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Supplementary information

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Copper-catalysed asymmetric cross-coupling reactions tolerant of highly reactive radicals

In the format provided by the authors and unedited

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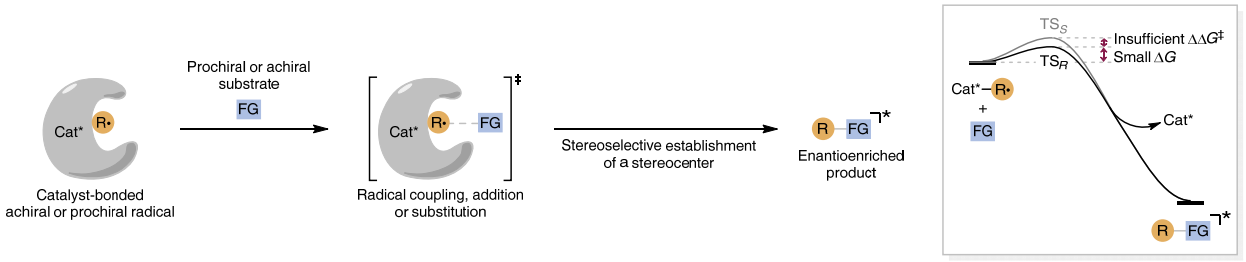
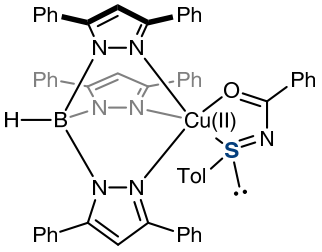
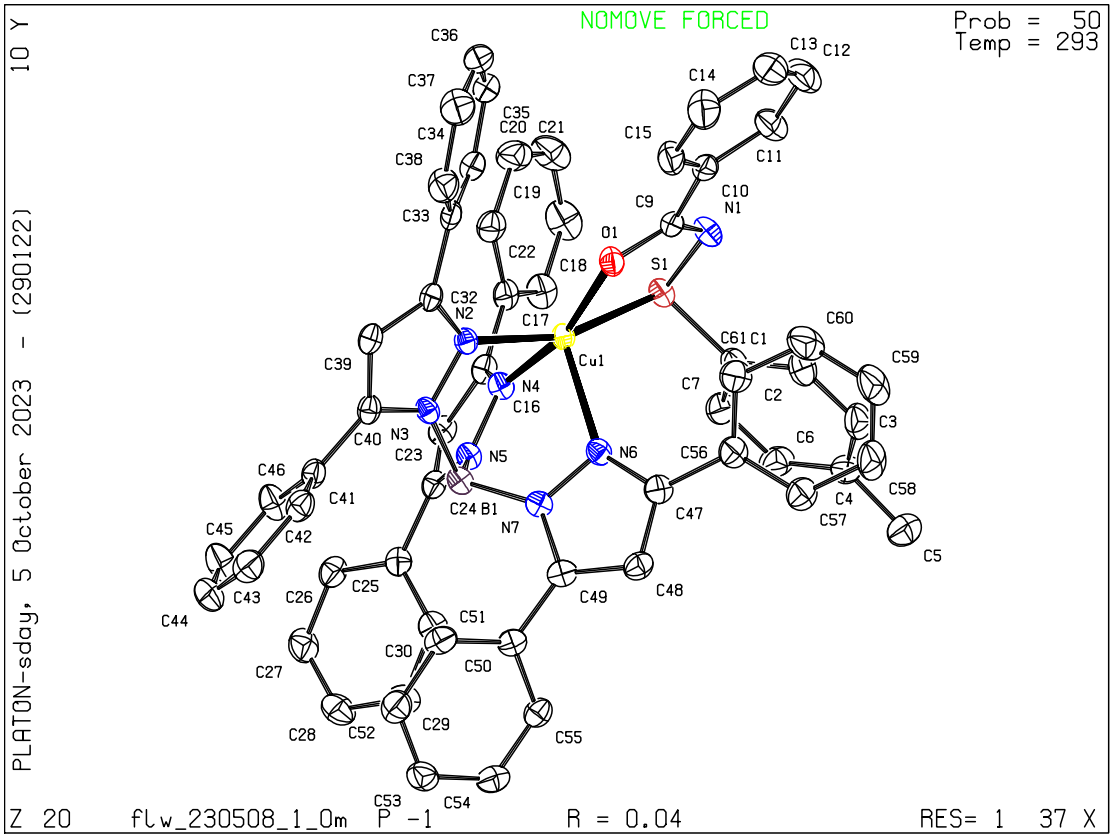
1. Supplementary figures for experiments



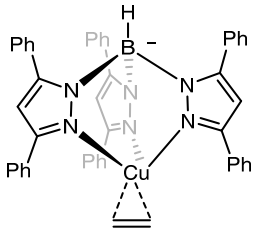
Supplementary Fig. 1 | Stereodiscrimination in elementary radical bond-forming reactions involving catalyst-bound radicals.



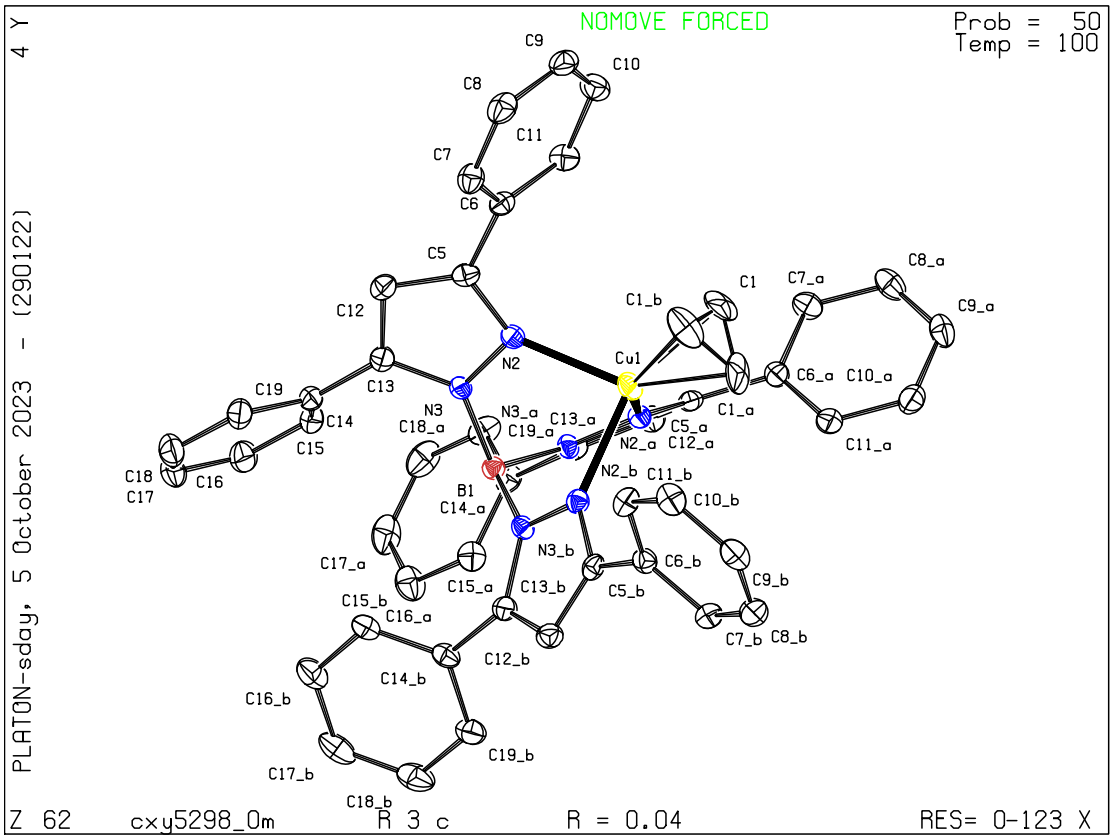
M1



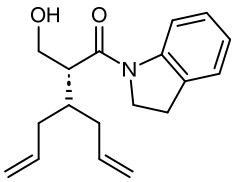
Supplementary Fig. 2 | The X-ray structure of M1 (CCDC no. 2289793).



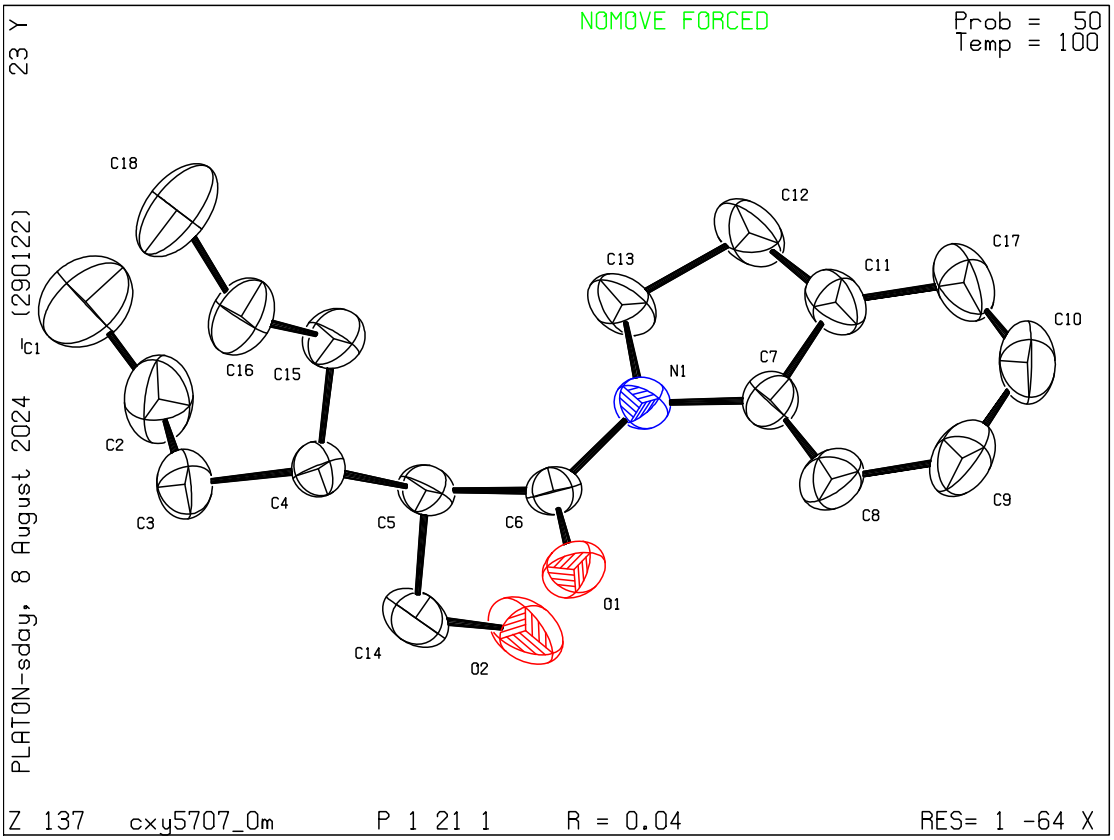
M2



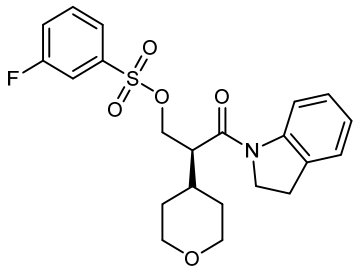
Supplementary Fig. 3 | The X-ray structure of M2. The corresponding monocrystal was consistent with that reported in the literature[1].



(*R*)-**S5**



Supplementary Fig. 4 | The X-ray structure of (*R*)-S5 (CCDC no. 2375977).



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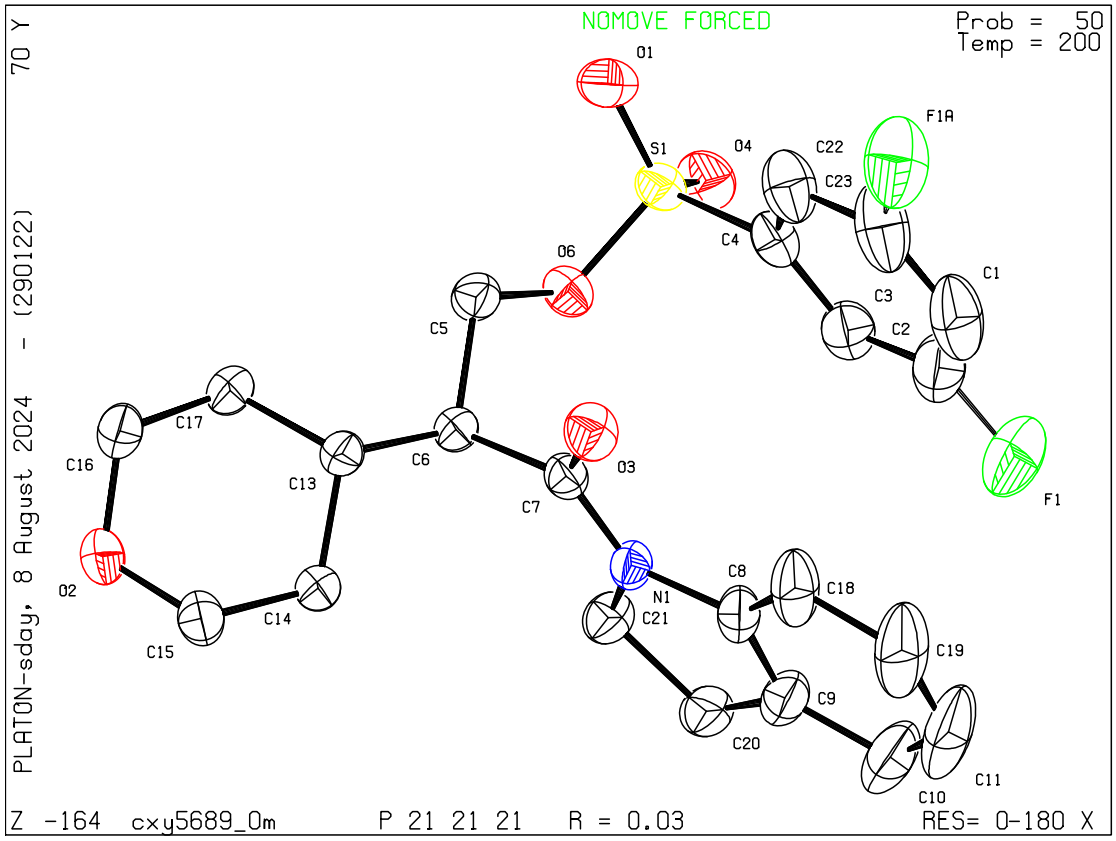
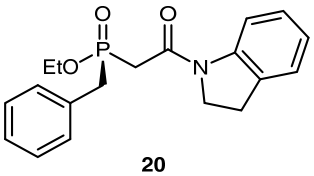


Supplementary Fig. 5 | The X-ray structure of 9 (CCDC no. 2375978).



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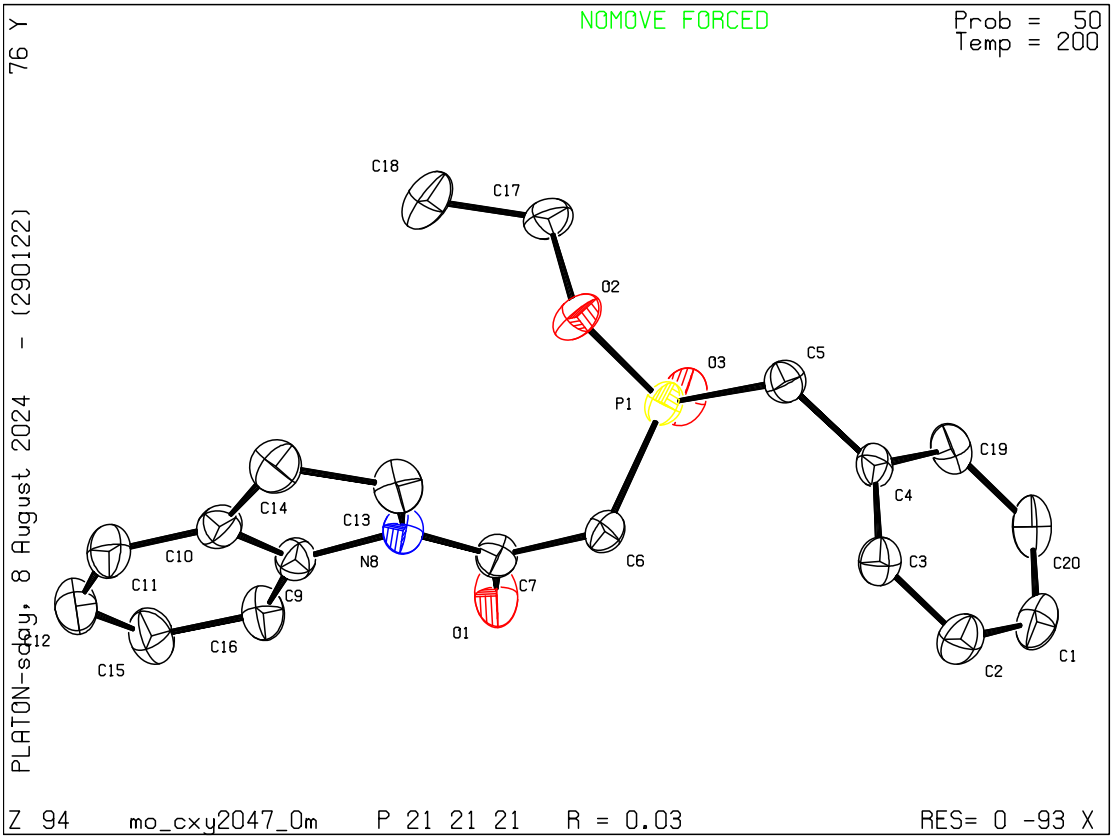
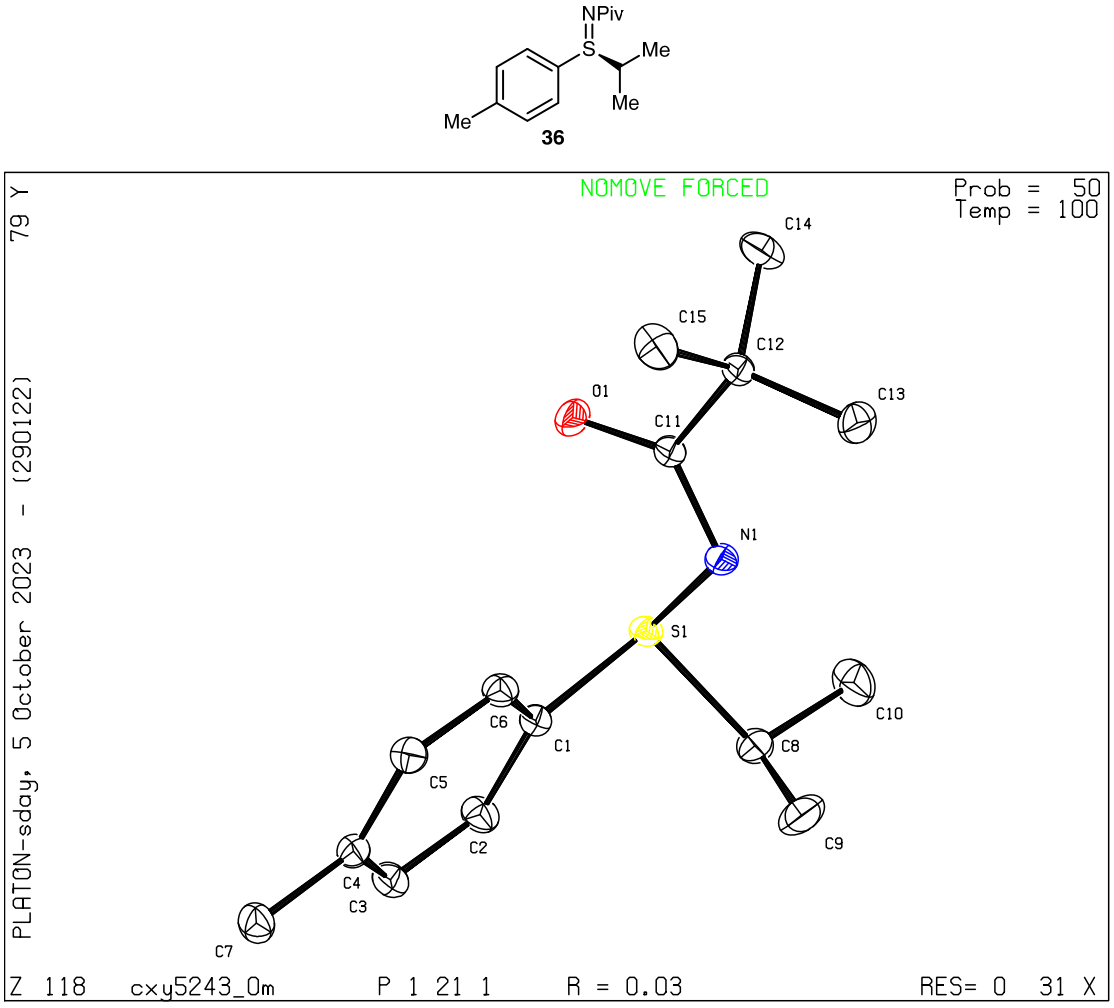
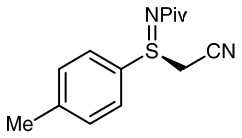


Supplementary Fig. 6 | The X-ray structure of 20 (CCDC no. 2375976).



Supplementary Fig. 7 | The X-ray structure of 36 (CCDC no. 2289792).



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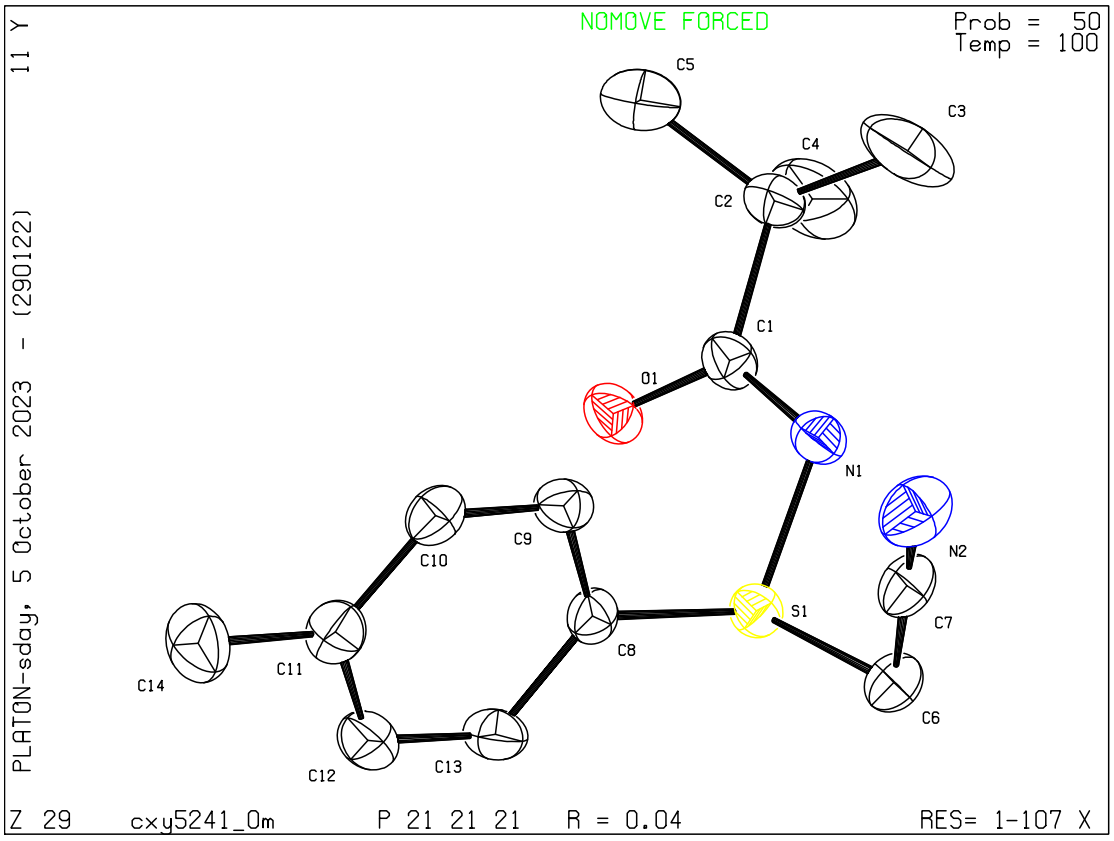
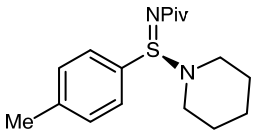


Supplementary Fig. 8 | The X-ray structure of 46 (CCDC no. 2289795).



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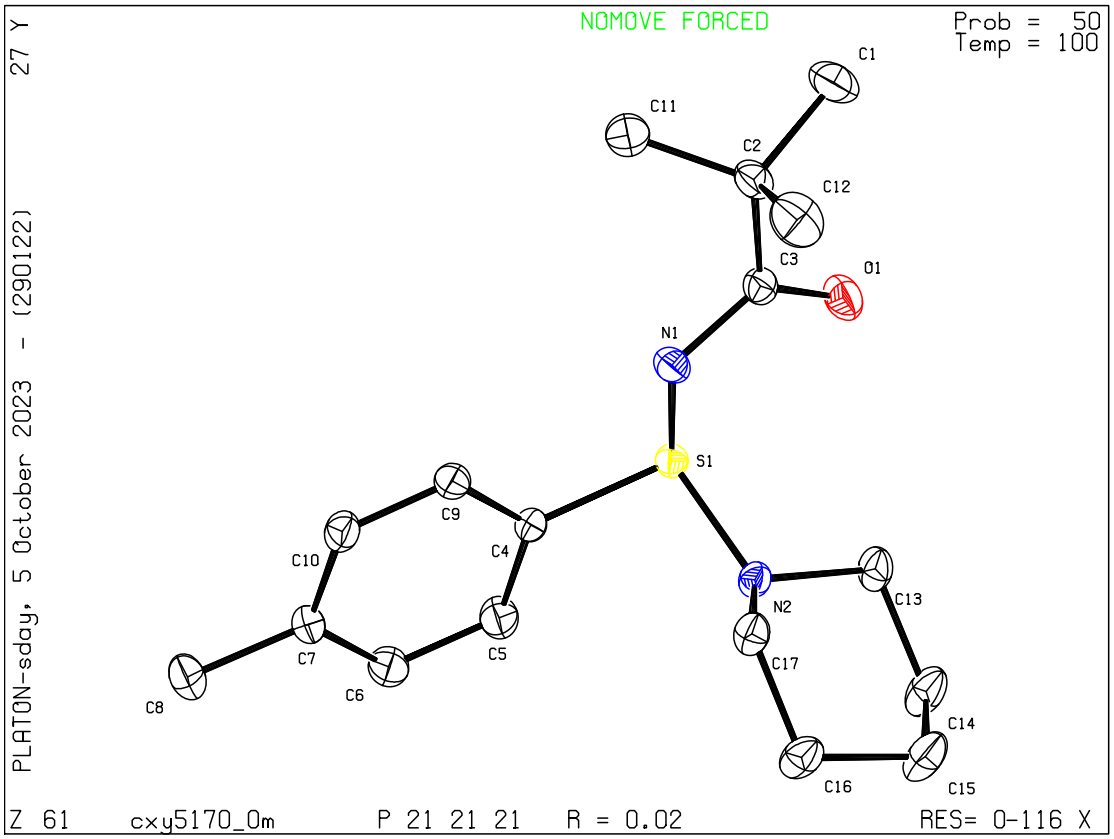
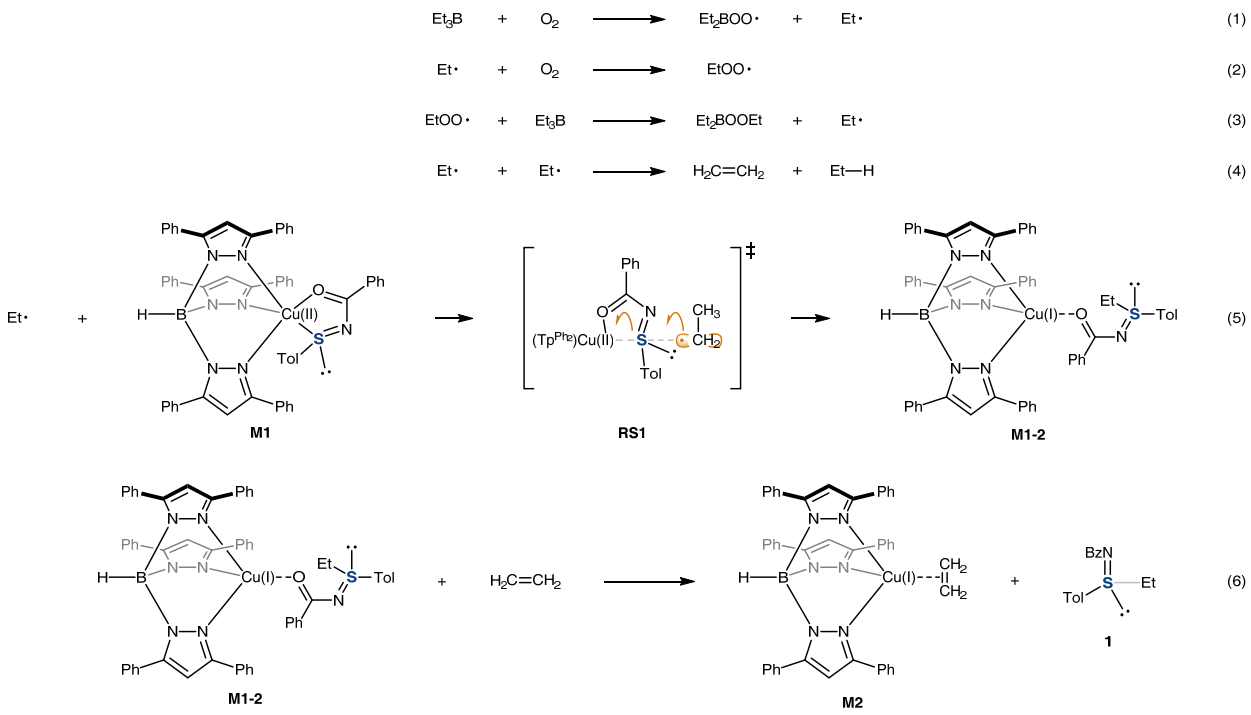
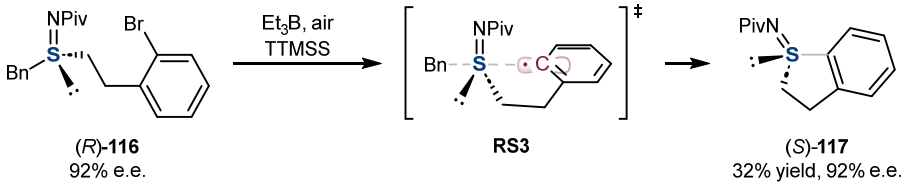


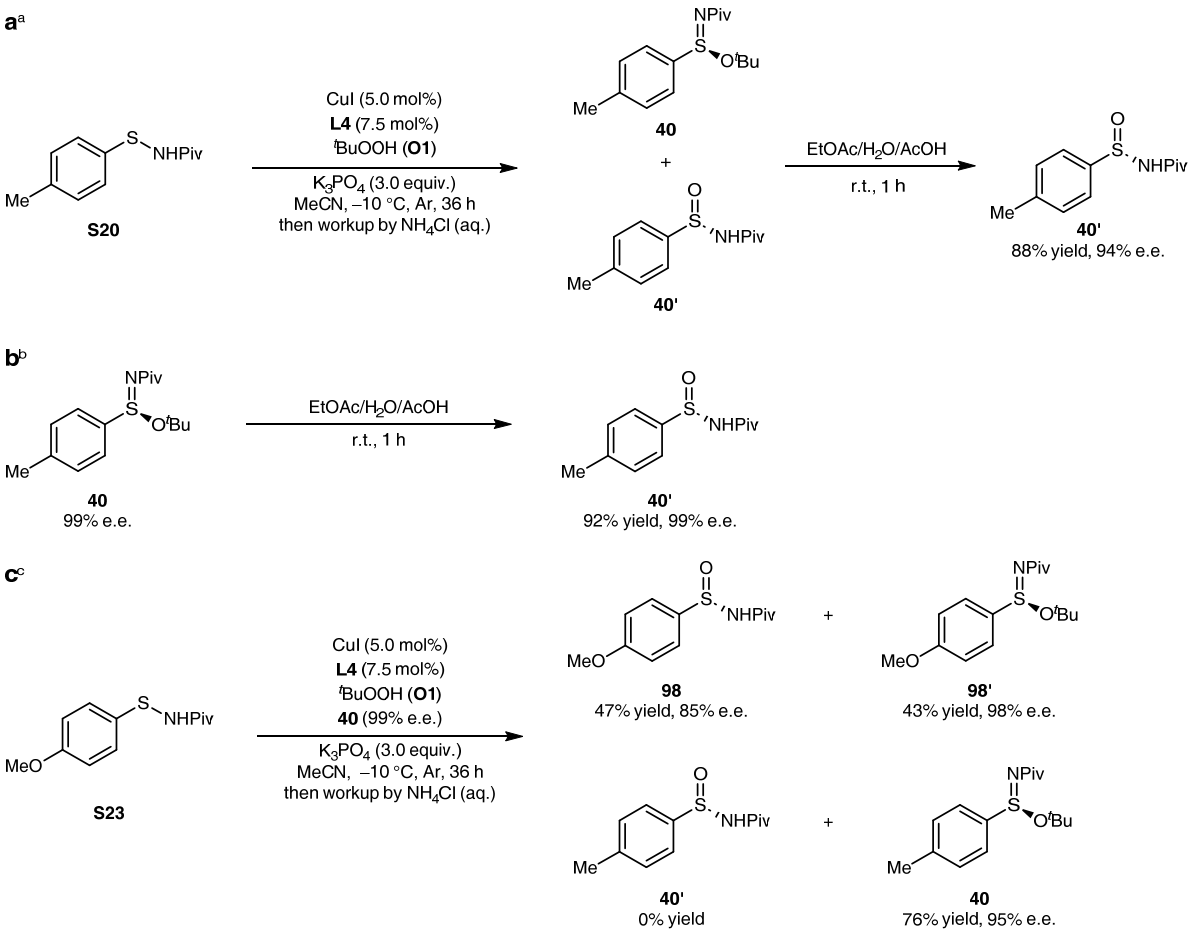
Supplementary Fig. 9 | The X-ray structure of 57 (CCDC no. 2289794).



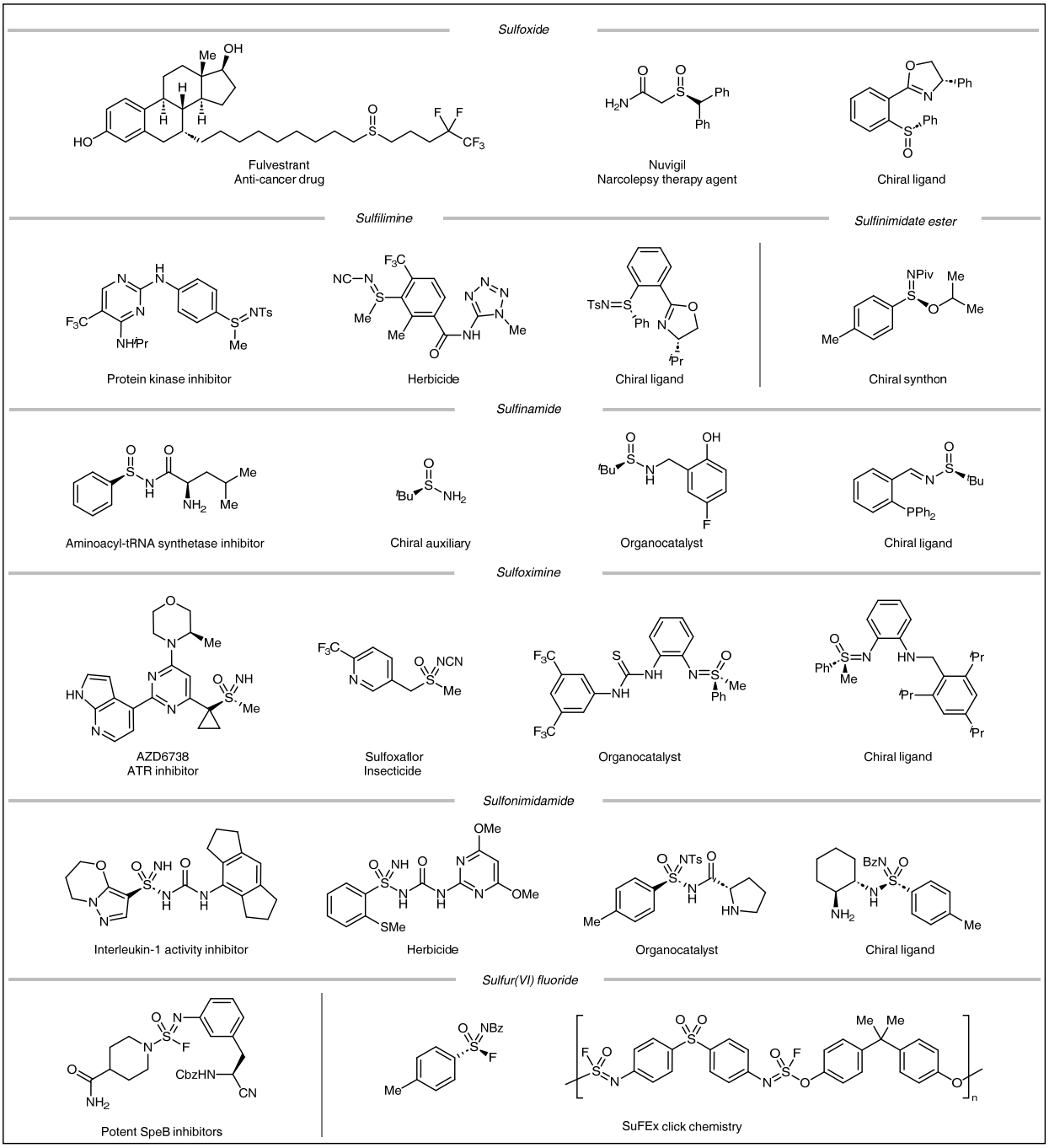
Supplementary Fig. 10 | Proposed mechanism for the formation of 1 and M2 from M1. According to the literature[2], ethyl radicals are generated from triethylborane in the presence of oxygen, as shown in equations (1–3). Under ambient conditions in air, the formation of ethylene in this system is well documented[3] and attributed to the disproportionation of ethyl radicals (equation (4)). We propose that the radical substitution of **M1** by ethyl radicals proceeds via transition state **RS1**, initially affording a labile, product-bound copper(I) complex (**M1-2**) (equation (5)). Subsequent ligand exchange between **M1-2** and in situ formed ethylene likely yields **M2** and product **1** (equation (6)). The favorable formation of **1** under similar conditions has been previously reported[1].



Supplementary Fig. 11 | The enantiospecific intramolecular homolytic substitution reaction of chiral sulfilimine. Conditions: (*R*)-**116** (92% e.e., 0.355 mmol, 1.0 equiv.), TTMSS (1.420 mmol, 4.0 equiv.), Et_3B (3.550 mmol, 10 equiv.), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in benzene (2.0 mL) under air at r.t. for 2 h. TTMSS, tris(trimethylsilyl)silane.



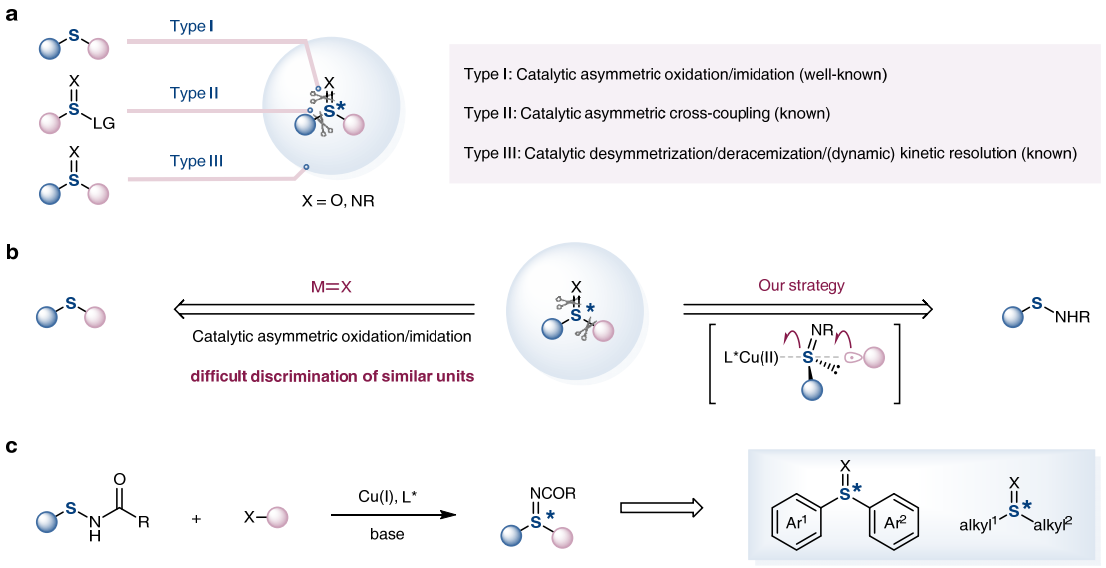
Supplementary Fig. 12 | The mechanistic study of O-centered radical. [a]Conditions: **S20** (0.20 mmol, 1.0 equiv.), **O1** (0.24 mmol, 1.2 equiv.), CuI (0.010 mmol, 5.0 mol%), **L4** (0.015 mmol, 7.5 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in MeCN (2.0 mL) under argon at –10 °C for 36 h. [b]Conditions: **40** (0.10 mmol) in a mixed solvent of EtOAc (1.5 mL), H_2O (1.0 mL), and AcOH (0.5 mL) at r.t. for 1 h. [c]Conditions: **S23** (0.10 mmol, 1.0 equiv.), **40** (99% e.e., 0.10 mmol, 1.0 equiv.), **O1** (0.12 mmol, 1.2 equiv.), CuI (0.0050 mmol, 5.0 mol%), **L4** (0.0075 mmol, 7.5 mol%), and K_3PO_4 (0.30 mmol, 3.0 equiv.) in MeCN (1.0 mL) at −10 °C for 36 h.



Supplementary Fig. 13 | Importance of S(IV) and S(VI) stereogenic centers.

Compounds possessing sulfur stereogenic centers play a pivotal role in asymmetric synthesis[4-5] and widely exist in bioactive molecules[6], pharmaceuticals[7-9], and agrochemicals[10-11]. However, enantioenriched S-chiral compounds are usually neglected in drug discovery[12-13], despite their potent physicochemical and pharmacokinetic properties. Among them, sulfoxides, sulfilimines, sulfinimidate esters, sulfinamides, and sulfinamidines are representative S(IV) scaffolds that, in addition to their bioactivity, are often used as chiral ligands, auxiliaries, or catalysts[5,14]. Moreover, they also serve as chiral synthons to access S(VI) stereogenic centers[15-16],

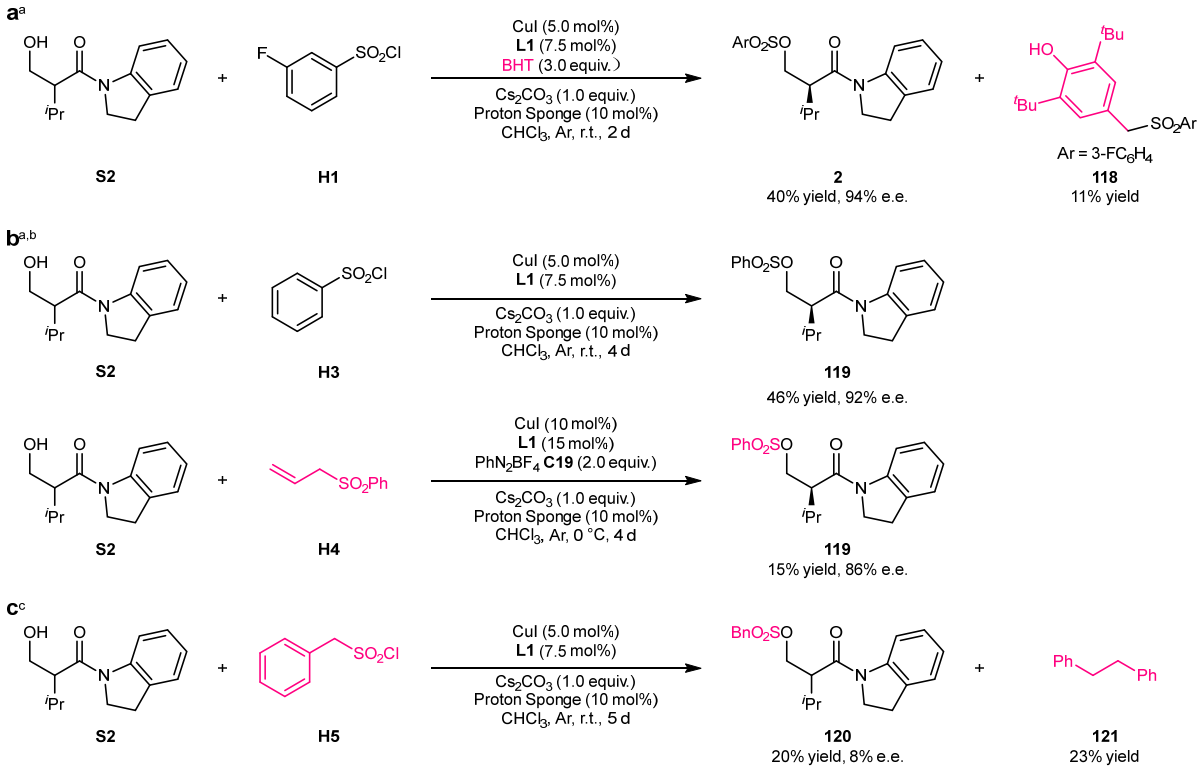
such as chiral sulfoximines and sulfur(VI) fluorides. While the former have been utilized in drug discovery[12,17-21], the latter have been used in SuFEx click chemistry in the area of biology and polymers[22-28]. Given the importance of enantioenriched sulfur stereogenic centers, it is highly desirable to develop a robust and universal catalytic asymmetric strategy to access all sorts of chiral sulfur centers.



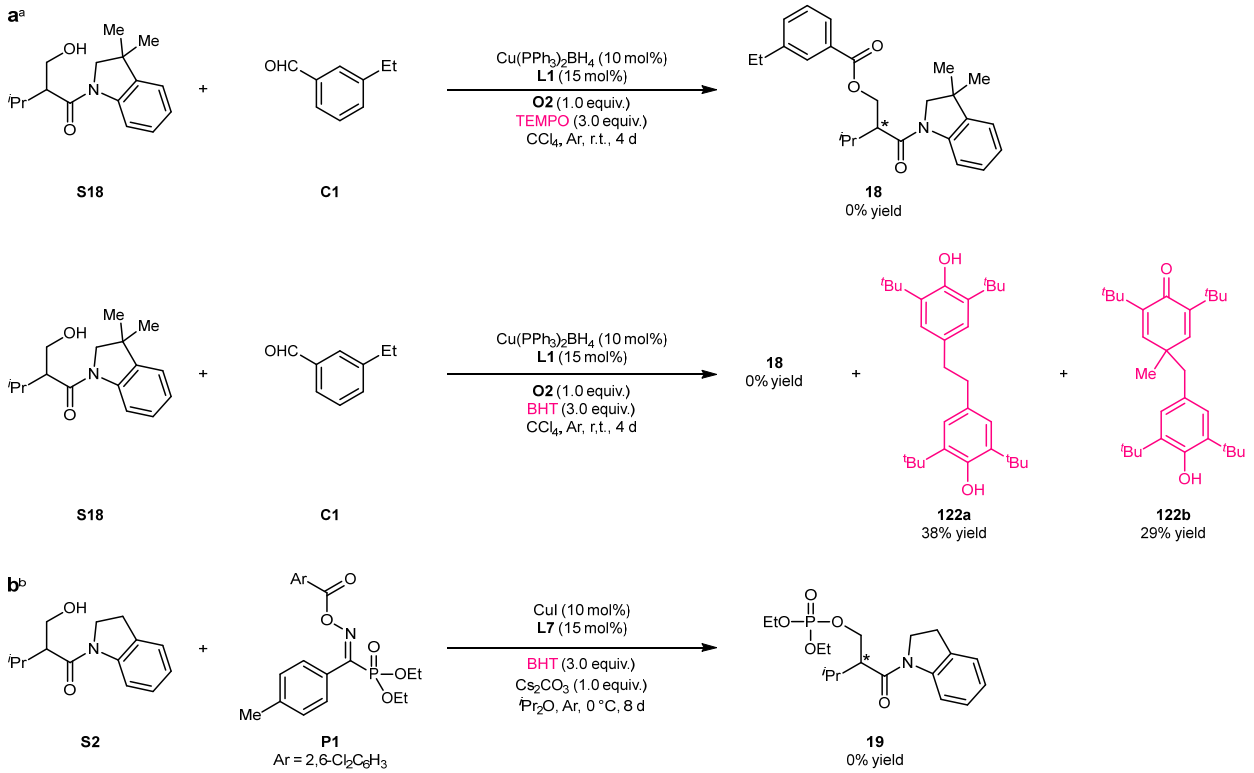
Supplementary Fig. 14 | Asymmetric synthesis of sulfilimine and sulfinamide. a, Of all the known catalytic asymmetric methods for S-chiral S(IV) compounds, the direct oxidation/imidation of sulfur is the most advanced and frequently employed approach. **b**, Challenges persist in obtaining S-chiral S(IV) compounds with similar *S*-substituents via direct oxidation/imidation. Therefore, we proposed an asymmetric radical substitution strategy for constructing S(IV) stereocenters de novo, of which the successful implementation would resolve the issue of stereodiscrimination. **c**, In this work, we disclose a copper-catalyzed enantioselective radical cross-coupling of *N*-acyl sulfenamides with a diverse range of aryl and alkyl halides, leading to highly enantioenriched S-chiral S(IV) compounds, particularly those bearing *S*-substituents of minimal differences.

S-chiral sulfilimines[29-30] and sulfinamides[31-32] possess S(IV)-stereogenic centers attached to nitrogen atoms. Unlike their corresponding oxygen analogues[16,33] (e.g., S-chiral sulfoxides and sulfinate esters), the asymmetric synthesis of S-chiral sulfilimines and sulfinamides has less precedent in the literature. Two strategies have been employed for their synthesis: i. enantiospecific functional group exchange from chiral S(IV) sources or chiral auxiliary-facilitated oxidation of S(II) sources; ii. asymmetric catalysis employing simple sulfide/sulfenamide starting materials (Supplementary Fig. 14a). Andersen's sulfinate[34] or Ellman auxiliary[9] are commonly used in the first strategy. While they generally work well for the synthesis of chiral sulfoxides and sulfinamides, tedious steps are required to access the corresponding sulfilimines. In comparison, asymmetric imidation[35] represents a more straightforward way to access sulfilimines from simple sulfides. In this aspect, the two *S*-substituents should be stereochemically differentiated as shown in Supplementary Fig. 14b. Accordingly, all the current methods largely only provide access to the aryl alkyl sulfilimines owing to the substantial differences between aryl and alkyl groups. However, the stereochemical differentiation of two aryl or alkyl groups with similar steric hindrance and electronic properties has thus far remained difficult, rendering the catalytic asymmetric sulfide imidation challenging. In this scenario, direct asymmetric S-alkylation or -arylation would elegantly circumvent this problem. To date, the state of the art for the formation of this chiral sulfur–carbon bond has been reported by Ellman[11] using donor-acceptor carbenes as

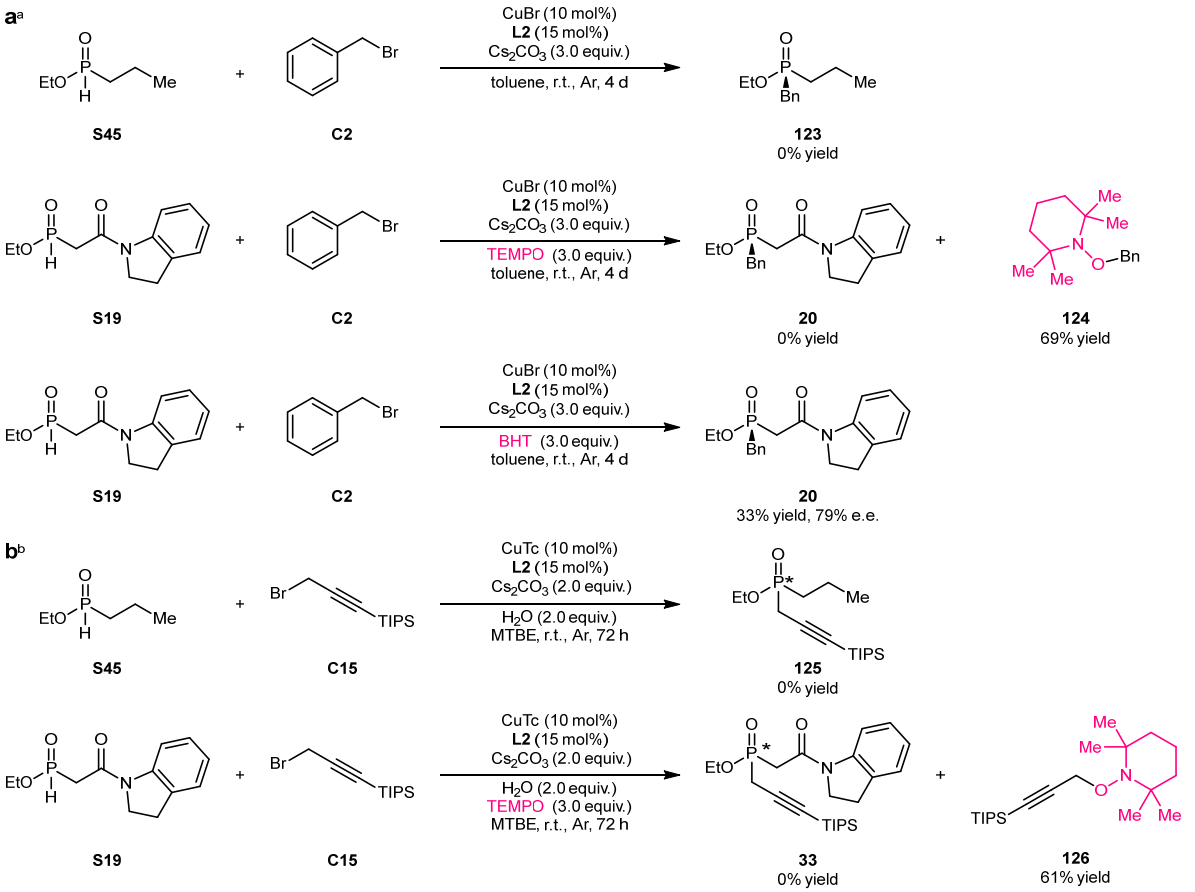
the alkylation reagents. Using our developed strategy, we can easily synthesize both bis-arylated and -alkylated sulfilimines in one step with excellent enantioselectivity (Supplementary Fig. 14c). More importantly, straightforward follow-up transformations can also lead to the corresponding valuable S-chiral sulfoxides, which are otherwise difficult to target using known methods. This clearly demonstrates that the current method would play a revolutionary role in the formation of chiral sulfur centers. Notably, during the preparation of this manuscript, several asymmetric catalytic methodologies for the synthesis of chiral sulfilimines from sulfenamides were independently reported[36-45].



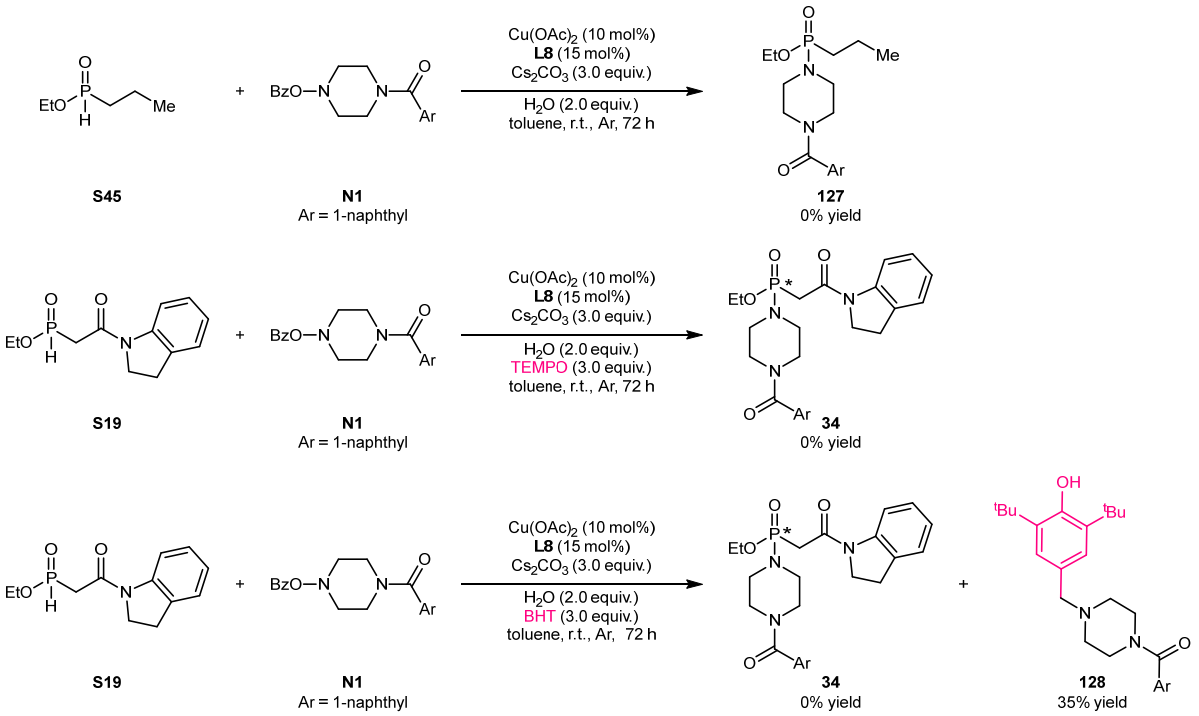
Supplementary Fig. 15 | Control experiments for sulfonyl radical in chiral C part. [a]Conditions: γ-aminocarbonyl alcohol **S2** (0.20 mmol, 1.0 equiv.), sulfonyl chloride **H1** or **H3** or **H5** (0.18 mmol, 0.9 equiv.), CuI (0.010 mmol, 5.0 mol%), **L1** (0.015 mmol, 7.5 mol%), proton sponge (0.020 mmol, 10 mol%), BHT (0 or 3.0 equiv.), and Cs_2CO_3 (0.20 mmol, 1.0 equiv.) in anhydrous anhydrous $CHCl_3$ (1.0 mL) under argon at r.t.. [b]Conditions: γ-aminocarbonyl alcohol **S2** (0.20 mmol, 1.0 equiv.), (allylsulfonyl)benzene **H4** (0.30 mmol, 1.5 equiv.), CuI (0.020 mmol, 10 mol%), **L1** (0.030 mmol, 15 mol%), proton sponge (0.020 mmol, 10 mol%), aryldiazonium tetrafluoroborate **C19** (0.40 mmol, 2.0 equiv.), and Cs_2CO_3 (0.20 mmol, 1.0 equiv.) in anhydrous anhydrous $CHCl_3$ (1.0 mL) under argon at 0 °C for 4 d.



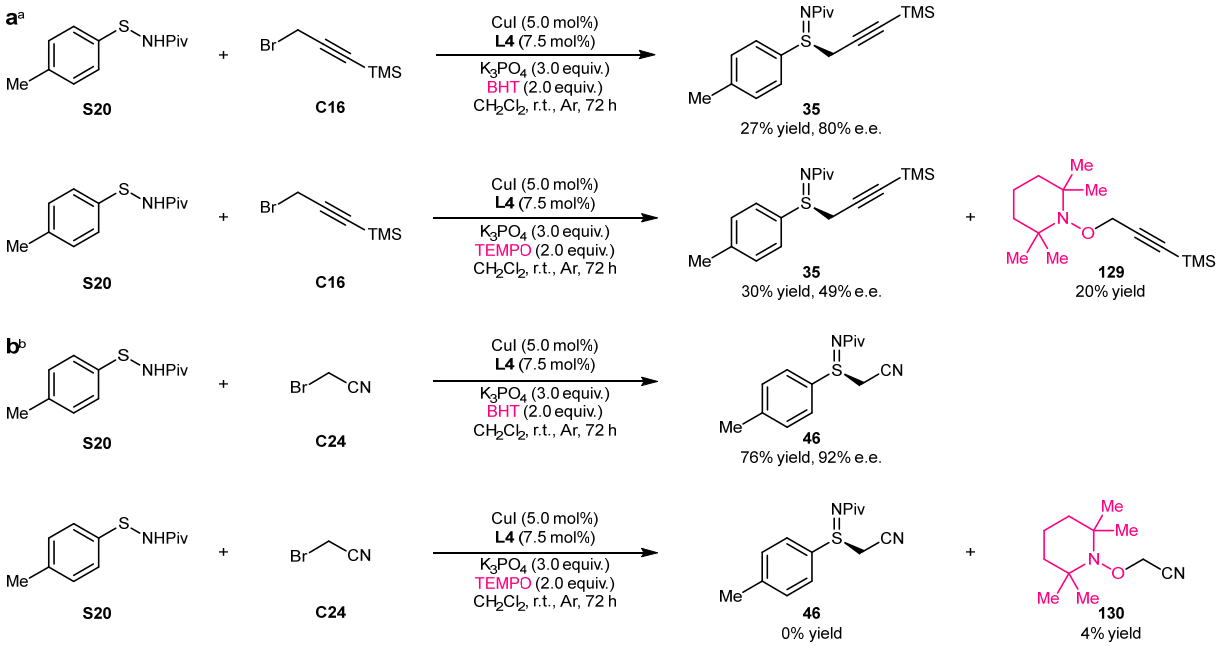
Supplementary Fig. 16 | Radical trapping experiments for C- or P-center radical in chiral C part. [a]Conditions: γ-aminocarbonyl alcohol **S18** (0.10 mmol, 1.0 equiv.), **O2** (0.10 mmol, 1.0 equiv.) and 3-ethylbenzaldehyde **C1** (0.06 mmol, 0.6 equiv.), $CuBH_4(PPh_3)_2$ (0.010 mmol, 10 mol %), **L1** (0.015 mmol, 15 mol%), BHT (0 or 3.0 equiv.), and Cs_2CO_3 (0.10 mmol, 1.0 equiv.) in anhydrous CCl_4 (1.0 mL) under argon at r.t. for 4 d. [b]Conditions: γ-aminocarbonyl alcohol **S2** (0.20 mmol, 1.0 equiv.), oxime phosphonate **P1** (0.20 mmol, 1.0 equiv.), CuI (0.02 mmol, 10 mol%), **L7** (0.03 mmol, 15 mol%), BHT (0.60 mmol, 3.0 equiv.), and Cs_2CO_3 (0.20 mmol, 1.0 equiv.) in anhydrous anhydrous $^iPr_2O$ (2.0 mL) under argon at 0 °C for 8 d.



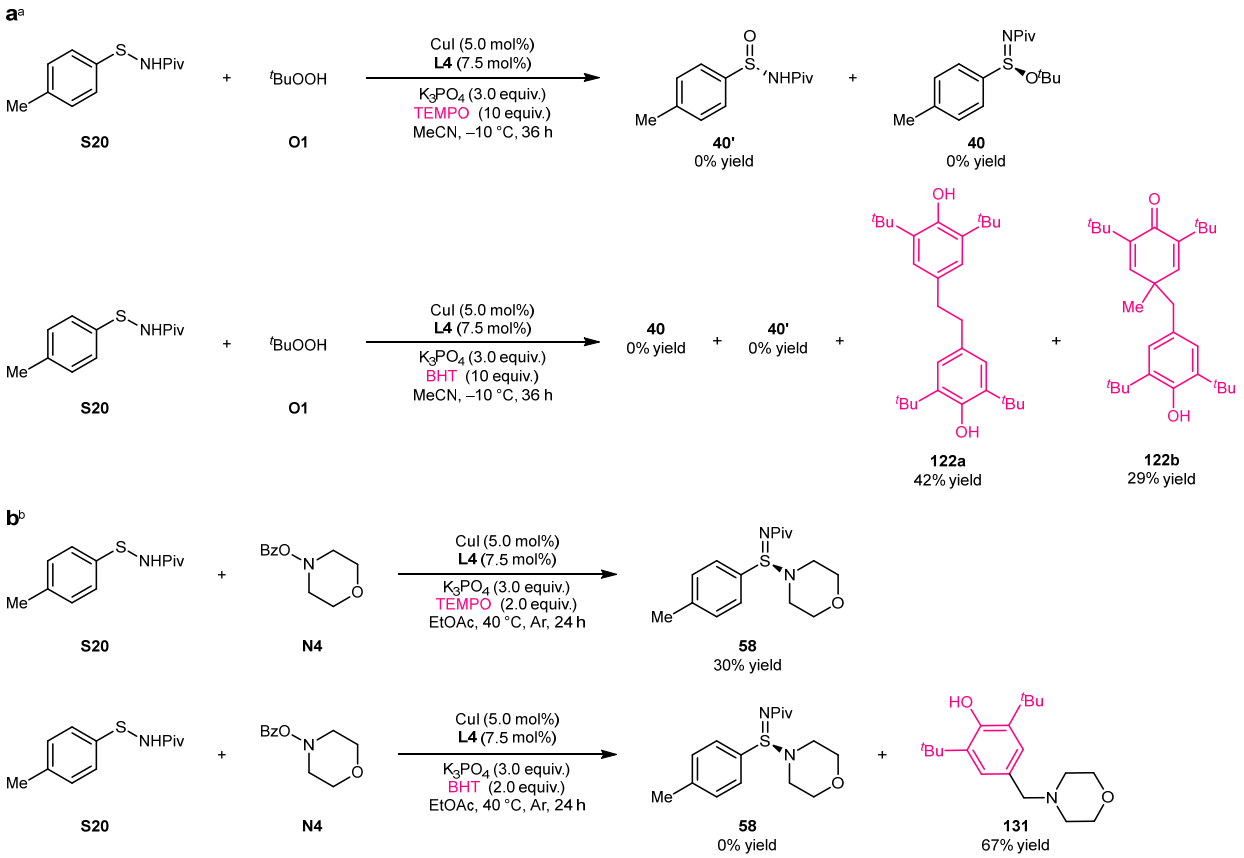
Supplementary Fig. 17 | Radical trapping experiments for C-centered radical in chiral P(V) part. [a]Conditions: **S19** or **S45** (0.10 mmol, 1.0 equiv.), **C2** (0.15 mmol, 1.5 equiv.), CuBr (0.010 mmol, 10 mol%), **L2** (0.015 mmol, 15 mol%), BHT or TEMPO (0 or 2.0 equiv.), and Cs_2CO_3 (0.30 mmol, 3.0 equiv.) in anhydrous toluene (4.0 mL) under argon at r.t. for 72 h; [b]Conditions: **S45** or **S19** (0.12 mmol, 1.2 equiv.), **C15** (0.10 mmol, 1.0 equiv.), CuTc (0.010 mmol, 10 mol%), **L2** (0.015 mmol, 15 mol%), H_2O (0.20 mmol, 2.0 equiv.), Cs_2CO_3 (0.20 mmol, 2.0 equiv.), and TEMPO (0 or 3.0 equiv.) in anhydrous MTBE (4.0 mL) under argon at r.t. for 72 h. BHT, butylated hydroxytoluene; TEMPO, 2,2,6,6-tetramethylpiperidinooxy; MTBE, *tert*-butyl methyl ether.



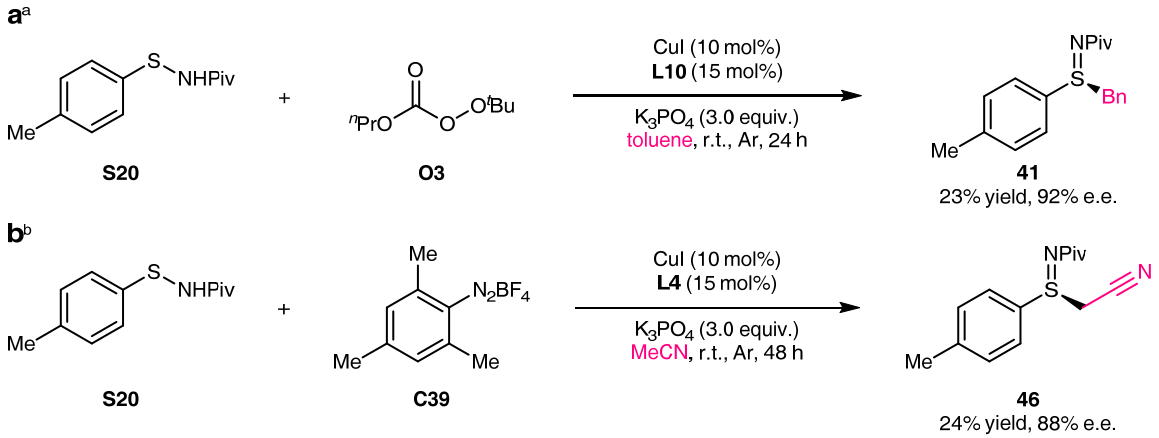
Supplementary Fig. 18 | Radical trapping experiments for N-centered radical in chiral P(V) part. Conditions: **S45** or **S19** (0.15 mmol, 1.5 equiv.), **N1** (0.10 mmol, 1.0 equiv.), $Cu(OAc)_2$ (0.010 mmol, 10 mol%), **L8** (0.015 mmol, 15 mol%), BHT or TEMPO (0 or 3.0 equiv.), H_2O (0.20 mmol, 2.0 equiv.), and Cs_2CO_3 (0.30 mmol, 3.0 equiv.) in anhydrous toluene (4.0 mL) under argon at r.t. for 72 h. BHT, butylated hydroxytoluene; TEMPO, 2,2,6,6-tetramethylpiperidinooxy.



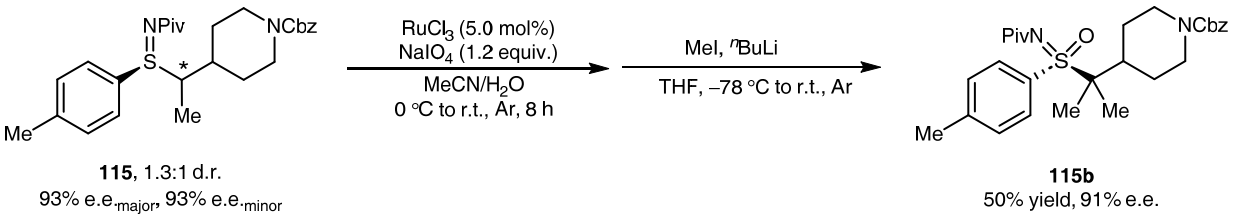
Supplementary Fig. 19 | Radical trapping experiments for C-centered radical in chiral S(IV) part. [a]Conditions: **S20** (0.20 mmol, 1.0 equiv.), **C16** (0.24 mmol, 1.2 equiv.), CuI (0.010 mmol, 5.0 mol%), **L4** (0.015 mmol, 7.5 mol%), BHT or TEMPO (2.0 equiv.), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in CH_2Cl_2 (2.0 mL) under argon at r.t. for 72 h; [b]Conditions: **S20** (0.20 mmol, 1.0 equiv.), **C24** (0.24 mmol, 1.2 equiv.), CuI (5.0 mol%), **L4** (7.5 mol%), BHT or TEMPO (2.0 equiv.), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in CH_2Cl_2 (2.0 mL) under argon at r.t. for 48 h; BHT, butylated hydroxytoluene; TEMPO, 2,2,6,6-tetramethylpiperidinooxy.



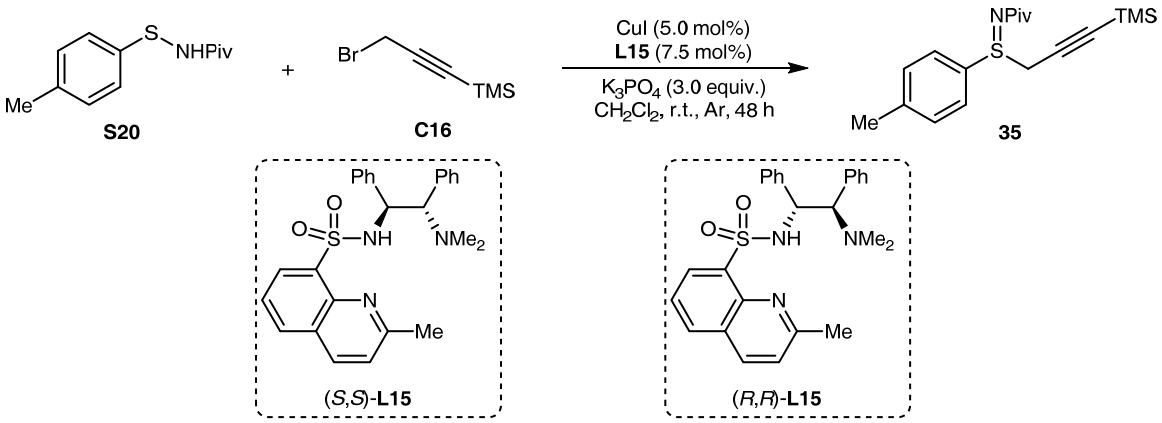
Supplementary Fig. 20 | Radical trapping experiments for N/O-centered radical in chiral S(IV) part. [a]Conditions: **S20** (0.20 mmol, 1.0 equiv.), **O1** (0.24 mmol, 1.2 equiv.), CuI (5.0 mol%), **L4** (7.5 mol%), BHT or TEMPO (10 equiv.), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in MeCN (2.0 mL) under argon at –10 °C for 36 h; [b]Conditions: **S20** (0.050 mmol, 1.0 equiv.), **N4** (0.075 mmol, 1.5 equiv.), CuI (0.00250 mmol, 5.0 mol%), **L4** (0.00375 mmol, 7.5 mol%), BHT or TEMPO (2.0 equiv.), and K_3PO_4 (0.15 mmol, 3.0 equiv.) in EtOAc (0.50 mL) under argon at 40 °C for 24 h. BHT, butylated hydroxytoluene; TEMPO, 2,2,6,6-tetramethylpiperidinooxy.



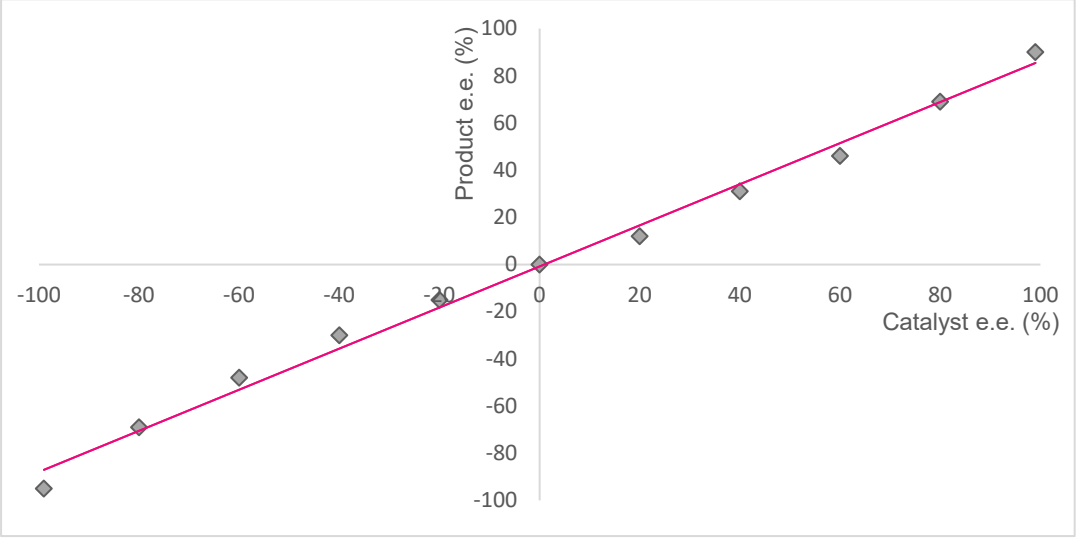
Supplementary Fig. 21 | Enantioselective radical S–C coupling of carbon radicals generated by hydrogen atom abstraction of hydrogen hydrocarbon solvents. [a]Conditions: **S20** (0.05 mmol, 1.0 equiv.), **O3** (0.10 mmol, 2.0 equiv.), CuI (0.0050 mmol, 10 mol%), **L10** (0.0075 mmol, 15 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in toluene (0.50 mL) under argon at r.t. for 24 h; [b]Conditions: **S20** (0.05 mmol, 1.0 equiv.), **C39** (0.25 mmol, 5.0 equiv.), CuI (0.0050 mmol, 10 mol%), **L4** (0.0075 mmol, 15 mol%), and K_3PO_4 (0.15 mmol, 3.0 equiv.) in MeCN (0.5 mL) under argon at r.t. for 48 h.



Supplementary Fig. 22 | Determination of stereocenter of 115, the poor diastereoselectivity of 115 was caused by carbon chiral center. Conditions: **115** (0.10 mmol, 1.0 equiv.), $RuCl_3$ (0.005 mmol, 5.0 mol%) and $NaIO_4$ (0.12 mmol, 1.2 equiv.) in MeCN (1.0 mL) and H_2O (2.0 mL) under argon at –10 °C for 8 h; then ^{n}BuLi (0.15 mmol, 1.5 equiv.) and MeI (0.15 mmol, 1.5 equiv.) at r.t. for 0.5 h.



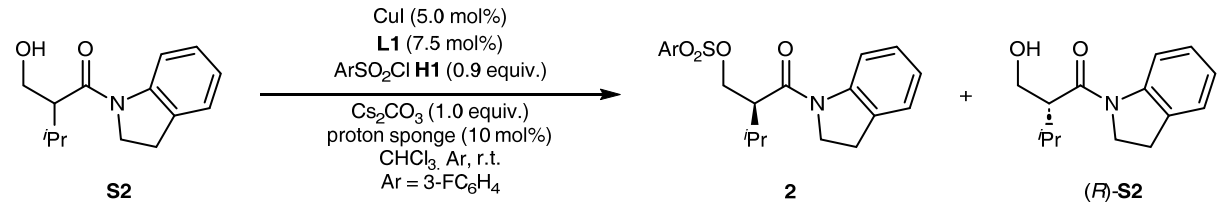
Entry	Catalyst e.e. (%)	Product e.e. (%)
1	99	90
2	80	69
3	60	46
4	40	31
5	20	12
6	0	0
7	–20	–15
8	–40	–30
9	–60	–48
10	–80	–69
11	–99	–95

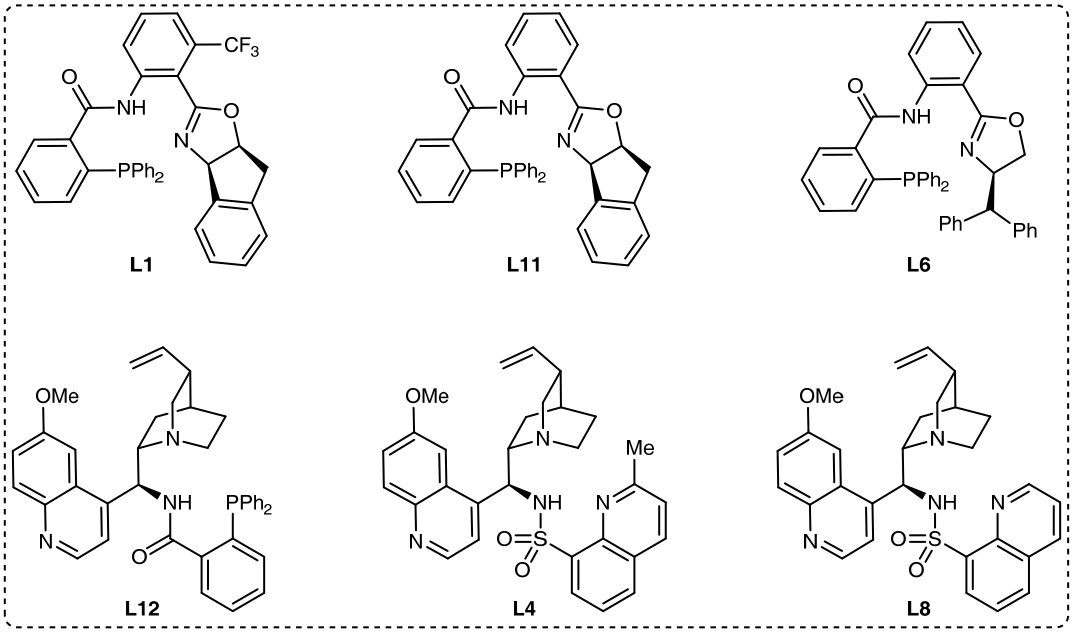


Supplementary Fig. 23 | The non-linear effect. The control experiments indicated a linear relationship between e.e. values of products and corresponding catalysts.

2. Supplementary tables for experiments

Supplementary Table 1 | Reaction condition optimization with γ-aminocarbonyl alcohol S2 and sulfonyl chloride H1



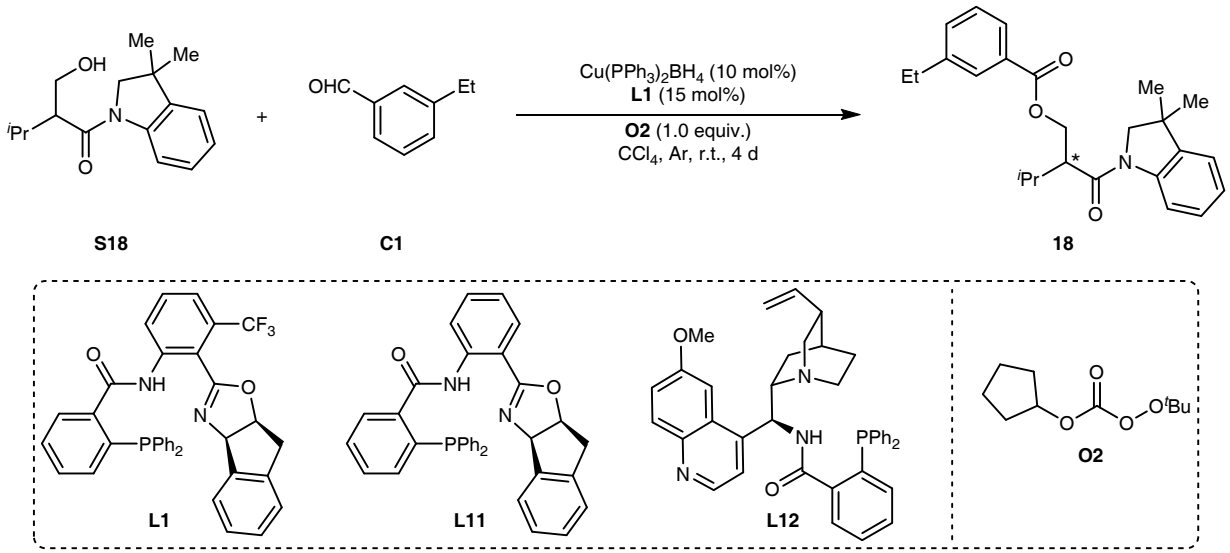


Entry	Variations	Yield (%)	E.e. of 2 (%)	E.e. of S2 (%)	*s* factor
1	None	47	92	92	79
2	Without CuI	10	14	0	N.D.
3	Without **L1**	15	0	0	N.D.
4	Without Cs_2CO_3	0	n.d.	n.d.	N.D.
5	Without CuI and **L1**	11	0	0	0
6	Without Proton Sponge	47	92	90	74
7	**L11** instead of **L1**	45	83	76	25
8	**L6** instead of **L1**	40	69	55	9
9	**L12** instead of **L1**	20	–54	–13	4
10	**L4** instead of **L1**	10	46	5	3
11	**L8** instead of **L1**	4	24	0	N.D.
12	$Cu(MeCN)_4PF_6$ instead of CuI	44	88	80	38
13	CuTc instead of CuI	43	92	84	64
14	$Cu(OTf)_2$ instead of CuI	46	82	91	32
15	K_2CO_3 instead of Cs_2CO_3	43	92	90	74
16	K_3PO_4 instead of Cs_2CO_3	46	91	92	70
17	Ag_2CO_3 instead of Cs_2CO_3	33	92	52	40

18	MeCN instead of $CHCl_3$	35	91	54	36
19	THF instead of $CHCl_3$	45	90	94	67
20	$PhCF_3$ instead of $CHCl_3$	50	81	94	33
21	MTBE instead of $CHCl_3$	43	90	88	55

Reaction conditions: **S2** (0.20 mmol, 1.0 equiv.), 3-fluorobenzenesulfonyl chloride **H1** (0.18 mmol, 0.9 equiv.), CuI (0.010 mmol, 5.0 mol%), **L1** (0.015 mmol, 7.5 mol%), Cs_2CO_3 (0.20 mmol, 1.0 equiv.) and proton sponge (0.020 mmol, 10 mol%) in $CHCl_3$ (1.0 mL) at r.t. for 48 h under argon. The yields are based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard and the e.e. values are based on HPLC analysis. Selectivity factor (s) = $\ln((1 - C)(1 - \text{e.e.}_S)]/\ln[(1 - C)(1 + \text{e.e.}_S))$, conversion ($C$) = $\text{e.e.}_S/(\text{e.e.}_S + \text{e.e.}_P)$. N.D., not determined.

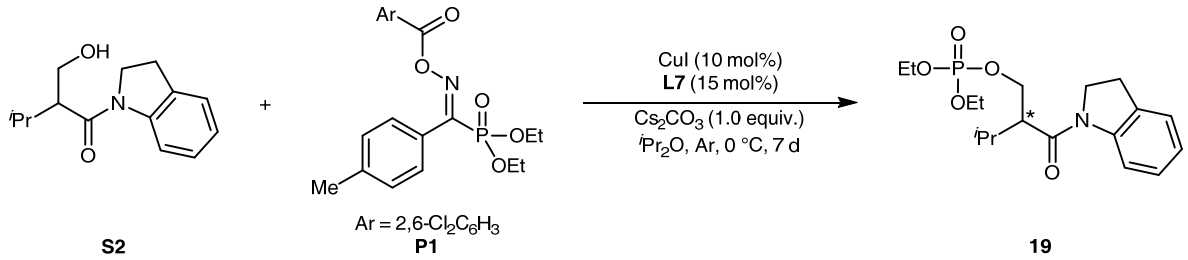
Supplementary Table 2 | Reaction condition optimization with γ-aminocarbonyl alcohol S18 and aldehyde C1



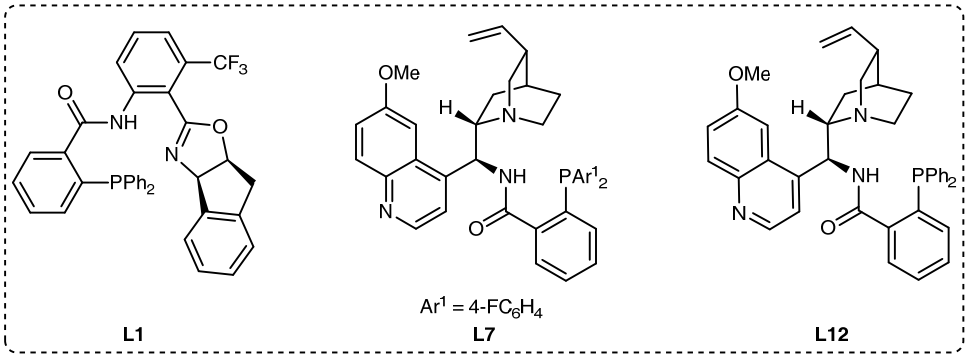
Entry	Variations	Conv. (%)	Yield (%)	E.e. (%)
1	None	40	27	90
2	Without $Cu(PPh_3)_2BH_4$	10	0	N.D.
3	Without **L1**	24	11	0
4	Without **O2**	0	0	N.D.
5	Without $Cu(PPh_3)_2BH_4$ and **L1**	0	0	N.D.
6	CuTc instead of $Cu(PPh_3)_2BH_4$	55	32	55
7	$Cu(OTf)_2$ instead of $Cu(PPh_3)_2BH_4$	26	5	5
8	CuI instead of $Cu(PPh_3)_2BH_4$	18	5	26
9	$Cu(MeCN)_4PF_6$ instead of $Cu(PPh_3)_2BH_4$	45	25	9
10	**L11** instead of **L1**	30	21	78
11	**L12** instead of **L1**	40	19	–38
12	LPO instead of **O2**	13	0	N.D.
13	THF instead of CCl_4	0	0	N.D.
14	CH_2Cl_2 instead of CCl_4	9	5	87
15	MTBE instead of CCl_4	24	12	89
16	At 0 °C & 7 d	42	35	90

Reaction conditions: **S18** (0.10 mmol, 1.0 equiv.), **C1** (0.06 mmol, 0.6 equiv.), CuI (0.010 mmol, 10 mol%), **L1** (0.015 mmol, 15 mol%), and **O2** (0.10 mmol, 1.0 equiv.) in CCl_4 (2.0 mL) at r.t. for 4 d under argon. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on chiral HPLC analysis. Conv., conversion; N.D., not determined.

Supplementary Table 3 | Reaction condition optimization with γ-aminocarbonyl alcohol S2 and oxime phosphonate P1



S2 P1 19

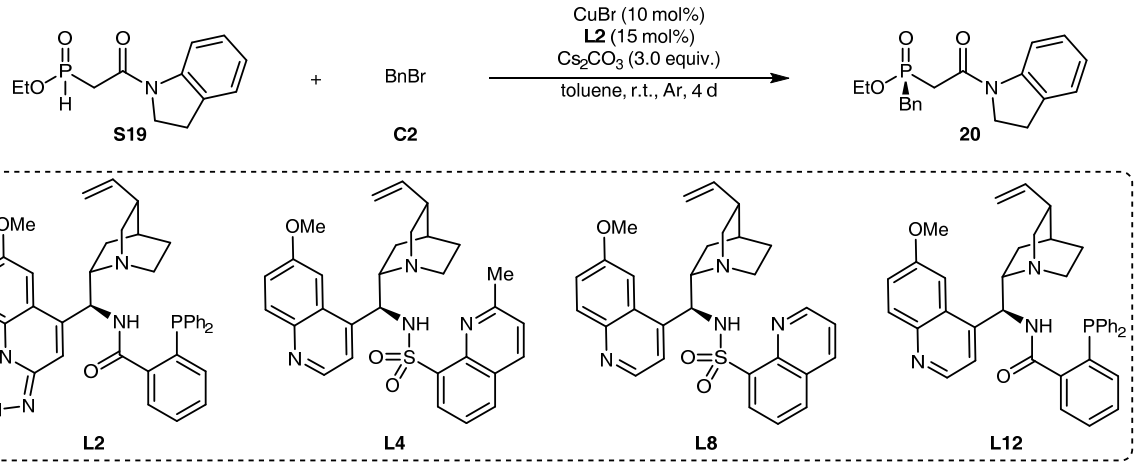


L1 L7 L12

Entry	Variations	Conv. (%)	Yield (%)	E.e. (%)
1	None	27	23	80
2	Without CuI	5	0	N.D.
3	Without **L7**	8	0	N.D.
4	Without Cs_2CO_3	9	0	N.D.
5	Without CuI and **L7**	0	0	N.D.
6	CuTc instead of CuI	10	5	54
7	$Cu(MeCN)_4PF_6$ instead of CuI	5	3	70
8	**L1** instead of **L7**	40	0	N.D.
9	**L12** instead of **L7**	20	11	61
10	K_2CO_3 instead of Cs_2CO_3	20	0	N.D.
11	K_3PO_4 instead of Cs_2CO_3	40	25	73
12	EtOAc instead of $^iPr_2O$	15	10	55
13	$PhCF_3$ instead of $^iPr_2O$	15	7	76
14	$CHCl_3$ instead of $^iPr_2O$	0	0	N.D.

Reaction conditions: **S2** (0.10 mmol, 1.0 equiv.), **P1** (0.10 mmol, 1.0 equiv.), CuI (0.010 mmol, 10 mol%), **L7** (0.015 mmol, 15 mol%), and Cs_2CO_3 (0.10 mmol, 1.0 equiv.) in $^iPr_2O$ (1.0 mL) at 0 °C for 7 d under argon. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on chiral HPLC analysis. N.D., not determined.

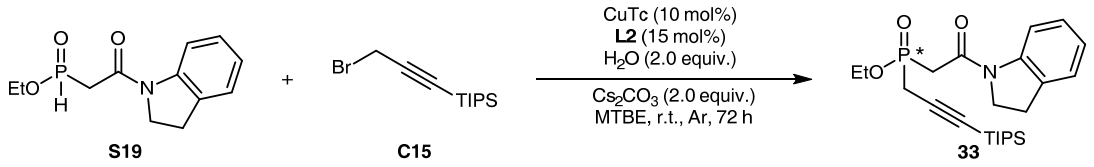
Supplementary Table 4 | Reaction condition optimization with *H*-phosphinate S19 and benzyl bromide C2

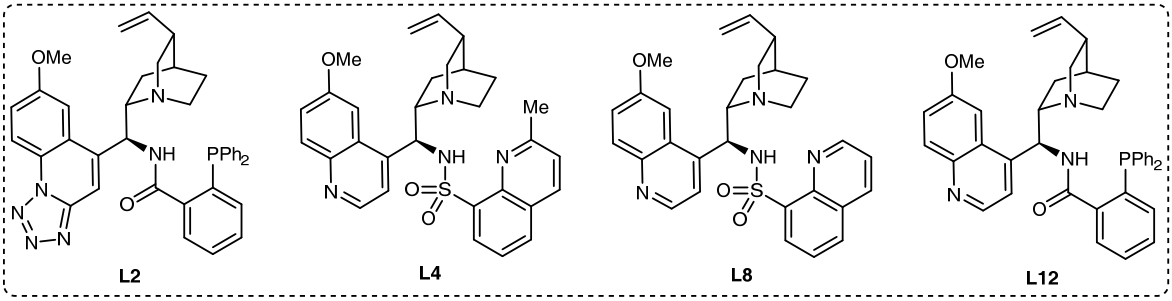


Entry	Variations	Yield (%)	E.e. (%)
1	None	68	90
2	Without CuBr	31	0
3	Without **L2**	30	0
4	Without Cs_2CO_3	0	N.D.
5	Without CuBr and **L2**	31	0
6	CuI instead of CuBr	43	86
7	$Cu(MeCN)_4PF_6$ instead of CuBr	61	71
8	CuTc instead of CuBr	15	10
9	**L4** instead of **L2**	34	23
10	**L8** instead of **L2**	40	26
11	**L12** instead of **L2**	71	80
12	K_2CO_3 instead of Cs_2CO_3	55	86
13	K_3PO_4 instead of Cs_2CO_3	26	71
14	KO^{t}Bu instead of Cs_2CO_3	0	N.D.
15	THF instead of toluene	32	82
16	CH_2Cl_2 instead of toluene	57	32
17	EtOAc instead of toluene	50	52
18	At 10 °C	44	89
19	At 0 °C	14	89

Reaction conditions: **S19** (0.10 mmol, 1.0 equiv.), **C2** (0.15 mmol, 1.5 equiv.), CuBr (0.010 mmol, 10 mol%), **L2** (0.015 mmol, 15 mol%), and Cs_2CO_3 (0.30 mmol, 3.0 equiv.) in toluene (4.0 mL) at r.t. for 4 d under argon. The yields are based on ^{31}P NMR analysis of the crude product using PPh_3 as an internal standard. The e.e. values are based on HPLC analysis. N.D., not determined.

Supplementary Table 5 | Reaction condition optimization with *H*-phosphinate S19 and (3-bromoprop-1-yn-1-yl)triisopropylsilane C15

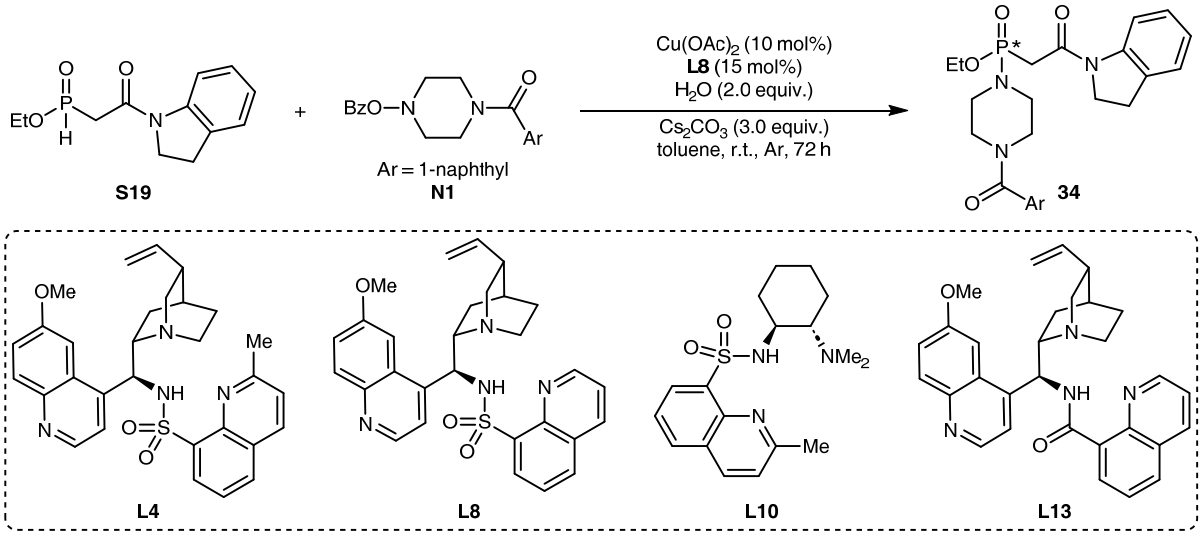




Entry	Variations	Yield (%)	E.e. (%)
1	None	60	90
2	Without CuTc	8	0
3	Without **L2**	33	0
4	Without Cs_2CO_3	0	N.D.
5	Without CuTc and **L2**	15	0
6	CuI instead of CuTc	30	70
7	$Cu(MeCN)_4BF_4$ instead of CuTc	26	63
8	CuOAc instead of CuTc	32	81
9	**L4** instead of **L2**	6	16
10	**L8** instead of **L2**	21	8
11	**L12** instead of **L2**	41	80
12	K_2CO_3 instead of Cs_2CO_3	5	51
13	K_3PO_4 instead of Cs_2CO_3	4	53
14	NaO^tBu instead of Cs_2CO_3	0	N.D.
15	THF instead of MTBE	40	70
16	toluene instead of MTBE	32	81
17	Without H_2O	6	77
18	1.0 equiv. H_2O	8	71
19	3.0 equiv. H_2O	70	85
20	4.0 equiv. H_2O	72	80

Reaction conditions: **S19** (0.12 mmol, 1.2 equiv.), **C15** (0.10 mmol, 1.0 equiv.), CuTc (0.010 mmol, 10 mol%), **L2** (0.015 mmol, 15 mol%), H_2O (0.20 mmol, 2.0 equiv.), and Cs_2CO_3 (0.20 mmol, 2.0 equiv.) in MTBE (4.0 mL) at r.t. for 72 h under argon. The yields are based on ^{31}P NMR analysis of the crude product using PPh_3 as an internal standard. The e.e. values are based on chiral HPLC analysis. N.D., not determined.

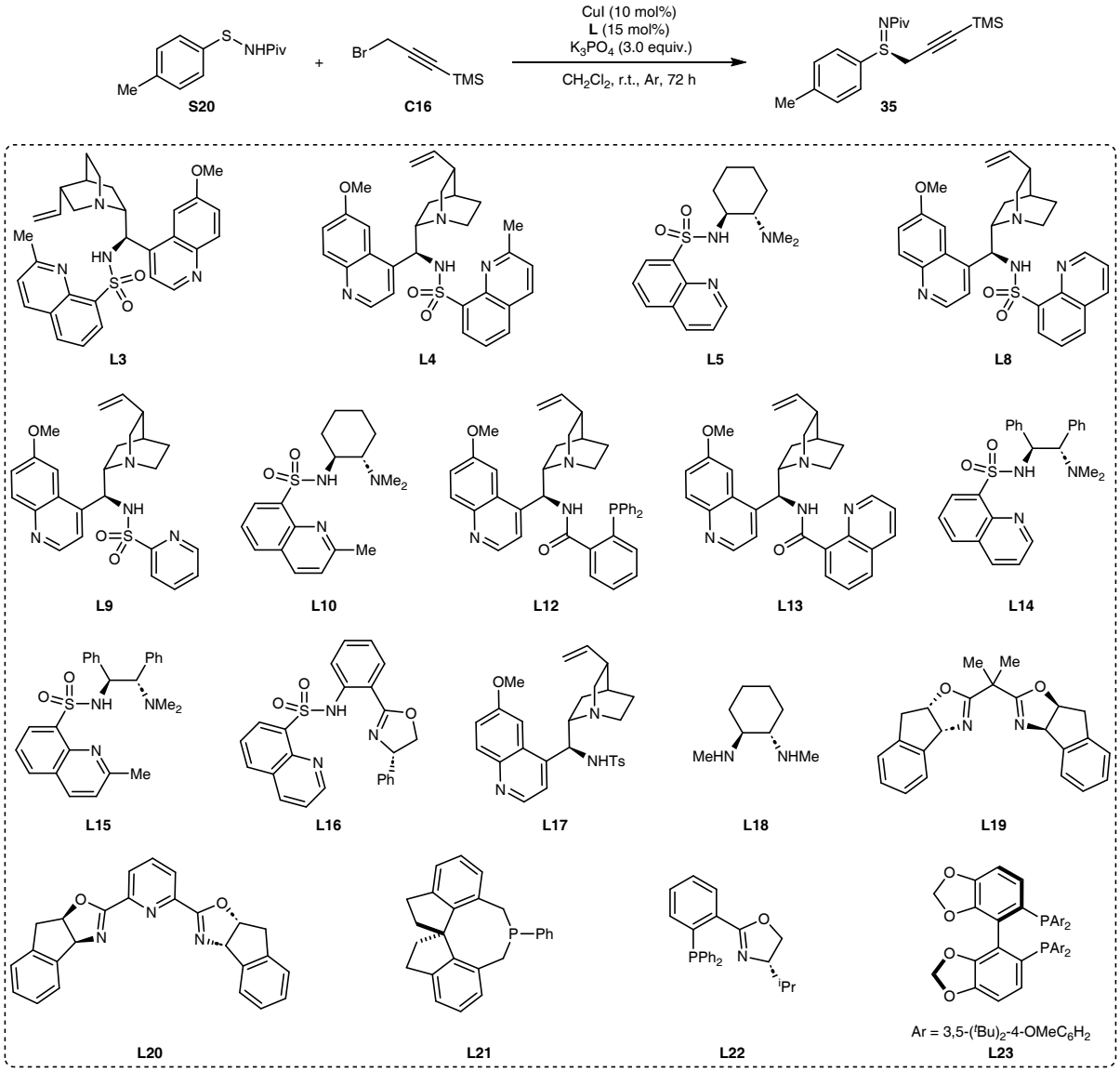
Supplementary Table 6 | Reaction condition optimization with *H*-phosphinate S19 and *O*-benzoylhydroxylamines N1



Entry	Variations	Yield (%)	E.e. (%)
1	None	40	85
2	Without $Cu(OAc)_2$	0	N.D.
3	Without **L8**	trace	N.D.
4	Without Cs_2CO_3	0	N.D.
5	Without $Cu(OAc)_2$ and **L8**	0	N.D.
6	CuI instead of $Cu(OAc)_2$	11	60
7	CuCN instead of $Cu(OAc)_2$	15	71
8	**L4** instead of **L8**	21	72
9	**L10** instead of **L8**	14	0
10	**L13** instead of **L8**	16	5
11	Na_2CO_3 instead of Cs_2CO_3	0	N.D.
12	K_3PO_4 instead of Cs_2CO_3	0	N.D.
13	NaO^tBu instead of Cs_2CO_3	0	N.D.
14	EtOAc instead of toluene	17	70
15	MTBE instead of toluene	25	80
16	DME instead of toluene	18	78
17	Without H_2O	6	56
18	1.0 equiv. H_2O	10	81
19	4.0 equiv. H_2O	24	82

Reaction conditions: **S19** (0.15 mmol, 1.5 equiv.), **N1** (0.10 mmol, 1.0 equiv.), $Cu(OAc)_2$ (0.010 mmol, 10 mol%), **L8** (0.015 mmol, 15 mol%), H_2O (0.20 mmol, 2.0 equiv.), and Cs_2CO_3 (0.30 mmol, 3.0 equiv.) in toluene (2.0 mL) at r.t. for 72 h under argon. The yields are based on ^{31}P NMR analysis of the crude product using PPh_3 as an internal standard. The e.e. values are based on chiral HPLC analysis. N.D., not determined.

Supplementary Table 7 | Reaction condition optimization with sulfenamide S20 and (3-bromoprop-1-yn-1-yl)trimethylsilane C16: screening of different ligands

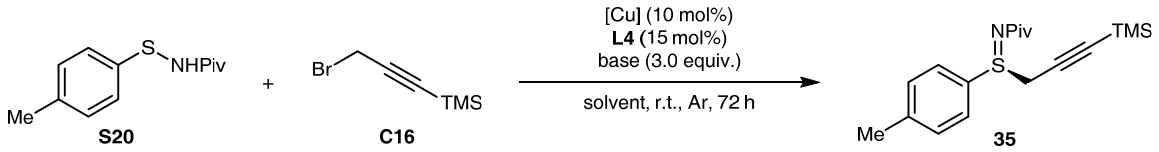


Entry	L	Yield (%)	E.e. (%)
1	**L3**	95	–98
2	**L4**	97	98
3	**L5**	96	70
4	**L8**	86	86
5	**L9**	97	94
6	**L10**	88	94
7	**L12**	81	5
8	**L13**	51	0
9	**L14**	98	86
10	**L15**	75	95

11	**L16**	94	71
12	**L17**	48	80
13	**L18**	27	15
14	**L19**	49	20
15	**L20**	50	0
16	**L21**	35	0
17	**L22**	54	0
18	**L23**	42	0

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **C16** (0.30 mmol, 1.5 equiv.), CuI (0.02 mmol, 10 mol%), **L** (0.03 mmol, 15 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in CH_2Cl_2 (2.0 mL) at r.t. for 72 h under argon. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis.

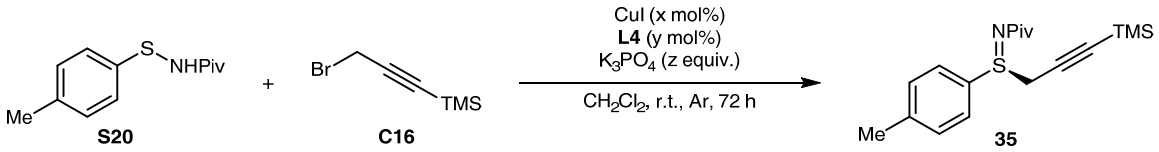
Supplementary Table 8 | Reaction condition optimization with sulfenamide S20 and (3-bromoprop-1-yn-1-yl)trimethylsilane C16: screening of copper, base, and solvent



Entry	[Cu]	Base	Solvent	Yield (%)	E.e. (%)
1	CuI	K_3PO_4	CH_2Cl_2	97	98
2	CuI	Cs_2CO_3	CH_2Cl_2	90	97
3	CuI	K_2CO_3	CH_2Cl_2	90	98
4	CuI	^{t}BuOK	CH_2Cl_2	0	N.D.
5	$CuBH_4(PPh_3)_2$	K_3PO_4	CH_2Cl_2	87	86
6	CuCN	K_3PO_4	CH_2Cl_2	90	98
7	$Cu(OTf)_2$	K_3PO_4	CH_2Cl_2	93	97
8	CuBr	K_3PO_4	CH_2Cl_2	92	98
9	CuI	K_3PO_4	MeCN	88	86
10	CuI	K_3PO_4	EtOAc	89	94
11	CuI	K_3PO_4	MTBE	90	94
12	CuI	K_3PO_4	$PhCF_3$	90	96
13	CuI	K_3PO_4	DMF	30	19

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **C16** (0.30 mmol, 1.5 equiv.), [Cu] (0.02 mmol, 10 mol%), **L4** (0.03 mmol, 15 mol%), and base (0.60 mmol, 3.0 equiv.) in solvent (2.0 mL) at r.t. for 72 h under argon. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis. N.D., not determined.

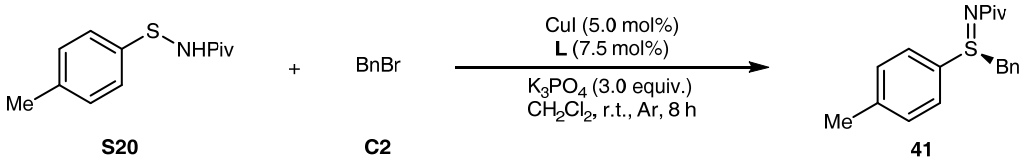
Supplementary Table 9 | Reaction condition optimization with sulfenamide S20 and (3-bromoprop-1-yn-1-yl)trimethylsilane C16: screening of ratio and temperature

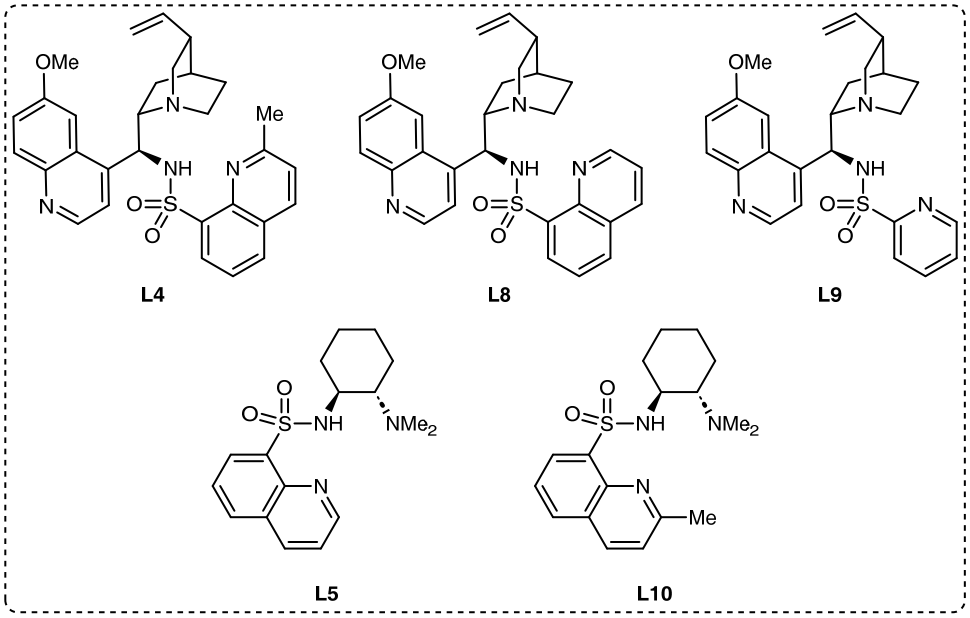


Entry	C16 (equiv.)	x	y	z	Yield (%)	E.e. (%)
1	1.5	10	15	3.0	97	98
2	1.2	10	15	3.0	95	98
3	1.0	10	15	3.0	88	98
4	1.2	10	15	1.5	72	98
5	1.2	10	15	1.0	68	98
6	1.2	5	7.5	3.0	96	98
7	1.2	2.5	3.75	3.0	54	90
8[a]	1.2	5	7.5	3.0	96	96
9[b]	1.2	5	7.5	3.0	80	98

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **C16**, CuI (x mol%), **L4** (y mol%), and K_3PO_4 (z equiv.) in CH_2Cl_2 (2.0 mL) at r.t. for 72 h under argon. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis. [a]Conducted at 40 °C. [b]Conducted at 10 °C.

Supplementary Table 10 | Reaction condition optimization with sulfenamide S20 and benzyl bromide C2: screening of ligand

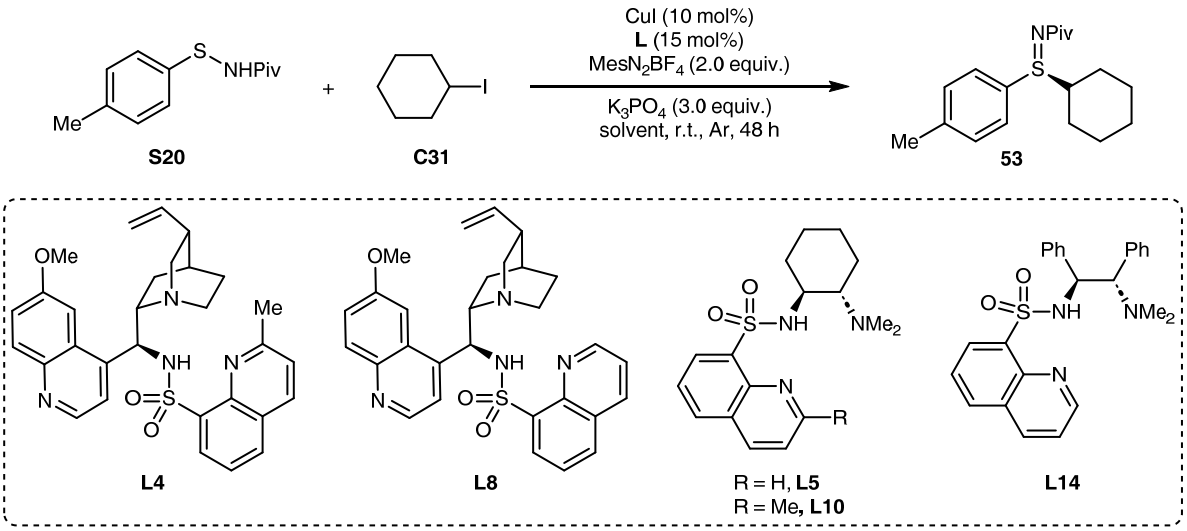




Entry	L	Yield (%)	E.e. (%)
1	**L4**	89	21
2	**L8**	68	70
3	**L9**	95	93
4	**L5**	86	71
5	**L10**	89	78

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **C2** (0.24 mmol, 1.2 equiv.), CuI (0.010 mmol, 5.0 mol%), **L** (0.010 mmol, 7.5 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in CH_2Cl_2 (2.0 mL) at r.t. for 8 h under argon. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis.

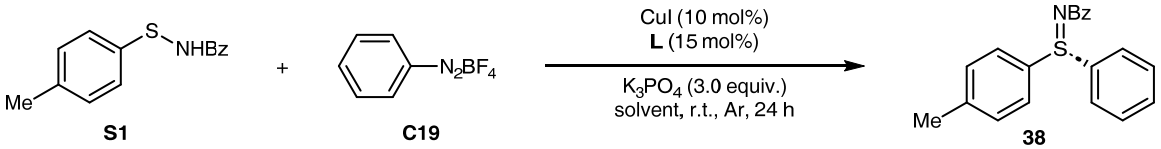
Supplementary Table 11 | Reaction condition optimization with sulfenamide S20 and cyclohexyl iodide C31: screening of ligand and solvent

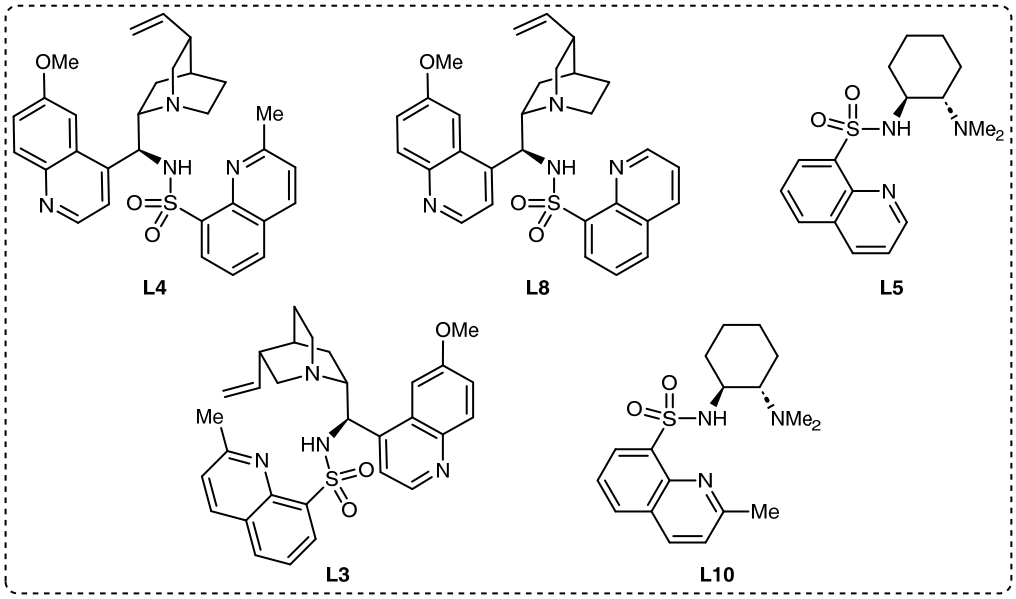


Entry	L	Solvent	Yield (%)	E.e. (%)
1	**L4**	CH_2Cl_2	0	N.D.
2	**L4**	MeCN	0	N.D.
3	**L4**	EtOAc	21	45
4	**L4**	PhF	12	66
5	**L4**	Cyclohexane	62	72
6	**L4**	$^{i}Pr_2O$	60	70
7	**L4**	MTBE	75	73
8	**L4**	DME	trace	N.D.
9	**L4**	THF	23	68
10	**L5**	MTBE	95	92
11	**L8**	MTBE	86	88
12	**L10**	MTBE	82	89
13	**L14**	MTBE	80	83

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **C31** (0.30 mmol, 1.5 equiv.), CuI (0.02 mmol, 10 mol%), **L** (0.03 mmol, 15 mol%), $MesN_2BF_4$ (0.40 mmol, 2.0 equiv.), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in solvent (4.0 mL) at r.t. for 48 h under argon. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis. N.D., not determined.

Supplementary Table 12 | Reaction condition optimization with sulfenamide S1 and benzenediazonium tetrafluoroborate C19: screening of ligand and solvent

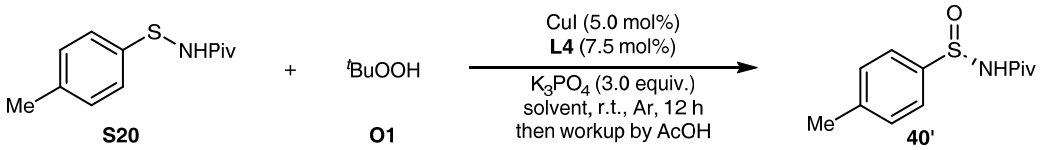




Entry	L	Solvent	Yield (%)	E.e. (%)
1	**L4**	PhF	15	–81
2	**L8**	PhF	18	–83
3	**L5**	PhF	20	–75
4	**L3**	PhF	21	86
5	**L10**	PhF	16	–81
6	**L3**	MeCN	21	28
7	**L3**	MTBE	6	0
8[a]	**L3**	PhF	22	91
9[a,b]	**L3**	PhF	40	94
10[a,c]	**L3**	PhF	55	95

Reaction conditions: **S1** (0.20 mmol, 1.0 equiv.), **C19** (0.30 mmol, 1.5 equiv.), CuI (0.02 mmol, 10 mol%), **L** (0.03 mmol, 15 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in solvent (2.0 mL) at r.t. for 24 h under argon. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis. [a]CuI, ligand, K_3PO_4, and PhF were premixed at 50 °C under Ar for 1 h. [b]CuI (0.04 mmol, 20 mol%), **L3** (0.06 mmol, 30 mol%). [c]CuI (0.06 mmol, 30 mol%), **L3** (0.09 mmol, 45 mol%).

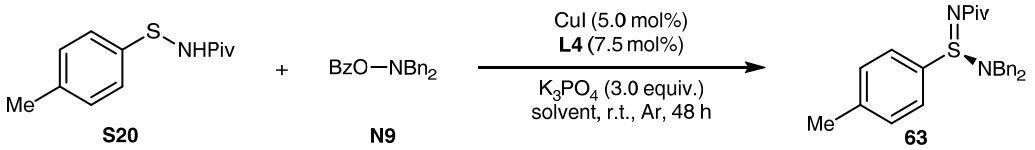
Supplementary Table 13 | Reaction condition optimization with sulfenamide S20 and *tert*-butyl hydroperoxide O1: screening of solvent and temperature



Entry	Solvent	Yield (%)	E.e. (%)
1	CH_2Cl_2	70	52
2	EtOAc	70	34
3	PhF	83	60
4	MTBE	33	36
5	MeCN	87	65
6[a]	MeCN	90	90
7[b]	MeCN	97	96

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.), CuI (0.010 mmol, 5.0 mol%), **L4** (0.015 mmol, 7.5 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in solvent (2.0 mL) at r.t. for 12 h under argon. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis. [a]Conducted at 0 °C for 18 h. [b]Conducted at −10 °C for 36 h.

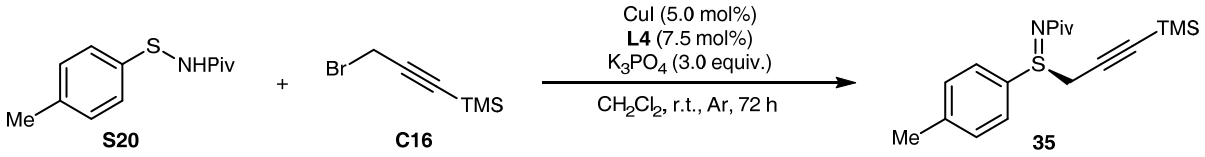
Supplementary Table 14 | Reaction condition optimization with sulfenamide S20 and *O*-benzoylhydroxylamines N9: screening of solvent



Entry	Solvent	Yield (%)	E.e. (%)
1	CH_2Cl_2	71	85
2	EtOAc	93	98
3	PhH	48	95
4	MTBE	87	98
5	$CHCl_3$	75	74
6	*n*-Hexane	0	N.D.
7	DMF	66	98
8	MeOH	6	96

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **N9** (0.30 mmol, 1.5 equiv.), CuI (0.010 mmol, 5.0 mol%), **L4** (0.015 mmol, 7.5 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in solvent (2.0 mL) for 48 h under argon. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis. N.D., not determined.

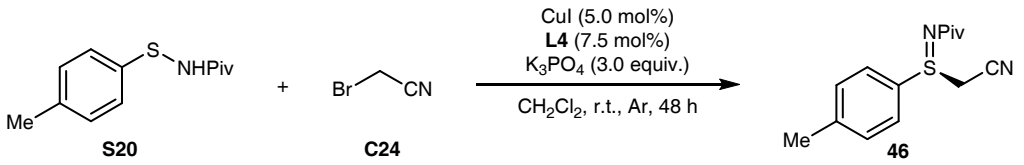
Supplementary Table 15 | Control experiments with sulfenamide S20 and 3-(trimethylsilyl)-propargyl bromide C16:



Entry	CuI	L4	K_3PO_4	Yield (%)	E.e. (%)
1	√	√	√	96	98
2	√	×	√	0	N.D.
3[a]	×	√	√	67	0
4	√	√	×	0	N.D.
5	×	×	√	0	N.D.

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **C16** (0.24 mmol, 1.2 equiv.), CuI (0.010 mmol, 5.0 mol%), **L4** (0.015 mmol, 7.5 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) for 72 h under argon. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis. [a]This result may be caused by quaternary ammonium salt in situ generated from **L3** and **C16**, which work as phase-transfer catalysis to promote the reaction, and a similar mechanism was reported in the previous literature[46]. n.d., not determined.

Supplementary Table 16 | Control experiments with sulfenamide S20 and bromoacetonitrile C24:



Entry	CuI	L4	K_3PO_4	Yield (%)	E.e. (%)
1	√	√	√	90	97
2	√	×	√	0	N.D.
3	×	√	√	0	N.D.
4	√	√	×	0	N.D.
5	×	×	√	0	N.D.

Reaction conditions: **S20** (0.20 mmol, 1.0 equiv.), **C24** (0.30 mmol, 1.5 equiv.), CuI (0.010 mmol, 5.0 mol%), **L4** (0.015 mmol, 7.5 mol%), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in CH_2Cl_2 (2.0 mL) for 48 h under argon. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The e.e. values are based on HPLC analysis. N.D., not determined.

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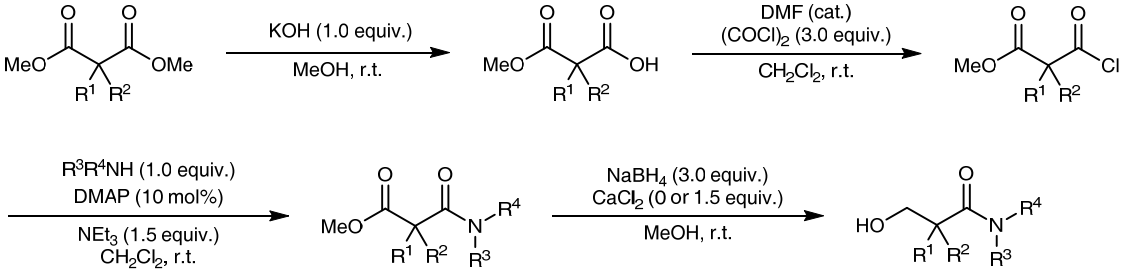
3. General Information

Most of the reactions were carried out under an argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated. CH_2Cl_2, THF, and DMF were purified and dried using a solvent-purification system that contained activated alumina under argon. CuI was purchased from Sigma-Aldrich. K_3PO_4 was purchased from J&K Scientific. Anhydrous CH_2Cl_2, MeCN, EtOAc, MTBE, and fluorobenzene were purchased from J&K Scientific. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). As the eluent, the petroleum ether (PE), ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), and methanol (CH_3OH) were purchased from Shanghai Titan Scientific Co. Ltd without further purification. Visualization on TLC was achieved by the use of UV light (254 nm), iodine on silica gel, or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, and 375 MHz for ^{19}F NMR, respectively, in $CDCl_3$, with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quart; p, pentet, m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (e.e.) was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector (at appropriate wavelength) or SHIMADZU LC-20AD with SPD-20AV detector or Waters instrument. Column conditions are reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα or Mo–Kα radiation.

4. Synthesis of γ-aminocarbonyl alcohols, *H*-phosphinates, and sulfenamides

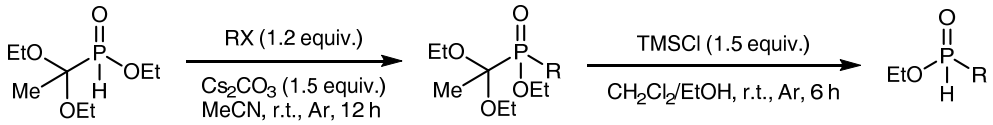


General procedure 1:

According to the literature reported procedure[47] with slight modification. A solution of KOH (1.12 g, 20 mmol) in MeOH (20 mL) was added to a stirred solution of methyl malonate (20 mmol) in MeOH (10 mL). The reaction mixture was stirred at r.t. for 24 h and then diluted with H_2O (50 mL) and extracted with EtOAc (3 x 20 mL). The aqueous layer was acidified to pH ca. 1-2 with 6 N HCl and extracted with CH_2Cl_2 (6 x 50 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$) and concentrated under reduced pressure to provide crude acid which was dissolved in CH_2Cl_2 (50 mL). Oxalyl chloride (7.62 g, 60 mmol) was added dropwise, followed by several drops of anhydrous DMF. The resulting mixture was stirred at r.t. for 3 h and then the reaction mixture was concentrated under reduced pressure to yield crude acid chloride, which was used in the next step without further purification.

Crude acid chloride (20 mmol) in anhydrous CH_2Cl_2 (20 mL) was dissolved in anhydrous CH_2Cl_2 (20 mL) and the resultant solution was cooled to 0 °C. Dry NEt_3 (3.04 g, 30 mmol) and DAMP (244.4 mg, 10 mol%) were added, followed by a solution of amine (20 mmol) in dry CH_2Cl_2 (20 mL). The reaction mixture was stirred at r.t. for 16 h. Upon completion (monitored by TLC), the reaction was quenched with H_2O, and extracted with CH_2Cl_2 three times (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired amide product.

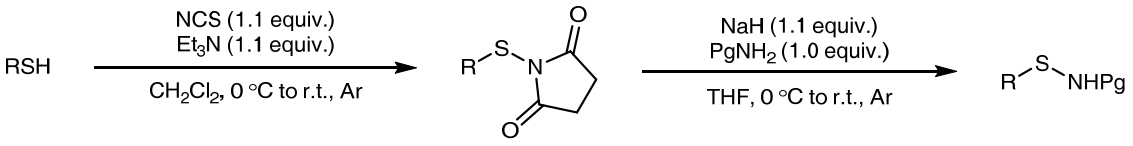
According to the literature reported procedure[48] with slight modification. Sodium borohydride (3.0 equiv.) was added to a suspension of the amide (1.0 equiv.) and calcium chloride (0 or 1.5 equiv.) in MeOH (0.2 M) at 0 °C and the resulting mixture gradually warmed to r.t. and stirred overnight. Upon completion (monitored by TLC), the reaction was quenched with sat. NH_4Cl (aq.), and extracted with CH_2Cl_2 three times (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired alcohol product.



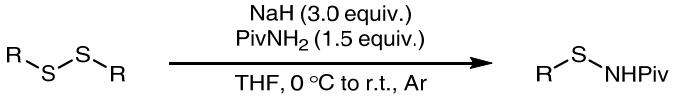
General procedure 2:

To a solution of Ciba–Geigy reagent ethyl (1,1-diethoxyethyl)-*H*-phosphinate (4.2 g, 20 mmol, 1.0 equiv.) in anhydrous MeCN (50 mL) was added R–X (24.0 mmol, 1.2 equiv.) and Cs_2CO_3 (1.5 equiv.) at 0 °C under an argon atmosphere. Then, the reaction mixture was stirred at r.t. for

overnight. Upon completion (monitored by TLC), the reaction was quenched with H_2O and extracted with EtOAc three times (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the alkylation phosphinate.
According to the literature reported procedure[49] with slight modification. To a solution of alkylation phosphinate (8.0 mmol) in 20 mL of 10% ethanol in dichloromethane was added chlorotrimethylsilane (12.0 mmol, 1.5 equiv.) under Ar and the clear solution was stirred for 16 h at r.t.. The solvent was removed in vacuo and the resulting oil was purified by column chromatography on silica gel to afford the desired product.

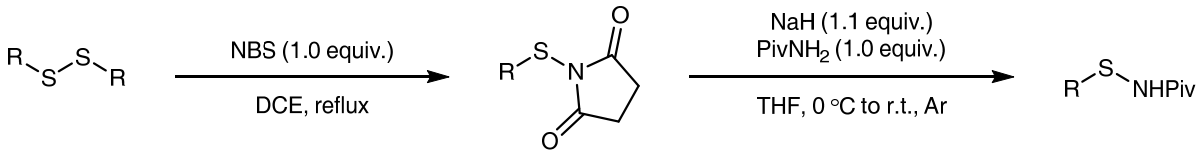


General procedure 3:
According to the literature reported procedure[50] with slight modification. To a solution of thiol (10.0 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.2 M, 50 mL) was added *N*-chlorosuccinimide (NCS) (11.0 mmol, 1.1 equiv.) slowly at 0 °C under an argon atmosphere. Then, the mixture was stirred at r.t. for 0.5 h. After that, triethylamine (11.0 mmol, 1.1 equiv.) was slowly added into the mixture under an ice bath, and the reaction mixture was stirred at r.t. overnight. Upon completion (monitored by TLC), the reaction was quenched with sat. $NaHCO_3$ aqueous solution and extracted with EtOAc three times (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was directly used in the next step without further purification.
To a solution of amide (1.0 equiv.) in anhydrous THF (0.33 M) was added sodium hydride (60% in mineral oil, 1.1 equiv.) slowly at 0 °C under an argon atmosphere. The reaction mixture was stirred at r.t. for 0.5 h. To the resulting solution was added the crude residue (1.0 equiv.) slowly at 0 °C, and then the reaction mixture was stirred at r.t. overnight. Upon completion (monitored by TLC), the reaction was quenched with sat. $NaHCO_3$ aqueous solution, and extracted with EtOAc three times (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.



General procedure 4:
According to the literature reported procedure[51] with slight modification. To a solution of pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.) in anhydrous THF (100 mL) was added sodium hydride (60% in mineral oil, 1.20 g, 30.0 mmol, 3.0 equiv.) slowly at 0 °C under an argon atmosphere. The reaction mixture was stirred at r.t. for 0.5 h. After that, disulfide (10.0 mmol, 1.0 equiv.) was slowly added into the mixture at 0 °C, and then the reaction mixture was stirred at r.t. overnight. Upon completion (monitored by TLC), the reaction was quenched with a sat. NH_4Cl aqueous solution and extracted with EtOAc three times (3 × 50 mL). The combined organic layers were washed

with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

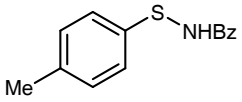


General procedure 5:

According to the literature reported procedure[52] with slight modification. To a solution of disulfides (10 mmol, 1.0 equiv.) in DCE (50 mL) was added *N*-bromosuccinimide (NBS, 10.0 mmol, 1.0 equiv.) at r.t. under an argon atmosphere. The reaction mixture was refluxed overnight. Upon completion (monitored by TLC), the reaction was cooled to r.t., quenched with sat. $NaHCO_3$ aqueous solution, and extracted with EtOAc three times (3×50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was directly used in the next step without further purification.

To a solution of pivalamide (1.0 equiv.) in anhydrous THF (0.33 M) was added sodium hydride (60% in mineral oil, 1.1 equiv.) slowly at 0 °C under an argon atmosphere. The reaction mixture was stirred at r.t. for 0.5 h. After that, to the resulting solution was added the crude product (1.0 equiv.) slowly at 0 °C. The reaction mixture was stirred at r.t. overnight. Upon completion (monitored by TLC), the reaction was quenched with sat. NH_4Cl aqueous solution and extracted with EtOAc three times (3×50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

***N*-(*p*-Tolylthio)benzamide (S1)**

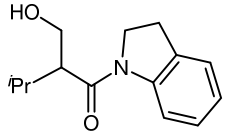


According to **General procedure 3** with methyl 4-methylbenzenethiol (1.24 g, 10 mmol, 1.0 equiv.) and benzamide (1.09 g, 9.0 mmol, 0.9 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.68 g, 69% overall yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 2H), 7.59 – 7.50 (m, 1H), 7.48 – 7.37 (m, 3H), 7.34 – 7.30 (m, 2H), 7.13 – 7.09 (m, 2H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 137.5, 135.1, 133.4, 132.3, 129.8, 128.7, 127.8, 127.2, 21.2.

2-(Hydroxymethyl)-1-(indolin-1-yl)-3-methylbutan-1-one (S2)



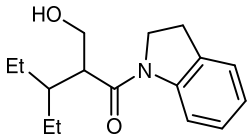
According to **General procedure 1** with 2-isopropylmalonic acid dimethyl ester (1.74 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.05 g, 45% overall yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.0 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.06 – 6.99 (m, 1H), 4.24 – 4.07 (m, 2H), 3.96 (dd, J = 10.9, 7.3 Hz, 1H), 3.84 (dd, J = 10.9, 3.4 Hz, 1H), 3.17 (t, J = 8.5 Hz, 2H), 2.90 (s, 1H), 2.63 – 2.54 (m, 1H), 2.26 – 2.11 (m, 1H), 1.08 – 0.94 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 142.8, 131.7, 127.6, 124.7, 124.1, 117.7, 62.2, 53.3, 48.8, 28.3, 28.0, 21.4, 20.1.

HRMS (ESI) m/z calcd. for $C_{14}H_{20}NO_2$ $[M + H]^+$ 234.1489, found 234.1489.

3-Ethyl-2-(hydroxymethyl)-1-(indolin-1-yl)pentan-1-one (S3)



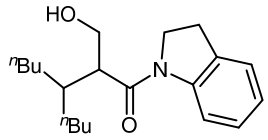
According to **General procedure 1** with dimethyl 2-(pentan-3-yl)malonate (2.02 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.05 g, 40% overall yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.0 Hz, 1H), 7.24 – 7.14 (m, 2H), 7.09 – 6.93 (m, 1H), 4.28 – 4.16 (m, 1H), 4.16 – 4.06 (m, 1H), 4.03 – 3.91 (m, 1H), 3.78 (dt, J = 11.8, 3.7 Hz, 1H), 3.17 (q, J = 7.6, 7.0 Hz, 2H), 3.01 – 2.60 (m, 2H), 1.90 – 1.79 (m, 1H), 1.68 – 1.56 (m, 1H), 1.46 – 1.28 (m, 3H), 0.95 – 0.81 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 142.9, 131.6, 127.6, 124.7, 124.1, 117.7, 61.7, 48.9, 48.6, 40.0, 28.1, 23.2, 21.3, 11.6, 10.1.

HRMS (ESI) m/z calcd. for $C_{16}H_{24}NO_2$ $[M + H]^+$ 262.1802, found 262.1802.

3-Butyl-2-(hydroxymethyl)-1-(indolin-1-yl)heptan-1-one (S4)



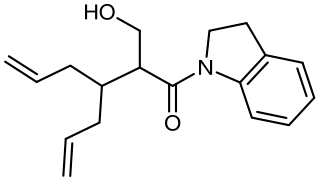
According to **General procedure 1** with dimethyl 2-(nonan-5-yl)malonate (2.58 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a colorless oil (0.95 g, 30% overall yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.08 – 6.99 (m, 1H), 4.26 – 4.15 (m, 1H), 4.15 – 4.06 (m, 1H), 4.04 – 3.96 (m, 1H), 3.77 (dd, *J* = 11.0, 3.3 Hz, 1H), 3.25 – 3.11 (m, 2H), 2.86 (td, *J* = 7.8, 3.4 Hz, 1H), 2.77 (s, 1H), 1.98 – 1.85 (m, 1H), 1.59 – 1.47 (m, 1H), 1.45 – 1.06 (m, 11H), 0.93 – 0.82 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 143.0, 131.6, 127.6, 124.7, 124.1, 117.7, 61.5, 49.7, 48.5, 37.5, 31.2, 29.5, 29.3, 28.5, 28.2, 23.2, 23.1, 14.2.

HRMS (ESI) m/z calcd. for $C_{20}H_{32}NO_2$ $[M + H]^+$ 318.2428, found 318.2428.

3-Allyl-2-(hydroxymethyl)-1-(indolin-1-yl)hex-5-en-1-one (S5)



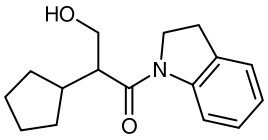
According to General procedure **1** with dimethyl 2-(hepta-1,6-dien-4-yl)malonate (2.26 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.14 g, 40% overall yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.08 – 6.99 (m, 1H), 5.86 – 5.70 (m, 2H), 5.15 – 4.98 (m, 4H), 4.20 – 4.04 (m, 2H), 3.99 (dd, *J* = 11.0, 7.3 Hz, 1H), 3.84 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.15 (t, *J* = 8.4 Hz, 2H), 2.89 – 2.79 (m, 1H), 2.38 (dd, *J* = 12.7, 6.0 Hz, 1H), 2.20 – 2.07 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 142.8, 136.4, 135.7, 131.7, 127.6, 124.7, 124.2, 117.7, 117.5, 117.3, 61.5, 48.6(2), 48.5(7), 37.1, 35.6, 33.9, 28.0.

HRMS (ESI) m/z calcd. for $C_{18}H_{24}NO_2$ $[M + H]^+$ 286.1802, found 286.1802.

2-Cyclopentyl-3-hydroxy-1-(indolin-1-yl)propan-1-one (S6)

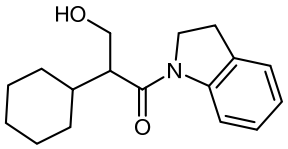


According to **General procedure 1** with dimethyl 2-cyclopentylmalonate (2.0 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (0.91 g, 35% overall yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.11 (m, 2H), 7.07 – 6.93 (m, 1H), 4.23 (dt, *J* = 10.2, 8.3 Hz, 1H), 4.17 – 4.06 (m, 1H), 3.93 (dd, *J* = 10.7, 7.7 Hz, 1H), 3.83 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.14 (t, *J* = 8.5 Hz, 2H), 2.98 (s, 1H), 2.77 – 2.68 (m, 1H), 2.30 – 2.18 (m, 1H), 1.94 – 1.77 (m, 2H), 1.71 – 1.48 (m, 4H), 1.26 – 1.16 (m, 2H).

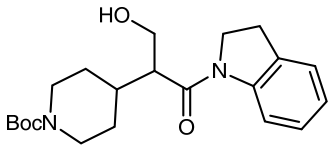
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 142.8, 131.8, 127.6, 124.7, 124.1, 117.6, 63.8, 52.1, 48.8, 40.3, 31.3, 30.6, 28.0, 24.9, 24.8.
HRMS (ESI) m/z calcd. for $C_{16}H_{22}NO_2$ $[M + H]^+$ 260.1645, found 260.1645.

2-Cyclohexyl-3-hydroxy-1-(indolin-1-yl)propan-1-one (S7)



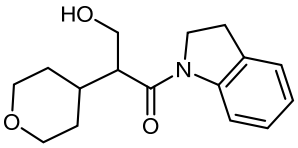
According to **General procedure 1** with dimethyl 2-cyclohexylmalonate (2.14 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.18 g, 43% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.0 Hz, 1H), 7.24 – 7.14 (m, 2H), 7.07 – 6.99 (m, 1H), 4.22 – 4.06 (m, 2H), 3.97 (dd, J = 10.9, 7.1 Hz, 1H), 3.83 (dd, J = 10.8, 3.3 Hz, 1H), 3.16 (t, J = 8.5 Hz, 2H), 3.02 (s, 1H), 2.69 – 2.58 (m, 1H), 1.95 – 1.83 (m, 2H), 1.79 – 1.60 (m, 4H), 1.29 – 0.95 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 142.7, 131.7, 127.6, 124.7, 124.1, 117.6, 61.9, 52.4, 48.8, 37.7, 31.8, 30.5, 28.0, 26.4, 26.3.
HRMS (ESI) m/z calcd. for $C_{17}H_{24}NO_2$ $[M + H]^+$ 274.1802, found 274.1802.

***tert*-Butyl 4-(3-hydroxy-1-(indolin-1-yl)-1-oxopropan-2-yl)piperidine-1-carboxylate (S8)**



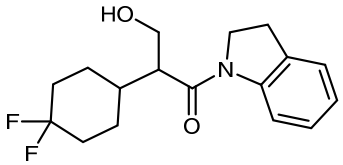
According to **General procedure 1** with dimethyl 2-(1-(*tert*-butoxycarbonyl)piperidin-4-yl)malonate (3.15 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 4/1) to afford the product as a colorless oil (1.47 g, 37% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 7.8 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.13 – 6.94 (m, 1H), 4.26 – 4.04 (m, 4H), 3.99 – 3.91 (m, 1H), 3.90 – 3.82 (m, 1H), 3.17 (t, J = 8.5 Hz, 2H), 3.07 (s, 1H), 2.75 – 2.58 (m, 3H), 2.10 – 2.02 (m, 1H), 1.89 – 1.84 (m, 1H), 1.71 – 1.63 (m, 1H), 1.44 (s, 9H), 1.30 – 1.15 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 154.8, 142.5, 131.7, 127.6, 124.8, 124.4, 117.6, 79.6, 61.6, 51.7, 48.8, 44.98 – 42.61 (br m), 36.0, 30.7, 29.7, 28.6, 28.0.
HRMS (ESI) m/z calcd. for $C_{21}H_{30}N_2NaO_4$ $[M + Na]^+$ 397.2098, found 397.2097.

3-Hydroxy-1-(indolin-1-yl)-2-(tetrahydro-2H-pyran-4-yl)propan-1-one (S9)



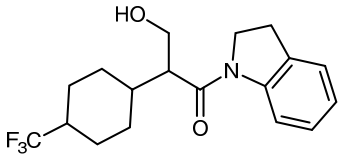
According to **General procedure 1** with dimethyl 2-(tetrahydro-*2H*-pyran-4-yl)malonate (2.16 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 4/1) to afford the product as a colorless oil (0.41 g, 15% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.09 – 6.94 (m, 1H), 4.20 (dt, *J* = 10.1, 8.3 Hz, 1H), 4.09 (dt, *J* = 10.0, 8.5 Hz, 1H), 3.99 – 3.81 (m, 4H), 3.43 – 3.24 (m, 3H), 3.16 (t, *J* = 8.5 Hz, 2H), 2.72 – 2.61 (m, 1H), 2.16 – 2.09 (m, 1H), 1.78 – 1.71 (m, 1H), 1.63 – 1.55 (m, 1H), 1.46 – 1.33 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 142.5, 131.7, 127.4, 124.7, 124.1, 117.5, 67.9, 67.8, 61.5, 52.1, 48.7, 35.0, 31.3, 30.6, 27.8.
HRMS (ESI) m/z calcd. for $C_{16}H_{22}NO_3$ $[M + H]^+$ 276.1594, found 276.1595.

2-(4,4-Difluorocyclohexyl)-3-hydroxy-1-(indolin-1-yl)propan-1-one (S10)



According to **General procedure 1** with dimethyl 2-(4,4-difluorocyclohexyl)malonate (2.50 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.55 g, 50% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.09 – 6.95 (m, 1H), 4.19 (dt, *J* = 10.1, 8.4 Hz, 1H), 4.07 (dt, *J* = 10.0, 8.5 Hz, 1H), 3.91 (dt, *J* = 10.7, 6.8 Hz, 1H), 3.83 (dt, *J* = 10.9, 3.2 Hz, 1H), 3.24 (s, 1H), 3.16 (t, *J* = 8.5 Hz, 2H), 2.70 – 2.60 (m, 1H), 2.12 – 1.92 (m, 4H), 1.83 – 1.62 (m, 3H), 1.44 – 1.27 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 142.5, 131.8, 127.6, 124.8, 124.4, 123.3 (dd, *J* = 242.7, 238.9 Hz), 117.6, 62.0, 51.2 (d, *J* = 2.3 Hz), 48.8, 35.7 (d, *J* = 1.5 Hz), 33.5 (ddd, *J* = 25.7, 22.7, 10.3 Hz), 27.9, 27.6 (d, *J* = 9.8 Hz), 26.4 (d, *J* = 10.0 Hz).
^{19}F NMR (375 MHz, $CDCl_3$) δ −91.54 (d, *J* = 235.3 Hz), −102.90 (d, *J* = 235.6 Hz).
HRMS (ESI) m/z calcd. for $C_{17}H_{22}F_2NO_2$ $[M + H]^+$ 310.1613, found 310.1612.

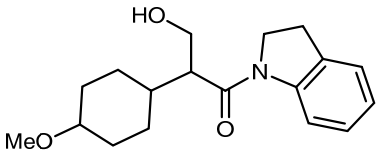
3-Hydroxy-1-(indolin-1-yl)-2-(4-(trifluoromethyl)cyclohexyl)propan-1-one (S11)



According to **General procedure 1** with dimethyl 2-(4-(trifluoromethyl)cyclohexyl)malonate (2.82 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 7/1) to afford the product as a white solid (1.33 g, 39% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.07 – 7.00 (m, 1H), 4.18 (dt, *J* = 10.1, 8.4 Hz, 1H), 4.14 – 4.05 (m, 1H), 3.96 (dd, *J* = 11.0, 7.1 Hz, 1H), 3.84 (dd, *J* = 10.9, 3.3 Hz, 1H), 3.17 (t, *J* = 8.5 Hz, 2H), 2.99 (s, 1H), 2.69 – 2.58 (m, 1H), 2.09 – 1.85 (m, 6H), 1.40 – 1.28 (m, 2H), 1.19 – 1.00 (m, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 142.6, 131.7, 127.7 (q, *J* = 278.7 Hz), 127.6, 124.8, 124.3, 117.6, 61.8, 51.9 (d, *J* = 2.4 Hz), 48.8, 41.9 (q, *J* = 26.6 Hz), 36.8, 29.9, 28.8, 28.0, 24.9 (q, *J* = 2.7 Hz), 24.8 (q, *J* = 2.7 Hz).

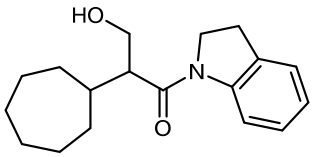
^{19}F NMR (375 MHz, CDCl3) δ −73.88.
HRMS (ESI) m/z calcd. for $C_{18}H_{23}F_3NO_2$ $[M + H]^+$ 342.1675, found 342.1675.

3-Hydroxy-1-(indolin-1-yl)-2-(4-methoxycyclohexyl)propan-1-one (S12)



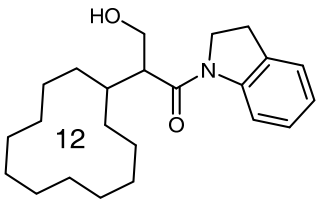
According to **General procedure 1** with dimethyl 2-(4-methoxycyclohexyl)malonate (2.44 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford the product as a colorless oil (1.37 g, 45% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.14 (m, 2H), 7.07 – 6.97 (m, 1H), 4.22 – 4.09 (m, 2H), 3.94 (dd, *J* = 10.9, 6.8 Hz, 1H), 3.85 (dd, *J* = 10.9, 3.2 Hz, 1H), 3.46 – 3.40 (m, 1H), 3.29 (s, 3H), 3.16 (t, *J* = 8.5 Hz, 2H), 3.05 (s, 1H), 2.74 – 2.59 (m, 1H), 2.01 – 1.92 (m, 2H), 1.89 – 1.84 (m, 1H), 1.73 – 1.65 (m, 1H), 1.51 – 1.33 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 142.7, 131.8, 127.6, 124.8, 124.2, 117.6, 74.8, 61.8, 55.8, 51.8, 48.8, 36.8, 29.4, 29.0, 28.0, 25.6, 24.3.
HRMS (ESI) m/z calcd. for $C_{18}H_{26}NO_3$ $[M + H]^+$ 304.1907, found 304.1909.

2-Cycloheptyl-3-hydroxy-1-(indolin-1-yl)propan-1-one (S13)



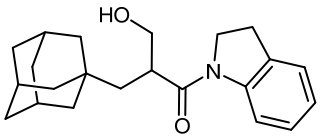
According to **General procedure 1** with dimethyl 2-cycloheptylmalonate (2.28 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.10 g, 38% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.10 – 6.91 (m, 1H), 4.23 – 4.06 (m, 2H), 3.99 (dd, *J* = 10.9, 7.5 Hz, 1H), 3.81 (dd, *J* = 10.9, 3.3 Hz, 1H), 3.17 (t, *J* = 8.5 Hz, 2H), 2.87 (s, 1H), 2.70 (td, *J* = 7.9, 3.3 Hz, 1H), 2.10 – 1.99 (m, 1H), 1.96 – 1.85 (m, 1H), 1.79 – 1.68 (m, 2H), 1.66 – 1.56 (m, 3H), 1.51 – 1.39 (m, 4H), 1.37 – 1.20 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 142.9, 131.7, 127.6, 124.7, 124.1, 117.7, 62.0, 52.7, 48.7, 39.1, 33.0, 31.3, 28.4, 28.3, 28.0, 26.7, 26.4.
HRMS (ESI) m/z calcd. for $C_{18}H_{26}NO_2$ $[M + H]^+$ 288.1958, found 288.1958.

2-Cyclododecyl-3-hydroxy-1-(indolin-1-yl)propan-1-one (S14)



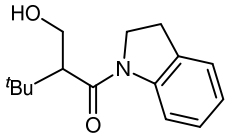
According to **General procedure 1** with dimethyl 2-cyclododecylmalonate (2.98 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (0.72 g, 20% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.06 – 6.99 (m, 1H), 4.27 – 4.17 (m, 1H), 4.15 – 4.05 (m, 1H), 3.96 (dt, *J* = 12.9, 6.8 Hz, 1H), 3.87 – 3.77 (m, 1H), 3.17 (t, *J* = 8.5 Hz, 2H), 2.90 (s, 1H), 2.82 – 2.72 (m, 1H), 2.12 – 1.99 (m, 1H), 1.66 – 1.08 (m, 22H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 142.9, 131.7, 127.6, 124.7, 124.0, 117.7, 62.3, 49.9, 48.7, 35.1, 28.1, 27.6, 25.5, 25.4, 25.3, 25.0, 23.2, 23.1(0), 23.0(6), 23.0, 22.5, 20.6.
HRMS (ESI) m/z calcd. for $C_{23}H_{36}NO_2$ $[M + H]^+$ 358.2741, found 358.2742.

3-(Adamantan-1-yl)-2-(hydroxymethyl)-1-(indolin-1-yl)propan-1-one (S15)



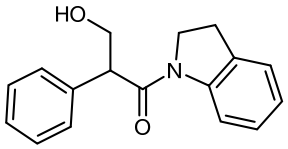
According to **General procedure 1** with dimethyl 2-((adamantan-1-yl)methyl)malonate (2.80 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (0.34 g, 10% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.05 – 6.97 (m, 1H), 4.42 – 4.28 (m, 1H), 4.20 – 4.08 (m, 1H), 3.77 (td, *J* = 9.7, 8.5, 4.2 Hz, 1H), 3.71 – 3.63 (m, 1H), 3.16 (t, *J* = 8.5 Hz, 2H), 3.03 – 2.89 (m, 2H), 1.96 – 1.89 (m, 3H), 1.82 – 1.73 (m, 1H), 1.72 – 1.64 (m, 3H), 1.62 – 1.48 (m, 6H), 1.45 – 1.36 (m, 3H), 1.14 (dd, *J* = 14.3, 3.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 143.2, 131.8, 127.6, 124.7, 123.9, 117.6, 66.2, 48.5, 43.4, 43.0, 41.6, 37.1, 32.7, 28.7, 28.1.
HRMS (ESI) m/z calcd. for $C_{22}H_{30}NO_2$ $[M + H]^+$ 340.2271, found 340.2271.

2-(Hydroxymethyl)-1-(indolin-1-yl)-3,3-dimethylbutan-1-one (S16)



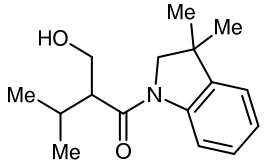
According to **General procedure 1** with dimethyl 2-neopentylmalonate (2.02 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.17 g, 47% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.12 (m, 2H), 7.06 – 6.91 (m, 1H), 4.25 (dt, *J* = 10.0, 8.0 Hz, 1H), 4.17 – 4.05 (m, 2H), 3.79 (dd, *J* = 10.3, 3.8 Hz, 1H), 3.19 – 3.05 (m, 2H), 2.86 – 2.44 (m, 2H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 143.0, 131.9, 127.4, 124.7, 123.8, 117.6, 62.2, 56.0, 49.3, 33.5, 28.5, 28.0.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}NO_2$ $[M + H]^+$ 248.1645, found 248.1645.

3-Hydroxy-1-(indolin-1-yl)-2-phenylpropan-1-one (S17)



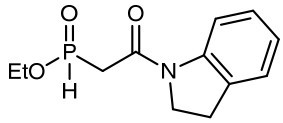
According to **General procedure 1** with dimethyl 2-phenylmalonate (2.08 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.07 g, 40% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.25 (m, 5H), 7.24 – 7.18 (m, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.05 – 6.98 (m, 1H), 4.26 – 4.14 (m, 1H), 4.10 – 3.95 (m, 2H), 3.84 – 3.75 (m, 1H), 3.61 (td, *J* = 10.4, 6.6 Hz, 1H), 3.19 (s, 1H), 3.12 – 3.02 (m, 1H), 2.94 (ddd, *J* = 16.4, 10.5, 6.3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 143.0, 135.5, 131.3, 129.2, 128.4, 127.8, 127.6, 124.7, 124.2, 117.4, 65.8, 54.9, 47.7, 28.0.
HRMS (ESI) m/z calcd. for $C_{17}H_{18}NO_2$ $[M + H]^+$ 268.1332, found 268.1332.

1-(3,3-Dimethylindolin-1-yl)-2-(hydroxymethyl)-3-methylbutan-1-one (S18)



According to **General procedure 1** with 2-isopropylmalonic acid dimethyl ester (1.74 g, 10 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 7/1) to afford the product as a white solid (1.05 g, 40% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.19 – 7.12 (m, 1H), 7.12 – 7.04 (m, 1H), 4.03 – 3.80 (m, 4H), 2.77 (s, 1H), 2.62 – 2.51 (m, 1H), 2.29 – 2.12 (m, 1H), 1.35 (s, 6H), 1.09 – 0.95 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 141.3, 140.9, 127.7, 124.3, 121.9, 117.6, 63.4, 62.1, 53.0, 40.1, 28.6, 28.2, 28.1, 21.3, 20.0.
HRMS (ESI) m/z calcd. for $C_{16}H_{24}NO_2$ $[M + H]^+$ 262.1802, found 262.1801.

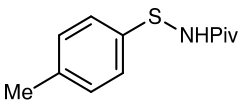
Ethyl (2-(indolin-1-yl)-2-oxoethyl)phosphinate (S19)



According to **General procedure 2** with ethyl (1,1-diethoxyethyl)-*H*-phosphinate (4.20 g, 20 mmol, 1.0 equiv.) and 2-chloro-1-(indolin-1-yl)ethan-1-one (4.70 g, 24.0 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 50/1) to afford the product as a white solid (1.21 g, 36% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.09 (m, 1.5H), 7.23 – 7.13 (m, 2H), 7.09 – 6.97 (m, 1H), 6.73 (t, *J* = 2.0 Hz, 0.5H), 4.64 – 3.67 (m, 4H), 3.50 – 2.58 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 4.0 Hz), 142.3, 131.6, 127.5, 124.7, 124.4, 117.2, 63.3 (d, *J* = 6.4 Hz), 48.9, 38.6 (d, *J* = 90.8 Hz), 27.8, 16.2 (d, *J* = 6.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 30.63.

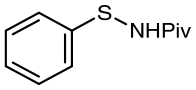
HRMS (ESI) *m/z* calcd. for $C_{12}H_{17}NO_3P$ $[M + H]^+$ 254.0941, found 254.0940.

***N*-(*p*-Tolylthio)pivalamide (S20)**



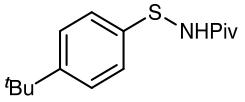
According to **General procedure 3** with 4-methylbenzenethiol (1.24 g, 10 mmol, 1.0 equiv.) and pivalamide (0.91 g, 9.0 mmol, 0.9 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to afford the product as a white solid (1.47 g, 66% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 2H), 7.12 – 7.05 (m, 3H), 2.30 (s, 3H), 1.25 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 137.0, 135.5, 129.7, 126.4, 39.9, 27.7, 21.1.

***N*-(Phenylthio)pivalamide (S21)**



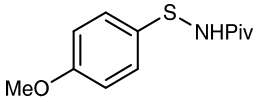
According to **General procedure 4** with 1,2-diphenyldisulfane (2.18 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on Al_2O_3 (PE/EtOAc = 5/1) to afford the product as a white solid (0.13 g, 6% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.25 – 7.15 (m, 3H), 6.90 (s, 1H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 139.1, 129.1, 126.8, 125.2, 40.1, 27.9.

***N*-((4-(*tert*-Butyl)phenyl)thio)pivalamide (S22)**



According to **General procedure 3** with 4-(*tert*-butyl)benzenethiol (1.66 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a white solid (1.11 g, 42% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.23 – 7.15 (m, 2H), 6.94 – 6.86 (m, 1H), 1.29 (s, 9H), 1.27 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 150.3, 135.6, 126.2, 125.9, 40.0, 34.6, 31.4, 27.9.

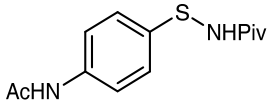
***N*-((4-Methoxyphenyl)thio)pivalamide (S23)**



According to **General procedure 3** with 4-methoxybenzenethiol (1.40 g, 10.0 mmol, 1.0 equiv.) and pivalamide (0.91 g, 9.0 mmol, 0.9 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a pink solid (1.53 g, 64% overall yield).

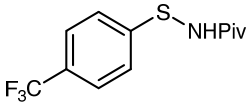
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 6.88 – 6.82 (m, 3H), 3.79 (s, 3H), 1.22 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 160.0, 131.6, 129.6, 114.7, 55.5, 39.9, 27.8.

***N*-((4-Acetamidophenyl)thio)pivalamide (S24)**



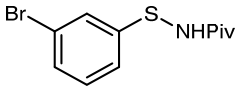
According to **General procedure 3** with *N*-(4-mercaptophenyl)acetamide (2.51 g, 15.0 mmol, 1.0 equiv.) and pivalamide (0.76 g, 7.5 mmol, 0.5 equiv.), the reaction mixture was purified by column chromatography on Al_2O_3 (PE/EtOAc = 1/1) to afford the product as a white solid (0.60 g, 15% overall yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.52 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 2.10 (s, 3H), 1.24 (s, 9H).
^{13}C NMR (100 MHz, CD_3OD) δ 183.4, 171.6, 138.9, 135.4, 127.6, 121.6, 40.9, 27.9, 23.8.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{19}N_2O_2S$ $[M + H]^+$ 267.1162, found 267.1159.

***N*-((4-(Trifluoromethyl)phenyl)thio)pivalamide (S25)**



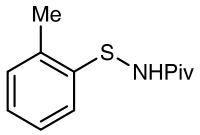
According to **General procedure 3** with 4-(trifluoromethyl)benzenethiol (1.78 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a white solid (1.36 g, 49% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 6.87 (s, 1H), 1.33 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 144.3 – 144.2 (m), 128.4 (q, J = 32.8 Hz), 126.0 (q, J = 3.8 Hz), 124.1 (d, J = 271.9 Hz), 123.4, 40.2, 27.9.
^{19}F NMR (375 MHz, $CDCl_3$) δ −62.48.

***N*-((3-Bromophenyl)thio)pivalamide (S26)**



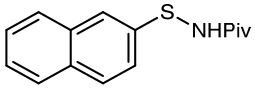
According to **General procedure 3** with 3-bromobenzenethiol (5.00 g, 26.4 mmol, 1.0 equiv.) and pivalamide (2.40 g, 23.8 mmol, 0.9 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (2.51 g, 33% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.19 – 7.09 (m, 2H), 6.87 (s, 1H), 1.31 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 141.5, 130.5, 129.6, 127.1, 123.2, 123.1, 40.2, 27.9.

***N*-(*o*-Tolylthio)pivalamide (S27)**



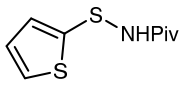
According to **General procedure 3** with 2-methylbenzenethiol (1.24 g, 10.0 mmol, 1.0 equiv.) and pivalamide (0.91 g, 9.0 mmol, 0.9 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to afford the product as a white solid (1.70 g, 76% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.02 (m, 4H), 6.76 (s, 1H), 2.32 (s, 3H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 137.5, 133.7, 130.4, 126.7, 126.2, 123.5, 40.2, 27.9, 19.1.

***N*-(Naphthalen-2-ylthio)pivalamide (S28)**



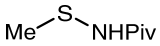
According to **General procedure 3** with naphthalene-2-thiol (1.6 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a white solid (1.71 g, 66% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.74 – 7.69 (m, 1H), 7.68 – 7.63 (m, 1H), 7.50 – 7.39 (m, 2H), 7.38 – 7.31 (m, 1H), 6.98 (s, 1H), 1.31 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 136.4, 133.6, 132.4, 129.0, 127.9, 127.5, 126.9, 126.2, 124.0, 123.7, 40.2, 27.9.

***N*-(Thiophen-2-ylthio)pivalamide (S29)**



According to **General procedure 3** with thiophene-2-thiol (2.32 g, 20.0 mmol, 1.0 equiv.) and pivalamide (1.66 g, 16.4 mmol, 0.82 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to afford the product as a yellow solid (1.60 g, 37% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 5.3 Hz, 1H), 7.38 (d, J = 3.0 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.82 (s, 1H), 1.18 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 136.8, 135.5, 132.2, 127.4, 39.9, 27.7.

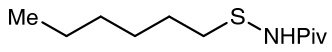
***N*-(Methylthio)pivalamide (S30)**



According to **General procedure 5** with 1,2-dimethyldisulfane (0.94 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a yellow solid (0.44 g, 30% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 1H), 2.41 (s, 3H), 1.22 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 39.8, 27.8, 23.1.

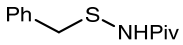
HRMS (ESI) *m/z* calcd. for $C_6H_{14}NOS$ $[M + H]^+$ 148.0791, found 148.0786.

***N*-(Hexylthio)pivalamide (S31)**



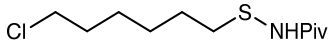
According to **General procedure 3** with hexane-1-thiol (1.18 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a yellow liquid (1.10 g, 51% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H), 2.73 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.49 (m, 2H), 1.45 – 1.34 (m, 2H), 1.34 – 1.25 (m, 4H), 1.23 (s, 9H), 0.93 – 0.81 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 39.7, 38.2, 31.3, 28.2, 27.6, 27.5, 22.4, 13.9.

***N*-(Benzylthio)pivalamide (S32)**



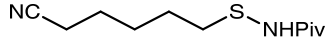
According to **General procedure 3** with phenylmethanethiol (1.24 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a light yellow solid (1.39 g, 62% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 5H), 6.16 (s, 1H), 3.93 (s, 2H), 1.14 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 136.3, 129.5, 128.6, 127.4, 42.0, 39.8, 27.7.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NOS$ $[M + H]^+$ 224.1104, found 224.1098.

***N*-((6-Chlorohexyl)thio)pivalamide (S33)**



According to **General procedure 3** with 6-chlorohexane-1-thiol (1.53 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a colorless liquid (1.08 g, 43% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H), 3.65 (t, *J* = 6.4 Hz, 1H), 2.71 (t, *J* = 7.4 Hz, 1H), 1.82 – 1.72 (m, 2H), 1.63 – 1.52 (m, 2H), 1.49 – 1.39 (m, 4H), 1.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 45.1, 39.9, 38.5, 32.5, 27.9, 27.8, 27.5, 26.6.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{21}ClNOS$ $[M + H]^+$ 252.1183, found 252.1177.

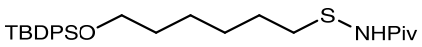
***N*-((5-Cyanopentyl)thio)pivalamide (S34)**



According to **General procedure 3** with 6-mercaptohexanenitrile (1.29 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a brown liquid (0.96 g, 42% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 1H), 2.89 – 2.64 (m, 2H), 2.38 (t, *J* = 6.8 Hz, 2H), 1.80 – 1.44 (m, 6H), 1.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 119.7, 39.8, 38.2, 27.7, 27.4, 26.7, 24.9, 17.0.

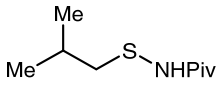
HRMS (ESI) *m/z* calcd. for $C_{11}H_{21}N_2OS$ $[M + H]^+$ 229.1369, found 229.1364.

***N*-((6-((*tert*-Butyldiphenylsilyl)oxy)hexyl)thio)pivalamide (S35)**



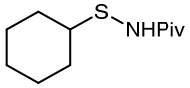
According to **General procedure 3** with 6-((*tert*-butyldiphenylsilyl)oxy)hexane-1-thiol (3.73 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a white solid (2.07 g, 44% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.60 (m, 4H), 7.48 – 7.31 (m, 6H), 6.47 – 6.33 (m, 1H), 3.65 (t, *J* = 6.4 Hz, 1H), 2.71 (t, *J* = 7.4 Hz, 1H), 1.64 – 1.46 (m, 4H), 1.46 – 1.32 (m, 4H), 1.22 (s, 9H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 135.6, 134.1, 129.6, 127.6, 63.8, 39.8, 38.4, 32.4, 28.5, 27.8, 27.6, 26.9, 25.4, 19.3.
HRMS (ESI) *m/z* calcd. for $KC_{27}H_{41}NO_2SSi$ $[M + K]^+$ 472.2700, found 472.2690.

***N*-(Isobutylthio)pivalamide (S36)**



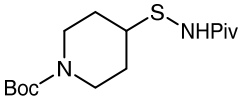
According to **General procedure 3** with 2-methylpropane-1-thiol (0.90 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a white solid (0.66 g, 35% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H), 2.63 (d, *J* = 6.8 Hz, 2H), 1.94 – 1.75 (m, 1H), 1.23 (s, 9H), 1.03 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 47. 8, 39.9, 27.8, 27.4, 22.0.
HRMS (ESI) *m/z* calcd. for $C_9H_{20}NOS$ $[M + H]^+$ 190.1260, found 190.1254.

***N*-(Cyclohexylthio)pivalamide (S37)**



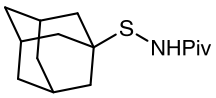
According to **General procedure 3** with cyclohexanethiol (1.16 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a white solid (1.12 g, 52% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 – 6.29 (s, 1H), 3.06 – 2.94 (m, 1H), 1.94 – 1.85 (m, 2H), 1.83 – 1.70 (m, 2H), 1.69 – 1.57 (m, 1H), 1.37 – 1.24 (m, 5H), 1.24 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 48.6, 40.0, 30.9, 27.9, 25.9, 25.8.

***tert*-Butyl 4-(pivalamidothio)piperidine-1-carboxylate (S38)**



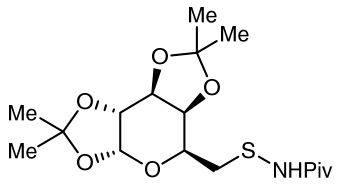
According to **General procedure A** with *tert*-butyl 4-mercaptopiperidine-1-carboxylate (2.17 g, 10.0 mmol, 1.0 equiv.) and pivalamide (0.91 g, 9.0 mmol, 0.9 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.68 g, 53% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (s, 1H), 4.06 – 4.01 (m, 2H), 3.11 (tt, *J* = 10.8, 3.9 Hz, 1H), 2.85 (t, *J* = 12.3 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.48 – 1.41 (m, 11H), 1.24 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 154.7, 79.8, 46.4, 44.1 – 42.3 (br m), 40.0, 30.0, 28.5, 27.9.

_N_-(((3_s_,5_s_,7_s_)-Adamantan-1-yl)thio)pivalamide (S39)



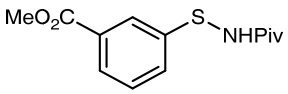
According to **General procedure 3** with (3*s*,5*s*,7*s*)-adamantane-1-thiol (1.68 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the product as a white solid (1.34 g, 50% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 2.12 – 1.97 (m, 3H), 1.86 – 1.76 (m, 6H), 1.76 – 1.54 (m, 6H), 1.26 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 50.8, 41.4, 40.1, 36.4, 29.5, 28.1.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{26}NOS$ $[M + H]^+$ 268.1730, found 268.1723.

_N_-((((3a_R_,5_S_,5a_R_,8a_S_,8b_R_)-2,2,7,7-Tetramethyltetrahydro-5_H_-bis([1,3]dioxolo)[4,5-_b_:4',5'-_d_]pyran-5-yl)methyl)thio)pivalamide (S40)



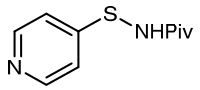
According to **General procedure 3** with ((3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-tetrahydro-*5H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methanethiol (2.76 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (1.24 g, 33% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 1H), 5.59 – 5.47 (m, 1H), 4.71 – 4.59 (m, 1H), 4.52 – 4.42 (m, 1H), 4.38 – 4.30 (m, 1H), 4.12 – 3.91 (m, 1H), 3.11 – 2.95 (m, 1H), 2.93 – 2.76 (m, 1H), 1.54 (s, 3H), 1.42 (s, 3H), 1.34 (s, 6H), 1.21 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 109.3, 108.7, 96.7, 71.7, 70.9, 70.5, 67.9, 39.8, 39.4, 27.7, 26.2, 26.1, 25.0, 24.6.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{30}NO_6S$ $[M + H]^+$ 376.1788, found 376.1791.

Methyl 3-(pivalamidothio)benzoate (S41)



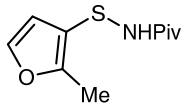
According to **General procedure 3** with methyl 3-mercaptobenzoate (1.68 g, 10.0 mmol, 1.0 equiv.) and pivalamide (0.91 g, 9.0 mmol, 0.9 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a white solid (0.37 g, 14% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.39 – 7.32 (m, 2H), 7.01 (s, 1H), 3.90 (s, 3H), 1.32 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 166.6, 140.0, 131.0, 129.2, 128.6, 127.6, 125.0, 52.4, 40.2, 27.8.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}NO_3S$ $[M + H]^+$ 268.1002, found 268.1003.

***N*-(Pyridin-4-ylthio)pivalamide (S42)**



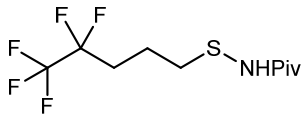
According to **General procedure 4** with 1,2-di(pyridin-4-yl)disulfane (2.20 g, 10.0 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on Al_2O_3 (PE/EtOAc = 3/1) to afford the product as a white solid (0.75 g, 36% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.26 (d, *J* = 5.4 Hz, 2H), 6.86 (d, *J* = 5.3 Hz, 2H), 1.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 152.2, 148.7, 116.7, 40.1, 27.6.

***N*-((2-Methylfuran-3-yl)thio)pivalamide (S43)**



According to **General procedure 3** with 2-methylfuran-3-thiol (1.14 g, 10.0 mmol, 1.0 equiv.) and pivalamide (0.91 g, 9.0 mmol, 0.9 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to afford the product as a white solid (0.15 g, 7% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.9 Hz, 1H), 6.62 (s, 1H), 6.48 (d, *J* = 2.0 Hz, 1H), 2.49 (s, 3H), 1.18 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 157.1, 140.9, 114.7, 114.4, 39.9, 27.8, 12.2.

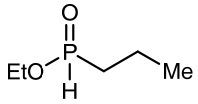
***N*-((4,4,5,5,5-pentafluoropentyl)thio)pivalamide (S44)**



According to **General procedure 3** with 4,4,5,5,5-pentafluoropentane-1-thiol (1.94 g, 10 mmol, 1.0 equiv.) and pivalamide (1.52 g, 15.0 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to yield the product as a yellow liquid (0.88 g, 30% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (s, 1H), 2.80 (t, *J* = 7.0 Hz, 2H), 2.34 – 2.16 (m, 2H), 1.93 – 1.81 (m, 2H), 1.23 (s, 9H).

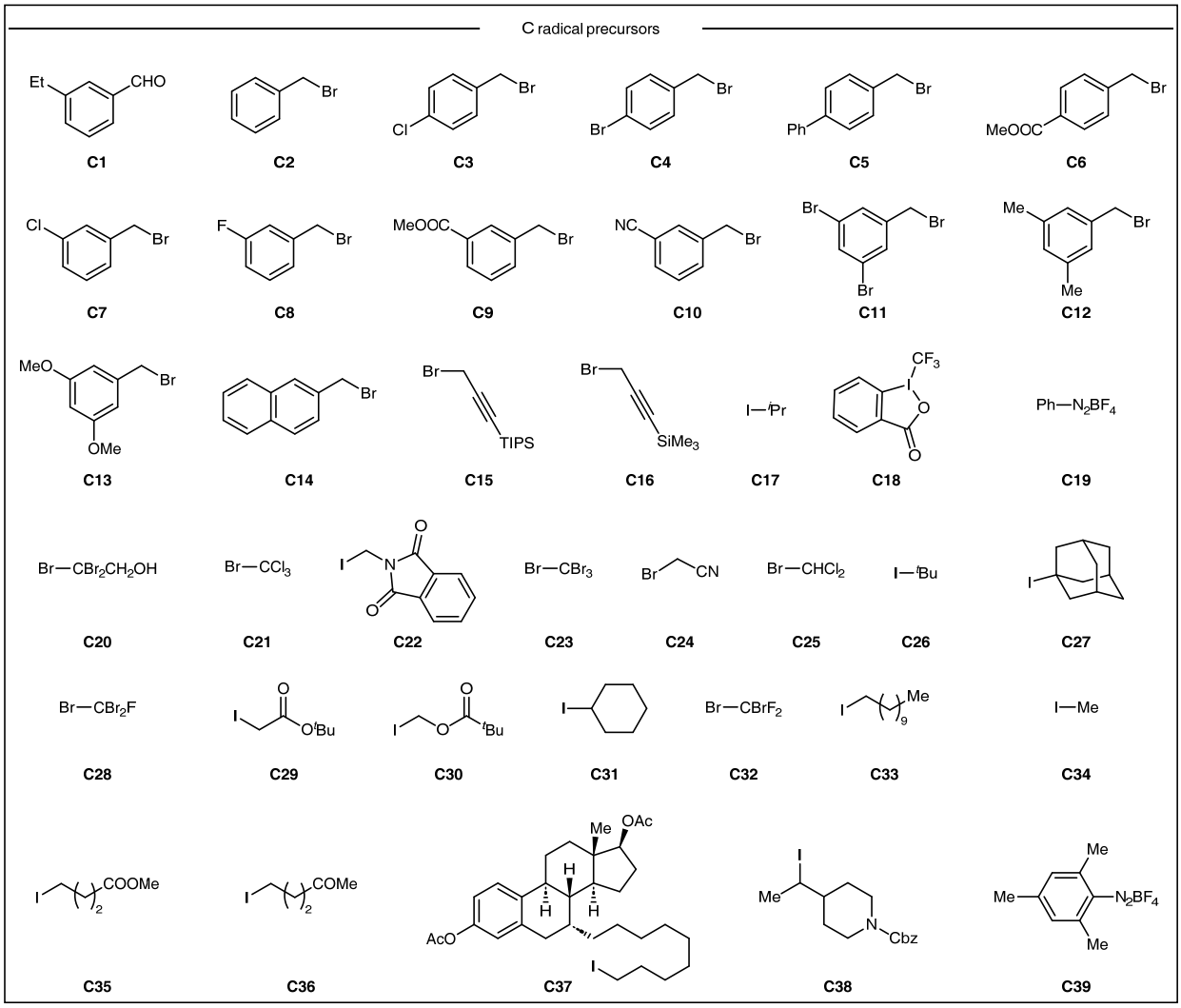
^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 118.9 (qt, *J* = 287.17 Hz, *J* = 34.96 Hz), 115.6 (tq, *J* = 251.7, *J* = 38.46), 39.6, 37.3, 29.0 (t, *J* = 21.9 Hz), 27.2, 18.5.
^{19}F NMR (375 MHz, $CDCl_3$) δ −85.41, −117.94 (t, *J* = 18.3 Hz).

Ethyl propylphosphinate (S45)

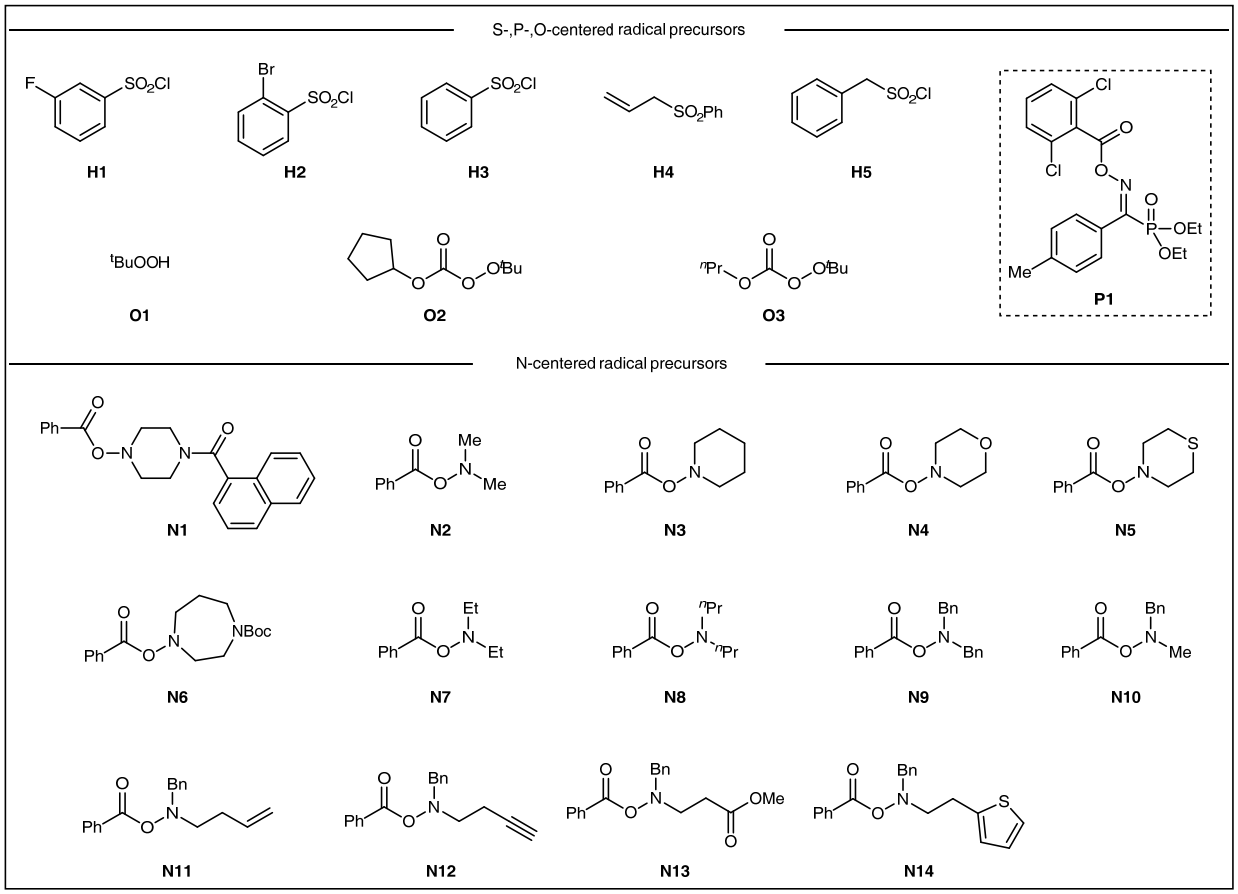


According to **General procedure 2** with ethyl (1,1-diethoxyethyl)-*H*-phosphinate (4.20 g, 20 mmol, 1.0 equiv.) and 1-iodopropane (4.10 g, 24.0 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (EtOAc) to afford the product as a colorless oil (435 mg, 20% overall yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.69 (m, 0.5H), 6.44 (t, *J* = 2.0 Hz, 0.5H), 4.30 – 3.99 (m, 2H), 1.90 – 1.51 (m, 4H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.09 – 1.02 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 62.3 (d, *J* = 6.9 Hz), 30.8 (d, *J* = 93.6 Hz), 16.3 (d, *J* = 6.1 Hz), 15.1 (d, *J* = 16.0 Hz), 14.5 (d, *J* = 2.9 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 38.58.

5. Synthesis of diverse radical precursors

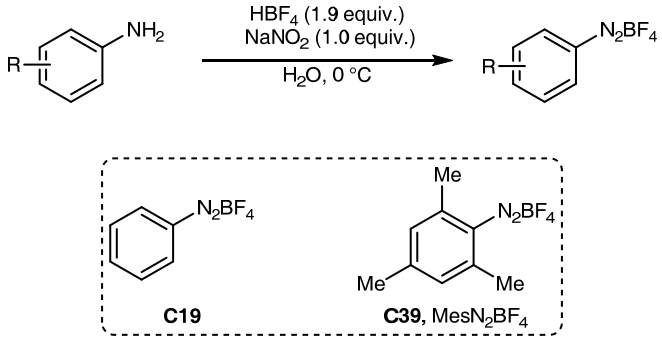


C1-C18, **C20-C21**, **C23-C35** were all purchased from commercial sources.



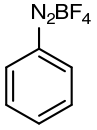
H1-**H5**, **O1** were all purchased from commercial sources.

Synthesis of C-centered radical precursors
Synthesis of aryldiazonium tetrafluoroborate



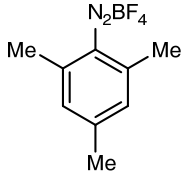
General procedure 6:
Aryldiazonium tetrafluoroborate was prepared from the corresponding arylamine according to the literature reported procedure[53]. The corresponding aniline (50 mmol) was dissolved in a mixture of water (20 mL) and 50% aqueous hydrofluoroboric acid (96.5 mmol, 1.9 equiv.). To this mixture was added a solution of $NaNO_2$ (50 mmol in 7.5 mL of water, 1.0 equiv.) slowly at 0 °C. The resulting reaction mixture was stirred at that temperature for 30 min and the precipitate was collected by filtration. The solid product was dissolved in minimum acetone and reprecipitated using diethyl ether to afford aryldiazonium tetrafluoroborate which was dried under vacuum without further purification.

1-Phenyl-2-(tetrafluoro-λ^5-boraneyl)diazene (C19)



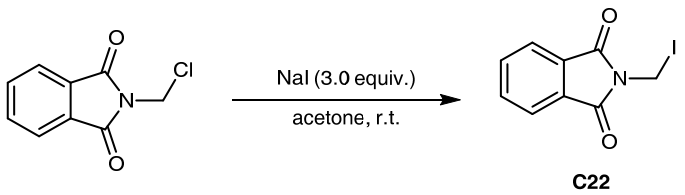
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.75 – 8.56 (m, 2H), 8.30 – 8.23 (m, 1H), 8.07 – 7.90 (m, 2H).

1-Mesityl-2-(tetrafluoro-λ^5-boraneyl)diazene (C39)



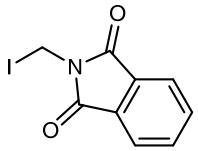
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 (s, 2H), 2.67 (s, 6H), 2.49 (s, 3H).

Synthesis of C22:



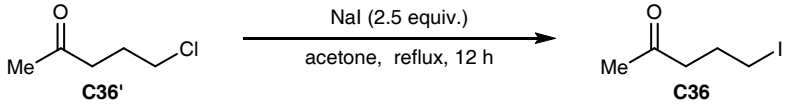
According to the literature reported procedure[54] with slight modification. A solution of 2-chloromethyl-isoindole-1,3-dione (6.0 g, 31 mmol) and sodium iodide (3.0 equiv., 13.8 g, 92 mmol) in acetone (44 mL) was stirred at r.t. in the dark for 4 h. After the addition of pentane (100 mL), the mixture was filtered and concentrated in vacuo to afford 2-iodomethyl-isoindole-1,3-dione (**C22**) as a white solid (7.0 g, 25 mmol, 40%).

2-(Iodomethyl)isoindoline-1,3-dione (C22)



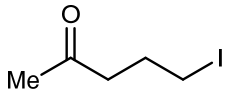
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.83 – 7.75 (m, 2H), 5.47 (s, 2H).

Synthesis of C36:



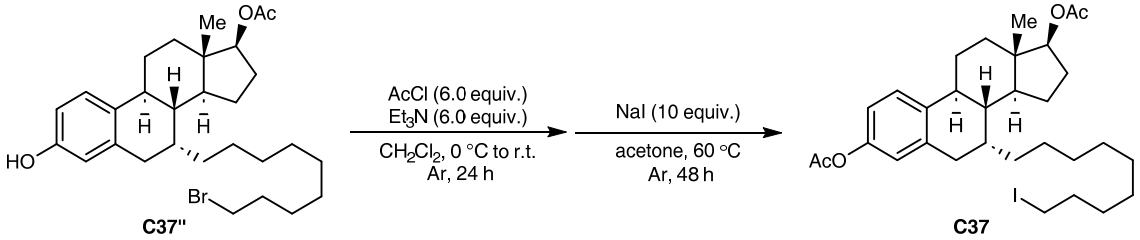
According to the literature reported procedure with slight modification. To a solution of a 5-chloropentan-2-one (0.60 g, 5.0 mmol, 1.0 equiv.) in dry acetone (10 mL) was added NaI (1.87 g, 12.5 mmol, 2.5 equiv.). After stirring at reflux for 12 h, the solvent was removed under reduced pressure, the residue was dissolved in water and extracted three times with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **C36** as a colorless oil (742 mg, 70% yield).

5-Iodopentan-2-one (C36)



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.32 – 3.16 (m, 2H), 2.91 – 2.52 (m, 2H), 2.24 – 2.14 (m, 3H), 2.13 – 1.99 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 43.8, 30.2, 27.1, 6.6.

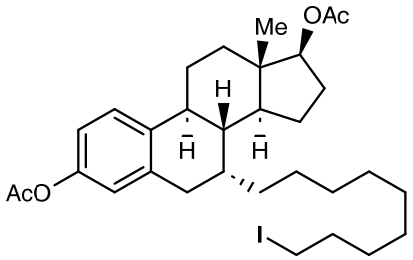
Synthesis of C37:



C37″ was synthesized according to the literature[55]. A solution of acetyl chloride (471.0 mg, 6.0 mmol, 6.0 equiv.) in dry CH_2Cl_2 (2.0 mL) was slowly added at 0 °C to an orange solution of **C37″** (519.6 mg, 1.0 mmol, 1.0 equiv.) and triethylamine (0.84 mL, 6.0 mmol, 6.0 equiv.) in dry CH_2Cl_2

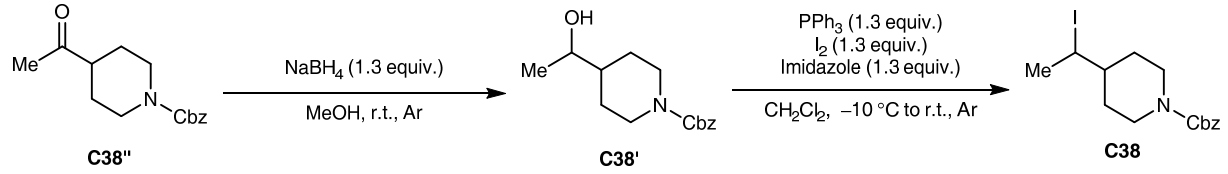
(8.0 mL), which resulted in a colorless precipitate. After the reaction mixture was stirred for 24 h at r.t., the formed triethylammonium chloride was removed by filtration. The combined organic layers were dried over sodium sulfate and concentrated without further purification.
To the above concentrated organic layer in acetone (30 mL) was added NaI (1.50 g, 10.0 mmol, 10 equiv.) under argon at 60 °C. Then, the reaction mixture was stirred at 60 °C for 48 h. Upon completion, the mixture was cooled to r.t. and concentrated in vacuo. Et_2O was added and the organic phase was washed with $Na_2S_2O_3$, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel to afford the desired product **C37** as a colorless oil.

(7*R*,8*R*,9*S*,13*S*,14*S*,17*S*)-7-(9-Iodononyl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diyl diacetate (C37)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford **C37** as colorless oil (493.2 mg, 81% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.84 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.78 (d, *J* = 2.5 Hz, 1H), 4.70 (dd, *J* = 9.1, 7.8 Hz, 1H), 3.18 (t, *J* = 7.0 Hz, 2H), 2.90 (dd, *J* = 17.0, 5.4 Hz, 1H), 2.82 – 2.68 (m, 1H), 2.43 – 2.12 (m, 6H), 2.06 (s, 3H), 1.93 – 1.72 (m, 4H), 1.71 – 1.59 (m, 2H), 1.57 – 1.31 (m, 8H), 1.32 – 1.12 (m, 10H), 1.11 – 0.94 (m, 1H), 0.82 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 169.9, 148.5, 137.2(3), 137.1(7), 127.1, 122.5, 118.7, 82.8, 46.3, 43.0, 41.4, 38.2, 37.1, 34.6, 33.6, 33.2, 30.6, 29.9, 29.7, 29.5, 28.6, 28.2, 27.6, 27.0, 25.7, 22.9, 21.3(0), 21.2(6), 12.1, 7.5.
HRMS (ESI) *m*/*z* calcd. for $C_{31}H_{45}INaO_4$ $[M + Na]^+$ 631.2255, found 631.2255.

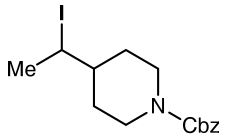
Synthesis of C38:



According to the literature reported procedure[56] with slight modification. Compound **C38″** (2.61 g, 10 mmol, 1.0 equiv.) was dissolved in dry MeOH (30 mL) in a round-bottomed flask equipped with a magnetic stirrer. To the resulting solution was added $NaBH_4$ (491 mg, 13.0 mmol, 1.3 equiv.) at 0 °C under an argon atmosphere and the reaction mixture was stirred at r.t. for 24 h. The reaction mixture was diluted with EtOAc and washed with water, brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product. The crude product was purified by silica gel chromatography to afford the desired product **C38′**.
According to the literature reported procedure[57] with slight modification. An oven-dried round-bottom flask equipped with a stirring bar was charged with an aliphatic alcohol **C38′** (1.32 g, 5.0

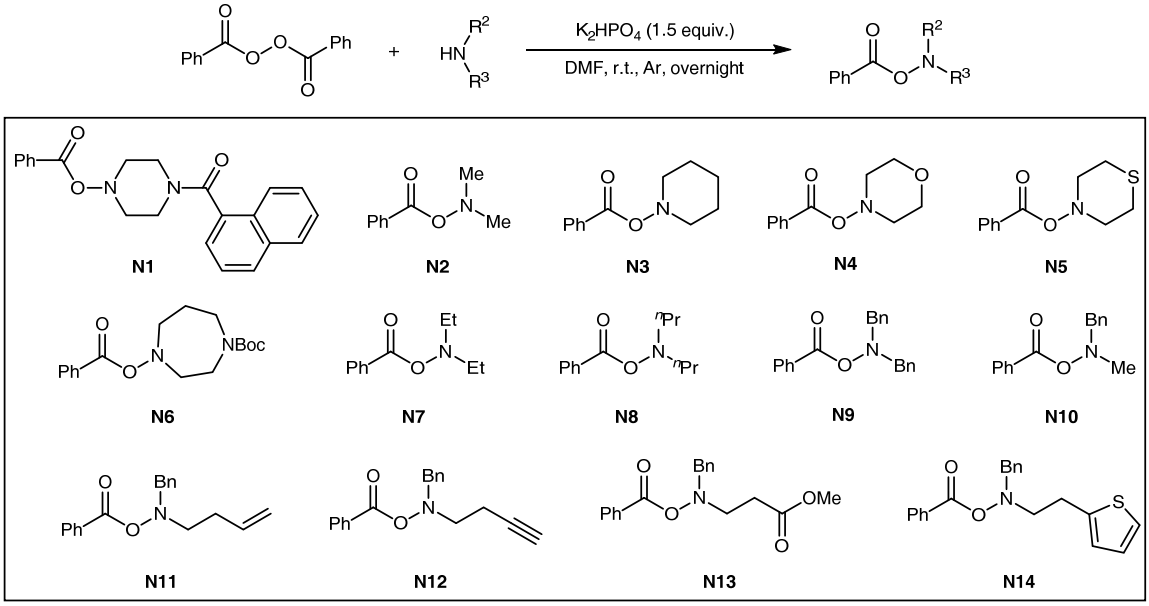
mmol, 1.0 equiv.), PPh_3 (1.70 g, 6.5 mmol, 1.3 equiv.) and imidazole (443 mg, 6.5 mmol, 1.3 equiv.). The flask was evacuated and refilled with argon three times, followed by the addition of dry CH_2Cl_2 (50 mL). To the resulting solution was added I_2 (1.65 g, 6.5 mmol, 1.3 equiv.) portion-wise. The reaction mixture was warmed to r.t. and allowed to stir overnight. After completion (monitored by TLC), the reaction was quenched with sat. $Na_2S_2O_3$ aqueous solution. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 three times (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by silica gel chromatography to afford the desired product **C38**.

Benzyl 4-(1-iodoethyl)piperidine-1-carboxylate (C38)



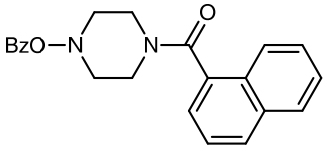
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 40/1) to afford **C38** as a colorless oil.
HPLC analysis: Chiralcel OD-H (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 18.82 min, t_R (minor) = 20.80 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 5.12 (s, 2H), 4.43 – 4.01 (m, 3H), 2.76 (d, *J* = 15.2 Hz, 2H), 1.90 (d, *J* = 7.0 Hz, 3H), 1.88 – 1.60 (m, 2H), 1.39 – 1.09 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 136.8, 128.5, 128.0, 127.9, 67.1, 45.0, 43.8, 43.7, 36.6, 32.0 – 29.8 (m), 25.7.
HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{21}NIO_2$ $[M + H]^+$ 374.0611, found 374.0615.
High enantiomeric **C38** with >99% e.e. was obtained through preparative HPLC (CHIRALPAK® OD-H, *n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min).

Synthesis of N-centered radical precursors



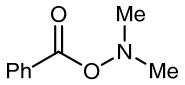
General procedure 7:
According to the literature reported procedure[58] with slight modification. An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with appropriate benzoyl peroxide (1.0 equiv.), dipotassium hydrogen phosphate (1.5 equiv.), appropriate secondary amine (1.0 equiv.), and anhydrous *N,N*-dimethylformamide (0.2 M). The reaction mixture was then stirred at r.t. overnight. Upon completion (monitored by TLC), the reaction mixture was quenched with water (5.0 mL), and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel using PE/CH_2Cl_2 as the eluent to afford the corresponding *O*-carboxylhydroxylamines **N1**–**N14**. The spectroscopic data of **N1**–**N11** is consistent with that reported in the literature, and the spectroscopic data of new compounds are shown below.

4-(1-Naphthoyl)piperazin-1-yl benzoate (N1)



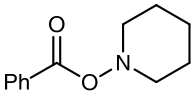
According to **General procedure 7** with naphthalen-1-yl(piperazin-1-yl)methanone (481 mg, 2.0 mmol, 1.0 equiv.) and BPO (484.5 mg, 2.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 1/1) to afford the product **N1** as a white solid (389 mg, 54% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.95 (m, 2H), 7.95 – 7.73 (m, 3H), 7.65 – 7.36 (m, 7H), 5.05 – 4.63 (m, 1H), 3.89 – 2.50 (m, 7H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 164.6, 133.6, 133.5, 129.6(3), 129.5(5), 128.9, 128.7, 128.6, 127.4, 126.7, 125.3, 124.6, 124.0, 56.7, 56.1, 45.5, 40.2.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}N_2NaO_3$ $[M + Na]^+$ 383.1366, found 383.1365.

***O*-Benzoyl-*N*,*N*-dimethylhydroxylamine (N2)**



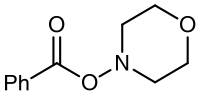
According to **General procedure 7** with dimethylamine (225 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N2** as a pare yellow liquid (340 mg, 41% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.86 (m, 2H), 7.66 – 7.51 (m, 1H), 7.49 – 7.37 (m, 2H), 2.90 (s, 6H).

Piperidin-1-yl benzoate (N3)



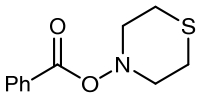
According to **General procedure 7** with piperidine (426 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N3** as a white solid (800 mg, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.92 (m, 2H), 7.58 – 7.48 (m, 1H), 7.46 – 7.38 (m, 2H), 3.56 – 3.45 (m, 2H), 2.97 – 2.56 (m, 2H), 1.89 – 1.75 (m, 4H), 1.73 – 1.60 (m, 1H), 1.42 – 1.19 (m, 1H).

Morpholino benzoate (N4)



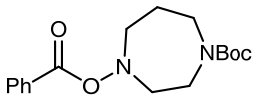
According to **General procedure 7** with morpholine (436 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N4** as a white solid (777 mg, 75% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.48 – 7.42 (m, 2H), 4.02 – 3.94 (m, 2H), 3.87 (t, J = 11.4 Hz, 2H), 3.52 – 3.40 (m, 2H), 3.05 (t, J = 8.9 Hz, 2H).

Thiomorpholino benzoate (N5)



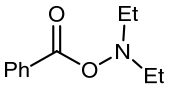
According to **General procedure 7** with thiomorpholine (516 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N5** as a white solid (615 mg, 55% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.62 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 3.91 – 3.48 (m, 2H), 3.43 – 3.11 (m, 2H), 3.10 – 2.69 (m, 4H).

***tert*-Butyl 4-(benzoyloxy)-1,4-diazepane-1-carboxylate (N6)**



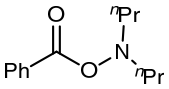
According to **General procedure 7** with *tert*-butyl 1,4-diazepane-1-carboxylate (1.0 g, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N6** as a white solid (960 mg, 60% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.39 (m, 2H), 3.76 – 3.45 (m, 4H), 3.41 – 3.25 (m, 4H), 2.12 – 1.98 (m, 2H), 1.49 (s, 9H).

***O*-Benzoyl-*N*,*N*-diethylhydroxylamine (N7)**



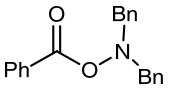
According to **General procedure 7** with diethylamine (366 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N7** as a pare yellow liquid (531 mg, 55% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.97 (m, 2H), 7.65 – 7.51 (m, 1H), 7.49 – 7.38 (m, 2H), 3.05 (q, *J* = 7.1 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 6H).

***O*-Benzoyl-*N*,*N*-dipropylhydroxylamine (N8)**



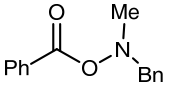
According to **General procedure 7** with dipropylamine (506 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N8** as a pare yellow liquid (509 mg, 46% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.59 – 7.52 (m, 1H), 7.47 – 7.41 (m, 2H), 2.99 – 2.87 (m, 4H), 1.75 – 1.50 (m, 4H), 0.94 (t, *J* = 7.5 Hz, 6H).

***O*-Benzoyl-*N*,*N*-dibenzylhydroxylamine (N9)**



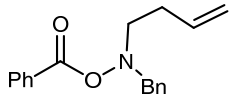
According to **General procedure 7** with dibenzylamine (986 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N9** as a white solid (509 mg, 46% yield).
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.56 – 7.41 (m, 5H), 7.40 – 7.18 (m, 8H), 4.20 (s, 4H).

***O*-Benzoyl-N-benzyl-*N*-methylhydroxylamine (N10)**



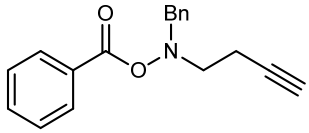
According to **General procedure 7** with *N*-methylbenzylamine (606 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N10** as a white solid (736 mg, 61% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.54 – 7.46 (m, 1H), 7.46 – 7.33 (m, 4H), 7.34 – 7.21 (m, 3H), 4.15 (s, 2H), 2.92 (s, 3H).

_O_-Benzoyl-_N_-benzyl-_N_-methylhydroxylamine (N11)



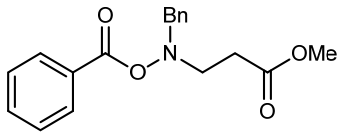
According to **General procedure 7** with *N*-benzylbut-3-en-1-amine (807 mg, 5.0 mmol, 1.0 equiv.) and BPO (1.21 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product **N11** as a white solid (704 mg, 50% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.81 (m, 2H), 7.55 – 7.45 (m, 1H), 7.45 – 7.32 (m, 4H), 7.32 – 7.19 (m, 3H), 5.91 – 5.70 (m, 1H), 5.09 – 4.93 (m, 2H), 4.18 (s, 2H), 3.13 – 3.00 (m, 2H), 2.44 – 2.34 (m, 2H).

_O_-Benzoyl-_N_-benzyl-_N_-(but-3-yn-1-yl)hydroxylamine (N12)



According to **General procedure 7** with *N*-benzylbut-3-yn-1-amine (318 mg, 2.0 mmol, 1.0 equiv.) and BPO (484.5 mg, 2.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/CH_2Cl_2 = 1/1) to afford the product as a colorless oil (305 mg, 34% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H), 7.54 – 7.46 (m, 1H), 7.43 – 7.33 (m, 4H), 7.33 – 7.19 (m, 3H), 4.19 (s, 2H), 3.24 – 3.16 (m, 2H), 2.53 (td, *J* = 7.5, 2.7 Hz, 2H), 1.92 (t, *J* = 2.7 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 135.1, 133.0, 129.6, 129.4, 129.0, 128.4, 127.8, 81.6, 69.5, 63.4, 56.6, 17.1.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{18}NO_2$ $[M + H]^+$ 280.1332, found 280.1330.

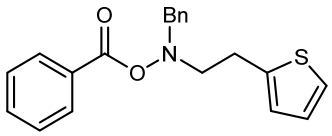
Methyl 3-((benzoyloxy)(benzyl)amino)propanoate (N13)



According to **General procedure 7** with methyl 3-(benzylamino)propanoate (1.5 g, 7.8 mmol, 1.2 equiv.) and BPO (1.57 g, 6.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 8/1) to afford the product as a colorless oil (1.17 g, 36% yield).

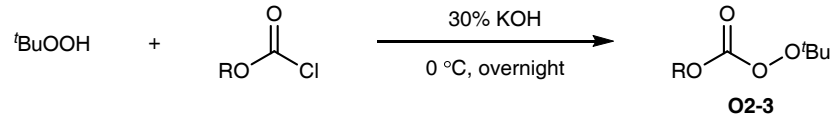
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.57 – 7.48 (m, 1H), 7.44 – 7.35 (m, 4H), 7.34 – 7.20 (m, 3H), 4.20 (s, 2H), 3.54 (s, 3H), 3.35 (t, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.1 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 165.0, 135.1, 133.1, 129.7, 129.4, 128.9, 128.4(1), 128.3(9), 127.9, 63.6, 53.5, 51.6, 32.2.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}NNaO_4$ $[M + Na]^+$ 336.1206, found 336.1208.

***O*-Benzoyl-*N*-benzyl-*N*-(2-(thiophen-2-yl)ethyl)hydroxylamine (N14)**



According to **General procedure 7** with *N*-benzyl-2-(thiophen-2-yl)ethan-1-amine (1.7 g, 7.92 mmol, 1.2 equiv.) and BPO (1.6 g, 6.6 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the product as a colorless oil (1.44 g, 41% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.56 – 7.48 (m, 1H), 7.44 – 7.35 (m, 4H), 7.32 – 7.21 (m, 3H), 7.11 – 7.05 (m, 1H), 6.90 – 6.84 (m, 1H), 6.84 – 6.79 (m, 1H), 4.21 (s, 2H), 3.35 – 3.26 (m, 2H), 3.20 – 3.12 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 141.6, 135.3, 133.1, 129.7, 129.5, 129.1, 128.5, 128.4, 127.9, 126.9, 125.1, 123.6, 63.7, 59.7, 27.9.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}NNaO_2S$ $[M + Na]^+$ 360.1029, found 360.1030.

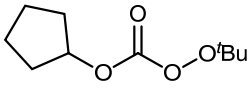
Synthesis of O-centered radical precursors:



O2-3

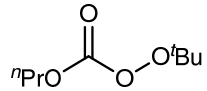
The synthesis of **O2** and **O3** was carried out according to a literature-reported procedure[59]. To a solution of 2-hydroperoxy-2-methylpropane (5.5 mmol, 1.1 equiv.) was added propyl carbonochloridate (5.0 mmol, 1.0 equiv.) dropwise at 0 °C. The reaction mixture was stirred for 0.5 h. To the resulting solution was added a KOH solution (30% in water) (6.5 mmol, 1.3 equiv.) dropwise. The reaction mixture was then stirred overnight at 0 °C. Upon completion (monitored by TLC), the reaction mixture was quenched with water (20 mL), and the aqueous layer was extracted with EtOAc (3 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford the crude product, which was purified by flash chromatography (PE/EtOAc = 20/1~8/1) to afford the desired product **O2** or **O3**.

***tert*-Butyl propyl carbonoperoxoate (O2)**



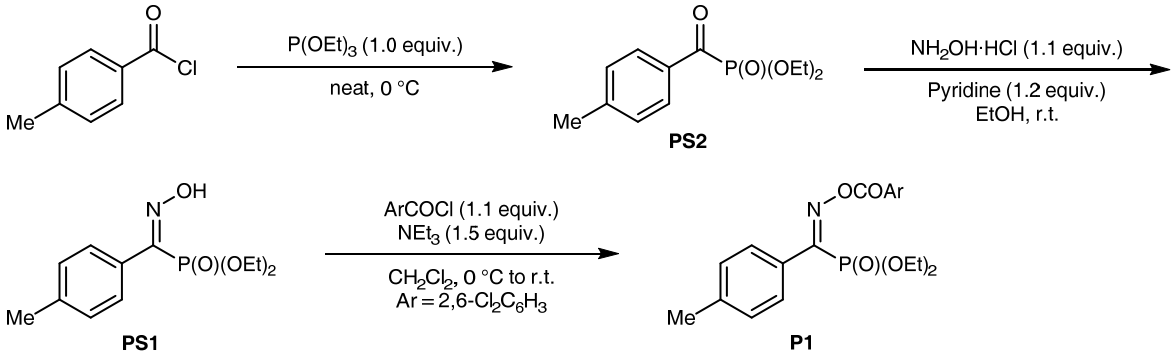
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (tt, *J* = 5.9, 2.6 Hz, 1H), 2.03 – 1.55 (m, 8H), 1.32 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 83.9, 82.6, 32.6, 26.0, 23.5.

***tert*-Butyl propyl carbonoperoxoate (O3)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (t, *J* = 6.7 Hz, 1H), 1.73 (h, *J* = 7.2 Hz, 1H), 1.34 (s, 4H), 0.97 (t, *J* = 7.5 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 84.1, 70.7, 25.9, 22.1, 10.1.

Synthesis of P-centered radical precursors:

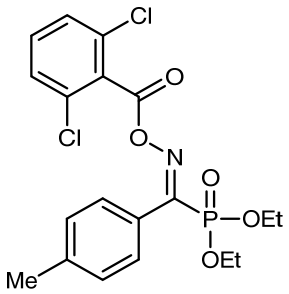


According to the literature reported procedure[60] with slight modification. To a 100 mL round bottom flask equipped with a magnetic stir bar was charged with benzoyl chloride (20.1 mmol, 1.05 equiv.) and the triethyl phosphate (20 mmol, 1.0 equiv.) at 0 °C, then the mixture was stirred for 2 h to give the **PS2**, which could be used for the next step without further purification.

The above afforded **PS2** was solved with EtOH (40 mL), and to the mixture was added hydroxylamine hydrochloride (22.0 mmol, 1.1 euqiv.) and pyridine (24.0 mmol, 1.2 equiv.). Then the mixture was stirred overnight at r.t.. Quenched the reaction with 1N HCl (aq.), and extracted with EtOAc, washed by water and brine. The organic phase was collected and the solvent was removed under vacuum to give the crude product **PS1**, which could be used for the next step without further purification.

The above afforded **PS1** was solved with CH_2Cl_2 (40 mL), and to the mixture was added triethylamine (24.0 mmol, 1.2 equiv.) and 2,6-dichlorobenzoyl chloride (22.0 mmol, 1.1 equiv.) at 0 °C. Then the mixture was allowed to r.t. and stirred overnight to give the final product **P1** (7.1 g, 80% yield) after purification by chromatography.

Diethyl (*E*)-((((2,6-dichlorobenzoyl)oxy)imino)(*p*-tolyl)methyl)phosphonate (P1)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.47 (m, 2H), 7.41 – 7.23 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.32 – 3.97 (m, 4H), 2.56 – 2.13 (m, 3H), 1.34 – 1.18 (m, 6H).

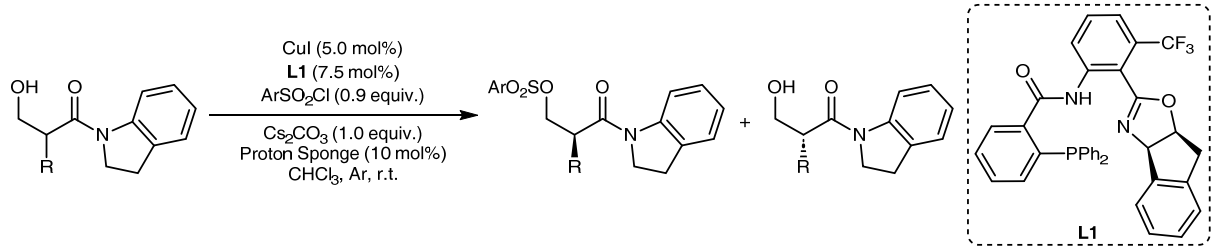
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 162.1, 162.0, 160.4, 160.2, 141.4, 141.2, 132.5, 132.3, 132.2, 132.0, 131.7, 131.5, 129.2(9), 129.2(6), 129.2, 128.8(9), 128.8(5), 128.0(0), 127.9(5), 125.9, 125.7, 64.6 (d, *J* = 6.6 Hz), 63.7 (d, *J* = 6.3 Hz), 21.6, 21.5, 16.2 (d, *J* = 6.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 5.04, 0.31.

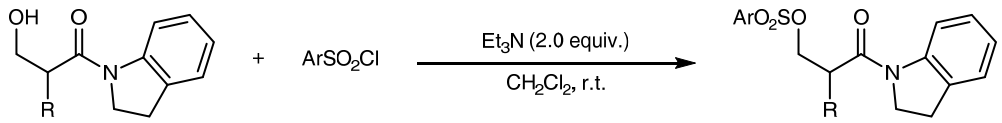
HRMS (ESI) *m/z* calcd. for $C_{19}H_{20}Cl_2NNaO_5P$ $[M + Na]^+$ 466.0348, found 466.0348.

6. Asymmetric radical coupling between radical acceptor and diverse radical precursors

General Procedure A:

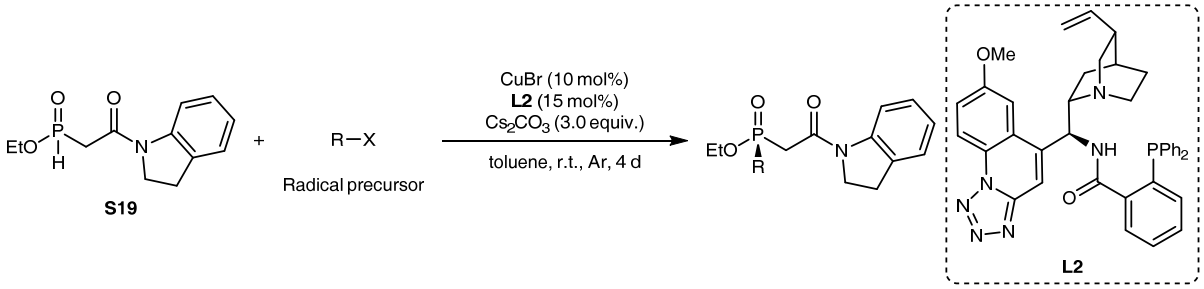


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L1** (9.1 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 1.0 equiv.), proton sponge (4.3 mg, 0.020 mmol, 10 mol%), γ-aminocarbonyl alcohol (0.20 mmol, 1.0 equiv.), and anhydrous $CHCl_3$ (1.0 mL). Then the corresponding sulfonyl chloride (0.18 mmol, 0.9 equiv.) was added and the reaction mixture was stirred at r.t.. Upon completion, the precipitate was filtered off and washed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.



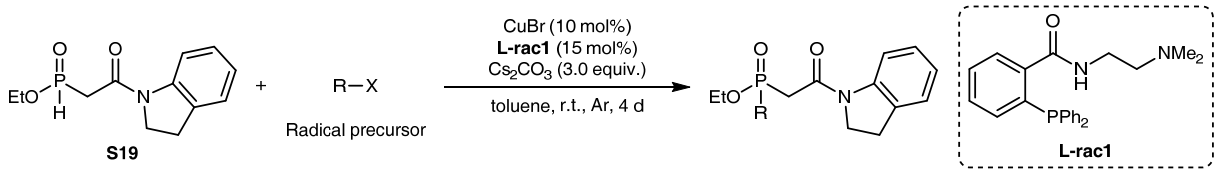
The racemates of products were prepared following the procedure: To a solution of γ-aminocarbonyl alcohol (0.10 mmol, 1.0 equiv.) and Et_3N (27.7 μL, 0.20 mmol, 2.0 equiv.) in dry CH_2Cl_2 (1.0 mL) was added the corresponding sulfonyl chloride (0.11 mmol, 1.1 equiv.). After stirring for 24 h, saturated NH_4Cl (aq.) was added to the above reaction solution to quench the reaction. Then, the mixture was extracted with CH_2Cl_2 and the combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The residue was purified by silica gel column chromatography to afford the desired racemate.

General procedure B:



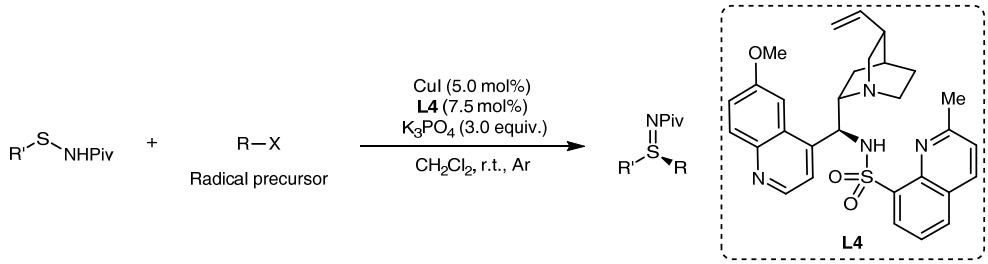
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuBr (1.42 mg, 0.010 mmol, 10 mol%), **L2** (9.8 mg, 0.015 mmol, 15 mol%), **S19** (25.6 mg, 0.10 mmol, 1.0 equiv.), radical precursor (0.15 mmol, 1.5 equiv.), and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then anhydrous toluene (4.0 mL) was added by syringe under argon and the reaction mixture was stirred at r.t.. Upon

completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

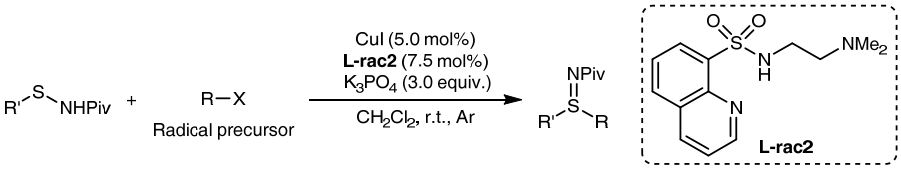


An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuBr (1.42 mg, 0.010 mmol, 10 mol%), **L-rac1** (5.6 mg, 0.015 mmol, 15 mol%), **S19** (25.6 mg, 0.10 mmol, 1.0 equiv.), radical precursor (0.15 mmol, 1.5 equiv.), and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then anhydrous toluene (4.0 mL) was added by syringe under argon and the reaction mixture was stirred at r.t.. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure C:

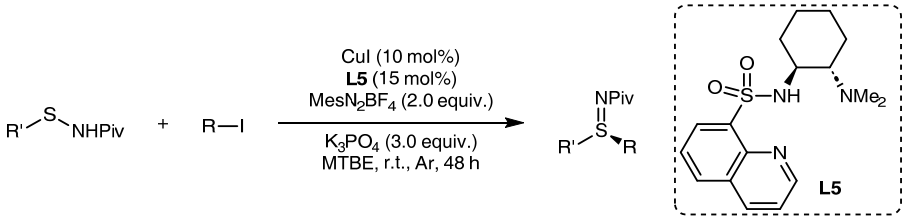


Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S** (0.20 mmol, 1.0 equiv.), CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L4** (7.9 mg, 0.015 mmol, 7.5 mol%), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.), and anhydrous CH_2Cl_2 (2.0 mL). Then, radical precursor (0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at r.t.. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

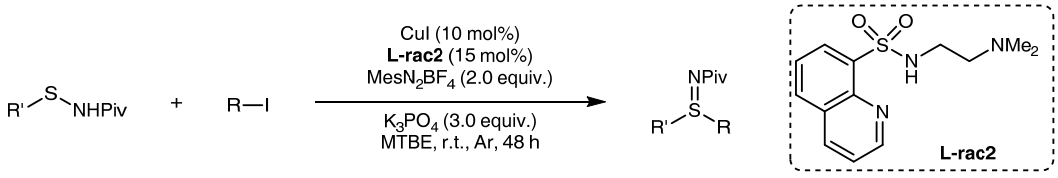


The racemates of products were prepared following the procedure: Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S** (0.20 mmol, 1.0 equiv.), CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L-rac2** (4.2 mg, 0.015 mmol, 7.5 mol%), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.), and anhydrous CH_2Cl_2 (2.0 mL). Then, radical precursor (0.24 mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at r.t.. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure D:

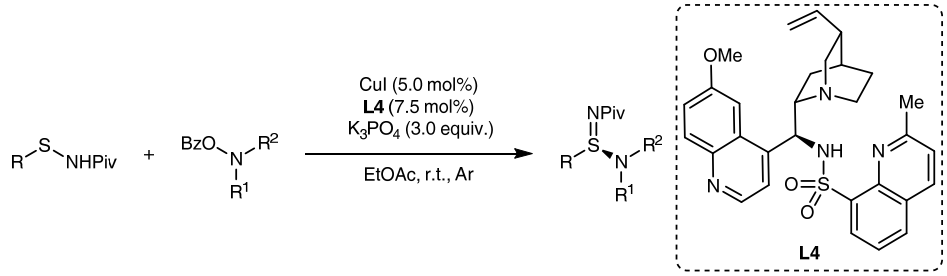


To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L5** (10.0 mg, 0.03 mmol, 15 mol%), sulfenamide **S** (0.20 mmol, 1.0 equiv.), alkyl iodide (0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (**C39**, 93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.



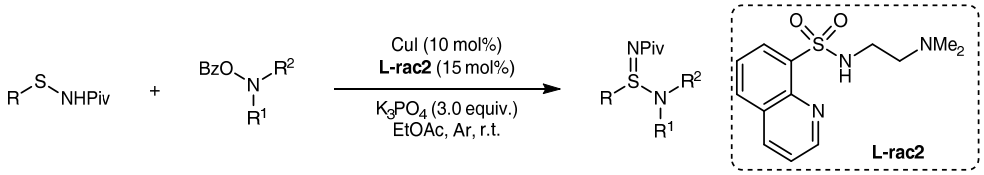
The racemates of products were prepared following the procedure: To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L-rac2** (8.4 mg, 0.03 mmol, 15 mol%), sulfenamide **S** (0.20 mmol, 1.0 equiv.), alkyl iodide (0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure E:



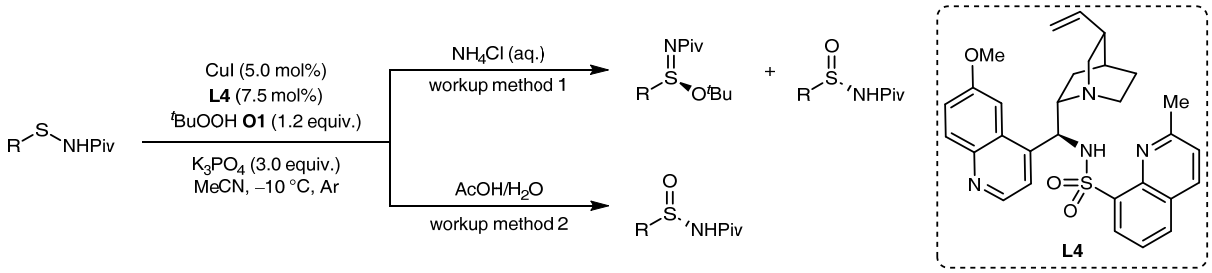
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.90 mg, 0.010 mmol, 5 mol%), **L4** (7.9 mg, 0.015 mmol, 7.5 mol%), sulfenamide **S** (0.20 mmol, 1.0 equiv.), *O*-benzoylhydroxylamine (0.30 mmol, 1.5 equiv.) and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then anhydrous EtOAc (2.0 mL) was added by syringe under argon and the reaction mixture was stirred at r.t.. Upon

completion, the precipitate was filtered off and washed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.



The racemates of products were prepared following the procedure: An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (0.95 mg, 0.0050 mmol, 10 mol%), **L-rac2** (2.1 mg, 0.0075 mmol, 15 mol%), sulfenamide **S** (0.050 mmol, 1.0 equiv.), *O*-benzoylhydroxylamine (0.075 mmol, 1.5 equiv.), and K_3PO_4 (31.8 mg, 0.15 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then anhydrous EtOAc (0.5 mL) was added by syringe under argon and the reaction mixture was stirred at r.t.. Upon completion, the precipitate was filtered off and washed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

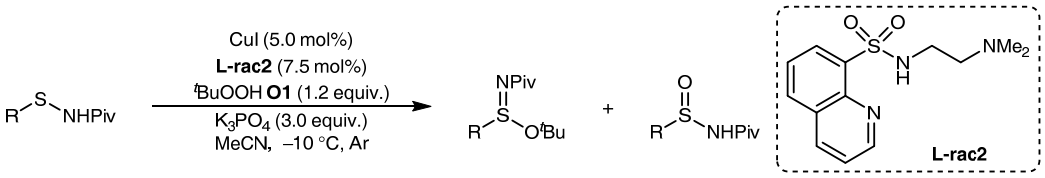
General procedure F:



Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S** (0.20 mmol, 1.0 equiv.), CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L4** (7.9 mg, 0.015 mmol, 7.5 mol%), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.), and anhydrous MeCN (2.0 mL). Then, *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at −10 °C for 36 h.

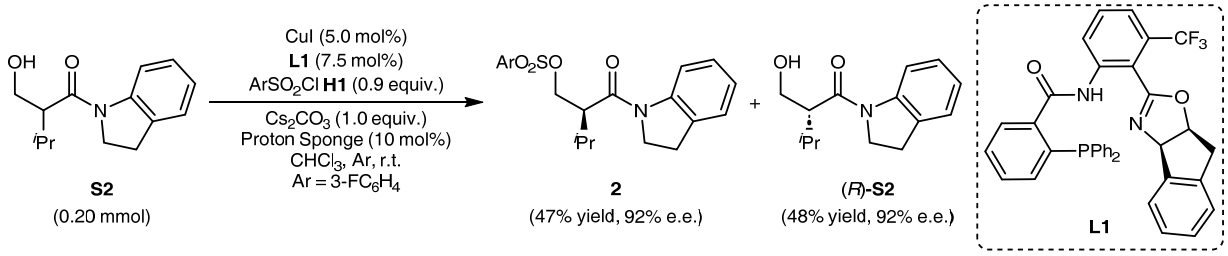
Workup method 1: the reaction was quenched with sat. aqueous NH_4Cl solution, and then extracted with EtOAc three times (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography or preparative thin-layer chromatography on silica gel to afford the desired products sulfinimidate ester and sulfinamide.

Workup method 2: 2.0 mL of mixture solvent (AcOH:H_2O = 1:2) was added and the reaction mixture was stirred at r.t. for another 1 h. Then the reaction mixture was extracted with EtOAc three times (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography or preparative thin-layer chromatography on silica gel to afford the desired product (sulfinamide).



The racemates of products were prepared following the procedure: Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S** (0.20 mmol, 1.0 equiv.), CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L-rac2** (2.1 mg, 0.0075 mmol, 7.5 mol%), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.), and anhydrous MeCN (2.0 mL). Then, *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at −10 °C for 36 h. Upon completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl aqueous solution, and extracted with EtOAc three times (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography or preparative thin-layer chromatography on silica gel to afford the desired products.

(*S*)-2-(Indoline-1-carbonyl)-3-methylbutyl 3-fluorobenzenesulfonate (2)



According to **General Procedure A** with **S2** (46.7 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 8/1) to afford **2** as a colorless oil (36.9 mg, 47% yield, 92% e.e.) and (*R*)-**S2** (23.3 mg, 48% yield, 92% e.e.).

HPLC analysis of **2**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.94 min, t_R (major)= 14.19 min.

HPLC analysis of (*R*)-**S2**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 12.39 min, t_R (minor)= 14.10 min.

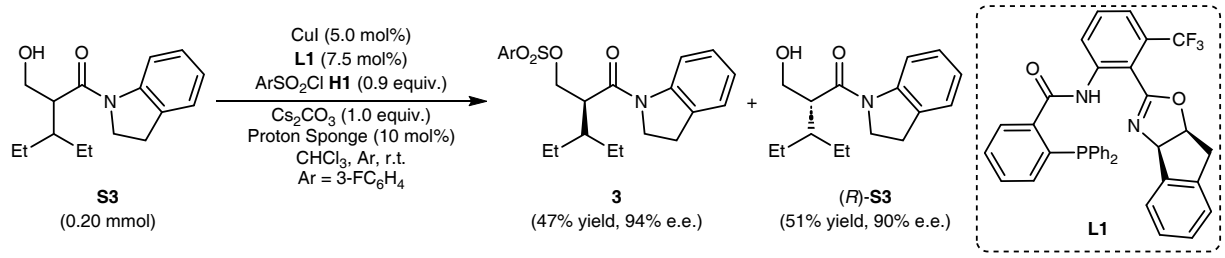
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.55 – 7.50 (m, 1H), 7.48 – 7.39 (m, 1H), 7.32 – 7.26 (m, 1H), 7.22 – 7.15 (m, 2H)), 7.07 – 7.01 (m, 1H), 4.38 (d, *J* = 7.1 Hz, 2H), 4.20 (td, *J* = 9.7, 7.4 Hz, 1H), 4.08 (td, *J* = 9.8, 7.3 Hz, 1H), 3.27 – 3.12 (m, 2H), 2.89 (q, *J* = 7.5 Hz, 1H), 1.97 (dq, *J* = 13.8, 6.8 Hz, 1H), 1.03 – 0.96 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 162.4 (d, *J* = 252.2 Hz), 142.7, 137.5 (d, *J* = 7.1 Hz), 131.7, 131.2 (d, *J* = 7.8 Hz), 127.6, 124.7, 124.2, 123.8 (d, *J* = 3.4 Hz), 121.2 (d, *J* = 21.1 Hz), 117.6, 115.4 (d, *J* = 24.7 Hz), 71.6, 51.1, 48.6, 29.1, 28.0, 21.0, 20.1.

^{19}F NMR (375 MHz, $CDCl_3$) δ −109.00.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}FNO_4S$ $[M + H]^+$ 392.1326, found 392.1325.

(*S*)-3-Ethyl-2-(indoline-1-carbonyl)pentyl 3-fluorobenzenesulfonate (3)



According to **General Procedure A** with **S3** (52.3 mg, 0.20 mmol, 1.0 equiv.), 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) and anhydrous $CHCl_3$ (0.5 mL) for 96 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 10/1) to afford **3** as a colorless oil (39.4 mg, 47% yield, 94% e.e.) and (*R*)-**S3** (26.6 mg, 51% yield, 90% e.e.).

HPLC analysis of **3**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.20 min, t_R (major)= 11.54 min.

HPLC analysis of (*R*)-**S3**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.67 min, t_R (major)= 7.60 min.

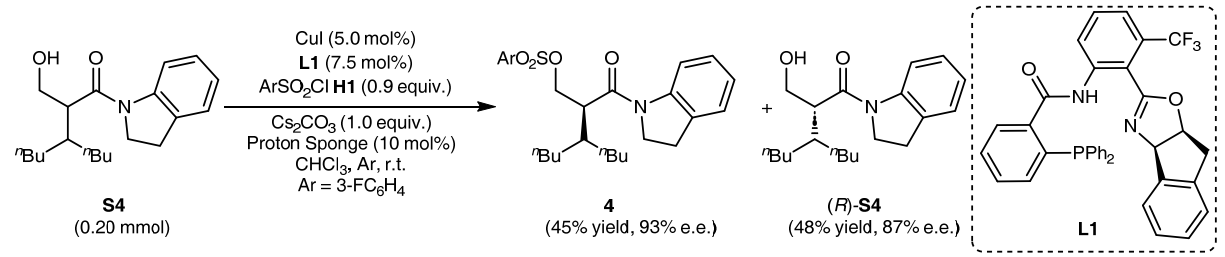
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.55 – 7.50 (m, 1H), 7.48 – 7.40 (m, 1H), 7.33 – 7.26 (m, 1H), 7.23 – 7.16 (m, 2H), 7.04 (td, *J* = 7.4, 1.1 Hz, 1H), 4.45 – 4.32 (m, 2H), 4.20 (td, *J* = 9.8, 7.4 Hz, 1H), 4.06 (td, *J* = 9.8, 7.3 Hz, 1H), 3.27 – 3.07 (m, 3H), 1.67 – 1.56 (m, 2H), 1.47 – 1.31 (m, 2H), 1.21 (dq, *J* = 14.5, 7.2 Hz, 1H), 0.92 – 0.82 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 162.4 (d, *J* = 252.1 Hz), 142.8, 137.6 (d, *J* = 7.2 Hz), 131.6, 131.1 (d, *J* = 7.8 Hz), 127.6, 124.7, 124.2, 123.8 (d, *J* = 3.5 Hz), 121.2 (d, *J* = 21.2 Hz), 117.6, 115.4 (d, *J* = 24.9 Hz), 71.2, 48.4, 46.8, 41.0, 28.1, 23.1, 21.5, 11.5, 10.2.

^{19}F NMR (375 MHz, $CDCl_3$) δ −109.04.

HRMS (ESI) m/z calcd. for $C_{22}H_{27}FNO_4S$ $[M + H]^+$ 420.1639, found 420.1641.

(*S*)-3-Butyl-2-(indoline-1-carbonyl)heptyl 3-fluorobenzenesulfonate (4)



According to **General Procedure A** with **S4** (63.5 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 84 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 10/1) to afford **4** as a white solid (42.8 mg, 45% yield, 93% e.e.) and (*R*)-**S4** (30.6 mg, 48% yield, 87% e.e.).

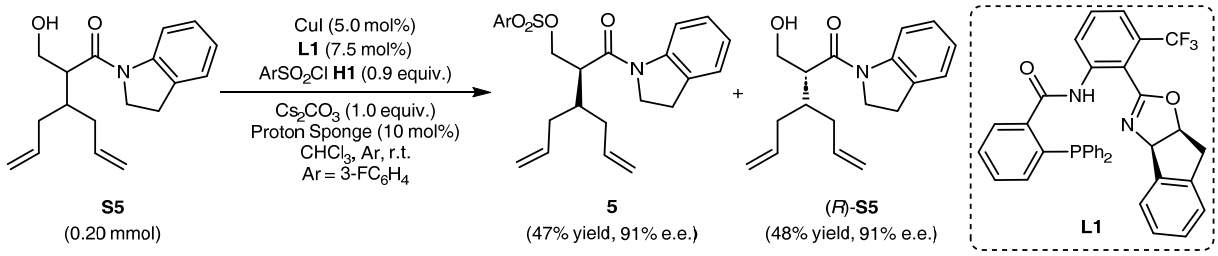
HPLC analysis of **4**: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.03 min, t_R (major)= 15.29 min.

HPLC analysis of (*R*)-**S4**: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.71 min, t_R (major)= 10.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.57 – 7.50 (m, 1H), 7.47 – 7.40 (m, 1H), 7.32 – 7.25 (m, 1H), 7.22 – 7.15 (m, 2H), 7.09 – 6.99JJI (m, 1H), 4.47 – 4.39 (m, 1H), 4.33 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.18 (td, *J* = 9.7, 7.2 Hz, 1H), 4.05 (td, *J* = 9.8, 7.2 Hz,

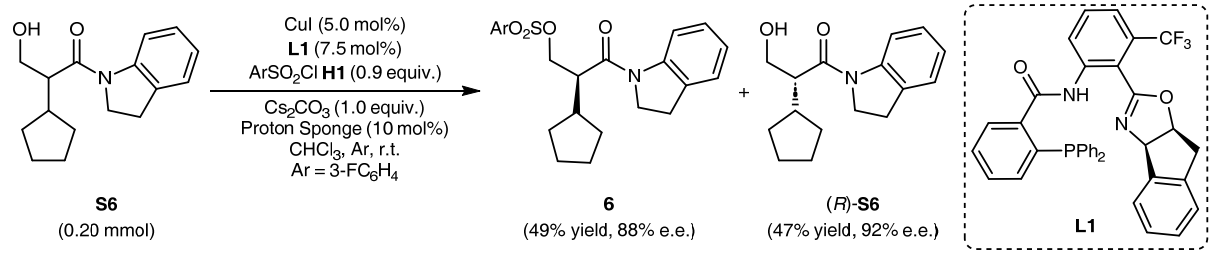
1H), 3.26 – 3.14 (m, 2H), 3.13 – 3.05 (m, 1H), 1.78 – 1.68 (m, 1H), 1.52 – 1.41 (m, 1H), 1.42 – 1.03 (m, 11H), 0.92 – 0.79 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 162.4 (d, J = 252.2 Hz), 142.9, 137.7 (d, J = 7.1 Hz), 131.6, 131.1 (d, J = 7.8 Hz), 127.6, 124.7, 124.1, 123.8 (d, J = 3.5 Hz), 121.2 (d, J = 21.1 Hz), 117.7, 115.4 (d, J = 24.8 Hz), 71.1, 48.4, 47.4, 38.5, 31.0, 29.4, 29.3, 28.5, 28.1, 23.1, 22.9, 14.1.
^{19}F NMR (375 MHz, $CDCl_3$) δ −109.05.
HRMS (ESI) m/z calcd. for $C_{26}H_{35}FNO_4S$ $[M + H]^+$ 476.2265, found 476.2269.

(*S*)-3-Allyl-2-(indoline-1-carbonyl)hex-5-en-1-yl 3-fluorobenzenesulfonate (5)



According to **General Procedure A** with **S5** (57.1 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 8/1) to afford **5** as a colorless oil (41.5 mg, 47% yield, 91% e.e.) and (*R*)-**S5** (27.2 mg, 48% yield, 91% e.e.).
HPLC analysis of **5**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.38 min, t_R (major)= 11.60 min.
HPLC analysis of (*R*)-**S5**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.44 min, t_R (major)= 11.28 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.3 Hz, 1H), 7.67 – 7.58 (m, 1H), 7.56 – 7.50 (m, 1H), 7.48 – 7.40 (m, 1H), 7.33 – 7.26 (m, 1H), 7.23 – 7.16 (m, 2H), 7.08 – 7.01 (m, 1H), 5.78 – 5.65 (m, 2H), 5.12 – 5.02 (m, 4H), 4.45 – 4.34 (m, 2H), 4.13 (td, J = 9.6, 7.6 Hz, 1H), 4.05 (td, J = 9.7, 7.2 Hz, 1H), 3.26 – 3.06 (m, 3H), 2.39 – 2.27 (m, 1H), 2.20 – 2.07 (m, 2H), 2.02 – 1.90 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 162.4 (d, J = 252.3 Hz), 142.7, 137.5 (d, J = 7.2 Hz), 135.7, 135.0, 131.7, 131.2 (d, J = 7.8 Hz), 127.6, 124.7, 124.3, 123.8 (d, J = 3.5 Hz), 121.2 (d, J = 21.2 Hz), 118.0, 117.6, 115.4 (d, J = 24.9 Hz), 70.8, 48.4, 46.5, 38.0, 35.4, 33.9, 28.0.
^{19}F NMR (375 MHz, $CDCl_3$) δ −108.95.
HRMS (ESI) m/z calcd. for $C_{24}H_{27}FNO_4S$ $[M + H]^+$ 444.1639, found 444.1641.

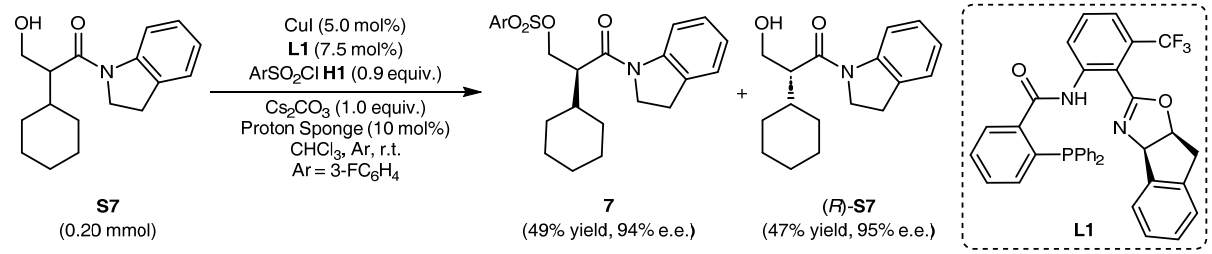
(*S*)-2-Cyclopentyl-3-(indolin-1-yl)-3-oxopropyl 3-fluorobenzenesulfonate (6)



According to **General Procedure A** with **S6** (51.9 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 40 h, the product mixture

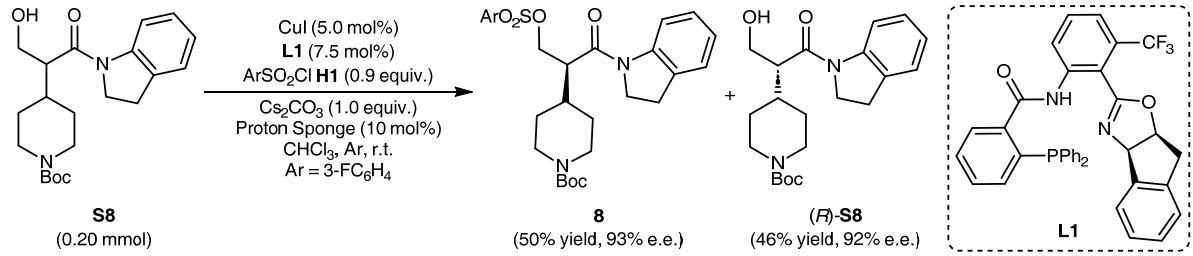
was purified by silica gel column chromatography (PE/Acetone = 8/1) to afford **6** as a white solid (40.7 mg, 49% yield, 88% e.e.) and (*R*)-**S6** (24.2 mg, 47% yield, 92% e.e.).
HPLC analysis of **6**: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.65 min, t_R (major)= 23.95 min.
HPLC analysis of (*R*)-**S6**: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.64 min, t_R (major)= 16.16 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.55 – 7.48 (m, 1H), 7.46 – 7.38 (m, 1H), 7.30 – 7.24 (m, 1H), 7.22 – 7.16 (m, 2H), 7.08 – 7.01 (m, 1H), 4.41 – 4.29 (m, 2H), 4.22 (td, *J* = 9.7, 7.3 Hz, 1H), 4.09 (td, *J* = 9.8, 7.4 Hz, 1H), 3.28 – 3.11 (m, 2H), 2.99 (td, *J* = 9.6, 4.9 Hz, 1H), 2.08 – 1.96 (m, 1H), 1.86 – 1.75 (m, 2H), 1.68 – 1.46 (m, 4H), 1.26 – 1.13 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 162.4 (d, *J* = 252.2 Hz), 142.7, 137.6 (d, *J* = 7.0 Hz), 131.7, 131.2 (d, *J* = 7.8 Hz), 127.6, 124.7, 124.2, 123.7 (d, *J* = 3.5 Hz), 121.2 (d, *J* = 21.1 Hz), 117.6, 115.4 (d, *J* = 24.9 Hz), 72.4, 49.9, 48.7, 40.4, 31.0, 30.5, 28.0, 25.0, 24.6.
^{19}F NMR (375 MHz, $CDCl_3$) δ −108.97.
HRMS (ESI) m/z calcd. for $C_{22}H_{25}FNO_4S$ $[M + H]^+$ 418.1483, found 418.1485.

(*S*)-2-Cyclohexyl-3-(indolin-1-yl)-3-oxopropyl 3-fluorobenzenesulfonate (7)



According to **General Procedure A** with **S7** (54.7 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 8/1) to afford **7** as a white solid (42.1 mg, 49% yield, 94% e.e.) and (*R*)-**S7** (25.6 mg, 47% yield, 95% e.e.).
HPLC analysis of **7**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.50 min, t_R (major)= 12.01 min.
HPLC analysis of (*R*)-**S7**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.12 min, t_R (minor)= 8.14 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.55 – 7.49 (m, 1H), 7.48 – 7.41 (m, 1H), 7.32 – 7.26 (m, 1H), 7.22 – 7.75 (m, 2H), 7.08 – 7.00 (m, 1H), 4.43 – 4.32 (m, 2H), 4.19 (td, *J* = 9.7, 7.4 Hz, 1H), 4.08 (td, *J* = 9.8, 7.3 Hz, 1H), 3.27 – 3.11 (m, 2H), 2.99 – 2.89 (m, 1H), 1.78 – 1.62 (m, 6H), 1.25 – 1.01 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 162.4 (d, *J* = 252.0 Hz), 142.7, 137.5 (d, *J* = 7.1 Hz), 131.7, 131.2 (d, *J* = 7.8 Hz), 127.6, 124.7, 124.2, 123.8 (d, *J* = 3.4 Hz), 121.2 (d, *J* = 21.1 Hz), 117.6, 115.4 (d, *J* = 24.8 Hz), 71.6, 50.4, 48.6, 38.7, 31.2, 30.7, 28.0, 26.21, 26.2, 26.1.
^{19}F NMR (375 MHz, $CDCl_3$) δ −109.03.
HRMS (ESI) m/z calcd. for $C_{23}H_{27}FNO_4S$ $[M + H]^+$ 432.1639, found 432.1640.

***tert*-Butyl (*S*)-4-(3-(((3-fluorophenyl)sulfonyl)oxy)-1-(indolin-1-yl)-1-oxopropan-2-yl)piperidine-1-carboxylate (8)**



According to **General Procedure A** with **S8** (74.9 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 40 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 5/1) to afford **8** as a light yellow oil (53.1 mg, 50% yield, 93% e.e.) and (*R*)-**S8** (34.3 mg, 46% yield, 92% e.e.).

HPLC analysis of **8**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.50 min, t_R (major)= 18.06 min.

HPLC analysis of (*R*)-**S8**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.65 min, t_R (major)= 10.83 min.

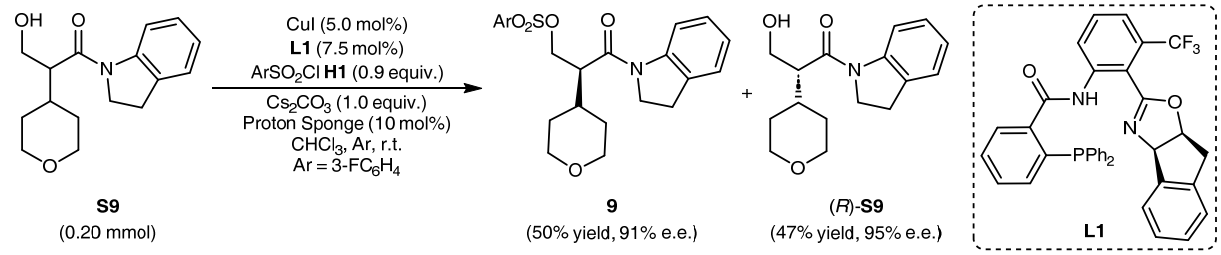
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.5 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.55 – 7.50 (m, 1H), 7.49 – 7.38 (m, 1H), 7.34 – 7.27 (m, 1H), 7.25 – 7.14 (m, 2H), 7.09 – 7.02 (m, 1H), 4.44 – 4.30 (m, 2H), 4.25 – 3.96 (m, 4H), 3.31 – 3.09 (m, 2H), 2.97 (td, *J* = 9.0, 5.0 Hz, 1H), 2.62 (t, *J* = 12.2 Hz, 2H), 1.88 – 1.78 (m, 1H), 1.74 – 1.62 (m, 2H), 1.44 (s, 9H), 1.31 – 1.20 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 162.4 (d, *J* = 252.5 Hz), 154.7, 142.5, 137.5 (d, *J* = 7.2 Hz), 131.7, 131.2 (d, *J* = 7.8 Hz), 127.6, 124.8, 124.5, 123.8 (d, *J* = 3.5 Hz), 121.3 (d, *J* = 21.1 Hz), 117.6, 115.4 (d, *J* = 24.9 Hz), 79.8, 71.0, 49.8, 48.7, 44.5 – 42.3 (br m), 37.1, 30.1, 29.8, 28.5, 28.0.

^{19}F NMR (375 MHz, $CDCl_3$) δ −108.82.

HRMS (ESI) m/z calcd. for $C_{27}H_{33}FN_2NaO_6S$ $[M + Na]^+$ 555.1936, found 555.1937.

(*S*)-3-(Indolin-1-yl)-3-oxo-2-(tetrahydro-2H-pyran-4-yl)propyl 3-fluorobenzenesulfonate (9)



According to **General Procedure A** with **S9** (55.1 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 60 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 6/1) to afford **9** as a white solid (43.5 mg, 50% yield, 91% e.e.) and (*R*)-**S9** (25.9 mg, 47% yield, 95% e.e.).

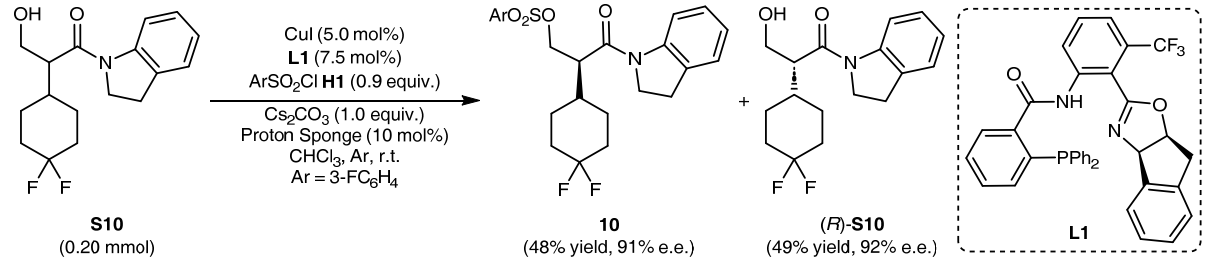
HPLC analysis of **9**: Chiralpak IB (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.67 min, t_R (major)= 15.56 min.

HPLC analysis of (*R*)-**S9**: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 23.38 min, t_R (major)= 29.85 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.9 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.55 – 7.49 (m, 1H), 7.47 – 7.40 (m, 1H), 7.32 – 7.26 (m, 1H), 7.22 – 7.16 (m, 2H), 7.09 – 7.02 (m, 1H), 4.43 – 4.31 (m, 2H), 4.21 (td, *J* = 9.7, 7.4 Hz, 1H), 4.08 (td, *J* = 9.8, 7.4 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.93 –

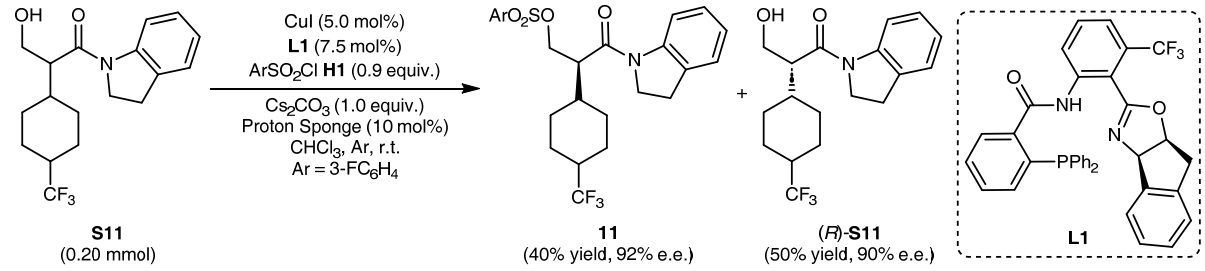
3.85 (m, 1H), 3.37 – 3.28 (m, 2H), 3.27 – 3.13 (m, 2H), 2.98 (td, *J* = 9.2, 4.8 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.67 – 1.54 (m, 2H), 1.51 – 1,38 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 162.4 (d, *J* = 252.3 Hz), 142.5, 137.4 (d, *J* = 7.0 Hz), 131.7, 131.2 (d, *J* = 7.7 Hz), 127.6, 124.8, 124.5, 123.7 (d, *J* = 3.5 Hz), 121.3 (d, *J* = 21.2 Hz), 117.6, 115.4 (d, *J* = 24.8 Hz), 70.9, 67.8, 67.6, 50.1, 48.7, 35.9, 30.8, 30.7, 28.0.
^{19}F NMR (375 MHz, $CDCl_3$) δ −108.83.
HRMS (ESI) m/z calcd. for $C_{22}H_{25}FNO_5S$ $[M + H]^+$ 434.1432, found 434.1432.

(*S*)-2-(4,4-Difluorocyclohexyl)-3-(indolin-1-yl)-3-oxopropyl 3-fluorobenzenesulfonate (10)



According to **General Procedure A** with **S10** (61.9 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 84 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 6/1) to afford **10** as a white solid (44.5 mg, 48% yield, 91% e.e.) and (*R*)-**S10** (30.4 mg, 49% yield, 92% e.e.).
HPLC analysis of **10**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.27 min, t_R (major)= 20.30 min.
HPLC analysis of (*R*)-**S10**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.67 min, t_R (major)= 11.40 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.54 – 7.49 (m, 1H), 7.48 – 7.40 (m, 1H), 7.32 – 7.26 (m, 1H),7.22 – 7.16 (m, 2H), 7.12 – 6.99 (m, 1H), 4.42 – 4.30 (m, 2H), 4.20 (td, *J* = 9.6, 7.5 Hz, 1H), 4.06 (td, *J* = 9.7, 7.4 Hz, 1H), 3.27 – 3.12 (m, 2H), 2.98 (td, *J* = 8.9, 5.1 Hz, 1H), 2.17 – 1.99 (m, 2H), 1.96 – 1.81 (m, 1H), 1.79 – 1.67 (m, 3H), 1.65 – 1.57 (m, 1H), 1.47 – 1.35 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 162.4 (d, *J* = 252.5 Hz), 142.5, 137.4 (d, *J* = 7.1 Hz), 131.7, 131.2 (d, *J* = 7.8 Hz), 127.6, 124.8, 124.5, 123.8 (d, *J* = 3.6 Hz), 122.8 (dd, *J* = 243.1, 239.0 Hz), 121.4 (d, *J* = 21.2 Hz), 117.6, 115.4 (d, *J* = 24.8 Hz), 71.1, 49.3 (d, *J* = 2.2 Hz), 48.7, 36.7 (d, *J* = 1.6 Hz), 33.4 (ddd, *J* = 25.5, 23.2, 7.1 Hz, 2C), 28.0, 27.2 (d, *J* = 9.9 Hz), 26.5 (d, *J* = 10.1 Hz).
^{19}F NMR (375 MHz, $CDCl_3$) δ −91.95 (d, *J* = 236.7 Hz), −103.01 (d, *J* = 236.9 Hz), −108.79.
HRMS (ESI) m/z calcd. for $C_{23}H_{25}F_3NO_4S$ $[M + H]^+$ 468.1451, found 468.1453.

(2*S*)-3-(Indolin-1-yl)-3-oxo-2-(4-(trifluoromethyl)cyclohexyl)propyl 3-fluorobenzenesulf onate (11)



According to **General Procedure A** with **S11** (68.2 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 8/1) to afford **11** as a white solid (39.9 mg, 40% yield, 92% e.e.) and (*R*)-**S11** (34.3 mg, 50% yield, 90% e.e.).

HPLC analysis of **11**: Chiralpak IB (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.15 min, t_R (major)= 18.13 min.

HPLC analysis of (*R*)-**S11**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.67 min, t_R (major)= 11.47 min.

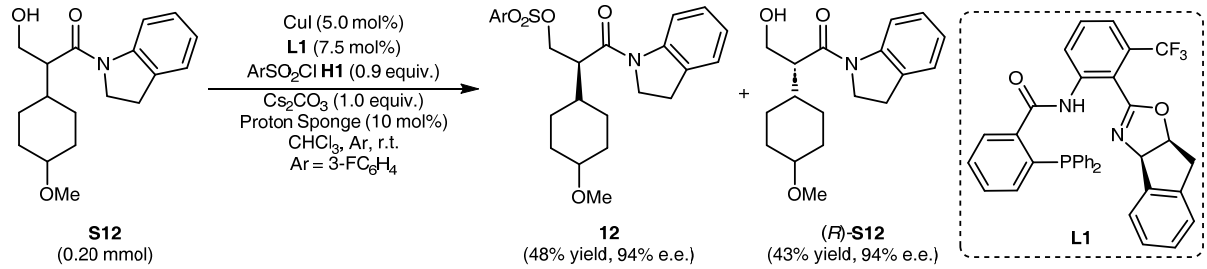
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.55 – 7.49 (m, 1H), 7.48 – 7.41 (m, 1H), 7.33 – 7.27 (m, 1H), 7.23 – 7.17 (m, 2H), 7.09 – 7.03 (m, 1H), 4.43 – 4.33 (m, 2H), 4.20 (td, *J* = 9.7, 7.3 Hz, 1H), 4.06 (td, *J* = 9.8, 7.2 Hz, 1H), 3.26 – 3.12 (m, 2H), 2.96 (td, *J* = 8.7, 5.2 Hz, 1H), 2.01 – 1.82 (m, 5H), 1.71 – 1.64 (m, 1H), 1.34 – 1.23 (m, 2H), 1.21 – 1.05 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 162.4 (d, *J* = 252.7 Hz), 142.5, 137.4 (d, *J* = 7.1 Hz), 131.7, 131.2 (d, *J* = 7.8 Hz), 127.7, 127.5 (q, *J* = 278.5 Hz), 124.8, 124.5, 123.8 (d, *J* = 3.6 Hz), 121.4 (d, *J* = 21.0 Hz), 117.6, 115.4 (d, *J* = 24.7 Hz), 71.1, 49.9, 48.7, 41.6 (q, *J* = 26.7 Hz), 37.8, 29.3, 28.9, 28.0, 24.8 – 24.6 (m, 2C).

^{19}F NMR (375 MHz, $CDCl_3$) δ −73.92, −108.84.

HRMS (ESI) m/z calcd. for $C_{24}H_{26}F_4NO_4S$ $[M + H]^+$ 500.1513, found 500.1514.

(2*S*)-3-(Indolin-1-yl)-2-(4-methoxycyclohexyl)-3-oxopropyl 3-fluorobenzenesulfonate (12)



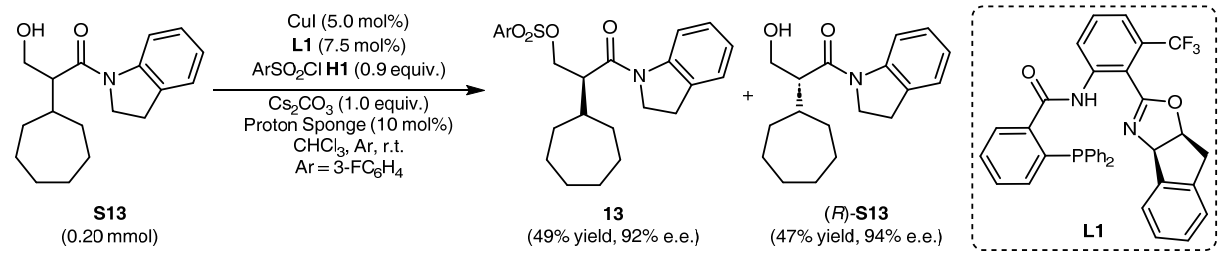
According to **General Procedure A** with **S12** (60.7 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 5/1) to afford **12** as a colorless oil (44.5 mg, 48% yield, 94% e.e.) and (*R*)-**S12** (25.8 mg, 43% yield, 94% e.e.).

HPLC analysis of **12**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.89 min, t_R (major)= 13.65 min.

HPLC analysis of (*R*)-**S12**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.46 min, t_R (major)= 12.69 min.

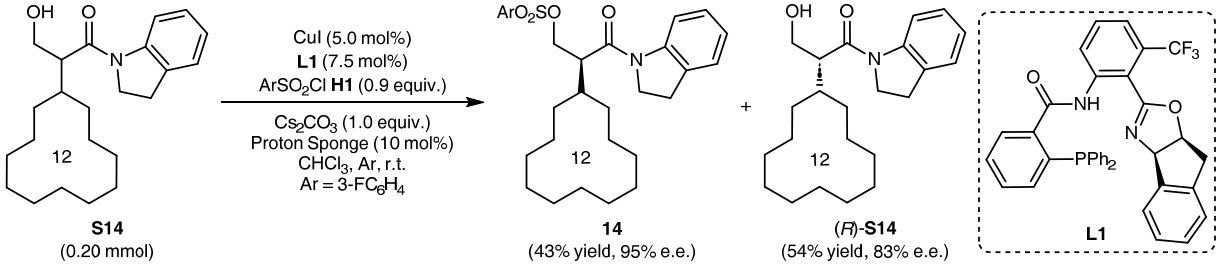
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.54 – 7.48 (m, 1H), 7.43 (td, *J* = 8.1, 5.2 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.23 – 7.16 (m, 2H), 7.08 – 7.01 (m, 1H), 4.46 – 4.39 (m, 1H), 4.38 – 4.31 (m, 1H), 4.22 – 4.06 (m, 2H), 3.44 – 3.37 (m, 1H), 3.27 (s, 3H), 3.20 – 3.15 (m, 1H), 2.96 (td, *J* = 9.7, 4.4 Hz, 1H), 1.98 – 1.82 (m, 2H), 1.76 – 1.62 (m, 2H), 1.53 – 1.30 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 162.4 (d, *J* = 252.2 Hz), 142.7, 137.6 (d, *J* = 7.3 Hz), 131.8, 131.1 (d, *J* = 7.8 Hz), 127.6, 124.8, 124.3, 123.8 (d, *J* = 3.5 Hz), 121.2 (d, *J* = 21.1 Hz), 117.6, 115.4 (d, *J* = 24.8 Hz), 74.3, 71.6, 55.8, 50.1, 48.6, 37.9, 29.1, 28.9, 28.0, 25.1, 24.5.
^{19}F NMR (375 MHz, $CDCl_3$) δ −109.02.
HRMS (ESI) m/z calcd. for $C_{24}H_{29}FNO_5S$ $[M + H]^+$ 462.1745, found 462.1747.

(*S*)-2-Cycloheptyl-3-(indolin-1-yl)-3-oxopropyl 3-fluorobenzenesulfonate (13)



According to **General Procedure A** with **S13** (57.5 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 84 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 6/1) to afford **13** as a white solid (43.9 mg, 49% yield, 92% e.e.) and (*R*)-**S13** (26.9 mg, 47% yield, 94% e.e.).
HPLC analysis of **13**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.52 min, t_R (major)= 11.57 min.
HPLC analysis of (*R*)-**S13**: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.17 min, t_R (major)= 8.65 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.55 – 7.50 (m, 1H), 7.47 – 7.40 (m, 1H), 7.32 – 7.25 (m, 1H), 7.22 – 7.16 (m, 2H), 7.08 – 7.00 (m, 1H), 4.45 – 4.34 (m, 2H), 4.24 – 4.14 (m, 1H), 4.06 (td, *J* = 9.6, 7.4 Hz, 1H), 3.25 – 3.12 (m, 2H), 2.98 (td, *J* = 7.9, 6.0 Hz, 1H), 1.89 – 1.75 (m, 2H), 1.72 – 1.53 (m, 5H), 1.49 – 1.31 (m, 5H), 1.30 – 1.18 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 162.4 (d, *J* = 252.2 Hz), 142.8, 137.6 (d, *J* = 7.2 Hz), 131.6, 131.1 (d, *J* = 7.8 Hz), 127.6, 124.7, 124.2, 123.7 (d, *J* = 3.5 Hz), 121.2 (d, *J* = 21.2 Hz), 117.6, 115.4 (d, *J* = 24.8 Hz), 71.6, 50.6, 48.5, 40.0, 32.6, 31.3, 28.1(3), 28.0(9), 28.0, 26.6, 26.3.
^{19}F NMR (375 MHz, $CDCl_3$) δ −109.04.
HRMS (ESI) m/z calcd. for $C_{24}H_{29}FNO_4S$ $[M + H]^+$ 446.1796, found 446.1797.

(*S*)-2-Cyclododecyl-3-(indolin-1-yl)-3-oxopropyl 3-fluorobenzenesulfonate (14)



According to **General Procedure A** with **S14** (71.5 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 84 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 5/1) to afford **14** as a white solid (44.5 mg, 43% yield, 95% e.e.) and (*R*)-**S14** (38.8 mg, 54% yield, 83% e.e.).

HPLC analysis of **14**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.28 min, t_R (major)= 10.31 min.

HPLC analysis of (*R*)-**S14**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.83 min, t_R (minor)= 12.34 min.

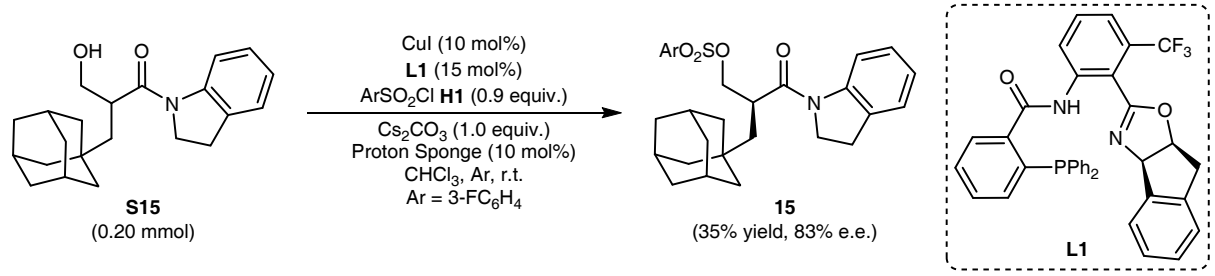
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.54 – 7.47 (m, 1H), 7.46 – 7.37 (m, 1H), 7.30 – 7.24 (m, 1H), 7.23 – 7.16 (m, 2H), 7.08 – 7.00 (m, 1H), 4.46 – 4.33 (m, 2H), 4.26 – 4.16 (m, 1H), 4.12 – 4.01 (m, 1H), 3.27 – 3.12 (m, 2H), 3.04 (td, *J* = 9.3, 4.3 Hz, 1H), 1.91 – 1.80 (m, 1H), 1.55 – 1.46 (m, 1H), 1.40 – 1.20 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 162.4 (d, *J* = 252.3 Hz), 142.8, 137.6 (d, *J* = 7.1 Hz), 131.7, 131.1 (d, *J* = 7.7 Hz), 127.6, 124.7, 124.2, 123.7 (d, *J* = 3.4 Hz), 121.2 (d, *J* = 21.1 Hz), 117.7, 115.4 (d, *J* = 24.8 Hz), 71.9, 48.5, 47.8, 36.0, 28.1, 27.3, 25.5, 25.3, 25.2, 24.9, 23.1, 23.0(4), 23.0(1), 22.9(6), 22.4, 20.7.

^{19}F NMR (375 MHz, $CDCl_3$) δ −108.99.

HRMS (ESI) m/z calcd. for $C_{29}H_{39}FNO_4S$ $[M + H]^+$ 516.2578, found 516.2582.

(*S*)-2-((Adamantan-1-yl)methyl)-3-(indolin-1-yl)-3-oxopropyl 3-fluorobenz enesulfonate (15)



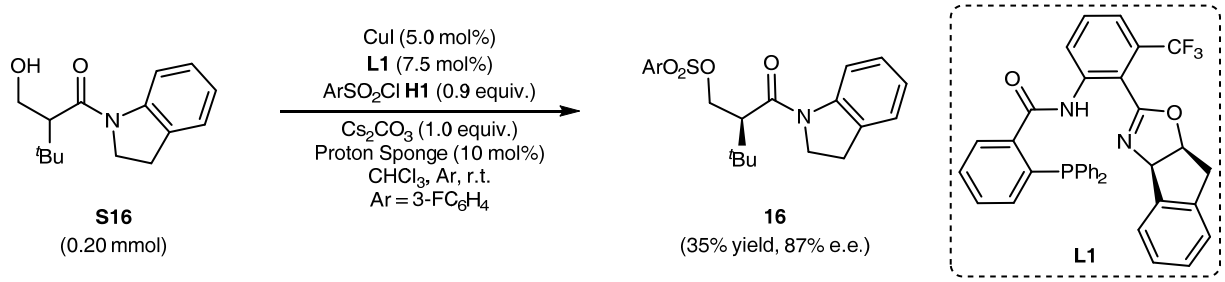
According to **General Procedure A** with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L1** (18.2 mg, 0.03 mmol, 15 mol%), **S15** (67.9 mg, 0.20 mmol, 1.0 equiv.) and 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) for 96 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 5/1) to afford **15** as a white solid (34.6 mg, 35% yield, 83% e.e.).

HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.96 min, t_R (major)= 12.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.53 – 7.46 (m, 1H), 7.44 – 7.36 (m, 1H), 7.28 – 7.23 (m, 1H), 7.22 – 7.16 (m, 2H), 7.08 – 7.02 (m, 1H), 4.30 (td, *J* =

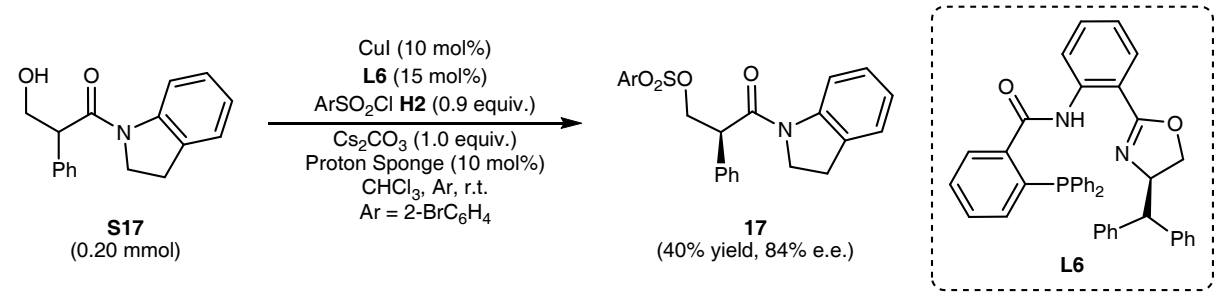
9.6, 6.9 Hz, 1H), 4.25 – 4.07 (m, 3H), 3.29 – 3.12 (m, 3H), 1.96 – 1.86 (m, 3H), 1.77 – 1.66 (m, 4H), 1.61 – 1.54 (m, 3H), 1.53 – 1.45 (m, 3H), 1.44 – 1.36 (m, 3H), 1.05 (dd, J = 14.3, 3.5 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 162.4 (d, J = 252.5 Hz), 142.9, 137.6 (d, J = 7.1 Hz), 131.7, 131.2 (d, J = 7.8 Hz), 127.6, 124.7, 124.2, 123.7 (d, J = 3.6 Hz), 121.2 (d, J = 21.2 Hz), 117.7, 115.3 (d, J = 24.8 Hz), 73.4, 48.4, 43.1, 42.8, 39.2, 36.9, 32.6, 28.6, 28.1.
^{19}F NMR (375 MHz, $CDCl_3$) δ −108.87.
HRMS (ESI) m/z calcd. for $C_{28}H_{33}FNO_4S$ $[M + H]^+$ 498.2109, found 498.2110.

(*S*)-2-(Indoline-1-carbonyl)-3,3-dimethylbutyl 3-fluorobenzenesulfonate (16)



According to **General Procedure A** with **S16** (67.9 mg, 0.20 mmol, 1.0 equiv.), 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) and dry $CHCl_3$ (0.5 mL) for 96 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 6/1) to afford **16** as a white solid (28.7 mg, 35% yield, 87% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.63 min, t_R (major)= 8.83 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.8 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.54 – 7.48 (m, 1H), 7.44 – 7.37 (m, 1H), 7.28 – 7.22 (m, 1H), 7.21 – 7.15 (m, 2H), 7.09 – 6.91 (m, 1H), 4.50 (dd, J = 10.3, 9.3 Hz, 1H), 4.41 (dd, J = 9.3, 3.5 Hz, 1H), 4.18 (td, J = 9.7, 7.5 Hz, 1H), 4.09 (td, J = 9.7, 7.4 Hz, 1H), 3.25 – 3.10 (m, 2H), 2.96 (dd, J = 10.3, 3.5 Hz, 1H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 162.4 (d, J = 252.2 Hz), 142.8, 137.8 (d, J = 7.1 Hz), 131.7, 131.2 (d, J = 7.8 Hz), 127.5, 124.7, 124.1, 123.7 (d, J = 3.5 Hz), 121.2 (d, J = 21.2 Hz), 117.7, 115.3 (d, J = 24.8 Hz), 71.7, 53.1, 49.2, 33.9, 28.2, 28.0.
^{19}F NMR (375 MHz, $CDCl_3$) δ −109.00.
HRMS (ESI) m/z calcd. for $C_{21}H_{25}FNO_4S$ $[M + H]^+$ 406.1483, found 406.1484.

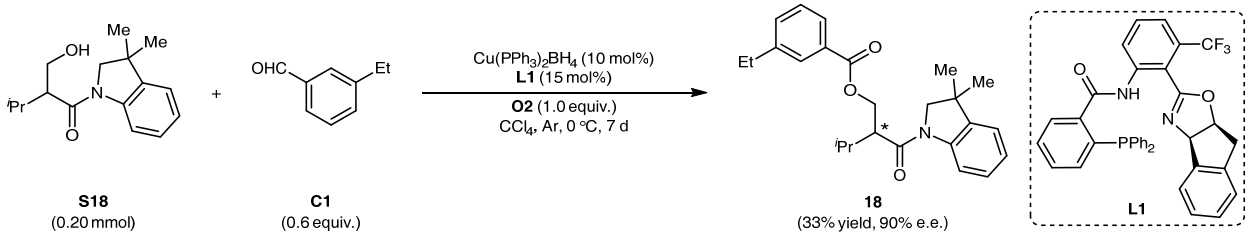
(*S*)-3-(Indolin-1-yl)-3-oxo-2-phenylpropyl 2-bromobenzenesulfonate (17)



According to **General Procedure A** with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L6** (18.5 mg, 0.03 mmol, 15 mol%), **S17** (53.5 mg, 0.20 mmol, 1.0 equiv.) and 2-bromobenzenesulfonyl chloride **H2**

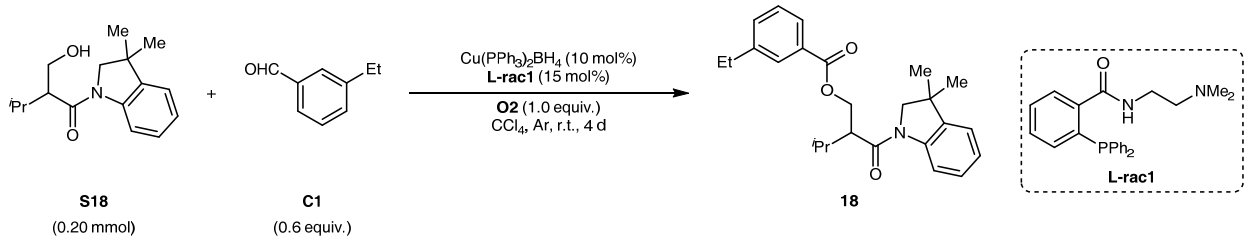
(46.0 mg, 0.18 mmol, 0.9 equiv.) for 96 h, the product mixture was purified by silica gel column chromatography (PE/Acetone = 5/1) to afford **17** as a white solid (38.7 mg, 40% yield, 84% e.e.).
HPLC analysis: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 25.89 min, t_R (major)= 29.14 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 1H), 8.11 – 8.07 (m, 1H), 7.77 – 7.63 (m, 1H), 7.49 – 7.39 (m, 2H), 7.35 – 7.26 (m, 5H), 7.21 – 7.15 (m, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.05 – 6.95 (m, 1H), 4.85 (dd, *J* = 9.8, 8.5 Hz, 1H), 4.33 (dd, *J* = 9.9, 5.6 Hz, 1H), 4.24 (dd, *J* = 8.5, 5.6 Hz, 1H), 4.14 (td, *J* = 10.3, 6.6 Hz, 1H), 3.76 (td, *J* = 10.4, 6.2 Hz, 1H), 3.14 (ddd, *J* = 16.5, 10.5, 6.2 Hz, 1H), 3.00 (ddd, *J* = 16.5, 10.6, 6.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 142.9, 135.9, 135.7, 134.7, 133.7, 132.1, 131.3, 129.4, 128.6, 128.5, 127.7, 127.6, 124.6, 124.3, 121.1, 117.4, 72.3, 51.3, 47.7, 28.0.
HRMS (ESI) m/z calcd. for $C_{23}H_{21}BrNO_4S$ $[M + H]^+$ 486.0369, found 486.0369.

2-(3,3-Dimethylindoline-1-carbonyl)-3-methylbutyl 3-ethylbenzoate (18)



S18 (0.20 mmol) **C1** (0.6 equiv.) **18** (33% yield, 90% e.e.)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (12.0 mg, 0.02 mmol, 10 mol %), **L1** (18.2 mg, 0.03 mmol, 15 mol%), γ-aminocarbonyl alcohol **S18** (52.2 mg, 0.20 mmol, 1.0 equiv.), and anhydrous CCl_4 (2.0 mL). Then, **O2** (40.4 mg, 0.20 mmol, 1.0 equiv.) and 3-ethylbenzaldehyde **C1** (16.2 mg, 0.12 mmol, 0.6 equiv.) were added to the mixture and the reaction mixture was stirred at 0 °C for 7 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The filtrate was evaporated and the residue was purified by flash column chromatography (EtOAc/PE = 1/10) to afford the **18** as a colorless liquid (26.0 mg, 33% yield, 90 % e.e.).

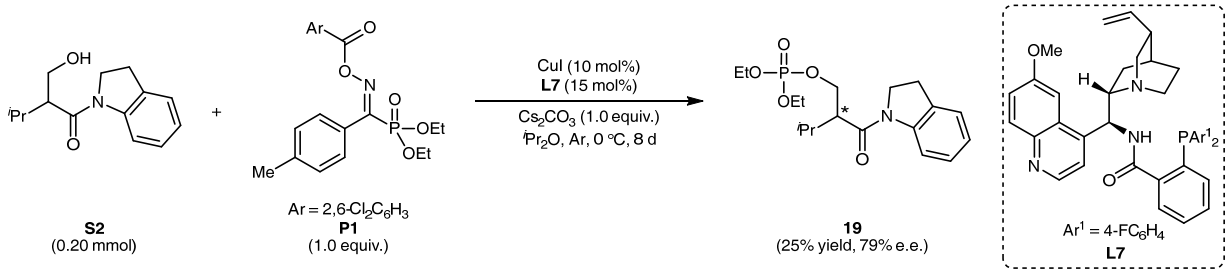


S18 (0.20 mmol) **C1** (0.6 equiv.) **18**

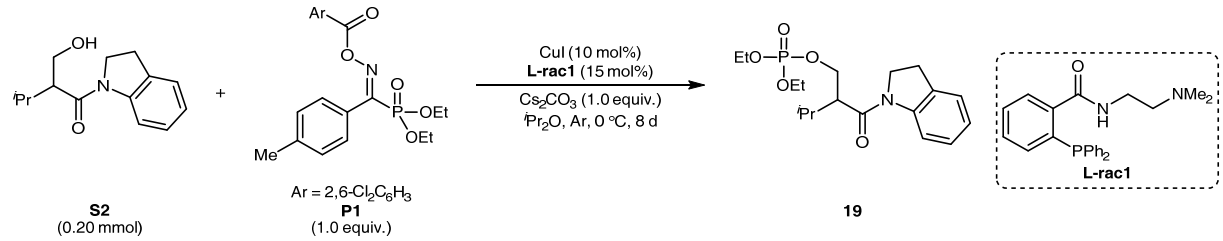
The racemates of products were prepared following the procedure: under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (12.0 mg, 0.02 mmol, 10 mol %), **L-rac1** (11.3 mg, 0.03 mmol, 15 mol%), γ-aminocarbonyl alcohol **S18** (52.2 mg, 0.20 mmol, 1.0 equiv.), and anhydrous CCl_4 (2.0 mL). Then, **O2** (40.4 mg, 0.20 mmol, 1.0 equiv.) and 3-ethylbenzaldehyde **C1** (16.2 mg, 0.12 mmol, 0.6 equiv.) were added to the mixture and the reaction mixture was stirred at 0 °C for 7 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The filtrate was evaporated and the residue was purified by flash column chromatography (EtOAc/PE = 1/10) to afford the desired product.

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/05, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 16.98 min, t_R (minor) = 12.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.64 (m, 2H), 7.35 – 7.27 (m, 1H), 7.27 – 7.18 (m, 2H), 7.15 – 7.02 (m, 2H), 4.75 (dd, *J* = 10.5, 4.7 Hz, 1H), 4.49 (t, *J* = 10.2 Hz, 1H), 3.85 (s, 2H), 2.98 – 2.88 (m, 1H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.23 – 2.09 (m, 1H), 1.33 (s, 3H), 1.17 (s, 3H), 1.15 – 1.07 (m, 6H), 1.07 – 1.02 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 166.7, 144.5, 141.5, 140.8, 132.7, 129.9, 129.0, 128.3, 127.8, 127.0, 124.2, 121.8, 117.5, 65.7, 63.6, 51.0, 40.0, 29.5, 28.5, 28.4, 21.2, 20.3, 15.4.
HRMS (ESI) m/z calcd. for $C_{25}H_{32}NO_3$+ $[M + H]^+$ 394.2377, found 394.2379.

(*S*)-Diethyl (2-(indoline-1-carbonyl)-3-methylbutyl) phosphate (19)



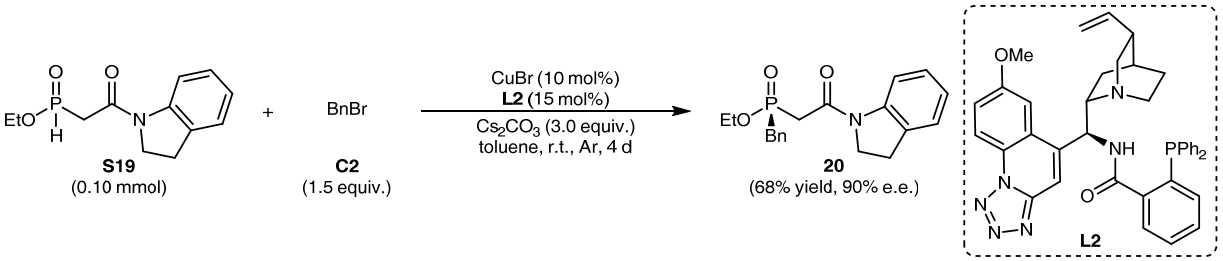
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L7** (19.4 mg, 0.03 mmol, 15 mol%), Cs_2CO_3 (65.1 mg, 0.20 mmol, 1.0 equiv.), γ-aminocarbonyl alcohol **S2** (46.7 mg, 0.20 mmol, 1.0 equiv.), oxime phosphonate **P1** (88.8 mg, 0.20 mmol, 1.0 equiv.), and anhydrous ^{i}Pr$_2$O (2.0 mL). Then the reaction mixture was stirred at 0 °C for 8 d. Upon completion, the precipitate was filtered off and washed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (EtOAc/PE = 2/1) to afford the **19** as a light yellow oil (18.5 mg, 25% yield, 79% e.e.).



The racemates of products were prepared following the procedure: under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L-rac1** (11.3 mg, 0.03 mmol, 15 mol%), γ-aminocarbonyl alcohol **S2** (46.7 mg, 0.20 mmol, 1.0 equiv.), oxime phosphonate **P1 (**88.8 mg, 0.20 mmol, 1.0 equiv.), and anhydrous ^{i}Pr$_2$O (2.0 mL). Then the reaction mixture was stirred at 0 °C for 8 d. Upon completion, the precipitate was filtered off and washed with EtOAc and concentrated *in vacuo*. The filtrate was evaporated and the residue was purified by flash column chromatography (EtOAc/PE = 2/1) to afford the desired product.

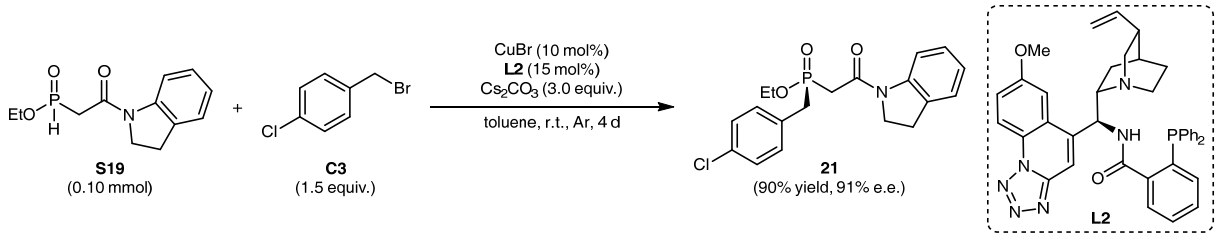
HPLC analysis: Chiralpak IA-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 15.15 min, t_R (minor) = 21.94 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 9.0 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.07 – 6.99 (m, 1H), 4.45 – 4.22 (m, 3H), 4.18 – 3.97 (m, 5H), 3.19 (t, *J* = 8.5 Hz, 2H), 2.95 – 2.83 (m, 1H), 2.03 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.34 – 1.18 (m, 6H), 1.06 – 0.86 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 143.0, 131.7, 127.6, 124.7, 124.0, 117.6, 68.2 (d, *J* = 5.8 Hz), 64.0 (t, *J* = 5.5 Hz), 52.2 (d, *J* = 6.8 Hz), 48.7, 29.1, 28.1, 21.2, 20.2, 16.2 (dd, *J* = 6.8, 4.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ –1.43.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{29}NO_5P$ $[M + H]^+$ 370.1778, found 370.1778.

Ethyl (*S*)-benzyl(2-(indolin-1-yl)-2-oxoethyl)phosphinate (20)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and (bromomethyl)benzene **C2** (25.5 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **20** as a white solid (23.4 mg, 68% yield, 90% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 28.98 min, t_R (major) = 30.70 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.09 (m, 7H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.27 – 3.92 (m, 4H), 3.40 (d, *J* = 17.7 Hz, 2H), 3.15 (t, *J* = 8.4 Hz, 2H), 3.01 (d, *J* = 17.1 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (d, *J* = 4.2 Hz), 142.7, 131.7, 131.3 (d, *J* = 8.2 Hz), 130.2 (d, *J* = 5.9 Hz), 128.8 (d, *J* = 3.0 Hz), 127.6, 127.1 (d, *J* = 3.5 Hz), 124.7, 124.3, 117.4, 61.6 (d, *J* = 7.0 Hz), 49.1, 37.4 (d, *J* = 82.8 Hz), 36.8 (d, *J* = 89.0 Hz), 27.9, 16.7 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 45.56.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}NO_3P$ $[M + H]^+$ 344.1410, found 344.1404.

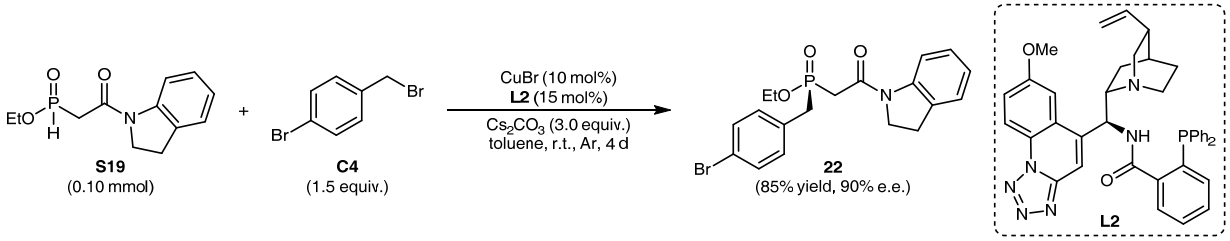
Ethyl (*S*)-(4-chlorobenzyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (21)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 1-(bromomethyl)-4-chlorobenzene **C3** (30.8 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the

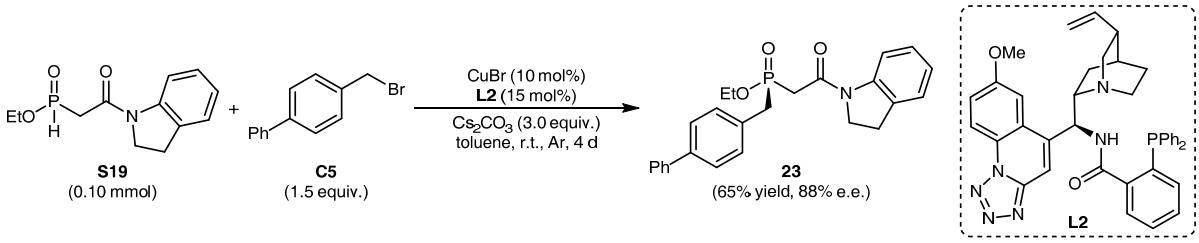
reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **21** as a colorless oil (34.0 mg, 90% yield, 91% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 11.22 min, t_R (minor) = 14.77 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.13 (m, 6H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.32 – 3.92 (m, 4H), 3.38 (d, *J* = 17.0 Hz, 2H), 3.17 (t, *J* = 8.5 Hz, 2H), 3.01 (d, *J* = 17.5 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 3.7 Hz), 142.6, 133.1 (d, *J* = 4.2 Hz), 131.7, 131.6 (d, *J* = 5.9 Hz), 129.9 (d, *J* = 8.2 Hz), 128.9 (d, *J* = 3.0 Hz), 127.6, 124.8, 124.4, 117.4, 61.7 (d, *J* = 6.9 Hz), 49.2, 37.4 (d, *J* = 83.0 Hz), 36.0 (d, *J* = 90.1 Hz), 28.0, 16.7 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 45.05.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}NO_3PCl$ $[M + H]^+$ 378.1020, found 378.1014.

Ethyl (*S*)-(4-bromobenzyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (22)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 1-bromo-4-(bromomethyl)benzene **C4** (37.5 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **22** as a white solid (35.9 mg, 85% yield, 90% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 10.60 min, t_R (minor) = 13.27 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.26 (m, 2H), 7.25 – 7.14 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 4.30 – 3.89 (m, 4H), 3.48 – 3.26 (m, 2H), 3.17 (t, *J* = 8.4 Hz, 2H), 3.01 (d, *J* = 17.5 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 3.7 Hz), 142.6, 132.0 (d, *J* = 5.9 Hz), 131.9 (d, *J* = 3.0 Hz), 131.8, 130.4 (d, *J* = 8.3 Hz), 127.6, 124.8, 124.4, 121.3 (d, *J* = 4.4 Hz), 117.4, 61.7 (d, *J* = 6.9 Hz), 49.2, 37.3 (d, *J* = 83.2 Hz), 36.1 (d, *J* = 90.0 Hz), 28.0, 16.7 (d, *J* = 5.6 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 45.03.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}NO_3PBr$ $[M + H]^+$ 422.0515, found 422.0509.

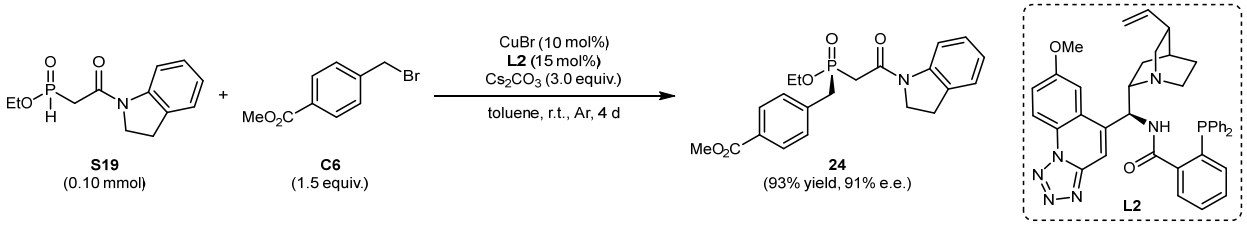
Ethyl (*S*)-([1,1'-biphenyl]-4-ylmethyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (23)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 4-(bromomethyl)-1,1'-biphenyl **C5** (37.1 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction

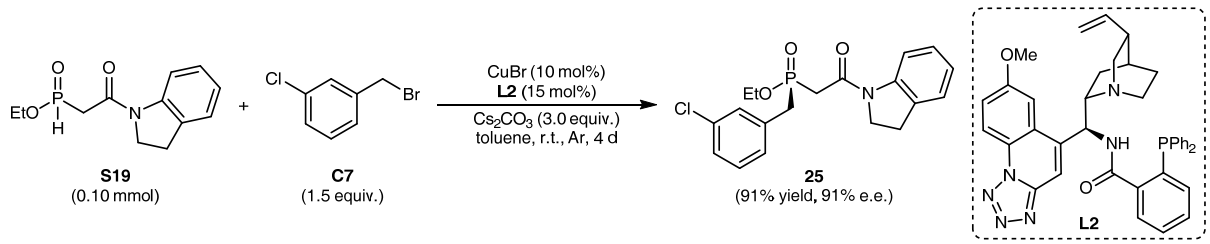
mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **23** as a white solid (27.3 mg, 65% yield, 88% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 14.60 min, t_R (minor) = 16.87 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.38 (m, 8H), 7.38 – 7.28 (m, 1H), 7.26 – 7.14 (m, 2H), 7.05 (t, *J* = 8.0 Hz, 1H), 4.21 – 3.98 (m, 4H), 3.45 (d, *J* = 17.9 Hz, 2H), 3.14 (t, *J* = 8.4 Hz, 2H), 3.05 (d, *J* = 17.2 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, *J* = 3.9 Hz), 142.7, 140.7 (d, *J* = 1.5 Hz), 140.0 (d, *J* = 3.8 Hz), 131.8, 130.7 (d, *J* = 5.9 Hz), 130.3 (d, *J* = 8.1 Hz), 128.9, 127.6, 127.4(8), 127.4(5), 127.1, 124.8, 124.4, 117.4, 61.7 (d, *J* = 6.8 Hz), 49.2, 37.5 (d, *J* = 82.6 Hz), 36.4 (d, *J* = 90.1 Hz), 28.0, 16.7 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 45.68.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}NO_3P$ $[M + H]^+$ 420.1723, found 420.1714.

Methyl (*S*)-4-((ethoxy(2-(indolin-1-yl)-2-oxoethyl)phosphoryl)methyl)benzoate (24)



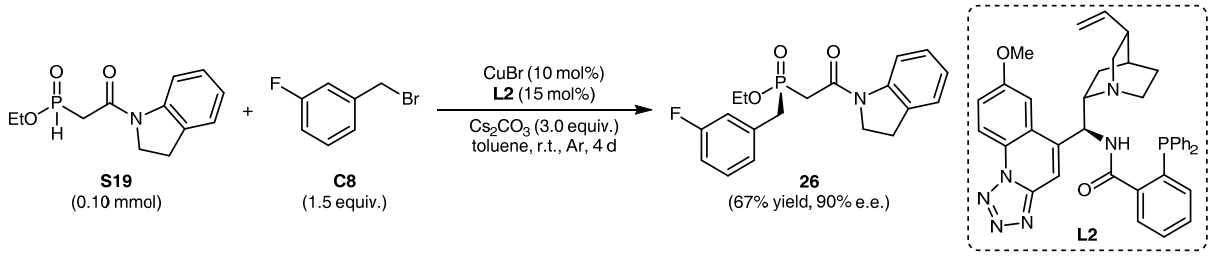
According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and methyl 4-(bromomethyl)benzoate **C6** (34.5 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **24** as a white solid (37.3 mg, 93% yield, 91% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 11.82 min, t_R (minor) = 16.89 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.49 (dd, *J* = 8.3, 2.4 Hz, 2H), 7.25 – 7.16 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 4.28 – 3.96 (m, 4H), 3.91 (s, 3H), 3.48 (d, *J* = 18.0 Hz, 2H), 3.17 (t, *J* = 8.4 Hz, 2H), 3.03 (d, *J* = 17.4 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 163.3 (d, *J* = 3.8 Hz), 142.6, 136.85 (d, *J* = 8.4 Hz), 131.8, 130.3 (d, *J* = 5.7 Hz), 130.0 (d, *J* = 2.9 Hz), 129.1 (d, *J* = 3.3 Hz), 127.6, 124.8, 124.5, 117.4, 61.8 (d, *J* = 6.9 Hz), 52.2, 49.2, 37.6 (d, *J* = 83.6 Hz), 36.9 (d, *J* = 89.1 Hz), 28.0, 16.7 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 44.75.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}NO_5P$ $[M + H]^+$ 402.1465, found 402.1457.

Ethyl (*S*)-(3-chlorobenzyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (25)



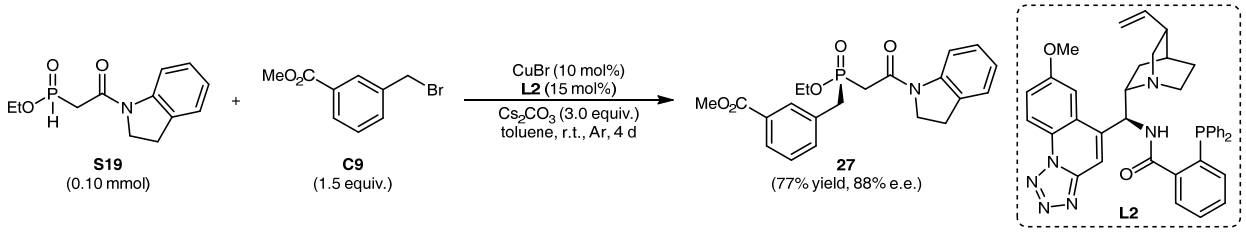
According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 1-(bromomethyl)-3-chlorobenzene **C7** (30.8 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **25** as a white solid (34.4 mg, 91% yield, 91% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 10.43 min, t_R (minor) = 13.57 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.40 (s, 1H), 7.35 – 7.15 (m, 5H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.33 – 3.96 (m, 4H), 3.39 (d, *J* = 17.7 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 3.03 (d, *J* = 17.5 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 3.8 Hz), 142.6, 134.5 (d, *J* = 3.5 Hz), 133.4 (d, *J* = 8.2 Hz), 131.8, 130.2 (d, *J* = 5.9 Hz), 130.0 (d, *J* = 3.0 Hz), 128.5 (d, *J* = 5.8 Hz), 127.6, 127.4 (d, *J* = 3.4 Hz), 124.8, 124.4, 117.4, 61.8 (d, *J* = 6.8 Hz), 49.2, 37.5 (d, *J* = 83.4 Hz), 36.4 (d, *J* = 89.9 Hz), 28.0, 16.7 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 44.94.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}NO_3PCl$ $[M + H]^+$ 378.1020, found 378.1016.

Ethyl (*S*)-(3-fluorobenzyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (26)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 1-(bromomethyl)-3-fluorobenzene **C8** (28.3 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **26** as a colorless oil (24.2 mg, 67% yield, 90% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 10.14 min, t_R (minor) = 12.69 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.11 (m, 5H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 8.4 Hz, 1H), 4.29 – 3.95 (m, 4H), 3.41 (d, *J* = 17.8 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 3.03 (d, *J* = 17.5 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 3.9 Hz), 162.9 (dd, *J* = 3.5, 246.3 Hz), 142.6, 133.8 (t, *J* = 8.2 Hz), 131.8, 130.2 (dd, *J* = 3.0, 8.4 Hz), 127.6, 126.0 (dd, *J* = 6.1, 3.0 Hz), 124.8, 124.4, 117.4, 117.2 (dd, *J* = 22.0, 5.8 Hz), 114.1 (dd, *J* = 21.0, 3.5 Hz), 61.7 (d, *J* = 6.9 Hz), 49.2, 37.5 (d, *J* = 83.4 Hz), 36.5 (dd, *J* = 90.1, 1.8 Hz), 28.0, 16.7 (d, *J* = 5.7 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 44.98.
^{19}F NMR (375 MHz, $CDCl_3$) δ –112.71.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}NO_3PF$ $[M + H]^+$ 362.1316, found 362.1309.

Methyl (*S*)-3-((ethoxy(2-(indolin-1-yl)-2-oxoethyl)phosphoryl)methyl)benzoate (27)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and methyl 3-(bromomethyl)benzoate **C9** (34.4 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **27** as a white solid (30.9 mg, 77% yield, 88% e.e.).

HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 13.95 min, t_R (minor) = 17.15 min.

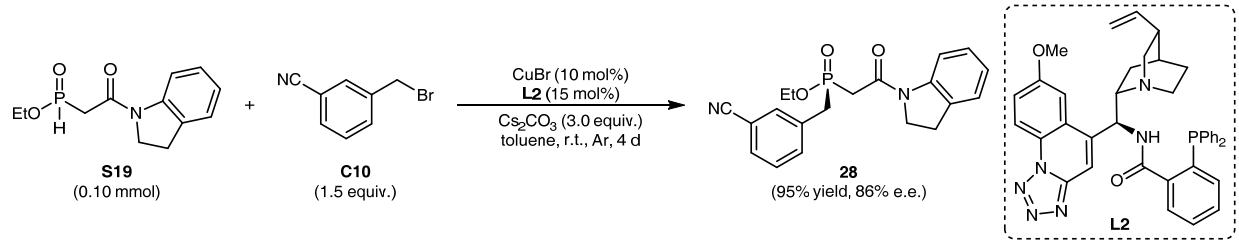
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.1 Hz, 1H), 8.03 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.20 – 3.98 (m, 4H), 3.87 (s, 3H), 3.46 (d, *J* = 17.5 Hz, 2H), 3.16 (t, *J* = 8.5 Hz, 2H), 3.03 (d, *J* = 17.4 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 163.4 (d, *J* = 3.9 Hz), 142.7, 134.8 (d, *J* = 5.6 Hz), 131.9 (d, *J* = 8.4 Hz), 131.7, 131.2 (d, *J* = 6.0 Hz), 130.7 (d, *J* = 2.8 Hz), 128.9 (d, *J* = 2.9 Hz), 128.4 (d, *J* = 3.3 Hz), 127.6, 124.8, 124.4, 117.5, 61.8 (d, *J* = 6.9 Hz), 52.2, 49.2, 37.7 (d, *J* = 83.2 Hz), 36.6 (d, *J* = 89.9 Hz), 28.0, 16.6 (d, *J* = 5.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 44.88.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}NO_5P$ $[M + H]^+$ 402.1465, found 402.1458.

Ethyl (*S*)-(3-cyanobenzyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (28)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 3-(bromomethyl)benzonitrile **C10** (29.4 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **28** as a white solid (35.0 mg, 95% yield, 86% e.e.).

HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 16.88 min, t_R (minor) = 31.69 min.

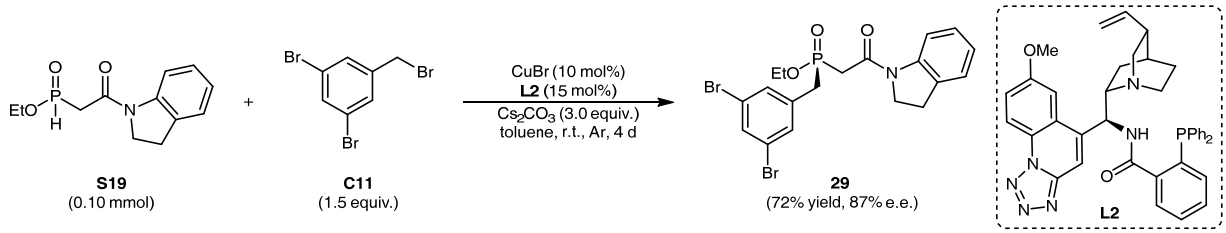
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.07 (t, *J* = 6.9 Hz, 1H), 4.30 – 3.95 (m, 4H), 3.56 – 3.33 (m, 2H), 3.20 (t, *J* = 8.5 Hz, 2H), 3.13 – 2.90 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 3.6 Hz), 142.5, 134.9 (d, *J* = 5.6 Hz), 133.7, 133.2 (d, *J* = 8.4 Hz), 131.7, 130.9 (d, *J* = 3.4 Hz), 129.5 (d, *J* = 2.9 Hz), 127.7, 124.8, 124.6, 118.6, 117.4, 112.9 (d, *J* = 3.0 Hz), 61.9 (d, *J* = 6.9 Hz), 49.2, 37.5 (d, *J* = 83.6 Hz), 36.1 (d, *J* = 89.7 Hz), 28.0, 16.7 (d, *J* = 5.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 44.41.

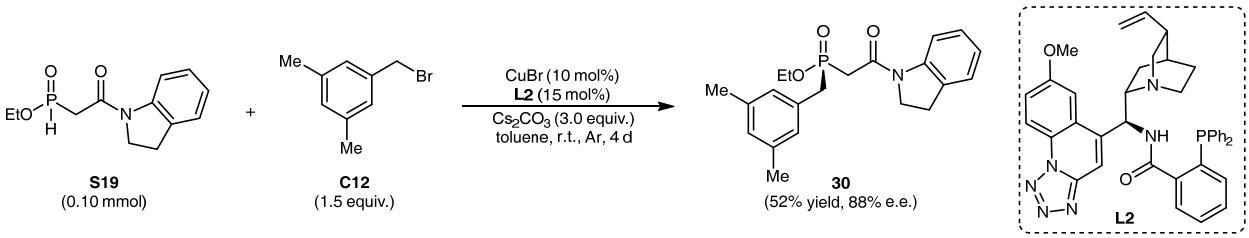
HRMS (ESI) *m/z* calcd. for $C_{20}H_{22}N_2O_3P$ $[M + H]^+$ 369.1363, found 369.1355.

Ethyl (*S*)-(3,5-dibromobenzyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (29)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 1,3-dibromo-5-(bromomethyl)benzene **C11** (49.3 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **29** as a white solid (36.1 mg, 72% yield, 87% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 10.72 min, t_R (minor) = 19.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.48 (m, 3H), 7.25 – 7.15 (m, 2H), 7.06 (t, *J* = 7.4, 1H), 4.30 – 3.97 (m, 4H), 3.36 (dd, *J* = 17.5, 2.7 Hz, 2H), 3.20 (t, *J* = 8.5 Hz, 2H), 3.05 (dd, *J* = 17.7, 4.8 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 3.7 Hz), 142.5, 135.4 (d, *J* = 8.3 Hz), 132.9 (d, *J* = 3.5 Hz), 132.0 (d, *J* = 5.9 Hz), 131.8, 127.7, 124.8, 124.5, 123.1 (d, *J* = 3.4 Hz), 117.5, 61.9 (d, *J* = 6.9 Hz), 49.3, 37.6 (d, *J* = 83.8 Hz), 35.9 (d, *J* = 89.6 Hz), 28.0, 16.7 (d, *J* = 5.7 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 44.20.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}NO_3PBr_2$ $[M + H]^+$ 499.9620, found 499.9611.

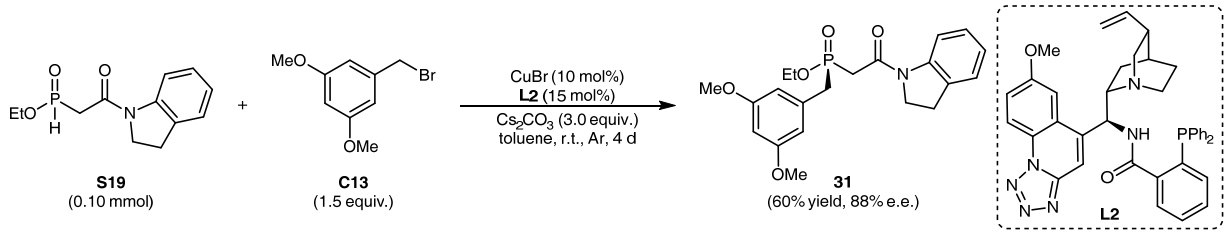
Ethyl (*S*)-(3,5-dimethylbenzyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (30)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 1-(bromomethyl)-3,5-dimethylbenzene **C12** (25.5 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **30** as a white solid (19.3 mg, 52% yield, 88% e.e.).
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 21.59 min, t_R (minor) = 26.16 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.13 (m, 2H), 7.10 – 6.95 (m, 3H), 6.87 (s, 1H), 4.24 – 3.87 (m, 4H), 3.32 (d, *J* = 17.8 Hz, 2H), 3.14 (t, *J* = 8.4 Hz, 2H), 3.02 (dd, *J* = 17.2, 2.9 Hz, 2H), 2.24 (s, 6H), 1.27 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, *J* = 4.1 Hz), 142.7, 138.3 (d, *J* = 3.1 Hz), 131.7, 130.9 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 3.6 Hz), 128.0 (d, *J* = 5.9 Hz), 127.6, 124.7, 124.3, 117.4, 61.6 (d, *J* = 6.9 Hz), 49.1, 37.5 (d, *J* = 82.4 Hz), 36.6 (d, *J* = 90.2 Hz), 28.0, 21.3, 16.7 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 45.81.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{27}NO_3P$ $[M + H]^+$ 372.1723, found 372.1725.

Ethyl (*S*)-(3,5-dimethoxybenzyl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (31)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 1-(bromomethyl)-3,5-dimethoxybenzene **C13** (34.6 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **31** as a white solid (24.2 mg, 60% yield, 88% e.e.).

HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 11.87 min, t_R (minor) = 13.37 min.

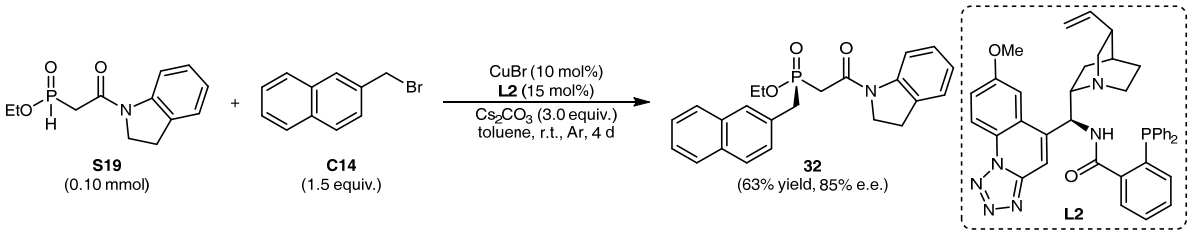
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.12 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.59 – 6.52 (m, 2H), 6.38 – 6.31 (m, 1H), 4.30 – 3.94 (m, 4H), 3.74 (s, 6H), 3.34 (d, *J* = 17.9 Hz, 2H), 3.16 (t, *J* = 8.5 Hz, 2H), 3.03 (d, *J* = 17.2 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (d, *J* = 4.0 Hz), 161.0 (d, *J* = 3.0 Hz), 142.7, 133.4 (d, *J* = 7.7 Hz), 131.8, 127.6, 124.8, 124.3, 117.4, 108.1 (d, *J* = 6.0 Hz), 99.6 (d, *J* = 3.4 Hz), 61.7 (d, *J* = 6.9 Hz), 55.4, 49.1, 37.6 (d, *J* = 21.9 Hz), 36.8 (d, *J* = 28.5 Hz), 28.0, 16.7 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 45.66.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{27}NO_5P$ $[M + H]^+$ 404.1621, found 404.1614.

Ethyl (*S*)-(2-(indolin-1-yl)-2-oxoethyl)(naphthalen-2-ylmethyl)phosphinate (32)



According to **General procedure B** with *H*-phosphinate **S19** (25.3 mg, 0.10 mmol, 1.0 equiv.) and 2-(bromomethyl)naphthalene **C14** (33.2 mg, 0.15 mmol, 1.5 equiv.) at r.t. for 4 d, the reaction mixture was purified by column chromatography on silica gel (EtOAc/MeOH = 40/1) to afford **32** as a white solid (24.7 mg, 63% yield, 85% e.e.).

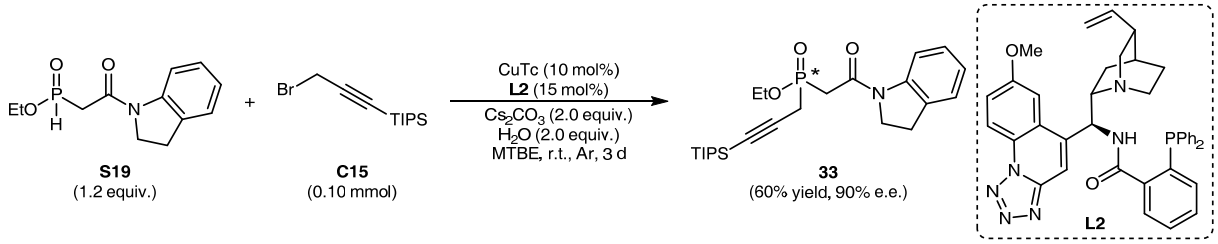
HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 280 nm), t_R (major) = 12.00 min, t_R (minor) = 14.62 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.67 (m, 4H), 7.58 – 7.37 (m, 3H), 7.25 – 7.19 (m, 1H), 7.15 (d, *J* = 6.2 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.27 – 3.87 (m, 4H), 3.57 (d, *J* = 17.9 Hz, 2H), 3.13 – 2.92 (m, 4H), 1.27 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, *J* = 3.9 Hz), 142.7, 133.5 (d, *J* = 3.1 Hz), 132.5 (d, *J* = 2.6 Hz), 131.8, 129.1 (d, *J* = 7.8 Hz), 128.8 (d, *J* = 8.5 Hz), 128.4 (d, *J* = 2.5 Hz), 128.2 (d, *J* = 4.6 Hz), 127.79 – 127.65 (m, 2C), 127.6, 126.3, 126.0 (d, *J* = 1.8 Hz), 124.8, 124.3, 117.4, 61.7 (d, *J* = 6.9 Hz), 49.1, 37.6 (d, *J* = 47.5 Hz), 36.7 (d, *J* = 54.5 Hz), 27.9, 16.7 (d, *J* = 5.8 Hz).

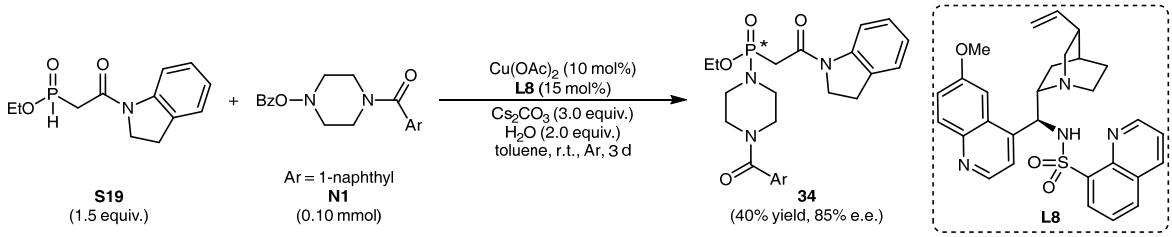
^{31}P NMR (162 MHz, $CDCl_3$) δ 45.74.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{25}NO_3P$ $[M + H]^+$ 394.1567, found 394.1562.

Ethyl (2-(indolin-1-yl)-2-oxoethyl)(3-(triisopropylsilyl)prop-2-yn-1-yl)phosphinate (33)

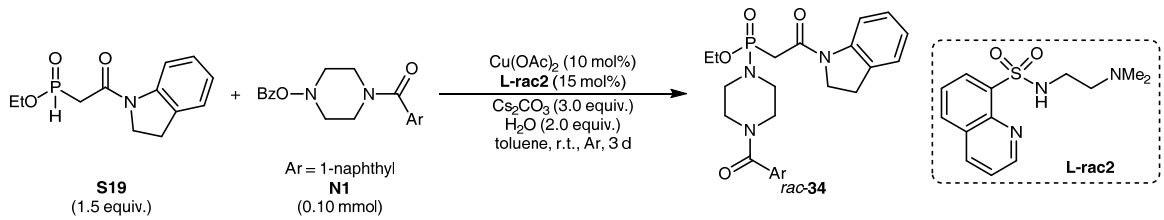


According to **General procedure B** with *H*-phosphinate **S19** (30.4 mg, 0.12 mmol, 1.2 equiv.), CuTc (1.91 mg, 0.01 mmol, 10 mol%), (3-bromoprop-1-yn-1-yl)triisopropylsilane **C15** (26.0 μL, 0.10 mmol, 1.0 equiv.), H_2O (3.6 μL, 0.20 mmol, 2.0 equiv.), Cs_2CO_3 (65.2 mg, 0.20 mmol, 2.0 equiv.) and anhydrous MTBE (4.0 mL) at r.t. for 3 d, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 1/2) to afford **33** as a white solid (24.7 mg, 60% yield, 90% e.e.).
HPLC analysis: Chiralpak IH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.23 min, t_R (minor) = 20.42 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.16 (m, 1H), 7.21 – 7.13 (m, 2H), 7.07 – 6.99 (m, 1H), 4.32 – 4.14 (m, 4H), 3.40 – 2.92 (m, 6H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.13 – 0.95 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 4.0 Hz), 142.6, 131.5, 127.5, 124.6, 124.3, 117.4, 97.6 (d, *J* = 11.7 Hz), 85.2 (d, *J* = 8.3 Hz), 62.0 (d, *J* = 6.9 Hz), 49.1, 36.8 (d, *J* = 90.1 Hz), 27.9, 22.3 (d, *J* = 93.0 Hz), 18.6, 16.5 (d, *J* = 6.2 Hz), 11.2.
^{31}P NMR (162 MHz, $CDCl_3$) δ 42.26.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{39}NO_3PSi$ $[M + H]^+$ 448.2431, found 448.2431.

Ethyl (4-(1-naphthoyl)piperazin-1-yl)(2-(indolin-1-yl)-2-oxoethyl)phosphinate (34)



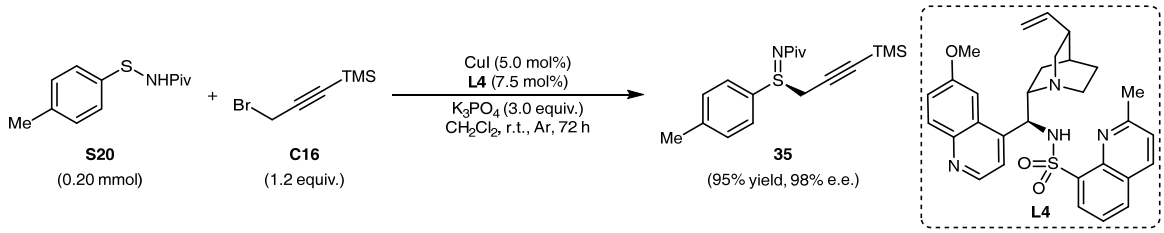
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (1.90 mg, 0.010 mmol, 10 mol%), **L8** (7.80 mg, 0.015 mmol, 15 mol%), **S19** (37.9 mg, 0.15 mmol, 1.5 equiv.), **N1** (36.0 mg, 0.10 mmol, 1.0 equiv.), H_2O (3.6 μL, 0.20 mmol, 2.0 equiv.) and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then anhydrous toluene (2.0 mL) was added by syringe under argon and the reaction mixture was stirred at r.t. for 3 d. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the residue was purified by silica gel column chromatography (EtOAc/MeOH = 20/1) to afford **34** as colorless oil (19.6 mg, 40% yield, 85% e.e.).



The racemates of products were prepared following the procedure: An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (1.90 mg, 0.010 mmol, 10 mol%), **L-rac2** (4.20 mg, 0.015 mmol, 15 mol%), **S19** (37.9 mg, 0.15 mmol, 1.5 equiv.), **N1** (36.0 mg, 0.10 mmol, 1.0 equiv.), H_2O (3.6 μL, 0.20 mmol, 2.0 equiv.) and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then anhydrous toluene (2.0 mL) was added by syringe under argon and the reaction mixture was stirred at r.t. for 3 d. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product *rac*-**34**.

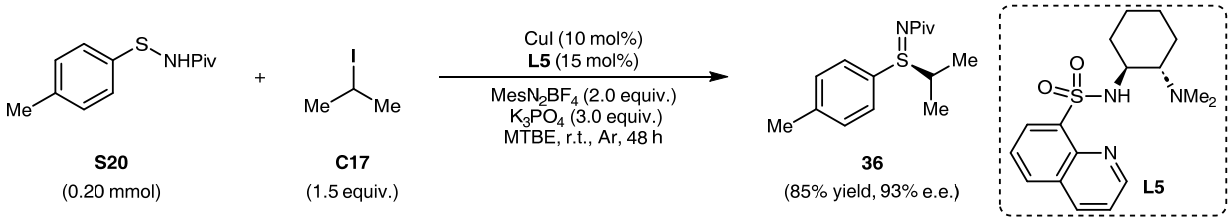
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min, λ = 280 nm), t_R (major) = 20.11 min, t_R (minor) = 27.38 min.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.96 – 7.78 (m, 3H), 7.64 – 7.37 (m, 4H), 7.24 – 7.12 (m, 2H), 7.07 – 6.98 (m, 1H), 4.63 – 4.35 (m, 1H), 4.24 – 3.79 (m, 5H), 3.60 – 2.89 (m, 10H), 1.44 – 1.26 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 163.3 (d, *J* = 4.6 Hz), 142.8, 133.9, 133.6, 131.9, 129.6, 129.4, 128.6, 127.6, 127.3, 126.6, 125.3, 124.8(3), 124.7(9), 124.3, 124.0, 117.2, 60.5 (d, *J* = 6.7 Hz), 49.2, 47.7, 44.8, 44.3, 42.2, 36.9 (d, *J* = 118.2 Hz), 28.0, 16.4 (d, *J* = 6.7 Hz)
^{31}P NMR (375 MHz, $CDCl_3$) δ 23.90.
HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{30}N_3NaO_4P$ $[M + Na]^+$ 514.1866, found 514.1869.

(*S*)-*N*-(*p*-Tolyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (35)



According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **35** as a colorless oil (63.4 mg, 95% yield, 98% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 7.06 min, t_R (major) = 10.04 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.97 (d, *J* = 15.7 Hz, 1H), 3.81 (d, *J* = 15.7 Hz, 1H), 2.42 (s, 3H), 1.24 (s, 9H), 0.09 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 143.3, 130.1, 129.5, 128.3, 94.9, 93.5, 42.0, 40.2, 28.8, 21.7, –0.3.
HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{28}NOSSi$ $[M + H]^+$ 334.1655, found 334.1651.

(*S*)-*N*-(Isopropyl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (36)



S20 (0.20 mmol) **C17** (1.5 equiv.) **36** (85% yield, 93% e.e.)

According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2-iodopropane **C17** (51.0 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **36** as a white solid (45.2 mg, 85% yield, 93% e.e.).

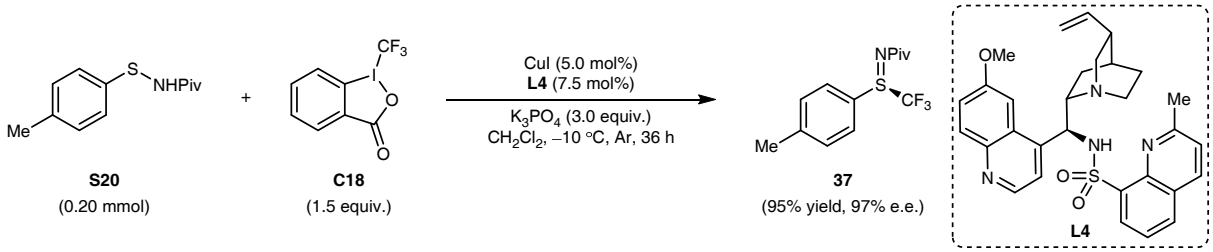
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 9.33 min, t_R (major) = 14.97 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.36 – 3.29 (m, 1H), 2.38 (s, 3H), 1.29 – 1.21 (m, 12H), 1.13 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 142.5, 130.1, 129.0, 128.1, 50.0, 40.4, 28.8, 21.5, 16.8, 16.1.

HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{24}NOS$ $[M + H]^+$ 266.1573, found 266.1573

***(R)*-*N*-(*p*-Tolyl(trifluoromethyl)-λ^4-sulfaneylidene)pivalamide (37)**



S20 (0.20 mmol) **C18** (1.5 equiv.) **37** (95% yield, 97% e.e.)

According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 1-(trifluoromethyl)-1λ^3-benzo[d][1,2]iodaoxol-3(1*H*)-one **C18** (94.8 mg, 0.30 mmol, 1.5 equiv.) at −10 °C for 36 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 5/1) to afford **37** as a light yellow oil (55.3 mg, 95% yield, 97% e.e.).

HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 6.31 min, t_R (major) = 11.68 min.

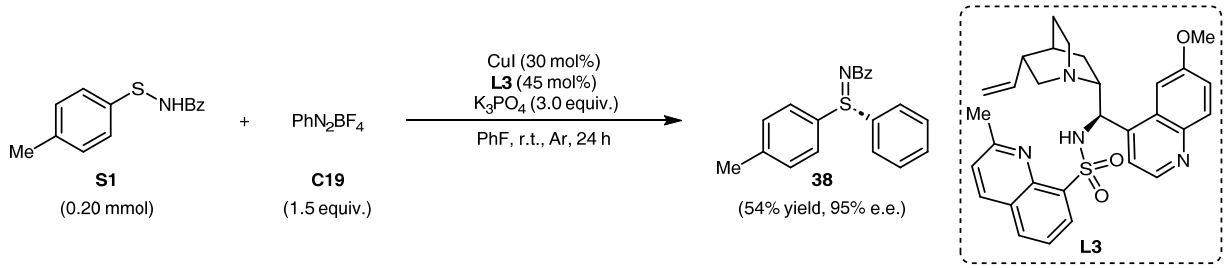
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 145.4, 130.9, 128.5, 124.6, 124.4 (q, *J* = 323.7 Hz), 40.5, 28.5, 21.8.

^{19}F NMR (375 MHz, $CDCl_3$) δ −64.91.

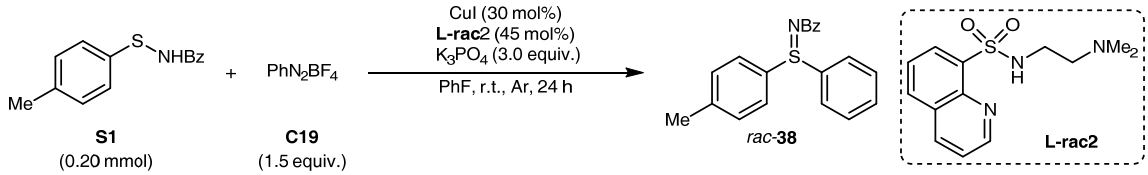
HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{17}F_3NOS$ $[M + H]^+$ 292.0977, found 292.0972.

(*R*)-*N*-(Phenyl(*p*-tolyl)- λ^4-sulfaneylidene)benzamide (38)



Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (11.4 mg, 0.06 mmol, 30 mol%), **L3** (38.8 mg, 0.09 mmol, 45 mol%) and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). Then, anhydrous fluorobenzene (PhF, 2.0 mL) was added and the reaction mixture was stirred at 50 °C for 1 h. After premixing, *N*-(*p*-tolylthio)benzamide **S1** (48.66 mg, 0.20 mmol, 1.0 equiv.) and benzenediazonium tetrafluoroborate **C19** (57.58 mg, 0.30 mmol, 1.5 equiv.) were added to the mixture under an argon atmosphere, and the reaction mixture was stirred at r.t. for 24 h. Then the reaction mixture was extracted with EtOAc three times (3 × 10 mL) and the combined organic layers were concentrated *in vacuo*. The filtrate was evaporated and the residue was purified by flash column chromatography (EtOAc/PE = 1/1) to afford the **38** as a white solid (34.5 mg, 54% yield, 95 % e.e.).

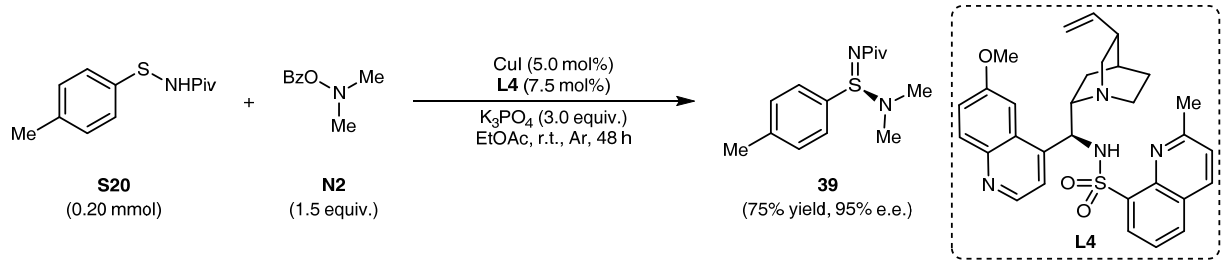
.



The racemates of products were prepared following the procedure: Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (11.4 mg, 0.06 mmol, 30 mol%), **L-rac2** (25.14 mg, 0.09 mmol, 45 mol%) and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). Then, anhydrous fluorobenzene (PhF, 2.0 mL) was added and the reaction mixture was stirred at 50 °C for 1 h. After premixing, *N*-(*p*-tolylthio)benzamide **S1** (48.66 mg, 0.20 mmol, 1.0 equiv.) and benzenediazonium tetrafluoroborate **C19** (57.58 mg, 0.30 mmol, 1.5 equiv.) were added under an argon atmosphere, and the reaction mixture was stirred at r.t. for 24 h. Then the reaction mixture was extracted with EtOAc three times (3 × 10 mL) and the combined organic layers were concentrated *in vacuo*. The filtrate was evaporated and the residue was purified by flash column chromatography or preparative thin-layer chromatography on silica gel to afford the desired product.

HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 21.00 min, t_R (minor) = 24.34 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.19 (m, 2H), 7.86 – 7.77 (m, 2H), 7.74 – 7.68 (m, 2H), 7.53 – 7.35 (m, 6H), 7.32 – 7.26 (m, 2H), 2.37 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 142.8, 136.8, 136.7, 133.2, 131.8, 130.9, 130.7, 129.9, 129.0, 128.1, 127.9, 127.8, 21.6.
HRMS (ESI) m/z calcd. for $C_{20}H_{17}NOS$ $[M + H]^+$ 320.1104, found 320.1099.

(*S*)-*N*-((Dimethylamino)(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (39)



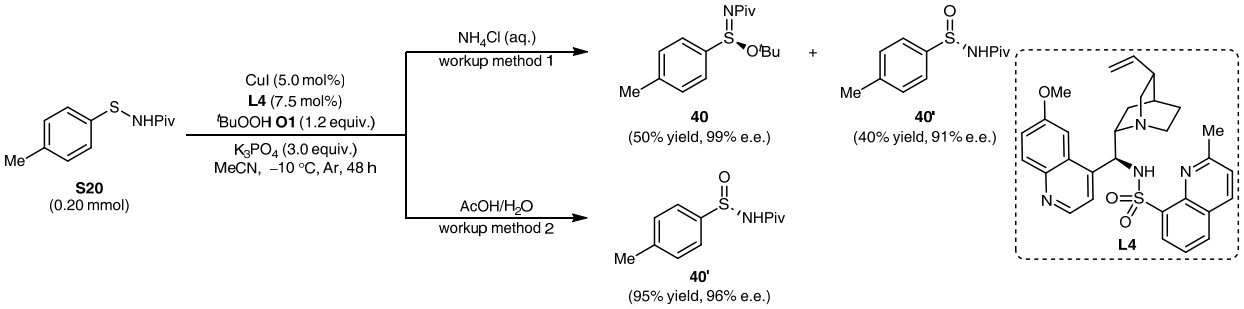
According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *O*-benzoyl-*N*,*N*-dimethylhydroxylamine **N2** (49.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 15/1) to afford the product **39** as a white solid (39.9 mg, 75% yield, 95% e.e.).

HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.16 min, t_R (major) = 9.28 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.34 – 7.28 (m, 2H), 2.68 (s, 6H), 2.41 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 141.9, 132.4, 129.9, 128.2, 40.9, 38.8, 28.8, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{23}N_2OS$ $[M + H]^+$ 267.1526, found 267.1524.



(*R*)-*tert*-Butyl *N*–(pivaloyl)-4-methylphenylsulfinimidate (40)

According to **General Procedure F** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.) for 48 h with workup method 1, the reaction mixture was purified by flash column chromatography on neutral alumina (PE/EtOAc = 3/1) to afford the product **40** as a white solid (29.5 mg, 50% yield, 99% e.e.).

HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 6.39 min, t_R (major) = 7.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H), 1.55 (s, 9H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 142.6, 136.5, 129.9, 127.2, 84.8, 41.1, 29.5, 28.2, 21.5.

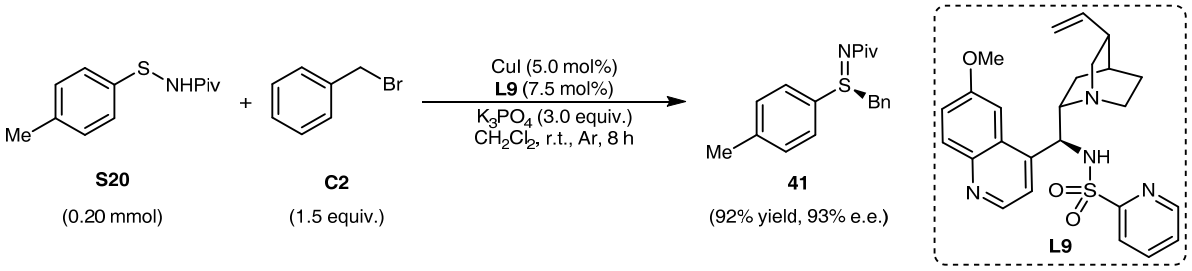
HRMS (ESI) *m/z* calcd. for $C_{16}H_{25}NNaO_2S$ $[M + Na]^+$ 318.1498, found 318.1498.

(*S*)-*N*-(*p*-Tolylsulfinyl)pivalamide (40')

According to **General Procedure F** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.) for 48 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 3/1) to afford the product **40'** as a white solid (workup method 1, 19.1 mg, 40% yield, 91% e.e.; workup method 2, 45.5 mg, 95% yield, 96% e.e.). The stereoconfiguration of **40'** was matched with literature report [61].

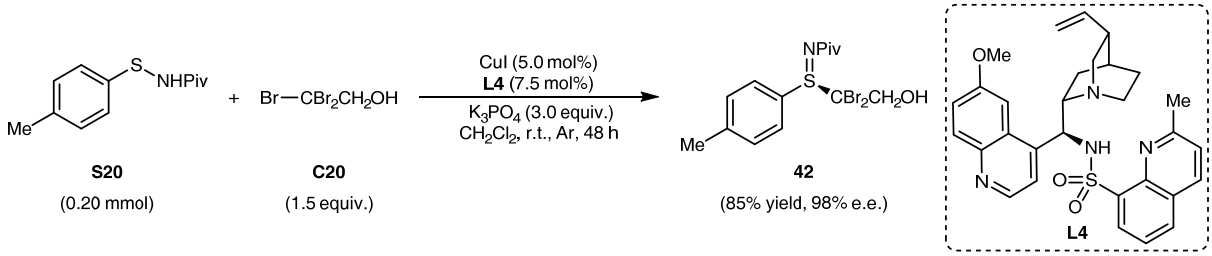
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 20.63 min, t_R (minor) = 23.88 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H), 1.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 142.4, 140.9, 130.1, 124.8, 39.8, 27.1, 21.5.
HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{18}NO_2S$ $[M + H]^+$ 240.1053, found 240.1049.

(*R*)-*N*-(Benzyl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (41)



According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.), benzyl bromide **C2** (51.3 mg, 0.30 mmol, 1.5 equiv.) and **L9** (7.0 mg, 0.015 mmol, 7.5 mol%) at r.t. for 8 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 1.5/1) to afford **41** as a white solid (57.7 mg, 92% yield, 93% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 6.51 min, t_R (major) = 10.14 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.24 – 7.15 (m, 4H), 6.90 (d, *J* = 7.2 Hz, 2H), 4.42 (d, *J* = 12.3 Hz, 1H), 4.15 (d, *J* = 12.3 Hz, 1H), 2.38 (s, 3H), 1.26 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 142.7, 130.9, 130.0, 129.3, 128.6(9), 128.6(6), 128.3, 128.0, 55.4, 40.2, 28.8, 21.6.
HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{24}NOS$ $[M + H]^+$ 314.1573, found 314.1567.

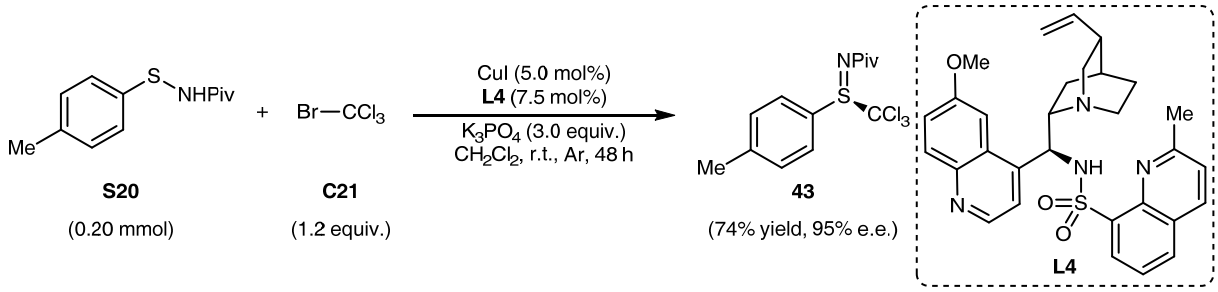
(*R*)-*N*-((1,1-Bibromo-2-hydroxyethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (42)



According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2,2,2-tribromoethanol **C20** (84.8 mg, 0.30 mmol, 1.5 equiv.) at r.t. for 48 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 4/1) to afford **42** as a light yellow oil (72.3 mg, 85% yield, 98% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 12.98 min, t_R (major) = 22.31 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 6.56 (dd, *J* = 10.1, 5.7 Hz, 1H), 4.24 – 4.05 (m, 2H), 2.48 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 145.2, 131.7, 129.6, 124.6, 84.8, 71.1, 41.2, 28.6, 21.9.
HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{20}Br_2NO_2S$ $[M + H]^+$ 423.9576, found 423.9578.

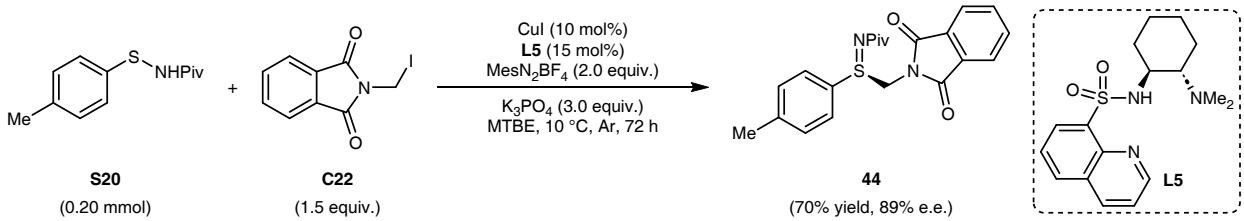
(*R*)-*N*-(*p*-Tolyl(trichloromethyl)-λ^4-sulfaneylidene)pivalamide (43)



S20 (0.20 mmol) **C21** (1.2 equiv.) **43** (74% yield, 95% e.e.)

According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and bromotrichloromethane **C21** (47.6 mg, 0.24 mmol, 1.2 equiv.) at r.t. for 48 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 4/1) to afford **43** as a light yellow oil (50.4 mg, 74% yield, 95% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 8.89 min, t_R (major) = 13.62 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 145.7, 130.5, 130.0, 127.8, 107.9, 41.4, 28.4, 21.9.
HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{17}Cl_3NOS$ $[M + H]^+$ 340.0091, found 340.0088.

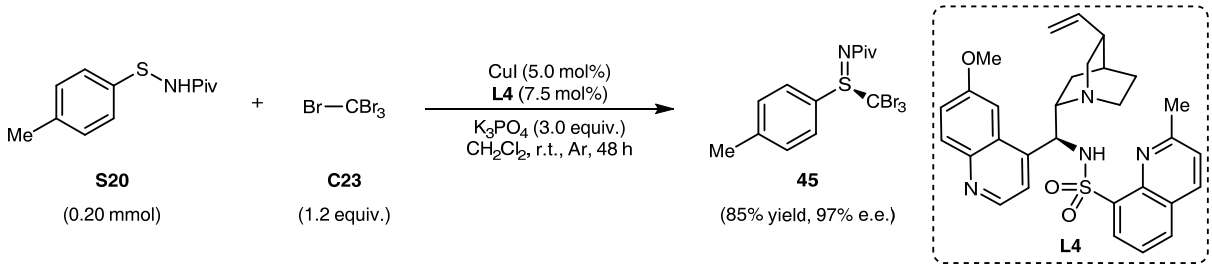
(*R*)-*N*-(((1,3-dioxoisoindolin-2-yl)methyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (44)



S20 (0.20 mmol) **C22** (1.5 equiv.) **44** (70% yield, 89% e.e.)

According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2-(iodomethyl)isoindoline-1,3-dione **C22** (86.1 mg, 0.30 mmol, 1.5 equiv.) for 72 h at 10 °C, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 3/2) to afford **44** as a pale yellow solid (53.5 mg, 70% yield, 89% e.e.).
HPLC analysis: Chiralpak IA-3 (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 19.62 min, t_R (major) = 12.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.79 – 7.73 (m, 2H), 7.69 – 7.62 (m, 2H), 7.30 – 7.24 (m, 2H), 5.13 (d, *J* = 12.2 Hz, 1H), 4.99 (d, *J* = 12.2 Hz, 1H), 2.38 (s, 3H), 1.17 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 166.2, 143.5, 134.7, 131.5, 130.5, 128.8, 127.9, 123.9, 54.9, 40.12, 28.5, 21.6.
HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{23}N_2O_3S$ $[M + H]^+$ 383.1424, found 383.1423.

(*R*)-*N*-(*p*-Tolyl(tribromomethyl)-λ^4-sulfaneylidene)pivalamide (45)



According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and carbon tetrabromide **C23** (79.6 mg, 0.24 mmol, 1.2 equiv.) at r.t. for 48 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 2/1) to afford **45** as a light yellow oil (80.6 mg, 85% yield, 97% e.e.).

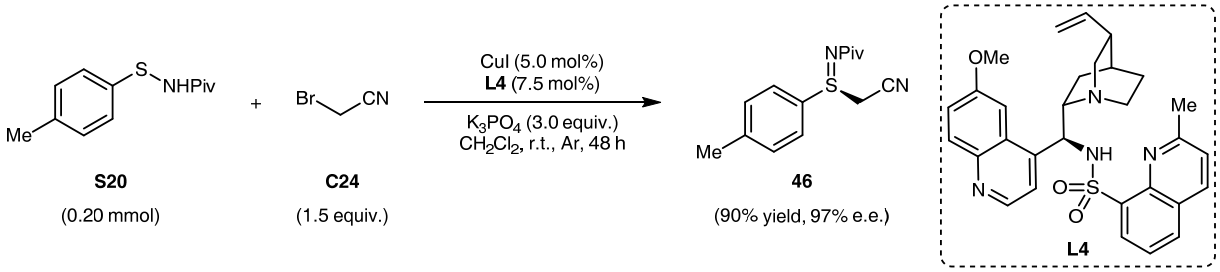
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 16.21 min, t_R (major) = 19.21 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 145.6, 130.8, 129.7, 129.2, 56.0, 41.5, 28.5, 21.9.

HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{17}Br_3NOS$ $[M + H]^+$ 471.8575, found 471.8569.

(*R*)-*N*-((Cyanomethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (46)



According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and bromoacetonitrile **C24** (36.0 mg, 0.30 mmol, 1.5 equiv.) at r.t. for 48 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 1.5/1) to afford **46** as a white solid (47.2 mg, 90% yield, 97% e.e.).

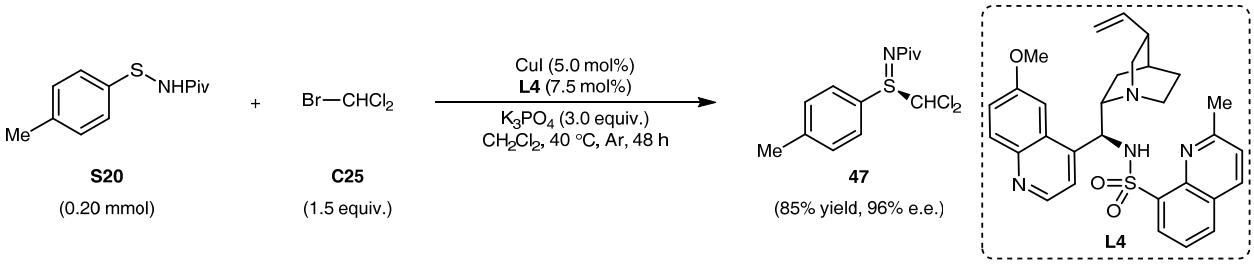
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 15.74 min, t_R (major) = 18.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.25 (d, *J* = 15.7 Hz, 1H), 3.87 (d, *J* = 15.7 Hz, 1H), 2.46 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 144.8, 131.0, 128.1, 127.5, 110.4, 40.4, 37.8, 28.6, 21.8.

HRMS (ESI) *m*/*z* calcd. for $C_{14}H_{19}N_2OS$ $[M + H]^+$ 263.1213, found 263.1209.

(*R*)-*N*-((Dichloromethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (47)



According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and bromodichloromethane **C25** (49.1 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 4/1) to afford **47** as a light yellow oil (52.1 mg, 85% yield, 96% e.e.).

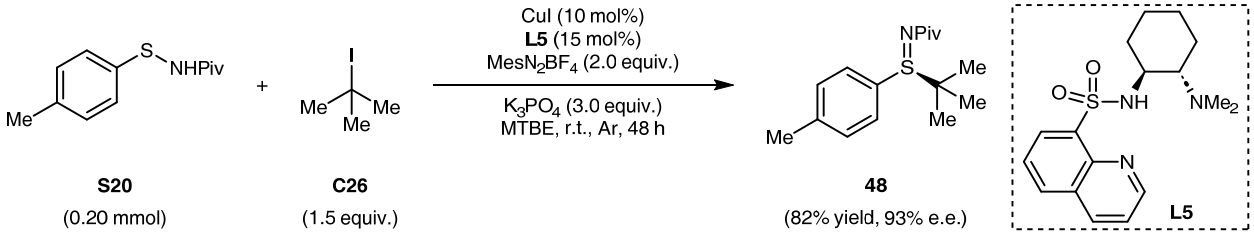
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 7.49 min, t_R (major) = 12.00 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 1H), 2.47 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 145.2, 131.3, 129.9, 122.7, 78.0, 40.4, 28.5, 21.8.

HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{18}Cl_2NOS$ $[M + H]^+$ 306.0481, found 306.0477.

(*S*)-*N*-(*tert*-Butyl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (48)



According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2-iodo-2-methylpropane **C26** (55.2 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **48** as a colorless oil (46.0 mg, 82% yield, 93% e.e.).

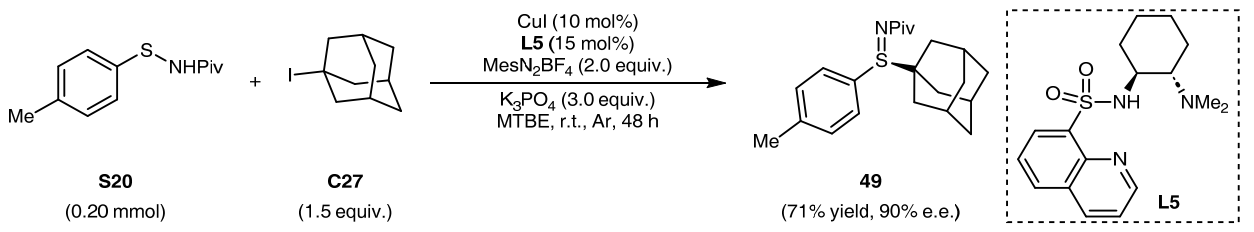
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 8.74 min, t_R (major) = 13.17 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 1.26 (s, 9H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 142.4, 129.6, 128.6, 128.3, 55.4, 40.5, 28.7, 24.3, 21.4.

HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{24}NOS$ $[M + H]^+$ 280.1730, found 280.1729.

(*S*)-*N*-(Adamantan-1-yl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (49)



According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 1-iodoadamantane **C27** (80.0 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **49** as a colorless oil (51.0 mg, 71% yield, 90% e.e.).

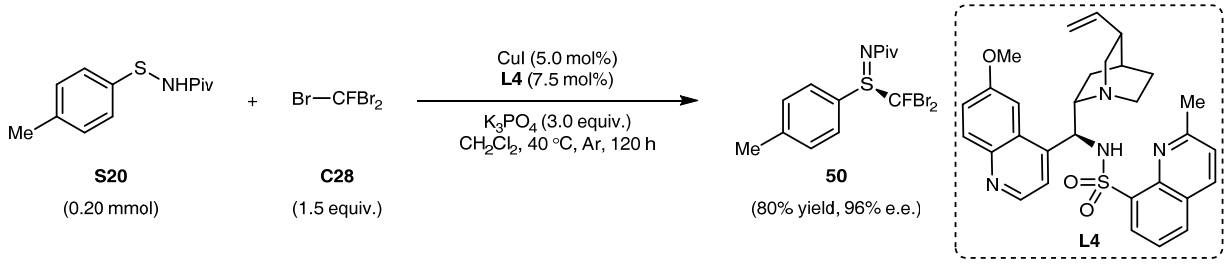
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 12.88 min, t_R (major) = 15.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 2.40 (s, 3H), 2.12 – 2.09 (m, 3H), 1.91 – 1.74 (m, 6H), 1.73 – 1.55 (m, 6H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 142.4, 129.6, 128.9, 126.7, 57.3, 40.7, 36.6, 36.1, 29.3, 28.9, 21.6.

HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{32}NOS$ $[M + H]^+$ 358.2199, found 358.2198.

(*R*)-*N*-((Dibromofluoromethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (50)



According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and fluorotribromomethane **C28** (81.2 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 120 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 3/1) to afford **50** as a light yellow oil (66.1 mg, 80% yield, 96% e.e.).

HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 9.87 min, t_R (major) = 15.46 min.

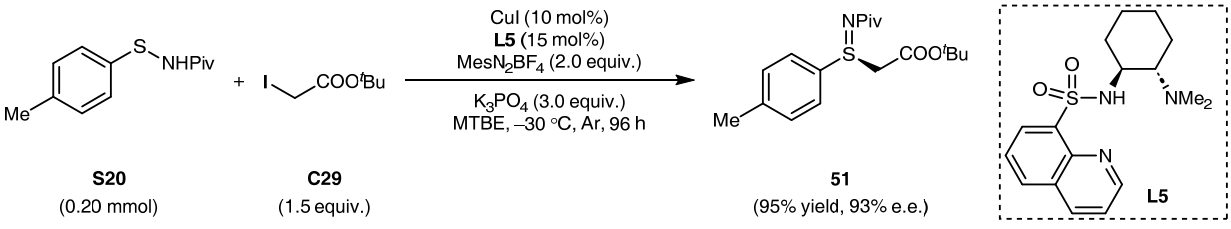
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 145.5, 130.2, 130.0 (d, *J* = 1.2 Hz), 127.4, 103.4 (d, *J* = 363.5 Hz), 41.2, 28.4, 21.9.

^{19}F NMR (375 MHz, $CDCl_3$) δ –53.19.

HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{17}Br_2FNOS$ $[M + H]^+$ 411.9376, found 411.9379.

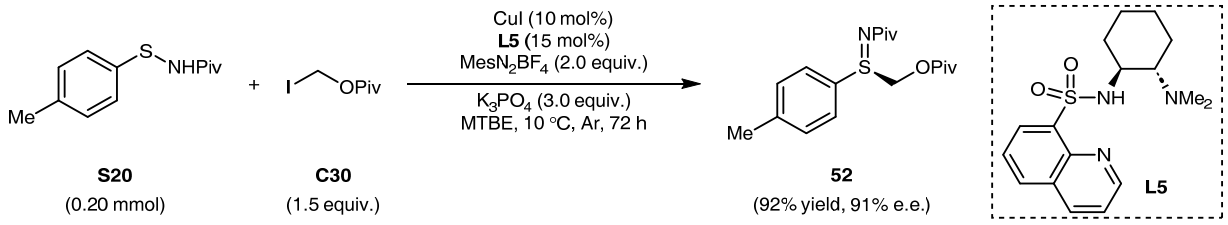
tert-Butyl (*S*)-2-(*N*-pivaloyl-*S*-(*p*-tolyl)sulfinimidoyl)acetate (51)



According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *tert*-butyl 2-iodoacetate **C29** (72.6 mg, 0.30 mmol, 1.5 equiv.) at –30 °C for 96 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 2/1) to afford **51** as colorless oil (64.1 mg, 95% yield, 93% e.e.).

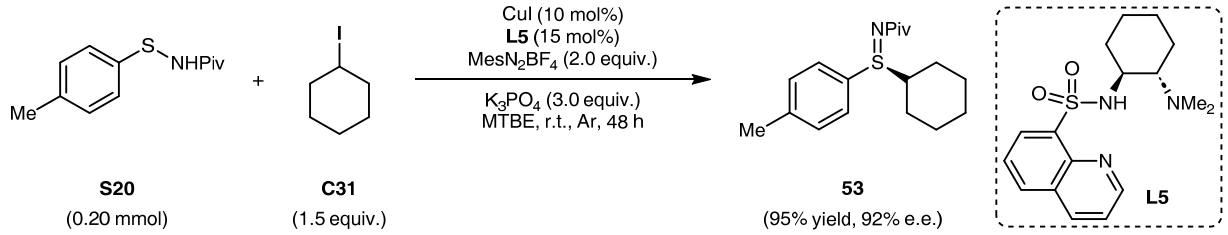
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 230 nm), t_R (minor) = 10.69 min, t_R (major) = 18.27 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.15 (d, *J* = 14.3 Hz, 1H), 3.64 (d, *J* = 12.1 Hz, 1H), 2.40 (s, 3H), 1.38 (s, 9H), 1.22 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 163.4, 143.3, 131.0, 130.5, 127.7, 83.8, 53.6, 40.0, 28.7, 28.0, 21.6.
HRMS (ESI) m/z calcd. for $C_{18}H_{28}NO_3S$ $[M + H]^+$ 338.1784, found 338.1781.

(*R*)-(*N*-pivaloyl-*S*-(*p*-tolyl)sulfinimidoyl)methyl pivalate (52)



According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and iodomethyl pivalate **C30** (72.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h at 10 °C, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 2/1) to afford **52** as a white solid (62.1 mg, 92% yield, 91% e.e.).
HPLC analysis: Chiralpak IA-3 (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 8.81 min, t_R (major) = 13.93 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.27 (q, *J* = 9.6 Hz, 2H), 2.41 (s, 3H), 1.24 (s, 9H), 1.14 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 176.6, 143.3, 130.5, 128.7, 127.7, 74.8, 40.2, 39.0, 28.7, 27.0, 21.6.
HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{28}NO_3S$ $[M + H]^+$ 338.1784, found 338.1781.

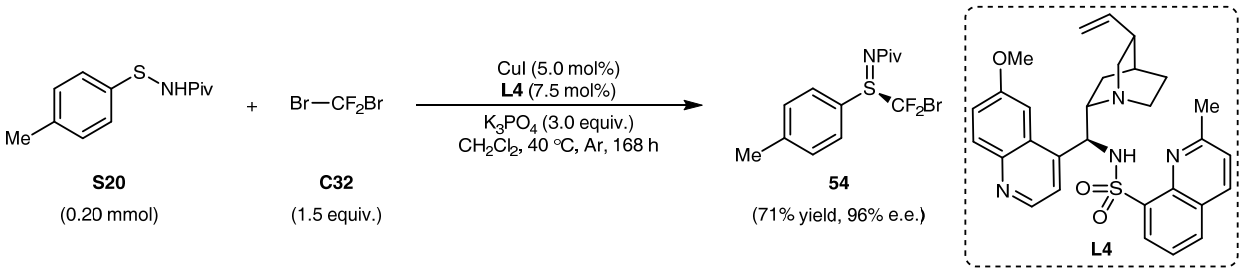
(*S*)-*N*-(Cyclohexyl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (53)



According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and iodocyclohexane **C31** (63.0 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **53** as a colorless oil (58.1 mg, 95% yield, 92% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 10.97 min, t_R (major) = 17.08 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.14 – 2.98 (m, 1H), 2.40 (s, 3H), 2.18 – 1.95 (m, 1H), 1.91 – 1.72 (m, 3H), 1.71 – 1.58 (m, 1H), 1.54 – 0.90 (m, 14H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 142.5, 130.2, 129.6, 128.1, 58.1, 40.3, 28.8, 27.0, 26.6, 25.5, 21.6.
HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{28}NOS$ $[M + H]^+$ 306.1886, found 306.1885.

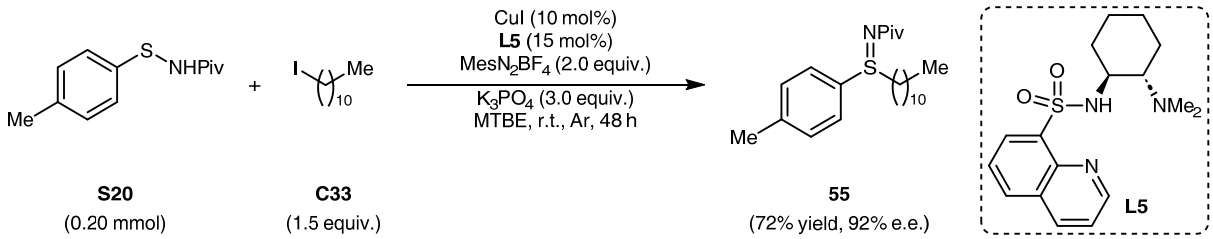
(*R*)-*N*-((Bromodifluoromethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (54)



S20 (0.20 mmol) C32 (1.5 equiv.) 54 (71% yield, 96% e.e.)

According to **General Procedure C** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and dibromodifluoromethane **C32** (62.9 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 168 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 5/1) to afford **54** as a light yellow oil (50.0 mg, 71% yield, 96% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 7.34 min, t_R (major) = 12.26 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 145.4, 130.6, 129.3, 125.5 (d, *J* = 1.4 Hz), 125.1 (dd, *J* = 355.7, 350.0 Hz), 40.9, 28.4, 21.8.
^{19}F NMR (375 MHz, $CDCl_3$) δ –44.94 (d, *J* = 134.9 Hz, 1F), –46.38 (d, *J* = 135.0 Hz, 1F).
HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{17}BrF_2NOS$ $[M + H]^+$ 352.0177, found 352.0179.

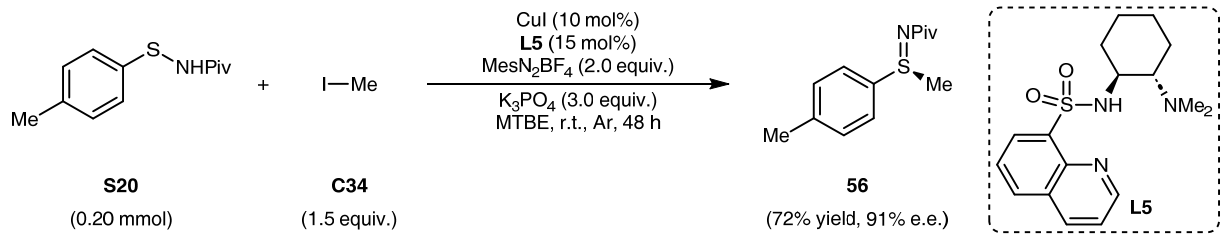
(*S*)-*N*-(Methyl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (55)



S20 (0.20 mmol) C33 (1.5 equiv.) 55 (72% yield, 92% e.e.)

According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 1-iodoundecane **C33** (84.7 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **55** as a colorless oil (54.4 mg, 72% yield, 92% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 9.42 min, t_R (major) = 11.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.14 – 2.78 (m, 2H), 2.38 (s, 3H), 1.64 – 1.47 (m, 2H), 1.39 – 1.09 (m, 25H), 0.86 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 142.5, 131.7, 130.4, 127.1, 49.5, 40.1, 32.0, 29.6(2), 29.5(5), 29.3(7), 29.3(5), 29.1, 28.8, 28.4, 23.1, 22.8, 21.5, 14.2.
HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{40}NOS$ $[M + H]^+$ 378.2825, found 378.2824.

(*S*)-*N*-(Methyl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (56)



According to **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and iodomethane **C34** (42.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **56** as a colorless oil (34.3 mg, 72% yield, 91% e.e.).

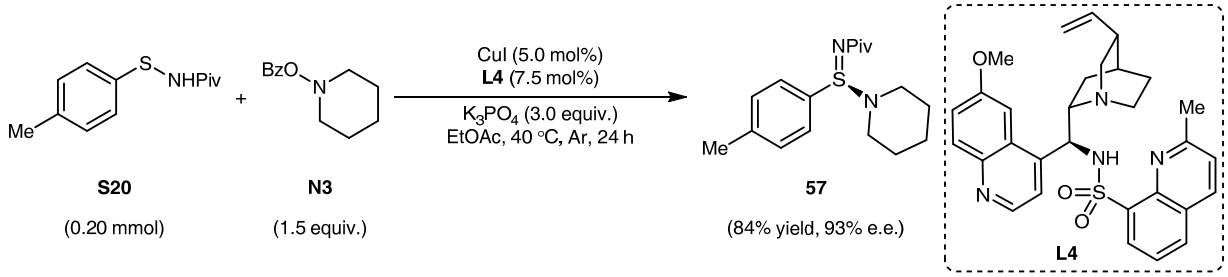
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 10.20 min, t_R (major) = 13.73 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.74 (s, 3H), 2.39 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 142.6, 133.3, 130.6, 126.6, 39.9, 35.0, 28.7, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{20}NOS$ $[M + H]^+$ 238.1260, found 238.1259.

(*S*)-*N*-(Piperidin-1-yl(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (57)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and piperidin-1-yl benzoate **N3** (61.6 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 10/1) to afford the product **57** as a white solid (51.4 mg, 84% yield, 93% e.e.).

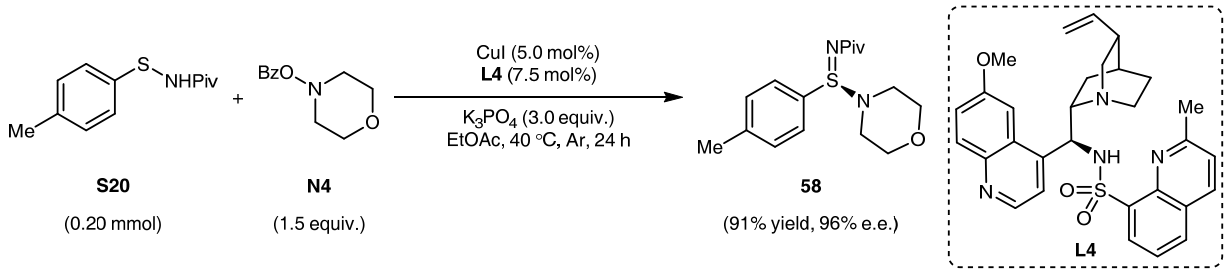
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.06 min, t_R (major) = 8.21 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.31 – 7.24 (m, 2H), 3.13 – 2.92 (m, 4H), 2.39 (s, 3H), 1.63 – 1.41 (m, 6H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 141.6, 132.4, 129.8, 128.2, 48.6, 40.9, 28.8, 26.3, 23.7, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{27}N_2OS$ $[M + H]^+$ 307.1839, found 307.1837.

(*S*)-*N*-(Morpholino(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (58)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and morpholino benzoate **N4** (62.2 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford the product **58** as a light yellow oil (56.3 mg, 91% yield, 96% e.e.).

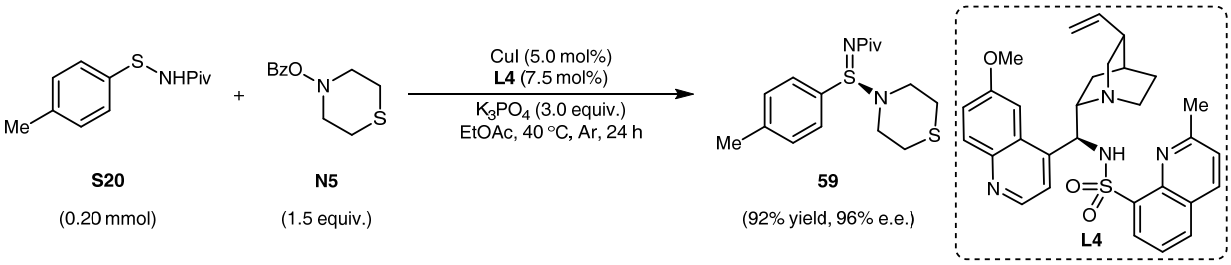
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.56 min, t_R (major) = 13.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 2H), 7.33 – 7.27 (m, 2H), 3.72 – 3.59 (m, 4H), 3.19 – 3.09 (m, 2H), 3.03 – 2.93 (m, 2H), 2.39 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 142.2, 131.1, 130.0, 128.3, 67.0, 47.3, 40.9, 28.7, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{25}N_2O_2S$ $[M + H]^+$ 309.1631, found 309.1630.

(*S*)-*N*-(Thiomorpholino(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (59)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and thiomorpholino benzoate **N5** (67.0 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 6/1) to afford the product **59** as a yellow oil (59.8 mg, 92% yield, 96% e.e.).

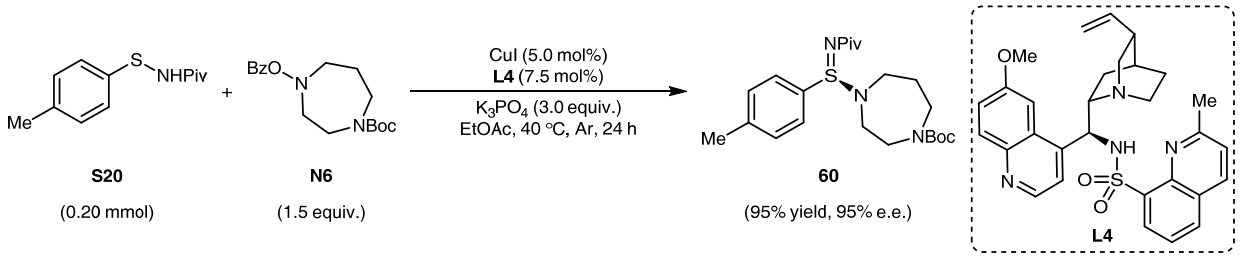
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.01 min, t_R (major) = 7.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.33 – 7.27 (m, 2H), 3.44 – 3.24 (m, 4H), 2.62 (t, *J* = 5.1 Hz, 4H), 2.40 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 142.1, 131.8, 130.0, 128.3, 49.9, 40.9, 28.7, 28.1, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{25}N_2OS_2$ $[M + H]^+$ 325.1403, found 325.1400.

***tert*-Butyl (*S*)-4-(*N*-pivaloyl-*S*-(*p*-tolyl)sulfinimidoyl)-1,4-diazepane-1-carboxylate (60)**



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *tert*-butyl 4-(benzoyloxy)-1,4-diazepane-1-carboxylate **N6** (96.1 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 6/1) to afford the product **60** as a colorless oil (80.1 mg, 95% yield, 95% e.e.).

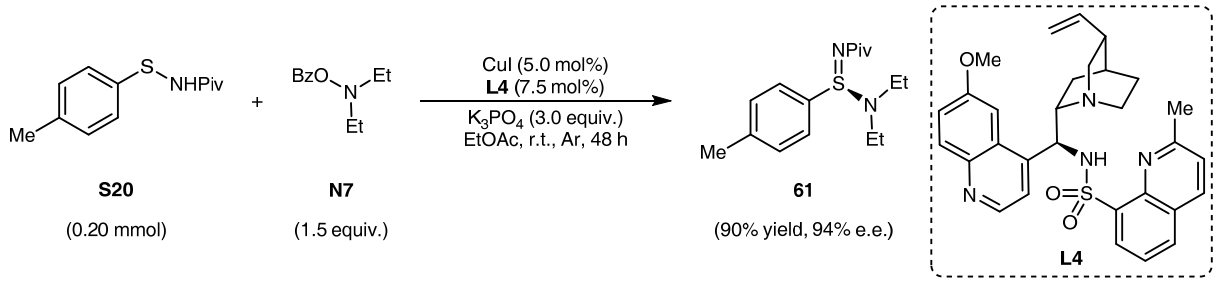
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.31 min, t_R (major) = 8.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 2H), 7.31 – 7.24 (m, 2H), 3.57 – 3.14 (m, 8H), 2.38 (s, 3H), 1.81 – 1.52 (m, 2H), 1.40 (d, *J* = 16.6 Hz, 9H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 155.2, 155.0, 142.0, 132.9, 129.9, 128.2, 79.7(3), 79.6(5), 50.9, 50.6, 50.3, 49.3, 48.3, 47.8, 46.0, 45.6, 40.8, 29.3, 29.0, 28.7, 28.5, 28.4, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{36}N_3O_3S$ $[M + H]^+$ 422.2472, found 422.2468.

(*S*)-*N*-((Diethylamino)(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (61)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *O*-benzoyl-*N*,*N*-diethylhydroxylamine **N7** (58.0 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 15/1) to afford the product **61** as a colorless oil (53.0 mg, 90% yield, 94% e.e.).

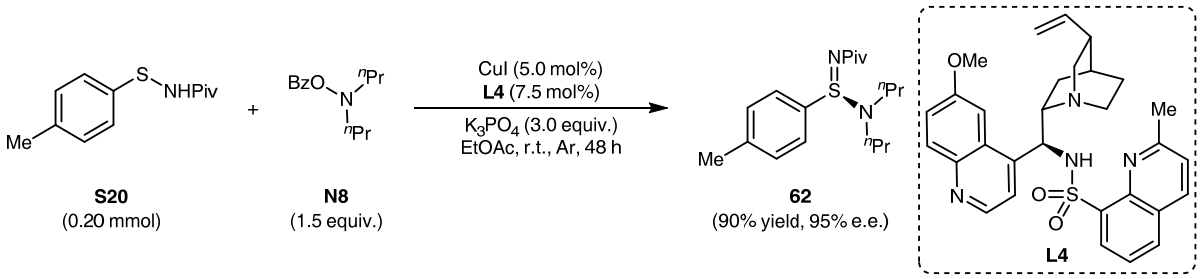
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.32 min, t_R (major) = 9.12 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.29 – 7.24 (m, 2H), 3.19 (dq, *J* = 14.2, 7.1 Hz, 2H), 3.04 (dq, *J* = 14.4, 7.2 Hz, 2H), 2.39 (s, 3H), 1.26 (s, 9H), 1.11 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 141.5, 133.5, 129.8, 128.3, 43.6, 40.7, 28.7, 21.4, 14.3.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{27}N_2OS$ $[M + H]^+$ 295.1839, found 295.1837.

(*S*)-*N*-((Dipropylamino)(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (62)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *O*-benzoyl-*N*,*N*-dipropylhydroxylamine **N8** (66.4 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 15/1) to afford the product **62** as a light yellow oil (58.1 mg, 90% yield, 95% e.e.).

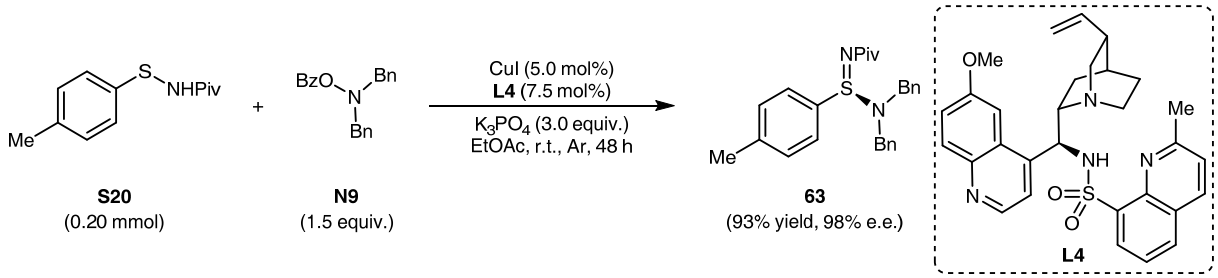
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.22 min, t_R (major) = 7.66 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2H), 7.30 – 7.24 (m, 2H), 3.10 (ddd, *J* = 14.4, 8.9, 5.8 Hz, 2H), 2.88 (ddd, *J* = 13.8, 9.0, 6.5 Hz, 2H), 2.39 (s, 3H), 1.64 – 1.41 (m, 4H), 1.26 (s, 9H), 0.80 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 141.6, 133.6, 129.8, 128.4, 51.5, 40.7, 28.8, 22.2, 21.4, 11.5.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{31}N_2OS$ $[M + H]^+$ 323.2152, found 323.2150.

(*S*)-*N*-((Dibenzylamino)(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (63)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *O*-benzoyl-*N*,*N*-dibenzylhydroxylamine **N9** (95.2 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 10/1) to afford the product **63** as a colorless oil (78.2 mg, 93% yield, 98% e.e.).

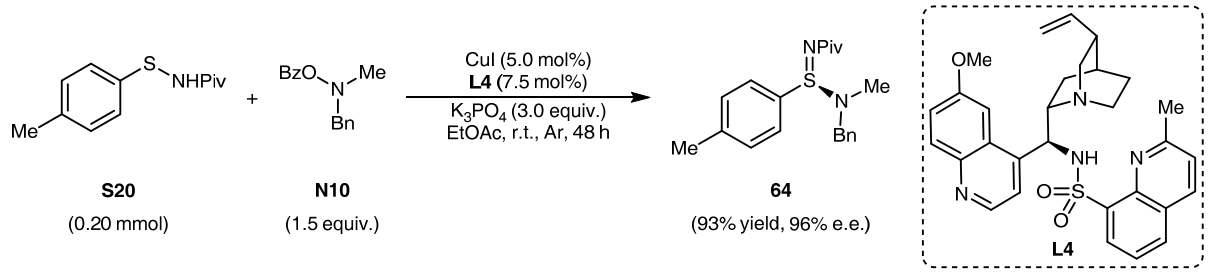
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.81 min, t_R (major) = 8.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.32 – 7.19 (m, 8H), 7.19 – 7.13 (m, 4H), 4.24 (d, *J* = 14.2 Hz, 2H), 4.02 (d, *J* = 14.2 Hz, 2H), 2.39 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 142.0, 137.1, 133.0, 129.9, 129.4, 128.5(2), 128.4(5), 127.7, 52.6, 41.0, 28.9, 21.5.

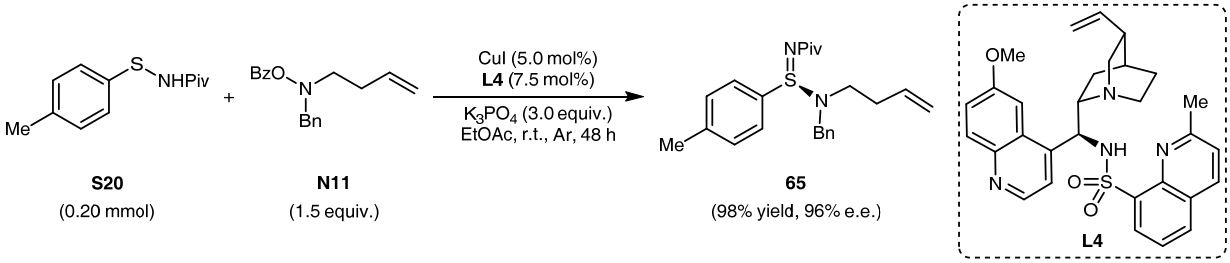
HRMS (ESI) *m/z* calcd. for $C_{26}H_{31}N_2OS$ $[M + H]^+$ 419.2152, found 419.2150.

(*S*)-*N*-((Benzyl(methyl)amino)(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (64)



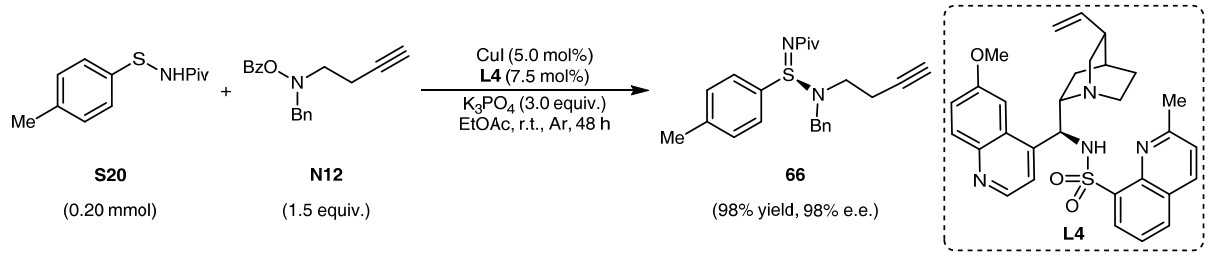
According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *O*-benzoyl-*N*-benzyl-*N*-methylhydroxylamine **N10** (72.4 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 10/1) to afford the product **64** as a colorless oil (63.8 mg, 93% yield, 96% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.70 min, t_R (major) = 13.46 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.22 (m, 7H), 4.51 (d, *J* = 14.3 Hz, 1H), 4.08 (d, *J* = 14.2 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 1.34 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 142.0, 137.3, 132.8, 130.0, 128.7, 128.6, 128.4, 127.7, 57.8, 41.0, 33.7, 28.9, 21.5.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}N_2OS$ $[M + H]^+$ 343.1839, found 343.1837.

(*S*)-*N*-((Benzyl(but-3-en-1-yl)amino)(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (65)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *O*-benzoyl-*N*-benzyl-*N*-(but-3-en-1-yl)hydroxylamine **N11** (84.4 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 3/1) to afford the product **65** as a light yellow oil (75.5 mg, 98% yield, 96% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.44 min, t_R (major) = 9.42 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.21 (m, 5H), 7.21 – 7.15 (m, 2H), 5.57 (ddt, *J* = 16.6, 9.6, 6.8 Hz, 1H), 5.00 – 4.92 (m, 2H), 4.21 – 4.07 (m, 2H), 3.29 (ddd, *J* = 13.8, 8.2, 5.7 Hz, 1H), 2.96 (ddd, *J* = 13.7, 8.4, 7.0 Hz, 1H), 2.41 (s, 3H), 2.38 – 2.17 (m, 2H), 1.33 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 142.0, 137.2, 135.5, 133.1, 129.9, 128.9, 128.6, 127.7, 116.8, 53.2, 49.0, 40.9, 33.1, 28.8, 21.5.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{31}N_2OS$ $[M + H]^+$ 383.2152, found 383.2149.

(*S*)-*N*-((Benzyl(but-3-yn-1-yl)amino)(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (66)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *O*-benzoyl-*N*-benzyl-*N*-(but-3-yn-1-yl)hydroxylamine **N12** (83.8 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 3/1) to afford the product **66** as a light yellow oil (74.8 mg, 98% yield, 98% e.e.).

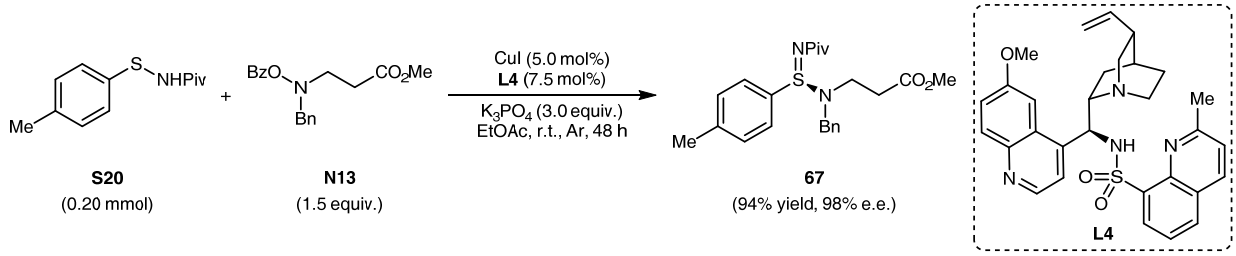
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.95 min, t_R (major) = 10.15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.21 (m, 5H), 7.21 – 7.15 (m, 2H), 4.22 – 4.06 (m, 2H), 3.47 (dt, *J* = 13.7, 6.7 Hz, 1H), 3.11 (dt, *J* = 14.1, 7.2 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.42 (s, 3H), 2.33 – 2.20 (m, 1H), 1.99 – 1.93 (m, 1H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 142.1, 136.7, 132.7, 129.9, 128.9, 128.6(4), 128.5(8), 127.8, 81.8, 70.1, 53.0, 48.6, 40.8, 28.8, 21.4, 19.1.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{29}N_2OS$ $[M + H]^+$ 381.1995, found 381.1992.

Methyl (*S*)-3-((*N*-benzyl-4-methyl-*N*'-pivaloylphenyl)sulfinoamidimidamido)propanoate (67)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20**(44.7 mg, 0.20 mmol, 1.0 equiv.) and methyl 3-((benzoyloxy)(benzyl)amino)propanoate **N13** (94.0 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford the product **67** as a colorless oil (78.1 mg, 94% yield, 98% e.e.).

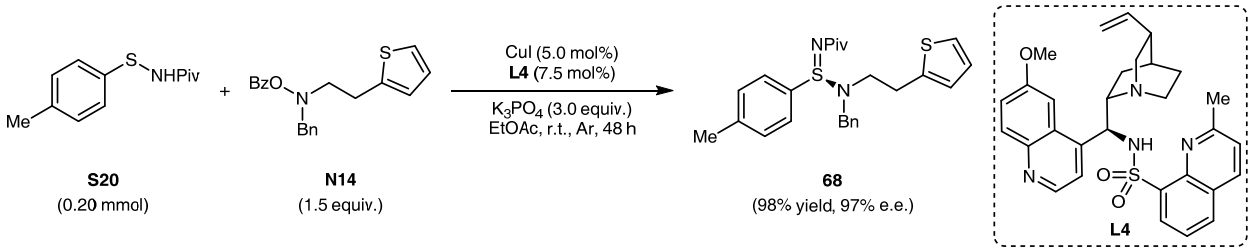
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.91 min, t_R (major) = 13.31 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.19 (m, 5H), 7.12 (d, *J* = 7.2 Hz, 2H), 4.09 (s, 2H), 3.62 – 3.47 (m, 4H), 3.24 (dt, *J* = 14.3, 7.3 Hz, 1H), 2.60 (dt, *J* = 15.1, 7.3 Hz, 1H), 2.45 (dt, *J* = 16.2, 7.1 Hz, 1H), 2.39 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 171.9, 142.2, 136.7, 132.6, 130.0, 128.8, 128.6, 128.5, 127.8, 53.1, 51.7, 45.7, 40.8, 33.7, 28.8, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{31}N_2O_3S$ $[M + H]^+$ 415.2050, found 415.2047.

(*S*)-*N*-((Benzyl(2-(thiophen-2-yl)ethyl)amino)(*p*-tolyl)-λ^4-sulfanylidene)pivalamide (68)



According to **General procedure E** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and *O*-benzoyl-*N*-benzyl-*N*-(2-(thiophen-2-yl)ethyl)hydroxylamine **N14** (101.2 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford vthe product **68** as a colorless oil (86.2 mg, 98% yield, 97% e.e.).

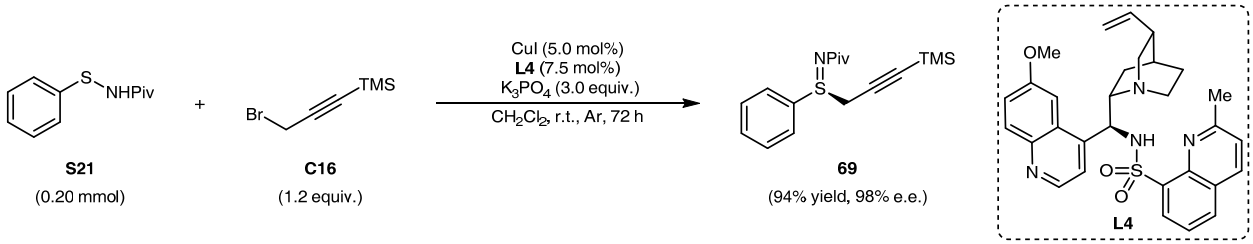
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.20 min, t_R (major) = 10.17 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.19 (m, 5H), 7.13 – 7.05 (m, 3H), 6.89 – 6.82 (m, 1H), 6.62 (d, *J* = 3.4 Hz, 1H), 4.09 (s, 2H), 3.53 (dt, *J* = 14.4, 7.2 Hz, 1H), 3.20 (ddd, *J* = 14.2, 8.3, 6.5 Hz, 1H), 3.02 (dt, *J* = 14.7, 7.3 Hz, 1H), 2.84 (dt, *J* = 14.8, 7.2 Hz, 1H), 2.37 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 142.0, 141.5, 136.8, 132.9, 129.9, 129.1, 128.6(4), 128.5(7), 127.9, 126.9, 125.5, 123.7, 53.2, 51.7, 40.9, 29.3, 28.9, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{31}N_2OS_2$ $[M + H]^+$ 439.1872, found 439.1872.

(*S*)-*N*-(Phenyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (69)



According to **General Procedure C** with *N*-(phenylthio)pivalamide **S21** (41.8 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **69** as a colorless oil (60.1 mg, 94% yield, 98% e.e.).

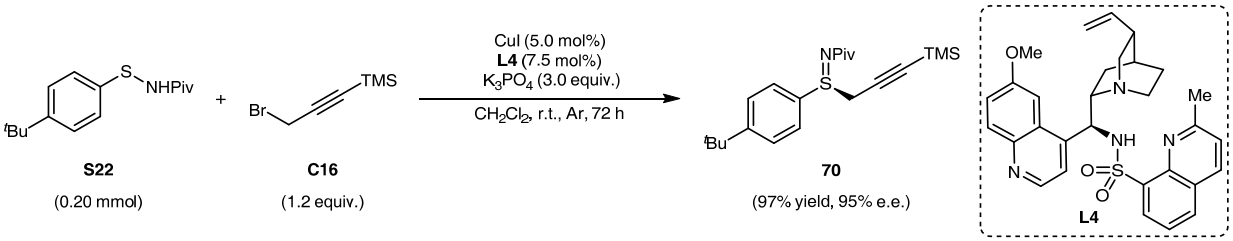
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 10.94 min, t_R (major) = 13.61 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.76 (m, 2H), 7.66 – 7.46 (m, 3H), 4.01 (d, *J* = 15.7 Hz, 1H), 3.86 (d, *J* = 15.7 Hz, 1H), 1.26 (s, 9H), 0.10 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 132.9, 132.6, 129.4, 128.3, 95.1, 93.3, 41.9, 40.3, 28.7, –0.3.

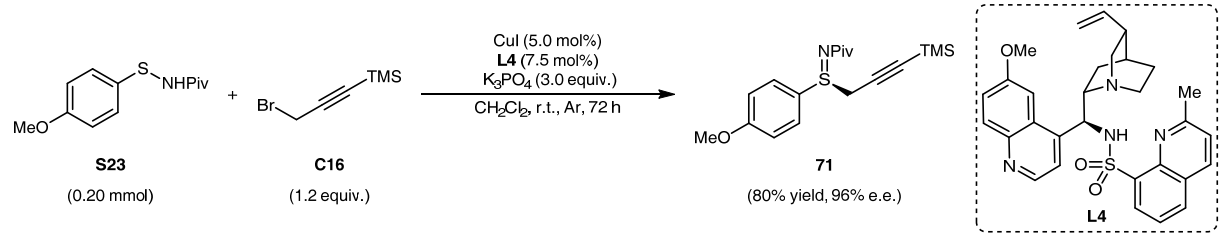
HRMS (ESI) *m/z* calcd. for $C_{17}H_{26}NOSSi$ $[M + H]^+$ 320.1499, found 320.1495.

(*S*)-*N*-((4-(*tert*-Butyl)phenyl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-pivalamide (70)



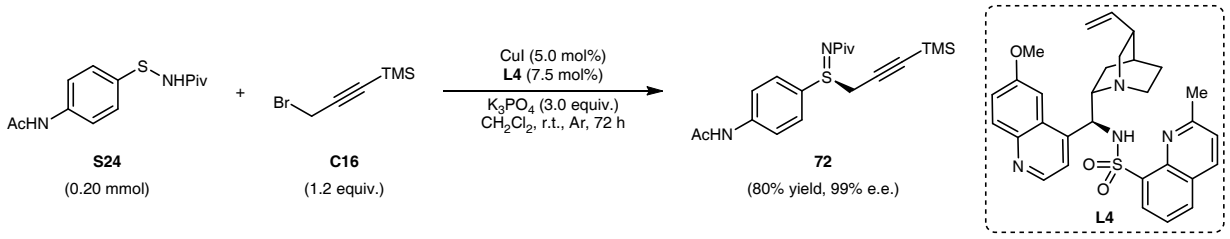
According to **General Procedure C** with *N*-((4-(*tert*-butyl)phenyl)thio)pivalamide **S22** (53.1 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **70** as a colorless oil (72.9 mg, 97% yield, 95% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 9.09 min, t_R (major) = 13.16 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 4.00 (d, *J* = 15.7 Hz, 1H), 3.81 (d, *J* = 15.7 Hz, 1H), 1.33 (s, 9H), 1.24 (s, 9H), 0.08 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 156.3, 129.4, 128.1, 126.5, 94.9, 93.6, 41.8, 40.2, 35.2, 31.2, 28.8, –0.3.
HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{34}NOSSi$ $[M + H]^+$ 376.2125, found 376.2119.

(*S*)-*N*-((4-Methoxyphenyl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (71)



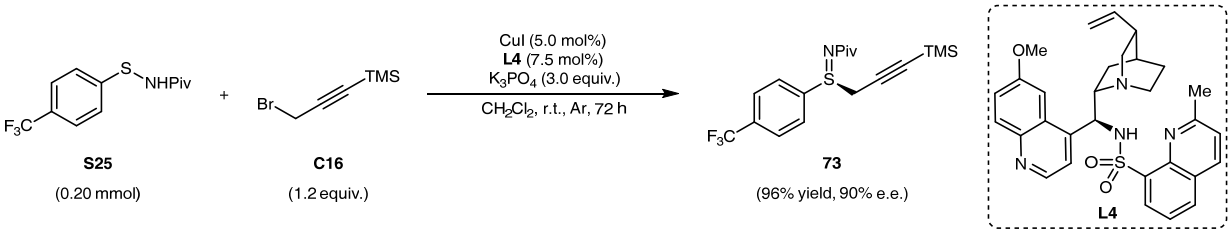
According to **General Procedure C** with *N*-((4-methoxyphenyl)thio)pivalamide **S23** (47.9 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 20/10/1) to afford **71** as a colorless oil (55.9 mg, 80% yield, 96% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 12.66 min, t_R (major) = 19.73 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.97 (d, *J* = 15.6 Hz, 1H), 3.84 (s, 3H), 3.79 (d, *J* = 15.7 Hz, 1H), 1.23 (s, 9H), 0.09 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 163.1, 130.2, 123.3, 114.9, 94.9, 93.5, 55.7, 42.1, 40.2, 28.7, –0.3.
HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{28}NO_2SSi$ $[M + H]^+$ 350.1605, found 350.1601.

(*S*)-*N*-((4-Acetamidophenyl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (72)



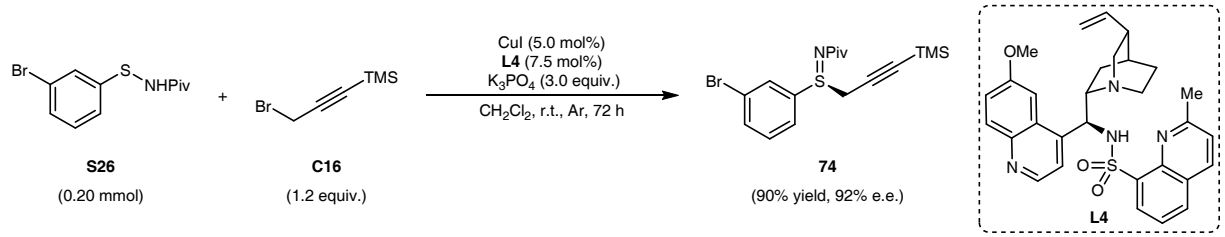
According to **General Procedure C** with *N*-((4-acetamidophenyl)thio)pivalamide **S24** (53.3 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 10/20/1) to afford **72** as a colorless oil (60.4 mg, 80% yield, 99% e.e.).
HPLC analysis: Chiralpak IE (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 270 nm), t_R (minor) = 33.56 min, t_R (major) = 47.04 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.54 – 7.35 (m, 4H), 3.87 (d, *J* = 15.7 Hz, 1H), 3.78 (d, *J* = 15.8 Hz, 1H), 2.18 (s, 3H), 1.27 (s, 9H), 0.09 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 169.5, 142.9, 127.9, 126.2, 120.0, 95.2, 93.2, 41.6, 40.2, 28.8, 24.6, –0.4.
HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{29}N_2O_2SSi$ $[M + H]^+$ 377.1714, found 377.1716.

(*S*)-*N*-((4-Methoxyphenyl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (73)



According to **General Procedure C** with *N*-((4-(trifluoromethyl)phenyl)thio)pivalamide **S25** (55.5 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **73** as a colorless oil (74.4 mg, 96% yield, 90% e.e.).
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 240 nm), t_R (minor) = 11.38 min, t_R (major) = 13.17 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 4.01 (d, *J* = 15.8 Hz, 1H), 3.90 (d, *J* = 15.9 Hz, 1H), 1.24 (s, 9H), 0.09 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 137.4, 134.4 (q, *J* = 33.0 Hz), 128.7, 126.3 (q, *J* = 3.8 Hz), 123.4 (q, *J* = 272.8 Hz), 95.9, 92.6, 41.8, 40.3, 28.7, –0.4.
^{19}F NMR (375 MHz, $CDCl_3$) δ –63.11.
HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{25}F_3NOSSi$ $[M + H]^+$ 388.1373, found 388.1368.

(*S*)-*N*-((3-Bromophenyl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (74)



According to **General Procedure C** with *N*-((3-bromophenyl)thio)pivalamide **S26** (57.6 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **74** as a colorless oil (71.6 mg, 90% yield, 92% e.e.).

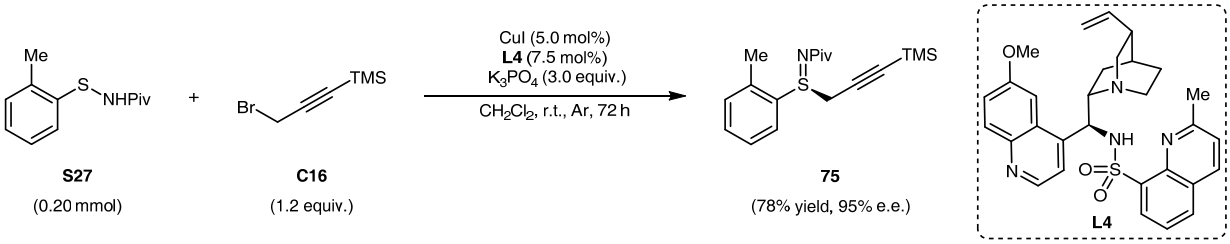
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 270 nm), t_R (minor) = 15.09 min, t_R (major) = 28.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 1H), 7.74 – 7.66 (m, 2H), 7.43 – 7.34 (m, 1H), 3.96 (d, *J* = 15.8 Hz, 1H), 3.88 (d, *J* = 15.8 Hz, 1H), 1.24 (s, 9H), 0.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 135.7, 135.0, 131.0, 130.7, 126.6, 123.3, 95.8, 92.7, 41.9, 40.2, 28.7, –0.3.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{25}BrNOSSi$ $[M + H]^+$ 398.0604, found 398.0600.

(*S*)-*N*-(*o*-Tolyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (75)



According to **General Procedure C** with *N*-(*o*-tolylthio)pivalamide **S27** (44.7 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **75** as a colorless oil (52.1 mg, 78% yield, 95% e.e.).

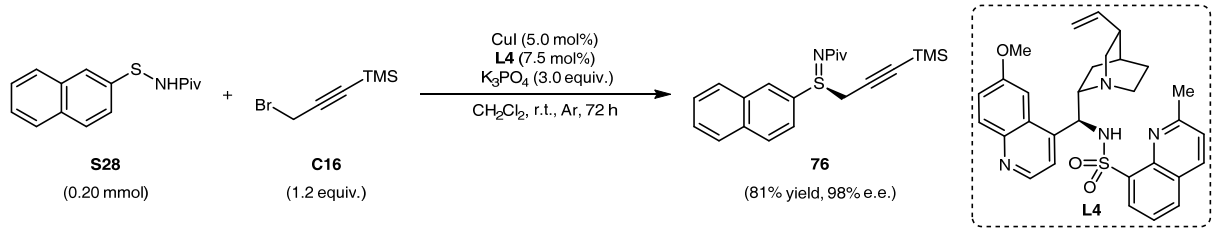
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 8.81 min, t_R (major) = 11.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.34 (m, 2H), 7.31 – 7.22 (m, 1H), 3.98 (d, *J* = 15.8 Hz, 1H), 3.90 (d, *J* = 15.8 Hz, 1H), 2.60 (s, 3H), 1.24 (s, 9H), 0.07 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 139.3, 132.5, 132.2, 130.8, 127.6, 127.2, 94.2, 93.1, 40.5, 40.1, 28.7, 19.8, –0.4.

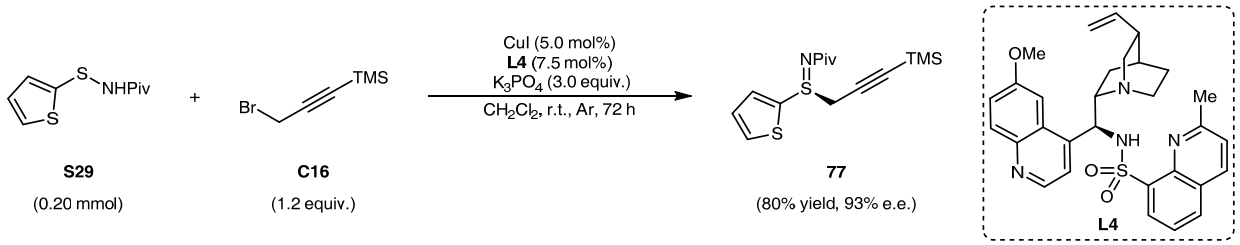
HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{28}NOSSi$ $[M + H]^+$ 334.1655, found 334.1652.

(*S*)-*N*-(Naphthalen-2-yl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (76)



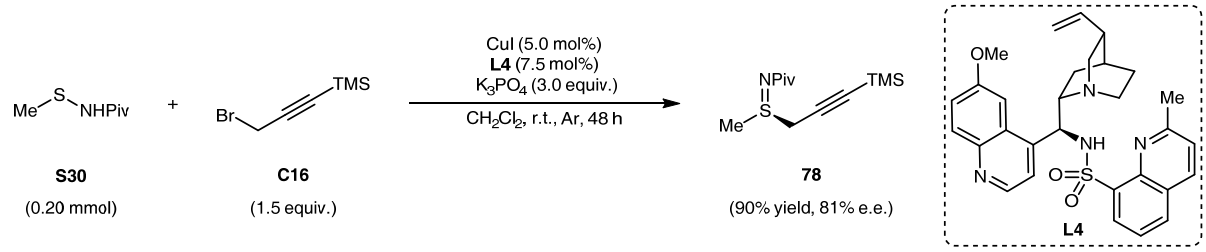
According to **General Procedure C** with *N*-(naphthalen-2-ylthio)pivalamide **S28** (51.9 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **76** as a colorless oil (59.9 mg, 81% yield, 98% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 12.25 min, t_R (major) = 16.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.95 – 7.84 (m, 3H), 7.65 – 7.56 (m, 2H), 4.08 (d, *J* = 15.7 Hz, 1H), 3.92 (d, *J* = 15.7 Hz, 1H), 1.29 (s, 9H), 0.02 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.86, 135.2, 132.6, 130.0, 129.8(4), 129.7(9), 128.8, 128.6, 128.2, 127.5, 122.9, 95.2, 93.3, 41.9, 40.3, 28.8, –0.4.
HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{28}NOSSi$ $[M + H]^+$ 370.1655, found 370.1652.

(*S*)-*N*-(Thiophen-2-yl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (77)



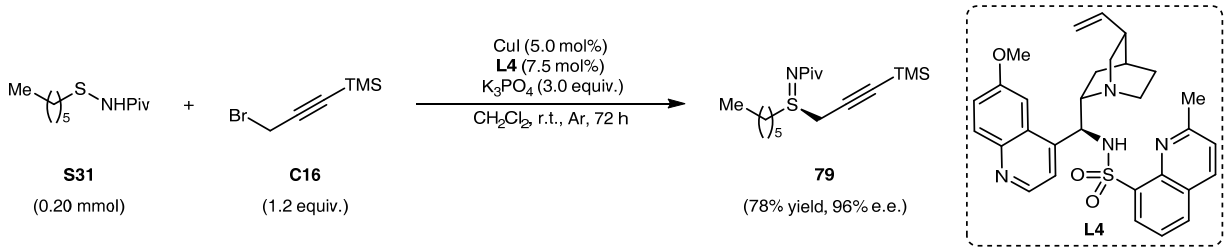
According to **General Procedure C** with *N*-(thiophen-2-ylthio)pivalamide **S29** (43.1 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 20/10/1) to afford **77** as a colorless oil (52.1 mg, 80% yield, 93% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 11.29 min, t_R (major) = 13.54 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 1H), 7.59 – 7.47 (m, 1H), 7.18 – 7.03 (m, 1H), 4.18 (d, *J* = 15.5 Hz, 1H), 3.84 (d, *J* = 15.5 Hz, 1H), 1.22 (s, 9H), 0.11 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 133.7, 133.0, 132.7, 127.3, 95.9, 93.1, 44.3, 40.2, 28.6, –0.3.
HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{24}NOS_2Si$ $[M + H]^+$ 326.1063, found 326.1059.

(*R*)-*N*-(Methyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (78)



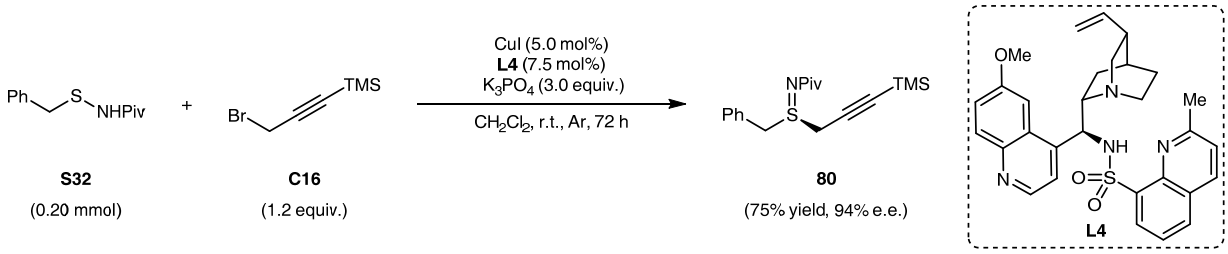
According to **General Procedure C** with *N*-(methylthio)pivalamide **S30** (29.5 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (57.3 mg, 0.3 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (PE/EtOAc/Et_3N = 30/30/1) to afford **78** as a yellow oil (46.3 mg, 90% yield, 81% e.e.).
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 33.40 min, t_R (major) = 35.45 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (d, *J* = 16.0 Hz, 1H), 3.75 (d, *J* = 16.0 Hz, 1H), 2.73 (s, 3H), 1.18 (s, 9H), 0.19 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 94. 8, 92.9, 39.8, 37.4, 28.6, 27.9, –0.3.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{25}NOSSi$ $[M + H]^+$ 258.1342, found 258.1338.

(*S*)-*N*-(Hexyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (79)



According to **General Procedure C** with *N*-(hexylthio)pivalamide **S31** (43.5 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **79** as a colorless oil (51.2 mg, 78% yield, 96% e.e.).
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 15.33 min, t_R (major) = 18.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (d, *J* = 16.1 Hz, 1H), 3.74 (d, *J* = 16.1 Hz, 1H), 3.16 – 2.98 (m, 2H), 1.77 – 1.65 (m, 2H), 1.50 – 1.37 (m, 2H), 1.34 – 1.24 (m, 4H), 1.16 (s, 9H), 0.93 – 0.83 (m, 3H), 0.16 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 94.3, 93.2, 42.6, 40.0, 35.5, 31.2, 28.6, 28.2, 23.0, 22.4, 14.0, –0.3.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{34}NOSSi$ $[M + H]^+$ 328.2125, found 328.2121.

(*S*)-*N*-(Benzyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (80)



S32 (0.20 mmol) + **C16** (1.2 equiv.) → **80** (75% yield, 94% e.e.)

According to **General Procedure C** with *N*-(benzylthio)pivalamide **S32**(44.7 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 20/10/1) to afford **80** as a colorless oil (50.0 mg, 75% yield, 94% e.e.).

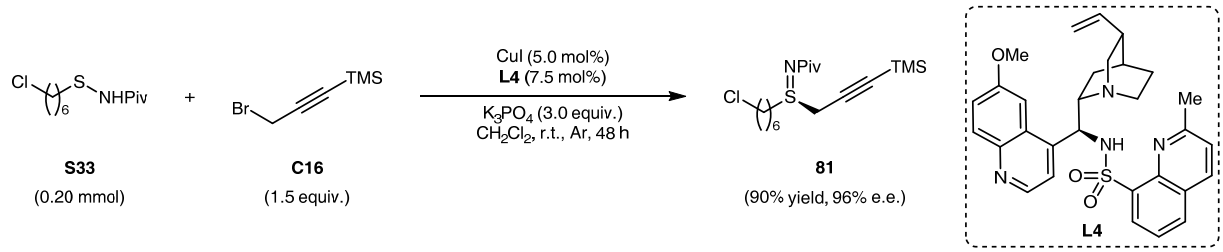
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min. λ = 254 nm), t_R (minor) = 9.99 min, t_R (major) = 11.31 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 3H), 7.34 – 7.28 (m, 2H), 4.44 (d, *J* = 13.0 Hz, 1H), 4.28 (d, *J* = 13.0 Hz, 1H), 3.68 (d, *J* = 16.3 Hz, 1H), 3.52 (d, *J* = 16.3 Hz, 1H), 1.17 (s, 9H), 0.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 130.9, 129.1, 128.9, 128.3, 94.9, 93.5, 46.5, 40.0, 33.0, 28.7, –0.2.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{28}NOSSi$ $[M + H]^+$ 334.1655, found 334.1651.

(*R*)-*N*-((6-Chlorohexyl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (81)



S33 (0.20 mmol) + **C16** (1.5 equiv.) → **81** (90% yield, 96% e.e.)

According to **General Procedure C** with *N*-((6-chlorohexyl)thio)pivalamide **S33** (50.4 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (57.3 mg, 0.3 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (PE/EtOAc/Et_3N = 30/30/1) to afford **81** as a yellow oil (65.2 mg, 90% yield, 96% e.e.).

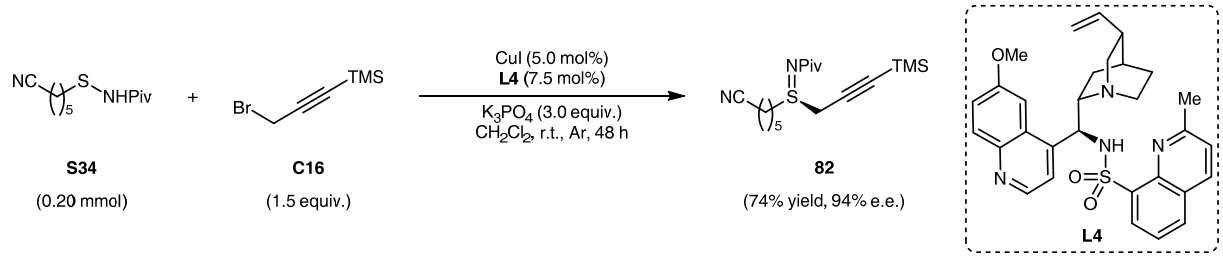
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 246 nm), t_R (minor) = 5.58 min, t_R (major) =7.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 – 3.86 (m, 1H), 3.83 – 3.69 (m, 1H), 3.60 – 3.47 (m, 2H), 3.15 – 2.94 (m, 2H), 1.86 – 1.71 (m, 4H), 1.60 – 1.40 (m, 4H), 1.23 – 1.10 (m, 9H), 0.26 – 0.10 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 94.4, 93.1, 44.8, 42.5, 40.0, 35.7, 32.2, 28.6, 27.8, 26.3, 23.0, –0.3.

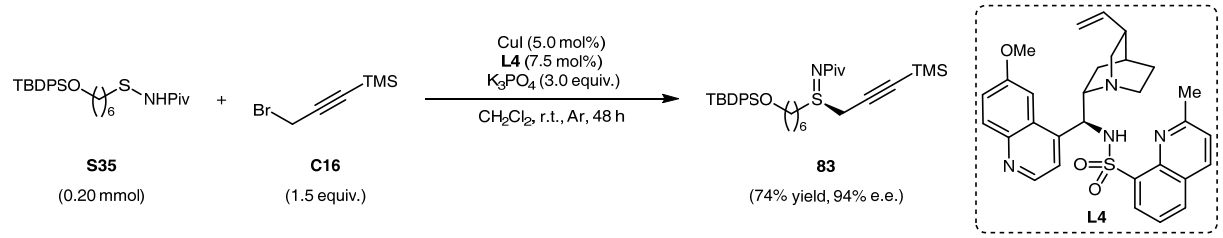
HRMS (ESI) *m/z* calcd. for $C_{17}H_{32}ClNOSSi$ $[M + H]^+$ 362.1735, found 362.1735.

(*R*)-*N*-((5-Cyanopentyl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (82)



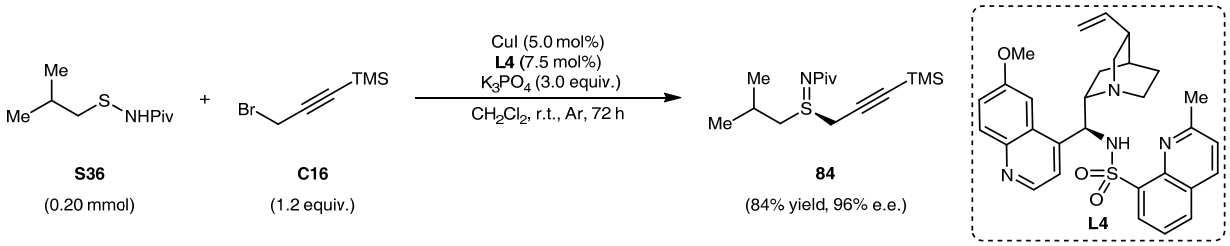
According to **General Procedure C** with *N*-((5-cyanopentyl)thio)pivalamide **S34** (45.7 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (57.3 mg, 0.3 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (PE/EtOAc/Et_3N = 30/30/1) to afford **82** as a yellow oil (50.0 mg, 74% yield, 94% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 31.06 min, t_R (major) = 51.20 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (d, *J* = 16.2 Hz, 1H), 3.76 (d, *J* = 16.1 Hz, 1H), 3.15 – 3.04 (m, 2H), 2.44 – 2.33 (m, 2H), 1.87 – 1.79 (m, 2H), 1.77 – 1.69 (m, 2H), 1.69 – 1.61 (m, 2H), 1.18 (s, 9H), 0.19 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 119.3, 94.8, 93.0, 42.4, 40.1, 36.0, 28.7, 27.7, 25.0, 22.6, 17.1, –0.2.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{30}N_2OSSi$ $[M + H]^+$ 339.1921, found 339.1915.

(*R*)-*N*-(2,2,15,15-Tetramethyl-14,14-diphenyl-13-oxa-6λ^4-thia-2,14-disilahexadec-3-yn-6-ylidene)pivalamide (83)



According to **General Procedure C** with *N*-((6-((*tert*-butyldiphenylsilyl)oxy)-hexyl)thio)pivalamide **S35** (94.4 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (57.3 mg, 0.3 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (PE/EtOAc/Et_3N = 100/500/1) to afford **83** as a colorless oil (85.8 mg, 74% yield, 94% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 245 nm), t_R (minor) = 9.92 min, t_R (major) = 13.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 4H), 7.58 – 7.42 (m, 6H), 3.99 (d, *J* = 16.2 Hz, 1H), 3.86 (d, *J* = 16.1 Hz, 1H), 3.80 – 3.70 (m, 2H), 3.22 – 3.08 (m, 2H), 1.87 – 1.78 (m, 2H), 1.72 – 1.60 (m, 2H), 1.59 – 1.46 (m, 4H), 1.28 (s, 9H), 1.15 (s, 9H), 0.27 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 135.7, 134.2, 129.7, 127.8, 94.5, 93.3, 63.8, 42.8, 40.1, 35.7, 32.3, 28.7, 28.5, 27.0, 25.5, 23.2, 19.4, –0.2.
HRMS (ESI) *m/z* calcd. for $C_{33}H_{52}NO_2SSi_2$ $[M + H]^+$ 582.3252, found 582.3266.

(*S*)-*N*-(Isobutyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (84)



According to **General Procedure C** with *N*-(isobutylthio)pivalamide **S36** (37.8 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 30/10/1) to afford **84** as a colorless oil (50.5 mg, 84% yield, 96% e.e.).

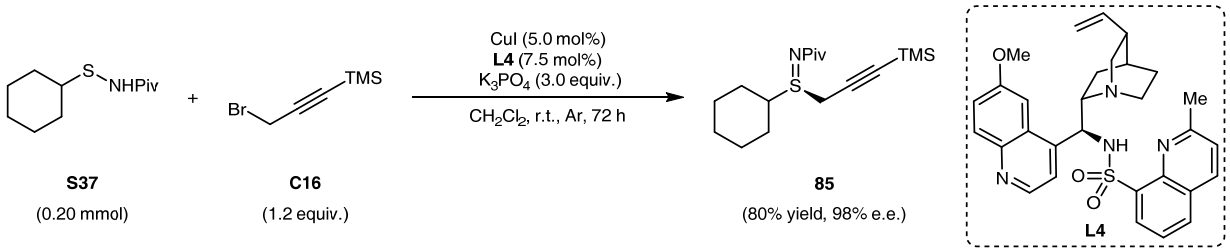
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 8.07 min, t_R (major) = 9.79 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (d, *J* = 16.1 Hz, 1H), 3.75 (d, *J* = 16.1 Hz, 1H), 3.11 – 2.81 (m, 2H), 2.22 – 2.08 (m, 1H), 1.16 (s, 9H), 1.08 (dd, *J* = 12.2, 6.7 Hz, 6H), 0.16 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 94.5, 93.4, 52.2, 40.1, 36.3, 28.7, 24.7, 22.5, 22.0, –0.2.

HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{30}NOSSi$ $[M + H]^+$ 300.1812, found 300.1815.

(*S*)-*N*-(Cyclohexyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (85)



According to **General Procedure C** with *N*-(cyclohexylthio)pivalamide **S37** (43.1 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 20/10/1) to afford **85** as a colorless oil (52.1 mg, 80% yield, 98% e.e.).

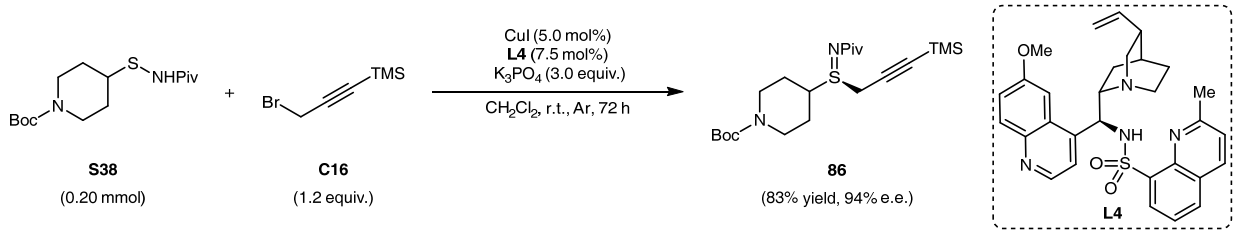
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 19.74 min, t_R (major) = 26.13 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06 – 3.63 (m, 2H), 3.29 – 3.19 (m, 1H), 2.20 – 1.94 (m, 2H), 1.94 – 1.81 (m, 2H), 1.78 – 1.47 (m, 3H), 1.46 – 1.20 (m, 3H), 1.16 (s, 9H), 0.16 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 94.0, 93.8, 52.9, 40.3, 33.3, 28.7, 27.6, 26.0, 25.7, 25.4(8), 25. 4(6), –0.2.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{32}NOSSi$ $[M + H]^+$ 326.1968, found 326.1965.

(*S*)-4-(*N*-Pivaloyl-*S*-(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfinimidoyl)piperidine-1-carboxylate (86)



According to **General Procedure C** with *tert*-butyl 4-(pivalamidothio)piperidine-1-carboxylate **S38** (63.3 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 20/10/1) to afford **86** as a colorless oil (71.2 mg, 83% yield, 94% e.e.).

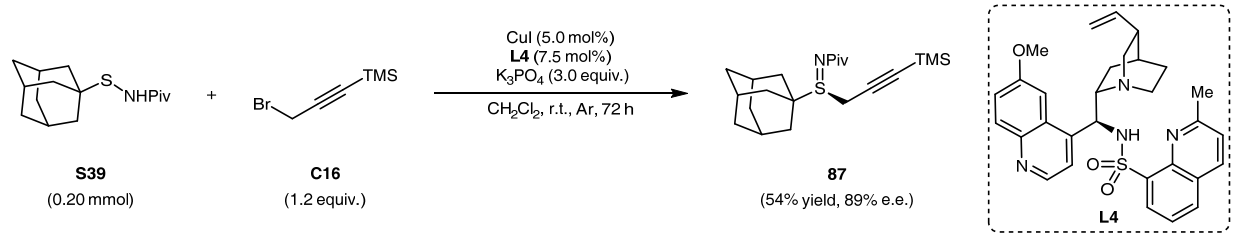
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 11.54 min, t_R (major) = 14.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 – 4.04 (m, 2H), 3.97 – 3.71 (m, 2H), 3.44 – 3.32 (m, 1H), 2.90 – 2.71 (m, 2H), 2.13 – 1.65 (m, 4H), 1.44 (s, 9H), 1.15 (s, 9H), 0.16 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 154.6, 94.7, 93.2, 80.3, 51.6, 42.9, 40.4, 33.7, 28.7, 28.5, 26.9, –0.3.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{38}N_2O_3SSiNa$ $[M + Na]^+$ 449.2265, found 449.2268.

(*S*)-*N*-Adamantan-1-yl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (87)



According to **General Procedure C** with *N*-(adamantan-1-ylthio)pivalamide **S39** (53.5 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc/Et_3N = 20/10/1) to afford **87** as a colorless oil (40.9 mg, 54% yield, 89% e.e.).

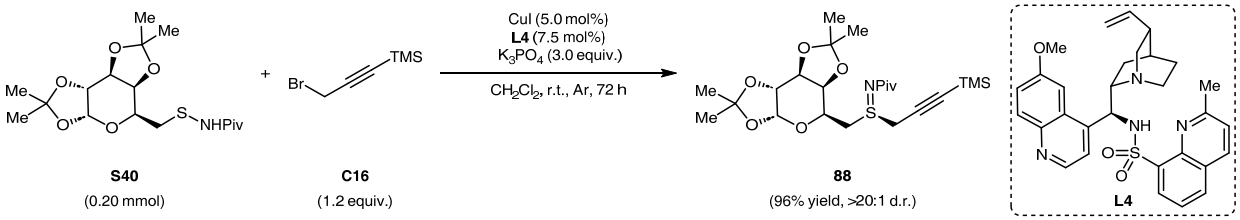
HPLC analysis: Chiralpak IE (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 24.11 min, t_R (major) = 36.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 – 3.61 (m, 2H), 2.23 – 2.15 (m, 3H), 2.15 – 2.06 (m, 3H), 2.05 – 1.96 (m, 3H), 1.83 – 1.72 (m, 6H), 1.19 (s, 9H), 0.14 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 95.3, 93.6, 56.8, 40.6, 37.1, 36.2, 30.4, 29.2, 28.9, –0.3.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{36}NOSSi$ $[M + H]^+$ 378.2281, found 378.2285.

***N*-((*S*)-(((*3*a*R*,*5S*,*5*a*R*,*8*a*S*,*8*b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo) [4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)pivalamide (88)**



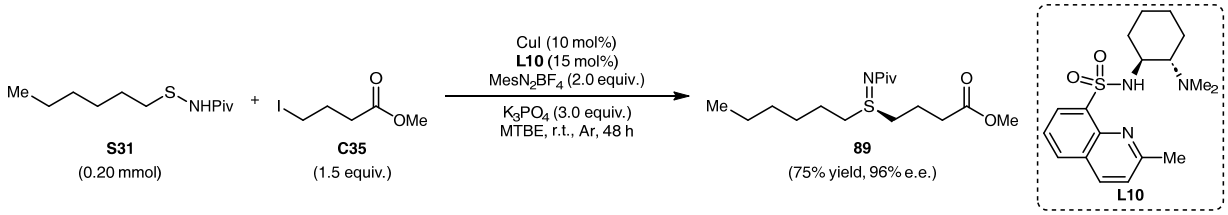
According to **General Procedure C** with *N*-((((*3*a*R*,*5S*,*5*a*R*,*8*a*S*,*8*b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)thio)pivalamide **S40** (75.1 mg, 0.20 mmol, 1.0 equiv.) and (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) for 72 h, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc/Et_3N = 75/25/1) to afford **88** as a light yellow solid (93.3 mg, 96% yield, >20:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (d, *J* = 4.9 Hz, 1H), 4.66 (dd, *J* = 7.8, 2.6 Hz, 1H), 4.36 – 4.26 (m, 2H), 4.22 (dd, *J* = 7.8, 2.0 Hz, 1H), 3.97 (s, 2H), 3.39 (dd, *J* = 13.3, 10.4 Hz, 1H), 3.20 (dd, *J* = 13.3, 2.3 Hz, 1H), 1.53 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H), 1.17 (s, 9H), 0.18 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 109.9, 109.3, 96.3, 94.6, 93.1, 72.7, 71.1, 70.4, 63.4, 44.6, 40.0, 36.6, 28.7, 26.3, 26.1, 25.0, 24.6, –0.2.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{40}NO_6SSi$ $[M + H]^+$ 486.2340, found 486.2346.

Methyl (*R*)-4-(*S*-hexyl-*N*-pivaloylsulfinimidoyl)butanoate (89)



According to **General Procedure D** with *N*-(hexylthio)pivalamide **S31** (43.5 mg, 0.20 mmol, 1.0 equiv.), methyl 4-iodobutanoate **C35** (68.4 mg, 0.30 mmol, 1.5 equiv.), **L10** (10.44 mg, 0.03 mmol, 15 mol%) for 48 h, the product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **89** as a colorless oil (47.6 mg, 75% yield, 96% e.e.).

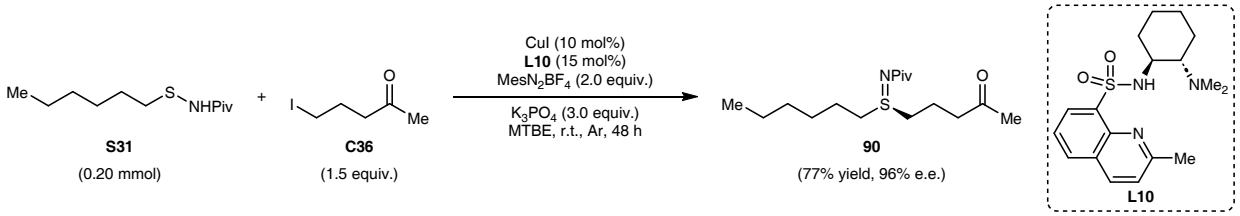
HPLC analysis: Chiralpak IG (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 224 nm), t_R (minor) = 12.41 min, t_R (major) = 17.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.06 – 2.91 (m, 3H), 2.89 – 2.79 (m, 1H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.04 (p, *J* = 7.0 Hz, 2H), 1.70 (p, *J* = 7.6 Hz, 2H), 1.51 – 1.37 (m, 2H), 1.37 – 1.24 (m, 4H), 1.19 (s, 9H), 0.92 – 0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 172.9, 51.9, 44.6, 43.5, 40.1, 32.3, 31.3, 28.7, 28.3, 23.2, 22.4, 18.8, 14.0.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{32}NO_3S$ $[M + H]^+$ 318.2097, found 318.2087.

(*R*)-*N*-(Hexyl(4-oxopentyl)-λ^4-sulfaneylidene)pivalamide (90)



According to **General Procedure D** with *N*-(hexylthio)pivalamide **S31** (43.5 mg, 0.20 mmol, 1.0 equiv.) and 5-iodopentan-2-one **C36** (63.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the product mixture was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 20/1) to afford **90** as a colorless liquid (46.4 mg, 77% yield, 96% e.e.).

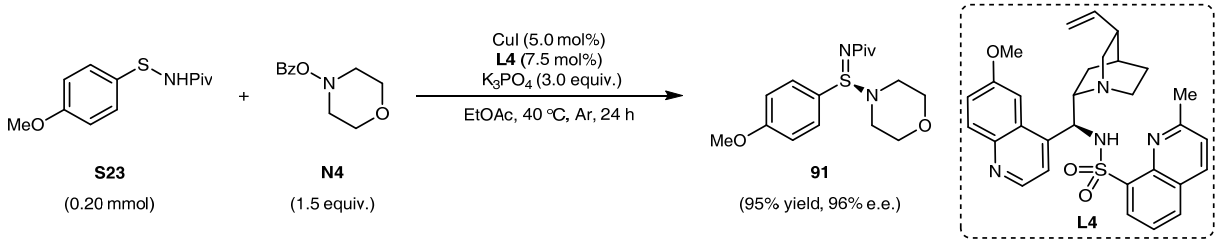
HPLC analysis: Chiralpak IG (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 226 nm), t_R (minor) = 12.20 min, t_R (major) = 14.99 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 – 2.89 (m, 3H), 2.90 – 2.79 (m, 1H), 2.68 (t, *J* = 6.7 Hz, 2H), 2.16 (s, 3H), 1.97 (p, *J* = 6.9 Hz, 2H), 1.70 (p, *J* = 7.6 Hz, 2H), 1.52 – 1.37 (m, 2H), 1.35 – 1.26 (m, 4H), 1.19 (s, 9H), 0.93 – 0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 191.0, 44.4, 43.7, 41.3, 40.0, 31.2, 30.0, 28.6, 28.2, 23.1, 22.3, 17.3, 13.9.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{32}NO_2S$ $[M + H]^+$ 302.2148, found 302.2140.

(*S*)-*N*-((4-Methoxyphenyl)(morpholino)-λ^4-sulfanylidene)pivalamide (91)



According to **General procedure E** with *N*-((4-methoxyphenyl)thio)pivalamide **S23** (47.9 mg, 0.20 mmol, 1.0 equiv.) and morpholino benzoate **N4** (62.2 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford the product **91** as a light yellow oil (61.7 mg, 95% yield, 96% e.e.).

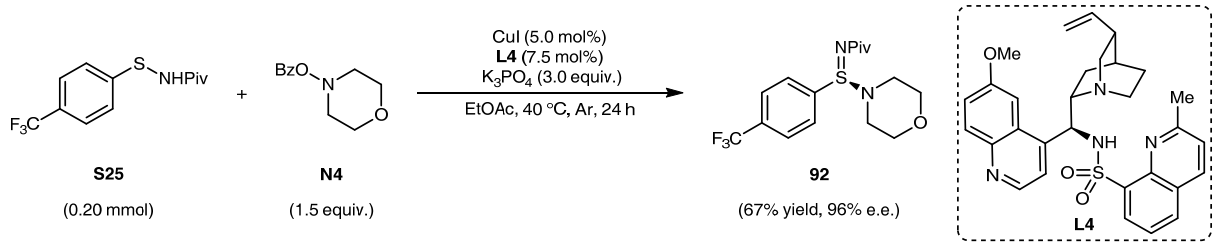
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.87 min, t_R (major) = 9.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.03 – 6.96 (m, 2H), 3.84 (s, 3H), 3.71 – 3.59 (m, 4H), 3.18 – 3.08 (m, 2H), 3.02 – 2.92 (m, 2H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 162.3, 130.1, 125.1, 114.7, 67.0, 55.6, 47.2, 41.0, 28.7.

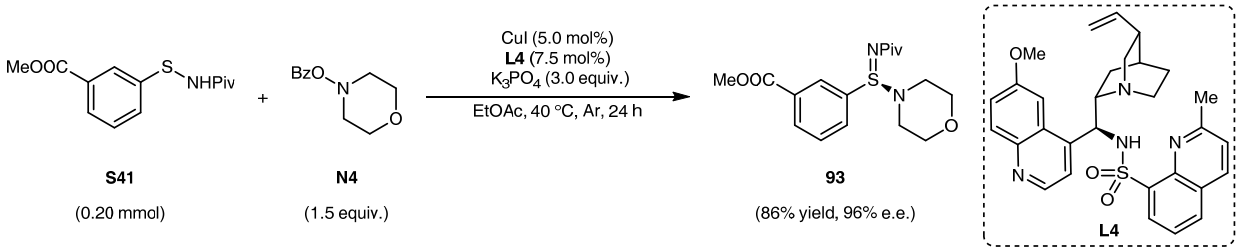
HRMS (ESI) *m/z* calcd. for $C_{16}H_{25}N_2O_3S$ $[M + H]^+$ 325.1580, found 325.1576.

(*S*)-*N*-(Morpholino(4-(trifluoromethyl)phenyl)-λ^4-sulfanylidene)pivalamide (92)



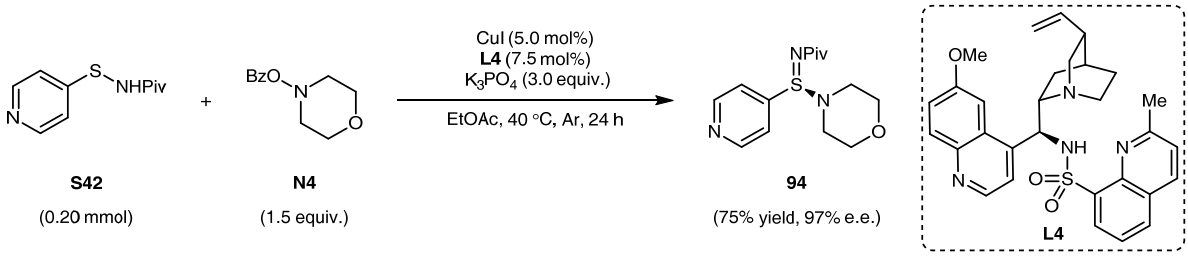
According to **General procedure E** with *N*-((4-(trifluoromethyl)phenyl)thio)pivalamide **S25** (55.5 mg, 0.20 mmol, 1.0 equiv.) and morpholino benzoate **N4** (62.2 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford the product **92** as a colorless oil (48.3 mg, 67% yield, 96% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 6.50 min, t_R (major) = 9.55 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 3.76 – 3.63 (m, 4H), 3.24 – 3.14 (m, 2H), 3.07 – 2.97 (m, 2H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 139.0, 133.6 (q, *J* = 32.8 Hz), 129.1, 126.3 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 67.0, 47.7, 41.0, 28.7.
^{19}F NMR (375 MHz, $CDCl_3$) δ –62.97.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{22}F_3N_2O_2S$ $[M + H]^+$ 363.1349, found 363.1346.

Methyl (*S*)-2-(*N*-pivaloylmorpholine-4-sulfinimidoyl)benzoate (93)



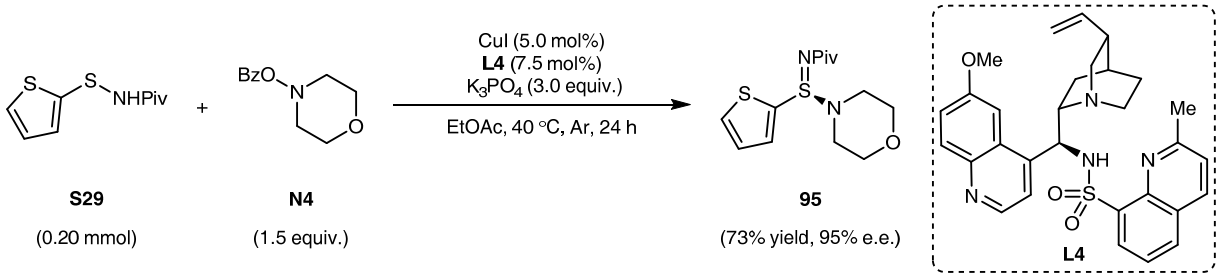
According to **General procedure E** with methyl 2-(pivalamidothio)benzoate **S41** (53.5 mg, 0.20 mmol, 1.0 equiv.) and morpholino benzoate **N4** (62.2 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford the product **93** as a colorless oil (60.6 mg, 86% yield, 96% e.e.).
HPLC analysis: Chiralpak IG (*n*-hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.51 min, t_R (major) = 15.59 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.48 (m, 1H), 8.20 – 8.15 (m, 1H), 8.15 – 8.10 (m, 1H), 7.66 – 7.56 (m, 1H), 3.95 (s, 3H), 3.71 – 3.65 (m, 4H), 3.23 – 2.95 (m, 4H), 1.28 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 165.8, 135.6, 132.7, 132.6, 131.5, 129.7, 129.5, 66.9, 52.7, 47.6, 41.0, 28.7.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}N_2O_4S$ $[M + H]^+$ 353.1530, found 353.1533.

(*S*)-*N*-(Morpholino(pyridin-4-yl)-λ^4-sulfanylidene)pivalamide (94)



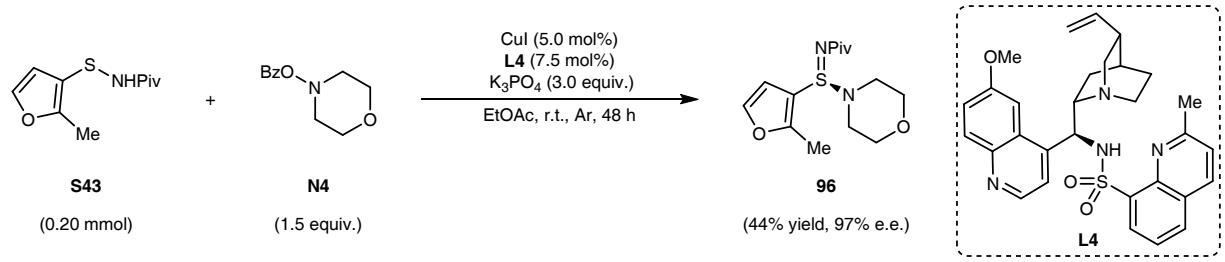
According to **General procedure E** with *N*-(pyridin-4-ylthio)pivalamide **S42** (42.1 mg, 0.20 mmol, 1.0 equiv.) and morpholino benzoate **N4** (62.2 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 1/1) to afford the product **94** as a colorless oil (44.1 mg, 75% yield, 97% e.e.).
HPLC analysis: Chiralpak IH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.63 min, t_R (major) = 9.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 – 8.76 (m, 2H), 7.86 – 7.80 (m, 2H), 3.71 (t, *J* = 4.8 Hz, 4H), 3.18 (dt, *J* = 12.5, 4.8 Hz, 2H), 3.04 (dt, *J* = 12.4, 4.8 Hz, 2H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 150.8, 145.2, 122.6, 67.0, 48.0, 41.0, 28.7.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{22}N_3O_2S$ $[M + H]^+$ 296.1427, found 296.1426.

(*S*)-*N*-(Morpholino(thiophen-2-yl)-λ^4-sulfanylidene)pivalamide (95)



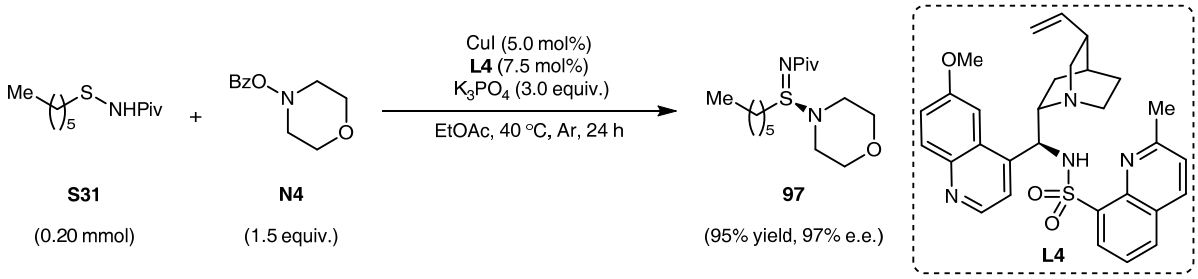
According to **General procedure E** with *N*-(thiophen-2-ylthio)pivalamide **S29** (43.1 mg, 0.20 mmol, 1.0 equiv.) and morpholino benzoate **N4** (62.2 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 2/1) to afford the product **95** as a light yellow oil (43.6 mg, 73% yield, 95% e.e.).
HPLC analysis: Chiralpak IG (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 9.56 min, t_R (minor) = 12.68 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 1H), 7.48 – 7.43 (m, 1H), 7.19 – 7.12 (m, 1H), 3.68 (t, *J* = 4.8 Hz, 4H), 3.23 – 3.02 (m, 4H), 1.25 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 136.7, 132.8, 131.3, 128.6, 67.0, 47.0, 40.7, 28.6.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{21}N_2O_2S_2$ $[M + H]^+$ 301.1039, found 301.1037.

(*S*)-*N*-((2-Methylfuran-3-yl)(morpholino)-λ^4-sulfaneylidene)pivalamide (96)



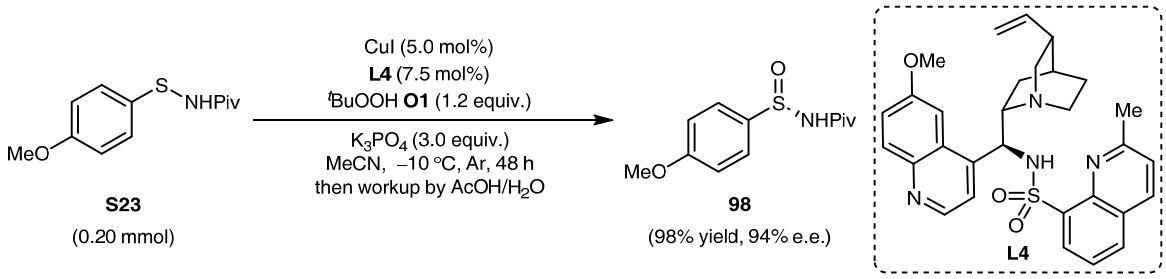
According to **General procedure E** with *N*-((2-methylfuran-3-yl)thio)pivalamide **S43** (42.7 mg, 0.20 mmol, 1.0 equiv.) and morpholino benzoate **N4** (62.2 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford the product **96** as a light yellow oil (26.3 mg, 44% yield, 97% e.e.).
HPLC analysis: Chiralpak IG (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.55 min, t_R (major) = 11.50 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* = 2.0 Hz, 1H), 3.67 (t, *J* = 4.8 Hz, 4H), 3.21 – 2.99 (m, 4H), 2.48 (s, 3H), 1.22 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 155.4, 141.4, 114.2, 110.8, 66.9, 47.1, 40.7, 28.7, 13.4.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{23}N_2O_3S$ $[M + H]^+$ 299.1424, found 299.1425.

(*S*)-*N*-(Hexyl(morpholino)-λ^4-sulfanylidene)pivalamide (97)



According to **General procedure E** with *N*-(hexylthio)pivalamide **S31** (43.5 mg, 0.20 mmol, 1.0 equiv.) and morpholino benzoate **N4** (62.2 mg, 0.30 mmol, 1.5 equiv.) at 40 °C for 24 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford the product **97** as a light yellow oil (57.5 mg, 95% yield, 97% e.e.).
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.87 min, t_R (minor) = 13.90 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (t, *J* = 4.8 Hz, 4H), 3.20 (dt, *J* = 12.4, 4.7 Hz, 2H), 3.01 (dt, *J* = 12.2, 4.8 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 1.72 – 1.54 (m, 2H), 1.47 – 1.34 (m, 2H), 1.33 – 1.22 (m, 4H), 1.17 (s, 9H), 0.90 – 0.82 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 66.9, 47.7, 45.8, 40.3, 31.3, 28.6, 28.0, 23.9, 22.4, 14.0.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{31}N_2O_2S$ $[M + H]^+$ 303.2101, found 303.2098.

(*S*)-*N*-((4-Methoxyphenyl)sulfinyl)pivalamide (98)



According to **General Procedure F** with *N*-((4-methoxyphenyl)thio)pivalamide **S23** (47.9 mg, 0.20 mmol, 1.0 equiv.) and *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.) for 48 h with workup method 2, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 2.5/1) to afford the product **98** as a white solid (50.0 mg, 98% yield, 94% e.e.).

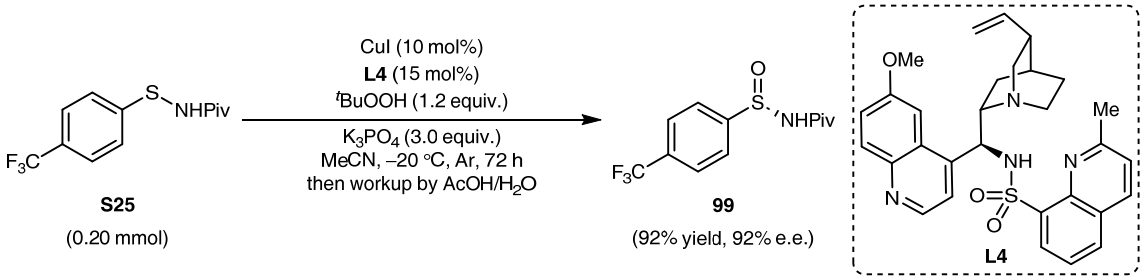
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 23.72 min, t_R (minor) = 27.40 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 162.5, 135.1, 126.6, 114.9, 55.7, 39.8, 27.1.

HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{18}NO_3S$ $[M + H]^+$ 256.1002, found 256.0999.

(*S*)-*N*-(Thiophen-2-ylsulfinyl)pivalamide (99)



According to **General Procedure F** with *N*-((4-(trifluoromethyl)phenyl) thio)pivalamide **S25** (55.5 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.), CuI (10 mol%) and **L4** (15 mol%) at –20 °C for 72 h with workup method 2, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 4/1) to afford the product **99** as a light yellow solid (54.0 mg, 92% yield, 92% e.e.).

HPLC analysis: Chiralcel OD-3 (*n*-hexane/*i*-PrOH = 50/50, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 5.57 min, t_R (major) = 20.42 min.

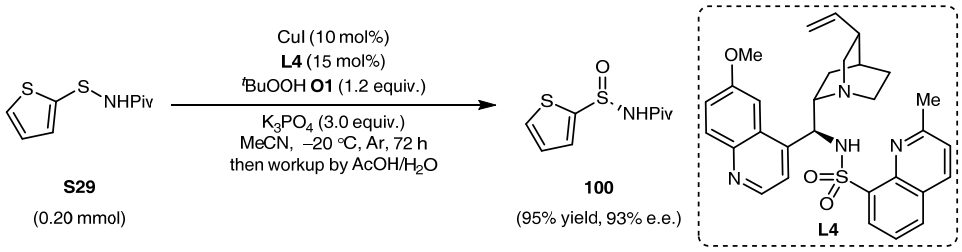
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.96 – 7.59 (m, 4H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 148.3, 133.9 (q, *J* = 33.0 Hz), 126.5 (q, *J* = 3.8 Hz), 125.7, 123.5 (q, *J* = 272.7 Hz), 40.0, 27.1.

^{19}F NMR (375 MHz, $CDCl_3$) δ –62.94.

HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{15}F_3NO_2S$ $[M + H]^+$ 294.0770, found 294.0767.

(*S*)-*N*-(Thiophen-2-ylsulfinyl)pivalamide (100)



According to **General Procedure F** with *N*-(thiophen-2-ylthio)pivalamide **S29** (43.1 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.), CuI (10 mol%) and **L4** (15 mol%) at –20 °C for 72 h with workup method 2, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 3/1) to afford the product **100** as a light yellow solid (44.0 mg, 95% yield, 93% e.e.).

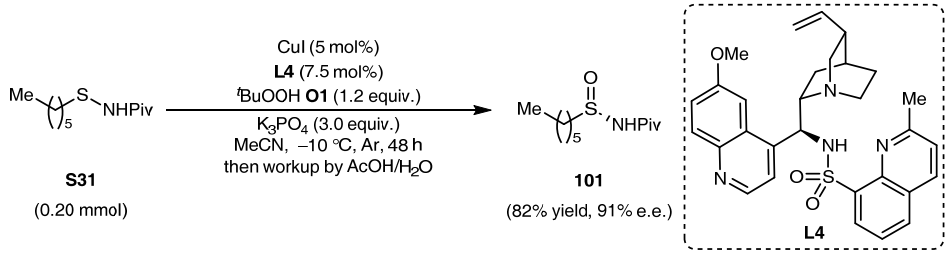
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 21.13 min, t_R (major) = 23.15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.43 (d, *J* = 3.6 Hz, 1H), 7.13 (t, *J* = 4.4 Hz, 1H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 146.1, 131.7, 130.2, 128.1, 39.8, 27.1.

HRMS (ESI) *m*/*z* calcd. for $C_9H_{14}NO_2S_2$ $[M + H]^+$ 232.0460, found 232.0459.

(*S*)-*N*-(Hexylsulfinyl)pivalamide (101)



According to **General Procedure F** with *N*-(hexylthio)pivalamide **S31** (43.5 mg, 0.20 mmol, 1.0 equiv.) and *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.) for 48 h with workup method 2, the reaction mixture was purified by flash column chromatography on silica gel (PE/EtOAc = 2/1) to afford the product **101** as a colorless liquid (38.3 mg, 82% yield, 91% e.e.).

HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 22.82 min, t_R (minor) = 25.52 min.

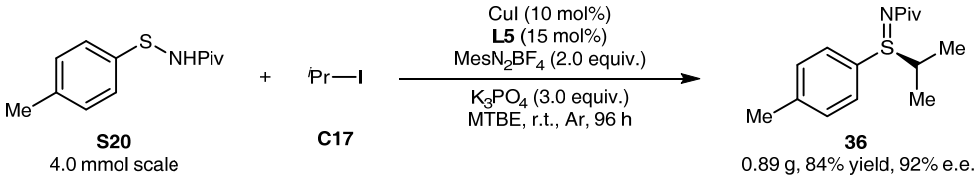
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 3.17 – 3.05 (m, 1H), 3.05 – 2.94 (m, 1H), 1.76 – 1.63 (m, 2H), 1.53 – 1.39 (m, 2H), 1.37 – 1.27 (m, 4H), 1.22 (s, 9H), 0.93 – 0.86 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 55.4, 39.9, 31.5, 28.3, 27.2, 22.7, 22.5, 14.0.

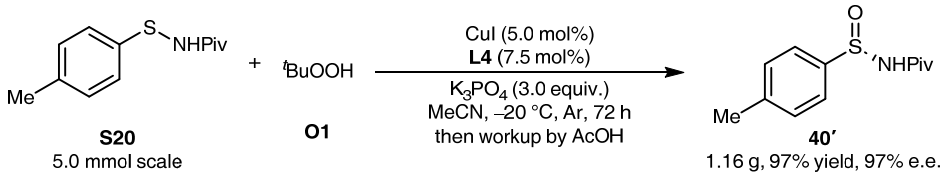
HRMS (ESI) *m*/*z* calcd. for $C_{11}H_{24}NO_2S$ $[M + H]^+$ 234.1522, found 234.1521.

7. Transformation

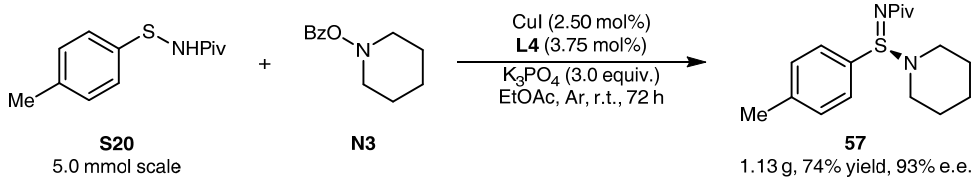
Gram-scale reaction



To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (76.0 mg, 0.4 mmol, 10 mol%), **L5** (200 mg, 0.6 mmol, 15 mol%), sulfenamide **S20** (0.89 g, 4.0 mmol, 1.0 equiv.), **C17** (1.02 g, 6.0 mmol, 1.5 equiv.), $MesN_2BF_4$ (**C39**, 1.87 g, 8.0 mmol, 2.0 equiv.), and K_3PO_4 (2.6 g, 12.0 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (40 mL). The reaction mixture was stirred at r.t. for 96 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **36** (0.84 g, 84% yield, 92% e.e.).



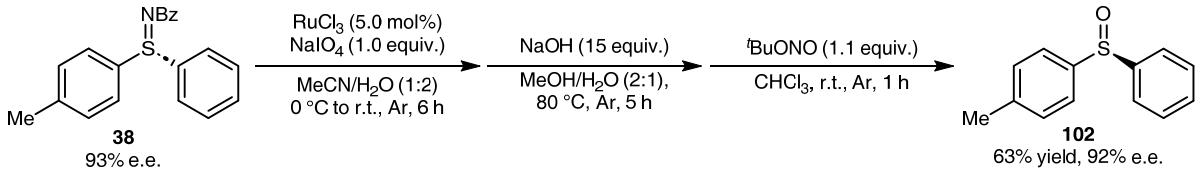
Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S20** (1.12 g, 5.0 mmol, 1.0 equiv.), CuI (47.6 mg, 0.250 mmol, 5.0 mol%), **L4** (198.2 mg, 0.375 mmol, 7.5 mol%), K_3PO_4 (3.18 g, 15.0 mmol, 3.0 equiv.), and anhydrous MeCN (50 mL). Then, *tert*-butyl hydroperoxide **O1** (70% in H_2O, 6.0 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at –20 °C for 72 h. Upon completion (monitored by TLC), a mixed solvent (50 mL, AcOH:H_2O = 1:2) was added and the reaction mixture was stirred at r.t. for 1 h. Then the reaction mixture was extracted with EtOAc three times (5 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel to afford the desired product **40′** (1.16 g, 97% yield, 97% e.e.).



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (23.8 mg, 0.125 mmol, 2.50 mol%), **L4** (99.1 mg, 0.188 mmol, 3.75 mol%), sulfenamide **S20** (1.12 g, 5.0 mmol, 1.0 equiv.), piperidin-1-yl benzoate **N3** (1.54 g, 7.5 mmol, 1.5 equiv.), and K_3PO_4 (3.18 g, 15.0 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then EtOAc (50 mL) was added by syringe under argon and the reaction mixture was stirred at r.t. for 72 h. Upon completion, the precipitate was filtered off and washed with EtOAc. The filtrate

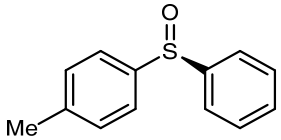
was evaporated and the residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 10:1) to afford the desired product **57** (1.13 g, 74%, 93% e.e.).

The synthesis of sulfoxide from sulfimide:

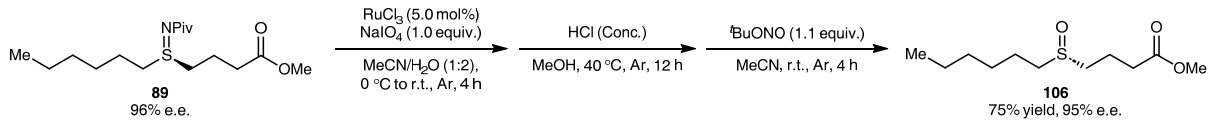


According to the literature reported procedure[50] with slight modification. To a solution of sulfimide **38** (31.9 mg, 0.10 mmol, 1.0 equiv.) in MeCN (1.0 mL) was added a predissolved solution of $NaIO_4$ (21.6 mg, 0.10 mmol, 1.0 equiv.) in H_2O (2.0 mL). This solution was cooled to 0 °C, and then $RuCl_3$ hydrate (1.0 mg, 0.005 mmol, 5.0 mol%) was added under argon. After stirring at 0 ºC to r.t. for 6 h, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.
To the above concentrated organic layer in MeOH (1.0 mL) and H_2O (0.5 mL) was added NaOH (60 mg, 1.50 mmol, 15 equiv.) under argon. The reaction mixture was heated to 80 °C for 5 h. After cooling to r.t., the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated without further purification.
According to the literature reported procedure[62] with slight modification. To the above concentrated organic layer in $CHCl_3$ (2.0 mL) was added ^{t}BuONO (11.4 mg, 0.11 mmol, 1.1 equiv.) under argon. The reaction mixture was stirred at r.t. for 1 h. Then, the reaction mixture was concentrated. Purification by silica gel chromatography afforded the product **102**.

(*R*)-1-Methyl-4-(phenylsulfinyl)benzene (102)



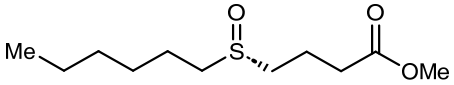
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 4/1) to afford **102** as light yellow solid (13.7 mg, 63% yield, 92% e.e.).
HPLC analysis: Chiralcel OD-H (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 28.52 min, t_R (minor) = 31.05 min.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.60 (m, 2H), 7.56 – 7.50 (m, 2H), 7.48 – 7.40 (m, 3H), 7.29 – 7.24 (m, 2H), 2.37 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 142.6, 141.8, 131.0, 130.2, 129.4, 125.1, 124.8, 21.5.



According to the literature reported procedure[50] with slight modification. To a solution of sulfimide **89** (63.5 mg, 0.20 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added a predissolved solution of $NaIO_4$ (43.0 mg, 0.20 mmol, 1.0 equiv.) in H_2O (4.0 mL). This solution was cooled to 0 °C, and then $RuCl_3$ hydrate (2.4 mg, 0.01 mmol, 5.0 mol%) was added under argon. After stirring

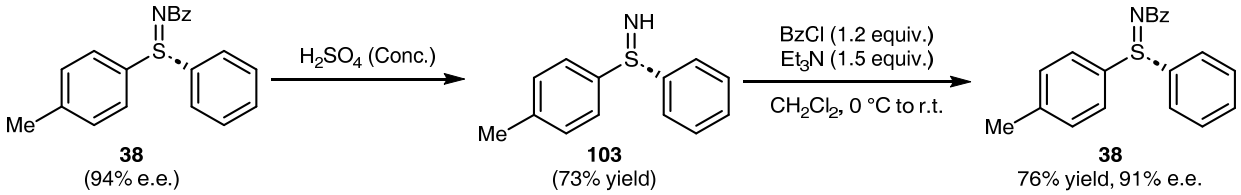
at 0 ºC to r.t. for 4 h, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.
According to the literature reported procedure[63] with slight modification. To the above concentrated organic layer in MeOH (1.0 mL) was added HCl (Conc., 0.5 mL) under argon. The reaction mixture was heated to 40 ºC for 12 h. After cooling to r.t., the reaction mixture was quenched with sat. Na_2CO_3 aqueous solution, and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated without further purification.
According to the literature reported procedure[62] with slight modification. To the above concentrated organic layer in MeCN (4.0 mL) was added ^{t}BuONO (22.7 mg, 0.22 mmol, 1.1 equiv.) under argon. The reaction mixture was stirred at r.t. for 4 h. Then, the reaction mixture was concentrated. Purification by silica gel column chromatography (PE/EtOAc = 1/2) to afford **106** as a white solid (35.2 mg, 75% yield, 95% e.e.).

Methyl (*S*)-4-(hexylsulfinyl)butanoate (106)



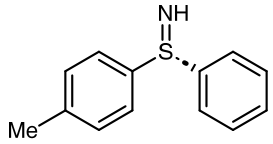
HPLC analysis: Chiralpak IG (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 210 nm), t_R (minor) = 15.36 min, t_R (major) = 16.38 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 2.84 – 2.60 (m, 4H), 2.53 (t, *J* = 7.1 Hz, 2H), 2.20 – 2.07 (m, 2H), 1.77 (q, *J* = 8.2 Hz, 2H), 1.57 – 1.17 (m, 6H), 0.99 – 0.82 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 52.6, 51.9, 51.3, 32.7, 31.4, 28.6, 22.6, 22.5, 18.3, 14.0.
HRMS (ESI) *m*/*z* calcd. for $C_{11}H_{23}O_3S$ $[M + H]^+$ 235.1362, found 235.1359.

The deprotection of diarylsulfimide:



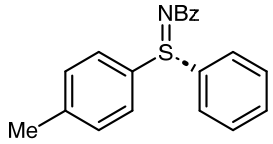
According to the literature reported procedure[64] with slight modification. An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with (*R*)-phenyl(*p*-tolyl)-λ^4-sulfanimine **38** (260 mg, 0.81 mmol) and 0.5 mL conc. H_2SO_4 under argon and the reaction mixture was stirred at r.t. for 1 h. Upon completion, the mixture was poured into ice water and washed with CH_2Cl_2 three times (3 × 10 mL). Then aqueous solution of NaOH (5.0 M) was added dropwise into the aqueous layer until basic. The solution was extracted with CH_2Cl_2 three times (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford the product **103** as a light yellow oil (127 mg, 0.59 mmol, 73% yield), which was pure enough.
To the above product in CH_2Cl_2 was added Et_3N (90.1 mg, 0.89 mmol, 1.5 equiv.) under argon. The mixture was cooled to 0 °C and BzCl (98.4 mg, 0.70 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was warmed to r.t. and stirred overnight. Upon completion, the mixture was concentrated and purification by silica gel chromatography to afford the product **38** (143 mg, 0.45 mmol, 76% yield, 91% e.e.).

(*R*)-phenyl(*p*-tolyl)-λ^4-sulfanimine (103)



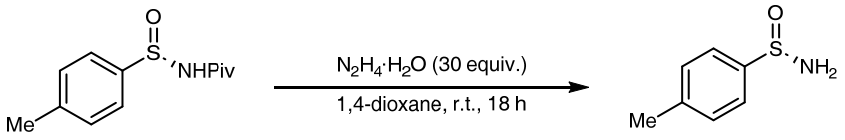
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.49 (m, 2H), 7.45 – 7.31 (m, 5H), 7.20 (d, J = 7.9 Hz, 2H), 2.53 (br s, 1H), 2.32 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 141.4, 141.1, 130.4, 130.1, 129.3, 126.2, 126.0, 21.4.
HRMS (ESI) *m*/*z* calcd. for $C_{13}H_{14}NS$ $[M + H]^+$ 216.0841, found 216.0841.

(*R*)-*N*-(phenyl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (38)



HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 22.11 min, t_R (minor) = 25.19 min.

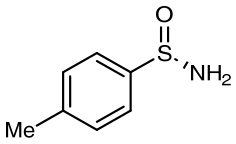
The deprotection of sulfinamide:



40' 97% e.e. **104** 77% yield, 96% e.e.

According to the literature reported procedure[65] with slight modification. To a solution of sulfinamide **40′** (47.9 mg, 0.20 mmol, 1.0 equiv.) in 1,4-dioxane (0.5 mL) was added $N_2H_4·H_2O$ (192.3 mg, 6.0 mmol, 30 equiv.), then the reaction mixture was stirred at r.t. for 18 h and a full consumption of **40′** was observed. Upon completion, the mixture was diluted with water (5.0 mL) and extracted with EtOAc (3 × 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford the desired product **104** as a white solid (23.9 mg, 77% yield, 96% e.e.).

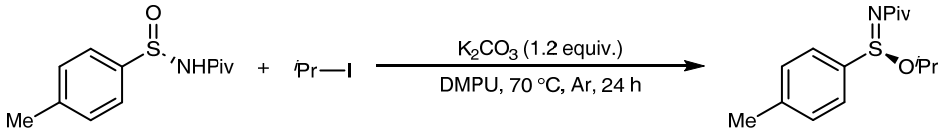
(*S*)-4-Methylbenzenesulfinamide (104)



HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 17.14 min t_R (major) =21.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.35 – 7.28 (m, 2H), 4.56 – 4.18 (m, 2H), 2.42 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.7, 129.7, 125.5, 21.5.

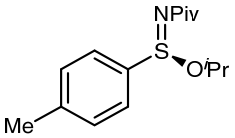
The synthesis of sulfinimidate ester from sulfinamide



40' 97% e.e. **C17** **105** 75% yield, 97% e.e.

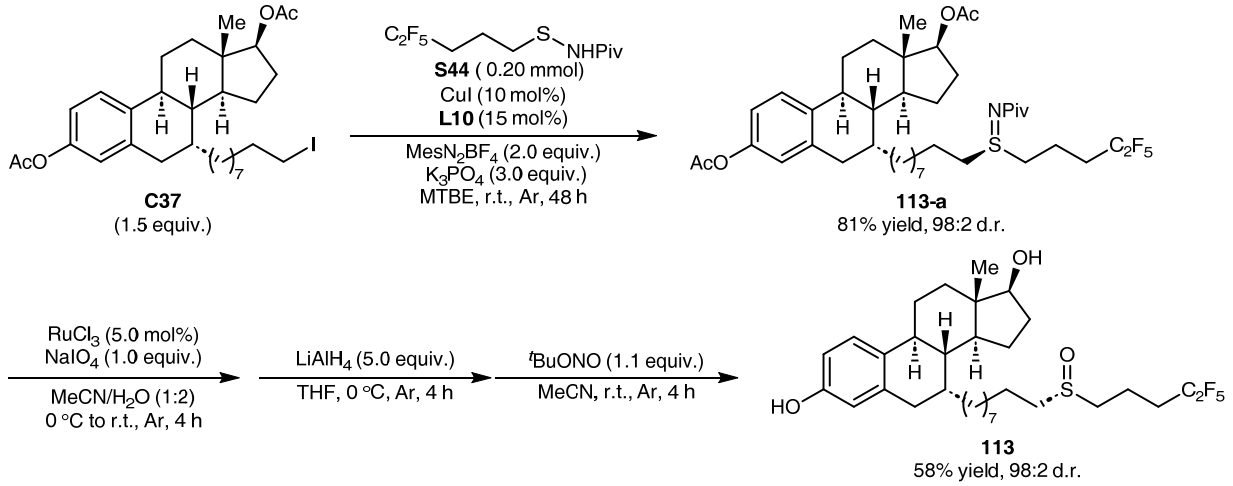
According to the literature reported procedure[64] with slight modification. Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfinamide **40′** (0.20 mmol, 1.0 equiv.), K_2CO_3 (33.2 mg, 0.24 mmol, 1.2 equiv.), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU, 1.0 mL). ^{i}PrI (**C17**, 68.0 mg, 0.40 mmol, 2.0 equiv.) was added. After stirring at 70 °C for 24 h, the reaction mixture was cooled to r.t. and quenched with sat. NH_4Cl aqueous solution. The mixture was extracted with EtOAc three times (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel to afford the alkylation product **105**.

Isopropyl (*S*)-*N*-(pivaloyl)-*p*-tolylsulfinimidate (105)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford **105** as a colorless oil (42.2 mg, 75% yield, 97% e.e.).
HPLC analysis: Chiralpak IG (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 9.17 min, t_R (major) = 14.83 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.92 (hept, J = 6.3 Hz, 1H), 2.43 (s, 3H), 1.39 (d, J = 6.3 Hz, 3H), 1.29 (s, 9H), 1.20 (d, J = 6.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 143.1, 134.8, 130.0, 127.7, 75.3, 41.0, 28.4, 23.8, 23.5, 21.6.
HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{24}NO_2S$ $[M + H]^+$ 282.1522, found 282.1524.

The synthesis of Fulvestrant



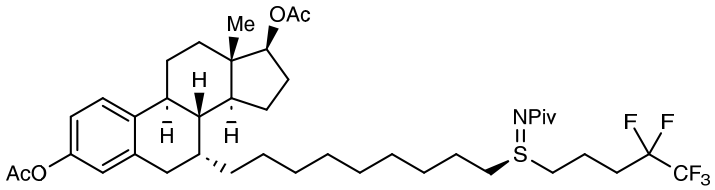
To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.80 mg, 0.02 mmol, 10 mol%), **L10** (10.44 mg, 0.03 mmol, 15 mol%), sulfenamide **S44** (58.7 mg, 0.20 mmol, 1.0 equiv.), **C37** (0.30 mmol, 1.5 equiv., 182.5 mg), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon for three times, anhydrous MTBE (4.0 mL) were added into the mixture and the reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **113-a** as colorless oil (125.3 mg, 81% yield, 98:2 d.r.).

According to the literature reported procedure[50] with slight modification. To a solution of **113-a** (154.8 mg, 0.20 mmol, 1.0 equiv.) in MeCN (4.0 mL) was added a predissolved solution of $NaIO_4$ (43.0 mg, 0.20 mmol, 1.0 equiv.) in H_2O (2.0 mL). This solution was cooled to 0 °C, and then $RuCl_3$ hydrate (2.4 mg, 0.01 mmol, 5.0 mol%) was added under argon. After stirring at 0 ºC to r.t. for 4 h, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.

According to the literature reported procedure[61] with slight modification. To the above concentrated organic layer in dry THF (8.0 mL) was added $LiAlH_4$ (38.0 mg, 1.0 mmol, 5.0 equiv.) under argon at 0 °C. Then, the reaction mixture was stirred at 0 °C for 4 h. Upon completion, the reaction mixture was quenched with 0.10 N HCl and extracted with EtOAc. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated without further purification.

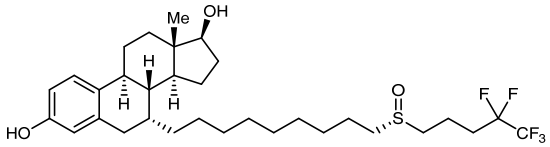
According to the literature reported procedure[62] with slight modification. To the above concentrated organic layer in MeCN (4.0 mL) was added ^{t}BuONO (26 μL, 0.22 mmol, 1.1 equiv.) under argon. The reaction mixture was stirred at r.t. for 4 h. Then, the reaction mixture was concentrated. Purification by purified by silica gel column chromatography (CH_2Cl_2/EtOAc = 1/1) to afford **113** as colorless oil (70.4 mg, 58% yield, 98:2 d.r.).

(7*R*,8*R*,9*S*,13*S*,14*S*,17*S*)-13-Methyl-7-(9-((*R*)-*S*-(4,4,5,5,5-pentafluoropentyl)-*N*-pivaloyl sulfinimidoyl)nonyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diyl diacetate (113-a)



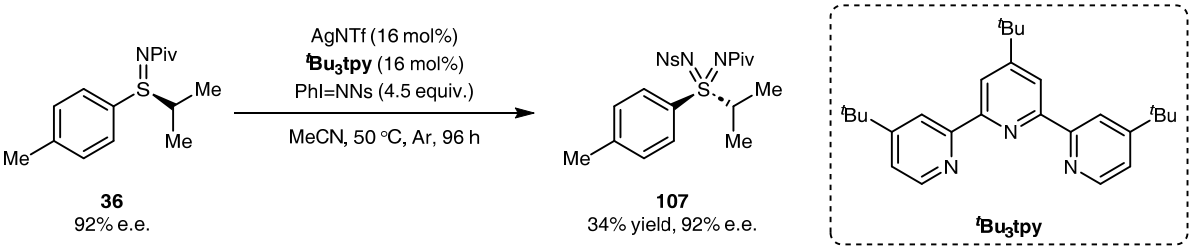
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 14.28 min, t_R (minor) = 18.08 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.76 (s, 1H), 4.67 (t, *J* = 8.4 Hz, 1H), 3.17 – 2.59 (m, 6H), 2.43 – 2.13 (m, 8H), 2.13 – 1.94 (m, 5H), 1.91 – 1.78 (m, 1H), 1.78 – 1.18 (m, 23H), 1.17 (s, 9H), 1.08 – 0.92 (m, 1H), 0.80 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 171.2, 169.8, 148.5, 137.1, 137.0, 127.0, 122.4, 118.7, 117.5 (qt, *J* = 285.2 Hz, *J* = 36.3 Hz), 115.2 (tq, *J* = 252.4 Hz, *J* = 37.9 Hz), 82.7, 46.2, 44.8, 43.1, 42.9, 41.4, 40.0, 38.1, 37.0, 34.5, 33.1, 29.8, 29.5, 29.4 (t, *J* = 22.1 Hz), 29.2, 29.0, 28.6, 28.5, 28.1, 27.5, 26.9, 25.6, 23.2, 22.8, 21.1(3), 21.1(0), 15.0, 12.0.
^{19}F NMR (375 MHz, $CDCl_3$) δ –85.45 (s, 3F), –118.26 (m, 2F).
HRMS (ESI) *m*/*z* calcd. for $C_{41}H_{60}NNaO_5S$ $[M + Na]^+$ 796.4005, found 796.4000.

(7*R*,8*R*,9*S*,13*S*,14*S*,17*S*)-13-Methyl-7-(9-((*S*)-(4,4,5,5,5-pentafluoropentyl)sulfinyl)nonyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol (113, fulvestrant)



HPLC analysis: Chiralcel OD-H (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 280 nm), t_R (minor) = 65.69 min, t_R (major) = 73.13 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 2.7 Hz, 1H), 3.74 (t, *J* = 8.4 Hz, 1H), 2.94 – 2.55 (m, 6H), 2.34 – 2.20 (m, 3H), 2.20 – 2.06 (m, 3H), 1.96 – 1.55 (m, 6H), 1.52 – 1.10 (m, 18H), 1.10 – 0.95 (m, 1H), 0.78 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) *δ* 154.3, 137.0, 131.2, 127.1, 118.2 (qt, *J* = 285.2 Hz, *J* = 36.2 Hz), 116.3,115.3 (tq, *J* = 252.5 Hz, *J* = 37.8 Hz), 113.2, 82.2, 53.6, 52.6, 51.0, 46.6, 43.5, 42.2, 38.4, 37.1, 34.9, 33.5, 30.7, 29.9, 29.8, 29.7, 29.5(0), 29.4(5) (t, *J* = 22.1 Hz), 29.3, 29.1, 28.9, 28.8, 28.7, 27.3(9), 27.3(6), 25.1, 22.7(8), 22.7(6), 14.8, 11.3.
^{19}F NMR (375 MHz, $CDCl_3$) δ –85.43 (s, 3F), –118.08 (m, 2F).
HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{47}F_5NaO_3S$ $[M + Na]^+$ 629.3058, found 629.3061.

The synthesis of sulfondiimine from sulfimide:

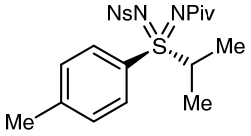


36
92% e.e.

107
34% yield, 92% e.e.

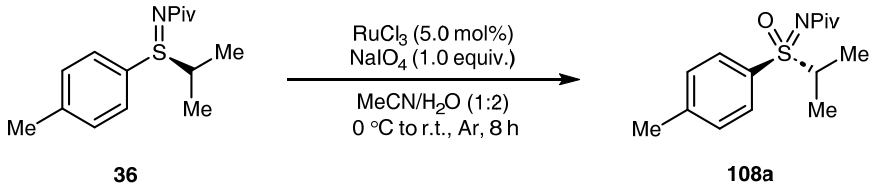
According to the literature reported procedure[66] with slight modification. To a solution of (*S*)-*N*-(isopropyl(p-tolyl)-λ^4-sulfaneylidene)pivalamide **36** (53.2 mg, 0.20 mmol, 1.0 equiv.), PhI=NNs (363.6 mg, 0.90 mmol, 4.5 equiv.), and AgNTf (12.4 mg, 0.032 mmol, 16 mol%) in MeCN (4.0 mL) was added 4-*tert*-butyl-2,6-bis(4-*tert*-butylpyridin-2-yl)pyridine (**^{t}Bu$_3$tpy**, 19.2 mg, 0.032 mmol, 16 mol%) under an argon atmosphere. The reaction mixture was heated to 50 °C and stirred for 96 h. After cooling to r.t., the reaction mixture was extracted with CH_2Cl_2 three times (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by silica gel chromatography to afford the product **107**.

(*R*)-*N*-(Isopropyl(((4-nitrophenyl)sulfonyl)imino)(*p*-tolyl)-λ^6-sulfaneylidene)pivalamide (107)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **107** as a colorless oil (31.8 mg, 34% yield, 92% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 230 nm), t_R (major) = 13.37 min, t_R (minor) = 15.56 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.9 Hz, 2H), 8.10 (d, *J* = 8.9 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 4.60 – 4.53 (m, 1H), 2.47 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.27 (d, *J* = 4.9 Hz, 3H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 149.7, 148.9, 146.2, 130.5, 129.6, 128.4, 123.8, 120.0, 59.7, 42.0, 27.7, 21.7, 16.1, 16.0.
HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{27}N_3O_5S_2Na$ $[M + Na]^+$ 488.1284, found 488.1284.

The synthesis of sulfoximine from sulfimide:

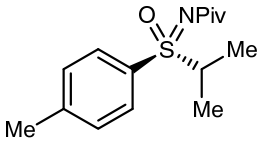


36
92% e.e.

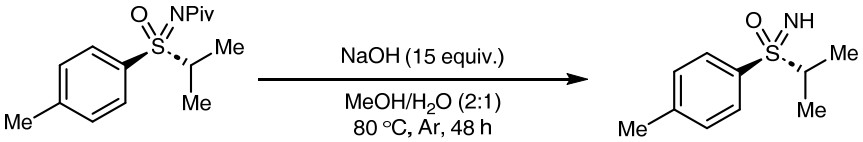
108a
94% yield, 92% e.e.

According to the literature reported procedure[50] with slight modification. To a solution of (*S*)-*N*-(isopropyl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide **36** (796 mg, 3.0 mmol, 1.0 equiv.) in MeCN (30 mL) was added a solution of $NaIO_4$ (642 mg, 3.0 mmol, 1.0 equiv.) in H_2O (60 mL). The reaction mixture was cooled to 0 °C, and then $RuCl_3$ hydrate (31.1 mg, 0.15 mmol, 5.0 mol%) was added. After stirring at r.t. for 8 h, the reaction mixture was extracted with CH_2Cl_2 three times (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by silica gel chromatography to afford the product **108a**.

(*R*)-*N*-(Isopropyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)pivalamide (108a)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford **108a** as a white solid (795 mg, 94% yield, 92% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 11.06 min, t_R (major) = 13.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.63 – 3.56 (m, 1H), 2.41 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 3H), 1.21 – 1.19 (m, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 144.4, 131.7, 130.0, 128.7, 55.9, 41.5, 27.8, 21.6, 15.8, 15.3.
HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{24}NO_2S$ $[M + H]^+$ 282.1522, found 282.1524.

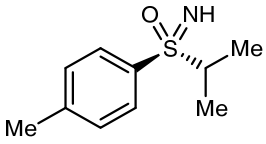


108a
92% e.e.

108
93% yield, 93% e.e.

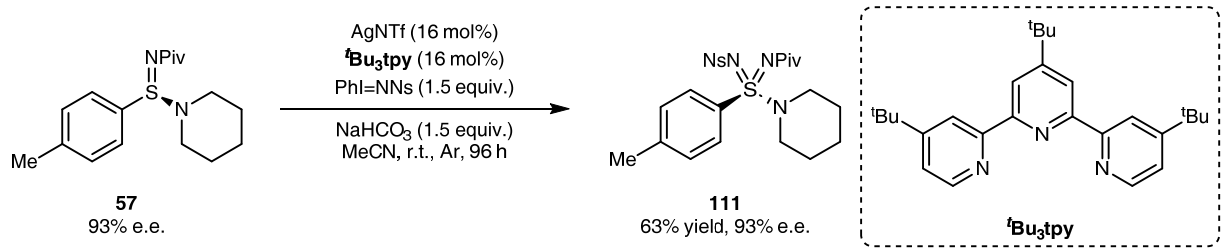
According to the literature reported procedure[50] with slight modification. To a solution of (*S*)-*N*-(isopropyl(oxo)(p-tolyl)-λ^6-sulfaneylidene)pivalamide **108a** (56.3 mg, 0.20 mmol, 1.0 equiv.) in MeOH (2.0 mL) and H_2O (1.0 mL) was added NaOH (120 mg, 3.0 mmol, 15.0 equiv.) under an argon atmosphere. The reaction mixture was heated to 80 °C and stirred for 48 h. After cooling to r.t., the reaction mixture was extracted with CH_2Cl_2 three times (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by silica gel chromatography to afford the desired product **108**.

(*R*)-Imino(isopropyl)(*p*-tolyl)-λ^6-sulfanone (108)



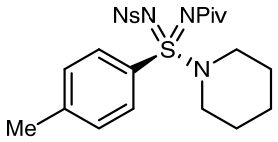
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 2/1) to afford **108** as a white solid (36.7 mg, 93% yield, 93% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 14.69 min, t_R (major) = 15.57 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.34 – 3.12 (m, 1H), 2.43 (s, 3H), 2.18 (s, 1H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 136.7, 129.7, 129.5, 56.6, 21.6, 16.6, 16.1.
HRMS (ESI) *m*/*z* calcd. for $C_{10}H_{16}NOS$ $[M + H]^+$ 198.0947, found 198.0948.

The synthesis of sulfondiimidamide from sulfinamidine:



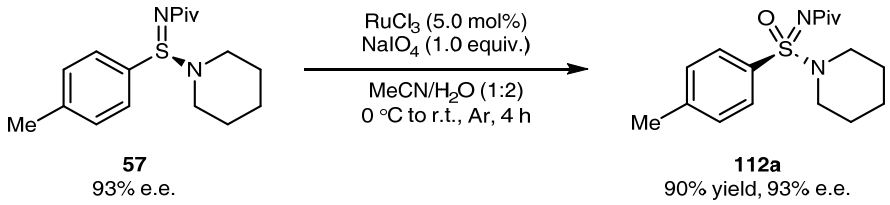
According to the literature reported procedure[66] with slight modification. To a solution of (*S*)-*N*-(piperidin-1-yl(p-tolyl)-λ^4-sulfaneylidene)pivalamide **57** (61.2 mg, 0.20 mmol, 1.0 equiv.), PhI=NNs (121.2 mg, 0.30 mmol, 1.5 equiv.), AgNTf (12.4 mg, 0.032 mmol, 16 mol%), and 4-*tert*-butyl-2,6-bis(4-*tert*-butylpyridin-2-yl)pyridine (^{t}Bu$_3$tpy, 19.2 mg, 0.032 mmol, 16 mol%) in MeCN (4.0 mL) was added $NaHCO_3$ (24.1 mg, 0.30 mmol, 1.5 equiv.). The reaction mixture was stirred at r.t. for 96 h. After cooling to r.t., the reaction mixture was extracted with CH_2Cl_2 three times (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by silica gel chromatography to afford the desired product **111**.

(*R*)-*N*-(Isopropyl(((4-nitrophenyl)sulfonyl)imino)(*p*-tolyl)-λ^6-sulfaneylidene)pivalamide (111)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford **111** as a colorless oil (62.3 mg, 63% yield, 93% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 11.49 min, t_R (minor) = 13.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.9 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.41 – 3.25 (m, 4H), 2.42 (s, 3H), 1.71 – 1.50 (m, 6H), 1.00 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 149.6, 148.8, 145.4, 132.4, 130.1, 128.5, 128.4, 123.8, 46.7, 42.0, 27.6, 25.5, 23.8, 21.7.
HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{30}N_4O_5S_2Na$ $[M + Na]^+$ 529.1550, found 529.1549.

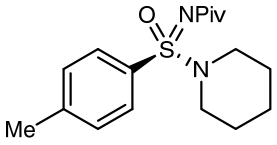
The synthesis of sulfonimidamide from sulfinamidine:



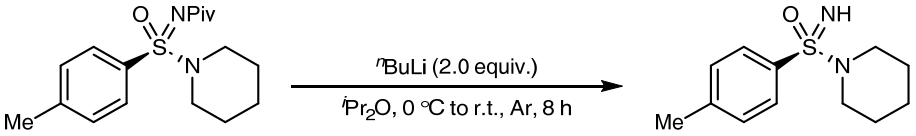
According to the literature reported procedure[50] with slight modification. To a solution of (*S*)-*N*-(piperidin-1-yl(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide **57** (61.2 mg, 0.20 mmol, 1.0 equiv.) in

MeCN (2.0 mL) was added a solution of $NaIO_4$ (42.8 mg, 0.20 mmol, 1.0 equiv.) in H_2O (4.0 mL). This solution was cooled to 0 °C, and then $RuCl_3$ hydrate (2.06 mg, 0.010 mmol, 5.0 mol%) was added under an argon atmosphere. After stirring at r.t. for 4 h, the reaction mixture was extracted with CH_2Cl_2 three times (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by silica gel chromatography to afford the desired product **112a**.

I-*N*-(Oxo(piperidin-1-yl)(*p*-tolyl)-λ^6-sulfaneylidene)pivalamide (112a)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 4/1) to afford **112a** as a colorless oil (58.2 mg, 90% yield, 93% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 10.89 min, t_R (major) = 12.49 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.16 – 3.06 (m, 4H), 2.42 (s, 3H), 1.69 – 1.56 (m, 4H), 1.51 – 1.43 (m, 2H), 1.22 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 143.7, 134.2, 129.8, 127.8, 46.4, 41.9, 27.9, 25.4, 23.8, 21.6.
HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{26}N_2O_2SNa$ $[M + Na]^+$ 345.1607, found 345.1604.

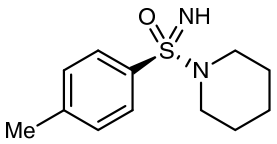


112a
93% e.e.

112
75% yield, 93% e.e.

To a solution of (*R*)-*N*-(oxo(piperidin-1-yl)(*p*-tolyl)-λ^6-sulfaneylidene)pivalamide **112a** (64.4 mg, 0.20 mmol, 1.0 equiv.) in $^iPr_2O$ (2.0 mL) was added ^{n}BuLi (0.40 mmol, 2.0 equiv., 2.4 M in hexane) at 0 °C under an argon atmosphere. The reaction mixture was stirred at r.t. for 8 h. After cooling to r.t., the reaction mixture was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 three times (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by silica gel chromatography to afford the desired product **112**.

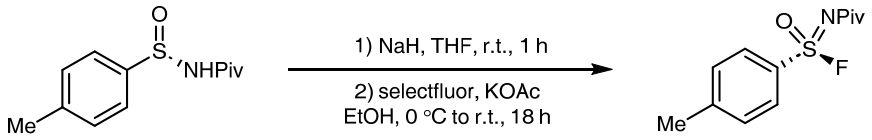
(*R*)-1-(4-Methylphenylsulfonimidoyl)piperidine (112)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 4/1) to afford **112** as a colorless oil (35.8 mg, 75% yield, 93% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 10.73 min, t_R (major) = 13.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.97 (t, *J* = 5.5 Hz, 4H), 2.42 (s, 3H), 1.72 – 1.52 (m, 4H), 1.48 – 1.29 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 133.4, 129.4, 128.2, 48.1, 25.8, 23.8, 21.6.
HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{18}N_2OSNa$ $[M + Na]^+$ 261.1032, found 261.1030.

The synthesis of sulfonimidoyl fluoride from sulfinamide

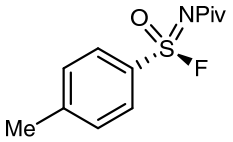


40'
97% e.e.

109
86% yield, 97% e.e.

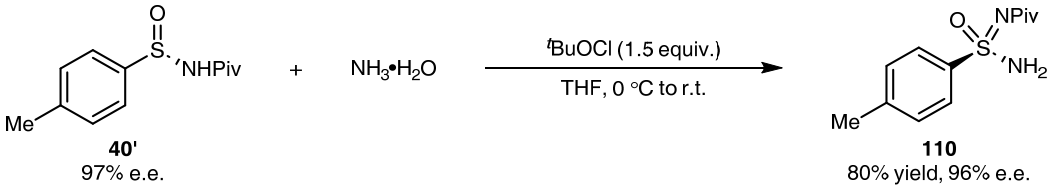
According to the literature reported procedure[24] with slight modification. To a solution of (*S*)-*N*-(*p*-tolylsulfinyl)pivalamide **40′** (119.7 mg, 0.50 mmol, 1.0 equiv.) in anhydrous THF (5.0 mL) was added NaH (60% in mineral oil, 22 mg, 0.55 mmol, 1.1 equiv.) at 0 °C. Then the reaction mixture was stirred for 1 h at r.t.. The reaction mixture was quenched with MeOH (1.0 mL) and concentrated under reduced pressure. The precipitate was washed with *n*-hexane to give the sulfinamide salt. Then the salt and potassium acetate (98.1 mg, 1.0 mmol, 2.0 equiv.) were dissolved in anhydrous ethanol (5.0 mL), followed by the addition of selectfluor (354.3 mg, 1.0 mmol, 2.0 equiv.) at 0 °C. The reaction mixture was allowed to warm up to r.t. and stirred for 24 h. The reaction was quenched by adding water (5.0 mL), extracted with CH_2Cl_2 three times (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by silica gel column chromatography to afford **109**.

(*R*)-4-Methyl-*N*-pivaloylbenzenesulfonimidoyl fluoride (109)



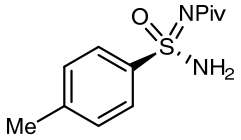
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20/1) to afford **109** as a white solid (44.3 mg, 86% yield, 97% e.e.).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 99/01, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 10.45 min, t_R (minor) = 12.25 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 2.49 (s, 3H), 1.25 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 147.0, 131.71 (d, *J* = 20.8 Hz), 130.3, 128.1, 42.4, 27.3, 22.0.
^{19}F NMR (375 MHz, $CDCl_3$) δ 65.91 (d, *J* = 37.9 Hz).
HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{17}FNO_2S$ $[M + H]^+$ 258.0959, found 258.0961.

The synthesis of sulfonimidamide from sulfinamide



According to the literature reported procedure[67] with slight modification. To a solution of (*S*)-*N*-(*p*-tolylsulfinyl)pivalamide **40′** (47.9 mg, 0.20 mmol, 1.0 equiv.) in dry THF (2.5 mL) was added ^{t}BuOCl (32.6 mg, 0.30 mmol, 1.5 equiv.) dropwise at 0 °C. After stirring at 0 °C for 2 h, an aqueous solution of $NH_3 \cdot H_2O$ (1.0 mL) was added at 0 °C, and the reaction mixture was stirred at r.t. for 45 min. Subsequently, water (15.0 mL) was added and the phases were separated. The aqueous phase was extracted four times with EtOAc (4 × 10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted once with EtOAc (10 mL). All organic phases were combined and dried over $MgSO_4$ and filtered. After removal of the solvent under reduced pressure, the crude residue was purified by silica gel column chromatography to afford **110**.

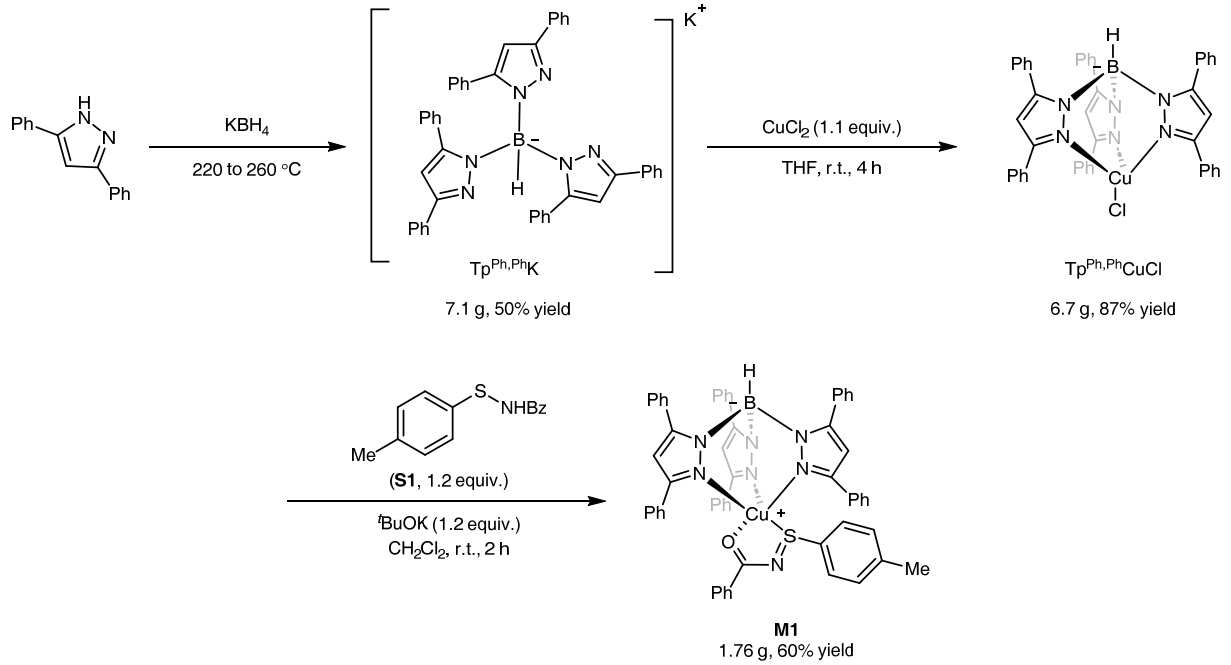
(*S*)-*N*-(Amino(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)pivalamide (110)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford **110** as a white solid (40.7 mg, 80% yield, 96% e.e.).
HPLC analysis: Chiralpak IH (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 8.75 min, t_R (minor) = 17.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.34 (s, 2H), 2.42 (s, 3H), 1.15 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 144.2, 138.7, 129.8, 126.5, 41.6, 27.6, 21.6.
HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{19}N_2O_2S$ $[M + H]^+$ 255.1162, found 255.1162.

8. Mechanistic studies

Preparation of sulfinimidoyl Cu(II) complexes:

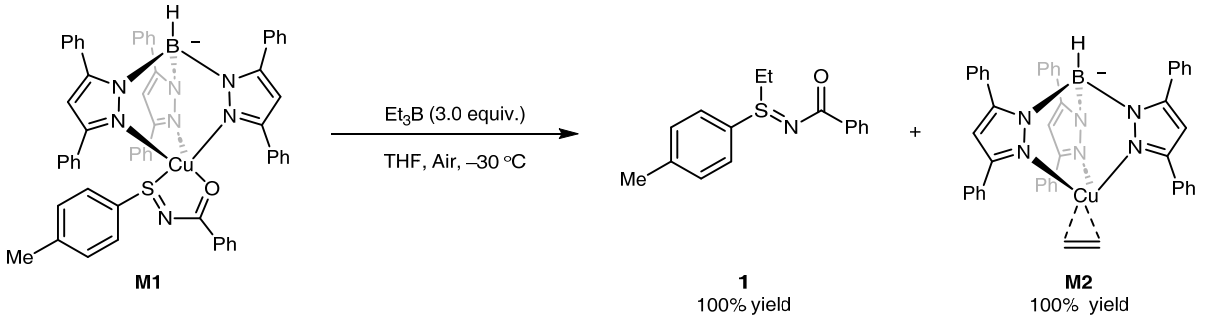


According to the literature reported procedure[68] with slight modification. In a 100 mL Schlenk reaction tube equipped with a Teflon stopcock and a magnetic stirring bar, 3,5-bis(phenyl)pyrazole (17.6 g, 80 mmol, 4.0 equiv.) was treated with KBH_4 (1.08 g, 20 mmol). The mixture was heated to 220 °C, wherein 3,5-bis(phenyl)pyrazole was found to gradually thaw and a small amount of bubble was observed. The Schlenk tube was equipped with liquid sealing to against excess pressure imposed by the released H_2. The mixture was then heated up to 260 °C and reacted until no H_2 bubble was produced. After cooling to r.t., the reaction residue was vigorously mixed with a boiling toluene (50 mL). The resulting suspension was then passed through a filter with Celite to remove the unreacted 3,5-bis(phenyl)pyrazole upon thermal filtration. The residue was washed with hexane to give a white solid of $Tp^{Ph,Ph}K$ (7.1 g, 50% yield). It was dried under a vacuum condition overnight and stored under Ar.

To a solution of $Tp^{Ph,Ph}K$ (7.1 g, 10 mmol, 1.0 equiv.) in THF (150 mL) was added $CuCl_2$ (1.48 g, 11 mmol, 1.1 equiv.). The reaction mixture was stirred at r.t. for 4 h and the resulting suspension was passed through a filter with Celite to remove the white precipitate. The filtrate was then concentrated, and recrystallized in hexane and acetone (1:10). Then the resulting suspension was passed through a filter to give a black solid of $Tp^{Ph,Ph}CuCl$ (6.7 g, 87% yield), and then dried under vacuum.

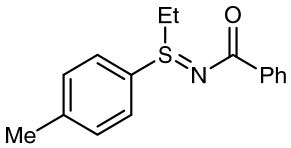
To a solution of **S1** (876 mg, 3.6 mmol, 1.2 equiv.) in CH_2Cl_2 (30 mL) was added ^{t}BuOK (404 mg, 3.6 mmol, 1.2 equiv.). The reaction mixture was stirred at r.t. for 1 h, and then $Tp^{Ph,Ph}CuCl$ (2.31 g, 3.0 mmol, 1.0 equiv.) was added and the reaction mixture was stirred at r.t. for another 2 h. Then the solvent was removed under reduced pressure to afford the crude mixture, which was purified by column chromatography on silica gel to afford the desired product **M1** as a purple solid (1.76 g, 60% yield).

Radical substitution reaction of ethyl radicals with sulfinimidoyl Cu(II) complexes



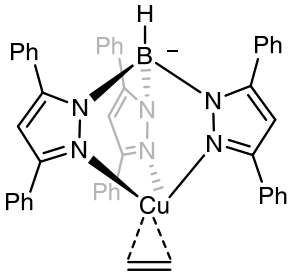
To a dark purple solution of **M1** (97.6 mg, 0.1 mmol) in THF (2.0 mL) was added Et_3B (1M in hexane, 0.3 mmol, 3.0 equiv.) at –30 °C, and the reaction mixture was stirred at that temperature for 3 h. The dark purple solution turned gradually to pale green with a large amount of white precipitate. The mixture was warmed to r.t. followed by the addition of Et_2O (3.0 mL) and the supernatant liquid was removed to afford the precipitate **M2**. The precipitate **M2** was washed with Et_2O for 3 times until there was no **1** in supernatant liquid (detected by TLC) and the residue was dried in a stream of argon. The yields of **1** and **M2** were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. White X-ray quality crystals of **M2** were grown from degassed CH_2Cl_2 under an argon atmosphere in the glovebox.
*Caution: the Cu(I) complex **(M2)** is air-stable in solid state but is air-sensitive in solution.*

***N*-(Ethyl(*p*-tolyl)-λ^4-sulfanylidene)benzamide (1)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 2H), 7.68 – 7.61 (m, 2H), 7.43 – 7.32 (m, 3H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.23 – 3.06 (m, 2H), 2.35 (s, 3H), 1.20 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 142.7, 136.7, 130.5, 130.4, 130.1, 128.7, 127.7, 127.3, 43.6, 21.4, 7.5.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}NOS$ $[M + H]^+$ 272.1104, found 272.1102.

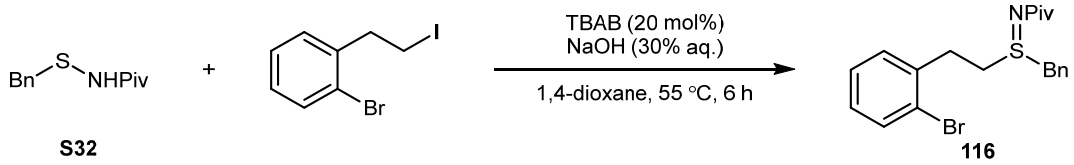
Cu(Tp^{Ph,Ph})(C_2H_4) (M2)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 6H), 7.44 – 7.33 (m, 9H), 7.26 – 7.19 (m, 3H), 7.06 – 7.00 (m, 6H), 7.00 – 6.91 (m, 6H), 6.36 (s, 3H), 3.53 (s, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 149.8, 134.8, 132.4, 130.0, 128.6, 128.1(4), 128.06, 127.7, 127.6, 105.6, 81.6.

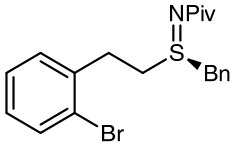
HRMS (ESI) *m/z* calcd. for $C_{45}H_{35}BCuN_6$ $[M - C_2H_4 + H]^+$ 733.2307, found 733.2301. The corresponding monocrystal was consistent with that reported in the literature.[1]

Enantiospecific intramolecular radical substitution reaction of chiral sulfilimine.

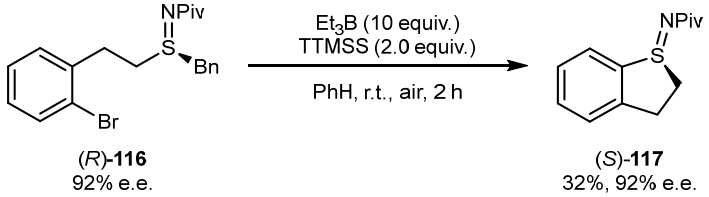


According to the literature reported procedure[46] with slight modification. *N*-(Benzylthio)pivalamide **S32** (1.1 g, 5.0 mmol) was dissolved in 1,4-dioxane (25.0 mL). To this solution was added a solution of 30% NaOH (2.0 g in 4.6 mL H_2O, 10.0 equiv.), 1-bromo-2-(2-iodoethyl)benzene (20 mmol, 4.0 equiv.), and TBAB (322 mg, 1.0 mmol, 0.2 equiv.) sequentially. The reaction mixture was stirred at 55 °C for 6 h and a full consumption of **S32** was observed. The solution was diluted with water (20 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel (30% EtOAc in hexane) to afford the desired product **116** as a white solid (1.38 g, 68%).
High enantiomeric (*R*)-**116** with 92% e.e. was obtained through preparative HPLC (CHIRALPAK® IC, *n*-hexane/*i*-PrOH = 70/30, flow rate 5.0 mL/min). The absolute configuration of (*R*)-**116** was determined by comparison with the known compound synthesized from a chiral source.

(*R*)-*N*-(Benzyl(2-bromophenethyl)-λ^4-sulfanylidene)pivalamide ((*R*)-116)



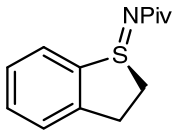
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.50 min, t_R (minor) = 8.14 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 1H), 7.36 – 7.29 (m, 3H), 7.27 – 7.22 (m, 2H), 7.20 – 7.16 (m, 2H), 7.09 – 7.02 (m, 1H), 4.30 (d, *J* = 12.9 Hz, 1H), 4.08 (d, *J* = 12.9 Hz, 1H), 3.19 – 2.96 (m, 4H), 1.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 137.5, 133.0, 131.0, 130.4, 128.8(4), 128.8(2), 128.7(5), 127.8, 124.2, 49.3, 41.5, 40.0, 29.8, 28.7.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{25}BrNOS$ $[M + H]^+$ 406.0835, found 406.0833.



According to the literature reported procedure[69] with slight modification. To a solution of (*R*)-**116** (92% e.e., 144 mg, 0.355 mmol, 1.0 equiv.) and tris(trimethylsilyl)silane (TTMSS, 353 mg, 1.42 mmol, 4.0 equiv.) in benzene (2.0 mL) was added Et_3B (1M in hexane, 3.55 mmol, 10 equiv.). The reaction mixture was stirred at r.t. for 2 h, and then concentrated under reduced pressure. The

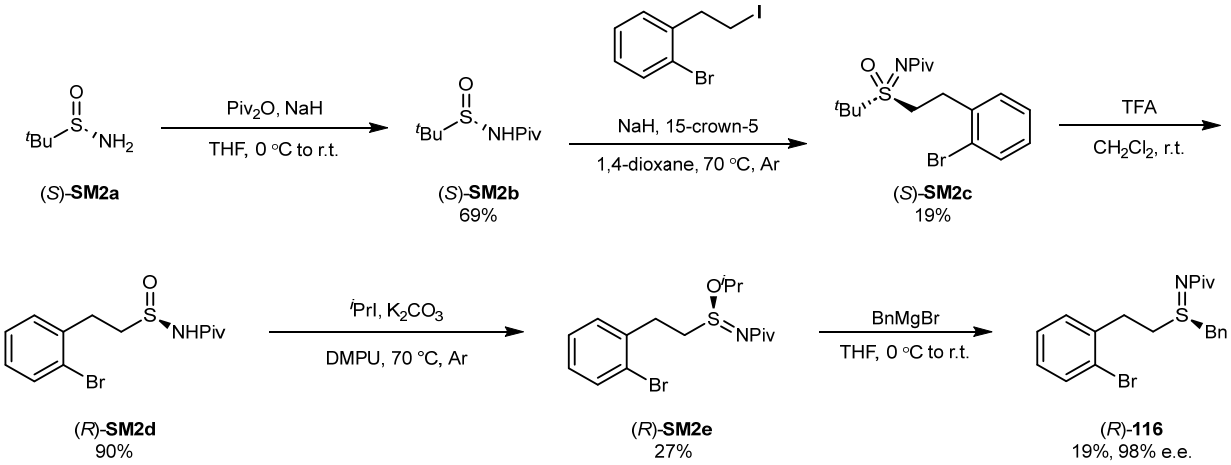
residue was purified by flash column chromatography on silica gel (5% MeOH in dichloromethane) to afford product **117** as a colorless oil (26.7 mg, 32% yield, 92% e.e.). The absolute configuration of (*S*)-**117** was determined by comparison of its derivative **117b** with the known compound synthesized from a chiral source.

(*S*)-*N*-(2,3-Dihydro-1λ^4-benzo[*b*]thiophen-1-ylidene)pivalamide (117)



HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 10.60 min, t_R (minor) = 13.46 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.43 – 7.33 (m, 2H), 3.79 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.64 (dt, *J* = 13.0, 7.6 Hz, 1H), 3.47 (ddd, *J* = 12.7, 7.9, 4.3 Hz, 1H), 3.32 (ddd, *J* = 15.9, 7.9, 4.4 Hz, 1H), 1.15 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 143.2, 136.7, 132.0, 128.6, 128.5, 125.9, 45.5, 39.8, 32.0, 28.7.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}NOS$ $[M + H]^+$ 236.1104, found 236.1105.

Determination of the absolute configuration of 116 and 117:
Determination of the configuration of **116**.



The synthesis of **SM2d** was according to the literature reported procedure[61].
To a solution of (*S*)-*N*-(*tert*-butylsulfinyl)pivalamide **SM2a** (2.67 g, 22.0 mmol) in anhydrous THF (100 mL) was added NaH (60% in mineral oil, 2.4 g, 60 mmol) at 0 °C. After stirring for 10 min at r.t., a solution of pivalic anhydride (3.73 g, 20 mmol) in anhydrous THF (50 mL) was added at r.t. in 2 h. After stirring vigorously for 1 h, the reaction mixture was quenched with MeOH at 0 °C, followed by the addition of brine and sat. NH_4Cl aqueous solution. The mixture was extracted with EtOAc three times (3 × 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and then concentrated to afford the crude product, which was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford product **SM2b** as a white solid (3.28 g, 69%).

To a solution of **SM2b** (1.64 g, 8.0 mmol) in anhydrous dioxane (48 mL) was added NaH (60% in mineral oil, 384 mg, 9.6 mmol, 1.2 equiv.) and 15-crown-5 (1.9 mL, 9.6 mmol, 1.2 equiv.) at r.t.. After stirring for 10 min, 1-bromo-2-(2-iodoethyl)benzene (4.98 g, 16 mmol, 2.0 equiv.) was added. The reaction mixture was stirred at 70 °C for 24 h and cooled to r.t.. Sat. NH_4Cl aqueous solution was added to quench the reaction and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 5/1) to afford the corresponding product **SM2c** as a white solid (600 mg, 18%).

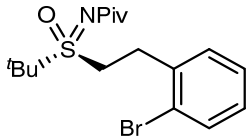
To a solution of compound **SM2c** (600 mg, 1.55 mmol) in CH_2Cl_2 (3.0 mL) was added TFA (176 μL, 2.30 mmol, 1.5 equiv.) at r.t.. After stirring for 40 min, the reaction mixture was diluted with CH_2Cl_2 and brine. The organic layer was separated and washed with sat. $NaHCO_3$ aqueous solution and brine. After drying with Na_2SO_4, the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel (PE/EtOAc = 1/1) to afford **SM2d** as a colorless oil (466 mg, 1.40 mmol, 90%).

The synthesis of **(*R*)-116** was according to the literature reported procedure[64].

To a tube equipped with a stir bar was added sulfinamide **SM2d** (66.4 mg, 0.20 mmol, 1.0 equiv.) and K_2CO_3 (33.2 mg, 0.24 mmol, 1.2 equiv.). The reaction vessel was then capped and backfilled with argon three times. To this mixture was added DMPU (1.0 mL), followed by the addition of *i*-PrI (40 μL, 0.40 mmol, 2.0 equiv.). After stirring for 48 h at 70 °C, the mixture was cooled to r.t. and quenched with sat. NH_4Cl aqueous solution. Then, the mixture was extracted with EtOAc three times (3 × 5.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and then concentrated to afford the crude product, which was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the alkylation product **SM2e** (20 mg, 27%).

A round-bottom flask with Mg turnings (24 mg, 1.0 mmol, 1.0 equiv.) was dried under vacuum with a hot gun. It was cooled to r.t. and was replaced with argon. After the addition of a grain of I_2, to this mixture was added a solution of benzyl bromide (171 mg, 1.0 mmol, 1.0 equiv. in 2.0 mL of THF) dropwise. After stirring for 3 h at 80 °C, the obtained solution of benzylmagnesium bromide was cooled to r.t.. To a solution of **SM2e** (20 mg, 0.053 mmol) in THF (2.0 mL) was added the freshly prepared benzylmagnesium bromide (0.2 mL) at 0 °C. The reaction mixture was stirred at r.t. overnight and quenched with sat. NH_4Cl aqueous solution. The mixture was extracted with EtOAc three times (3 × 5.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by preparative TLC (PE/EtOAc = 3/1) to afford the corresponding product (*R*)-**116** (4 mg, 19%, 98% e.e.).

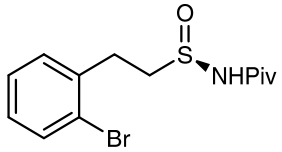
(*S*)-*N*-((2-Bromophenethyl)(*tert*-butyl)(oxo)-λ⁶-sulfanylidene)pivalamide (**SM2c**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 1H), 7.43 – 7.36 (m, 1H), 7.31 – 7.23 (m, 1H), 7.15 – 7.07 (m, 1H), 3.76 – 3.55 (m, 2H), 3.47 – 3.17 (m, 2H), 1.49 (s, 9H), 1.21 (s, 9H).

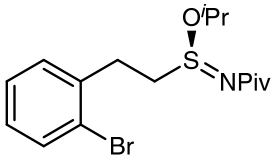
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 137.8, 133.0, 131.6, 128.9, 128.3, 124.3, 62.2, 46.3, 41.8, 30.9, 28.0, 23.5.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{27}BrNO_2S$ $[M + H]^+$ 388.0940, found 388.0943.

(*R*)-*N*-((2-Bromophenethyl)sulfinyl)pivalamide (SM2d)



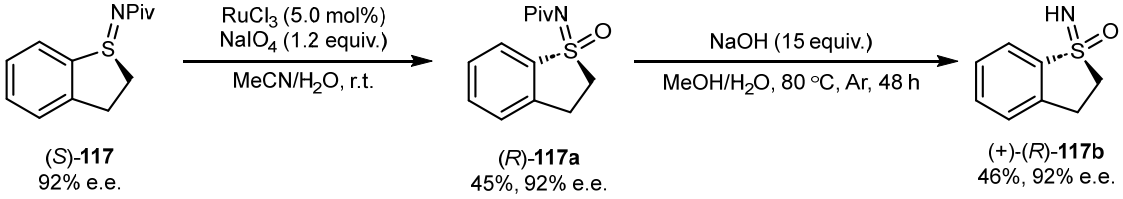
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.57 – 7.51 (m, 1H), 7.26 – 7.22 (m, 2H), 7.16 – 7.06 (m, 1H), 3.40 – 3.25 (m, 2H), 3.22 – 3.04 (m, 2H), 1.21 (s, 10H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 137.6, 133.3, 131.0, 129.0, 128.1, 124.4, 54.4, 39.9, 29.3, 27.2.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{19}BrNO_2S$ $[M + H]^+$ 332.0314, found 332.0317.

Isopropyl (*R*)-*N*-(pivaloyl)-(2-bromophenethyl)sulfinimidate (SM2e)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 1H), 7.31 – 7.22 (m, 2H), 7.17 – 7.08 (m, 1H), 4.84 (hept, *J* = 6.2 Hz, 1H), 3.37 – 3.08 (m, 4H), 1.35 (d, *J* = 6.2 Hz, 3H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 137.8, 133.3, 130.8, 128.9, 128.0, 124.5, 77.0, 50.2, 40.6, 30.0, 28.4, 23.5(2), 23.4(5).
HRMS (ESI) *m/z* calcd. for $C_{16}H_{25}BrNO_2S$ $[M + H]^+$ 374.0784, found 374.0788.

Determination of the absolute configuration of 117.



(*S*)-**117**
92% e.e.

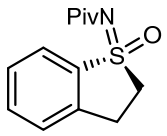
(*R*)-**117a**
45%, 92% e.e.

(+)-(*R*)-**117b**
46%, 92% e.e.

The synthesis of **117b** was according to the literature reported procedure[50] with slight modification. To a solution of **117** (27.1 mg, 0.115 mmol, 1.0 equiv.) in MeCN (1.0 mL) was added a solution of $NaIO_4$ (29.5 mg, 0.138 mmol, 1.2 equiv.) in H_2O (2.0 mL). The solution was cooled to 0 °C, followed by the addition of $RuCl_3$ hydrate (1.2 mg, 0.00575 mmol, 5.0 mol%) under argon. After stirring at r.t. for 8 h, the reaction mixture was extracted with CH_2Cl_2 three times (3 × 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford **117a** as a colorless oil (13 mg, 45% yield, 92% e.e.).
To a solution of **117a** (13 mg, 0.052 mmol, 1.0 equiv.) in MeOH (0.5 mL) and H_2O (0.25 mL) was added NaOH (31.2 mg, 0.780 mmol, 15.0 equiv.) under argon. The reaction mixture was heated

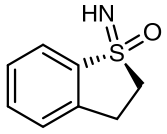
to 80 °C and stirred at that temperature for 48 h. After cooling to r.t., the reaction mixture was extracted with CH_2Cl_2 three times (3 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product. Purification by preparative TLC (PE/EtOAc = 2/1) afforded product (*R*)-**117b** as a pale yellow oil (4.0 mg, 46%, 92% e.e.). The absolute configuration of (*R*)-**117b** was determined by comparing its optical rotation with that reported in the literature[70].

(*R*)-*N*-(1-Oxido-2,3-dihydro-1λ^4-benzo[b]thiophen-1-ylidene)pivalamide (117a)



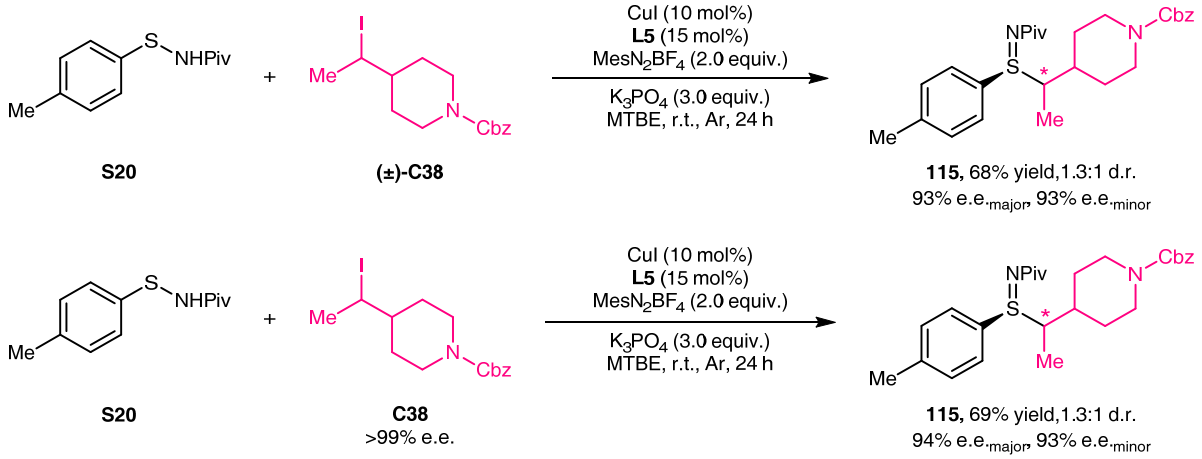
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.01 min, t_R (minor) = 14.57 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 1H), 7.64 – 7.56 (m, 1H), 7.52 – 7.44 (m, 1H), 7.43 – 7.37 (m, 1H), 4.01 – 3.90 (m, 1H), 3.71 – 3.60 (m, 1H), 3.52 – 3.45 (m, 2H), 1.17 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 138.9, 137.5, 134.1, 128.9, 127.0, 124.4, 52.1, 41.1, 27.8, 27.1.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}NO_2S$ $[M + H]^+$ 252.1053, found 252.1055.

(*R*)-1-Imino-2,3-dihydro-1*H*-1λ^4-benzo[*b*]thiophene 1-oxide (117b)



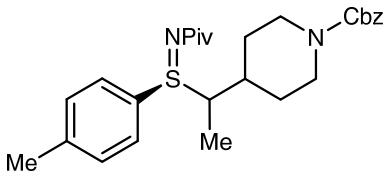
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 22.04 min, t_R (major) = 28.53 min.
$[\alpha]_D^{21}$ = 20 (*c* 0.3, acetone)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.51 – 7.43 (m, 1H), 7.41 – 7.35 (m, 1H), 3.62 – 3.55 (m, 2H), 3.42 (t, *J* = 6.9 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 137.3, 132.7, 128.7, 127.1, 121.0, 55.0, 26.3.
HRMS (ESI) *m/z* calcd. for $C_8H_{10}NOS$ $[M + H]^+$ 168.0478, found 168.0480.
The absolute configuration of (*R*)-**117b** was determined by comparing its optical rotation with that reported in the literature[70].

The control experiments using enantioenriched and racemic alkyl iodide C38.



To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.80 mg, 0.02 mmol, 10 mol%), **L5** (10.0 mg, 0.03 mmol, 15 mol%), sulfenamide **S20** (44.6 mg, 0.20 mmol, 1.0 equiv.), second alkyl iodide **C38** (0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Anhydrous MTBE (4.0 mL) was added and the reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **115**.

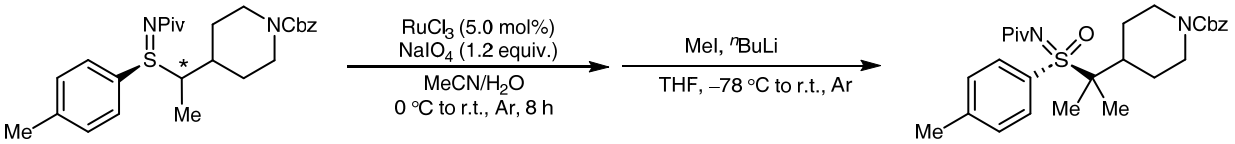
Benzyl (*E*)-4-(1-(*N*-pivaloyl-S-(*p*-tolyl)sulfinimidoyl)ethyl)piperidine-1-carboxylate (115)



According to the **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (44.7 mg, 0.20 mmol, 1.0 equiv.) and racemic second alkyl iodide **C38** (56.0 mg, 0.30 mmol, 1.5 equiv.) for 24 h, The product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **115** as a colorless oil (63.7 mg, 68% yield, 1.3:1 d.r., 93% e.e.$_{major}$, 93% e.e.$_{minor}$).
According to the **General Procedure D** with *N*-(*p*-tolylthio)pivalamide **S20** (11.2 mg, 0.05 mmol, 1.0 equiv.) and chiral second alkyl iodide **C38** (14.0 mg, 0.3 mmol, 1.5 equiv.) for 24 h, The product mixture was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford **115** as a colorless oil (16.2 mg, 69% yield, 1.3:1 d.r., 94% e.e.$_{major}$, 93% e.e.$_{minor}$).
HPLC analysis (from racemic **C38**): Chiralcel OD-H (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major 1) = 27.14 min, t_R (major 2) = 29.38 min, t_R (minor 1) = 42.08 min, t_R (minor 2) = 49.82 min.
HPLC analysis (from chiral **C38**): Chiralcel OD-H (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major 1) = 27.44 min, t_R (major 2) = 29.80 min, t_R (minor 1) = 42.24 min, t_R (minor 2) = 49.97 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2.6H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.27 (m, 16H), 5.12 (s, 5H), 4.24 (s, 5H), 3.35 – 3.02 (m, 1.3H), 2.91 – 2.57 (m, 6H), 2.40 (d, *J* = 2.1 Hz,

6.9H), 2.16 – 1.65 (m, 9H), 1.59 – 1.31 (m, 4H), 1.26 (s, 9H), 1.23 (s, 12H), 1.17 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 7.0 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 190.1, 155.2(3), 155.2(0), 143.0, 142.2, 136.8, 130.4, 130.3, 128.6, 128.5, 128.1, 128.0, 127.2, 67.2(1), 67.2(0), 62.8, 59.8, 59.7, 44.2, 44.1, 44.0, 43.9, 40.6, 40.3, 37.8, 36.4, 28.9(3), 28.8(6), 28.8, 26.9, 21.6, 21.5, 9.9, 9.2.
HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{37}N_2O_3S$ $[M + H]^+$ 469.2519, found 469.2517.

Determining the origin of the diastereoselectivity of 115:

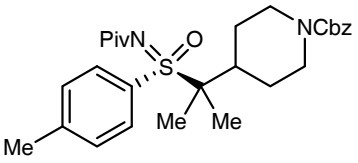


115, 1.3:1 d.r.
93% e.e.$_{major}$, 93% e.e.$_{minor}$

115b
50% yield, 91% e.e.

According to the literature reported procedure[50] with slight modification. To a solution of **115** (46.9 mg, 0.10 mmol, 1.0 equiv.) in MeCN (1.0 mL) was added a solution of $NaIO_4$ (25.9 mg, 0.12 mmol, 1.2 equiv.) in H_2O (2.0 mL). The solution was cooled to 0 °C, and then $RuCl_3$ hydrate (1.0 mg, 0.005 mmol, 5.0 mol%) was added under argon. After stirring at r.t. for 8 h, the reaction mixture was extracted with CH_2Cl_2 three times (3 × 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude sulfoximine **115a** without further purification.
According to the literature reported procedure[71] with slight modification. To a solution of sulfoximine **115a** in anhydrous THF (1.0 mL) was added ^{n}BuLi (94 μL, 1.6 M in hexanes, 0.15 mmol) dropwise at −78 °C. The reaction mixture was stirred for 30 min, followed by the addition of MeI (21.3 mg, 0.15 mmol). The reaction mixture was stirred at −78 °C for another 15 min. Then the reaction mixture was warmed to r.t. and stirred for an additional 30 min at that temperature. After that, the reaction was quenched with saturated NH_4Cl aqueous solution. The layers were separated and the aqueous layers were extracted with CH_2Cl_2 three times (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product, which was purified by silica gel chromatography to afford the desired product **115b** (24.9 mg, 50%, 91% e.e.).

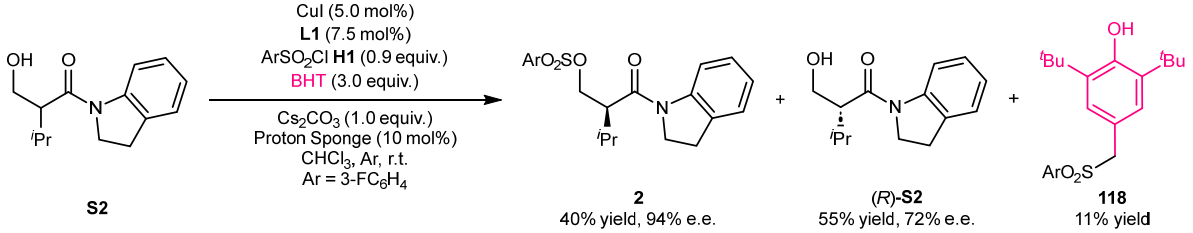
Benzyl (*R*)-4-(2-(4-methyl-*N*-pivaloylphenylsulfonimidoyl)propan-2-yl)piperidine-1-carboxylate (115b)



HPLC analysis: Chiralpak OD-H (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 16.84 min, t_R (minor) = 19.53 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.41 – 7.28 (m, 7H), 5.12 (s, 2H), 4.37 – 4.15 (m, 2H), 2.86 – 2.63 (m, 2H), 2.43 (s, 3H), 2.39 – 2.27 (m, 1H), 2.18 – 1.97 (m, 2H), 1.37 (qd, J = 12.5, 4.2 Hz, 2H), 1.28 (s, 3H), 1.21 (s, 9H), 1.16 (s, 3H).

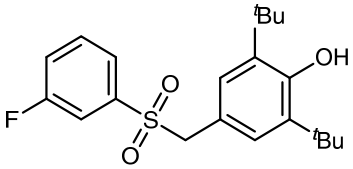
^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 155.3, 144.6, 136.9, 131.5, 130.1, 129.9, 128.6, 128.2, 128.1, 67.5, 67.2, 44.5, 44.4, 41.9, 40.4, 28.1, 27.9, 21.7.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{39}N_2O_4S$ $[M + H]^+$ 499.2625, found 499.2623.

Control experiments of chiral C center

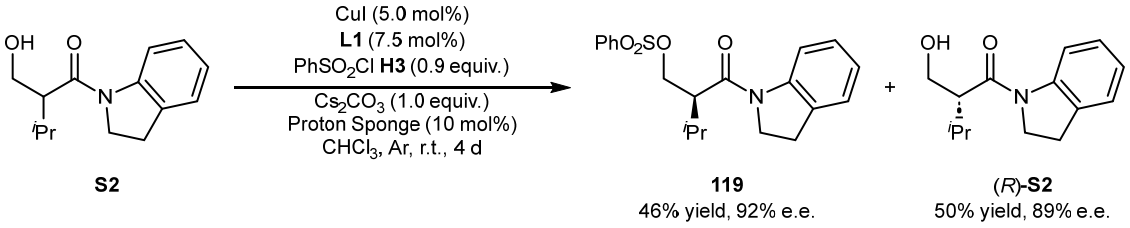


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L1** (9.1 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (65.1 mg, 0.20 mmol, 1.0 equiv.), proton sponge (4.3 mg, 0.020 mmol, 0.10 equiv.), γ-aminocarbonyl alcohol **S2** (46.7 mg, 0.20 mmol, 1.0 equiv.), BHT (132.1 mg, 0.60 mmol, 3.0 equiv.) and anhydrous $CHCl_3$ (1.0 mL). Then the 3-fluorobenzenesulfonyl chloride **H1** (23.9 μL, 0.18 mmol, 0.9 equiv.) was added and the reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed with EtOAc. The yields are based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard and the e.e. values are based on HPLC analysis. The yield of **118** is based on **H1**.

2,6-Di-*tert*-butyl-4-(((3-fluorophenyl)sulfonyl)methyl)phenol (118)



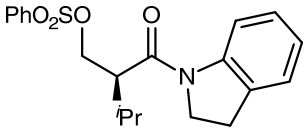
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 2H), 7.32 – 7.26 (m, 1H), 7.25 – 7.17 (m, 1H), 6.78 (s, 2H), 5.29 (s, 1H), 4.23 (s, 2H), 1.33 (s, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 252.1 Hz), 154.6, 140.1 (d, J = 6.4 Hz), 136.4, 130.6 (d, J = 7.5 Hz), 127.7, 124.7 (d, J = 3.5 Hz), 120.7 (d, J = 21.3 Hz), 118.5, 116.5 (d, J = 24.3 Hz), 63.3, 34.3, 30.2.
^{19}F NMR (375 MHz, $CDCl_3$) δ −110.13.
HRMS (ESI) m/z calcd. for $C_{21}H_{27}FNaO_3S$ $[M + H]^+$ 401.1557, found 401.1558.



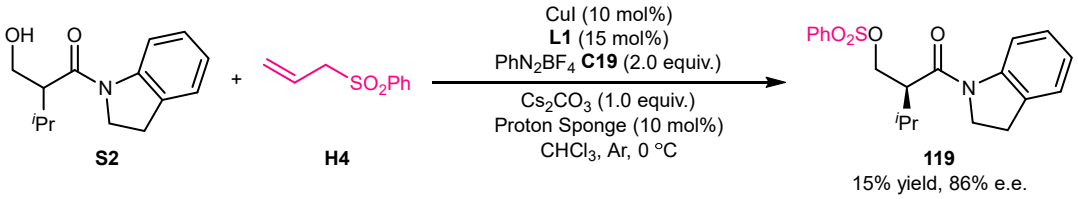
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L1** (9.1 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 1.0 equiv.), proton sponge (4.3 mg, 0.020 mmol, 10 mol%), γ-aminocarbonyl alcohol **S2** (46.7 mg, 0.20 mmol, 1.0 equiv.) and anhydrous $CHCl_3$ (1.0 mL). Then the benzenesulfonyl chloride **H3** (23.0 μL, 0.18 mmol, 0.9 equiv.) was added and the reaction mixture was stirred at r.t. for 4 d. Upon completion, the precipitate was filtered off and washed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography

on silica gel (PE/Acetone = 8/1) to afford **119** (34.5 mg, 46% yield, 92% e.e.) as a colorless oil and (*R*)-**S2** (23.5 mg, 50% yield, 89% e.e.).

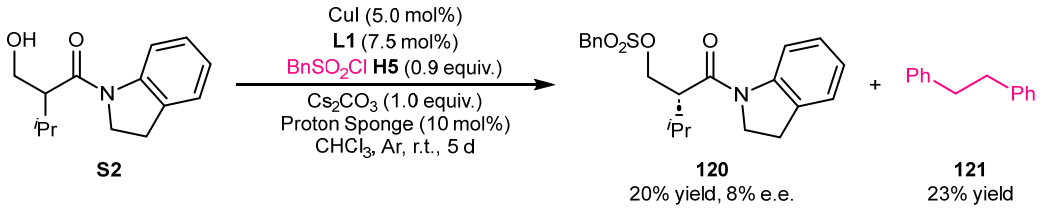
(*S*)-2-(Indoline-1-carbonyl)-3-methylbutyl benzenesulfonate (119)



HPLC analysis of **119**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.77 min, t_R (major)= 17.95 min.
HPLC analysis of (*R*)-**S2**: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 12.93 min, t_R (minor)= 14.86 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.64 – 7.56 (m, 1H), 7.51 – 7.43 (m, 2H), 7.24 – 7.15 (m, 2H), 7.09 – 6.97 (m, 1H), 4.41 – 4.30 (m, 2H), 4.19 (td, *J* = 9.6, 7.4 Hz, 1H), 4.06 (td, *J* = 9.7, 7.5 Hz, 1H), 3.27 – 3.09 (m, 2H), 2.88 (td, *J* = 8.5, 5.5 Hz, 1H), 2.04 – 1.90 (m, 1H), 1.05 – 0.92 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 142.8, 135.7, 133.9, 131.7, 129.3, 127.9, 127.5, 124.7, 124.1, 117.6, 71.1, 51.1, 48.6, 29.1, 28.0, 21.0, 20.0.
HRMS (ESI) m/z calcd. for $C_{20}H_{24}NO_4S$ $[M + H]^+$ 374.1421, found 374.1422.



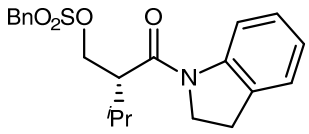
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L1** (18.2 mg, 0.030 mmol, 15 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 1.0 equiv.), proton sponge (4.3 mg, 0.020 mmol, 10 mol%), γ-aminocarbonyl alcohol **S2** (46.7 mg, 0.20 mmol, 1.0 equiv.) and anhydrous $CHCl_3$ (1.0 mL). Then the (allylsulfonyl)benzene **H4** (46.0 μL, 0.30 mmol, 1.5 equiv.) and aryldiazonium tetrafluoroborate **C19** (76.8 mg, 0.40 mmol, 2.0 equiv.) were added and the reaction mixture was stirred at 0 °C for 96 h. Upon completion, the precipitate was filtered off and washed with EtOAc. The yields are based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard and the e.e. values are based on HPLC analysis.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L1** (9.1 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 1.0 equiv.), Proton Sponge (4.3 mg, 0.020 mmol, 10 mol%), γ-aminocarbonyl alcohol **S2** (46.7 mg, 0.20 mmol, 1.0 equiv.) and anhydrous $CHCl_3$ (1.0 mL). Then

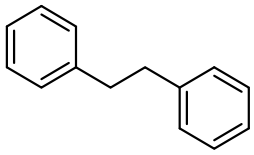
the benzylsulfonyl chloride **H5** (34.3 mg, 0.18 mmol, 0.9 equiv.) was added and the reaction mixture was stirred at r.t. for 5 d. Upon completion, the precipitate was filtered off and washed with EtOAc. The yields are based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard and the e.e. values are based on HPLC analysis. The yield of **121** is based on **H5**.

2-(Indoline-1-carbonyl)-3-methylbutyl phenylmethanesulfonate (120)

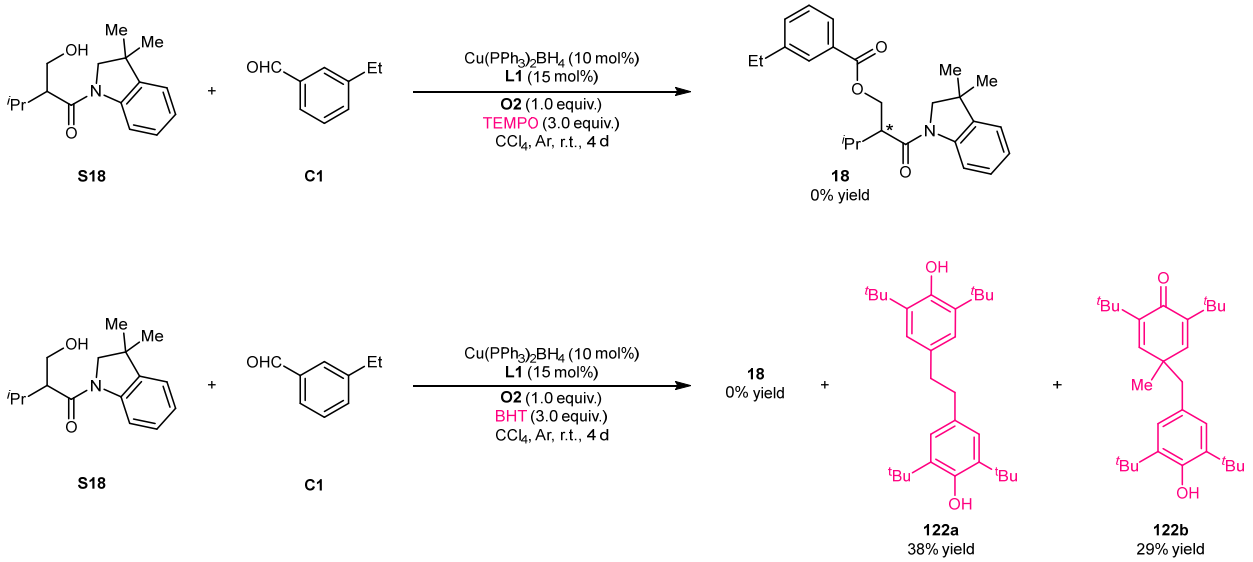


HPLC analysis: Chiralpak IB (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 22.40 min, t_R (minor)= 29.11 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 7.16 – 7.10 (m, 2H), 7.09 – 7.02 (m, 1H), 4.48 (t, *J* = 10.0 Hz, 1H), 4.37 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.28 (s, 2H), 4.00 (t, *J* = 8.5 Hz, 2H), 3.18 – 3.00 (m, 2H), 2.89 – 1.78 (m, 1H), 2.07 – 1.91 (m, 1H), 1.03 – 0.93 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 142.8, 131.8, 130.7, 128.9, 128.7, 127.7, 127.5, 124.7, 124.2, 117.5, 71.1, 56.3, 51.1, 48.4, 29.2, 27.9, 20.9, 19.9.
HRMS (ESI) m/z calcd. for $C_{21}H_{26}NO_4S$ $[M + H]^+$ 388.1577, found 388.1578.

1,2-Diphenylethane (121)

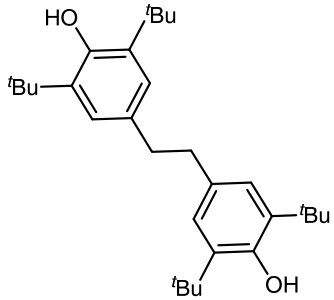


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 4H), 7.21 – 7.13 (m, 6H), 2.91 (s, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 128.6, 128.5, 126.0, 38.1.
The NMR data of **121** is consistent with that reported in the literature.[72]



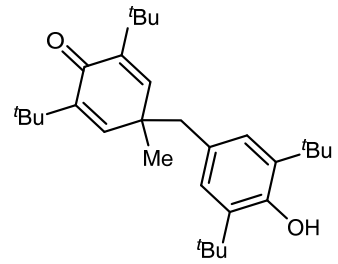
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (9.1 mg, 0.015 mmol, 15 mol%), γ-aminocarbonyl alcohol **S18** (26.1 mg, 0.10 mmol, 1.0 equiv.), TEMPO or BHT (3.0 equiv.), and anhydrous CCl_4 (1.0 mL). Then, **O2** (20.2 mg, 0.10 mmol, 1.0 equiv.) and 3-ethylbenzaldehyde **C1** (8.1 mg, 0.06 mmol, 0.6 equiv.) were added to the mixture and the reaction mixture was stirred at r.t. for 4 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated in vacuo. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard and the e.e. values are based on HPLC analysis. The yield of **122a** and **122b** are based on **O2**.

4,4'-(Ethane-1,2-diyl)bis(2,6-di-*tert*-butylphenol) (122a)

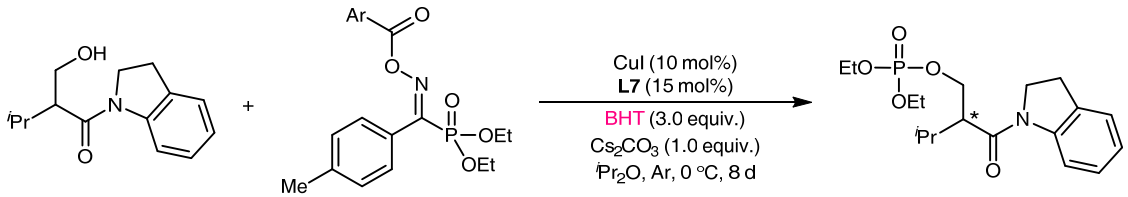


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 4H), 5.02 (s, 2H), 2.81 (s, 4H), 1.43 (s, 36H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 135.8, 132.9, 125.0, 38.2, 34.4, 30.5.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{46}NaO_2$ $[M + Na]^+$ 461.3390, found 461.3387.

2,6-Di-*tert*-butyl-4-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-4-methylcyclohexa-2,5-dien-1-one (122b)



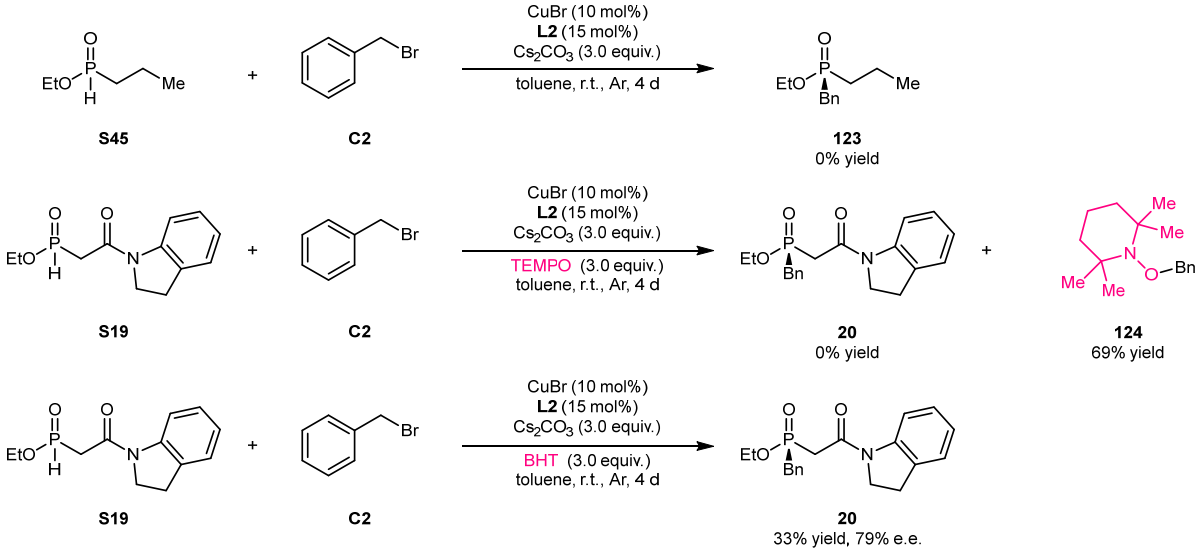
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 6.51 (s, 2H), 5.04 (s, 1H), 2.74 (s, 2H), 1.40 (s, 18H), 1.21 (s, 3H), 1.18 (s, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 146.8, 145.9, 135.3, 132.7, 127.9, 126.6, 48.2, 41.1, 34.7, 34.3, 30.4, 29.6, 26.4.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{47}O_2$ $[M + H]^+$ 439.3571, found 439.3586.



S2 **P1** Ar = 2,6-$Cl_2C_6H_3$ **19** 0% yield

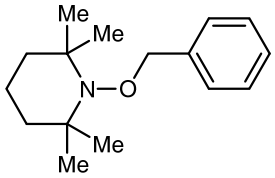
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L7** (19.4 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (65.1 mg, 0.20 mmol, 1.0 equiv.), γ-aminocarbonyl alcohol **S2** (46.7 mg, 0.20 mmol, 1.0 equiv.), oxime phosphonate **P1 (**88.8 mg, 0.20 mmol, 1.0 equiv.), BHT (132.1 mg, 0.60 mmol, 3.0 equiv.) and anhydrous $^{i}Pr_2O$ (2.0 mL). Then the reaction mixture was stirred at 0 °C for 8 d. Upon completion, the precipitate was filtered off and washed with EtOAc. The yields are based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

Control experiments of chiral P(V) center

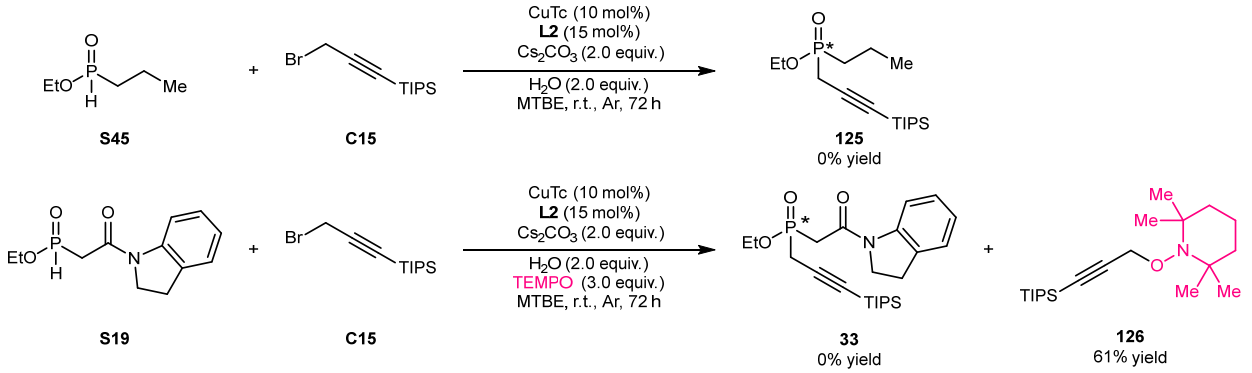


An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuBr (1.42 mg, 0.010 mmol, 10 mol%), **L2** (9.8 mg, 0.0150 mmol, 15 mol%), *H*-phosphinate **S45** or **S19** (0.10 mmol, 1.0 equiv.), **C2** (25.6 mg, 0.15 mmol, 1.5 equiv.), and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then anhydrous toluene (4.0 mL) was added by syringe under argon and the reaction mixture was stirred at r.t.. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The yields are based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. The yield of **124** are based on **S19**.

1-(Benzyloxy)-2,2,6,6-tetramethylpiperidine (124)

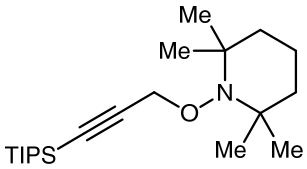


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 5H), 4.83 (s, 2H), 1.73 – 1.30 (m, 6H), 1.26 (s, 6H), 1.15 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 128.4, 127.6, 127.4, 78.9, 60.2, 39.9, 33.2, 20.5, 17.3.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{26}NO$ $[M + H]^+$ 248.1936, found 248.2009.
The NMR data of **124** is consistent with that reported in the literature.[73]

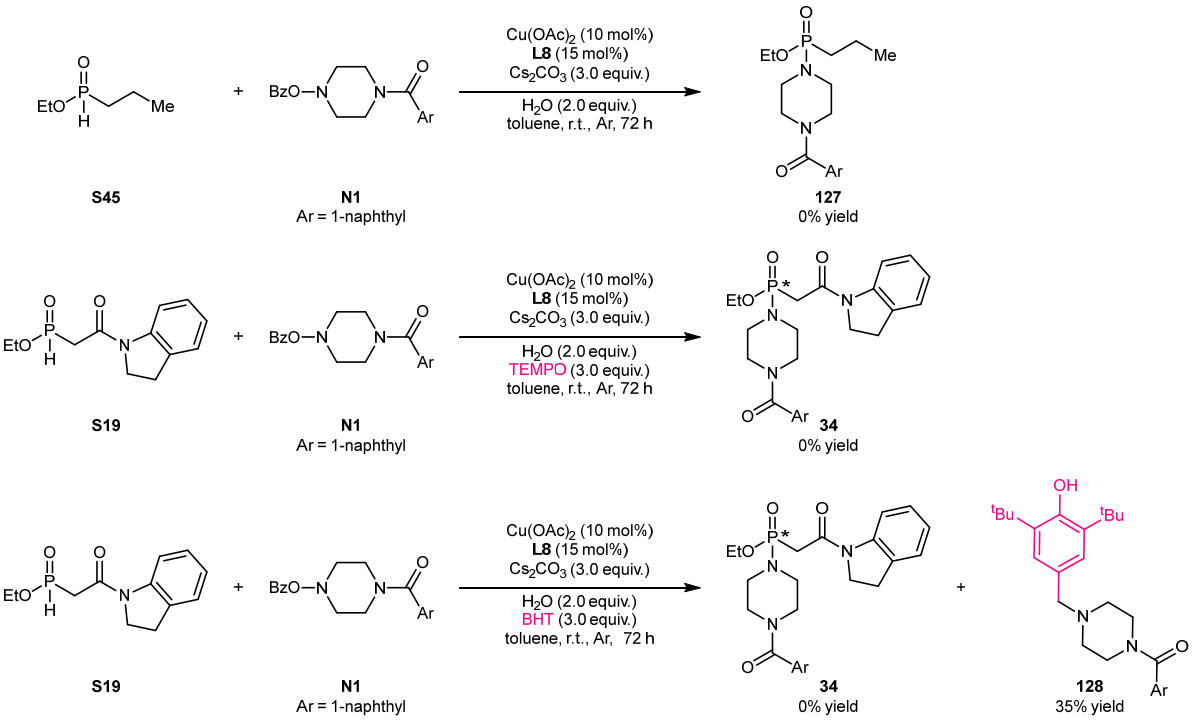


Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **S45** or **S19** (0.12 mmol, 1.2 equiv.), CuTc (1.91 mg, 0.010 mmol, 10 mol%), **L2** (9.80 mg, 0.015 mmol, 15 mol%), H_2O (3.6 μL, 0.20 mmol, 2.0 equiv.), Cs_2CO_3 (65.2 mg, 0.20 mmol, 2.0 equiv.), TEMPO (0 or 2.0 equiv.) and anhydrous MTBE (4.0 mL). Then, (3-bromoprop-1-yn-1-yl)triisopropylsilane **C15** (26.0 μL, 0.10 mmol, 1.0 equiv.) was added and the reaction mixture was stirred at at r.t. for 72 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard, and the yield of **126** is based on **S19**.

2,2,6,6-Tetramethyl-1-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)piperidine (126)

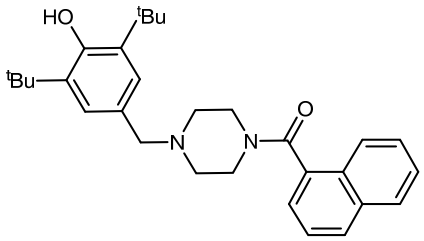


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (s, 2H), 1.62 – 1.23 (m, 6H), 1.19 (s, 6H), 1.14 – 1.02 (m, 27H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 104.2, 86.9, 66.9, 59.9, 39.8, 33.2, 20.1, 18.7, 17.3, 11.4.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{42}NOSi$ $[M + H]^+$ 352.3030, found 352.3031.



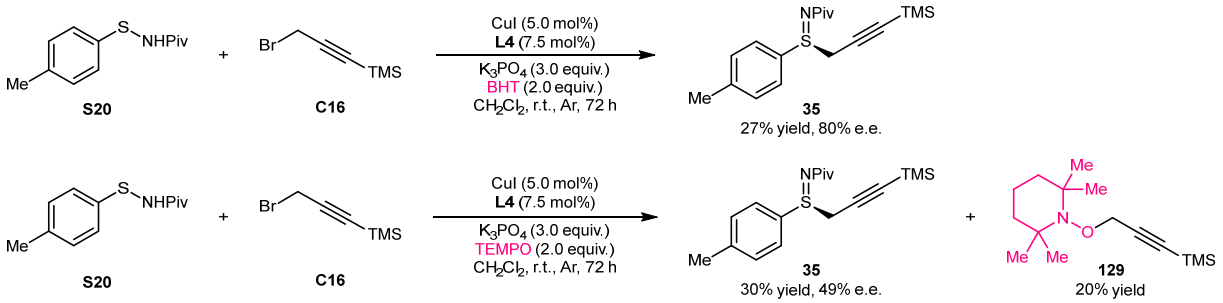
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (1.90 mg, 0.010 mmol, 10 mol%), **L8** (7.80 mg, 0.015 mmol, 15 mol%), **S45** or **S19** (0.15 mmol, 1.5 equiv.), **N1** (36.0 mg, 0.10 mmol, 1.0 equiv.), BHT or TEMPO (0 or 3.0 equiv.) and Cs_2CO_3 (97.6 mg, 0.30 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then anhydrous toluene (2.0 mL) and H_2O (3.6 μL, 0.20 mmol, 2.0 equiv.) were added by syringe under argon and the reaction mixture was stirred at r.t. for 72 h. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard, and the yield of **128** is based on **S19**.

(4-(3,5-Di-*tert*-butyl-4-hydroxybenzyl)piperazin-1-yl)(naphthalen-1-yl)methanone (128)



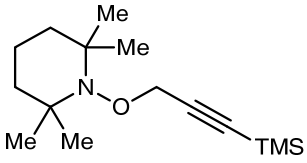
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.78 (m, 3H), 7.62 – 7.44 (m, 3H), 7.43 – 7.36 (m, 1H), 7.06 (s, 2H), 5.13 (s, 1H), 4.09 – 3.78 (m, 2H), 3.44 (s, 2H), 3.29 – 3.06 (m, 2H), 2.71 – 2.49 (m, 2H), 2.35 – 2.12 (m, 2H), 1.42 (s, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 153.1, 135.8, 134.5, 133.6, 129.7, 129.2, 128.5, 128.1, 127.1, 126.6, 125.9, 125.3, 125.0, 123.9, 63.2, 53.6, 53.0, 47.4, 42.0, 34.4, 30.5.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{39}N_2O_2$ $[M + H]^+$ 459.3006, found 459.3005.

Control experiments of chiral S(IV) center

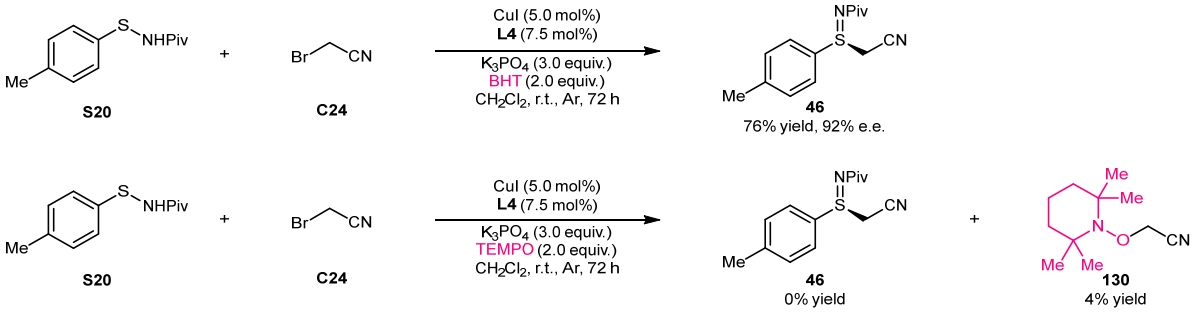


To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.90 mg, 0.020 mmol, 5.0 mol%), **L4** (7.9 mg, 0.015 mmol, 7.5 mol%), sulfenamide **S20** (44.6 mg, 0.20 mmol, 1.0 equiv.), (3-bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.), TEMPO or BHT (0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Anhydrous CH_2Cl_2 (2.0 mL) was added and the reaction mixture was stirred at r.t. for 72 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2, then the filtrate was evaporated. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard and the $^{e.e.}$ values are based on HPLC analysis. The yield of **129** is based on **C16**.

2,2,6,6-Tetramethyl-1-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)piperidine (129)



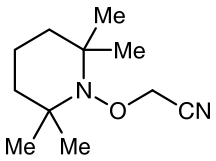
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (s, 2H), 1.47 – 1.39 (m, 4H), 1.33 – 1.24 (m, 2H), 1.18 (s, 6H), 1.11 (s, 6H), 0.18 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 102.0, 90.7, 66.3, 59.9, 39.8, 33.1, 20.2, 17.2, 0.1.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{30}NOSi$ $[M + H]^+$ 268.2091, found 268.2088.



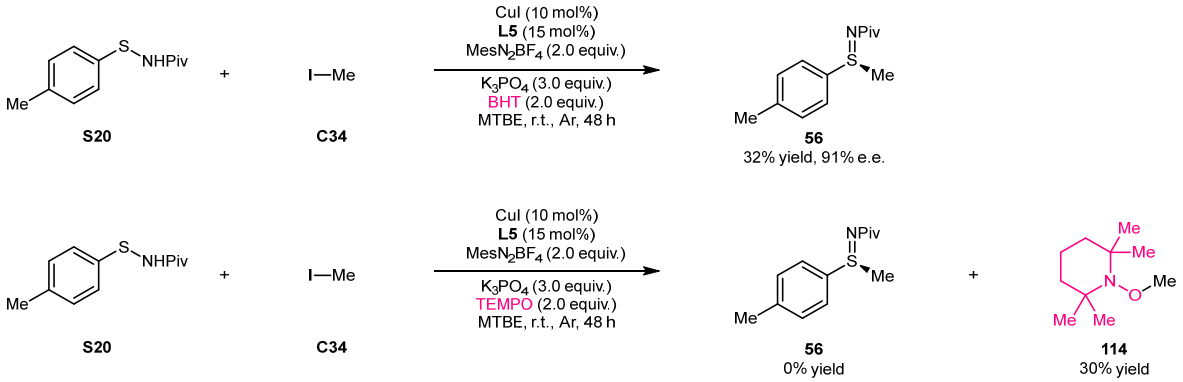
To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.90 mg, 0.010 mmol, 5.0 mol%), **L4** (7.9 mg, 0.015 mmol, 7.5 mol%), sulfenamide **S20** (44.6 mg, 0.20 mmol, 1.0 equiv.), bromoacetonitrile **C24** (36.0 mg, 0.24 mmol, 1.5 equiv.), TEMPO or BHT (0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Anhydrous CH_2Cl_2 (2.0 mL) was added and the reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2,

and then the filtrate was evaporated. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard and the e.e. values are based on HPLC analysis. The yield of **130** is based on **C24**.

2-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)acetonitrile (130)

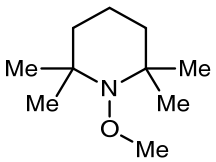


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (s, 2H), 1.72 – 1.24 (m, 6H), 1.20 (s, 6H), 1.10 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 116.2, 62.8, 60.5, 39.7, 33.1, 20.0, 17.0.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{21}N_2O$ $[M + H]^+$ 197.1648, found 197.1645.
The NMR data of **130** is consistent with that reported in the literature.[74]

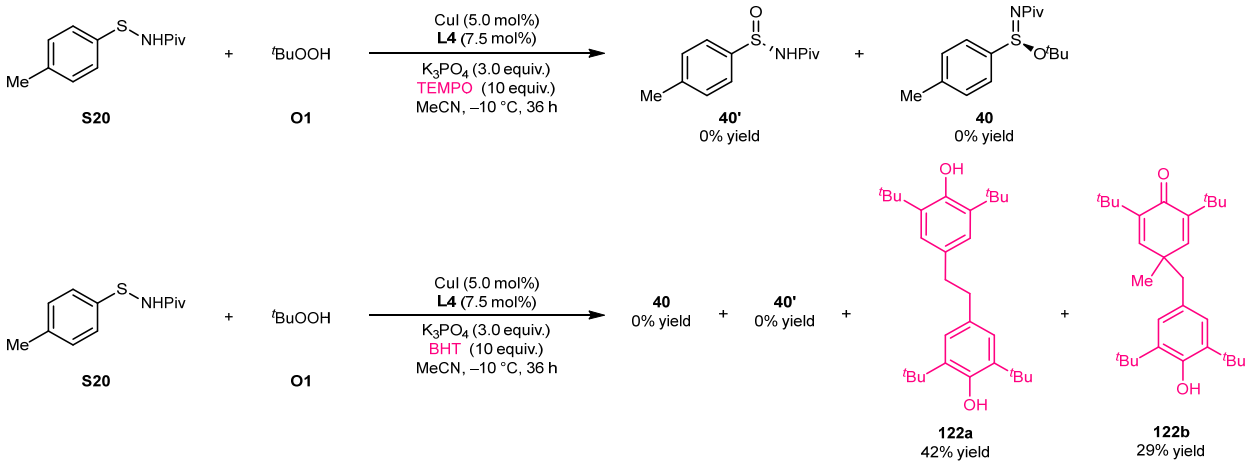


To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.80 mg, 0.02 mmol, 10 mol%), **L5** (10.0 mg, 0.03 mmol, 15 mol%), sulfenamide **S20** (44.6 mg, 0.20 mmol, 1.0 equiv.), iodomethane **C34** (0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), TEMPO or BHT (0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Anhydrous MTBE (4.0 mL) was added and the reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2, then the filtrate was evaporated. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard and the e.e. values are based on HPLC analysis. The yield of **114** is based on **C34**.

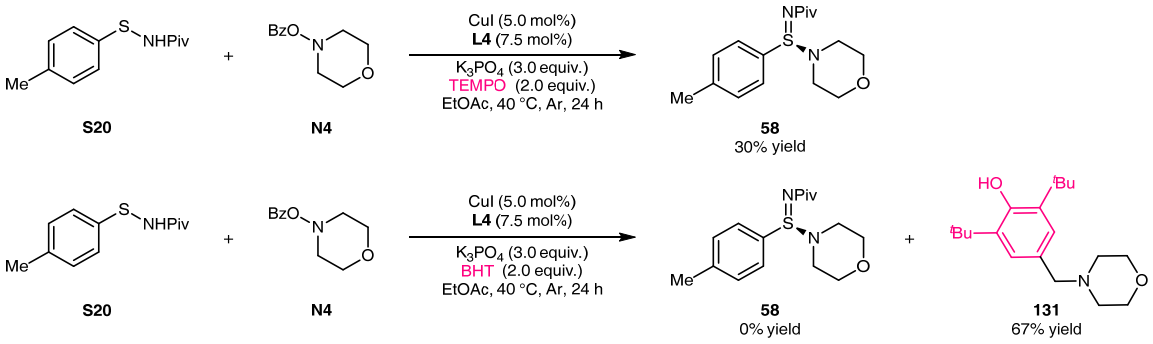
1-Methoxy-2,2,6,6-tetramethylpiperidine (114)



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 3H), 1.62 – 1.21 (m, 6H), 1.15 (s, 6H), 1.05 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 65.4, 59.8, 39.8, 33.1, 20.1, 17.2.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{22}NO$ $[M + H]^+$ 172.1696, found 172.1696.
The NMR data of **114** is consistent with that reported in the literature.[74]

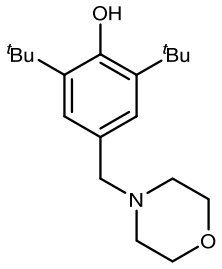


Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S20** (0.20 mmol, 1.0 equiv.), CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L4** (7.9 mg, 0.015 mmol, 7.5 mol%), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.), TEMPO or BHT (2.0 mmol, 10.0 equiv.), and anhydrous MeCN (2.0 mL). Then, *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at –10 °C for 36 h. Upon completion (monitored by TLC), the reaction was quenched with a saturated aqueous solution of NH_4Cl, and extracted with EtOAc three times (3 × 10 mL). The combined organic layers were concentrated in vacuo. The yield is based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard and the yields of **122a** and **122b** are based on **S20**.



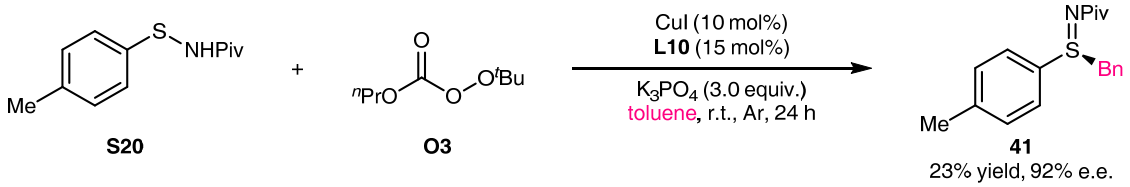
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (0.48 mg, 0.00250 mmol, 5.0 mol%), **L4** (1.98 mg, 0.00375 mmol, 7.5 mol%), **S20** (11.17 mg, 0.050 mmol, 1.0 equiv.), **N4** (15.54 mg, 0.075 mmol, 1.5 equiv.), BHT or TEMPO (0.10 mmol, 2.0 equiv.), and K_3PO_4 (31.8 mg, 0.150 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then EtOAc (0.5 mL) was added by syringe under argon and the reaction mixture was stirred at 40 °C for 24 h. Upon completion, the precipitate was filtered off and washed with EtOAc. The filtrate was evaporated and the yields are based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard the yield of **131** is based on **N4**.

2,6-Di-*tert*-butyl-4-(morpholinomethyl)phenol (131)

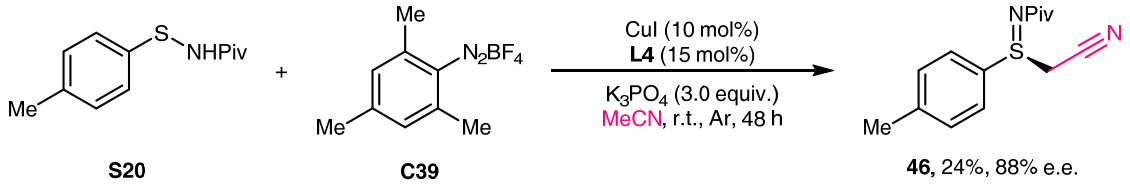


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 2H), 5.14 (s, 1H), 3.72 (t, J = 4.7 Hz, 4H), 3.43 (s, 2H), 2.54 – 2.33 (m, 4H), 1.44 (s, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 135.5, 127.8, 125.9, 67.0, 63.6, 53.4, 34.2, 30.3.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{32}NO_2$ $[M + H]^+$ 306.2428, found 306.3423.
The NMR data of **131** is consistent with that reported in the literature.[75]

Radical verification experiment:

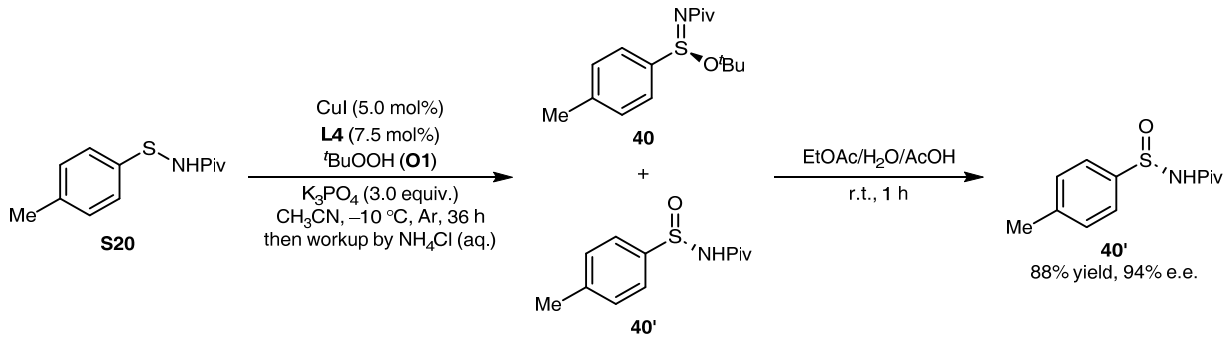


An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (0.95 mg, 0.0050 mmol, 10 mol%), **L10** (3.86 mg, 0.0075 mmol, 15 mol%), sulfenamide **S20** (11.2 mg, 0.05 mmol, 1.0 equiv.), and K_3PO_4 (31.8 mg, 0.15 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then toluene (0.5 mL) and *tert*-butyl propyl carbonoperoxoate **O3** (17.62 mg, 0.10 mmol, 2.0 equiv.) were added by syringe under argon and the reaction mixture was stirred at r.t. for 24 h. Upon completion, the precipitate was filtered off and washed with EtOAc, and the filtrate was evaporated. The yield of **41** was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. E.e. value was based on HPLC analysis.



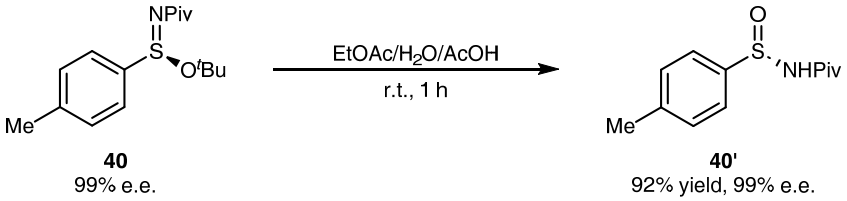
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (0.95 mg, 0.0050 mmol, 10 mol%), **L4** (3.86mg, 0.0075 mmol, 15 mol%), sulfenamide **S20** (11.2 mg, 0.05 mmol, 1.0 equiv.), $MesN_2BF_4$ **C39** (58.5 mg, 0.25 mmol, 5.0 equiv.) and K_3PO_4 (31.8 mg, 0.15 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then MeCN (0.5 mL) was added by syringe under argon and the reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed with EtOAc, and the filtrate was evaporated. The yield of **46** was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. E.e. value was based on HPLC analysis.

The mechanistic study of O radical:

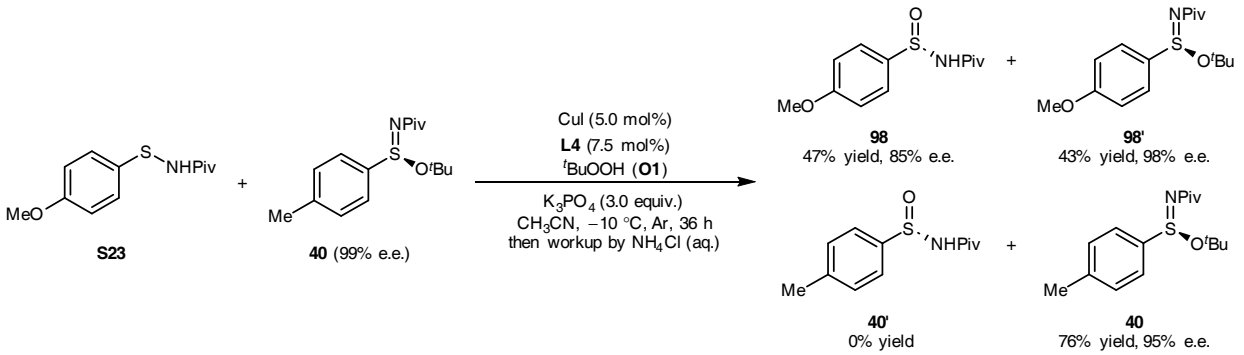


Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S20** (0.20 mmol, 1.0 equiv.), CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L4** (7.9 mg, 0.015 mmol, 7.5 mol%), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.), and anhydrous MeCN (2.0 mL). Then, *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at −10 °C for 36 h. Upon completion (monitored by TLC), the reaction was quenched with sat. NH_4Cl aqueous solution, and extracted with EtOAc three times (3 × 10 mL). The combined organic layers were concentrated *in vacuo*, and the filtrate was evaporated to afford the crude residue **40** and **40′**.

To a solution of the crude residue in EtOAc (1.5 mL) was added H_2O (1.0 mL) and AcOH (0.5 mL). The reaction mixture was then stirred at r.t. for 1 h. Upon completion (monitored by TLC), the reaction was quenched with H_2O and extracted with EtOAc three times (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The yield is based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard and the e.e. value is based on HPLC analysis.

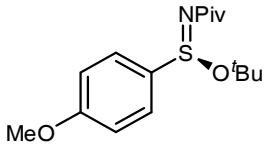


To a solution of **40** (29.5 mg, 0.10 mmol, 1.0 equiv.) in EtOAc (1.5 mL) was added H_2O (1.0 mL) and AcOH (0.5 mL). The reaction mixture was stirred at r.t. for 1 h. Upon completion (monitored by TLC), the reaction was quenched with H_2O and extracted with EtOAc three times (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product. The yield is based on ^1H NMR analysis of the crude product using dibromomethane as an internal standard and the e.e. value is based on HPLC analysis.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S23** (0.10 mmol, 1.0 equiv.), sulfinimidate ester **40** (0.10 mmol, 1.0 equiv.), CuI (0.95 mg, 0.0050 mmol, 5.0 mol%), **L4** (3.9 mg, 0.0075 mmol, 7.5 mol%), K_3PO_4 (63.7 mg, 0.30 mmol, 3.0 equiv.), and anhydrous MeCN (1.0 mL). Then, *tert*-butyl hydroperoxide **O1** (70% in H_2O, 0.12 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at −10 °C for 36 h. Upon completion (monitored by TLC), the reaction was quenched with sat. NH_4Cl aqueous solution, and extracted with EtOAc three times (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product. The yields are based on ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard and the e.e. values are based on HPLC analysis.

(*R*)-*tert*-Butyl *N*–(pivaloyl)-4-methoxyphenylsulfinimidate (98')

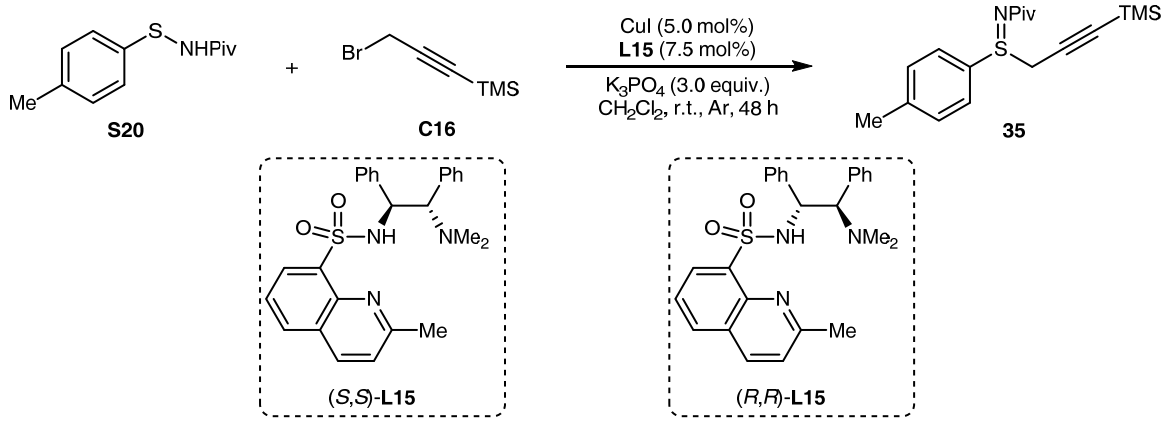


HPLC analysis: Chiralpak IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 10.34 min, t_R (major) = 14.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H), 1.55 (s, 9H), 1.27 (s, 9H).

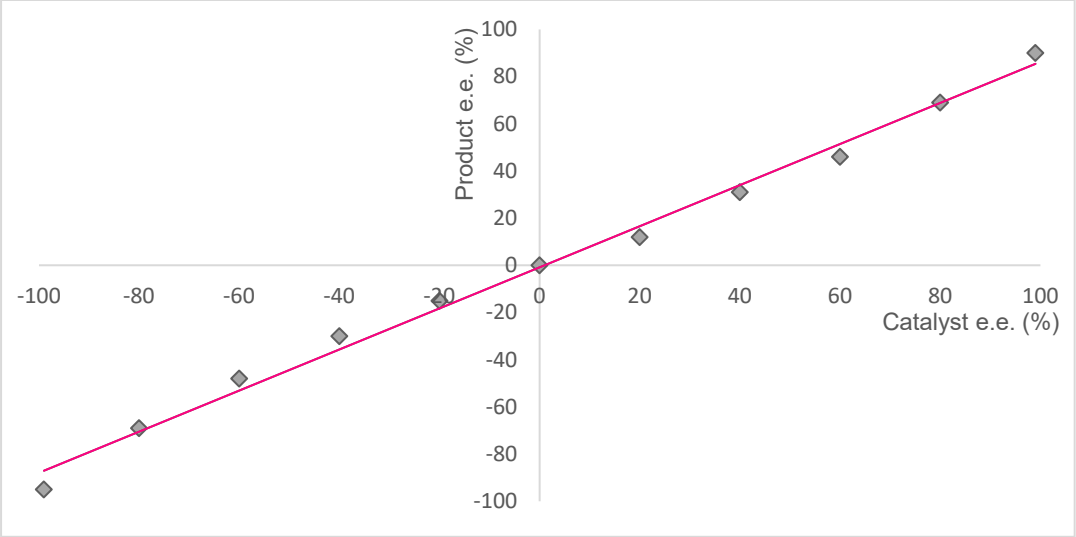
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 162.6, 130.6, 129.0, 114.6, 84.5, 55.6, 41.0, 29.5, 28.1.

The non-linear effect of catalyst:



Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S20** (0.20 mmol, 1.0 equiv.), CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L15** (6.7 mg, 0.015 mmol, 7.5 mol%), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.), and anhydrous CH_2Cl_2 (2.0 mL). (3-Bromoprop-1-yn-1-yl)trimethylsilane **C16** (45.9 mg, 0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at r.t. for 48 h. Upon completion (monitored by TLC), product **35** was separated by preparative TLC on silica gel. The e.e. value of product **35** was then determined by HPLC, which indicated a linear relationship between the e.e. value of product **35** and the corresponding catalyst. The catalyst **L15** with different e.e. values was prepared by mixing (*S*,*S*)-**L15** (99% e.e.) and (*R*,*R*)-**L15** (99% e.e.) in appropriate ratios.

Entry	Catalyst e.e. (%)	Product e.e. (%)
1	99	90
2	80	69
3	60	46
4	40	31
5	20	12
6	0	0
7	–20	–15
8	–40	–30
9	–60	–48
10	–80	–69
11	–99	–95


Product e.e. (%)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-100
-80
-60
-40
-20
0
20
40
60
80
100
Catalyst e.e. (%)

9. Computational details

All density functional theory (DFT) calculation results were obtained with the Gaussian 16 program[76]. The default G16 SCF convergence criteria (scf=tight), optimization convergence criteria, and integral grid parameters (int=(ultrafine,acc2e=12)) for Gaussian 16 were applied unless otherwise stated. The (5d,7f) keyword in Gaussian 16 was used. Geometry optimizations were conducted with the B3LYP functional[77-78], employing the D3 version of Grimme's dispersion corrections[79] with Becke-Johnson damping[80]. The def2-SVP basis set[81-82] was used for all atoms. Single-point energies and solvent effects in dichloromethane (DCM) were also evaluated using the B3LYP functional with Grimme's dispersion corrections and Becke-Johnson damping. The def2-TZVP basis set[81-82] was used for all atoms. Solvation energies in geometry optimizations and single-point energy calculations were obtained with a self-consistent reaction field (SCRF) using the SMD implicit solvent model[83]. The solvent-accessible surface is used in geometry optimization (surface = SAS). Frequency analyses were also performed at the same level of theory as geometry optimizations, using the harmonic oscillator model to confirm whether the optimized stationary points are local minima or transition states, as well as to evaluate zero-point vibrational energies and thermal corrections for enthalpies and free energies at 298.15 K. Mulliken spin distributions were obtained at the same level of theory as geometry optimizations. NBO analysis was performed using NBO7 program[84]. Cartesian coordinates of the computed species are included in the Computational Archives.

In addition, geometry optimizations, frequency analyses, and single-point energy calculations of open-shell transition states and local minima were carried out with unrestricted DFT methods, while same computations for closed-shell structures were performed with restricted DFT methods. A wavefunction stability test at the same level of theory as geometry optimizations was employed to ensure that the SCF-converged wavefunction was stable.

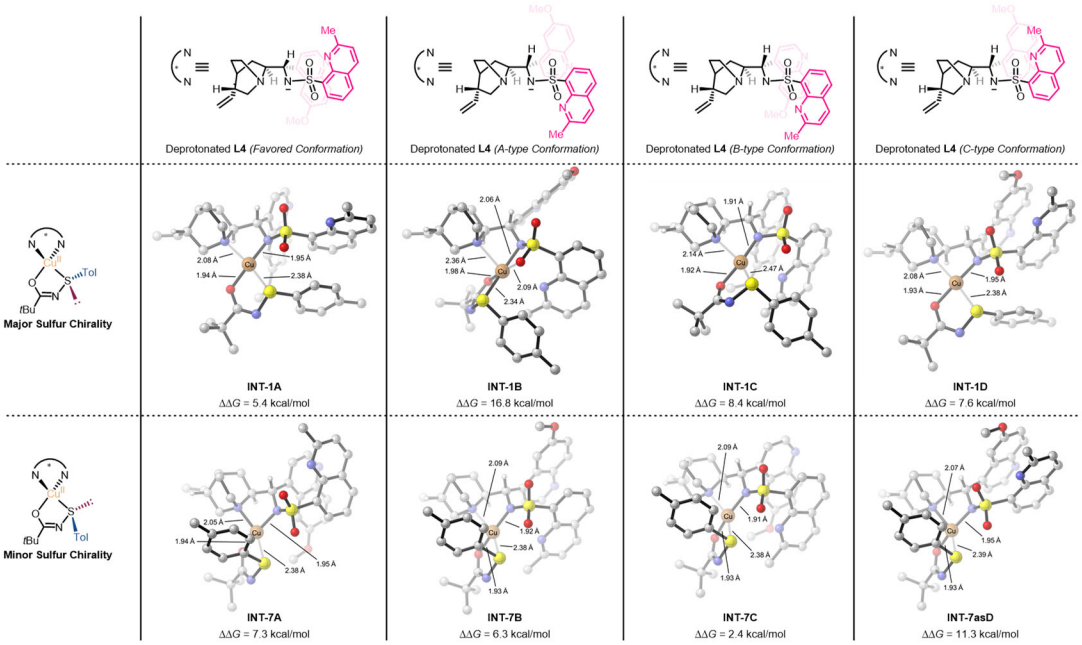
Configurational and conformational searches were performed with the Conformer-Rotamer Ensemble Sampling Tool (CREST, version 2.12)[85] using the xTB program package (version 6.4.0)[86]. The conformers generated by CREST were optimized at the GFN2-xTB level, based on proposed initial structures. Solvation effects in ether, instead of dichloromethane, were calculated with the GBSA implicit solvation model. An energy window of 6.0 kcal/mol, an RMSD threshold of 0.25 Å, and a "--mdlen" (MD length in picoseconds) parameter of 6.0 were used for sampling. For conformational sampling of transition state structures, atoms involved in forming/cleaving bonds were constrained using a force constant of 1.0 Hartree/Bohr. The "--cluster" keyword was used to apply the default clustering algorithm. The "--noreftopo" keyword was also applied to ensure the successful initial geometry optimization with xTB.

The 3D diagrams of optimized structures shown in this Supplementary Information were generated with CYLview software[87]. Graphs of frontier orbitals were generated with VMD[88].

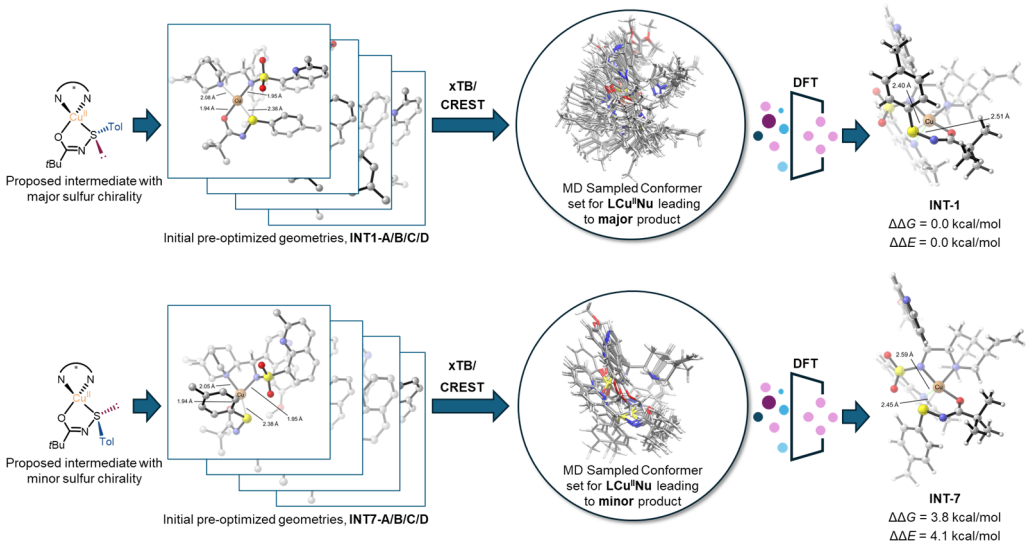
Configurational and Conformational Searches for L4Cu(II)Nu Species

The configurational and conformational searches for the key **L4**Cu(II)Nu species were based on manually defined conformational space and xTB/CREST sampling methods. Initially, considering different sulfur-centered chiralities and rotations of the two substituted quinoline rings, eight possible isomers (**INT-1A** to **INT-1D** and **INT-7A** to **INT-7D**; Supplementary Fig. 24 and Supplementary Table 19) were identified.

However, some isomers may be omitted by using only manually defined conformational space. Hence, the xTB/CREST programs were employed (Supplementary Fig. 25 and Supplementary Table 20). Starting from the eight possible isomers (**INT-1A** to **INT-1D** and **INT-7A** to **INT-7D**), 28 isomers for the **L4**Cu(II)Nu intermediate leading to the experimentally observed sulfur-centered chirality were identified (Supplementary Tables 17 and 19), and 13 isomers for the **L4**Cu(II)Nu intermediate leading to the opposite sulfur-centered chirality were identified (Supplementary Tables 18 and 19). Among them, **INT-1** is the most favorable. The corresponding intermediate, maintaining similar conformational features but possessing the opposite sulfur chirality to **INT-1**, is **INT-7**. **INT-1** is used as the reference intermediate in energy evaluations for subsequent mechanistic studies.



Supplementary Fig. 24 | Proposed configurational and conformational isomers of L4Cu(II)Nu intermediates INT-1 and INT-7. Free energies are given relative to **INT-1**. Trivial hydrogen atoms in the 3D structures are omitted for clarity.



Supplementary Fig. 25 | Combined DFT and xTB/CREST workflow for the configurational and conformational searches of key L4Cu(II)Nu intermediates responsible for C–S bond formation. Free energies and electronic energies are given relative to **INT-1.**

Supplementary Table 17 | Identified isomers of INT-1 that lead to the major product with the experimentally observed sulfur-centered chirality. Free energies are given relative to **INT-1**.

Isomer No.	ΔΔ*G* /kcal/mol	**Isomer No.**	ΔΔ*G* /kcal/mol
INT-1	0.0	**INT-1_No-12**	15.0
INT-1A	5.4	**INT-1_No-13**	16.7
INT-1B	16.8	**INT-1_No-14**	16.8
INT-1C	8.4	**INT-1_No-15**	19.3
INT-1D	7.6	**INT-1_No-16**	20.4
INT-1_No-01	7.2	**INT-1_No-17**	8.4
INT-1_No-02	7.7	**INT-1_No-18**	10.1
INT-1_No-03	5.4	**INT-1_No-19**	7.6
INT-1_No-04	5.3	**INT-1_No-20**	8.2
INT-1_No-05	16.7	**INT-1_No-21**	3.7
INT-1_No-06	16.5	**INT-1_No-22**	3.8
INT-1_No-07	17.5	**INT-1_No-23**	5.2
INT-1_No-08	16.4	**INT-1_No-24**	1.3
INT-1_No-09	16.7	**INT-1_No-25**	0.3
INT-1_No-10	19.1	**INT-1_No-26**	1.7
INT-1_No-11	18.0	**INT-1_No-27**	1.9

Supplementary Table 18 | Identified isomers of INT-7 that lead to the minor product with the sulfur-centered chirality opposite to the experimentally observed configuration. Free energies are given relative to **INT-1**.

Isomer No.	ΔΔ*G* /kcal/mol	Isomer No.	ΔΔ*G* /kcal/mol
INT-7	3.8	**INT-7_No-05**	5.2
INT-7A	7.3	**INT-7_No-06**	6.3
INT-7B	6.3	**INT-7_No-07**	6.2
INT-7C	2.4	**INT-7_No-08**	3.8
INT-7D	11.3	**INT-7_No-09**	4.4
INT-7_No-01	3.8	**INT-7_No-10**	4.2
INT-7_No-02	6.9	**INT-7_No-11**	4.9
INT-7_No-03	6.3	**INT-7_No-12**	5.7
INT-7_No-04	6.6		

Mechanistic Studies on the C–S Bond Formation Step

Two main possibilities for the key, final radical termination (C–S bond formation) step are considered: a) an S_H1 mechanism involving Cu–S cleavage and subsequent radical coupling of a *S*-based radical (Supplementary Fig. 26, path A); b) an S_H2 mechanism involving direct attack of an outer-sphere-generated radical on the Cu–S bond (Supplementary Fig. 26, path B).

We tried to obtain the proposed Cu(I)-coordinated *S*-based radical intermediate involved in the S_H1 mechanism. The key intermediate **INT-1** (**L4**Cu(II)Nu) has a Cu–S bond length of 2.40 Å. Natural population analysis (NPA) reveals a spin density of 0.520 on the Cu center, with the remaining spin delocalized over the coordinating N, O, and S atoms (Supplementary Fig. 27b, left and Supplementary Table 20). This confirms **INT-1** as a Cu(II)-centered radical. Upon stretching the Cu–S atom distance to 3.40 Å from **INT-1**, the potential energy increases by 14.4 kcal/mol (Supplementary Figs. 27a and 27b and Supplementary Tables 20 and 21). In this Cu–S-elongated structure (**INT-1_R1**), the Cu spin density slightly increases to 0.560, while the S atom retains a small spin density (0.010) (Supplementary Fig. 27b, structure on the right). Additionally, starting from the proposed intermediate with separated Cu and S atoms, **INT-1_R2** was independently obtained with a DFT-optimized separated Cu–S length of 3.54 Å. This **INT-1_R2** shows spin densities of 0.575 (Cu) and 0.031 (S), maintaining Cu-radical character (Supplementary Fig. 27c). These results reveal that the Cu(I)-coordinated *S*-based radical intermediate is unstable.

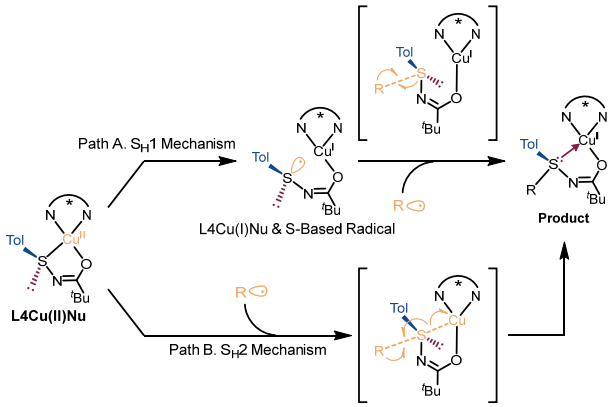
In addition, sequential, facile radical substitution involving **INT-1** and the cyanomethyl radical **INT-2**, with an activation barrier of 0.7 kcal/mol (electronic energy change from **INT-3** to **TS-4**), is more favorable than the endergonic Cu–S dissociation (an endergonic electronic energy change of 14.4 kcal/mol; Supplementary Fig. 28 and Supplementary Table 20). These results rule out the S_H1 mechanism involving *S*-radical formation.

For path B, the S_H2 (bimolecular homolytic substitution) pathway in Supplementary Fig. 26, the Cu(II) intermediate **INT-1** and cyanomethyl radical **INT-2** first generate the open-shell singlet diradical complex **INT-3**. **INT-3** then undergoes C–S bond formation via an open-shell singlet transition state, **TS-4**, generating **INT-5** with the newly formed C–S bond, which eventually liberates the observed product (Supplementary Fig. 29 and Supplementary Table 20). Spin population analysis by NPA (natural population analysis) reveals the open-shell singlet diradical nature of **TS-4** (Supplementary Fig. 30 and Supplementary Table 20). Canonical frontier bonding orbitals (SOMO-alpha and SOMO-beta, where SOMO stands for singly occupied molecular orbital) in the C–S bond formation transition state **TS-4** confirm the interaction between the SOMO of the cyanomethyl radical and the anti-bonding orbital of the Cu–S bond (Supplementary Fig. 30), which is consistent with the nature of radical substitution[89]. For the minor pathway leading to the byproduct with the opposite configuration, **INT-1** undergoes a configuration shift via **TS-6**, affording **INT-7** with the opposite sulfur chirality. Subsequent C–S bond formation via **TS-8** generates **INT-9**, which eventually liberates the minor byproduct (Supplementary Fig. 29). The configuration shift transition state **TS-6** is 7.4 kcal/mol less favorable than the S_H2 transition state **TS-4** (**TS-6** vs **TS-4**; Supplementary Fig. 29). This energy difference indicates that radical substitution is facile from **INT-1**, and the formation of the byproduct with the minor configuration from the configuration flip of **INT-1** is unlikely.

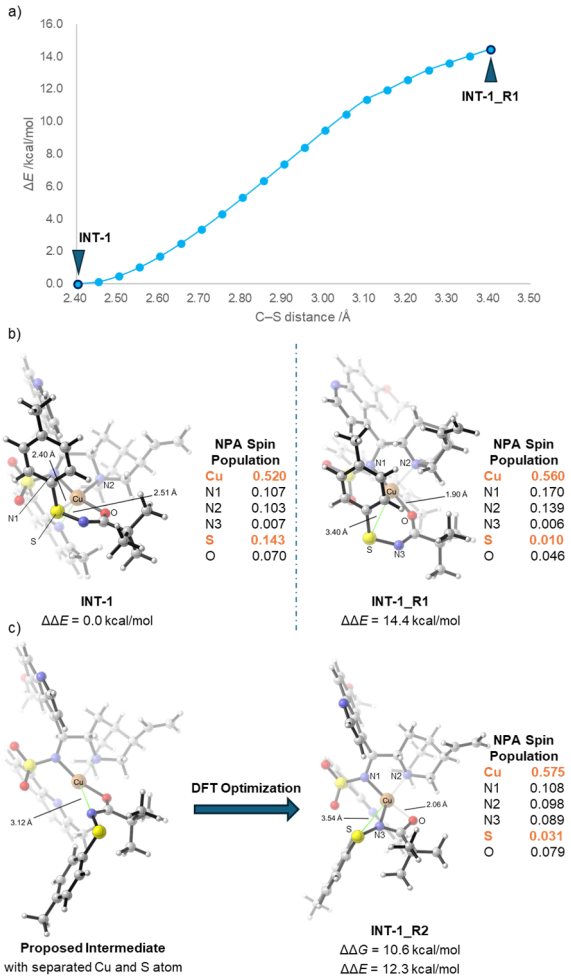
Furthermore, radical substitution involving the tribromomethyl radical **INT-10** is barrierless compared to the configuration shift, which requires a free energy barrier of 13.3 kcal/mol from **INT-1** (Supplementary Fig. 31 and Supplementary Table 20). Starting from a proposed complex of **INT-1** and **INT-10**, the potential energy decreases as the carbon atom of the tribromomethyl radical and the S atom of the nucleophile approach, indicating that a transition state for C–S bond

formation cannot be located on the potential energy surface (Supplementary Fig. 32 and Supplementary Table 22). This discussion shows that C–S bond formation is facile with **INT-1** and tribromomethyl radical **INT-10**.

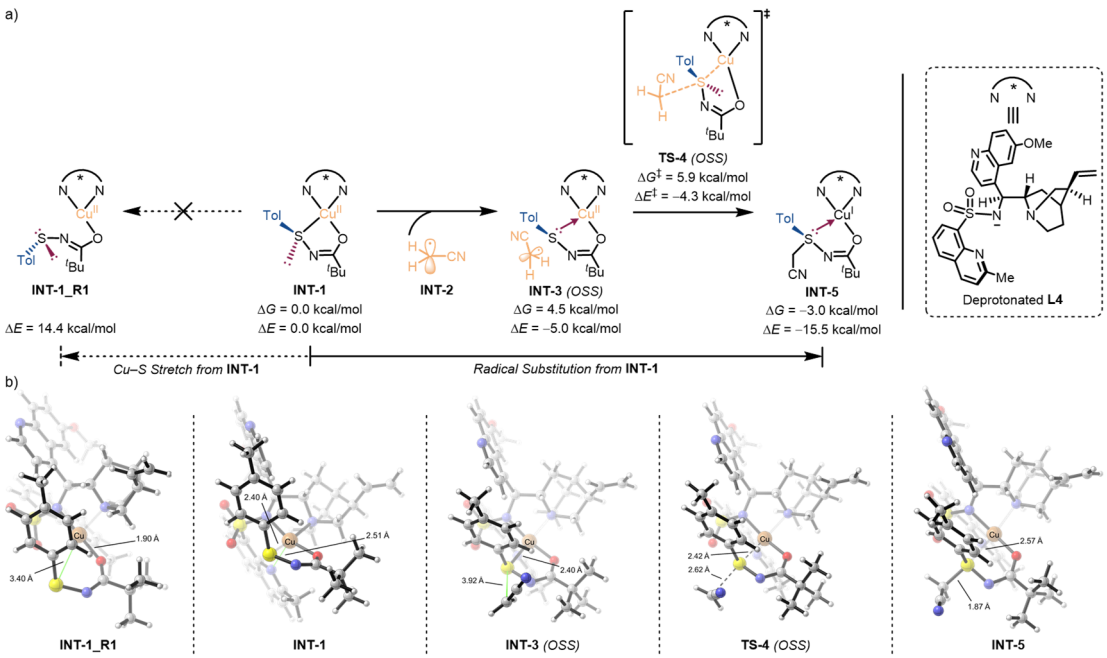
To sum up, C–S bond formation favors a facile S_H2-type radical substitution for both cyanomethyl radical and tribromomethyl radical. Furthermore, the formation of the byproduct with the minor configuration from the configuration flip of **INT-1** is kinetically unfavorable.



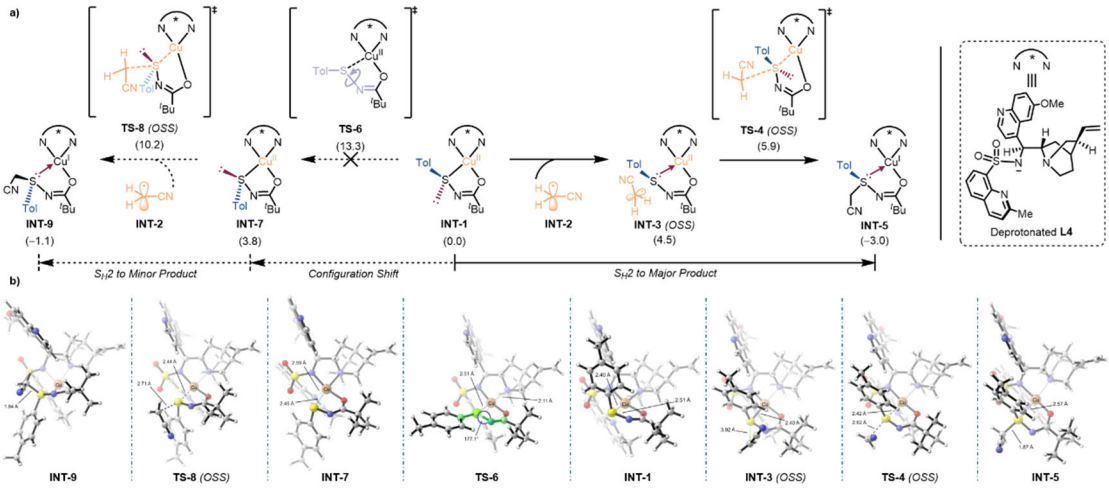
Supplementary Fig. 26 | Proposed C–S bond formation pathways.



Supplementary Fig. 27 | a, Electronic energy profile along the Cu–S stretch. **b**, Key intermediate and spin population based on natural population analysis (NPA). **c**, Independently identified configurational isomer of L*Cu(II)Nu species **INT-1** with a Cu–S distance of 3.54 Å and its NPA spin population. Relative free energies and electronic energies are given relative to **INT-1**. The scan along the C–S distance was performed using the internal procedure of Gaussian 16, starting from **INT-1** at the same level of theory as the geometry optimization, with a scan step size of 0.05 Å. Electronic energies from the scan are listed in Supplementary Table 21.

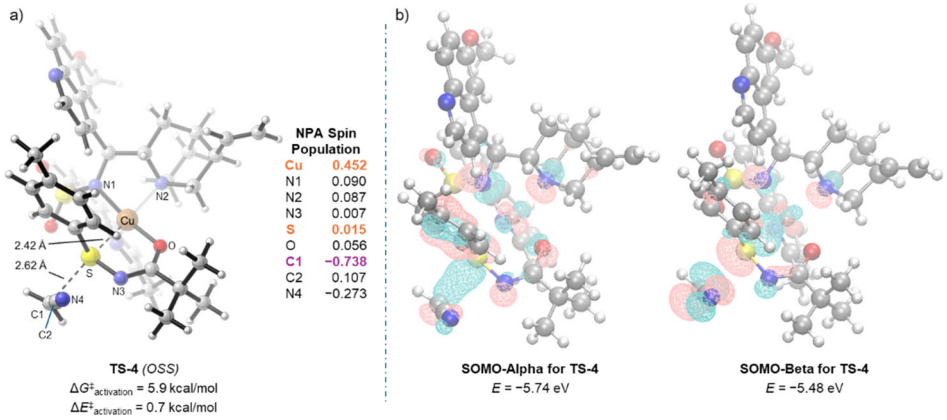


Supplementary Fig. 28 | a, Energy diagram comparing the Cu–S stretch pathway and the operative radical substitution pathway. **b**, 3D structures of the calculated intermediates and transition state. Electronic energies and free energies are given relative to the sum of **INT-1** and the cyanomethyl radical **INT-2**.

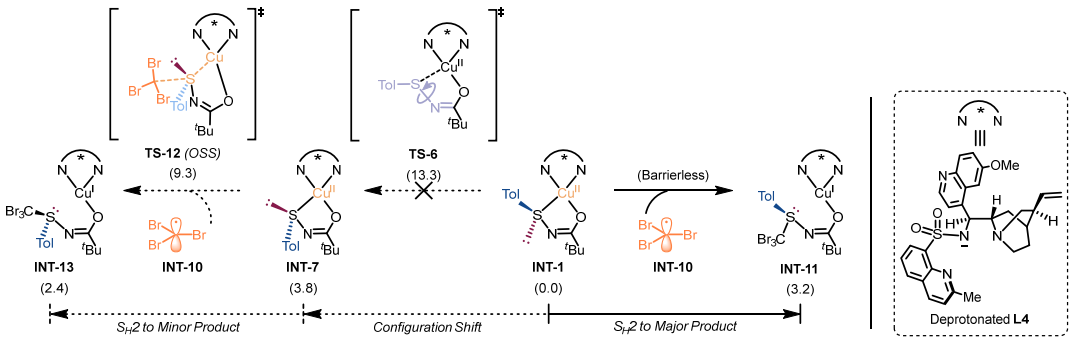


Supplementary Fig. 29 | a, Free energy diagram for radical substitution pathways of the cyanomethyl radical leading to the major product **46** and its stereoisomer. **b**, 3D structures of key configuration shift and radical substitution transition states. Free energies in parentheses are in

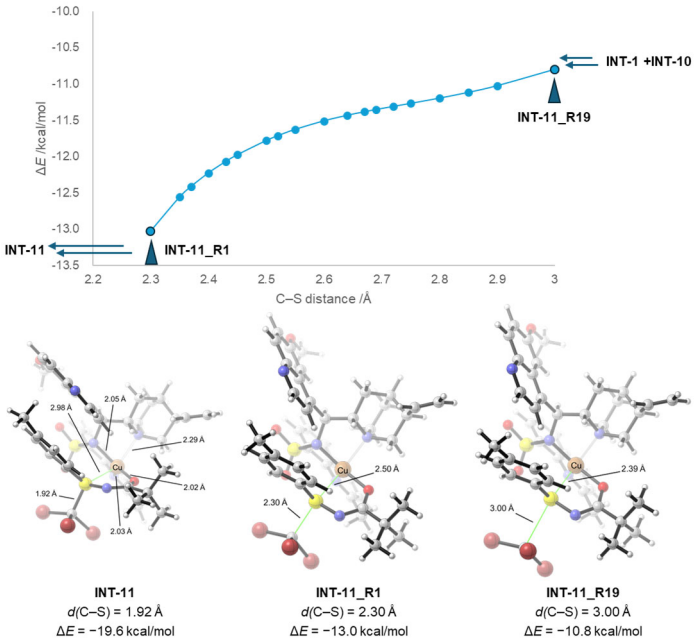
kcal/mol, relative to the sum of the LCu(II)Nu intermediate **INT-1** and the cyanomethyl radical **INT-2**.



Supplementary Fig. 30 | a, 3D structures of the key radical substitution transition state **TS-4** and NPA spin populations. **b**, Canonical SOMOs for **TS-4**. The activation energy ($\Delta E^{\ddagger}_{\text{activation}}$) is given relative to the reactant adduct **INT-3**. The activation free energy ($\Delta G^{\ddagger}_{\text{activation}}$) is given relative to the sum of **INT-1** and **INT-2**. The isovalues of the corresponding orbitals are set to 0.04 for clarity.



Supplementary Fig. 31 | Free energy diagram for the radical substitution pathways of the tribromomethyl radical INT-10 leading to the major product 45 and its stereoisomer. Free energies in parentheses are in kcal/mol, relative to the sum of the LCu(II)Nu intermediate **INT-1** and the tribromomethyl radical **INT-10**.



Supplementary Fig. 32 | Electronic energy changes along the carbon–sulfur distance during radical substitution by the tribromomethyl radical. Electronic energies are given relative to the sum of **INT-1** and the tribromomethyl radical **INT-10**. Electronic energies from the scan curve are listed in Supplementary Table 22.

Table of Energies

Supplementary Table 19 | Energies from Supplementary Tables 17 and 18 and Supplementary Fig. 24. Zero-point correction (***ZPE***), thermal correction to enthalpy (***TCH***), thermal correction to Gibbs free energy (***TCG***), energies (***E***), enthalpies (***H***), and Gibbs free energies (***G***) (in Hartree) for the structures calculated at the B3LYP-D3(BJ)/Def2-TZVP-SMD(Dichloromethane)// B3LYP-D3(BJ)/Def2-SVP-SMD(Dichloromethane) level of theory are listed.

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*
INT-1	0.825067	0.876828	0.737628	−4641.622035	−4640.745207	−4640.884407
INT-1A	0.824851	0.876885	0.736699	−4641.612461	−4640.735576	−4640.875762
INT-1B	0.824005	0.876276	0.733974	−4641.591659	−4640.715383	−4640.857685
INT-1C	0.825989	0.877356	0.741034	−4641.612048	−4640.734692	−4640.871014
INT-1D	0.825096	0.876728	0.738498	−4641.610784	−4640.734056	−4640.872286
INT-1_No-01	0.824672	0.876644	0.737260	−4641.610155	−4640.733511	−4640.872895
INT-1_No-02	0.824832	0.876743	0.737683	−4641.609839	−4640.733096	−4640.872156
INT-1_No-03	0.824850	0.876885	0.736693	−4641.612465	−4640.735580	−4640.875772
INT-1_No-04	0.824935	0.876968	0.736147	−4641.612111	−4640.735143	−4640.875964
INT-1_No-05	0.823989	0.876273	0.733815	−4641.591673	−4640.715400	−4640.857858
INT-1_No-06	0.824385	0.876526	0.735510	−4641.593560	−4640.717034	−4640.858050
INT-1_No-07	0.823687	0.876058	0.733233	−4641.589785	−4640.713727	−4640.856552
INT-1_No-08	0.824202	0.876431	0.734544	−4641.592837	−4640.716406	−4640.858293
INT-1_No-09	0.824239	0.876420	0.733681	−4641.591508	−4640.715088	−4640.857827
INT-1_No-10	0.824048	0.876262	0.734805	−4641.588733	−4640.712471	−4640.853928
INT-1_No-11	0.824241	0.876344	0.735777	−4641.591564	−4640.715220	−4640.855787
INT-1_No-12	0.823583	0.875819	0.734407	−4641.594856	−4640.719037	−4640.860449
INT-1_No-13	0.823985	0.876016	0.736256	−4641.594042	−4640.718026	−4640.857786
INT-1_No-14	0.823833	0.875925	0.735469	−4641.593117	−4640.717192	−4640.857648
INT-1_No-15	0.824622	0.876334	0.738043	−4641.591752	−4640.715418	−4640.853709
INT-1_No-16	0.824372	0.876178	0.737504	−4641.589440	−4640.713262	−4640.851936
INT-1_No-17	0.825992	0.877357	0.741057	−4641.612045	−4640.734688	−4640.870988
INT-1_No-18	0.826104	0.877378	0.741655	−4641.609892	−4640.732514	−4640.868237
INT-1_No-19	0.825098	0.876730	0.738506	−4641.610782	−4640.734052	−4640.872276
INT-1_No-20	0.825329	0.876905	0.738836	−4641.610117	−4640.733212	−4640.871281
INT-1_No-21	0.826255	0.877444	0.742887	−4641.621421	−4640.743977	−4640.878534
INT-1_No-22	0.826229	0.877484	0.742449	−4641.620737	−4640.743253	−4640.878288
INT-1_No-23	0.826361	0.877443	0.743489	−4641.619608	−4640.742165	−4640.876119
INT-1_No-24	0.824900	0.876755	0.737102	−4641.619473	−4640.742718	−4640.882371
INT-1_No-25	0.825039	0.876817	0.737067	−4641.620942	−4640.744125	−4640.883875
INT-1_No-26	0.825170	0.876864	0.738367	−4641.620056	−4640.743192	−4640.881689
INT-1_No-27	0.825065	0.876826	0.737675	−4641.619090	−4640.742264	−4640.881415
INT-7	0.823941	0.875659	0.737050	−4641.615445	−4640.739786	−4640.878395
INT-7A	0.824383	0.876453	0.735559	−4641.608272	−4640.731819	−4640.872713
INT-7A	0.824898	0.876834	0.737279	−4641.611687	−4640.734853	−4640.874408
INT-7B	0.825305	0.876925	0.740156	−4641.620780	−4640.743855	−4640.880624
INT-7C	0.825166	0.876817	0.738891	−4641.605216	−4640.728399	−4640.866325

INT-7_No-01	0.825629	0.877099	0.740381	−4641.618653	−4640.741554	−4640.878272
INT-7_No-02	0.824936	0.876790	0.738519	−4641.611939	−4640.735149	−4640.873420
INT-7_No-03	0.824899	0.876834	0.737289	−4641.611685	−4640.734851	−4640.874396
INT-7_No-04	0.824681	0.876694	0.736357	−4641.610316	−4640.733622	−4640.873959
INT-7_No-05	0.825218	0.876840	0.739592	−4641.615657	−4640.738817	−4640.876065
INT-7_No-06	0.824900	0.876835	0.737289	−4641.611685	−4640.734850	−4640.874396
INT-7_No-07	0.824622	0.876664	0.736324	−4641.610852	−4640.734188	−4640.874528
INT-7_No-08	0.825626	0.877096	0.740370	−4641.618651	−4640.741555	−4640.878281
INT-7_No-09	0.825815	0.877210	0.740917	−4641.618261	−4640.741051	−4640.877344
INT-7_No-10	0.825089	0.876916	0.736330	−4641.614058	−4640.737142	−4640.877728
INT-7_No-11	0.825293	0.877018	0.737103	−4641.613733	−4640.736715	−4640.876630
INT-7_No-12	0.825279	0.877021	0.736871	−4641.612197	−4640.735176	−4640.875326

Supplementary Table 20 | Energies from Supplementary Figs. 25 and 27 to 31. Zero-point correction (***ZPE***), thermal correction to enthalpy (***TCH***), thermal correction to Gibbs free energy (***TCG***), energies (***E***), enthalpies (***H***), and Gibbs free energies (***G***) (in Hartree) of the structures calculated at the B3LYP-D3(BJ)/Def2-TZVP-SMD(Dichloromethane)// B3LYP-D3(BJ)/Def2-SVP-SMD(Dichloromethane) level of theory are listed.

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
INT-1_R1	/	/	/	−4641.599086	/	/	
INT-1_R2	0.824679	0.876803	0.734888	−4641.602422	−4640.725619	−4640.867534	
INT-1	0.825067	0.876828	0.737628	−4641.622035	−4640.745207	−4640.884407	
INT-2	0.030930	0.035510	0.006653	−132.159833	−132.124323	−132.153180	
INT-3	0.857657	0.914615	0.762409	−4773.789820	−4772.875205	−4773.027411	
TS-4	0.858203	0.914127	0.765387	−4773.790510	−4772.876383	−4773.025123	94.7*i*
INT-5	0.860868	0.916892	0.767130	−4773.806507	−4772.889615	−4773.039377	
TS-6	0.824335	0.875791	0.736107	−4641.599261	−4640.723470	−4640.863154	152.5*i*
INT-7	0.823941	0.875659	0.737050	−4641.615445	−4640.739786	−4640.878395	
TS-8	0.858083	0.914063	0.764468	−4773.782793	−4772.868730	−4773.018325	31.6*i*
INT-9	0.860549	0.916811	0.765811	−4773.802109	−4772.885298	−4773.036298	
INT-10	0.005432	0.011577	-0.026785	−7760.619682	−7760.608105	−7760.646467	
INT-11	0.831356	0.890023	0.733842	−12402.256582	−12401.366559	−12401.522740	
TS-12	0.830550	0.889241	0.730052	−12402.243014	−12401.353773	−12401.512962	18.2*i*
INT-13	0.830925	0.889938	0.731669	−12402.255668	−12401.365730	−12401.523999	

Supplementary Table 21 | Electronic energy changes along the carbon–sulfur stretch for the proposed intermediate of INT-1_R2 in Supplementary Fig. 27. Electronic energies are calculated at the B3LYP-D3(BJ)/Def2-SVP-SMD(dichloromethane) level of theory.

C–S Distance / Å	Δ*E* /Hartree	ΔΔ*E* /kcal/mol
2.40 (**INT-1**)	−4638.617306	0.0
2.45	−4638.617101	0.1
2.50	−4638.616536	0.5
2.55	−4638.615682	1.0
2.60	−4638.614597	1.7
2.65	−4638.613332	2.5
2.70	−4638.611930	3.4
2.75	−4638.610426	4.3
2.80	−4638.608846	5.3
2.85	−4638.607215	6.3
2.90	−4638.605552	7.4
2.95	−4638.603872	8.4
3.00	−4638.602190	9.5
3.05	−4638.600581	10.5
3.10	−4638.599161	11.4
3.15	−4638.598236	12.0
3.20	−4638.597225	12.6
3.25	−4638.596270	13.2
3.30	−4638.595578	13.6
3.35	−4638.594898	14.1
3.40	−4638.594240	14.5

Supplementary Table 22 | Electronic energy changes along the carbon–sulfur distance during radical substitution by the tribromomethyl radical in Supplementary Fig. 32. Electronic energies are calculated at the B3LYP-D3(BJ)/Def2-SVP-SMD(dichloromethane) level of theory.

Structure	C–S Distance / Å	Δ*E* /Hartree	ΔΔ*E* /kcal/mol
INT-1 + INT-10	/	−12398.252353	0.0
INT-11	1.92	−12398.283600	−19.6
INT-11_R1	2.30	−12398.273107	−13.0
INT-11_R2	2.35	−12398.272362	−12.6
INT-11_R3	2.37	−12398.272130	−12.4
INT-11_R4	2.40	−12398.271834	−12.2
INT-11_R5	2.43	−12398.271583	−12.1
INT-11_R6	2.45	−12398.271437	−12.0
INT-11_R7	2.50	−12398.271125	−11.8
INT-11_R8	2.52	−12398.271020	−11.7
INT-11_R9	2.55	−12398.270882	−11.6
INT-11_R10	2.60	−12398.270694	−11.5
INT-11_R11	2.64	−12398.270573	−11.4
INT-11_R12	2.67	−12398.270495	−11.4
INT-11_R13	2.69	−12398.270446	−11.4
INT-11_R14	2.72	−12398.270378	−11.3
INT-11_R15	2.75	−12398.270311	−11.3
INT-11_R16	2.80	−12398.270196	−11.2
INT-11_R17	2.85	−12398.270070	−11.1
INT-11_R18	2.90	−12398.269923	−11.0
INT-11_R19	3.00	−12398.269564	−10.8

10. References

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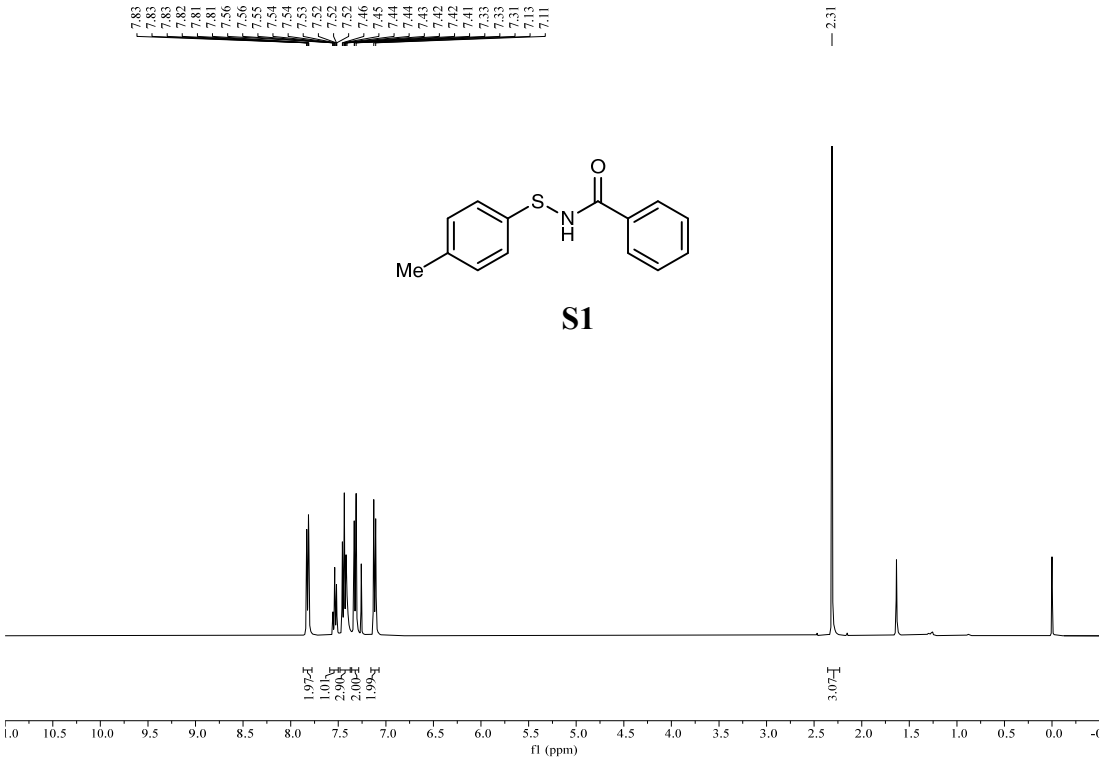
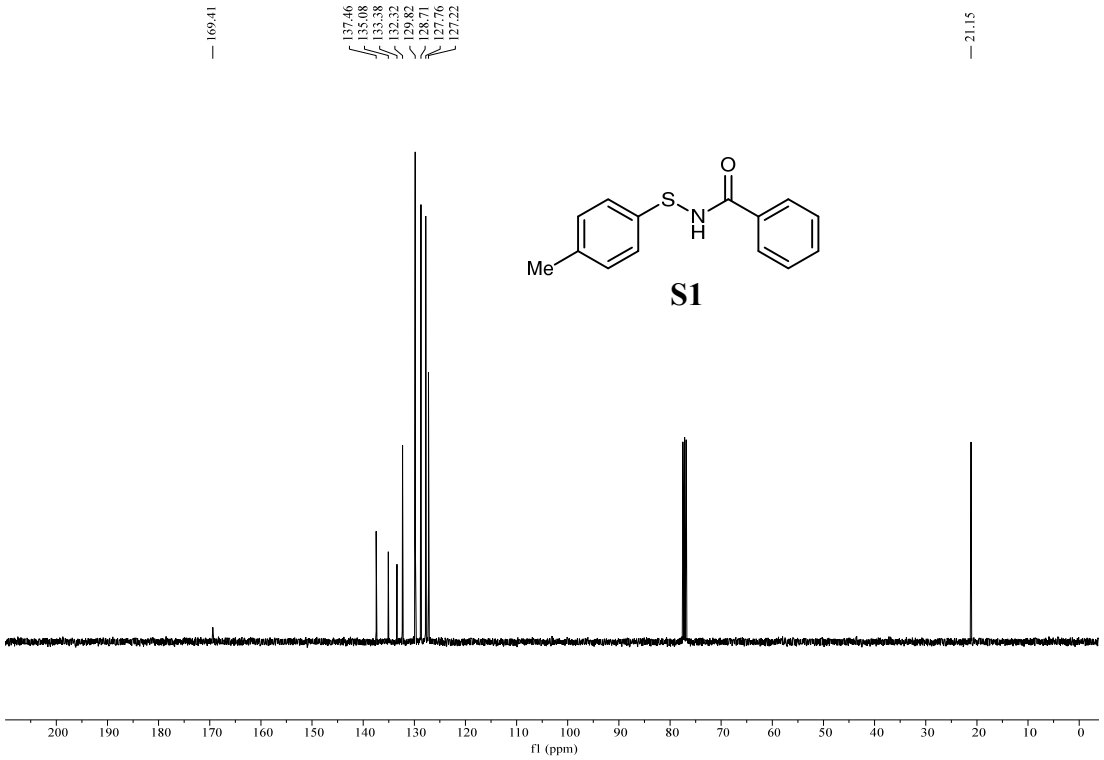
11. NMR spectra

^{1}H NMR of S1 (400 MHz, $CDCl_3$)



S1

^{13}C NMR of S1 (100 MHz, $CDCl_3$)



S1

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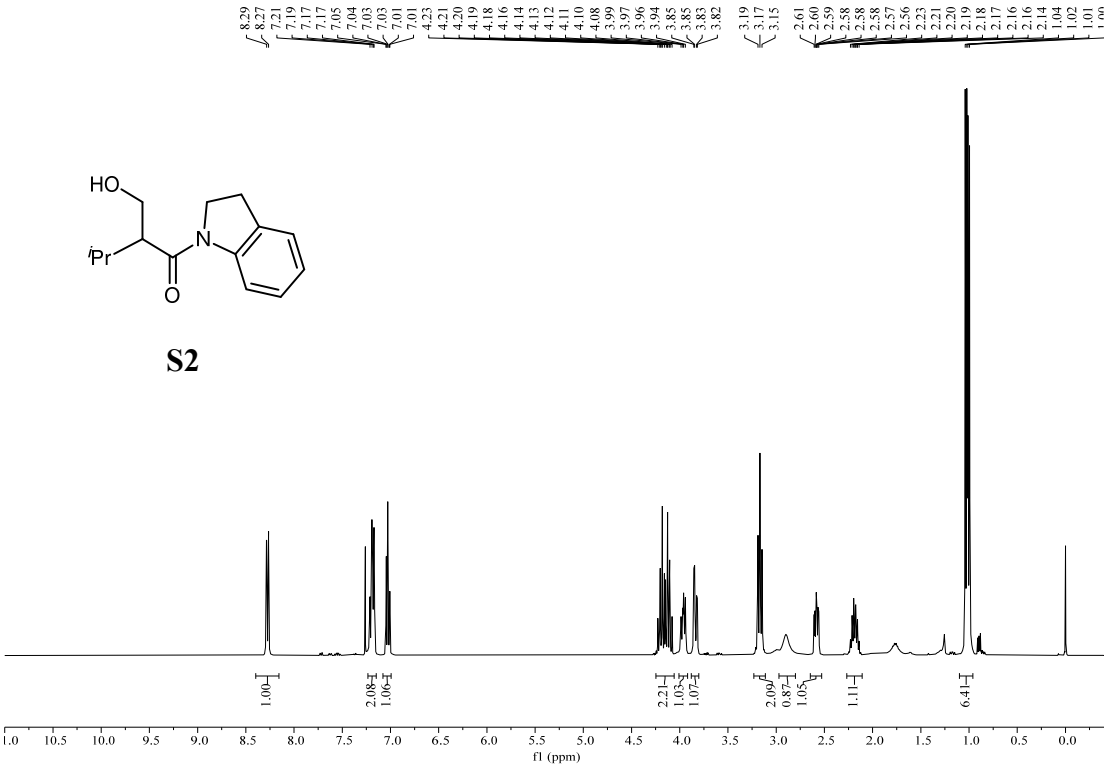

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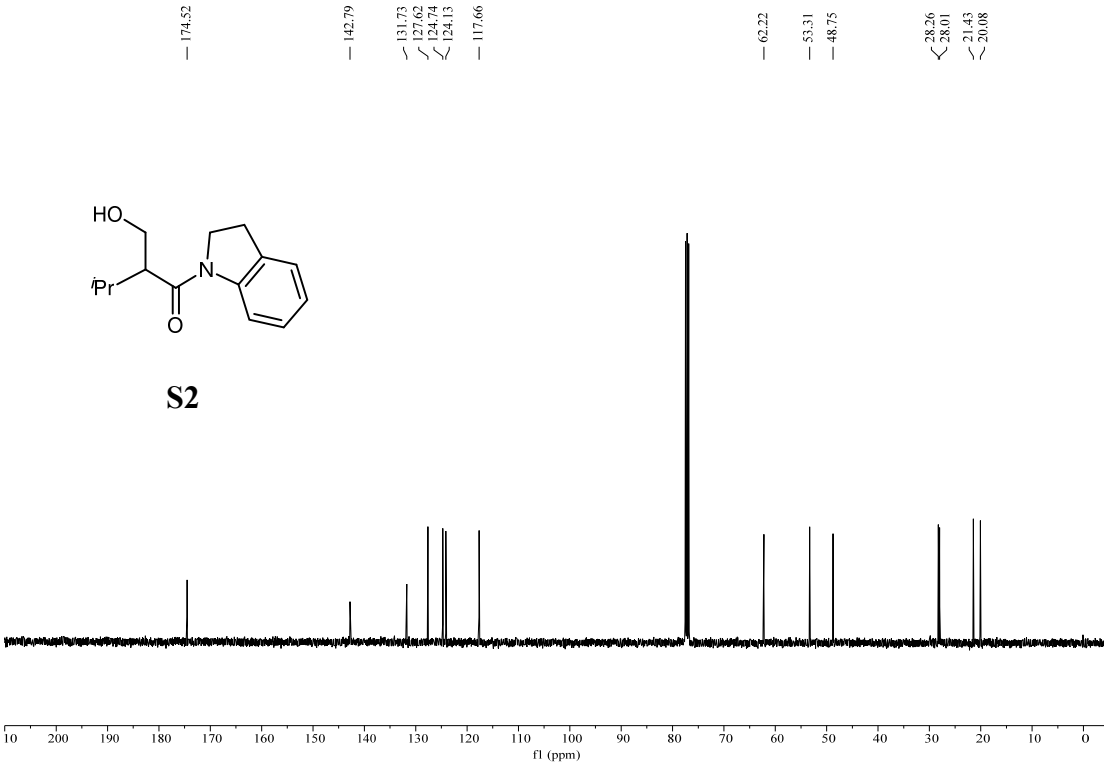

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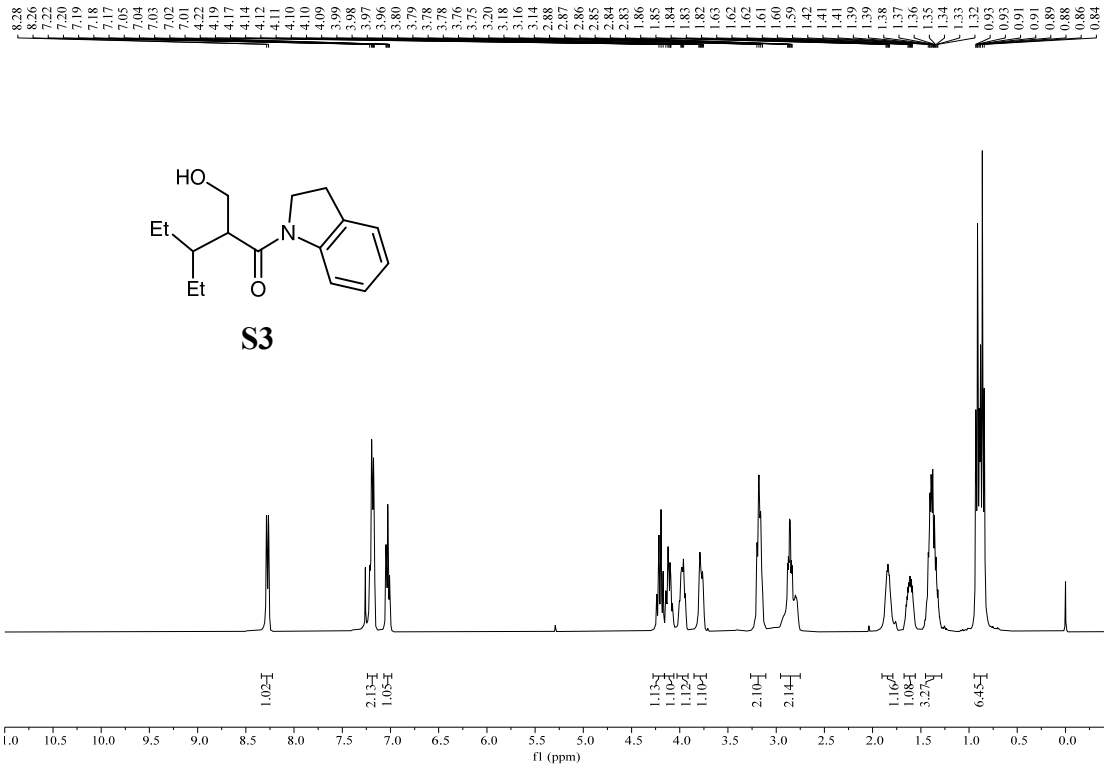

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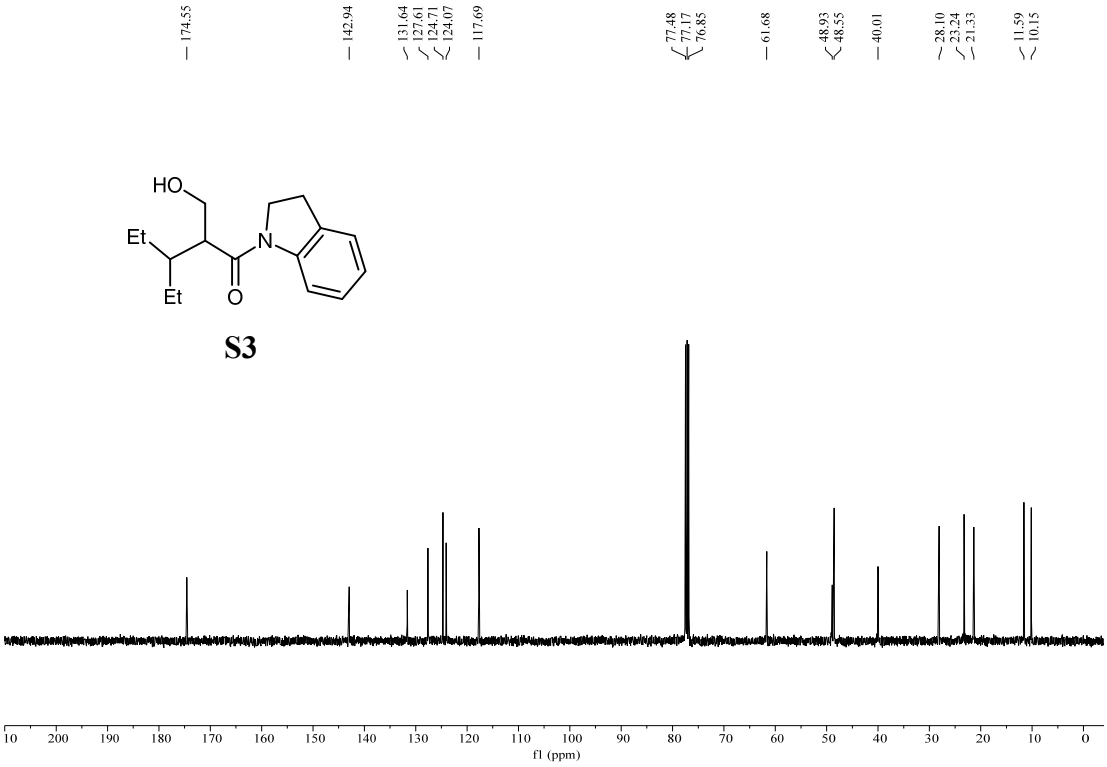

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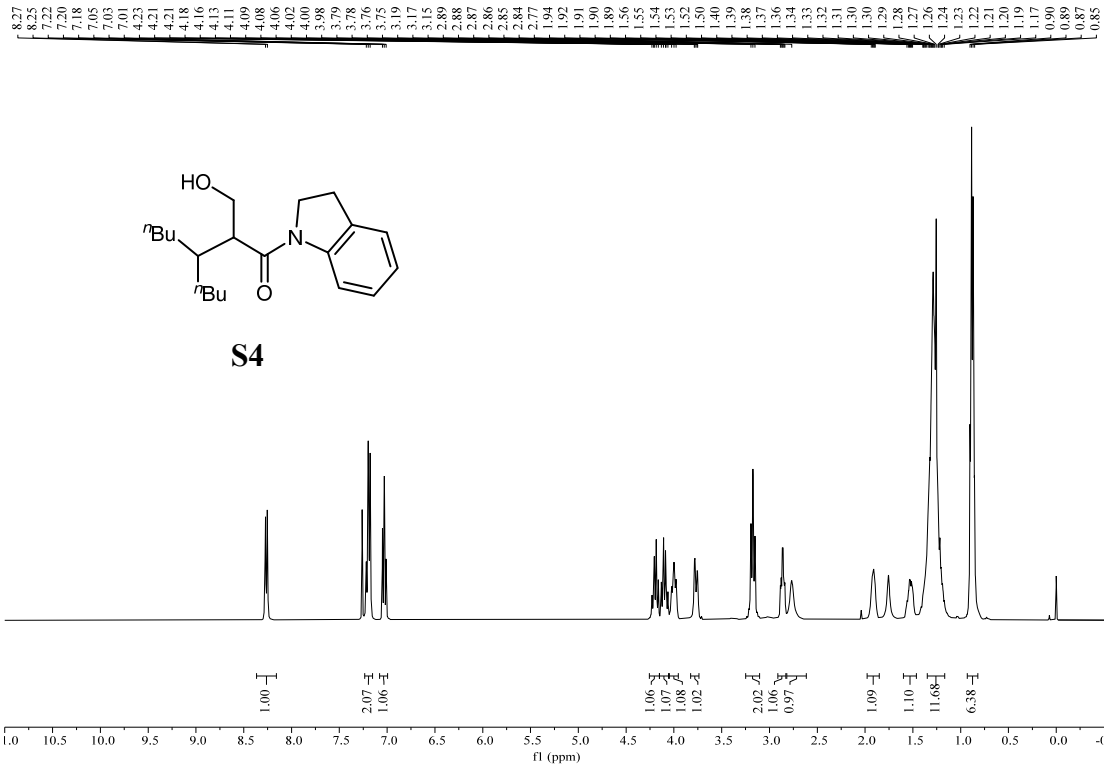

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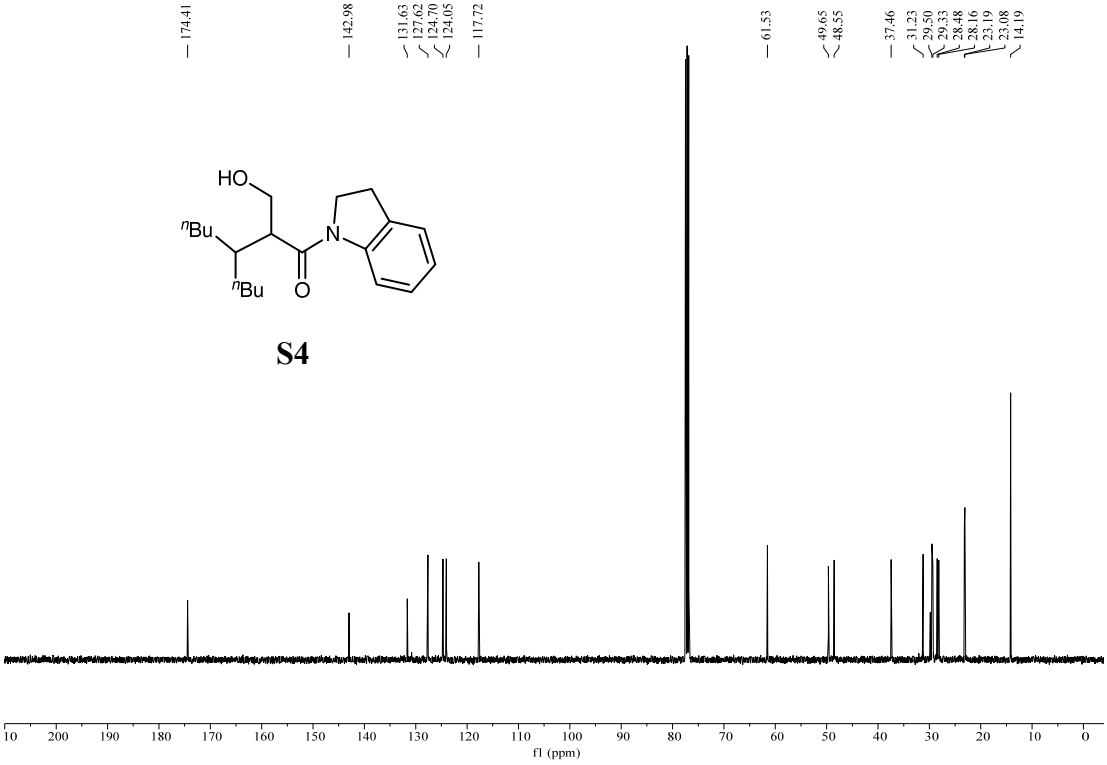

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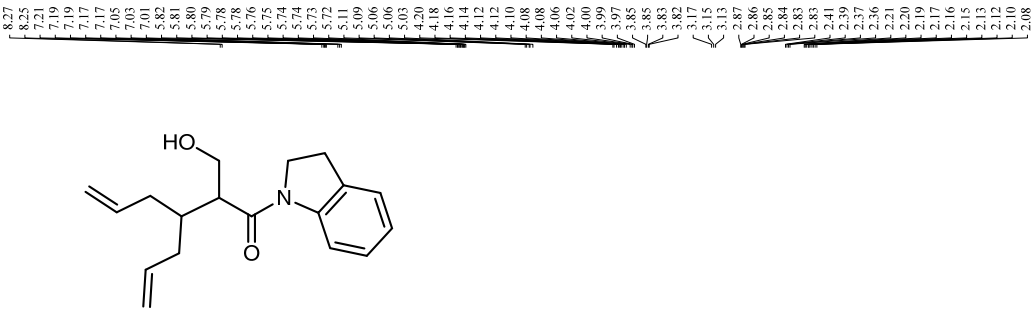
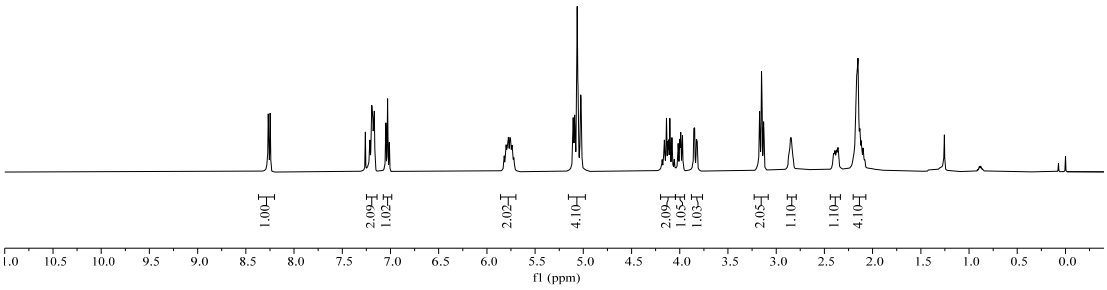


S5



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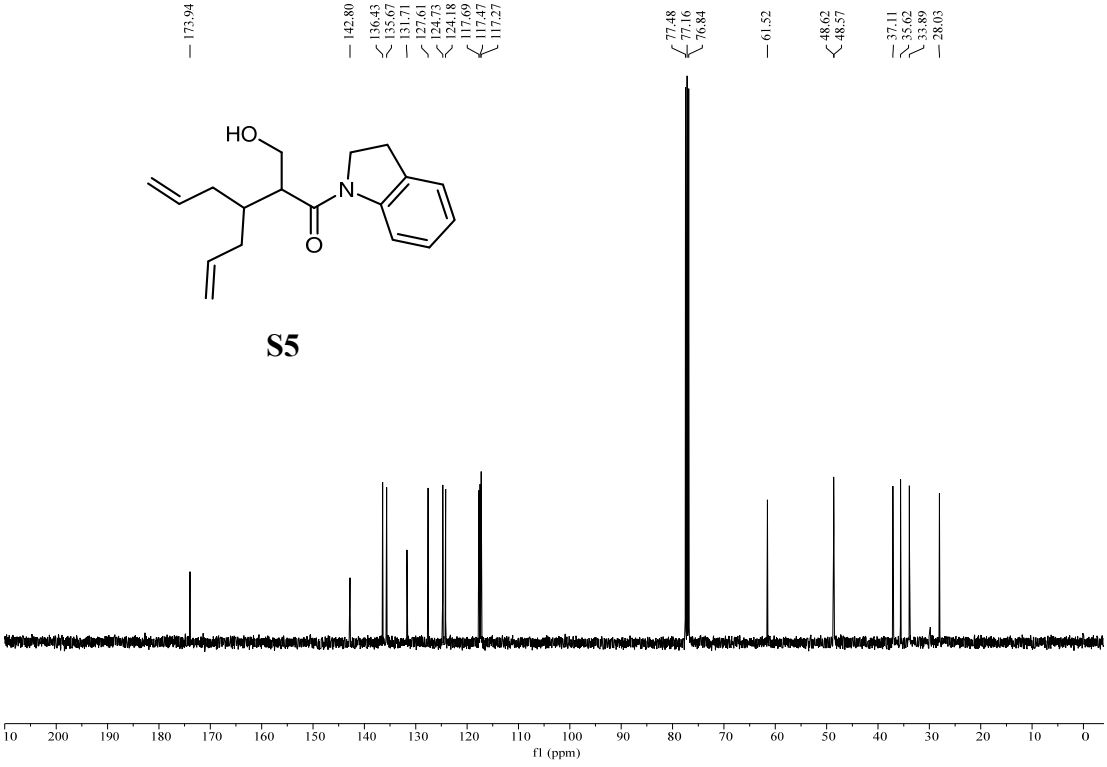

S5

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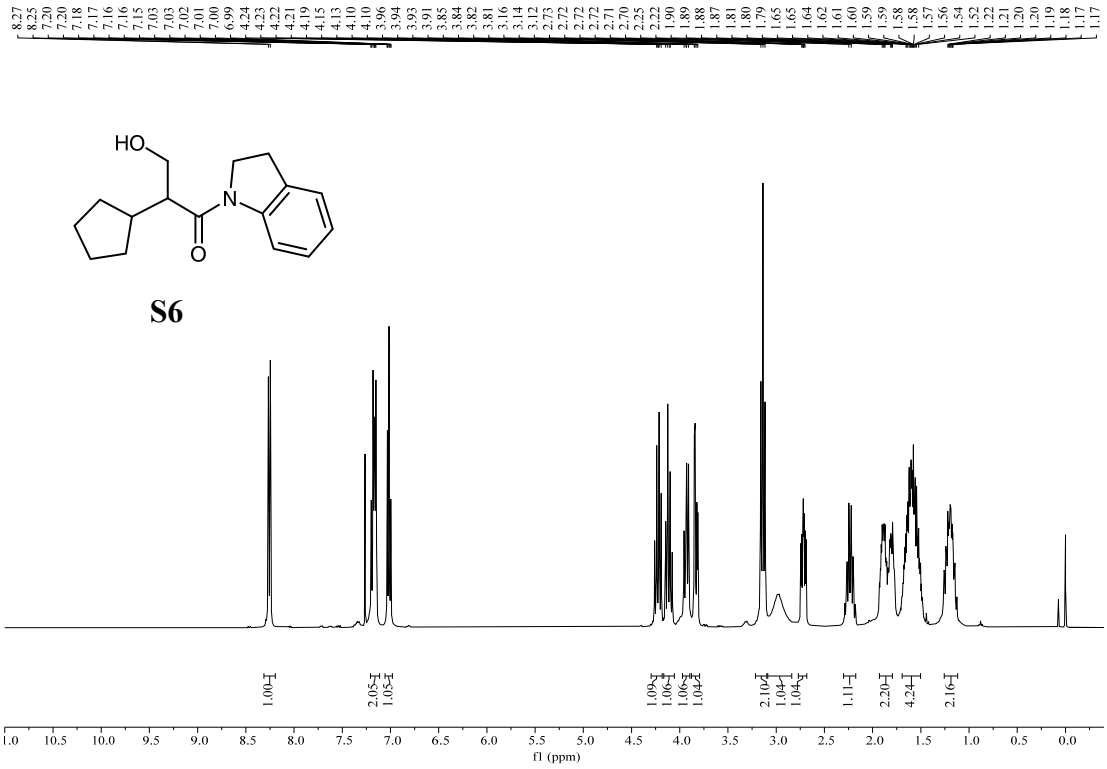

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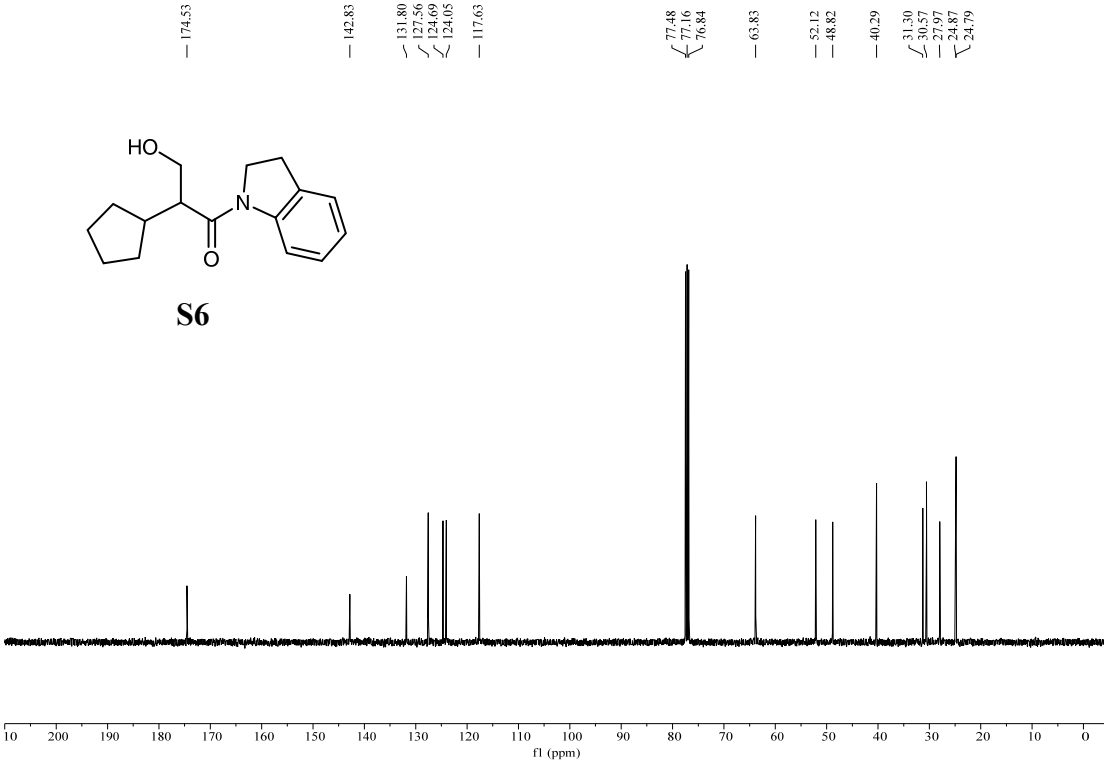

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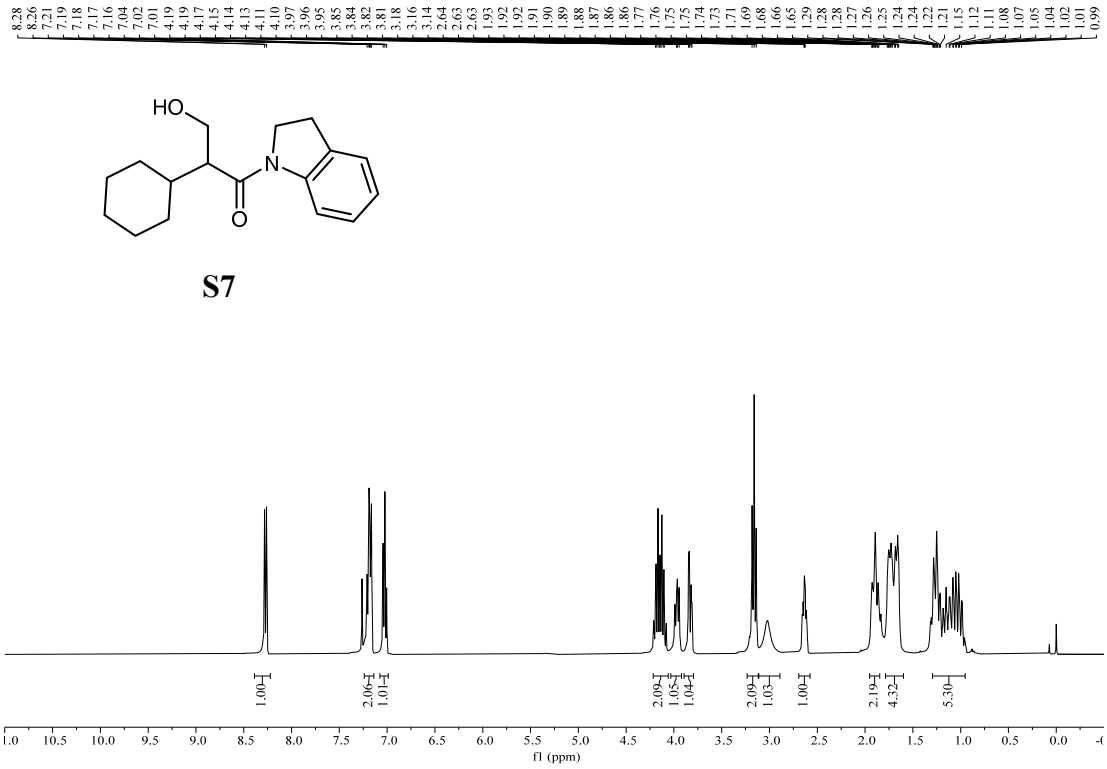

S7

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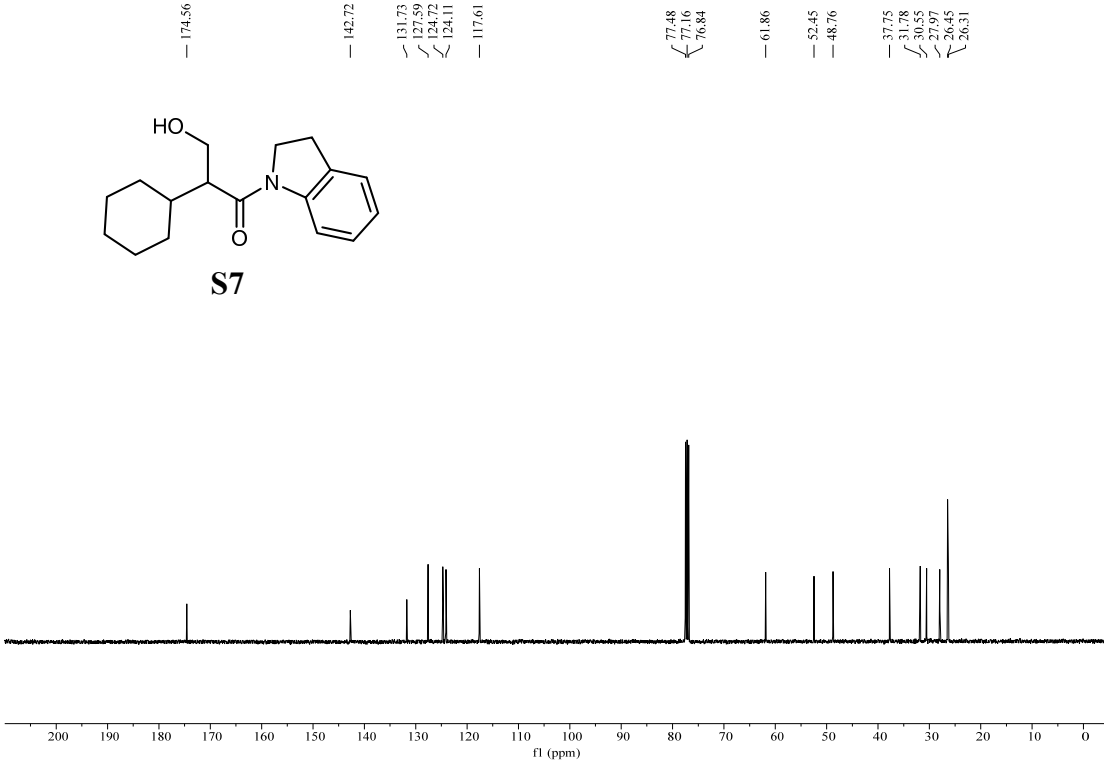

S7

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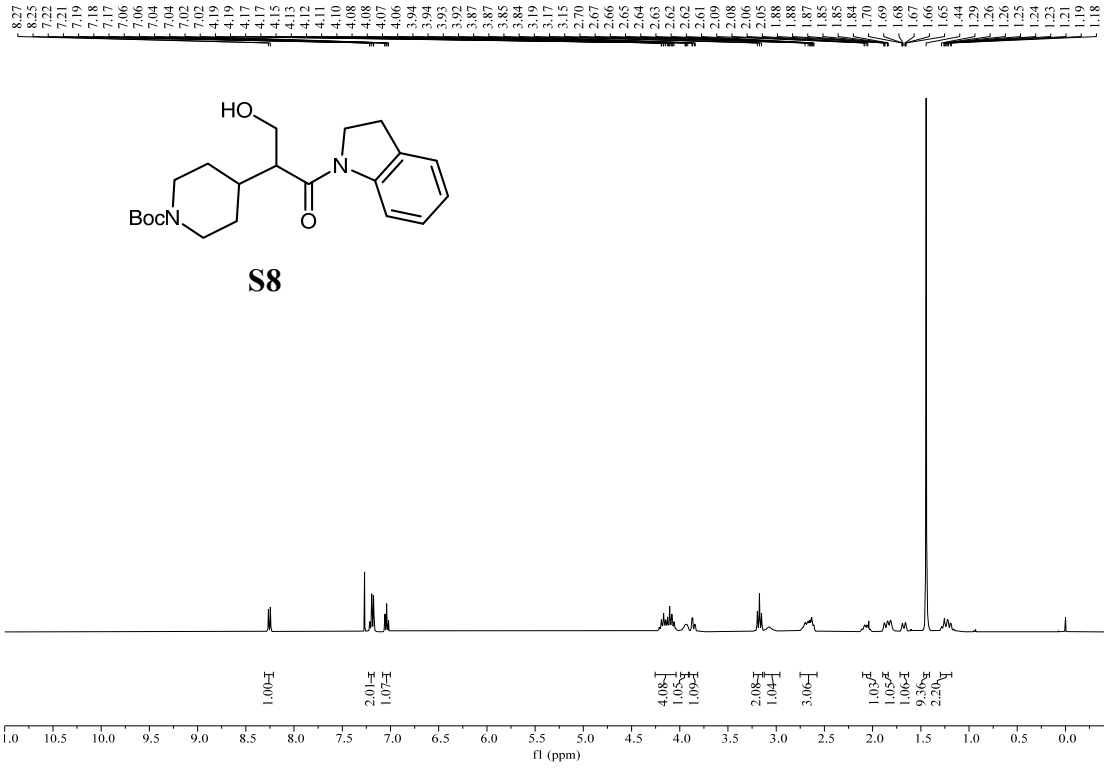

S8

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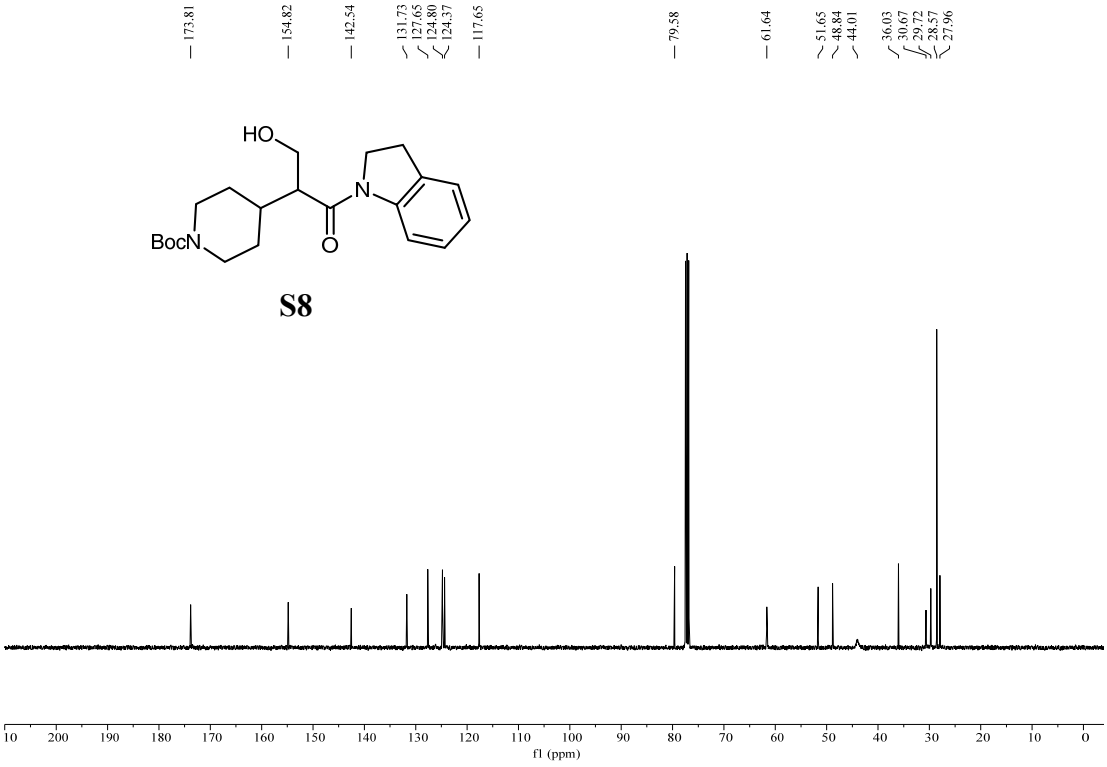

S8

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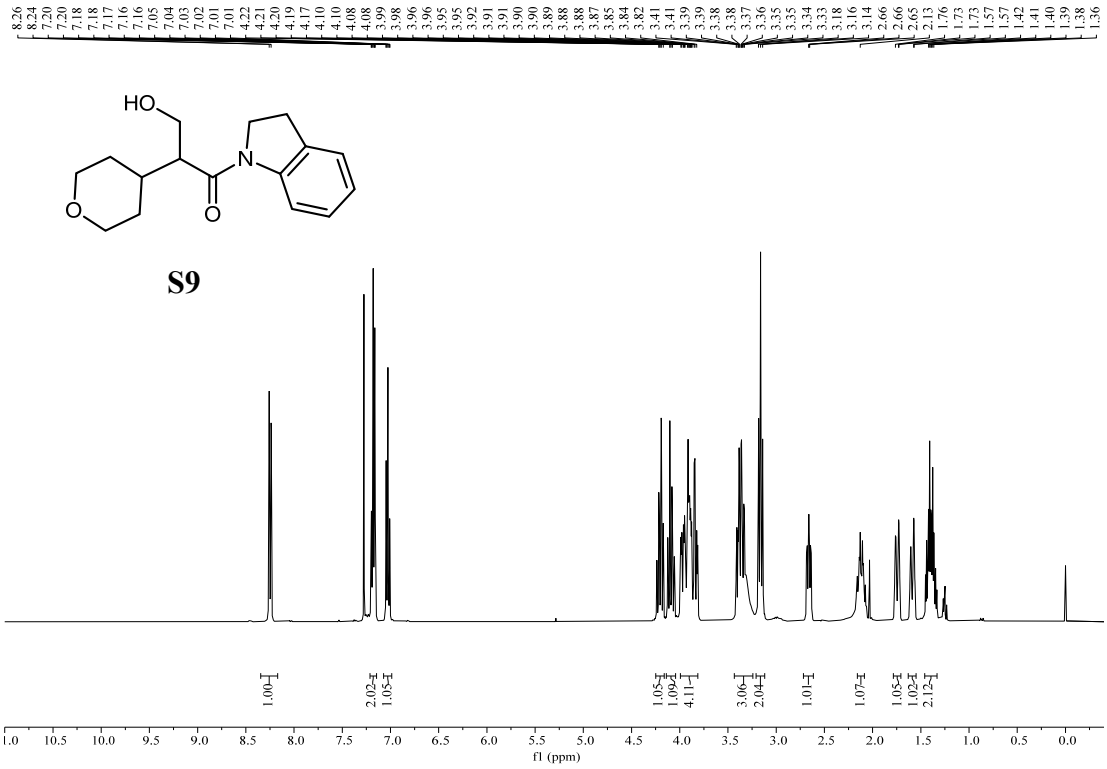

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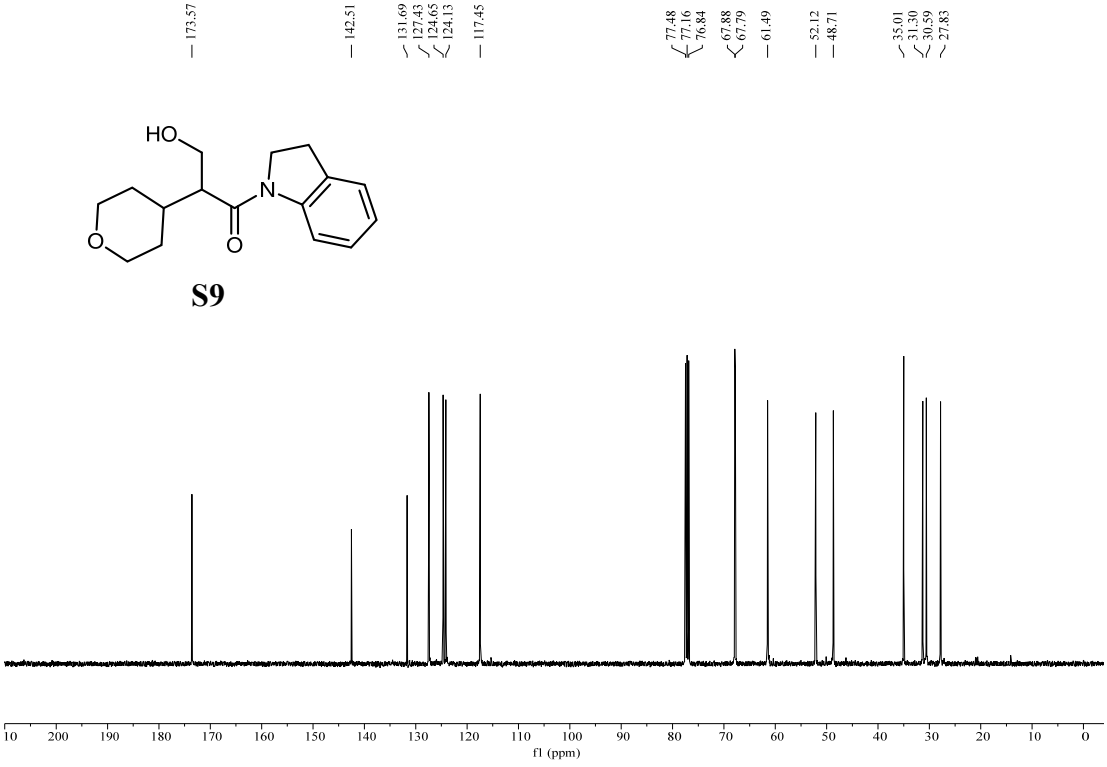
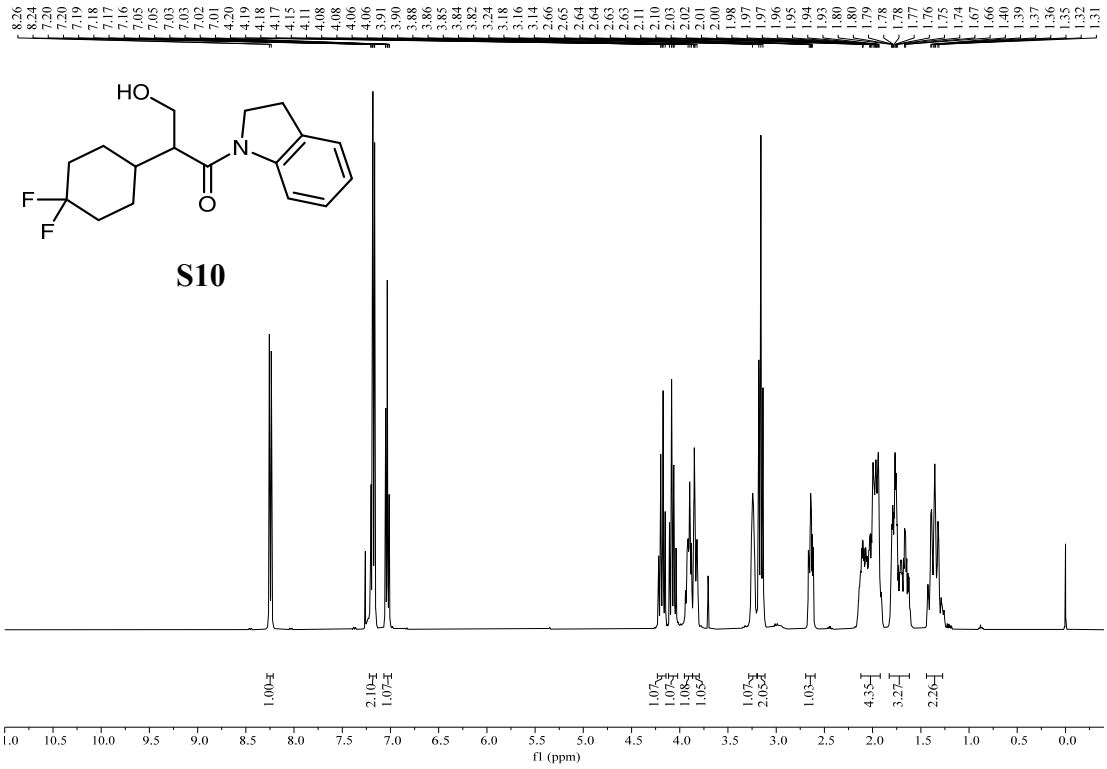
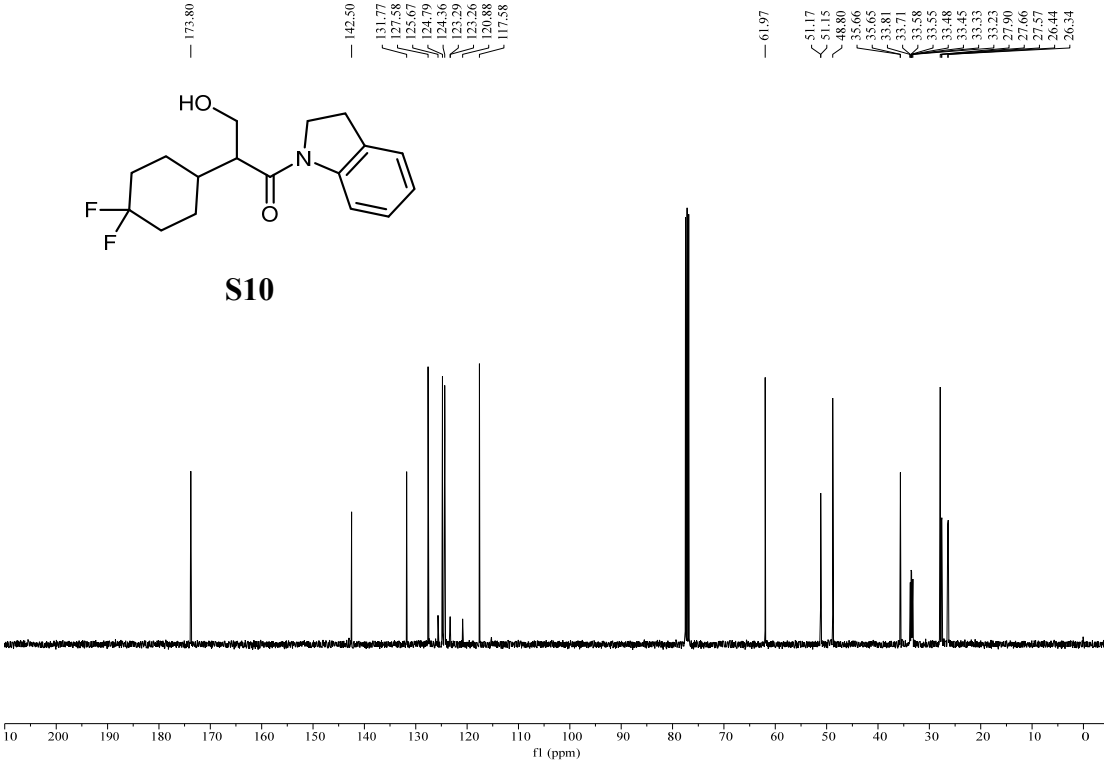


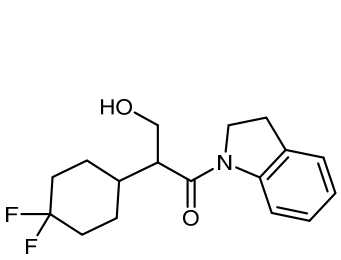
^{1}H NMR of S10 (400 MHz, $CDCl_3$)



^{13}C NMR of S10 (100 MHz, $CDCl_3$)

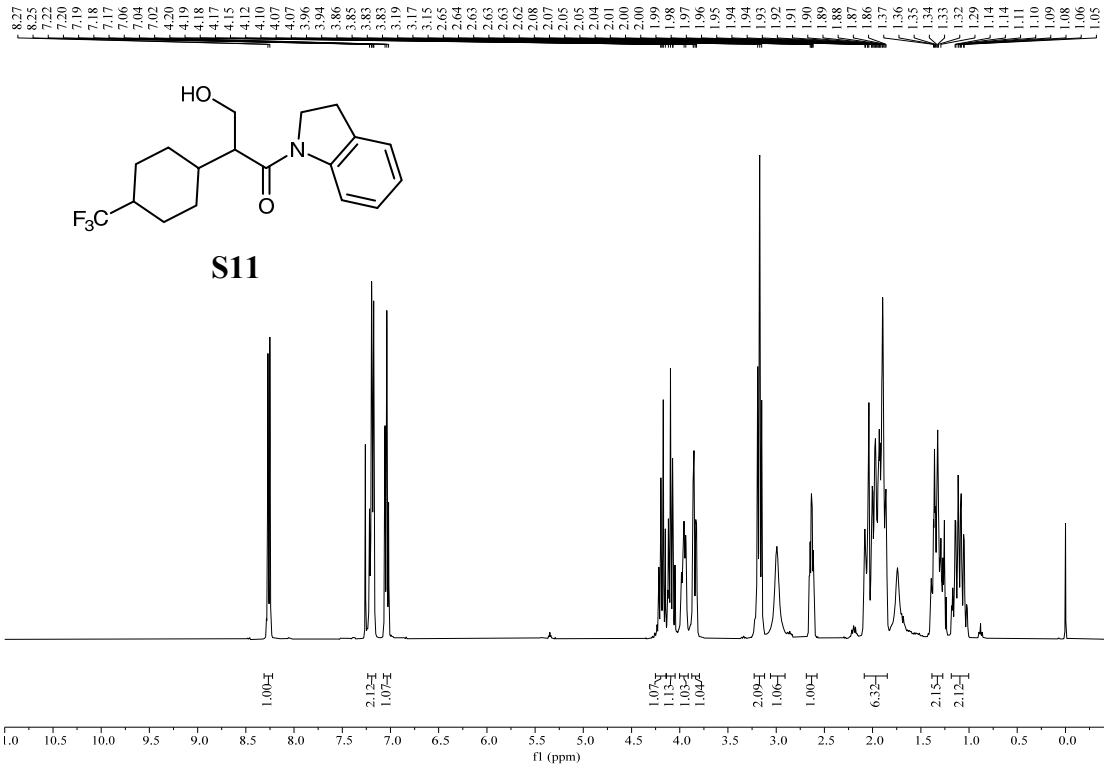


^{19}F NMR of S10 (375 MHz, $CDCl_3$)

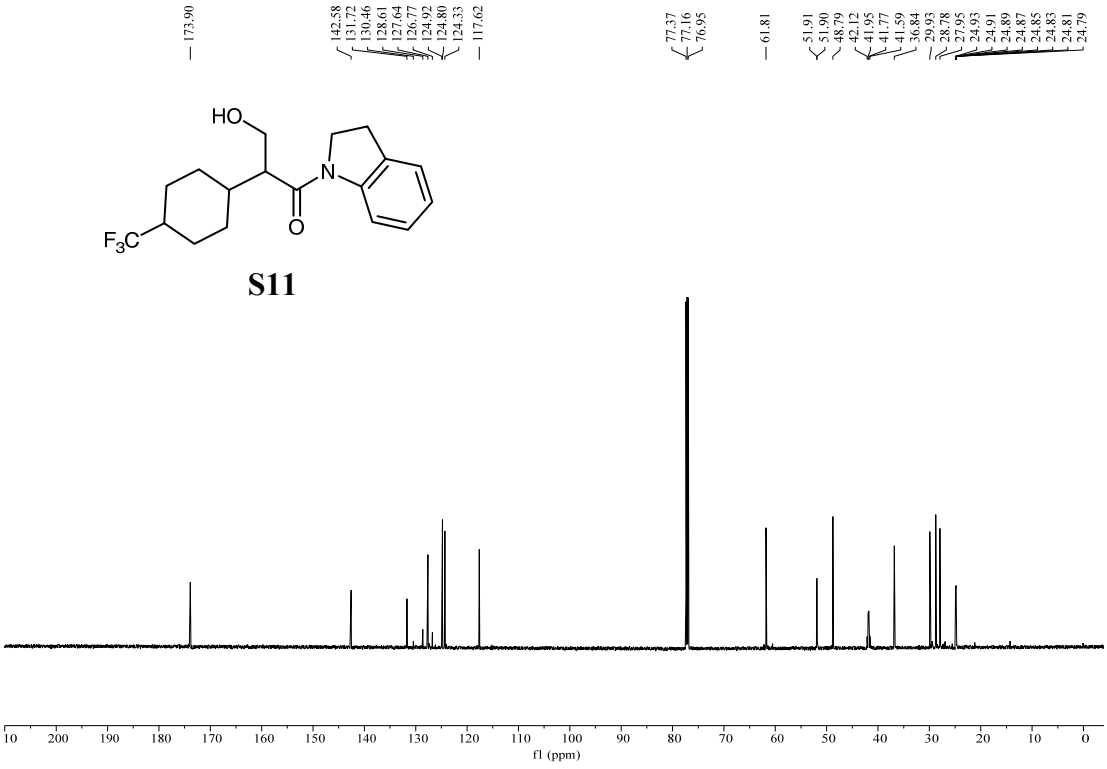


S10

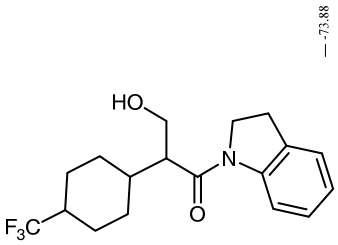
^{1}H NMR of S11 (400 MHz, $CDCl_3$)



^{13}C NMR of S11 (150 MHz, $CDCl_3$)

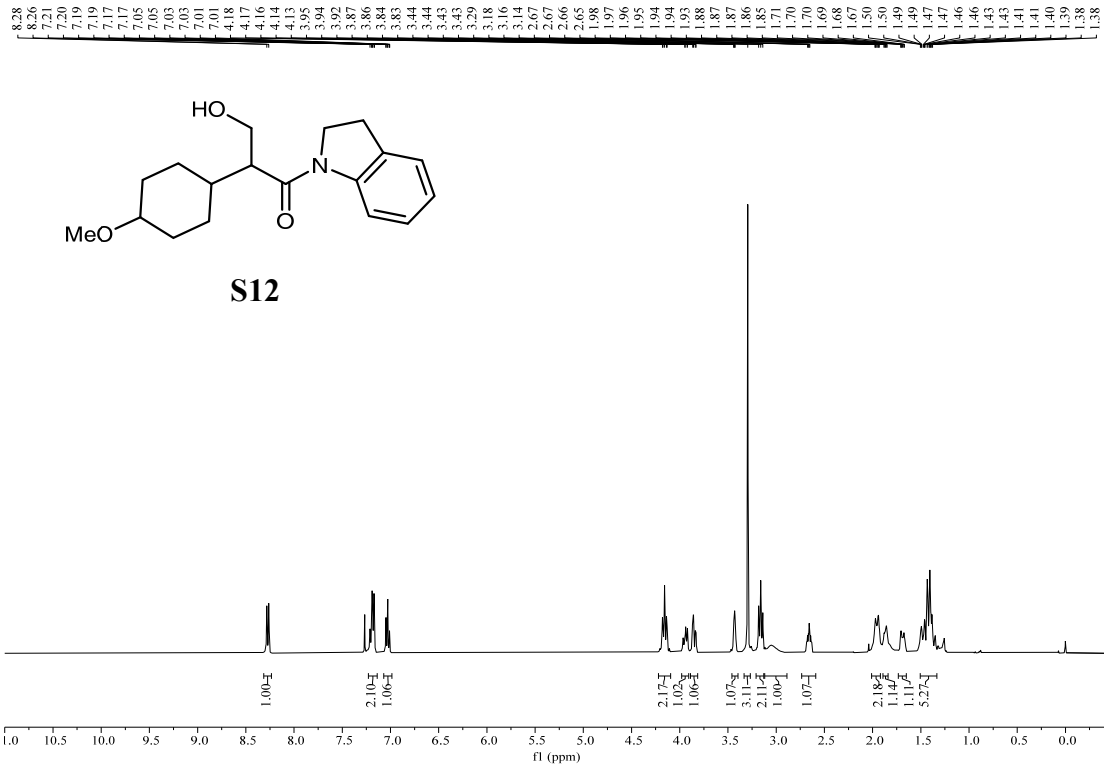


^{19}F NMR of S11 (375 MHz, $CDCl_3$)



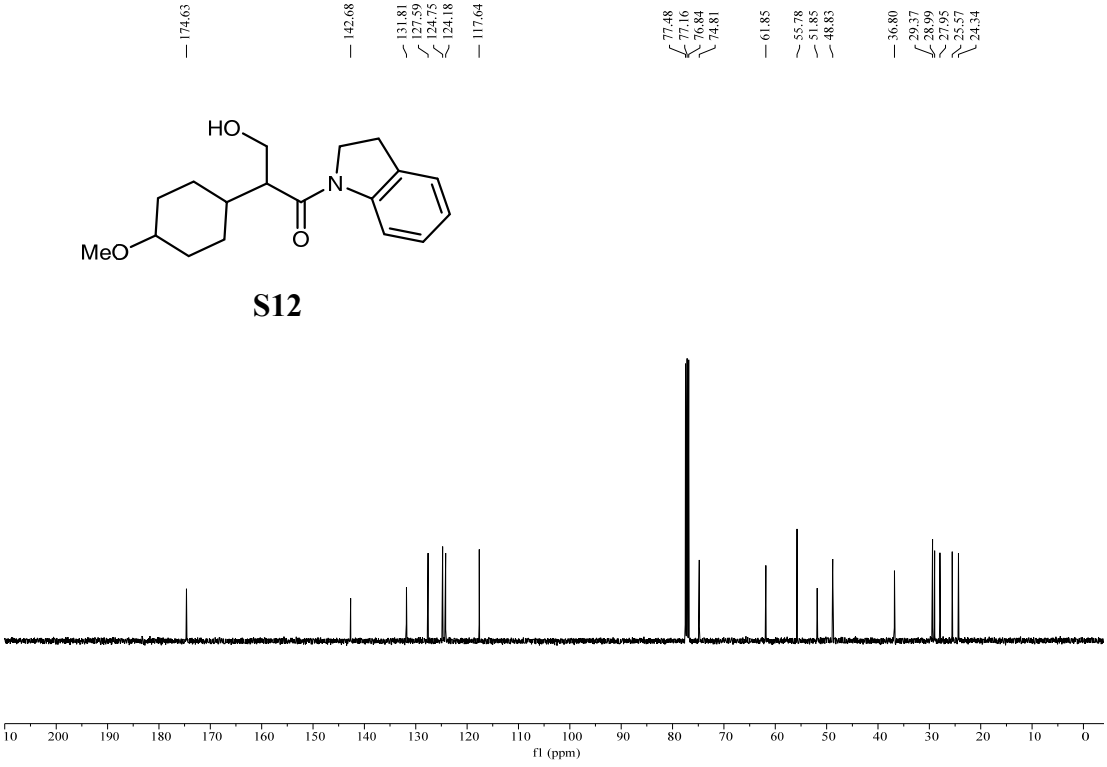
S11

^{1}H NMR of S12 (400 MHz, $CDCl_3$)



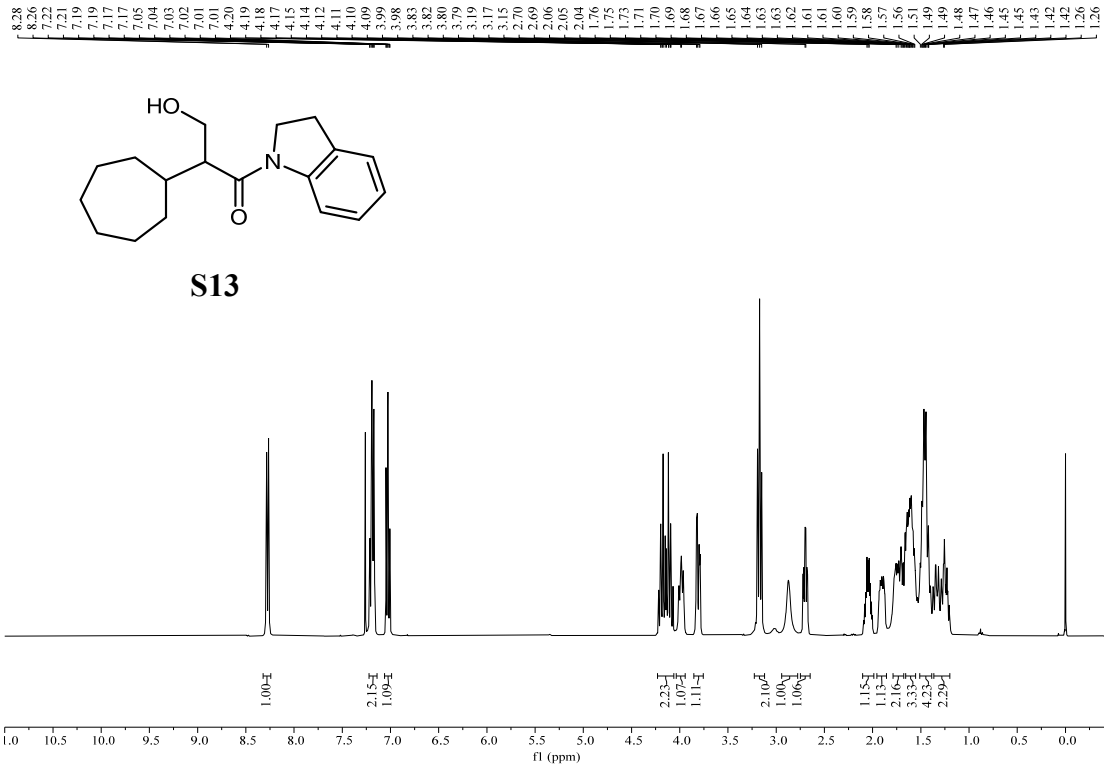
S12

^{13}C NMR of S12 (100 MHz, $CDCl_3$)

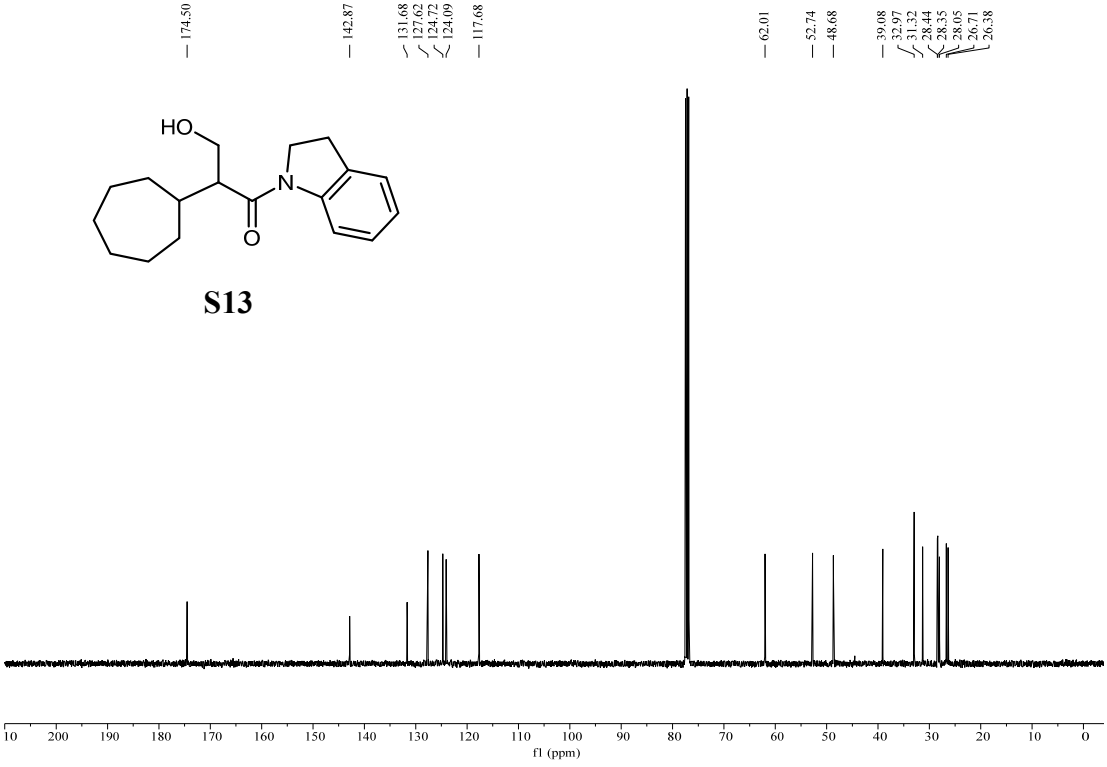


S12

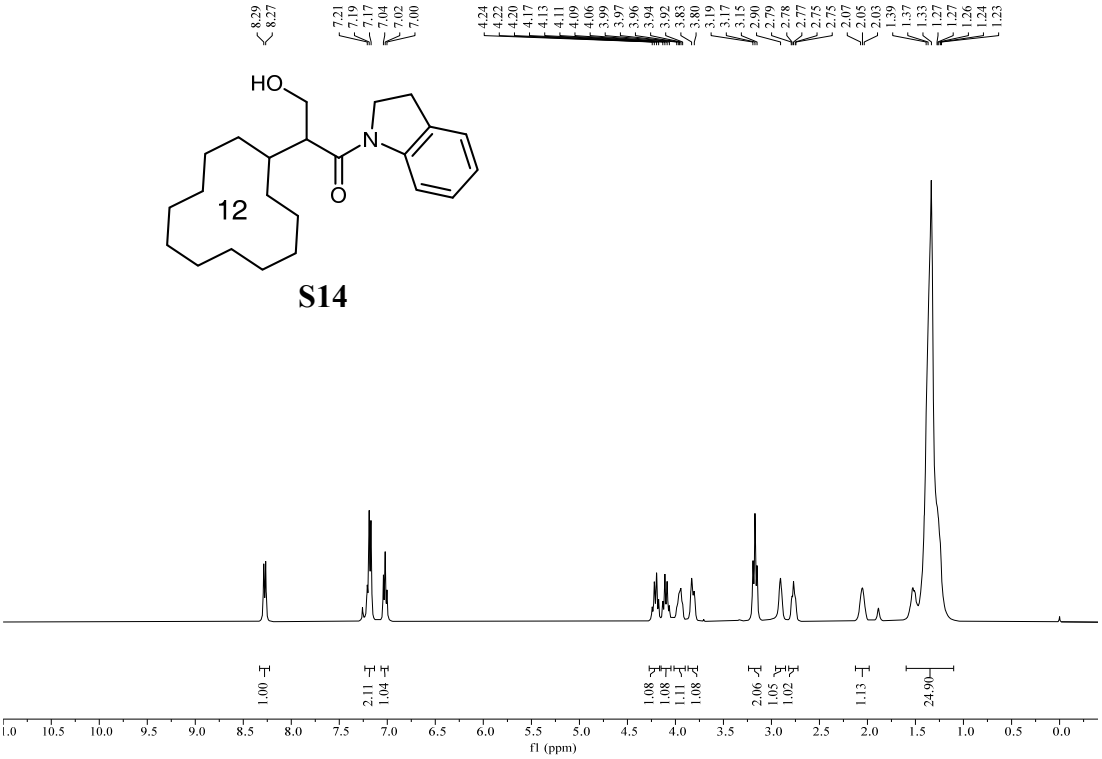
^{1}H NMR of S13 (400 MHz, $CDCl_3$)



^{13}C NMR of S13 (100 MHz, $CDCl_3$)

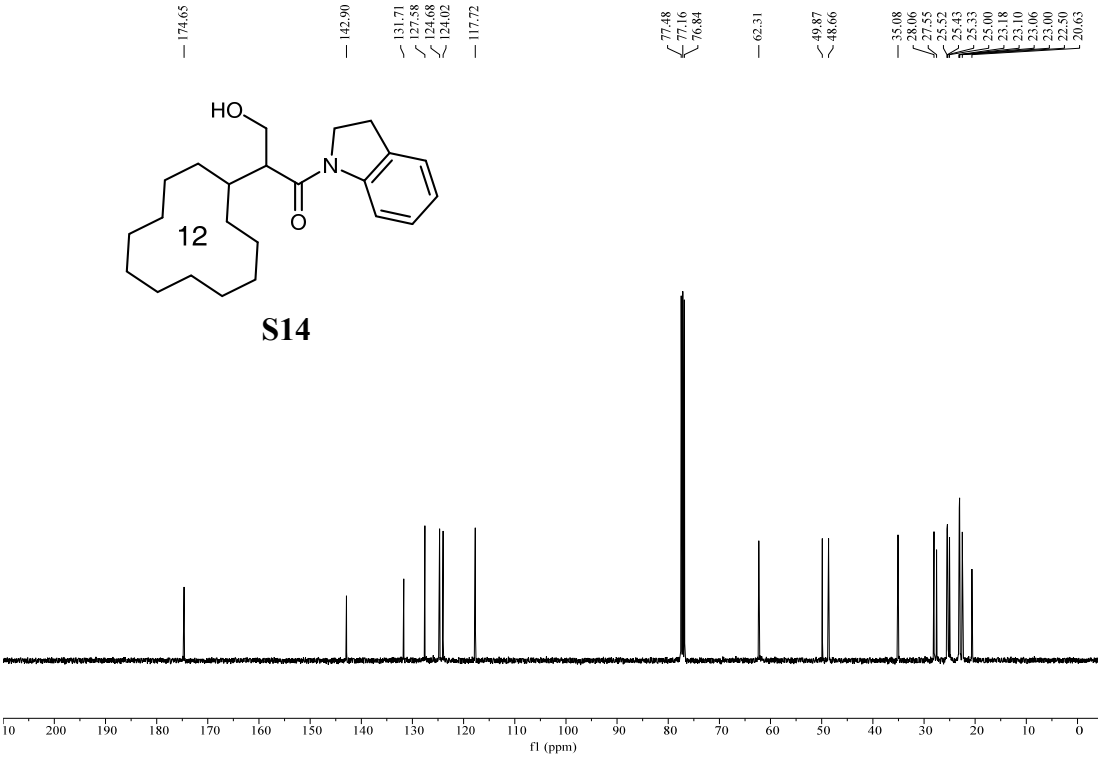


^{1}H NMR of S14 (400 MHz, $CDCl_3$)



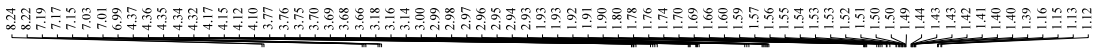
S14

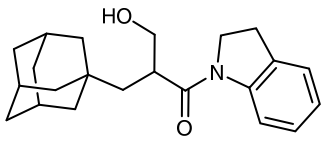
^{13}C NMR of S14 (100 MHz, $CDCl_3$)



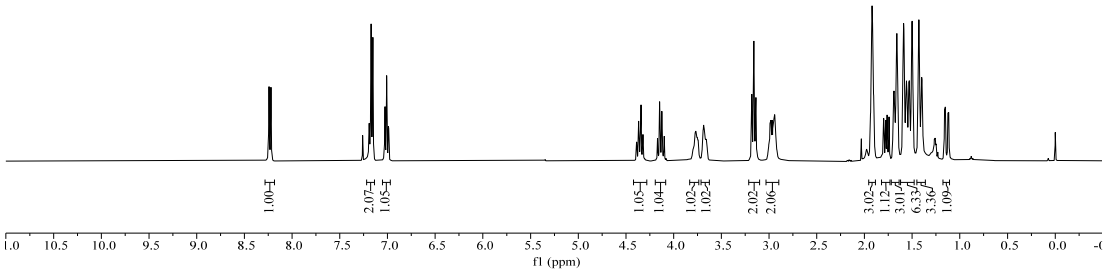
S14

^{1}H NMR of S15 (400 MHz, $CDCl_3$)

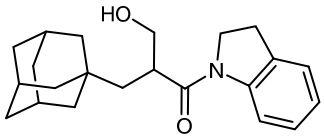




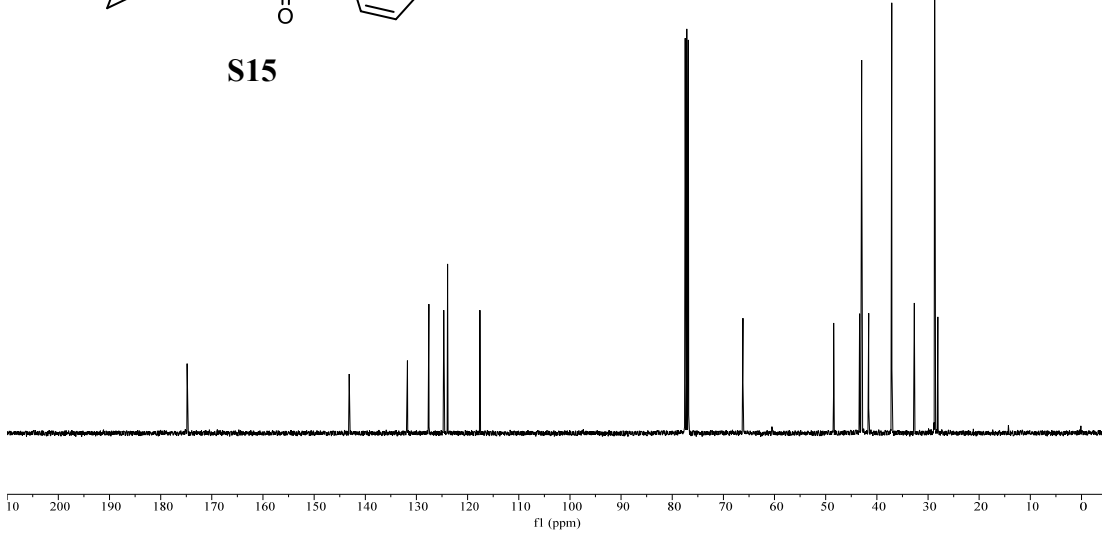
S15



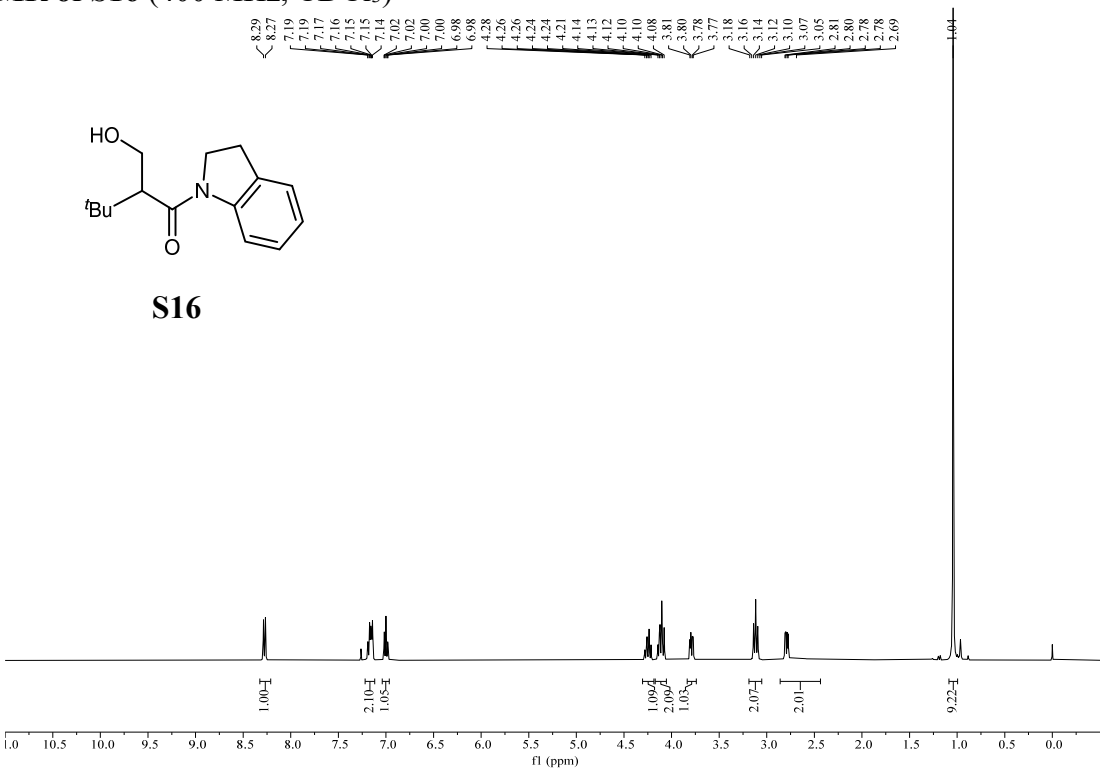
^{13}C NMR of S15 (100 MHz, $CDCl_3$)



S15

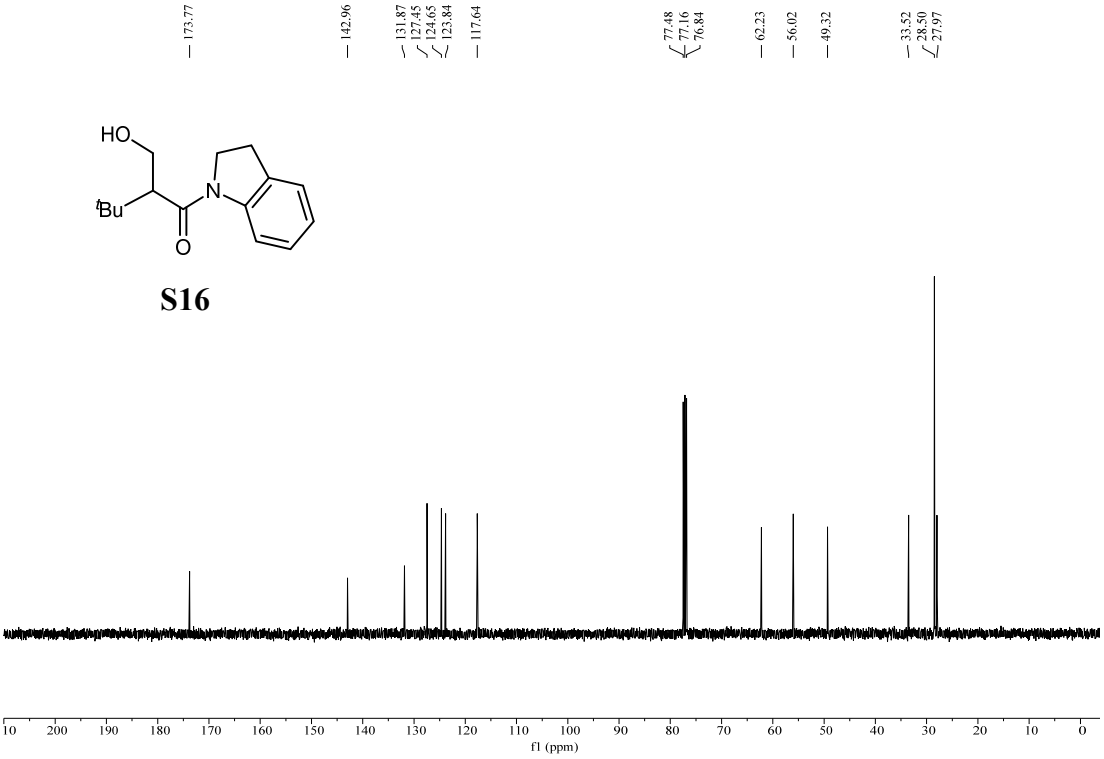


^{1}H NMR of S16 (400 MHz, $CDCl_3$)



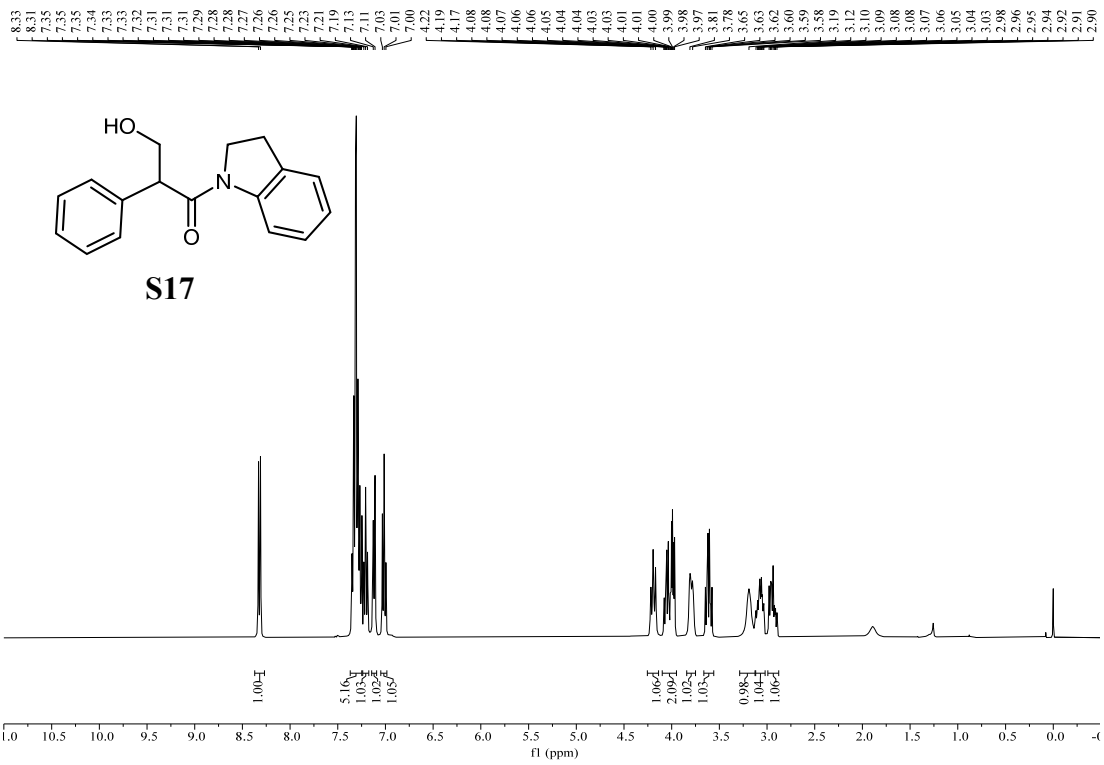
S16

^{13}C NMR of S16 (100 MHz, $CDCl_3$)

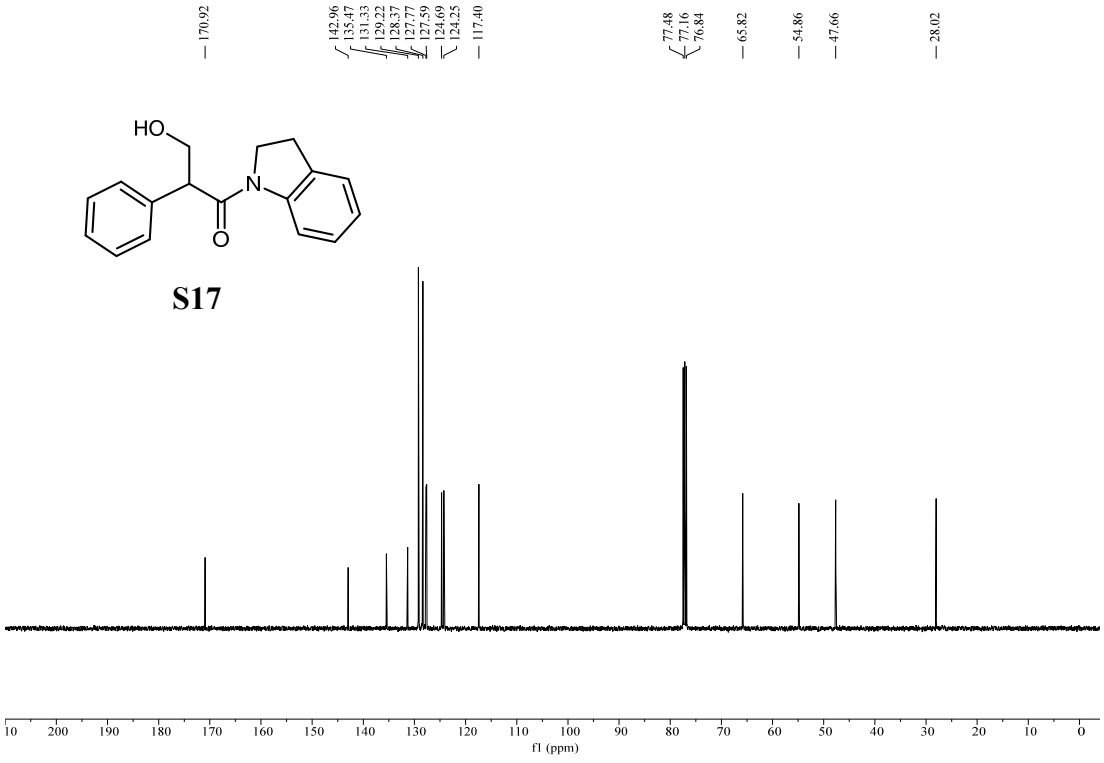


S16

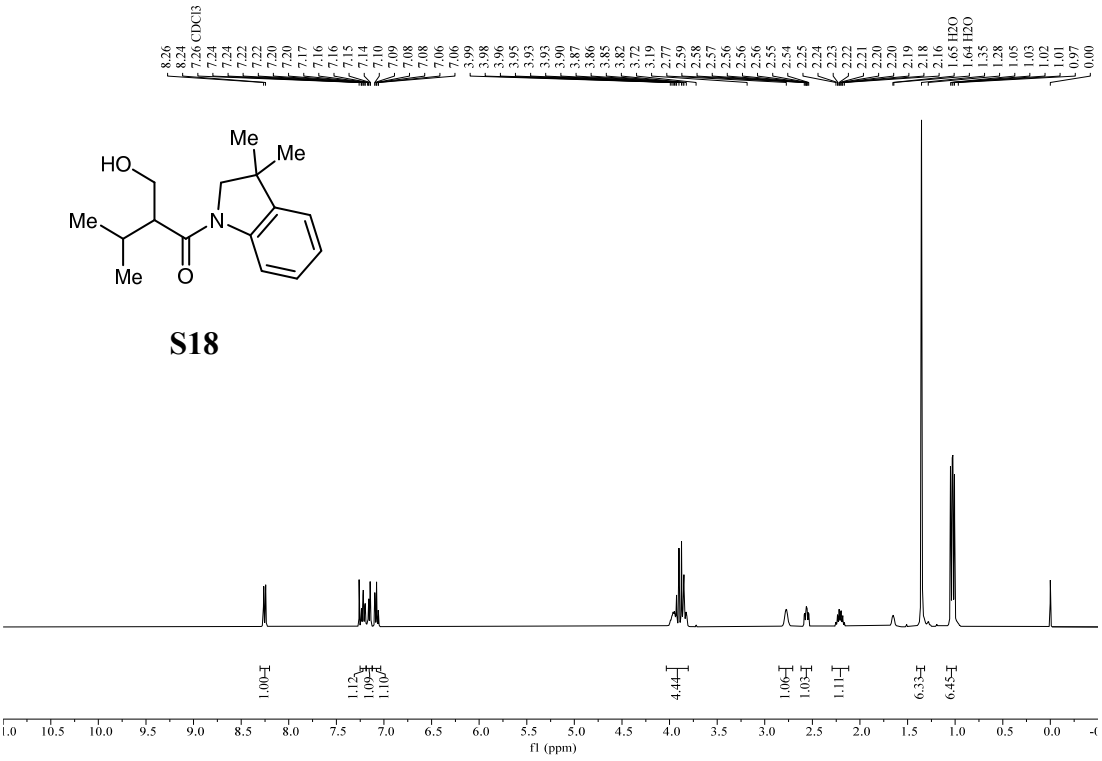
^{1}H NMR of S17 (400 MHz, $CDCl_3$)



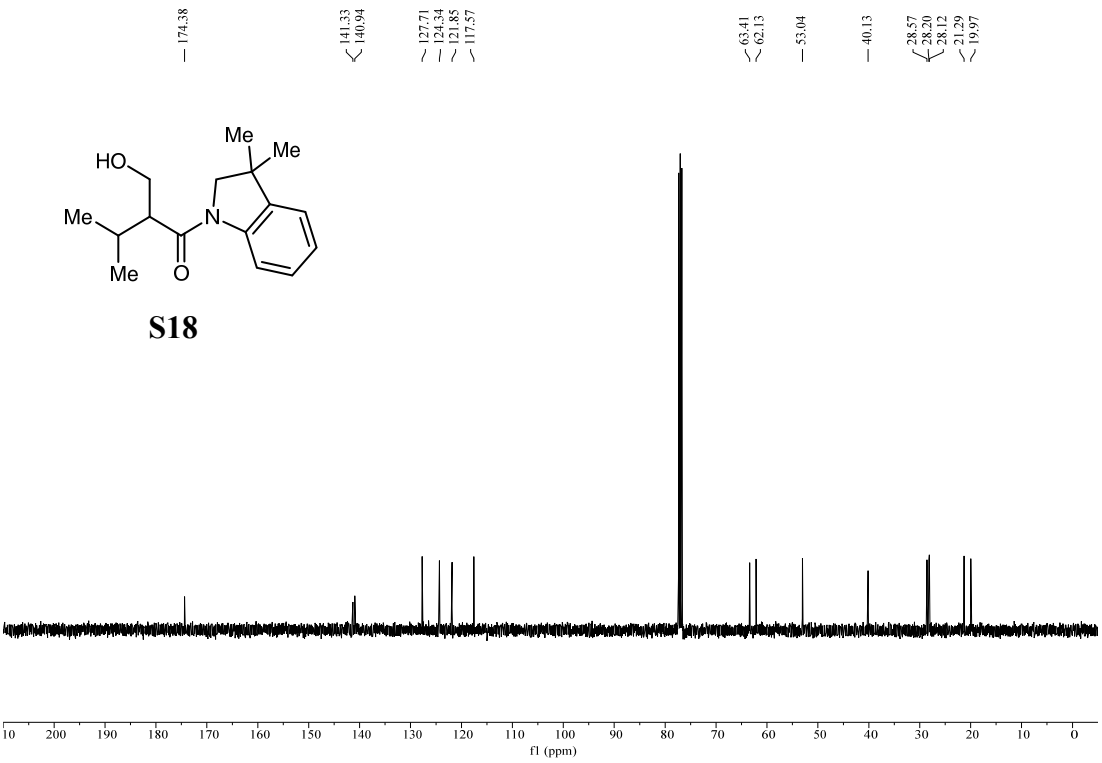
^{13}C NMR of S17 (100 MHz, $CDCl_3$)



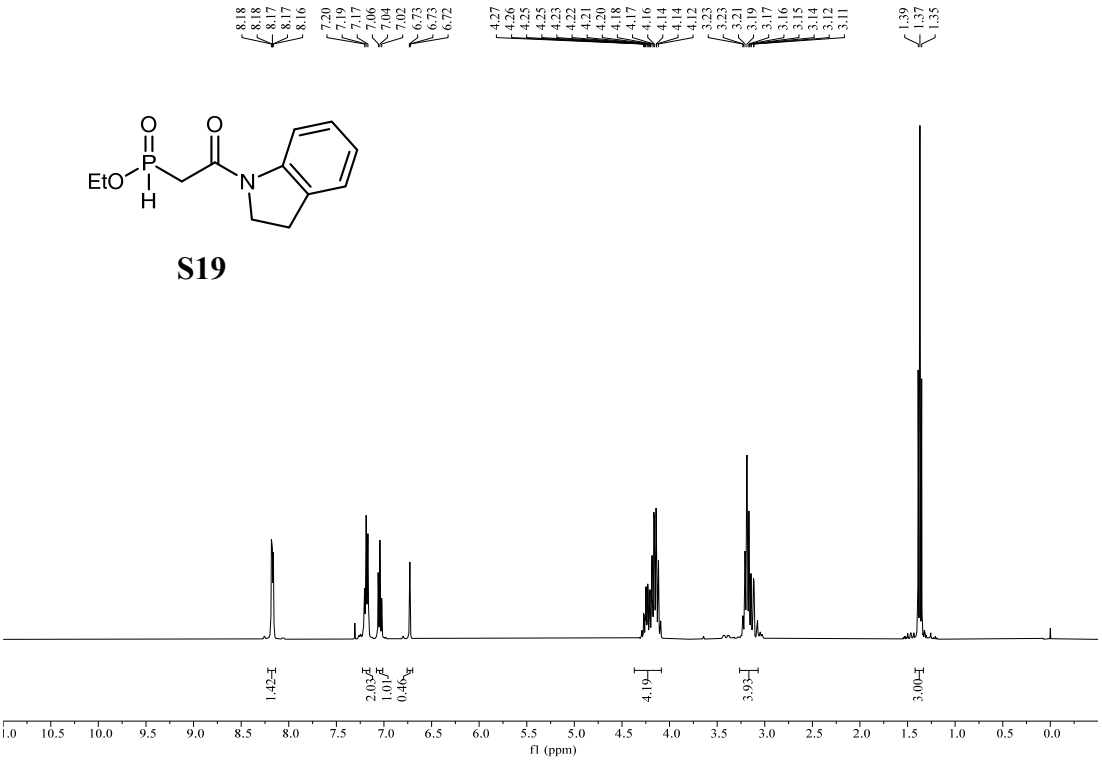
^{1}H NMR of S18 (400 MHz, $CDCl_3$)



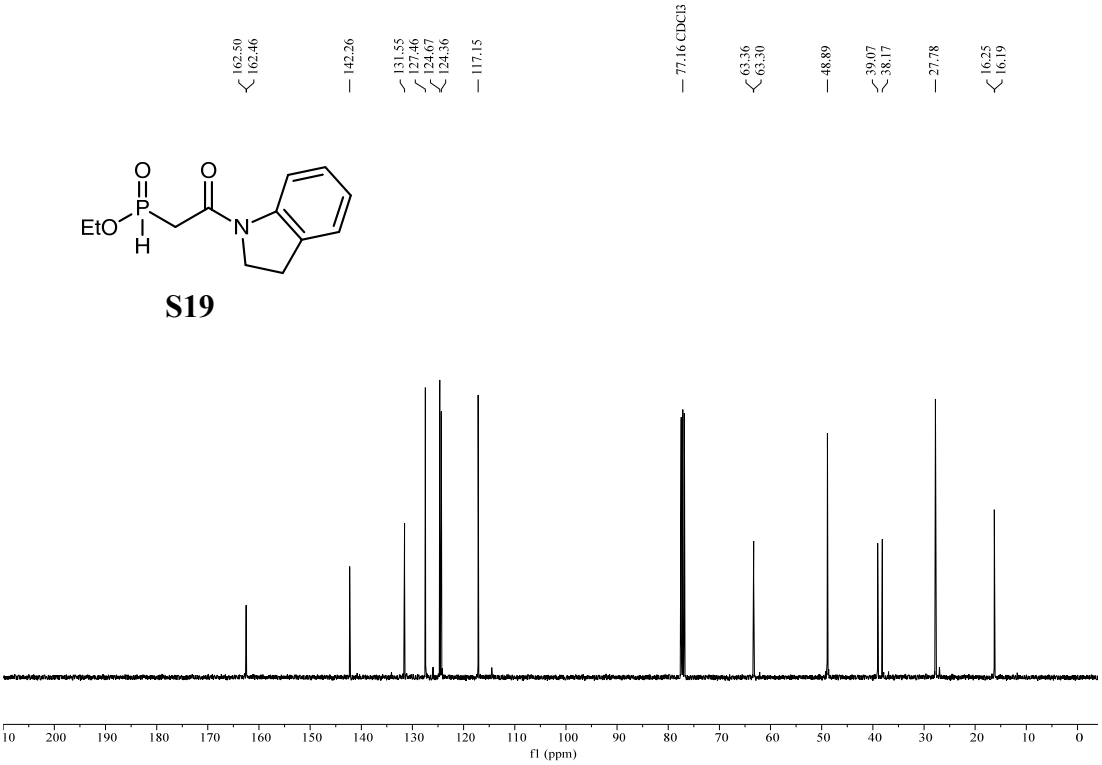
^{13}C NMR of S18 (100 MHz, $CDCl_3$)



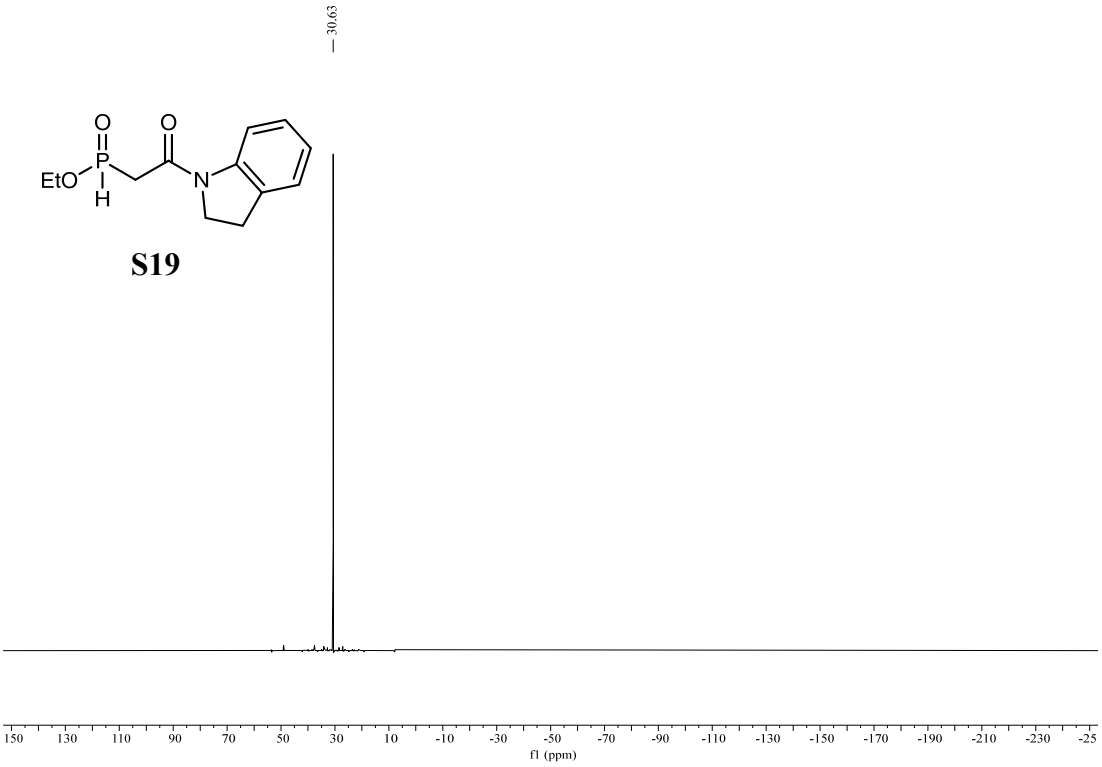
^{1}H NMR of S19 (400 MHz, $CDCl_3$)



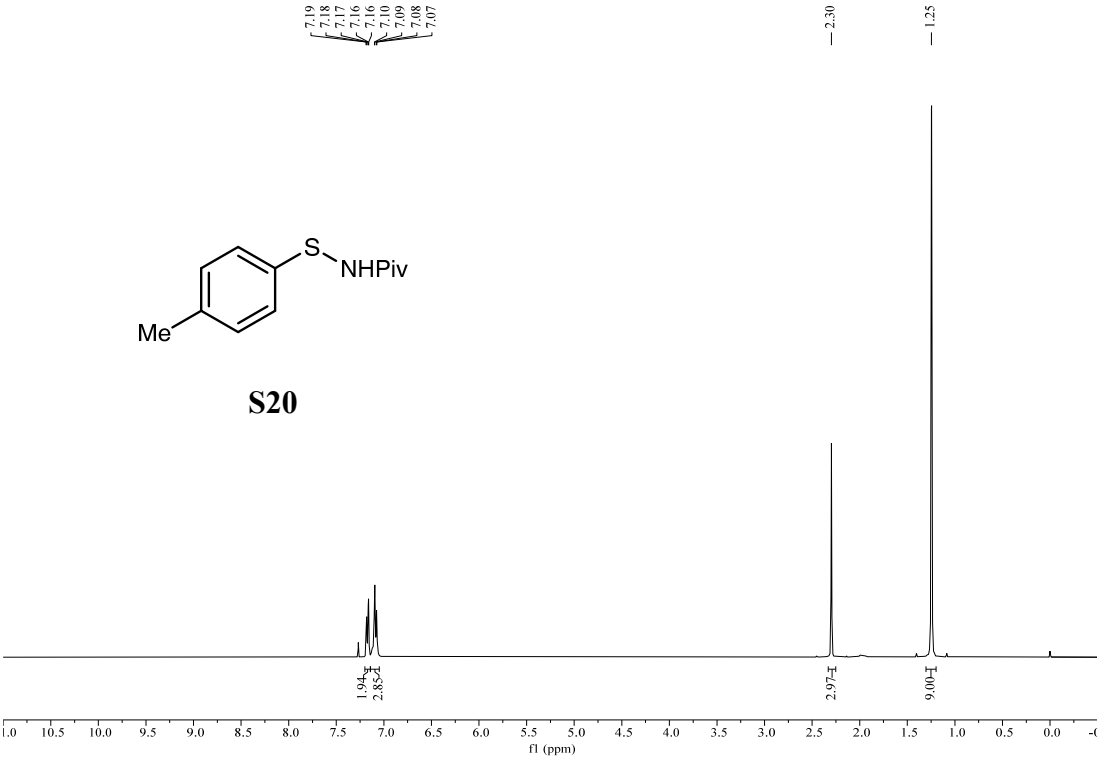
^{13}C NMR of S19 (100 MHz, $CDCl_3$)



^{31}P NMR of S19 (162 MHz, $CDCl_3$)

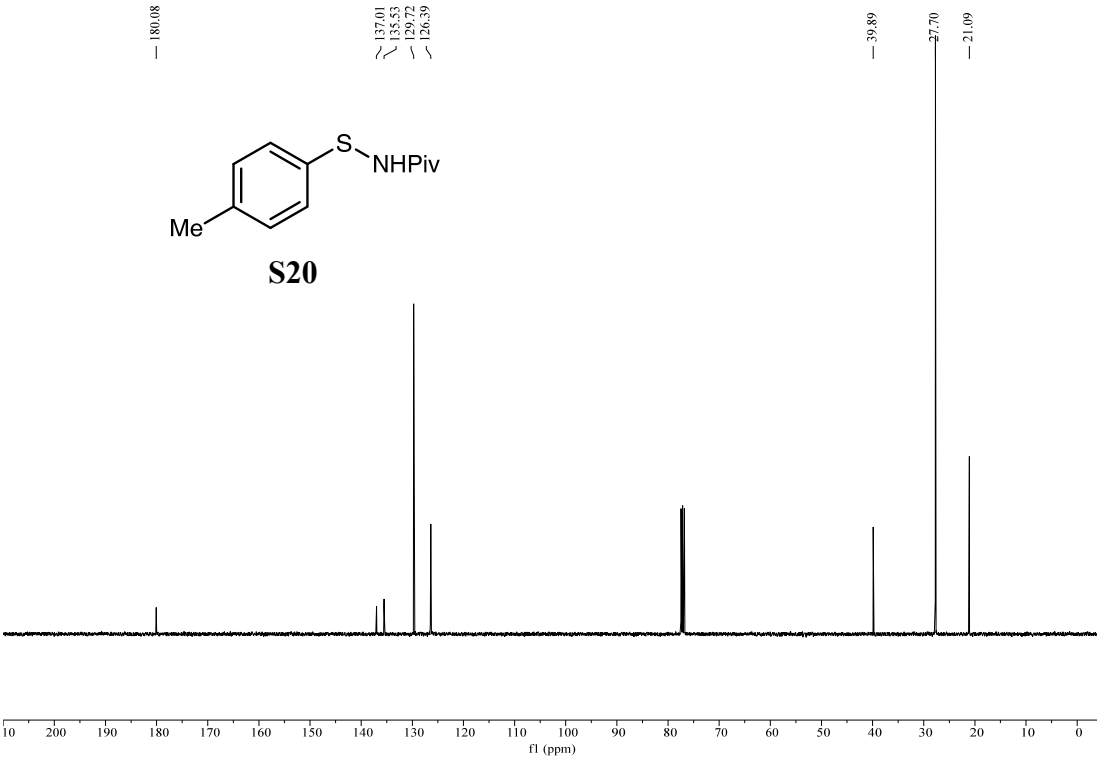


^{1}H NMR of S20 (400 MHz, $CDCl_3$)



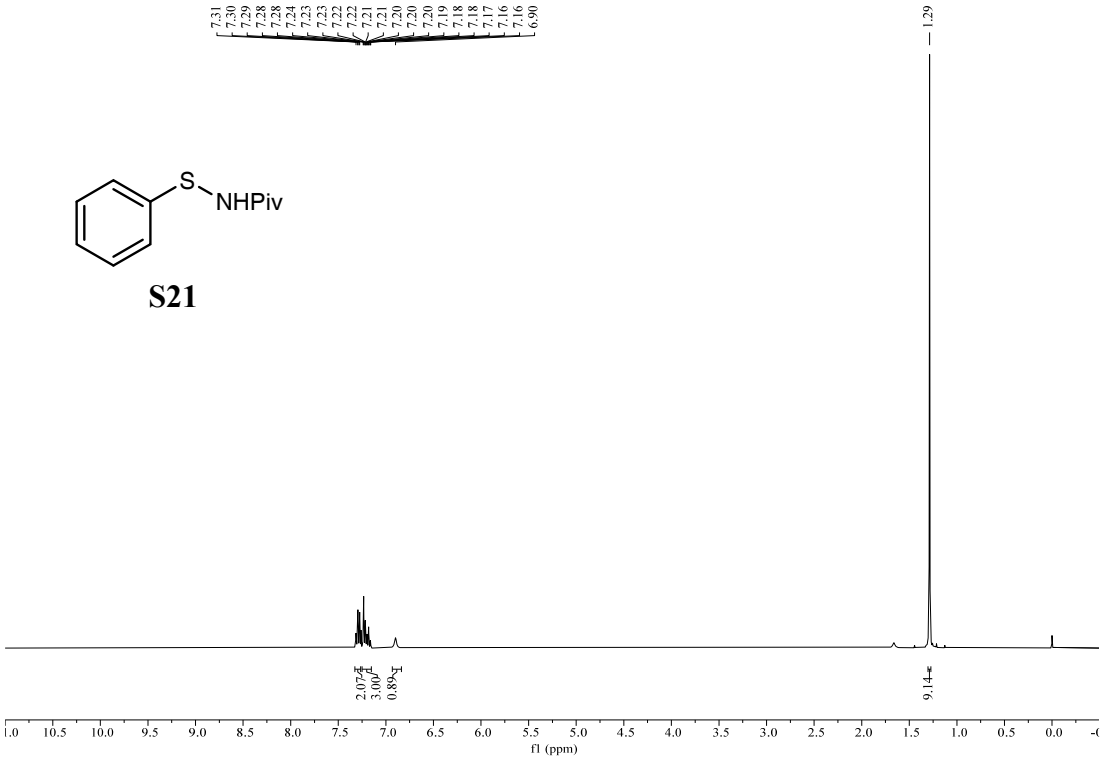
S20

^{13}C NMR of S20 (100 MHz, $CDCl_3$)



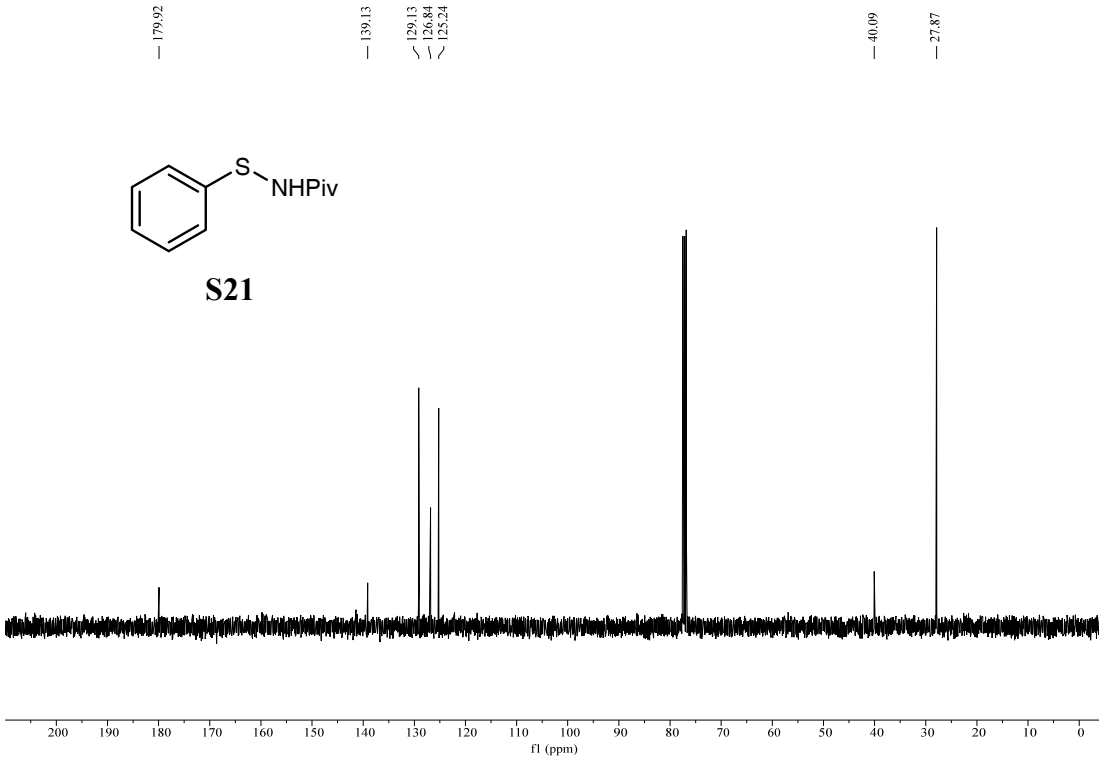
S20

^{1}H NMR of S21 (400 MHz, $CDCl_3$)



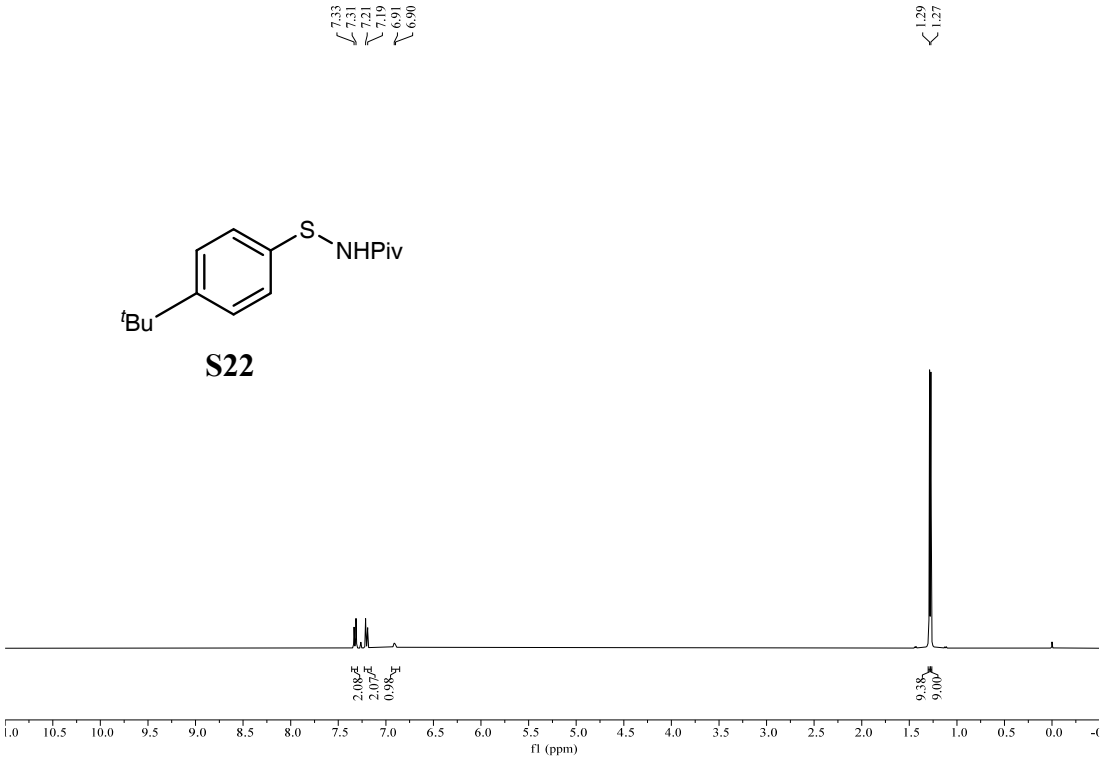
S21

^{13}C NMR of S21 (100 MHz, $CDCl_3$)

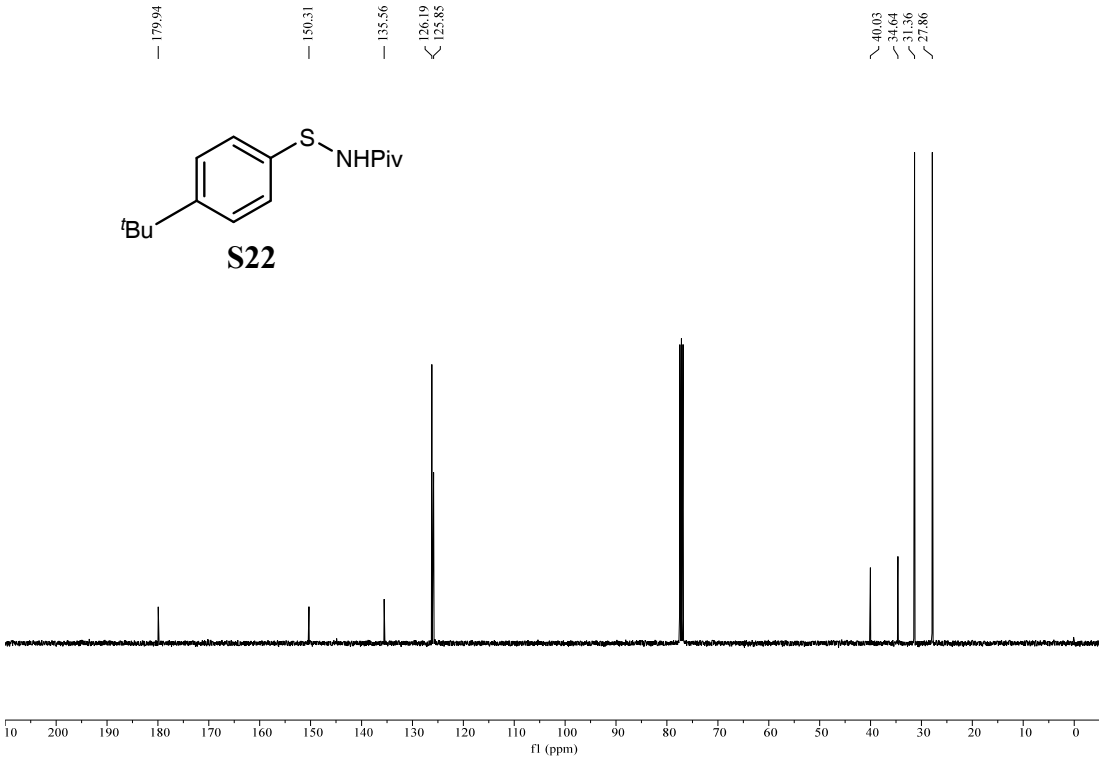


S21

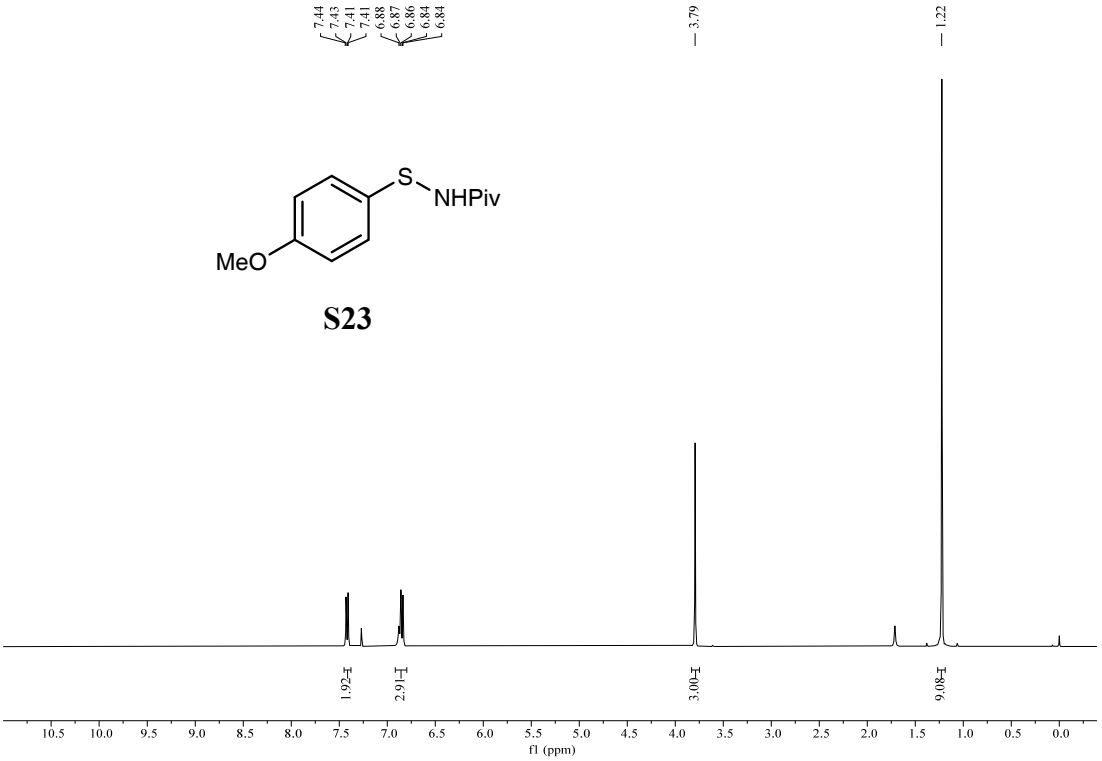
^{1}H NMR of S22 (400 MHz, $CDCl_3$)



^{13}C NMR of S22 (100 MHz, $CDCl_3$)

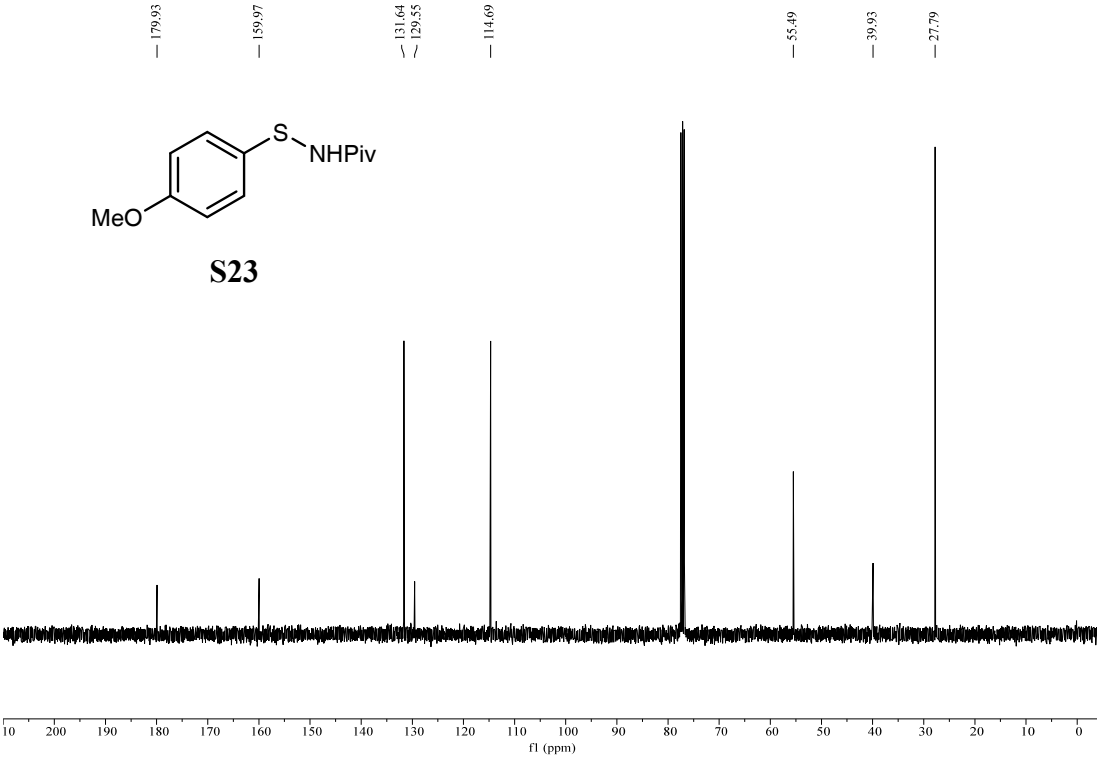


^{1}H NMR of S23 (400 MHz, $CDCl_3$)



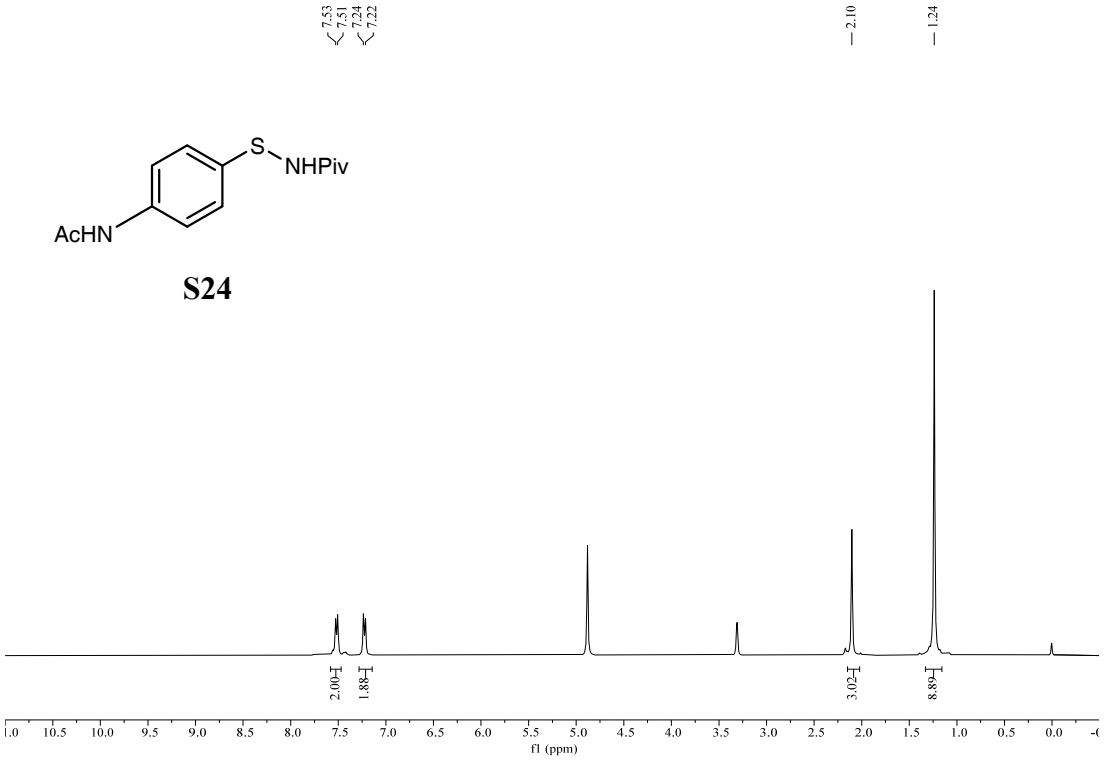
S23

^{13}C NMR of S23 (100 MHz, $CDCl_3$)



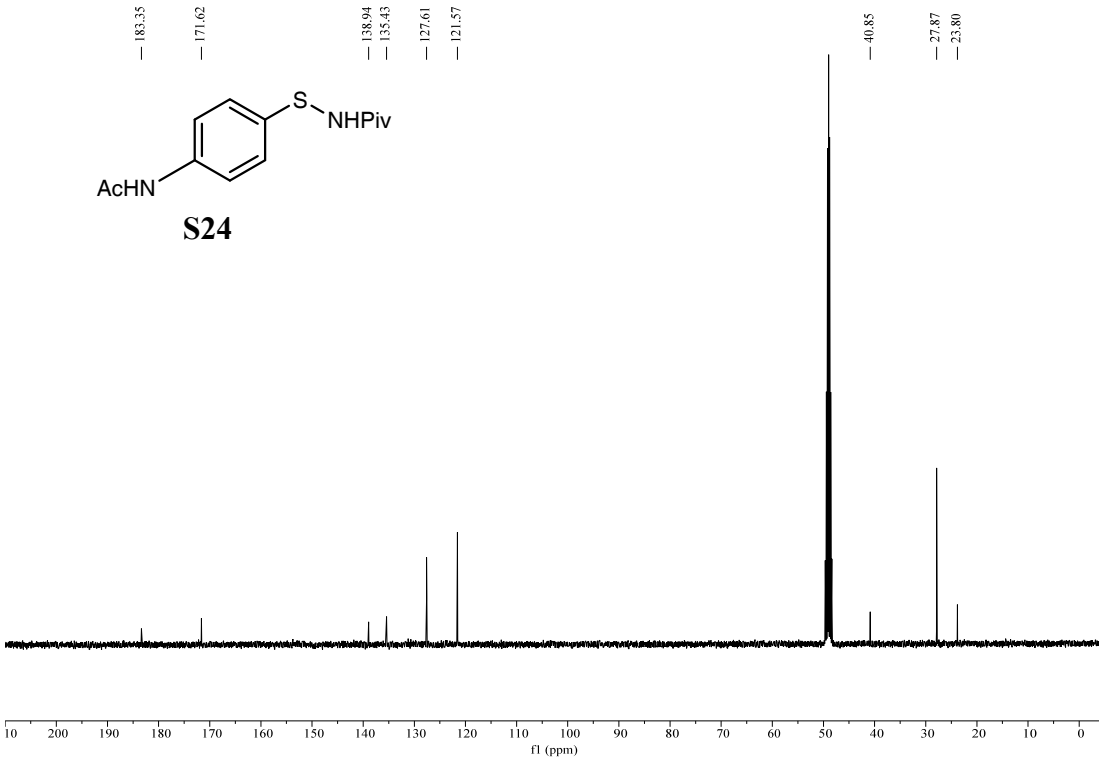
S23

^{1}H NMR of S24 (400 MHz, CD_3OD)



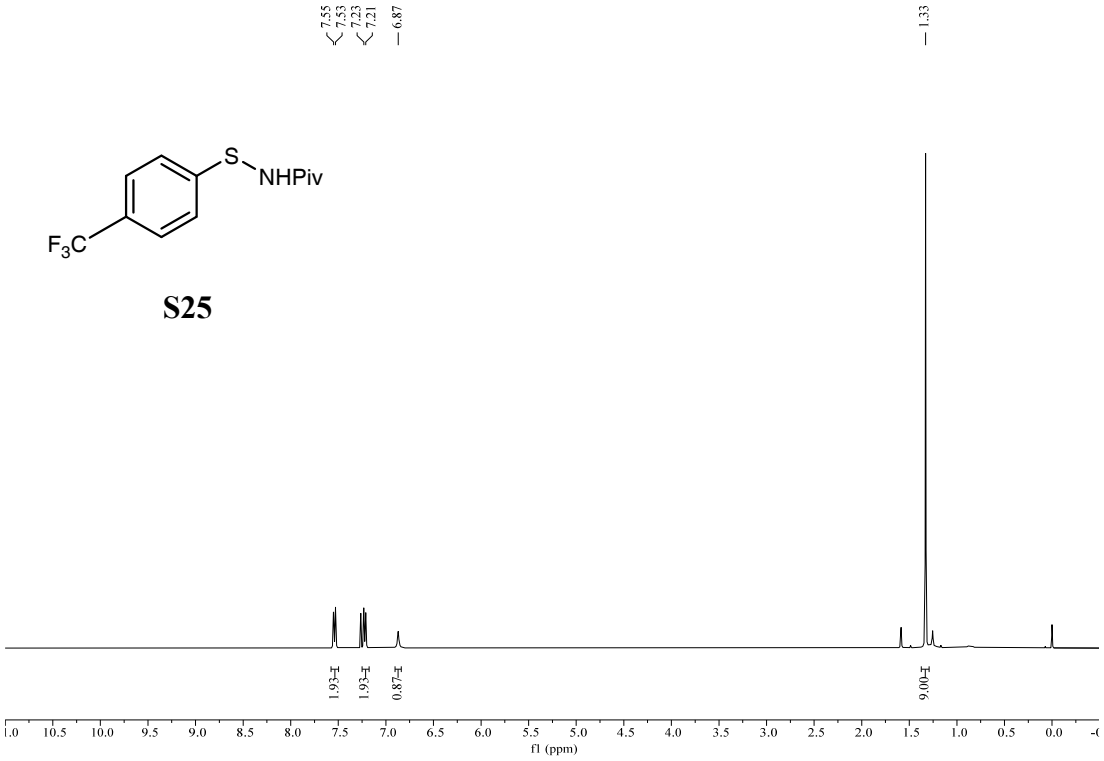
S24

^{13}C NMR of S24 (100 MHz, CD_3OD)



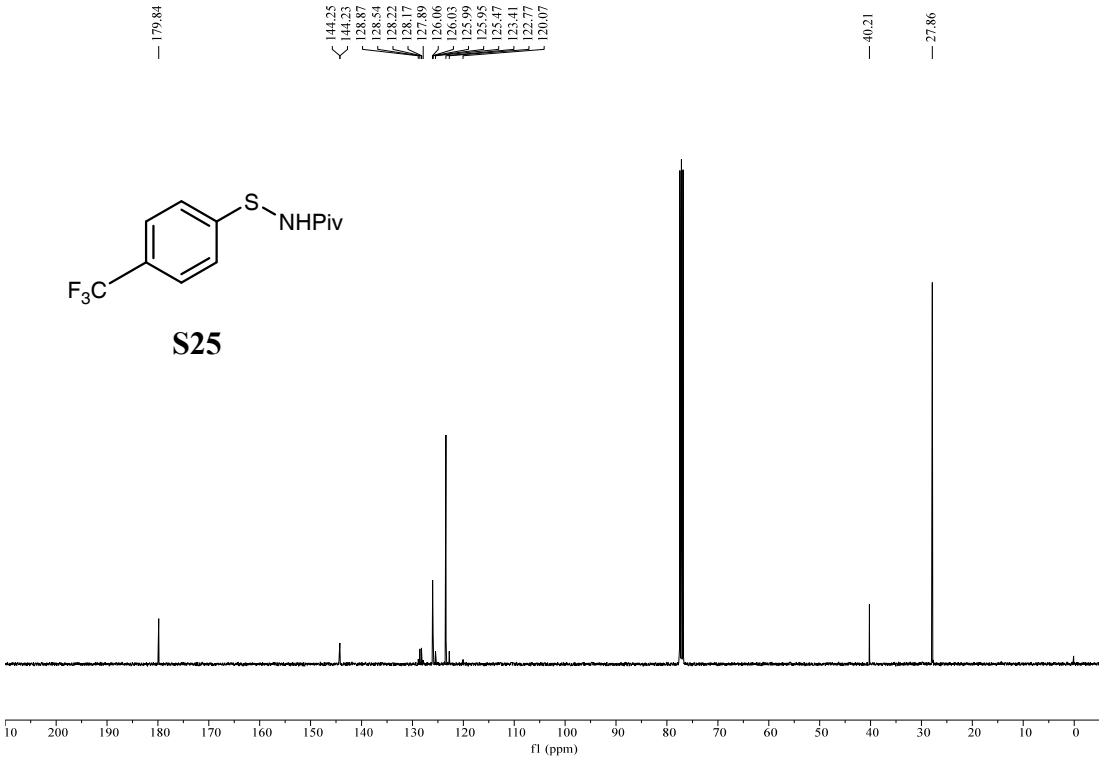
S24

^{1}H NMR of S25 (400 MHz, $CDCl_3$)



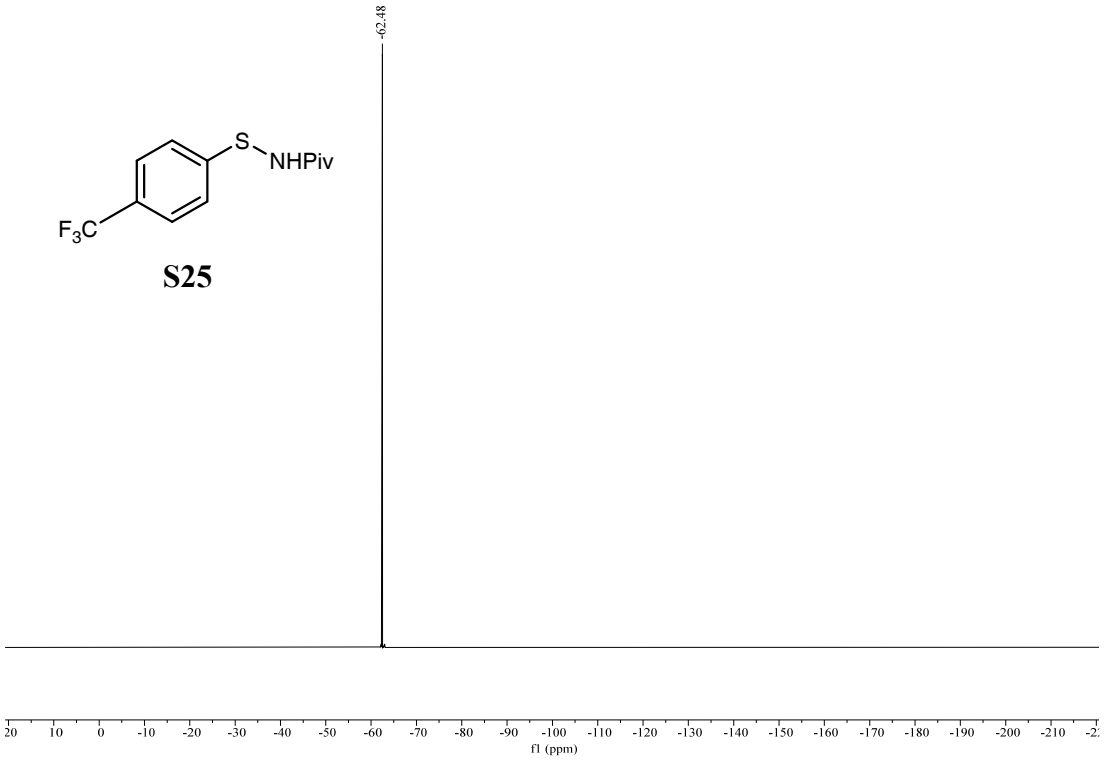
S25

^{13}C NMR of S25 (100 MHz, $CDCl_3$)



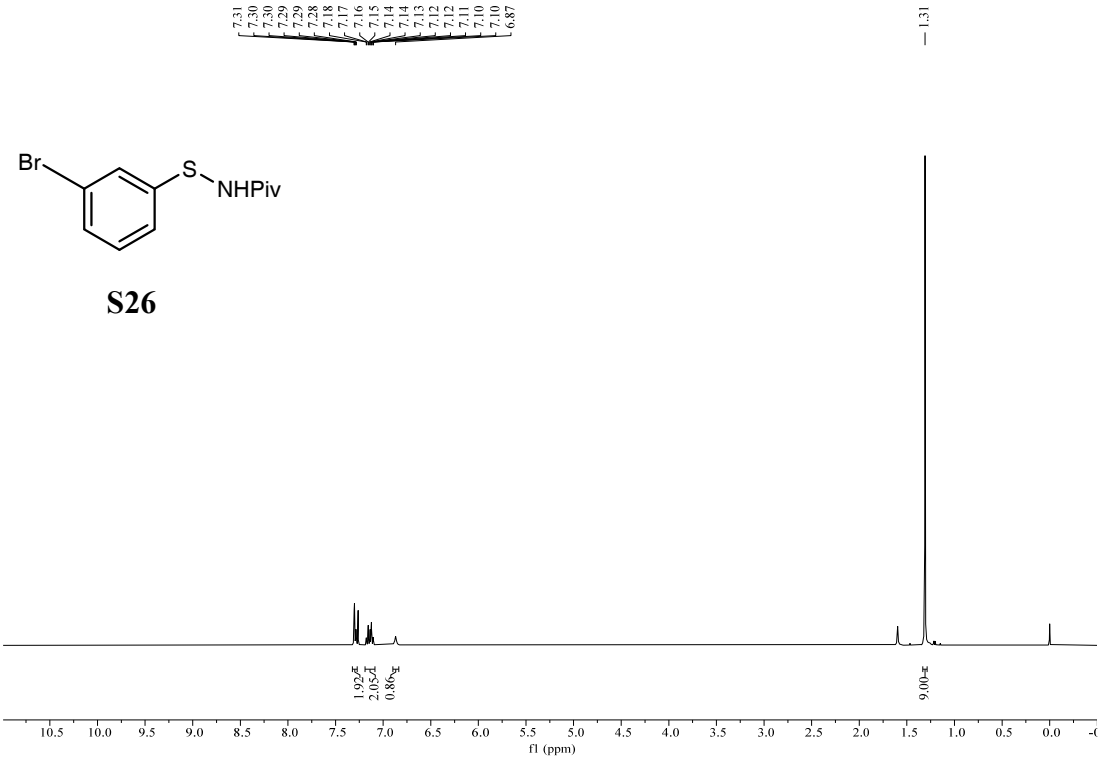
S25

^{19}F NMR of S25 (375 MHz, $CDCl_3$)

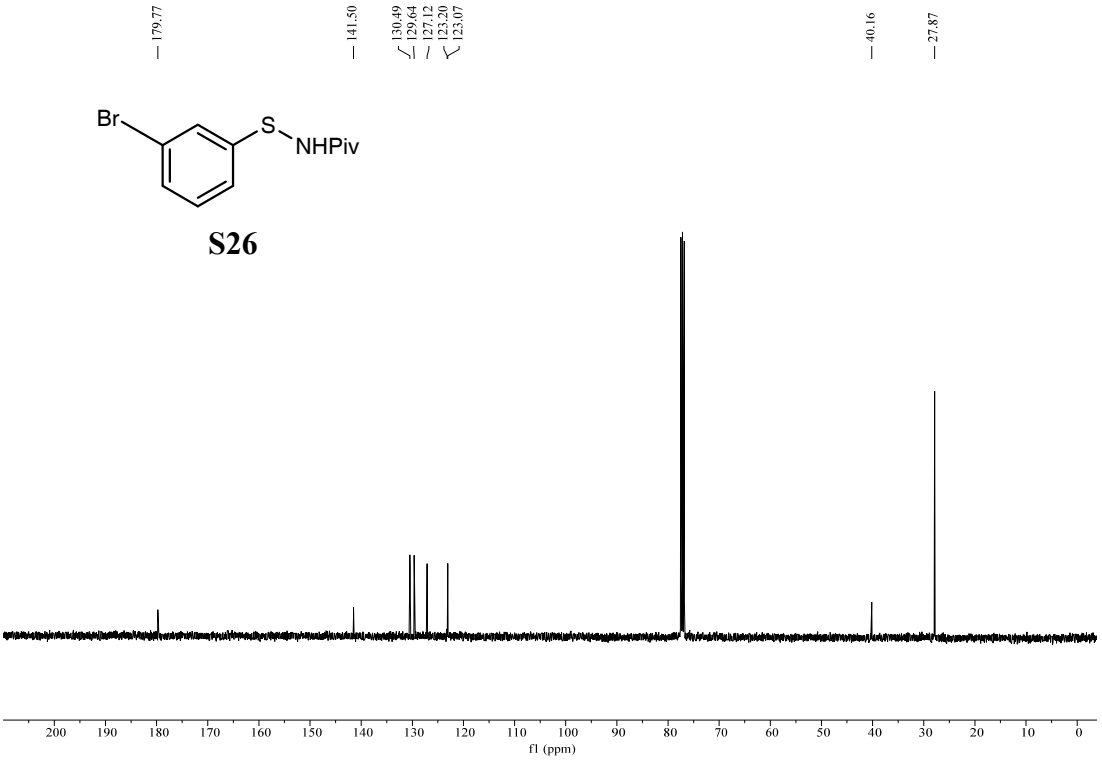


S25

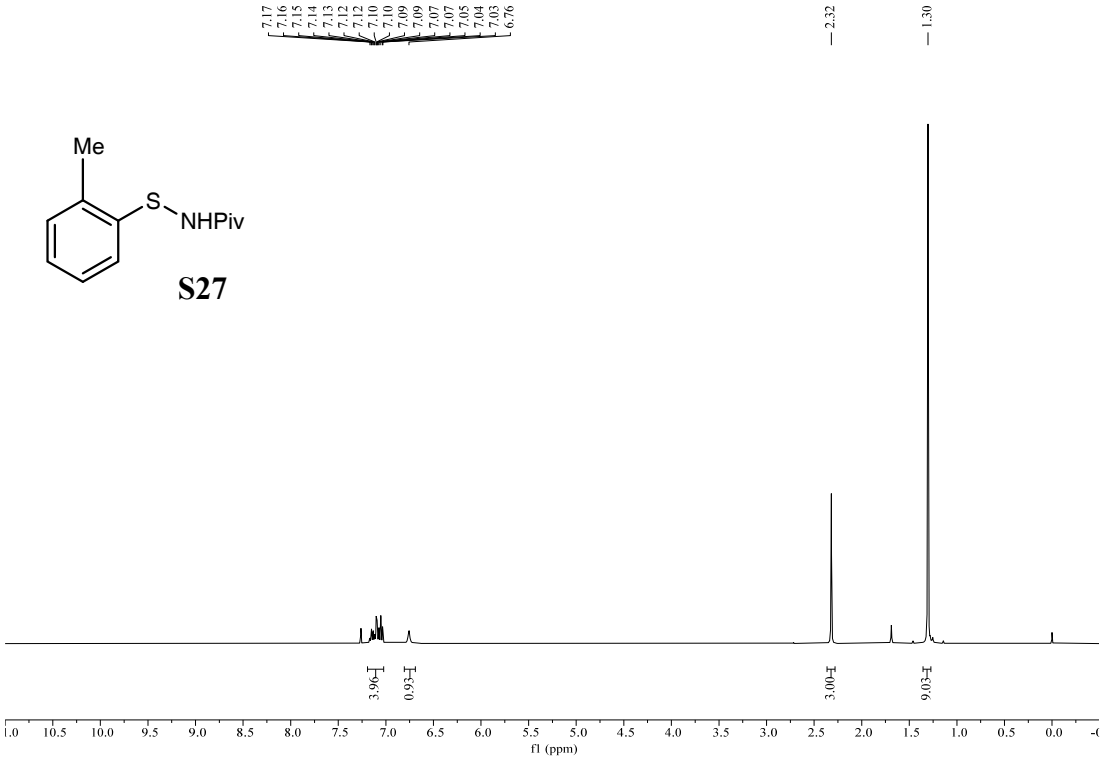
^{1}H NMR of S26 (400 MHz, $CDCl_3$)



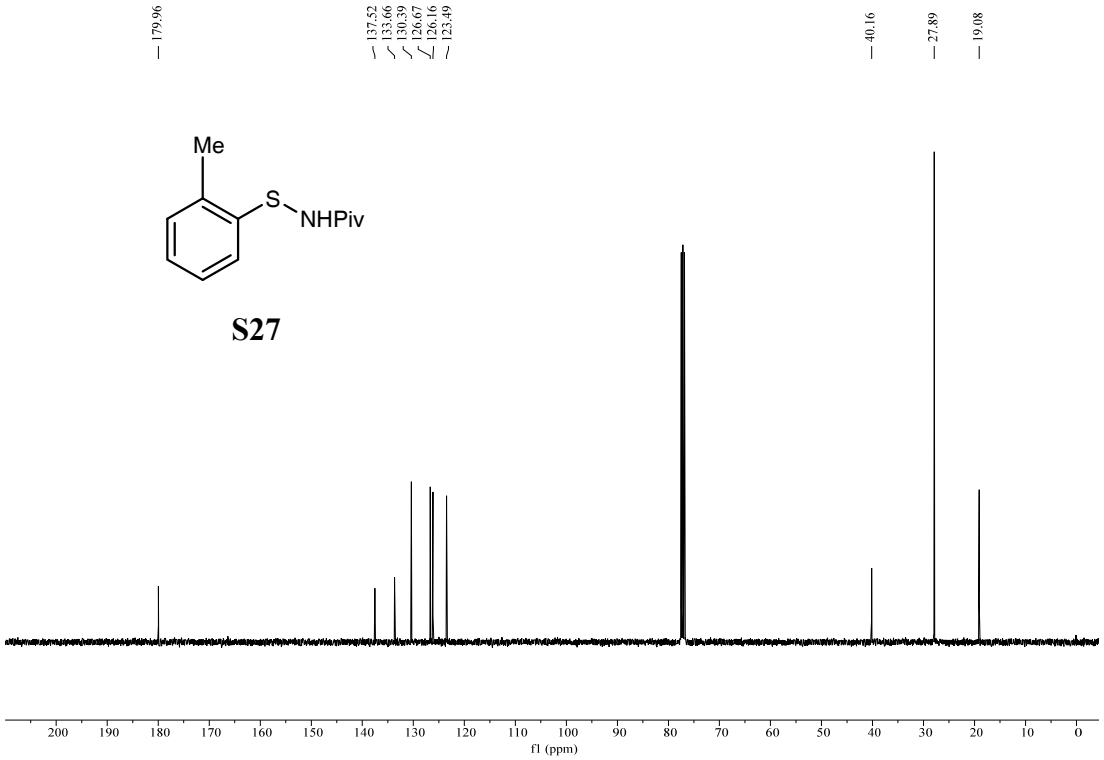
^{13}C NMR of S26 (100 MHz, $CDCl_3$)



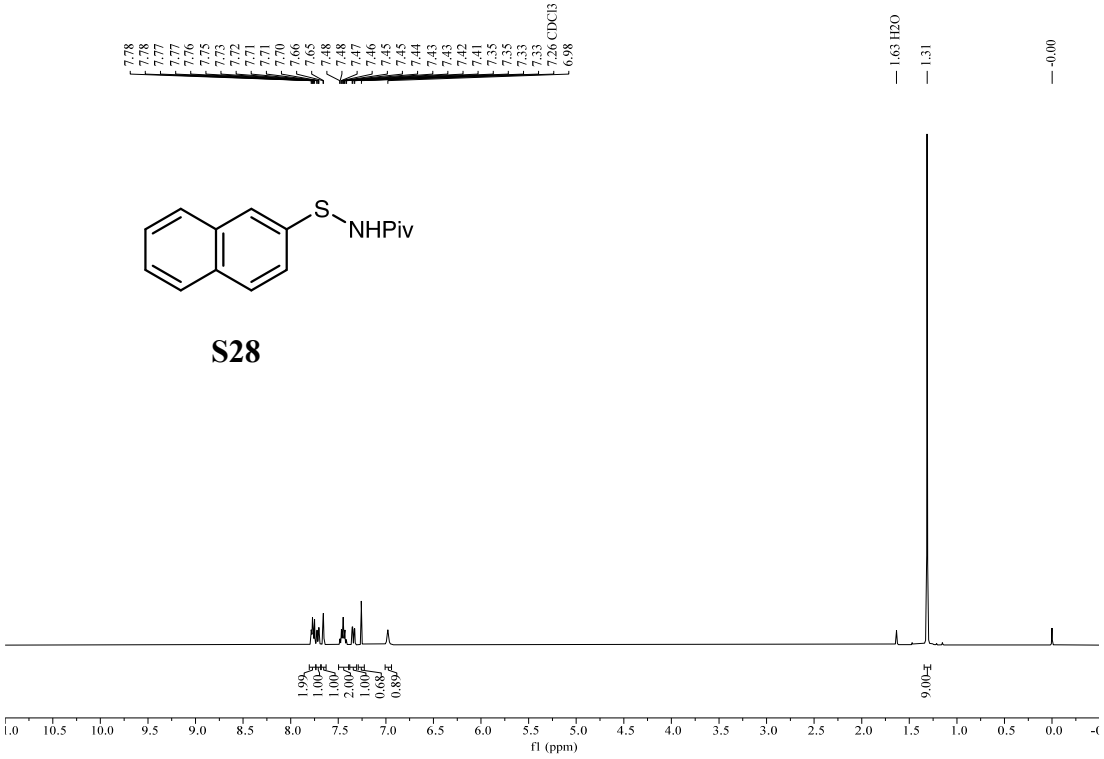
^{1}H NMR of S27 (400 MHz, $CDCl_3$)



^{13}C NMR of S27 (100 MHz, $CDCl_3$)

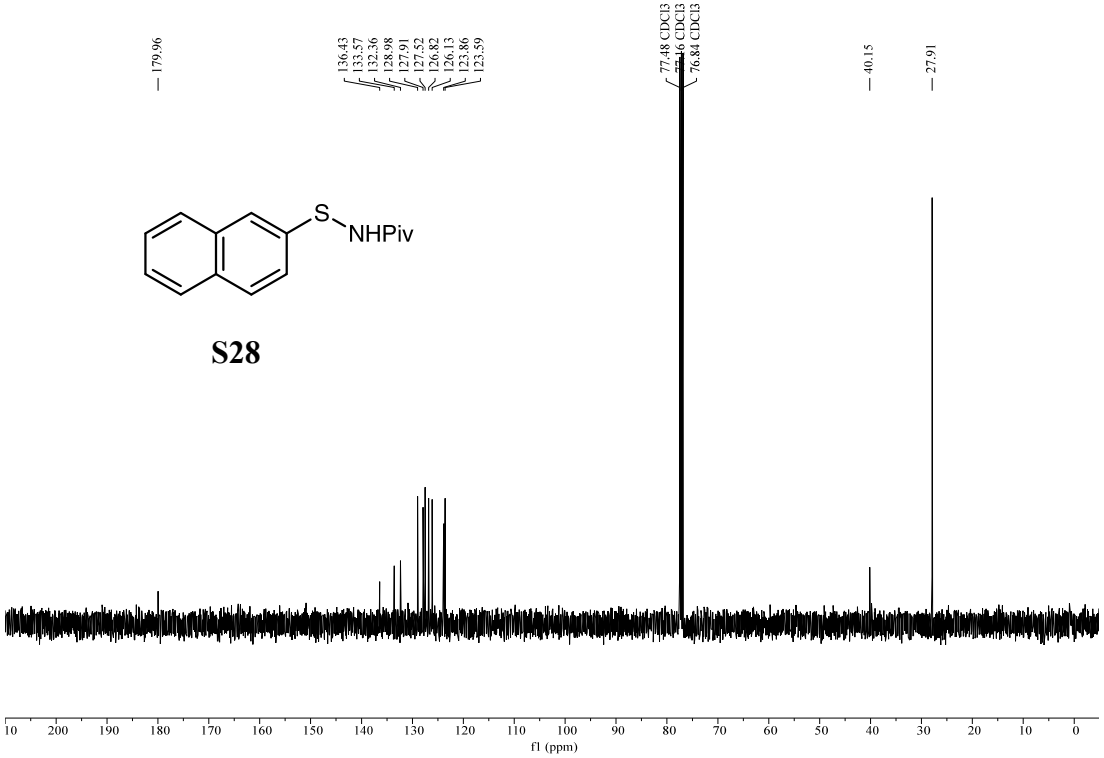


^{1}H NMR of S28 (400 MHz, $CDCl_3$)



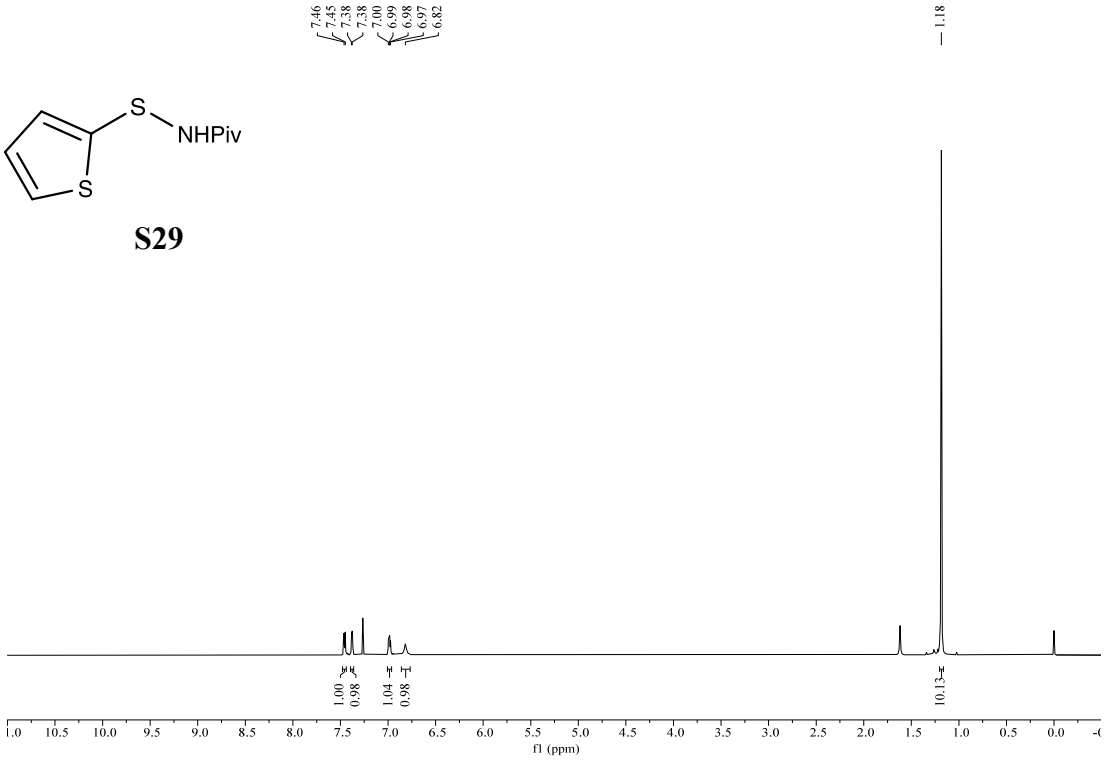
S28

^{13}C NMR of S28 (100 MHz, $CDCl_3$)



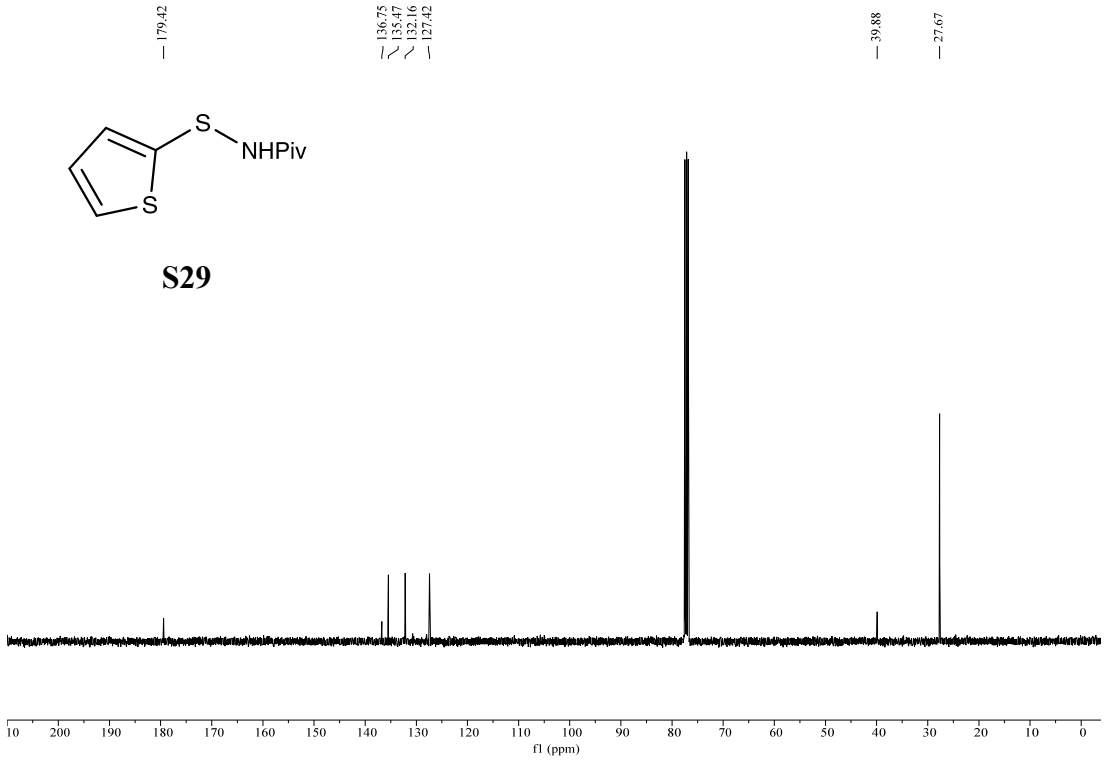
S28

^{1}H NMR of S29 (400 MHz, $CDCl_3$)



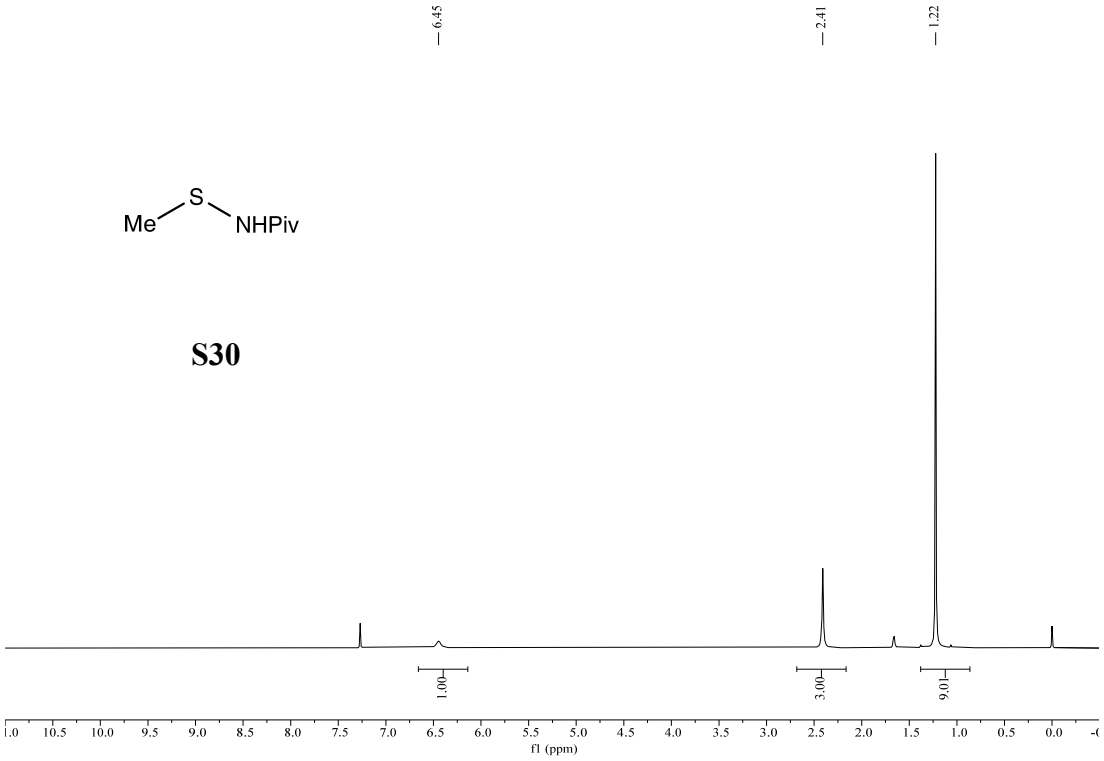
S29

^{13}C NMR of S29 (100 MHz, $CDCl_3$)

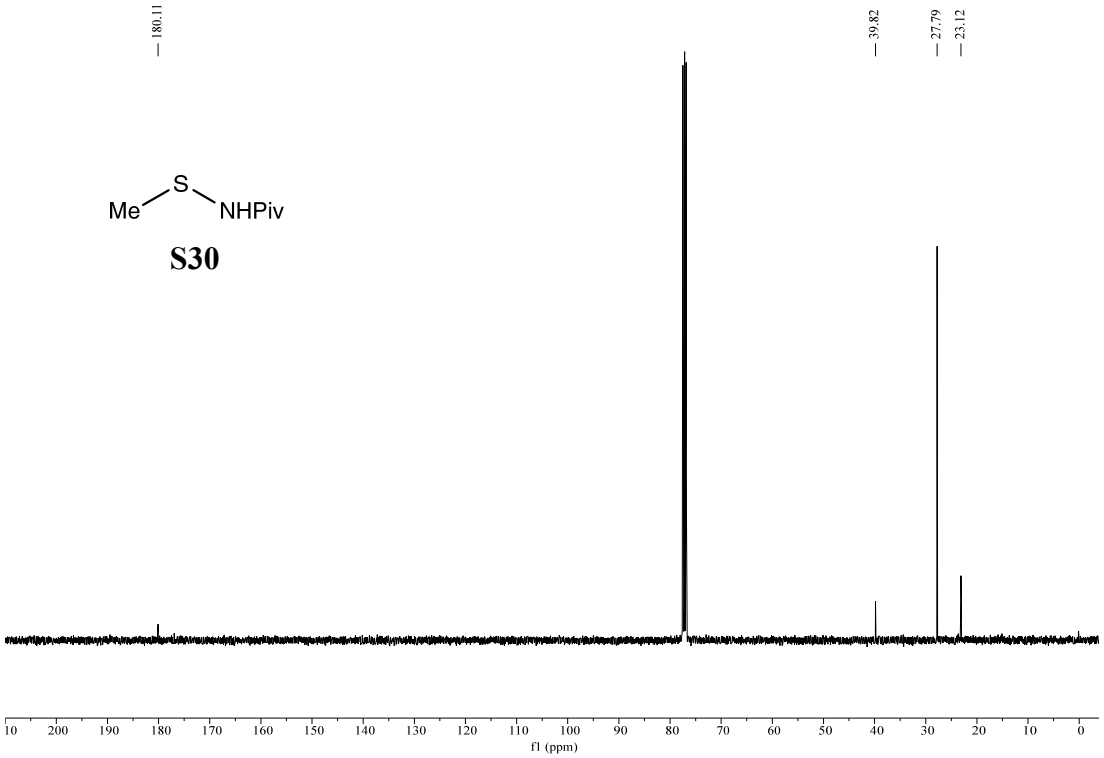


S29

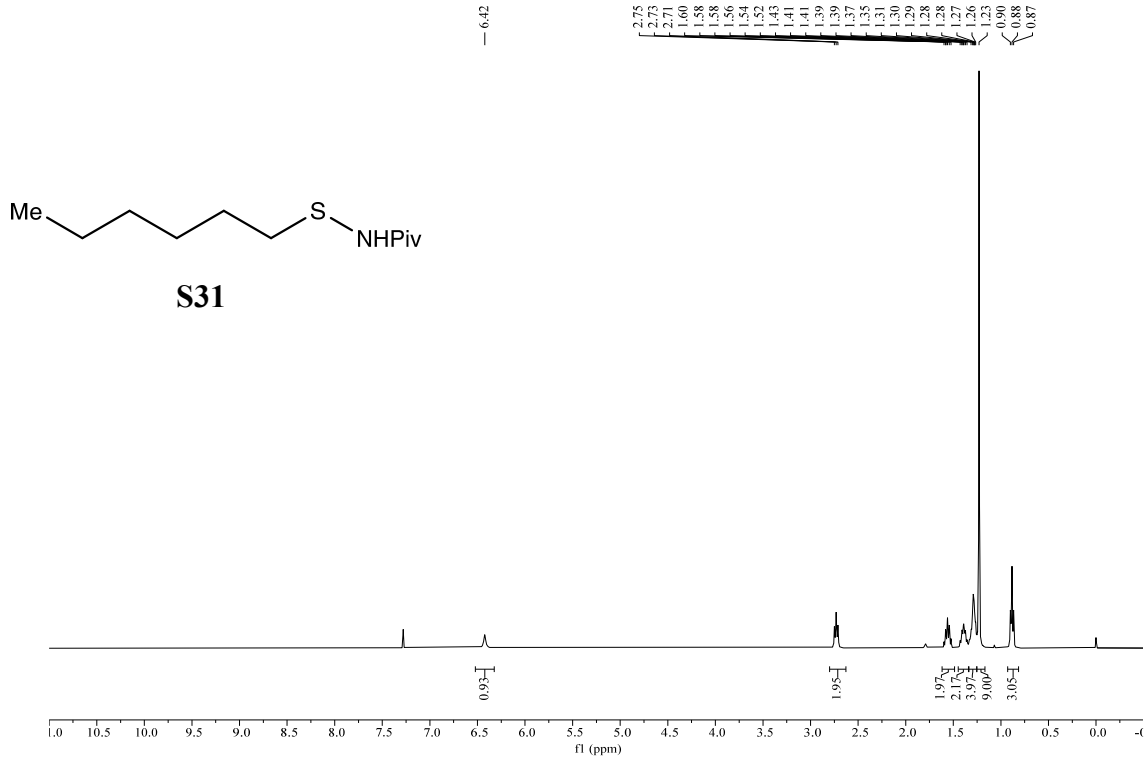
^{1}H NMR of S30 (400 MHz, $CDCl_3$)



^{13}C NMR of S30 (100 MHz, $CDCl_3$)

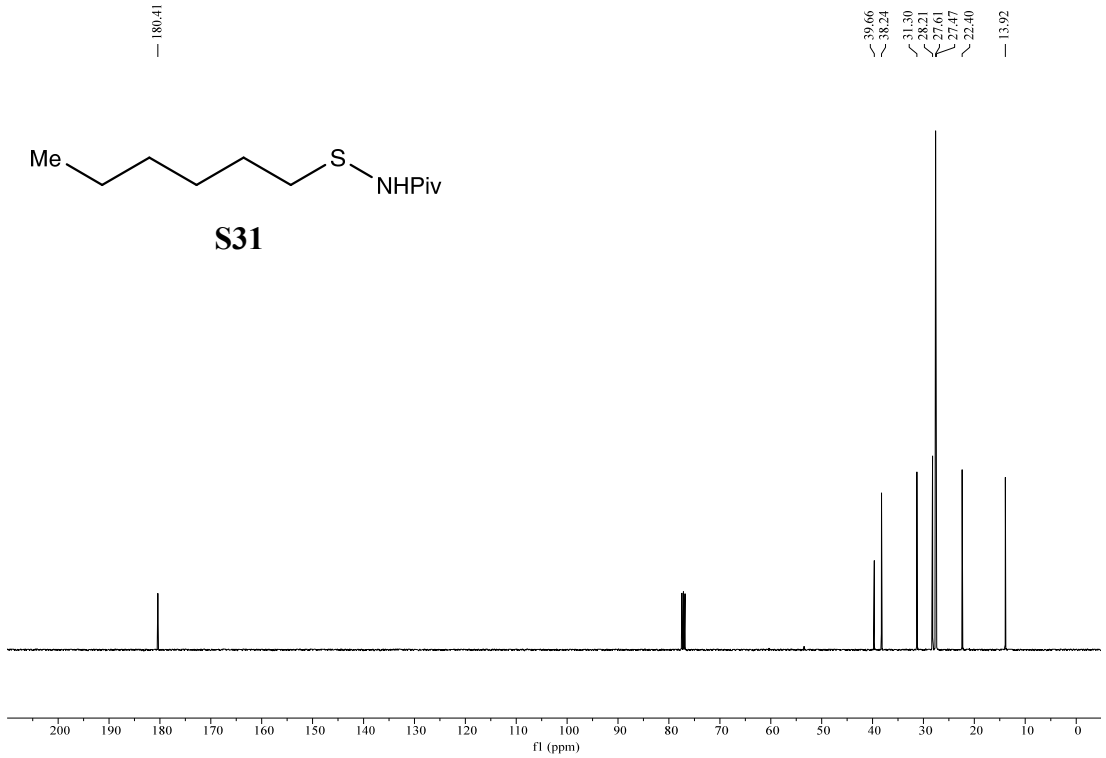


^{1}H NMR of S31 (400 MHz, $CDCl_3$)



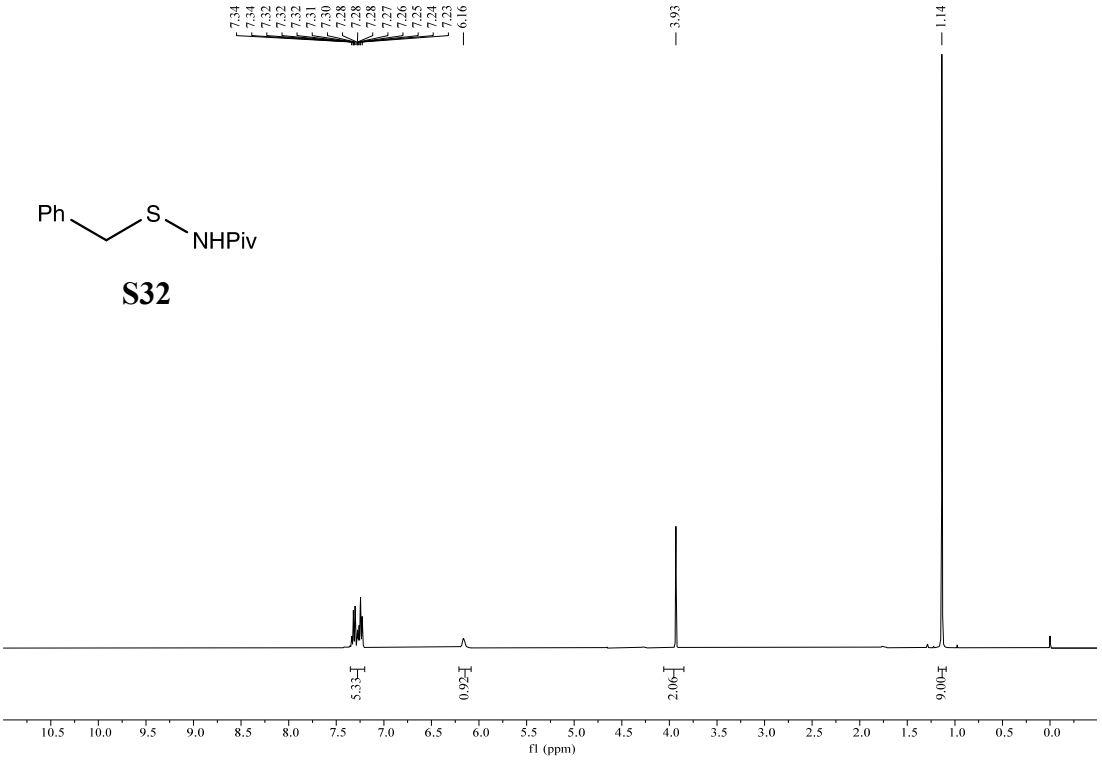
S31

^{13}C NMR of S31 (100 MHz, $CDCl_3$)

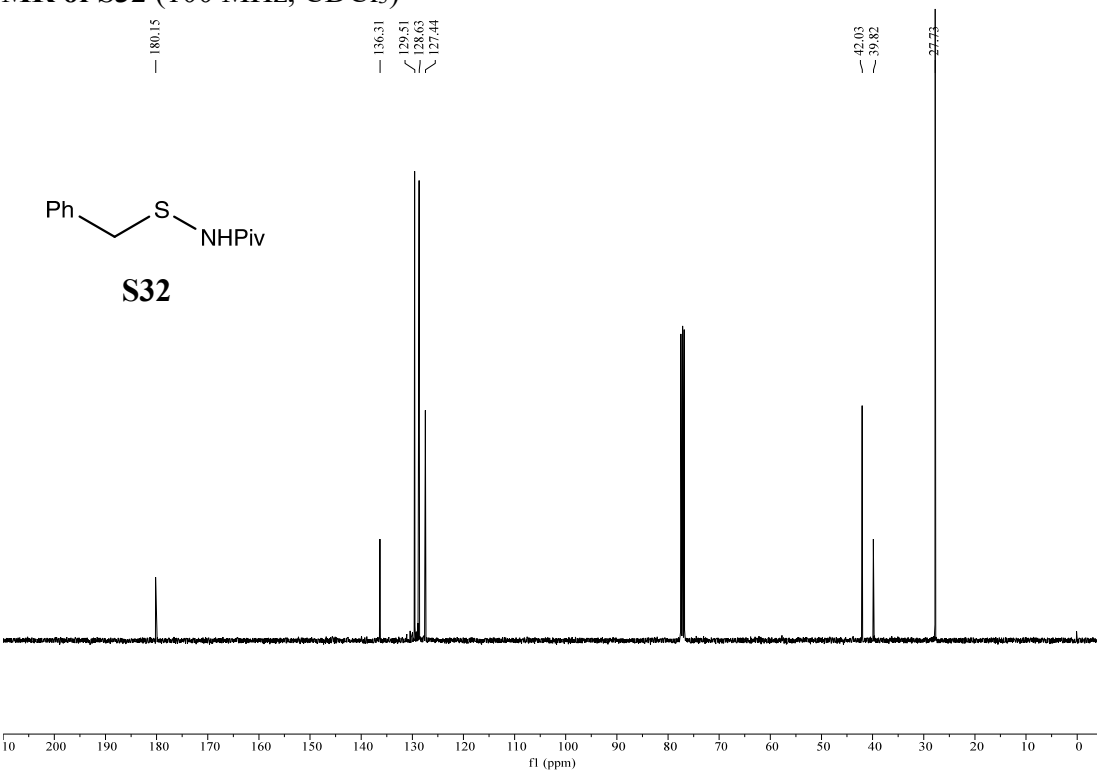


S31

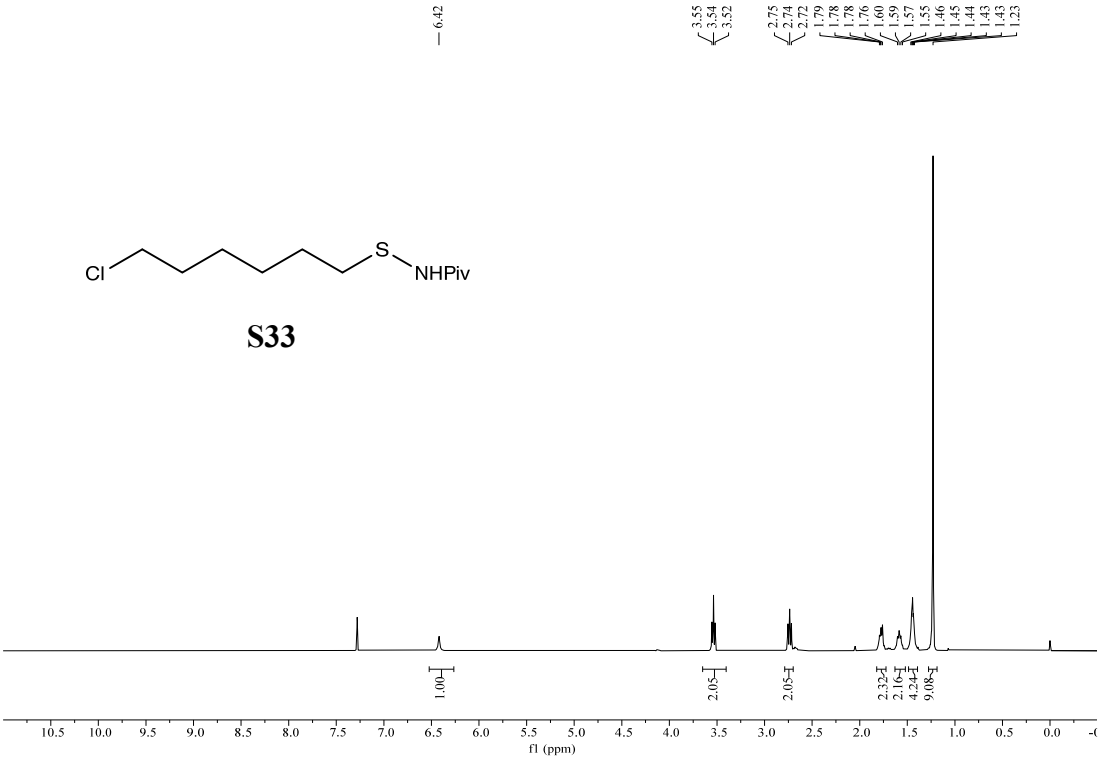
^{1}H NMR of S32 (400 MHz, $CDCl_3$)



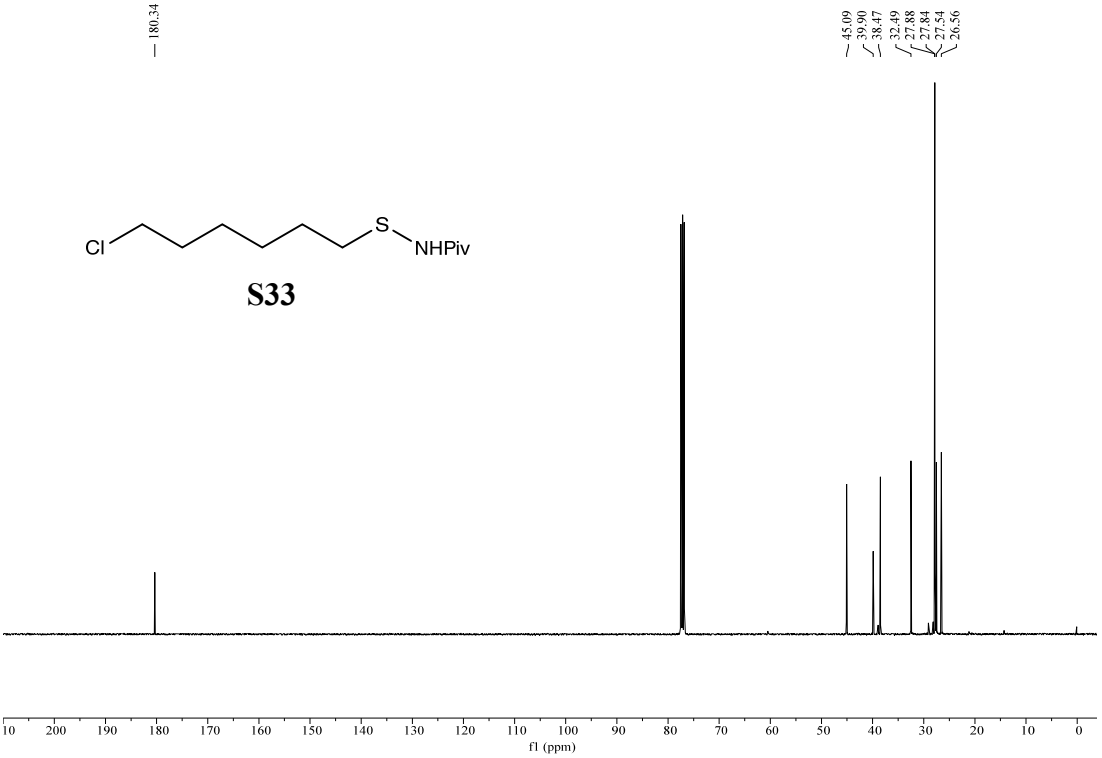
^{13}C NMR of S32 (100 MHz, $CDCl_3$)



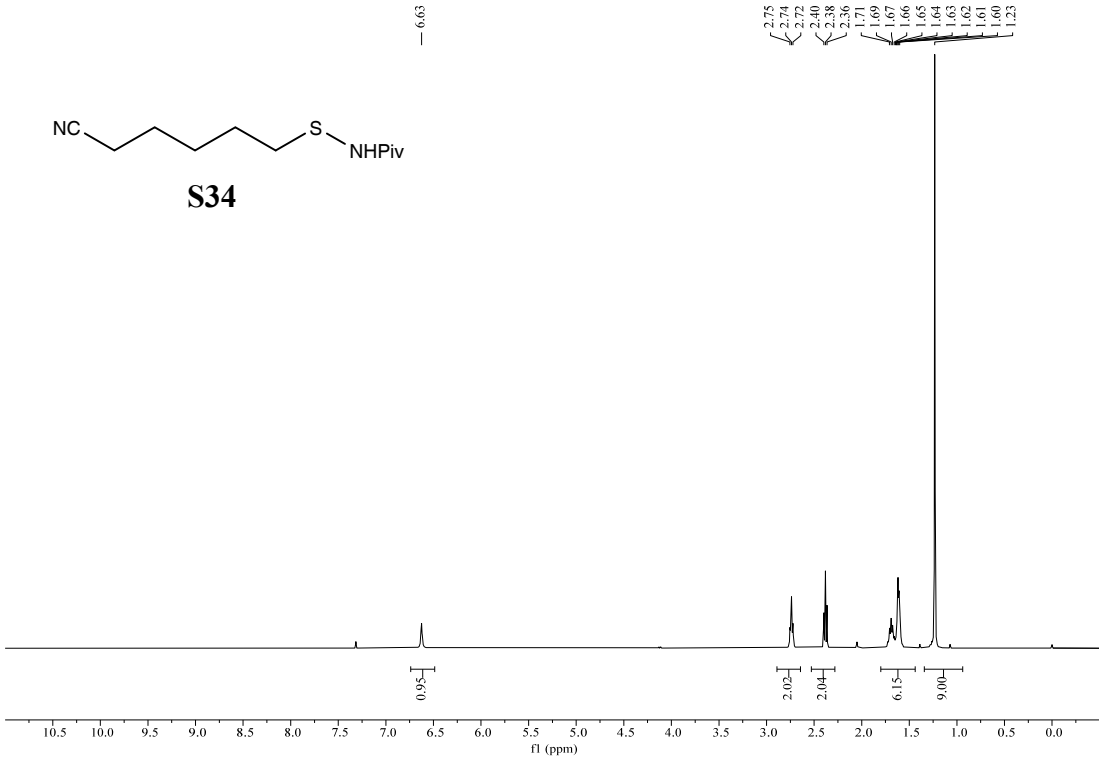
^{1}H NMR of S33 (400 MHz, $CDCl_3$)



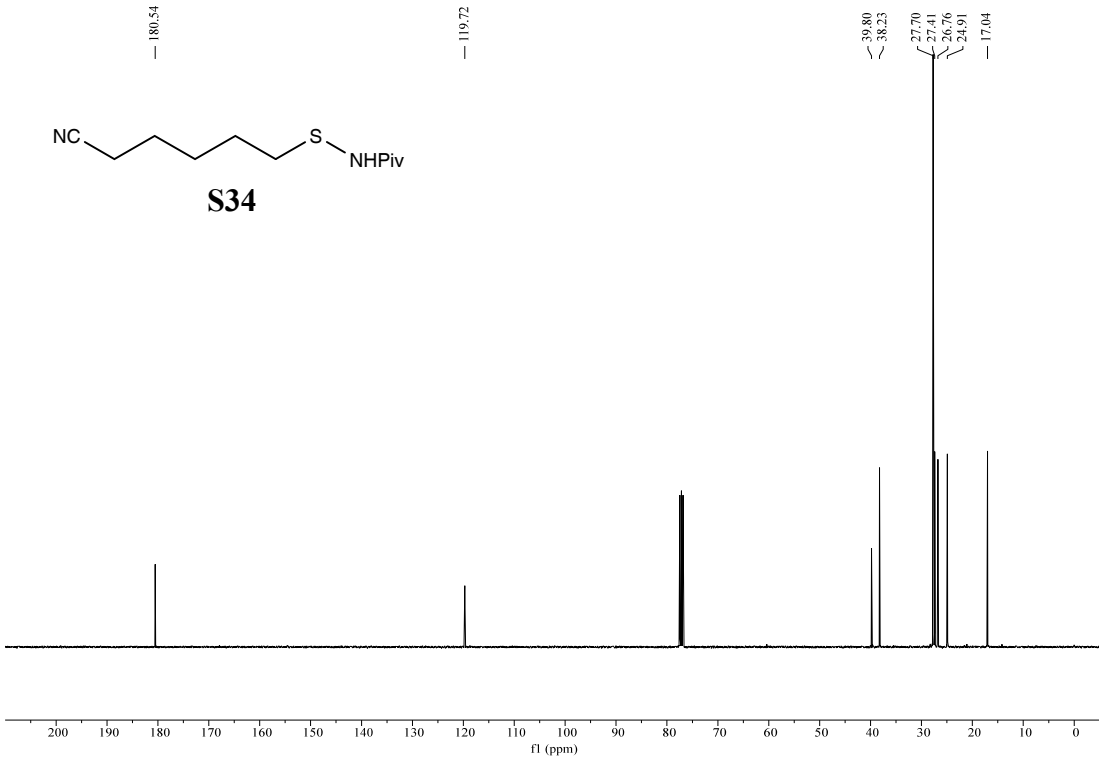
^{13}C NMR of S33 (100 MHz, $CDCl_3$)



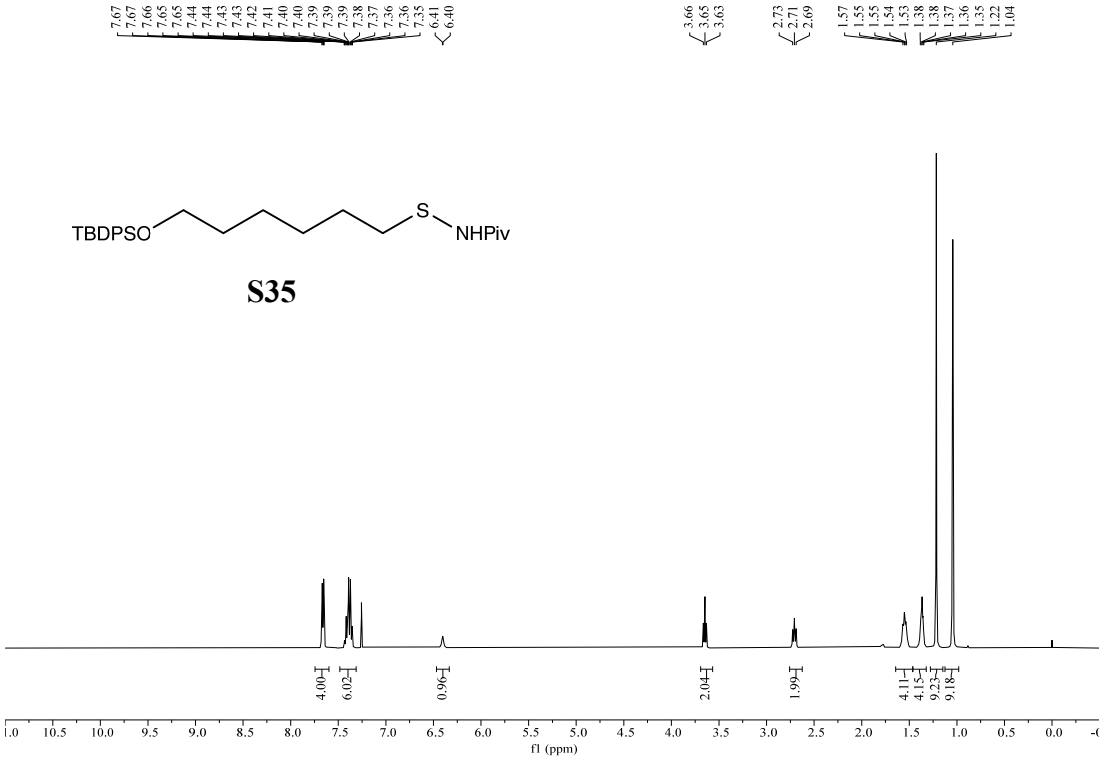
^{1}H NMR of S34 (400 MHz, $CDCl_3$)



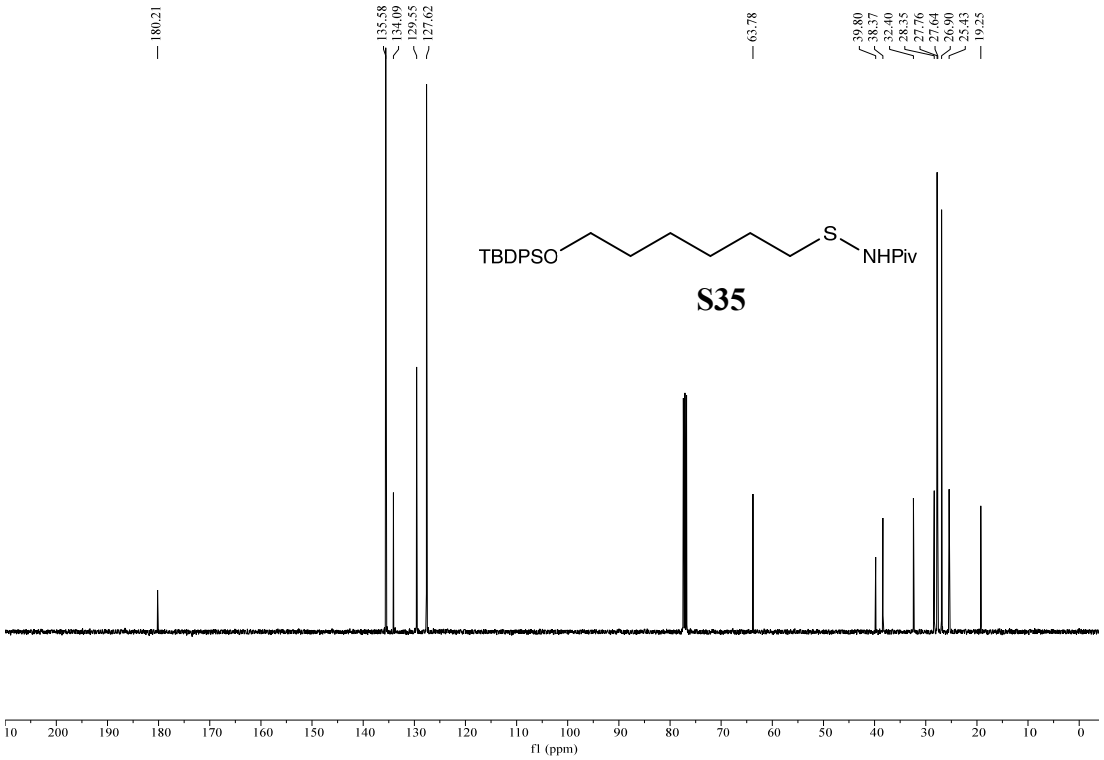
^{13}C NMR of S34 (100 MHz, $CDCl_3$)



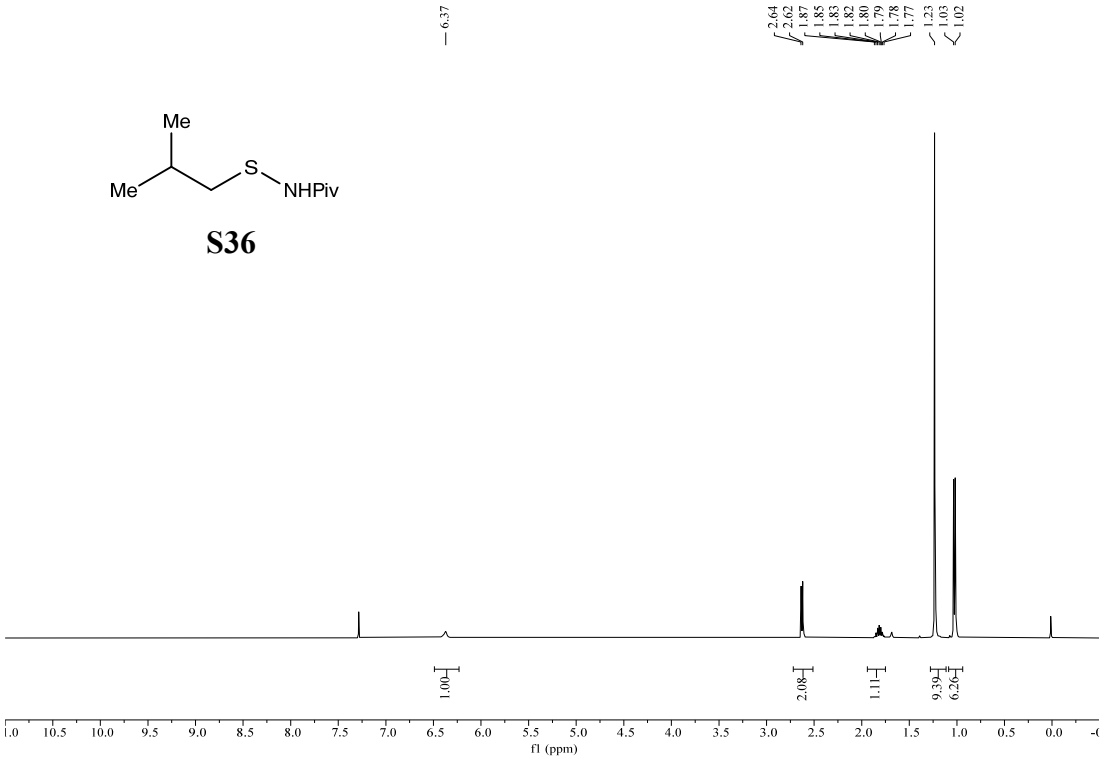
^{1}H NMR of S35 (400 MHz, $CDCl_3$)



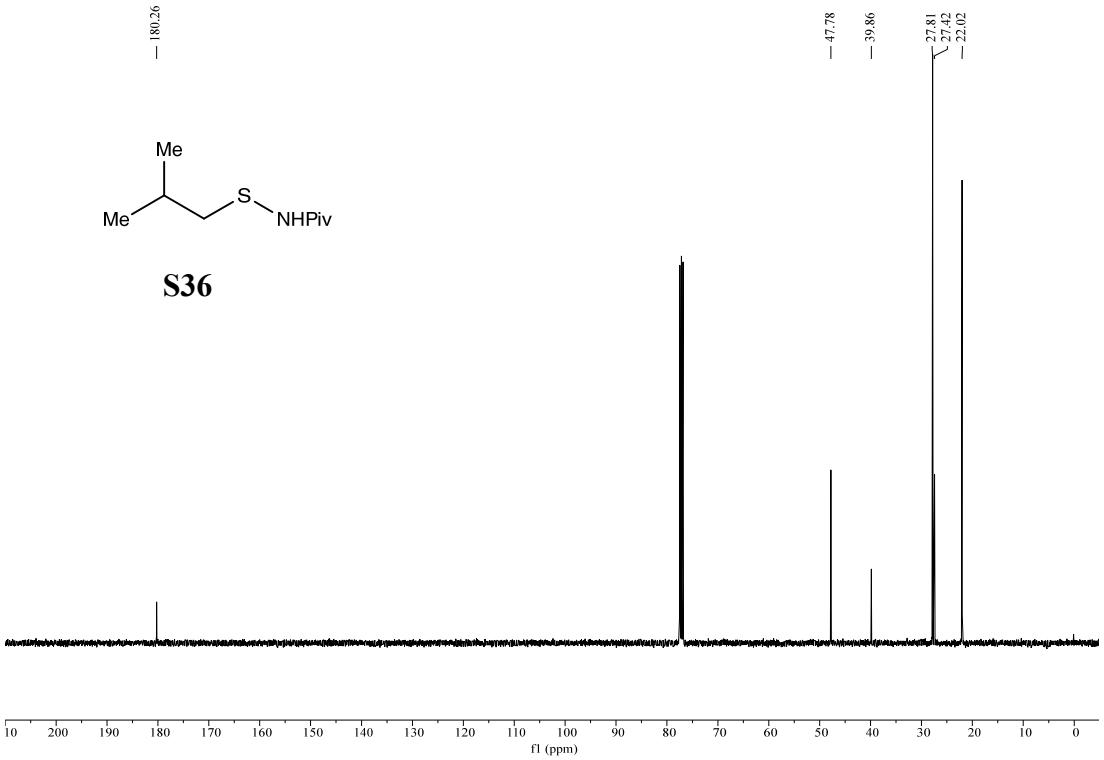
^{13}C NMR of S35 (100 MHz, $CDCl_3$)



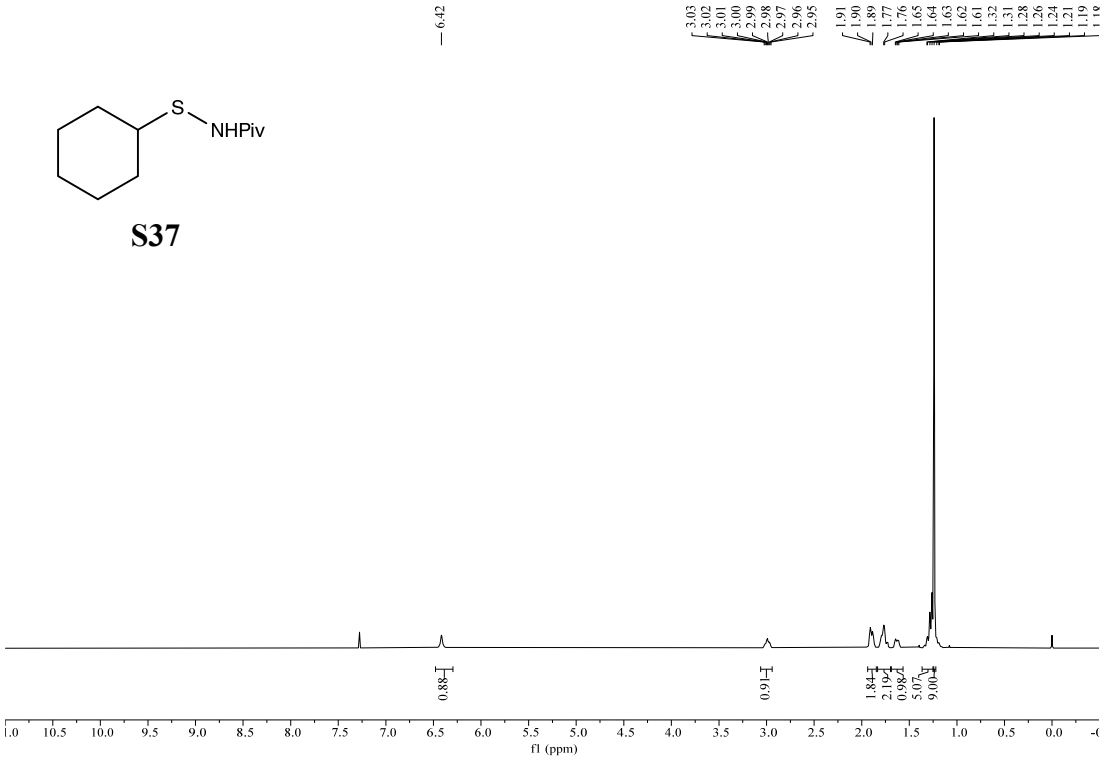
^{1}H NMR of S36 (400 MHz, $CDCl_3$)



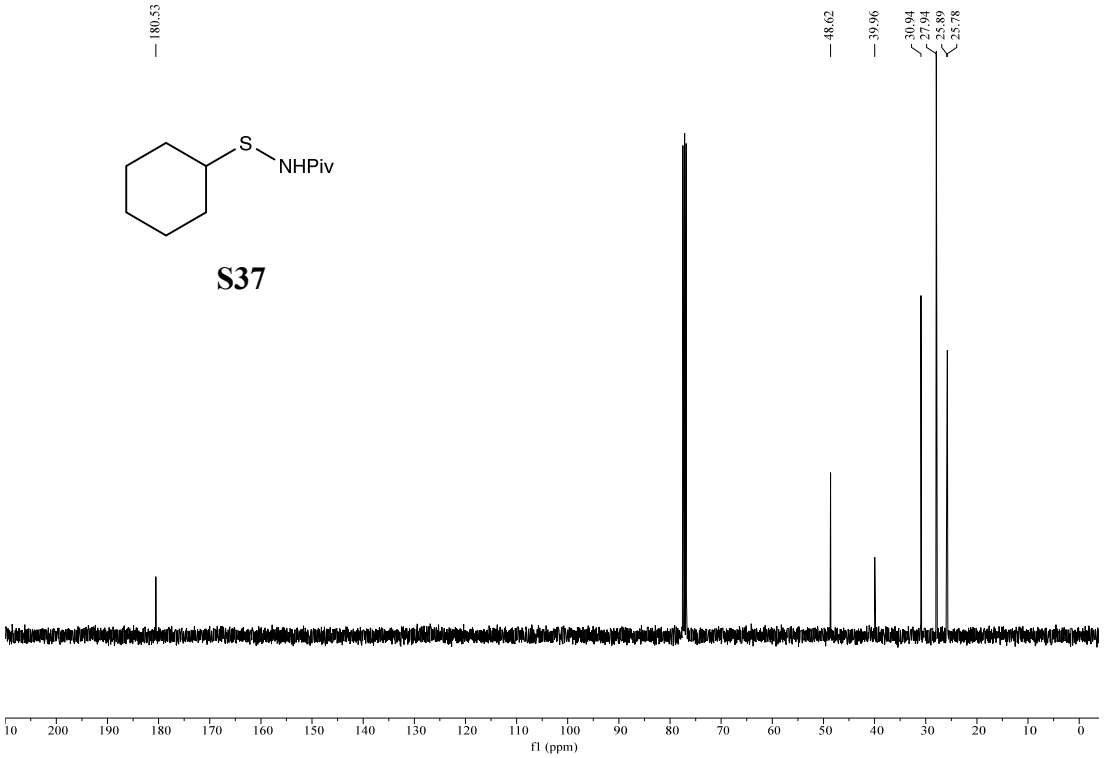
^{13}C NMR of S35 (100 MHz, $CDCl_3$)



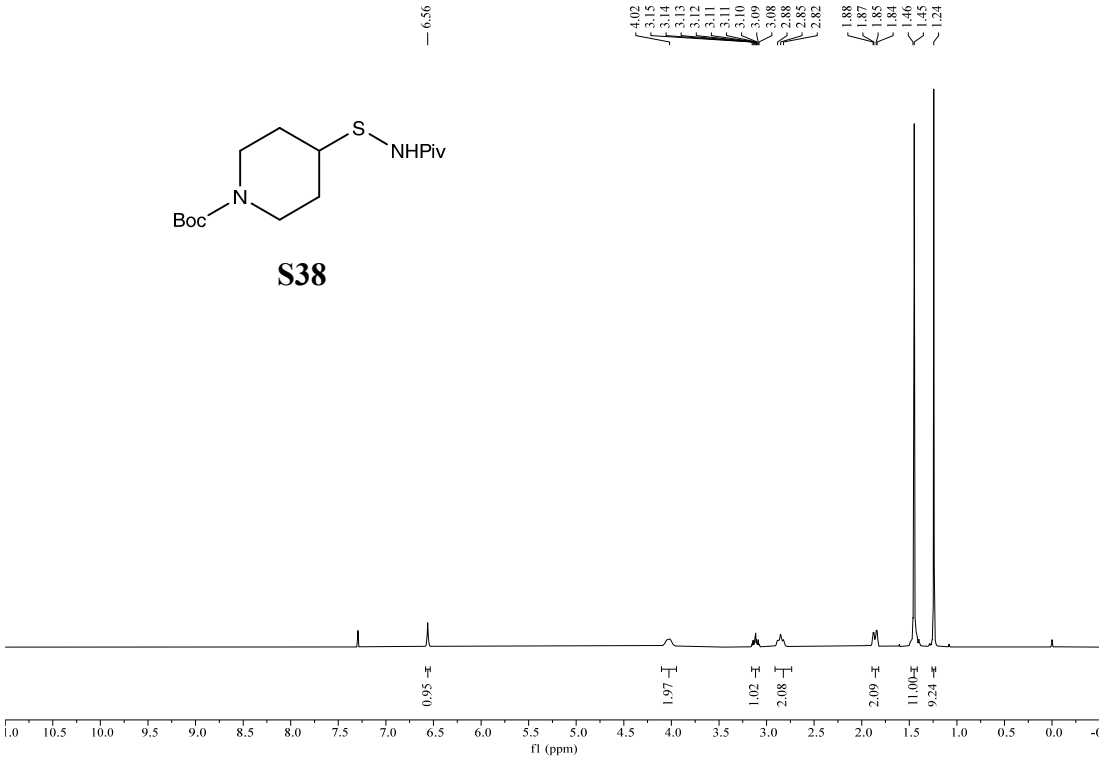
^{1}H NMR of S37 (400 MHz, $CDCl_3$)



^{13}C NMR of S37 (100 MHz, $CDCl_3$)

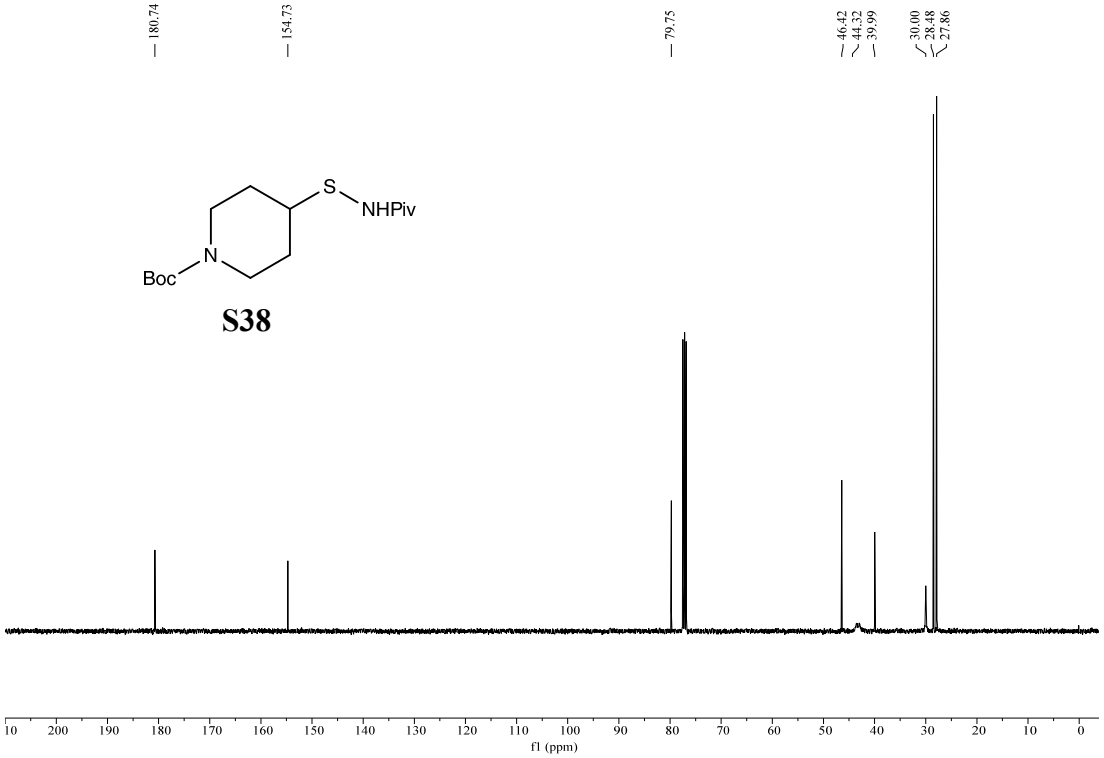


^{1}H NMR of S38 (400 MHz, $CDCl_3$)



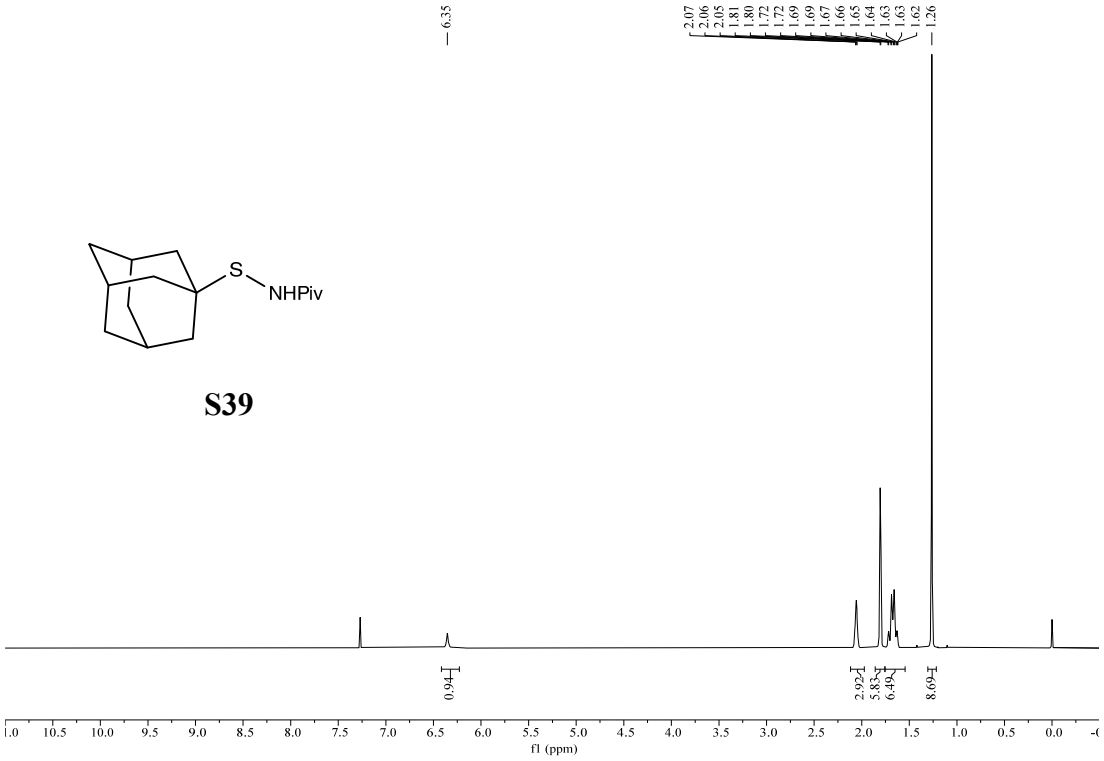
S38

^{13}C NMR of S38 (100 MHz, $CDCl_3$)



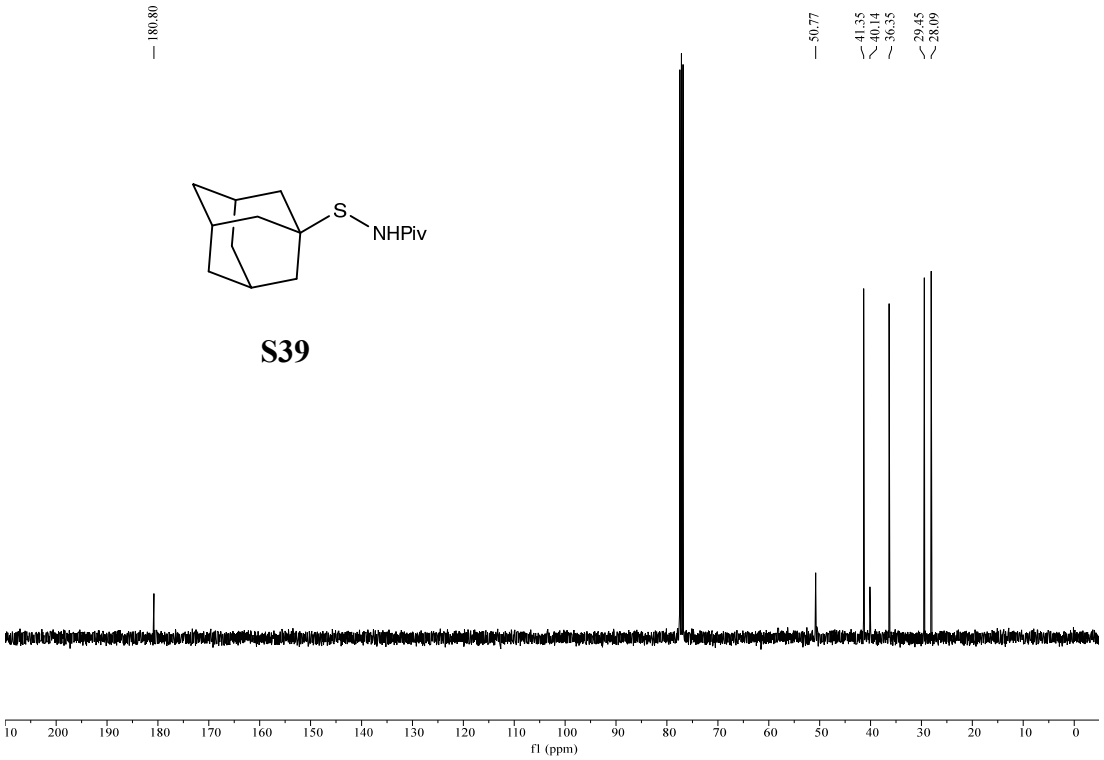
S38

^{1}H NMR of S39 (400 MHz, $CDCl_3$)



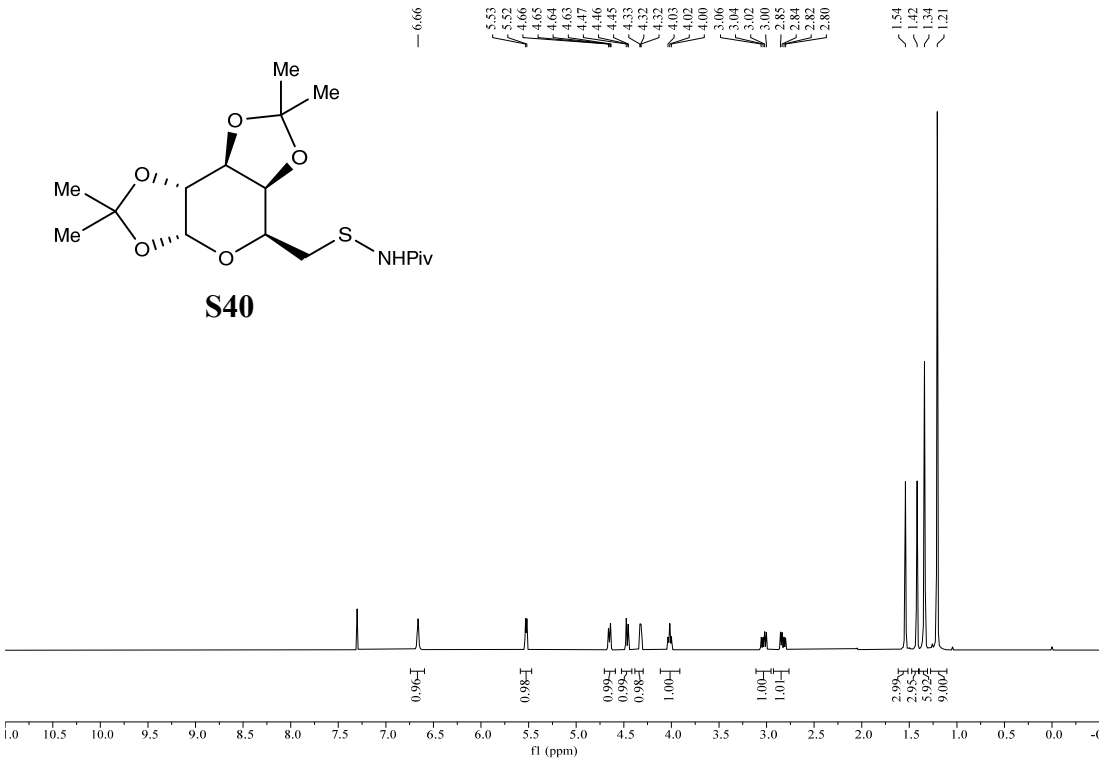
S39

^{13}C NMR of S39 (100 MHz, $CDCl_3$)



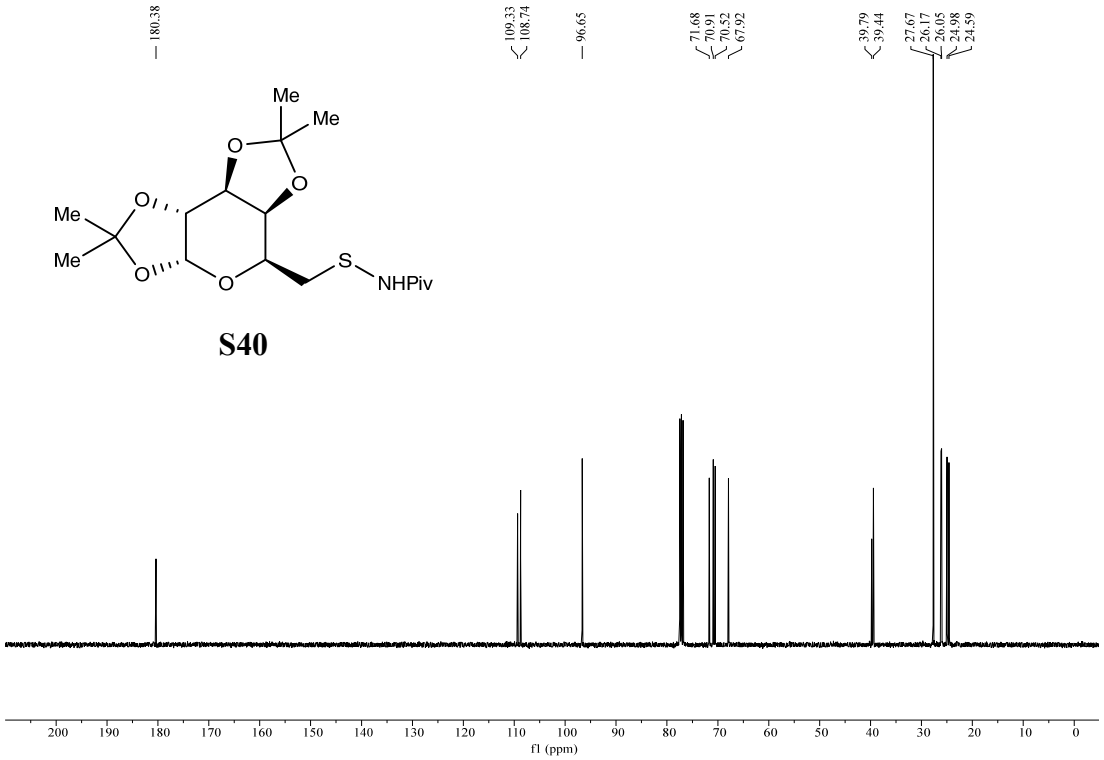
S39

^{1}H NMR of S40 (400 MHz, $CDCl_3$)



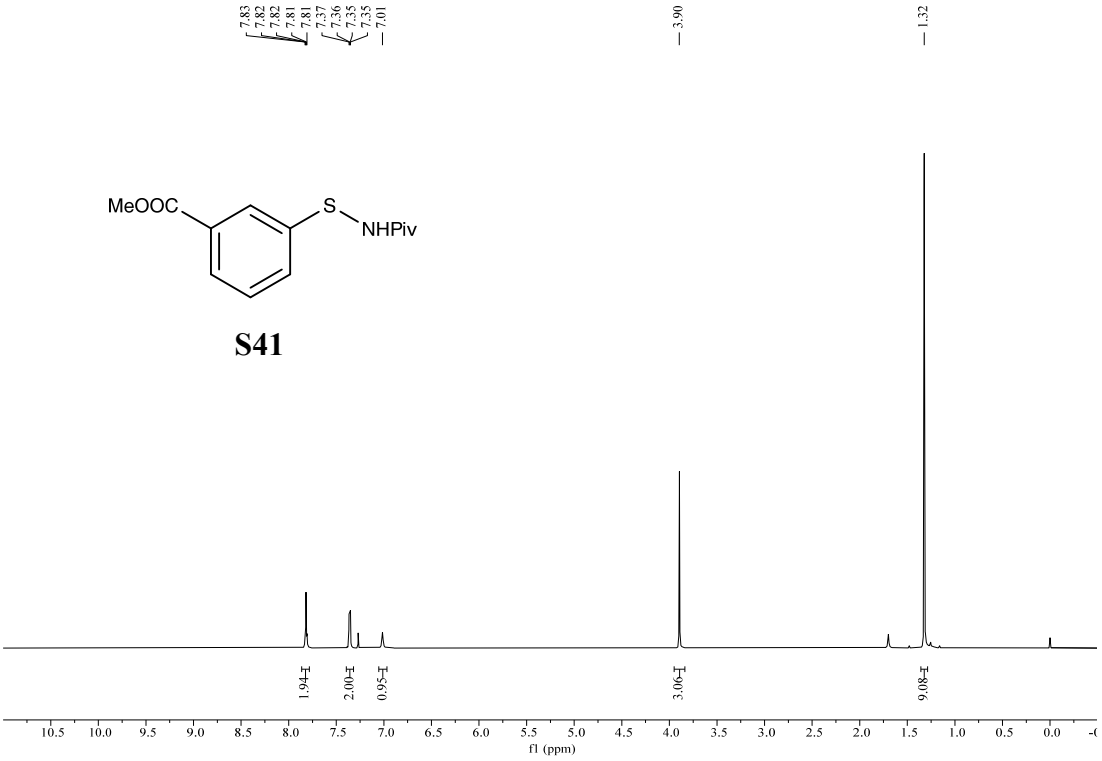
S40

^{13}C NMR of S40 (100 MHz, $CDCl_3$)



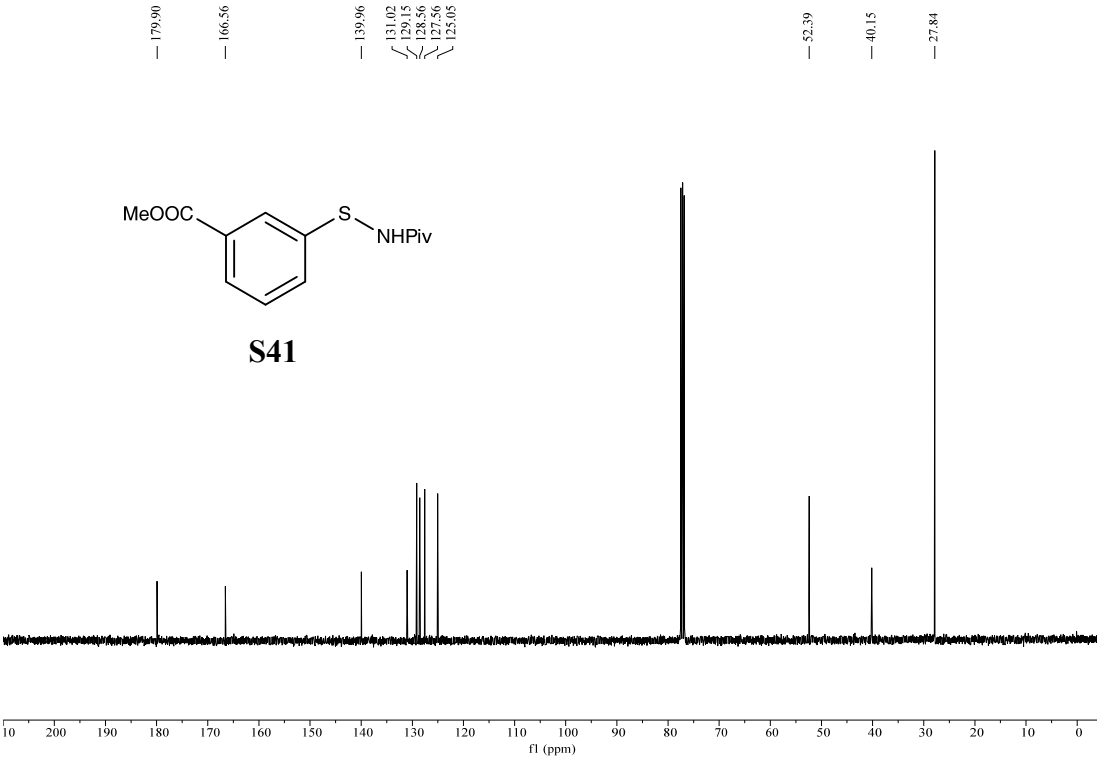
S40

^{1}H NMR of S41 (400 MHz, $CDCl_3$)



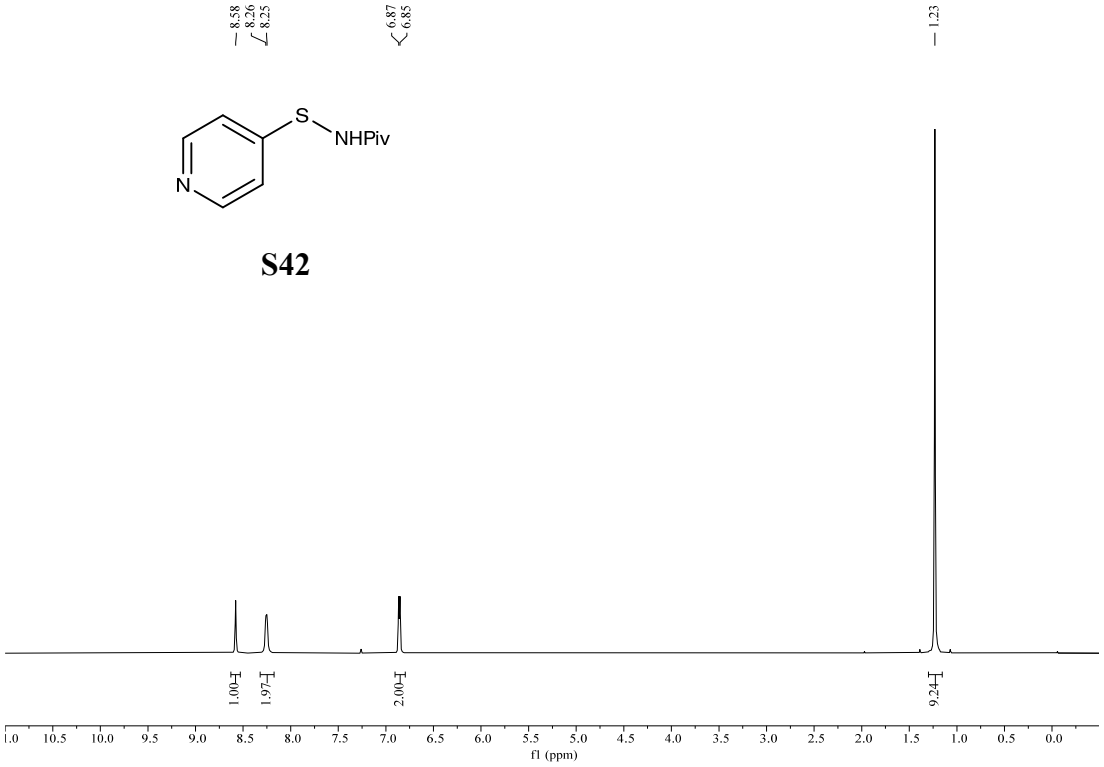
S41

^{13}C NMR of S41 (100 MHz, $CDCl_3$)



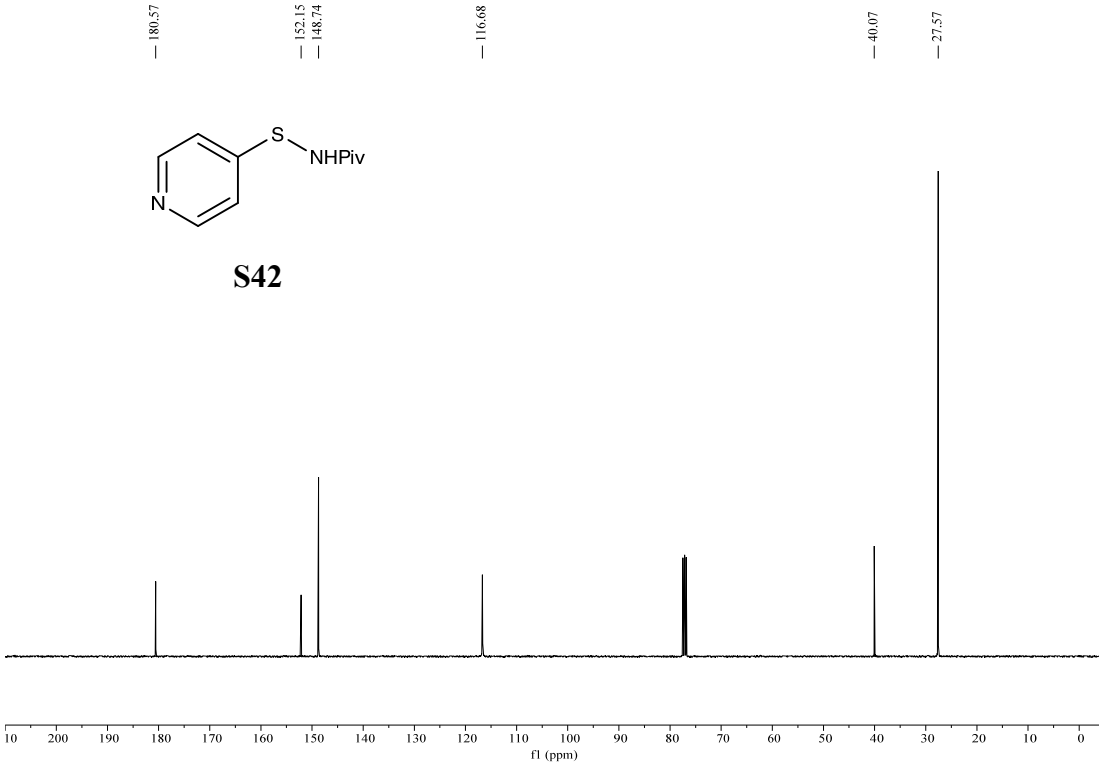
S41

^{1}H NMR of S42 (400 MHz, $CDCl_3$)



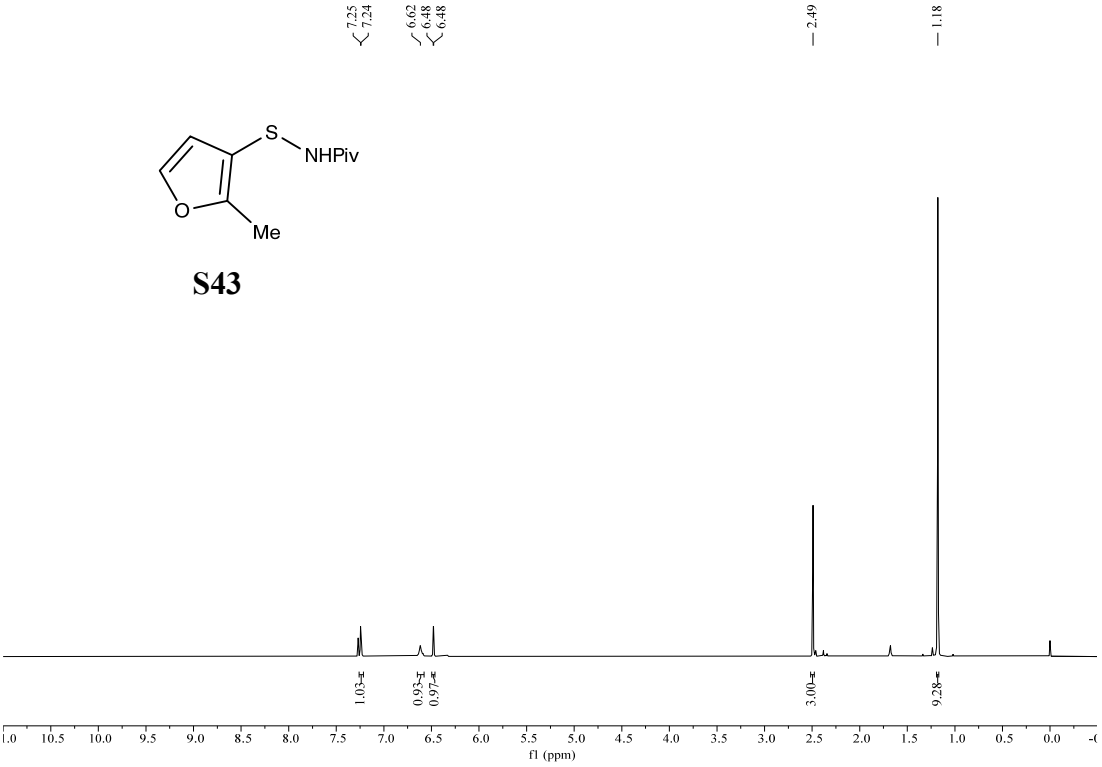
S42

^{13}C NMR of S42 (100 MHz, $CDCl_3$)



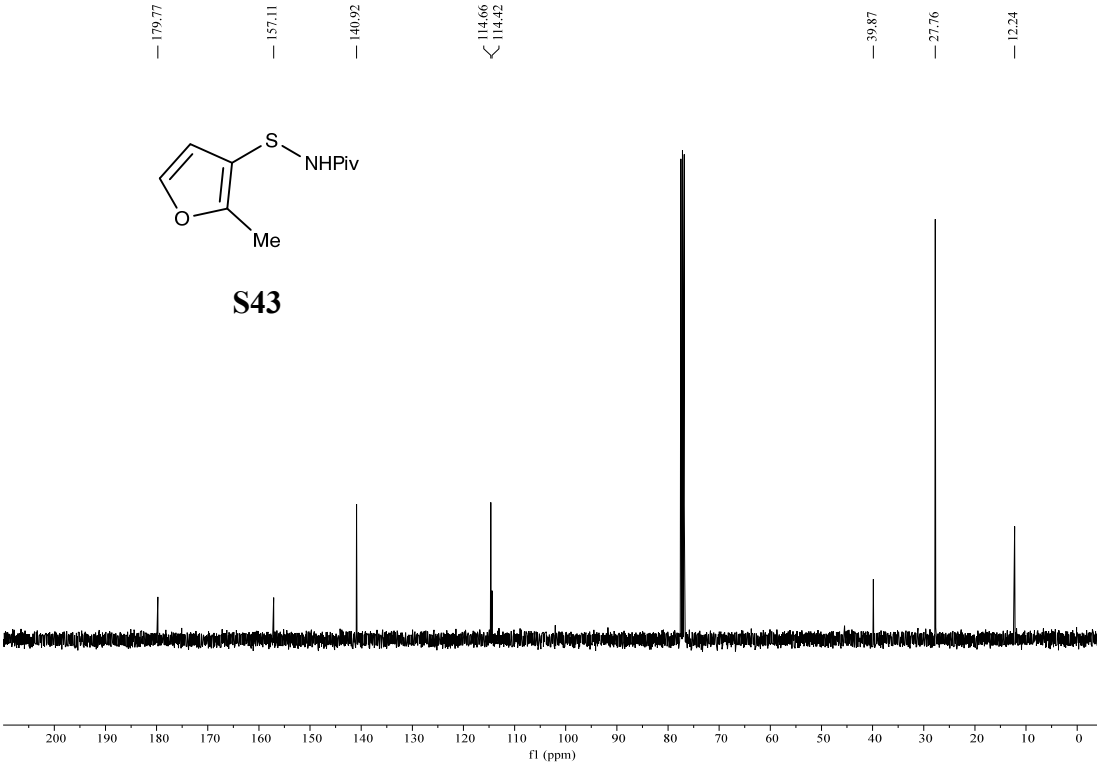
S42

^{1}H NMR of S43 (400 MHz, $CDCl_3$)



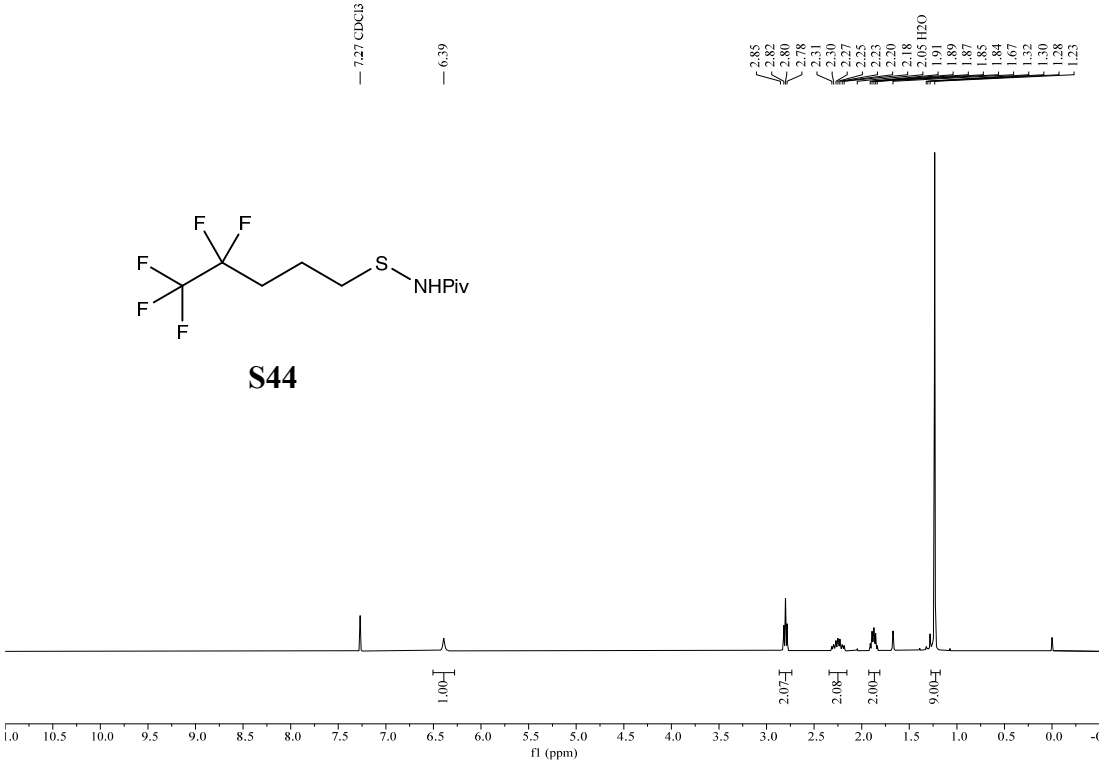
S43

^{13}C NMR of S43 (100 MHz, $CDCl_3$)



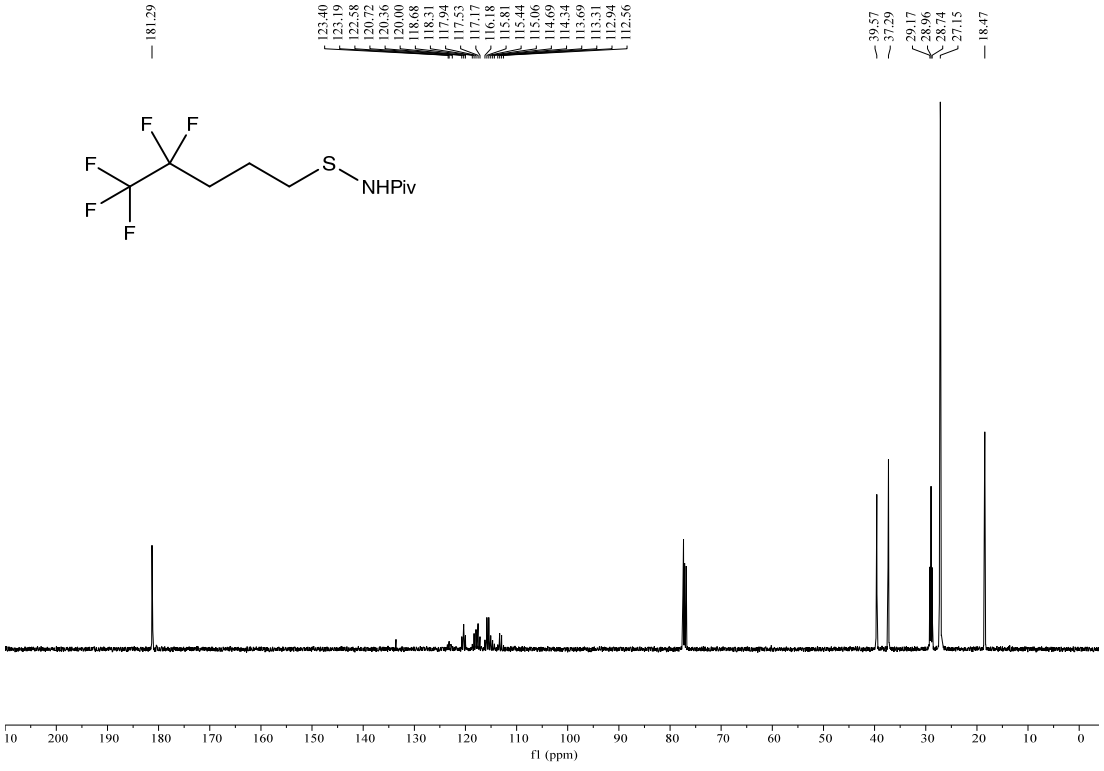
S43

^{1}H NMR of S44 (400 MHz, $CDCl_3$)

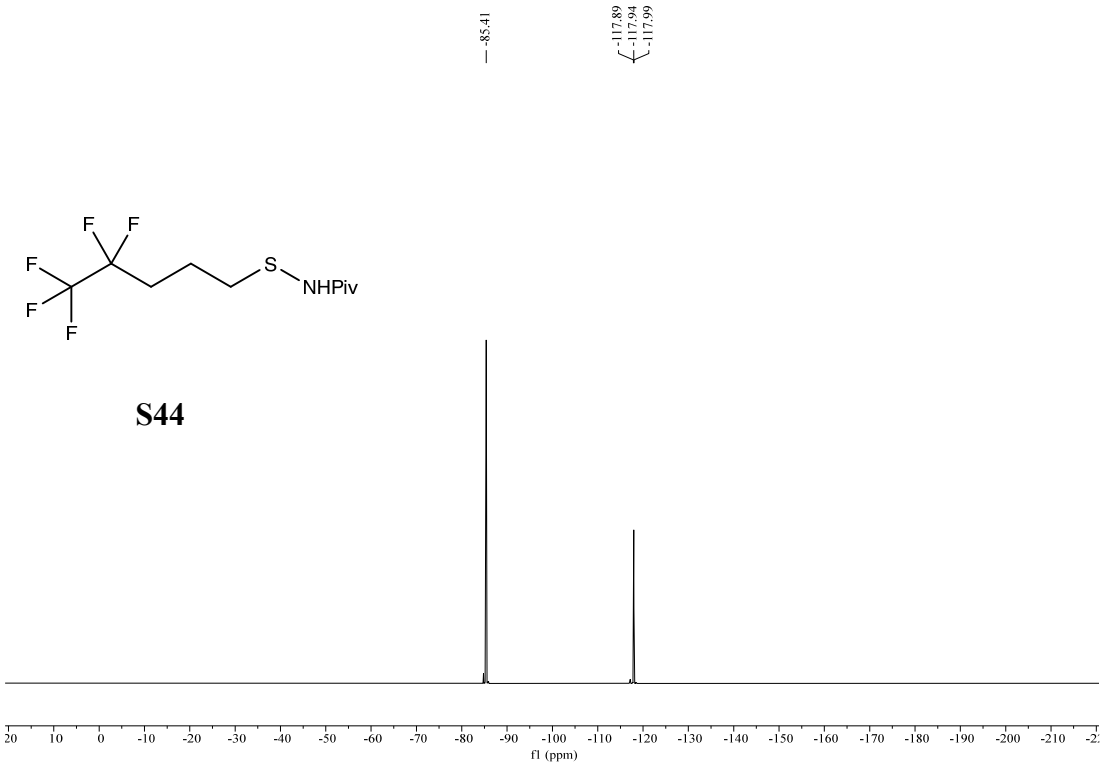


S44

^{13}C NMR of S44 (100 MHz, $CDCl_3$)

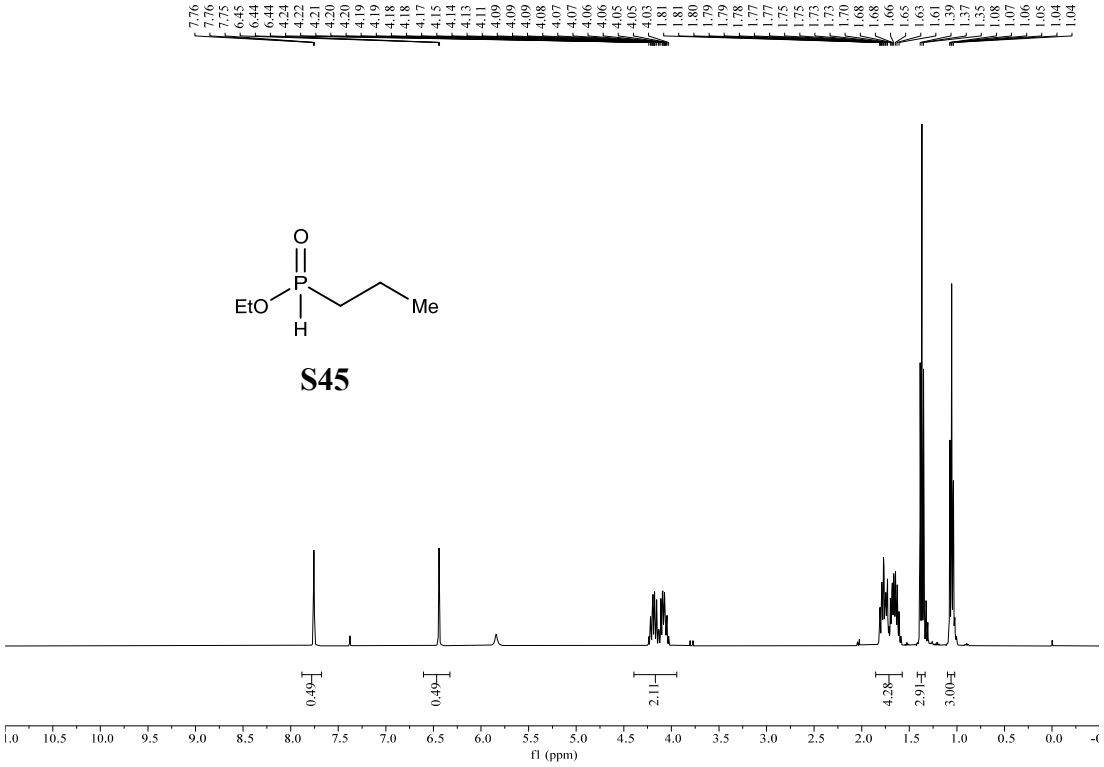


^{19}F NMR of S44 (375 MHz, $CDCl_3$)



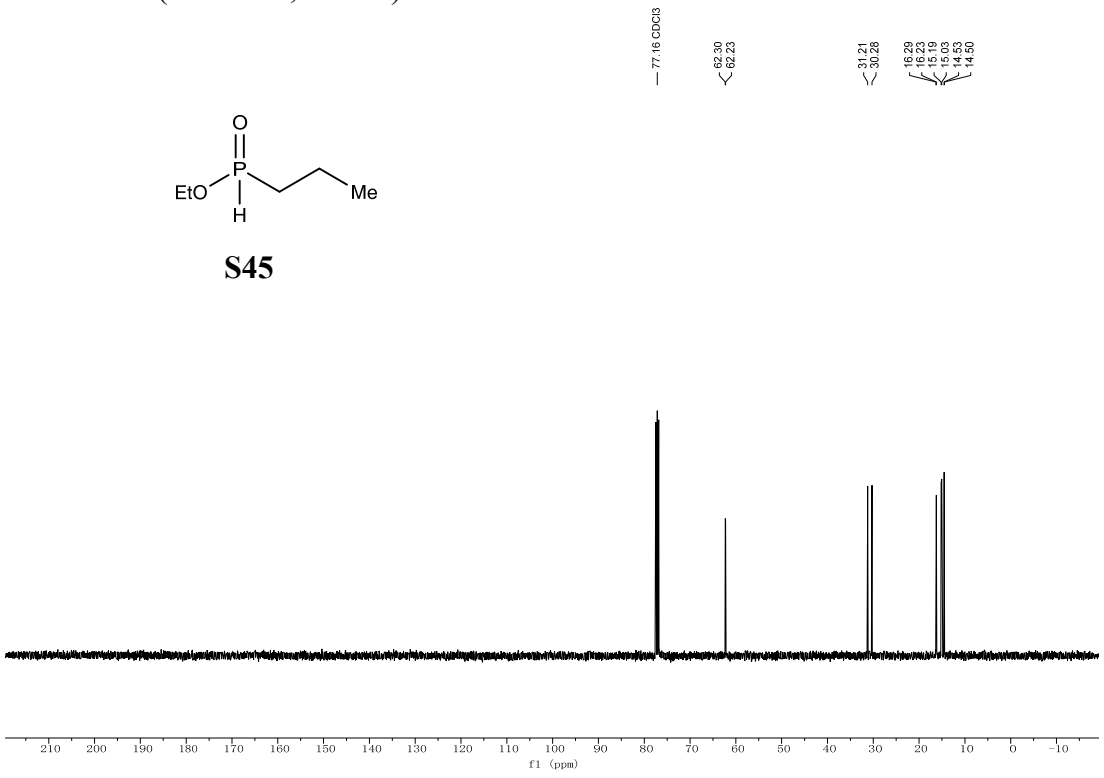
S44

^{1}H NMR of S45 (400 MHz, $CDCl_3$)



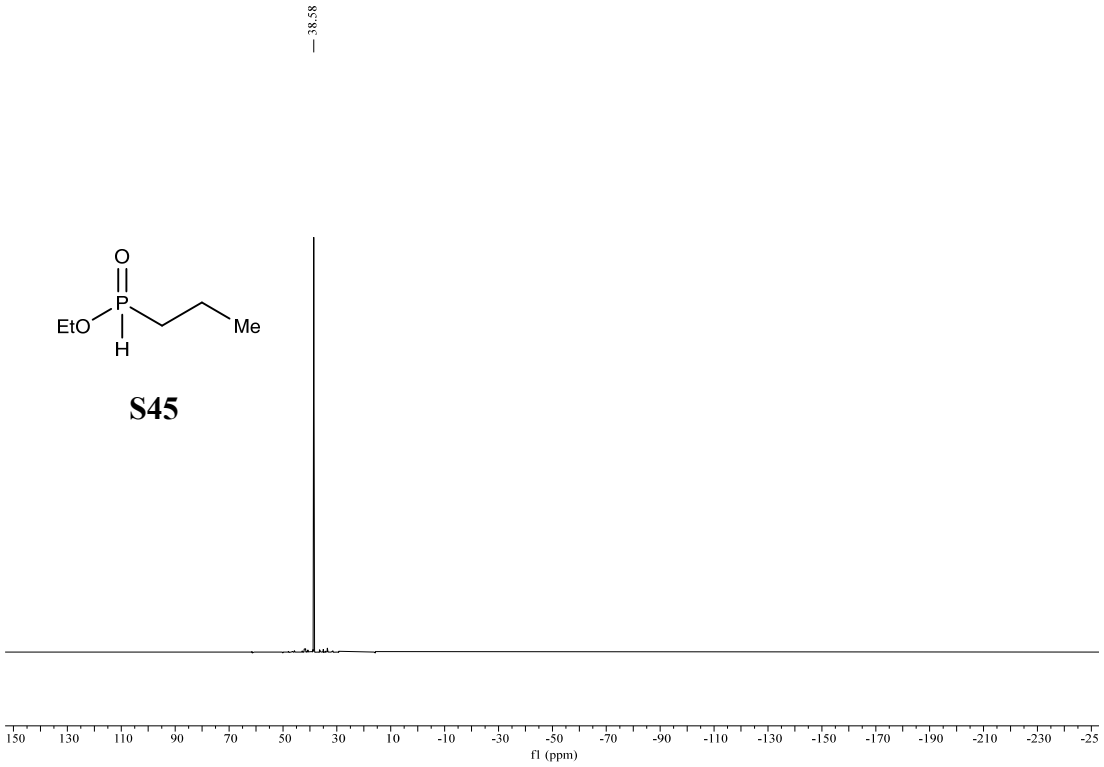
S45

^{13}C NMR of S45 (100 MHz, $CDCl_3$)



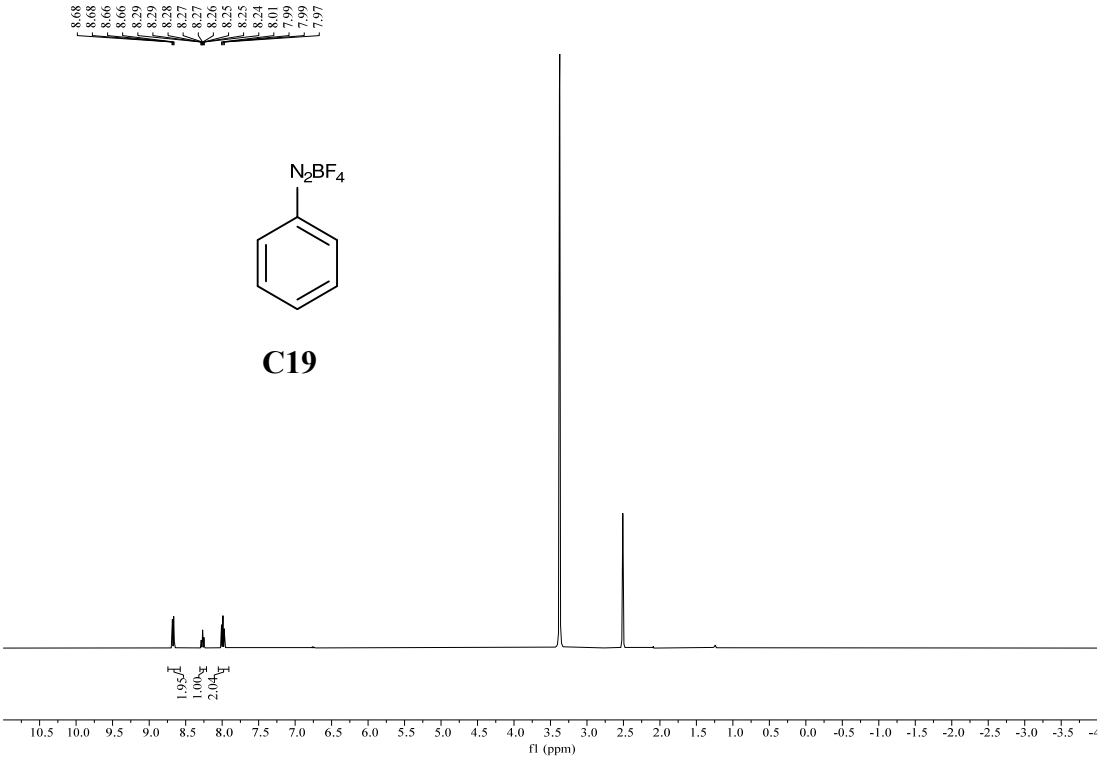
S45

^{31}P NMR of S45 (162I MHz, $CDCl_3$)



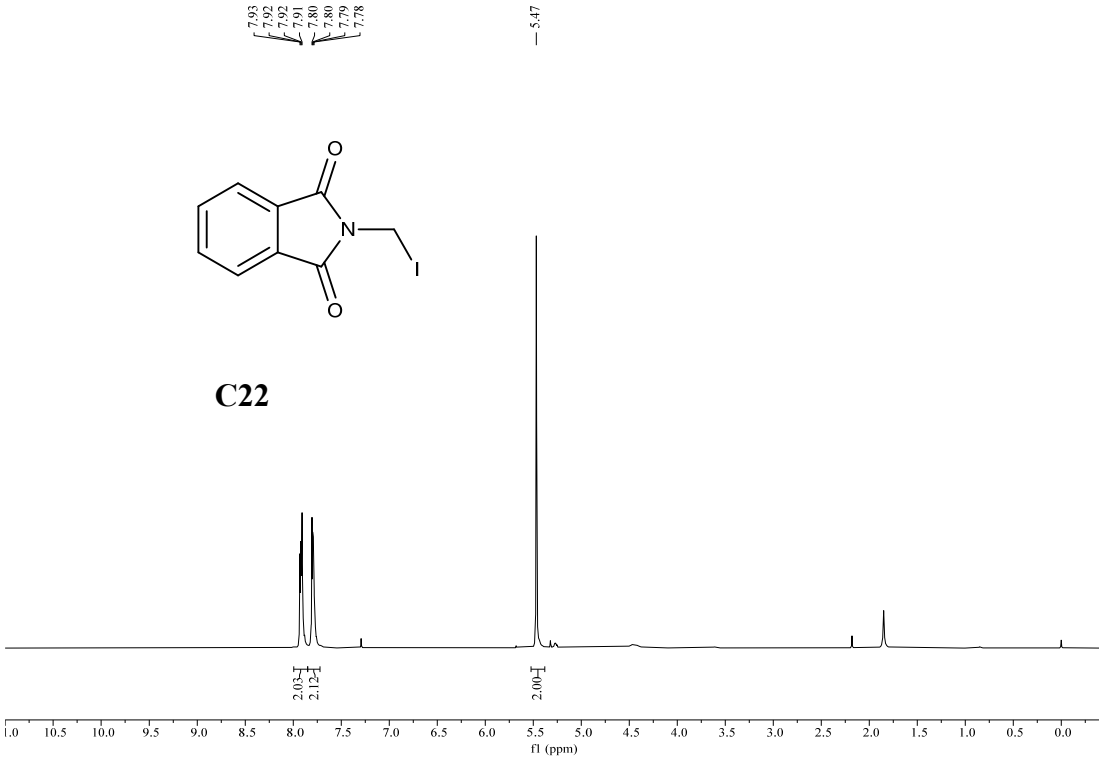
S45

[1]H NMR of C19 (400 MHz, DMSO-*d*6)

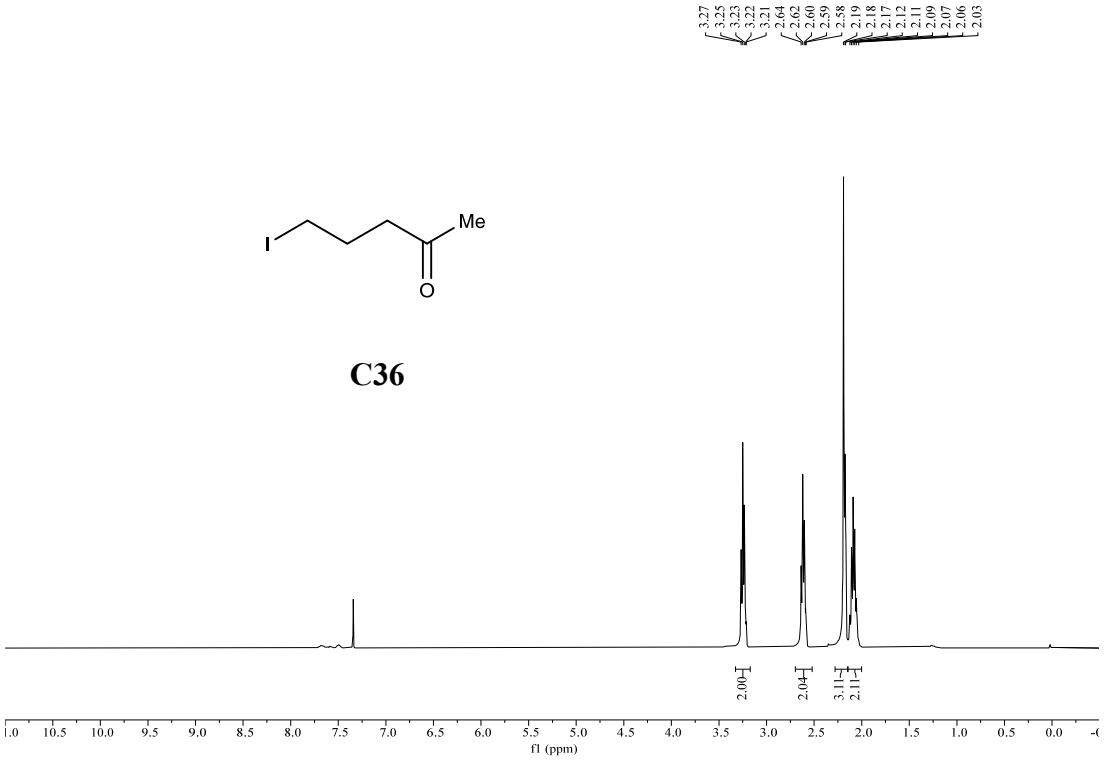


C19

^{1}H NMR of C22 (400 MHz, $CDCl_3$)

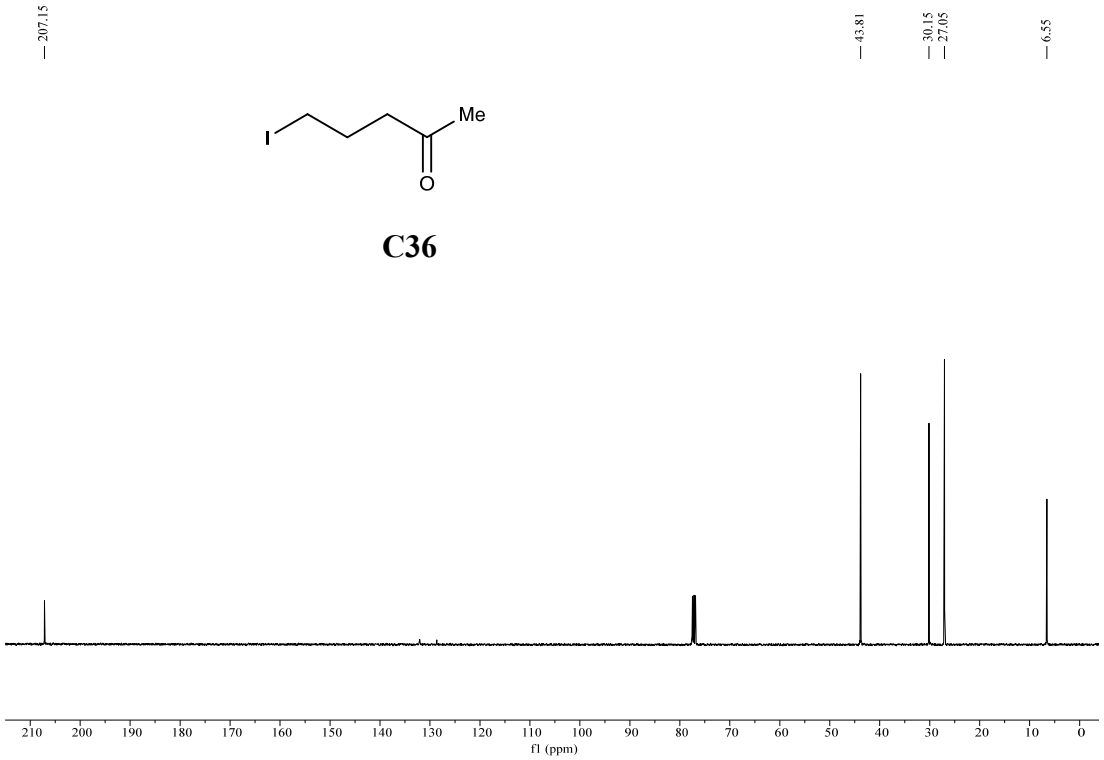


^{1}H NMR of C36 (400 MHz, $CDCl_3$)



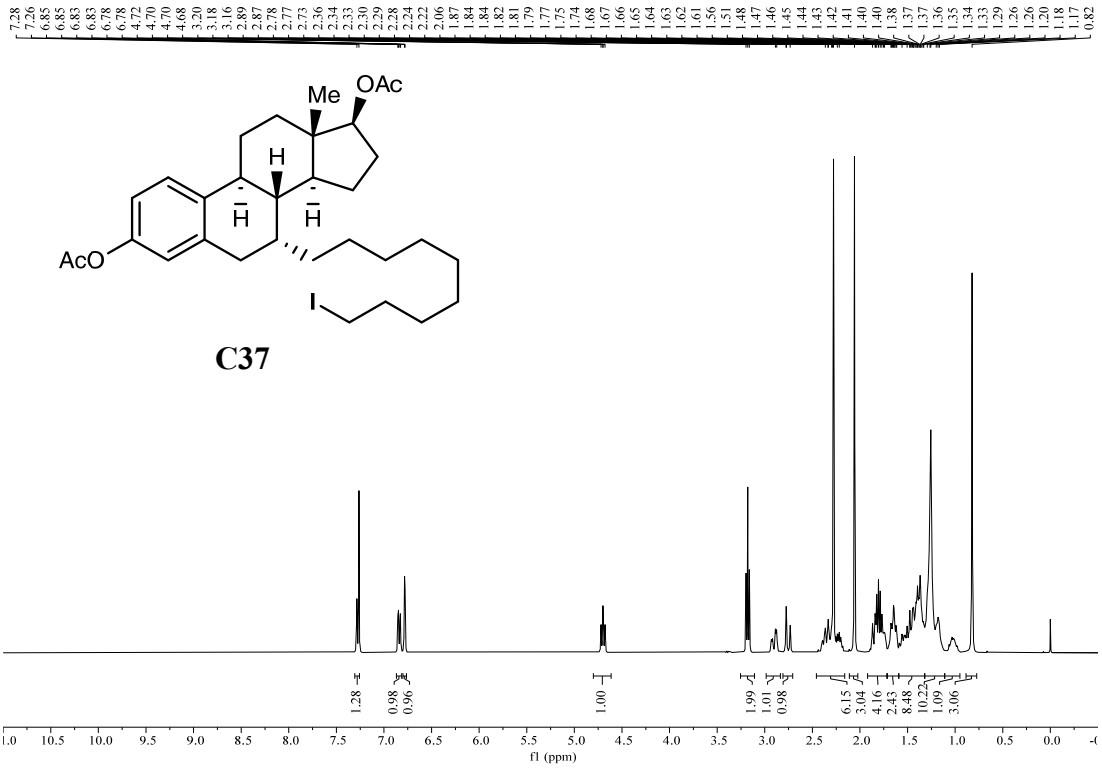
C36

^{13}C NMR of C36 (100 MHz, $CDCl_3$)

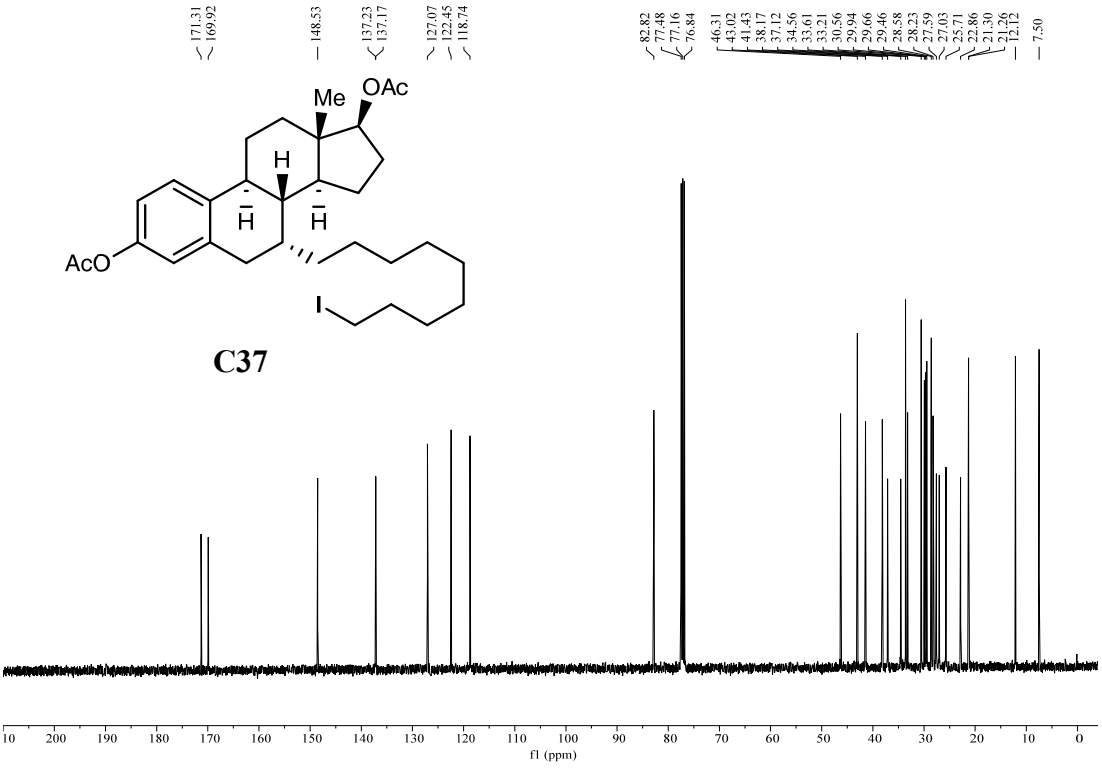


C36

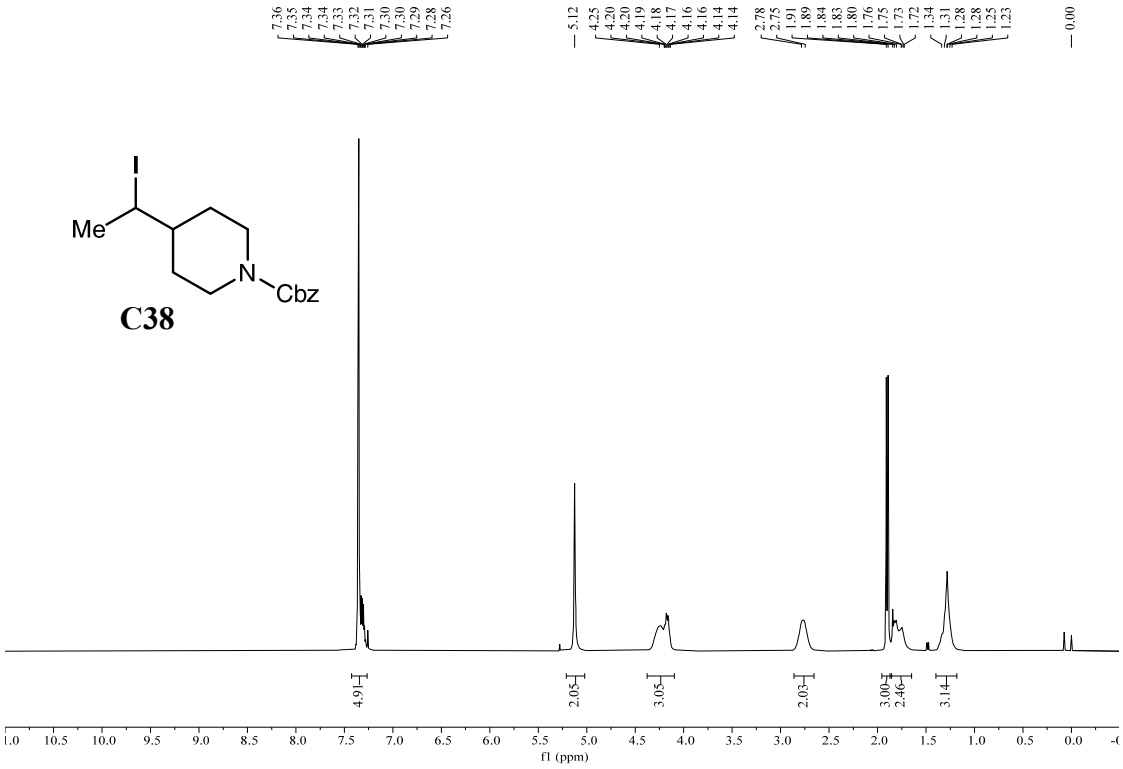
^{1}H NMR of C37 (400 MHz, $CDCl_3$)



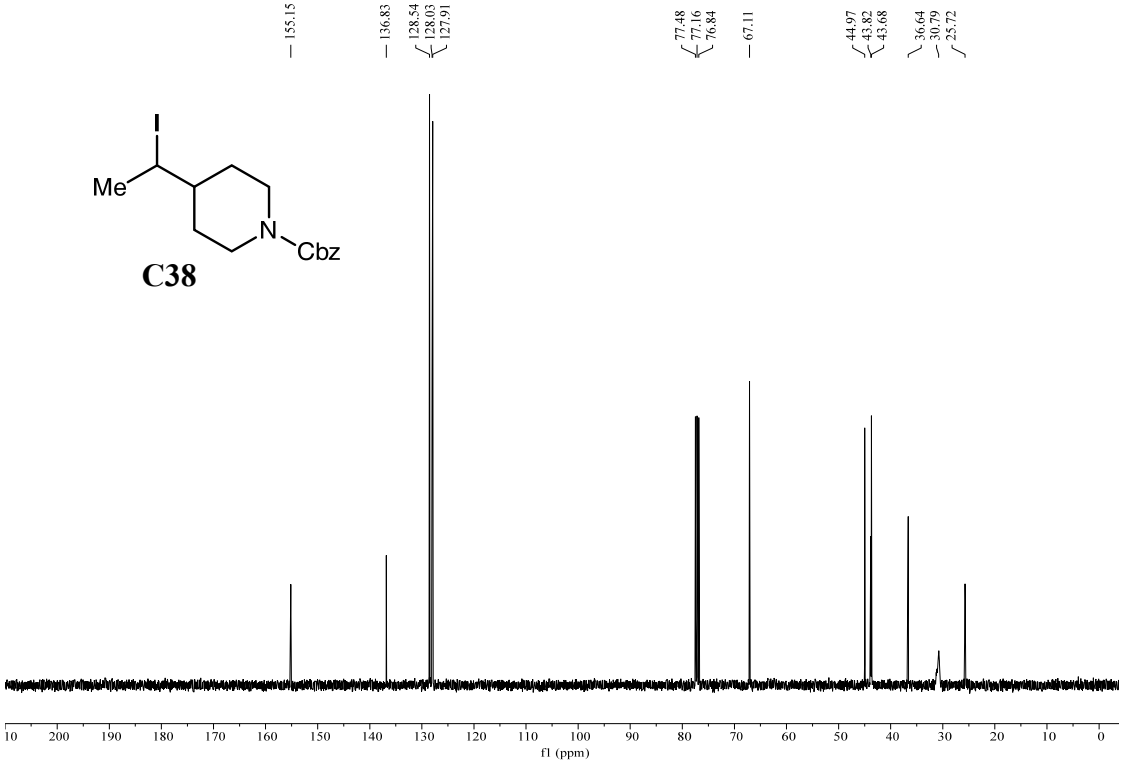
^{13}C NMR of C37 (100 MHz, $CDCl_3$)



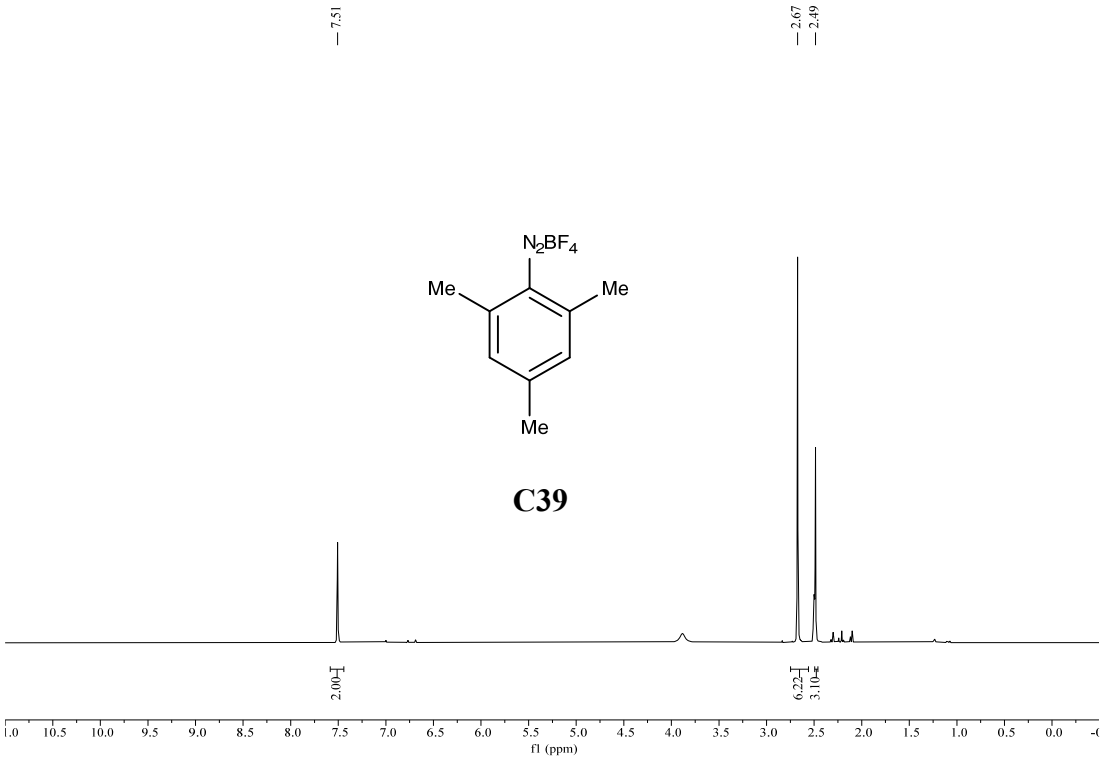
^{1}H NMR of C38 (400 MHz, $CDCl_3$)



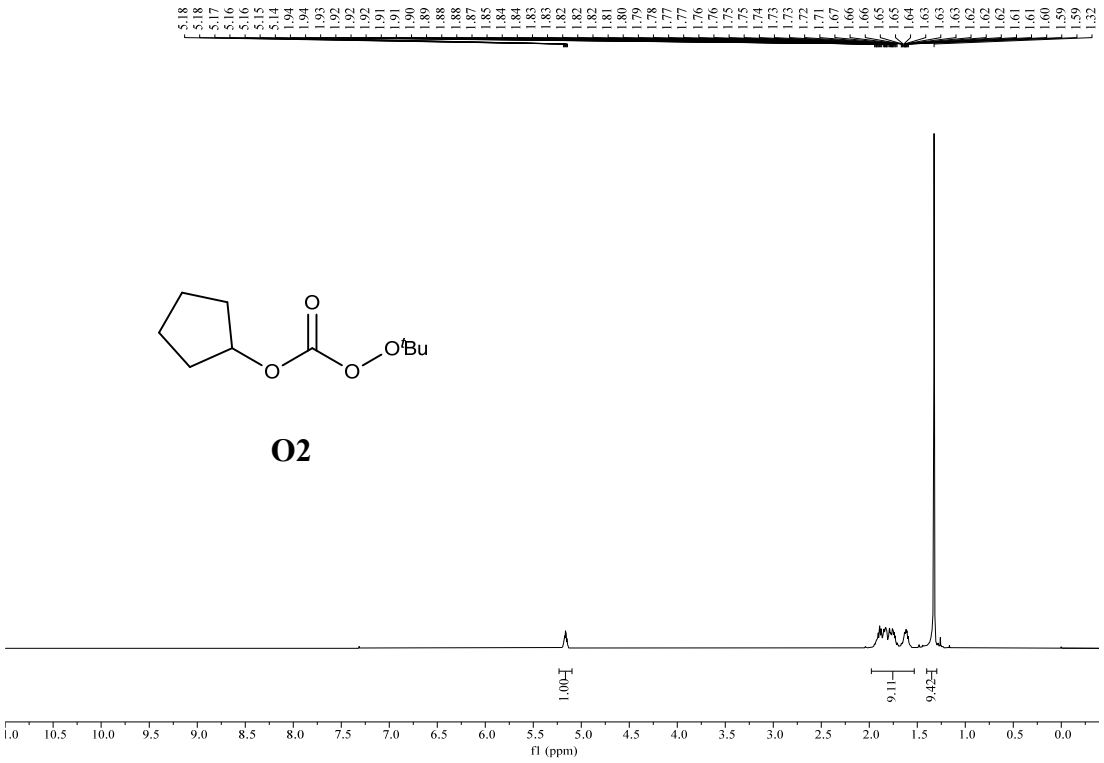
^{13}C NMR of C38 (100 MHz, $CDCl_3$)



^{1}H NMR of C39 (400 MHz, DMSO-*d*6)

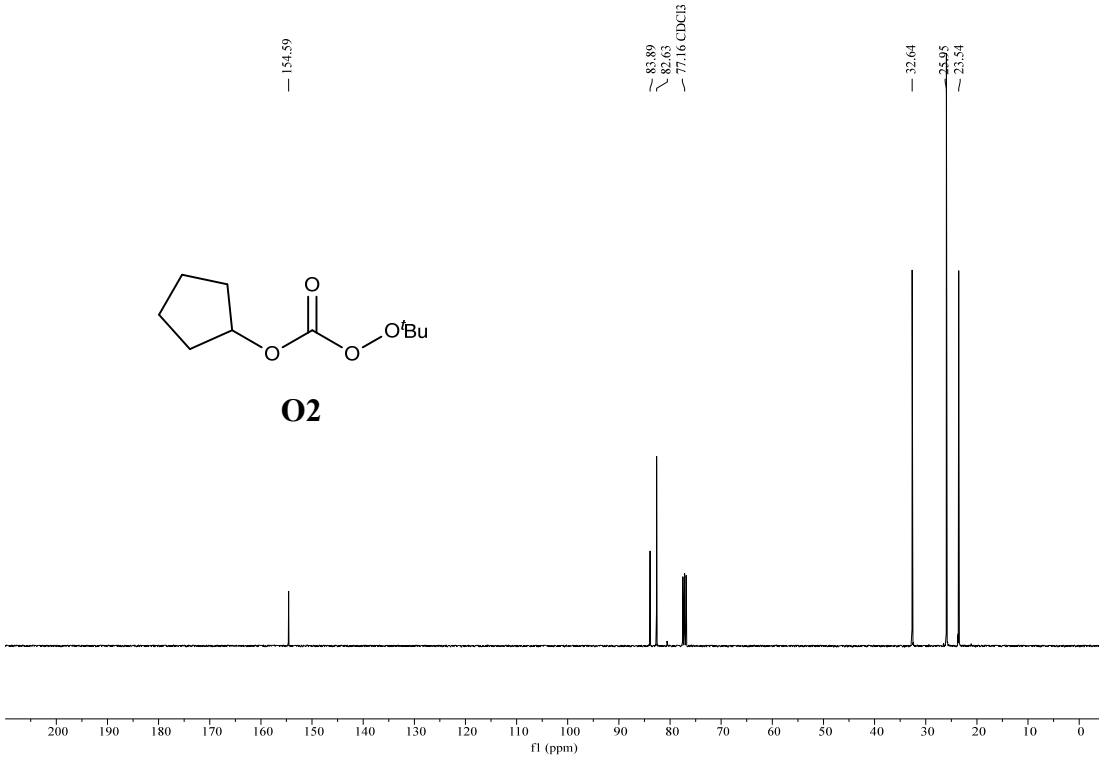


^{1}H NMR of O2 (400 MHz, $CDCl_3$)



O2

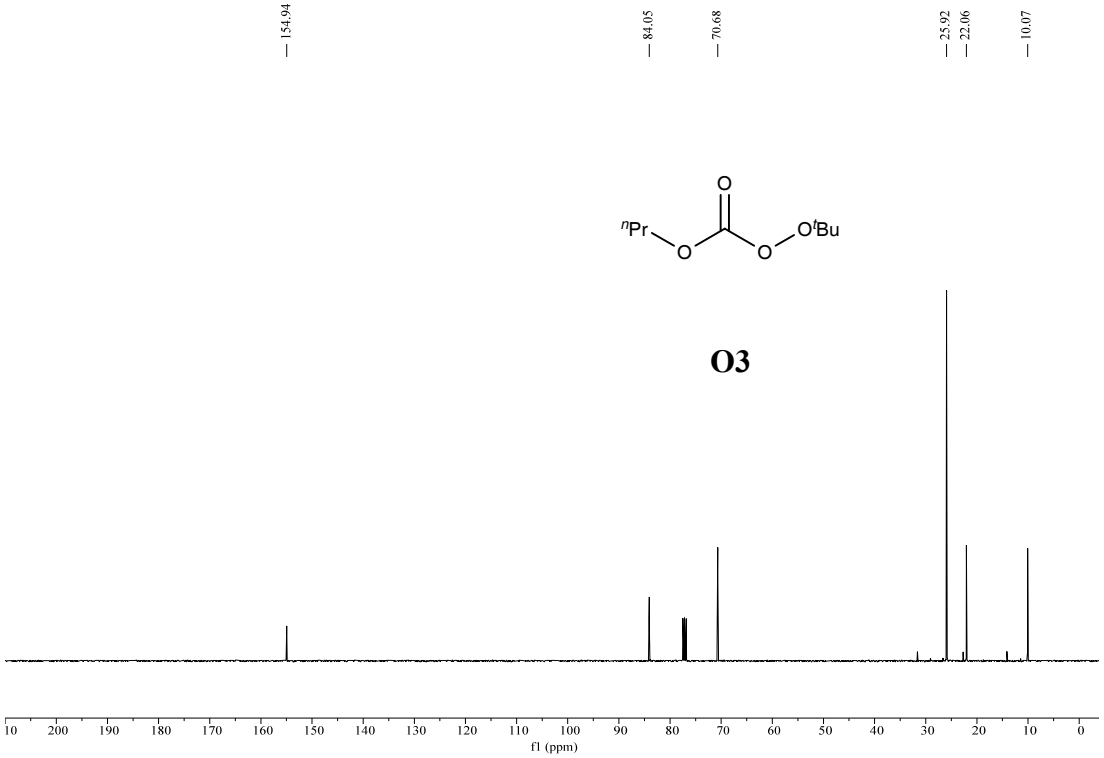
^{13}C NMR of O2 (100 MHz, $CDCl_3$)



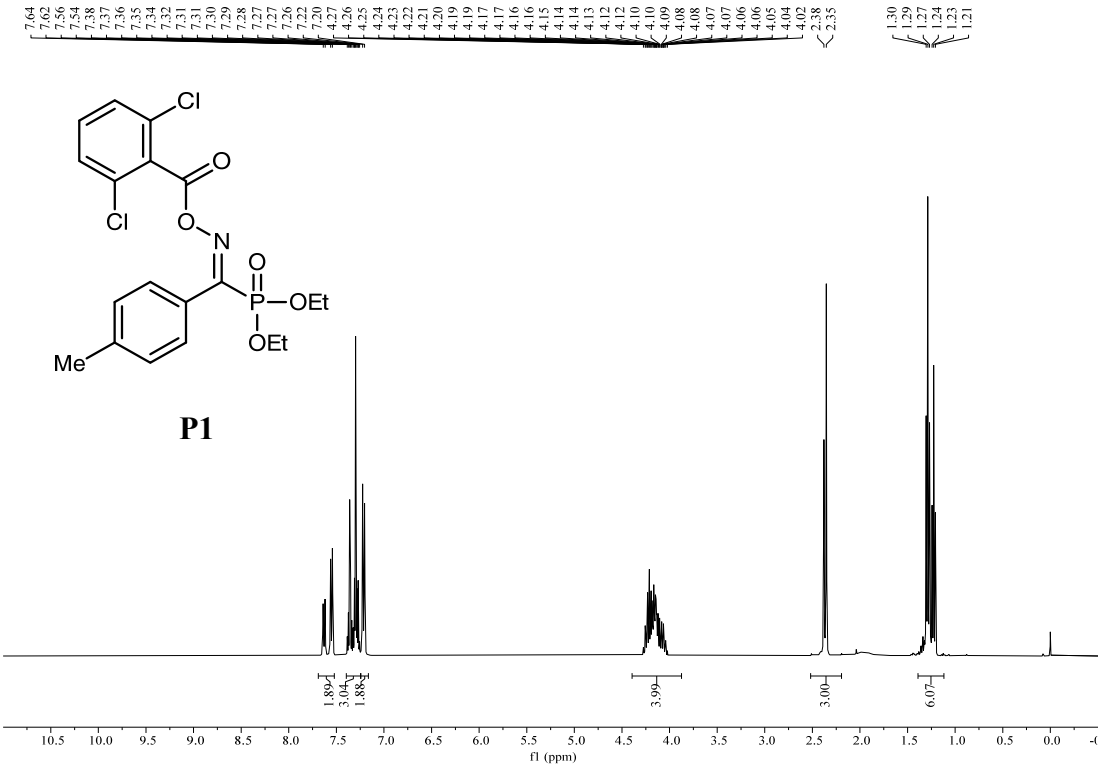
O2

^{1}H NMR of O3 (400 MHz, $CDCl_3$)

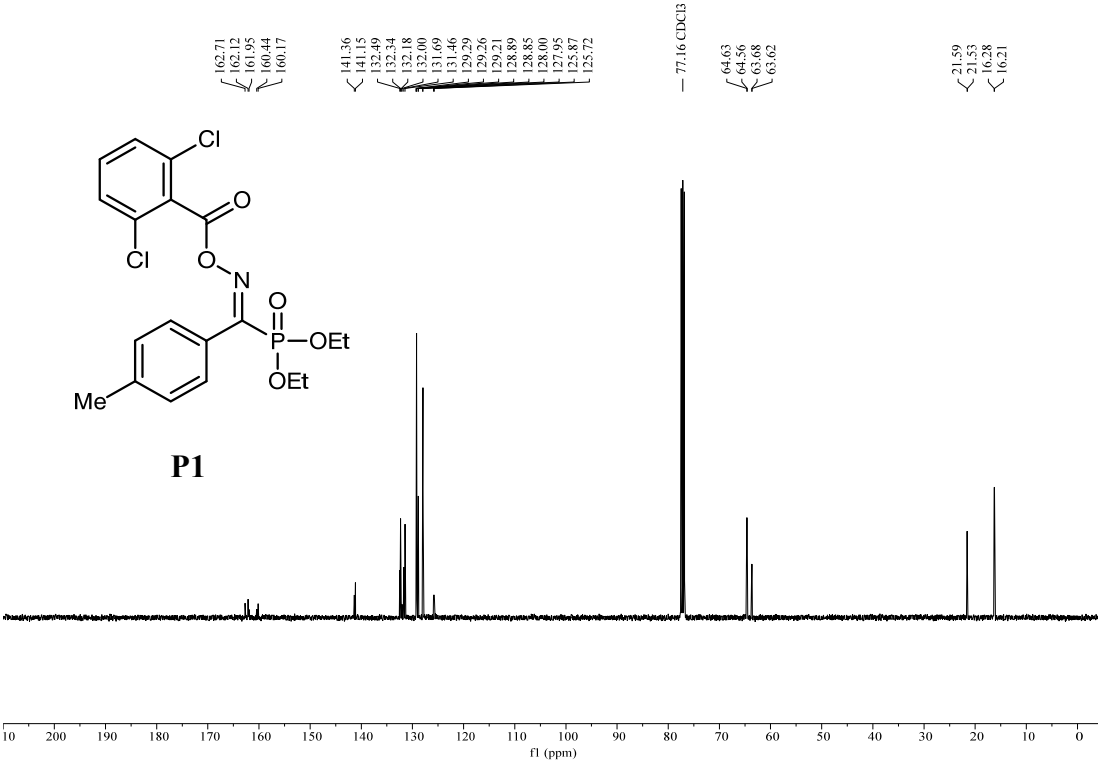
^{13}C NMR of O3 (100 MHz, $CDCl_3$)



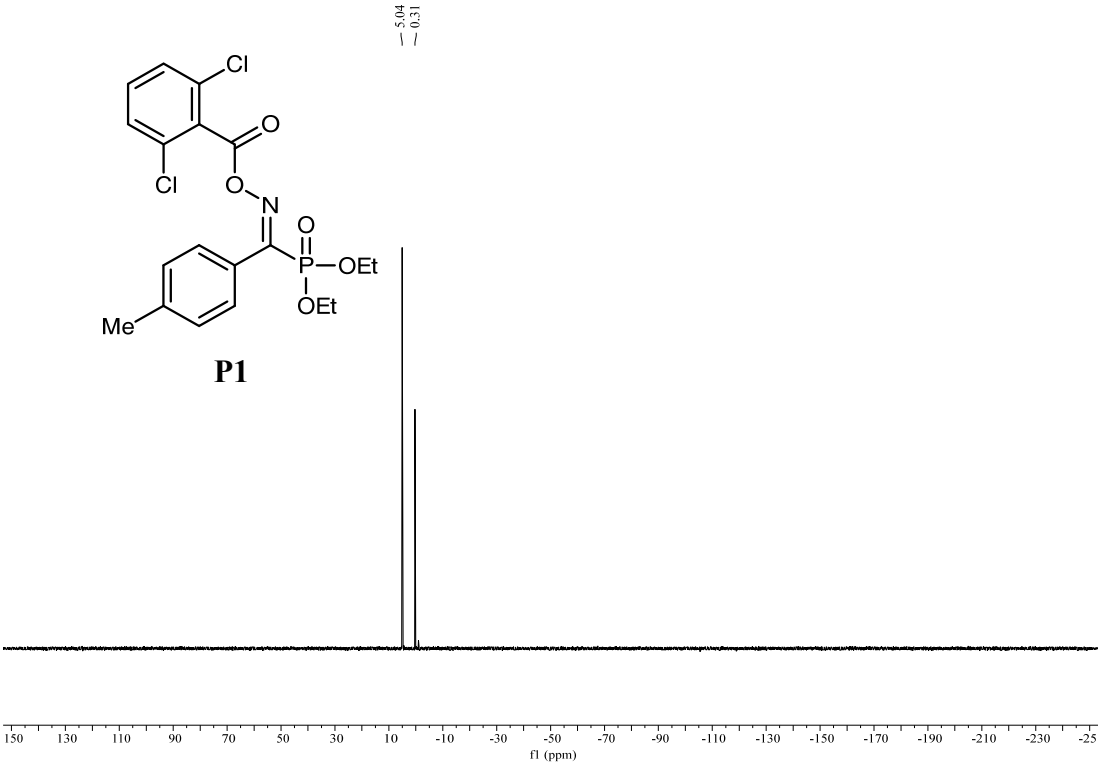
^{1}H NMR of P1 (400 MHz, $CDCl_3$)



^{13}C NMR of P1 (100 MHz, $CDCl_3$)

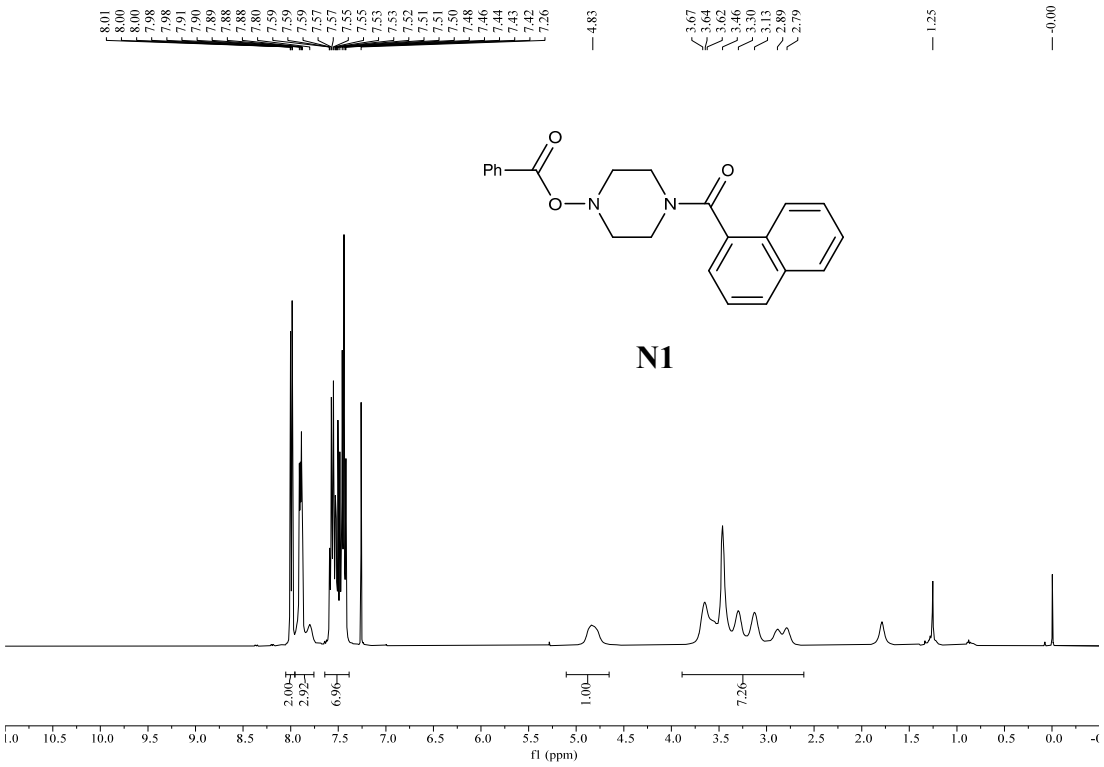


^{31}P NMR of P1 (162 MHz, $CDCl_3$)

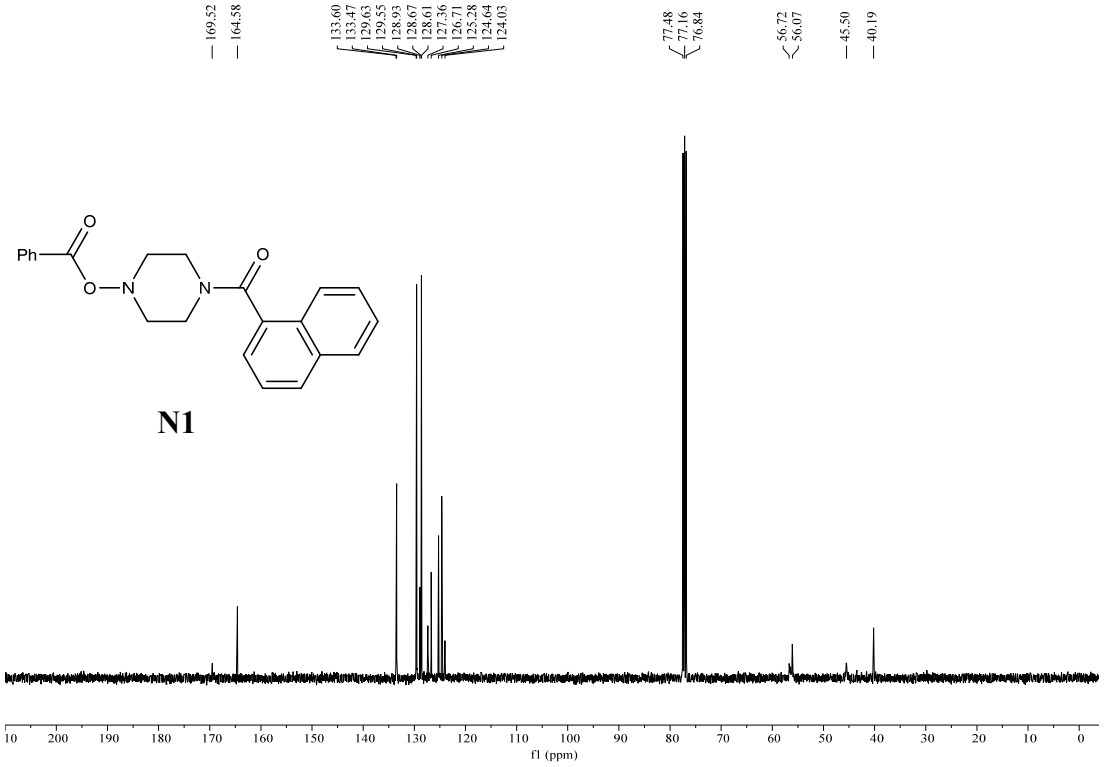


P1

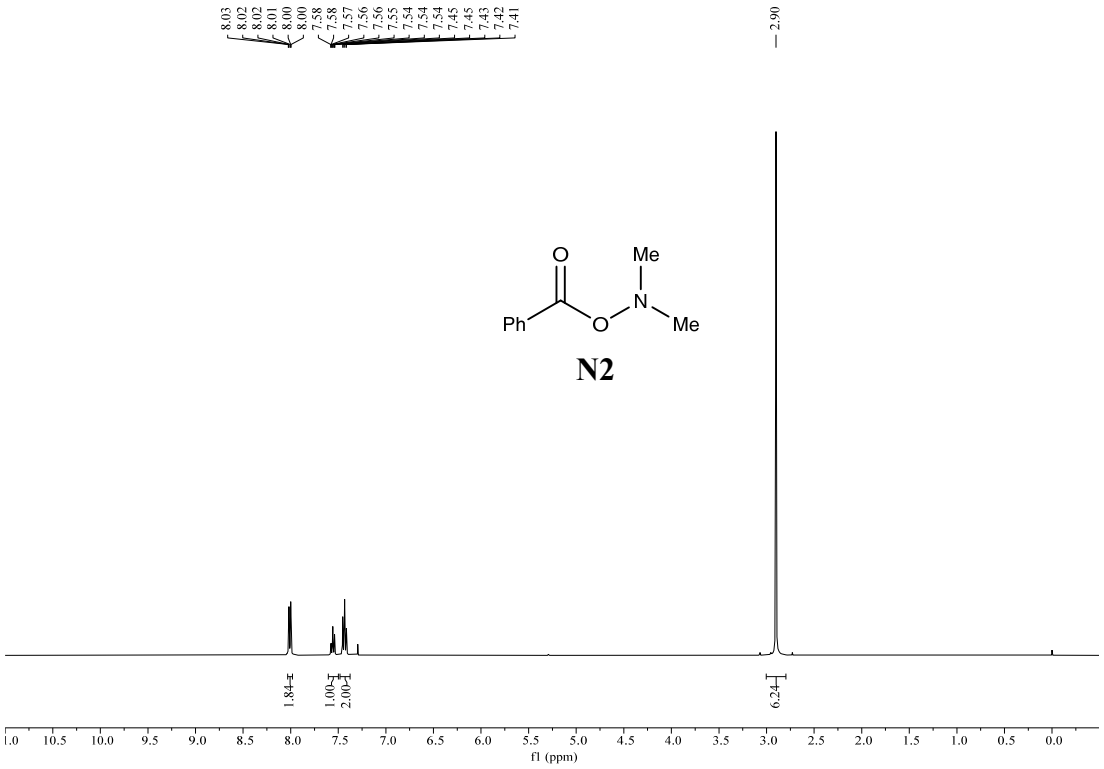
^{1}H NMR of N1 (400 MHz, $CDCl_3$)



^{13}C NMR of N1 (100 MHz, $CDCl_3$)

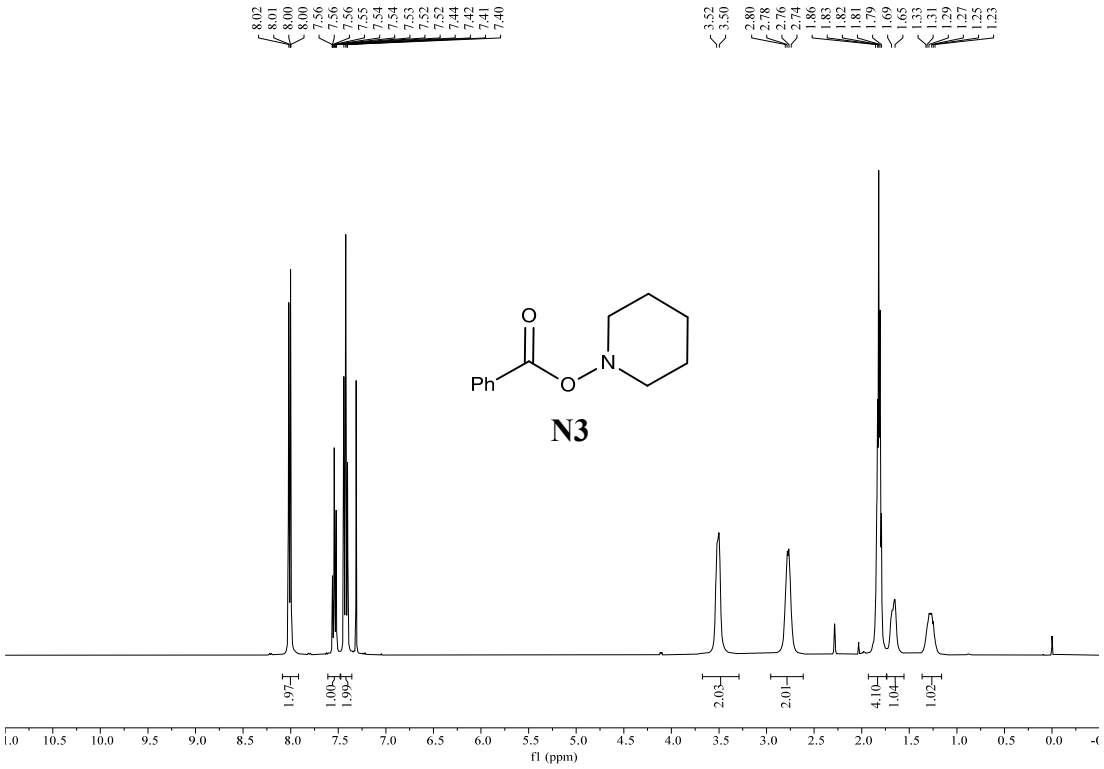


^{1}H NMR of N2 (400 MHz, $CDCl_3$)

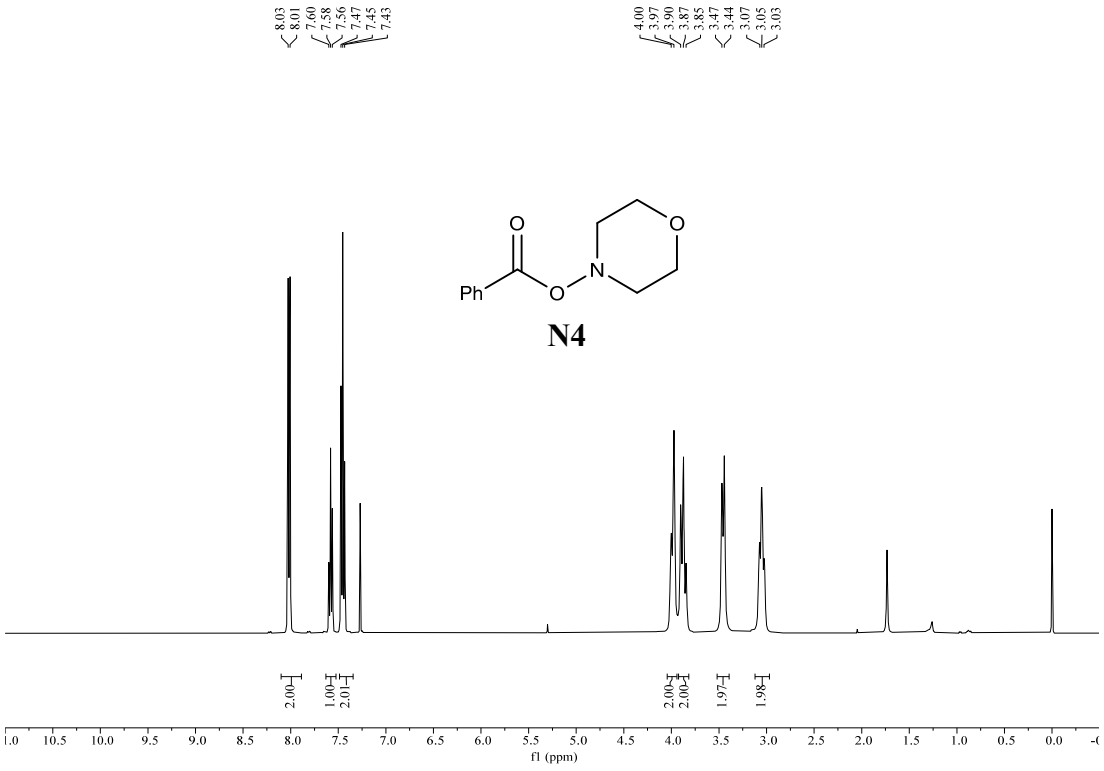


N2

^{1}H NMR of N3 (400 MHz, $CDCl_3$)

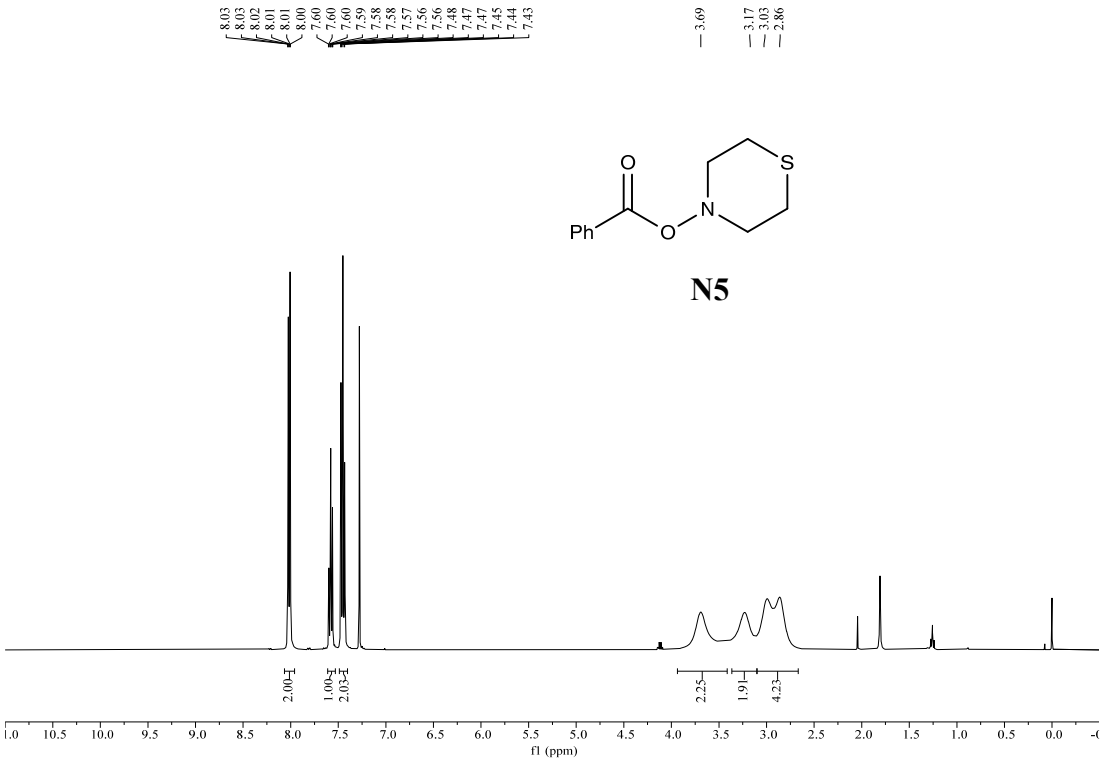


^{1}H NMR of N4 (400 MHz, $CDCl_3$)

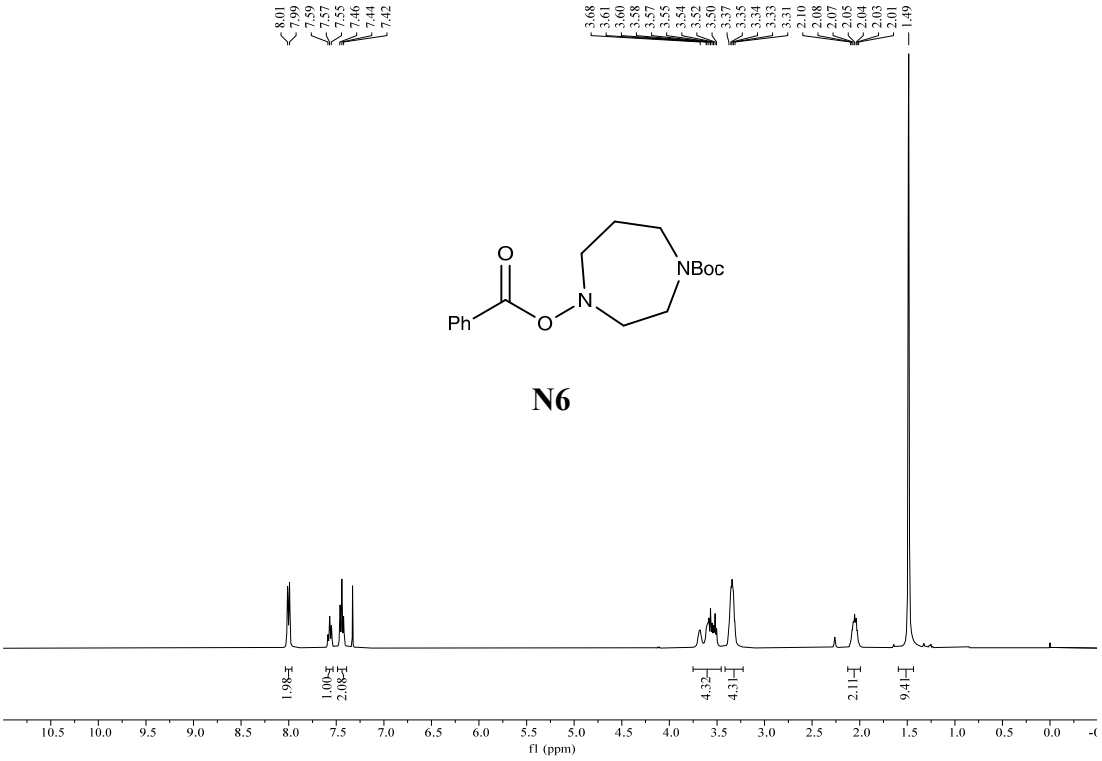


N4

^{1}H NMR of N5 (400 MHz, $CDCl_3$)

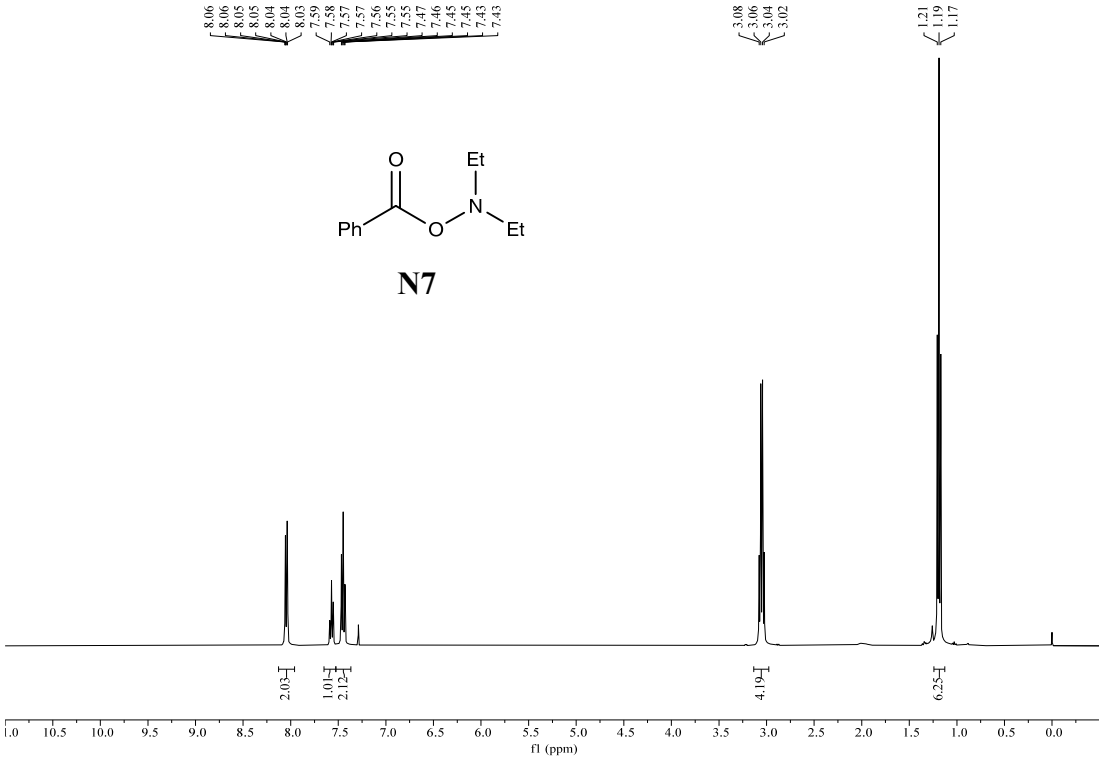


^{1}H NMR of N6 (400 MHz, $CDCl_3$)

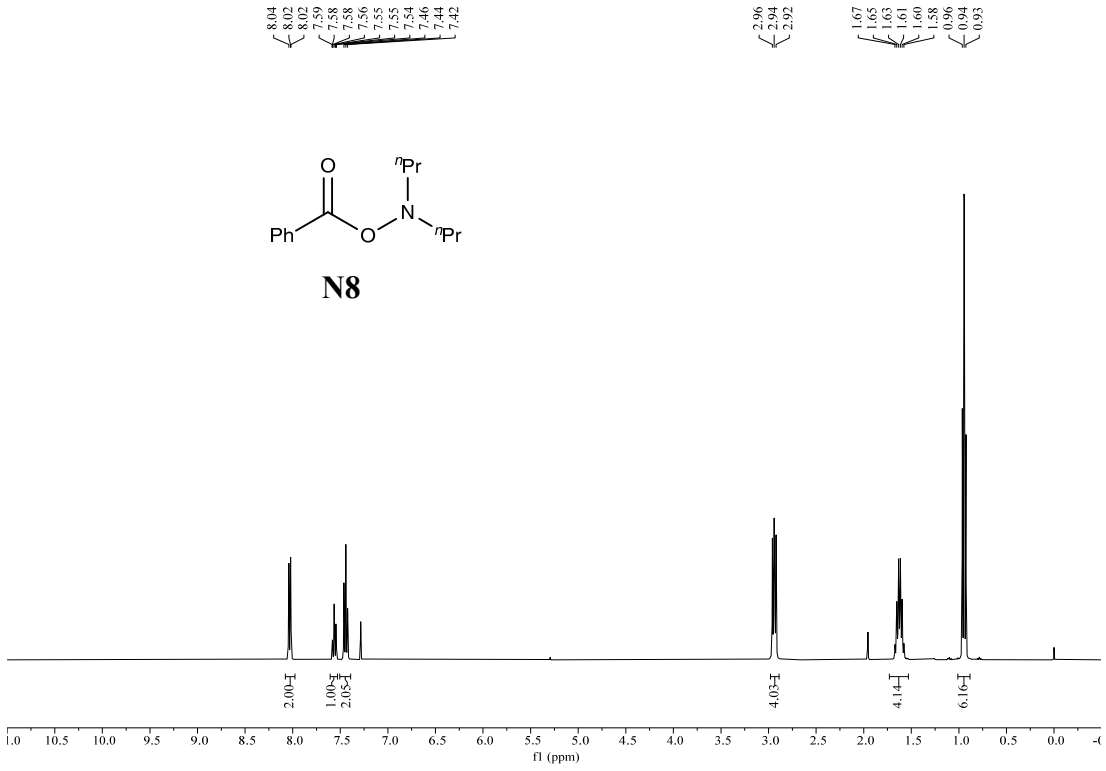


N6

^{1}H NMR of N7 (400 MHz, $CDCl_3$)

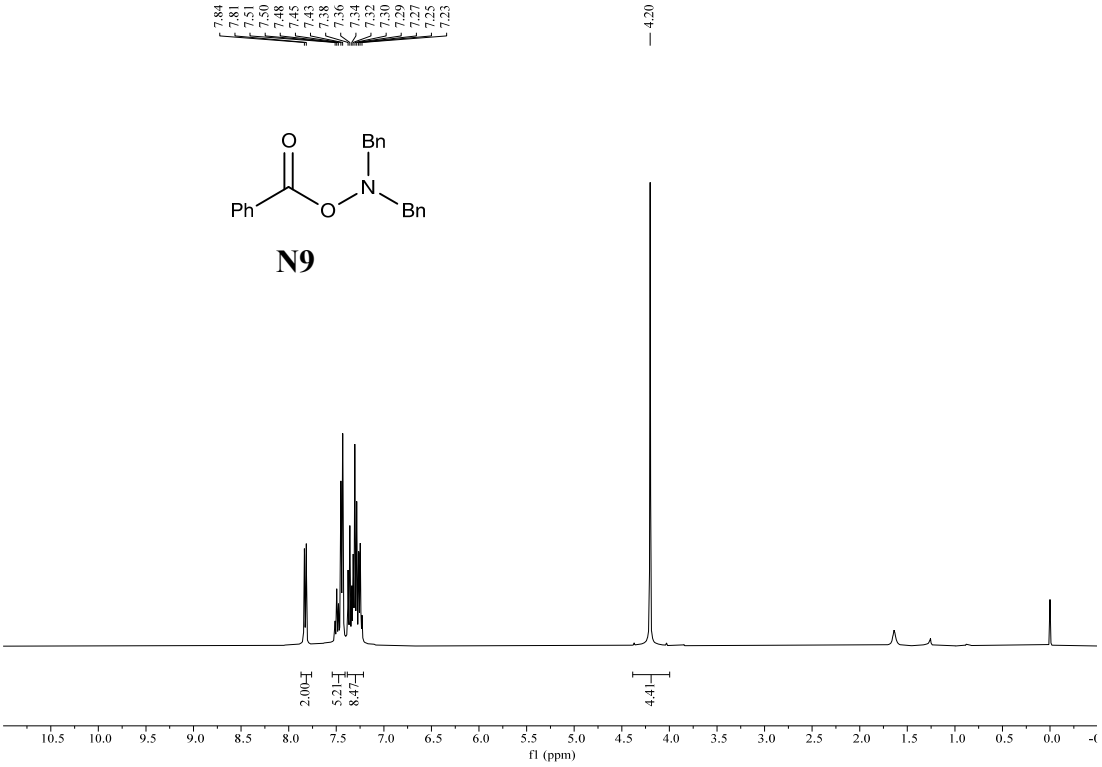


^{1}H NMR of N8 (400 MHz, $CDCl_3$)



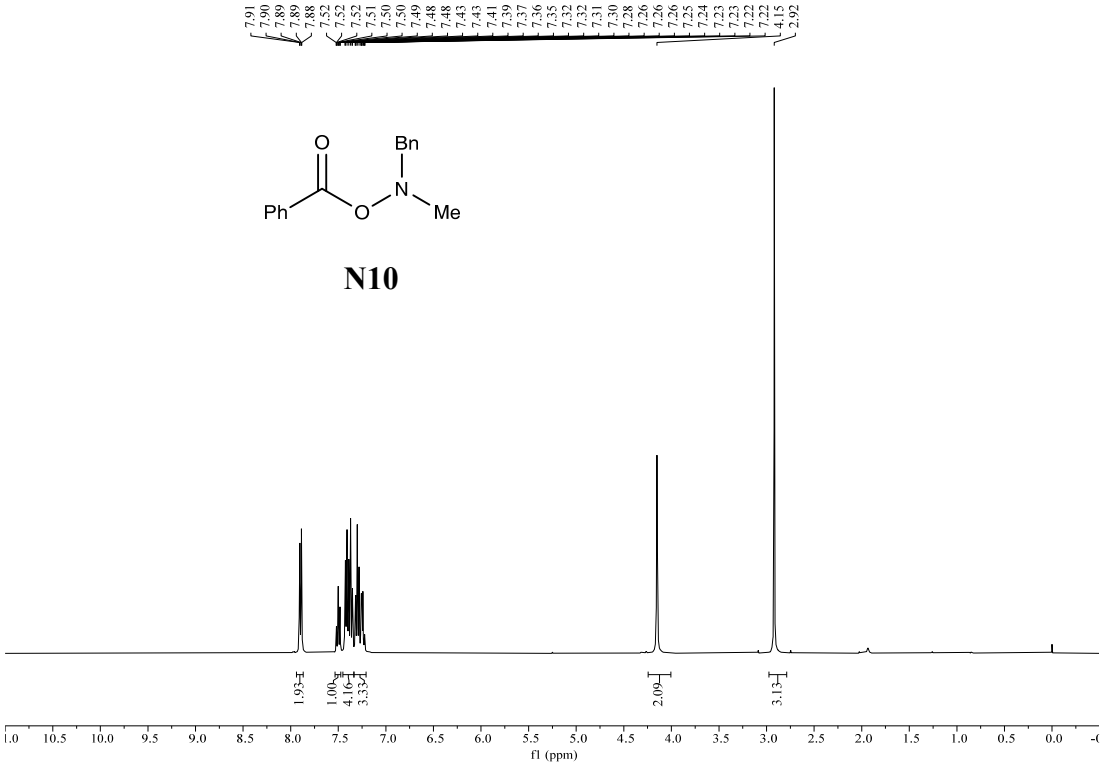
N8

^{1}H NMR of N9 (400 MHz, $CDCl_3$)



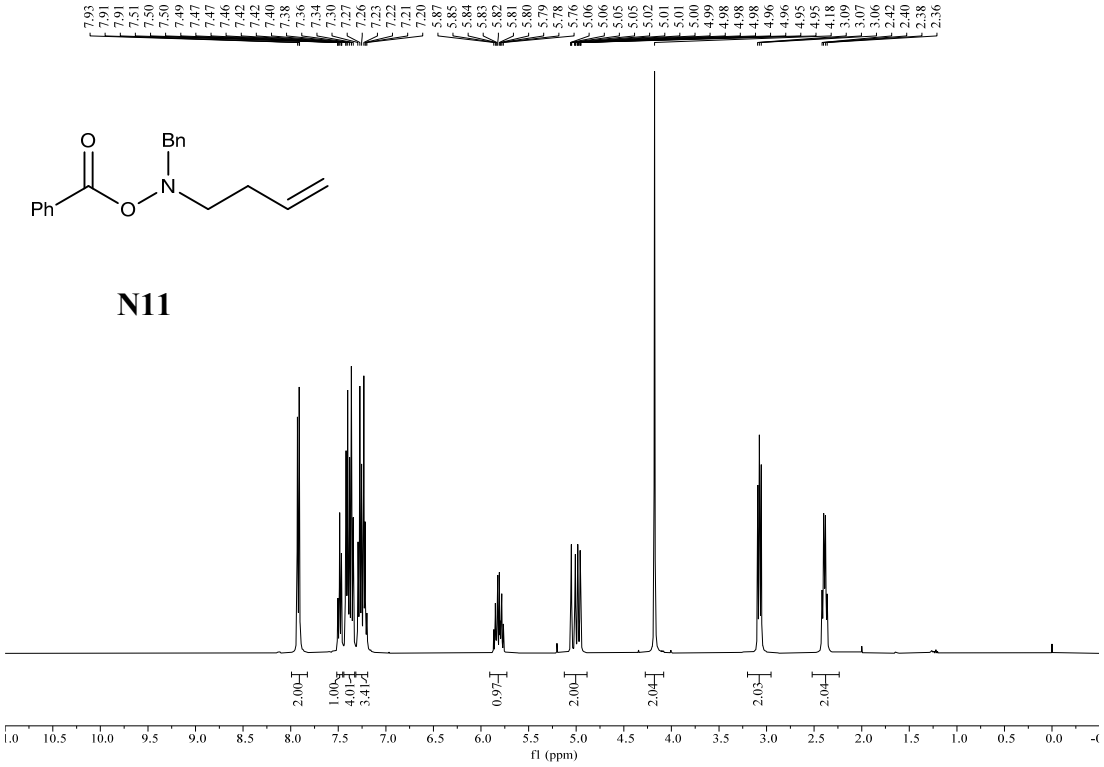
N9

^{1}H NMR of N10 (400 MHz, $CDCl_3$)

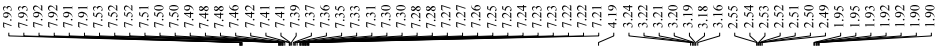


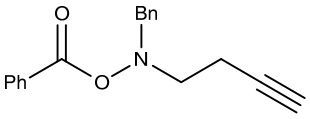
N10

^{1}H NMR of N11 (400 MHz, $CDCl_3$)

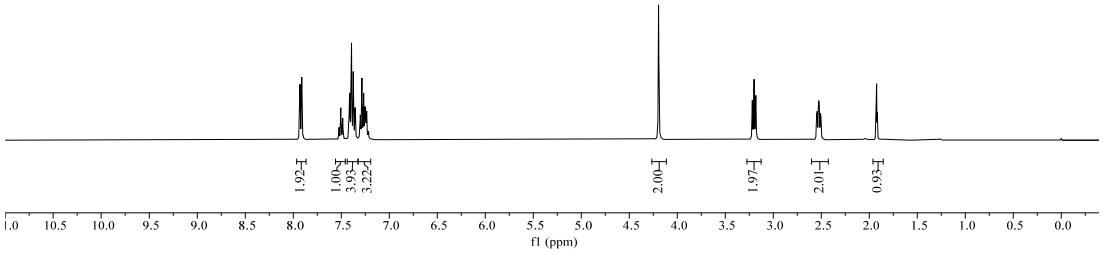


^{1}H NMR of N12 (400 MHz, $CDCl_3$)

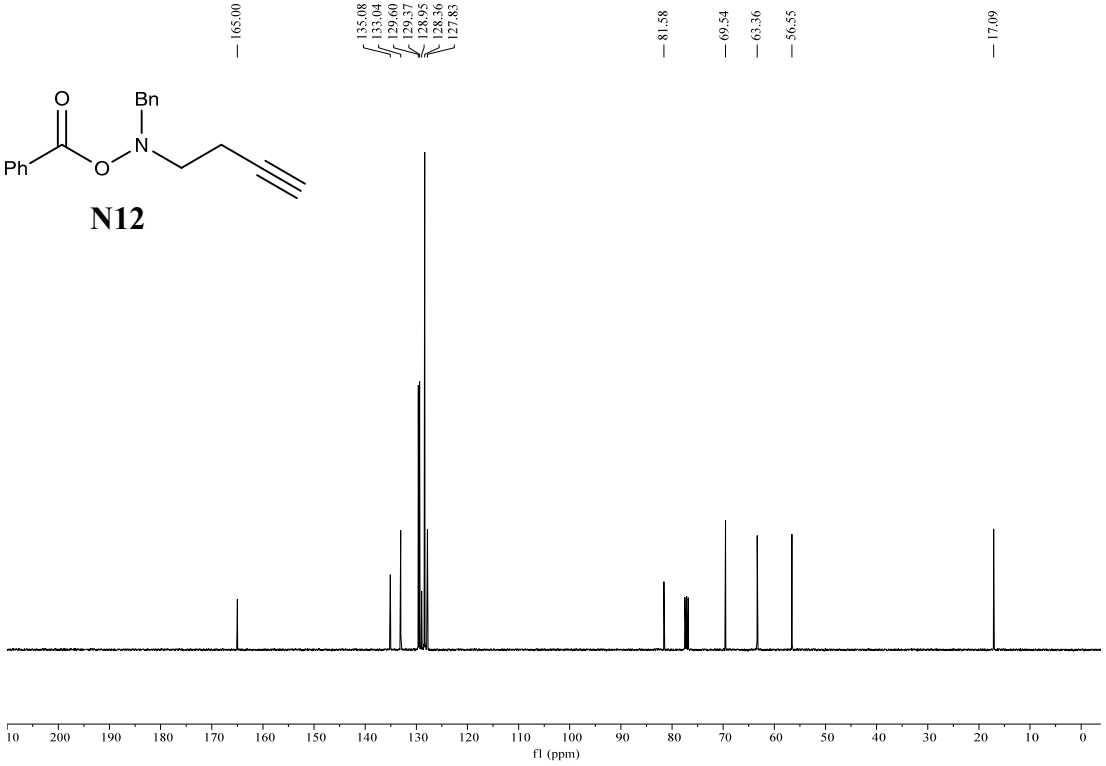




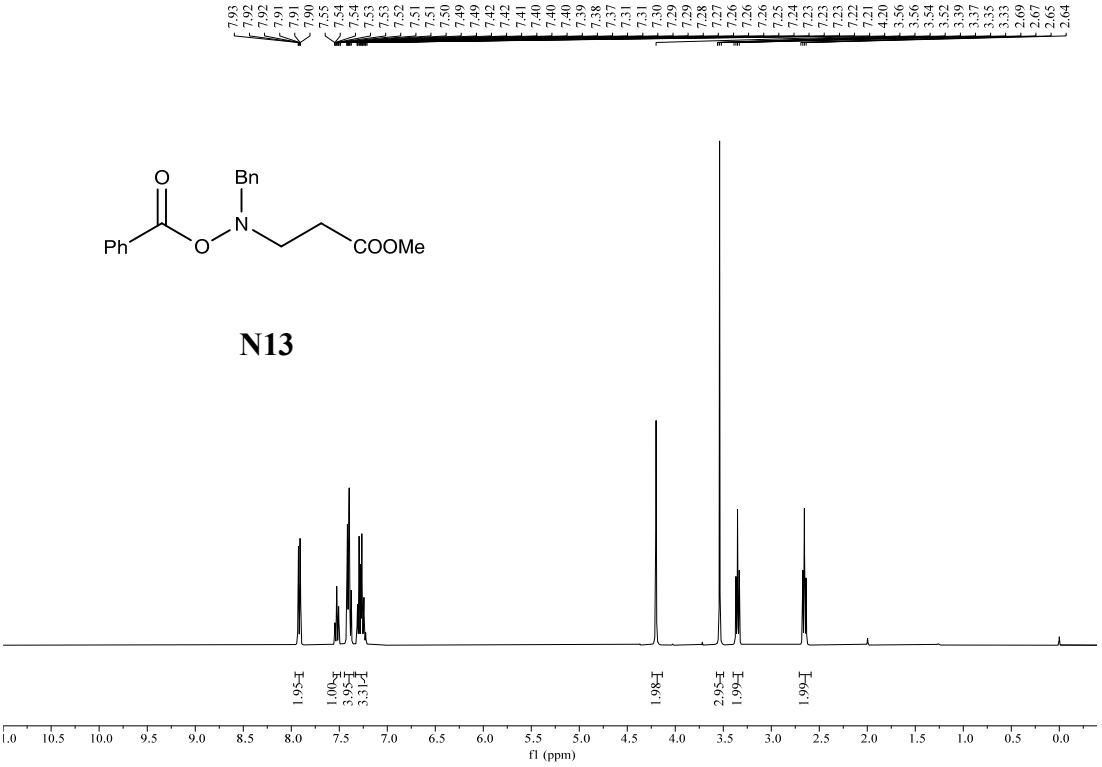
N12



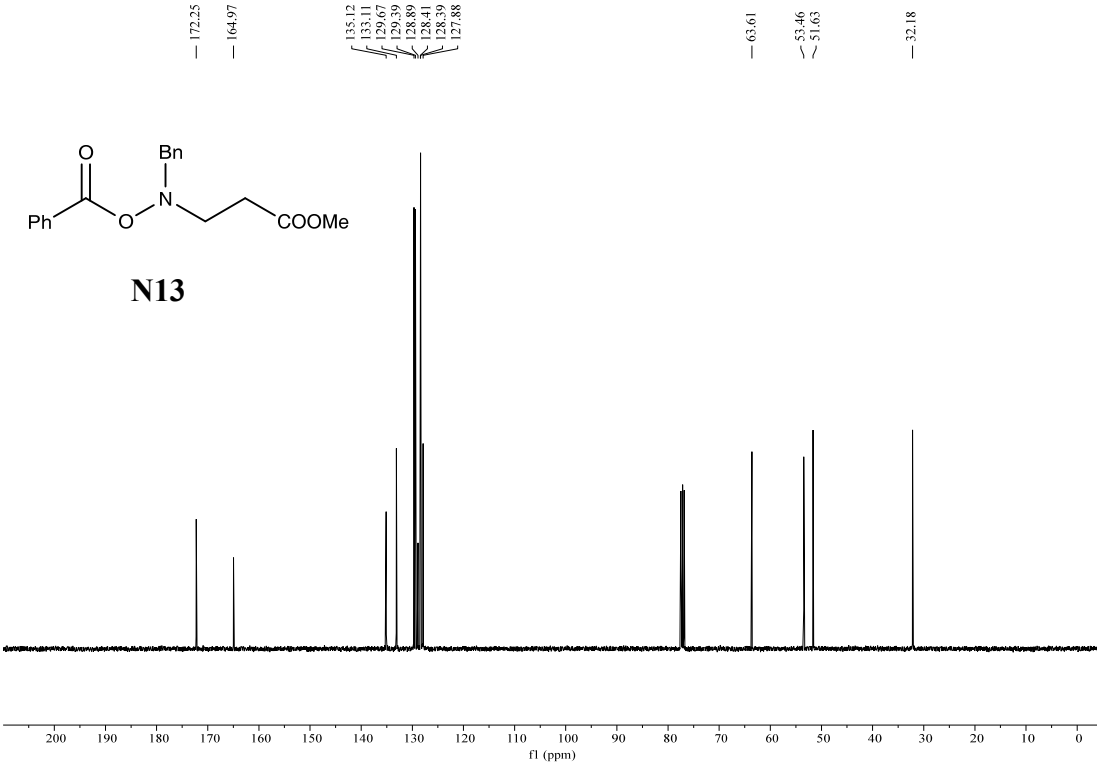
^{13}C NMR of N12 (100 MHz, $CDCl_3$)



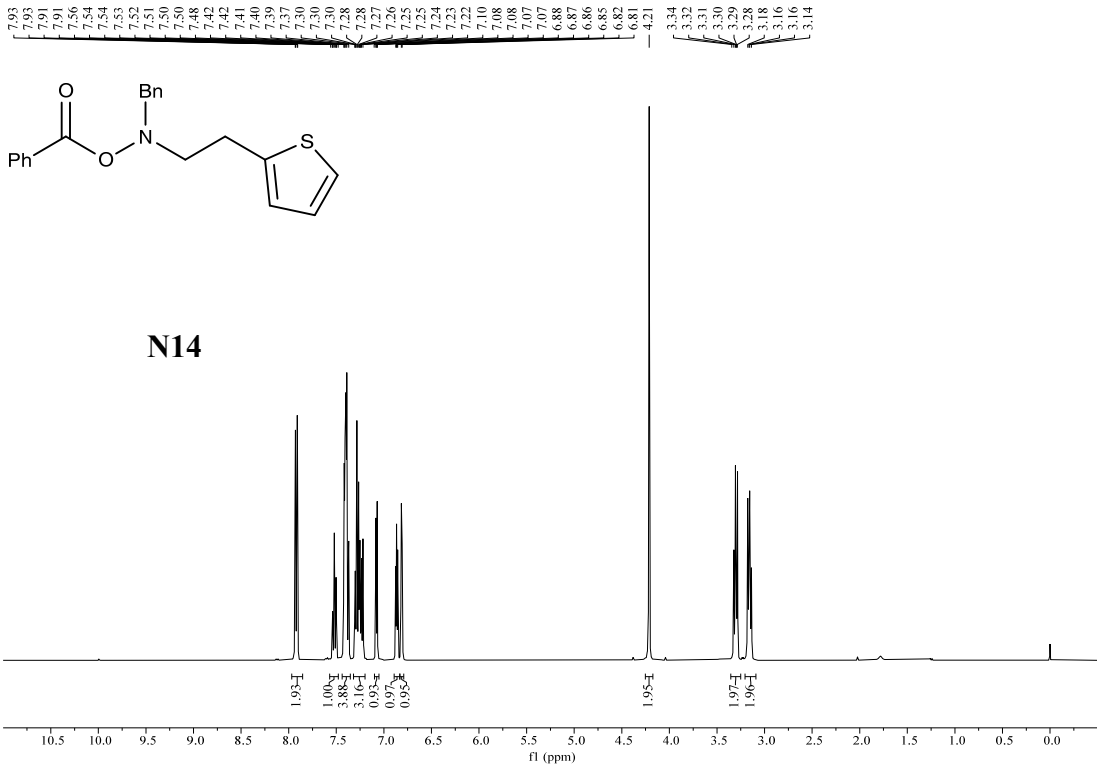
^{1}H NMR of N13 (400 MHz, $CDCl_3$)



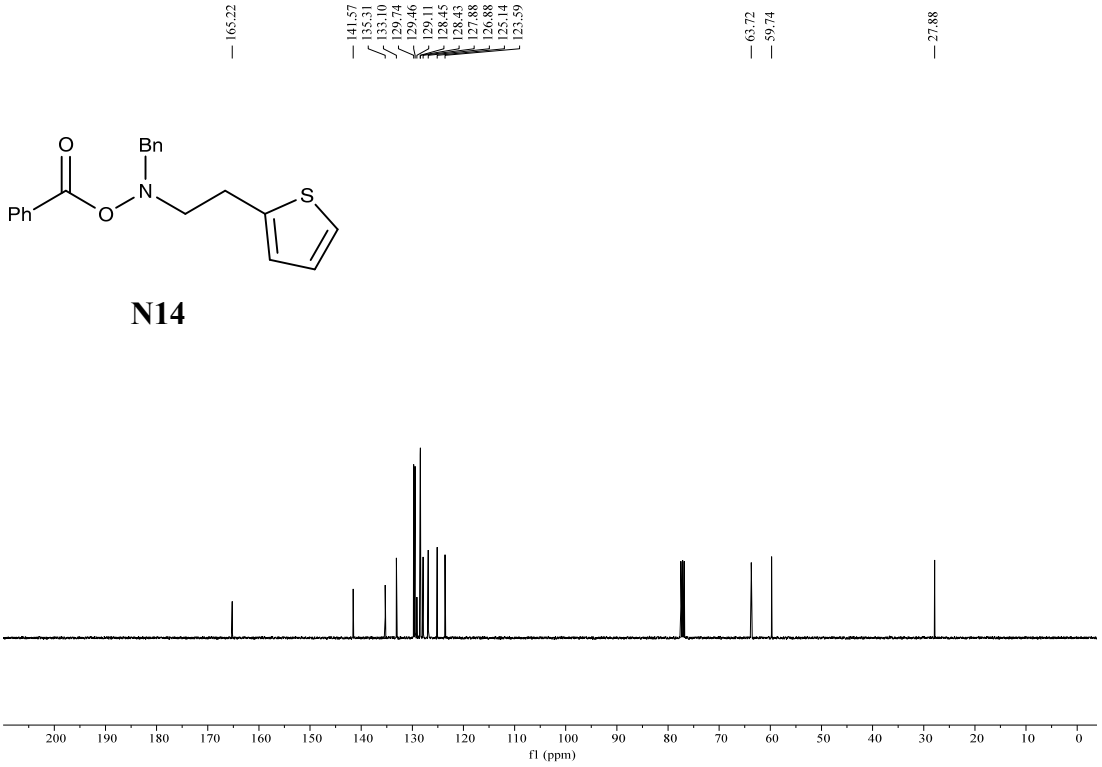
^{13}C NMR of N13 (100 MHz, $CDCl_3$)



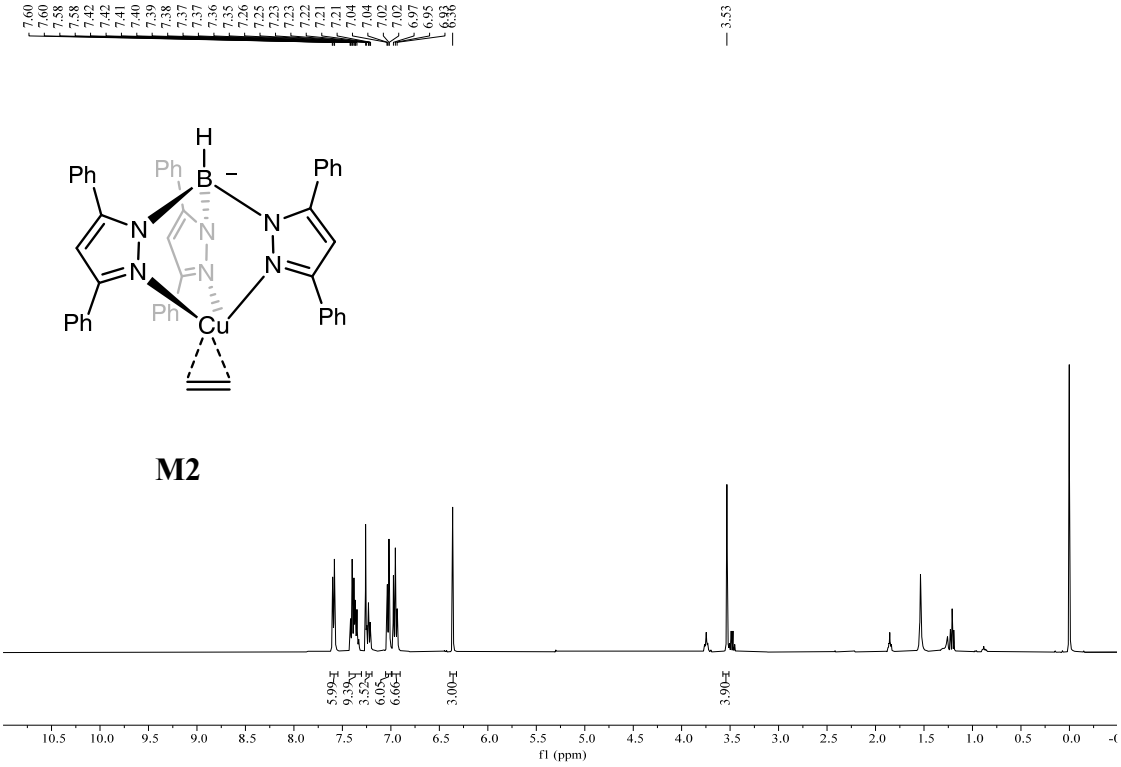
^{1}H NMR of N14 (400 MHz, $CDCl_3$)



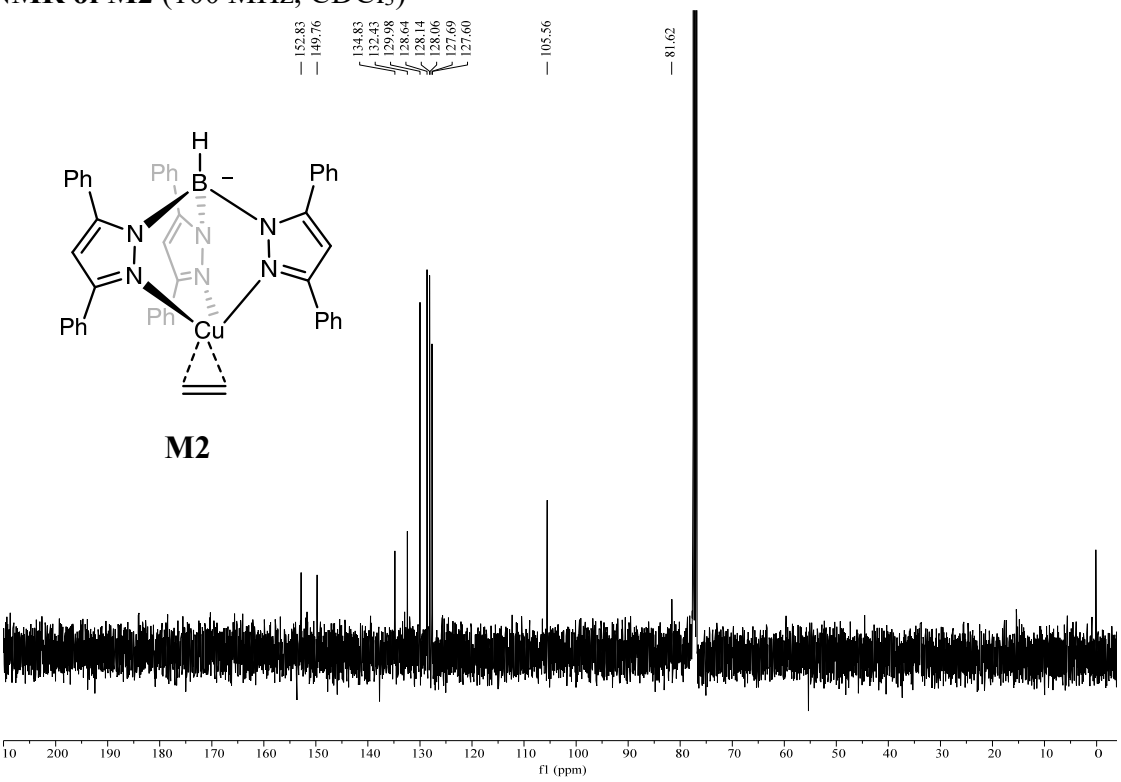
^{13}C NMR of N14 (100 MHz, $CDCl_3$)



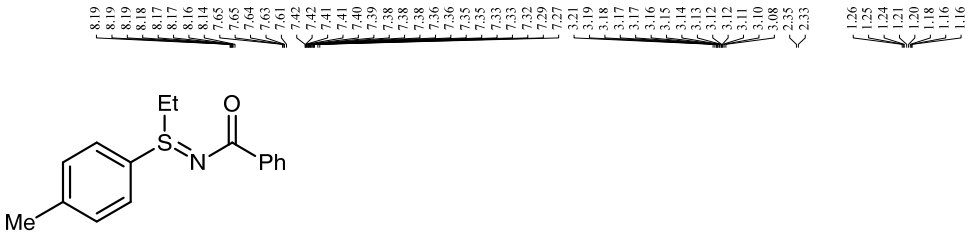
^{1}H NMR of M2 (400 MHz, $CDCl_3$)



^{13}C NMR of M2 (100 MHz, $CDCl_3$)



^{1}H NMR of 1 (400 MHz, $CDCl_3$)



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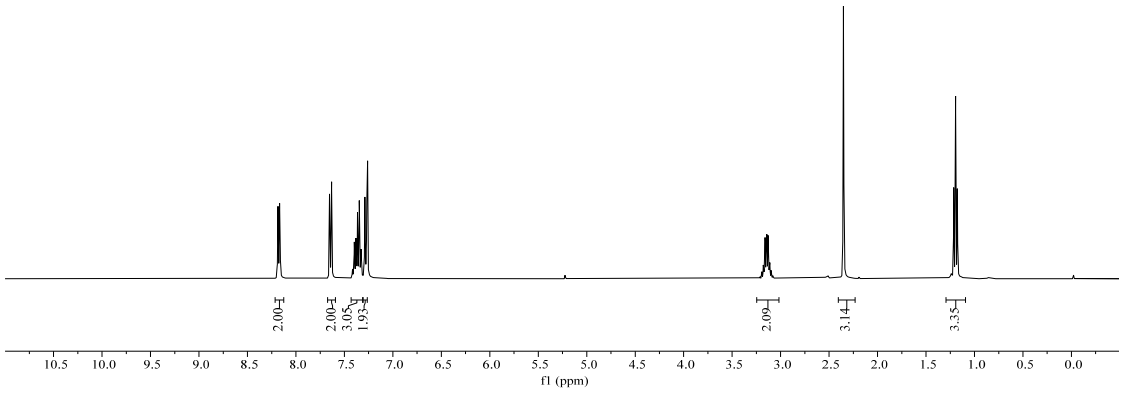
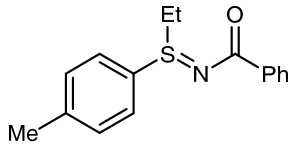


^{13}C NMR of 1 (100 MHz, $CDCl_3$)



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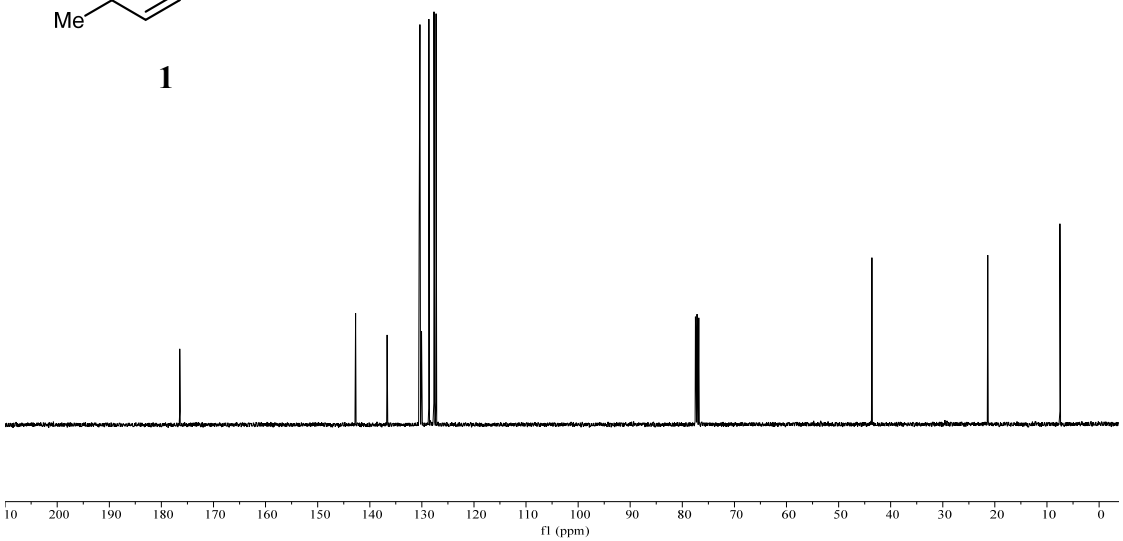
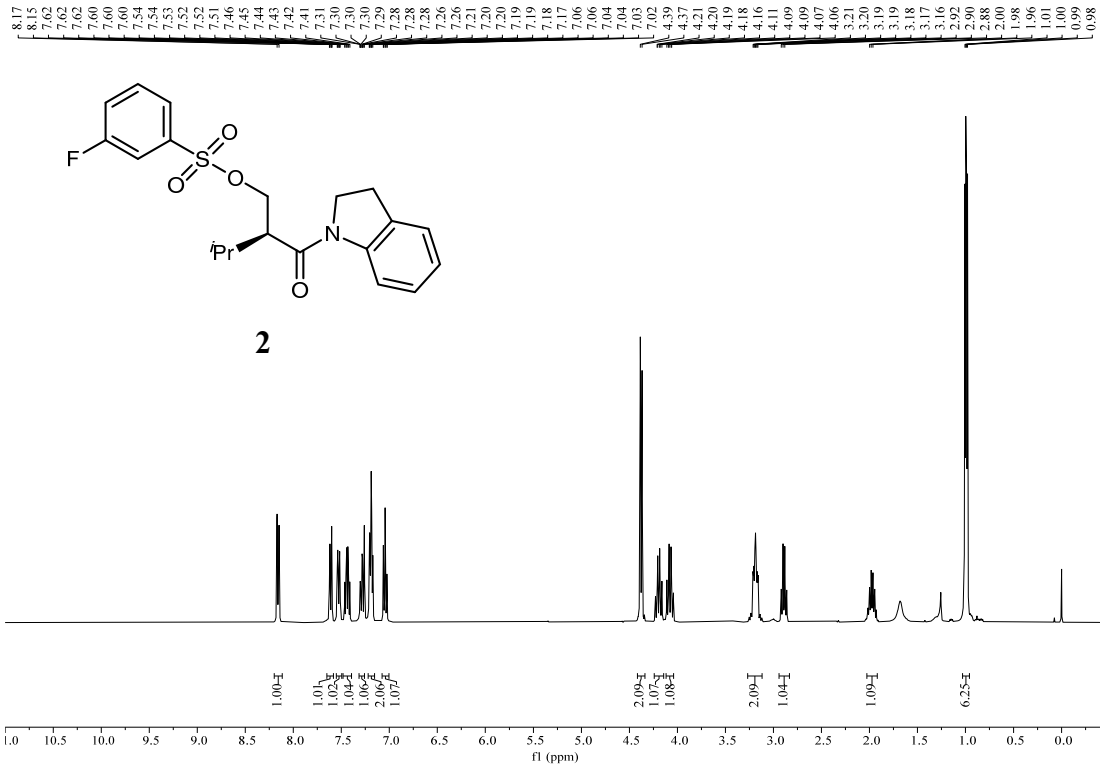
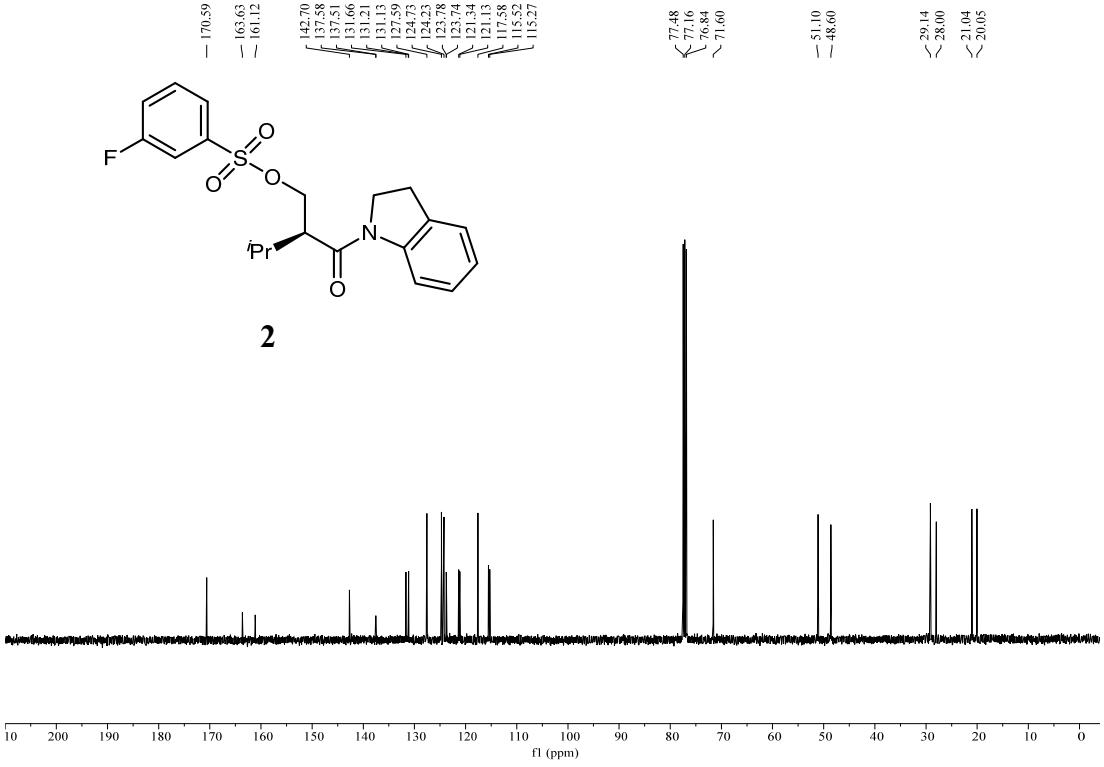


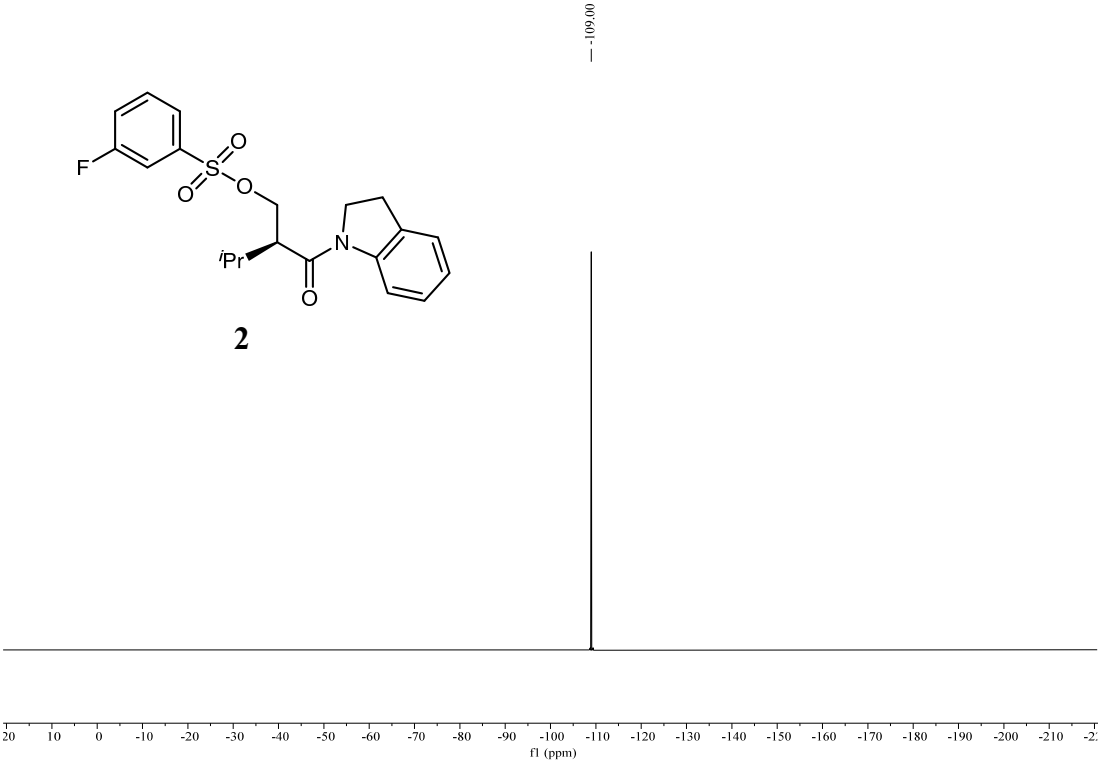
^{1}H NMR of 2 (400 MHz, $CDCl_3$)



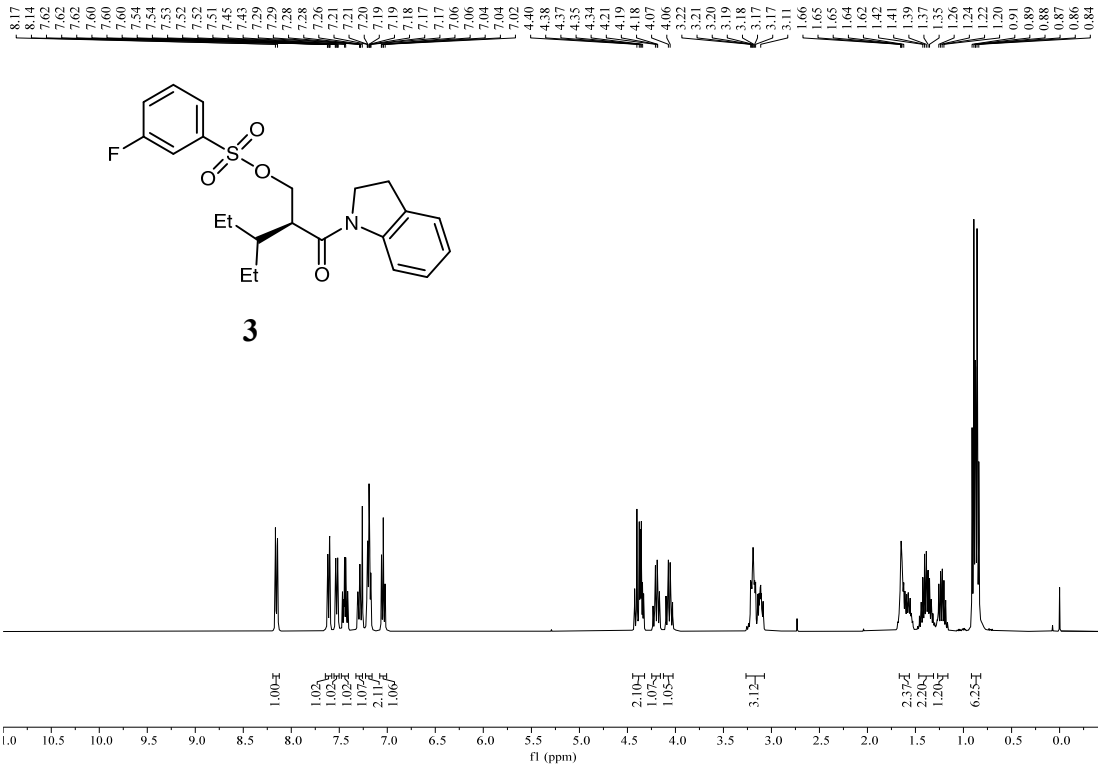
^{13}C NMR of 2 (100 MHz, $CDCl_3$)



^{19}F NMR of 2(375 MHz, $CDCl_3$)

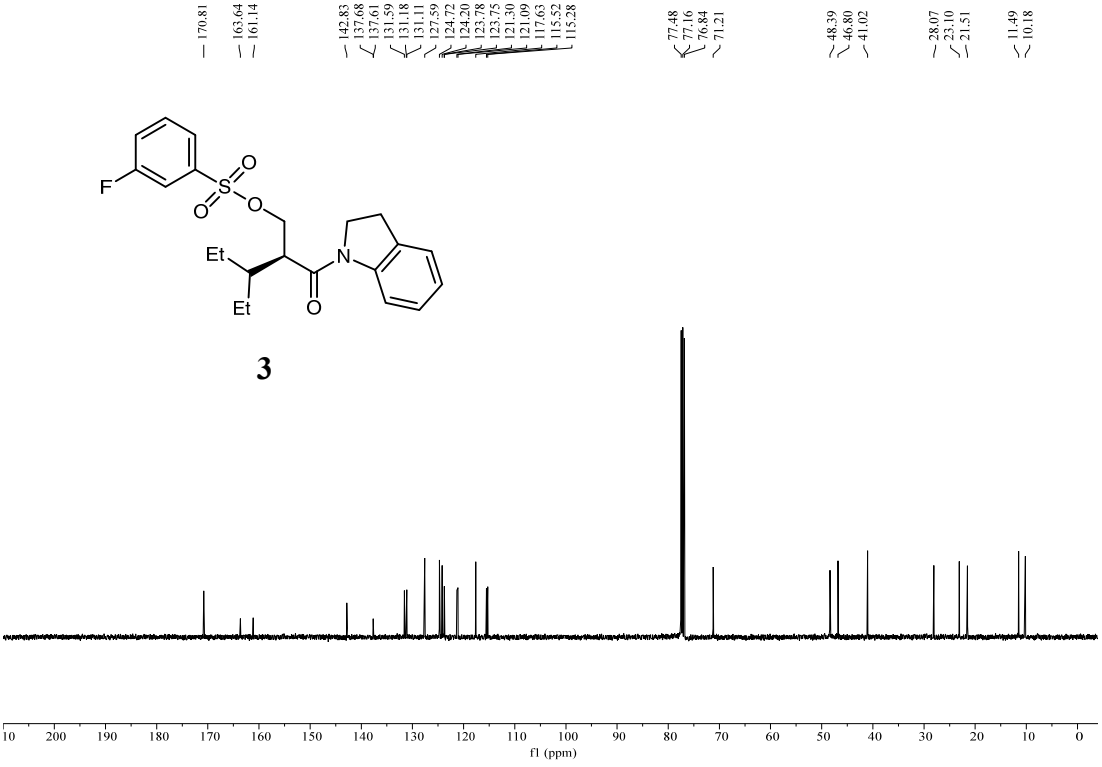


^{1}H NMR of 3 (400 MHz, $CDCl_3$)



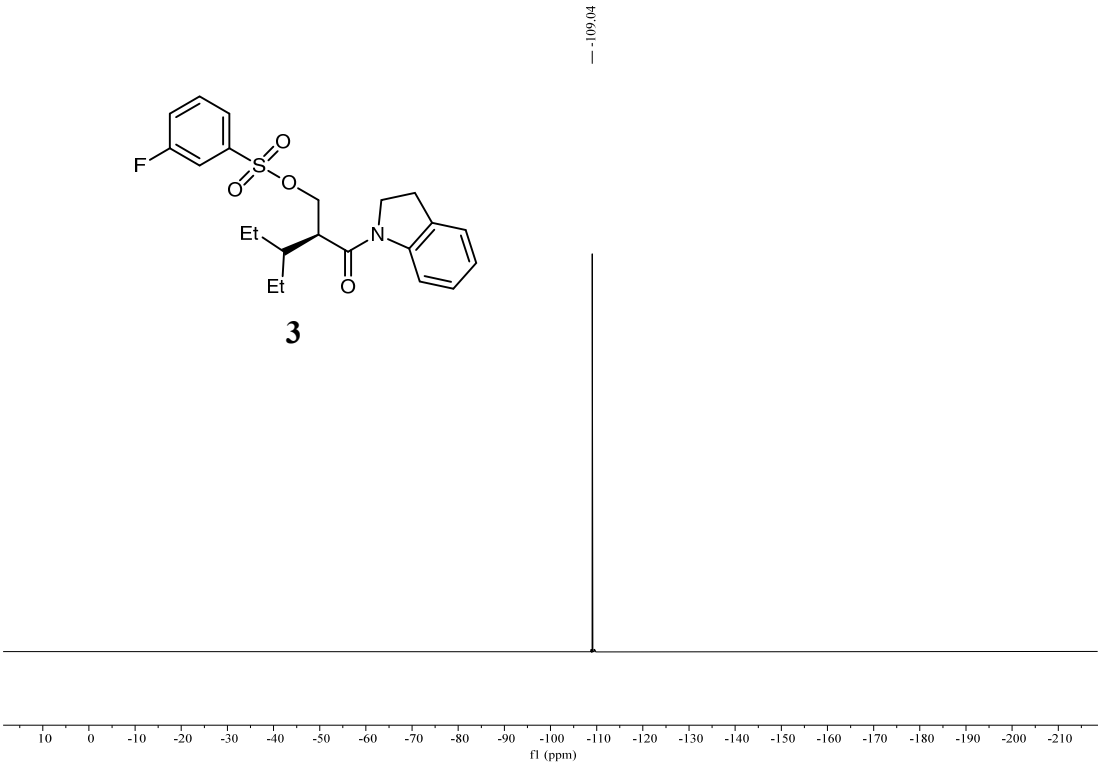
3

^{13}C NMR of 3 (100 MHz, $CDCl_3$)



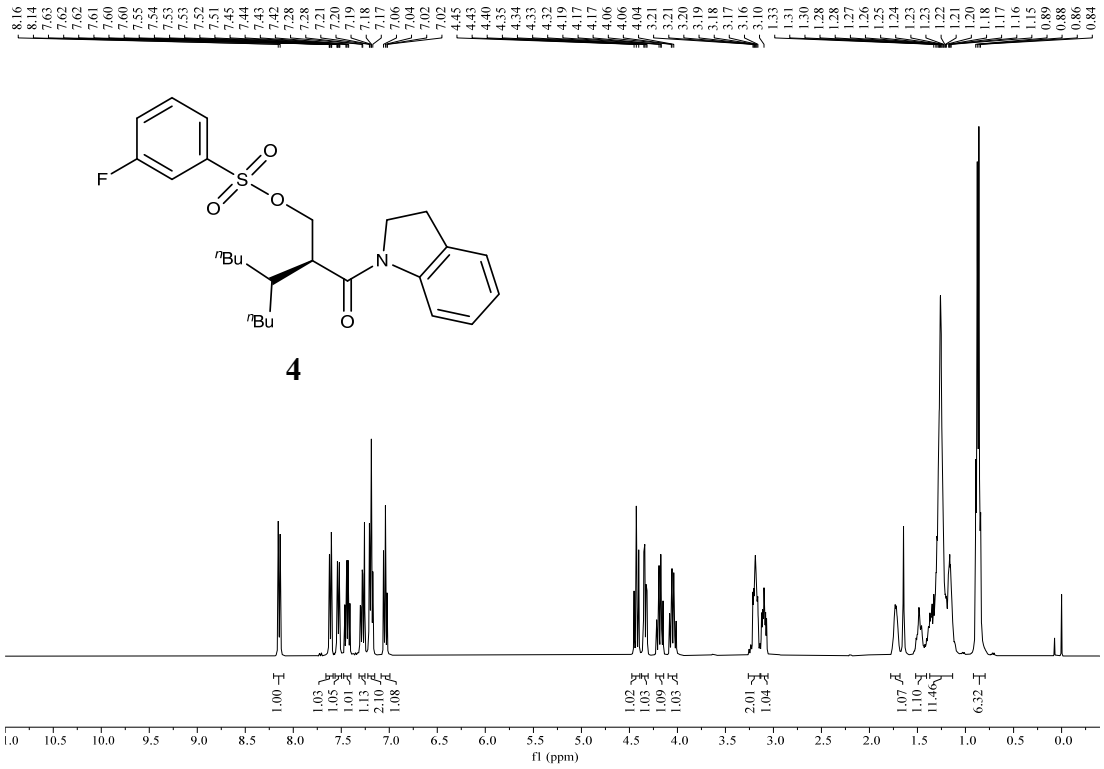
3

^{19}F NMR of 3 (375 MHz, $CDCl_3$)

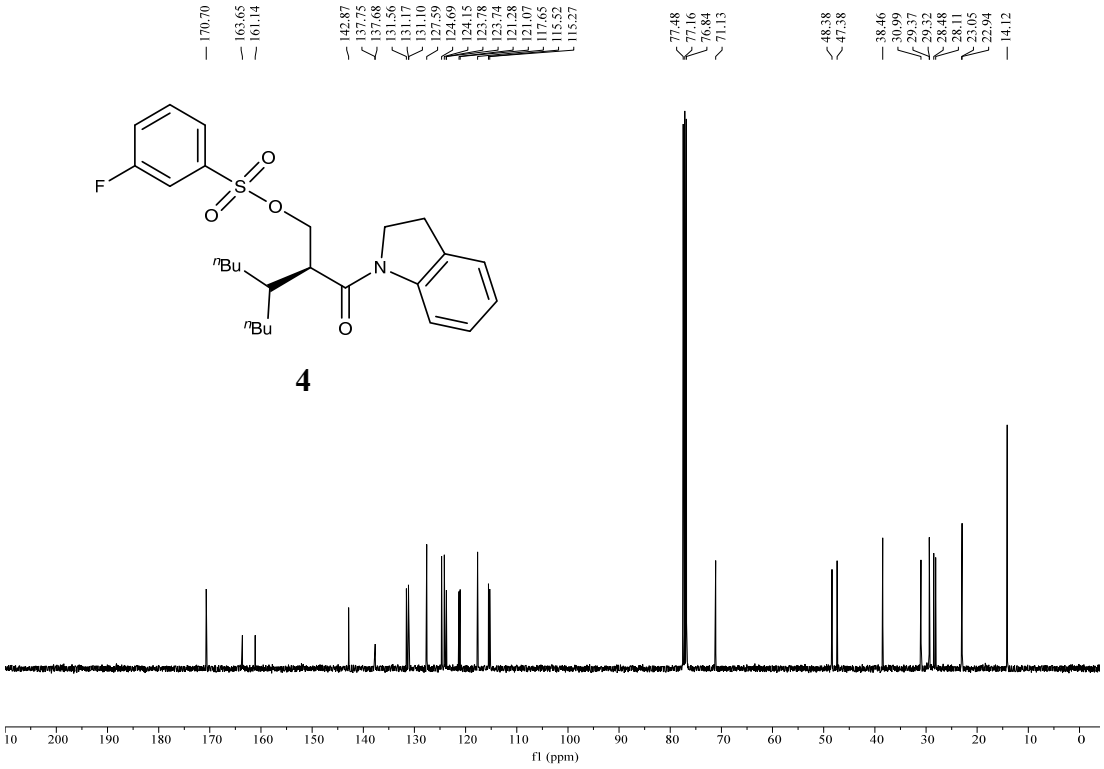


3

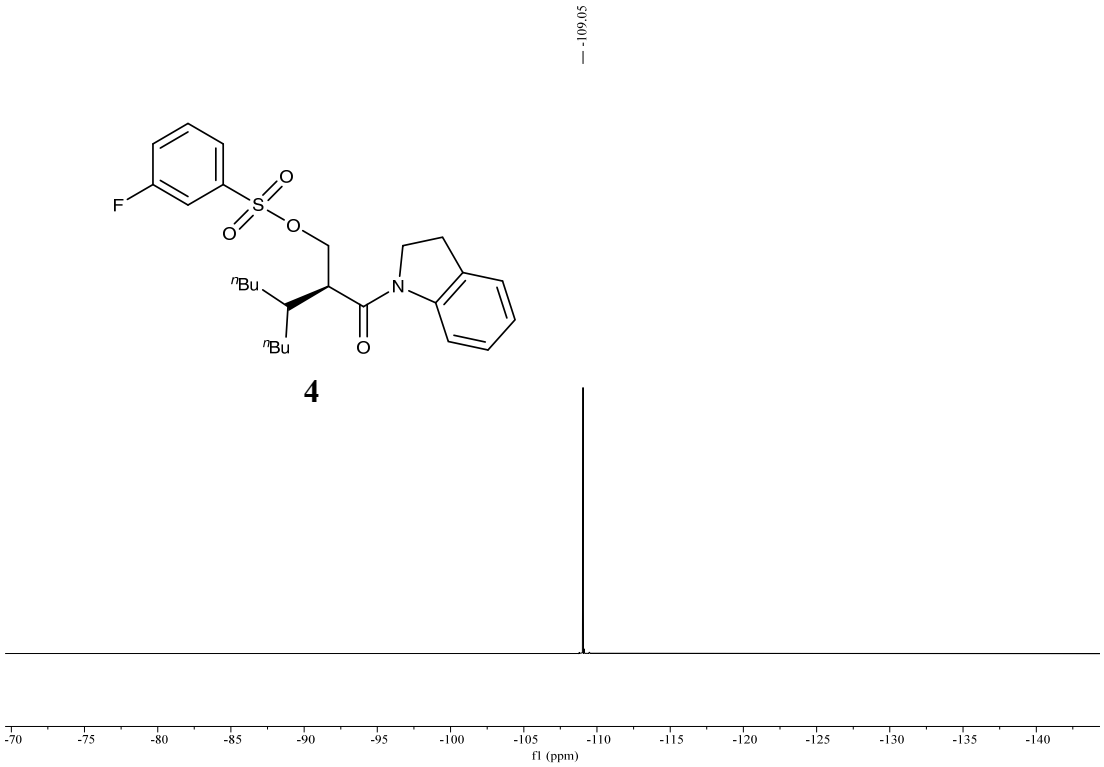
^{1}H NMR of 4 (400 MHz, $CDCl_3$)



^{13}C NMR of 4 (100 MHz, $CDCl_3$)

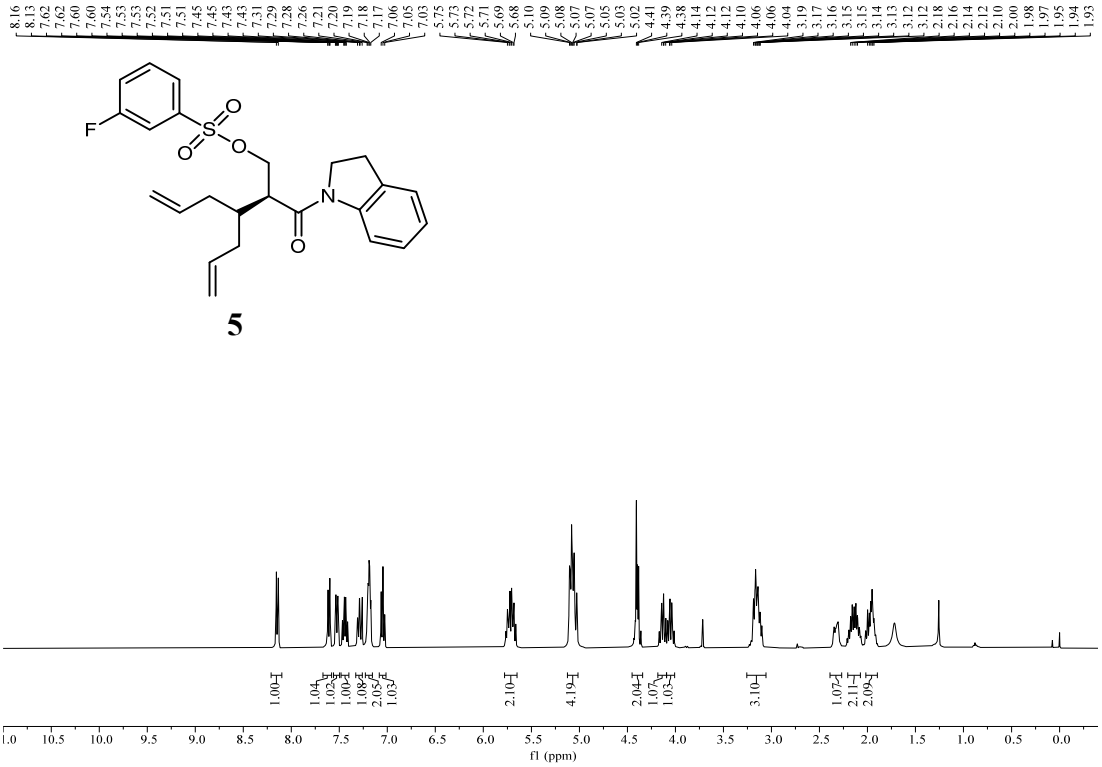


^{19}F NMR of 4 (375 MHz, $CDCl_3$)

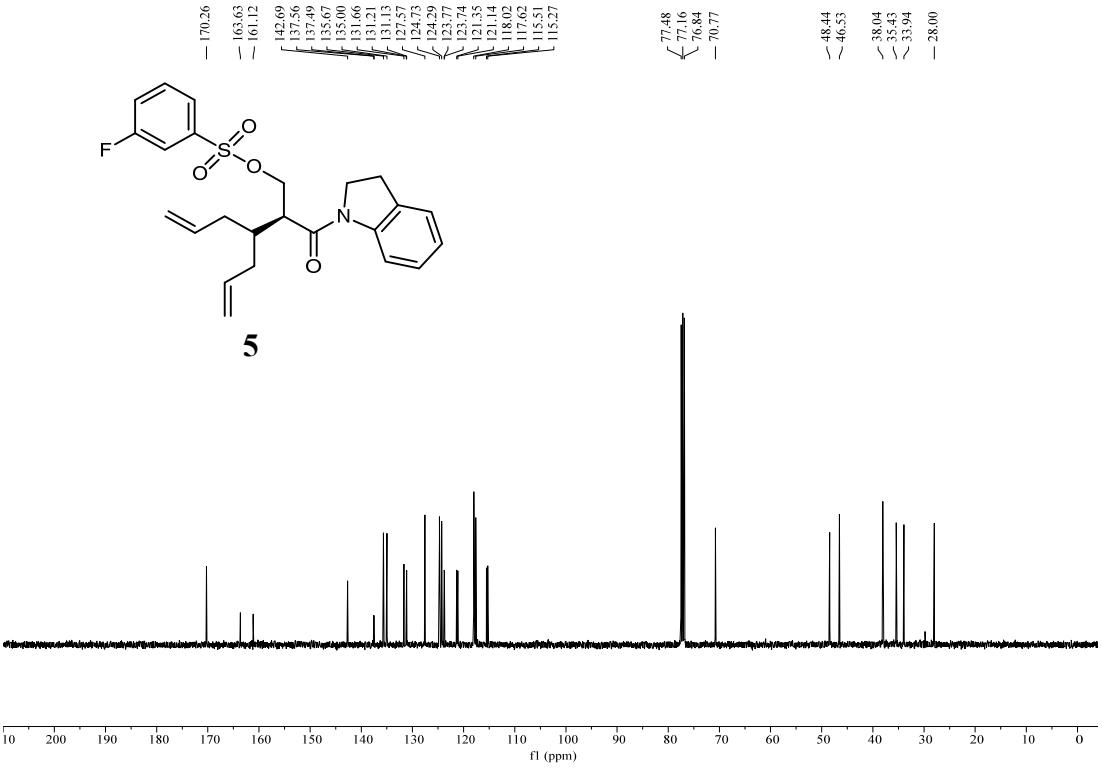


4

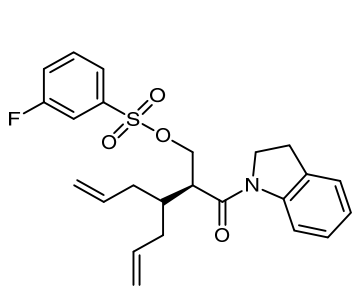
^{1}H NMR of 5 (400 MHz, $CDCl_3$)



^{13}C NMR of 5 (100 MHz, $CDCl_3$)

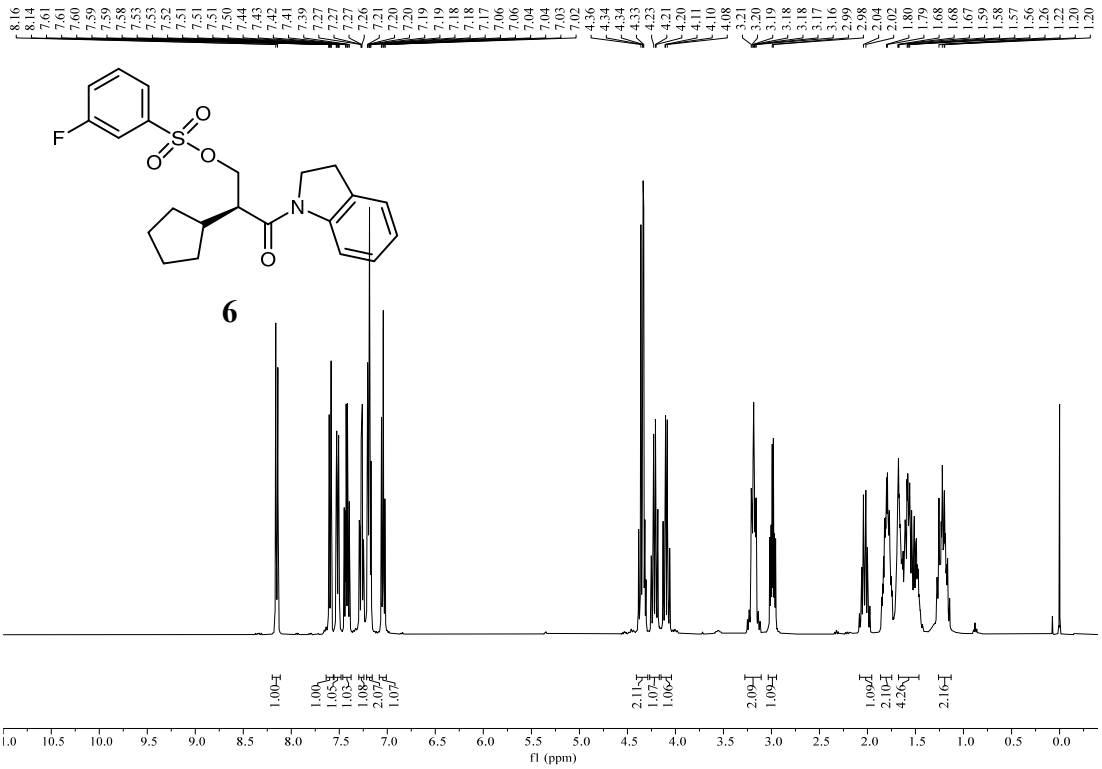


^{19}F NMR of 5 (375 MHz, $CDCl_3$)

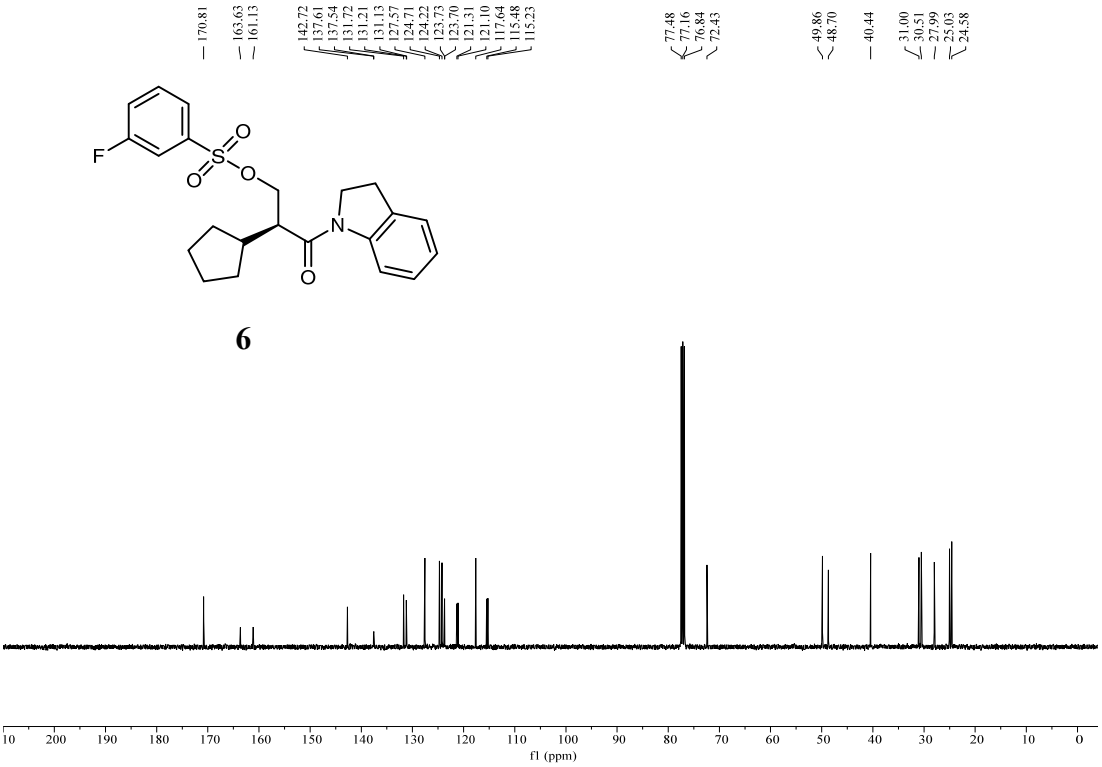


5

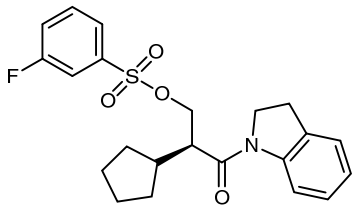
^{1}H NMR of 6 (400 MHz, $CDCl_3$)



^{13}C NMR of 6 (100 MHz, $CDCl_3$)

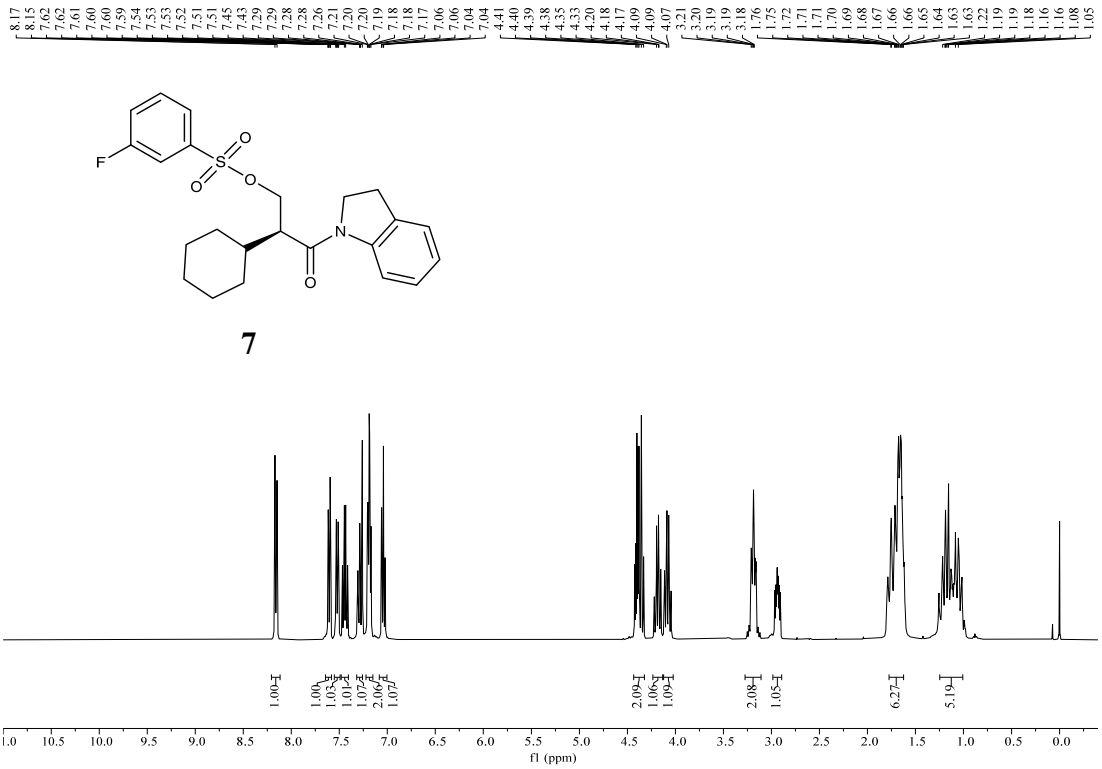


^{19}F NMR of 6 (375 MHz, $CDCl_3$)



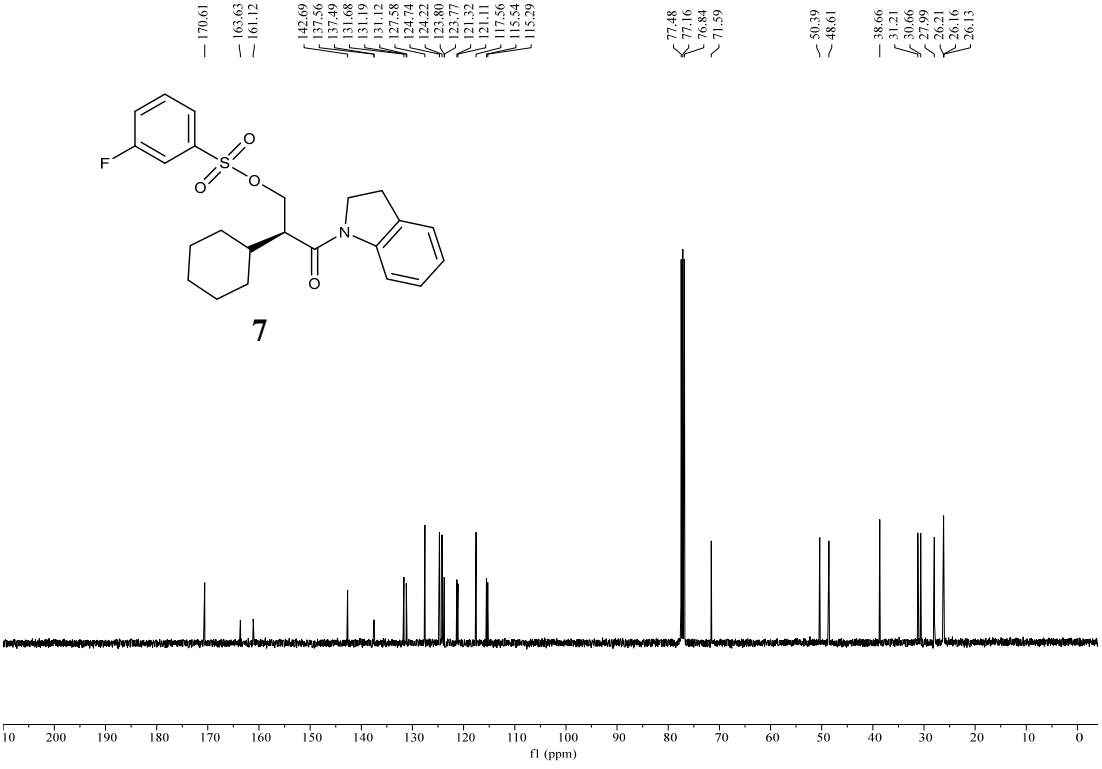
6

^{1}H NMR of 7 (400 MHz, $CDCl_3$)



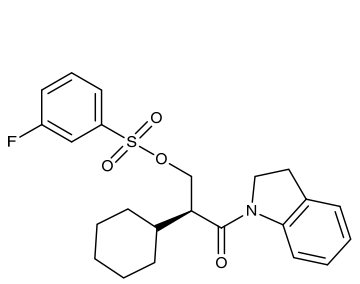
7

^{13}C NMR of 7 (100 MHz, $CDCl_3$)



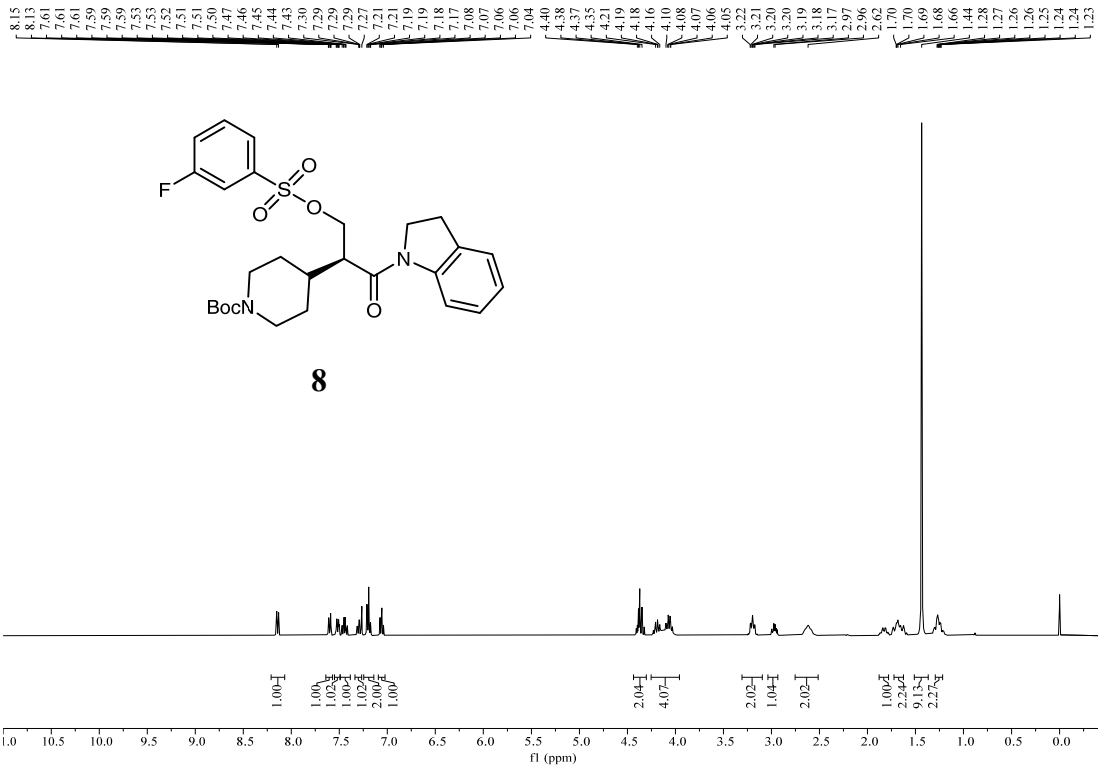
7

^{19}F NMR of 7 (375 MHz, $CDCl_3$)



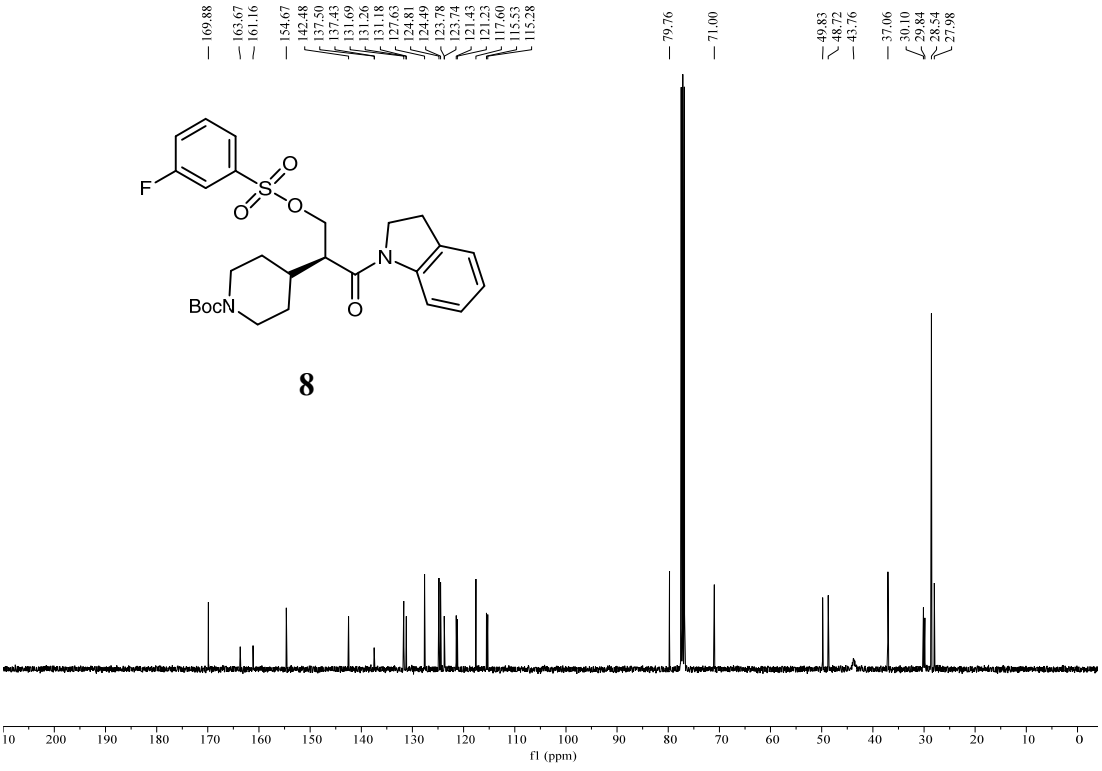
7

^{1}H NMR of 8 (400 MHz, $CDCl_3$)



8

^{13}C NMR of 8 (100 MHz, $CDCl_3$)

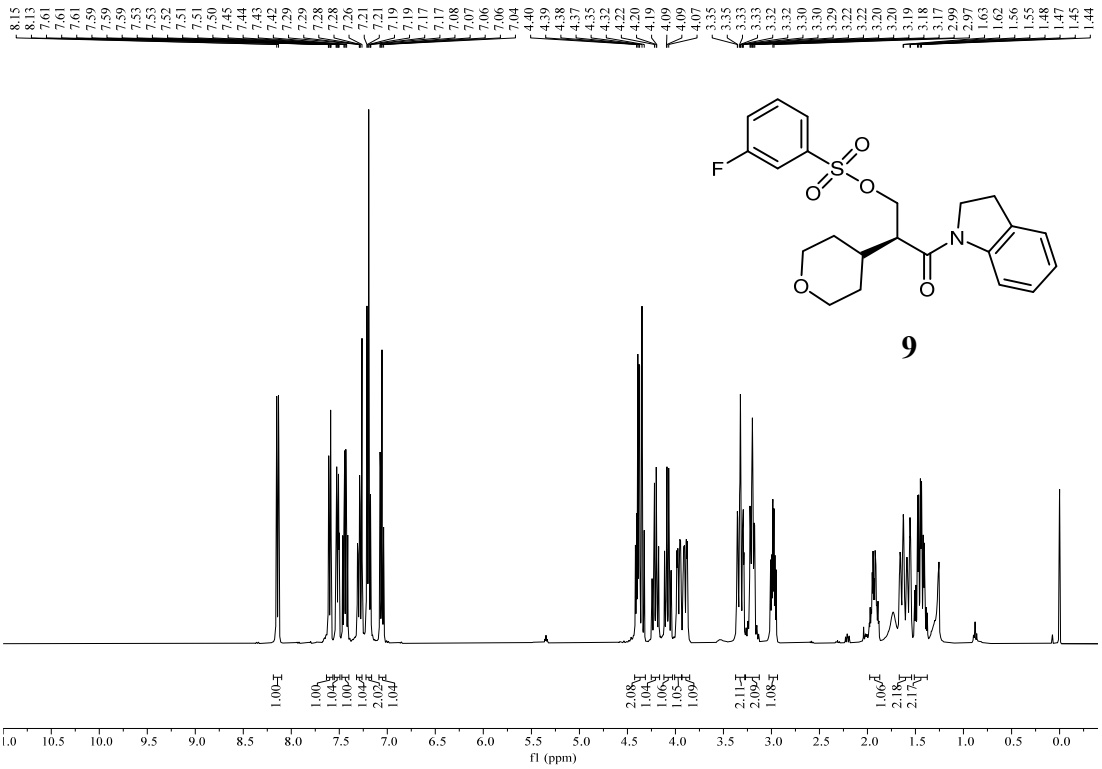


8

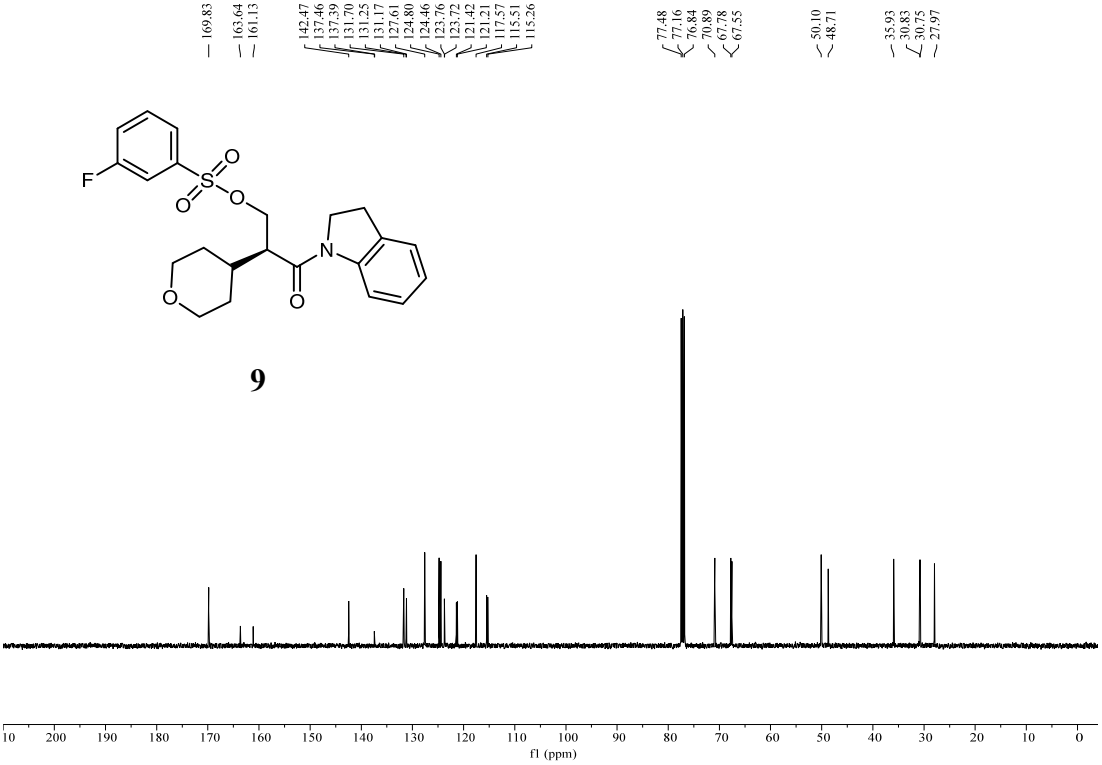
^{19}F NMR of 8 (375 MHz, $CDCl_3$)

8

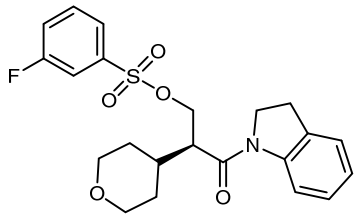
^{1}H NMR of 9 (400 MHz, $CDCl_3$)



^{13}C NMR of 9 (100 MHz, $CDCl_3$)

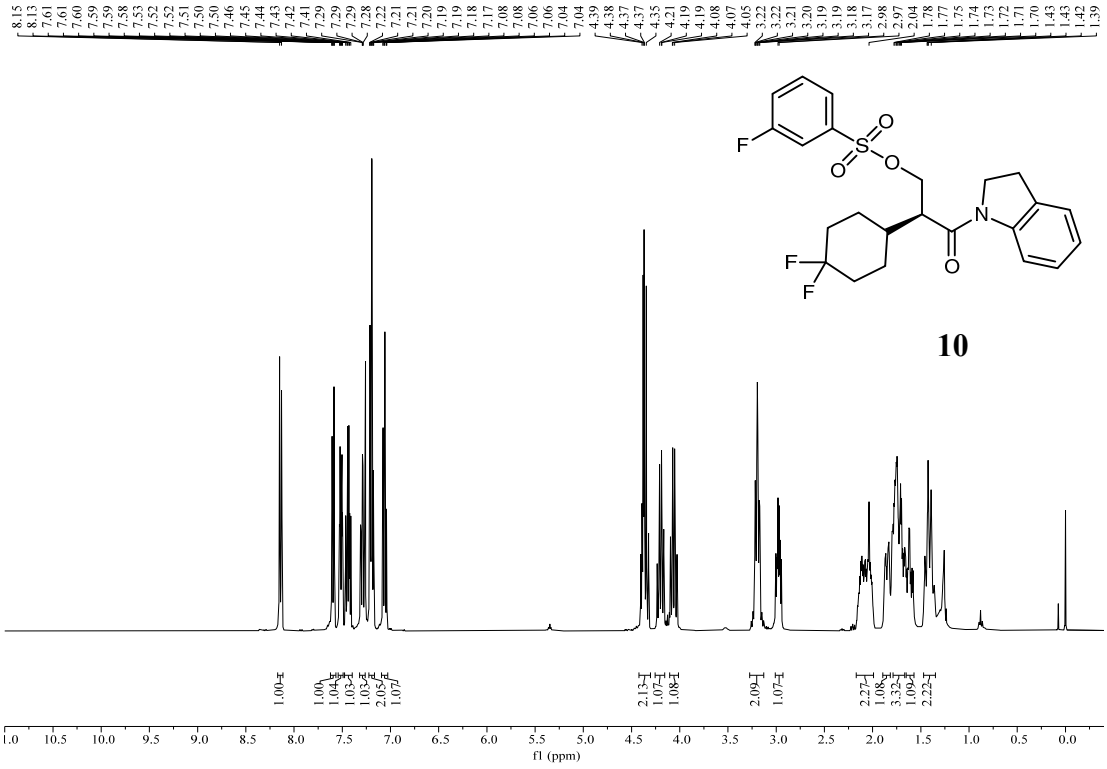


^{19}F NMR of 9 (375 MHz, $CDCl_3$)

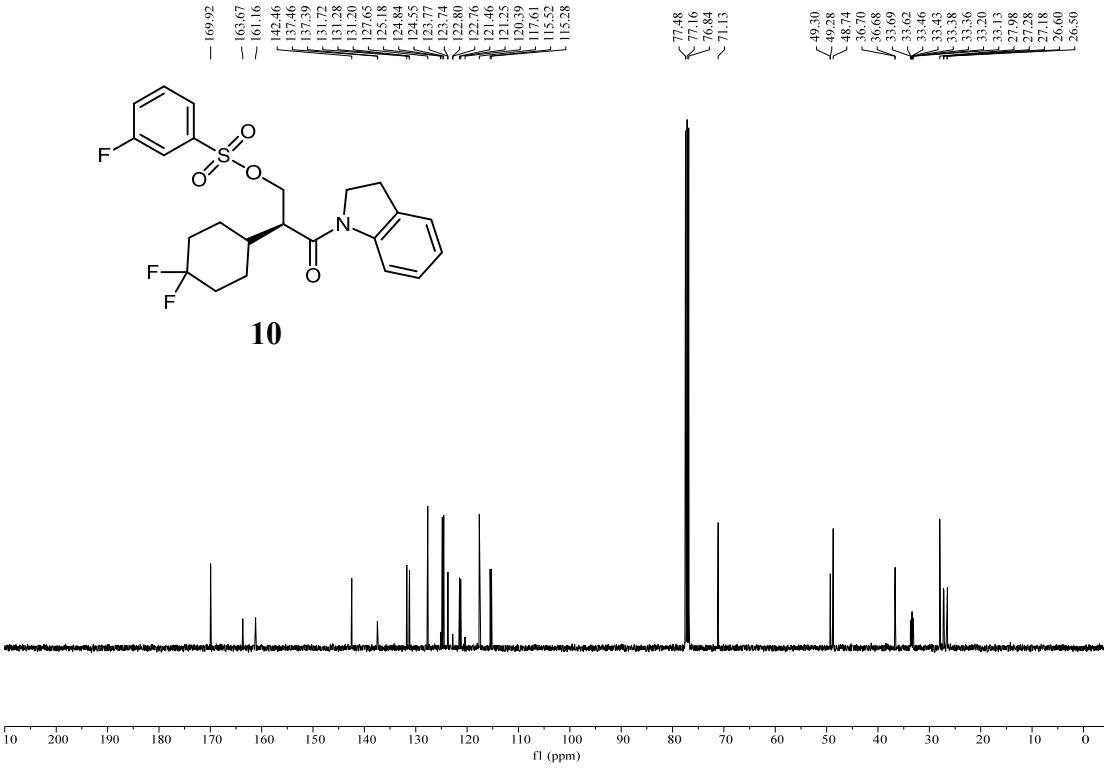


9

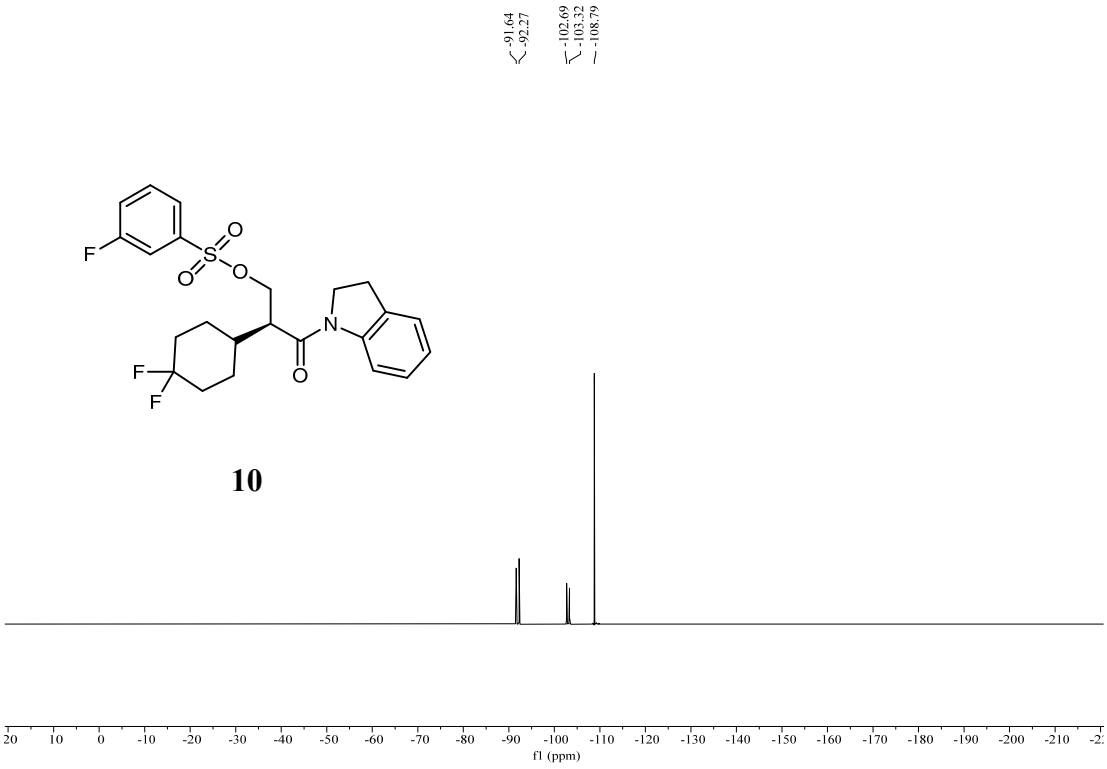
^{1}H NMR of 10 (400 MHz, $CDCl_3$)



^{13}C NMR of 10 (100 MHz, $CDCl_3$)

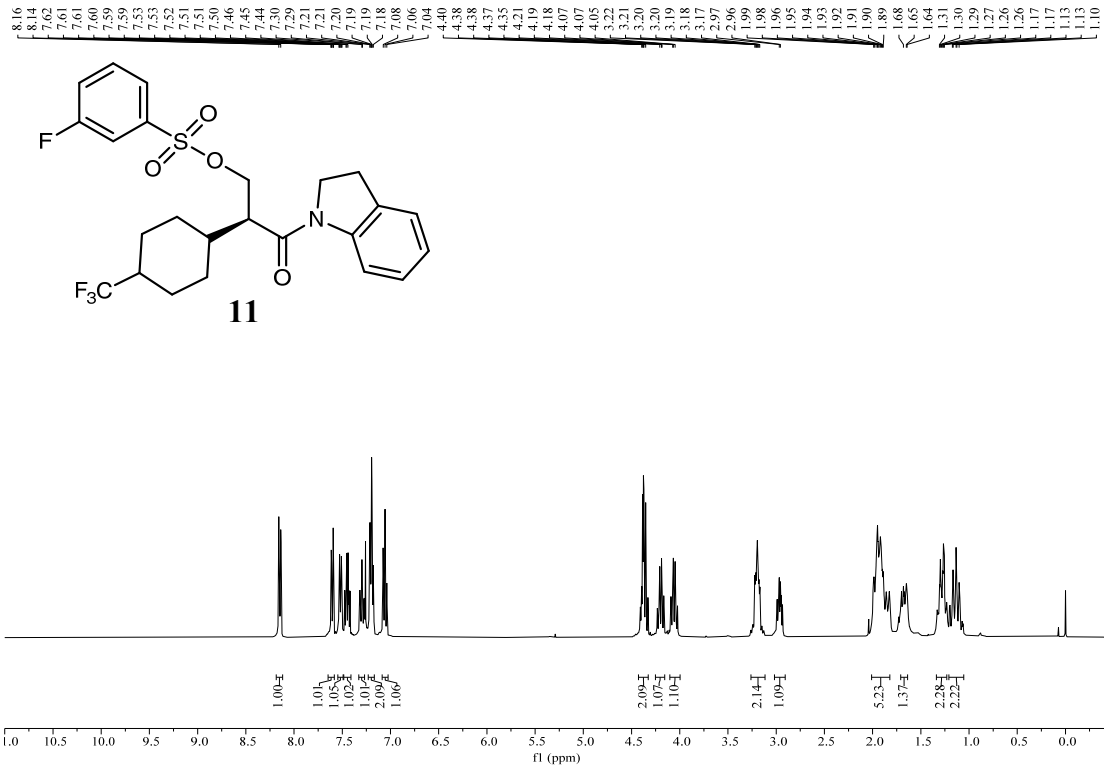


^{19}F NMR of 10 (375 MHz, $CDCl_3$)

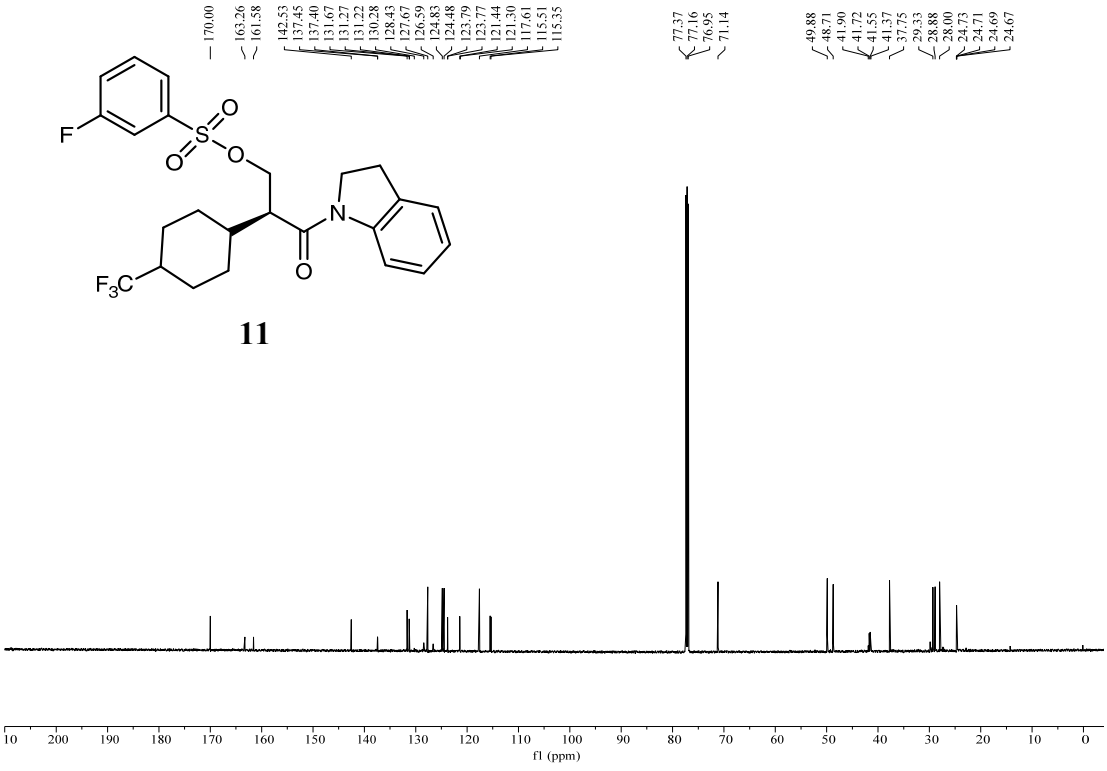


10

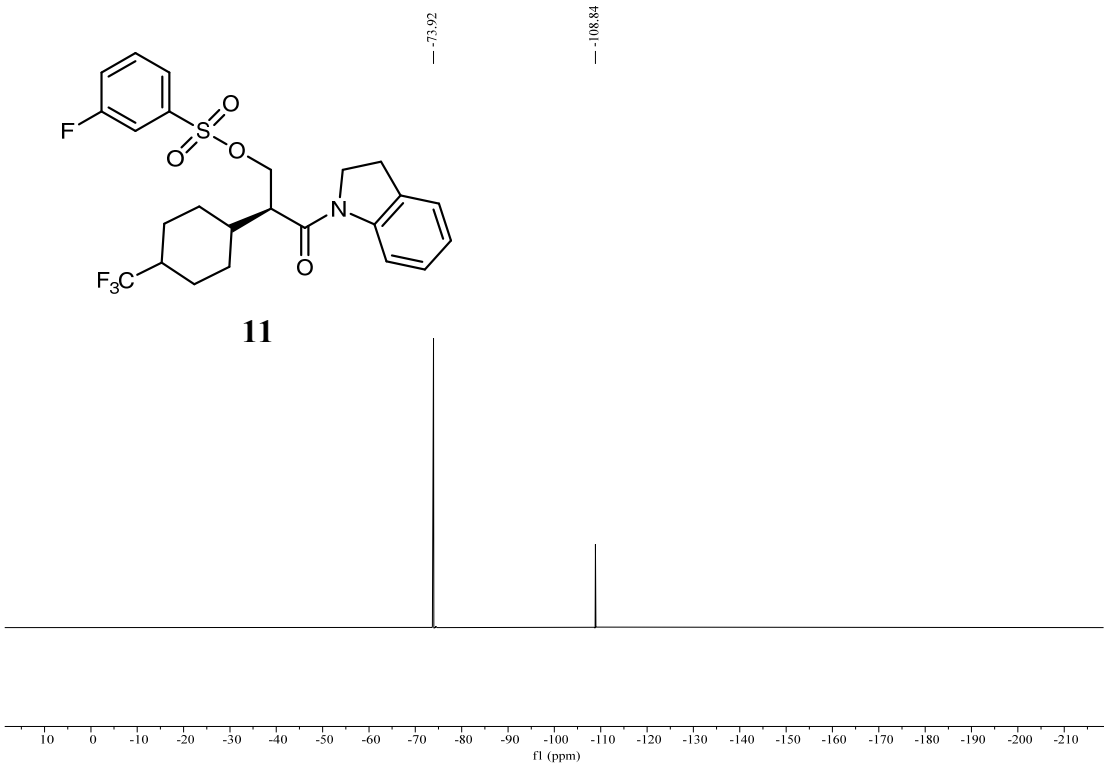
^{1}H NMR of 11 (400 MHz, $CDCl_3$)



^{13}C NMR of 11 (150 MHz, $CDCl_3$)

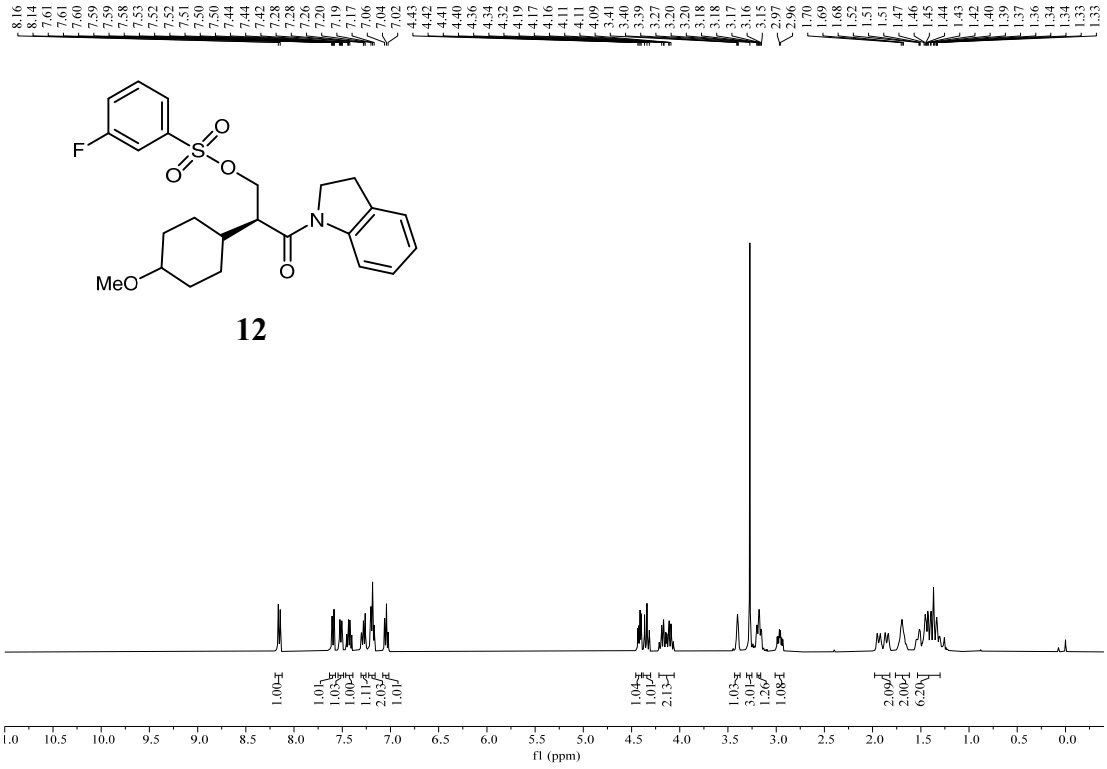


^{19}F NMR of 11 (375 MHz, $CDCl_3$)



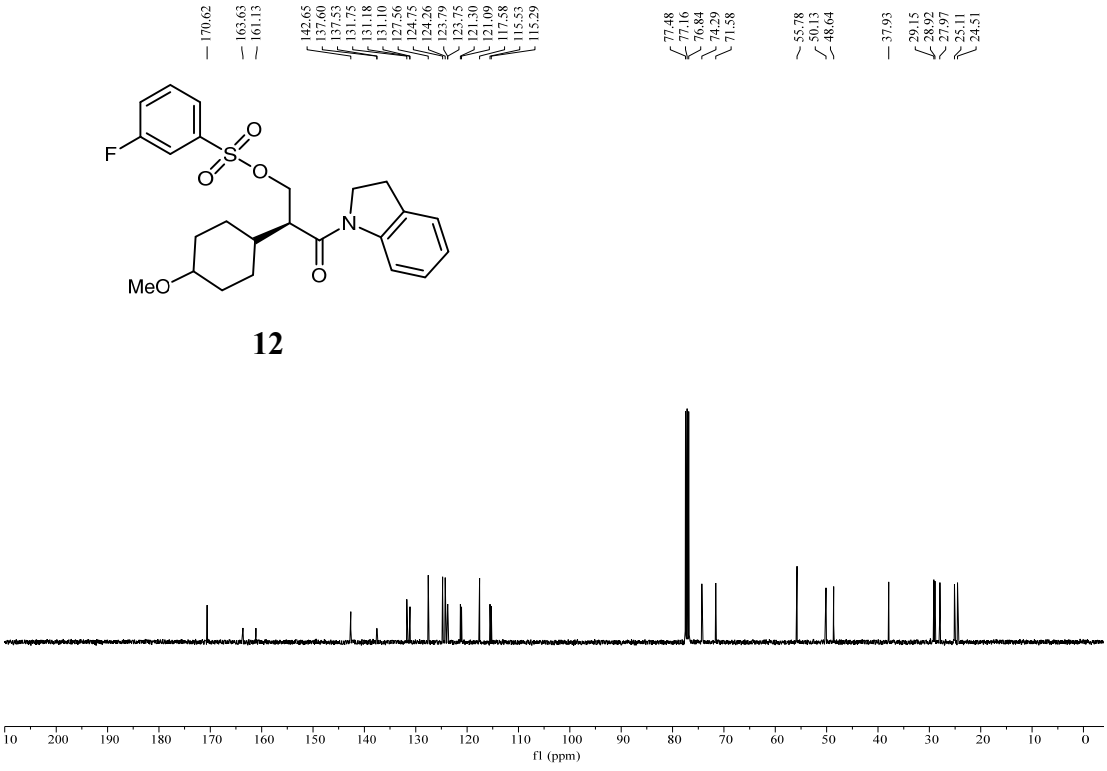
11

^{1}H NMR of 12 (400 MHz, $CDCl_3$)



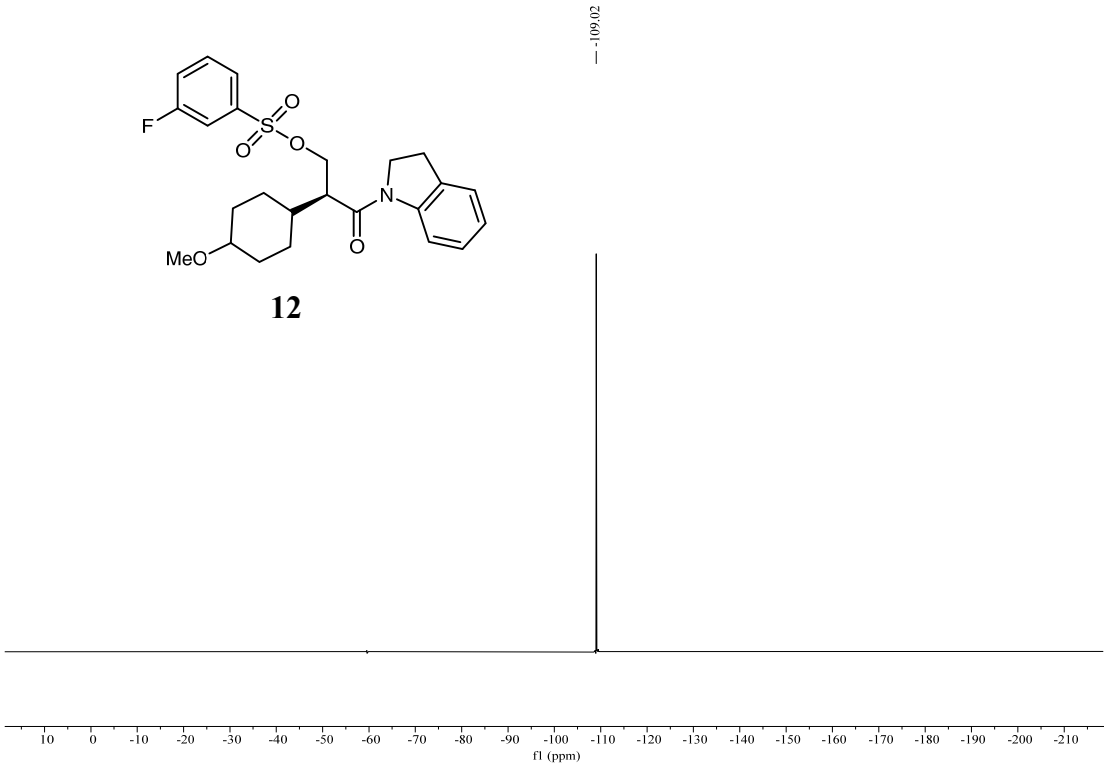
12

^{13}C NMR of 12 (100 MHz, $CDCl_3$)



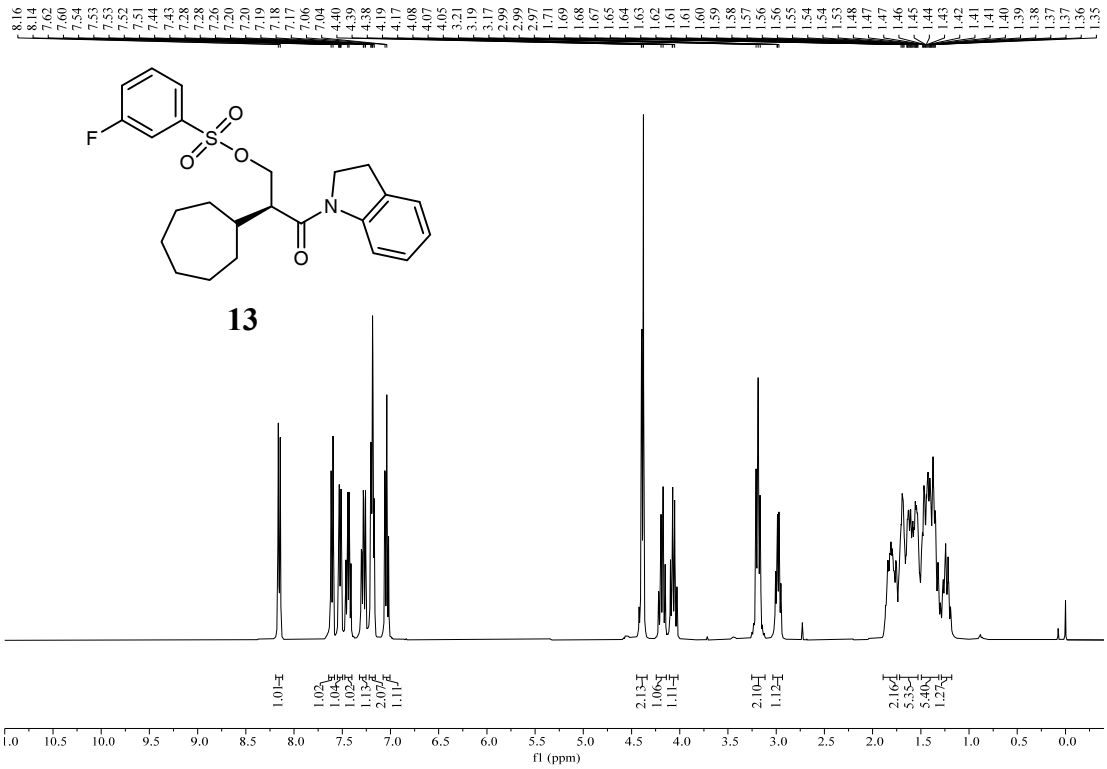
12

^{19}F NMR of 12 (375 MHz, $CDCl_3$)

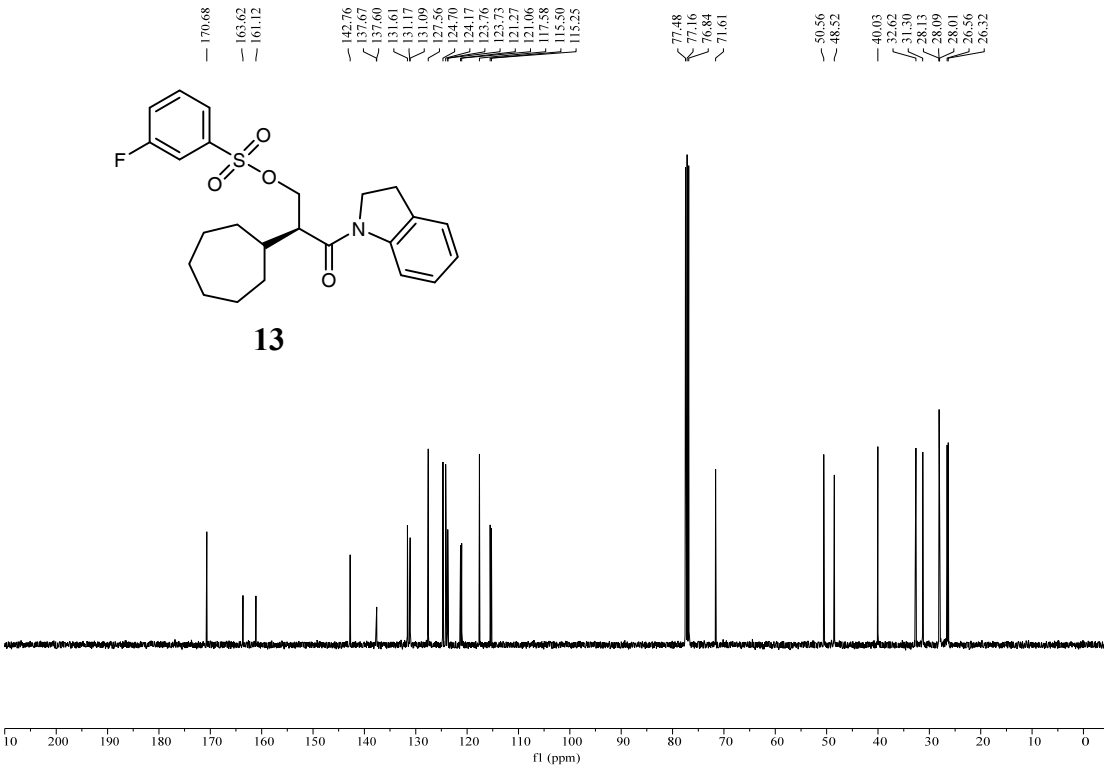


12

^{1}H NMR of 13 (400 MHz, $CDCl_3$)



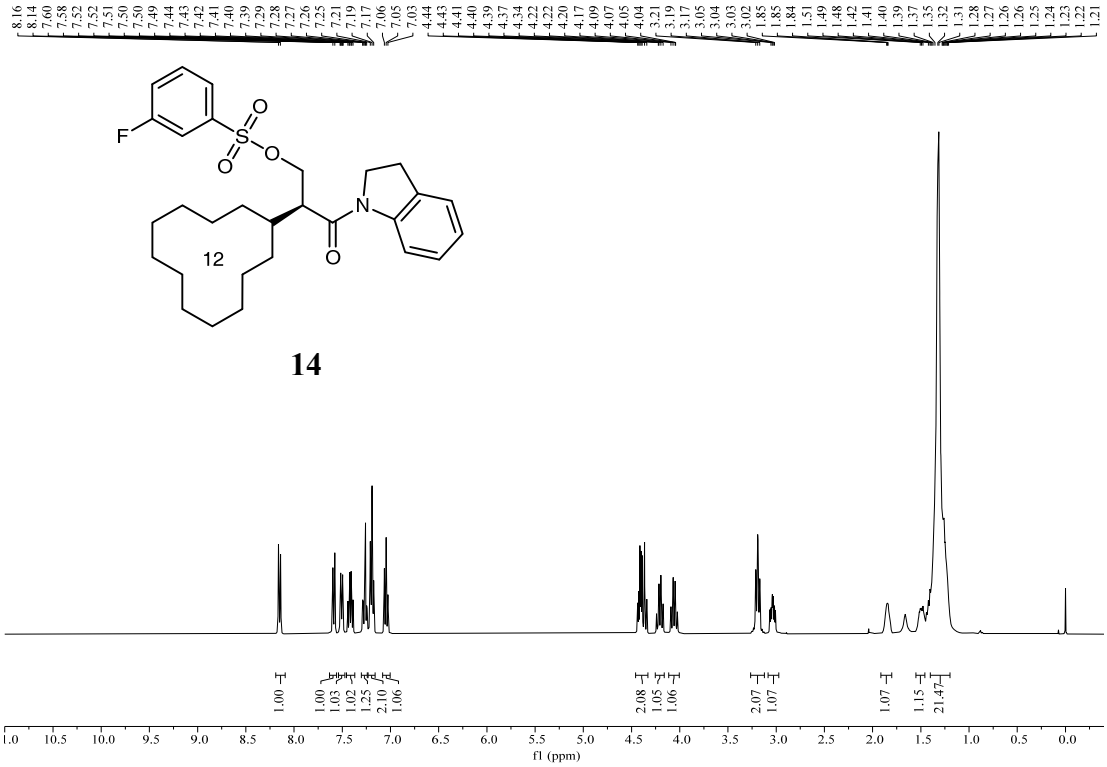
^{13}C NMR of 13 (100 MHz, $CDCl_3$)



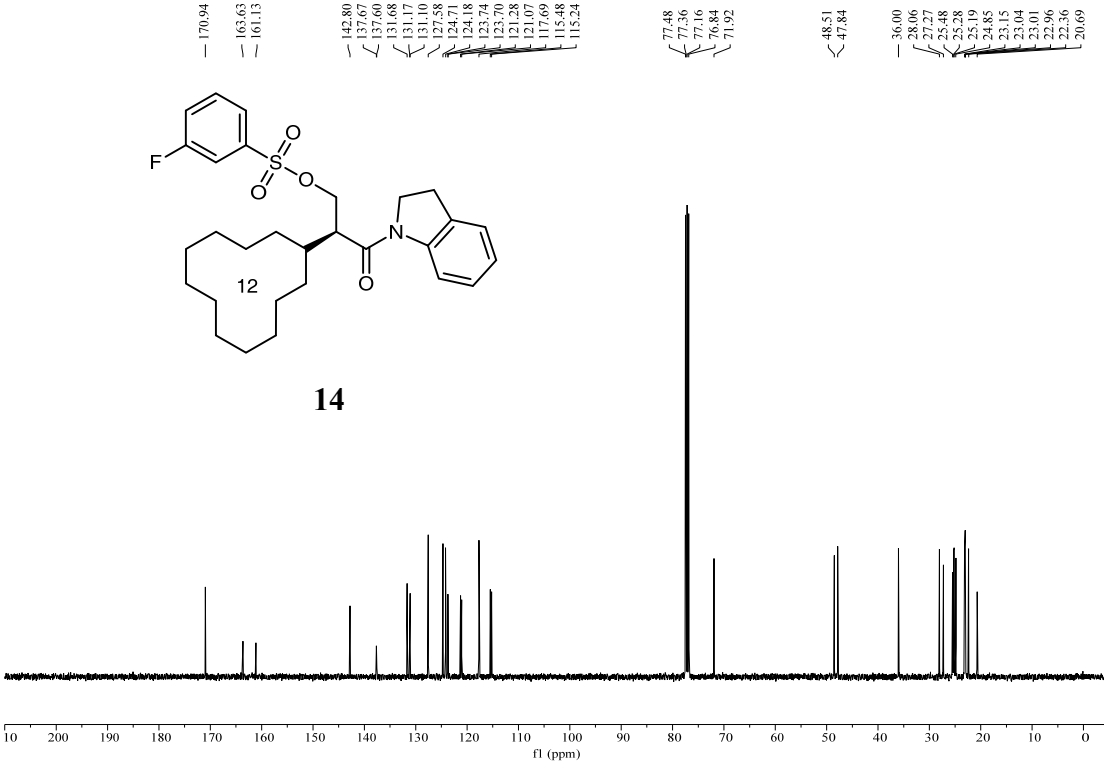
^{19}F NMR of 13 (375 MHz, $CDCl_3$)

13

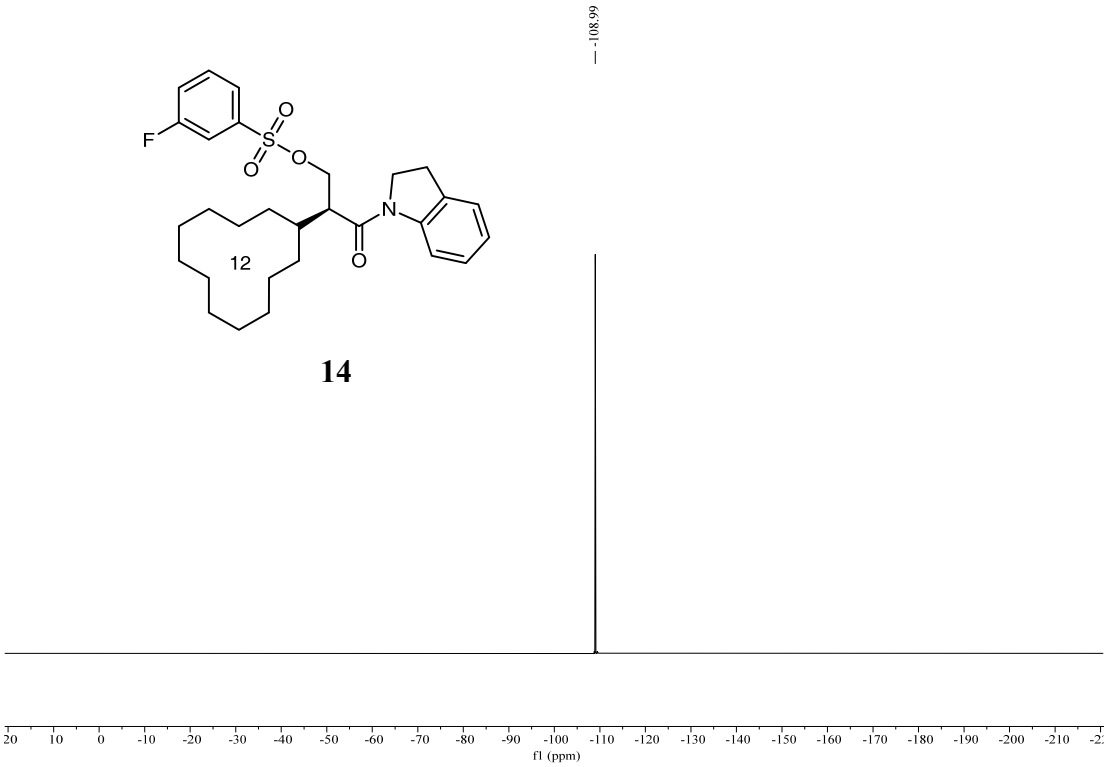
^{1}H NMR of 14 (400 MHz, $CDCl_3$)



^{13}C NMR of 14 (100 MHz, $CDCl_3$)

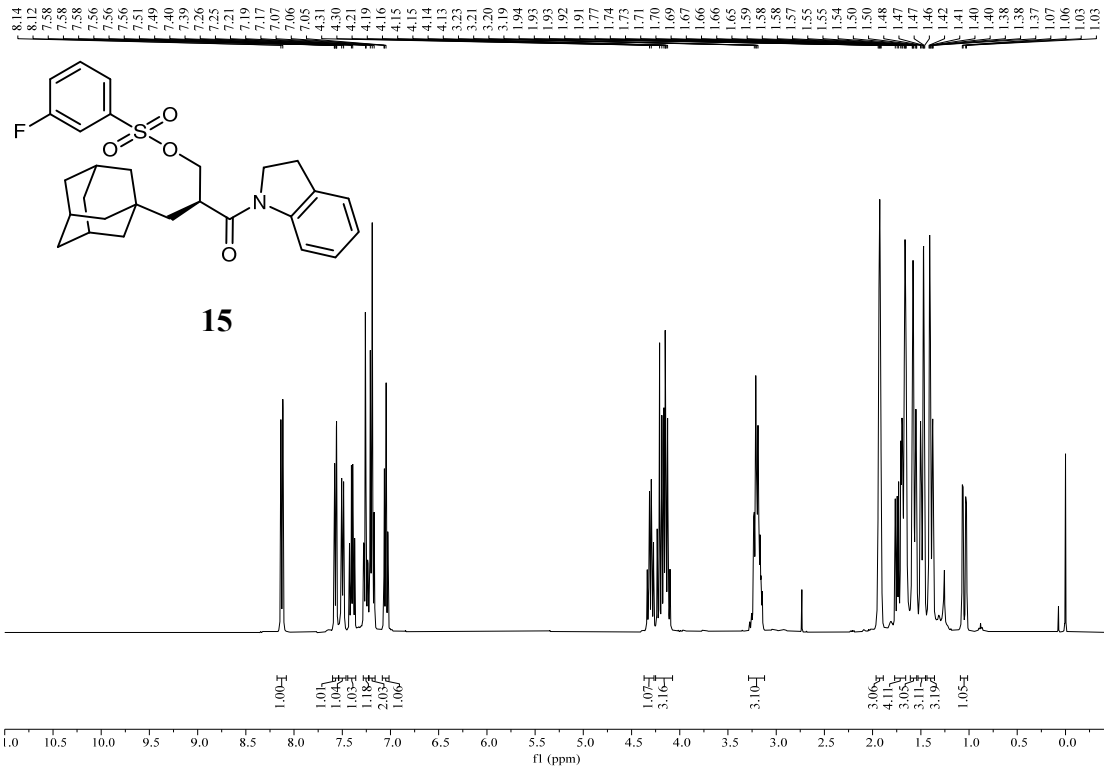


^{19}F NMR of 14 (375 MHz, $CDCl_3$)

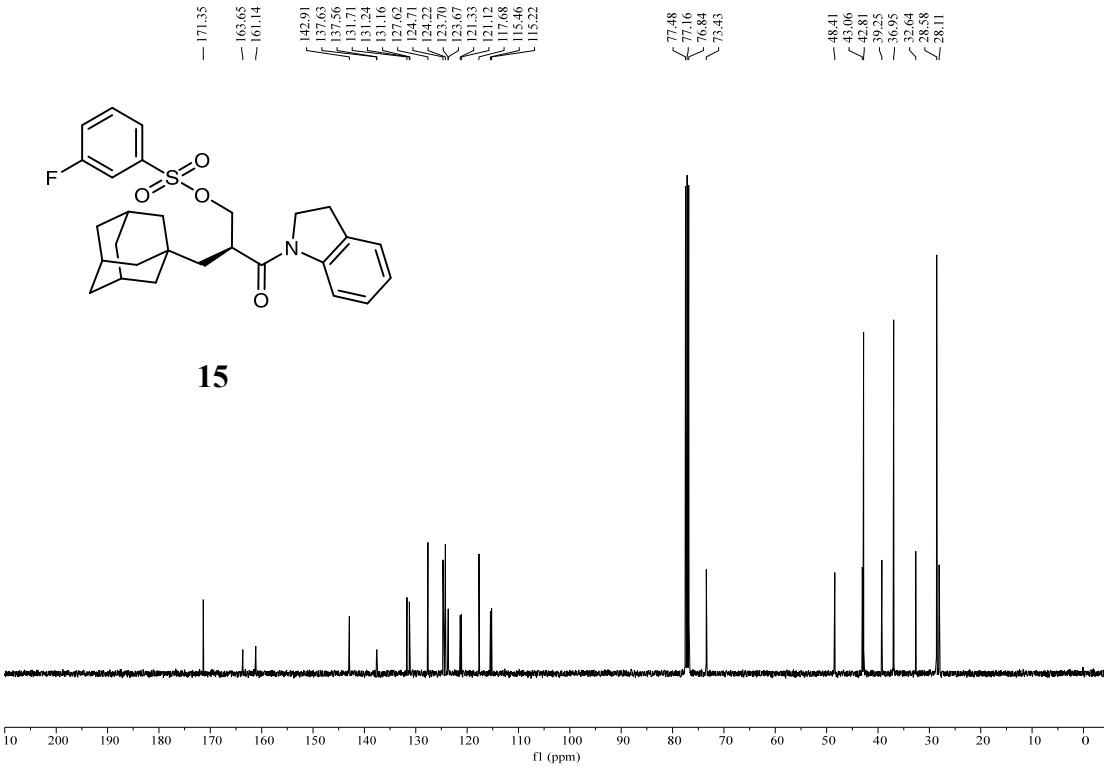


14

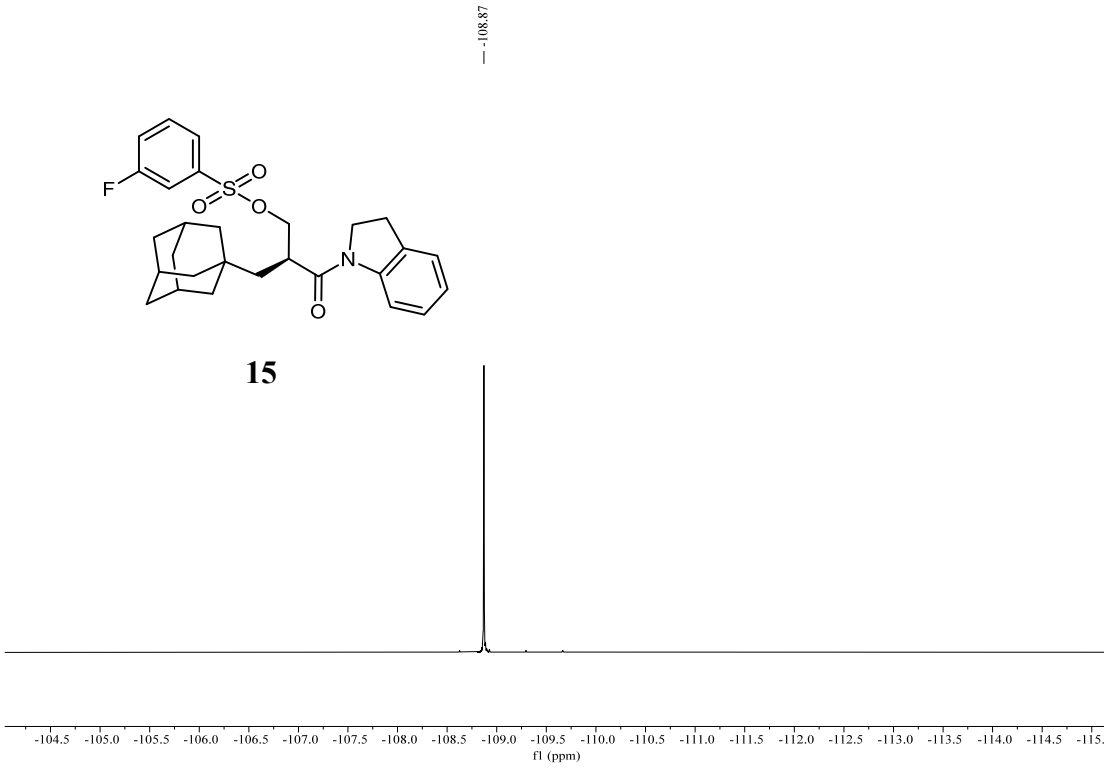
^{1}H NMR of 15 (400 MHz, $CDCl_3$)



^{13}C NMR of 15 (100 MHz, $CDCl_3$)

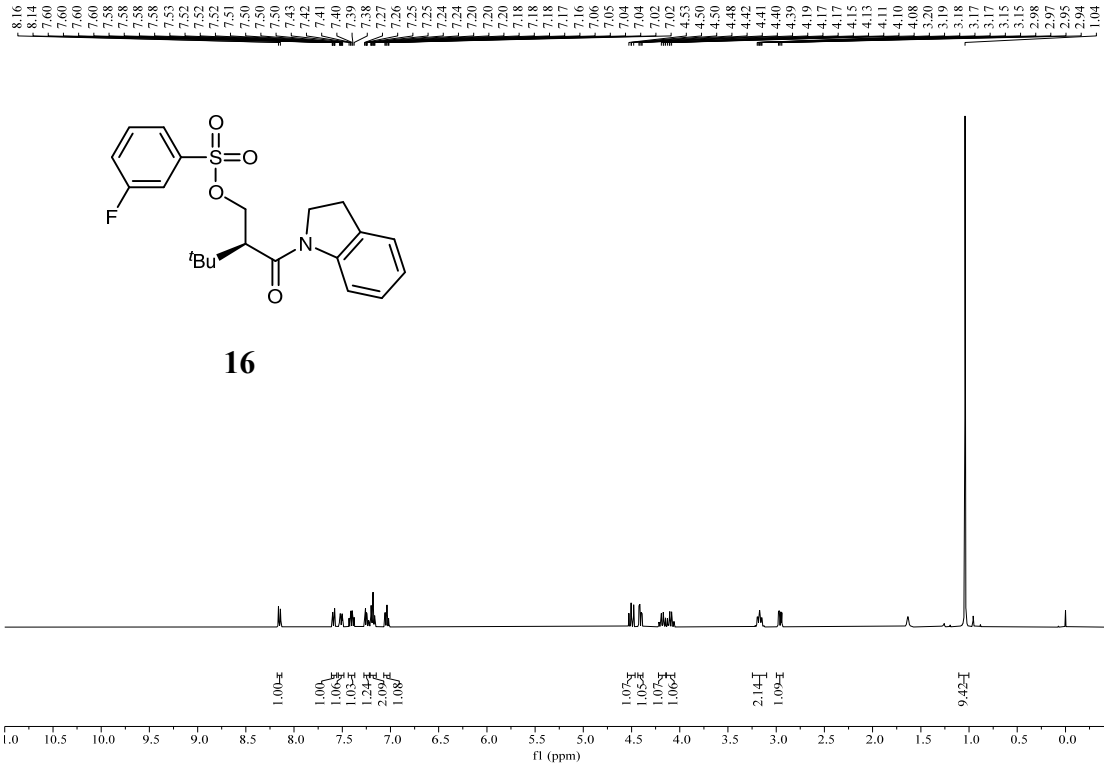


^{19}F NMR of 15 (375 MHz, $CDCl_3$)



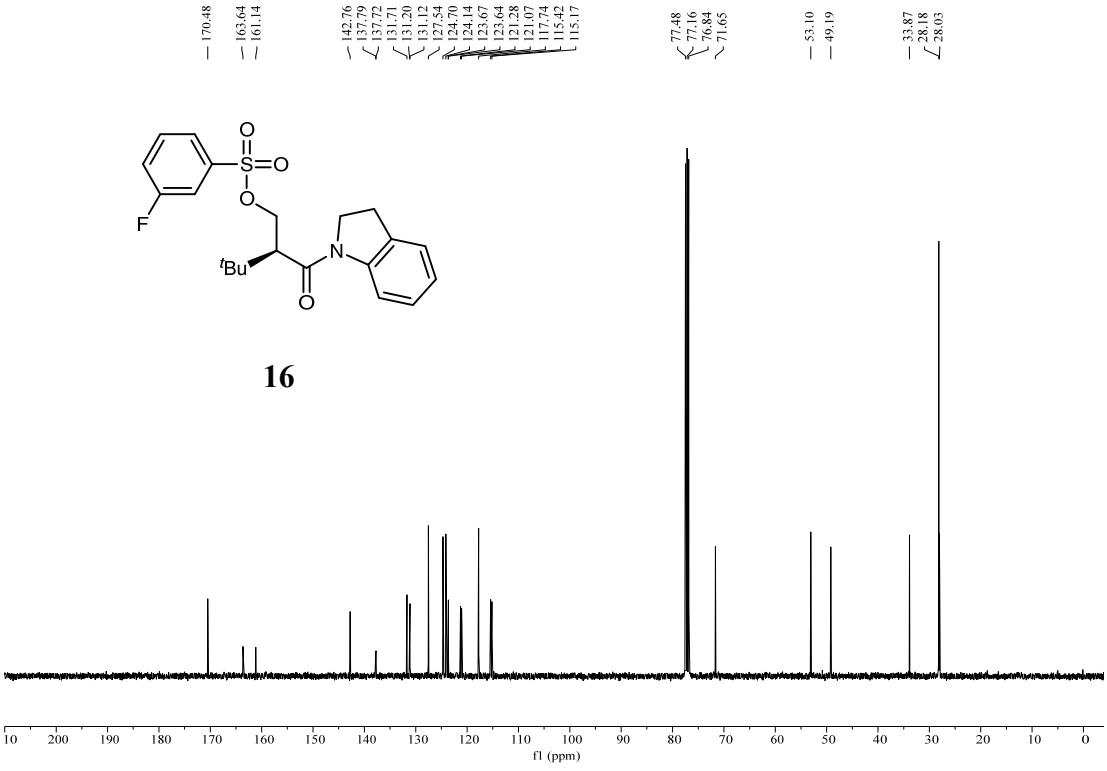
15

^{1}H NMR of 16 (400 MHz, $CDCl_3$)



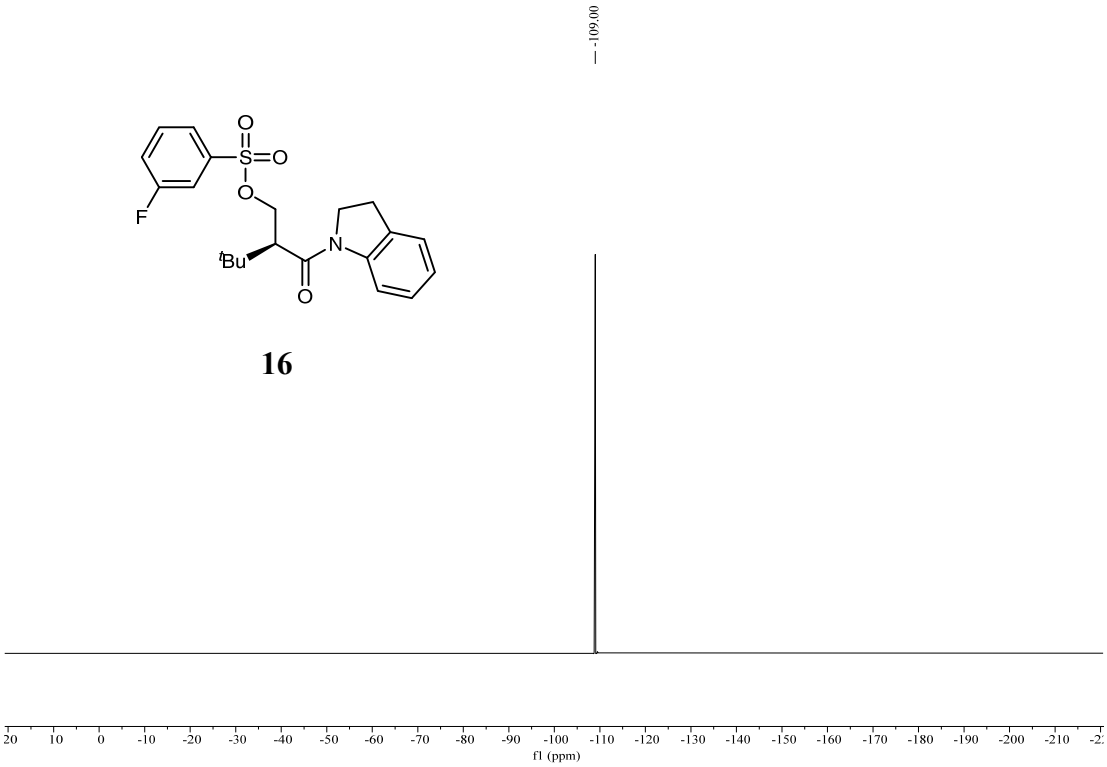
16

^{13}C NMR of 16 (100 MHz, $CDCl_3$)



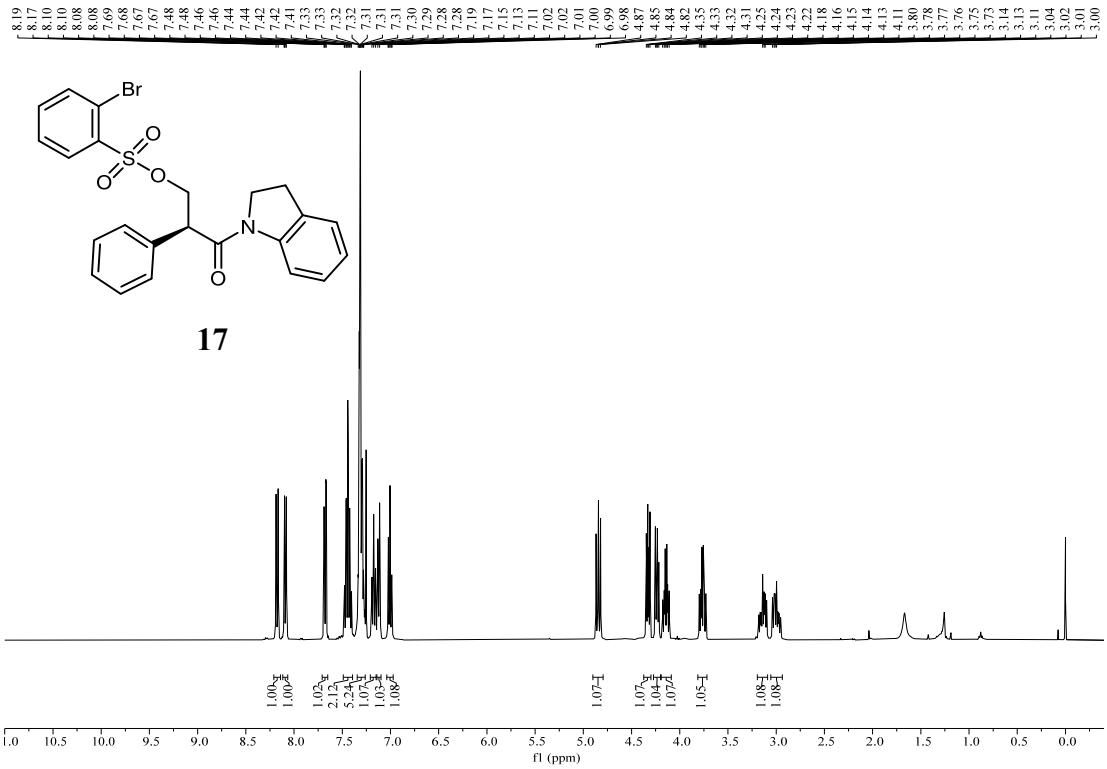
16

^{19}F NMR of 16 (375 MHz, $CDCl_3$)

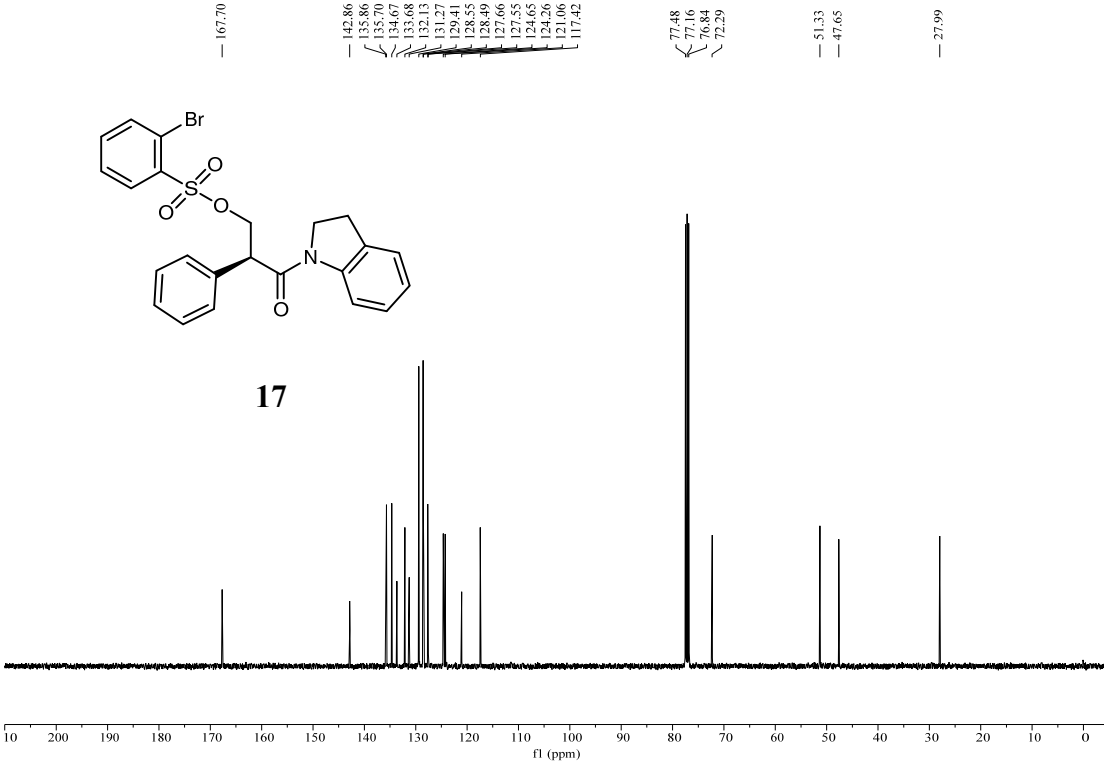


16

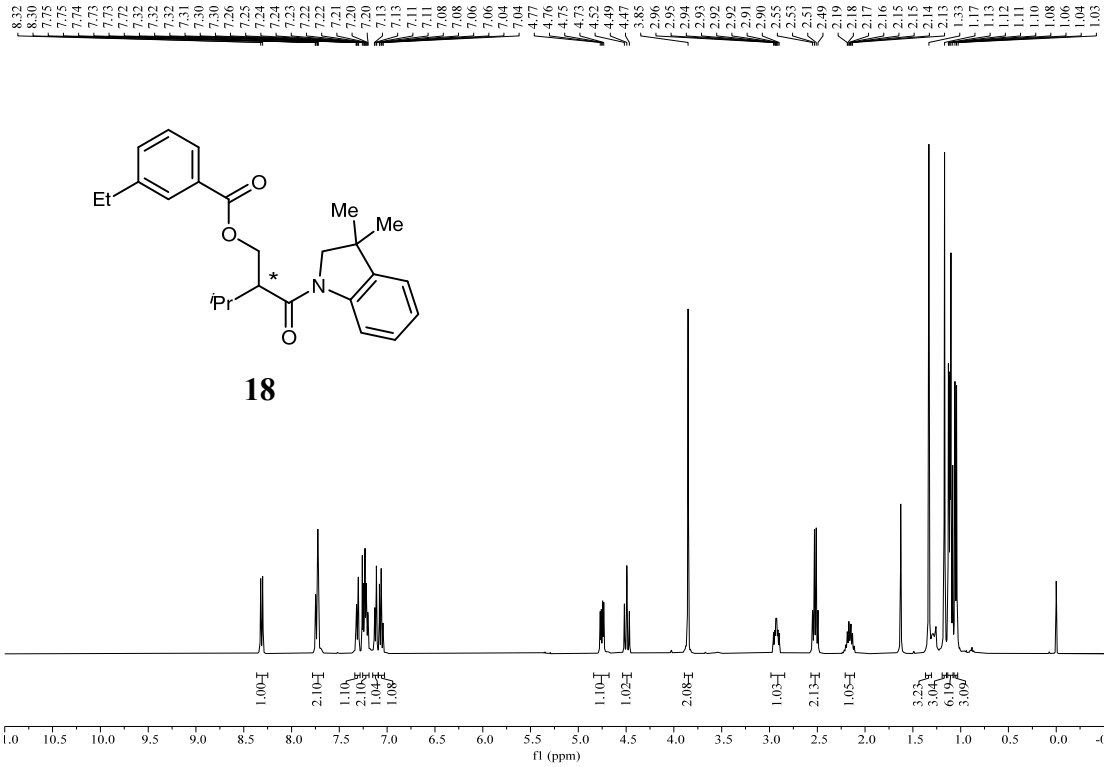
^{1}H NMR of 17 (400 MHz, $CDCl_3$)



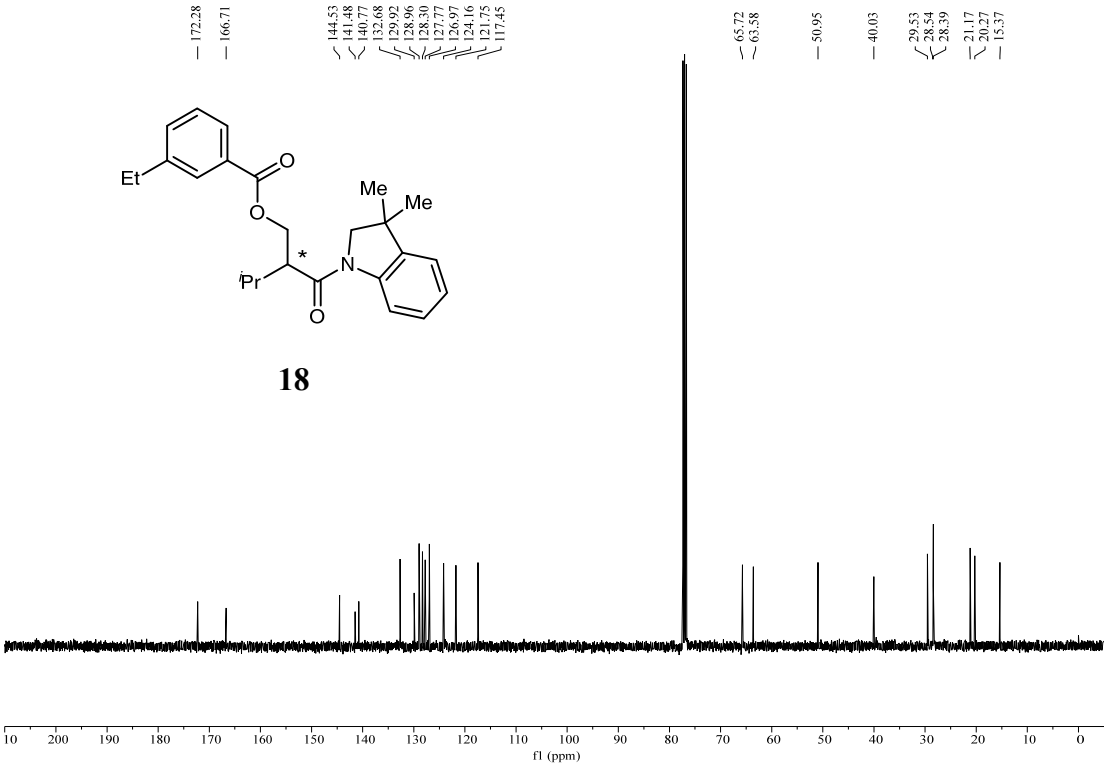
^{13}C NMR of 17 (100 MHz, $CDCl_3$)



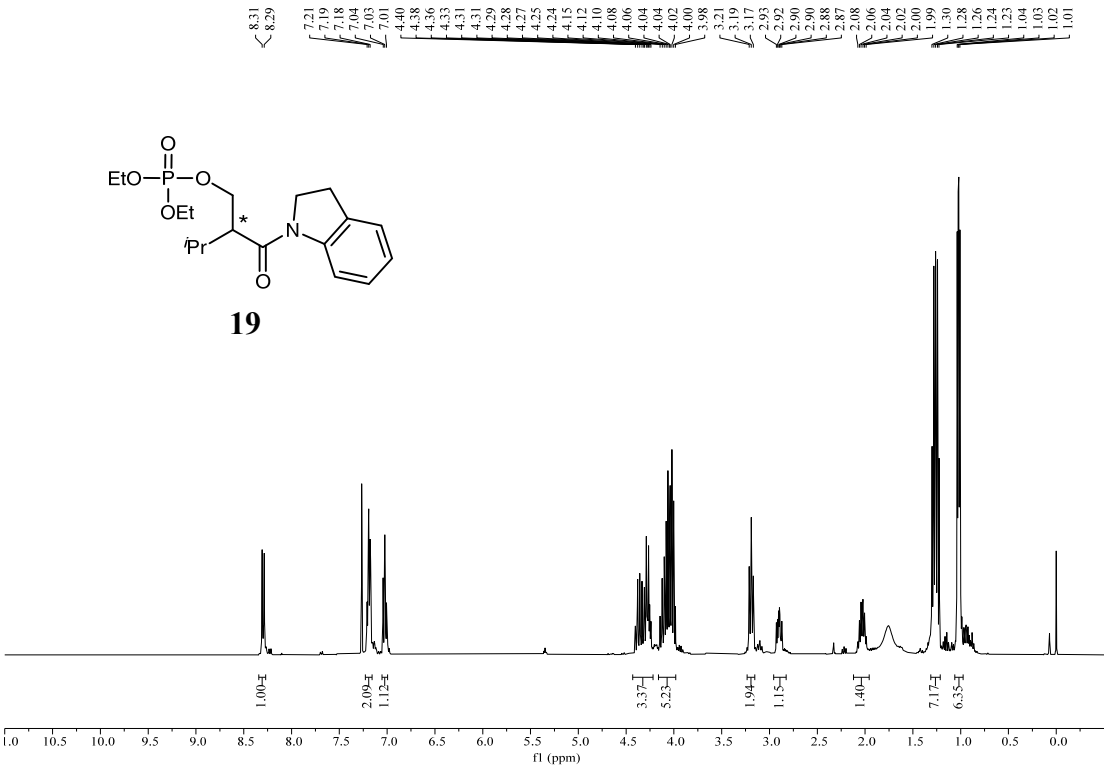
^{1}H NMR of 18 (400 MHz, $CDCl_3$)



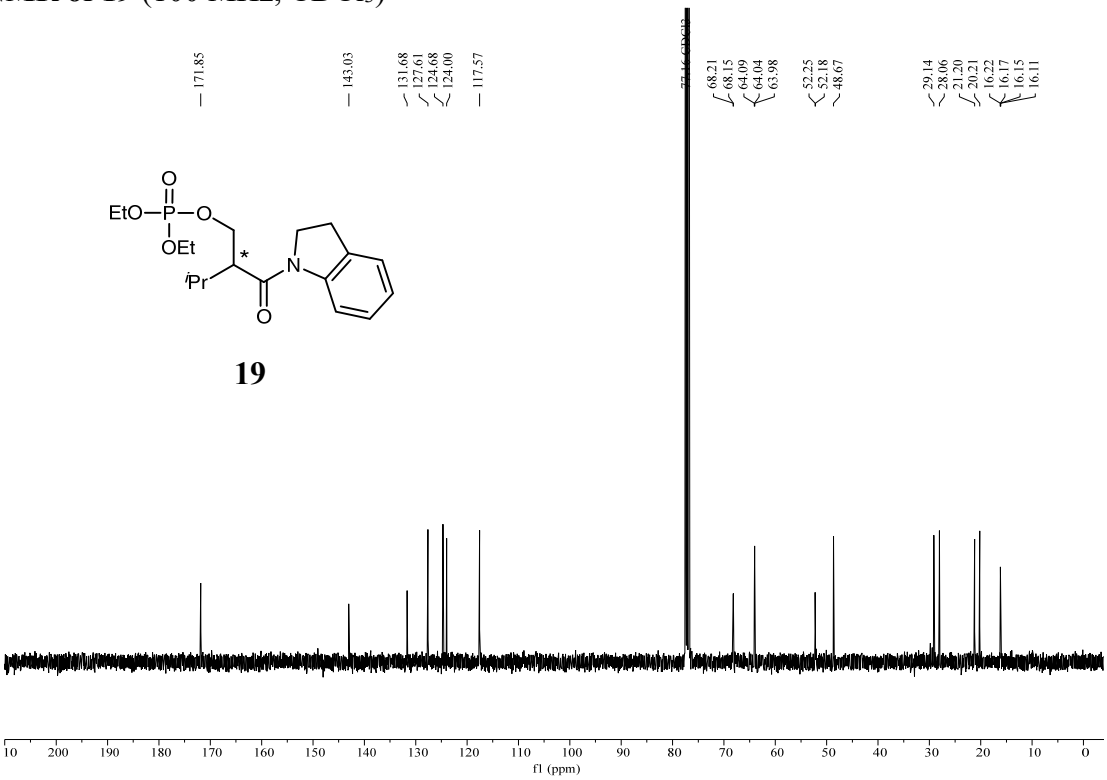
^{13}C NMR of 18 (100 MHz, $CDCl_3$)



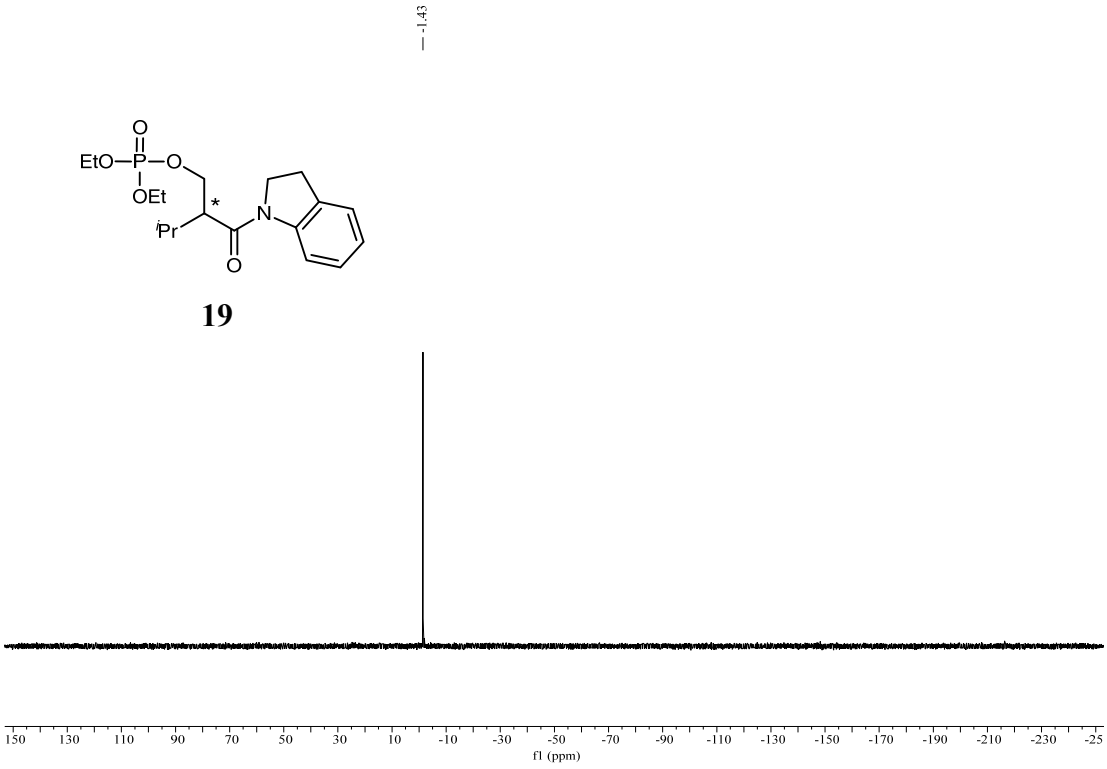
^{1}H NMR of 19 (400 MHz, $CDCl_3$)



^{13}C NMR of 19 (100 MHz, $CDCl_3$)

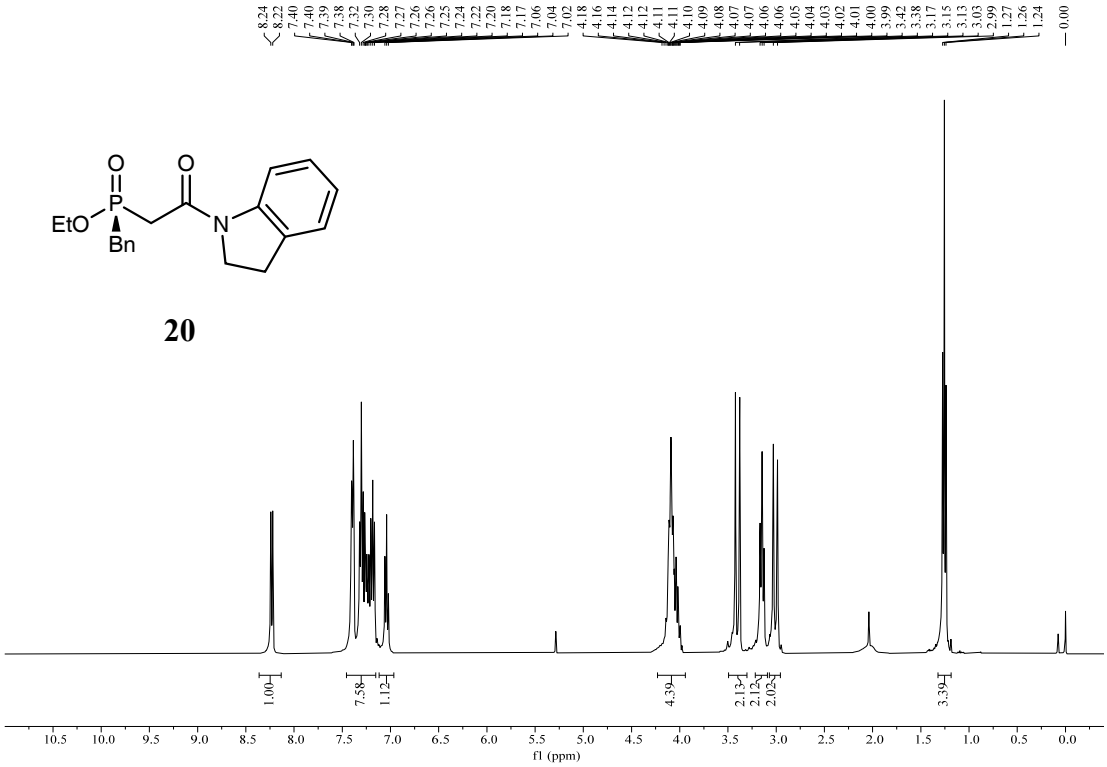


^{31}P NMR of 19 (162 MHz, $CDCl_3$)



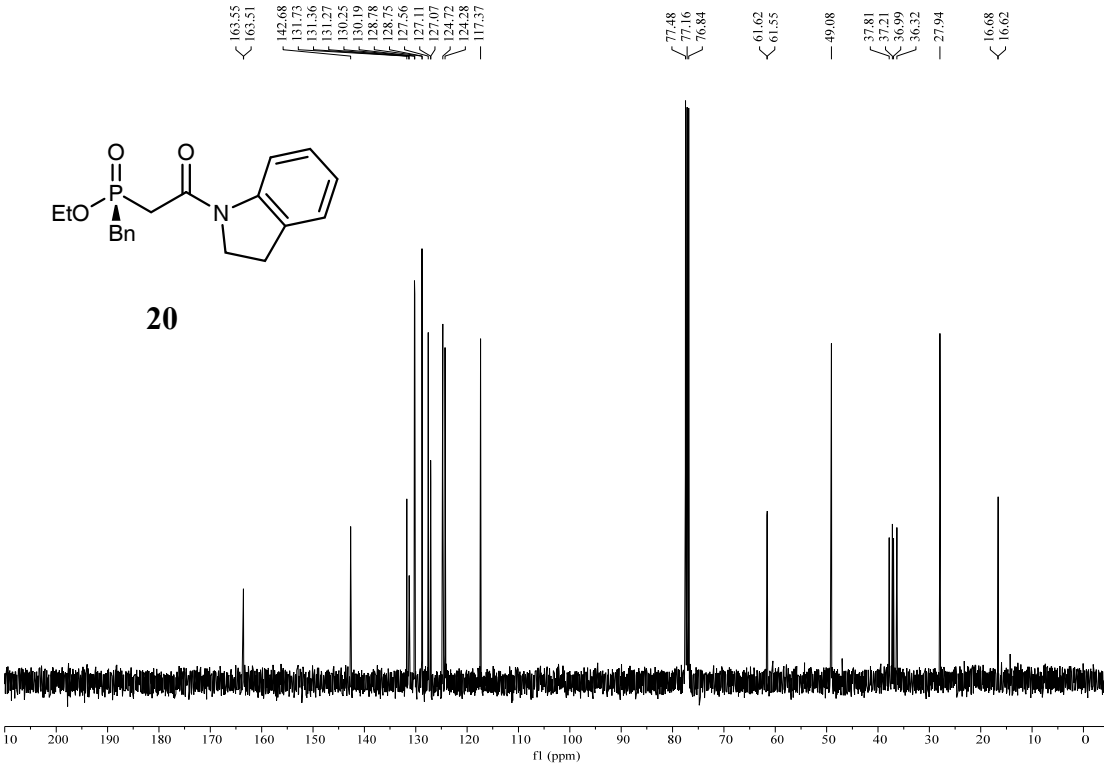
19

^{1}H NMR of 20 (400 MHz, $CDCl_3$)



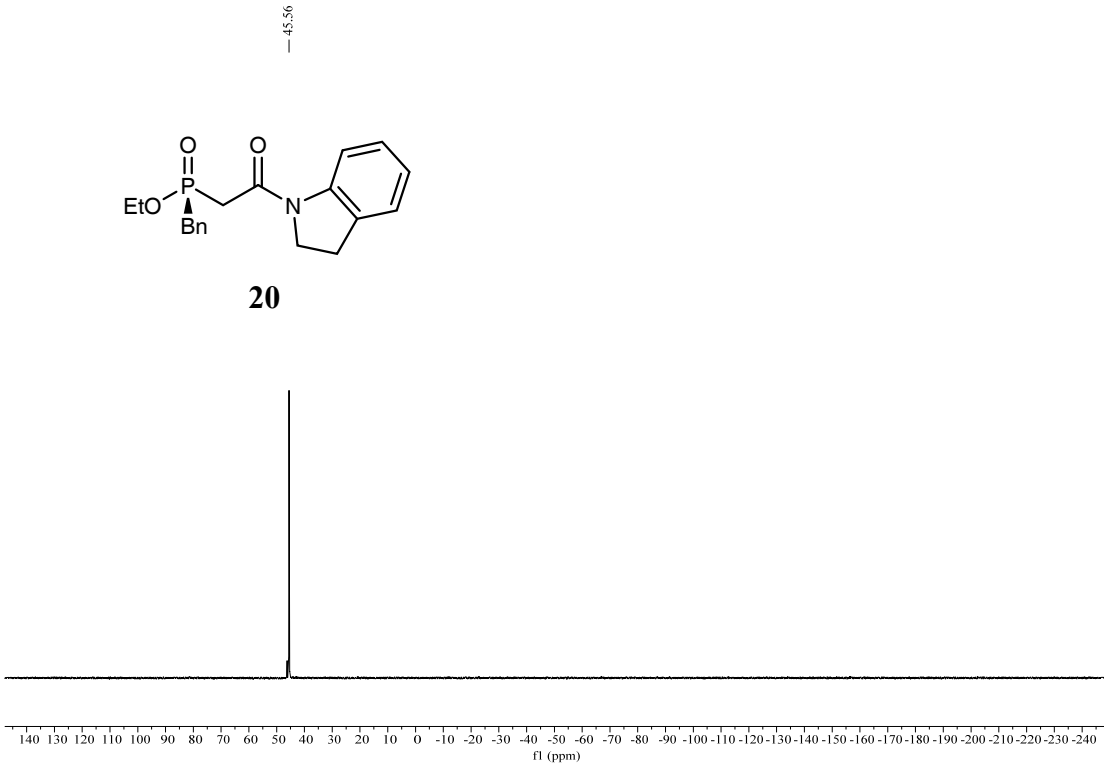
20

^{13}C NMR of 20 (100 MHz, $CDCl_3$)



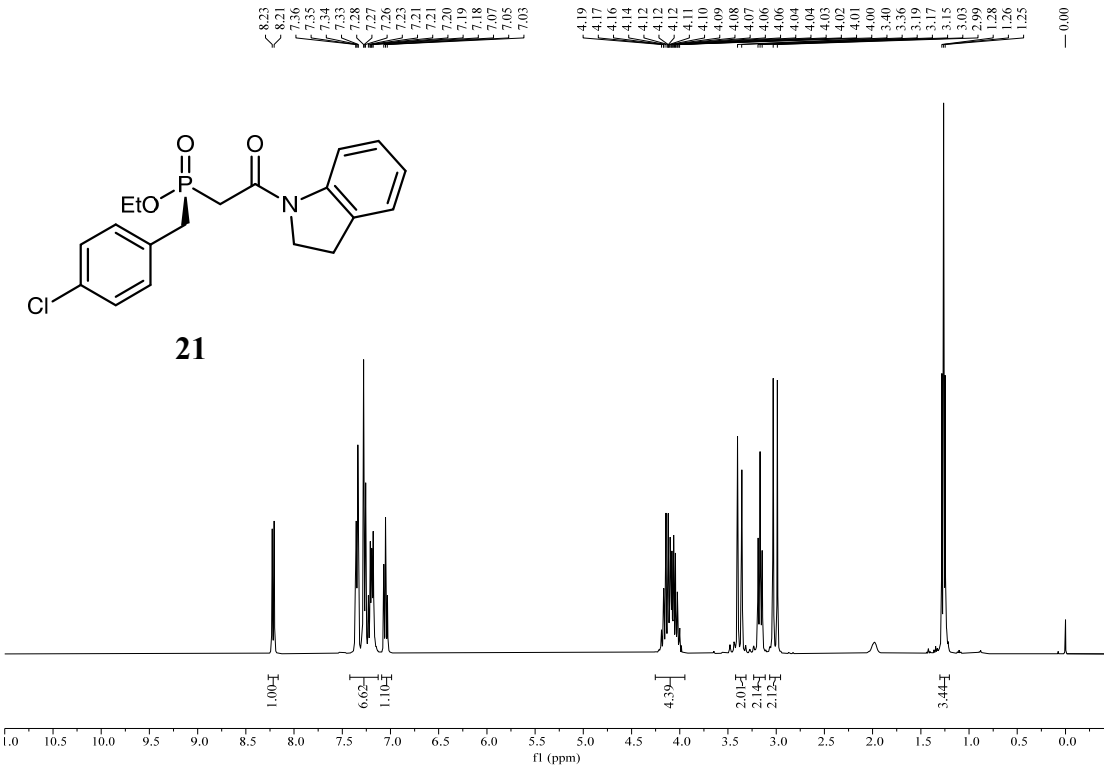
20

^{31}P NMR of 20 (162 MHz, $CDCl_3$)

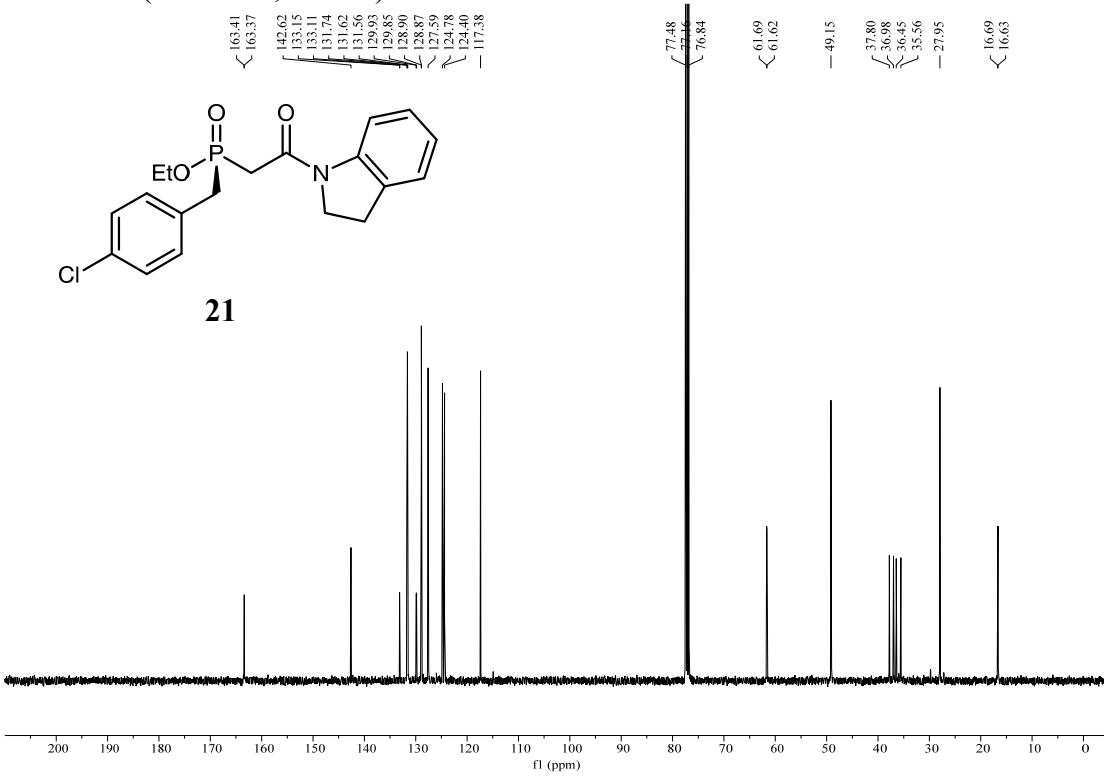


20

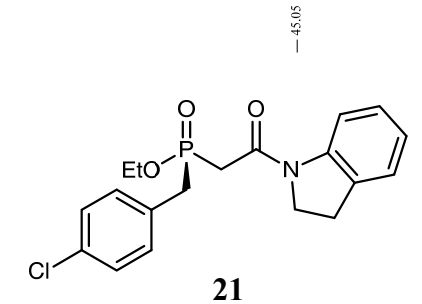
^{1}H NMR of 21 (400 MHz, $CDCl_3$)



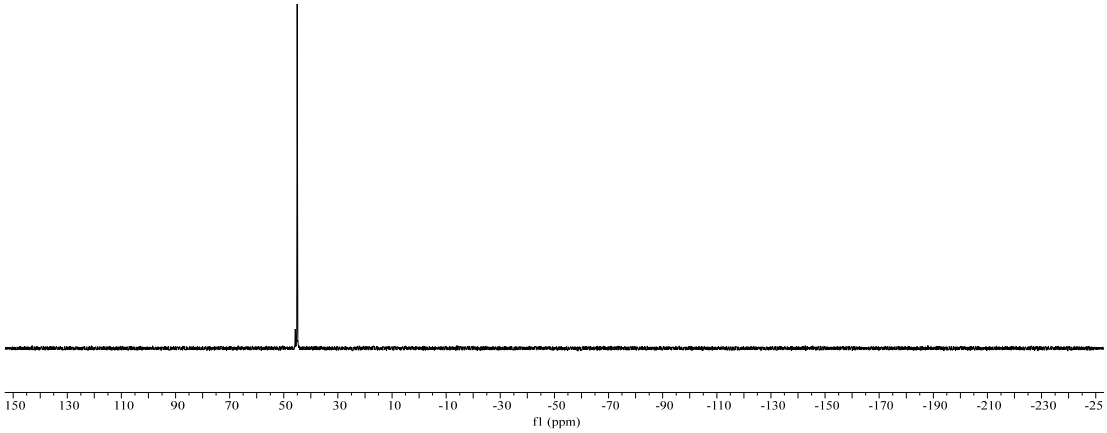
^{13}C NMR of 21 (100 MHz, $CDCl_3$)



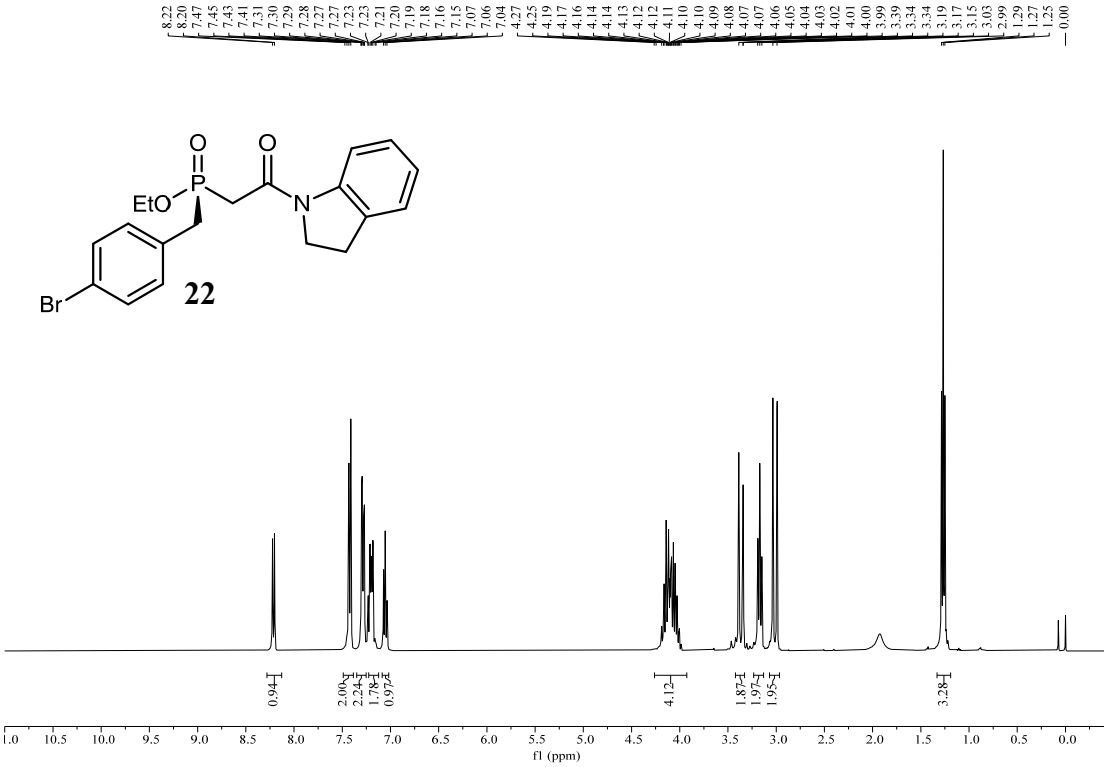
^{31}P NMR of 21 (162 MHz, $CDCl_3$)



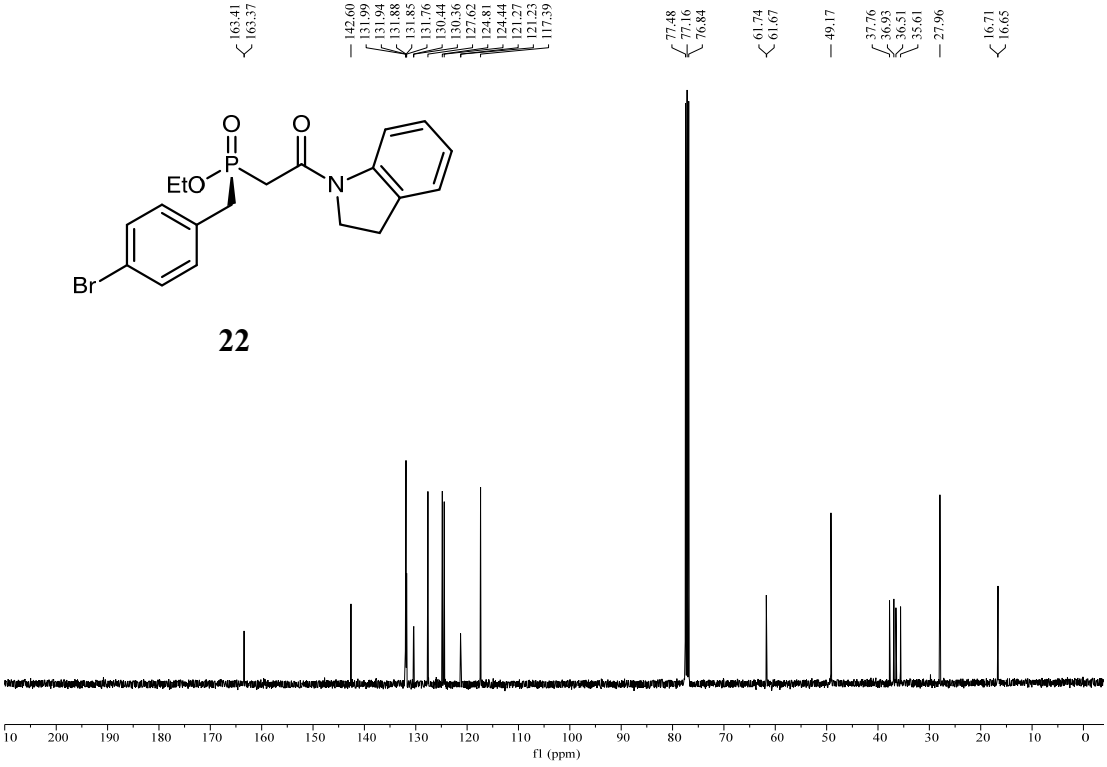
21



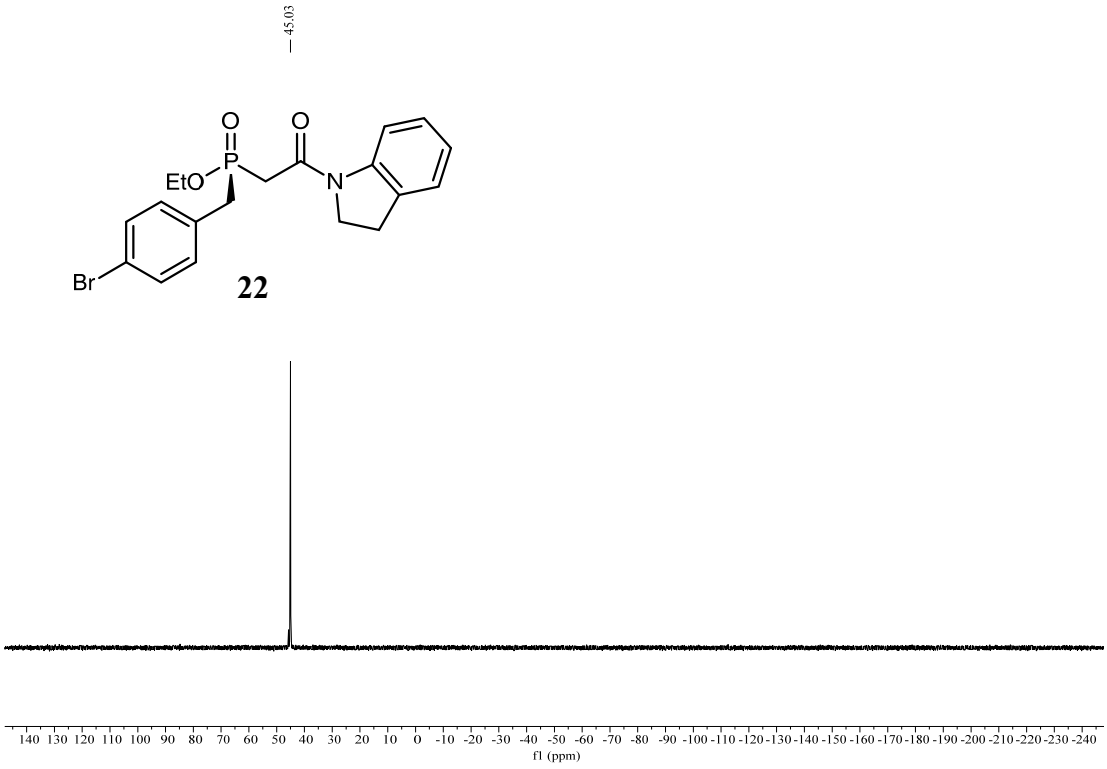
^{1}H NMR of 22 (400 MHz, $CDCl_3$)



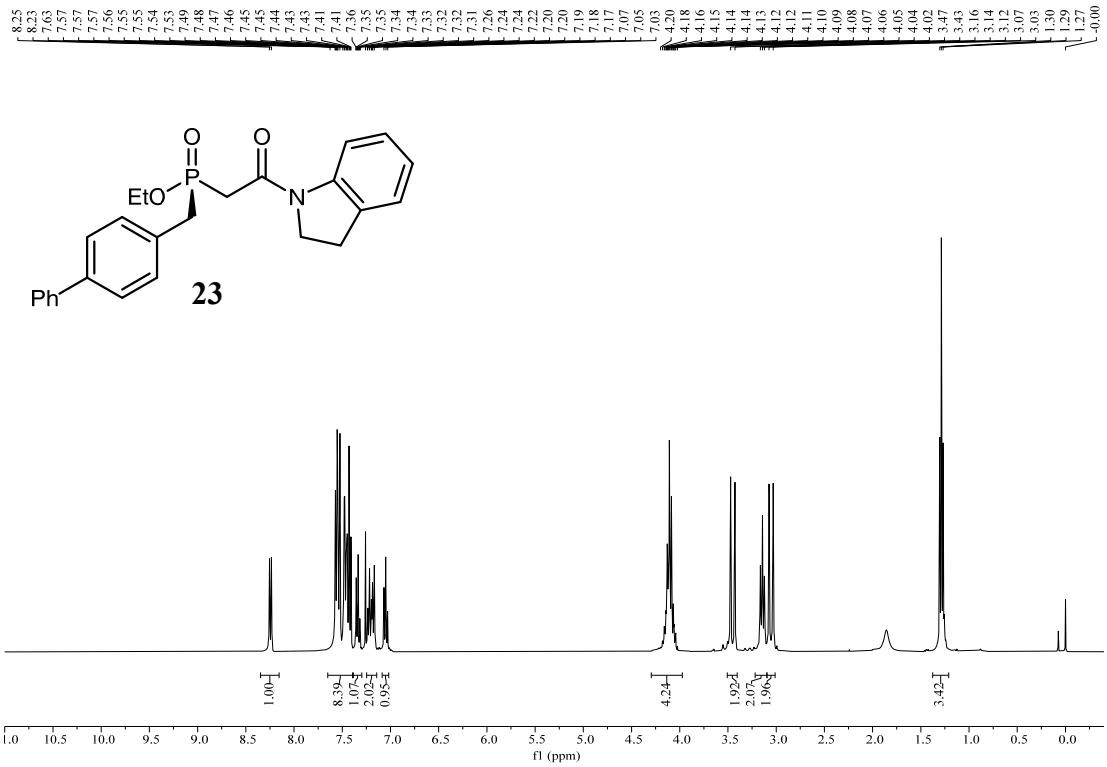
^{13}C NMR of 22 (100 MHz, $CDCl_3$)



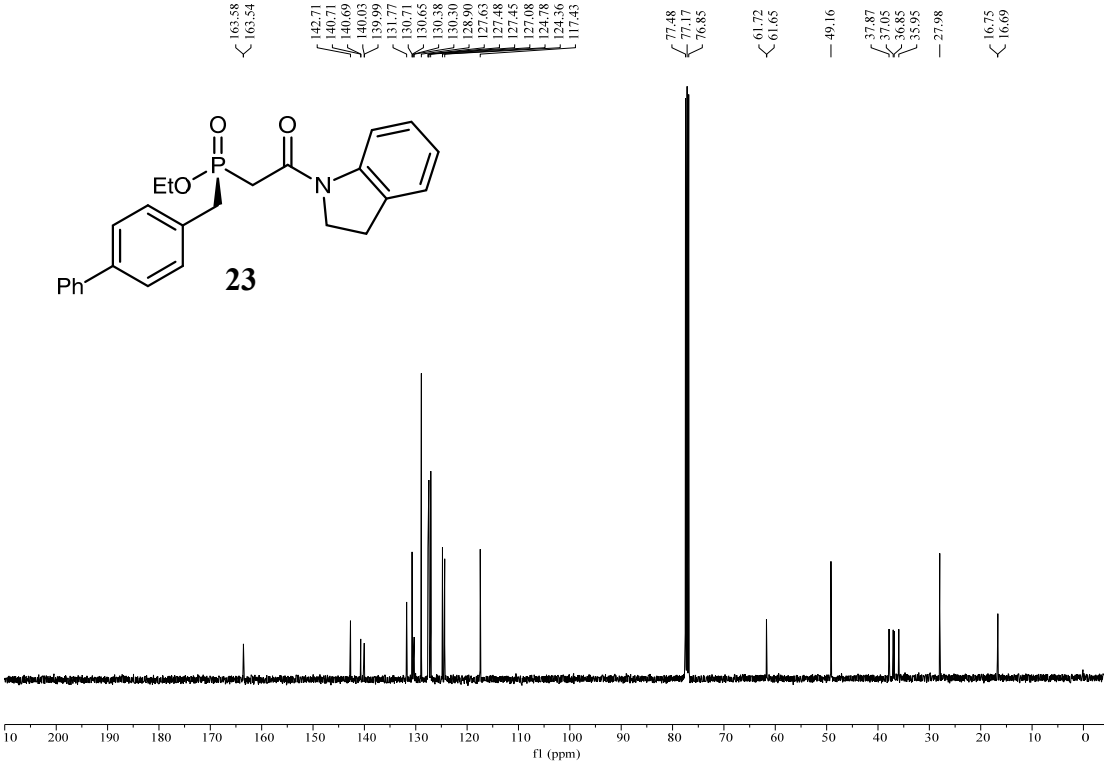
^{31}P NMR of 22 (162 MHz, $CDCl_3$)



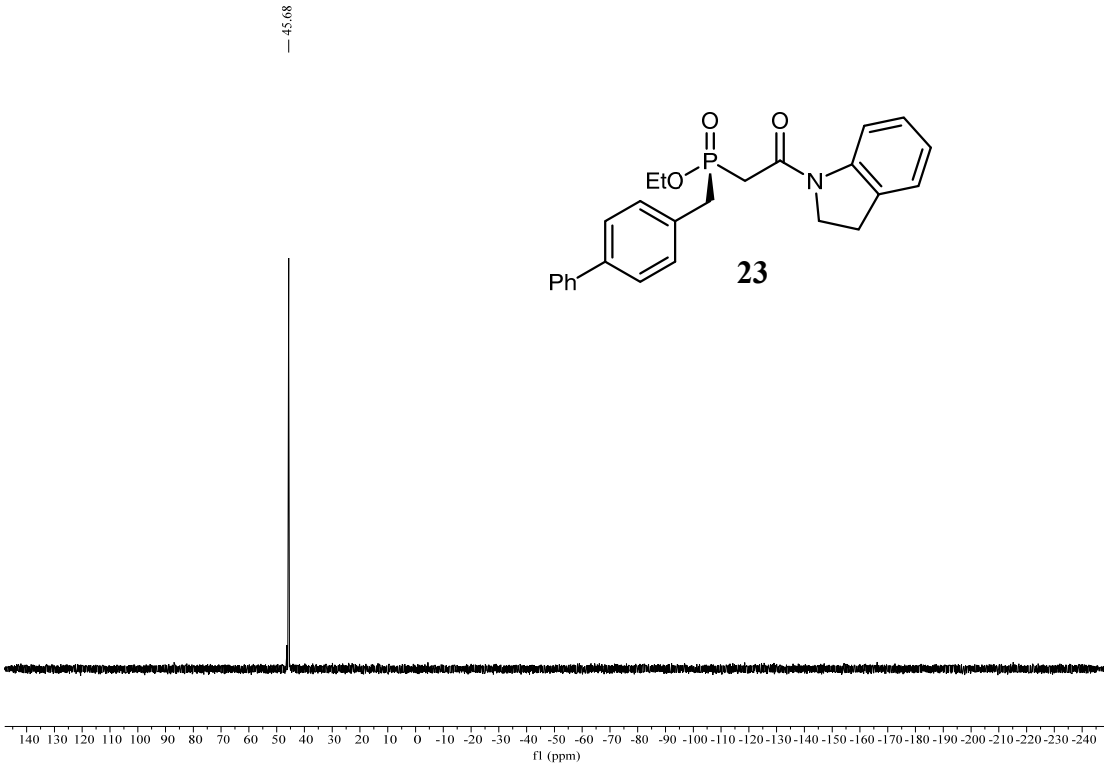
^{1}H NMR of 23 (400 MHz, $CDCl_3$)



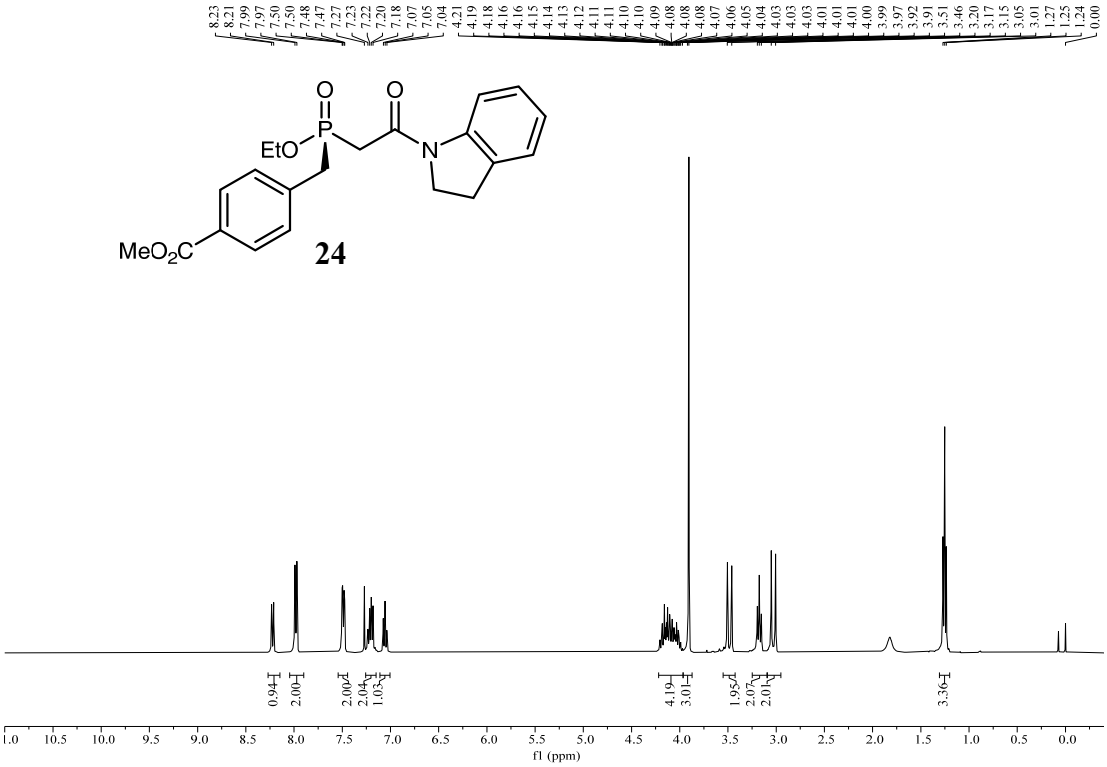
^{13}C NMR of 23 (100 MHz, $CDCl_3$)



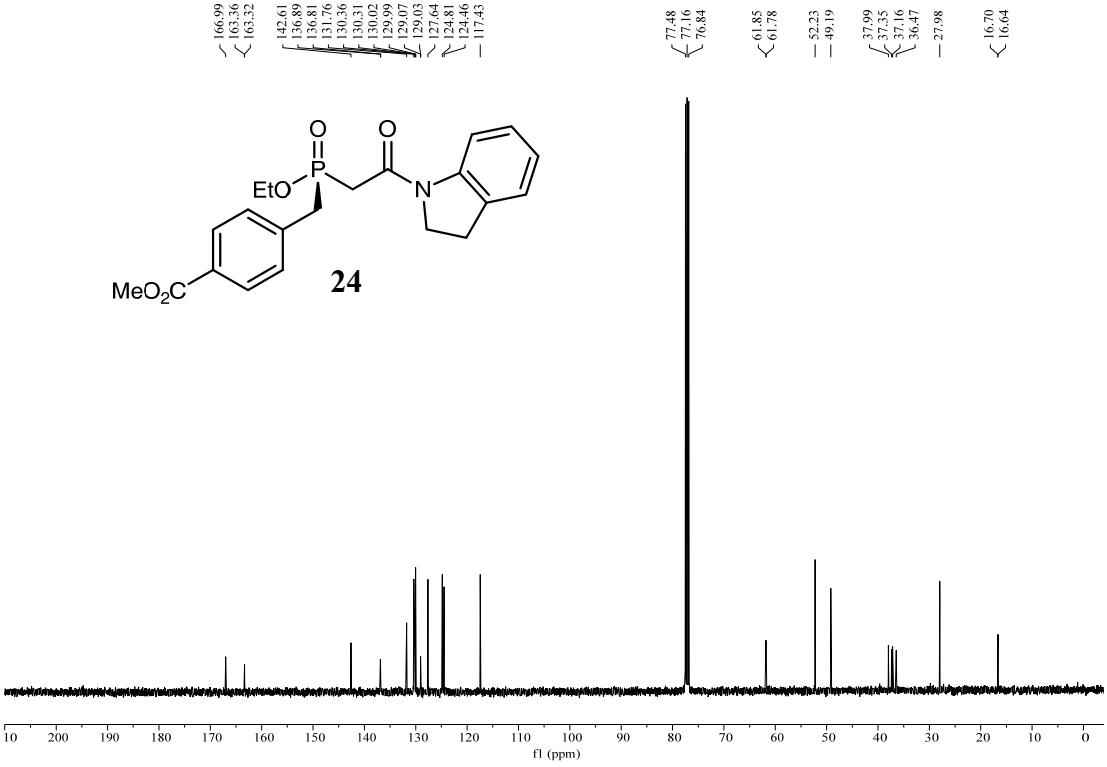
^{31}P NMR of 23 (162 MHz, $CDCl_3$)



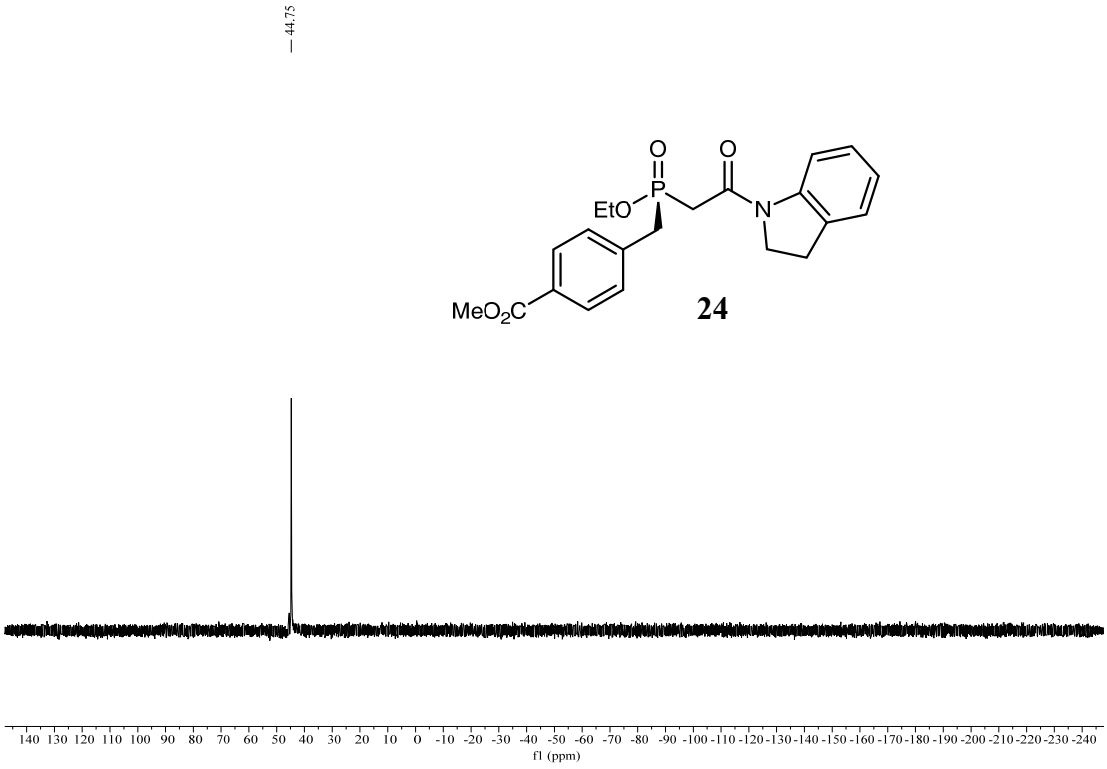
^{1}H NMR of 24 (400 MHz, $CDCl_3$)



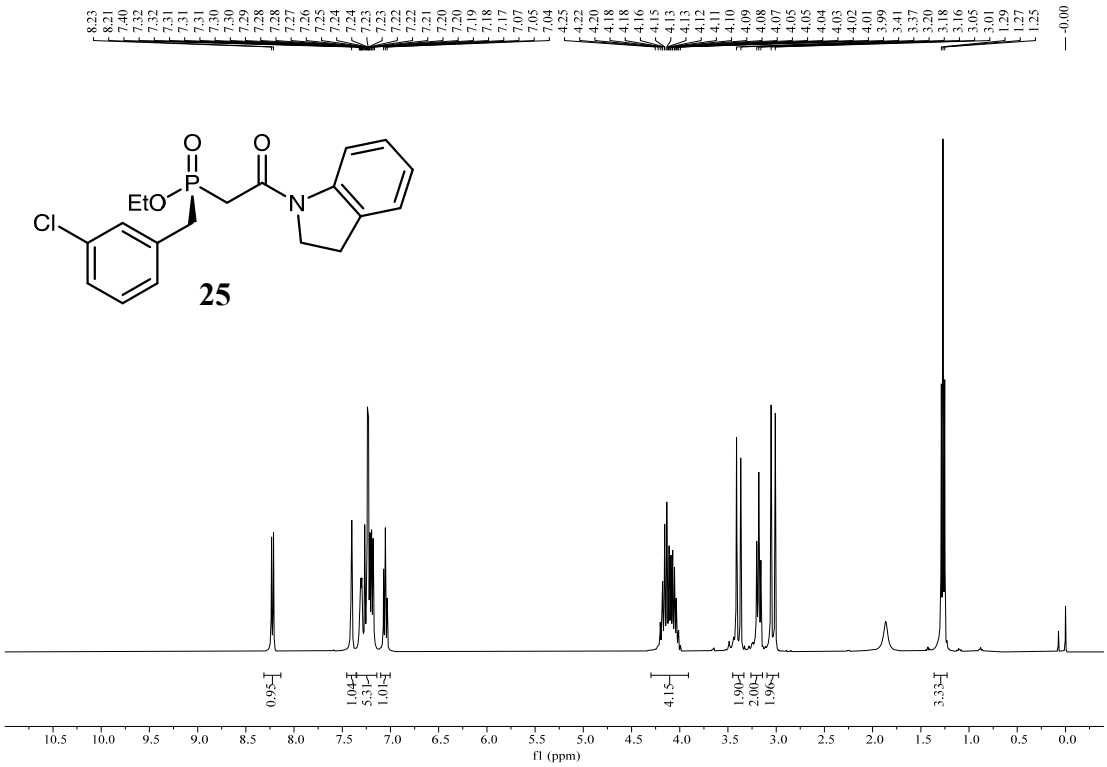
^{13}C NMR of 24 (100 MHz, $CDCl_3$)



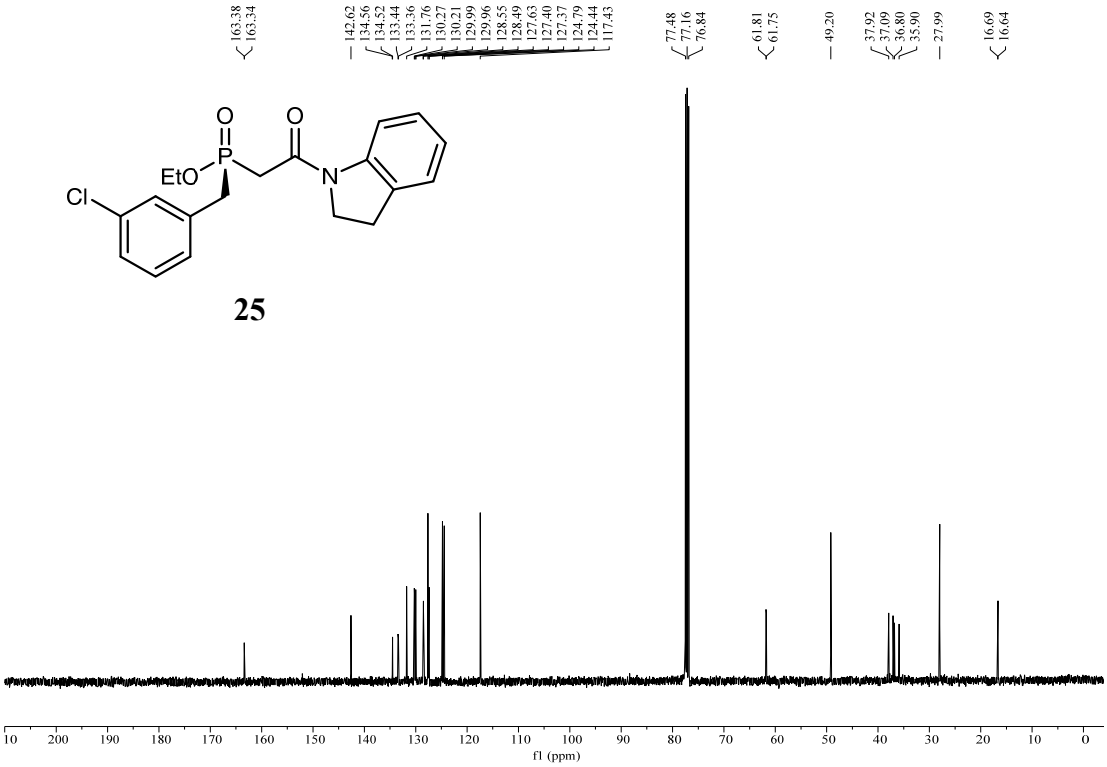
^{31}P NMR of 24 (162 MHz, $CDCl_3$)



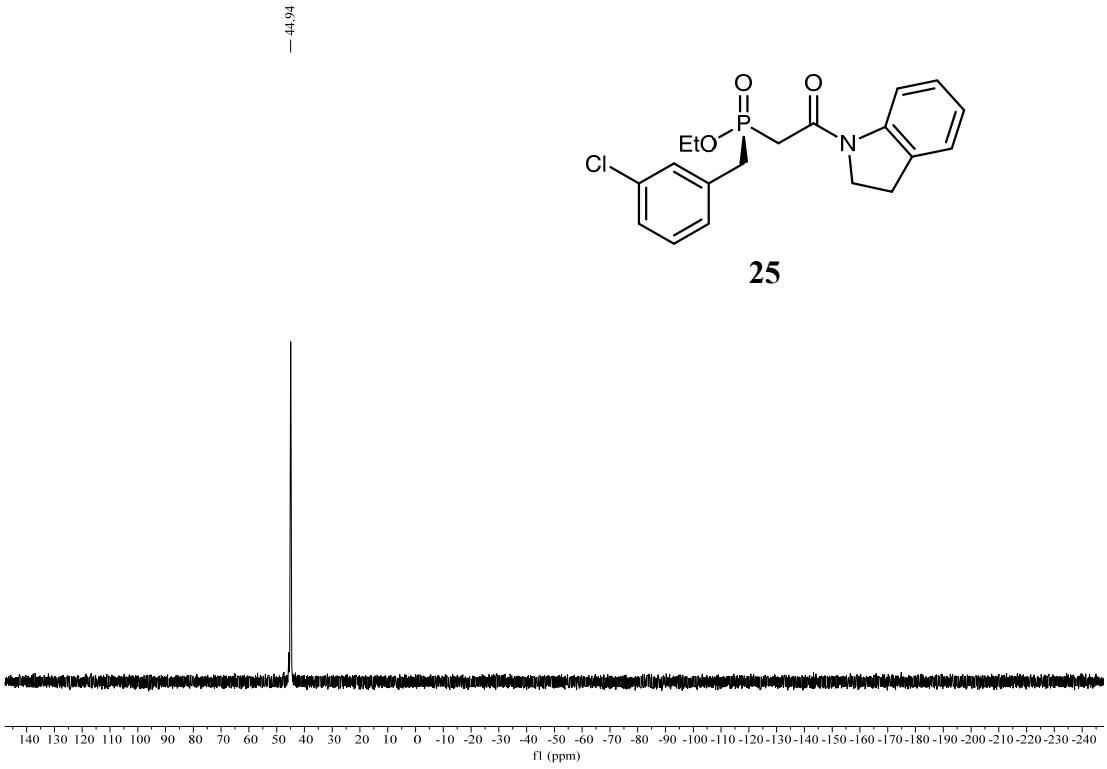
^{1}H NMR of 25 (400 MHz, $CDCl_3$)



^{13}C NMR of 25 (100 MHz, $CDCl_3$)

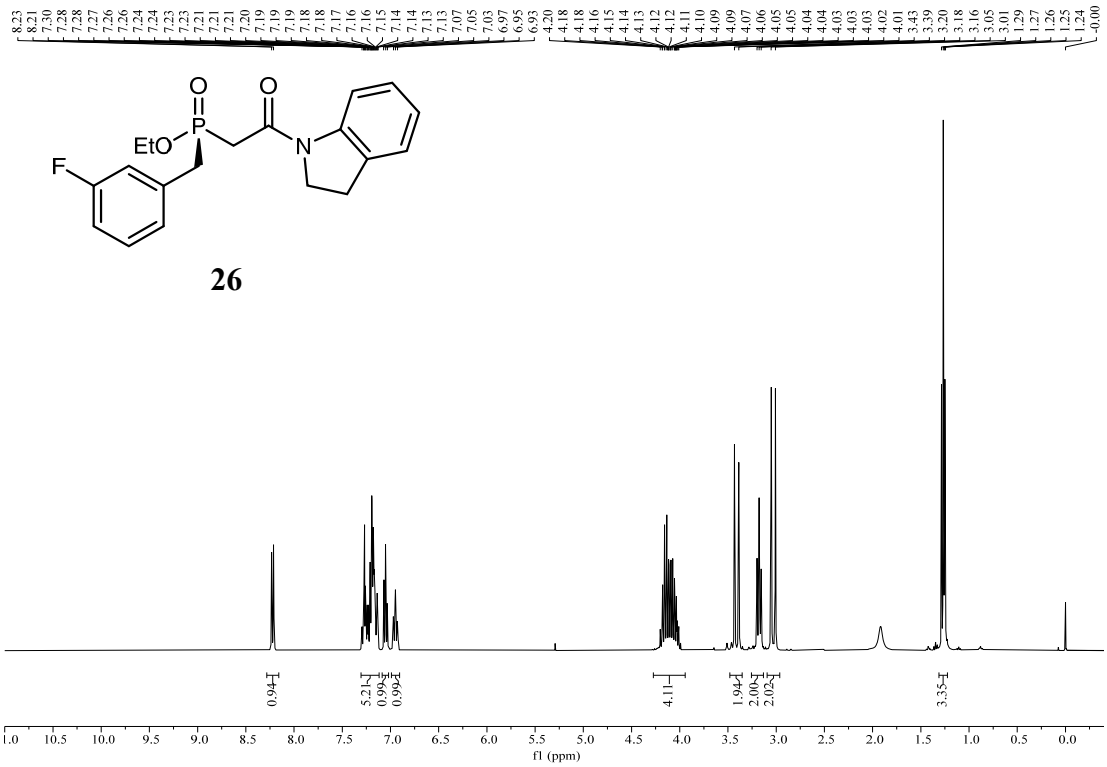


^{31}P NMR of 25 (162 MHz, $CDCl_3$)

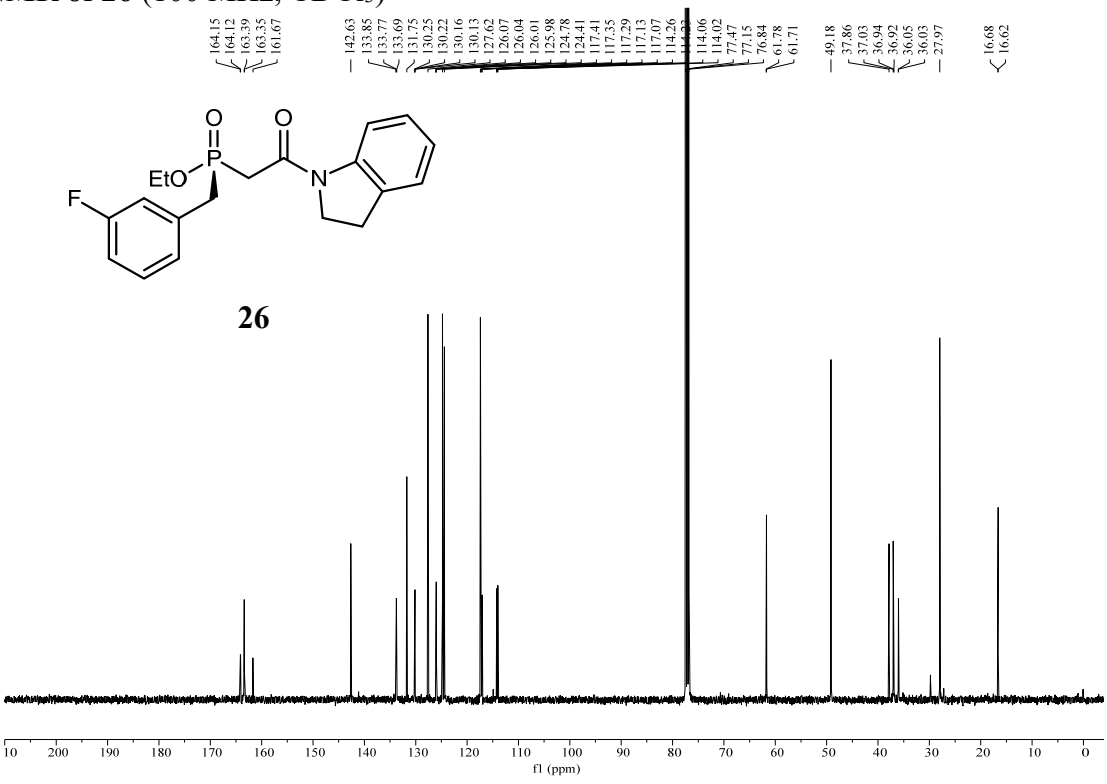


25

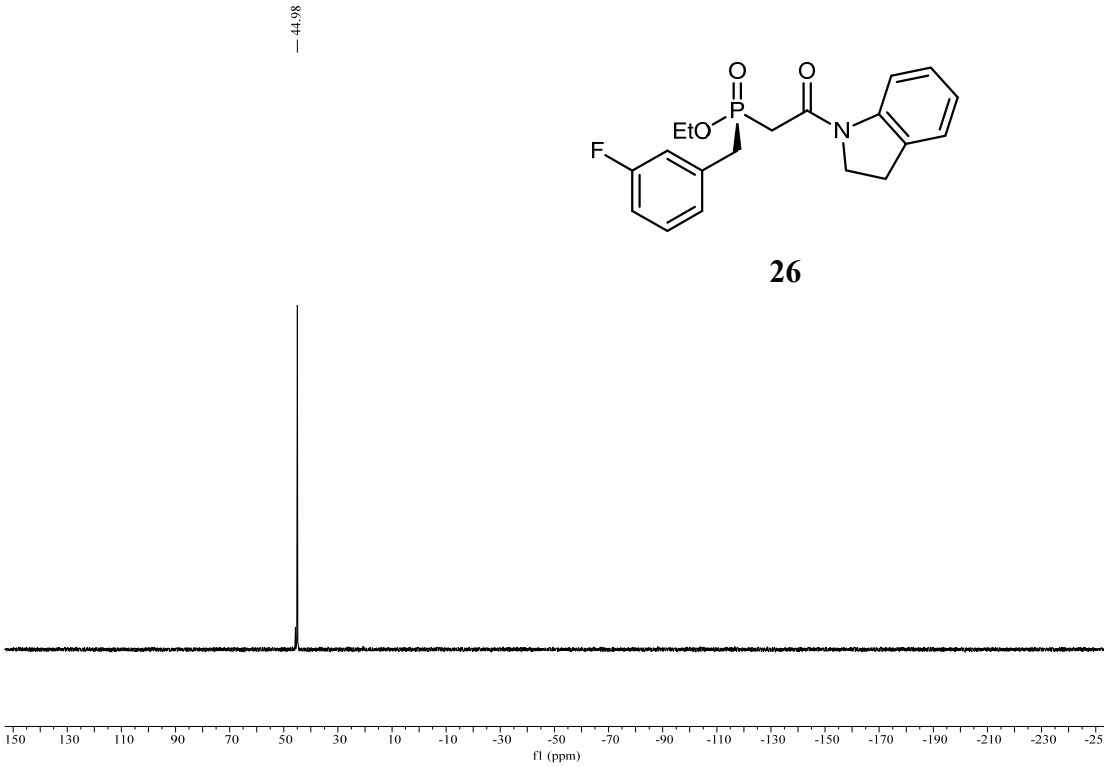
^{1}H NMR of 26 (400 MHz, $CDCl_3$)



^{13}C NMR of 26 (100 MHz, $CDCl_3$)

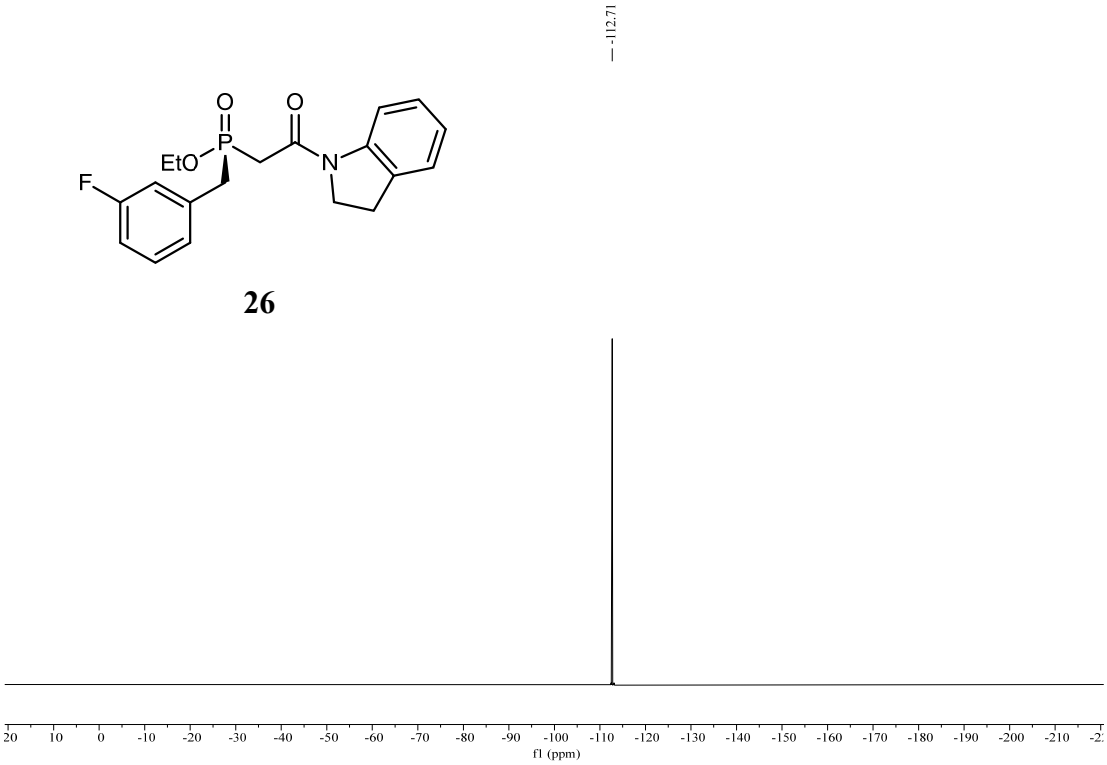


^{31}P NMR of 26 (162 MHz, $CDCl_3$)



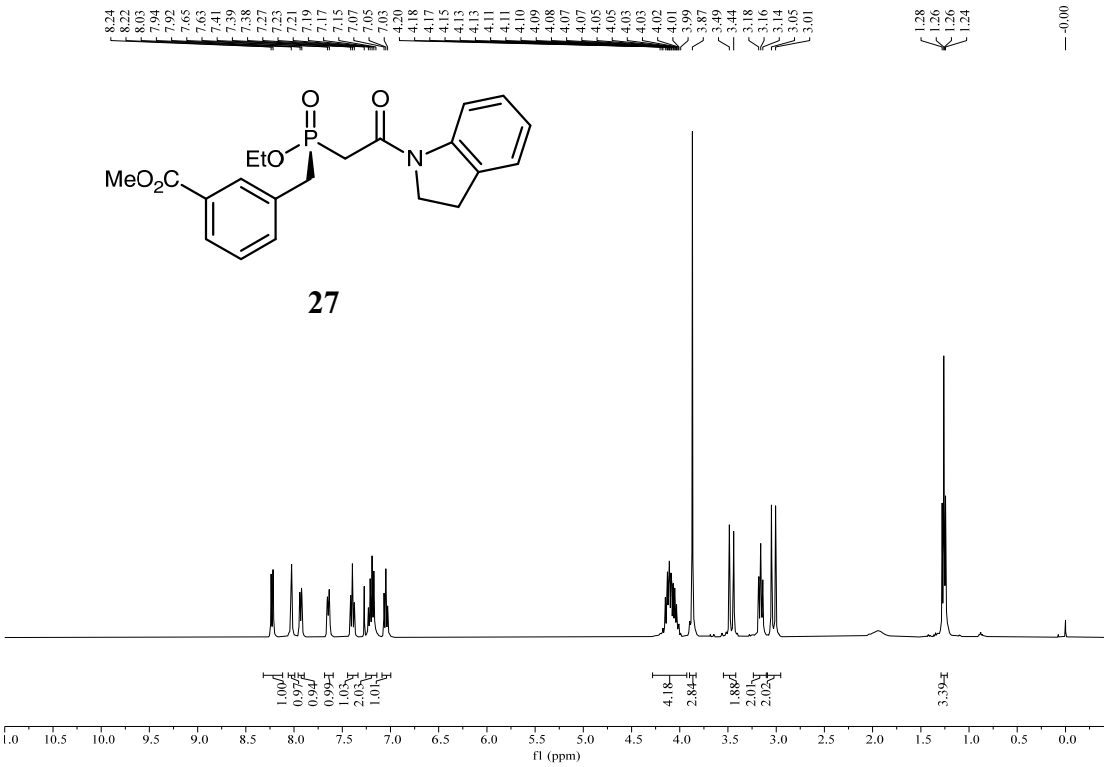
26

^{19}F NMR of 26 (375 MHz, $CDCl_3$)



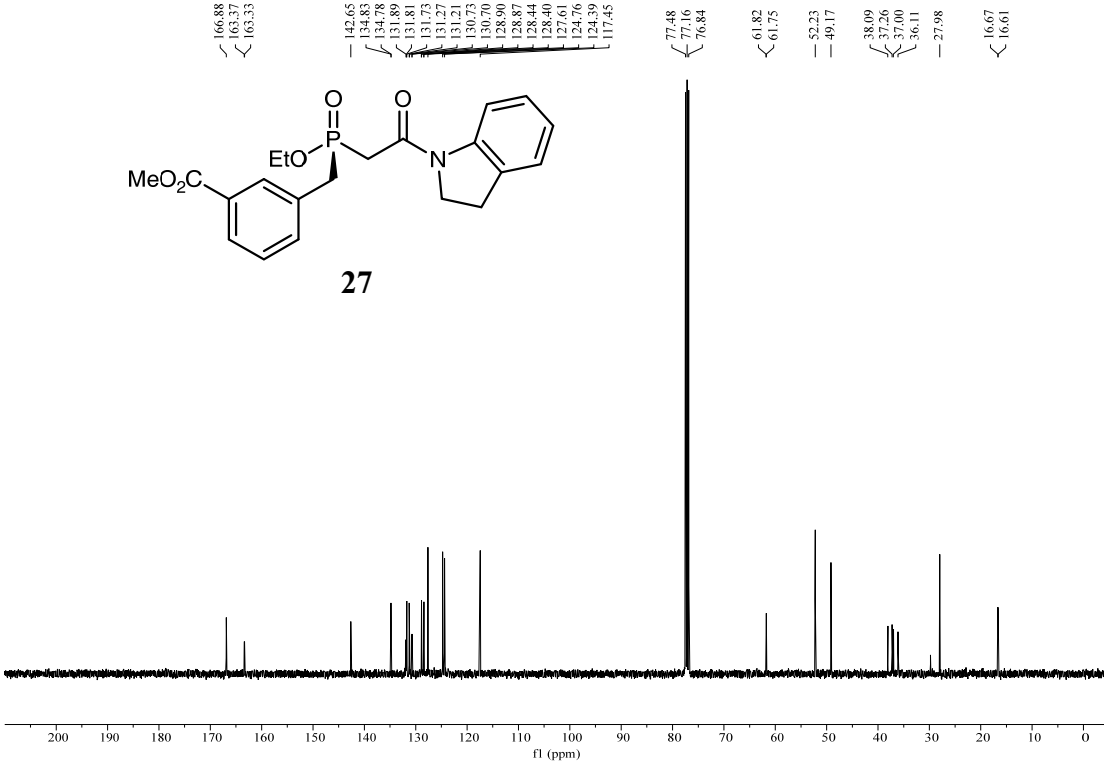
26

^{1}H NMR of 27 (400 MHz, $CDCl_3$)



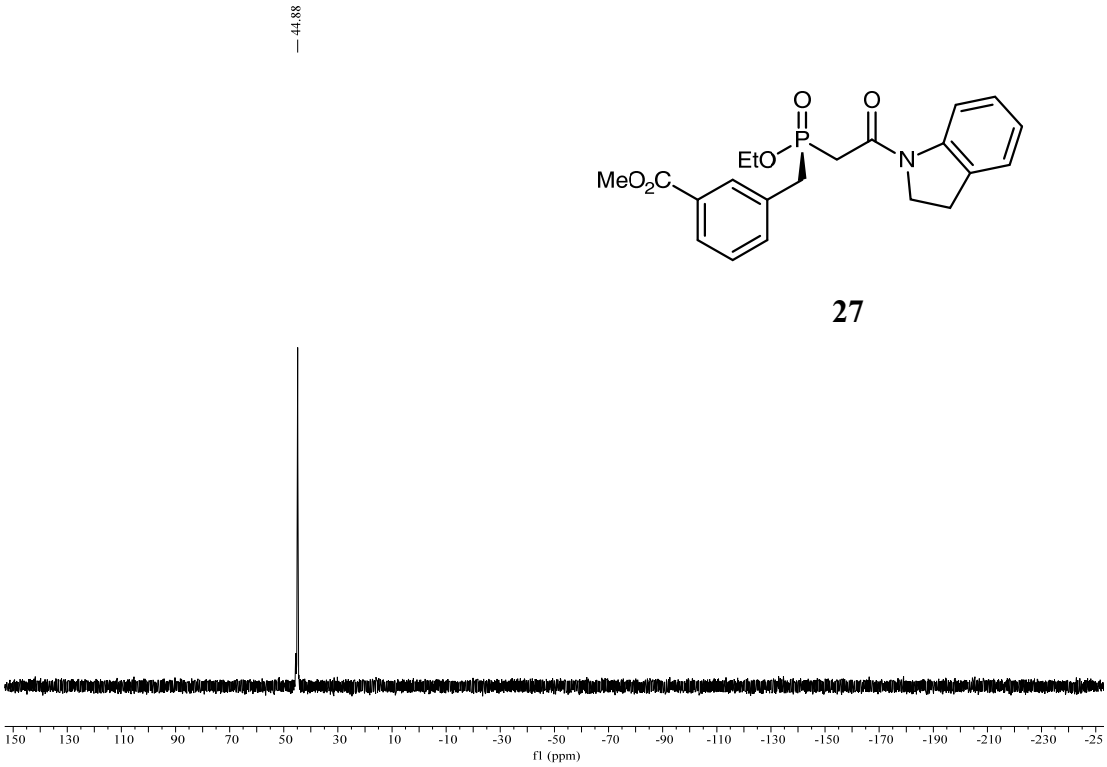
27

^{13}C NMR of 27 (100 MHz, $CDCl_3$)



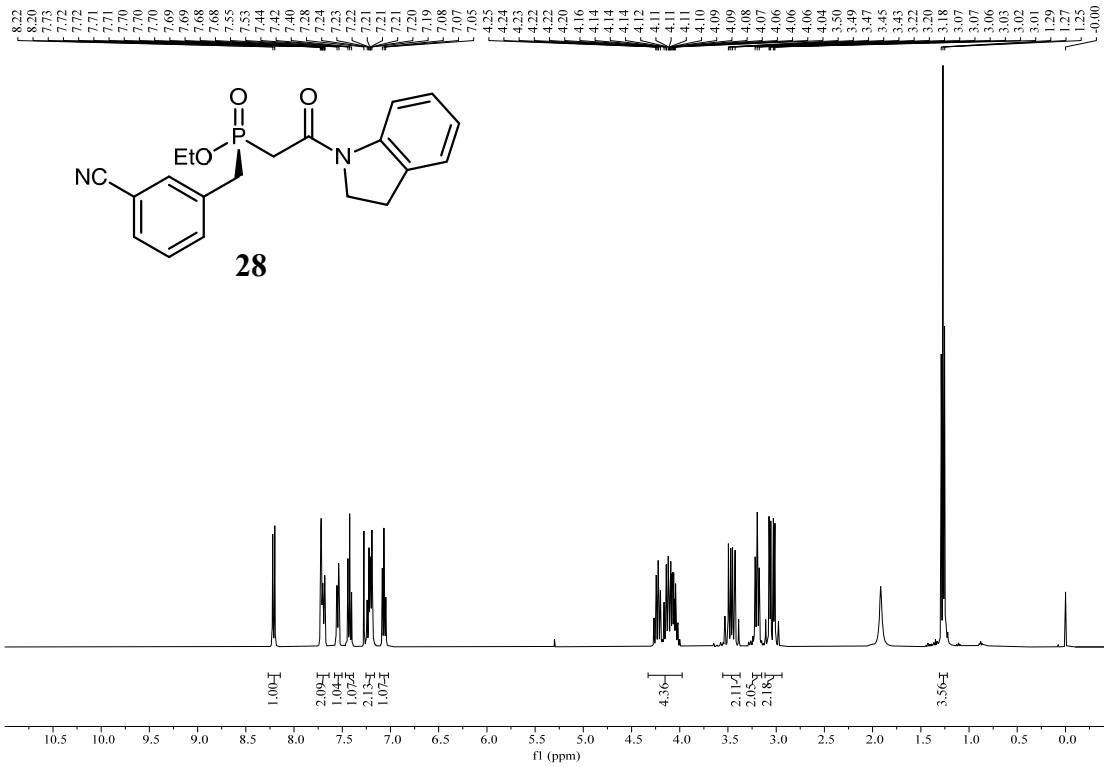
27

^{31}P NMR of 27 (162 MHz, $CDCl_3$)

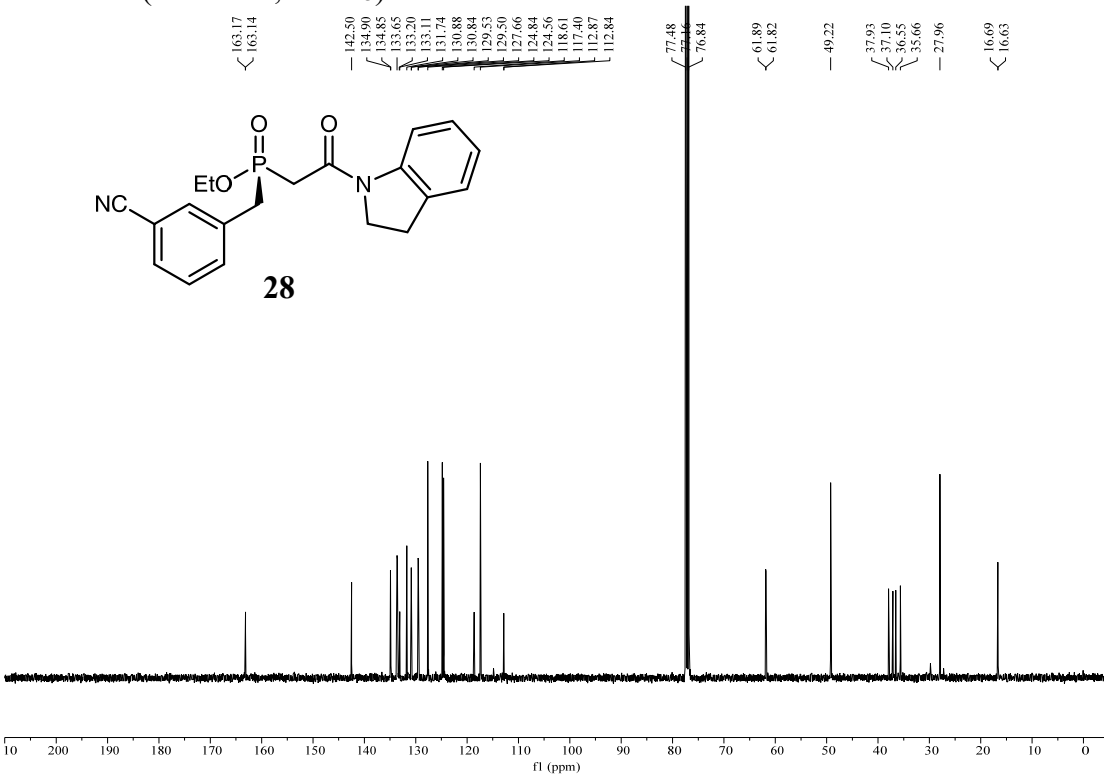


27

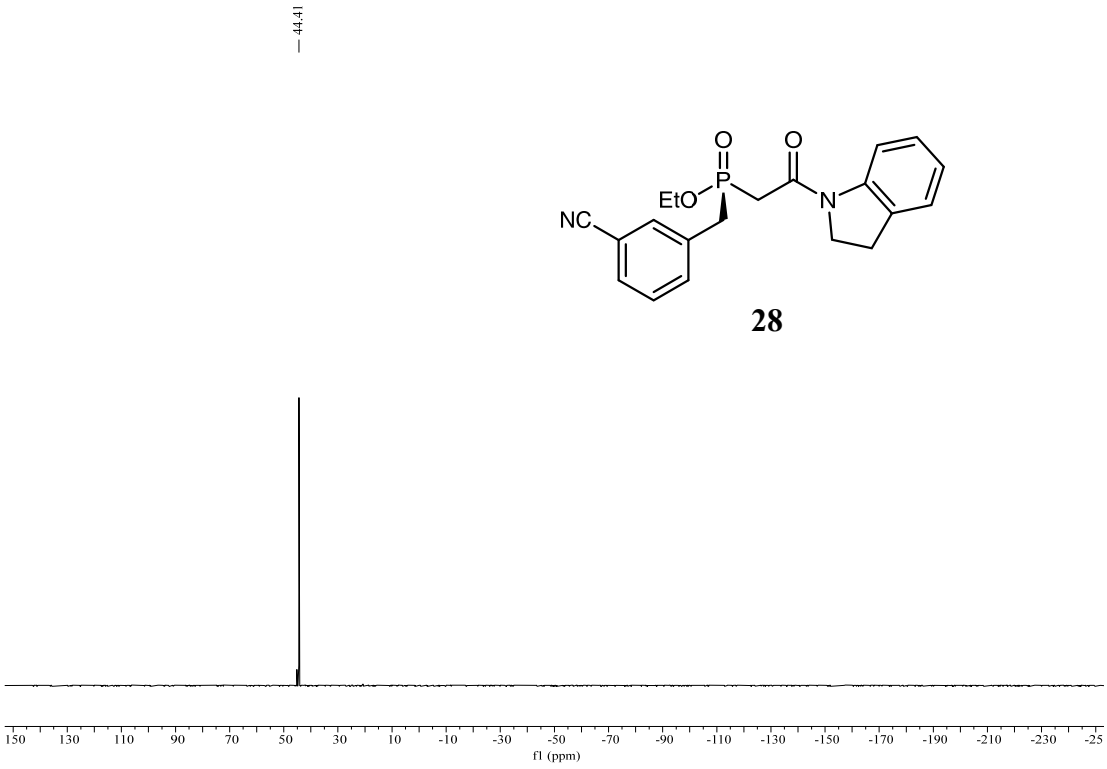
^{1}H NMR of 28 (400 MHz, $CDCl_3$)



^{13}C NMR of 28 (100 MHz, $CDCl_3$)

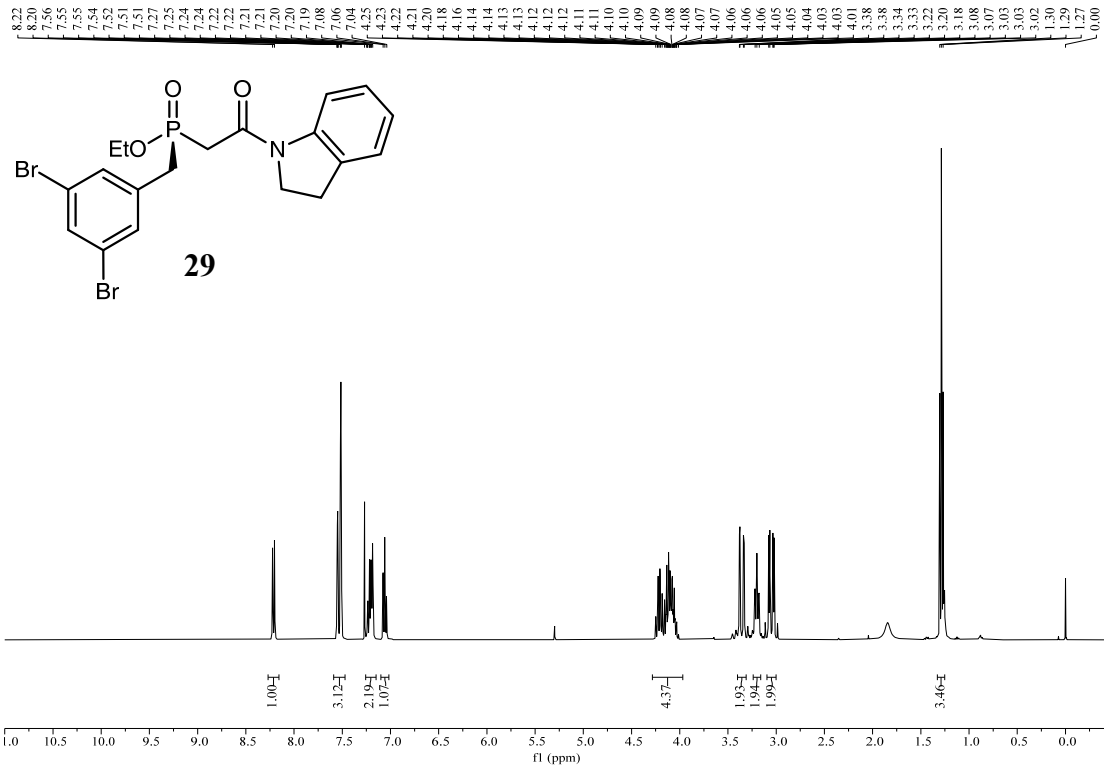


^{31}P NMR of 28 (162 MHz, $CDCl_3$)

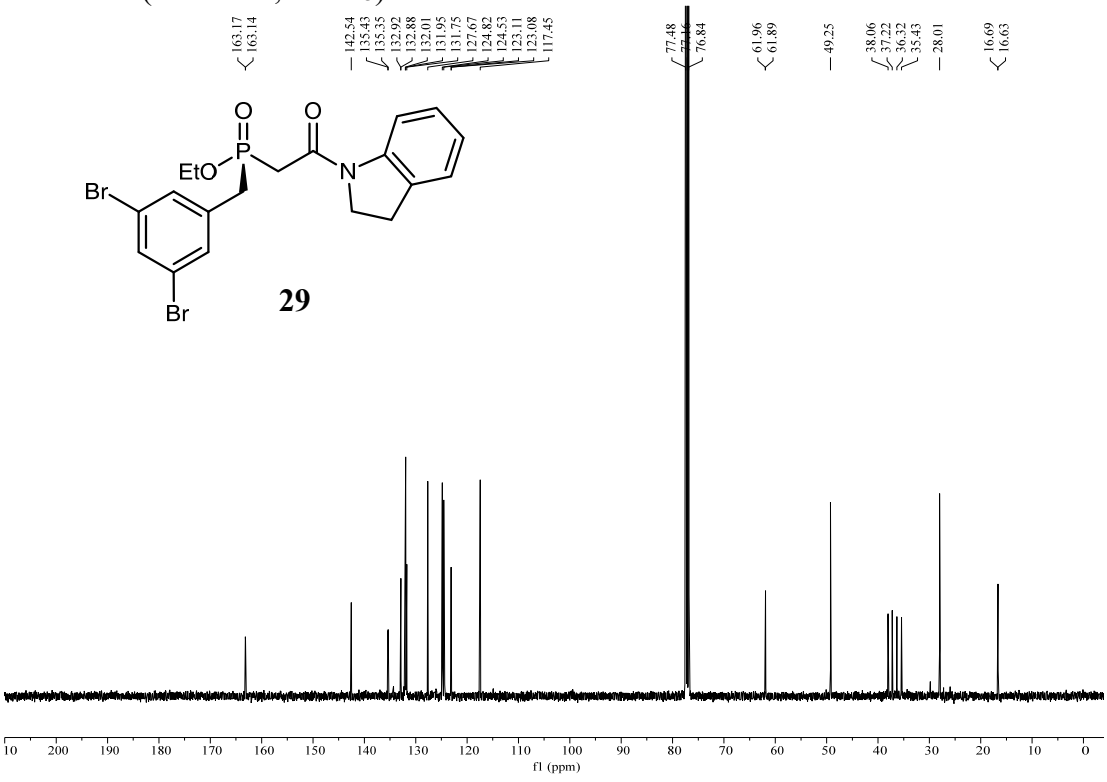


28

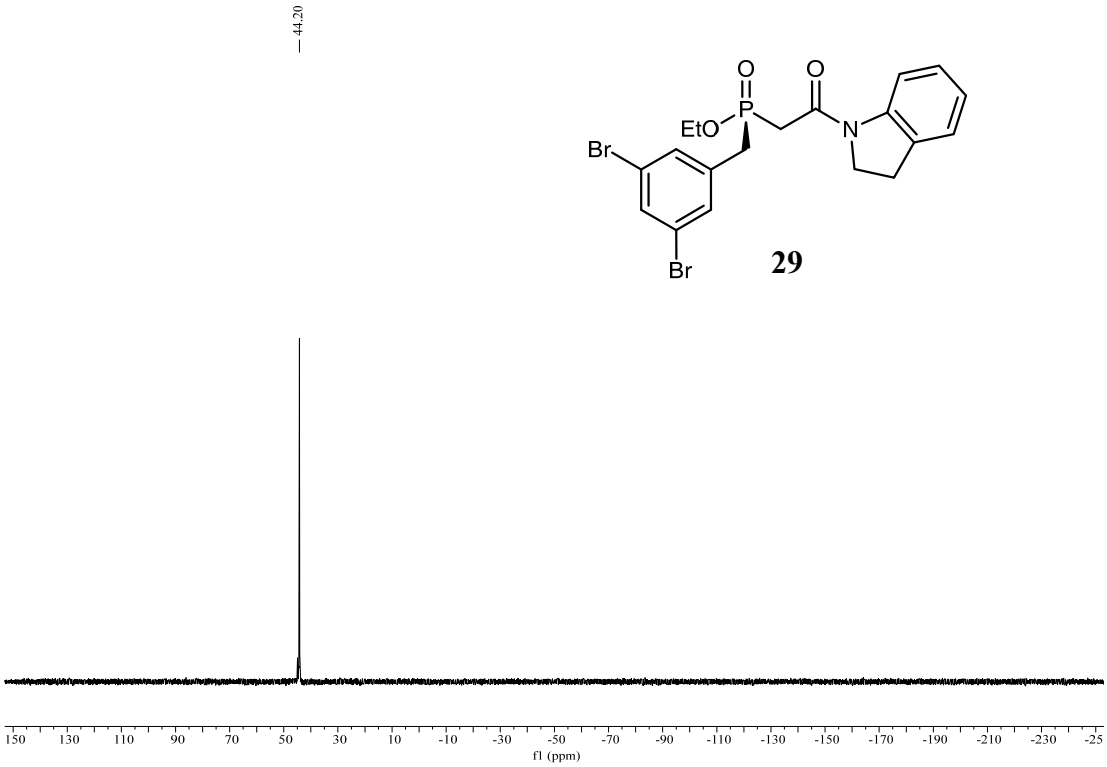
^{1}H NMR of 29 (400 MHz, $CDCl_3$)



^{13}C NMR of 29 (100 MHz, $CDCl_3$)

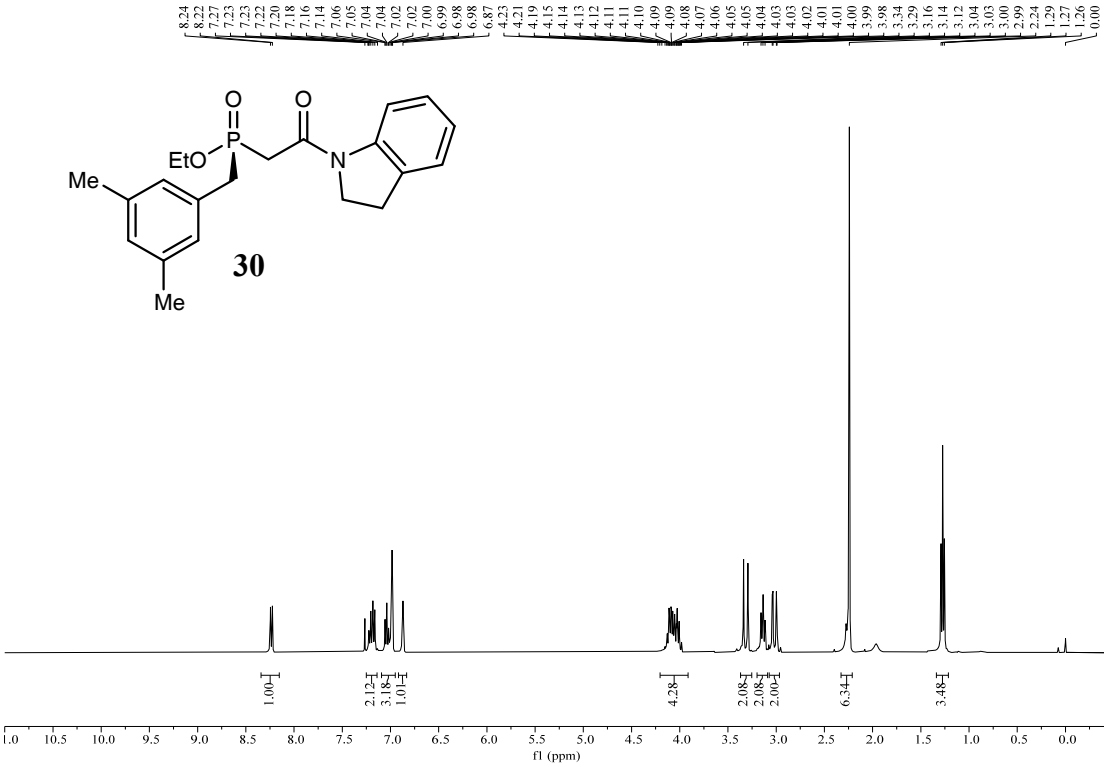


^{31}P NMR of 29 (162 MHz, $CDCl_3$)

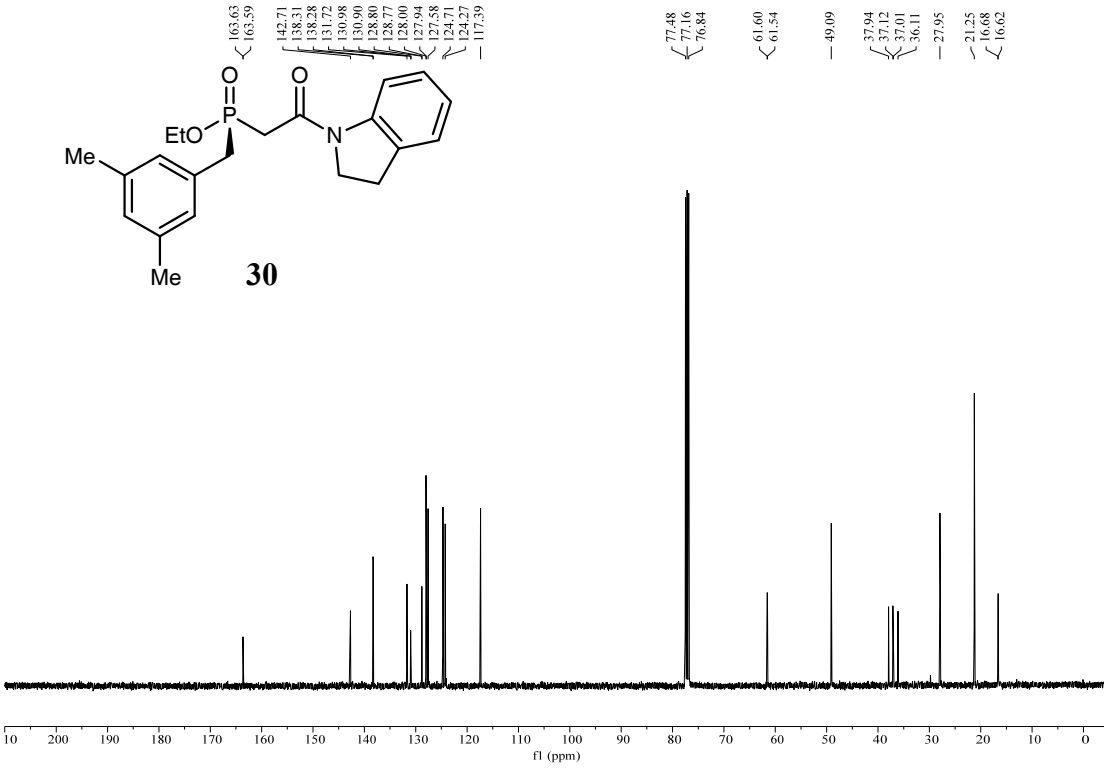


29

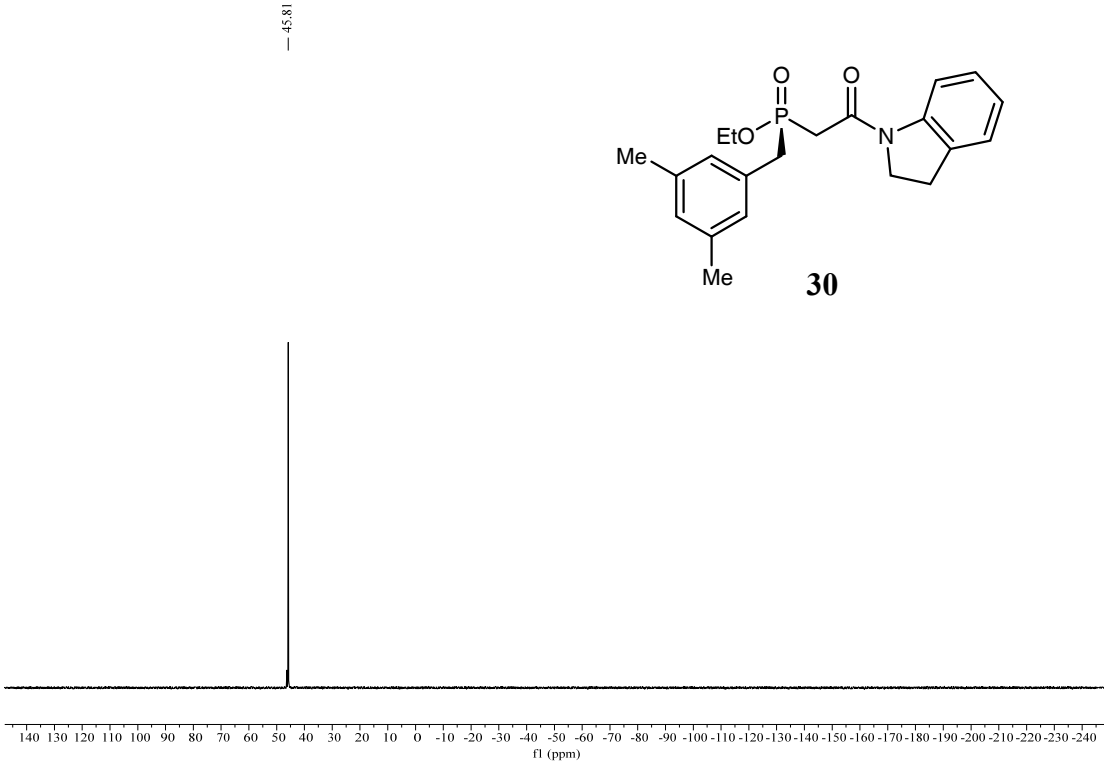
^{1}H NMR of 30 (400 MHz, $CDCl_3$)



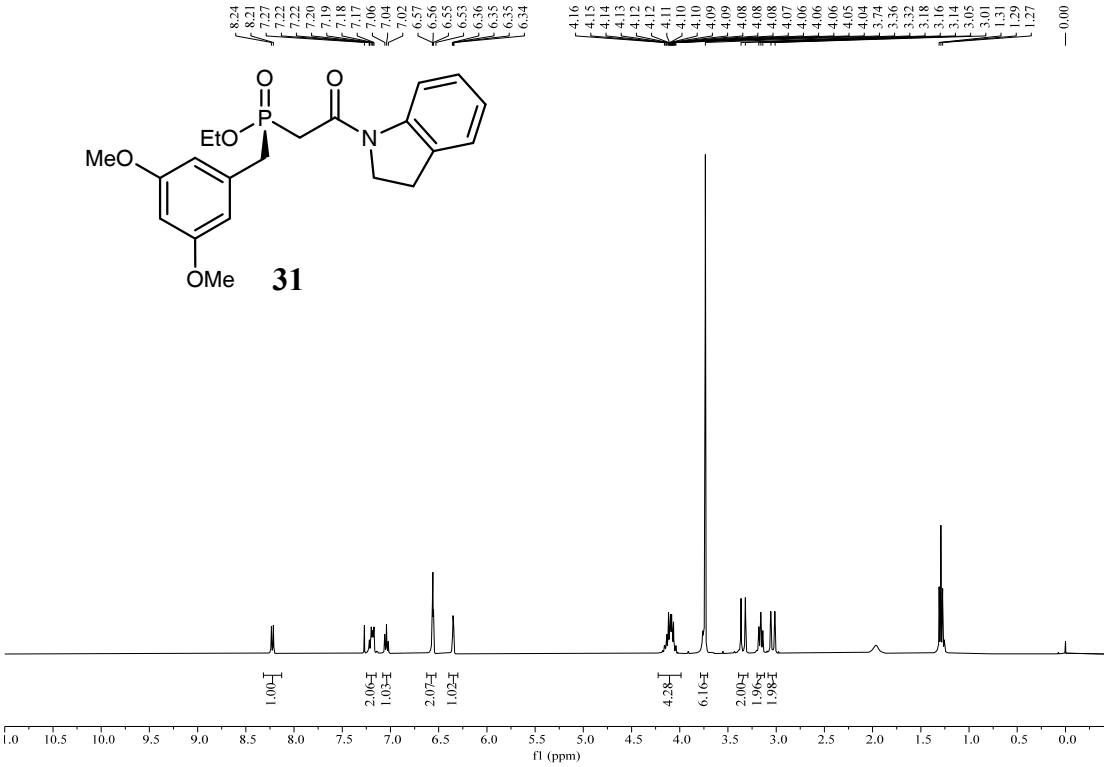
^{13}C NMR of 30 (100 MHz, $CDCl_3$)



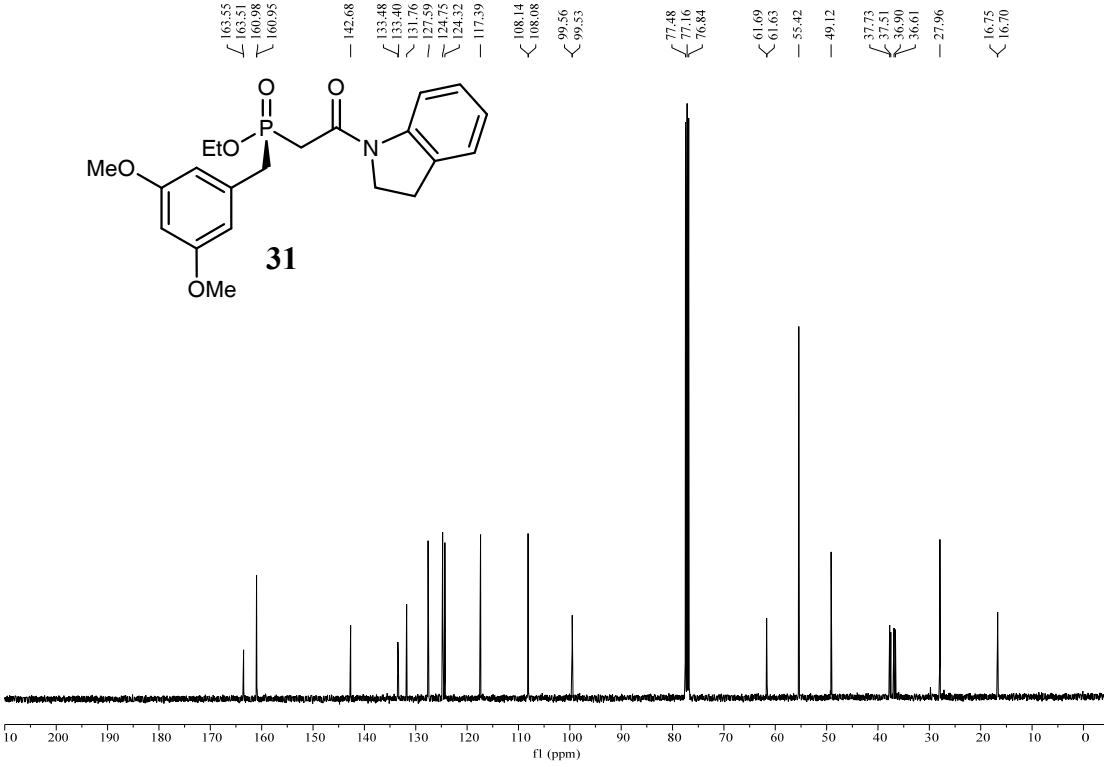
^{31}P NMR of 30 (162 MHz, $CDCl_3$)



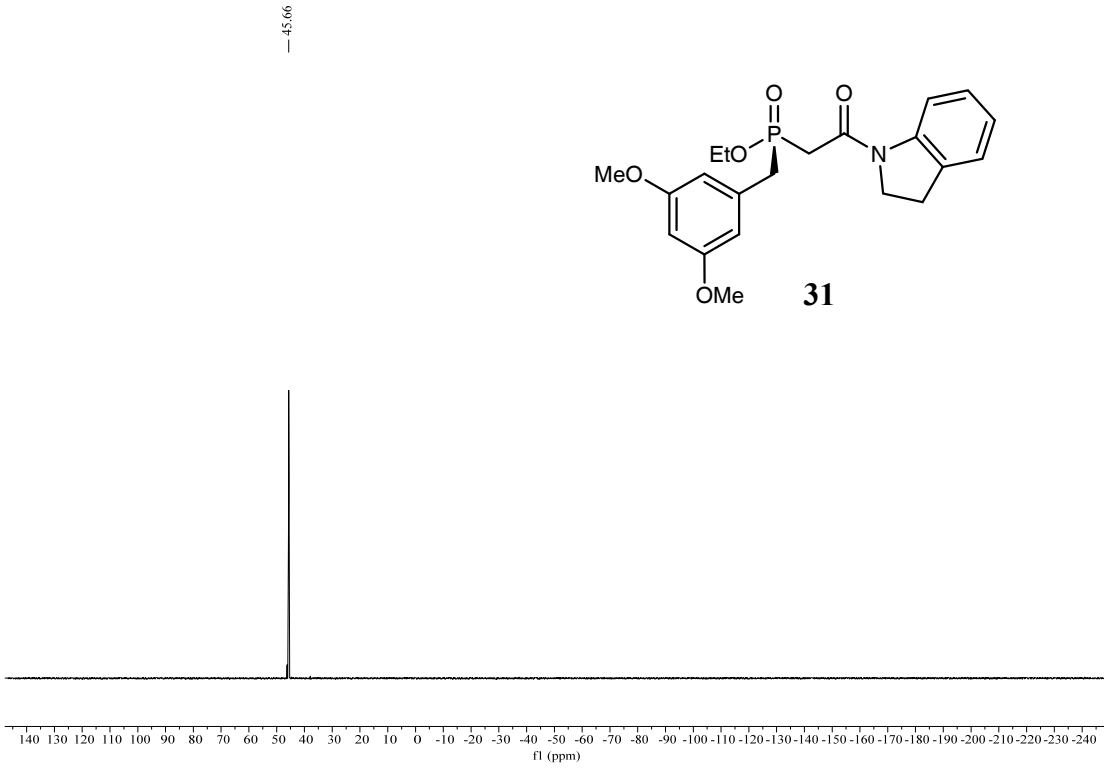
^{1}H NMR of 31 (400 MHz, $CDCl_3$)



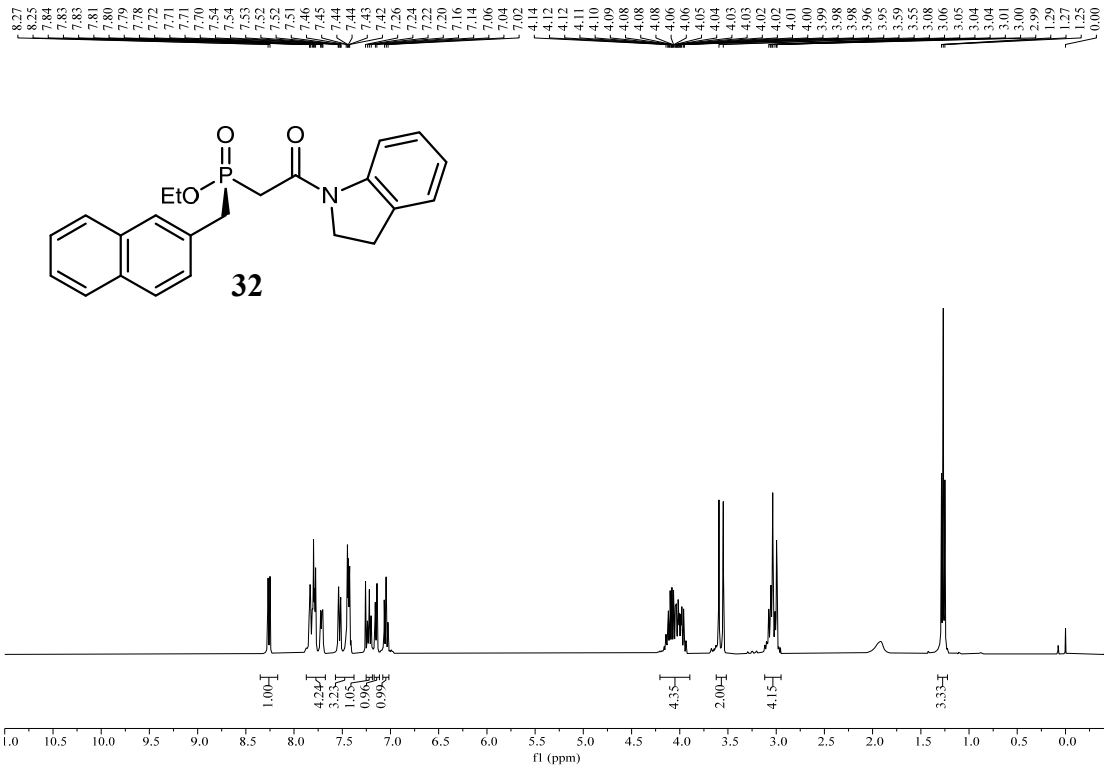
^{13}C NMR of 31 (100 MHz, $CDCl_3$)



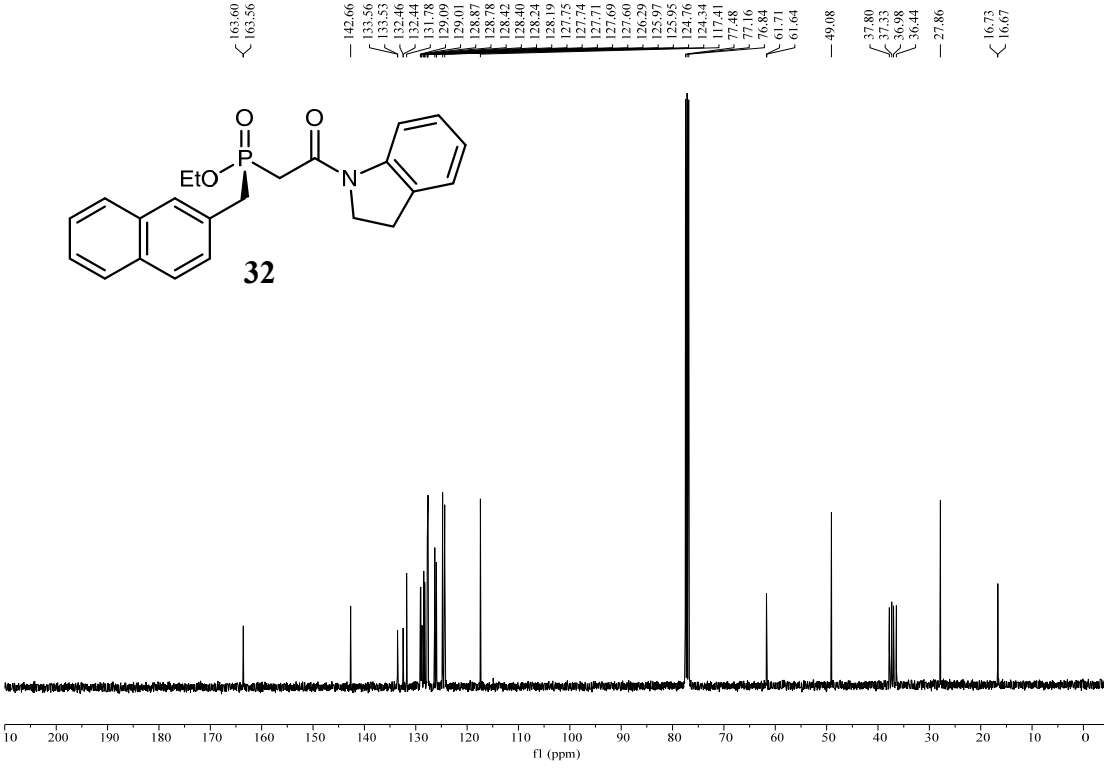
^{31}P NMR of 31 (162 MHz, $CDCl_3$)



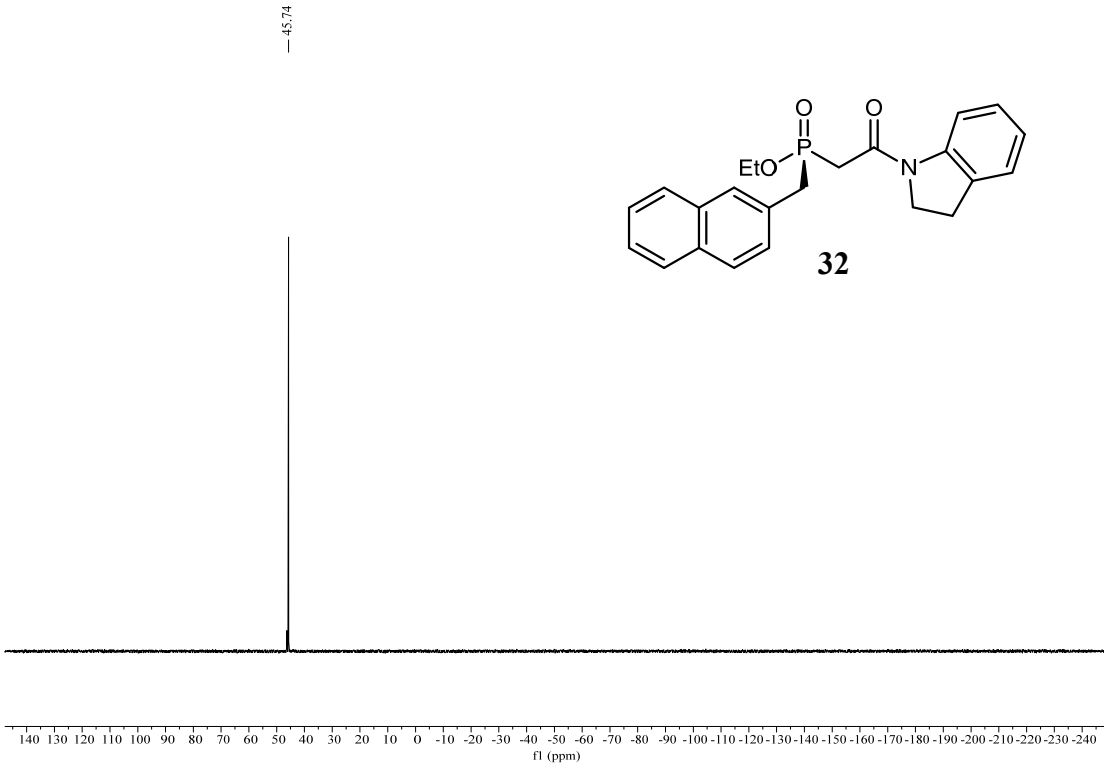
^{1}H NMR of 32 (400 MHz, $CDCl_3$)



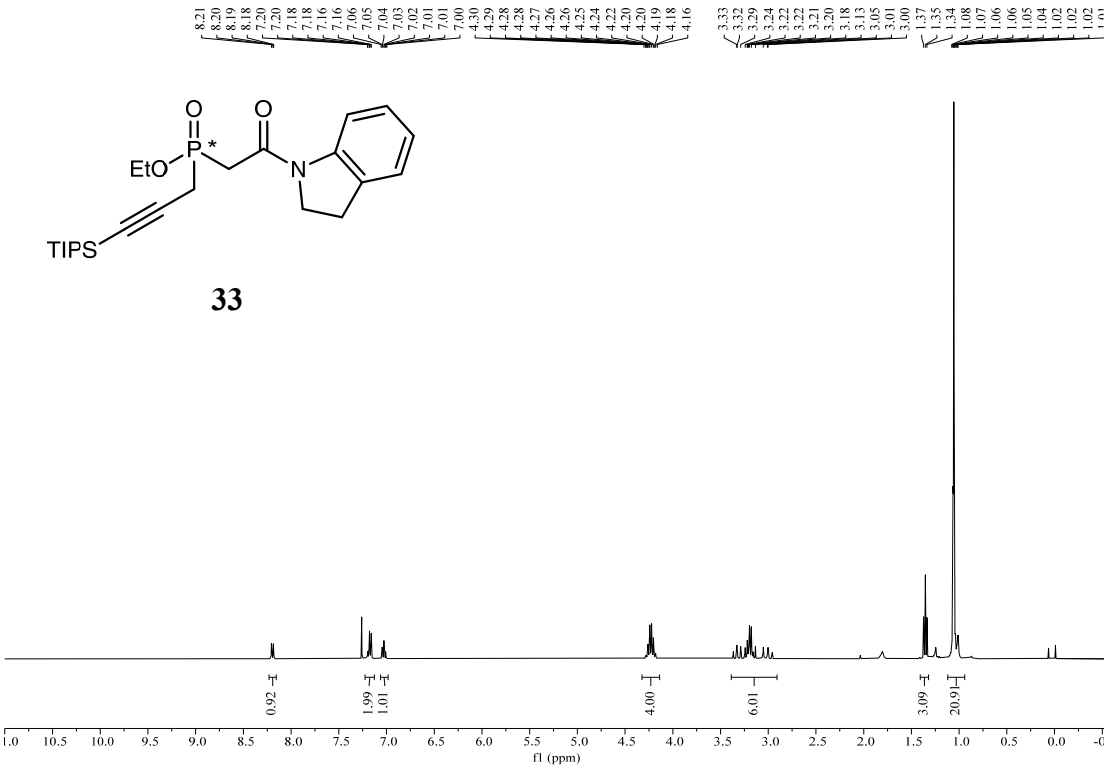
^{13}C NMR of 32 (100 MHz, $CDCl_3$)



^{31}P NMR of 32 (162 MHz, $CDCl_3$)

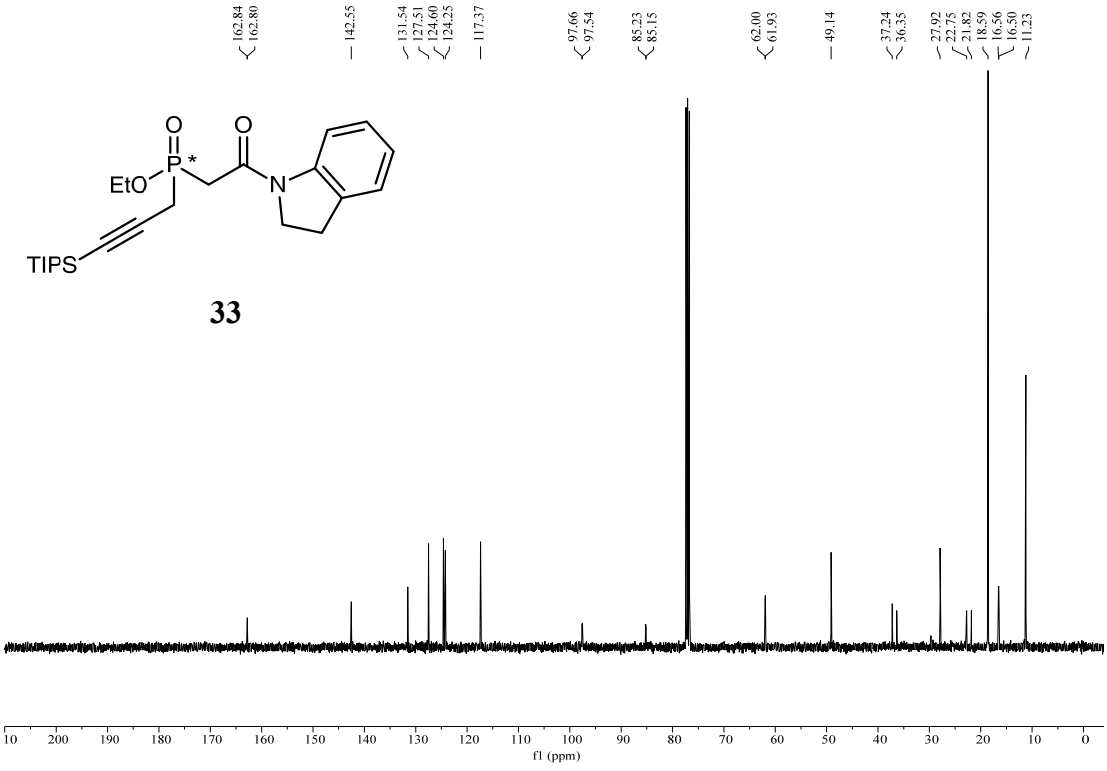


^{1}H NMR of 33 (400 MHz, $CDCl_3$)



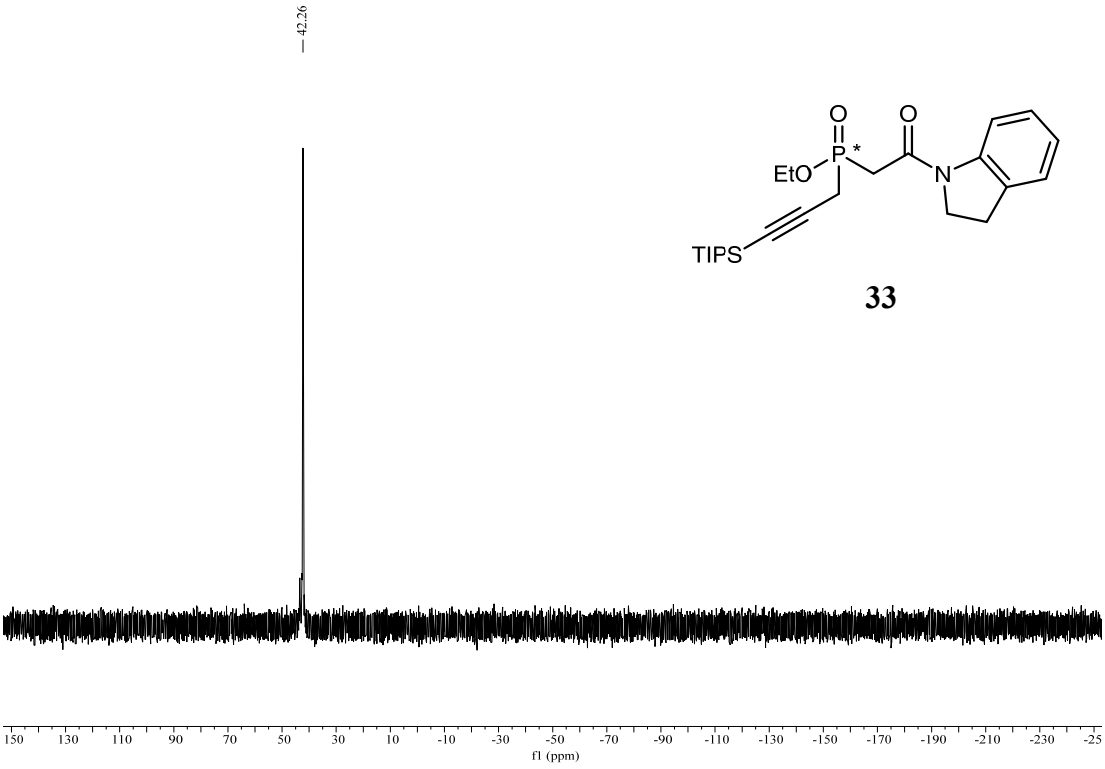
33

^{13}C NMR of 33 (100 MHz, $CDCl_3$)



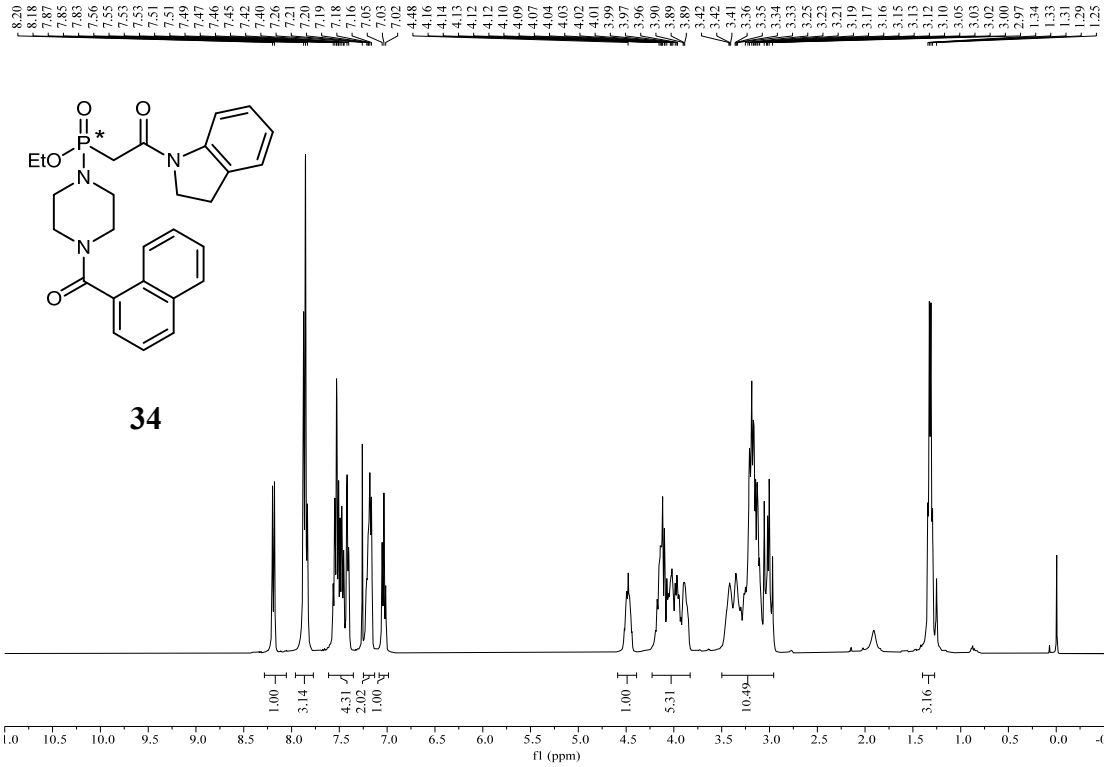
33

^{31}P NMR of 33 (162 MHz, $CDCl_3$)

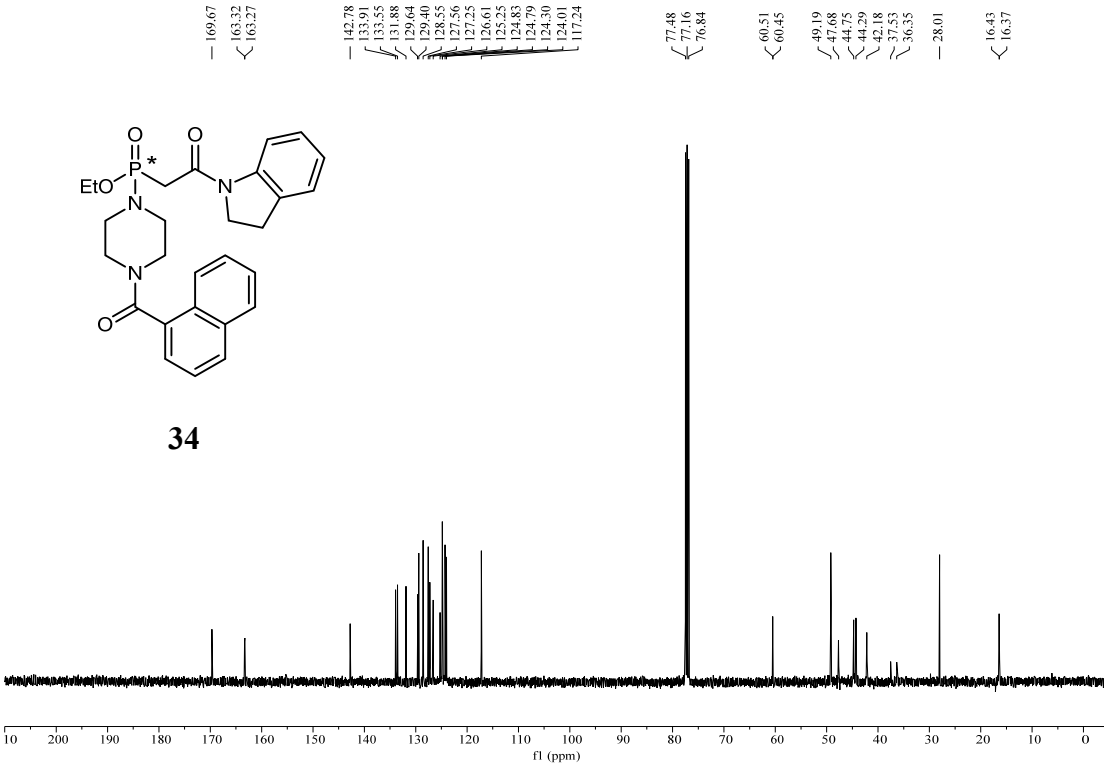


33

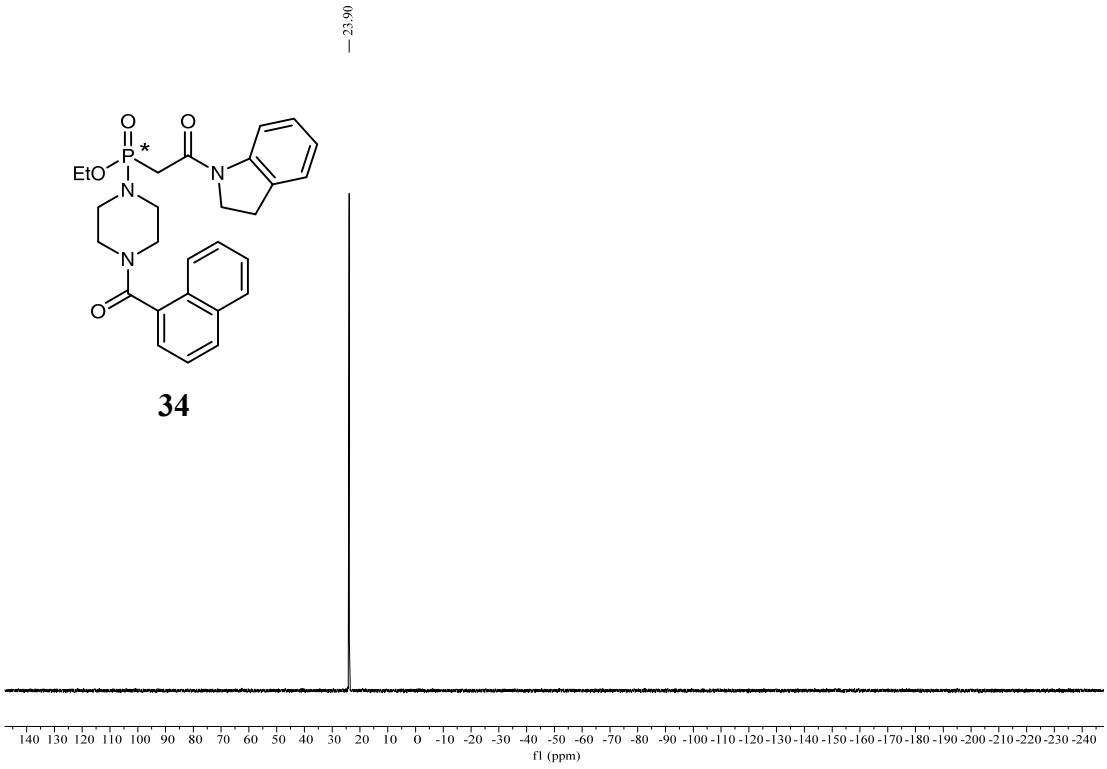
^{1}H NMR of 34 (400 MHz, $CDCl_3$)



^{13}C NMR of 34 (100 MHz, $CDCl_3$)

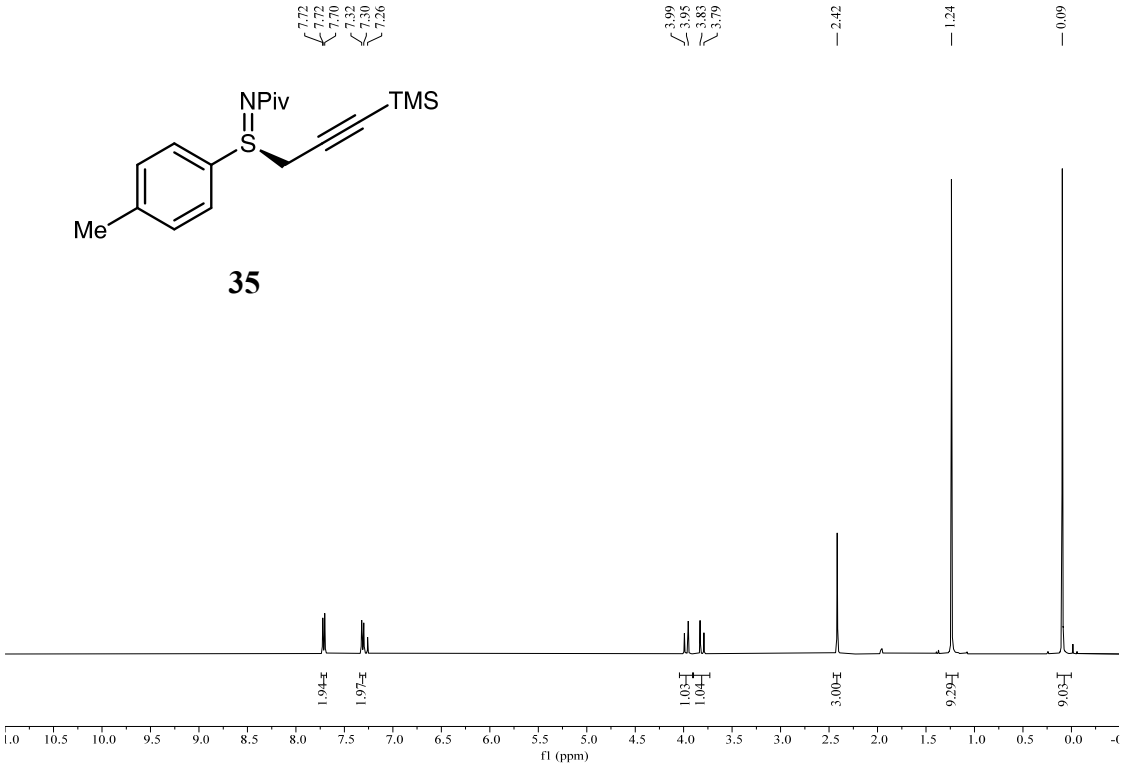


^{31}P NMR of 34 (162 MHz, $CDCl_3$)

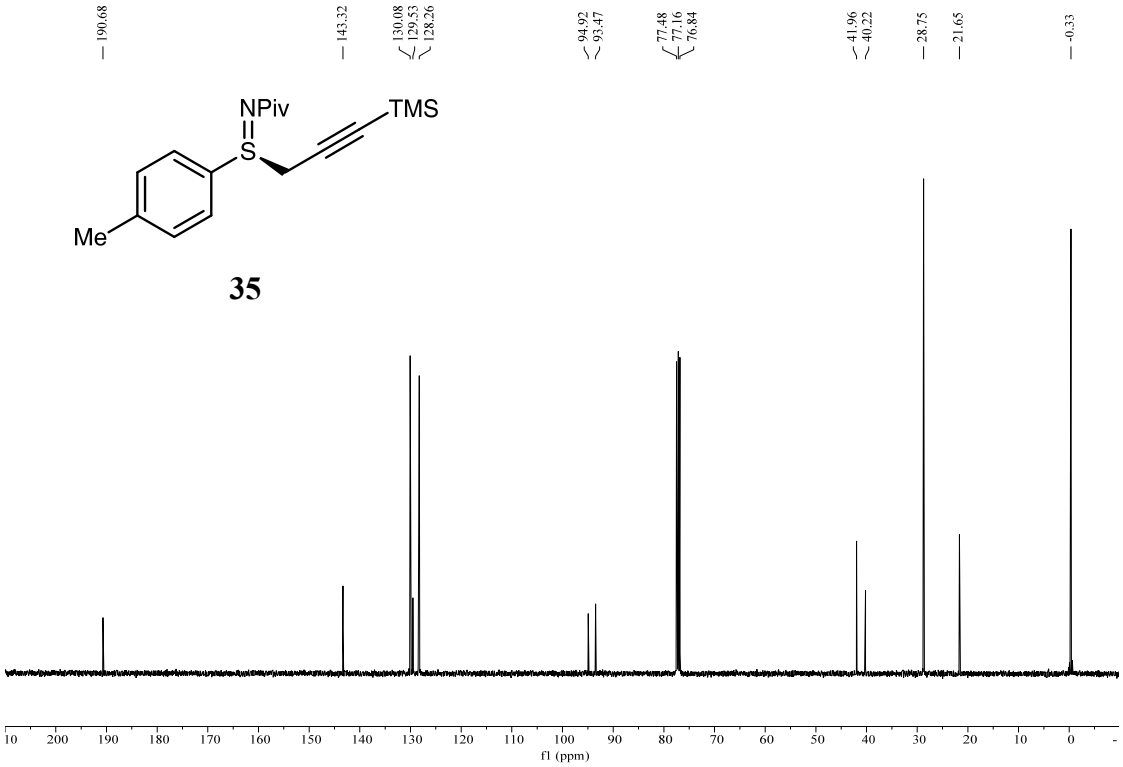


34

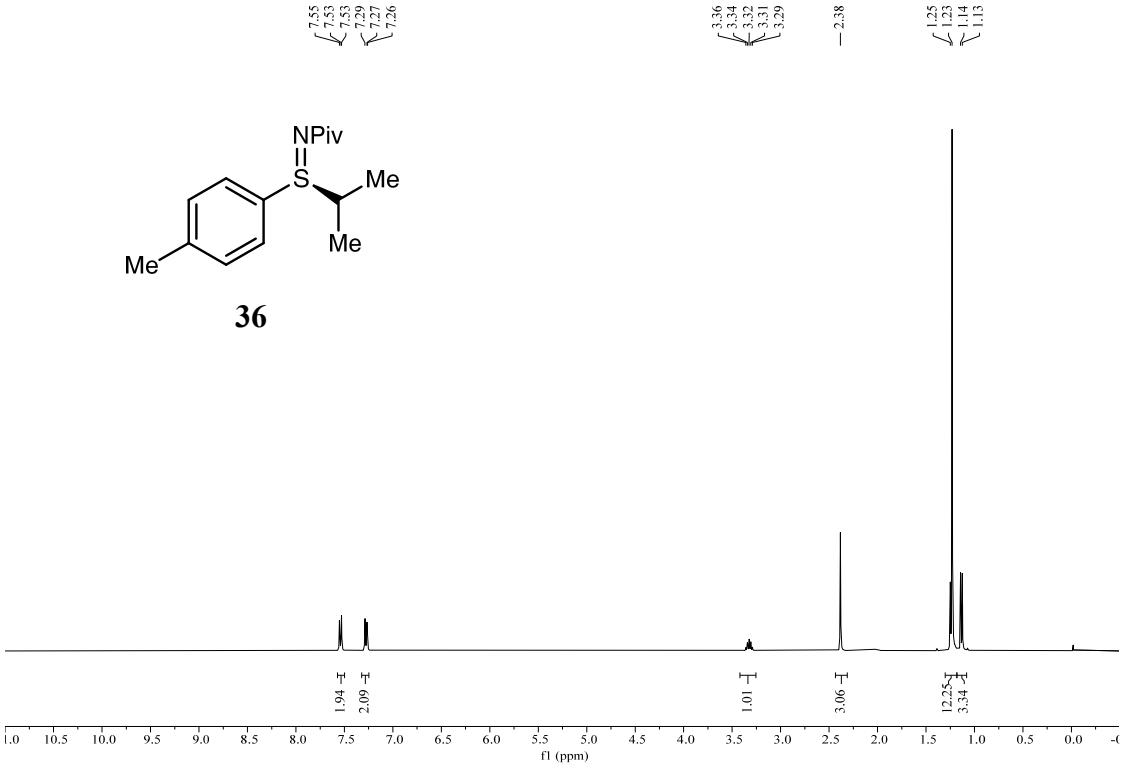
^{1}H NMR of 35 (400 MHz, $CDCl_3$)



^{13}C NMR of 35 (100 MHz, $CDCl_3$)

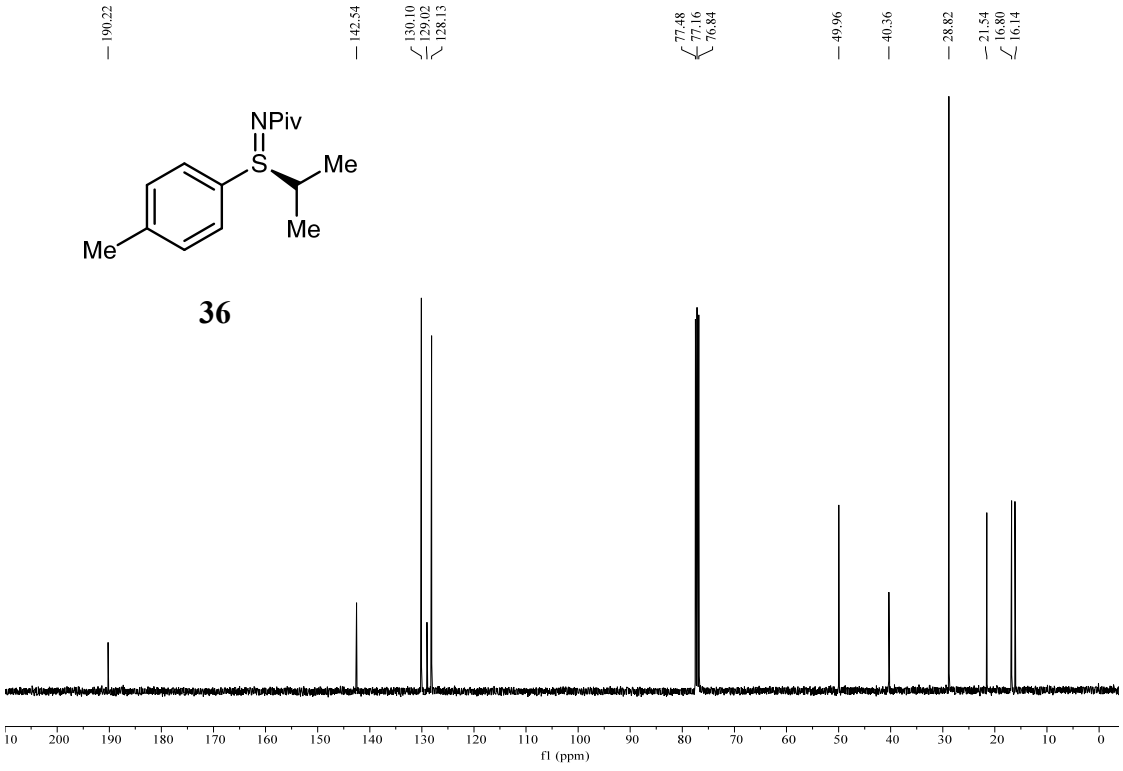


^{1}H NMR of 36 (400 MHz, $CDCl_3$)



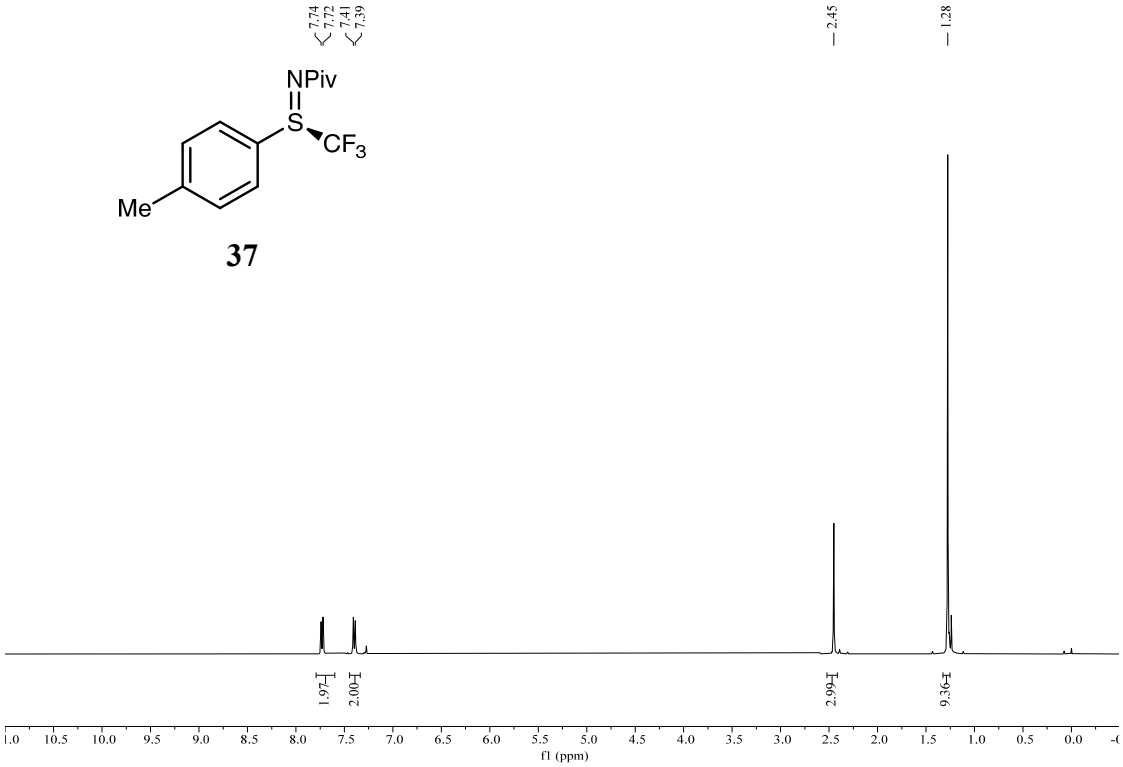
36

^{13}C NMR of 36 (100 MHz, $CDCl_3$)



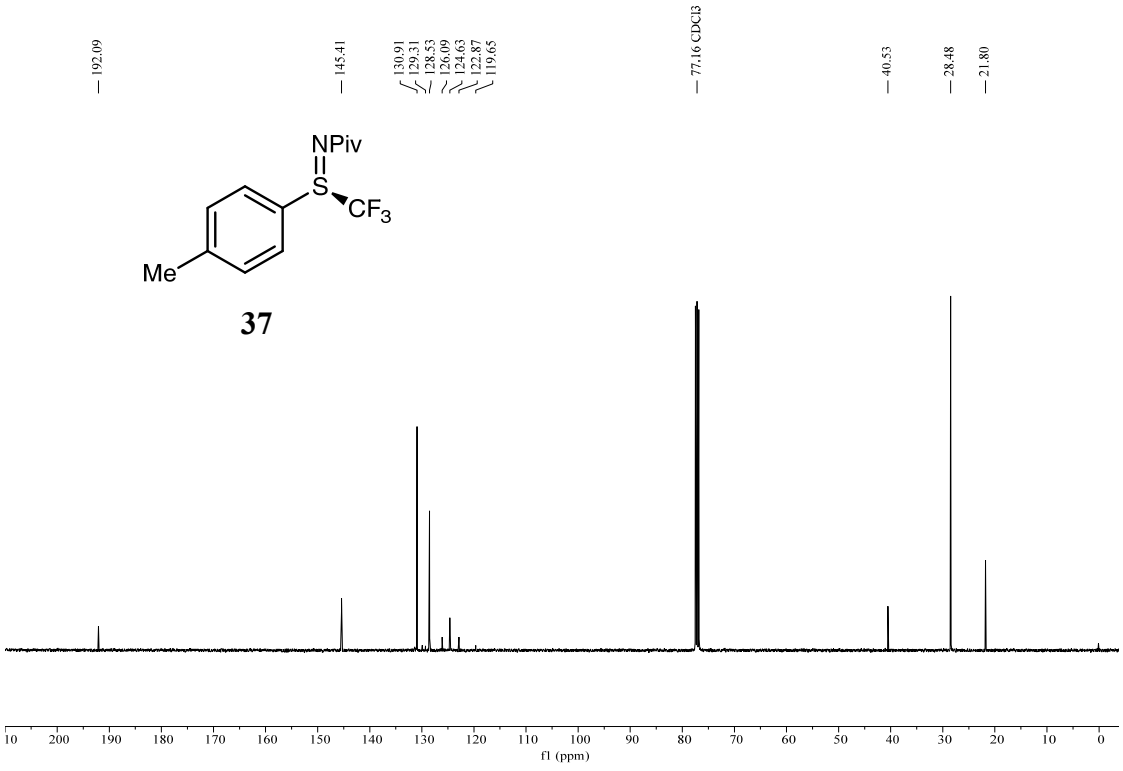
36

^{1}H NMR of 37 (400 MHz, $CDCl_3$)



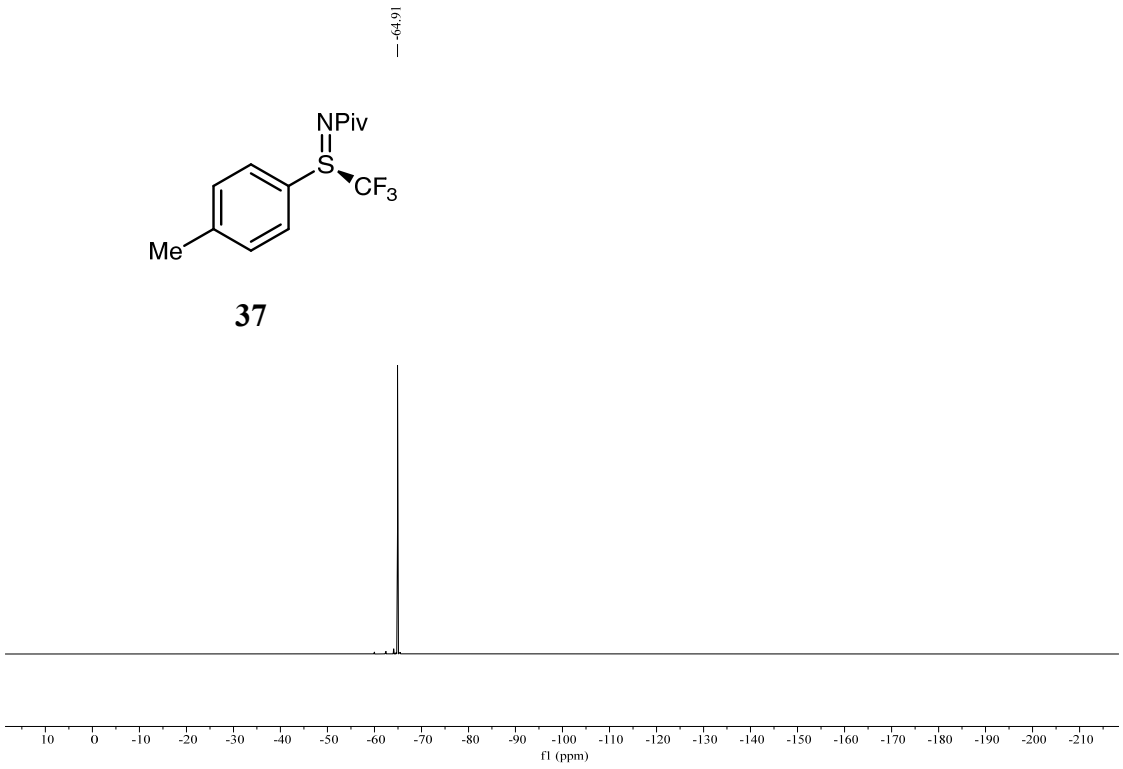
37

^{13}C NMR of 37 (100 MHz, $CDCl_3$)



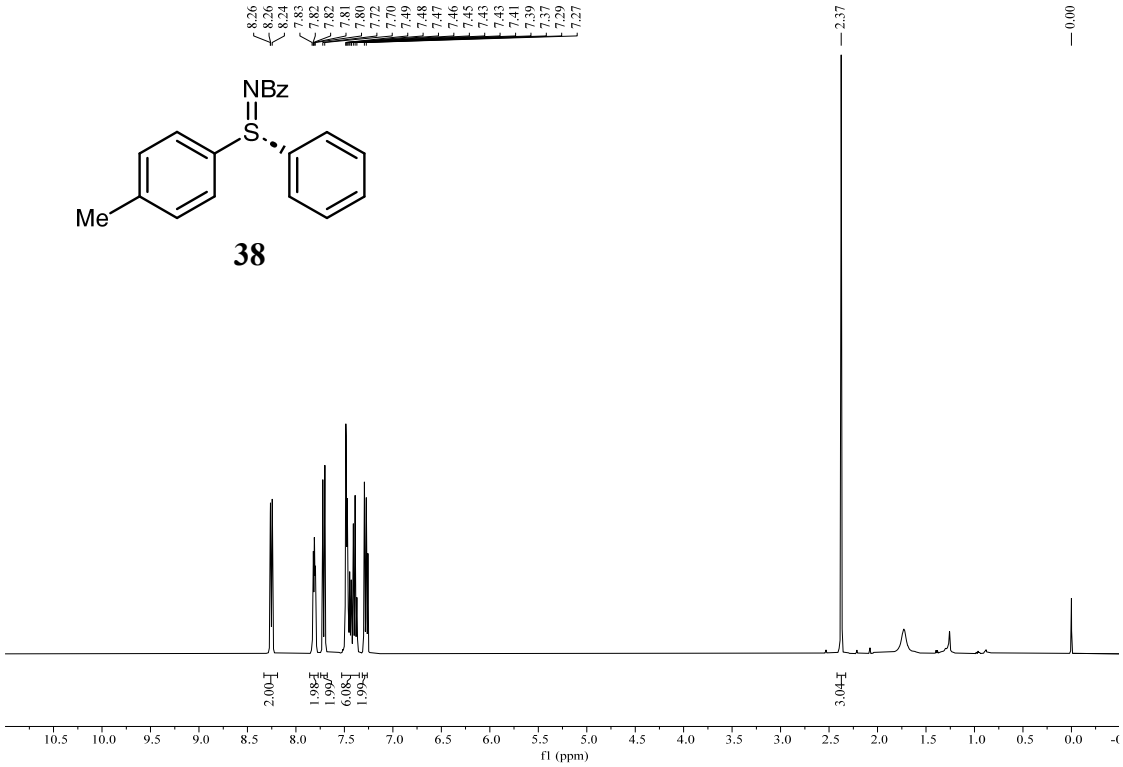
37

^{19}F NMR of 37 (375 MHz, $CDCl_3$)

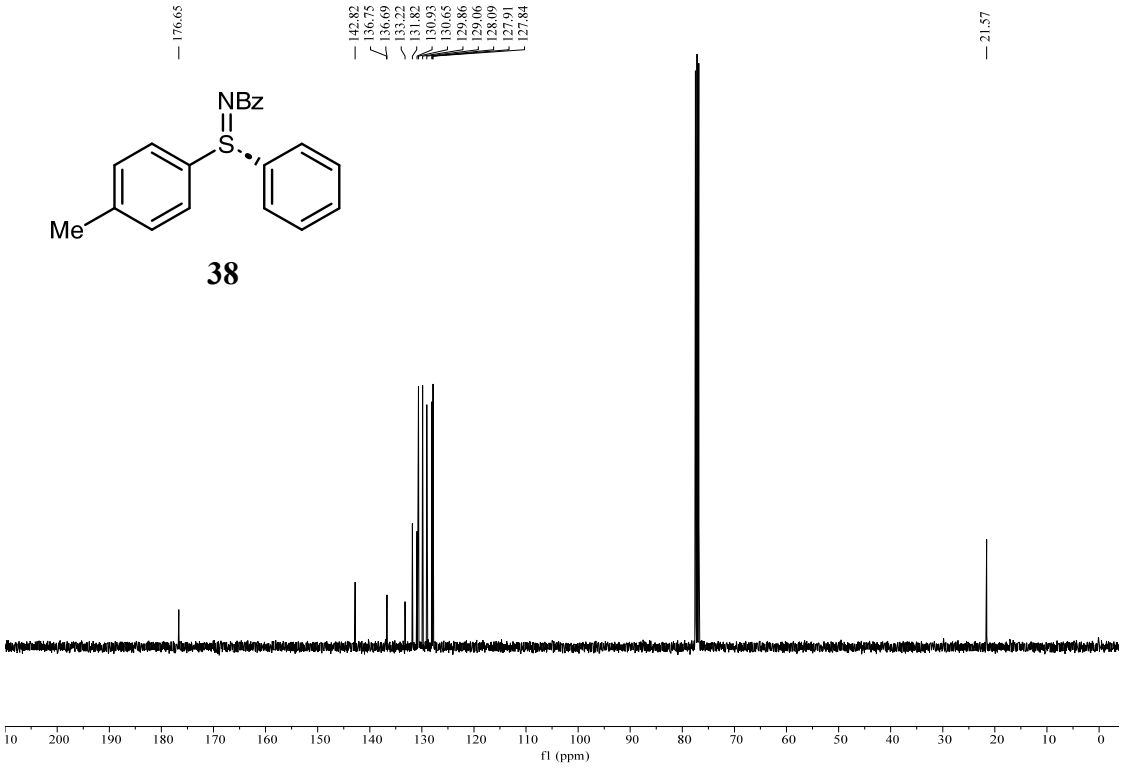


37

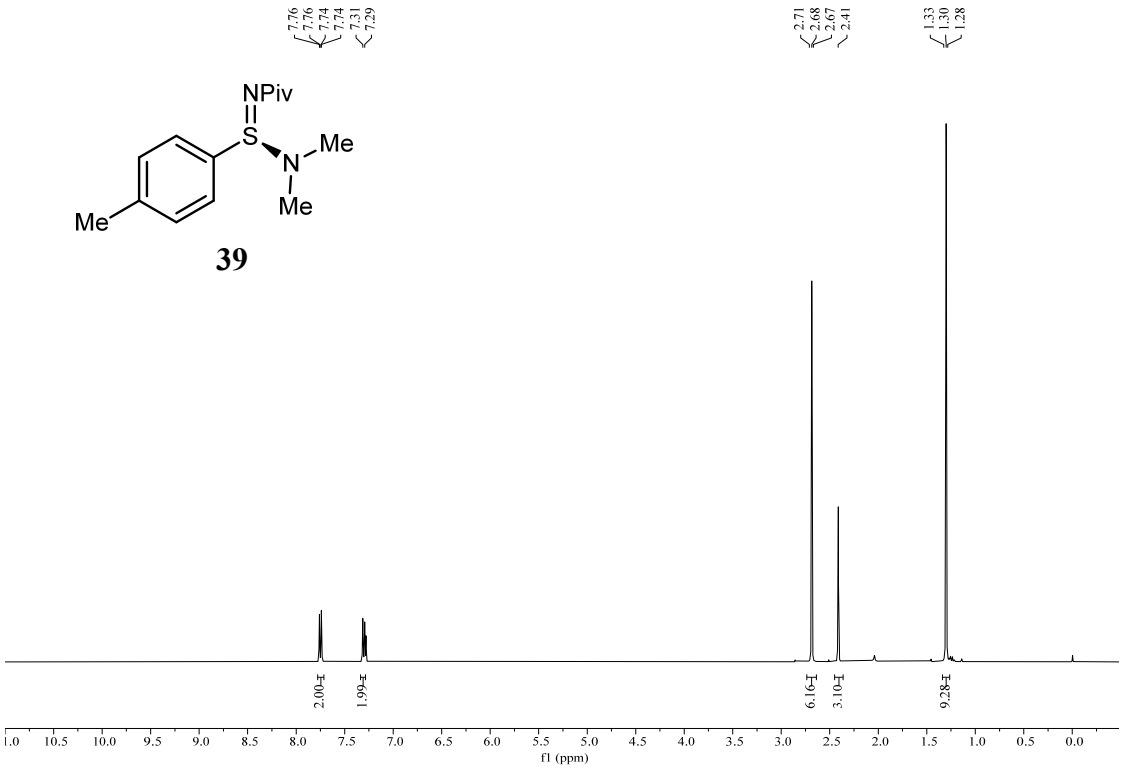
^{1}H NMR of 38 (400 MHz, $CDCl_3$)



^{13}C NMR of 38 (100 MHz, $CDCl_3$)

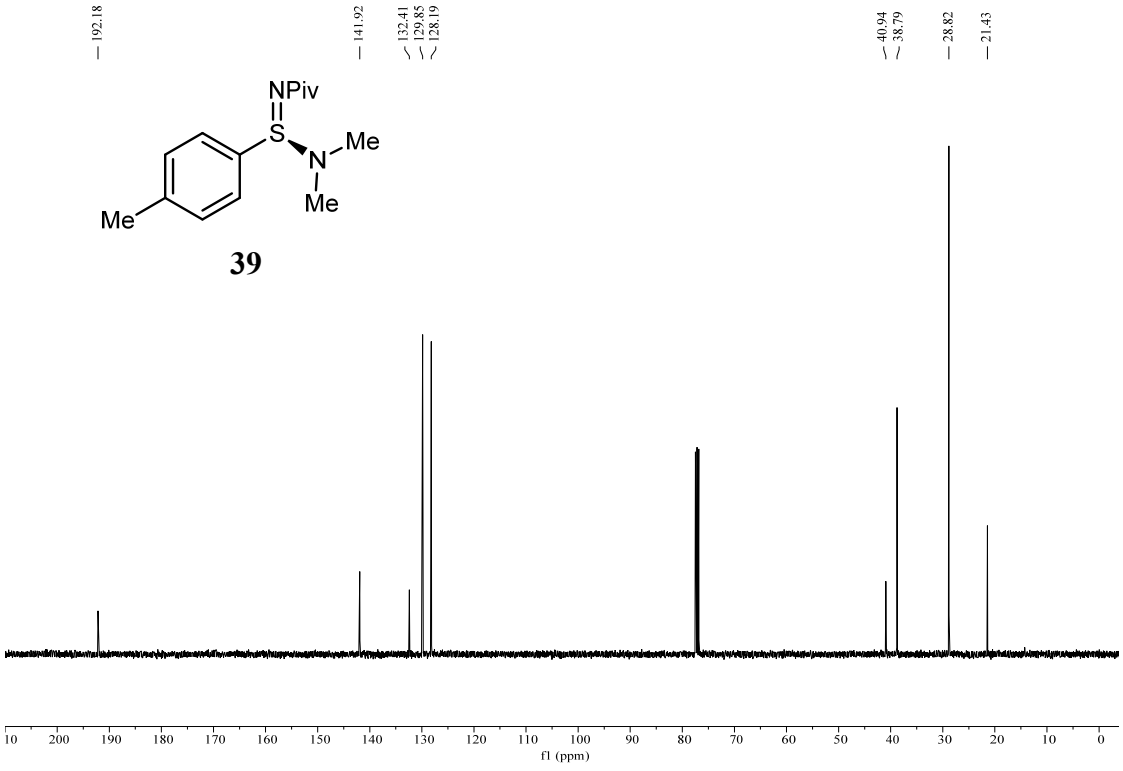


^{1}H NMR of 39 (400 MHz, $CDCl_3$)



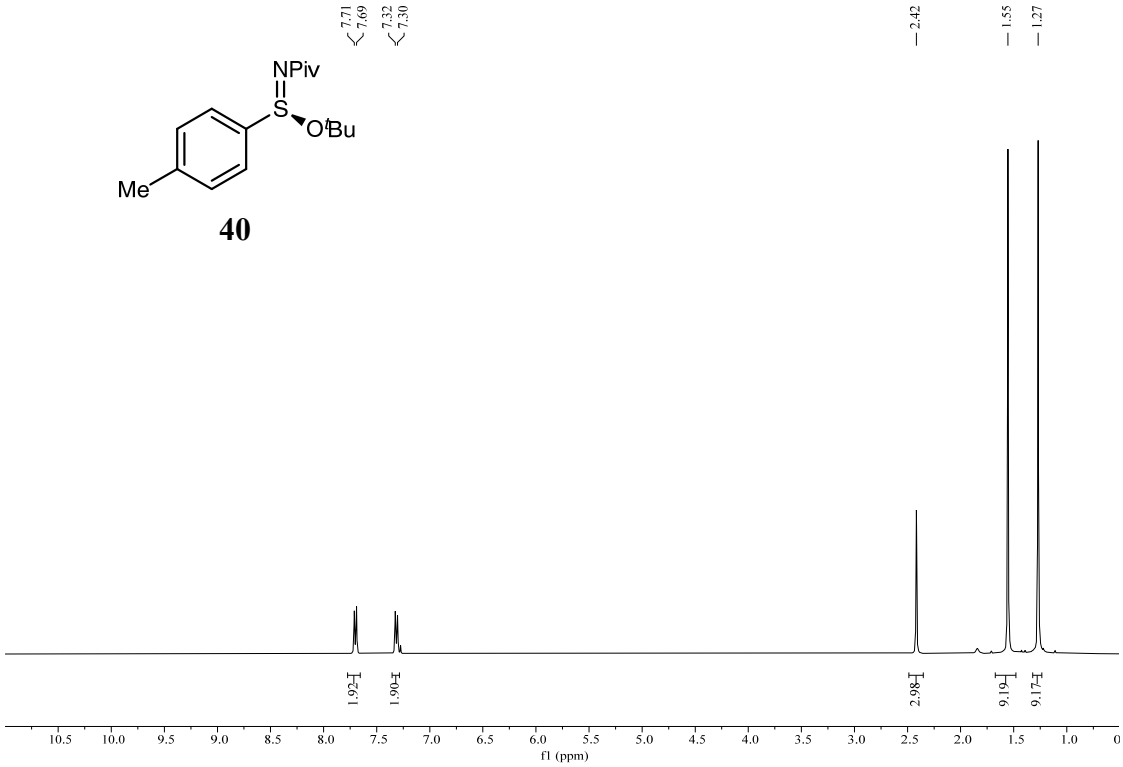
39

^{13}C NMR of 39 (100 MHz, $CDCl_3$)



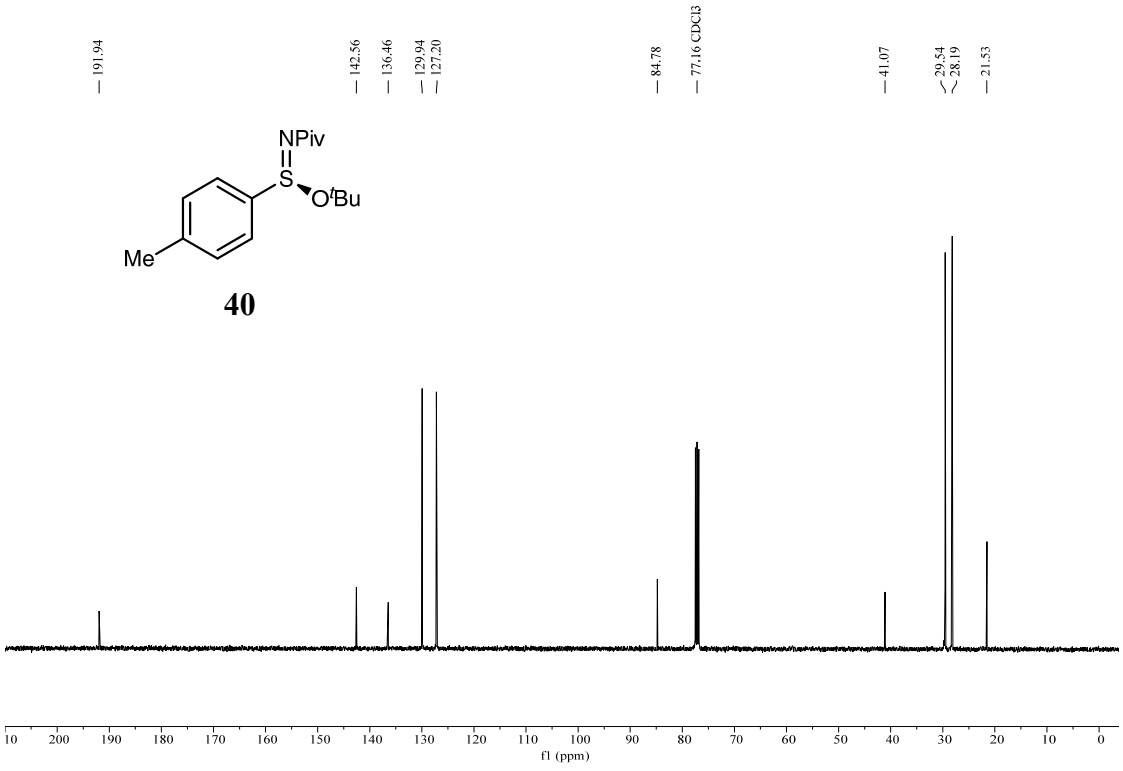
39

^{1}H NMR of 40 (400 MHz, $CDCl_3$)



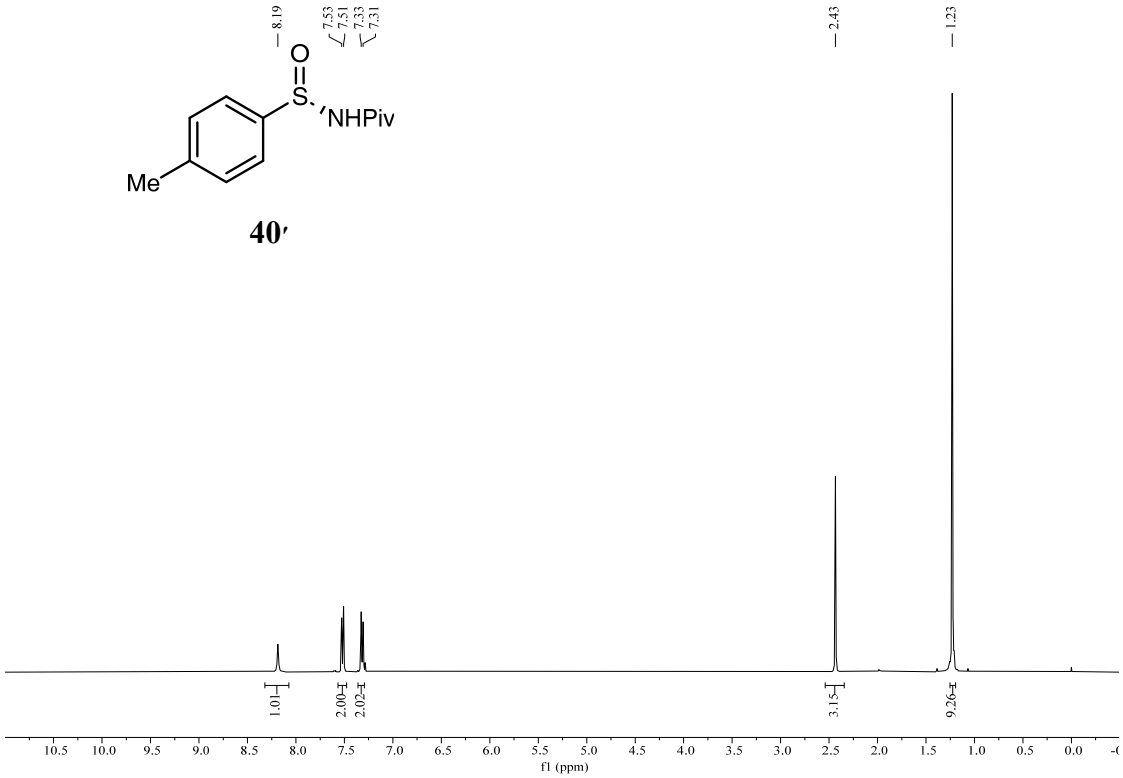
40

^{13}C NMR of 40 (100 MHz, $CDCl_3$)



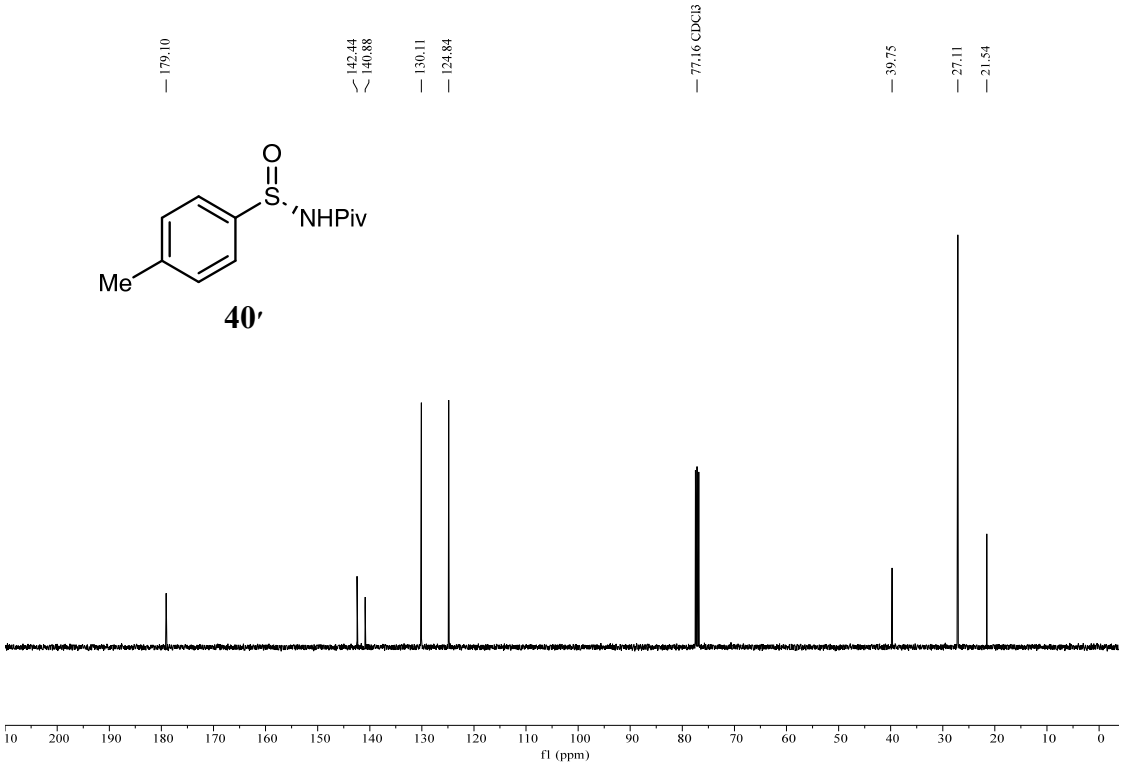
40

^{1}H NMR of 40′ (400 MHz, $CDCl_3$)



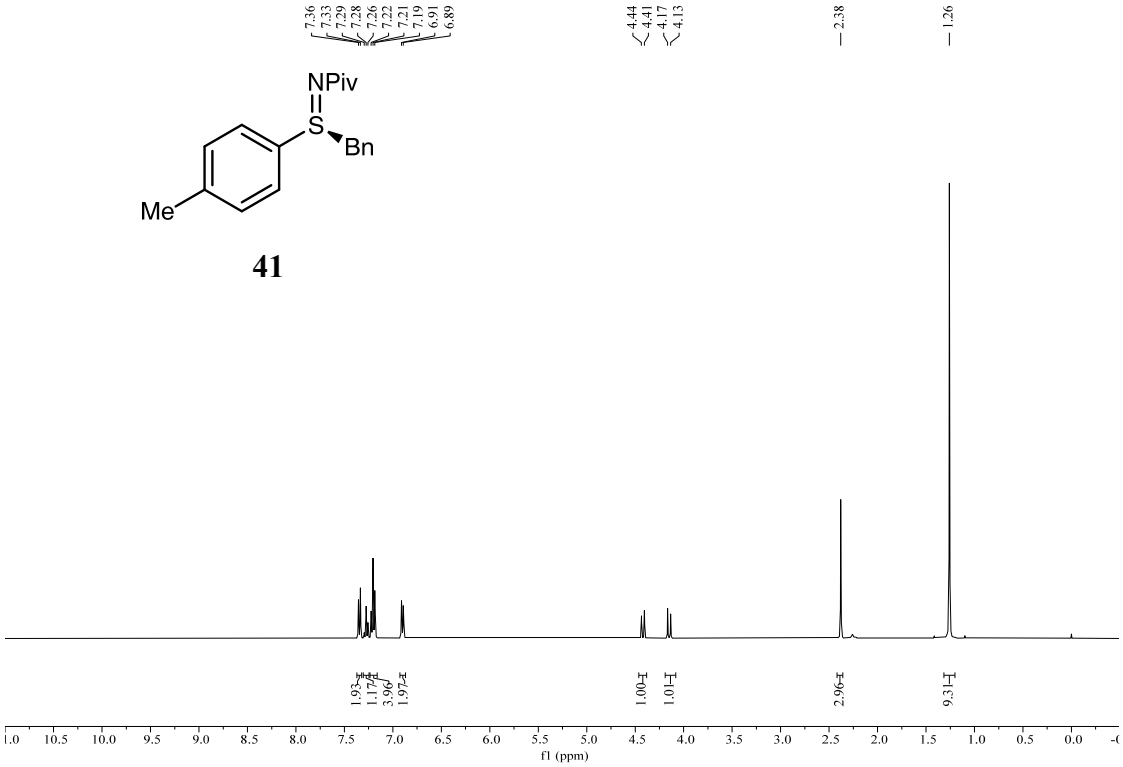
40′

^{13}C NMR of 40′ (100 MHz, $CDCl_3$)



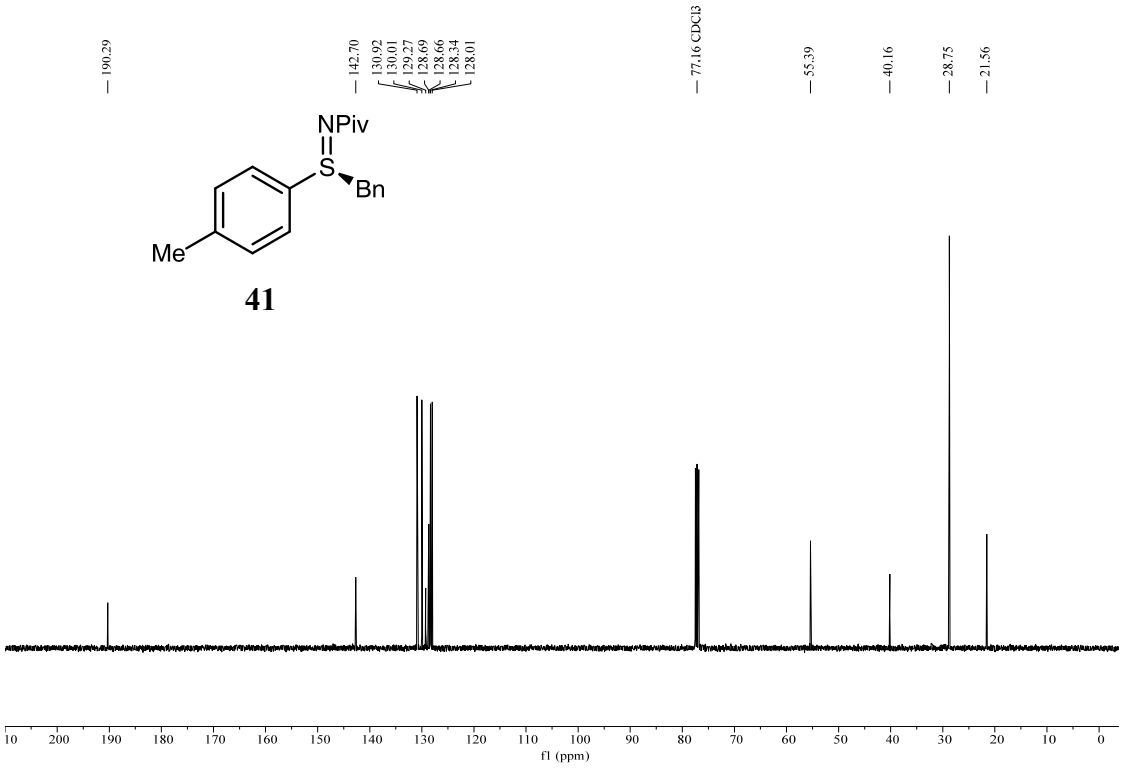
40′

^{1}H NMR of 41 (400 MHz, $CDCl_3$)



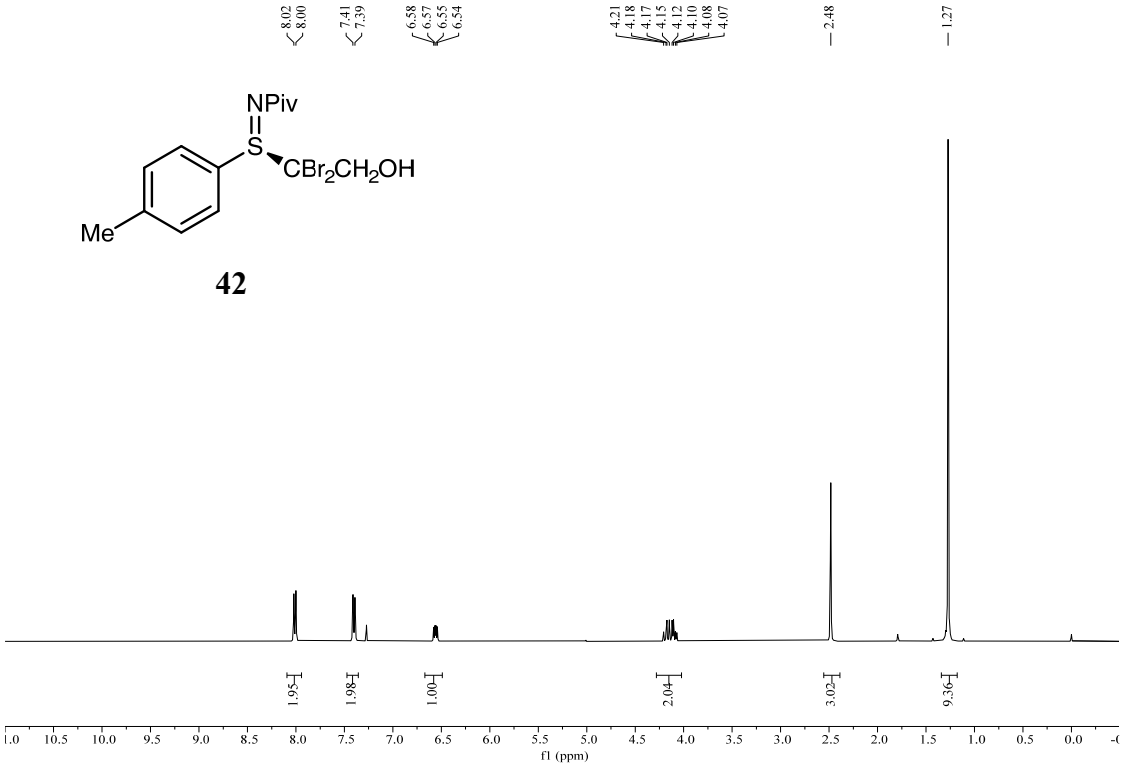
41

^{13}C NMR of 41 (100 MHz, $CDCl_3$)



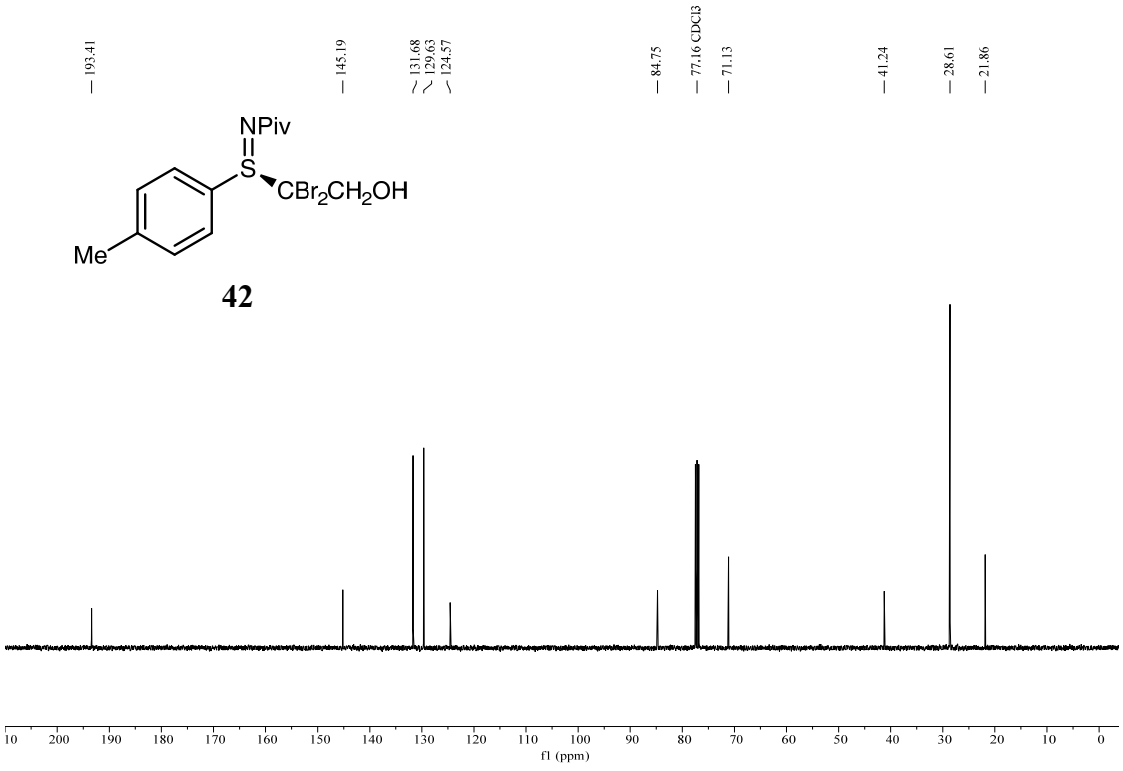
41

^{1}H NMR of 42 (400 MHz, $CDCl_3$)



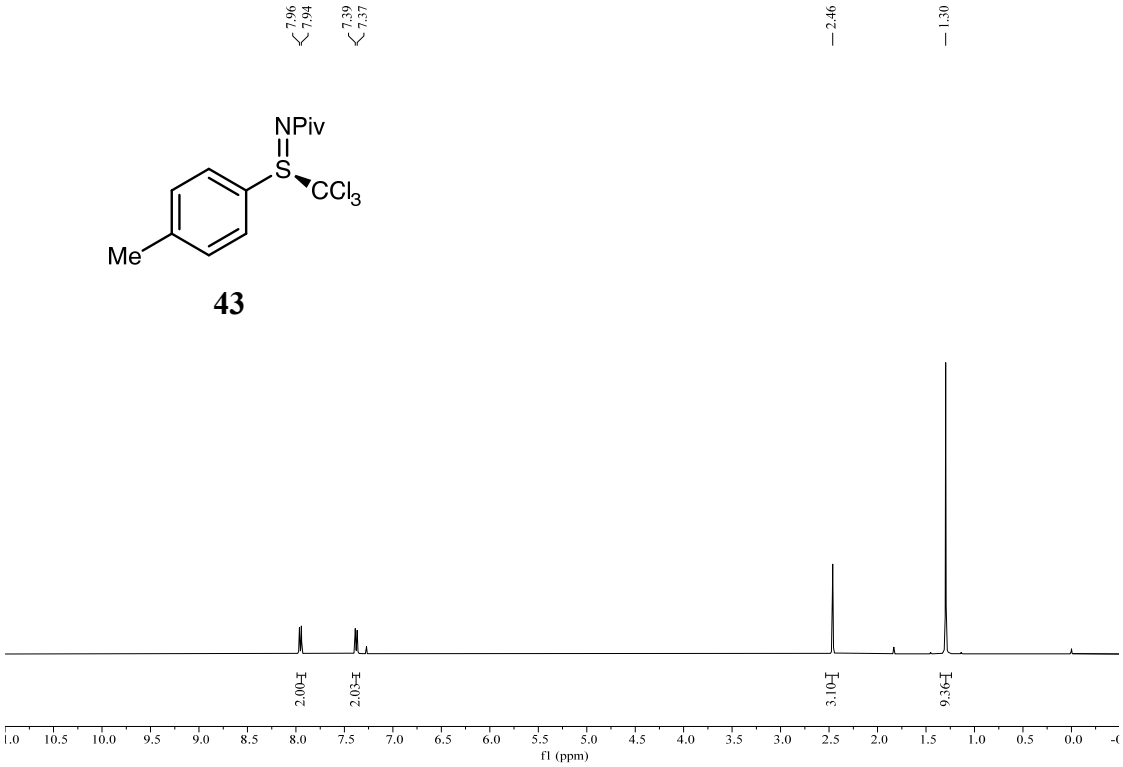
42

^{13}C NMR of 42 (100 MHz, $CDCl_3$)



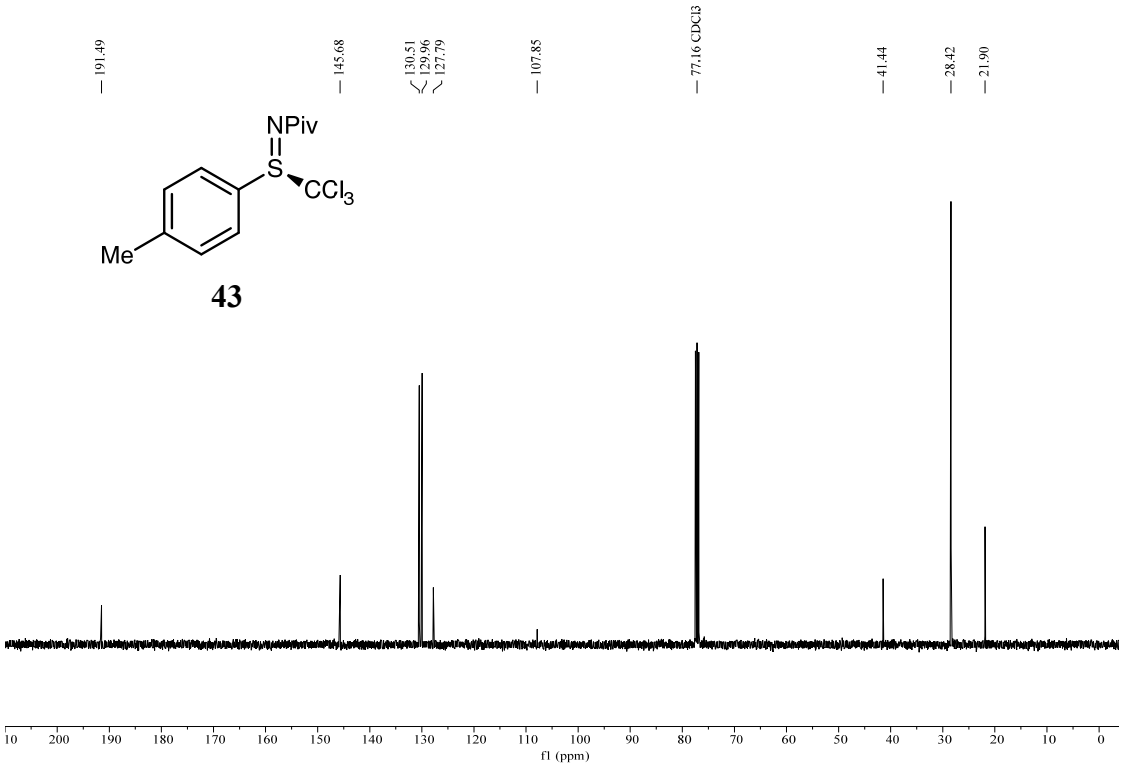
42

^{1}H NMR of 43 (400 MHz, $CDCl_3$)



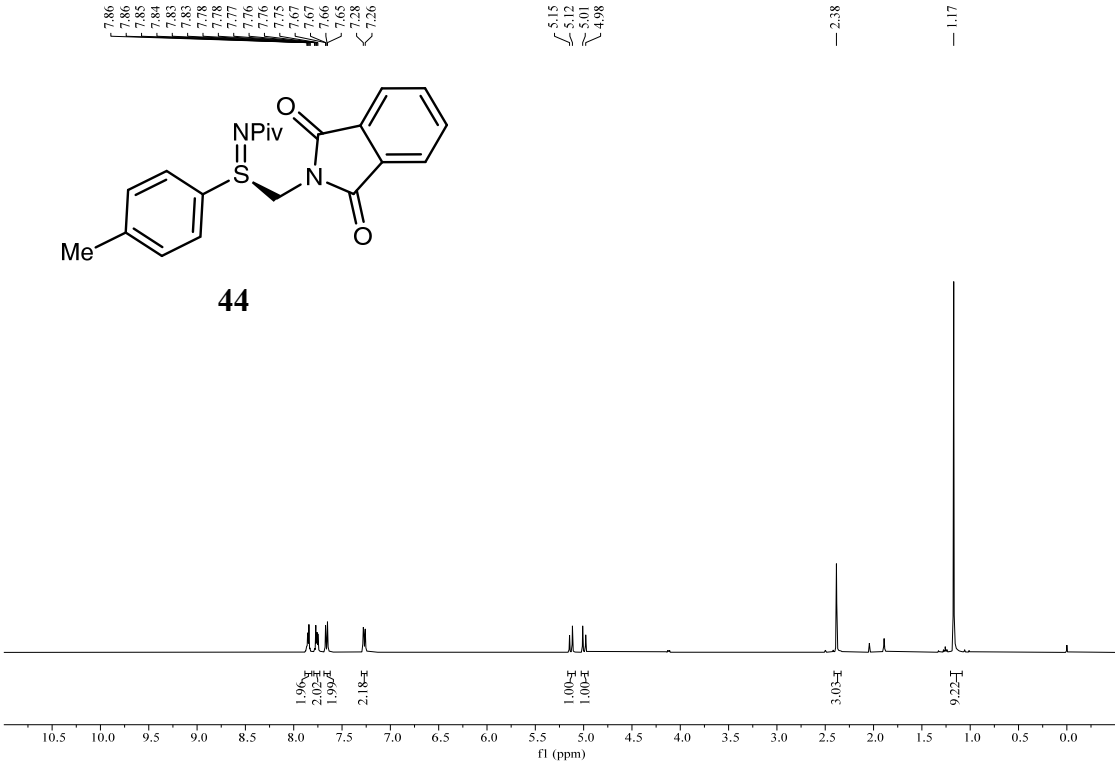
43

^{13}C NMR of 43 (100 MHz, $CDCl_3$)



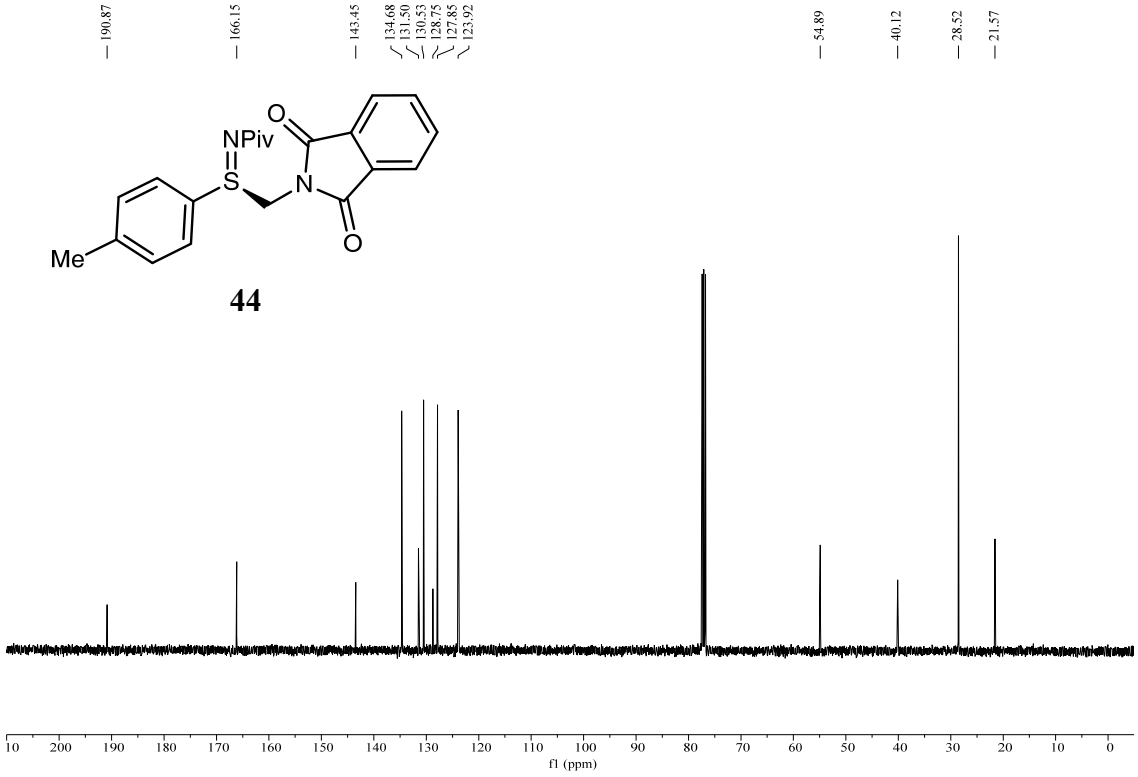
43

^{1}H NMR of 44 (400 MHz, $CDCl_3$)



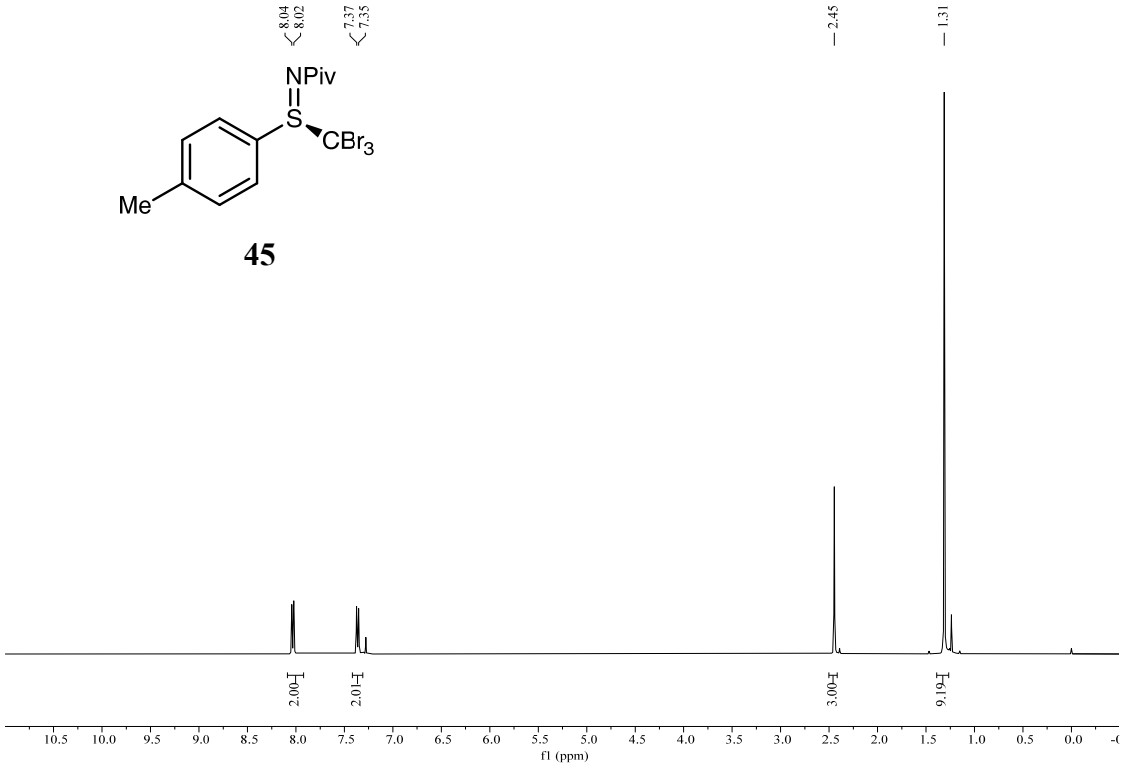
44

^{13}C NMR of 44 (100 MHz, $CDCl_3$)



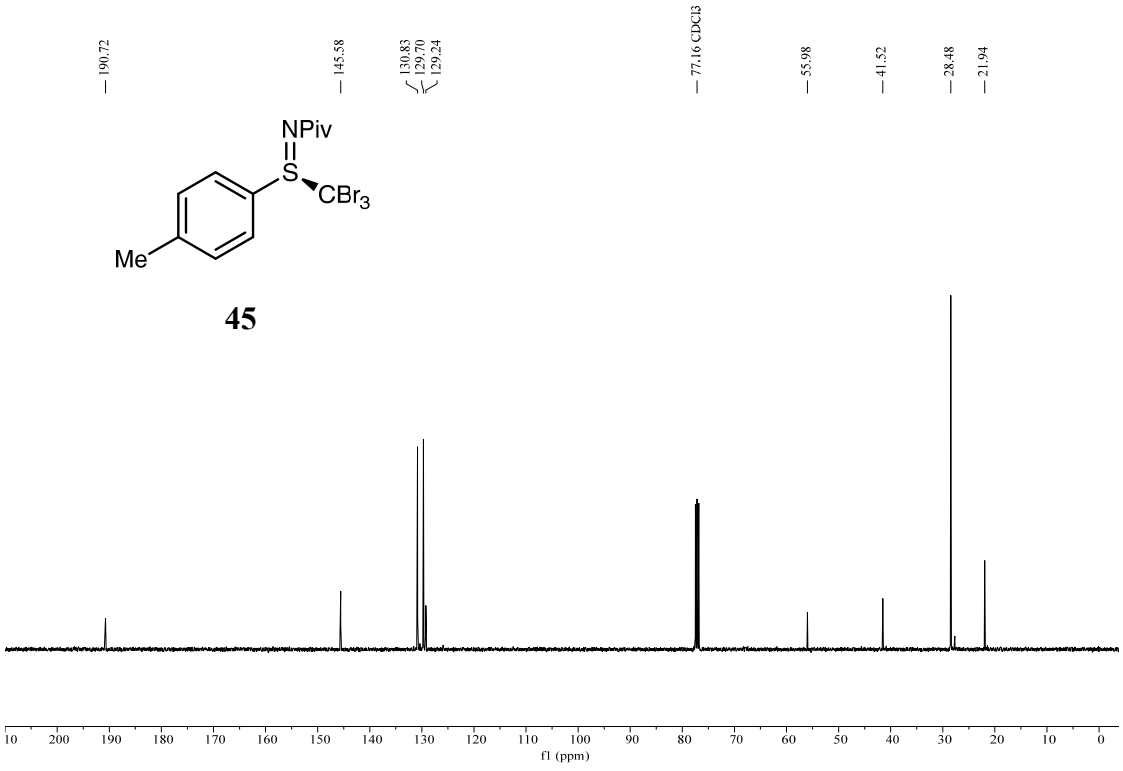
44

^{1}H NMR of 45 (400 MHz, $CDCl_3$)



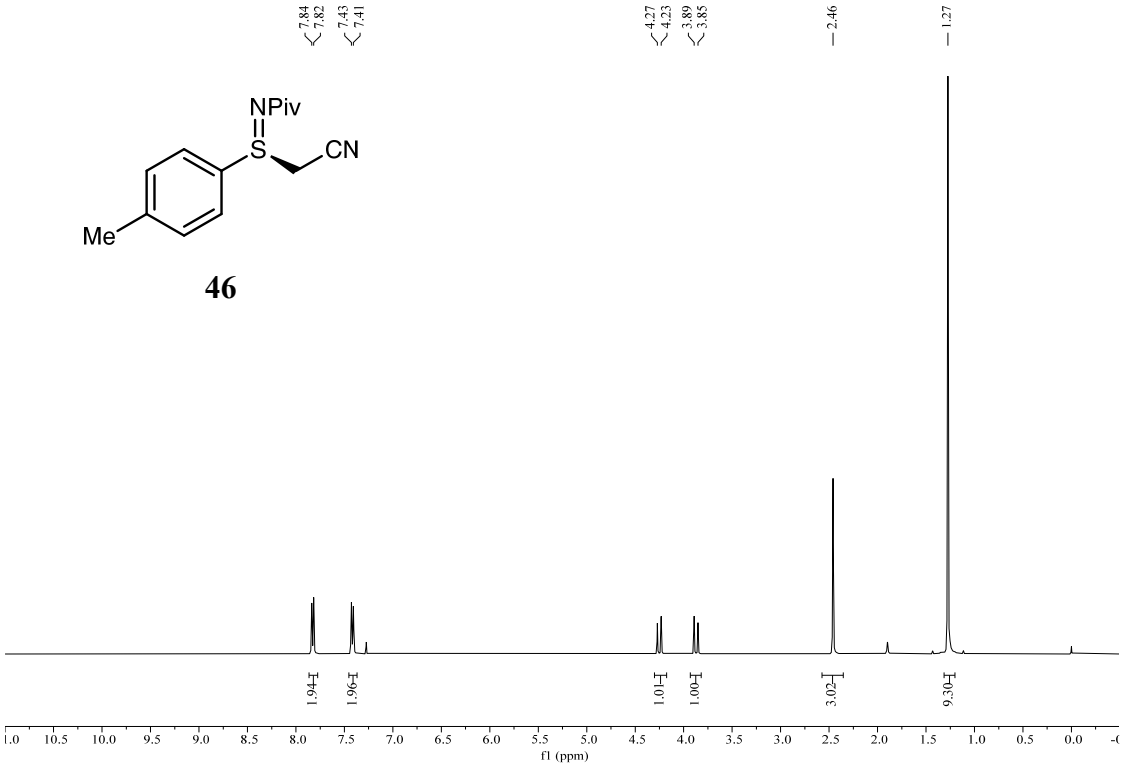
45

^{13}C NMR of 45 (100 MHz, $CDCl_3$)



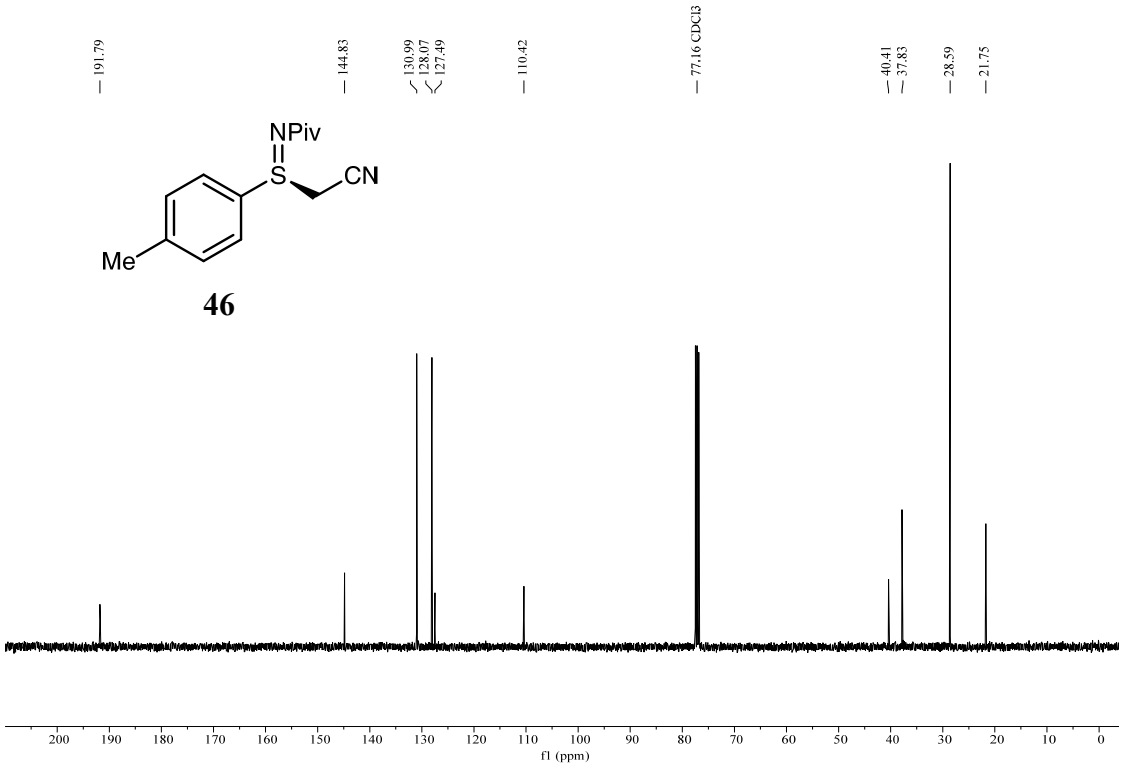
45

^{1}H NMR of 46 (400 MHz, $CDCl_3$)



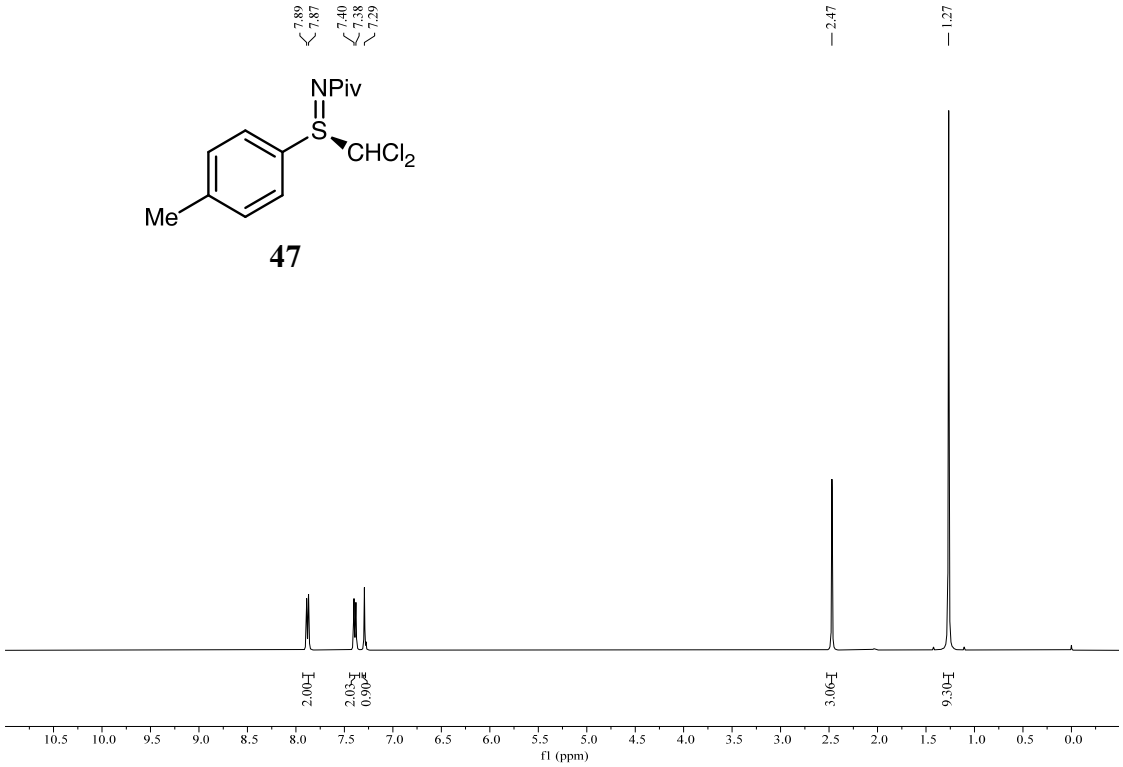
46

^{13}C NMR of 46 (100 MHz, $CDCl_3$)



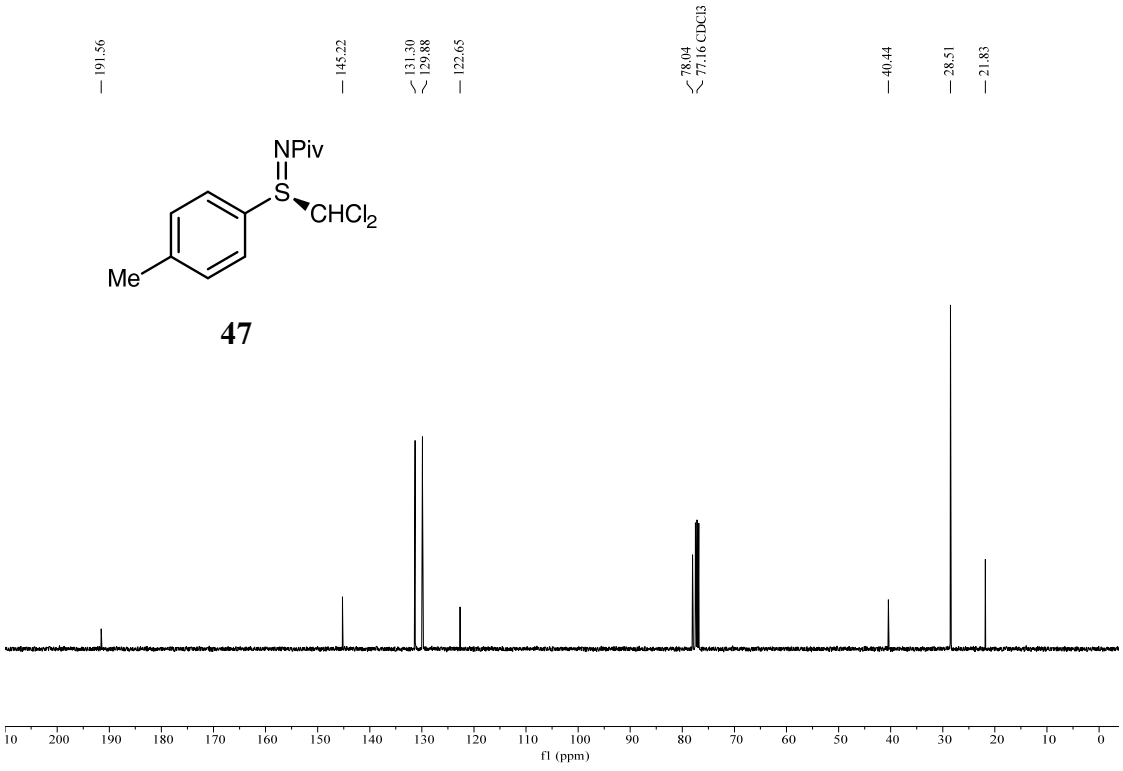
46

^{1}H NMR of 47 (400 MHz, $CDCl_3$)



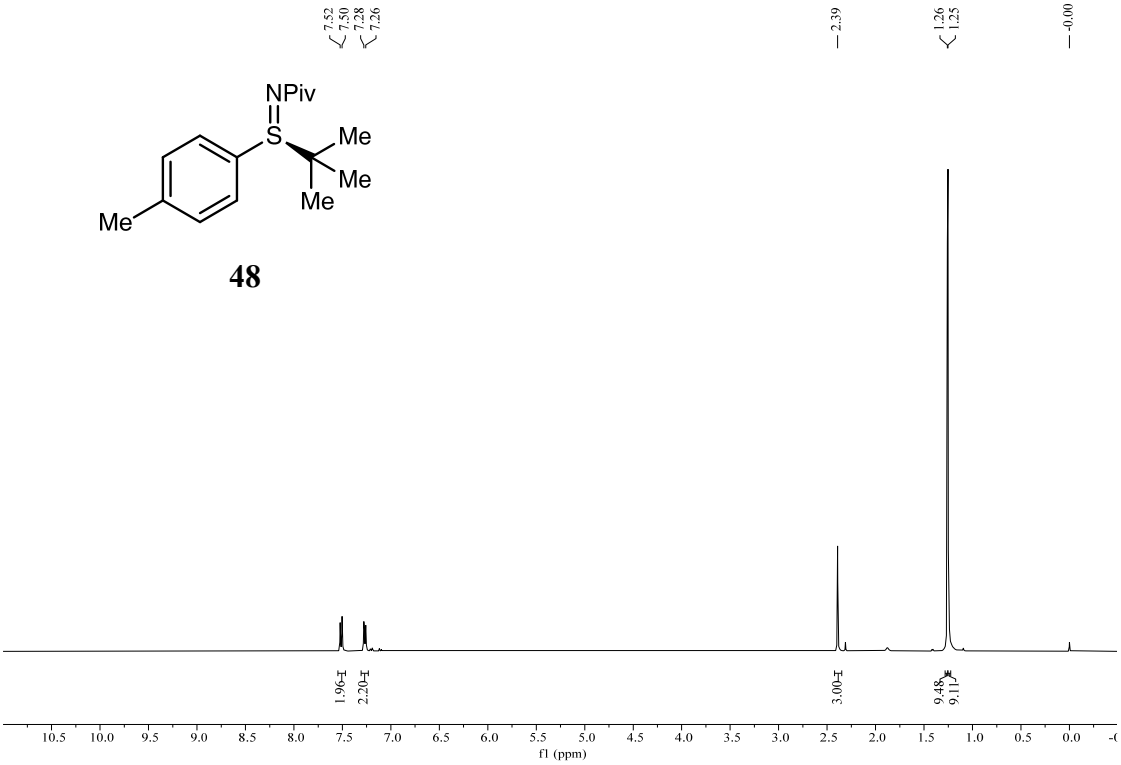
47

^{13}C NMR of 47 (100 MHz, $CDCl_3$)



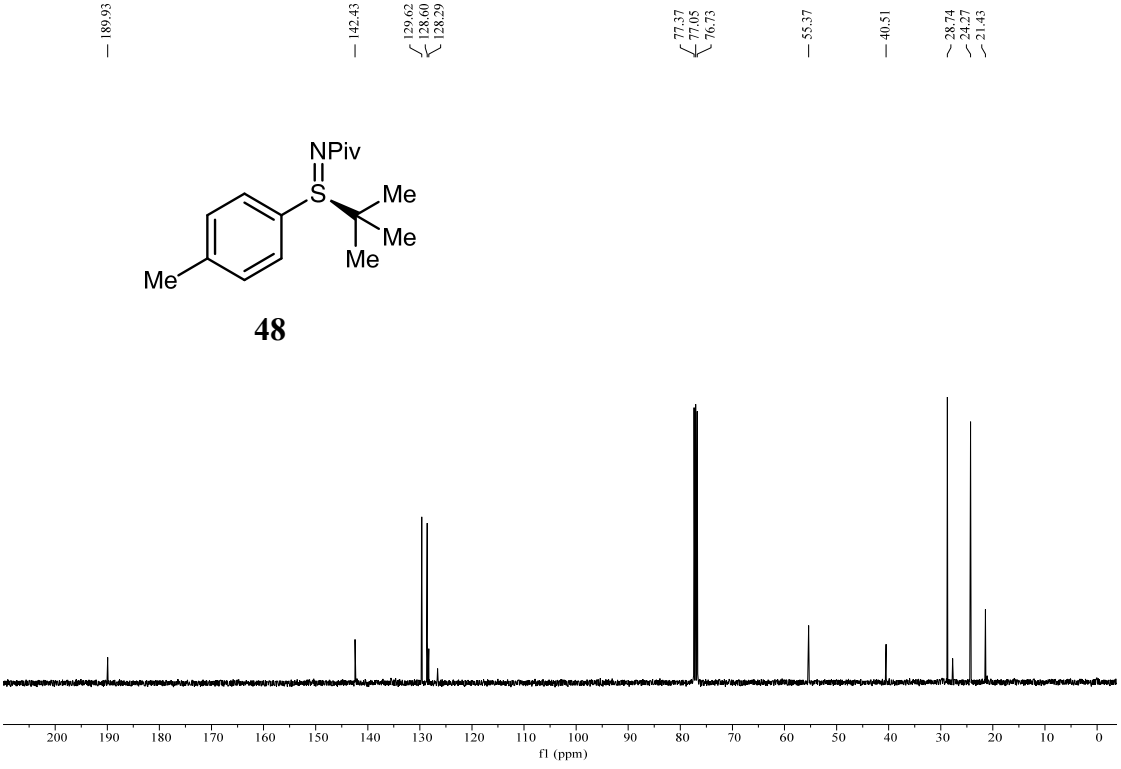
47

^{1}H NMR of 48 (400 MHz, $CDCl_3$)



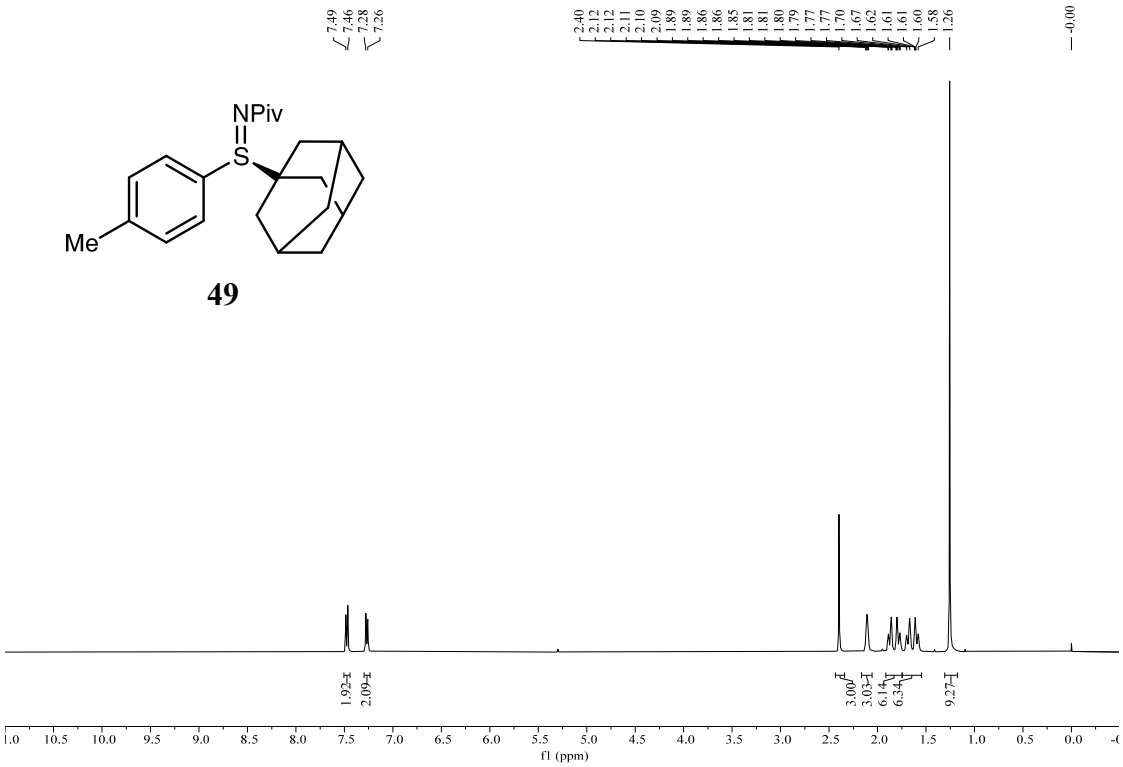
48

^{13}C NMR of 48 (100 MHz, $CDCl_3$)

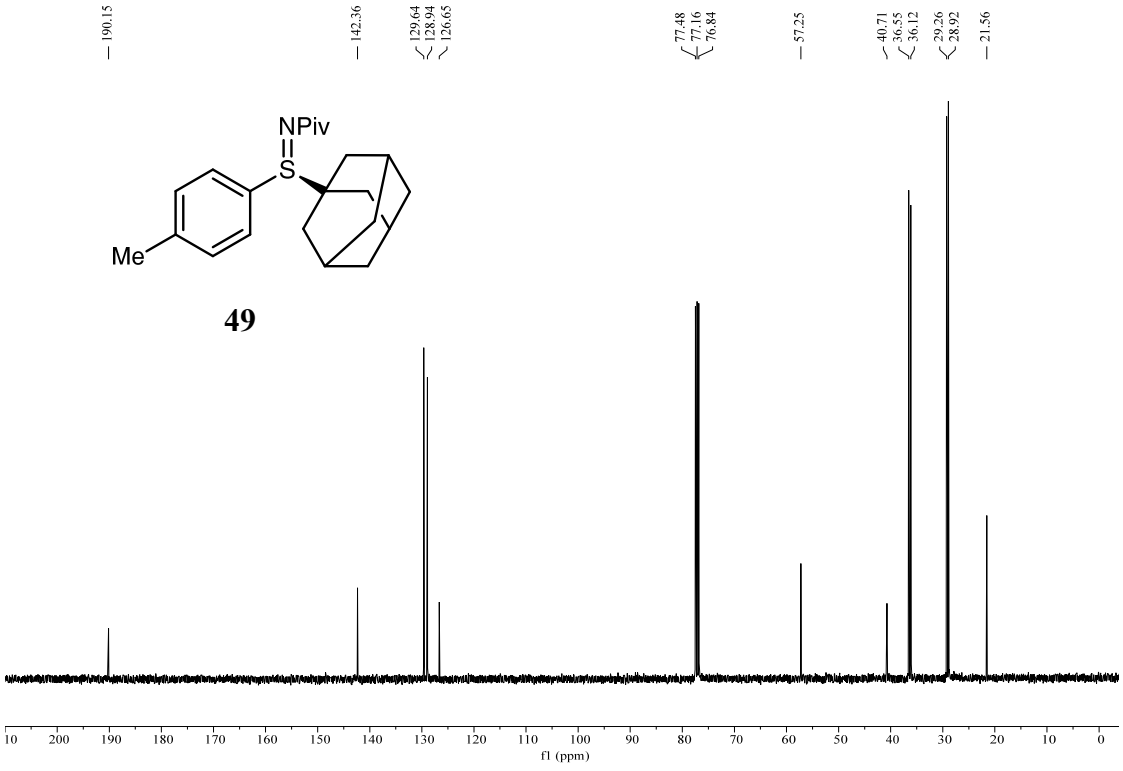


48

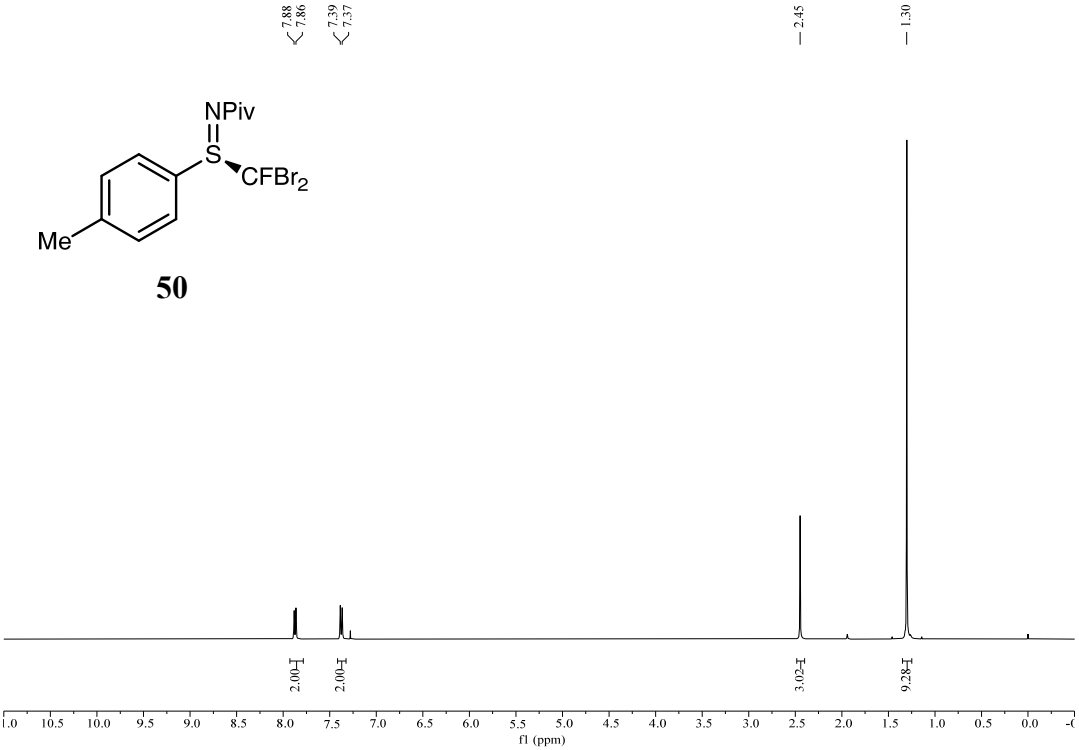
^{1}H NMR of 49 (400 MHz, $CDCl_3$)



^{13}C NMR of 49 (100 MHz, $CDCl_3$)

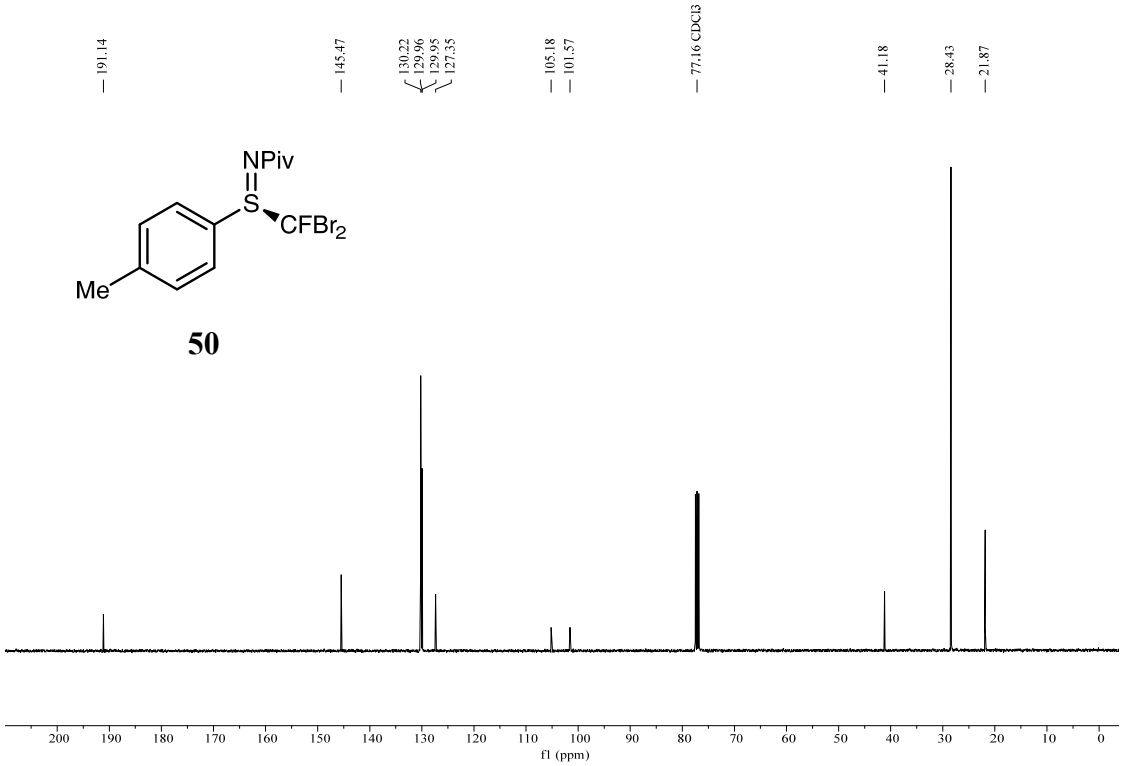


^{1}H NMR of 50 (400 MHz, $CDCl_3$)



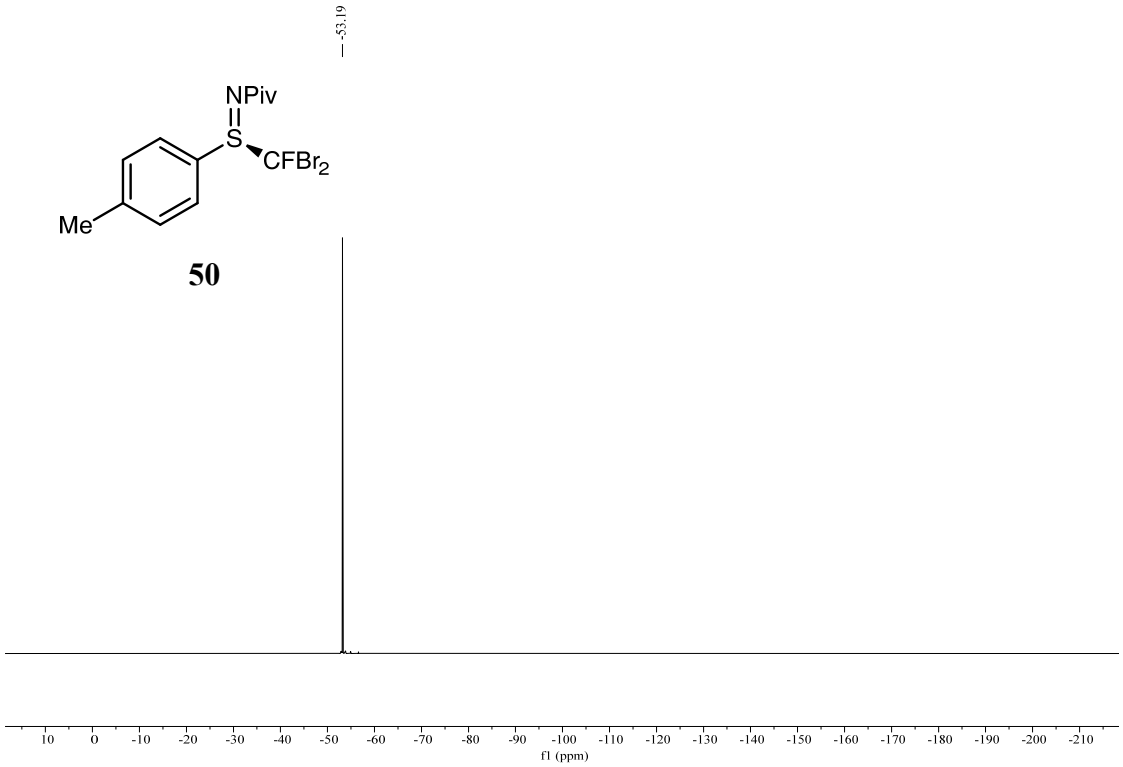
50

^{13}C NMR of 50 (100 MHz, $CDCl_3$)

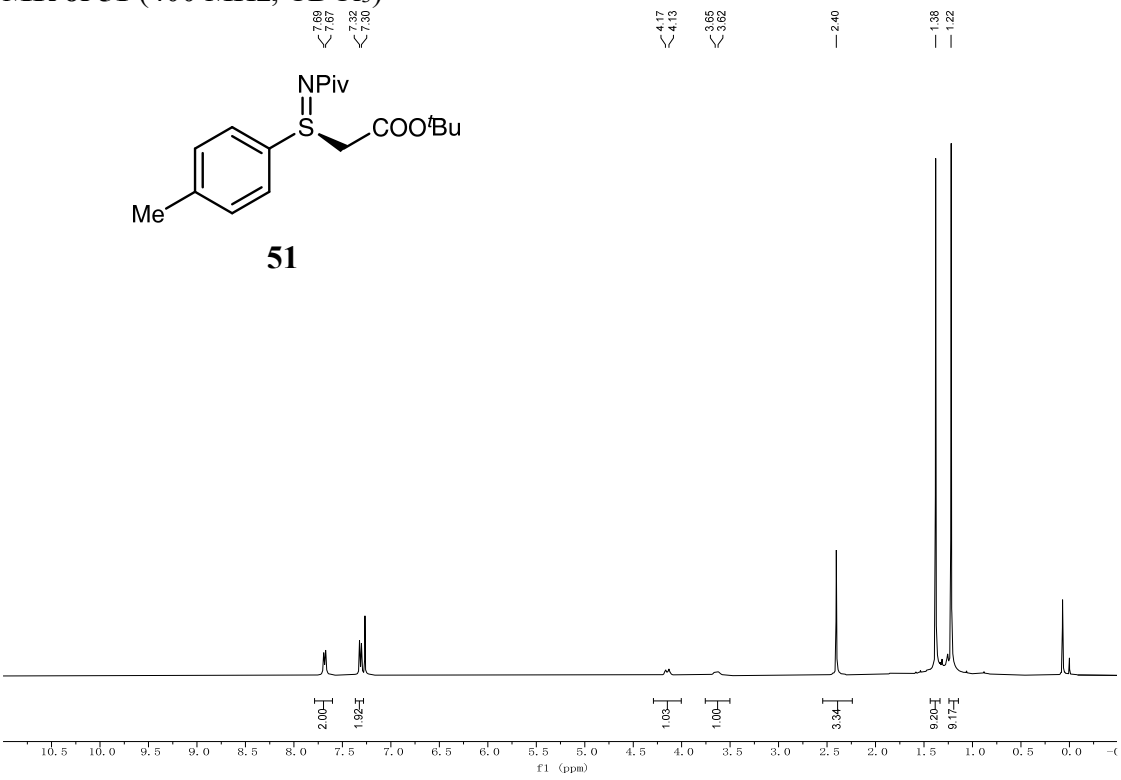


50

^{19}F NMR of 50 (375 MHz, $CDCl_3$)

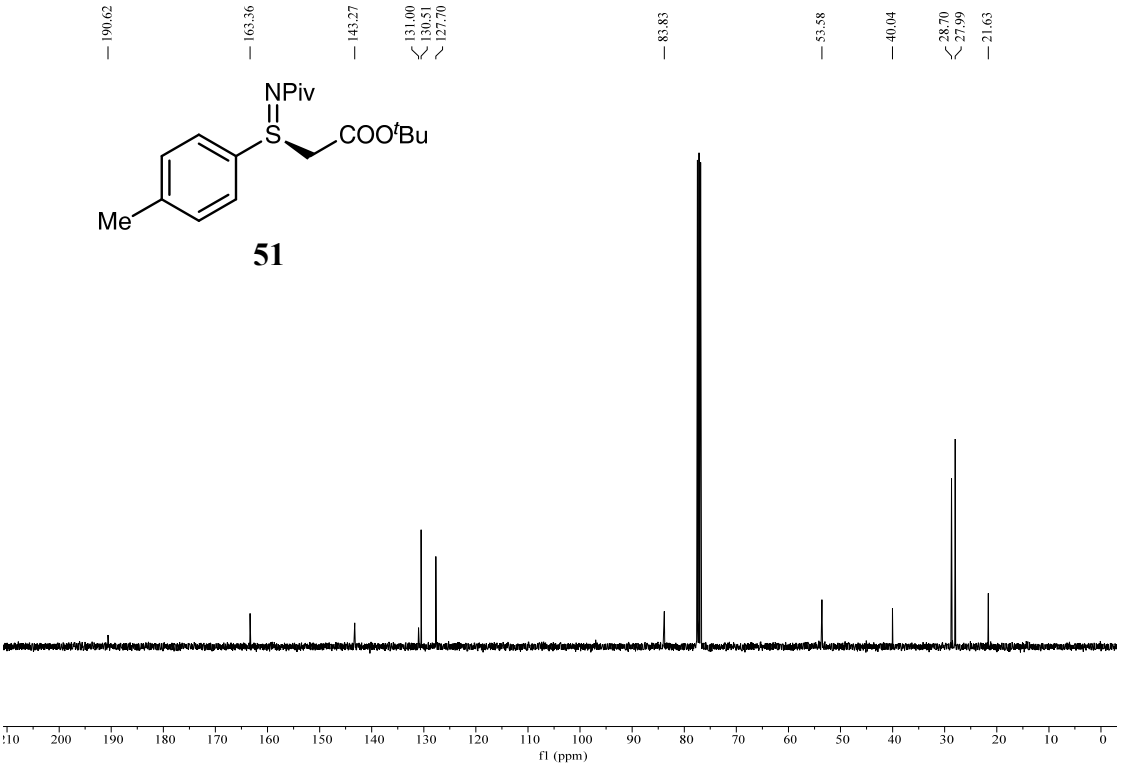


^{1}H NMR of 51 (400 MHz, $CDCl_3$)



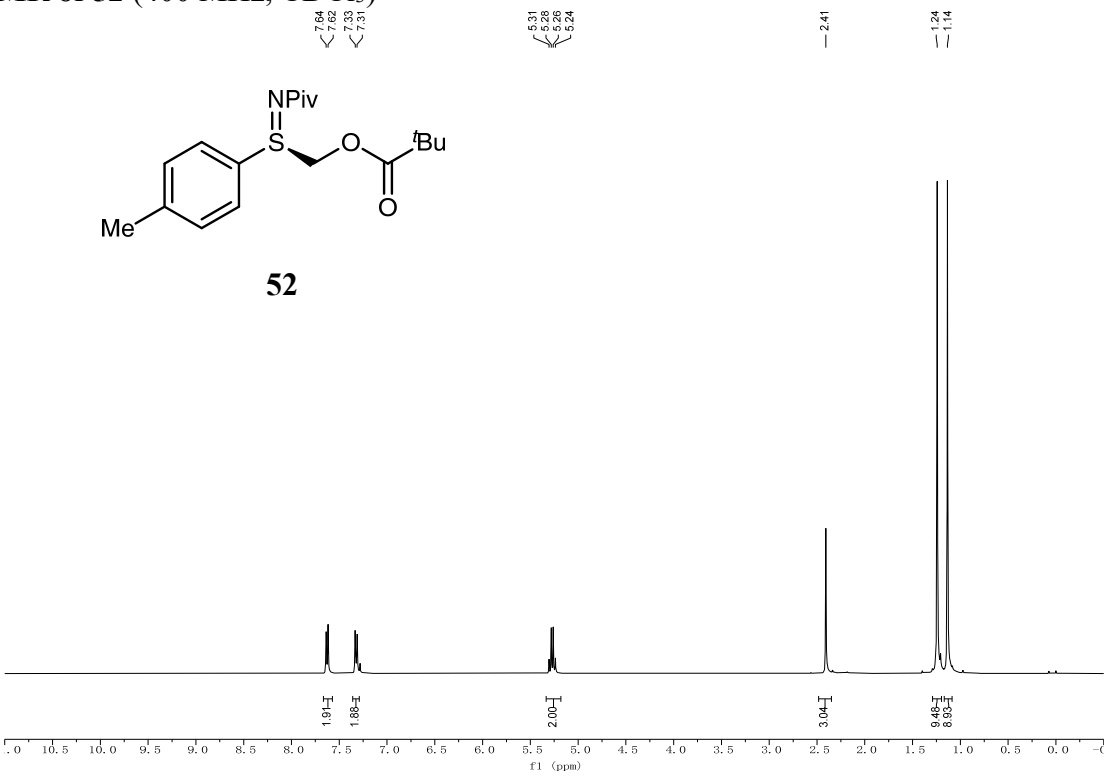
51

^{13}C NMR of 51 (100 MHz, $CDCl_3$)

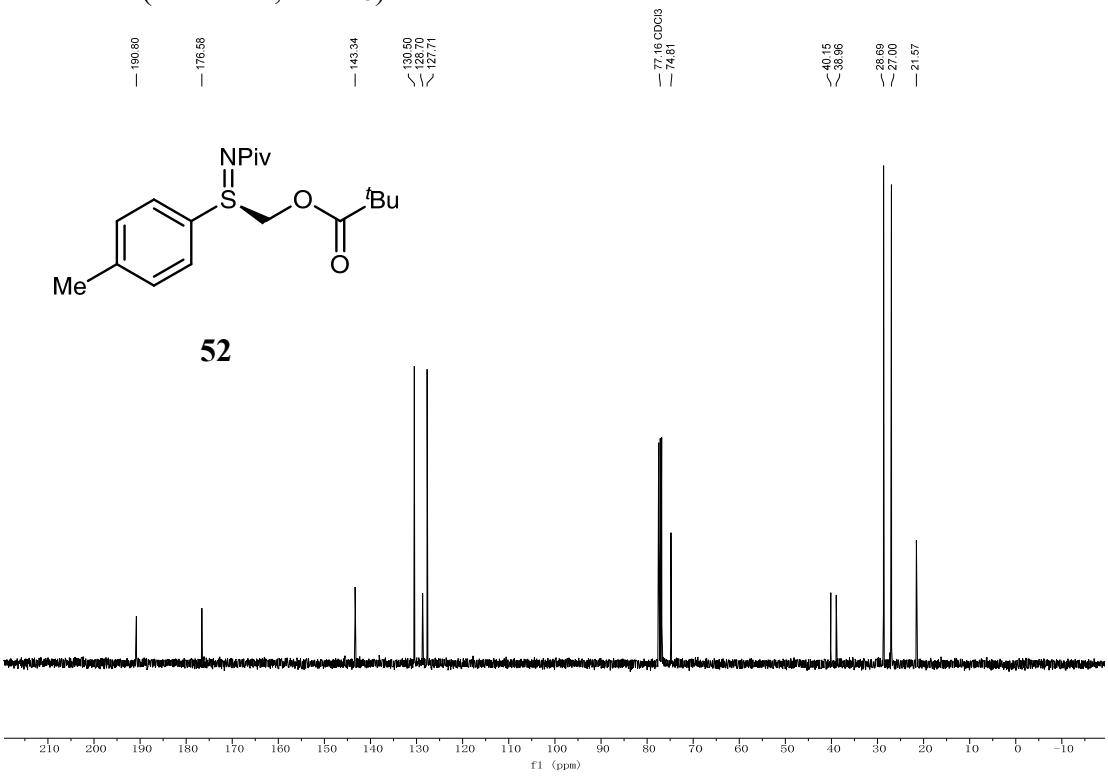


51

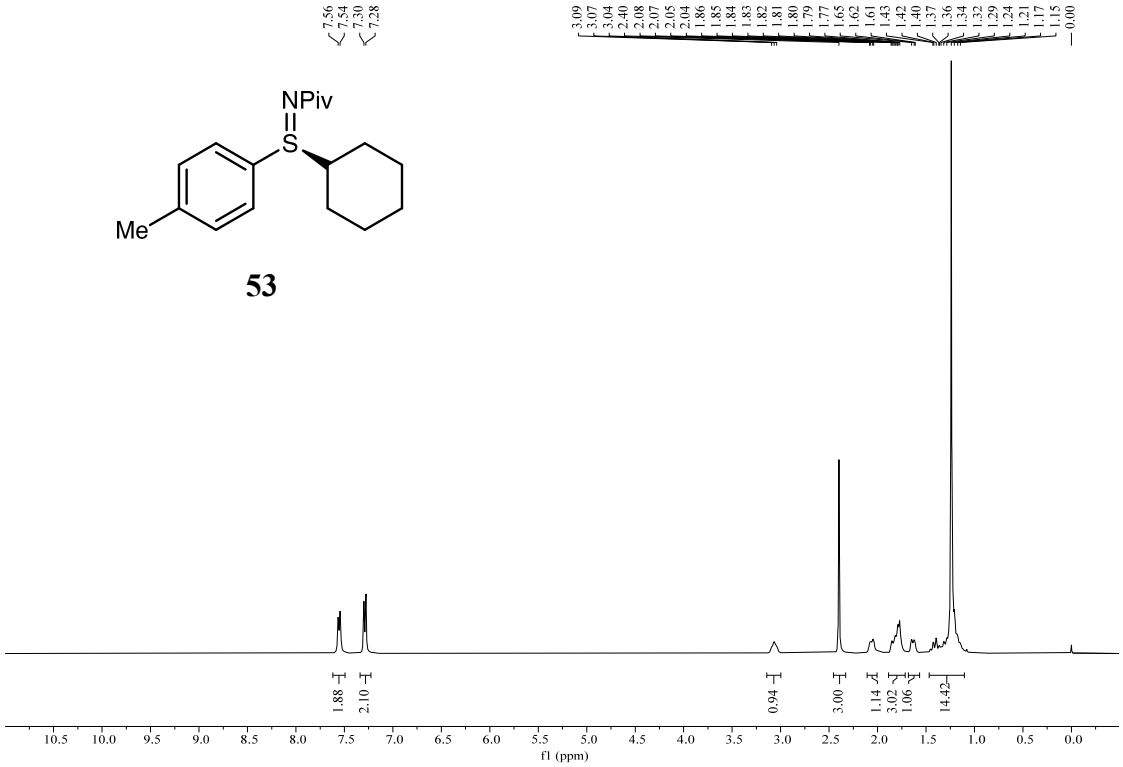
^{1}H NMR of 52 (400 MHz, $CDCl_3$)



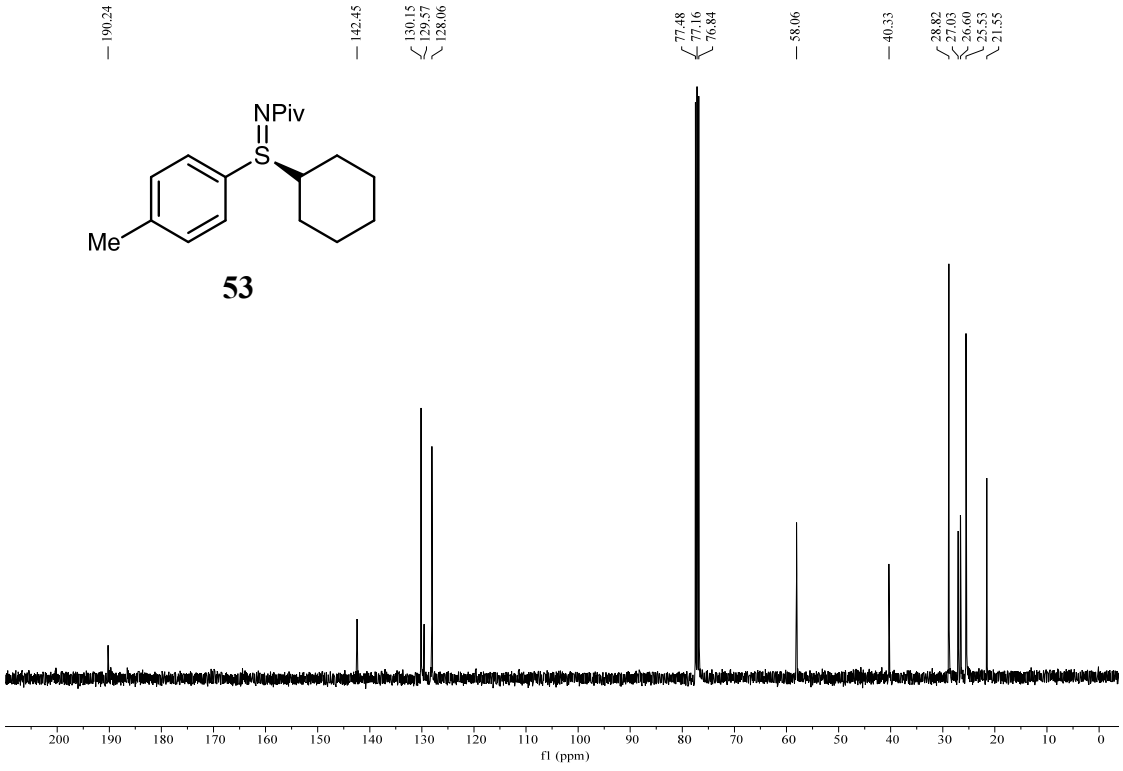
^{13}C NMR of 52 (100 MHz, $CDCl_3$)



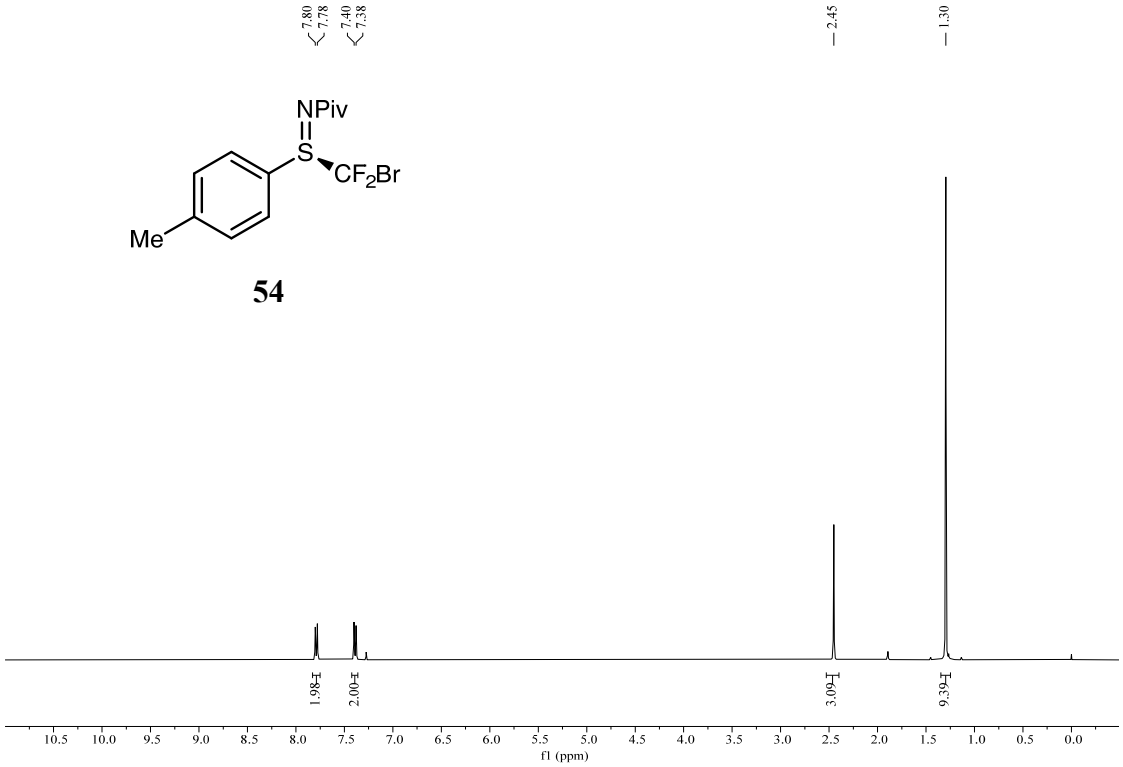
^{1}H NMR of 53 (400 MHz, $CDCl_3$)



^{13}C NMR of 53 (100 MHz, $CDCl_3$)

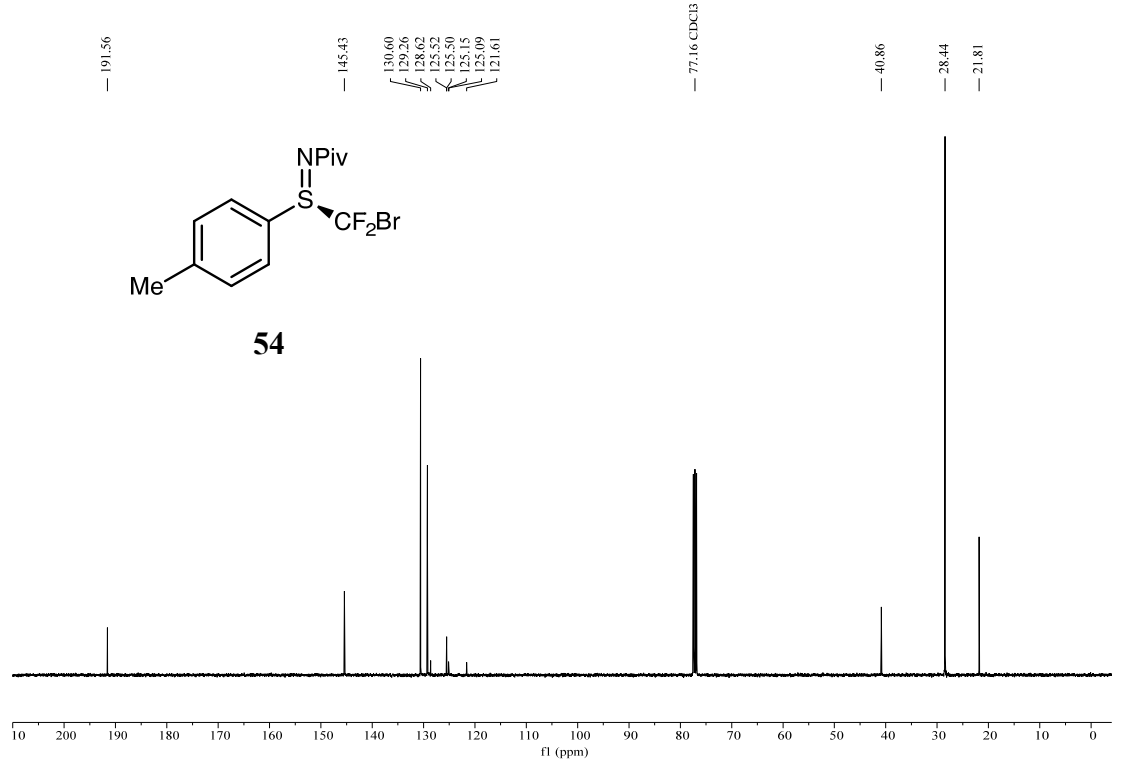


^{1}H NMR of 54 (400 MHz, $CDCl_3$)



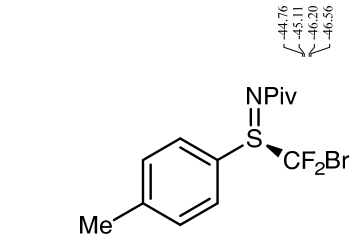
54

^{13}C NMR of 54 (100 MHz, $CDCl_3$)

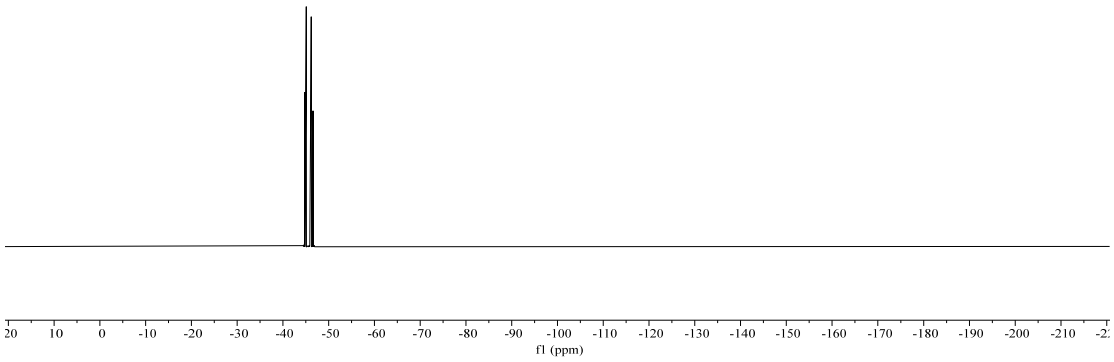


54

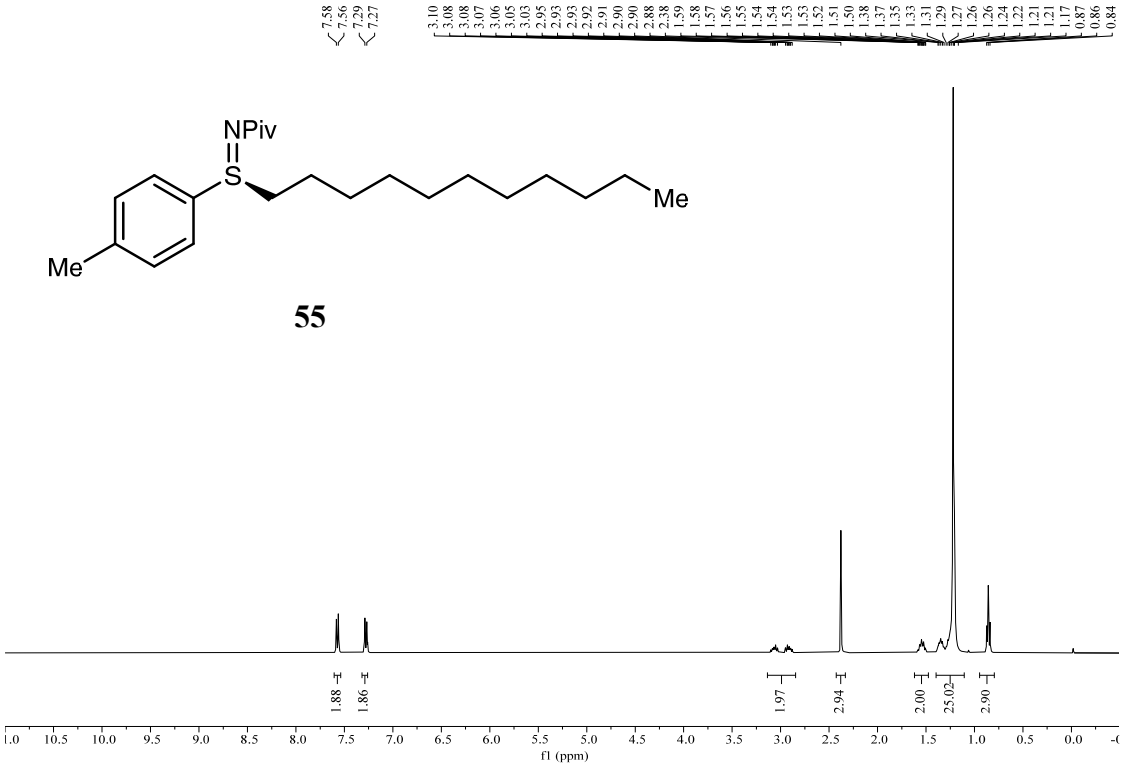
^{19}F NMR of 54 (375 MHz, $CDCl_3$)



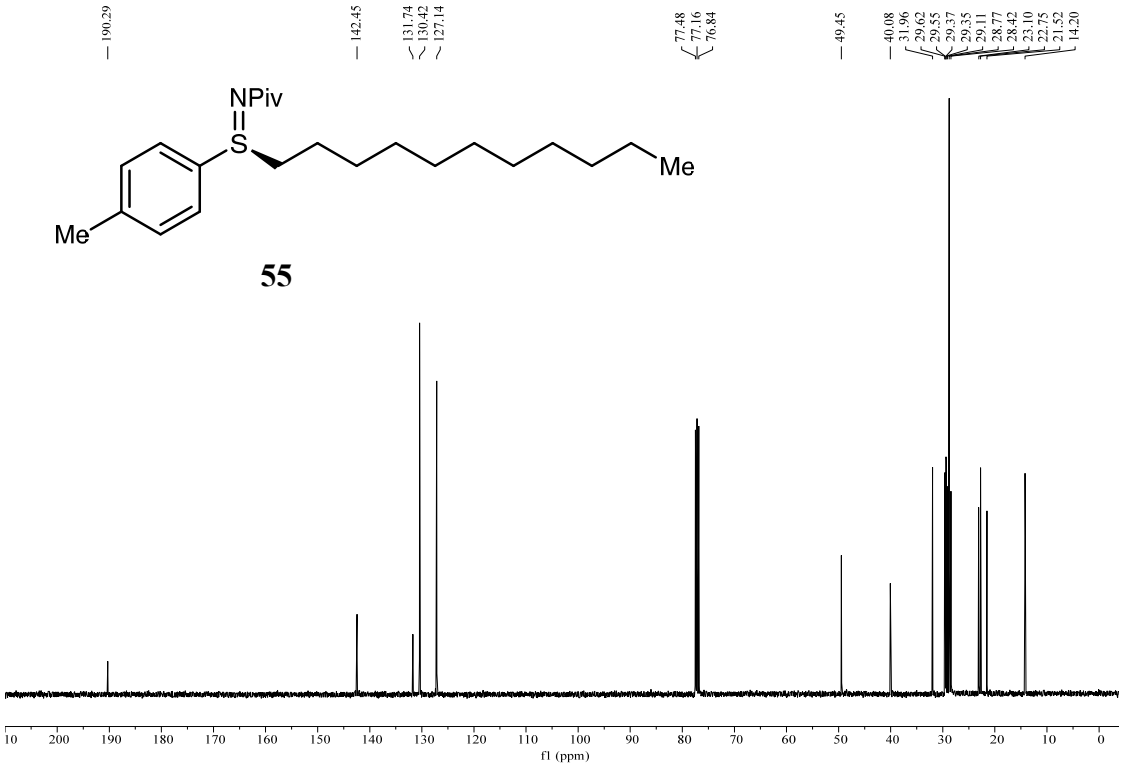
54



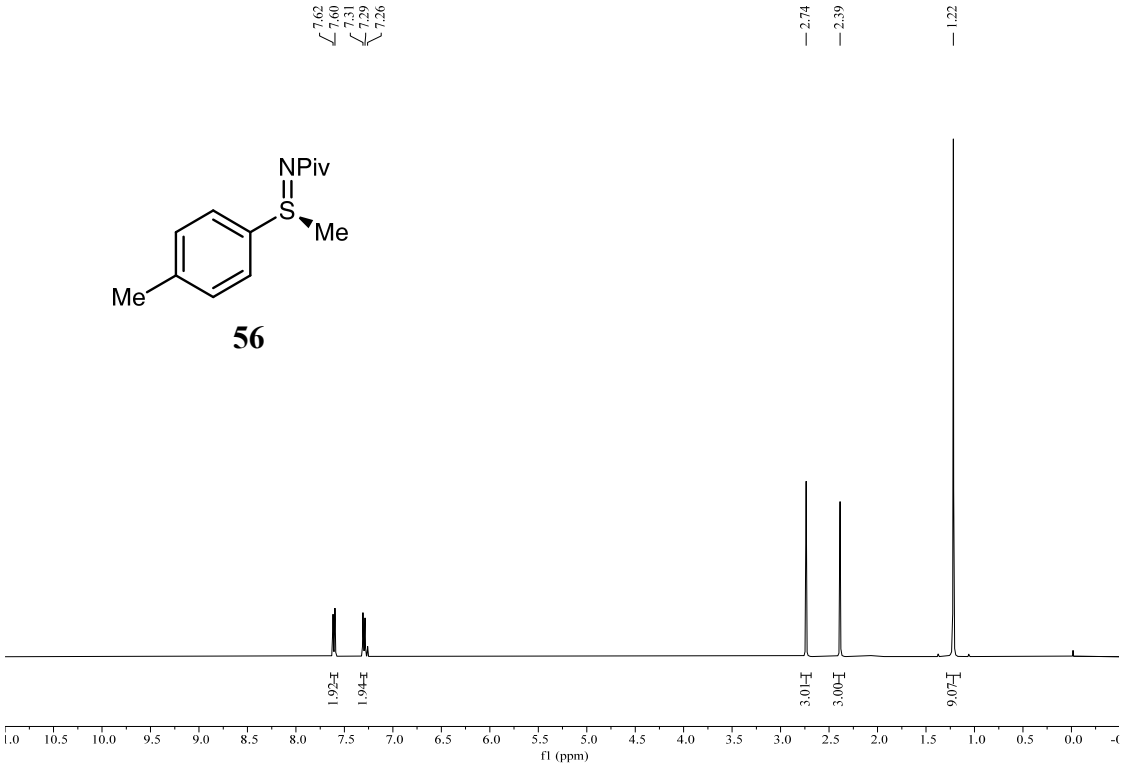
^{1}H NMR of 55 (400 MHz, $CDCl_3$)



^{13}C NMR of 55 (100 MHz, $CDCl_3$)

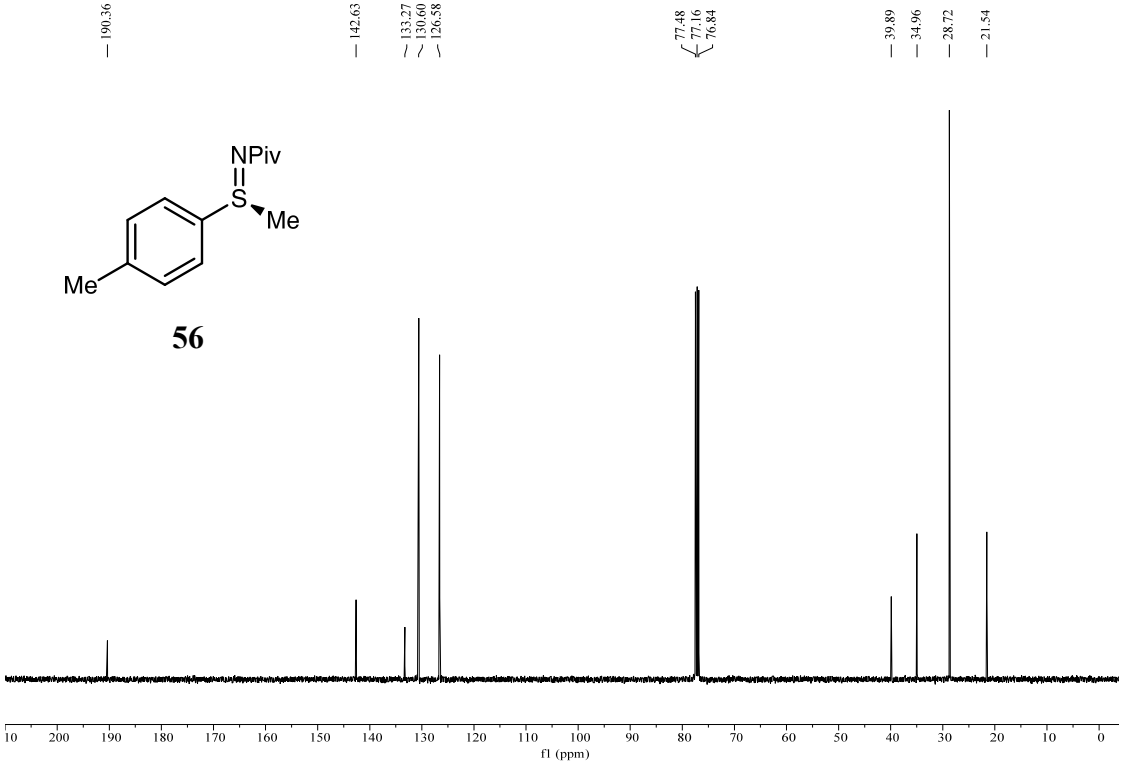


^{1}H NMR of 56 (400 MHz, $CDCl_3$)



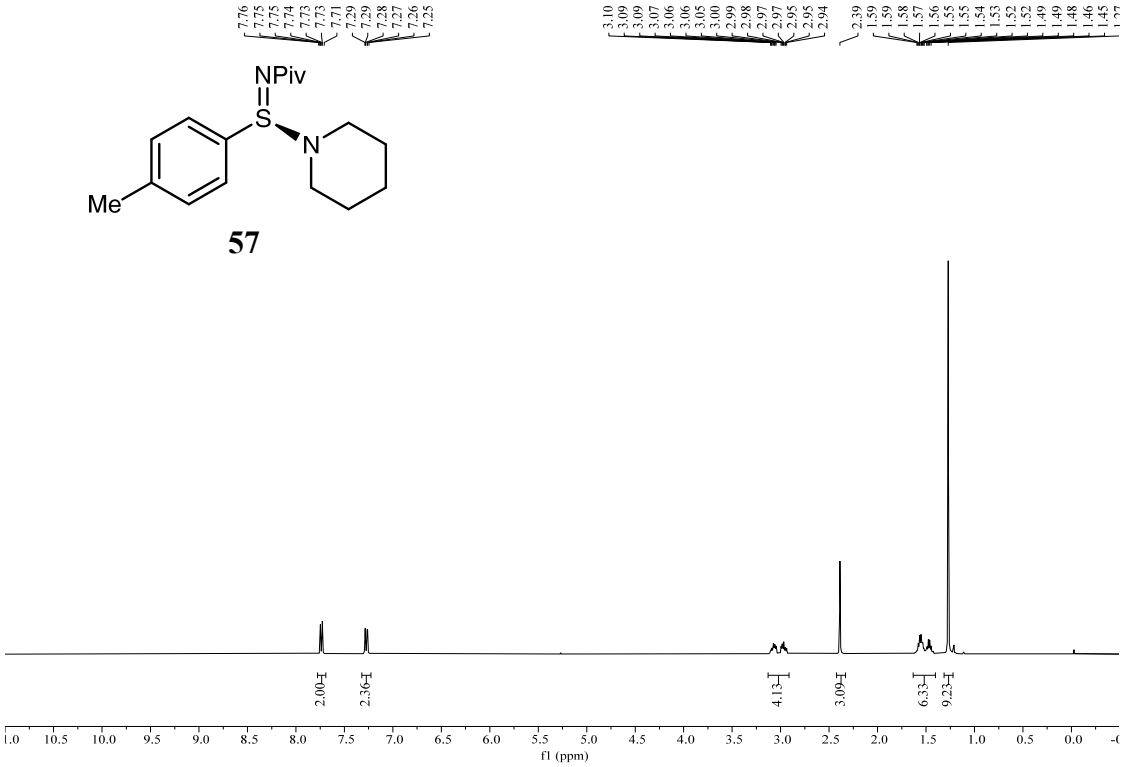
56

^{13}C NMR of 56 (100 MHz, $CDCl_3$)

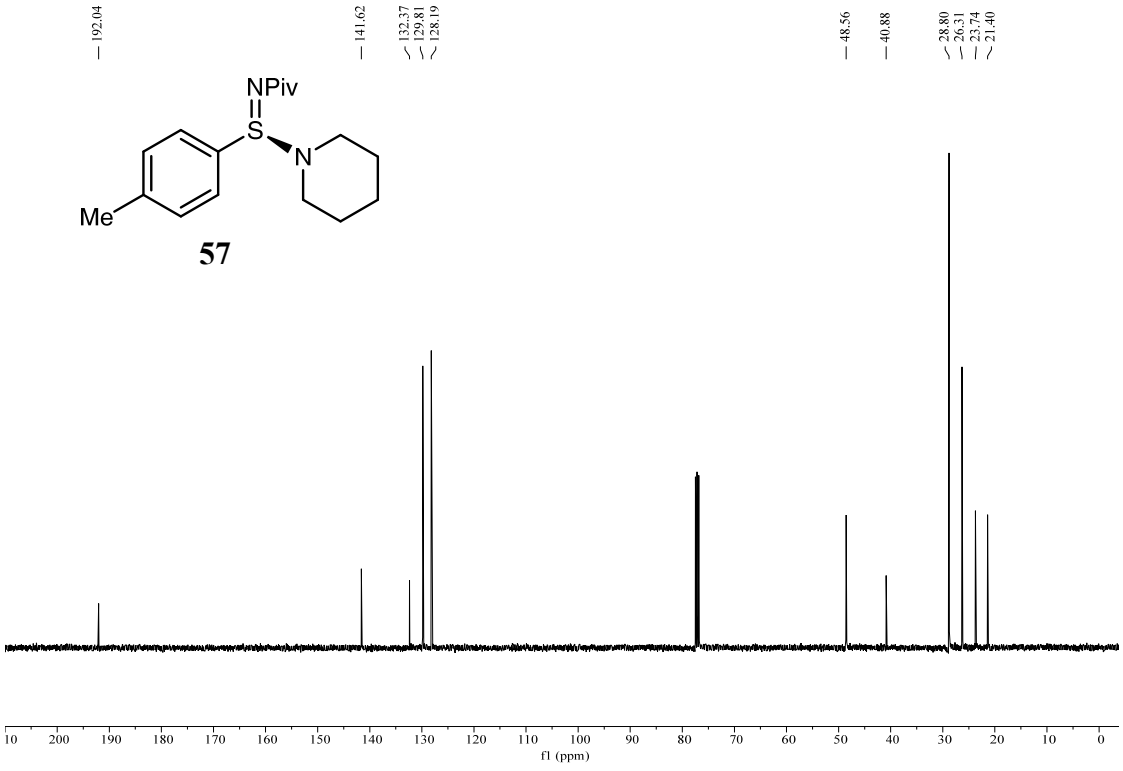


56

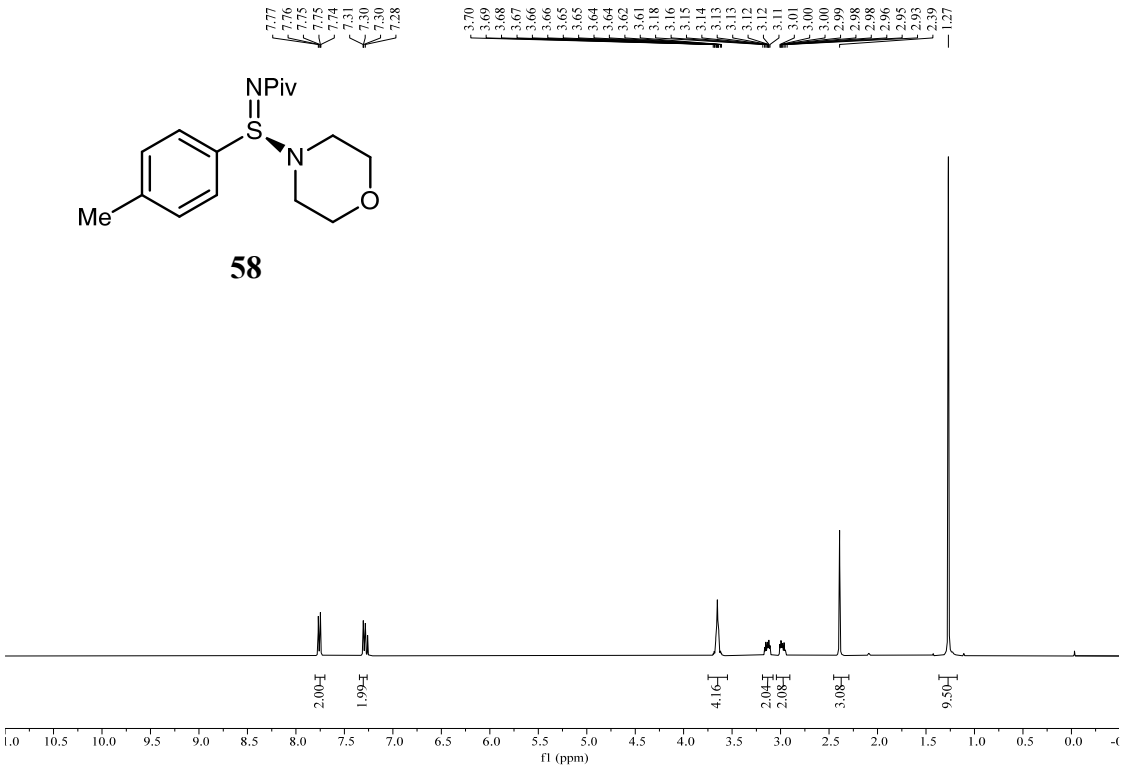
^{1}H NMR of 57 (400 MHz, $CDCl_3$)



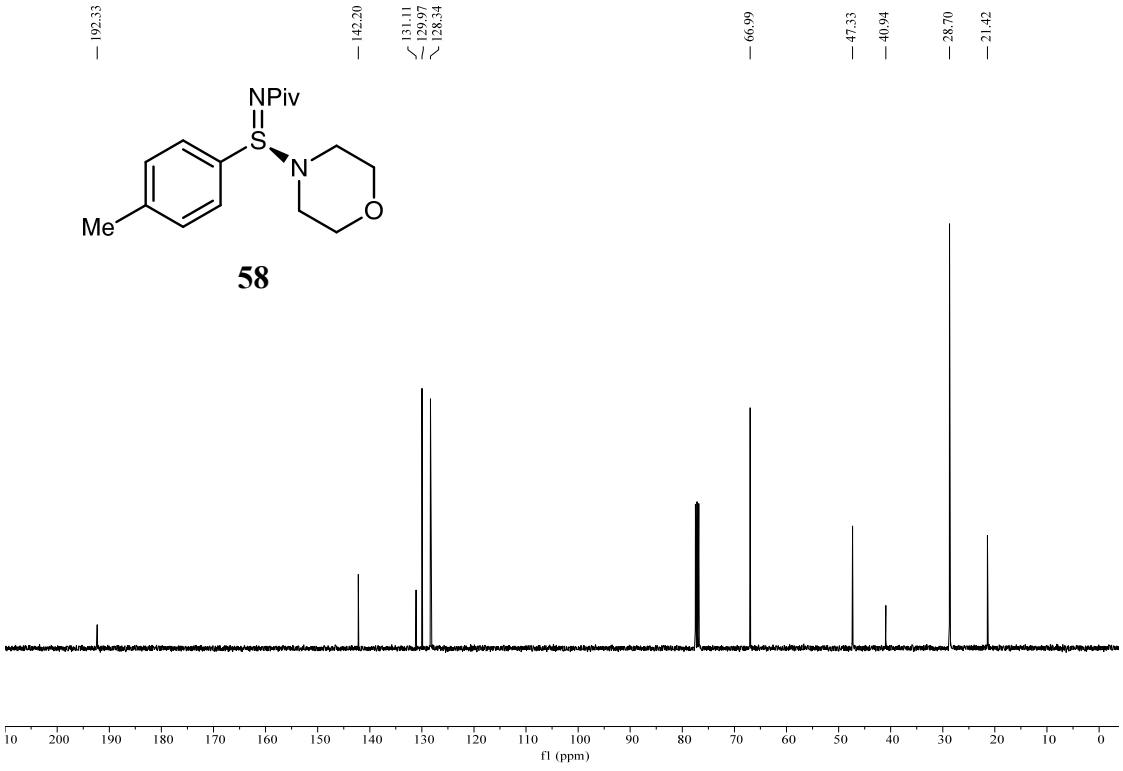
^{13}C NMR of 57 (100 MHz, $CDCl_3$)



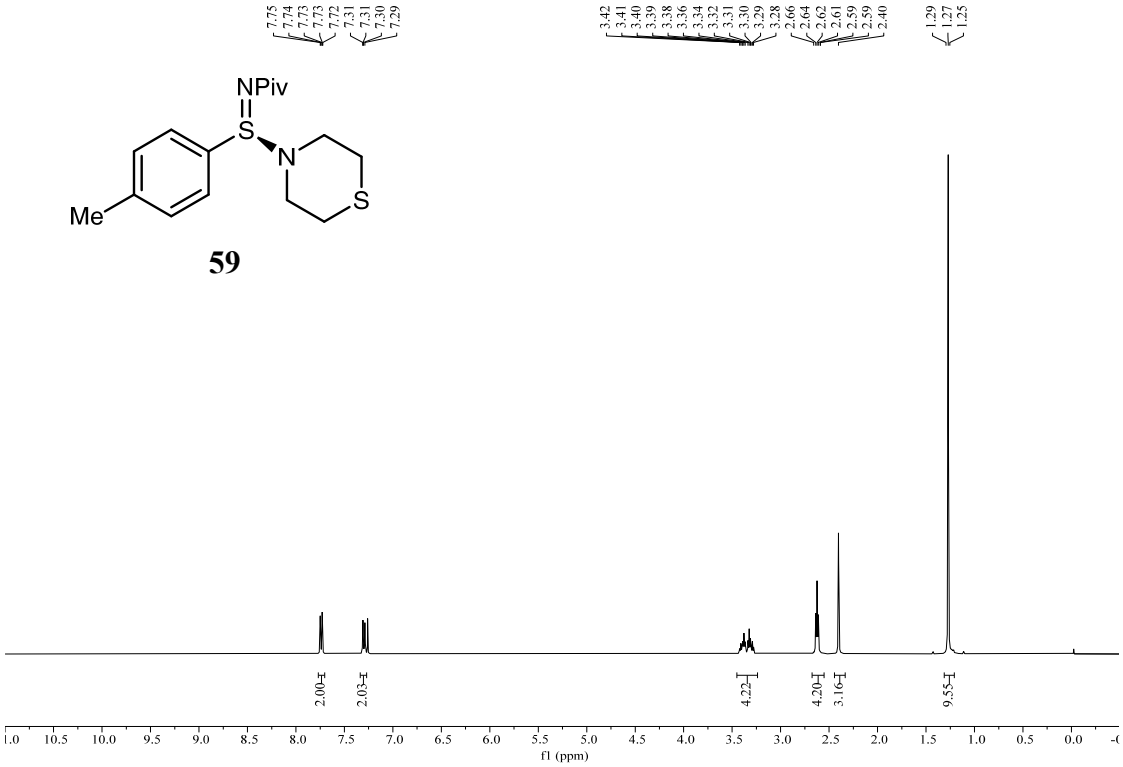
^{1}H NMR of 58 (400 MHz, $CDCl_3$)



^{13}C NMR of 58 (100 MHz, $CDCl_3$)

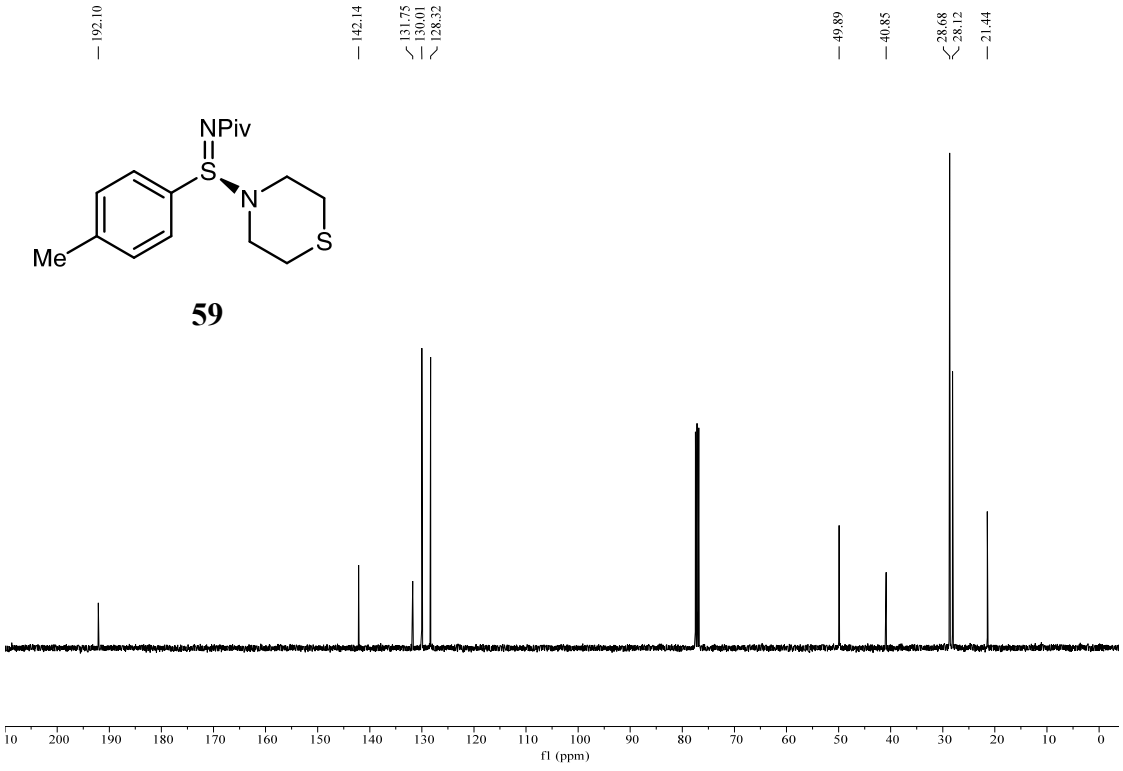


^{1}H NMR of 59 (400 MHz, $CDCl_3$)



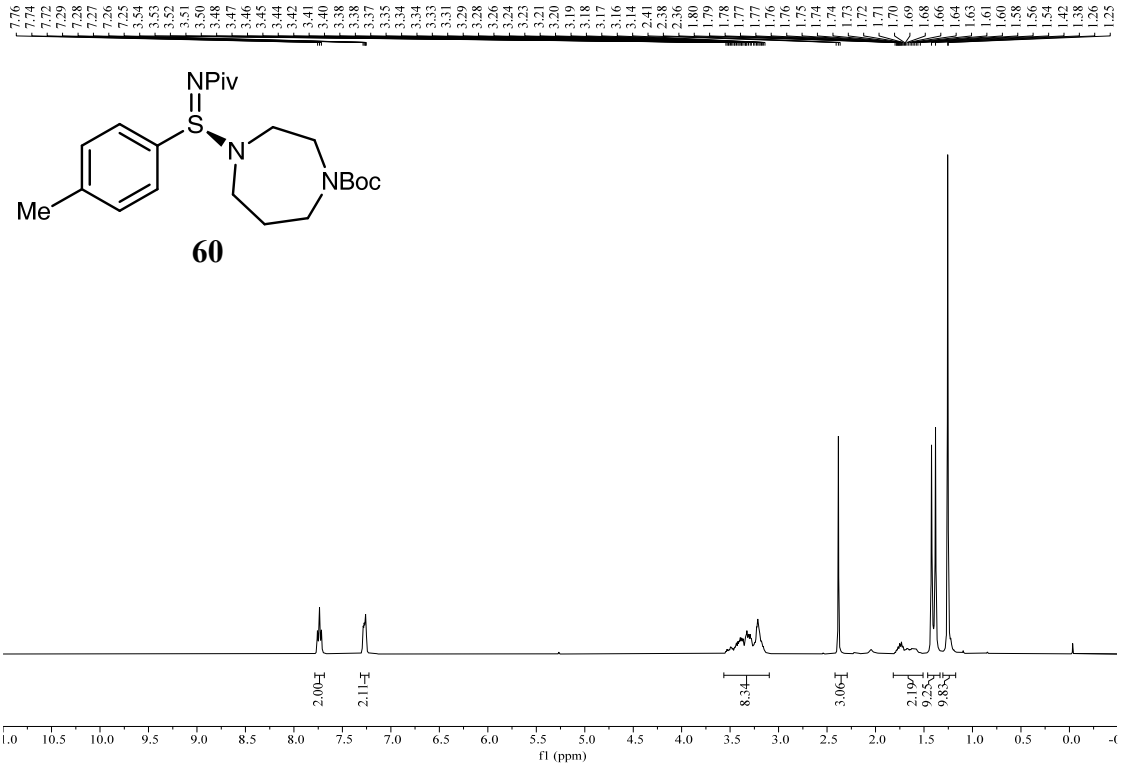
59

^{13}C NMR of 59 (100 MHz, $CDCl_3$)

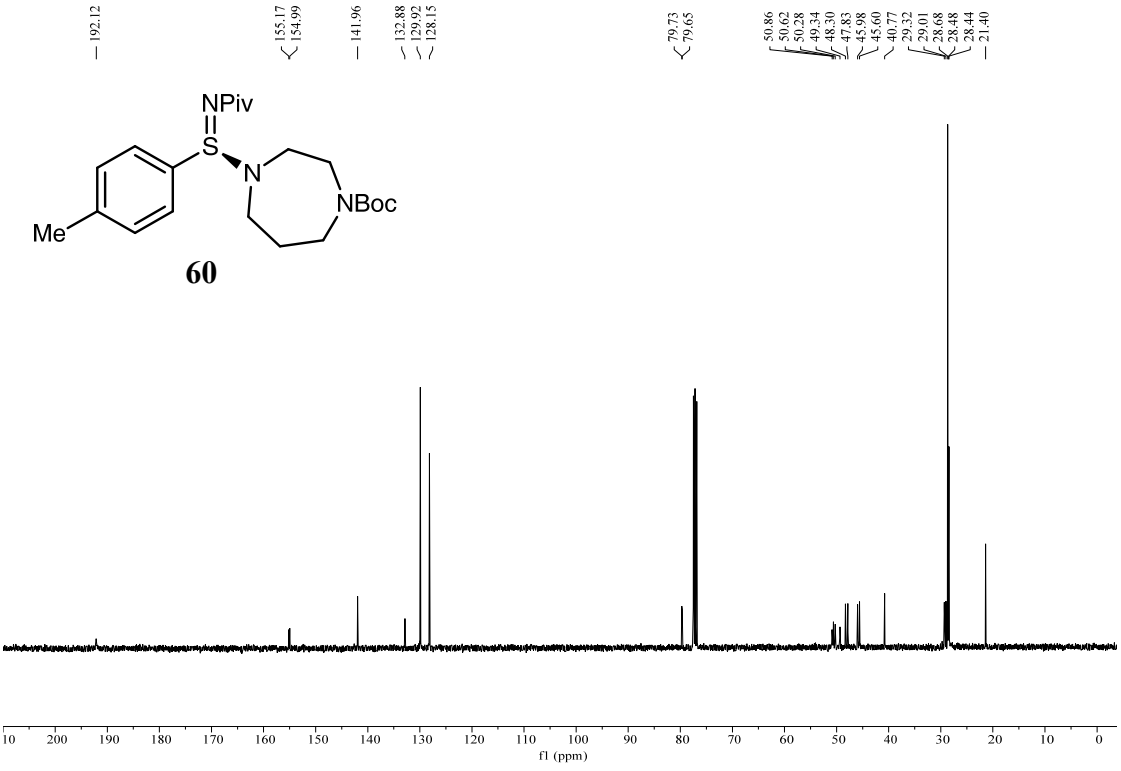


59

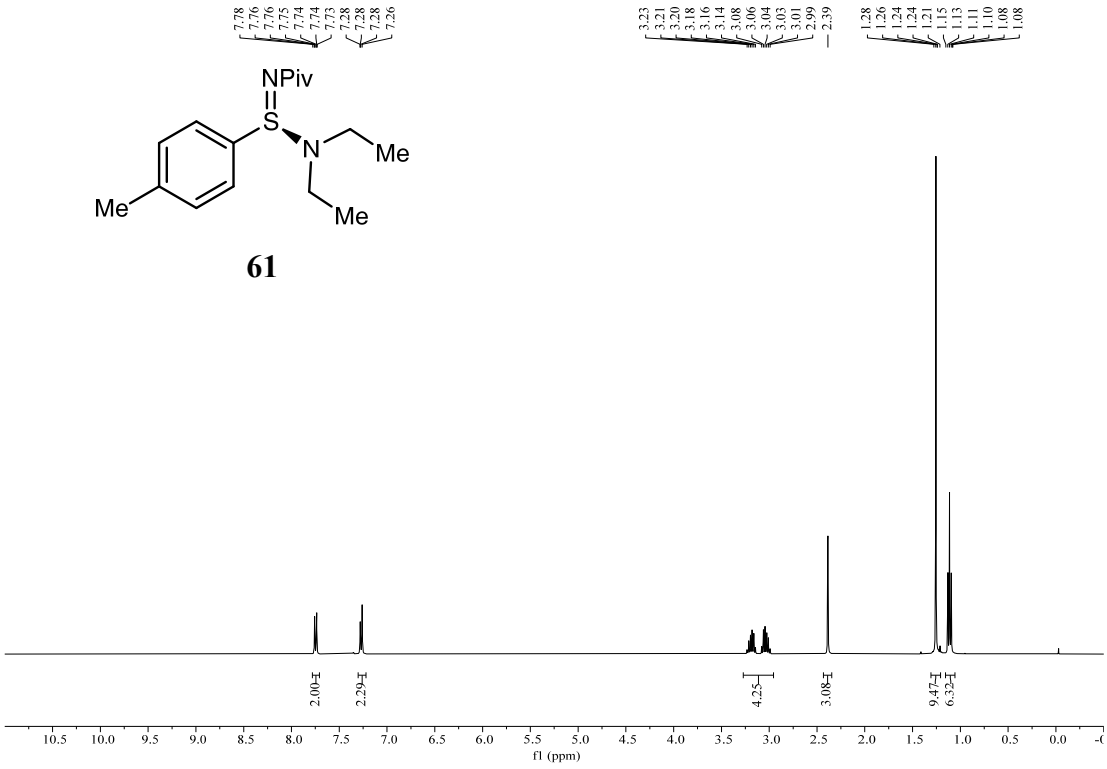
^{1}H NMR of 60 (400 MHz, $CDCl_3$)



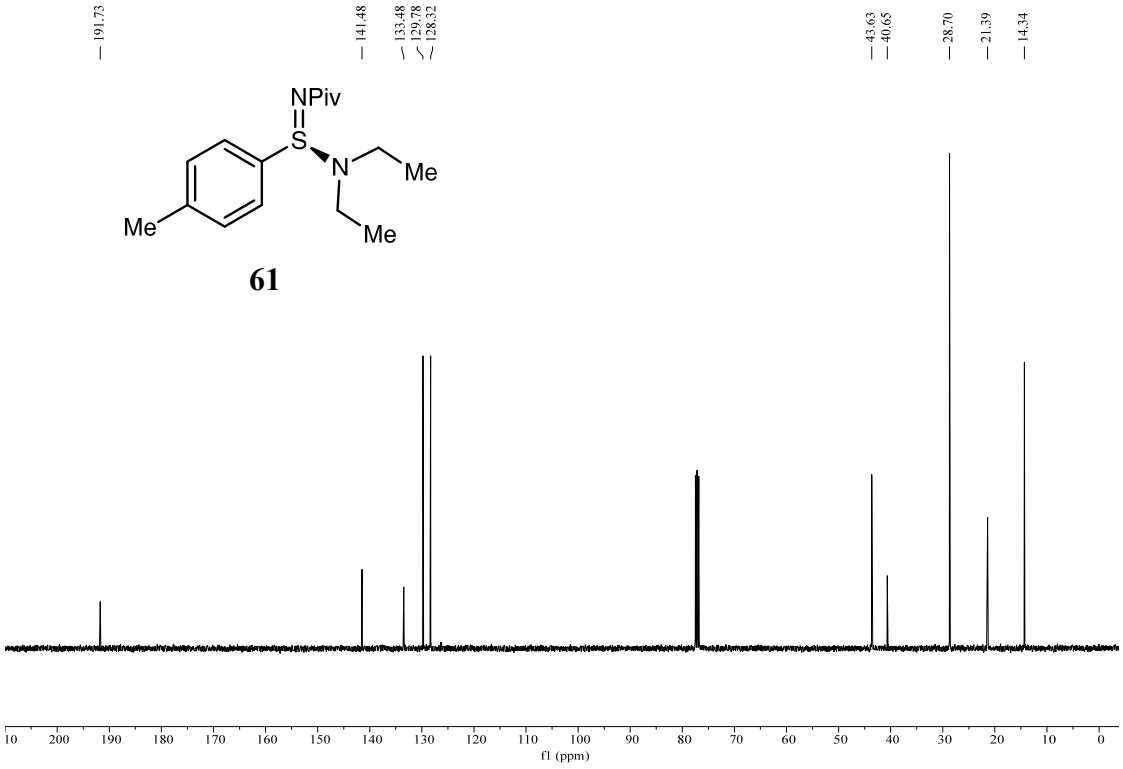
^{13}C NMR of 60 ($CDCl_3$)



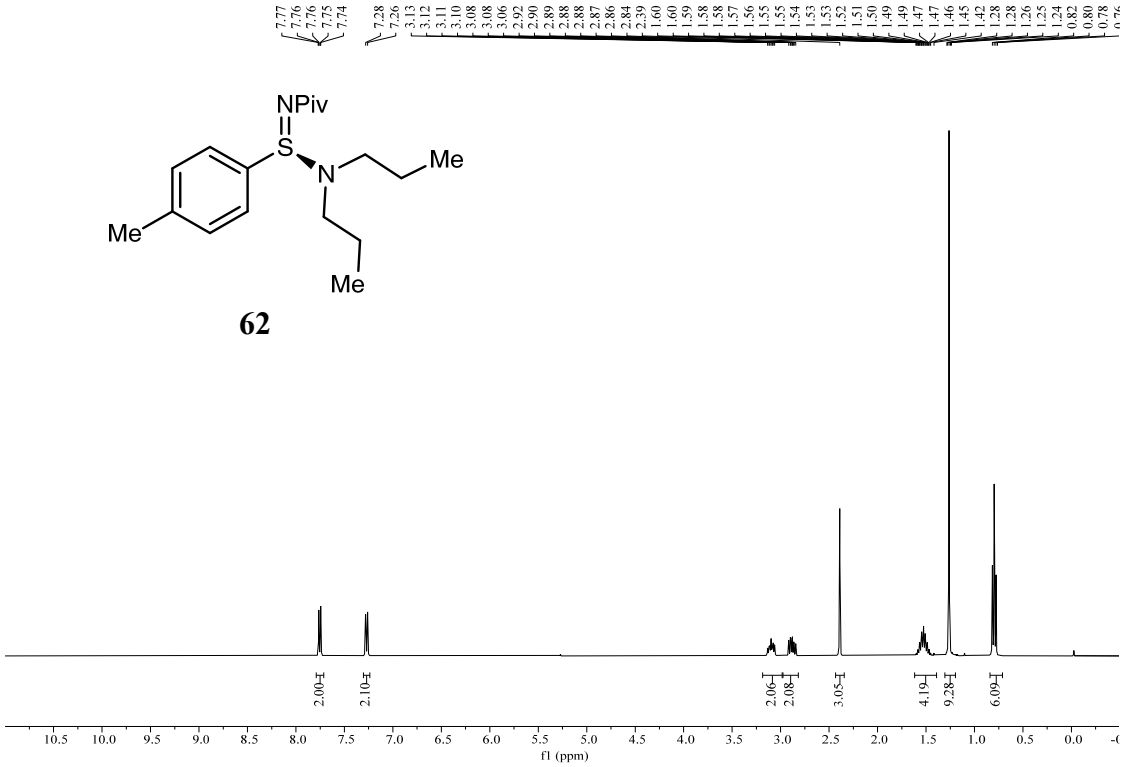
^{1}H NMR of 61 (400 MHz, $CDCl_3$)



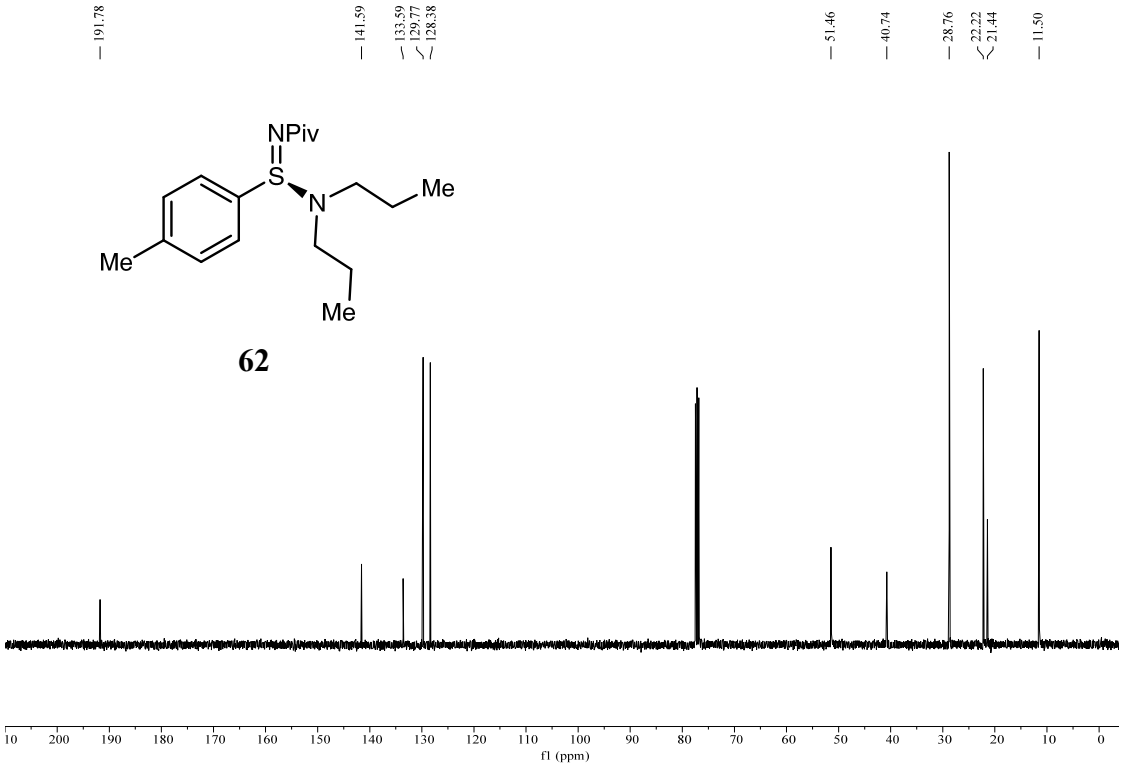
^{13}C NMR of 61 (100 MHz, $CDCl_3$)



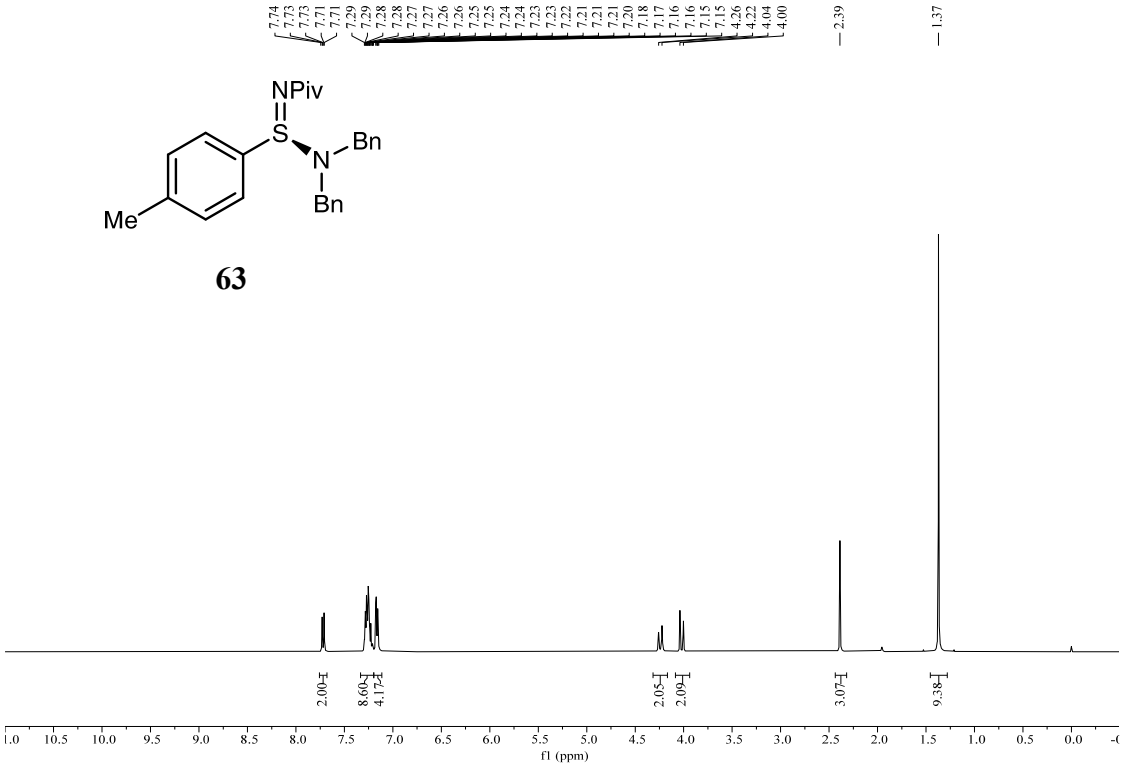
^{1}H NMR of 62 (400 MHz, $CDCl_3$)



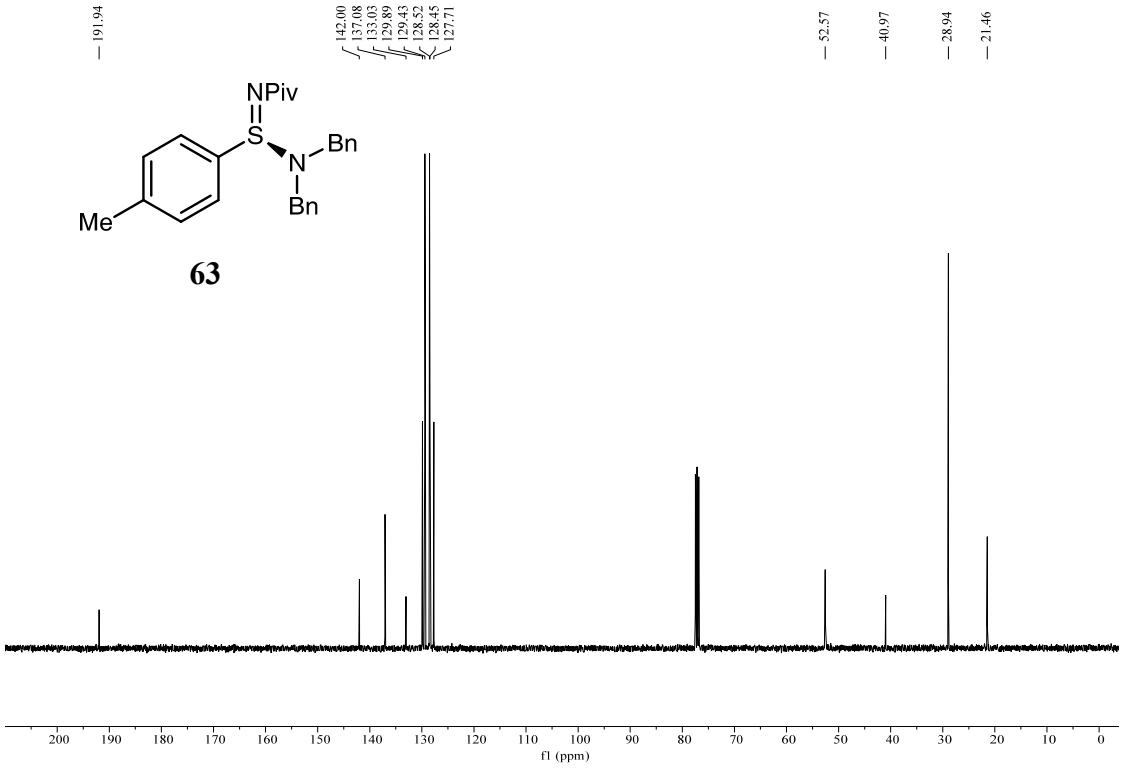
^{13}C NMR of 62 (100 MHz, $CDCl_3$)



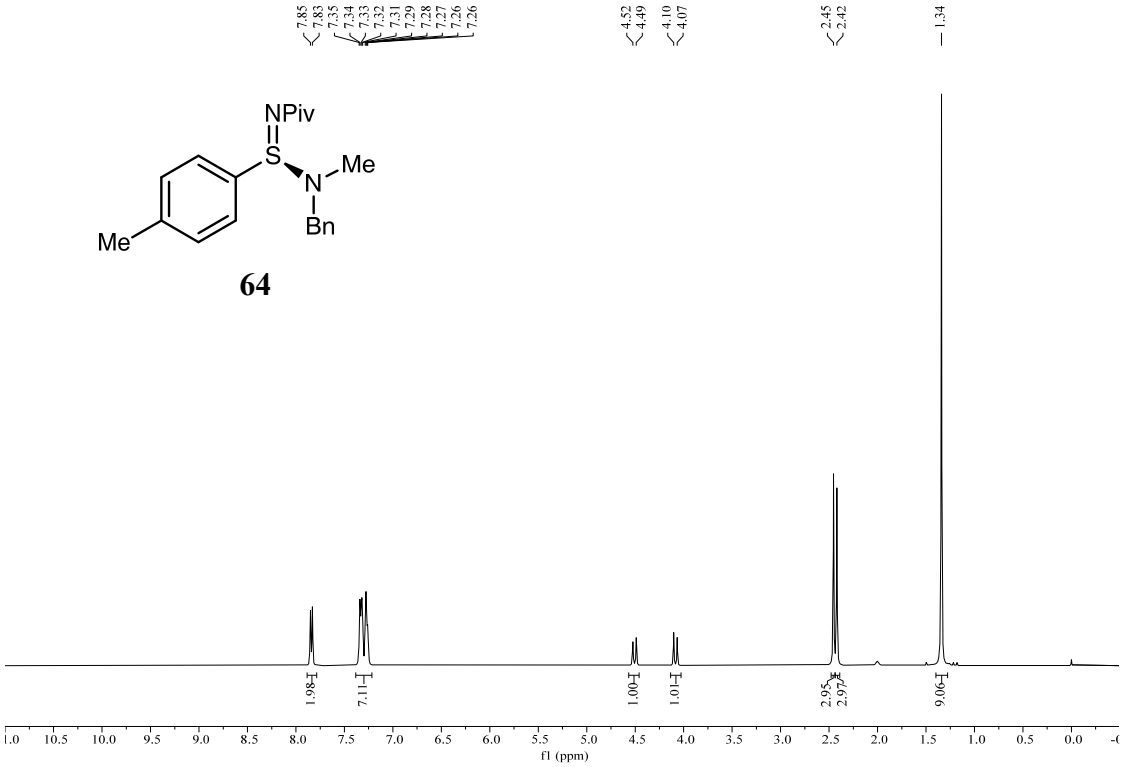
^{1}H NMR of 63 (400 MHz, $CDCl_3$)



^{13}C NMR of 63 (100 MHz, $CDCl_3$)

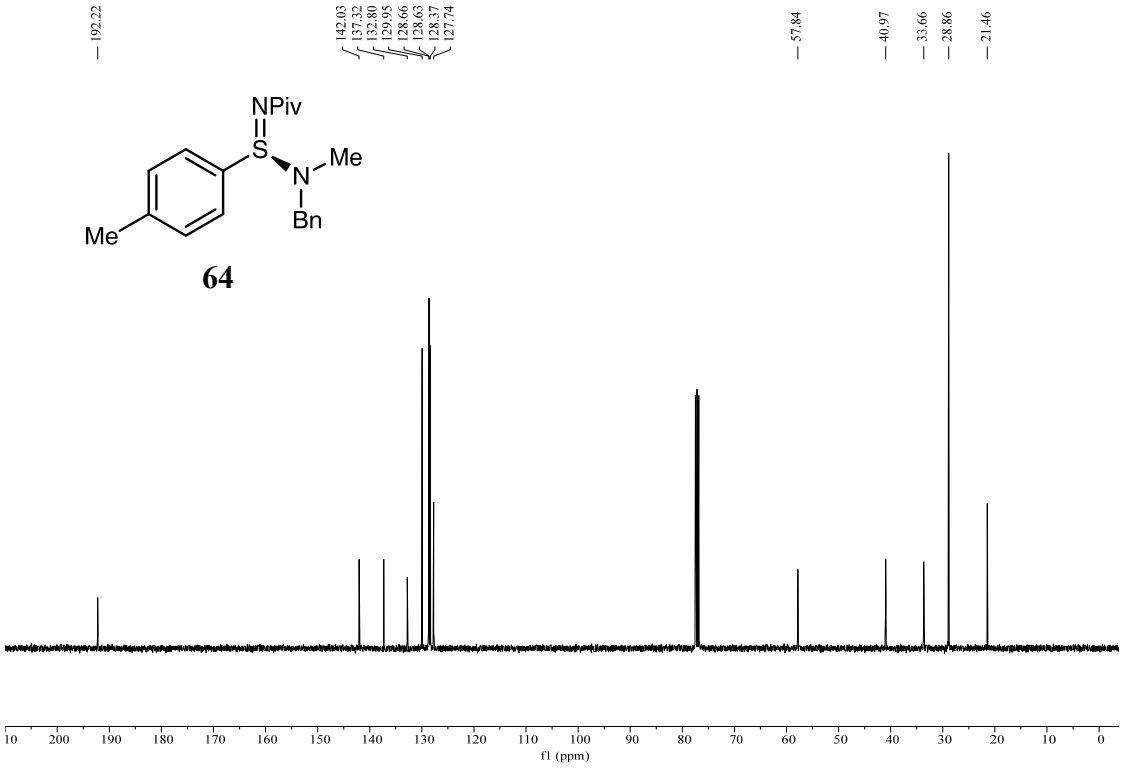


^{1}H NMR of 64 (400 MHz, $CDCl_3$)



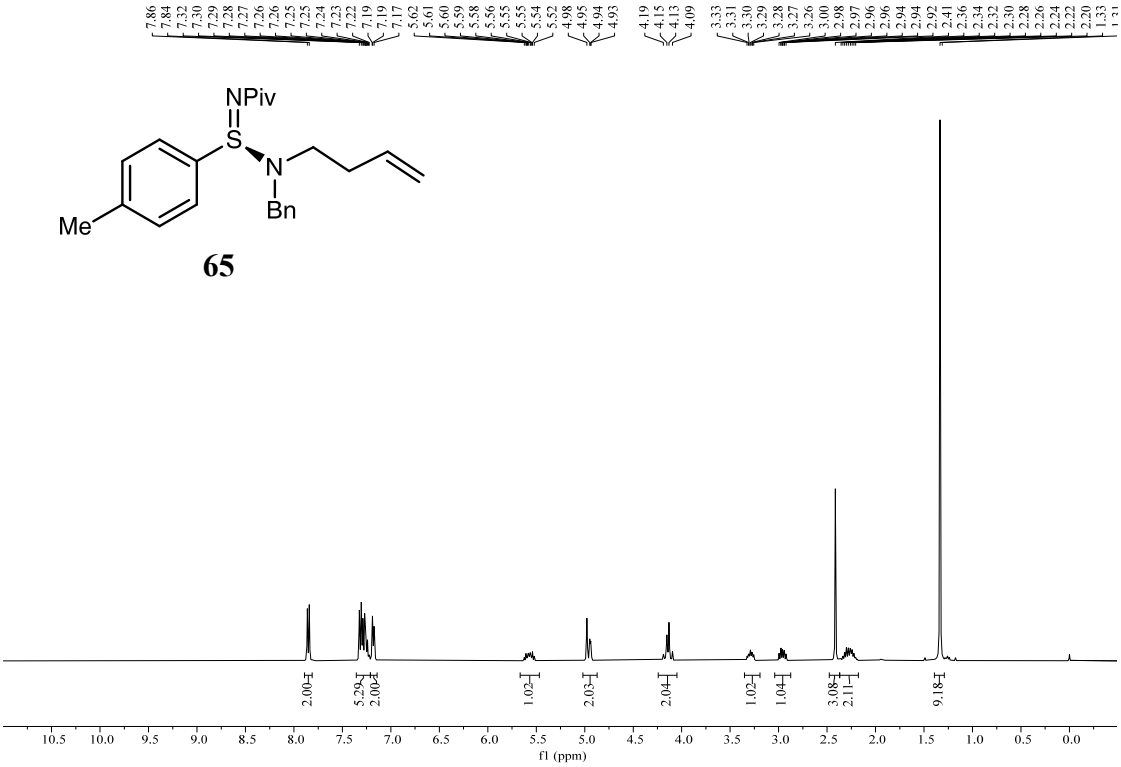
64

^{13}C NMR of 64 (100 MHz, $CDCl_3$)

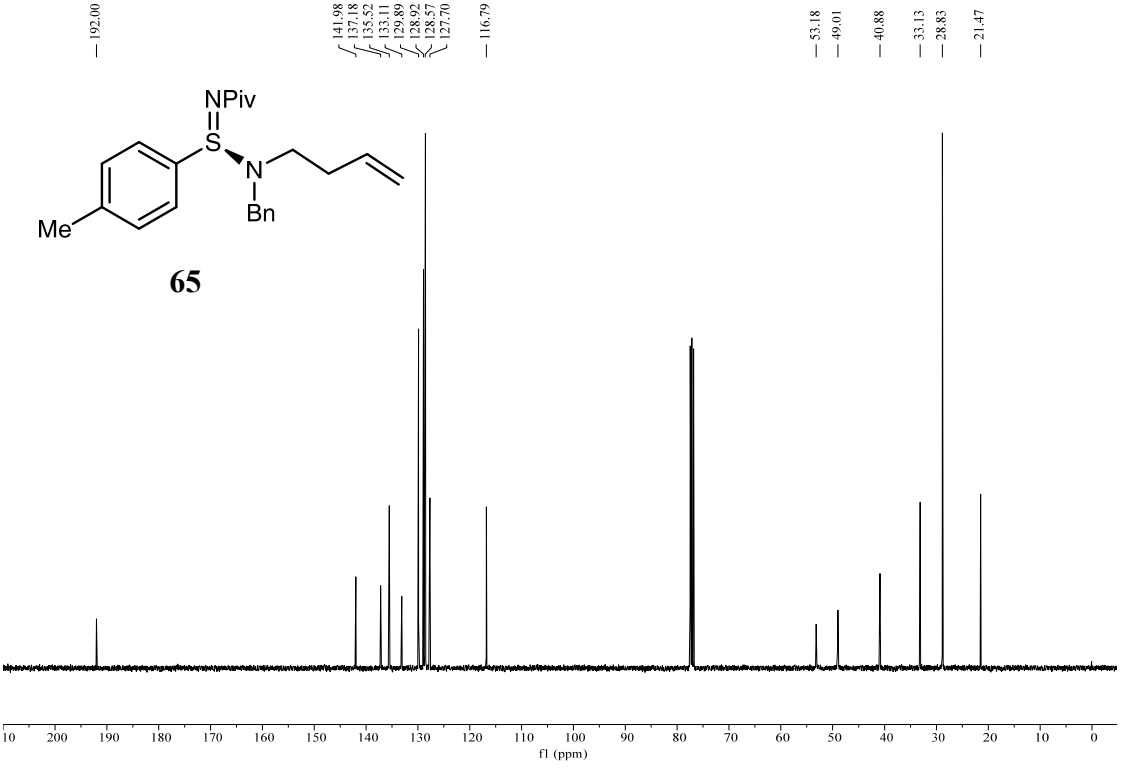


64

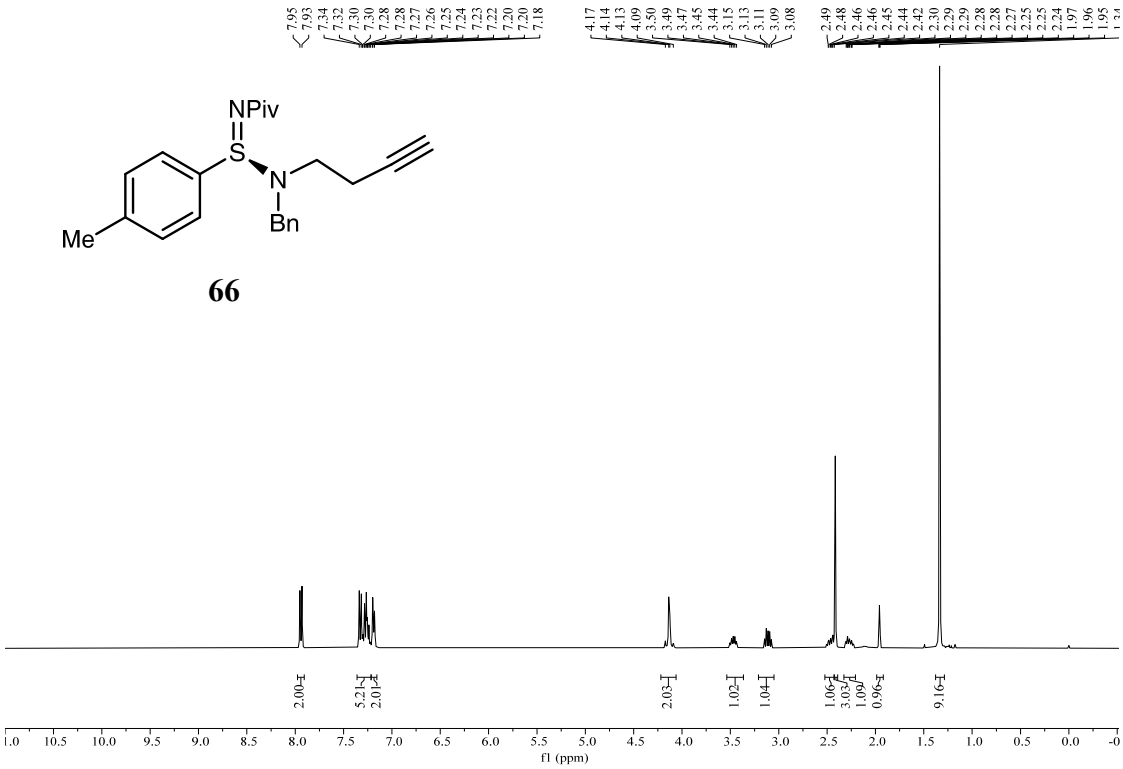
^{1}H NMR of 65 (400 MHz, $CDCl_3$)



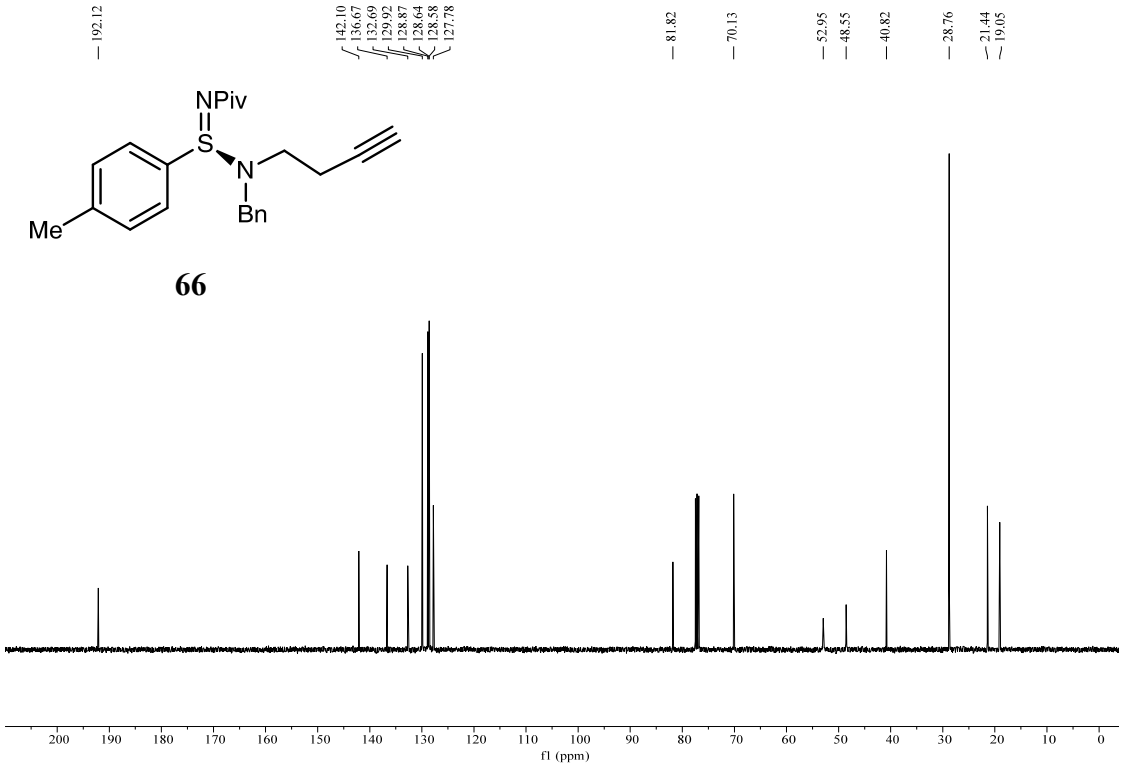
^{13}C NMR of 65 (100 MHz, $CDCl_3$)



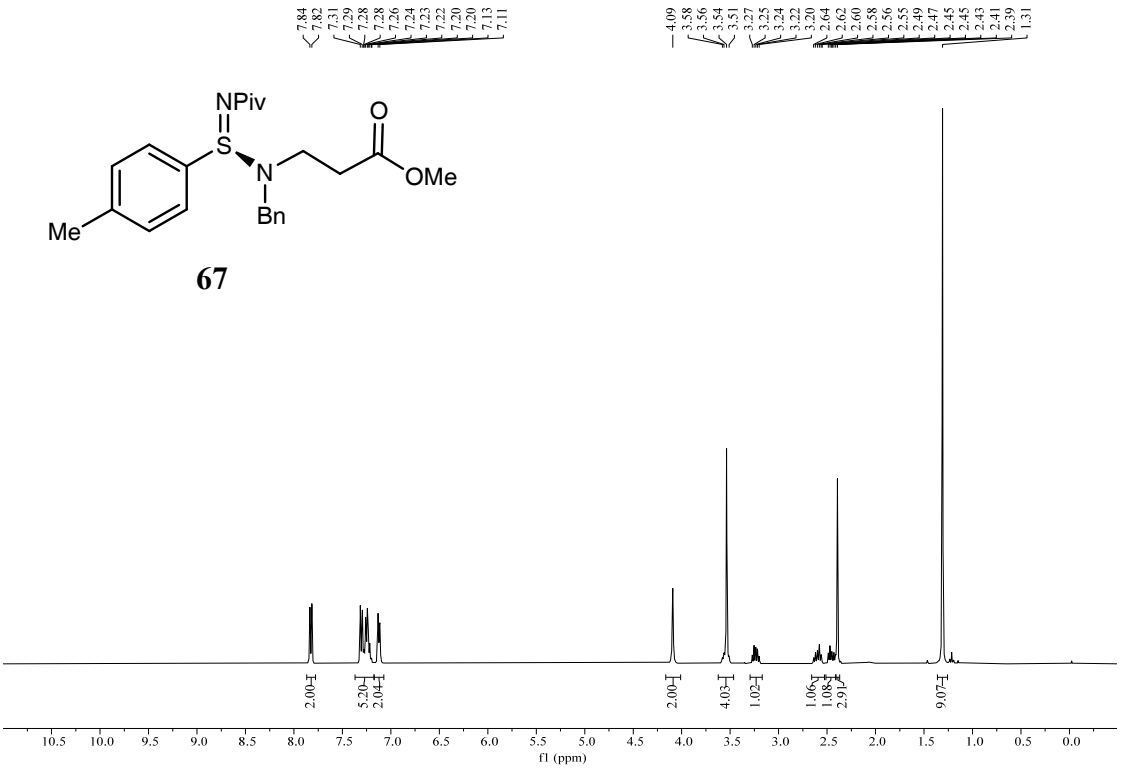
^{1}H NMR of 66 (400 MHz, $CDCl_3$)



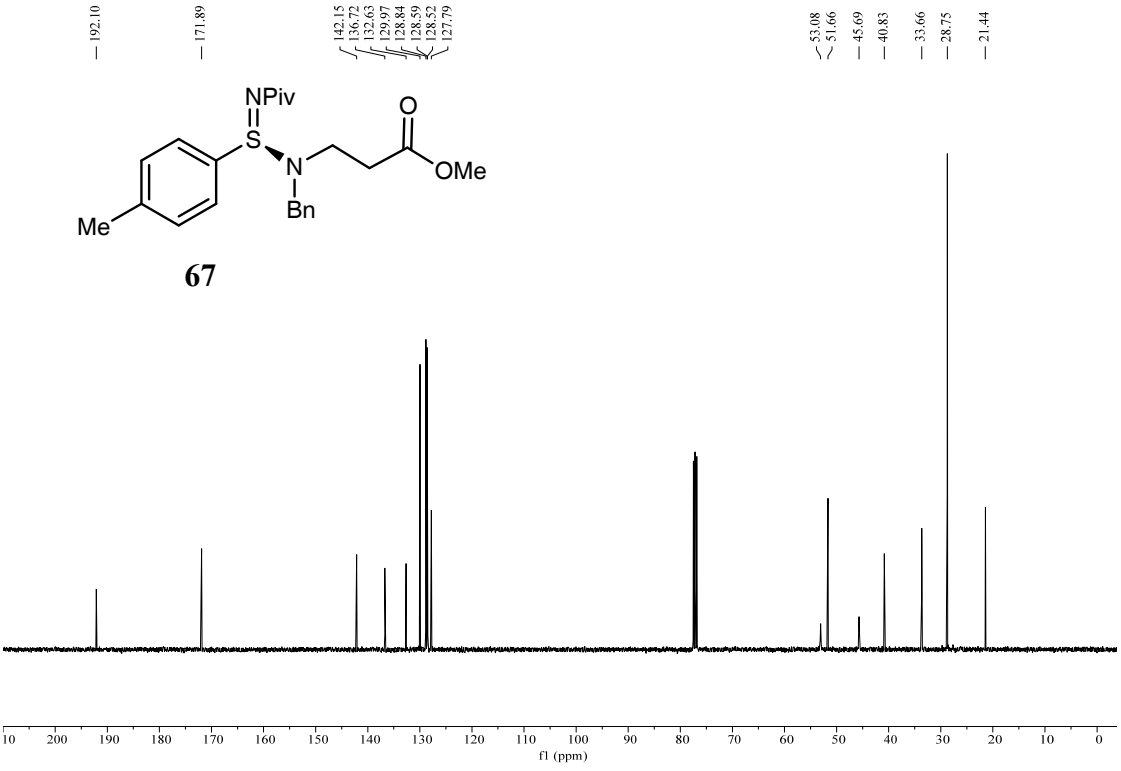
^{13}C NMR of 66 (100 MHz, $CDCl_3$)



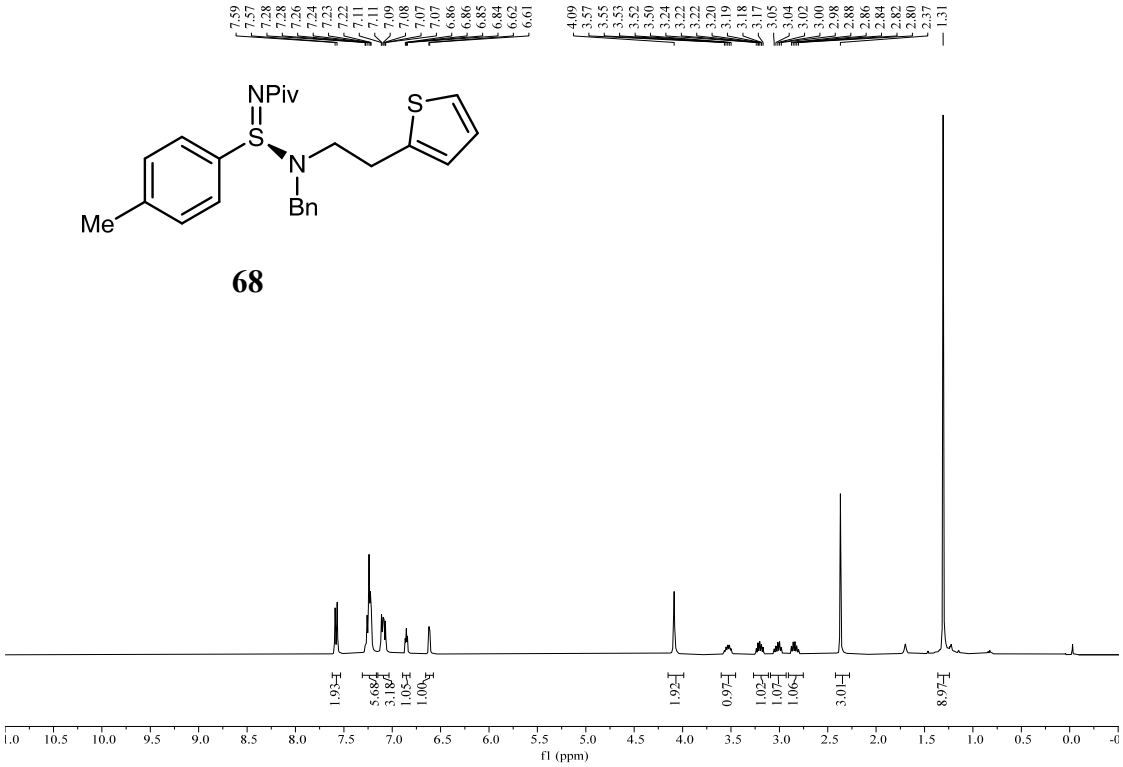
^{1}H NMR of 67 (400 MHz, $CDCl_3$)



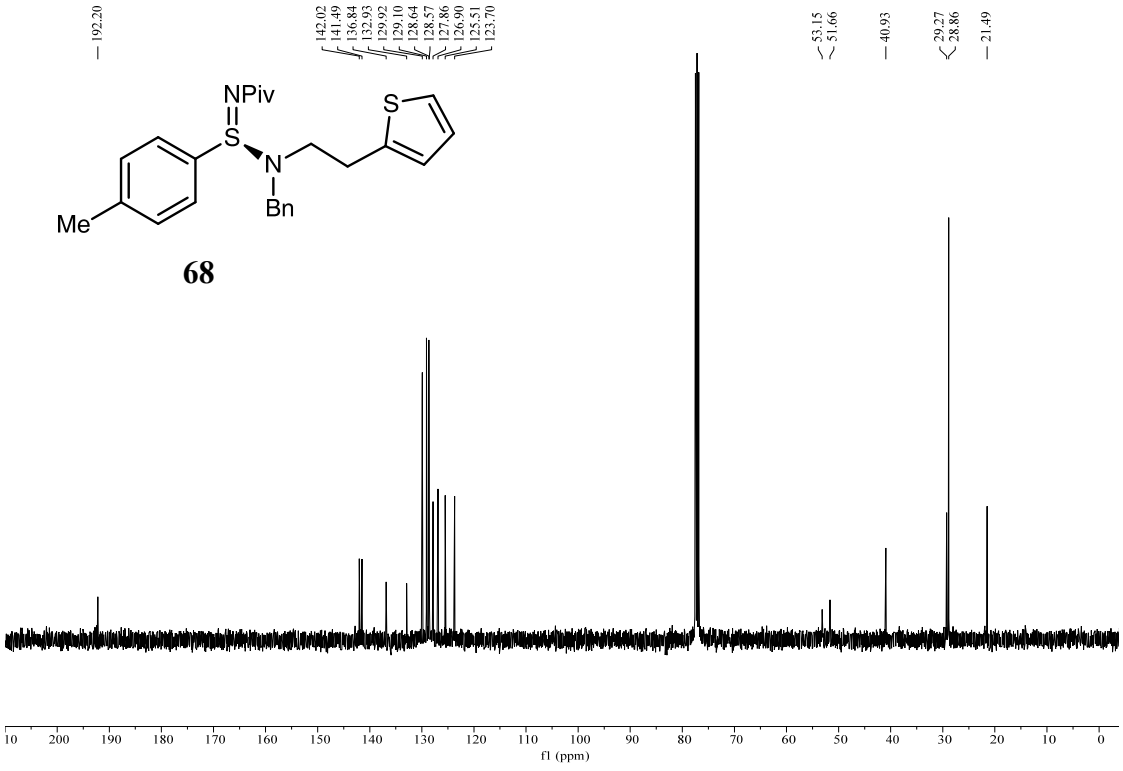
^{13}C NMR of 67 (100 MHz, $CDCl_3$)



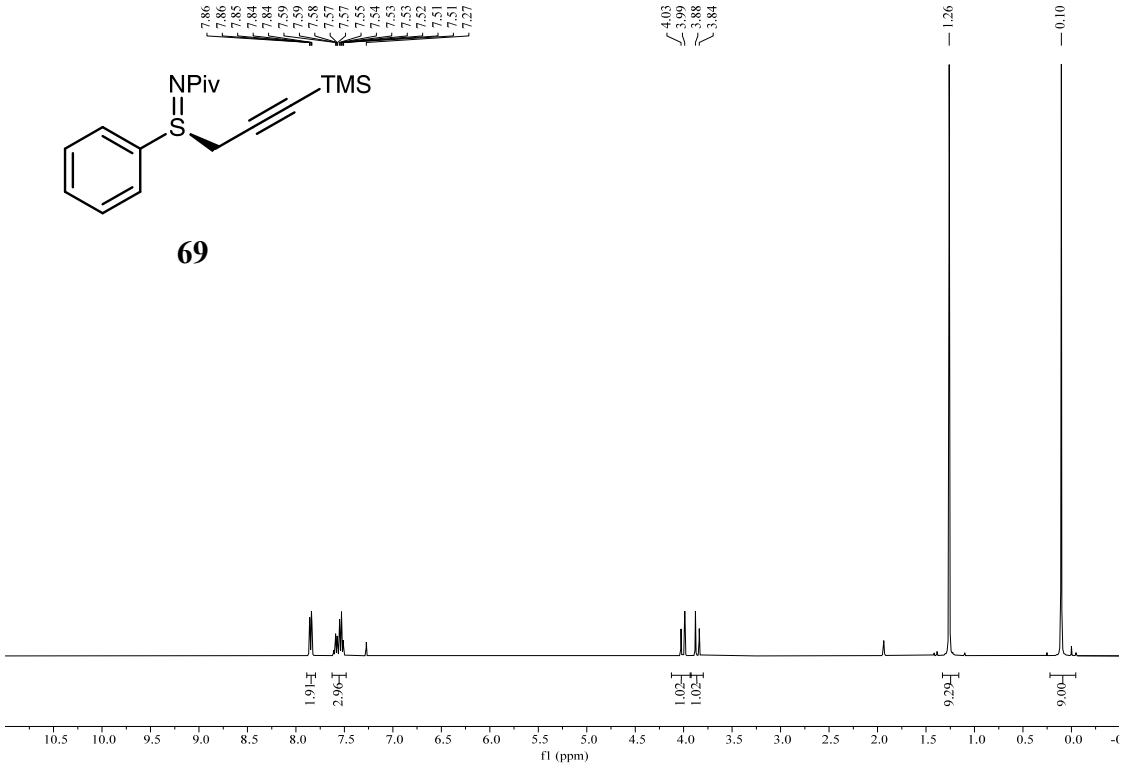
^{1}H NMR of 68 (400 MHz, $CDCl_3$)



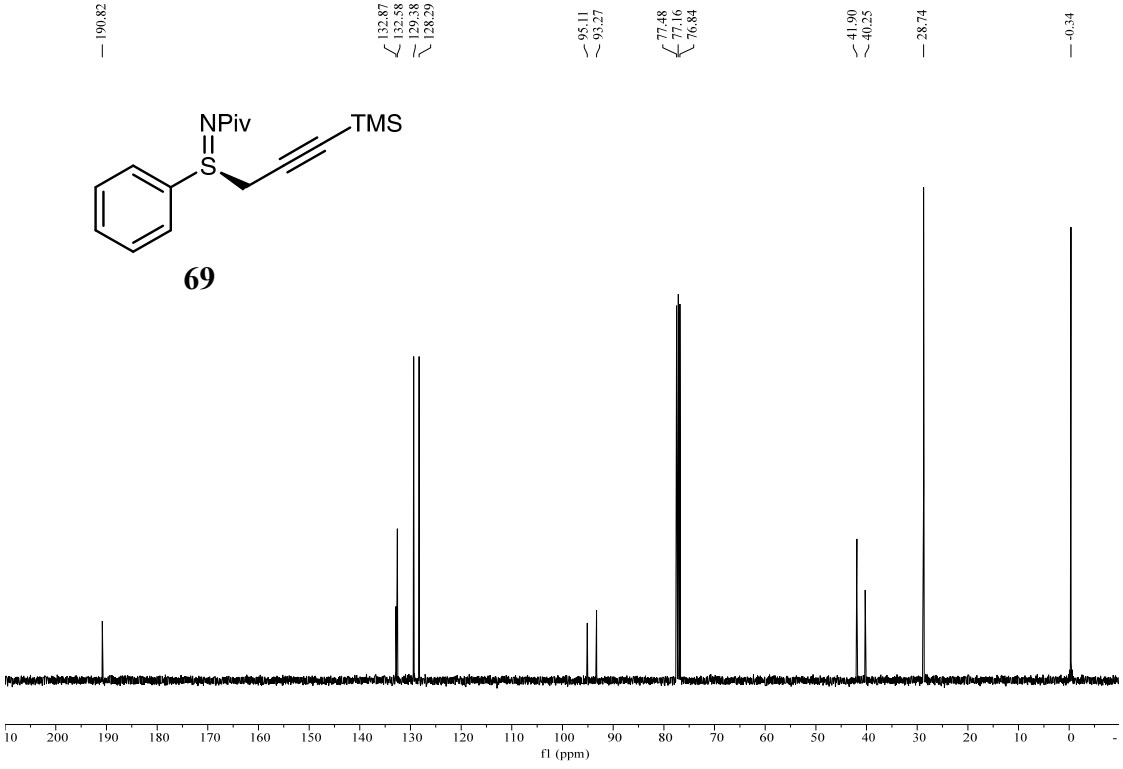
^{13}C NMR of 68 (100 MHz, $CDCl_3$)



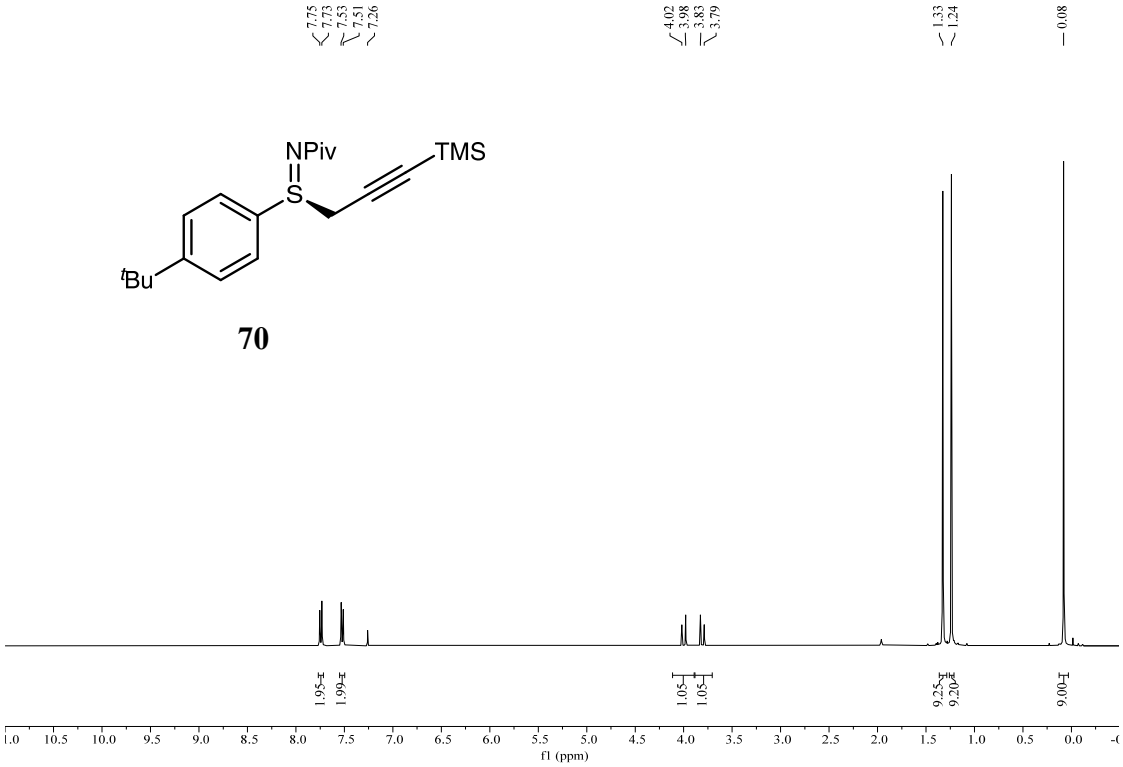
^{1}H NMR of 69 (400 MHz, $CDCl_3$)



^{13}C NMR of 69 (100 MHz, $CDCl_3$)

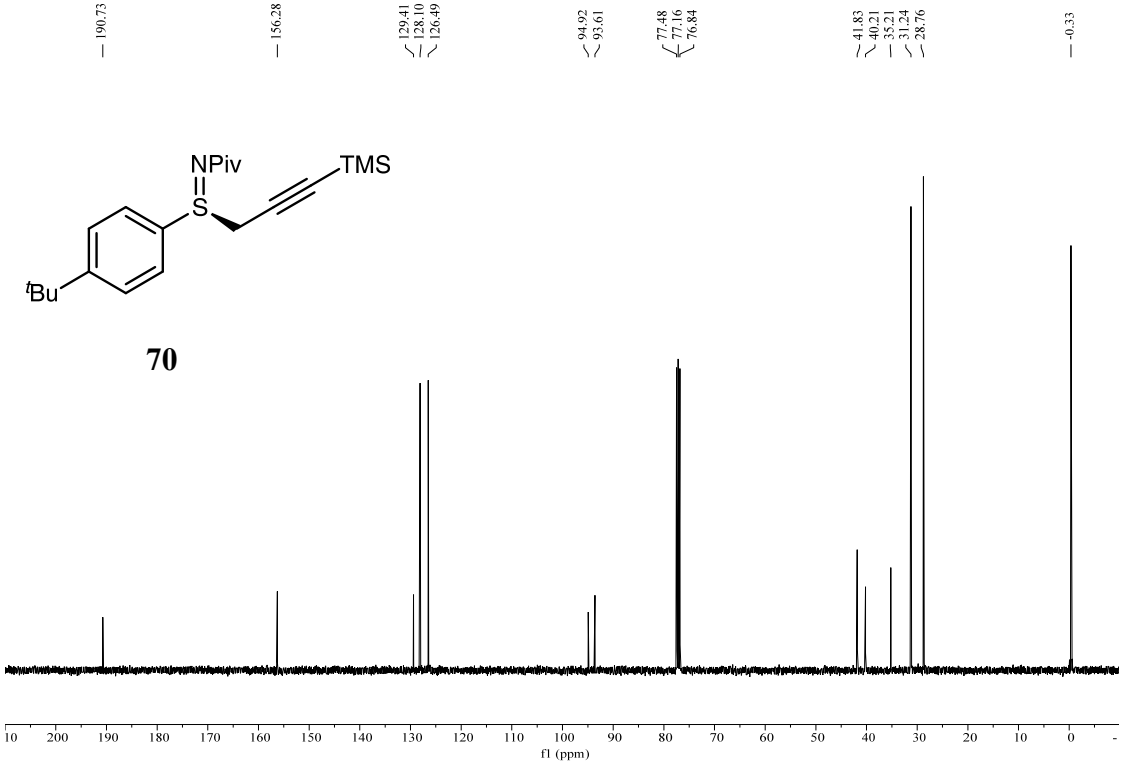


^{1}H NMR of 70 (400 MHz, $CDCl_3$)



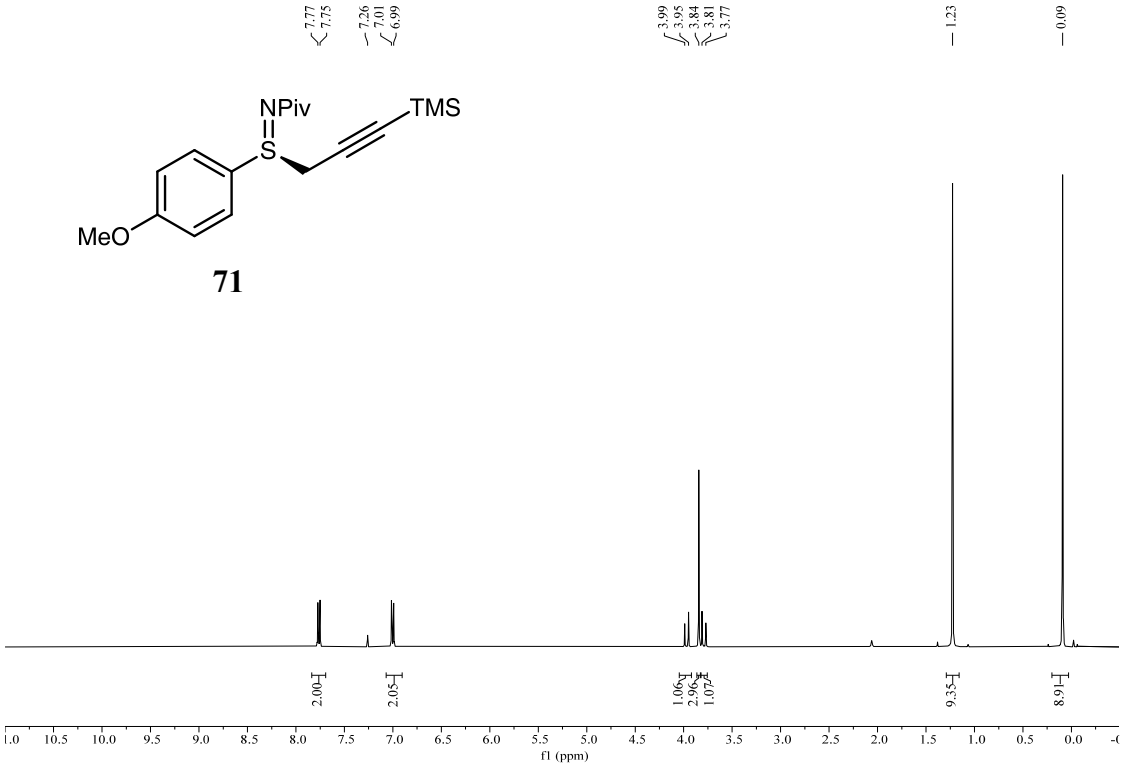
70

^{13}C NMR of 70 (100 MHz, $CDCl_3$)



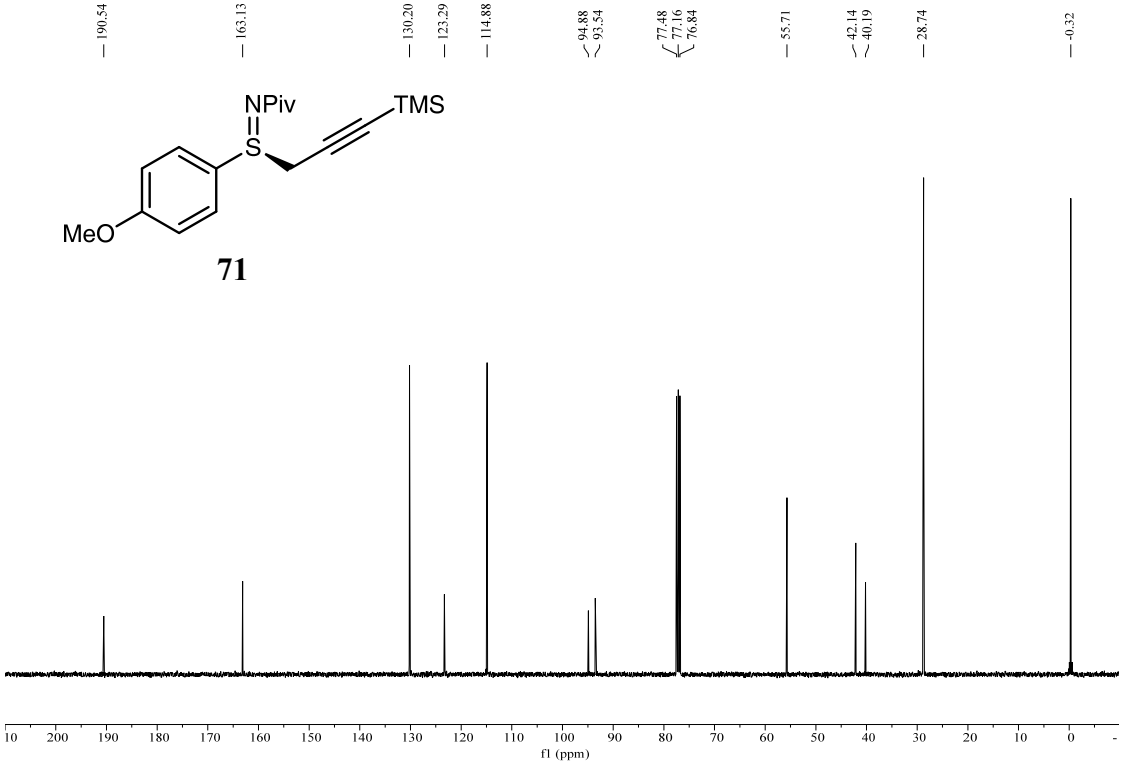
70

^{1}H NMR of 71 (400 MHz, $CDCl_3$)



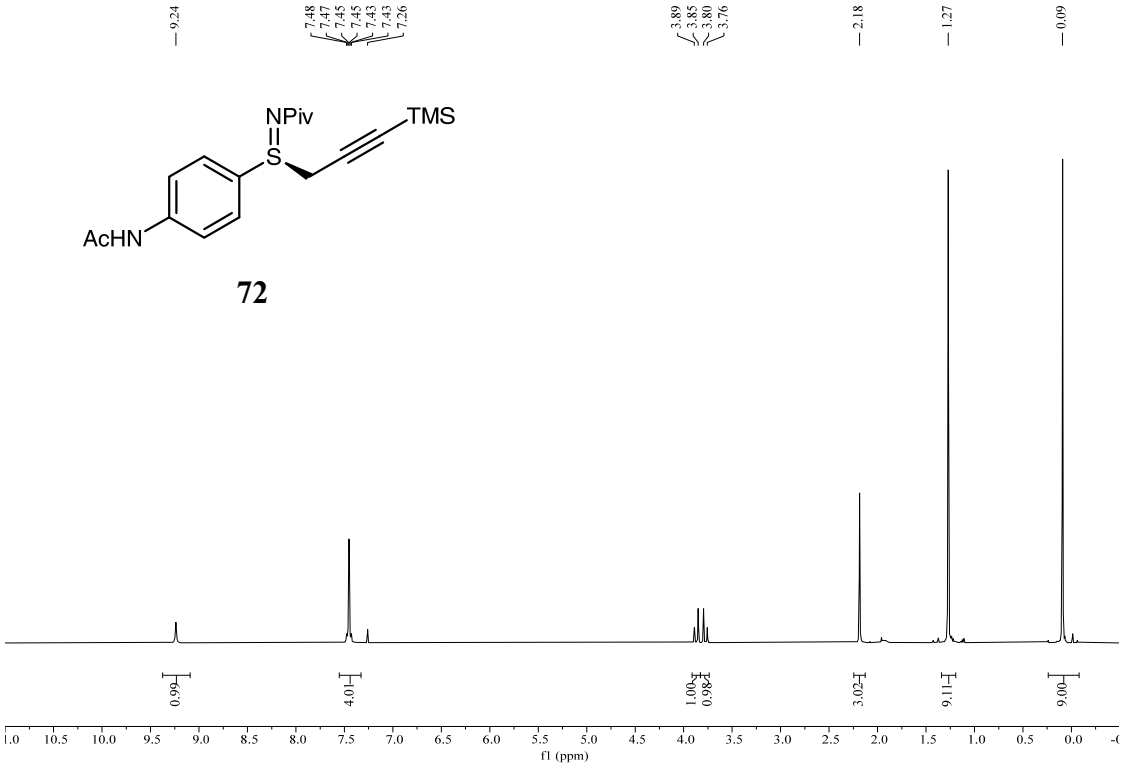
71

^{13}C NMR of 71 (100 MHz, $CDCl_3$)



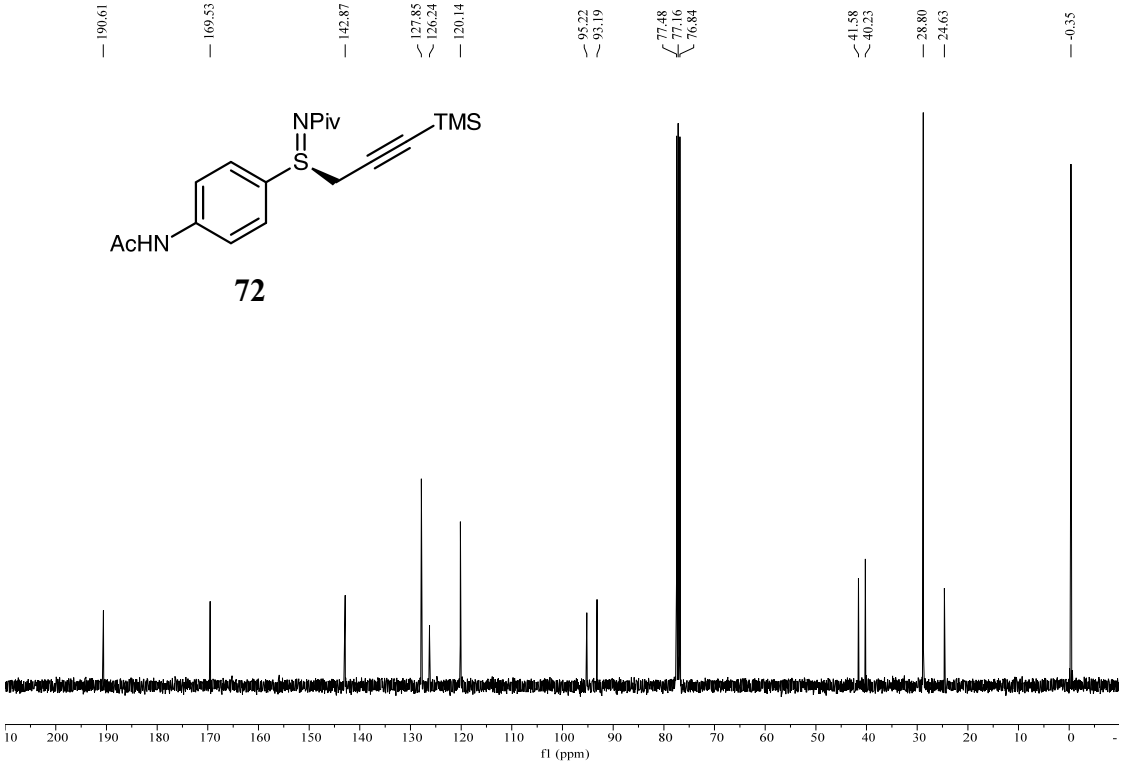
71

^{1}H NMR of 72 (400 MHz, $CDCl_3$)



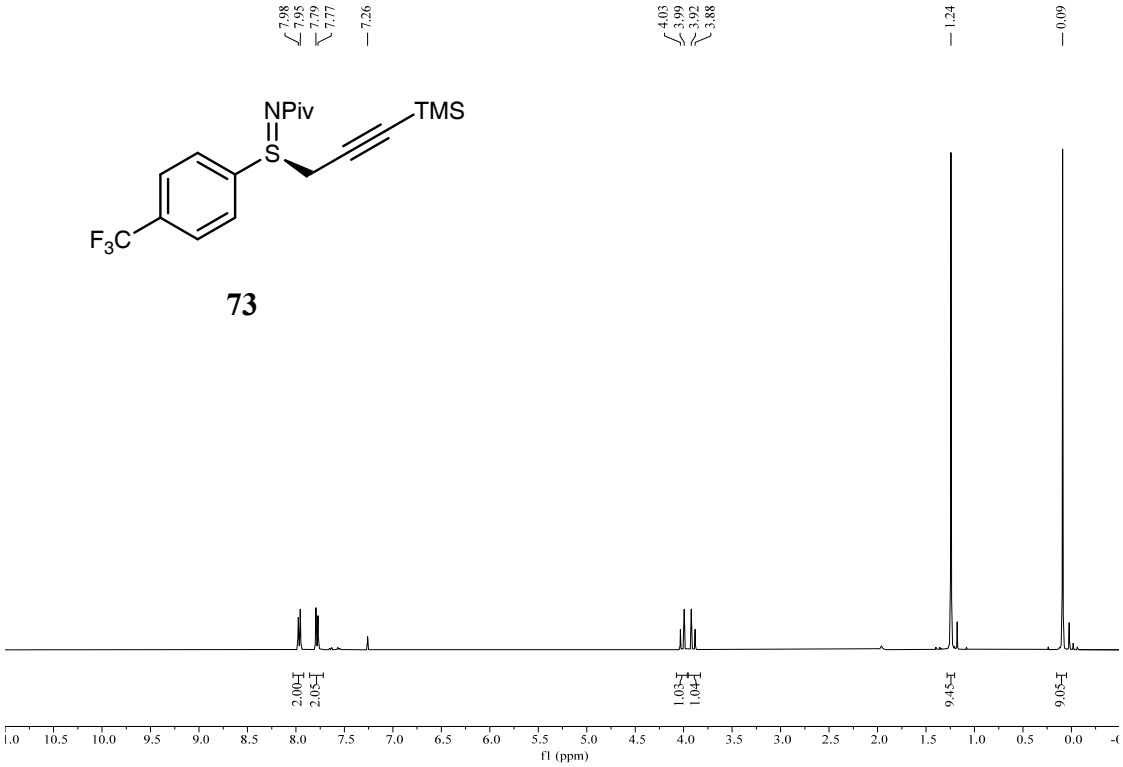
72

^{13}C NMR of 72 (100 MHz, $CDCl_3$)



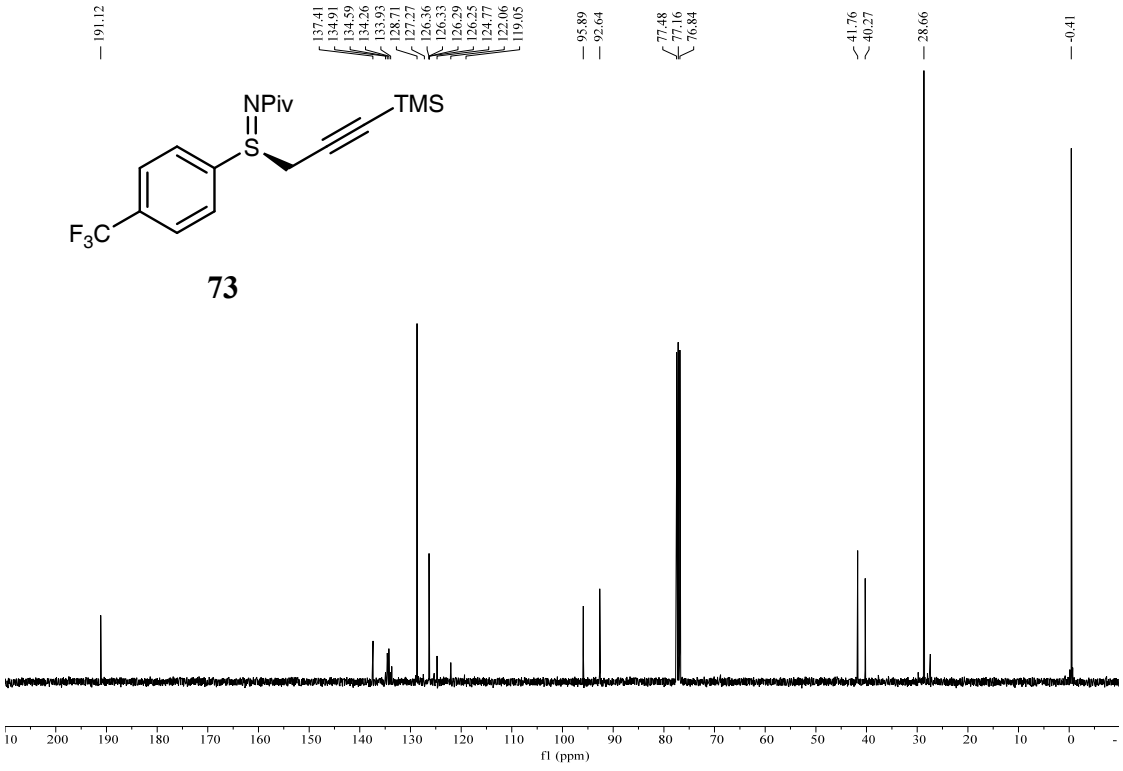
72

^{1}H NMR of 73 (400 MHz, $CDCl_3$)



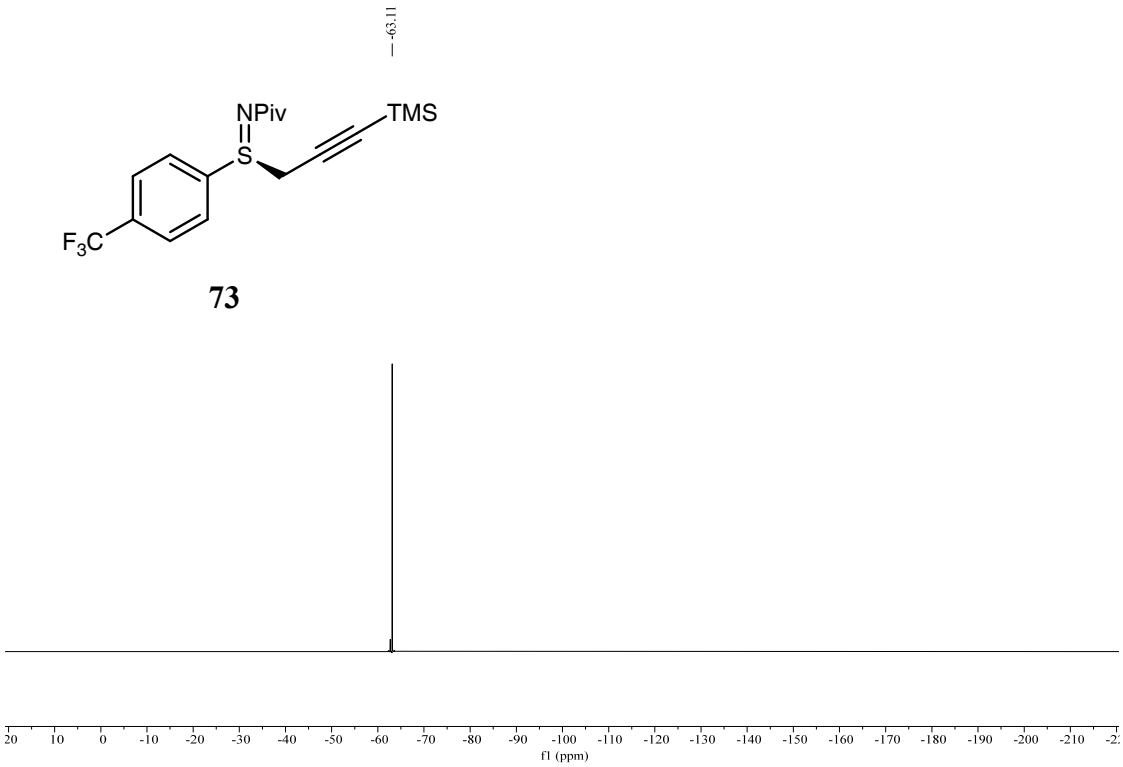
73

^{13}C NMR of 73 (100 MHz, $CDCl_3$)



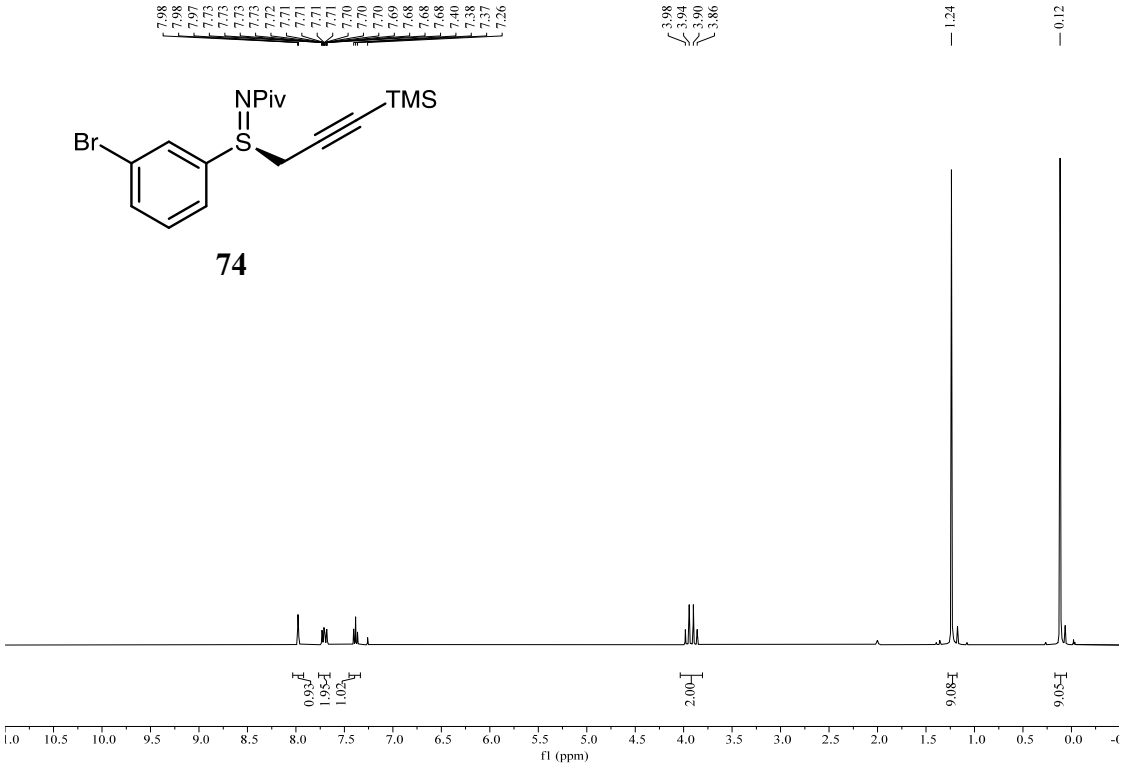
73

^{19}F NMR of 73 (375 MHz, $CDCl_3$)

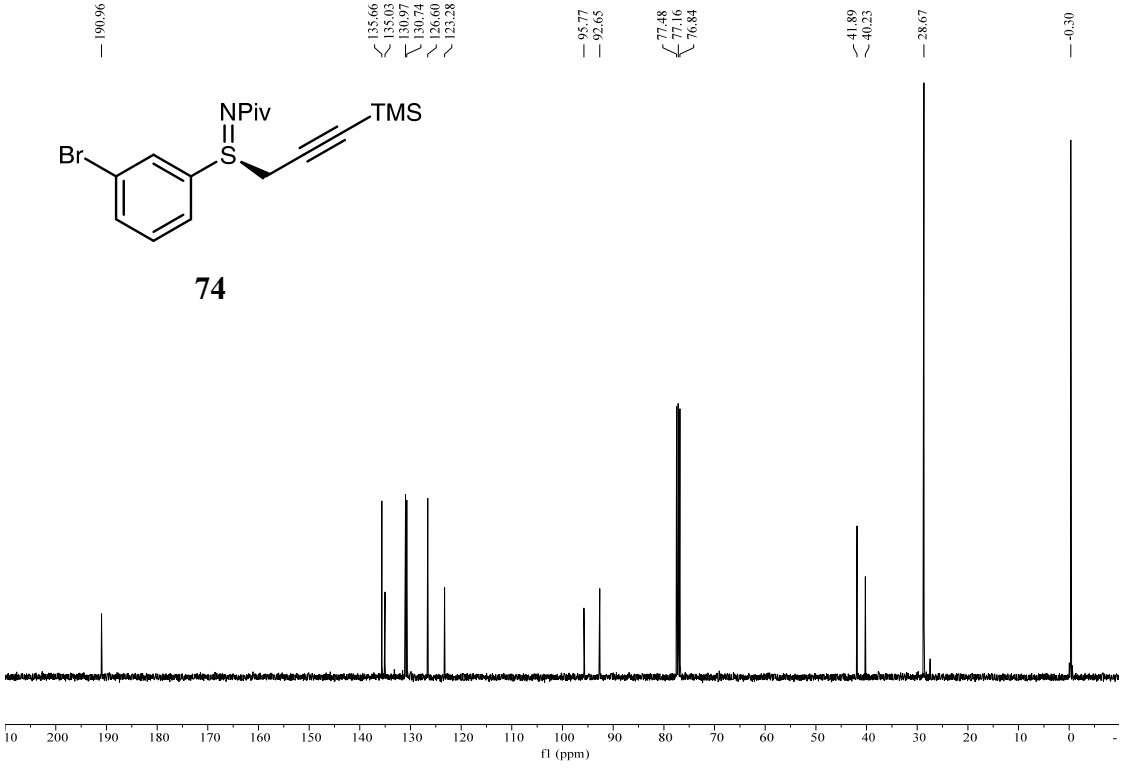


73

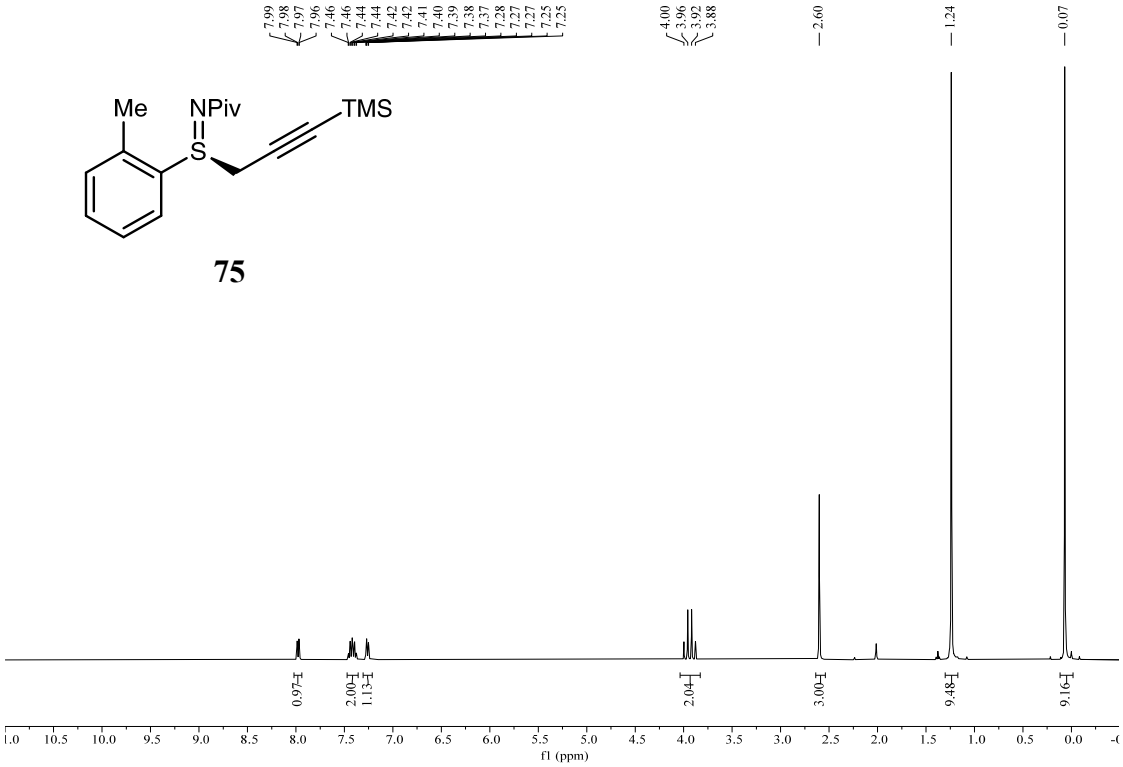
^{1}H NMR of 74 (400 MHz, $CDCl_3$)



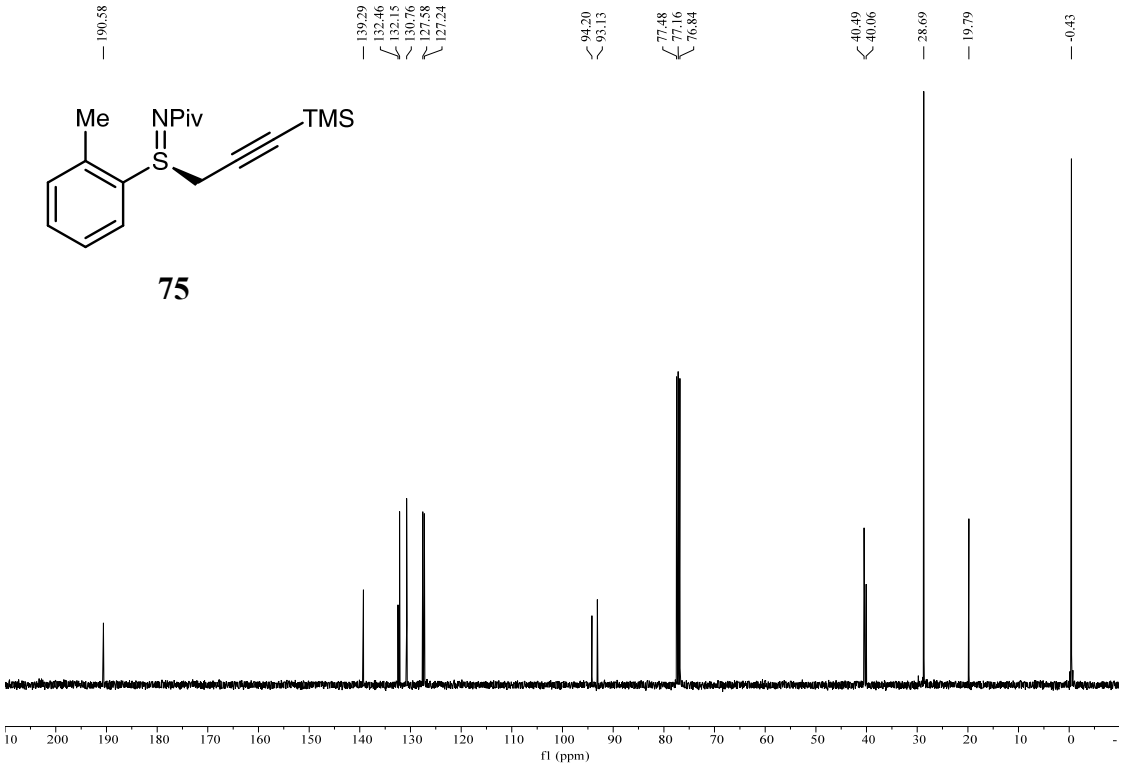
^{13}C NMR of 74 (100 MHz, $CDCl_3$)



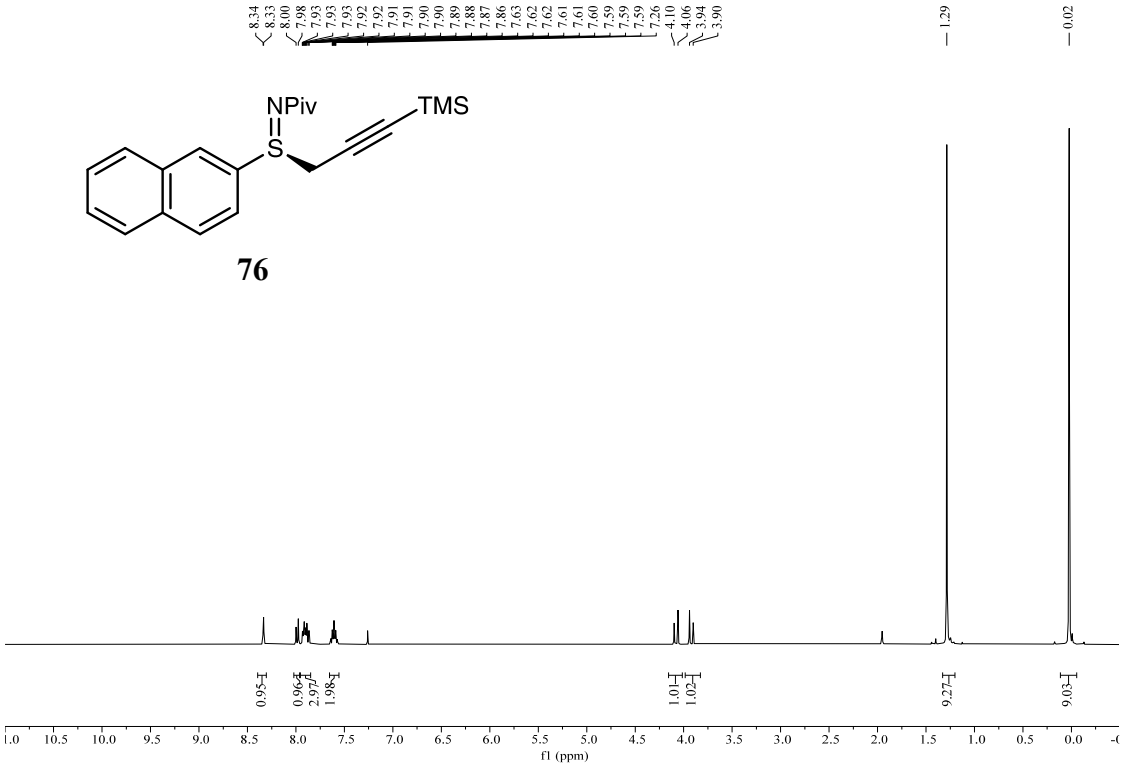
^{1}H NMR of 75 (400 MHz, $CDCl_3$)



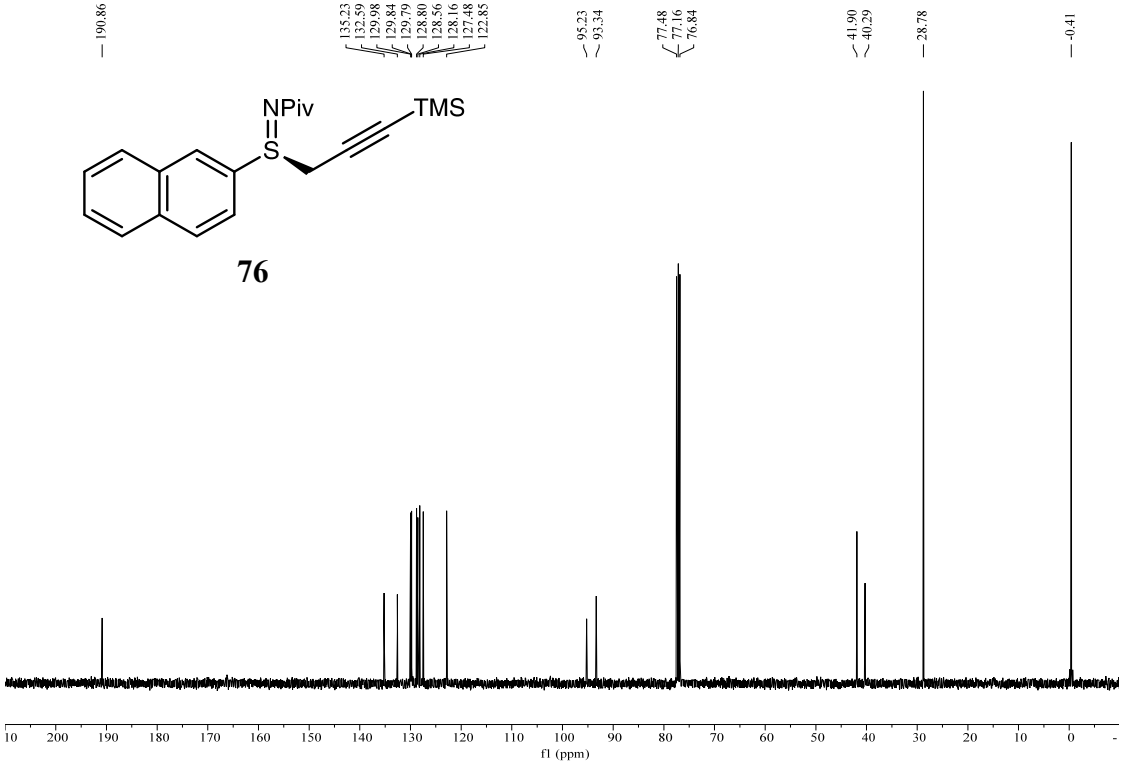
^{13}C NMR of 75 (100 MHz, $CDCl_3$)



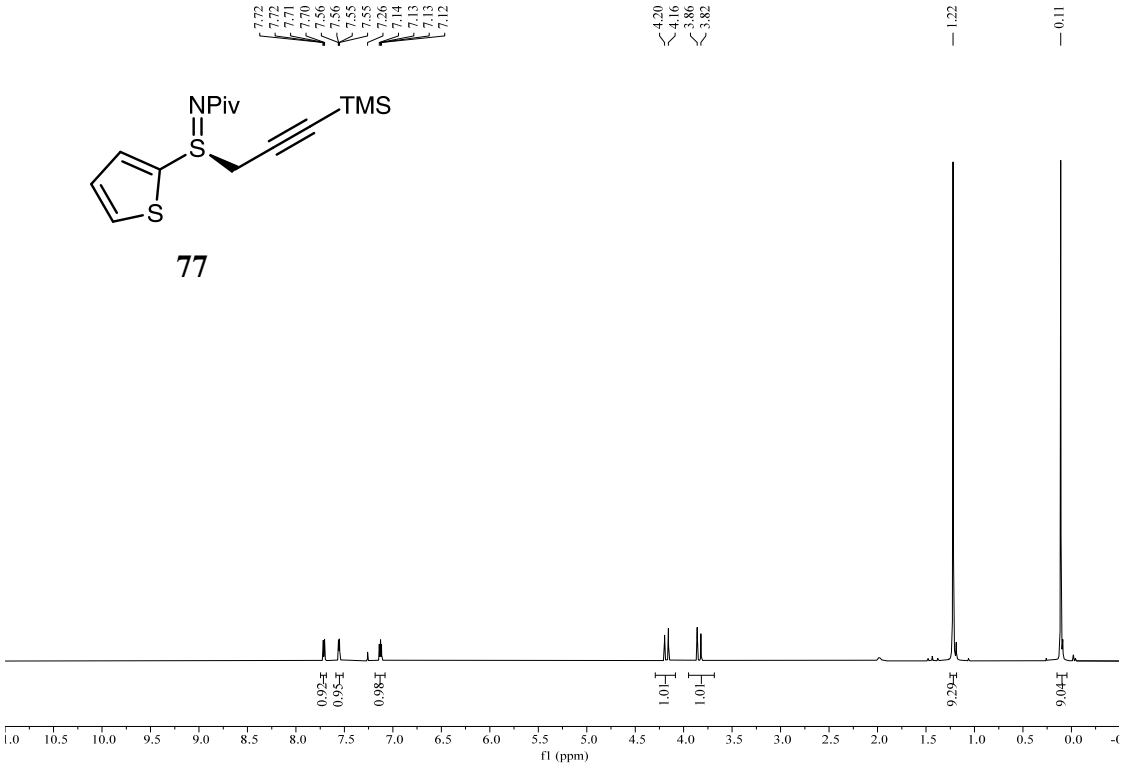
^{1}H NMR of 76 (400 MHz, $CDCl_3$)



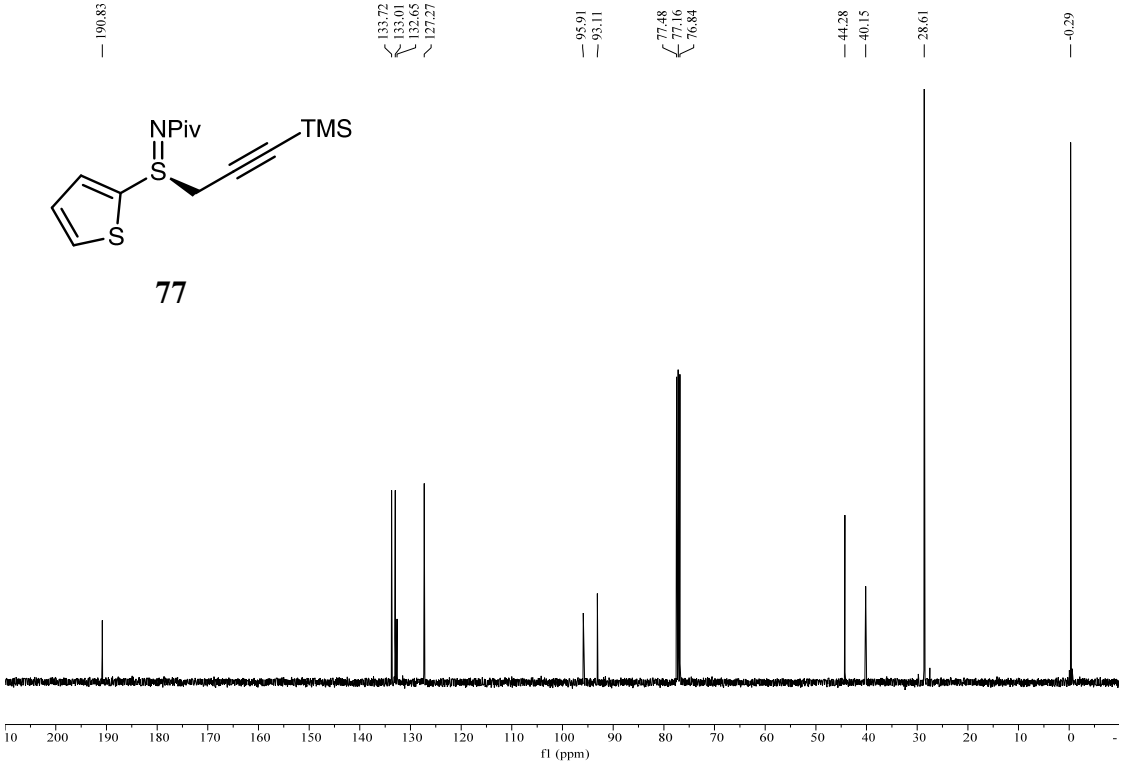
^{13}C NMR of 76 (100 MHz, $CDCl_3$)



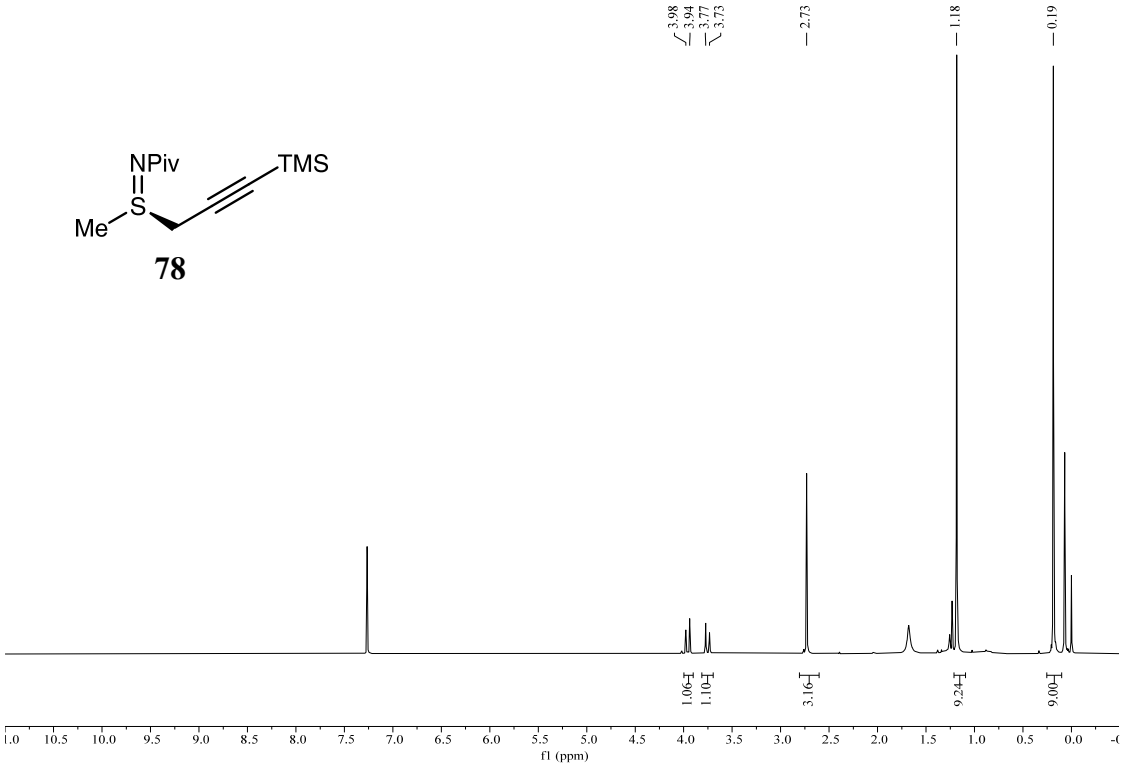
^{1}H NMR of 77 (400 MHz, $CDCl_3$)



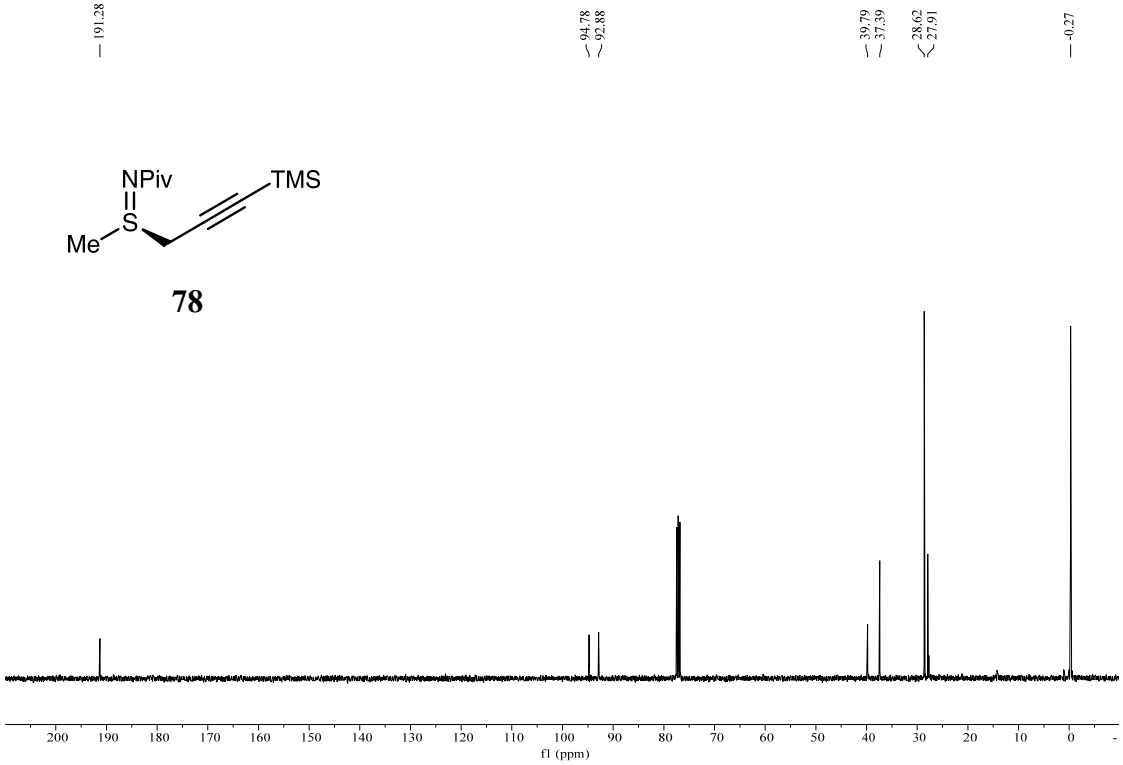
^{13}C NMR of 77 (100 MHz, $CDCl_3$)



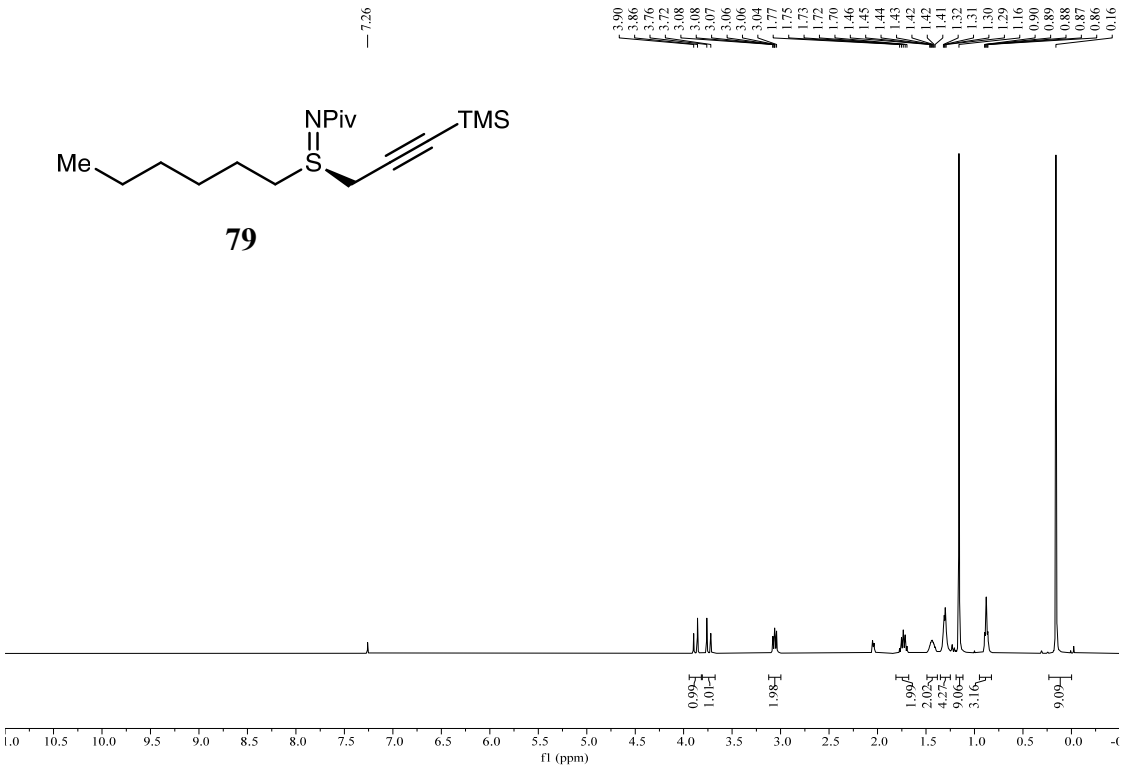
^{1}H NMR of 78 (400 MHz, $CDCl_3$)



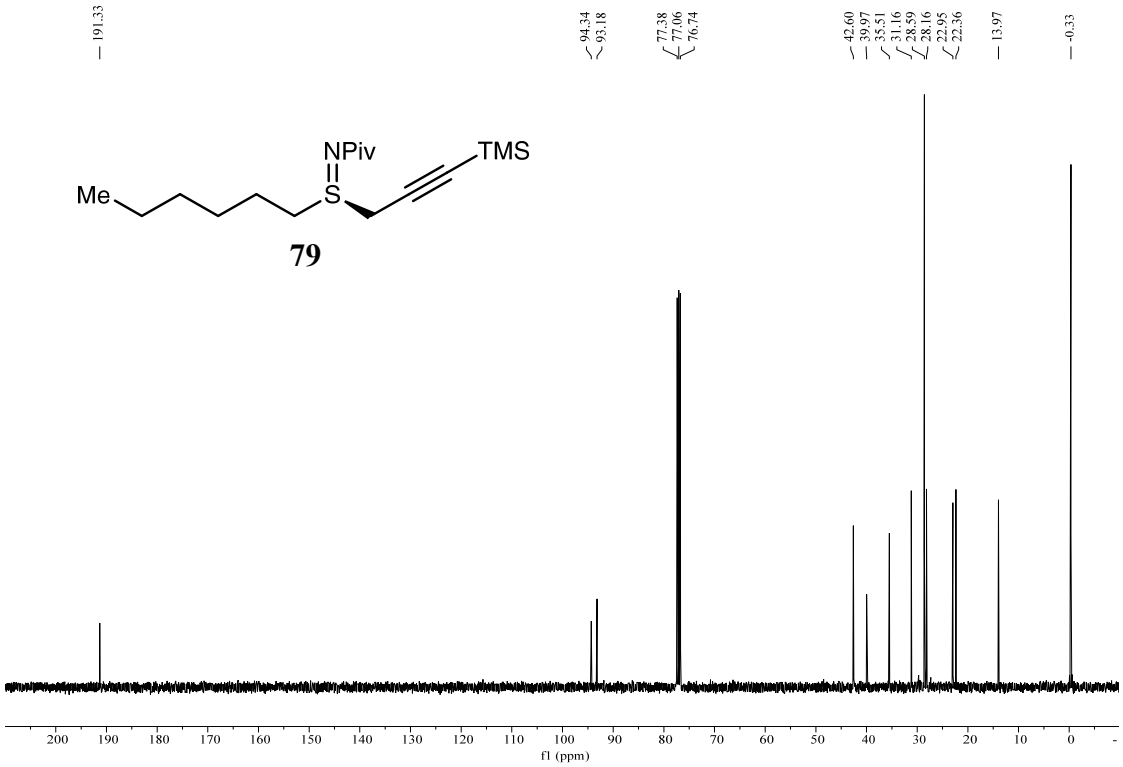
^{13}C NMR of 78 (100 MHz, $CDCl_3$)



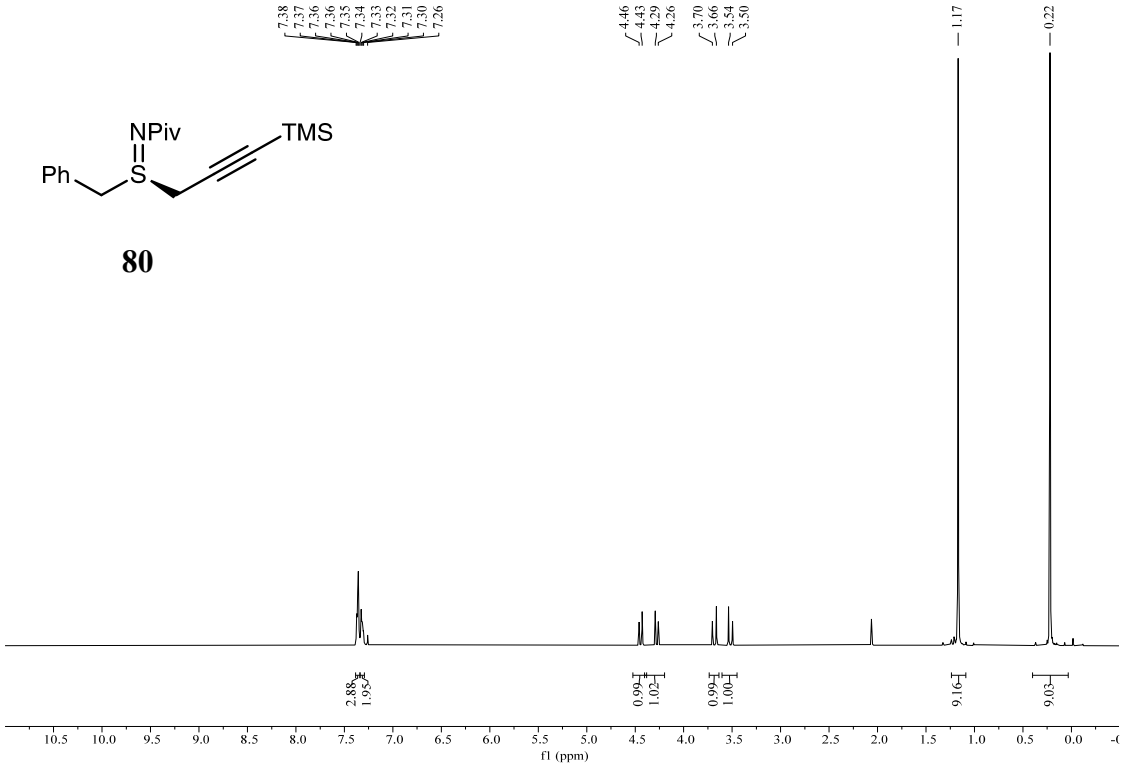
^{1}H NMR of 79 (400 MHz, $CDCl_3$)



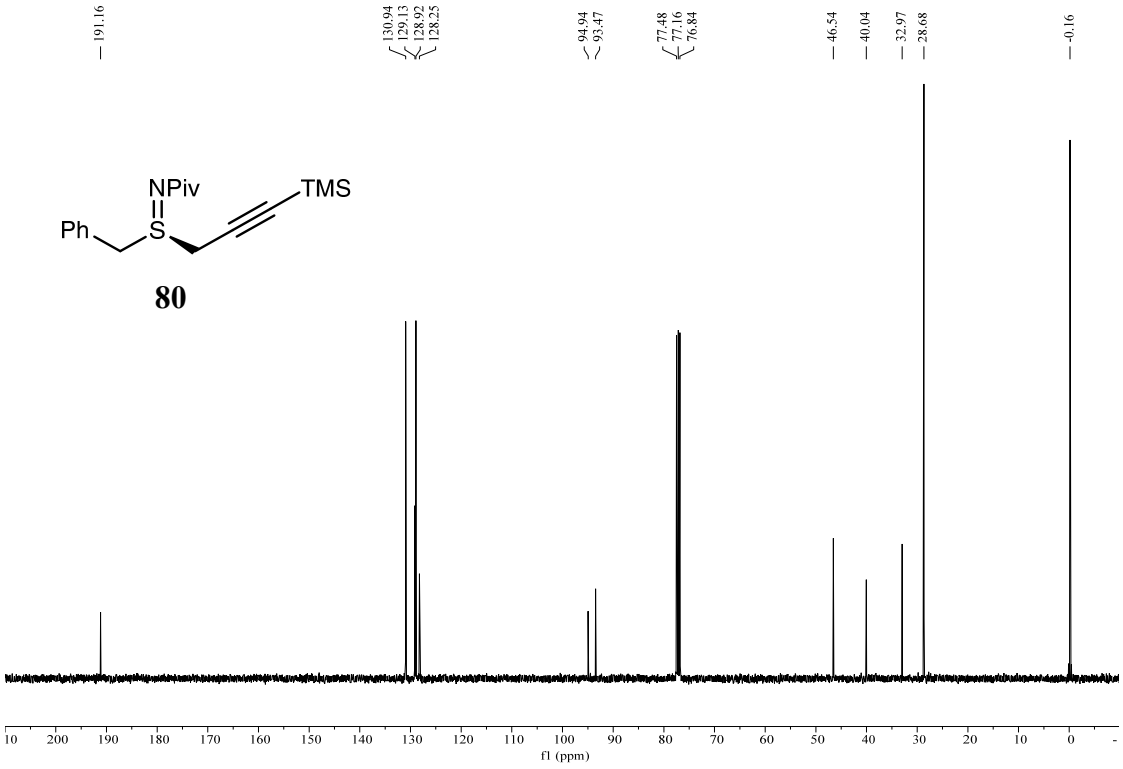
^{13}C NMR of 79 (100 MHz, $CDCl_3$)



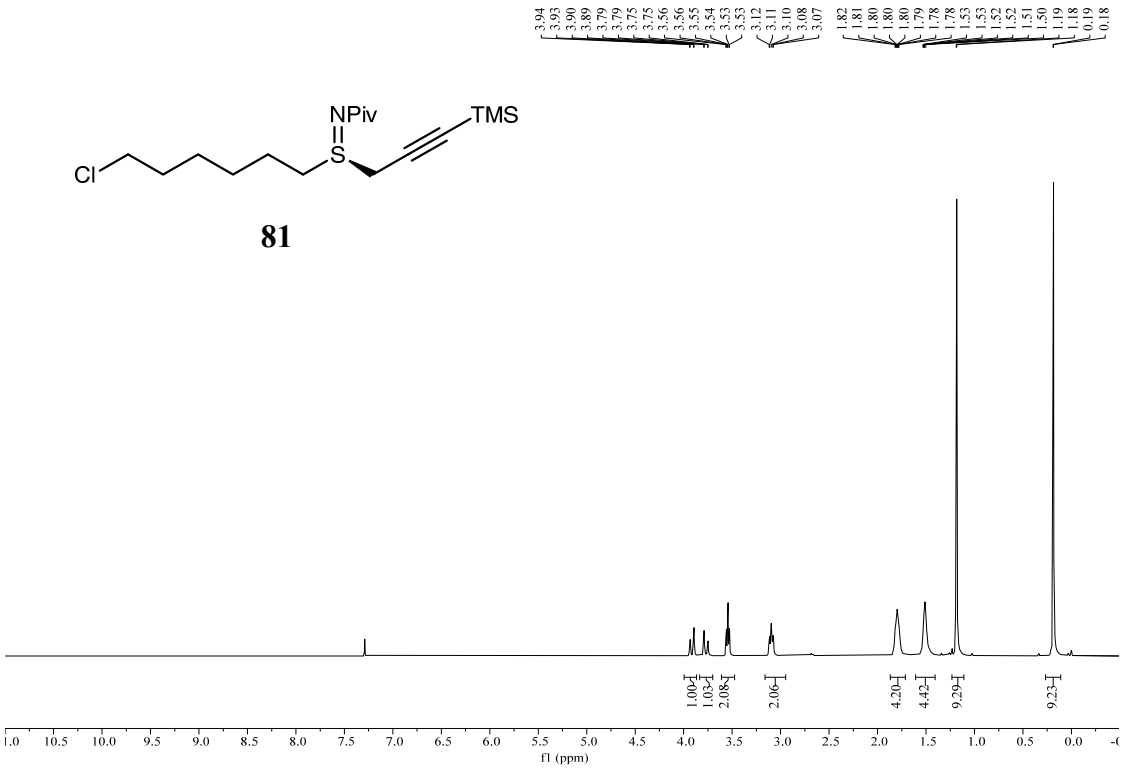
^{1}H NMR of 80 (400 MHz, $CDCl_3$)



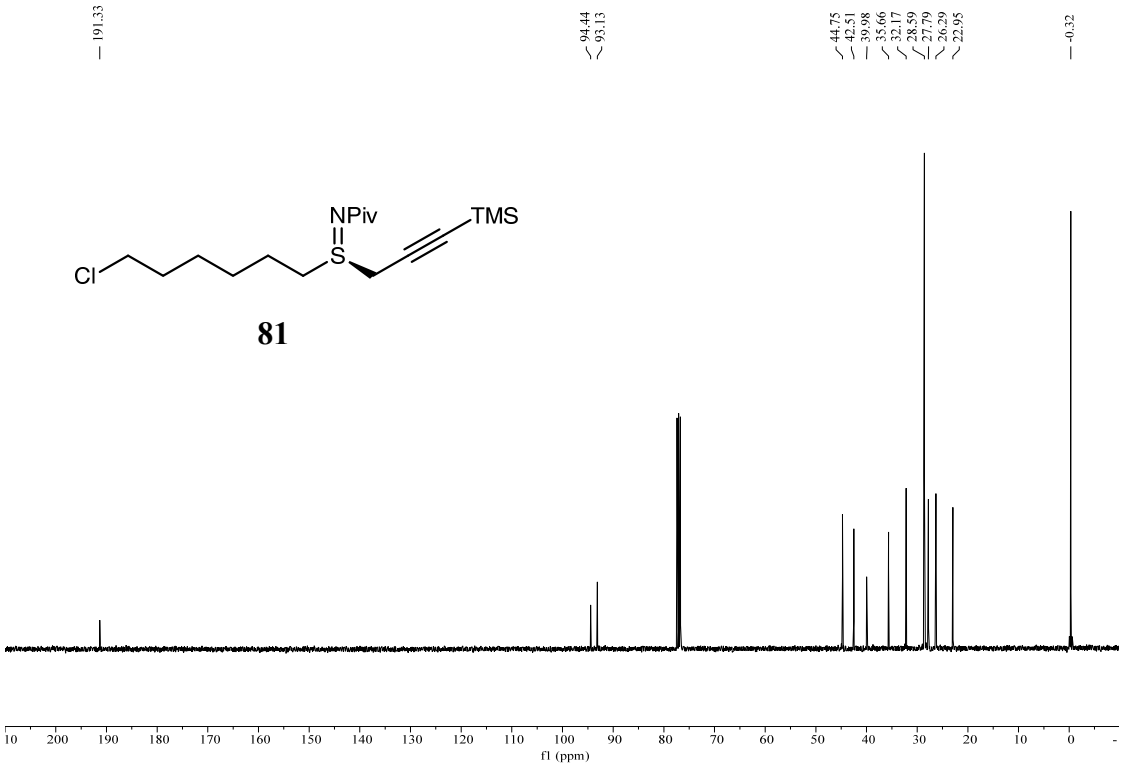
^{13}C NMR of 80 (100 MHz, $CDCl_3$)



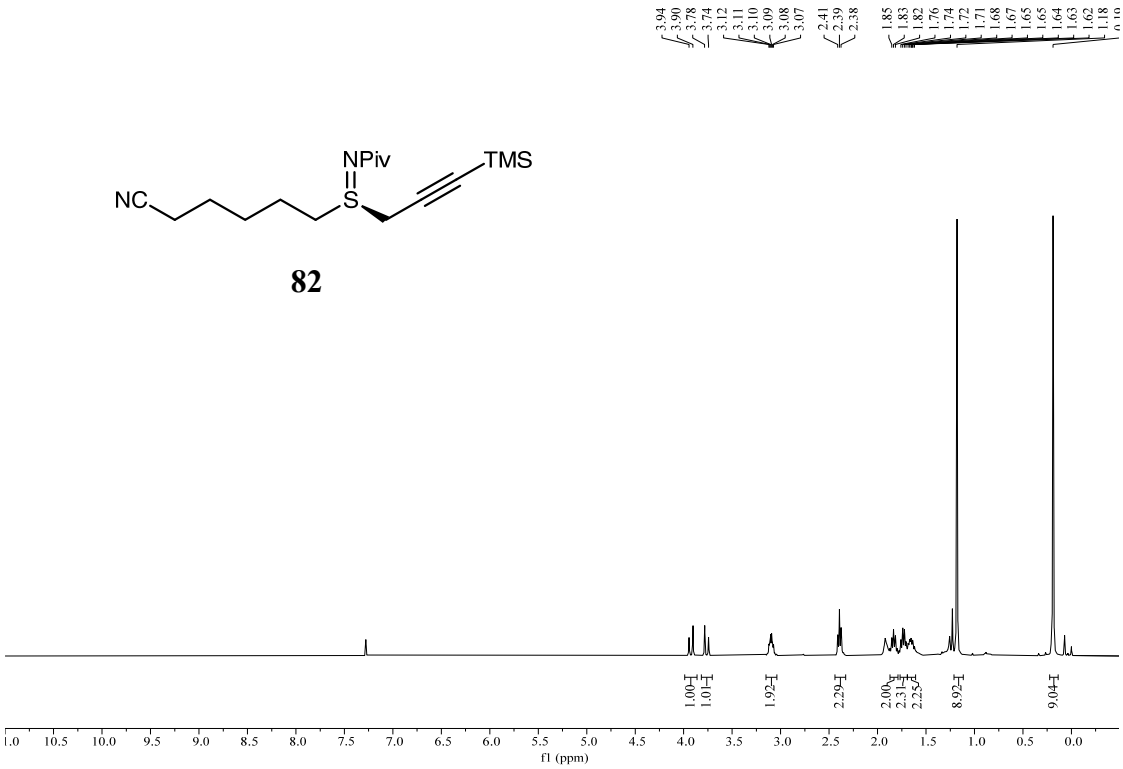
^{1}H NMR of 81 (400 MHz, $CDCl_3$)



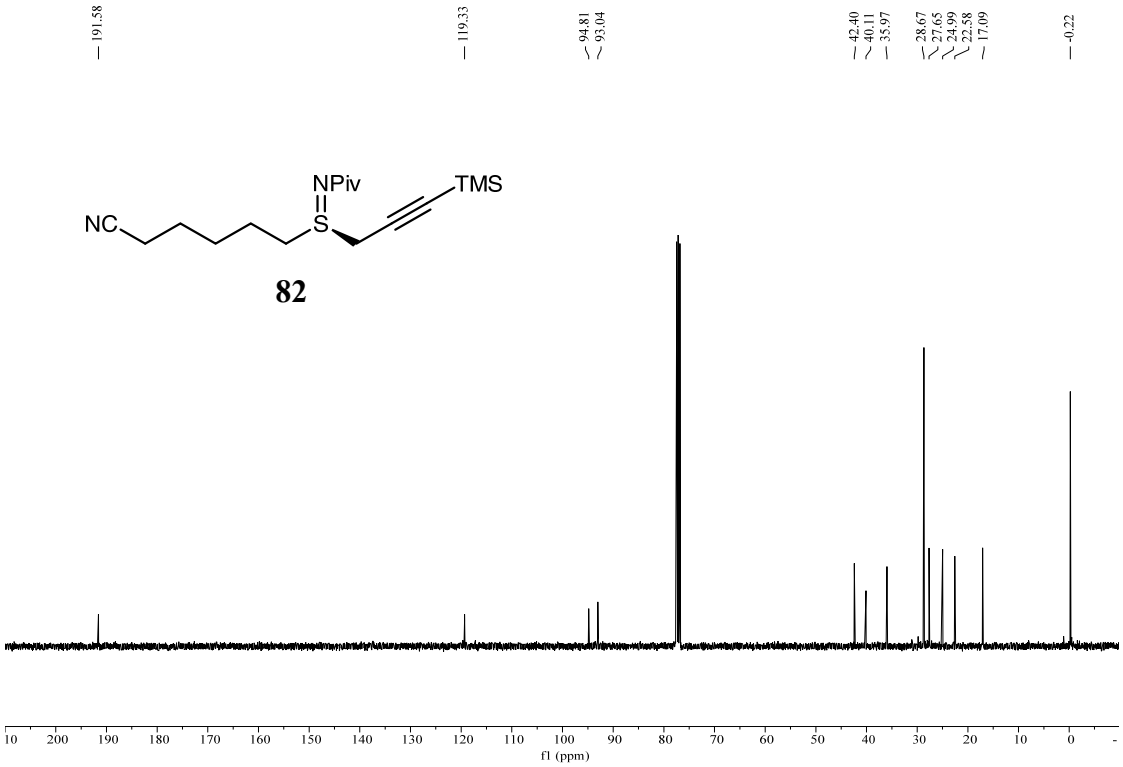
^{13}C NMR of 81 (100 MHz, $CDCl_3$)



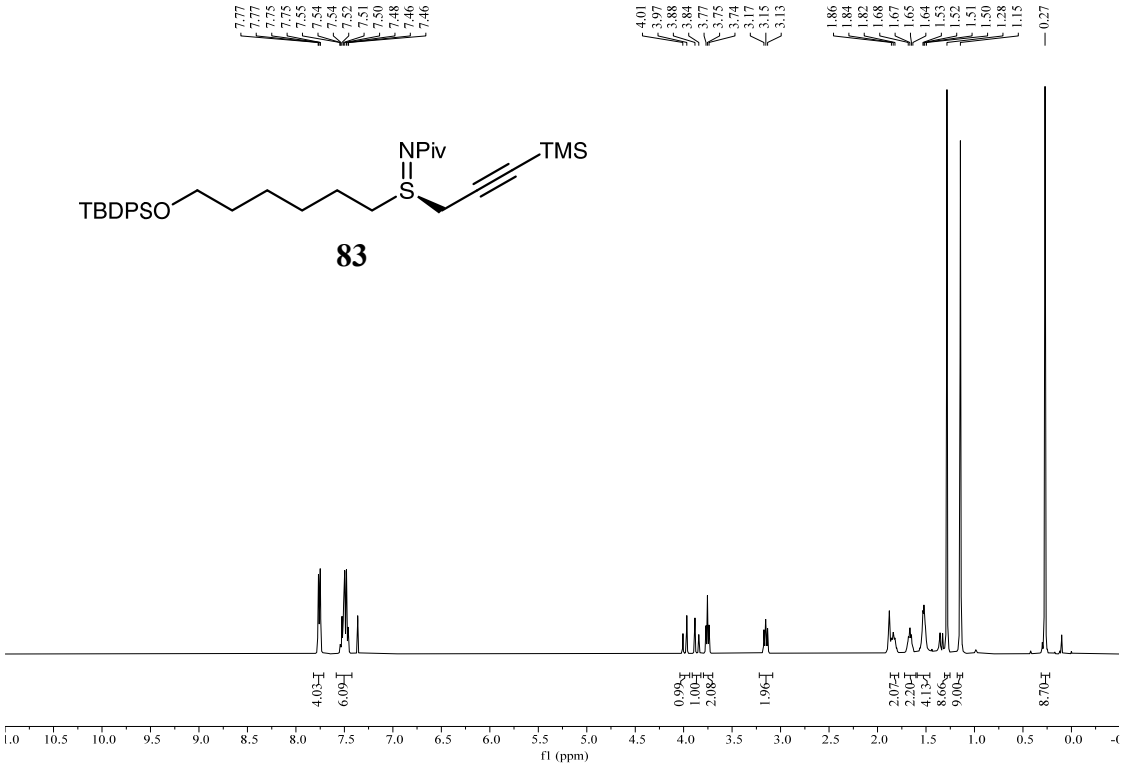
^{1}H NMR of 82 (400 MHz, $CDCl_3$)



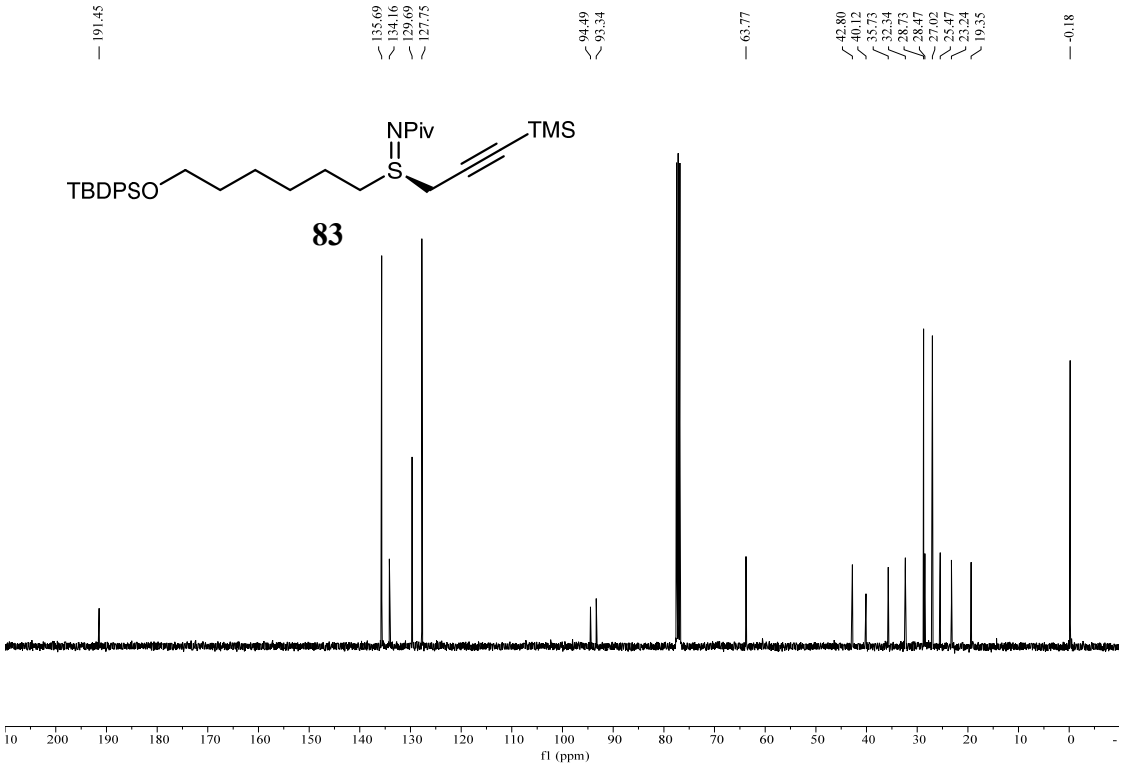
^{13}C NMR of 82 (100 MHz, $CDCl_3$)



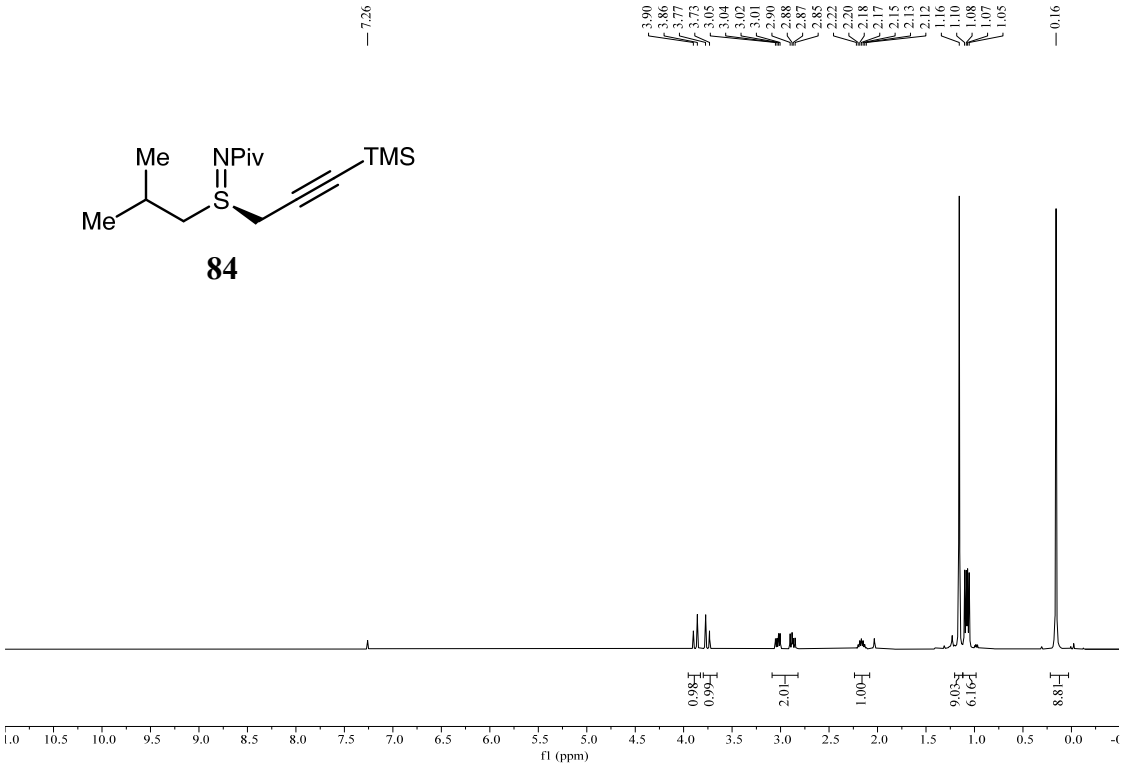
^{1}H NMR of 83 (400 MHz, $CDCl_3$)



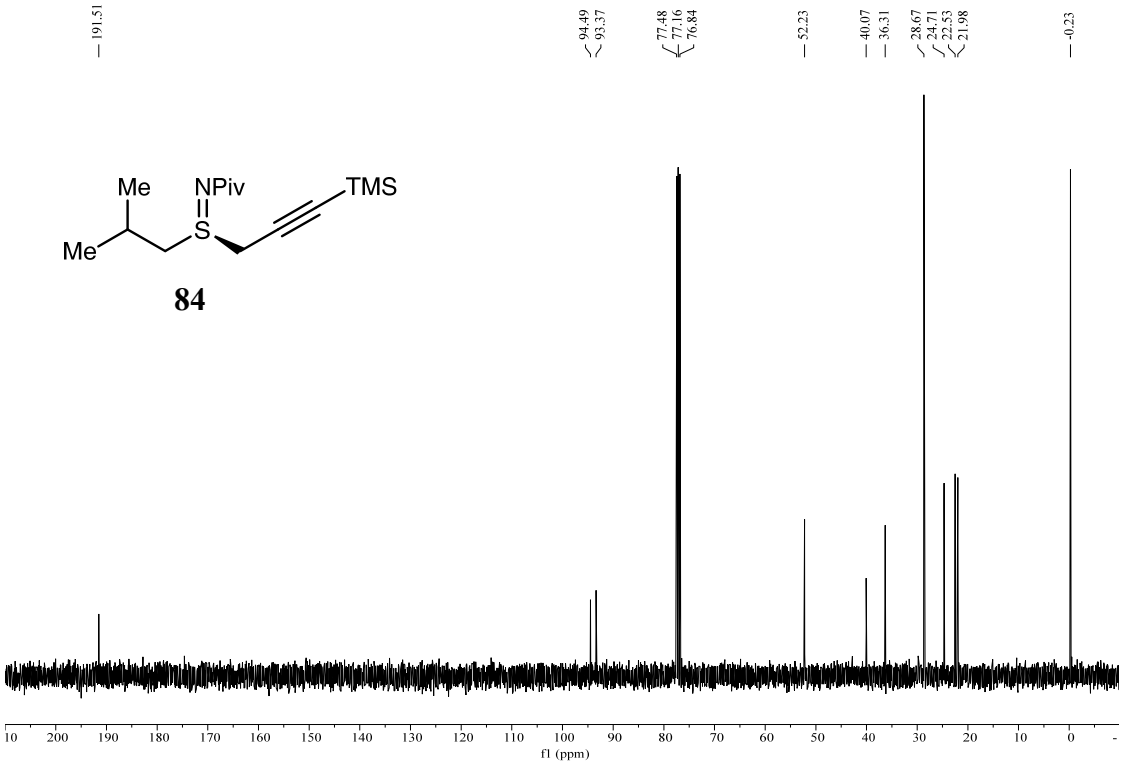
^{13}C NMR of 83 (100 MHz, $CDCl_3$)



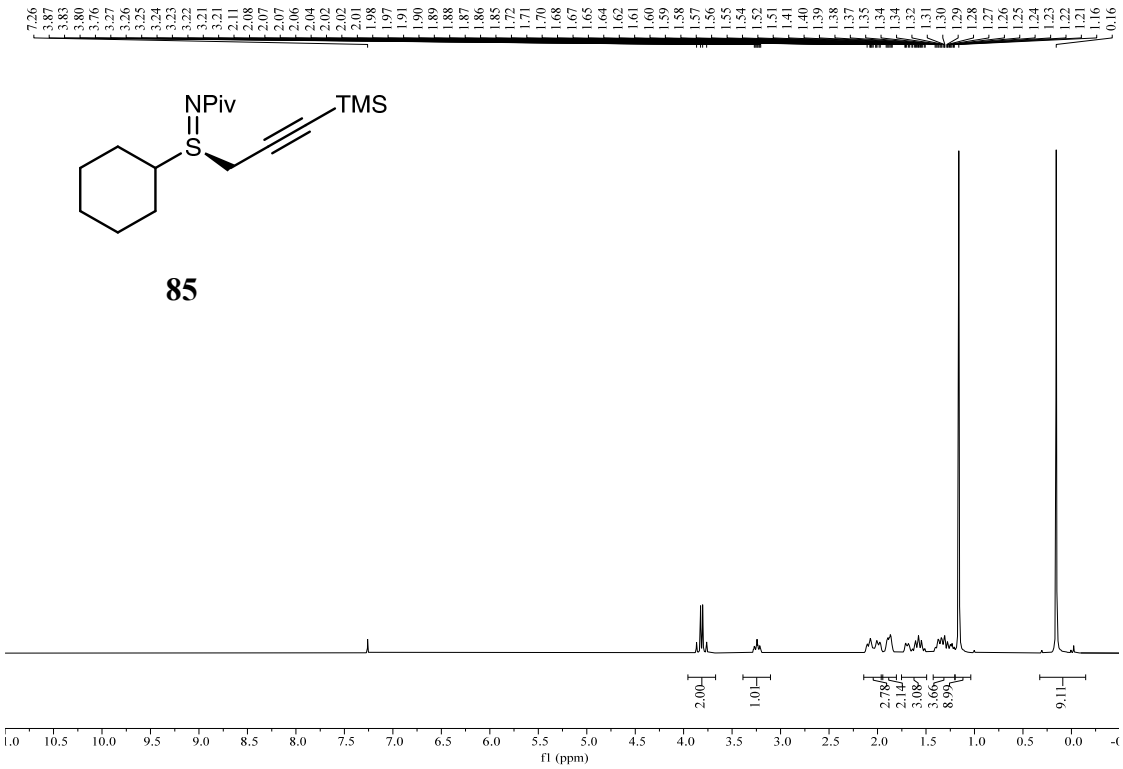
^{1}H NMR of 84 (400 MHz, $CDCl_3$)



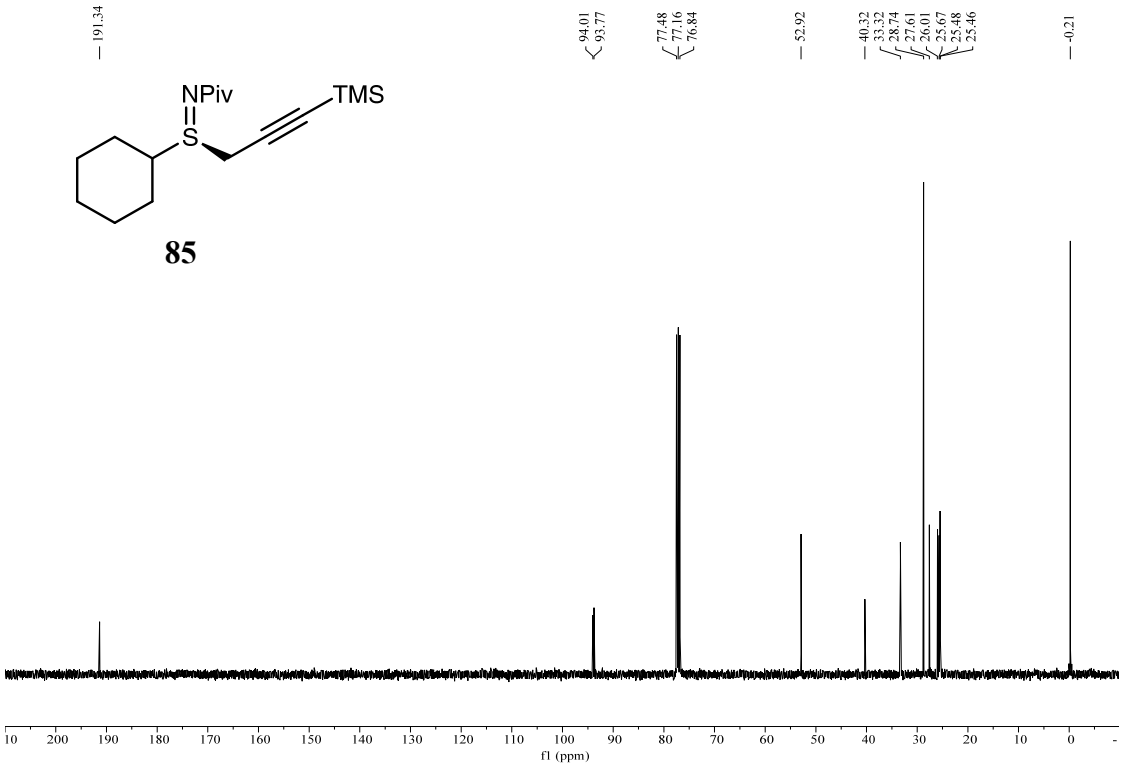
^{13}C NMR of 84 (100 MHz, $CDCl_3$)



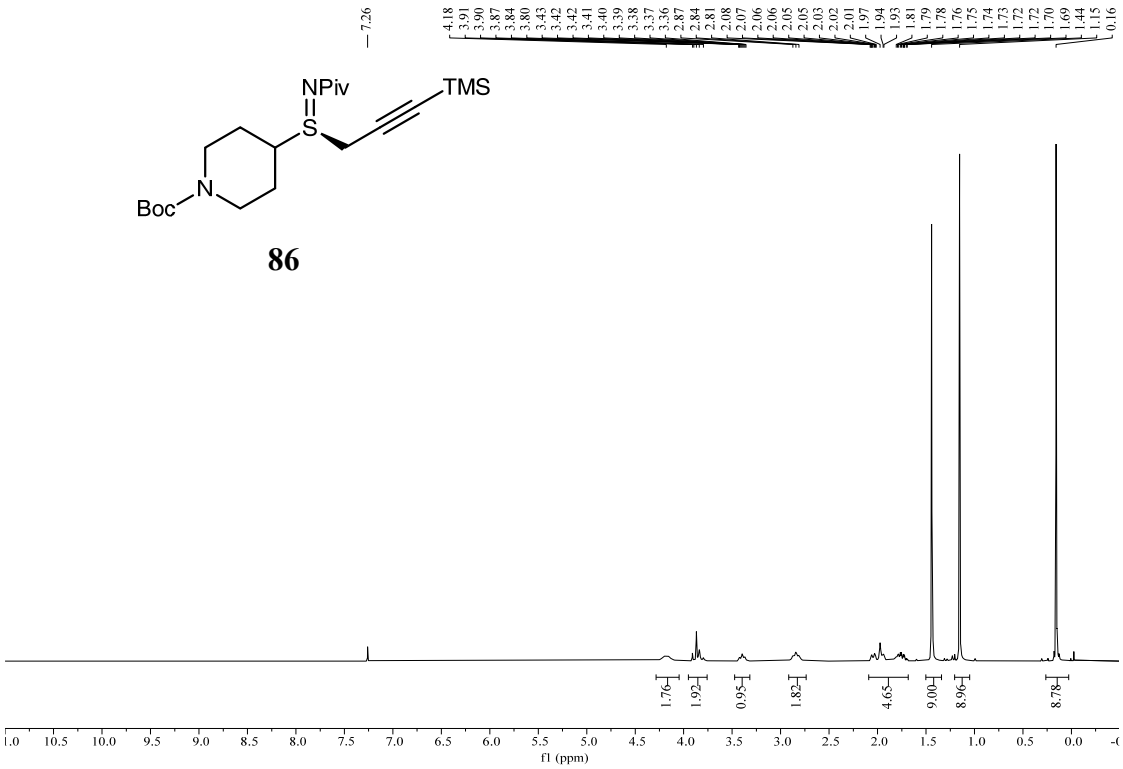
^{1}H NMR of 85 (400 MHz, $CDCl_3$)



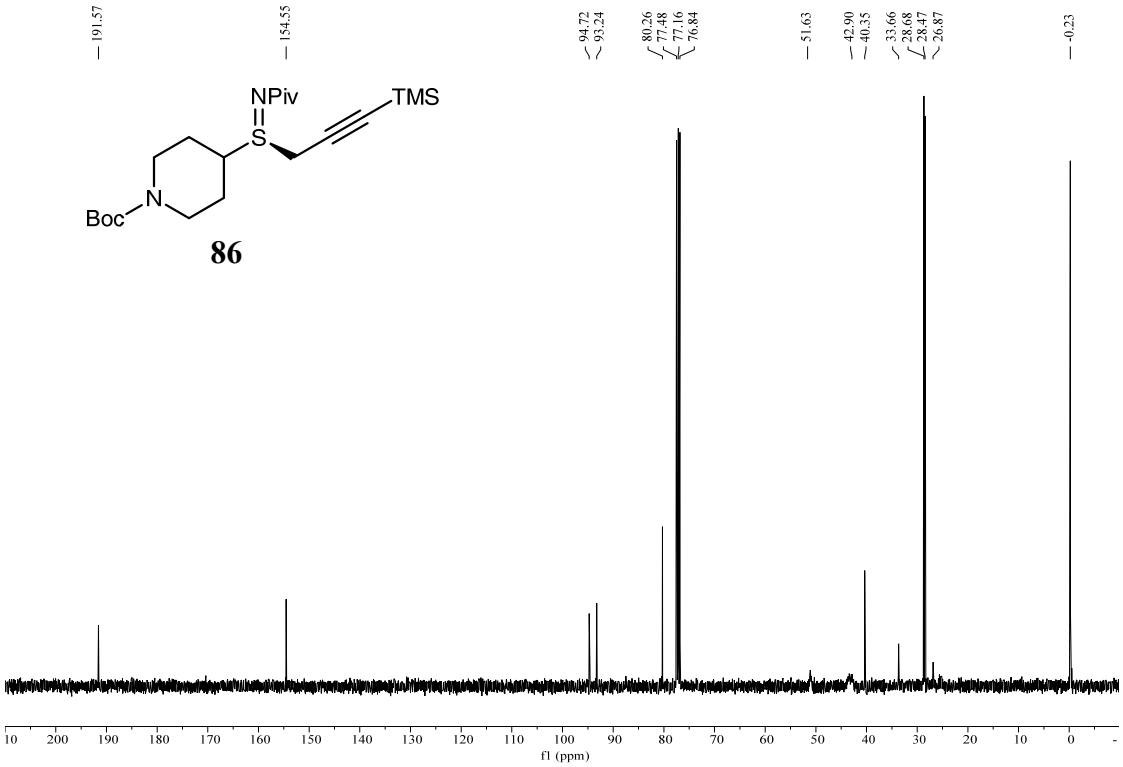
^{13}C NMR of 85 (100 MHz, $CDCl_3$)



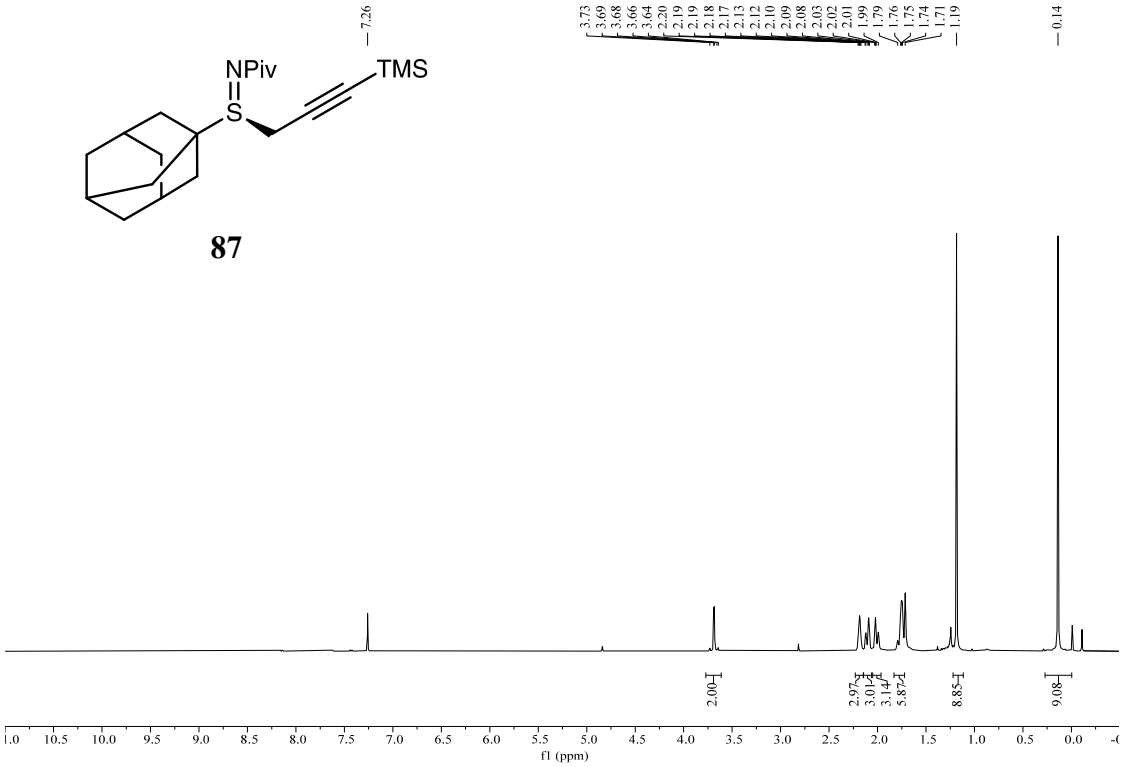
^{1}H NMR of 86 (400 MHz, $CDCl_3$)



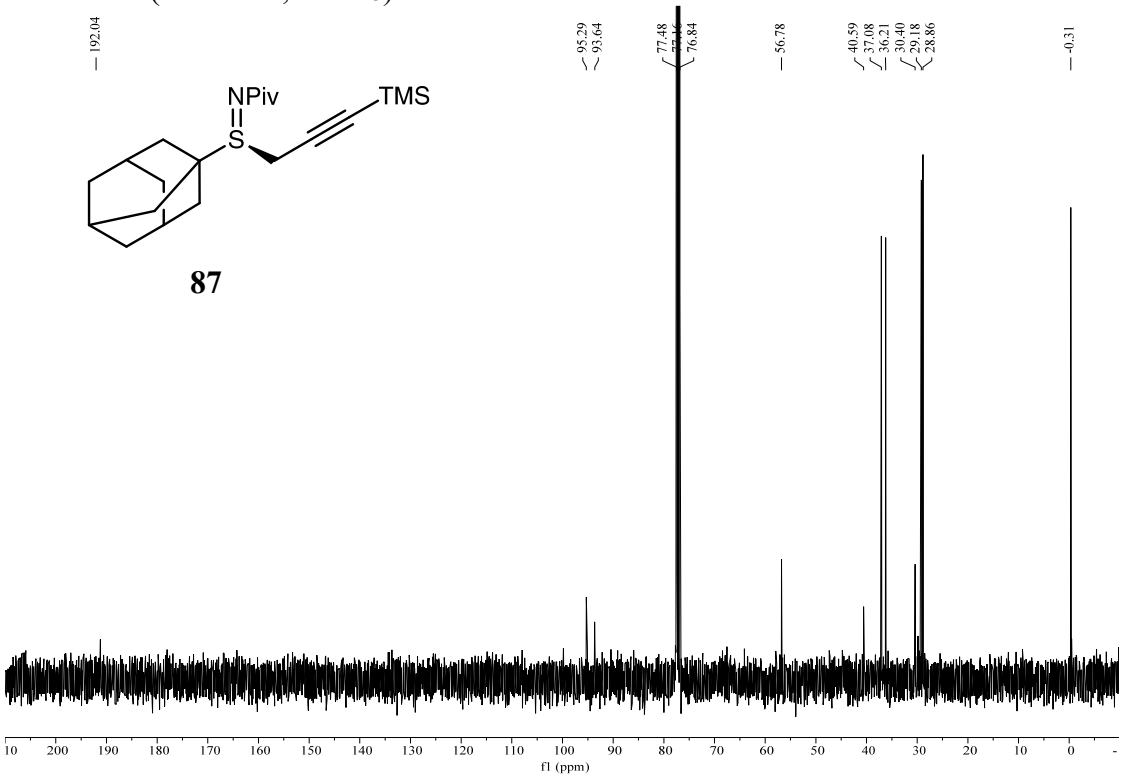
^{13}C NMR of 86 (100 MHz, $CDCl_3$)



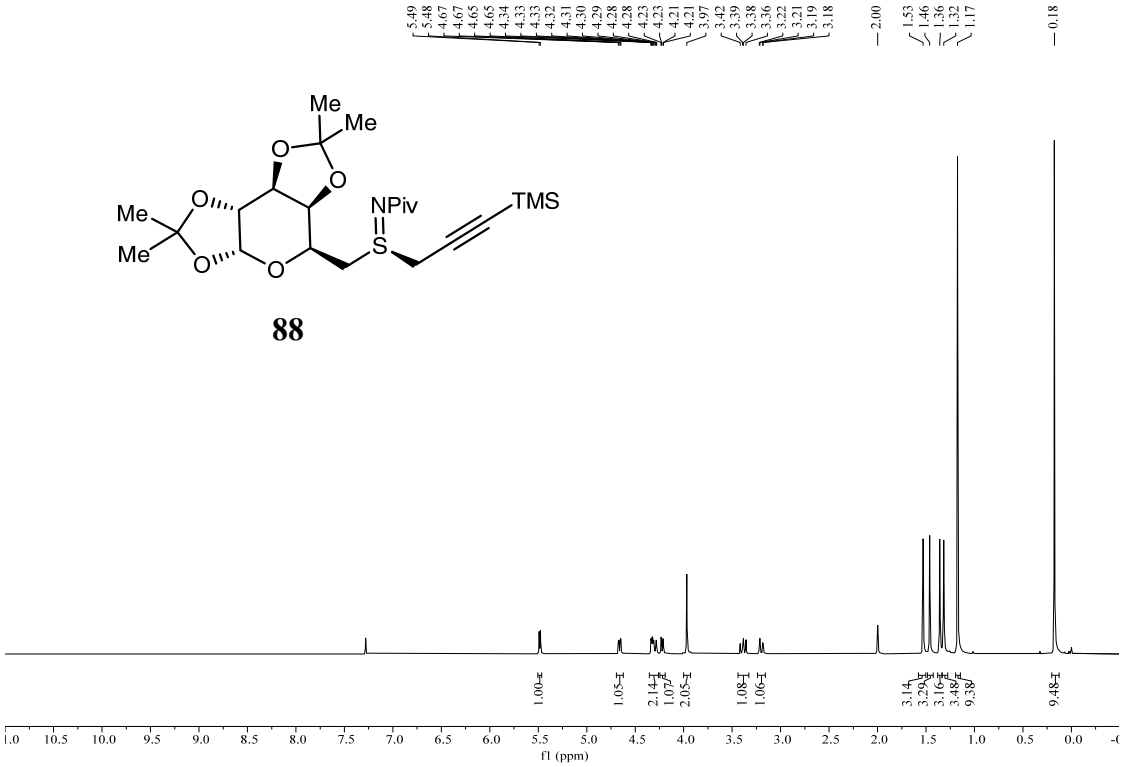
^{1}H NMR of 87 (400 MHz, $CDCl_3$)



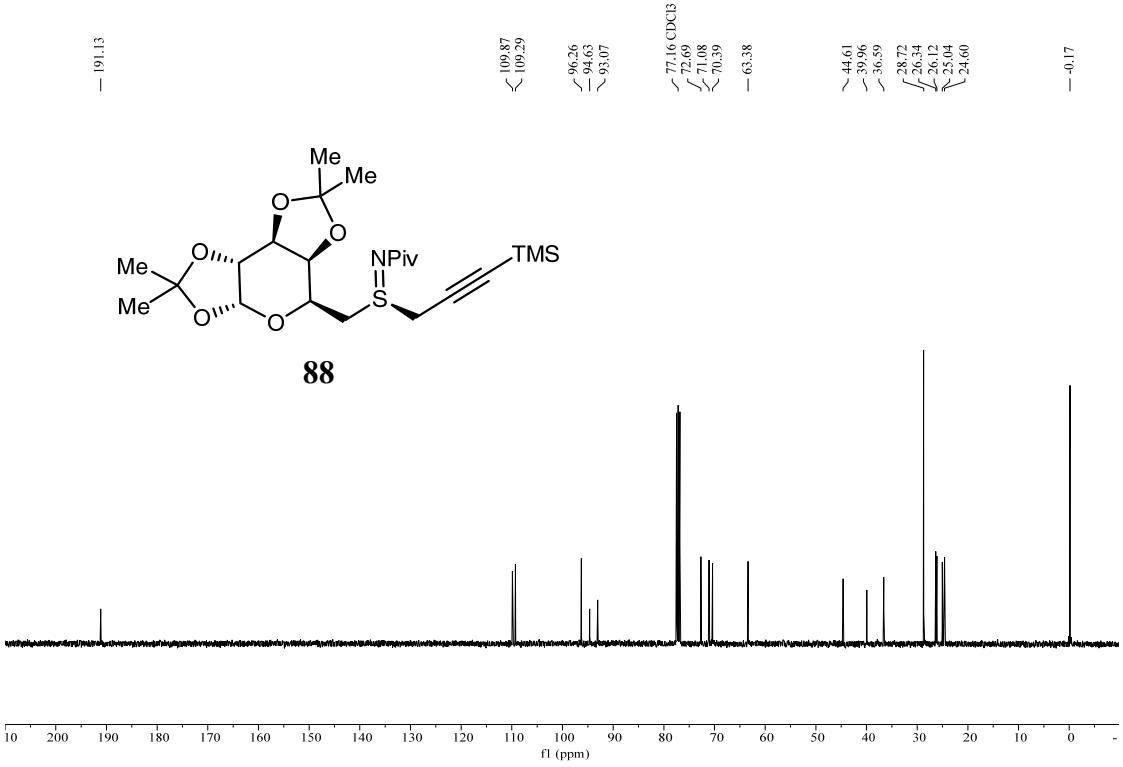
^{13}C NMR of 87 (100 MHz, $CDCl_3$)



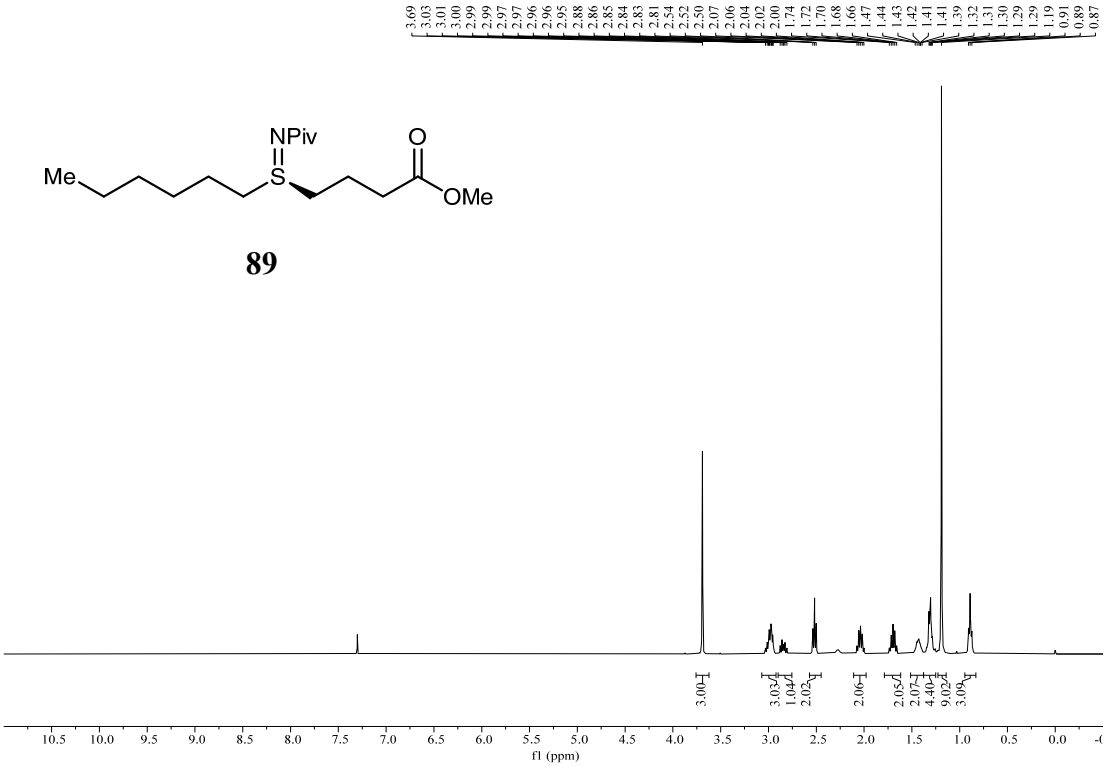
^{1}H NMR of 88 (400 MHz, $CDCl_3$)



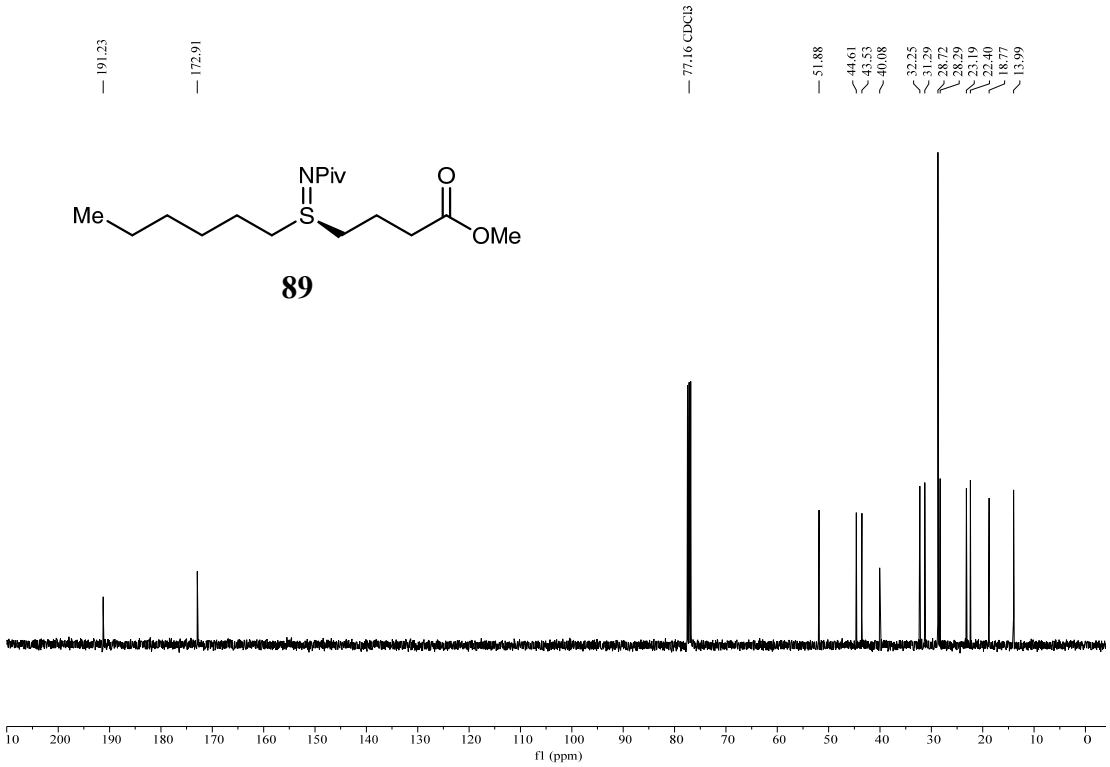
^{13}C NMR of 88 (100 MHz, $CDCl_3$)



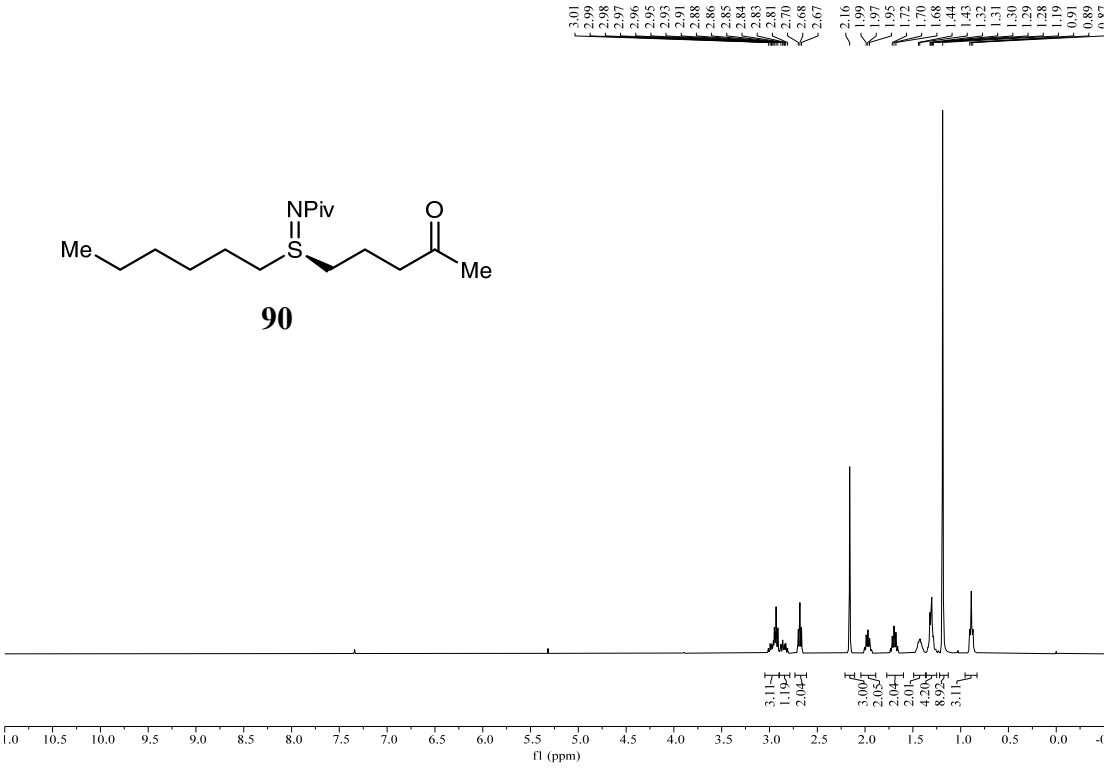
^{1}H NMR of 89 (400 MHz, $CDCl_3$)



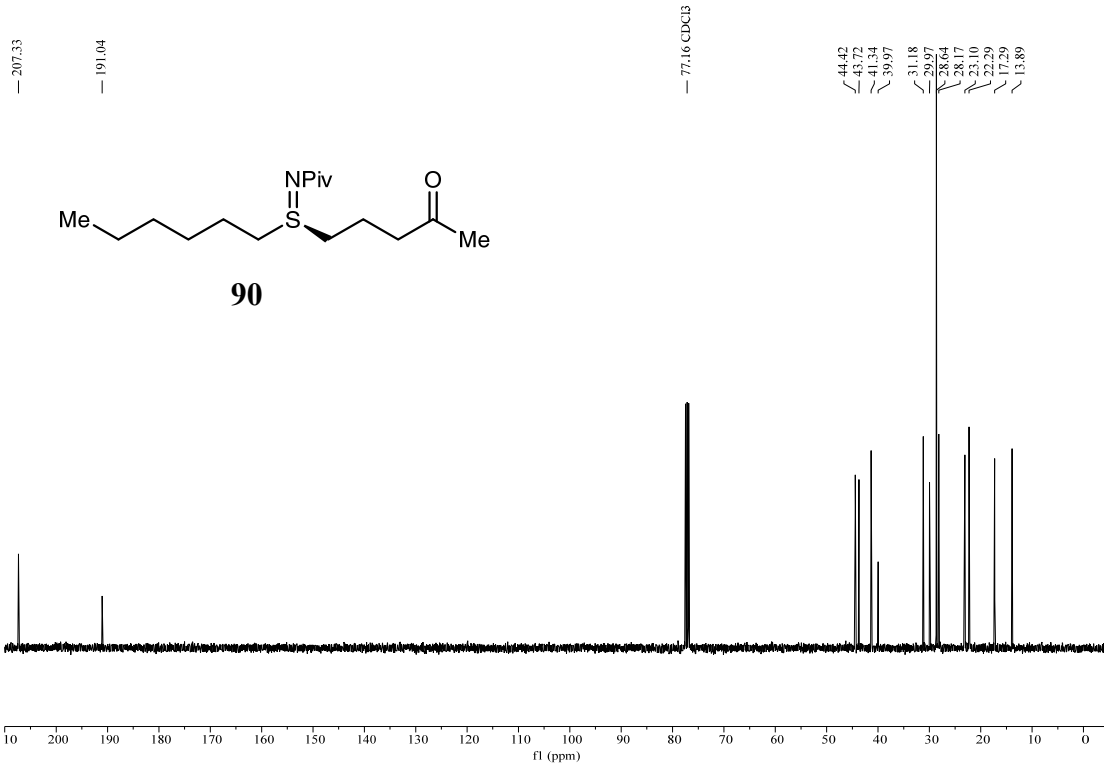
^{13}C NMR of 89 (100 MHz, $CDCl_3$)



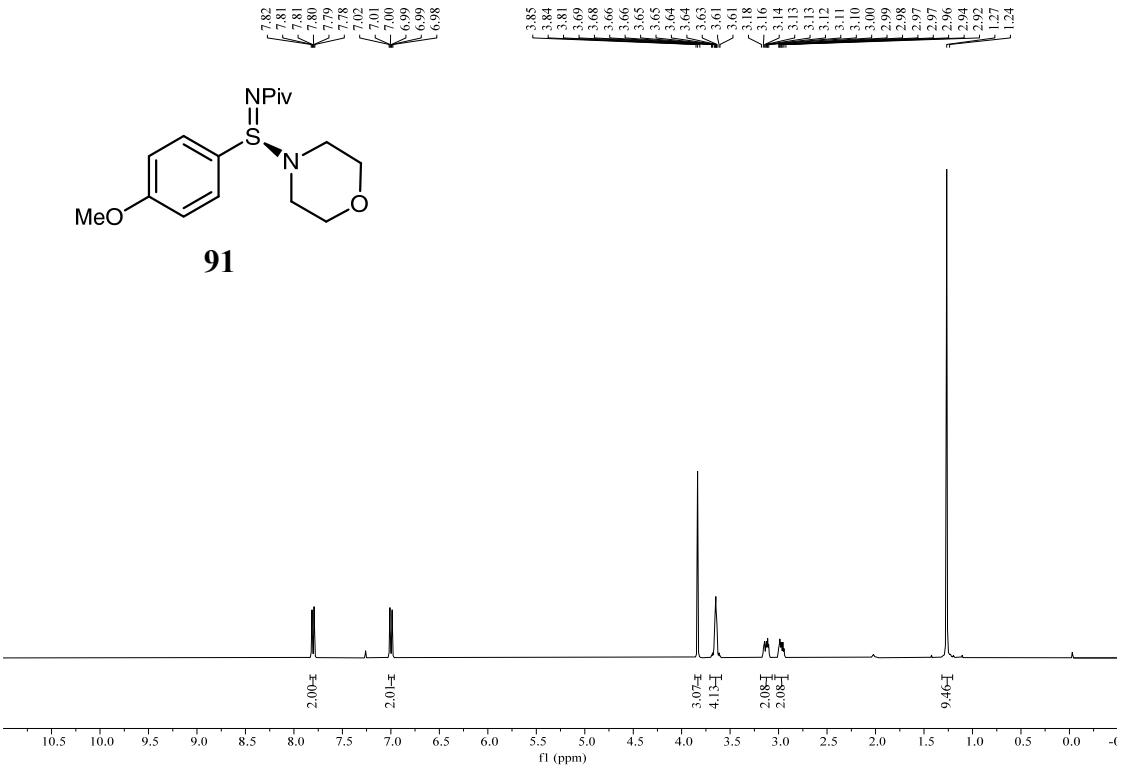
^{1}H NMR of 90 (400 MHz, $CDCl_3$)



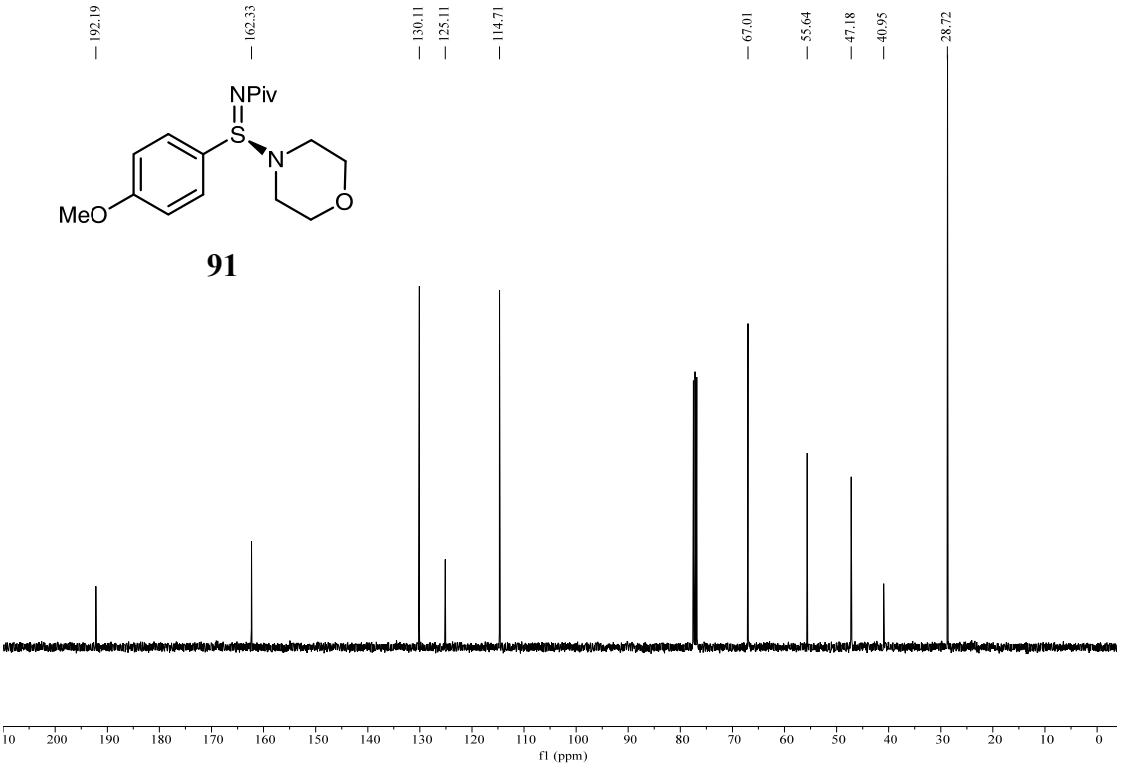
^{13}C NMR of 90 (100 MHz, $CDCl_3$)



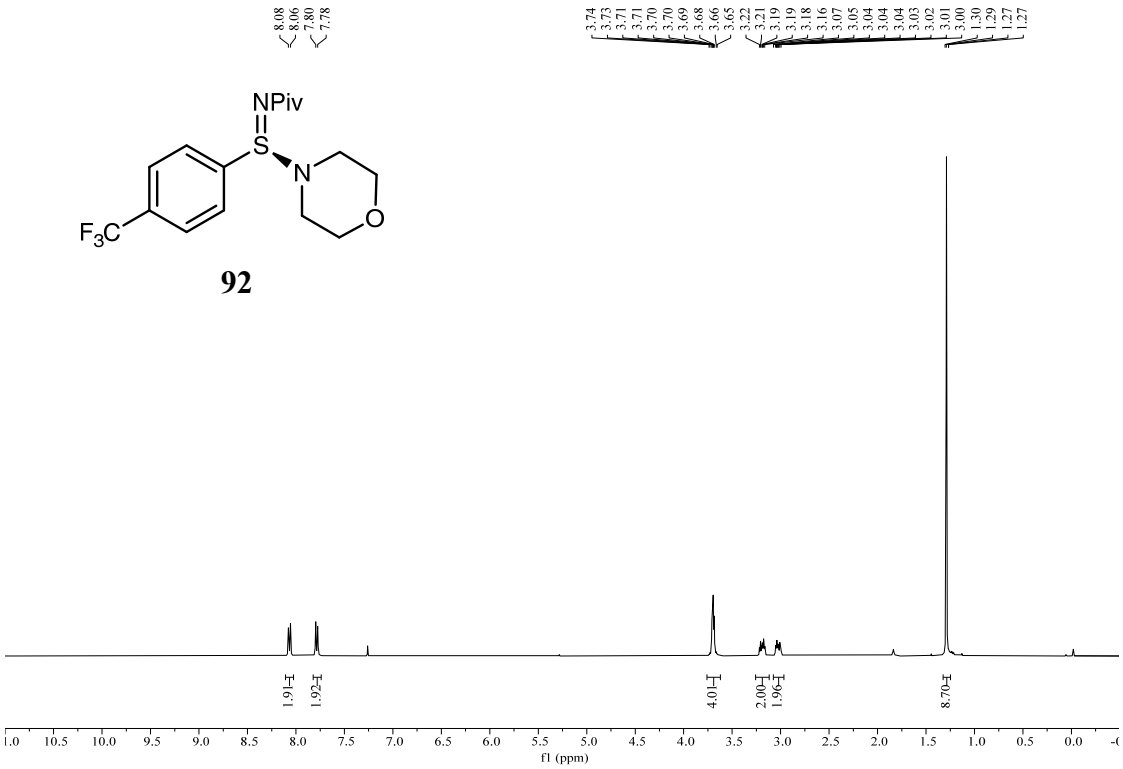
^{1}H NMR of 91 (400 MHz, $CDCl_3$)



^{13}C NMR of 91 (100 MHz, $CDCl_3$)

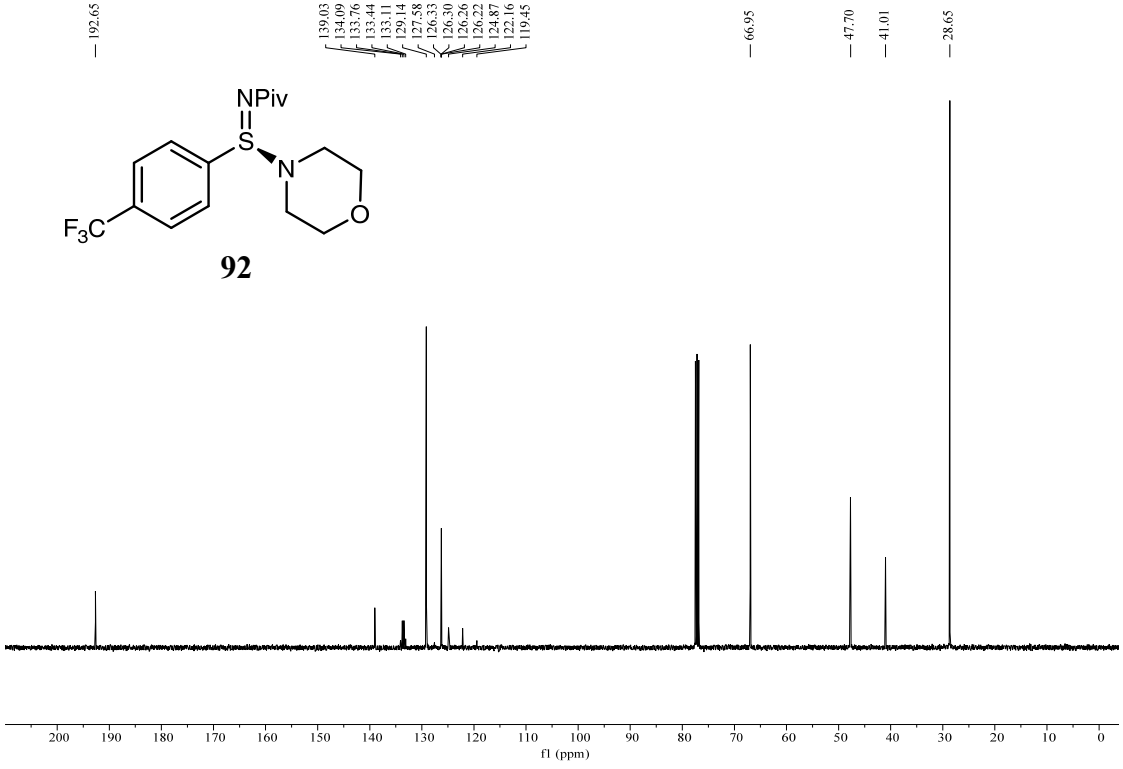


^{1}H NMR of 92 (400 MHz, $CDCl_3$)



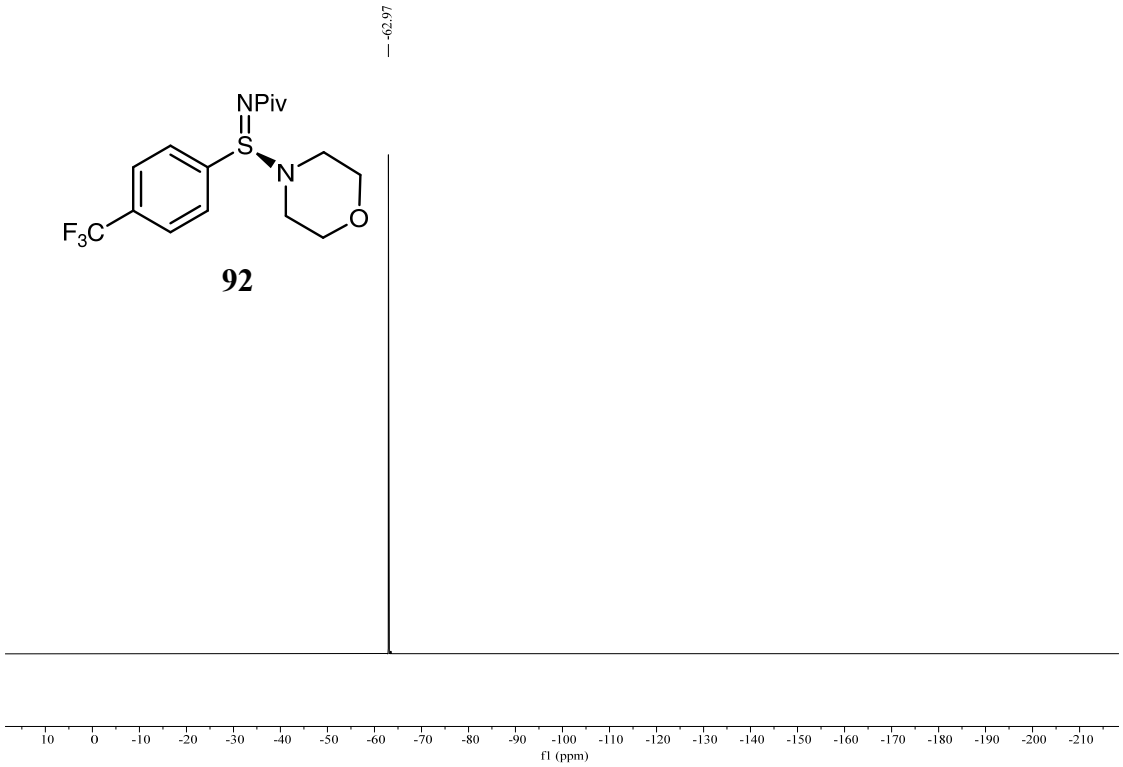
92

^{13}C NMR of 92 (100 MHz, $CDCl_3$)

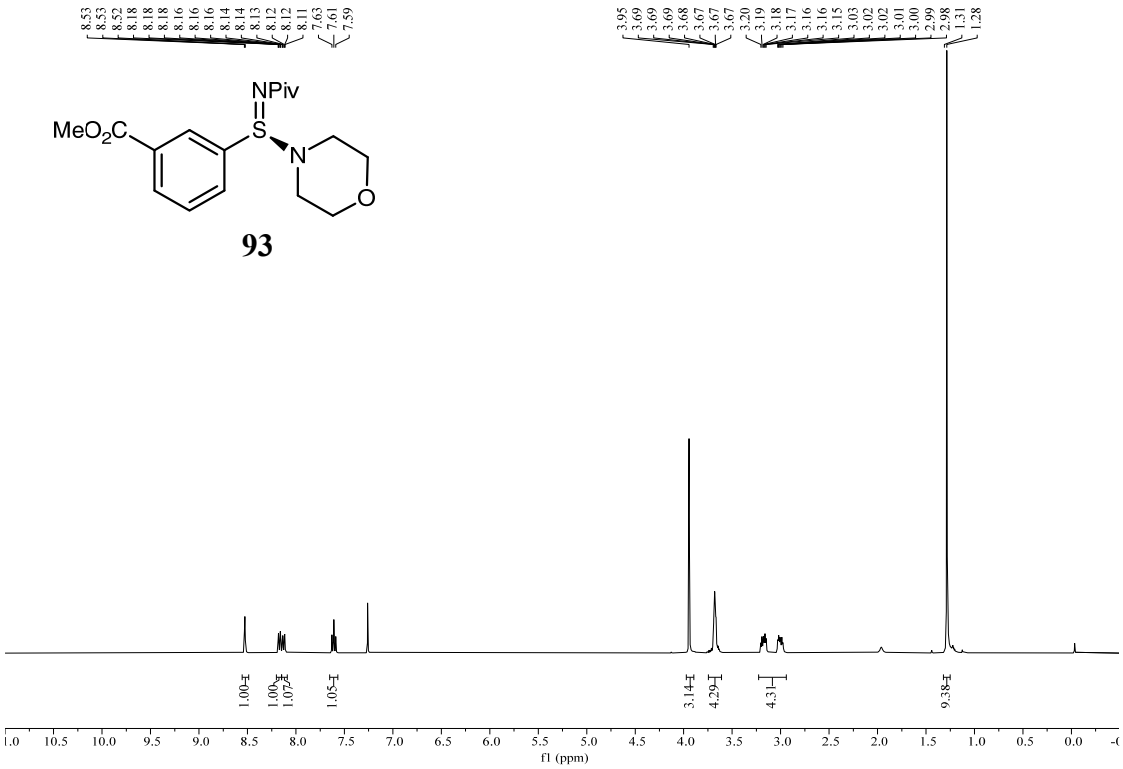


92

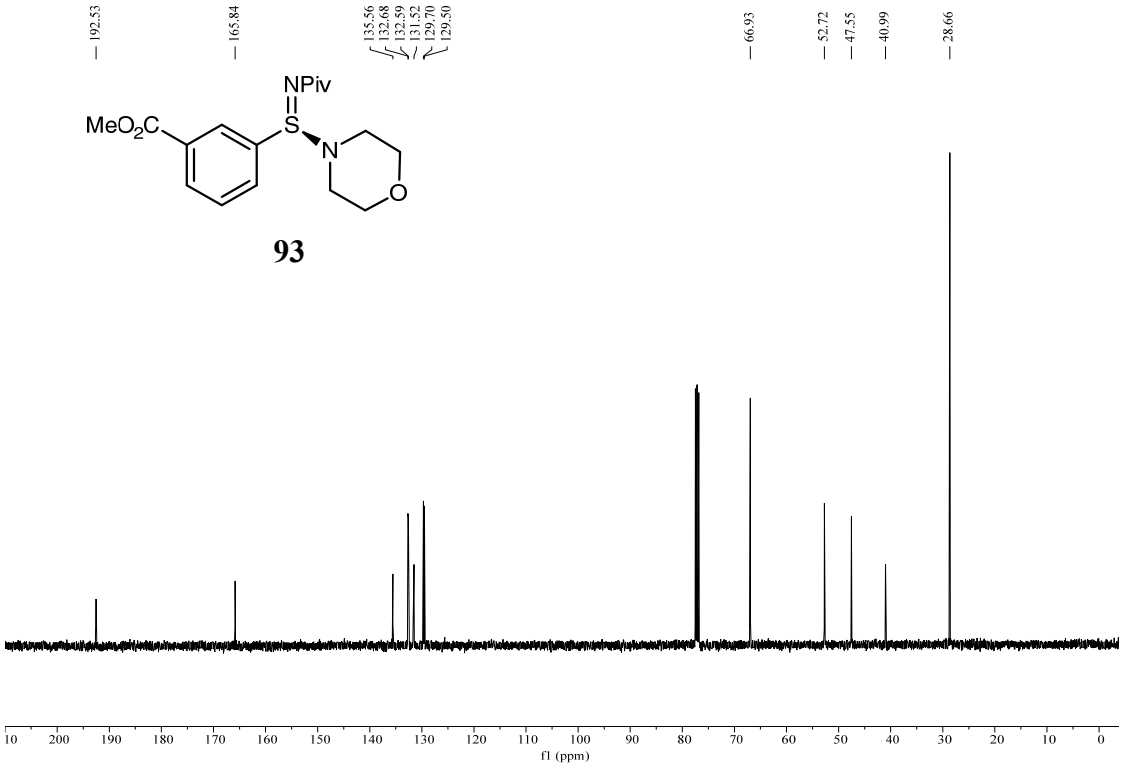
^{19}F NMR of 92 (375 MHz, $CDCl_3$)



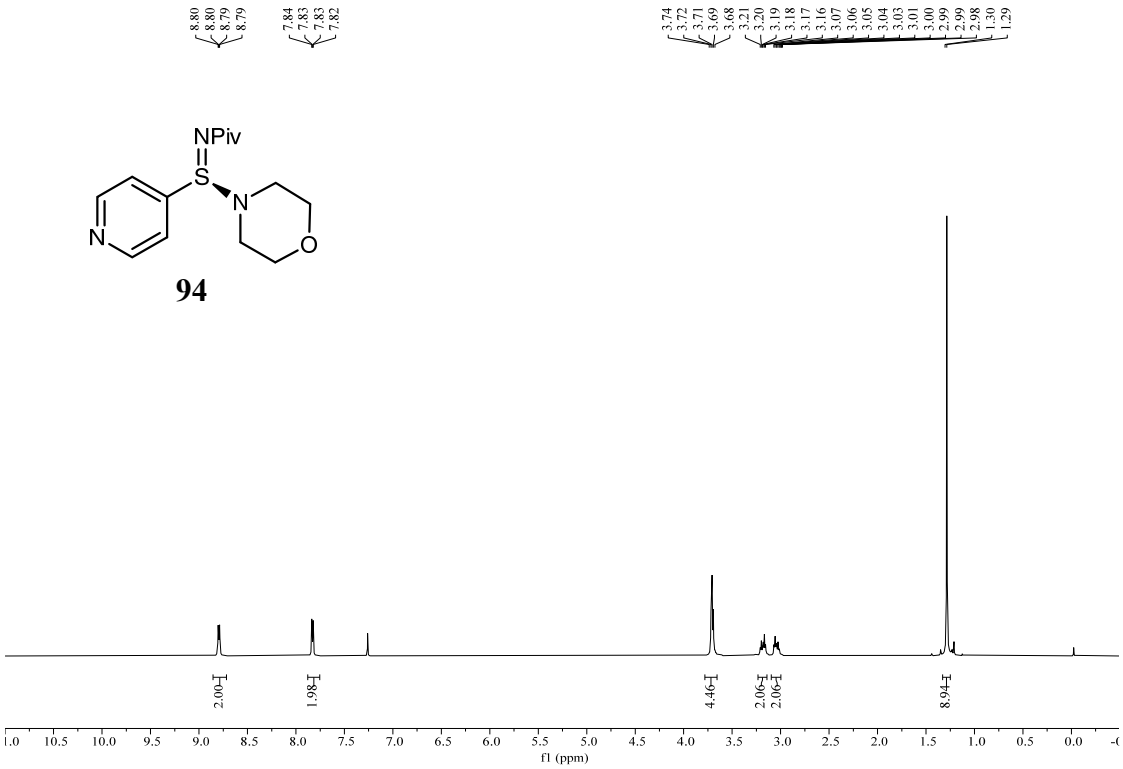
^{1}H NMR of 93 (400 MHz, $CDCl_3$)



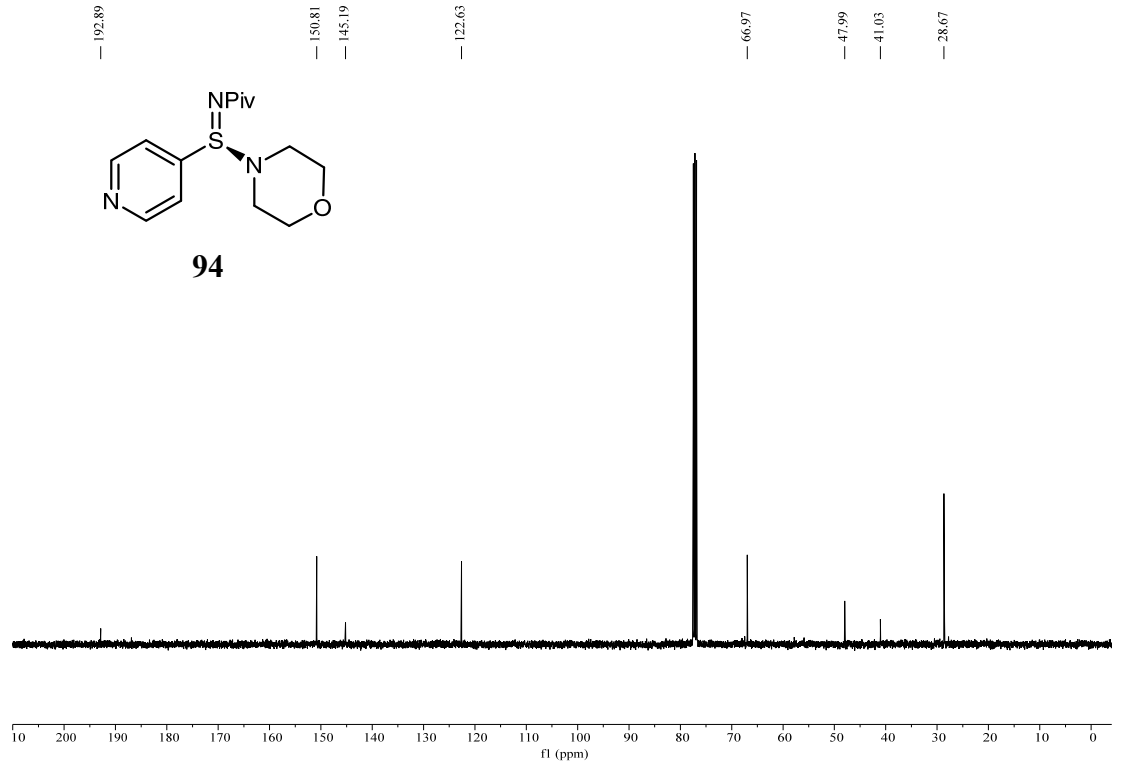
^{13}C NMR of 93 (100 MHz, $CDCl_3$)



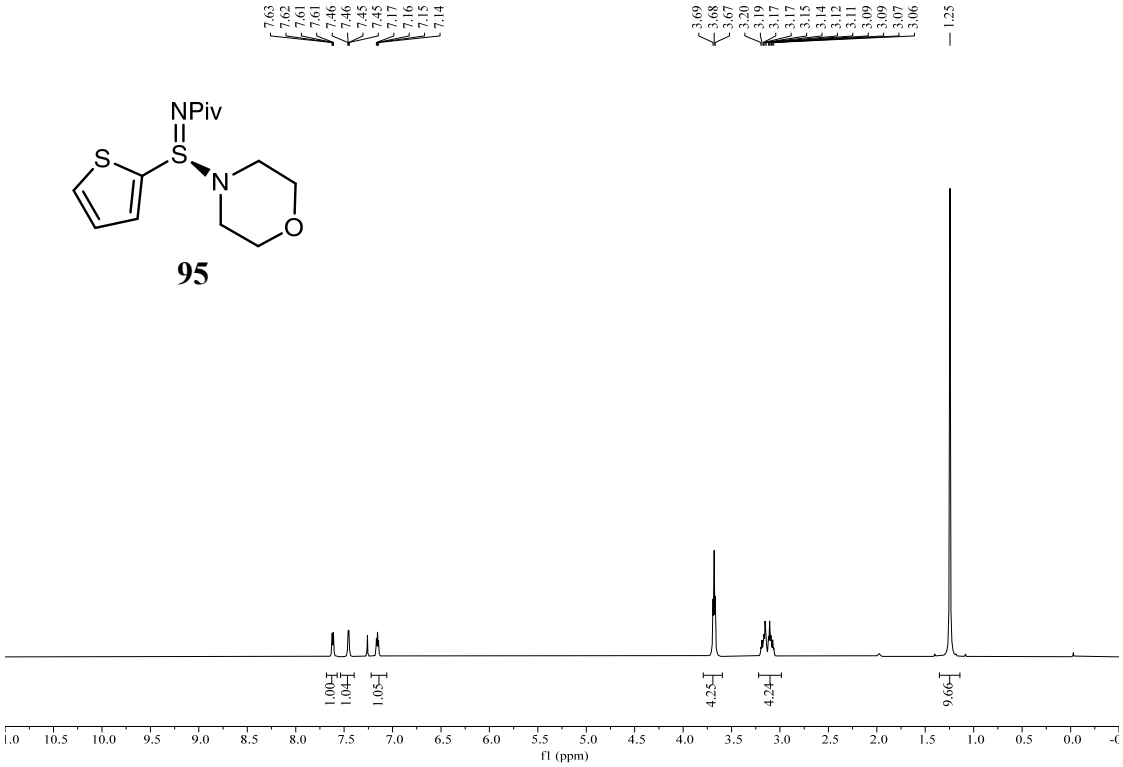
^{1}H NMR of 94 (400 MHz, $CDCl_3$)



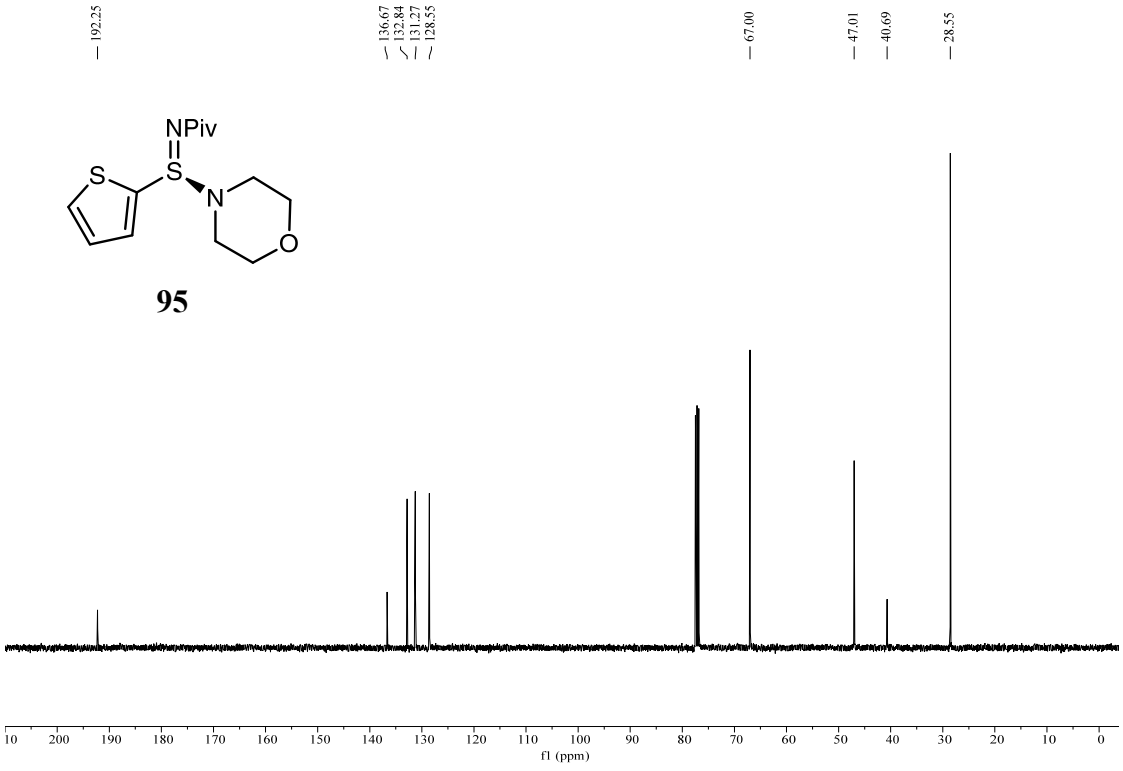
^{13}C NMR of 94 (100 MHz, $CDCl_3$)



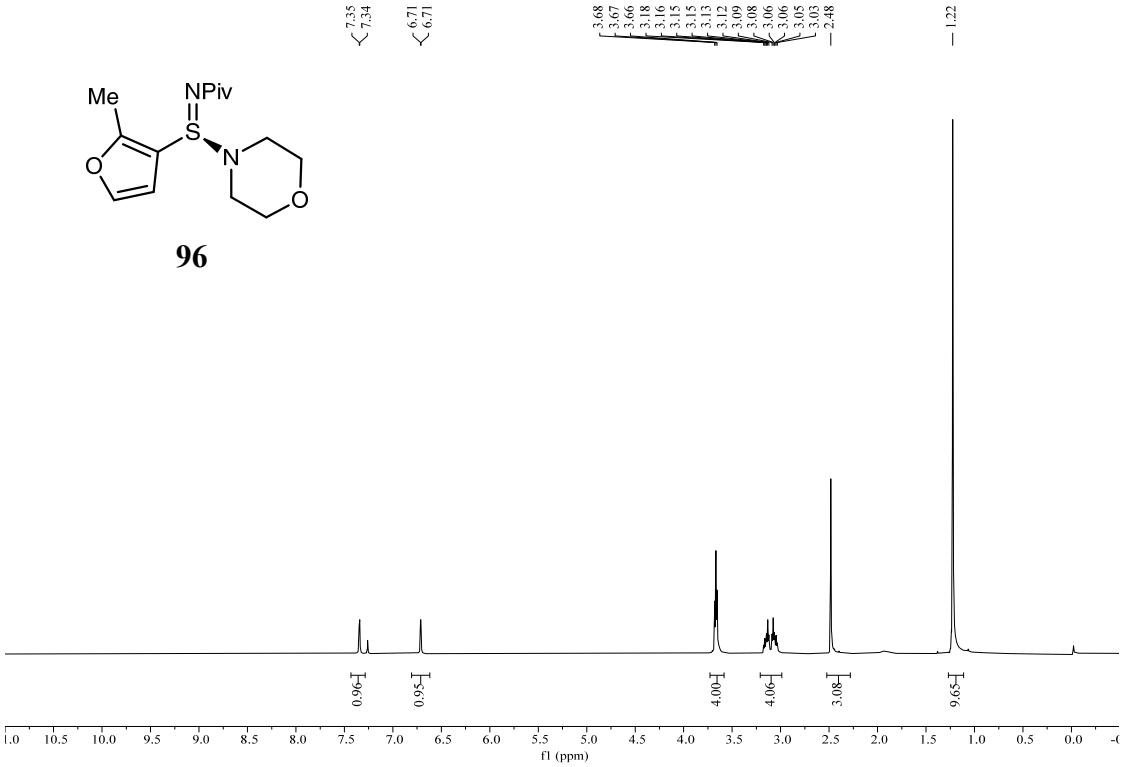
^{1}H NMR of 95 (400 MHz, $CDCl_3$)



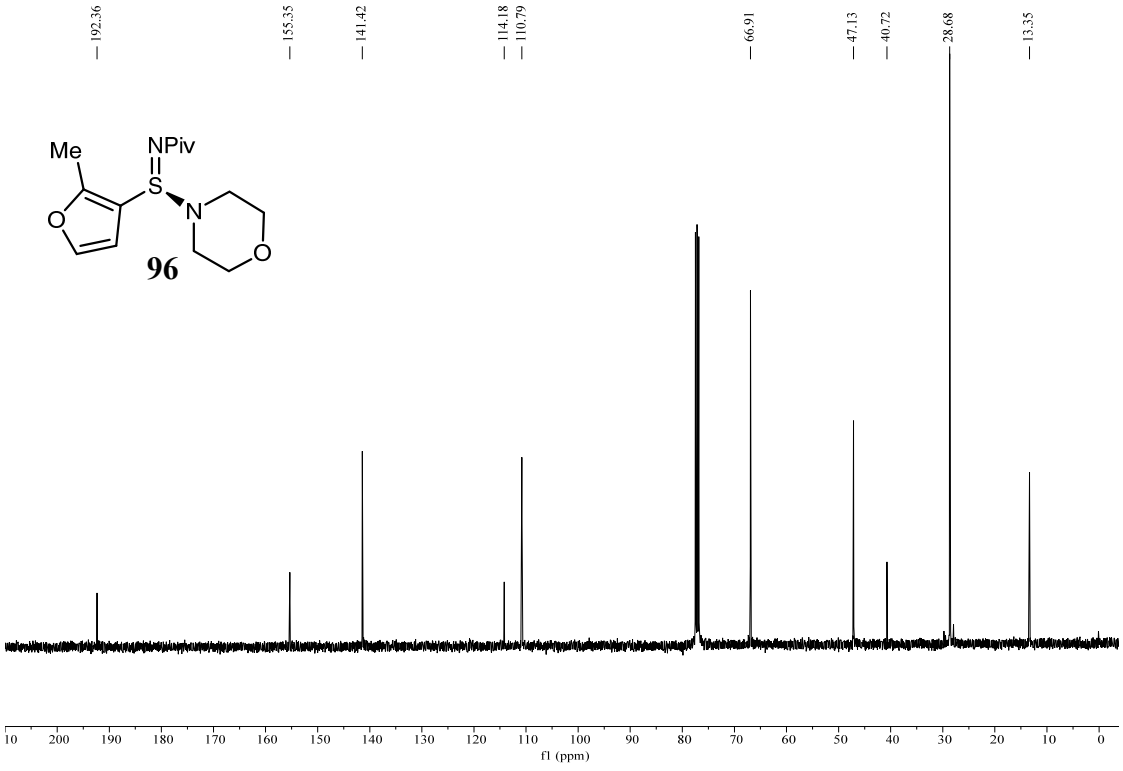
^{13}C NMR of 95 ($CDCl_3$)



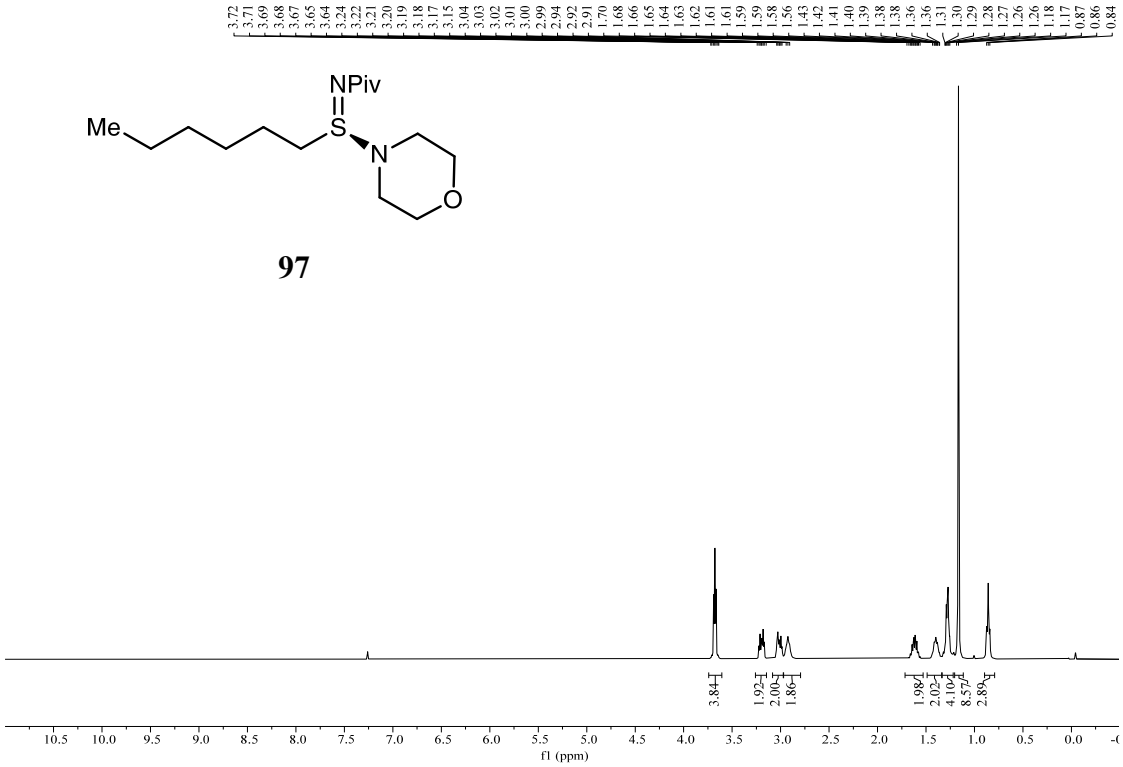
^{1}H NMR of 96 (400 MHz, $CDCl_3$)



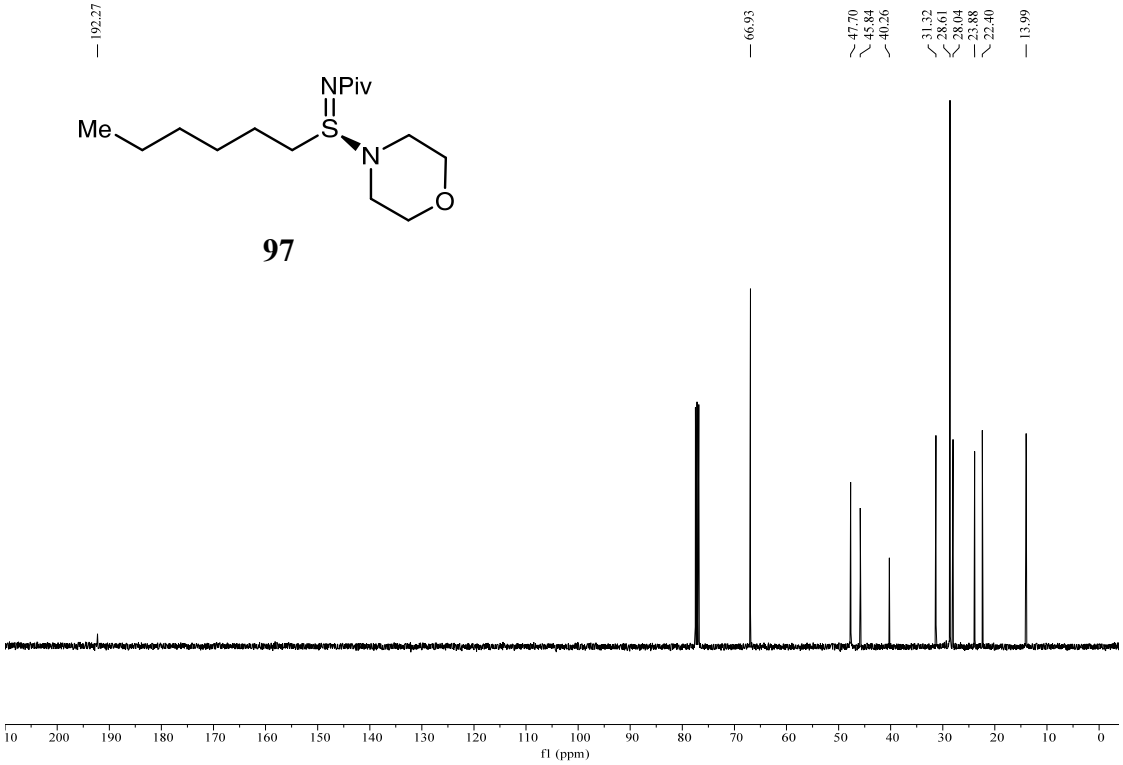
^{13}C NMR of 96 (100 MHz, $CDCl_3$)



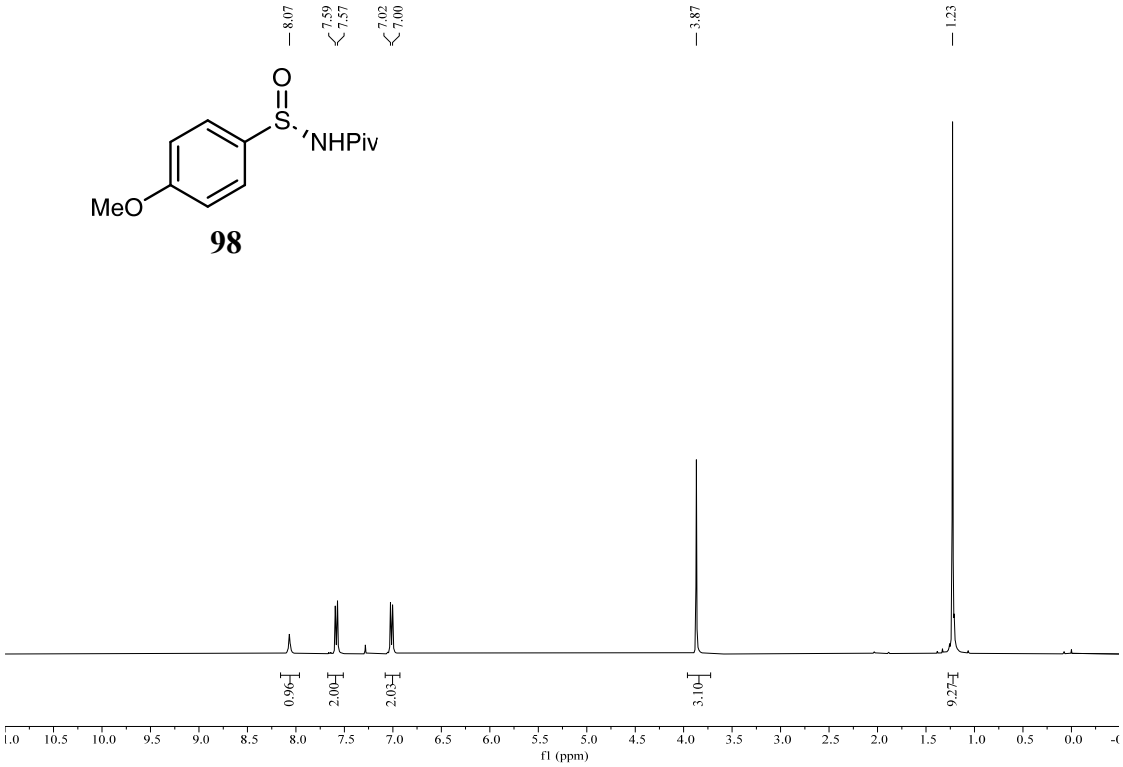
^{1}H NMR of 97 (400 MHz, $CDCl_3$)



^{13}C NMR of 97 (100 MHz, $CDCl_3$)

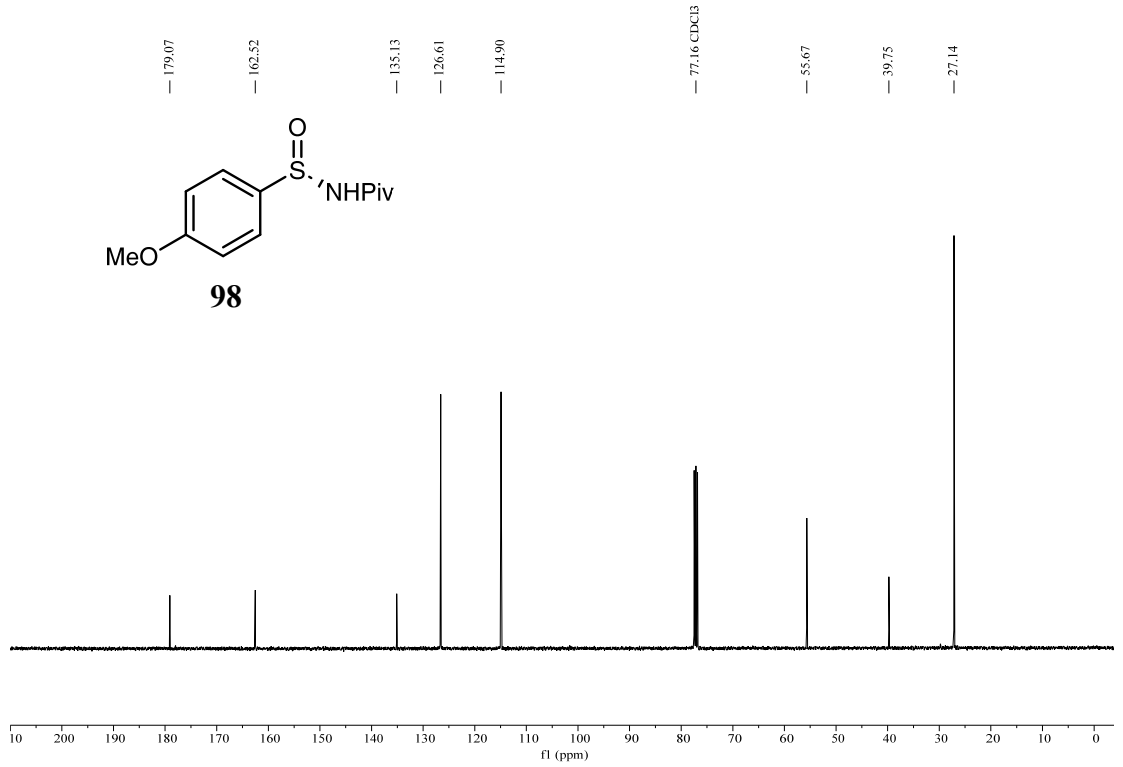


^{1}H NMR of 98 (400 MHz, $CDCl_3$)



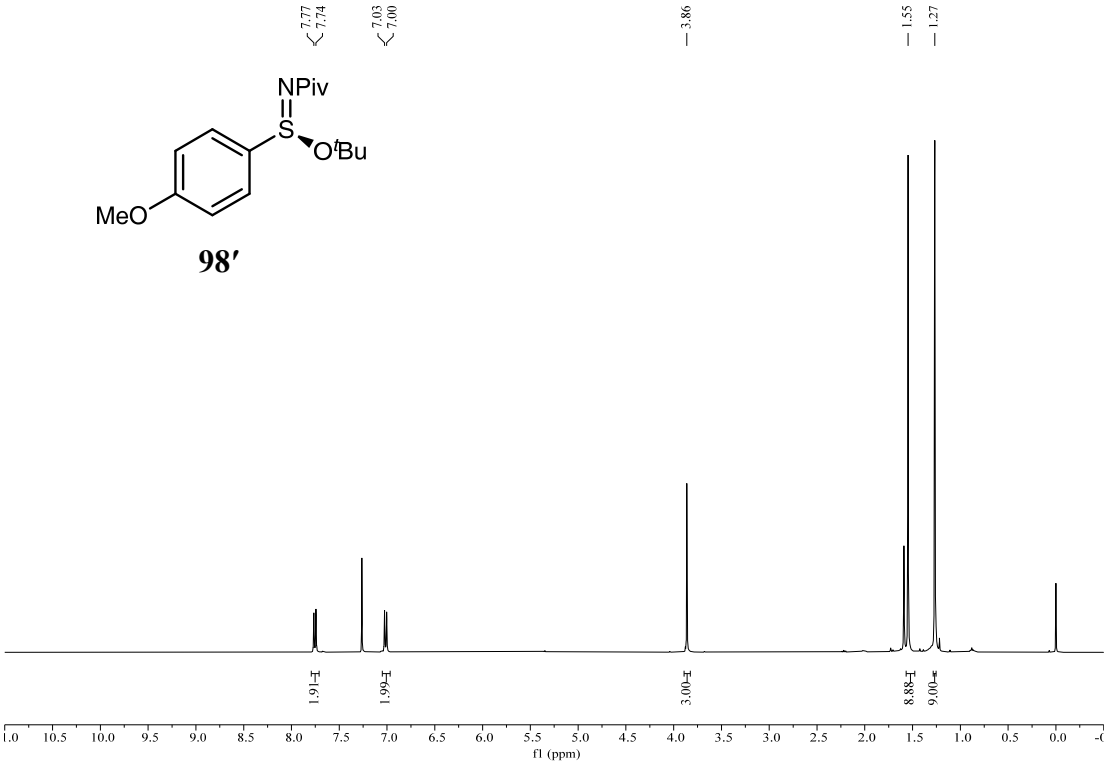
98

^{13}C NMR of 98 (100 MHz, $CDCl_3$)



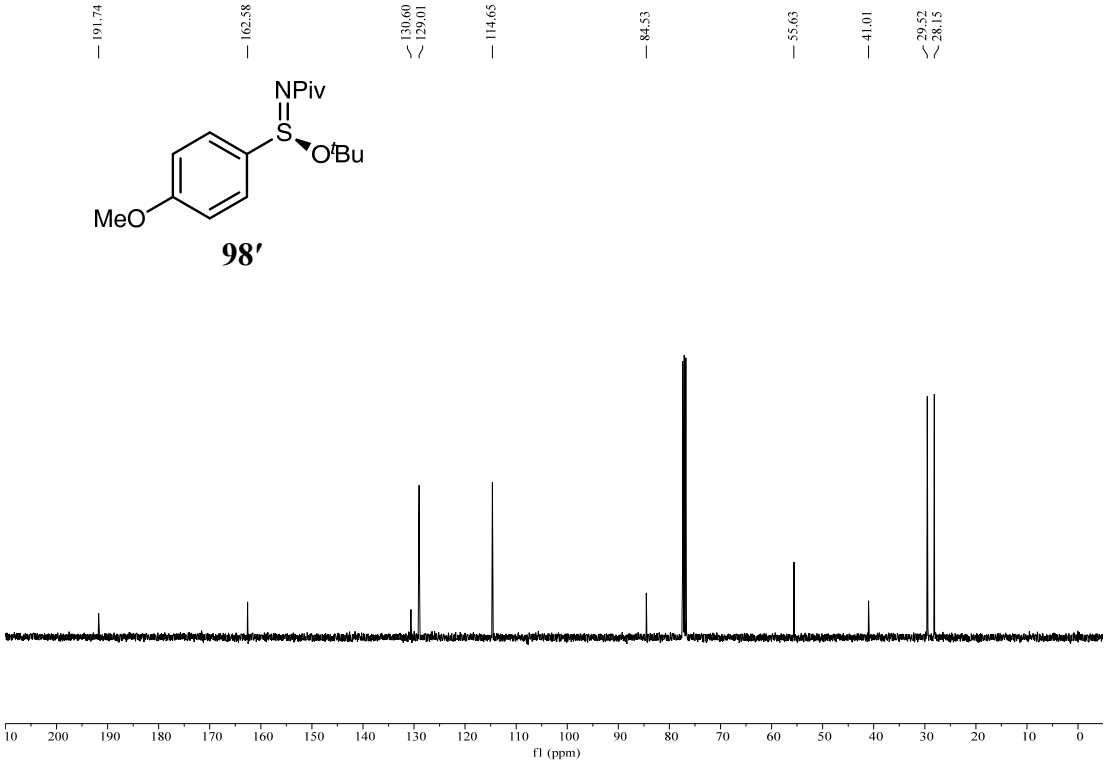
98

^{1}H NMR of 98′ (400 MHz, $CDCl_3$)



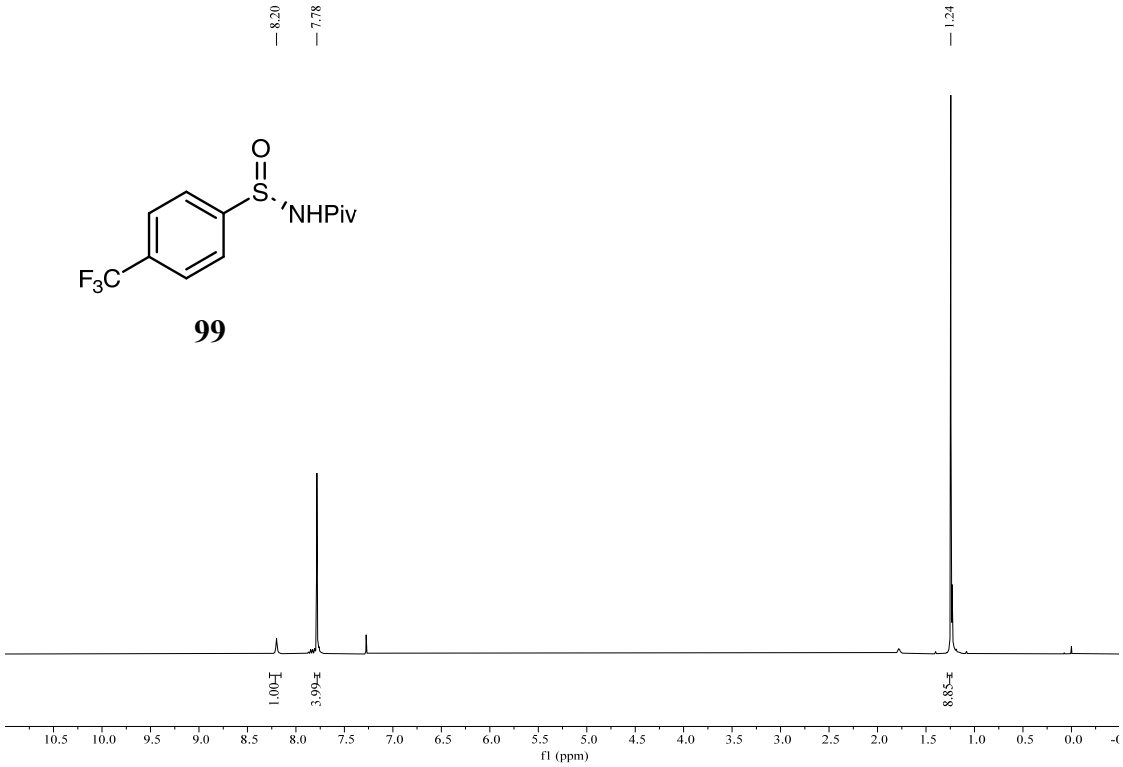
98′

^{13}C NMR of 98′ (100 MHz, $CDCl_3$)

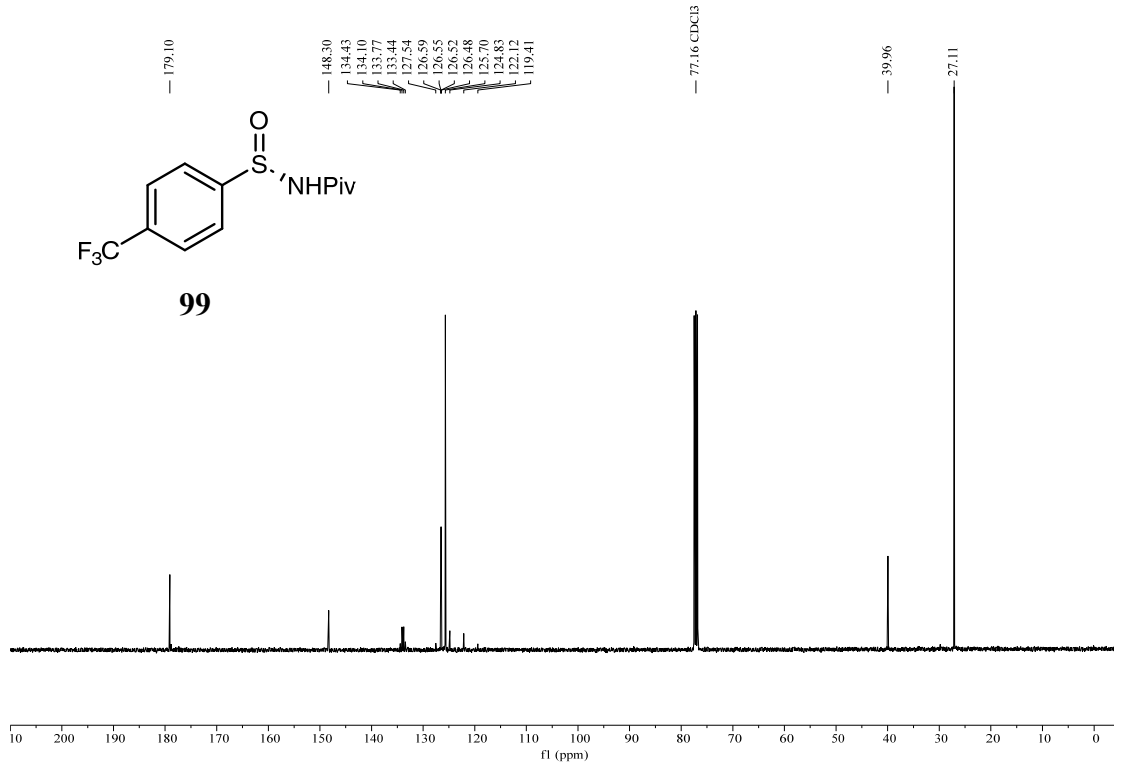


98′

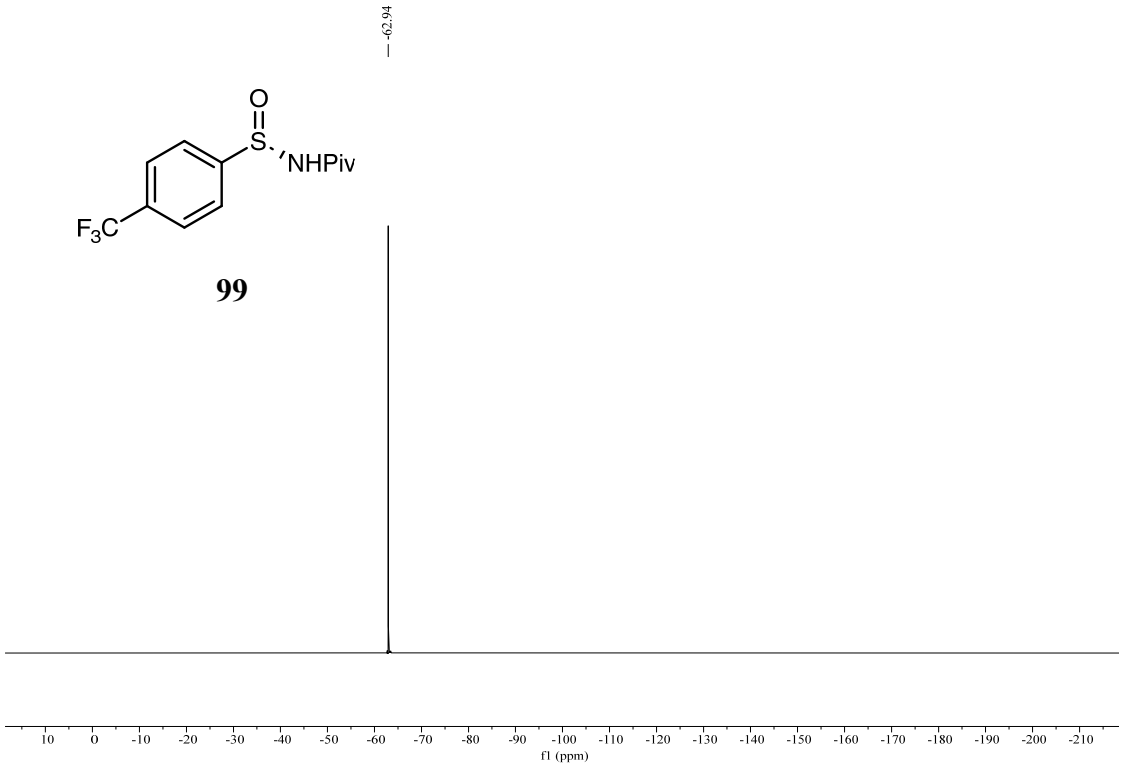
^{1}H NMR of 99 (400 MHz, $CDCl_3$)



^{13}C NMR of 99 (100 MHz, $CDCl_3$)

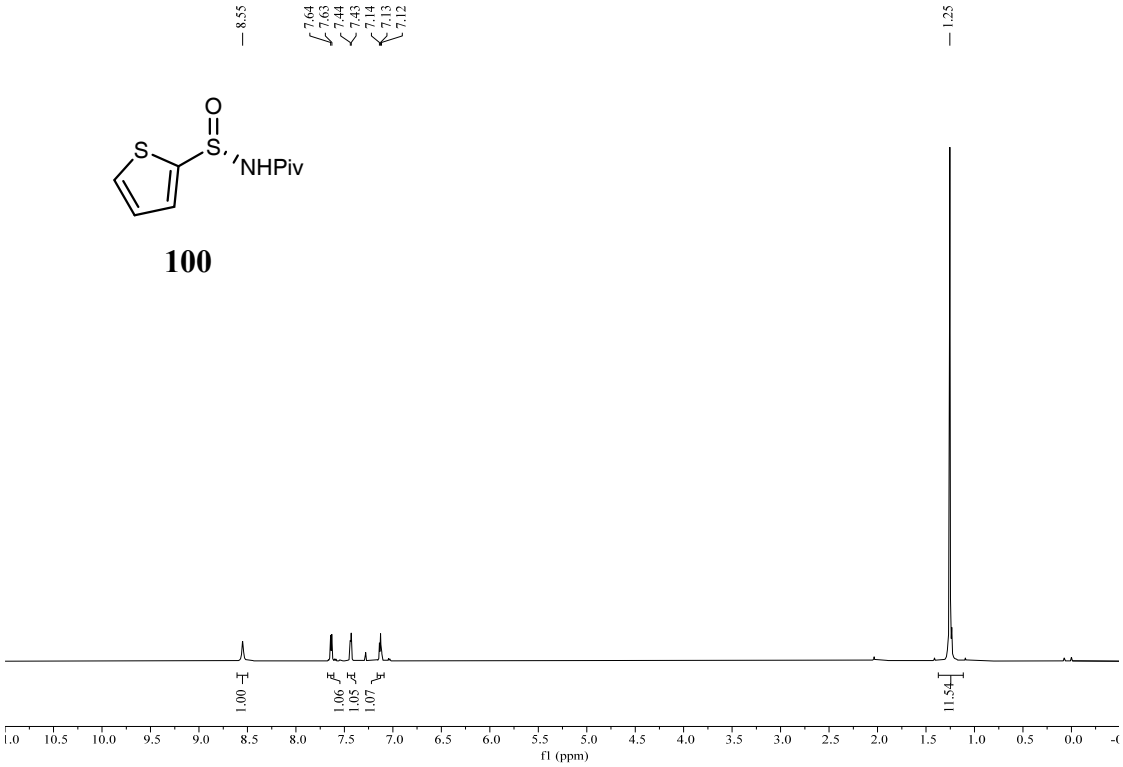


^{19}F NMR of 99 (375 MHz, $CDCl_3$)



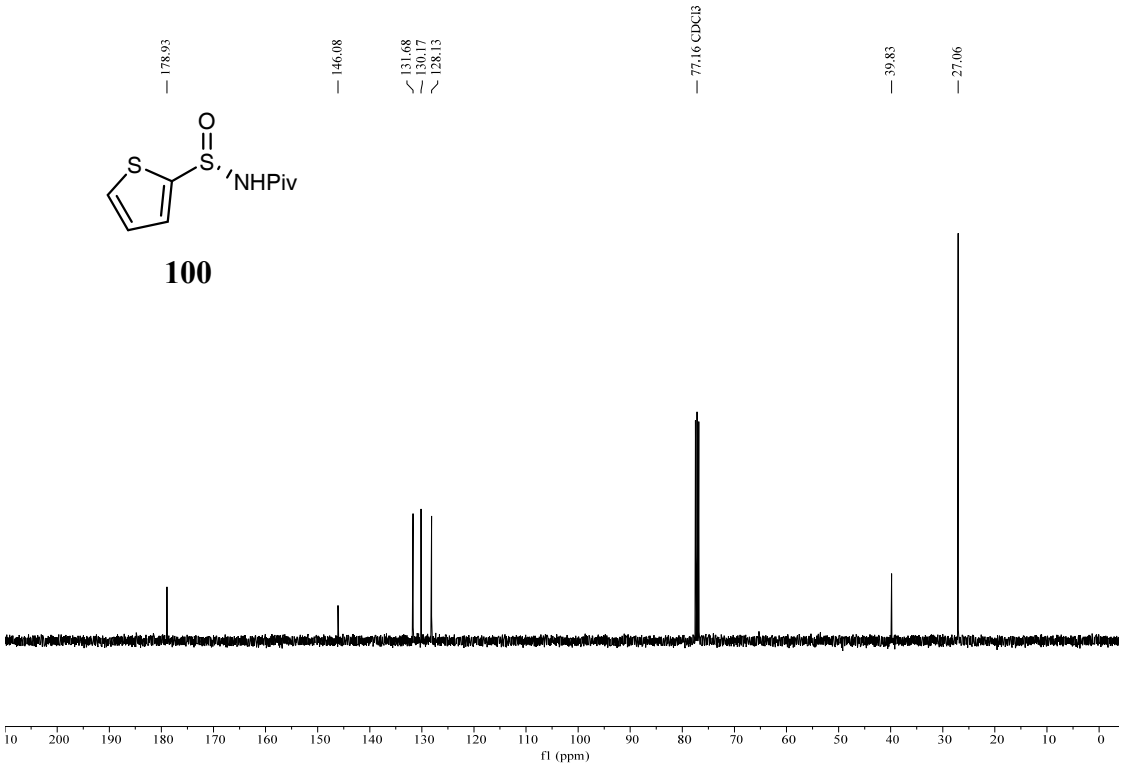
99

^{1}H NMR of 100 (400 MHz, $CDCl_3$)



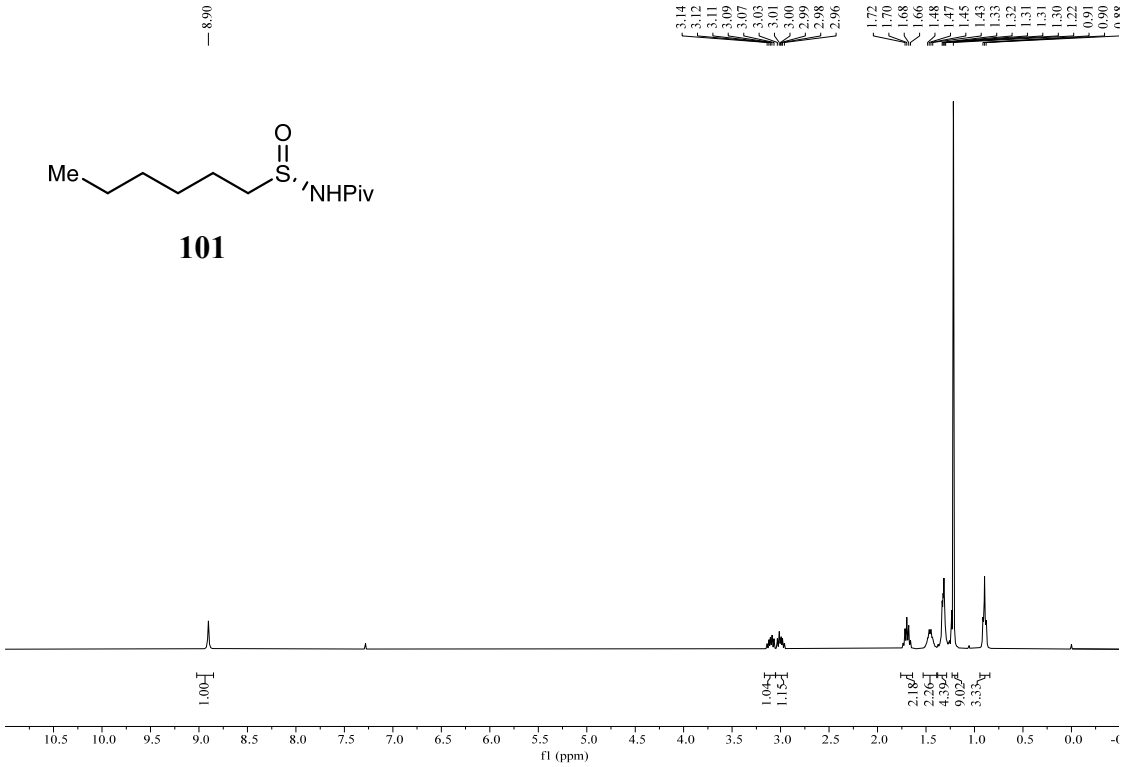
100

^{13}C NMR of 100 (100 MHz, $CDCl_3$)



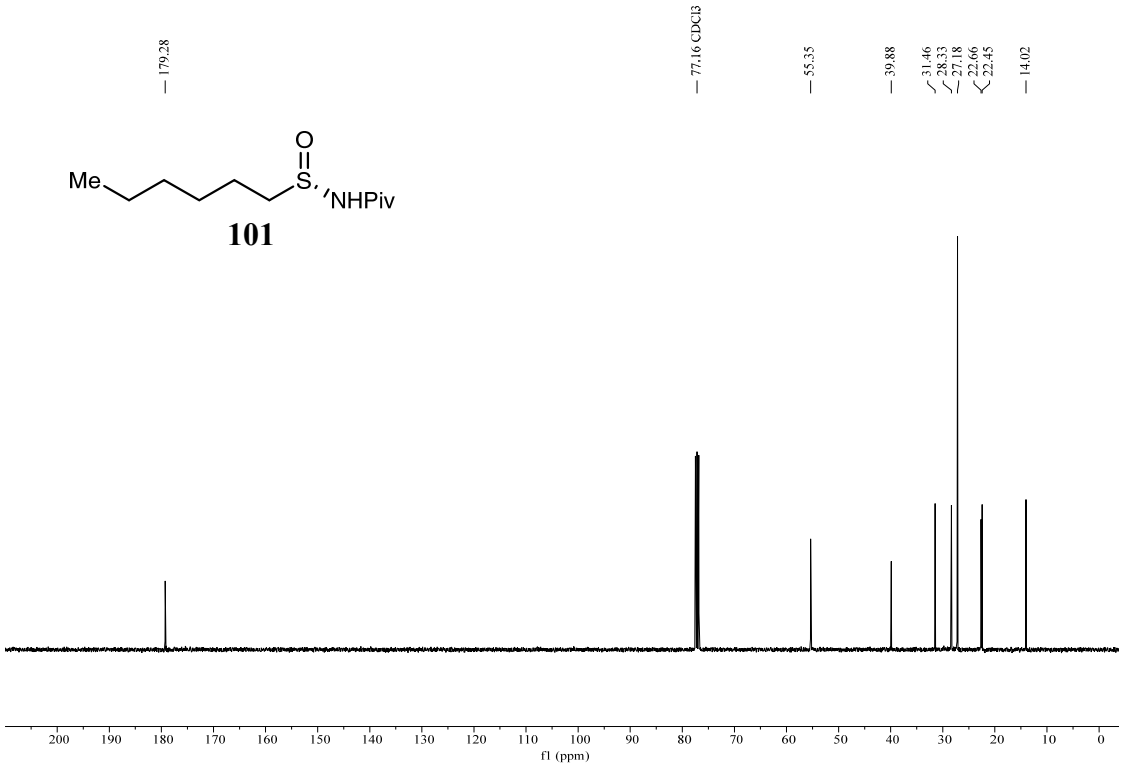
100

^{1}H NMR of 101 (400 MHz, $CDCl_3$)



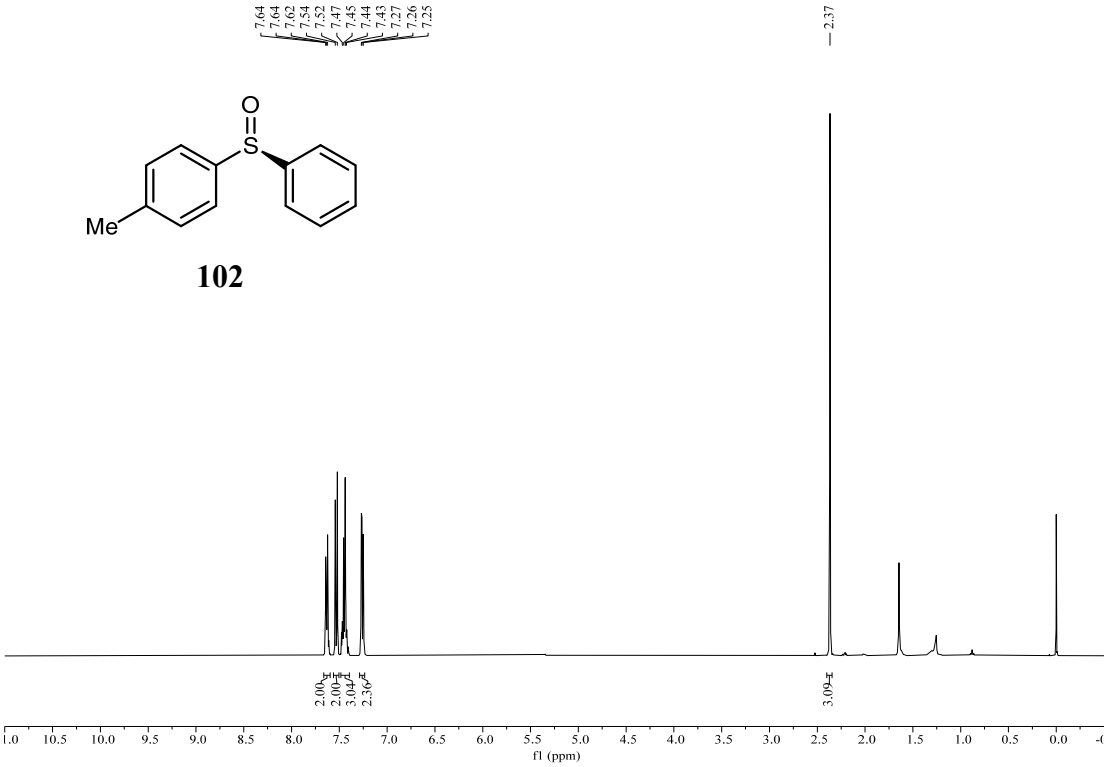
101

^{13}C NMR of 101 (100 MHz, $CDCl_3$)



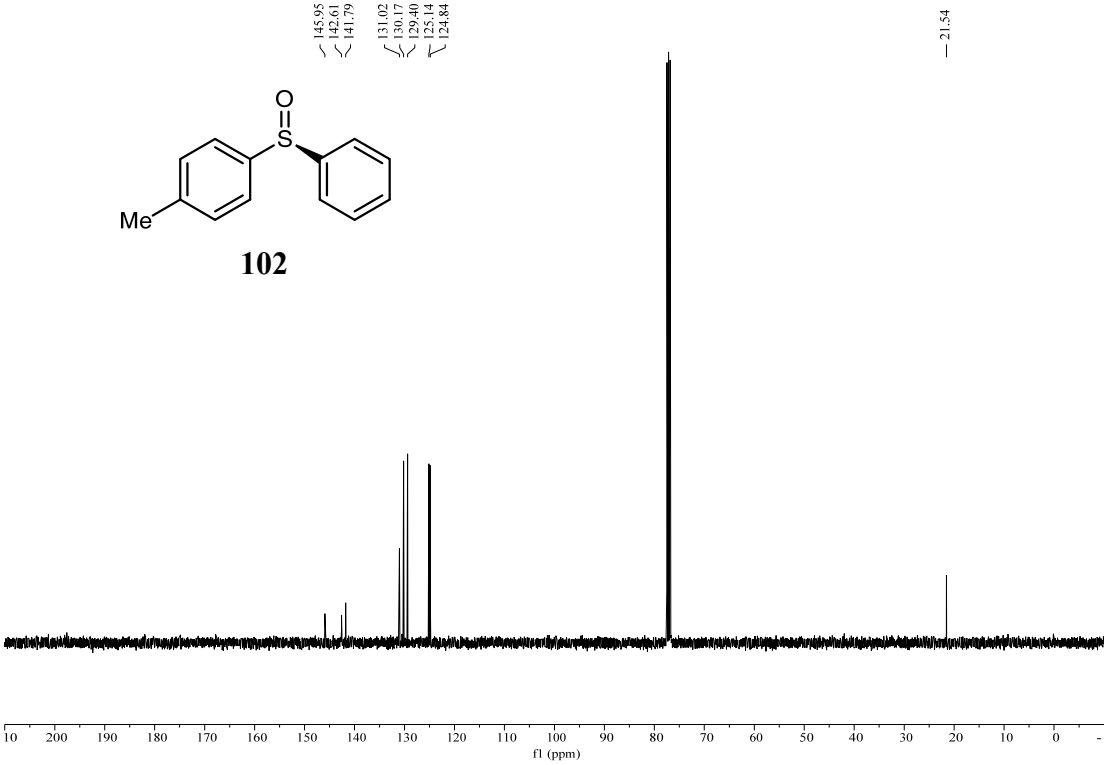
101

^{1}H NMR of 102 (400 MHz, $CDCl_3$)



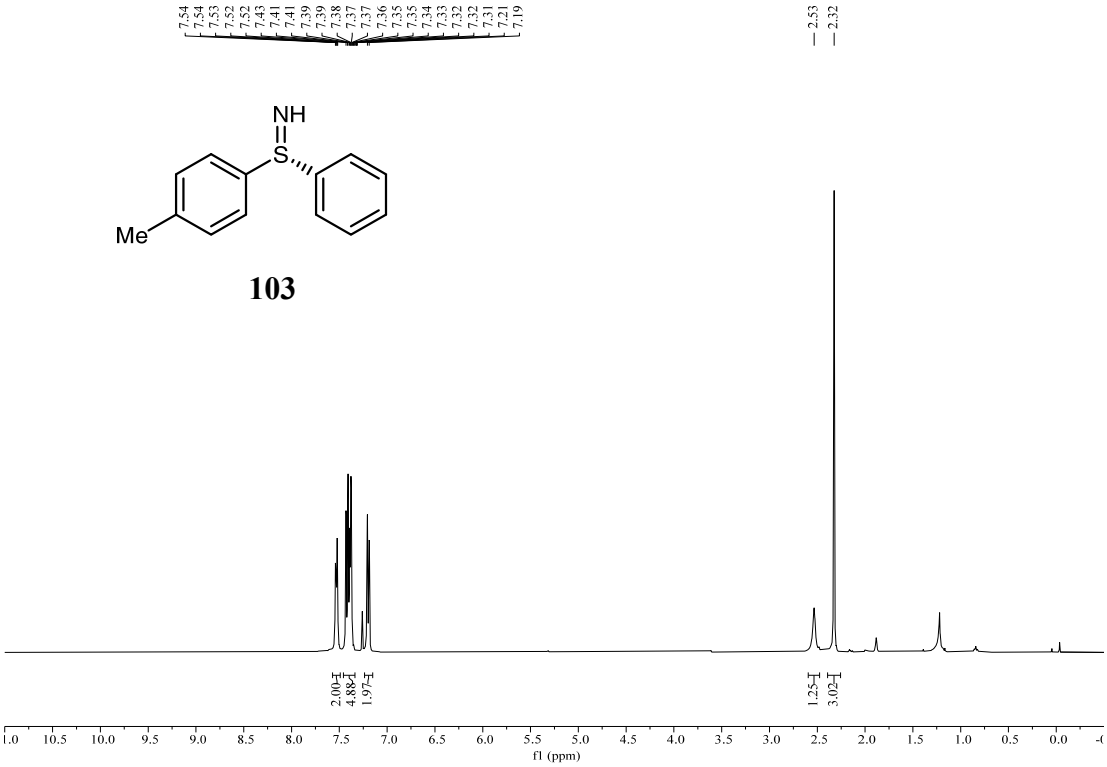
102

^{13}C NMR of 102 (100 MHz, $CDCl_3$)



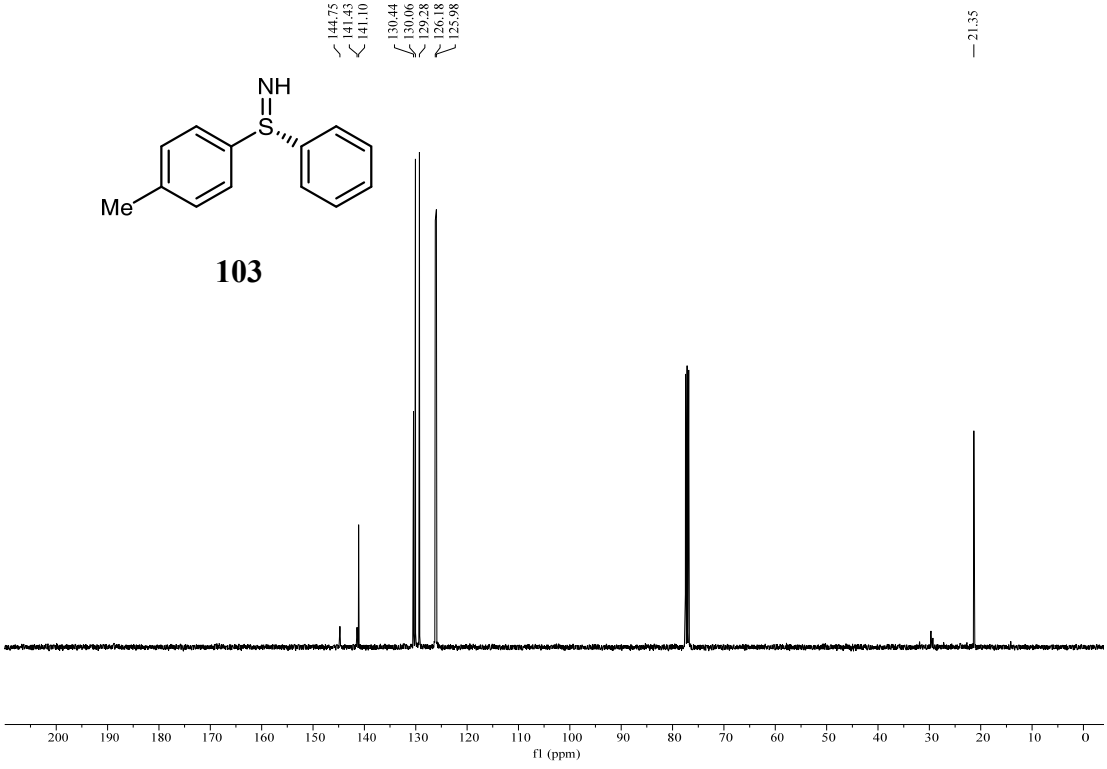
102

^{1}H NMR of 103 (400 MHz, $CDCl_3$)



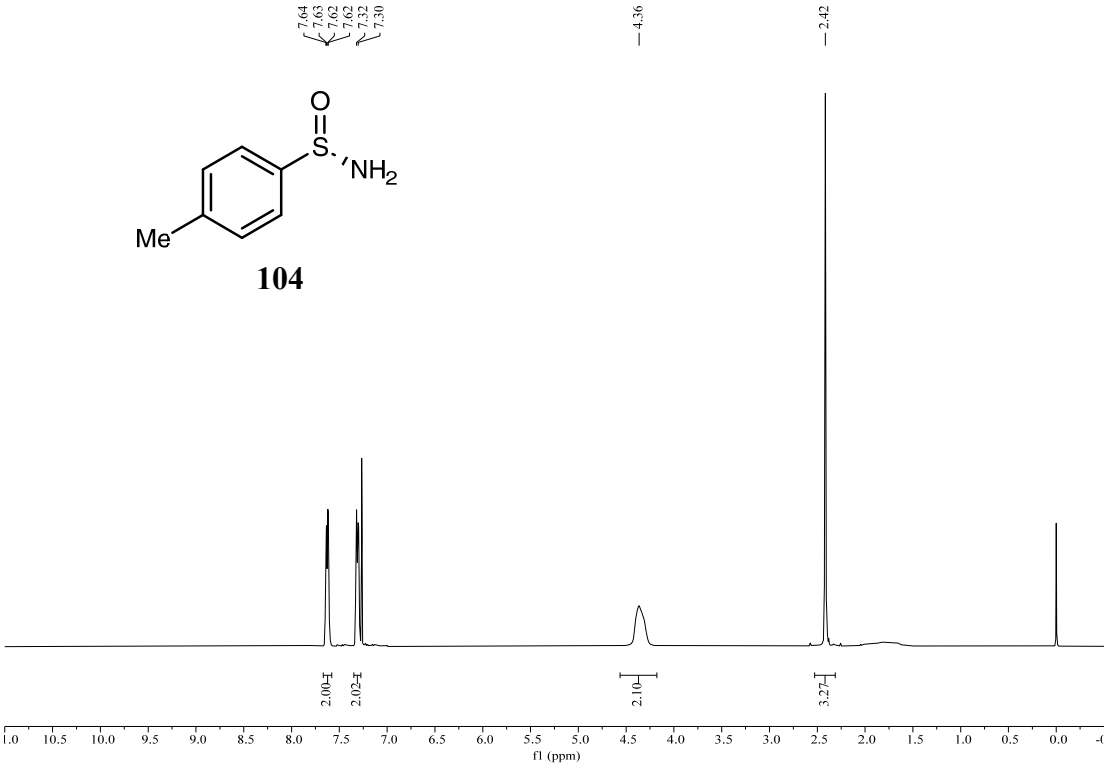
103

^{13}C NMR of 103 (100 MHz, $CDCl_3$)



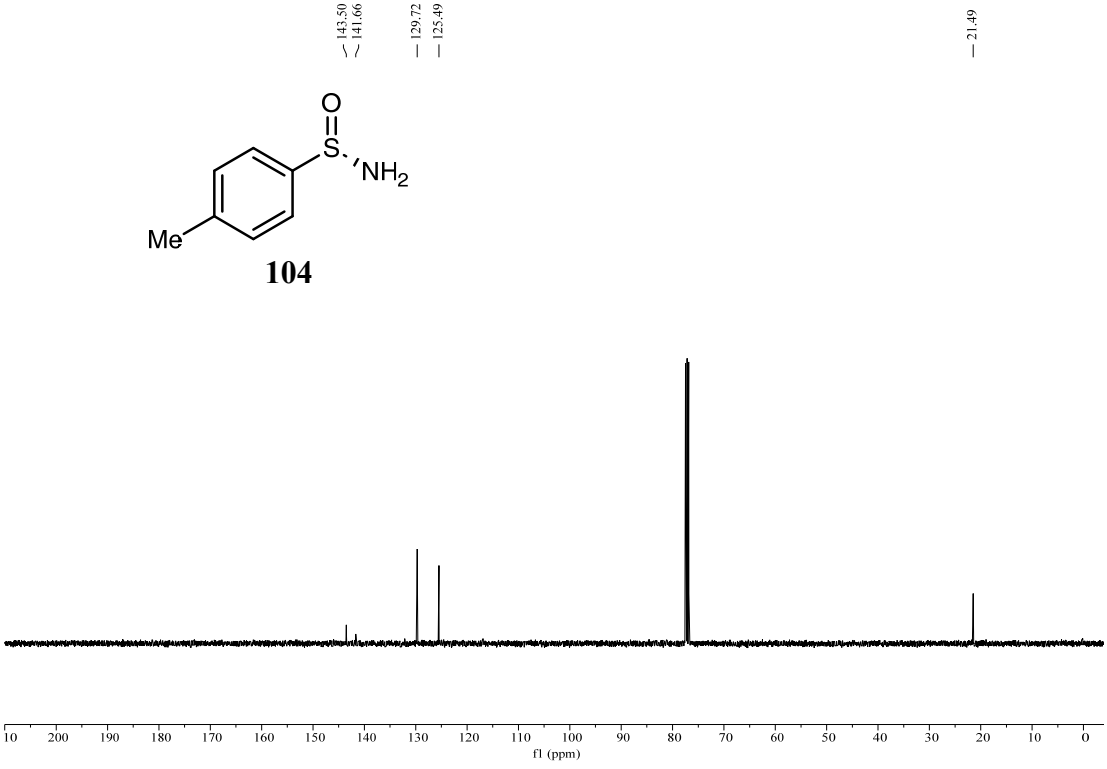
103

^{1}H NMR of 104 (400 MHz, $CDCl_3$)



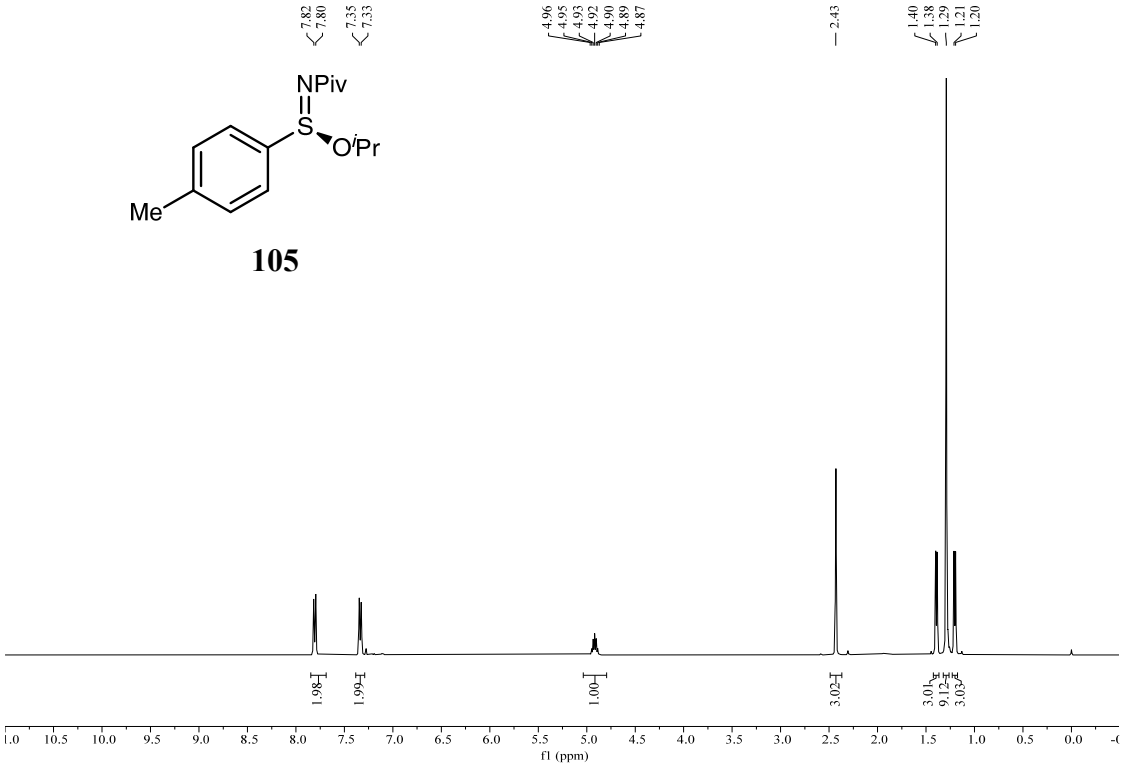
104

^{13}C NMR of 104 (100 MHz, $CDCl_3$)



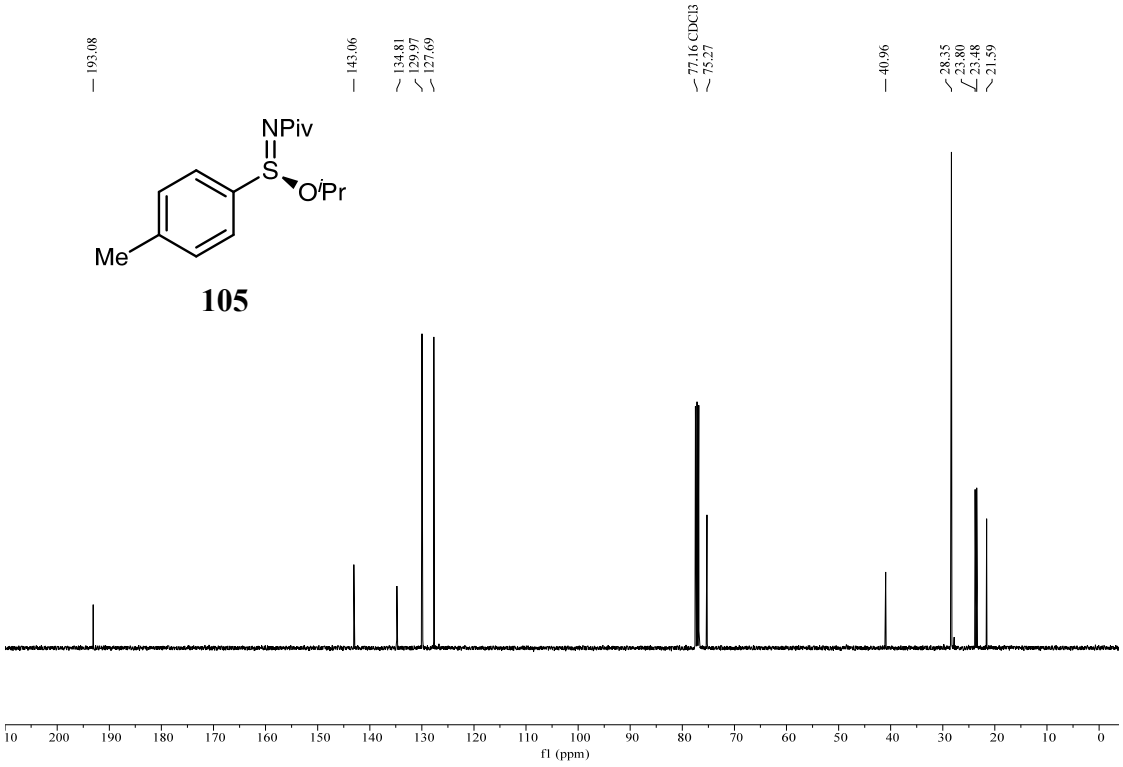
104

^{1}H NMR of 105 (400 MHz, $CDCl_3$)



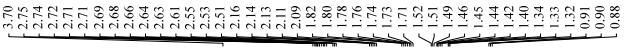
105

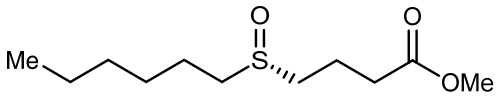
^{13}C NMR of 105 (100 MHz, $CDCl_3$)



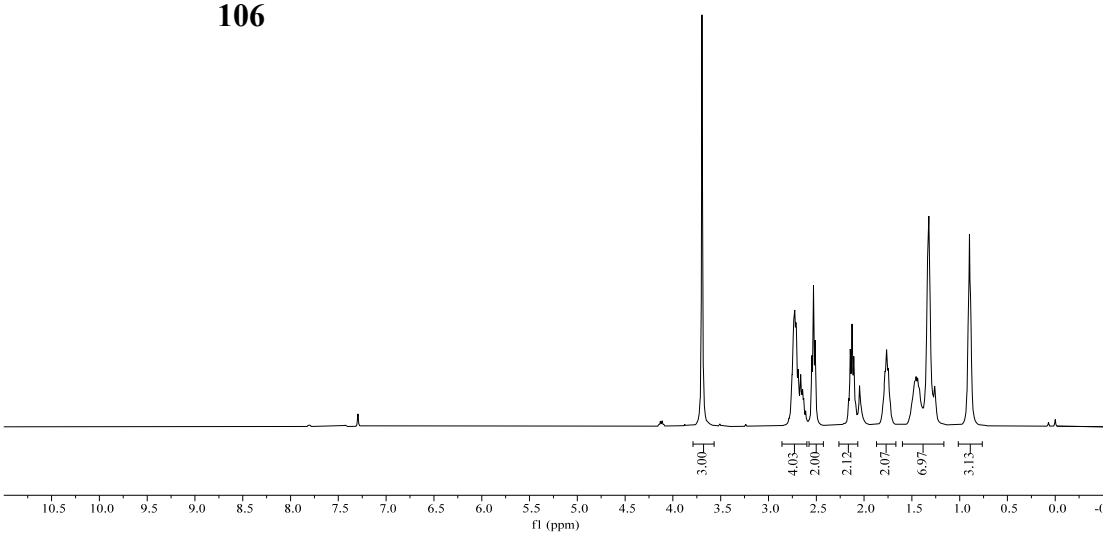
105

^{1}H NMR of 106 (400 MHz, $CDCl_3$)

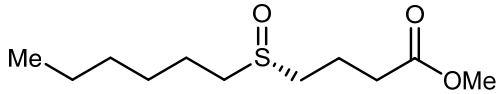




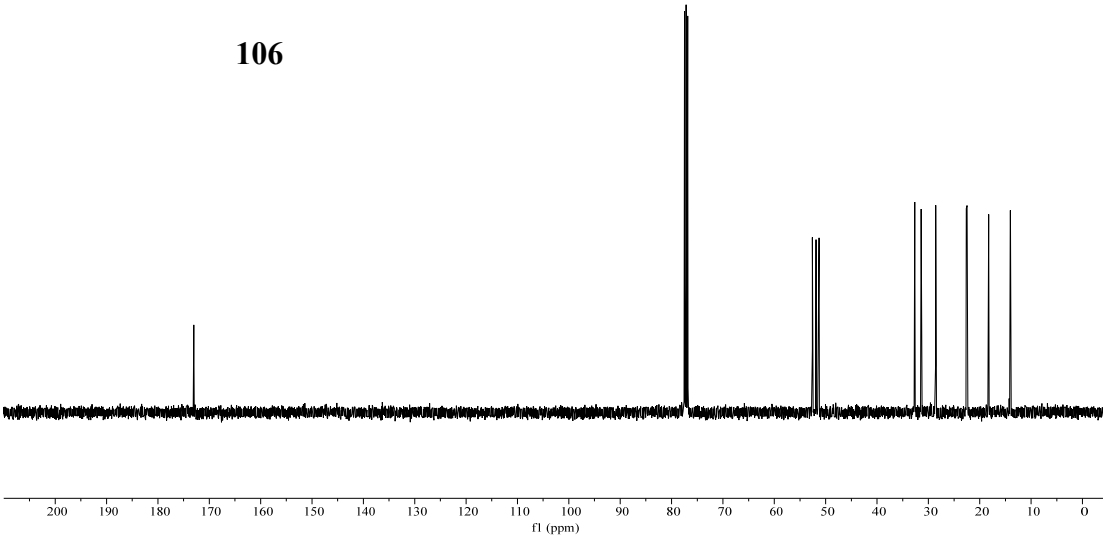
106



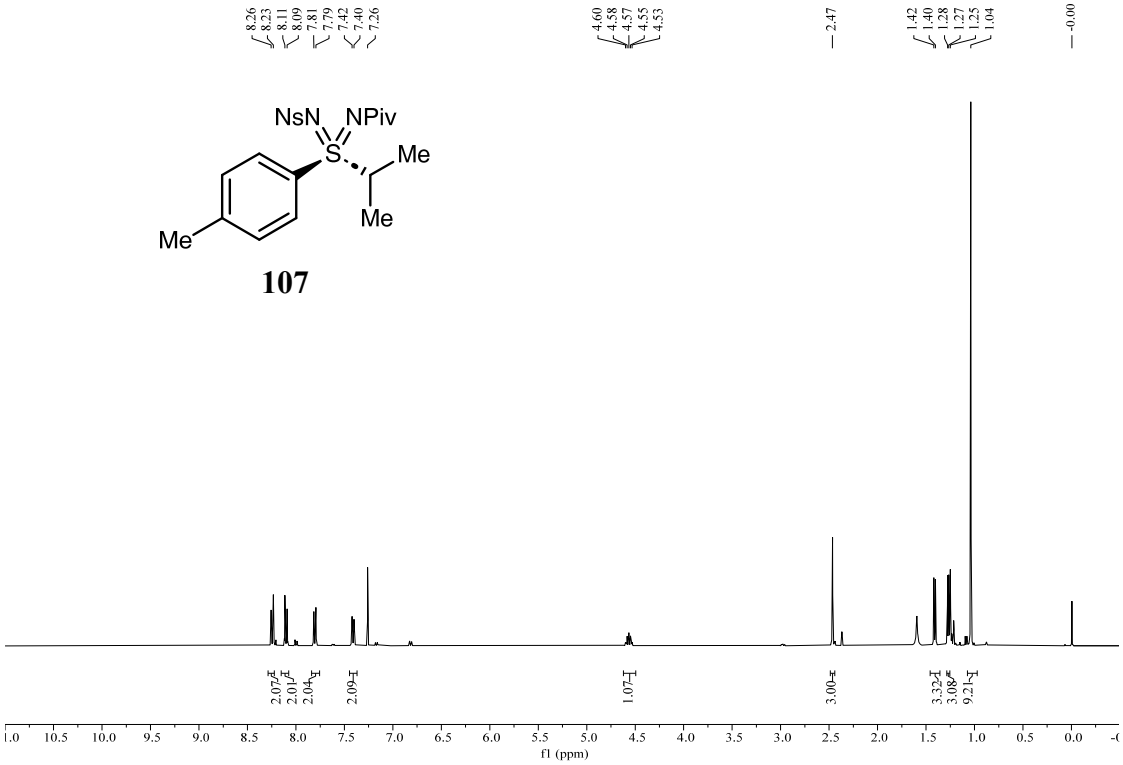
^{13}C NMR of 106 (100 MHz, $CDCl_3$)



106

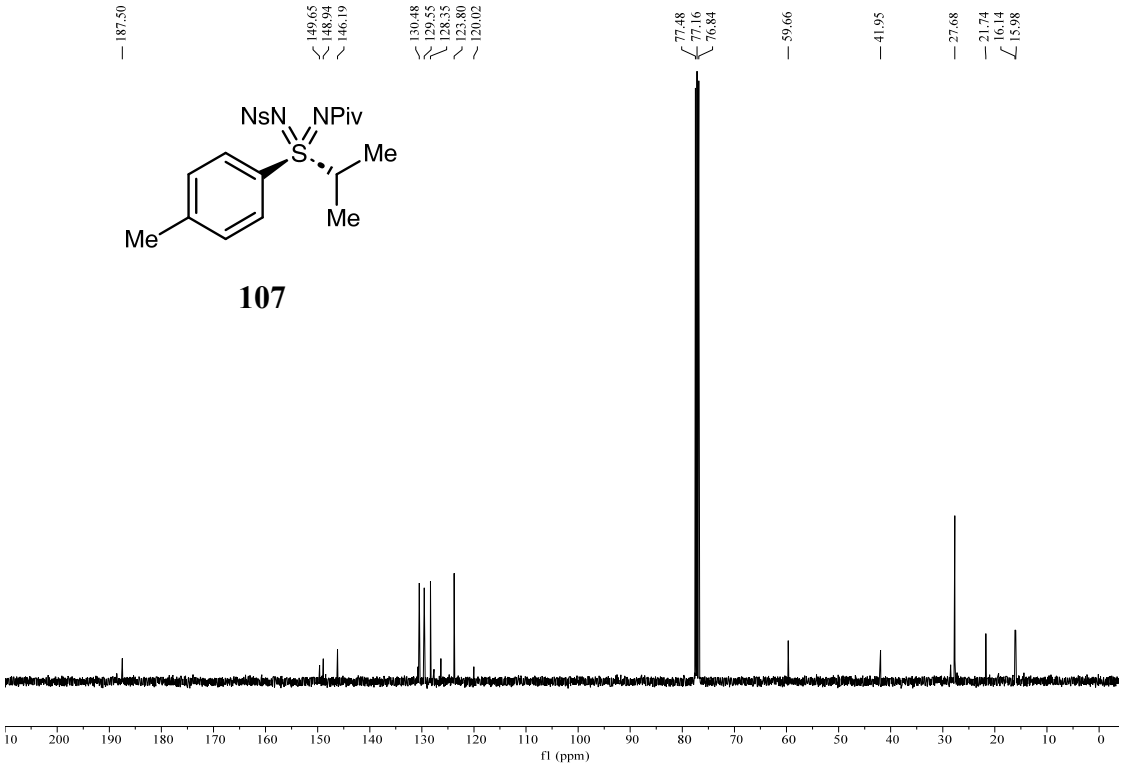


^{1}H NMR of 107 (400 MHz, $CDCl_3$)



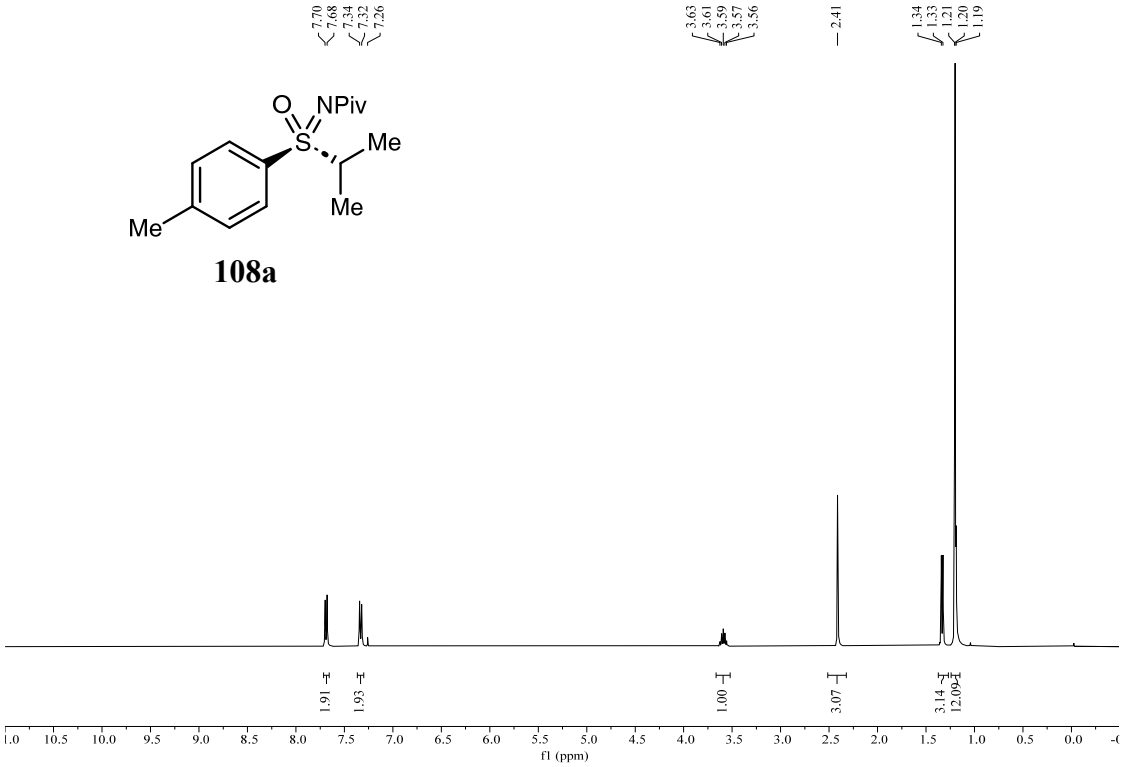
107

^{13}C NMR of 107 (100 MHz, $CDCl_3$)



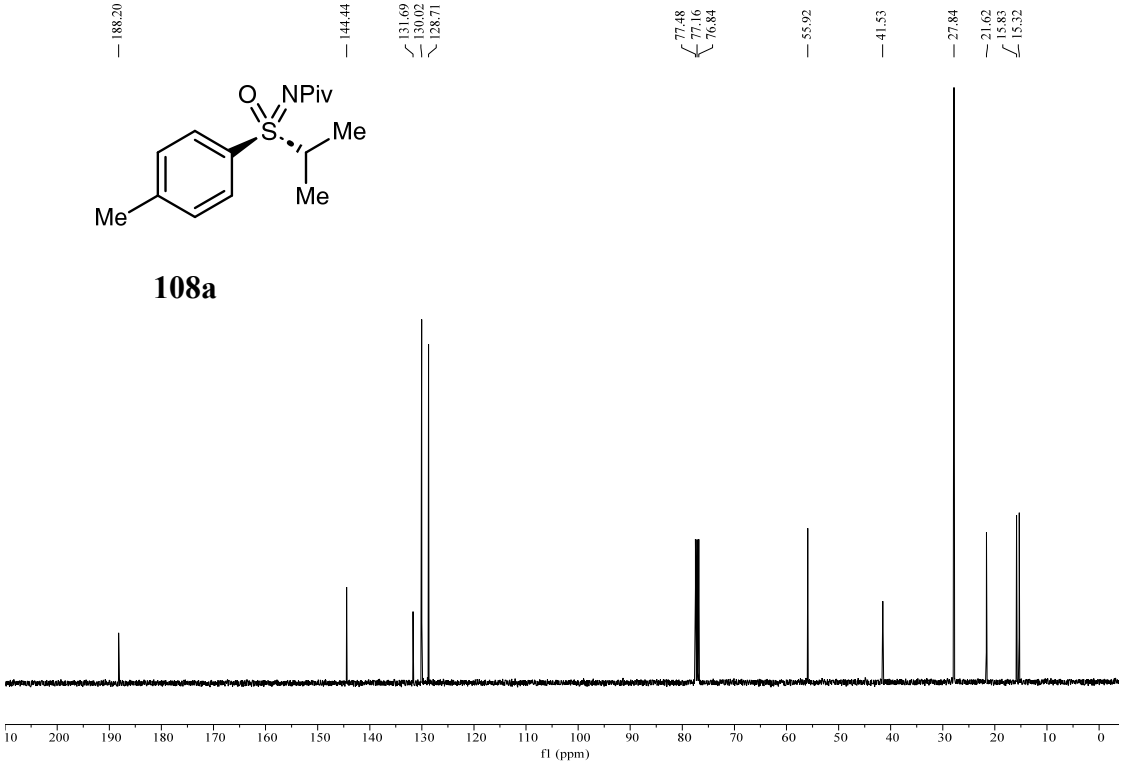
107

^{1}H NMR of 108a (400 MHz, $CDCl_3$)



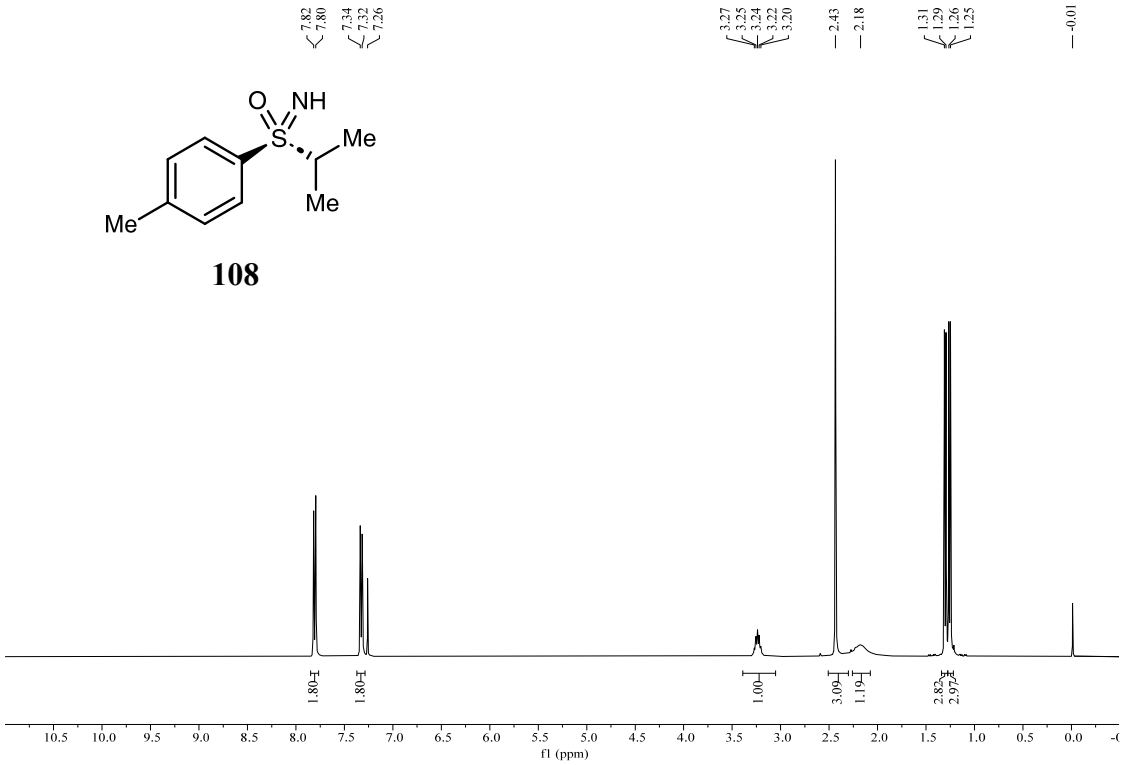
108a

^{13}C NMR of 108a (100 MHz, $CDCl_3$)



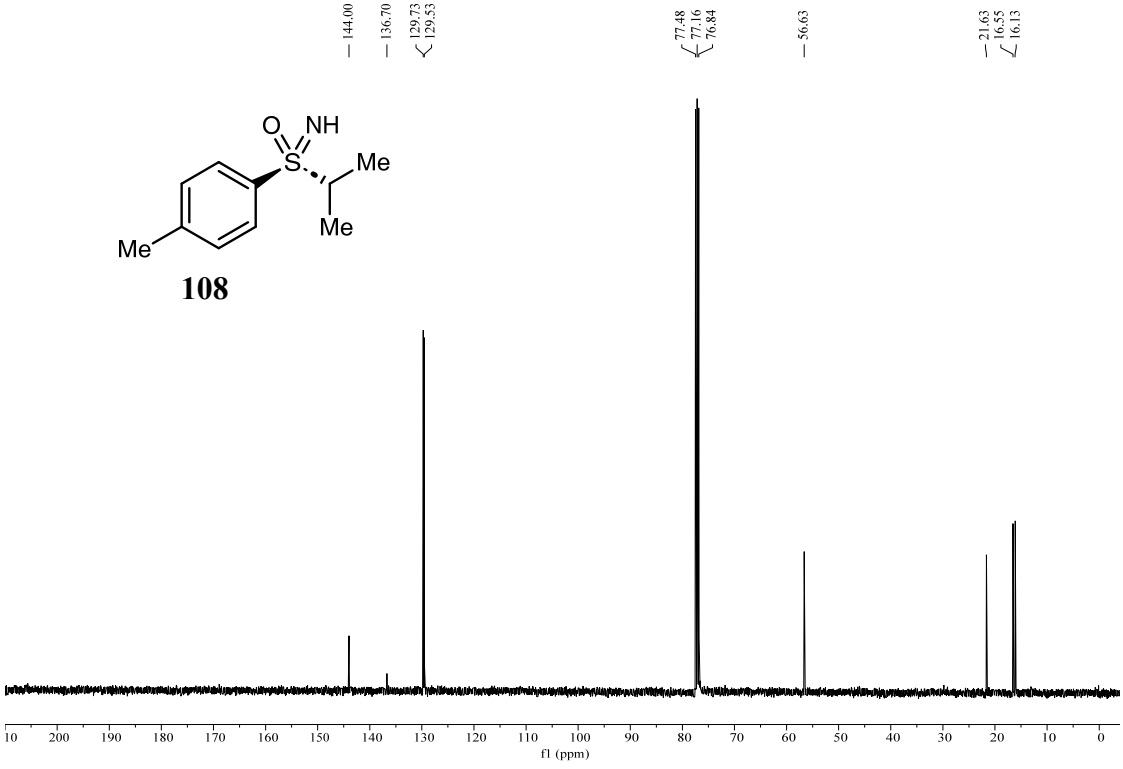
108a

^{1}H NMR of 108 (400 MHz, $CDCl_3$)



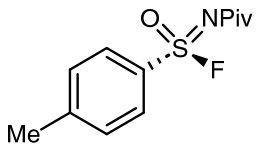
108

^{13}C NMR of 108 (100 MHz, $CDCl_3$)



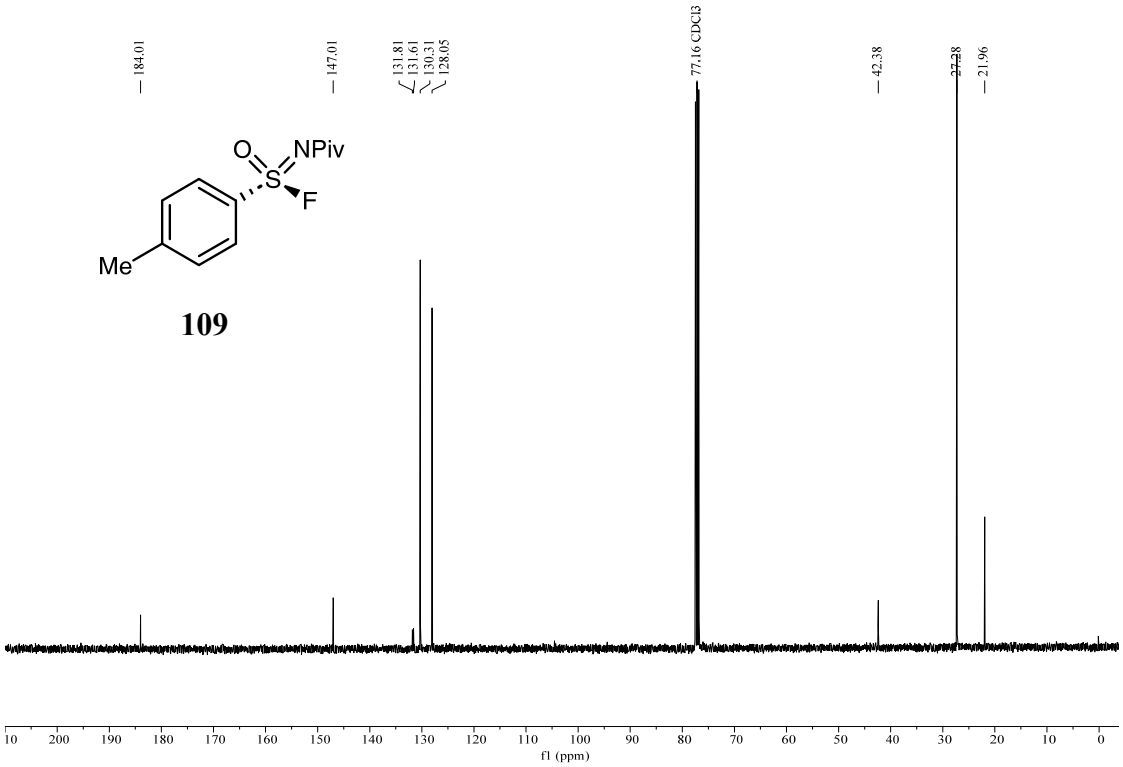
108

^{1}H NMR of 109 (400 MHz, $CDCl_3$)



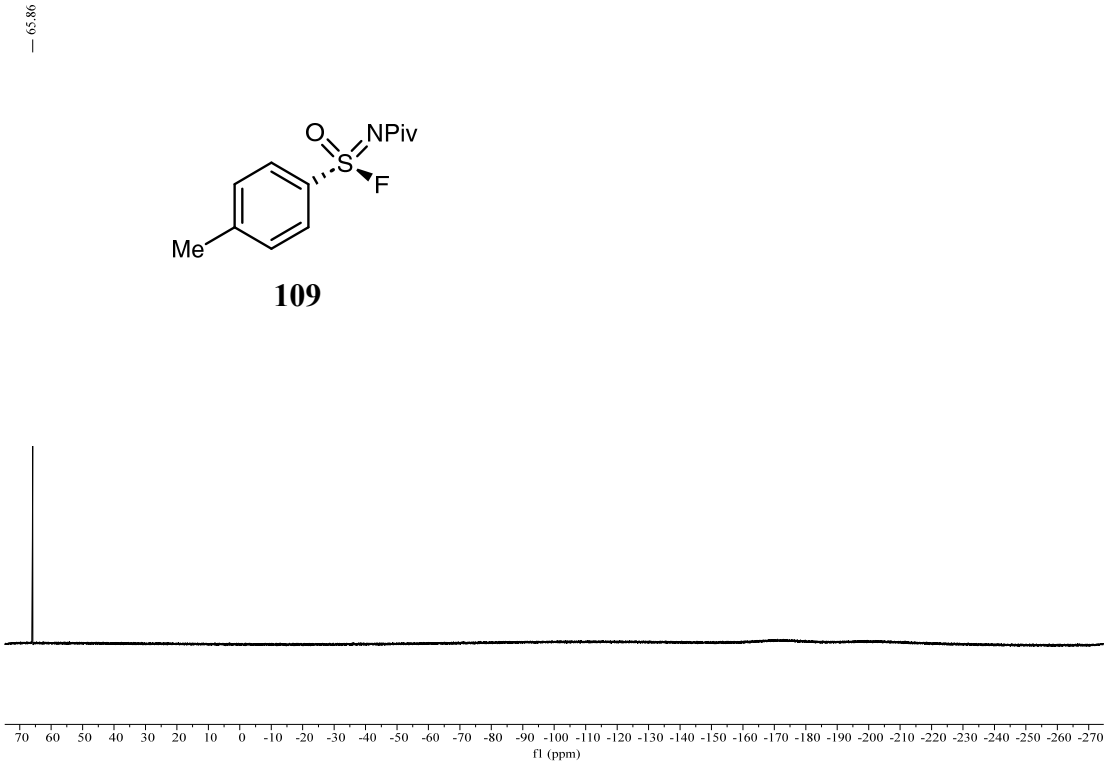
109

^{13}C NMR of 109 (100 MHz, $CDCl_3$)



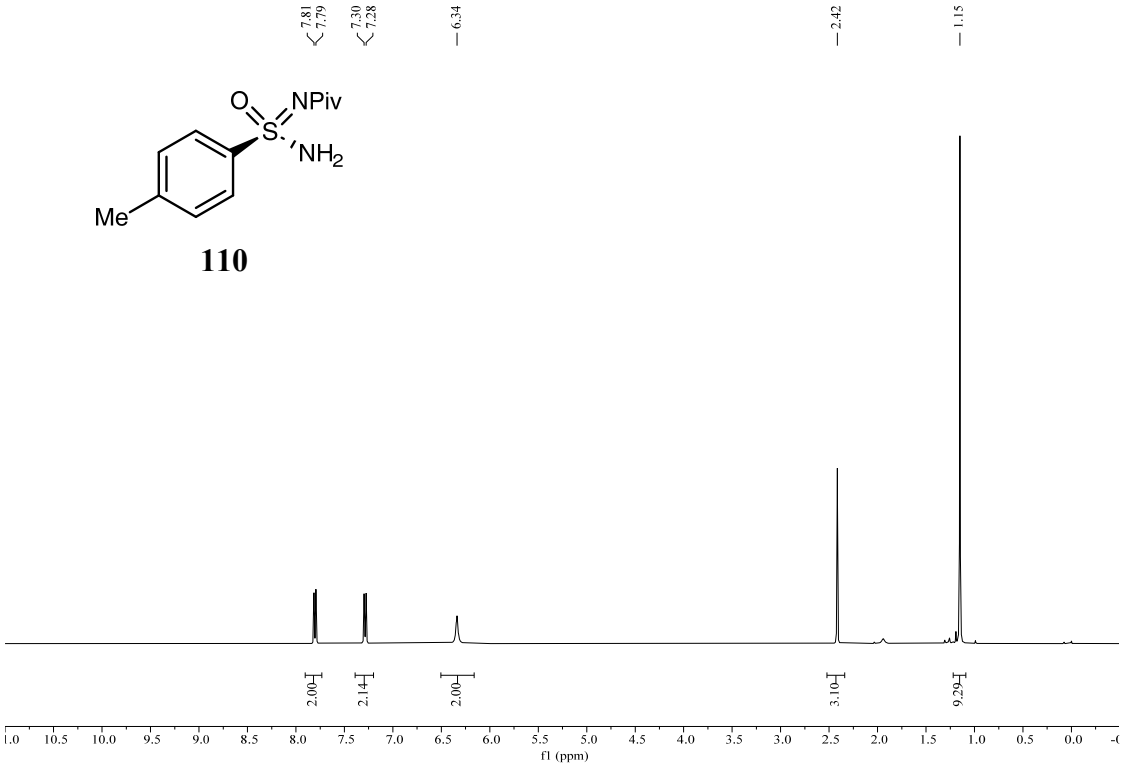
109

^{19}F NMR of 109 (375 MHz, $CDCl_3$)



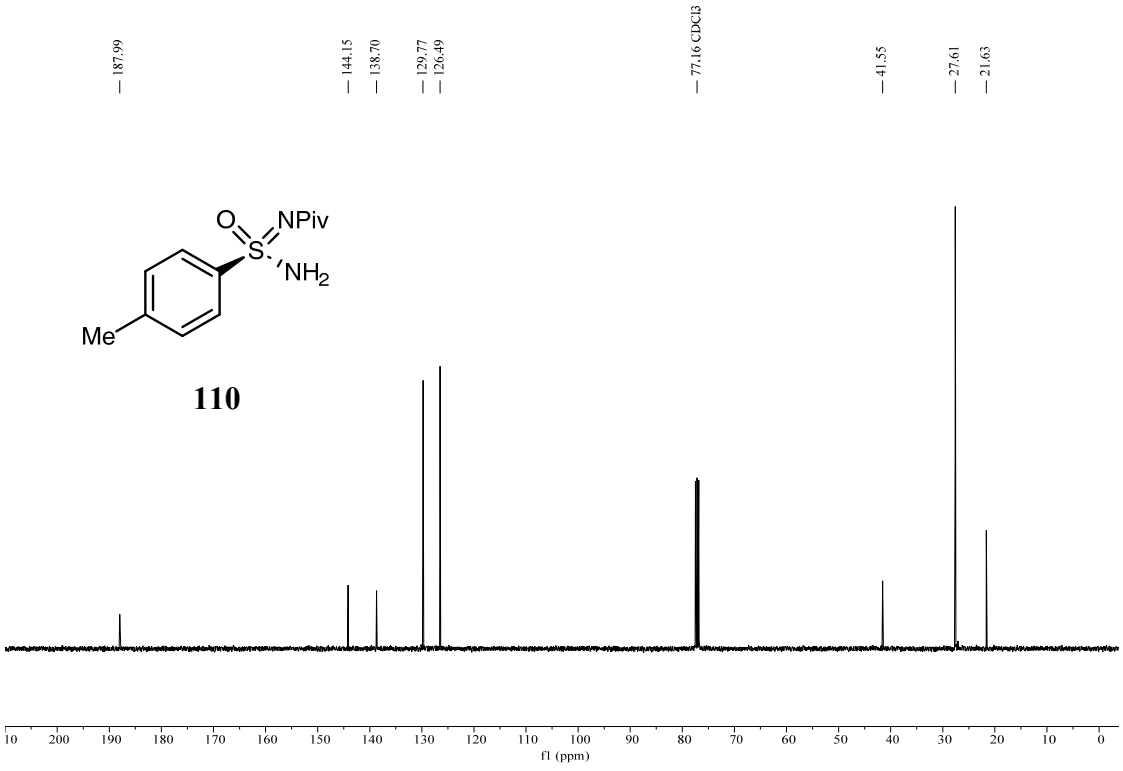
109

^{1}H NMR of 110 (400 MHz, $CDCl_3$)



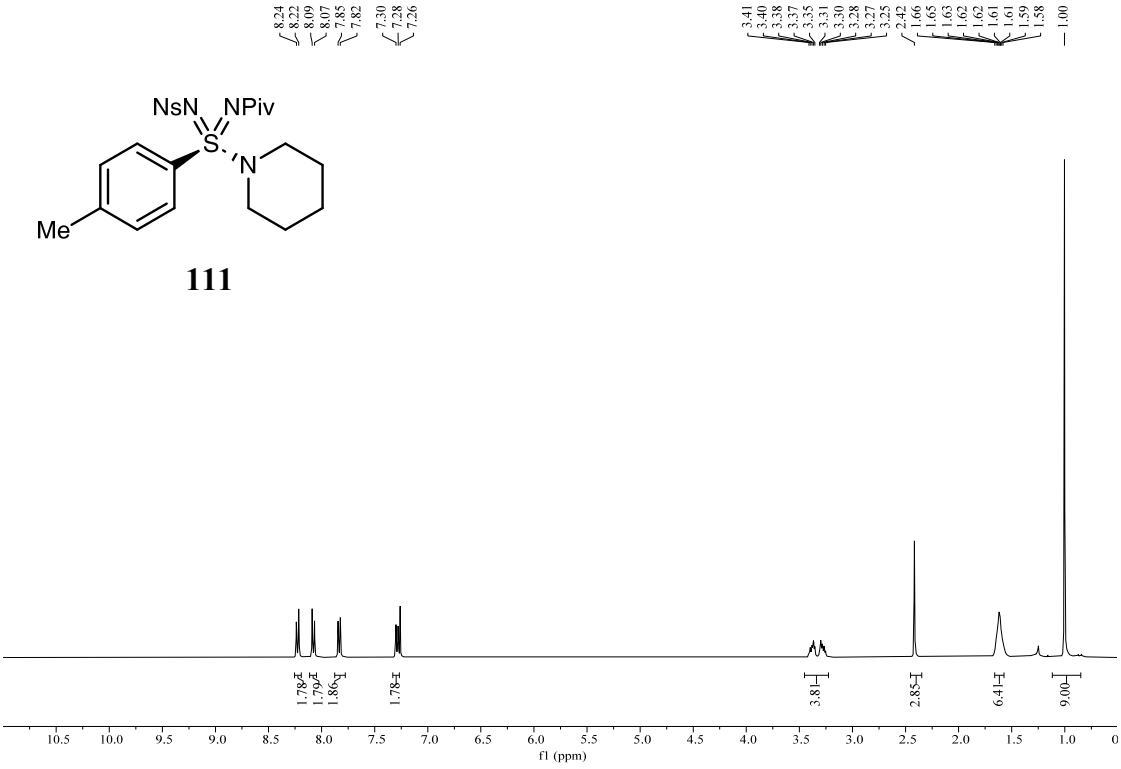
110

^{13}C NMR of 110 (100 MHz, $CDCl_3$)



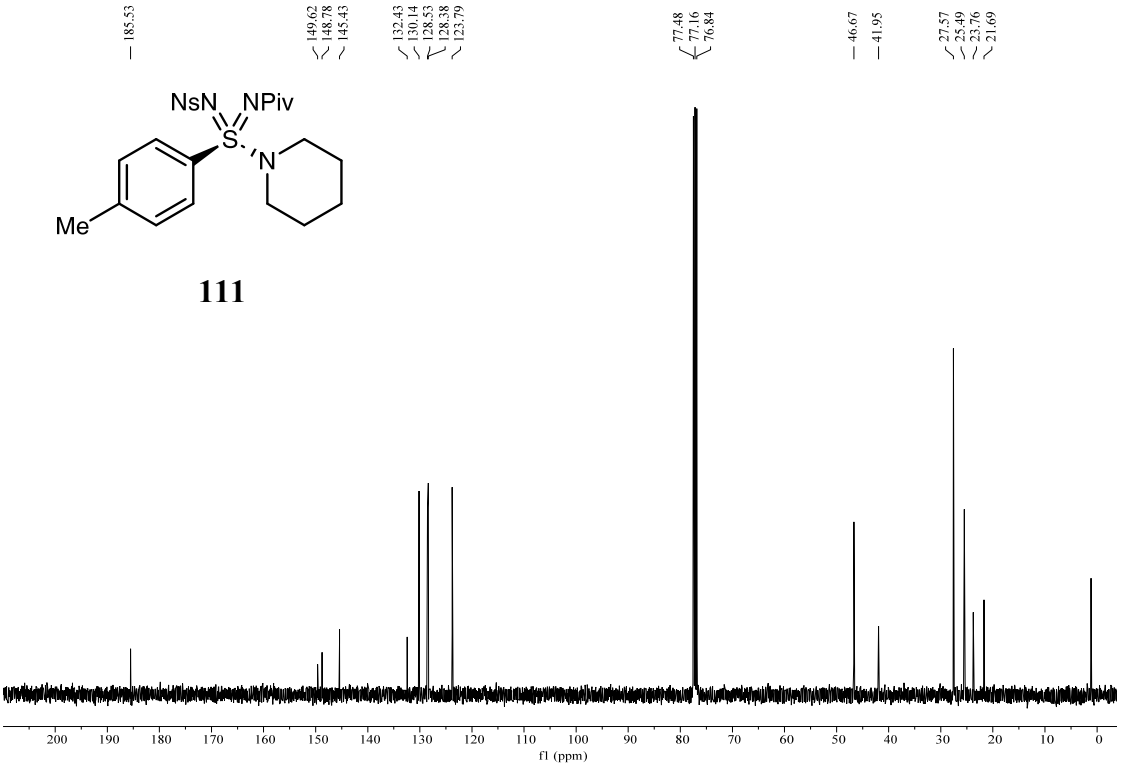
110

^{1}H NMR of 111 (400 MHz, $CDCl_3$)



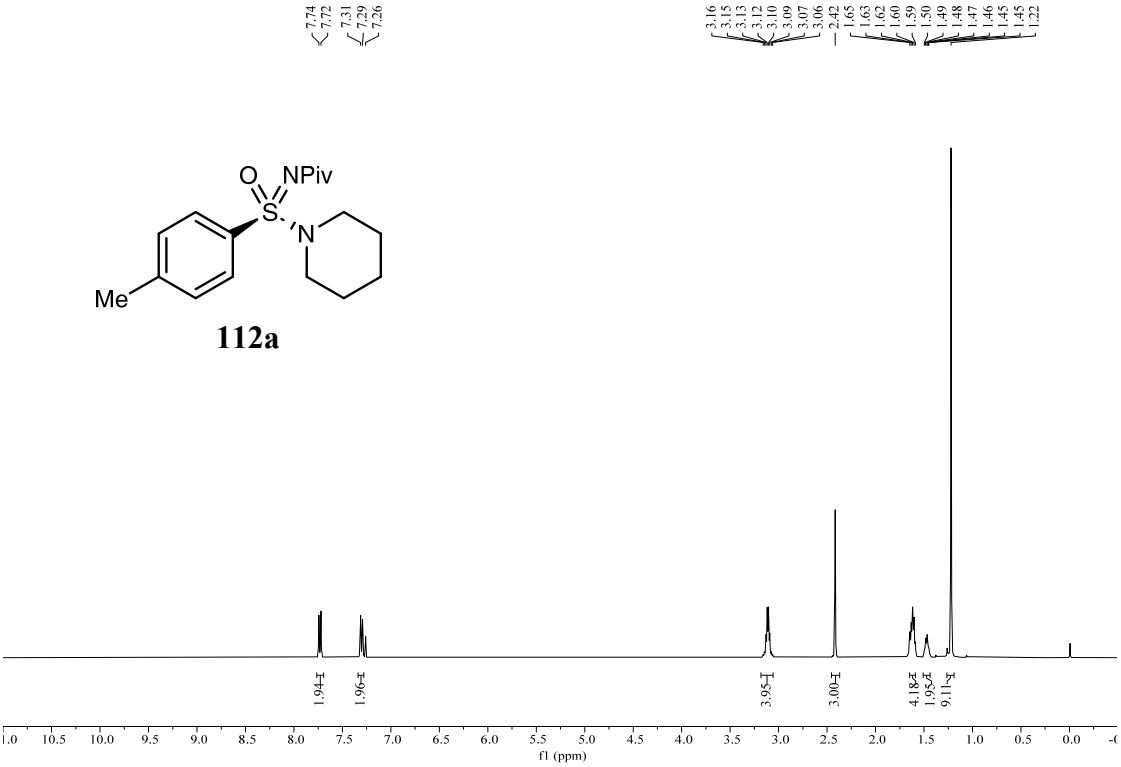
111

^{13}C NMR of 111 (100 MHz, $CDCl_3$)



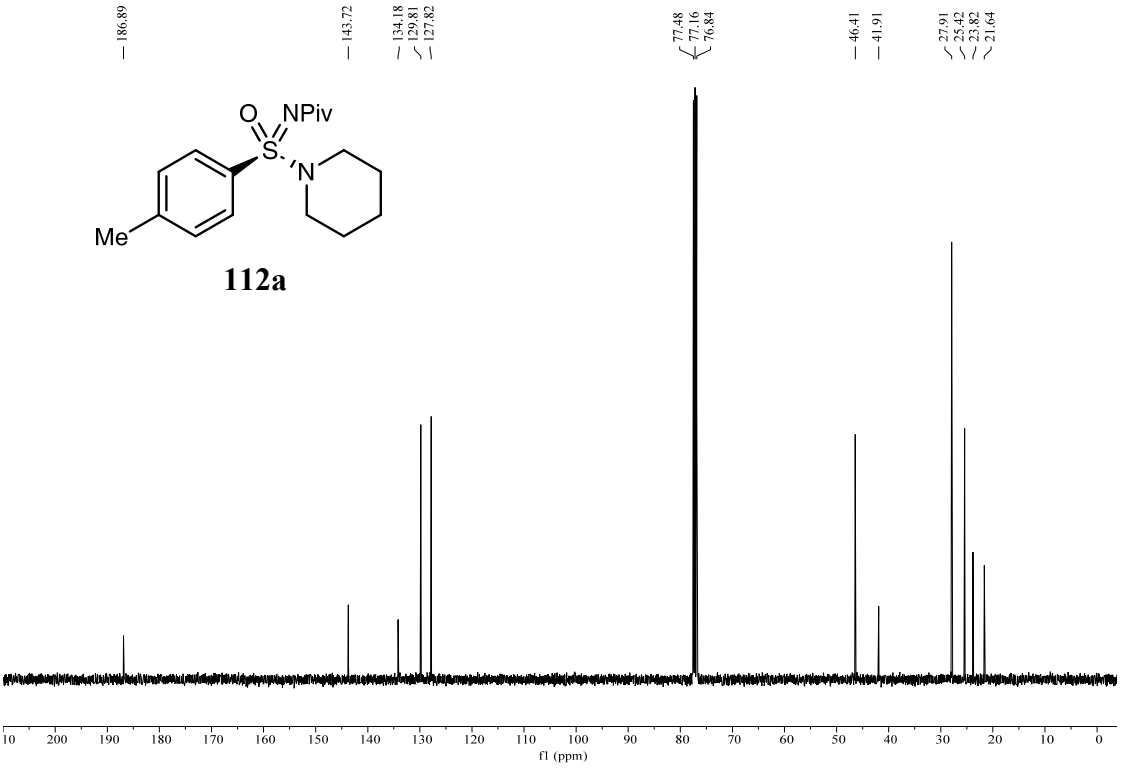
111

^{1}H NMR of 112a (400 MHz, $CDCl_3$)



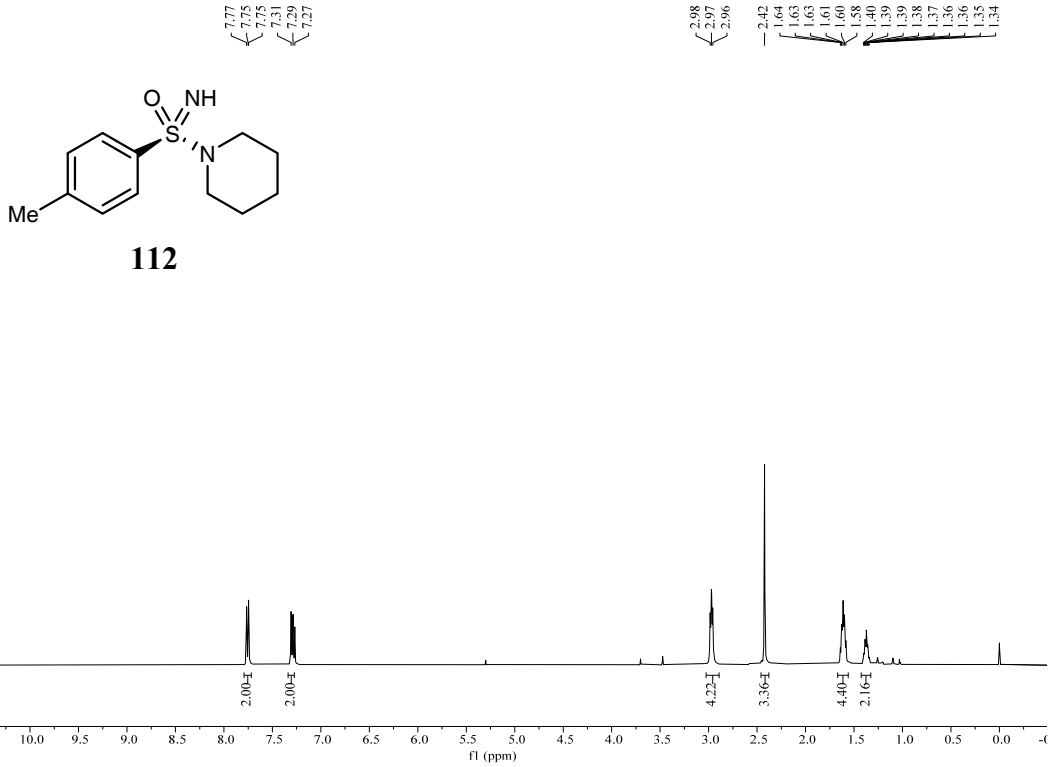
112a

^{13}C NMR of 112a (100 MHz, $CDCl_3$)



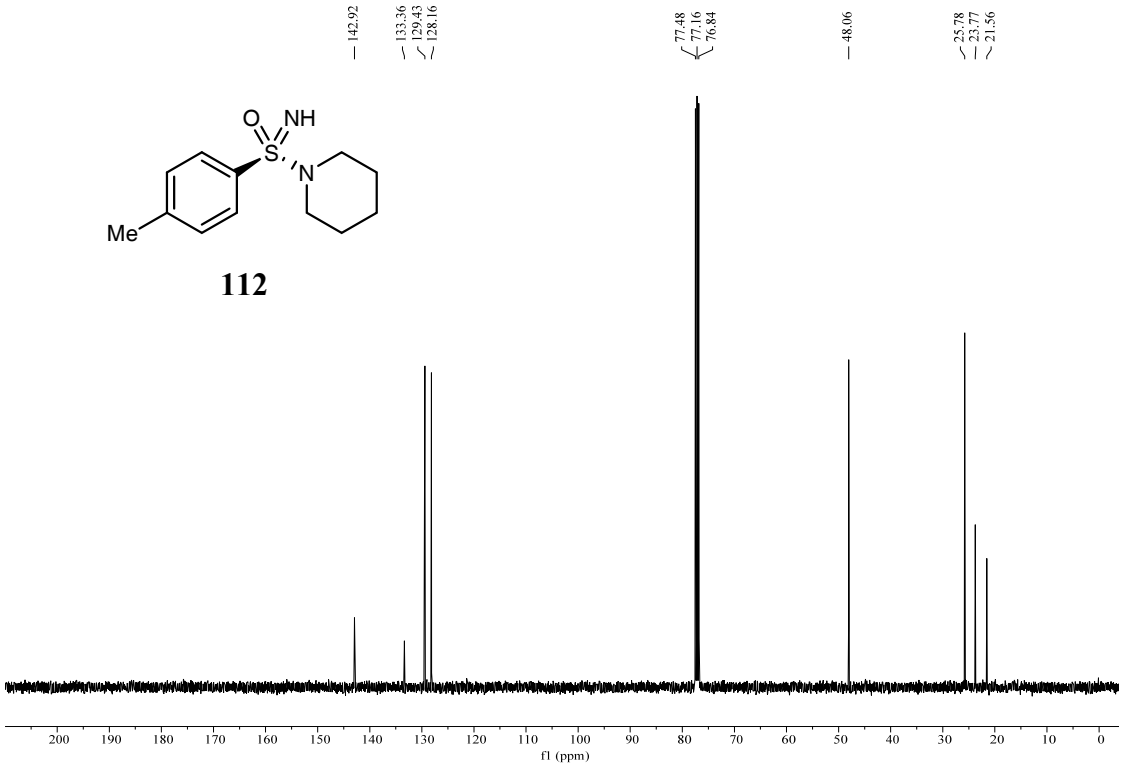
112a

^{1}H NMR of 112 (400 MHz, $CDCl_3$)



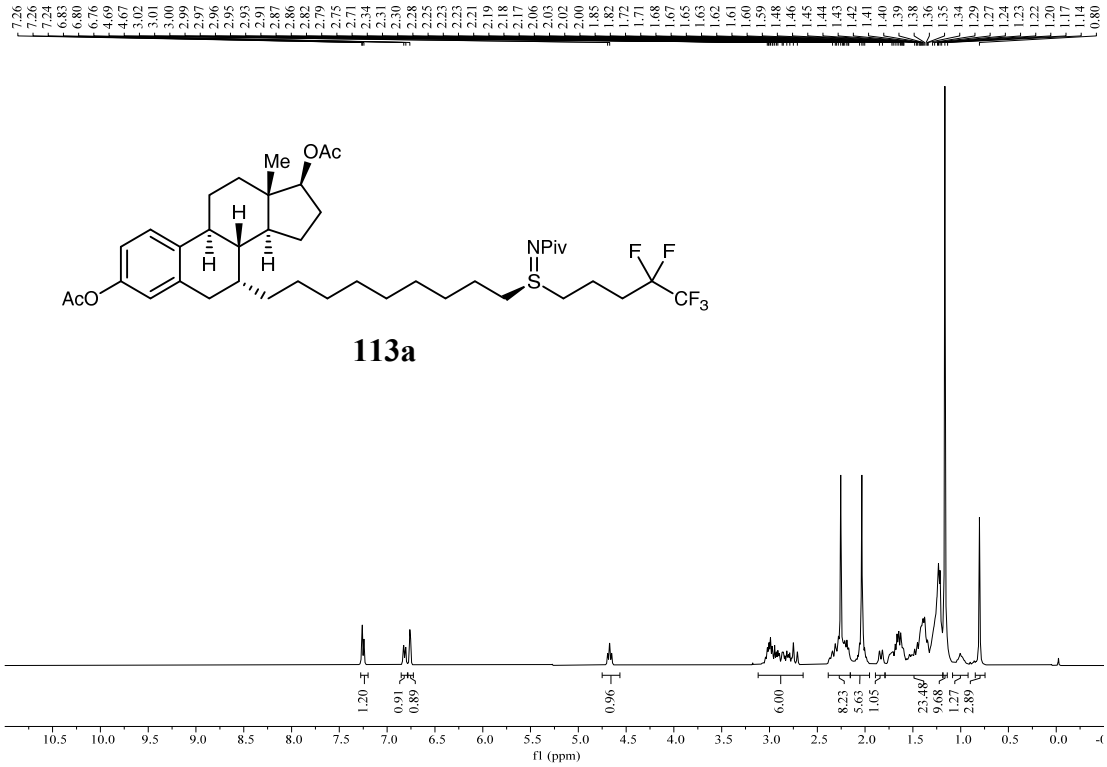
112

^{13}C NMR of 112 (100 MHz, $CDCl_3$)



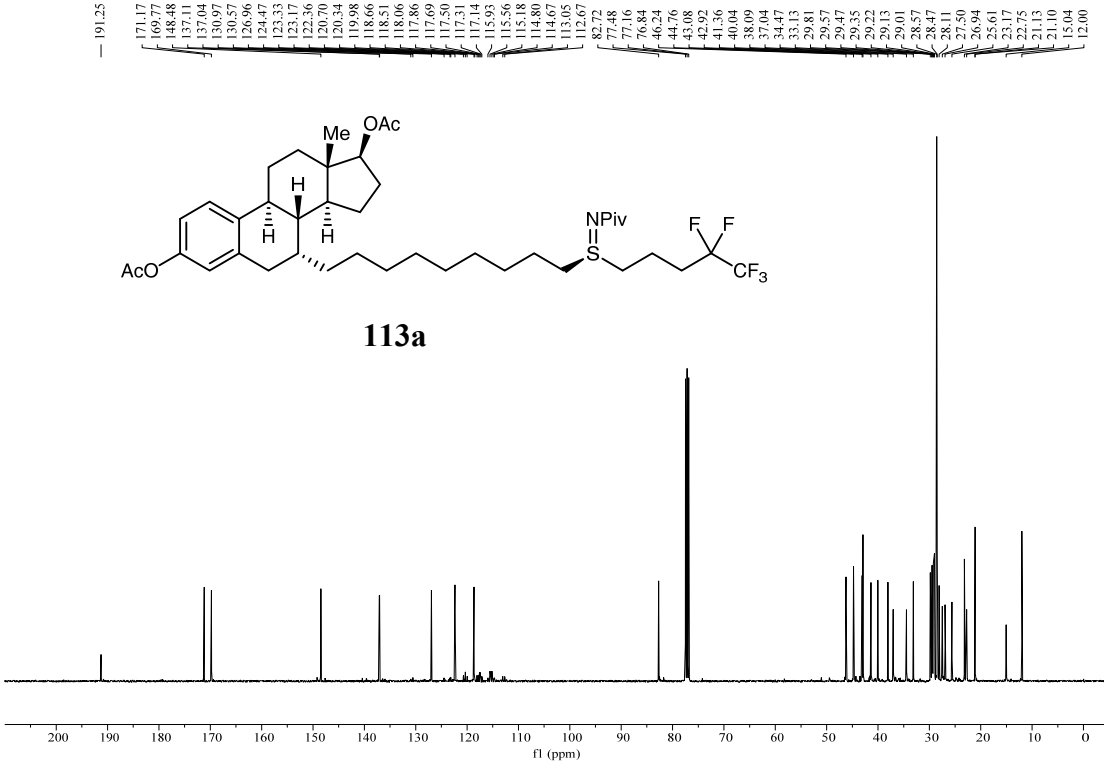
112

^{1}H NMR of 113a (400 MHz, $CDCl_3$)



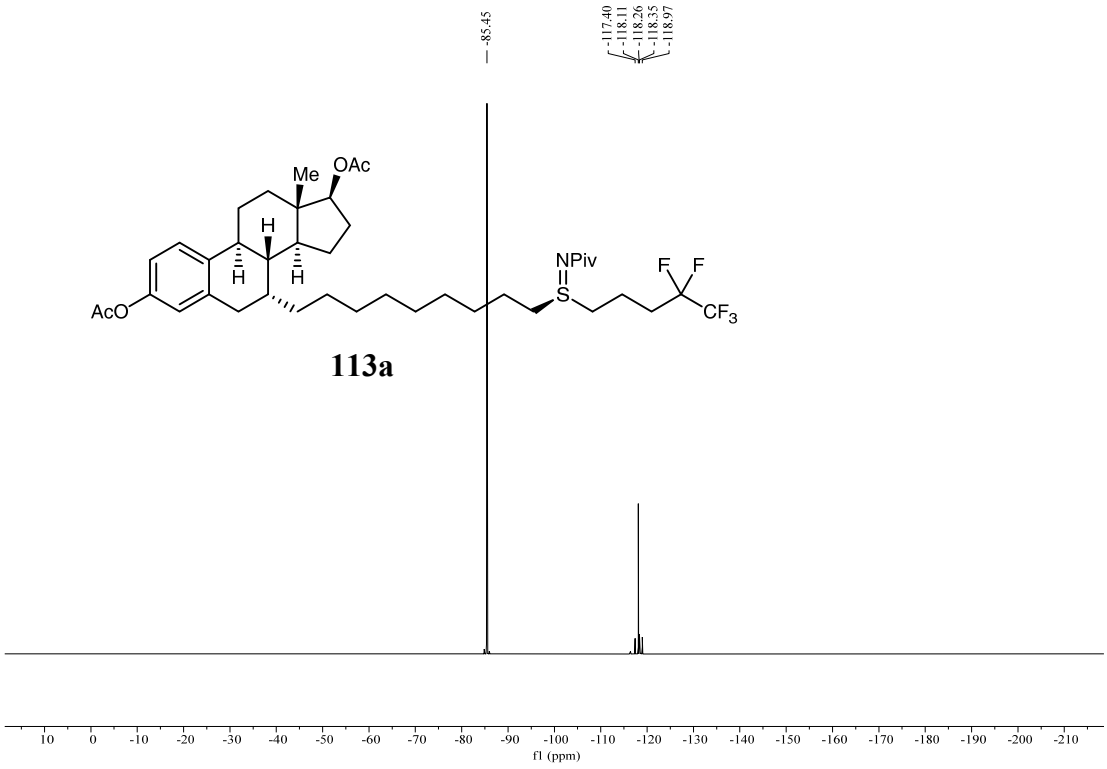
113a

^{13}C NMR of 113a (100 MHz, $CDCl_3$)



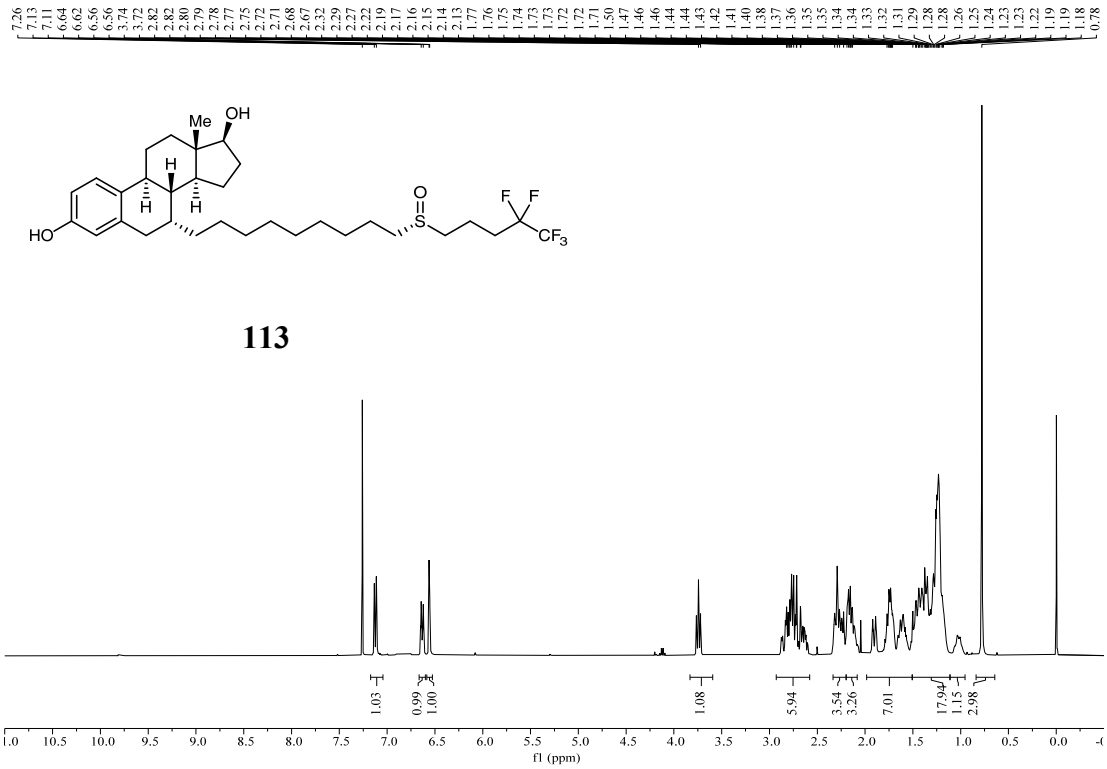
113a

^{19}F NMR of 113a (375 MHz, $CDCl_3$)



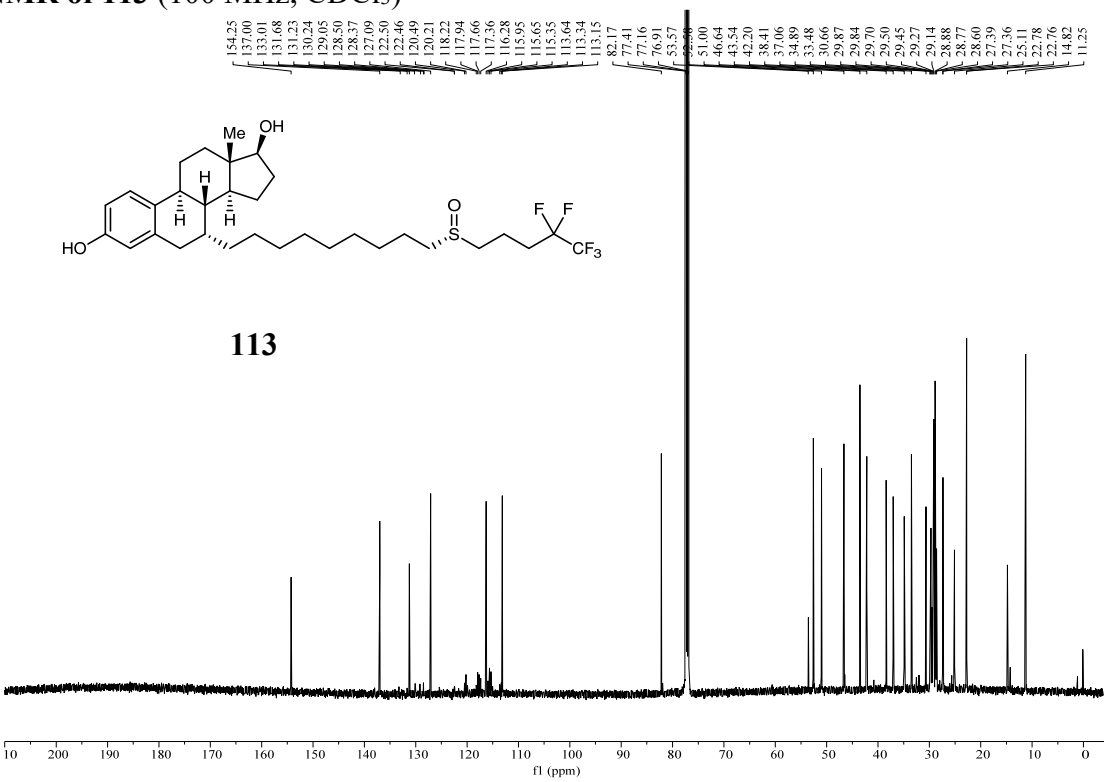
113a

^{1}H NMR of 113 (400 MHz, $CDCl_3$)



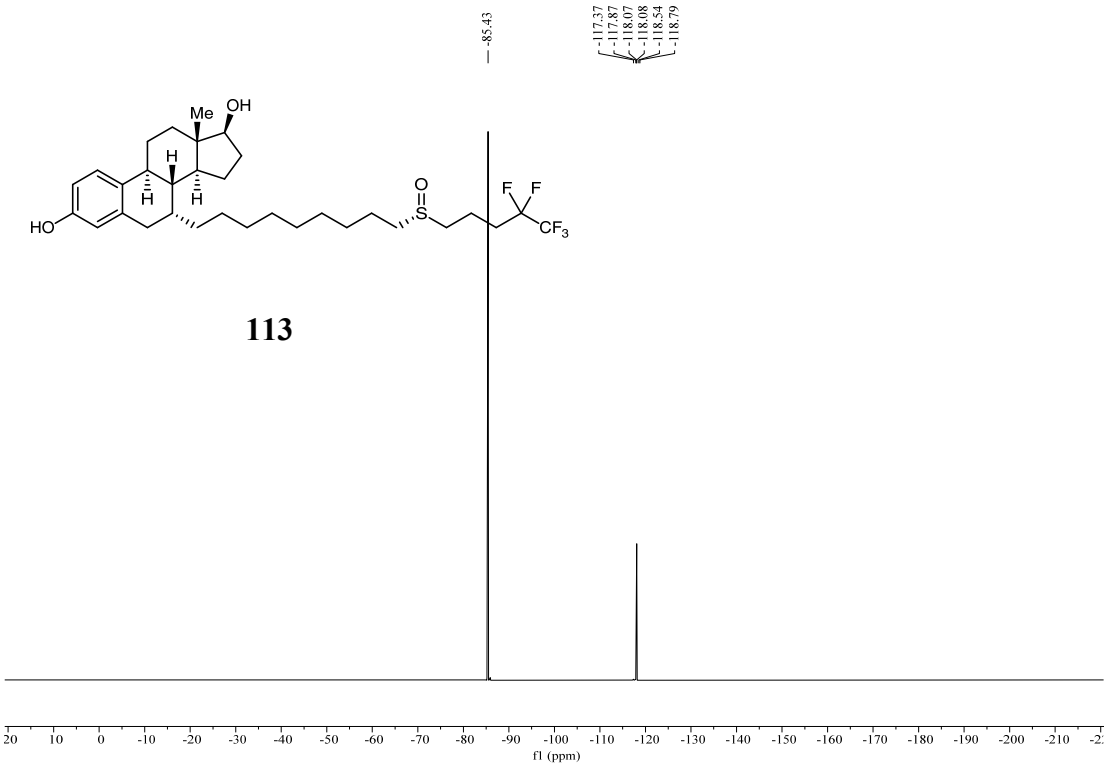
113

^{13}C NMR of 113 (100 MHz, $CDCl_3$)



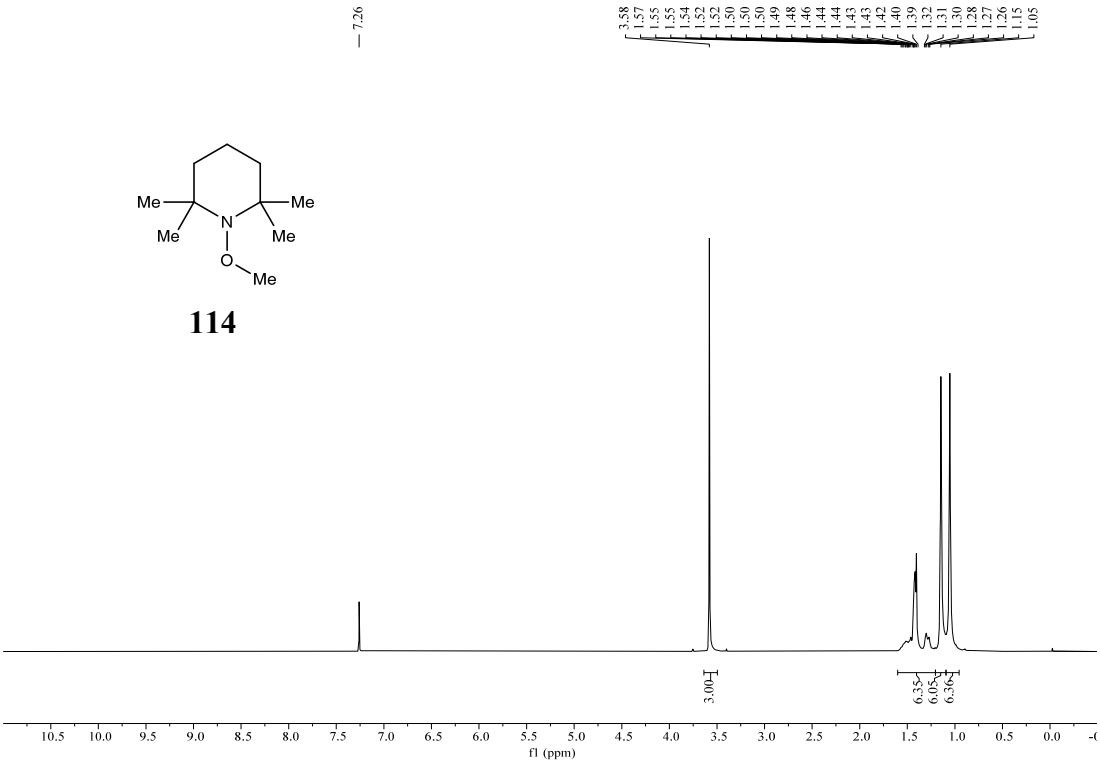
113

^{19}F NMR of 113 (375 MHz, $CDCl_3$)



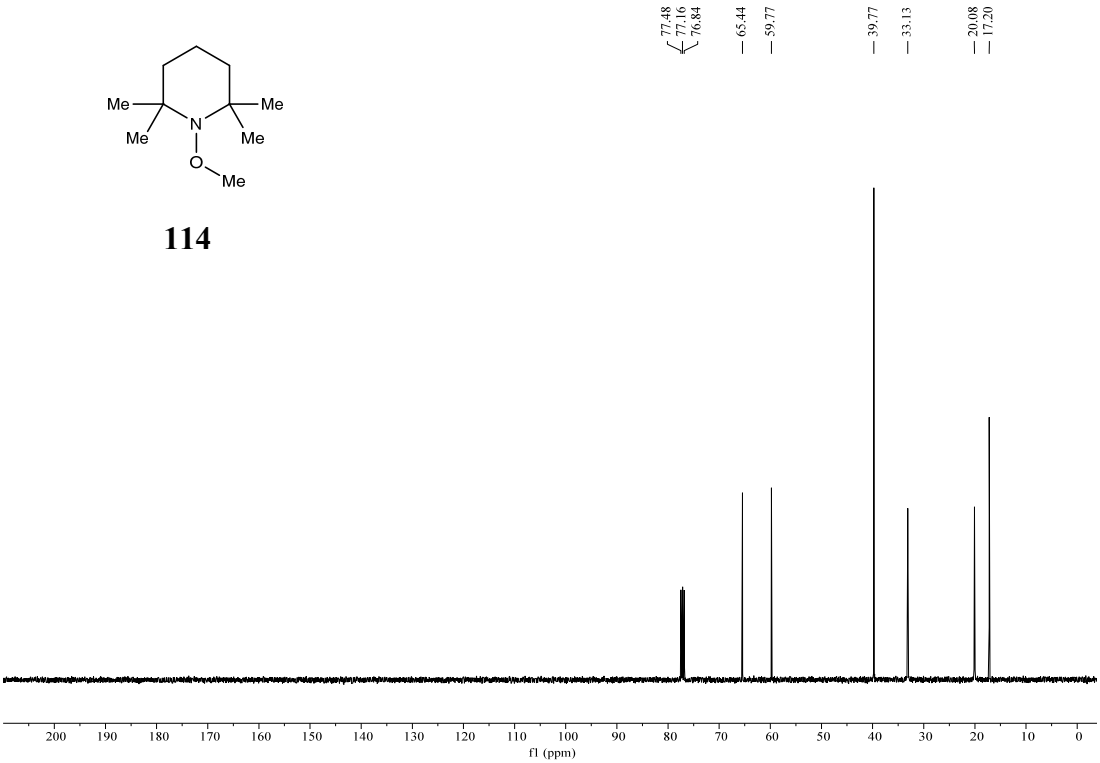
113

^{1}H NMR of 114 (400 MHz, $CDCl_3$)



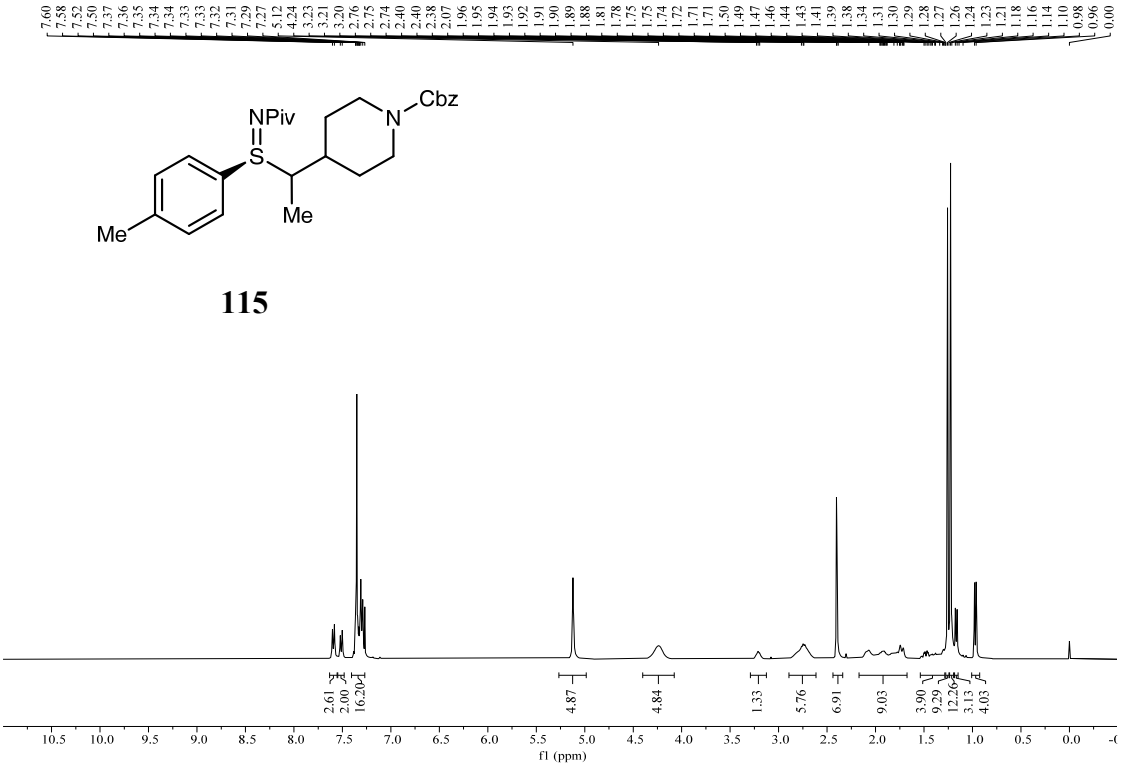
114

^{13}C NMR of 114 (100 MHz, $CDCl_3$)



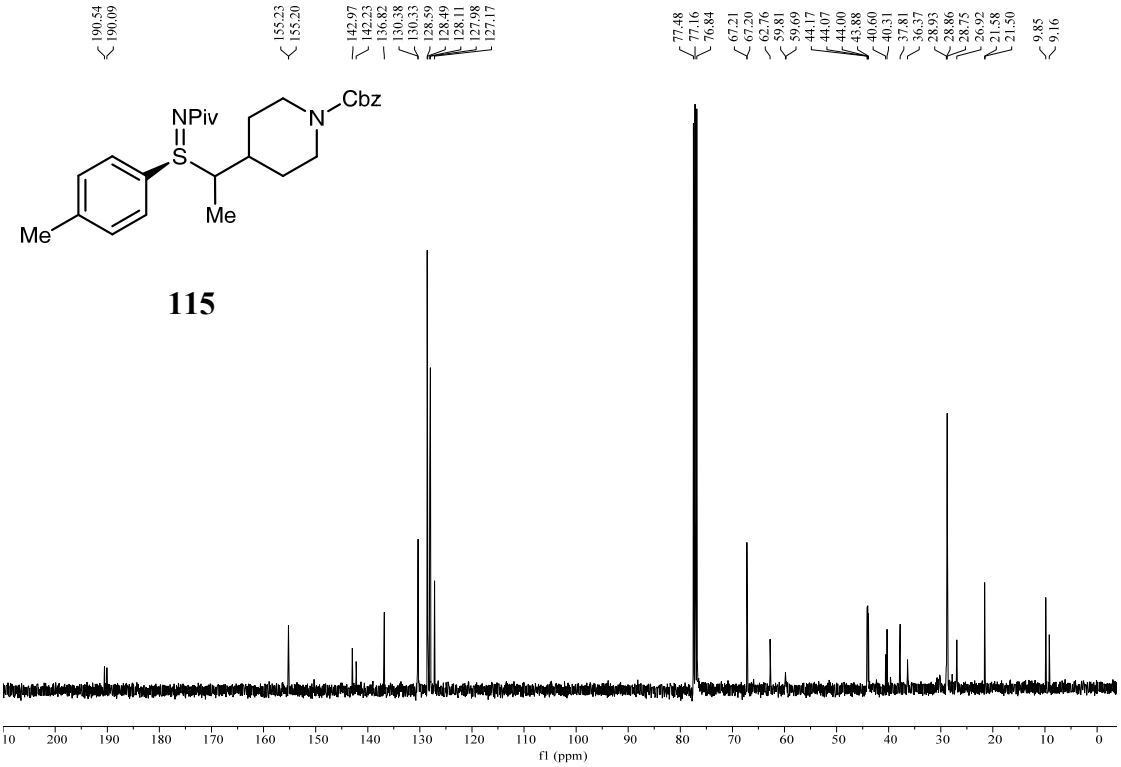
114

^{1}H NMR of 115 (400 MHz, $CDCl_3$)



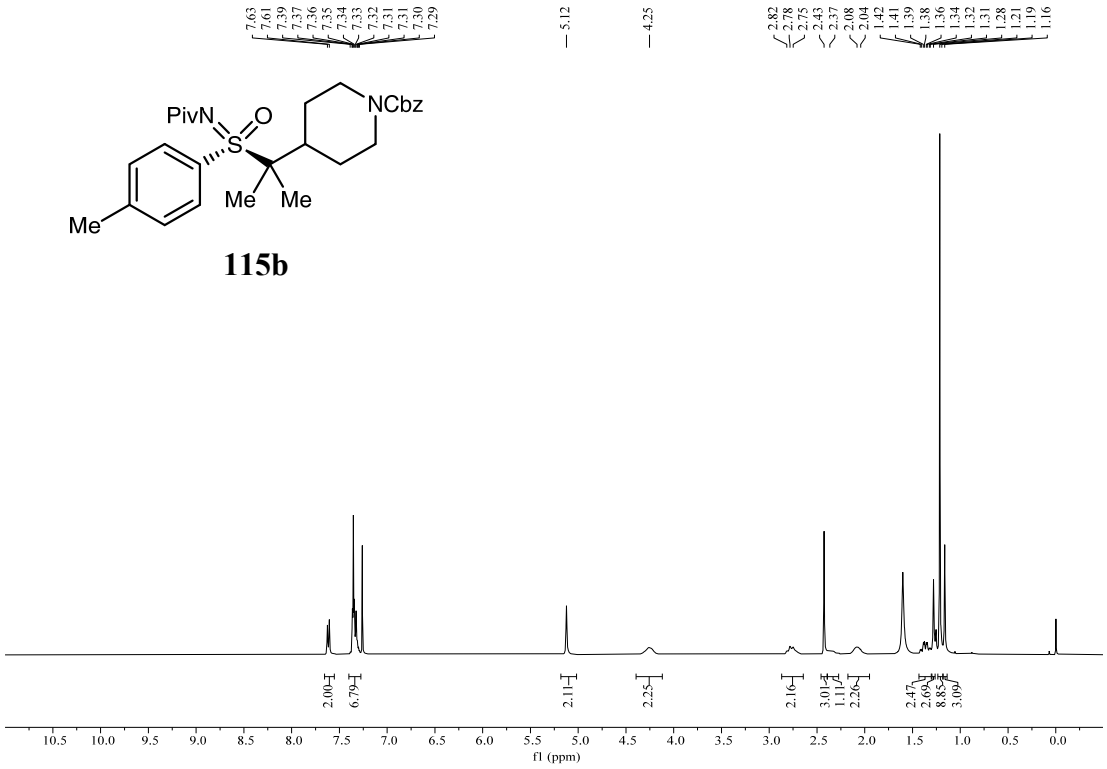
115

^{13}C NMR of 115 (100 MHz, $CDCl_3$)



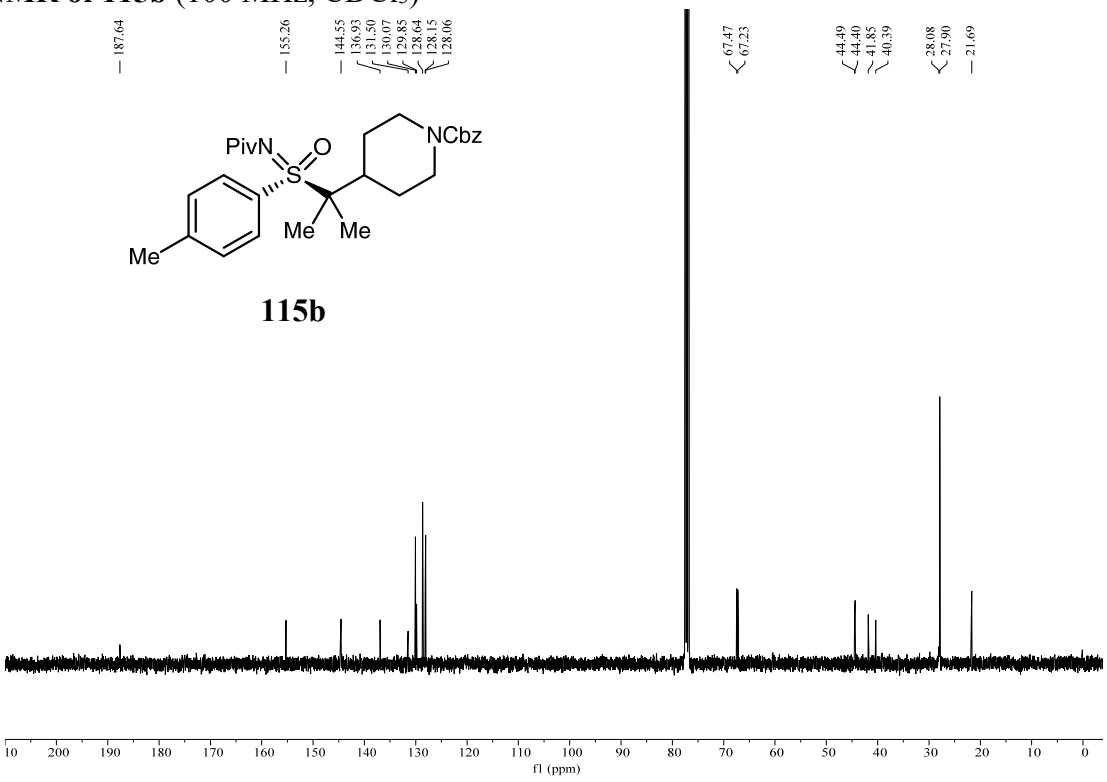
115

^{1}H NMR of 115b (400 MHz, $CDCl_3$)



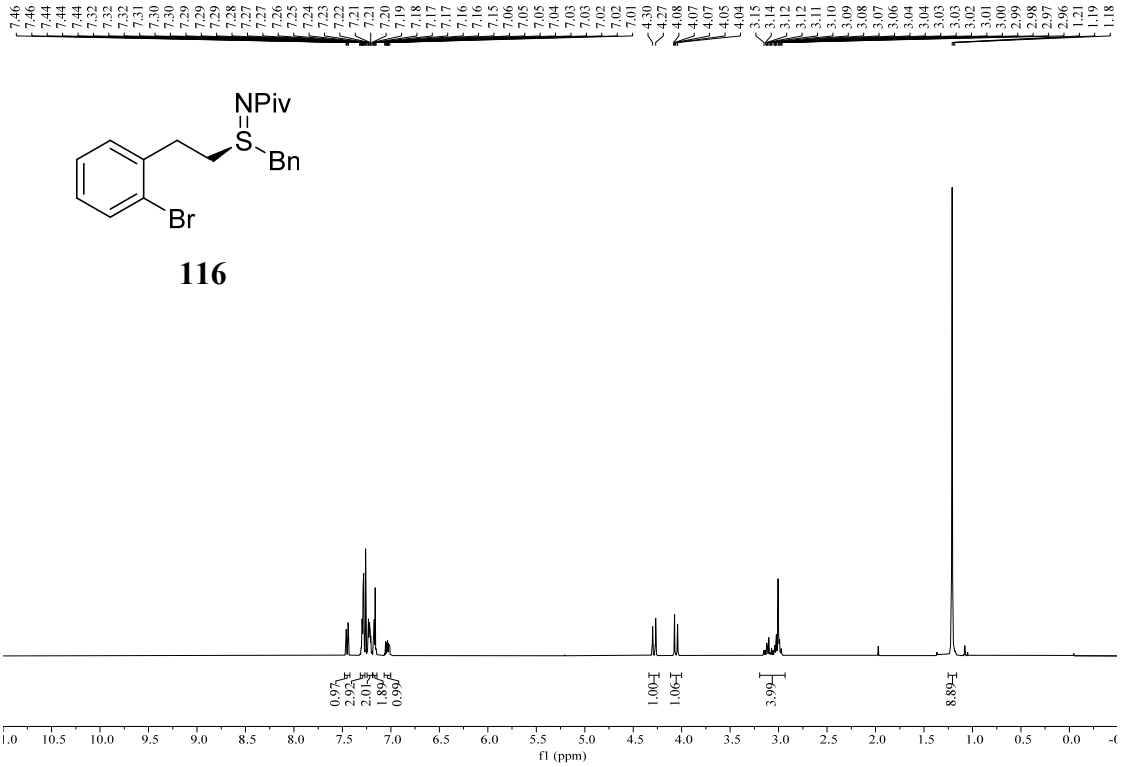
115b

^{13}C NMR of 115b (100 MHz, $CDCl_3$)

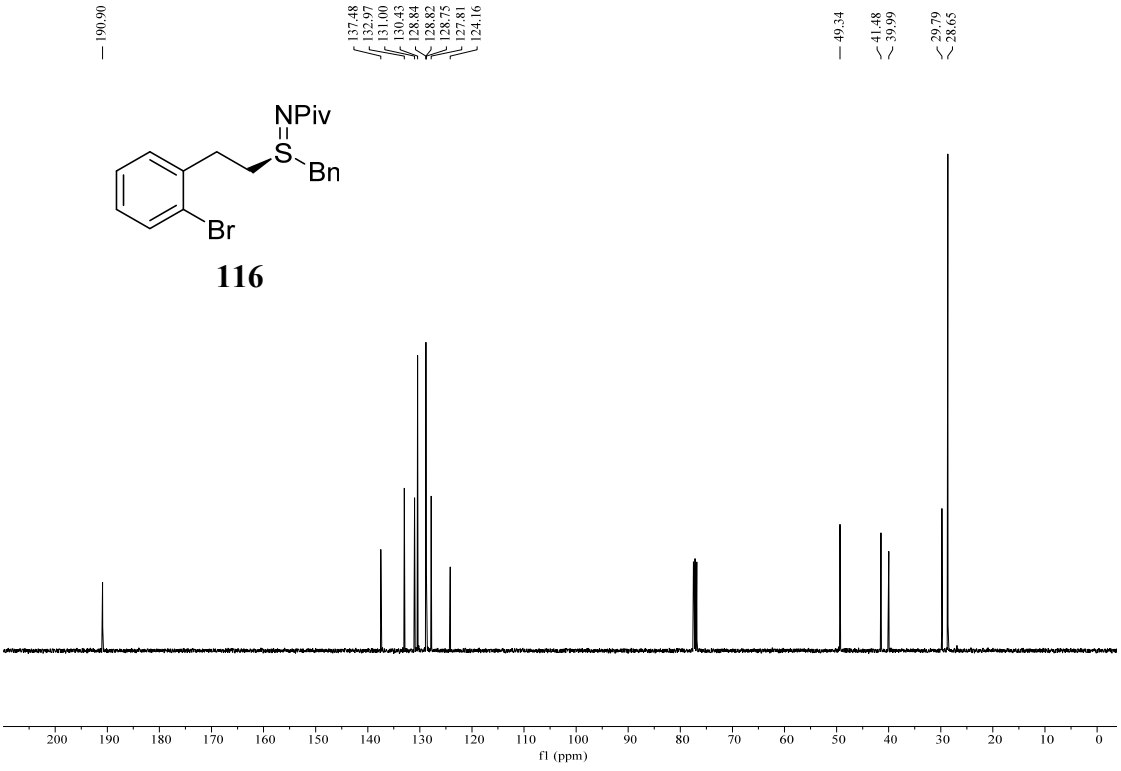


115b

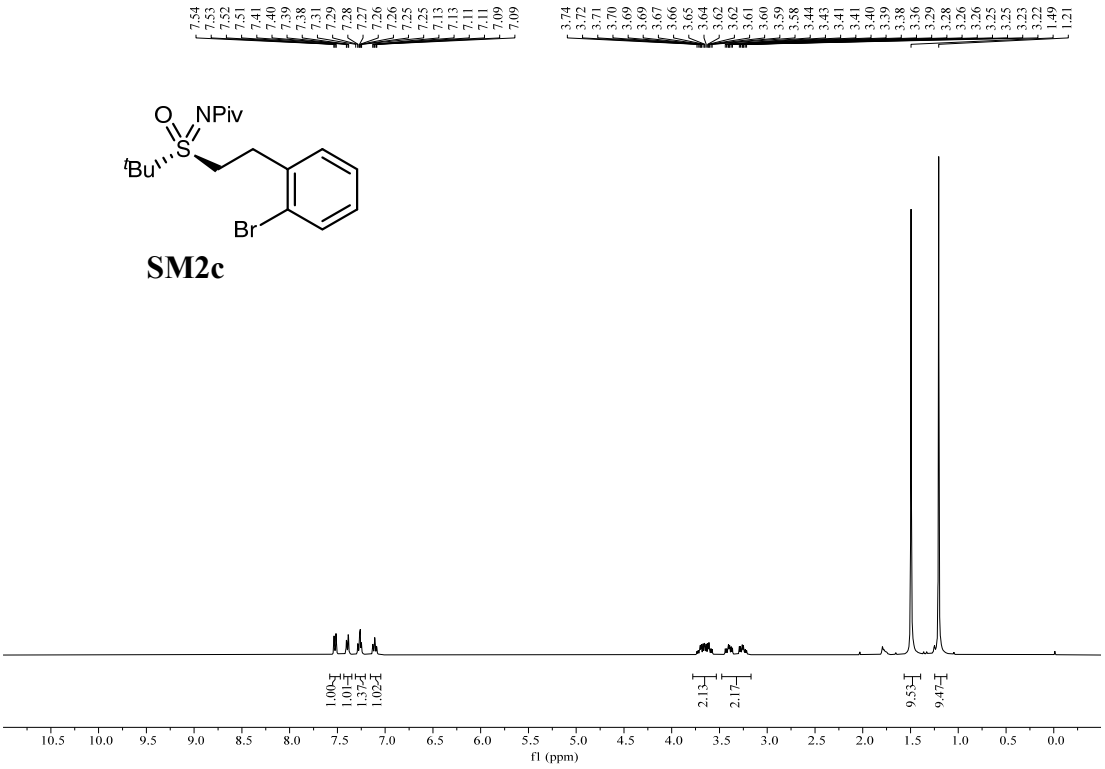
^{1}H NMR of 116 (400 MHz, $CDCl_3$)



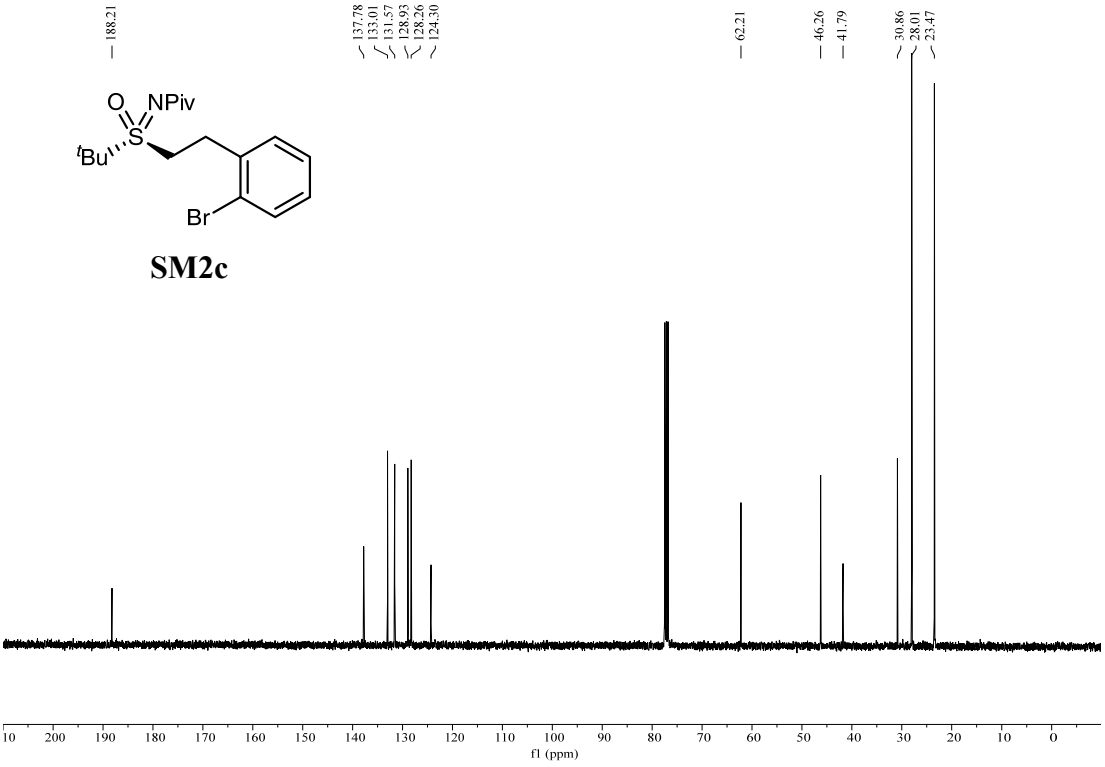
^{13}C NMR of 116 (100 MHz, $CDCl_3$)



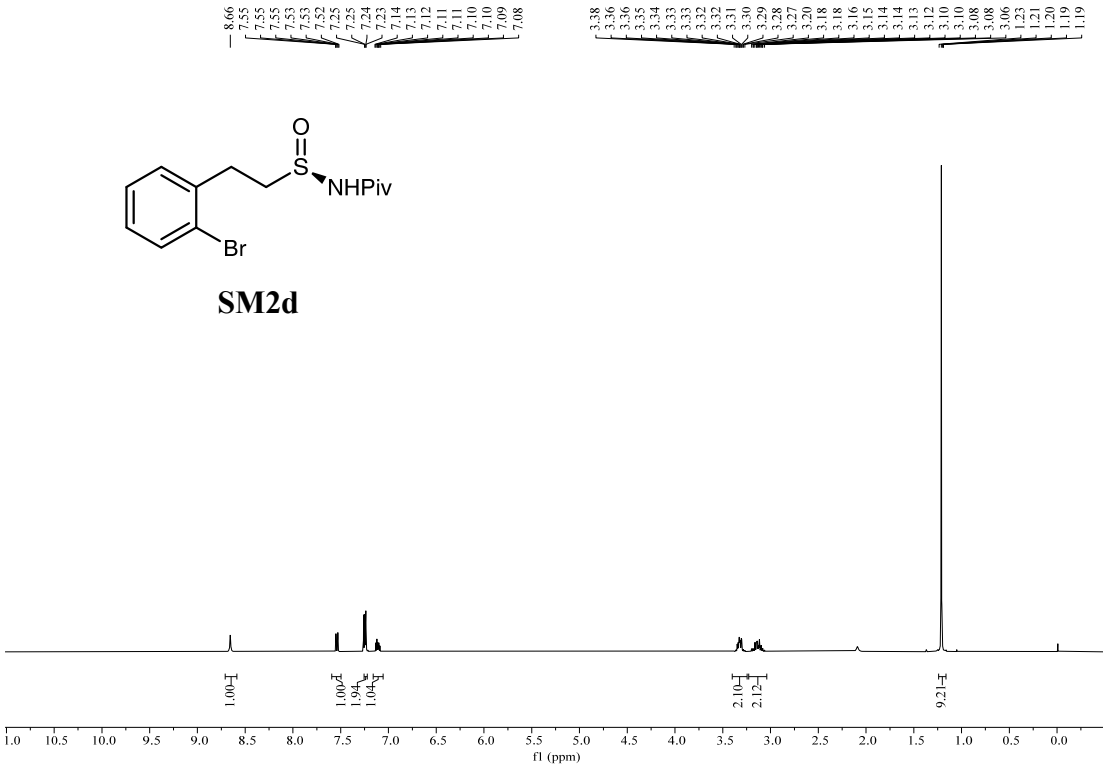
^{1}H NMR of SM2c (400 MHz, $CDCl_3$)



^{13}C NMR of SM2c (100 MHz, $CDCl_3$)

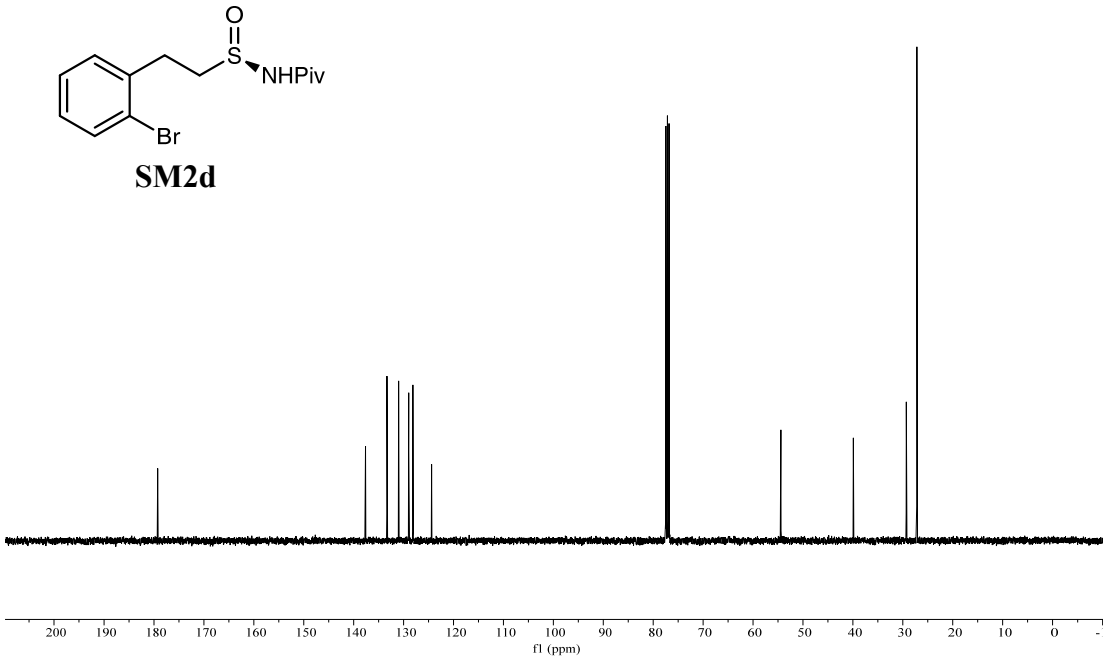


^{1}H NMR of SM2d (400 MHz, $CDCl_3$)



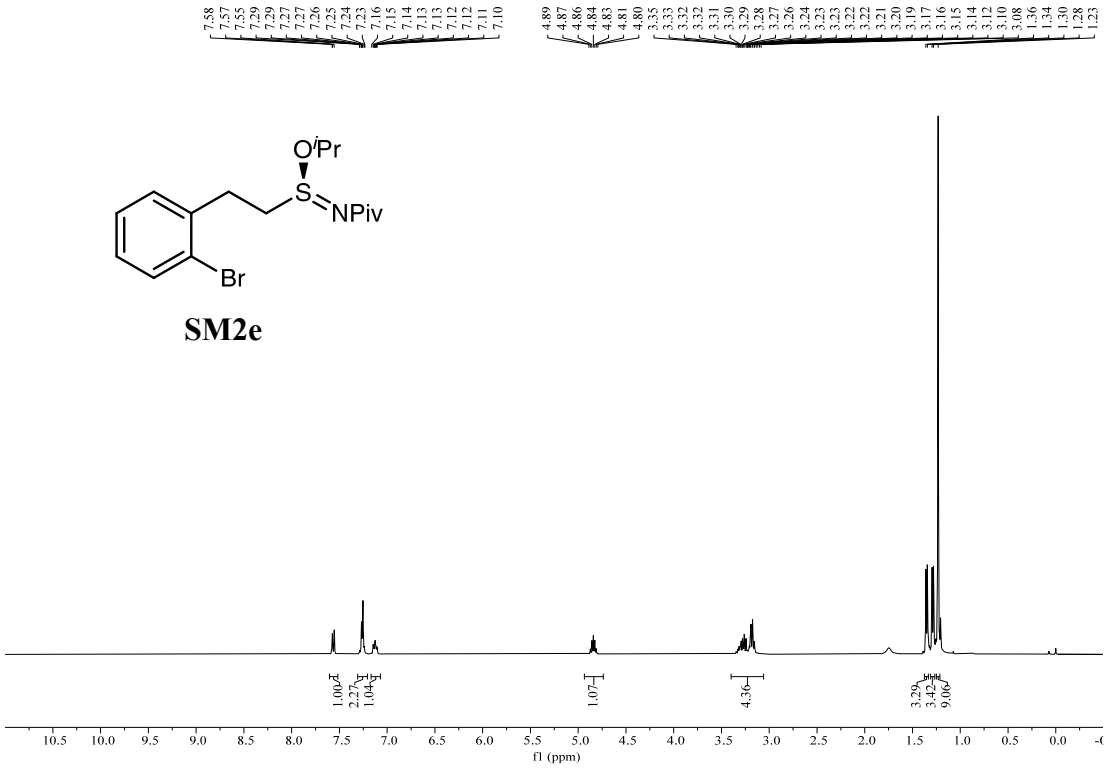
SM2d

^{13}C NMR of SM2d (100 MHz, $CDCl_3$)

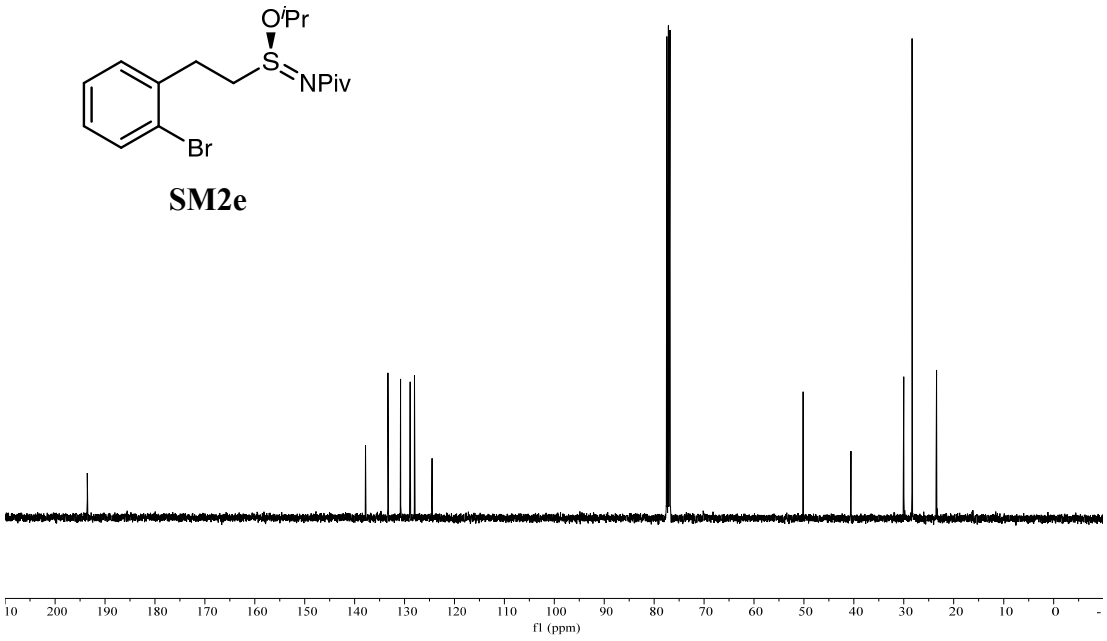


SM2d

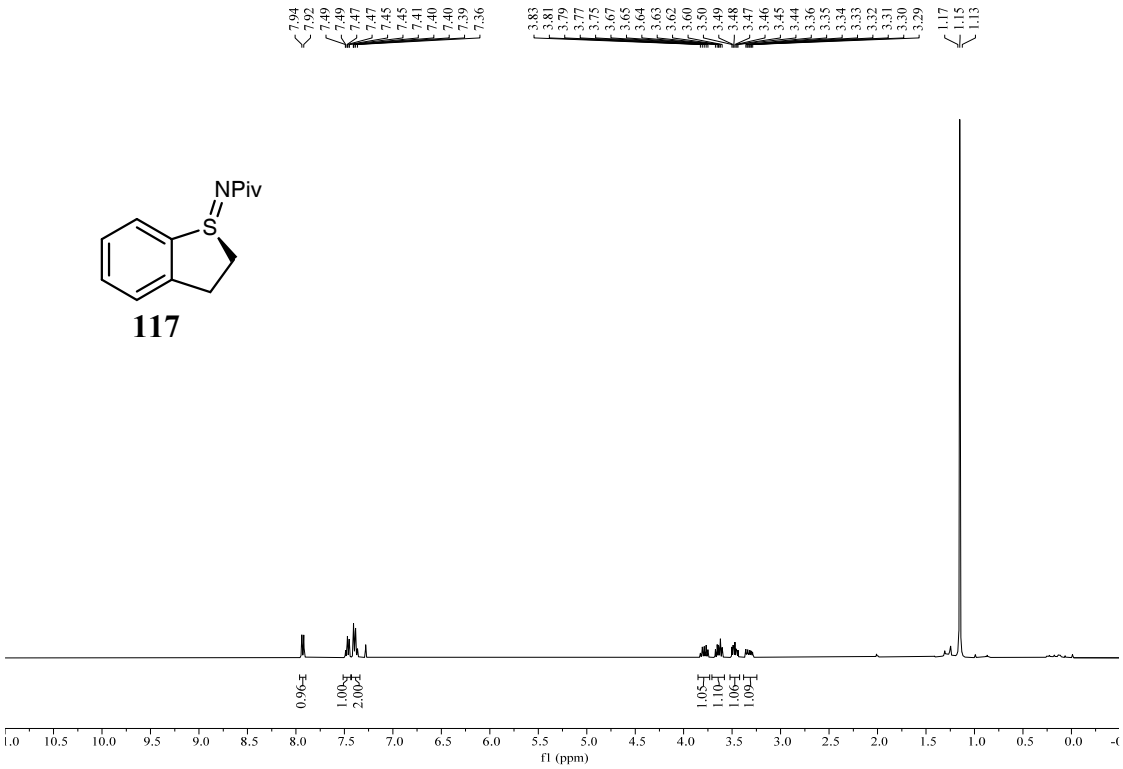
^{1}H NMR of SM2e (400 MHz, $CDCl_3$)



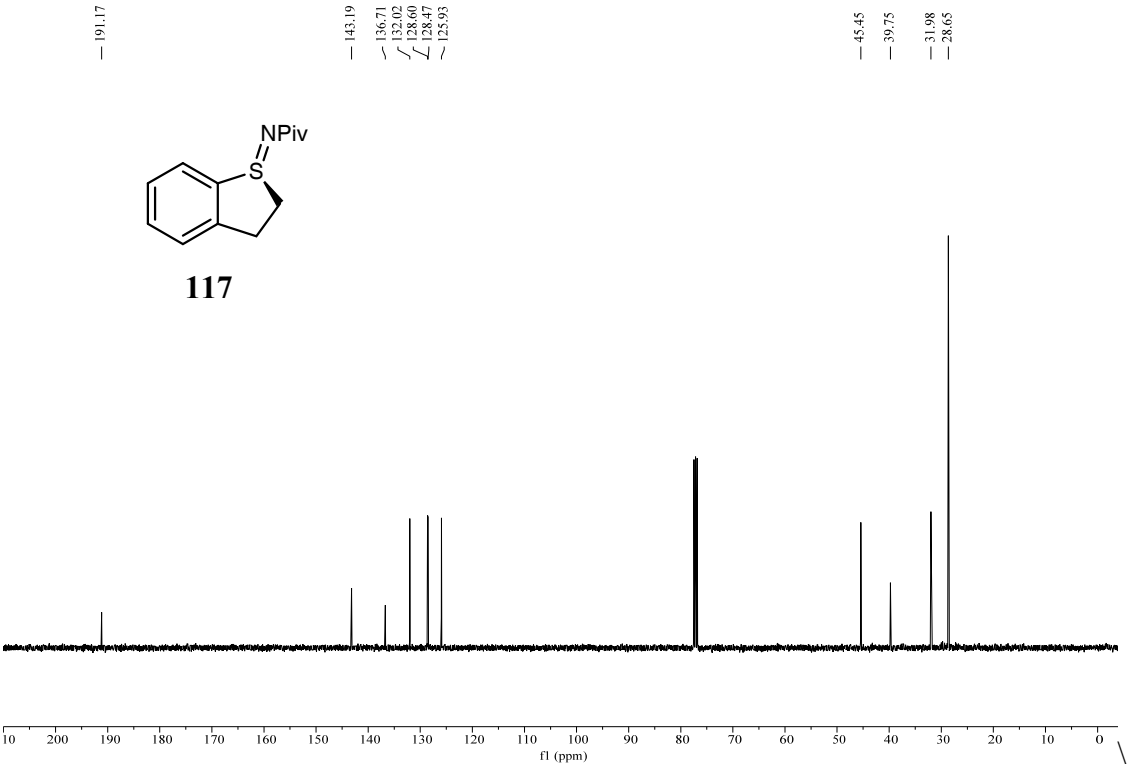
^{13}C NMR of SM2e (100 MHz, $CDCl_3$)



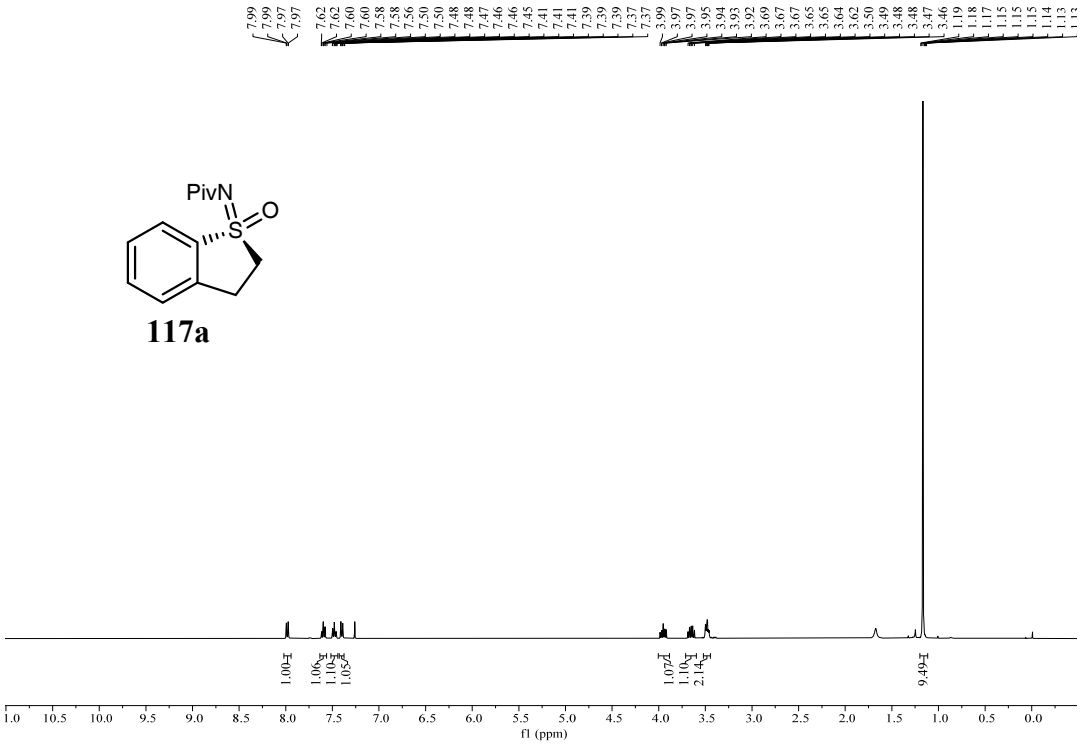
^{1}H NMR of 117 (400 MHz, $CDCl_3$)



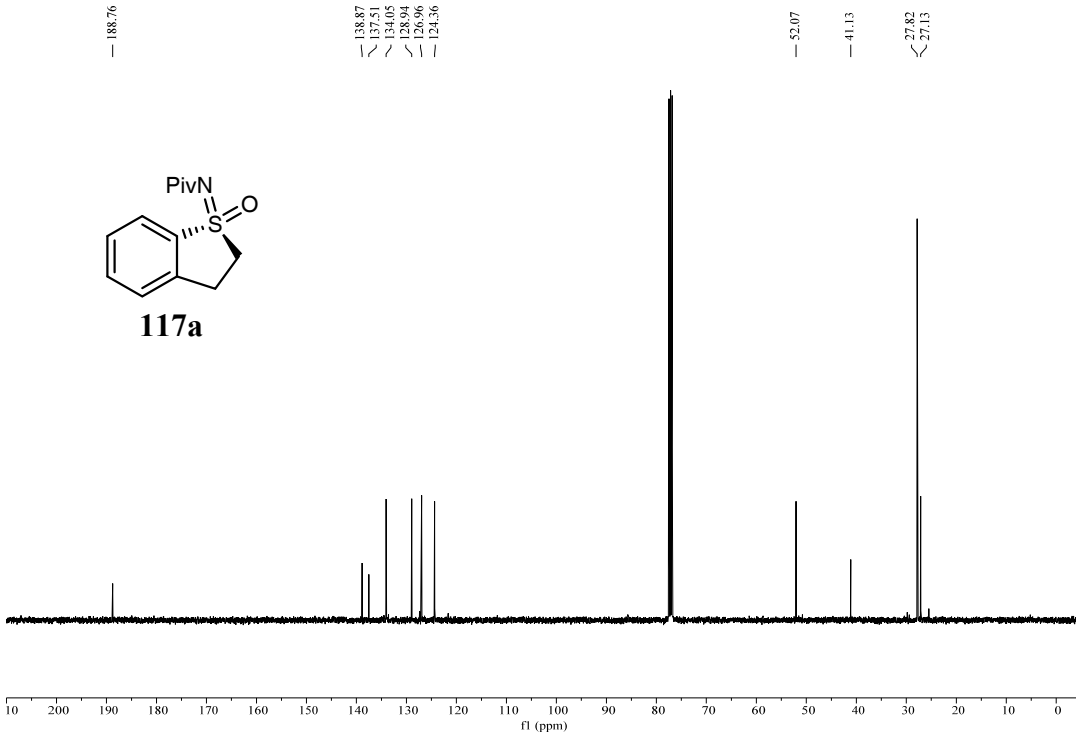
^{13}C NMR of 117 (100 MHz, $CDCl_3$)



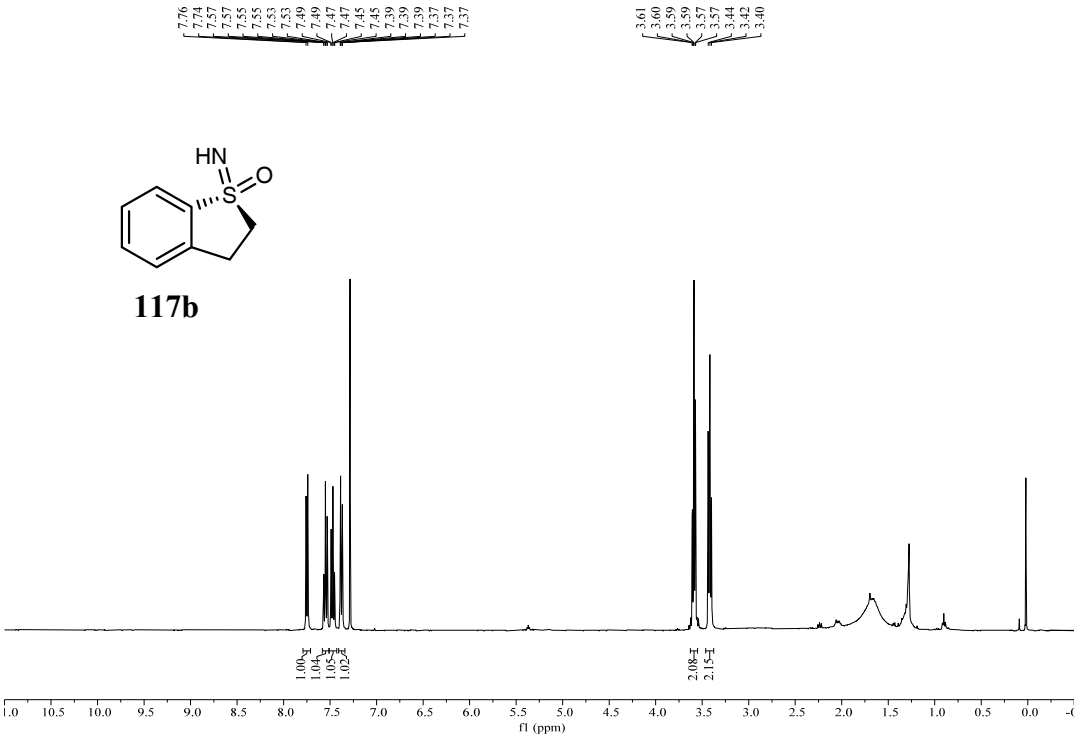
^{1}H NMR of 117a (400 MHz, $CDCl_3$)



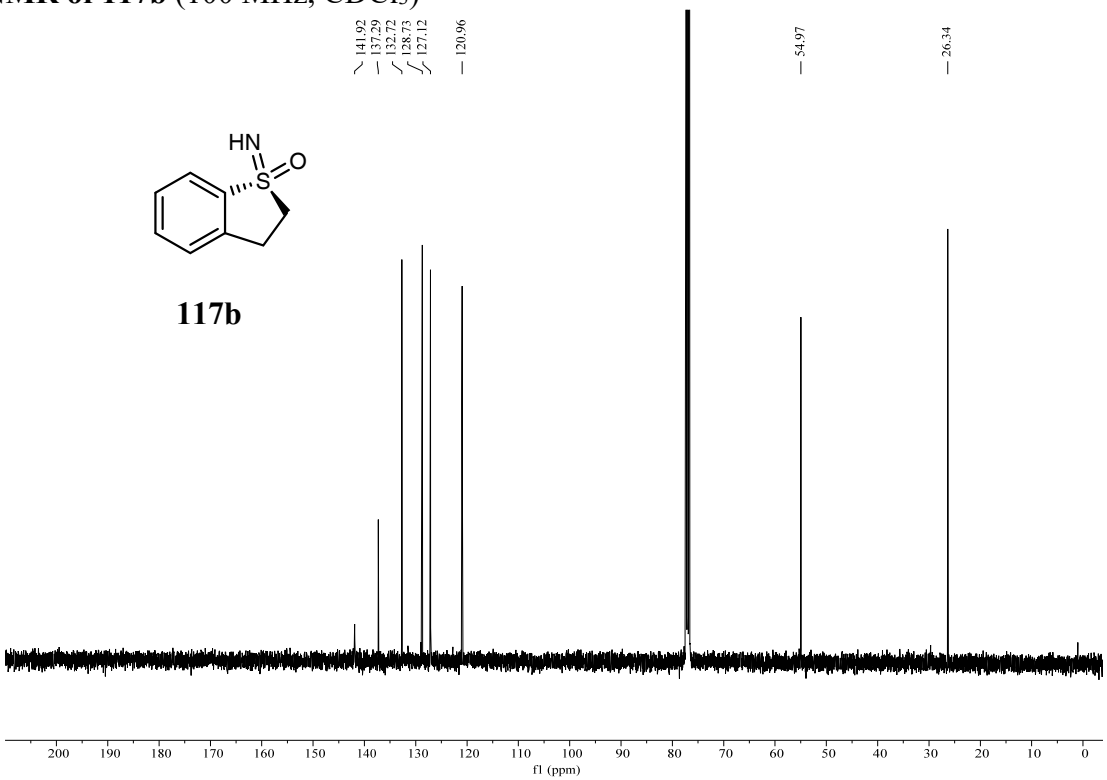
^{13}C NMR of 117a (100 MHz, $CDCl_3$)



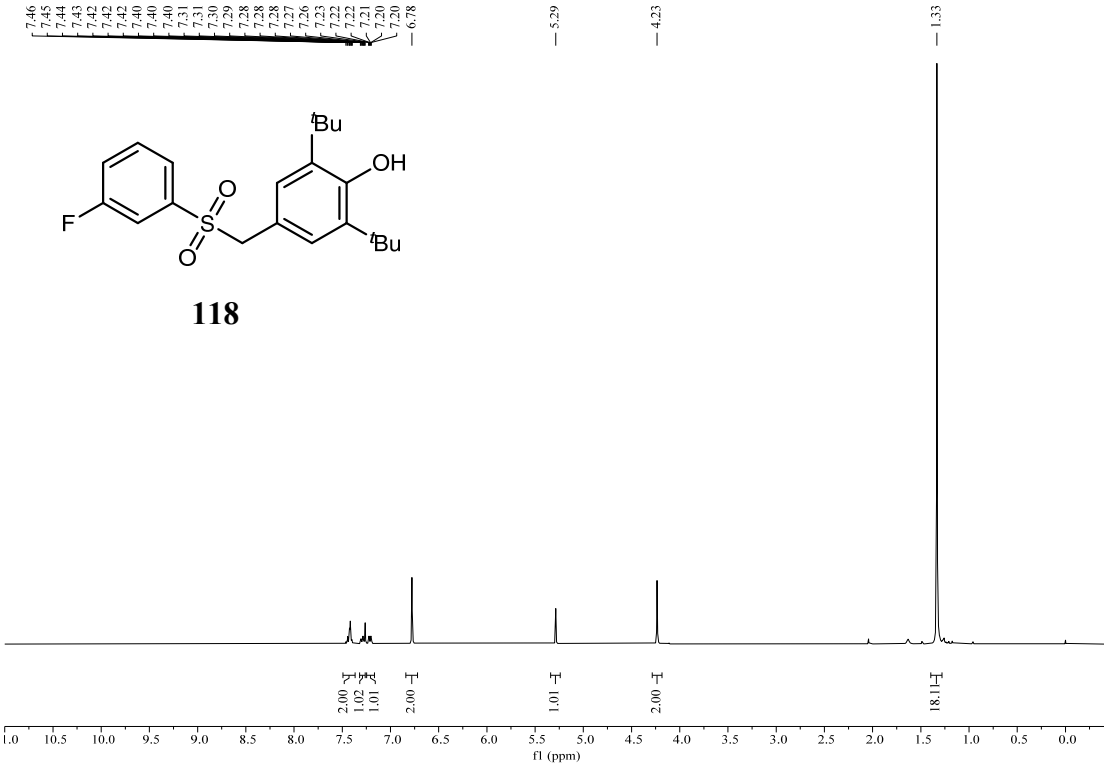
^{1}H NMR of 117b (400 MHz, $CDCl_3$)



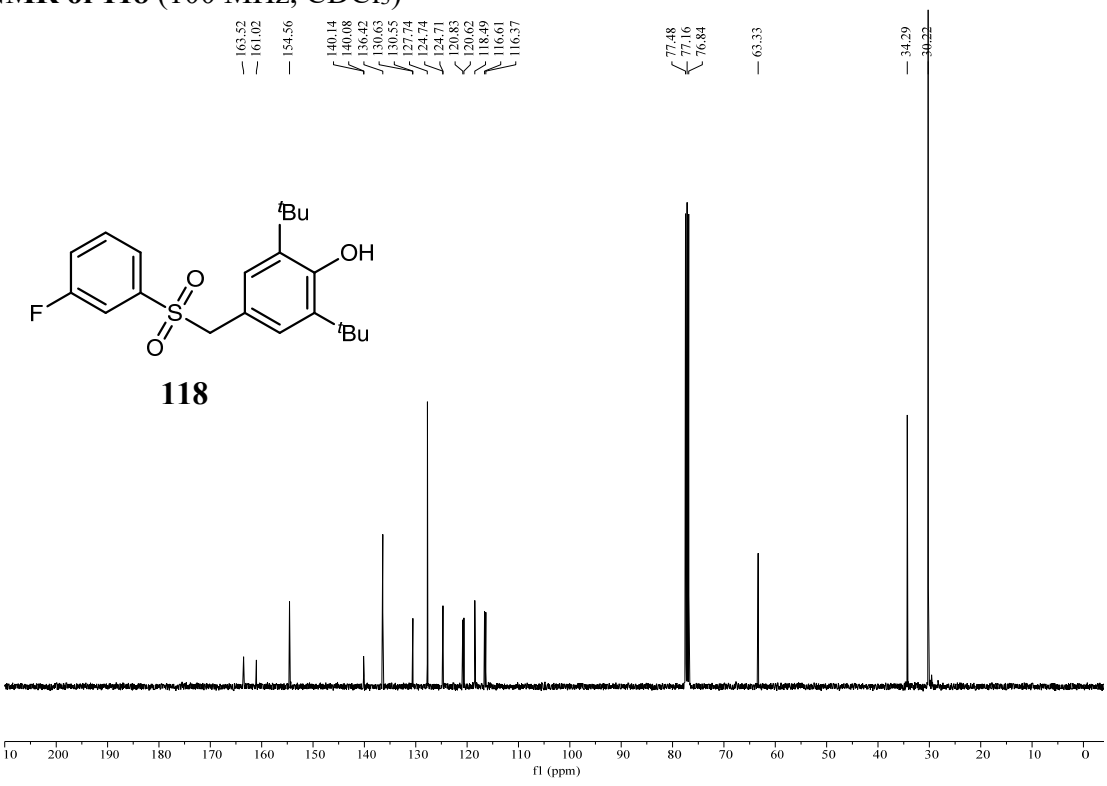
^{13}C NMR of 117b (100 MHz, $CDCl_3$)



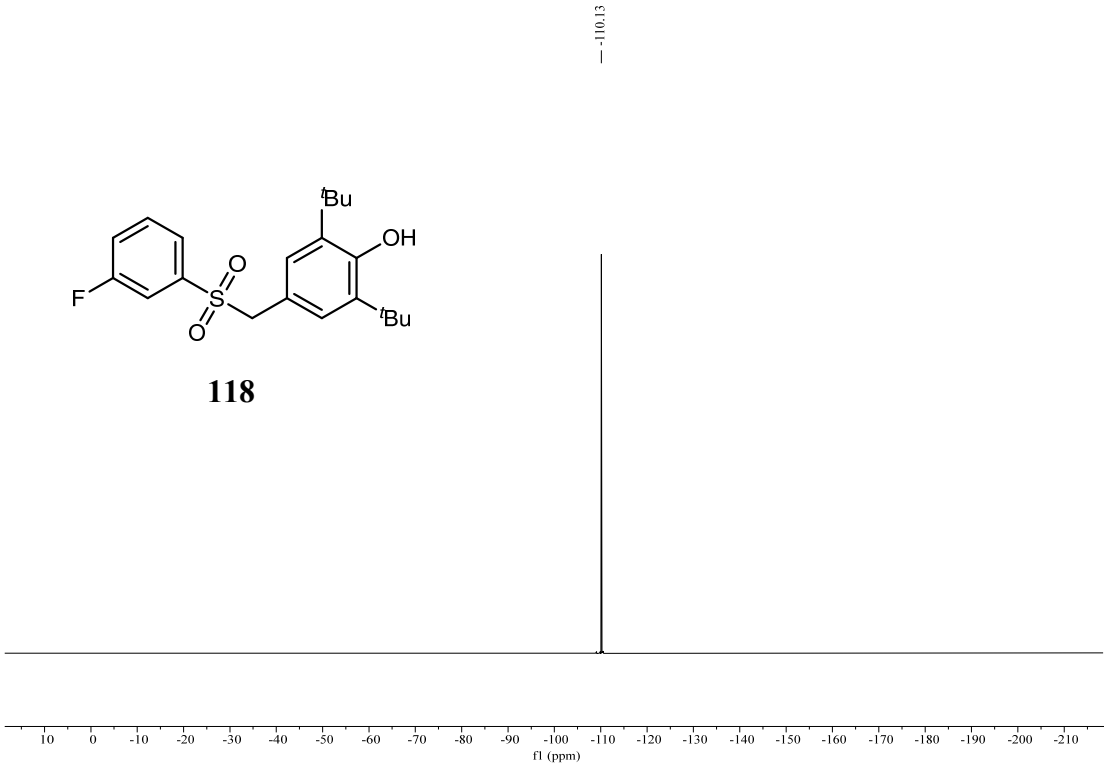
^{1}H NMR of 118 (400 MHz, $CDCl_3$)



^{13}C NMR of 118 (100 MHz, $CDCl_3$)

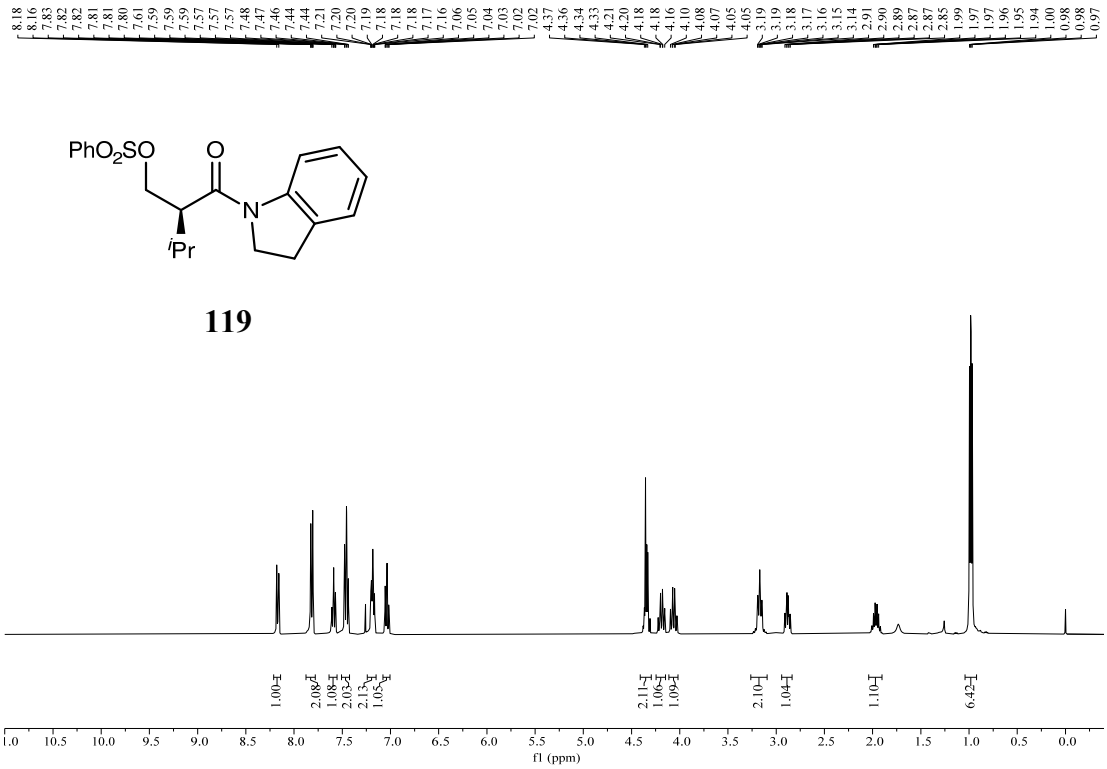


^{19}F NMR of 118 (375 MHz, $CDCl_3$)

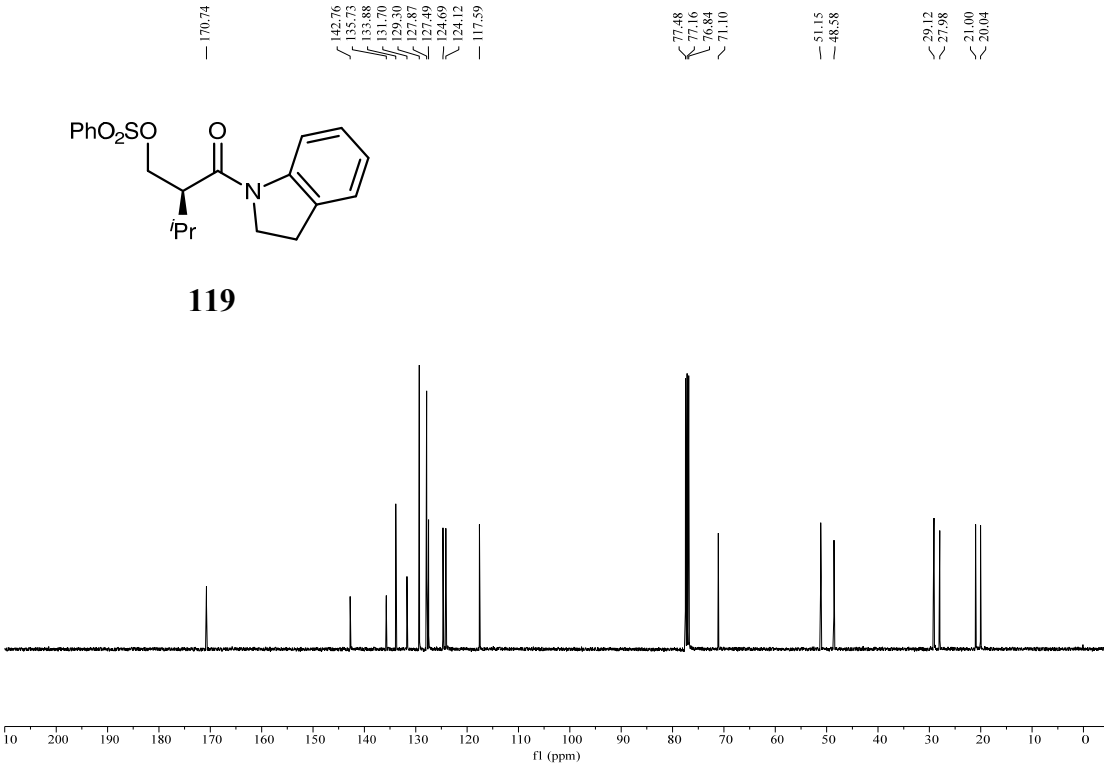


118

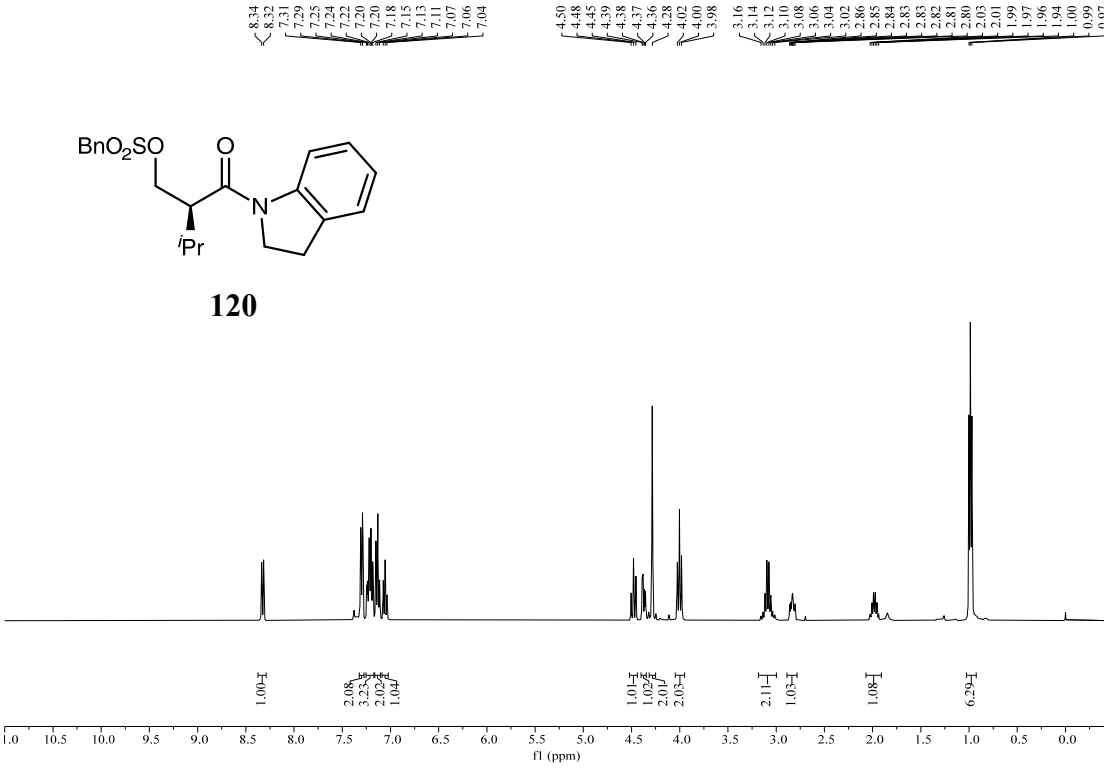
^{1}H NMR of 119 (400 MHz, $CDCl_3$)



^{13}C NMR of 119 (100 MHz, $CDCl_3$)

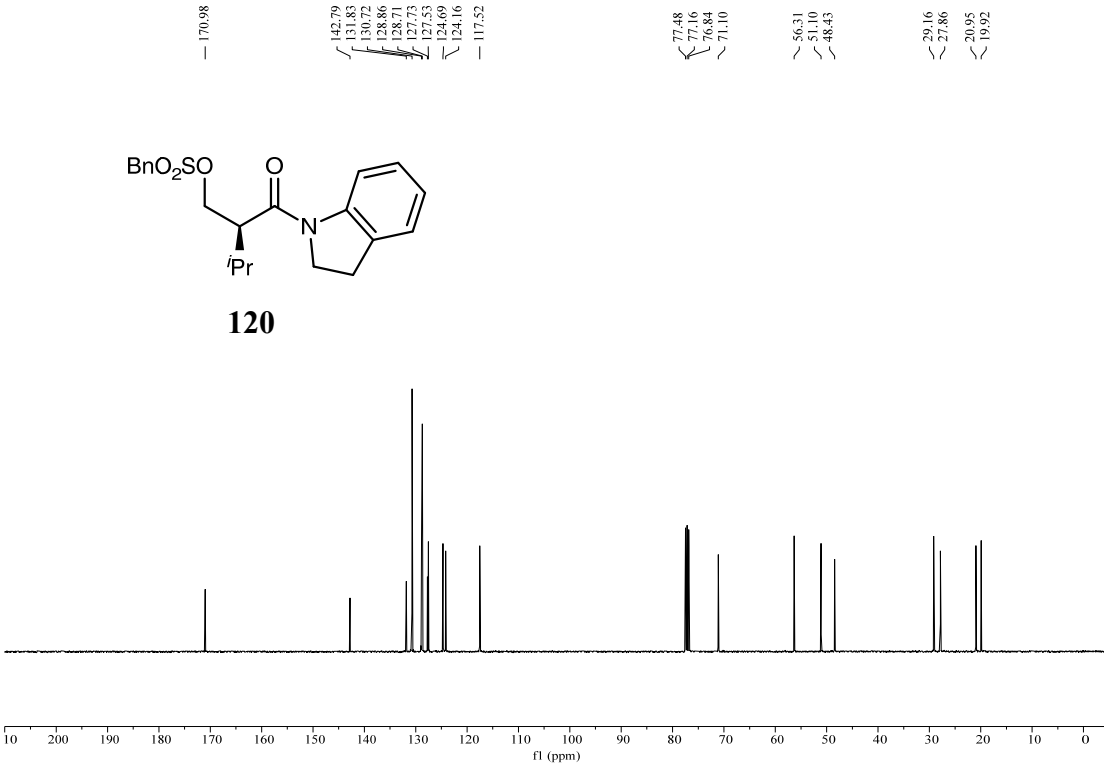


^{1}H NMR of 120 (400 MHz, $CDCl_3$)



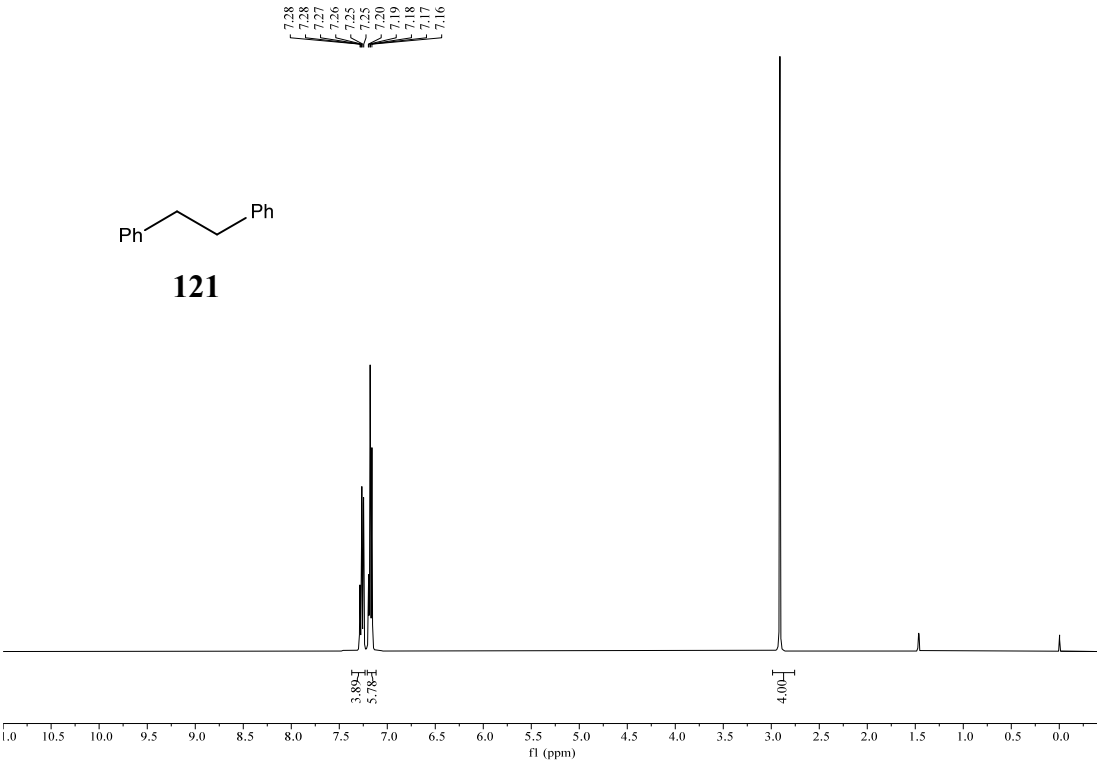
120

^{13}C NMR of 120 (100 MHz, $CDCl_3$)

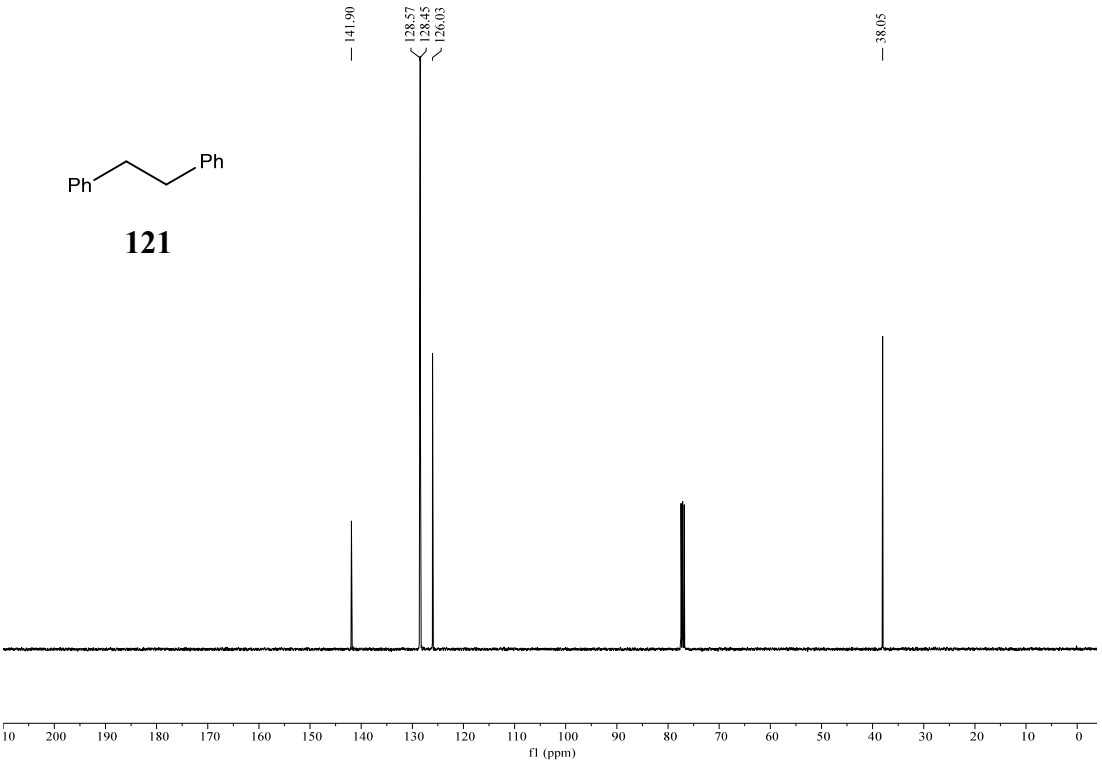


120

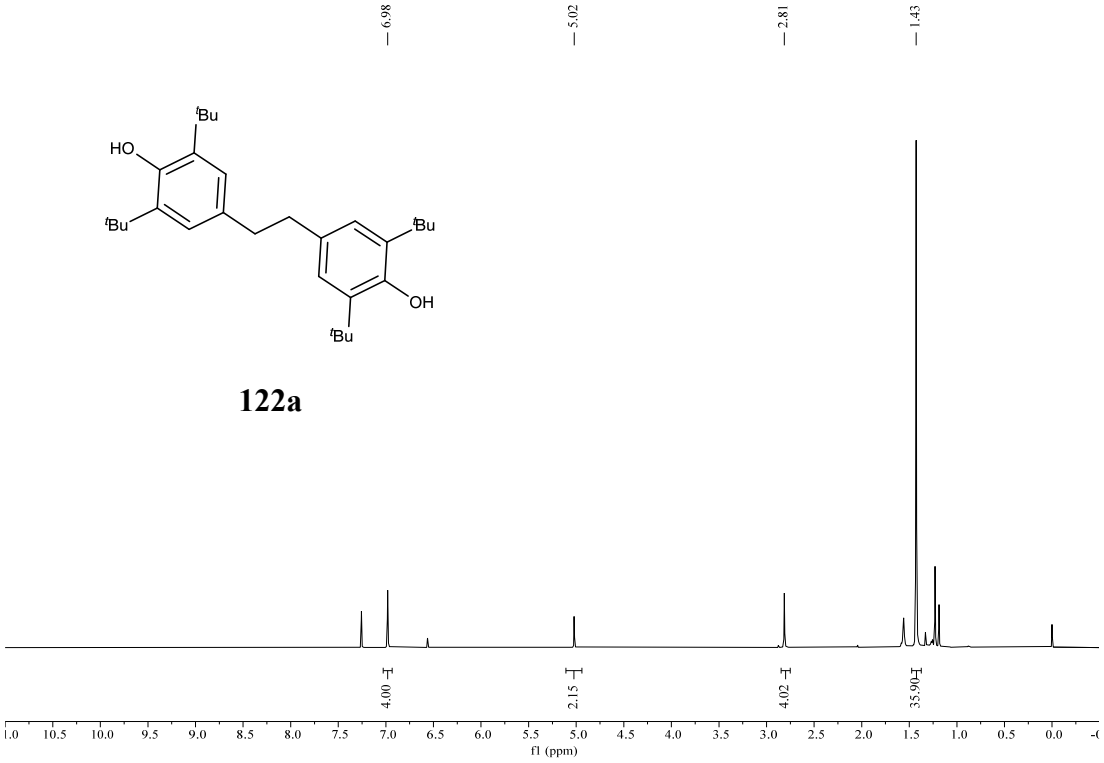
^{1}H NMR of 121 (400 MHz, $CDCl_3$)



^{13}C NMR of 121 (100 MHz, $CDCl_3$)

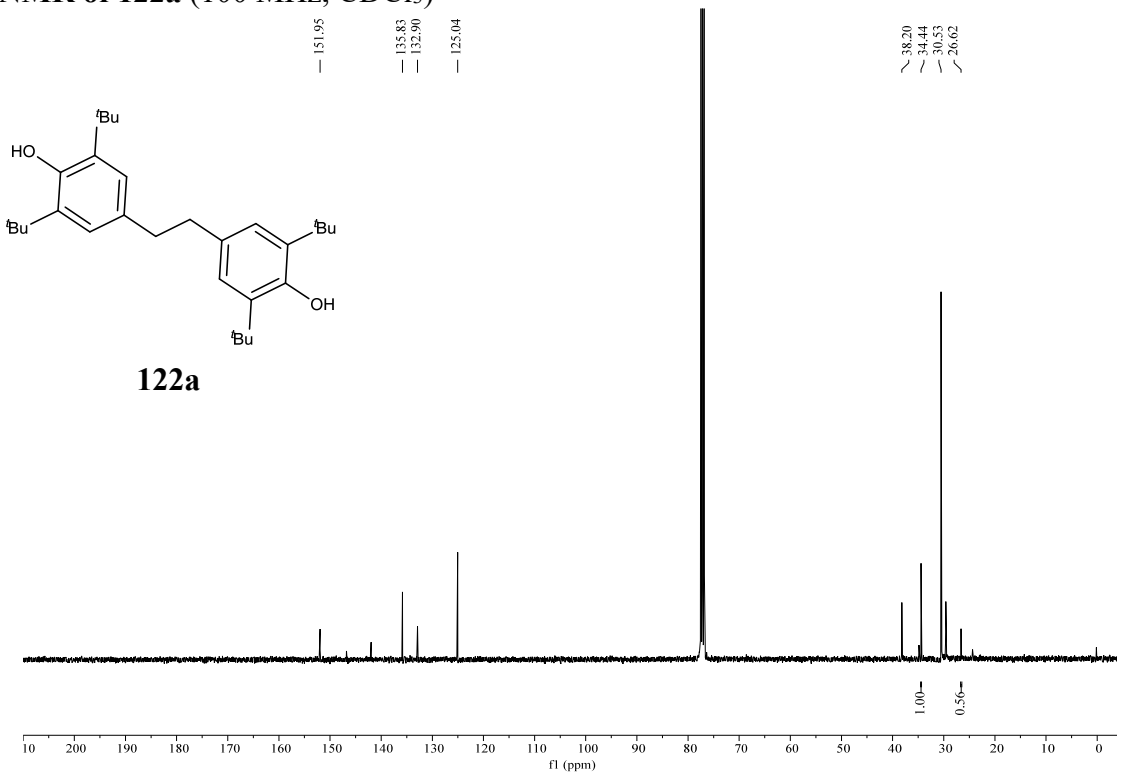


^{1}H NMR of 122a (400 MHz, $CDCl_3$)



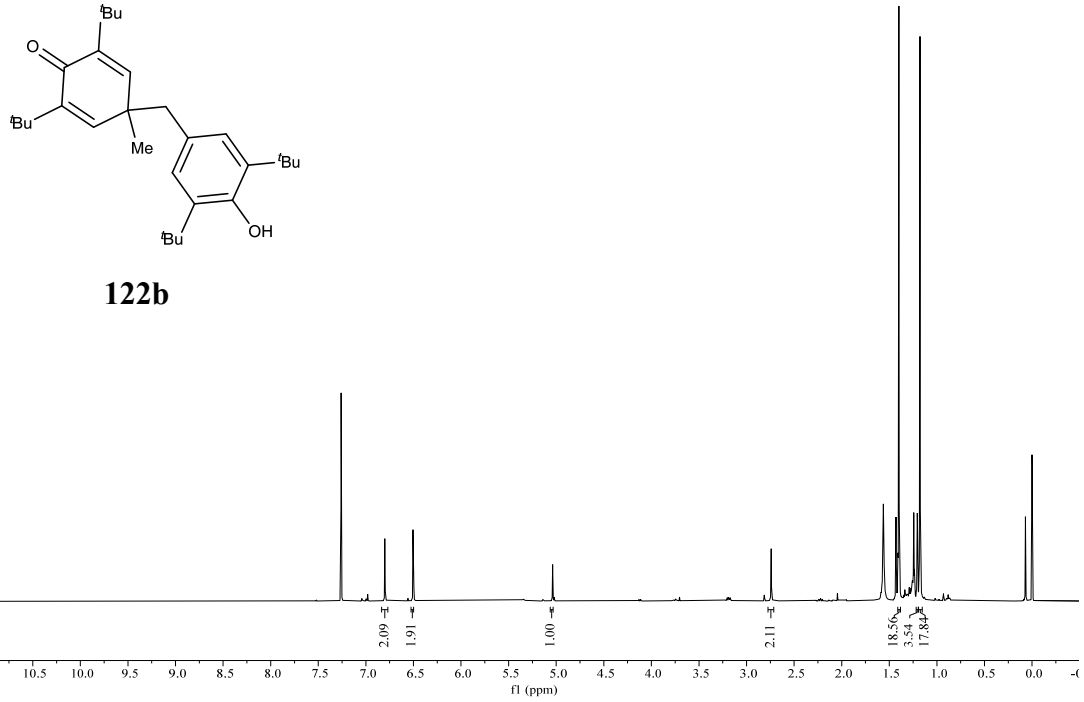
122a

^{13}C NMR of 122a (100 MHz, $CDCl_3$)



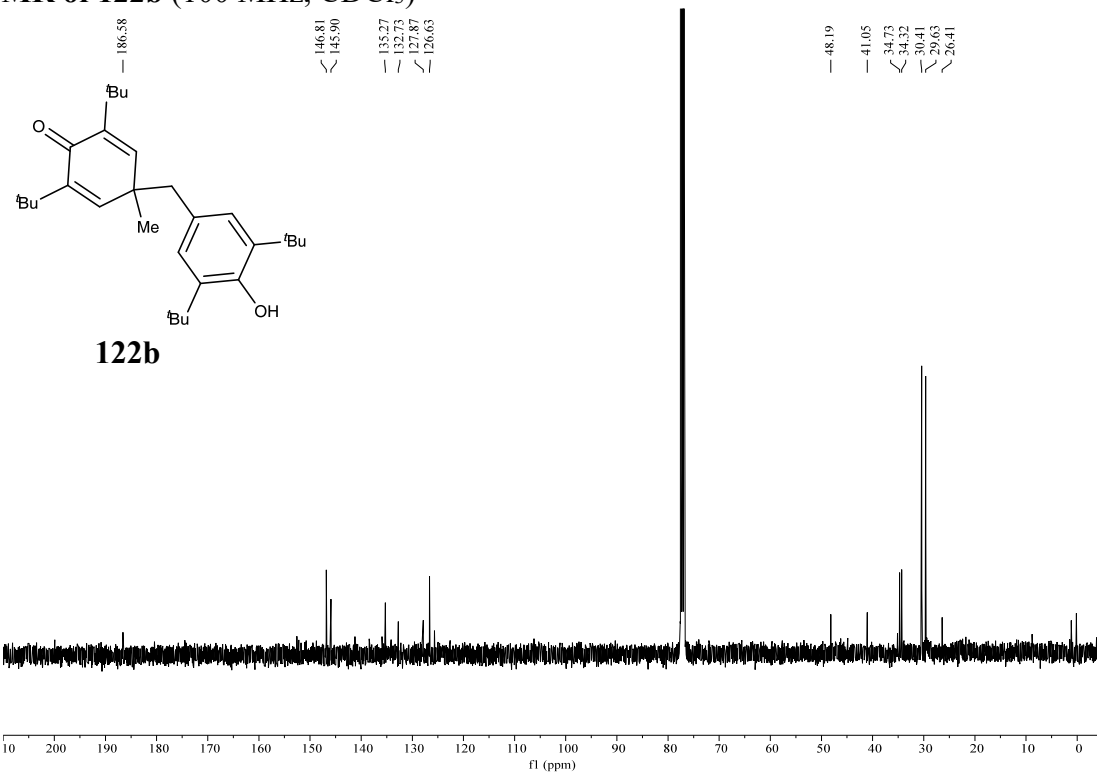
122a

^{1}H NMR of 122b (400 MHz, $CDCl_3$)



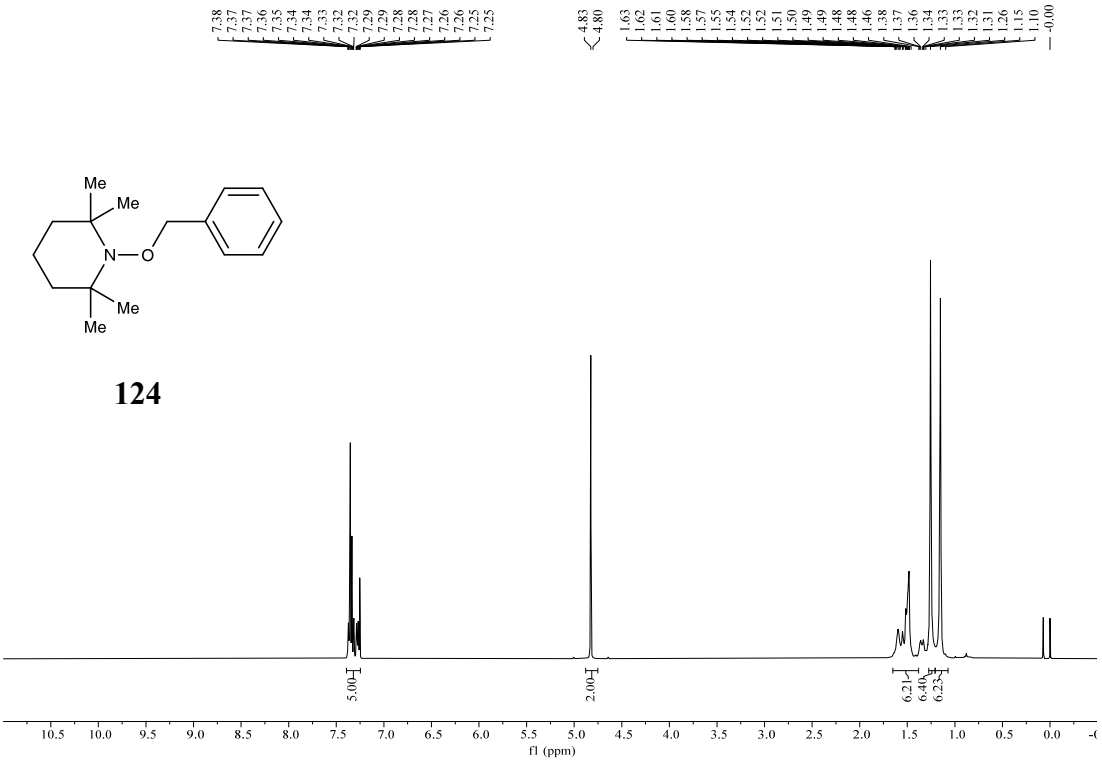
122b

^{13}C NMR of 122b (100 MHz, $CDCl_3$)

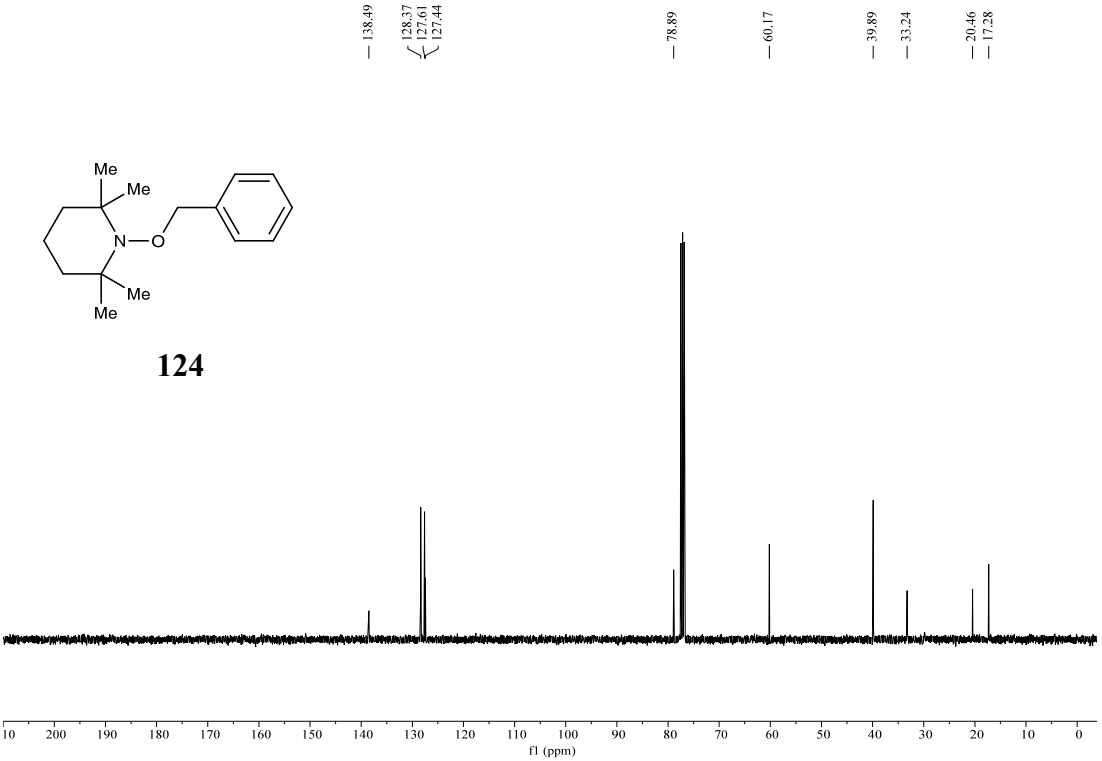


122b

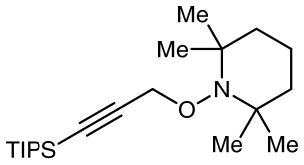
^{1}H NMR of 124 (400 MHz, $CDCl_3$)



^{13}C NMR of 124 (100 MHz, $CDCl_3$)

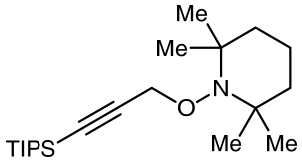


^{1}H NMR of 126 (400 MHz, $CDCl_3$)



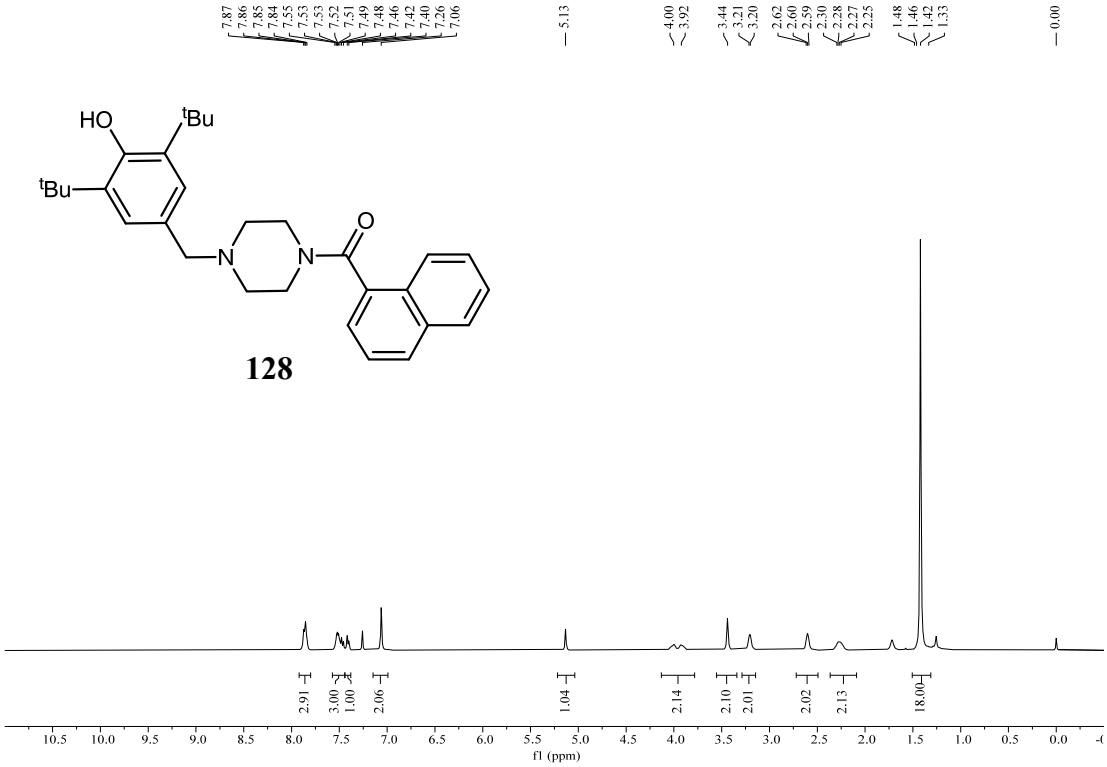
126

^{13}C NMR of 126 (100 MHz, $CDCl_3$)

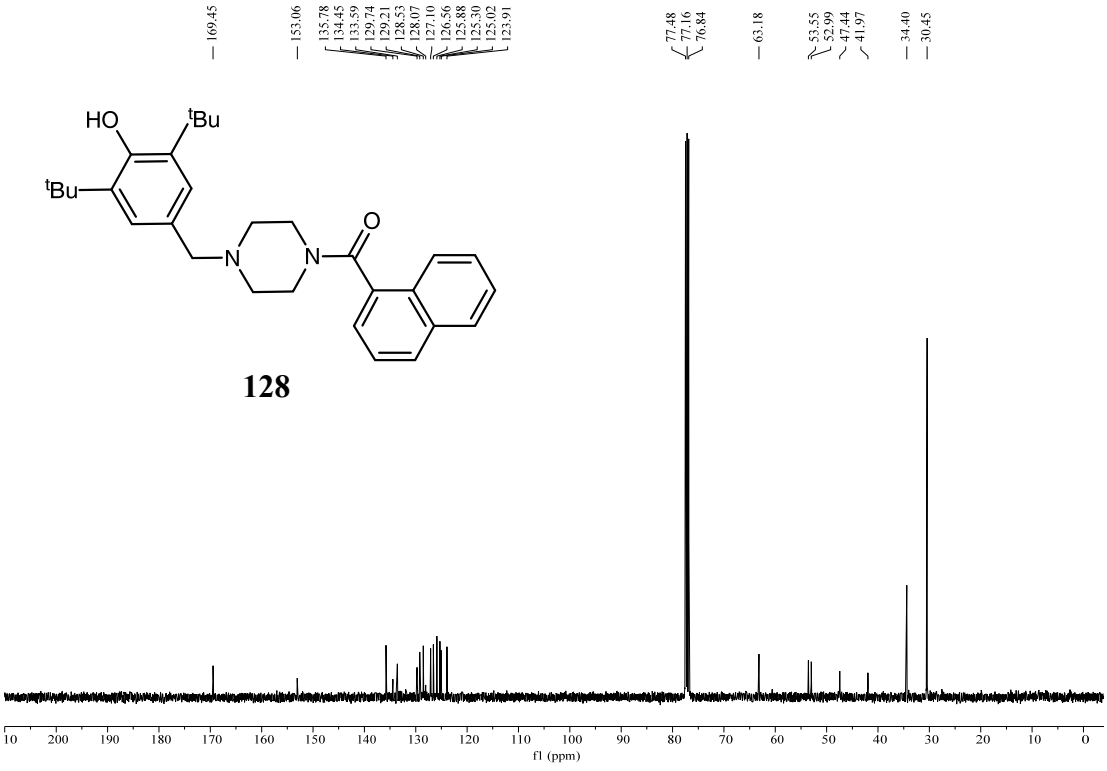


126

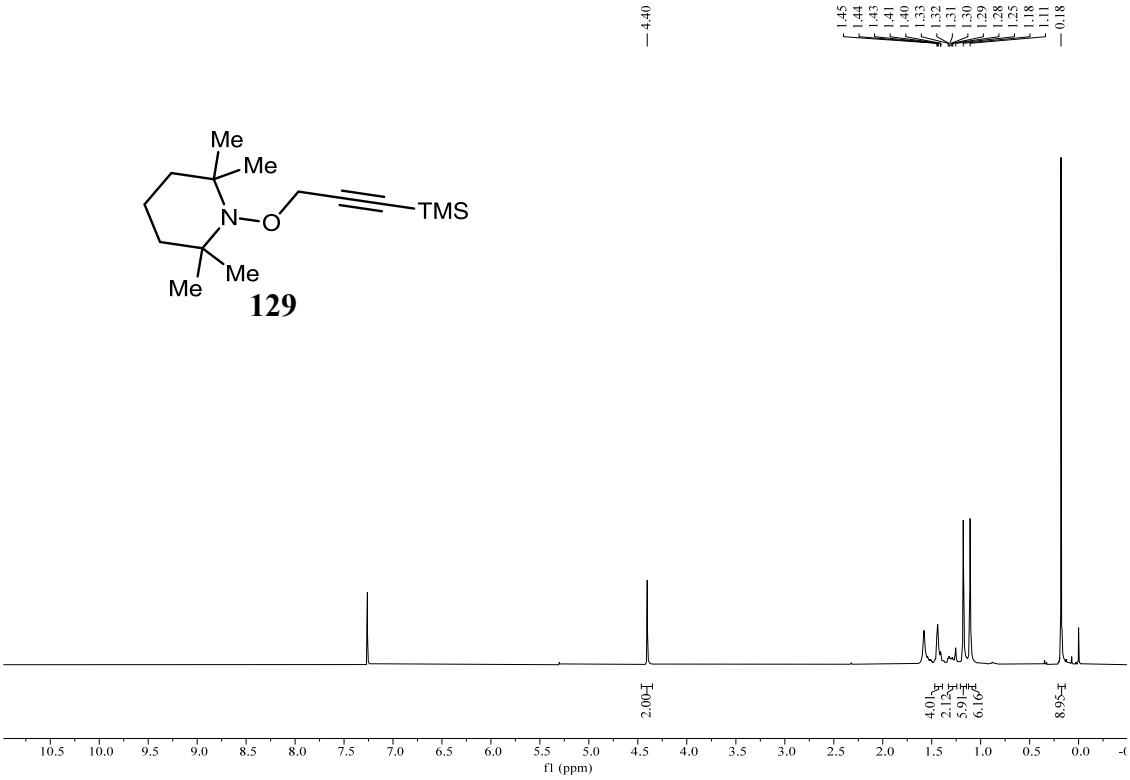
^{1}H NMR of 128 (400 MHz, $CDCl_3$)



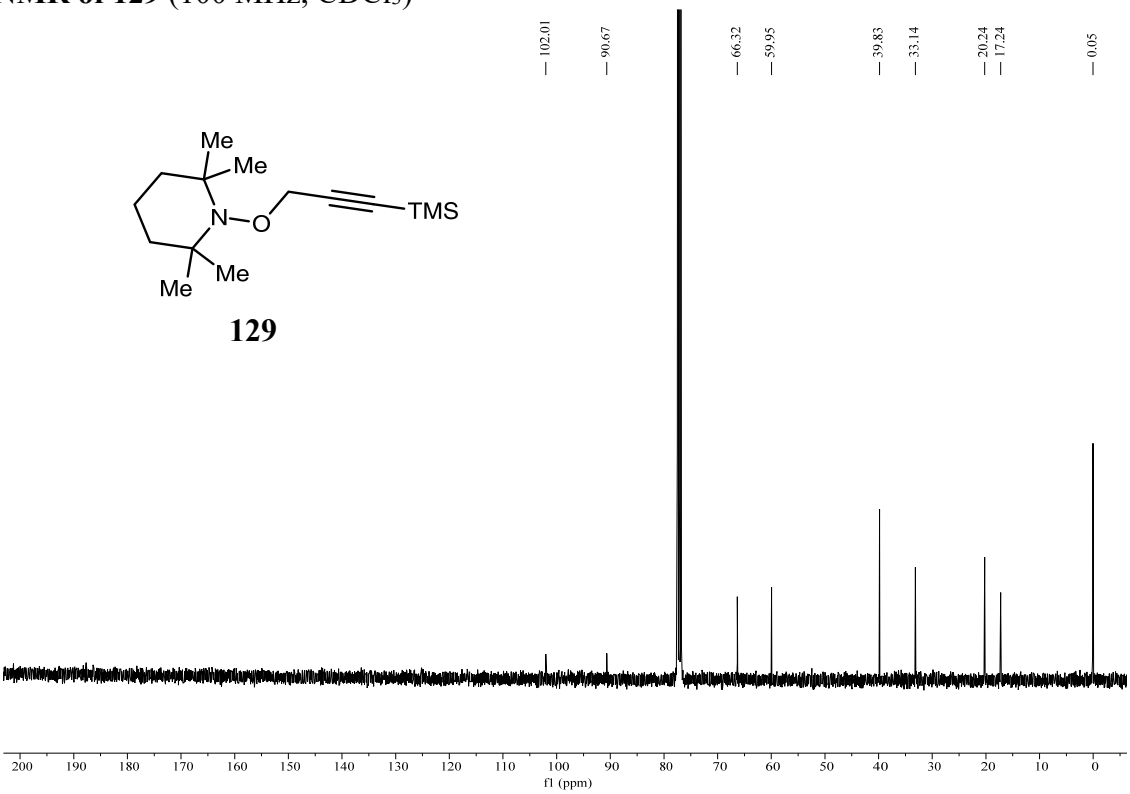
^{13}C NMR of 128 (100 MHz, $CDCl_3$)



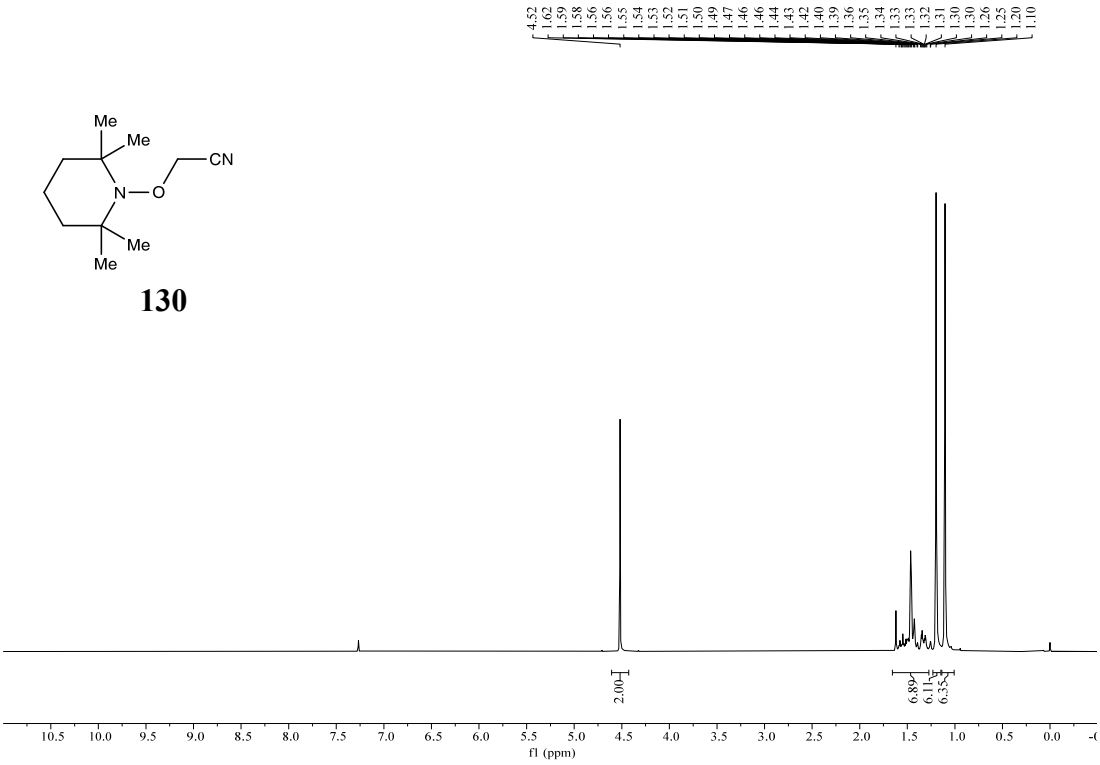
^{1}H NMR of 129 (400 MHz, $CDCl_3$)



^{13}C NMR of 129 (100 MHz, $CDCl_3$)

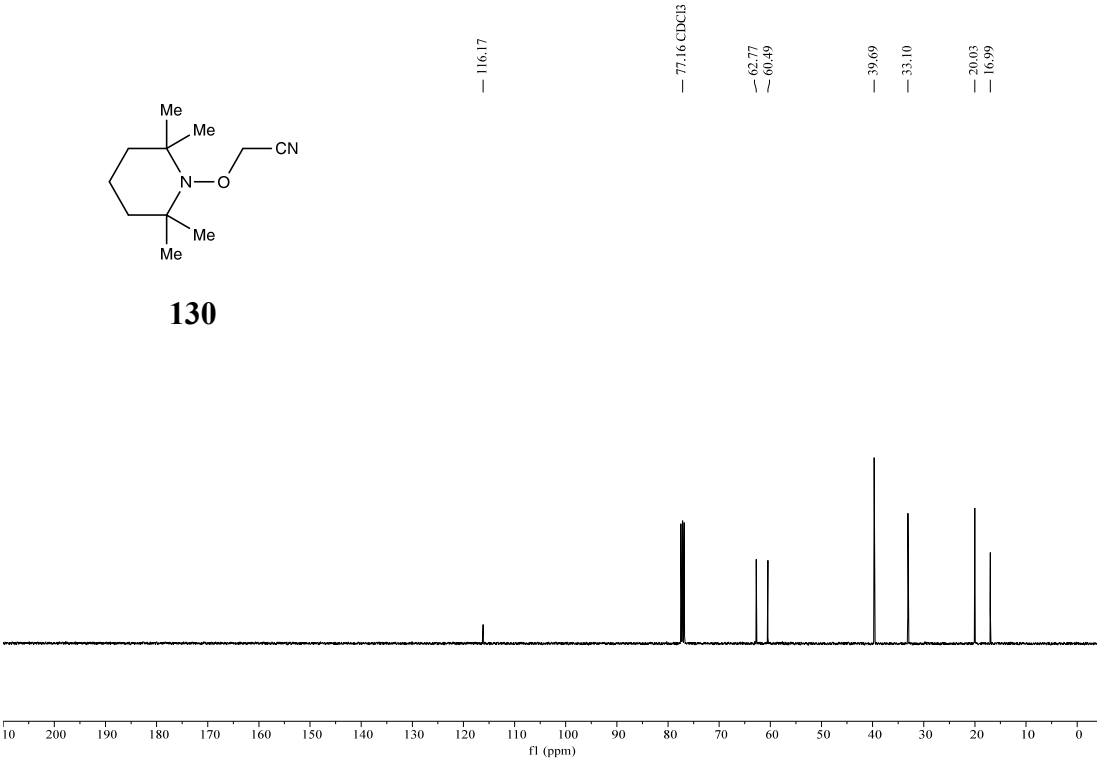


^{1}H NMR of 130 (400 MHz, $CDCl_3$)



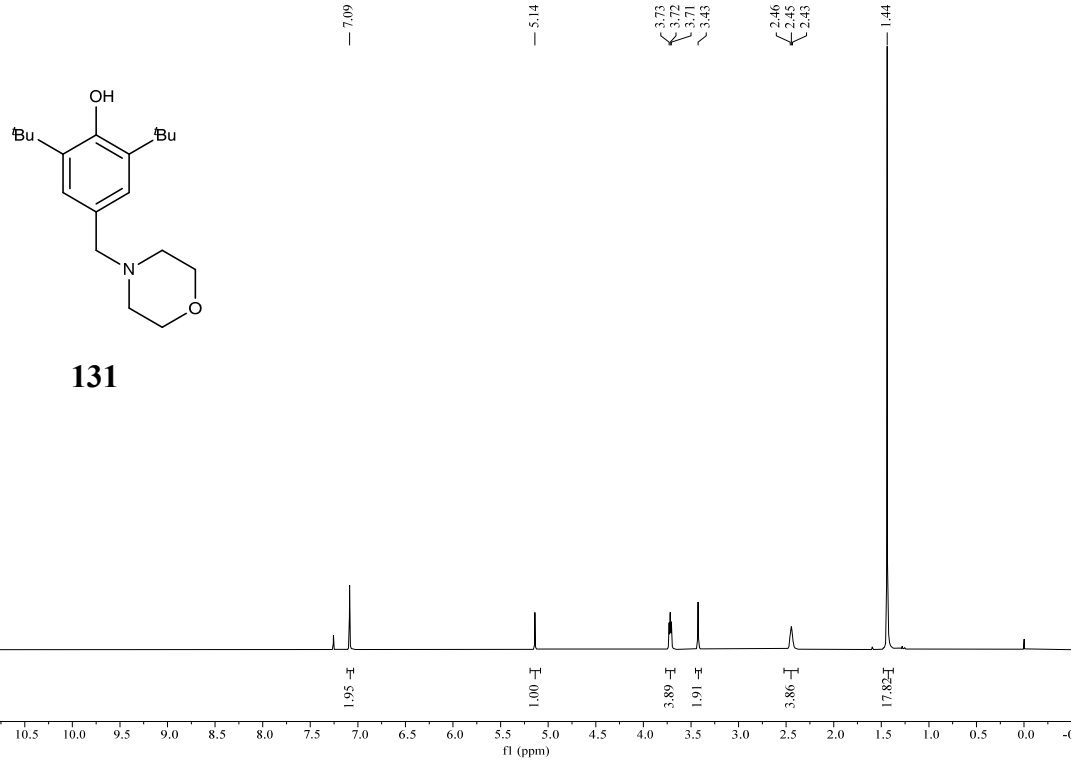
130

^{13}C NMR of 130 (100 MHz, $CDCl_3$)



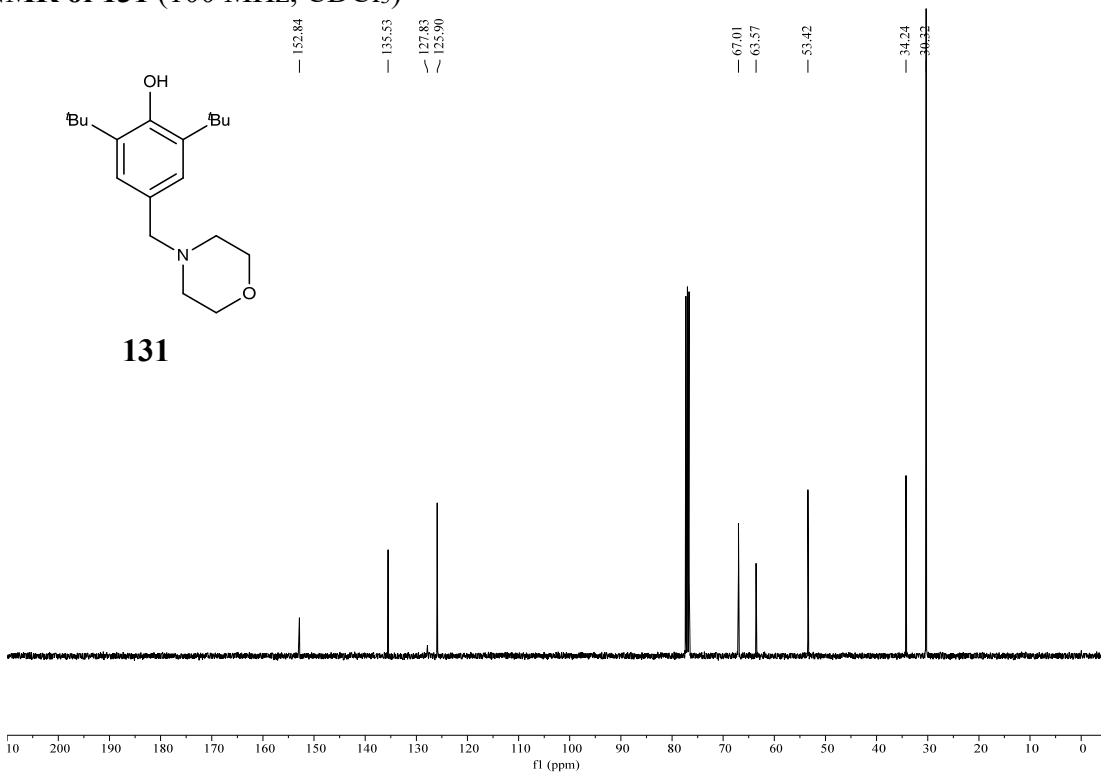
130

^{1}H NMR of 131 (400 MHz, $CDCl_3$)



131

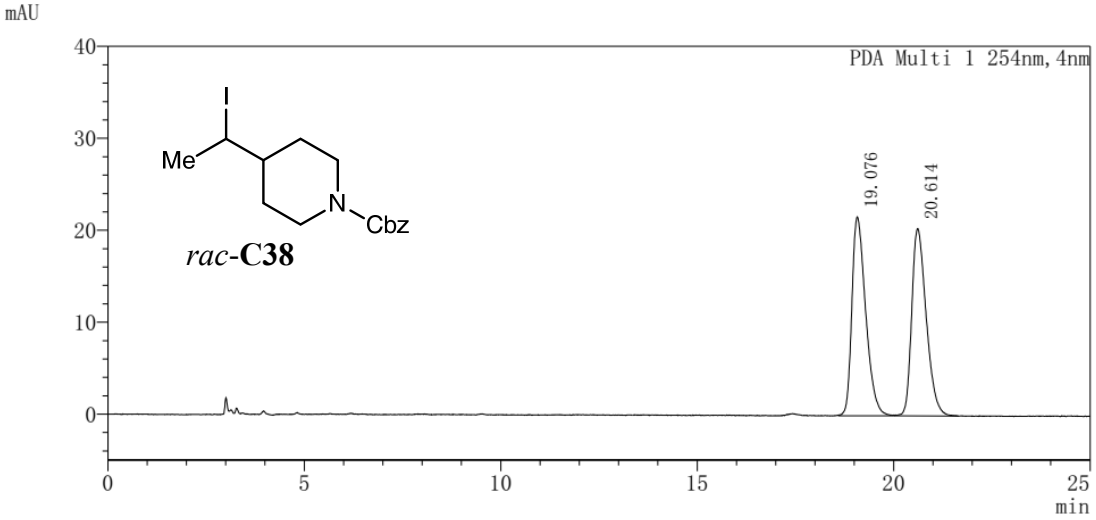
^{13}C NMR of 131 (100 MHz, $CDCl_3$)



131

12. HPLC spectra

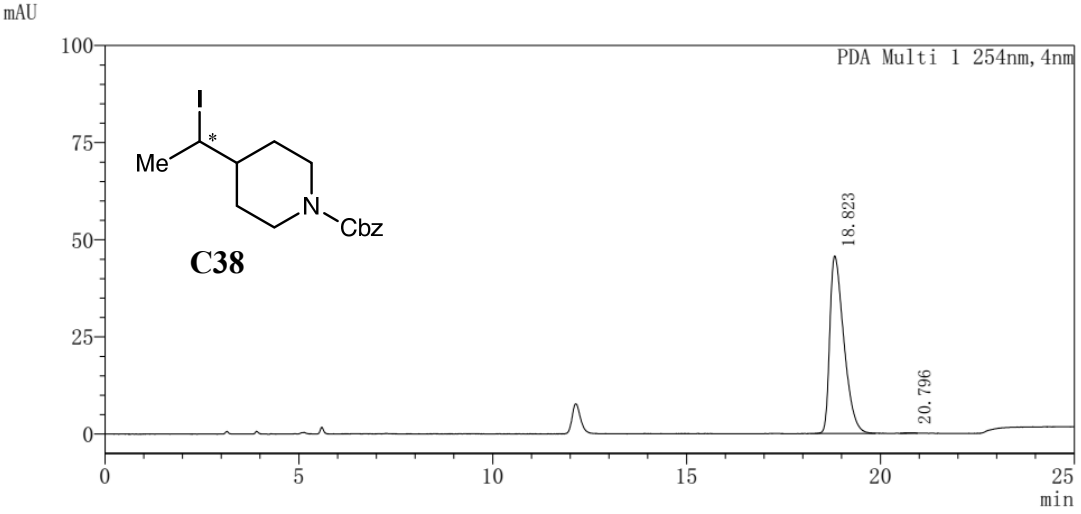
HPLC of C38



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.076	528520	50.199
2	20.614	524339	49.801

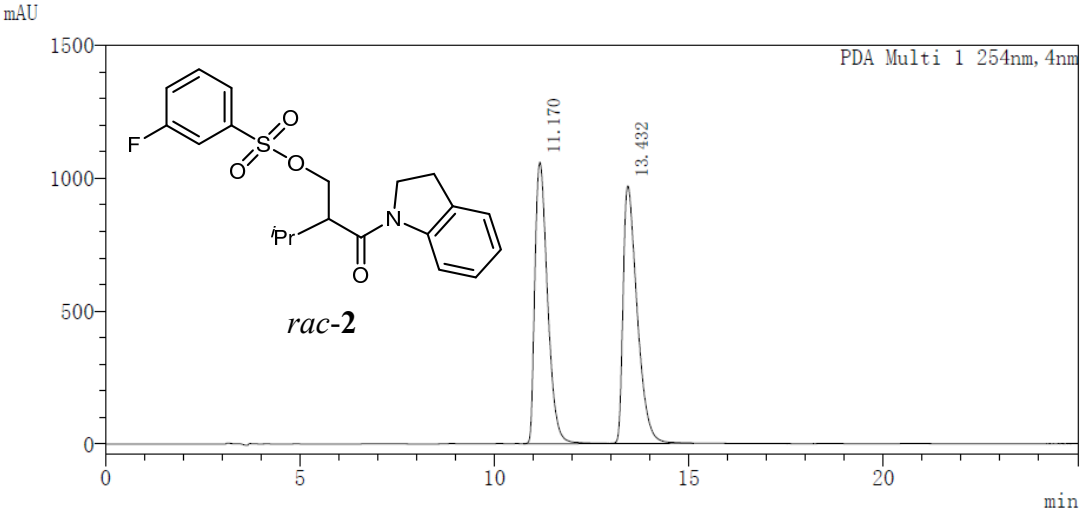


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.823	1152460	99.857
2	20.796	1647	0.143

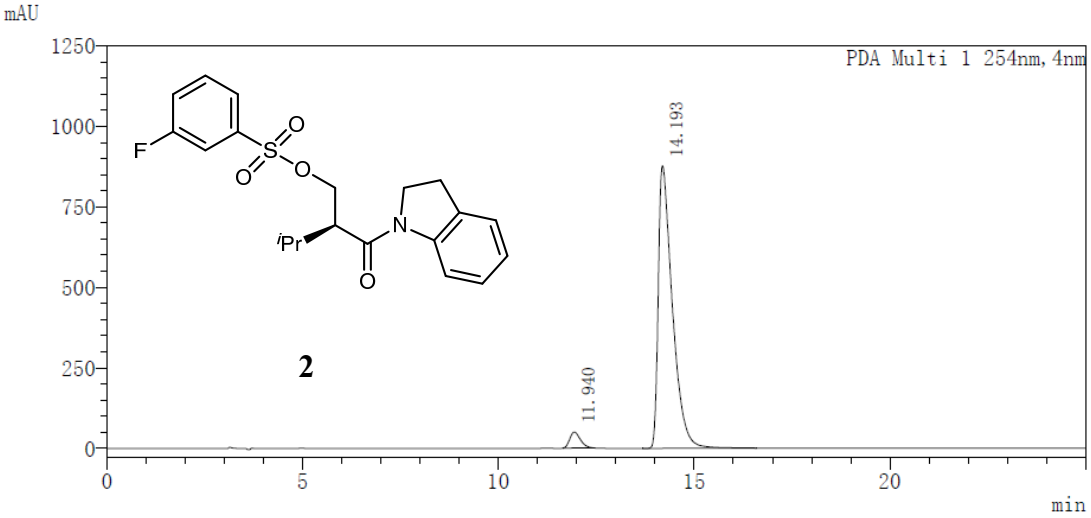
HPLC of 2



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.170	23997980	49.641
2	13.432	24344668	50.359

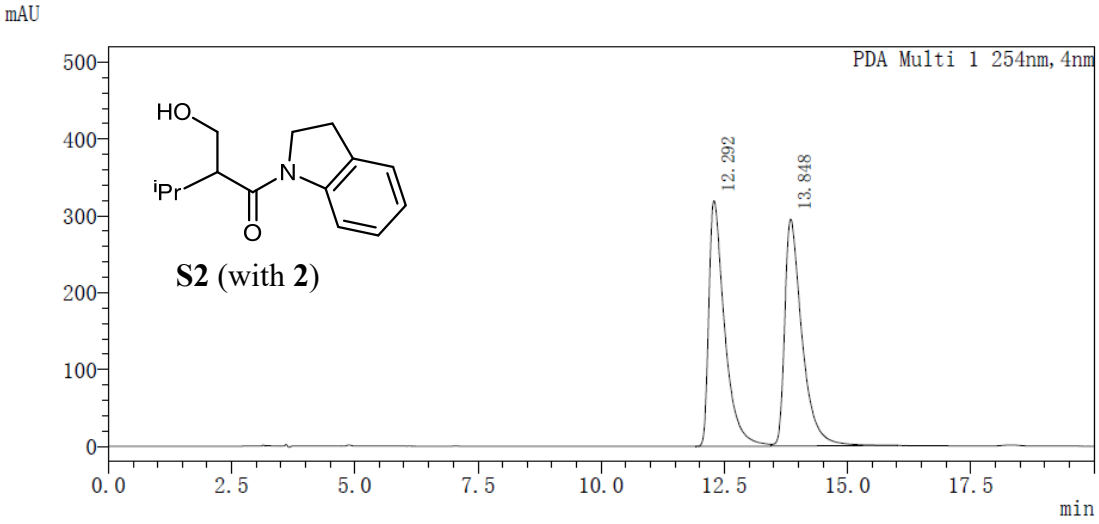


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.940	927787	4.054
2	14.193	21959835	95.946

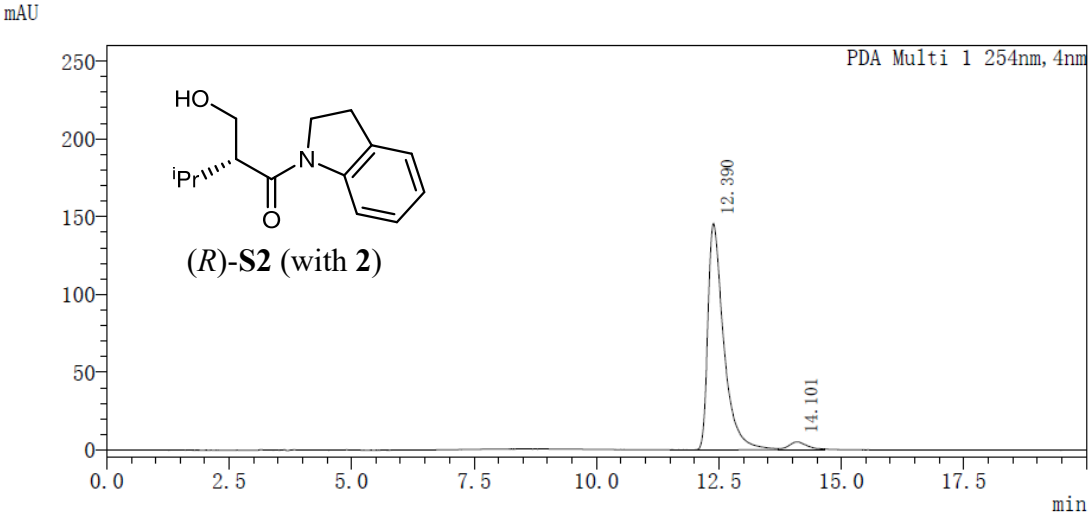
HPLC of S2



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.292	7131722	49.660
2	13.848	7229508	50.340

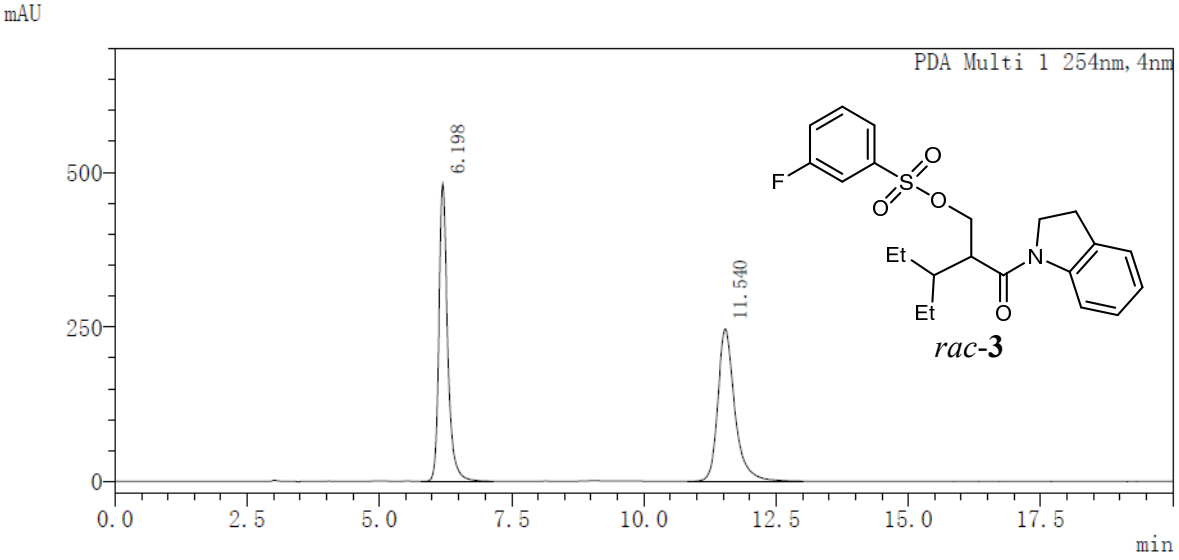


Peak Table

PDA Ch1 254nm

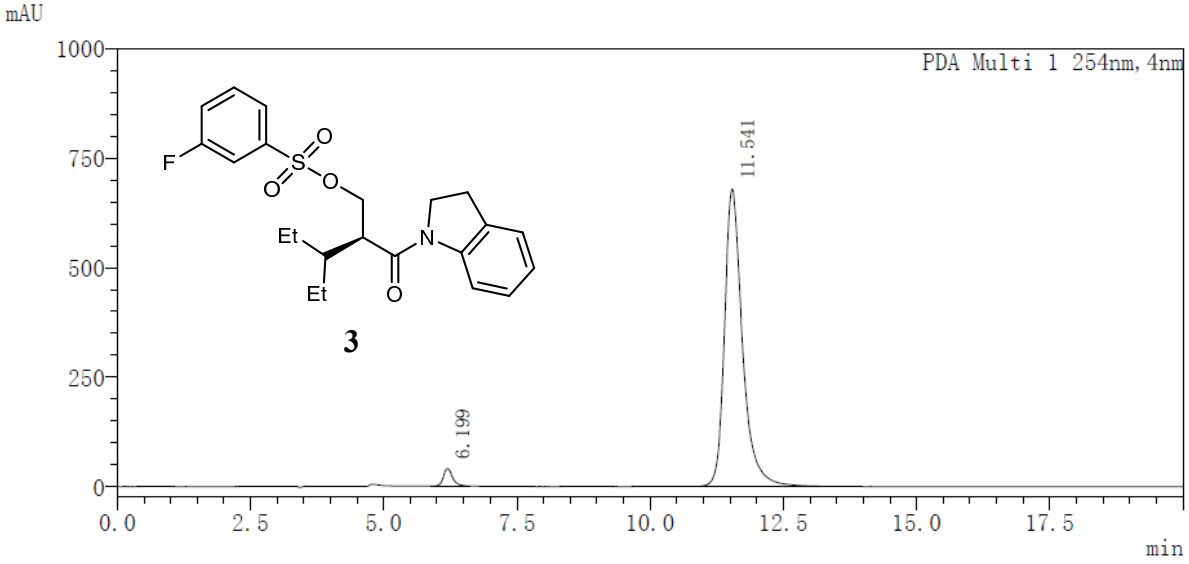
Peak#	Ret. Time	Area	Area%
1	12.390	3287106	95.999
2	14.101	137008	4.001

HPLC of 3



PDA Ch1 254nm

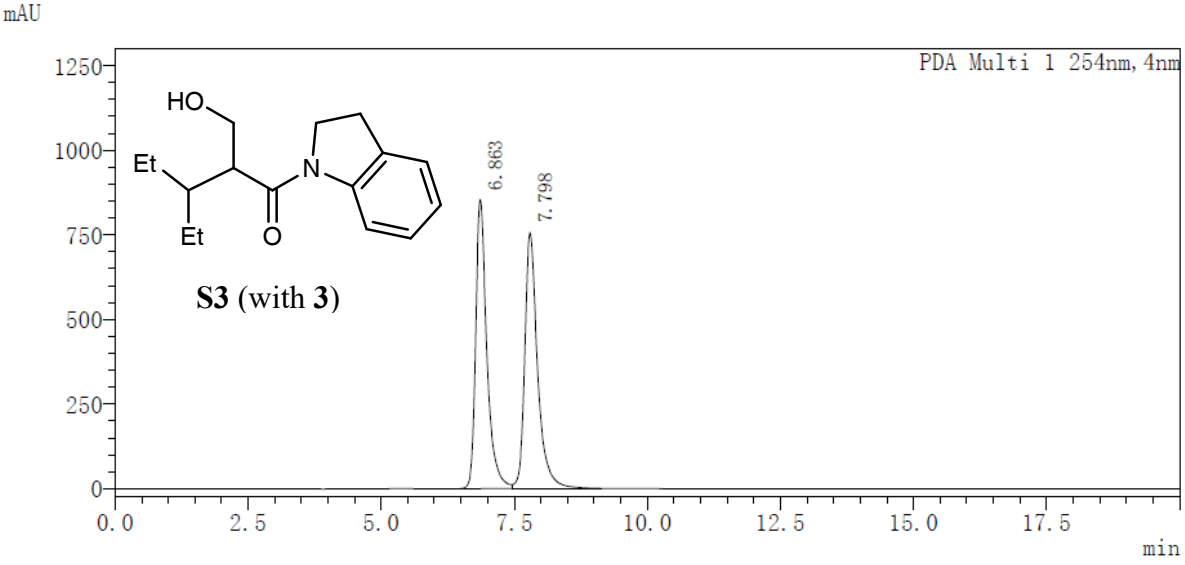
T	Hight	Area	Area%
6.198	481868	5516235	50.060
11.540	246675	5502942	49.940



PDA Ch1 254nm

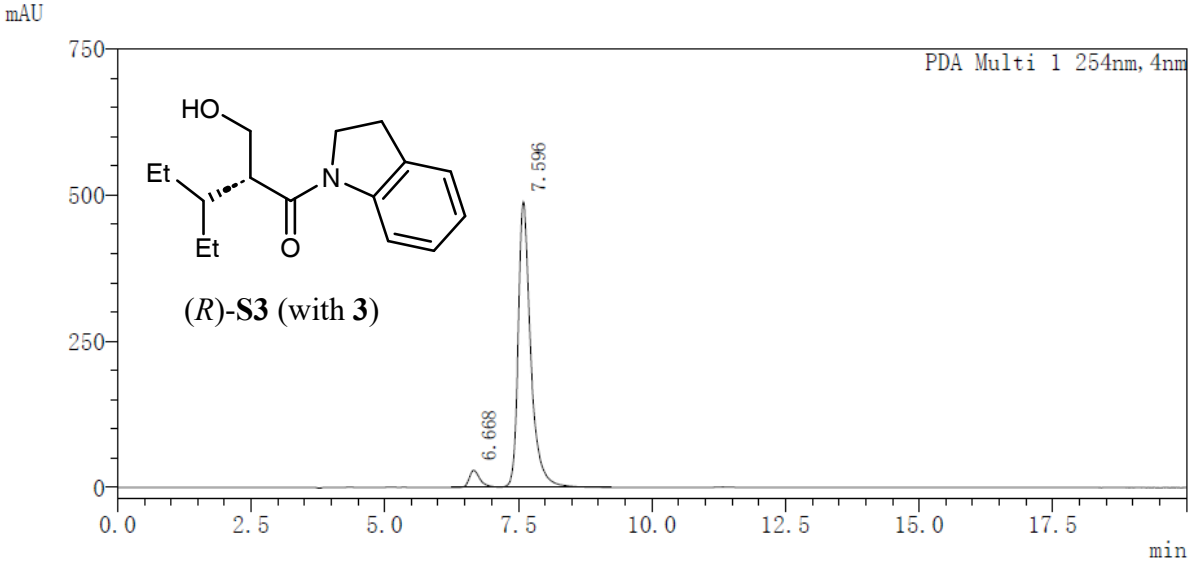
T	Hight	Area	Area%
6.199	40364	480034	2.921
11.541	679548	15955118	97.079

HPLC of S3



PDA Ch1 254nm

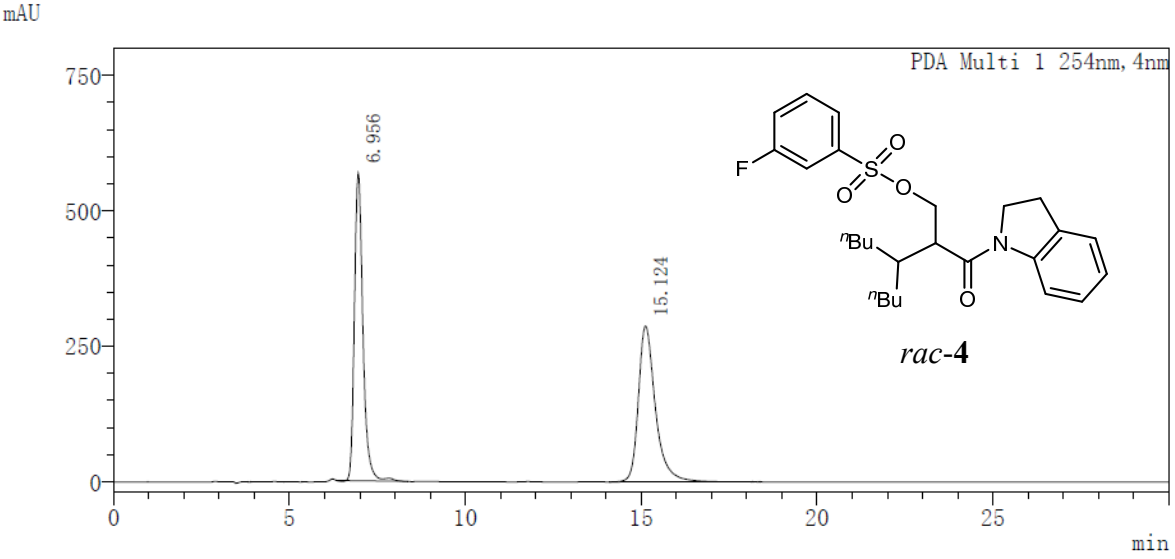
T	Hight	Area	Area%
6.863	853792	12450013	49.612
7.798	754962	12644676	50.388



PDA Ch1 254nm

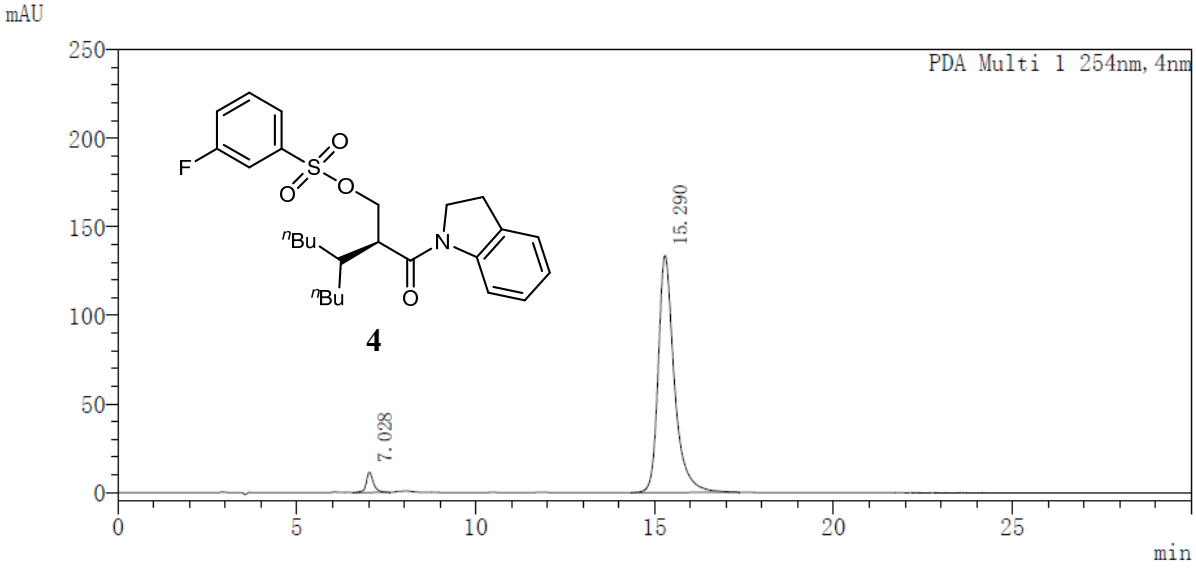
T	Hight	Area	Area%
6.668	29582	417099	4.979
7.596	488827	7960758	95.021

HPLC of 4



PDA Ch1 254nm

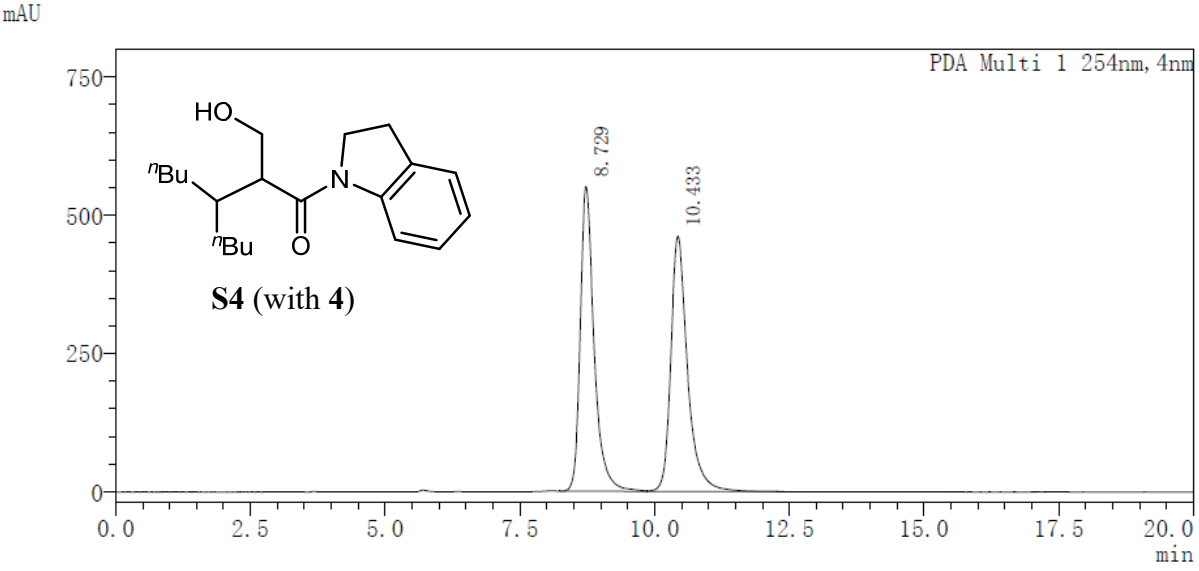
T	Hight	Area	Area%
6.956	567702	9602612	49.860
15.124	287662	9656485	50.140



PDA Ch1 254nm

T	Hight	Area	Area%
7.028	11419	160011	3.685
15.290	133731	4182789	96.315

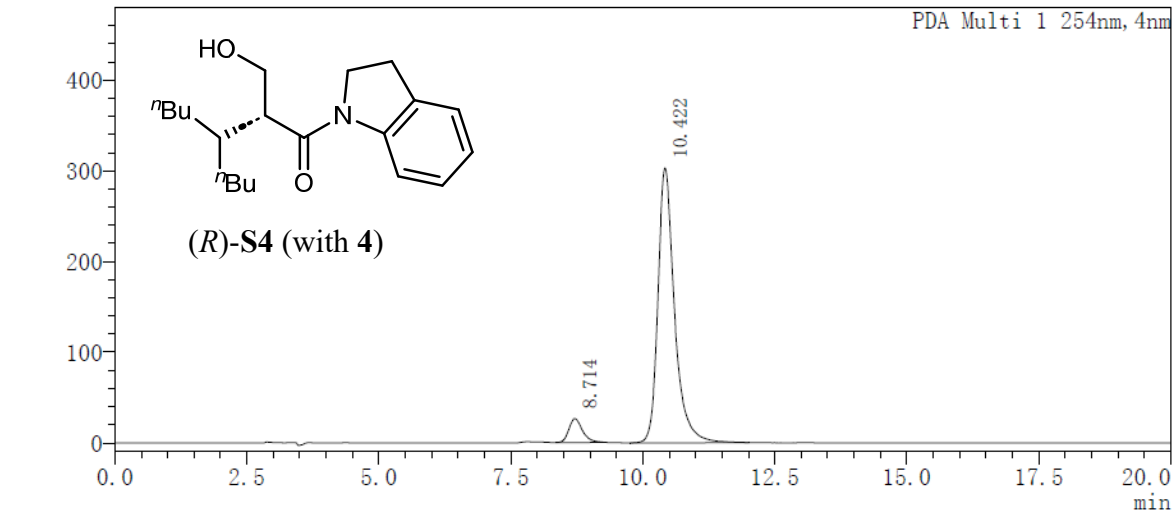
HPLC of S4



S4 (with **4**)

PDA Ch1 254nm

T	Hight	Area	Area%
8.729	551137	9869447	49.784
10.433	461451	9955079	50.216

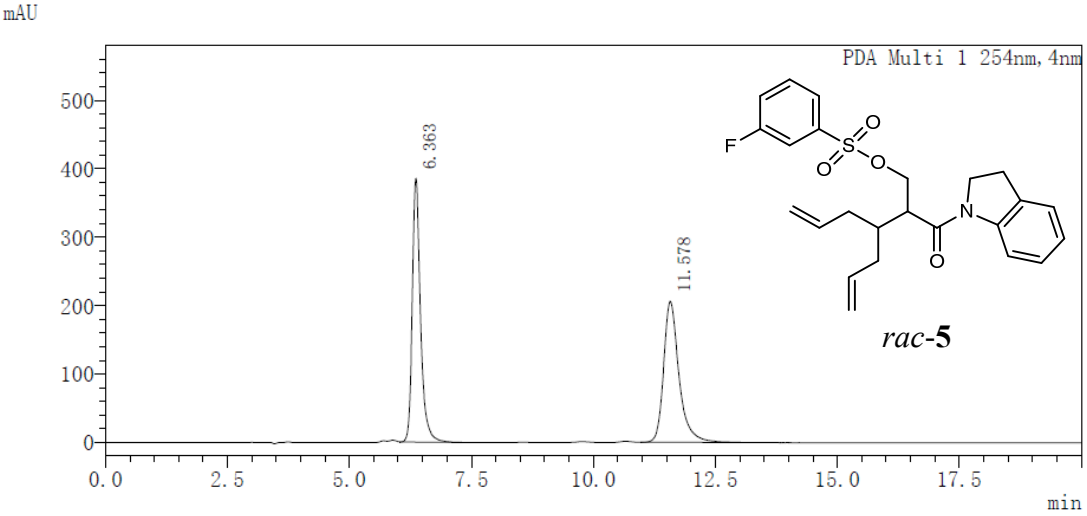


(*R*)-**S4** (with **4**)

PDA Ch1 254nm

T	Hight	Area	Area%
8.714	26267	465683	6.568
10.422	303124	6624031	93.432

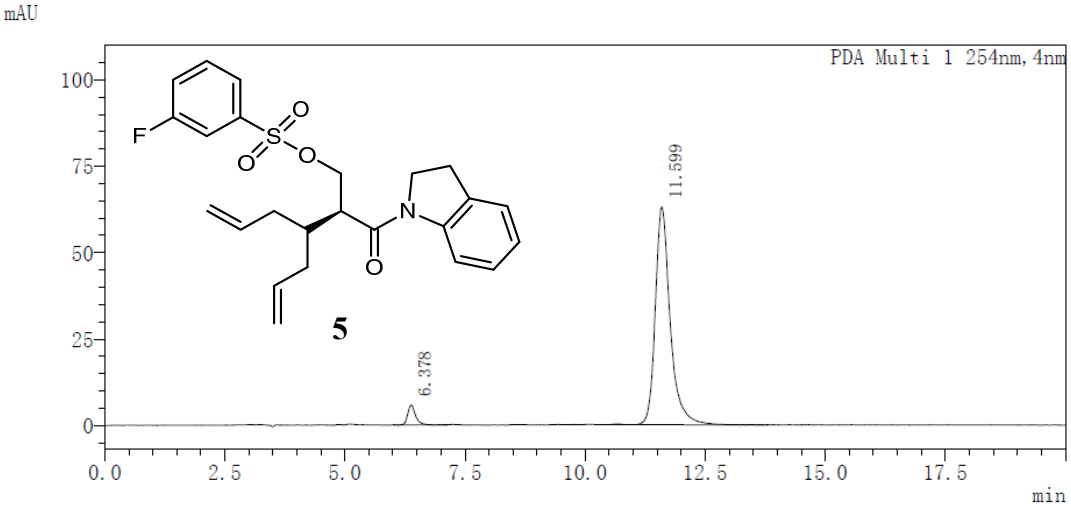
HPLC of 5



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.363	4519926	49.892
2	11.578	4539531	50.108

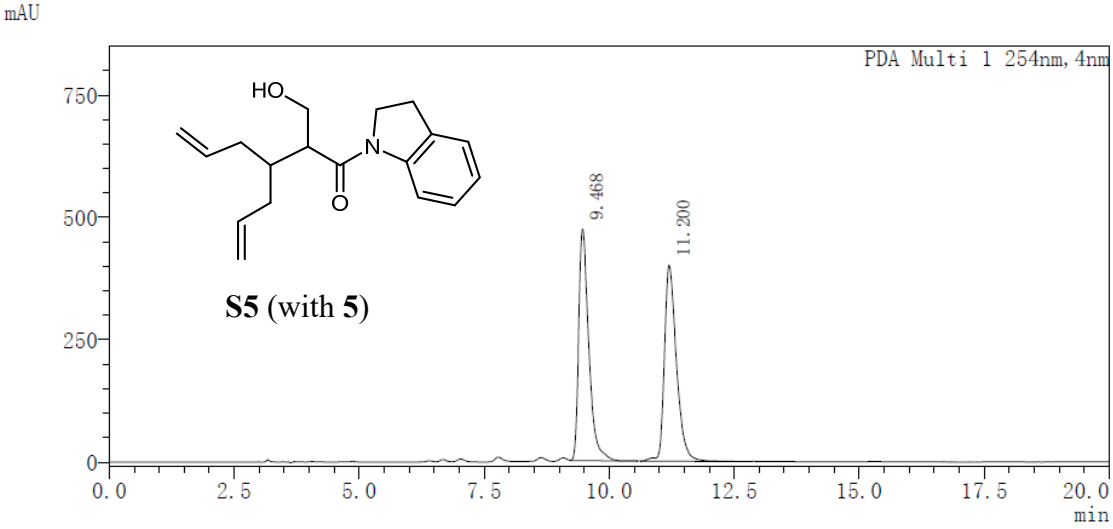


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.378	64976	4.528
2	11.599	1370155	95.472

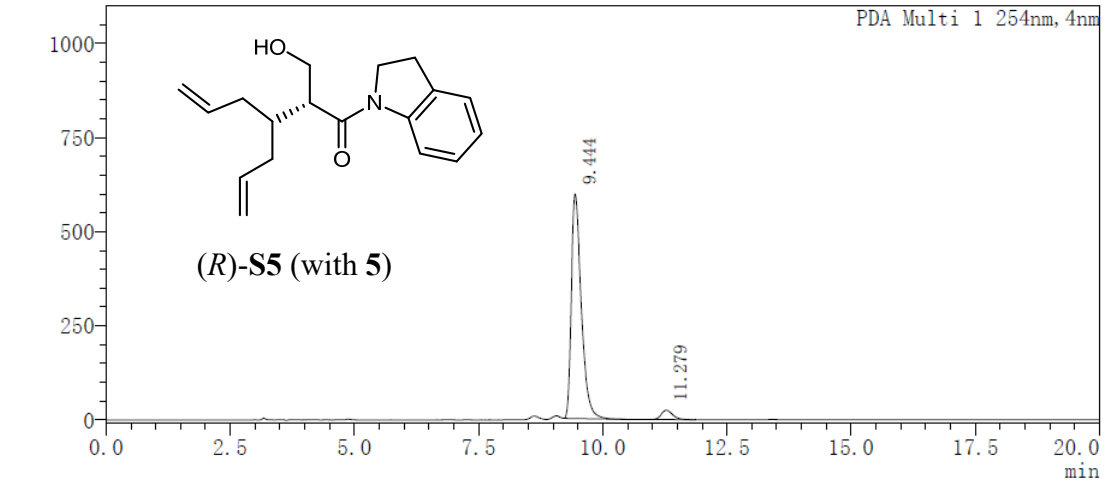
HPLC of S5



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.468	6659147	49.742
2	11.200	6728161	50.258

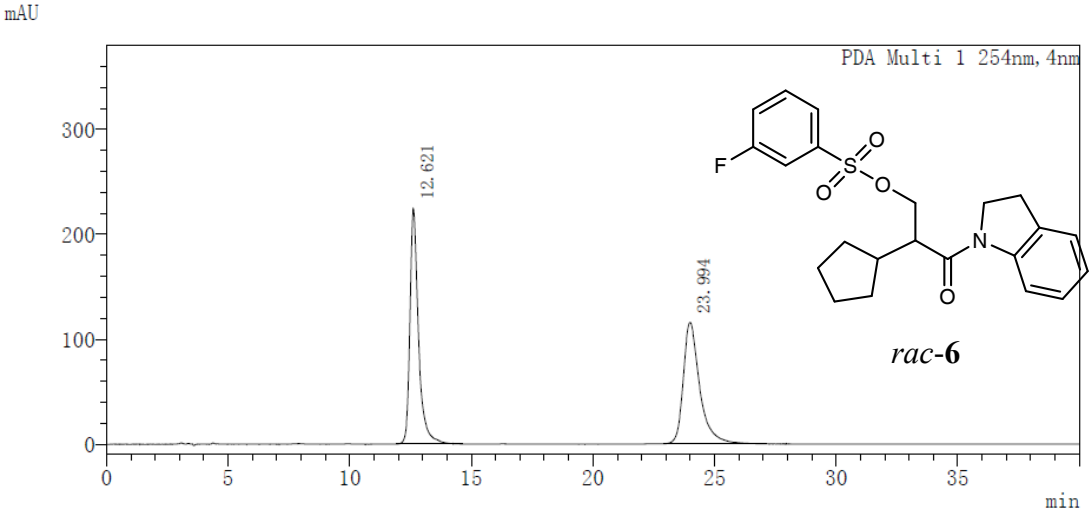


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.444	8297700	95.429
2	11.279	397452	4.571

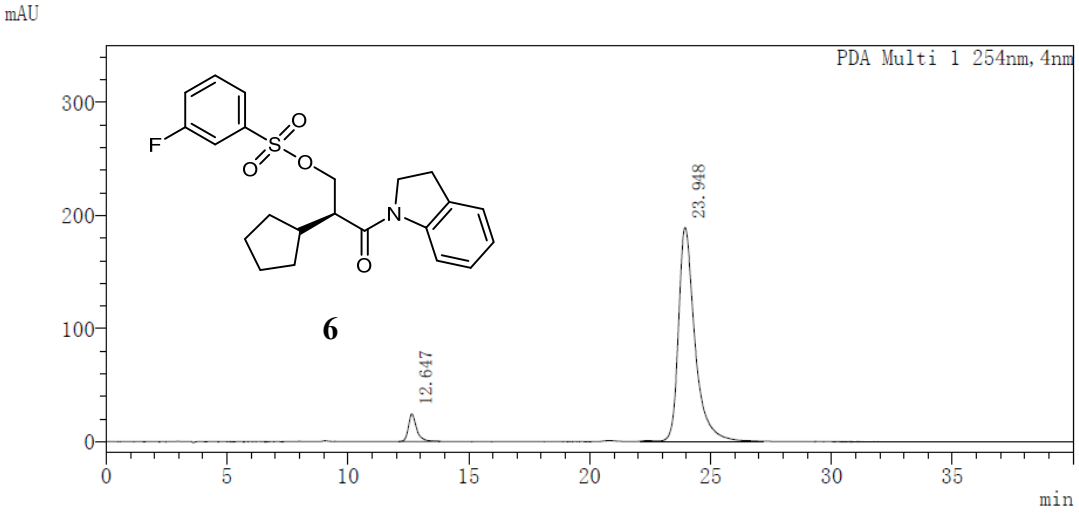
HPLC of 6



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.621	5522970	50.327
2	23.994	5451192	49.673

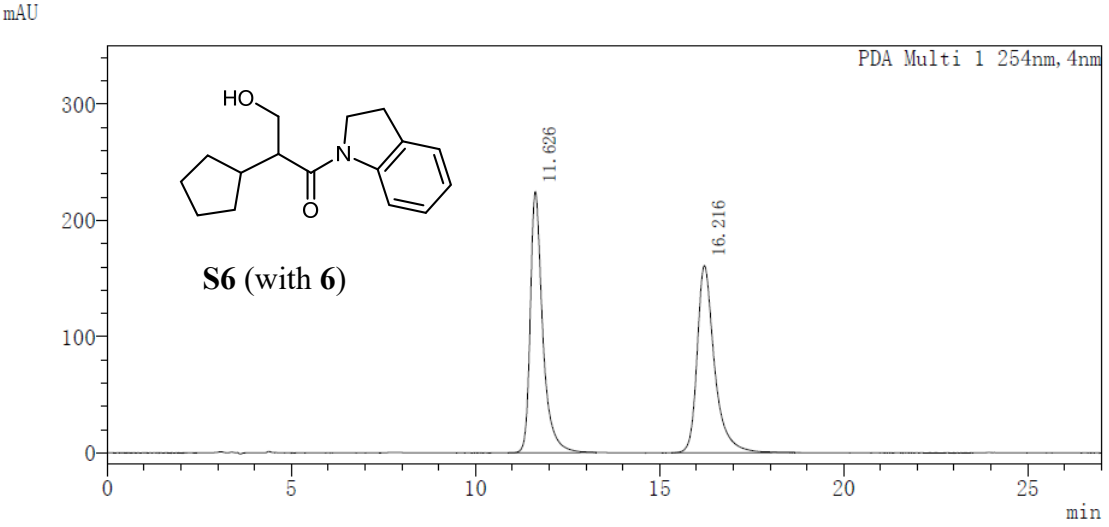


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.647	577577	6.069
2	23.948	8939275	93.931

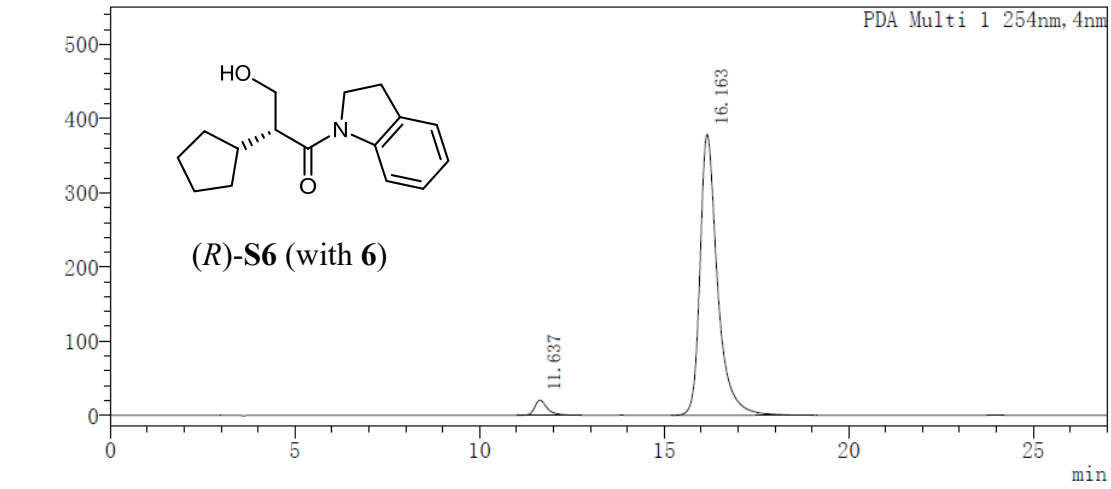
HPLC of S6



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.626	5290179	49.903
2	16.216	5310829	50.097

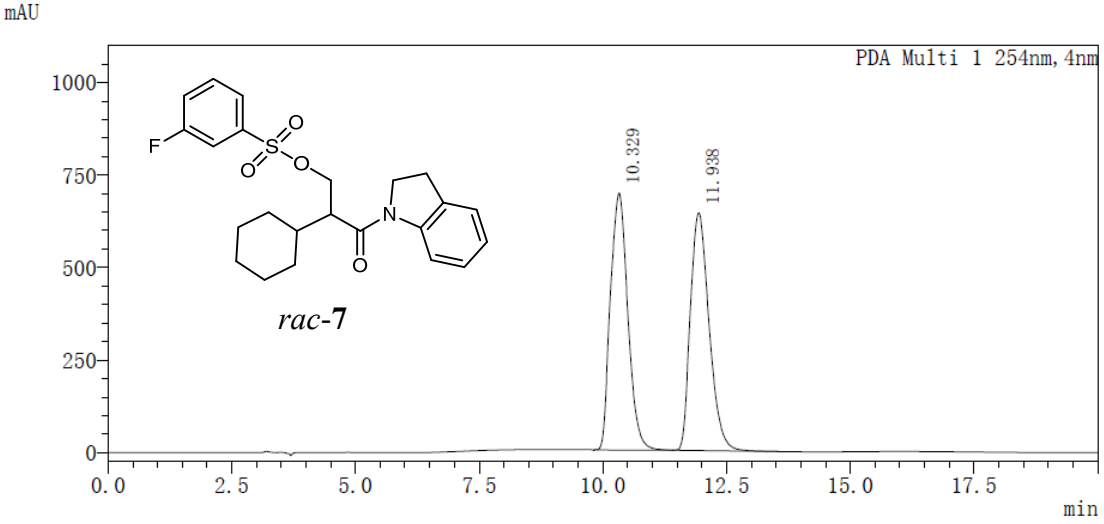


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.637	491547	3.787
2	16.163	12487638	96.213

HPLC of 7

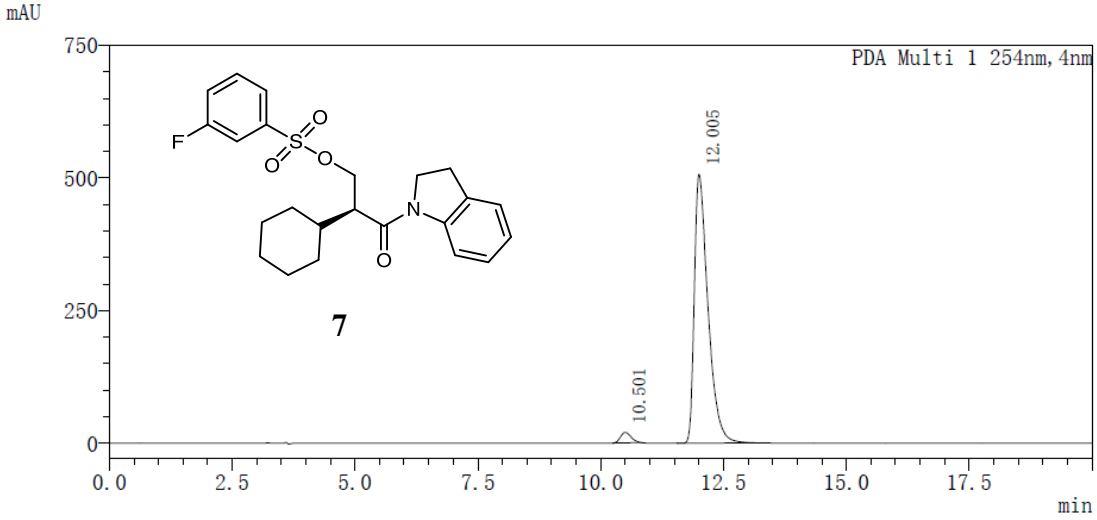


rac-7

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.329	16981465	50.015
2	11.938	16970953	49.985



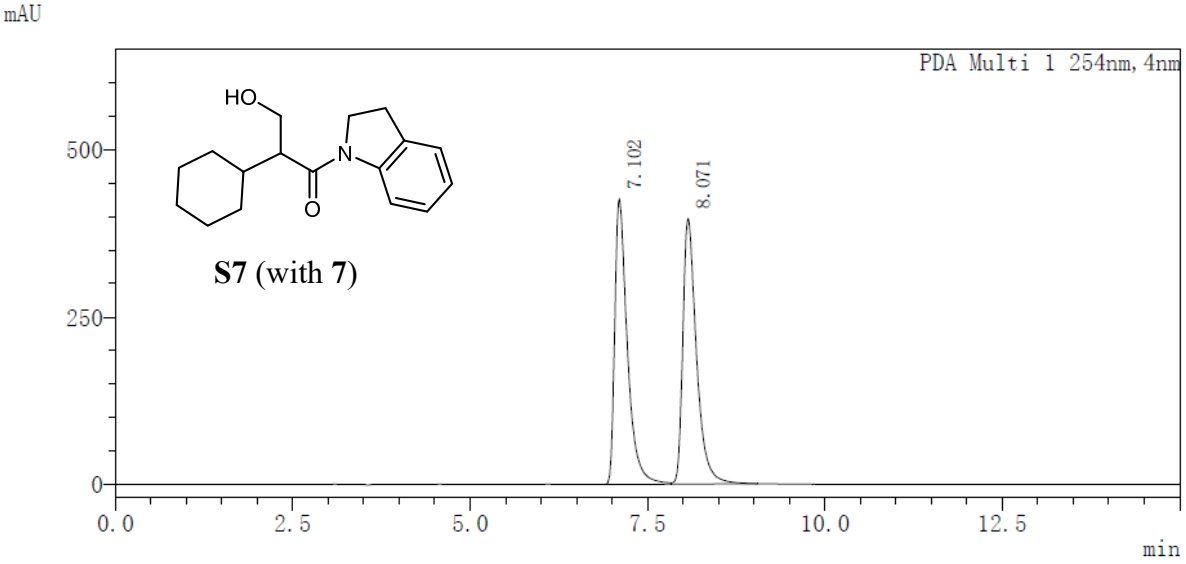
7

Peak Table

PDA Ch1 254nm

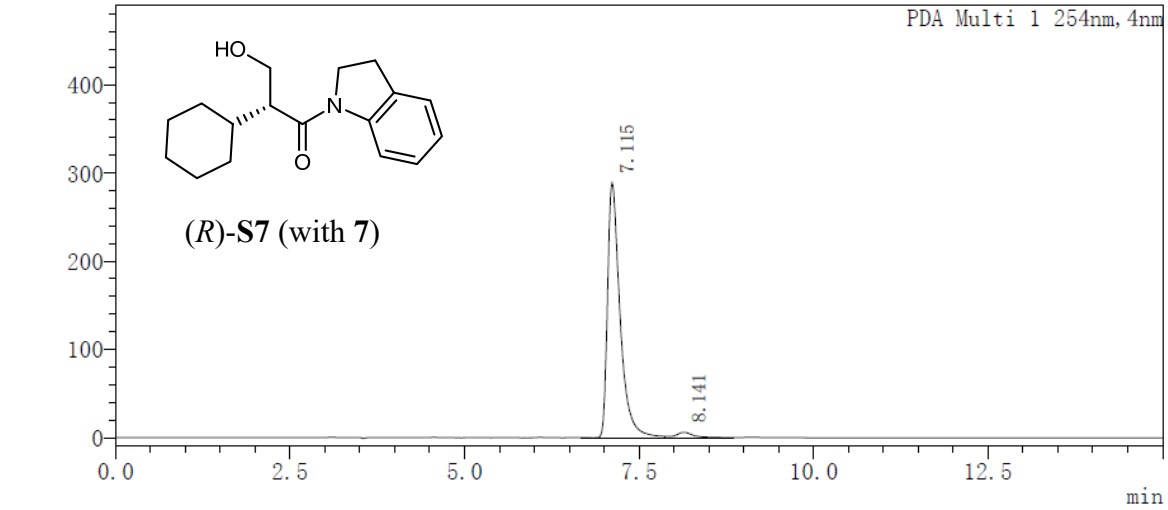
Peak#	Ret. Time	Area	Area%
1	10.501	301211	2.979
2	12.005	9811535	97.021

HPLC of S7



PDA Ch1 254nm

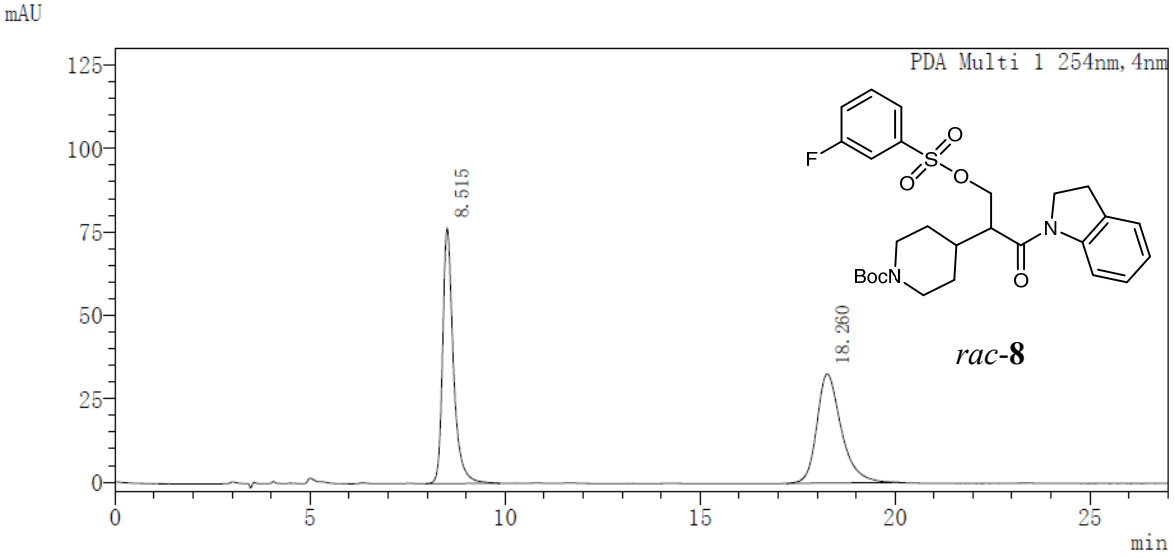
T	Hight	Area	Area%
7.102	425782	5283720	49.877
8.071	396127	5309707	50.123



PDA Ch1 254nm

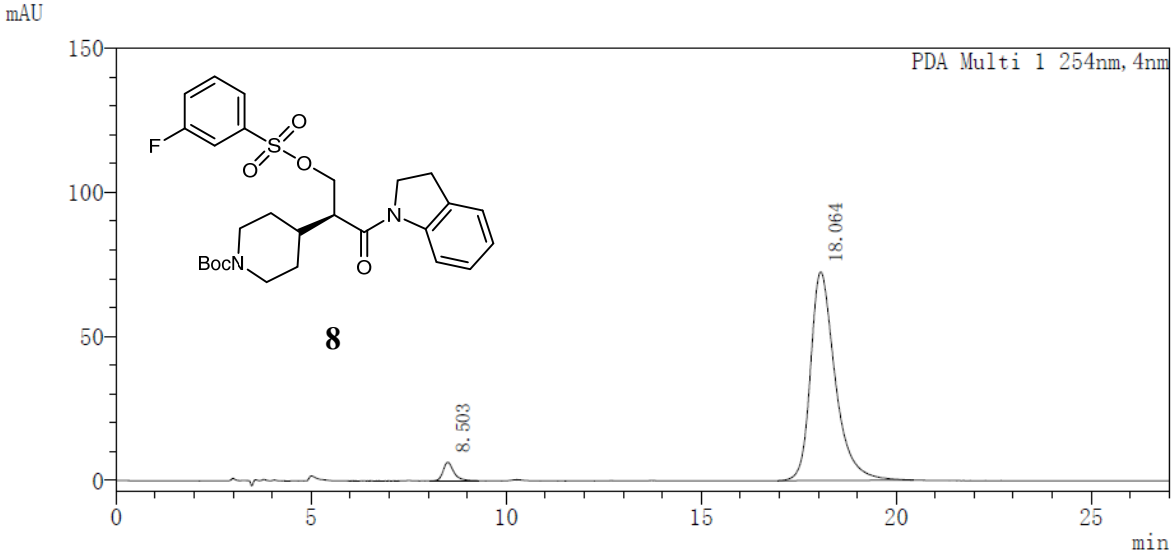
T	Hight	Area	Area%
7.115	288501	3611953	97.270
8.141	6044	101374	2.730

HPLC of 8



PDA Ch1 254nm

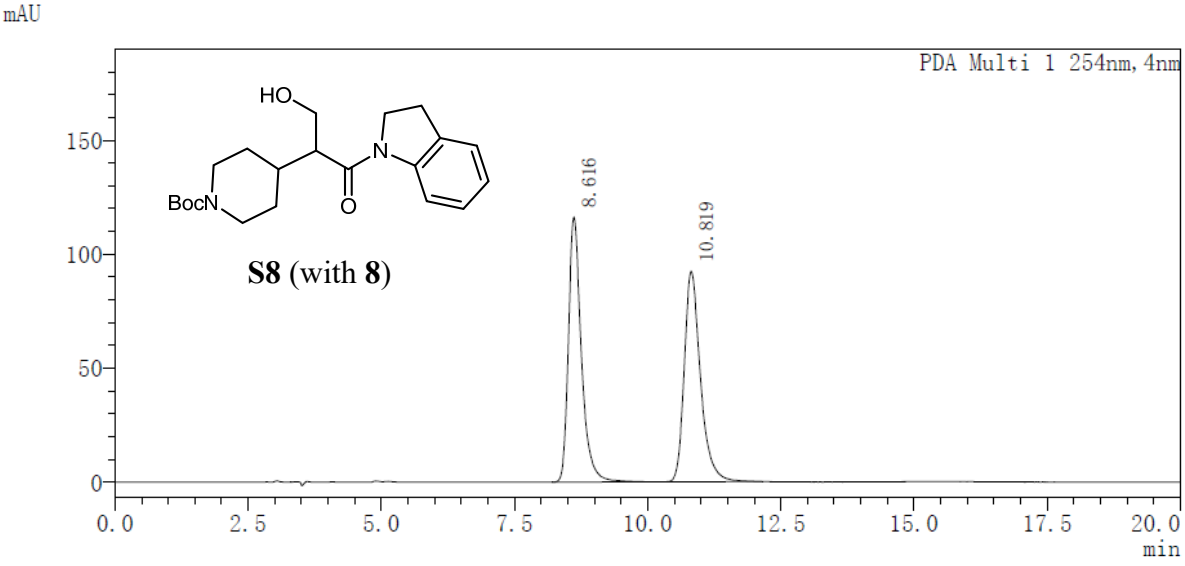
T	Hight	Area	Area%
8.515	76525	1462189	50.620
18.260	32685	1426396	49.380



PDA Ch1 254nm

T	Hight	Area	Area%
8.503	6439	121831	3.687
18.064	72385	3182252	96.313

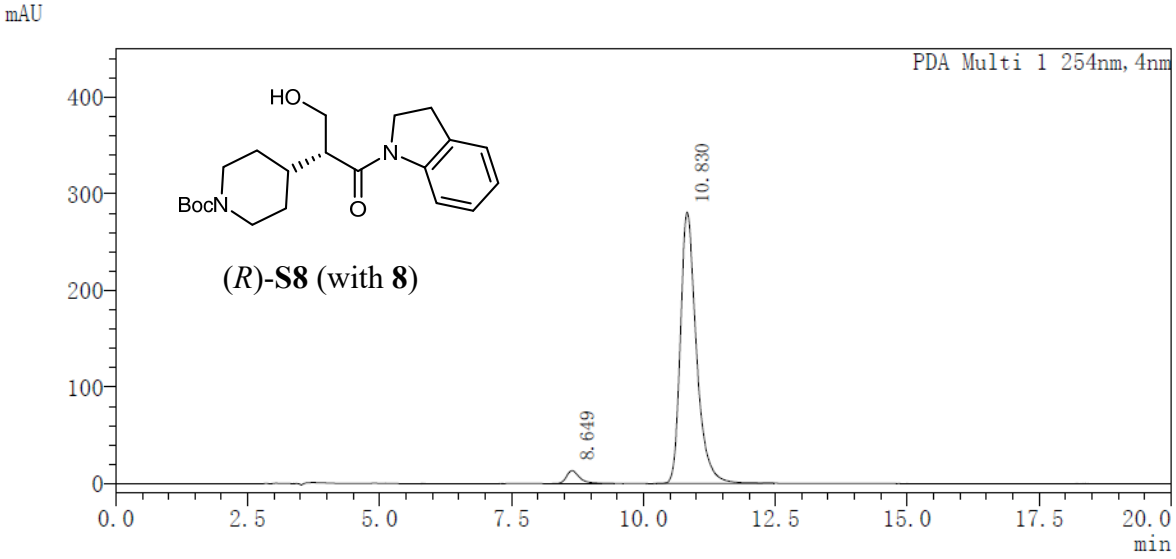
HPLC of S8



S8 (with **8**)

PDA Ch1 254nm

T	Hight	Area	Area%
8.616	116303	1965397	50.093
10.819	92315	1958114	49.907

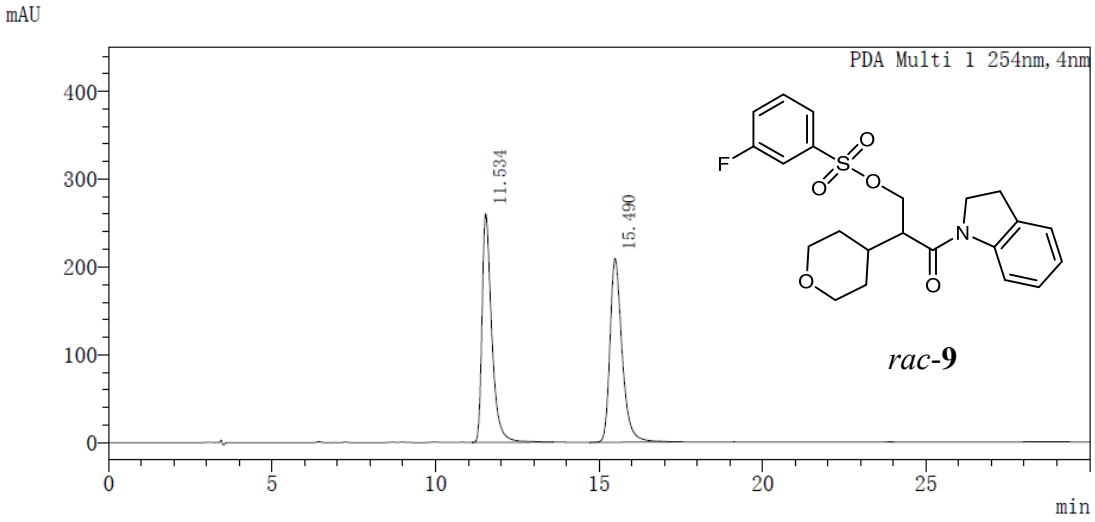


(*R*)-**S8** (with **8**)

PDA Ch1 254nm

T	Hight	Area	Area%
8.649	13428	236556	3.835
10.830	280599	5931335	96.165

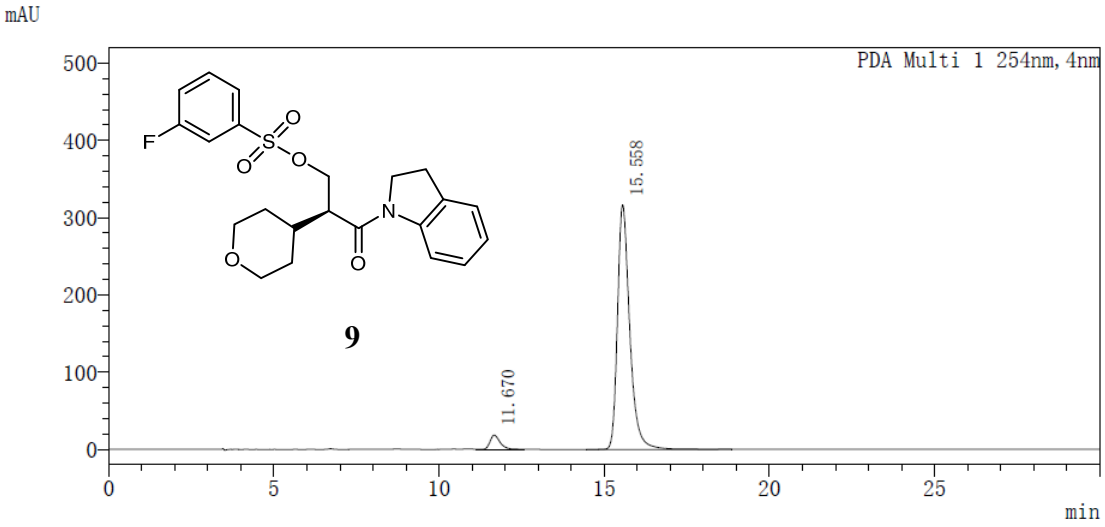
HPLC of 9



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.534	5389432	49.957
2	15.490	5398717	50.043

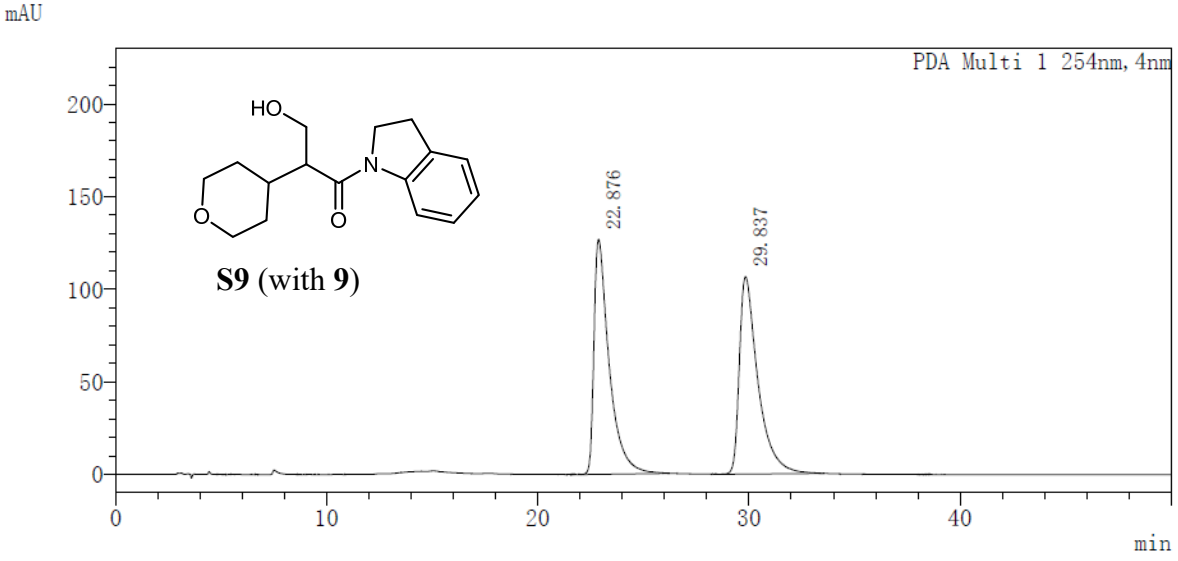


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.670	389678	4.545
2	15.558	8184879	95.455

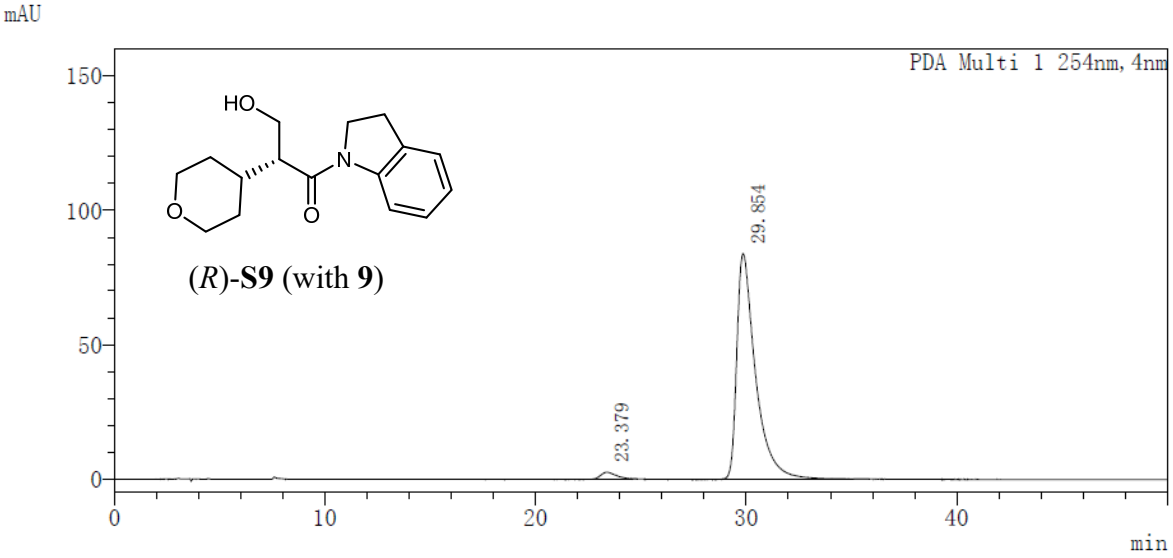
HPLC of S9



S9 (with **9**)

PDA Ch1 254nm

T	Hight	Area	Area%
22.876	126718	6348759	49.356
29.837	106567	6514449	50.644

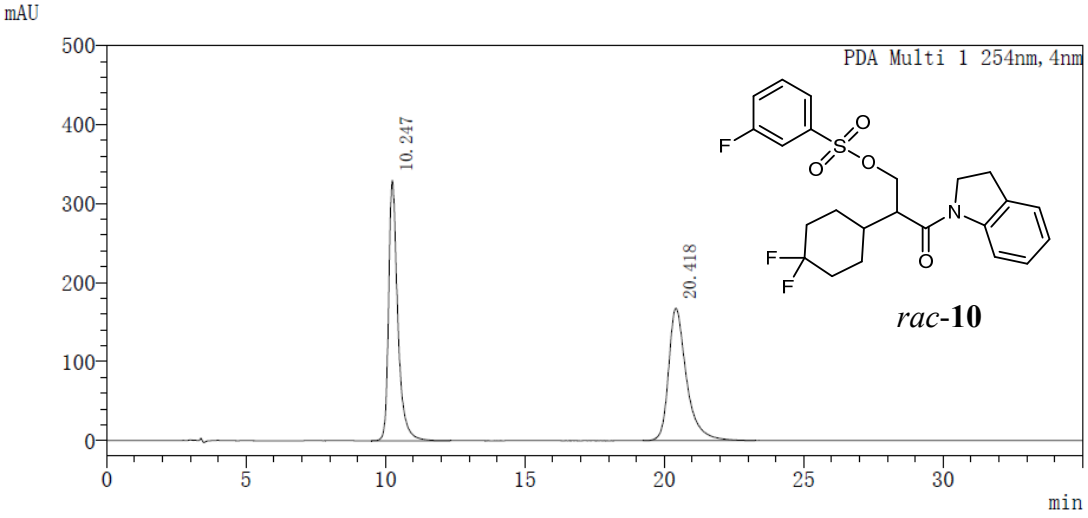


(*R*)-**S9** (with **9**)

PDA Ch1 254nm

T	Hight	Area	Area%
23.379	2593	134701	2.520
29.854	84002	5211320	97.480

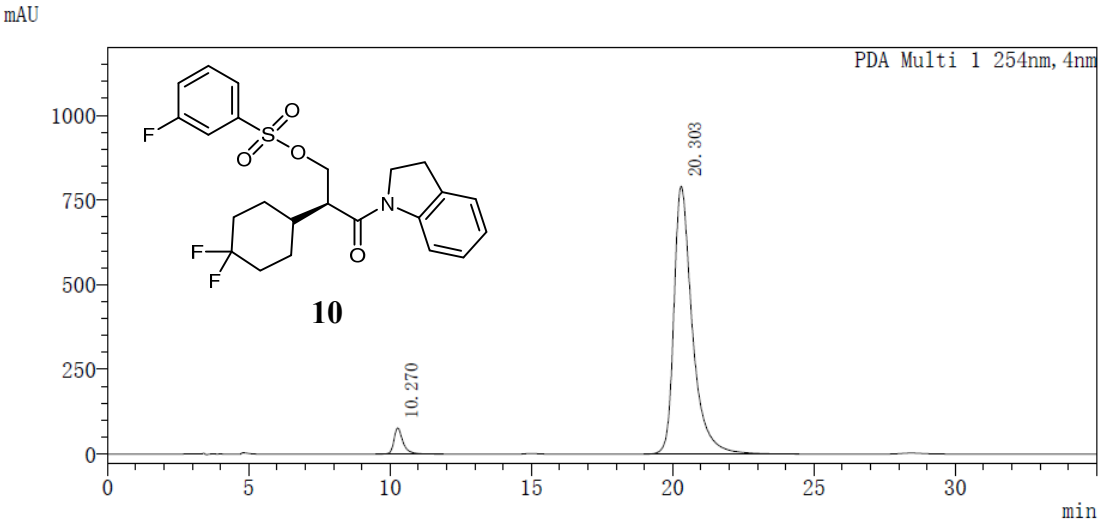
HPLC of 10



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.247	7563221	50.172
2	20.418	7511351	49.828

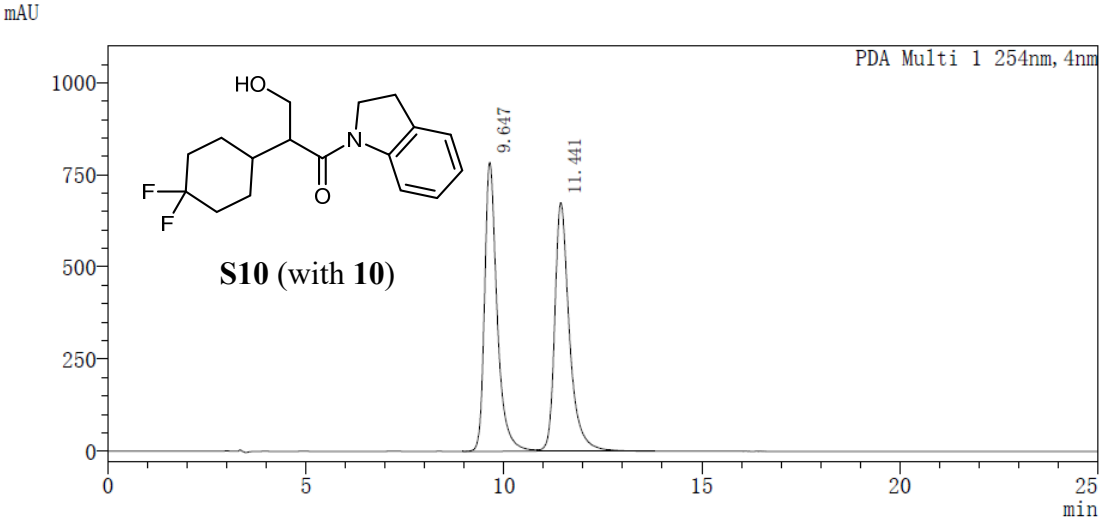


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.270	1729383	4.598
2	20.303	35880644	95.402

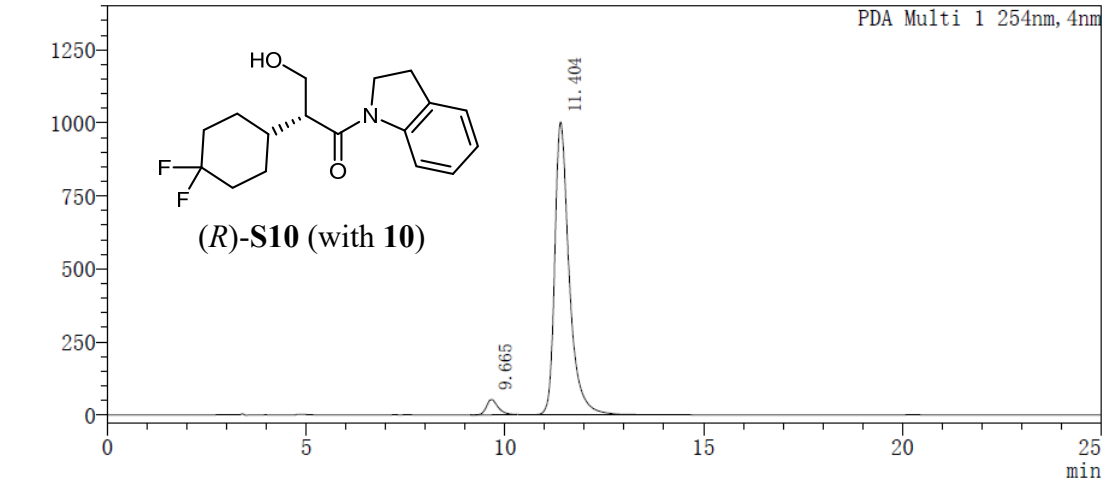
HPLC of S10



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.647	17330789	49.852
2	11.441	17433433	50.148

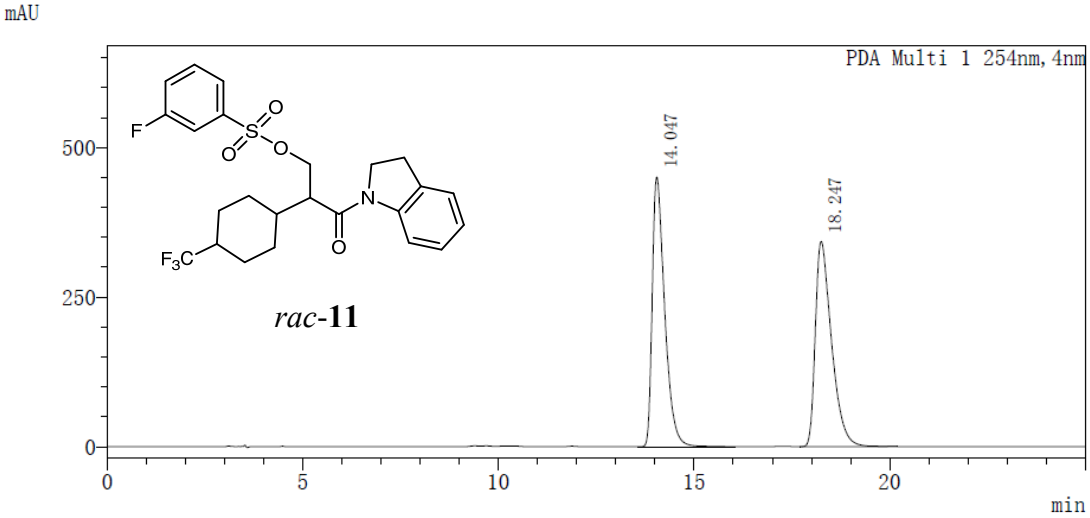


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.665	1067364	4.038
2	11.404	25367501	95.962

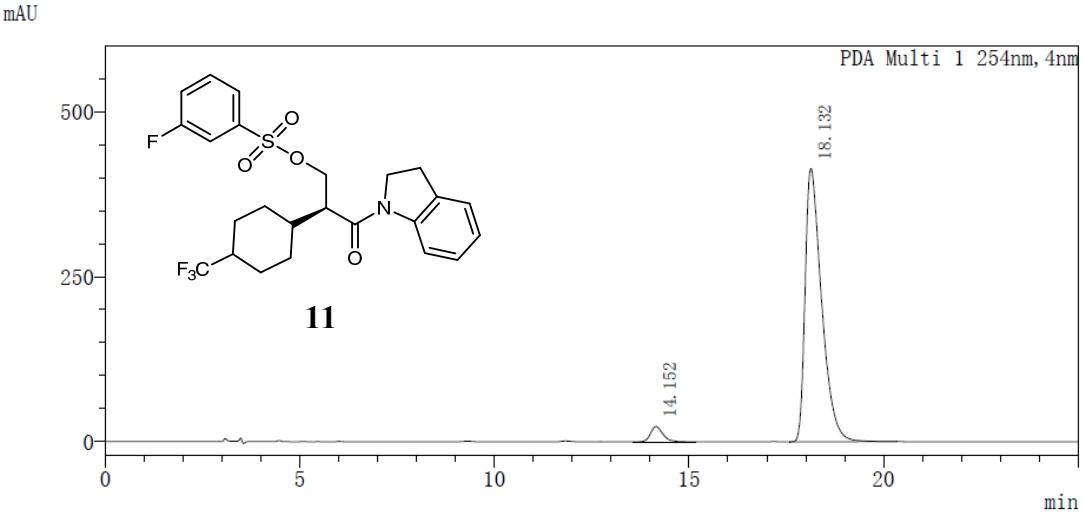
HPLC of 11



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.047	9980967	50.164
2	18.247	9915849	49.836

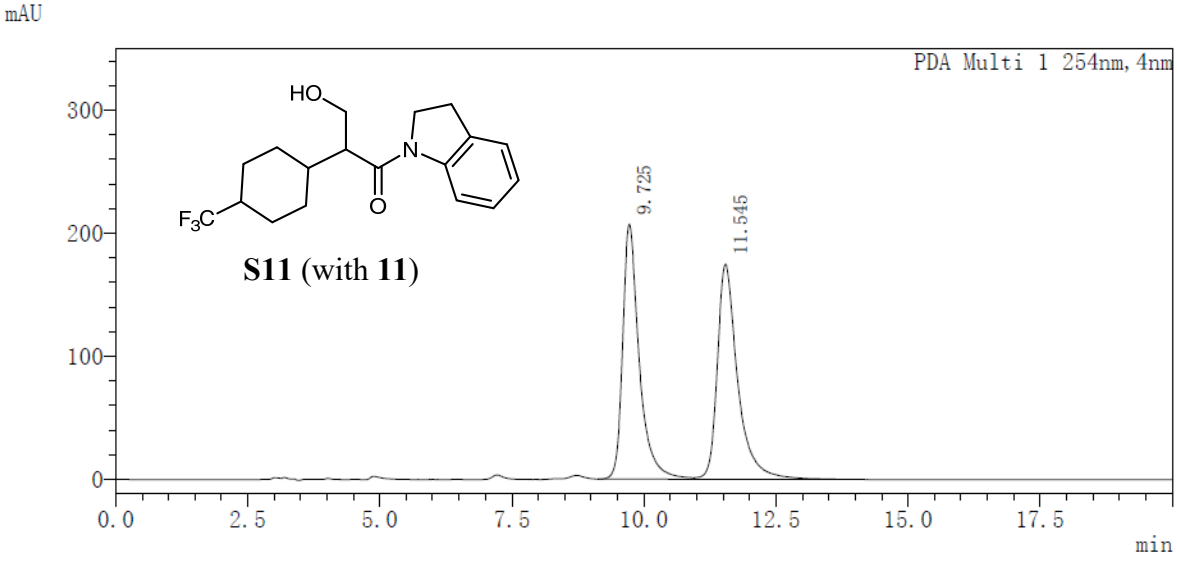


Peak Table

PDA Ch1 254nm

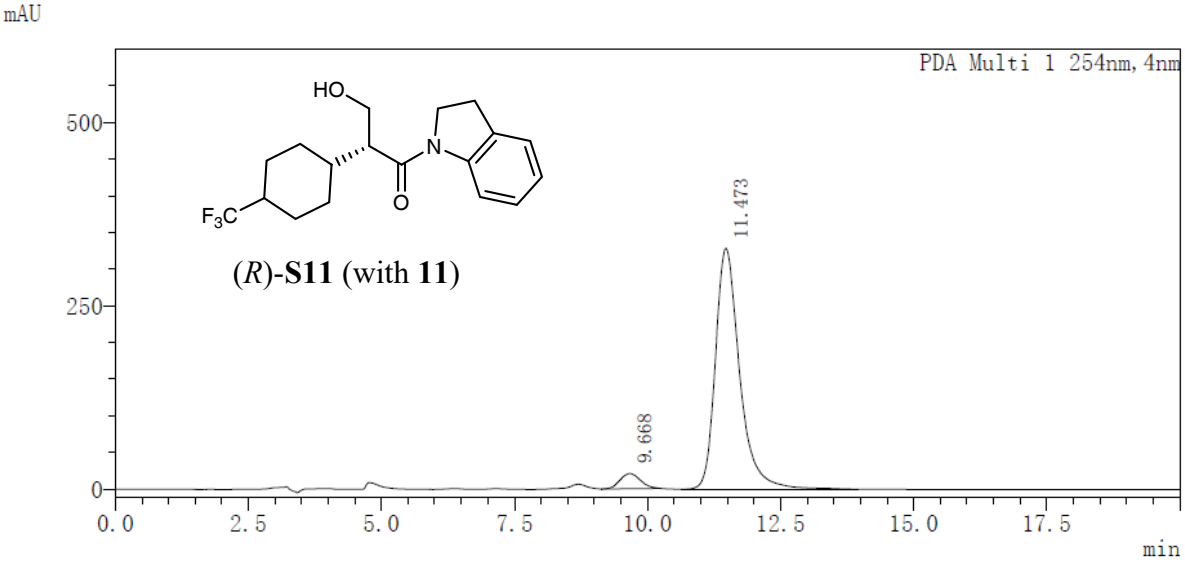
Peak#	Ret. Time	Area	Area%
1	14.152	514228	4.027
2	18.132	12254461	95.973

HPLC of S11



PDA Ch1 254nm

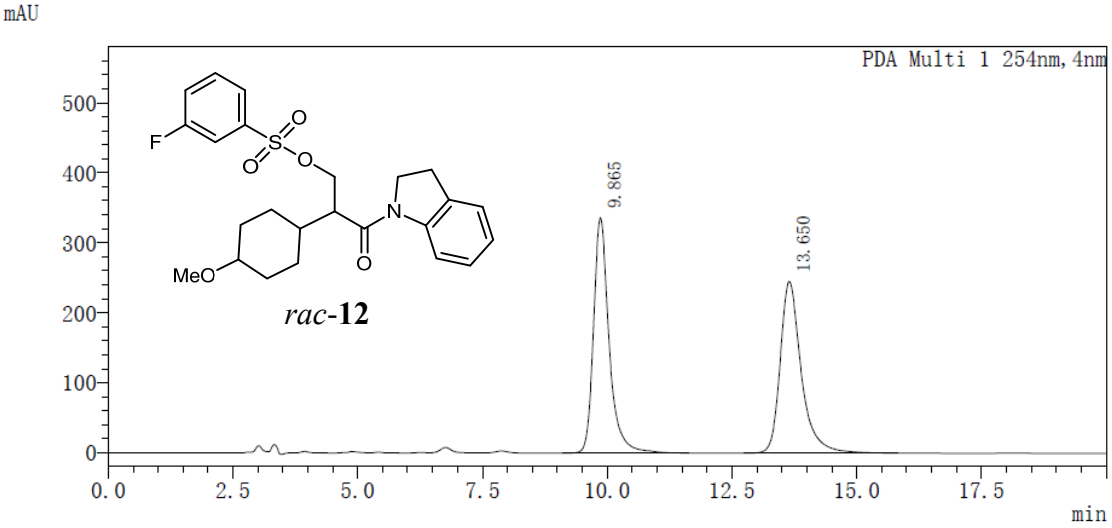
T	Hight	Area	Area%
9.725	207037	4519364	49.057
11.545	174804	4693056	50.943



PDA Ch1 254nm

T	Hight	Area	Area%
9.668	20534	551133	5.023
11.473	328369	10421021	94.977

HPLC of 12

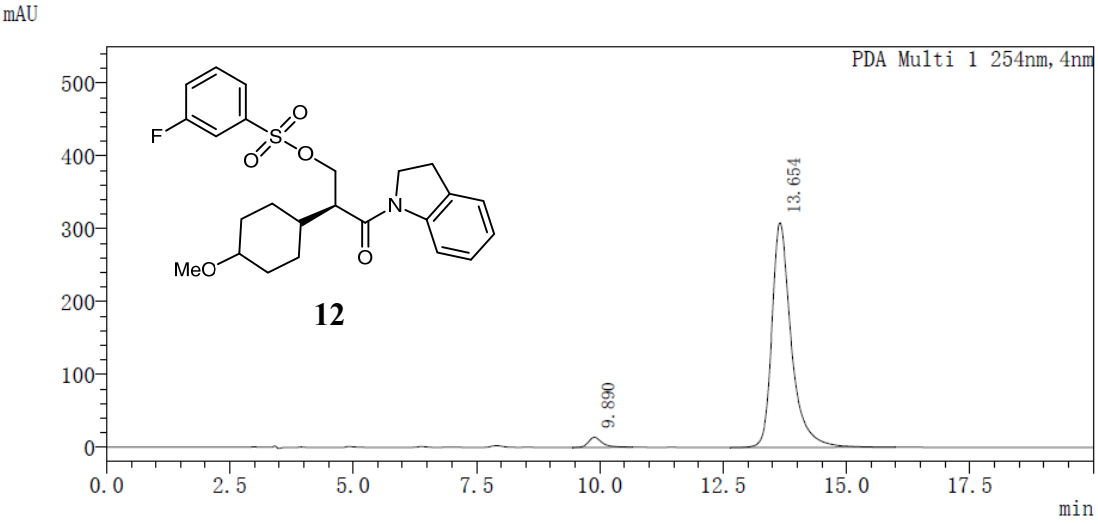


rac-**12**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.865	7301811	50.315
2	13.650	7210274	49.685



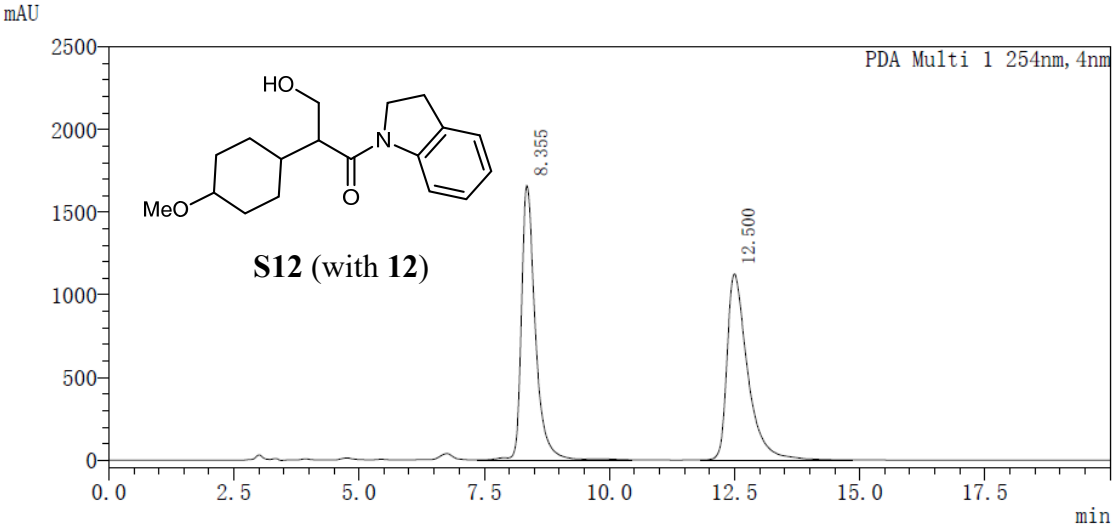
12

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.890	264616	3.033
2	13.654	8460574	96.967

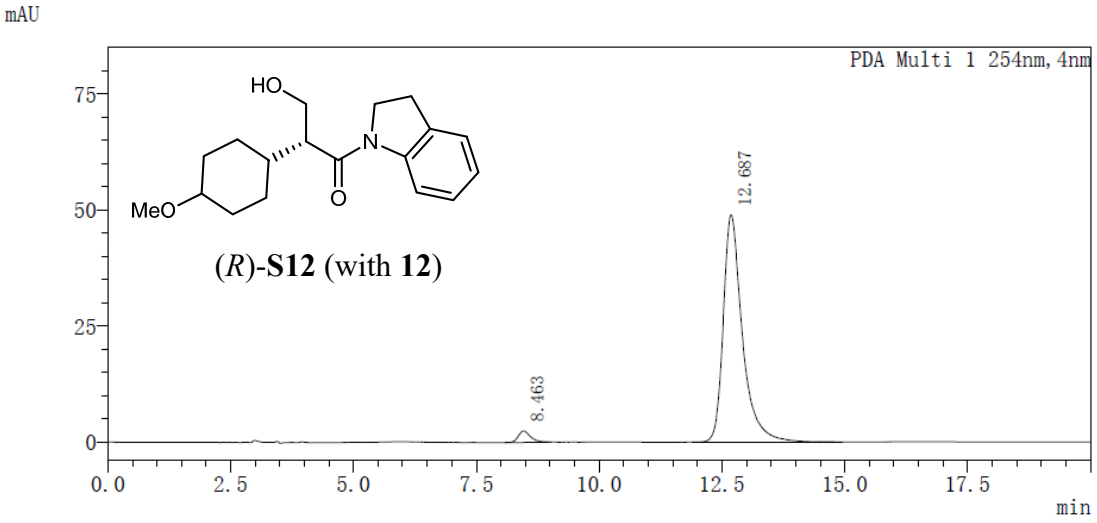
HPLC of S12



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.355	31983413	49.702
2	12.500	32367334	50.298

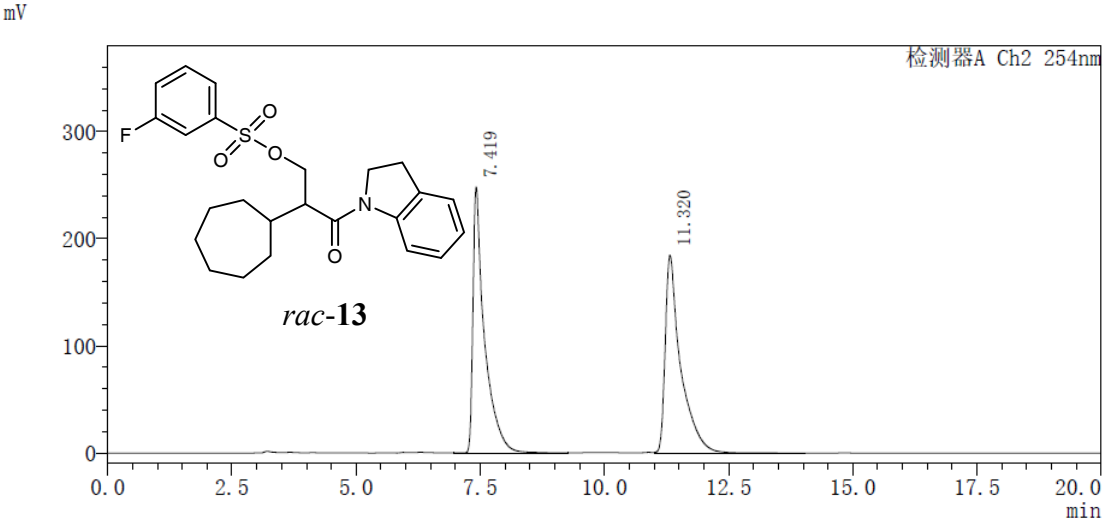


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.463	42253	3.072
2	12.687	1333061	96.928

HPLC of 13

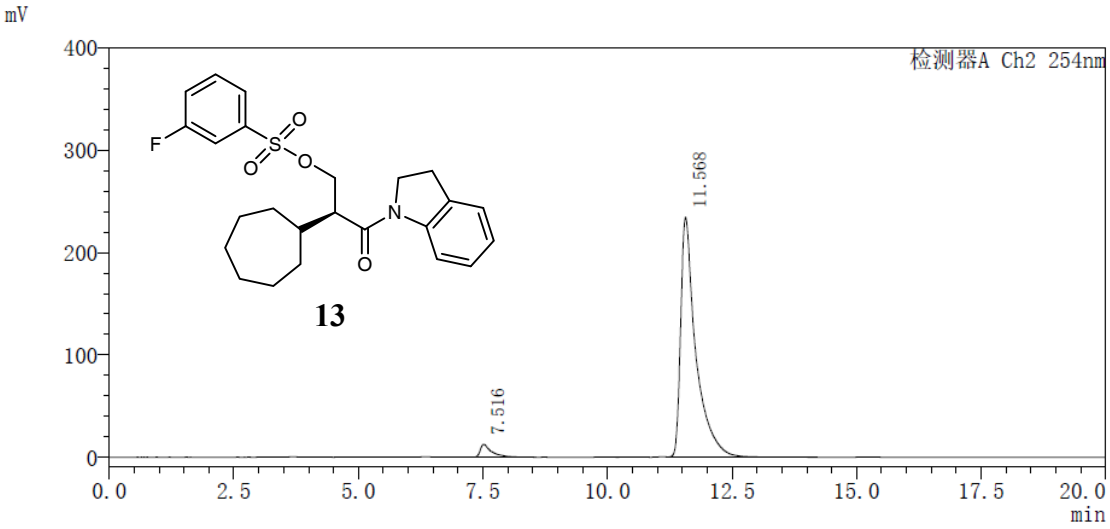


rac-**13**

Peak Table

检测器A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	7.419	4032361	50.205
2	11.320	3999353	49.795



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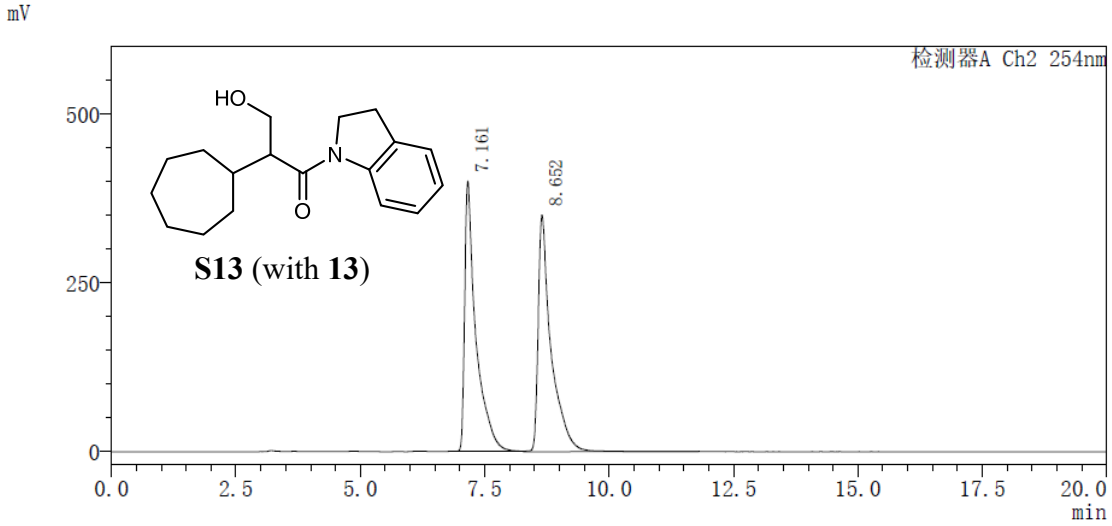
Peak Table

检测器A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	7.516	200717	3.887
2	11.568	4963557	96.113

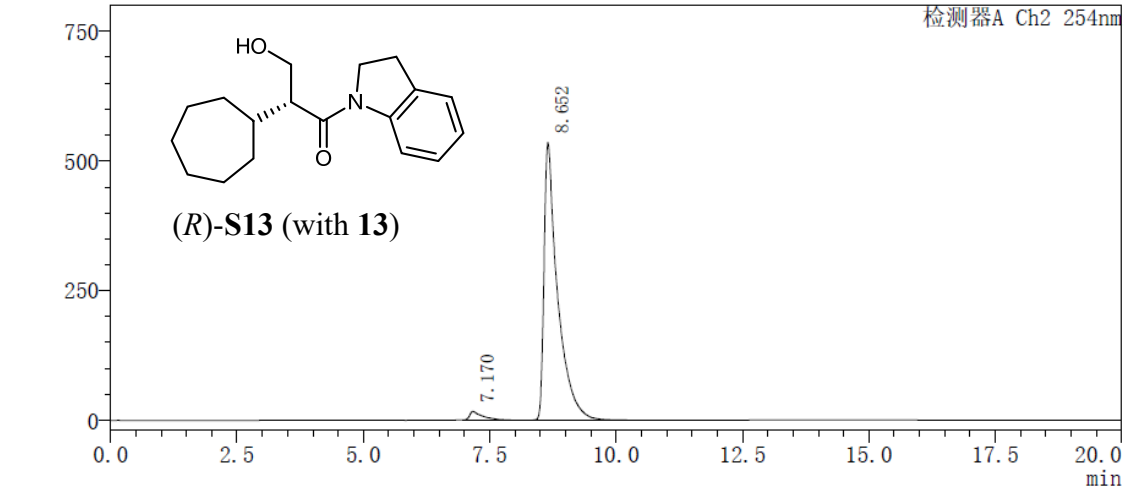
HPLC of S13



Peak Table

检测器A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	7.161	6289302	49.841
2	8.652	6329551	50.159

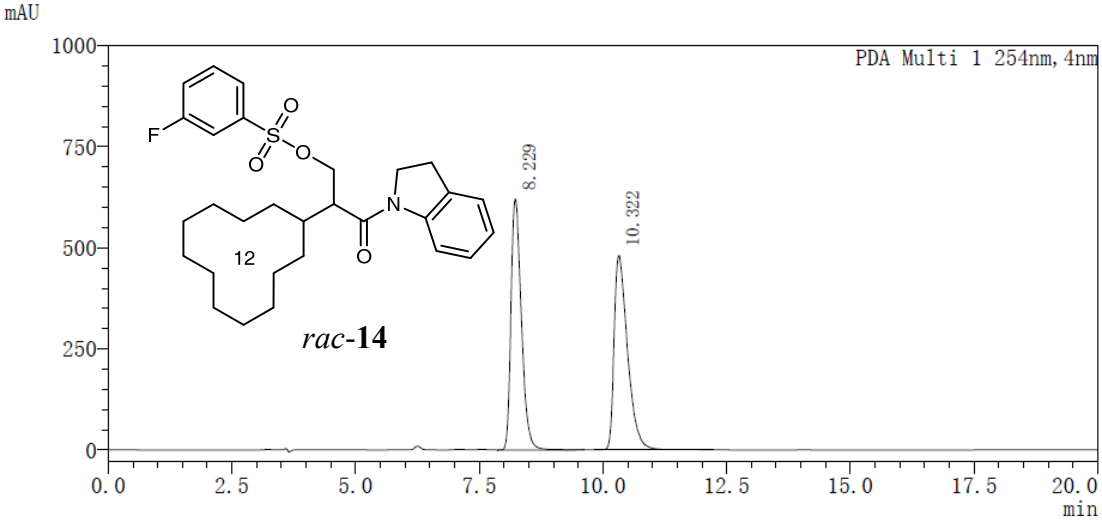


Peak Table

检测器A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	7.170	310467	3.009
2	8.652	10008232	96.991

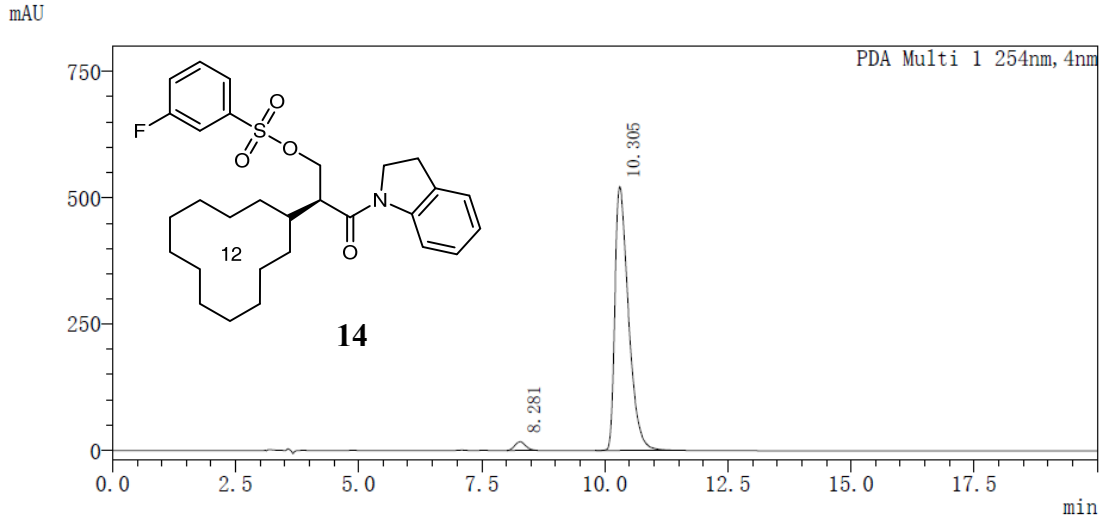
HPLC of 14



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.229	9087067	49.920
2	10.322	9116334	50.080

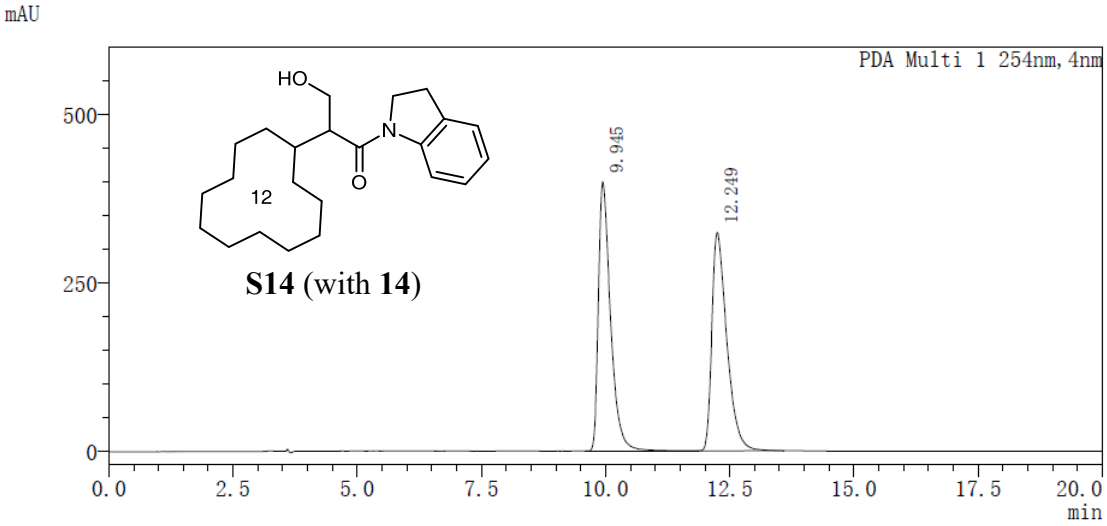


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.281	260884	2.526
2	10.305	10065730	97.474

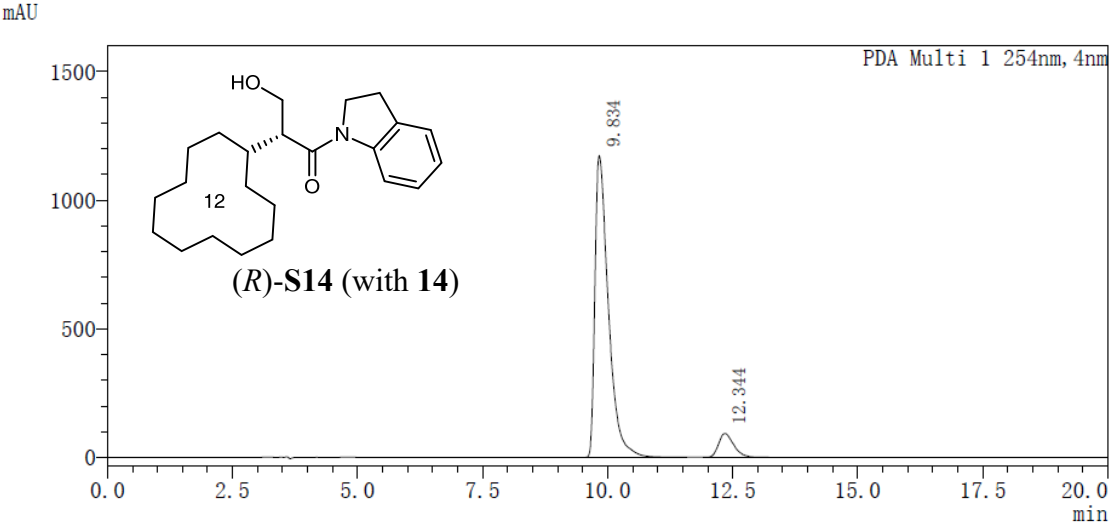
HPLC of S14



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.945	6809951	50.149
2	12.249	6769366	49.851

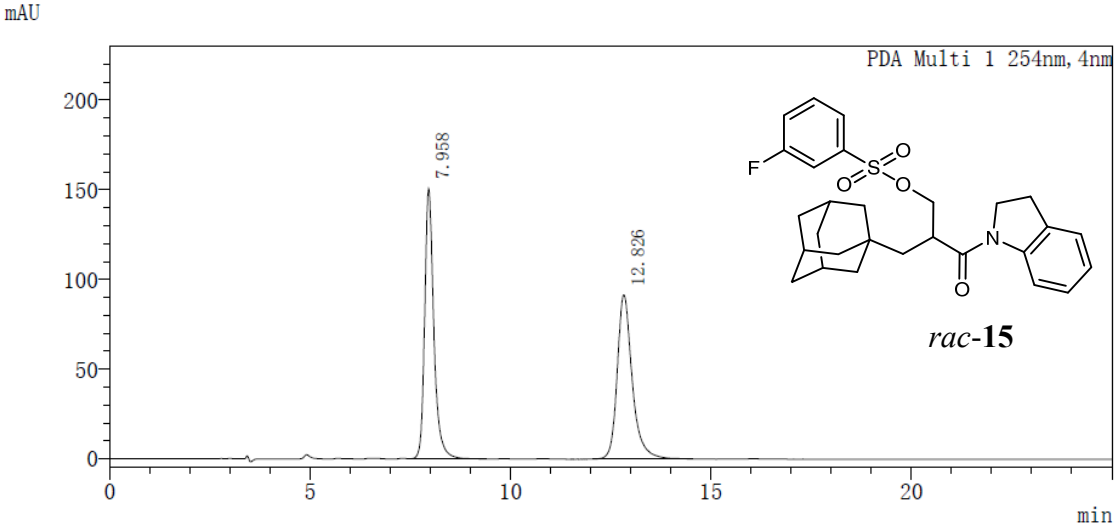


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.834	22114326	91.653
2	12.344	2013984	8.347

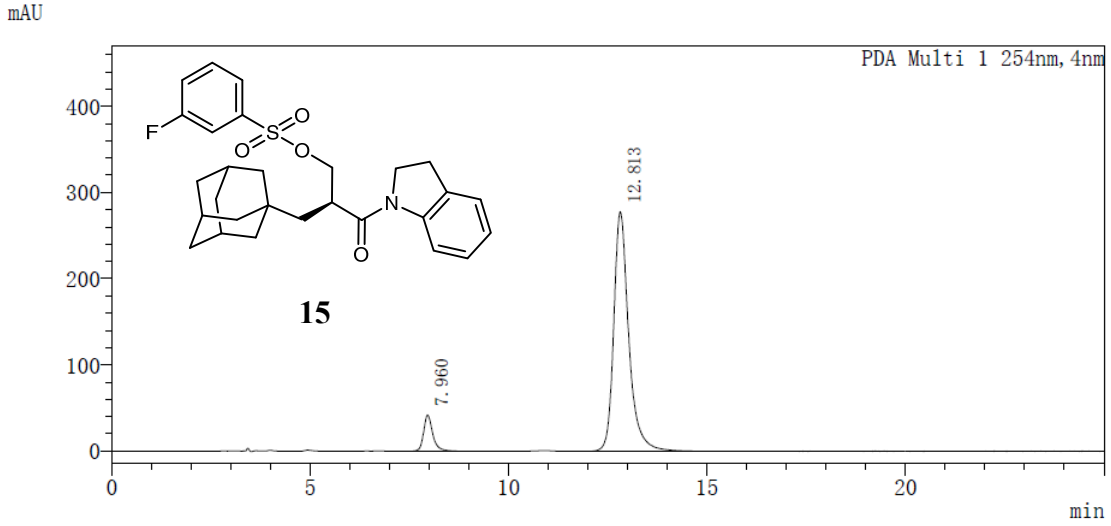
HPLC of 15



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.958	2413117	50.182
2	12.826	2395647	49.818

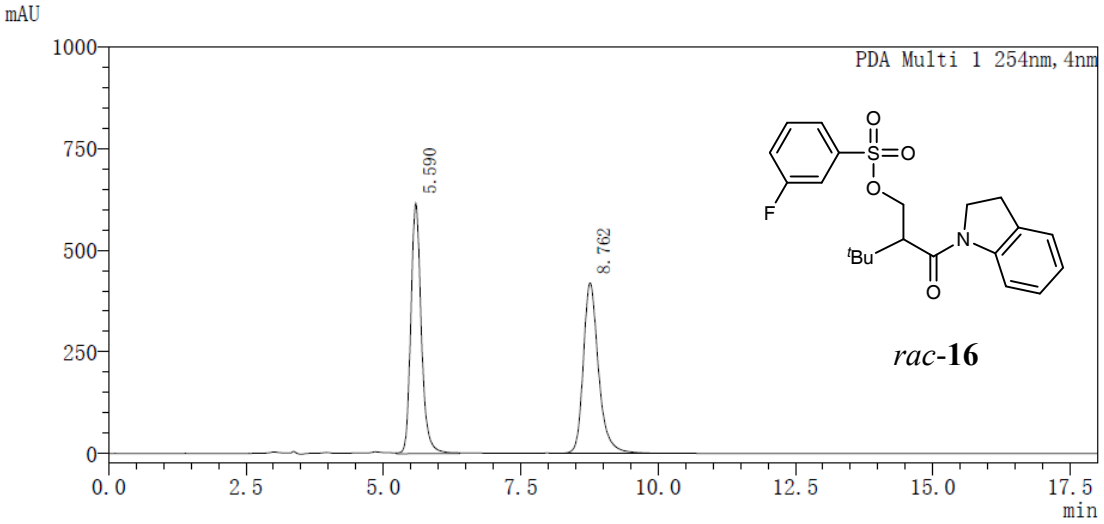


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.960	673309	8.446
2	12.813	7298883	91.554

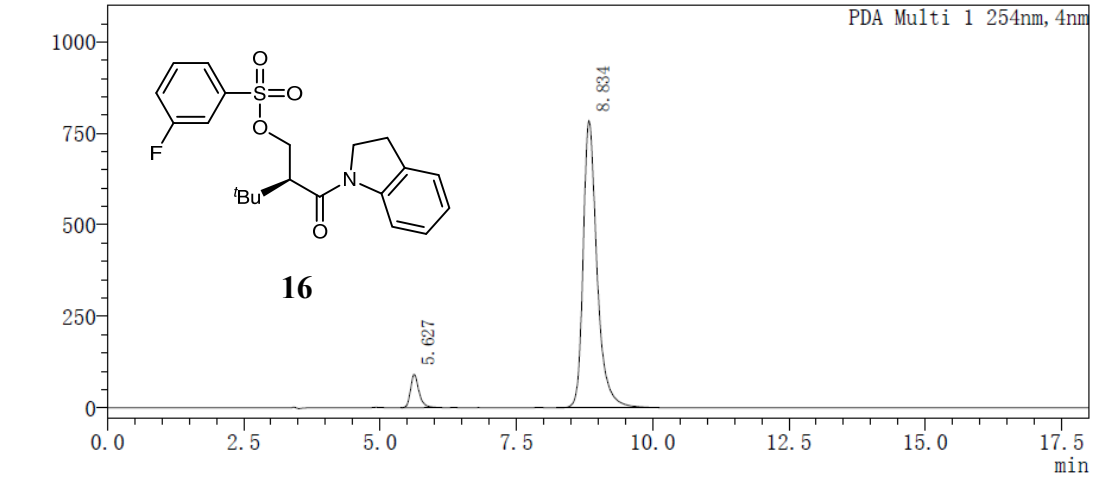
HPLC of 16



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.590	8185111	50.357
2	8.762	8069090	49.643

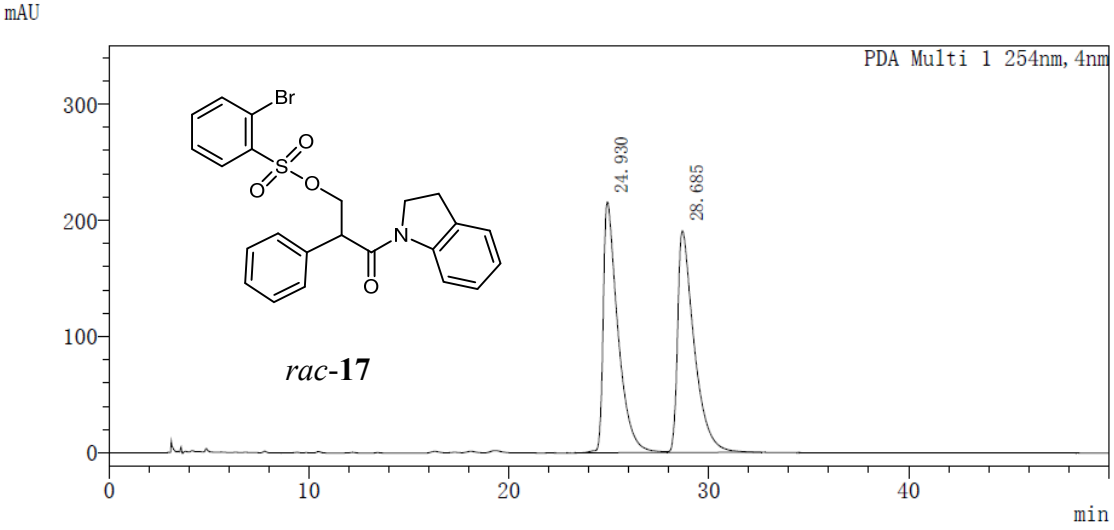


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.627	981797	6.570
2	8.834	13960972	93.430

HPLC of 17



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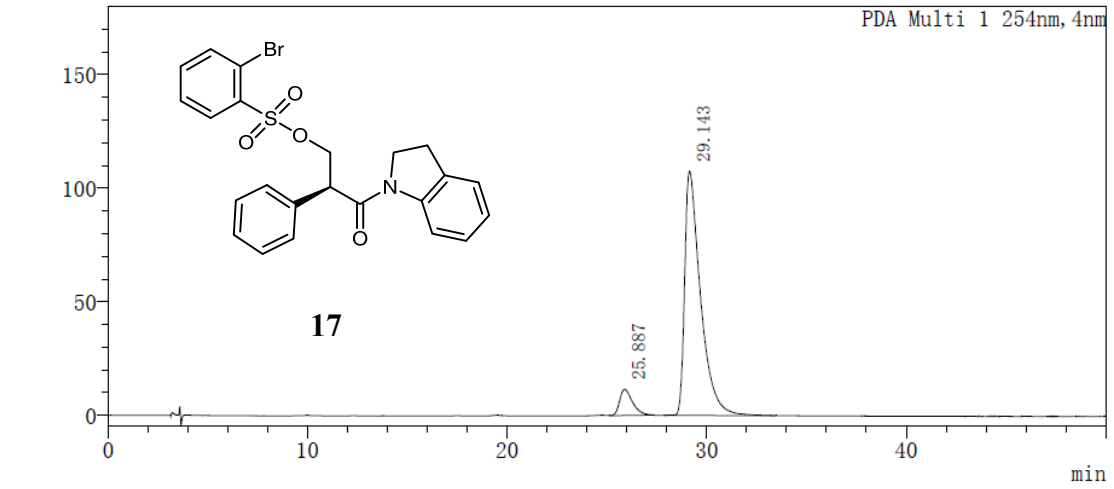
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.930	11011774	50.144
2	28.685	10948656	49.856



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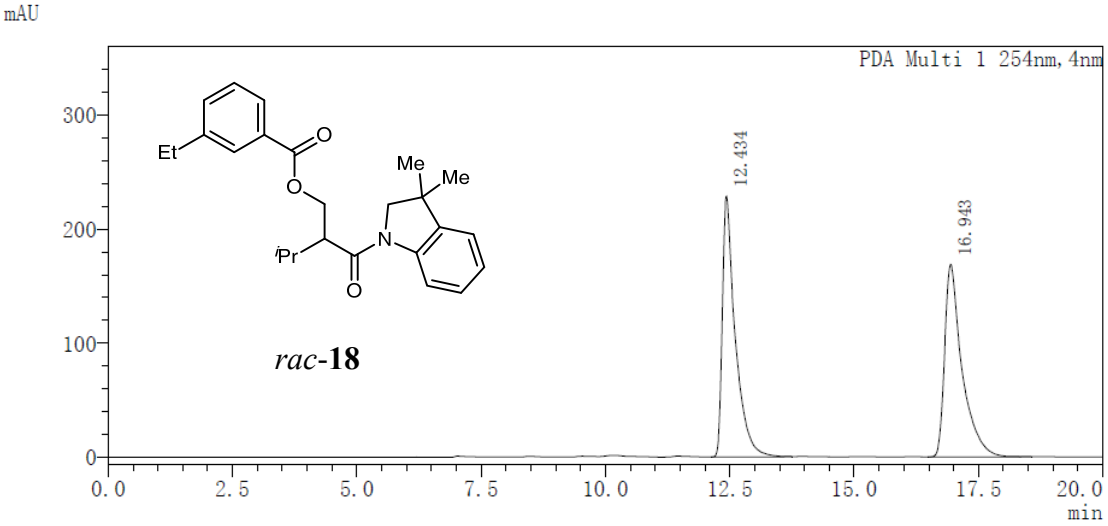
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.887	513001	7.932
2	29.143	5954588	92.068

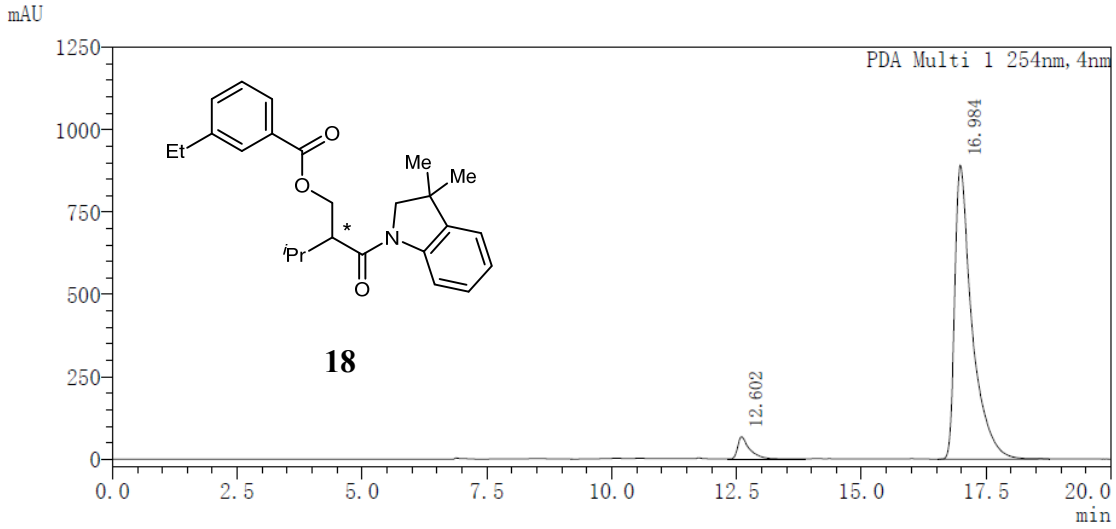
HPLC of 18



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.434	4124909	50.106
2	16.943	4107468	49.894

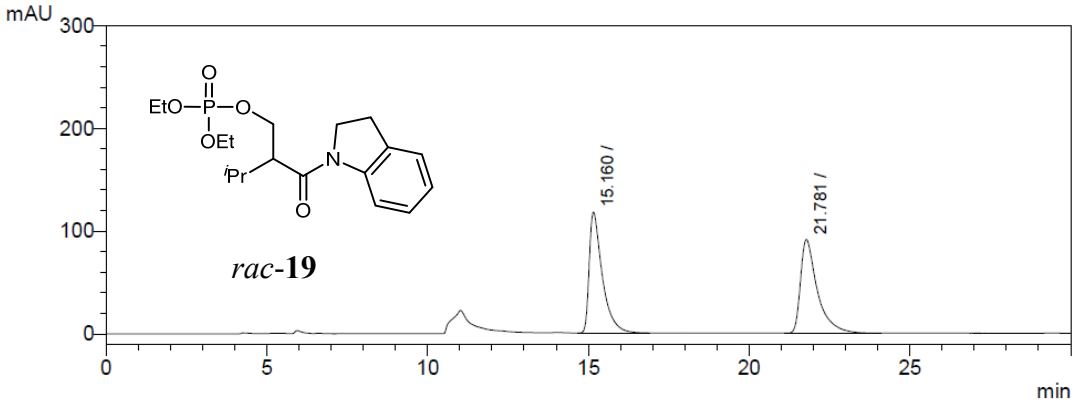


Peak Table

PDA Ch1 254nm

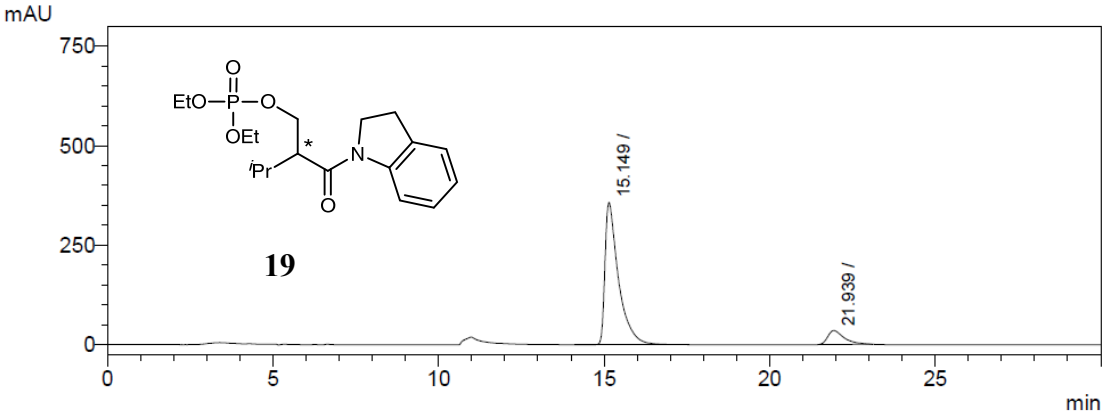
Peak#	Ret. Time	Area	Area%
1	12.602	1129825	5.006
2	16.984	21441578	94.994

HPLC of 19



PDA Ch1 254nm

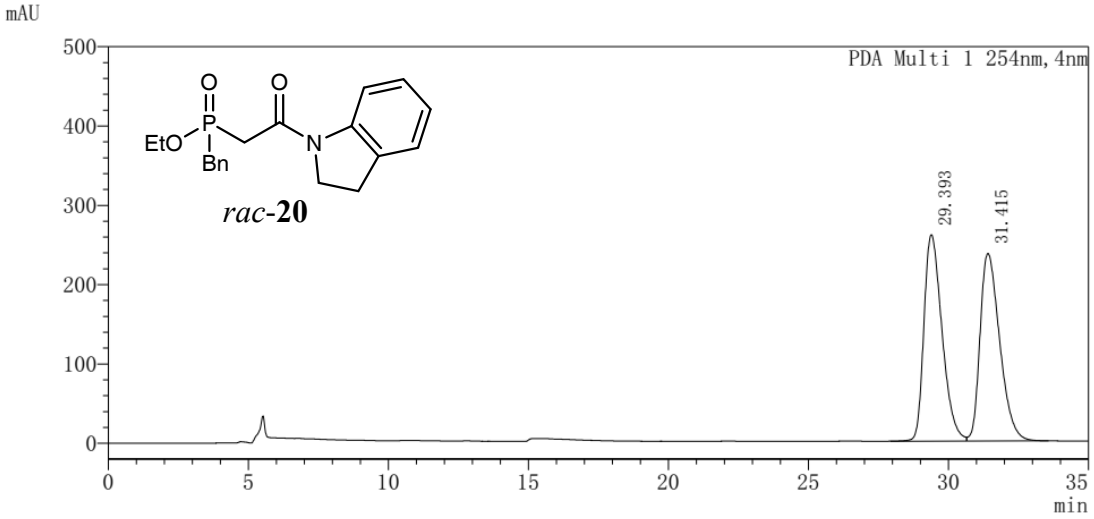
Peak#	Ret. Time	Area	Area%
1	15.160	3314619	49.950
2	21.781	3321271	50.050



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.149	10157516	89.553
2	21.939	1185004	10.447

HPLC of 20

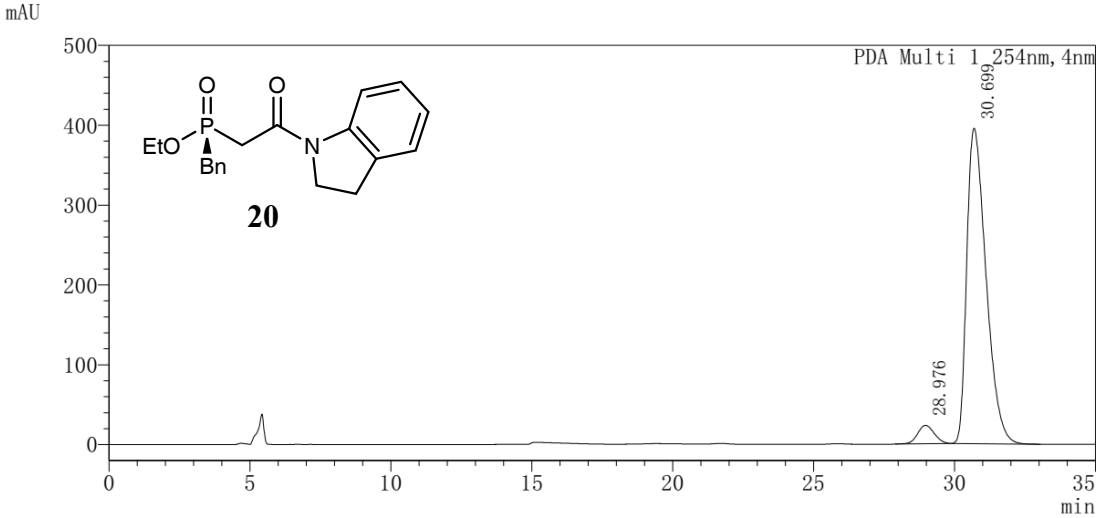


rac-**20**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	29.393	11721510	50.342
2	31.415	11562222	49.658



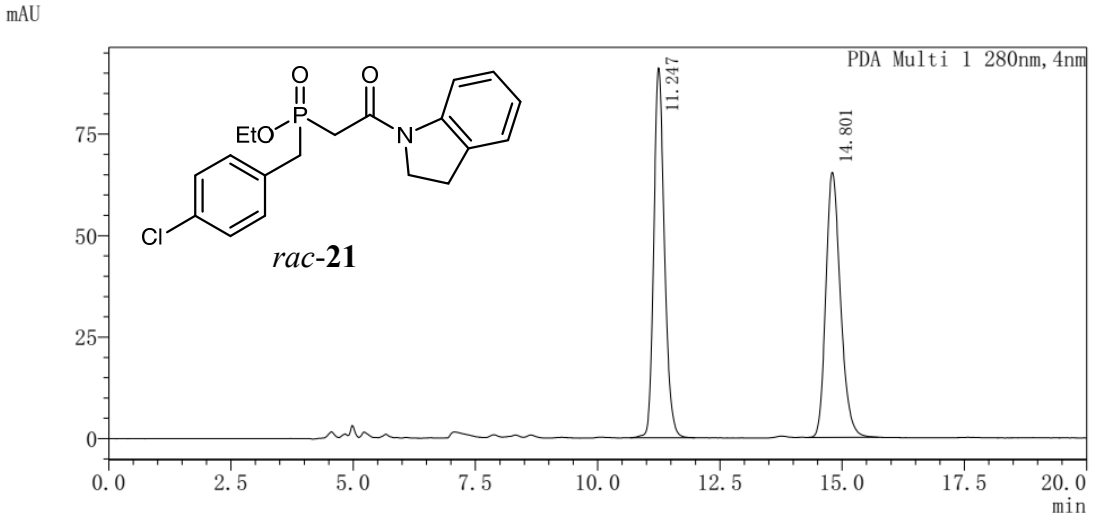
20

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.976	943662	4.780
2	30.699	18798592	95.220

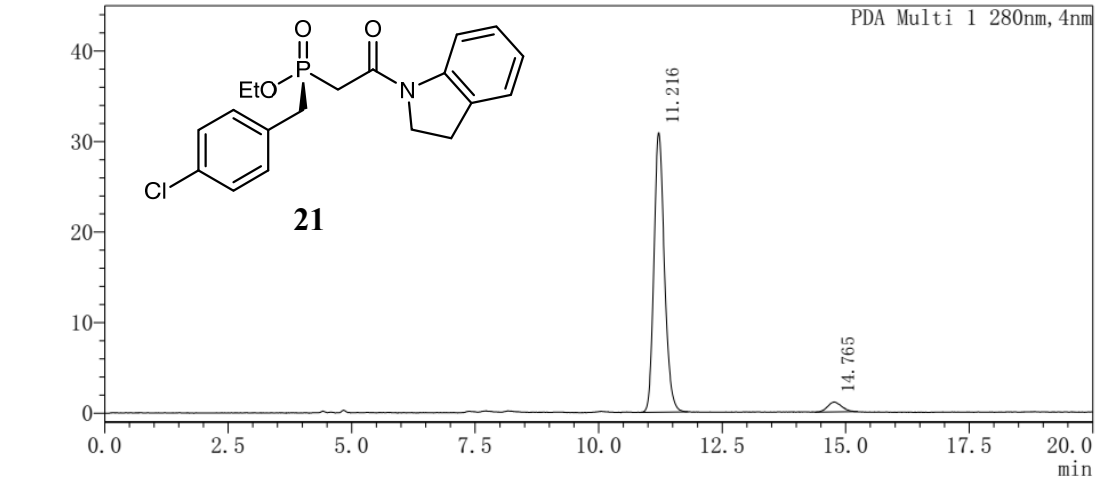
HPLC of 21



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	11.247	1382257	50.341
2	14.801	1363521	49.659

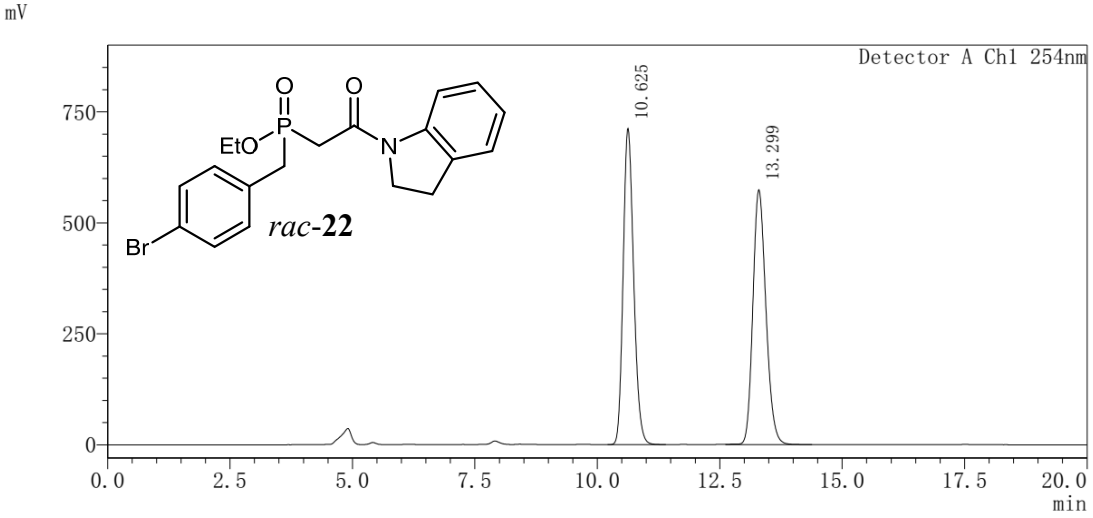


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	11.216	457080	95.475
2	14.765	21665	4.525

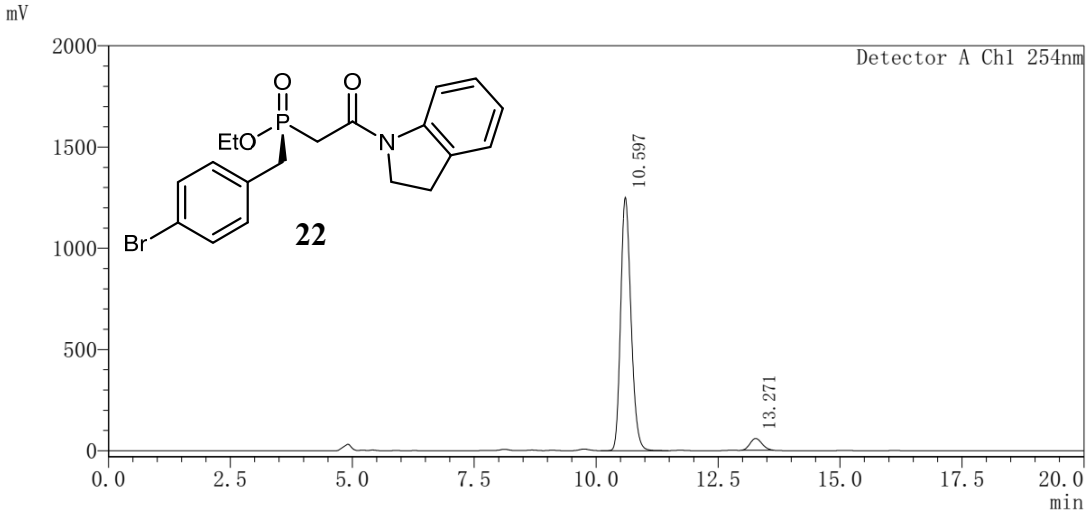
HPLC of 22



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.625	10660470	49.975
2	13.299	10671240	50.025

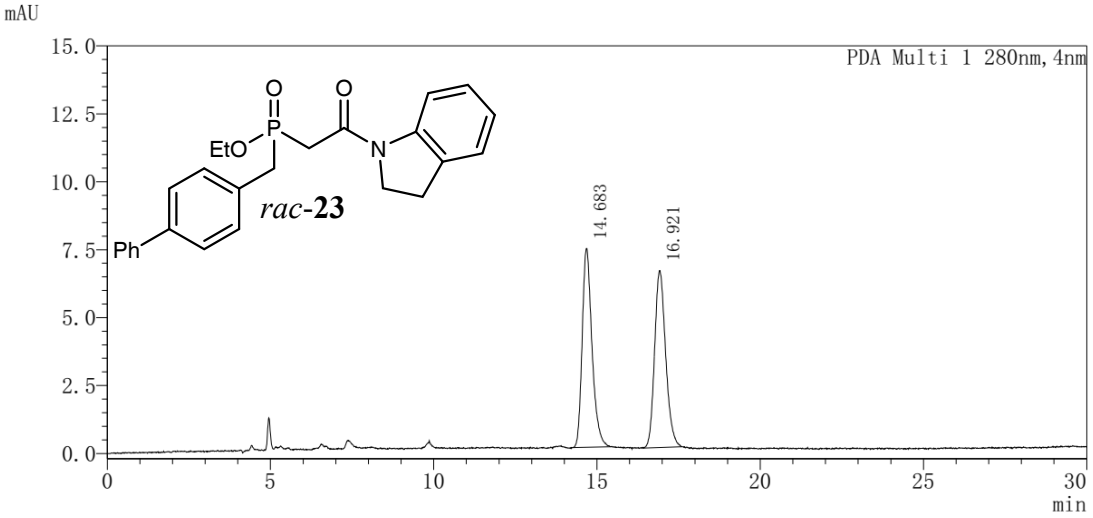


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.597	18477271	94.918
2	13.271	989318	5.082

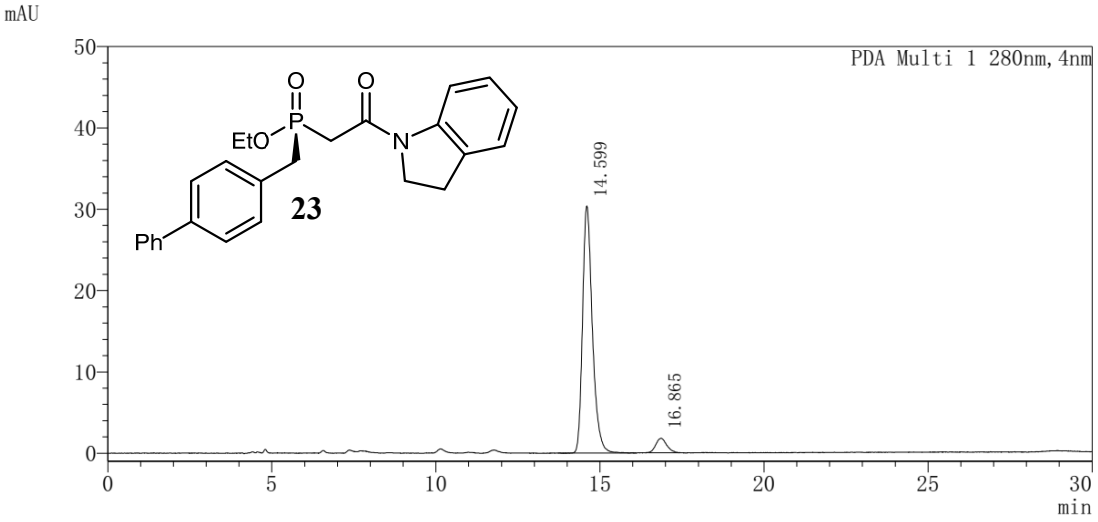
HPLC of 23



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	14.683	153084	49.925
2	16.921	153546	50.075

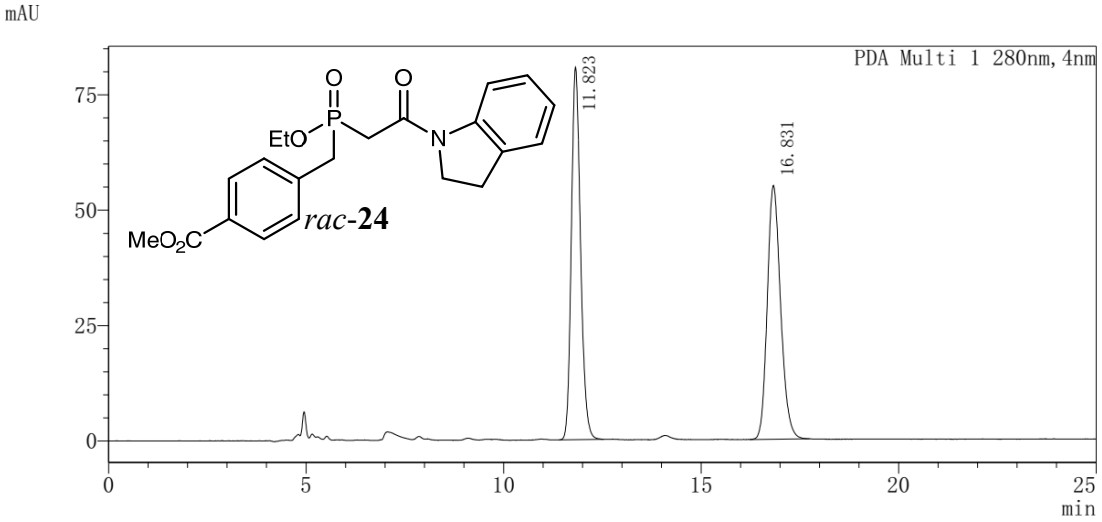


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	14.599	632183	93.904
2	16.865	41039	6.096

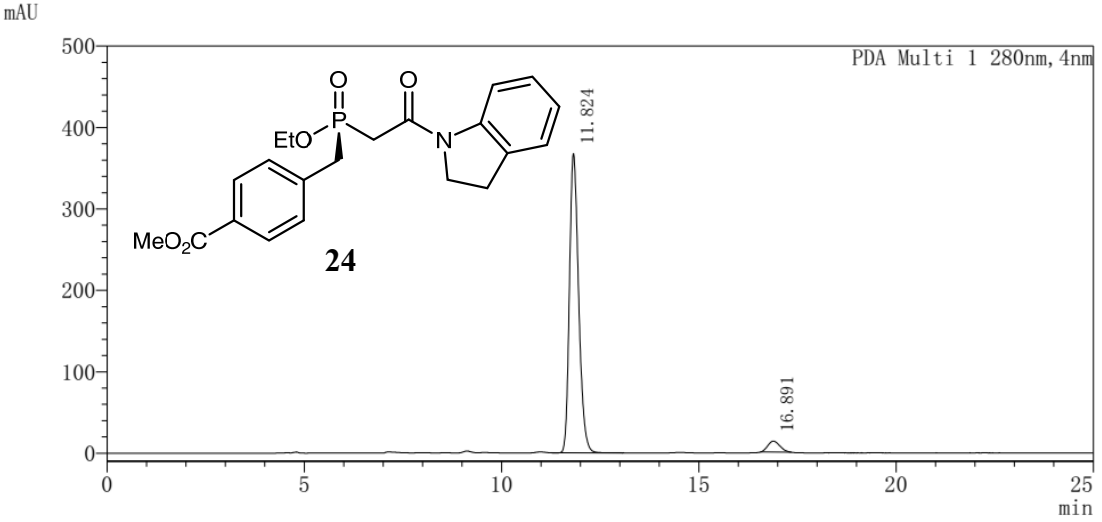
HPLC of 24



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	11.823	1307521	50.334
2	16.831	1290172	49.666

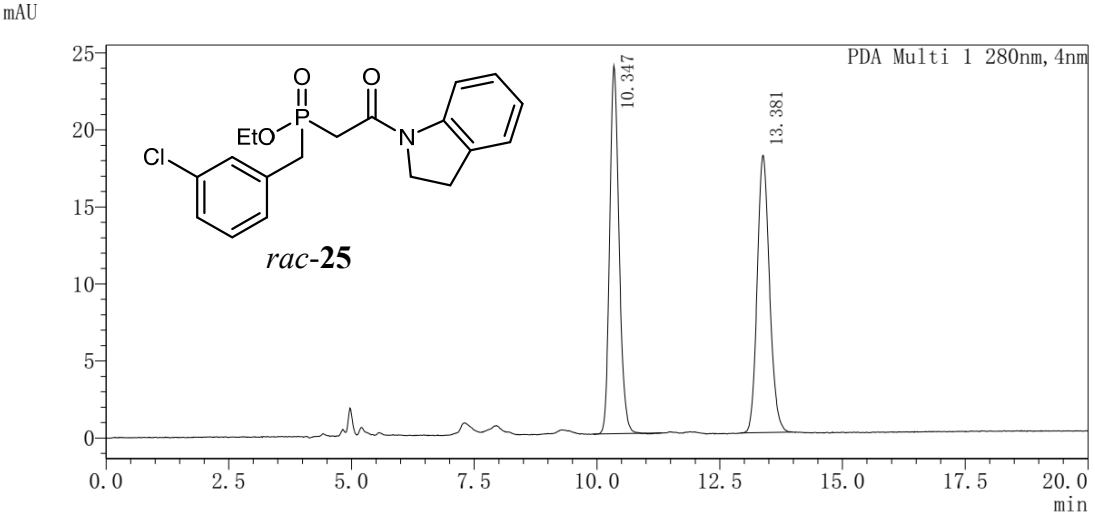


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	11.824	5955177	95.371
2	16.891	289069	4.629

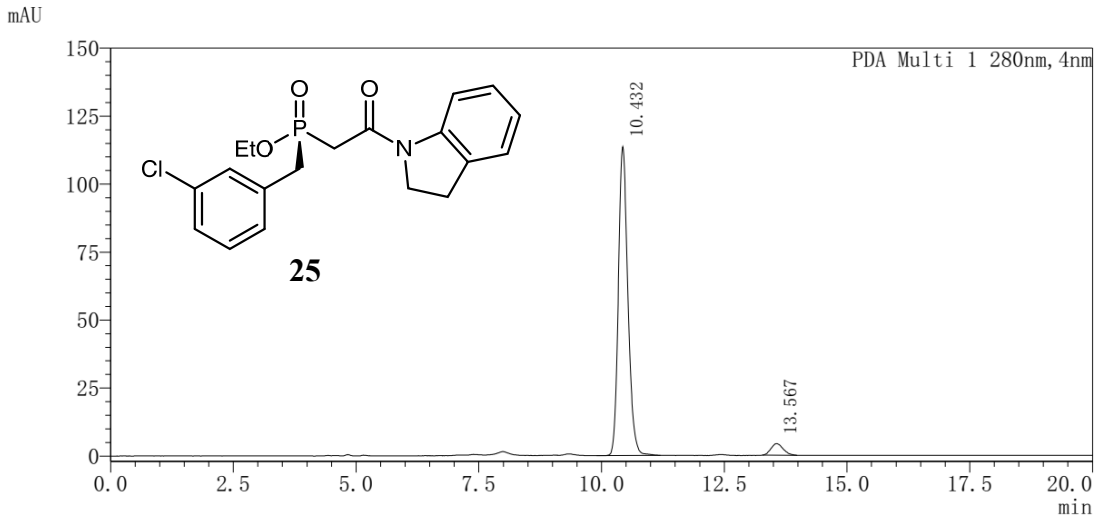
HPLC of 25



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	10.347	316272	50.211
2	13.381	313614	49.789

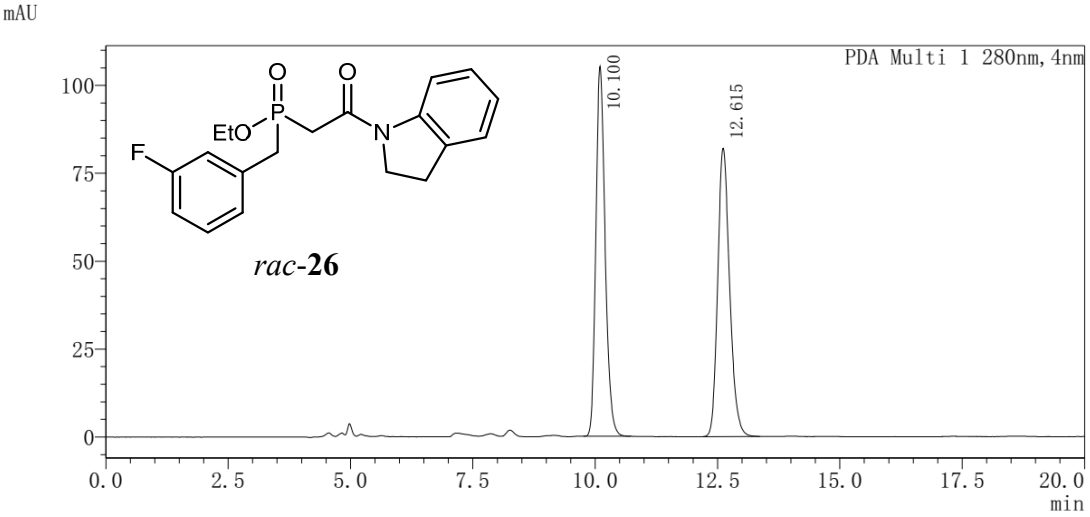


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	10.432	1530070	95.415
2	13.567	73528	4.585

HPLC of 26



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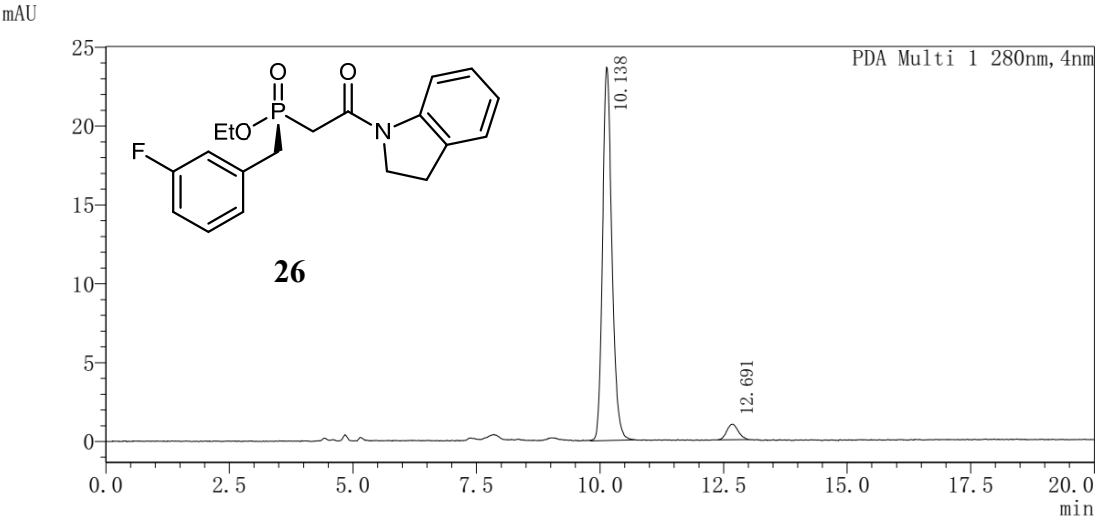
Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	10.100	1388298	49.996
2	12.615	1388516	50.004



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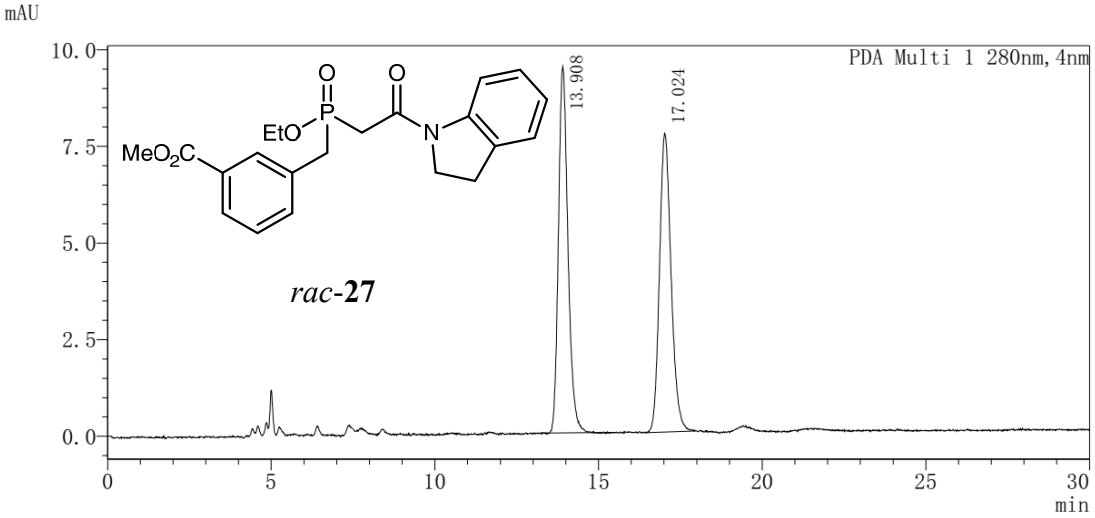
Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	10.138	311038	95.103
2	12.691	16015	4.897

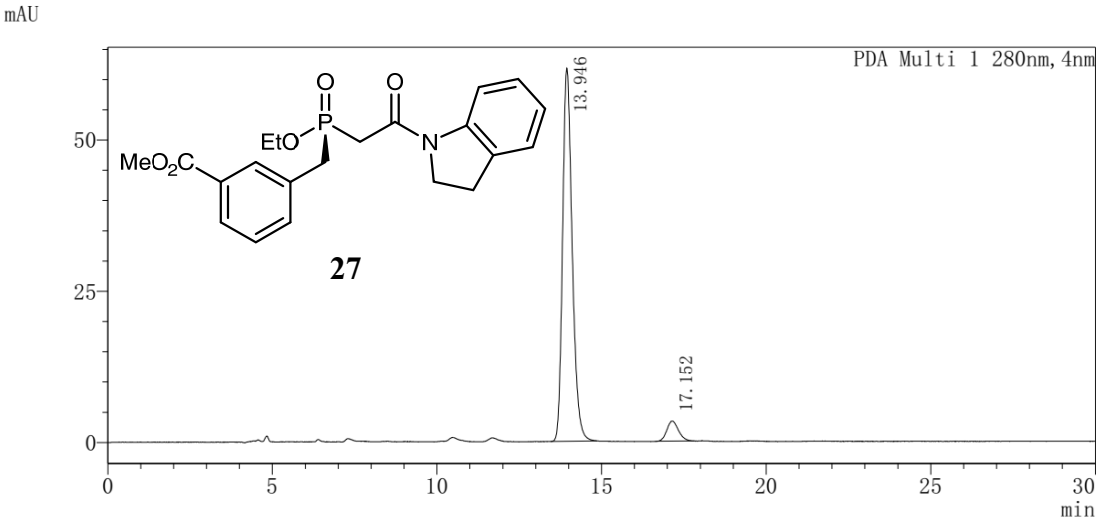
HPLC of 27



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	13.908	191259	50.012
2	17.024	191169	49.988

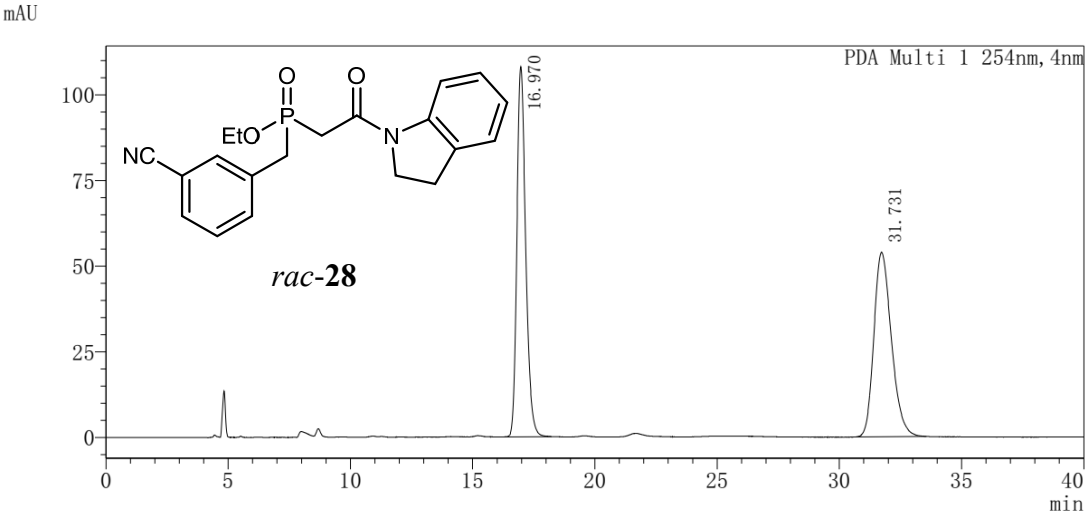


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	13.946	1254973	93.846
2	17.152	82293	6.154

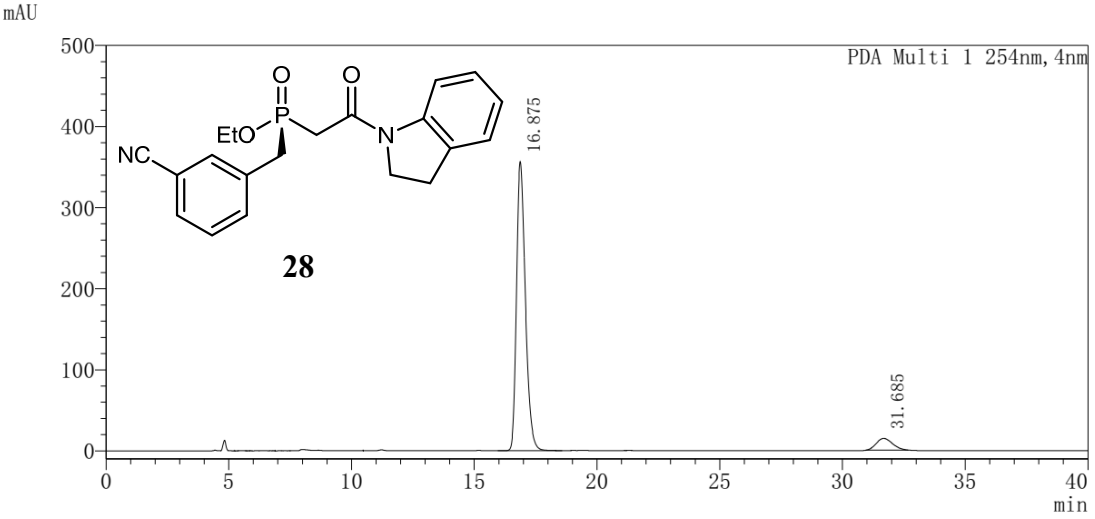
HPLC of 28



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.970	2702871	50.119
2	31.731	2690068	49.881

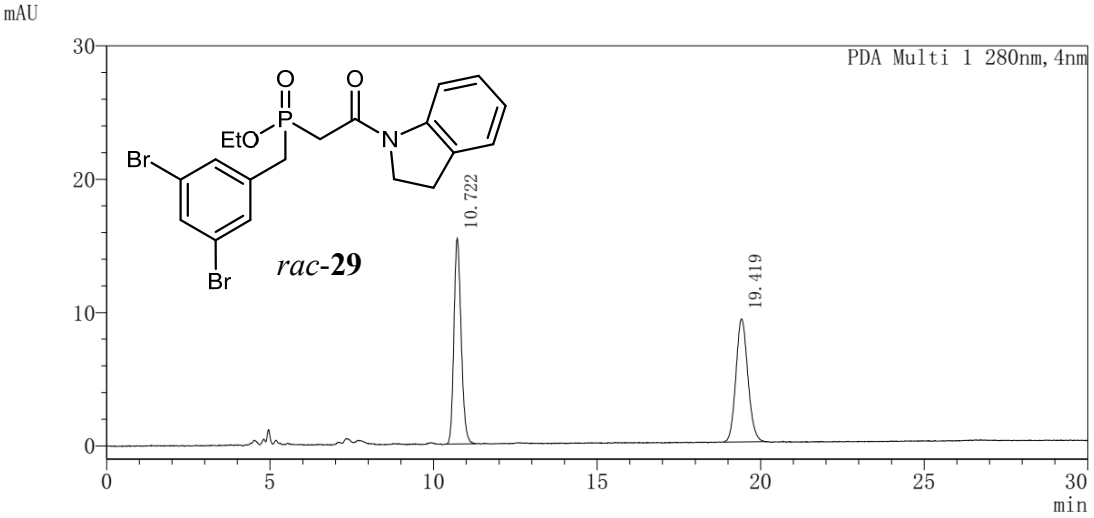


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.875	8979244	93.081
2	31.685	667447	6.919

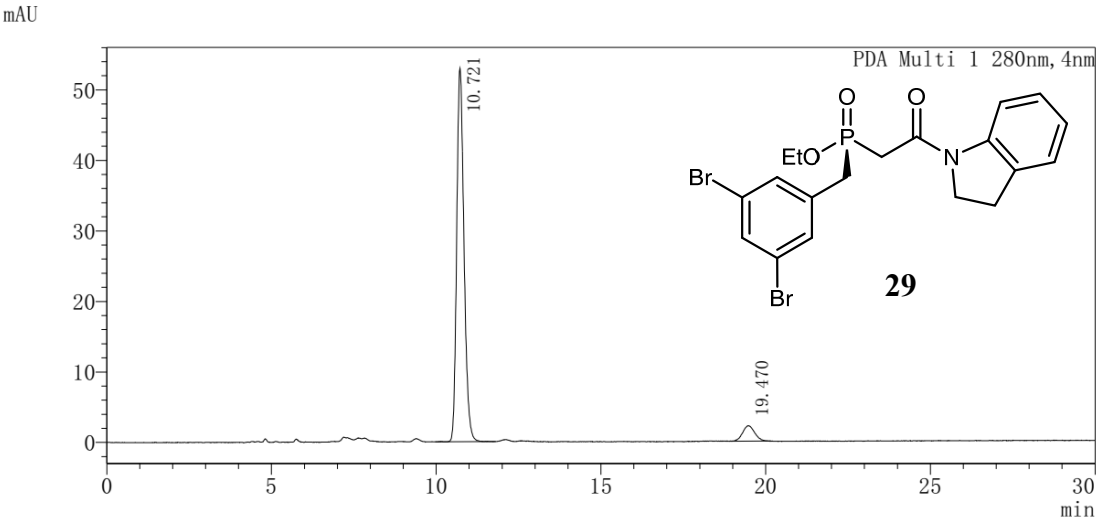
HPLC of 29



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	10.722	237159	50.230
2	19.419	234987	49.770

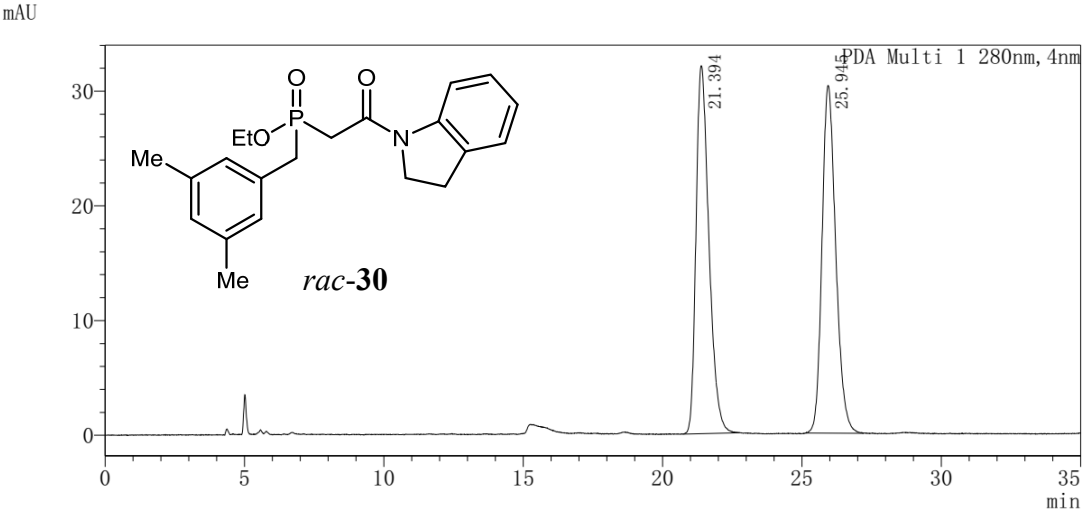


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	10.721	813747	93.599
2	19.470	55652	6.401

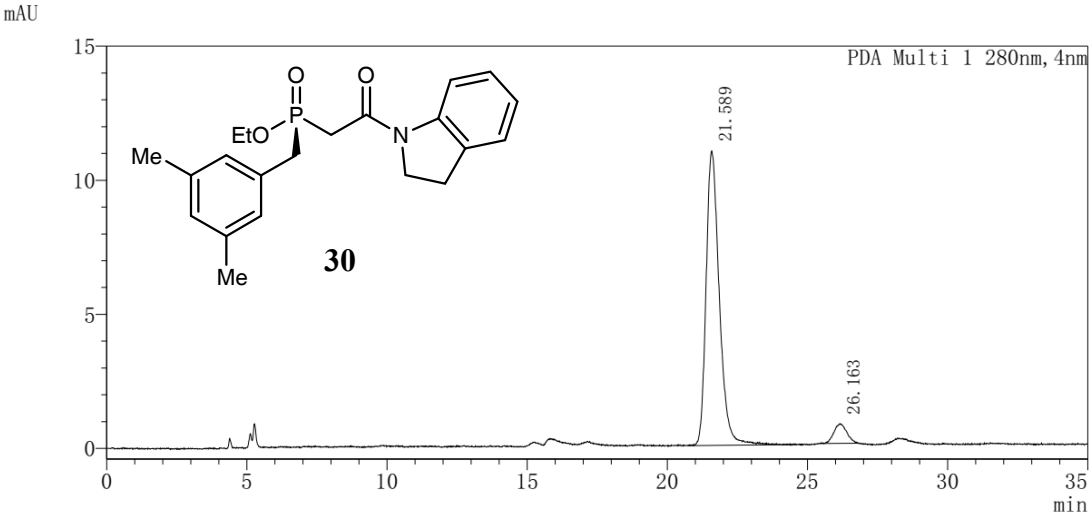
HPLC of 30



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	21.394	1030951	49.794
2	25.945	1039492	50.206

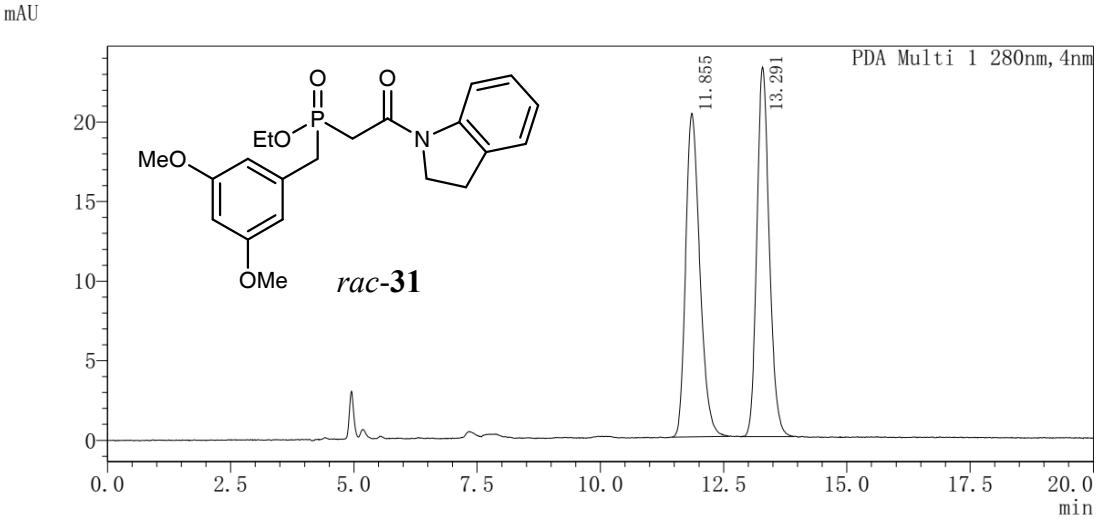


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	21.589	360629	93.838
2	26.163	23681	6.162

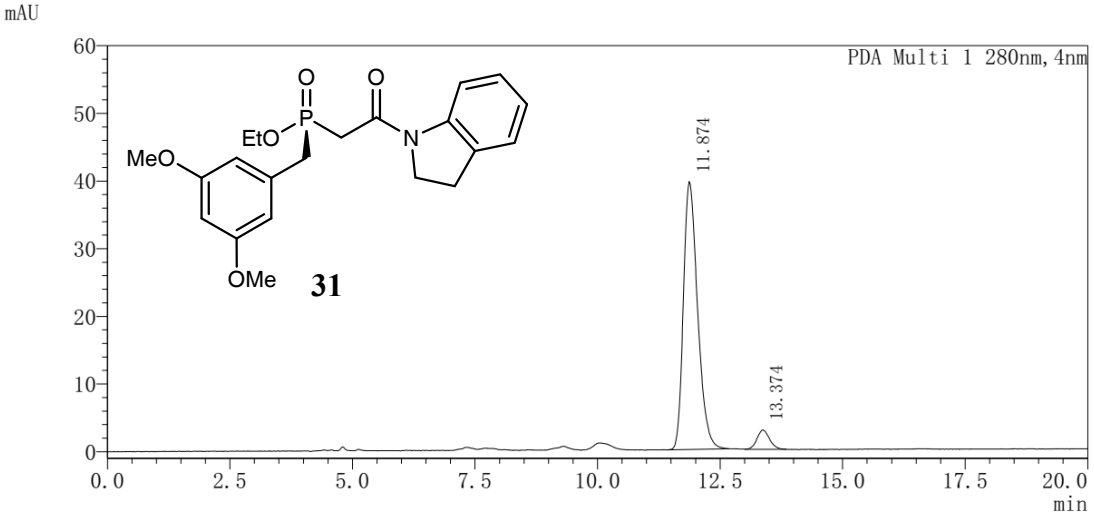
HPLC of 31



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	11.855	406485	49.961
2	13.291	407112	50.039

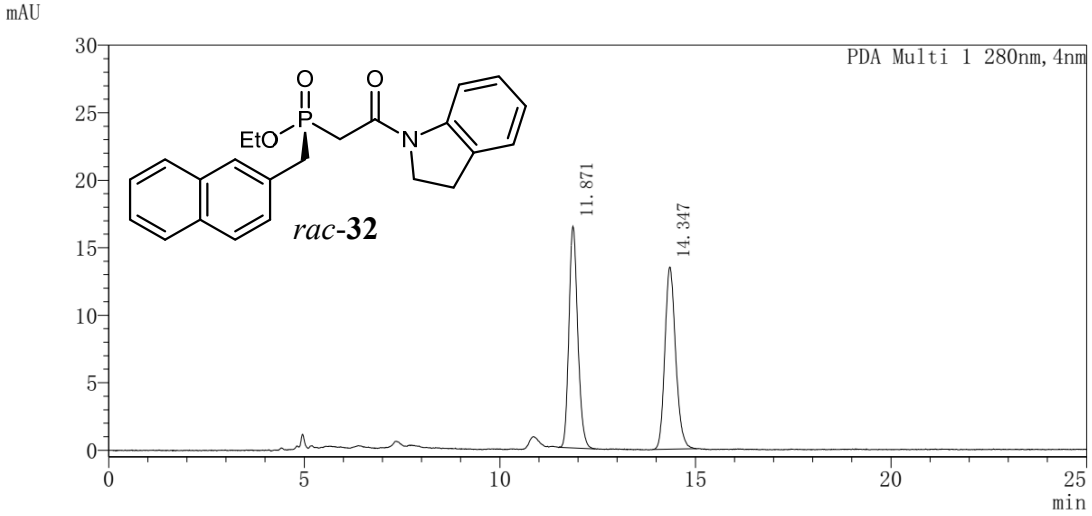


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	11.874	796467	94.052
2	13.374	50372	5.948

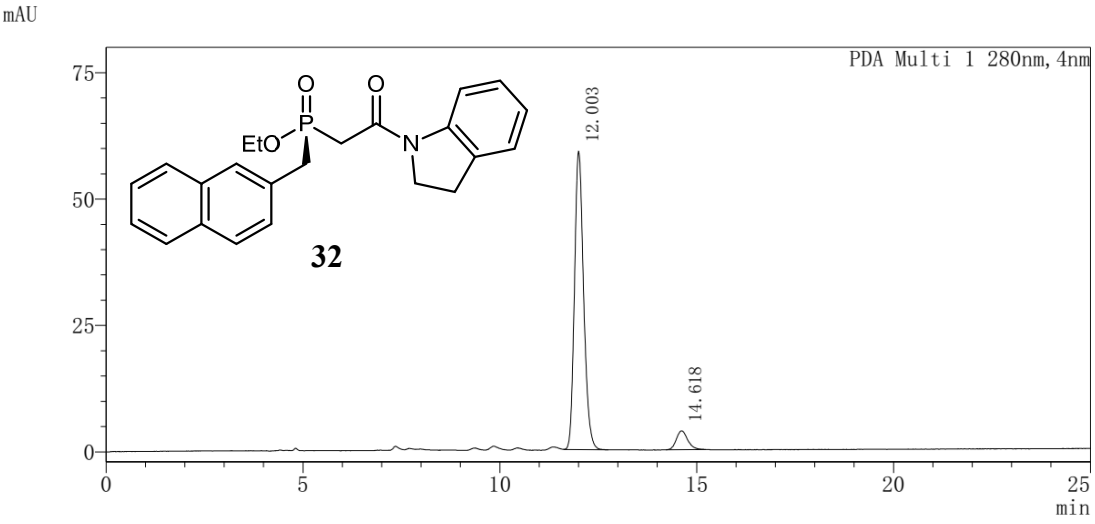
HPLC of 32



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	11.871	258246	49.908
2	14.347	259203	50.092

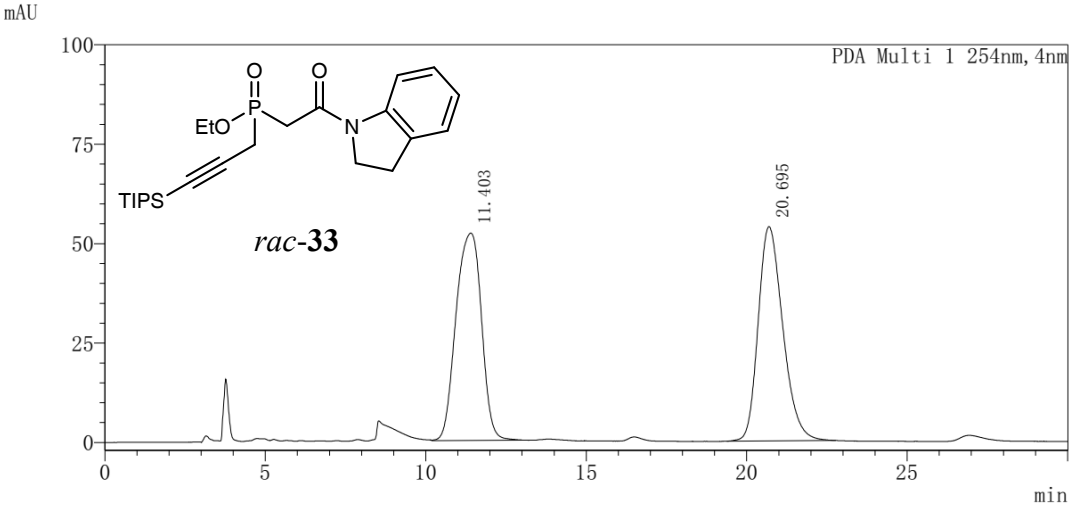


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	12.003	954583	92.674
2	14.618	75458	7.326

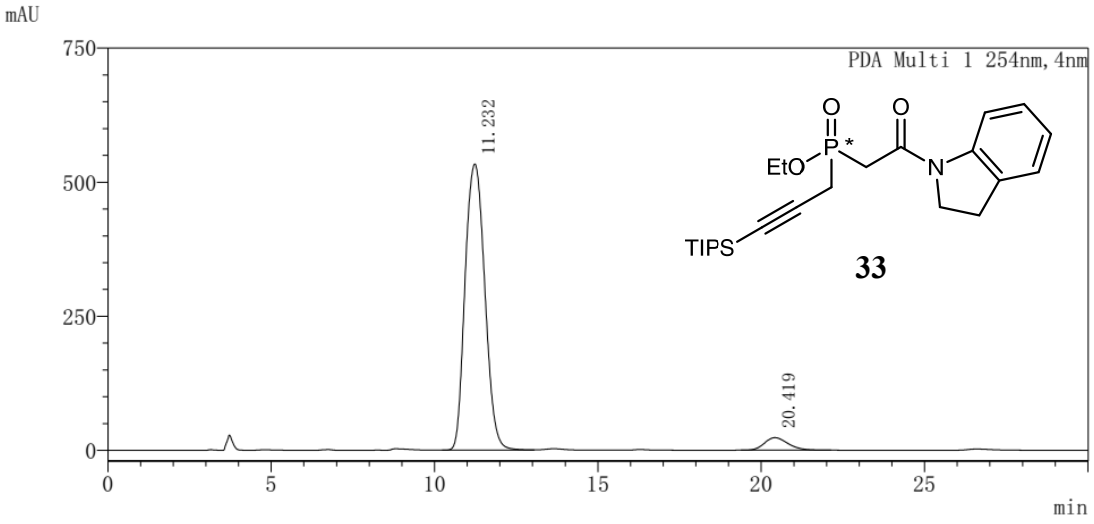
HPLC of 33



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.403	2880581	50.006
2	20.695	2879871	49.994

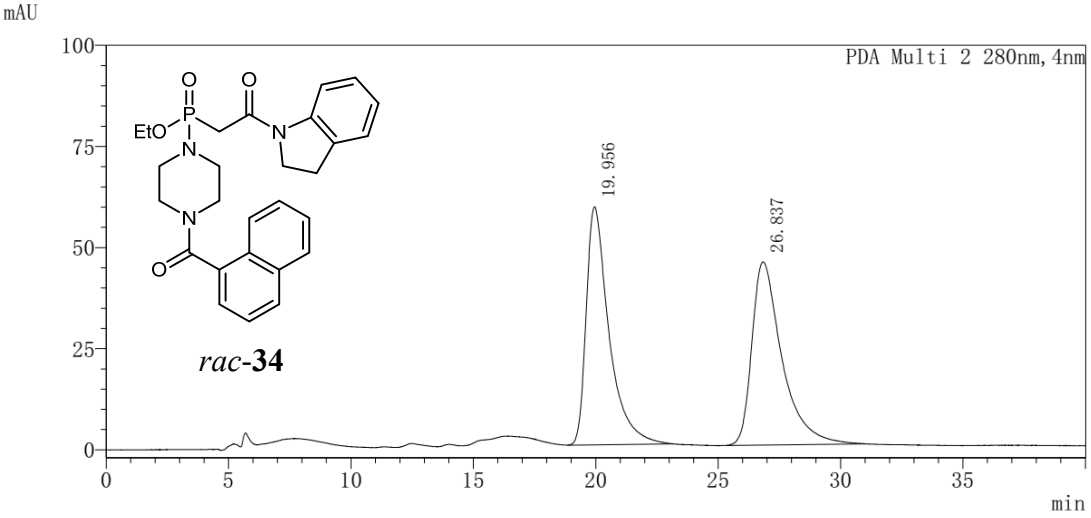


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.232	22447638	95.020
2	20.419	1176407	4.980

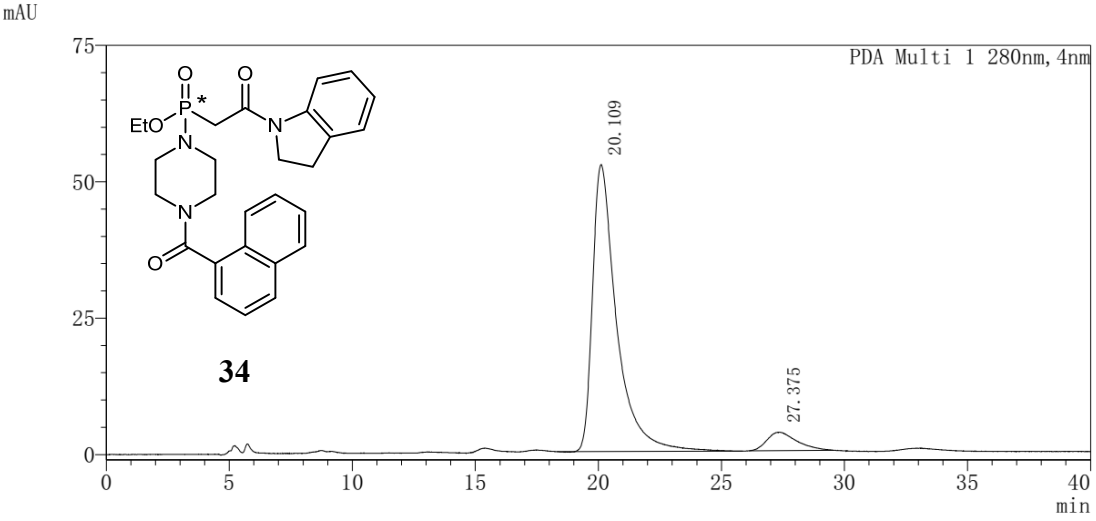
HPLC of 34



Peak Table

PDA Ch2 280nm

Peak#	Ret. Time	Area	Area%
1	19.956	3812649	49.609
2	26.837	3872800	50.391

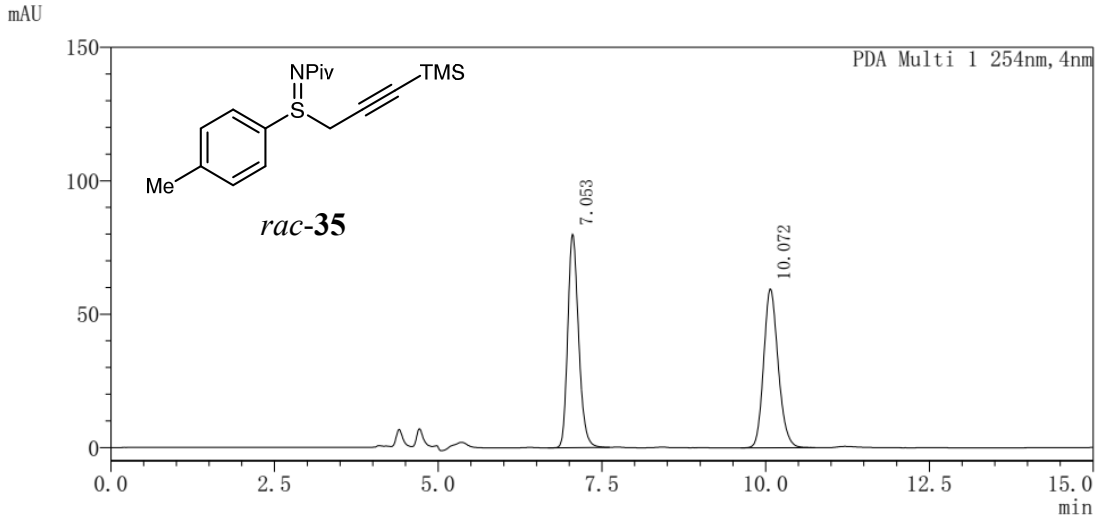


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	20.109	3578678	92.566
2	27.375	287387	7.434

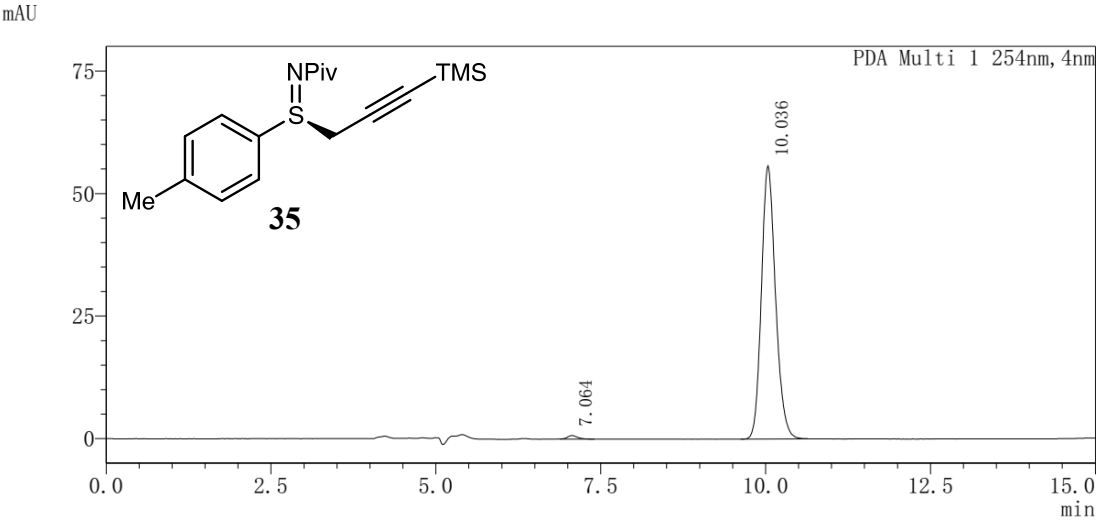
HPLC of 35



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.053	924422	50.156
2	10.072	918672	49.844

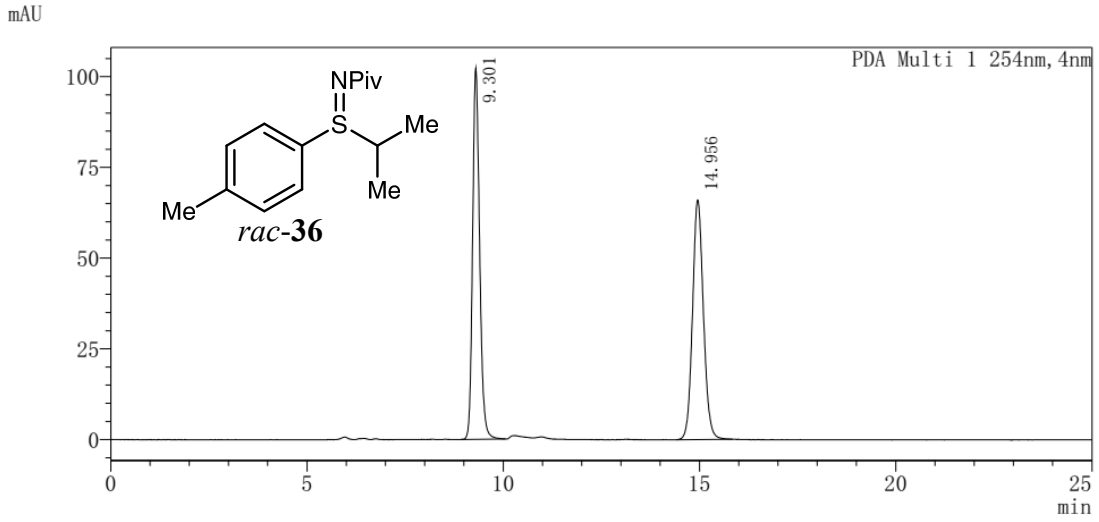


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.064	7879	0.938
2	10.036	831800	99.062

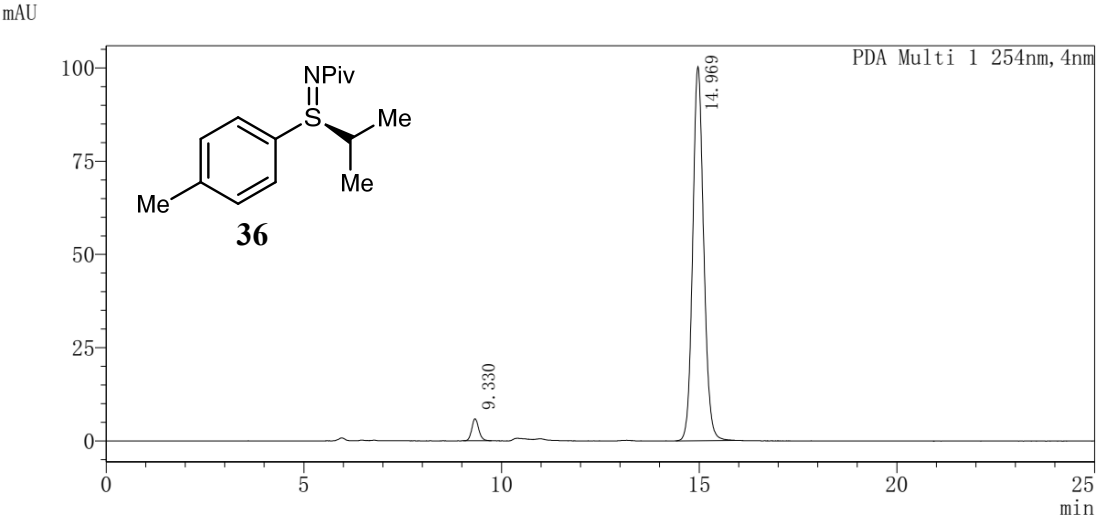
HPLC of 36



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.301	1269773	49.867
2	14.956	1276548	50.133

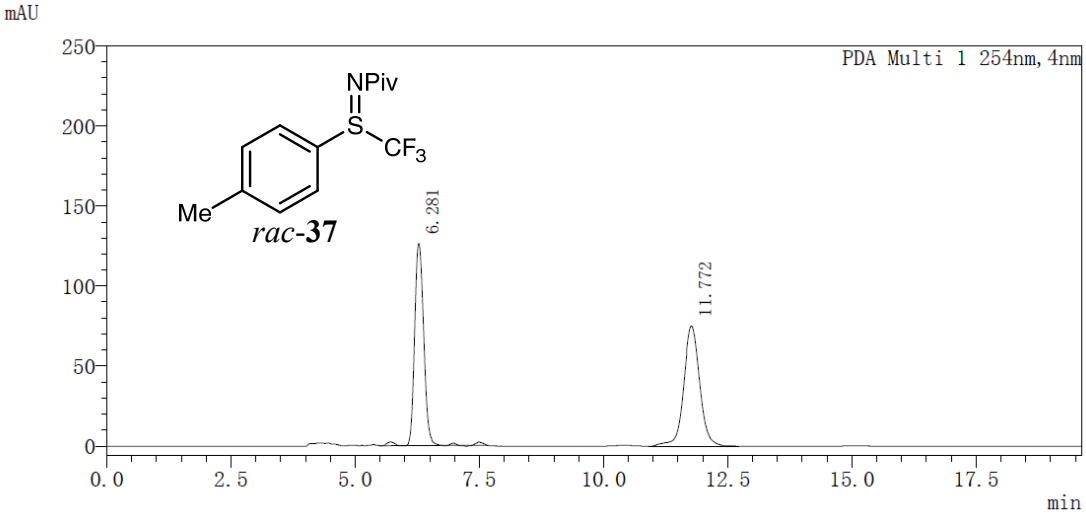


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.330	73486	3.653
2	14.969	1938287	96.347

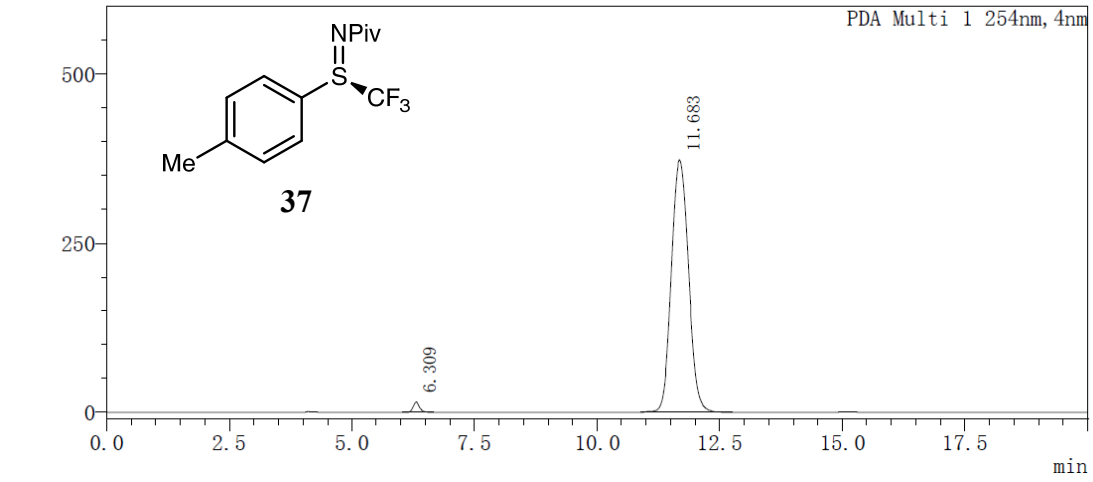
HPLC of 37



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.281	1606804	48.876
2	11.772	1680719	51.124

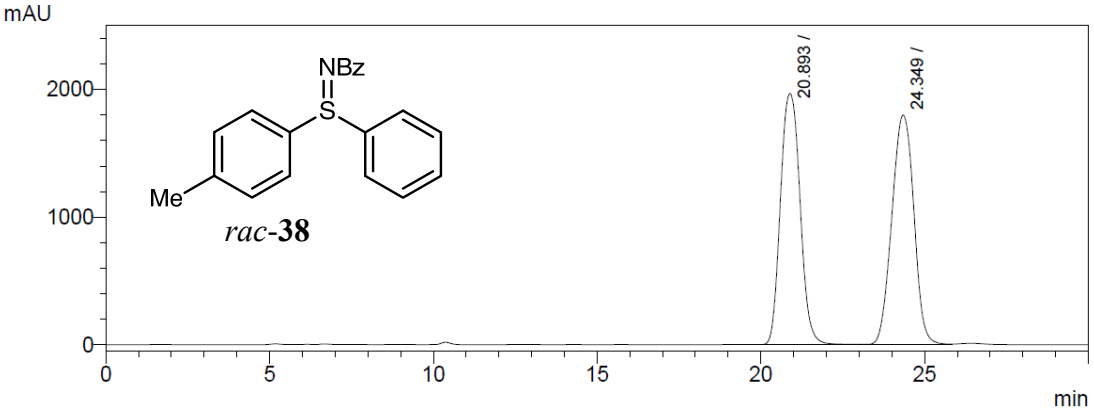


Peak Table

PDA Ch1 254nm

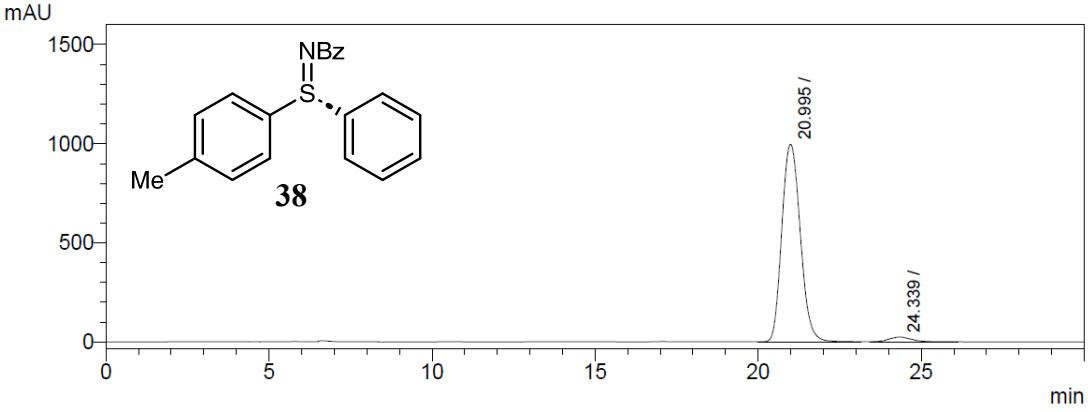
Peak#	Ret. Time	Area	Area%
1	6.309	140994	1.527
2	11.683	9092483	98.473

HPLC of 38



PDA Ch1 254nm

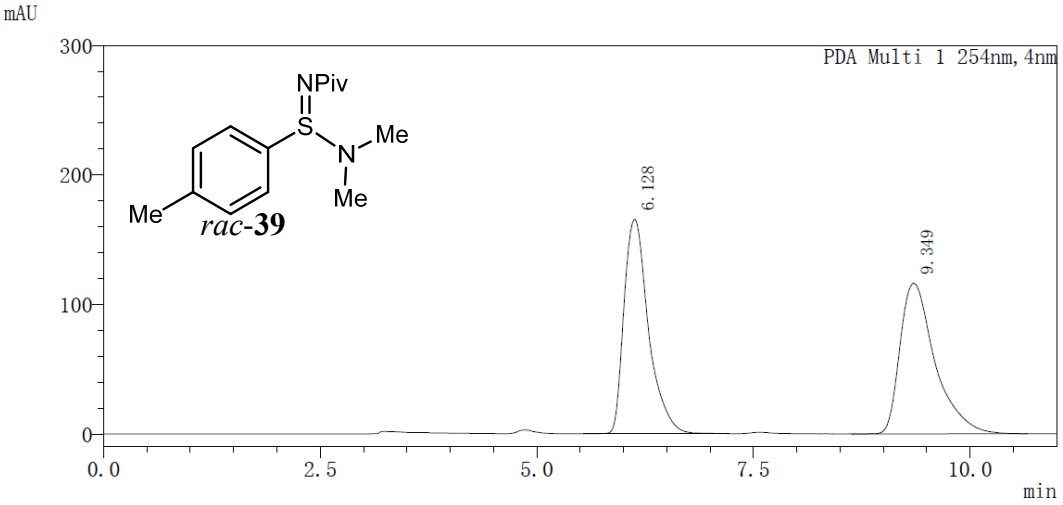
Peak#	Ret. Time	Area	Area%
1	20.893	82444333	49.396
2	24.349	84459366	50.604



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.995	39271076	97.255
2	24.339	1108322	2.745

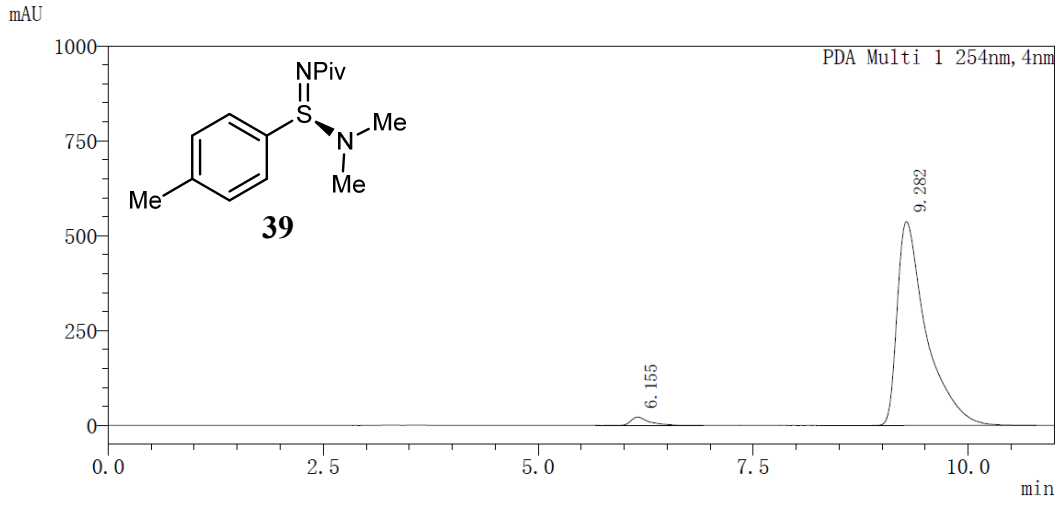
HPLC of 39



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.128	3268039	50.014
2	9.349	3266163	49.986

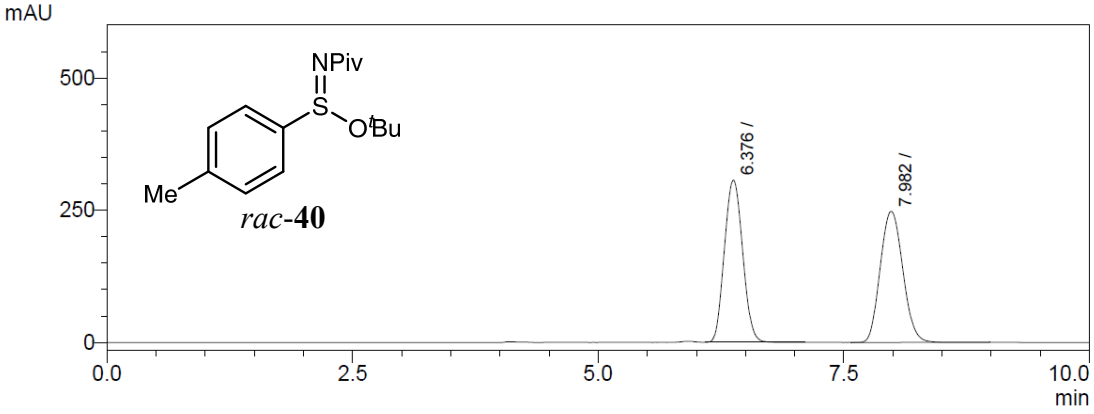


Peak Table

PDA Ch1 254nm

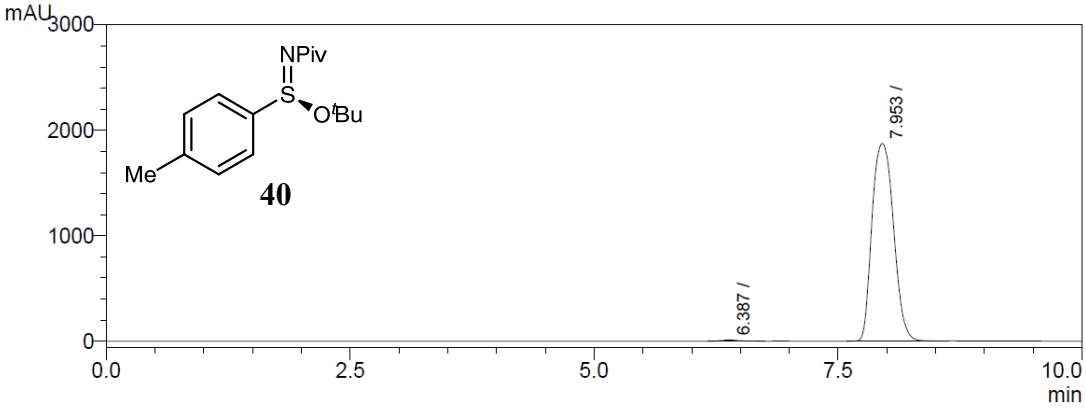
Peak#	Ret. Time	Area	Area%
1	6.155	324414	2.508
2	9.282	12613052	97.492

HPLC of 40



PDA Ch1 254nm

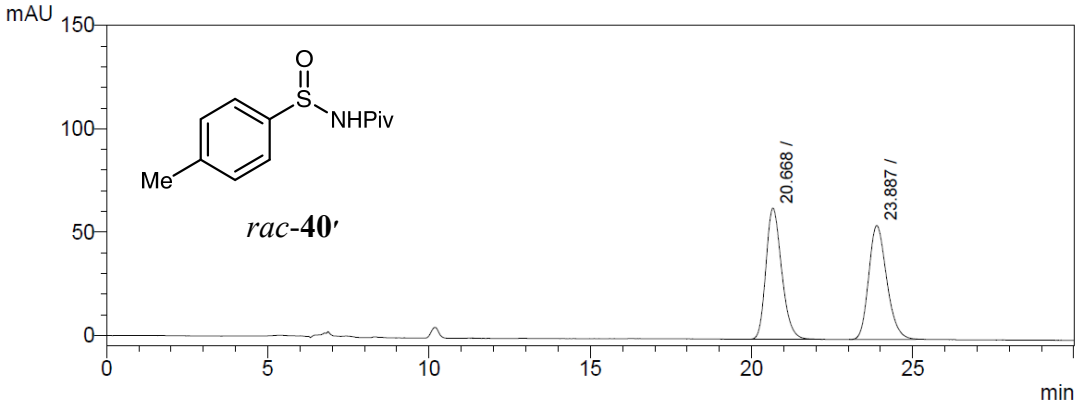
Peak#	Ret. Time	Area	Area%
1	6.376	3972487	50.031
2	7.982	3967563	49.969



PDA Ch1 254nm

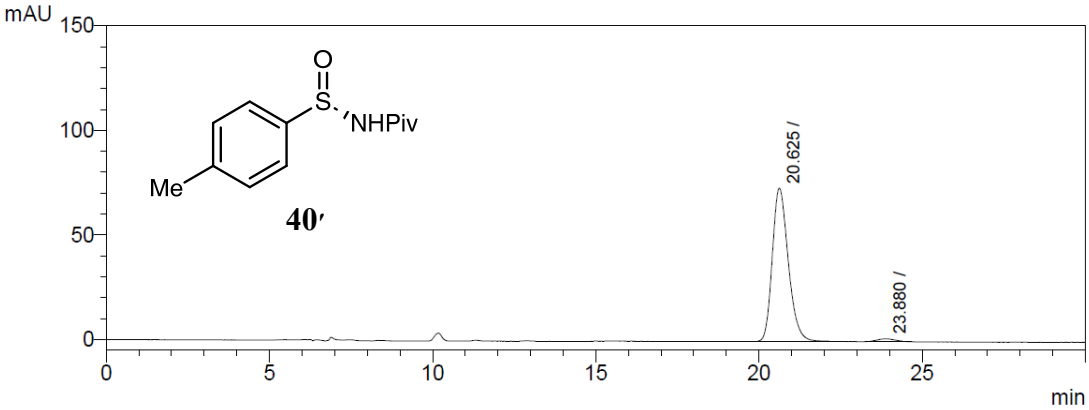
Peak#	Ret. Time	Area	Area%
1	6.387	149849	0.516
2	7.953	28897698	99.484

HPLC of 40′



PDA Ch1 254nm

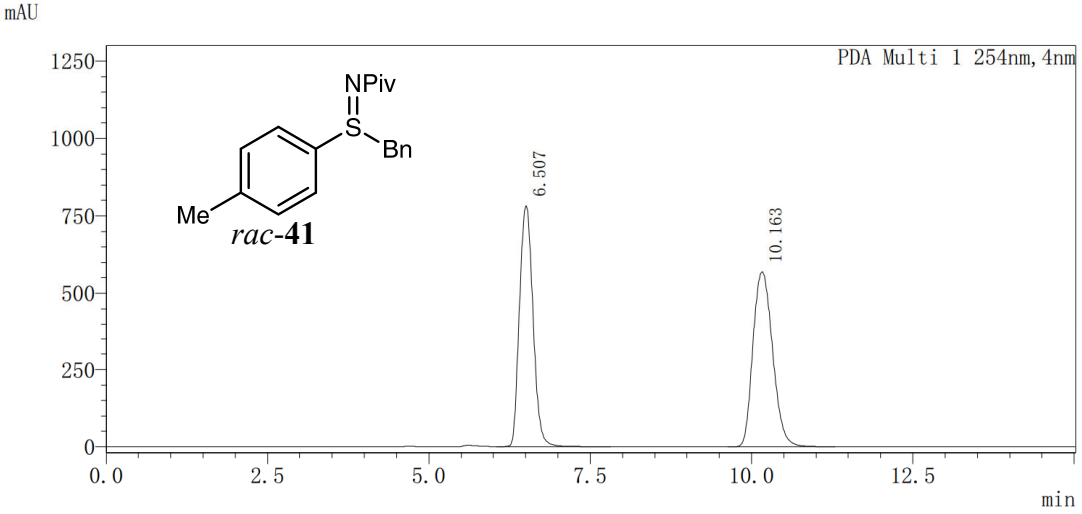
Peak#	Ret. Time	Area	Area%
1	20.668	2155840	50.042
2	23.887	2152234	49.958



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.625	2489291	97.903
2	23.880	53318	2.097

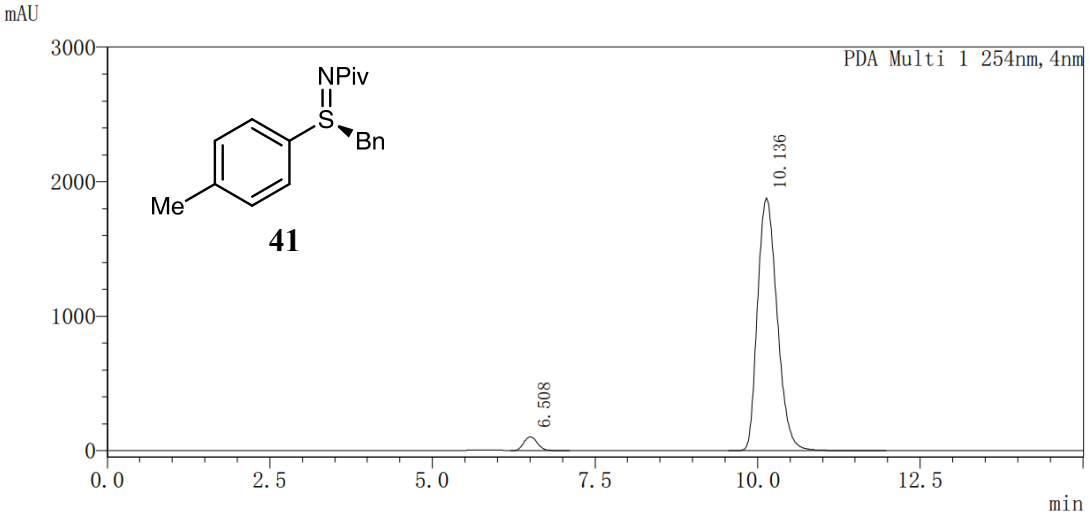
HPLC of 41



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.507	11449566	48.684
2	10.163	12068331	51.316

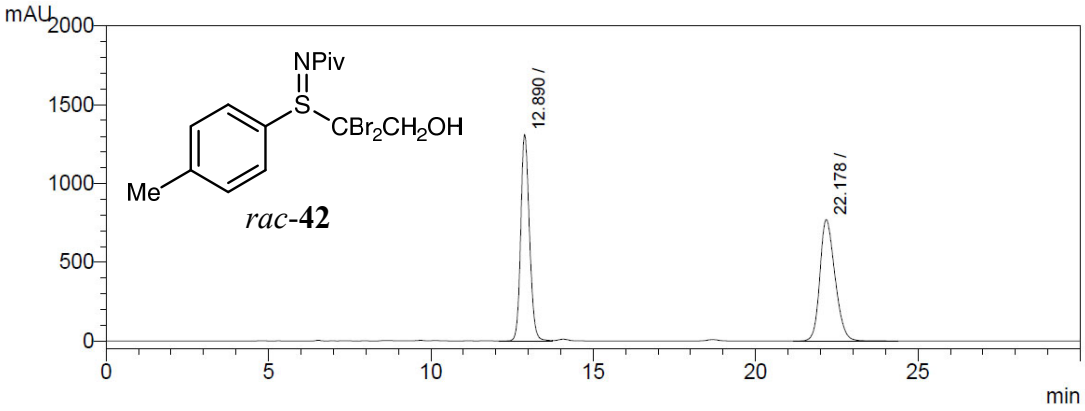


Peak Table

PDA Ch1 254nm

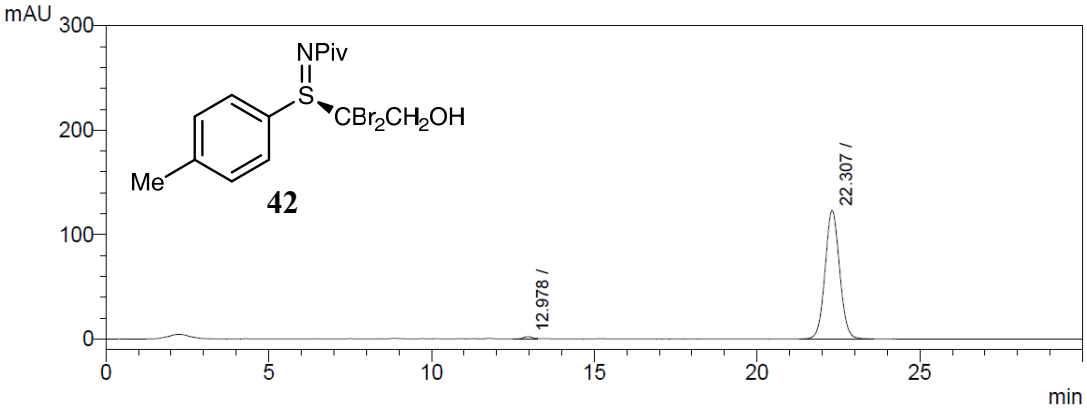
Peak#	Ret. Time	Area	Area%
1	6.508	1470270	3.598
2	10.136	39389958	96.402

HPLC of 42



PDA Ch1 254nm

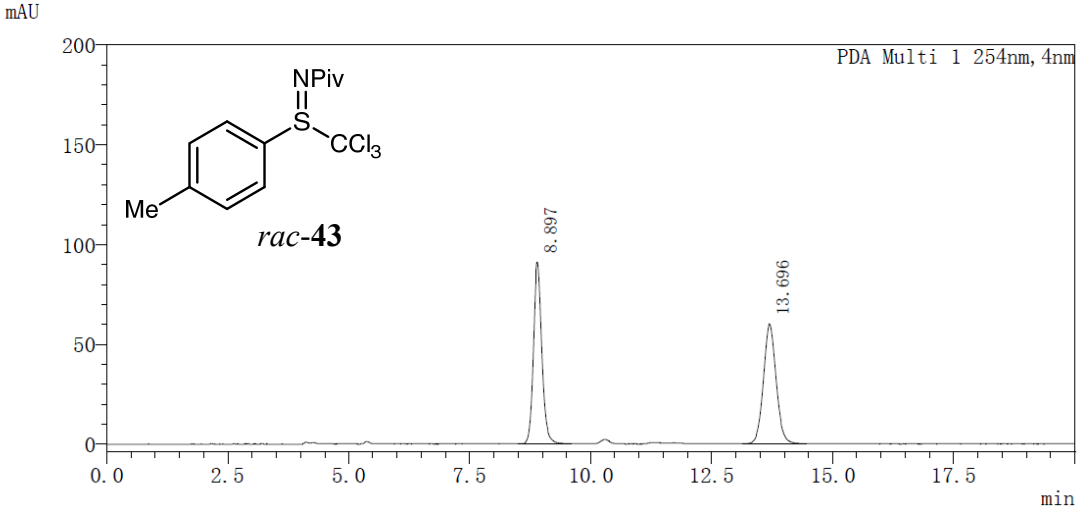
Peak#	Ret. Time	Area	Area%
1	12.890	24451369	49.486
2	22.178	24959593	50.514



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.978	41621	1.078
2	22.307	3818485	98.922

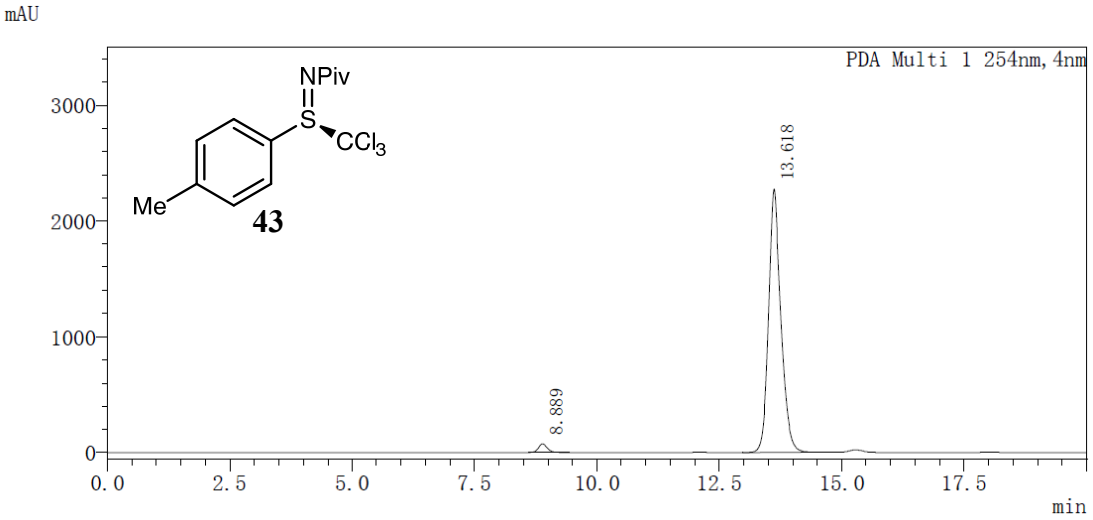
HPLC of 43



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.897	1102620	50.043
2	13.696	1100723	49.957

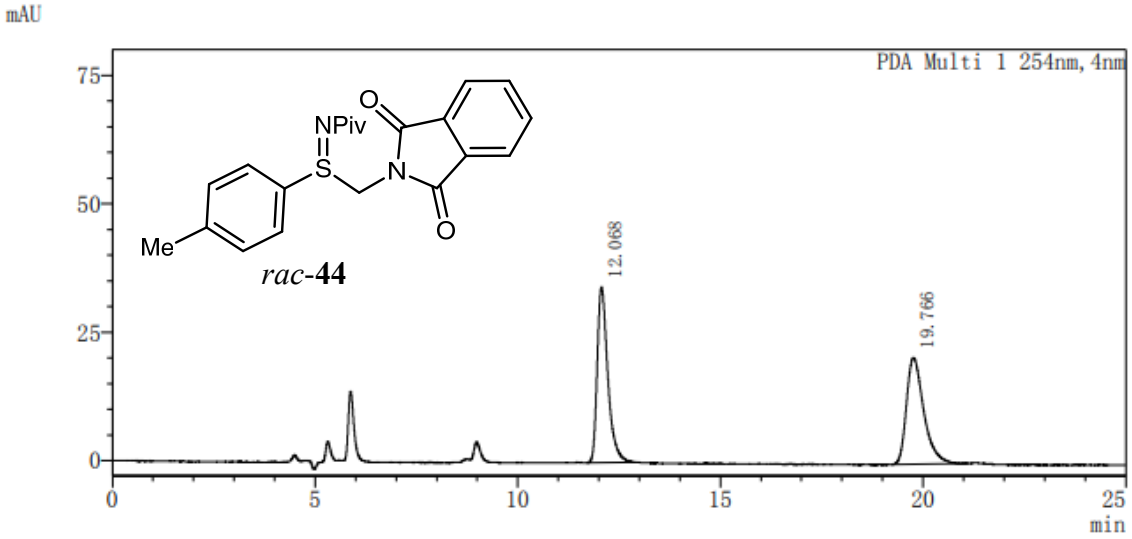


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.889	932253	2.297
2	13.618	39646576	97.703

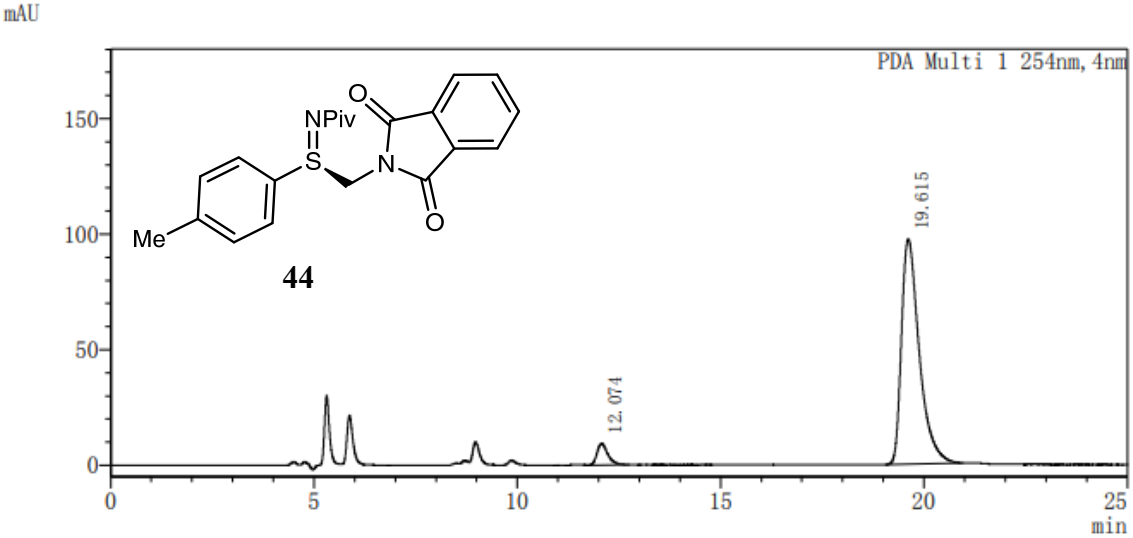
HPLC of 44



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.068	625341	50.241
2	19.766	619348	49.759

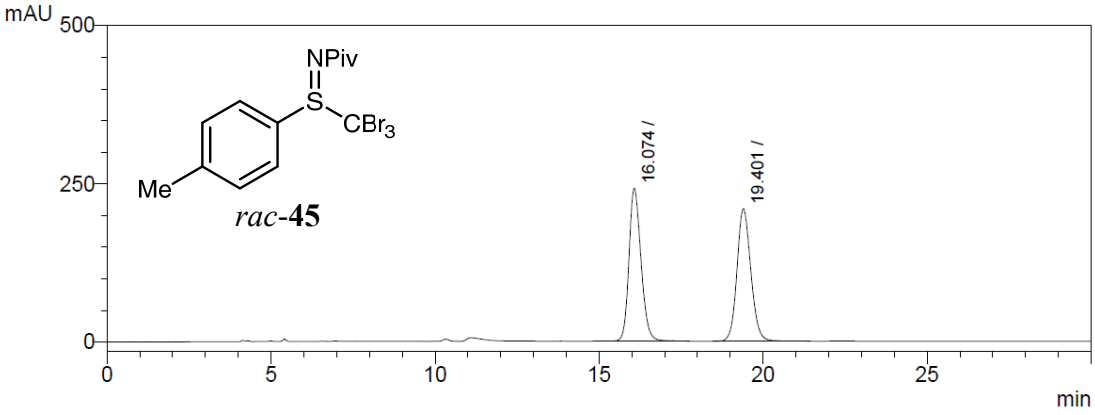


Peak Table

PDA Ch1 254nm

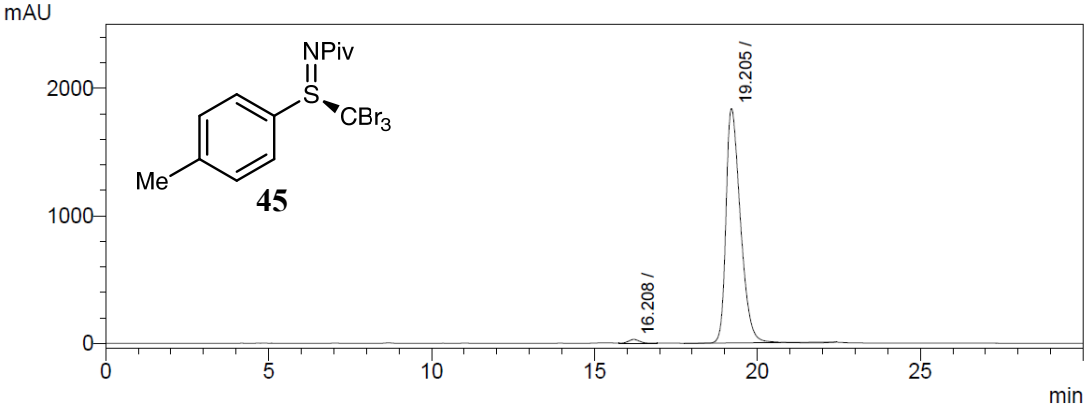
Peak#	Ret. Time	Area	Area%
1	12.074	170725	5.442
2	19.615	2966719	94.558

HPLC of 45



PDA Ch1 254nm

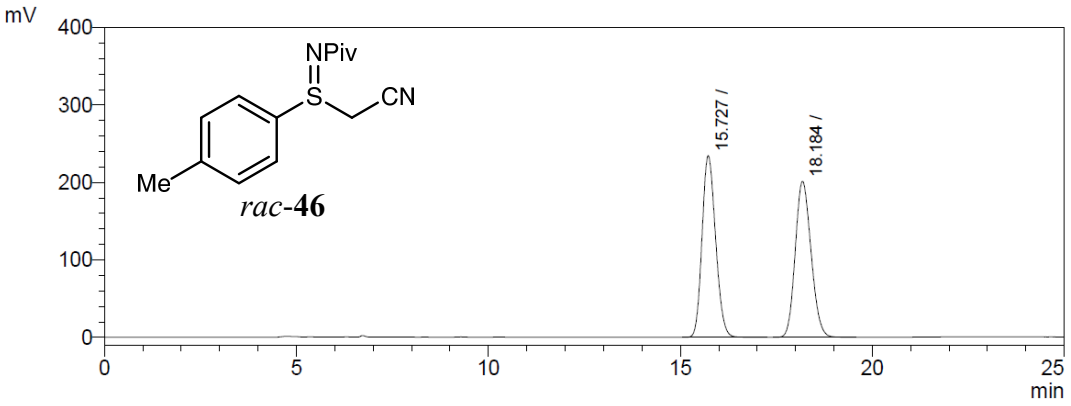
Peak#	Ret. Time	Area	Area%
1	16.074	6179380	50.035
2	19.401	6170711	49.965



PDA Ch1 254nm

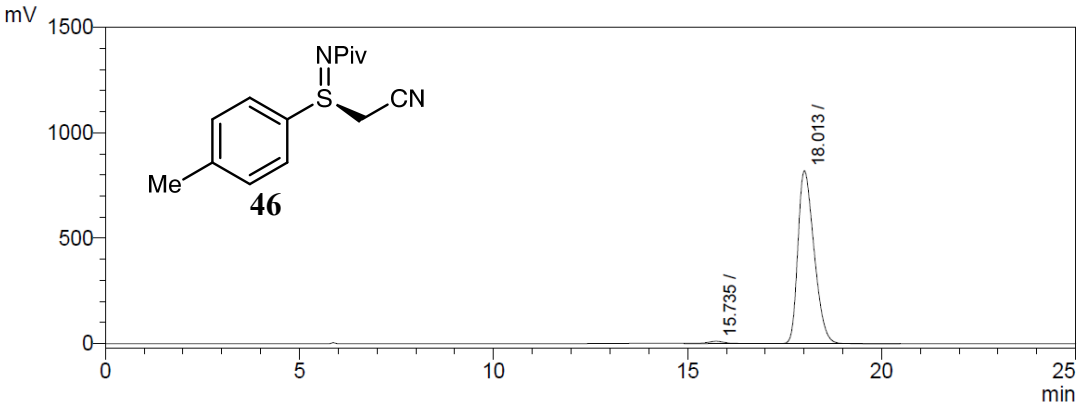
Peak#	Ret. Time	Area	Area%
1	16.208	716015	1.254
2	19.205	56404753	98.746

HPLC of 46



检测器A Ch1 254nm

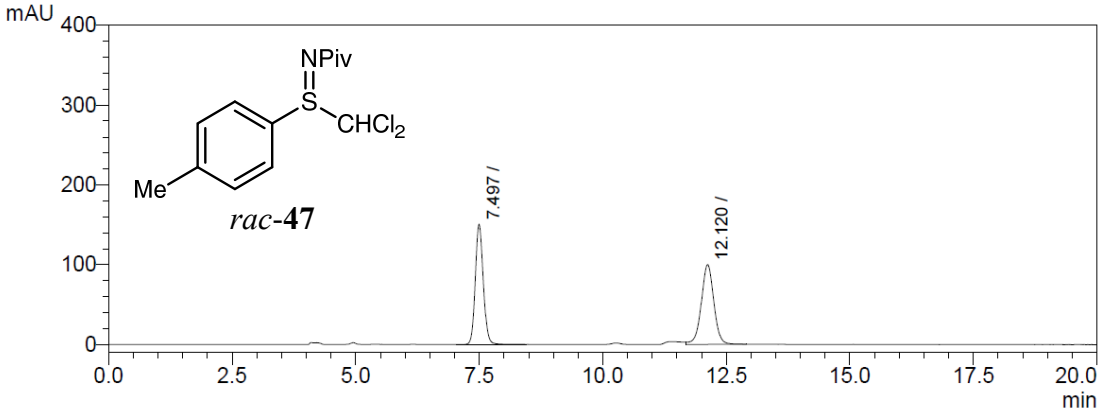
Peak#	Ret. Time	Area	Area%
1	15.727	5780549	49.961
2	18.184	5789592	50.039



检测器A Ch1 254nm

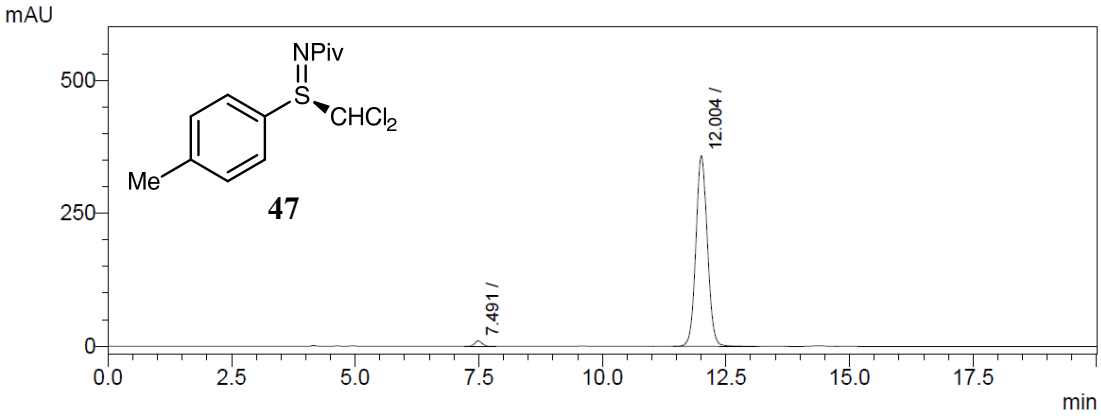
Peak#	Ret. Time	Area	Area%
1	15.735	377464	1.565
2	18.013	23744057	98.435

HPLC of 47



PDA Ch1 254nm

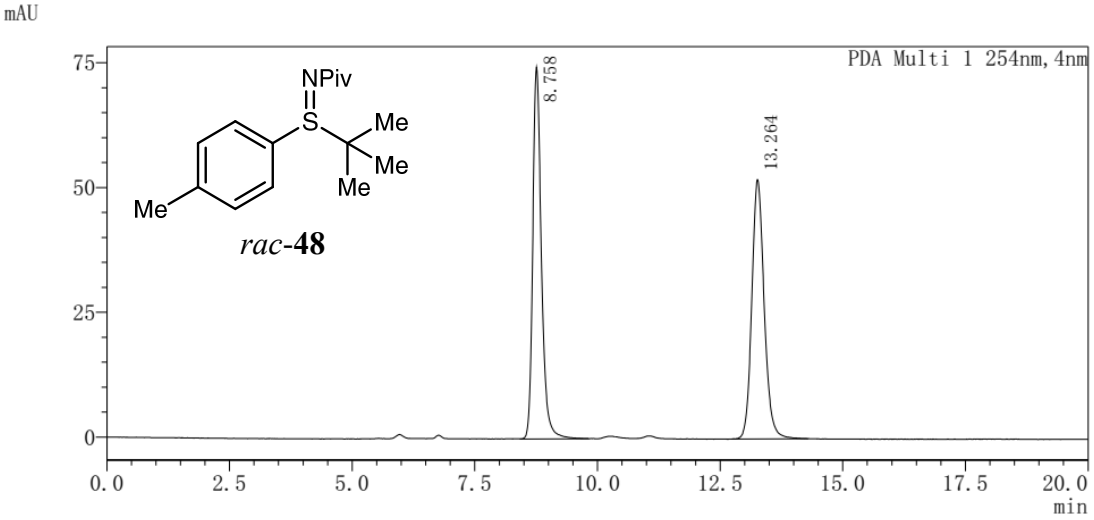
Peak#	Ret. Time	Area	Area%
1	7.497	1706892	49.185
2	12.120	1763478	50.815



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.491	110317	1.862
2	12.004	5814708	98.138

HPLC of 48

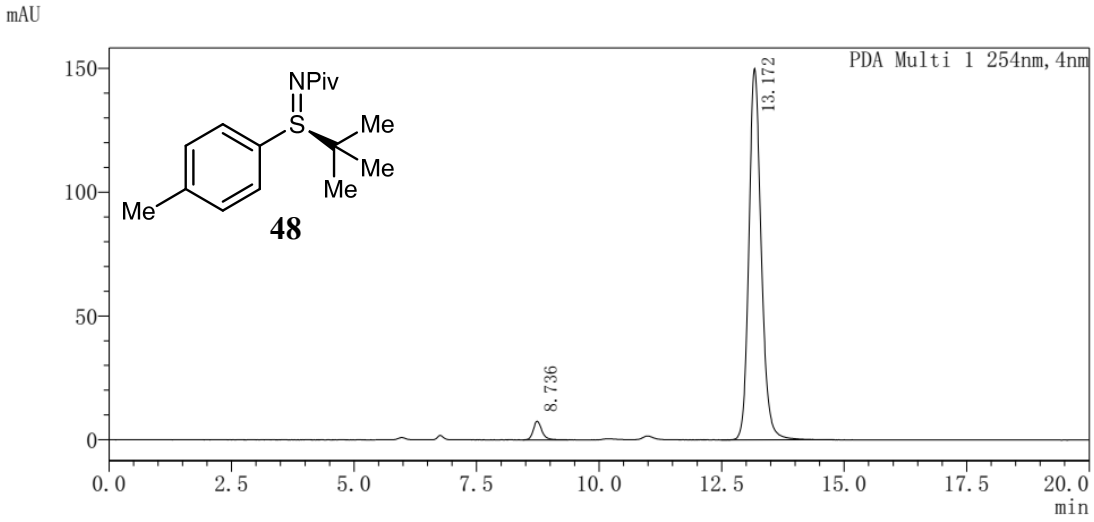


rac-**48**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.758	912198	49.969
2	13.264	913325	50.031



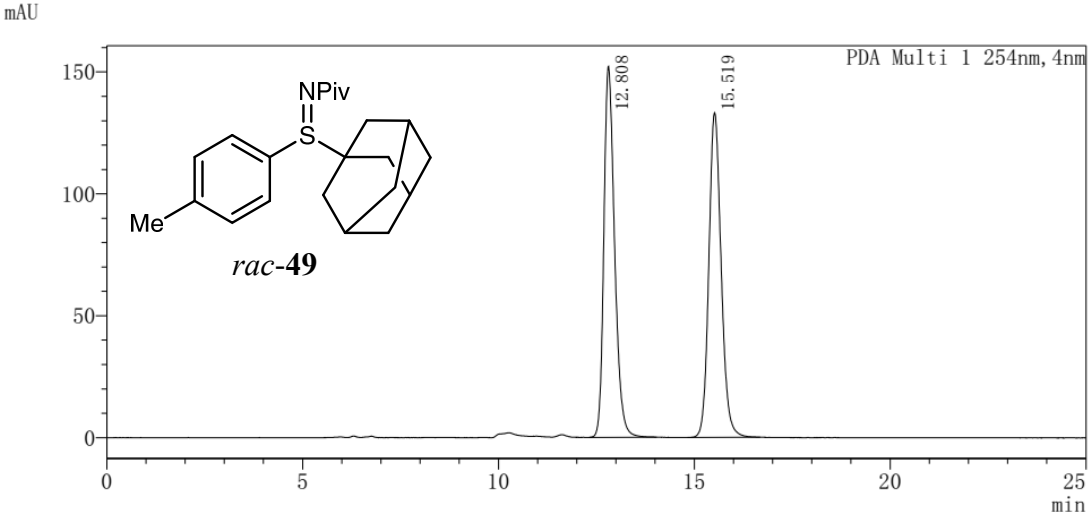
48

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.736	92311	3.391
2	13.172	2629885	96.609

HPLC of 49

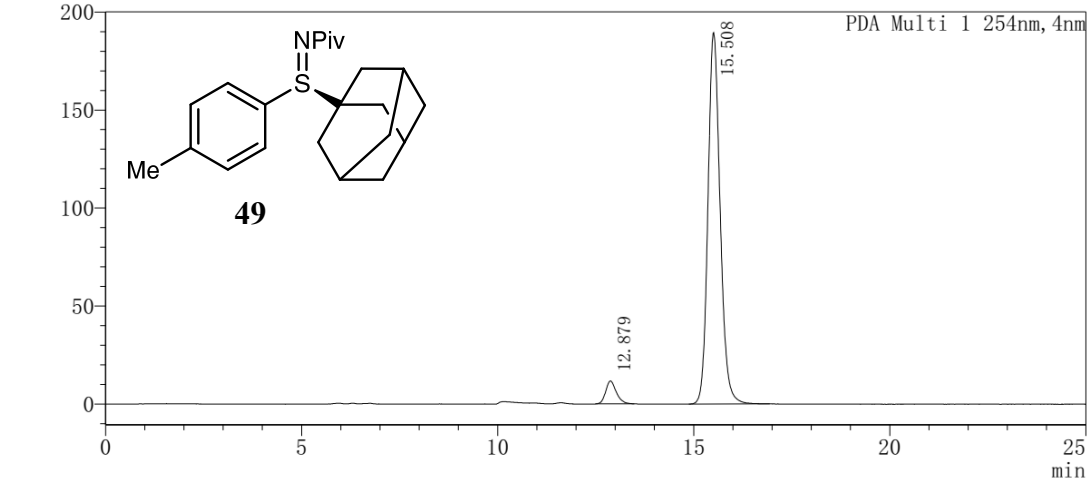


rac-**49**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.808	2904290	49.866
2	15.519	2919879	50.134



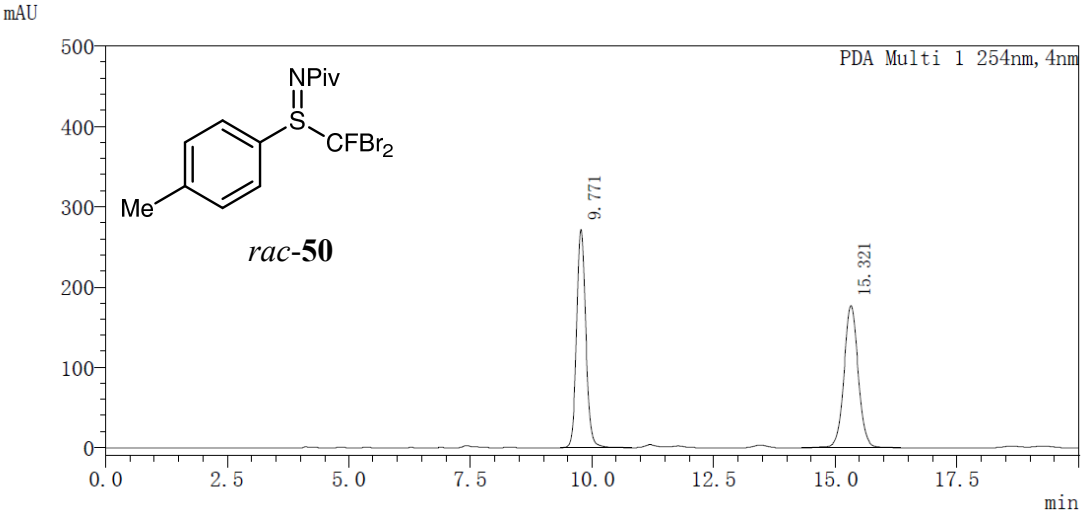
49

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.879	220447	5.110
2	15.508	4093867	94.890

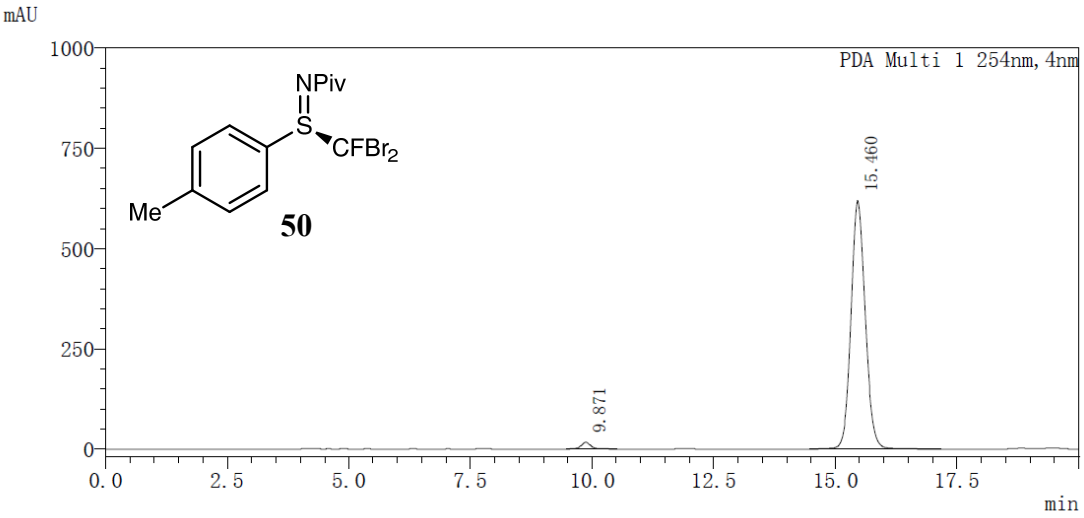
HPLC of 50



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.771	3563529	49.747
2	15.321	3599807	50.253

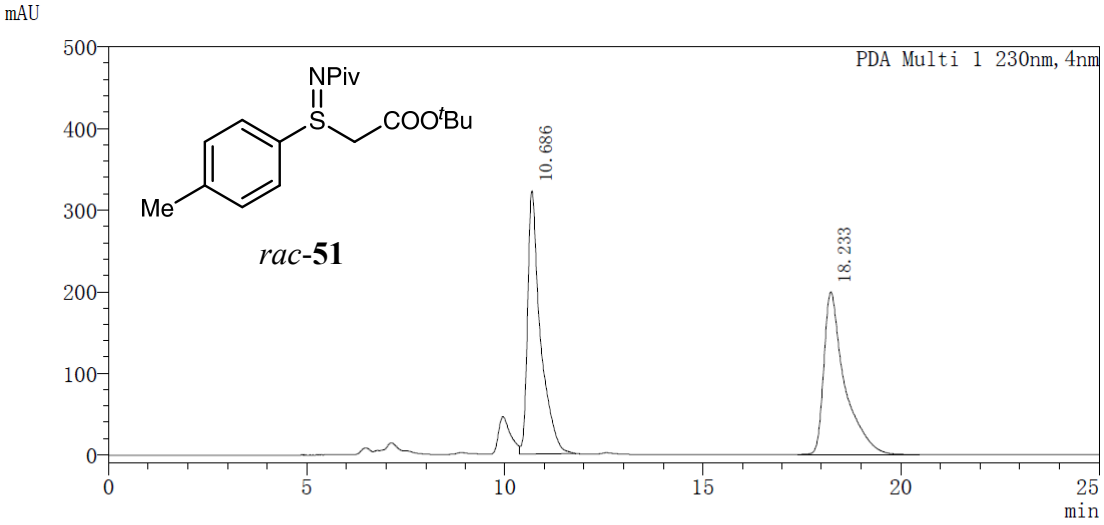


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.871	234546	1.818
2	15.460	12665457	98.182

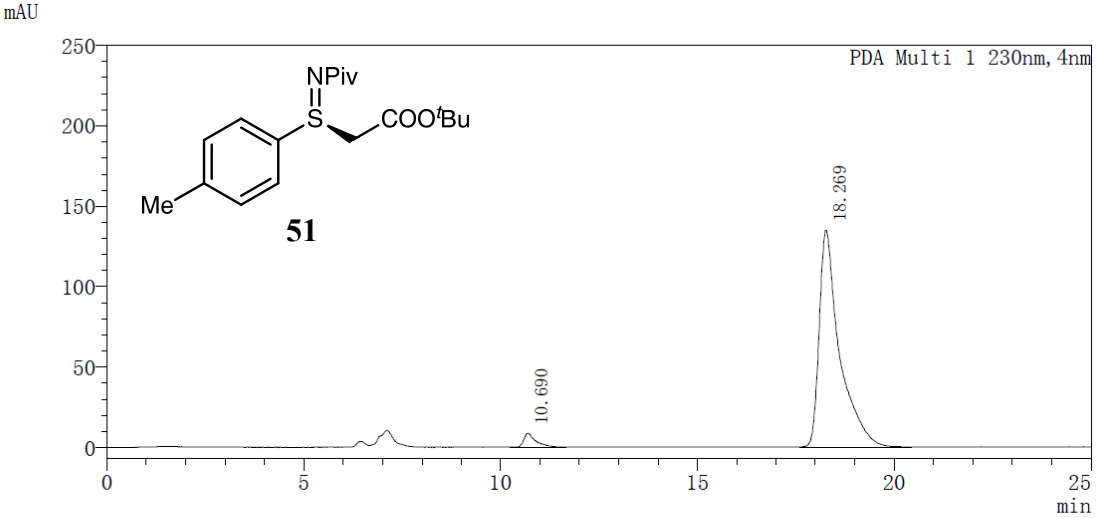
HPLC of 51



Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	10.686	7246052	49.976
2	18.233	7253146	50.024

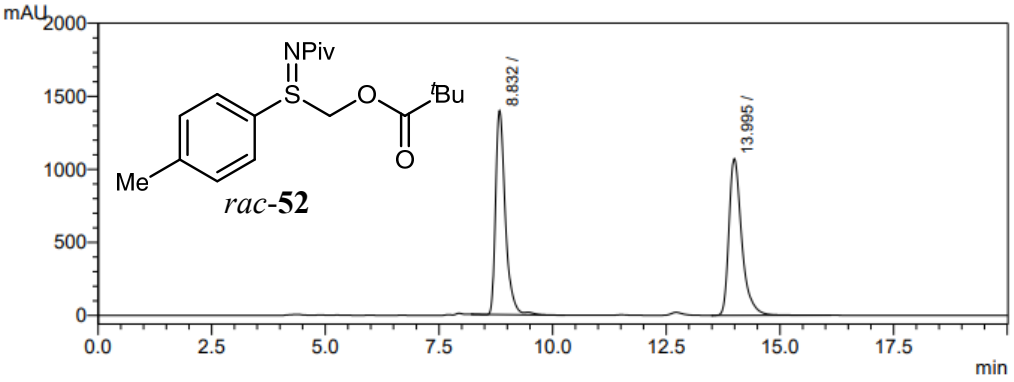


Peak Table

PDA Ch1 230nm

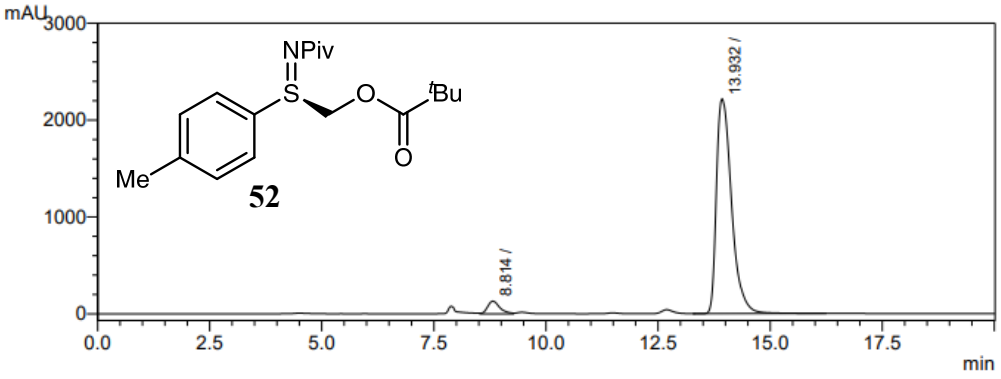
Peak#	Ret. Time	Area	Area%
1	10.690	179675	3.582
2	18.269	4836319	96.418

HPLC of 52



PDA Ch1 227nm

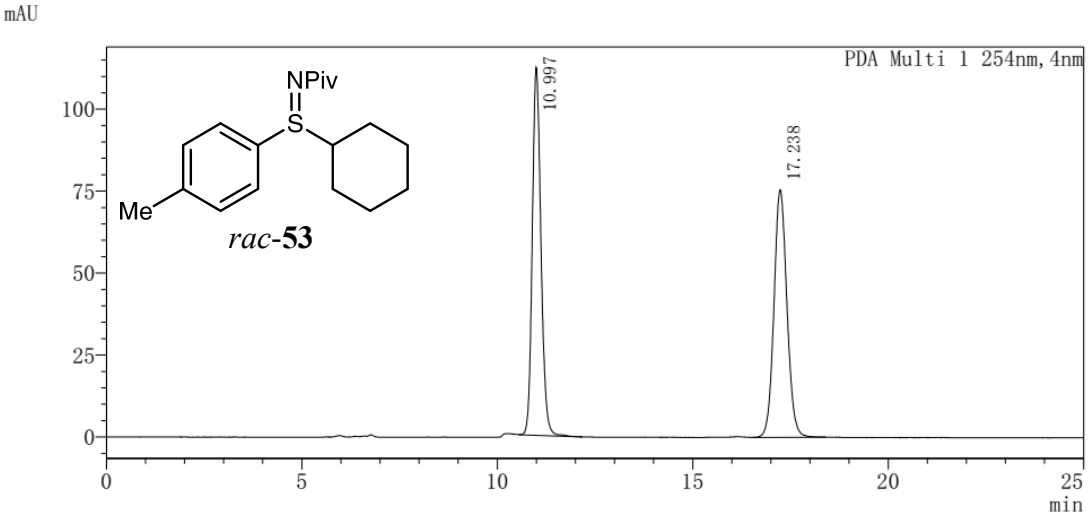
Peak#	Ret. Time	Area	Area%
1	8.832	20937401	49.822
2	13.995	21086733	50.178



PDA Ch1 227nm

Peak#	Ret. Time	Area	Area%
1	8.814	2474625	4.524
2	13.932	52221423	95.476

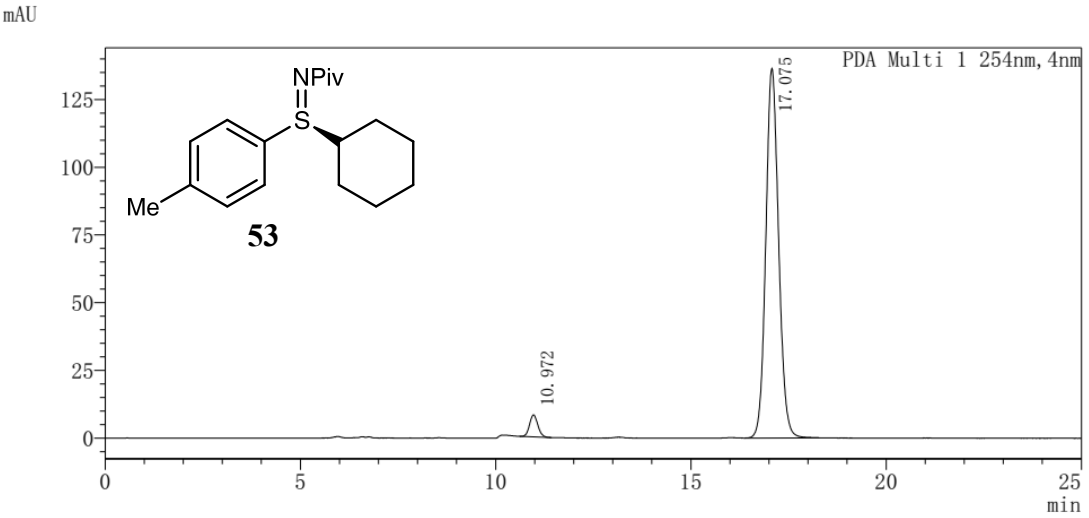
HPLC of 53



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.997	1728035	49.774
2	17.238	1743739	50.226

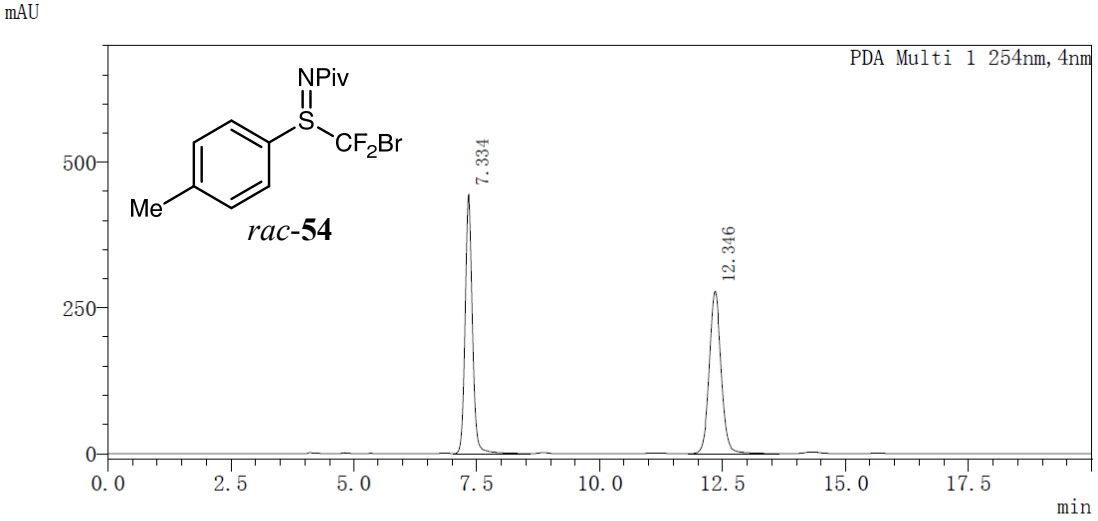


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.972	121329	3.751
2	17.075	3113325	96.249

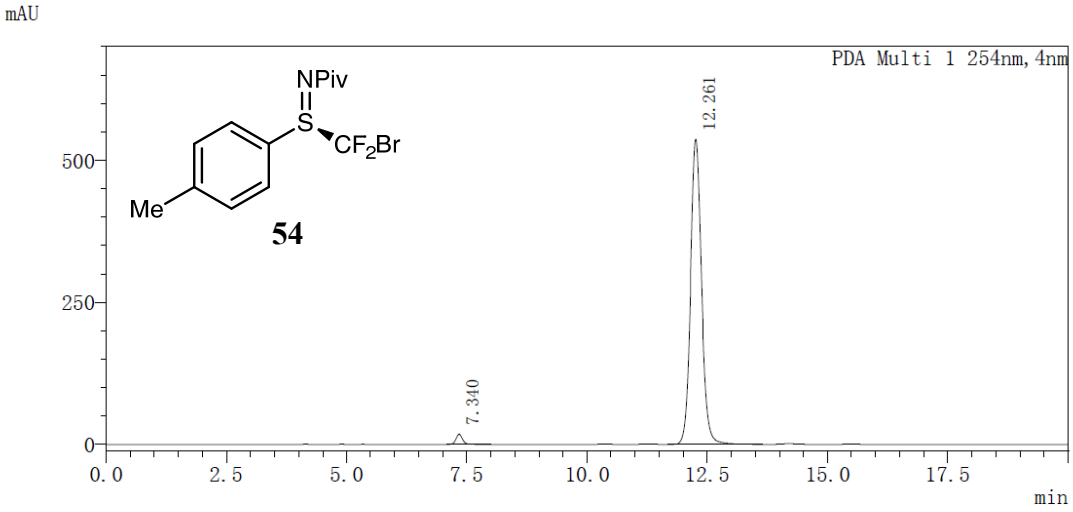
HPLC of 54



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.334	4650513	49.893
2	12.346	4670429	50.107

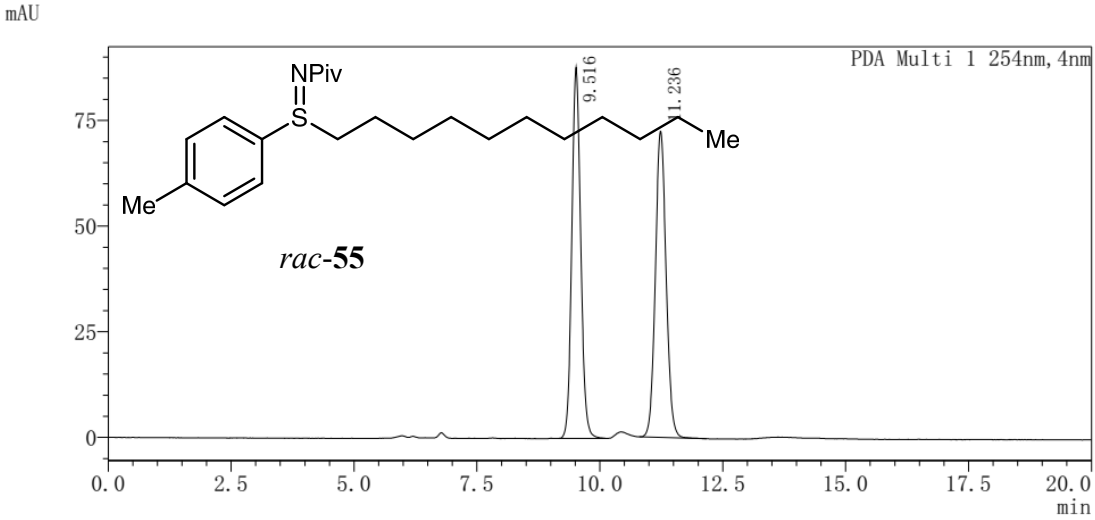


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.340	174039	2.014
2	12.261	8466356	97.986

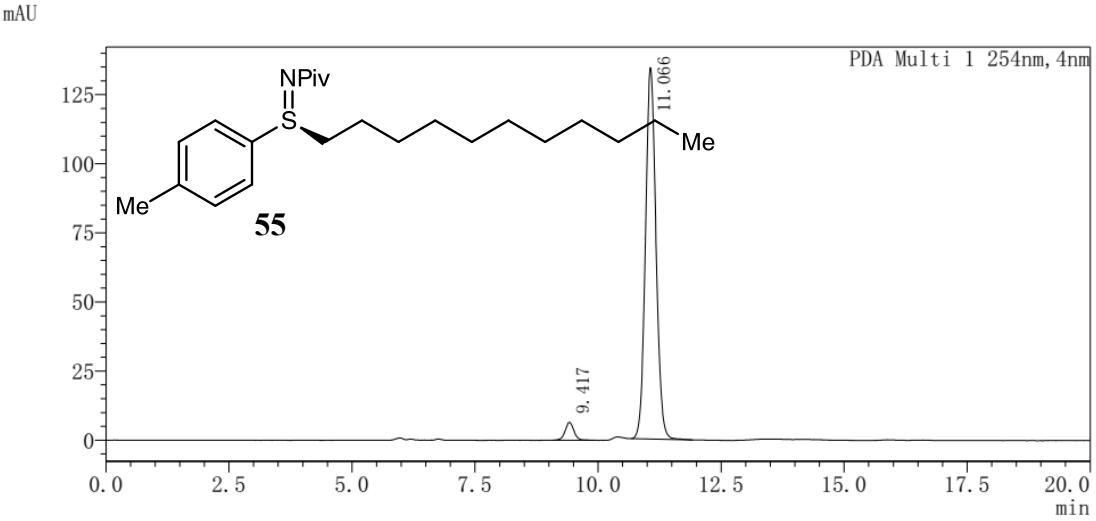
HPLC of 55



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.516	1107184	50.115
2	11.236	1102115	49.885

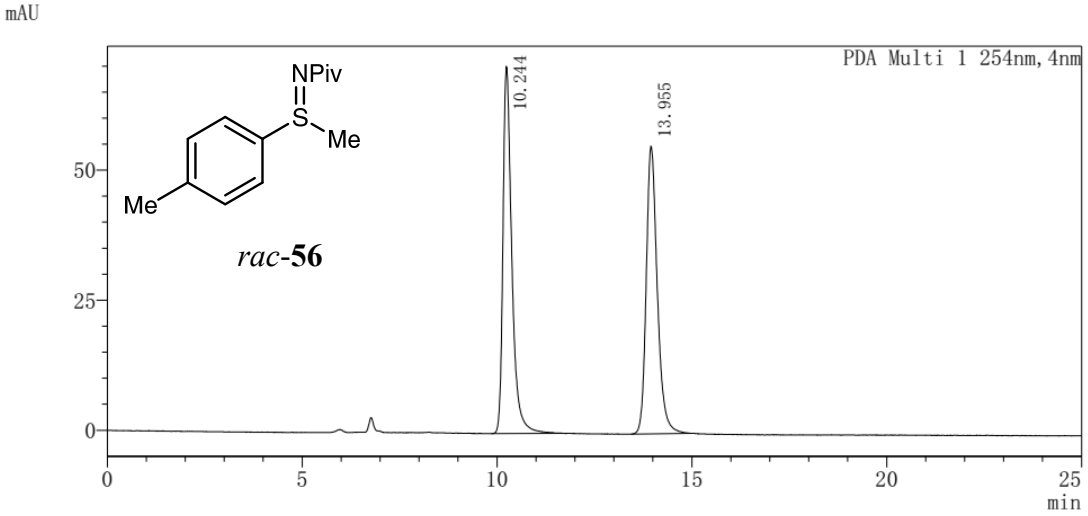


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.417	81672	3.928
2	11.066	1997574	96.072

HPLC of 56

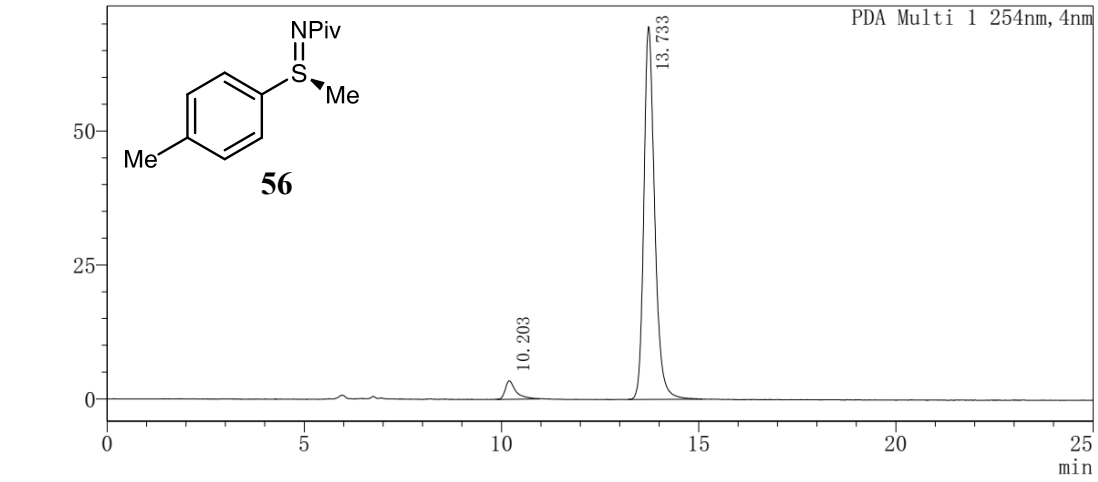


rac-**56**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.244	1119850	50.658
2	13.955	1090774	49.342



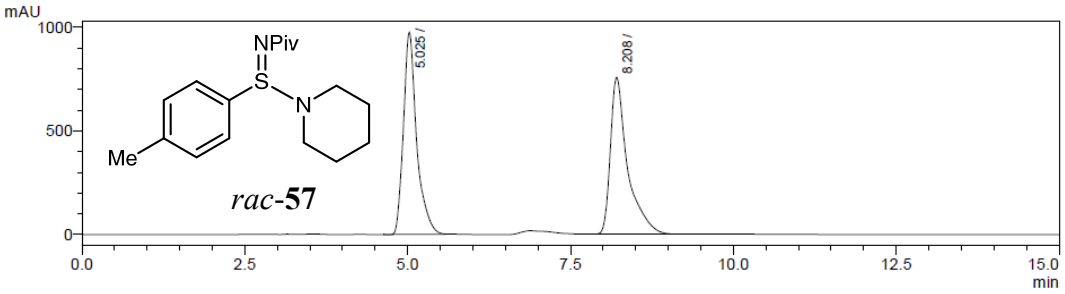
56

Peak Table

PDA Ch1 254nm

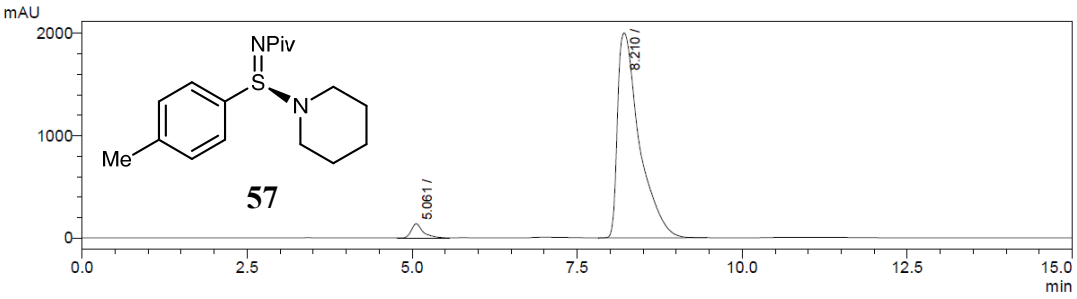
Peak#	Ret. Time	Area	Area%
1	10.203	64491	4.626
2	13.733	1329455	95.374

HPLC of 57



PDA Ch1 254nm

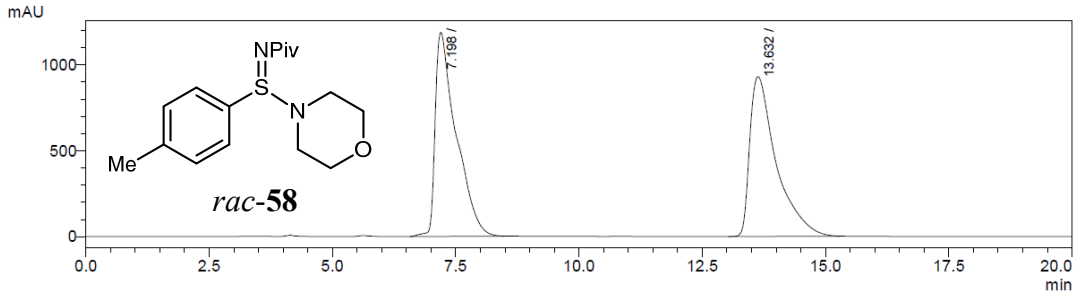
Peak#	Ret. Time	Area	Area%
1	5.025	13776938	49.878
2	8.208	13844449	50.122



PDA Ch1 254nm

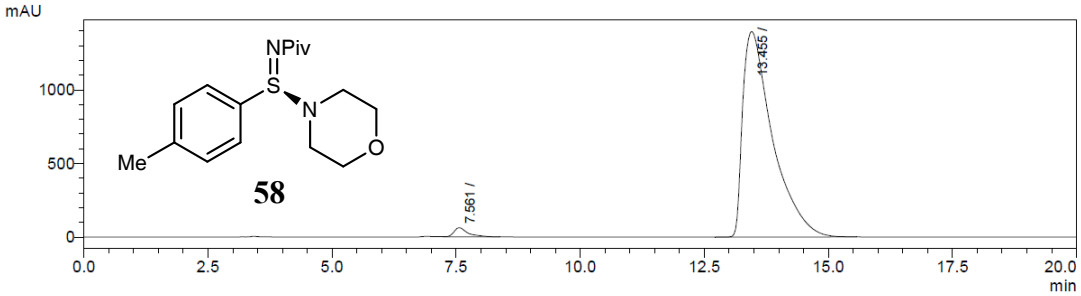
Peak#	Ret. Time	Area	Area%
1	5.061	1709751	3.585
2	8.210	45976221	96.415

HPLC of 58



PDA Ch1 254nm

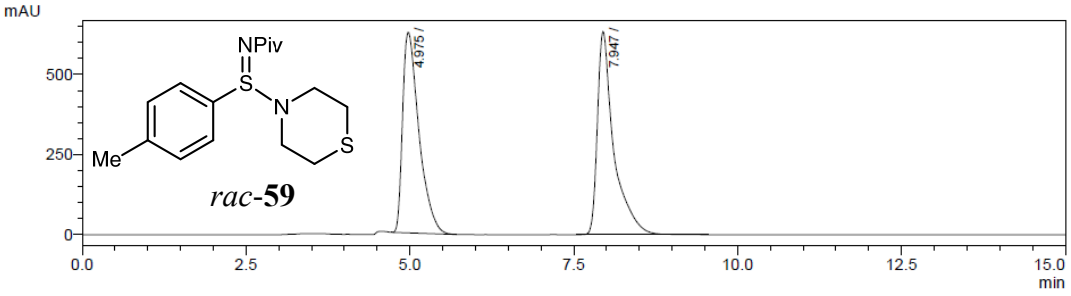
Peak#	Ret. Time	Area	Area%
1	7.198	35063568	50.306
2	13.632	34636634	49.694



PDA Ch1 254nm

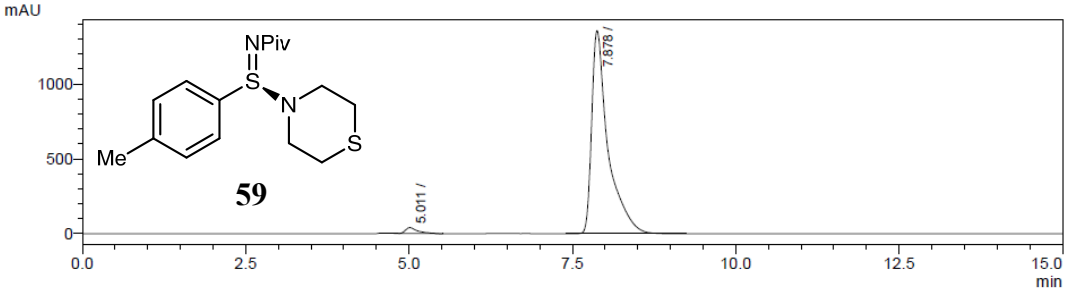
Peak#	Ret. Time	Area	Area%
1	7.561	1172955	1.969
2	13.455	58405130	98.031

HPLC of 59



PDA Ch1 254nm

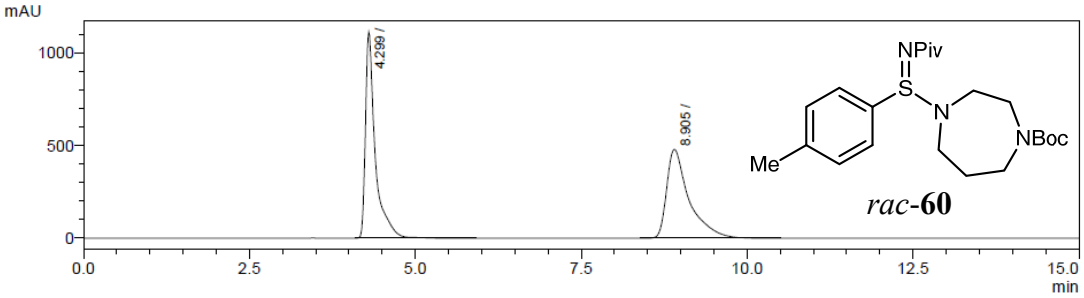
Peak#	Ret. Time	Area	Area%
1	4.975	10842486	49.679
2	7.947	10982692	50.321



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.011	492019	2.043
2	7.878	23590112	97.957

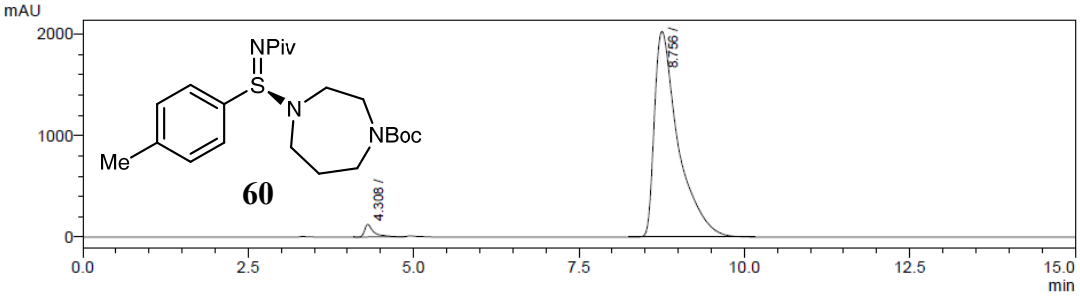
HPLC of 60



rac-**60**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.299	11425402	50.440
2	8.905	11225926	49.560

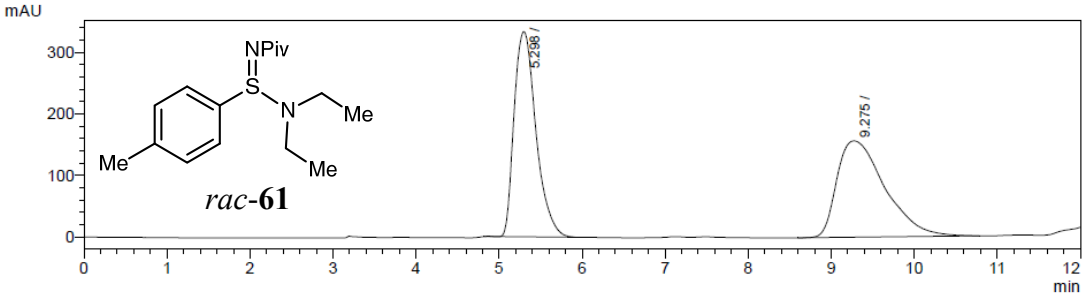


60

PDA Ch1 254nm

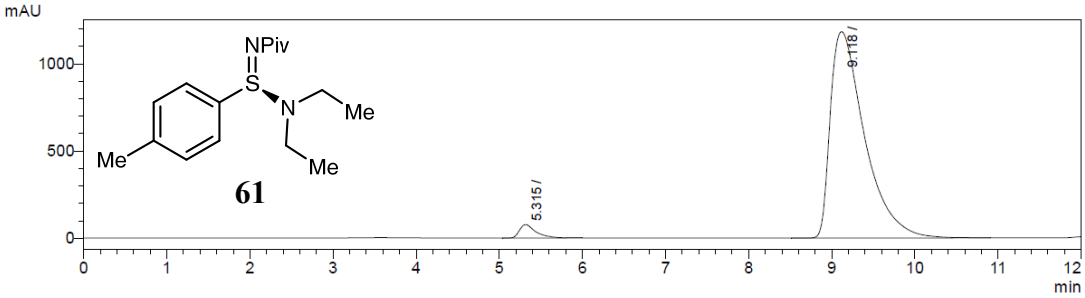
Peak#	Ret. Time	Area	Area%
1	4.308	1185960	2.285
2	8.756	50705968	97.715

HPLC of 61



PDA Ch1 254nm

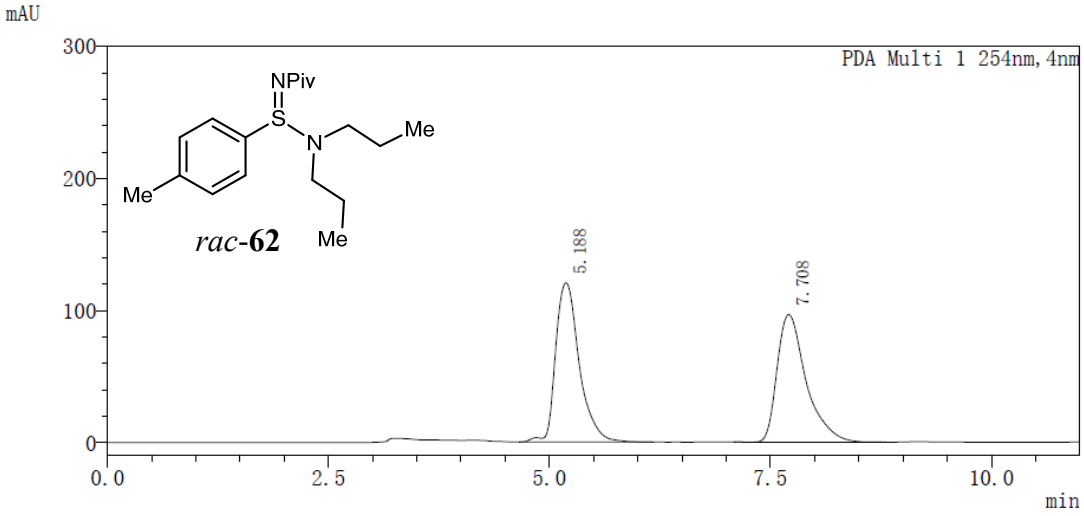
Peak#	Ret. Time	Area	Area%
1	5.298	6100530	49.310
2	9.275	6271372	50.690



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.315	1075156	3.073
2	9.118	33909346	96.927

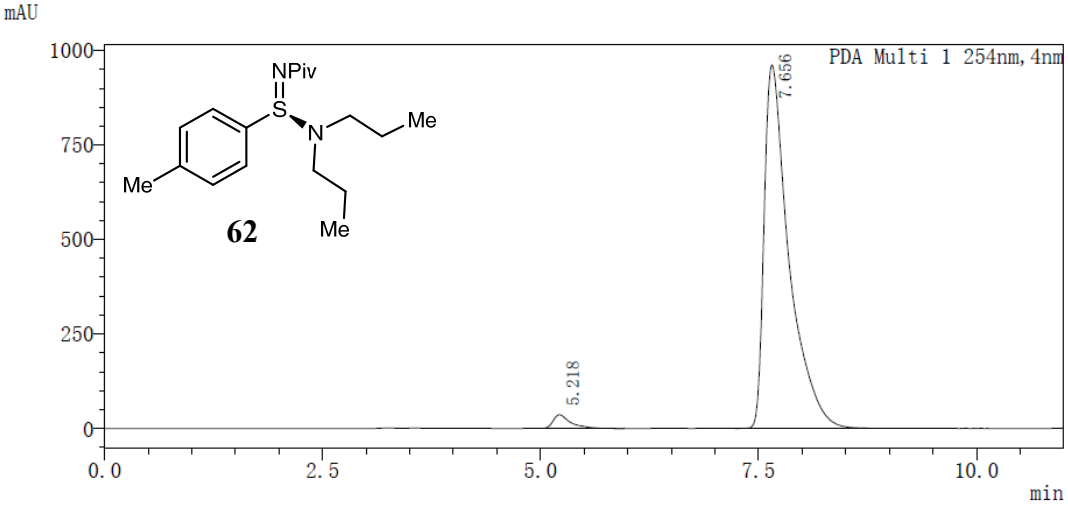
HPLC of 62



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.188	2249901	50.402
2	7.708	2214040	49.598

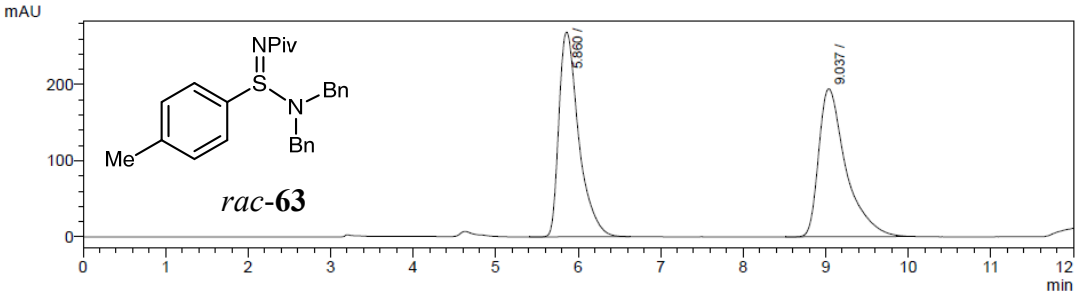


Peak Table

PDA Ch1 254nm

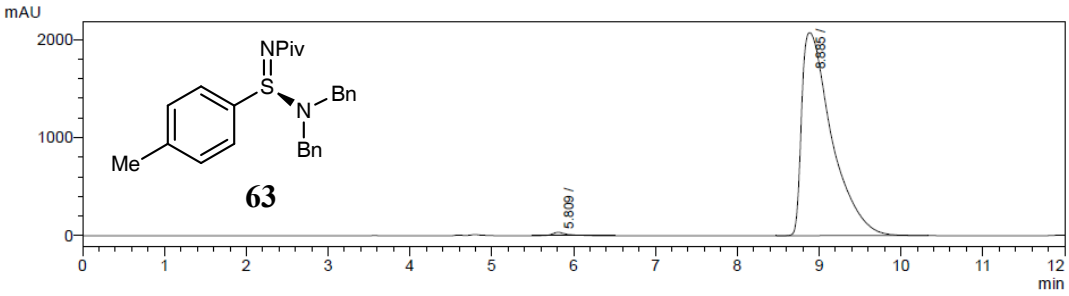
Peak#	Ret. Time	Area	Area%
1	5.218	488568	2.494
2	7.656	19101700	97.506

HPLC of 63



PDA Ch1 254nm

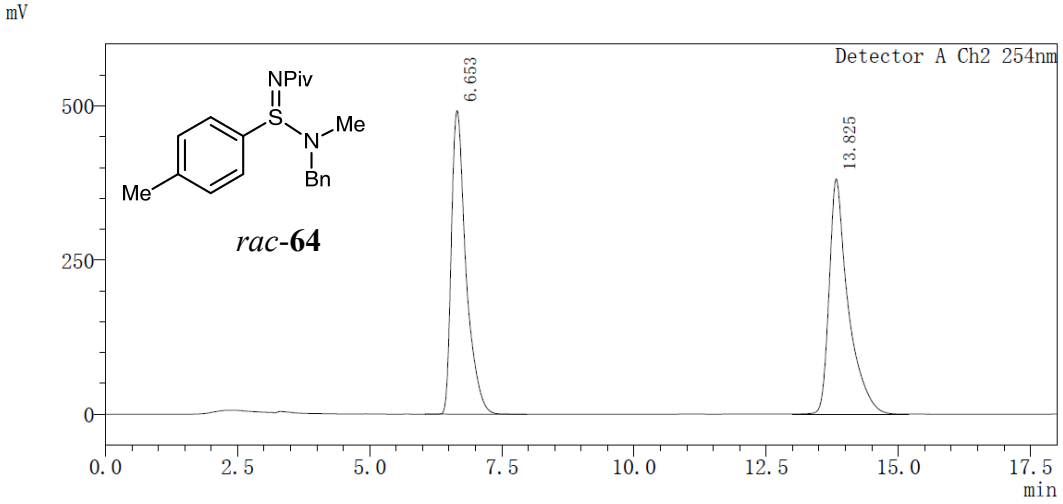
Peak#	Ret. Time	Area	Area%
1	5.860	4488666	50.152
2	9.037	4461527	49.848



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.809	450523	0.850
2	8.885	52525284	99.150

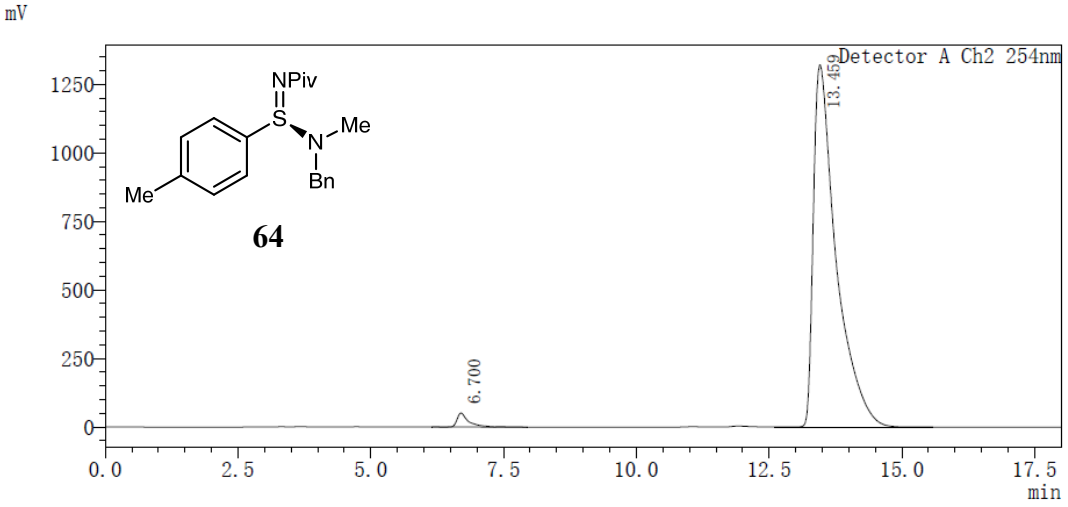
HPLC of 64



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	6.653	9481344	49.804
2	13.825	9555969	50.196

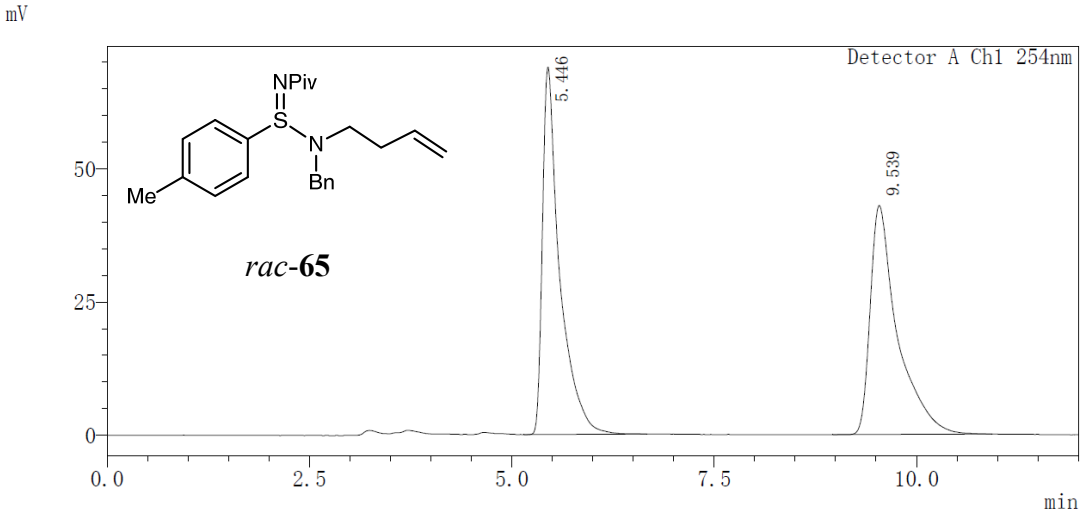


Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	6.700	780428	1.941
2	13.459	39435361	98.059

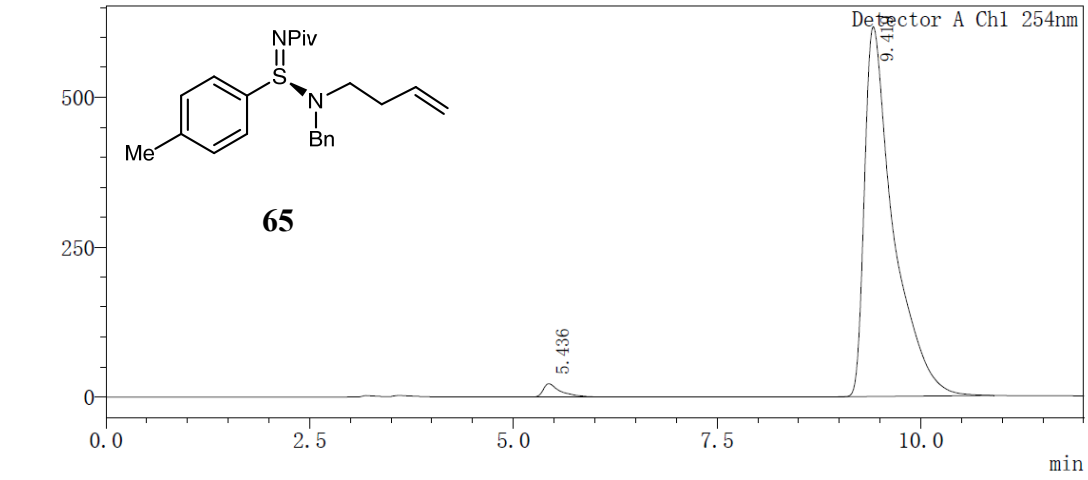
HPLC of 65



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.446	1023615	50.552
2	9.539	1001278	49.448

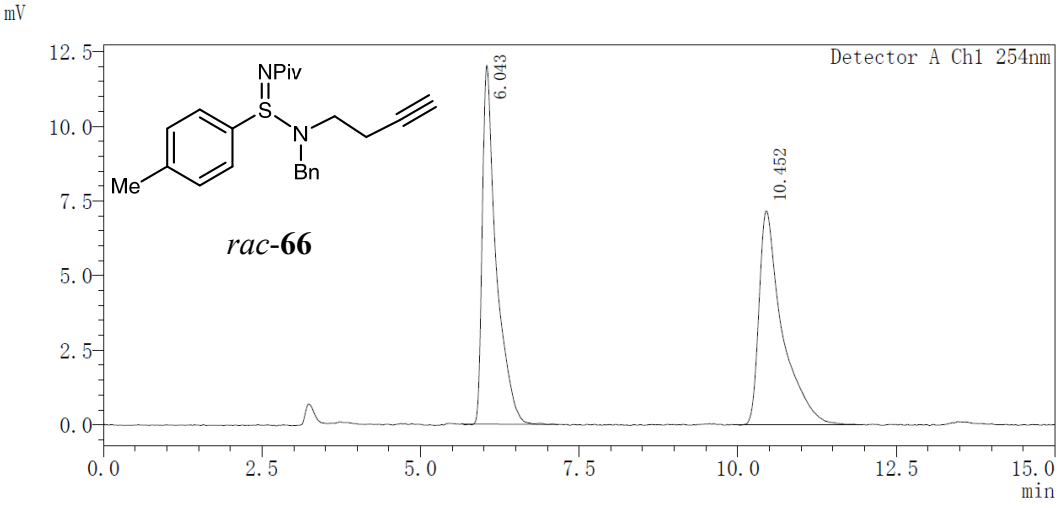


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.436	315074	2.028
2	9.419	15223640	97.972

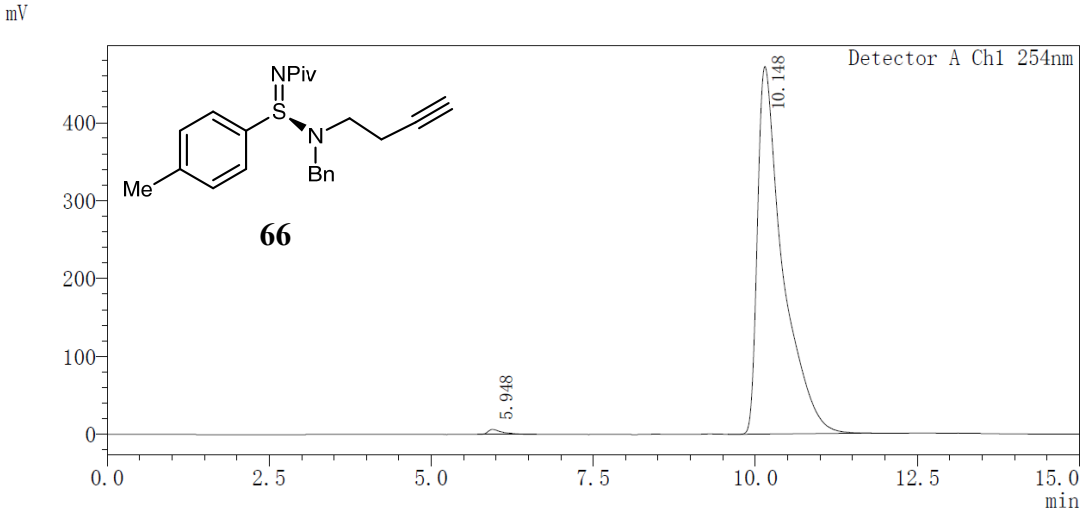
HPLC of 66



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.043	181107	49.780
2	10.452	182706	50.220

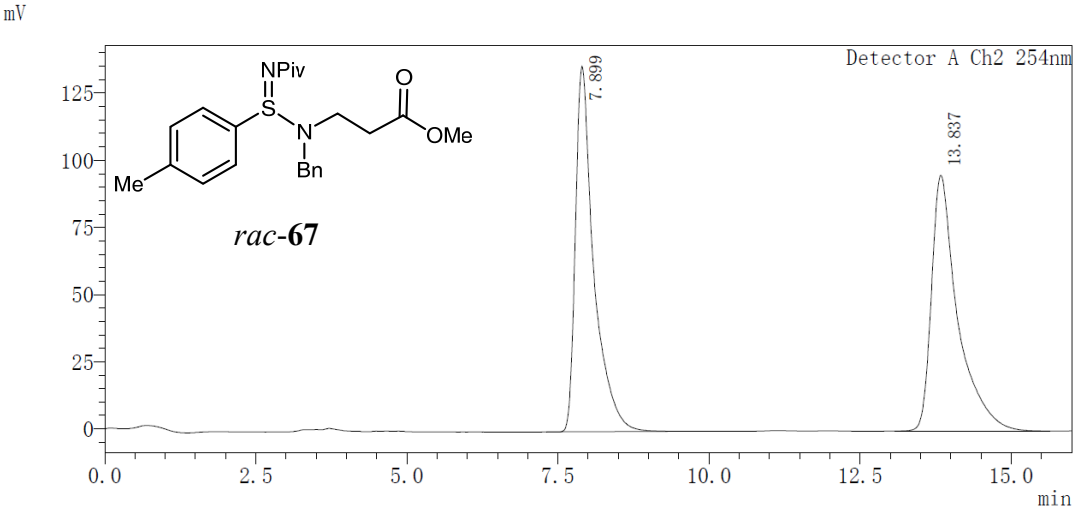


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.948	103054	0.800
2	10.148	12778110	99.200

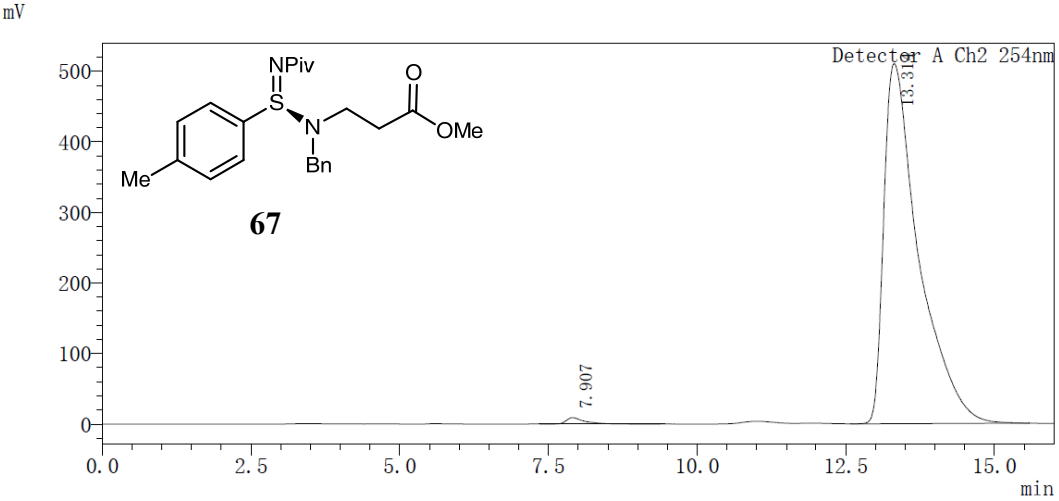
HPLC of 67



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	7.899	2871888	49.920
2	13.837	2881090	50.080

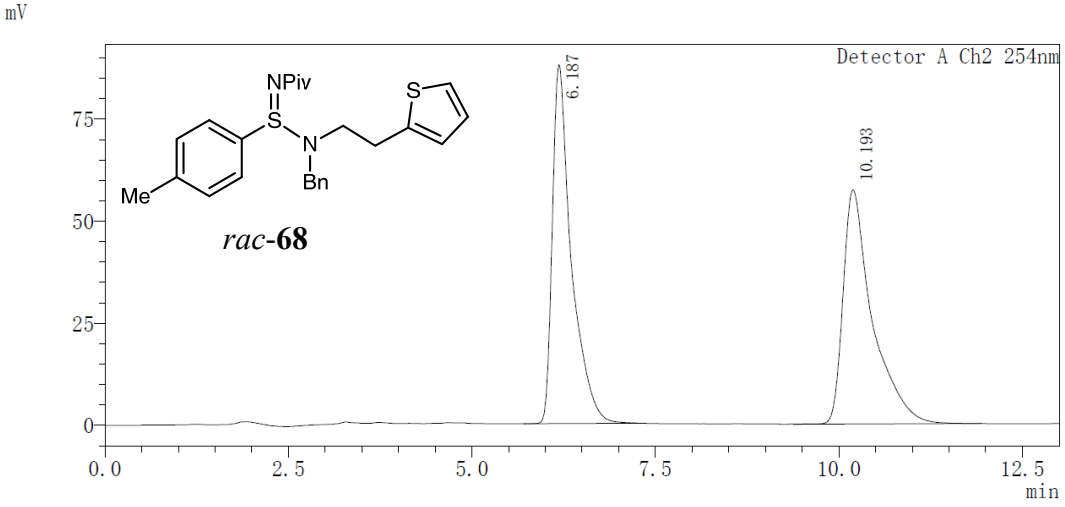


Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	7.907	191007	0.907
2	13.314	20860901	99.093

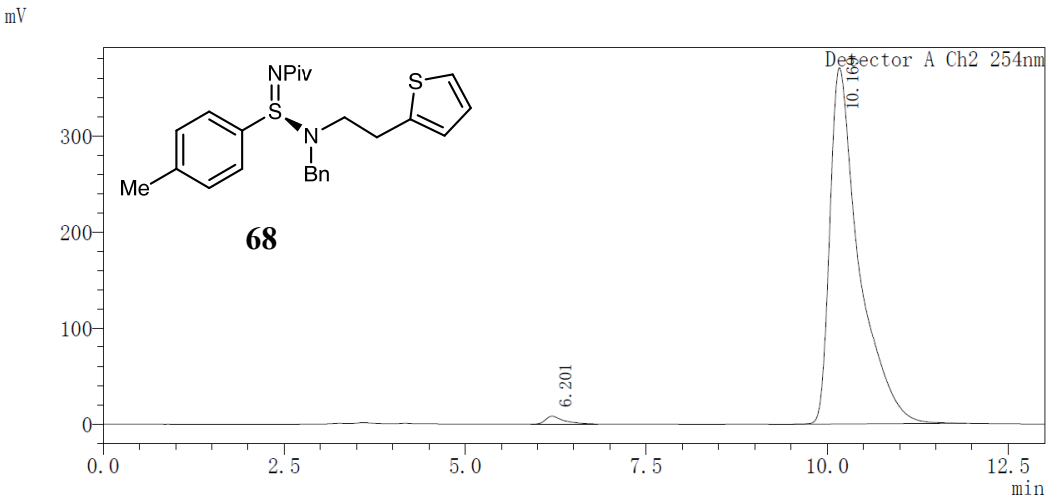
HPLC of 68



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	6.187	1584023	49.952
2	10.193	1587052	50.048

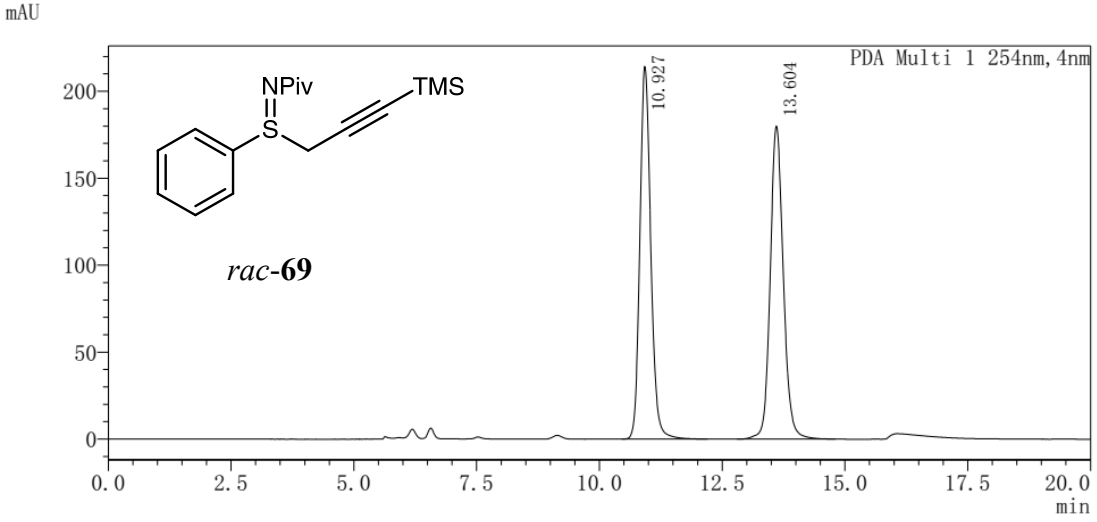


Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	6.201	139679	1.324
2	10.169	10413251	98.676

HPLC of 69

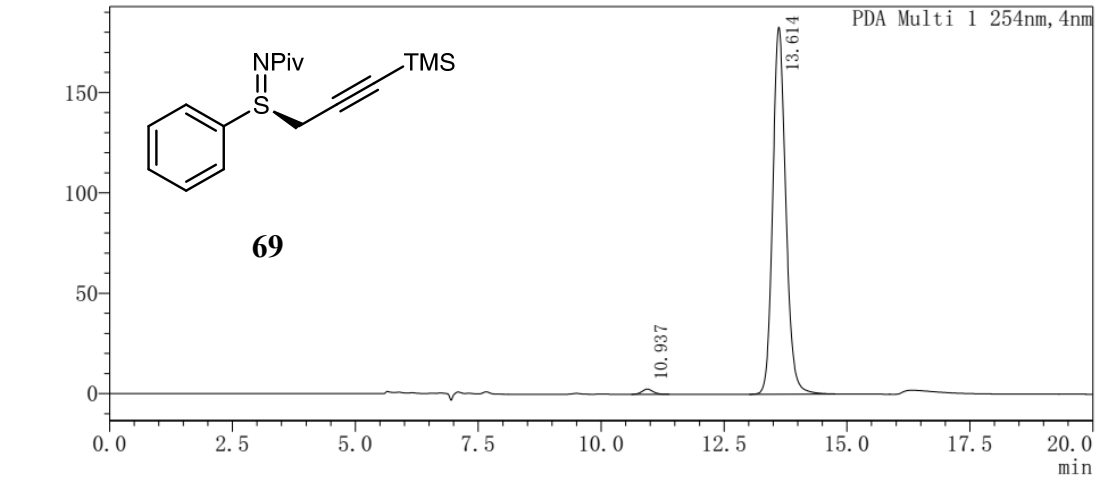


rac-**69**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.927	3310651	49.736
2	13.604	3345737	50.264



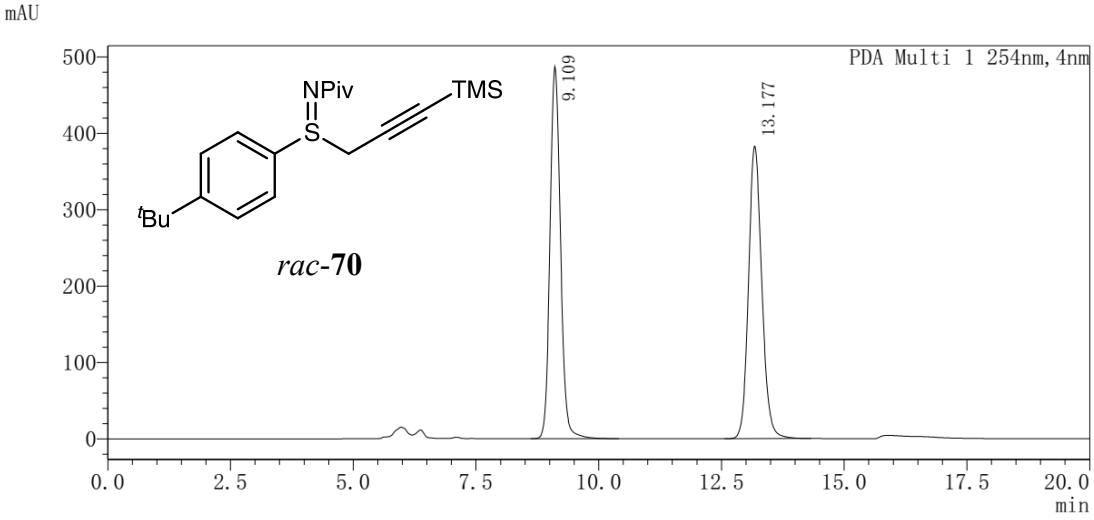
69

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.937	39296	1.148
2	13.614	3382944	98.852

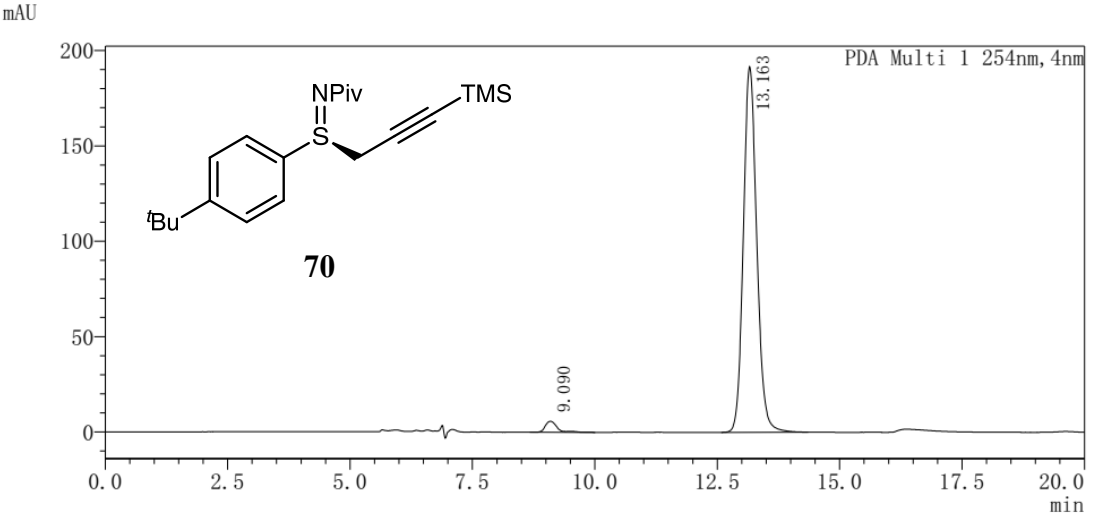
HPLC of 70



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.109	7258586	50.136
2	13.177	7219223	49.864

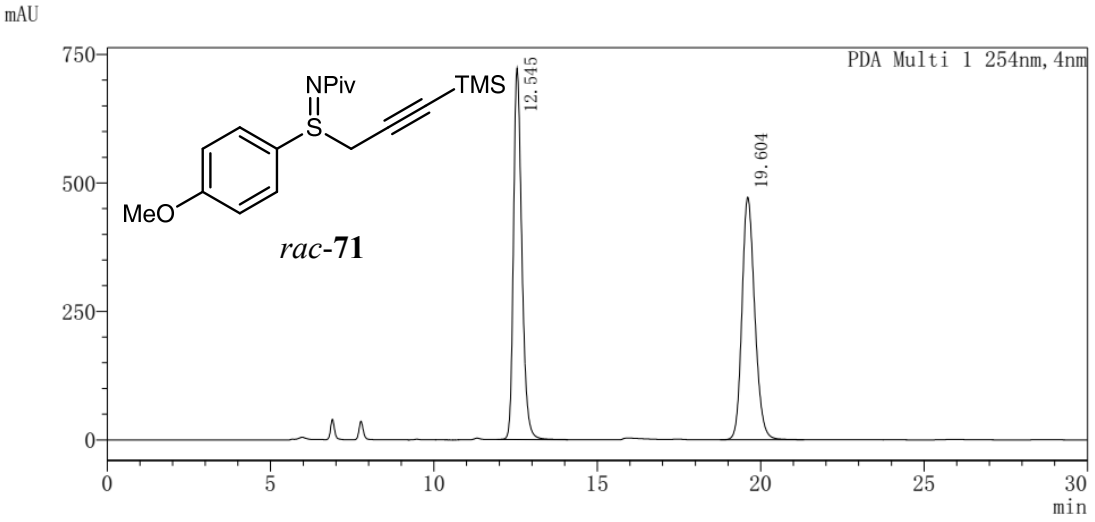


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.090	96986	2.589
2	13.163	3649573	97.411

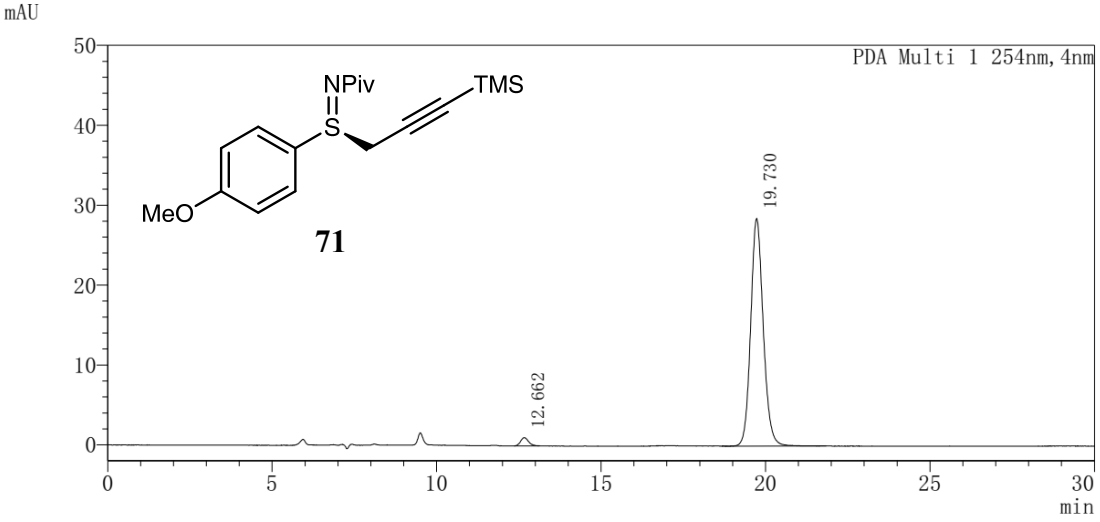
HPLC of 71



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.545	12830959	49.976
2	19.604	12843448	50.024

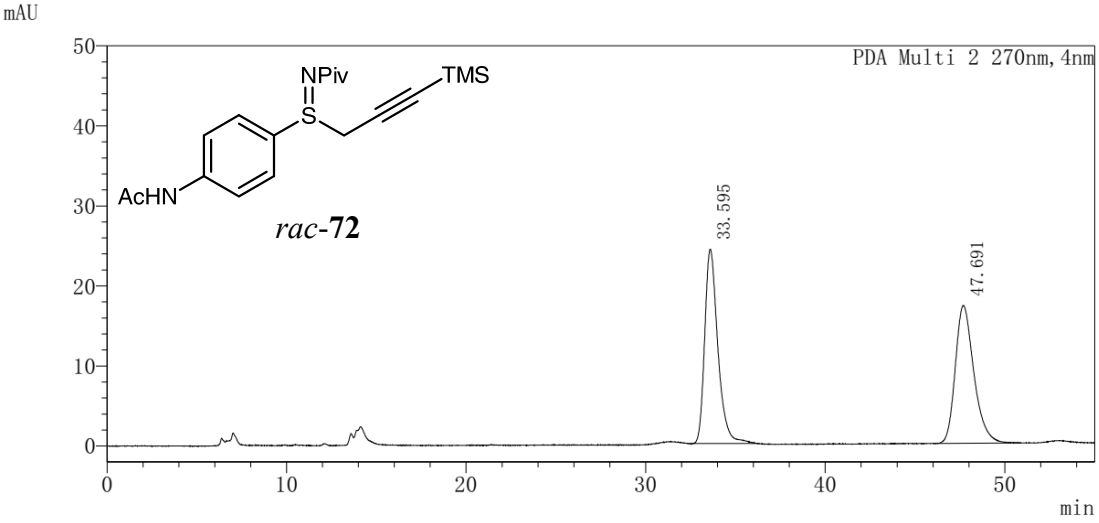


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.662	17223	2.226
2	19.730	756453	97.774

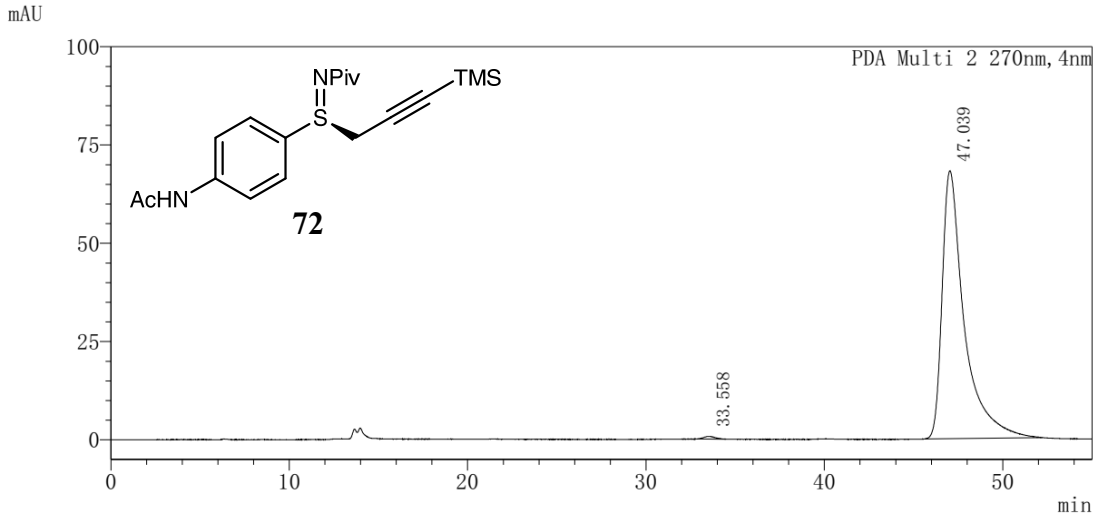
HPLC of 72



Peak Table

PDA Ch2 270nm

Peak#	Ret. Time	Area	Area%
1	33.595	1237726	50.031
2	47.691	1236201	49.969

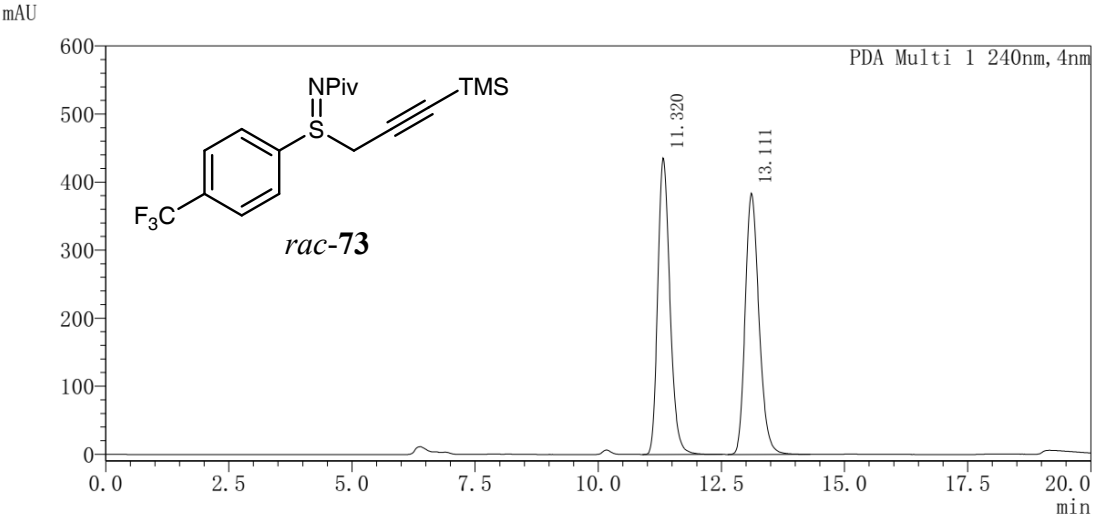


Peak Table

PDA Ch2 270nm

Peak#	Ret. Time	Area	Area%
1	33.558	29716	0.504
2	47.039	5871236	99.496

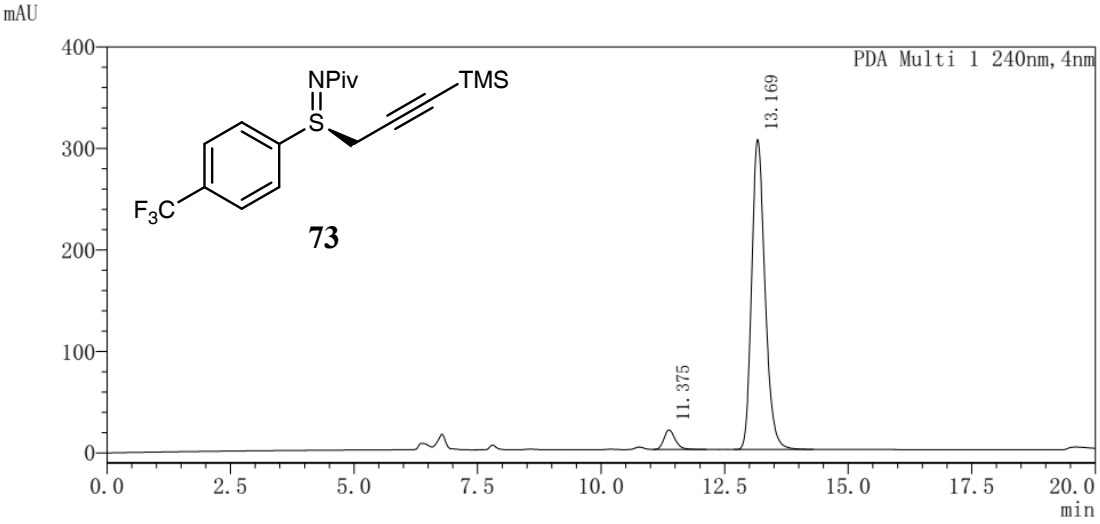
HPLC of 73



Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%
1	11.320	7485634	49.993
2	13.111	7487745	50.007

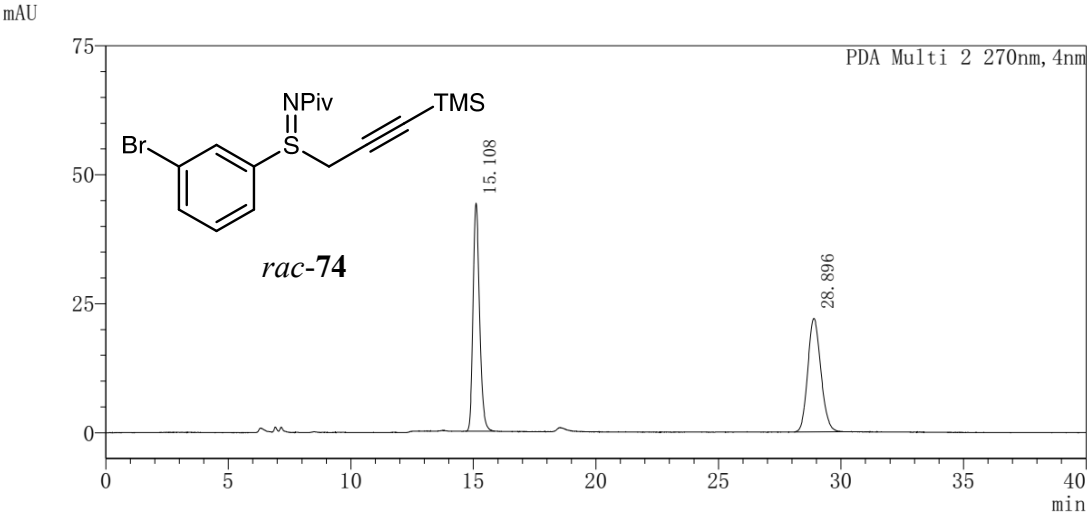


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%
1	11.375	305165	5.049
2	13.169	5738928	94.951

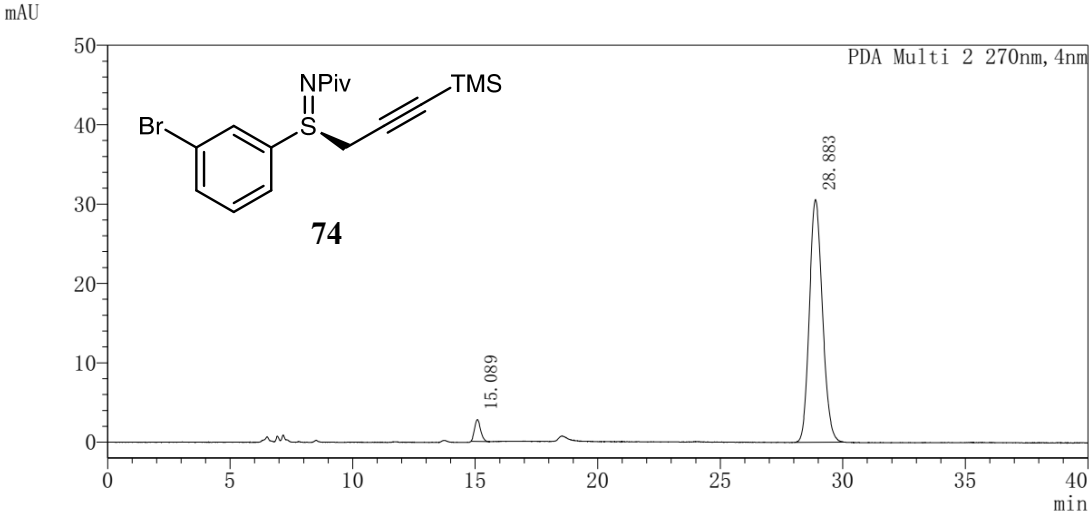
HPLC of 74



Peak Table

PDA Ch2 270nm

Peak#	Ret. Time	Area	Area%
1	15.108	818696	50.092
2	28.896	815676	49.908

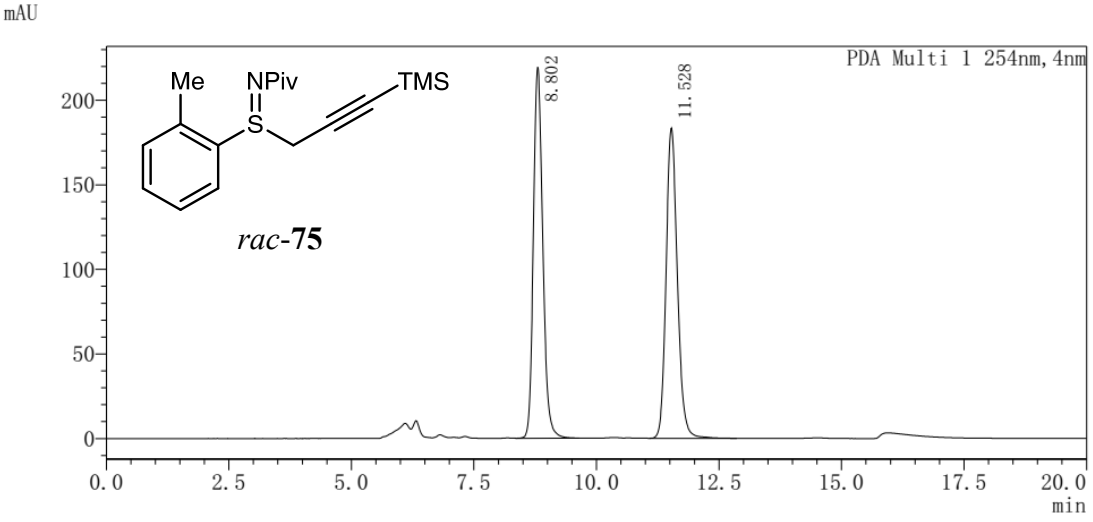


Peak Table

PDA Ch2 270nm

Peak#	Ret. Time	Area	Area%
1	15.089	47088	3.981
2	28.883	1135635	96.019

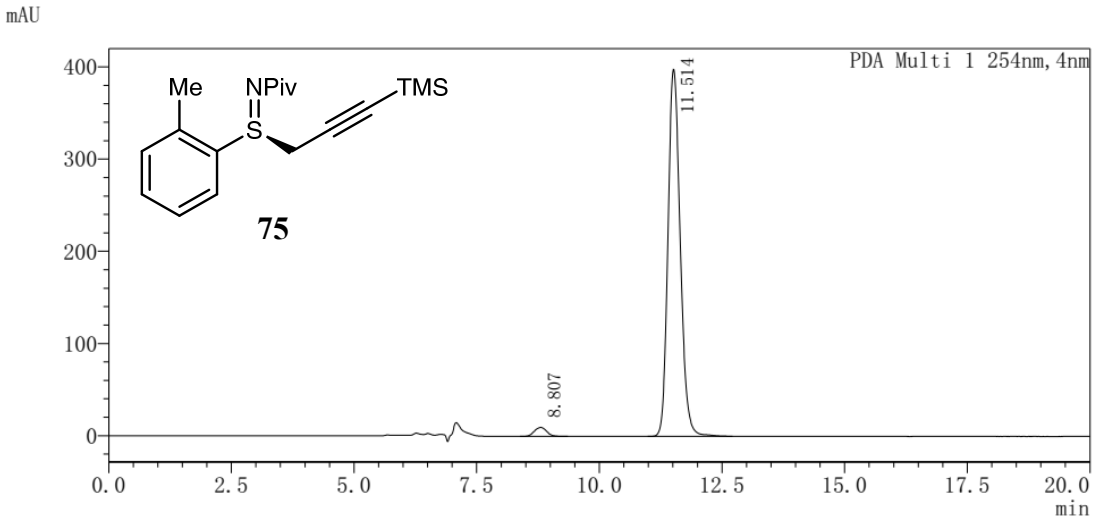
HPLC of 75



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.802	2931633	49.883
2	11.528	2945340	50.117

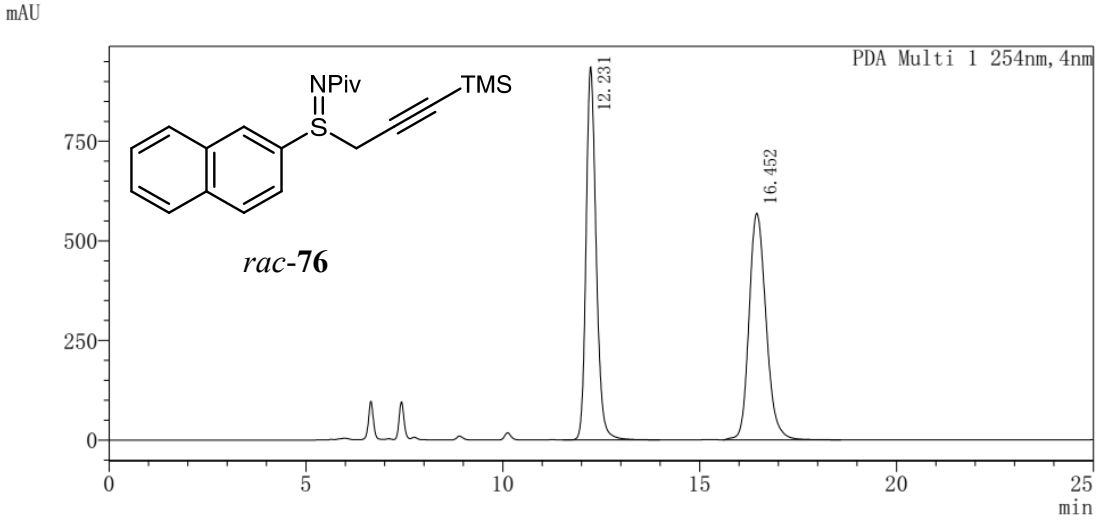


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.807	169231	2.389
2	11.514	6913585	97.611

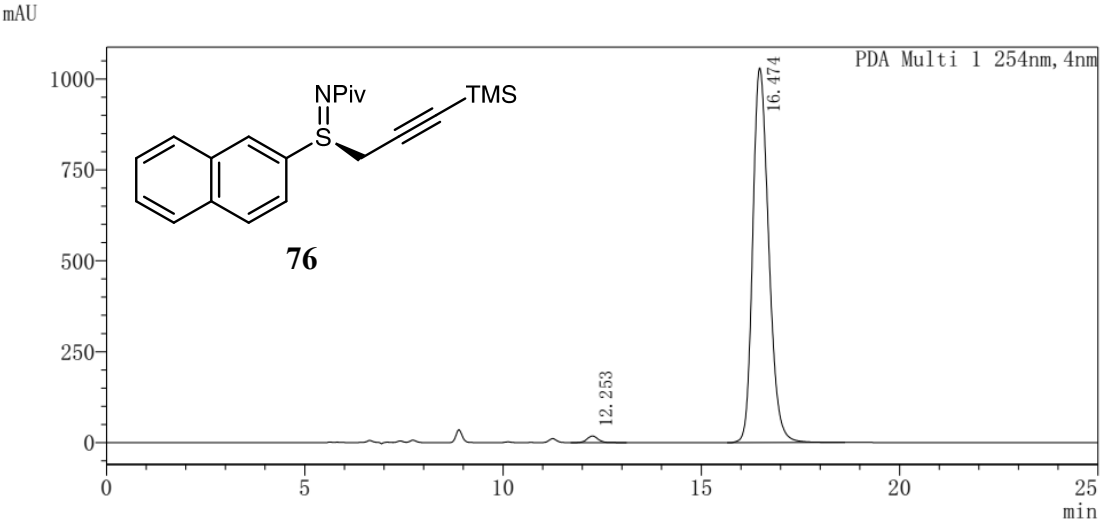
HPLC of 76



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.231	16696156	49.416
2	16.452	17090827	50.584

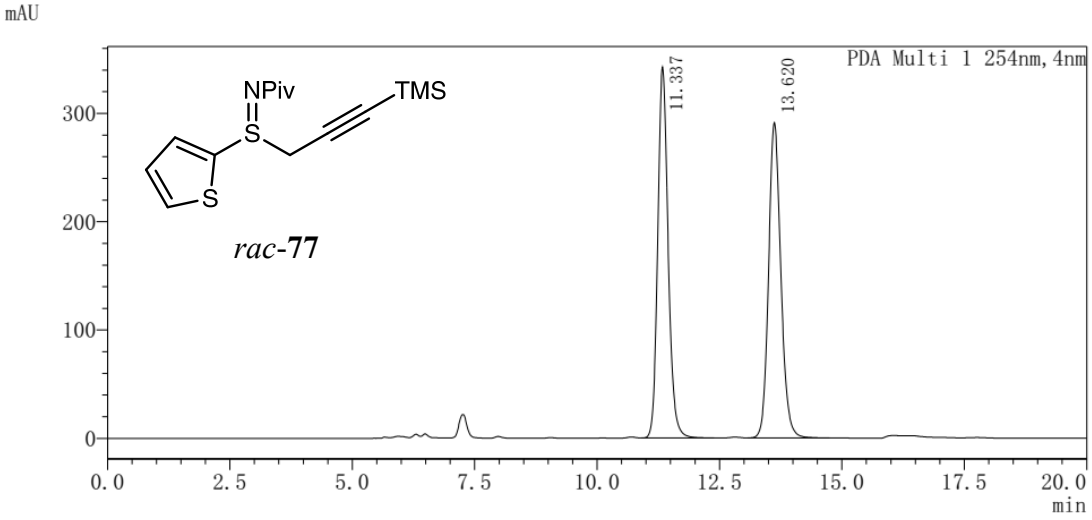


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.253	363241	1.244
2	16.474	28843084	98.756

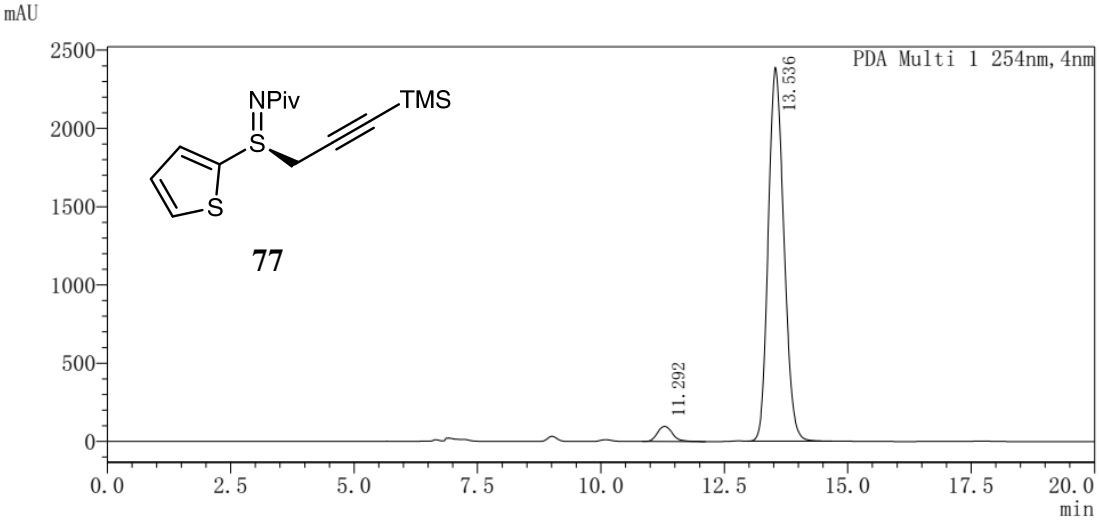
HPLC of 77



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.337	5062484	49.930
2	13.620	5076582	50.070

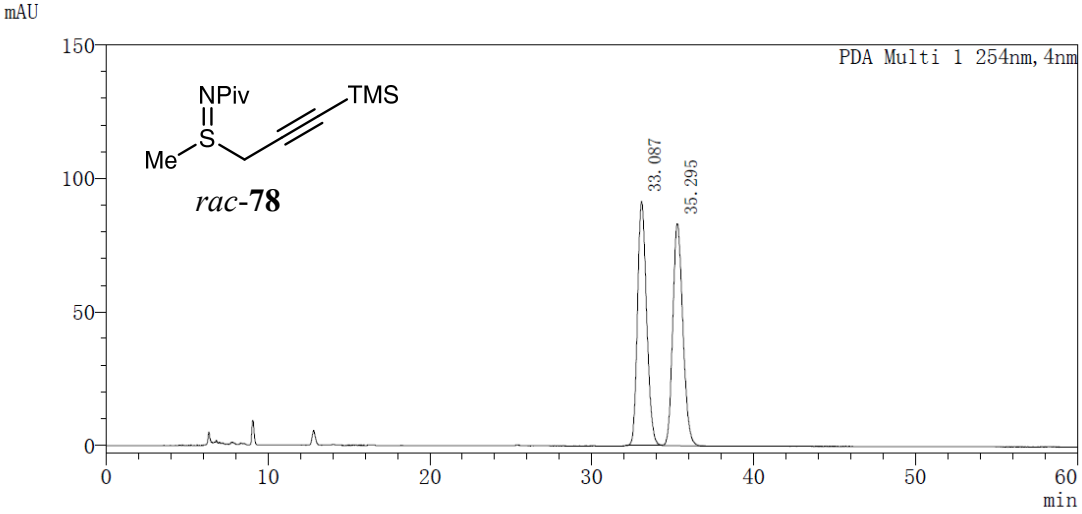


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.292	2035825	3.729
2	13.536	52561458	96.271

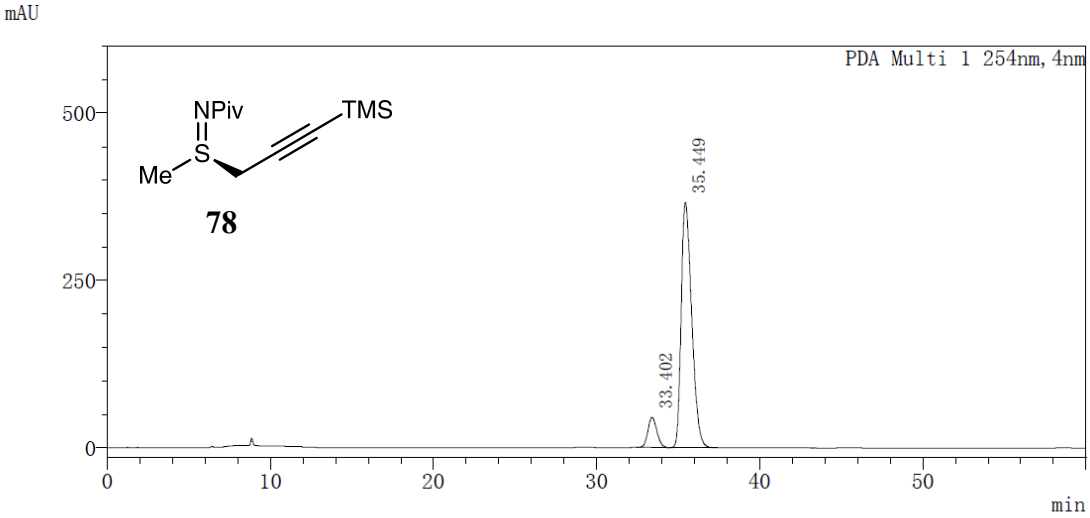
HPLC of 78



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	33.087	3609207	49.966
2	35.295	3614117	50.034

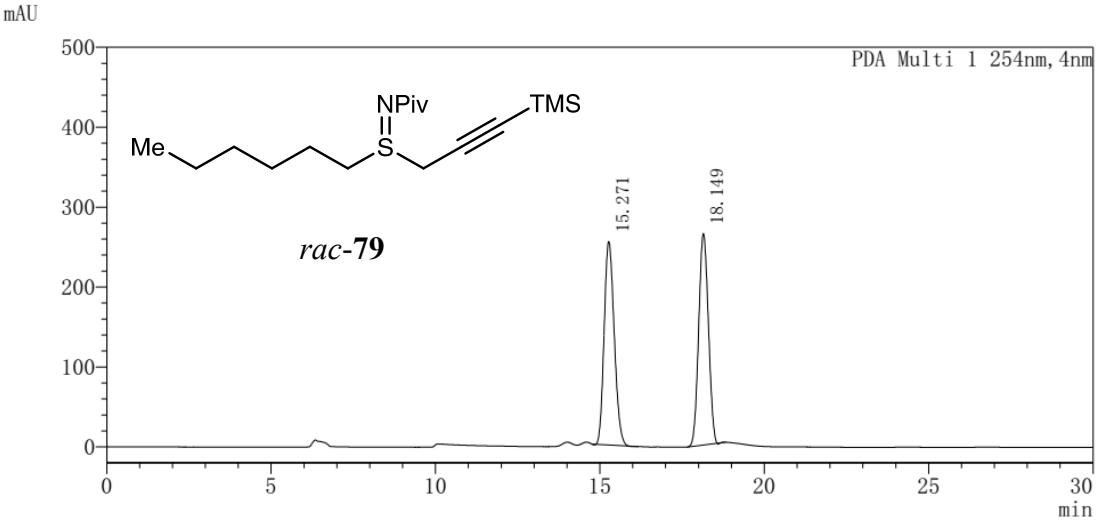


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	33.402	1712184	9.429
2	35.449	16446184	90.571

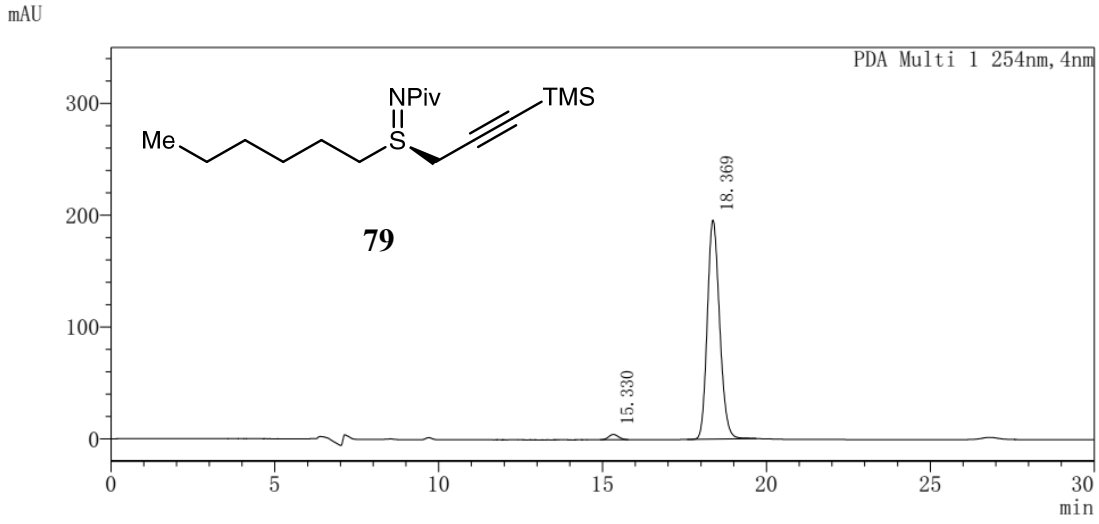
HPLC of 79



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.271	5416040	50.004
2	18.149	5415101	49.996

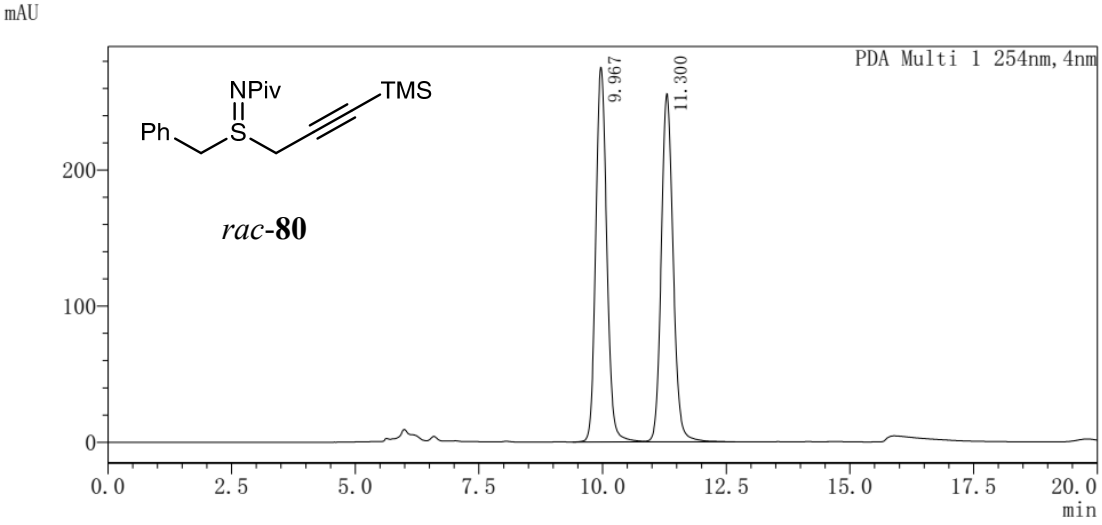


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.330	98497	1.891
2	18.369	5110801	98.109

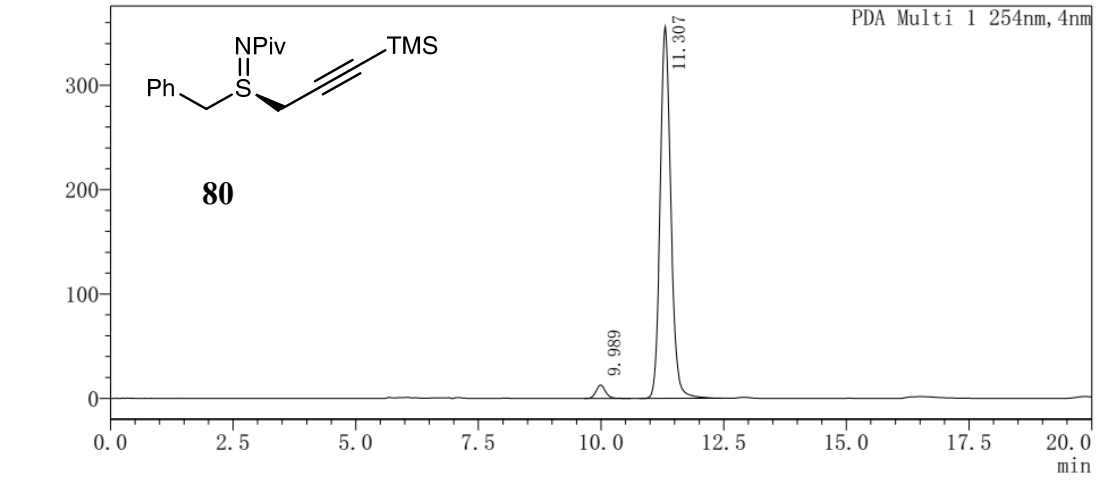
HPLC of 80



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.967	4289840	50.029
2	11.300	4284904	49.971

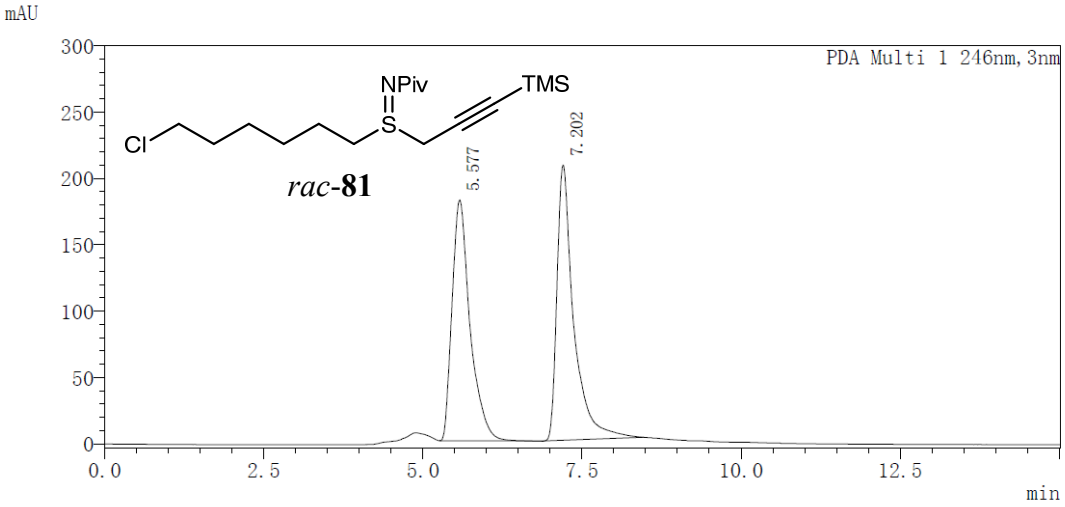


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.989	172957	3.094
2	11.307	5417489	96.906

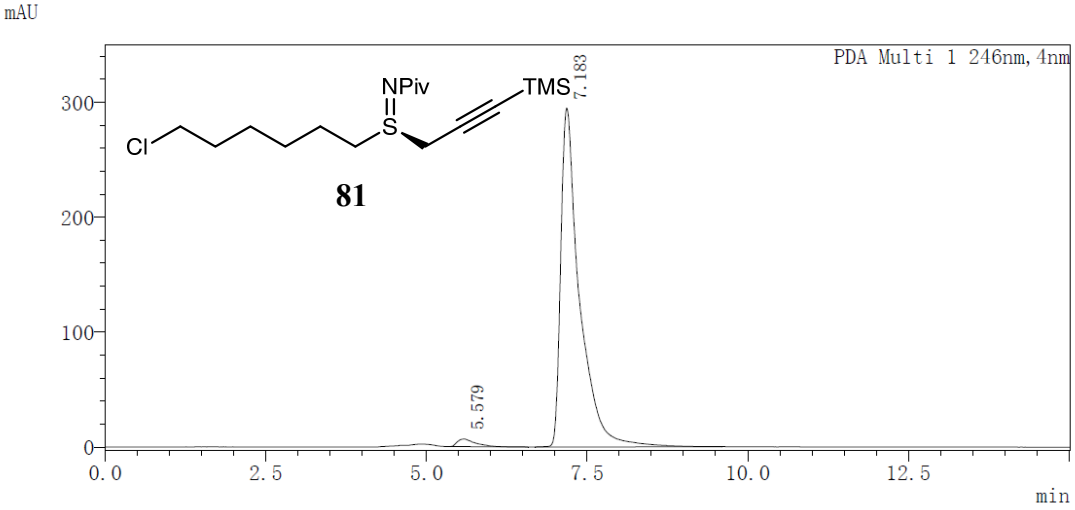
HPLC of 81



Peak Table

PDA Ch1 246nm

Peak#	Ret. Time	Area	Area%
1	5.577	3570063	48.433
2	7.202	3801094	51.567

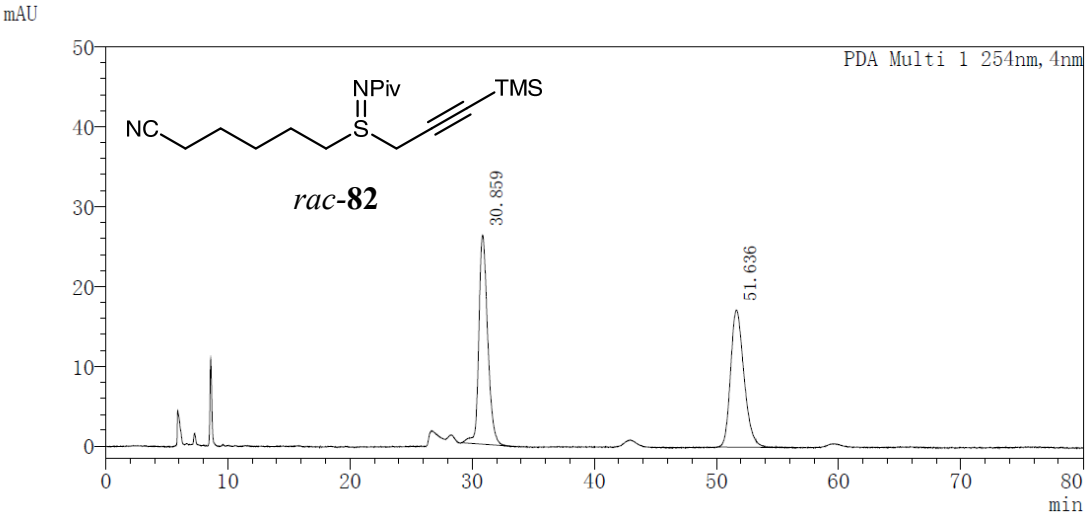


Peak Table

PDA Ch1 246nm

Peak#	Ret. Time	Area	Area%
1	5.579	132830	2.161
2	7.183	6012802	97.839

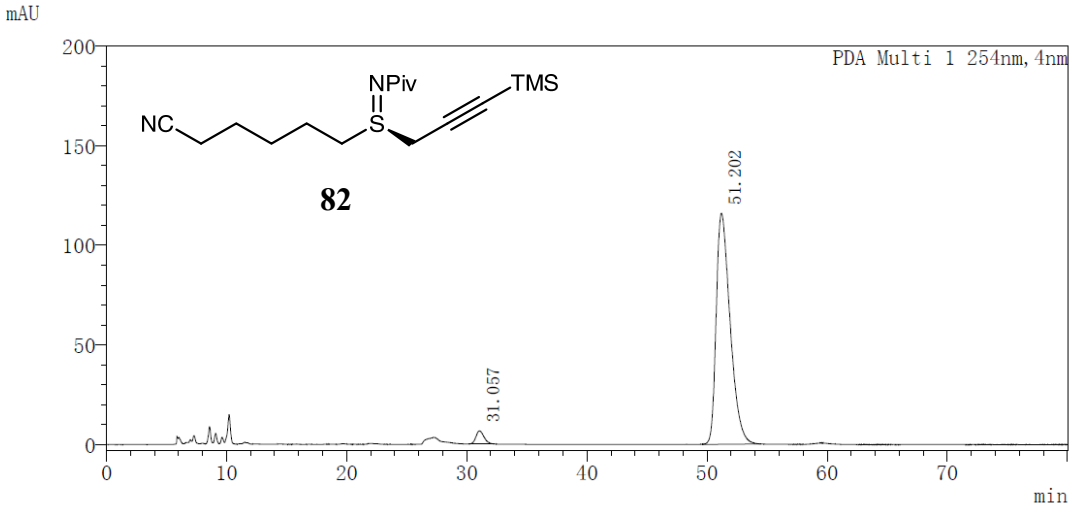
HPLC of 82



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	30.859	1318595	50.108
2	51.636	1312908	49.892

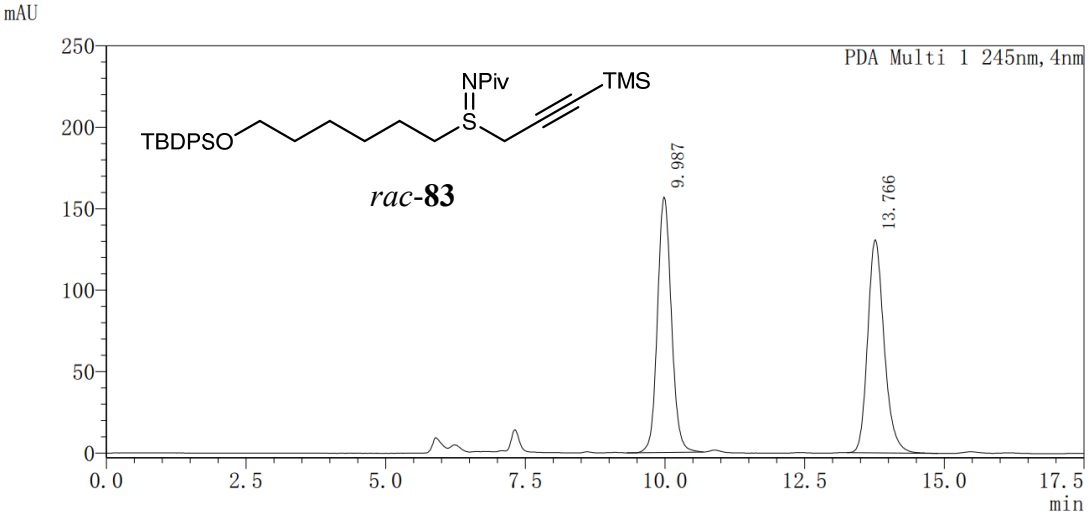


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	31.057	305188	3.164
2	51.202	9339746	96.836

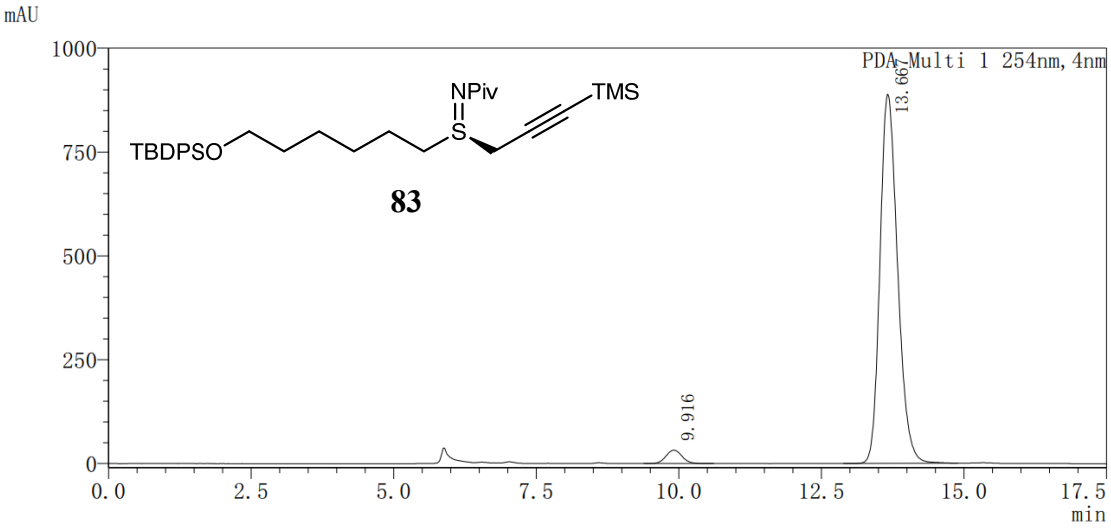
HPLC of 83



Peak Table

PDA Ch1 245nm

Peak#	Ret. Time	Area	Area%
1	9.987	2717266	50.244
2	13.766	2690842	49.756

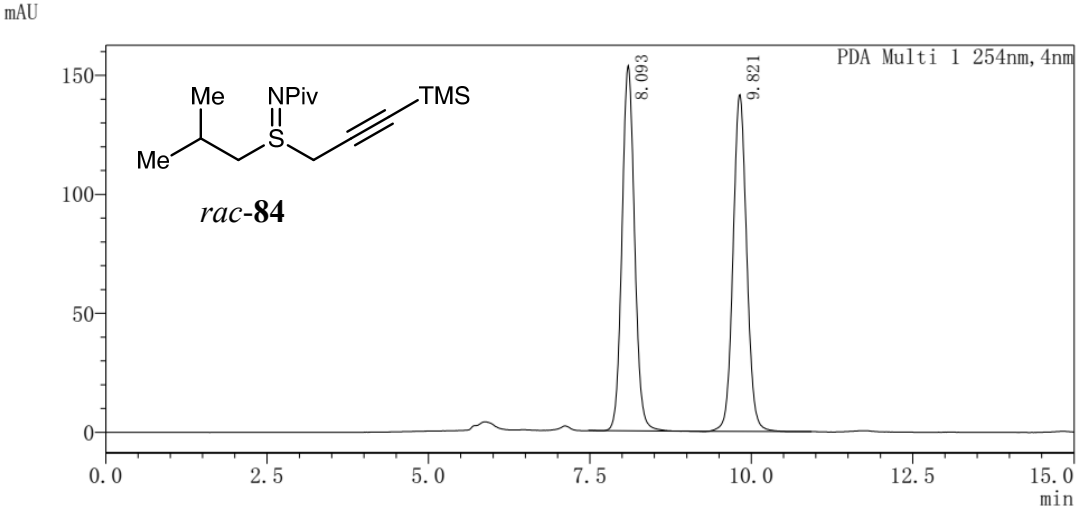


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.916	631581	3.192
2	13.667	19156708	96.808

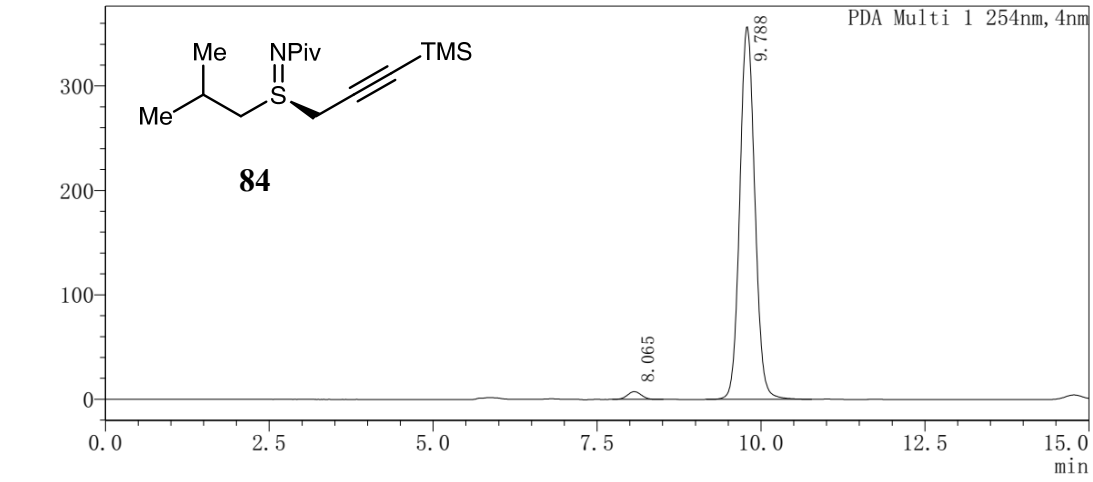
HPLC of 84



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.093	2088936	50.058
2	9.821	2084115	49.942

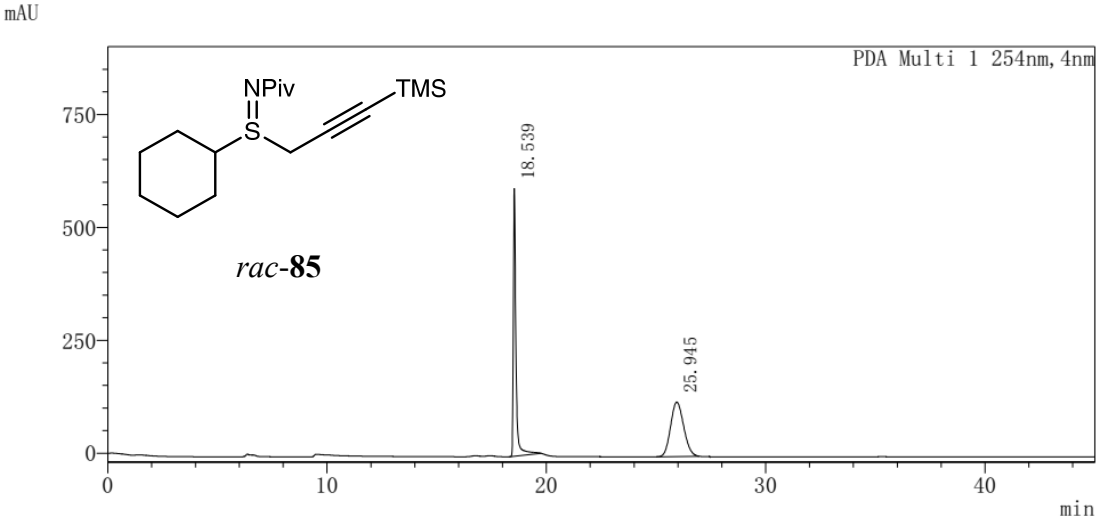


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.065	110014	1.890
2	9.788	5710652	98.110

HPLC of 85

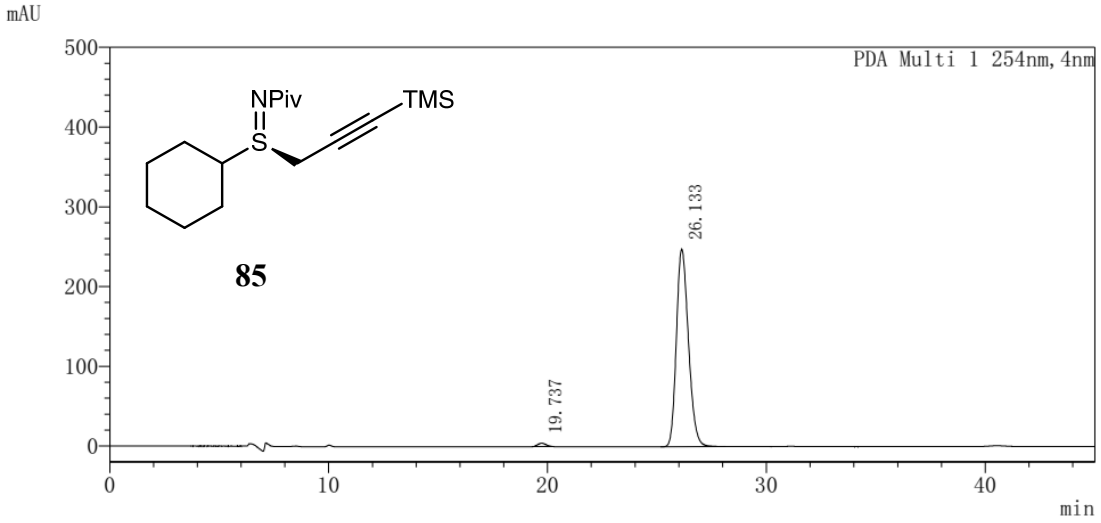


rac-**85**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.539	4916783	49.598
2	25.945	4996521	50.402



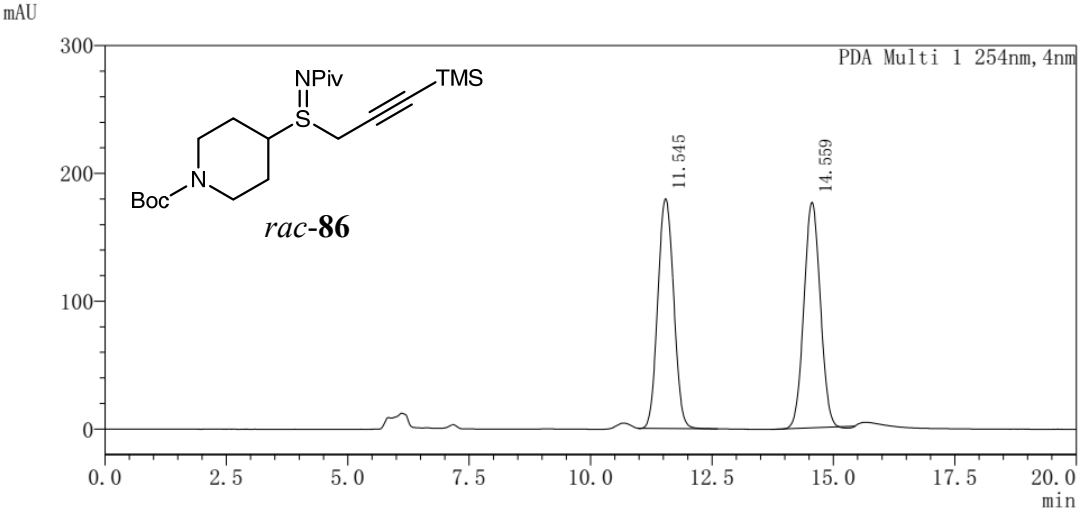
85

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.737	103943	1.084
2	26.133	9483346	98.916

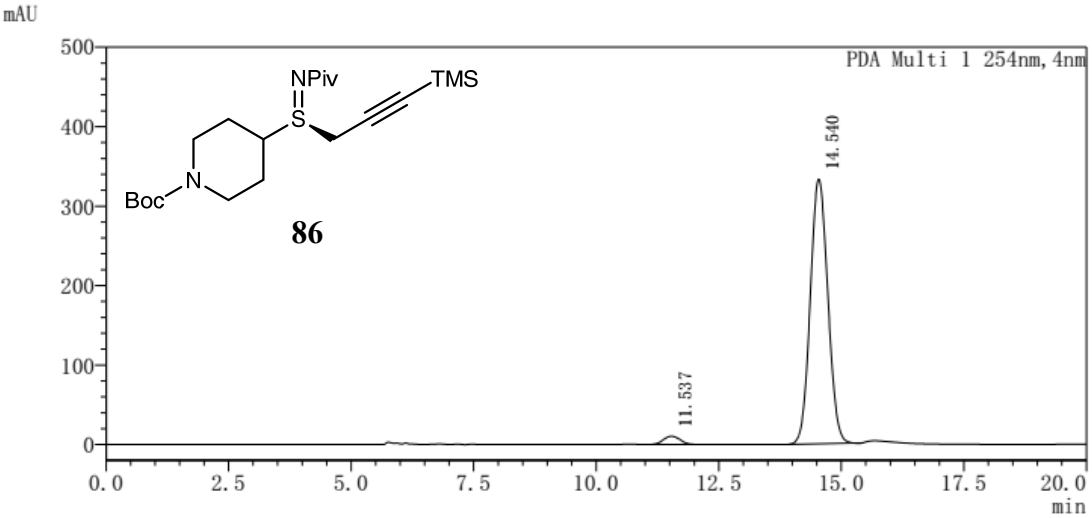
HPLC of 86



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.545	4105368	49.906
2	14.559	4120868	50.094

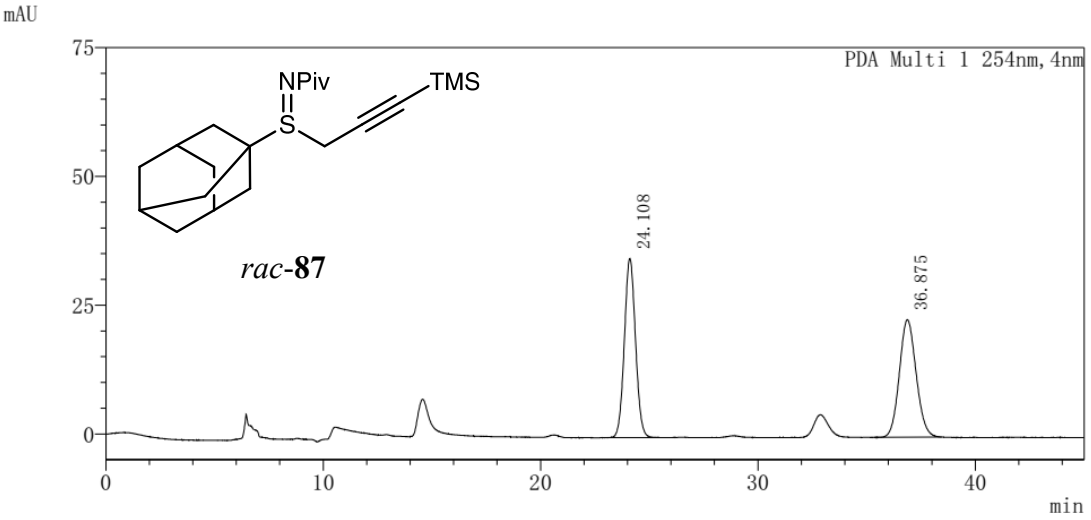


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.537	246990	2.892
2	14.540	8292314	97.108

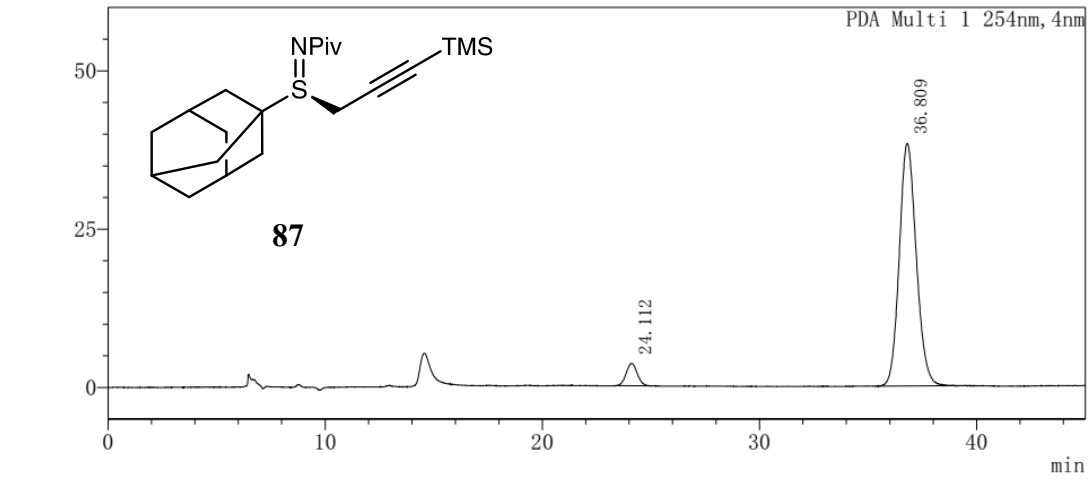
HPLC of 87



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.108	1237222	50.250
2	36.875	1224888	49.750

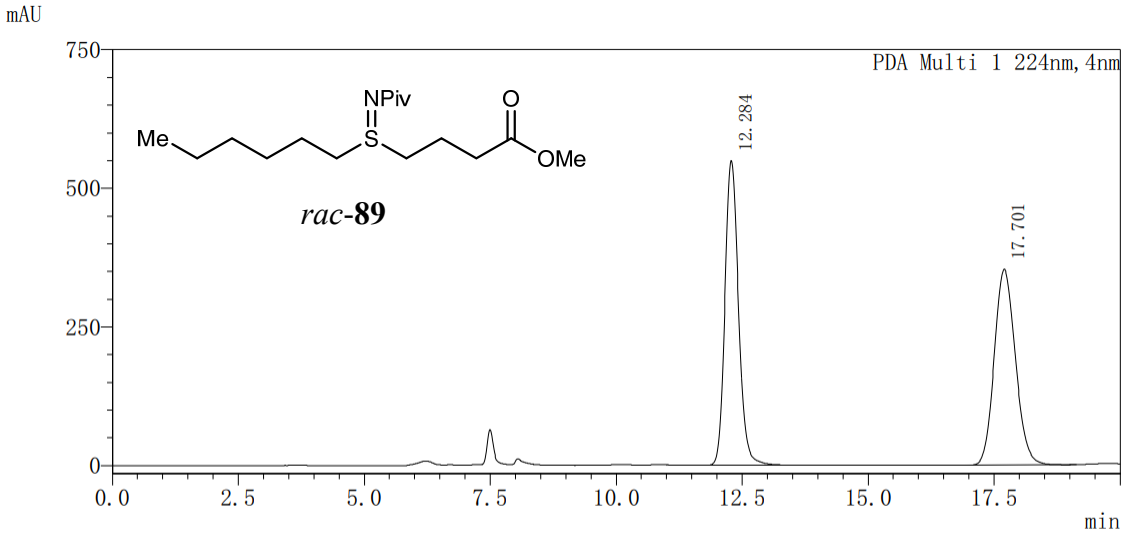


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.112	125019	5.659
2	36.809	2084282	94.341

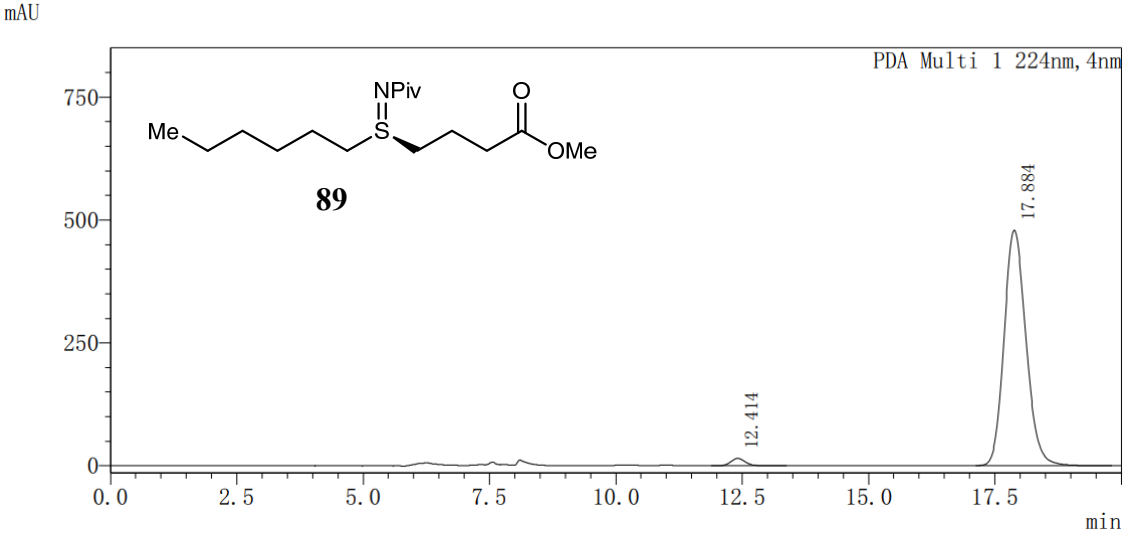
HPLC of 89



Peak Table

PDA Ch1 224nm

Peak#	Ret. Time	Area	Area%
1	12.284	10265418	49.857
2	17.701	10324455	50.143

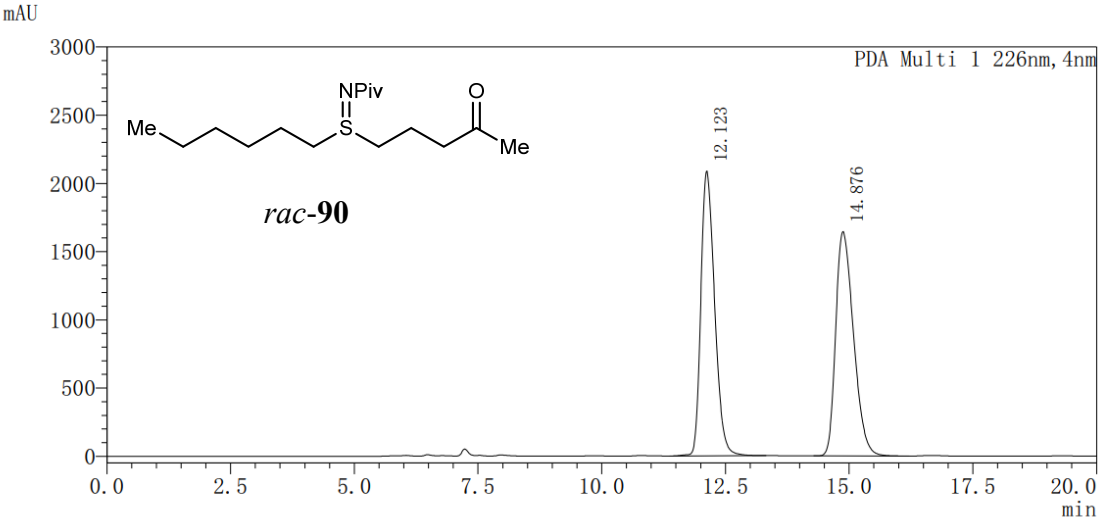


Peak Table

PDA Ch1 224nm

Peak#	Ret. Time	Area	Area%
1	12.414	285800	1.942
2	17.884	14429689	98.058

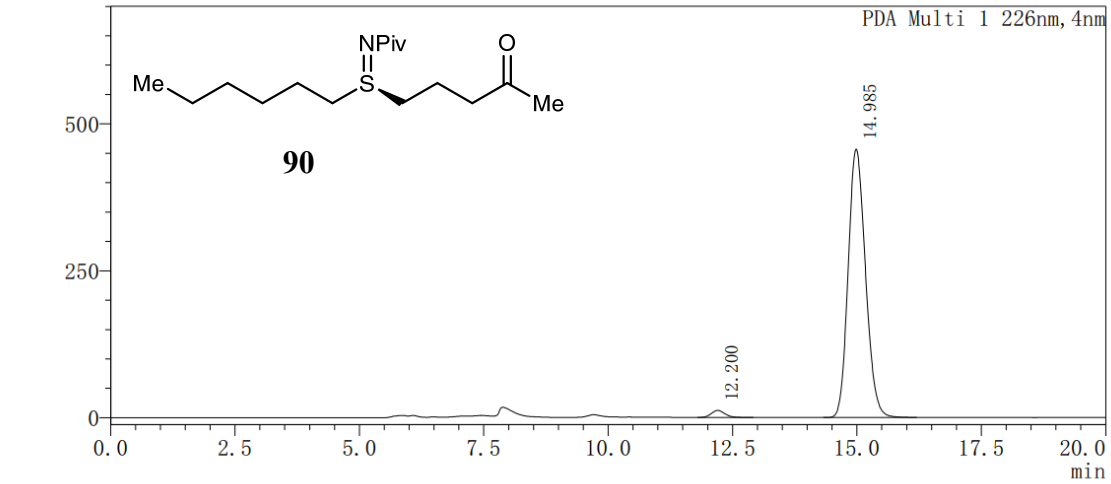
HPLC of 90



Peak Table

PDA Ch1 226nm

Peak#	Ret. Time	Area	Area%
1	12.123	40443708	49.535
2	14.876	41202881	50.465

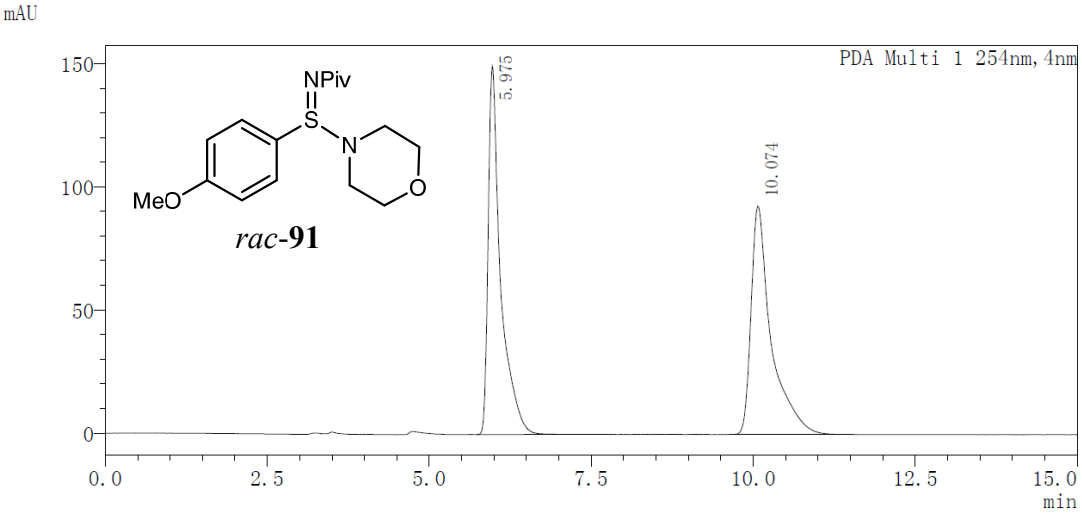


Peak Table

PDA Ch1 226nm

Peak#	Ret. Time	Area	Area%
1	12.200	225610	1.998
2	14.985	11066397	98.002

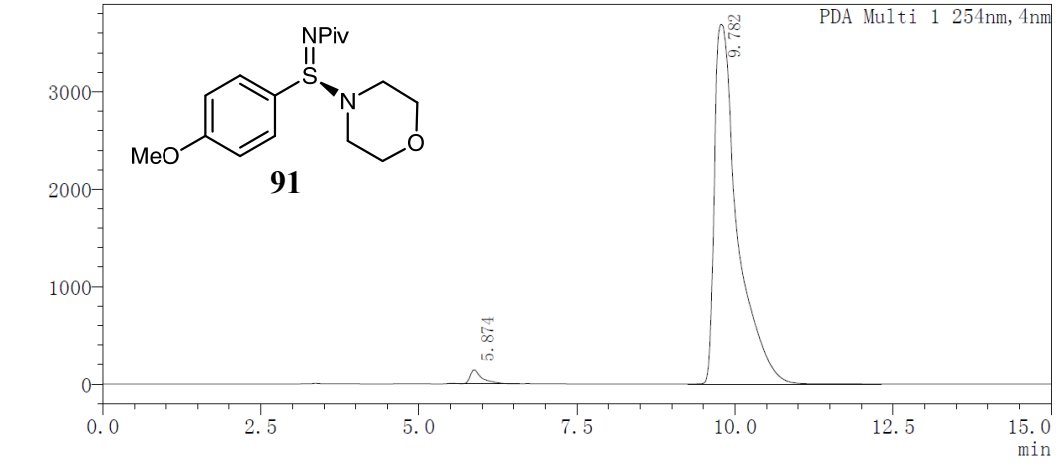
HPLC of 91



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.975	2000691	50.063
2	10.074	1995687	49.937

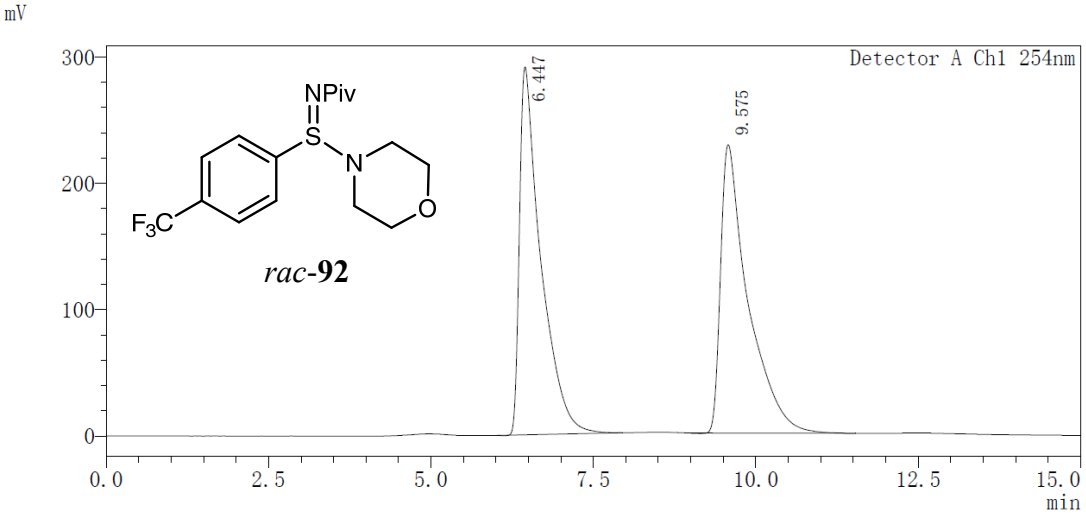


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.874	1928267	2.022
2	9.782	93443289	97.978

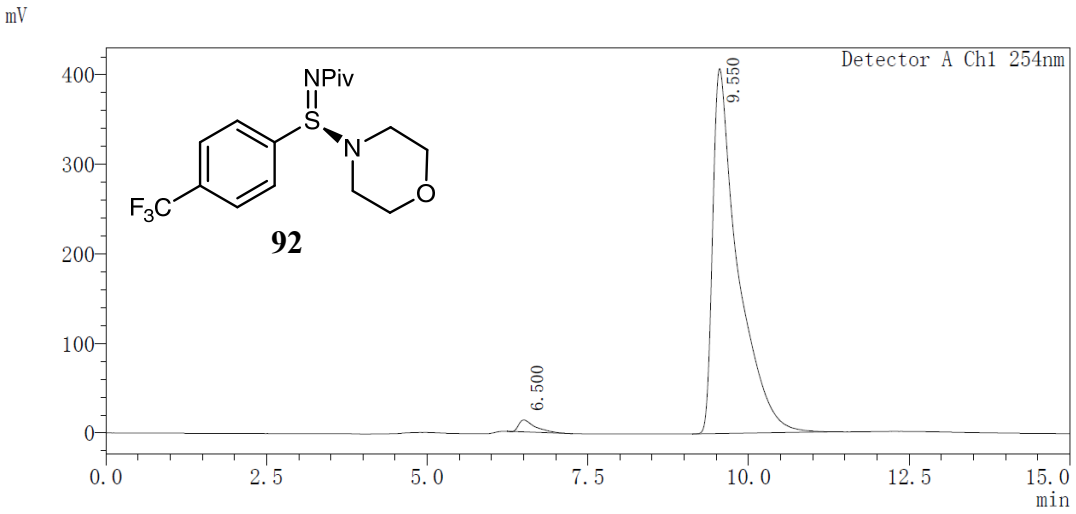
HPLC of 92



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.447	6651746	49.771
2	9.575	6713072	50.229

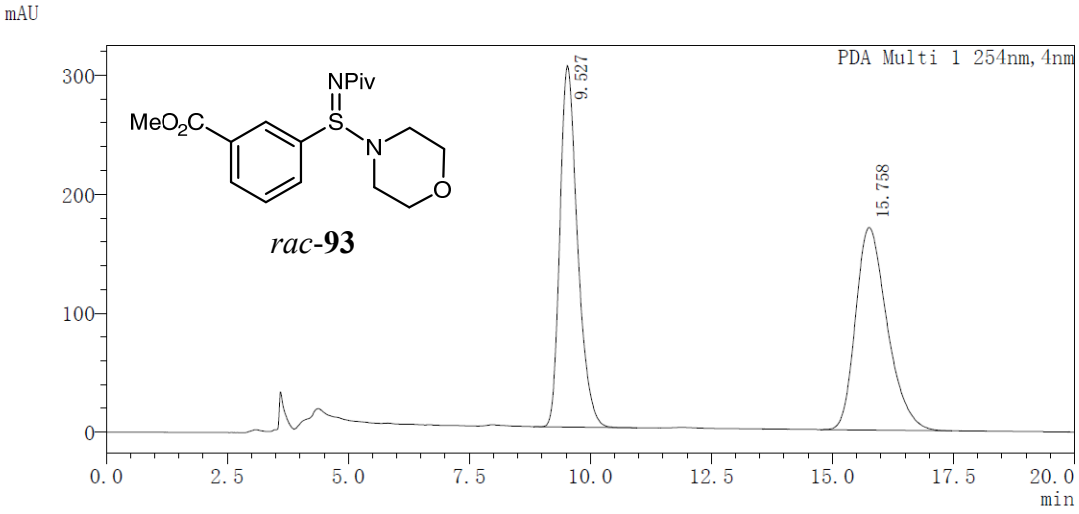


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.500	236271	2.074
2	9.550	11154585	97.926

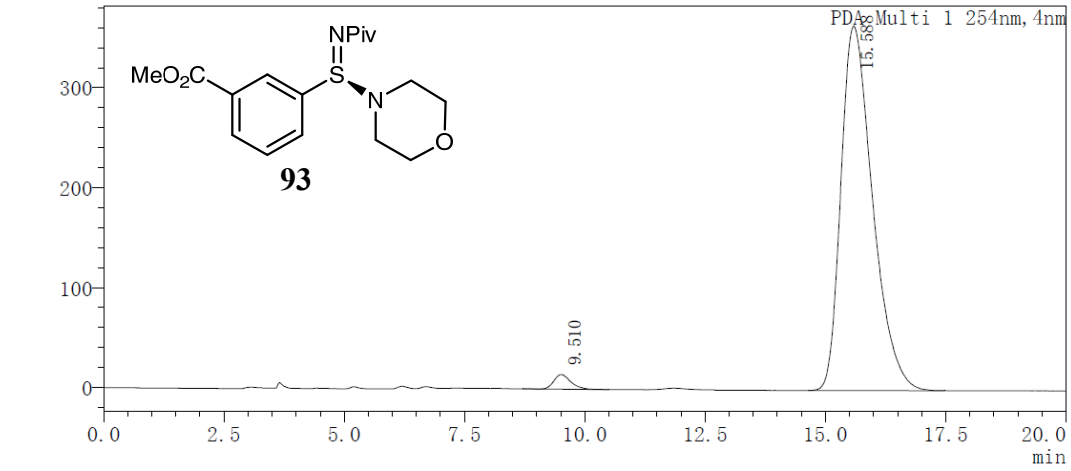
HPLC of 93



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.527	7704427	49.882
2	15.758	7740808	50.118

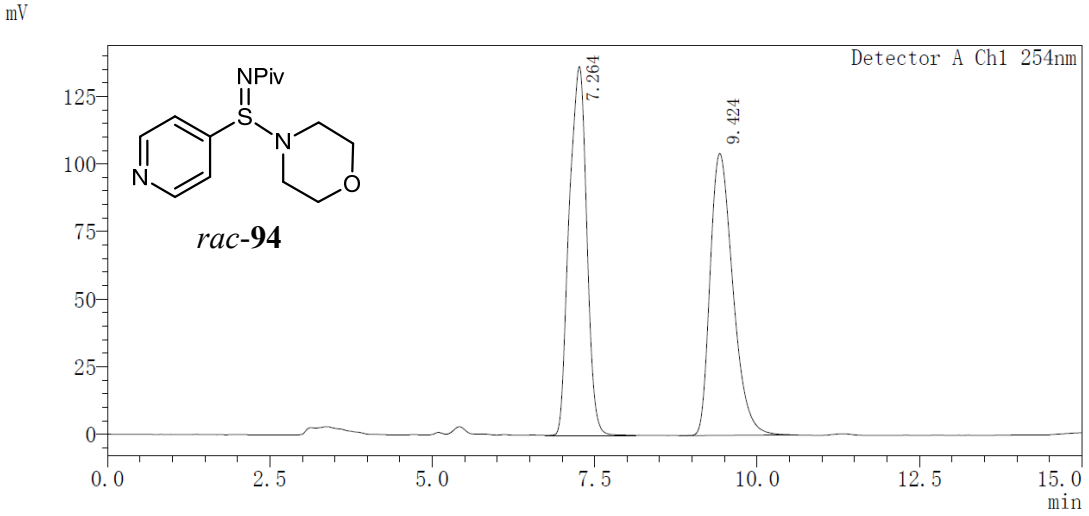


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.510	359545	2.110
2	15.588	16681194	97.890

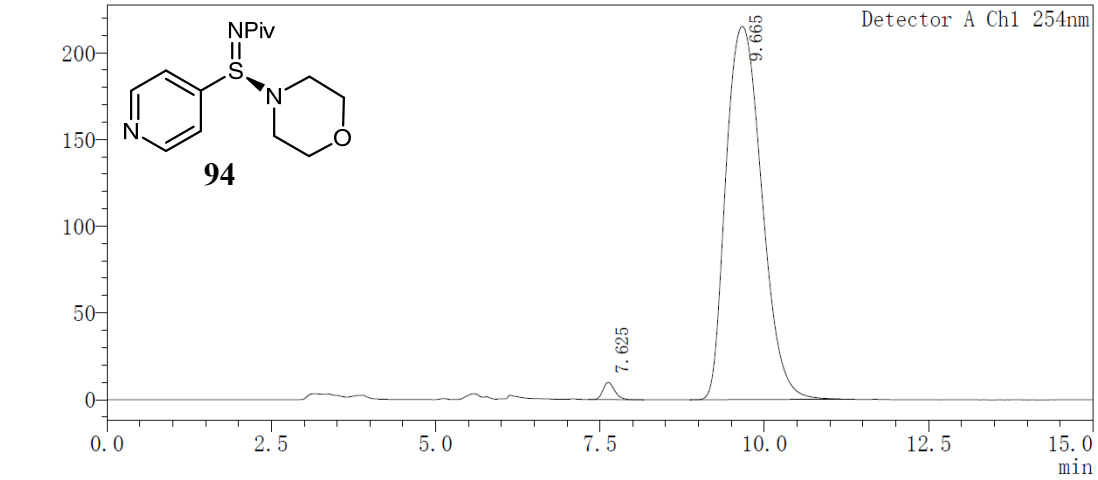
HPLC of 94



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.264	2563601	50.172
2	9.424	2545989	49.828

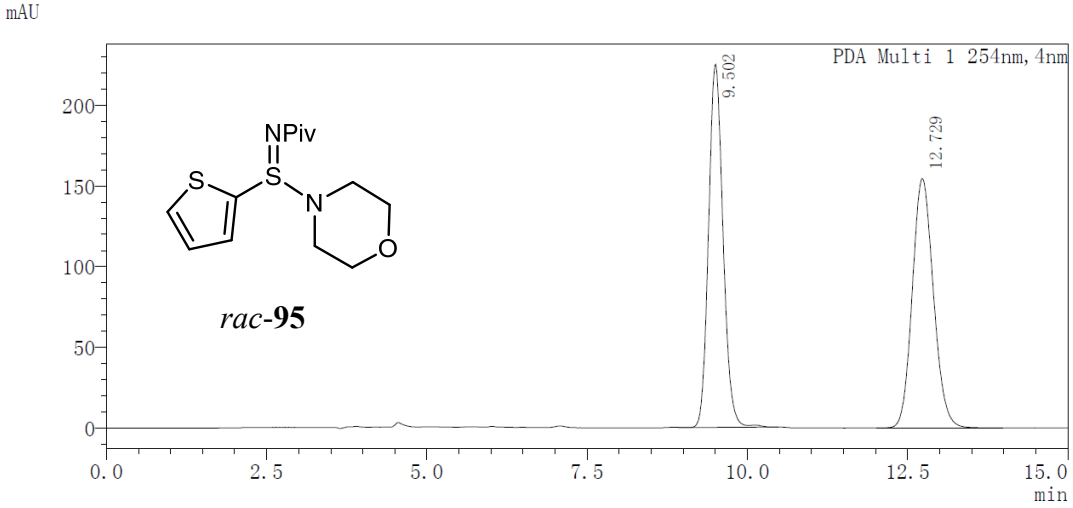


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.625	122718	1.478
2	9.665	8178846	98.522

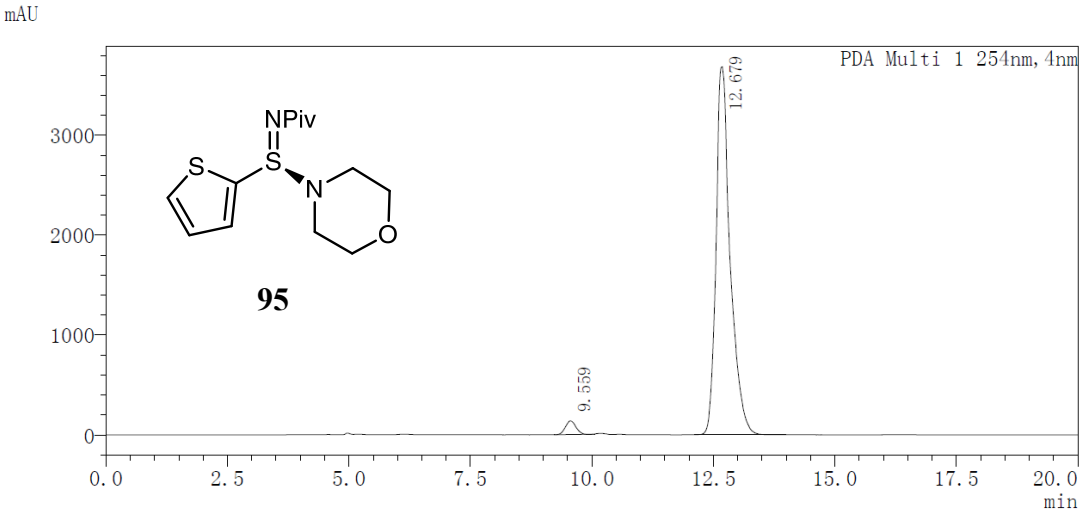
HPLC of 95



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.502	3535729	49.891
2	12.729	3551190	50.109

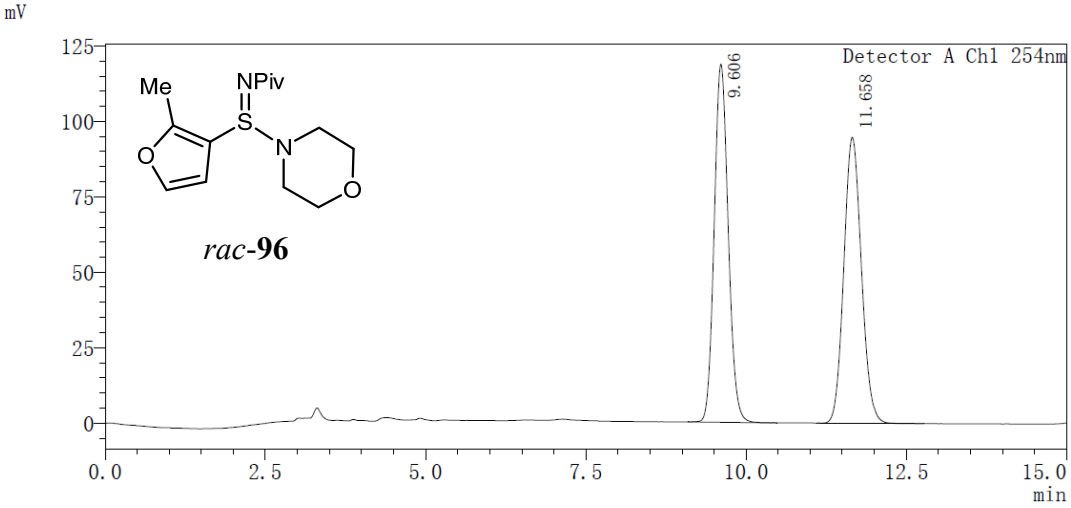


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.559	2000690	2.616
2	12.679	74465439	97.384

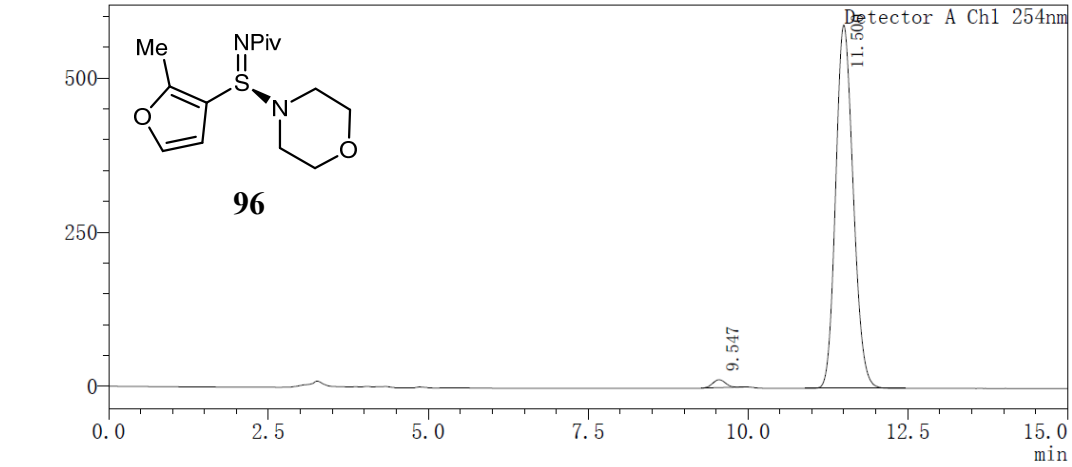
HPLC of 96



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.606	1808073	49.983
2	11.658	1809308	50.017

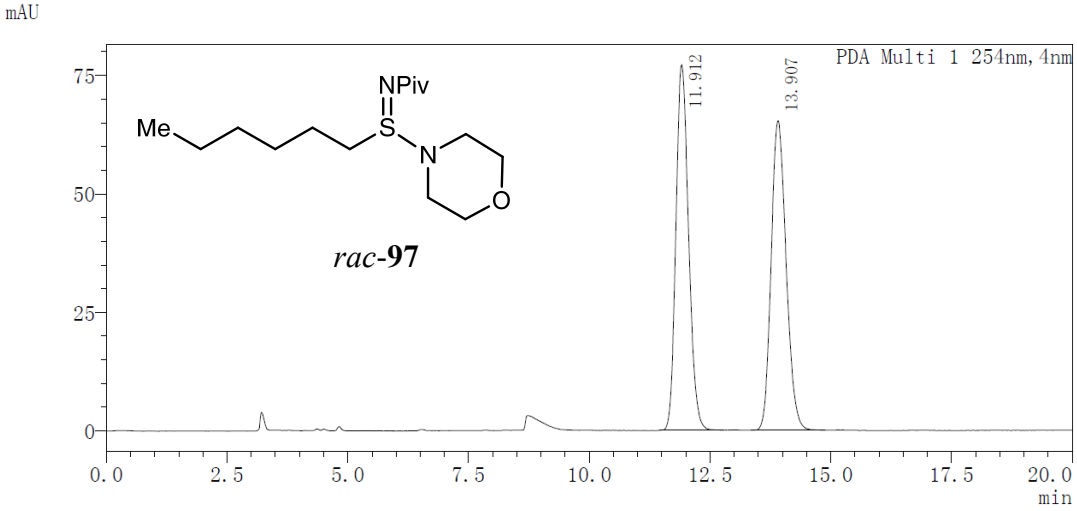


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.547	179395	1.565
2	11.500	11283436	98.435

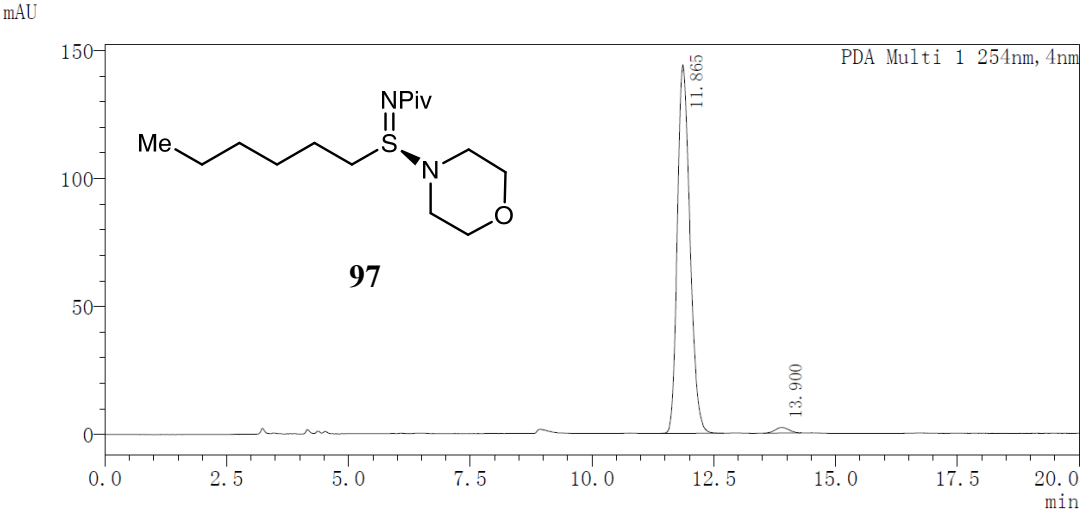
HPLC of 97



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.912	1409156	49.944
2	13.907	1412298	50.056

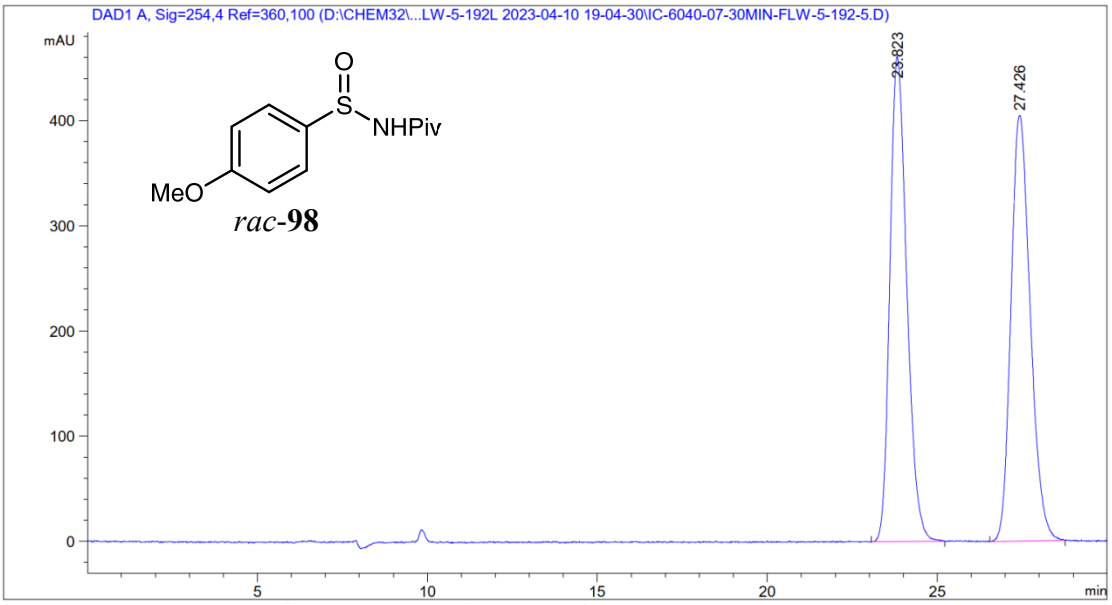


Peak Table

PDA Ch1 254nm

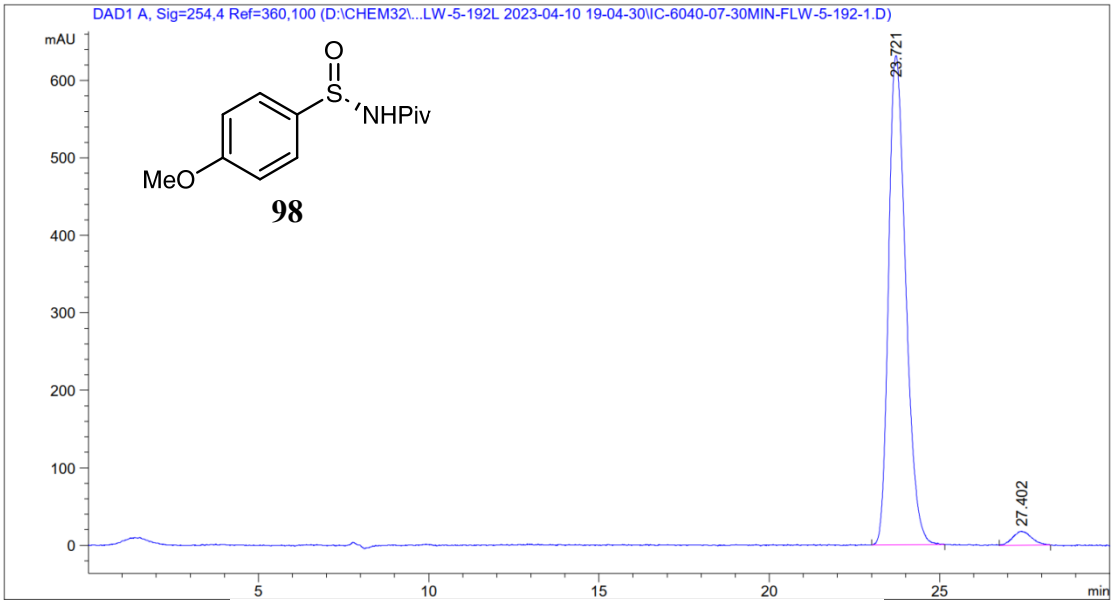
Peak#	Ret. Time	Area	Area%
1	11.865	2591355	98.299
2	13.900	44838	1.701

HPLC of 98



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

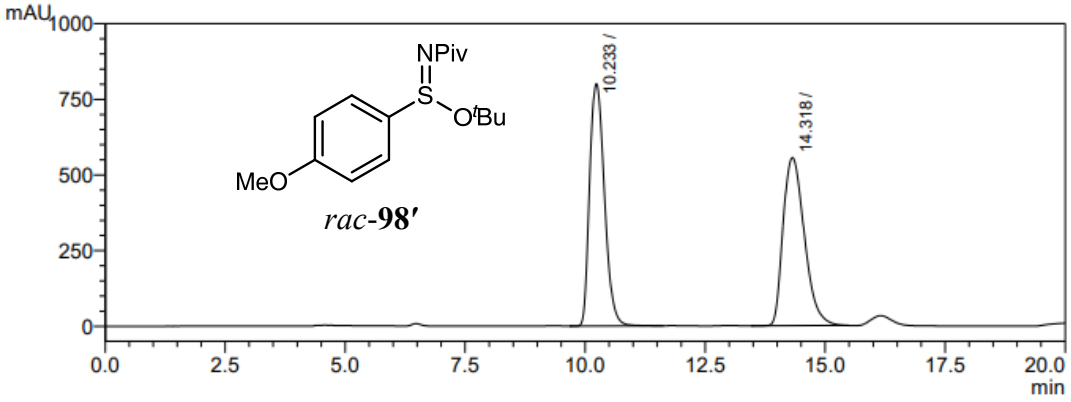
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.823	VV R	0.5170	1.59321e4	461.23090	49.8838
2	27.426	BB	0.5411	1.60063e4	405.01511	50.1162
Totals :				3.19384e4	866.24600	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.721	BV R	0.5063	2.21073e4	631.34106	96.9648
2	27.402	VV R	0.4562	692.01086	18.17536	3.0352
Totals :				2.27993e4	649.51643	

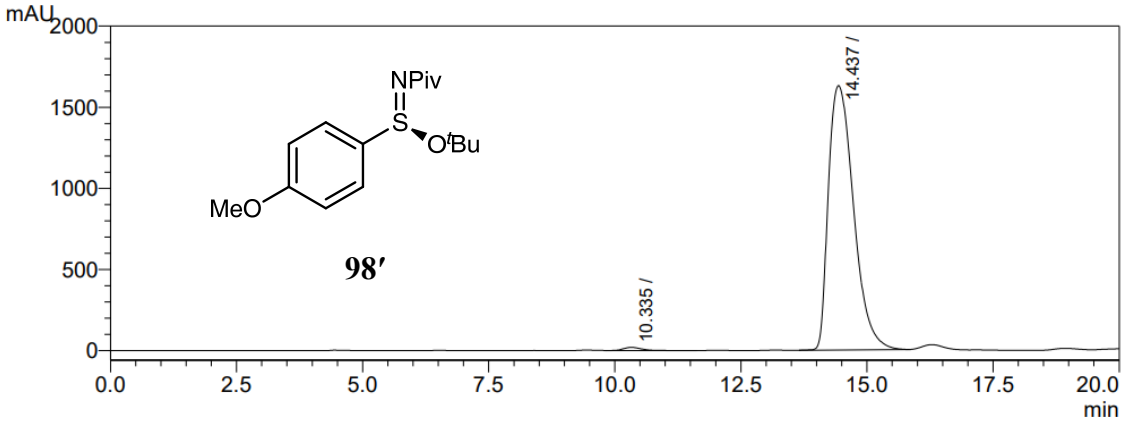
HPLC of 98′



rac-**98′**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.233	17236450	50.070
2	14.318	17188452	49.930

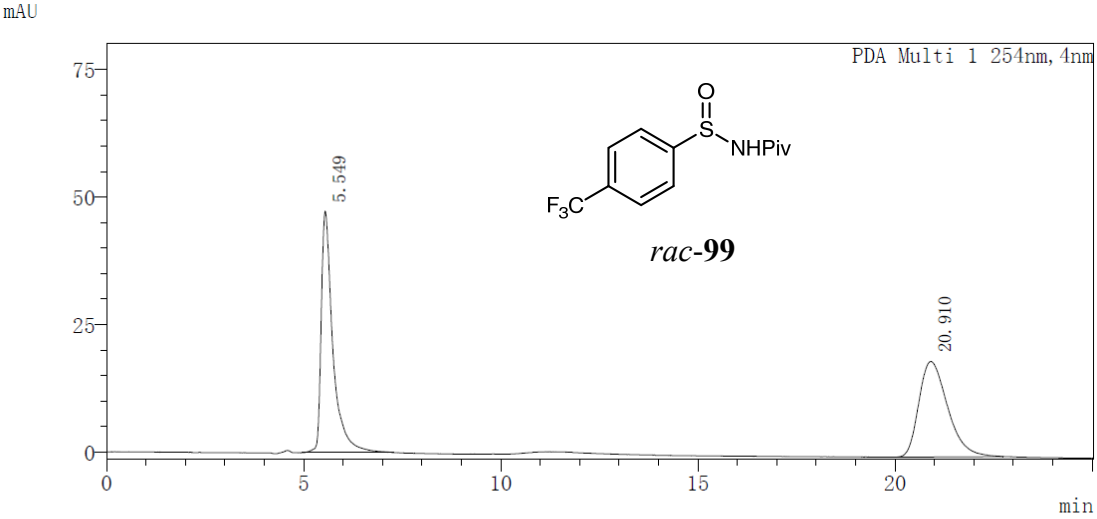


98′

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.335	465521	0.815
2	14.437	56634777	99.185

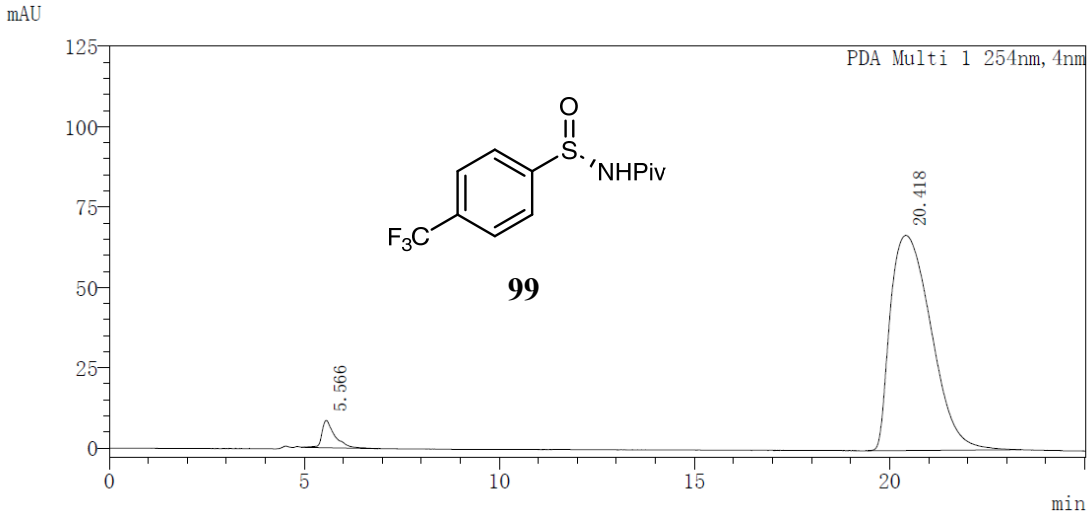
HPLC of 99



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.549	977425	50.702
2	20.910	950373	49.298

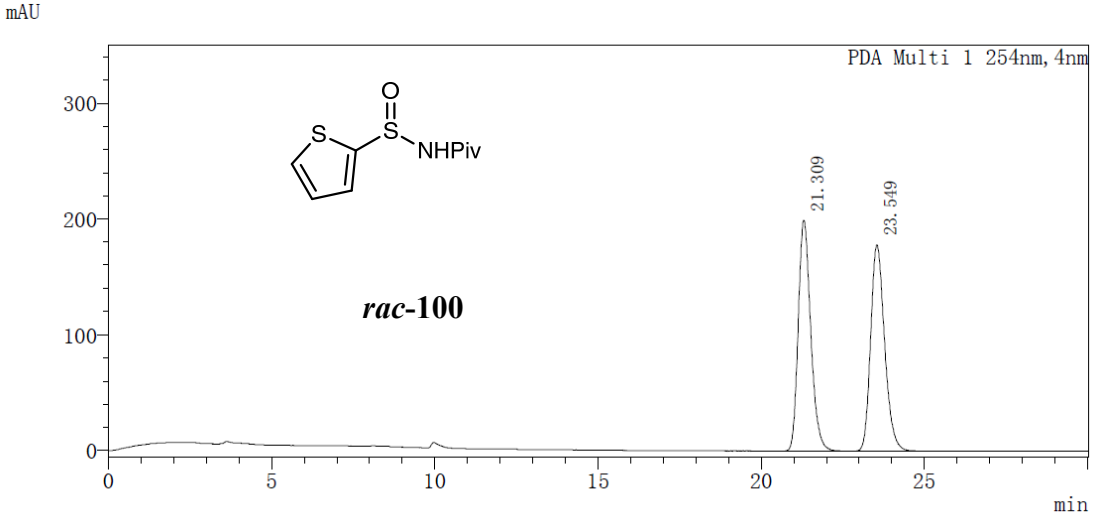


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.566	196417	3.867
2	20.418	4882458	96.133

HPLC of 100

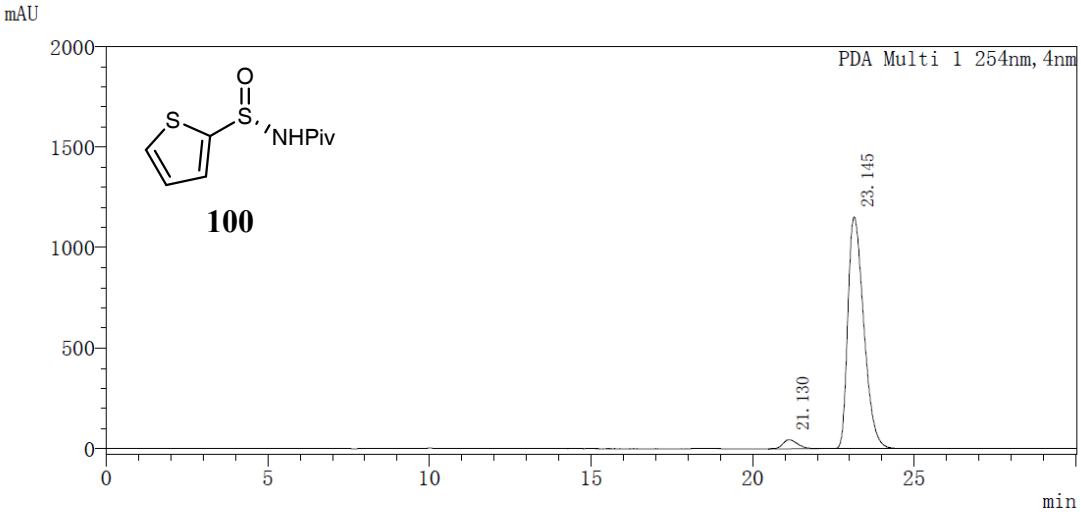


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.309	5312692	50.023
2	23.549	5307835	49.977

HPLC of 100

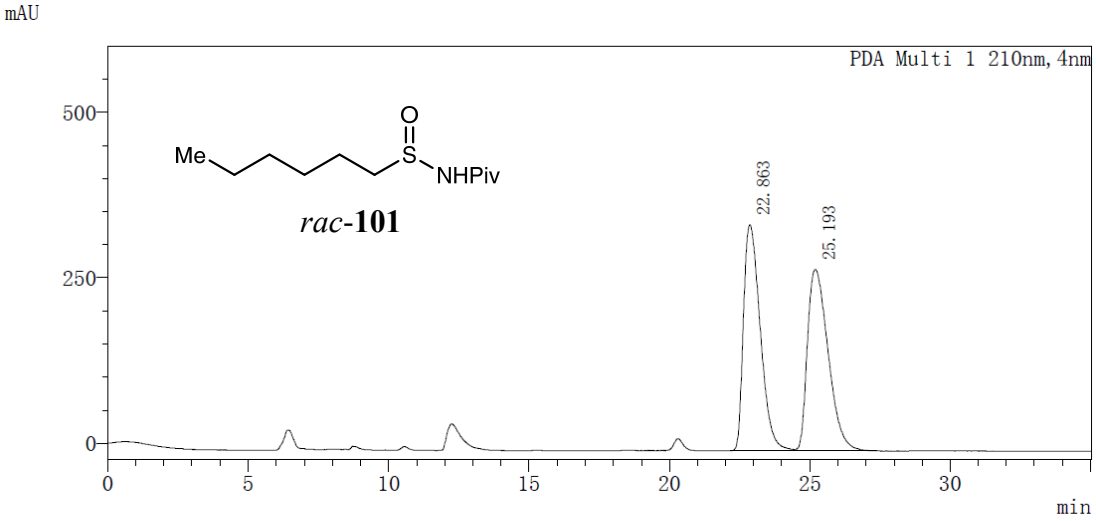


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.130	1435863	3.503
2	23.145	39555901	96.497

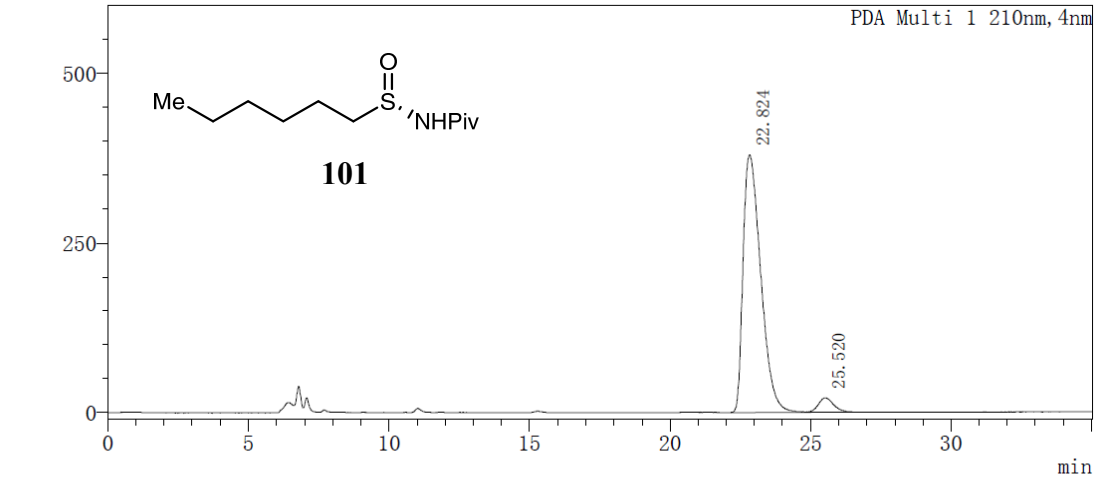
HPLC of 101



Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%
1	22.863	14243350	50.170
2	25.193	14146748	49.830

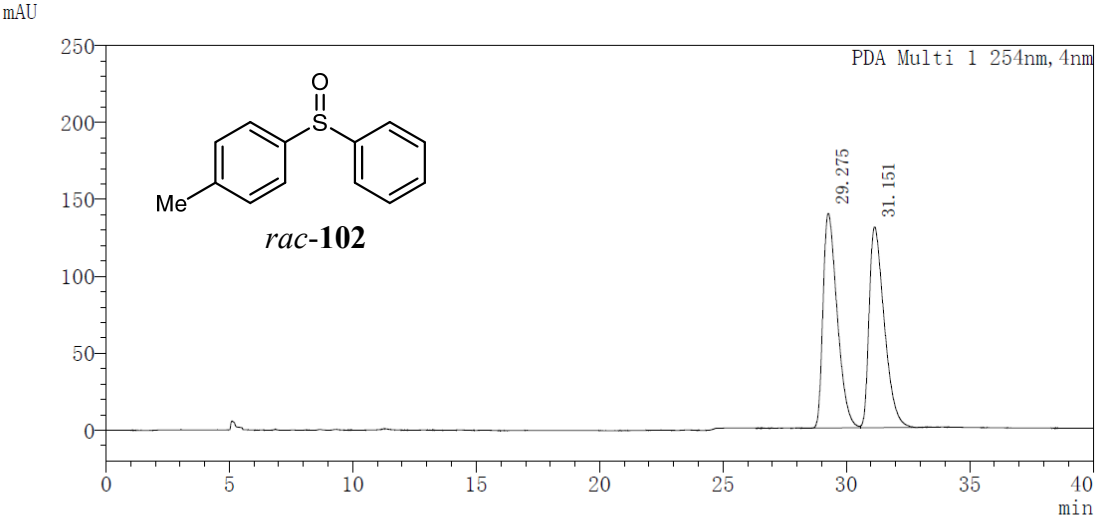


Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%
1	22.824	16603383	95.605
2	25.520	763343	4.395

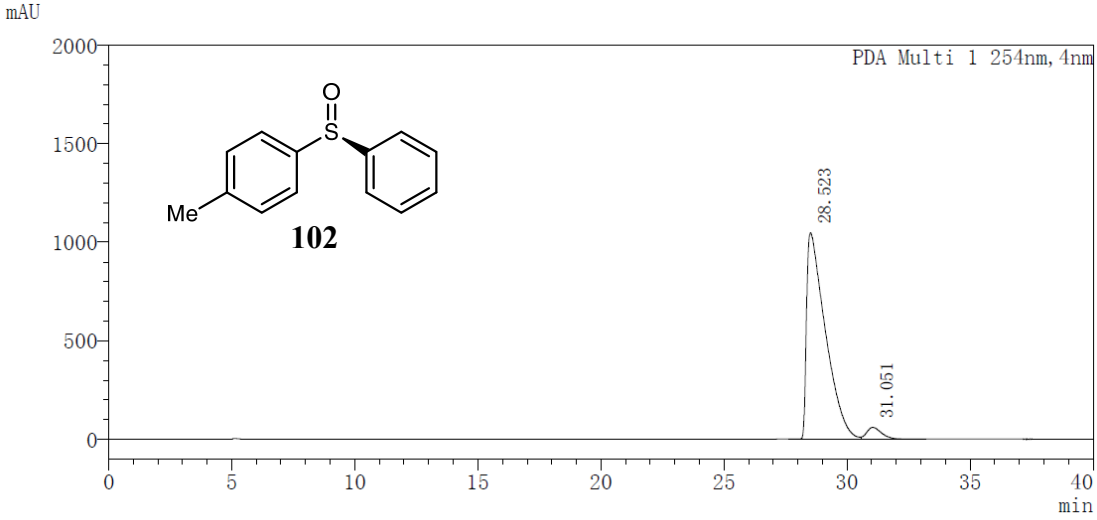
HPLC of 102



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	29.275	5563281	50.035
2	31.151	5555585	49.965

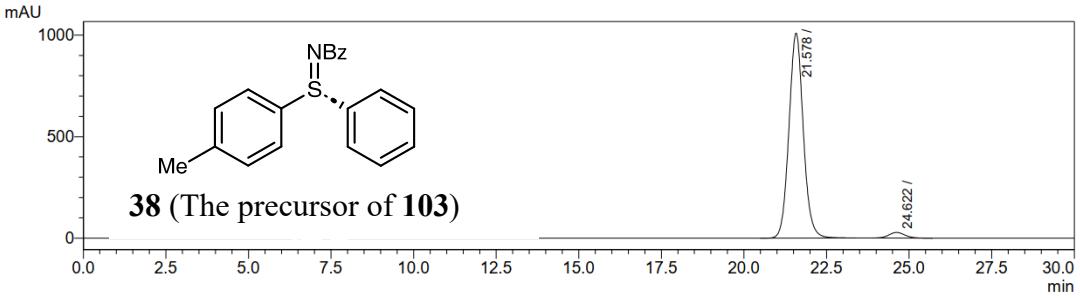


Peak Table

PDA Ch1 254nm

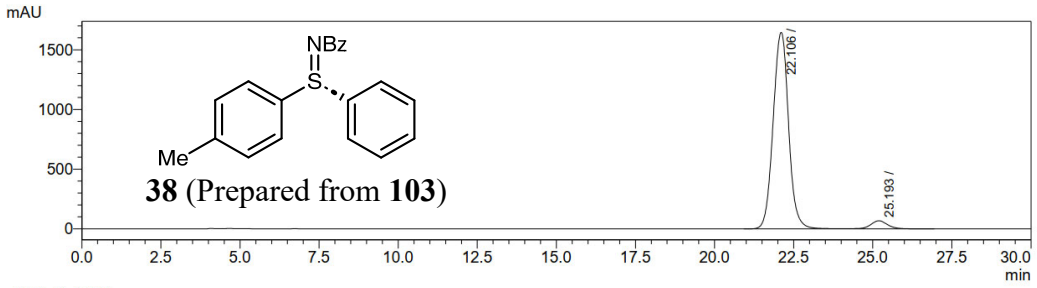
Peak#	Ret. Time	Area	Area%
1	28.523	55694287	95.792
2	31.051	2446446	4.208

HPLC of 103



PDA Ch1 254nm

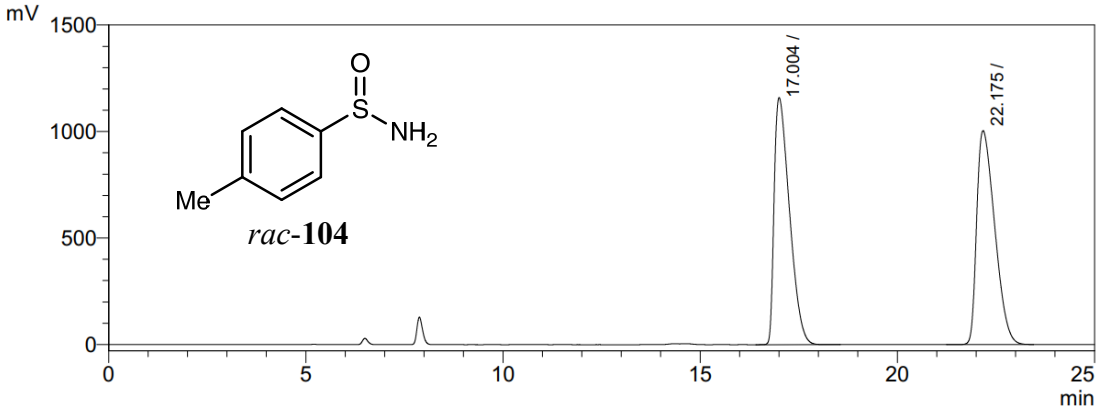
Peak#	Ret. Time	Area	Area%
1	21.578	30537294	97.079
2	24.622	918765	2.921



PDA Ch1 254nm

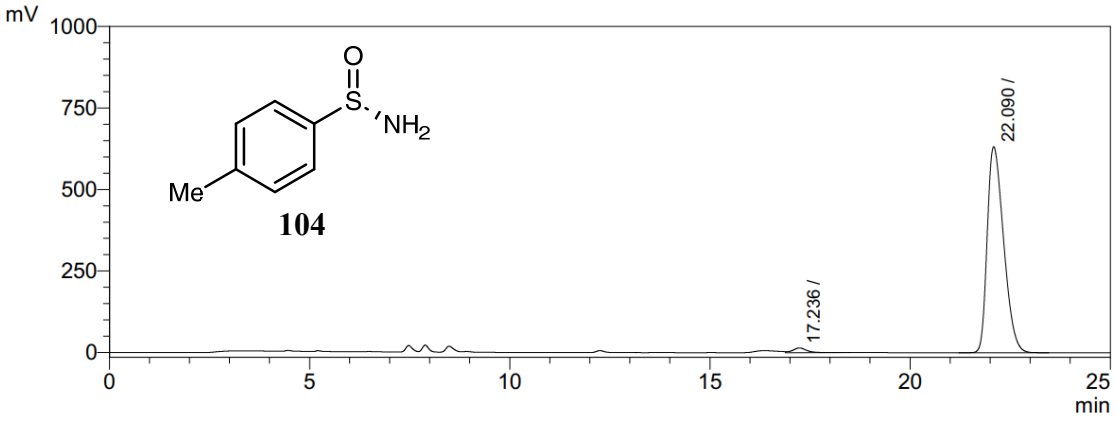
Peak#	Ret. Time	Area	Area%
1	22.106	55860618	95.517
2	25.193	2622006	4.483

HPLC of 104



检测器A Ch1 254nm

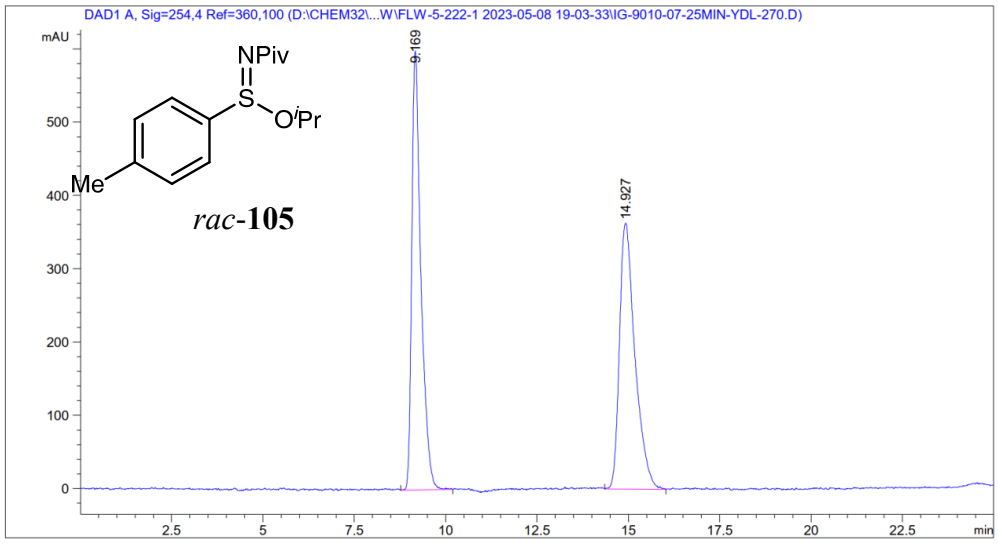
Peak#	Ret. Time	Area	Area%
1	17.004	31338519	49.579
2	22.175	31871251	50.421



检测器A Ch1 254nm

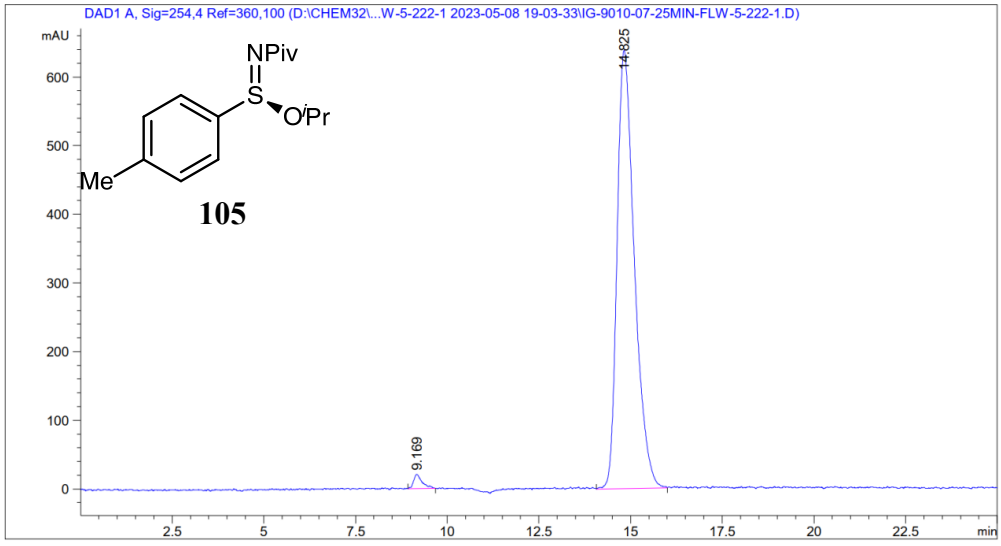
Peak#	Ret. Time	Area	Area%
1	17.236	349559	1.907
2	22.090	17976568	98.093

HPLC of 105



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

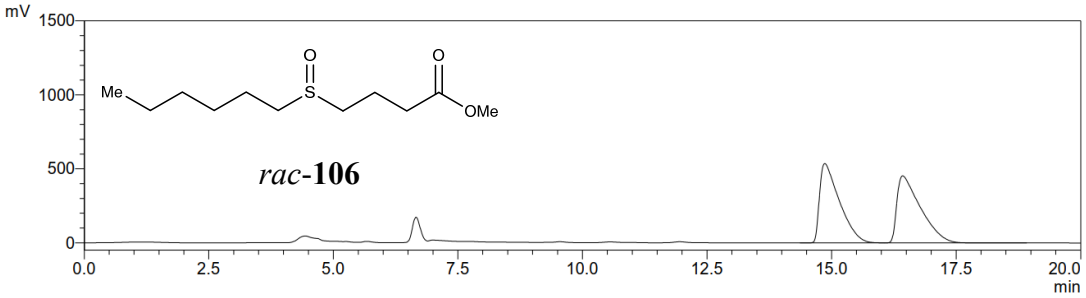
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.169	VV R	0.2528	1.04086e4	598.27026	49.3640
2	14.927	VV R	0.4150	1.06768e4	362.73062	50.6360
Totals :				2.10854e4	961.00089	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

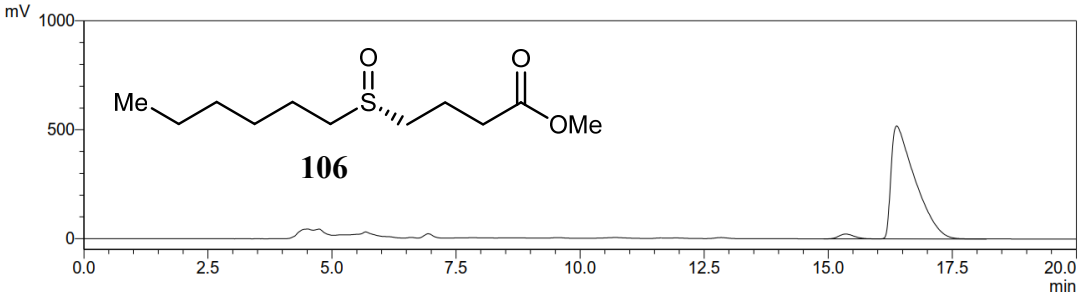
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.169	VV R	0.2049	340.24985	20.91678	1.6023
2	14.825	VV R	0.4599	2.08951e4	637.93341	98.3977
Totals :				2.12353e4	658.85019	

HPLC of 106



Detector A Ch1 210nm

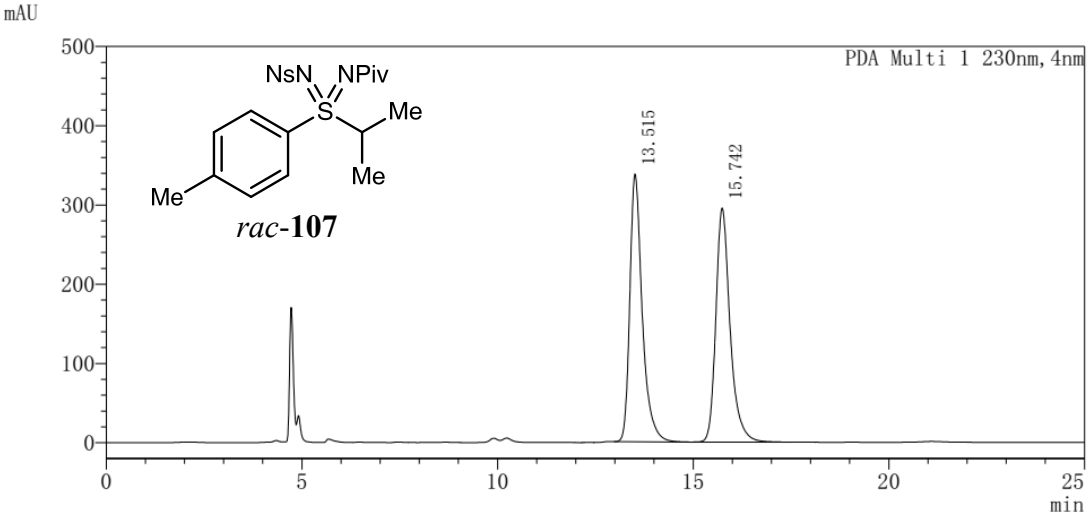
Peak#	Ret. Time	Area	Area%
1	14.864	14931775	49.934
2	16.427	14971155	50.066



Detector A Ch1 210nm

Peak#	Ret. Time	Area	Area%
1	15.355	478539	2.669
2	16.381	17452645	97.331

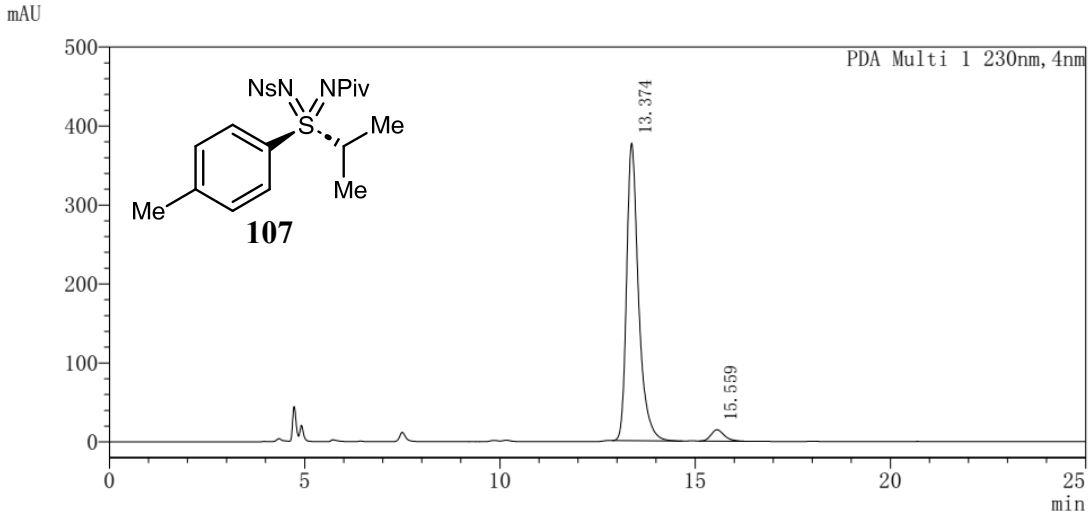
HPLC of 107



Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	13.515	7446464	49.851
2	15.742	7491043	50.149

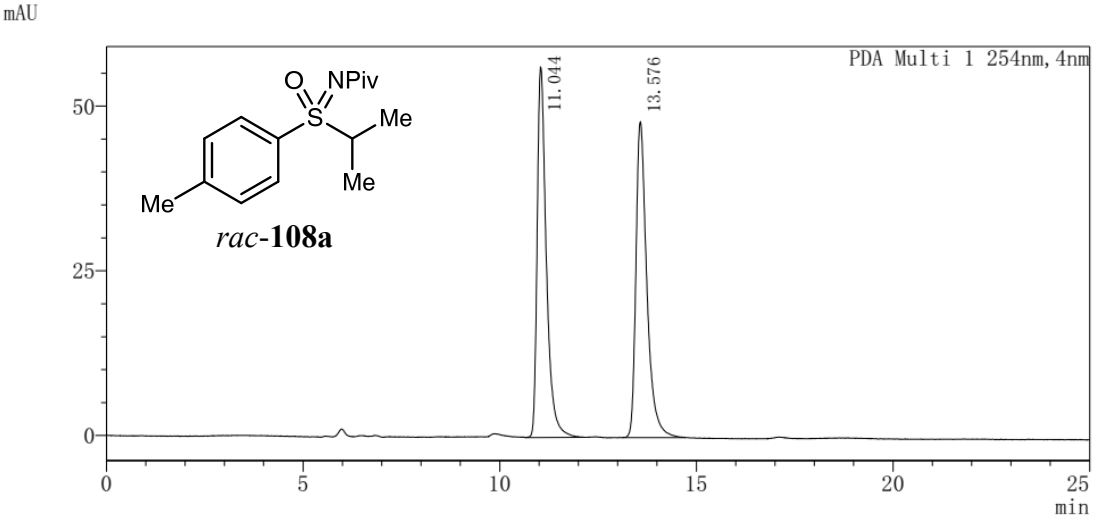


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	13.374	8020826	95.886
2	15.559	344177	4.114

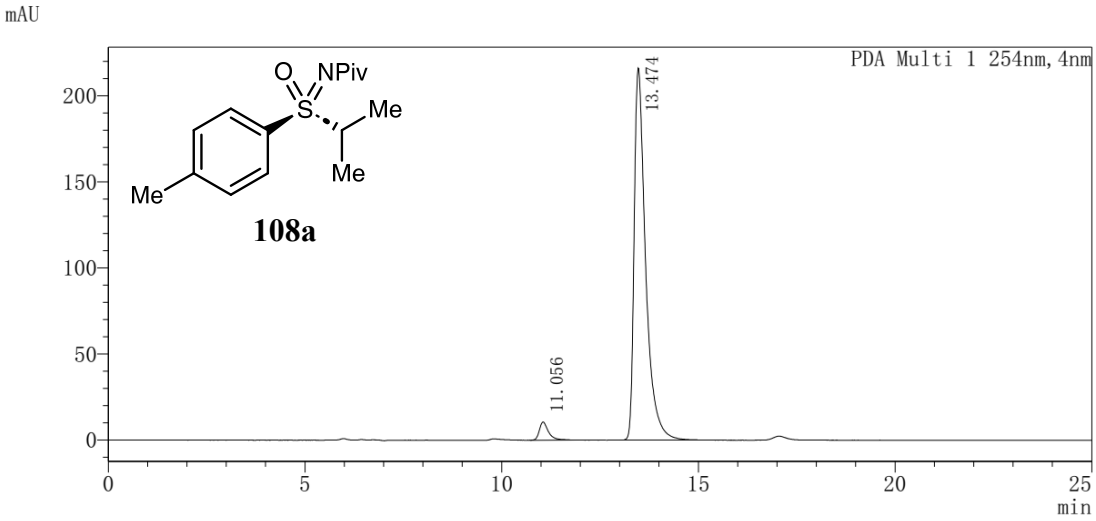
HPLC of 108a



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.044	910709	49.555
2	13.576	927048	50.445

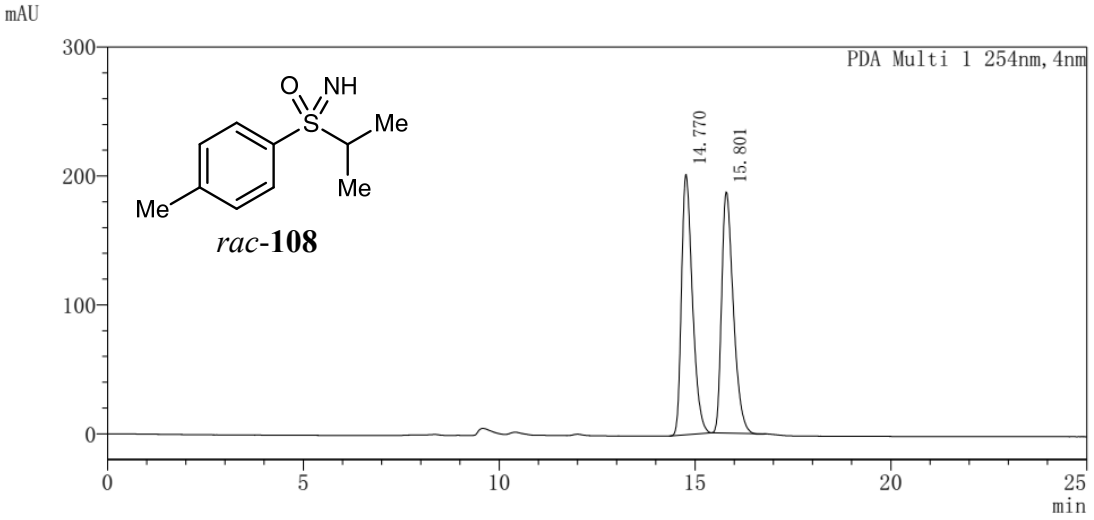


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.056	172198	3.783
2	13.474	4379463	96.217

HPLC of 108

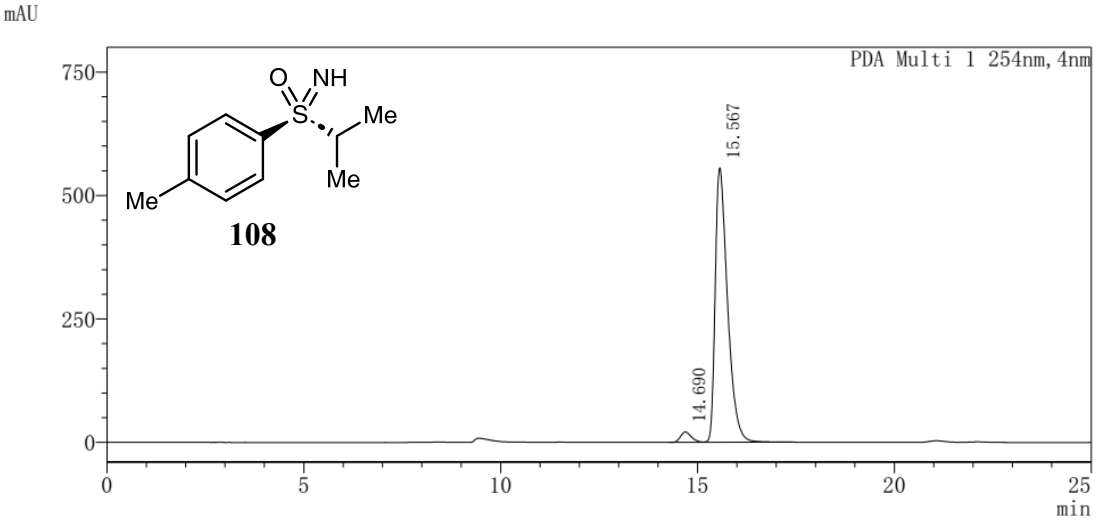


rac-**108**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.770	3921486	50.170
2	15.801	3894987	49.830



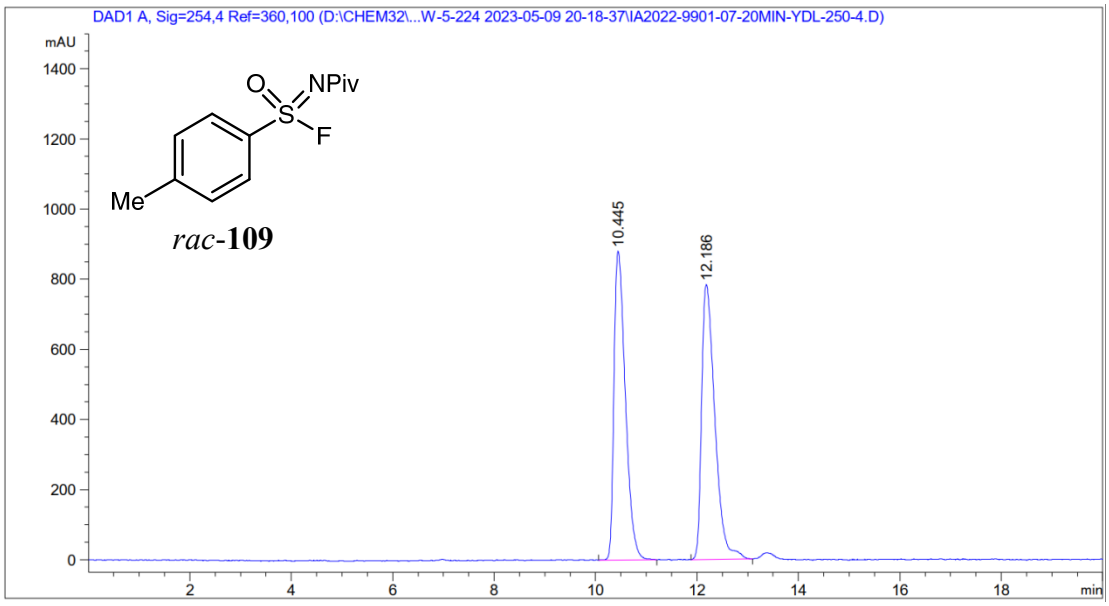
108

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.690	407229	3.257
2	15.567	12097843	96.743

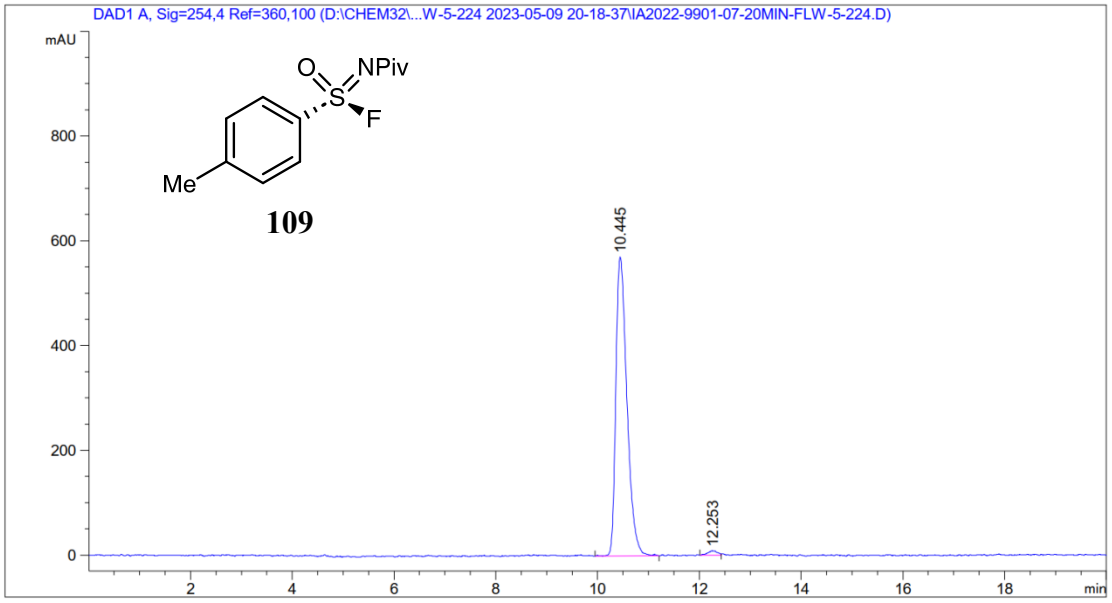
HPLC of 109



rac-**109**

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.445	VV R	0.2399	1.37359e4	880.97089	49.1631
2	12.186	BB	0.2674	1.42036e4	783.71619	50.8369
Totals :				2.79395e4	1664.68707	

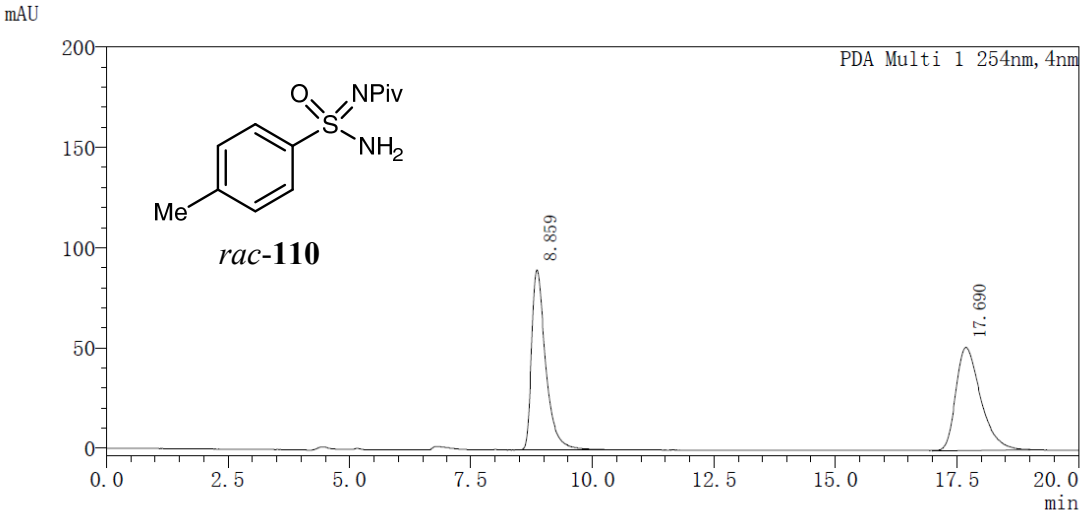


109

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.445	VV R	0.2346	8657.74805	571.04645	98.6895
2	12.253	BV	0.1645	114.96727	8.57088	1.3105
Totals :				8772.71532	579.61732	

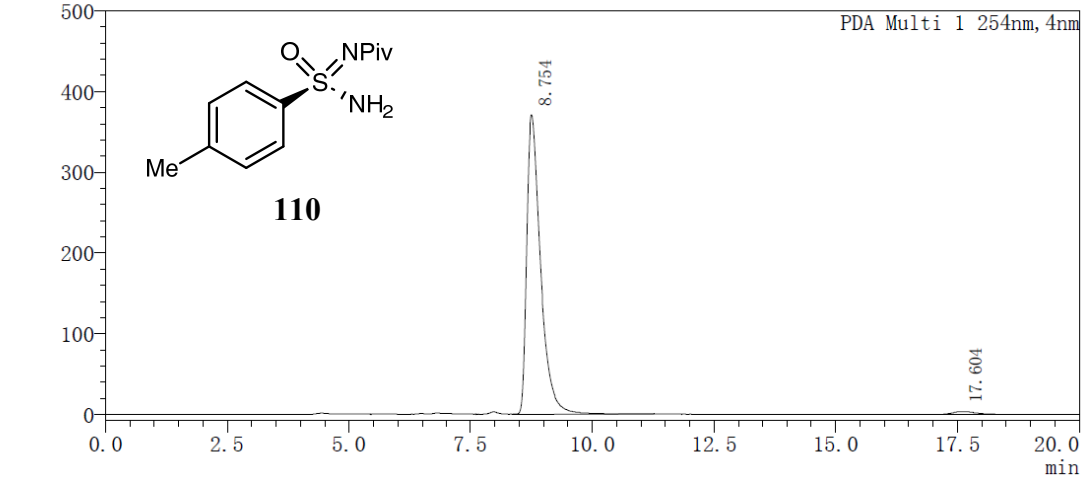
HPLC of 110



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.859	1813771	49.752
2	17.690	1831834	50.248

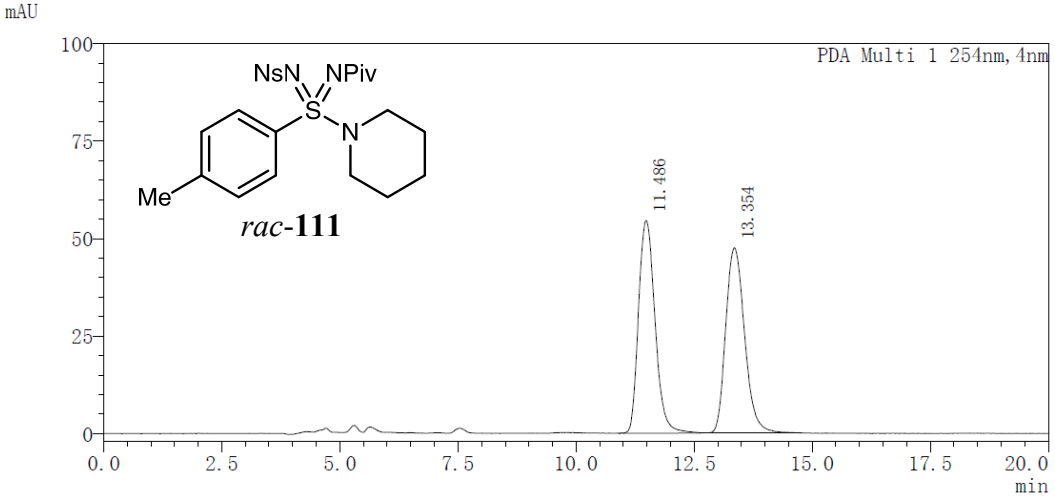


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.754	7370390	98.249
2	17.604	131351	1.751

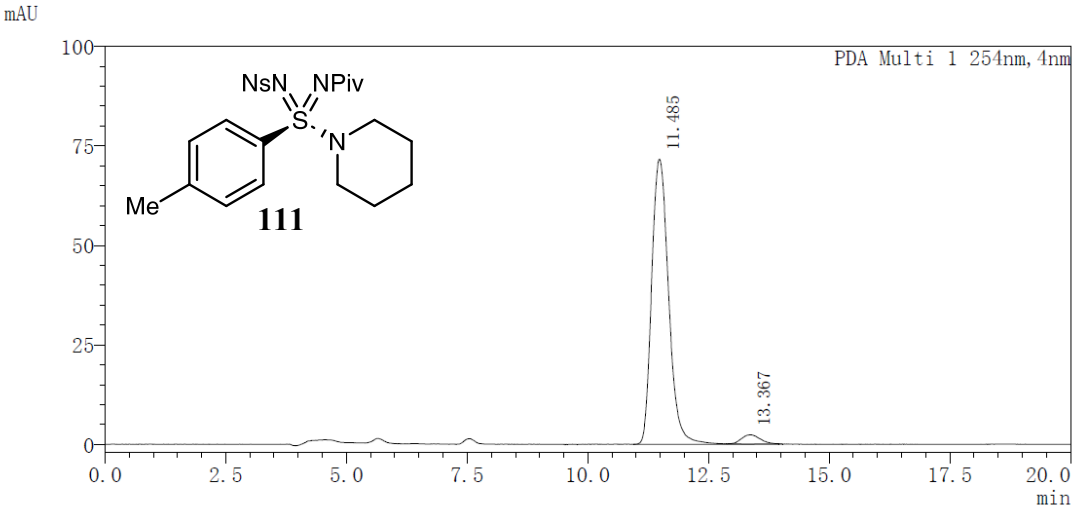
HPLC of 111



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.486	1329696	50.073
2	13.354	1325816	49.927

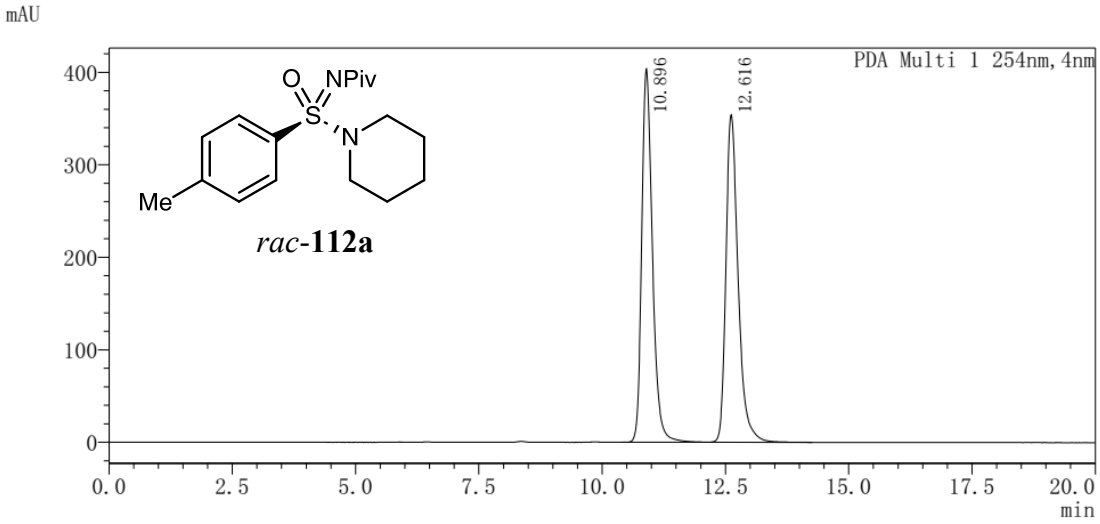


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.485	1747659	96.564
2	13.367	62192	3.436

HPLC of 112a

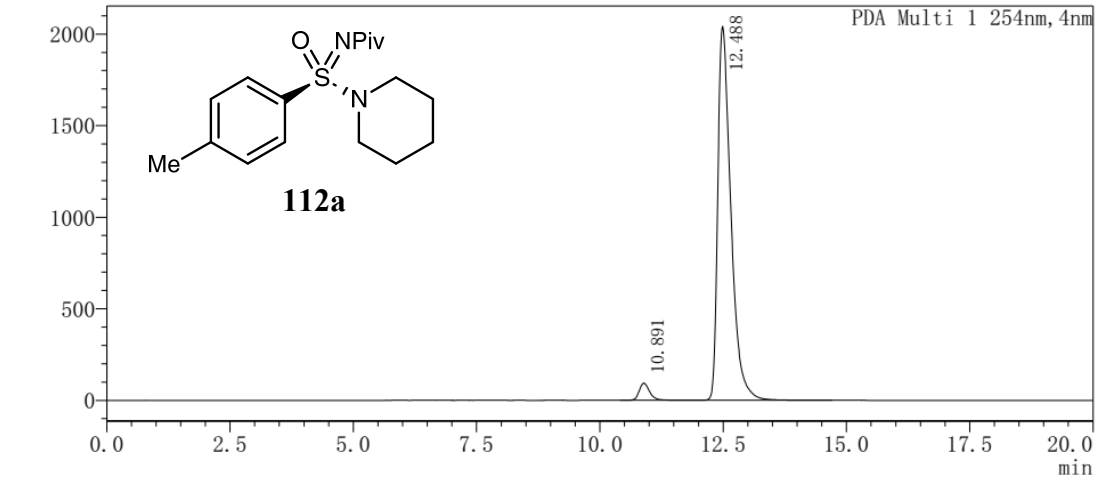


rac-**112a**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.896	6096391	49.963
2	12.616	6105528	50.037



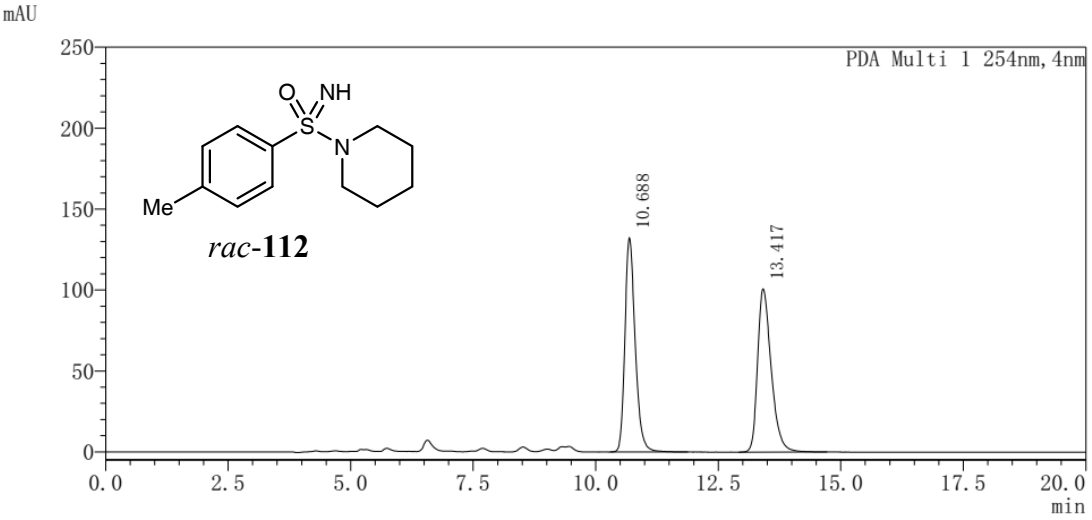
112a

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.891	1401150	3.583
2	12.488	37703542	96.417

HPLC of 112

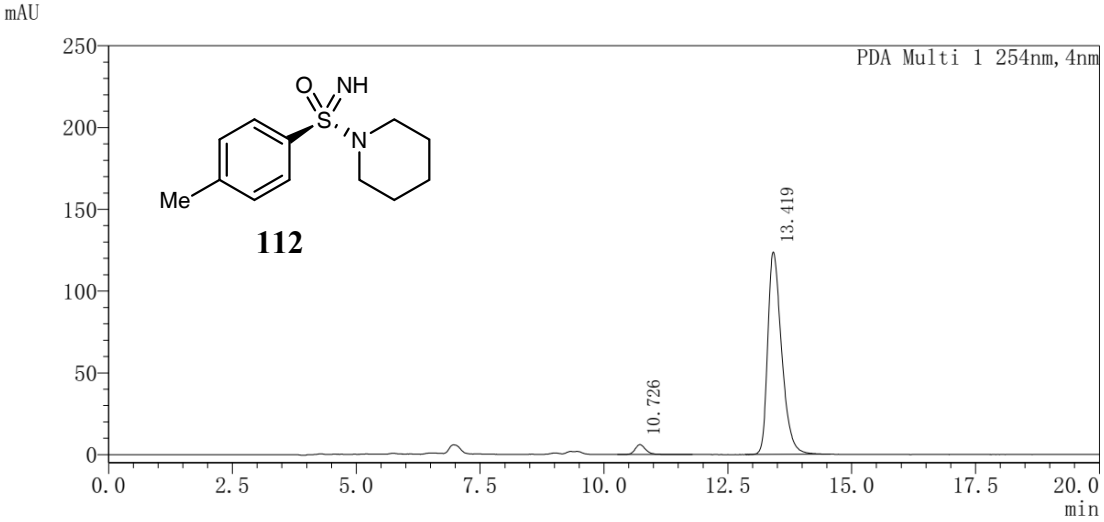


rac-**112**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.688	1934255	49.775
2	13.417	1951717	50.225



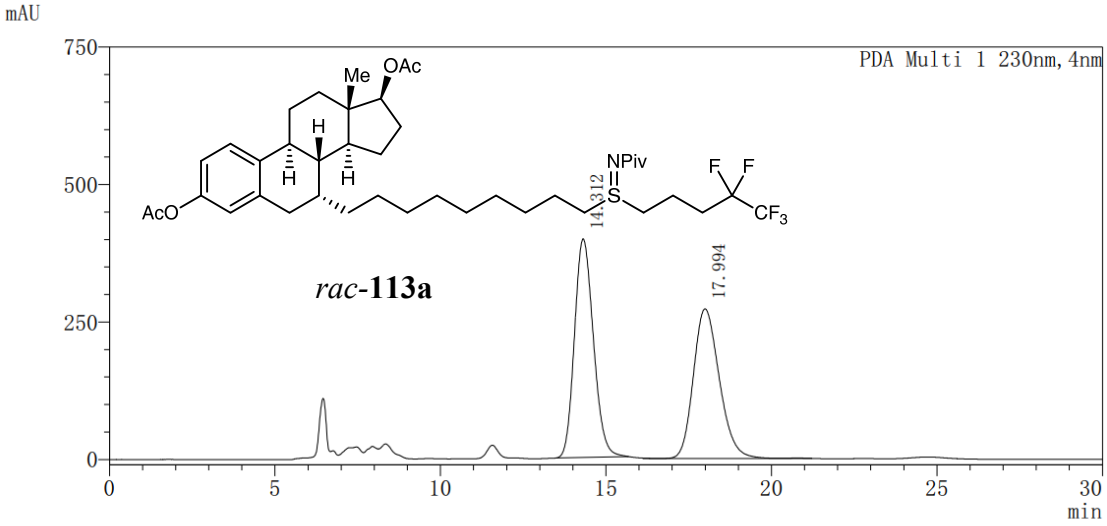
112

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.726	88872	3.545
2	13.419	2418021	96.455

HPLC of 113a

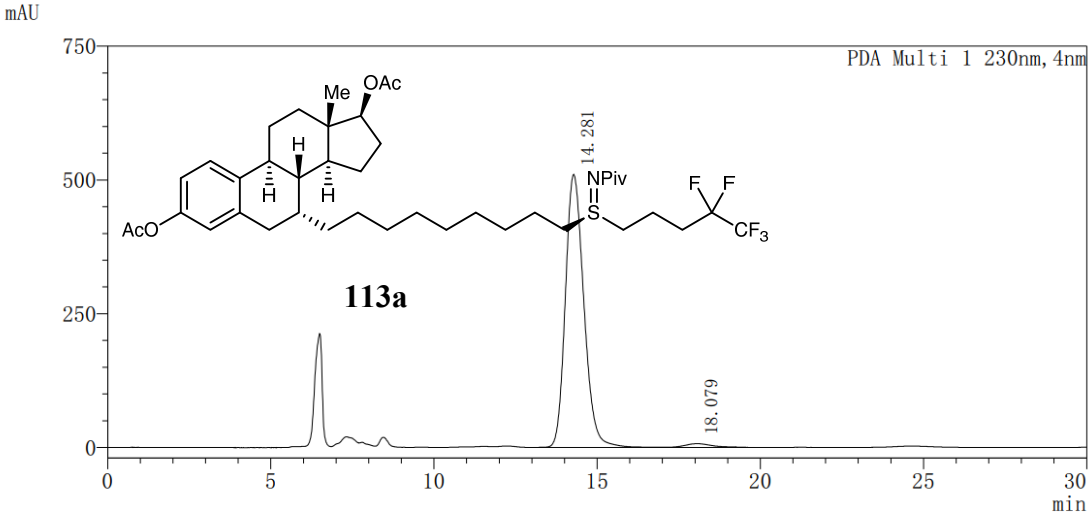


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	14.312	15833805	51.562
2	17.994	14874718	48.438

HPLC of 113a

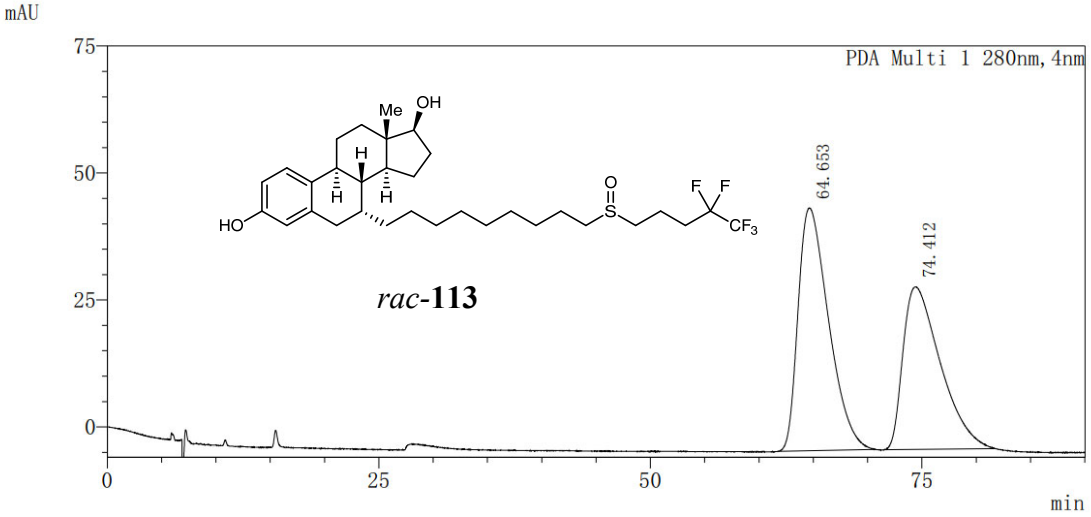


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	14.281	20077786	97.939
2	18.079	422431	2.061

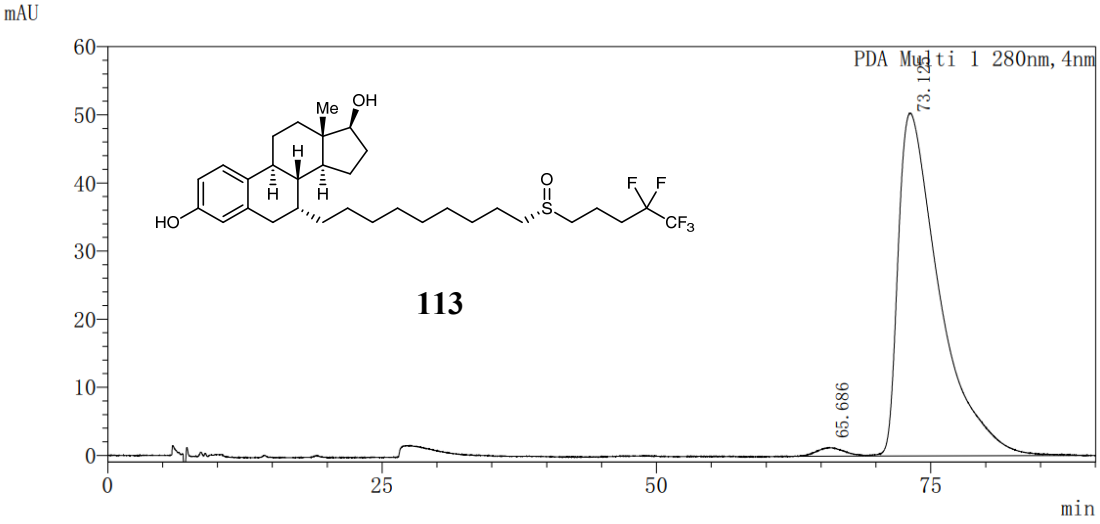
HPLC of 113



Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	64.653	9317310	54.880
2	74.412	7660359	45.120

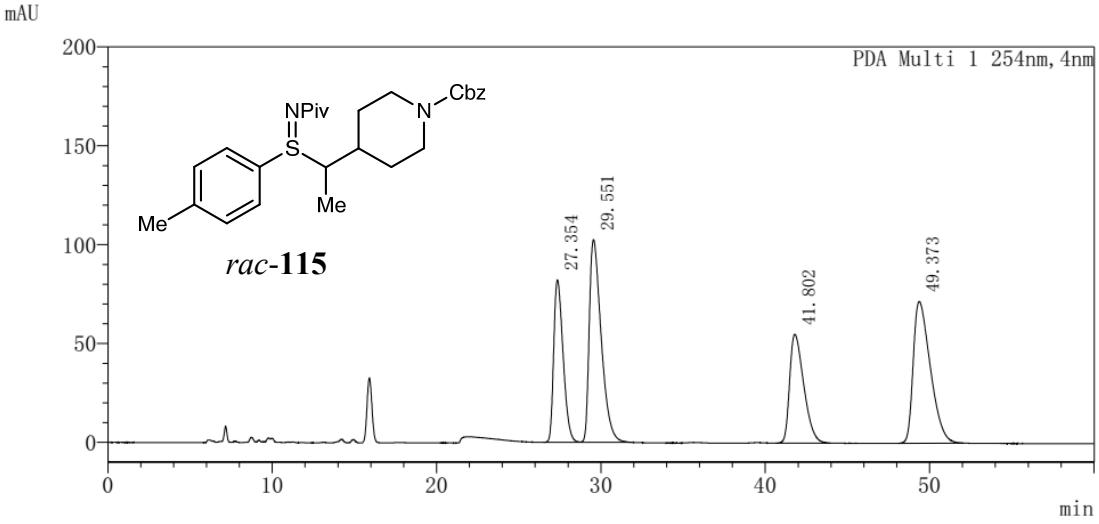


Peak Table

PDA Ch1 280nm

Peak#	Ret. Time	Area	Area%
1	65.686	230267	1.720
2	73.125	13157999	98.280

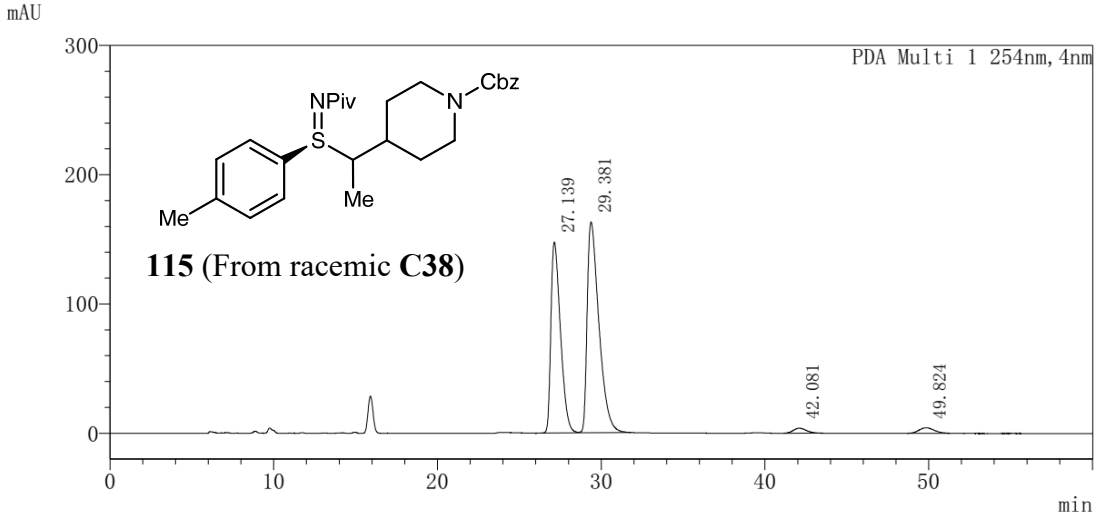
HPLC of 115



Peak Table

PDA Ch1 254nm

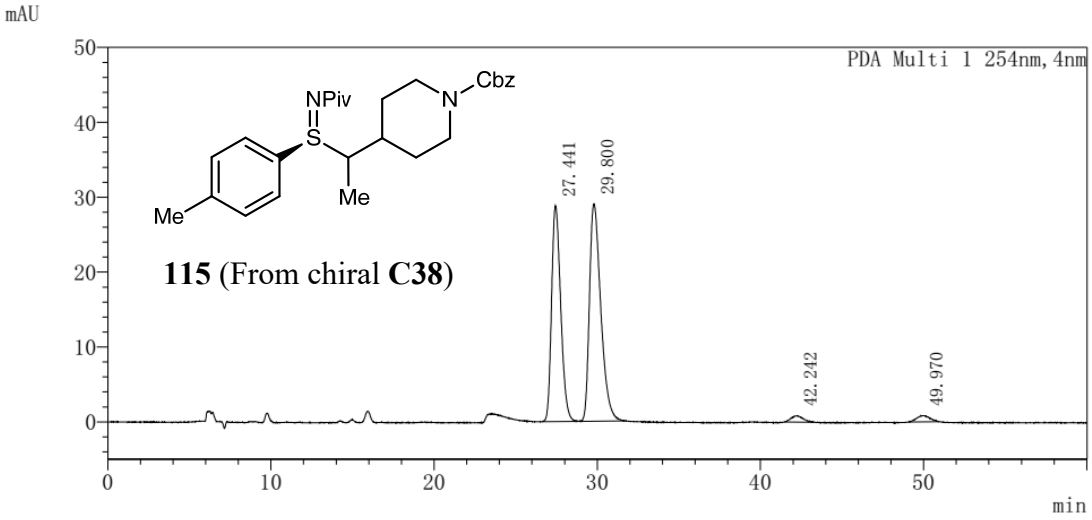
Peak#	Ret. Time	Area	Area%
1	27.354	3271464	19.331
2	29.551	5174668	30.577
3	41.802	3289366	19.437
4	49.373	5187837	30.655



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.139	5992931	40.962
2	29.381	8147233	55.687
3	42.081	214267	1.465
4	49.824	275969	1.886

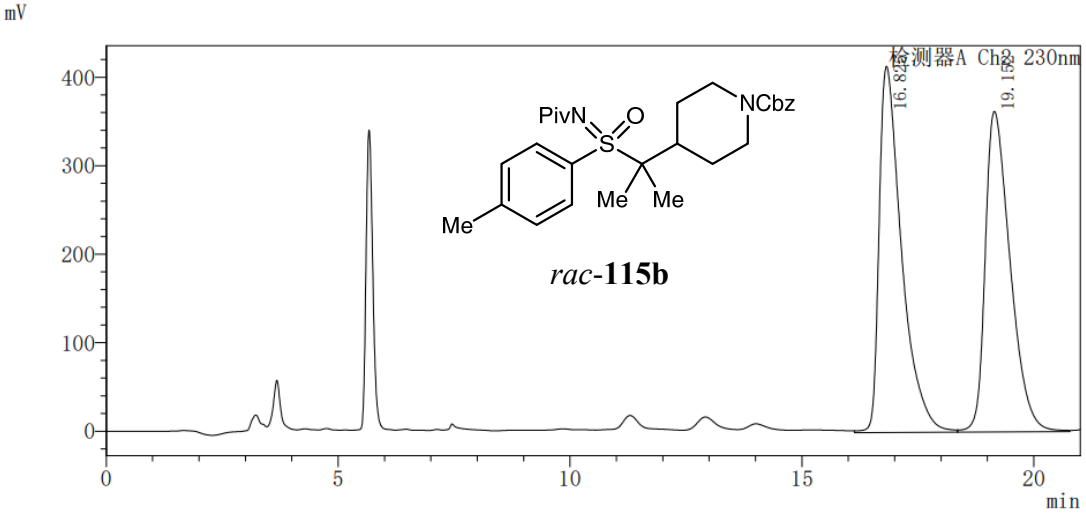


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.441	1119858	42.937
2	29.800	1399180	53.646
3	42.242	42328	1.623
4	49.970	46797	1.794

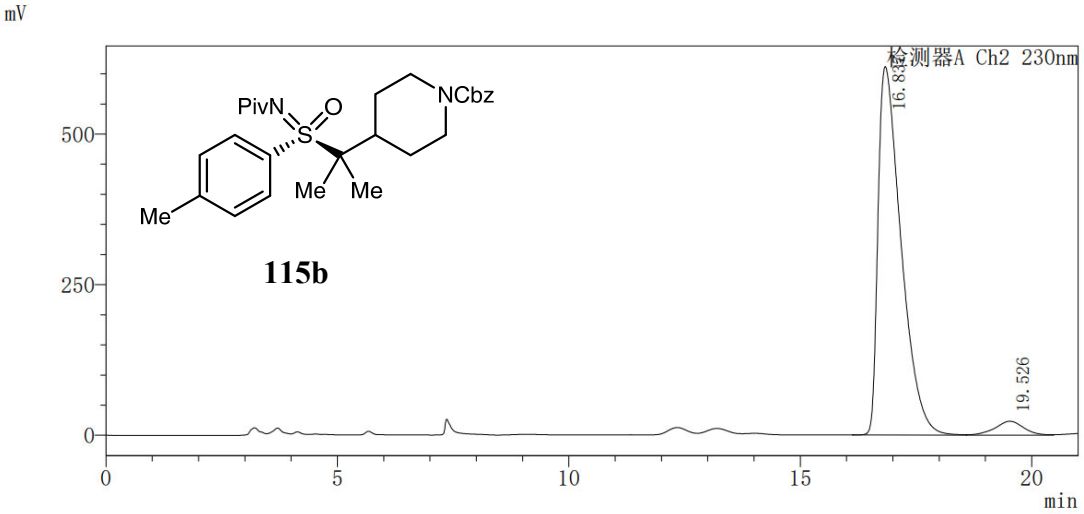
HPLC of 115b



Peak Table

Detector A Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	16.825	13969619	50.715
2	19.152	13575944	49.285

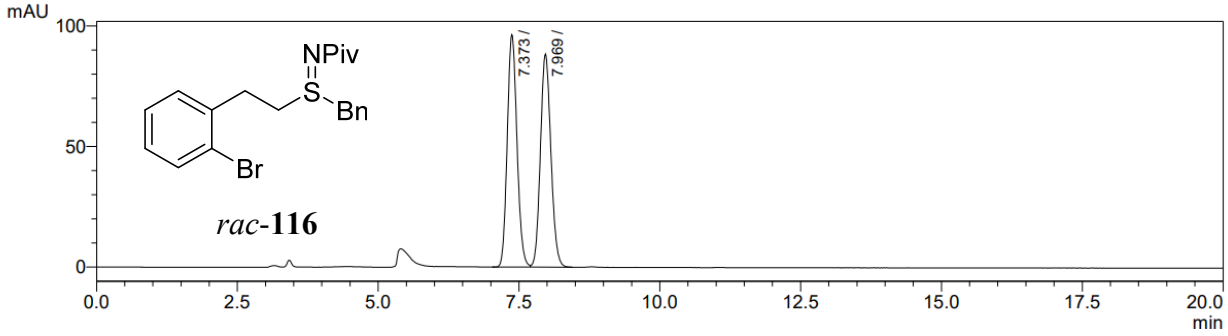


Peak Table

Detector A Ch2 230nm

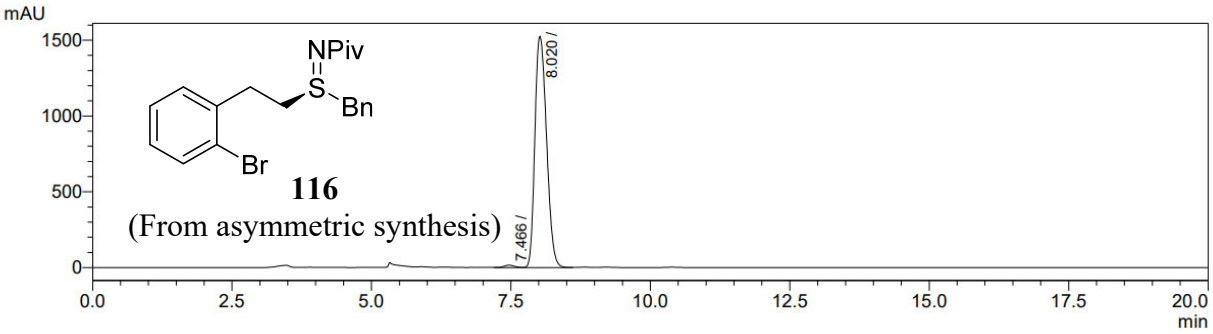
Peak#	Ret. Time	Area	Area%
1	16.837	21144431	95.534
2	19.526	988391	4.466

HPLC of 116



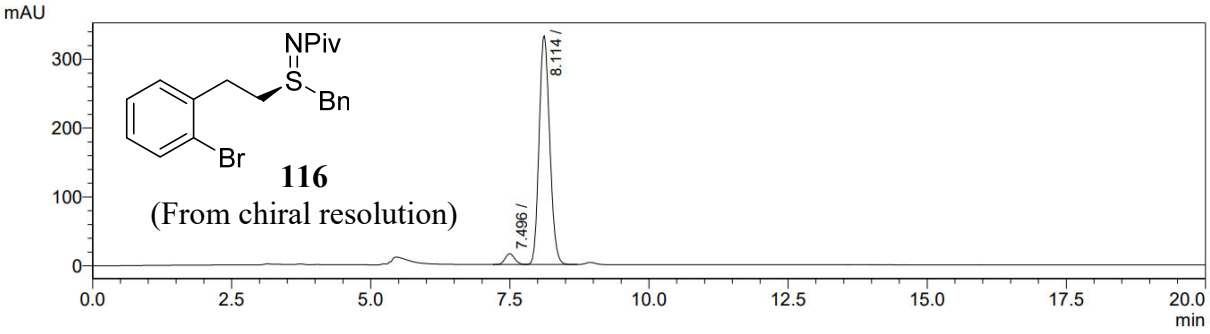
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.373	1158885	50.300
2	7.969	1145045	49.700



PDA Ch1 254nm

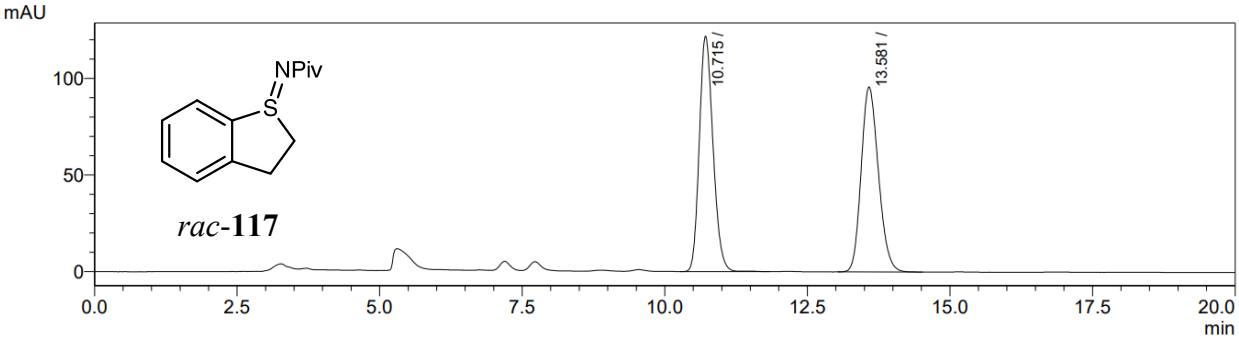
Peak#	Ret. Time	Area	Area%
1	7.466	209735	0.937
2	8.020	22166548	99.063



PDA Ch1 254nm

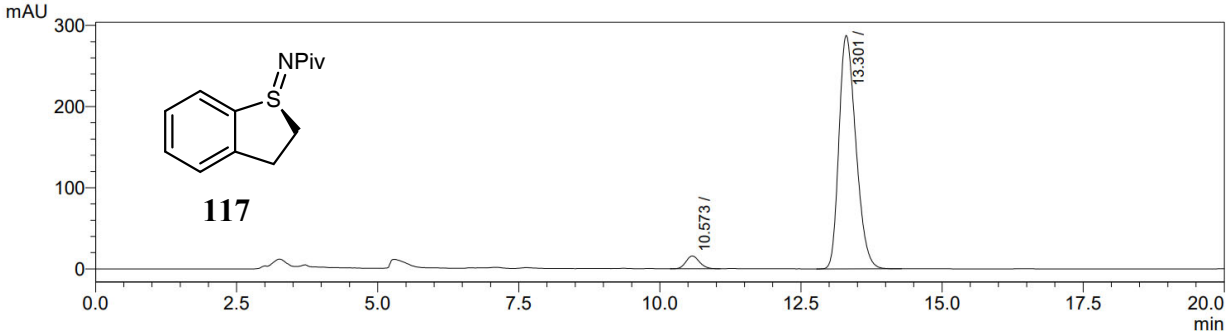
Peak#	Ret. Time	Area	Area%
1	7.496	190232	4.138
2	8.114	4407043	95.862

HPLC of 117



PDA Ch1 254nm

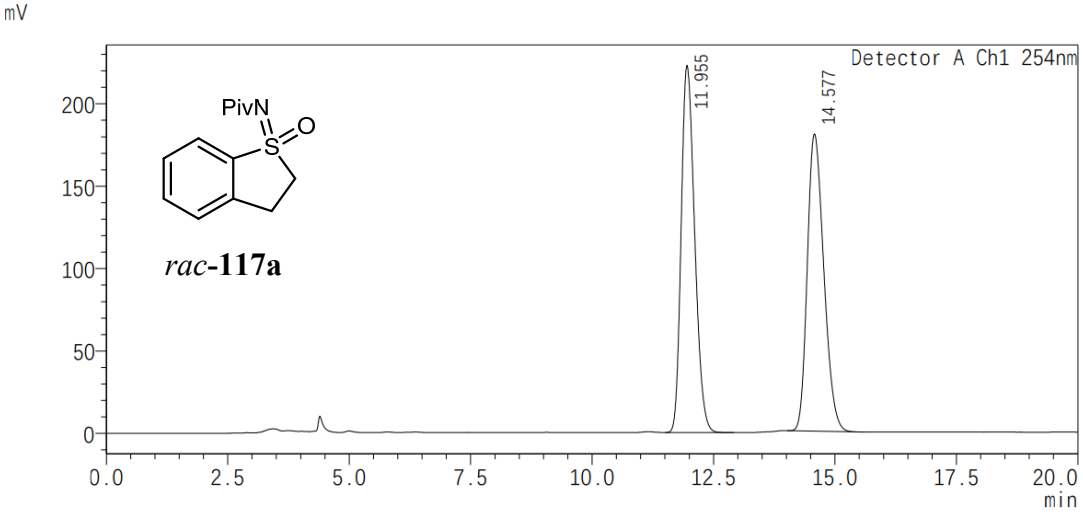
Peak#	Ret. Time	Area	Area%
1	10.715	2044769	50.353
2	13.581	2016126	49.647



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.573	262488	4.194
2	13.301	5995780	95.806

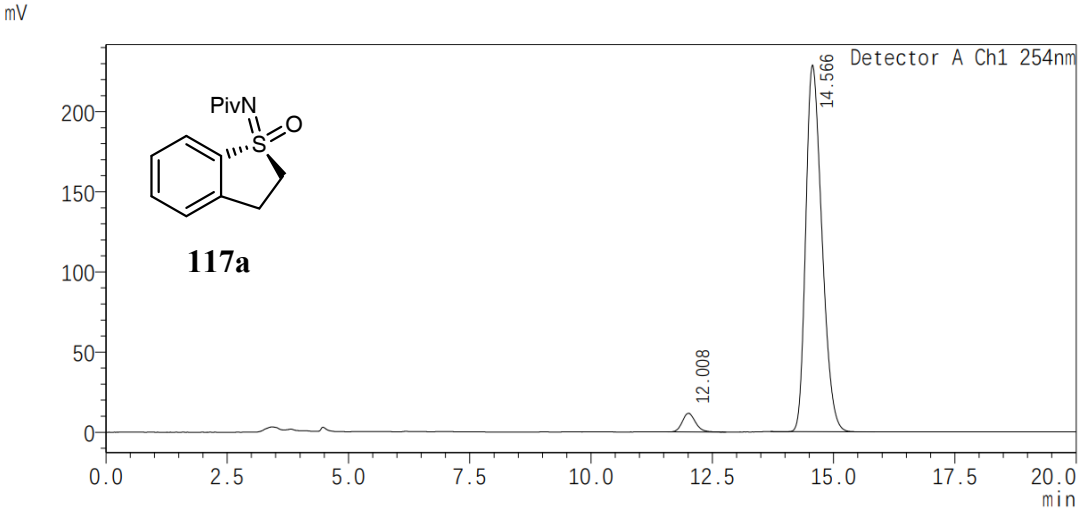
HPLC of 117a



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.955	4275374	50.046
2	14.577	4267545	49.954

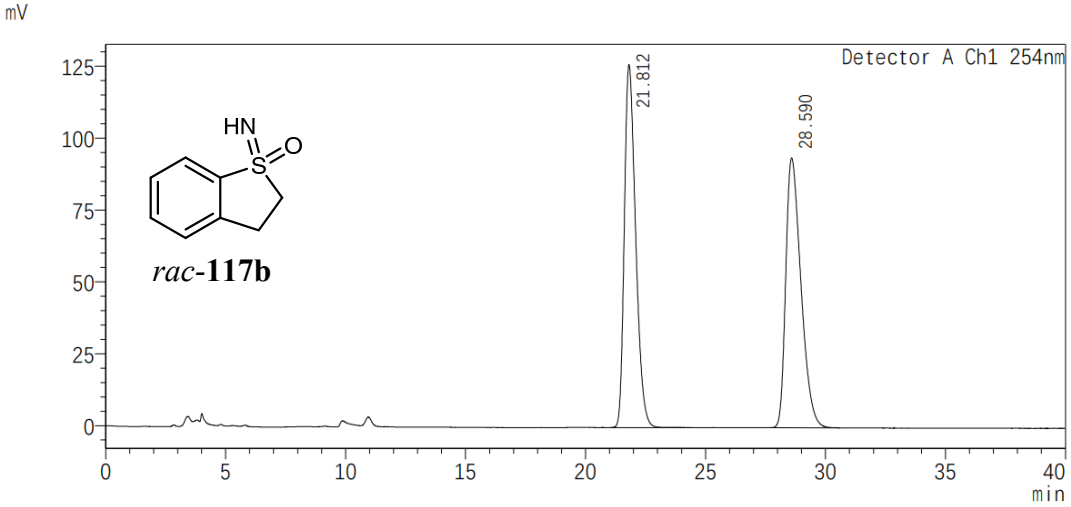


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.008	216225	3.914
2	14.566	5308741	96.086

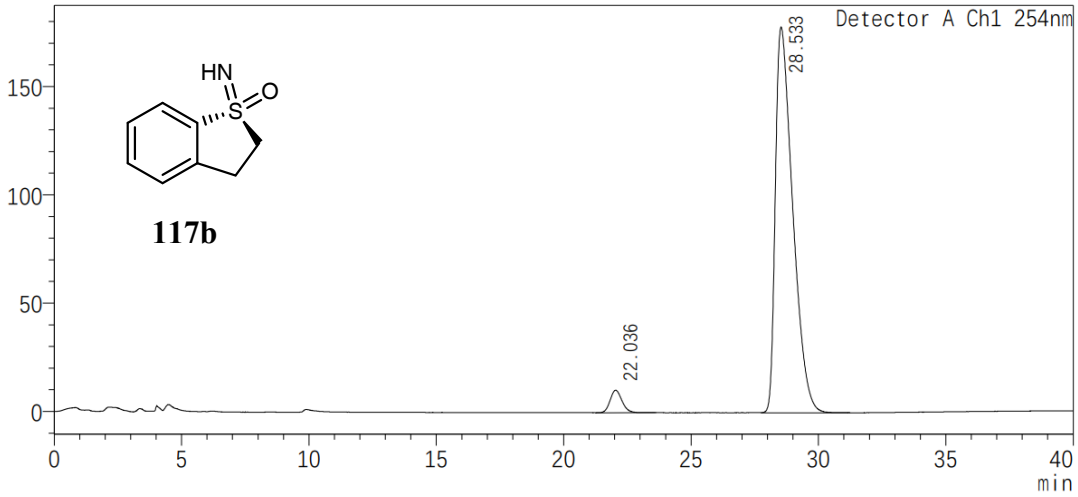
HPLC of 117b



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.812	4130452	49.978
2	28.590	4134027	50.022

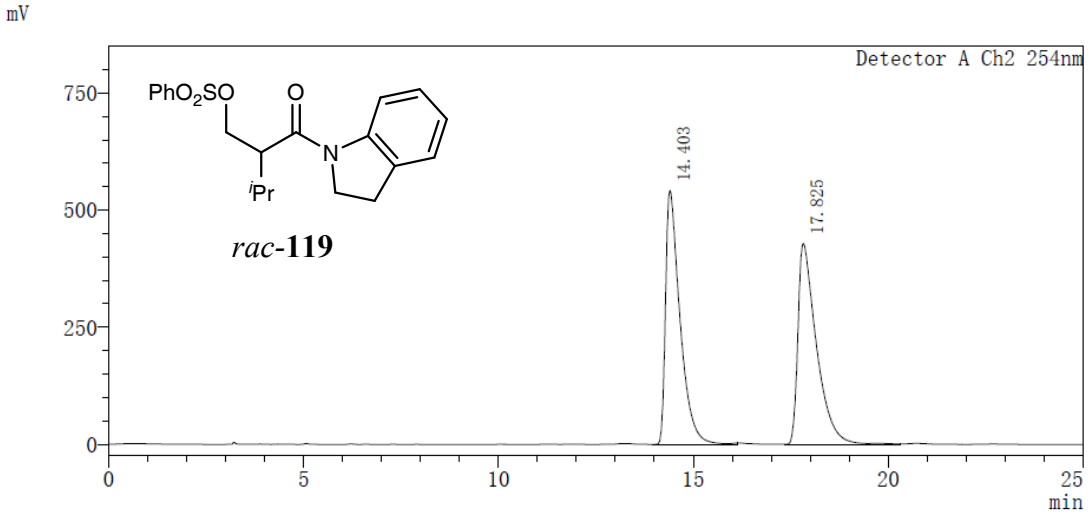


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.036	335419	3.821
2	28.533	8443100	96.179

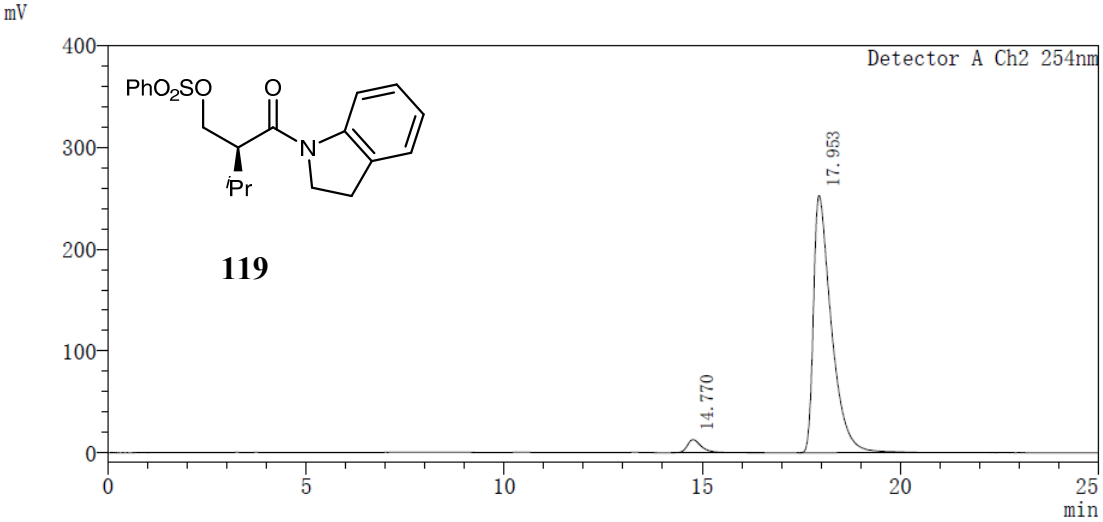
HPLC of 119



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	14.403	14023626	49.618
2	17.825	14239764	50.382

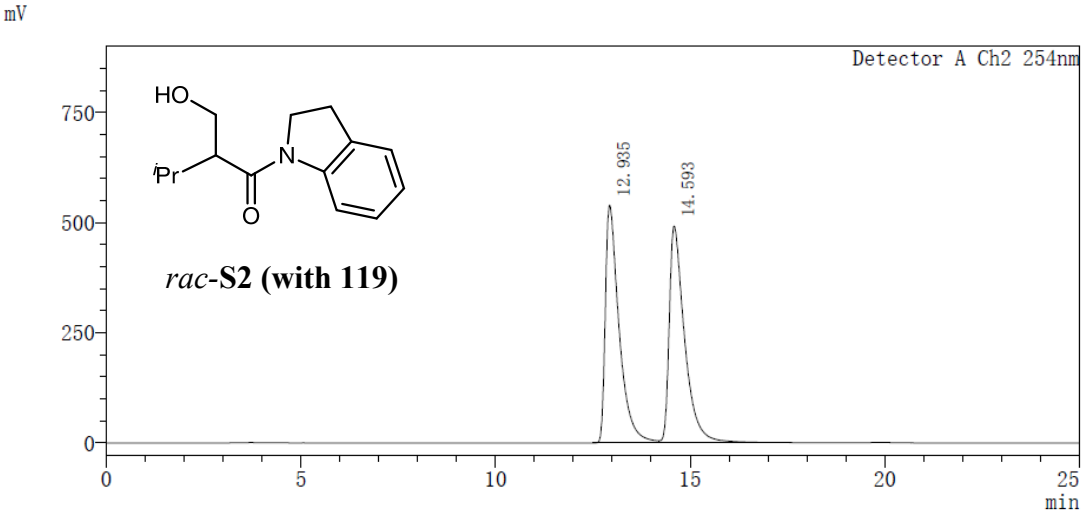


Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	14.770	319806	3.863
2	17.953	7959382	96.137

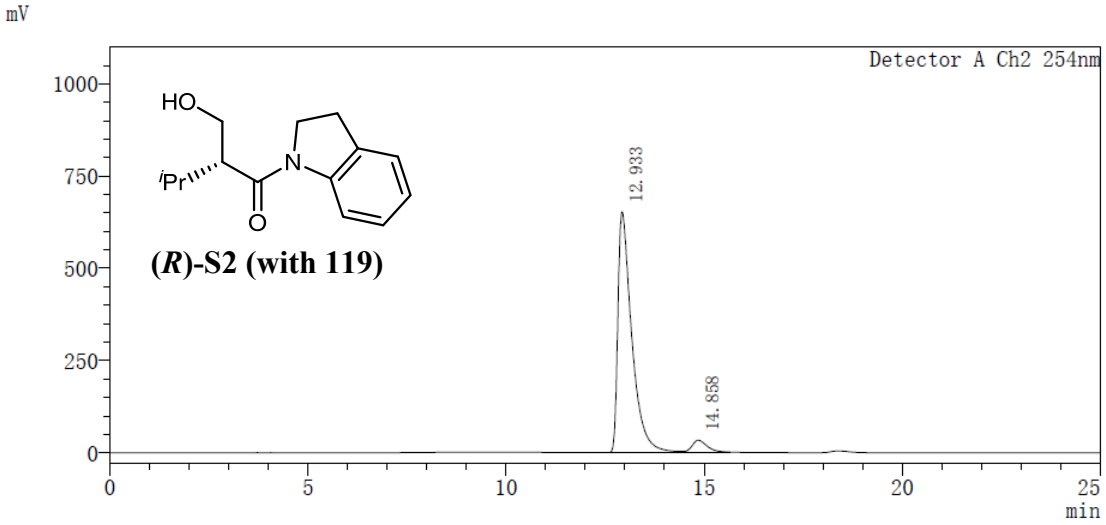
HPLC of S2



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	12.935	13266477	49.415
2	14.593	13580349	50.585

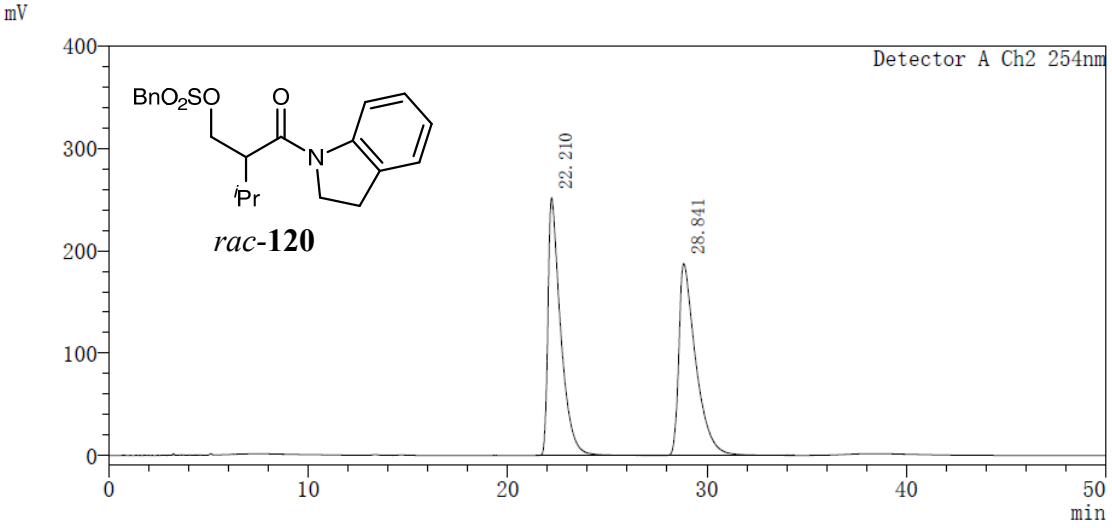


Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	12.933	15903250	94.459
2	14.858	932944	5.541

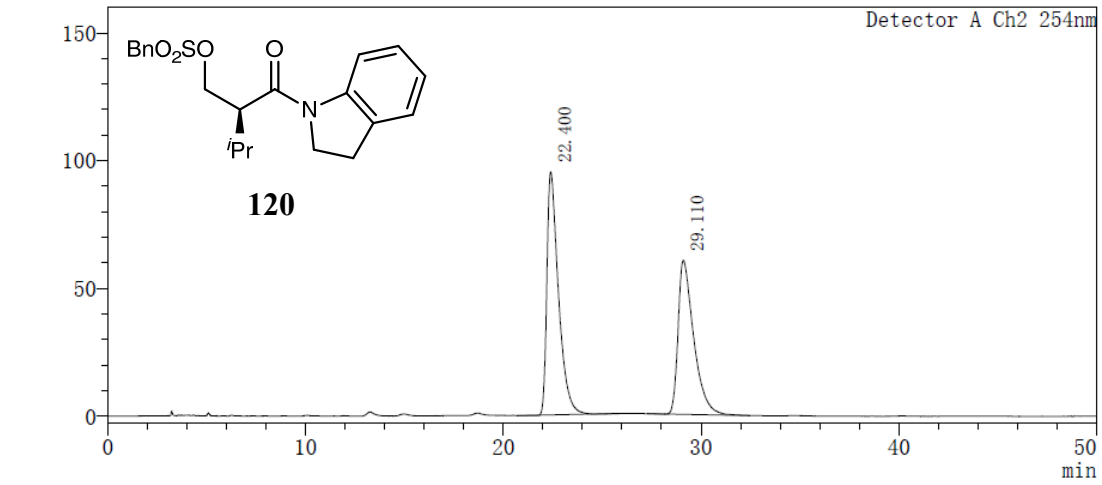
HPLC of 120



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	22.210	11099399	50.064
2	28.841	11071130	49.936



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	22.400	3866049	53.903
2	29.110	3306133	46.097