Supporting Information for

Enantioconvergent Cu-Catalyzed Radical C–N Coupling of Racemic Secondary Alkyl Halides to Access α-Chiral Primary Amines

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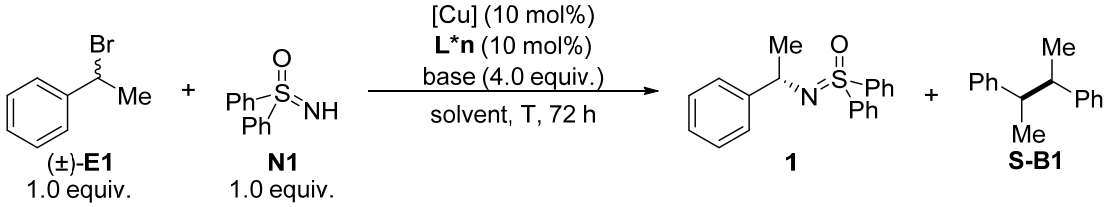
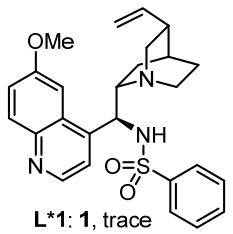
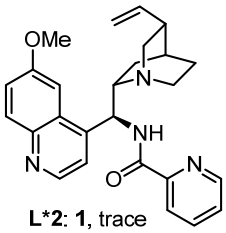
Table S1. Reaction Condition Optimization with Benzyl Bromide[a]

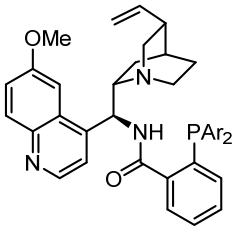




L*1: 1, trace



L*2: 1, trace

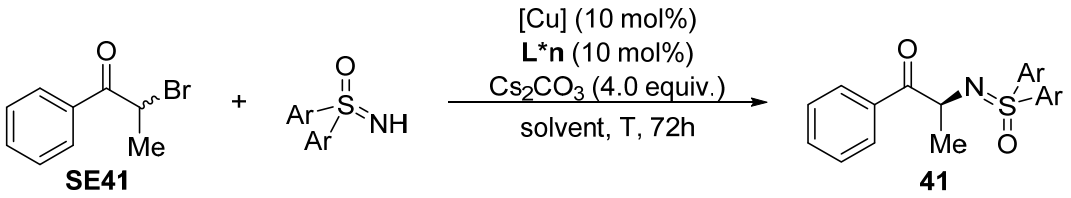


L*3, Ar = Ph
L*4, Ar = 1-naphthyl
L*5, Ar = 3,5-$Ph_2C_6H_3$
L*6, Ar = 3,5-(3,5-$Me_2C_6H_3)_2C_6H_3$
L*7, Ar = 3,5-(3,5-^{t}Bu$_2C_6H_3)_2C_6H_3$

entry	[Cu]	L*n	base	solvent	T (°C)	yield (%)	e.e. (%)
1	CuTc	**L*1**	Cs_2CO_3	Et_2O	r. t.	trace[b]	–
2	CuTc	**L*2**	Cs_2CO_3	Et_2O	r. t.	trace[b]	–
3	CuTc	**L*3**	Cs_2CO_3	Et_2O	r. t.	15[b]	61
4	CuTc	**L*4**	Cs_2CO_3	Et_2O	r. t.	trace	–
5	CuTc	**L*5**	Cs_2CO_3	Et_2O	r. t.	67	83
6	CuTc	**L*5**	Cs_2CO_3	THF	r. t.	trace	–
7	CuTc	**L*5**	Cs_2CO_3	benzene	r. t.	< 5	–
8	CuTc	**L*6**	Cs_2CO_3	Et_2O	r. t.	91	91
9	CuI	**L*6**	Cs_2CO_3	Et_2O	r. t.	trace	–
10	$Cu(PPh_3)_3Br$	**L*6**	Cs_2CO_3	Et_2O	r. t.	37	78
11	$Cu(^iPrCOO)_2$	**L*6**	Cs_2CO_3	Et_2O	r. t.	14	92
12	CuTc	**L*6**	K_2CO_3	Et_2O	r. t.	trace	–
13	CuTc	**L*6**	KOH	Et_2O	r. t.	< 5	67
14	CuTc	**L*6**	Cs_2CO_3	Et_2O	40	49	78
15	CuTc	**L*6**	Cs_2CO_3	Et_2O	0	85	95
16	CuTc	**L*7**	Cs_2CO_3	Et_2O	r. t.	81	97

[a]Reaction conditions: (±)-**E1** (0.025 mmol), **N1** (1.0 equiv.), [Cu] (10 mol%), **L*n** (10 mol%), and base (4.0 equiv.) in solvent (0.5 mL) at room temperature for 72 h under argon; Yield of **1** was isolated; Ee was based on HPLC analysis. [b]The yield of **S-B1** was based on ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard: 10% yield by **L*1**, trace by **L*2**, 13% yield by **L*3**.

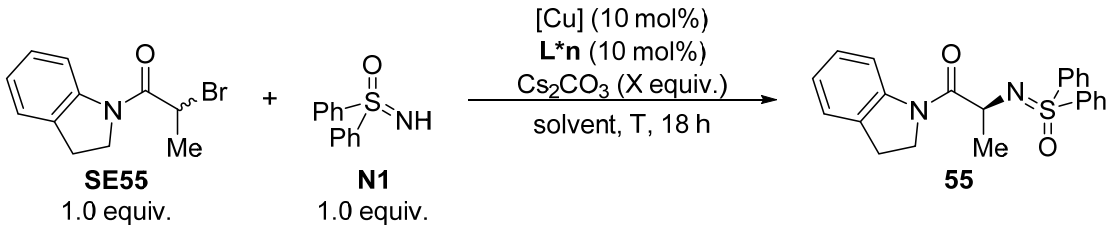
Table S2. Reaction Condition Optimization with α-Arylcarbonyl Alkyl Bromide[a]



entry	[Cu]	L*n	Ar	solvent	T (°C)	yield (%)	e.e. (%)
1	CuTc	**L*5**	Ph	Et_2O	r. t.	26	34
2	CuTc	**L*5**	Ph	THF	r. t.	41	20
3	CuTc	**L*5**	Ph	dioxane	r. t.	50	5
4	CuTc	**L*5**	Ph	benzene	r. t.	17	32
5	$Cu(HFacac)_2$	**L*5**	Ph	Et_2O	r. t.	88	53
6	$Cu(HFacac)_2$	**L*6**	Ph	Et_2O	r. t.	83	56
7	$Cu(HFacac)_2$	**L*7**	Ph	Et_2O	r. t.	82	63
8	$Cu(HFacac)_2$	**L*7**	4-MeOPh	Et_2O	r. t.	63	84
9	$Cu(HFacac)_2$	**L*7**	4-MeOPh	Et_2O	10	69	90
10	$Cu(HFacac)_2$	**L*7**	4-MeOPh	Et_2O	0	55	91
11	$Cu(HFacac)_2$	**L*7**	4-MeOPh	Et_2O	0	80	91

[a]Reaction conditions: (±)-**SE41** (0.025 mmol), sulfoximine (1.1 equiv.), [Cu] (10 mol%), **L*n** (10 mol%) and base (4.0 equiv.) in solvent (0.5 mL) for 72 h under argon; Yield of **41** was isolated; Ee was based on HPLC analysis.

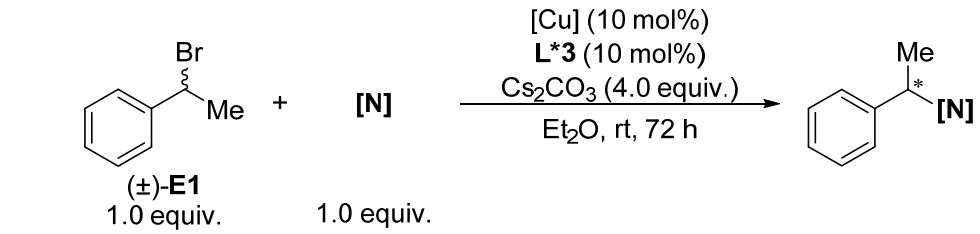
Table S3. Reaction Condition Optimization with α-Aminocarbonyl Alkyl Bromide[a]

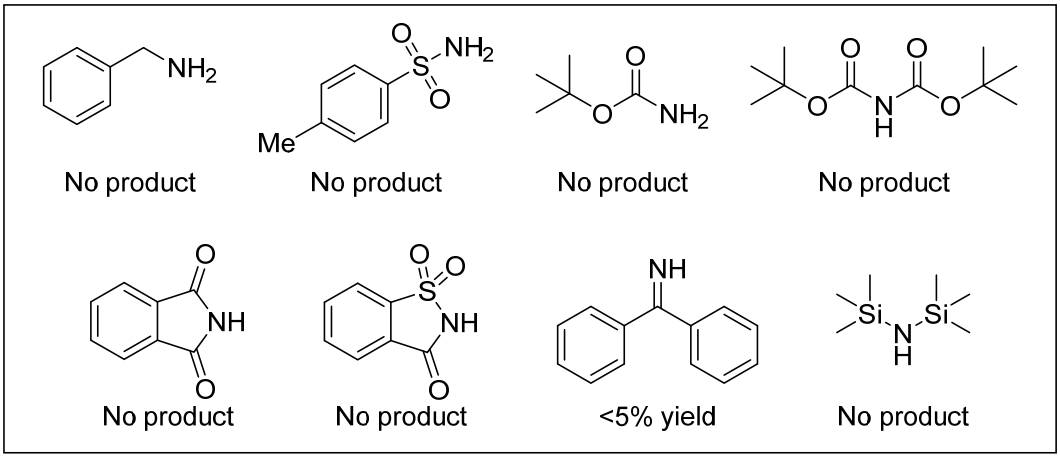


entry	[Cu]	L*n	X	solvent	T (°C)	yield (%)	e.e. (%)
1	CuTc	**L*5**	4.0	Et_2O	r. t.	60	44
2	CuTc	**L*5**	4.0	CH_2Cl_2	r. t.	71	17
3	CuTc	**L*5**	4.0	Dioxane	r. t.	52	25
4	CuTc	**L*5**	4.0	Benzene	r. t.	36	13
5	CuTc	**L*6**	4.0	Et_2O	r. t.	71	75
6	CuI	**L*5**	4.0	Et_2O	r. t.	56	61
7	$Cu(PPh_3)_3Br$	**L*5**	4.0	Et_2O	r. t.	70	44
8	$Cu(^iPrCOO)_2$	**L*5**	4.0	Et_2O	r. t.	83	48
9	$Cu(HFacac)_2$	**L*5**	4.0	Et_2O	r. t.	90	77
10	$Cu(HFacac)_2$	**L*6**	4.0	Et_2O	r. t.	91	94
11	$Cu(HFacac)_2$	**L*6**	4.0	Et_2O	0	85	96
12	$Cu(HFacac)_2$	**L*6**	2.5	Et_2O	r. t.	95	94
13	$Cu(HFacac)_2$	**L*6**	2.0	Et_2O	r. t.	83	93

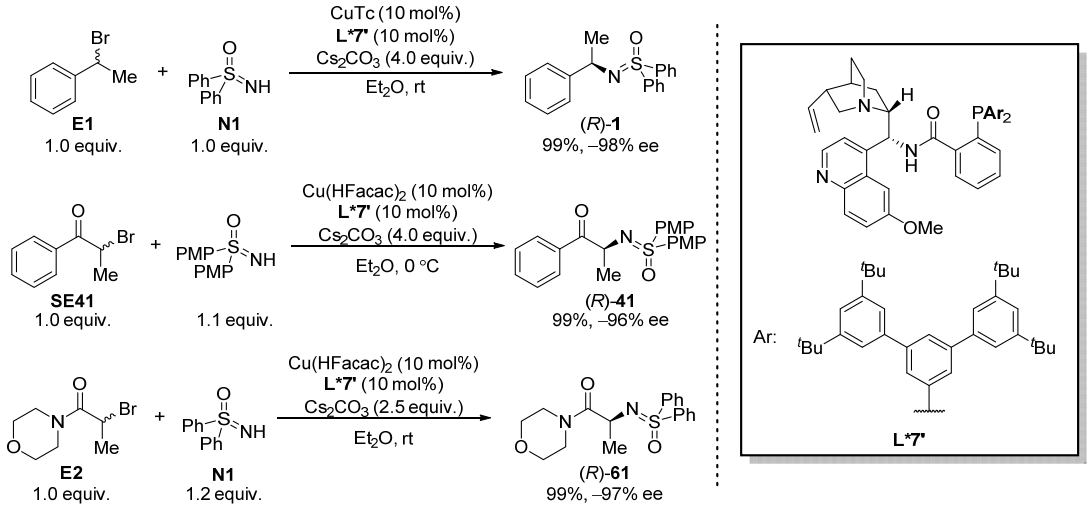
[a]Reaction conditions: (±)-**SE55** (0.025 mmol), **N1** (1.0 equiv.), [Cu] (10 mol%), **L*n** (10 mol%), and base (4.0 equiv.) in solvent (0.5 mL) for 72 h under argon; Yield of **55** was isolated; Ee was based on HPLC analysis.

Scheme S1. The Attempt of Other Common Ammonia Surrogates

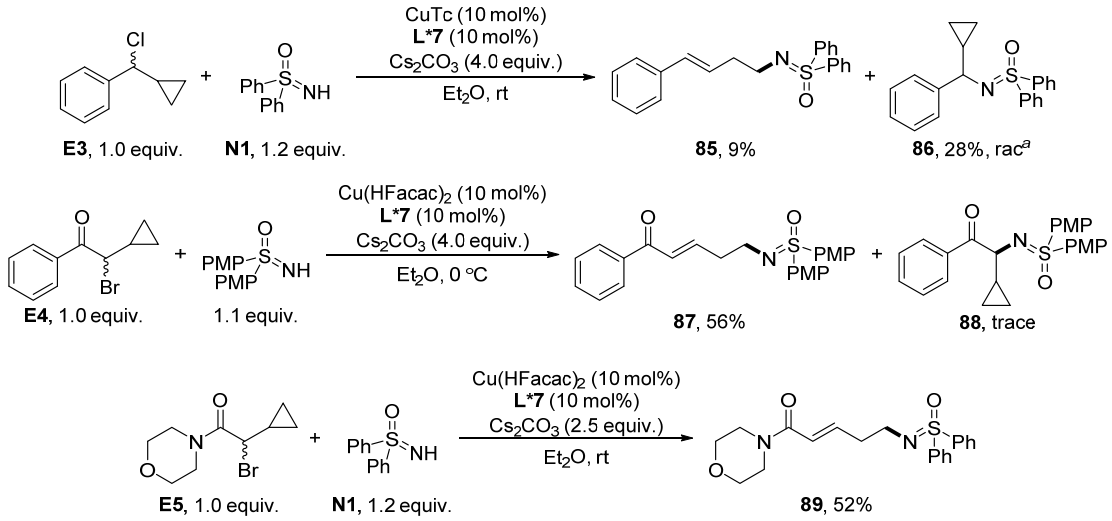




Scheme S2. The Synthesis of Antipodes



Scheme S3. Radical Clock Experiments



[a]The complete loss of enantioselectivity indicates that **86** might have formed through facile direct substitution reactions between **E3** and **N1** due to the doubly activated nature of **E3**.

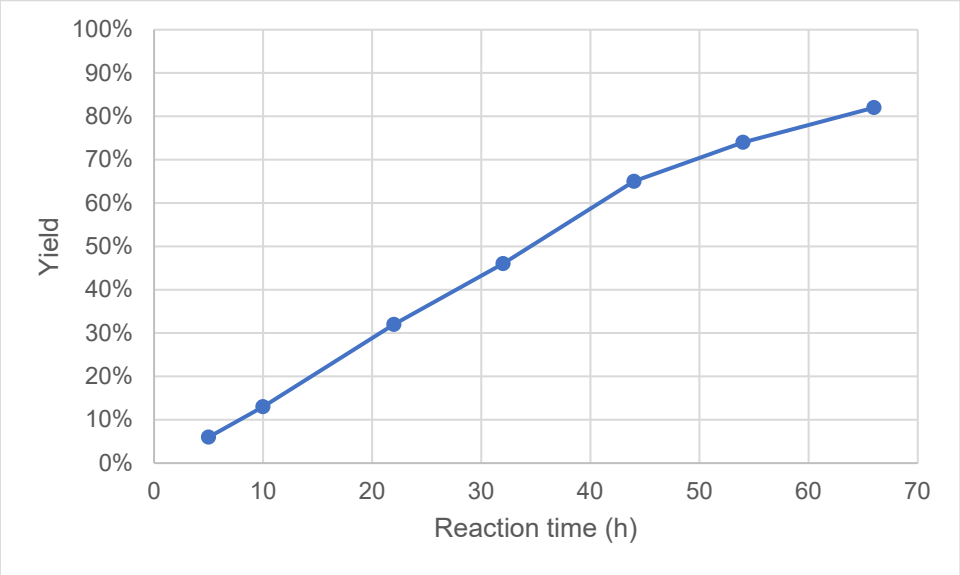
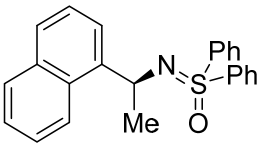


Figure S1. The time-course profile of the model reaction under the optimal conditions.



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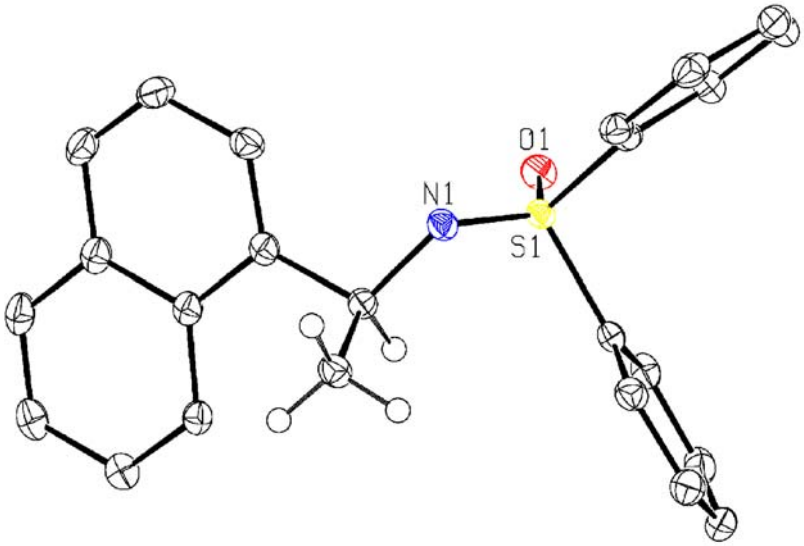
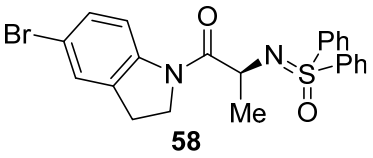


Figure S2. The X-ray structure of **26**.



58

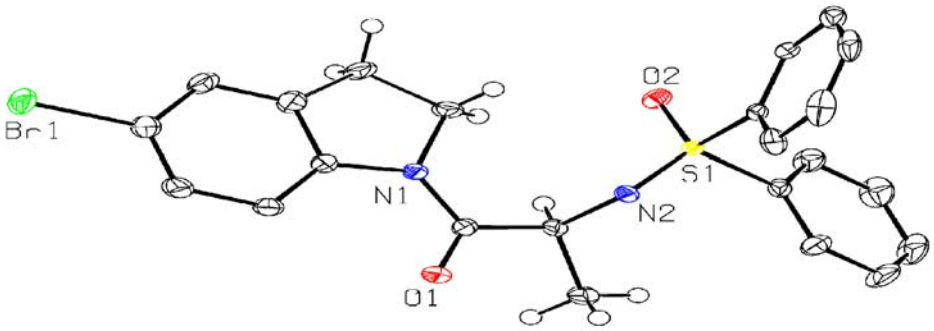
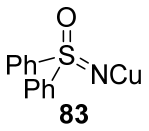


Figure S3. The X-ray structure of **58**.



83

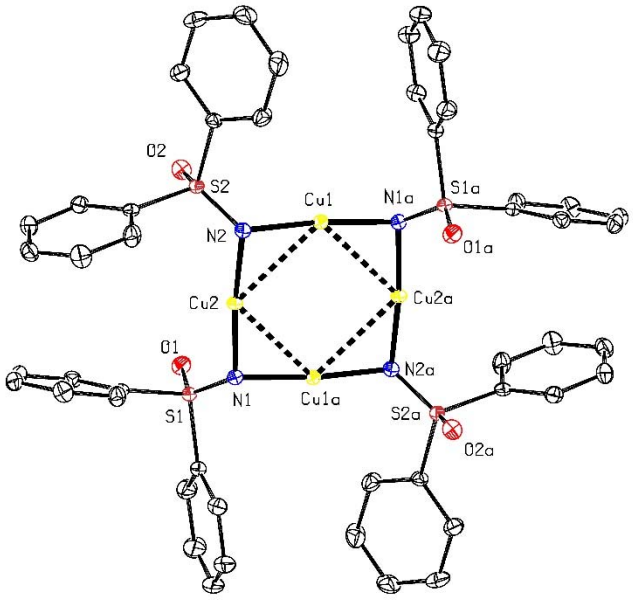


Figure S4. The X-ray structure of **83**.

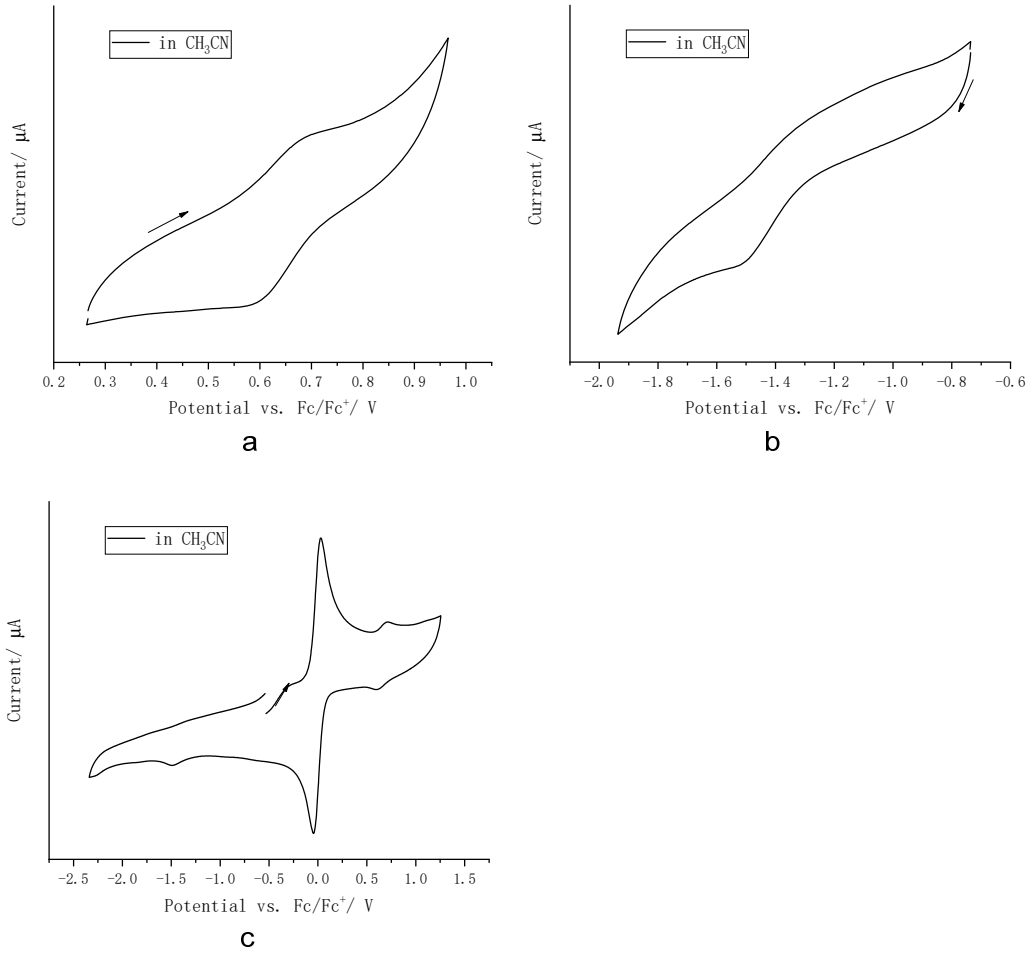


Figure S5. Cyclic voltammograms of compound **83** were measured in CH_3CN in the presence of $TBAPF_6$ (0.1 M) with scan rates of 100 mV s^{-1}. Potentials are given vs. the ferrocene/ferrocenium (Fc/Fc^+) couple. (a) and (b) are the scan spectra of corresponding oxidation and reduction, respectively. (c) is the whole scan spectrum of **83** with Fc/Fc^+ in CH_3CN.

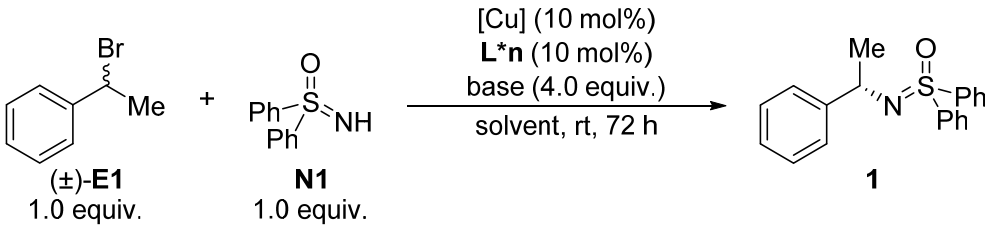
General information

Most of reactions were carried out under 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. Copper(I) thiophene-2-carboxylate (CuTc, CAS No. 68986-76-5) was purchased from Bide Pharmatech Ltd. Copper(II) hexafluoroacetylacetonate ($Cu(HFacac)_2$, CAS No. 14781-45-4) was purchased from TCI. Cs_2CO_3 was purchased from Bide Pharmatech Ltd. and treated by hot gun (approximate 500 to 600 °C) for 5 minutes in vacuum. Anhydrous diethyl ether (Et_2O) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd, which was treated by 4 Å Molecular sieve and distilled after refluxing with sodium and benzophenone. 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), hexane, ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2) and methanol were purchased from Shanghai Titan Scientific Co. Ltd without further purification. Visualization on TLC was achieved by use of UV light (254 nm), iodine on silica gel or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ^1H NMR, 100 or 150 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR and 162 MHz or 243 MHz for ^{31}P NMR, respectively, in $CDCl_3$, CD_3OD, C_6D_6, D_2O or DMSO-d_6 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, quarter; p, pentet, m, multiplet; br, broad), 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 (ee) value was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector (at appropriate wavelength) or SHIMADZU LC-20AD with SPD-20AV detector. Column conditions are reported in

the experimental section below. Specific optical rotation was measured on a Rudolph-Autopol I. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα radiation.

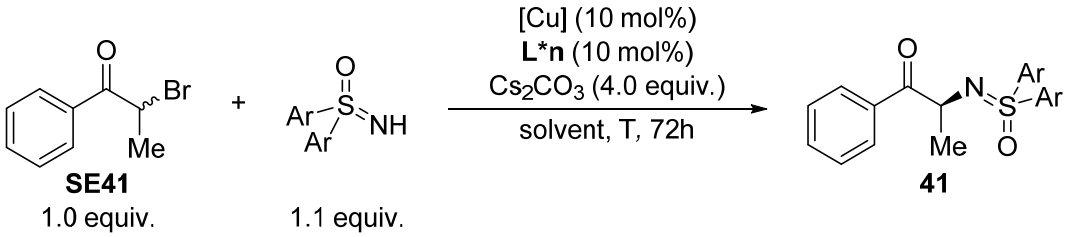
General procedure for reaction condition screening.

General procedure for Supplementary Table 1.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone **N1** (5.4 mg, 0.025 mmol, 1.0 equiv.), [Cu] (0.0025 mmol, 10 mol%), chiral ligand **L*n** (0.0025 mmol, 10 mol%), base (0.10 mmol, 4.0 equiv.) and anhydrous solvent (0.5 mL). To this solution was added (1-bromoethyl)benzene (4.6 mg, 0.025 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 72 h. The precipitate was diluted with EtOAc, filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

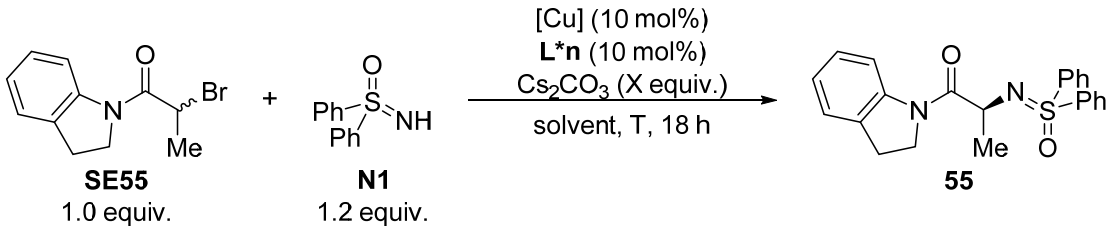
General procedure for Supplementary Table 2.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfoximine (0.028 mmol, 1.1 equiv.), [Cu] (0.0025 mmol, 10 mol%), chiral ligand **L*n** (0.0025 mmol, 10 mol%), Cs_2CO_3 (32.6 mg, 0.10 mmol, 4.0 equiv.) and anhydrous solvent (0.5 mL). To this solution was added 2-bromo-1-phenylpropan-1-one (5.3 mg, 0.025 mmol, 1.0 equiv.) and the reaction mixture was stirred for 72 h. The precipitate was diluted with EtOAc, filtered through

a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

General procedure for Supplementary Table 3.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone (6.5 mg, 0.030 mmol, 1.2 equiv.), [Cu] (0.0025 mmol, 10 mol%), chiral ligand **L*n** (0.0025 mmol, 10 mol%), Cs_2CO_3 (X equiv.) and anhydrous solvent (0.5 mL). Then, 2-bromo-1-(indolin-1-yl)propan-1-one (6.3 mg, 0.025 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 18 h. The precipitate was diluted with EtOAc, filtered off and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford the desired product.

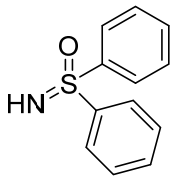
The synthesis of starting materials.

All the benzylic halides were synthesized following the literatures.[1]

The Synthesis of sulfoximines.

General procedure SM A: To a solution of sulfide or sulfoxide (1.0 equiv.) in methanol were added $PhI(OAc)_2$ (2.5 equiv.) and ammonium carbamate (2.0 equiv.) at 0 °C. The reaction mixture was warmed up to room temperature and stirred overnight. After that, the solvent was removed by evaporator and the residue was dissolved in CH_2Cl_2. The organic phase was washed with water, dried over 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.

Iminodiphenyl-λ^6-sulfanone (N1)



N1

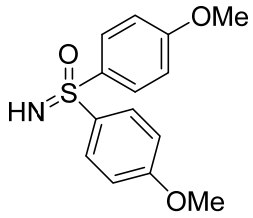
According to **General procedure SM A** with sulfinyldibenzene (2.02 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **N1** as a white powder (1.87 g, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 7.91 (m, 4H), 7.67 – 7.37 (m, 6H), 2.74 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 132.6, 129.1, 127.9.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{12}NOS$ $[M + H]^+$ 218.0634, found 218.0633.

Iminobis(4-methoxyphenyl)-λ^6-sulfanone (SN2)



SN2

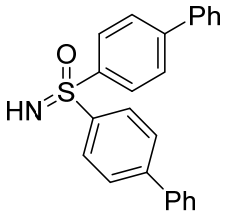
According to **General procedure SM A** with 4,4'-sulfinylbis(methoxybenzene) (2.62 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **SN2** as a yellow powder (2.22 g, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 4H), 6.93 (d, *J* = 8.5 Hz, 4H), 3.82 (s, 6H), 2.92 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 135.6, 129.8, 114.3, 55.6.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{16}NO_3S$ $[M + H]^+$ 278.0845, found 278.0844.

di([1,1'-Biphenyl]-4-yl)(imino)-λ^6-sulfanone (SN3)



SN3

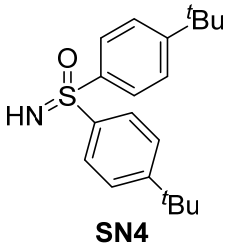
According to **General procedure SM A** with 4,4''-sulfinyld^{i}1,1'-biphenyl (3.54 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/3) to yield the product **SN3** as a white powder (2.44 g, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 4H), 7.81 – 7.65 (m, 4H), 7.65 – 7.53 (m, 4H), 7.53 – 7.36 (m, 6H), 3.16 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 142.1, 139.4, 129.0, 128.47, 128.46, 127.9, 127.4.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{20}NOS$ $[M + H]^+$ 370.1260, found 370.1258.

bis(4-(*tert*-Butyl)phenyl)(imino)-λ^6-sulfanone (SN4)



SN4

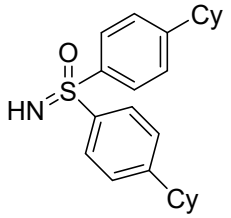
According to **General procedure SM A** with 4,4'-sulfinylbis(*tert*-butylbenzene) (3.14 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **SN4** as a white powder (2.66 g, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 4H), 7.47 (d, *J* = 8.5 Hz, 4H), 2.94 (brs, 1H), 1.29 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 140.6, 127.8, 126.1, 35.0, 31.1.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{28}NOS$ $[M + H]^+$ 330.1886, found 330.1883.

bis(4-Cyclohexylphenyl)(imino)-λ^6-sulfanone (SN5)



SN5

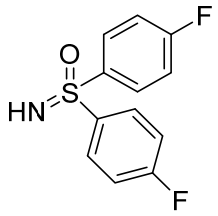
According to **General procedure SM A** with 4,4'-sulfinylbis(cyclohexylbenzene) (3.66 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **SN5** as a white powder (3.16 g, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 4H), 2.86 (brs, 1H), 2.63 – 2.38 (m, 2H), 1.77 (dd, *J* = 33.6, 10.8 Hz, 10H), 1.50 – 1.09 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 140.9, 128.0, 127.6, 44.4, 34.09, 34.07, 26.7, 26.0.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{32}NOS$ $[M + H]^+$ 382.2199, found 382.2195.

bis(4-Fluorophenyl)(imino)-λ^6-sulfanone (SN6)



SN6

According to **General procedure SM A** with bis(4-fluorophenyl)sulfane (2.22 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **SN6** as a yellow oil (2.28 g, 90% yield).

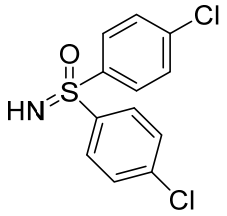
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.95 (m, 4H), 7.22 – 7.06 (m, 4H), 3.23 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2 (d, *J* = 255.1 Hz), 139.3 (d, *J* = 3.1 Hz), 130.6 (d, *J* = 9.5 Hz), 116.4 (d, *J* = 22.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –105.6 (tt, *J* = 8.2, 4.8 Hz, 2F).

HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}F_2NOS$ $[M + H]^+$ 254.0446, found 254.0444.

bis(4-Chlorophenyl)(imino)-λ^6-sulfanone (SN7)



SN7

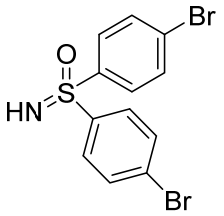
According to **General procedure SM A** with bis(4-chlorophenyl)sulfane (2.54 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **SN7** as a yellow powder (2.48 g, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 4H), 7.49 – 7.42 (m, 4H), 3.15 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.6, 129.6, 129.4.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}Cl_2NOS$ $[M + H]^+$ 285.9855, found 285.9854.

bis(4-Bromophenyl)(imino)-λ^6-sulfanone (SN8)



SN8

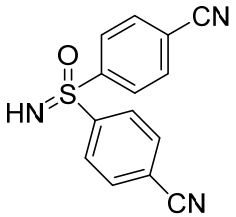
According to **General procedure SM A** with bis(4-bromophenyl)sulfane (3.42 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **SN8** as an orange powder (3.36 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 4H), 7.58 (d, *J* = 8.3 Hz, 4H), 3.27 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 132.5, 129.5, 128.1.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}Br_2NOS$ $[M + H]^+$ 373.8844, found 373.8844.

4,4'-Sulfonimidoyldibenzonitrile (N2)



N2

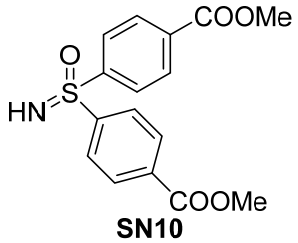
According to **General procedure SM A** with 4,4'-sulfinyldibenzonitrile (2.52 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **N2** as a yellow powder (2.32 g, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.11 (m, 4H), 7.95 – 7.77 (m, 4H), 3.36 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 133.2, 128.8, 117.09, 117.05.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}N_3OS$ $[M + H]^+$ 268.0539, found 268.0538.

Dimethyl 4,4'-sulfonimidoyldibenzoate (SN10)



SN10

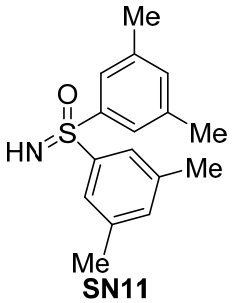
According to **General procedure SM A** with dimethyl 4,4'-sulfinyldibenzoate (3.18 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **SN10** as a white powder (2.73 g, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.06 (m, 8H), 3.94 (s, 6H), 3.28 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 146.7, 134.1, 130. 5, 128.1, 52.7.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}NO_5S$ $[M + H]^+$ 334.0744, found 334.0742.

bis(3,5-Dimethylphenyl)(imino)-λ^6-sulfanone (SN11)



SN11

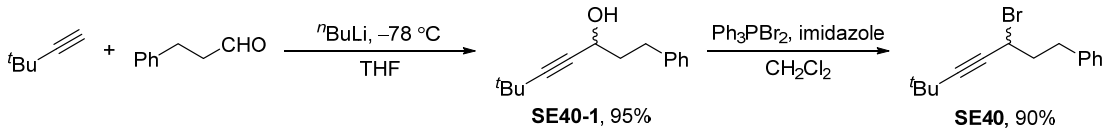
According to **General procedure SM A** with dimethyl 5,5'-sulfinylbis(1,3-dimethylbenzene) (2.58 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **SN11** as a white powder (1.97 g, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 4H), 7.11 (s, 2H), 2.98 (s, 1H), 2.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 139.1, 134.2, 125.4, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{20}NOS$ $[M + H]^+$ 274.1260, found 274.1258.

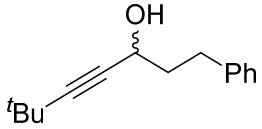
The synthesis of SE40.



To a solution of ^{n}BuLi (5.0 mL, 12.0 mmol, 1.2 equiv., 2.4 M in hexane) in THF (5.0 mL) was added 3,3-dimethylbut-1-yne (984.0 mg, 12.0 mmol, 1.2 equiv.) dropwise with vigorously stirring at −78 °C under an argon atmosphere. After that, the mixture was warmed up to room temperature, stirred for another 30 min, and cooled down to −78 °C again. To this solution was added 3-phenylpropanal (1.34 g, 10.0 mmol, 1.0 equiv.) dropwise. The reaction mixture was warmed up to room temperature and stirred for another 2 h. The reaction was quenched with slow addition of ice. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford the crude product **SE40-1** (2.05 g, 95% yield) as a colorless oil, which was immediately applied to the next step without further purification.

The crude **SE40-1** (2.05 g) was dissolved in CH_2Cl_2 (20.0 mL) and cooled down to 0 °C. To this solution were added imidazole (775.2 mg, 11.4 mmol, 1.2 equiv.) and PPh_3Br_2 (4.79 g, 11.4 mmol, 1.2 equiv.) sequentially at that temperature and the reaction mixture was warmed up to room temperature and stirred for another 3 h. The mixture was filtered through a short pad of Celite and washed with Et_2O. The combined organic phase was concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford the desired product **SE40** (2.38 g, 90% yield) as a colorless oil.

6,6-Dimethyl-1-phenylhept-4-yn-3-ol (SE40-1)

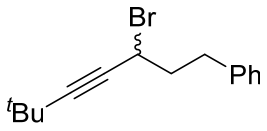


SE40-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 4.40 (q, *J* = 6.0 Hz, 1H), 2.83 (t, *J* = 7.9 Hz, 2H), 2.08 – 1.96 (m, 2H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 128.5, 128.4, 125.9, 94.2, 79.5, 61.9, 39.8, 31.6, 31.1, 27.4.

(3-Bromo-6,6-dimethylhept-4-yn-1-yl)benzene (SE40)



SE40

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 2H), 7.28 – 7.18 (m, 3H), 4.53 (t, *J* = 6.7 Hz, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.44 – 2.22 (m, 2H), 1.27 (s, 9H).

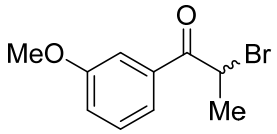
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 128.60, 128.55, 126.2, 96.7, 77.8, 41.8, 37.8, 33.5, 30.8, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{19}$ $[M - Br]^+$ 199.1481, found 199.1482.

The synthesis of α-bromo ketones.

General procedure SM B: To a solution of ketone (1.0 equiv.) in Et_2O was added bromine (10.0 equiv.) dropwise at room temperature and the reaction mixture was stirred for another 1 h. Upon completion (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ solution and extracted with Et_2O three times. The combined organic phase was washed with $Na_2S_2O_3$ solution and brine, then dried over Na_2SO_4 and concentrated to afford the residue. The residue was purified by flash column chromatography on silica gel to afford the desired product.

2-Bromo-1-(3-methoxyphenyl)propan-1-one (SE44)



SE44

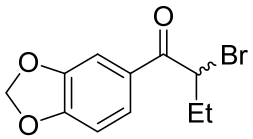
According to **General procedure SM B** with 1-(3-methoxyphenyl)propan-1-one (1.64 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product **SE44** as a colorless oil (2.01 g, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 1H), 7.57 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.15 (ddd, *J* = 8.2, 2.7, 0.9 Hz, 1H), 5.30 (q, *J* = 6.6 Hz, 1H), 3.88 (s, 3H), 1.92 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 159.9, 135.4, 129.7, 121.3, 120.2, 113.3, 55.5, 41.6, 20.2.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{12}BrO_2$ $[M + H]^+$ 243.0015, found 243.0015.

1-(Benzo[*d*][1,3]dioxol-5-yl)-2-bromobutan-1-one (SE45)



SE45

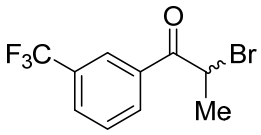
According to **General procedure SM B** with 1-(benzo[*d*][1,3]dioxol-5-yl)butan-1-one (1.92 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product **SE45** as a colorless oil (1.92 g, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 1H), 7.53 – 7.47 (m, 1H), 6.92 – 6.84 (m, 1H), 6.07 (s, 2H), 5.05 – 4.95 (m, 1H), 2.32 – 2.04 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 152.3, 148.4, 129.2, 125.2, 108.7, 108.1, 102.1, 49.0, 27.1, 12.2.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}BrO_3$ $[M + H]^+$ 270.9964 & 272.9944, found 270.9963 & 272.9942.

2-Bromo-1-(3-(trifluoromethyl)phenyl)propan-1-one (SE46)



SE46

According to **General procedure SM B** with 1-(3-(trifluoromethyl)phenyl)propan-1-one (2.02 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE46** as a colorless oil (2.49 g, 89% yield).

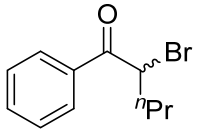
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.22 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 5.30 (d, *J* = 6.8 Hz, 1H), 1.94 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 134.7, 132.0, 131.4 (q, *J* = 33.0 Hz), 130.0 (q, *J* = 3.6 Hz), 129.4, 125.8 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 272.6 Hz), 41.2, 19.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{10}H_9BrF_3O$ $[M + H]^+$ 280.9783, found 280.9783.

2-Bromo-1-phenylpentan-1-one (SE50)



SE50

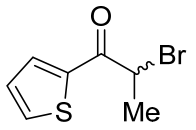
According to **General procedure SM B** with 1-phenylpentan-1-one (1.62 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE50** as a colorless oil (1.34 g, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H), 7.68 – 7.58 (m, 1H), 7.57 – 7.46 (m, 2H), 5.18 (dd, *J* = 7.8, 6.5 Hz, 1H), 2.27 – 2.08 (m, 2H), 1.70 – 1.36 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 134.5, 133.7, 128.9, 128.8, 47.1, 35.5, 20.8, 13.6.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}BrO$ $[M + H]^+$ 241.0223, found 241.0221.

2-Bromo-1-(thiophen-2-yl)propan-1-one (SE51)



SE51

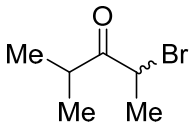
According to **General procedure SM B** with 1-(thiophen-2-yl)propan-1-one (1.40 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product **SE51** as a colorless oil (1.70 g, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.70 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.16 (dd, *J* = 5.0, 3.9 Hz, 1H), 5.15 (q, *J* = 6.7 Hz, 1H), 1.90 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 140.9, 134.9, 133.1, 128.3, 42.5, 20.4.

HRMS (ESI) *m/z* calcd. for C_7H_8BrOS $[M + H]^+$ 218.9474, found 218.9474.

2-Bromo-4-methylpentan-3-one (SE53)



SE53

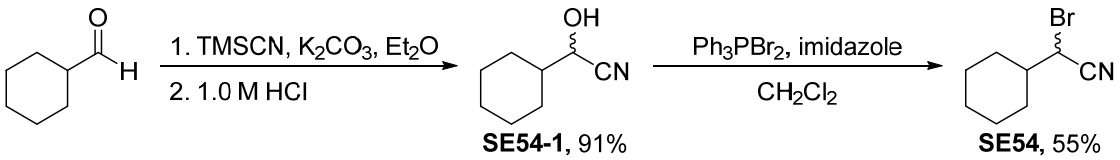
To a solution of lithium bis(trimethylsilyl)amide (LiHMDS) (2.0 mmol, 20 mol%) in THF was added 2-methylpentan-3-one (1.00 g, 10.0 mmol, 1.0 equiv.) dropwise at −78 °C. The reaction mixture was then warmed up to 0 °C and stirred for 10 min. After cooling down to −78 °C, bromine (1.60 g, 10.0 mmol, 1.0 equiv.) was added dropwise and the mixture was stirred for another 10 min at that temperature. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with Et_2O. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 4/1) to yield the product **SE53** as a colorless oil (1.37 g, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (d, *J* = 6.8 Hz, 1H), 3.11 (hept, *J* = 6.8 Hz, 1H), 1.74 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.14 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 45.9, 37.5, 20.1, 19.5, 18.7.

HRMS (ESI) *m/z* calcd. for $C_6H_{11}O$ $[M - Br]^+$ 99.0804, found 99.0810.

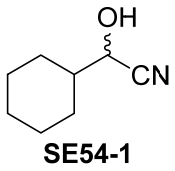
The synthesis of SE54.



To a mixture of cyclohexanecarbaldehyde (1.68 g, 15.0 mmol, 1.0 equiv.) and K_2CO_3 (0.41 g, 3.0 mmol, 0.2 equiv.) in Et_2O (30.0 mL) was added trimethylsilyl cyanide (1.63 g, 16.5 mmol, 1.1 equiv.) and the mixture was stirred at room temperature overnight. After completion (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ solution and extracted with Et_2O three times. The combined organic phase was washed with brine and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE54-1** as a colorless oil (1.90 g, 91% yield).

To a solution of **SE54-1** (0.70 g, 5.0 mmol, 1.0 equiv.) in CH_2Cl_2 (25.0 mL) were added triphenylphosphine dibromide (2.53 g, 6.0 mmol, 1.2 equiv.) and imidazole (0.41 g, 6.0 mmol, 1.2 equiv.) with vigorously stirring at 0 °C under argon. Then the reaction mixture was allowed to warm to room temperature and stirred overnight. After completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 three times. The combined organic phase was washed with brine and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **SE54** as a yellow oil (0.55 g, 55% yield).

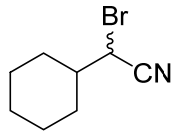
2-Cyclohexyl-2-hydroxyacetonitrile (SE54-1)



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (d, *J* = 6.4 Hz, 1H), 3.95 (brs, 1H), 1.96 – 1.63 (m, 6H), 1.34 – 1.02 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 119.5, 66.1, 42.1, 28.2, 27.9, 25.9, 25.43, 25.41.

2-Bromo-2-cyclohexylacetonitrile (SE54)



SE54

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (d, *J* = 5.7 Hz, 1H), 2.10 – 1.93 (m, 2H), 1.92 – 1.87 (m, 3H), 1.77 – 1.68 (m, 1H), 1.41 – 1.12 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 116.6, 42.7, 34.3, 30.4, 29.5, 25.6, 25.5.

HRMS (ESI) *m/z* calcd. for $C_8H_{13}BrN$ $[M + H]^+$ 202.0226, found 202.0225.

The synthesis of α-bromo amides.

General procedure SM C: To a solution of Et_3N (1.52 g, 15.0 mmol, 1.5 equiv.) and amine (10.0 mmol, 1.0 equiv.) in THF (5.0 mL) was added 2-bromopropanoyl bromide (2.59 g, 12.0 mmol, 1.2 equiv.) dropwise at 0 °C. Then the reaction mixture was warmed up to room temperature and stirred for 3 h. After completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl solution and extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel to afford the desired product.

General procedure SM D: To a solution of 2-bromo aliphatic acid (5.0 mmol, 1.0 equiv.) and Et_3N (1.52 g, 15.0 mmol, 3.0 equiv.) in THF (10.0 mL) was added pivaloyl chloride (603.0 mg, 5.0 mmol, 1.0 equiv.) dropwise at 0 °C. The reaction mixture was stirred at that temperature for 4 h, and then LiCl (0.21 g, 5.0 mmol, 1.0 equiv.) and morpholine (0.44 g, 5.0 mmol, 1.0 equiv.) were added sequentially. The mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with 1.0 M aqueous HCl solution and extracted with EtOAc three times. The combined organic phase was washed with 1.0 M aqueous NaOH solution and brine, dried over Na_2SO_4, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel to afford the desired product.

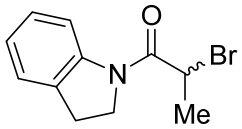
General procedure SM E: To a solution of aliphatic acid (10.0 mmol, 1.0 equiv.) and hexamethylphosphoramide (HMPA) (0.5 mL) in THF (30.0 mL) was added lithium diisopropylamide (LDA) (11.0 mL, 11.0 mmol, 1.1 equiv., 1.0 M in THF) at −10 °C. After being stirred for 2 h at −10 °C, the reaction mixture was cooled down to −78 °C and treated with a solution of carbon tetrabromide (7.30 g, 22.0 mmol, 2.2 equiv.) in THF (3.0 mL). The solution was warmed up to room temperature over 1 h and stirred for another 1 h at room temperature. The reaction was quenched with brine, acidified with 2.0 M aqueous HCl solution, and extracted with Et_2O three times. The combined organic phase was dried over magnesium sulfate, filtered and concentrated to afford the crude bromo acid, which was immediately used in the next step without further

purification.

To a solution of the above bromo acid in CH_2Cl_2 (10.0 mL) was added oxalyl chloride (2.52 g, 20.0 mmol, 2.0 equiv.) and a drop of DMF at room temperature. The reaction mixture was stirred for 2 h at room temperature. Then the solvent was removed under reduced pressure to afford the bromo acyl chloride, which was immediately used in the next step without further purification.

To a solution of morpholine (1.74 g, 20.0 mmol, 2.0 equiv.) and Et_3N (2.02 g, 20.0 mmol, 2.0 equiv.) in CH_2Cl_2 (20.0 mL) was added the above bromo acidic chloride at 0 °C. The mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with brine and extracted with EtOAc three times. The combined organic phase was dried over magnesium sulfate, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel to yield the product.

2-Bromo-1-(indolin-1-yl)propan-1-one (SE55)



SE55

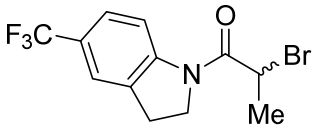
According to **General procedure SM C** with indoline (1.19 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE55** as a pink amorphous powder (2.20 g, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.17 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.59 (q, *J* = 6.6 Hz, 1H), 4.40 (td, *J* = 10.0, 6.8 Hz, 1H), 4.08 (td, *J* = 10.0, 6.9 Hz, 1H), 3.38 – 3.17 (m, 2H), 1.94 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 142.7, 131.5, 127.7, 124.6, 124.4, 117.6, 47.8, 40.9, 28.1, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{13}BrNO$ $[M + H]^+$ 254.0175, found 254.0175.

2-Bromo-1-(5-(trifluoromethyl)indolin-1-yl)propan-1-one (SE57)



SE57

According to **General procedure SM C** with 5-(trifluoromethyl)indoline (1.87 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE57** as a pink amorphous powder (2.73 g, 85% yield).

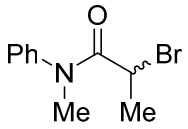
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 9.3 Hz, 1H), 7.46 (s, 1H), 4.58 (q, *J* = 6.6 Hz, 1H), 4.48 (td, *J* = 10.1, 6.9 Hz, 1H), 4.17 – 4.11 (m, 1H), 3.40 – 3.18 (m, 2H), 1.93 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 145.6, 132.2, 126.2 (dd, *J* = 64.8, 32.2 Hz), 125.3 (dd, *J* = 7.7, 3.9 Hz), 124.2 (q, *J* = 270.0 Hz), 122.0 – 120.7 (m), 117.2, 48.1, 40.5, 27.8, 21.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –61.8 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{12}H_{12}BrF_3NO$ $[M + H]^+$ 322.0049, found 322.0049.

2-Bromo-*N*-methyl-*N*-phenylpropanamide (SE59)



SE59

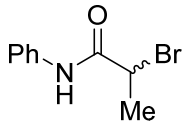
According to **General procedure SM C** with *N*-methylaniline (1.07 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE59** as a brown amorphous powder (1.88 g, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.33 (m, 3H), 7.33 – 7.19 (m, 2H), 4.26 (q, *J* = 6.7 Hz, 1H), 3.27 (s, 3H), 1.71 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 142.9, 123.0, 128.5, 127.1, 39.1, 38.1, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}BrNO$ $[M + H]^+$ 242.0175, found 242.0174.

2-Bromo-*N*-phenylpropanamide (SE60)



SE60

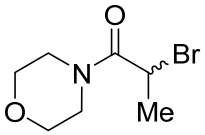
According to **General procedure SM C** with aniline (0.93 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE60** as a white amorphous powder (1.88 g, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.30 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.66 – 4.53 (m, 1H), 2.01 – 1.89 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 137.2, 129.1, 125.1, 120.5, 44.8, 22.6.

HRMS (ESI) *m/z* calcd. for $C_9H_{11}BrNO$ $[M + H]^+$ 228.0019, found 228.0018.

2-Bromo-1-morpholinopropan-1-one (E2)



E2

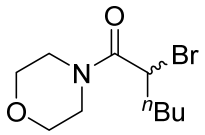
According to **General procedure SM C** with morpholine (0.87 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **E2** as a colorless oil (2.03 g, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 – 4.46 (m, 1H), 3.88 – 3.54 (m, 6H), 3.53 – 3.37 (m, 2H), 1.81 (t, *J* = 6.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 66.6, 66.3, 46.5, 42.6, 37.7, 21.5.

HRMS (ESI) *m/z* calcd. for $C_7H_{13}BrNO_2$ $[M + H]^+$ 222.0124, found 222.0124.

2-Bromo-1-morpholinohexan-1-one (SE62)



SE62

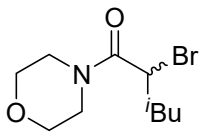
According to **General procedure SM D** with 2-bromohexanoic acid (0.97 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE62** as a colorless oil (0.82 g, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (t, *J* = 7.1 Hz, 1H), 3.86 – 3.39 (m, 8H), 2.24 – 1.97 (m, 2H), 1.49 – 1.25 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 66.7, 66.3, 46.6, 43.5, 42.6, 34.4, 29.7, 22.2, 13.9.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{19}BrNO_2$ $[M + H]^+$ 264.0594, found 264.0594.

2-Bromo-4-methyl-1-morpholinopentan-1-one (SE63)



SE63

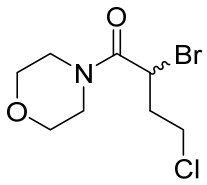
According to **General procedure SM D** with 2-bromo-4-methylpentanoic acid (0.97 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE63** as a colorless oil (0.68 g, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (dd, *J* = 8.0, 6.6 Hz, 1H), 3.87 – 3.41 (m, 8H), 2.06 – 1.71 (m, 3H), 1.01 – 0.86 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 66.7, 66.3, 52.2, 46.6, 43.1, 41.8, 26.1, 22.5, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{19}BrNO_2$ $[M + H]^+$ 264.0594, found 264.0594.

2-Bromo-4-chloro-1-morpholinobutan-1-one (SE64)



SE64

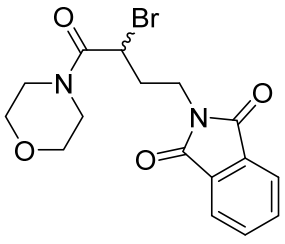
A mixture of 4-chlorobutanoic acid (1.22 g, 10.0 mmol, 1.0 equiv.), PBr_3 (0.54 g, 2.0 mmol, 0.2 equiv.) and Br_2 (3.20 g, 20.0 mmol, 2.0 equiv.) was refluxed overnight. After concentration under reduced pressure, the crude bromo acetyl bromide was obtained and dissolved in CH_2Cl_2 (10.0 mL). To this solution were added morpholine (1.04 g, 12.0 mmol, 1.2 equiv.) and Et_3N (3.03 g, 30.0 mmol, 3.0 equiv.) sequentially at room temperature and the reaction mixture was stirred overnight. The reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 three times. The combined organic phase was 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 (petroleum ether/EtOAc = 5/1) to afford the desired product **SE64** as a colorless oil (1.10 g, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (t, *J* = 6.9 Hz, 1H), 3.85 – 3.44 (m, 10H), 2.57 – 2.43 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 66.6, 66.3, 46.6, 42.7, 42.5, 39.8, 36.9.

HRMS (ESI) *m/z* calcd. for $C_8H_{14}BrClNO_2$ $[M + H]^+$ 269.9891, found 269.9890.

2-(3-Bromo-4-morpholino-4-oxobutyl)isoindoline-1,3-dione (SE65)



SE65

According to **General procedure SM D** with 2-bromo-4-(1,3-dioxoisoindolin-2-yl)butanoic acid (1.56 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the

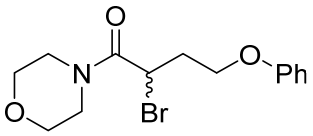
product **SE65** as a brown amorphous powder (0.78 g, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.77 – 7.71 (m, 2H), 4.49 – 4.38 (m, 1H), 3.92 – 3.43 (m, 10H), 2.83 – 2.60 (m, 1H), 2.38 – 2.19 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 166.2, 134.1, 132.0, 123.3, 66.6, 66.4, 46.3, 42.6, 39.4, 35.3, 33.8.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}BrN_2O_4$ $[M + H]^+$ 381.0444, found 381.0442.

2-Bromo-1-morpholino-4-phenoxybutan-1-one (SE66)



SE66

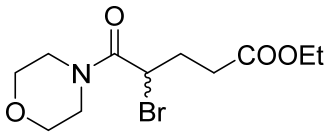
According to **General procedure SM E** with 4-phenoxybutanoic acid (1.80 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE66** as a red oil (1.96 g, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 6.98 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.91 (dt, *J* = 7.8, 1.0 Hz, 2H), 4.80 (dt, *J* = 7.9, 5.9 Hz, 1H), 4.25 – 4.02 (m, 2H), 3.87 – 3.41 (m, 8H), 2.68 – 2.35 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 158.6, 129.6, 121.2, 114.5, 66.72, 66.69, 63.9, 46.5, 42.8, 42.7, 34.3.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}BrNO_3$ $[M + H]^+$ 328.0543, found 328.0543.

Ethyl 4-bromo-5-morpholino-5-oxopentanoate (SE67)



SE67

According to **General procedure SM E** with 5-ethoxy-5-oxopentanoic acid (1.60 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE67** as a red oil (1.14

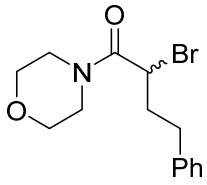
g, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 – 4.61 (m, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.86 – 3.45 (m, 8H), 2.61 – 2.48 (m, 2H), 2.44 – 2.31 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 167.0, 66.6, 60.6, 46.5, 42.7, 42.3, 31.4, 29.7, 14.2.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{19}BrNO_4$ $[M + H]^+$ 308.0492, found 308.0491.

2-Bromo-1-morpholino-4-phenylbutan-1-one (SE68)



SE68

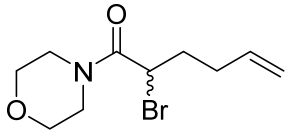
According to **General procedure SM E** with 4-phenylbutanoic acid (1.64 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE68** as a colorless oil (1.87 g, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.12 (m, 5H), 4.28 – 4.23 (m, 1H), 3.91 – 3.28 (m, 8H), 2.88 – 2.75 (m, 2H), 2.56 – 2.27 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 140.2, 128.6, 126.4, 66.7, 66.2, 52.6, 46.5, 42.2, 36.0, 33.3.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}BrNO_2$ $[M + H]^+$ 312.0594, found 312.0593.

2-Bromo-1-morpholinohex-5-en-1-one (SE69)



SE69

According to **General procedure SM E** with hex-5-enoic acid (1.14 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE69** as a red oil (1.49 g, 57%

yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.63 (m, 1H), 5.09 – 4.93 (m, 2H), 4.38 – 4.28 (m, 1H), 3.82 – 3.32 (m, 8H), 2.26 – 2.07 (m, 4H).

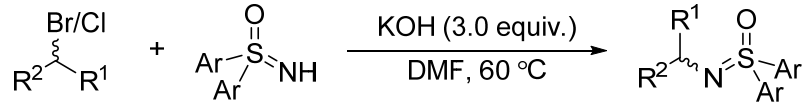
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 136.6, 116.2, 66.6, 66.3, 46.5, 42.6, 42.4, 33.5, 31.4.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{17}BrNO_2$ $[M + H]^+$ 262.0437, found 262.0437.

Enantioconvergent N-alkylation reactions.

All the racemic products were prepared by S_N2 reaction without further optimization.

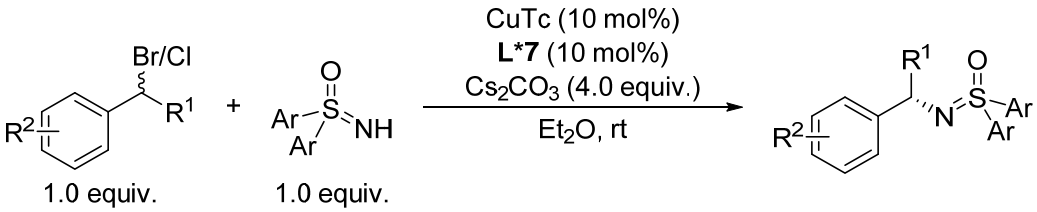
General procedure:



To a mixture of alkyl halides (3.0 equiv.) and sulfoximine (1.0 equiv.) in DMF was added KOH (3.0 equiv.). The reaction mixture was then warmed up to 60 °C and stirred for 3–12 h. After cooling to room temperature, the solution was diluted with H_2O and extracted with EtOAc three times. The combined organic phase was 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 to afford the desired products.

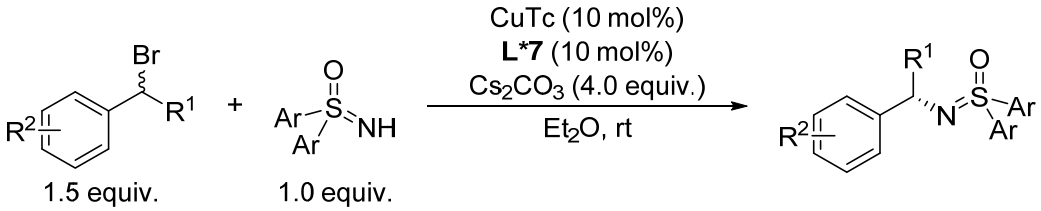
Enantioconvergent N-alkylation: scope of sulfoximines. (Figure 2B)

General procedure A:



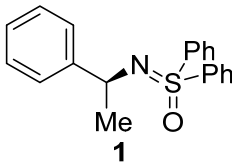
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.9 mg, 0.020 mmol, 10 mol%), chiral ligand **L*7** (27.3 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added alkyl halide (0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 30 to 96 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc. The mixture was then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

General procedure B:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfoximine (0.20 mmol, 1.0 equiv.), CuTc (3.9 mg, 0.020 mmol, 10 mol%), chiral ligand **L*7** (27.3 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added benzyl bromide (0.30 mmol, 1.5 equiv.) and the reaction mixture was stirred at room temperature for 3 to 5 d. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, then filtered through a pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

(*S*)-Diphenyl((1-phenylethyl)imino)-λ^6-sulfanone (1)



1

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **1** as a colorless oil (51.8 mg, 81% yield, 97% ee).

$[\alpha]_D^{20}$ = −37 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 38.53 min, t_R (minor) = 49.20 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.04 (m, 2H), 7.95 – 7.79 (m, 2H), 7.58 – 7.44 (m, 6H), 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.20 (m, 1H), 4.44 (q, *J* = 6.6 Hz, 1H), 1.59 (d, *J* = 6.6 Hz, 3H).

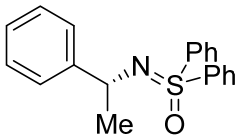
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 141.5, 140.8, 132.4, 132.3, 129.1, 129.0, 128.9, 128.5, 128.2, 126.4, 126.2, 54.2, 28.2.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{20}NOS$ $[M + H]^+$ 322.1260, found 322.1258.

According to **General procedure A** with (1-chloroethyl)benzene (28.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product as a colorless oil (45.6 mg, 71% yield, 93% ee).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 29.91 min, t_R (minor) = 44.48 min.

(*R*)-Diphenyl((1-phenylethyl)imino)-λ^6-sulfanone ((*R*)-1)

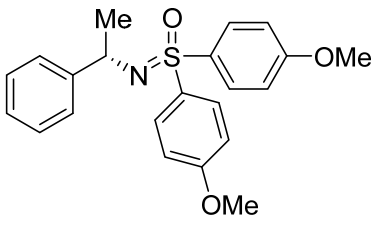


(*R*)-**1**

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*7'** for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product (*R*)-**1** as a colorless oil (63.6 mg, 99% yield, 98% ee).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 24.87 min, t_R (major) = 27.64 min.

(*S*)-bis(4-Methoxyphenyl)((1-phenylethyl)imino)-λ^6-sulfanone (2)



2

According to **General procedure B** with iminobis(4-methoxyphenyl)-λ^6-sulfanone (55.4 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **2** as a colorless oil (75.6 mg, 99% yield, 98% ee).

[α]$_D^{20}$ = –32 (*c* 1.6, CH_2Cl_2).

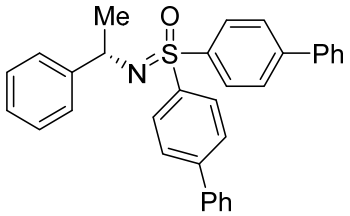
HPLC analysis: Chiralcel ID (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 13.36 min, t_R (minor) = 17.99 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.75 – 7.67 (m, 2H), 7.46 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 6.96 – 6.89 (m, 2H), 6.88 – 6.79 (m, 2H), 4.37 (q, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 1.54 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.7, 147.9, 133.7, 132.7, 130.9, 130.4, 128.3, 126.4, 114.4, 114.3, 55.7, 55.6, 54.2, 28.4.

HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{24}NO_3S$ $[M + H]^+$ 382.1471, found 382.1467.

(*S*)-di([1,1'-Biphenyl]-4-yl)((1-phenylethyl)imino)-λ^6-sulfanone (3)



3

According to **General procedure B** with di([1,1'-biphenyl]-4-yl)(imino)-λ^6-sulfanone (73.8 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **3** as a colorless oil (55.8 mg, 59% yield, 97% ee).

[α]$_D^{20}$ = –9 (*c* 2.0, CH_2Cl_2).

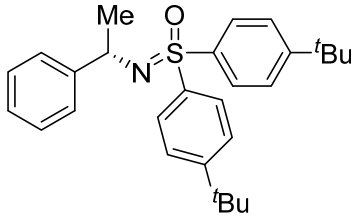
HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 12.65 min, t_R (minor) = 16.82 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.11 (m, 2H), 7.95 – 7.88 (m, 2H), 7.73 – 7.66 (m, 2H), 7.63 – 7.52 (m, 6H), 7.50 – 7.42 (m, 6H), 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.20 (m, 1H), 4.50 (q, *J* = 6.6 Hz, 1H), 1.62 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 145.5, 145.3, 140.3, 139.62, 139.59, 129.6, 129.12, 129.10, 129.06, 128.48, 128.46, 128.3, 127.91, 127.89, 127.5, 127.4, 126.5, 126.4, 54.4, 28.4.

HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{28}NOS$ $[M + H]^+$ 474.1886, found 474.1884.

(*S*)-bis(4-(*tert*-Butyl)phenyl)((1-phenylethyl)imino)-λ^6-sulfanone (4)



4

According to **General procedure B** with bis(4-(*tert*-butyl)phenyl)(imino)-λ^6-sulfanone (65.8 mg, 0.20 mmol, 1.0 equiv.) at 0 °C for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **4** as a colorless oil (77.9 mg, 90% yield, 92% ee).

$[\alpha]_D^{20}$ = –40 (*c* 0.6, CH_2Cl_2).

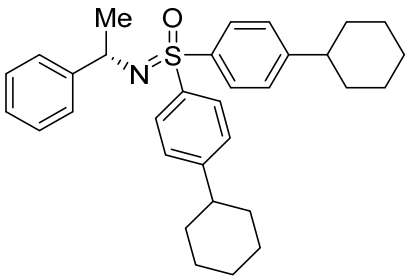
HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.80 min, t_R (minor) = 7.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.76 – 7.69 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.16 (m, 1H), 4.41 (q, *J* = 6.6 Hz, 1H), 1.55 (d, *J* = 6.6 Hz, 3H), 1.30 (s, 9H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 155.9, 147.9, 138.8, 137.9, 128.8, 128.4, 128.2, 126.4, 126.3, 126.2, 126.1, 54.1, 35.2, 35.1, 31.23, 31.21, 28.3.

HRMS (ESI) *m*/*z* calcd. for $C_{28}H_{36}NOS$ $[M + H]^+$ 434.2512, found 434.2508.

(*S*)-bis(4-Cyclohexylphenyl)((1-phenylethyl)imino)-λ^6-sulfanone (5)



5

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and bis(4-cyclohexylphenyl)(imino)-λ^6-sulfanone (76.2 mg, 0.20 mmol, 1.0 equiv.) for 3 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **5** as a colorless oil (50.4 mg, 52% yield, 92% ee).

$[\alpha]_D^{20}$ = −17 (*c* 2.0, CH_2Cl_2).

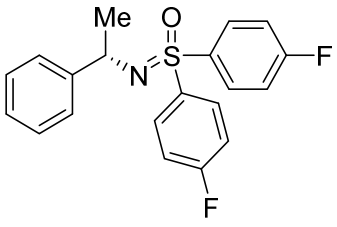
HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.41 min, t_R (minor) = 9.35 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.75 – 7.66 (m, 2H), 7.44 – 7.38 (m, 2H), 7.29 (m, 4H), 7.23 – 7.15 (m, 3H), 4.39 (q, *J* = 6.6 Hz, 1H), 2.59 – 2.41 (m, 2H), 1.90 – 1.68 (m, 10H), 1.54 (d, *J* = 6.6 Hz, 3H), 1.44 – 1.13 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 152.8, 147.9, 139.1, 138.3, 129.1, 128.6, 128.2, 127.6, 126.4, 126.3, 54.2, 44.61, 44.56, 34.3, 34.2, 28.3, 26.8, 26.1.

HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{40}NOS$ $[M + H]^+$ 486.2825, found 486.2822.

(*S*)-bis(4-Fluorophenyl)((1-phenylethyl)imino)-λ^6-sulfanone (6)



6

According to **General procedure B** with bis(4-fluorophenyl)(imino)-λ^6-sulfanone (50.6 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **6** as a colorless oil (58.5 mg, 82% yield, 98% ee).

[α]$_D^{20}$ = –44 (*c* 0.3, CH_2Cl_2).

HPLC analysis: Chiralcel IG (hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.93 min, t_R (minor) = 10.40 min.

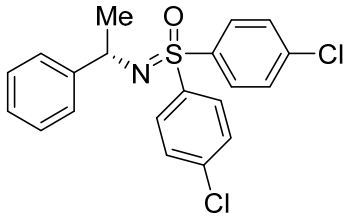
^{1}H NMR (400 MHz,) δ 8.08 – 7.99 (m, 2H), 7.82 – 7.72 (m, 2H), 7.42 – 7.34 (m, 2H), 7.30 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 – 7.11 (m, 2H), 7.08 – 7.00 (m, 2H), 4.37 (q, *J* = 6.6 Hz, 1H), 1.54 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ165.3 (d, *J* = 254.7 Hz), 165.2 (d, *J* = 254.6 Hz), 147.3, 137.5 (d, *J* = 2.8 Hz), 136.8 (d, *J* = 3.2 Hz), 131.7 (d, *J* = 9.4 Hz), 131.2 (d, *J* = 9.4 Hz), 128.4, 126.7, 126.3, 116.6, 116.3, 54.4, 28.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ –106.0 (tt, *J* = 8.2, 5.2 Hz, 1F), –106.1 (tt, *J* = 8.3, 5.0 Hz, 1F).

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{18}F_2NOS$ $[M + H]^+$ 358.1072, found 358.1067.

(*S*)-bis(4-Chlorophenyl)((1-phenylethyl)imino)- λ^6-sulfanone (7)



7

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and bis(4-chlorophenyl)(imino)-λ^6-sulfanone (57.0 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **7** as a colorless oil (56.0 mg, 72% yield, 94% ee).

[α]$_D^{20}$ = –18 (*c* 2.0, CH_2Cl_2).

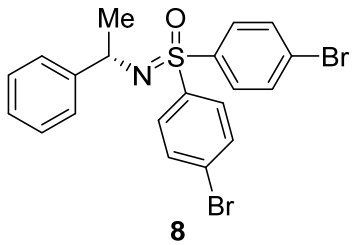
HPLC analysis: Chiralcel IG (hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.20 min, t_R (minor) = 13.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.74 – 7.65 (m, 2H), 7.47 – 7.41 (m, 2H), 7.40 – 7.34 (m, 3H), 7.33 – 7.27 (m, 3H), 7.24 – 7.18 (m, 1H), 4.38 (q, *J* = 6.6 Hz, 1H), 1.54 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 139.9, 139.4, 139.27, 139.25, 130.4, 130.0, 129.5, 128.4, 126.7, 126.3, 54.4, 28.2.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{18}Cl_2NOS$ $[M + H]^+$ 390.0481, found 390.0477.

(*S*)-bis(4-Bromophenyl)((1-phenylethyl)imino)-λ^6-sulfanone (8)



8

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and bis(4-bromophenyl)(imino)- λ^6-sulfanone (74.6 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **8** as a colorless oil (44.8 mg, 47% yield, 96% ee).

$[\alpha]_D^{20}$ = –3 (*c* 1.9, CH_2Cl_2).

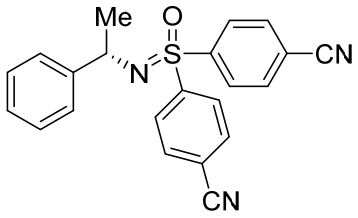
HPLC analysis: Chiralcel IG (hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.39 min, t_R (minor) = 10.53 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.66 – 7.58 (m, 4H), 7.54 – 7.47 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 4.37 (q, *J* = 6.6 Hz, 1H), 1.54 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 140.5, 139.8, 132.6, 130.6, 130.1, 128.4, 128.0, 127.9, 126.7, 126.3, 54.4, 28.2.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{18}Br_2NOS$ $[M + H]^+$ 477.9470, found 477.9469.

(*S*)-4,4'-((1-Phenylethyl)sulfonimidoyl)dibenzonitrile (9)



9

According to **General procedure B** with 4,4'-sulfonimidoyldibenzonitrile **N2** (53.4 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **9** as a colorless oil (33.4 mg, 45% yield, 90% ee).

$[\alpha]_D^{20}$ = –3 (*c* 1.7, CH_2Cl_2).

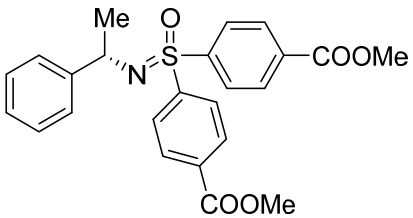
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.02 min, t_R (major) = 14.15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.10 (m, 2H), 7.89 – 7.82 (m, 2H), 7.83 – 7.75 (m, 2H), 7.69 – 7.62 (m, 2H), 7.35 – 7.25 (m, 4H), 7.26 – 7.17 (m, 1H), 4.41 (q, *J* = 6.6 Hz, 1H), 1.55 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 145.0, 144.8, 133.2, 133.1, 129.7, 129.3, 128.6, 127.1, 126.2, 117.3, 116.9, 116.7, 54.5, 27.9.

HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{18}N_3OS$ $[M + H]^+$ 372.1165, found 372.1161.

Dimethyl 4,4'-((1-phenylethyl)sulfonimidoyl)(*S*)-dibenzoate (10)



10

According to **General procedure B** with Dimethyl 4,4'-sulfonimidoyldibenzoate (66.6 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product **10** as a colorless oil (40.2 mg, 46% yield, 97% ee).

$[\alpha]_D^{20}$ = –30 (*c* 0.3, CH_2Cl_2).

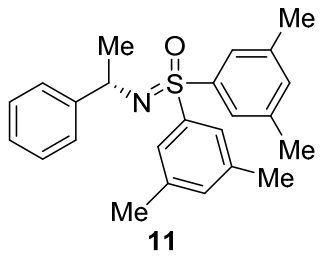
HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 20.26 min, t_R (minor) = 26.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.07 (m, 4H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.90 – 7.82 (m, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 4.40 (q, *J* = 6.6 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 1.55 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 147.0, 145.1, 144.7, 134.0, 133.9, 130.5, 130.4, 129.1, 128.7, 128.4, 126.8, 126.3, 54.5, 52.8, 52.7, 28.1.

HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{24}NO_5S$ $[M + H]^+$ 438.1370, found 438.1367.

(*S*)-bis(3,5-Dimethylphenyl)((1-phenylethyl)imino)-λ^6-sulfanone (11)



11

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and bis(3,5-dimethylphenyl)(imino)-λ^6-sulfanone (54.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **11** as a colorless oil (45.2 mg, 60% yield, 90% ee).

$[\alpha]_D^{20}$ = –33 (*c* 2.0, CH_2Cl_2).

HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.99 min, t_R (minor) = 8.95 min.

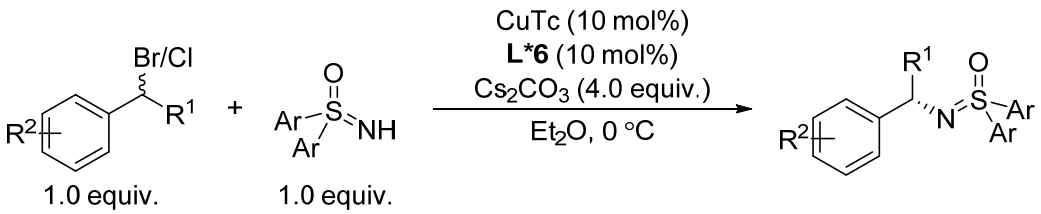
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.43 – 7.37 (m, 4H), 7.33 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 7.13 – 7.09 (m, 1H), 7.08 – 7.03 (m, 1H), 4.37 (q, *J* = 6.6 Hz, 1H), 2.35 (s, 6H), 2.24 (s, 6H), 1.56 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 141.3, 140.7, 139.04, 138.97, 134.2, 134.0, 128.2, 126.6, 126.5, 126.4, 125.9, 54.3, 28.2, 21.4, 21.3.

HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{28}NOS$ $[M + H]^+$ 378.1886, found 378.1882.

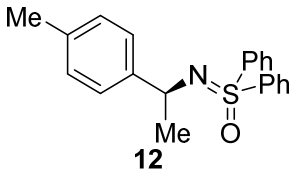
Enantioconvergent N-alkylation: scope of benzyl and propargyl halides. (Figure 2B)

General procedure C:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.9 mg, 0.020 mmol, 10 mol%), chiral ligand **L*6** (27.3 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added alkyl halide (0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at 0 °C for 30–96 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

(*S*)-Diphenyl((1-(*p*-tolyl)ethyl)imino)-λ^6-sulfanone (12)



12

According to **General procedure A** with 1-(1-bromoethyl)-4-methylbenzene (39.6 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **12** as a colorless oil (60.3 mg, 90% yield, >99% ee).

$[\alpha]_D^{20} = -50$ (*c* 1.0, CH_2Cl_2).

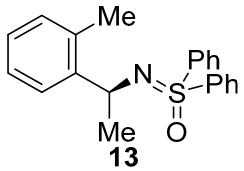
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 44.39 min, t_R (minor) = 66.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.98 (m, 2H), 7.89 – 7.77 (m, 2H), 7.52 – 7.40 (m, 4H), 7.40 – 7.34 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 4.36 (q, *J* = 6.6 Hz, 1H), 2.33 (s, 3H), 1.54 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 141.6, 140.8, 135.8, 132.3, 132.2, 129.1, 129.03, 128.97, 128.9, 128.5, 126.1, 54.0, 28.3, 21.1.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}NOS$ $[M + H]^+$ 336.1417, found 336.1415.

(*S*)-Diphenyl((1-(*o*-tolyl)ethyl)imino)-λ^6-sulfanone (13)



13

According to **General procedure A** with 1-(1-bromoethyl)-2-methylbenzene (39.6 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **13** as a colorless oil (61.0 mg, 91% yield, >99% ee).

$[\alpha]_D^{20}$ = 7 (*c* 1.0, CH_2Cl_2).

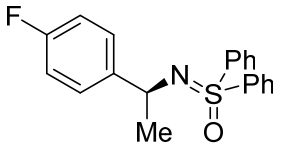
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 32.31 min, t_R (minor) = 47.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.06 (m, 2H), 7.92 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.58 – 7.42 (m, 4H), 7.40 – 7.27 (m, 3H), 7.15 (td, *J* = 7.4, 1.5 Hz, 1H), 7.05 (dd, *J* = 7.7, 1.4 Hz, 1H), 4.65 (q, *J* = 6.5 Hz, 1H), 2.04 (s, 3H), 1.54 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 141.5, 141.0, 133.4, 132.4, 132.2, 129.9, 129.02, 128.99, 128.9, 128.4, 126.6, 126.3, 126.1, 50.3, 27.3, 19.0.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}NOS$ $[M + H]^+$ 336.1417, found 336.1415.

(*S*)-((1-(4-Fluorophenyl)ethyl)imino)diphenyl-λ^6-sulfanone (14)



14

According to **General procedure A** with 1-(1-bromoethyl)-4-fluorobenzene (40.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **14** as a colorless oil (63.1 mg, 93% yield, 96% ee).

[α]$_D^{20}$ = –58 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 40.70 min, t_R (minor) = 50.64 min.

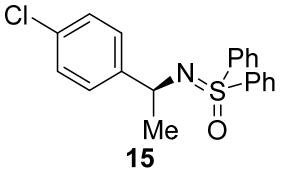
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.00 (m, 2H), 7.91 – 7.81 (m, 2H), 7.58 – 7.45 (m, 4H), 7.44 – 7.34 (m, 4H), 7.00 (t, *J* = 8.6 Hz, 2H), 4.41 (q, *J* = 6.6 Hz, 1H), 1.56 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 243.7 Hz), 143.3 (d, *J* = 3.0 Hz), 141.3, 140.8, 132.4, 132.3, 129.09, 129.07, 128.8, 128.4, 127.7 (d, *J* = 7.8 Hz), 114.8 (d, *J* = 21.0 Hz), 53.5, 28.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ –117.2 (td, *J* = 8.9, 4.4 Hz, 1F).

HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}FNOS$ $[M + H]^+$ 340.1166, found 340.1164.

(*S*)-((1-(4-Chlorophenyl)ethyl)imino)diphenyl-λ^6-sulfanone (15)



15

According to **General procedure A** with 1-(1-bromoethyl)-4-chlorobenzene (43.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **15** as a colorless oil (66.0 mg, 93% yield, >99% ee).

[α]$_D^{20}$ = –118 (*c* 1.0, CH_2Cl_2).

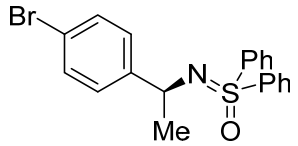
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 41.11 min, t_R (minor) = 55.00 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.57 – 7.45 (m, 4H), 7.46 – 7.32 (m, 4H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.39 (q, *J* = 6.6 Hz, 1H), 1.56 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 141.3, 140.7, 132.5, 132.4, 131.9, 129.1, 128.8, 128.4, 128.3, 127.7, 53.6, 28.1.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}ClNOS$ $[M + H]^+$ 356.0870, found 356.0868.

(*S*)-((1-(4-Bromophenyl)ethyl)imino)diphenyl-λ^6-sulfanone (16)



16

According to **General procedure A** with 1-bromo-4-(1-bromoethyl)benzene (52.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **16** as a colorless oil (66.2 mg, 83% yield, 97% ee).

$[\alpha]_D^{20}$ = −123 (*c* 1.0, CH_2Cl_2).

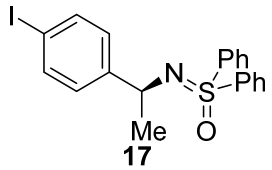
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 43.10 min, t_R (minor) = 60.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.36 (m, 8H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 2H), 4.38 (q, *J* = 6.6 Hz, 1H), 1.55 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 141.3, 140.7, 132.5, 132.4, 131.2, 129.1, 128.8, 128.4, 128.1, 120.0, 53.7, 28.1.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}BrNOS$ $[M + H]^+$ 400.0365 & 402.0345, found 400.0364 & 402.0341.

(*S*)-((1-(4-Iodophenyl)ethyl)imino)diphenyl-λ^6-sulfanone (17)



17

According to **General procedure A** with 1-(1-bromoethyl)-4-iodobenzene (62.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **17** as a yellow oil (71.5 mg, 80% yield, 98% ee).

[α]$_D^{20}$ = −76 (*c* 1.0, CH_2Cl_2).

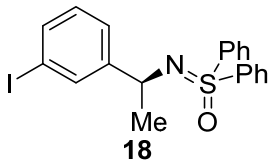
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 45.58 min, t_R (minor) = 62.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 2H), 7.84 – 7.78 (m, 2H), 7.64 – 7.58 (m, 2H), 7.55 – 7.43 (m, 4H), 7.42 – 7.34 (m, 2H), 7.20 – 7.14 (m, 2H), 4.33 (q, *J* = 6.6 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 141.2, 140.7, 137.2, 132.5, 132.4, 129.1, 128.8, 128.4, 91.6, 53.8, 28.0.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}INOS$ $[M + H]^+$ 448.0227, found 448.0225.

(*S*)-((1-(3-Iodophenyl)ethyl)imino)diphenyl-λ^6-sulfanone (18)



18

According to **General procedure A** with 1-(1-bromoethyl)-3-iodobenzene (62.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **18** as a yellow oil (71.5 mg, 80% yield, 97% ee).

[α]$_D^{20}$ = −16 (*c* 0.9, CH_2Cl_2).

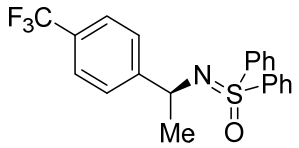
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 39.88 min, t_R (minor) = 46.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.4 Hz, 2H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.75 (s, 1H), 7.60 – 7.31 (m, 8H), 7.05 (t, *J* = 7.7 Hz, 1H), 4.35 (q, *J* = 6.6 Hz, 1H), 1.55 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 140.1, 139.6, 134.4, 134.3, 131.5, 131.4, 129.0, 128.1, 128.0, 127.7, 127.3, 124.6, 93.3, 52.5, 26.9.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}INOS$ $[M + H]^+$ 448.0227, found 448.0225.

(*S*)-Diphenyl((1-(4-(trifluoromethyl)phenyl)ethyl)imino)-λ^6-sulfanone (19)



19

According to **General procedure A** with 1-(1-bromoethyl)-4-(trifluoromethyl)benzene (50.4 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **19** as a colorless oil (73.9 mg, 95% yield, 98% ee).

$[\alpha]_D^{20}$ = −11 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.3 mL/min, λ = 230 nm), t_R (major) = 49.46 min, t_R (minor) = 58.97 min.

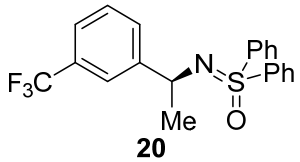
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.45 (m, 8H), 7.45 – 7.37 (m, 2H), 4.46 (q, *J* = 6.6 Hz, 1H), 1.58 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5 (d, *J* = 1.1 Hz), 141.2, 140.6, 132.5, 132.4, 129.14, 129.12, 128.7, 128.4, 128.2 (q, *J* = 24.0 Hz), 126.6, 125.2 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270.0 Hz), 53.8, 28.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.2 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{21}H_{19}F_3NOS$ $[M + H]^+$ 390.1134, found 390.1132.

(*S*)-Diphenyl((1-(3-(trifluoromethyl)phenyl)ethyl)imino)-λ^6-sulfanone (20)



20

According to **General procedure A** with 1-(1-bromoethyl)-3-(trifluoromethyl)benzene (52.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **20** as a colorless oil (73.9 mg, 95% yield, 98% ee).

[α]$_D^{20}$ = –23 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.3 mL/min, λ = 230 nm), t_R (major) = 43.16 min, t_R (minor) = 50.19 min.

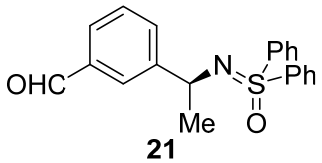
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.88 – 7.80 (m, 2H), 7.70 – 7.61 (m, 2H), 7.56 – 7.37 (m, 8H), 4.47 (q, *J* = 6.6 Hz, 1H), 1.59 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 141.2, 140.6, 132.5, 132.4, 130.3 (q, *J* = 31.9 Hz), 129.8 (d, *J* = 1.4 Hz), 129.14, 129.10, 128.7, 128.6, 128.4, 124.4 (q, *J* = 270.0 Hz), 128.6, 123.2 (dq, *J* = 10.8, 3.8 Hz), 53.8, 27.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.4 (s, 3F)

HRMS (ESI) *m/z* calcd. for $C_{21}H_{19}F_3NOS$ $[M + H]^+$ 390.1134, found 390.1132.

(*S*)-3-(1-((Oxodiphenyl-λ^6-sulfaneylidene)amino)ethyl)benzaldehyde (21)



21

According to **General procedure A** with 3-(1-bromoethyl)benzaldehyde (42.4 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **21** as a yellow oil (55.8 mg, 80% yield, 97% ee).

[α]$_D^{20}$ = –59 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm),

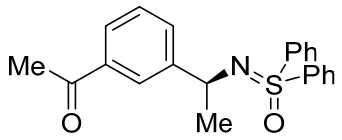
t_R (major) = 36.15 min, t_R (minor) = 39.79 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.10 – 8.00 (m, 2H), 7.92 (s, 1H), 7.89 – 7.82 (m, 2H), 7.75 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.58 – 7.44 (m, 5H), 7.44 – 7.36 (m, 2H), 4.49 (q, *J* = 6.6 Hz, 1H), 1.59 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 148.7, 141.1, 140.7, 136.4, 132.7, 132.6, 132.4, 129.2, 129.1, 128.9, 128.7, 128.4, 127.8, 53.7, 27.9.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}NO_2S$ $[M + H]^+$ 350.1209, found 350.1208.

(*S*)-((1-(3-Acetylphenyl)ethyl)imino)diphenyl-λ^6-sulfanone (22)



22

According to **General procedure A** with 1-(3-(1-bromoethyl)phenyl)ethan-1-one (45.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **22** as a colorless oil (63.2 mg, 87% yield, 98% ee).

$[\alpha]_D^{20}$ = –46 (*c* 1.0, CH_2Cl_2).

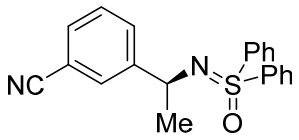
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 97/3, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 67.42 min, t_R (minor) = 73.93 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.97 (s, 1H), 7.88 – 7.80 (m, 3H), 7.73 – 7.68 (m, 1H), 7.58 – 7.35 (m, 7H), 4.48 (q, *J* = 6.6 Hz, 1H), 2.61 (s, 3H), 1.59 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 148.1, 141.2, 140.7, 137.1, 132.5, 132.4, 131.2, 129.13, 129.10, 128.8, 128.5, 128.4, 126.5, 126.3, 53.9, 28.0, 26.8.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}NO_2S$ $[M + H]^+$ 364.1366, found 364.1358.

(*S*)-3-(1-((Oxodiphenyl-λ^6-sulfaneylidene)amino)ethyl)benzonitrile (23)



23

According to **General procedure A** with 3-(1-bromoethyl)benzonitrile (41.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **23** as a colorless oil (65.7 mg, 95% yield, 92% ee).

$[\alpha]_D^{20}$ = −17 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 98/2, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 28.68 min, t_R (minor) = 35.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.73 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.45 (m, 5H), 7.45 – 7.34 (m, 3H), 4.41 (q, *J* = 6.6 Hz, 1H), 1.53 (d, *J* = 6.6 Hz, 3H).

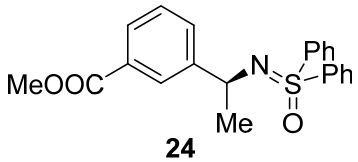
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 141.0, 140.6, 132.6, 132.5, 131.0, 130.2, 130.1, 129.21, 129.17, 129.0, 128.6, 128.4, 119.3, 112.1, 53.4, 27.9.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{19}N_2OS$ $[M + H]^+$ 347.1213, found 347.1210.

According to **General procedure A** with 3-(1-chloroethyl)benzonitrile (33.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **23** as a colorless oil (62.3 mg, 90% yield, 96% ee).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 98/2, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 28.29 min, t_R (minor) = 35.67 min.

Methyl (*S*)-3-(1-((oxodiphenyl-λ^6-sulfaneylidene)amino)ethyl)benzoate (24)



24

According to **General procedure A** with methyl 3-(1-bromoethyl)benzoate (48.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **24** as a yellow oil (70.5 mg, 93% yield, 96% ee).

$[\alpha]_D^{20}$ = −12 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 98/2, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 48.26 min, t_R (major) = 58.05 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 3H), 7.94 – 7.87 (m, 1H), 7.87 – 7.80 (m, 2H), 7.73 – 7.67 (m, 1H), 7.57 – 7.43 (m, 4H), 7.43 – 7.34 (m, 3H), 4.47 (q, *J* = 6.6 Hz, 1H), 3.92 (s, 3H), 1.58 (d, *J* = 6.6 Hz, 3H).

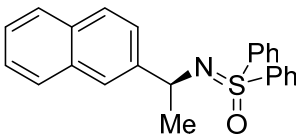
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 147.9, 141.3, 140.7, 132.5, 132.3, 131.0, 123.0, 129.10, 129.08, 128.8, 128.4, 128.3, 127.7, 127.5, 53.9, 52.0, 28.0.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}NO_3S$ $[M + H]^+$ 380.1315, found 380.1312.

According to **General procedure A** with methyl 3-(1-chloroethyl)benzoate (39.6 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **24** as a yellow oil (58.4 mg, 77% yield, 97% ee).

HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 98/2, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 52.88 min, t_R (major) = 64.56 min.

(*S*)-((1-(Naphthalen-2-yl)ethyl)imino)diphenyl-λ^6-sulfanone (25)



25

According to **General procedure A** with 2-(1-bromoethyl)naphthalene (46.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **25** as a colorless oil (63.8 mg, 86% yield, 93% ee).

$[\alpha]_D^{20}$ = −8 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 98/2, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 18.74 min, t_R (minor) = 34.32 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.92 – 7.80 (m, 6H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.41 (m, 6H), 7.41 – 7.32 (m, 2H), 4.62 (q, *J* = 6.6 Hz, 1H), 1.69 (d, *J* = 6.7 Hz, 3H).

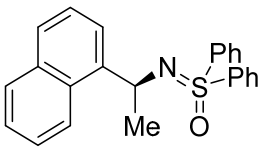
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 141.5, 140.8, 133.5, 132.6, 132.4, 132.3, 129.10, 129.07, 129.0, 128.5, 127.94, 127.93, 127.6, 125.8, 125.3, 125.2, 124.3, 54.5, 28.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{22}NOS$ $[M + H]^+$ 372.1417, found 372.1415.

According to **General procedure A** with 2-(1-chloroethyl)naphthalene (38.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **25** as a colorless oil (60.1 mg, 81% yield, 96% ee).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 98/2, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 28.38 min, t_R (minor) = 35.84 min.

(*S*)-((1-(Naphthalen-1-yl)ethyl)imino)diphenyl-λ^6-sulfanone (26)



26

According to **General procedure A** with 1-(1-bromoethyl)naphthalene (46.8 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **26** as a colorless oil (53.4 mg, 72% yield, 95% ee).

X-ray quality crystals were obtained by slow evaporation of solvent from a saturated solution in a mixture of toluene/hexane.

$[\alpha]_D^{20}$ = 4 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel OD3 (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254

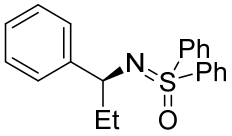
nm), t_R (major) = 18.40 min, t_R (minor) = 20.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.06 (m, 3H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.36 (m, 7H), 7.34 – 7.25 (m, 2H), 5.22 (q, *J* = 6.6 Hz, 1H), 1.75 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 141.7, 140.8, 133.9, 132.4, 132.2, 130.3, 129.03, 129.00, 128.82, 128.76, 128.4, 127.0, 125.8, 125.4, 125.1, 123.8, 123.7, 51.3, 27.8.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{22}NOS$ $[M + H]^+$ 372.1417, found 372.1414.

(*S*)-Diphenyl((1-phenylpropyl)imino)-λ^6-sulfanone (27)



27

According to **General procedure A** with (1-bromopropyl)benzene (39.2 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **26** as a colorless oil (53.6 mg, 80% yield, 95% ee).

$[\alpha]_D^{20}$ = −51 (*c* 1.0, CH_2Cl_2).

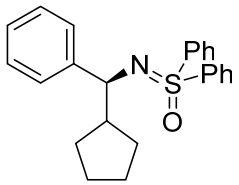
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (minor) = 21.76 min, t_R (major) = 37.32 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.01 (m, 2H), 7.84 – 7.72 (m, 2H), 7.57 – 7.40 (m, 4H), 7.41 – 7.27 (m, 6H), 7.26 – 7.17 (m, 1H), 4.10 (t, *J* = 6.7 Hz, 1H), 2.02 – 1.79 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 141.4, 141.0, 132.3, 132.2, 129.01, 128.99, 128.9, 128.5, 128.0, 126.9, 126.4, 60.5, 34.3, 11.0.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}NOS$ $[M + H]^+$ 336.1417, found 336.1414.

(*S*)-((Cyclopentyl(phenyl)methyl)imino)diphenyl-λ^6-sulfanone (28)



28

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), CuTc (15.4 mg, 0.080 mmol, 40 mol%), chiral ligand **L*6** (81.9 mg, 0.080 mmol, 40 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added (bromo(cyclopentyl)methyl)benzene (47.6 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 5 d. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the desired product **28** as a colorless oil (61.5 mg, 82% yield, 92% ee).

$[\alpha]_D^{20}$ = –47 (*c* 0.6, CH_2Cl_2).

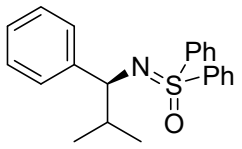
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 21.68 min, t_R (major) = 25.37 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.93 (m, 2H), 7.77 – 7.63 (m, 2H), 7.53 – 7.35 (m, 4H), 7.31 – 7.13 (m, 7H), 3.88 (d, *J* = 8.4 Hz, 1H), 2.32 (h, *J* = 8.1 Hz, 1H), 1.98 (td, *J* = 7.4, 6.4, 3.5 Hz, 1H), 1.75 – 1.38 (m, 5H), 1.39 – 1.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 141.3, 141.2, 132.2, 132.0, 129.03, 128.95, 128.7, 128.5, 127.9, 127.2, 126.2, 63.7, 49.7, 30.8, 30.0, 25.3, 25.1.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}NOS$ $[M + H]^+$ 376.1730, found 376.1727.

(*S*)-((2-Methyl-1-phenylpropyl)imino)diphenyl-λ^6-sulfanone (29)



29

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), CuTc (15.4 mg, 0.080 mmol, 40 mol%), chiral ligand **L*6** (81.9 mg, 0.080 mmol, 40 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added (1-bromo-2-methylpropyl)benzene (42.4 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 5 d. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the desired product **29** as a colorless oil (27.9 mg, 40% yield, 91% ee).

$[\alpha]_D^{20}$ = −7 (*c* 1.0, CH_2Cl_2).

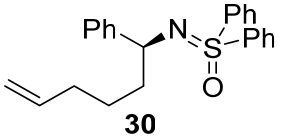
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 16.71 min, t_R (minor) = 17.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.74 – 7.64 (m, 2H), 7.53 – 7.36 (m, 4H), 7.31 – 7.13 (m, 7H), 3.82 (d, *J* = 7.0 Hz, 1H), 2.02 (h, *J* = 6.8 Hz, 1H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 141.4, 141.2, 132.2, 132.0, 129.0, 128.9, 128.7, 128.5, 127.7, 127.6, 126.2, 65.1, 36.8, 19.8, 19.7.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}NOS$ $[M + H]^+$ 350.1573, found 350.1571.

(*S*)-Diphenyl((1-phenylhex-5-en-1-yl)imino)-λ^6-sulfanone (30)



30

According to **General procedure C** with (1-bromohex-5-en-1-yl)benzene (47.6 mg,

0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **30** as a colorless oil (39.1 mg, 52% yield, 92% ee).

$[\alpha]_D^{20}$ = –5 (*c* 1.0, CH_2Cl_2).

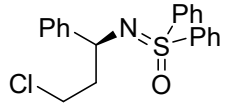
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 30.13 min, t_R (minor) = 33.86 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.40 (m, 4H), 7.40 – 7.25 (m, 6H), 7.25 – 7.17 (m, 1H), 5.79 (ddt, *J* = 16.7, 8.9, 6.5 Hz, 1H), 5.04 – 4.85 (m, 2H), 4.17 (t, *J* = 6.8 Hz, 1H), 2.04 (q, *J* = 7.3 Hz, 2H), 2.00 – 1.76 (m, 2H), 1.62 – 1.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 141.4, 141.0, 139.1, 132.3, 132.2, 129.0, 128.9, 128.5, 128.1, 126.8, 126.4, 114.3, 58.9, 41.0, 33.7, 25.8.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}NOS$ $[M + H]^+$ 376.1730, found 376.1728.

(*S*)-((3-Chloro-1-phenylpropyl)imino)diphenyl-λ^6-sulfanone (31)



31

According to **General procedure C** with (1-bromo-3-chloropropyl)benzene (46.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **31** as a colorless oil (56.8 mg, 77% yield, 94% ee).

$[\alpha]_D^{20}$ = –9 (*c* 1.0, CH_2Cl_2).

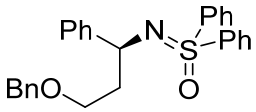
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 97/3, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 18.62 min, t_R (major) = 32.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 2H), 7.84 – 7.70 (m, 2H), 7.55 – 7.39 (m, 4H), 7.39 – 7.16 (m, 7H), 4.37 (dd, *J* = 8.2, 4.9 Hz, 1H), 3.93 – 3.75 (m, 1H), 3.67 – 3.51 (m, 1H), 2.44 – 2.25 (m, 1H), 2.25 – 2.08 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 141.0, 140.6, 132.5, 132.4, 129.1, 129.0, 128.9, 128.5, 128.3, 126.8, 126.7, 56.1, 43.9, 42.6.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}ClNOS$ $[M + H]^+$ 370.1027, found 370.1021.

(*S*)-((3-(Benzyloxy)-1-phenylpropyl)imino)diphenyl-λ^6-sulfanone (32)



32

According to **General procedure C** with (3-(benzyloxy)-1-bromopropyl)benzene (60.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **32** as a colorless oil (68.8 mg, 78% yield, 92% ee).

$[\alpha]_D^{20}$ = −14 (*c* 1.0, CH_2Cl_2).

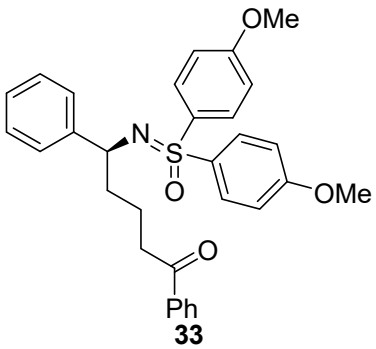
HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.36 min, t_R (minor) = 11.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.82 – 7.73 (m, 2H), 7.56 – 7.41 (m, 4H), 7.40 – 7.26 (m, 11H), 7.26 – 7.19 (m, 1H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.43 (dd, *J* = 8.3, 5.4 Hz, 1H), 3.88 – 3.74 (m, 1H), 3.63 – 3.50 (m, 1H), 2.29 – 2.17 (m, 1H), 2.17 – 2.03 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 141.2, 140.8, 138.9, 132.3, 132.2, 129.03, 128.96, 128.9, 128.6, 128.2, 128.1, 127.7, 127.3, 126.8, 126.5, 72.8, 67.6, 55.9, 41.1.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{28}NO_2S$ $[M + H]^+$ 442.1835, found 442.1834.

(*S*)-bis(4-Methoxyphenyl)((5-oxo-1,5-diphenylpentyl)imino)-λ^6-sulfanone (33)



33

According to **General procedure C** with 5-bromo-1,5-diphenylpentan-1-one (63.4 mg, 0.20 mmol, 1.0 equiv.) and iminobis(4-methoxyphenyl)-λ^6-sulfanone (55.4 mg, 0.20

mmol, 1.0 equiv.) for 96 h at 0 °C, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **33** as a yellow oil (57.5 mg, 56% yield, 84% ee).

[α]$_D^{20}$ = –0.1 (*c* 1.0, CH_2Cl_2).

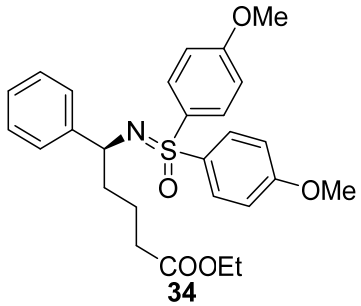
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 75/25, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 16.69 min, t_R (minor) = 19.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 4H), 7.69 – 7.63 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.15 (m, 1H), 6.94 – 6.87 (m, 2H), 6.83 – 6.74 (m, 2H), 4.17 (dd, *J* = 7.2, 5.1 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 2.97 – 2.87 (m, 2H), 2.01 – 1.72 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 162.6, 162.5, 146.4, 137.1, 133.3, 132.77, 132.76, 130.8, 130.3, 128.5, 128.1, 126.8, 126.4, 114.2, 114.1, 58.7, 55.54, 55.52, 41.0, 38.5, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{32}NO_4S$ $[M + H]^+$ 514.2047, found 514.2045.

Ethyl (*S*)-5-((bis(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)amino)-5-phenylpentanoate (34)



34

According to **General procedure C** with ethyl 5-bromo-5-phenylpentanoate (56.8 mg, 0.20 mmol, 1.0 equiv.) and iminobis(4-methoxyphenyl)-λ^6-sulfanone (55.4 mg, 0.20 mmol, 1.0 equiv.) at room temperature for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **34** as a yellow oil (76.0 mg, 79% yield, 87% ee).

[α]$_D^{20}$ = –35 (*c* 0.3, CH_2Cl_2).

HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254

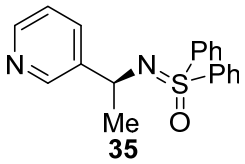
nm), t_R (major) = 14.61 min, t_R (minor) = 24.34 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.82 (m, 2H), 7.70 – 7.58 (m, 2H), 7.34 – 7.23 (m, 4H), 7.22 – 7.15 (m, 1H), 6.96 – 6.87 (m, 2H), 6.83 – 6.74 (m, 2H), 4.16 – 4.02 (m, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 2.34 – 2.16 (m, 2H), 1.96 – 1.66 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 162.6, 162.5, 146.4, 133.3, 132.8, 130.8, 130.3, 128.1, 126.8, 126.4, 114.2, 114.1, 60.1, 58.6, 55.6, 55.5, 40.9, 34.2, 21.9, 14.2.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{32}NO_5S$ $[M + H]^+$ 482.1996, found 482.1991.

(*S*)-Diphenyl((1-(pyridin-3-yl)ethyl)imino)-λ^6-sulfanone (35)



35

According to **General procedure C** with 3-(1-bromoethyl)pyridine (37.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **35** as a red oil (53.4 mg, 83% yield, 93% ee).

$[\alpha]_D^{20}$ = –9 (*c* 1.0, CH_2Cl_2).

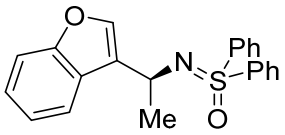
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 85/15, flow rate 0.7 mL/min, λ = 230 nm), t_R (major) = 19. 80 min, t_R (minor) = 24.55 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.3 Hz, 1H), 8.48 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.11 – 7.99 (m, 2H), 7.93 – 7.75 (m, 3H), 7.58 – 7.45 (m, 4H), 7.45 – 7.37 (m, 2H), 7.30 – 7.21 (m, 1H), 4.44 (q, *J* = 6.6 Hz, 1H), 1.58 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 147.9, 142.6, 141.1, 140.6, 133.9, 132.6, 132.5, 129.2, 129.1, 128.7, 128.4, 123.3, 51.9, 27.8.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}N_2OS$ $[M + H]^+$ 323.1213, found 323.1211.

(*S*)-((1-(Benzofuran-3-yl)ethyl)imino)diphenyl-λ^6-sulfanone (36)



36

According to **General procedure A** with 3-(1-bromoethyl)benzofuran (44.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **36** as a colorless oil (62.0 mg, 86% yield, 97% ee).

[α]$_D^{20}$ = −70 (*c* 0.9, CH_2Cl_2).

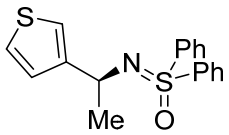
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 85/15, flow rate 0.3 mL/min, λ = 254 nm), t_R (major) = 21.07 min, t_R (minor) = 22.23 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.3 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.74 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64 (s, 1H), 7.56 – 7.44 (m, 5H), 7.44 – 7.36 (m, 2H), 7.34 – 7.19 (m, 2H), 4.70 (q, *J* = 6.6 Hz, 1H), 1.73 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 141.3, 141.1, 140.7, 132.5, 132.4, 129.11, 129.10, 128.7, 128.4, 126.70, 126.66, 124.0, 122.2, 120.8, 111.5, 46.4, 26.2.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}NO_2S$ $[M + H]^+$ 362.1209, found 362.1207.

(*S*)-Diphenyl((1-(thiophen-3-yl)ethyl)imino)-λ^6-sulfanone (37)



37

According to **General procedure A** with 3-(1-bromoethyl)thiophene (38.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **37** as a red oil (62.1 mg, 95% yield, 97% ee).

[α]$_D^{20}$ = −129 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.92 min, t_R (major) = 9.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.4 Hz, 2H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.37 (m, 6H), 7.28 – 7.24 (m, 1H), 7.20 – 7.14 (m, 2H), 4.51 (q, *J* = 6.6 Hz, 1H), 1.61 (d, *J* = 6.6 Hz, 3H).

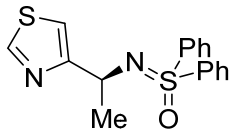
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 141.4, 140.7, 132.4, 132.3, 129.1, 128.8, 128.5, 126.6, 125.3, 119.6, 50.2, 27.0.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{18}NOS_2$ $[M + H]^+$ 328.0824, found 328.0822.

According to **General procedure A** with 3-(1-chloroethyl)thiophene (29.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **37** as a red oil (39.2 mg, 60% yield, 93% ee).

HPLC analysis: Chiralcel ID (hexane/^{i}PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 11.94 min, t_R (minor) = 14.74 min.

(*S*)-Diphenyl((1-(thiazol-4-yl)ethyl)imino)-λ^6-sulfanone (38)



38

According to **General procedure C** with 4-(1-bromoethyl)thiazole (38.2 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **38** as a coloress oil (55.8 mg, 85% yield, 82% ee).

$[\alpha]_D^{20}$ = –39 (*c* 0.8, CH_2Cl_2).

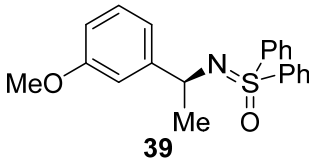
HPLC analysis: Chiralcel AD3 (hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 28.02 min, t_R (major) = 32.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.2 Hz, 1H), 8.03 (dd, *J* = 20.5, 6.6 Hz, 4H), 7.59 – 7.40 (m, 7H), 4.65 (q, *J* = 6.6 Hz, 1H), 1.68 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 152.3, 141.1, 140.6, 132.50, 132.46, 129.17, 129.15, 128.8, 128.5, 113.3, 51.4, 25.6.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}N_2OS_2$ $[M + H]^+$ 329.0777, found 329.0775.

(*S*)-((1-(3-Methoxyphenyl)ethyl)imino)diphenyl-λ^6-sulfanone (39)



39

According to **General procedure A** with 1-(1-chloroethyl)-3-methoxybenzene (34.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **39** as a colorless oil (51.2 mg, 73% yield, 98% ee).

$[\alpha]_D^{20}$ = −37 (*c* 1.0, CH_2Cl_2).

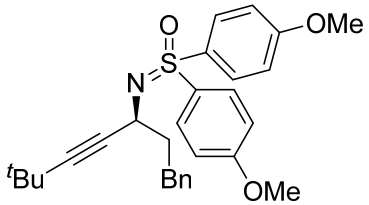
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 98/2, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 35.99 min, t_R (minor) = 41.71 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.03 (m, 2H), 7.93 – 7.80 (m, 2H), 7.57 – 7.35 (m, 6H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.09 – 7.03 (m, 1H), 7.03 – 6.98 (m, 1H), 6.84 – 6.74 (m, 1H), 4.41 (q, *J* = 6.6 Hz, 1H), 3.83 (s, 3H), 1.58 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 149.3, 141.5, 140.8, 132.4, 132.3, 129.13, 129.05, 129.0, 128.4, 118.7, 111.9, 111.8, 55.2, 54.2, 28.2.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}NO_2S$ $[M + H]^+$ 352.1366, found 352.1364.

(*S*)-((6,6-Dimethyl-1-phenylhept-4-yn-3-yl)imino)bis(4-methoxyphenyl)-λ^6-sulfanone (40)



40

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminobis(4-methoxyphenyl)-λ^6-sulfanone (55.4 mg, 0.20 mmol, 1.0 equiv.), $Cu(PPh_3)_3Br$ (37.2 mg, 0.040 mmol, 20 mol%), chiral ligand

L*4 (28.4 mg, 0.040 mmol, 20 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added (3-bromo-6,6-dimethylhept-4-yn-1-yl)benzene (111.2 mg, 0.40 mmol, 2.0 equiv.) and the reaction mixture was stirred at room temperature for 7 d. The precipitate was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford the desired product **40** as a colorless oil (38.9 mg, 41% yield, 50% conversion, 80% ee).

$[\alpha]_D^{20}$ = –10 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IF (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.59 min, t_R (minor) = 9.77 min.

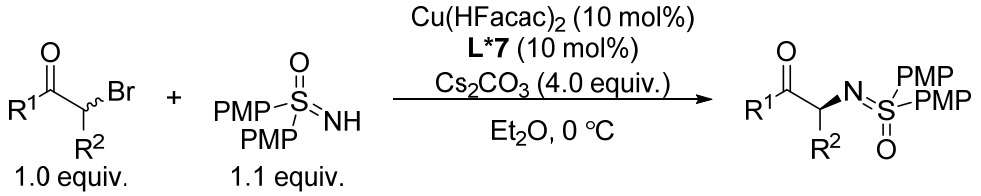
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.87 (m, 4H), 7.30 – 7.22 (m, 4H), 7.20 – 7.14 (m, 1H), 7.00 – 6.90 (m, 4H), 3.98 (t, *J* = 6.7 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.91 – 2.78 (m, 2H), 2.17 – 2.04 (m, 2H), 1.20 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 162.6, 142.5, 133.5, 133.2, 131.0, 130.0, 128.6, 128.2, 125.4, 114.17, 114.15, 91.3, 80.9, 55.6, 45.3, 41.5, 32.5, 31.2, 27.3.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{34}NO_3S$ $[M + H]^+$ 476.2254, found 476.2263.

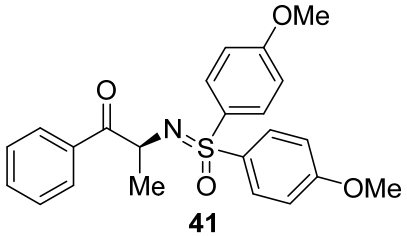
Enantioconvergent N-alkylation: scope of secondary α-bromoketones. (Figure 3A)

General procedure D:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminobis(4-methoxyphenyl)-λ^6-sulfanone (60.9 mg, 0.22 mmol, 1.1 equiv.), $Cu(HFacac)_2$ (8.8 mg, 0.020 mmol, 10 mol%), chiral ligand **L*7** (27.3 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (4.0 mL). To this solution was added α-bromo ketone (0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at 0 °C for 72 h or more. Upon completion (monitored by TLC), the precipitate was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

(*S*)-bis(4-Methoxyphenyl)((1-oxo-1-phenylpropan-2-yl)imino)-λ^6-sulfanone (41)



41

According to **General procedure D** with 2-bromo-1-phenylpropan-1-one (42.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **41** as a yellow oil (65.4 mg, 80% yield, 91% ee).

$[\alpha]_D^{20}$ = –0.1 (*c* 1.0, CH_2Cl_2).

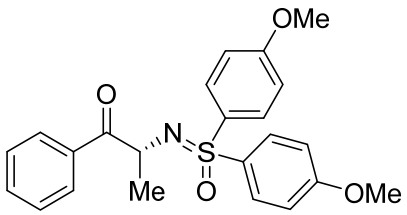
HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 29.03 min, t_R (minor) = 36.90 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.98 – 7.90 (m, 2H), 7.79 – 7.71 (m, 2H), 7.57 – 7.49 (m, 1H), 7.45 – 7.38 (m, 2H), 6.98 – 6.90 (m, 2H), 6.90 – 6.82 (m, 2H), 4.72 (q, *J* = 6.9 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.54 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 162.8, 162.7, 135.8, 133.3, 132.60, 132.57, 130.4, 130.3, 129.2, 128.3, 114.32, 114.26, 55.6, 55.5, 55.4, 22.2.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}NO_4S$ $[M + H]^+$ 410.1421, found 410.1419.

(*R*)-bis(4-Methoxyphenyl)((1-oxo-1-phenylpropan-2-yl)imino)-λ^6-sulfanone ((*R*)-41)

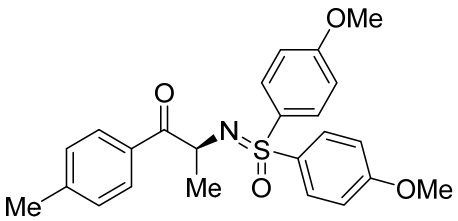


(R)-**41**

According to **General procedure D** with 2-bromo-1-phenylpropan-1-one (42.6 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*7'** for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product (*R*)-**41** as a yellow oil (81.2 mg, 99% yield, 96% ee).

HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 29.11 min, t_R (major) = 36.78 min.

(*S*)-bis(4-Methoxyphenyl)((1-oxo-1-(*p*-tolyl)propan-2-yl)imino)-λ^6-sulfanone (42)



42

According to **General procedure D** with 2-bromo-1-(*p*-tolyl)propan-1-one (45.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **42** as

a yellow oil (67.7 mg, 80% yield, 92% ee).

$[\alpha]_D^{20}$ = –70 (*c* 1.0, CH_2Cl_2).

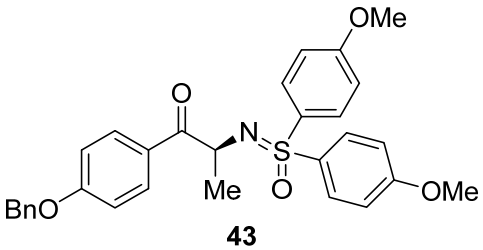
HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 31.44 min, t_R (minor) = 38.38 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 4H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.70 (q, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.39 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 162.8, 162.6, 143.3, 133.3, 133.0, 132.6, 130.5, 130.3, 129.3, 129.0, 114.32, 114.25, 55.6, 55.5, 55.3, 22.4, 21.6.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}NO_4S$ $[M + H]^+$ 424.1577, found 424.1575.

(*S*)-((1-(4-(Benzyloxy)phenyl)-1-oxopropan-2-yl)imino)bis(4-methoxyphenyl)-λ^6-sulfanone (43)



43

According to **General procedure D** with 1-(4-(benzyloxy)phenyl)-2-bromopropan-1-one (63.8 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **43** as a white amorphous solid (98.9 mg, 96% yield, 94% ee).

$[\alpha]_D^{20}$ = –72 (*c* 1.0, CH_2Cl_2).

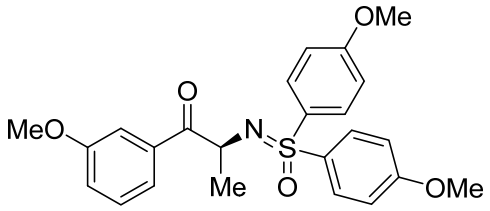
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 18.48 min, t_R (major) = 20.31 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.54 – 7.33 (m, 5H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.14 (s, 2H), 4.68 (q, *J* = 6.8 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 162.8, 162.7, 162.3, 136.3, 133.3, 132.6, 131.6, 130.5, 130.3, 128.7, 128.6, 128.2, 127.5, 114.33, 114.30, 114.27, 70.1, 55.60, 55.55, 55.3, 22.5.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{30}NO_5S$ $[M + H]^+$ 516.1839, found 516.1838.

(*S*)-bis(4-Methoxyphenyl)((1-(3-methoxyphenyl)-1-oxopropan-2-yl)imino)-λ^6-sulfanone (44)



44

According to **General procedure D** with 2-bromo-1-(3-methoxyphenyl)propan-1-one (48.4 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **44** as a colorless oil (67.6 mg, 77% yield, 94% ee).

$[\alpha]_D^{20}$ = −16 (*c* 1.0, CH_2Cl_2).

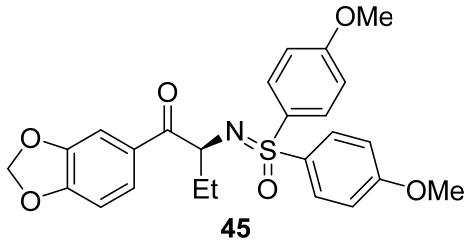
HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 29.88 min, t_R (minor) = 37.45 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.77 – 7.70 (m, 2H), 7.61 – 7.53 (m, 2H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.11 – 7.01 (m, 1H), 6.94 – 6.89 (m, 2H), 6.88 – 6.79 (m, 2H), 4.69 (q, *J* = 6.9 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 1.51 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 162.8, 162.7, 159.6, 137.1, 133.3, 132.6, 130.4, 130.3, 129.2, 121.7, 119.3, 114.32, 114.25, 113.3, 55.6, 55.5, 55.4, 55.3, 22.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}NO_5S$ $[M + H]^+$ 440.1526, found 440.1523.

(*S*)-((1-(Benzo[*d*][1,3]dioxol-5-yl)-1-oxobutan-2-yl)imino)bis(4-methoxyphenyl)-λ^6-sulfanone (45)



45

According to **General procedure D** with 1-(benzo[*d*][1,3]dioxol-5-yl)-2-bromobutan-1-one (54.0 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*6** for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **45** as a colorless oil (65.4 mg, 70% yield, 87% ee).

[α]$_D^{20}$ = −12 (*c* 1.0, CH_2Cl_2).

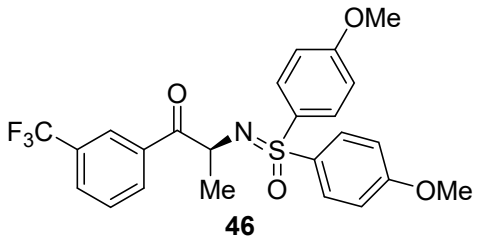
HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 39.80 min, t_R (minor) = 48.11 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.75 – 7.67 (m, 3H), 7.54 (d, *J* = 1.7 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.86 – 6.80 (m, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.01 (s, 2H), 4.29 (dd, *J* = 7.6, 6.3 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.02 – 1.80 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 162.7, 162.6, 151.3, 147.8, 133.0, 132.8, 130.6, 130.5, 130.3, 125.4, 114.3, 109.1, 107.6, 101.7, 62.2, 55.6, 55.5, 29.6, 11.0.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}NO_6S$ $[M + H]^+$ 468.1475, found 468.1474.

(*S*)-bis(4-Methoxyphenyl)((1-oxo-1-(3-(trifluoromethyl)phenyl)propan-2-yl)imino)-λ^6-sulfanone (46)



46

According to **General procedure D** with 2-bromo-1-(3-(trifluoromethyl)phenyl)propan-1-one (56.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the

reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **46** as a colorless oil (66.8 mg, 70% yield, 94% ee).

$[\alpha]_D^{20}$ = –6 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.29 min, t_R (minor) = 12.15 min.

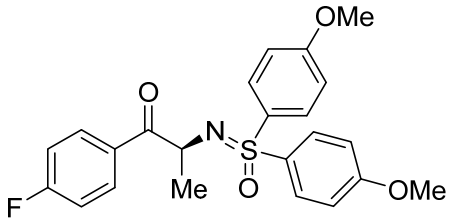
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.36 (m, 1H), 8.34 – 8.24 (m, 1H), 7.91 – 7.83 (m, 2H), 7.80 – 7.75 (m, 1H), 7.75 – 7.67 (m, 2H), 7.59 – 7.52 (m, 1H), 6.98 – 6.90 (m, 2H), 6.89 – 6.79 (m, 2H), 4.60 (q, *J* = 6.9 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 162.9, 162.8, 136.2, 132.8, 132.7, 132.4, 130.7 (q, *J* = 32.5 Hz), 130.3, 130.2, 129.1 – 128.8 (m), 128.9, 126.54 – 126.24 (m), 123.9 (q, *J* = 271.0 Hz), 114.4, 114.3, 56.0, 55.60, 55.55, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{24}H_{23}F_3NO_4S$ $[M + H]^+$ 478.1294, found 478.1294.

(*S*)-((1-(4-Fluorophenyl)-1-oxopropan-2-yl)imino)bis(4-methoxyphenyl)-λ^6-sulfanone (47)



47

According to **General procedure D** with 2-bromo-1-(4-fluorophenyl)propan-1-one (46.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **47** as a yellow oil (60.6 mg, 71% yield, 91% ee).

$[\alpha]_D^{20}$ = –59 (*c* 0.7, CH_2Cl_2).

HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 22.57 min, t_R (minor) = 24.84 min.

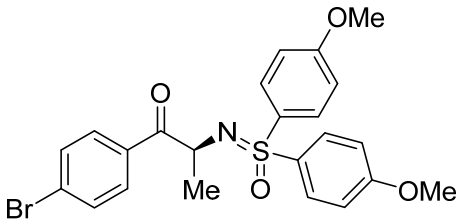
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 2H), 7.94 – 7.87 (m, 2H), 7.79 – 7.71 (m, 2H), 7.13 – 7.04 (m, 2H), 6.97 – 6.90 (m, 2H), 6.90 – 6.83 (m, 2H), 4.63 (q, *J* = 6.9 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 165.4 (d, *J* = 254.1 Hz), 162.8, 162.7, 133.1, 132.6, 132.0 (d, *J* = 9.1 Hz), 131.9 (d, *J* = 3.0 Hz), 130.33, 130.28, 115.3 (d, *J* = 21.6 Hz), 114.33, 114.31, 55.7, 55.59, 55.55, 22.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –106.0 (tt, *J* = 8.2, 5.5 Hz, 1F).

HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}FNO_4S$ $[M + H]^+$ 428.1326, found 428.1323.

(*S*)-((1-(4-Bromophenyl)-1-oxopropan-2-yl)imino)bis(4-methoxyphenyl)-λ^6-sulfanone (48)



48

According to **General procedure D** with 2-bromo-1-(4-bromophenyl)propan-1-one (58.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **48** as a colorless oil (68.2 mg, 70% yield, 91% ee).

$[\alpha]_D^{20}$ = –253 (*c* 0.4, CH_2Cl_2).

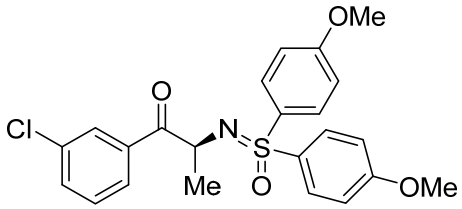
HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 26.29 min, t_R (minor) = 50.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.61 (q, *J* = 6.9 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 1.51 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 162.8, 162.7, 134.3, 133.0, 132.5, 131.5, 131.0, 130.31, 130.26, 127.7, 114.3, 55.7, 55.61, 55.58, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}BrNO_4S$ $[M + H]^+$ 488.0526 & 490.0505, found 488.0524 & 490.0499.

(*S*)-((1-(3-Chlorophenyl)-1-oxopropan-2-yl)imino)bis(4-methoxyphenyl)-λ^6-sulfanone (49)



49

According to **General procedure D** with 2-bromo-1-(3-chlorophenyl)propan-1-one (49.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **49** as a yellow oil (84.2 mg, 95% yield, 90% ee).

[α]$_D^{20}$ = –70 (*c* 0.8, CH_2Cl_2).

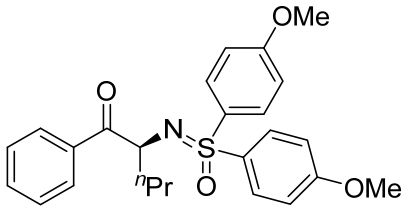
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 26.47 min, t_R (minor) = 33.30 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 1.8 Hz, 1H), 7.95 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 2H), 7.53 – 7.44 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.61 (q, *J* = 6.8 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 162.9, 162.7, 137.3, 134.4, 132.9, 132.5, 132.4, 130.31, 130.28, 129.6, 129.3, 127.4, 114.4, 114.3, 55.60, 55.56, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}ClNO_4S$ $[M + H]^+$ 444.1031, found 444.1031.

(*S*)-bis(4-Methoxyphenyl)((1-oxo-1-phenylpentan-2-yl)imino)-λ^6-sulfanone (50)



50

According to **General procedure D** with 2-bromo-1-phenylpentan-1-one (48.0 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*6** for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **50** as a white amorphous solid (68.2 mg, 78% yield, 92% ee).

[α]$_D^{20}$ = 0.5 (*c* 1.0, CH_2Cl_2).

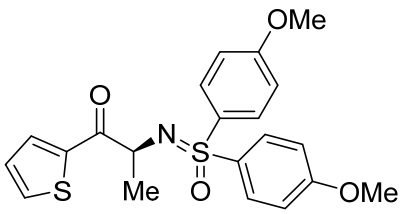
HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 21.29 min, t_R (minor) = 26.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.99 – 7.92 (m, 2H), 7.76 – 7.68 (m, 2H), 7.56 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 6.97 – 6.90 (m, 2H), 6.87 – 6.80 (m, 2H), 4.47 (t, *J* = 6.9 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 1.95 – 1.81 (m, 2H), 1.65 – 1.54 (m, 1H), 1.47 – 1.37 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 162.8, 162.6, 136.1, 133.1, 132.7, 132.5, 130.6, 130.4, 129.1, 128.2, 114.3, 114.2, 60.5, 55.6, 55.5, 38.3, 19.7, 13.9.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{28}NO_4S$ $[M + H]^+$ 438.1734, found 438.1733.

(*S*)-bis(4-Methoxyphenyl)((1-oxo-1-(thiophen-2-yl)propan-2-yl)imino)-λ^6-sulfanone (51)



51

According to **General procedure D** with 2-bromo-1-(thiophen-2-yl)propan-1-one (43.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **51** as a colorless oil (68.0 mg, 82% yield, 94% ee).

[α]$_D^{20}$ = –63 (*c* 1.0, CH_2Cl_2).

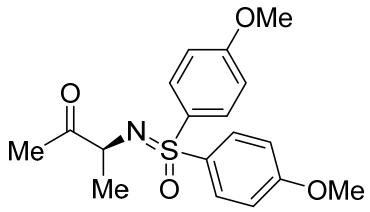
HPLC analysis: Chiralcel IE (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 24.03 min, t_R (minor) = 27.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.82 – 7.75 (m, 2H), 7.61 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.10 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.91 – 6.84 (m, 2H), 4.42 (q, *J* = 6.8 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 162.8, 162.7, 141.0, 133.8, 133.6, 133.0, 132.3, 130.5, 130.3, 127.7, 114.4, 114.3, 57.5, 55.60, 55.57, 23.0.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}NO_4S_2$ $[M + H]^+$ 416.0985, found 416.0983.

(*S*)-bis(4-Methoxyphenyl)((3-oxobutan-2-yl)imino)-λ^6-sulfanone (52)



52

According to **General procedure D** with 3-bromobutan-2-one (45.0 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **52** as a yellow oil (42.3 mg, 61% yield, 72% ee).

$[\alpha]_D^{20}$ = −1 (*c* 1.0, CH_2Cl_2).

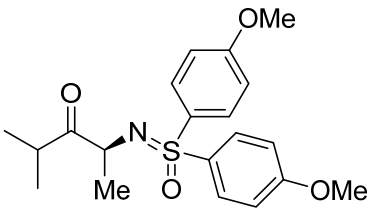
HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 21.16 min, t_R (major) = 22.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 7.64 (m, 4H), 7.09 – 6.78 (m, 4H), 3.85 (s, 3H), 3.84 (s, 3H), 3.69 (q, *J* = 6.8 Hz, 1H), 2.35 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0, 162.9, 162.8, 132.5, 132.3, 130.4, 130.3, 114.5, 114.4, 59.6, 55.6, 25.9, 21.1.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NO_4S$ $[M + H]^+$ 348.1264, found 348.1262.

(*S*)-bis(4-Methoxyphenyl)((4-methyl-3-oxopentan-2-yl)imino)-λ^6-sulfanone (53)



53

According to **General procedure D** with 2-bromo-4-methylpentan-3-one (35.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **52** as a colorless oil (58.5 mg, 78% yield, 89% ee).

$[\alpha]_D^{20}$ = −3 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.52 min, t_R (major) = 12.73 min.

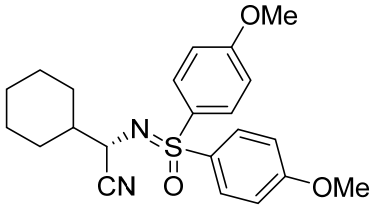
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.88 – 7.81 (m, 2H), 6.99 – 6.91 (m, 4H), 3.90 – 3.82 (m, 7H), 3.32 (p, *J* = 6.8 Hz, 1H), 1.37 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.5, 162.8, 162.7, 133.0, 132.5, 130.39, 130.37, 114.4, 114.3, 57.9, 55.6, 35.7, 21.2, 19.1, 18.9.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}NO_4S$ $[M + H]^+$ 376.1577, found 376.1575.

Enantioconvergent N-alkylation: scope of secondary α-bromonitrile. (Figure 3A)

(*S*)-2-((bis(4-Methoxyphenyl)(oxo)-λ^6-sulfaneylidene)amino)-2-cyclohexylacetonitrile (54)



54

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminobis(4-methoxyphenyl)-λ^6-sulfanone (60.9 mg, 0.22 mmol, 1.1 equiv.), $Cu(PPh_3)_3Br$ (18.6 mg, 0.020 mmol, 10 mol%), chiral ligand **L*7** (30.0 mg, 0.022 mmol, 11 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (4.0 mL). To this solution was added 2-bromo-2-cyclohexylacetonitrile (40.2 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at 0 °C for 5 d. Upon completion (monitored by TLC), the precipitate was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the desired product **54** as a colorless oil (54.1 mg, 68% yield, 90% ee).

$[\alpha]_D^{20}$ = 14 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel ID (hexane/^{i}PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 14.77 min, t_R (minor) = 16.93 min.

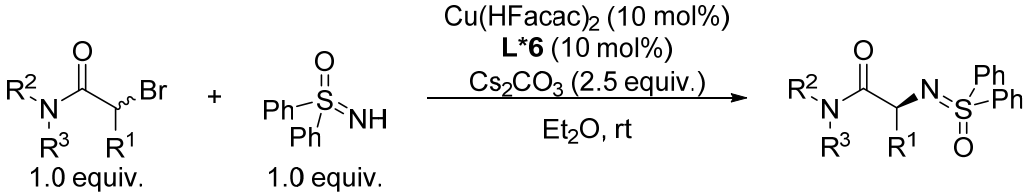
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 14.5, 8.9 Hz, 4H), 6.98 (dd, *J* = 12.7, 9.0 Hz, 4H), 3.85 (s, 6H), 3.80 (d, *J* = 6.4 Hz, 1H), 2.12 – 2.03 (m, 1H), 1.96 (d, *J* = 12.3 Hz, 1H), 1.82 – 1.68 (m, 3H), 1.36 – 1.09 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 163.1, 132.0, 131.4, 130.8, 130.1, 120.5, 114.7, 114.4, 55.7, 55.6, 50.4, 43.5, 29.4, 28.9, 26.2, 25.8.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}N_2O_3S$ $[M + H]^+$ 399.1737, found 399.1735.

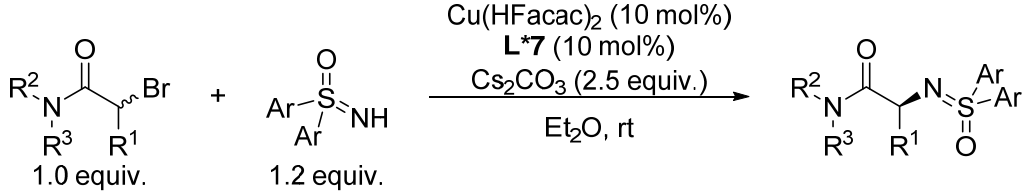
Enantioconvergent N-alkylation: scope of secondary α-bromo amides. (Figure 3A)

General procedure E:



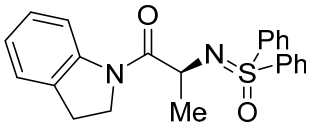
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), $Cu(HFacac)_2$ (8.8 mg, 0.020 mmol, 10 mol%), chiral ligand **L*6** (20.5 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (163.0 mg, 0.50 mmol, 2.5 equiv.) and anhydrous Et_2O (4.0 mL). Then, α-bromo amide (0.20 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 36 h or more. Upon completion (monitored by TLC), the precipitate was filtered off and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure F:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfoximine (0.24 mmol, 1.2 equiv.), $Cu(HFacac)_2$ (8.8 mg, 0.020 mmol, 10 mol%), chiral ligand **L*7** (27.3 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (163.0 mg, 0.50 mmol, 2.5 equiv.) and anhydrous Et_2O (4.0 mL). Then, α-bromo amide (0.20 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 36 h or more. Upon completion (monitored by TLC), the precipitate was filtered off and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford the desired product.

(*S*)-((1-(Indolin-1-yl)-1-oxopropan-2-yl)imino)diphenyl-λ^6-sulfanone (55)



55

According to **General procedure E** with 2-bromo-1-(indolin-1-yl)propan-1-one (50.6 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **55** as a white amorphous solid (74.8 mg, 96% yield, 94% ee).

[α]$_D^{20}$ = –114 (*c* 1.0, CH_2Cl_2).

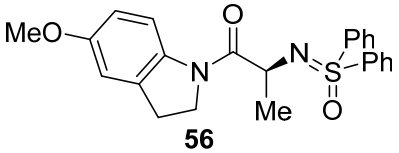
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 20.34 min, t_R (major) = 31.38 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 6.9 Hz, 2H), 7.96 (d, *J* = 6.7 Hz, 2H), 7.56 – 7.33 (m, 6H), 7.23 – 7.09 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.31 (q, *J* = 6.6 Hz, 1H), 4.16 – 3.95 (m, 2H), 3.17 – 2.92 (m, 2H), 1.46 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 143.3, 141.7, 141.2, 132.6, 132.5, 131.4, 129.12, 129.09, 128.41, 128.35, 127.4, 124.4, 123.6, 117.6, 52.0, 47.7, 28.2, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}N_2O_2S$ $[M + H]^+$ 391.1475, found 391.1472.

(*S*)-((1-(5-Methoxyindolin-1-yl)-1-oxopropan-2-yl)imino)diphenyl-λ^6-sulfanone (56)



56

According to **General procedure E** with 2-bromo-1-(5-methoxyindolin-1-yl)propan-1-one (56.6 mg, 0.20 mmol, 1.0 equiv.) for 30 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **56** as a yellow amorphous solid (78.1 mg, 93% yield, 93% ee).

[α]$_D^{20}$ = –56 (*c* 0.7, CH_2Cl_2).

HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 70/30, flow rate 0.6 mL/min, λ = 254

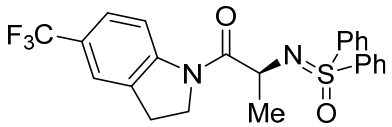
nm), t_R (minor) = 36.70 min, t_R (major) = 46.77 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.14 (m, 1H), 8.04 (d, *J* = 6.9 Hz, 2H), 7.95 (d, *J* = 6.8 Hz, 2H), 7.55 – 7.34 (m, 6H), 6.70 (s, 2H), 4.28 (q, *J* = 6.5 Hz, 1H), 4.12 – 3.92 (m, 2H), 3.77 (s, 3H), 3.11 – 2.87 (m, 2H), 1.45 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 156.3, 141.6, 141.2, 136.9, 133.0, 132.6, 132.5, 129.12, 129.08, 128.39, 128.37, 118.2, 111.8, 110.6, 55.6, 51.8, 47.9, 28.4, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_2O_3S$ $[M + H]^+$ 421.1580, found 421.1574.

(*S*)-((1-oxo-1-(5-(Trifluoromethyl)indolin-1-yl)propan-2-yl)imino)diphenyl-λ^6-sulfanone (57)



57

According to **General procedure E** with 2-bromo-1-(5-(trifluoromethyl)indolin-1-yl)propan-1-one (64.4 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **57** as a white amorphous solid (83.3 mg, 91% yield, 94% ee).

$[\alpha]_D^{20}$ = –425 (*c* 0.6, CH_2Cl_2).

HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 70/30, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 17.91 min, t_R (major) = 20.29 min.

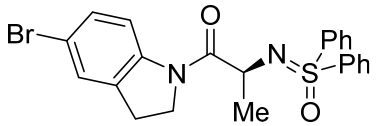
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 6.7 Hz, 2H), 7.96 (d, *J* = 6.5 Hz, 2H), 7.56 – 7.32 (m, 8H), 4.31 (q, *J* = 6.6 Hz, 1H), 4.17 (t, *J* = 8.5 Hz, 2H), 3.21 – 3.00 (m, 2H), 1.45 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 146.2, 141.5, 141.1, 132.7, 132. 6, 132.1, 129.2, 129.1, 128.4, 128.2, 125.4 (q, *J* = 32.0 Hz), 125.1 (q, *J* = 3.9 Hz), 124.4 (q, *J* = 270.0 Hz), 121.4 (d, *J* = 4.1 Hz), 117.2, 52.0, 48.1, 27.9, 20.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ –61.6 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{24}H_{22}F_3N_2O_2S$ $[M + H]^+$ 459.1349, found 459.1342.

(*S*)-((1-(5-Bromoindolin-1-yl)-1-oxopropan-2-yl)imino)diphenyl-λ^6-sulfanone (58)



58

According to **General procedure E** with 2-bromo-1-(5-bromoindolin-1-yl)propan-1-one (66.6 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **58** as a white amorphous solid (91.7 mg, 98% yield, 94% ee).

X-ray quality crystals were obtained by slow evaporation of solvent from a saturated solution in a mixture of CH_2Cl_2/hexane.

[α]$_D^{20}$ = –46 (*c* 0.5, CH_2Cl_2).

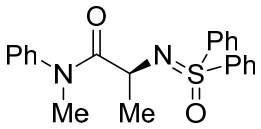
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 70/30, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 24.31 min, t_R (major) = 29.96 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 1H), 7.99 (dd, *J* = 27.4, 7.6 Hz, 4H), 7.61 – 7.36 (m, 6H), 7.32 – 7.14 (m, 2H), 4.28 (q, *J* = 6.6 Hz, 1H), 4.18 – 3.98 (m, 2H), 3.19 – 2.89 (m, 2H), 1.43 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 142.5, 141.6, 141.1, 133.8, 132.6, 132.5, 130.2, 129.2, 129.1, 128.4, 128.3, 127.4, 118.9, 116.0, 51.9, 47.9, 28.0, 20.7.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{22}BrN_2O_2S$ $[M + H]^+$ 469.0580, found 469.0577.

(*S*)-*N*-Methyl-2-((oxodiphenyl-λ^6-sulfaneylidene)amino)-*N*-phenylpropanamide (59)



59

According to **General procedure F** with 2-bromo-*N*-methyl-*N*-phenylpropanamide (48.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **59** as an amorphous solid (55.2 mg, 73% yield, 93% ee).

[α]$_D^{20}$ = 0.1 (*c* 1.0, CH_2Cl_2).

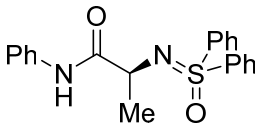
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 70/30, flow rate 0.6 mL/min, λ = 230 nm), t_R (minor) = 34.32 min, t_R (major) = 43.04 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.37 (m, 6H), 7.20 (s, 3H), 6.76 (s, 2H), 3.95 (q, *J* = 6.8 Hz, 1H), 3.19 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 143.4, 141.5, 141.0, 132.42, 132.38, 129.5, 129.1, 129.0, 128.9, 128.4, 127.6, 127.2, 49.2, 37.7, 22.4.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{23}N_2O_2S$ $[M + H]^+$ 379.1475, found 379.1469.

(*S*)-2-((Oxodiphenyl-λ^{6}-sulfaneylidene)amino)-*N*-phenylpropanamide (60)



60

According to **General procedure F** with 2-bromo-*N*-methyl-*N*-phenylpropanamide (48.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **60** as a colorless oil (35.6 mg, 49% yield, 72% ee).

$[\alpha]_D^{20}$ = –31 (*c* 1.0, CH_2Cl_2).

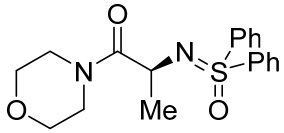
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.04 min, t_R (major) = 17.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.11 – 7.94 (m, 4H), 7.69 – 7.51 (m, 8H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 3.89 (q, *J* = 6.9 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 140.2, 139.7, 138.0, 133.11, 133.05, 129.6, 129.4, 129.0, 128.5, 128.3, 124.1, 119.7, 54.9, 22.7.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}N_2O_2S$ $[M + H]^+$ 365.1318, found 365.1313.

(*S*)-((1-Morpholino-1-oxopropan-2-yl)imino)diphenyl-λ^6-sulfanone (61)



61

According to **General procedure F** with 2-bromo-1-morpholinopropan-1-one **E2** (44.2 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **61** as a colorless oil (68.0 mg, 95% yield, 95% ee).

[α]$_D^{20}$ = 27 (*c* 1.0, CH_2Cl_2).

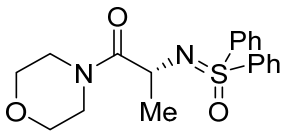
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 80/20, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 32.31 min, t_R (major) = 40.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.86 (m, 4H), 7.57 – 7.40 (m, 6H), 4.24 (q, *J* = 6.7 Hz, 1H), 3.88 – 3.45 (m, 8H), 1.39 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5 141.2, 140.9, 132.6, 129.2 128.4 128.3, 66.9, 66.7, 51.6, 46.2, 42.6, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}N_2O_3S$ $[M + H]^+$ 359.1424, found 359.1419.

(*R*)-((1-Morpholino-1-oxopropan-2-yl)imino)diphenyl-λ^6-sulfanone ((*R*)-61)

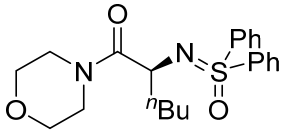


(*R*)-**61**

According to **General procedure F** with 2-bromo-1-morpholinopropan-1-one **E2** (44.2 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*7'** for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product (*R*)-**61** as a colorless oil (68.1 mg, 99% yield, 97% ee).

HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 80/20, flow rate 0.8 mL/min, λ = 230 nm), t_R (major) = 31.16 min, t_R (minor) = 42.41 min.

(*S*)-((1-Morpholino-1-oxohexan-2-yl)imino)diphenyl-λ^6-sulfanone (62)



62

According to **General procedure F** with 2-bromo-1-morpholinohexan-1-one (52.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **62** as a colorless oil (68.1 mg, 85% yield, 89% ee).

[α]$_D^{20}$ = –20 (*c* 1.0, CH_2Cl_2).

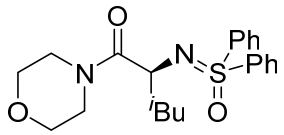
HPLC analysis: Chiralcel OZ3 (hexane/^{i}PrOH = 80/20, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 15.98 min, t_R (major) = 18.14 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.89 (m, 4H), 7.59 – 7.39 (m, 6H), 4.00 (t, *J* = 7.2 Hz, 1H), 3.88 – 3.74 (m, 1H), 3.71 – 3.39 (m, 7H), 1.91 – 1.70 (m, 2H), 1.53 – 1.39 (m, 1H), 1.38 – 1.16 (m, 3H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 141.1, 140.6, 132.60, 132.59, 129.1, 128.6, 128.4, 66.9, 66.6, 56.6, 46.2, 42.5, 35.3, 28.6, 22.5, 14.0.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{29}N_2O_3S$ $[M + H]^+$ 401.1893, found 401.1888.

(*S*)-((4-Methyl-1-morpholino-1-oxopentan-2-yl)imino)diphenyl-λ^6-sulfanone (63)



63

According to **General procedure F** with 2-bromo-4-methyl-1-morpholinopentan-1-one (52.6 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **63** as a colorless oil (63.2 mg, 79% yield, 91% ee).

[α]$_D^{20}$ = –13 (*c* 1.0, CH_2Cl_2).

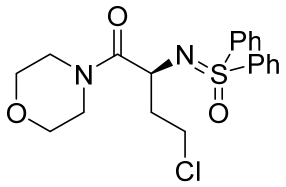
HPLC analysis: Chiralcel AZ3 (hexane/^{i}PrOH = 80/20, flow rate 0.6 mL/min, λ = 230 nm), t_R (minor) = 35.34 min, t_R (major) = 41.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 14.1, 7.3 Hz, 4H), 7.62 – 7.38 (m, 6H), 4.08 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.84 – 3.33 (m, 8H), 1.90 – 1.67 (m, 2H), 1.65 – 1.53 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 141.1, 140.6, 132.62, 132.61, 129.2, 129.1, 128.6, 128.4, 66.9, 66.5, 54.4, 46.2, 44.4, 42.5, 24.7, 23.2, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{29}N_2O_3S$ $[M + H]^+$ 401.1893, found 401.1888.

(*S*)-((4-Chloro-1-morpholino-1-oxobutan-2-yl)imino)diphenyl-λ^6-sulfanone (64)



64

According to **General procedure F** with 2-bromo-4-chloro-1-morpholinobutan-1-one (53.8 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **64** as a yellow oil (62.5 mg, 77% yield, 93% ee).

$[\alpha]_D^{20}$ = 5 (*c* 1.0, CH_2Cl_2).

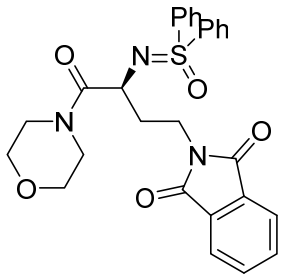
HPLC analysis: Chiralcel IF (hexane/^{i}PrOH = 70/30, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 14.79 min, t_R (minor) = 16.52 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.60 – 7.43 (m, 6H), 4.35 (dd, *J* = 8.3, 5.3 Hz, 1H), 3.88 – 3.78 (m, 1H), 3.72 – 3.25 (m, 9H), 2.33 – 2.13 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 140.9, 140.5, 132.83, 132.76, 129.24, 129.21, 128.6, 128.4, 66.8, 66.5, 51.3, 46.1, 42.4, 42.3, 37.8.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}ClN_2O_3S$ $[M + H]^+$ 407.1191, found 407.1188.

(*S*)-2-(4-Morpholino-4-oxo-3-((oxodiphenyl-λ^6-sulfaneylidene)amino)butyl) isoindoline-1,3-dione (65)



65

According to **General procedure F** with 2-(3-bromo-4-morpholino-4-oxobutyl)isoindoline-1,3-dione (76.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/5) to yield the product **65** as an amorphous solid (62.0 mg, 60% yield, 88% ee).

[α]$_D^{20}$ = −18 (*c* 0.9, CH_2Cl_2).

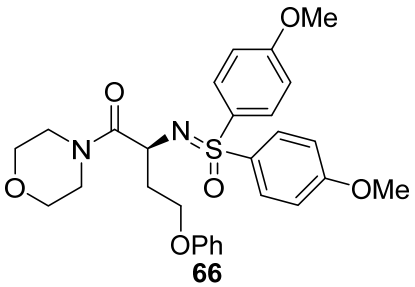
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 60/40, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 19.59 min, t_R (major) = 27.62 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.64 – 7.32 (m, 6H), 4.13 (t, *J* = 7.0 Hz, 1H), 3.93 – 3.36 (m, 10H), 2.35 (dt, *J* = 13.4, 6.8 Hz, 1H), 2.11 – 1.99 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 168.2, 140.8, 140.6, 133.9, 132.8, 132.6, 132.1, 129.2, 128.5, 128.2, 123.1, 66.7, 66.5, 53.4, 46.2, 42.5, 35.5, 33.6.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{28}N_3O_5S$ $[M + H]^+$ 518.1744, found 518.1741.

(*S*)-bis(4-Methoxyphenyl)((1-morpholino-1-oxo-4-phenoxybutan-2-yl)imino)-λ^6-sulfanone (66)



66

According to **General procedure F** with 2-bromo-1-morpholino-4-phenoxybutan-1-one (65.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **66** as a colorless oil (84.8 mg, 81% yield, 89% ee).

[α]$_D^{20}$ = 3 (*c* 1.0, CH_2Cl_2).

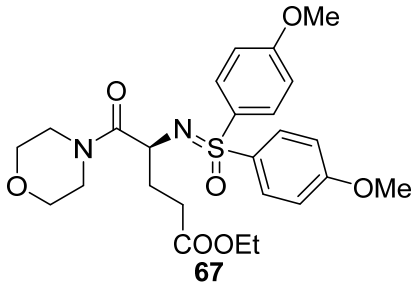
HPLC analysis: Chiralcel ID (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 32.61 min, t_R (major) = 56.48 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.9, 1.2 Hz, 4H), 7.36 – 7.20 (m, 2H), 7.06 – 6.69 (m, 7H), 4.36 (dd, *J* = 8.3, 5.7 Hz, 1H), 4.39 – 4.19 (m, 1H), 4.11 – 4.01 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.77 – 3.35 (m, 8H), 2.41 – 2.16 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 162.8, 158.8, 132.9, 132.3, 130.4, 130.3, 129.4, 120.6, 114.5, 114.4, 114.3, 66.9, 66.5, 64.4, 55.60, 55.55, 52.0, 46.1, 42.5, 34.9.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{33}N_2O_6S$ $[M + H]^+$ 525.2054, found 525.2048.

Ethyl (*S*)-4-((bis(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)amino)-5-morpholino-5-oxopentanoate (67)



67

According to **General procedure F** with ethyl 4-bromo-5-morpholino-5-oxopentanoate (61.4 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **67** as a colorless oil (66.6 mg, 66% yield, 88% ee).

[α]$_D^{20}$ = 4 (*c* 1.0, CH_2Cl_2).

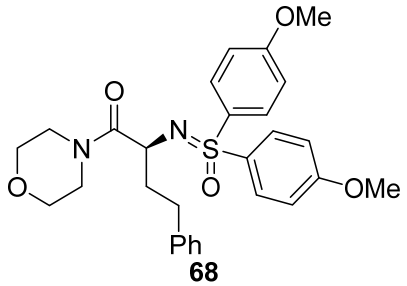
HPLC analysis: Chiralcel ID (hexane/^{i}PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 37.86 min, t_R (major) = 75.79 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.80 (d, *J* = 8.9 Hz, 2H), 6.92 (dd, *J* = 8.9, 6.3 Hz, 4H), 4.18 – 4.01 (m, 3H), 3.82 (s, 6H), 3.81 – 3.71 (m, 1H), 3.69 – 3.54 (m, 4H), 3.54 – 3.37 (m, 3H), 2.63 – 2.43 (m, 2H), 2.15 – 1.95 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 172.2, 162.9, 162.8, 132.8, 132.4, 130.5, 130.4, 114.4, 114.3, 66.9, 66.6, 60.3, 55.61, 55.59, 54.7, 46.1, 42.5, 30.7, 29.9, 14.2.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{33}N_2O_7S$ $[M + H]^+$ 505.2003, found 505.1998.

(*S*)-bis(4-Methoxyphenyl)((1-morpholino-1-oxo-4-phenylbutan-2-yl)imino)-λ^6-sulfanone (68)



68

According to **General procedure C** with 2-bromo-1-morpholino-4-phenylbutan-1-one (62.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **68** as a colorless oil (65.0 mg, 65% yield, 89% ee).

$[\alpha]_D^{20}$ = –0.4 (*c* 0.3, CH_2Cl_2).

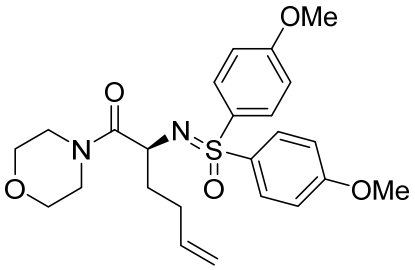
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.69 min, t_R (major) = 18.84 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.75 (m, 4H), 7.39 – 7.08 (m, 5H), 6.92 (dd, *J* = 9.0, 0.9 Hz, 4H), 3.99 (dd, *J* = 7.6, 6.4 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.73 – 3.30 (m, 8H), 3.01 – 2.75 (m, 1H), 2.72 – 2.60 (m, 1H), 2.17 – 2.07 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 162.8, 141.8, 132.8, 132.5, 130.4, 130.3, 128.56, 128.3, 125.8, 114.4, 114.3, 66.9, 66.6, 55.8, 55.6, 46.1, 42.5, 37.0, 32.6.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{33}N_2O_5S$ $[M + H]^+$ 509.2105, found 509.2103.

(*S*)-bis(4-Methoxyphenyl)((1-morpholino-1-oxohex-5-en-2-yl)imino)-λ^6-sulfanone (69)



69

According to **General procedure F** with 2-bromo-1-morpholinohex-5-en-1-one (52.2 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **69** as a colorless oil (71.4 mg, 78% yield, 90% ee).

$[\alpha]_D^{20}$ = −3 (*c* 1.0, CH_2Cl_2).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 16.58 min, t_R (major) = 18.86 min.

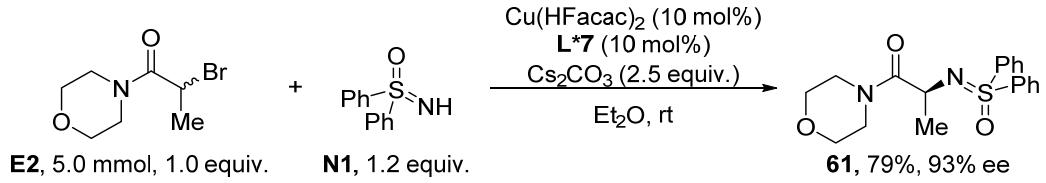
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 11.5, 8.9 Hz, 4H), 6.92 (dd, *J* = 8.9, 1.8 Hz, 4H), 5.78 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.24 – 4.70 (m, 2H), 4.00 (dd, *J* = 7.9, 6.4 Hz, 1H), 3.82 (s, 6H), 3.81 – 3.39 (m, 8H), 2.33 – 2.18 (m, 1H), 2.17 – 2.04 (m, 1H), 1.98 – 1.80 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 162.80, 162.78, 138.1, 133.0, 132.6, 130.4, 130.3, 115.0, 114.4, 114.3, 67.0, 66.7, 56.0, 55.6, 46.2, 42.5, 34.7, 30.6.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{31}N_2O_5S$ $[M + H]^+$ 459.1948, found 459.1942.

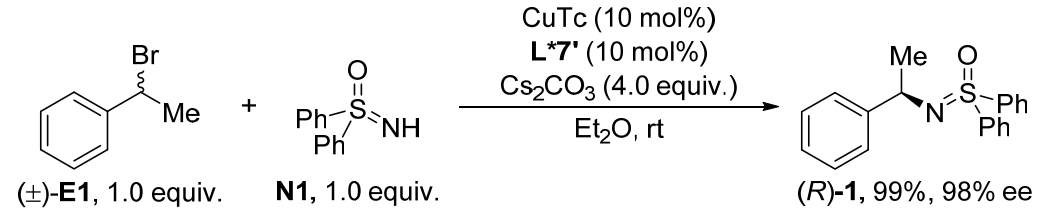
Demonstration of synthetic potentials. (Figure 4)

A gram-scale experiment. (Figure 4A)



According to **General procedure F** with 2-bromo-1-morpholinopropan-1-one **E2** (1.11 g, 5.0 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **61** as a colorless oil (1.41 g, 79% yield, 93% ee).

Synthesis of the antipodes of products. (Figure 4B)

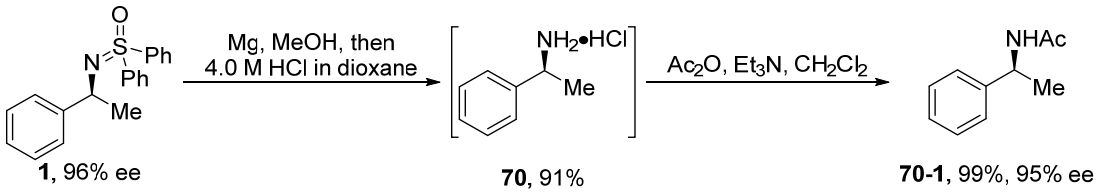


According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*7'** (27.3 mg, 0.020 mmol, 10 mol%) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product (*R*)-**1** as a colorless oil (63.6 mg, 99% yield, 98% ee).

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 24.87 min, t_R (major) = 27.64 min.

Conversion of enantioenriched sulfoximines to chiral primary amines. (Figure 4C)

Deprotection of benzyl products to primary amine (90)
Procedure a:

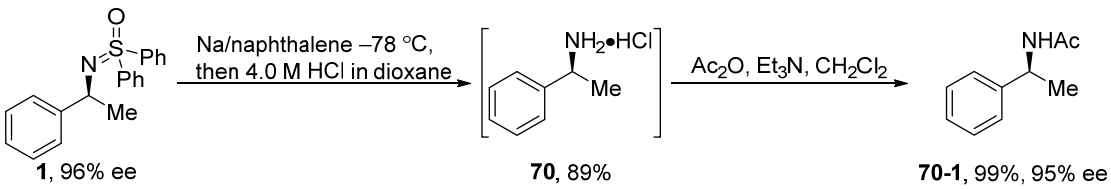


To a flamed dried flask charged with a stir bar were added **1** (18.3 mg, 0.057 mmol, 1.0 equiv., 96% ee), Mg (13.7 mg, 0.57 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The mixture was stirred at room temperature until Mg disappeared.

Upon completion (monitored by TLC), HCl (0.31 mL, 1.25 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added to the mixture at 0 °C, and the mixture was warmed up to room temperature to afford a homogeneous solution in 10 min. The mixture was stirred for another 1 h, then concentrated under reduced pressure to afford the crude product **70** (8.1 mg, 91% crude yield, determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard).

To a solution of the crude **70** (6.3 mg, 0.052 mmol, 1.0 equiv.) in CH_2Cl_2 (2.0 mL) were added Et_3N (21.0 mg, 0.21 mmol, 4.0 equiv.) and Ac_2O (21.4 mg, 0.21 mmol, 4.0 equiv.) sequentially. The reaction was stirred at room temperature for 12 h, and then quenched with saturated NH_4Cl solution. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the desired product **70-1** as a yellow oil (8.4 mg, 99% yield, 95% ee).

Procedure b:

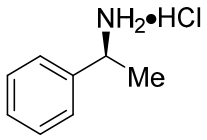


To a solution of **1** (64.2 mg, 0.20 mmol, 1.0 equiv., 96% ee) in THF (5.0 mL) was added the freshly prepared Na/naphthalene reagent (4.0 mL, 2.0 mmol, 10.0 equiv., 0.5 M in THF) dropwise with vigorously stirring at –78 °C under argon. The reaction was stirred at –78 °C for 10 min and quenched with MeOH. Then, the mixture was concentrated in

vacuum and redissolved in HCl (1.1 mL, 4.4 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane). After stirring for another 3 h, the mixture was concentrated under reduced pressure to afford the crude product **70** (27.9 mg, 89% crude yield, determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard).

To a solution of the crude **70** in CH_2Cl_2 (10.0 mL) were added Et_3N (80.8 mg, 0.80 mmol, 4.0 equiv.) and Ac_2O (81.6 mg, 0.80 mmol, 4.0 equiv.) sequentially. The mixture was stirred at room temperature for 12 h. Then the reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to afford the desired product **70-1** as a yellow oil (28.7 mg, 99% yield, 95% ee).

(*S*)-Chloro(1-phenylethyl)-λ^5-azane (70)

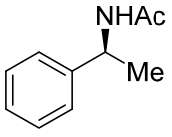


70

^{1}H NMR (400 MHz, MeOD) δ 7.48 – 7.27 (m, 5H), 4.39 (q, *J* = 6.9 Hz, 1H), 1.57 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, MeOD) δ 138.5, 128.9, 128.7, 126.5, 51.1, 19.7.

(*S*)-*N*-(1-Phenylethyl)acetamide (70-1)



70-1

$[\alpha]_D^{20}$ = –77 (*c* 0.4, CH_2Cl_2).

HPLC analysis: Chiralcel AD3 (hexane/^{i}PrOH = 90/10, flow rate 0.5 mL/min, λ = 210 nm), t_R (minor) = 11.15 min, t_R (major) = 13.16 min. (**procedure a**)

HPLC analysis: Chiralcel AD3 (hexane/^{i}PrOH = 90/10, flow rate 0.5 mL/min, λ = 210 nm), t_R (minor) = 11.52 min, t_R (major) = 14.12 min. (**procedure b**)

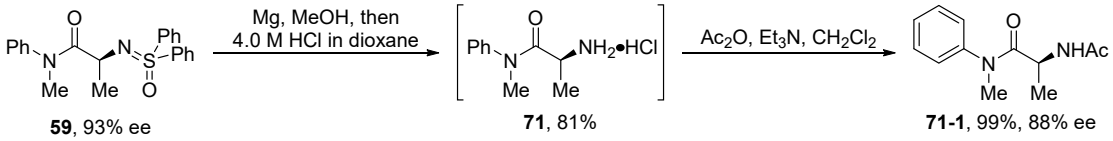
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 5.77 (brs, 1H), 5.22 – 5.07 (m, 1H), 2.00 (s, 3H), 1.51 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 143.2, 128.7, 127.4, 126.2, 48.8, 23.5, 21.7.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}NO$ $[M + H]^+$ 164.1070, found 164.1069.

Deprotection of amide product to primary amine (71)

Procedure a:

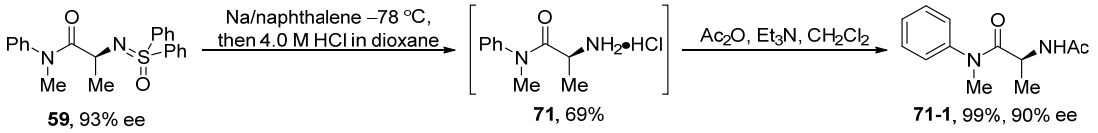


To a flamed dried flask charged with a stir bar were added **59** (37.8 mg, 0.10 mmol, 1.0 equiv., 93% ee), Mg (24.0 mg, 1.0 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The mixture was stirred at room temperature until Mg disappeared.

Upon completion (monitored by TLC), HCl (0.55 mL, 2.2 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added to the mixture at 0 °C, and the reaction was warmed up to room temperature to afford a homogeneous solution in 10 min. After stirring for another 1 h, the solvent was removed under reduced pressure to afford the crude product **71** (17.3 mg, 81% crude yield, determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard).

Then, CH_2Cl_2 (5.0 mL), Et_3N (40.0 mg, 0.40 mmol, 4.0 equiv.), and Ac_2O (40.8 mg, 0.40 mmol, 4.0 equiv.) were added to the crude **71** sequentially. The mixture was stirred at room temperature for 12 h and quenched with saturated NH_4Cl solution. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography (petroleum ether/EtOAc = 1/1) to yield the desired product **71-1** as a yellow oil (17.8 mg, 99% yield, 88% ee).

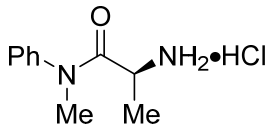
Procedure b:



To a solution of **59** (75.6 mg, 0.20 mmol, 1.0 equiv., 93% ee) in THF were added the freshly prepared Na/naphthalene reagent (4.0 mL, 2.0 mmol, 10.0 equiv., 0.5 M in THF) dropwise vigorously stirring at −78 °C under argon. The reaction mixture was stirred at −78 °C for 10 min and quenched with MeOH (The color was disappeared). Then, the mixture was concentrated in vacuum and redissolved in HCl (0.30 mL, 1.2 mmol, 6.0 equiv., 4.0 M in 1,4-dioxane). The reaction mixture was stirred for another 3 h. The mixture was concentrated under reduced pressure to afford the crude product **71** (29.5 mg, 68% crude yield, determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard).

To a solution of the crude **71** (24.2 mg, 0.14 mmol, 1.0 equiv.) in CH_2Cl_2 (5.0 mL) were added Et_3N (56.6 mg, 0.56 mmol, 4.0 equiv.) and Ac_2O (57.4 mg, 0.56 mmol, 4.0 equiv.) sequentially. The reaction was stirred at room temperature for 12 h, then quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product **71-1** as a yellow oil (30.5 mg, 99% yield, 90% ee).

(*S*)-2-(Chloro-λ^5-azaneyl)-*N*-methyl-*N*-phenylpropanamide (71)

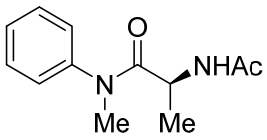


71

^{1}H NMR (400 MHz, MeOD) δ 7.60 – 7.52 (m, 2H), 7.51-7.43 (m, 3H), 3.97 (q, *J* = 6.9 Hz, 1H), 3.30 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, MeOD) δ 169.4, 141.7, 130.2, 128.8, 127.4, 47.2, 37.3, 15.5.

(*S*)-2-Acetamido-*N*-methyl-*N*-phenylpropanamide (71-1)



71-1

$[\alpha]_D^{20}$ = 73 (*c* 1.5, CH_2Cl_2).

HPLC analysis: Chiralcel ADH (hexane/^{i}PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.42 min, t_R (major) = 5.54 min. (**Procedure a**)

HPLC analysis: Chiralcel ADH (hexane/^{i}PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.05 min, t_R (major) = 4.97 min. (**Procedure b**)

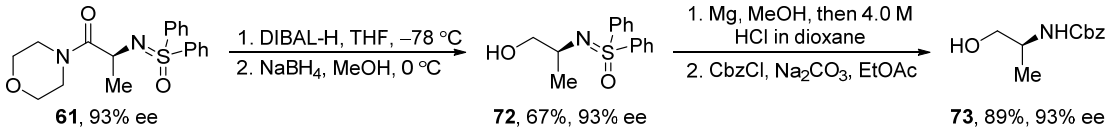
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.41 – 7.37 (m, 1H), 7.31 – 7.24 (m, 2H), 6.65 (brs, 1H), 4.59 (q, *J* = 7.0 Hz, 1H), 3.27 (s, 3H), 1.96 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.5, 142.6, 130.1, 128.5, 127.4, 46.0, 37.9, 23.1, 18.7.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{17}N_2O_2$ $[M + H]^+$ 221.1285, found 221.1281.

Conversion of enantioenriched sulfoximines to valuable chiral building blocks. (Figure 4D)

The synthesis of 73.



61, 93% ee **72**, 67%, 93% ee **73**, 89%, 93% ee

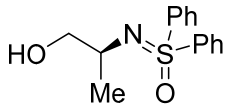
To a solution of **61** (71.6 mg, 0.20 mmol, 1.0 equiv.) in THF (3.0 mL) was added DIBAL-H (0.22 mL, 0.22 mmol, 1.1 equiv., 1.0 M in hexane) dropwise at −78 °C. The reaction mixture was stirred for 1 h and another portion of DIBAL-H (60.0 μL, 0.060 mmol, 0.3 equiv., 1.0 M in hexane) was added to the above solution. Upon completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated to afford the crude product, which was dissolved in MeOH (5.0 mL). To this solution was added $NaBH_4$ (15.2 mg, 0.40 mmol, 2.0 equiv.) at 0 °C. After stirring for 10 min, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 three times. The combined organic layer was 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 (petroleum ether/EtOAc = 1/1) to yield the desired product **72** as a yellow oil (36.9 mg, 67% yield, 93% ee).

To a flamed flask charged with a stir bar were added **72** (36.9 mg, 0.13 mmol, 1.0 equiv., 93% ee), Mg (64.8 mg, 2.7 mmol, 20.0 equiv.) and anhydrous MeOH (2.0 mL) under argon. The mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (1.4 mL, 5.6 mmol, 44.0 equiv., 4.0 M in 1,4-dioxane) was added to the reaction mixture at 0 °C and the reaction was stirred at room temperature to afford a homogenous solution in 10 min.

Upon completion (monitored by TLC), the solvent was removed under reduced pressure. The residue was dissolved in EtOAc (2.0 mL), followed by the addition of a solution of Na_2CO_3 (42.4 mg, 0.40 mmol, 3.0 equiv.) in H_2O (5.0 mL) and CbzCl (34.0

μl, 0.16 mmol, 1.2 equiv.). The reaction was stirred for 1 h and quenched with H_2O. The mixture was extracted with EtOAc three times. The combined organic layer was 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 (petroleum ether/EtOAc = 1/1) to afford the desired product **73** as a light yellow oil (24.2 mg, 89% yield, 93% ee).

(*S*)-((1-Hydroxypropan-2-yl)imino)diphenyl-λ^6-sulfanone (72)



72

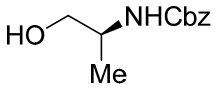
HPLC analysis: Chiralcel OD3 (hexane/^{i}PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 10.77 min, t_R (minor) = 12.39 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.99 – 7.90 (m, 2H), 7.59 – 7.44 (m, 6H), 3.56 (dd, *J* = 10.7, 3.7 Hz, 1H), 3.49 (dd, *J* = 10.7, 7.7 Hz, 1H), 3.39 – 3.28 (m, 1H), 2.93 (brs, 1H), 1.22 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 140.5, 132.6, 132.6, 129.3, 129.2, 128.7, 128.5, 68.7, 53.3, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{18}NO_2S$ $[M + H]^+$ 276.1053, found 276.1059.

Benzyl (*S*)-(1-hydroxypropan-2-yl)carbamate (73)



73

$[\alpha]_D^{20}$ = –4 (*c* 1.2, CH_2Cl_2).

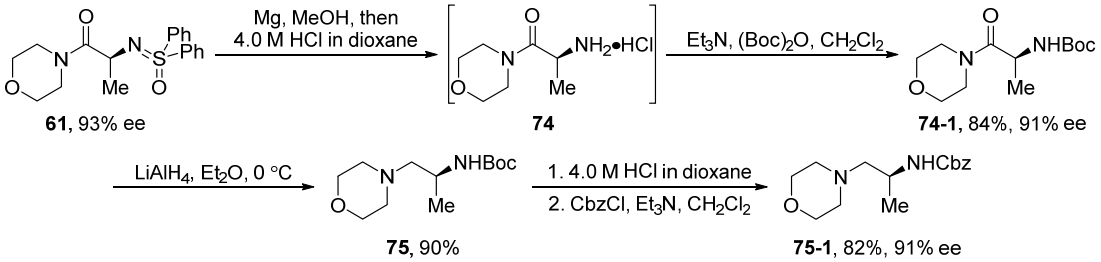
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 90/10, flow rate 0.8 mL/min, λ = 210 nm), t_R (major) = 17.73 min, t_R (minor) = 21.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.27 (m, 5H), 5.09 (s, 2H), 5.03 – 4.86 (m, 1H), 3.93 – 3.74 (m, 1H), 3.64 (dd, *J* = 11.0, 3.9 Hz, 1H), 3.51 (dd, *J* = 11.0, 5.9 Hz, 1H), 2.57 (brs, 1H), 1.16 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 136.4, 128.6, 128.2, 128.1, 77.1, 66.9, 49.0, 17.3.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{16}NO_3$ $[M + H]^+$ 210.1125, found 210.1131.

The synthesis of 75.



To a flamed flask charged with a stir bar were added **61** (358.0 mg, 1.0 mmol, 1.0 equiv., 93% ee), Mg (240.0 mg, 10.0 mmol, 10.0 equiv.) and anhydrous MeOH (10.0 mL) under argon. The reaction mixture was stirred at room temperature until Mg disappeared (Note: *Ice bath needed if the reaction was too violent!*).

Upon completion (monitored by TLC), HCl (5.5 mL, 22.0 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added dropwise to the mixture at 0 °C, then the mixture was warmed up to room temperature to afford a homogeneous solution in 30 min. Upon completion (monitored by TLC), the solvent was removed under reduced pressure to afford the crude **74**.

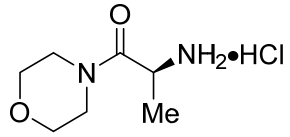
To the crude **74**, CH_2Cl_2 (20.0 mL), Et_3N (505.0 mg, 5.0 mmol, 5.0 equiv.) and $(Boc)_2O$ (654.0 mg, 3.0 mmol, 3.0 equiv.) were added sequentially. The mixture was stirred at room temperature for 3 h. Then the reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the desired product **74-1** as a colorless oil (218.0 mg, 84% yield in three steps, 91% ee).

To a solution of $LiAlH_4$ (11.3 mg, 0.30 mmol, 2.0 equiv.) in Et_2O (4.0 mL) was added the solution of **74-1** (38.7 mg, 0.15 mmol, 1.0 equiv.) in Et_2O (2.0 mL) dropwise at 0 °C under argon. The resulting mixture was slowly warmed up to room temperature and stirred for 3 h. Upon completion (monitored by TLC), the reaction was quenched with

Na_2SO_4•$10H_2O$, dried with Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the desired product **75** as a yellow oil (32.8 mg, 90% yield). To the solution of **75** (32.8 mg, 0.13 mmol, 1.0 equiv.) in 1,4-dioxane (2.0 mL) was added HCl (0.33 mL, 1.3 mmol, 10.0 equiv., 4.0 M HCl in 1,4-dioxane) and the resulting mixture was stirred at room temperature. Upon completion (monitored by TLC), the mixture was concentrated to afford the residue, which was directly used in the next step without further purification.

The residue and Et_3N (72.0 μL, 0.52 mmol, 4.0 equiv.) were dissolved in CH_2Cl_2 (5.0 mL) and cooled down to 0 °C. To this solution was added CbzCl (73.0 μL, 0.52 mmol, 4.0 equiv.) and the reaction mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with brine and extracted with CH_2Cl_2 three times. The combined organic layer was 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 (petroleum ether/EtOAc = 1/2) to yield the desired product **75-1** as a light yellow oil (29.6 mg, 82% yield, 91% ee).

(*S*)-2-Amino-1-morpholinopropan-1-one hydrochloride (74)

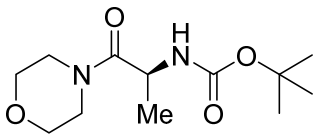


74

^{1}H NMR (400 MHz, CD_3OD) δ 4.41 – 4.29 (m, 1H), 3.63 – 3.55 (m, 5H), 3.50 – 3.41 (m, 3H), 1.37 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 168.1, 66.2, 46.7, 45.6, 42.4, 15.5.

***tert*-Butyl (*S*)-(1-morpholino-1-oxopropan-2-yl)carbamate (74-1)**



74-1

$[\alpha]_D^{20}$ = 5 (*c* 5.7, CH_2Cl_2).

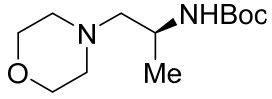
HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 17.35 min, t_R (minor) = 21.74 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (d, *J* = 7.7 Hz, 1H), 4.60 (p, *J* = 7.0 Hz, 1H), 3.78 – 3.63 (m, 5H), 3.63 – 3.53 (m, 2H), 3.53 – 3.43 (m, 1H), 1.44 (s, 9H), 1.30 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 155.1, 79.6, 66.8, 66.6, 45.9, 42.4, 28.3, 19.2.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{23}N_2O_4$ $[M + H]^+$ 259.1652, found 259.1658.

tert-Butyl (*S*)-(1-morpholinopropan-2-yl)carbamate (75)



75

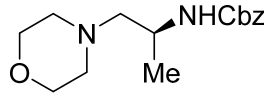
$[\alpha]_D^{20}$ = 2 (*c* 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (brs, 1H), 3.86 – 3.42 (m, 5H), 2.59 – 2.46 (m, 2H), 2.45 – 2.36 (m, 2H), 2.35 – 2.27 (m, 1H), 2.27 – 2.18 (m, 1H), 1.45 (s, 9H), 1.15 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 79.2, 67.0, 64.2, 53.8, 43.5, 28.5, 19.6.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{25}N_2O_3$ $[M + H]^+$ 245.1860, found 245.1856.

Benzyl (*S*)-(1-morpholinopropan-2-yl)carbamate (75-1)



75-1

$[\alpha]_D^{20}$ =12 (*c* 1.5, CH_2Cl_2).

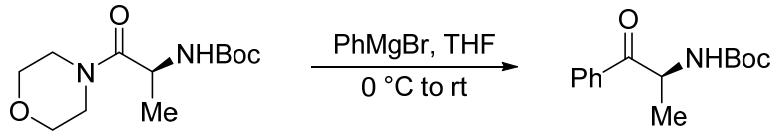
HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm), t_R (minor) = 10.10 min, t_R (major) = 13.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 5.19 – 5.00 (m, 3H), 3.89 – 3.73 (m, 1H), 3.72 – 3.57 (m, 4H), 2.60 – 2.44 (m, 2H), 2.43 – 2.21 (m, 4H), 1.19 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 136.7, 128.5, 128.11, 128.09, 66.9, 66.5, 63.9, 53.7, 44.0, 19.5.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{23}N_2O_3$ $[M + H]^+$ 279.1703, found 279.1699.

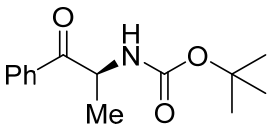
The synthesis of 76.



74-1, 91% ee **76**, 95%, 91% ee

To a solution of **74-1** (773.0 mg, 3.0 mmol, 1.0 equiv.) in anhydrous THF (15.0 mL) was added phenylmagnesium bromide (9.0 mL, 9.0 mmol, 3.0 equiv., 1.0 M in THF) dropwise at 0 °C under argon. Then the reaction mixture was stirred at 0 °C for 2 h. Upon completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the desired product **76** as a colorless oil (709.0 mg, 95% yield, 91% ee).

***tert*-Butyl (*S*)-(1-oxo-1-phenylpropan-2-yl)carbamate (76)**



76

$[\alpha]_D^{20}$ = –4 (*c* 4.8, CH_2Cl_2).

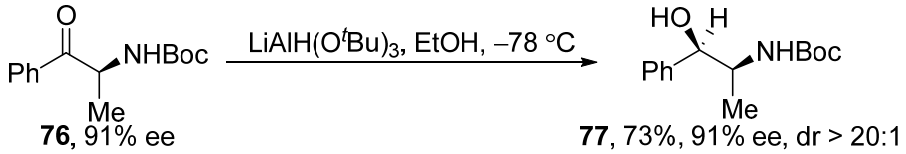
HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.04 min, t_R (major) = 8.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.64 – 7.55 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 5.60 (d, *J* = 6.5 Hz, 1H), 5.38 – 5.24 (m, 1H), 1.47 (s, 9H), 1.41 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 155.2, 134.2, 133.7, 128.8, 128.7, 79.7, 51.1, 28.4, 19.9.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}NO_3Na$ $[M + Na]^+$ 272.1257, found 272.1262.

The synthesis of 77.

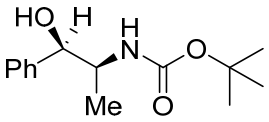


76, 91% ee

77, 73%, 91% ee, dr > 20:1

To a flamed tube charged with a stir bar and rubber plug were added Lithium tri-*tert*-butoxyaluminum hydride (406.0 mg, 1.6 mmol, 8.0 equiv.), anhydrous EtOH (2.0 mL) under argon and the mixture was cooled down to –78 °C. To this solution was added a solution of **76** (49.8 mg, 0.20 mmol, 1.0 equiv.) in anhydrous EtOH (1.0 mL) dropwise. The reaction mixture was stirred at −78 °C for 0.5 h. Upon completion (monitored by TLC), the reaction was quenched with 10% citric acid, and extracted with EtOAc three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford crude product (the dr was determined by ^{1}H NMR). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product **77** as a colorless oil (36.6 mg, 73% yield, 91% ee, dr > 20:1).

***tert*-Butyl ((1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)carbamate (77)**



77

[α]$_D^{20}$ = −54 (*c* 1.8, CH_2Cl_2).

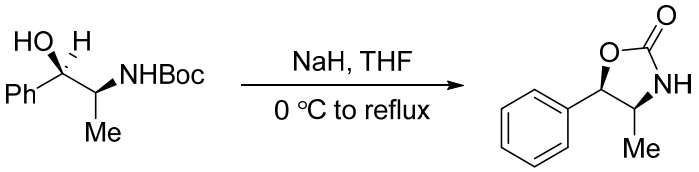
HPLC analysis: Chiralcel ODH (hexane/^{i}PrOH = 92/8, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 7.21 min, t_R (major) = 7.84 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.25 (m, 1H), 4.85 (d, *J* = 2.2 Hz, 1H), 4.77 (d, *J* = 7.9 Hz, 1H), 4.00 (brs, 1H), 3.49 (brs, 1H), 1.47 (s, 9H), 0.99 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 140.9, 128.1, 127.4, 126.3, 79.8, 76.8, 52.0, 28.4, 14.7.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{21}NO_3Na$ $[M + Na]^+$ 274.1414, found 274.1419.

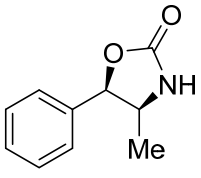
The assignment of relative configuration was determined by 2D NMR analysis of the cyclization product.



77 **77-1**, 87%

To an oven dried round bottom flask was added sodium hydride (60% dispersion in mineral oil, 7.4 mg, 0.18 mmol, 1.2 equiv.). To this flask was added a solution of Boc-protected amino alcohol **77** (38.9 mg, 0.15 mmol, 1.0 equiv.) in THF (2.0 mL) slowly at 0 °C under argon. Then the flask was equipped with a reflux condenser and the reaction mixture was heated to reflux with stirring until the starting material was completely consumed (monitored by TLC). The mixture was cooled down to room temperature, quenched with saturated aqueous NH_4Cl solution, and transferred to a separatory funnel. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum/EtOAc = 3/1) to afford the pure product **77-1** as a yellow oil (23.1 mg, 87% yield).

(4*S*,5*R*)-4-Methyl-5-phenyloxazolidin-2-one (77-1)



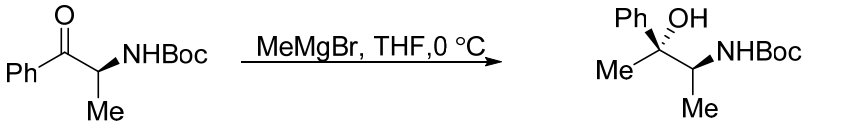
77-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 3H), 7.34 – 7.29 (m, 2H), 6.28 (s, 1H), 5.73 (d, *J* = 8.0 Hz, 1H), 4.32 – 4.13 (m, 1H), 0.83 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 134.9, 128.53, 128.50, 126.0, 81.0, 52.4, 17.5.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{12}NO_2$ $[M + H]^+$ 170.0863, found 170.0861.

The synthesis of 78.

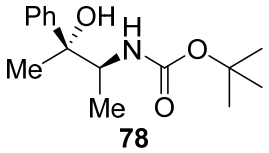


76, 91% ee

78, 83%, 91% ee, dr > 20:1

To a solution of **76** (49.8 mg, 0.20 mmol, 1.0 equiv.) in anhydrous THF (2.0 mL) was added methyl magnesium bromide (0.80 mL, 2.4 mmol, 12.0 equiv., 3.0 M in THF) dropwise at 0 °C under argon and then the mixture was stirred at 0 °C for 2 h. Upon completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl solution, and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford crude product (the dr was determined by ^{1}H NMR). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product **78** as a colorless oil (43.8 mg, 83% yield, 91% ee).

***tert*-Butyl ((2*S*,3*R*)-3-hydroxy-3-phenylbutan-2-yl)carbamate (78)**



78

$[\alpha]_D^{20}$ = –3 (*c* 2.2, CH_2Cl_2).

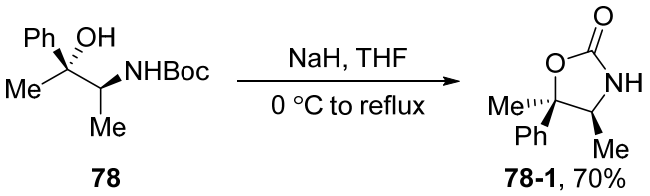
HPLC analysis: Chiralcel IC (hexane/^{i}PrOH = 93/7, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 7.69 min, t_R (minor) = 8.29 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.28 – 7.23 (m, 1H), 4.89 (d, *J* = 9.3 Hz, 1H), 4.07 – 3.96 (m, 1H), 2.80 (brs, 1H), 1.59 (s, 3H), 1.49 (s, 9H), 0.91 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 145.5, 128.2, 126.7, 125.1, 79.5, 77.1, 54.6, 28.5, 28.3, 16.1.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{23}NO_3Na$ $[M + Na]^+$ 288.1570, found 288.1576.

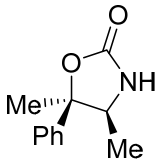
The assignment of relative configuration was determined by 2D NMR analysis of the cyclization product.



78 **78-1**, 70%

To an oven dried round bottom flask was added sodium hydride (60% dispersion in mineral oil, 3.6 mg, 0.090 mmol, 1.2 equiv.). To this flask was added a solution of Boc-protected amino alcohol **78** (19.8 mg, 0.075 mmol, 1.0 equiv.) in THF (1.0 mL) slowly at 0 °C under argon. Then the flask was equipped with a reflux condenser and the reaction mixture was heated to reflux with stirring until the starting material had been completely consumed (monitored by TLC). The mixture was cooled down to room temperature, quenched with saturated aqueous NH_4Cl solution, and transferred to a separatory funnel. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford the pure product **78-1** as a yellow oil (10.0 mg, 70% yield).

(4*S*,5*R*)-4,5-Dimethyl-5-phenyloxazolidin-2-one (78-1)



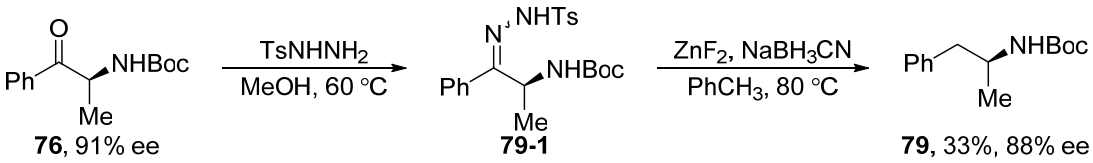
78-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 5.91 (s, 1H), 3.98 – 3.79 (m, 1H), 1.83 (s, 3H), 0.77 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 139.5, 128.3, 127.8, 125.2, 86.5, 58.3, 27.6, 19.0.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}NO_2$ $[M + H]^+$ 192.1019, found 192.1016.

The synthesis of 79.

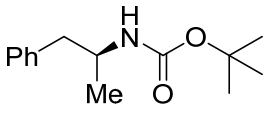


76, 91% ee **79-1** **79**, 33%, 88% ee

To a flask charged with a stir bar were added **76** (49.8 mg, 0.20 mmol, 1.0 equiv.), 4-methylbenzenesulfonhydrazide (44.6 mg, 0.24 mmol, 1.2 equiv.) and MeOH (2.0 mL). The reaction mixture was stirred at 60 °C for 12 h. Upon completion (monitored by TLC), the reaction was concentrated to afford the crude product **79-1**, which was directly used in the next step without further purification.

To a flask charged with a stir bar were added the above crude product **79-1**, ZnF_2 (82.4 mg, 0.80 mmol, 4.0 equiv.), $NaBH_3CN$ (100.8 mg, 1.6 mmol, 8.0 equiv.) and toluene (2.0 mL). Then the reaction mixture was stirred at 80 °C for 24 h. Upon completion (monitored by TLC), the reaction was quenched with 10% aqueous NaOH solution and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the desired product **79** as a white solid (15.4 mg, 33% yield in two steps, 88% ee).

***tert*-Butyl (*S*)-(1-phenylpropan-2-yl)carbamate (79)**



79

$[\alpha]_D^{20}$ = –3 (*c* 0.5, CH_2Cl_2).

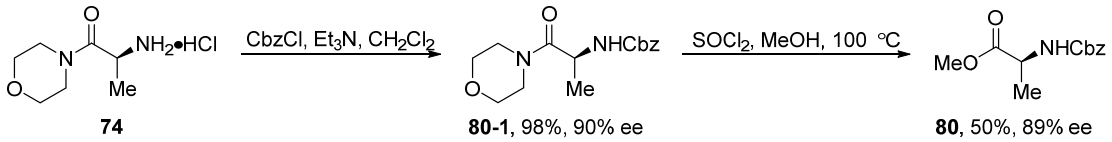
HPLC analysis: Chiralcel OD3 (hexane/^{i}PrOH = 99/1, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 8.53 min, t_R (minor) = 9.14 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 4.40 (brs, 1H), 3.91 (brs, 1H), 2.84 (dd, *J* = 13.2, 5.3 Hz, 1H), 2.65 (dd, *J* = 13.3, 7.4 Hz, 1H), 1.42 (s, 9H), 1.08 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 138.3, 129.5, 128.3, 126.3, 79.1, 47.5, 43.0, 28.4, 20.2.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{21}NO_2Na$ $[M + Na]^+$ 258.1465, found 258.1470.

The synthesis of 80.

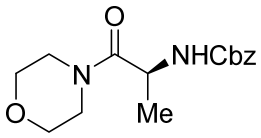


74 **80-1**, 98%, 90% ee **80**, 50%, 89% ee

To a solution of **74** (31.0 mg, 0.16 mmol, 1.0 equiv.) in CH_2Cl_2 was added CH_2Cl_2 (5.0 mL), Et_3N (0.11 mL, 0.80 mmol, 4.0 equiv.) and the mixture was cooled to 0 °C. To this solution was added CbzCl (136.0 mg, 0.80 mmol, 4.0 equiv.) and the reaction mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with brine and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the desired product **80-1** as a yellow oil (45.6 mg, 98% yield, 90% ee).

To a solution of **80-1** (45.6 mg, 0.16 mmol, 1.0 equiv., 90% ee) in MeOH (0.3 mL) was added $SOCl_2$ (56.0 μL, 0.80 mmol, 5.0 equiv.) at 0 °C under argon. The reaction mixture was refluxed at 100 °C for 48 h, then cooled down to room temperature. The solvent was removed under reduced pressure. The residue was diluted with CH_2Cl_2, saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 three times. The combined organic layer was 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 (petroleum ether/EtOAc = 3/1) to yield the desired product **80** as a yellow oil (19.0 mg, 50% yield, 89% ee).

Benzyl (*S*)-(1-morpholino-1-oxopropan-2-yl)carbamate (80-1)



80-1

$[\alpha]_D^{20}$ = 13 (*c* 2.0, CH_2Cl_2).

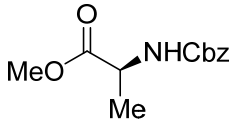
HPLC analysis: Chiralcel AD (hexane/^{i}PrOH = 75/25, flow rate 0.8 mL/min, λ = 210 nm), t_R (major) = 14.97 min, t_R (minor) = 16.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 6.01 – 5.80 (m, 1H), 5.11 (s, 2H), 4.77 – 4.58 (m, 1H), 3.77 – 3.44 (m, 8H), 1.34 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 155.6, 136.4, 128.5, 128.1, 128.0, 66.79, 66.76, 66.5, 46.5, 45.9, 42.4, 19.2.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{21}N_2O_4$ $[M + H]^+$ 293.1496, found 293.1491.

Methyl ((benzyloxy)carbonyl)-*L*-alaninate (80)



80

$[\alpha]_D^{20}$ = –4 (*c* 0.5, CH_2Cl_2).

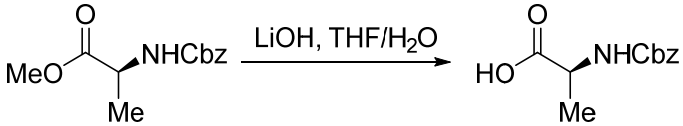
HPLC analysis: Chiralcel IB (hexane/^{i}PrOH = 90/10, flow rate 0.8 mL/min, λ = 210 nm), t_R (major) = 10.36 min, t_R (minor) = 12.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 5.41 (brs, 1H), 5.10 (s, 2H), 4.47 – 4.30 (m, 1H), 3.73 (s, 3H), 1.40 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 155.6, 136.3, 128.5, 128.2, 128.1, 66.9, 52.5, 49.6, 18.6.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{16}NO_4$ $[M + H]^+$ 238.1074, found 238.1075.

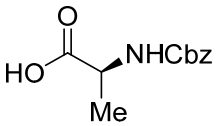
The hydrolysis of 80



80 **80-2**

To a solution of **80** (16.6 mg, 0.070 mmol, 1.0 equiv.) in co-solvent of THF (1.0 mL) and H_2O (1.0 mL) was added LiOH (3.4 mg, 0.14 mmol, 20.0 equiv.) in one portion at room temperature. The mixture was stirred at room temperature for 3 h. After completion (monitored by TLC), 3.0 M aqueous HCl solution was added and the mixture was extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated to afford the product **80-2** as a colorless oil (10.0 mg, 61% yield).

((Benzyloxy)carbonyl)-*L*-alanine (80-2)



80-2

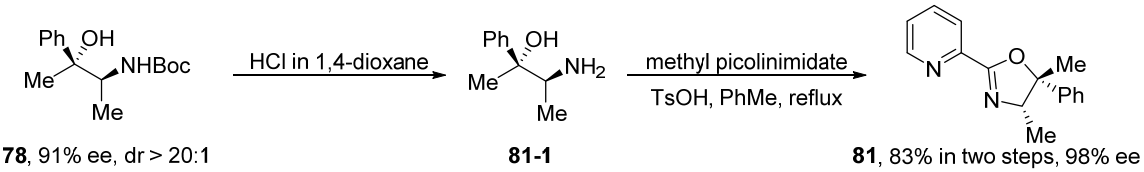
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 5.33 (d, *J* = 7.8 Hz, 1H), 5.20 – 5.01 (m, 2H), 4.50 – 4.34 (m, 1H), 1.46 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 155.9, 136.1, 128.6, 128.3, 128.2, 67.2, 49.5, 18.4.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{13}NO_4Na$ $[M + Na]^+$ 246.0737, found 246.0742.

Synthesis of novel chiral ligands. (Figure 4E)

The synthesis of 81 (Pyrox).

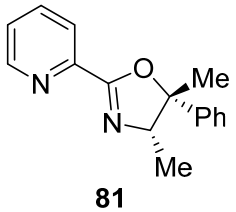


78, 91% ee, dr > 20:1 **81-1** **81**, 83% in two steps, 98% ee

The compound **78** (110.0 mg, 0.42 mmol, 1.0 equiv.) was dissolved in HCl (0.53 mL, 2.1 mmol, 5.0 equiv., 4.0 M in 1,4-dioxane) and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed by evaporator to afford the crude product **81-1**, which was directly used in next step without further purification.

To the residue were added methyl picolinimidate (57.1 mg, 0.42 mmol, 1.0 equiv.), TsOH (7.2 mg, 0.042 mmol, 10 mol%) and toluene (1.0 mL) and the reaction mixture was refluxed for 5 h. After cooling down to room temperature, 1.0 M aqueous NaOH solution was added and the product was extracted with EtOAc three times. The combined organic phase was 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 (MeOH/CH_2Cl_2 = 1/20) to afford **81** as a colorless oil (87.8 mg, 83% yield in two steps, 98% ee).

(4*S*,5*R*)-4,5-Dimethyl-5-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (81)



81

$[\alpha]_D^{20}$ = –303 (*c* 5.0, CH_2Cl_2).

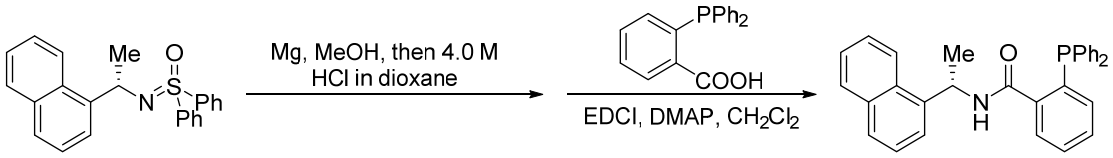
HPLC analysis: Chiralcel IF (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, λ = 260 nm), tR (minor) = 6.87 min, tR (major) = 8.49 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 3.6, 1.1 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.73 (td, *J* = 7.8, 1.8 Hz, 1H), 7.38 – 7.16 (m, 6H), 4.25 (q, *J* = 7.0 Hz, 1H), 1.80 (s, 3H), 0.79 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 150.0, 147.0, 140.9, 136.6, 128.0, 127.2, 125.5, 125.4, 123.8, 90.2, 72.2, 27.9, 19.0.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{17}N_2O$ $[M + H]^+$ 253.1335, found 253.1340.

The synthesis of 82 (N, P-ligand).

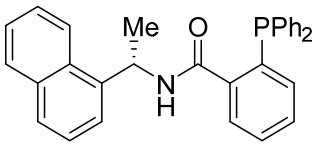


26, 98% ee **82**, 81%, 97% ee

To a flamed dried flask charged with a stir bar were added **26** (30.0 mg, 0.081 mmol, 1.0 equiv., 98% ee), Mg (19.4 mg, 0.81 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The reaction mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.45 mL, 1.8 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added at 0 °C and the reaction mixture was stirred at room temperature to afford a homogenous solution in 10 min. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na_2CO_3 solution and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated to afford the crude product.

Without further purification, the obtained crude product, 2-(diphenylphosphaneyl)benzoic acid (25.0 mg, 0.081 mmol, 1.0 equiv.), EDCI (18.6 mg, 0.097 mmol, 1.2 equiv.) and DMAP (0.99 mg, 0.0081 mmol, 0.1 equiv.) were dissolved in CH_2Cl_2 (5.0 mL) and the reaction mixture was stirred overnight. Upon completion, the reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product **82** as a white solid (30.0 mg, 81% yield, 97% ee).

(*S*)-2-(Diphenylphosphaneyl)-*N*-(1-(naphthalen-1-yl)ethyl)benzamide (82)



82

[α]$_D^{20}$ = 15 (*c* 1.5, CH_2Cl_2).

HPLC analysis: Chiralcel ID (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 16.82 min, t_R (major) = 22.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.55 – 7.50 (m, 1H), 7.45 – 7.39 (m, 1H), 7.39 – 7.26 (m, 11H), 7.26 – 7.19 (m, 2H), 7.00 – 6.91 (m, 1H), 6.25 (d, *J* = 8.2 Hz, 1H), 6.11 – 5.99 (m, 1H), 1.59 (d, *J* = 6.7 Hz, 3H).

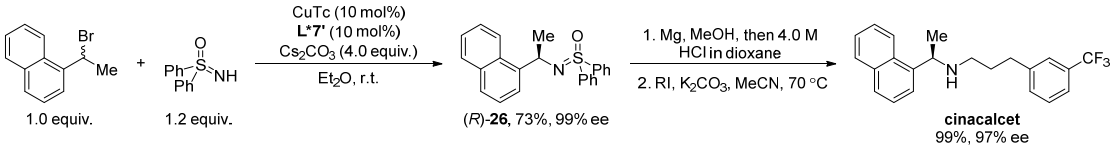
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 142.2, 142.1, 141.8, 137.74, 137.69, 137.62, 137.57, 136.8, 136.6, 134.3, 134.0, 133.9, 133.8, 133.7, 129.9, 128.7, 128.54, 128.53, 128.48, 128.4, 128.2, 127.7, 127.3, 127.2, 126.9, 64.9, 50.8, 39.0, 17.0, 12.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ −10.7.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{27}NOP$ $[M + H]^+$ 460.1825, found 460.1827.

Expedient synthesis of highly enantioenriched commercial drugs. (Figure 4F)

The synthesis of cinacalcet.

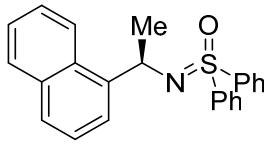


According to **General procedure A** with 1-(1-bromoethyl)naphthalene (23.4 mg, 0.10 mmol, 1.0 equiv.) and chiral ligand **L*7'** for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the product (*R*)-**26** as a white solid (27.1 mg, 73% yield, 99% ee).

To a flamed dried flask charged with a stir bar were added (*R*)-**26** (27.1 mg, 0.073 mmol, 1.0 equiv., 99% ee), Mg (17.5 mg, 0.73 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.40 mL, 1.6 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added to the mixture at 0 °C and the reaction mixture was stirred at room temperature to afford a homogeneous solution in 10 min. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na_2CO_3 solution and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuum.

Without further purification, the residue was dissolved in MeCN (1.0 mL). To this solution were added K_2CO_3 (30.2 mg, 0.22 mmol, 3.0 equiv.) and 1-(3-iodopropyl)-3-(trifluoromethyl)benzene (22.9 mg, 0.073 mmol, 1.0 equiv.) under argon, and then the reaction mixture was refluxed at 70 °C for 24 h. Upon completion (monitored by TLC), the reaction was diluted with EtOAc and filtered through a short pad of Celite. The filtrate was evaporated to afford the crude product, which was purified by column chromatography on silica gel (MeOH/CH_2Cl_2 = 1/10) to afford the desired product **cinacalcet** as a yellow oil (25.8 mg, 99% yield, 97% ee).

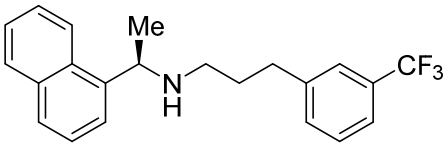
(*R*)-((1-(Naphthalen-1-yl)ethyl)imino)diphenyl-λ^6-sulfanone ((*R*)-26)



(*R*)-**26**

HPLC analysis: Chiralcel OD3 (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 19.50 min, t_R (major) = 21.47 min.

(*R*)-*N*-(1-(Naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (cinacalcet)



cinacalcet

[α]$_D^{20}$ = 4.7 (*c* 2.5, CH_2Cl_2).

HPLC analysis: Chiralcel IG (hexane/^{i}PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 10.97 min, t_R (minor) = 12.41 min.

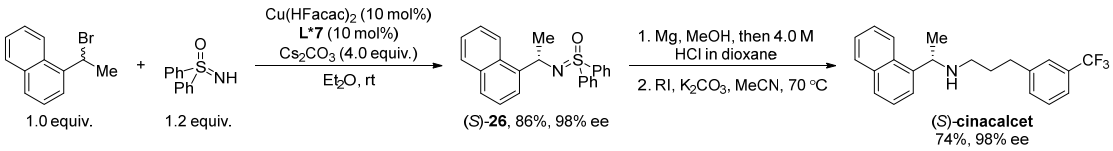
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.79 (t, *J* = 8.1 Hz, 2H), 7.59 – 7.45 (m, 3H), 7.42 – 7.34 (m, 2H), 7.33 – 7.20 (m, 2H), 4.78 (q, *J* = 6.6 Hz, 1H), 2.77 – 2.55 (m, 4H), 2.07 – 1.87 (m, 2H), 1.62 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 134.0, 131.7 (d, *J* = 1.0 Hz), 131.2, 130.6 (q, *J* = 32.0 Hz), 129.2, 128.7, 127.9, 126.2, 125.8, 125.6, 125.0 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.0 Hz), 123.3, 122.8 (q, *J* = 4.5, 3.9 Hz), 123.3, 122.5, 53.7, 46.8, 33.2, 30.6, 23.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.5 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{22}H_{23}F_3N$ $[M + H]^+$ 358.1777, found 358.1779.

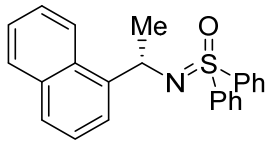
The synthesis of (*S*)-cinacalcet.



According to **General procedure A** with 1-(1-bromoethyl)naphthalene (23.4 mg, 0.10 mmol, 1.0 equiv.) and $Cu(HFacac)_2$ (4.4 mg, 0.10 mmol, 10 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the product (*S*)-**26** as a white solid (31.9 mg, 86% yield, 98% ee).

To a flamed dried flask charged with a stir bar were added (*S*)-**26** (31.9 mg, 0.086 mmol, 1.0 equiv., 98% ee), Mg (20.6 mg, 0.86 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The reaction mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.47 mL, 1.9 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added to the reaction mixture at 0 °C and then the mixture was warmed up to room temperature to afford a homogeneous solution in 10 min. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na_2CO_3 solution and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuum. Without further purification, the residue was dissolved in MeCN (1.0 mL). To this solution were added K_2CO_3 (35.9 mg, 0.26 mmol, 3.0 equiv.) and 1-(3-iodopropyl)-3-(trifluoromethyl)benzene (27.0 mg, 0.086 mmol, 1.0 equiv.) under argon, and then the reaction mixture was refluxed at 70 °C for 24 h. Upon completion (monitored by TLC), the reaction was diluted with EtOAc and filtered through a short pad of Celite. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/10) to afford the desired product (*S*)-**cinacalcet** as a yellow oil (22.7 mg, 74% yield, 98% ee).

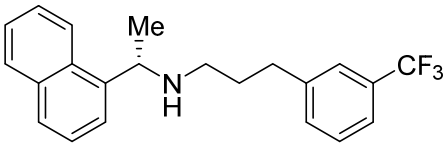
(*S*)-((1-(Naphthalen-1-yl)ethyl)imino)diphenyl-λ^6-sulfanone ((*S*)-26)



(*S*)-**26**

HPLC analysis: Chiralcel OD3 (hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 19.20 min, t_R (minor) = 21.64 min.

(*S*)-*N*-(1-(Naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine ((*S*)-cinacalcet)

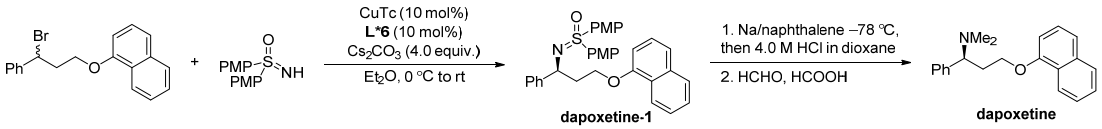


(*S*)-**cinacalcet**

[α]$_D^{20}$ = –23 (*c* 1.3, CH_2Cl_2).

HPLC analysis: Chiralcel IG (hexane/^{i}PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 11.33 min, t_R (major) = 12.91 min.

The synthesis of dapoxetine.



1.0 equiv. 1.2 equiv. **dapoxetine-1** 63%, 92% ee **dapoxetine** 71%, 93% ee

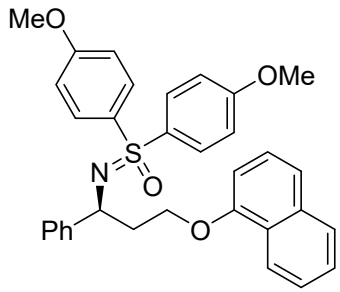
According to **General procedure C** with 1-(3-bromo-3-phenylpropoxy)naphthalene (34.0 mg, 0.10 mmol, 1.0 equiv.) and iminobis(4-methoxyphenyl)-λ^6-sulfanone (27.7 mg, 0.10 mmol, 1.0 equiv.) at 0 °C for 5 d and room temperature for another 2 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the **dapoxetine-1** as a white solid (34.0 mg, 63% yield, 92% ee).

To a solution of the above sulfoximine (34.0 mg, 0.063 mmol, 1.0 equiv., 92% ee) in THF (3.0 mL) was added the freshly prepared Na/naphthalene reagent (1.30 mL, 0.63

mmol, 10.0 equiv., 0.5 M in THF) dropwise with vigorously stirring at −78 °C under argon. The reaction mixture was stirred at −78 °C for another 10 min and quenched with MeOH (The color was disappeared). Then, the mixture was warmed up to 0 °C, followed by the addition of HCl (0.16 mL, 0.63 mmol, 10.0 equiv., 4.0 M in 1,4-dioxane) and the reaction mixture was stirred for another 3 h. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na_2CO_3 solution and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuum.

The residue was transferred to a Schlenk tube. Then HCHO (0.023 mL, 0.32 mmol, 5.0 equiv., 37% in water) and HCO_2H (1.0 mL) were added under argon. The reaction mixture was refluxed at 100 °C for 24 h. Upon completion (monitored by TLC), the reaction was cooled down to room temperature and treated with 2.0 M aqueous NaOH solution. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (MeOH/CH_2Cl_2 = 1/10) to afford the desired product **dapoxetine** as a brown oil (13.6 mg, 71% yield, 93% ee).

(*S*)-bis(4-Methoxyphenyl)((3-(naphthalen-1-yloxy)-1-phenylpropyl)imino)-λ⁶-sulfanone (dapoxetine-1)



dapoxetine-1

HPLC analysis: Chiralcel IA (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.42 min, t_R (major) = 13.60 min.

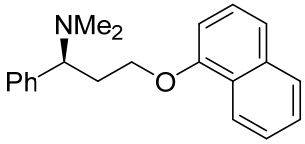
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.87 – 7.78 (m, 3H), 7.73 – 7.64 (m, 2H), 7.51 – 7.31 (m, 8H), 7.28 – 7.23 (m, 1H), 6.86 (dd, *J* = 7.0, 1.6 Hz, 1H),

6.81 – 6.75 (m, 2H), 6.75 – 6.70 (m, 2H), 4.60 (dd, *J* = 8.2, 5.4 Hz, 1H), 4.51 (ddd, *J* = 9.3, 7.9, 4.9 Hz, 1H), 4.17 (dt, *J* = 9.4, 5.5 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 2.54 – 2.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 154.8, 146.4, 134.5, 132.7, 132.5, 130.6, 130.5, 128.3, 127.3, 126.8, 126.6, 126.2, 126.1, 125.7, 124.8, 122.3, 119.8, 114.2, 114.1, 104.6, 65.0, 56.0, 55.5, 55.4, 40.9.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{32}NO_4S$ $[M + H]^+$ 538.2047, found 538.2060.

(*S*)-*N*,*N*-Dimethyl-3-(naphthalen-1-yloxy)-1-phenylpropan-1-amine (Dapoxetine)



dapoxetine

$[\alpha]_D^{20}$ = −1 (*c* 0.5, CH_2Cl_2).

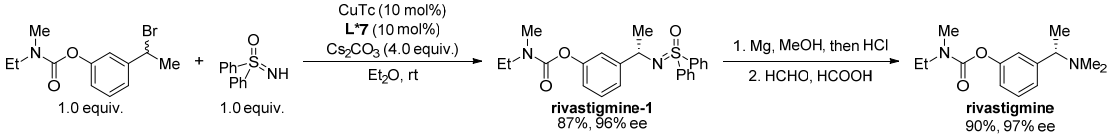
HPLC analysis: Chiralcel OD3 (hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 240 nm), t_R (major) = 5.61 min, t_R (minor) = 7.10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.86 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.66 – 7.54 (m, 2H), 7.54 – 7.47 (m, 2H), 7.47 – 7.35 (m, 3H), 7.35 – 7.23 (m, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 5.55 (dd, *J* = 8.2, 4.7 Hz, 1H), 2.62 (t, *J* = 7.3 Hz, 2H), 2.52 – 2.38 (m, 1H), 2.34 (s, 6H), 2.25 – 2.14 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 142.0, 134.6, 128.7, 127.6, 126.4, 126.1, 125.93, 125.86, 125.2, 122.2, 120.1, 107.0, 78.4, 56.2, 45.7, 37.3.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}NO$ $[M + H]^+$ 306.1852, found 306.1859.

The synthesis of rivastigmine.



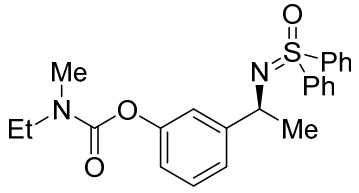
According to **General procedure A** with 3-(1-bromoethyl)phenyl

ethyl(methyl)carbamate (28.5 mg, 0.10 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the **rivastigmine-1** as a yellow solid (36.7 mg, 87% yield, 96% ee).

To a flamed dried flask charged with a stir bar were added the above sulfoximine (27.4 mg, 0.065 mmol, 1.0 equiv., 96% ee), Mg (15.0 mg, 0.65 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The reaction mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), the reaction mixture was cooled down to at 0 °C and HCl (0.36 mL, 22.0 equiv., 1.4 mmol, 4.0 M in 1,4-dioxane) was added. The mixture was stirred at room temperature to afford a homogeneous solution in 10 min. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na_2CO_3 solution and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuum.

The residue was transferred to a Schlenk tube. Then HCHO (0.025 mL, 0.33 mmol, 5.0 equiv., 37% in water) and HCO_2H (1.0 mL) were added under argon. The mixture was refluxed at 100 °C for 24 h. Upon completion (monitored by TLC), the reaction was cooled down to room temperature and treated with 2.0 M aqueous NaOH solution. The mixture was extracted with CH_2Cl_2 three times, 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 (MeOH/CH_2Cl_2 = 1/10) to afford the desired product **rivastigmine** as a colorless oil (14.6 mg, 90% yield, 97% ee).

(*S*)-3-(1-((Oxodiphenyl-λ^6-sulfaneylidene)amino)ethyl)phenyl ethyl(methyl)carbamate (rivastigmine-1)



rivastigmine-1

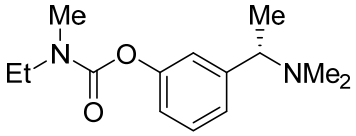
HPLC analysis: Chiralcel ID (hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 18.91 min, t_R (minor) = 22.14 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.87 – 7.78 (m, 2H), 7.53 – 7.33 (m, 6H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.20 (dd, *J* = 6.6, 1.9 Hz, 2H), 7.02 – 6.94 (m, 1H), 4.39 (q, *J* = 6.6 Hz, 1H), 3.44 (dq, *J* = 21.9, 7.2 Hz, 2H), 3.02 (d, *J* = 27.4 Hz, 3H), 1.55 (d, *J* = 6.6 Hz, 3H), 1.30 – 1.12 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.5, 151.5, 149.0, 141.5, 140.6, 132.39, 132.3, 129.12, 129.05, 129.0, 128.8, 128.4, 122.9, 119.7, 119.5, 53.9, 44.1, 34.2, 33.9, 28.1, 13.3, 12.5.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{27}N_2O_3S$ $[M + H]^+$ 423.1737, found 423.1745.

(*S*)-3-(1-(Dimethylamino)ethyl)phenyl ethyl(methyl)carbamate (Rivastigmine)



rivastigmine

$[\alpha]_D^{20}$ = −12 (*c* 0.7, CH_2Cl_2).

HPLC analysis: Chiralcel ODH (hexane/^{i}PrOH/TFA/DEA = 80/20/2/1, flow rate 1.0 mL/min, λ = 210 nm), t_R (minor) = 9.56 min, t_R (major) = 16.01 min.

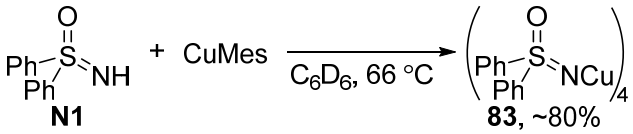
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.12 (m, 1H), 4.05 (q, *J* = 7.2 Hz, 1H), 3.49 (q, *J* = 7.1 Hz, 1H), 3.41 (q, *J* = 7.2 Hz, 1H), 3.04 (d, *J* = 53.1 Hz, 3H), 2.58 (s, 6H), 1.82 – 1.68 (m, 3H), 1.30 – 1.16 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.2, 154.1, 151.9, 136.9, 130.0, 125.43, 125.41, 122.9, 122.8, 122.31, 122.28, 65.8, 44.20, 44.15, 41.0, 34.3, 33.9, 17.84, 17.81, 13.3, 12.5.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{23}N_2O_2$ $[M + H]^+$ 251.1754, found 251.1755.

Mechanistic investigations. (Figure 5)

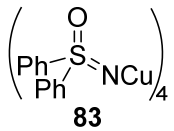
Synthesis of the sulfoximiato complex of Cu(I). (Figure 5A)



To a mixture of sulfoximine **N1** (21.7 mg, 0.10 mmol, 1.0 equiv.) and CuMes (Mesityl Copper) (18.2 mg, 0.10 mmol, 1.0 equiv.) were added C_6D_6 (benzene-d_6) (1.0 mL) under argon atmosphere, and the mixture was stirred at 66 °C overnight. After completion (monitored by ^{1}H NMR), the mixture was filtered in argon atmosphere and washed with anhydrous benzene. Next, the mixture thus obtained was transferred to a flask and volatiles were evaporated under reduced pressure to afford analytically pure **83** (~80% yield) as a crystalline solid.

The thus obtained product **83** was mixed with anhydrous DMSO at 100 °C in a glovebox and filtered to remove any remaining solids. The resulting solution was transferred to an NMR tube, and then stayed at 70 °C for 1 month to afford the X-ray quality crystals.

((Oxodiphenyl-λ^6-sulfaneylidene)amino)copper (83)



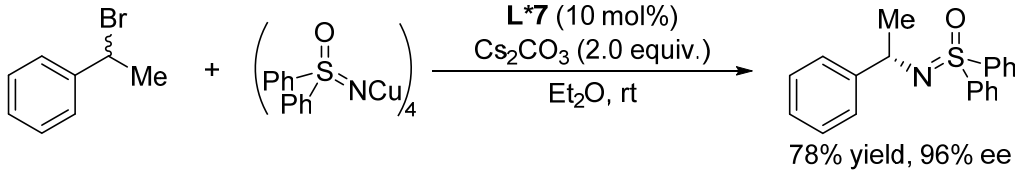
83

^{1}H NMR (600 MHz, DMSO-d_6, 100 °C) δ 7.97 – 7.75 (m, 16H), 7.50 – 7.22 (m, 24H)

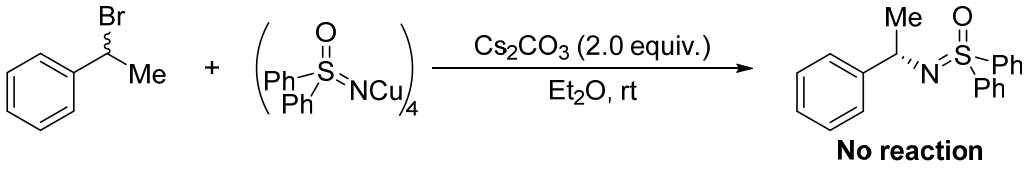
^{13}C NMR (150 MHz, DMSO-d_6, 100 °C) δ 147.8, 132.1, 129.2, 127.1.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{11}CuNOS$ $[M + H]^+$ 279.9852, found 279.9838.

The effect of chiral ligand in the stoichiometric reaction of the sulfoximinato complex with alkyl bromide. (Figure 5B)

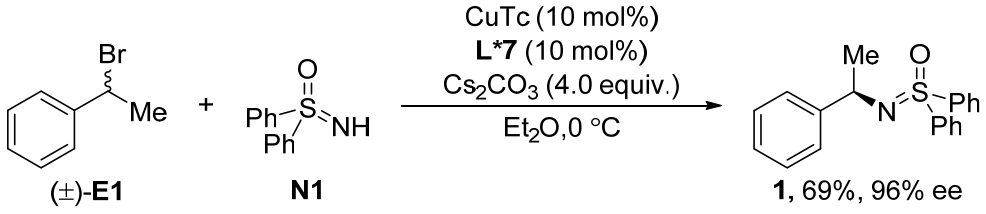


To the **83** (14.0 mg, 0.013 mmol, 0.25 equiv.) was added (1-bromoethyl)benzene (9.2 mg, 0.050 mmol, 1.0 equiv.), chiral ligand **L*7** (6.8 mg, 0.0050 mmol, 10 mol%), Cs_2CO_3 (32.6 mg, 0.10 mmol, 2.0 equiv.) and anhydrous Et_2O (1.0 mL) and stirred at room temperature for 72 h. The mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product and purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **1** as a colorless oil (12.5 mg, 78% yield, 96% ee).

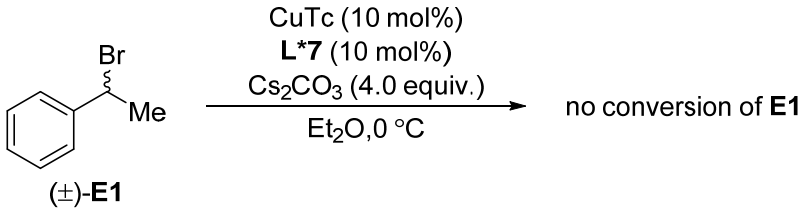


To the **83** (14.0 mg, 0.013 mmol, 0.25 equiv.) was added (1-bromoethyl)benzene (9.2 mg, 0.050 mmol, 1.0 equiv.), Cs_2CO_3 (32.6 mg, 0.10 mmol, 2.0 equiv.) and anhydrous Et_2O (1.0 mL) and stirred at room temperature for 72 h. The mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product and determined by ^1H NMR spectra. There is no reaction happened without the chiral ligand.

The effect of sulfoximine on the reaction initiation. (Figure 5C)



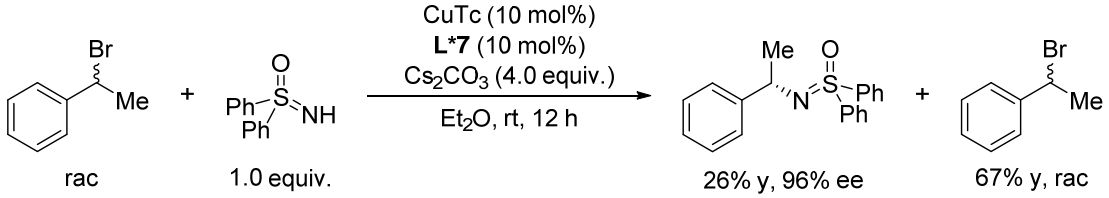
According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*7** at 0 °C for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **1** as a colorless oil (44.3 mg, 69% yield, 96% ee).



In absence of sulfoximine **N1**, according to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*7** at 0 °C for 72 h, there is no conversion of **E1**.

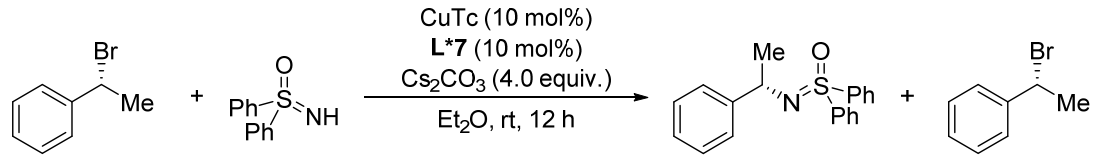
The stereochemistry of alkyl bromide during the reaction. (Figure 5D)

Racemic benzylic bromide



According to **General procedure A** with *rac*-(1-bromoethyl)benzene **E1** (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*7** at room temperature for 12 h, the reaction mixture was diluted with EtOAc and filtrated through a pad of Celite, then concentrated in vacuum. The yield of **E1** was determined by ^{1}H NMR spectra with 1,3,5-trimethoxybenzene as an internal standard, the product **1** as a colorless oil was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) as a colorless oil (16.6 mg, 26% yield, 96% ee).

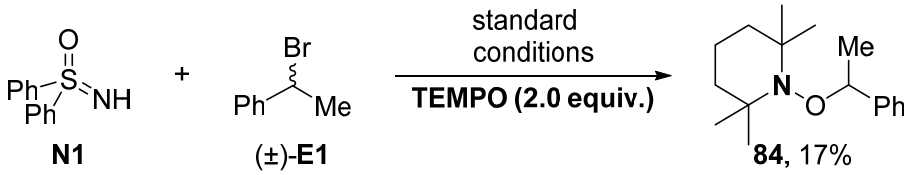
Chiral benzylic bromide



(*R*)-**E1**, 73% ee 1.0 equiv. 21% y, 96% ee 61% y, 73% ee

According to **General procedure A** with (*R*)-(1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand **L*7** at room temperature for 12 h, the reaction mixture was diluted with EtOAc and filtrated through a pad of Celite, then concentrated in vacuum. The yield of (*R*)-**E1** was determined by ^{1}H NMR spectra with 1,3,5-trimethoxybenzene as an internal standard, the product **1** (13.5 mg, 21% yield, 96% ee) as a colorless oil was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 5/1).

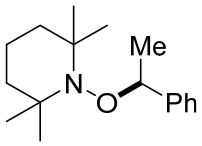
Radical trap experiment with TEMPO. (Figure 5E)



N1 (±)-**E1** **84**, 17%

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone **N1** (26.0 mg, 0.12 mmol, 1.2 equiv.), $Cu(HFacac)_2$ (4.4 mg, 0.010 mmol, 10 mol%), chiral ligand **L*7** (13.6 mg, 0.010 mmol, 10 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 2.0 equiv.), TEMPO (31.3 mg, 0.20 mmol, 2.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added (*R*)-(1-bromoethyl)benzene (18.4 mg, 0.10 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 96 h. The precipitate was diluted with EtOAc, and then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated under reduce pressure and the residue was purified by column chromatography on neutral alumina (petroleum) to afford **84** as a yellow oil (4.4 mg, 17% yield).

2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (84)



84

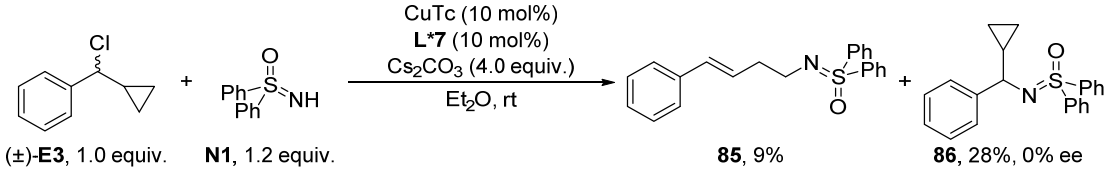
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.27 – 7.20 (m, 1H), 4.80 (q, *J* = 6.7 Hz, 1H), 1.53 – 1.02 (m, 18H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 128.0, 126.8, 126.6, 83.1, 59.7, 53.4, 40.4, 34.5, 34.1, 23.6, 20.4, 17.2.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{28}NO$ $[M + H]^+$ 262.2165, found 262.2161.

Radical clock experiment. (Supplementary Scheme S3)

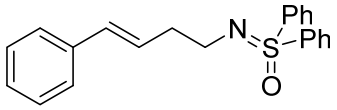
Benzyl chloride



(±)-**E3**, 1.0 equiv. **N1**, 1.2 equiv. **85**, 9% **86**, 28%, 0% ee

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone **N1** (52.0 mg, 0.24 mmol, 1.2 equiv.), CuTc (3.8 mg, 0.020 mmol, 10 mol%), chiral ligand **L*7** (27.3 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added (chloro(cyclopropyl)methyl)benzene **E3** (33.2 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 96 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, and then filtered through Celite and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the desired product **85** as a yellow oil (6.0 mg, 9% yield) and **86** as a yellow oil (19.1 mg, 28% yield, 0% ee).

(*E*)-Diphenyl((4-phenylbut-3-en-1-yl)imino)-λ^6-sulfanone (85)



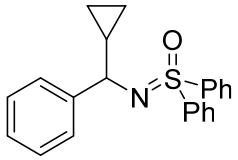
85

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.91 (m, 4H), 7.53 – 7.41 (m, 6H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.15 (m, 1H), 6.51 – 6.41 (m, 1H), 6.30 (dt, *J* = 15.9, 6.9 Hz, 1H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.62 – 2.51 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 137.8, 132.4, 131.1, 129.1, 128.9, 128.6, 128.5, 128.4, 127.6, 126.9, 126.03, 125.99, 43.9, 36.6.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}NOS$ $[M + H]^+$ 348.1417, found 348.1411.

((Cyclopropyl(phenyl)methyl)imino)diphenyl-λ^6-sulfanone (86)



86

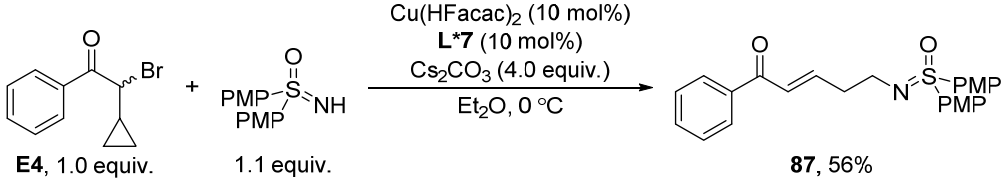
HPLC analysis: Chiralcel ID (hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_{R1} = 8.17 min, t_{R2} = 9.82 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.80 – 7.70 (m, 2H), 7.53 – 7.37 (m, 6H), 7.36 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 3.61 (d, *J* = 7.6 Hz, 1H), 1.36 – 1.17 (m, 1H), 0.58 – 0.50 (m, 1H), 0.50 – 0.39 (m, 2H), 0.39 – 0.30 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 141.7, 140.9, 132.3, 132.2, 128.94, 128.92, 128.6, 128.1, 126.8, 126.5, 62.9, 21.1, 4.8, 4.1.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}NOS$ $[M + H]^+$ 348.1417, found 348.1411.

α-Bromo ketone

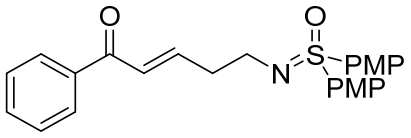


E4, 1.0 equiv. 1.1 equiv. **87**, 56%

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a

magnetic stir bar was charged with iminobis(4-methoxyphenyl)-λ^6-sulfanone (60.9 mg, 0.22 mmol, 1.1 equiv.), $Cu(HFacac)_2$ (8.8 mg, 0.020 mmol, 10 mol%), chiral ligand **L*7** (27.3 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (4.0 mL). To this solution was added 2-bromo-2-cyclopropyl-1-phenylethan-1-one **E4** (47.6 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at 0 °C for 72 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, and then filtered through a short pad of Celite and washed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **87** as a colorless oil (48.7 mg, 56% yield).

(*E*)-bis(4-Methoxyphenyl)((5-oxo-5-phenylpent-3-en-1-yl)imino)-λ^6-sulfanone (87)



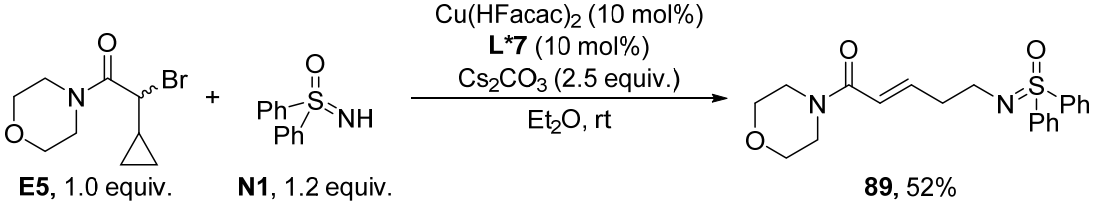
87

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.91 – 7.83 (m, 4H), 7.59 – 7.52 (m, 1H), 7.52 – 7.44 (m, 2H), 7.20 – 7.10 (m, 1H), 7.02 – 6.95 (m, 1H), 6.95 – 6.89 (m, 4H), 3.82 (s, 6H), 3.24 (t, *J* = 6.9 Hz, 2H), 2.73 – 2.61 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 162.7, 148.3, 138.0, 132.6, 132.5, 130.4, 128.6, 128.5, 127.1, 114.4, 55.6, 42.7, 36.3.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}NO_4S$ $[M + H]^+$ 436.1577, found 436.1575.

α-Bromo amide

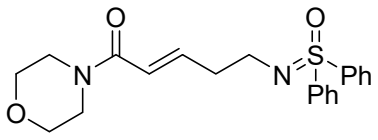


E5, 1.0 equiv. **N1**, 1.2 equiv. **89**, 52%

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a

magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone **N1** (13.0 mg, 0.060 mmol, 1.2 equiv.), $Cu(HFacac)_2$ (2.39 mg, 0.0050 mmol, 10 mol%), chiral ligand **L*7** (6.8 mg, 0.0050 mmol, 10 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 4.0 equiv.) and anhydrous Et_2O (1.0 mL). To this solution was added alkyl halide 2-bromo-2-cyclopropyl-1-morpholinoethan-1-one **E5** (12.4 mg, 0.050 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 96 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, and then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to afford the desired product **89** as a yellow oil (10.0 mg, 52% yield).

(*E*)-((5-Morpholino-5-oxopent-3-en-1-yl)imino)diphenyl-λ^6-sulfanone (89)



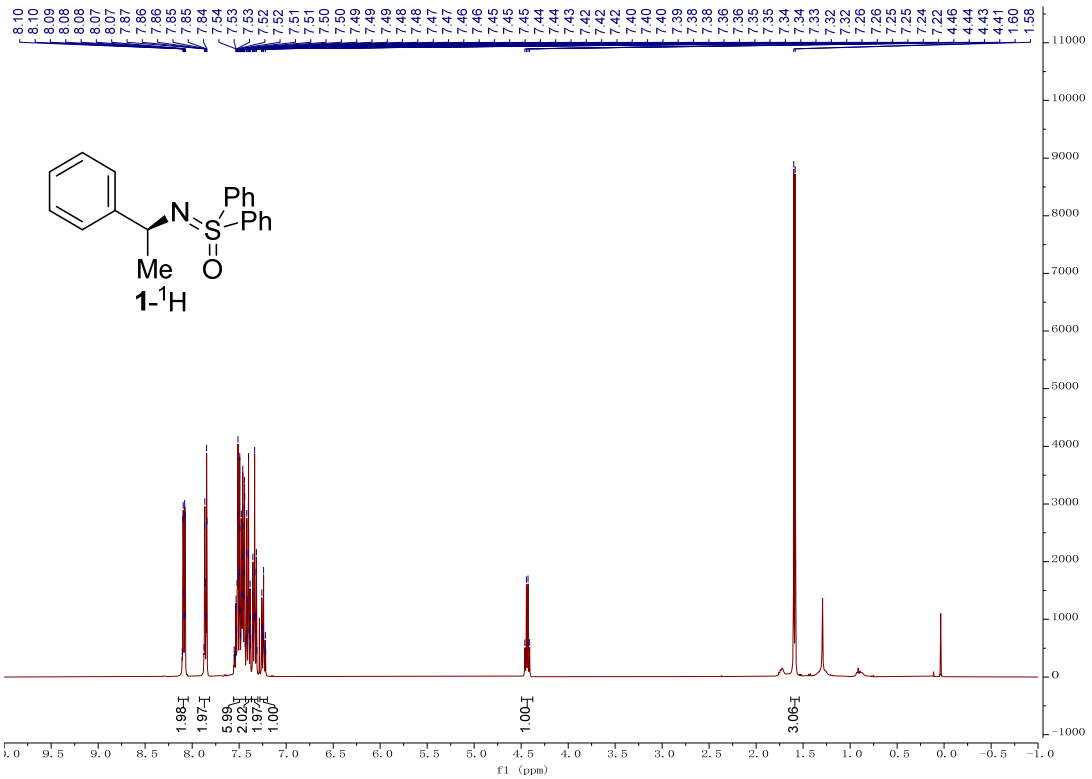
89

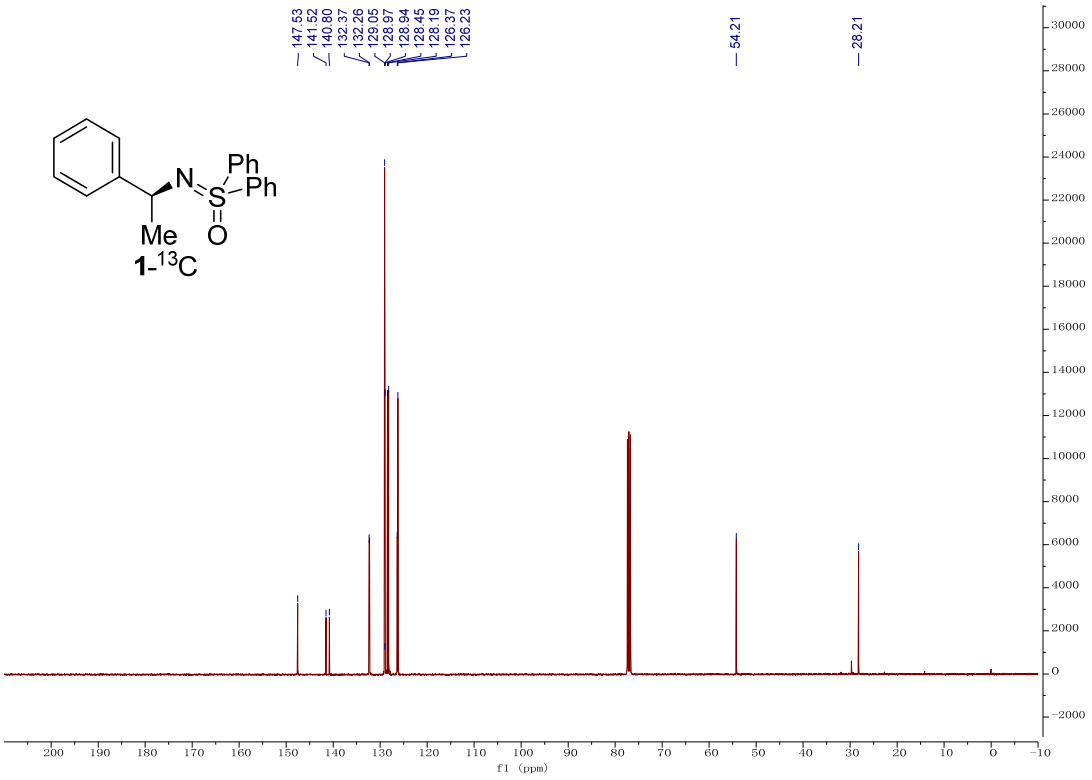
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.93 (m, 4H), 7.59 – 7.42 (m, 6H), 6.95 (dt, *J* = 15.2, 6.9 Hz, 1H), 6.32 (d, *J* = 15.2 Hz, 1H), 3.81 – 3.45 (m, 8H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.65 – 2.53 (m, 2H).

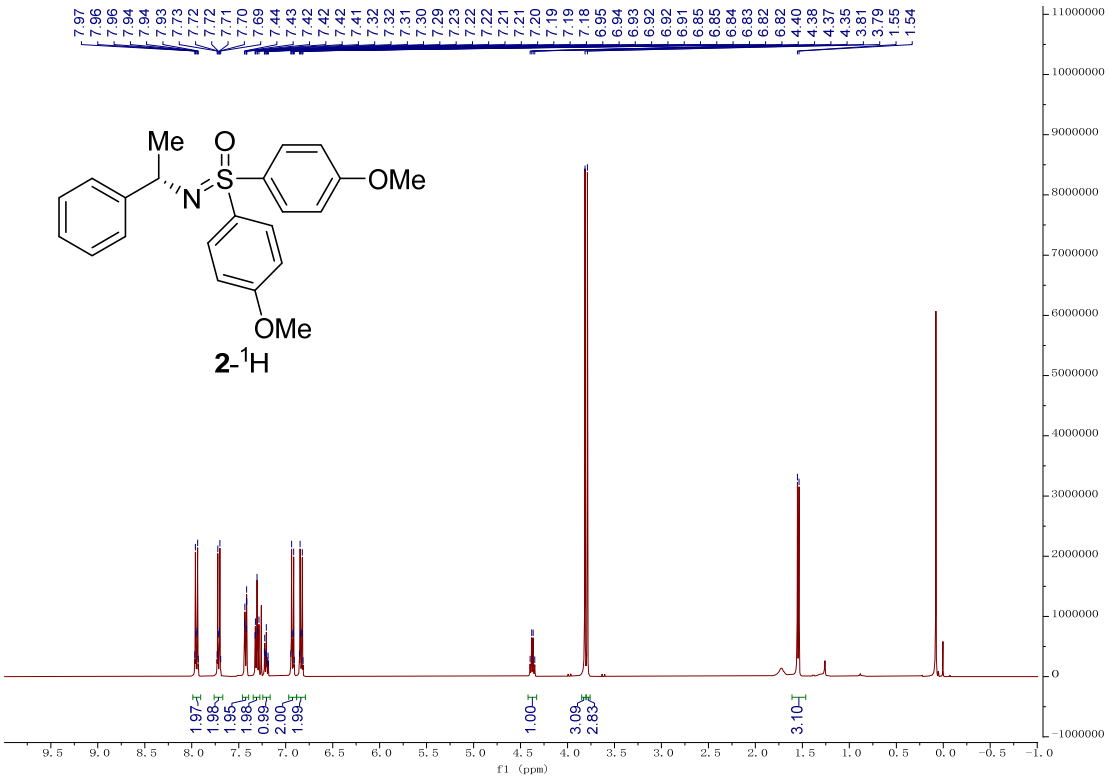
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 144.7, 140.6, 132.5, 129.2, 128.5, 121.0, 66.9, 46.2, 42.7, 36.0.

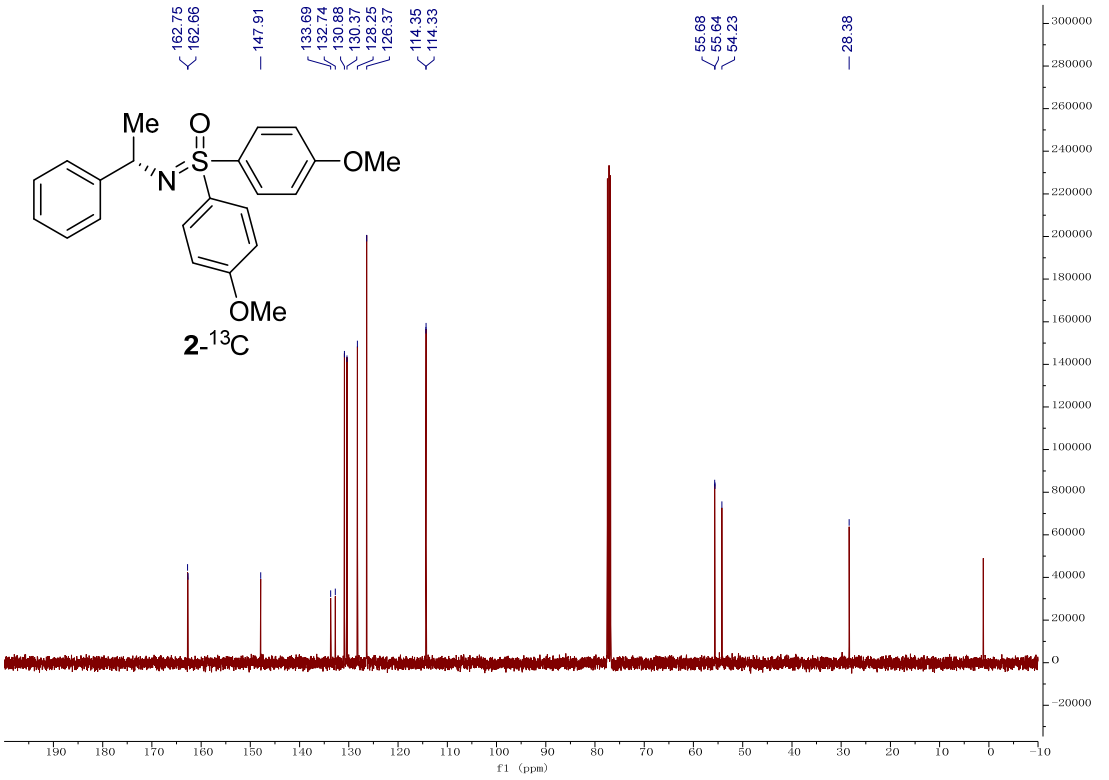
HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}N_2O_3S$ $[M + H]^+$ 385.1580, found 385.1575.

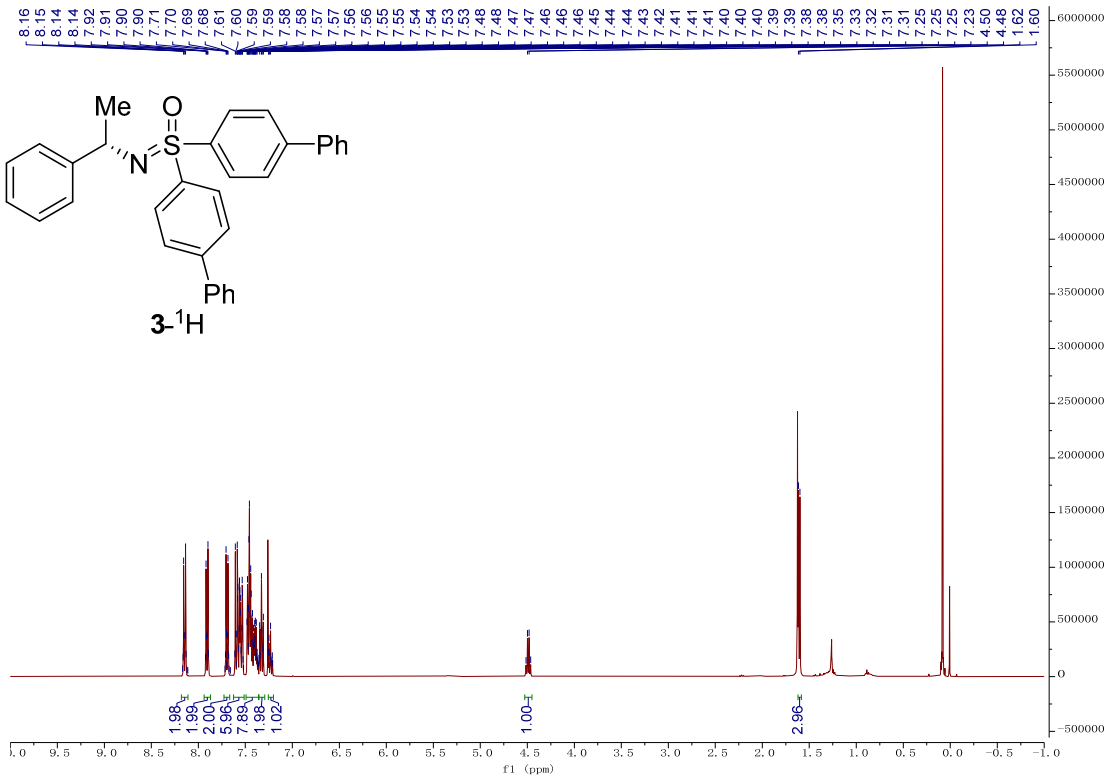
NMR spectra

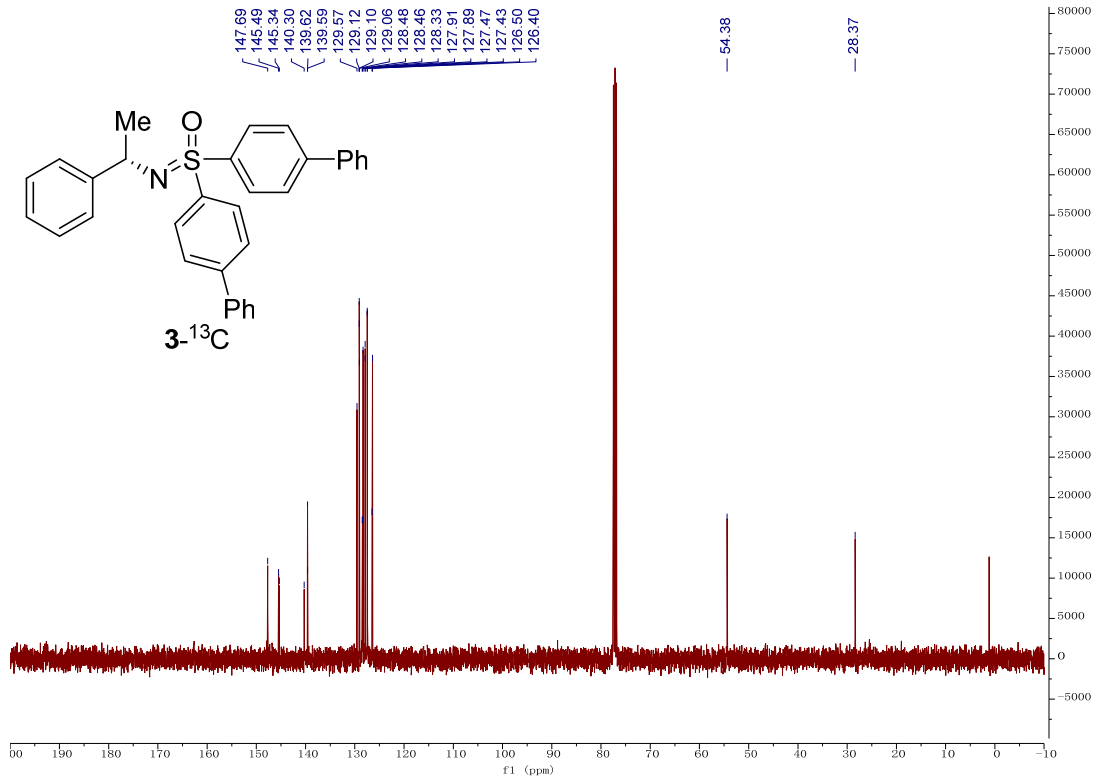


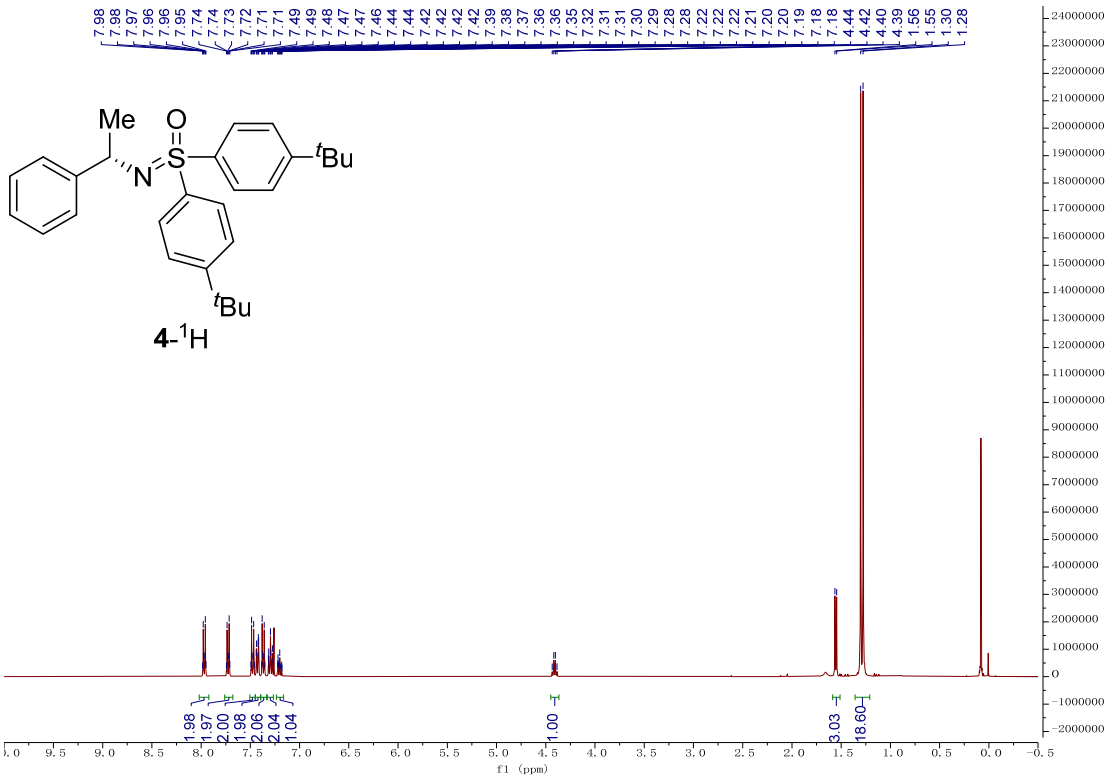



7.97 7.96 7.96 7.94 7.94 7.93 7.73 7.72 7.72 7.71 7.70 7.69 7.44 7.43 7.42 7.42 7.42 7.41 7.32 7.32 7.31 7.30 7.29 7.23 7.22 7.22 7.21 7.21 7.20 7.19 7.19 7.18 6.95 6.94 6.93 6.92 6.92 6.91 6.85 6.85 6.84 6.83 6.82 6.82 4.40 4.38 4.37 4.35 3.81 3.79 1.55 1.54
Me
O
S
N
OMe
OMe
2-1H
1.97 1.98 1.95 1.98 0.99 2.00 1.99 1.00 3.09 2.83 3.10
f1 (ppm)

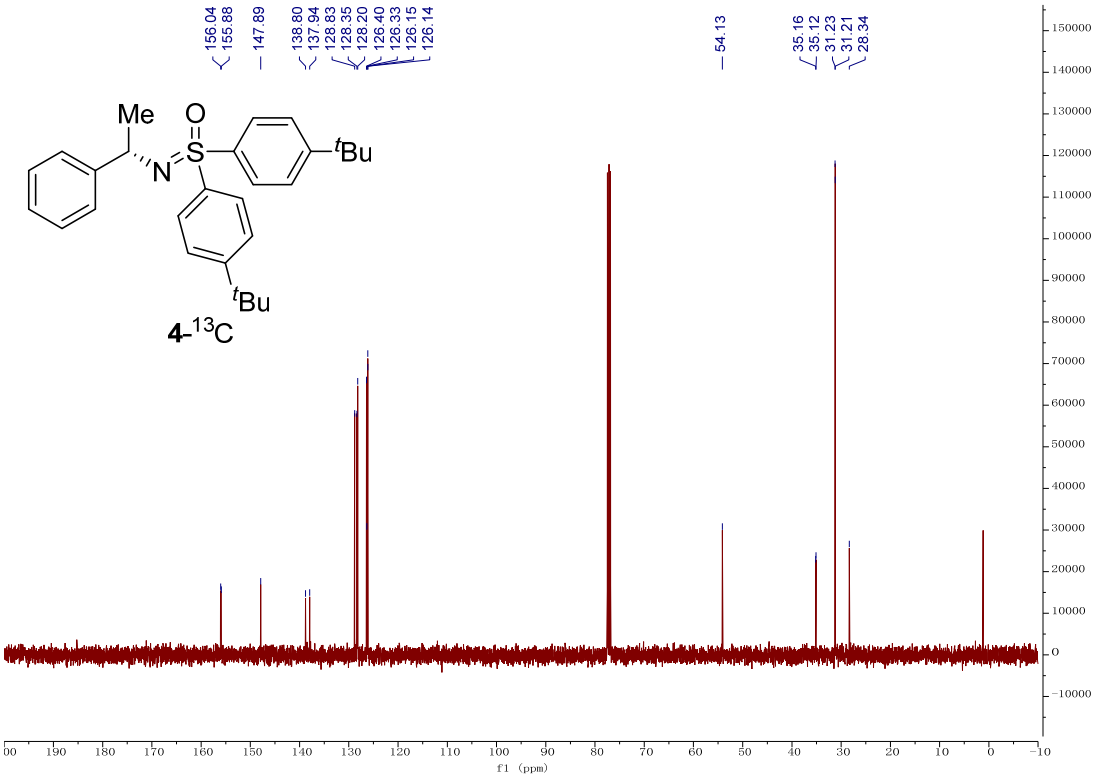

162.75 162.66 147.91 133.69 132.74 130.88 130.37 128.25 126.37 114.35 114.33 55.68 55.64 54.23 28.38
Me
O
S
N
OMe
OMe
2-13C
f1 (ppm)


Me
O
N
S
Ph
Ph
3-1H
f1 (ppm)

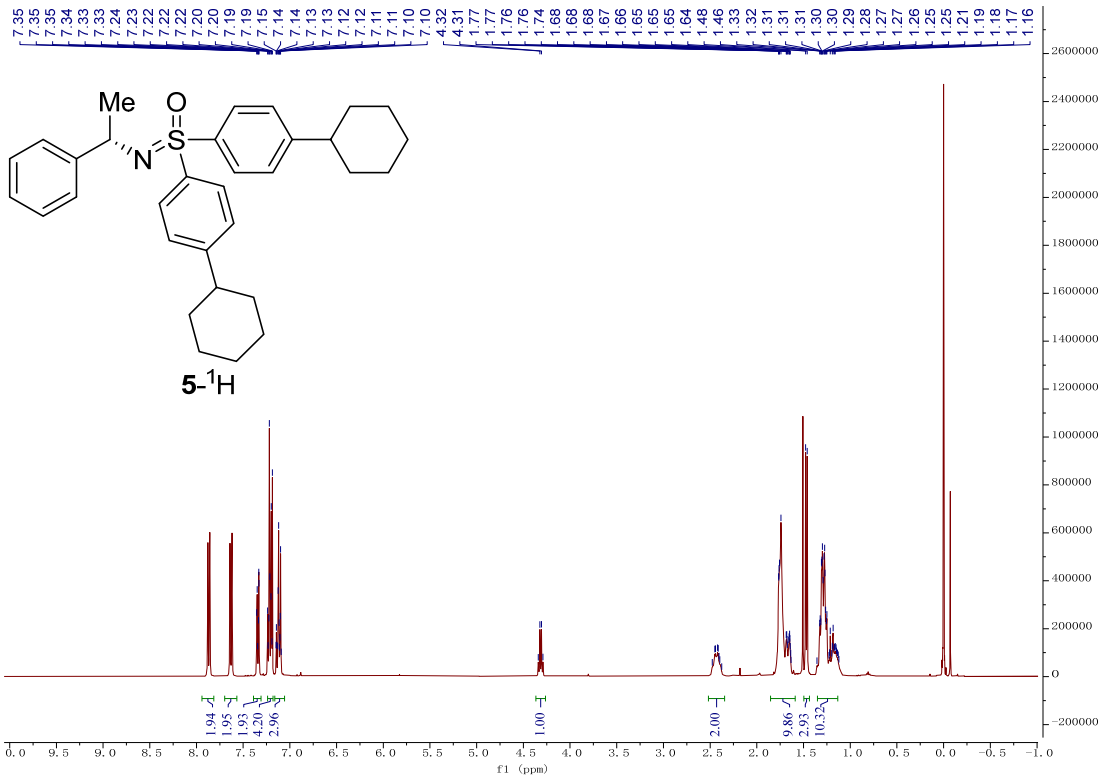

Me
O
N
S
Ph
Ph
3-13C
54.38
28.37
f1 (ppm)

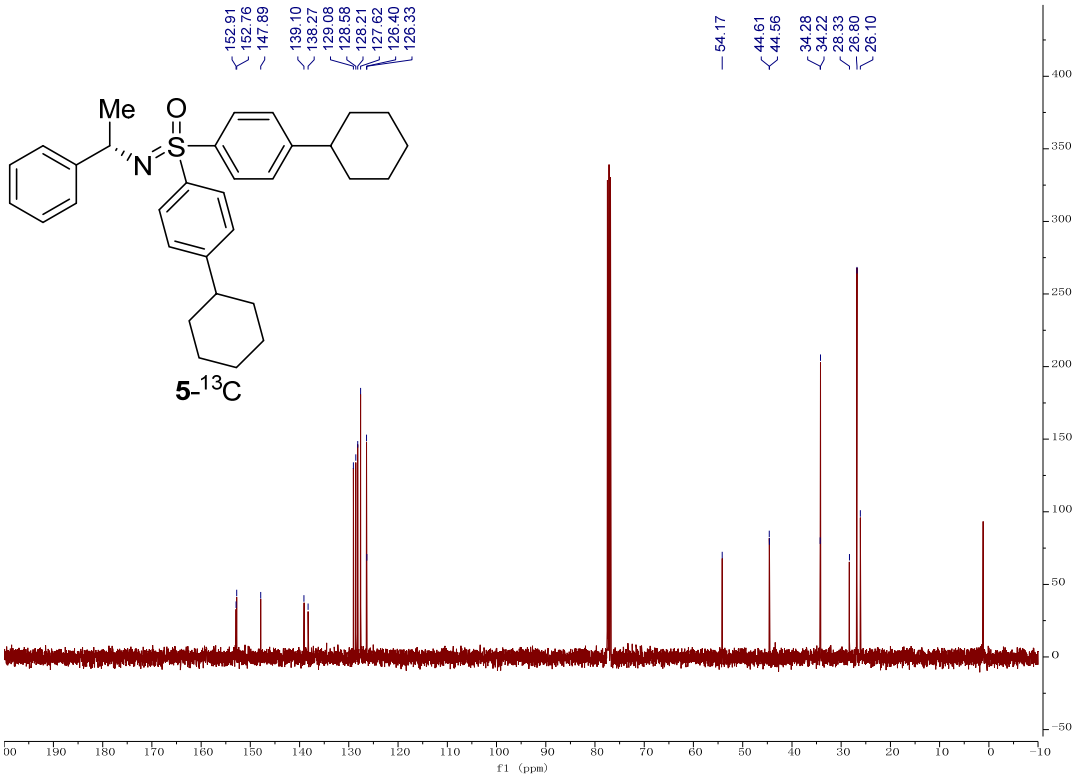

7.98 7.98 7.97 7.96 7.96 7.95 7.74 7.74 7.73 7.72 7.71 7.71 7.49 7.49 7.48 7.47 7.47 7.46 7.44 7.44 7.42 7.42 7.42 7.39 7.38 7.37 7.36 7.36 7.35 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.22 7.22 7.21 7.20 7.20 7.19 7.18 4.44 4.42 4.40 4.39 1.56 1.55 1.30 1.28
Me
O
S
N
tBu
tBu
1.98 1.97 2.00 1.98 2.06 2.04 1.04
1.00
3.03 18.60
f1 (ppm)

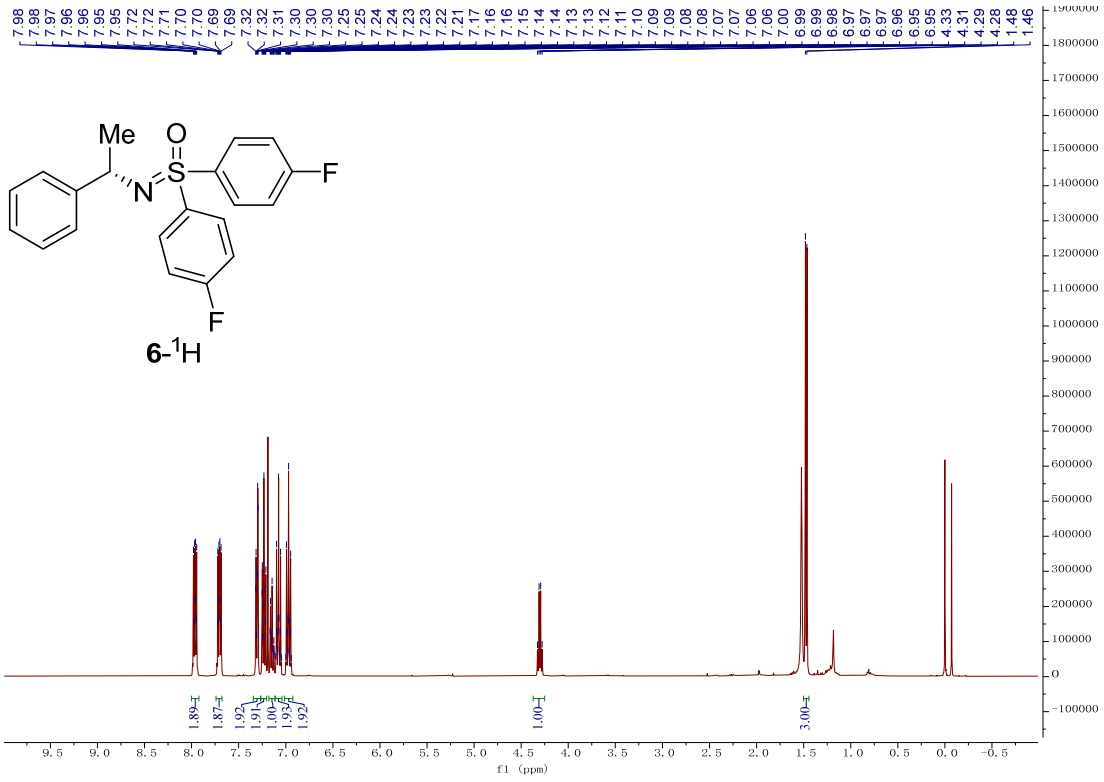
4-^{1}H

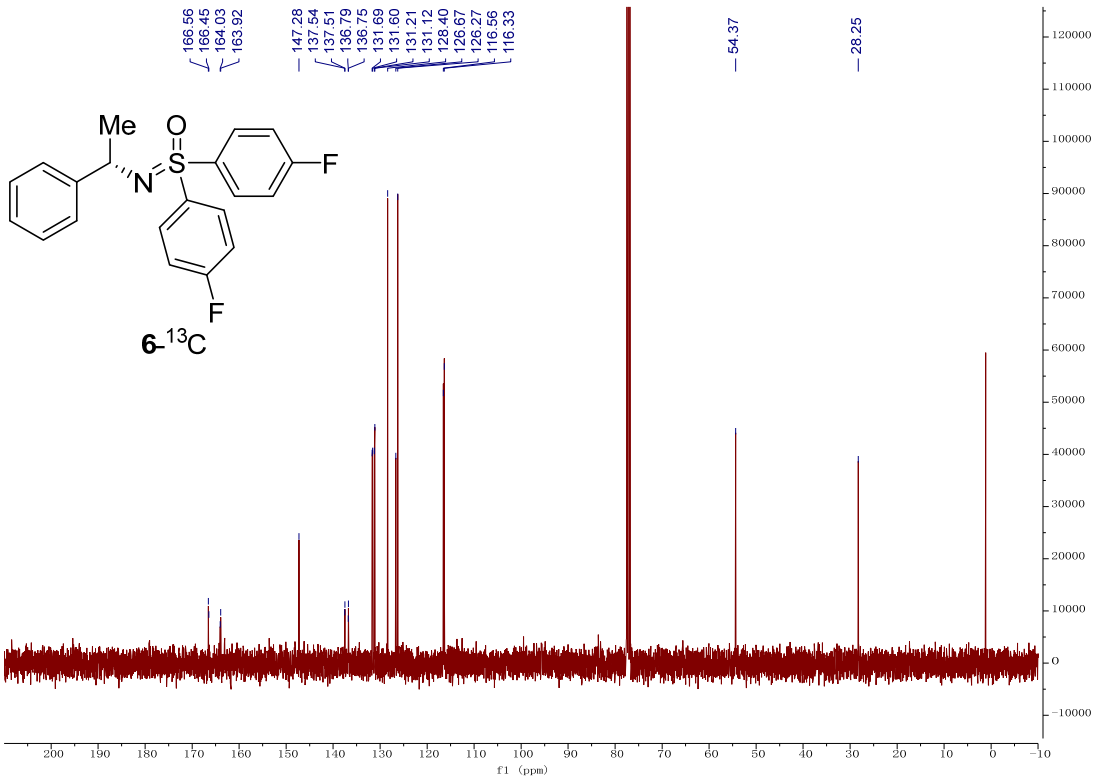

156.04 155.88 147.89 138.80 137.94 128.83 128.35 128.20 126.40 126.33 126.15 126.14
54.13
35.16 35.12 31.23 31.21 28.34
Me
O
S
N
tBu
tBu
f1 (ppm)

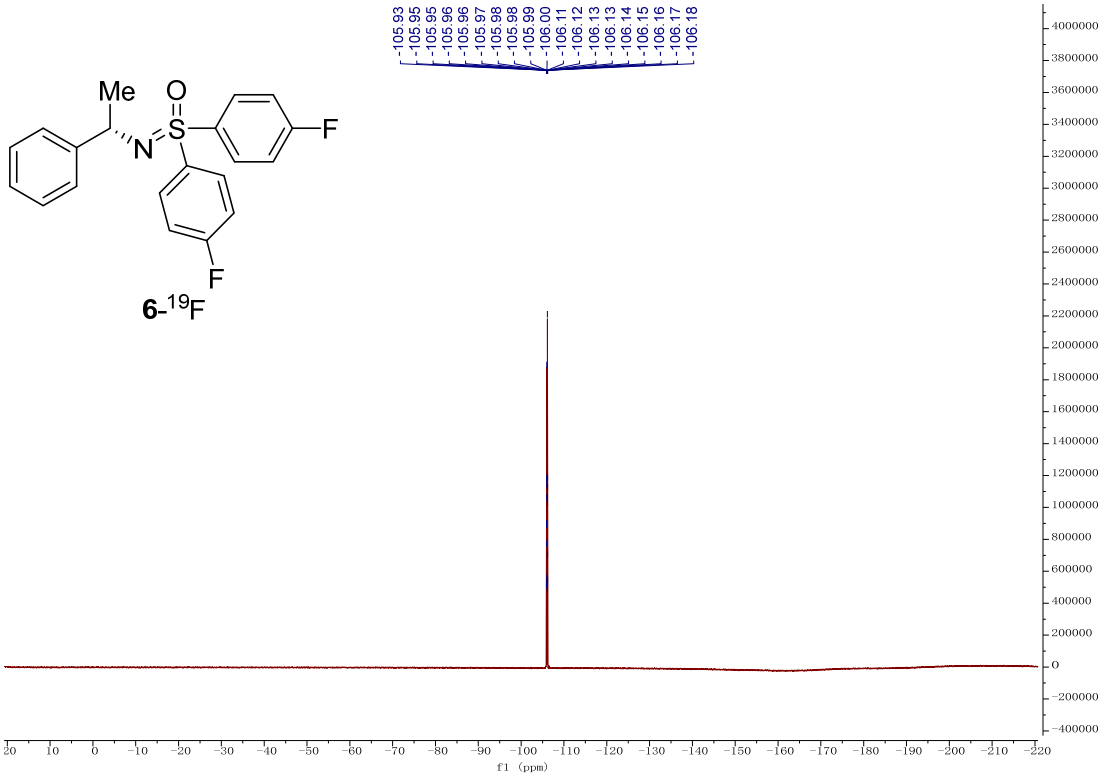
4-^{13}C

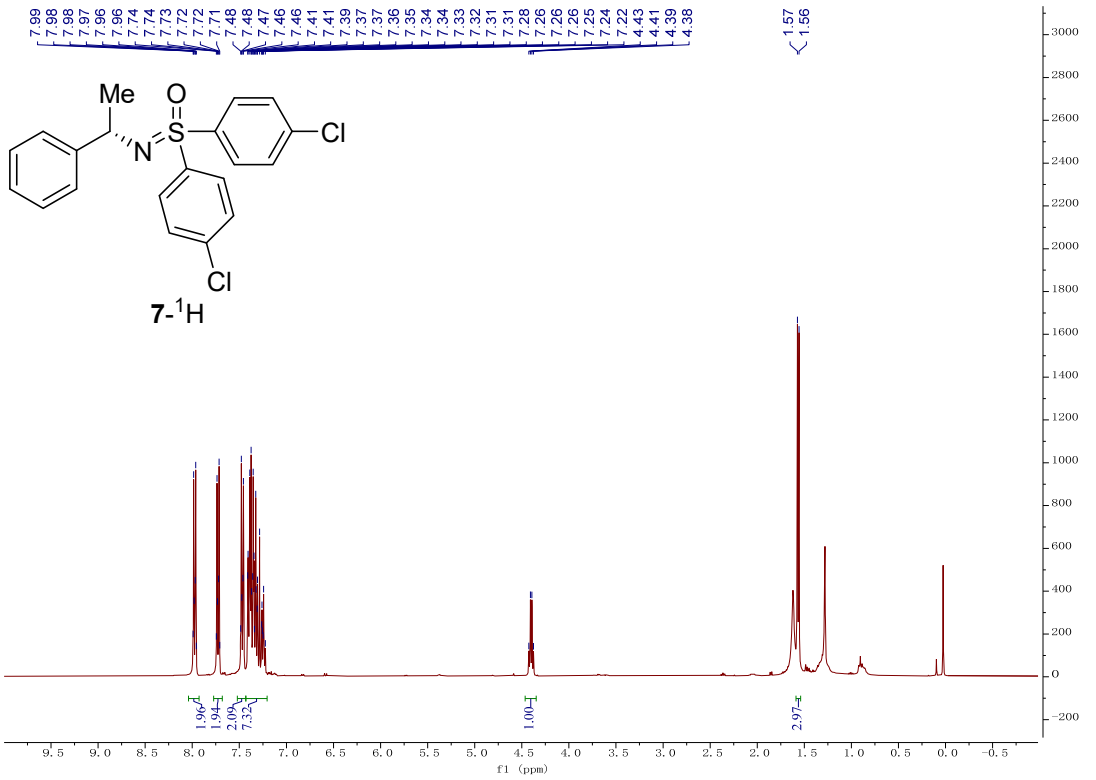

Me
O
S
N
5-1H
f1 (ppm)

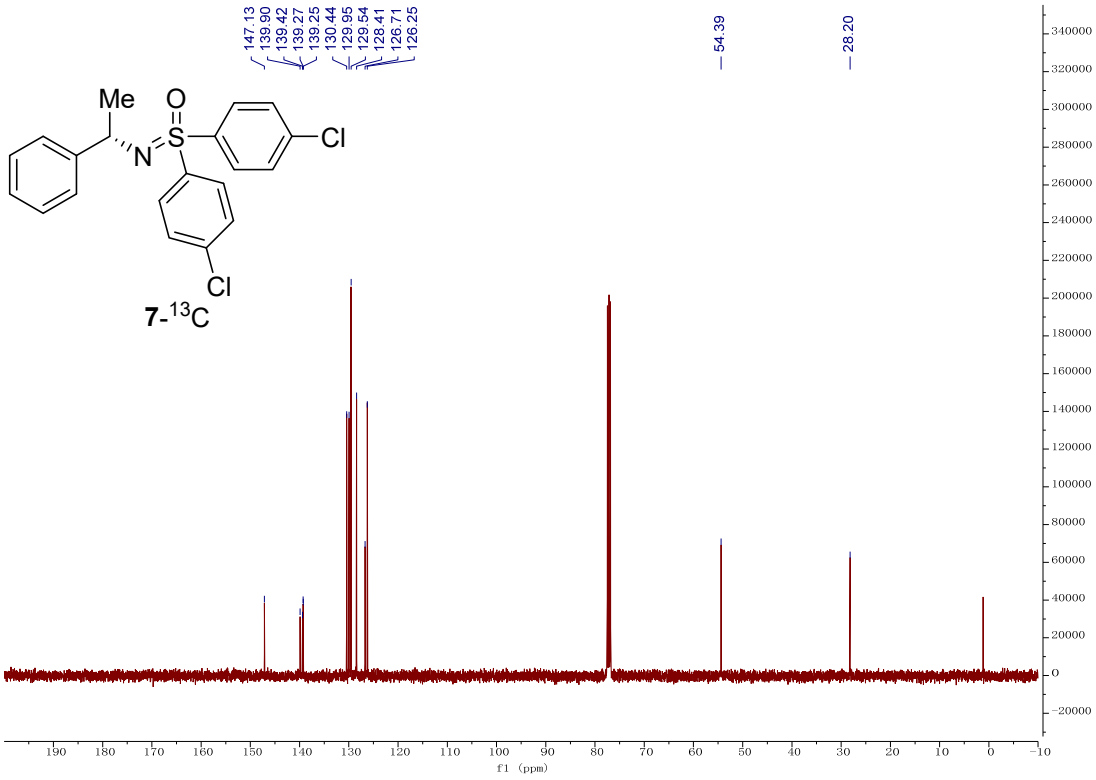

Me
O
S
N
5-13C
f1 (ppm)

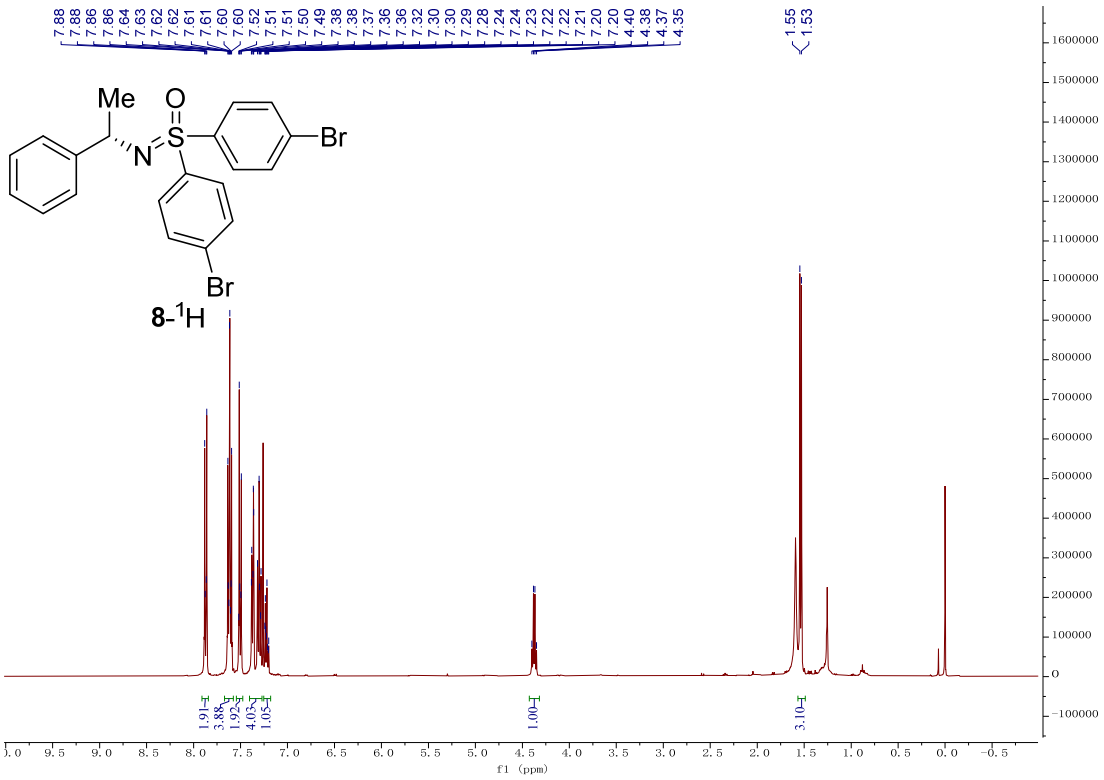

Me
O
S
N
F
F
6-1H
f1 (ppm)

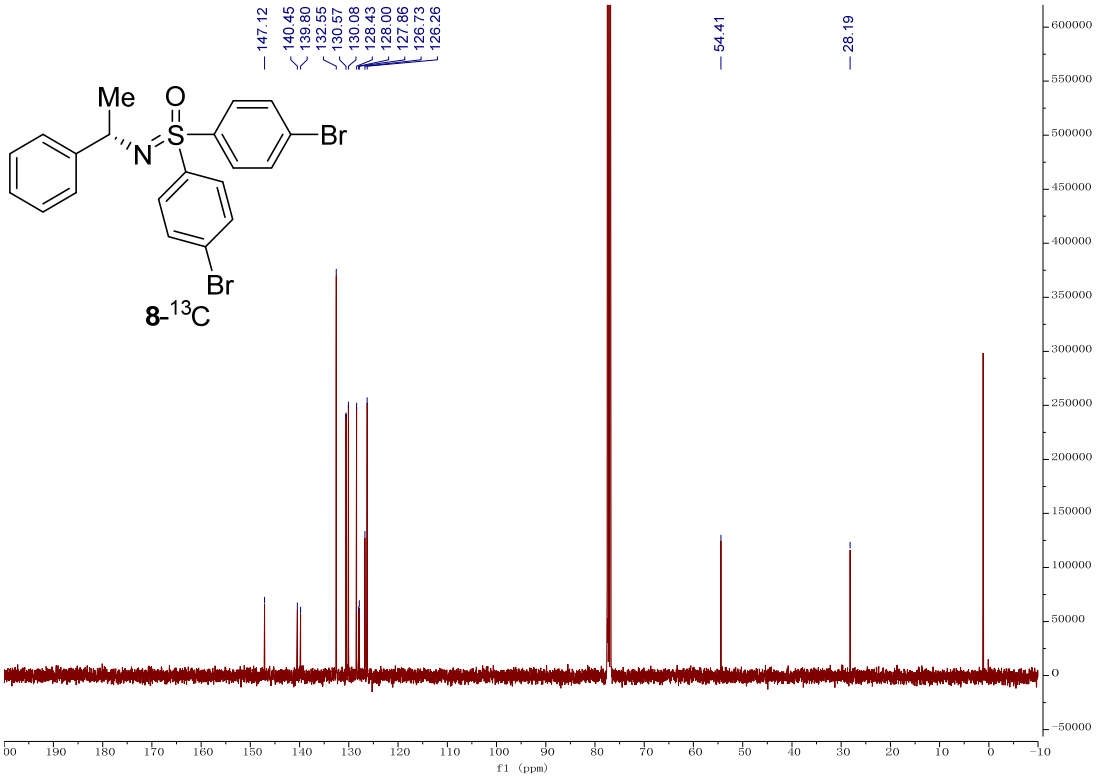

Me
O
S
N
F
F
6-13C
f1 (ppm)

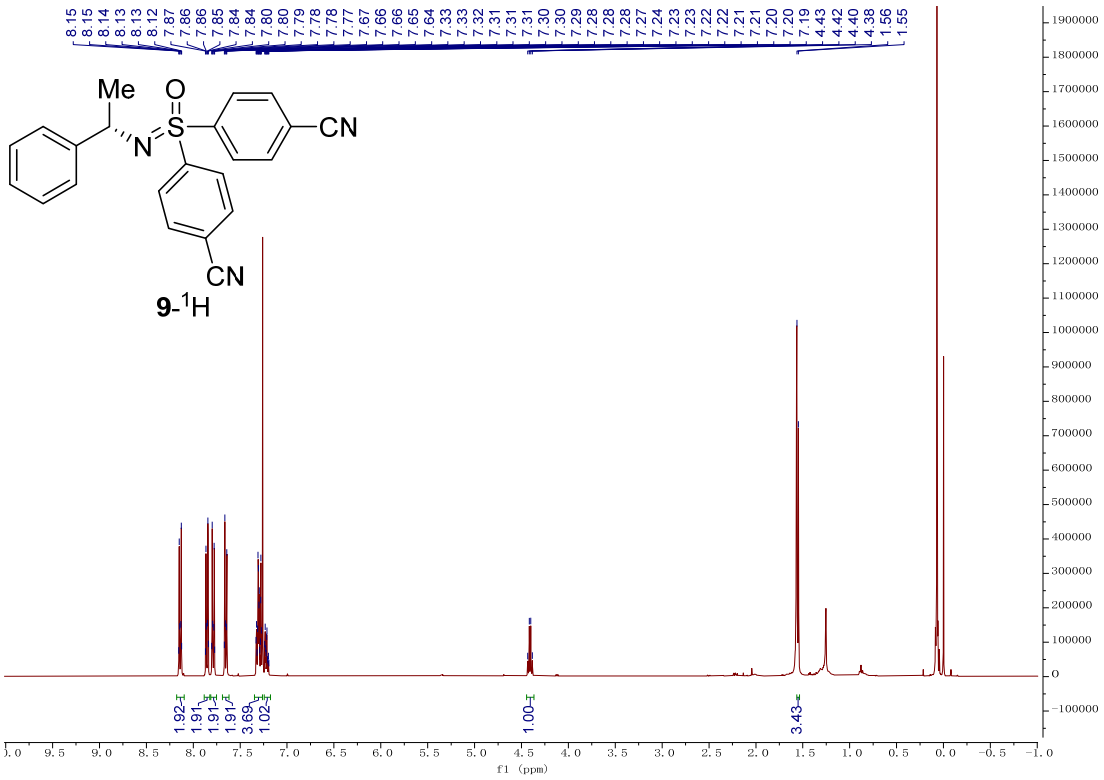

-105.93
-105.95
-105.95
-105.96
-105.96
-105.97
-105.98
-105.98
-105.99
-106.00
-106.11
-106.12
-106.13
-106.13
-106.14
-106.15
-106.16
-106.17
-106.18
Me
O
S
N
F
F
6-19F
4000000
3800000
3600000
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
-400000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

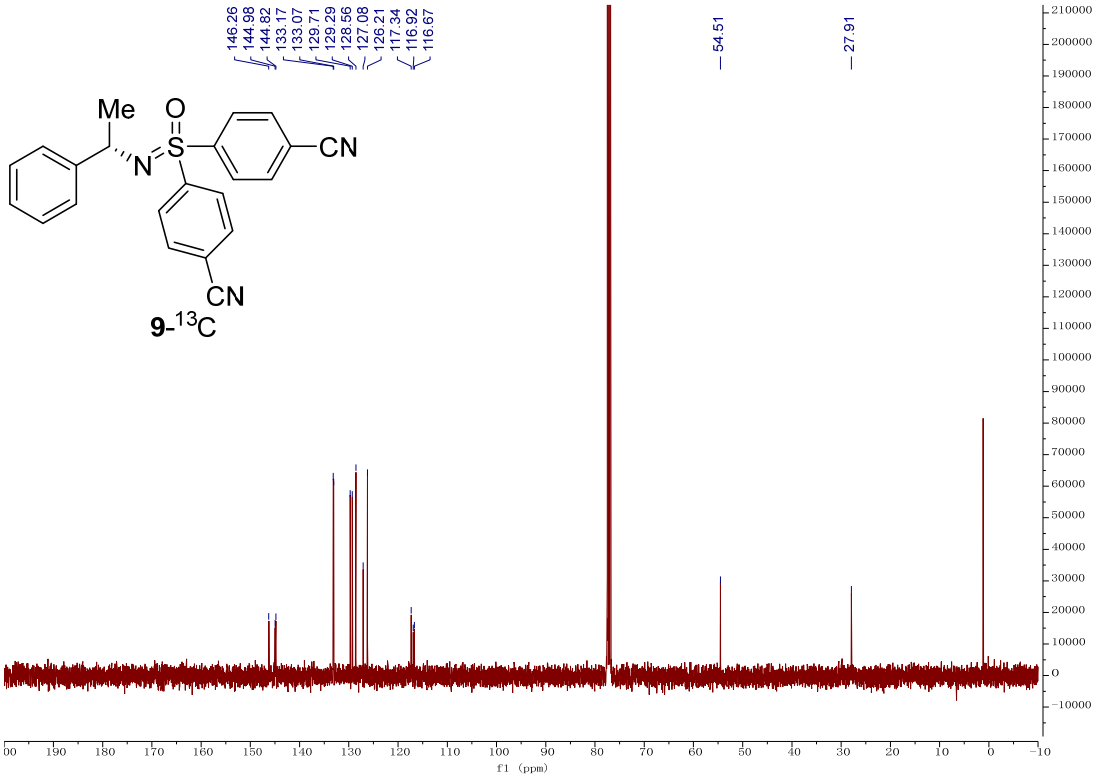

7.99
7.98
7.98
7.97
7.96
7.96
7.74
7.74
7.73
7.72
7.72
7.71
7.48
7.48
7.47
7.46
7.46
7.41
7.41
7.39
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.28
7.26
7.26
7.25
7.24
7.22
4.43
4.41
4.39
4.38
1.57
1.56
Me
O
S
N
Cl
Cl
7-1H
1.96
1.94
2.09
7.32
1.00
2.97
f1 (ppm)

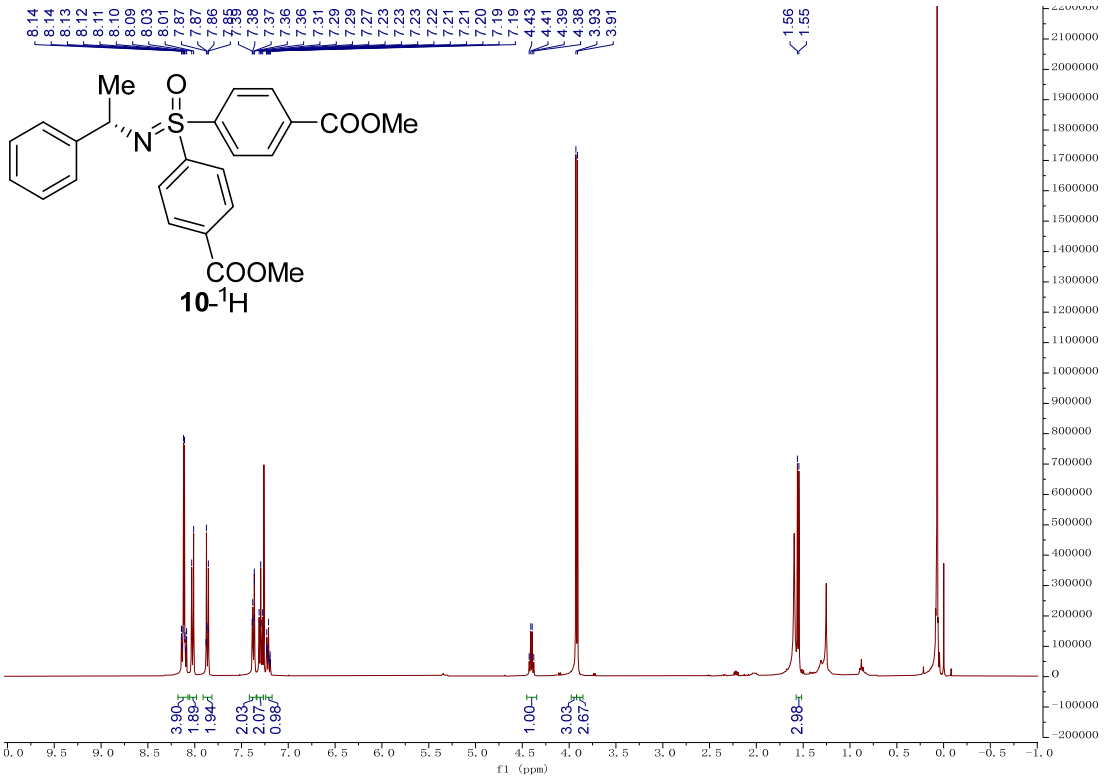

147.13
139.90
139.42
139.27
139.25
130.44
129.95
129.54
128.41
126.71
126.25
54.39
28.20
Me
O
S
N
Cl
Cl
7-13C
f1 (ppm)

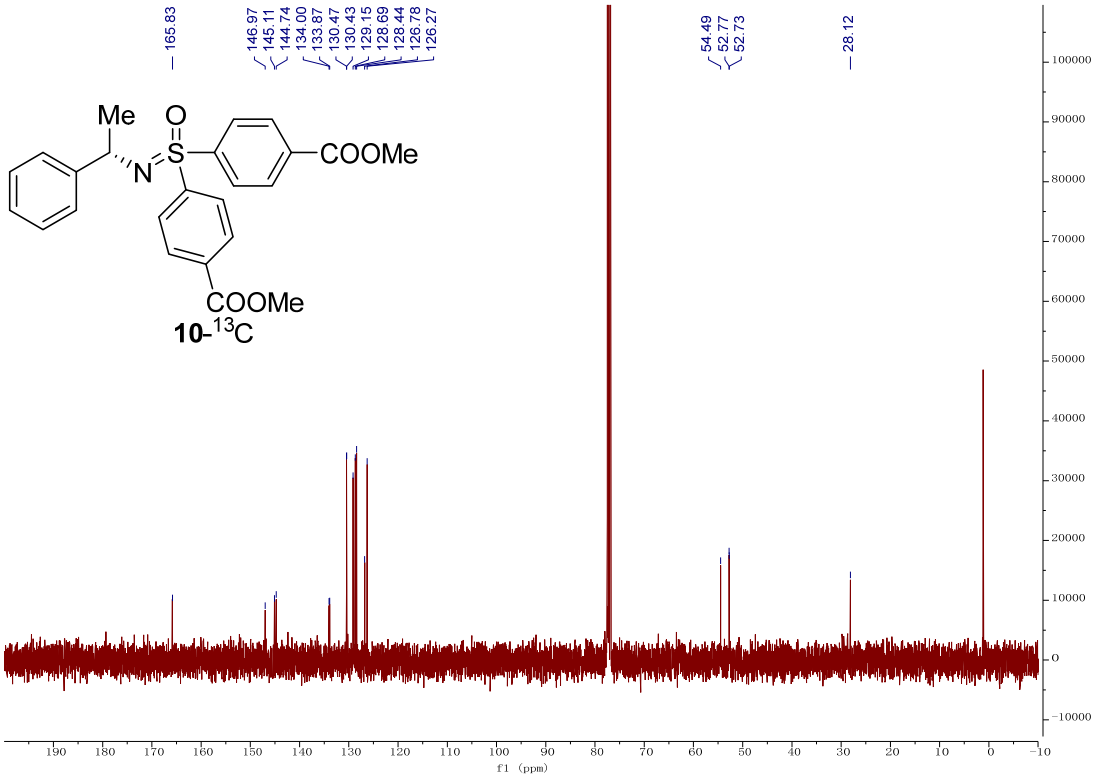

Me
O
N
S
Br
Br
8-1H
7.88
7.88
7.86
7.86
7.64
7.63
7.62
7.62
7.61
7.61
7.60
7.60
7.52
7.51
7.51
7.50
7.49
7.38
7.38
7.37
7.36
7.36
7.32
7.30
7.30
7.29
7.28
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.20
4.40
4.38
4.37
4.35
1.55
1.53
1.91
3.88
1.92
4.03
1.05
1.00
3.10
f1 (ppm)

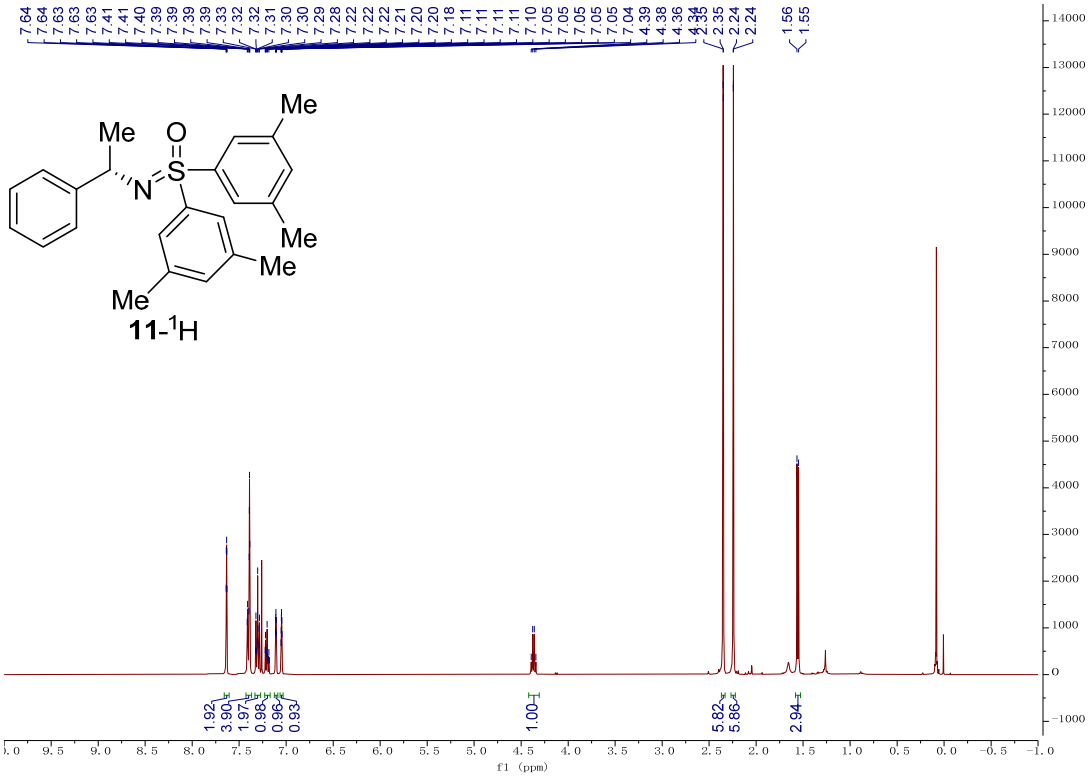

Me
O
N
S
Br
Br
8-13C
147.12
140.45
139.80
132.55
130.57
130.08
128.43
128.00
127.86
126.73
126.26
54.41
28.19
f1 (ppm)

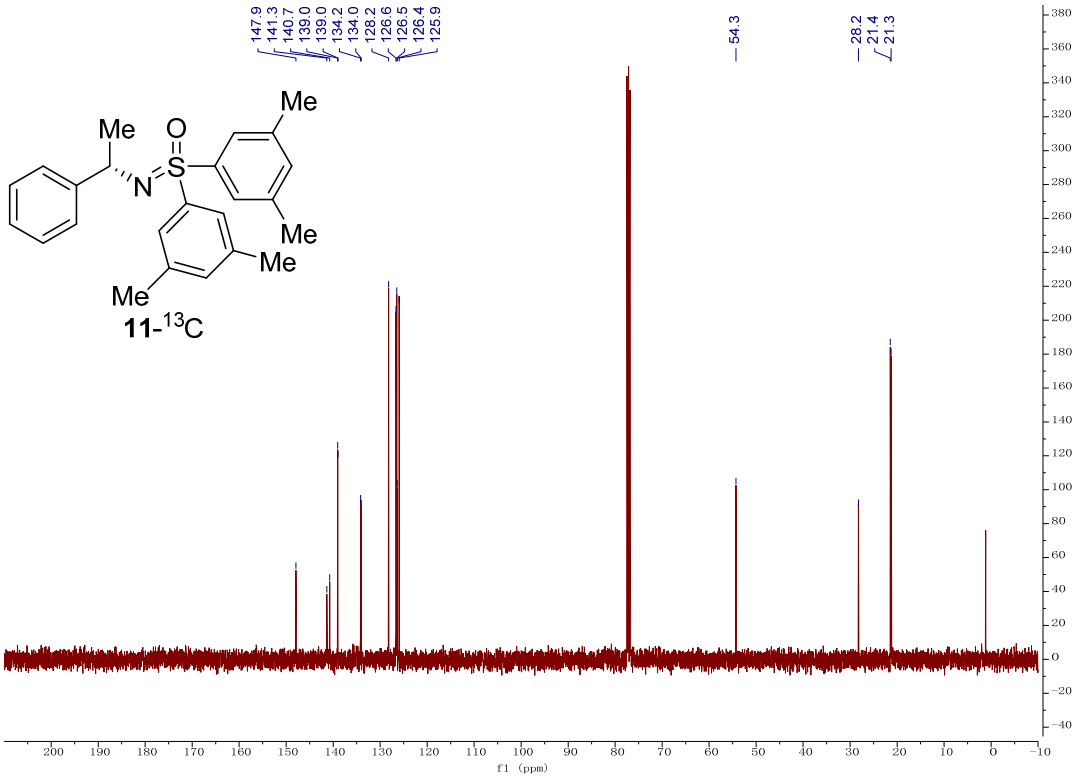

Me
O
N
S
CN
CN
9-1H
f1 (ppm)

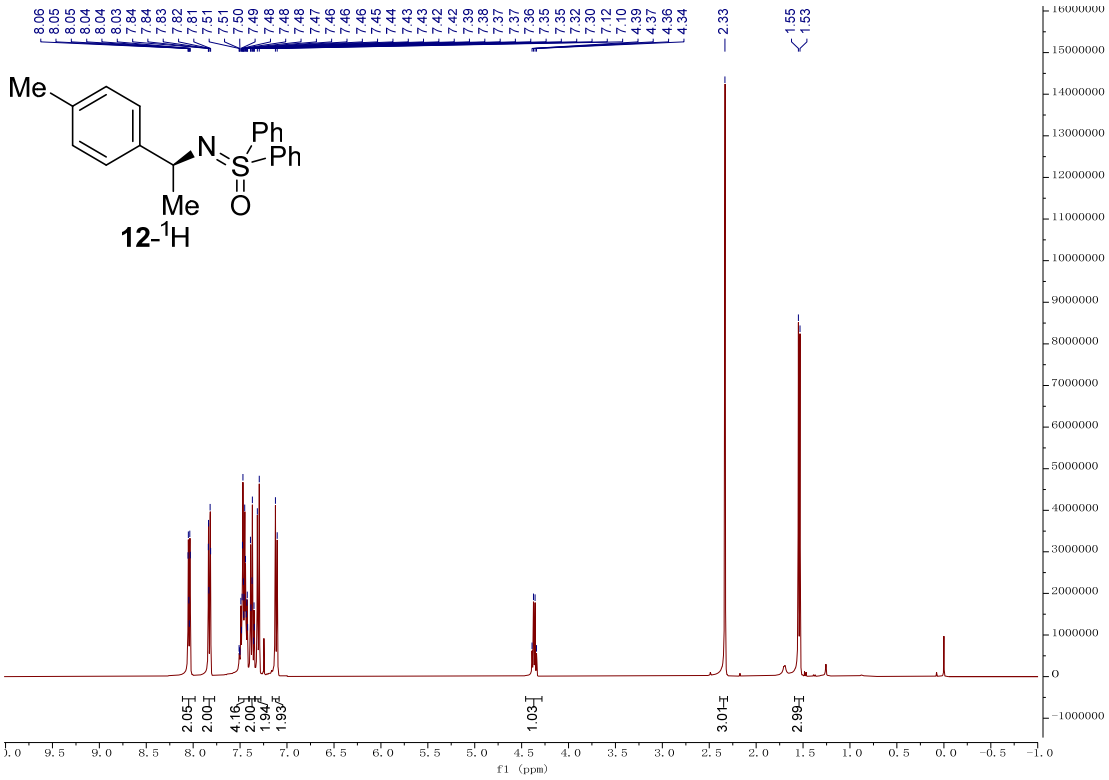

Me
O
N
S
CN
CN
9-13C
f1 (ppm)

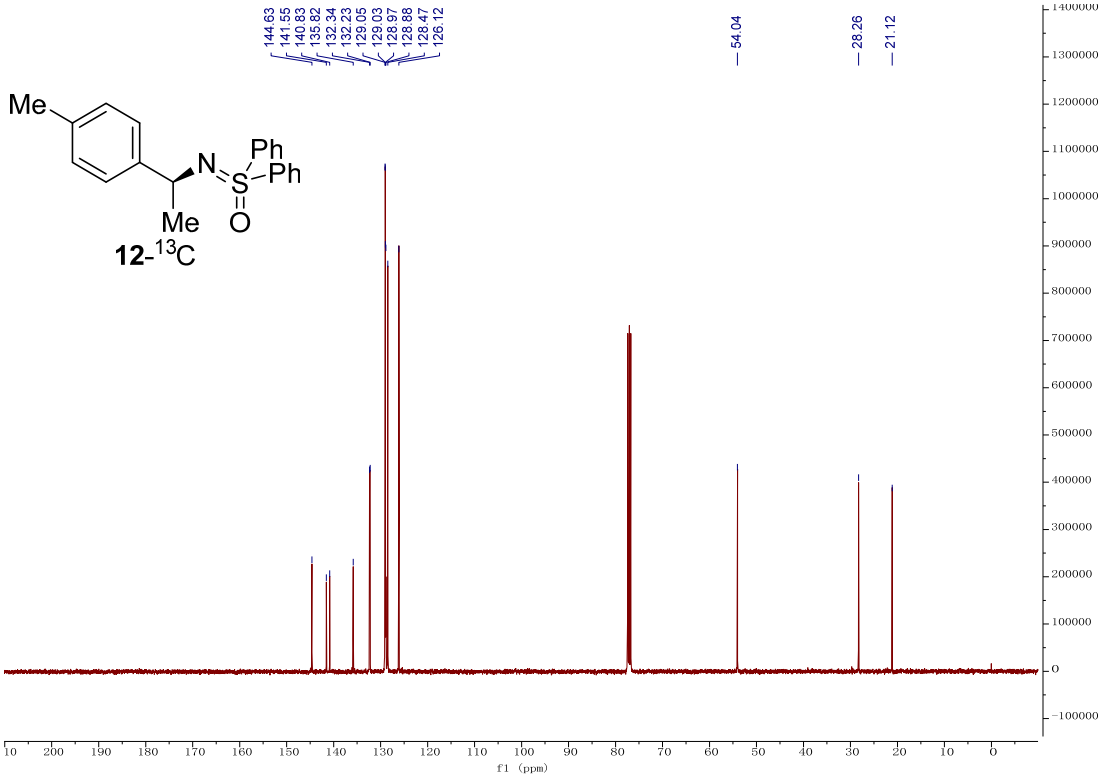

Me
O
N
S
COOMe
COOMe
10-1H
8.14
8.14
8.13
8.12
8.11
8.10
8.09
8.03
8.01
7.87
7.87
7.86
7.38
7.37
7.36
7.36
7.31
7.29
7.29
7.27
7.23
7.23
7.22
7.21
7.20
7.19
7.19
4.43
4.41
4.39
4.38
3.93
3.91
1.56
1.55
3.90
1.89
1.94
2.03
2.07
0.98
1.00
3.03
2.67
2.98
f1 (ppm)

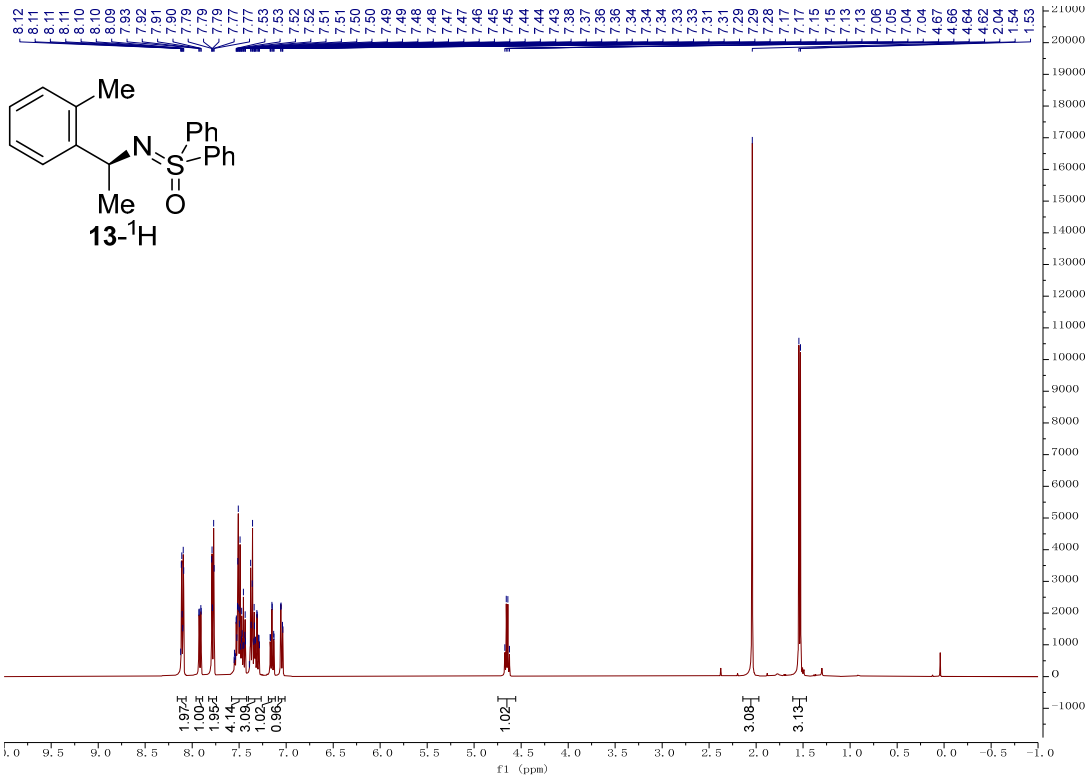

Me
O
N
S
COOMe
COOMe
10-13C
165.83
146.97
145.11
144.74
134.00
133.87
130.47
130.43
129.15
128.69
128.44
126.78
126.27
54.49
52.77
52.73
28.12
f1 (ppm)

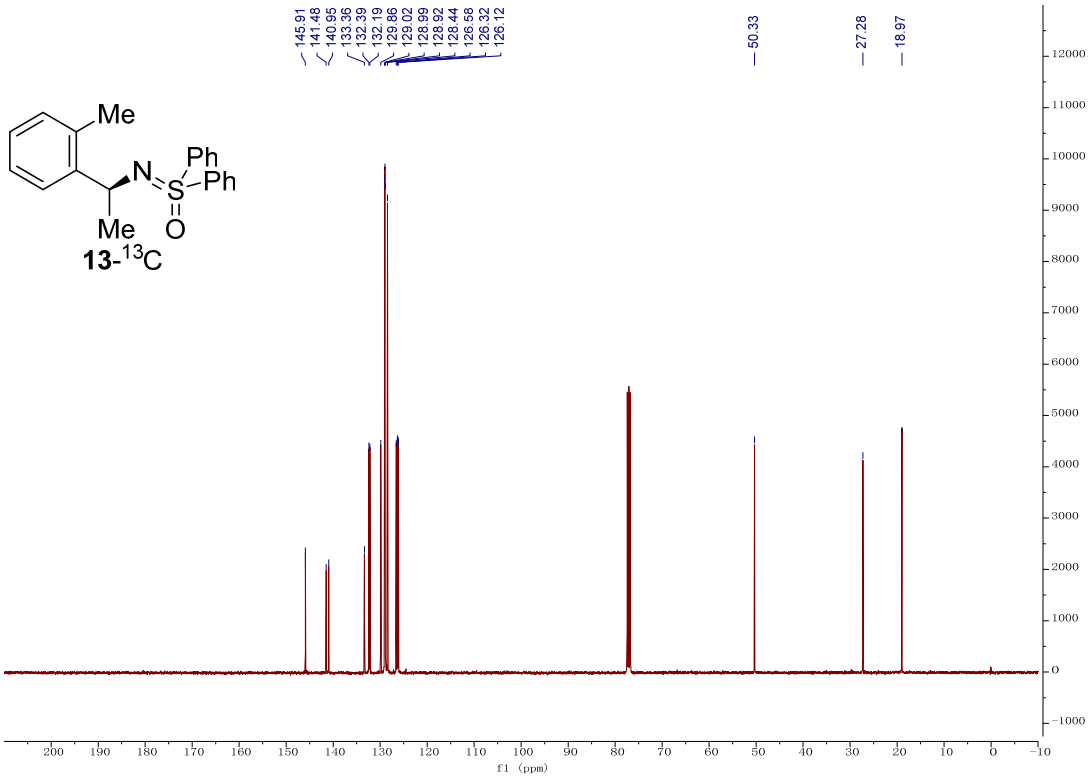

Me
O
N
S
Me
Me
Me
Me
11-1H
f1 (ppm)

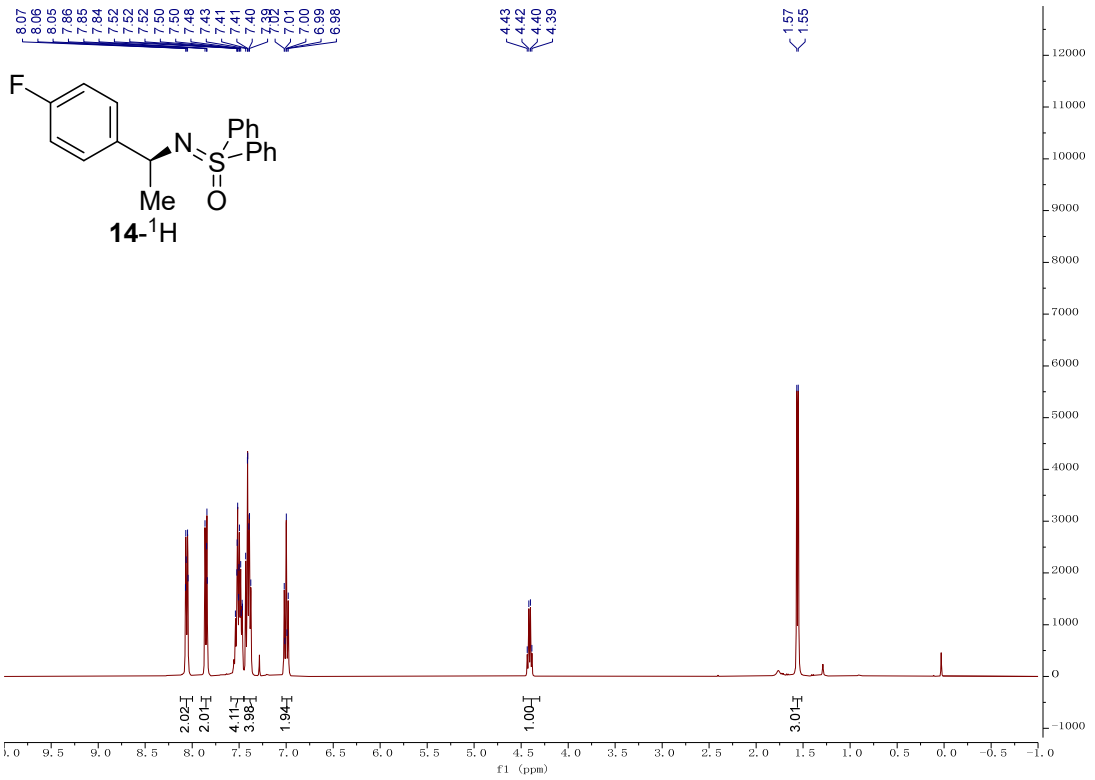

Me
O
N
S
Me
Me
Me
Me
11-13C
f1 (ppm)

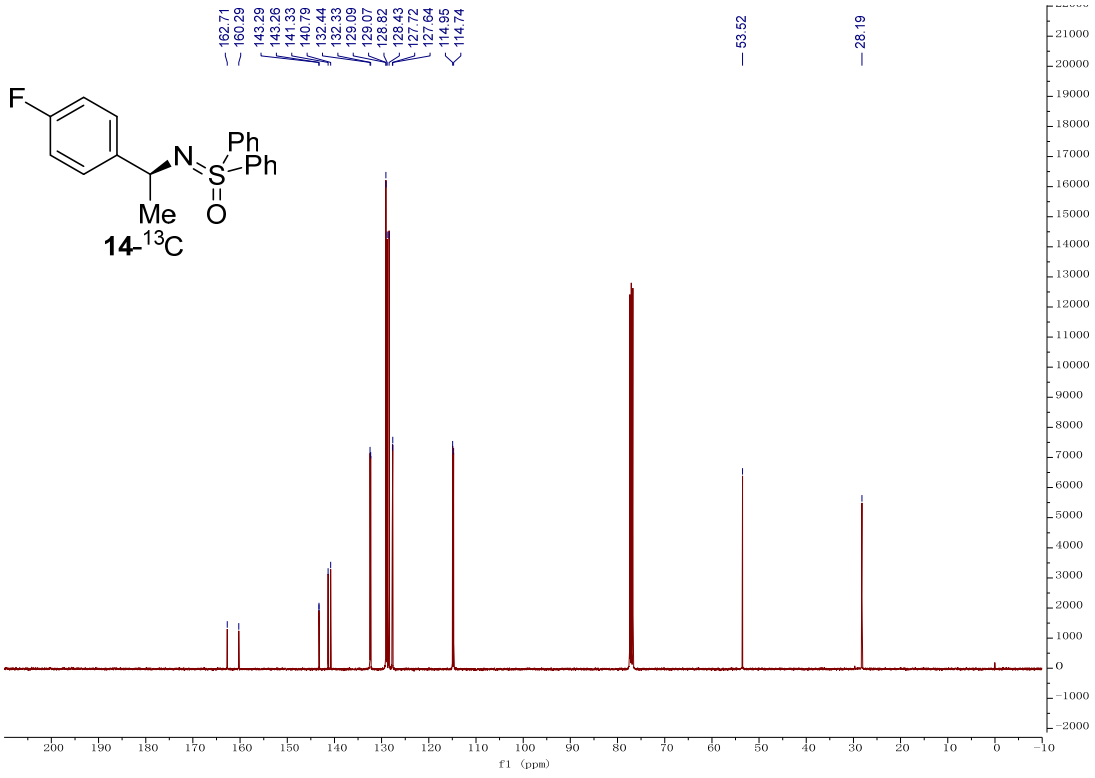

8.06 8.05 8.05 8.04 8.04 8.03 7.84 7.84 7.83 7.82 7.81 7.51 7.51 7.50 7.49 7.48 7.48 7.48 7.47 7.46 7.46 7.46 7.45 7.44 7.43 7.43 7.42 7.42 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.32 7.30 7.12 7.10 4.39 4.37 4.36 4.34
2.33
1.55 1.53
Me
N
S
Ph
Ph
O
Me
12-1H
2.05 2.00 4.16 2.00 1.94 1.93 1.03 3.01 2.99
f1 (ppm)

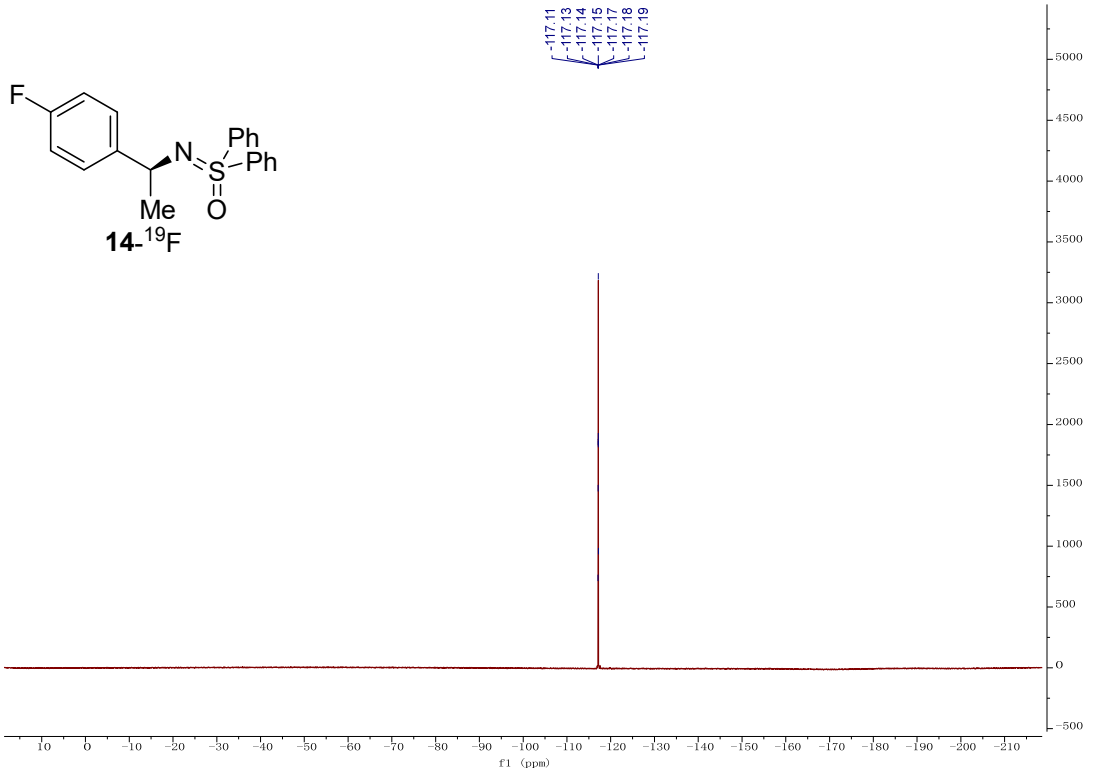

144.63 141.55 140.83 135.82 132.34 132.23 129.05 129.03 128.97 128.88 128.47 126.12
54.04
28.26
21.12
Me
N
S
Ph
Ph
O
Me
12-13C
f1 (ppm)


Me
Ph
N
S
Ph
Me
O
13-1H
f1 (ppm)

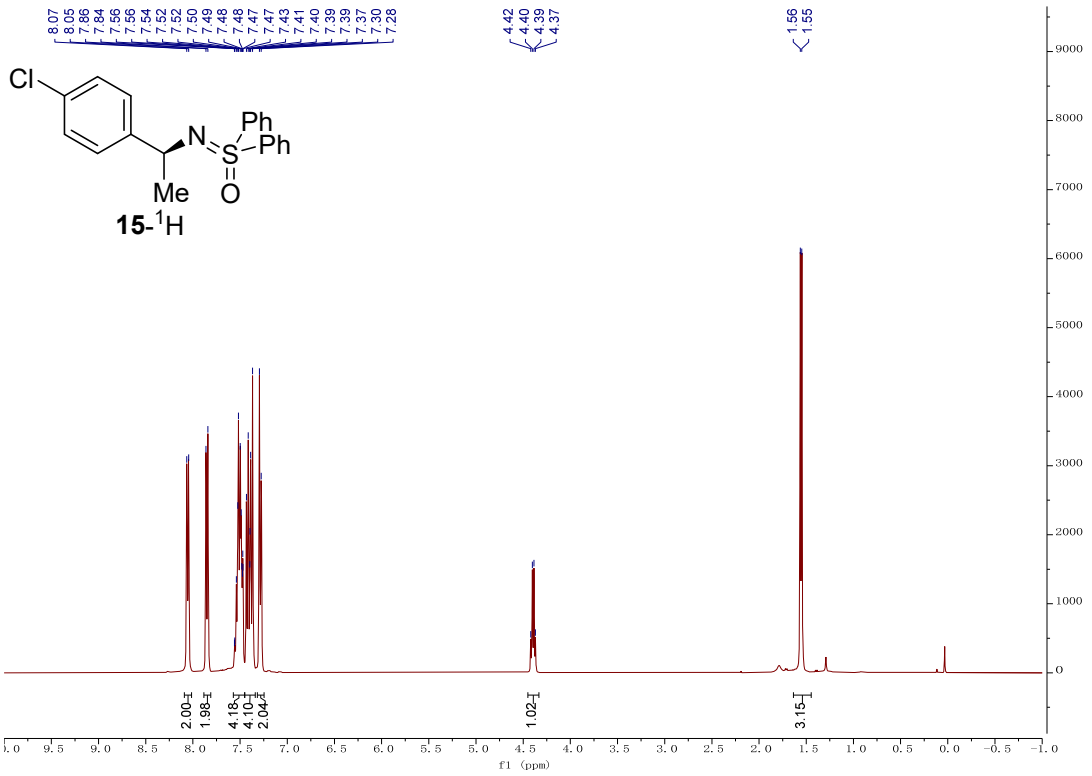

Me
Ph
N
S
Ph
Me
O
13-13C
f1 (ppm)

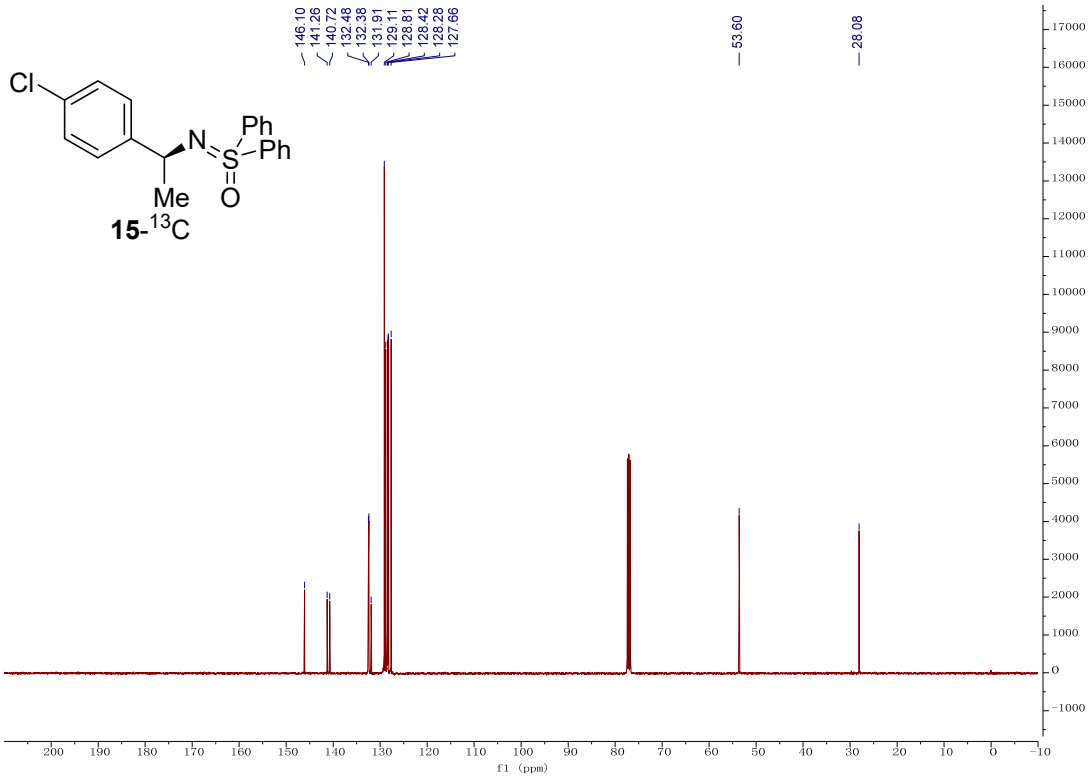

8.07
8.06
8.05
7.86
7.85
7.84
7.52
7.52
7.52
7.50
7.50
7.48
7.43
7.41
7.41
7.40
7.39
7.02
7.01
7.00
6.99
6.98
4.43
4.42
4.40
4.39
1.57
1.55
F
N
S
Ph
Ph
O
Me
14-1H
2.02
2.01
4.11
3.98
1.94
1.00
3.01
f1 (ppm)

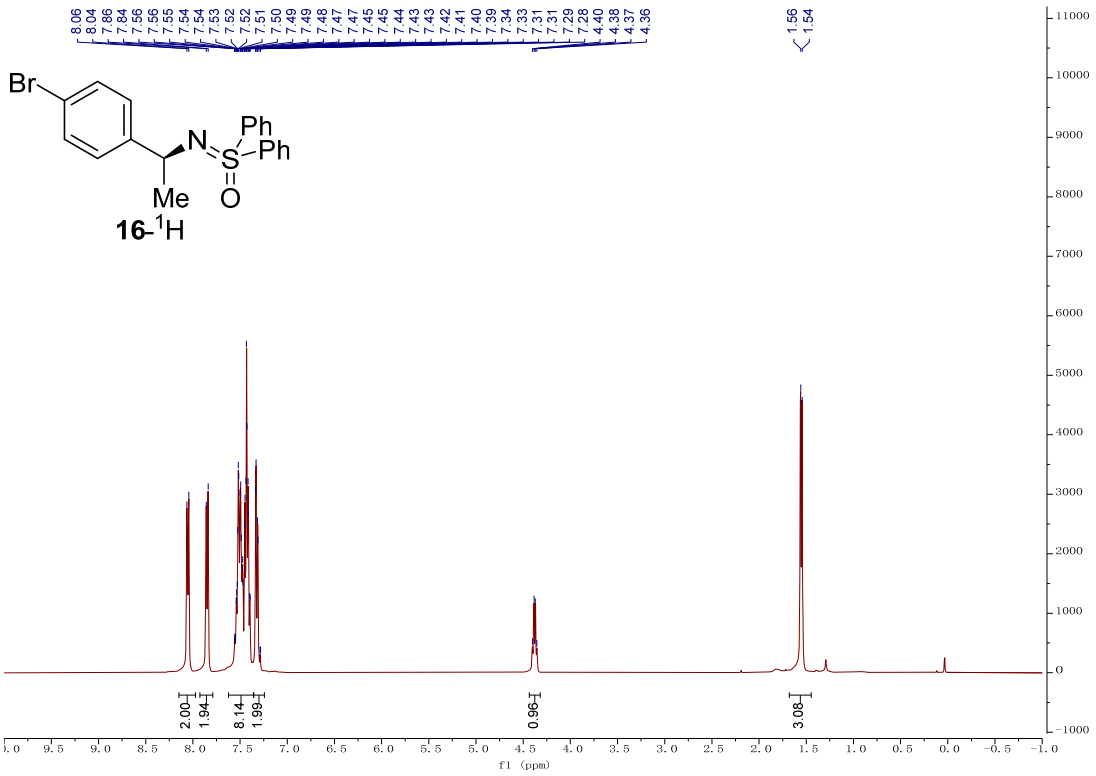

162.71
160.29
143.29
143.26
141.33
140.79
132.44
132.33
129.09
129.07
128.82
128.43
127.72
127.64
114.95
114.74
53.52
28.19
F
N
S
Ph
Ph
O
Me
14-13C
f1 (ppm)


F
N
S
Ph
Ph
O
Me
-117.11
-117.13
-117.14
-117.15
-117.17
-117.18
-117.19
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

14-^{19}F


8.07
8.05
7.86
7.84
7.56
7.54
7.52
7.52
7.50
7.49
7.48
7.48
7.47
7.47
7.43
7.41
7.40
7.39
7.39
7.37
7.30
7.28
4.42
4.40
4.39
4.37
1.56
1.55
Cl
N
S
Ph
Ph
O
Me
15-1H
2.00
1.98
4.18
4.10
2.04
1.02
3.15
f1 (ppm)


146.10
141.26
140.72
132.48
132.38
131.91
129.11
128.81
128.42
128.28
127.66
53.60
28.08
Cl
N
S
Ph
Ph
O
Me
15-13C
f1 (ppm)


8.06
8.04
7.86
7.84
7.56
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.49
7.49
7.48
7.47
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7.41
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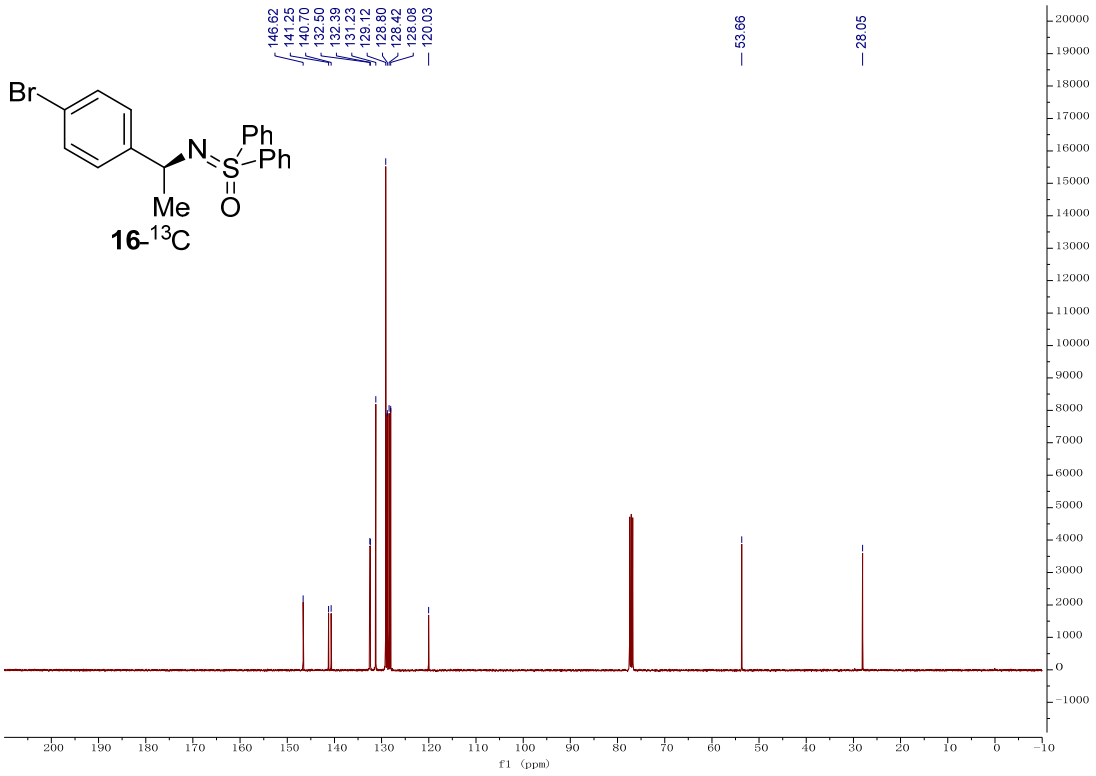
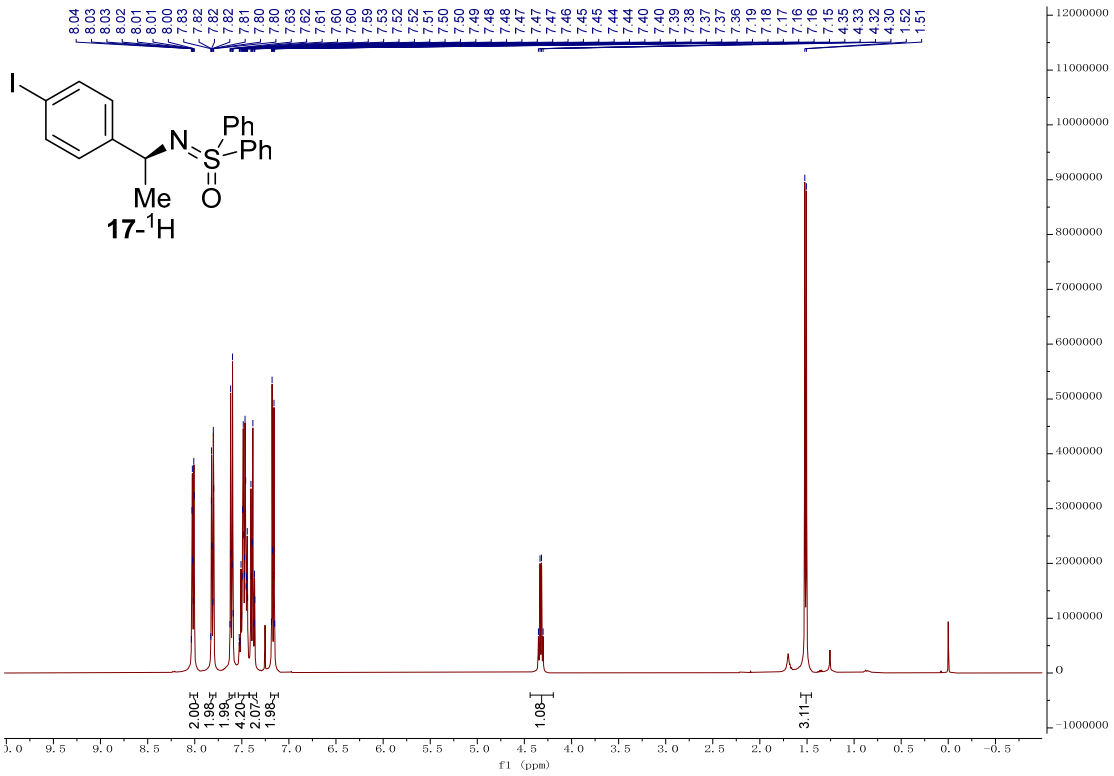
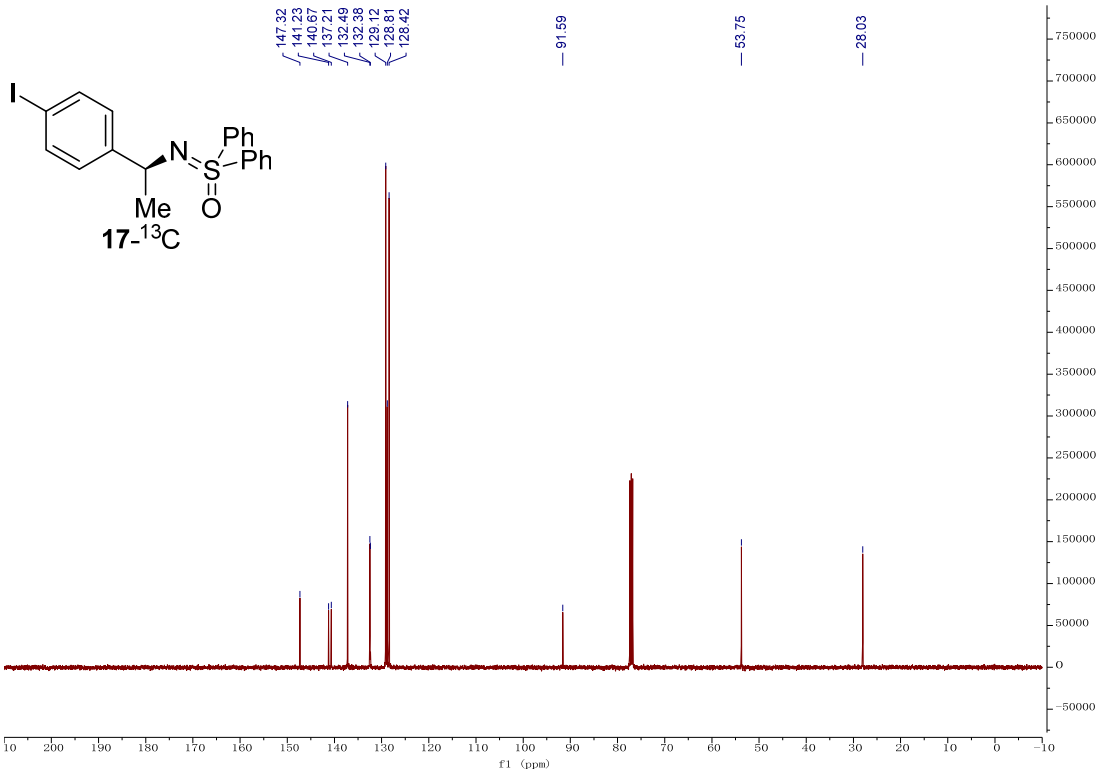
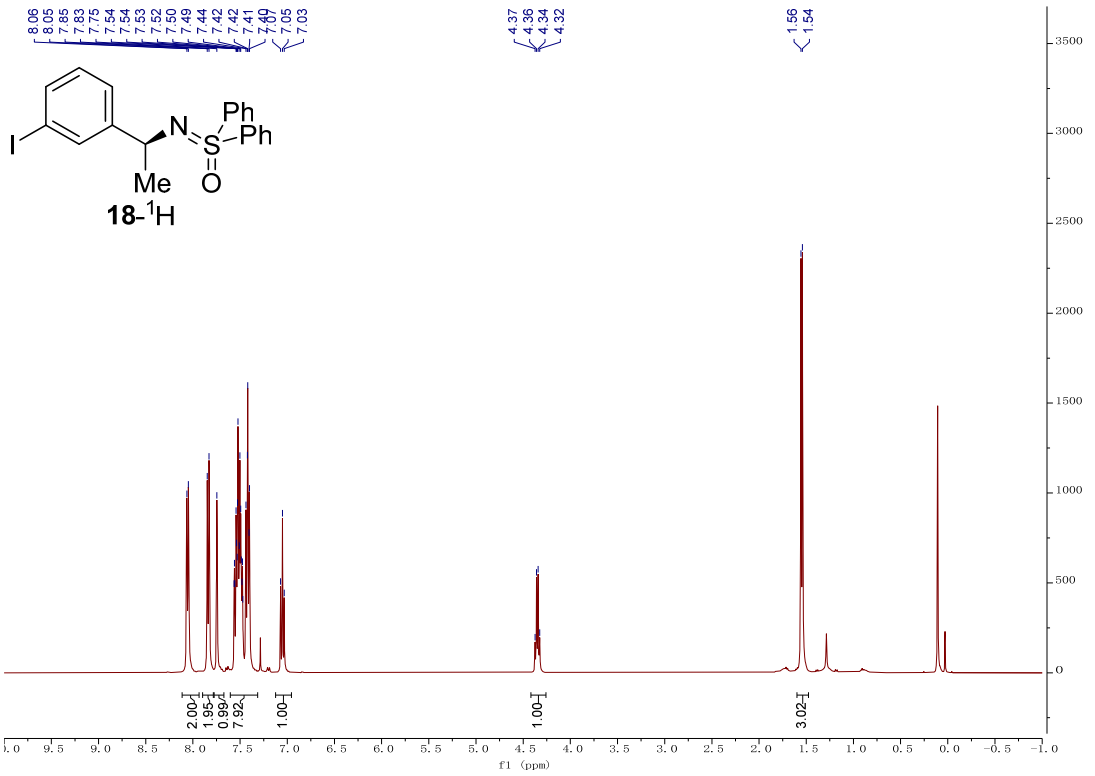
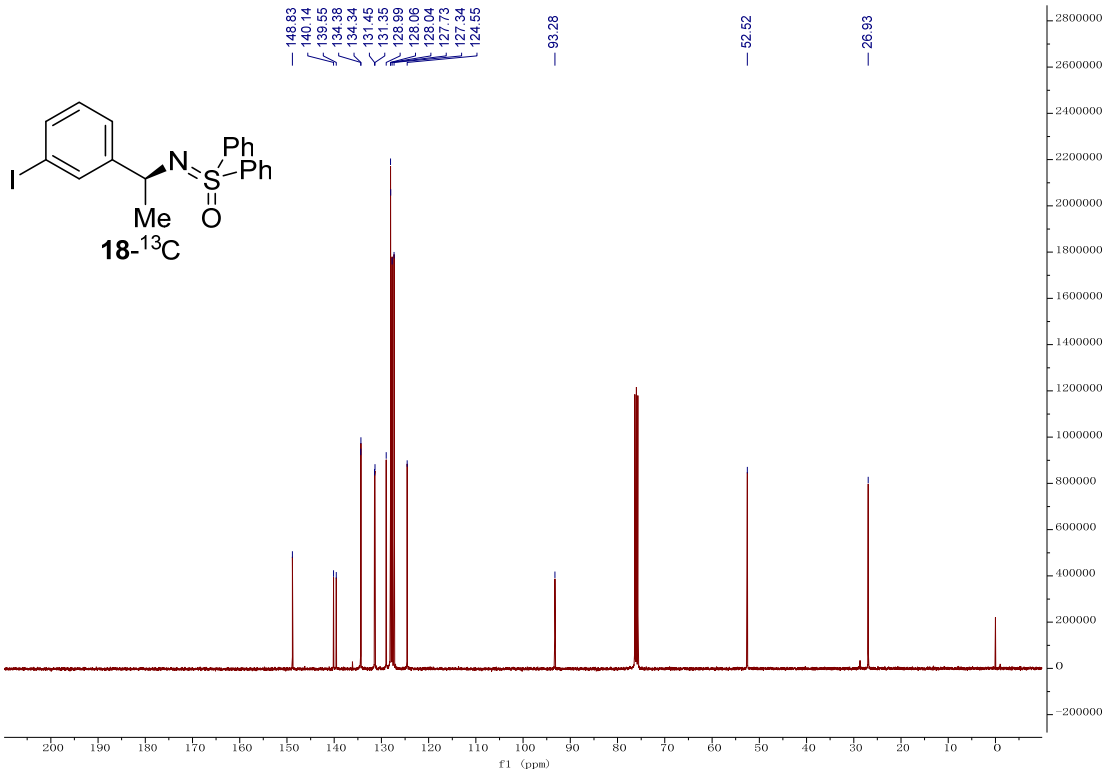
7.39
7.34
7.33
7.31
7.31
7.29
7.28
4.40
4.38
4.37
4.36
1.56
1.54
Br
N
S
Ph
Ph
O
Me
16-1H
2.00
1.94
8.14
1.99
0.96
3.08
f1 (ppm)

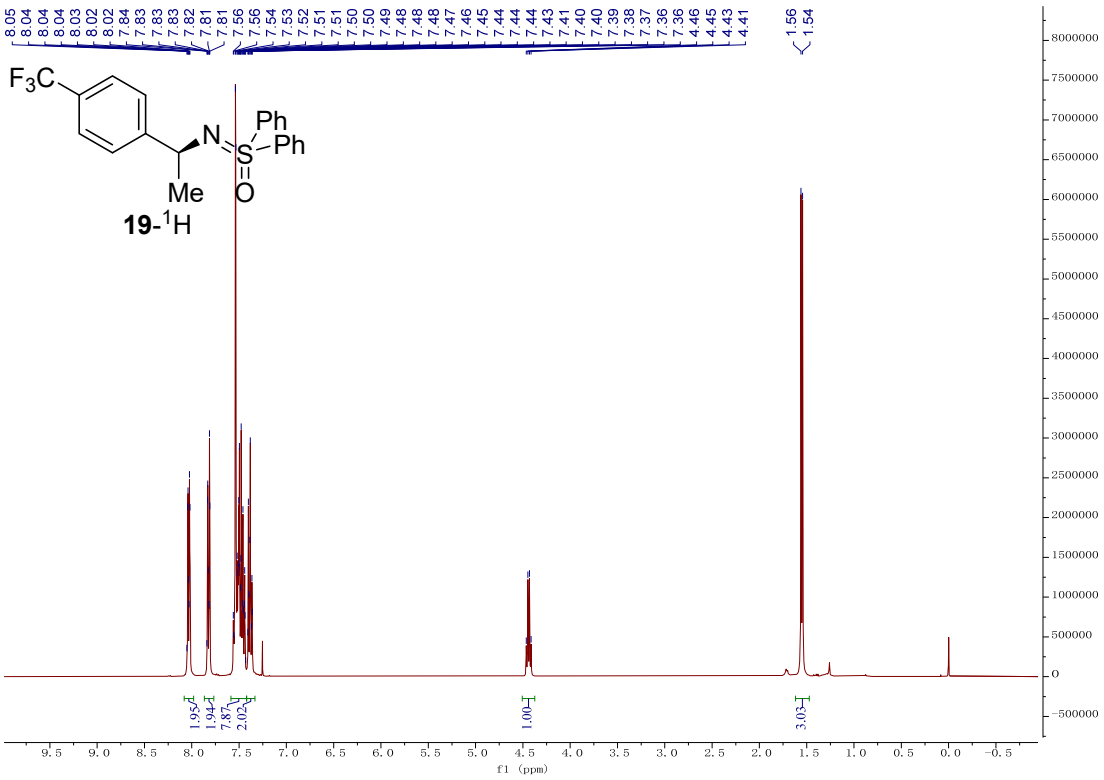

146.62
141.25
140.70
132.50
132.39
131.23
129.12
128.80
128.42
128.08
120.03
53.66
28.05
Br
N
S
Ph
Ph
O
Me
16-13C
f1 (ppm)

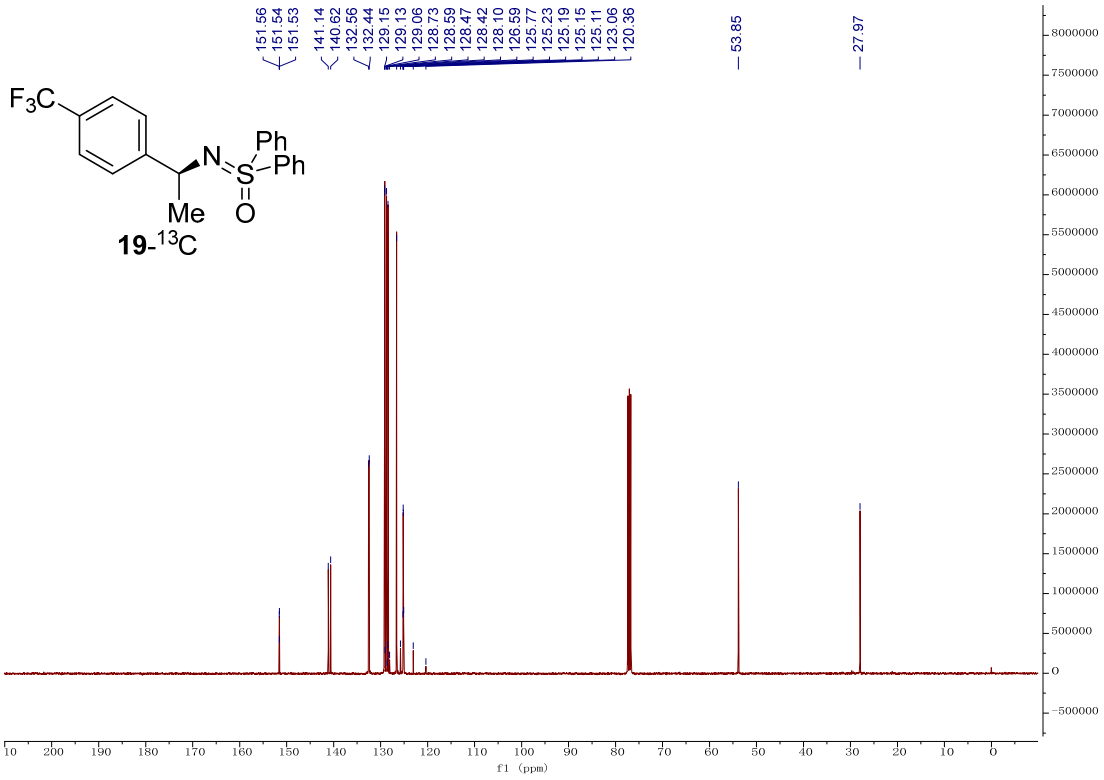

8.04 8.03 8.03 8.02 8.01 8.01 8.00 7.83 7.82 7.82 7.81 7.80 7.80 7.63 7.62 7.61 7.60 7.60 7.59 7.53 7.52 7.52 7.51 7.50 7.50 7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.45 7.45 7.44 7.44 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.19 7.18 7.17 7.16 7.16 7.15 4.35 4.33 4.32 4.30 1.52 1.51
I
N
S
Ph
Ph
O
Me
17-1H
2.00 1.98 1.99 4.20 2.07 1.98 1.08 3.11
f1 (ppm)

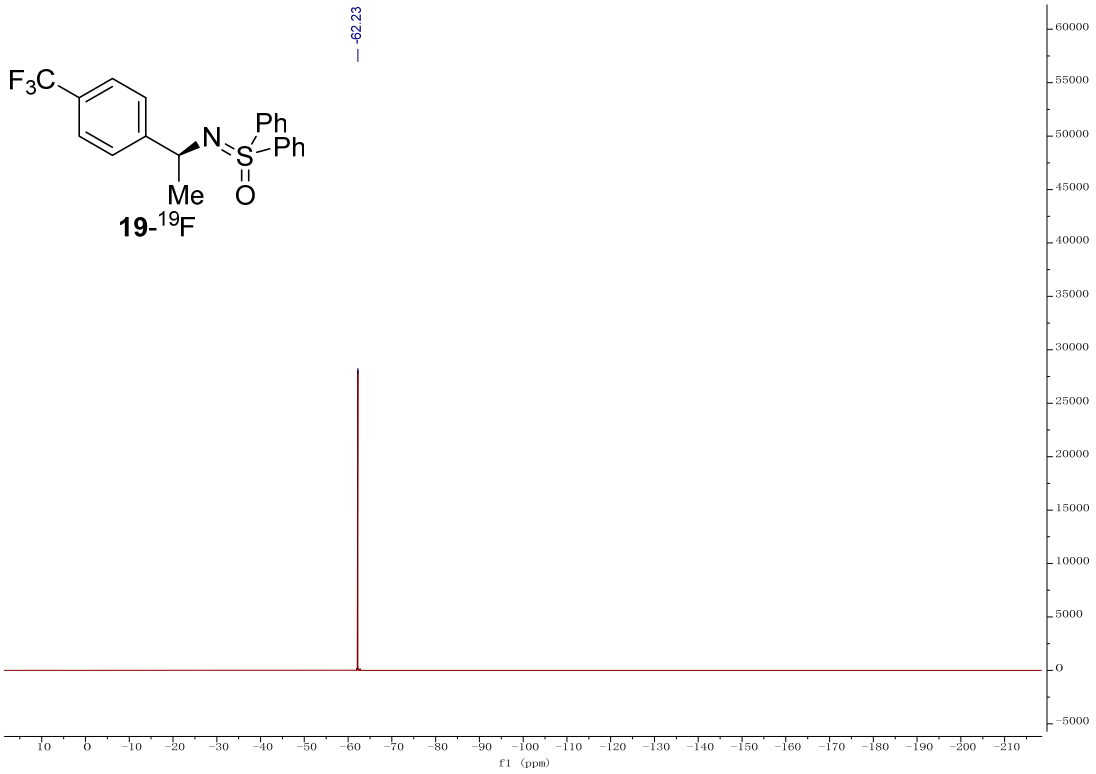

147.32 141.23 140.67 137.21 132.49 132.38 129.12 128.81 128.42 91.59 53.75 28.03
I
N
S
Ph
Ph
O
Me
17-13C
f1 (ppm)

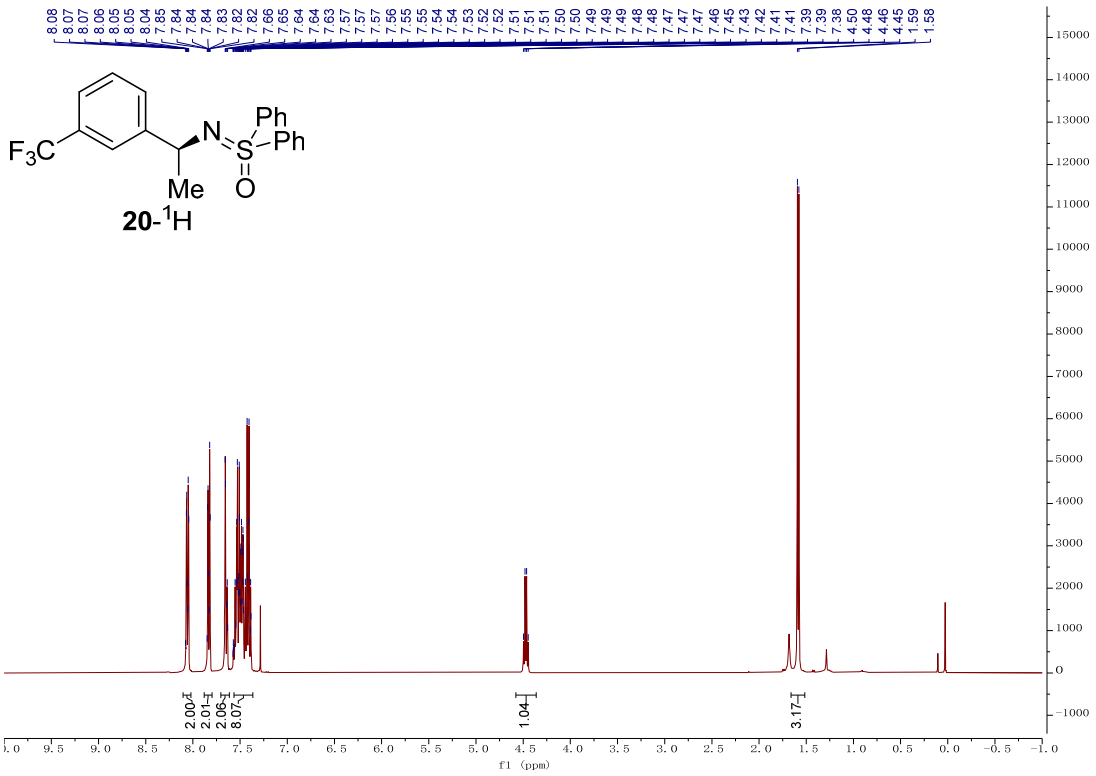

8.06
8.05
7.85
7.83
7.75
7.54
7.54
7.53
7.52
7.50
7.49
7.44
7.42
7.42
7.41
7.40
7.07
7.05
7.03
4.37
4.36
4.34
4.32
1.56
1.54
Ph
Ph
N
S
O
I
Me
18-1H
2.00
1.95
0.99
7.92
1.00
1.00
3.02
f1 (ppm)

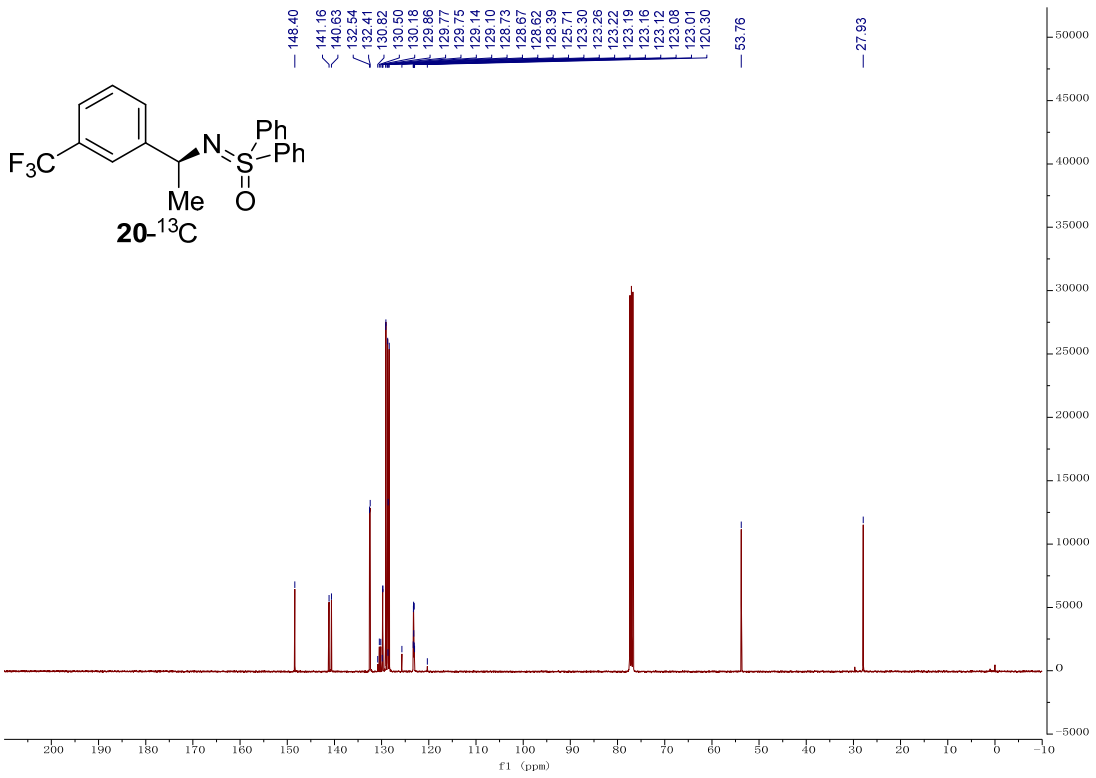

148.83
140.14
139.55
134.38
134.34
131.45
131.35
128.99
128.06
128.04
127.73
127.34
124.55
93.28
52.52
26.93
Ph
Ph
N
S
O
I
Me
18-13C
f1 (ppm)

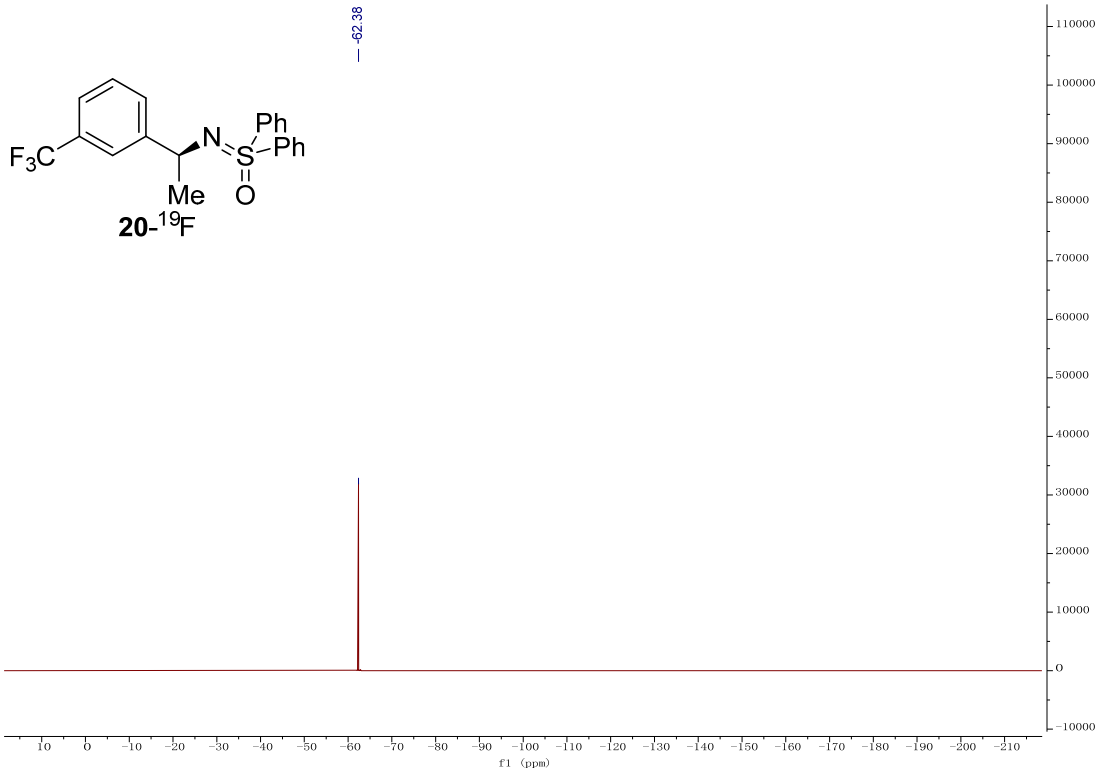

8.05 8.04 8.04 8.04 8.03 8.02 8.02 7.84 7.83 7.83 7.82 7.81 7.81 7.56 7.56 7.54 7.53 7.52 7.51 7.51 7.50 7.50 7.49 7.48 7.48 7.48 7.47 7.46 7.45 7.44 7.44 7.44 7.43 7.41 7.40 7.40 7.39 7.38 7.37 7.36 7.36 4.46 4.45 4.43 4.41 1.56 1.54
F3C
N
S
Ph
Ph
O
Me
19-1H
1.95 1.94 7.87 2.02 1.00 3.03
f1 (ppm)

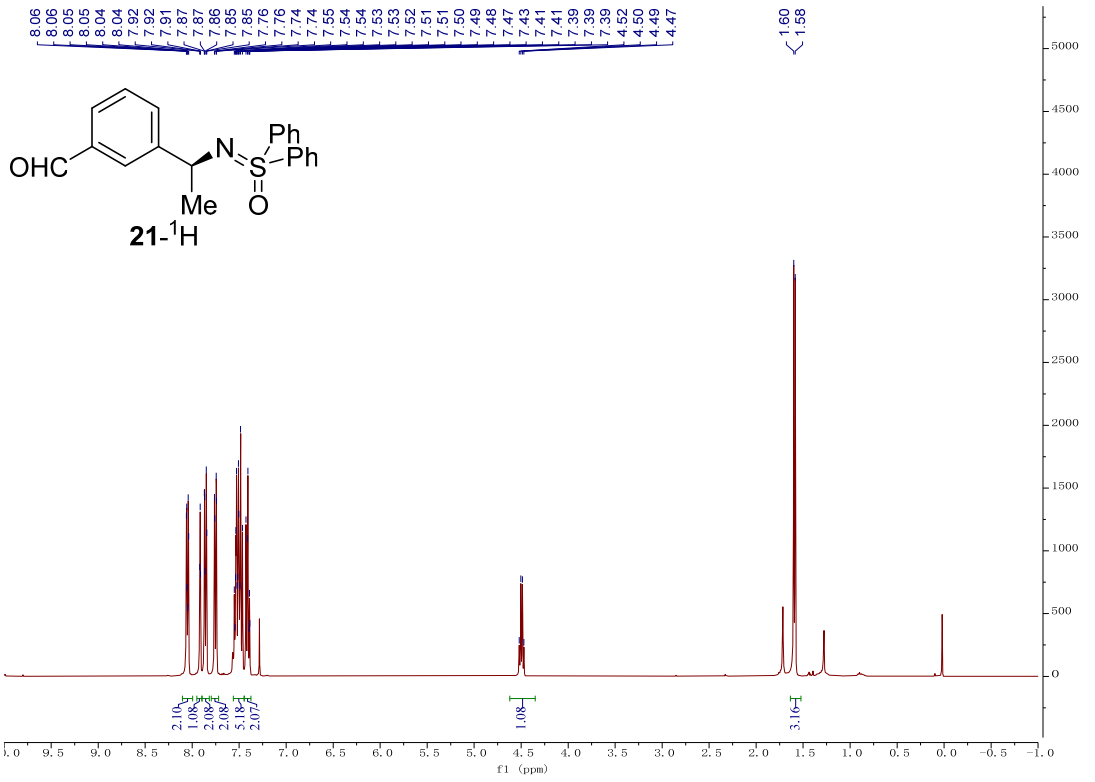

151.56 151.54 151.53 141.14 140.62 132.56 132.44 129.15 129.13 129.06 128.73 128.59 128.47 128.42 128.10 126.59 125.77 125.23 125.19 125.15 125.11 123.06 120.36 53.85 27.97
F3C
N
S
Ph
Ph
O
Me
19-13C
f1 (ppm)

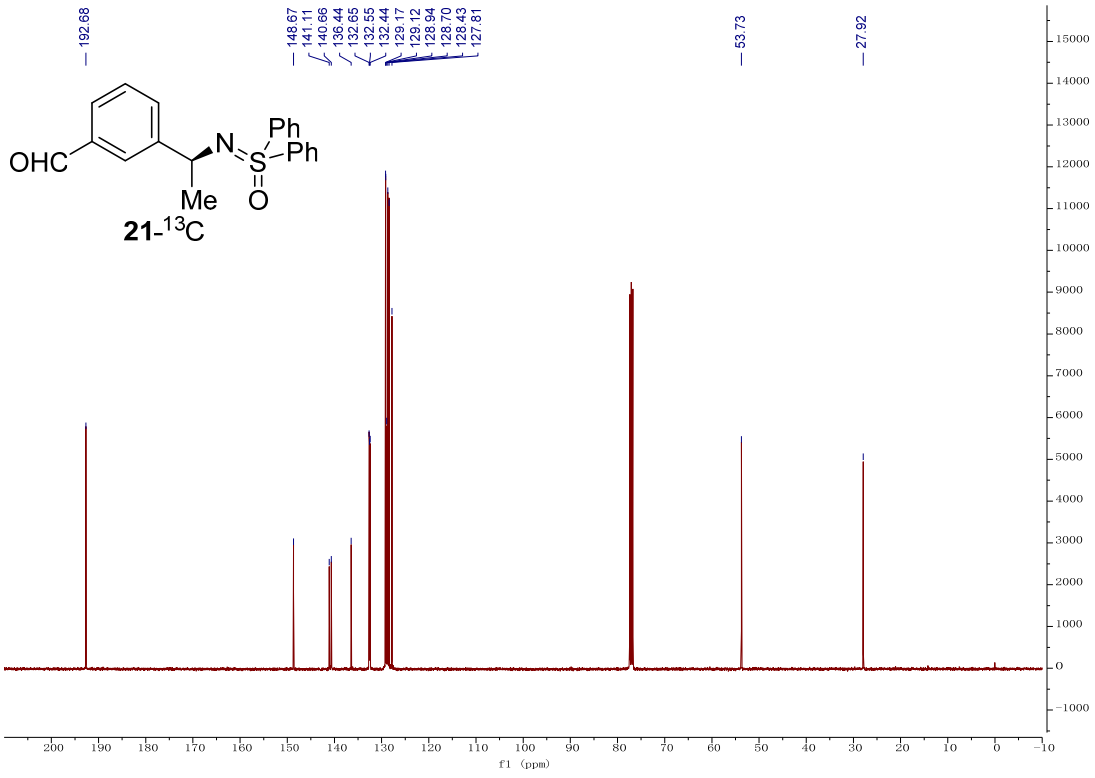

F3C
N
S
Ph
Ph
O
Me
19-19F
-62.23
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.08 8.07 8.07 8.06 8.05 8.05 8.04 7.85 7.84 7.84 7.84 7.83 7.82 7.82 7.66 7.65 7.64 7.64 7.63 7.57 7.57 7.57 7.56 7.55 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.45 7.43 7.42 7.41 7.41 7.39 7.39 7.38 4.50 4.48 4.46 4.45 1.59 1.58
F3C
N
S
Ph
Ph
O
Me
20-1H
2.00
2.01
2.06
8.07
1.04
3.17
f1 (ppm)


148.40 141.16 140.63 132.54 132.41 130.82 130.50 130.18 129.86 129.77 129.75 129.14 129.10 128.73 128.67 128.62 128.39 125.71 123.30 123.26 123.22 123.19 123.16 123.12 123.08 123.01 120.30 53.76 27.93
F3C
N
S
Ph
Ph
O
Me
20-13C
f1 (ppm)


-62.38
Ph
Ph
N
S
O
F3C
Me
20-19F
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.06
8.06
8.05
8.05
8.04
8.04
7.92
7.92
7.91
7.87
7.87
7.86
7.85
7.85
7.76
7.76
7.74
7.74
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.48
7.47
7.43
7.41
7.41
7.39
7.39
4.52
4.50
4.49
4.47
1.60
1.58
OHC
N
S
Ph
Ph
O
Me
21-1H
2.10
1.08
2.08
2.08
5.18
2.07
1.08
3.16
f1 (ppm)


192.68
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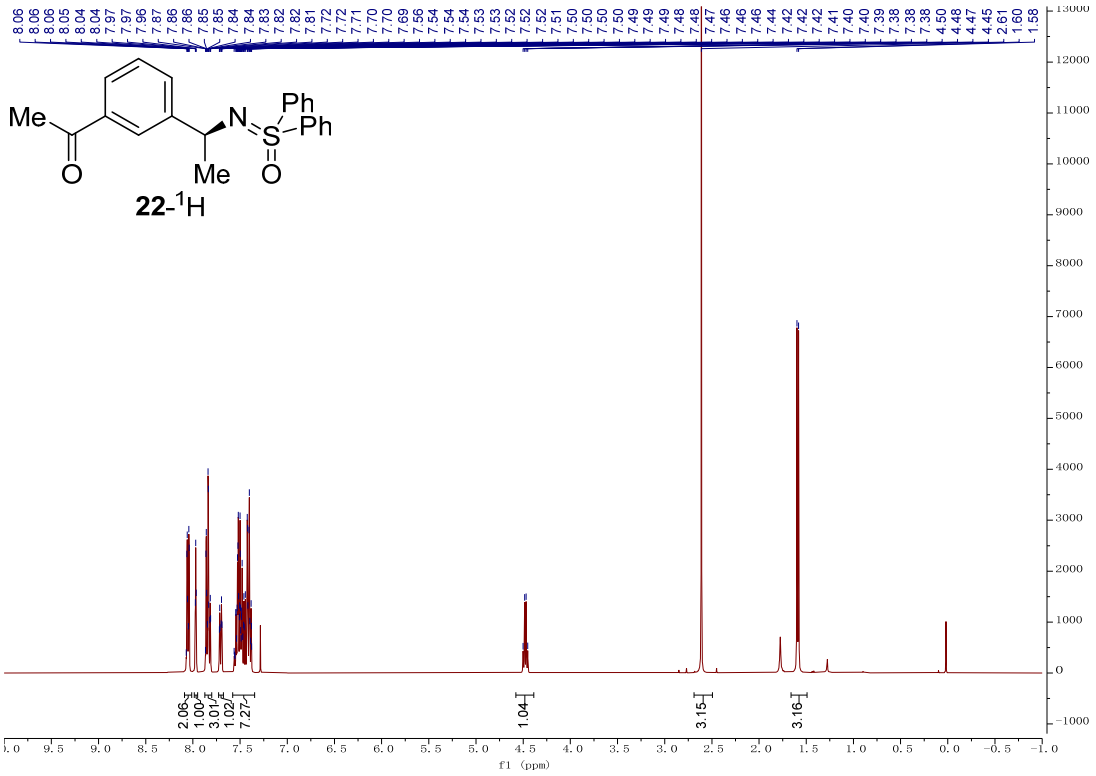
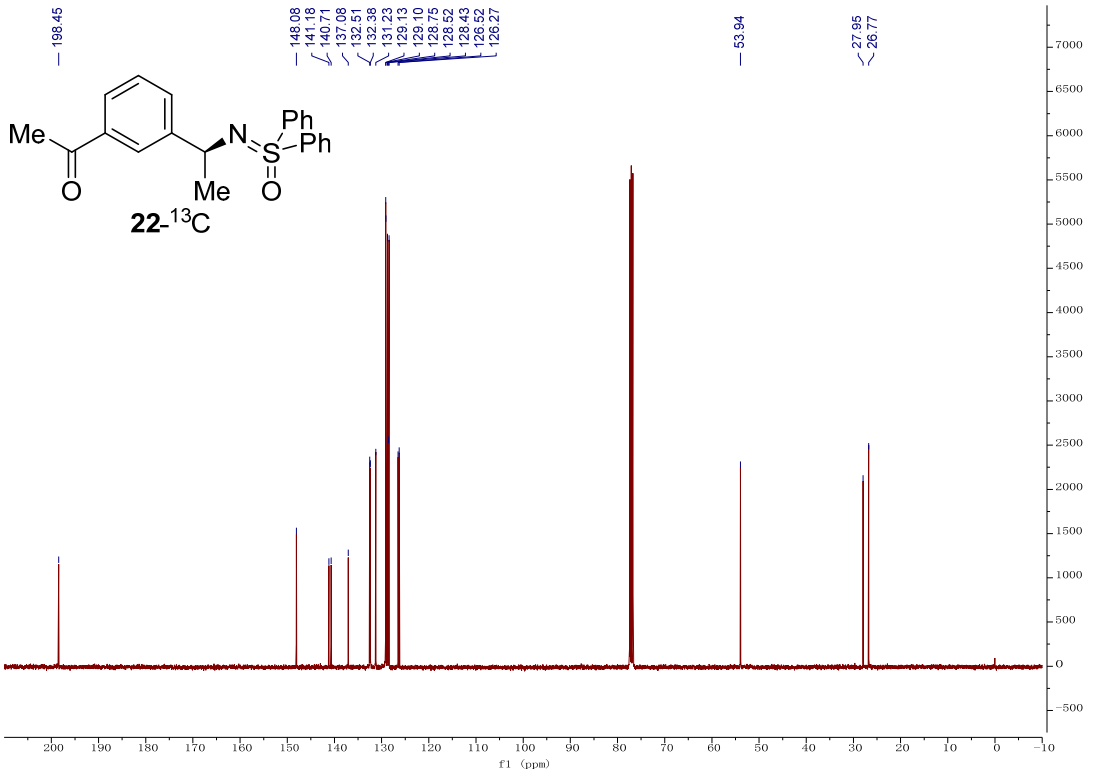
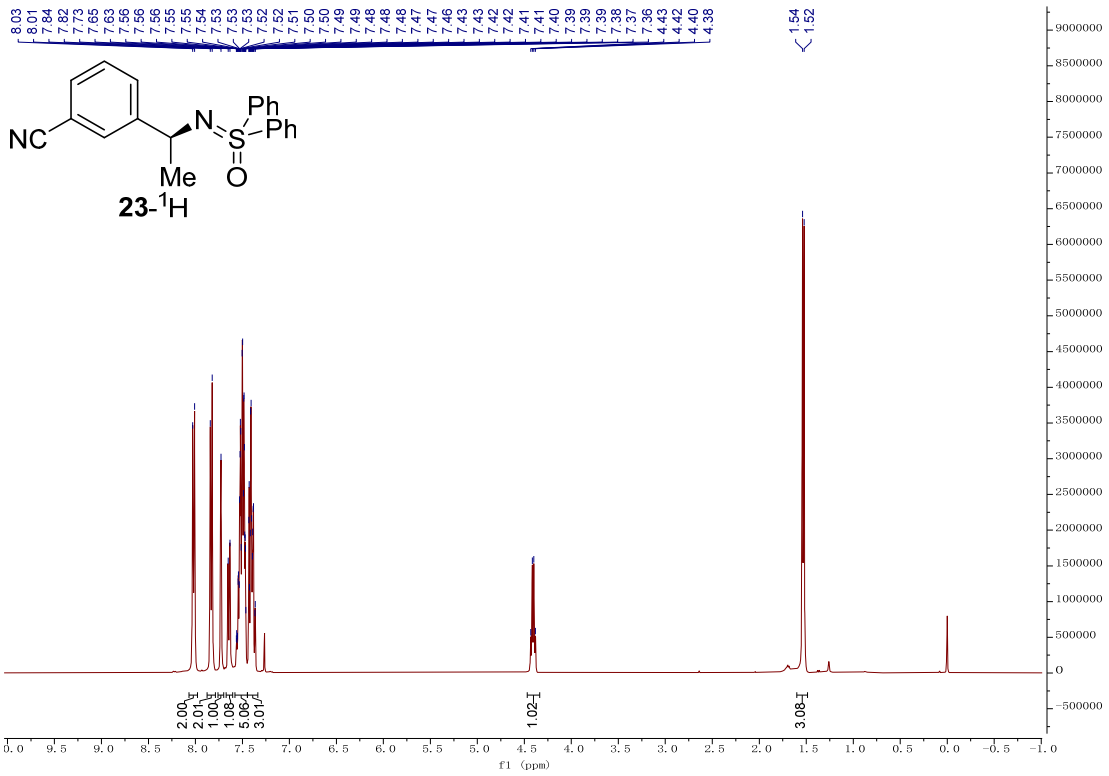
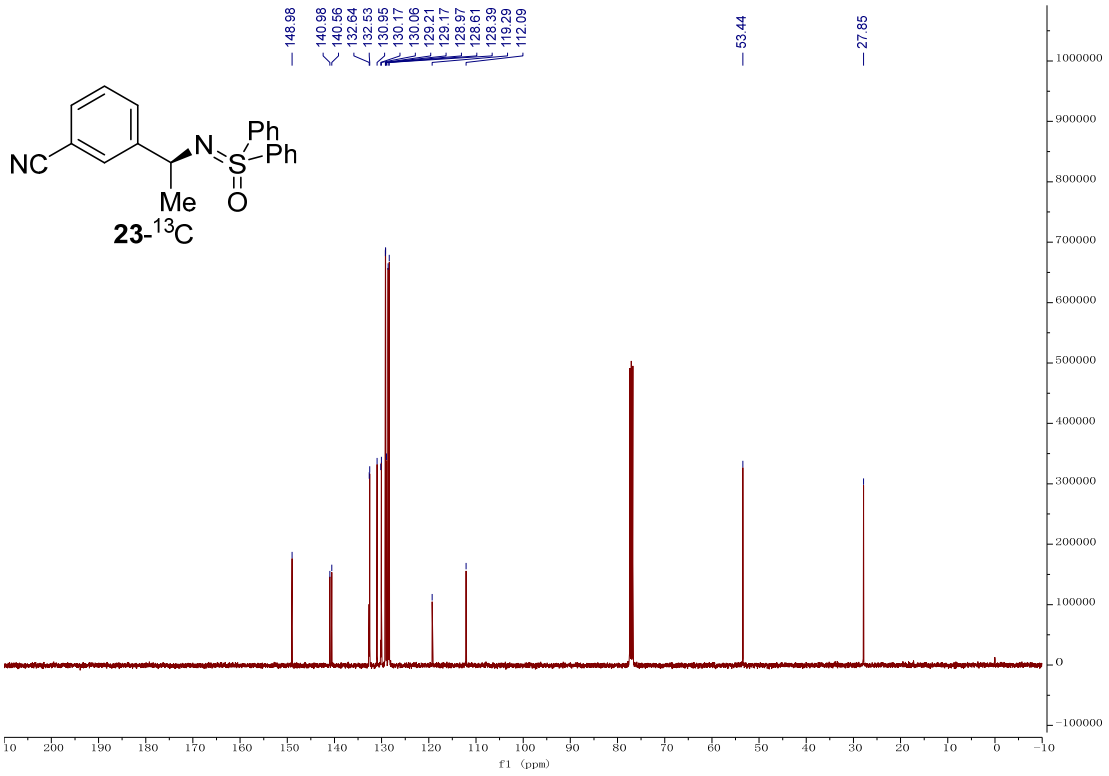
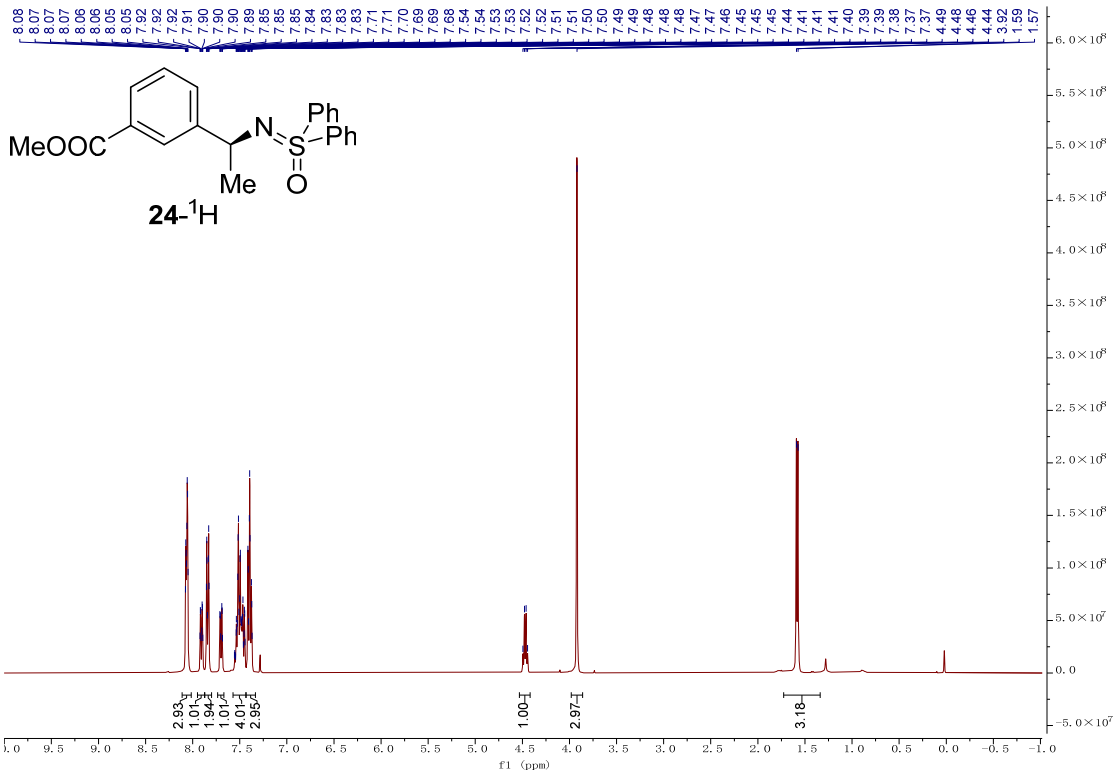
141.11
140.66
136.44
132.65
132.55
132.44
129.17
129.12
128.94
128.70
128.43
127.81
53.73
27.92
OHC
N
S
Ph
Ph
O
Me
21-13C
f1 (ppm)

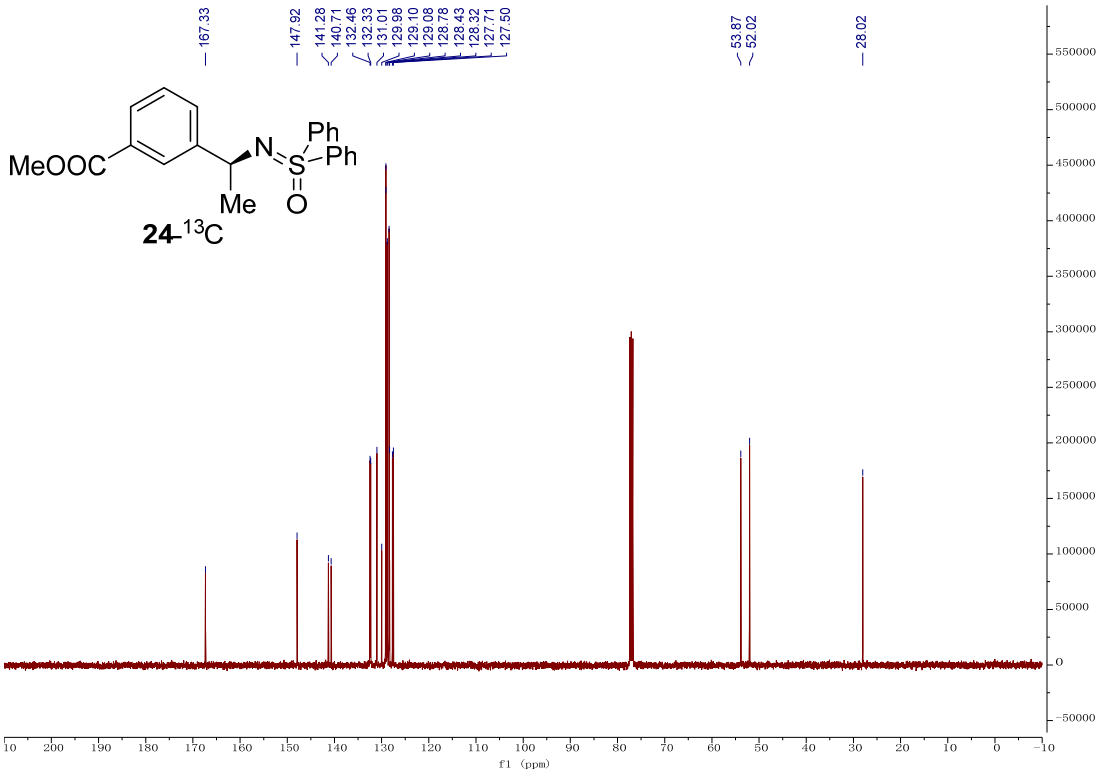

Me
O
N
S
Ph
Ph
O
Me
22-1H
f1 (ppm)

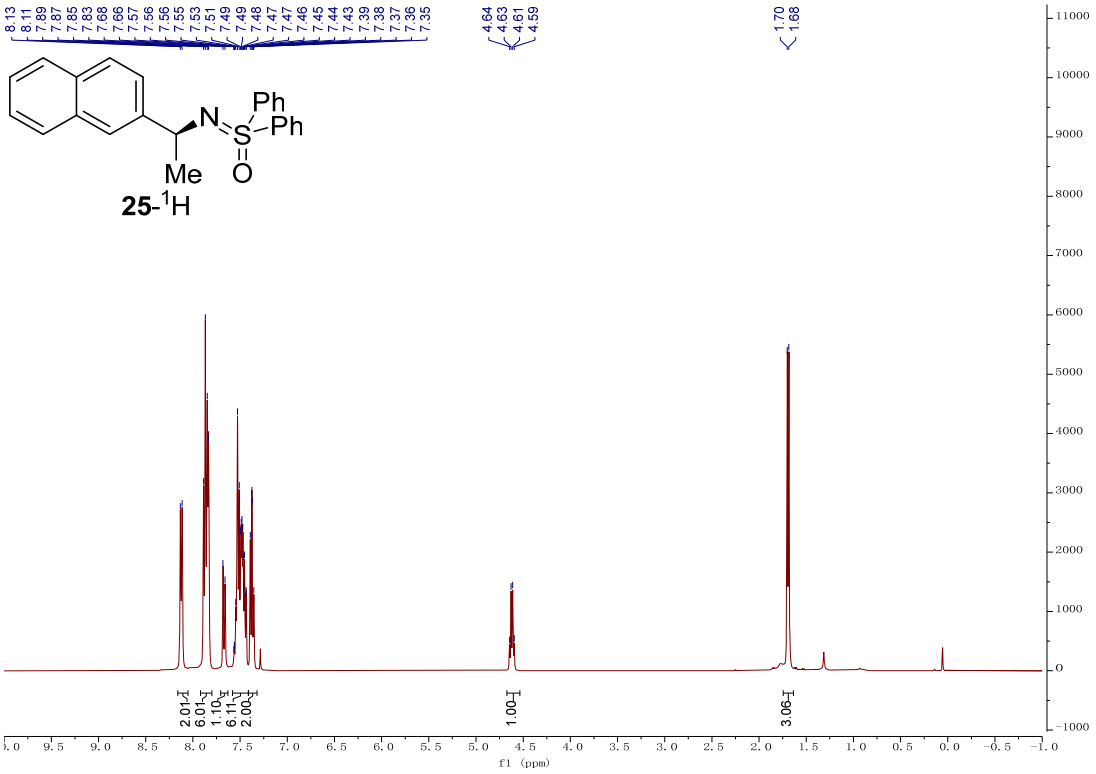

Me
O
N
S
Ph
Ph
O
Me
22-13C
f1 (ppm)


8.03 8.01 7.84 7.82 7.73 7.65 7.63 7.56 7.56 7.56 7.55 7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.46 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.37 7.36 4.43 4.42 4.40 4.38
1.54 1.52
NC
N
S
Ph
Ph
O
Me
23-1H
2.00 2.01 1.00 1.08 5.06 3.01
1.02
3.08
f1 (ppm)


148.98 140.98 140.56 132.64 132.53 130.95 130.17 130.06 129.21 129.17 128.97 128.61 128.39 119.29 112.09
53.44
27.85
NC
N
S
Ph
Ph
O
Me
23-13C
f1 (ppm)


MeOOC
N
S
Ph
Ph
O
Me
24-1H
f1 (ppm)


MeOOC
N
S
Ph
Ph
O
Me
24-13C
f1 (ppm)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8.11
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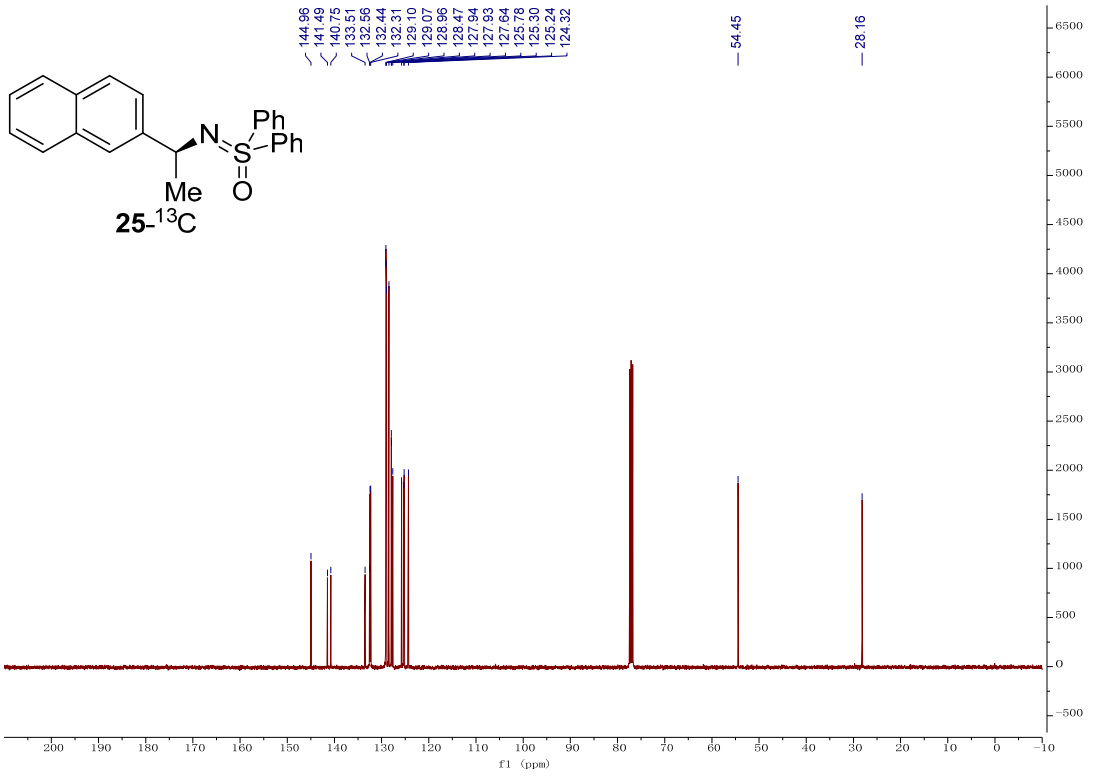
7.87
7.85
7.83
7.68
7.66
7.57
7.56
7.56
7.55
7.53
7.51
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.39
7.38
7.37
7.36
7.35
4.64
4.63
4.61
4.59
1.70
1.68
Ph
N
S
Ph
O
Me
25-1H
2.01
6.01
1.10
6.11
2.00
1.00
3.06
f1 (ppm)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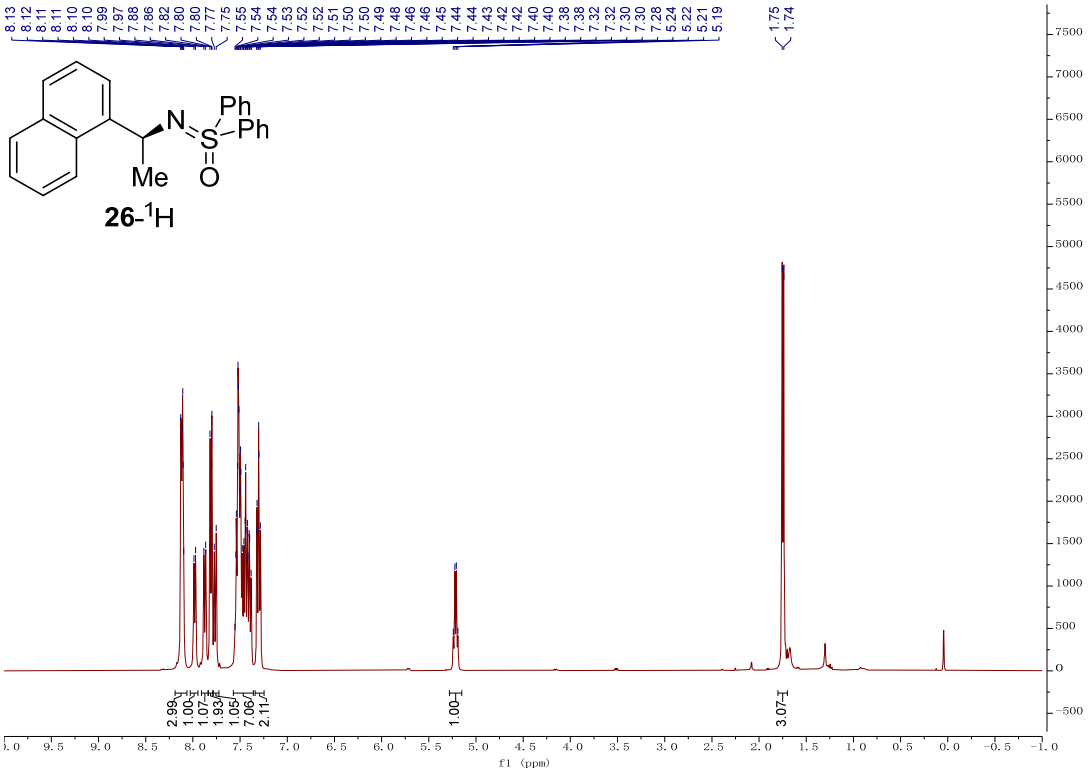
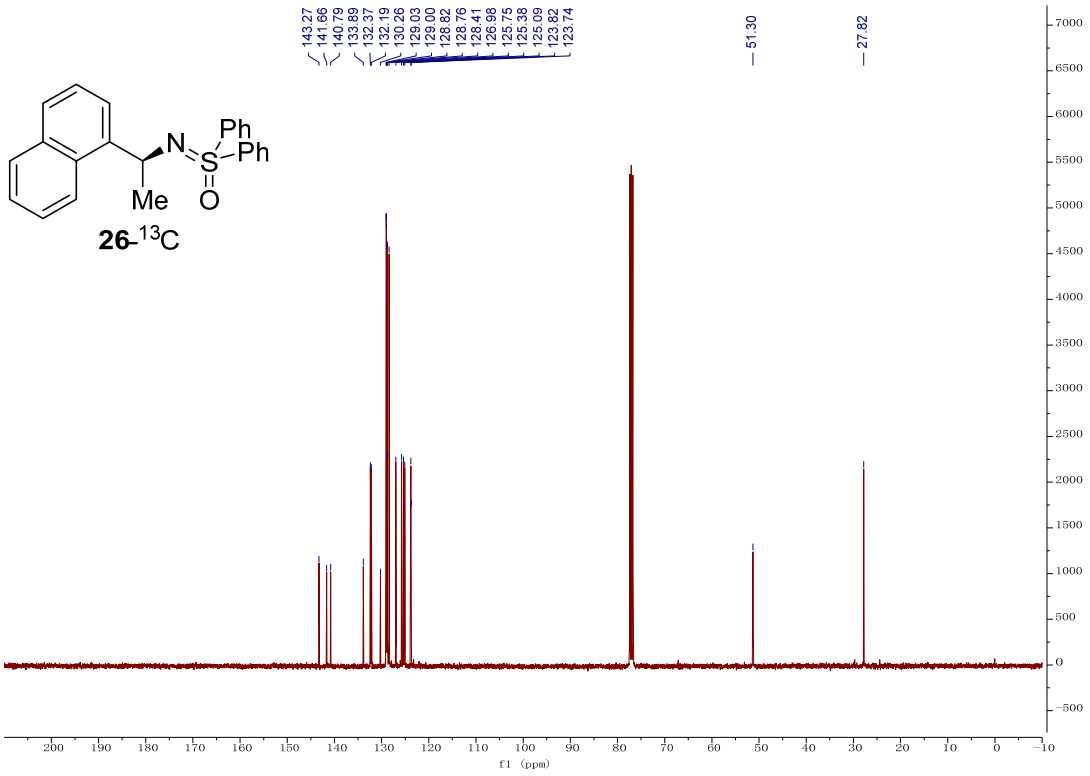
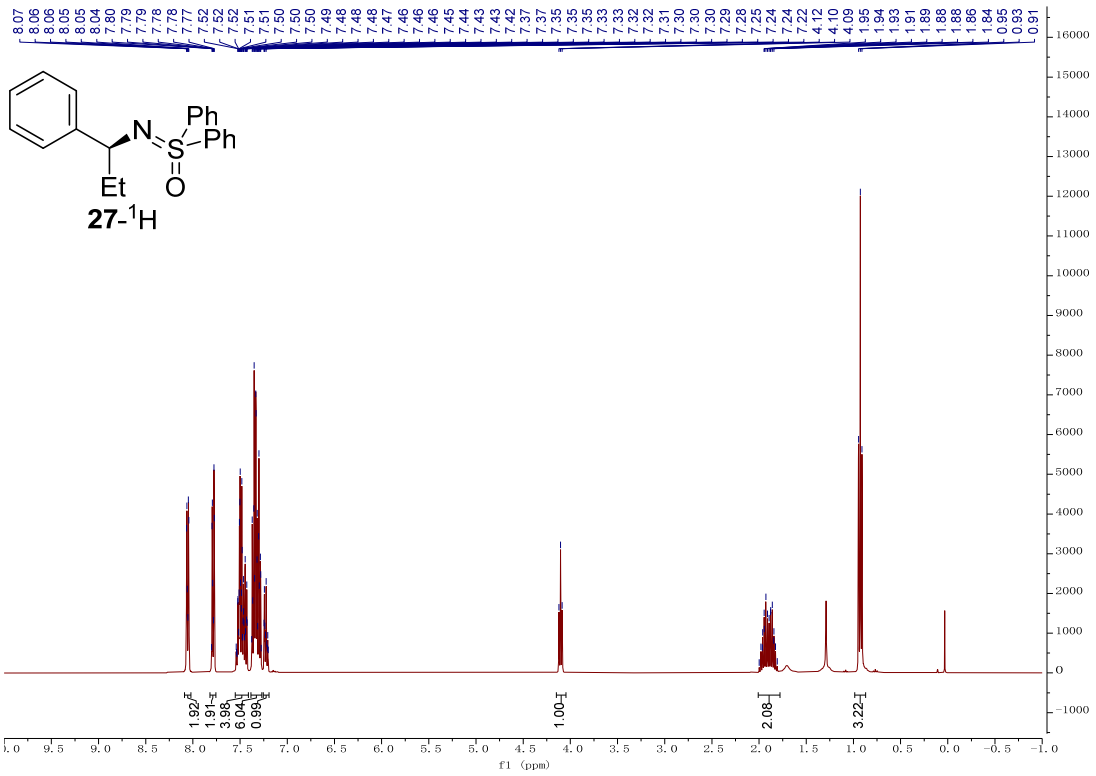
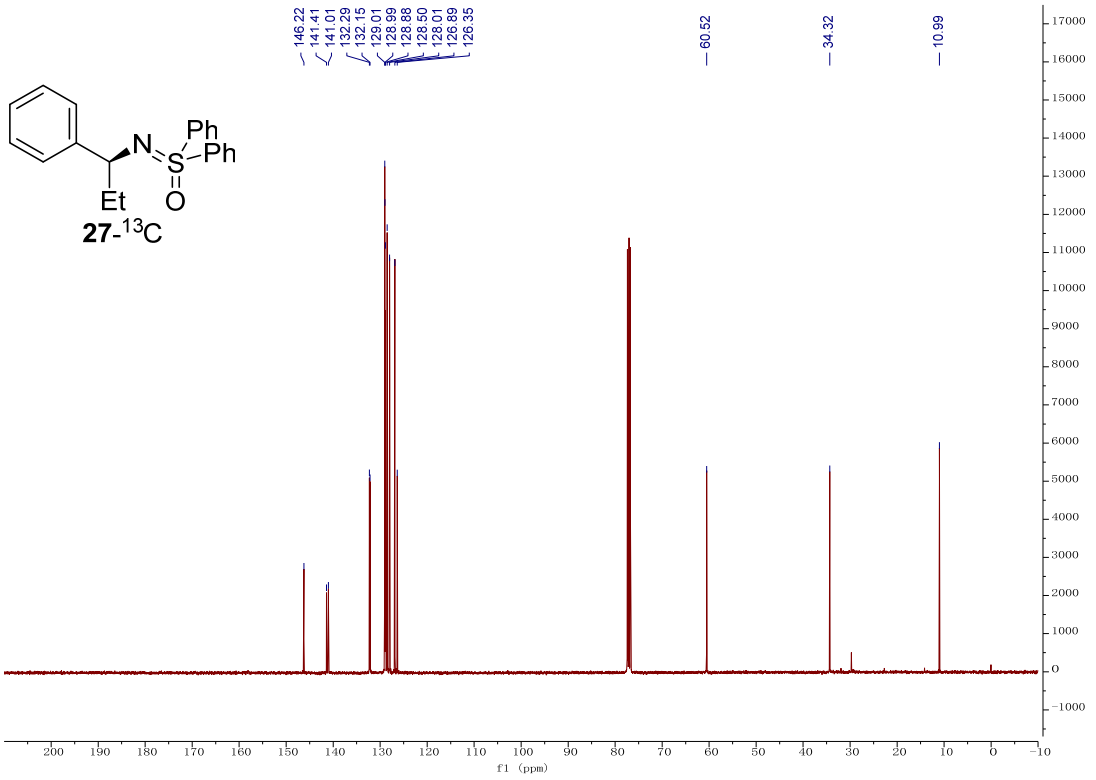
141.49
140.75
133.51
132.56
132.44
132.31
129.10
129.07
128.96
128.47
127.94
127.93
127.64
125.78
125.30
125.24
124.32
54.45
28.16
Ph
N
S
Ph
O
Me
25-13C
f1 (ppm)


Ph
Ph
N
S
O
Me
26-1H
f1 (ppm)


Ph
Ph
N
S
O
Me
26-13C
f1 (ppm)


Ph
Ph
N
S
O
Et
27-1H
f1 (ppm)


Ph
Ph
N
S
O
Et
27-13C
146.22
141.41
141.01
132.29
132.15
129.01
128.99
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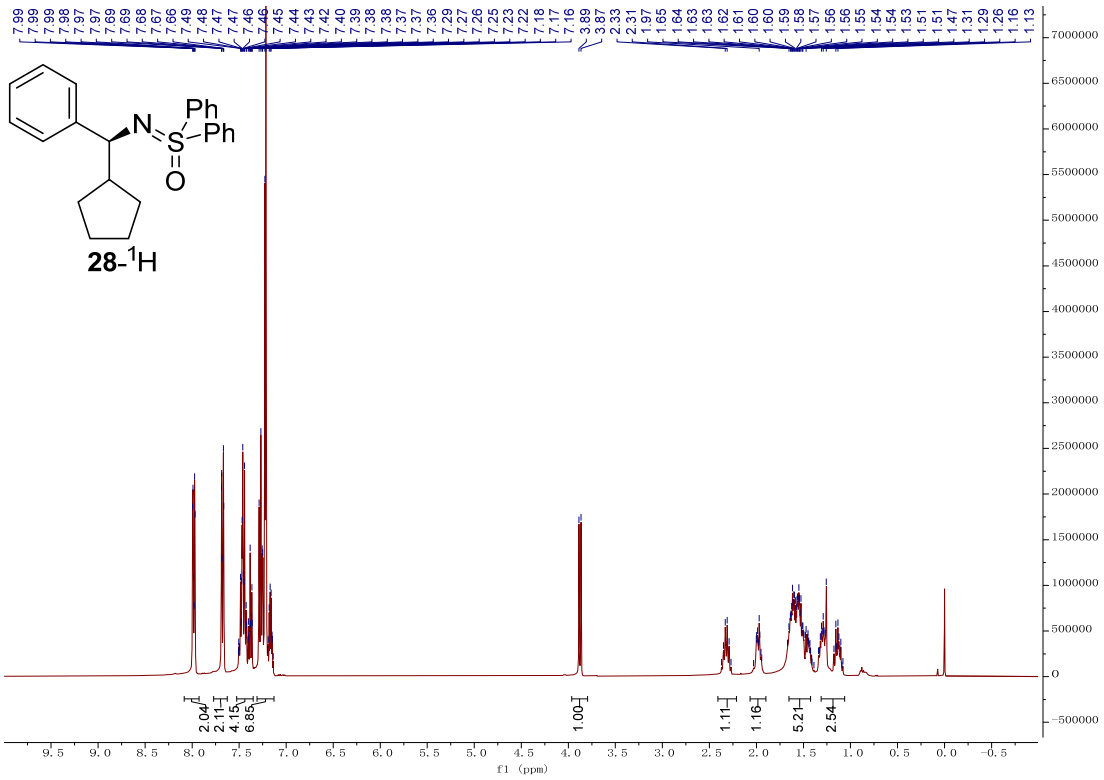
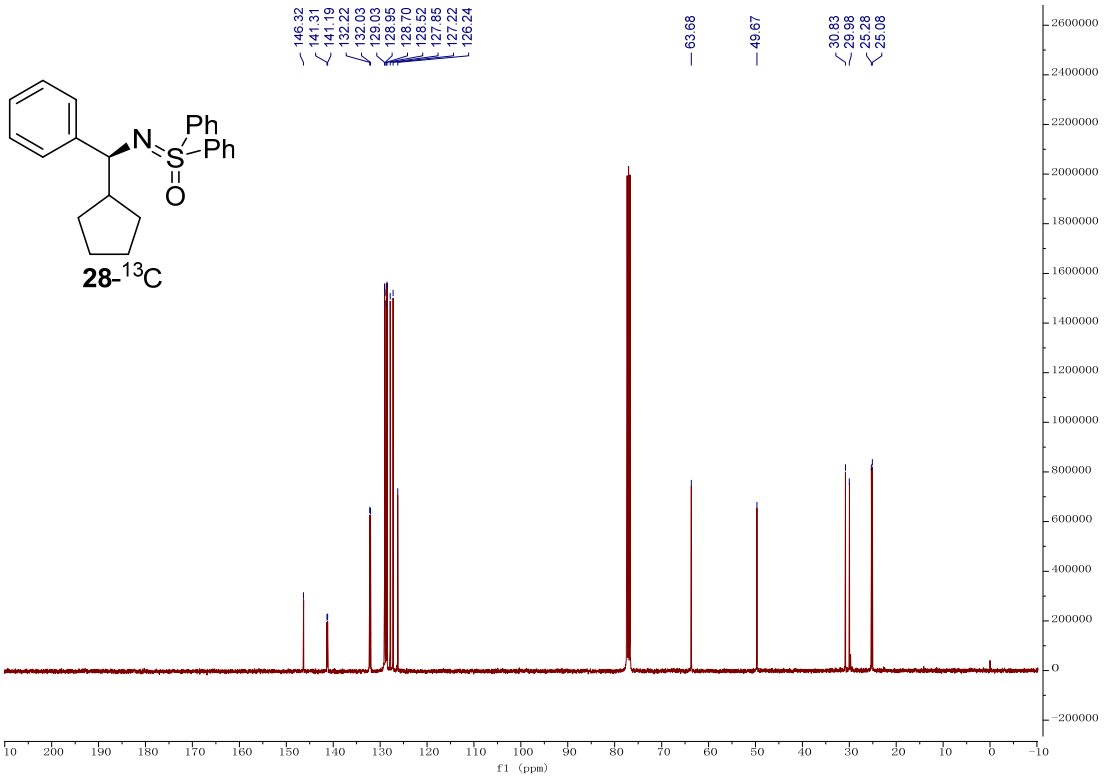
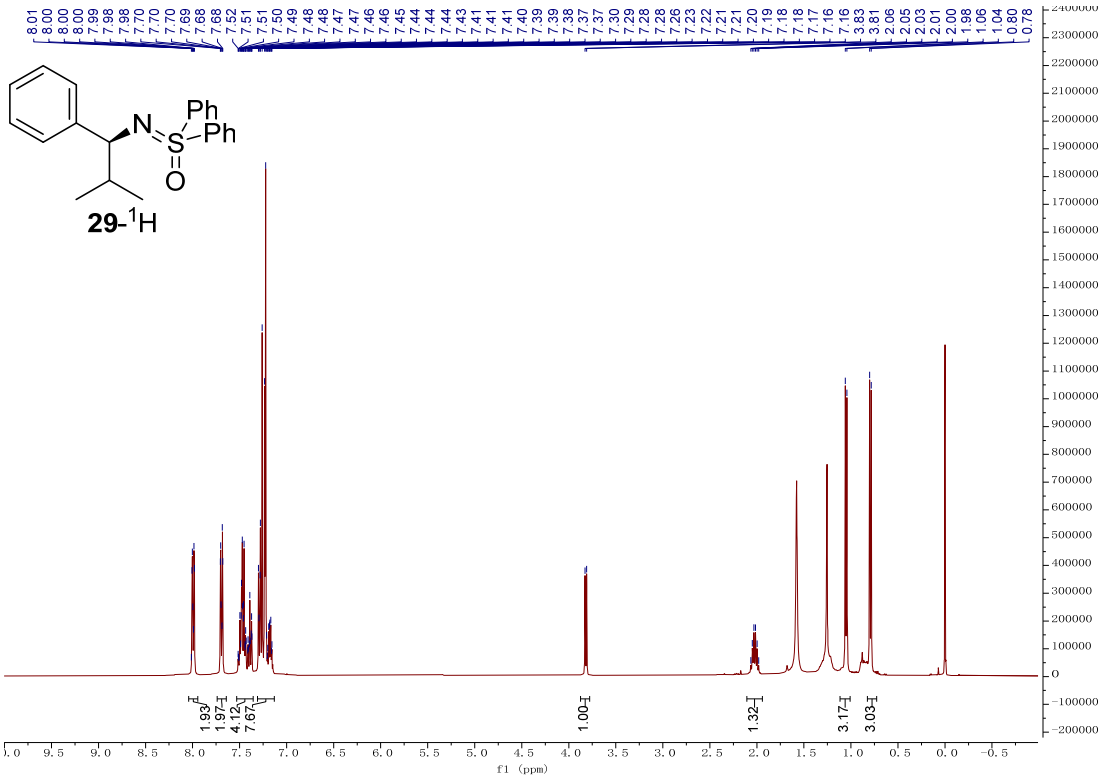
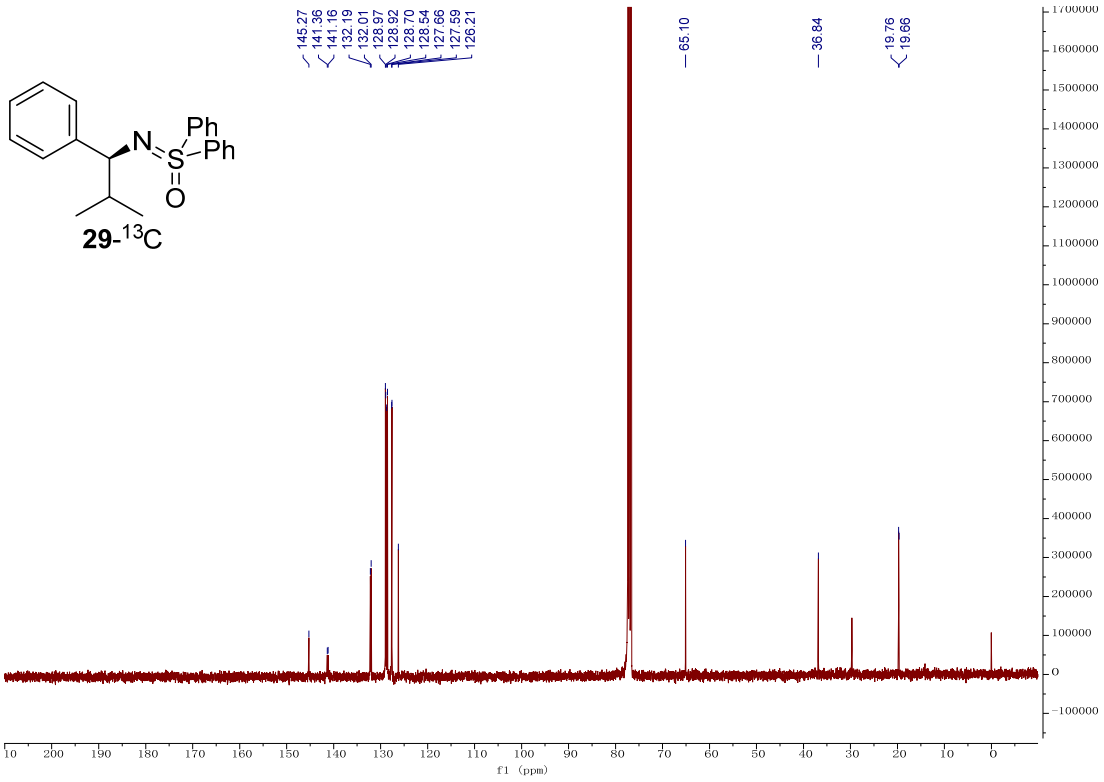
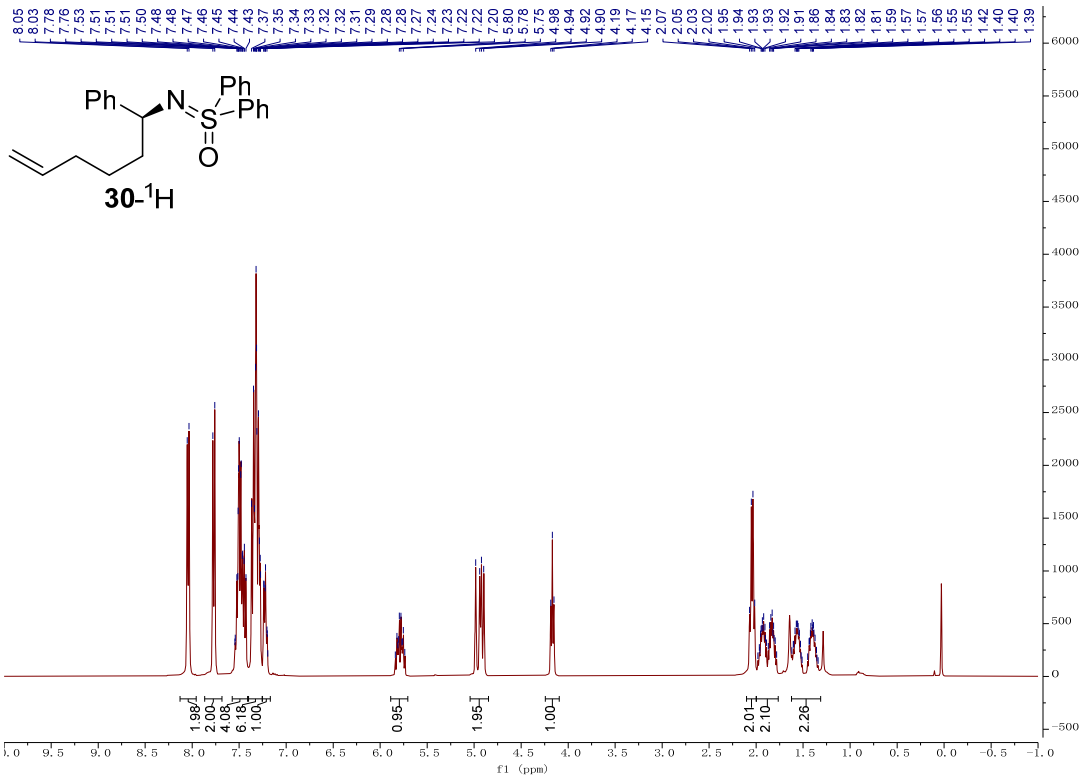
126.35
60.52
34.32
10.99
f1 (ppm)

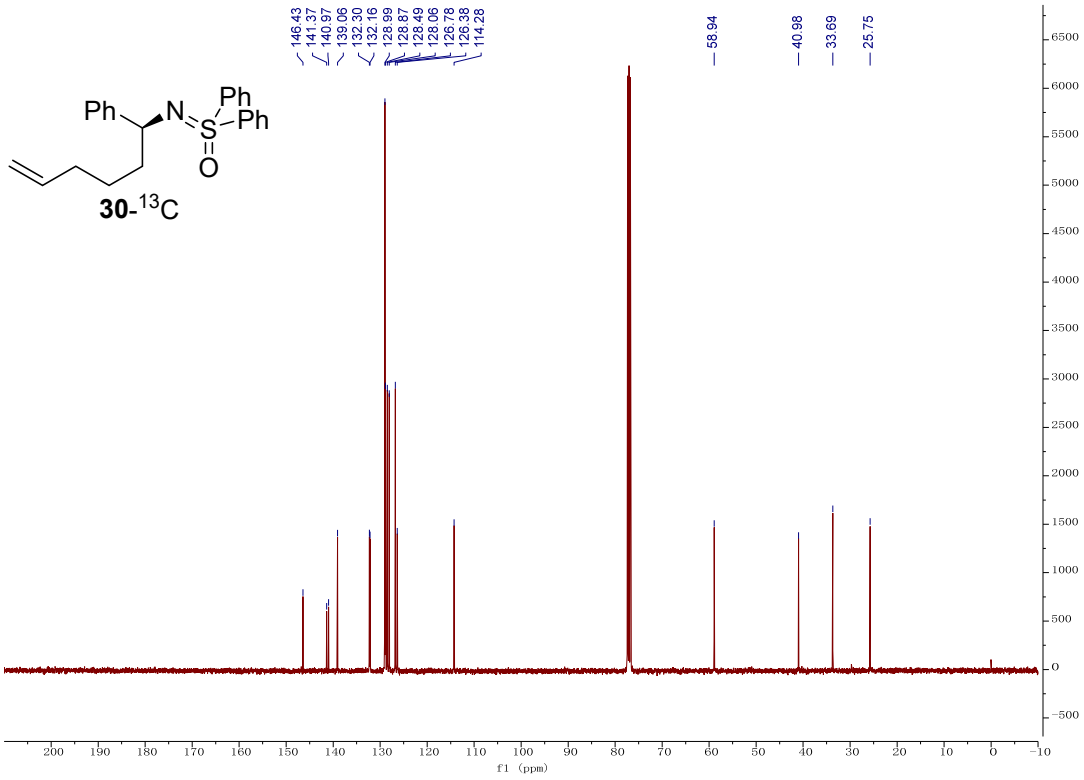

28-1H
f1 (ppm)

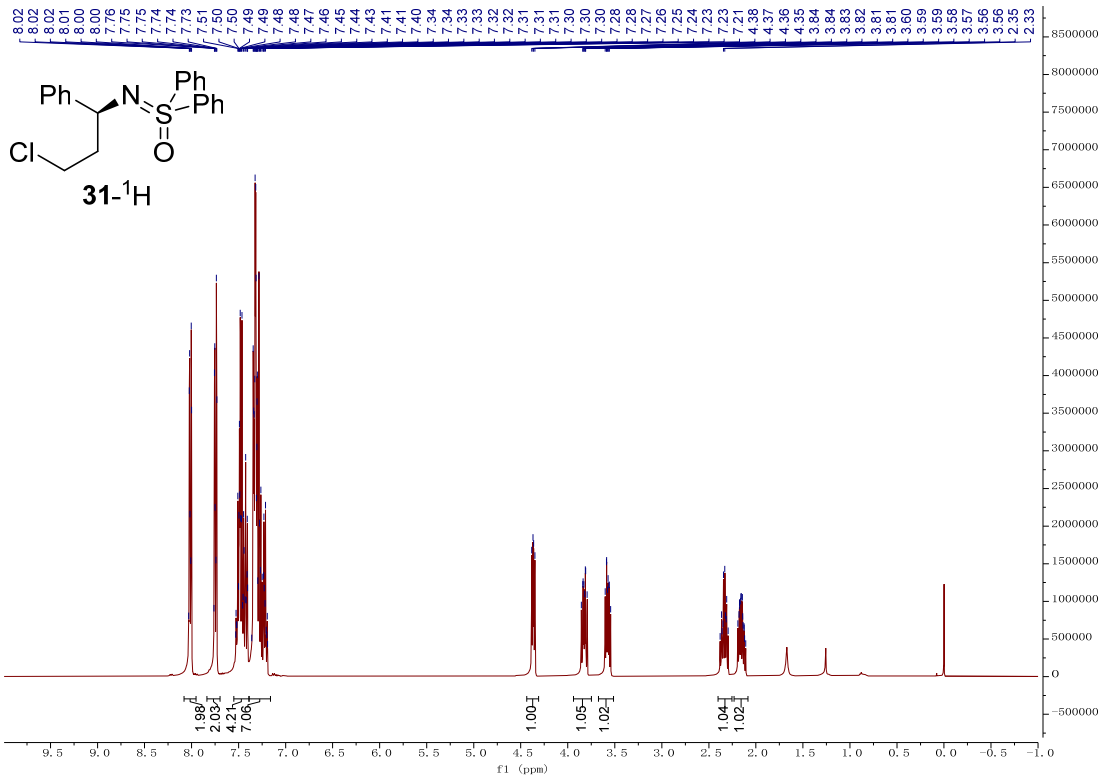

28-13C
f1 (ppm)

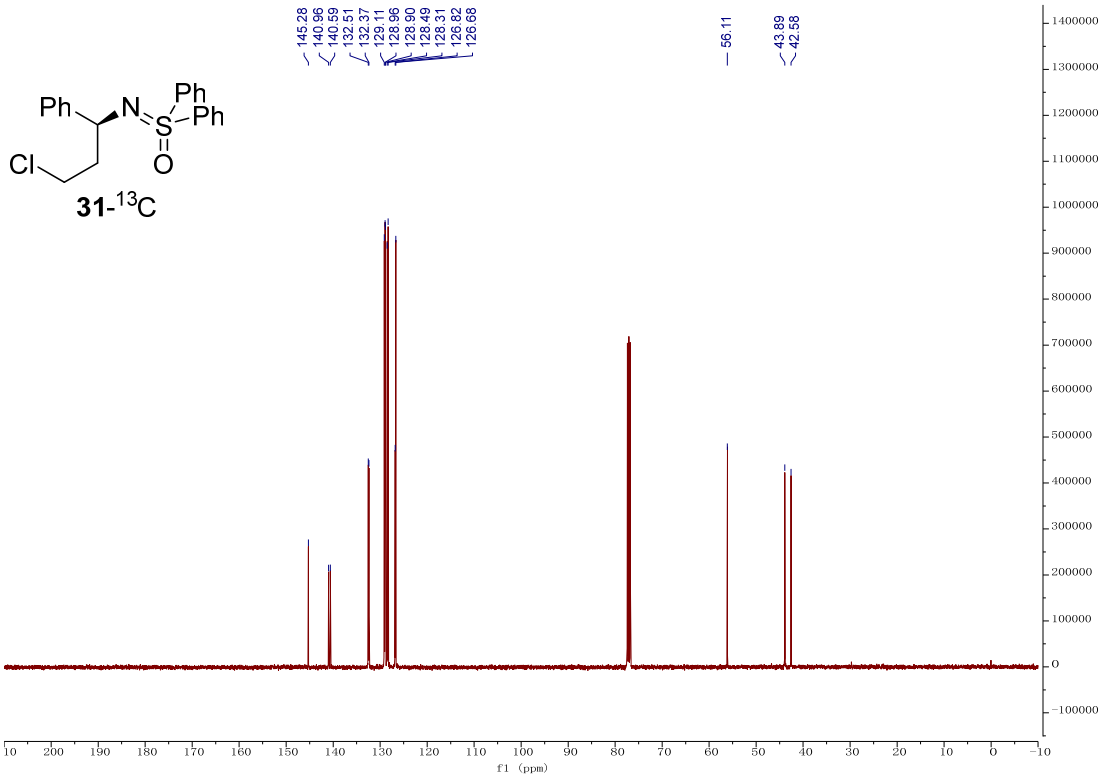

Ph
Ph
N
S
O
29-1H
f1 (ppm)

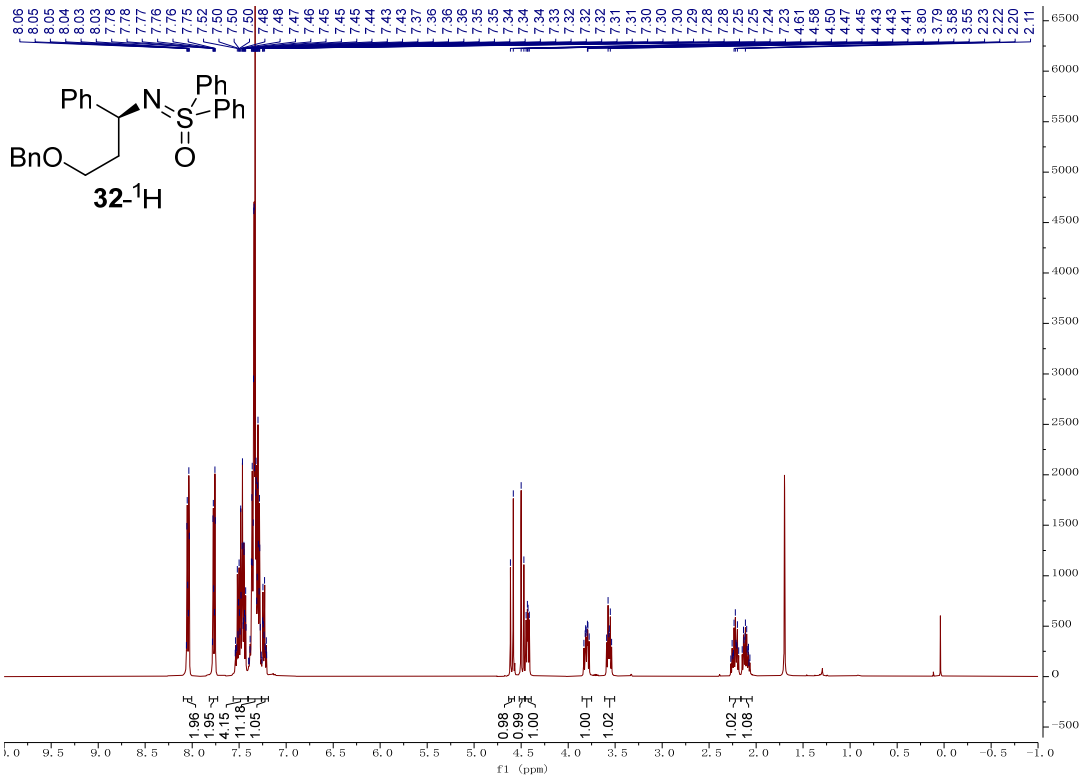

Ph
Ph
N
S
O
29-13C
f1 (ppm)

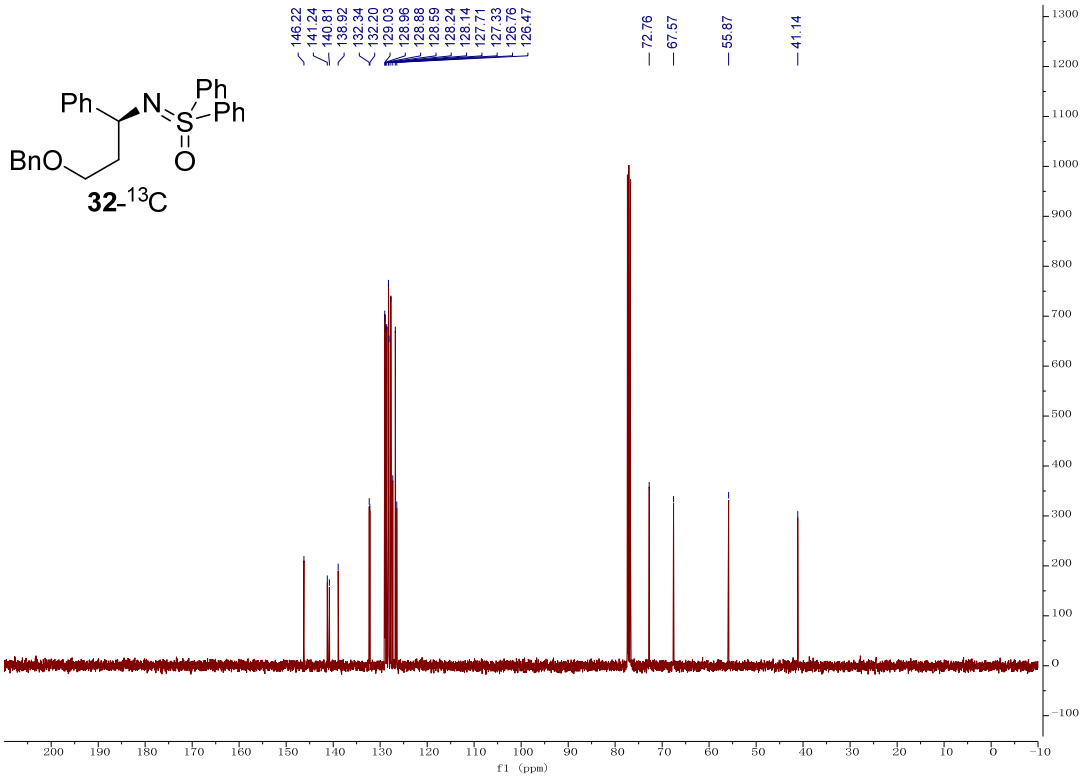

Ph
N
S
O
Ph
Ph
30-1H
f1 (ppm)

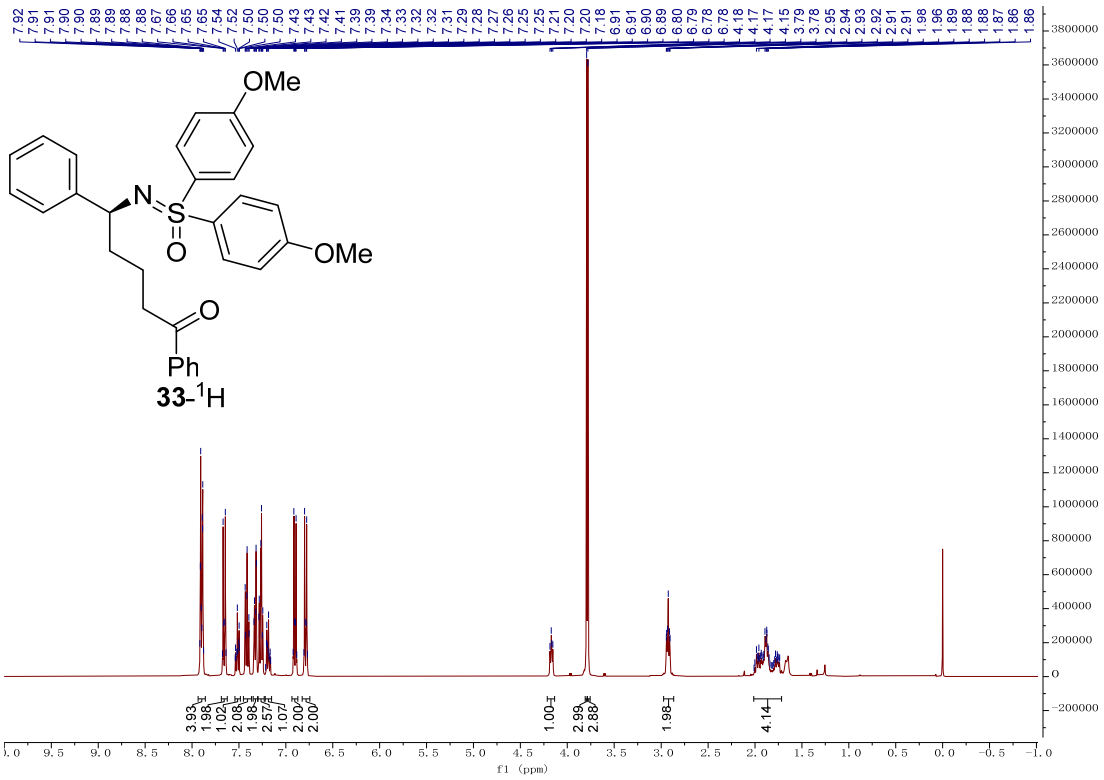

Ph
N
S
O
Ph
Ph
30-13C
f1 (ppm)

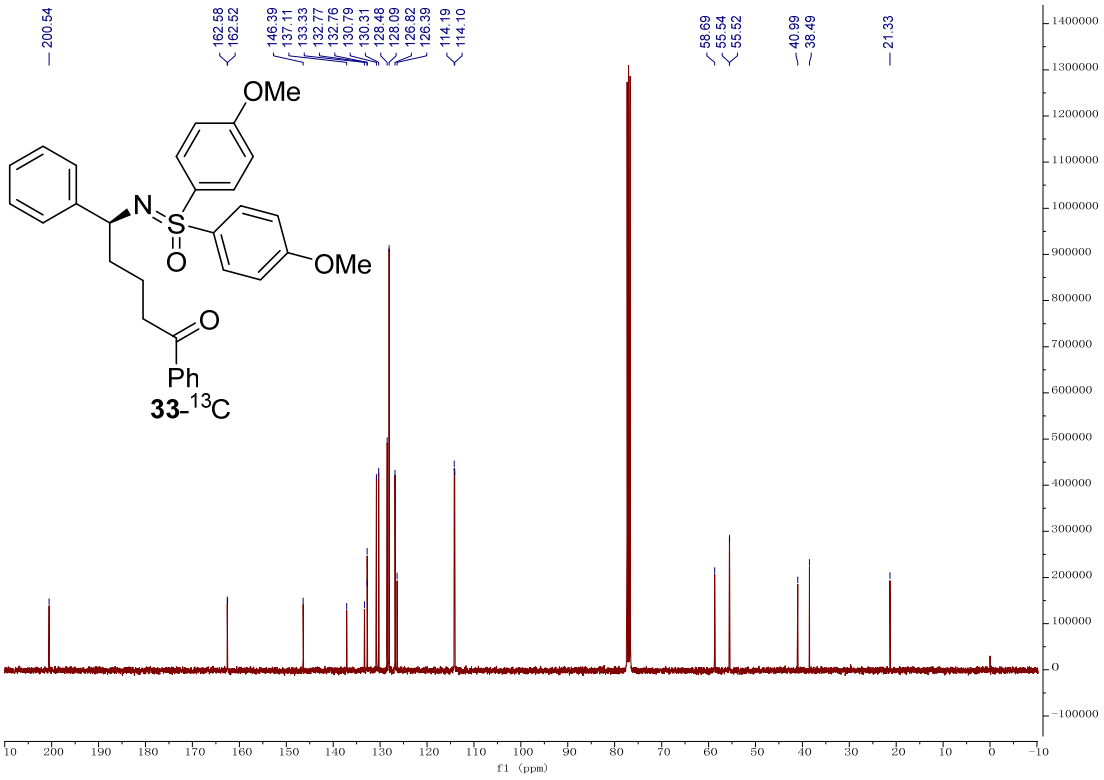

Ph
N
S
Ph
Ph
O
Cl
31-1H
f1 (ppm)

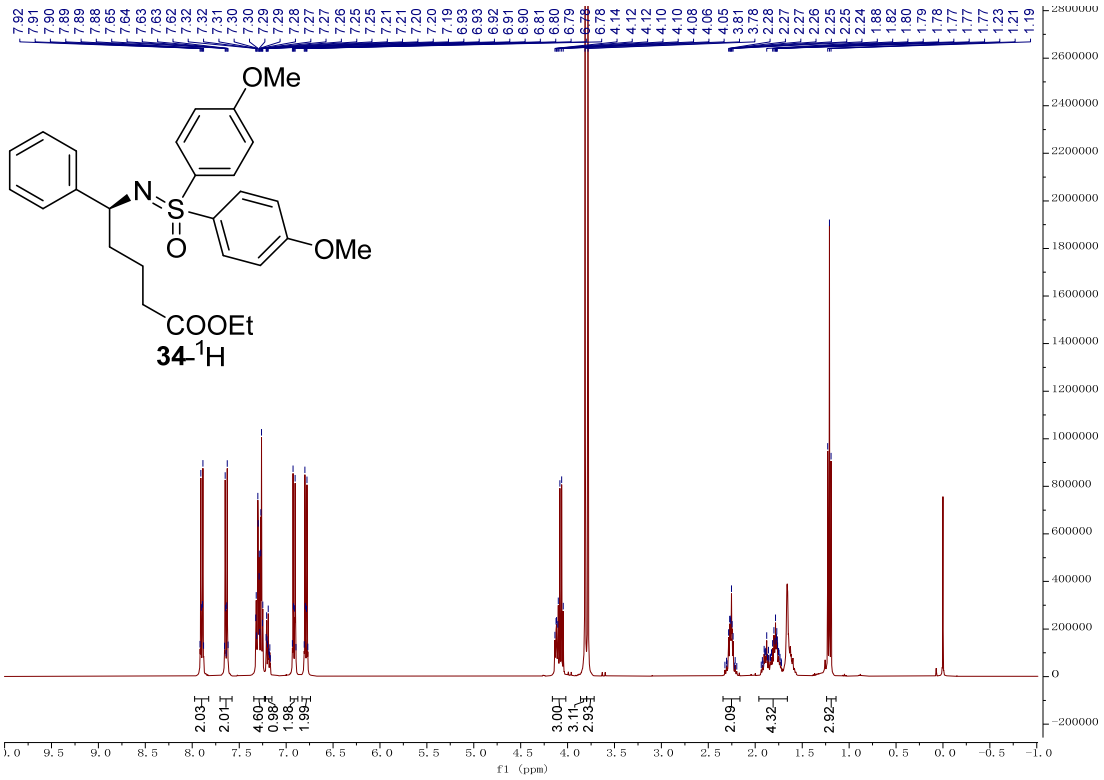

Ph
N
S
Ph
Ph
O
Cl
31-13C
f1 (ppm)

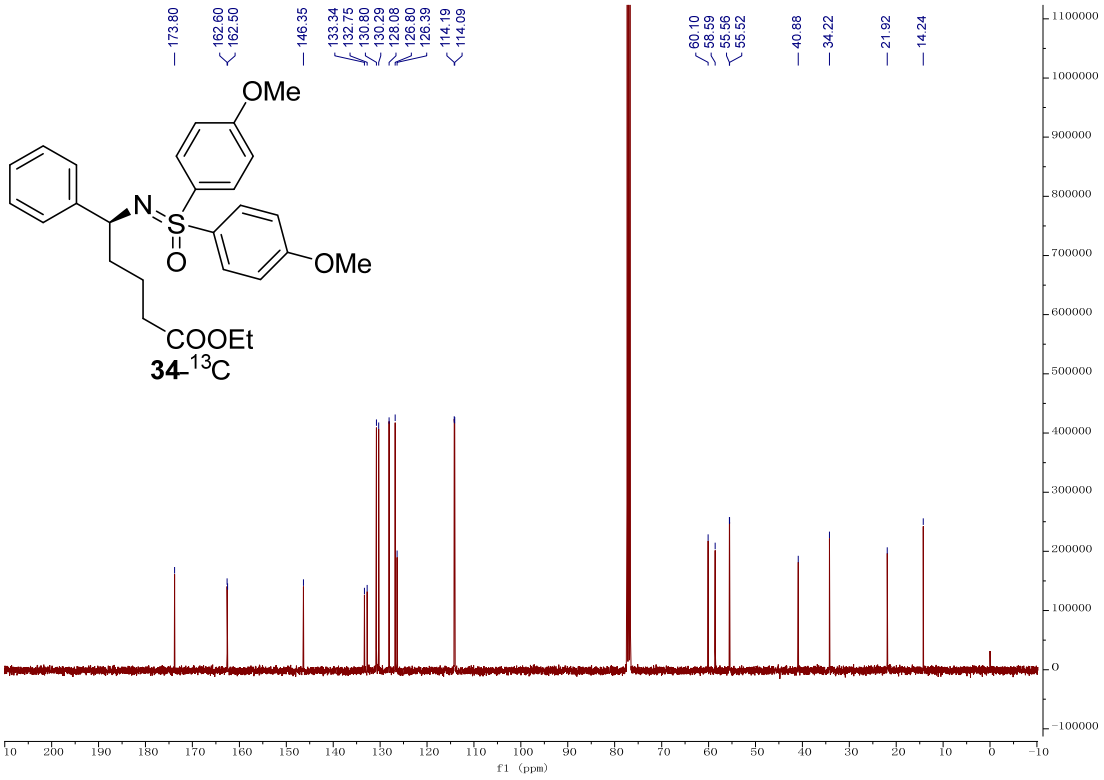

Ph
N
S
Ph
Ph
O
BnO
32-1H
f1 (ppm)

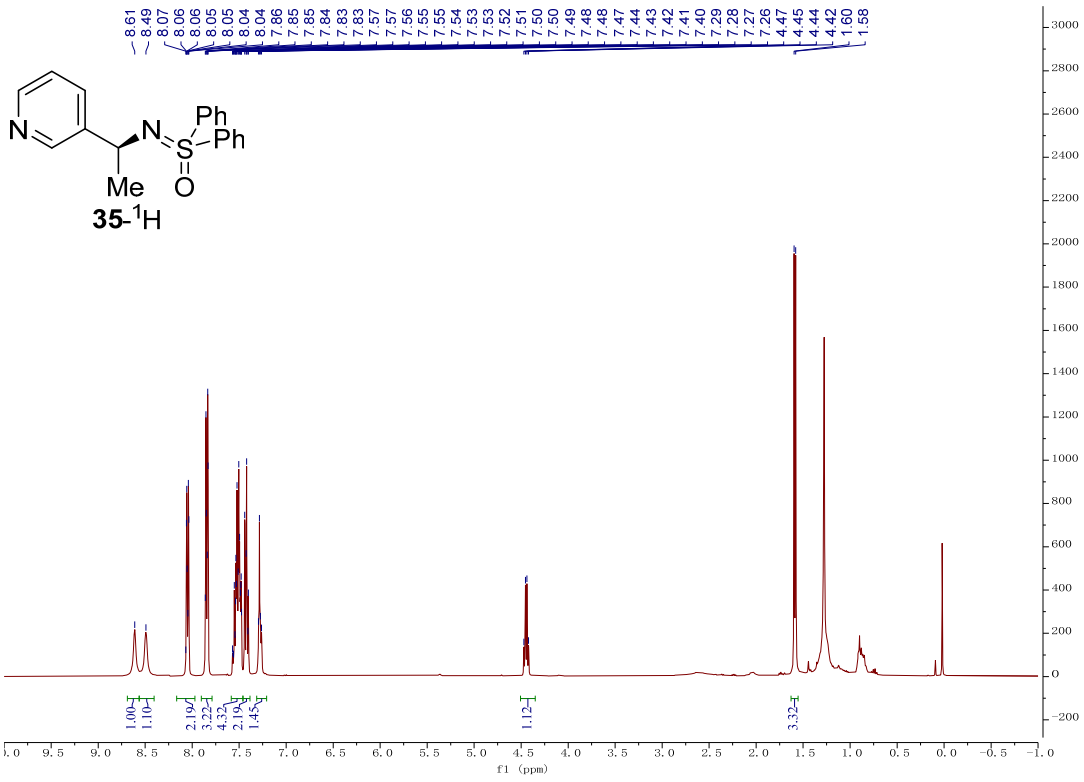

Ph
N
S
Ph
Ph
O
BnO
32-13C
f1 (ppm)

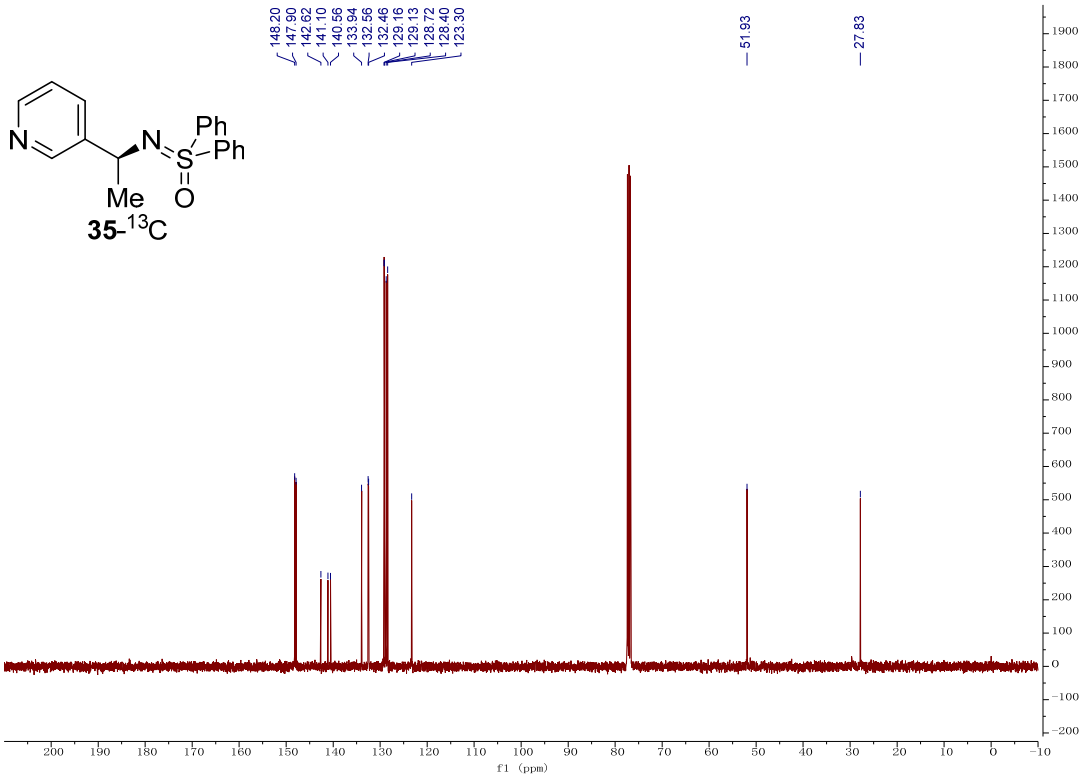

OMe
N
S
O
OMe
O
Ph
33-1H
f1 (ppm)

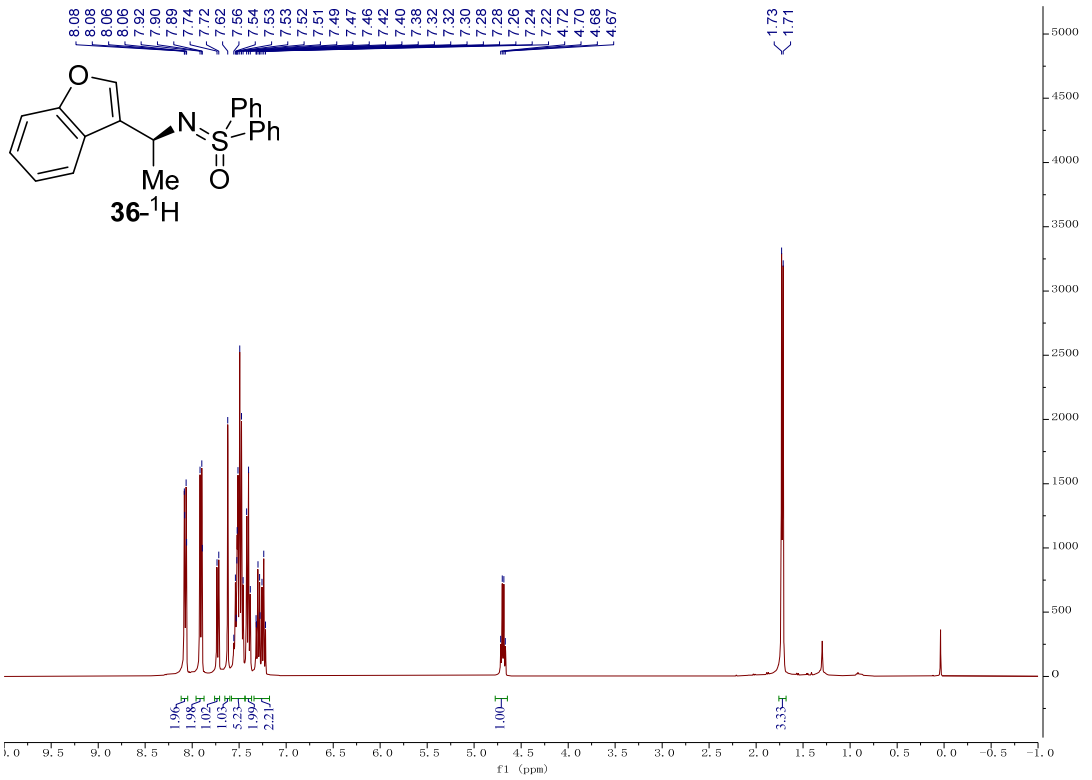

OMe
N
S
O
OMe
O
Ph
33-13C
f1 (ppm)

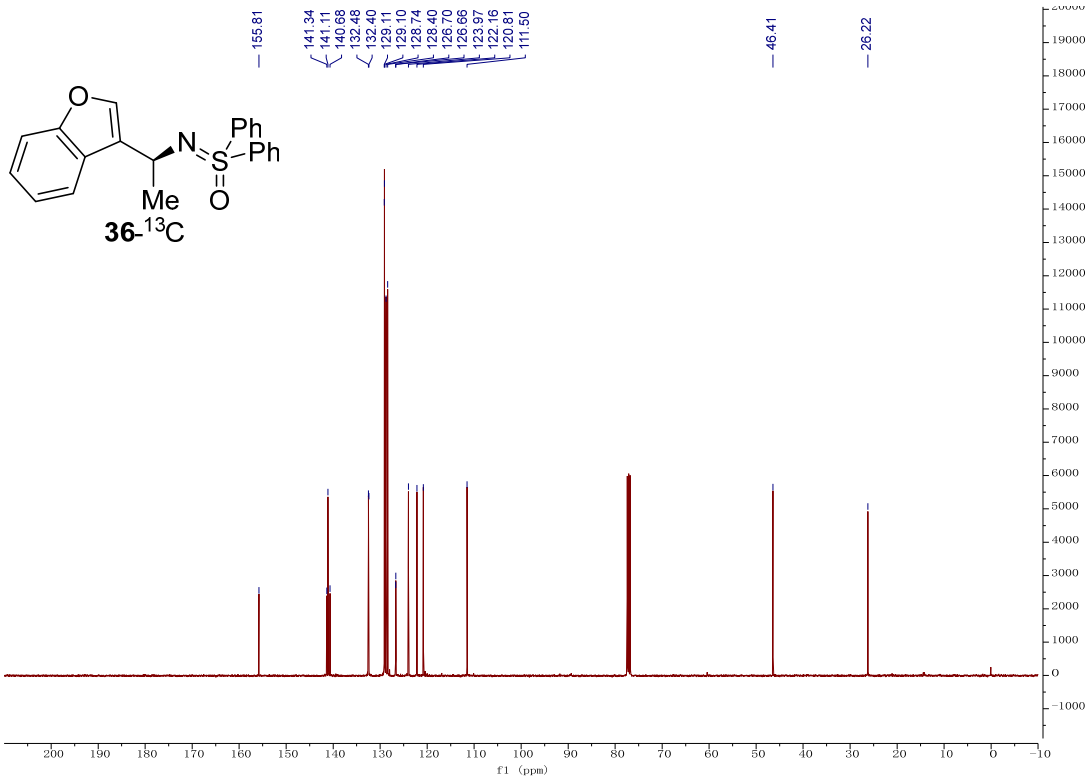

OMe
N
S
O
OMe
COOEt
34-1H
f1 (ppm)

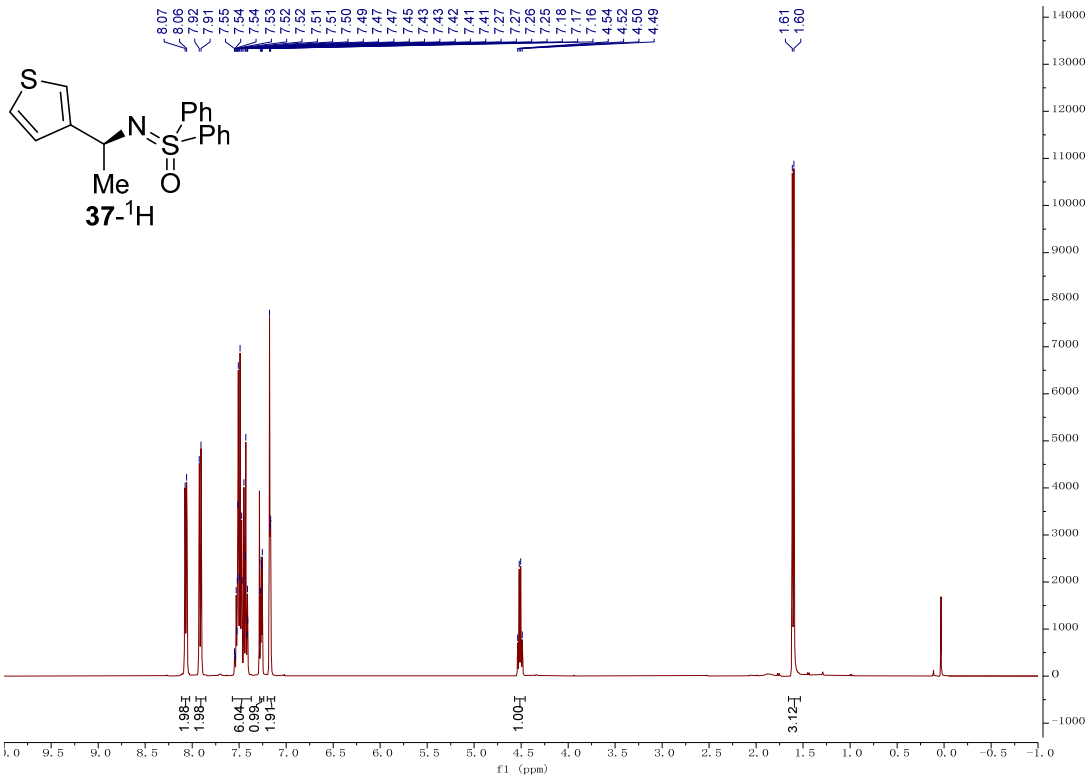

OMe
N
S
O
OMe
COOEt
34-13C
f1 (ppm)

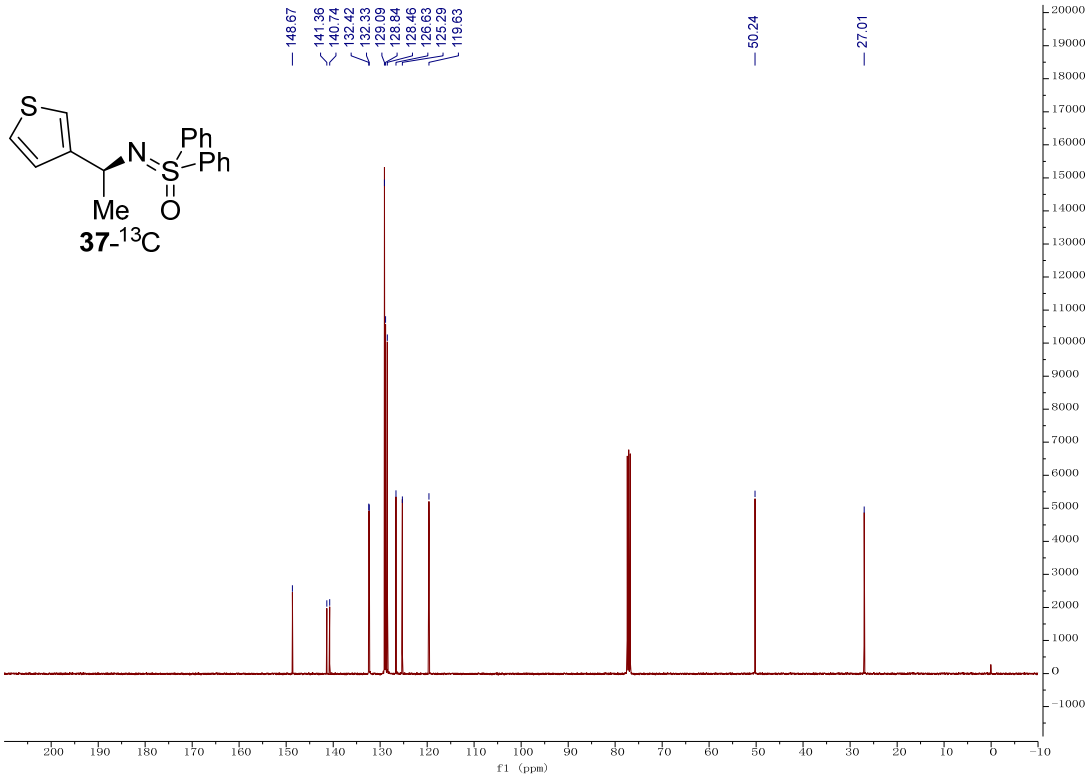

8.61
8.49
8.07
8.06
8.06
8.05
8.05
8.04
8.04
7.86
7.85
7.85
7.84
7.83
7.83
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.44
7.43
7.42
7.41
7.40
7.29
7.28
7.27
7.26
4.47
4.45
4.44
4.42
1.60
1.58
N
N
S
Ph
Ph
O
Me
35-1H
1.00
1.10
2.19
3.22
4.32
2.19
1.45
1.12
3.32
f1 (ppm)

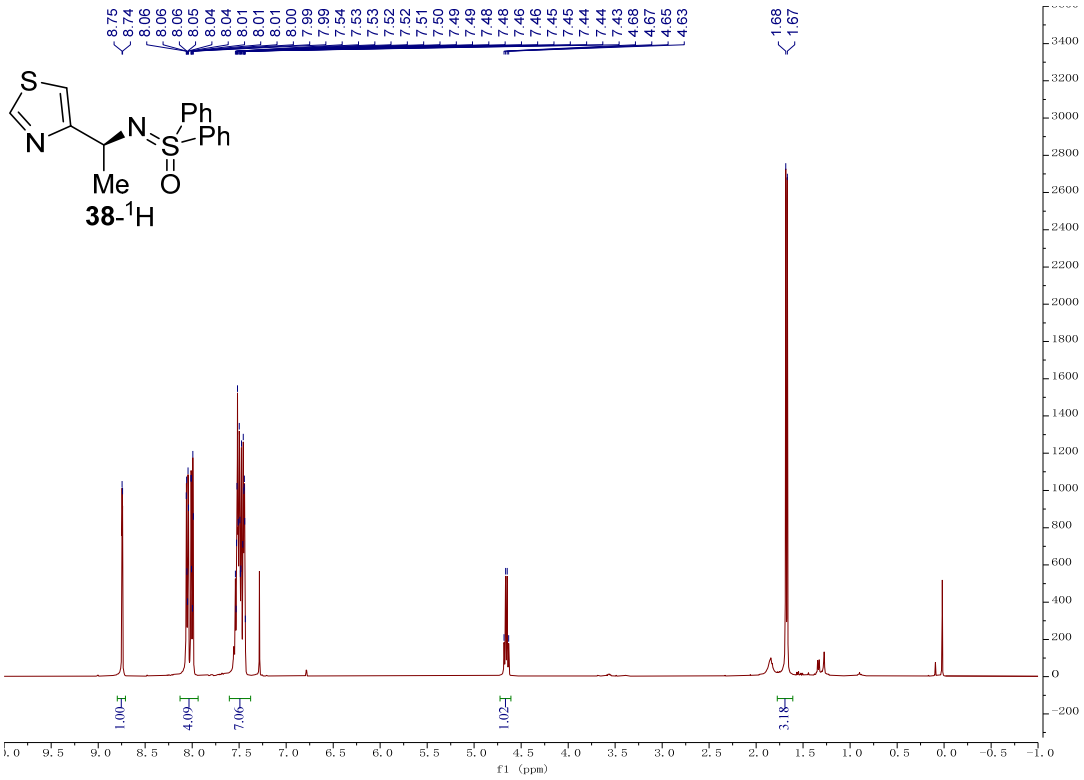

148.20
147.90
142.62
141.10
140.56
133.94
132.56
132.46
129.16
129.13
128.72
128.40
123.30
51.93
27.83
N
N
S
Ph
Ph
O
Me
35-13C
f1 (ppm)

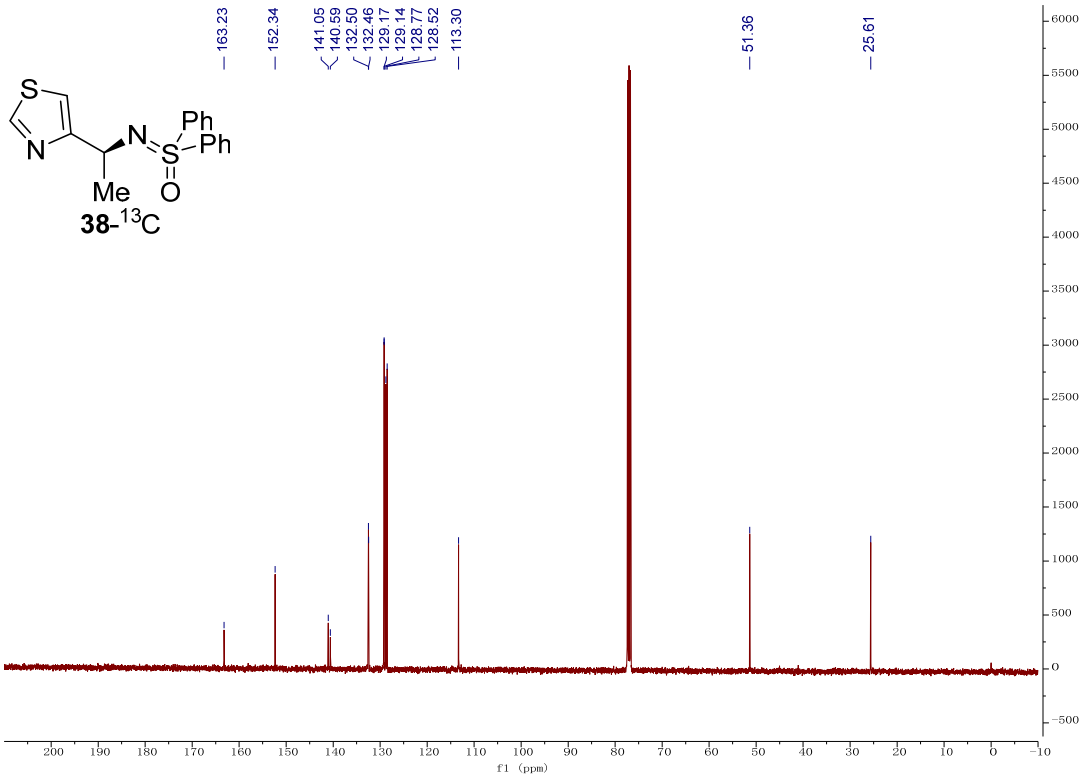

8.08
8.08
8.06
8.06
7.92
7.90
7.89
7.74
7.72
7.62
7.56
7.54
7.53
7.53
7.52
7.51
7.49
7.47
7.46
7.42
7.40
7.38
7.32
7.32
7.30
7.28
7.28
7.26
7.24
7.22
4.72
4.70
4.68
4.67
1.73
1.71
O
N
S
Ph
Ph
O
Me
36-1H
1.96
1.98
1.02
1.03
5.23
1.99
2.21
1.00
3.33
f1 (ppm)

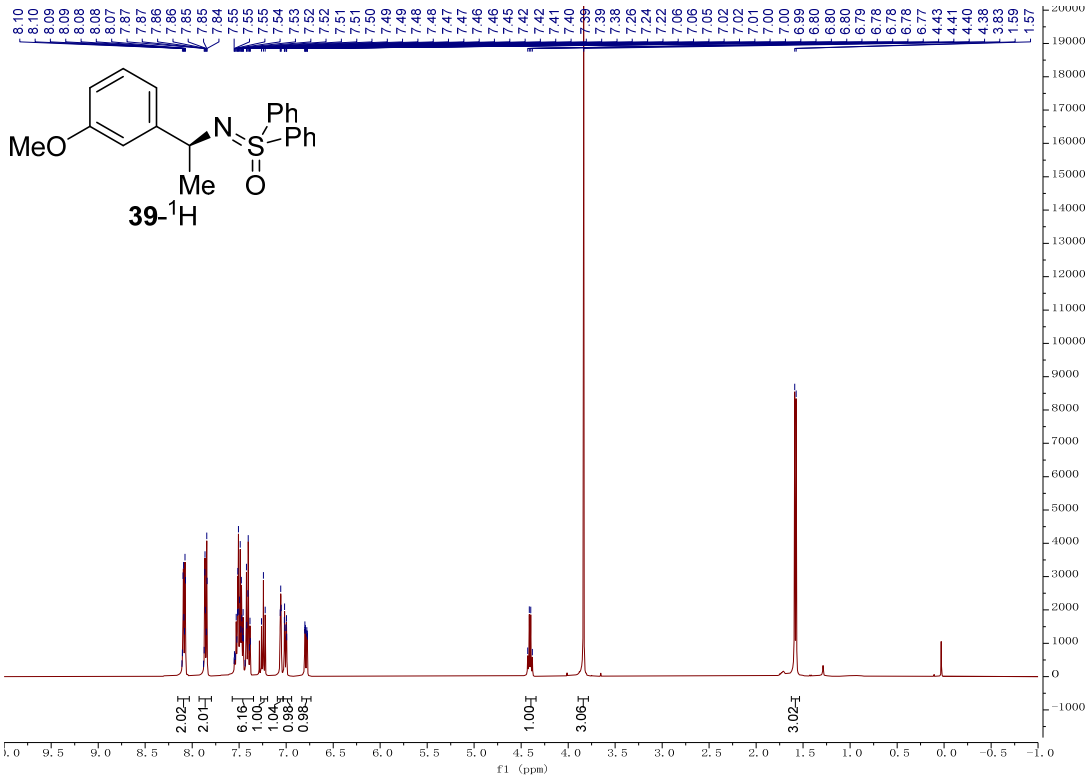

155.81
141.34
141.11
140.68
132.48
132.40
129.11
129.10
128.74
128.40
126.70
126.66
123.97
122.16
120.81
111.50
46.41
26.22
O
N
S
Ph
Ph
O
Me
36-13C
f1 (ppm)

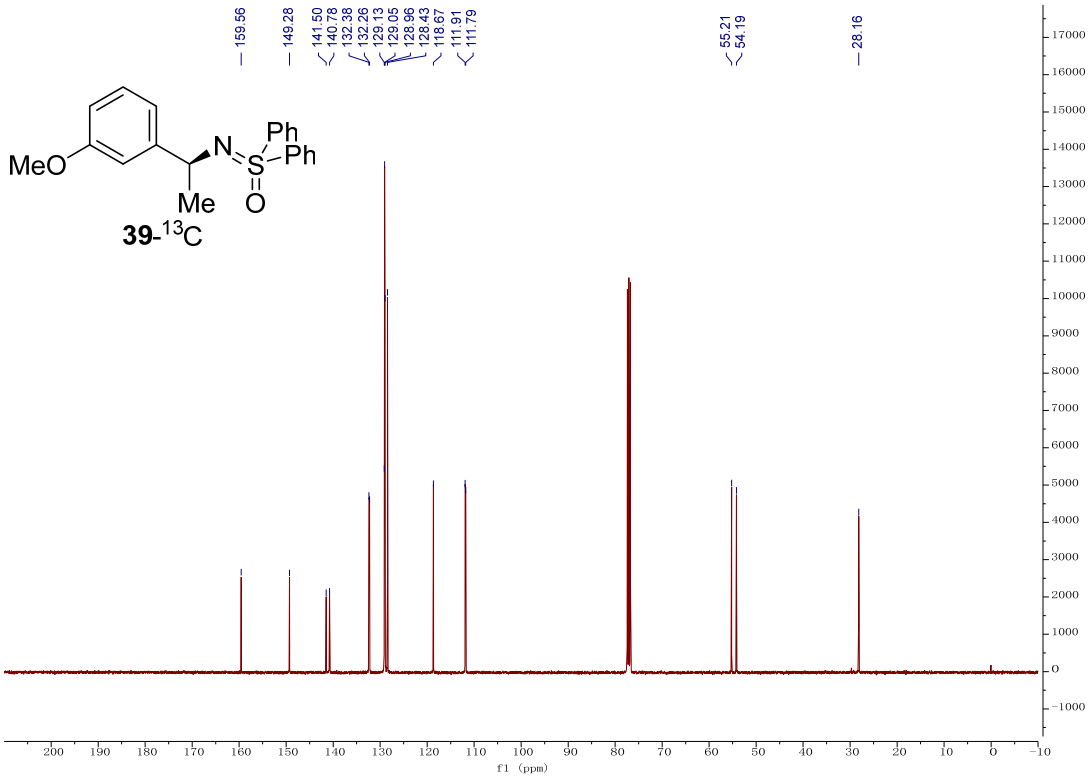

8.07
8.06
7.92
7.91
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.49
7.47
7.47
7.45
7.43
7.43
7.42
7.41
7.41
7.27
7.26
7.25
7.18
7.17
7.16
4.54
4.52
4.50
4.49
1.61
1.60
S
N
Ph
Ph
S
O
Me
37-1H
1.98
1.98
6.04
0.98
1.91
1.00
3.12
f1 (ppm)

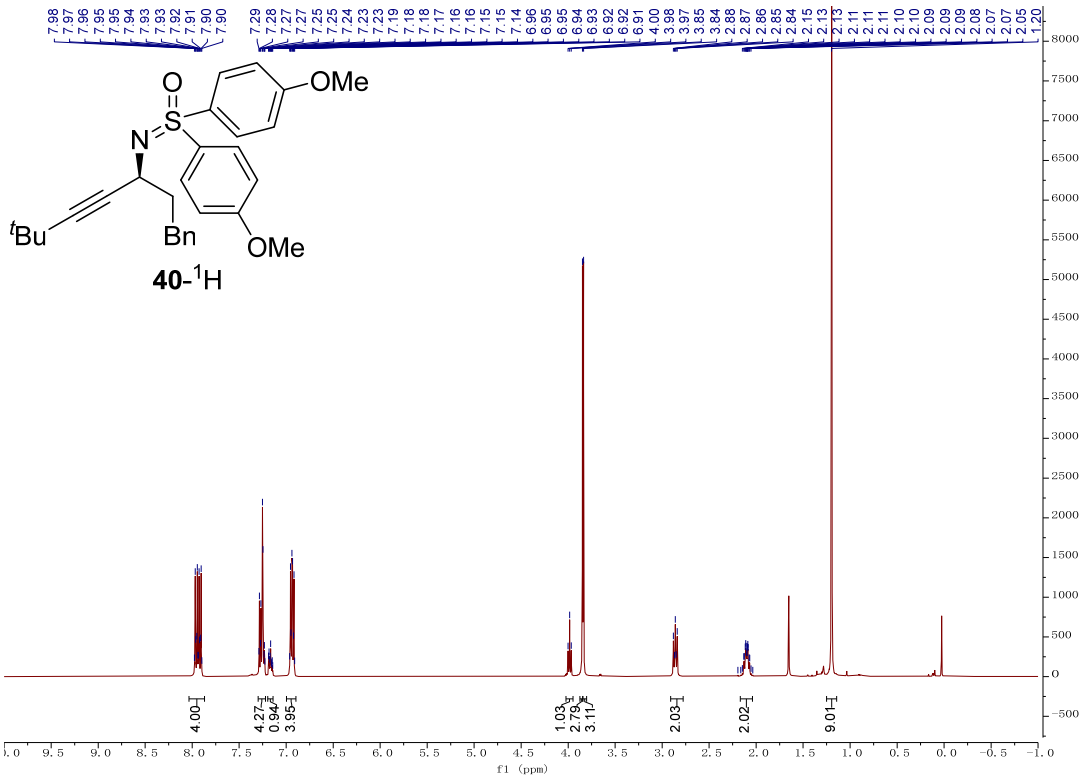

148.67
141.36
140.74
132.42
132.33
129.09
128.84
128.46
126.63
125.29
119.63
50.24
27.01
S
N
Ph
Ph
S
O
Me
37-13C
f1 (ppm)

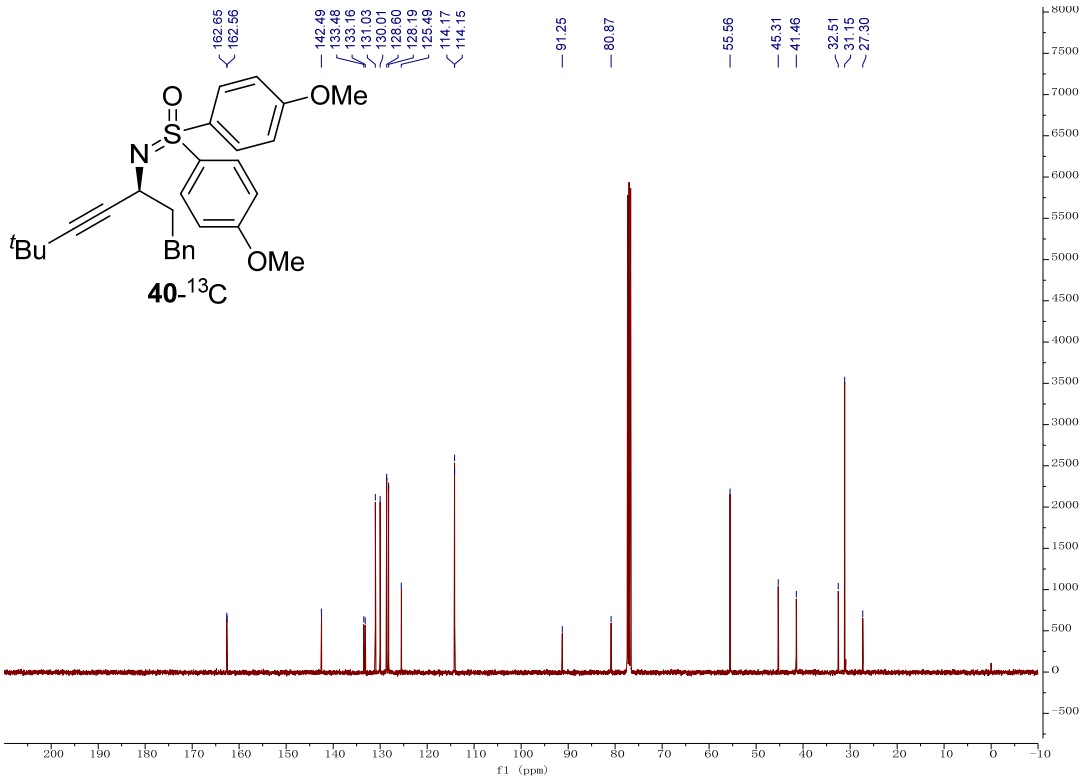

8.75
8.74
8.06
8.06
8.06
8.05
8.04
8.04
8.01
8.01
8.01
8.00
7.99
7.99
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.49
7.49
7.48
7.48
7.46
7.46
7.45
7.45
7.44
7.44
7.43
4.68
4.67
4.65
4.63
1.68
1.67
S
N
N
S
Ph
Ph
O
Me
38-1H
1.00
4.09
7.06
1.02
3.18
f1 (ppm)

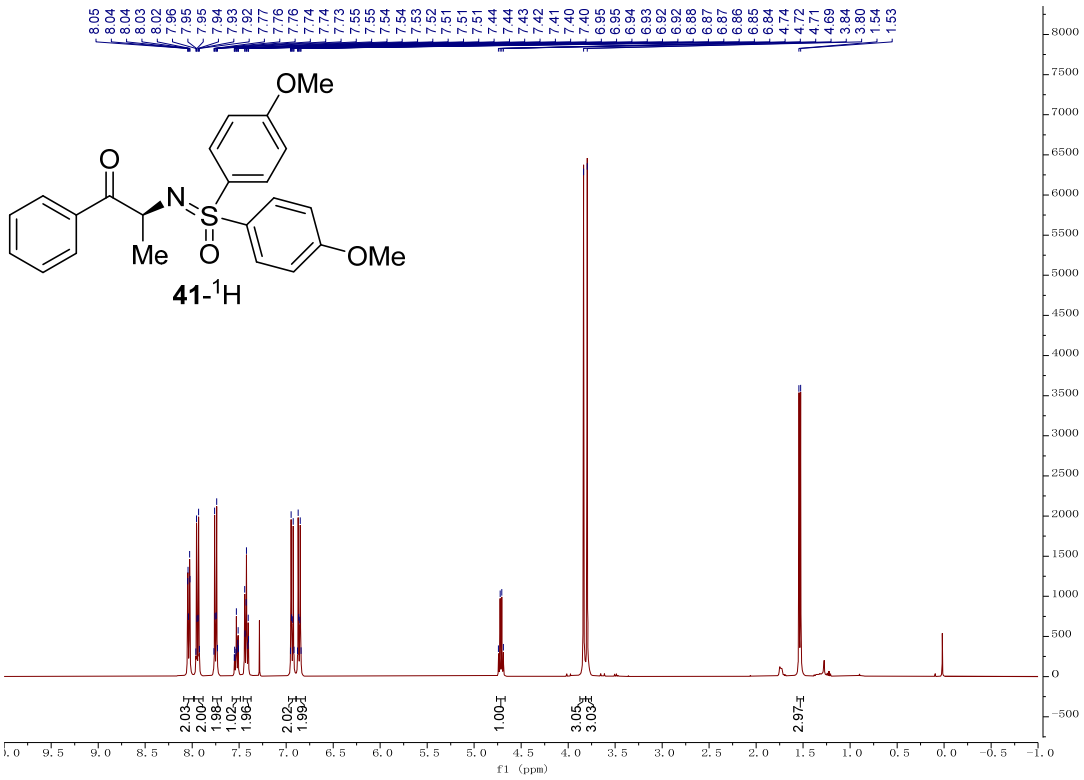

163.23
152.34
141.05
140.59
132.50
132.46
129.17
129.14
128.77
128.52
113.30
51.36
25.61
S
N
N
S
Ph
Ph
O
Me
38-13C
f1 (ppm)

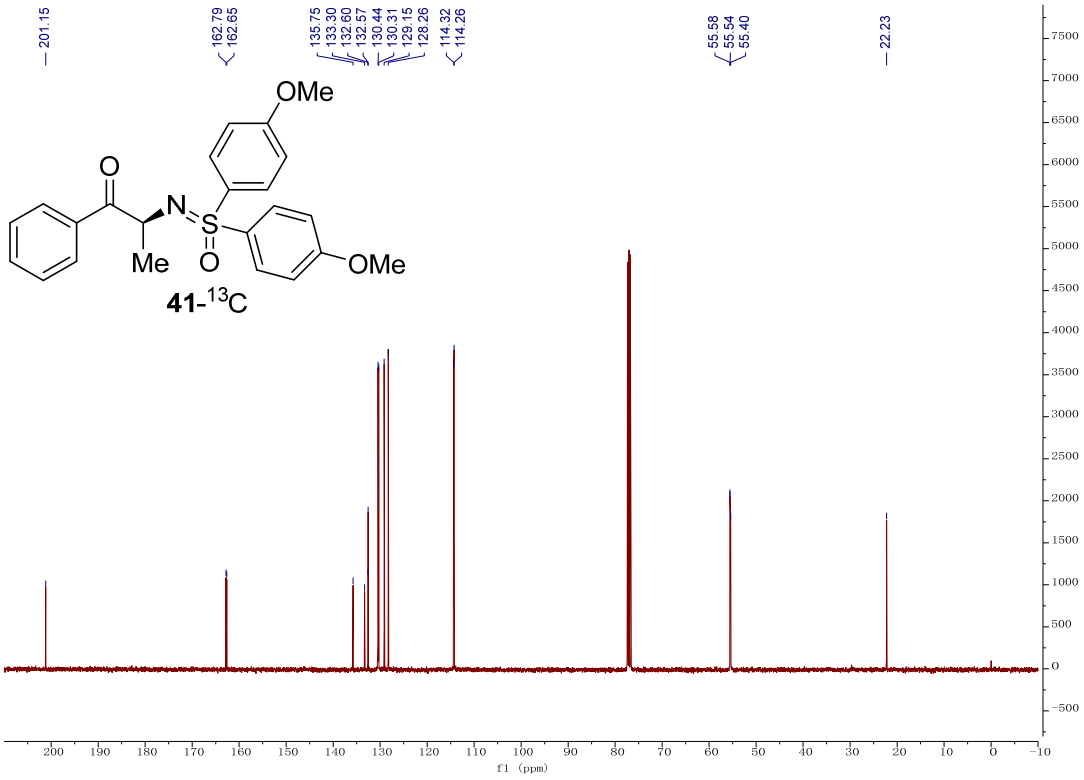

MeO
N
S
Ph
Ph
O
Me
39-1H
f1 (ppm)

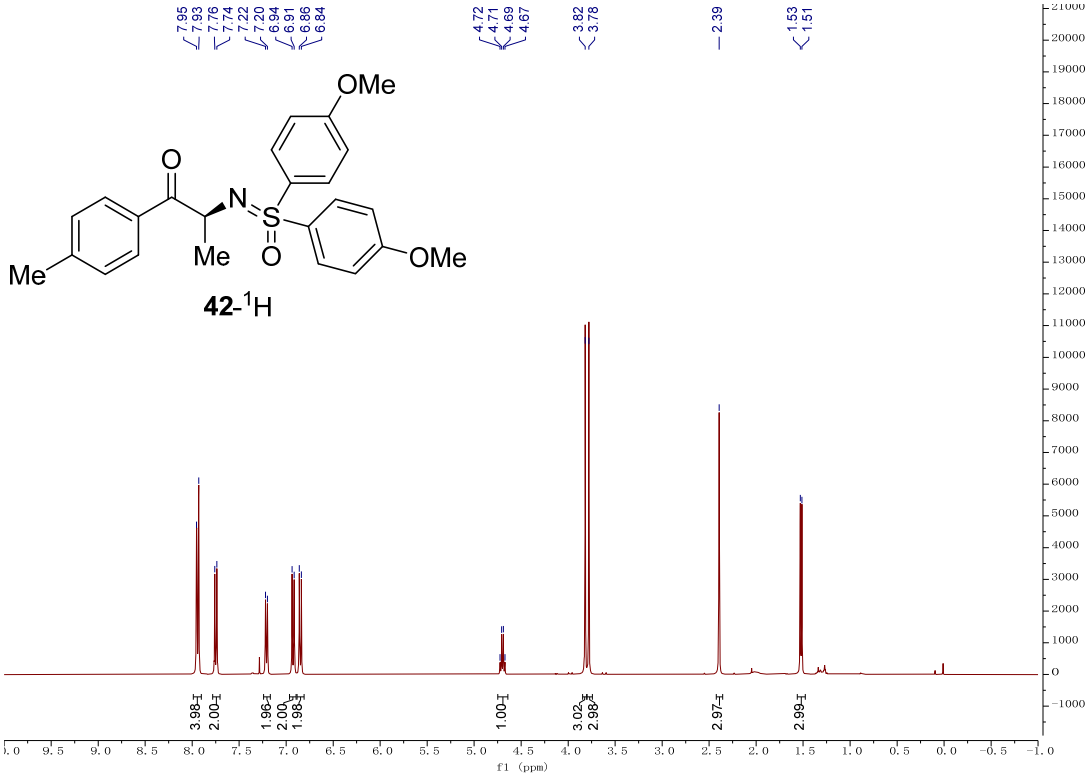

MeO
N
S
Ph
Ph
O
Me
39-13C
f1 (ppm)

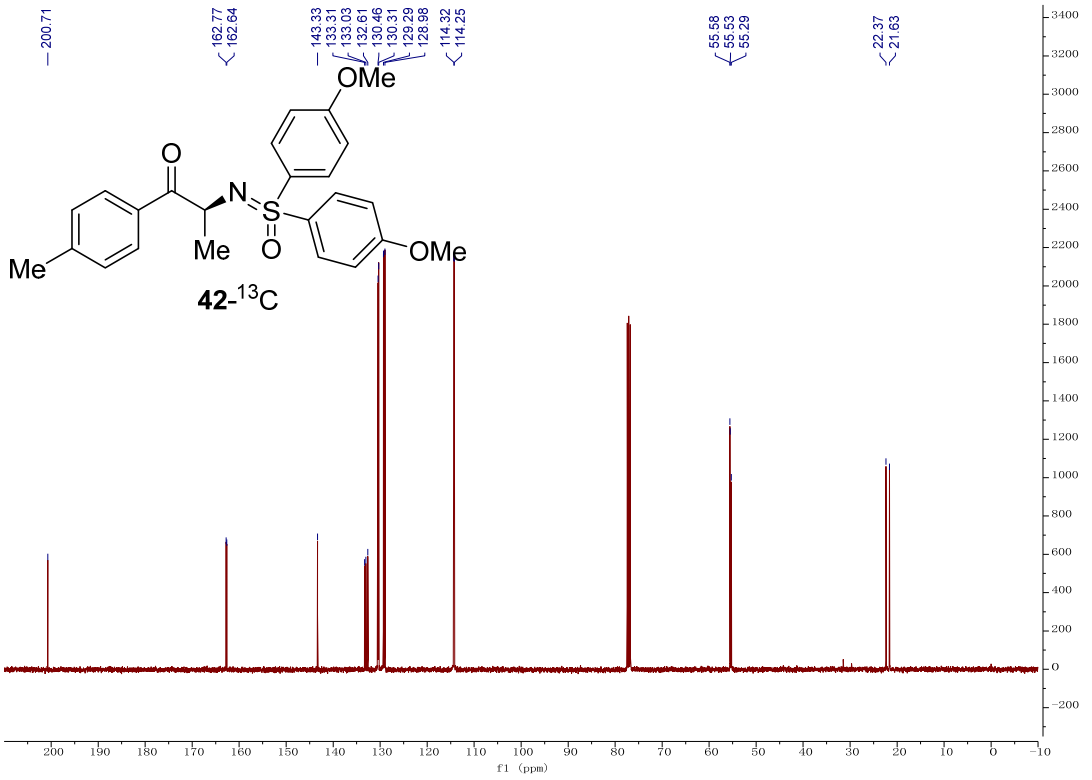

OMe
O
S
N
tBu
Bn
OMe
40-1H
f1 (ppm)

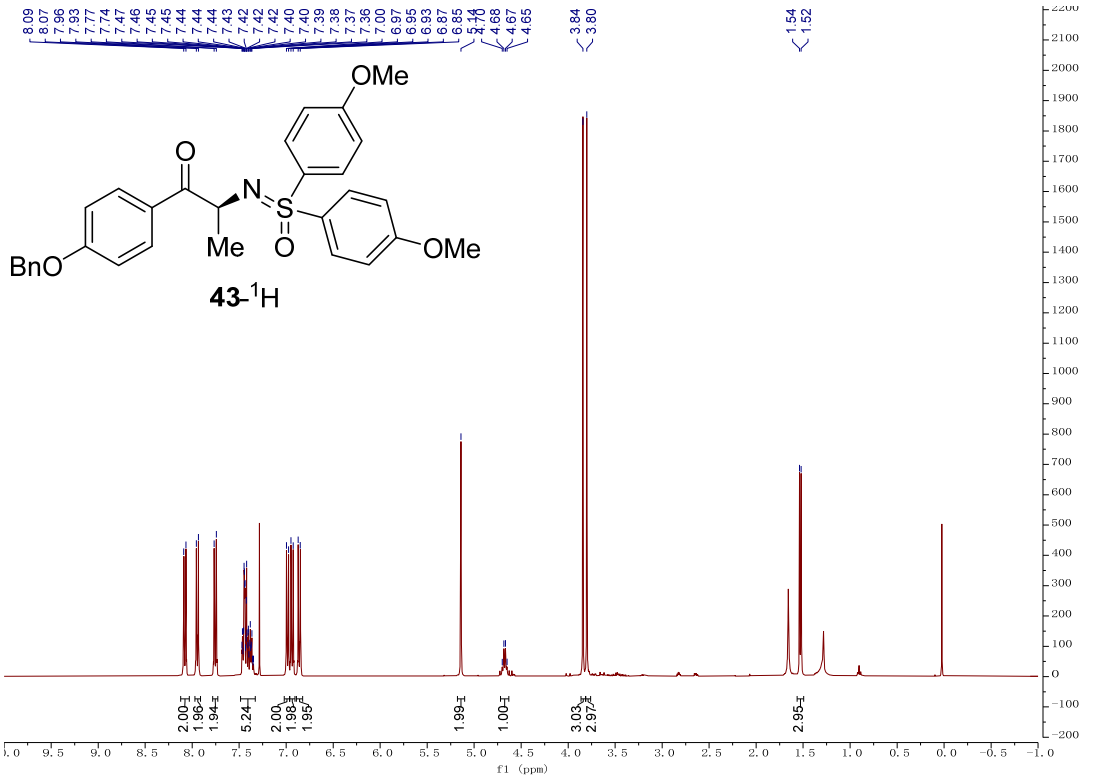

OMe
O
S
N
tBu
Bn
OMe
40-13C
f1 (ppm)

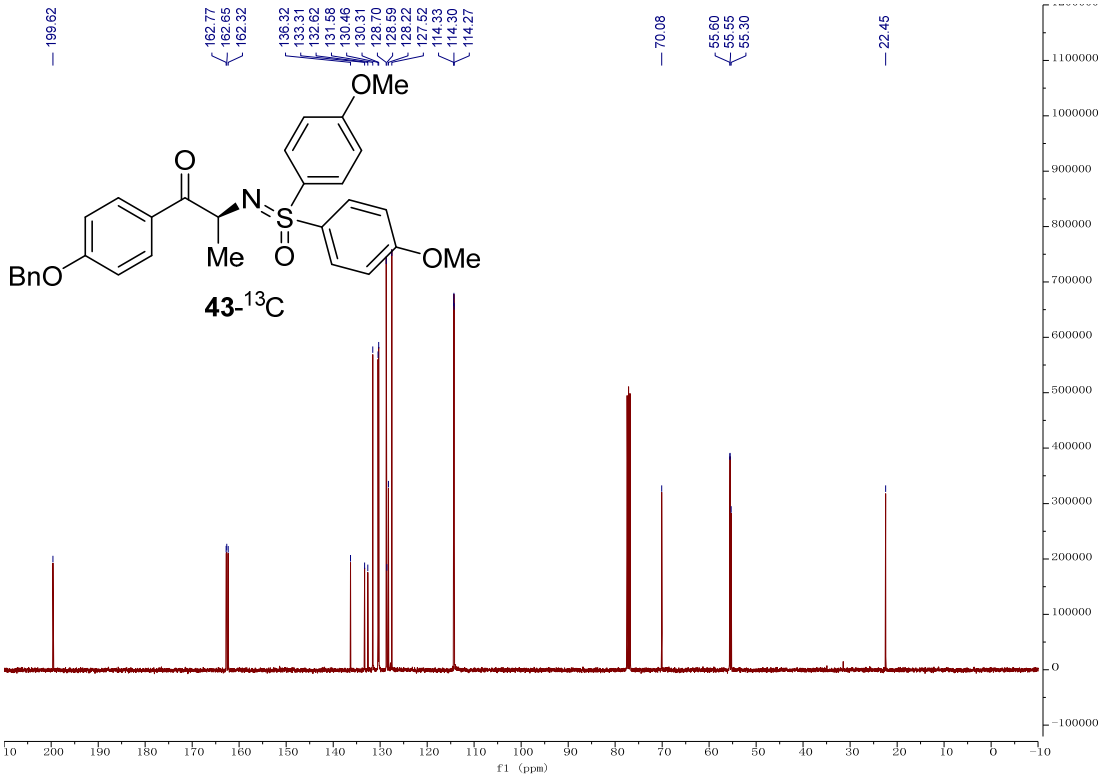

8.05 8.04 8.04 8.03 8.02 7.96 7.95 7.95 7.94 7.93 7.92 7.77 7.76 7.76 7.74 7.74 7.73 7.55 7.55 7.54 7.54 7.53 7.52 7.51 7.51 7.51 7.44 7.44 7.43 7.42 7.41 7.40 7.40 6.95 6.95 6.94 6.93 6.92 6.92 6.88 6.87 6.87 6.86 6.85 6.84 4.74 4.72 4.71 4.69 3.84 3.80 1.54 1.53
OMe
O
N
S
O
Me
OMe
41-1H
2.03 2.00 1.98 1.02 1.96 2.02 1.99 1.00 3.05 3.03 2.97
f1 (ppm)

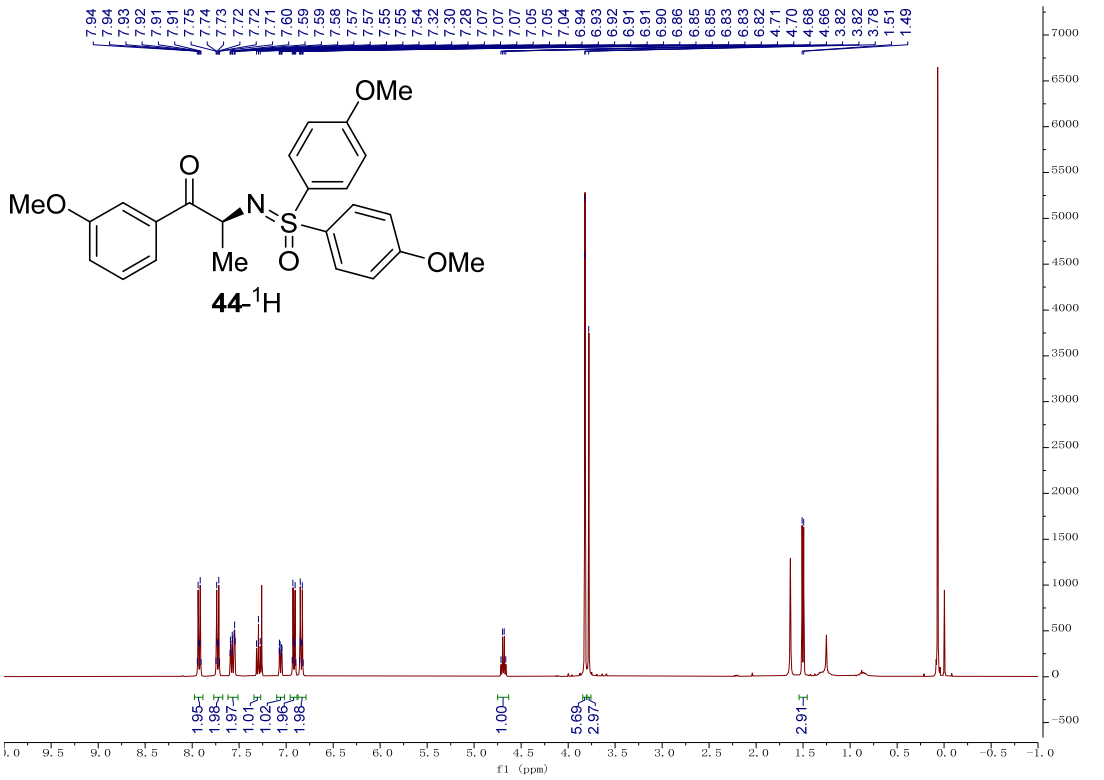

201.15
162.79 162.65
135.75 133.30 132.60 132.57 130.44 130.31 129.15 128.26
114.32 114.26
55.58 55.54 55.40
22.23
OMe
O
N
S
O
Me
OMe
41-13C
f1 (ppm)

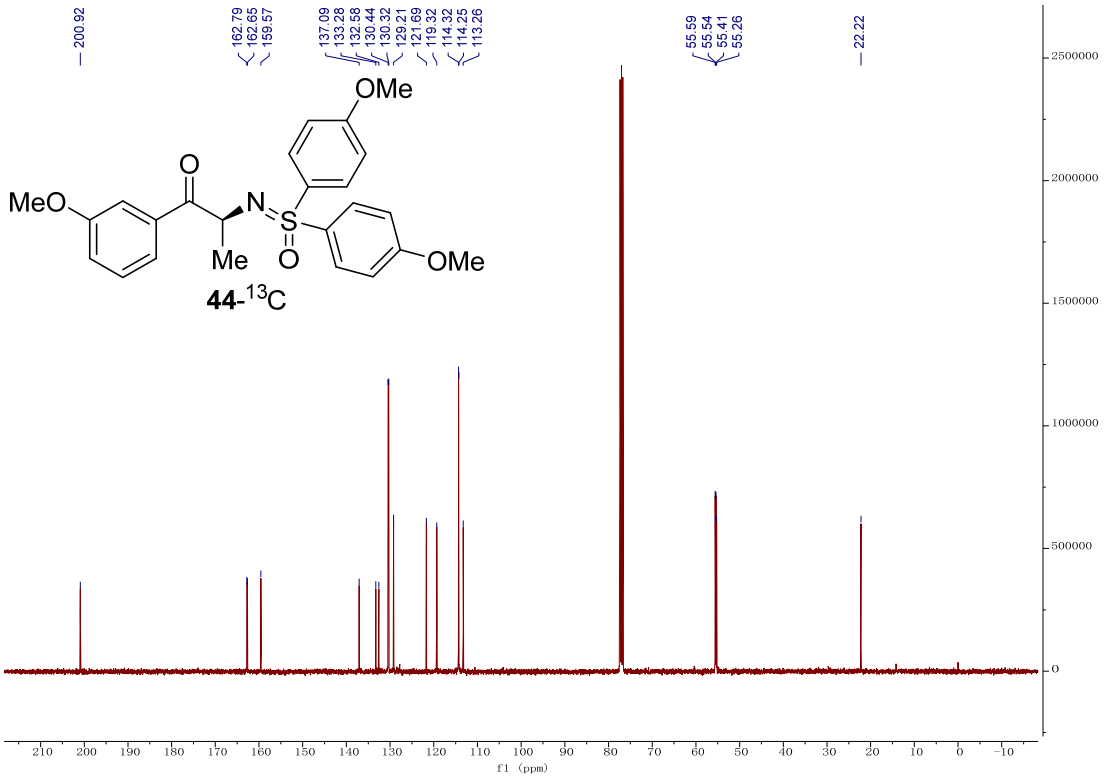

7.95
7.93
7.76
7.74
7.22
7.20
6.94
6.91
6.86
6.84
4.72
4.71
4.69
4.67
3.82
3.78
2.39
1.53
1.51
OMe
O
N
S
O
Me
Me
O
OMe
42-1H
3.98
2.00
1.96
2.00
1.98
1.00
3.02
2.98
2.97
2.99
f1 (ppm)

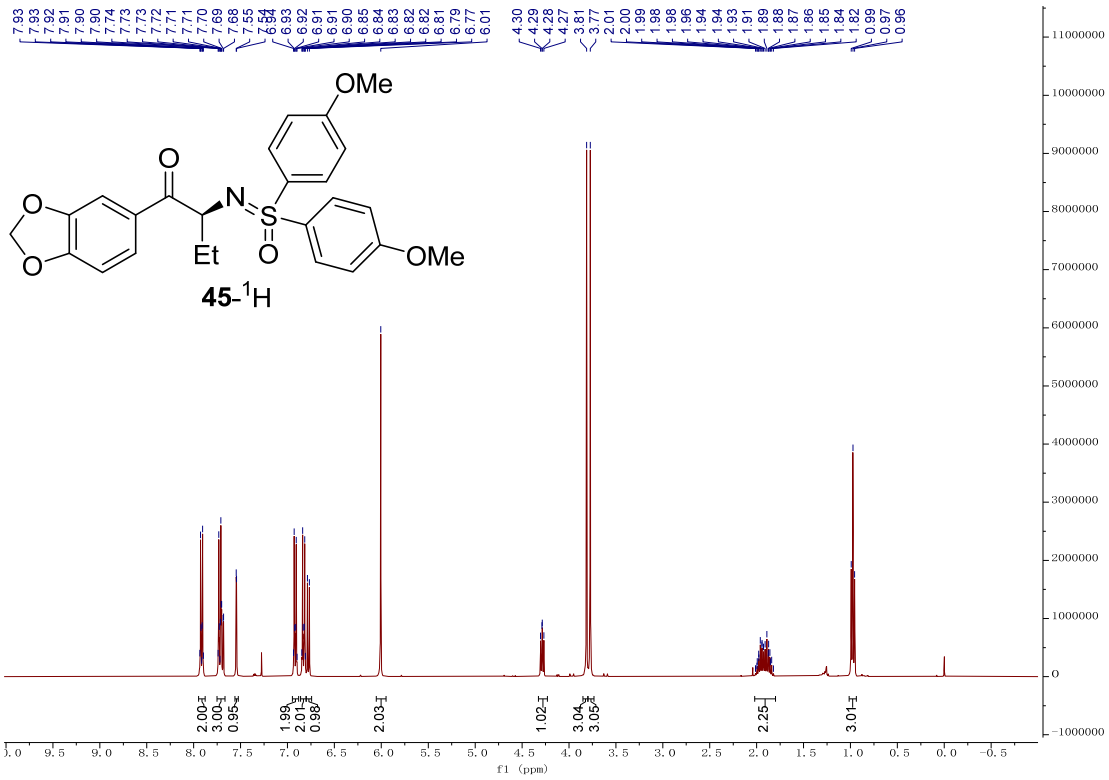

200.71
162.77
162.64
143.33
133.31
133.03
132.61
130.46
130.31
129.29
128.98
114.32
114.25
55.58
55.53
55.29
22.37
21.63
OMe
O
N
S
O
Me
Me
O
OMe
42-13C
f1 (ppm)

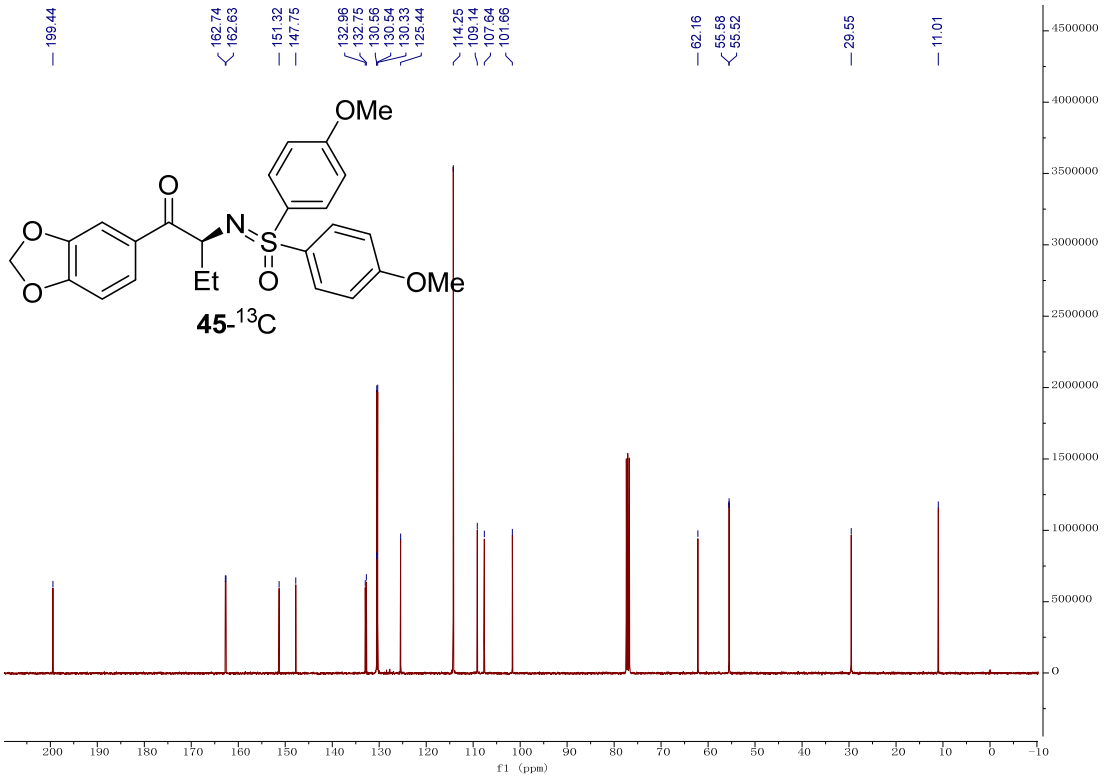

8.09
8.07
7.96
7.93
7.77
7.74
7.47
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.39
7.38
7.37
7.36
7.00
6.97
6.95
6.93
6.87
6.85
5.14
5.10
4.68
4.67
4.65
3.84
3.80
1.54
1.52
OMe
O
N
S
O
Me
O
OMe
BnO
43-1H
2.00
1.96
1.94
5.24
2.00
1.98
1.95
1.99
1.00
3.03
2.97
2.95
f1 (ppm)

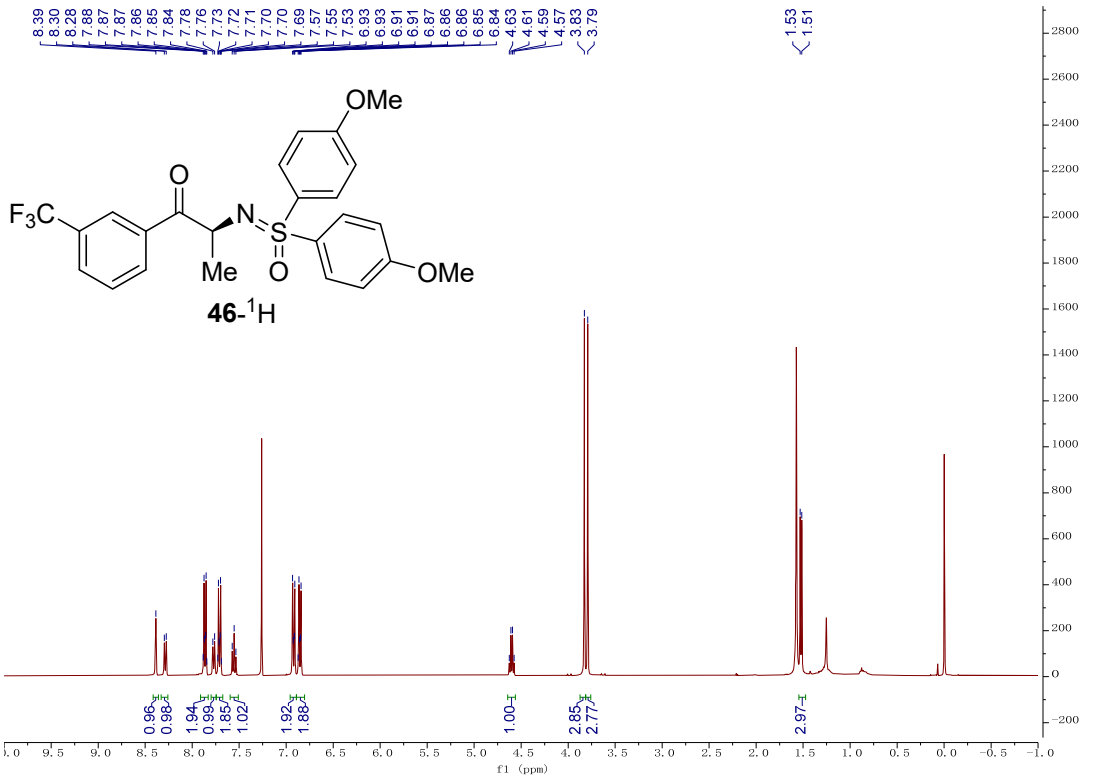

199.62
162.77
162.65
162.32
136.32
133.31
132.62
131.58
130.46
130.31
128.70
128.59
128.22
127.52
114.33
114.30
114.27
70.08
55.60
55.55
55.30
22.45
OMe
O
N
S
O
Me
O
OMe
BnO
43-13C
f1 (ppm)


7.94 7.94 7.93 7.92 7.91 7.91 7.75 7.74 7.73 7.72 7.72 7.71 7.60 7.59 7.59 7.58 7.57 7.57 7.55 7.55 7.54 7.32 7.30 7.28 7.07 7.07 7.05 7.05 7.04 6.94 6.93 6.92 6.91 6.91 6.90 6.86 6.85 6.85 6.83 6.83 6.82 4.71 4.70 4.68 4.66 3.82 3.82 3.78 1.51 1.49
OMe
O
MeO
N
S
O
Me
OMe
44-1H
1.95 1.98 1.97 1.01 1.02 1.96 1.98 1.00 5.69 2.97 2.91
f1 (ppm)


200.92
162.79 162.65 159.57
137.09 133.28 132.58 130.44 130.32 129.21 121.69 119.32 114.32 114.25 113.26
55.59 55.54 55.41 55.26
22.22
OMe
O
MeO
N
S
O
Me
OMe
44-13C
f1 (ppm)


OMe
O
N
S
O
Et
O
OMe
O
O
45-1H
f1 (ppm)


OMe
O
N
S
O
Et
O
OMe
O
O
45-13C
f1 (ppm)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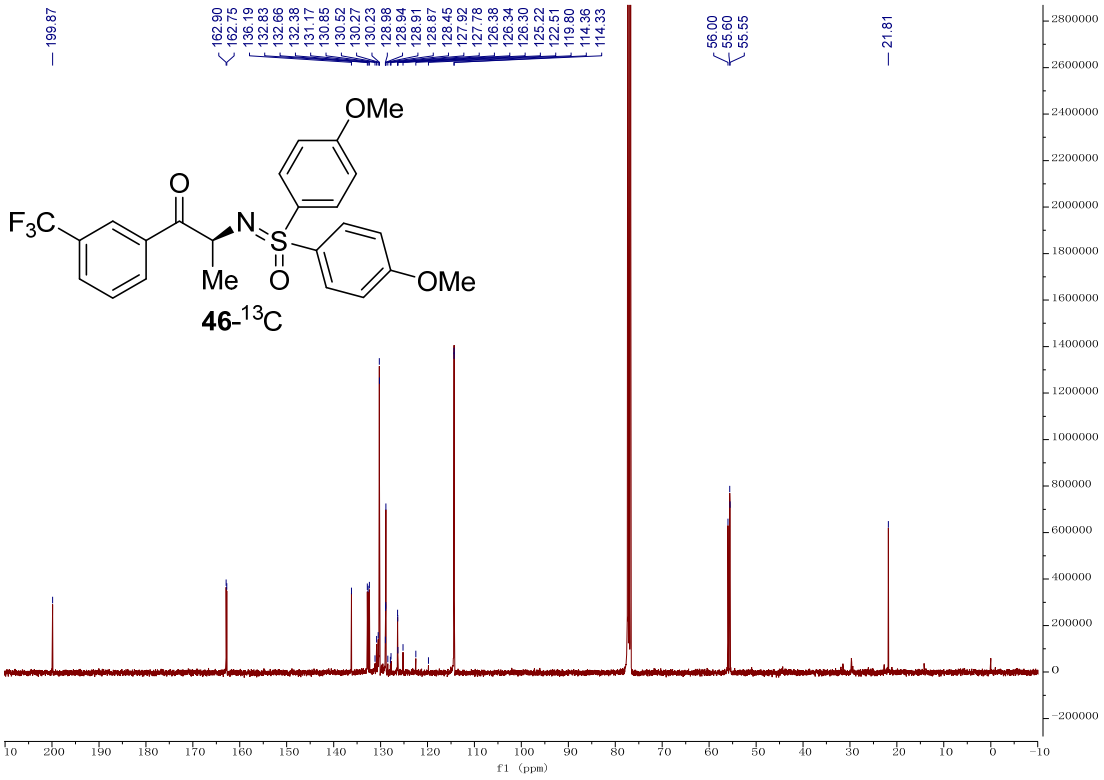
8.30
8.28
7.88
7.87
7.87
7.86
7.85
7.84
7.78
7.76
7.73
7.72
7.71
7.70
7.70
7.69
7.57
7.55
7.53
6.93
6.93
6.91
6.91
6.87
6.86
6.86
6.85
6.84
4.63
4.61
4.59
4.57
3.83
3.79
1.53
1.51
OMe
O
F3C
N
S
Me
O
OMe
46-1H
0.96
0.98
1.94
0.99
1.85
1.02
1.92
1.88
1.00
2.85
2.77
2.97
f1 (ppm)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162.90
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132.66
132.38
131.17
130.85
130.52
130.27
130.23
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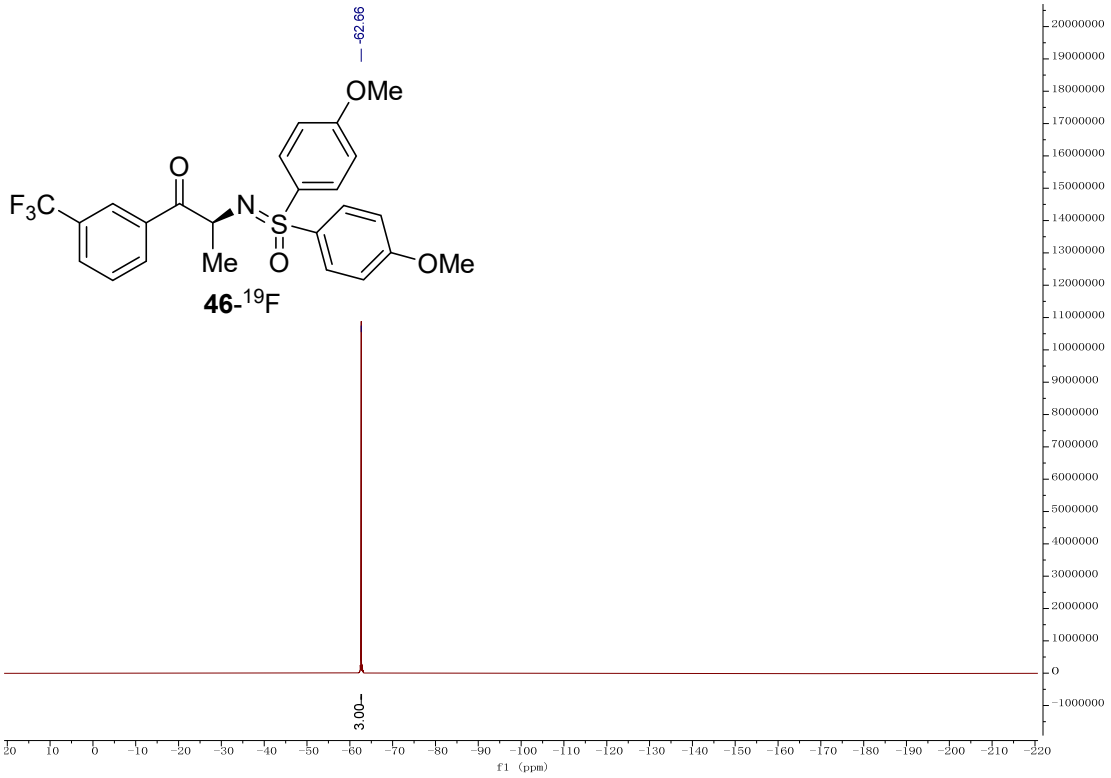
128.94
128.91
128.87
128.45
127.92
127.78
126.38
126.34
126.30
125.22
122.51
119.80
114.36
114.33
56.00
55.60
55.55
21.81
OMe
O
F3C
N
S
Me
O
OMe
46-13C
f1 (ppm)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O
F3C
N
S
Me
O
OMe
46-19F
3.00
20000000
19000000
18000000
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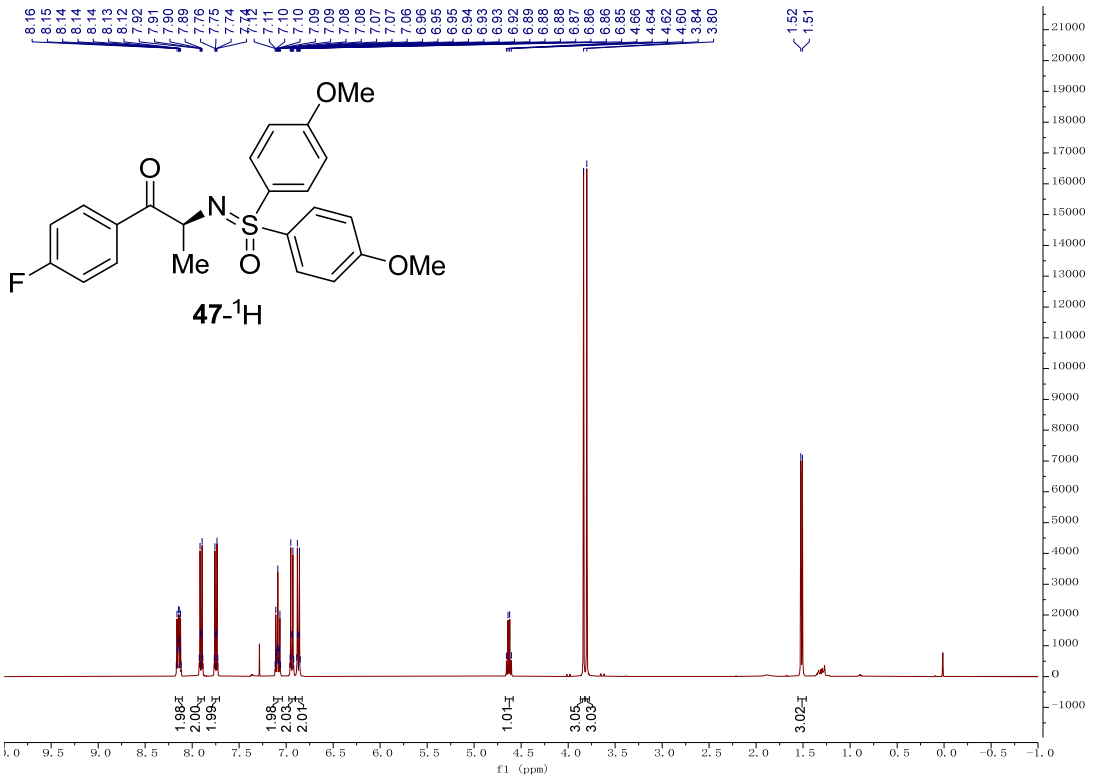
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


8.16
8.15
8.14
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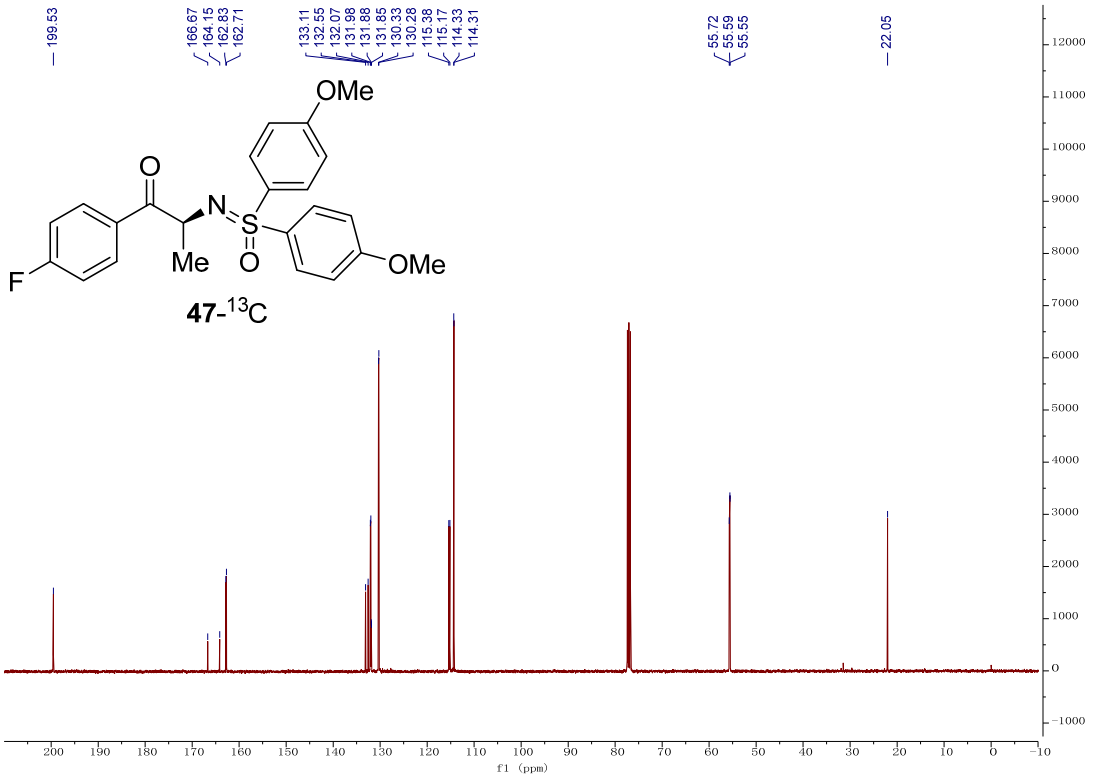
8.13
8.12
7.92
7.91
7.90
7.89
7.78
7.75
7.74
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.07
7.06
6.96
6.95
6.95
6.94
6.93
6.93
6.92
6.89
6.88
6.88
6.87
6.86
6.86
6.85
4.66
4.64
4.62
4.60
3.84
3.80
1.52
1.51
OMe
O
N
S
O
Me
OMe
F
47-1H
1.98
2.00
1.99
1.98
2.03
2.01
1.01
3.05
3.03
3.02
f1 (ppm)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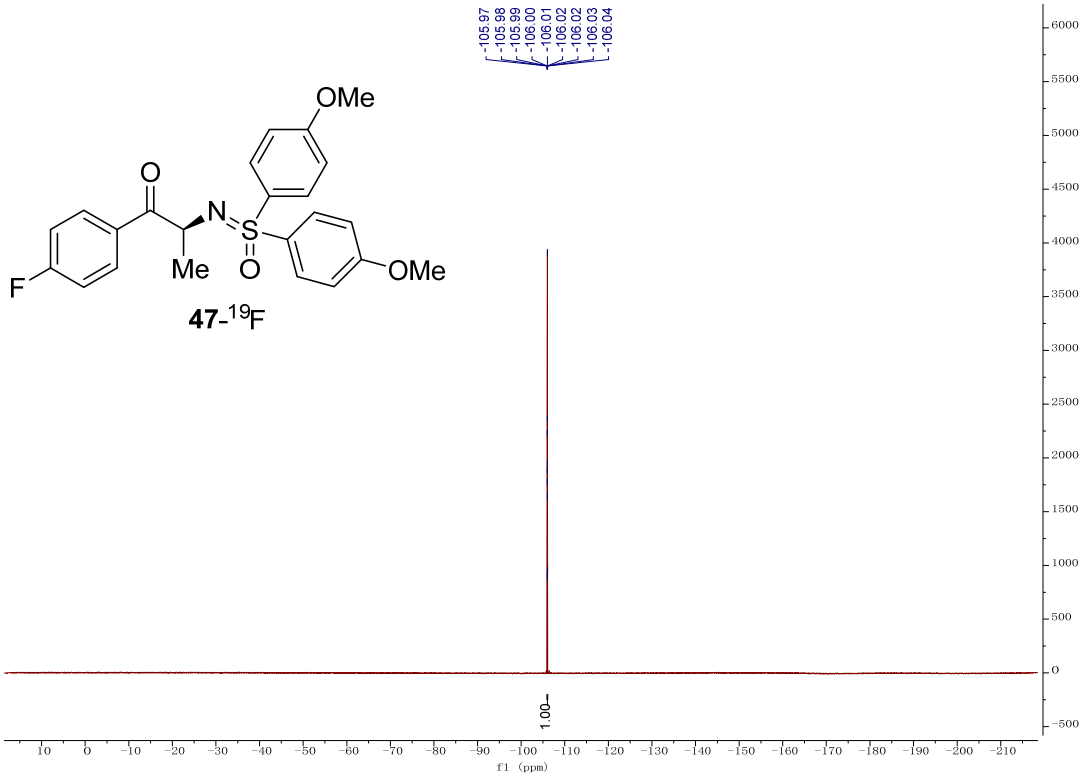
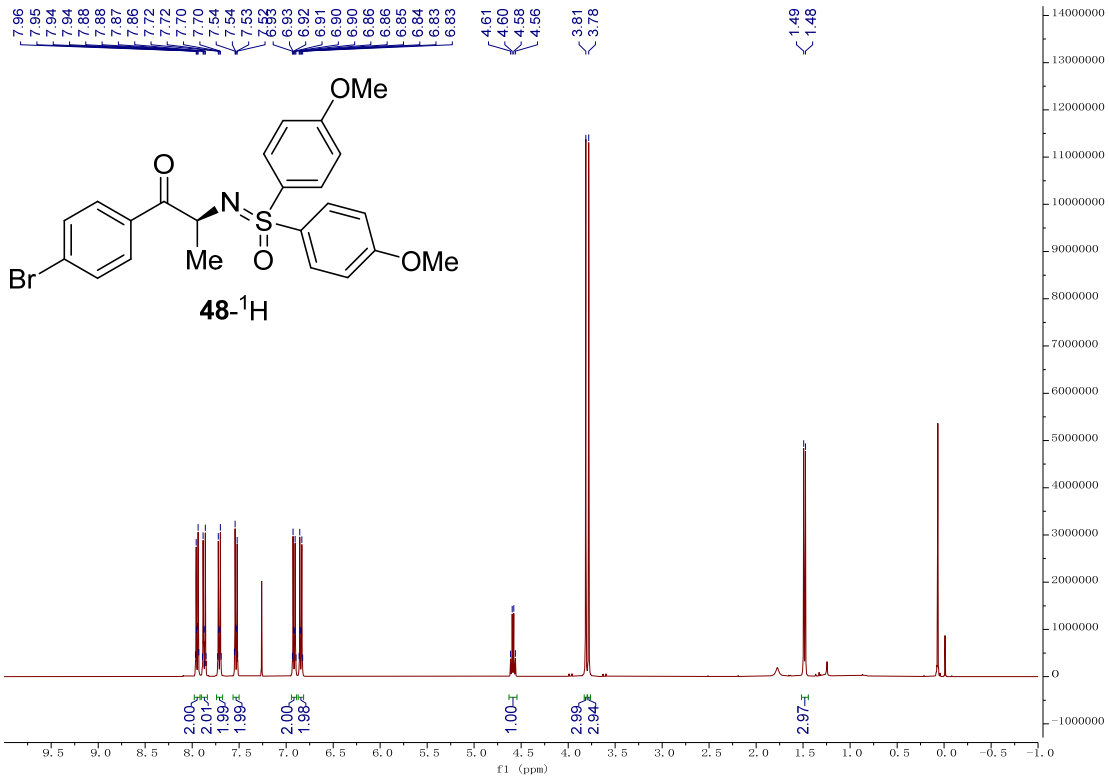
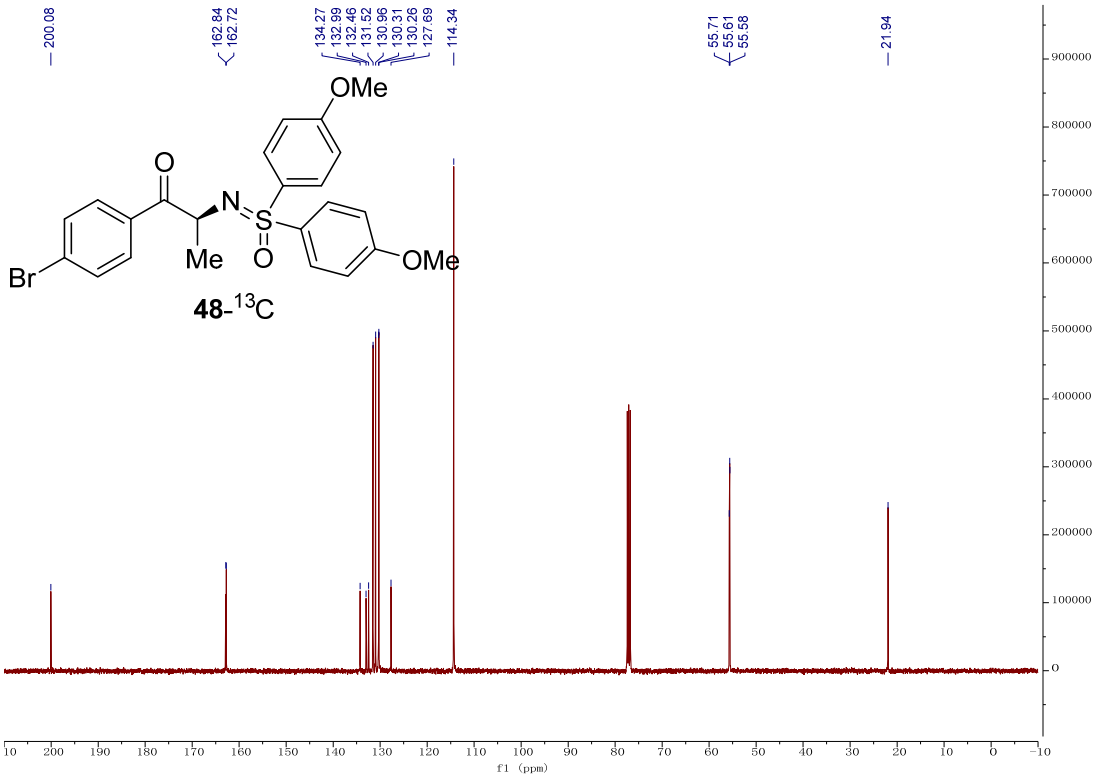
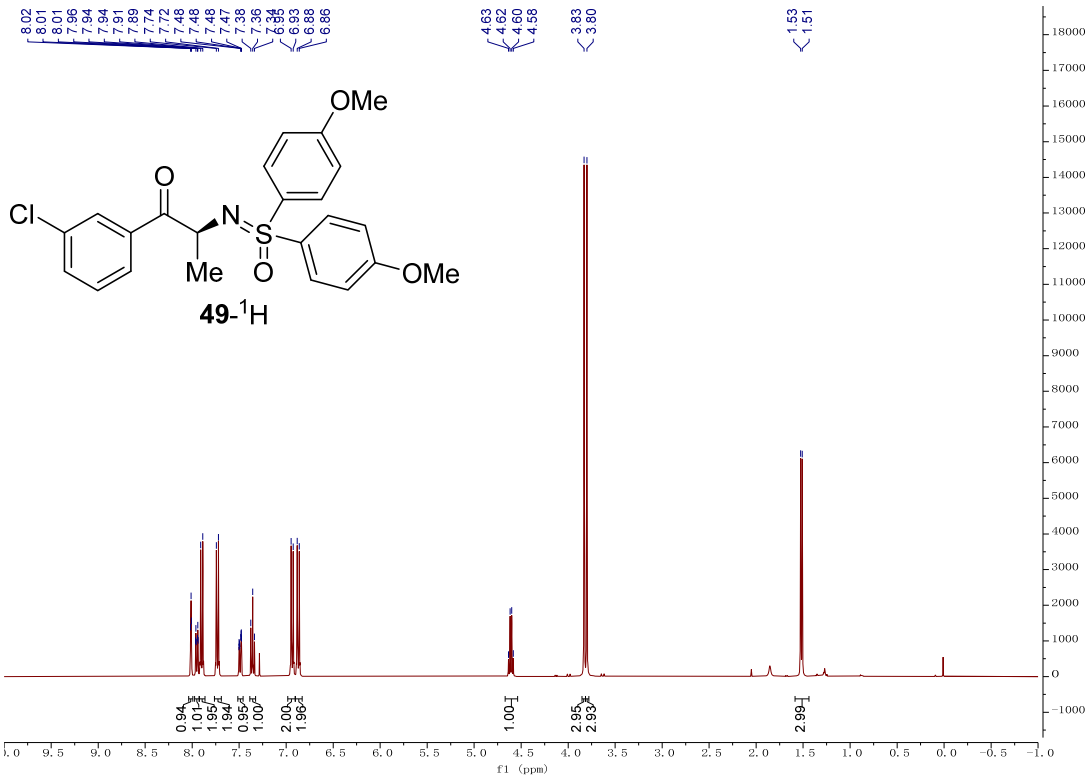
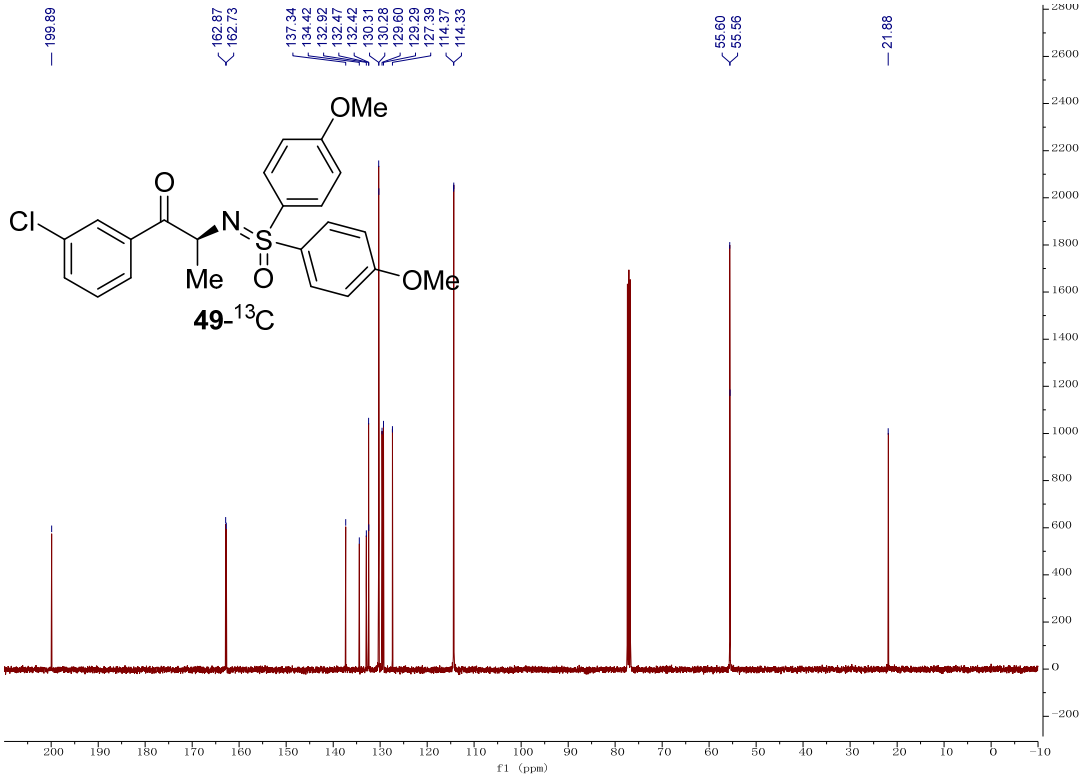
166.67
164.15
162.83
162.71
133.11
132.55
132.07
131.98
131.88
131.85
130.33
130.28
115.38
115.17
114.33
114.31
55.72
55.59
55.55
22.05
OMe
O
N
S
O
Me
OMe
F
47-13C
f1 (ppm)

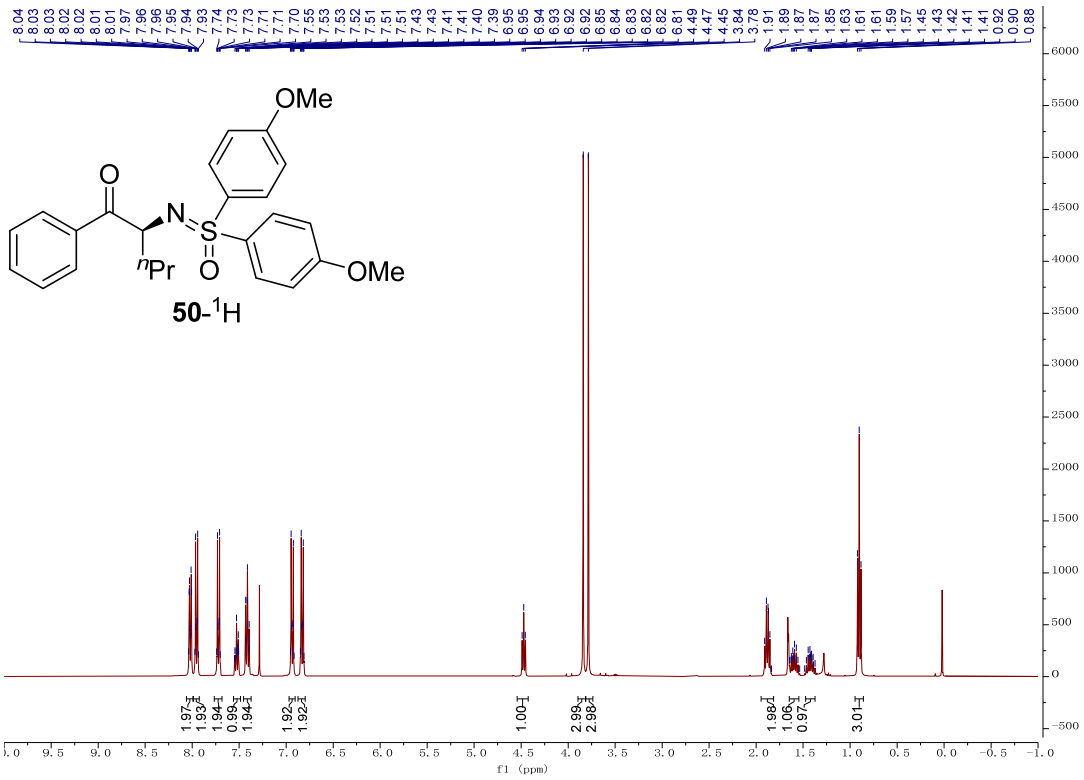

-105.97
-105.98
-105.99
-106.00
-106.01
-106.02
-106.02
-106.03
-106.04
OMe
O
N
S
O
Me
OMe
F
47-19F
1.00
f1 (ppm)

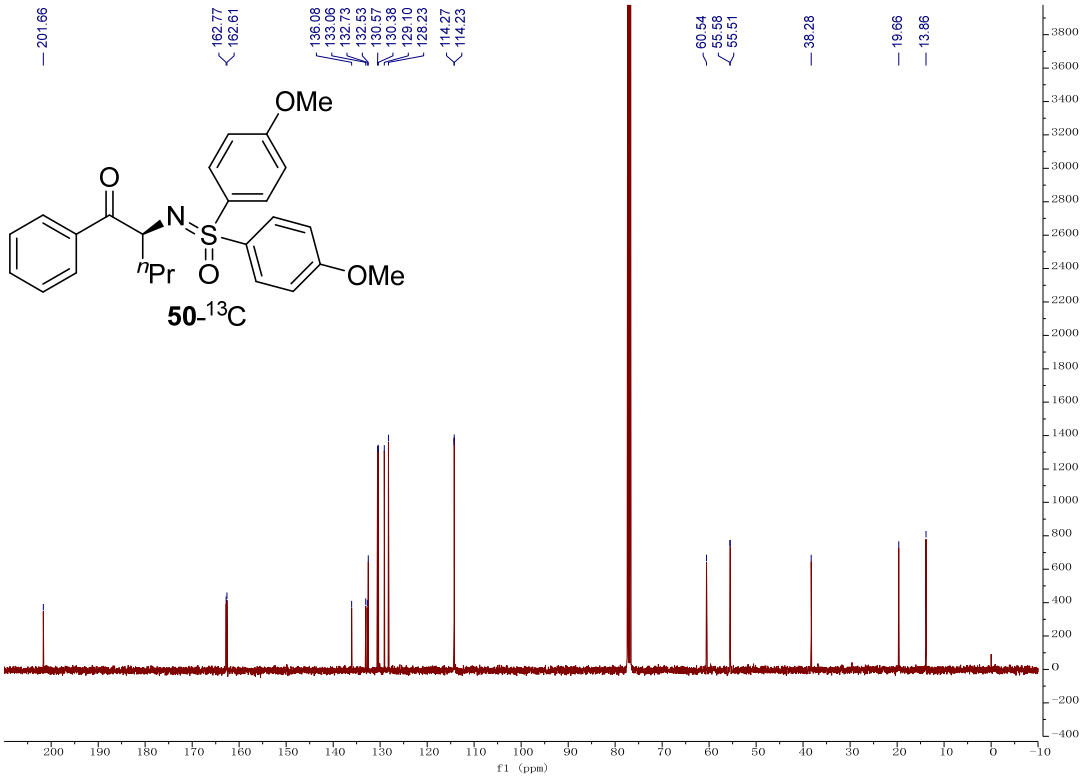

7.96
7.95
7.94
7.94
7.88
7.88
7.87
7.86
7.72
7.72
7.70
7.70
7.54
7.54
7.53
7.52
6.93
6.93
6.92
6.91
6.90
6.90
6.86
6.86
6.85
6.84
6.83
6.83
4.61
4.60
4.58
4.56
3.81
3.78
1.49
1.48
OMe
O
N
S
O
Me
Br
OMe
48-1H
2.00
2.01
1.99
1.99
2.00
1.98
1.00
2.99
2.94
2.97
f1 (ppm)

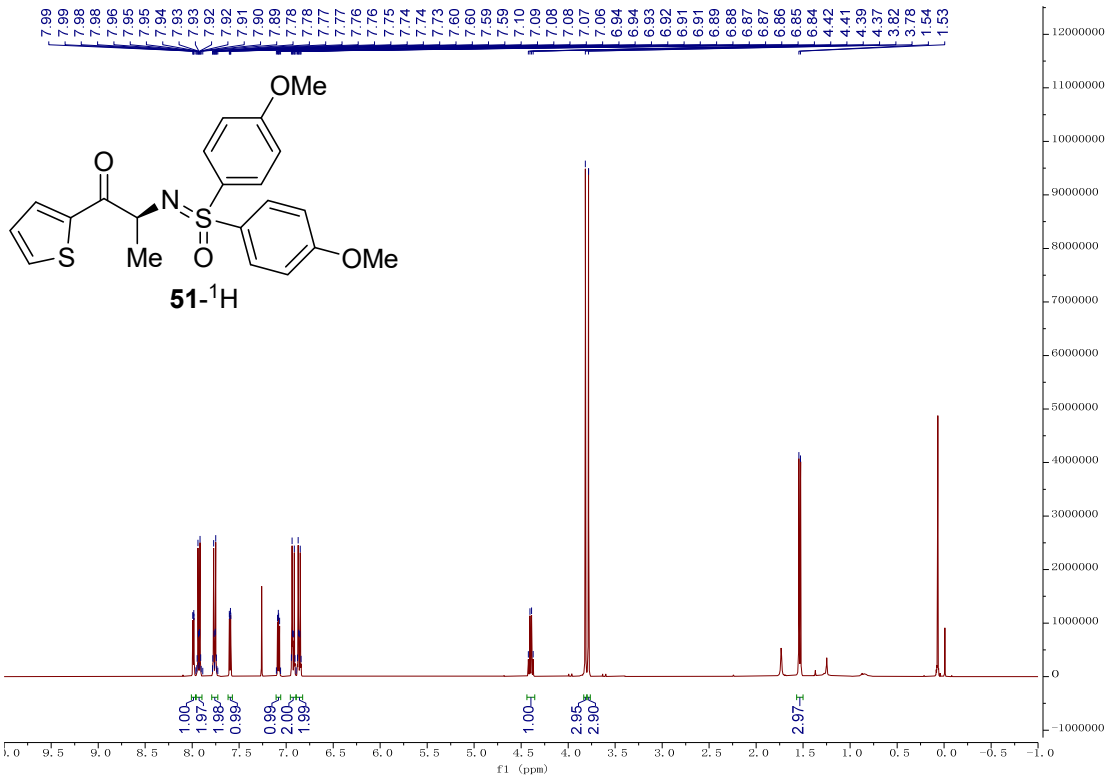

200.08
162.84
162.72
134.27
132.99
132.46
131.52
130.96
130.31
130.26
127.69
114.34
55.71
55.61
55.58
21.94
OMe
O
N
S
O
Me
Br
OMe
48-13C
f1 (ppm)

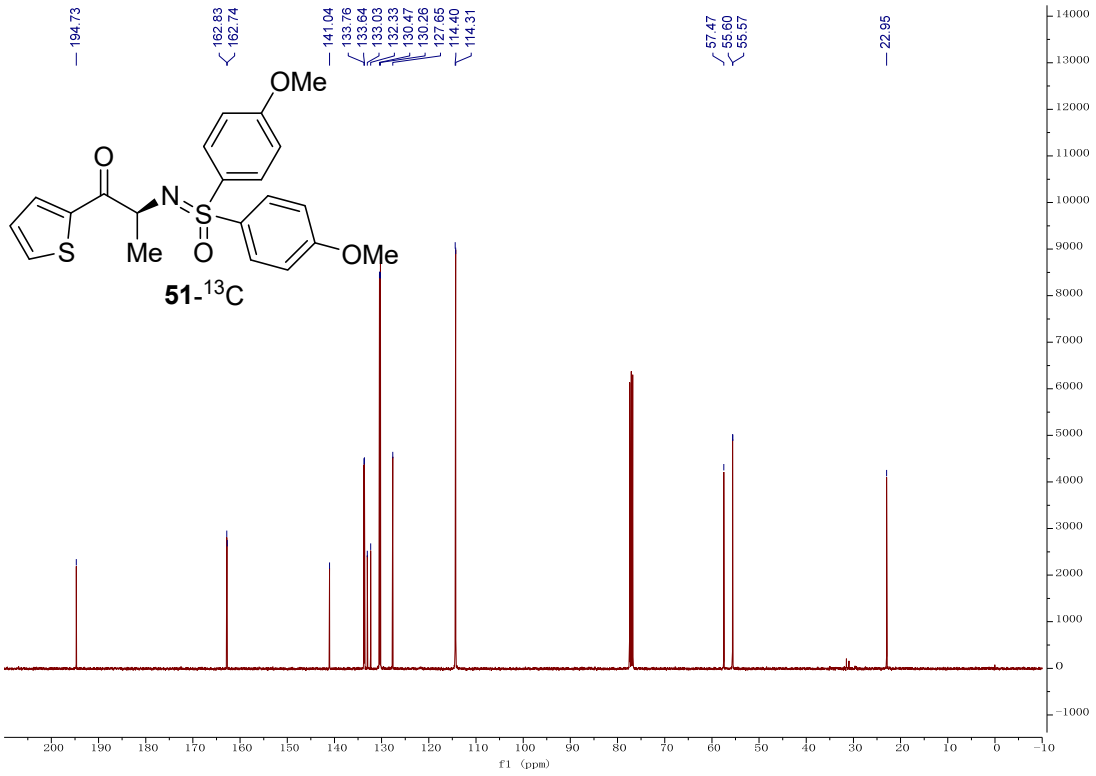

8.02
8.01
8.01
7.96
7.94
7.94
7.91
7.89
7.74
7.72
7.48
7.48
7.48
7.47
7.38
7.36
6.94
6.93
6.88
6.86
4.63
4.62
4.60
4.58
3.83
3.80
1.53
1.51
OMe
O
Cl
N
S
O
Me
OMe
49-1H
0.94
1.01
1.95
1.94
0.95
1.00
2.00
1.96
1.00
2.95
2.93
2.99
f1 (ppm)

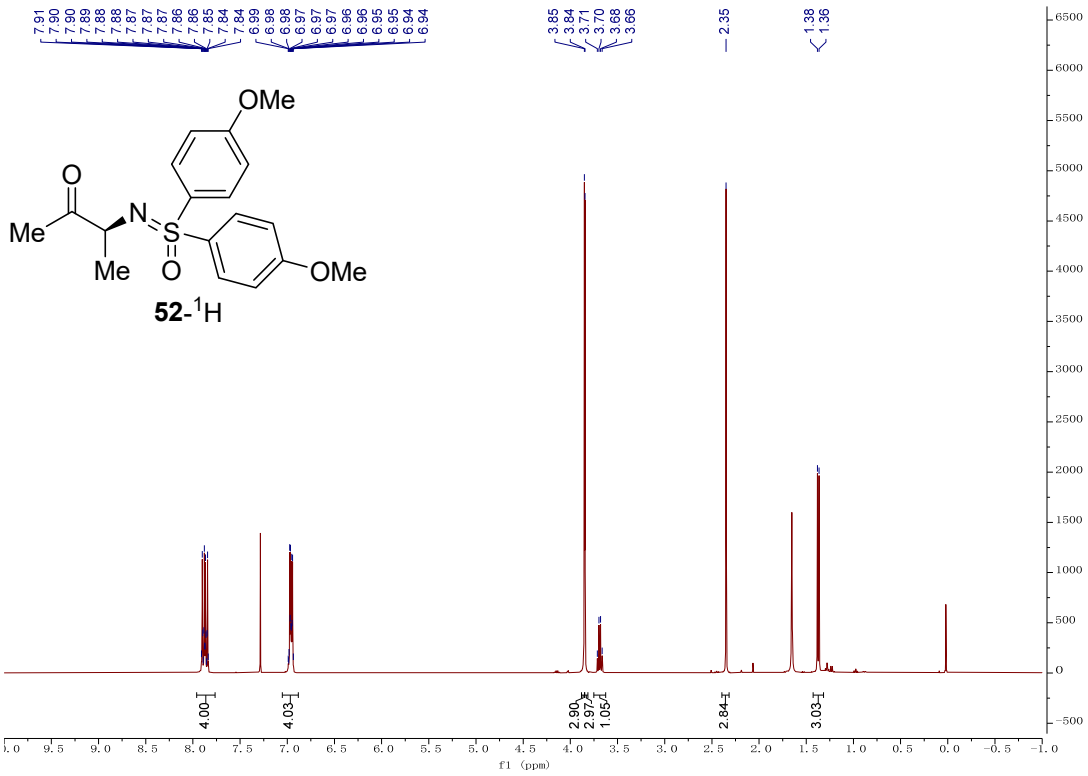

199.89
162.87
162.73
137.34
134.42
132.92
132.47
132.42
130.31
130.28
129.60
129.29
127.39
114.37
114.33
55.60
55.56
21.88
OMe
O
Cl
N
S
O
Me
OMe
49-13C
f1 (ppm)


OMe
O
N
S
O
nPr
OMe
50-1H
f1 (ppm)


OMe
O
N
S
O
nPr
OMe
50-13C
f1 (ppm)


7.99 7.99 7.98 7.98 7.96 7.95 7.95 7.94 7.93 7.93 7.92 7.92 7.91 7.90 7.89 7.78 7.78 7.77 7.77 7.76 7.76 7.75 7.74 7.74 7.73 7.60 7.60 7.59 7.59 7.10 7.09 7.08 7.08 7.07 7.06 6.94 6.94 6.93 6.92 6.91 6.91 6.89 6.88 6.87 6.87 6.86 6.85 6.84 4.42 4.41 4.39 4.37 3.82 3.78 1.54 1.53
OMe
O
N
S
O
Me
S
OMe
51-1H
1.00 1.97 1.98 0.99 0.99 2.00 1.99 1.00 2.95 2.90 2.97
f1 (ppm)


194.73
162.83 162.74
141.04
133.76 133.64 133.03 132.33 130.47 130.26 127.65 114.40 114.31
57.47 55.60 55.57
22.95
OMe
O
N
S
O
Me
S
OMe
51-13C
f1 (ppm)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7.89
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7.88
7.87
7.87
7.87
7.86
7.86
7.85
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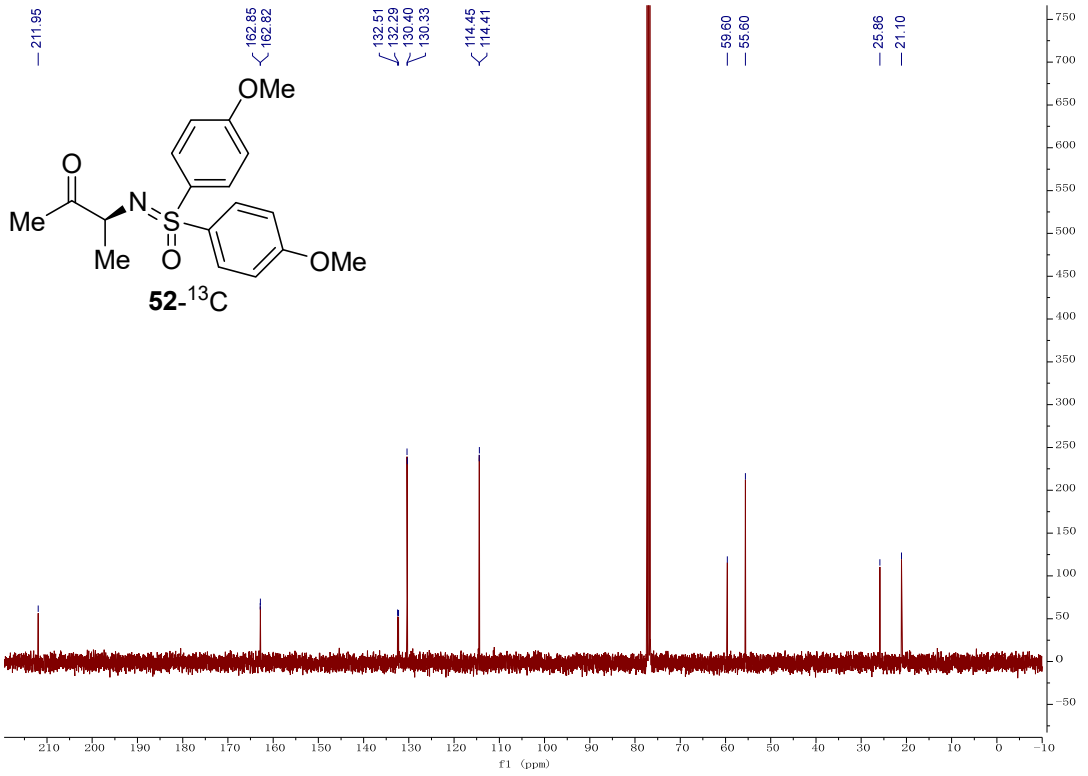
7.84
6.99
6.98
6.98
6.97
6.97
6.97
6.96
6.96
6.95
6.95
6.94
6.94
3.85
3.84
3.71
3.70
3.68
3.66
2.35
1.38
1.36
OMe
O
N
S
Me
Me
O
OMe
52-1H
4.00
4.03
2.90
2.97
1.05
2.84
3.03
f1 (ppm)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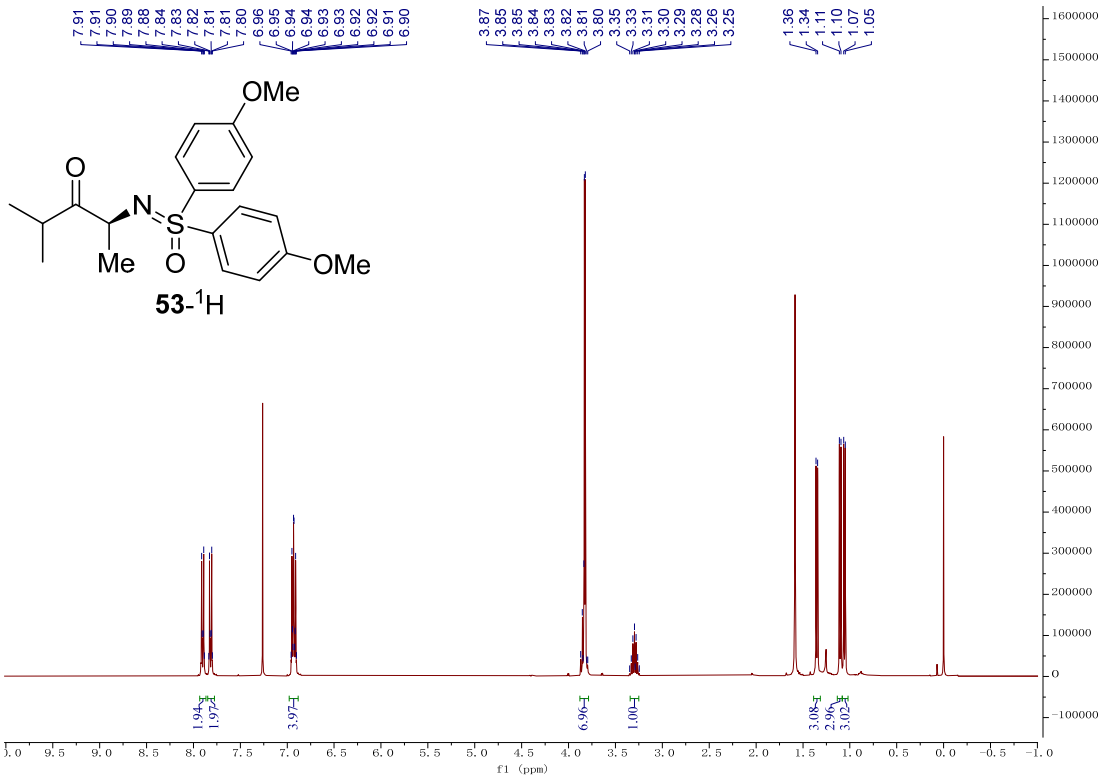
162.85
162.82
132.51
132.29
130.40
130.33
114.45
114.41
59.60
55.60
25.86
21.10
OMe
O
N
S
Me
Me
O
OMe
52-13C
f1 (ppm)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7.89
7.88
7.84
7.83
7.82
7.81
7.81
7.80
6.96
6.95
6.94
6.94
6.93
6.93
6.92
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6.91
6.90
3.87
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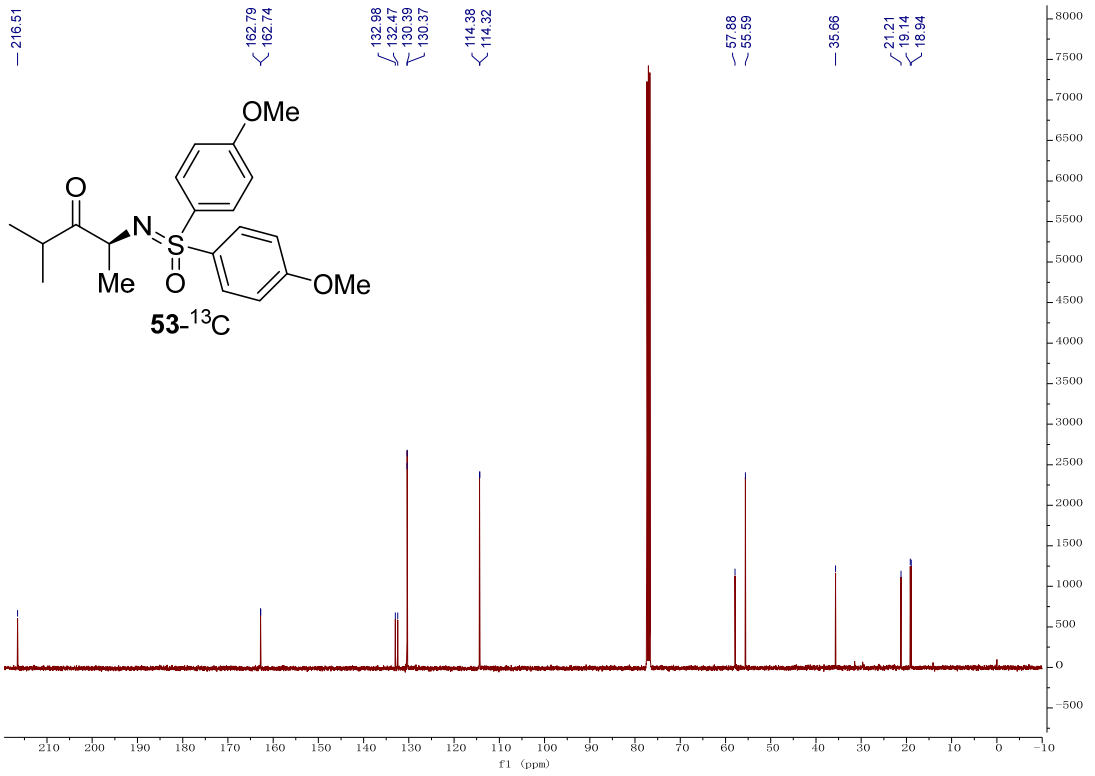
3.84
3.83
3.82
3.81
3.80
3.35
3.33
3.31
3.30
3.29
3.28
3.26
3.25
1.36
1.34
1.11
1.10
1.07
1.05
OMe
O
N
S
O
Me
OMe
53-1H
1.94
1.97
3.97
6.96
1.00
3.08
2.96
3.02
f1 (ppm)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162.74
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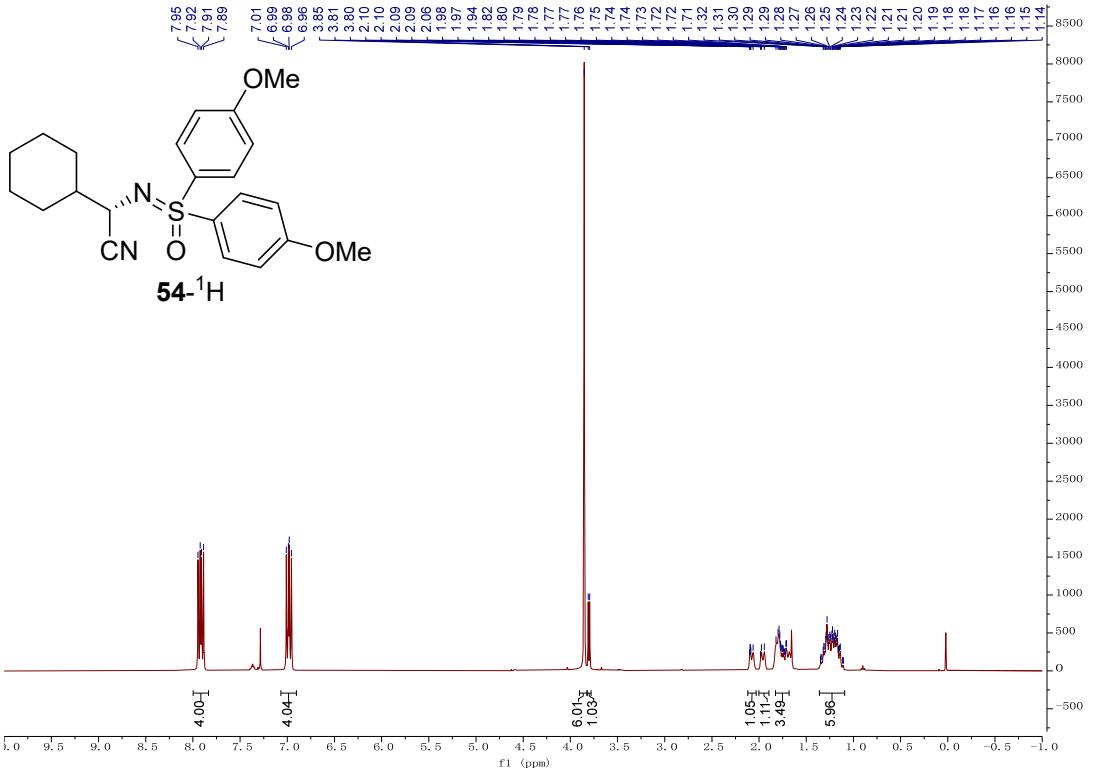
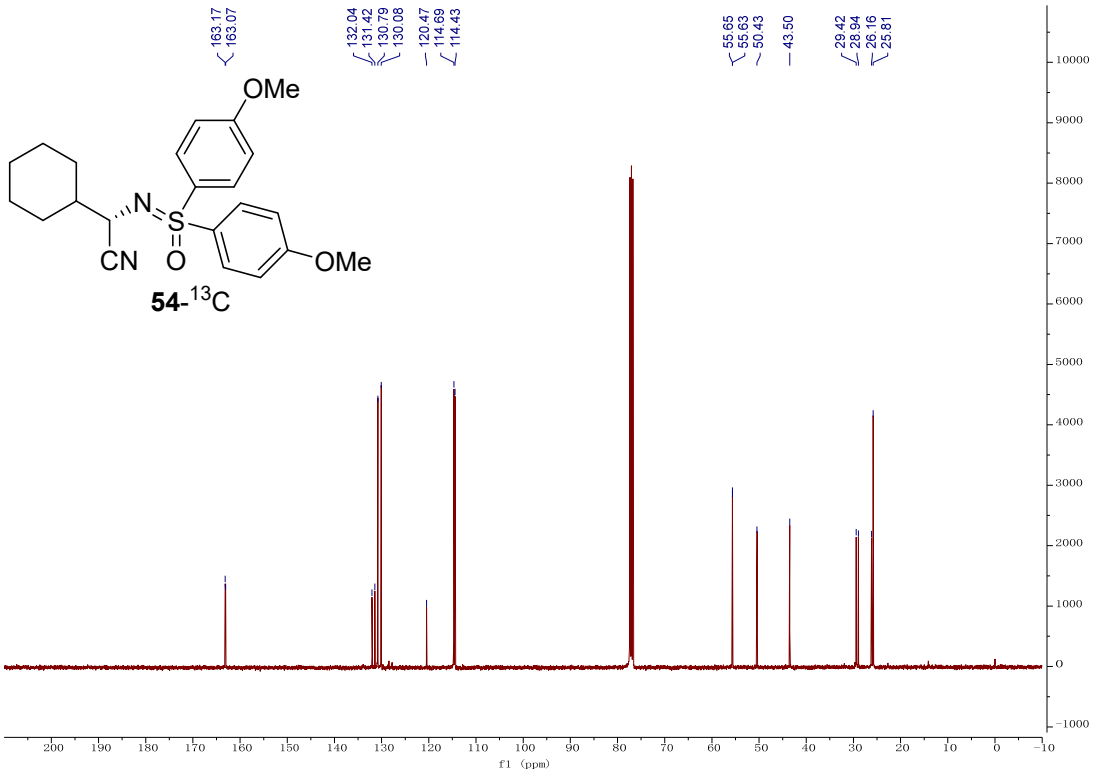
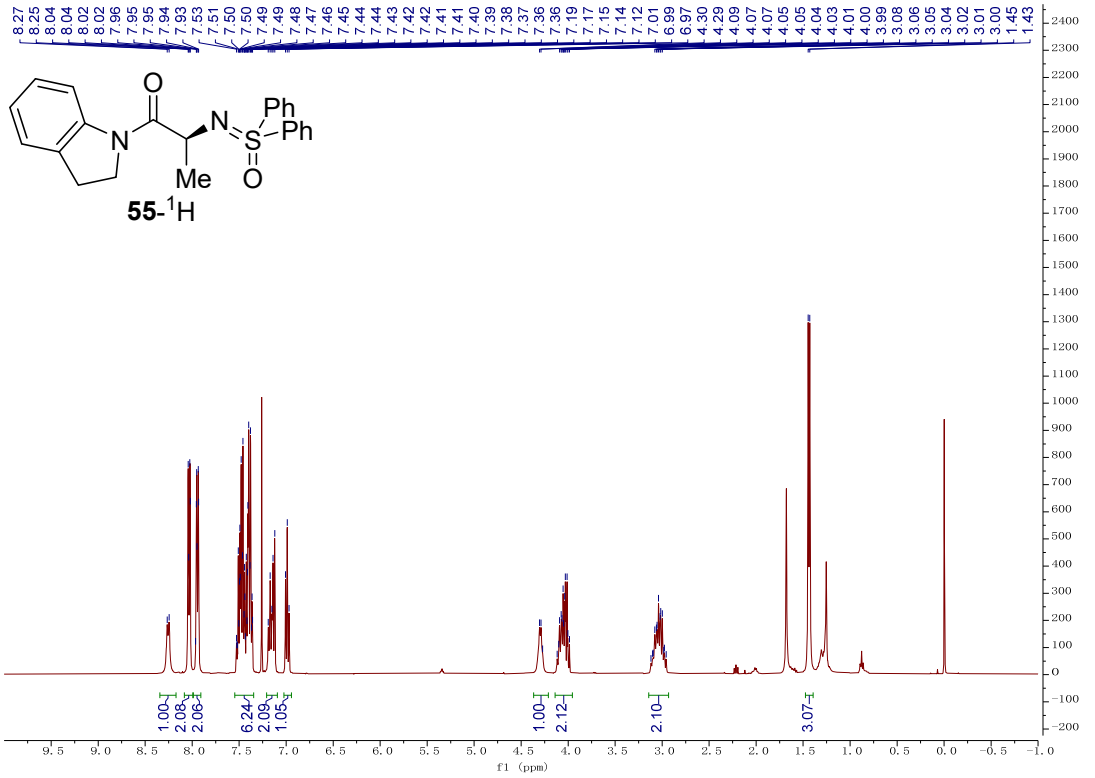
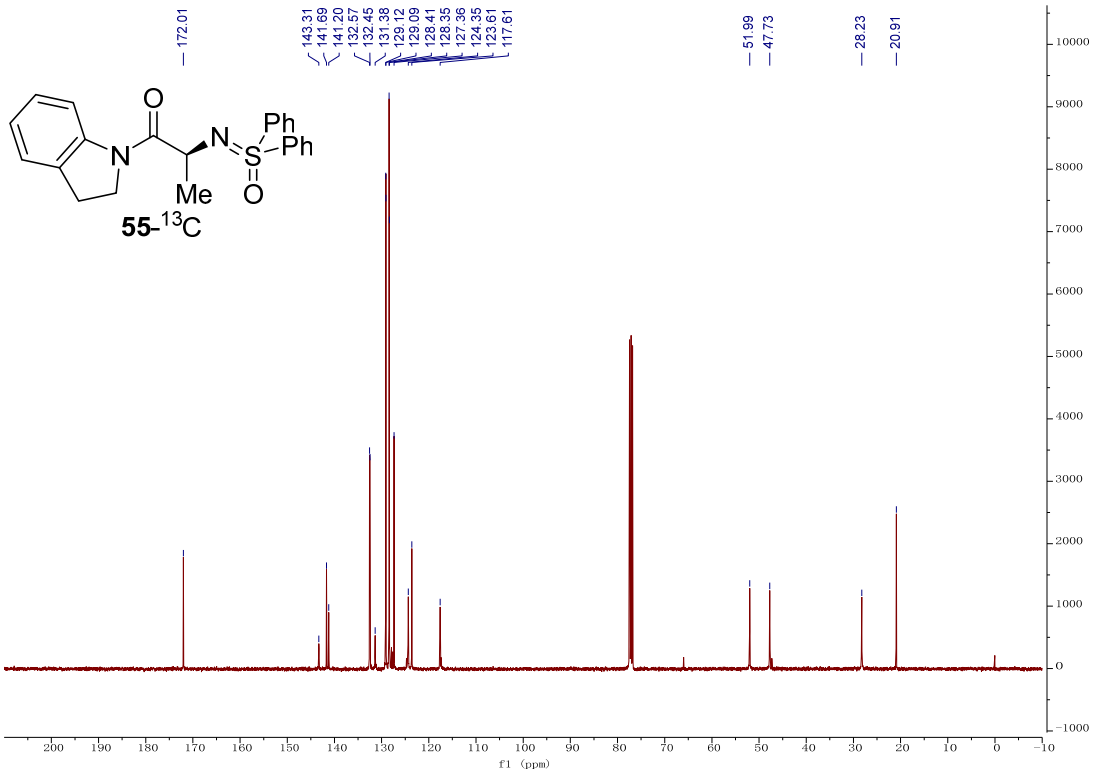
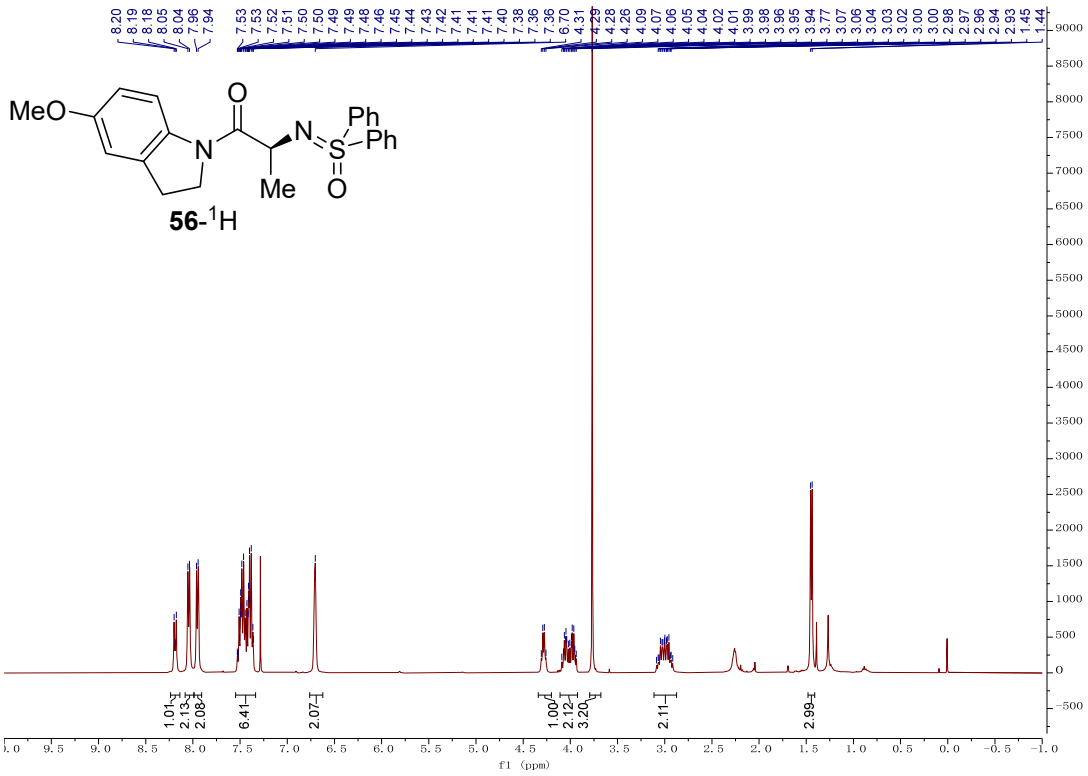
132.47
130.39
130.37
114.38
114.32
57.88
55.59
35.66
21.21
19.14
18.94
OMe
O
N
S
O
Me
OMe
53-13C
f1 (ppm)

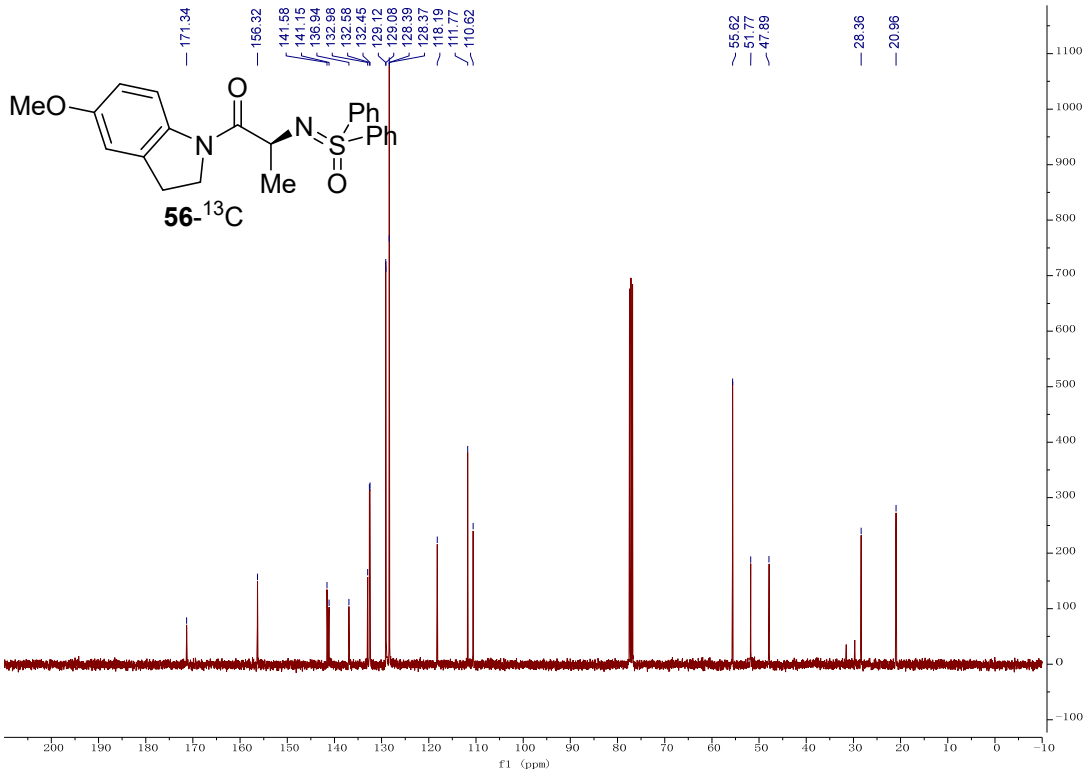

OMe
N
S
O
CN
OMe
54-1H
f1 (ppm)

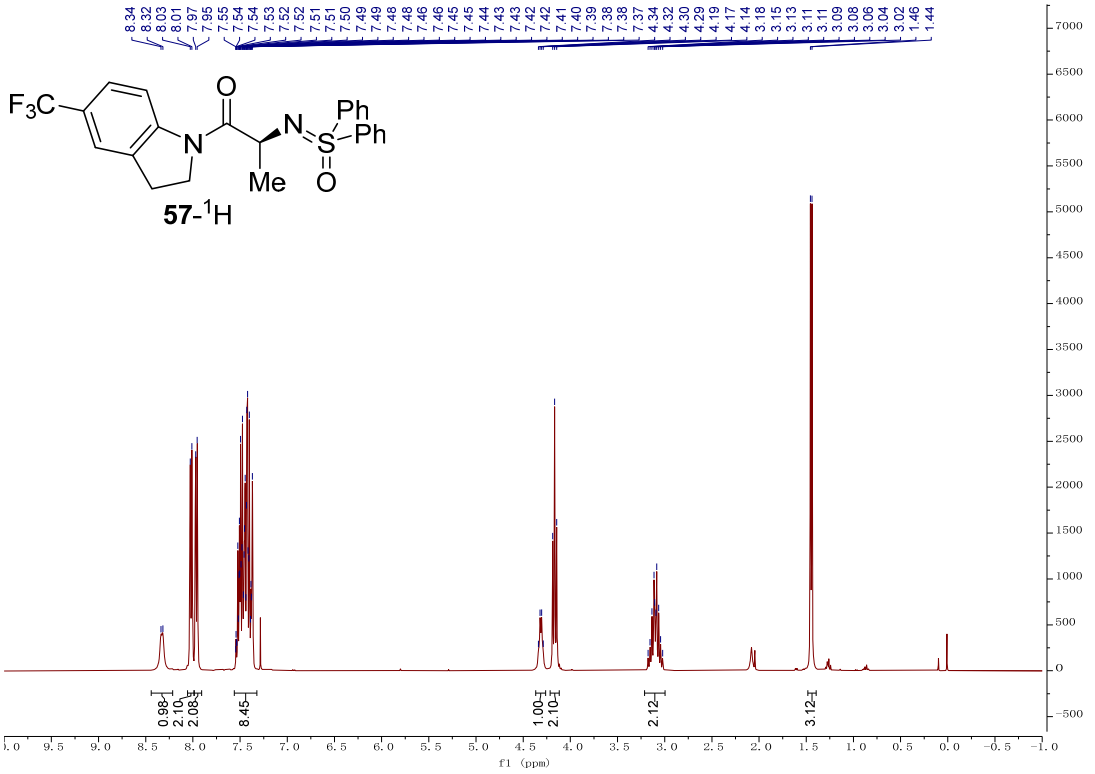

OMe
N
S
O
CN
OMe
54-13C
f1 (ppm)

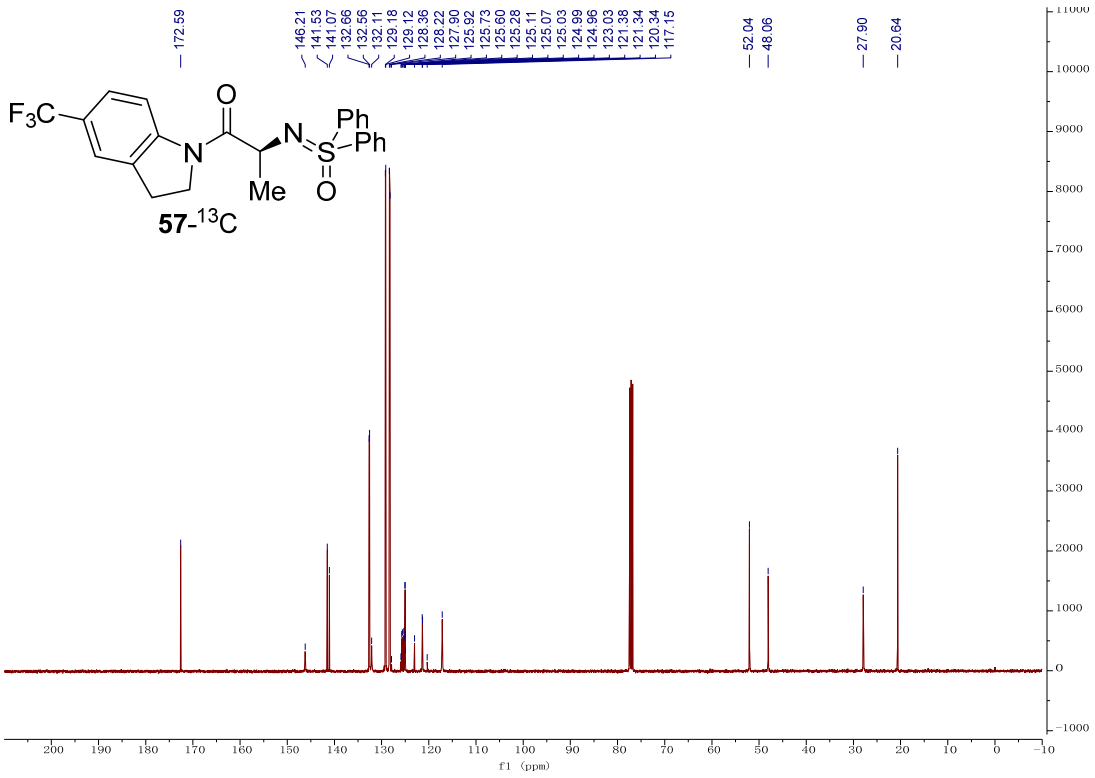

8.27 8.25 8.04 8.04 8.02 8.02 7.96 7.95 7.95 7.94 7.93 7.53 7.51 7.50 7.50 7.49 7.49 7.48 7.47 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.41 7.40 7.39 7.38 7.37 7.36 7.36 7.19 7.17 7.15 7.14 7.12 7.01 6.99 6.97 4.30 4.29 4.09 4.07 4.07 4.05 4.05 4.04 4.03 4.01 4.00 3.99 3.08 3.06 3.05 3.04 3.02 3.01 3.00 1.45 1.43
O
N
N
S
Ph
Ph
O
Me
55-1H
1.00 2.08 2.06 6.24 2.09 1.05 1.00 2.12 2.10 3.07
f1 (ppm)

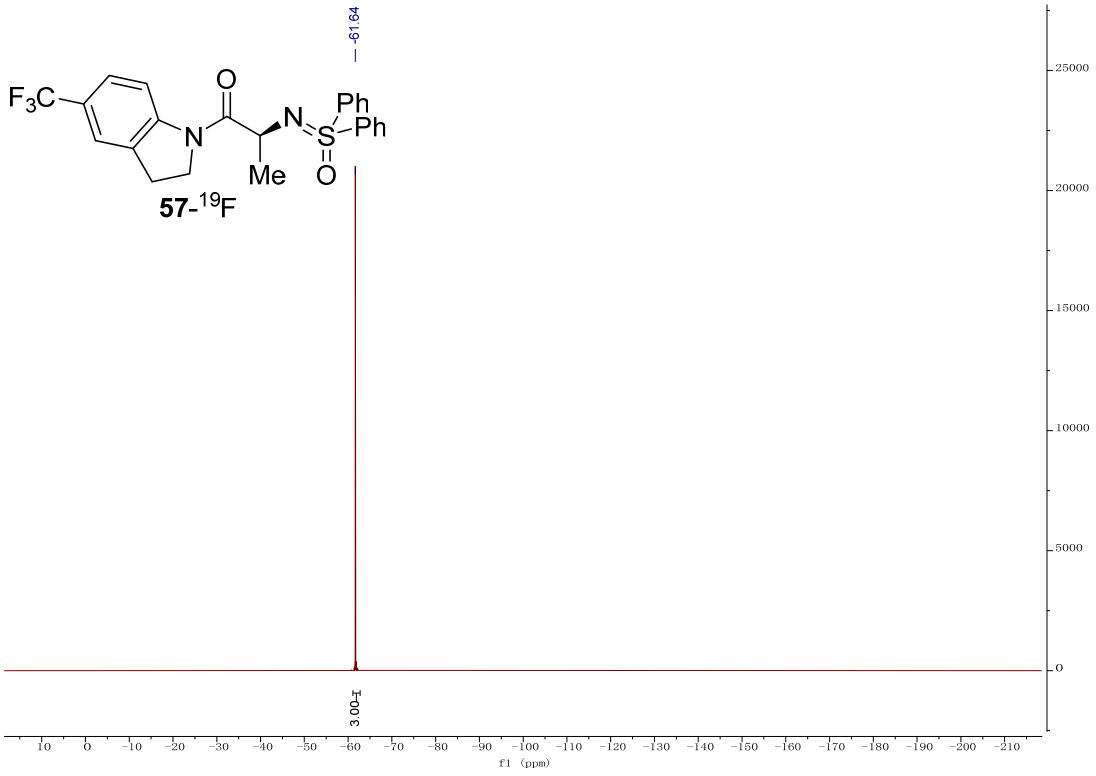

172.01
143.31 141.69 141.20 132.57 132.45 131.38 129.12 129.09 128.41 128.35 127.36 124.35 123.61 117.61
51.99 47.73 28.23 20.91
O
N
N
S
Ph
Ph
O
Me
55-13C
f1 (ppm)

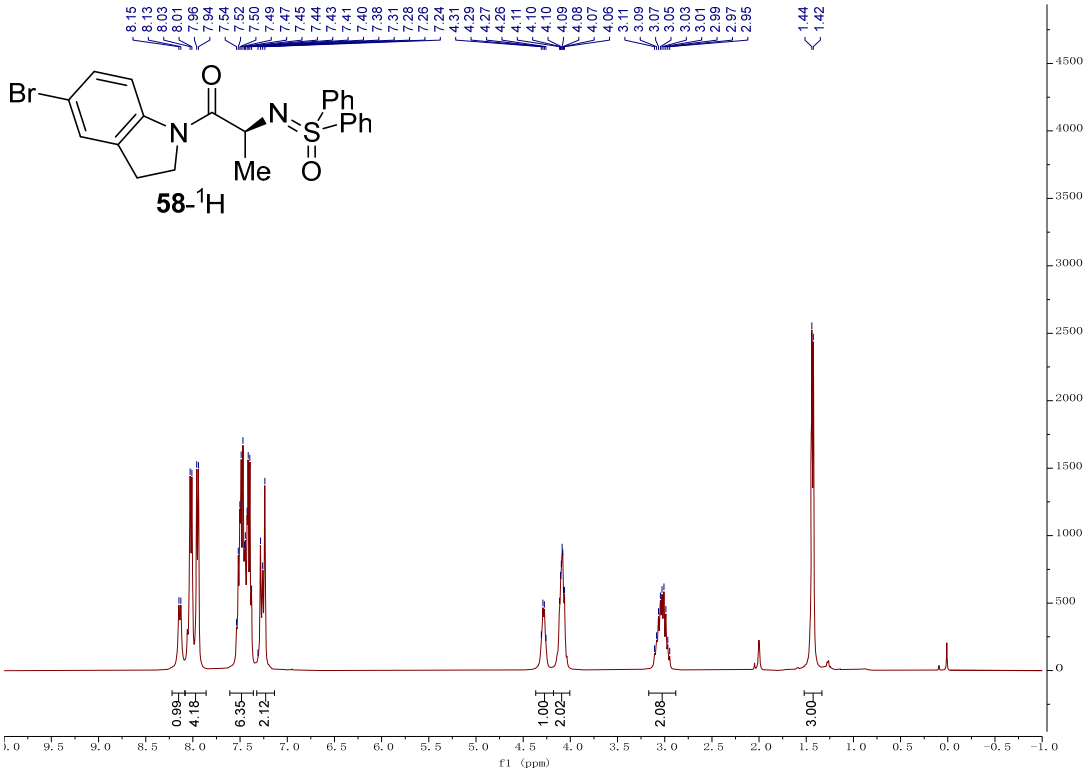

MeO
O
N
N
S
Ph
Ph
O
Me
56-1H
f1 (ppm)


MeO
O
N
N
S
Ph
Ph
O
Me
56-13C
f1 (ppm)

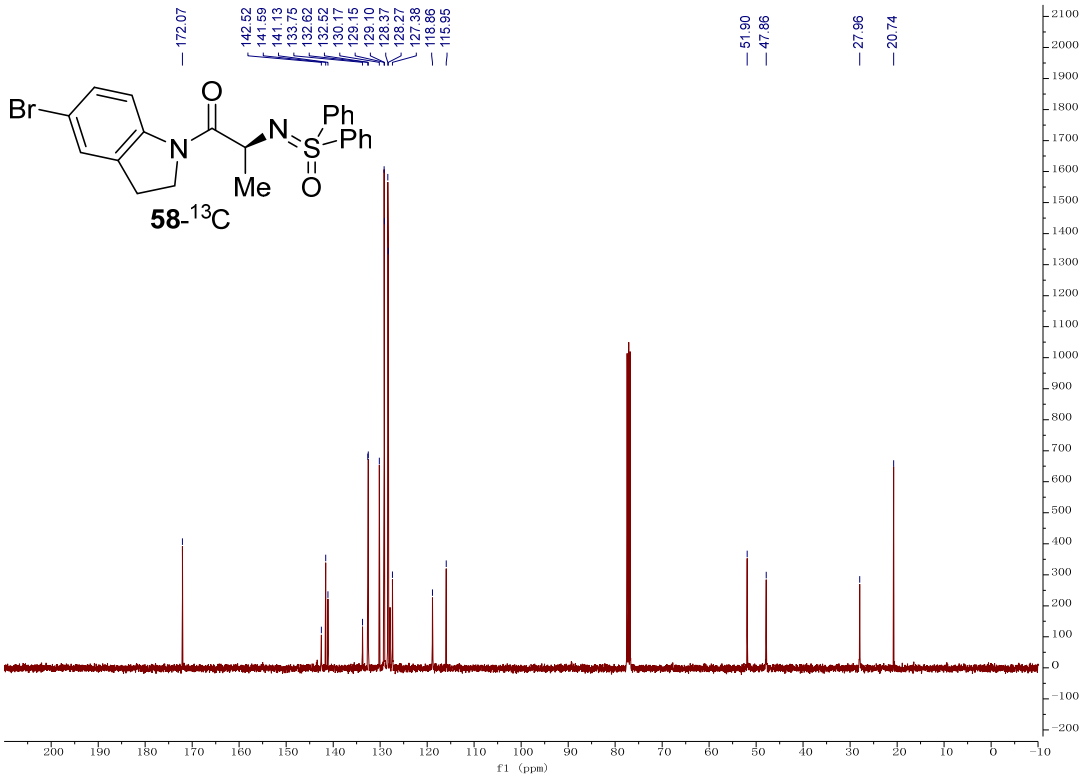

8.34 8.32 8.03 8.01 7.97 7.95 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.51 7.50 7.49 7.49 7.48 7.48 7.46 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.40 7.39 7.38 7.38 7.37 4.34 4.32 4.30 4.29 4.19 4.17 4.14 3.18 3.15 3.13 3.11 3.11 3.09 3.08 3.06 3.04 3.02 1.46 1.44
F3C
O
N
N
S
Ph
Ph
O
Me
57-1H
0.98 2.10 2.08 8.45 1.00 2.10 2.12 3.12
f1 (ppm)


172.59
146.21 141.53 141.07 132.66 132.56 132.11 129.18 129.12 128.36 128.22 127.90 125.92 125.73 125.60 125.28 125.11 125.07 125.03 124.99 124.96 123.03 121.38 121.34 120.34 117.15
52.04 48.06
27.90 20.64
F3C
O
N
N
S
Ph
Ph
O
Me
57-13C
f1 (ppm)

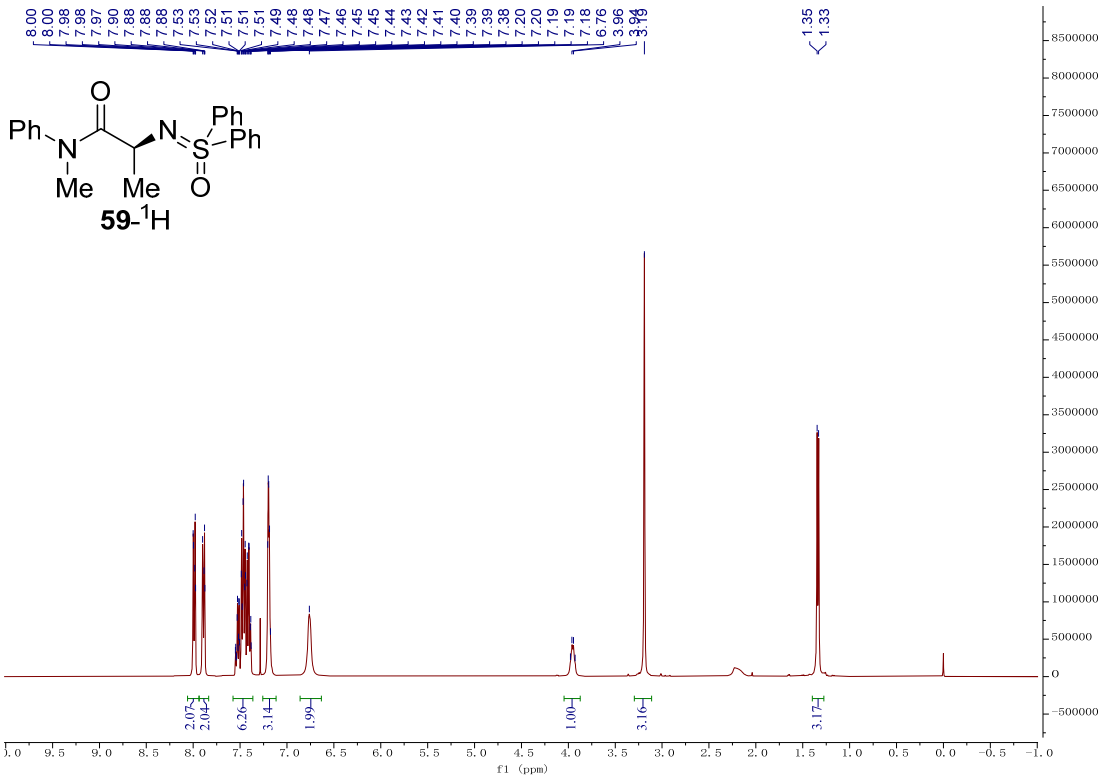

-61.64
F3C
O
N
N
S
Ph
Ph
Me
O
57-19F
25000
20000
15000
10000
5000
0
3.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

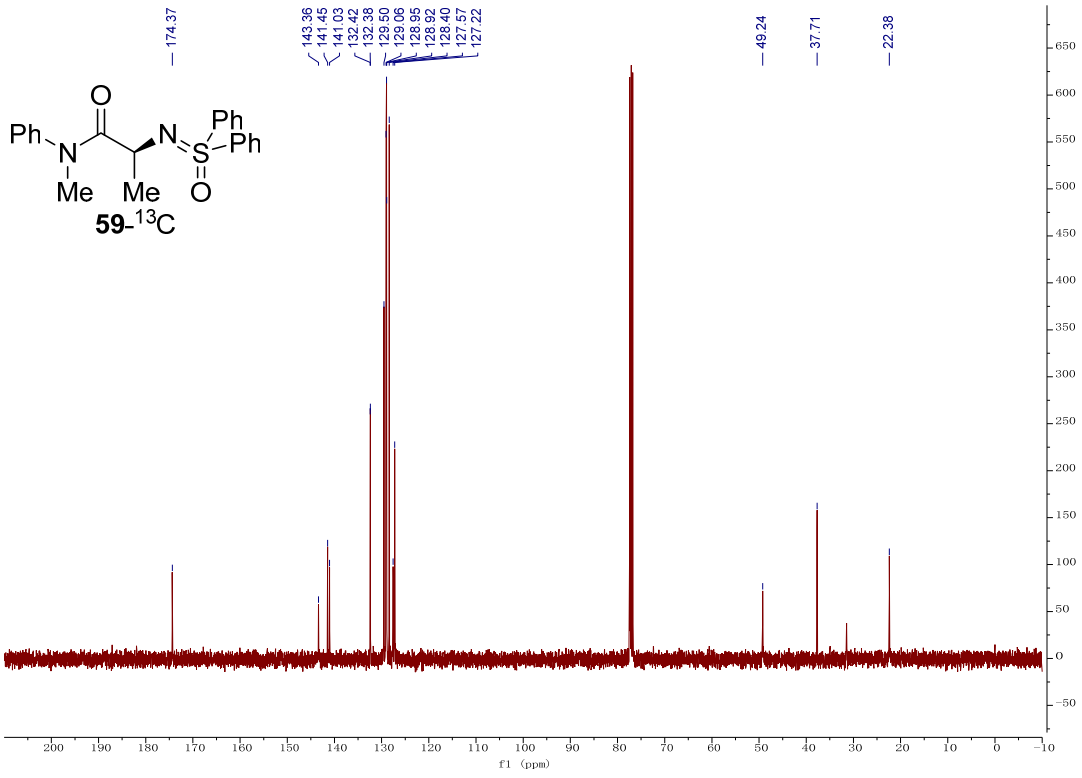

8.15
8.13
8.03
8.01
7.96
7.94
7.54
7.52
7.50
7.49
7.47
7.45
7.44
7.43
7.41
7.40
7.38
7.31
7.28
7.26
7.24
4.31
4.29
4.27
4.26
4.11
4.10
4.10
4.09
4.08
4.07
4.06
3.11
3.09
3.07
3.05
3.03
3.01
2.99
2.97
2.95
1.44
1.42
Br
O
N
Ph
N
S
Ph
Me
O
0.99
4.18
6.35
2.12
1.00
2.02
2.08
3.00
f1 (ppm)

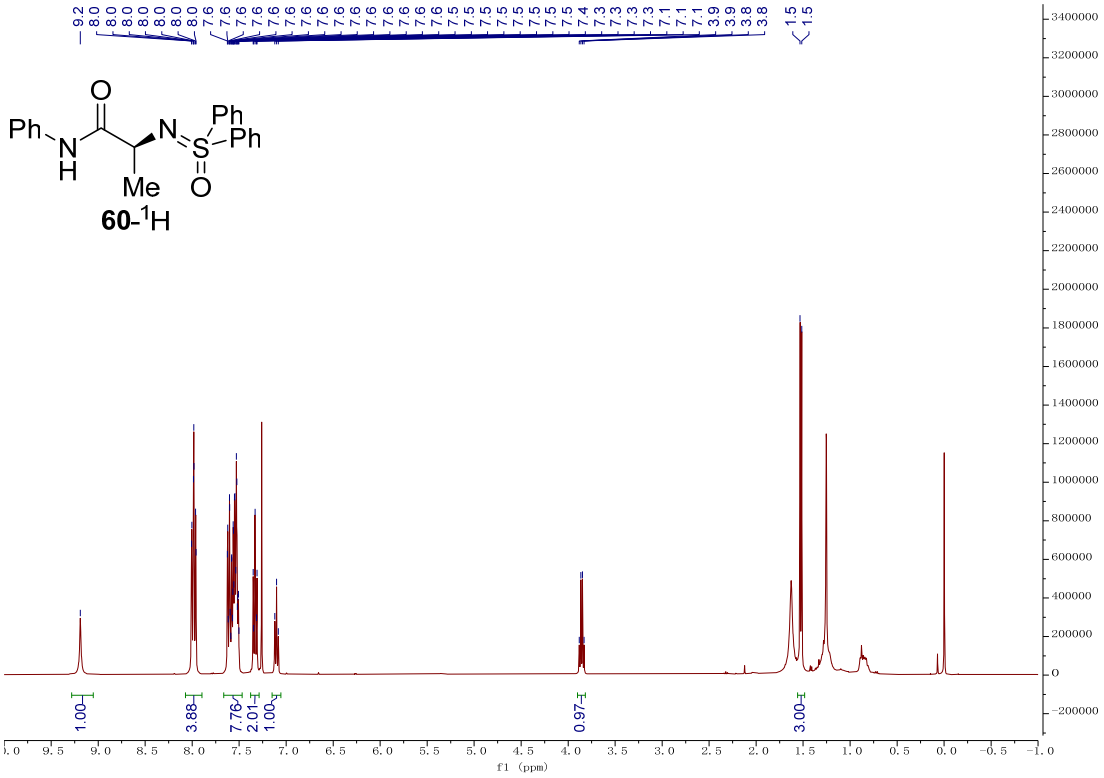
58-^{1}H


172.07
142.52
141.59
141.13
133.75
132.62
132.52
130.17
129.15
129.10
128.37
128.27
127.38
118.86
115.95
51.90
47.86
27.96
20.74
Br
O
N
Ph
N
S
Ph
Me
O
f1 (ppm)

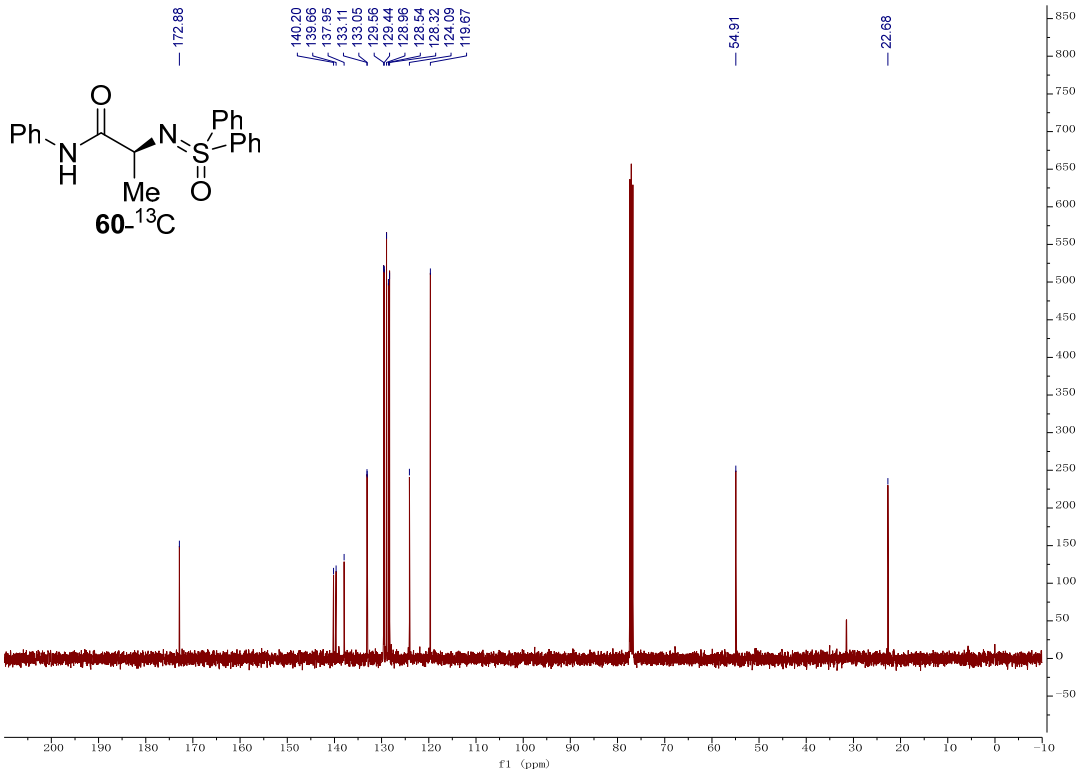
58-^{13}C


59-1H
f1 (ppm)

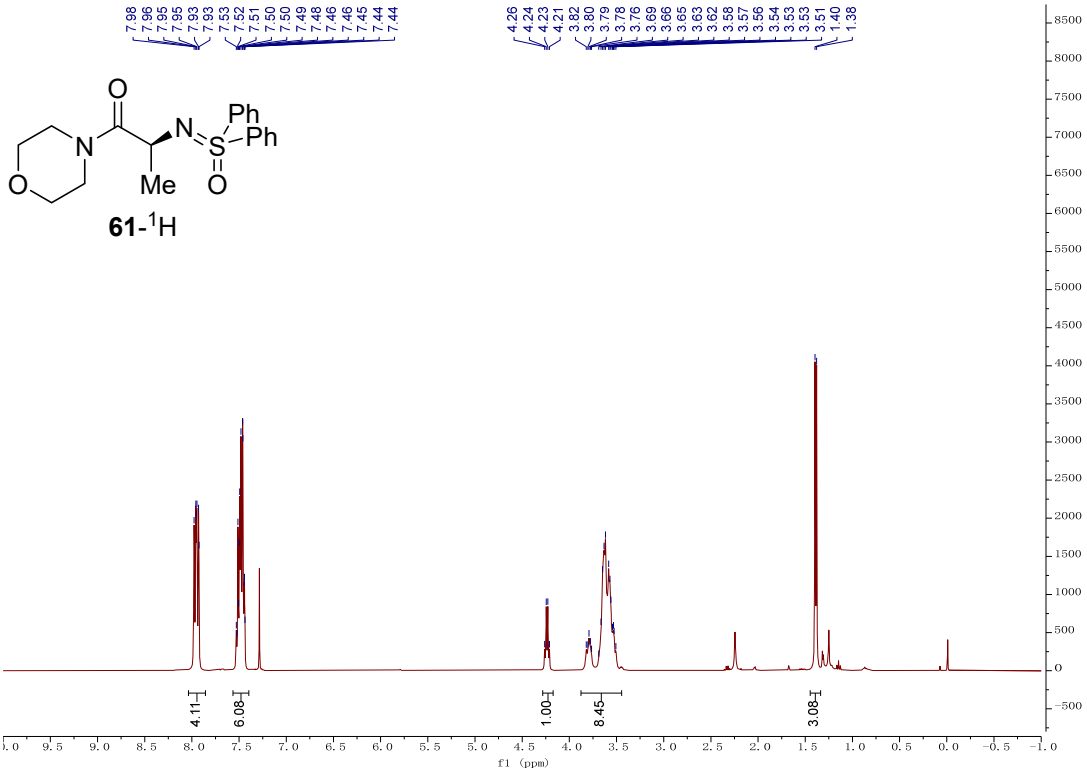

59-13C
f1 (ppm)


9.2
8.0
7.6
7.5
7.4
7.3
7.1
3.9
3.8
1.5
1.00
3.88
7.76
2.01
1.00
0.97
3.00
f1 (ppm)

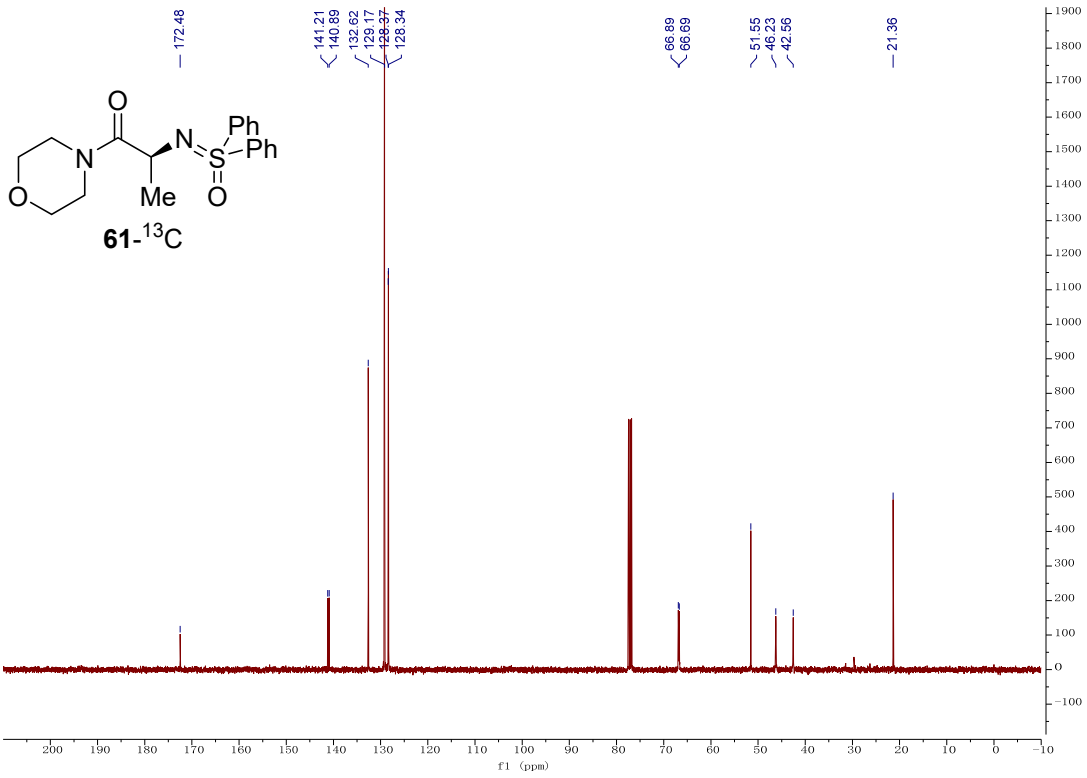
60-^{1}H


172.88
140.20
139.66
137.95
133.11
133.05
129.56
129.44
128.96
128.54
128.32
124.09
119.67
54.91
22.68
f1 (ppm)

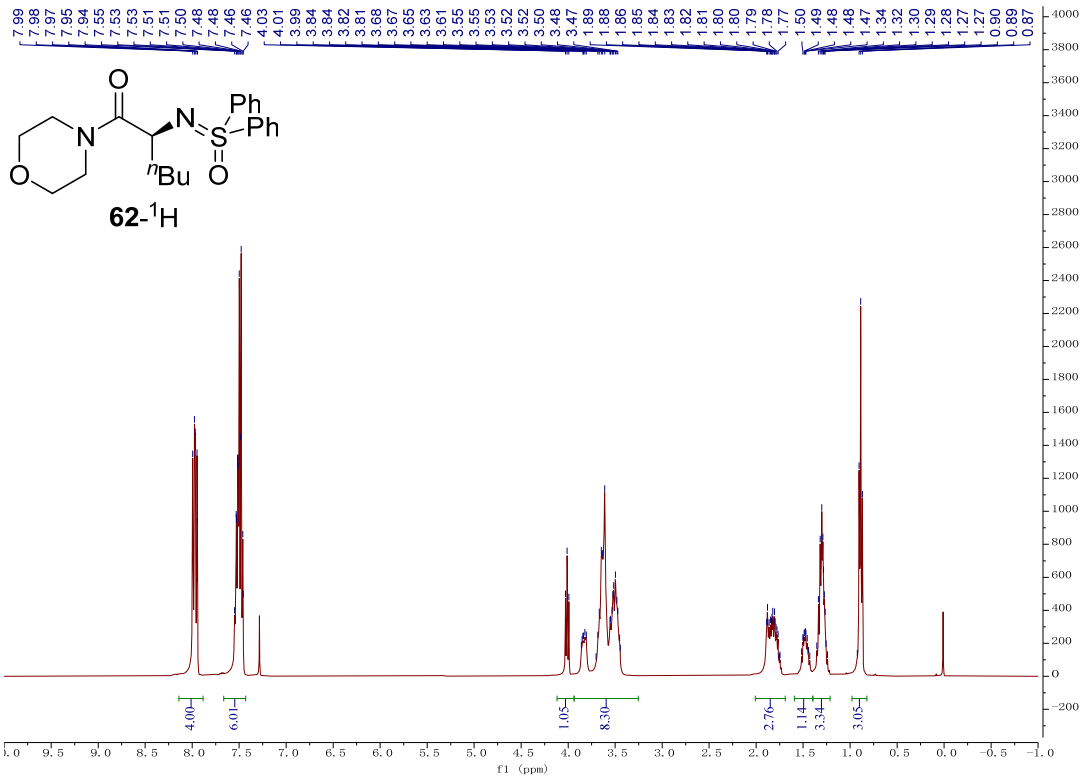
60-^{13}C


7.98
7.96
7.95
7.95
7.93
7.93
7.53
7.52
7.51
7.50
7.50
7.49
7.48
7.46
7.46
7.45
7.44
7.44
4.26
4.24
4.23
4.21
3.82
3.80
3.79
3.78
3.76
3.69
3.66
3.65
3.63
3.62
3.58
3.57
3.56
3.54
3.53
3.53
3.51
1.40
1.38
O
N
O
Me
N
S
Ph
Ph
O
4.11
6.08
1.00
8.45
3.08
f1 (ppm)

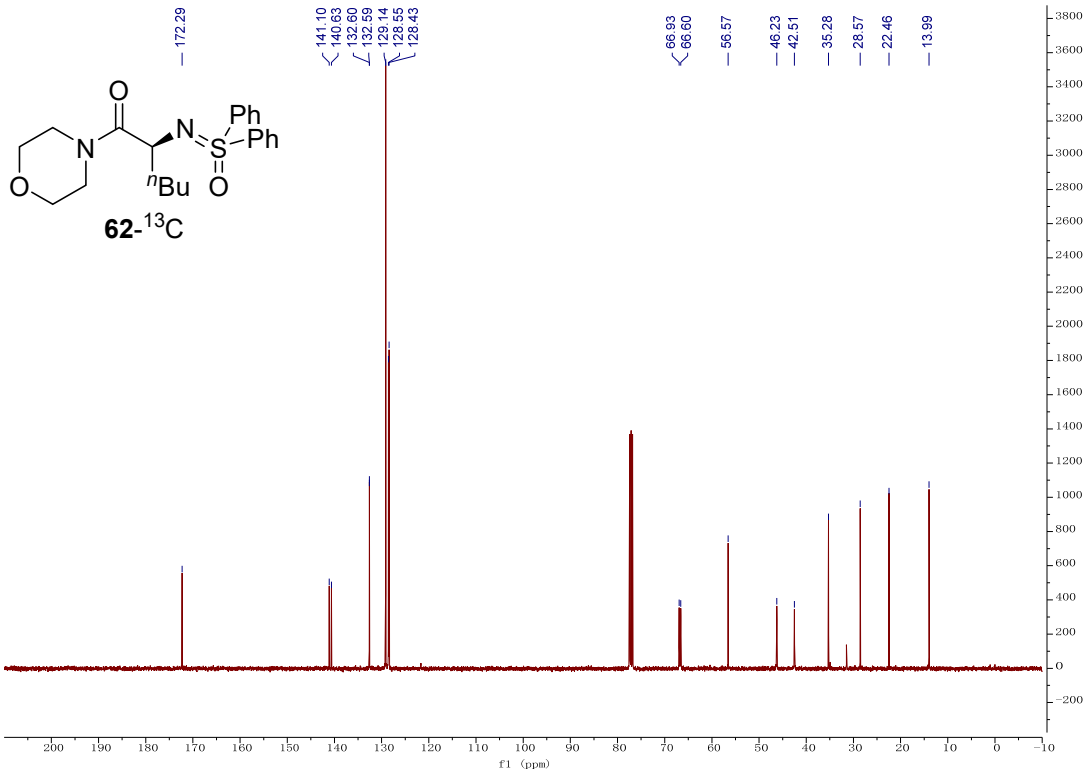
61-^{1}H


172.48
141.21
140.89
132.62
129.17
128.37
128.34
66.89
66.69
51.55
46.23
42.56
21.36
O
N
O
Me
N
S
Ph
Ph
O
f1 (ppm)

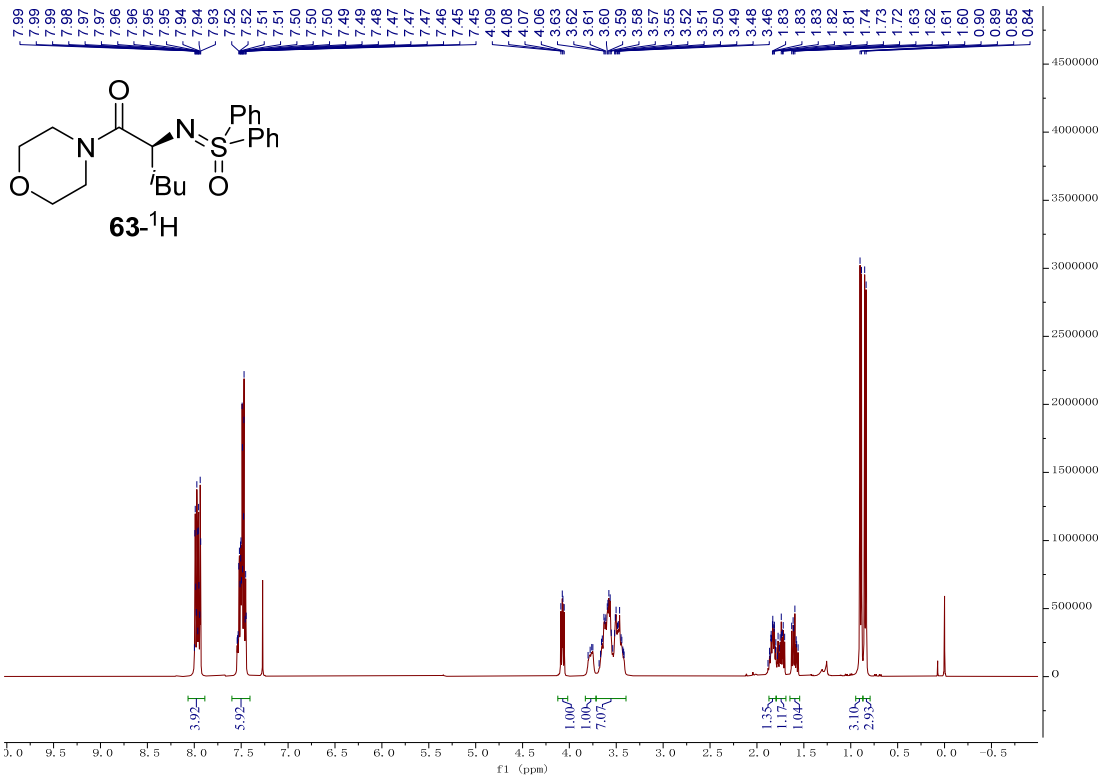
61-^{13}C

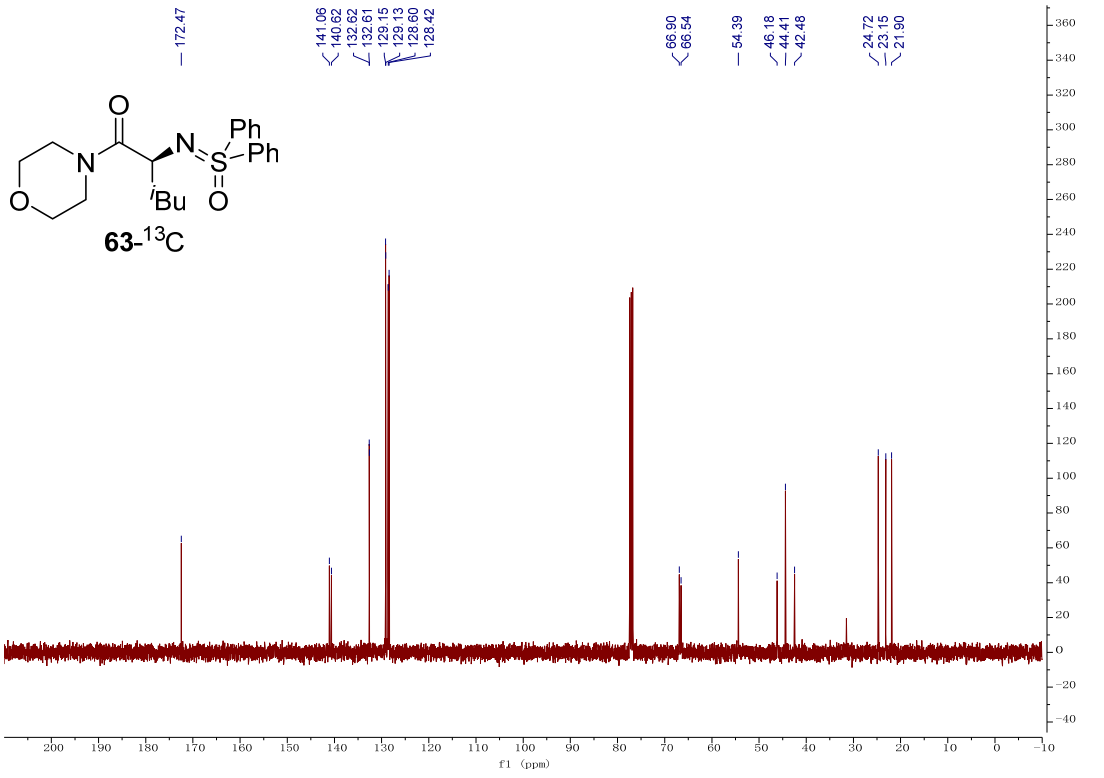

7.99 7.98 7.97 7.95 7.94 7.55 7.53 7.53 7.51 7.51 7.50 7.48 7.48 7.46 7.46 7.46
4.03 4.01 3.99 3.84 3.84 3.82 3.81 3.68 3.67 3.65 3.63 3.61 3.55 3.55 3.53 3.52 3.50 3.48 3.47
1.89 1.88 1.86 1.85 1.84 1.83 1.82 1.81 1.80 1.80 1.79 1.78 1.77
1.50 1.49 1.48 1.48 1.47 1.34 1.32 1.30 1.29 1.28 1.27 1.27 0.90 0.89 0.87
O
N
O
Ph
N
S
Ph
O
nBu
4.00
6.01
1.05
8.30
2.76
1.14
3.34
3.05
f1 (ppm)

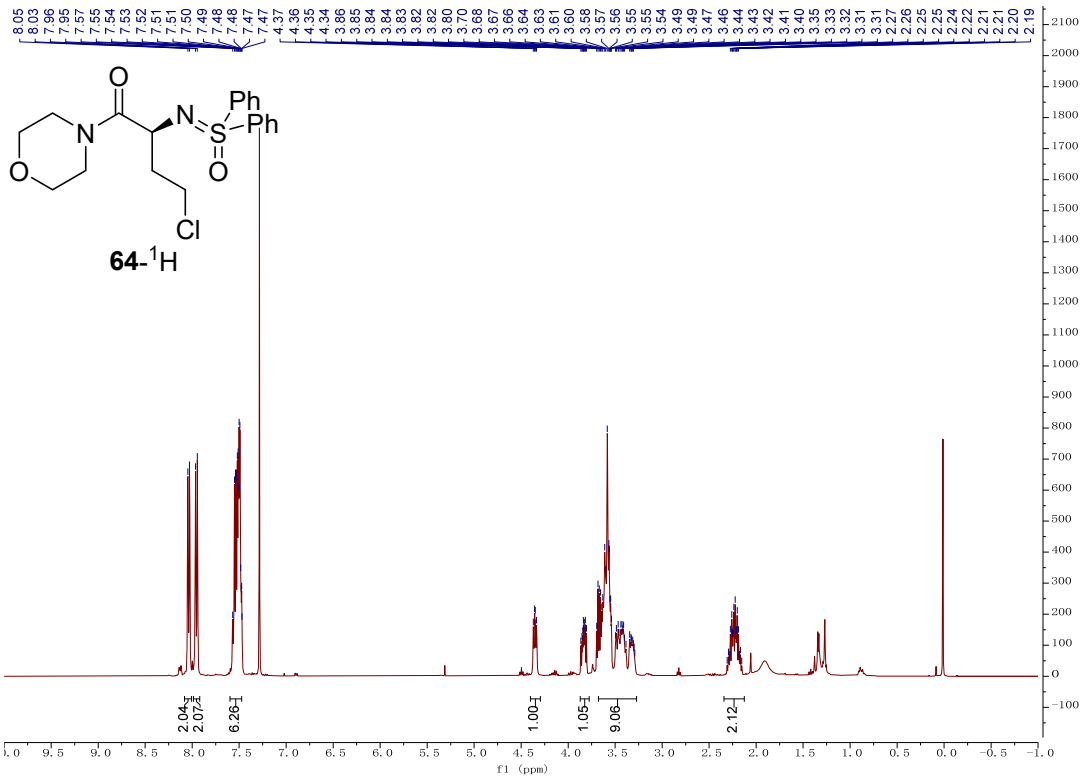
62-^{1}H

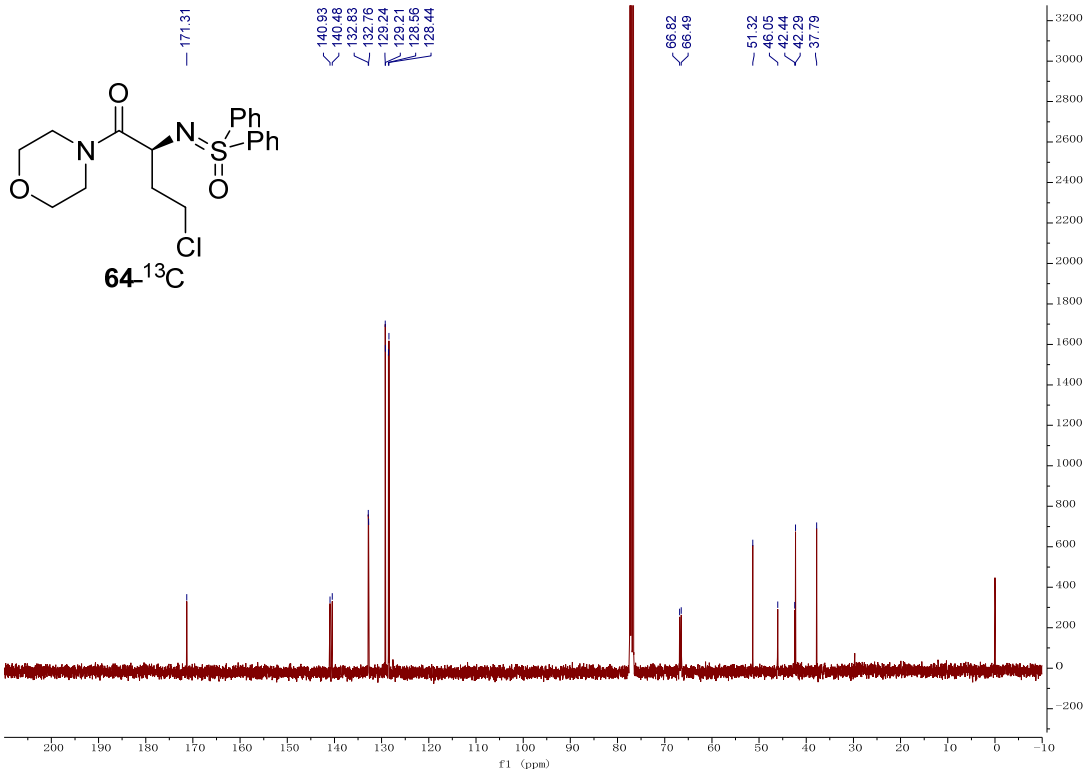

172.29
141.10 140.63 132.60 132.59 129.14 128.55 128.43
66.93 66.60 56.57 46.23 42.51 35.28 28.57 22.46 13.99
O
N
O
Ph
N
S
Ph
O
nBu
f1 (ppm)

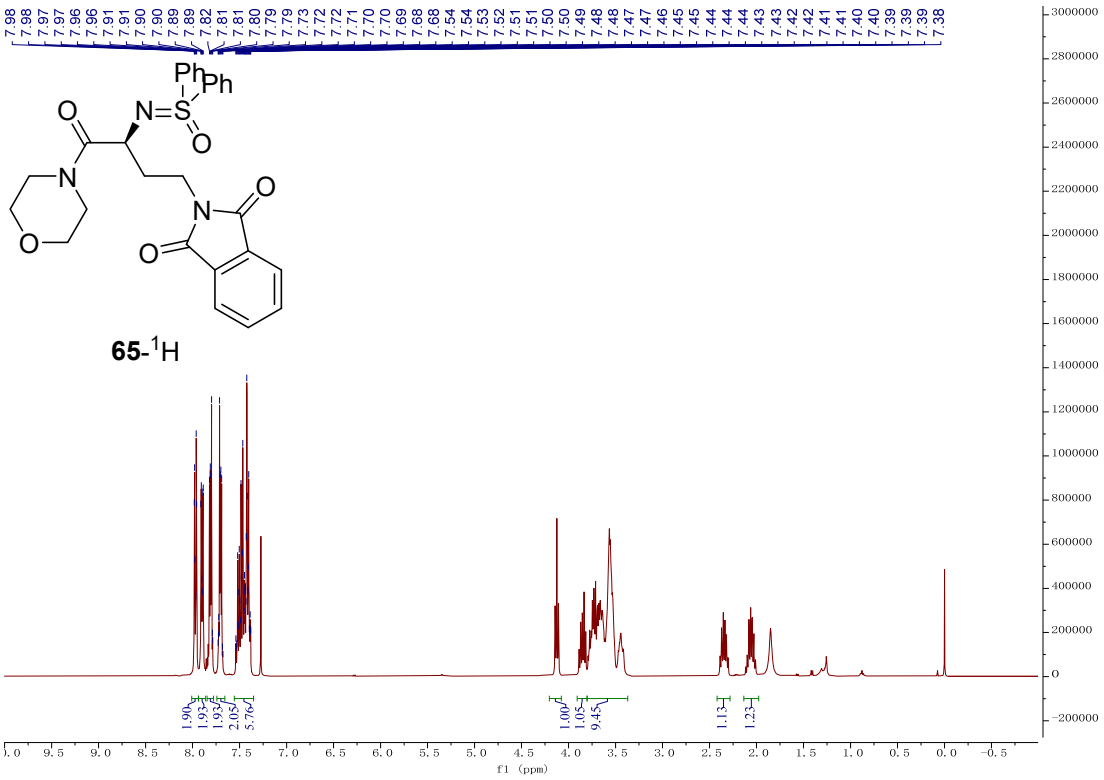
62-^{13}C

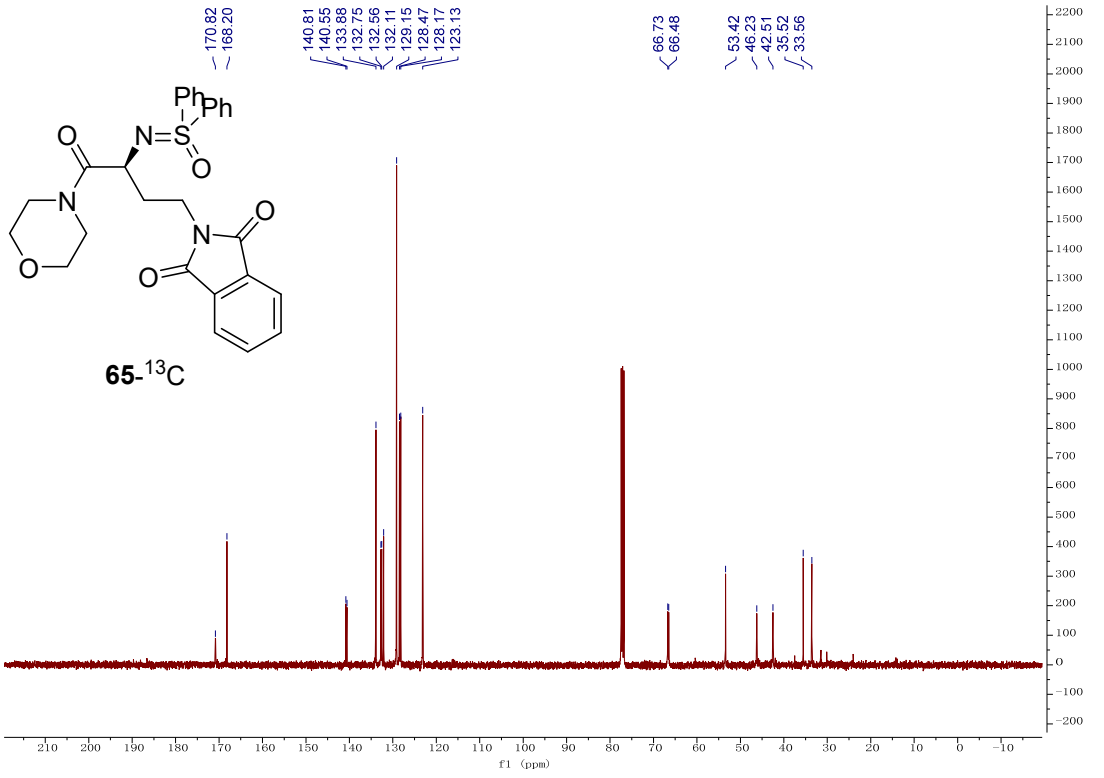

7.99 7.99 7.99 7.98 7.97 7.97 7.96 7.96 7.95 7.95 7.94 7.94 7.93 7.52 7.51 7.51 7.50 7.50 7.50 7.49 7.49 7.48 7.47 7.47 7.47 7.46 7.45 7.45
4.09 4.08 4.07 4.06 3.63 3.62 3.61 3.60 3.59 3.58 3.57 3.55 3.52 3.51 3.50 3.49 3.48 3.46
1.83 1.83 1.83 1.82 1.81 1.74 1.73 1.72 1.63 1.62 1.61 1.60 0.90 0.89 0.85 0.84
O
N
O
N
S
Ph
Ph
O
iBu
63-1H
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
3.92
5.92
1.00
1.00
7.07
1.35
1.17
1.04
3.10
2.93
f1 (ppm)

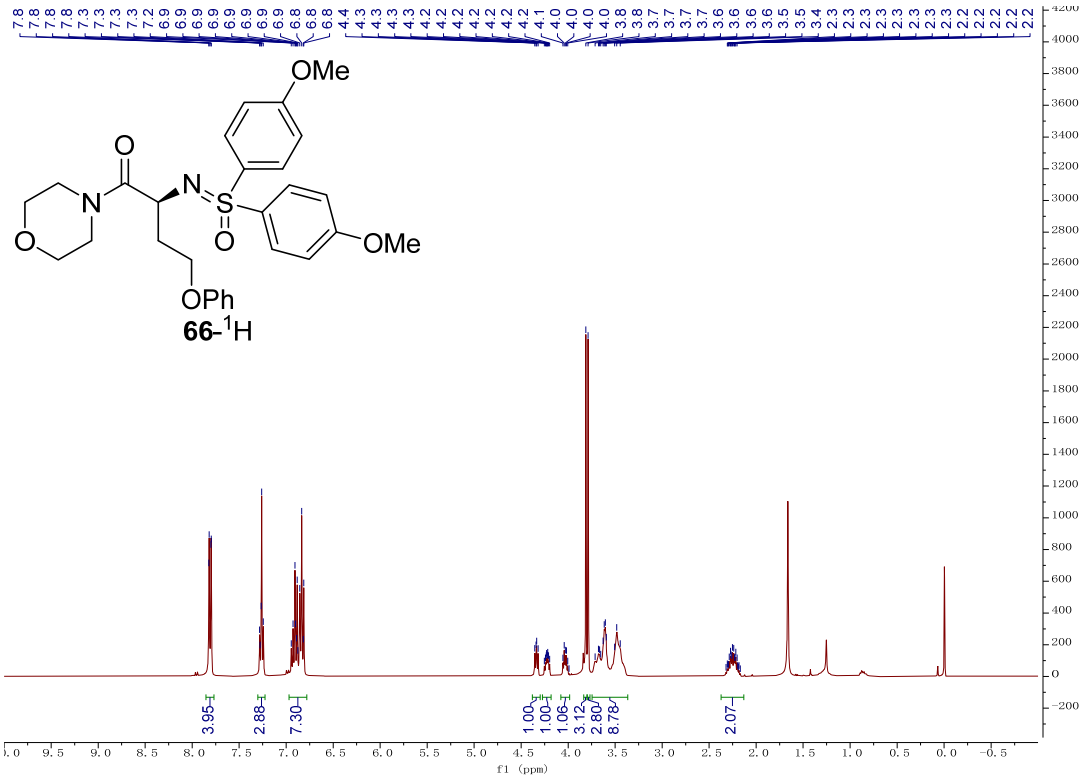

172.47
141.06
140.62
132.62
132.61
129.15
129.13
128.60
128.42
66.90
66.54
54.39
46.18
44.41
42.48
24.72
23.15
21.90
O
N
O
N
S
Ph
Ph
O
iBu
63-13C
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)

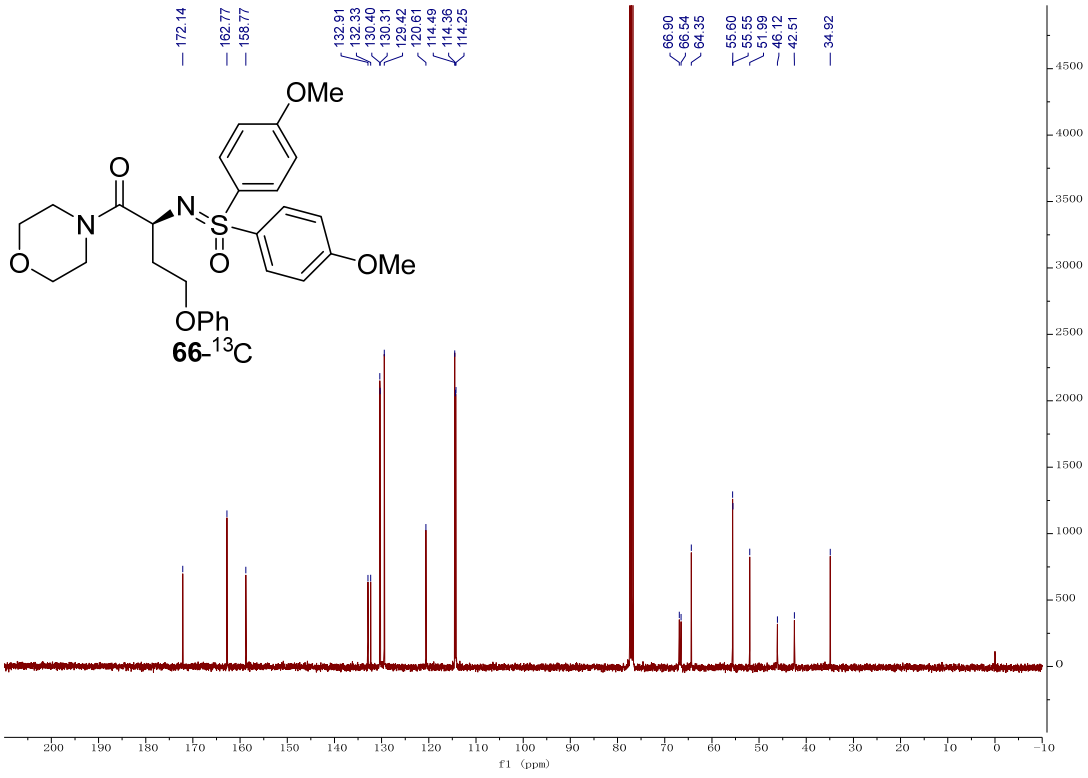

64-1H
f1 (ppm)

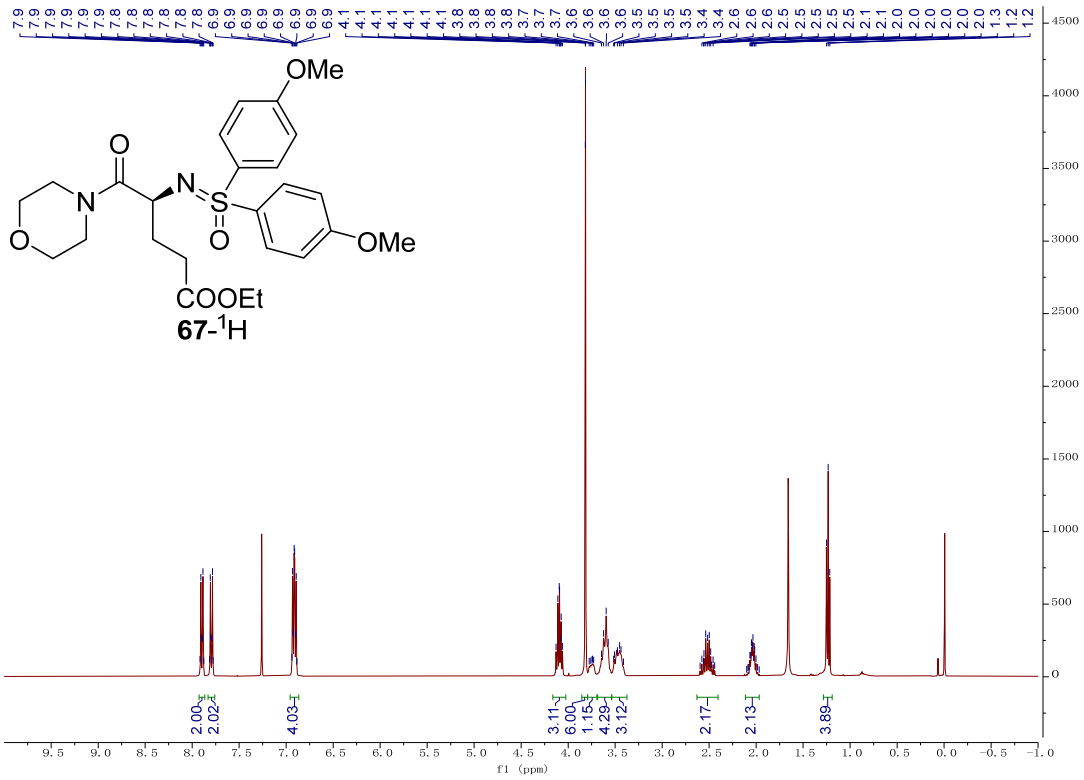

64-13C
f1 (ppm)

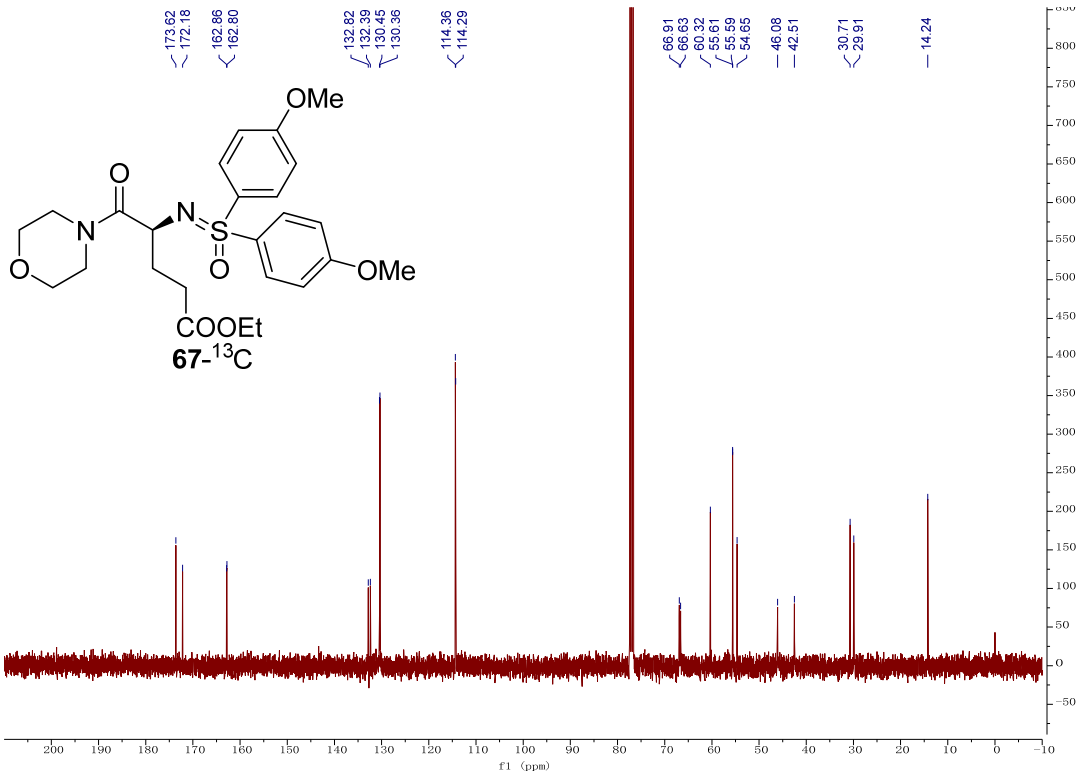

65-1H
f1 (ppm)

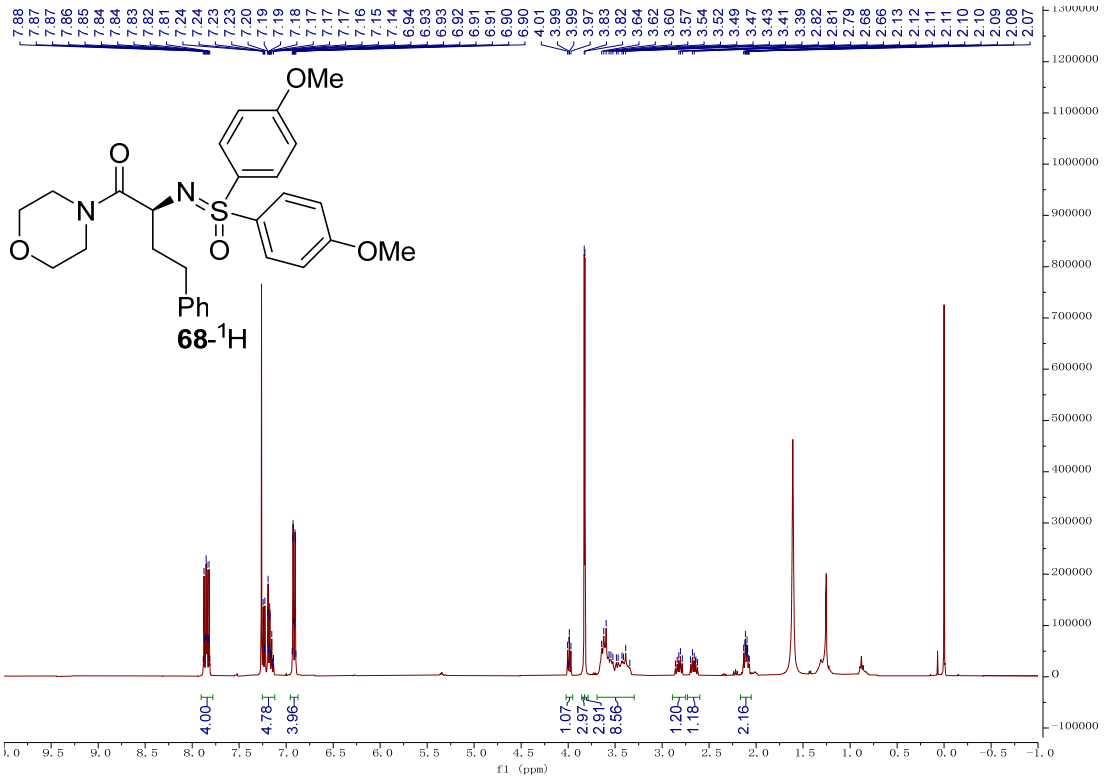

65-13C
f1 (ppm)

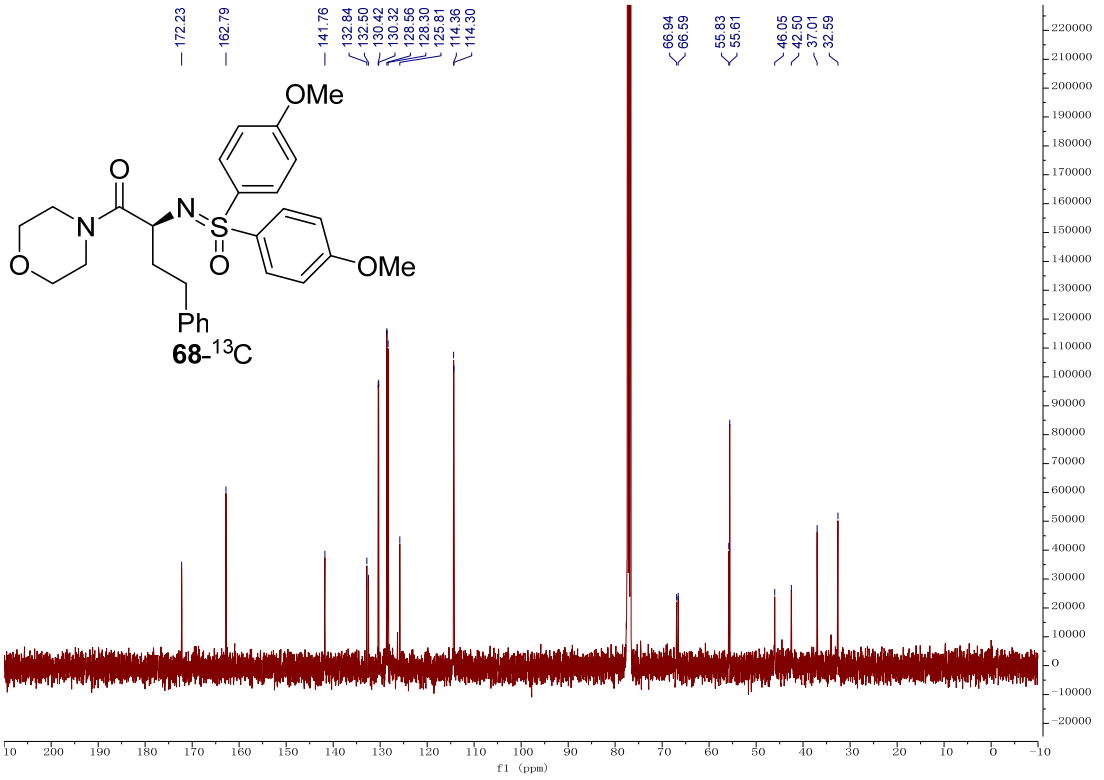

OMe
O
N
S
O
OMe
O
N
OPh
66-1H
f1 (ppm)

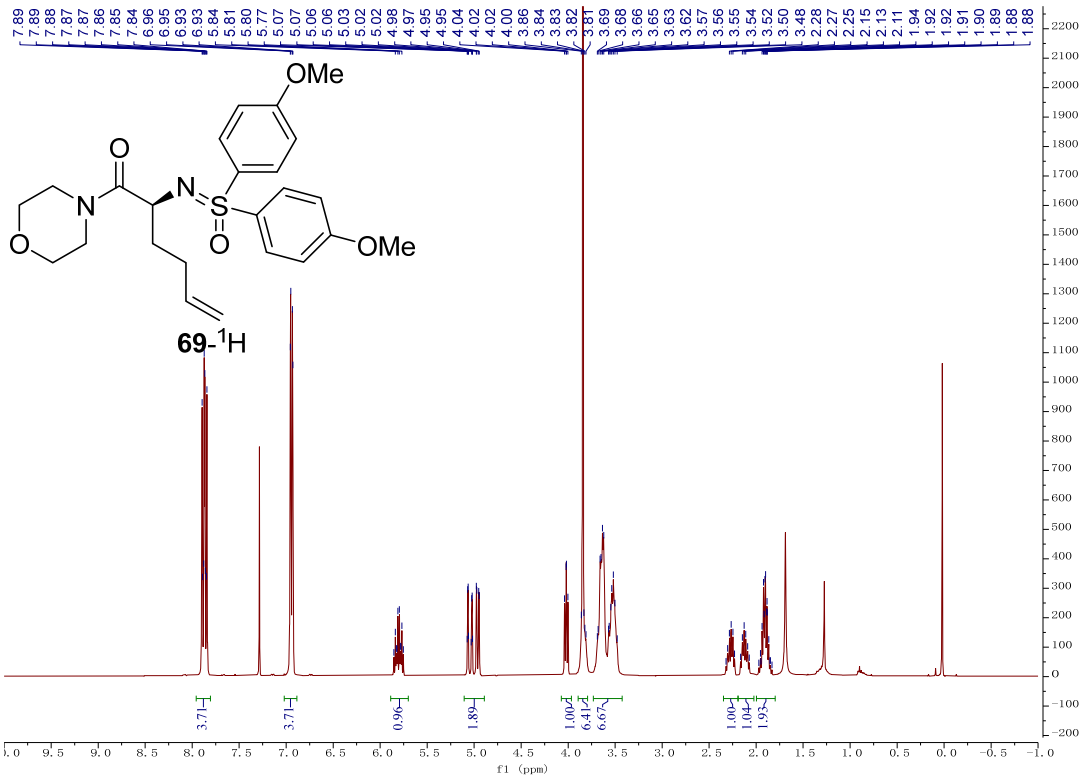

172.14
162.77
158.77
132.91
132.33
130.40
130.31
129.42
120.61
114.49
114.36
114.25
66.90
66.54
64.35
55.60
55.55
51.99
46.12
42.51
34.92
OMe
O
N
S
O
OMe
O
N
OPh
66-13C
f1 (ppm)

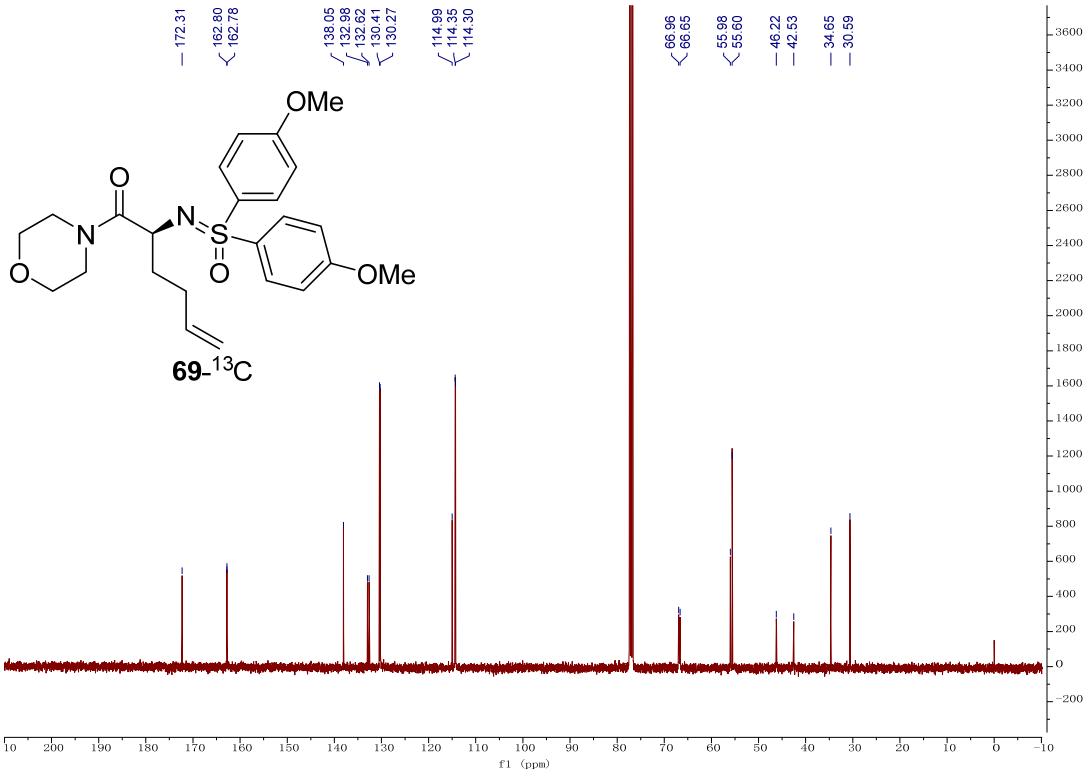

OMe
O
N
S
O
OMe
COOEt
67-1H
f1 (ppm)

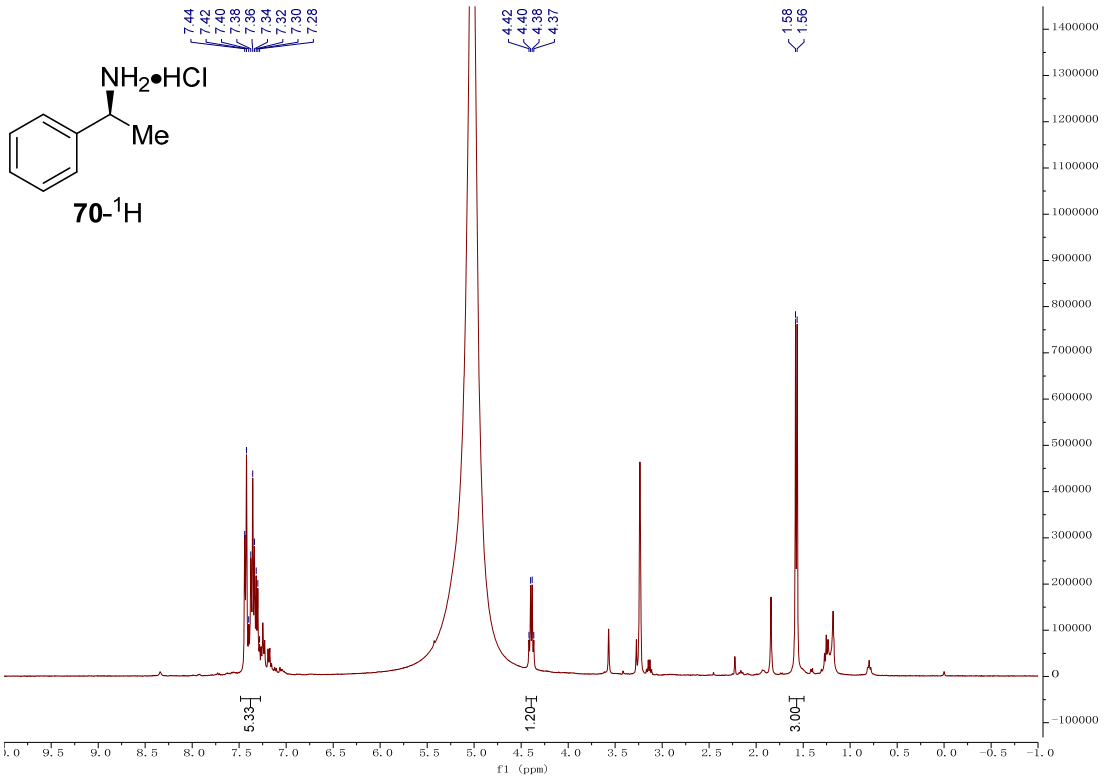

OMe
O
N
S
O
OMe
COOEt
67-13C
f1 (ppm)

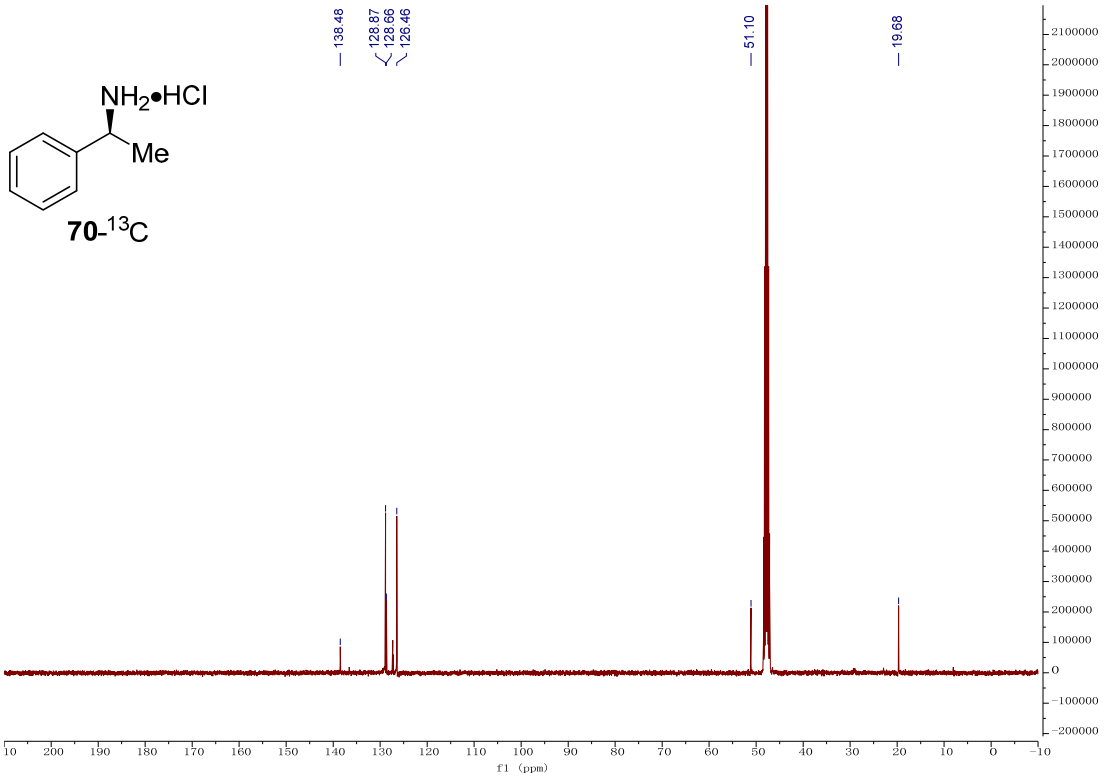

OMe
O
N
S
O
OMe
O
Ph
68-1H
f1 (ppm)

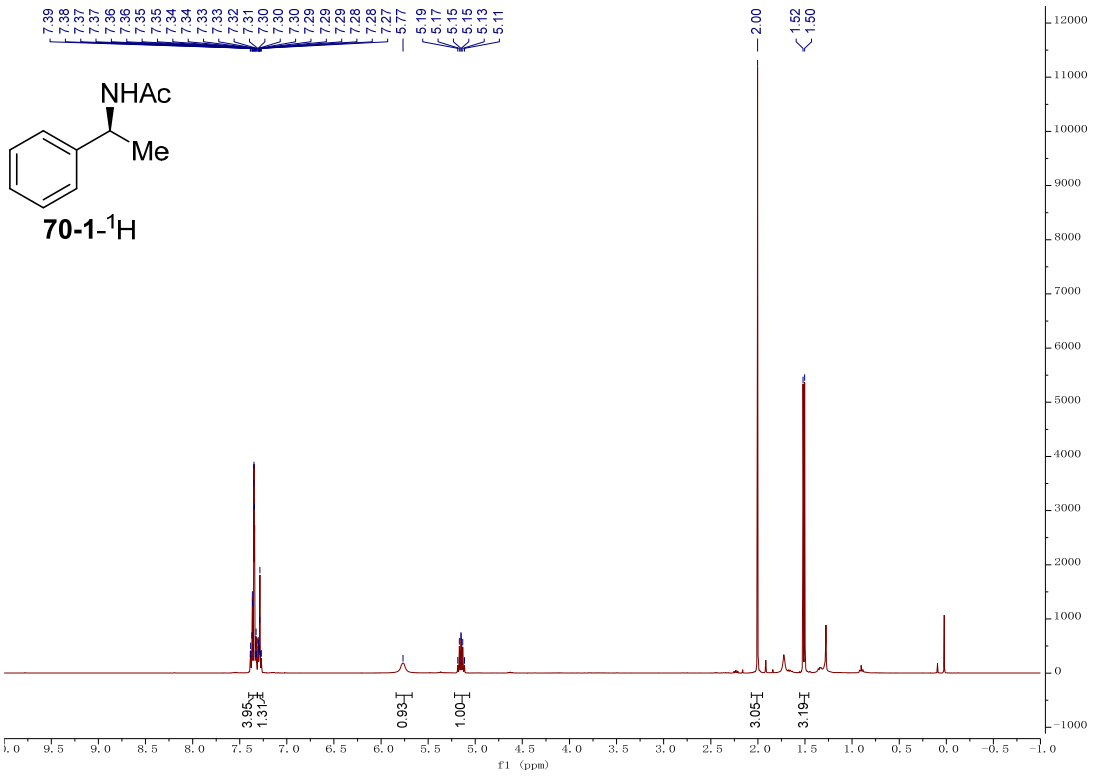

OMe
O
N
S
O
OMe
O
Ph
68-13C
f1 (ppm)

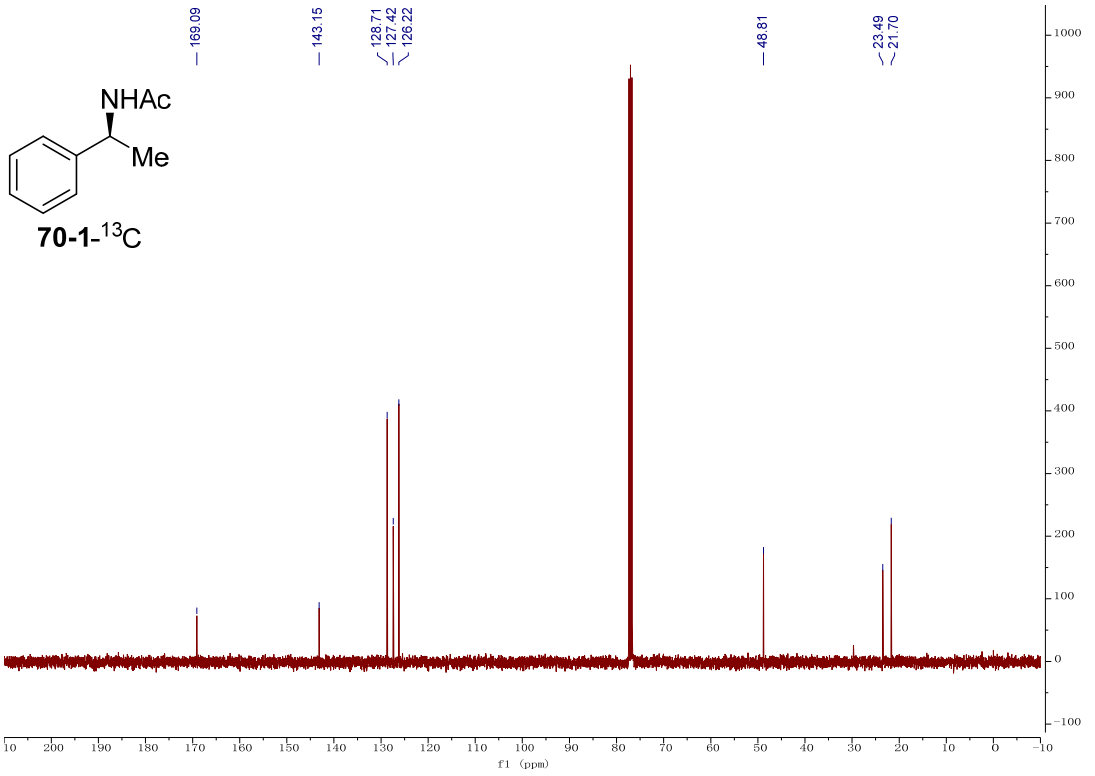

OMe
O
N
S
O
N
O
OMe
69-1H
f1 (ppm)

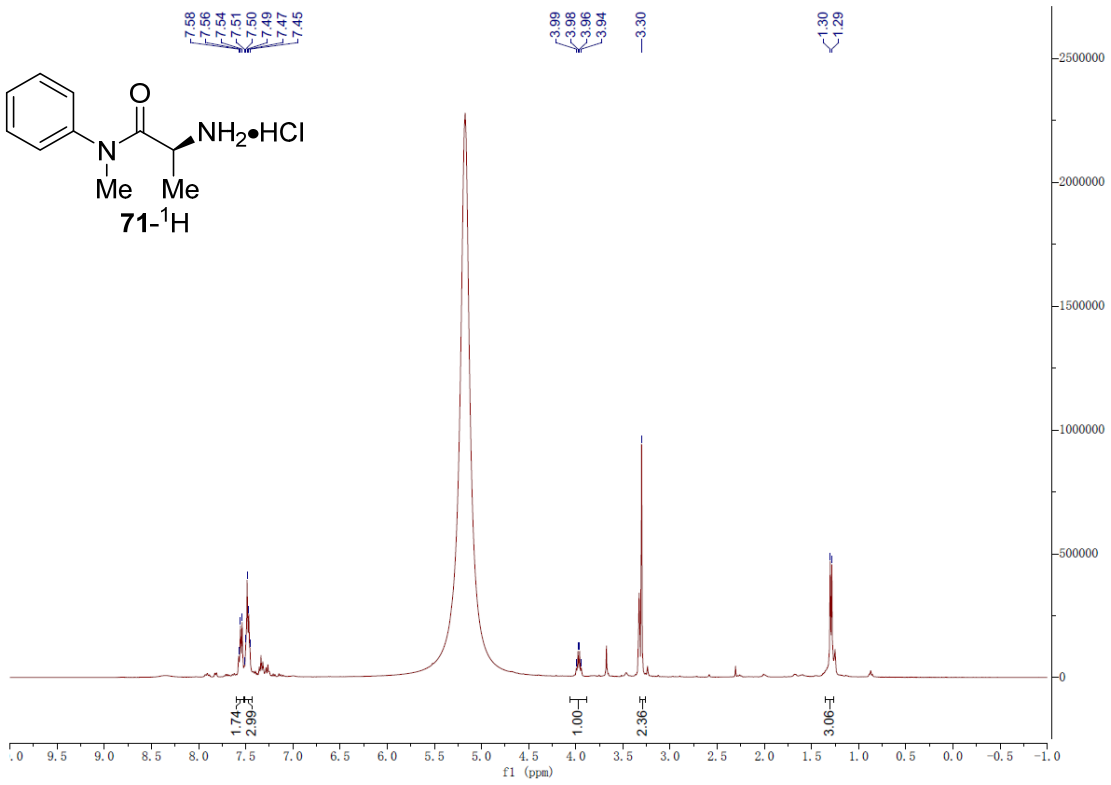

OMe
O
N
S
O
N
O
OMe
69-13C
f1 (ppm)

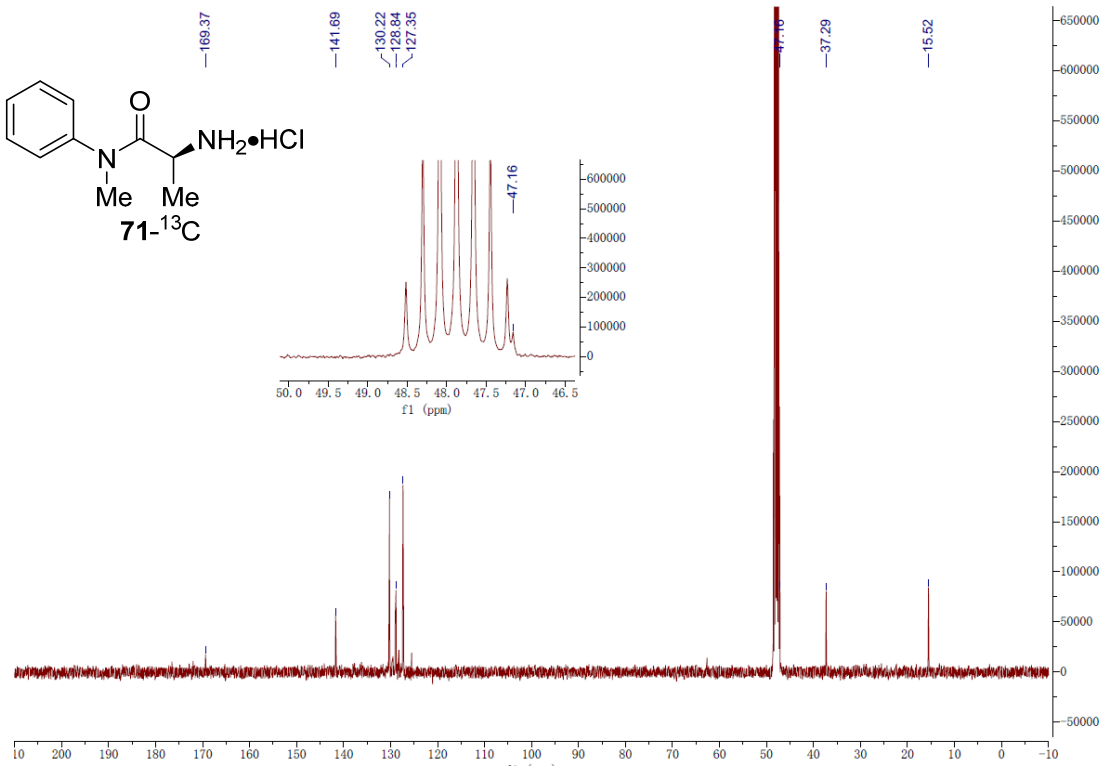

7.44
7.42
7.40
7.38
7.36
7.34
7.32
7.30
7.28
4.42
4.40
4.38
4.37
1.58
1.56
NH2•HCl
Me
70-1H
5.33
1.20
3.00
f1 (ppm)

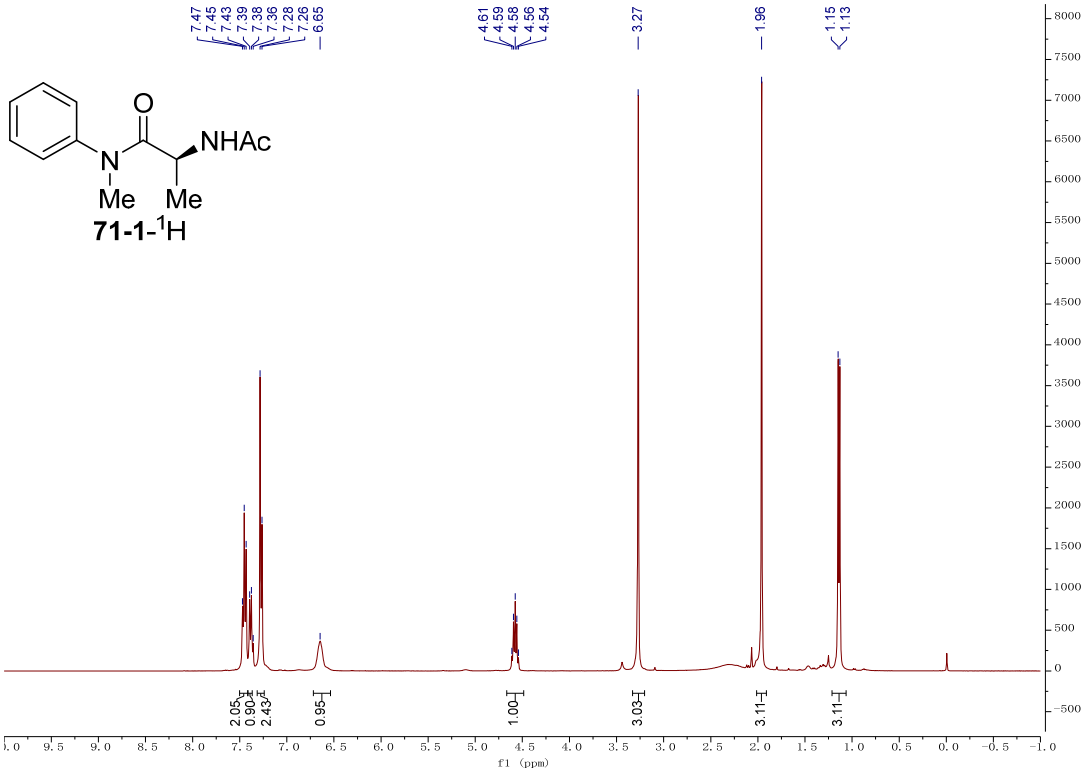

138.48
128.87
128.66
126.46
51.10
19.68
NH2•HCl
Me
70-13C
f1 (ppm)

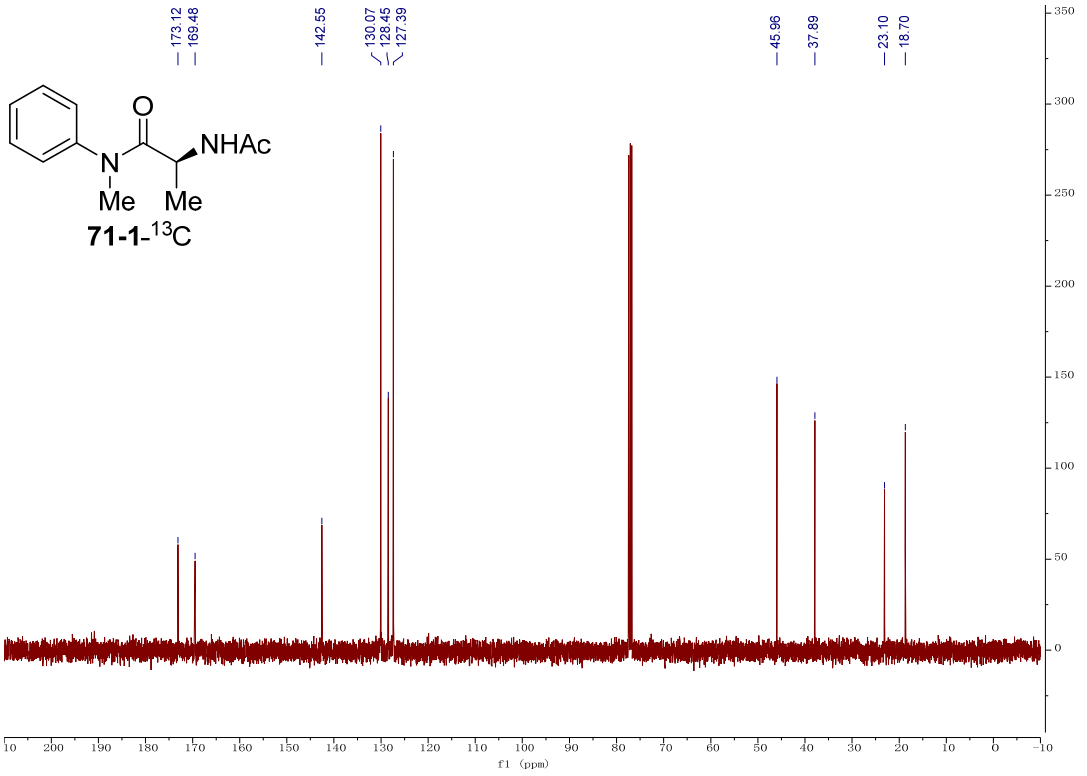

NHAc
Me
70-1-1H
f1 (ppm)

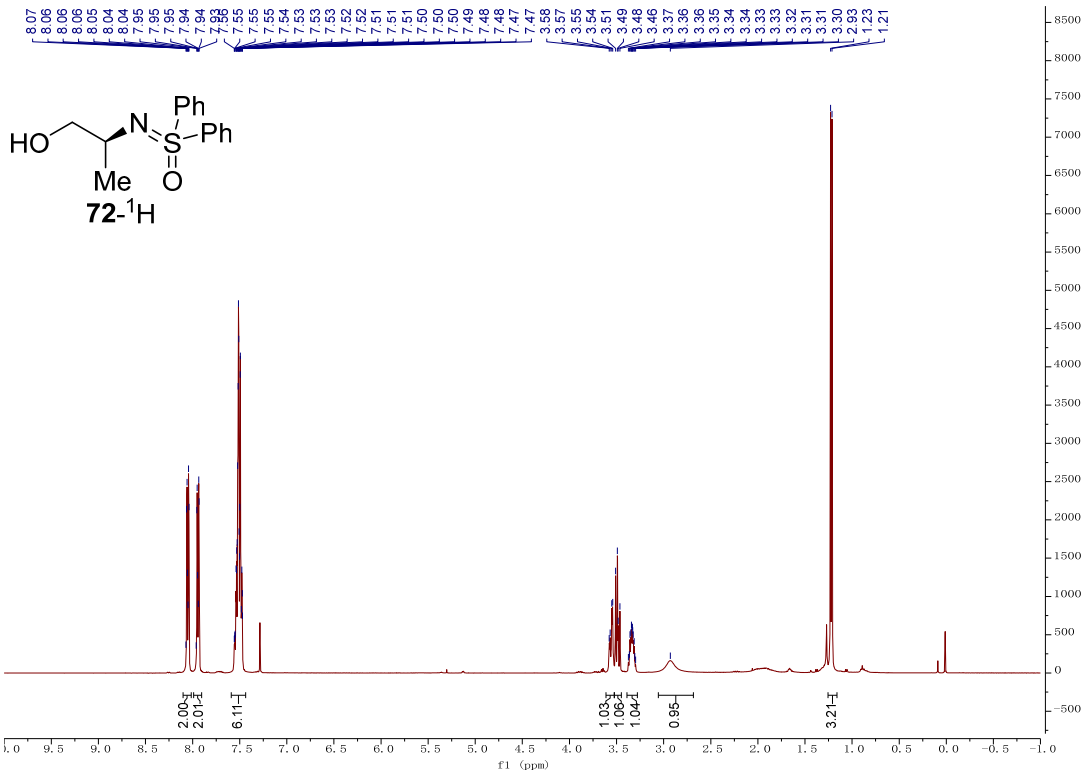

NHAc
Me
70-1-13C
f1 (ppm)

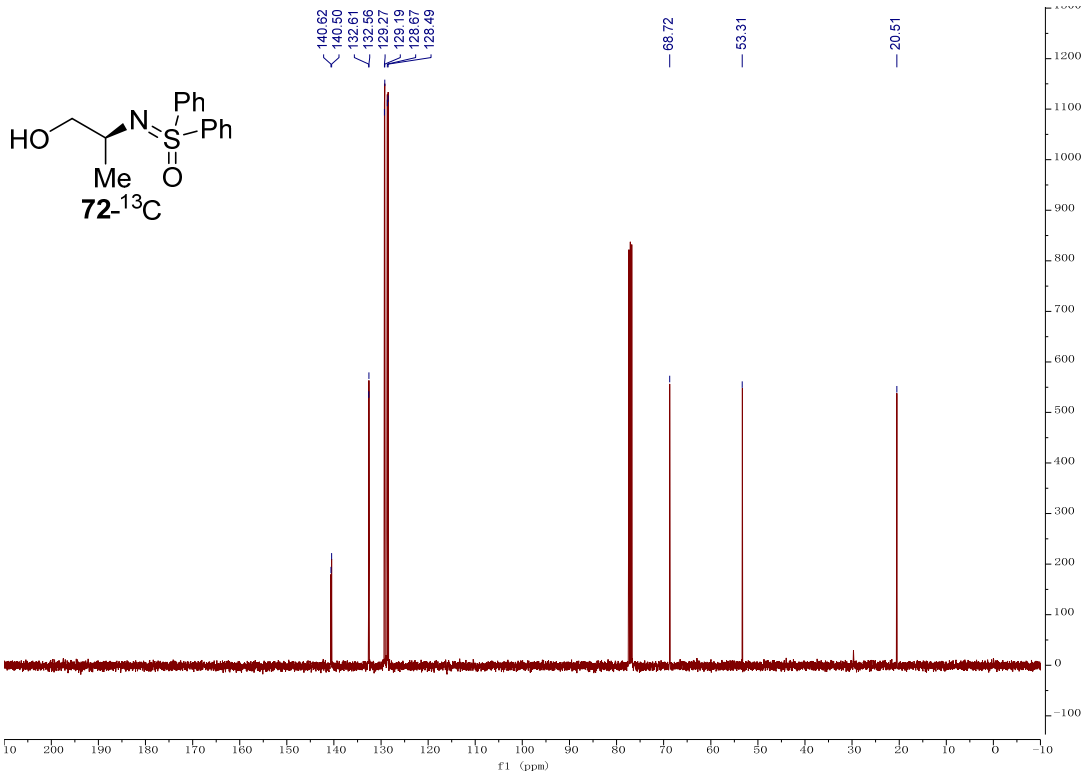

7.58
7.56
7.54
7.51
7.50
7.49
7.47
7.45
3.99
3.98
3.96
3.94
3.30
1.30
1.29
O
N
Me
Me
NH2•HCl
71-1H
1.74
2.99
1.00
2.36
3.06
f1 (ppm)

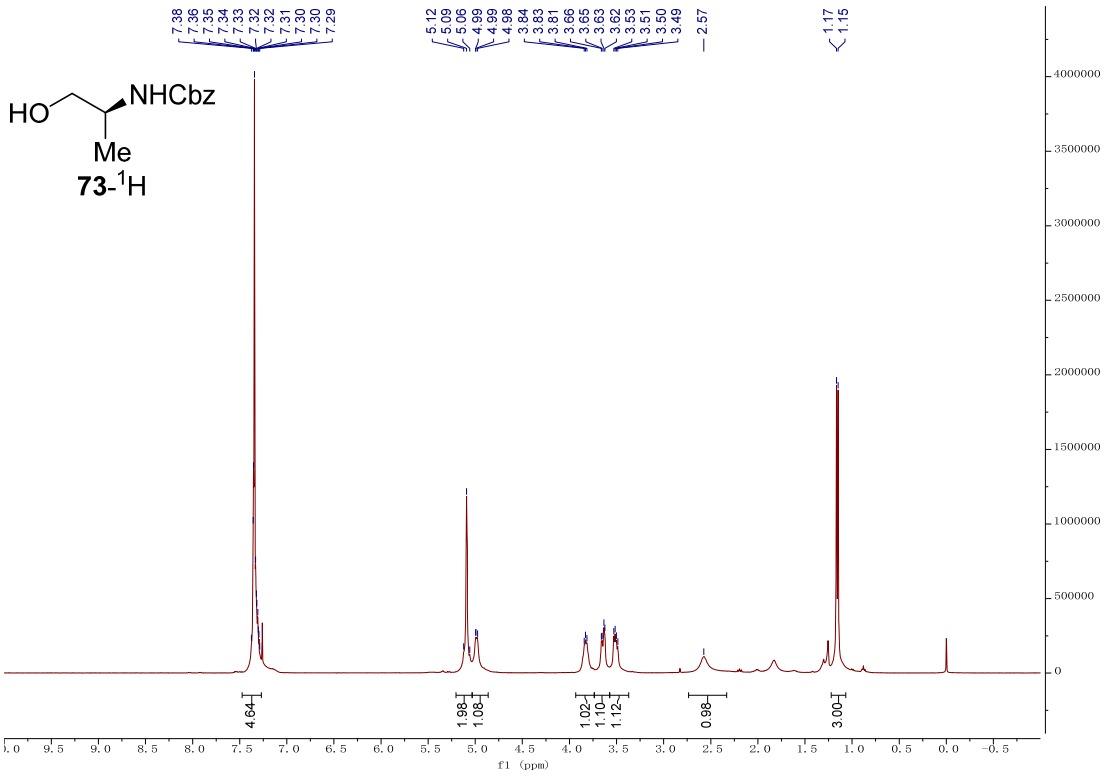

169.37
141.69
130.22
128.84
127.35
47.16
37.29
15.52
O
N
Me
Me
NH2•HCl
71-13C
f1 (ppm)

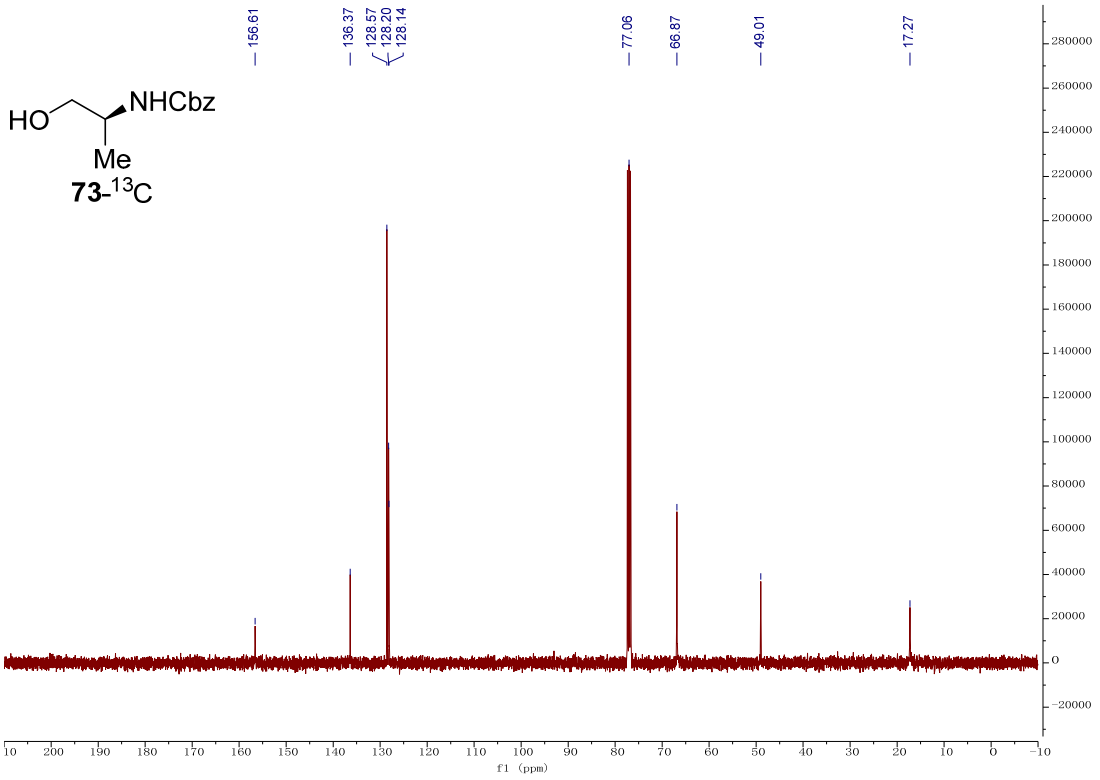

7.47
7.45
7.43
7.39
7.38
7.36
7.28
7.26
6.65
4.61
4.59
4.58
4.56
4.54
3.27
1.96
1.15
1.13
O
NHAc
N
Me
Me
71-1-1H
2.05
0.90
2.43
0.95
1.00
3.03
3.11
3.11
f1 (ppm)

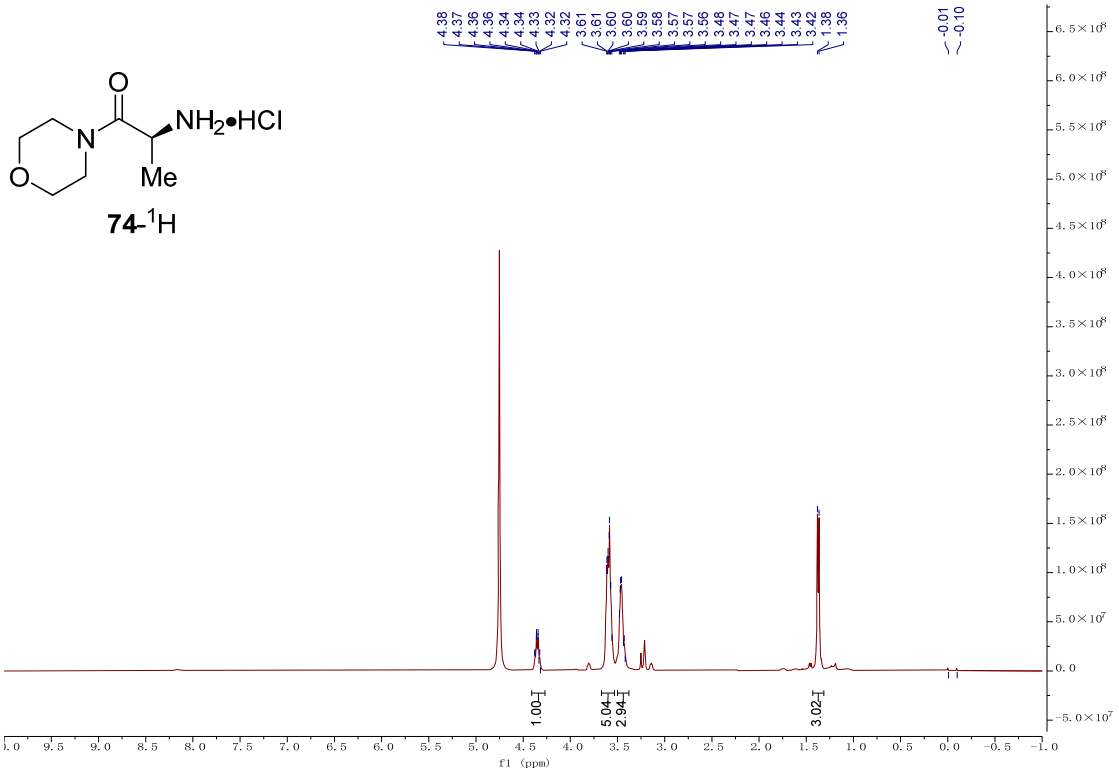

173.12
169.48
142.55
130.07
128.45
127.39
45.96
37.89
23.10
18.70
O
NHAc
N
Me
Me
71-1-13C
f1 (ppm)

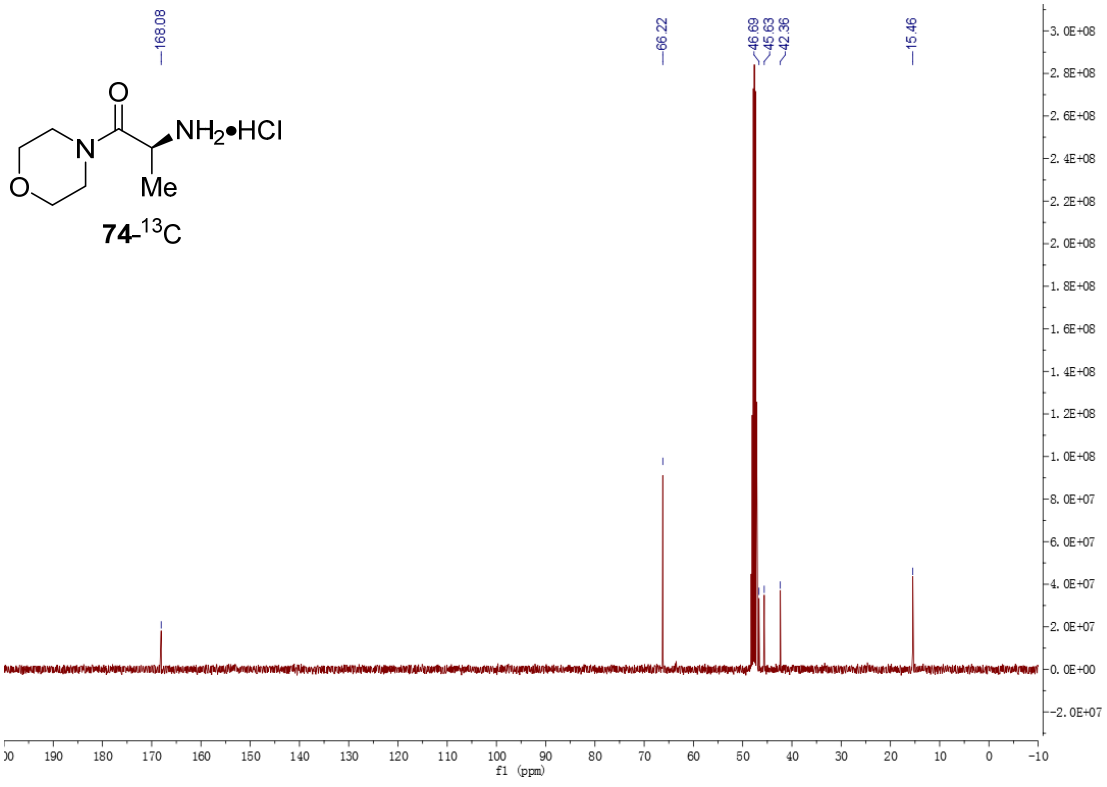

8.07 8.06 8.06 8.06 8.05 8.04 8.04 7.95 7.95 7.95 7.94 7.94 7.93 7.93 7.55 7.55 7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.51 7.51 7.50 7.50 7.50 7.49 7.48 7.48 7.47 7.47 3.58 3.57 3.55 3.54 3.51 3.49 3.48 3.46 3.37 3.36 3.36 3.35 3.34 3.34 3.33 3.32 3.31 3.31 3.30 2.93 1.23 1.21
HO
N
S
Ph
Ph
O
Me
72-1H
2.00
2.01
6.11
1.03
1.06
1.04
0.95
3.21
f1 (ppm)

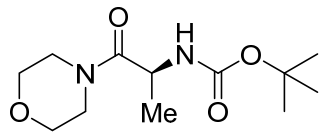

140.62
140.50
132.61
132.56
129.27
129.19
128.67
128.49
68.72
53.31
20.51
HO
N
S
Ph
Ph
O
Me
72-13C
f1 (ppm)


HO
NHCbz
Me
73-1H
7.38
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
5.12
5.09
5.06
4.99
4.99
4.98
3.84
3.83
3.81
3.66
3.65
3.63
3.62
3.53
3.51
3.50
3.49
2.57
1.17
1.15
4.64
1.98
1.08
1.02
1.10
1.12
0.98
3.00
f1 (ppm)

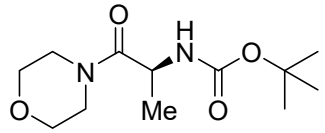

HO
NHCbz
Me
73-13C
156.61
136.37
128.57
128.20
128.14
77.06
66.87
49.01
17.27
f1 (ppm)


O
N
O
NH2•HCl
Me
74-1H
4.38
4.37
4.36
4.36
4.34
4.34
4.33
4.32
4.32
3.61
3.61
3.60
3.60
3.59
3.58
3.57
3.57
3.56
3.48
3.47
3.47
3.46
3.44
3.43
3.42
1.38
1.36
-0.01
-0.10
1.00
5.04
2.94
3.02
f1 (ppm)

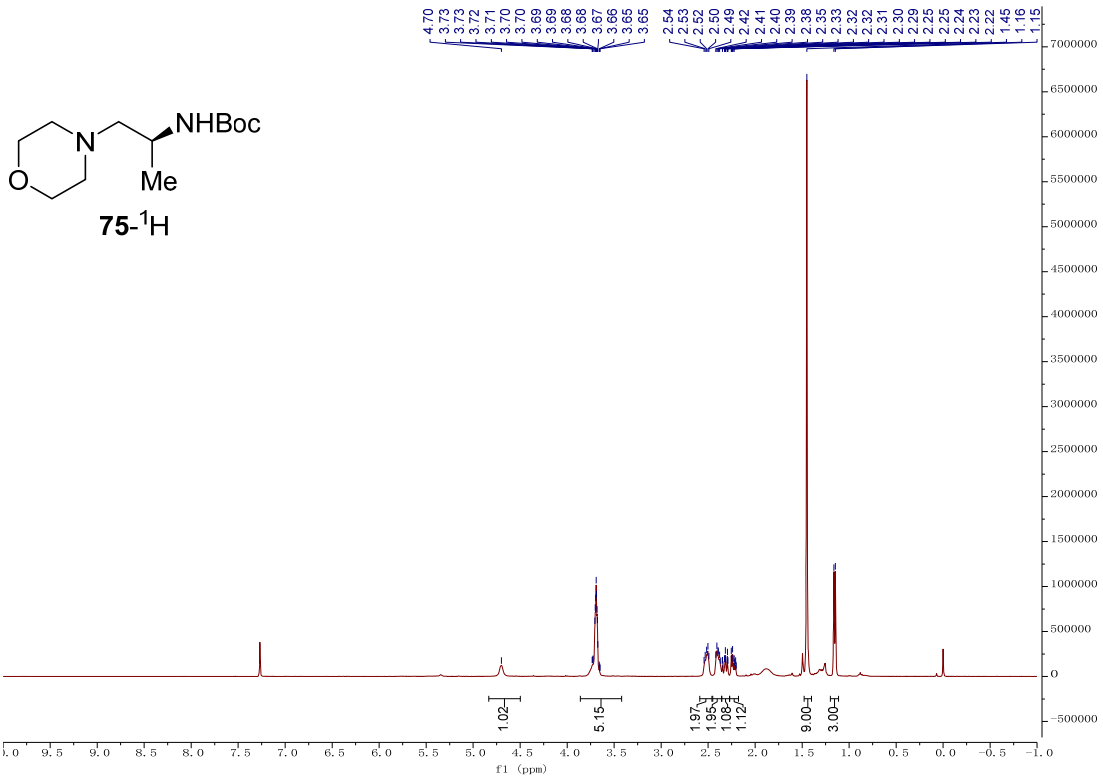

O
N
O
NH2•HCl
Me
74-13C
168.08
66.22
46.69
45.63
42.36
15.46
f1 (ppm)

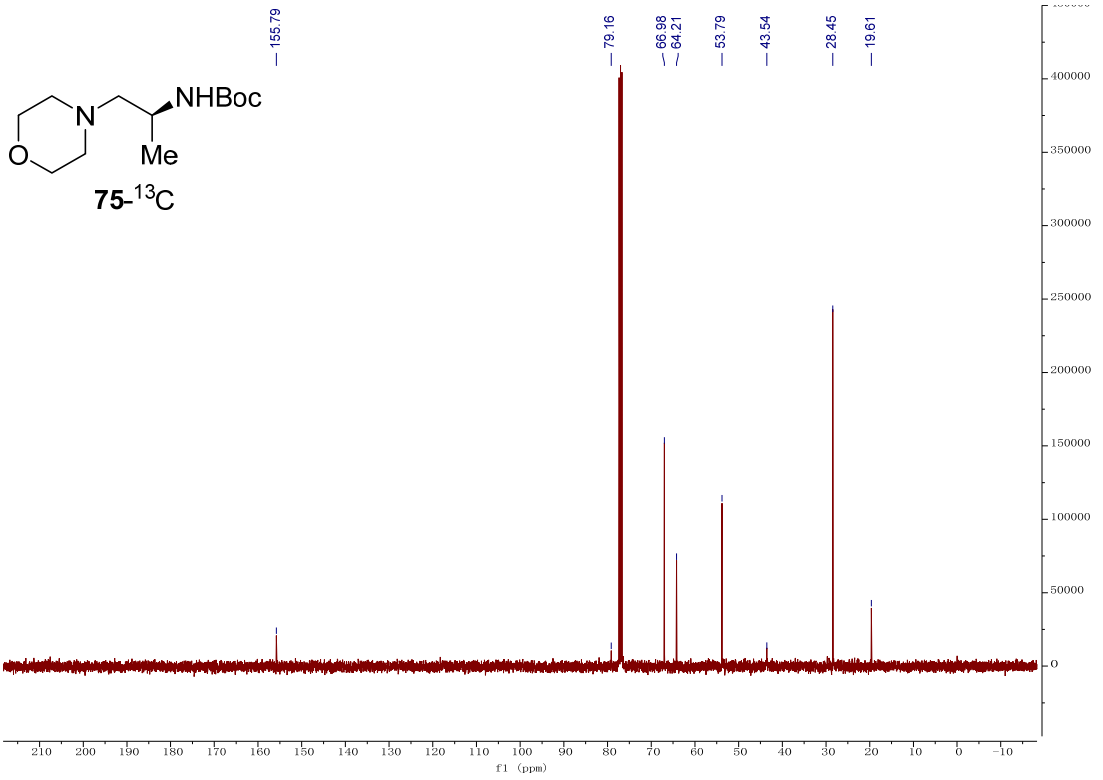


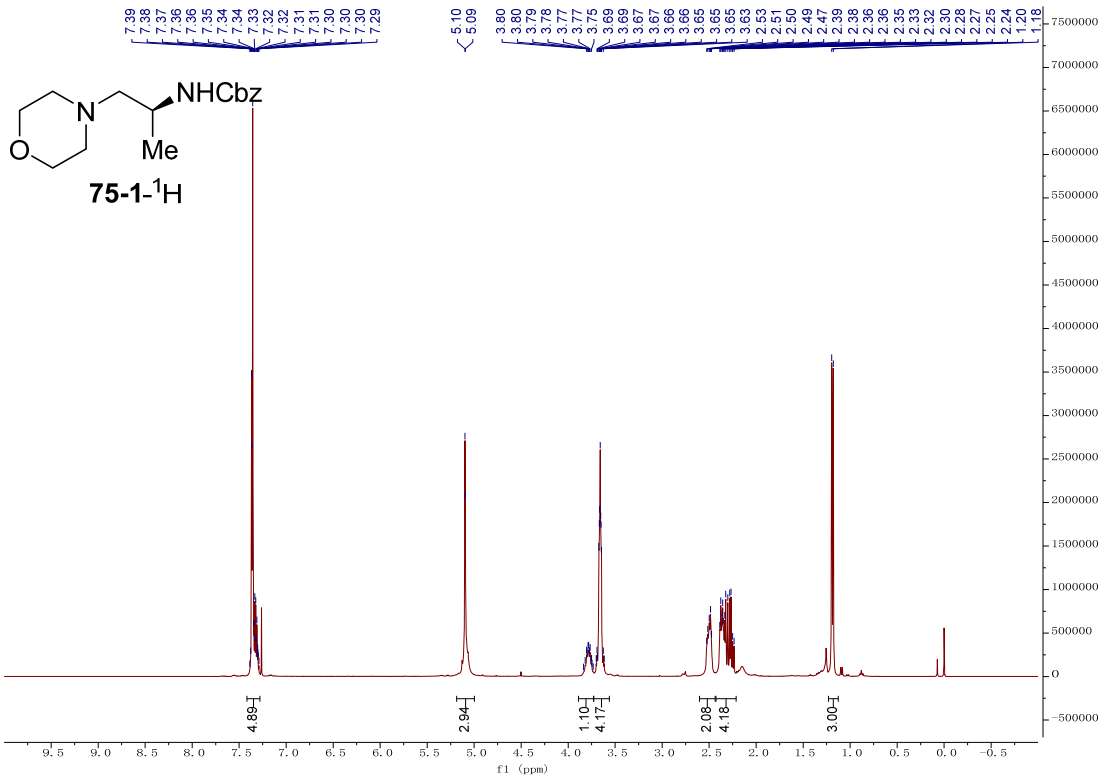
74-1-^{1}H

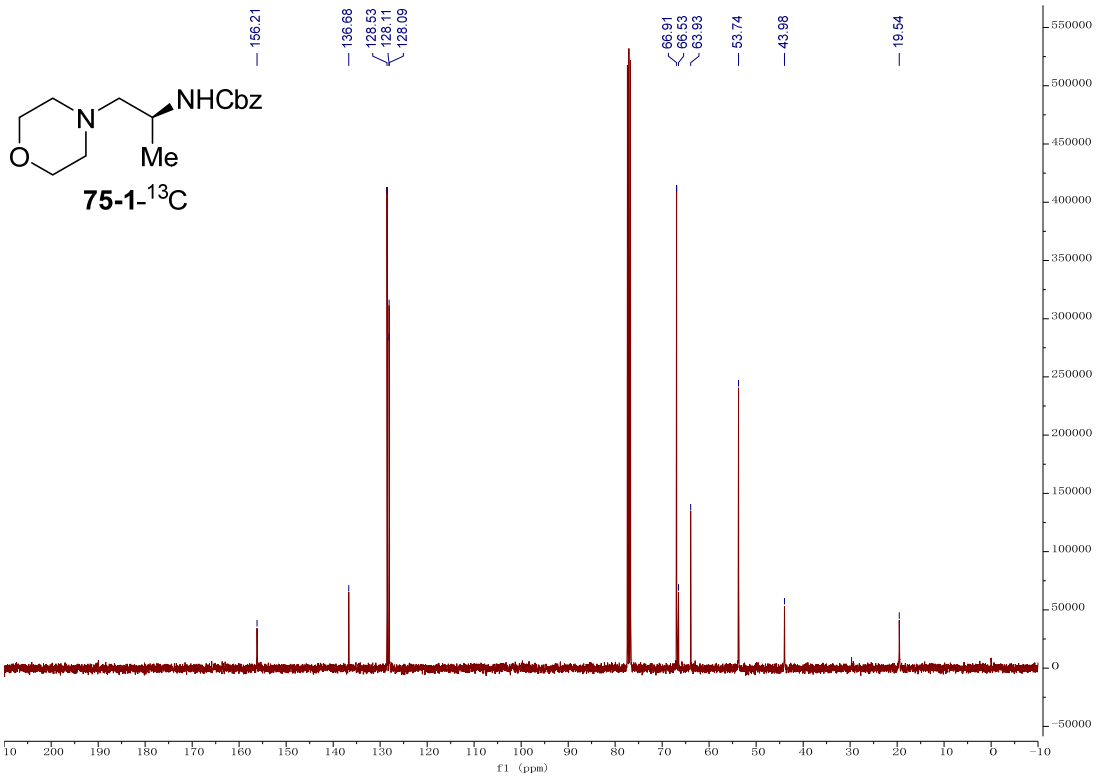


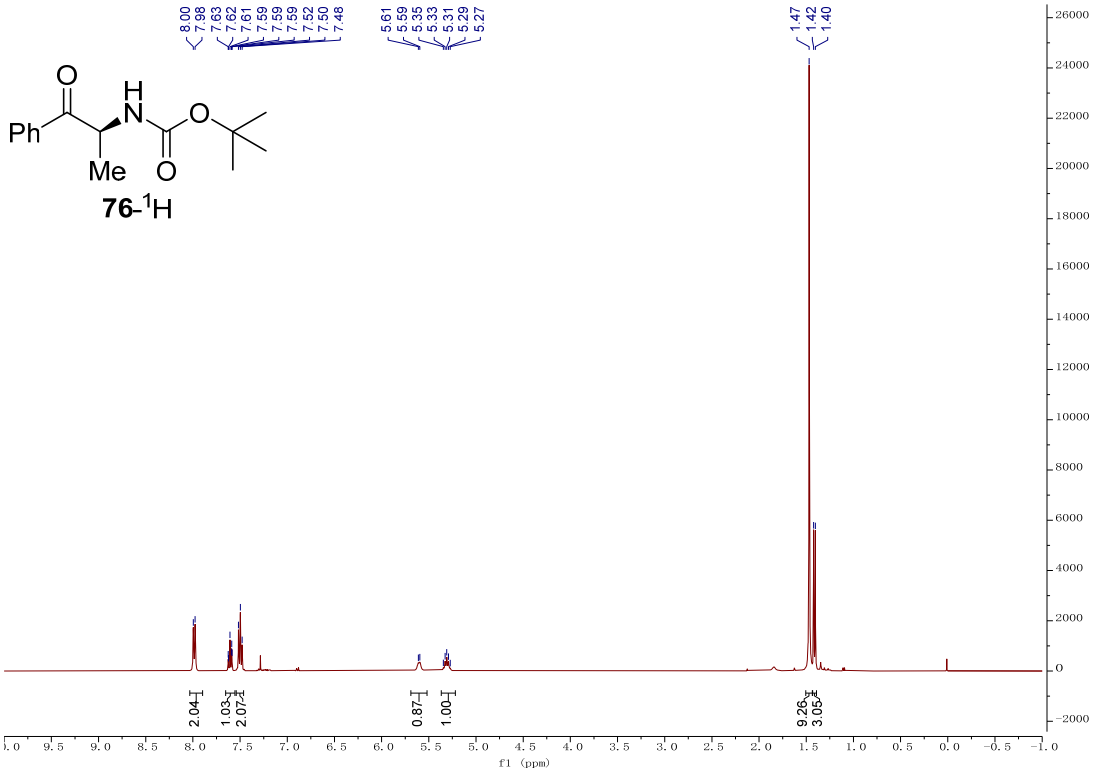
74-1-^{13}C


NHBoc
N
O
Me
75-1H
4.70 3.73 3.73 3.72 3.71 3.70 3.70 3.69 3.69 3.68 3.68 3.67 3.66 3.65 3.65
2.54 2.53 2.52 2.50 2.49 2.42 2.41 2.40 2.39 2.38 2.35 2.33 2.32 2.31 2.30 2.29 2.25 2.25 2.24 2.23 2.22 1.45 1.16 1.15
1.02 5.15 1.97 1.95 1.08 1.12 9.00 3.00
f1 (ppm)

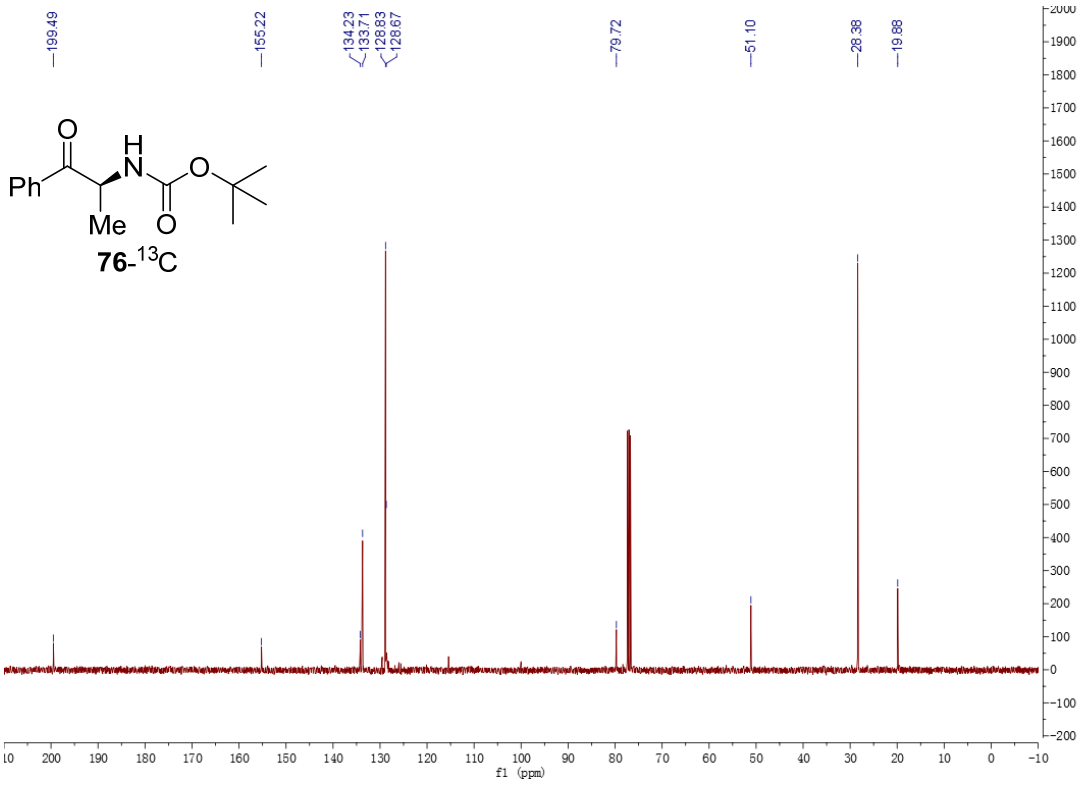

NHBoc
N
O
Me
75-13C
155.79 79.16 66.98 64.21 53.79 43.54 28.45 19.61
f1 (ppm)


NHCbz
N
O
Me
75-1-1H
7.39 7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29
5.10 5.09
3.80 3.80 3.79 3.78 3.77 3.77 3.75 3.69 3.69 3.67 3.67 3.66 3.66 3.65 3.65 3.63 2.53 2.51 2.50 2.49 2.47 2.39 2.38 2.36 2.36 2.35 2.33 2.32 2.30 2.28 2.27 2.25 2.24 1.20 1.18
4.89 2.94 1.10 4.17 2.08 4.18 3.00
f1 (ppm)

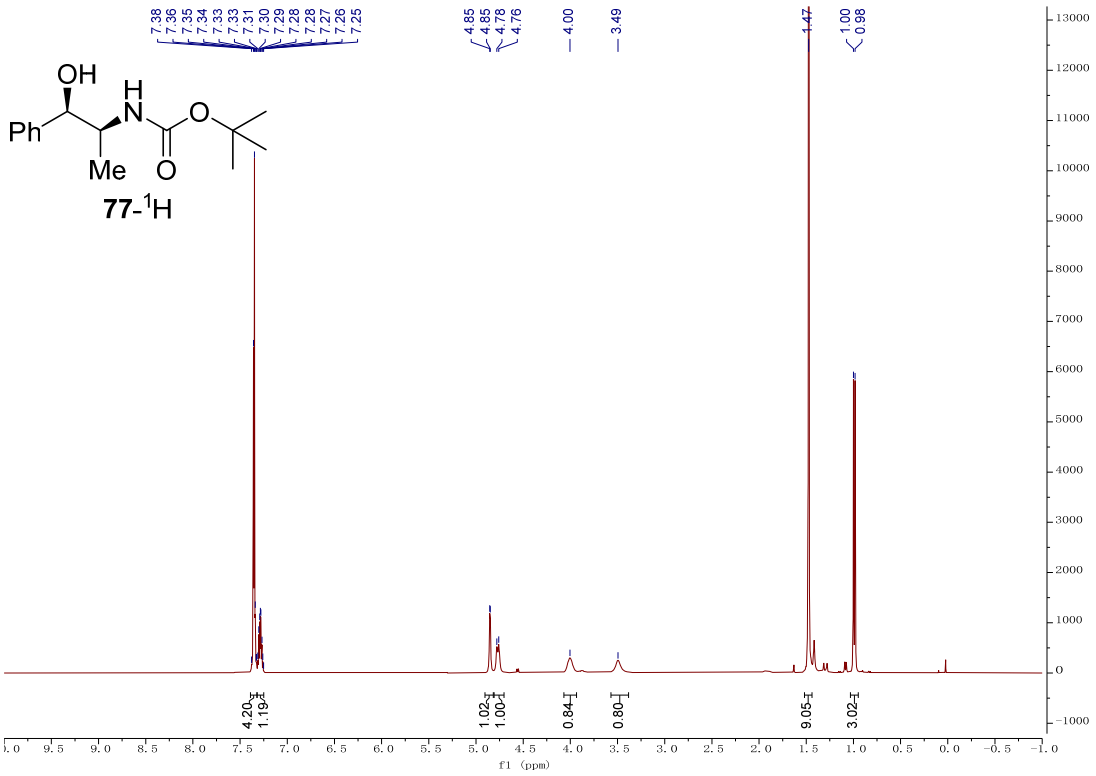

NHCbz
N
O
Me
75-1-13C
156.21 136.68 128.53 128.11 128.09 66.91 66.53 63.93 53.74 43.98 19.54
f1 (ppm)

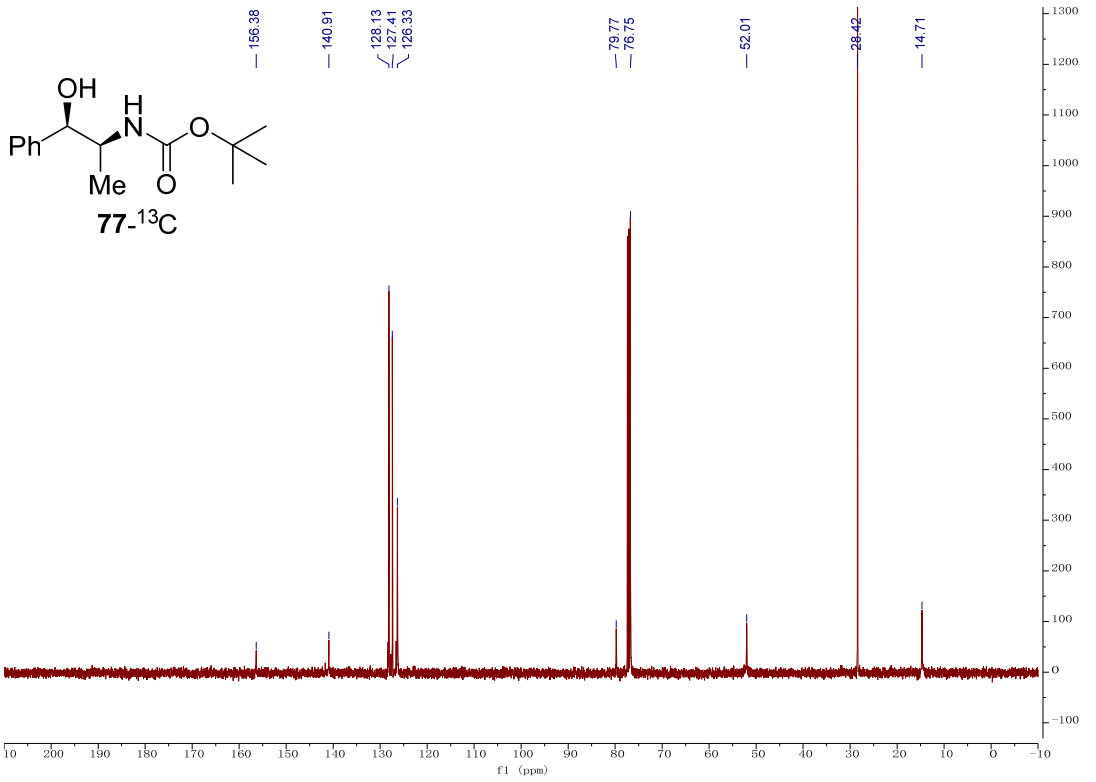

8.00
7.98
7.63
7.62
7.61
7.59
7.59
7.59
7.52
7.50
7.48
5.61
5.59
5.35
5.33
5.31
5.29
5.27
1.47
1.42
1.40
2.04
1.03
2.07
0.87
1.00
9.26
3.05
f1 (ppm)

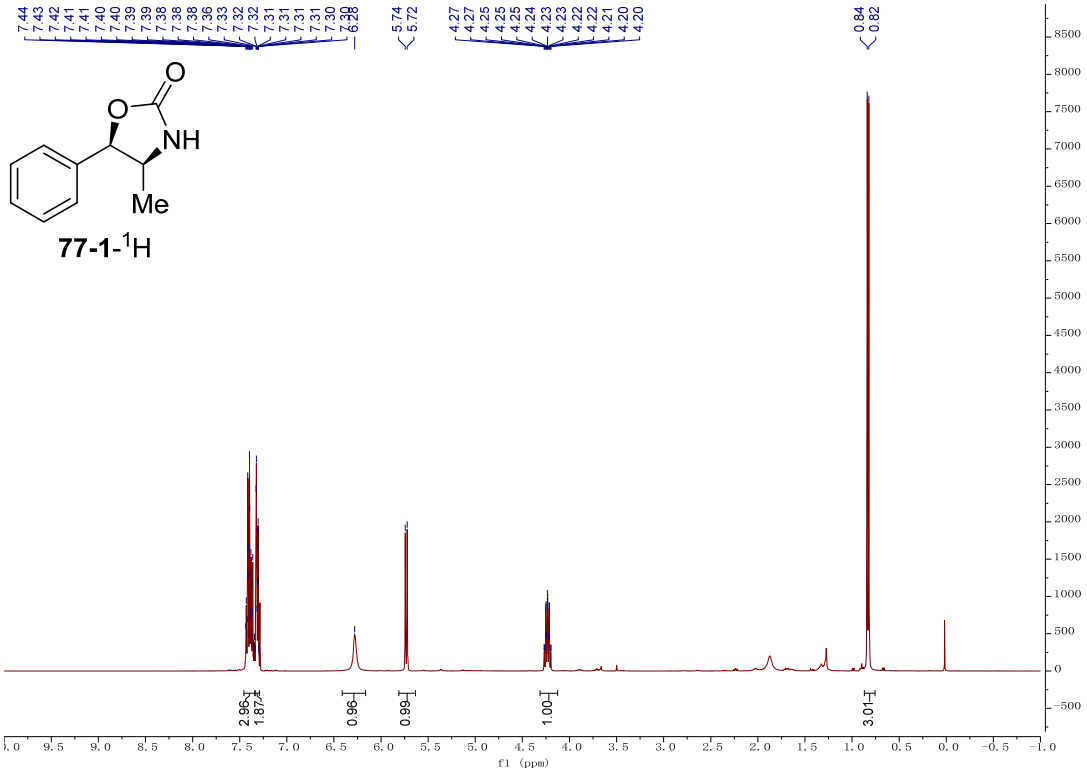
76-^{1}H


199.49
155.22
134.23
133.71
128.83
128.67
79.72
51.10
28.38
19.88
f1 (ppm)

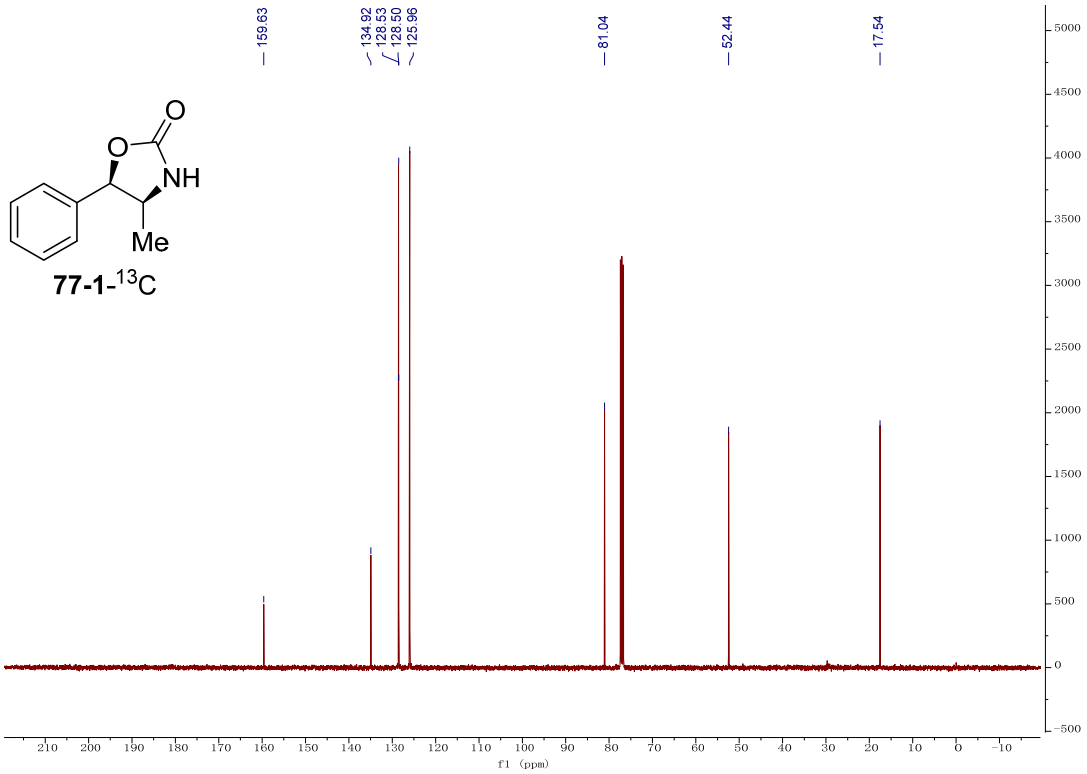
76-^{13}C


7.38
7.36
7.35
7.34
7.33
7.33
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.25
4.85
4.85
4.78
4.76
4.00
3.49
1.47
1.00
0.98
OH
H
N
O
Ph
Me
O
77-1H
4.20
1.19
1.02
1.00
0.84
0.80
9.05
3.02
f1 (ppm)

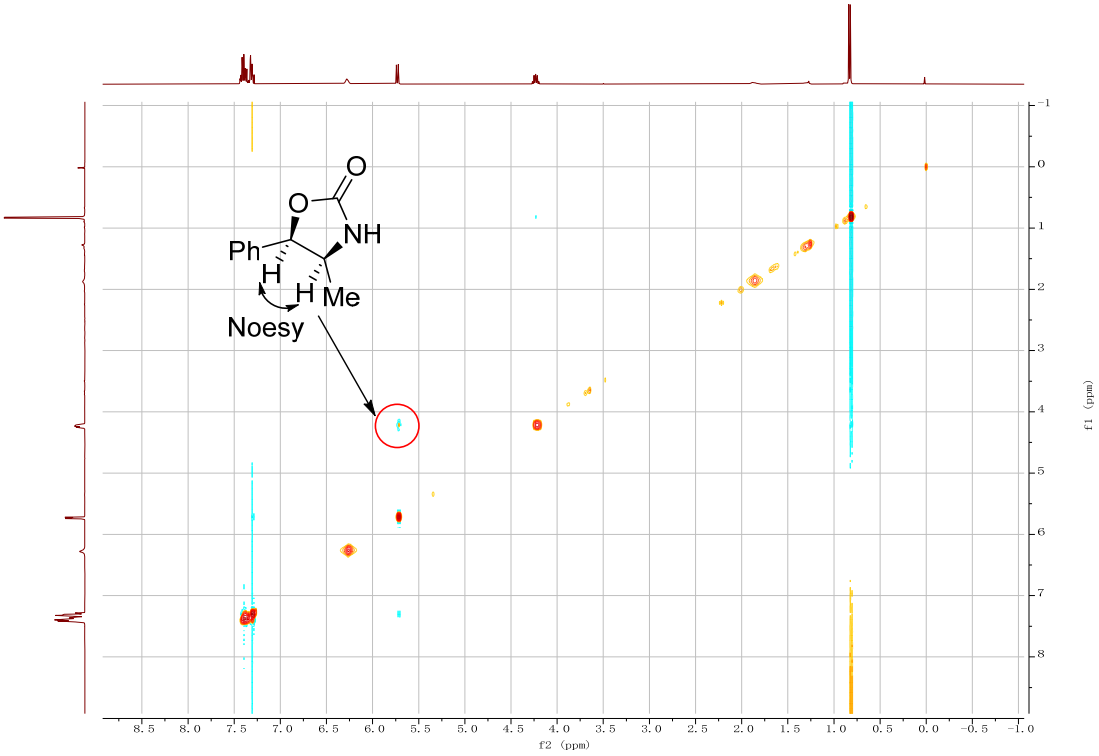

156.38
140.91
128.13
127.41
126.33
79.77
76.75
52.01
28.42
14.71
OH
H
N
O
Ph
Me
O
77-13C
f1 (ppm)

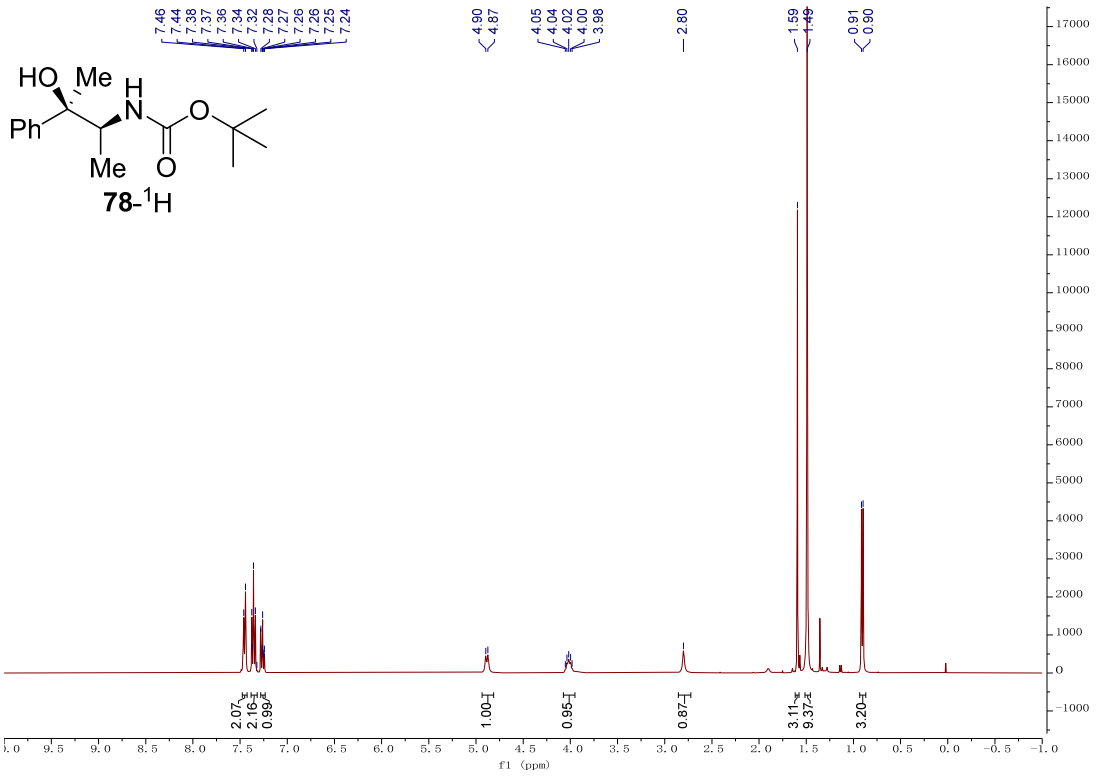


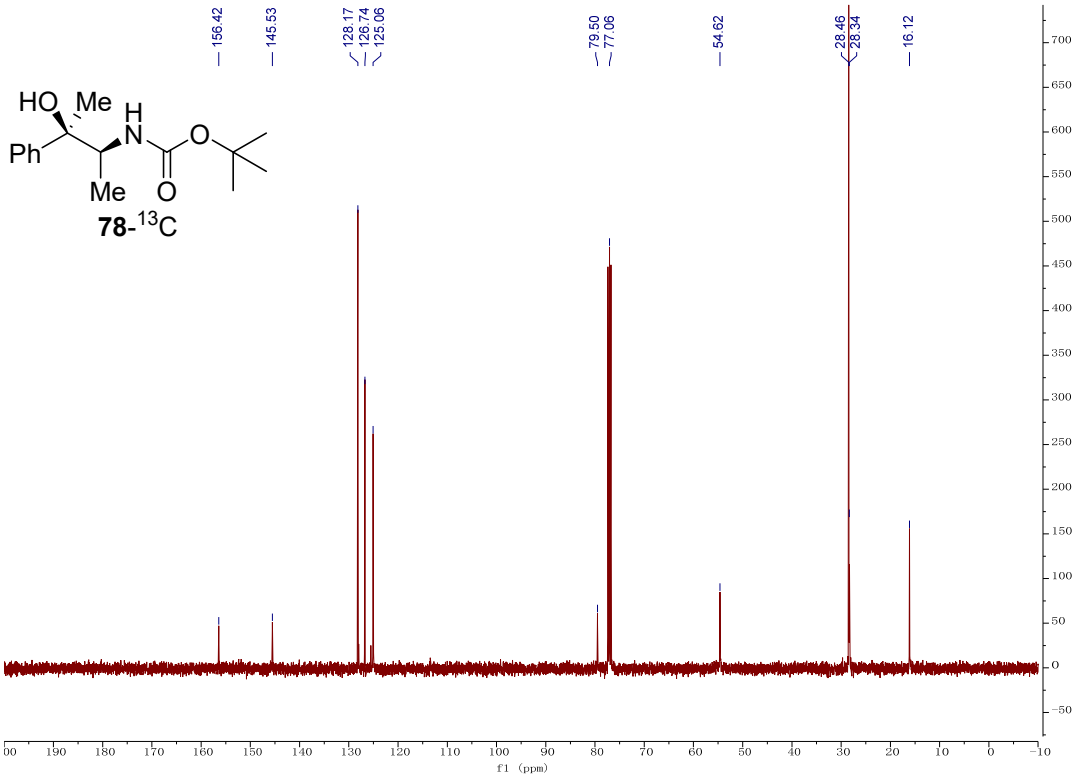
77-1-^{1}H

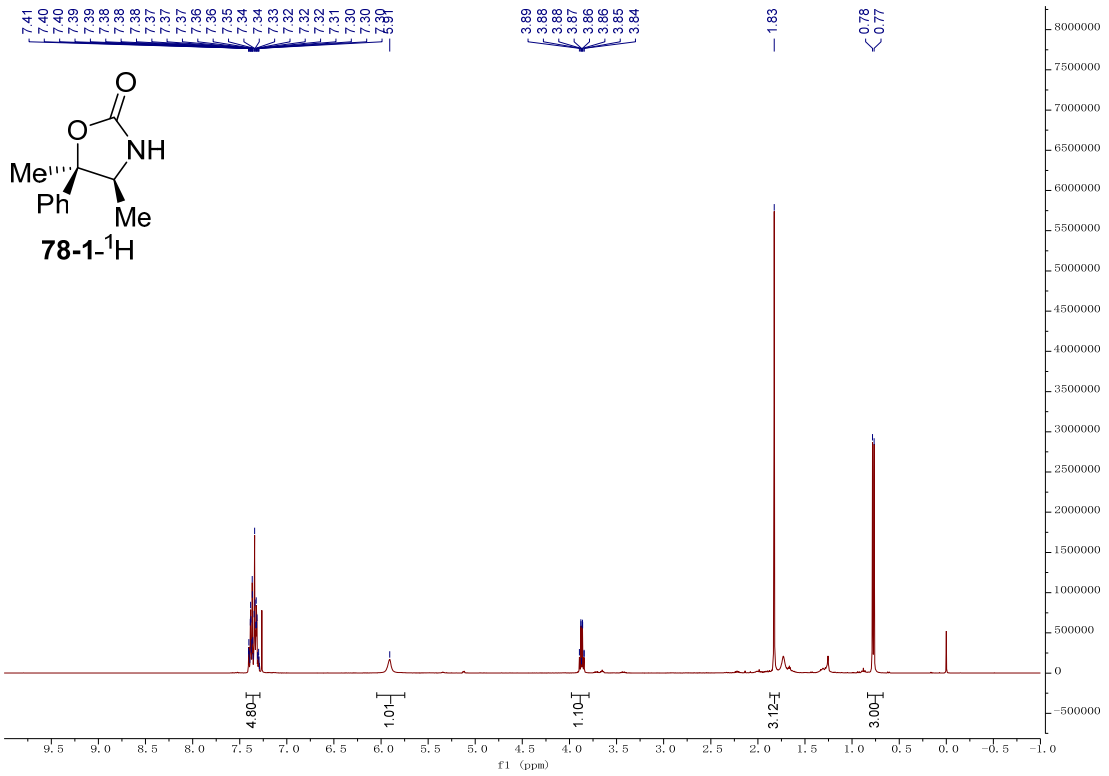


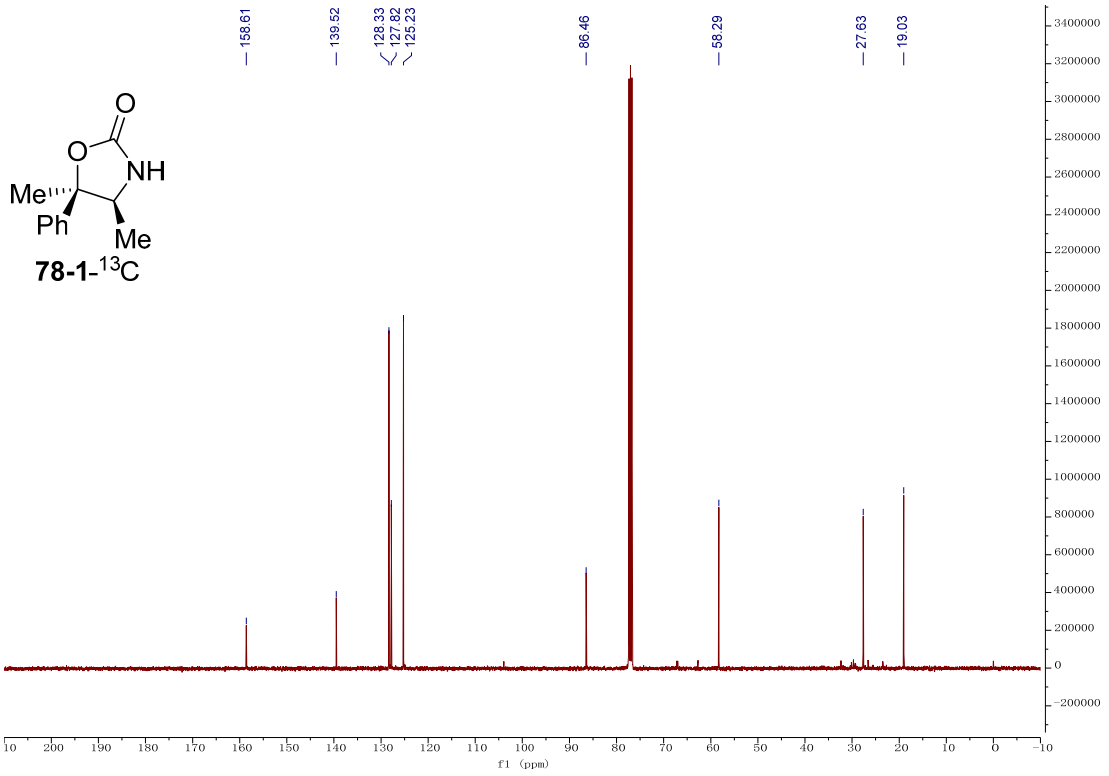
77-1-^{13}C

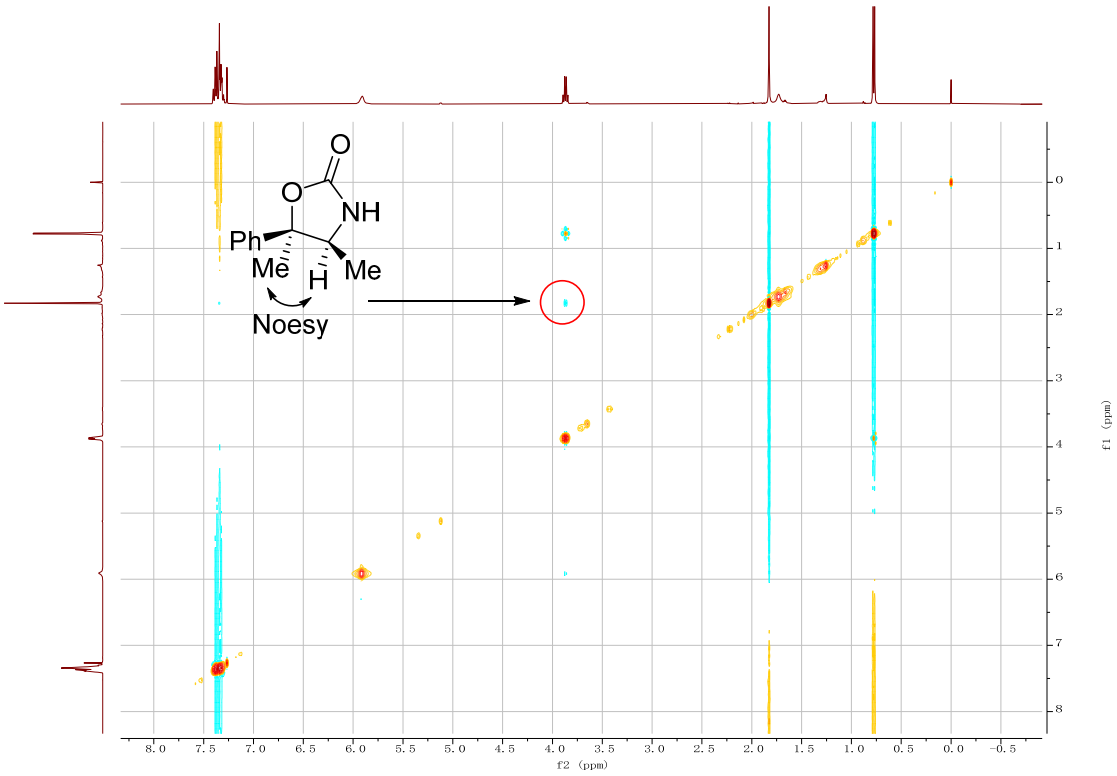

O
O
NH
Ph
H
H
Me
Noesy
f2 (ppm)
f1 (ppm)

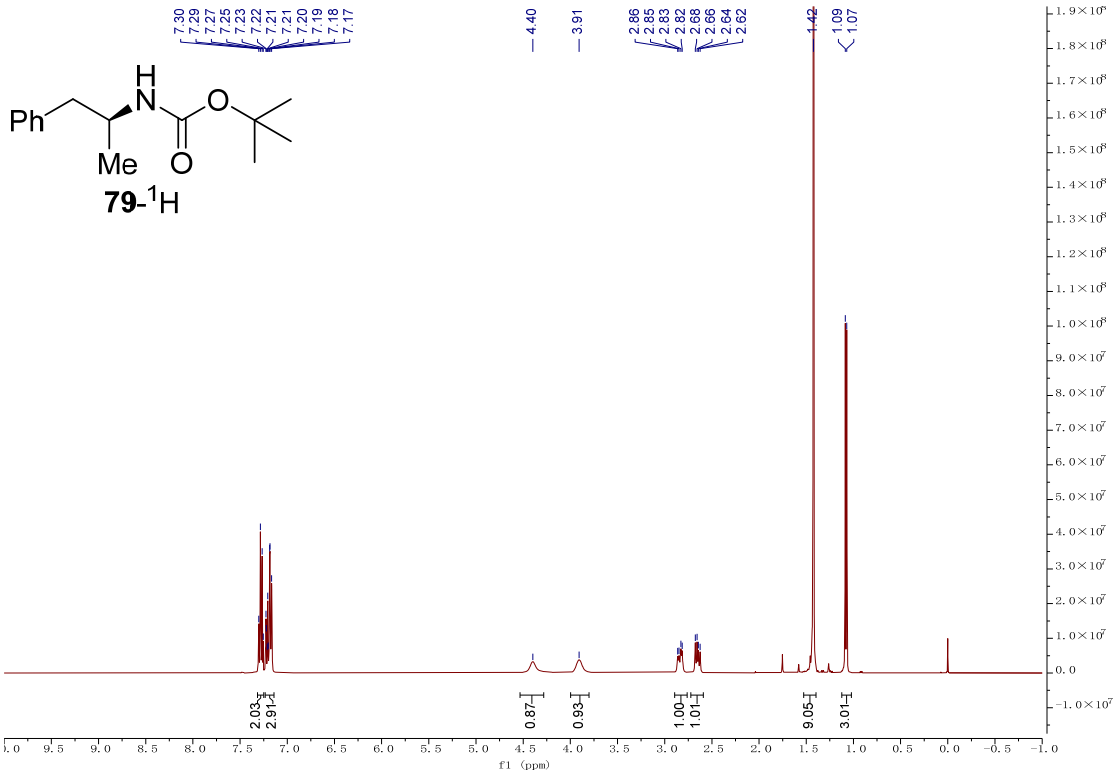

7.46
7.44
7.38
7.37
7.36
7.34
7.32
7.28
7.27
7.26
7.26
7.25
7.24
4.90
4.87
4.05
4.04
4.02
4.00
3.98
2.80
1.59
1.49
0.91
0.90
HO
Me
H
N
O
Ph
Me
O
78-1H
2.07
2.16
0.99
1.00
0.95
0.87
3.11
9.37
3.20
f1 (ppm)

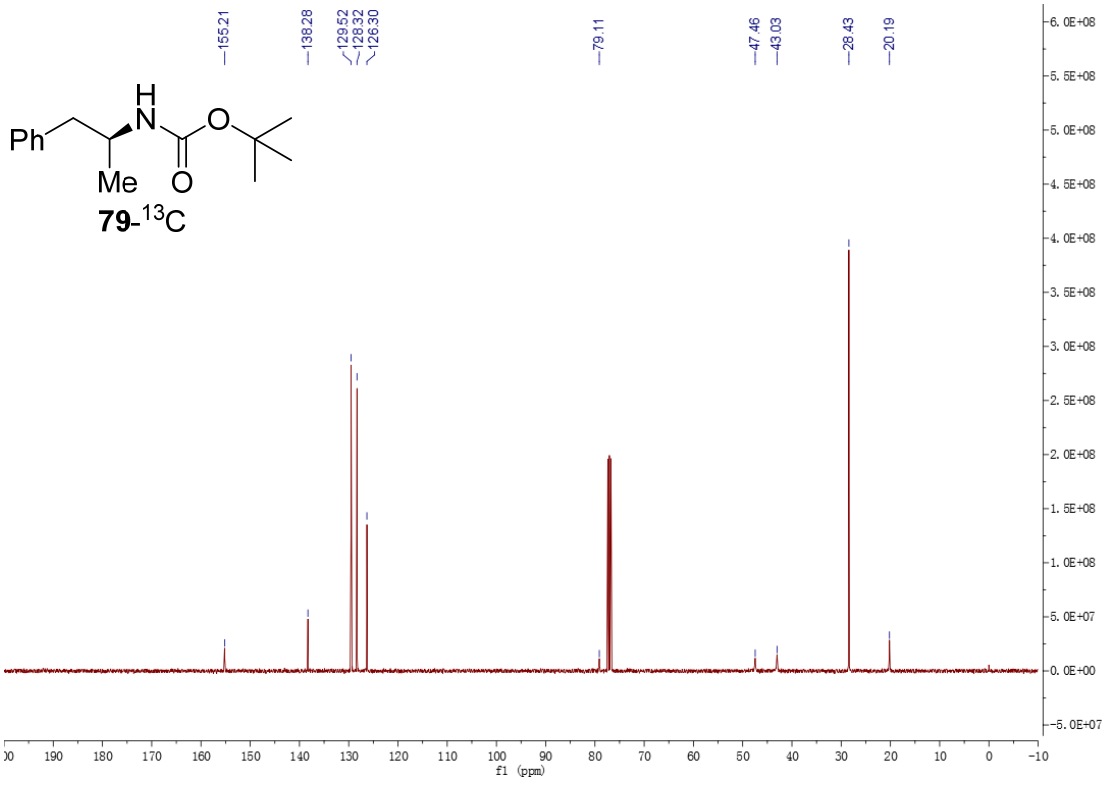

156.42
145.53
128.17
126.74
125.06
79.50
77.06
54.62
28.46
28.34
16.12
HO
Me
H
N
O
Ph
Me
O
78-13C
f1 (ppm)

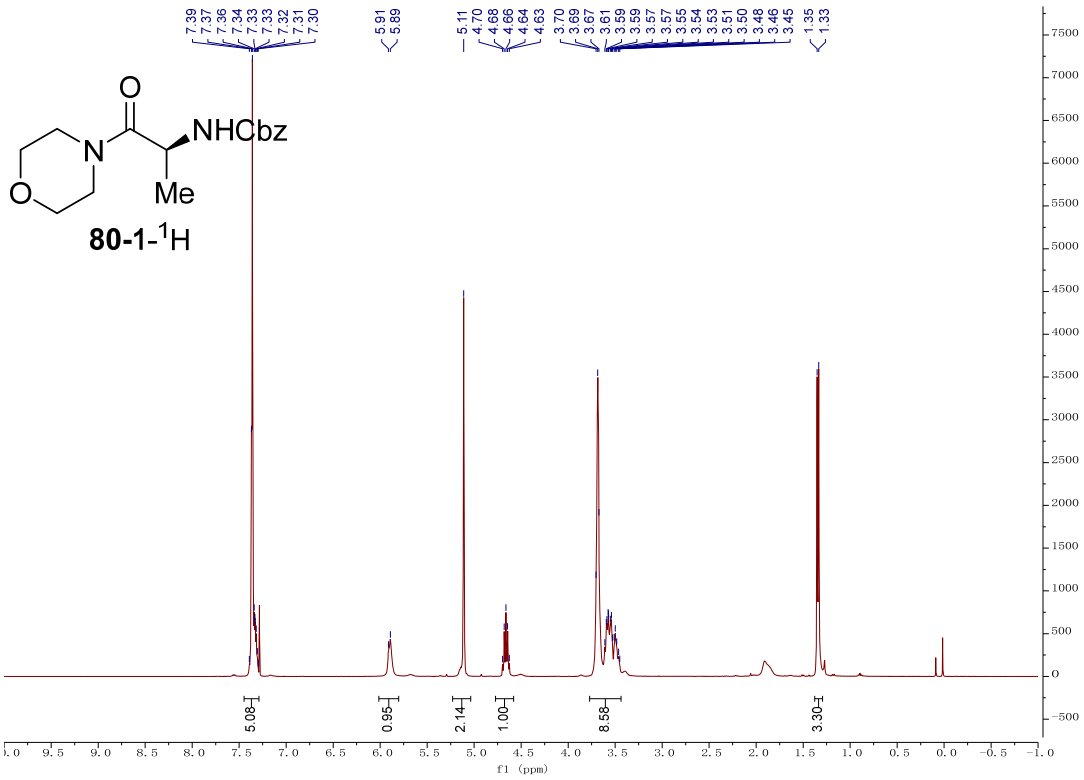

7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
5.90
3.89
3.88
3.88
3.87
3.86
3.86
3.85
3.84
1.83
0.78
0.77
O
O
NH
Me
Ph
Me
78-1-1H
4.80
1.01
1.10
3.12
3.00
f1 (ppm)


158.61
139.52
128.33
127.82
125.23
86.46
58.29
27.63
19.03
O
O
NH
Me
Ph
Me
78-1-13C
f1 (ppm)

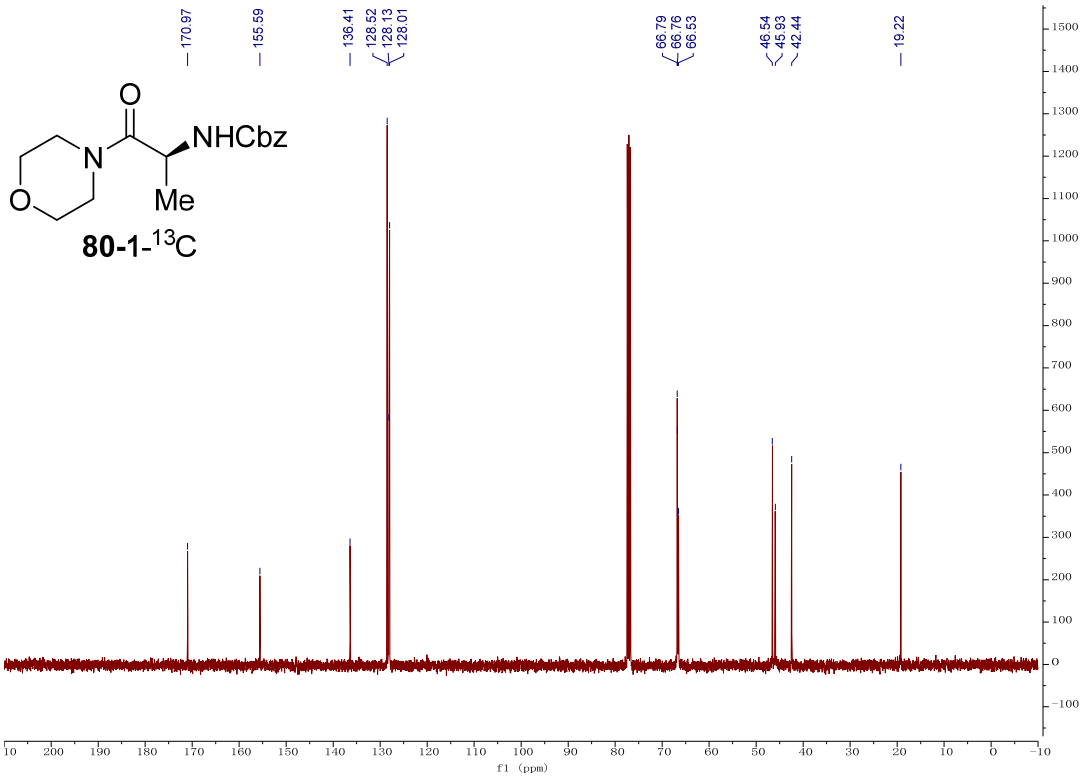

O
O
NH
Ph
Me
H
Me
Noesy
f2 (ppm)
f1 (ppm)


Ph
H
N
O
Me
O
79-1H
7.30
7.29
7.27
7.25
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.17
4.40
3.91
2.86
2.85
2.83
2.82
2.68
2.66
2.64
2.62
1.42
1.09
1.07
2.03
2.91
0.87
0.93
1.00
1.01
9.05
3.01
f1 (ppm)

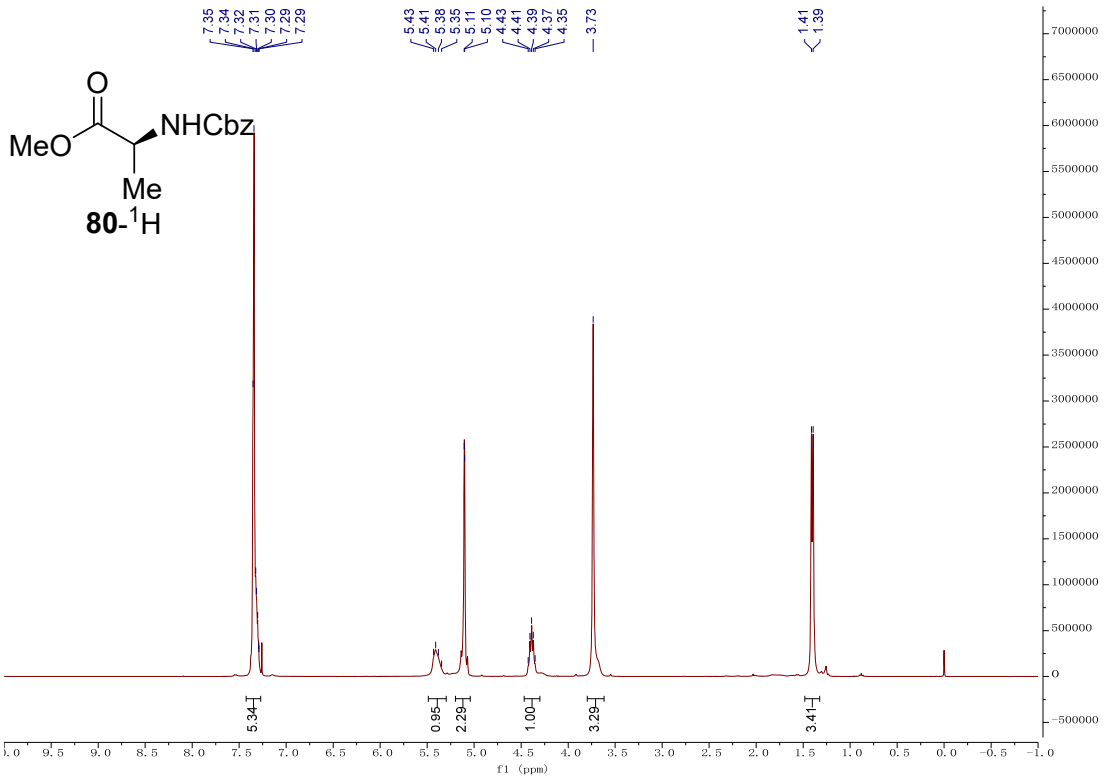

Ph
H
N
O
Me
O
79-13C
155.21
138.28
129.52
128.32
126.30
79.11
47.46
43.03
28.43
20.19
f1 (ppm)

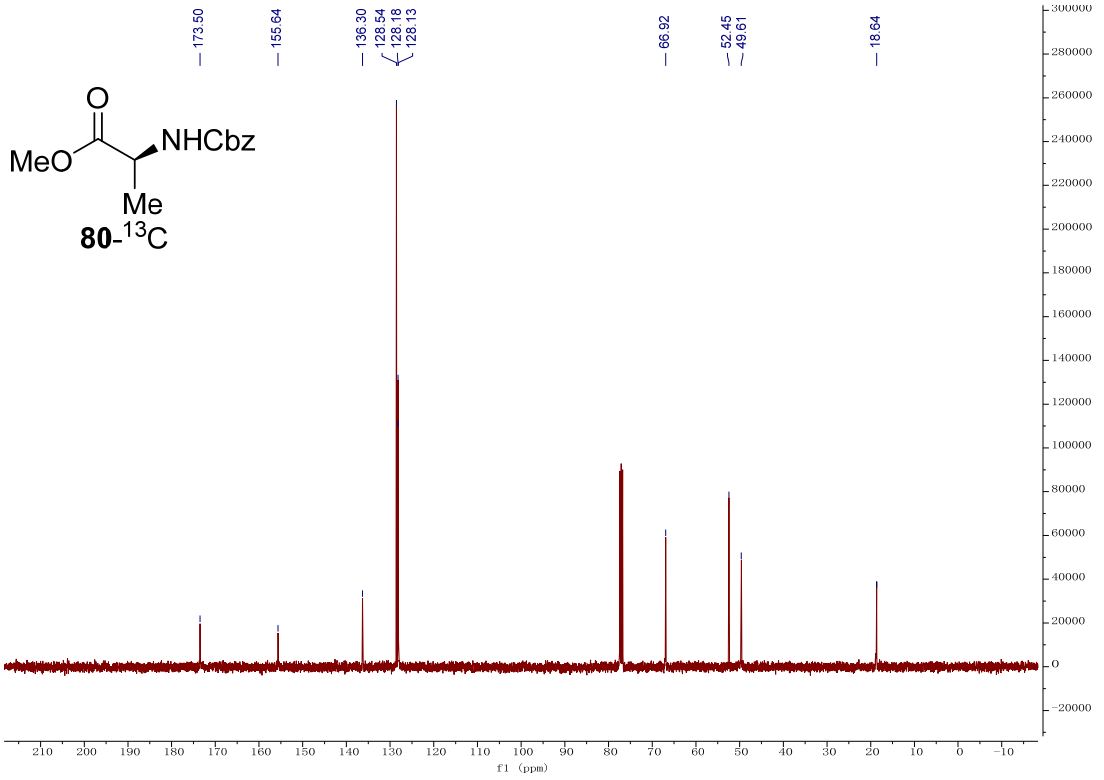


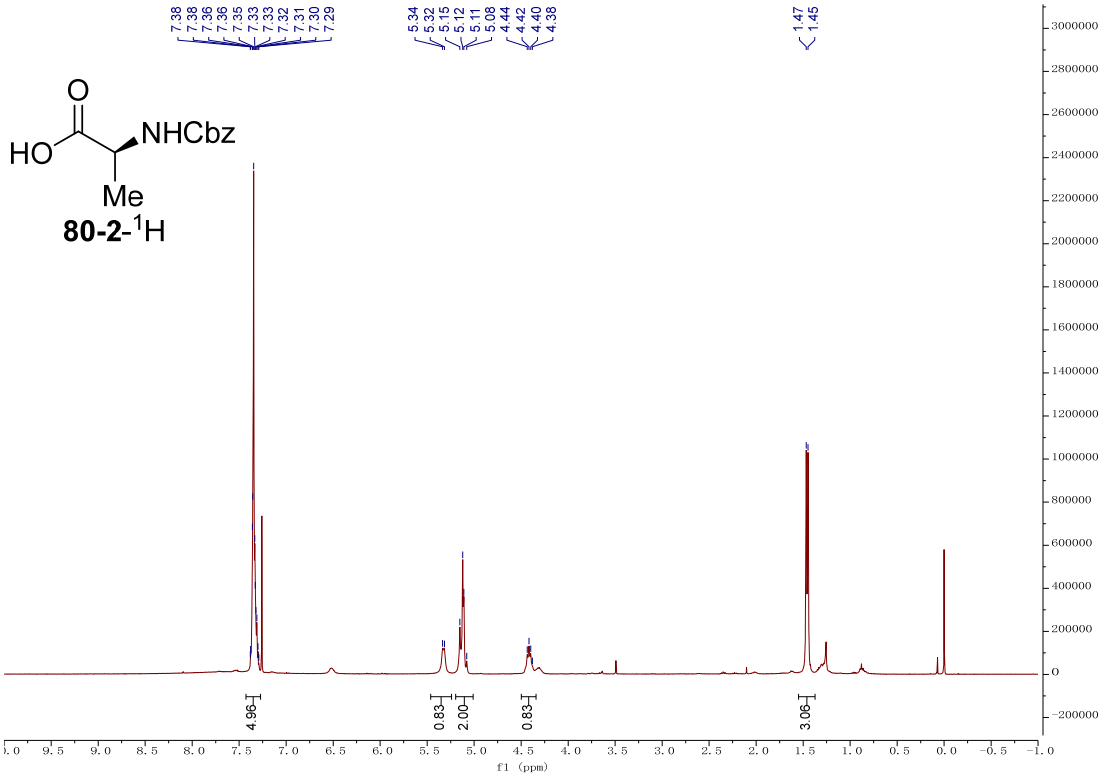
80-1-^{1}H

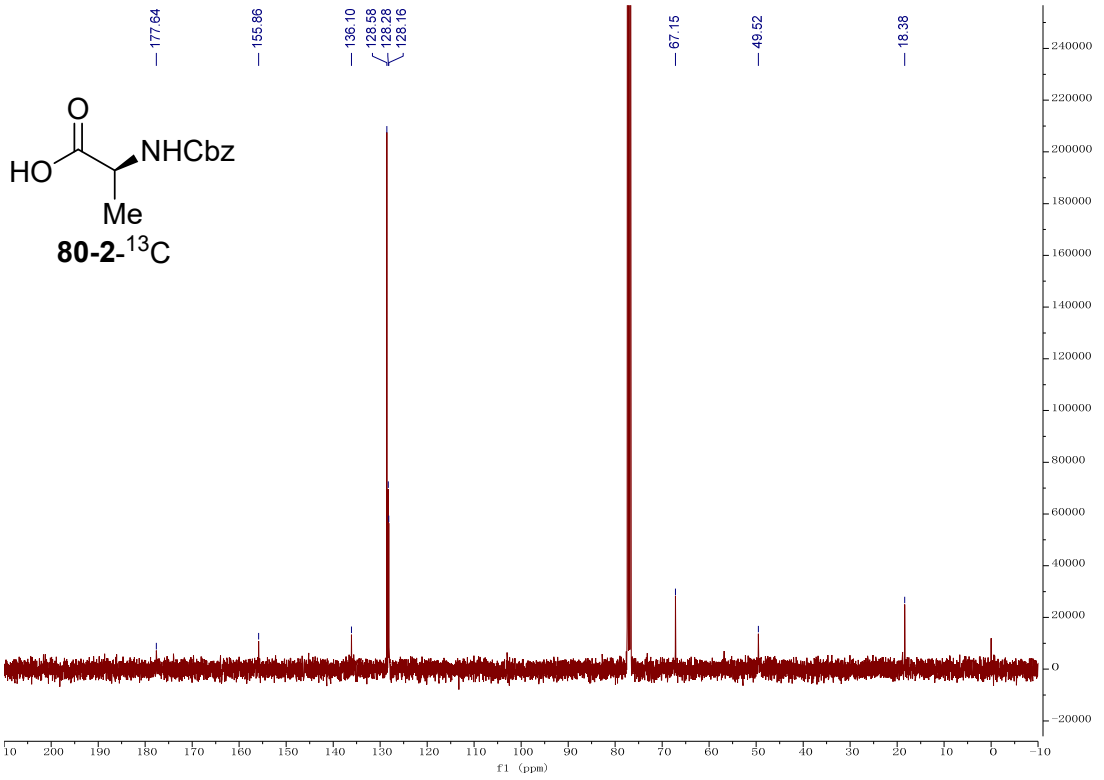


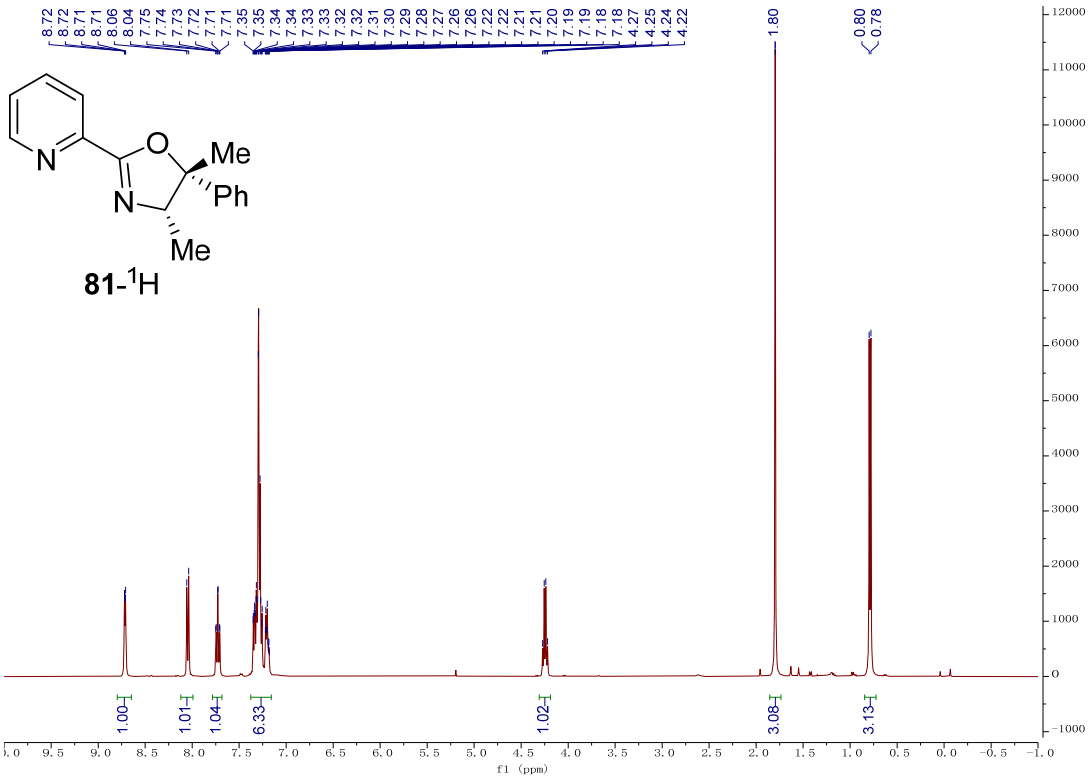
80-1-^{13}C


7.35
7.34
7.32
7.31
7.30
7.29
7.29
5.43
5.41
5.38
5.35
5.11
5.10
4.43
4.41
4.39
4.37
4.35
3.73
1.41
1.39
O
MeO
NHCbz
Me
80-1H
5.34
0.95
2.29
1.00
3.29
3.41
f1 (ppm)

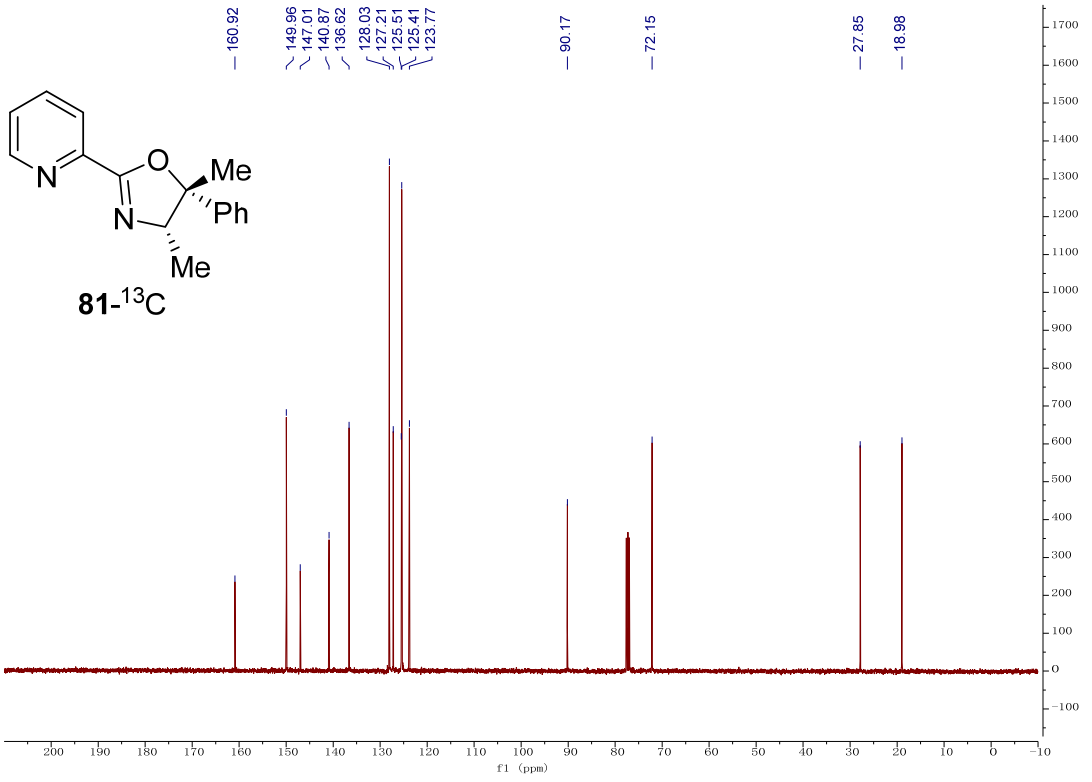

173.50
155.64
136.30
128.54
128.18
128.13
66.92
52.45
49.61
18.64
O
MeO
NHCbz
Me
80-13C
f1 (ppm)


7.38
7.38
7.36
7.36
7.35
7.33
7.33
7.32
7.31
7.30
7.29
5.34
5.32
5.15
5.12
5.11
5.08
4.44
4.42
4.40
4.38
1.47
1.45
O
HO
NHCbz
Me
80-2-1H
4.96
0.83
2.00
0.83
3.06
f1 (ppm)

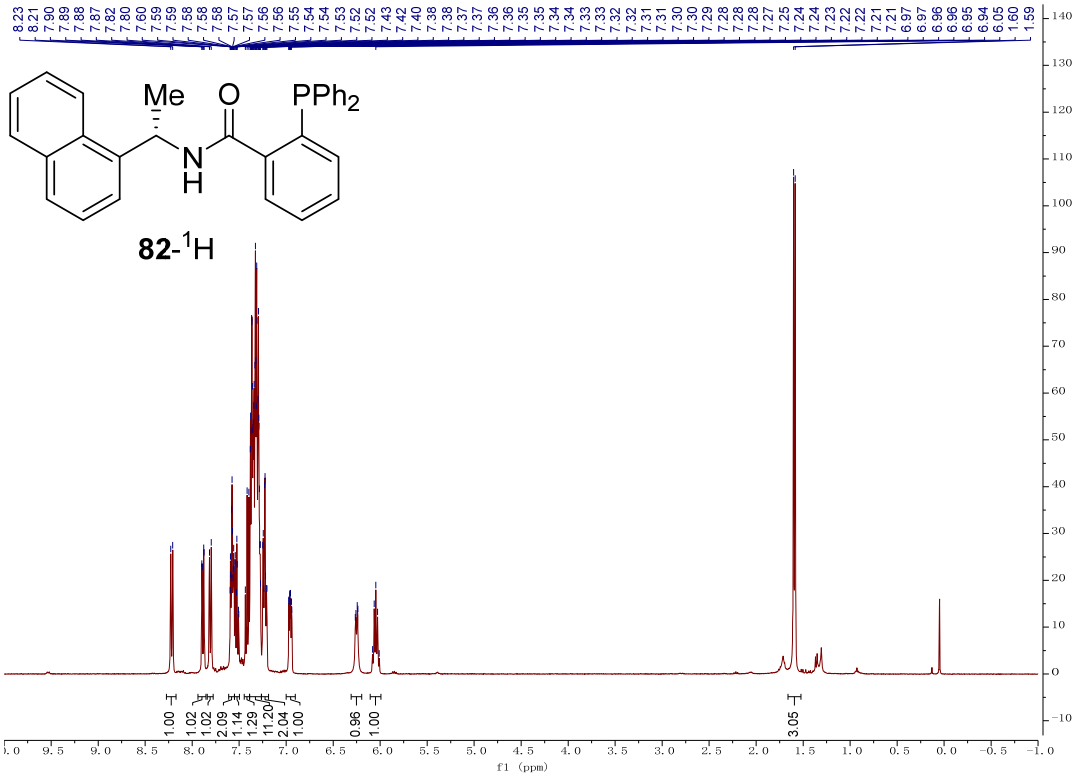

177.64
155.86
136.10
128.58
128.28
128.16
67.15
49.52
18.38
O
HO
NHCbz
Me
80-2-13C
f1 (ppm)

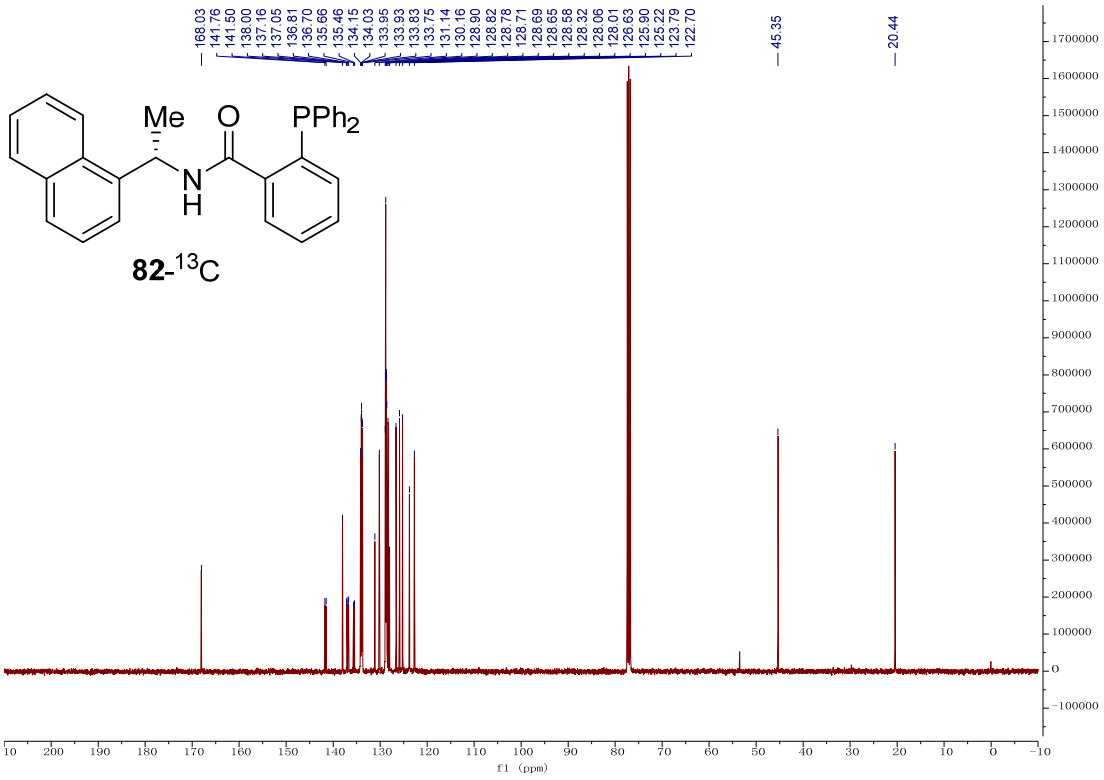

8.72
8.72
8.71
8.71
8.06
8.04
7.75
7.74
7.73
7.72
7.71
7.71
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.26
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
4.27
4.25
4.24
4.22
1.80
0.80
0.78
N
O
Me
N
Ph
Me
1.00
1.01
1.04
6.33
1.02
3.08
3.13
f1 (ppm)

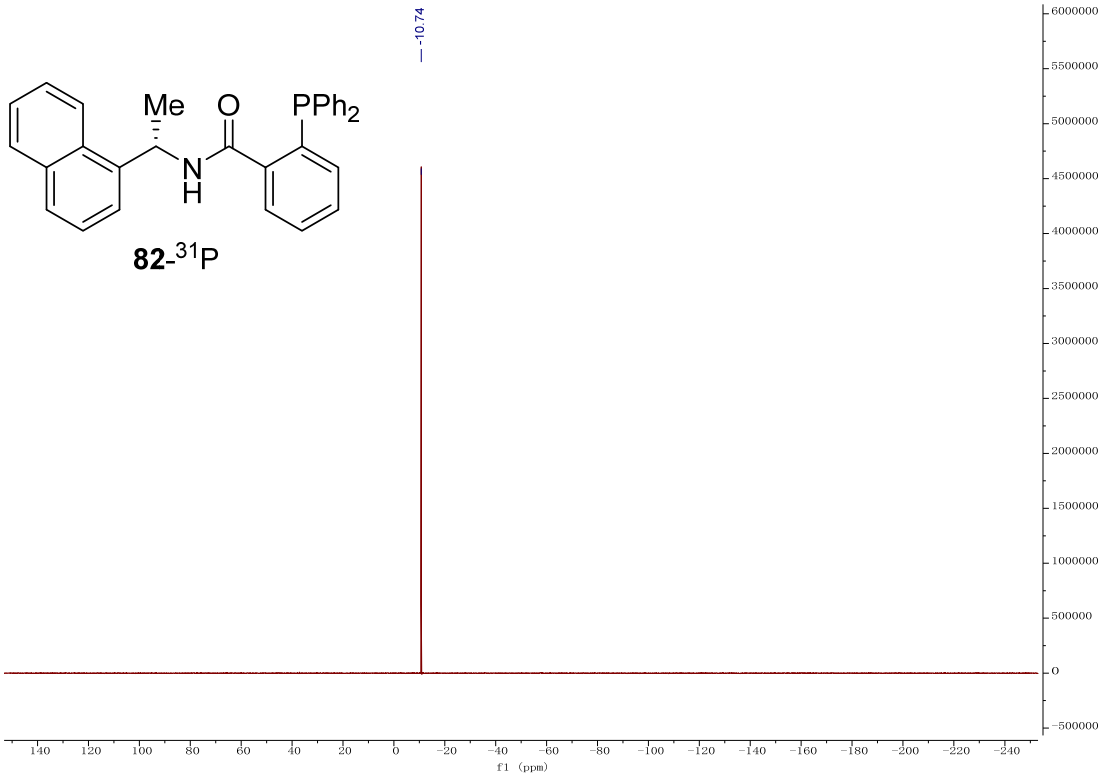
81-^{1}H

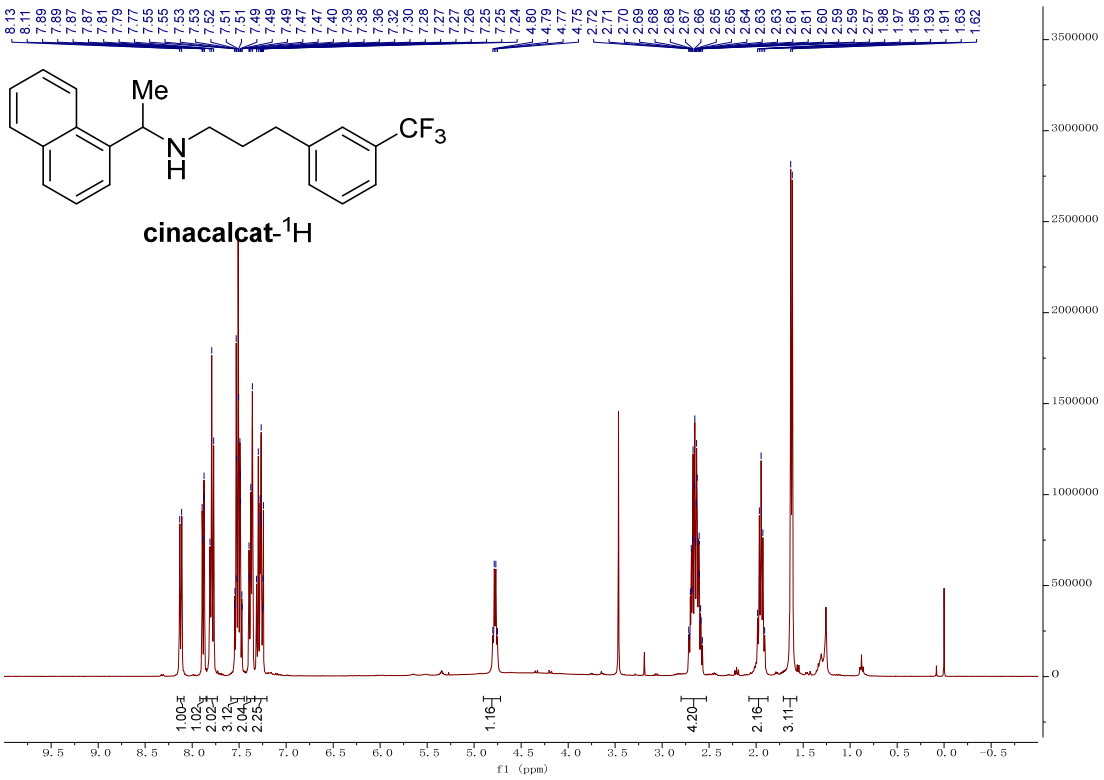

160.92
149.96
147.01
140.87
136.62
128.03
127.21
125.51
125.41
123.77
90.17
72.15
27.85
18.98
N
O
Me
N
Ph
Me
f1 (ppm)

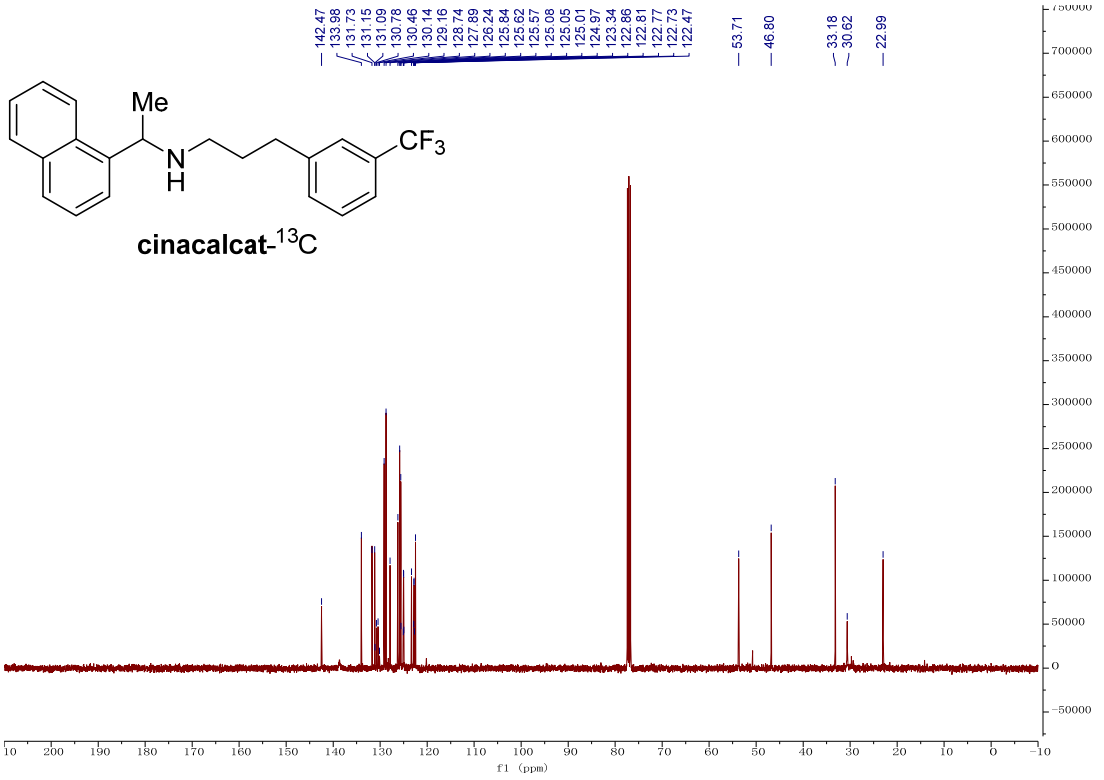
81-^{13}C

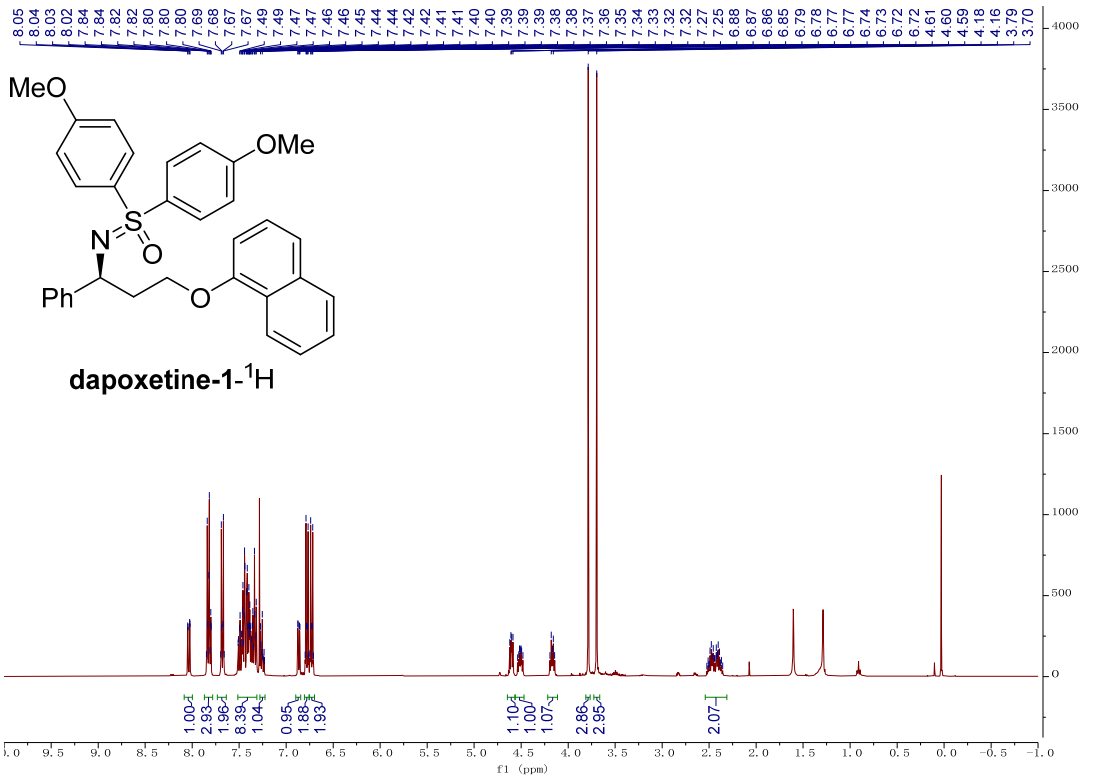

Me
O
PPh2
N
H
82-1H
f1 (ppm)

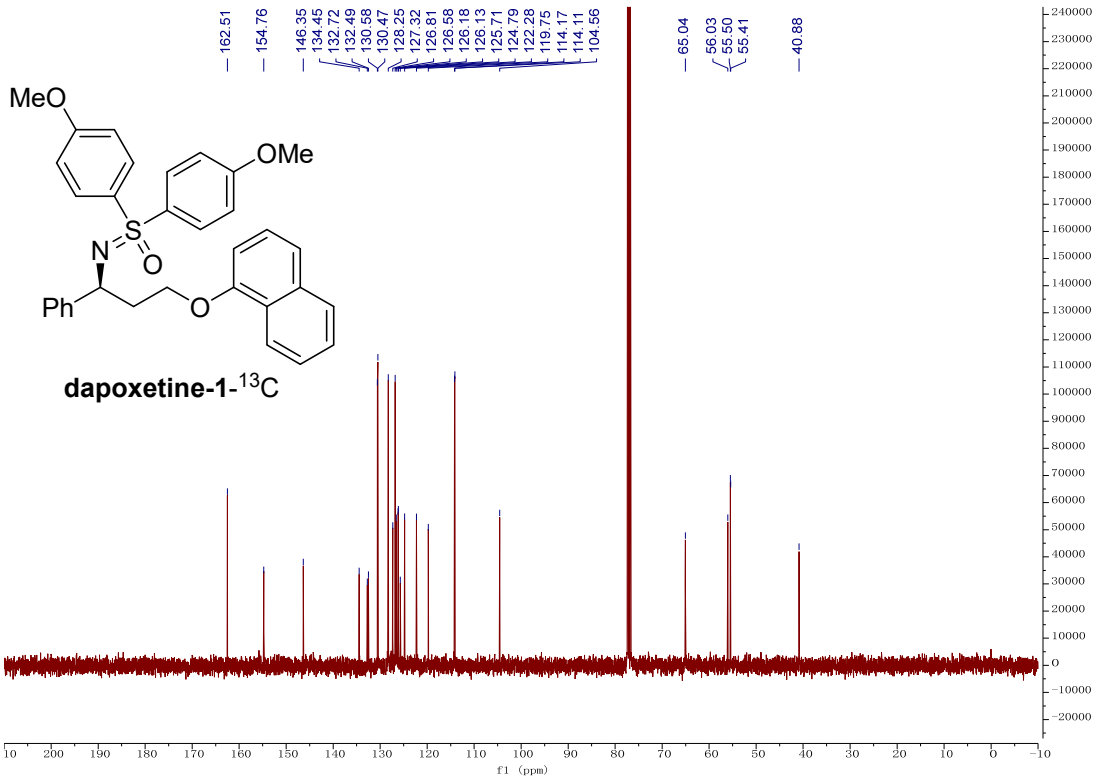

Me
O
PPh2
N
H
82-13C
f1 (ppm)

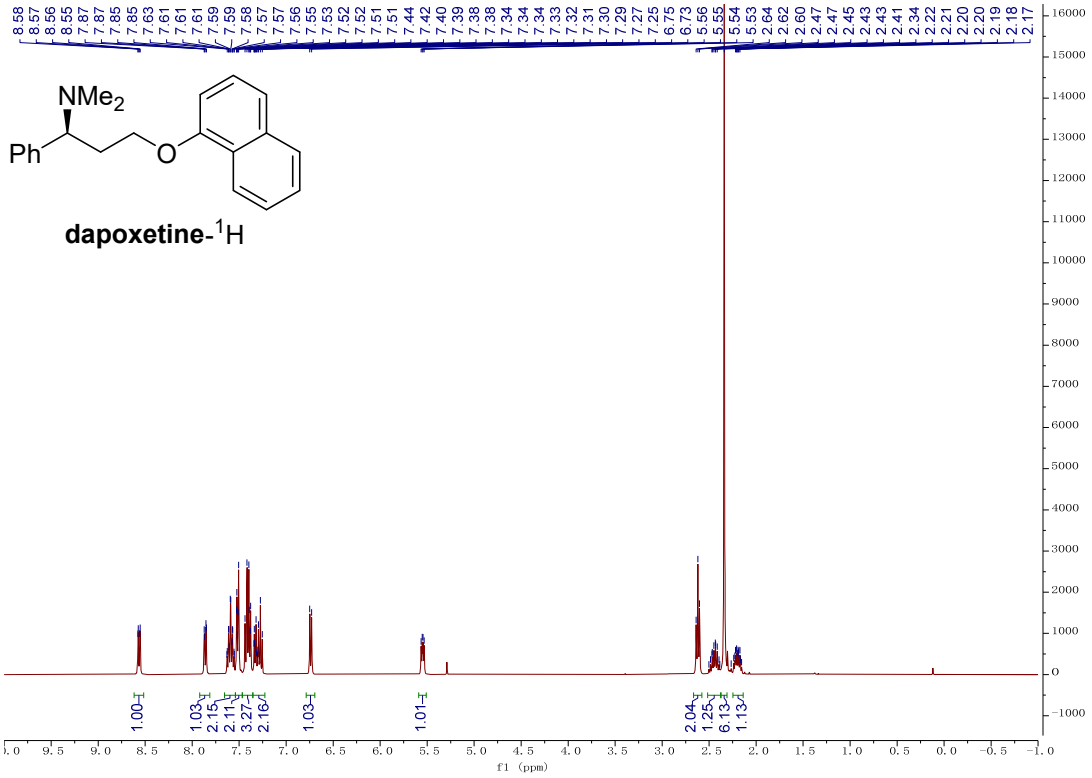

Me
O
PPh2
N
H
82-31P
-10.74
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

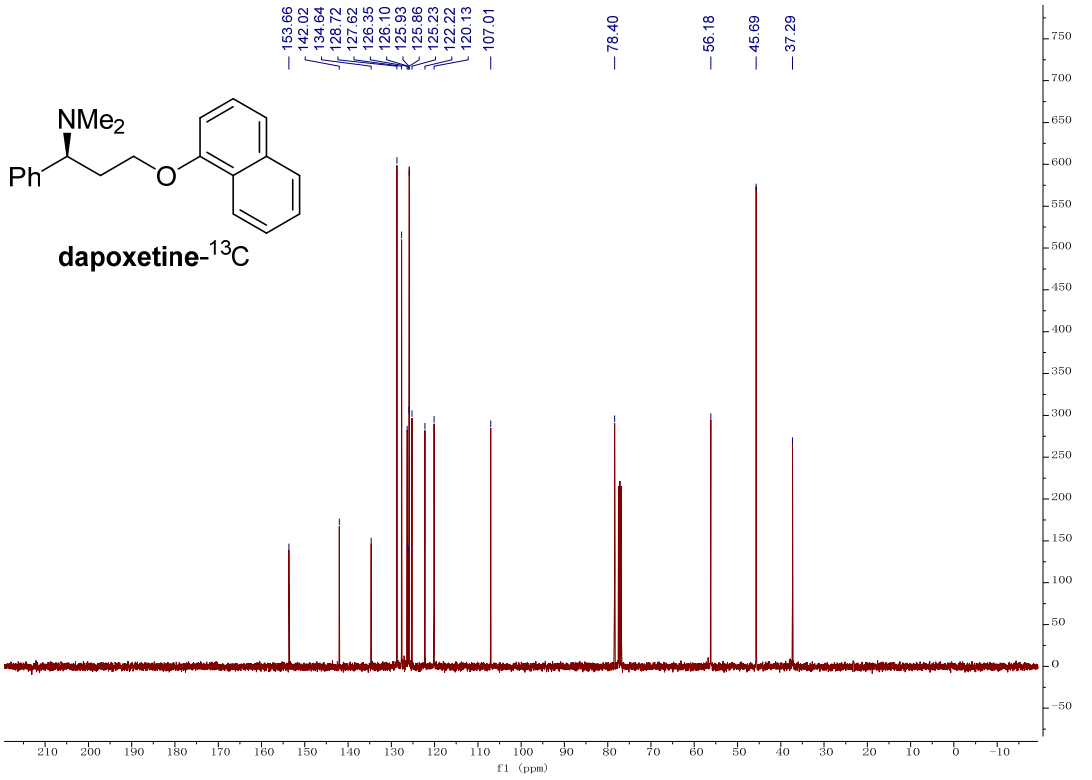

Me
N
H
CF3
cinacalcat-1H
f1 (ppm)

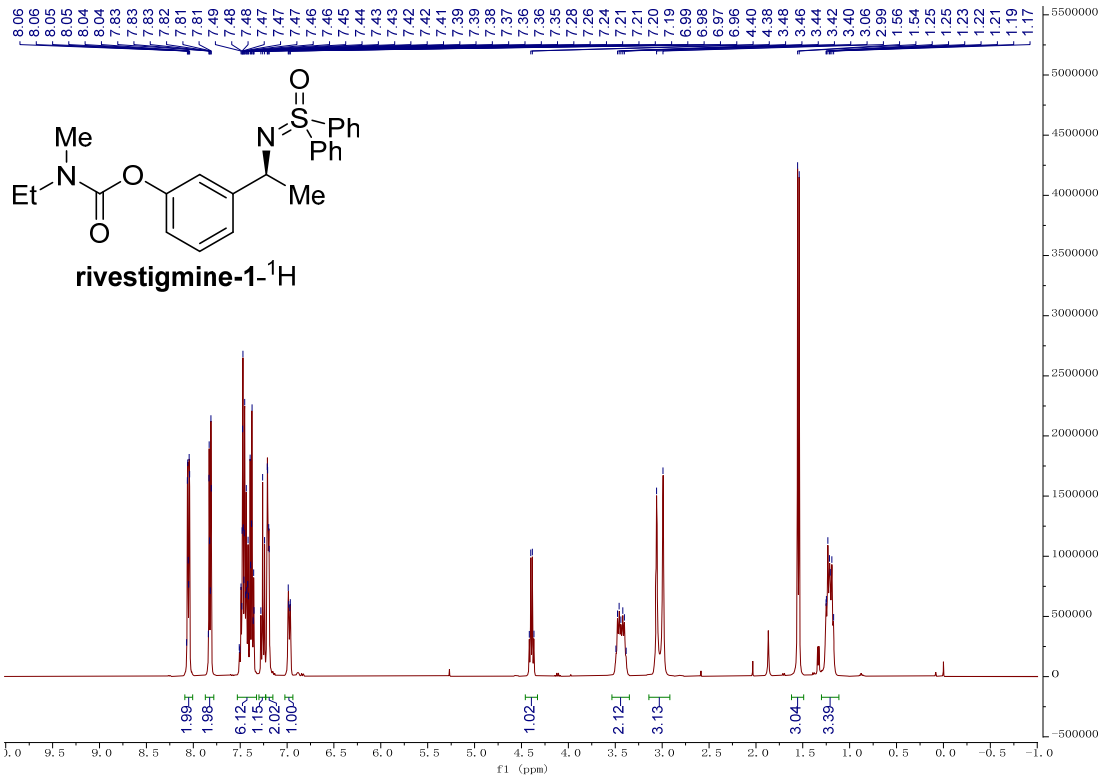

Me
N
H
CF3
cinacalcat-13C
f1 (ppm)

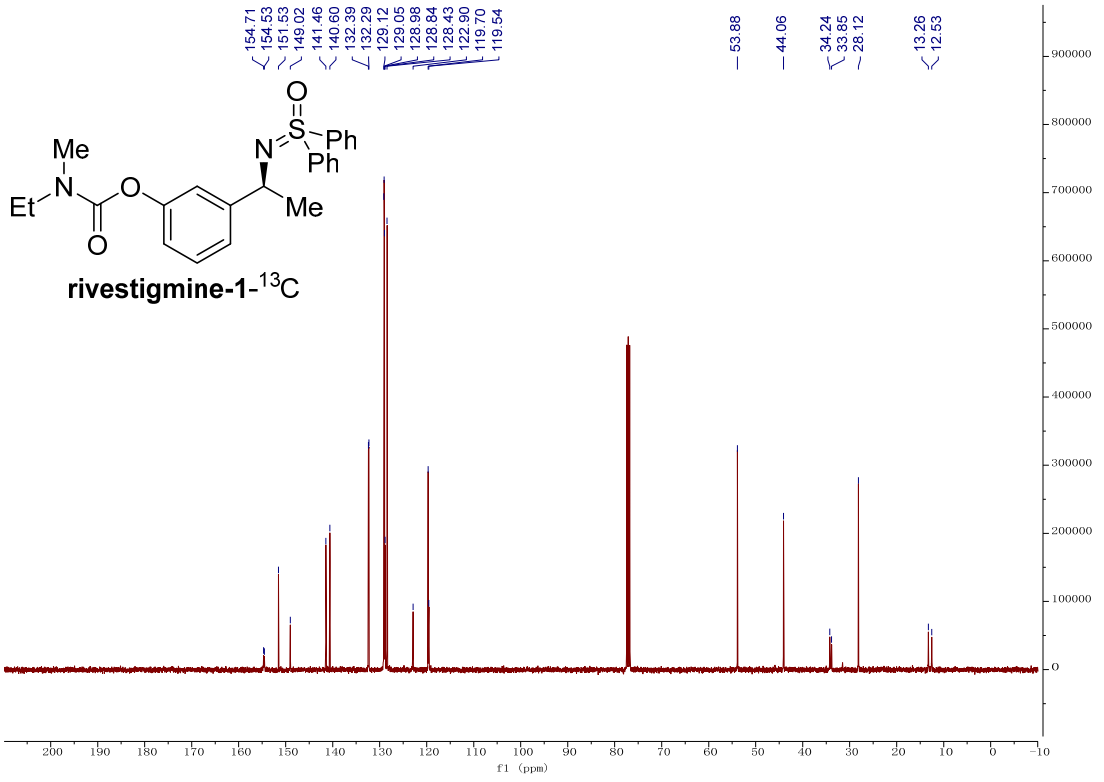

MeO
OMe
N
S
O
Ph
O
dapoxetine-1-1H
f1 (ppm)

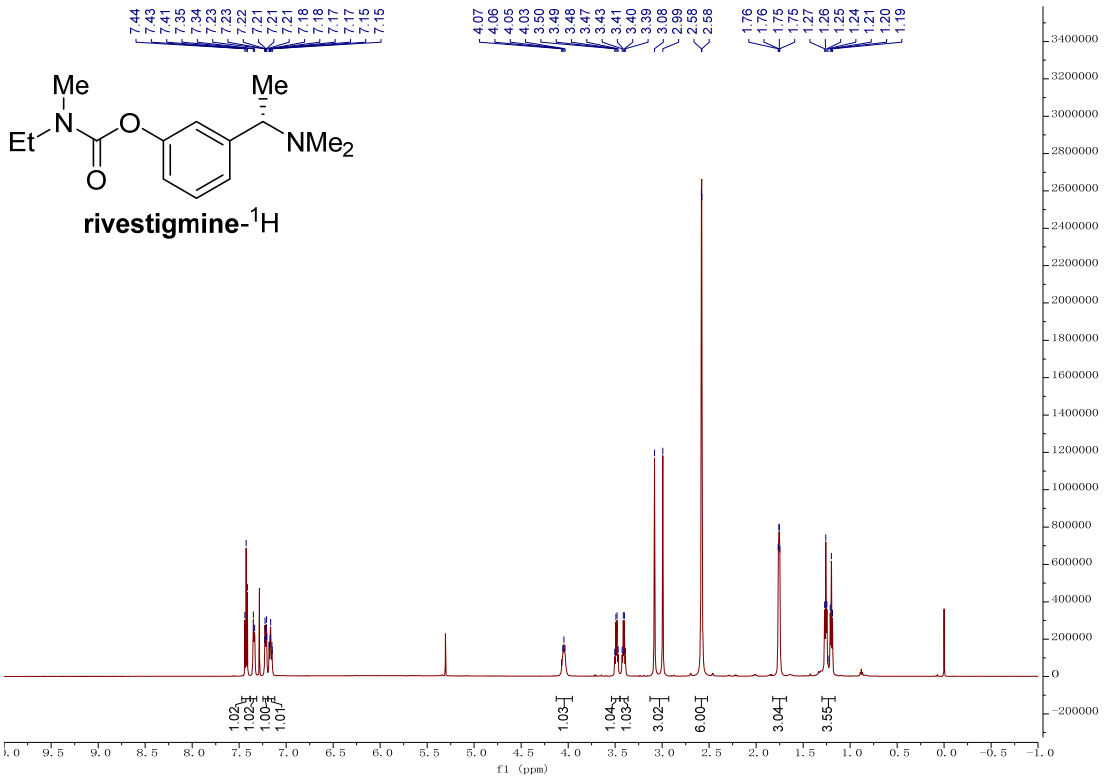

MeO
OMe
N
S
O
Ph
O
dapoxetine-1-13C
f1 (ppm)

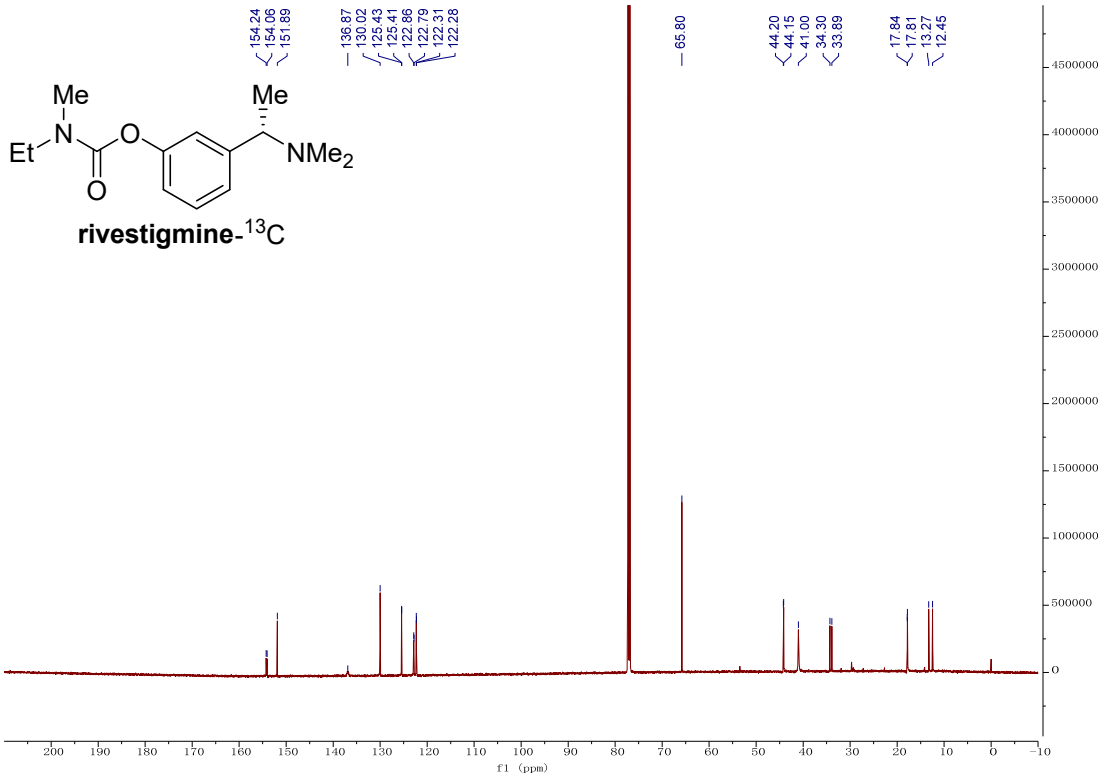

NMe2
Ph
O
dapoxetine-1H
f1 (ppm)

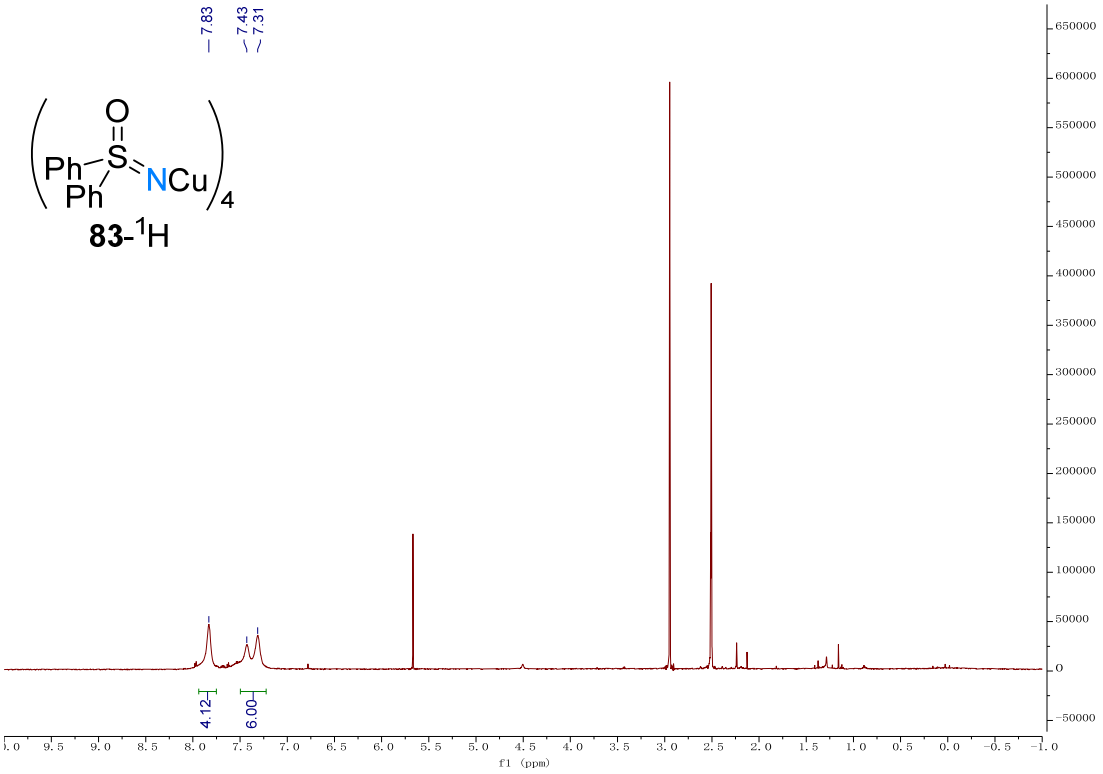

NMe2
Ph
O
dapoxetine-13C
153.66
142.02
134.64
128.72
127.62
126.35
126.10
125.93
125.86
125.23
122.22
120.13
107.01
78.40
56.18
45.69
37.29
f1 (ppm)


rivestigmine-1-1H
f1 (ppm)

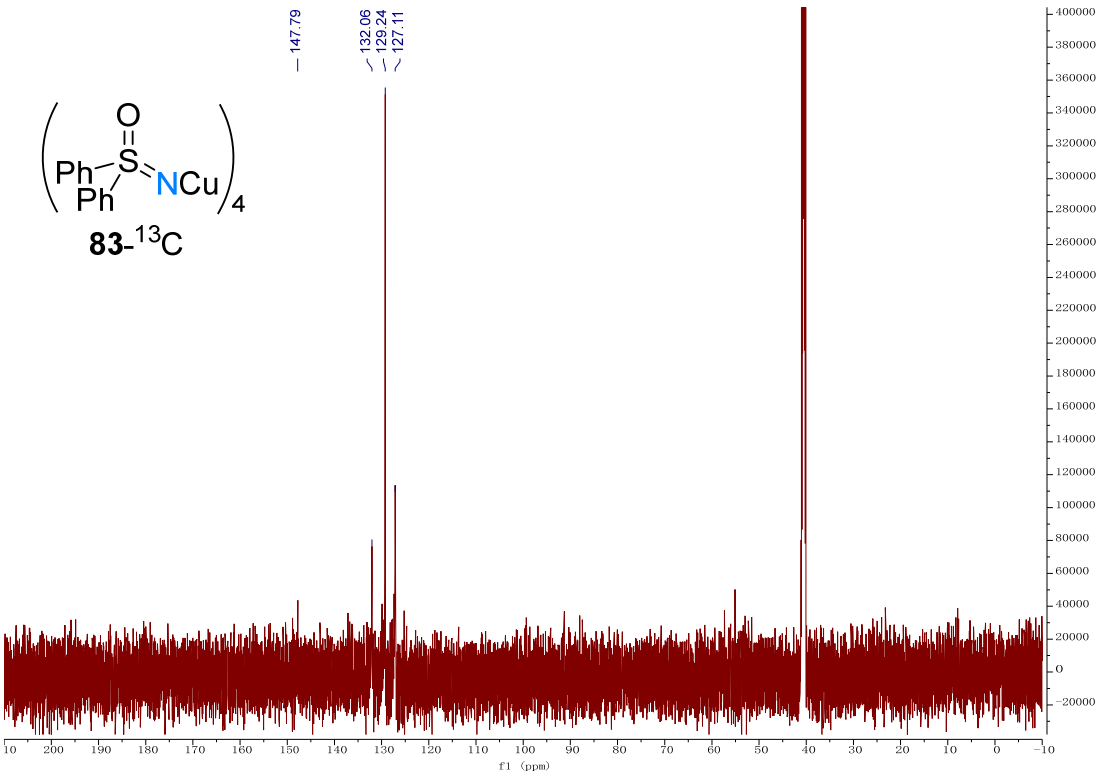

rivestigmine-1-13C
f1 (ppm)


Me
Et
N
O
O
Me
NMe2
rivestigmine-1H
f1 (ppm)

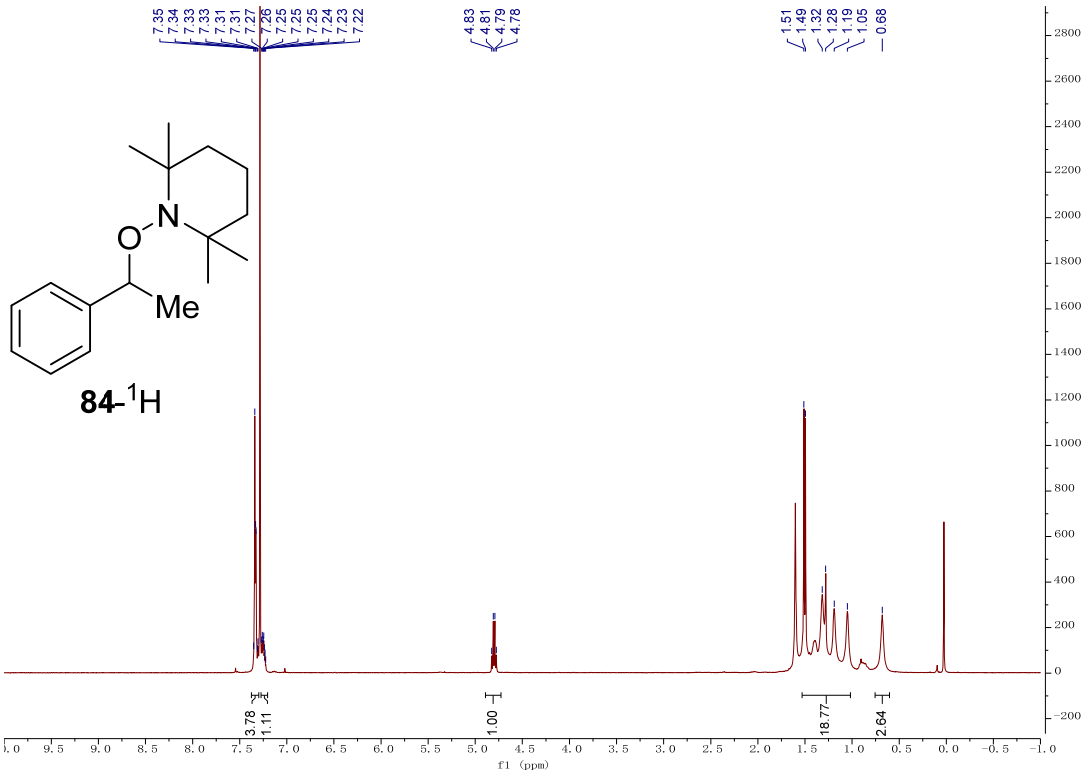

Me
Et
N
O
O
Me
NMe2
rivestigmine-13C
f1 (ppm)

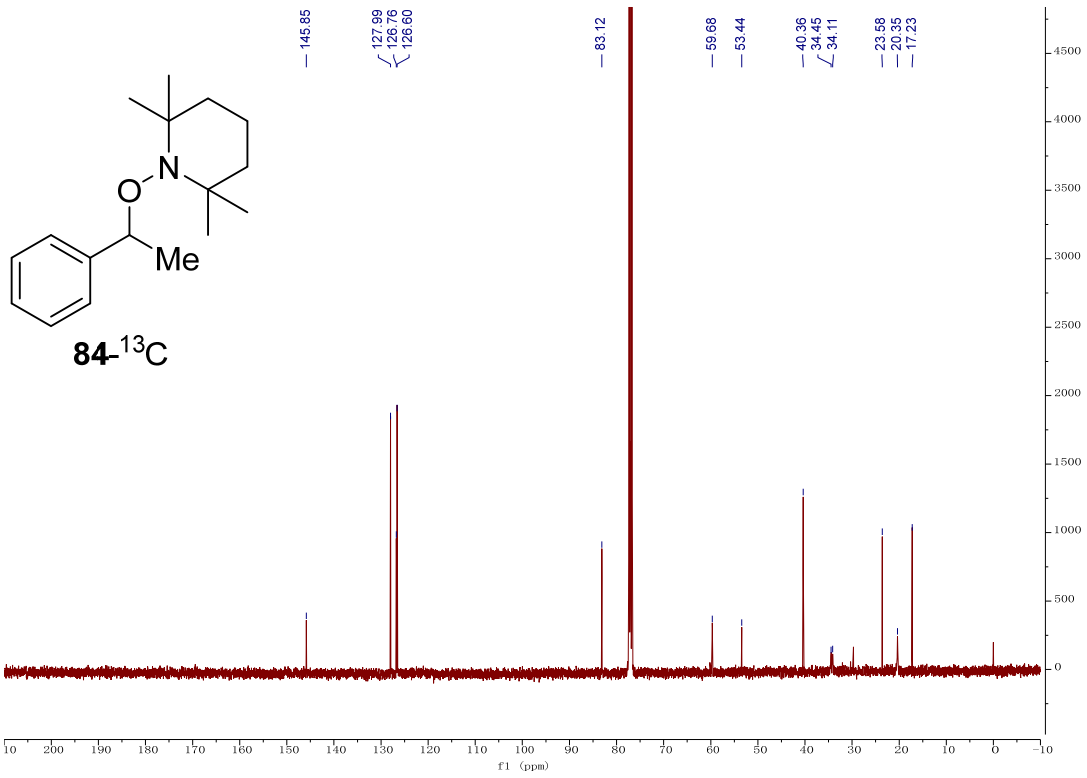


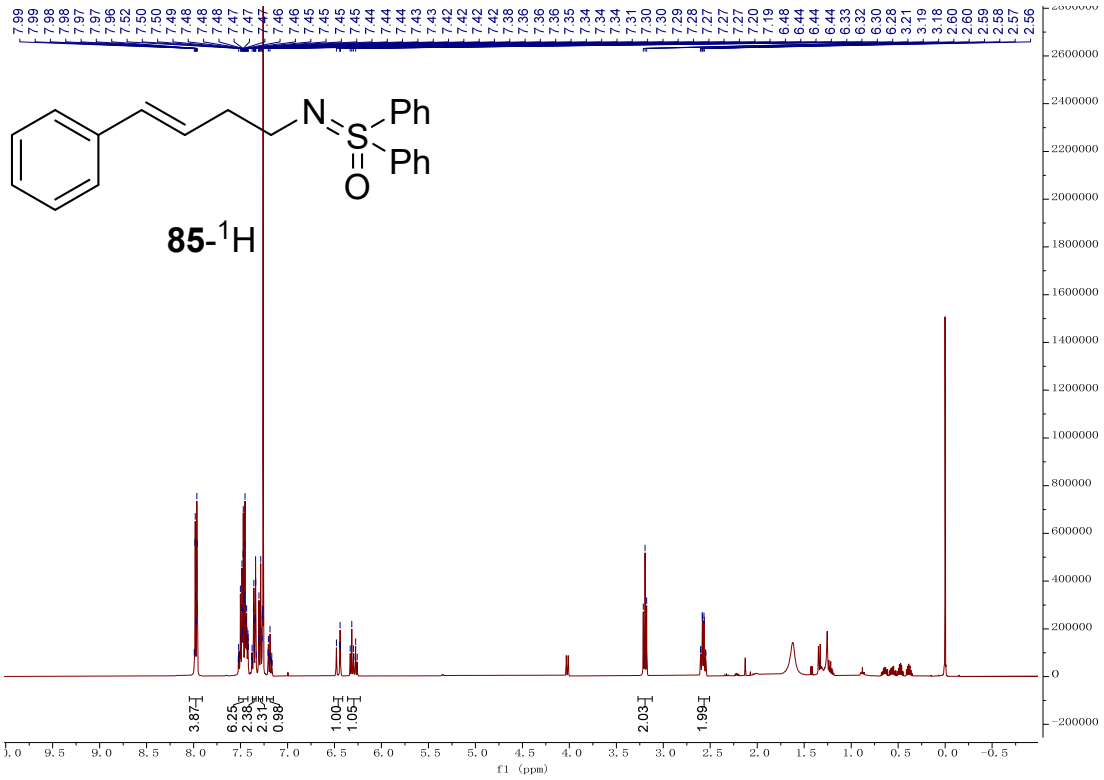
83-^{1}H

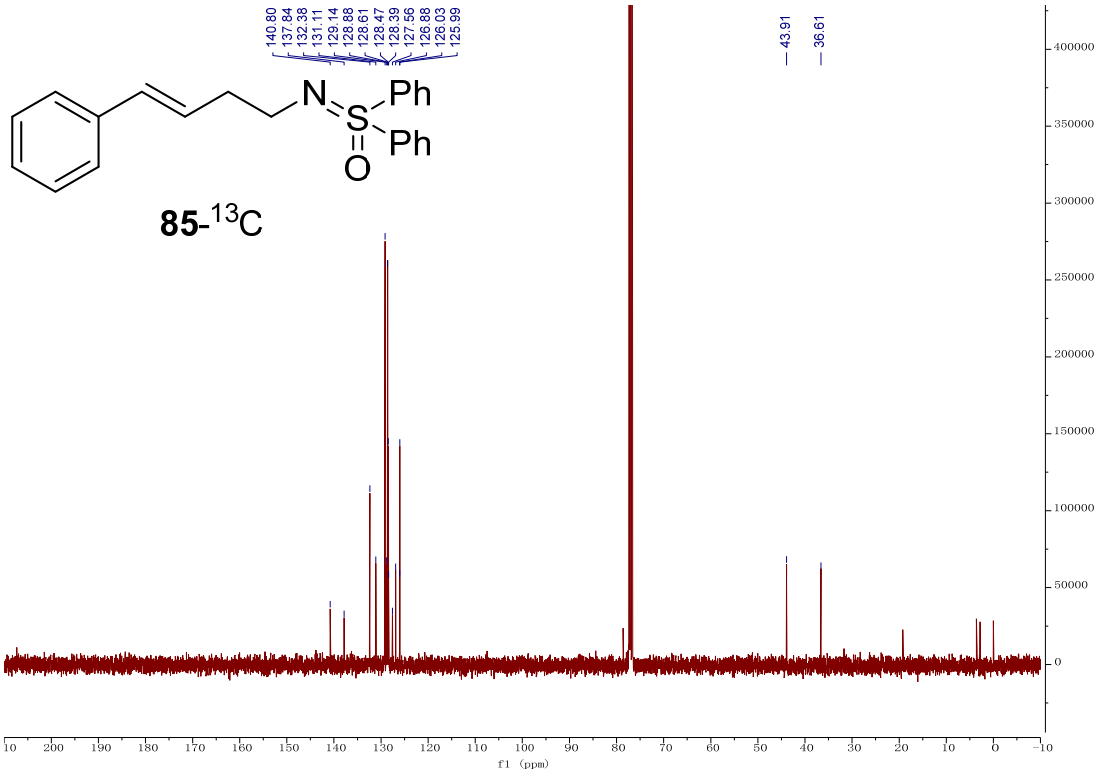


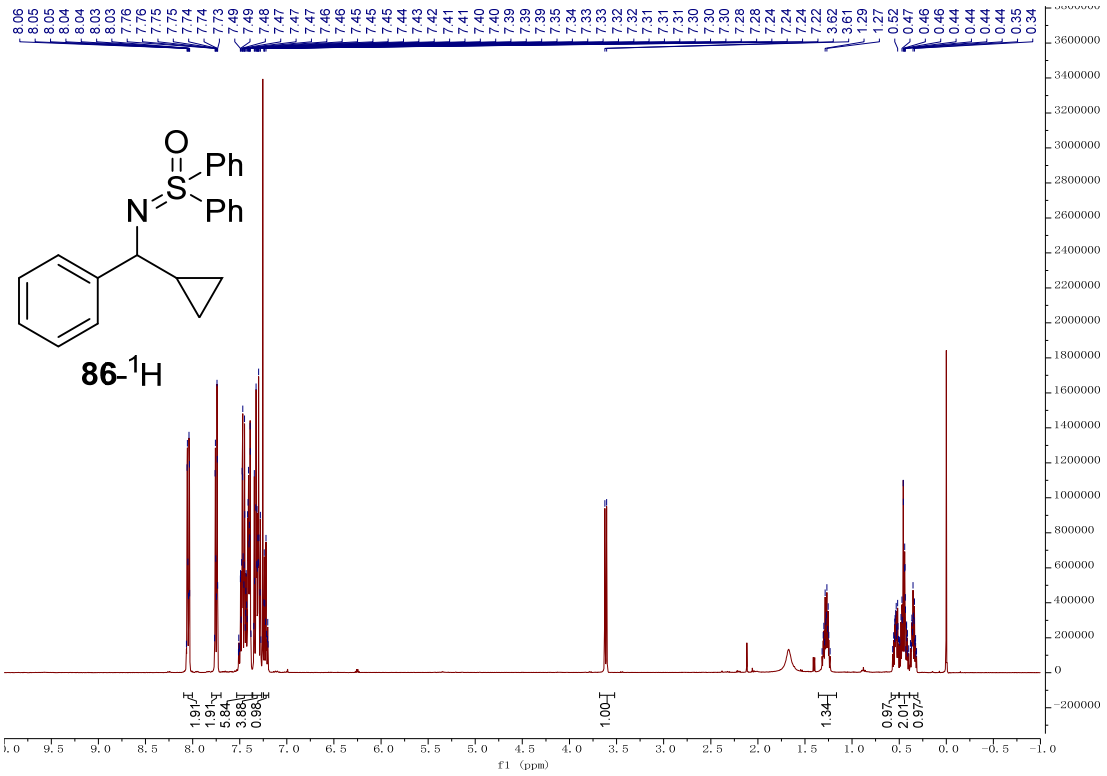
83-^{13}C

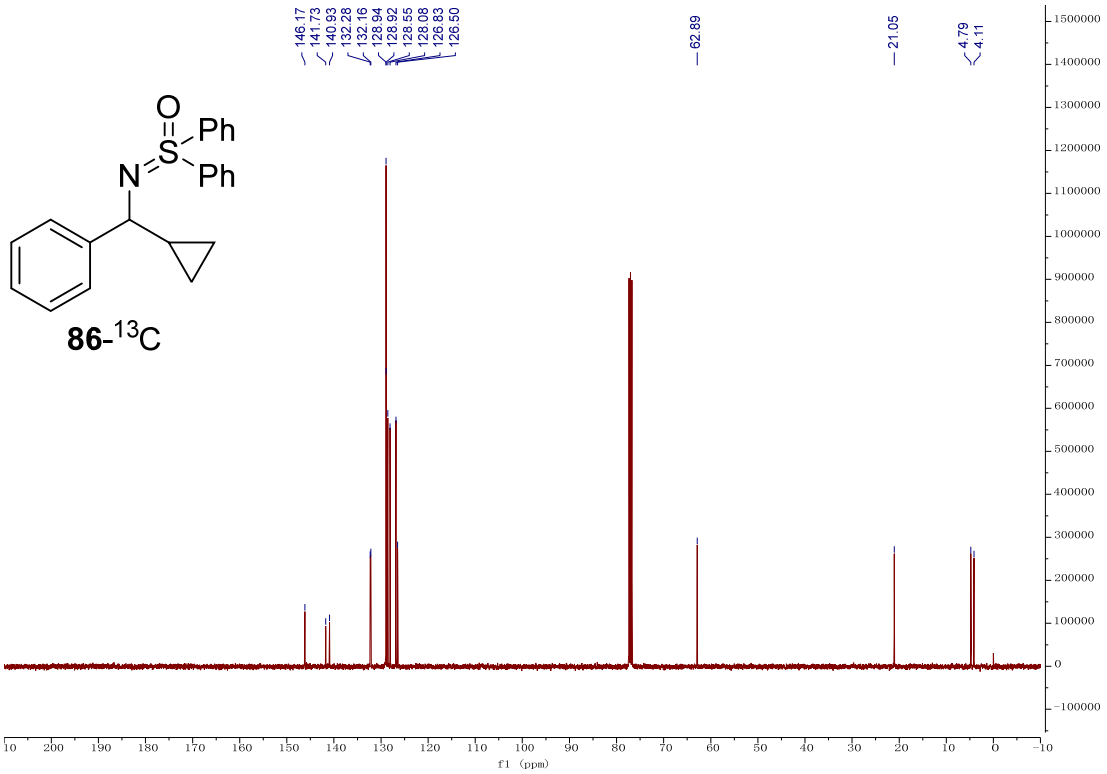

7.35
7.34
7.33
7.33
7.31
7.31
7.27
7.26
7.25
7.25
7.24
7.23
7.22
4.83
4.81
4.79
4.78
1.51
1.49
1.32
1.28
1.19
1.05
0.68
N
O
Me
84-1H
3.78
1.11
1.00
18.77
2.64
f1 (ppm)

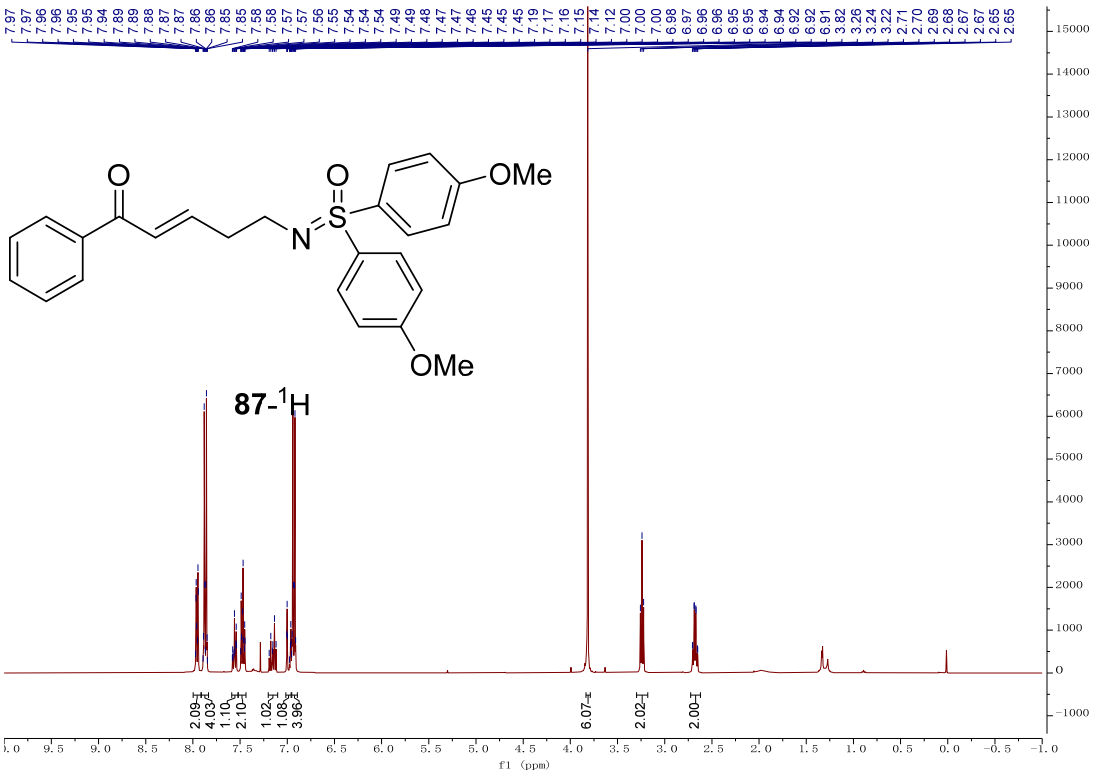

145.85
127.99
126.76
126.60
83.12
59.68
53.44
40.36
34.45
34.11
23.58
20.35
17.23
N
O
Me
84-13C
f1 (ppm)

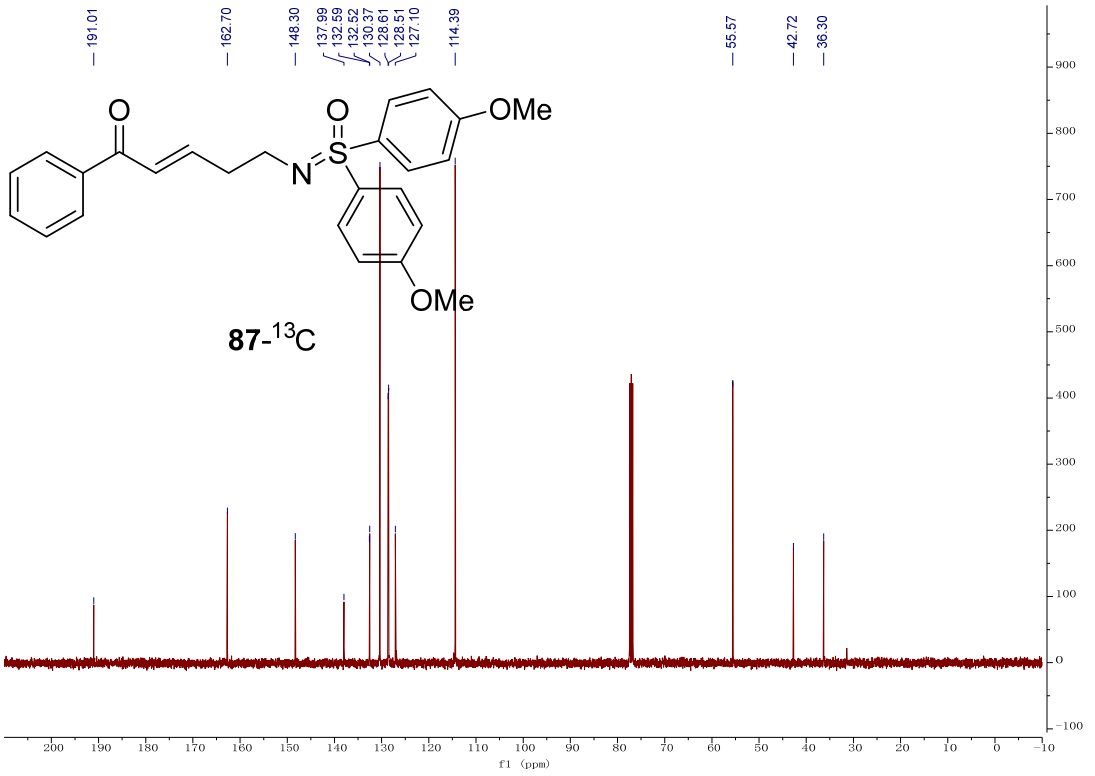

85-1H
N
S
O
Ph
Ph
3.87
6.25
2.38
2.31
0.98
1.00
1.05
2.03
1.99
f1 (ppm)

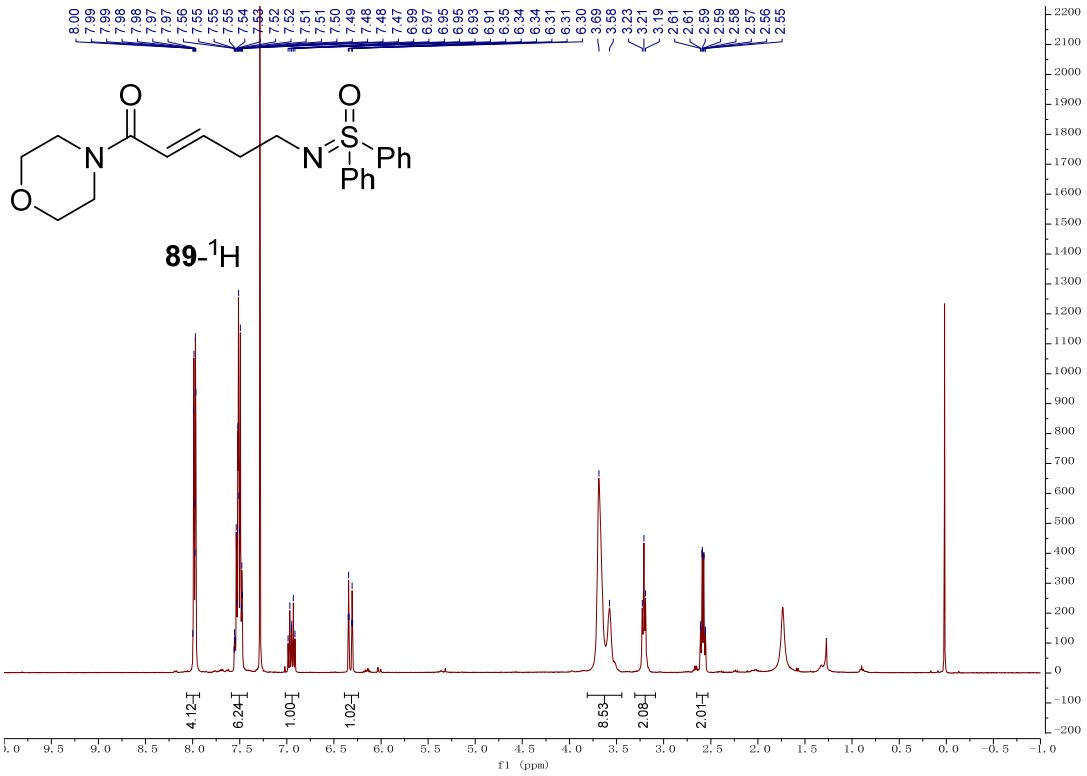

85-13C
N
S
O
Ph
Ph
140.80
137.84
132.38
131.11
129.14
128.88
128.61
128.47
128.39
127.56
126.88
126.03
125.99
43.91
36.61
f1 (ppm)

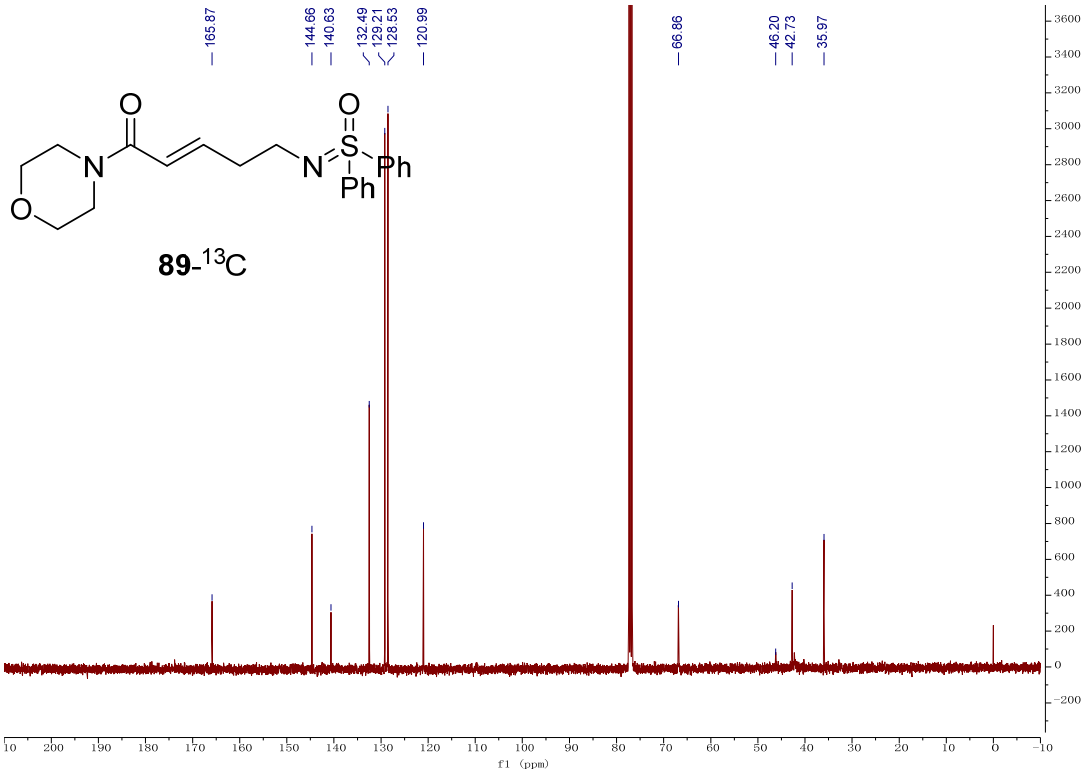

8.06 8.05 8.05 8.04 8.04 8.03 8.03 7.76 7.76 7.75 7.75 7.74 7.74 7.73 7.49 7.49 7.48 7.47 7.47 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.28 7.28 7.24 7.24 7.24 7.22 3.62 3.61 1.29 1.27 0.52 0.47 0.46 0.46 0.44 0.44 0.44 0.44 0.35 0.34
O
Ph
S
N
Ph
86-1H
1.91
1.91
5.84
3.88
0.98
1.00
1.34
0.97
2.01
0.97
f1 (ppm)


146.17
141.73
140.93
132.28
132.16
128.94
128.92
128.55
128.08
126.83
126.50
62.89
21.05
4.79
4.11
O
Ph
S
N
Ph
86-13C
f1 (ppm)

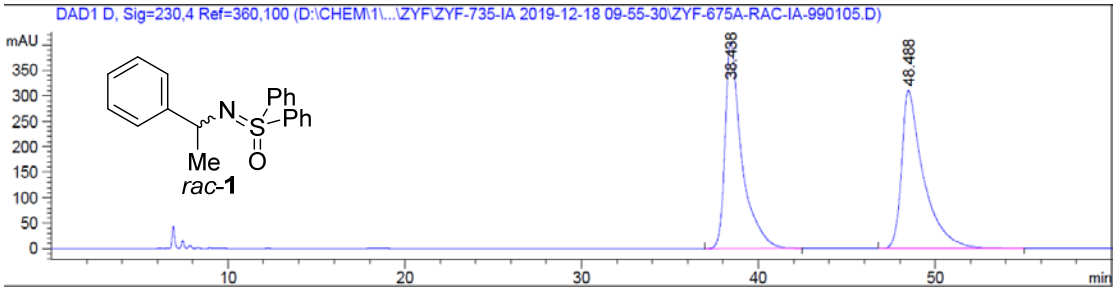

87-1H
f1 (ppm)


87-13C
f1 (ppm)


8.00 7.99 7.99 7.98 7.98 7.97 7.97 7.56 7.55 7.55 7.54 7.53 7.52 7.52 7.51 7.51 7.50 7.49 7.48 7.48 7.47 6.99 6.97 6.95 6.95 6.93 6.91 6.35 6.34 6.34 6.31 6.30 3.69 3.58 3.23 3.21 3.19 2.61 2.61 2.59 2.59 2.58 2.57 2.56 2.55
O
N
O
S
N
Ph
Ph
89-1H
4.12 6.24 1.00 1.02 8.53 2.08 2.01
f1 (ppm)

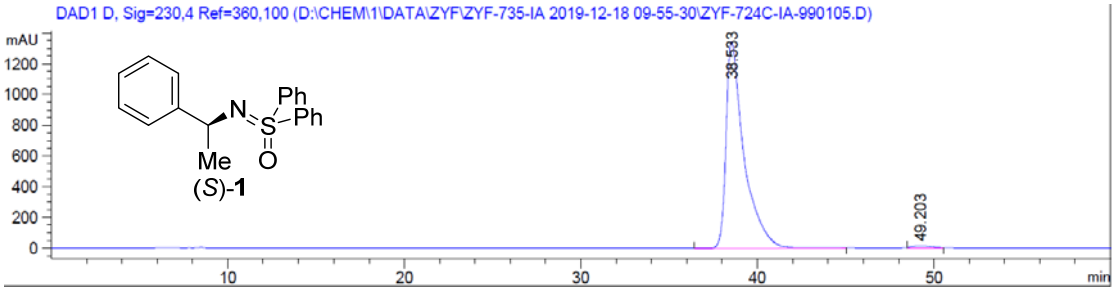

165.87 144.66 140.63 132.49 129.21 128.53 120.99 66.86 46.20 42.73 35.97
O
N
O
S
N
Ph
Ph
89-13C
f1 (ppm)

HPLC spectra



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

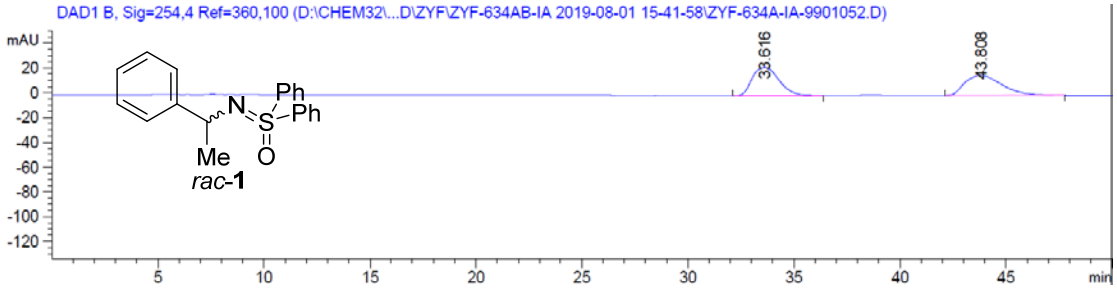
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.438	BB	0.9406	2.64790e4	405.10440	49.9046
2	48.488	BB	1.2155	2.65803e4	309.63678	50.0954
Totals :				5.30594e4	714.74118	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

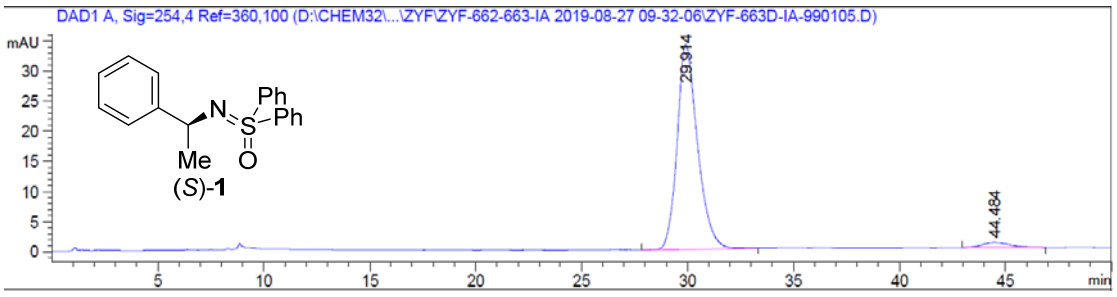
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.533	MM R	1.1878	9.59549e4	1346.36279	98.6305
2	49.203	MM R	1.2988	1332.36206	17.09709	1.3695
Totals :				9.72873e4	1363.45988	

The chloro substrate



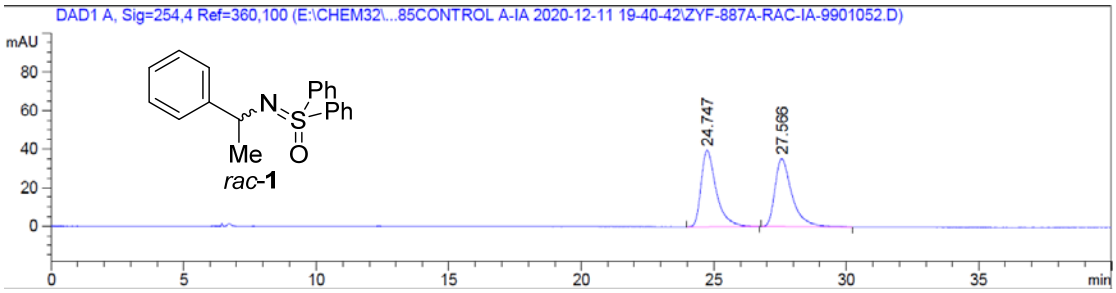
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.616	BB	1.3648	1980.41125	22.59015	50.4214
2	43.808	BB	1.4772	1947.30835	16.16784	49.5786
Totals :				3927.71960	38.75799	



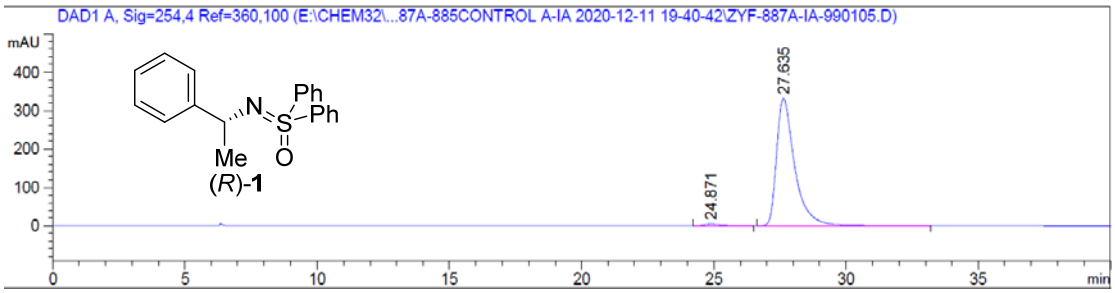
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.914	MM R	1.1173	2280.56177	34.01930	96.4924
2	44.484	MM R	1.5993	82.90019	8.63910e-1	3.5076
Totals :				2363.46196	34.88321	



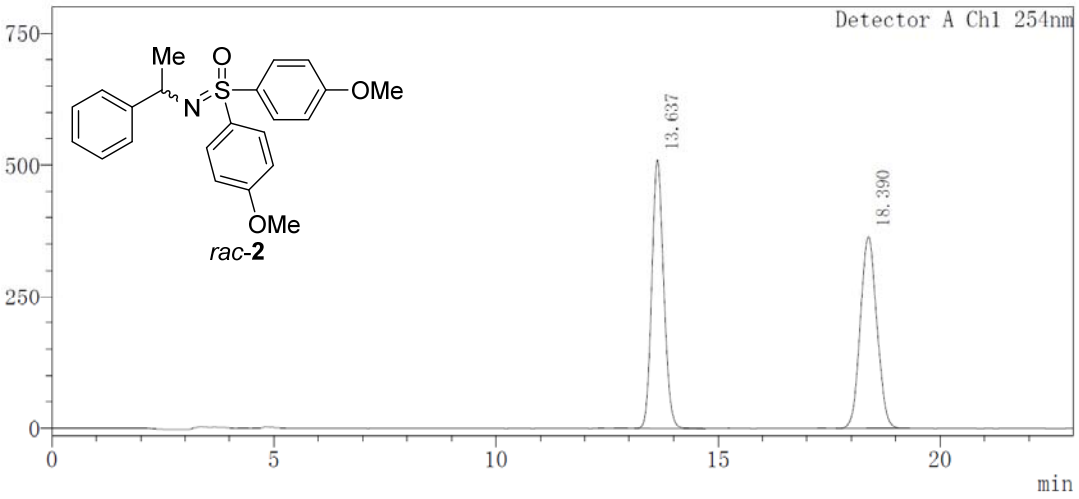
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.747	MM R	0.6640	1574.53088	39.52412	49.9293
2	27.566	MM R	0.7456	1578.99146	35.29557	50.0707
Totals :				3153.52234	74.81970	



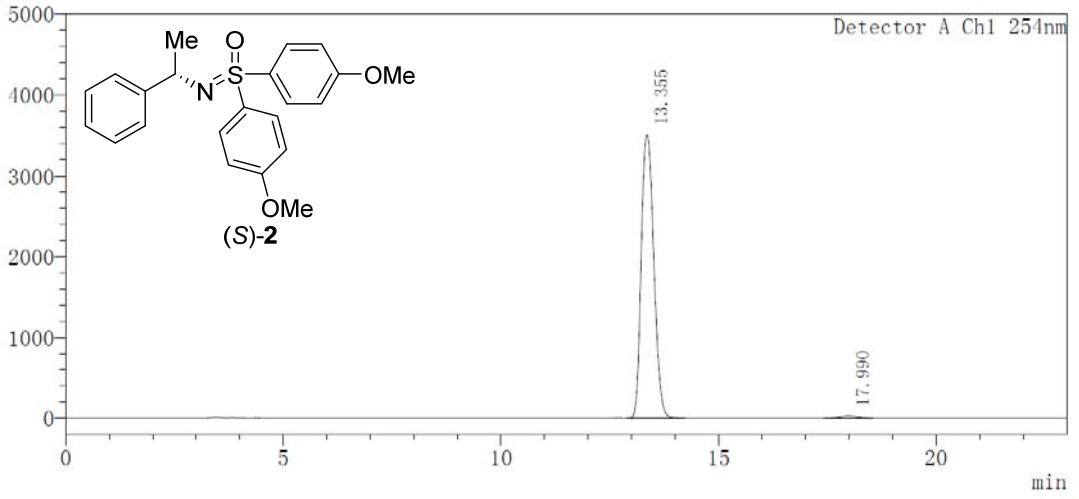
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.871	MM R	0.6997	148.49786	3.53742	0.9373
2	27.635	MM R	0.7920	1.56954e4	330.28882	99.0627
Totals :				1.58439e4	333.82623	



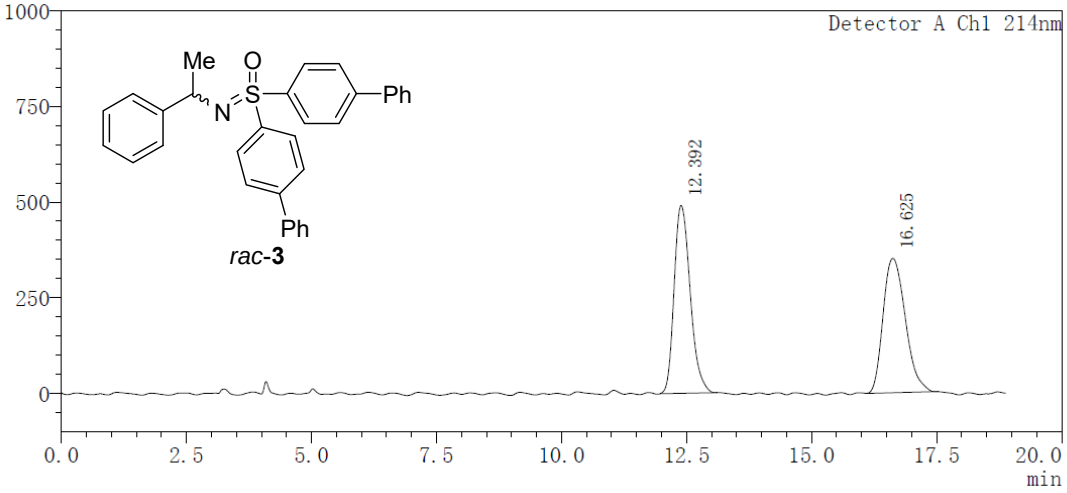
Detector A Ch1 254nm

T	Hight	Area	Area%
13.637	510495	9493266	50.139
18.390	364930	9440755	49.861



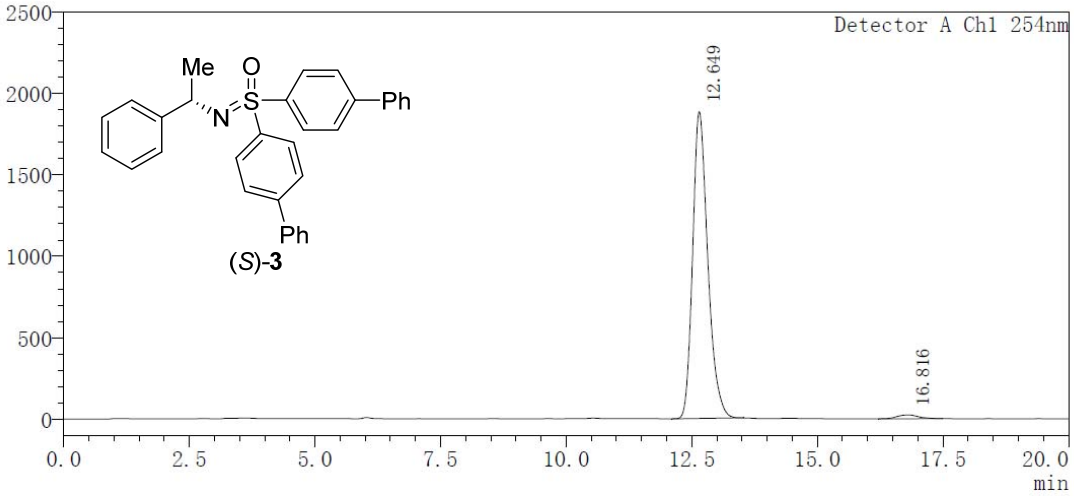
Detector A Ch1 254nm

T	Hight	Area	Area%
13.355	3502104	70381731	98.961
17.990	30743	738945	1.039



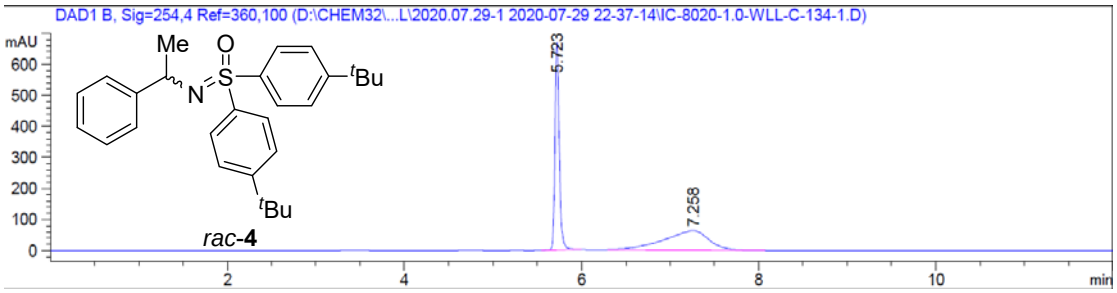
Detector A Ch1 214nm

T	Hight	Area	Area%
12.392	491084	11007992	50.260
16.625	351148	10894037	49.740



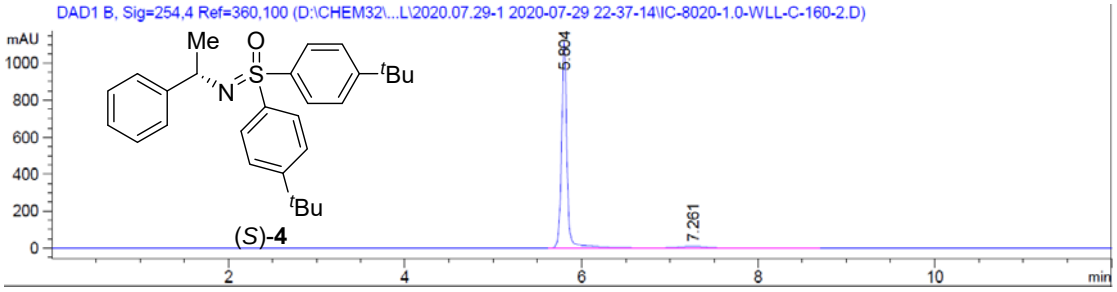
Detector A Ch1 254nm

T	Hight	Area	Area%
12.649	1884452	39552324	98.284
16.816	23385	690431	1.716



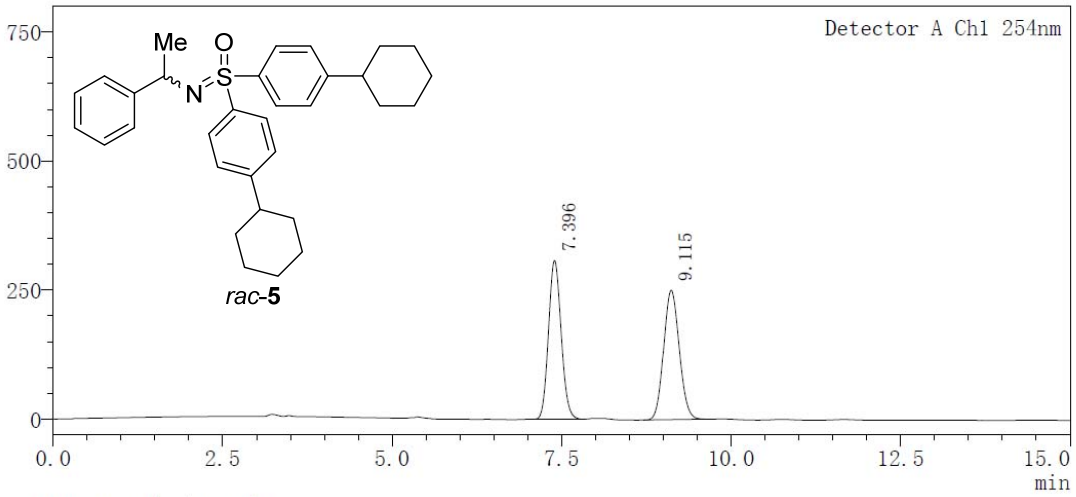
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.723	MM R	0.0556	2255.44287	676.06622	50.1071
2	7.258	MM R	0.6017	2245.80444	62.21108	49.8929
Totals :				4501.24731	738.27731	



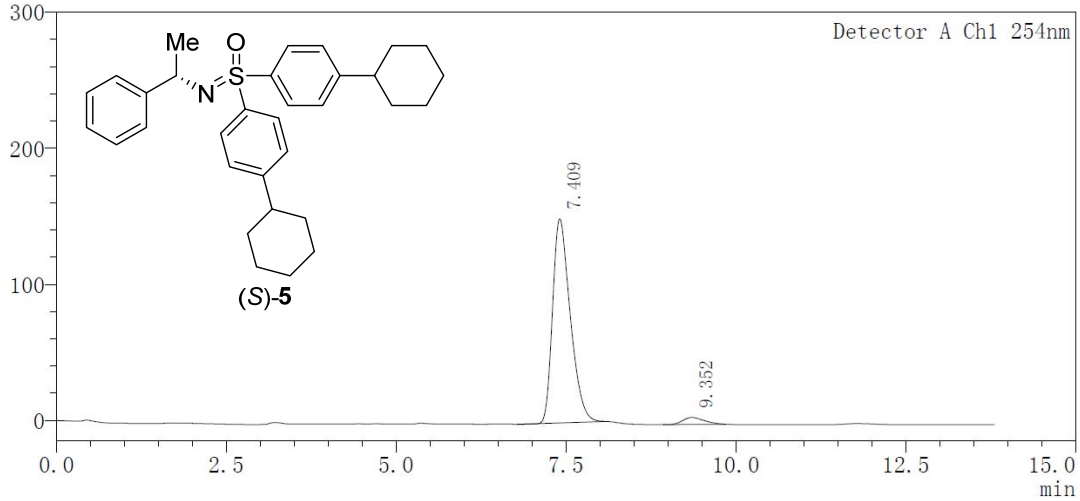
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.804	VV	0.0706	4808.30762	1108.69519	96.2177
2	7.261	VB	0.3402	189.01508	8.22201	3.7823
Totals :				4997.32269	1116.91720	



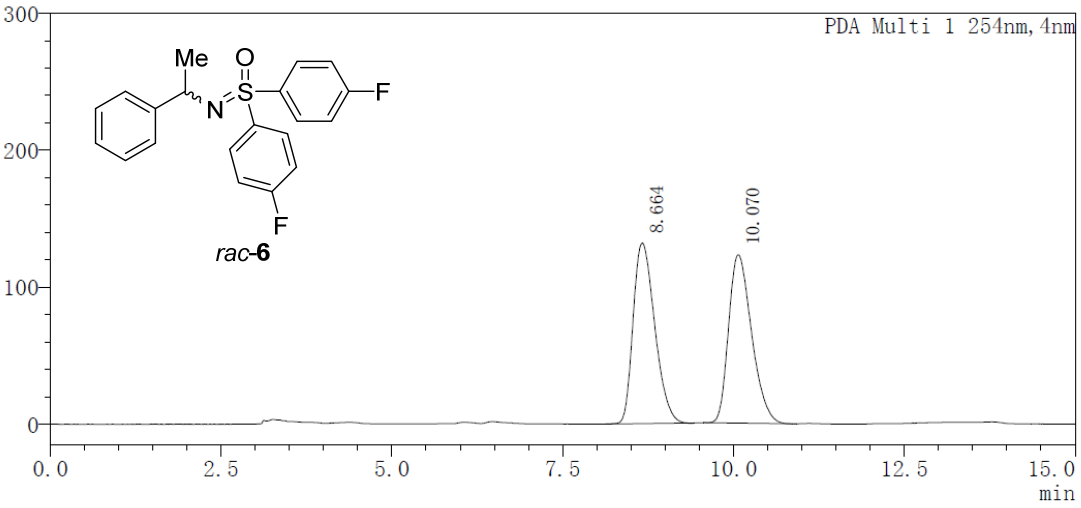
Detector A Ch1 254nm

T	Hight	Area	Area%
7.396	307196	3999559	49.992
9.115	250454	4000794	50.008



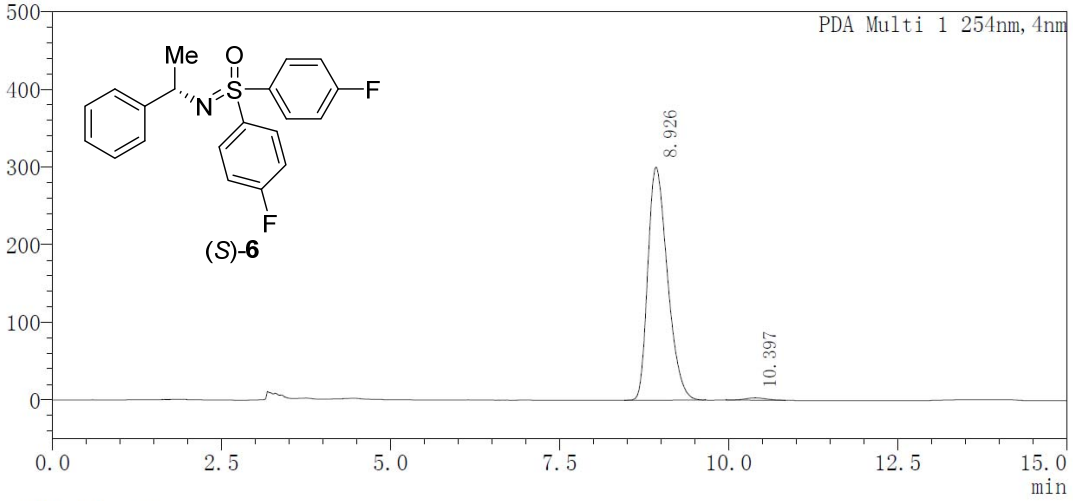
Detector A Ch1 254nm

T	Hight	Area	Area%
7.409	150093	2714811	96.045
9.352	5132	111790	3.955



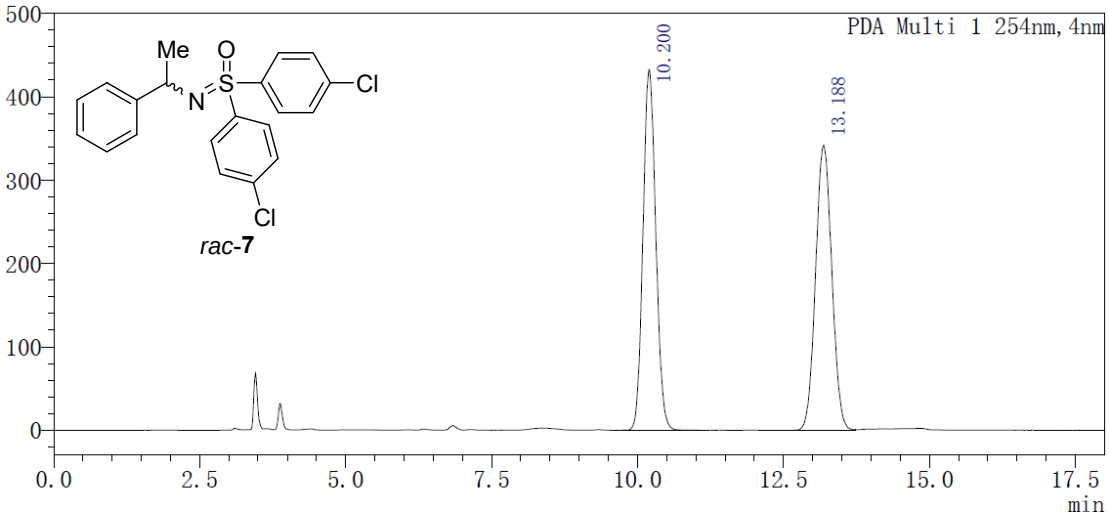
PDA Ch1 254nm

T	Hight	Area	Area%
8.664	132790	2925166	50.164
10.070	123895	2906037	49.836



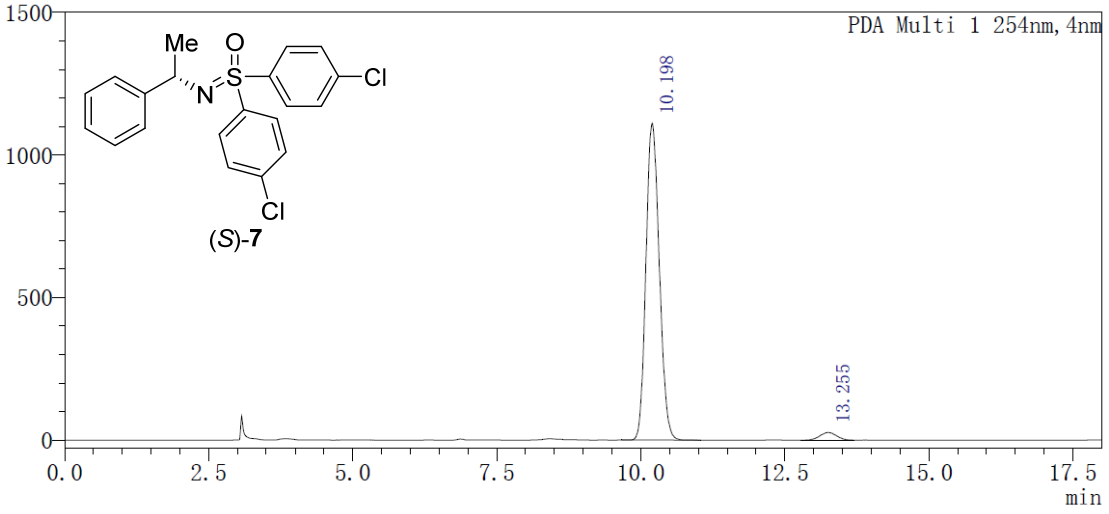
PDA Ch1 254nm

T	Hight	Area	Area%
8.926	302236	6107282	99.003
10.397	2929	61533	0.997



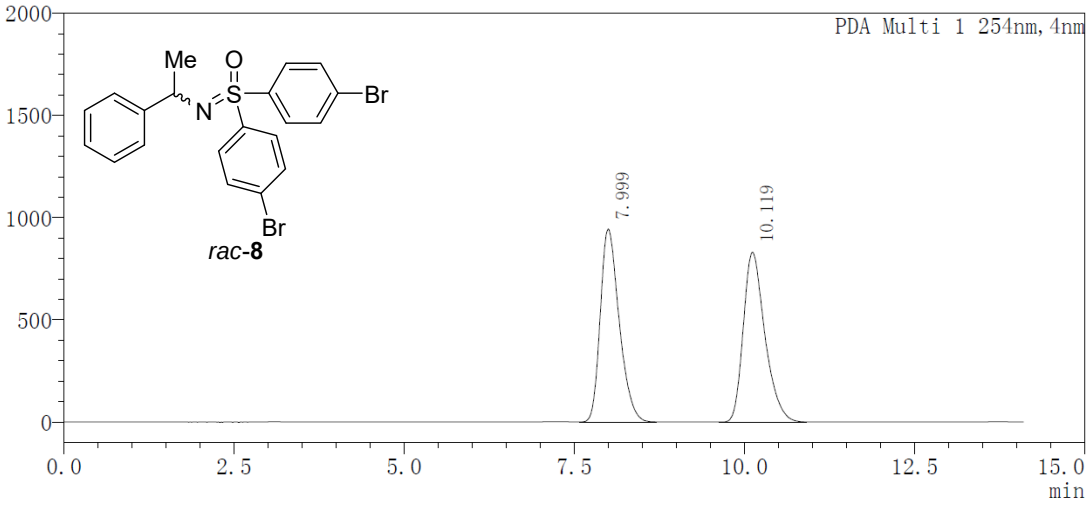
PDA Ch1 254nm

T	Hight	Area	Area%
10.200	432739	6610182	49.955
13.188	341888	6622120	50.045



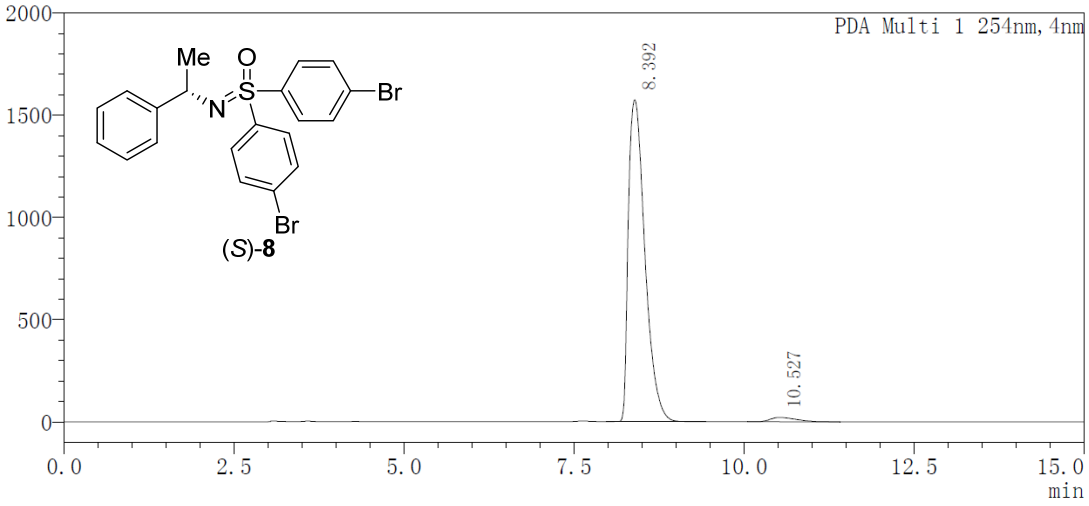
PDA Ch1 254nm

T	Hight	Area	Area%
10.198	1110338	17941633	97.093
13.255	26823	537218	2.907



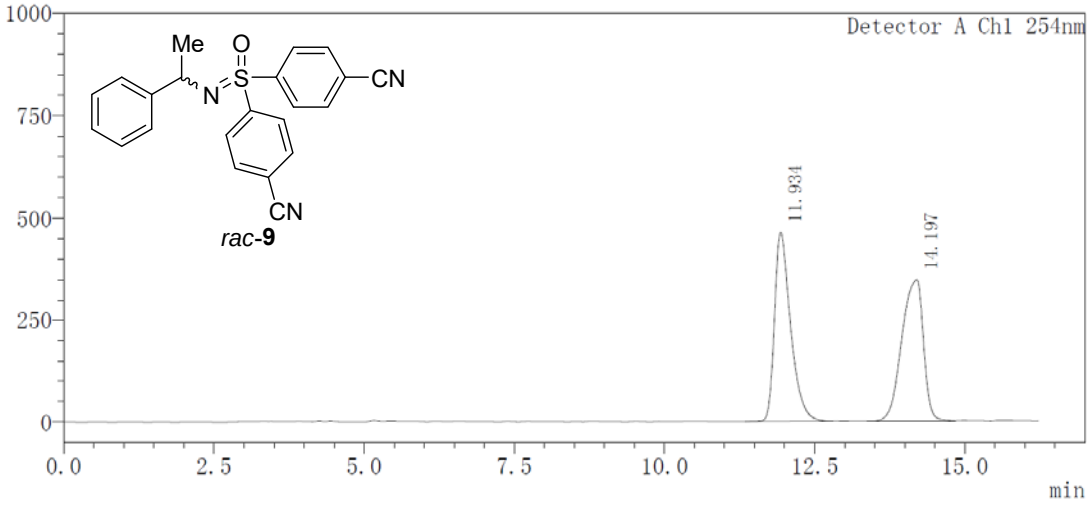
PDA Ch1 254nm

T	Hight	Area	Area%
7.999	946385	18309104	49.863
10.119	833051	18409790	50.137



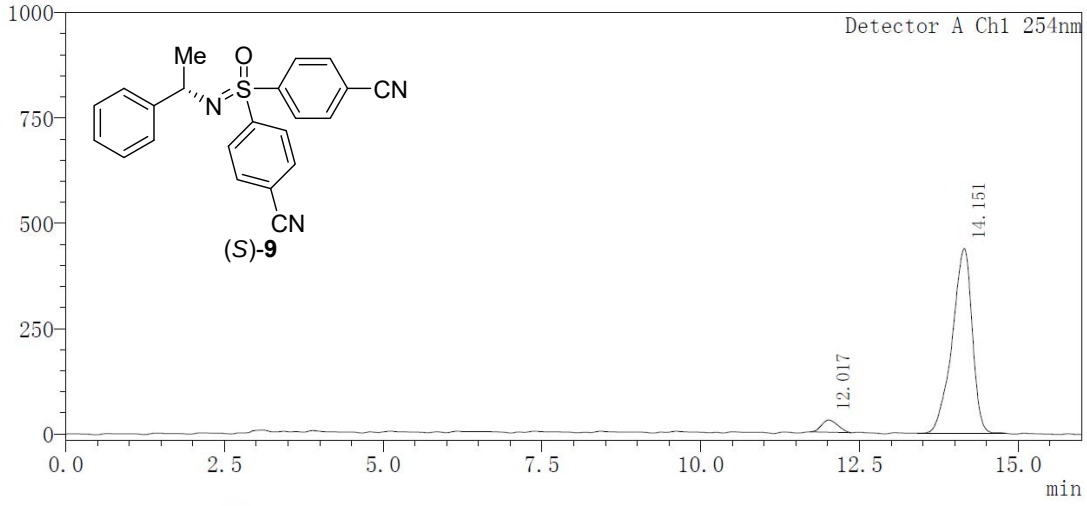
PDA Ch1 254nm

T	Hight	Area	Area%
8.392	1576839	26740303	97.907
10.527	22032	571566	2.093



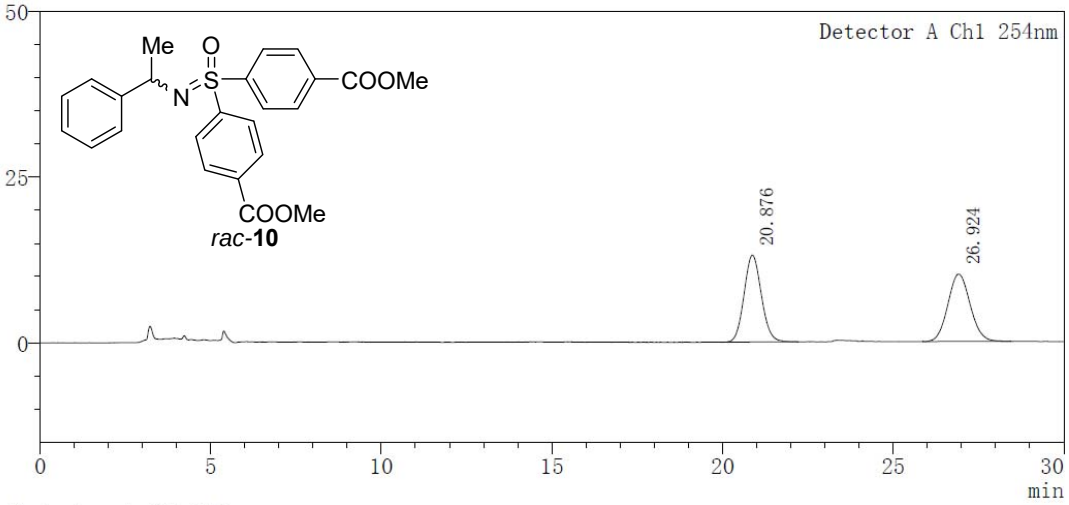
Detector A Ch1 254nm

T	Hight	Area	Area%
11.934	465189	8655013	49.972
14.197	348051	8664557	50.028



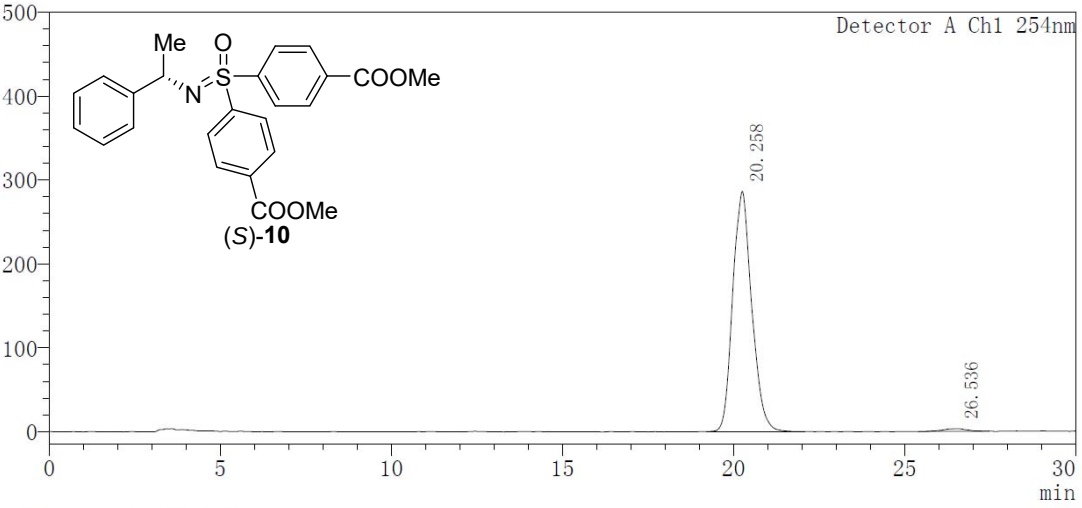
Detector A Ch1 254nm

T	Hight	Area	Area%
12.017	28689	508968	5.019
14.151	438602	9632378	94.981



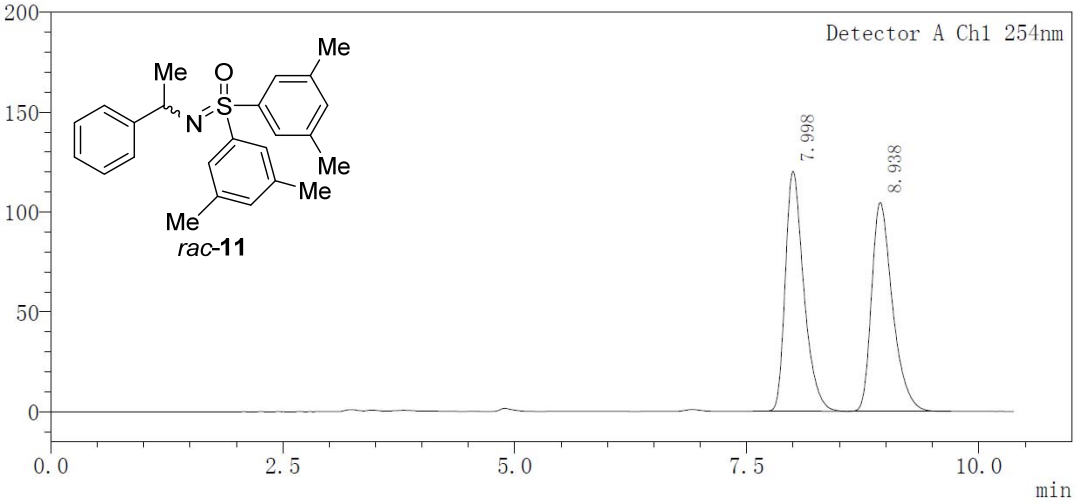
Detector A Ch1 254nm

T	Hight	Area	Area%
20.876	13098	462973	50.106
26.924	10166	461007	49.894



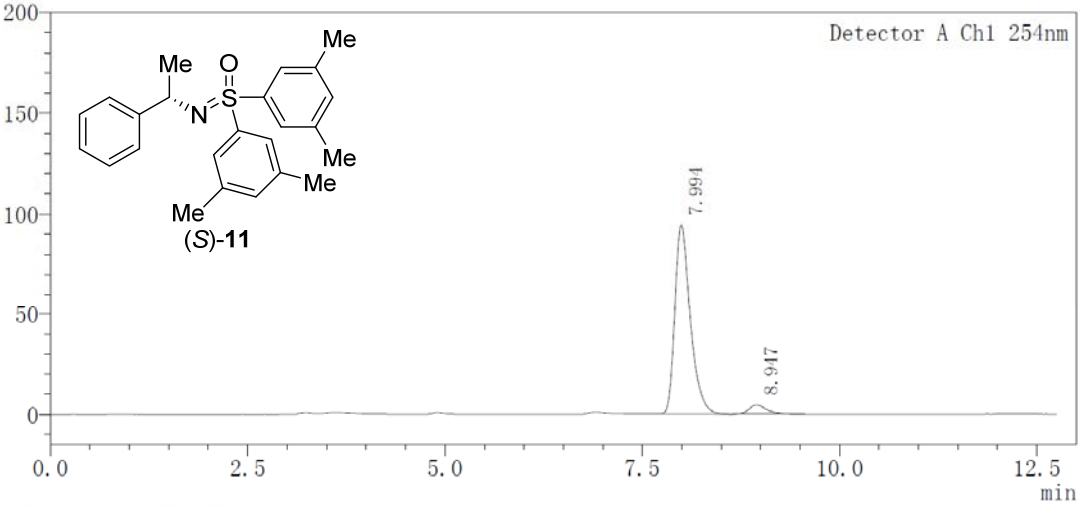
Detector A Ch1 254nm

T	Hight	Area	Area%
20.258	286267	11077365	98.612
26.536	3323	155893	1.388



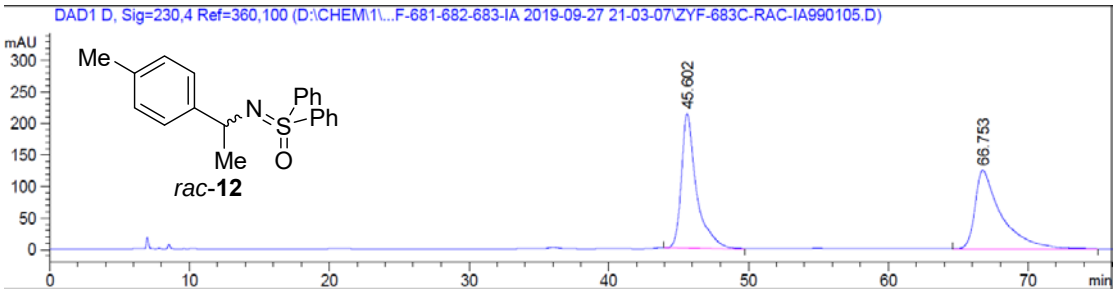
Detector A Ch1 254nm

T	Hight	Area	Area%
7.998	120094	1664901	50.301
8.938	104492	1644990	49.699



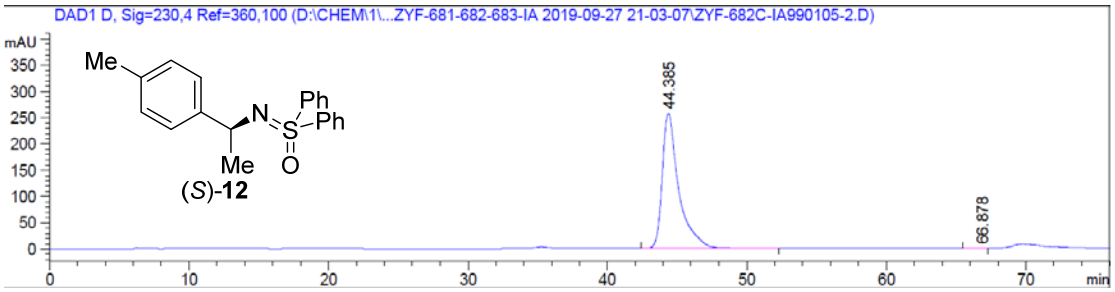
Detector A Ch1 254nm

T	Hight	Area	Area%
7.994	94380	1286878	94.760
8.947	4654	71164	5.240



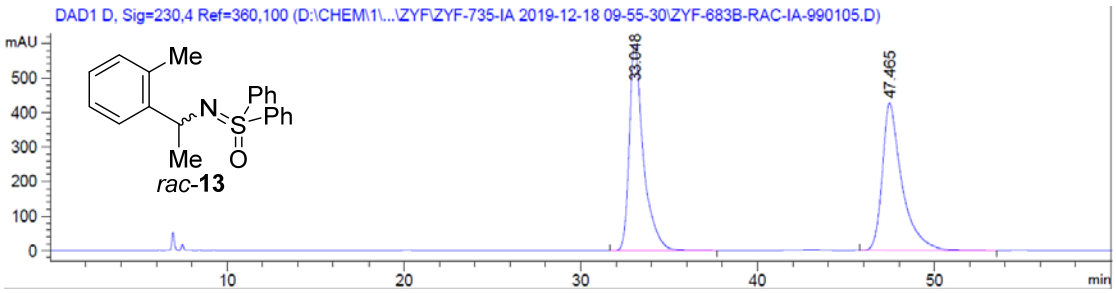
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.602	MM R	1.2519	1.60955e4	214.28592	49.9729
2	66.753	BB	1.8005	1.61129e4	124.78596	50.0271
Totals :				3.22084e4	339.07188	



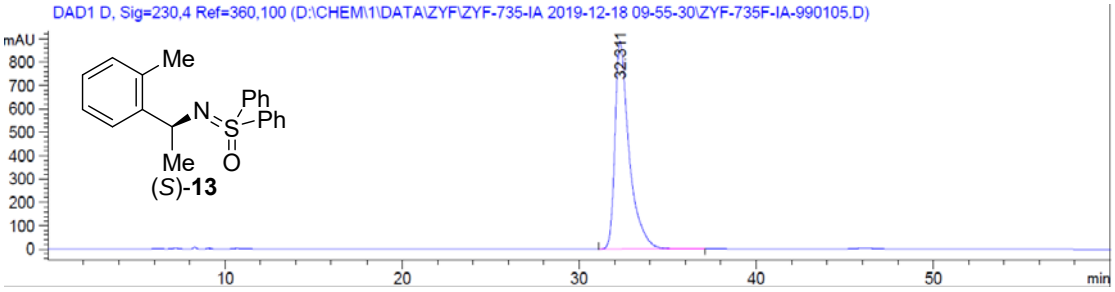
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.385	BB	1.1909	2.12108e4	257.52716	99.9702
2	66.878	MM R	1.8231	6.32561	5.78282e-2	0.0298
Totals :				2.12171e4	257.58499	



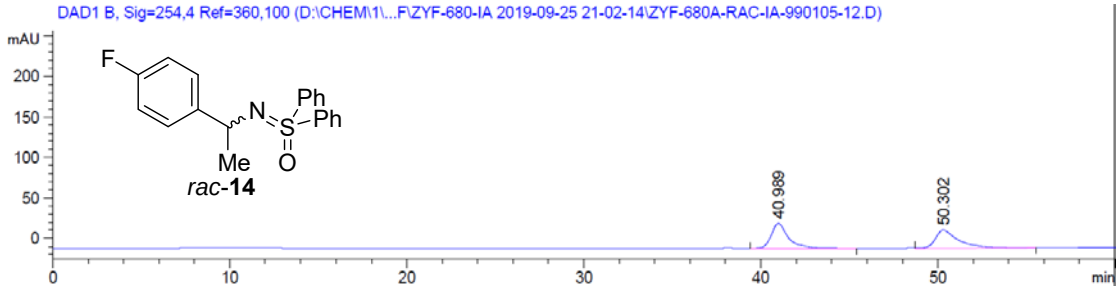
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.048	BB	0.8069	3.31078e4	598.92108	50.0171
2	47.465	BB	1.1145	3.30852e4	426.74246	49.9829
Totals :				6.61931e4	1025.66354	



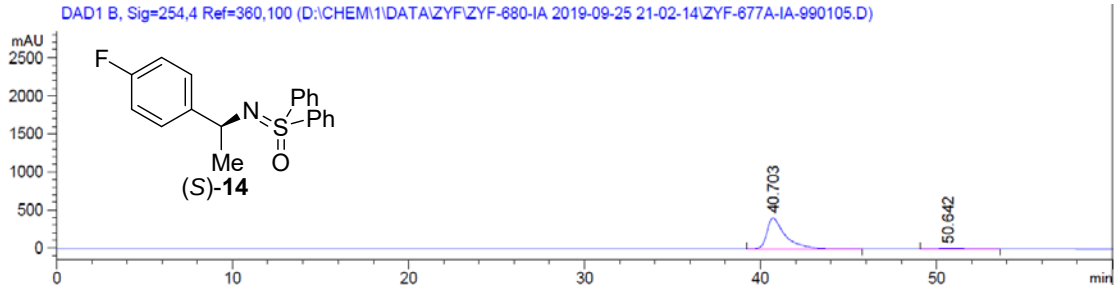
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.311	BB	0.8144	4.94108e4	889.06995	100.0000
Totals :				4.94108e4	889.06995	



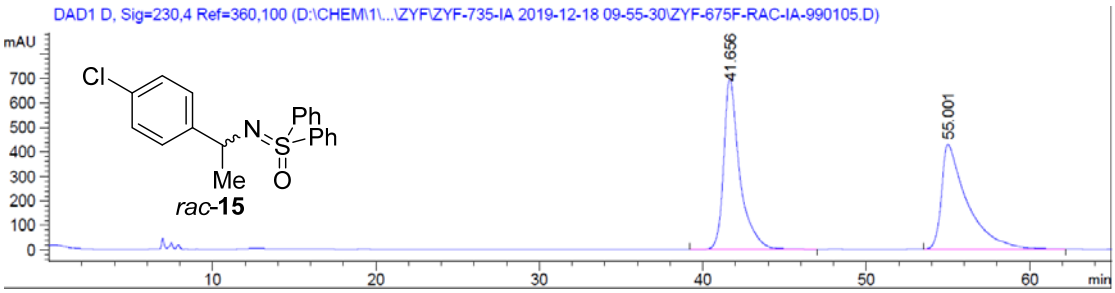
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.989	BB	0.9750	2047.65356	30.82331	49.8954
2	50.302	MM R	1.5217	2056.23633	22.52057	50.1046
Totals :				4103.88989	53.34387	



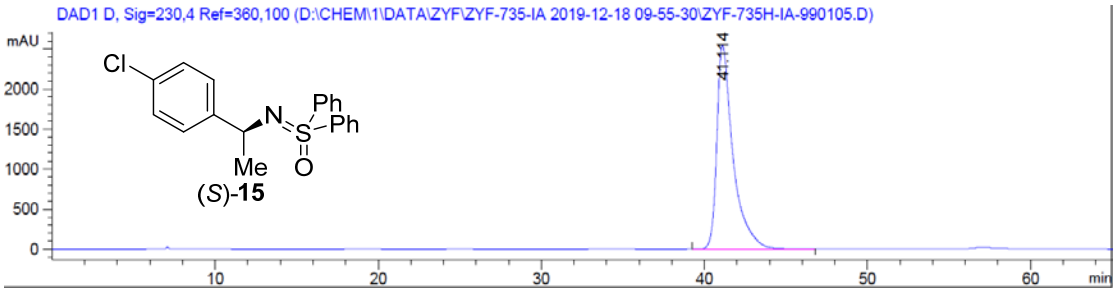
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.703	BB	1.0338	2.90297e4	404.24634	97.8410
2	50.642	BB	1.2200	640.57184	7.17219	2.1590
Totals :				2.96703e4	411.41853	



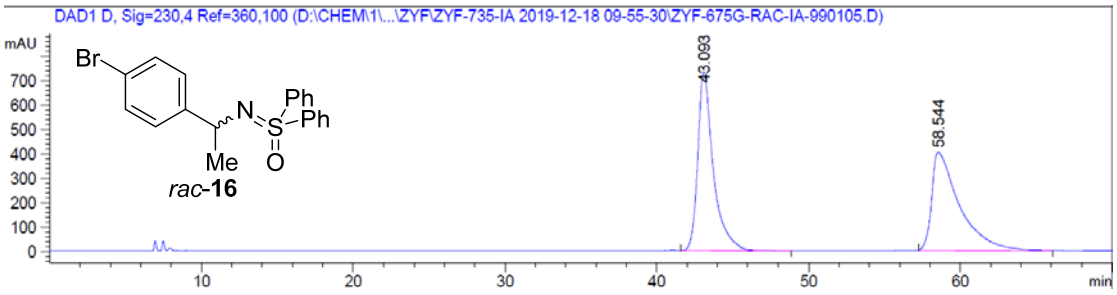
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.656	BB	0.9840	4.73538e4	699.32672	50.4262
2	55.001	BB	1.4967	4.65534e4	428.10934	49.5738
Totals :				9.39072e4	1127.43607	



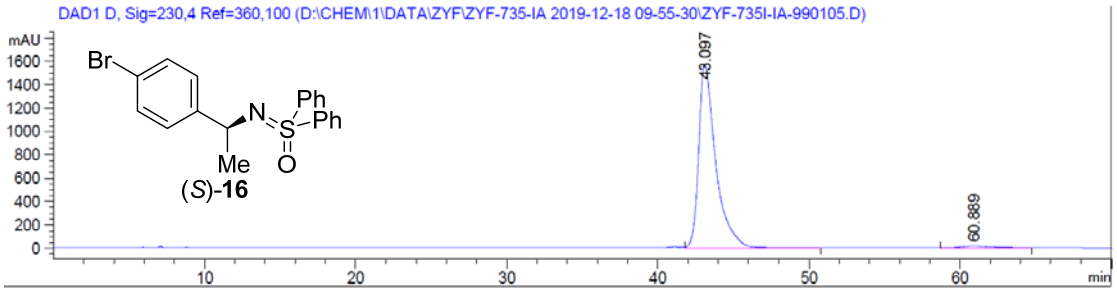
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.114	BB	1.0079	1.75803e5	2545.18359	100.0000
Totals :				1.75803e5	2545.18359	



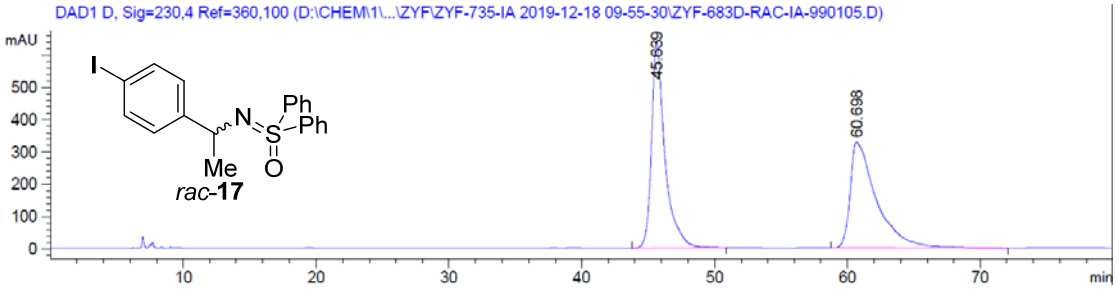
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.093	BB	1.0348	5.21301e4	732.02399	50.2237
2	58.544	MM R	2.1345	5.16658e4	403.41370	49.7763
Totals :				1.03796e5	1135.43768	



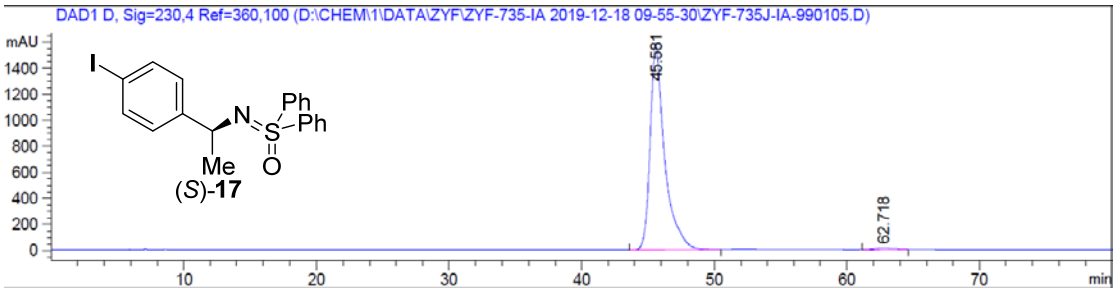
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.097	MM R	1.3261	1.25414e5	1576.22388	98.3707
2	60.889	BB	1.5686	2077.17212	16.36729	1.6293
Totals :				1.27491e5	1592.59117	



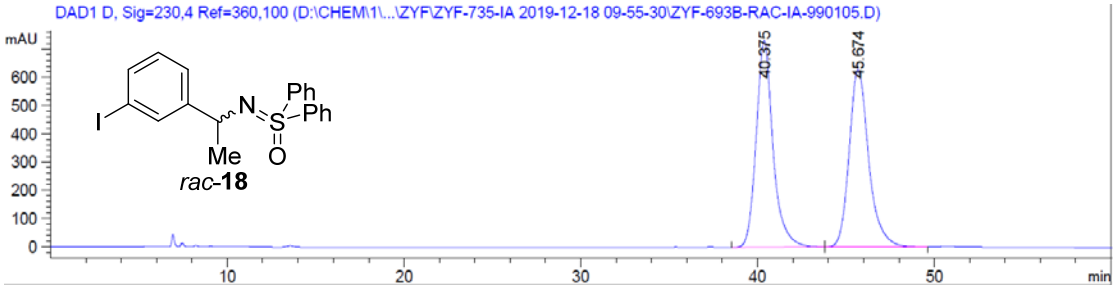
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.639	BB	1.0081	4.47529e4	639.79907	49.9349
2	60.698	BB	1.7749	4.48695e4	328.21915	50.0651
Totals :				8.96224e4	968.01822	



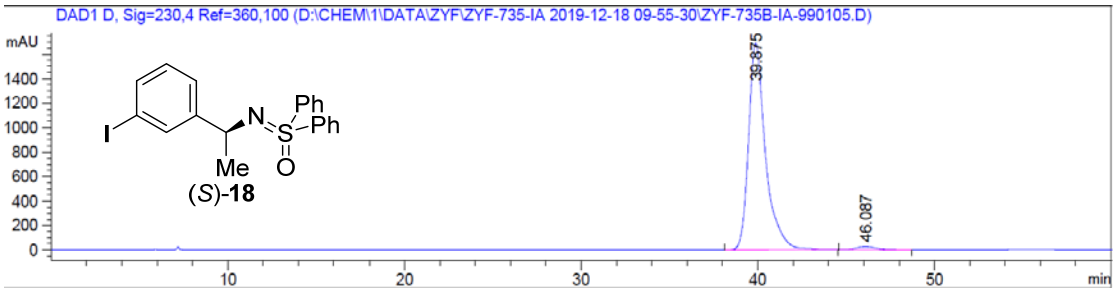
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.581	BB	1.1007	1.20058e5	1586.75171	98.7816
2	62.718	MM R	1.9474	1480.82922	12.67355	1.2184
Totals :				1.21539e5	1599.42526	



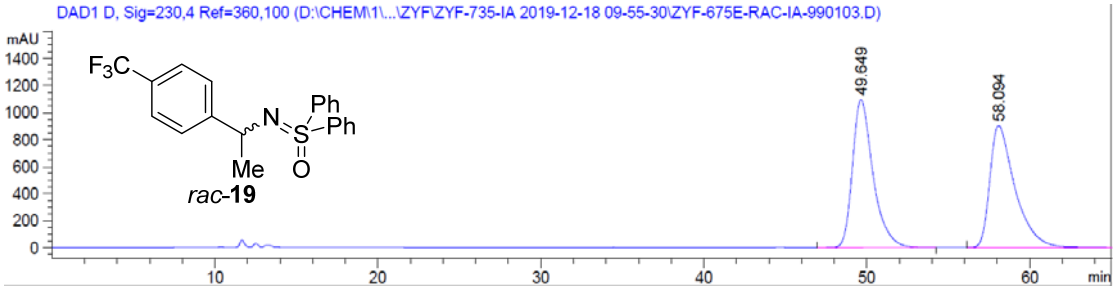
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.375	BB	0.9944	4.86179e4	732.44867	50.2278
2	45.674	BB	1.1659	4.81770e4	627.34558	49.7722
Totals :				9.67948e4	1359.79425	



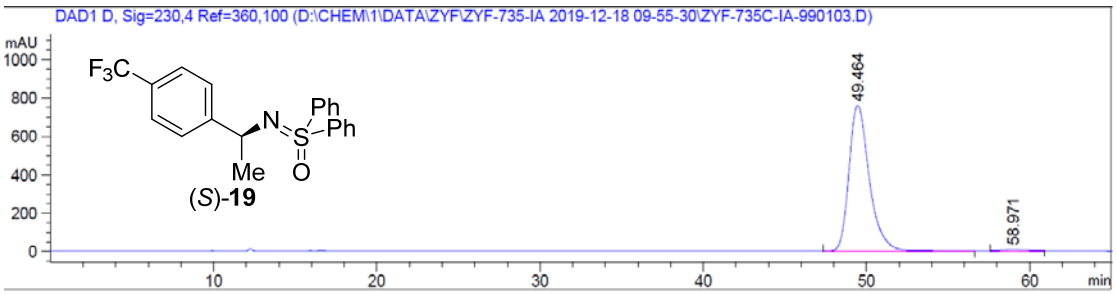
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.875	BB	0.9887	1.12532e5	1685.98218	98.3010
2	46.087	BB	1.1229	1945.00818	25.35567	1.6990
Totals :				1.14477e5	1711.33785	



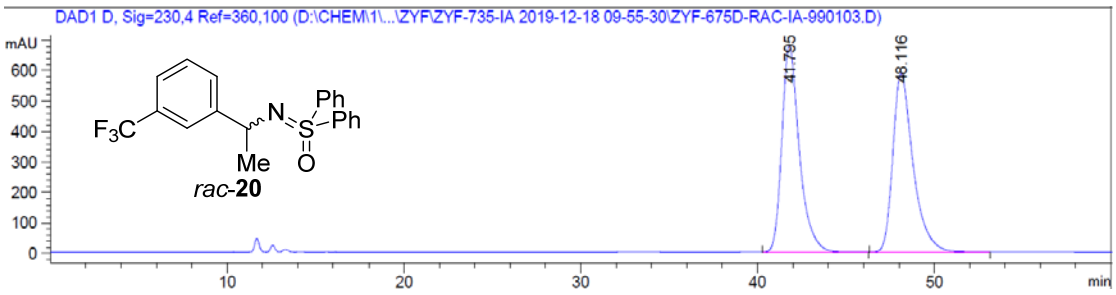
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.649	BB	1.3174	9.58099e4	1092.21545	49.8488
2	58.094	BB	1.5854	9.63913e4	900.07635	50.1512
Totals :				1.92201e5	1992.29181	



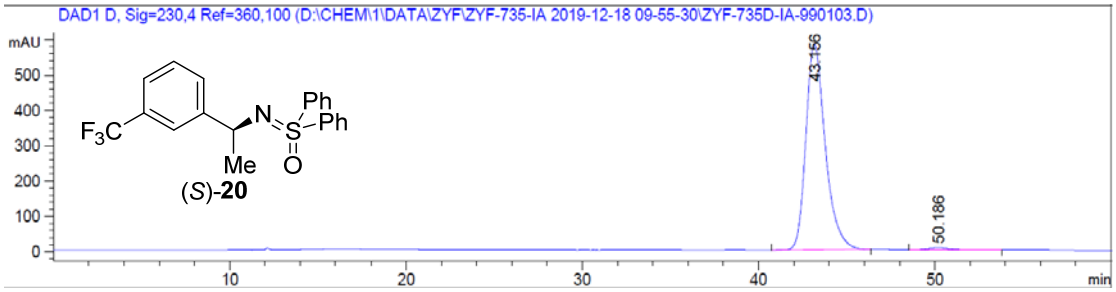
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.464	BB	1.3153	6.54396e4	757.93567	98.8920
2	58.971	MM R	1.8881	733.16608	6.47184	1.1080
Totals :				6.61728e4	764.40751	



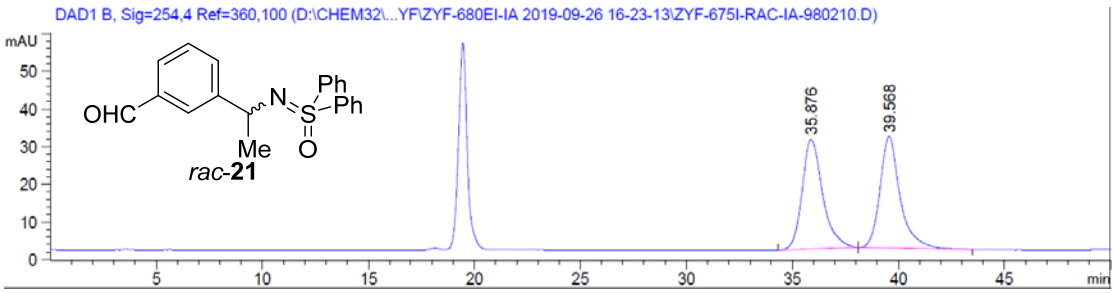
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.795	BB	1.0321	4.64648e4	677.55920	49.9437
2	48.116	BB	1.1927	4.65696e4	585.01495	50.0563
Totals :				9.30345e4	1262.57416	



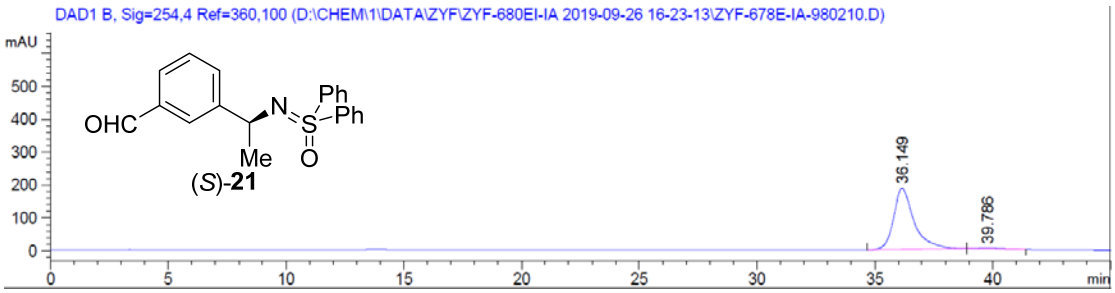
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.156	BB	1.1629	4.45228e4	583.03094	98.8820
2	50.186	BB	1.1637	503.37344	5.60514	1.1180
Totals :				4.50262e4	588.63609	



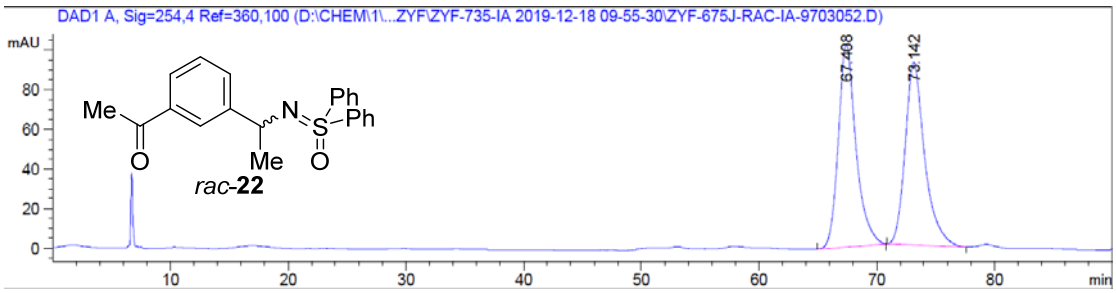
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.876	BB	1.0115	1953.82703	29.02003	50.0781
2	39.568	BB	0.9743	1947.72913	29.57620	49.9219
Totals :				3901.55615	58.59623	



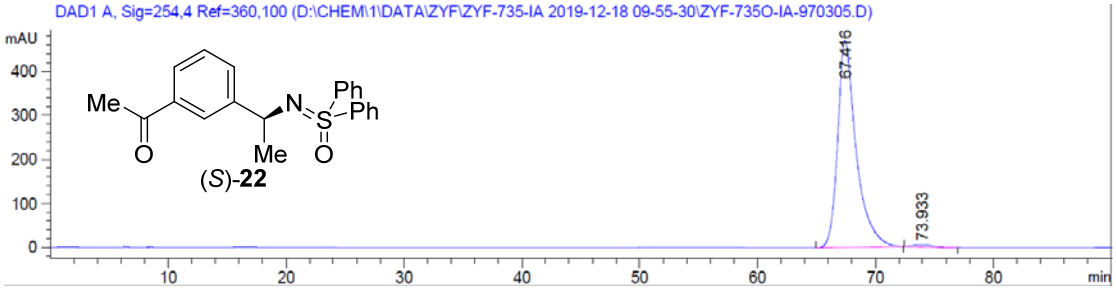
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.149	BB	0.8902	1.11870e4	185.33284	98.5339
2	39.786	BB	0.8560	166.45030	2.88983	1.4661
Totals :				1.13534e4	188.22267	



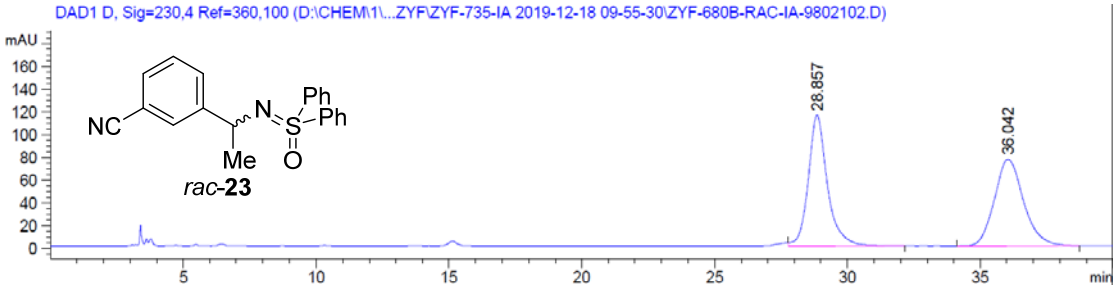
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.408	BB	1.5413	1.06781e4	102.50818	50.0453
2	73.142	BB	1.7148	1.06588e4	92.47124	49.9547
Totals :				2.13369e4	194.97942	



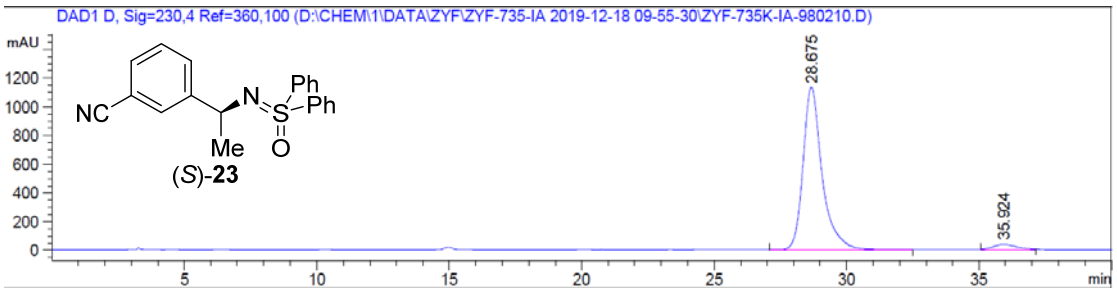
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.416	BB	1.5810	5.09481e4	469.87244	98.8052
2	73.933	MM R	1.9635	616.10785	5.22972	1.1948
Totals :				5.15642e4	475.10215	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

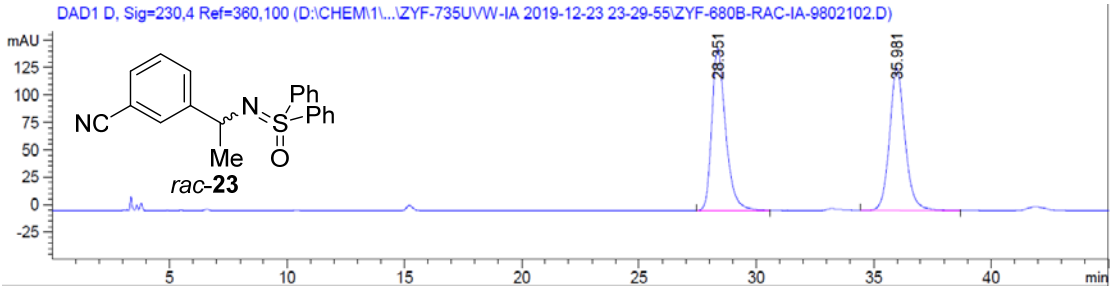
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.857	FM R	0.8307	5726.69385	114.89928	49.8968
2	36.042	BB	1.1223	5750.37793	75.69331	50.1032
Totals :				1.14771e4	190.59259	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

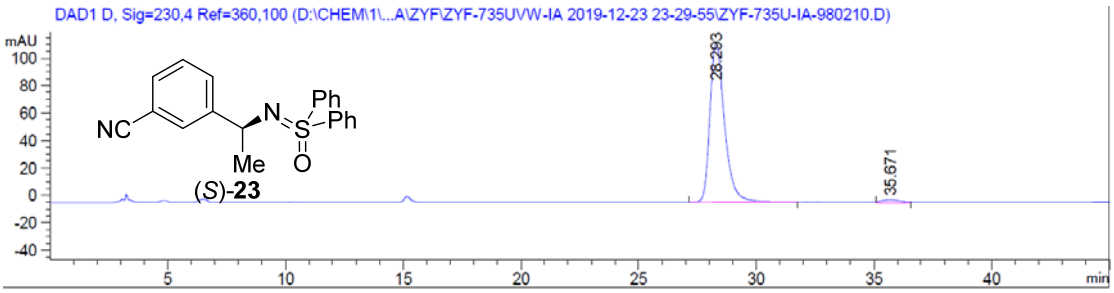
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.675	MM R	0.8402	5.73416e4	1137.46777	96.1699
2	35.924	MM R	0.9996	2283.73438	38.07840	3.8301
Totals :				5.96253e4	1175.54618	

The chloro substrates



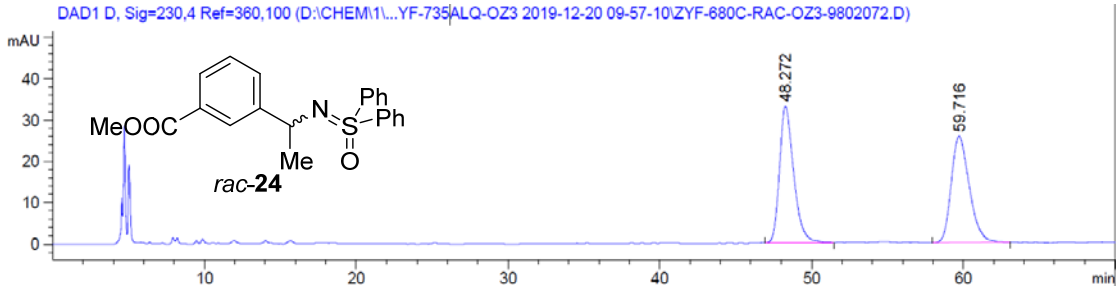
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.351	MM R	0.6905	6129.36133	147.93439	50.5681
2	35.981	MM R	0.7676	5991.64551	130.09331	49.4319
Totals :				1.21210e4	278.02769	



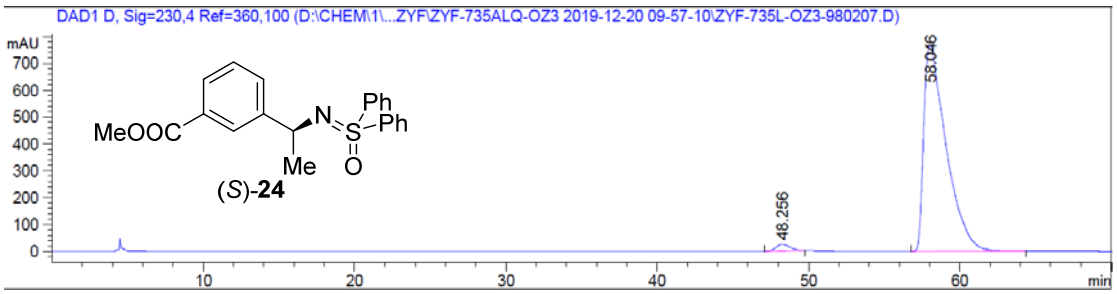
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.293	BB	0.6580	5021.50195	116.23598	97.8208
2	35.671	MM R	0.9252	111.86822	2.01512	2.1792
Totals :				5133.37017	118.25111	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

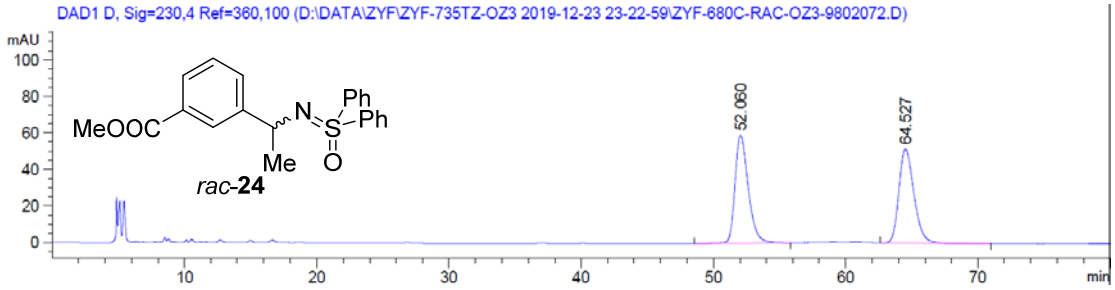
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.272	BB	0.9574	2136.25806	33.08049	50.0096
2	59.716	BB	1.2536	2135.43652	25.74644	49.9904
Totals :				4271.69458	58.82693	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

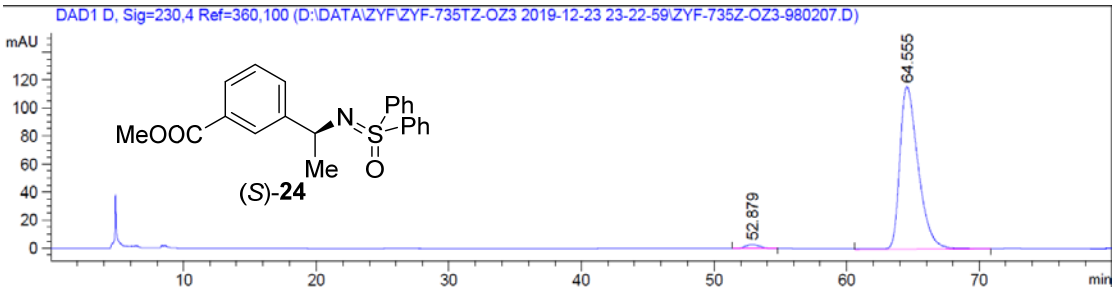
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.256	BB	0.9586	1555.43750	25.61066	1.9405
2	58.046	BB	1.4289	7.86011e4	768.74951	98.0595
Totals :				8.01566e4	794.36017	

The chloro substrates



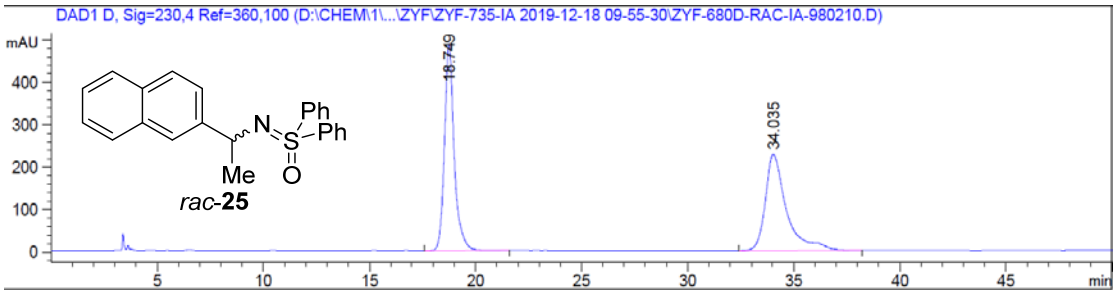
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.060	BB	1.0606	4097.68799	59.12556	50.0616
2	64.527	VB	1.2186	4087.59766	51.68767	49.9384
Totals :				8185.28564	110.81322	



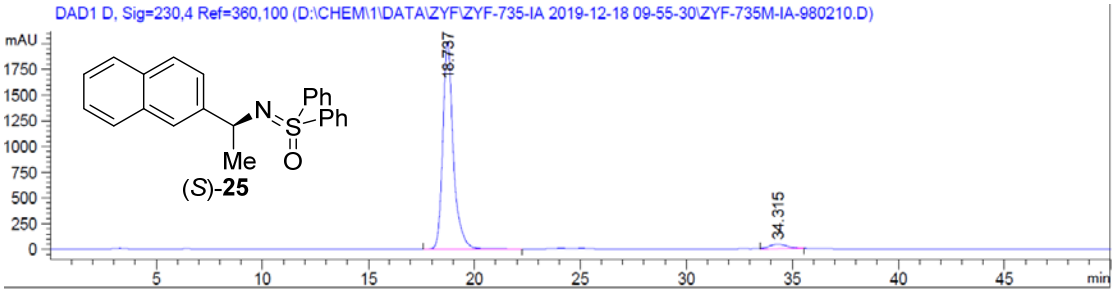
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.879	BB	1.1448	197.45909	2.70134	1.7432
2	64.555	MM R	1.6012	1.11300e4	115.84959	98.2568
Totals :				1.13274e4	118.55094	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

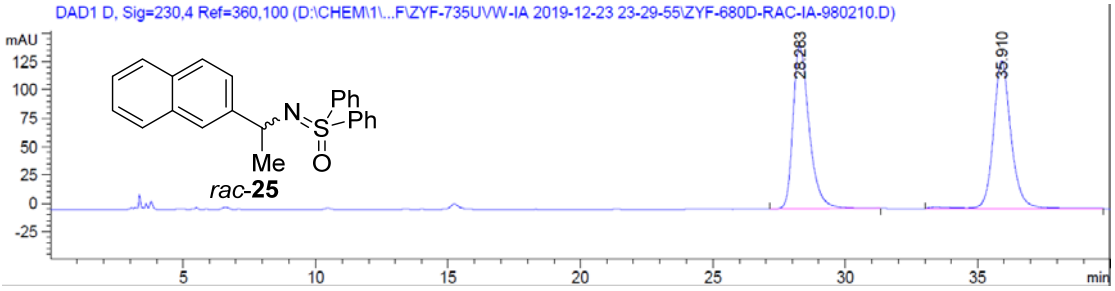
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.749	BB	0.4716	1.55100e4	486.97626	49.7060
2	34.035	BB	1.0074	1.56935e4	226.75638	50.2940
Totals :				3.12035e4	713.73264	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

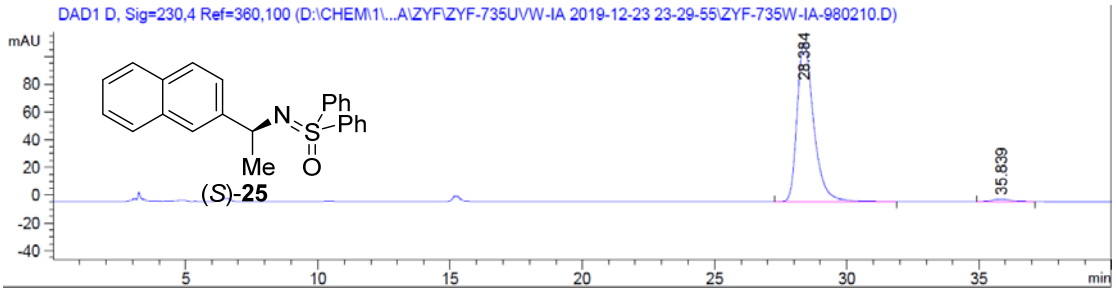
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.737	BB	0.5158	6.94171e4	2015.63318	96.4782
2	34.315	MM R	0.9429	2533.97803	44.78920	3.5218
Totals :				7.19511e4	2060.42238	

The chloro substrates



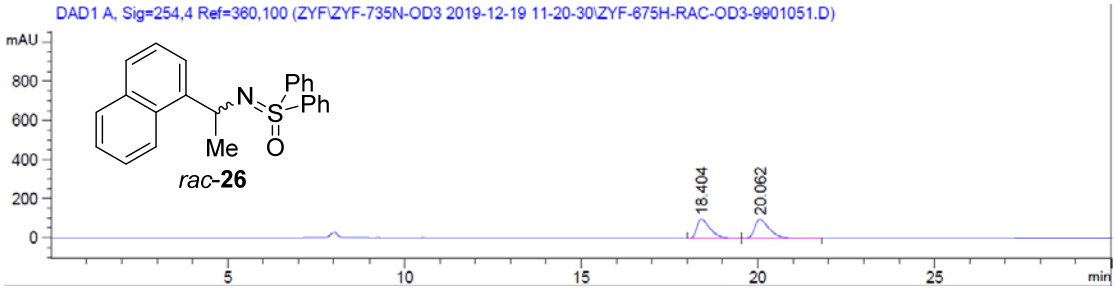
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.283	BB	0.6514	6109.99902	143.31752	49.9649
2	35.910	MM R	0.7831	6118.59473	130.22910	50.0351
Totals :				1.22286e4	273.54662	



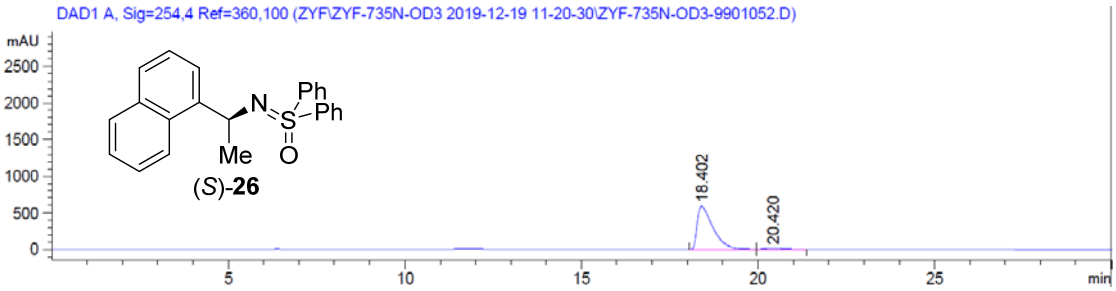
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.384	BB	0.6669	5033.23438	114.93758	98.1808
2	35.839	MM R	0.8933	93.26212	1.74008	1.8192
Totals :				5126.49649	116.67767	



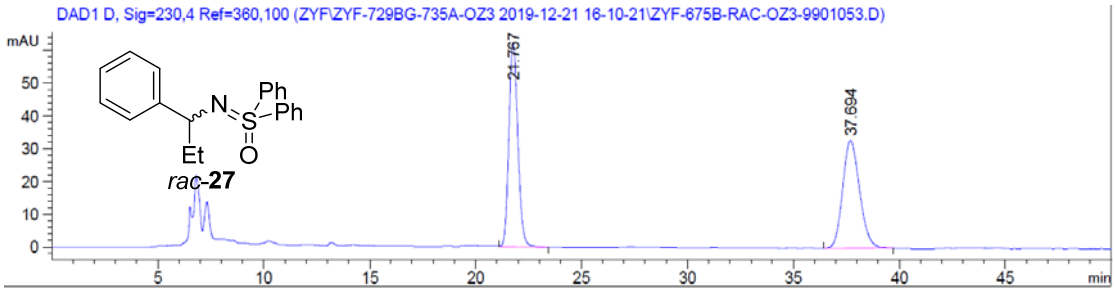
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.404	BB	0.3829	2473.65405	97.85881	48.0628
2	20.062	BB	0.4221	2673.05542	96.21078	51.9372
Totals :				5146.70947	194.06960	



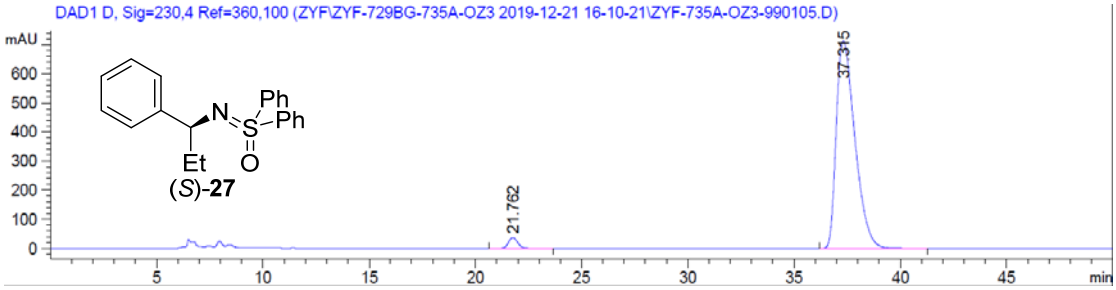
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.402	BB	0.4603	1.80370e4	587.29456	97.7450
2	20.420	BB	0.4677	416.12219	13.49546	2.2550
Totals :				1.84531e4	600.79001	



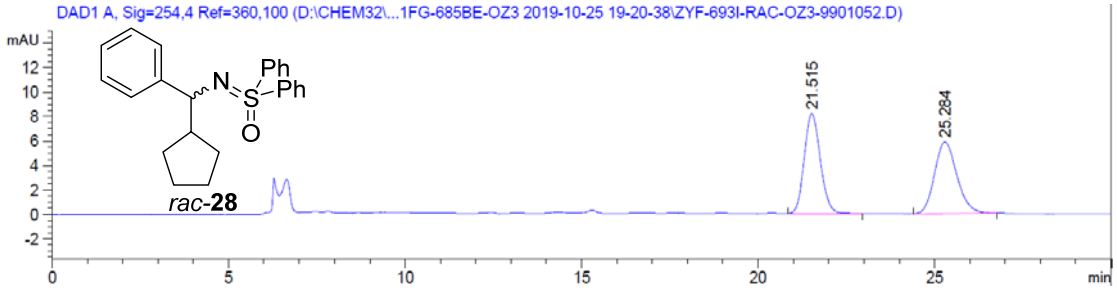
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.767	BB	0.4553	1823.32922	62.33519	49.8722
2	37.694	BB	0.8559	1832.67224	32.89739	50.1278
Totals :				3656.00146	95.23259	



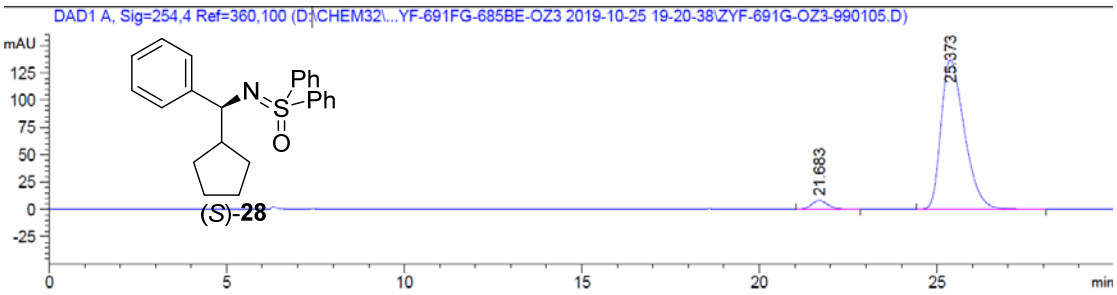
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.762	BB	0.4681	1132.11426	37.29874	2.5412
2	37.315	BB	0.9319	4.34174e4	713.48608	97.4588
Totals :				4.45495e4	750.78482	



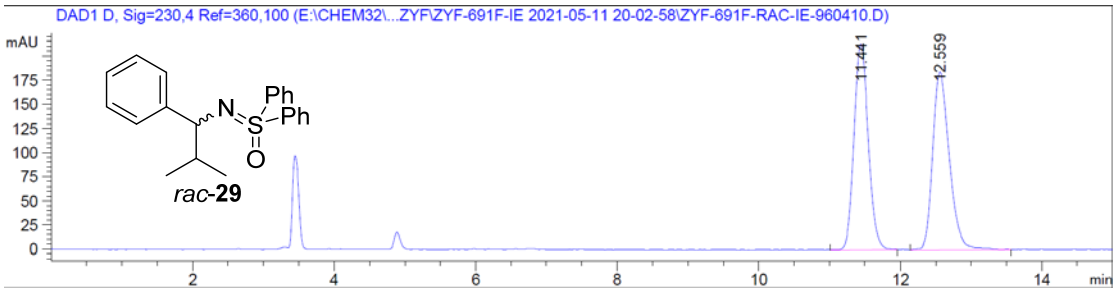
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.515	BB	0.4792	258.25525	8.16025	50.1547
2	25.284	BB	0.6283	256.66193	5.84520	49.8453
Totals :				514.91718	14.00546	



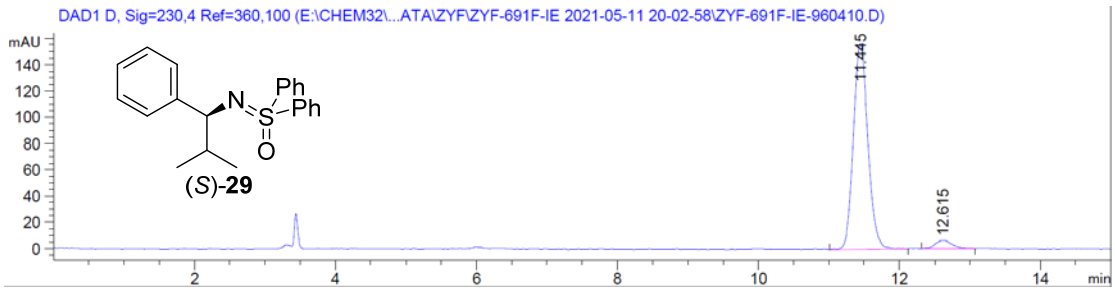
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.683	BB	0.4986	259.50281	8.12478	3.9846
2	25.373	BB	0.6991	6253.09863	136.85159	96.0154
Totals :				6512.60144	144.97638	



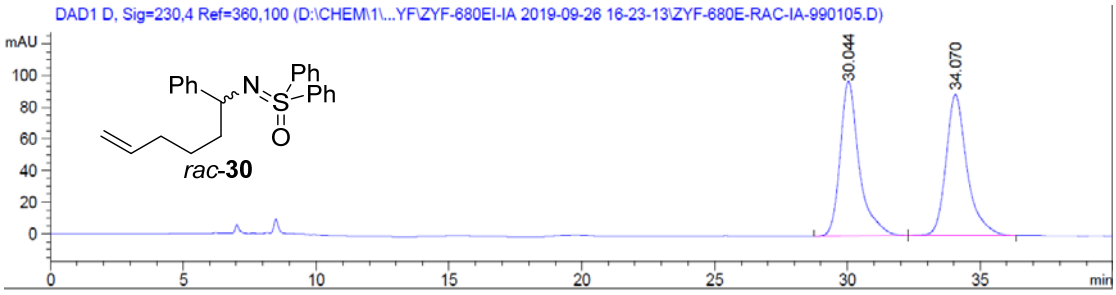
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.441	VB R	0.2171	2982.91162	213.39357	49.6558
2	12.559	BV R	0.2514	3024.26807	184.36650	50.3442
Totals :				6007.17969	397.76007	



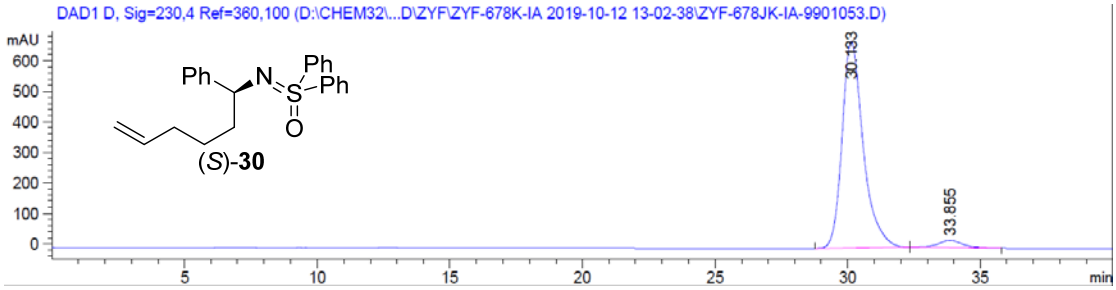
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.445	VV R	0.2203	2229.56519	156.41428	95.4798
2	12.615	BV R	0.2109	105.55209	6.31776	4.5202
Totals :				2335.11728	162.73204	



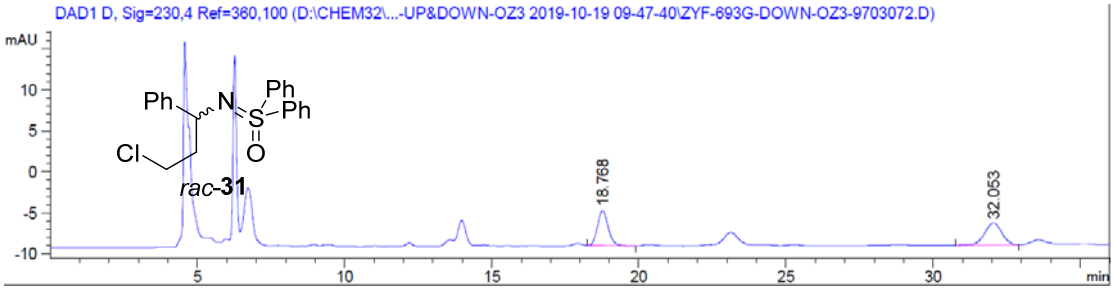
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.044	BB	0.7378	4879.53418	97.84650	49.9359
2	34.070	BB	0.8223	4892.06494	88.85565	50.0641
Totals :				9771.59912	186.70215	



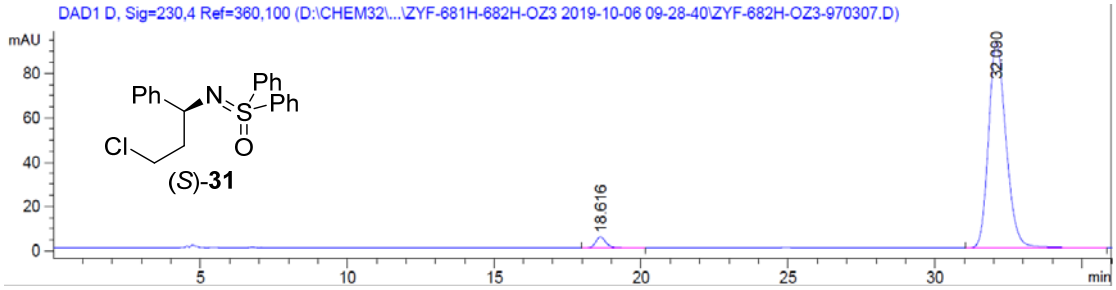
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.133	BB	0.8345	3.75098e4	676.94598	96.1263
2	33.855	BB	0.9708	1511.58765	23.30194	3.8737
Totals :				3.90213e4	700.24793	



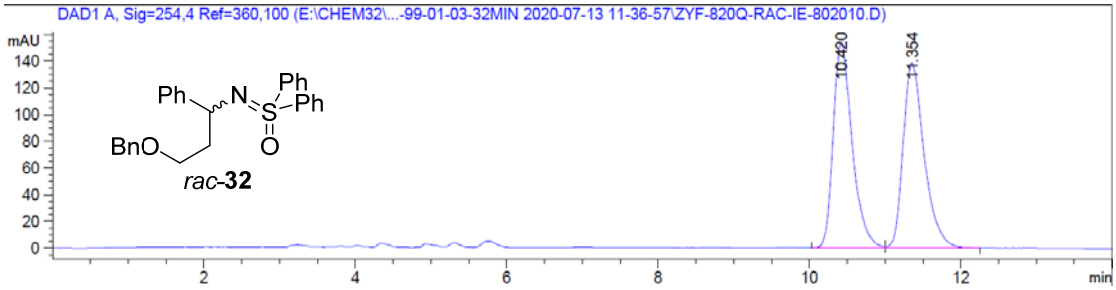
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.768	BB	0.3886	108.87351	4.28319	49.9965
2	32.053	BB	0.6003	108.88895	2.68982	50.0035
Totals :				217.76246	6.97301	



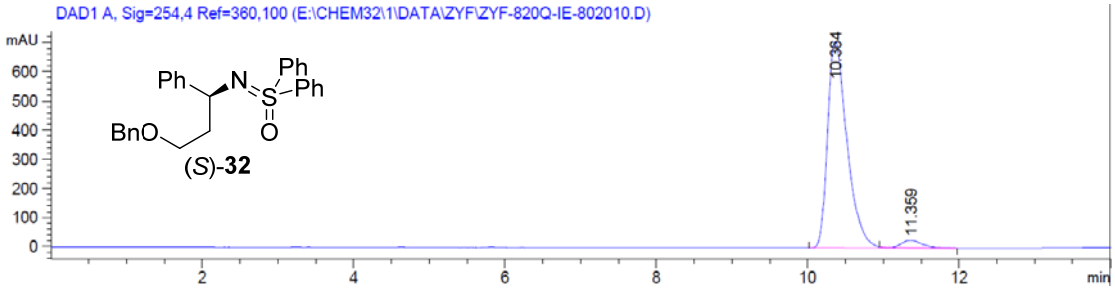
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.616	BB	0.3733	118.72488	4.92329	2.9877
2	32.090	BB	0.6309	3855.07568	93.14317	97.0123
Totals :				3973.80057	98.06646	



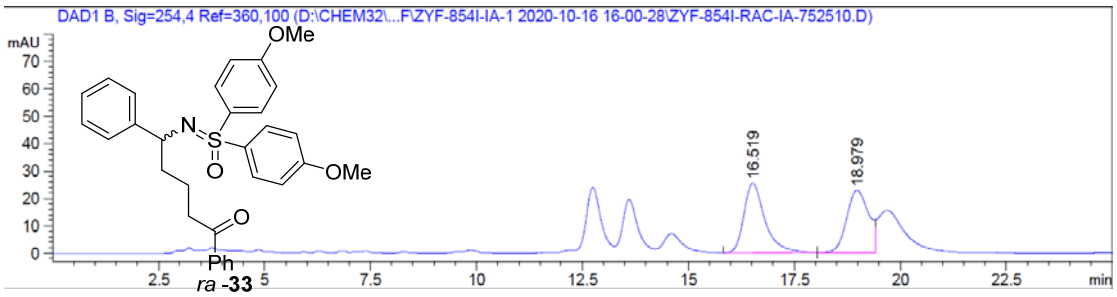
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.420	BV	0.2626	2675.26025	154.08708	49.9445
2	11.354	VB	0.2940	2681.20068	138.40616	50.0555
Totals :				5356.46094	292.49324	



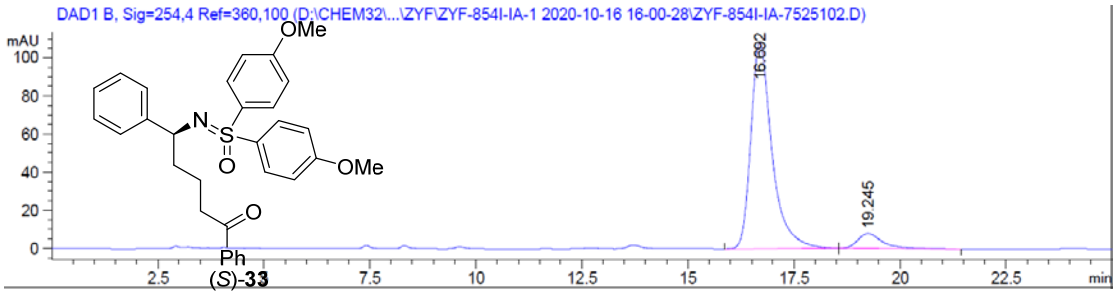
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.364	BV R	0.2705	1.26594e4	708.36725	95.9999
2	11.359	VB E	0.2869	527.49170	27.85690	4.0001
Totals :				1.31869e4	736.22415	



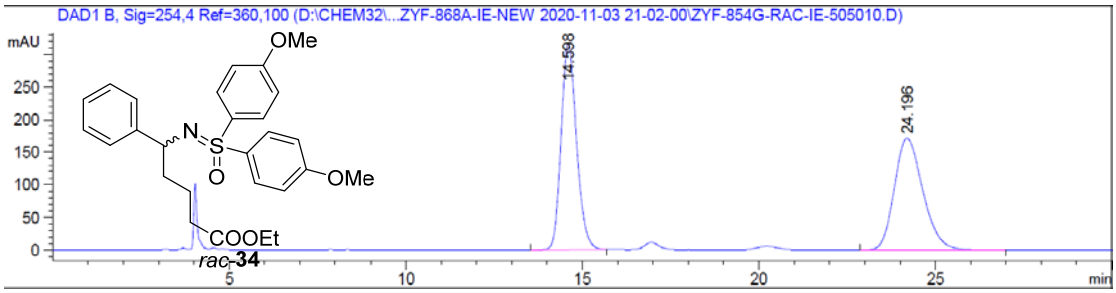
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.519	BB	0.5106	865.13348	25.32464	51.5652
2	18.979	MF R	0.5972	812.61371	22.67711	48.4348
Totals :				1677.74719	48.00175	



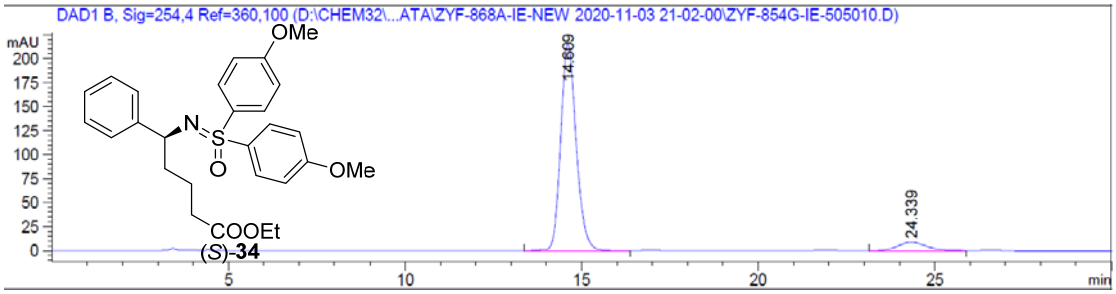
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.692	BB	0.5201	3743.00073	108.06425	92.0698
2	19.245	BB	0.6071	322.39331	7.88378	7.9302
Totals :				4065.39404	115.94804	



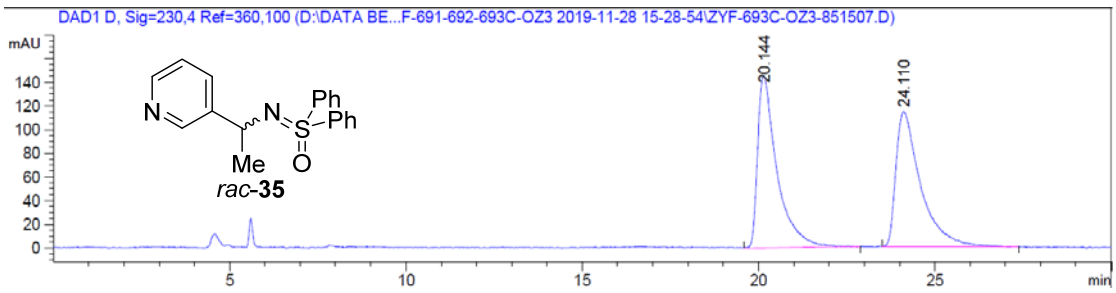
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.598	BB	0.4667	9575.00879	316.68216	49.9300
2	24.196	BB	0.8595	9601.86816	171.41501	50.0700
Totals :				1.91769e4	488.09717	



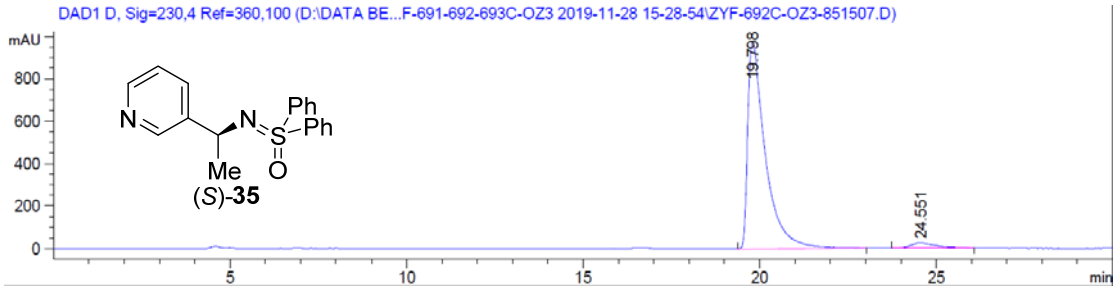
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.609	BB	0.4661	6544.97900	215.62640	93.3042
2	24.339	BB	0.7912	469.68518	8.51898	6.6958
Totals :				7014.66418	224.14538	



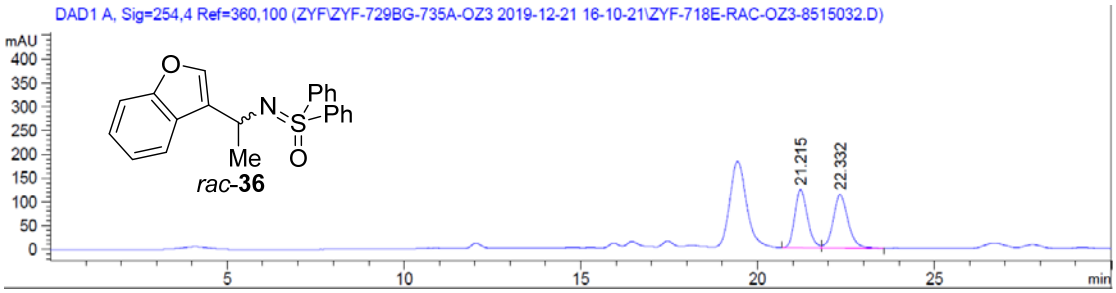
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.144	MM R	0.6378	5559.21582	145.26801	50.0233
2	24.110	MM R	0.8111	5554.03613	114.12766	49.9767
Totals :				1.11133e4	259.39566	



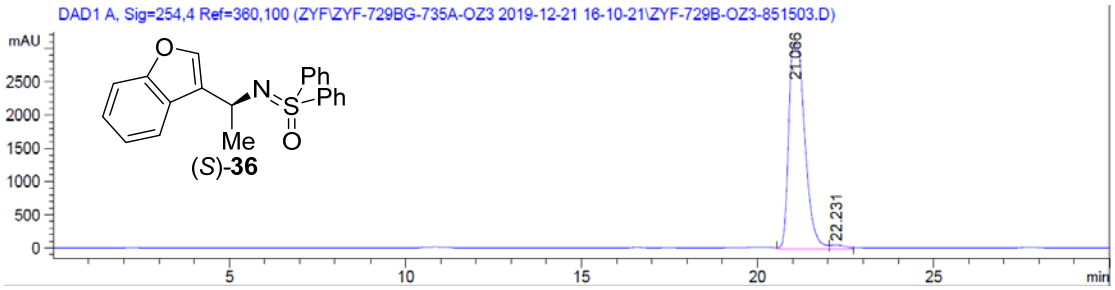
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.798	MM R	0.5759	3.37381e4	976.34192	96.5905
2	24.551	VV R	0.6152	1190.90613	23.03533	3.4095
Totals :				3.49291e4	999.37724	



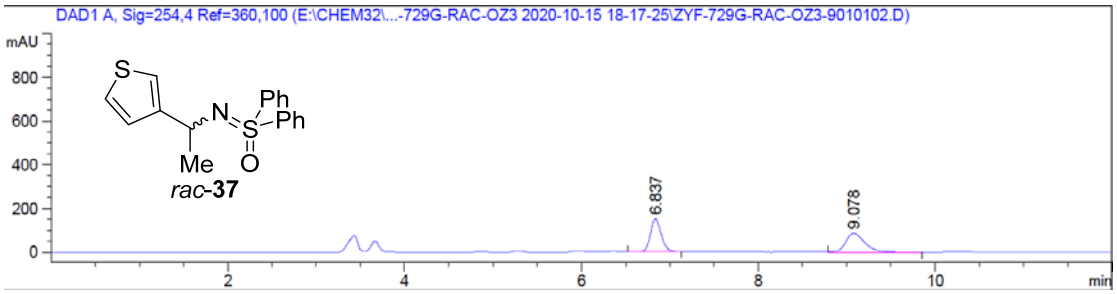
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.215	BV	0.3814	3039.37671	122.54710	48.1928
2	22.332	VB	0.4413	3267.32495	112.35404	51.8072
Totals :				6306.70166	234.90115	



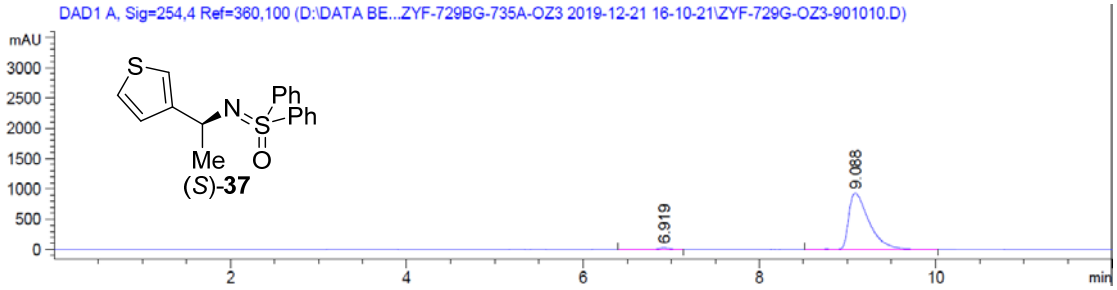
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.066	MF R	0.5276	9.81674e4	3100.98804	98.3851
2	22.231	FM R	0.5109	1611.29407	52.56573	1.6149
Totals :				9.97787e4	3153.55377	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

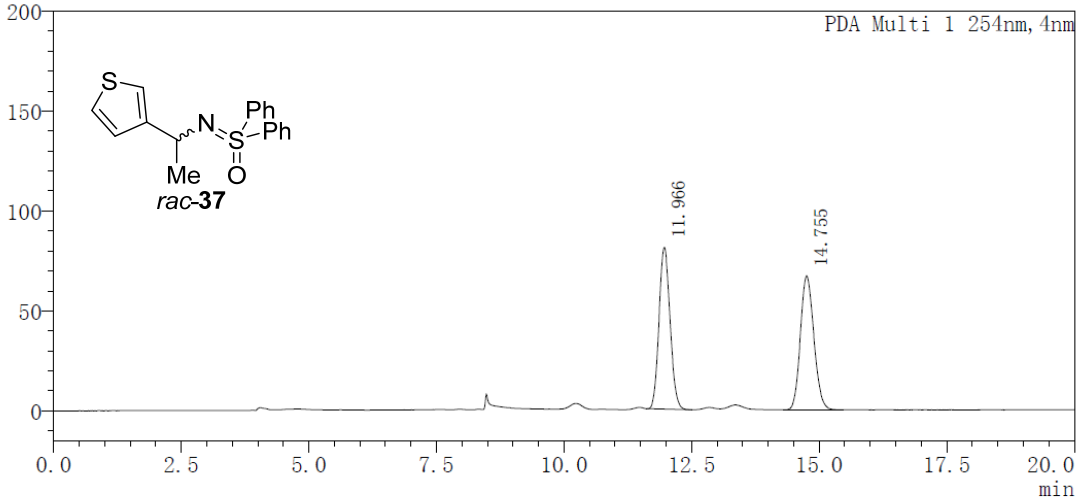
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.837	BV	0.1306	1266.32959	149.78006	50.2411
2	9.078	FM R	0.2444	1254.17615	85.54153	49.7589
Totals :				2520.50574	235.32159	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

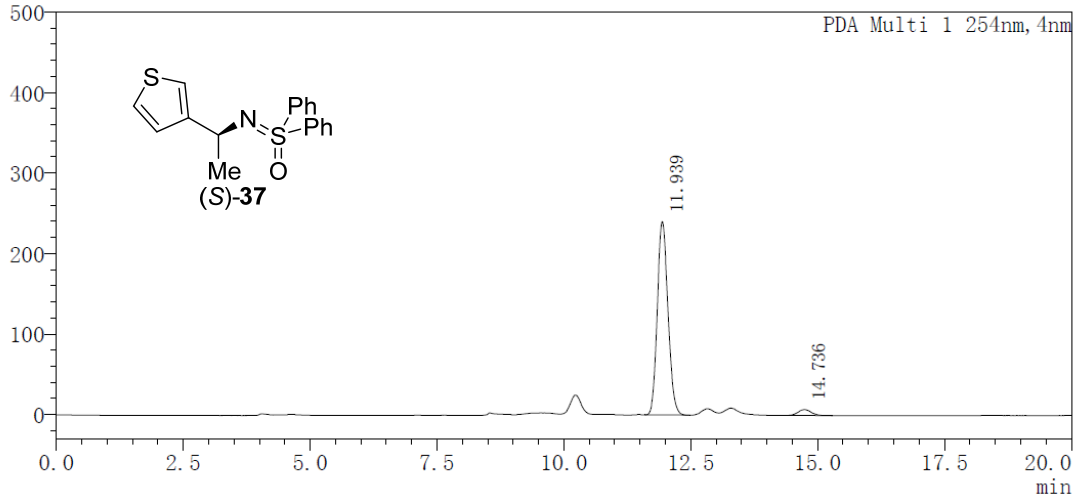
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.919	VB R	0.1385	253.80870	25.32936	1.6773
2	9.088	VB R	0.2391	1.48784e4	931.92694	98.3227
Totals :				1.51322e4	957.25631	

The chloro substrates



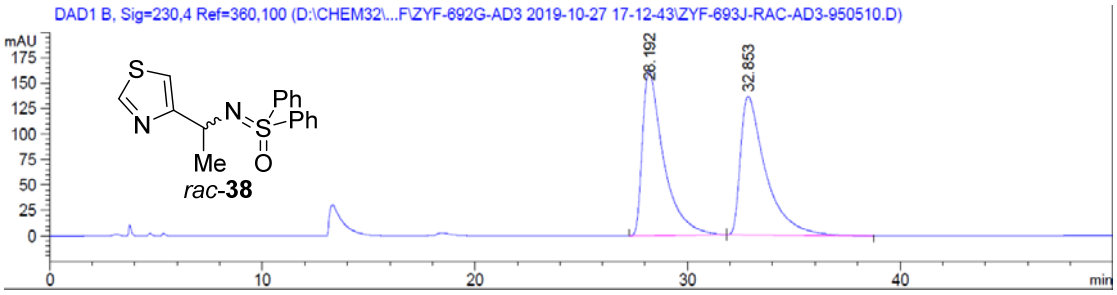
PDA Ch1 254nm

T	Hight	Area	Area%
11.966	80963	1222148	49.733
14.755	67136	1235276	50.267



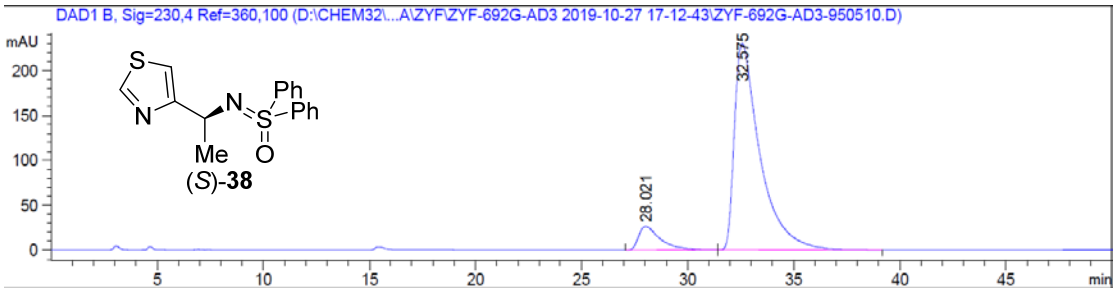
PDA Ch1 254nm

T	Hight	Area	Area%
11.939	240169	3516618	96.441
14.736	7294	129790	3.559



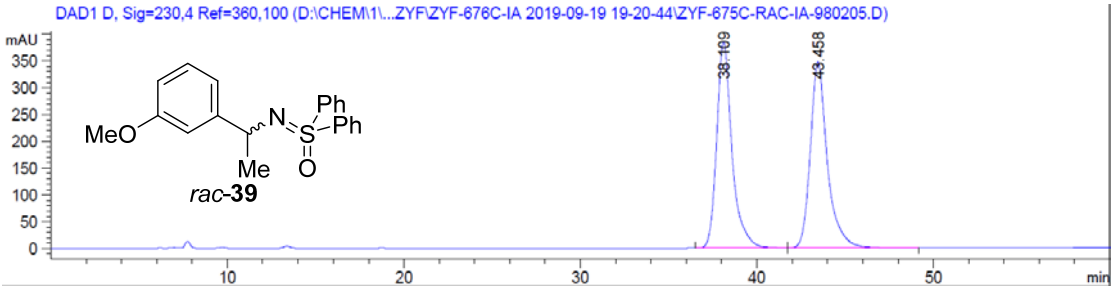
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.192	BB	1.0071	1.12106e4	161.65407	50.0206
2	32.853	BB	1.1941	1.12014e4	136.10995	49.9794
Totals :				2.24120e4	297.76402	



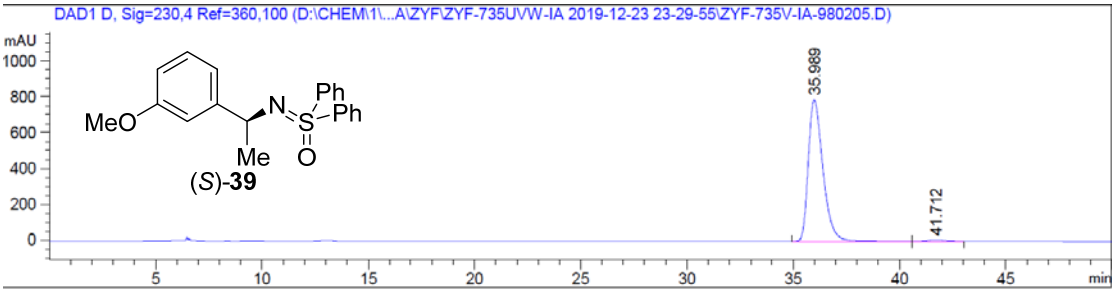
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.021	BB	0.9845	1880.88208	26.42155	8.8784
2	32.575	BB	1.2218	1.93040e4	229.84904	91.1216
Totals :				2.11848e4	256.27059	



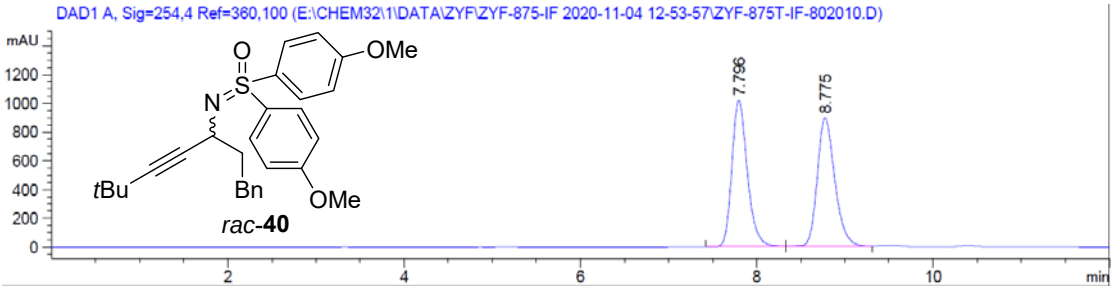
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.109	BB	0.8982	2.31619e4	385.91211	49.8754
2	43.458	BB	0.9896	2.32776e4	347.45084	50.1246
Totals :				4.64394e4	733.36295	



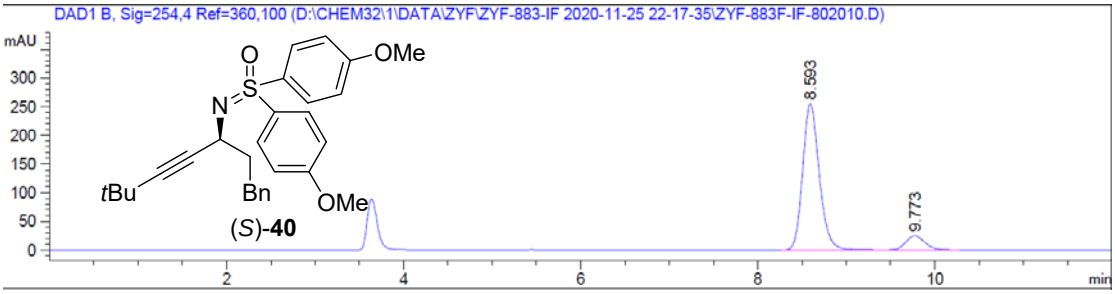
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.989	BB	0.7353	3.79174e4	790.89185	98.7748
2	41.712	BB	0.7907	470.32013	8.75555	1.2252
Totals :				3.83877e4	799.64740	



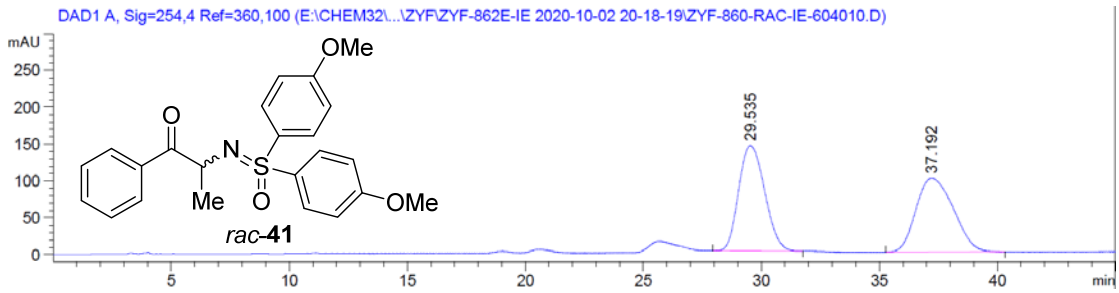
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.796	BV	0.1867	1.24916e4	1021.04315	49.8337
2	8.775	MF R	0.2331	1.25750e4	899.07648	50.1663
Totals :				2.50666e4	1920.11963	



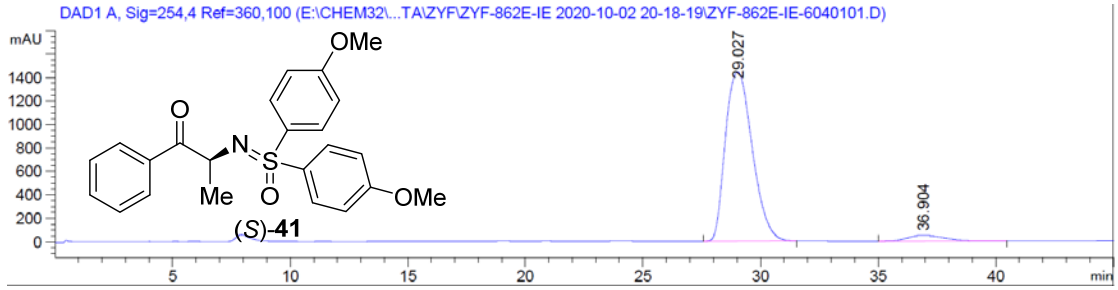
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.593	MM R	0.2178	3335.70874	255.23349	89.8878
2	9.773	MM R	0.2517	375.26151	24.85266	10.1122
Totals :				3710.97025	280.08615	



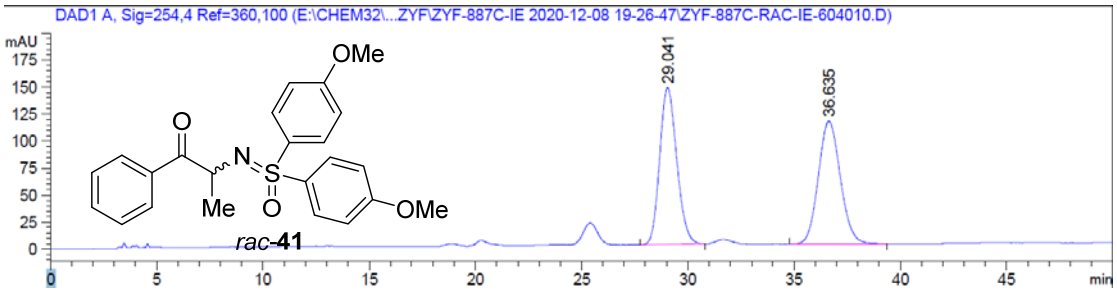
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.535	MM R	1.2789	1.09749e4	143.02078	49.9306
2	37.192	MM R	1.8234	1.10054e4	100.59306	50.0694
Totals :				2.19802e4	243.61384	



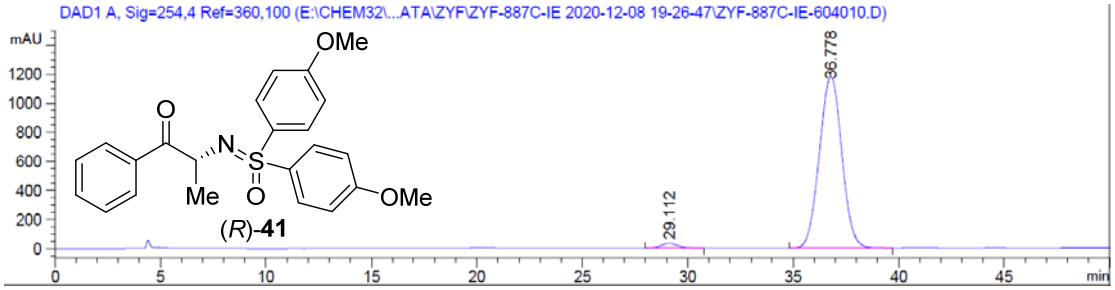
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.027	BB	1.2470	1.14457e5	1440.47339	95.5742
2	36.904	BB	1.5689	5300.26172	48.27670	4.4258
Totals :				1.19758e5	1488.75009	



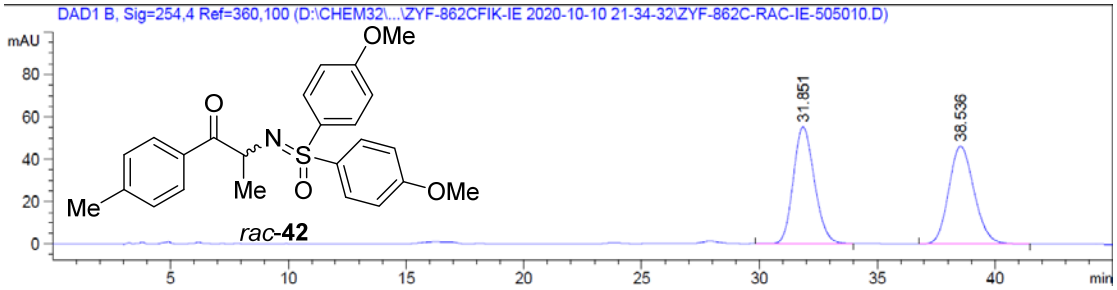
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.041	BB	0.8583	8115.31836	145.15533	49.8196
2	36.635	BB	1.0869	8174.07910	113.67123	50.1804
Totals :				1.62894e4	258.82657	



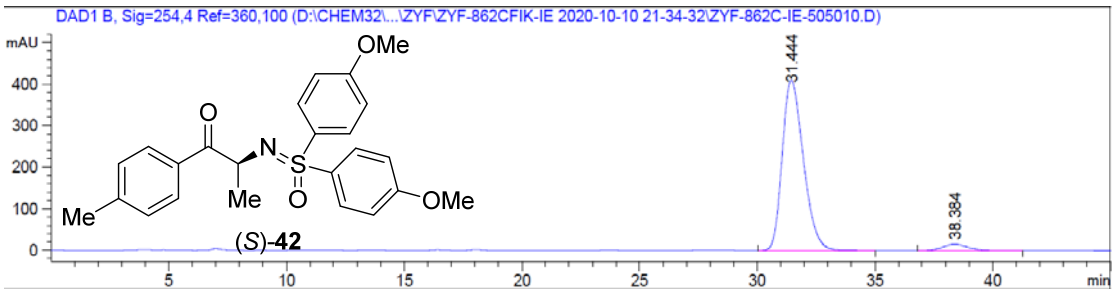
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.112	BB	0.8420	1914.09485	33.93956	2.1425
2	36.778	BB	1.1471	8.74266e4	1181.75098	97.8575
Totals :				8.93406e4	1215.69054	



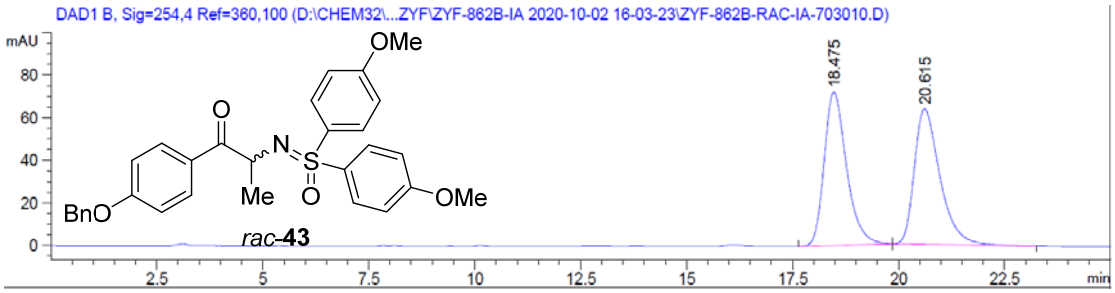
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.851	MM R	1.0371	3421.27783	54.98359	49.6998
2	38.536	BB	1.1333	3462.61279	46.25860	50.3002
Totals :				6883.89063	101.24219	



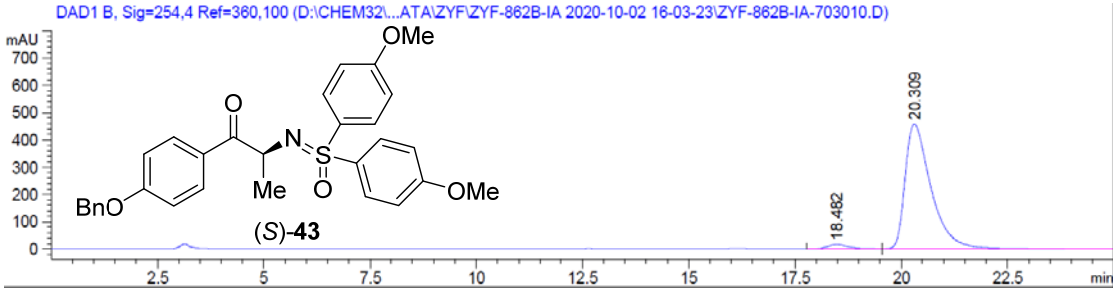
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.444	MM R	1.0545	2.60207e4	411.25116	95.8009
2	38.384	BB	1.0603	1140.54004	15.21855	4.1991
Totals :				2.71612e4	426.46971	



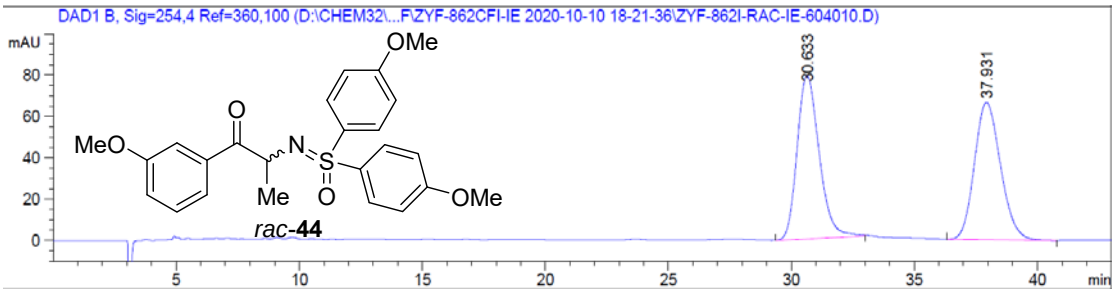
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.475	BB	0.5582	2645.55542	72.07307	49.7634
2	20.615	BB	0.6366	2670.70923	63.50843	50.2366
Totals :				5316.26465	135.58151	



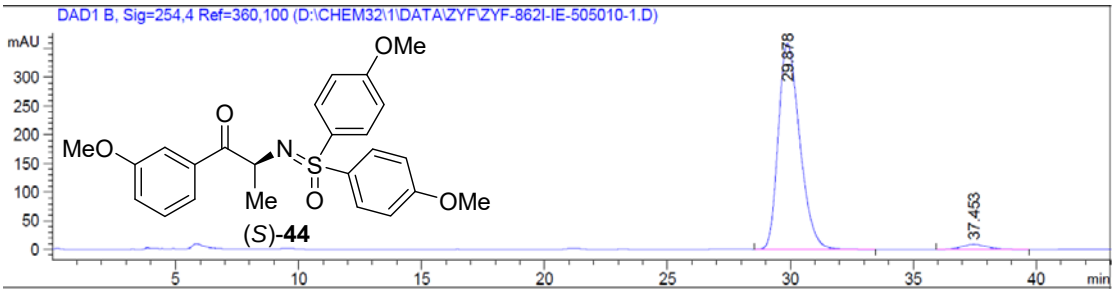
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.482	BB	0.5492	570.25281	15.72108	2.8574
2	20.309	BBA	0.6349	1.93869e4	457.05188	97.1426
Totals :				1.99571e4	472.77296	



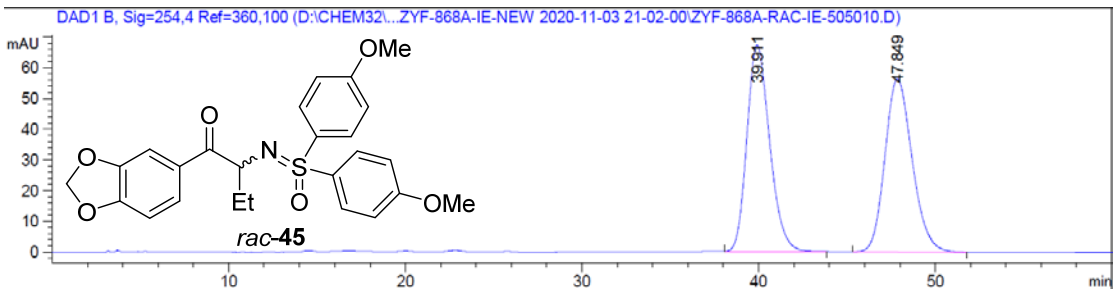
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.633	MM R	1.0364	4920.84277	79.13699	50.1795
2	37.931	BB	1.1316	4885.63672	66.30952	49.8205
Totals :				9806.47949	145.44650	



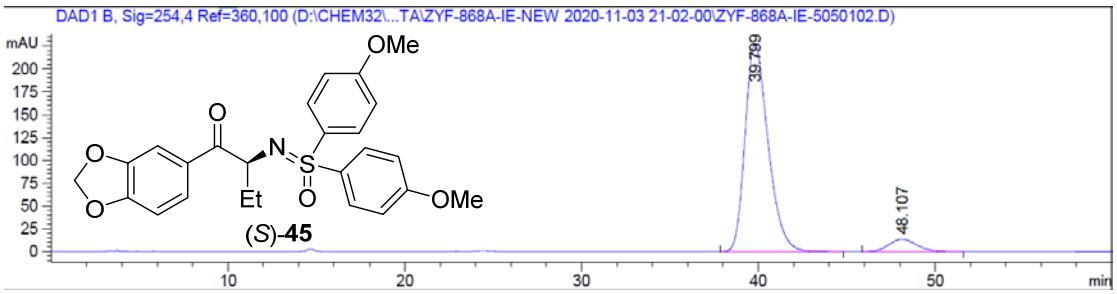
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.878	BB	0.9392	2.17582e4	358.95581	97.1445
2	37.453	BB	0.9753	639.57898	8.70349	2.8555
Totals :				2.23978e4	367.65930	



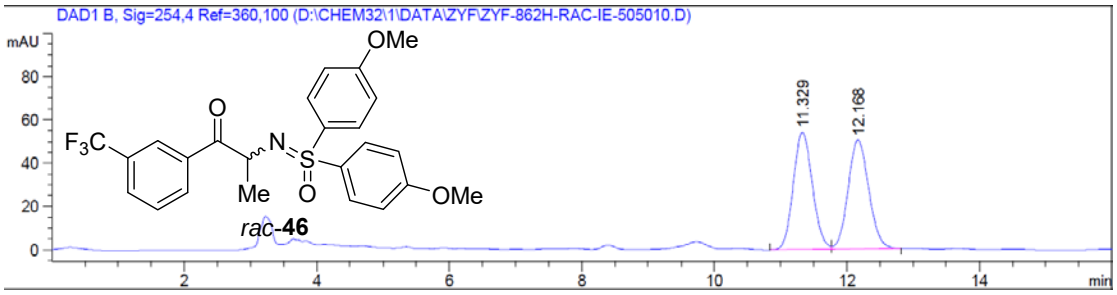
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.911	BB	1.3251	6002.48193	67.13322	49.9175
2	47.849	BB	1.5796	6022.32422	56.31431	50.0825
Totals :				1.20248e4	123.44753	



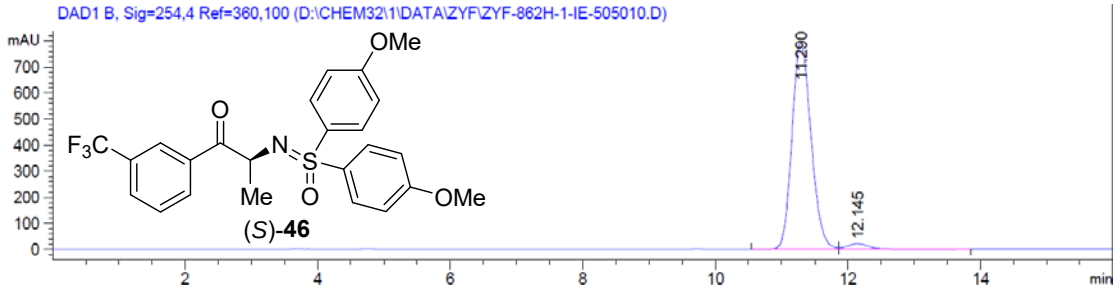
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.799	BB	1.3961	2.05143e4	226.62315	93.4253
2	48.107	BB	1.2723	1443.66357	13.47137	6.5747
Totals :				2.19580e4	240.09452	



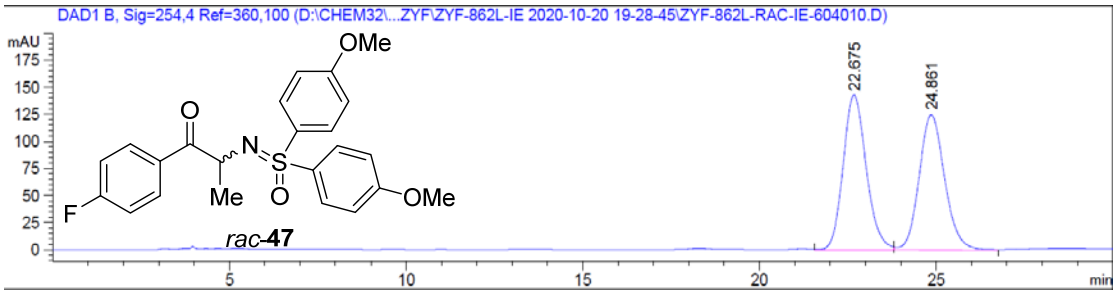
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.329	BV	0.3120	1088.28418	54.26349	50.0097
2	12.168	VB	0.3343	1087.86206	50.29762	49.9903
Totals :				2176.14624	104.56111	



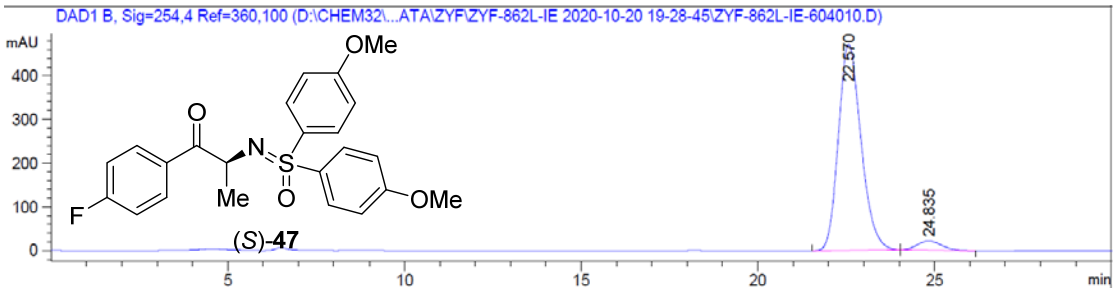
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.290	BV	0.3108	1.58914e4	796.49493	96.9539
2	12.145	VB	0.3487	499.27292	21.67608	3.0461
Totals :				1.63907e4	818.17102	



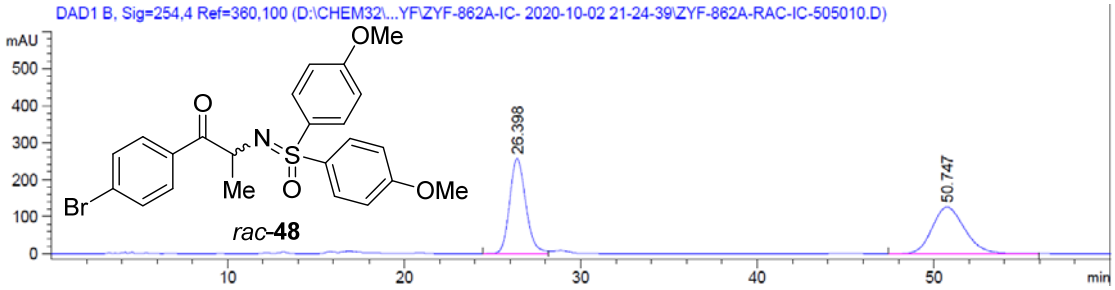
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.675	MF R	0.7582	6511.51270	143.14381	50.8488
2	24.861	FM R	0.8381	6294.13281	125.16263	49.1512
Totals :				1.28056e4	268.30644	



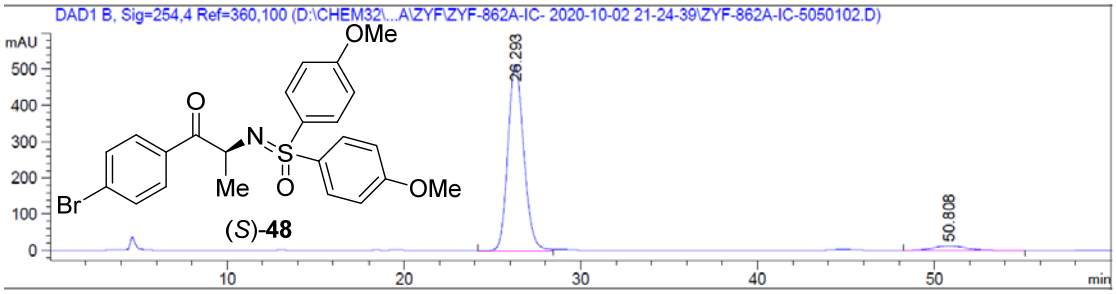
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.570	BB	0.6844	2.09530e4	471.54083	95.4709
2	24.835	BB	0.7300	993.99774	21.15985	4.5291
Totals :				2.19470e4	492.70068	



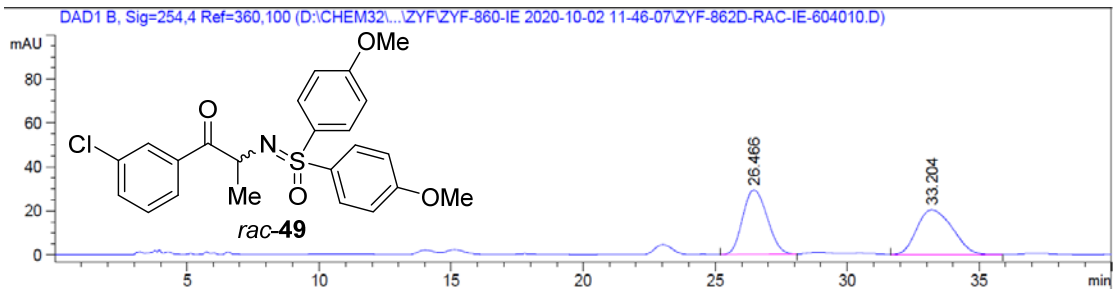
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.398	MF R	1.0654	1.64059e4	256.63904	50.4365
2	50.747	MM R	2.1406	1.61219e4	125.52304	49.5635
Totals :				3.25278e4	382.16208	



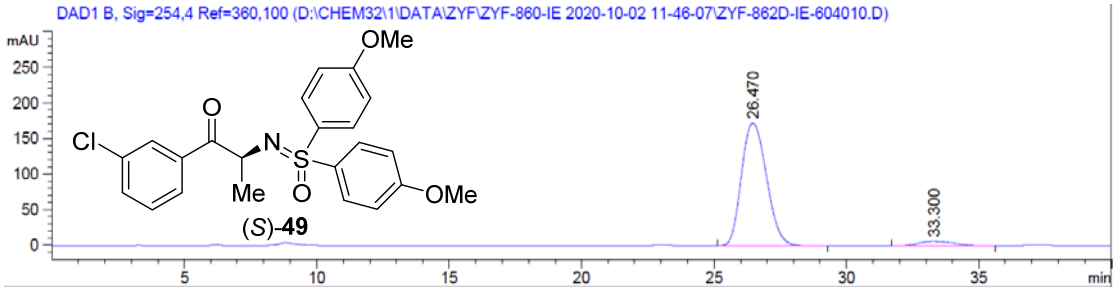
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.293	MF R	1.0451	3.22819e4	514.80560	95.4730
2	50.808	BB	1.5019	1530.70703	12.00249	4.5270
Totals :				3.38126e4	526.80809	



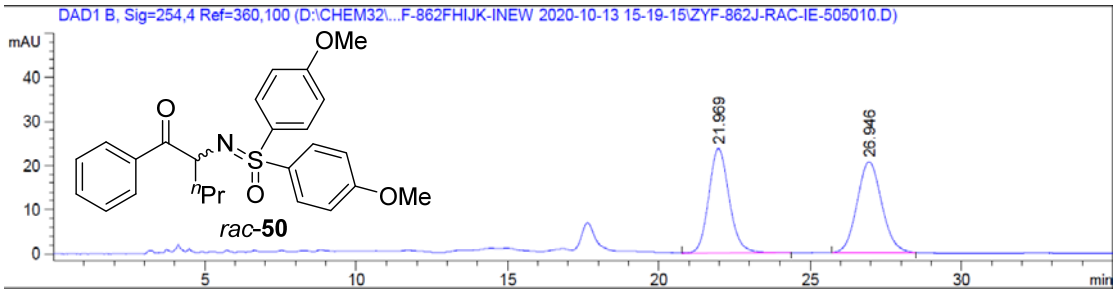
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.466	BB	1.0199	1884.78296	29.24394	49.8201
2	33.204	BB	1.2652	1898.39380	20.37167	50.1799
Totals :				3783.17676	49.61562	



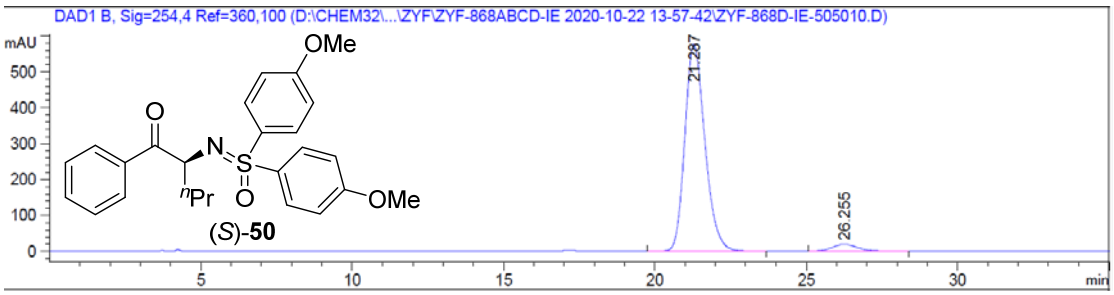
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.470	BB	1.0425	1.12698e4	171.99257	95.2291
2	33.300	BB	1.1026	564.61102	6.05098	4.7709
Totals :				1.18344e4	178.04355	



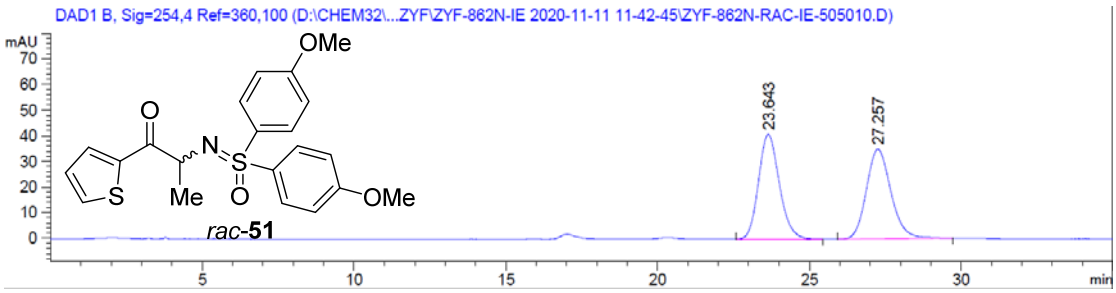
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.969	MM R	0.7818	1110.04211	23.66327	48.5844
2	26.946	MM R	0.9496	1174.72986	20.61849	51.4156
Totals :				2284.77197	44.28176	



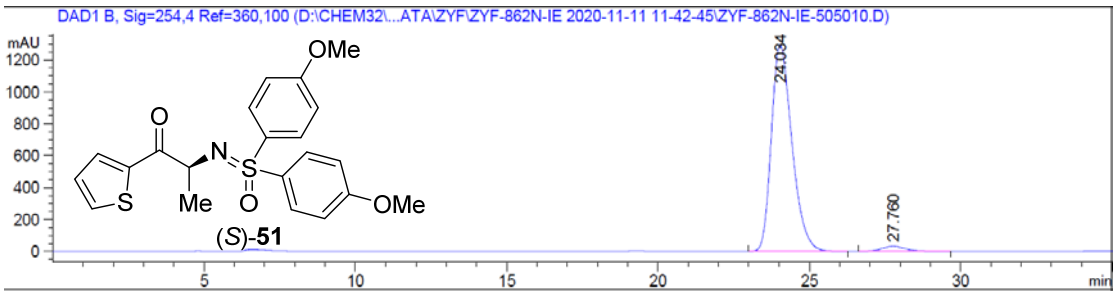
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.287	BB	0.7122	2.66140e4	576.90405	96.0370
2	26.255	BB	0.8477	1098.22229	19.48231	3.9630
Totals :				2.77122e4	596.38636	



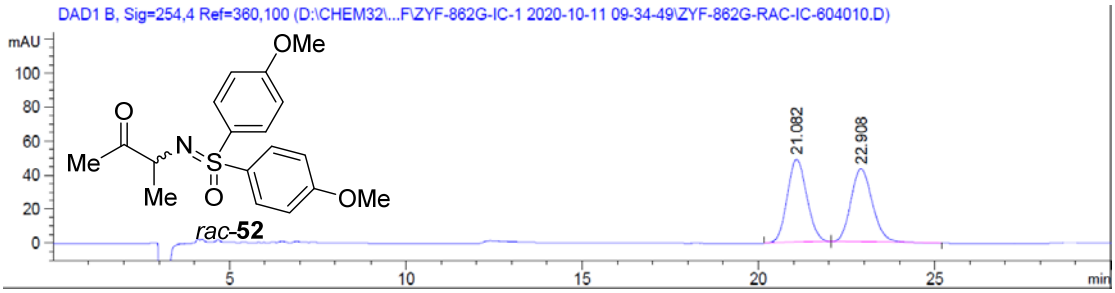
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.643	BB	0.7330	1950.66357	40.85941	49.8128
2	27.257	BB	0.8601	1965.32861	34.94857	50.1872
Totals :				3915.99219	75.80798	



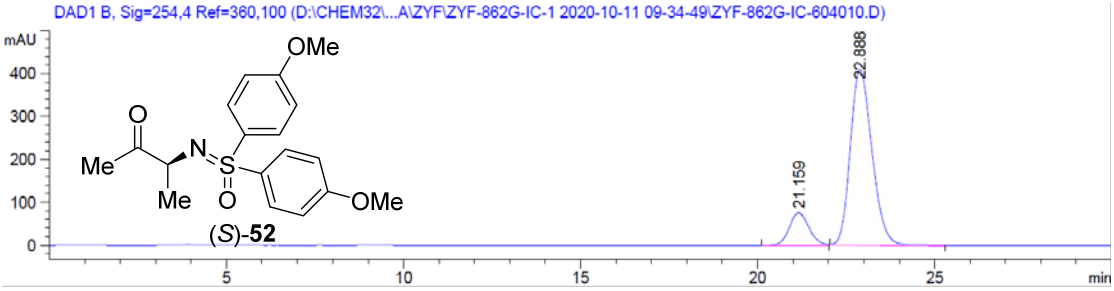
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.034	BB	0.7291	6.12202e4	1296.05078	97.2223
2	27.760	BB	0.8265	1749.10547	32.36598	2.7777
Totals :				6.29693e4	1328.41676	



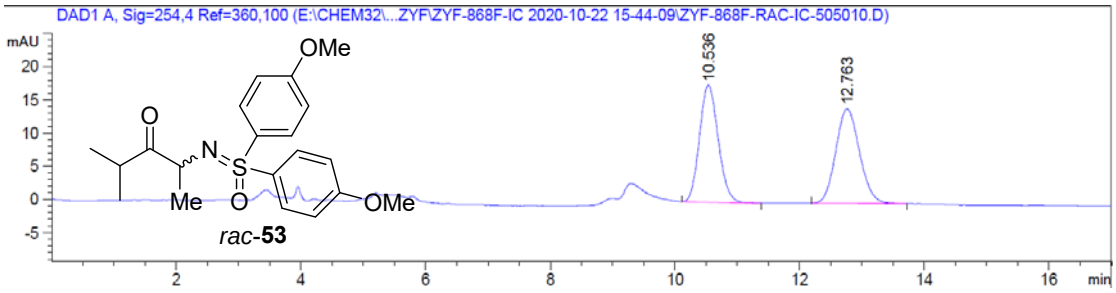
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.082	BB	0.5987	1888.84814	48.89371	50.8365
2	22.908	BB	0.6550	1826.68787	43.05470	49.1635
Totals :				3715.53601	91.94841	



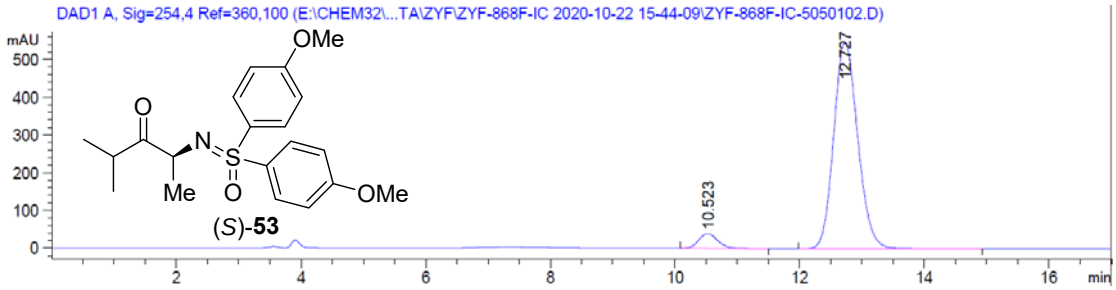
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.159	BV	0.5961	2911.27686	75.79636	14.2366
2	22.888	MM R	0.7123	1.75379e4	410.34650	85.7634
Totals :				2.04492e4	486.14286	



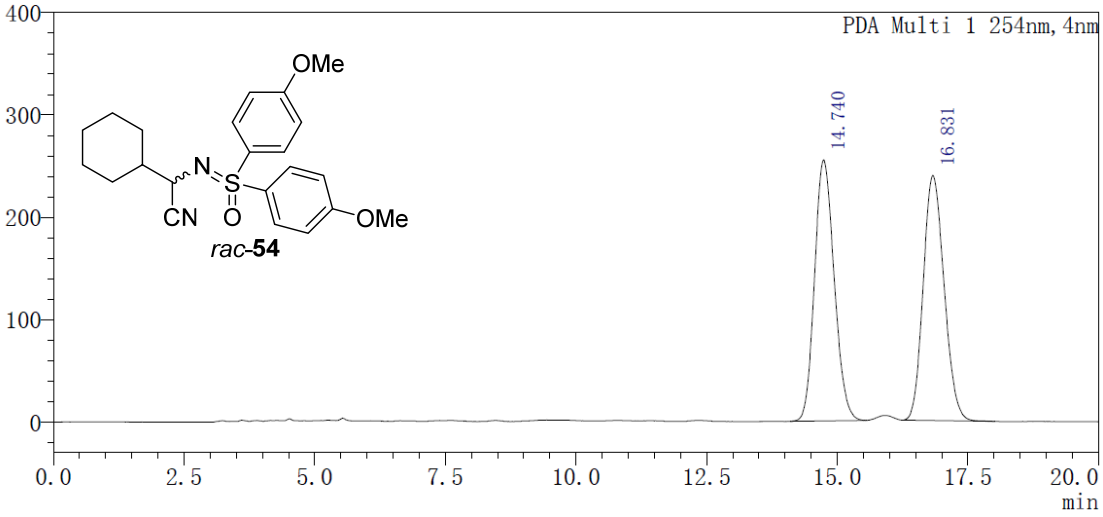
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.536	BB	0.3258	368.51419	17.63574	49.4100
2	12.763	BB	0.4030	377.31476	14.24509	50.5900
Totals :				745.82895	31.88083	



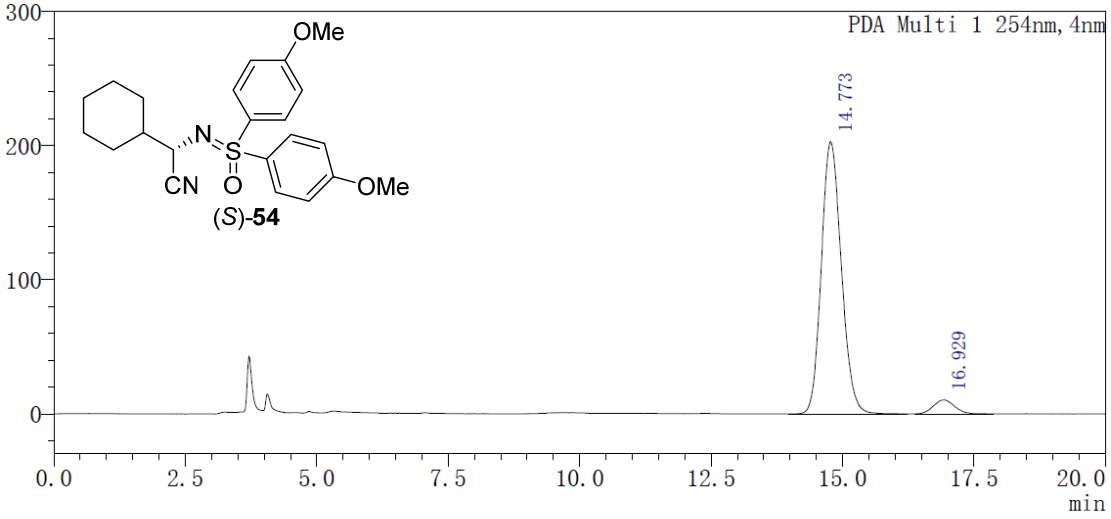
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.523	BB	0.3275	823.33551	39.12523	5.3343
2	12.727	BB	0.4129	1.46114e4	548.26465	94.6657
Totals :				1.54347e4	587.38988	



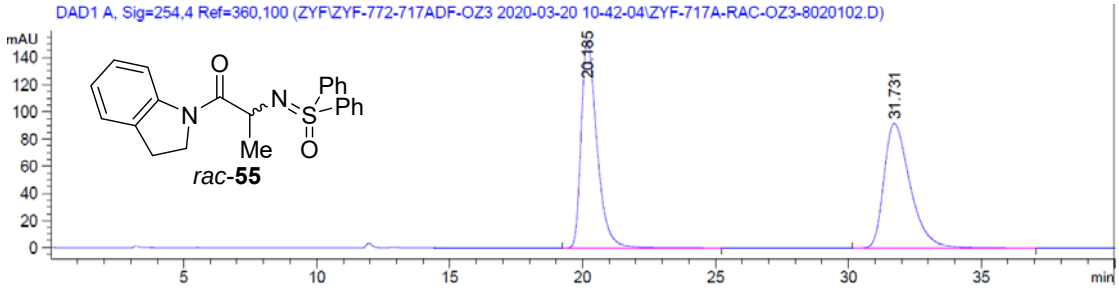
PDA Ch1 254nm

T	Hight	Area	Area%
14.740	254960	6665061	50.040
16.831	239342	6654400	49.960



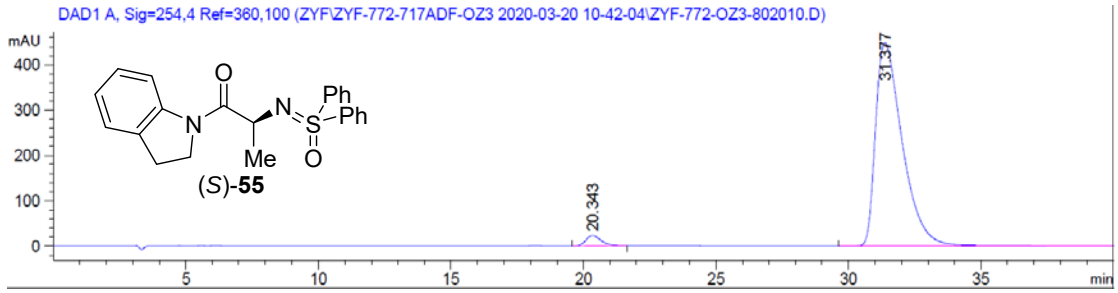
PDA Ch1 254nm

T	Hight	Area	Area%
14.773	203106	5376705	94.900
16.929	10396	288924	5.100



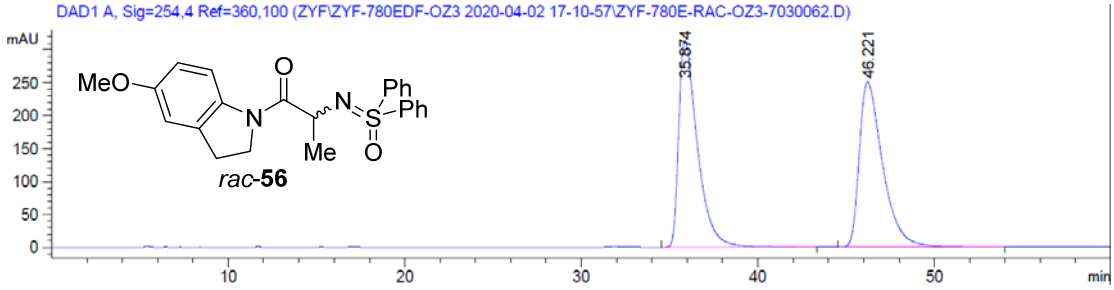
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.185	BB	0.6327	6343.55273	152.69914	50.0737
2	31.731	BB	1.0440	6324.86963	92.00576	49.9263
Totals :				1.26684e4	244.70490	



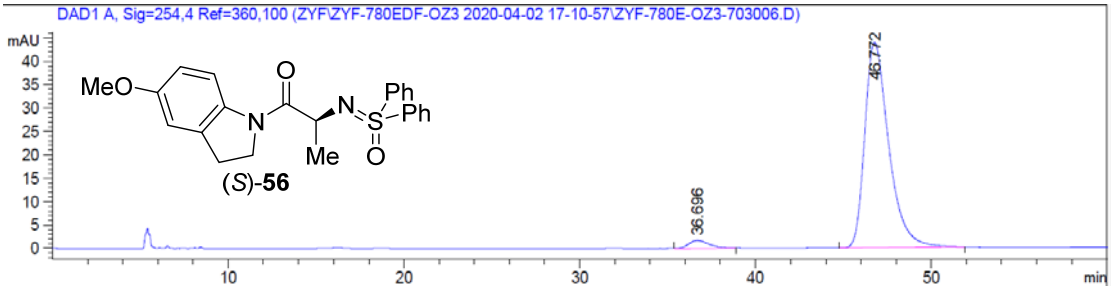
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.343	BB	0.6215	919.85565	22.95653	2.8282
2	31.377	BBA	1.0759	3.16047e4	448.60132	97.1718
Totals :				3.25245e4	471.55785	



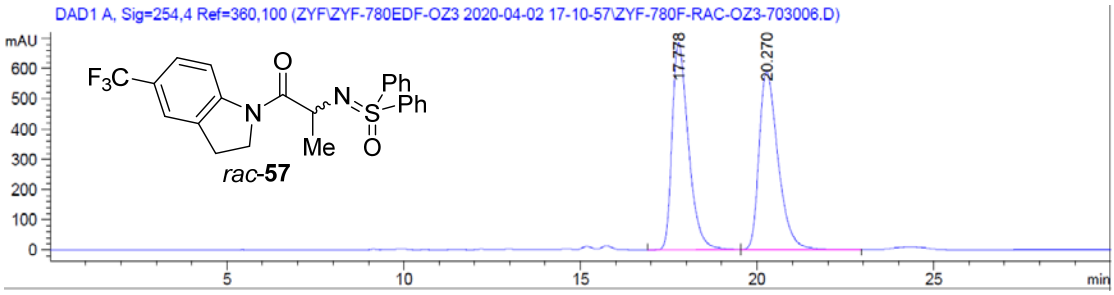
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.874	BB	1.1008	2.29967e4	313.88516	50.0245
2	46.221	BB	1.3728	2.29742e4	250.30614	49.9755
Totals :				4.59708e4	564.19130	



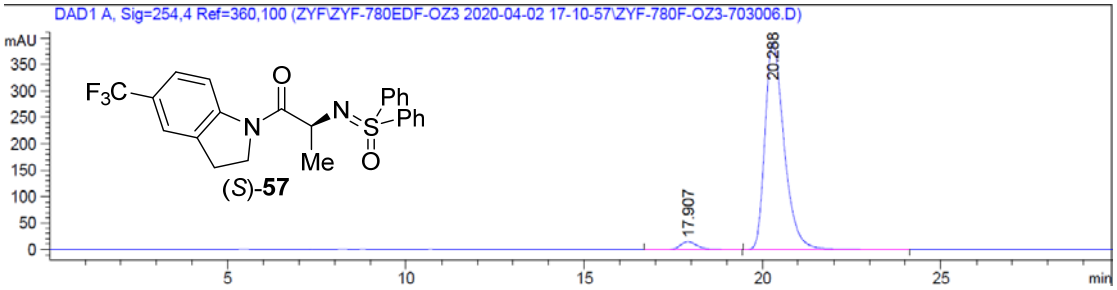
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.696	MM R	1.3398	139.82149	1.73928	3.2541
2	46.772	BB	1.4236	4156.90283	43.86626	96.7459
Totals :				4296.72432	45.60554	



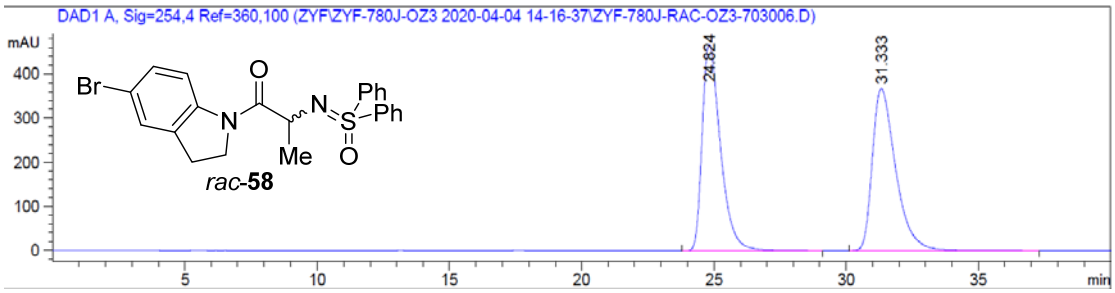
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.778	BB	0.4894	2.18919e4	683.92426	49.9939
2	20.270	BB	0.5687	2.18972e4	590.33777	50.0061
Totals :				4.37892e4	1274.26202	



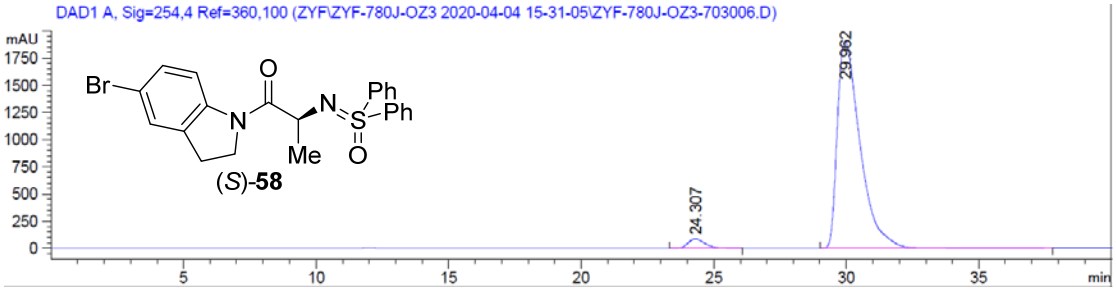
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.907	BB	0.5053	479.34879	14.51269	3.1842
2	20.288	BB	0.5704	1.45744e4	391.46890	96.8158
Totals :				1.50538e4	405.98159	



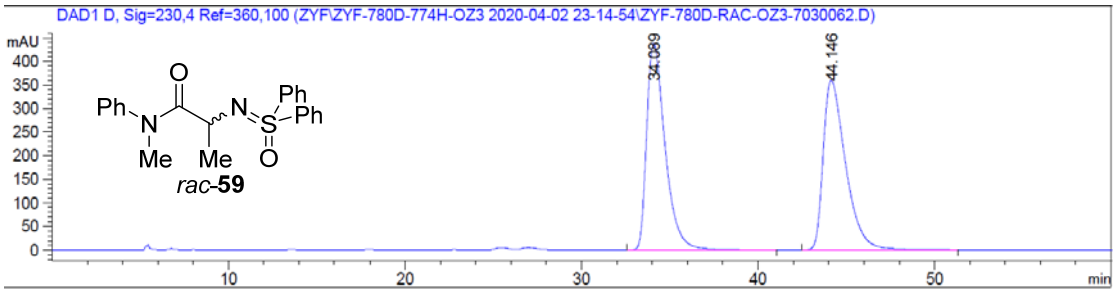
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.824	BB	0.7283	2.25128e4	468.75302	49.9218
2	31.333	BB	0.9383	2.25833e4	367.82880	50.0782
Totals :				4.50962e4	836.58182	



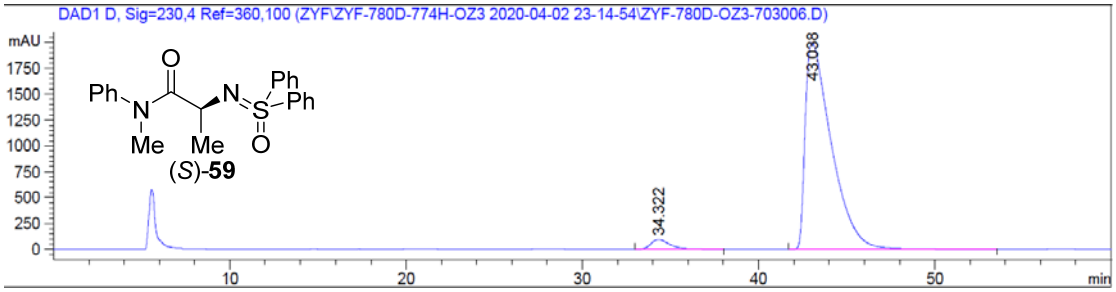
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.307	BB	0.6759	3803.23779	86.00909	3.2335
2	29.962	BB	0.9036	1.13816e5	1903.54834	96.7665
Totals :				1.17620e5	1989.55743	



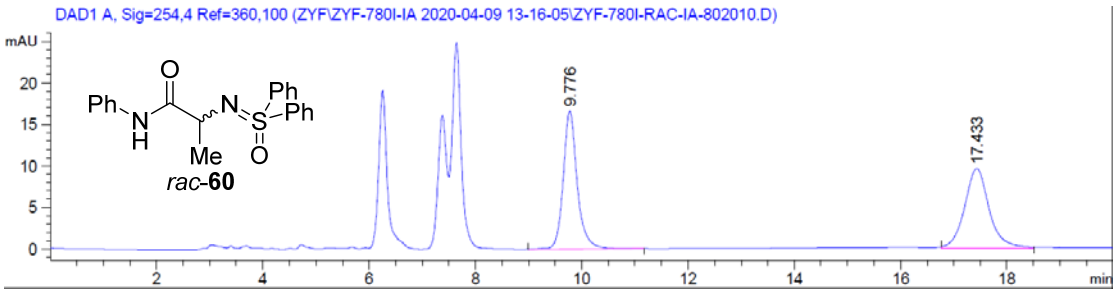
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.089	BB	1.0990	3.17399e4	438.23398	50.1479
2	44.146	BB	1.3293	3.15526e4	359.74316	49.8521
Totals :				6.32925e4	797.97714	



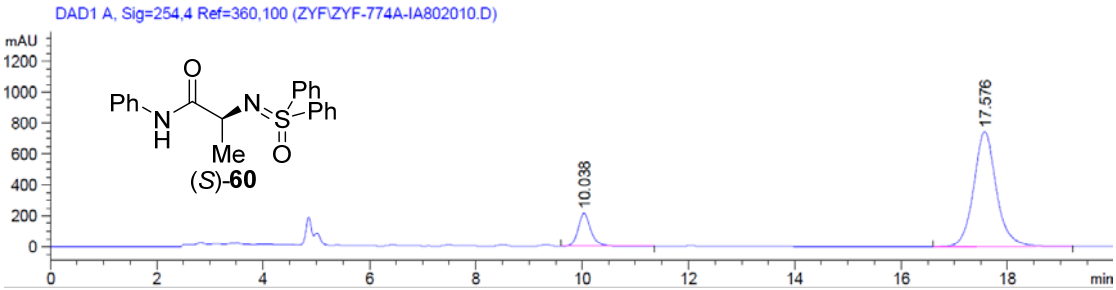
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.322	BB	1.1008	6925.98096	94.96967	3.2618
2	43.038	BB	1.5221	2.05411e5	1996.93567	96.7382
Totals :				2.12337e5	2091.90533	



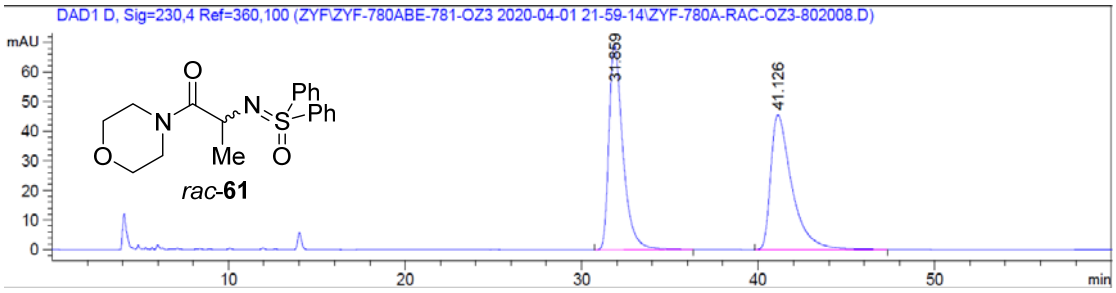
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.776	BB	0.2733	304.83850	16.67424	49.6669
2	17.433	MM R	0.5366	308.92709	9.59446	50.3331
Totals :				613.76559	26.26871	



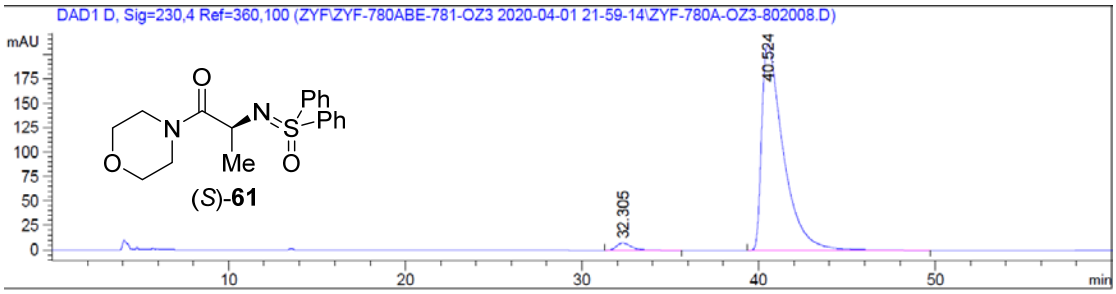
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.038	VB	0.2495	3579.75122	213.58316	14.0347
2	17.576	BB	0.4462	2.19267e4	743.28137	85.9653
Totals :				2.55064e4	956.86453	



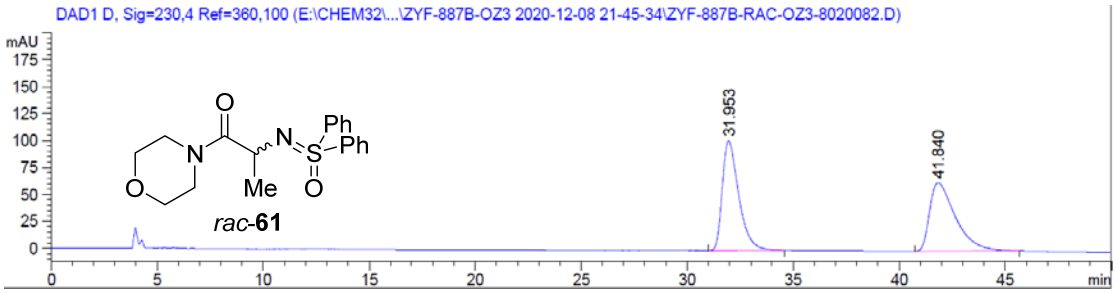
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.859	BB	0.8262	3821.35596	69.63688	50.1127
2	41.126	BB	1.2262	3804.16870	45.55674	49.8873
Totals :				7625.52466	115.19362	



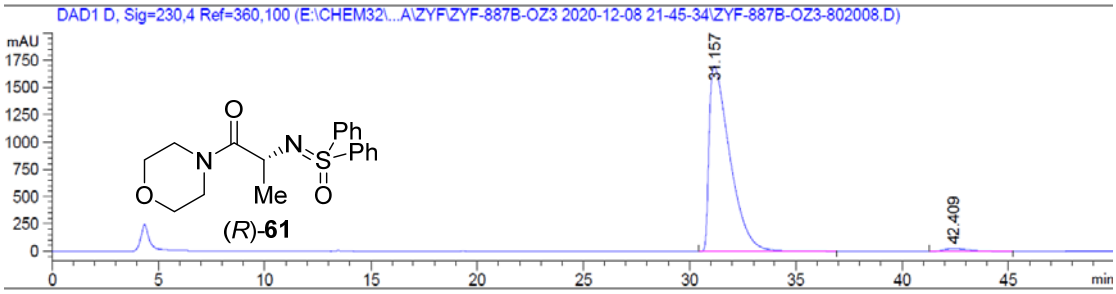
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.305	BB	0.8846	435.88144	7.27951	2.3709
2	40.524	BB	1.2470	1.79486e4	211.29892	97.6291
Totals :				1.83844e4	218.57843	



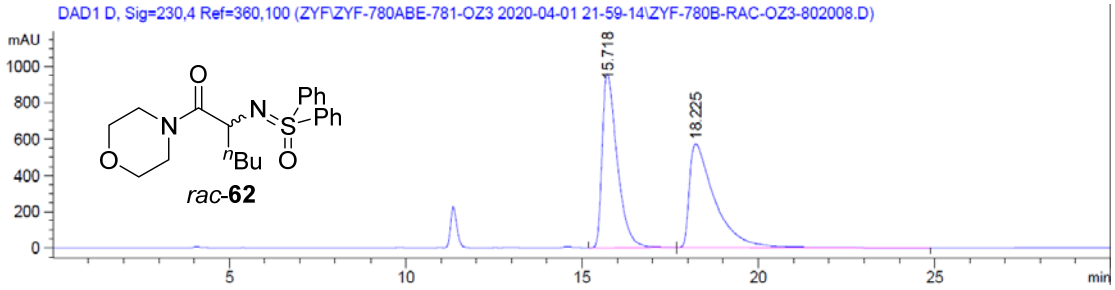
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.953	BB	0.8065	5487.00049	101.52797	50.3826
2	41.840	BB	1.1660	5403.65625	63.68179	49.6174
Totals :				1.08907e4	165.20976	



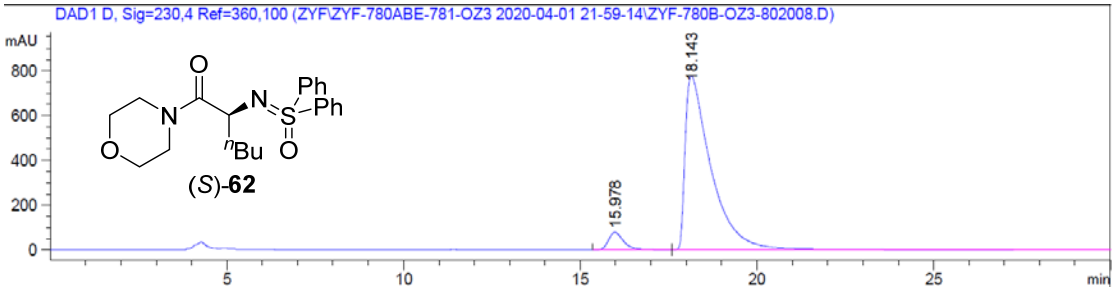
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.157	BB	0.9566	1.14461e5	1693.32275	98.3787
2	42.409	BB	1.0001	1886.37891	22.54610	1.6213
Totals :				1.16347e5	1715.86886	



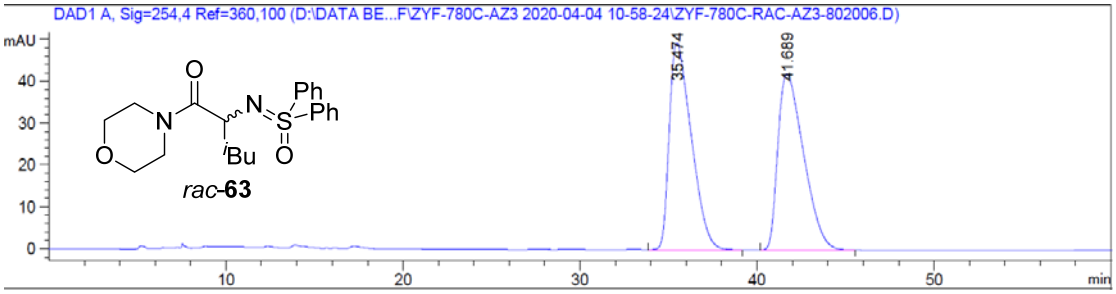
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.718	BB	0.4477	2.84080e4	958.70557	49.9325
2	18.225	BB	0.7223	2.84848e4	570.66528	50.0675
Totals :				5.68928e4	1529.37085	



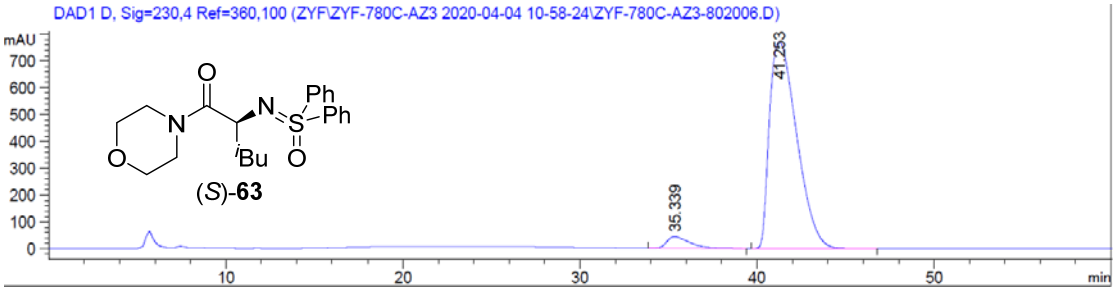
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.978	BB	0.4512	2303.86816	77.87305	5.4955
2	18.143	BB	0.7341	3.96186e4	777.97815	94.5045
Totals :				4.19224e4	855.85120	



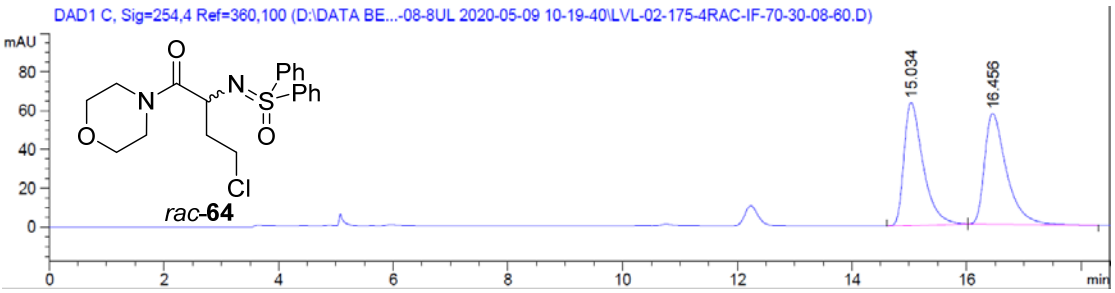
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.474	BB	1.2847	4265.30273	49.43028	50.1837
2	41.689	BB	1.5054	4234.07715	42.02741	49.8163
Totals :				8499.37988	91.45770	



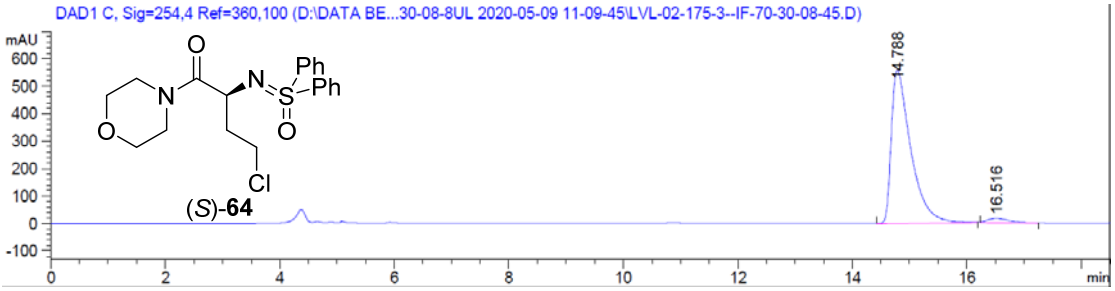
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.339	BB	1.2765	3862.34229	44.07092	4.4777
2	41.253	BB	1.6708	8.23952e4	772.25165	95.5223
Totals :				8.62575e4	816.32257	



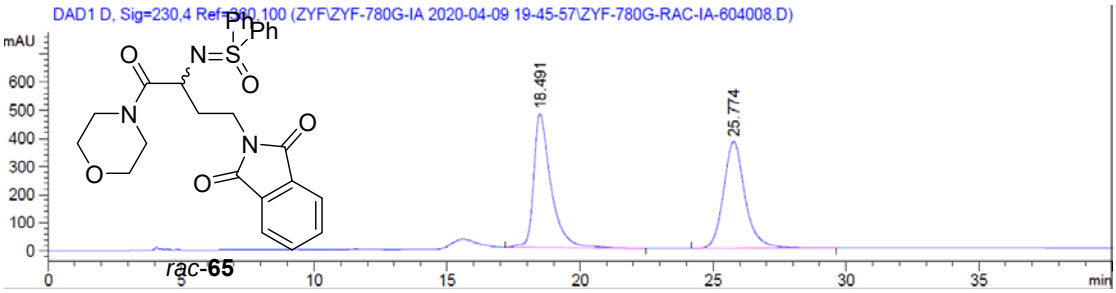
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.034	BB	0.3481	1467.87512	63.41177	49.1827
2	16.456	BB	0.3975	1516.65771	57.17370	50.8173
Totals :				2984.53284	120.58548	



Signal 3: DAD1 C, Sig=254,4 Ref=360,100

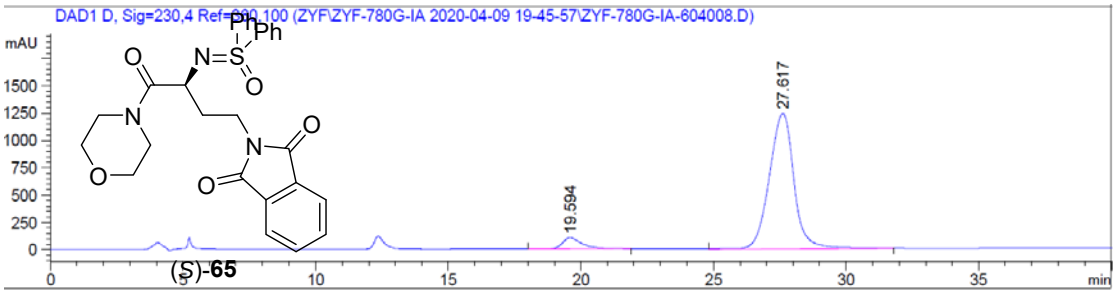
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.788	MM R	0.3944	1.32235e4	558.75153	96.6281
2	16.516	MM R	0.4690	461.44833	16.39979	3.3719
Totals :				1.36849e4	575.15131	



rac-**65**

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

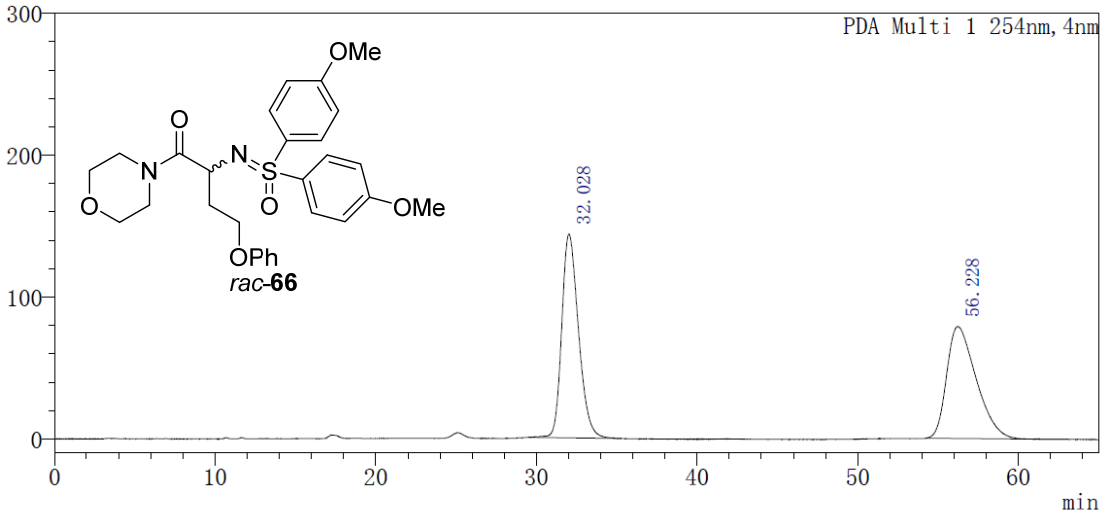
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.491	BB	0.6596	2.15415e4	476.30225	50.0235
2	25.774	BB	0.8526	2.15213e4	380.09293	49.9765
Totals :				4.30627e4	856.39517	



(*S*)-**65**

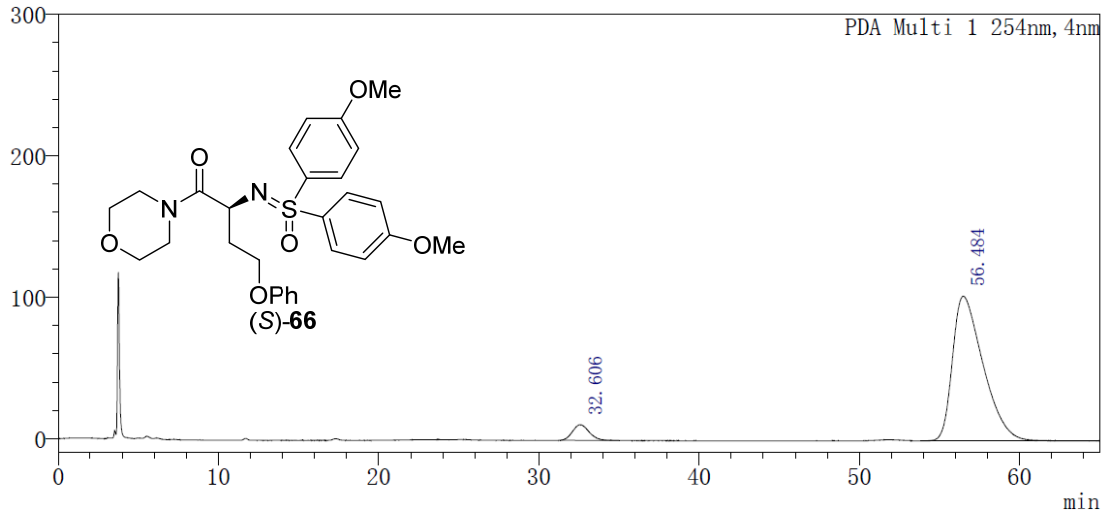
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.594	MM R	0.8162	4951.76563	101.10960	5.7893
2	27.617	MM R	1.0835	8.05810e4	1239.46155	94.2107
Totals :				8.55328e4	1340.57115	



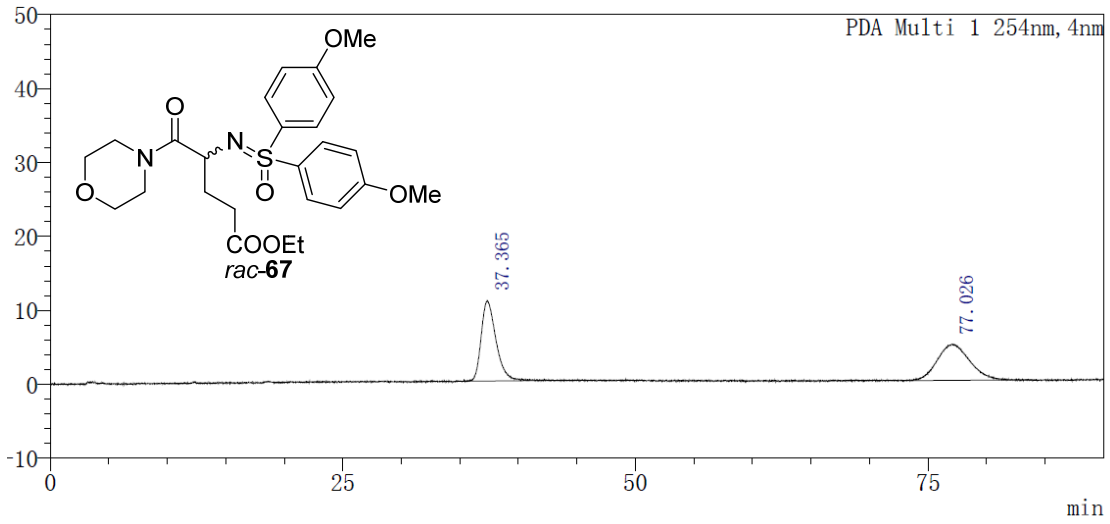
PDA Ch1 254nm

T	Hight	Area	Area%
32.028	143628	10415151	50.853
56.228	78944	10065707	49.147



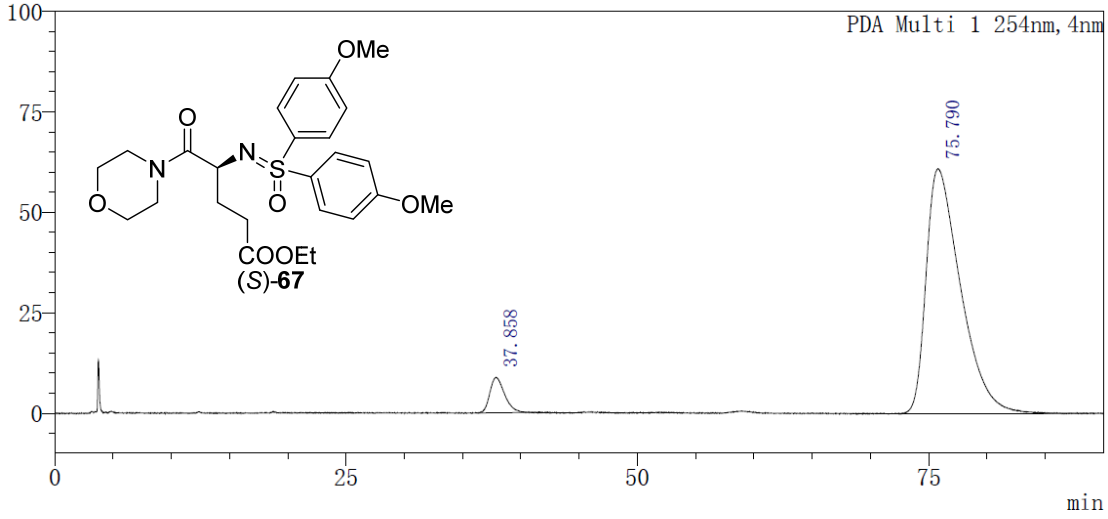
PDA Ch1 254nm

T	Hight	Area	Area%
32.606	11098	800369	5.571
56.484	102296	13566611	94.429



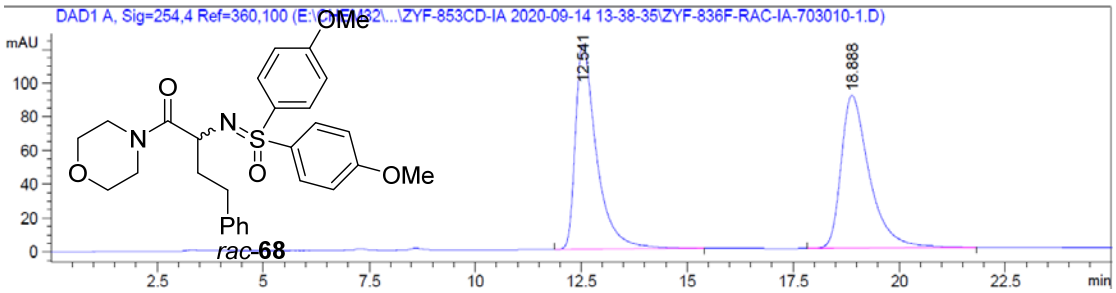
PDA Ch1 254nm

T	Hight	Area	Area%
37.365	10851	957714	50.678
77.026	4869	932104	49.322



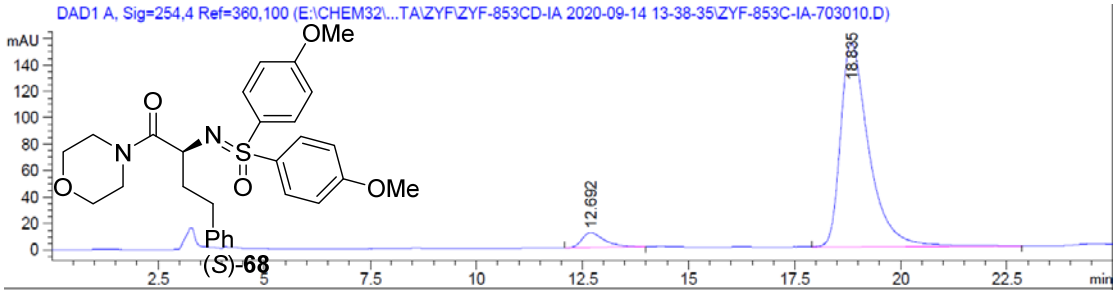
PDA Ch1 254nm

T	Hight	Area	Area%
37.858	8818	772369	5.789
75.790	60974	12569681	94.211



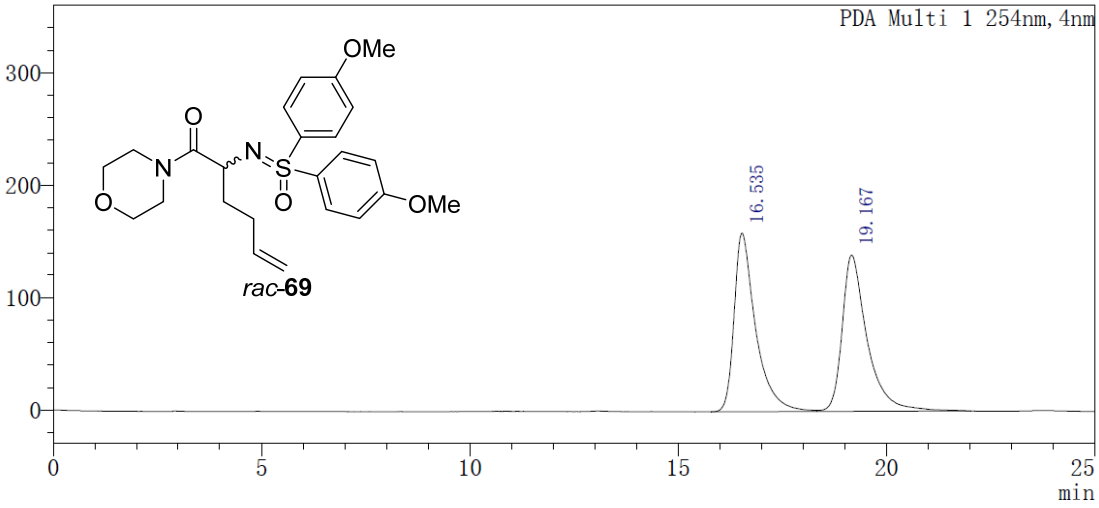
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.541	BB	0.5149	4212.57129	121.39346	50.0658
2	18.888	BB	0.6893	4201.50000	90.55860	49.9342
Totals :				8414.07129	211.95206	



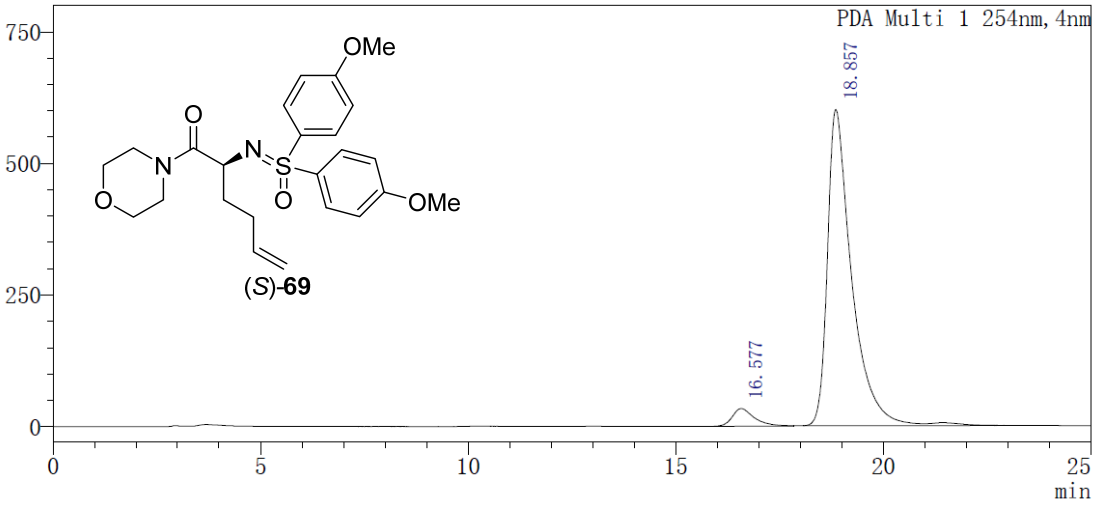
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.692	BB	0.5434	413.00174	11.16825	5.3754
2	18.835	MM R	0.7810	7270.23926	155.13843	94.6246
Totals :				7683.24100	166.30668	



PDA Ch1 254nm

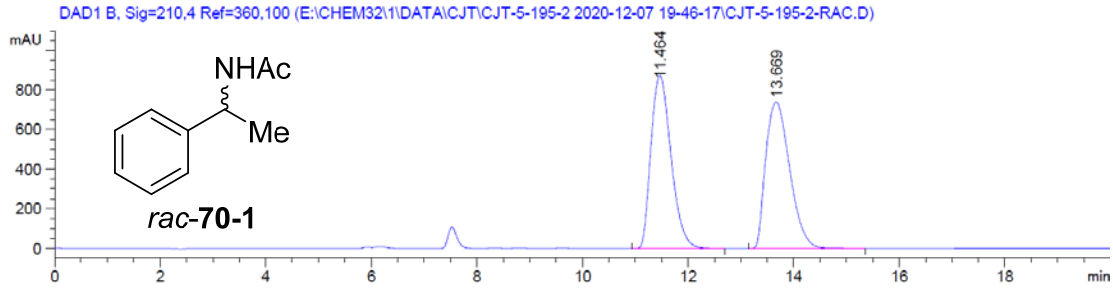
T	Hight	Area	Area%
16.535	159075	5738111	49.656
19.167	139082	5817665	50.344



PDA Ch1 254nm

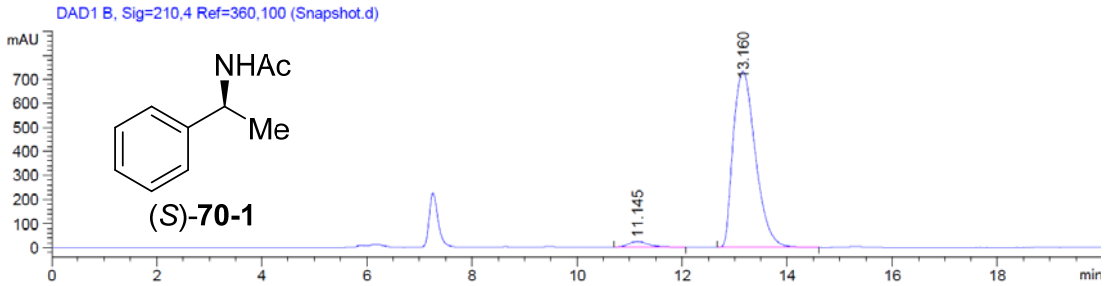
T	Hight	Area	Area%
16.577	33637	1254881	4.857
18.857	600831	24582029	95.143

70-1 Procedure a:



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

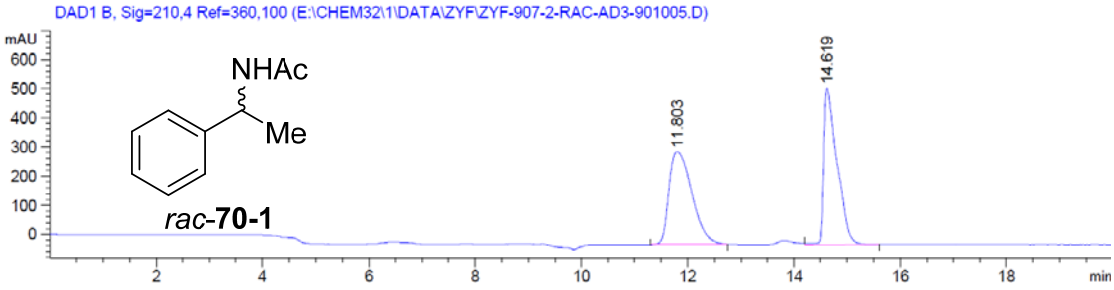
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.464	BB	0.4172	2.31839e4	874.91003	49.7112
2	13.669	BB	0.5023	2.34533e4	742.92719	50.2888
Totals :				4.66372e4	1617.83722	



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

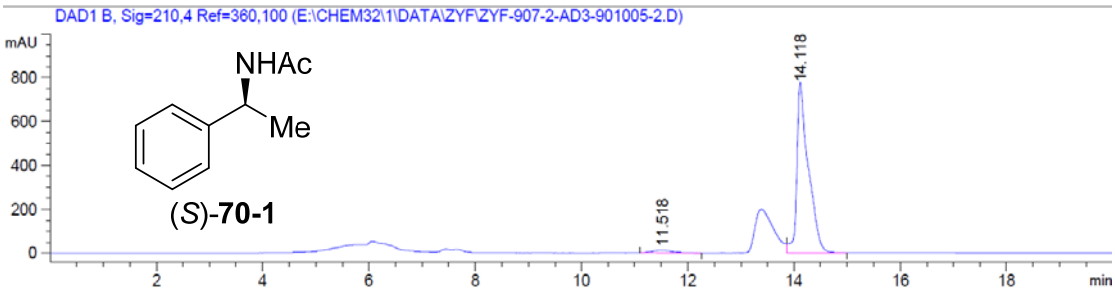
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.145	BB	0.3908	579.53302	22.62584	2.6287
2	13.160	BB	0.4706	2.14666e4	730.92181	97.3713
Totals :				2.20461e4	753.54766	

70-1 Procedure b:



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

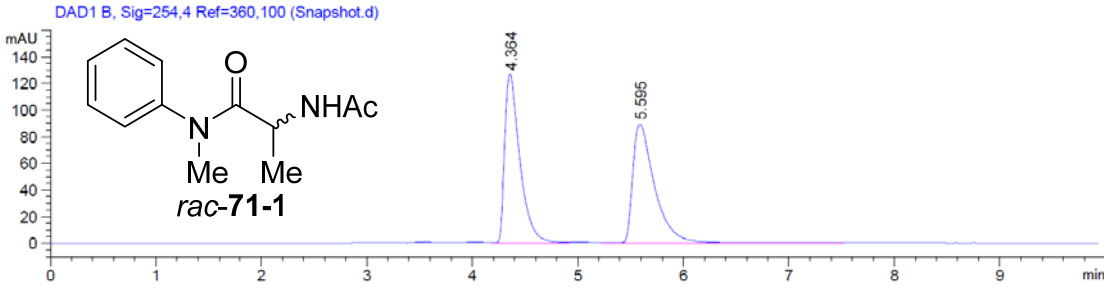
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.803	MM R	0.5035	9622.04785	318.52432	50.7779
2	14.619	FM R	0.2890	9327.25293	537.85400	49.2221
Totals :				1.89493e4	856.37833	



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

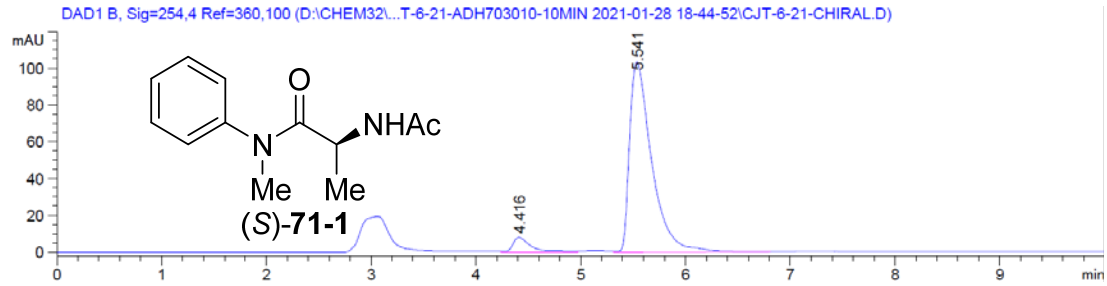
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.518	BV R	0.3523	329.84317	12.01479	2.7470
2	14.118	VB	0.2047	1.16775e4	780.02032	97.2530
Totals :				1.20074e4	792.03511	

71-1 procedure a:



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

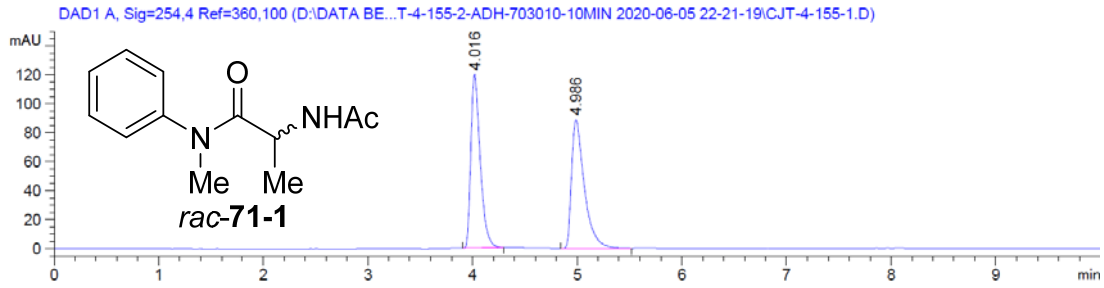
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.364	VV	0.1529	1263.34778	126.13493	49.8266
2	5.595	BB	0.2146	1272.14270	89.09251	50.1734
Totals :				2535.49048	215.22743	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

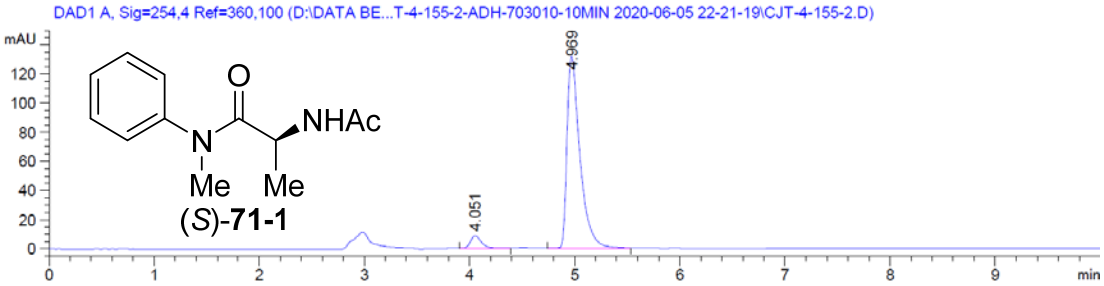
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.416	VV	0.1779	94.88505	7.80298	5.9097
2	5.541	VB	0.2187	1510.70288	103.27180	94.0903
Totals :				1605.58793	111.07478	

71-1 procedure b:



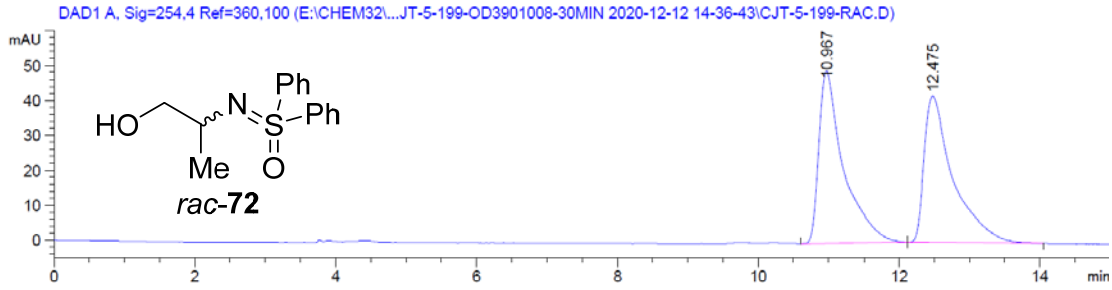
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.016	BB	0.0944	744.98492	119.97974	49.7860
2	4.986	BB	0.1268	751.38831	88.73402	50.2140
Totals :				1496.37323	208.71376	



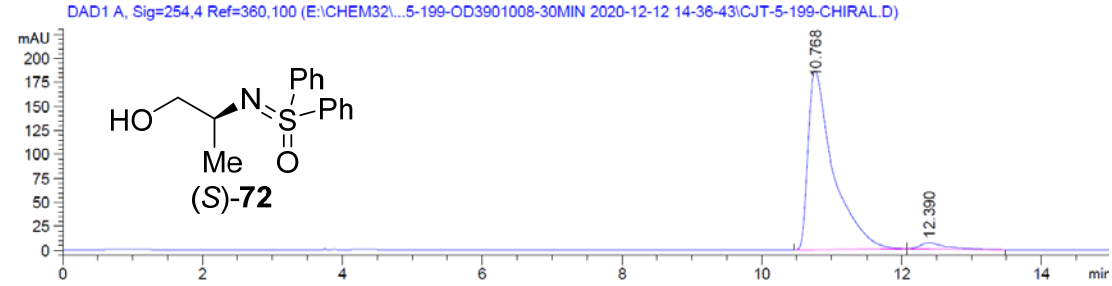
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.051	BB	0.1086	61.60689	8.70290	5.2014
2	4.969	BB	0.1275	1122.81873	131.60585	94.7986
Totals :				1184.42562	140.30875	



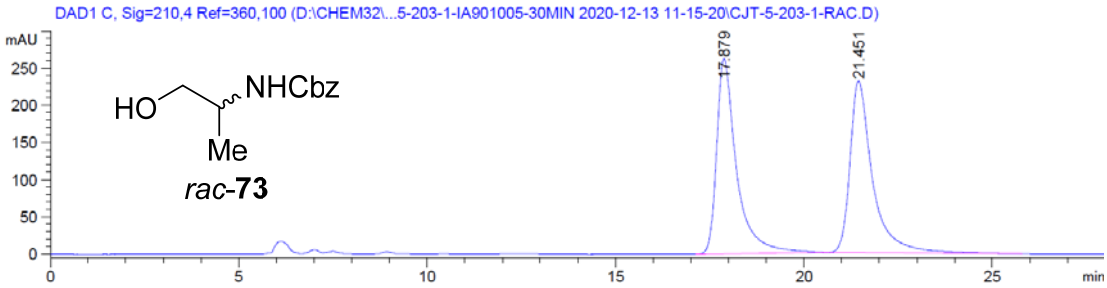
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.967	BB	0.3470	1197.34814	49.35469	50.0541
2	12.475	BB	0.4105	1194.76099	41.91695	49.9459
Totals :				2392.10913	91.27163	



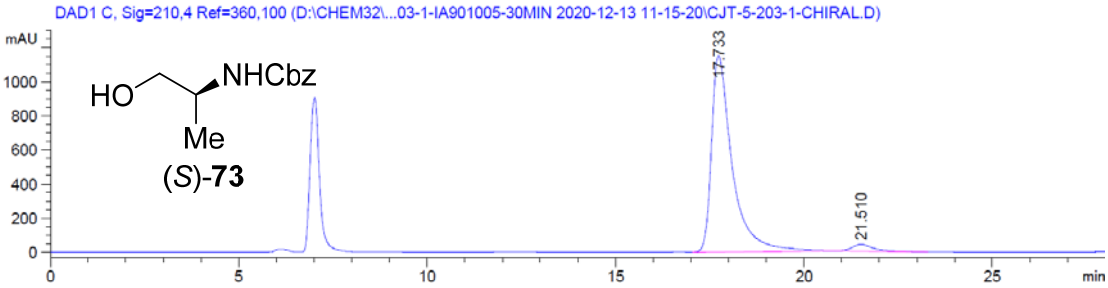
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.768	BB	0.3610	4674.11084	186.11456	96.6247
2	12.390	BB	0.3648	163.27538	6.41850	3.3753
Totals :				4837.38622	192.53306	



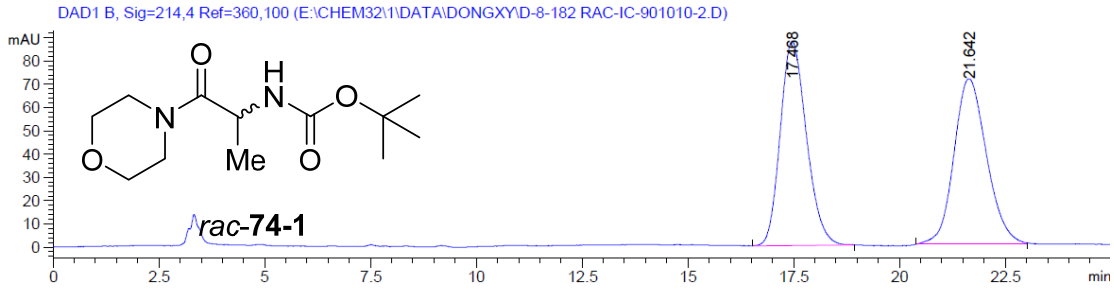
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.879	BB	0.5361	9619.58008	262.16507	50.0112
2	21.451	BB	0.6099	9615.27930	230.85823	49.9888
Totals :				1.92349e4	493.02330	



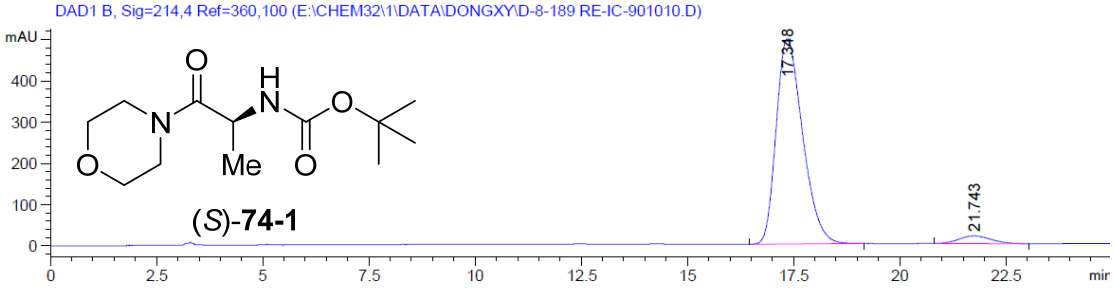
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.733	BB	0.5624	4.39897e4	1149.79004	96.6062
2	21.510	BB	0.5807	1545.38208	39.64761	3.3938
Totals :				4.55351e4	1189.43765	



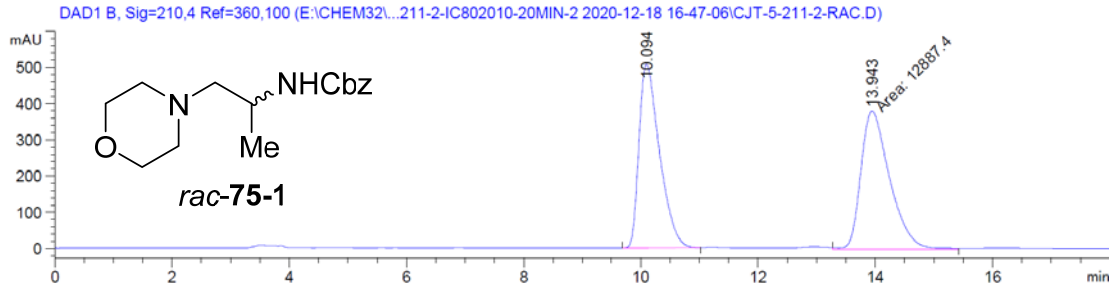
Signal 2: DAD1 B, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.468	BB	0.6521	3776.80518	87.75518	49.8942
2	21.642	MM R	0.8907	3792.81567	70.97343	50.1058
Totals :				7569.62085	158.72861	



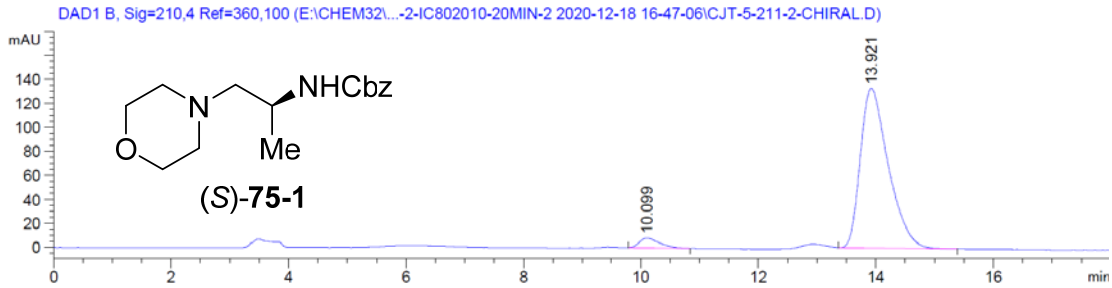
Signal 2: DAD1 B, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.348	BB	0.6713	2.15294e4	497.04449	95.6299
2	21.743	BB	0.6155	983.86243	18.89479	4.3701
Totals :				2.25133e4	515.93929	



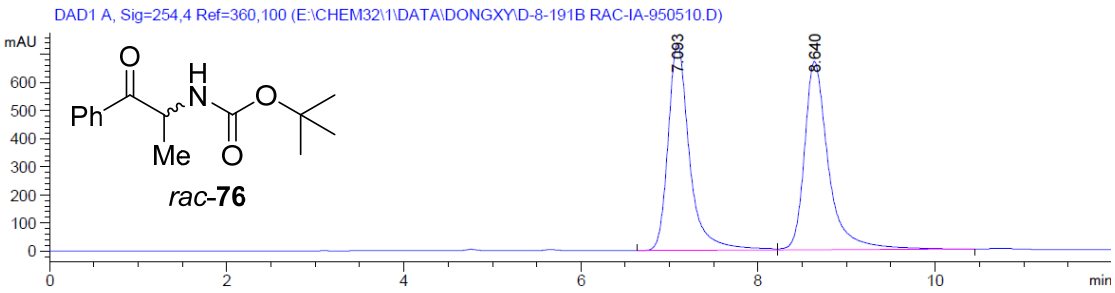
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.094	BB	0.3651	1.22806e4	506.03769	48.7944
2	13.943	MM	0.5663	1.28874e4	379.29300	51.2056
Totals :				2.51680e4	885.33069	



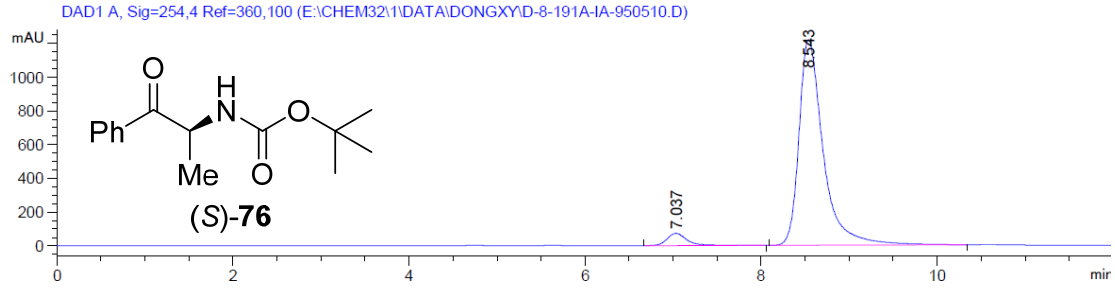
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.099	BB	0.3491	199.66264	8.28641	4.3393
2	13.921	BB	0.4980	4401.57178	133.03854	95.6607
Totals :				4601.23442	141.32495	



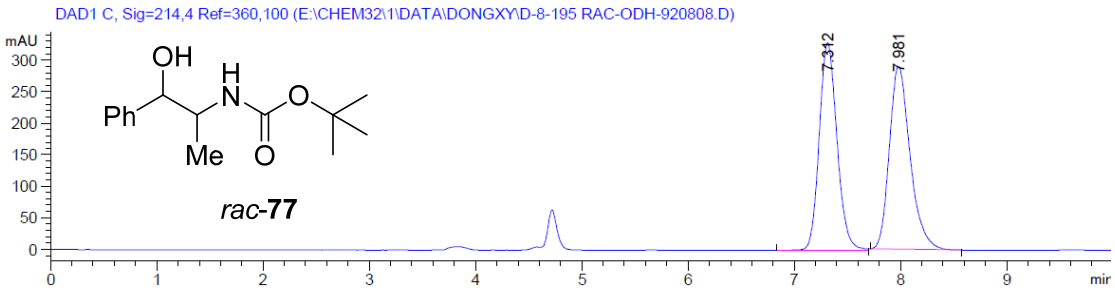
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.093	BV	0.2510	1.23022e4	735.97424	49.3968
2	8.640	VB	0.2814	1.26027e4	670.08380	50.6032
Totals :				2.49049e4	1406.05804	



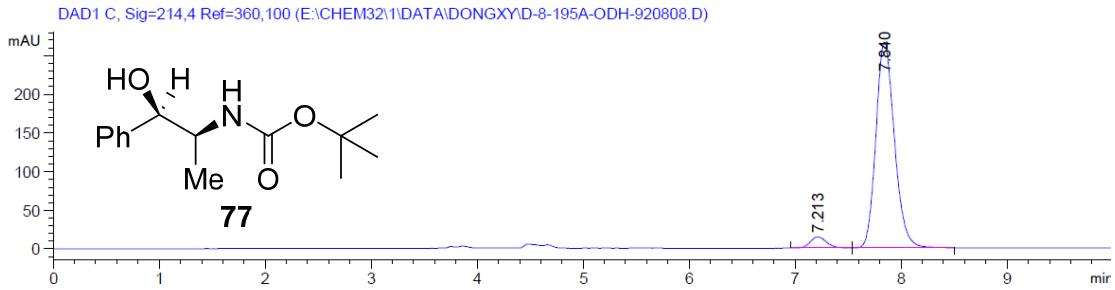
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.037	BB	0.2389	1142.35095	72.09510	4.6600
2	8.543	BB	0.2877	2.33717e4	1218.81848	95.3400
Totals :				2.45140e4	1290.91358	



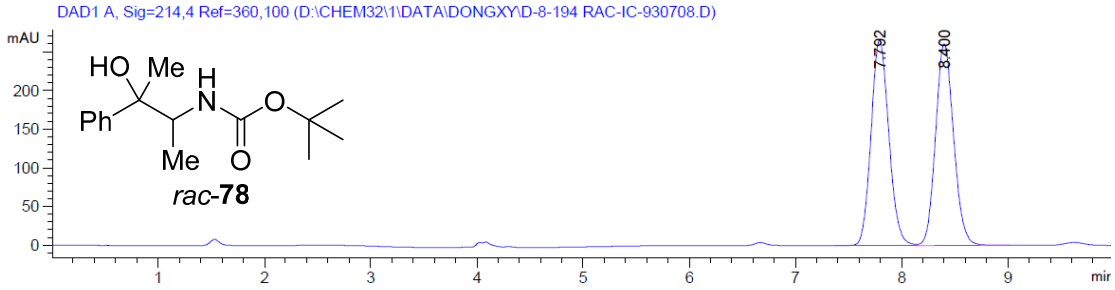
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.312	BV	0.1792	3813.89136	329.09067	49.2725
2	7.981	MM R	0.2260	3926.50757	289.60992	50.7275
Totals :				7740.39893	618.70059	



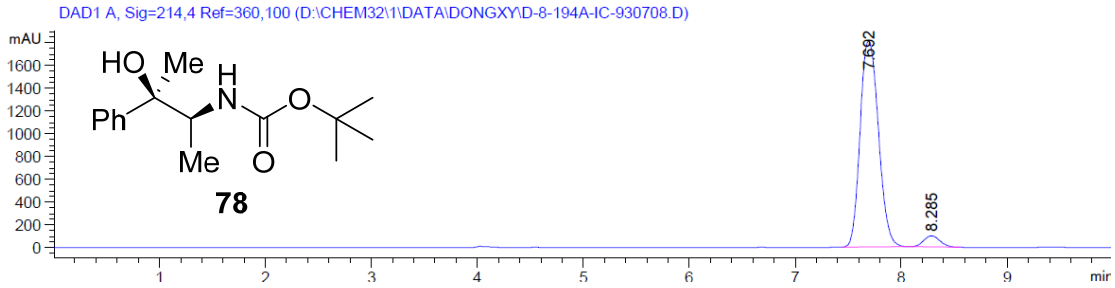
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.213	BB	0.1655	155.55150	14.45717	4.5762
2	7.840	BB	0.1879	3243.57764	266.63788	95.4238
Totals :				3399.12914	281.09505	



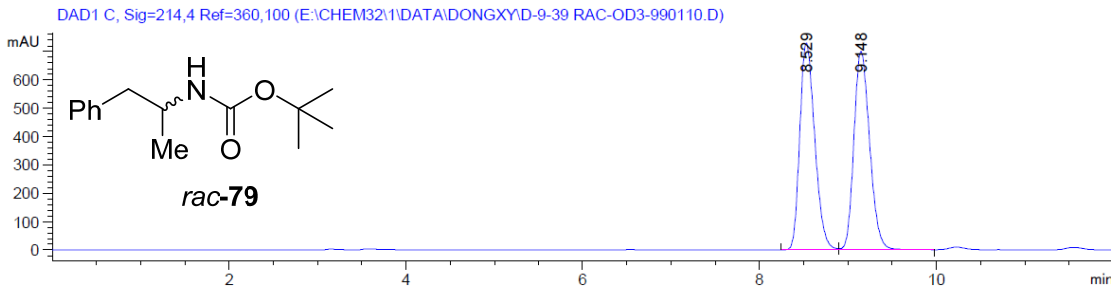
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.792	BV	0.1819	3095.37964	265.76370	50.1003
2	8.400	VB	0.1819	3082.98071	260.90656	49.8997
Totals :				6178.36035	526.67026	



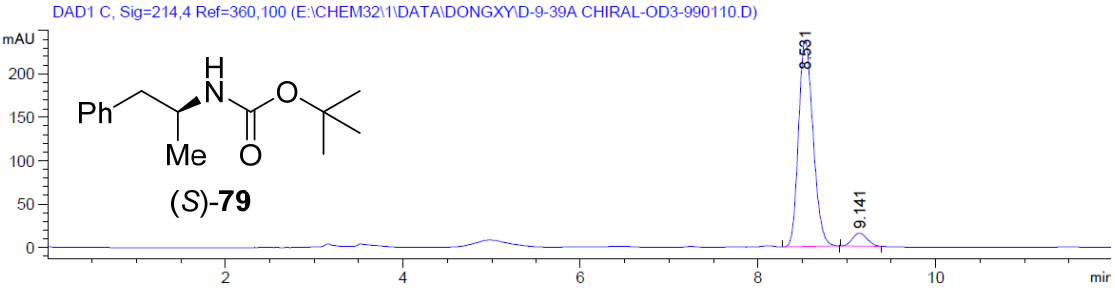
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.692	MM R	0.2005	2.18047e4	1812.46399	95.3332
2	8.285	MM R	0.1811	1067.38721	98.22916	4.6668
Totals :				2.28720e4	1910.69315	



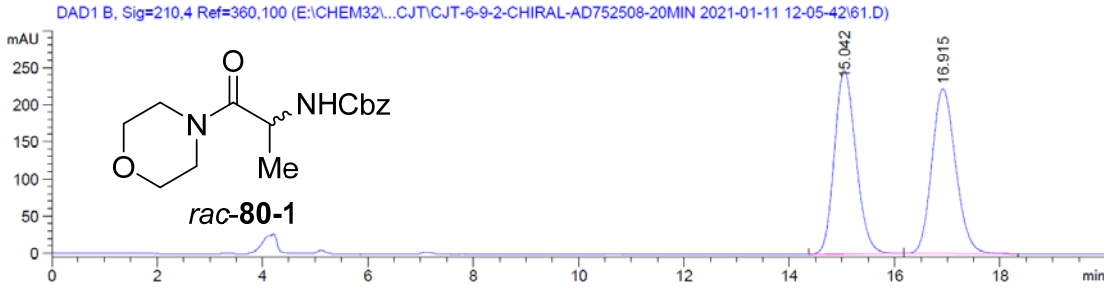
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.529	BV	0.1831	8572.78613	729.68750	49.7934
2	9.148	VB	0.1922	8643.93066	699.47711	50.2066
Totals :				1.72167e4	1429.16461	



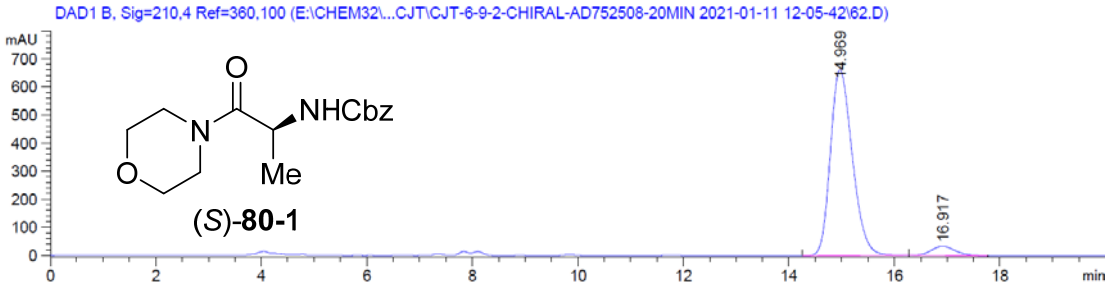
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.531	MM R	0.1893	2705.58447	238.17113	94.0151
2	9.141	MM R	0.1908	172.23415	15.04331	5.9849
Totals :				2877.81862	253.21444	



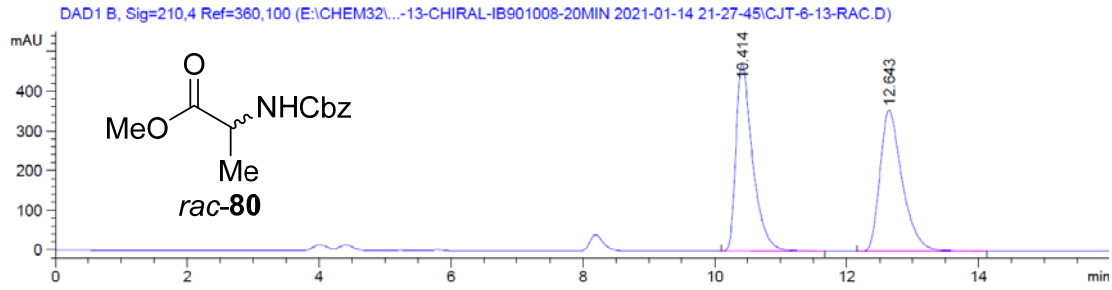
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.042	BB	0.4386	6992.24902	246.74162	50.0895
2	16.915	BB	0.4900	6967.25537	222.10153	49.9105
Totals :				1.39595e4	468.84315	



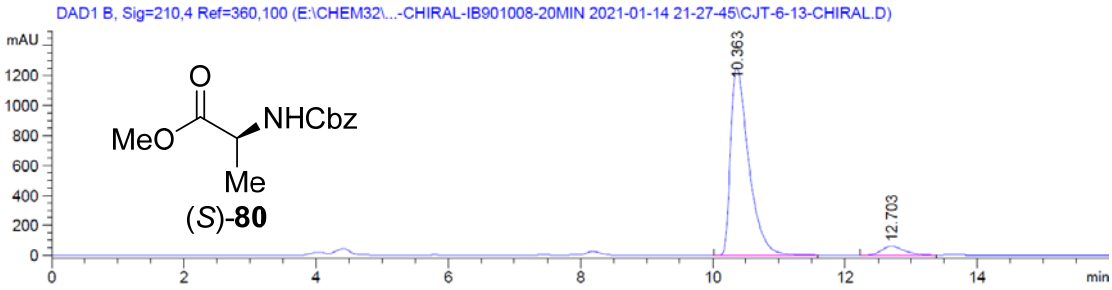
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.969	BB	0.4478	1.90429e4	661.55133	94.9757
2	16.917	BB	0.4606	1007.38684	32.59061	5.0243
Totals :				2.00503e4	694.14194	



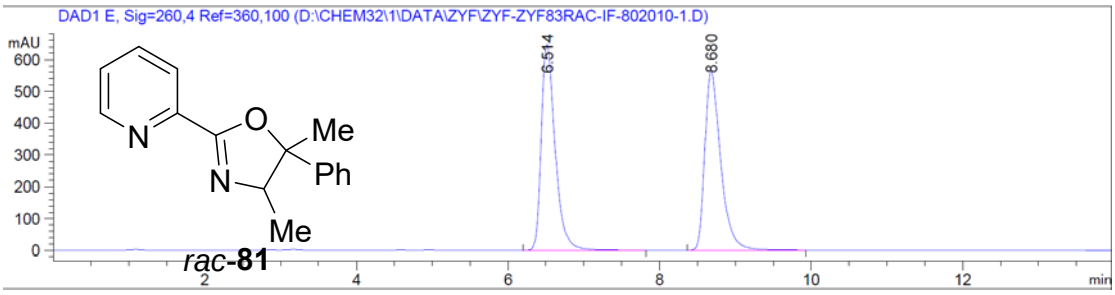
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.414	BB	0.2596	8253.10645	472.80496	49.7137
2	12.643	BB	0.3499	8348.16602	355.62445	50.2863
Totals :				1.66013e4	828.42941	



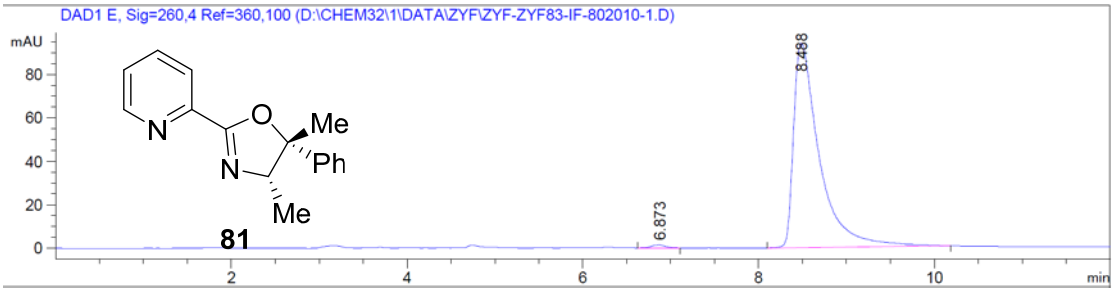
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.363	BB	0.2866	2.37640e4	1257.01978	94.6372
2	12.703	BB	0.3499	1346.63257	58.63842	5.3628
Totals :				2.51106e4	1315.65819	



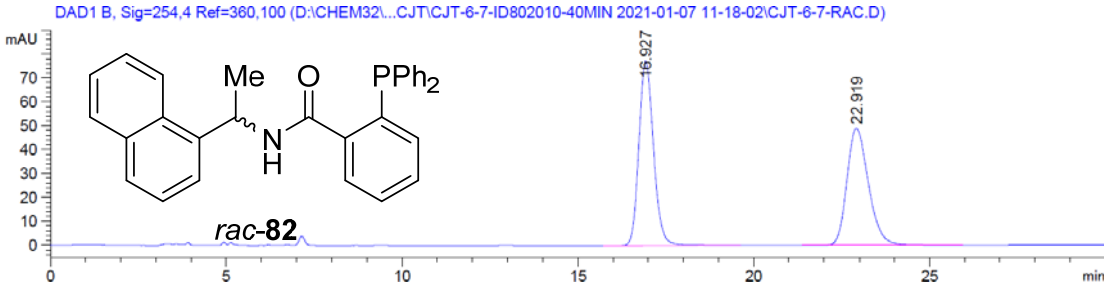
Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.514	BB	0.1940	8223.98730	648.10333	49.9683
2	8.680	BB	0.2205	8234.40723	563.55042	50.0317
Totals :				1.64584e4	1211.65375	



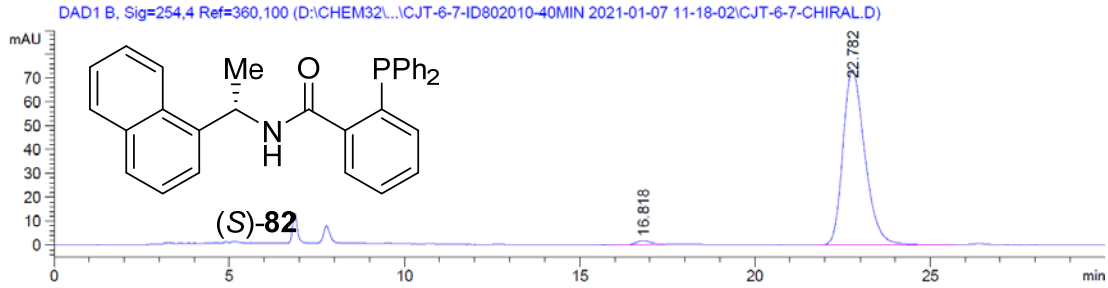
Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.873	BB	0.1661	16.02410	1.43743	0.8243
2	8.488	BB	0.2987	1927.99121	94.22214	99.1757
Totals :				1944.01531	95.65957	



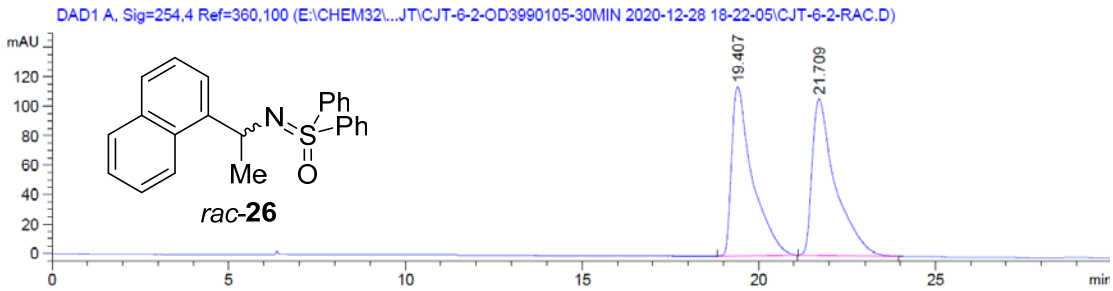
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.927	BB	0.4460	2238.84741	77.27638	51.7104
2	22.919	BB	0.6580	2090.74072	48.98307	48.2896
Totals :				4329.58813	126.25945	



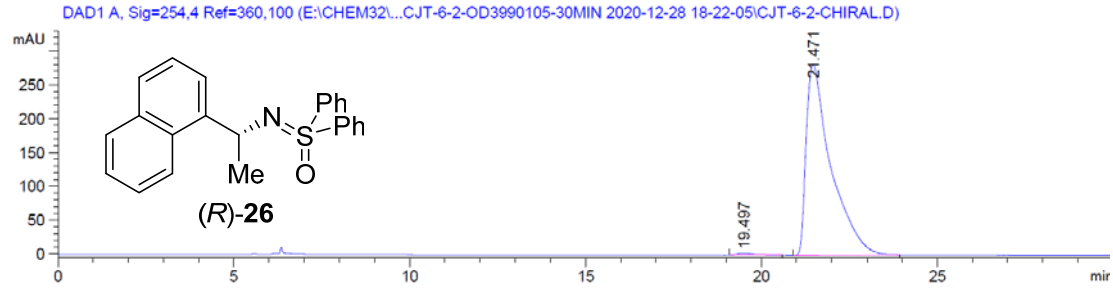
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.818	BV	0.4647	51.80617	1.69436	1.6029
2	22.782	BV	0.6651	3180.30957	73.46073	98.3971
Totals :				3232.11574	75.15510	



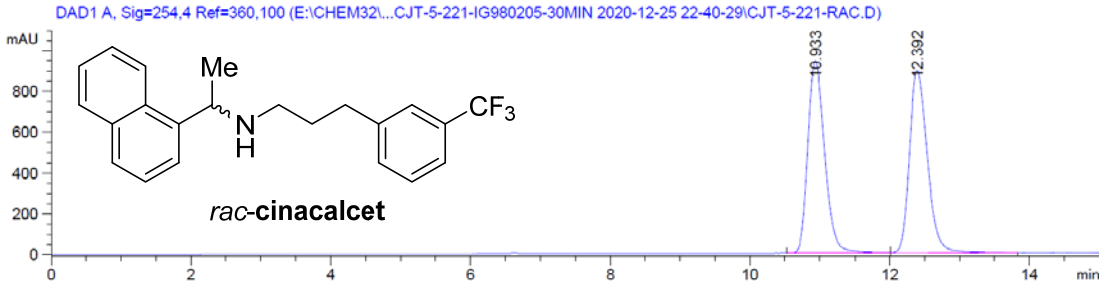
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.407	BB	0.5808	4695.06787	114.88725	49.1627
2	21.709	BB	0.6496	4855.00000	106.15434	50.8373
Totals :				9550.06787	221.04159	



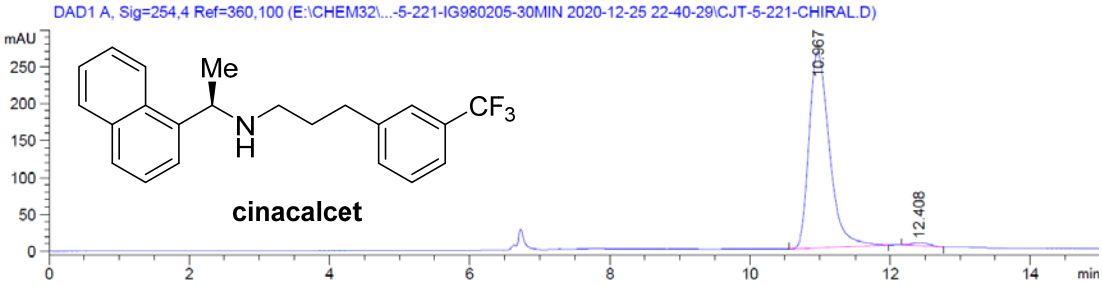
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.497	BB	0.4310	97.29700	2.70886	0.7042
2	21.471	BB	0.6988	1.37202e4	281.41525	99.2958
Totals :				1.38175e4	284.12412	



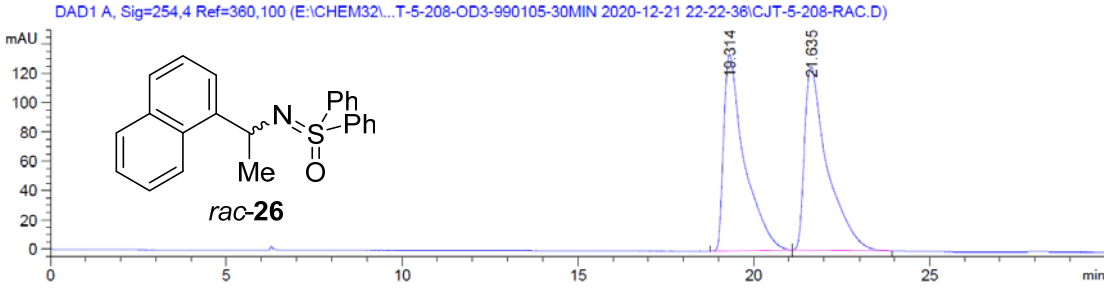
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.933	BV	0.2603	1.58807e4	943.72546	49.9267
2	12.392	VB	0.2778	1.59274e4	894.22443	50.0733
Totals :				3.18081e4	1837.94989	



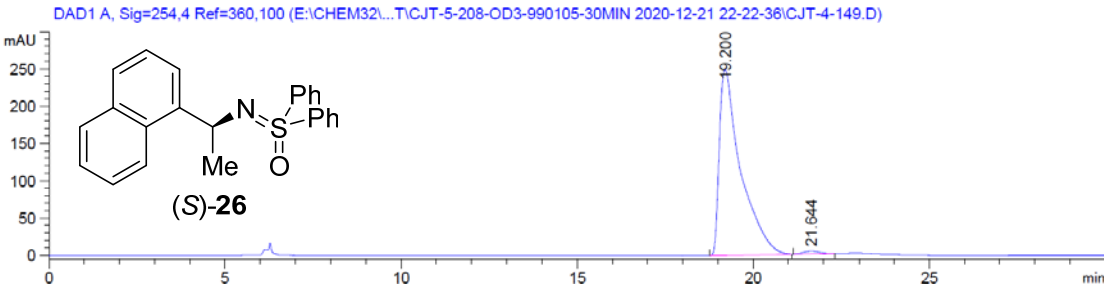
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.967	BB	0.3131	5354.47510	265.73593	98.6960
2	12.408	BB	0.2321	70.74434	4.20884	1.3040
Totals :				5425.21944	269.94477	



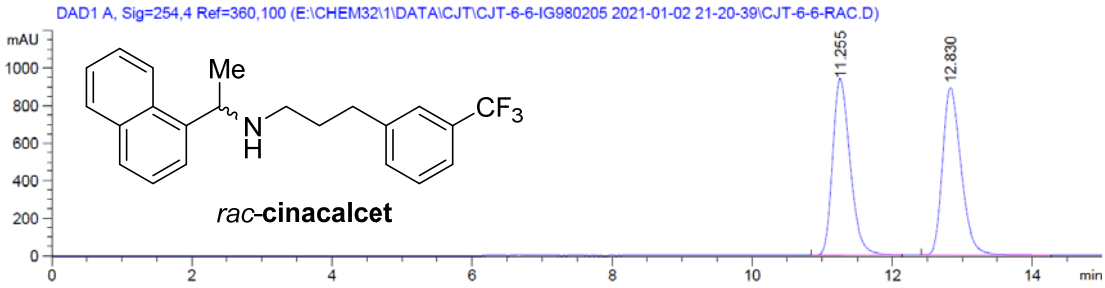
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.314	BB	0.5793	5479.00537	134.48413	49.1944
2	21.635	BB	0.6429	5658.46143	125.29555	50.8056
Totals :				1.11375e4	259.77968	



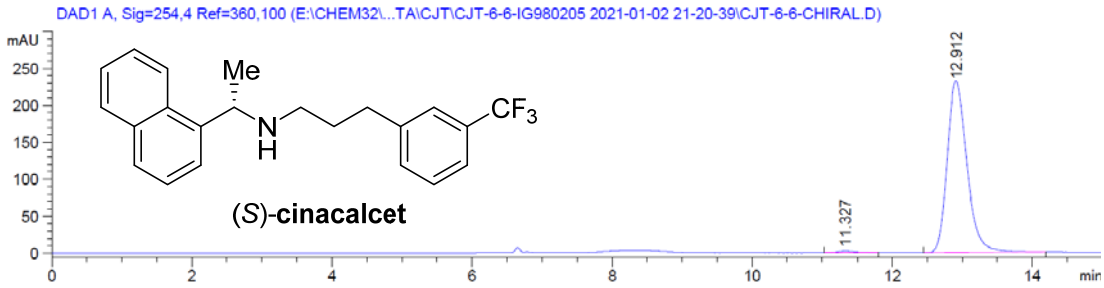
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.200	BB	0.6046	1.04809e4	249.24472	98.8089
2	21.644	BB	0.3911	126.33920	3.90864	1.1911
Totals :				1.06072e4	253.15336	



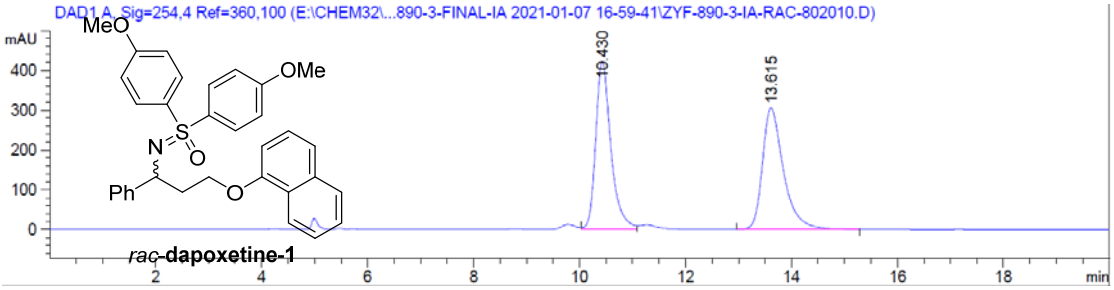
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.255	BB	0.2685	1.63785e4	943.45209	49.8839
2	12.830	BB	0.2847	1.64547e4	894.31372	50.1161
Totals :				3.28332e4	1837.76581	



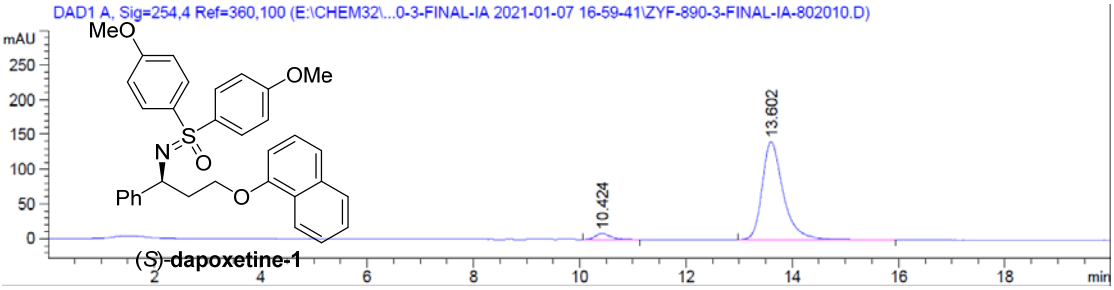
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.327	BB	0.2238	46.54716	2.58846	1.0121
2	12.912	BB	0.3006	4552.39404	232.29883	98.9879
Totals :				4598.94120	234.88728	



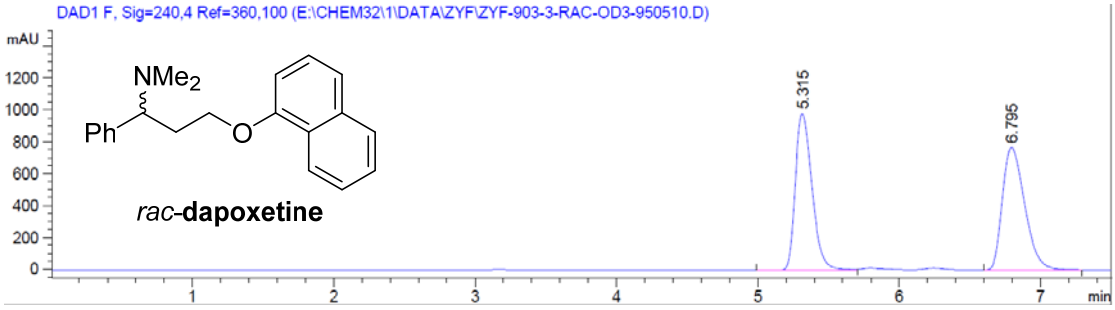
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.430	MF R	0.3324	8408.82520	421.64929	49.9769
2	13.615	BB	0.4160	8416.61035	304.95752	50.0231
Totals :				1.68254e4	726.60681	



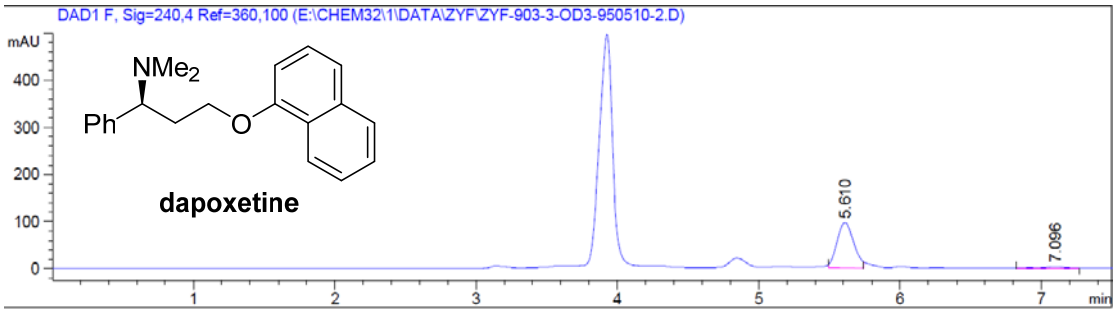
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.424	BB	0.2914	165.50771	8.41813	4.0920
2	13.602	BB	0.4154	3879.13306	140.79268	95.9080
Totals :				4044.64076	149.21081	



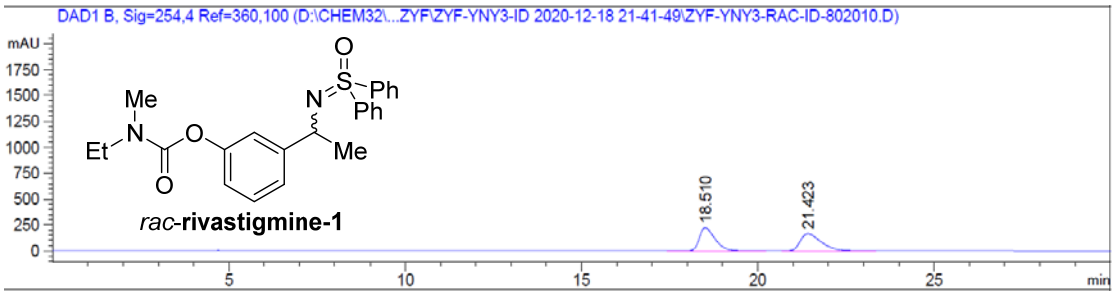
Signal 5: DAD1 F, Sig=240,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.315	MF R	0.1363	8028.58691	981.92572	48.7460
2	6.795	MM R	0.1823	8441.67676	771.74994	51.2540
Totals :				1.64703e4	1753.67566	



Signal 5: DAD1 F, Sig=240,4 Ref=360,100

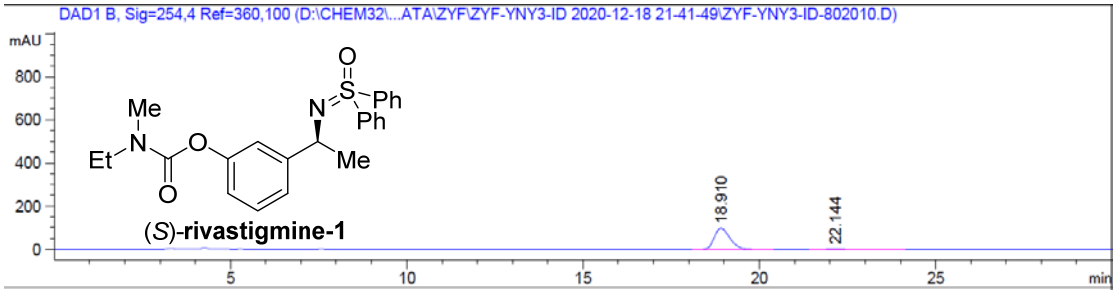
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.610	FM R	0.1367	788.99292	96.20926	96.5057
2	7.096	MM R	0.1442	28.56778	3.30167	3.4943
Totals :				817.56070	99.51093	



rac-**rivastigmine-1**

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

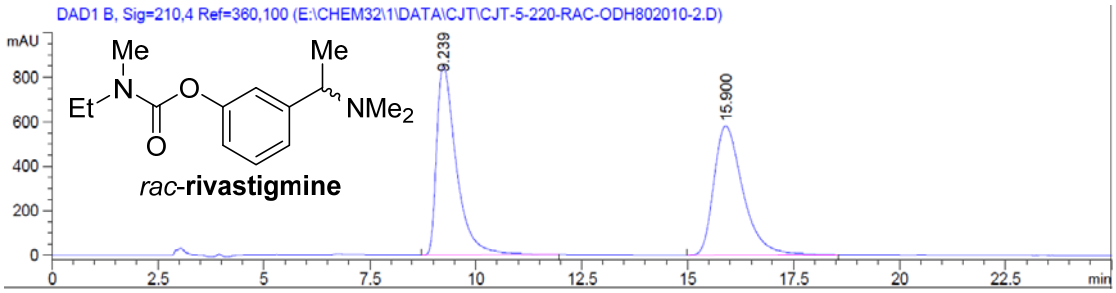
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.510	BV	0.4722	6791.69678	222.45860	50.1599
2	21.423	VB	0.6242	6748.38721	165.32813	49.8401
Totals :				1.35401e4	387.78673	



(*S*)-**rivastigmine-1**

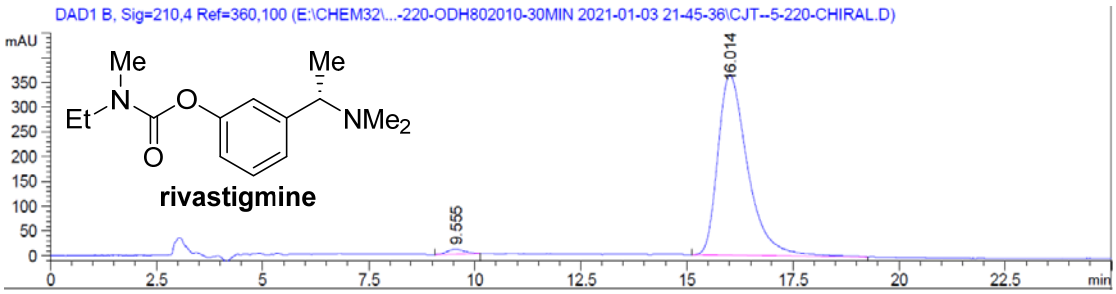
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.910	BV	0.4723	2979.02002	97.55349	98.1745
2	22.144	VB	0.6112	55.39318	1.31574	1.8255
Totals :				3034.41320	98.86923	



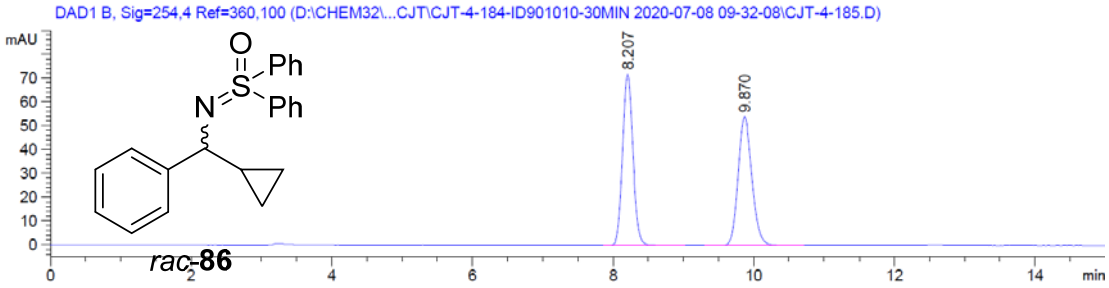
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.239	BV R	0.4819	2.73700e4	849.41785	49.7320
2	15.900	BB	0.7230	2.76650e4	579.42853	50.2680
Totals :				5.50350e4	1428.84637	



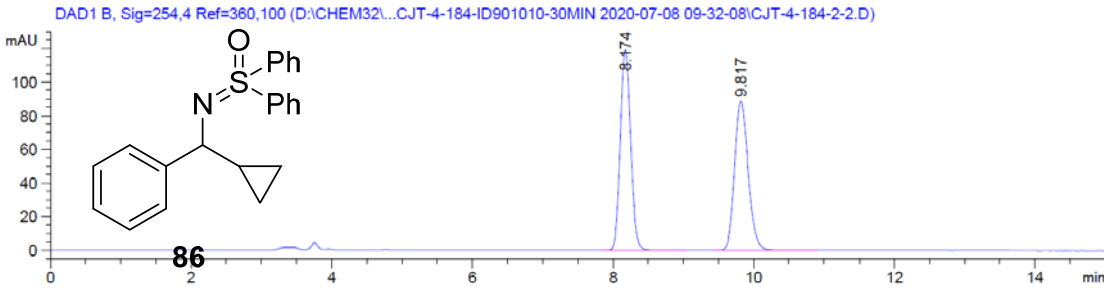
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.555	BB	0.3444	285.78000	9.91021	1.5771
2	16.014	BB	0.7124	1.78343e4	363.49234	98.4229
Totals :				1.81201e4	373.40255	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.207	BB	0.1593	732.68152	71.68010	49.9665
2	9.870	BV	0.2149	733.66266	53.88187	50.0335
Totals :				1466.34418	125.56197	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.174	BV	0.1584	1210.50232	119.30834	50.3436
2	9.817	BV	0.2133	1193.97937	88.53080	49.6564
Totals :				2404.48169	207.83914	

References

1. Dong, X.-Y.; Zhang, Y.-F.; Ma, C.-L.; Gu, Q.-S.; Wang, F.-L.; Li, Z.-L.; Jiang, S.-P.; Liu, X.-Y. A General Asymmetric Copper-Catalysed Sonogashira C(sp^3)–C(sp) Coupling. *Nat. Chem.* **2019**, *11*, 1158–1166.