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Supplementary information

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Enantioselective synthesis of sulfur-stereogenic alkyl sulfilimines with C(sp^3)–H-derived alkyl radicals using copper catalysis

In the format provided by the authors and unedited

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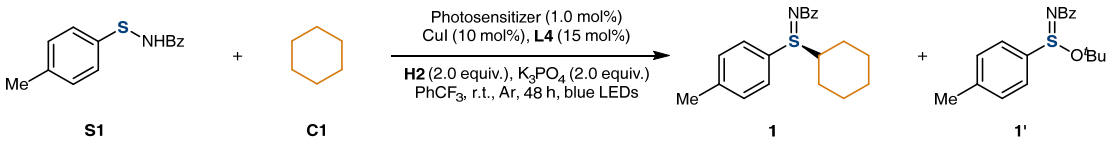
1. Supplementary tables for experiments

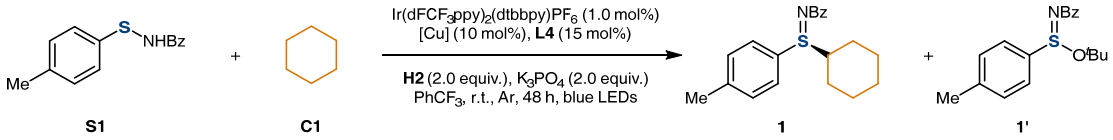
Supplementary Table 1 | Screening of photosensitizers with S1 and C1[a]



Entry	PS	Yield of 1 (%)	E.e. of 1 (%)	Yield of 1' (%)
1	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	65	97	10
2	*fac*-$Ir(ppy)_3$	51	96	6
3	$Ru(4,4'\text{-}dtbbpy)_3(PF_6)_2$	42	96	9
4	Mes-Arc$^+BF_4^-$	45	97	12
5	4-CzIPN	50	97	8
6	eosin Y	33	95	13
7	TPT$^+BF_4^-$	38	97	14

[a]Reaction conditions: **S1** (0.20 mmol), **C1** (40 equiv.), CuI (10 mol%), **L4** (15 mol%), **H2** (2.0 equiv.), PS (1.0 mol%), and K_3PO_4 (2.0 equiv.) in $PhCF_3$ (2.0 mL) at r.t. under blue LED irradiation for 48 h under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. values were based on chiral HPLC analysis. Bz, benzoyl; ^{t}Bu, *tert*-butyl; PS, photosensitizer; $dFCF_3ppy$, 3,5-difluoro-2-(5-(trifluoromethyl)pyridin-2-yl)phenyl; dtbbpy, 4,4′-di-*tert*-butyl-2,2′-dipyridyl; ppy, (pyridin-2-yl)phenyl; Mes-Arc$^+BF_4^-$, 9-mesityl-10-methylacridinium tetrafluoroborate; 4-CzIPN, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene; eosin Y, bromoeosin; TPT$^+BF_4^-$, 2,4,6-triphenylpyrylium tetrafluoroborate.

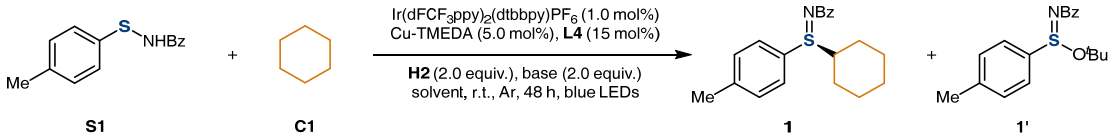
Supplementary Table 2 | Screening of copper salts with S1 and C1[a]



Entry	[Cu]	Yield of 1 (%)	E.e. of 1 (%)	Yield of 1' (%)
1	CuI	65	97	10
2	CuOAc	34	23	6
3	$Cu(CH_3CN)_4PF_6$	74	96	12
4	$Cu(OAc)_2$	38	37	5
5[b]	Cu-TMEDA	76	97	16

[a]Reaction conditions: **S1** (0.20 mmol), **C1** (40 equiv.), [Cu] (10 mol%), **L4** (15 mol%), **H2** (2.0 equiv.), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (1.0 mol%), and K_3PO_4 (2.0 equiv.) in $PhCF_3$ (2.0 mL) at r.t. under blue LED irradiation for 48 h under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. values were based on chiral HPLC analysis. [b]Cu-TMEDA (5.0 mol%, di-μ-hydroxo-bis[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) copper(II)] chloride).

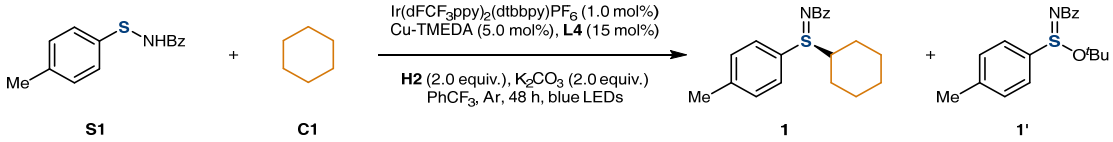
Supplementary Table 3 | Screening of solvents and bases with S1 and C1[a]



Entry	Solvent	Base	Yield of 1 (%)	E.e. of 1 (%)	Yield of 1' (%)
1	$PhCF_3$	K_3PO_4	76	97	16
2	PhF	K_3PO_4	66	97	13
3	PhCl	K_3PO_4	61	97	11
4	PhH	K_3PO_4	66	97	16
5	$PhCF_3$	Cs_2CO_3	62	94	17
6	$PhCF_3$	K_2CO_3	84	97	8
7	$PhCF_3$	Na_2CO_3	78	95	15
8	$PhCF_3$	Li_2CO_3	79	59	14
9	$PhCF_3$	$KHCO_3$	78	94	15

[a]Reaction conditions: **S1** (0.20 mmol), **C1** (40 equiv.), Cu-TMEDA (5.0 mol%), **L4** (15 mol%), **H2** (2.0 equiv.), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (1.0 mol%), and base (2.0 equiv.) in solvent (2.0 mL) at r.t. under blue LED irradiation for 48 h under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. values were based on chiral HPLC analysis.

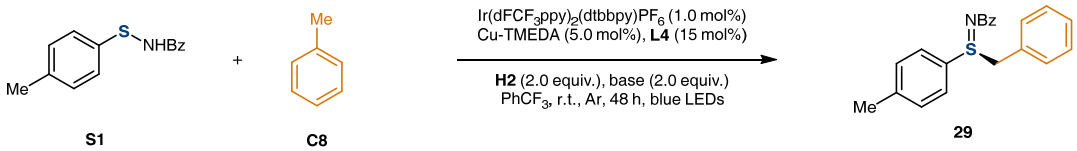
Supplementary Table 4 | Control experiments with S1 and C1[a]



Entry	PS	[Cu]	L4	Base	Light	Temp. (°C)	Yield of 1 (%)	E.e. of 1 (%)	Yield of 1' (%)
1[b]	√	√	√	√	√	r.t.	84	97	8
2[c]	√	√	√	√	√	20	88	95	3
3[b]	×	√	√	√	√	r.t.	17	95	7
4[b]	√	×	√	√	√	r.t.	50	2	12
5[b]	√	√	×	√	√	r.t.	45	0	5
6[b]	√	×	×	√	√	r.t.	20	0	5
7[b]	√	√	√	×	√	r.t.	60	92	6
8[b]	√	√	√	√	×	r.t.	14	97	4
9[b]	×	√	√	√	×	r.t.	15	97	8
10[d]	×	√	√	√	√	40	56	94	10
11[d]	×	√	√	√	×	30	36	97	18
12[d]	×	√	√	√	×	35	42	97	14
13[d]	×	√	√	√	×	40	53	95	16
14[d]	×	√	√	√	×	45	60	96	15
15[d]	×	√	√	√	×	50	65	96	16

[a]Reaction conditions: **S1** (0.20 mmol), **C1** (40 equiv.), Cu-TMEDA (5.0 mol%), **L4** (15 mol%), **H2** (2.0 equiv.), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (1.0 mol%), and K_2CO_3 (2.0 equiv.) in $PhCF_3$ (2.0 mL) at r.t. under blue LED irradiation for 48 h under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. values were based on chiral HPLC analysis. [b]R.t. denotes room temperature (ca. 20 °C) under efficient ventilation. [c]R.t. denotes room temperature (ca. 20 °C) under a water bath. [d]A heating block was used for reactions conducted at elevated temperature. Temp., temperature.

Supplementary Table 5 | Screening of bases with S1 and C8[a]

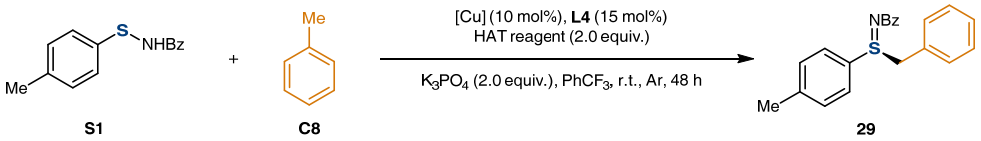


S1 C8 29

Entry	Base	Yield of 29 (%)	E.e. of 29 (%)
1	K_2CO_3	53	95
2	Cs_2CO_3	45	89
3	K_3PO_4	56	95
4	Na_2CO_3	50	94
5[b]	K_3PO_4	41	95

[a]Reaction conditions: **S1** (0.20 mmol), **C8** (40 equiv.), Cu-TMEDA (5.0 mol%), **L4** (15 mol%), **H2** (2.0 equiv.), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (1.0 mol%), and base (2.0 equiv.) in $PhCF_3$ (2.0 mL) at r.t. for 48 h under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. values were based on chiral HPLC analysis. [b]Without $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ and blue LED irradiation.

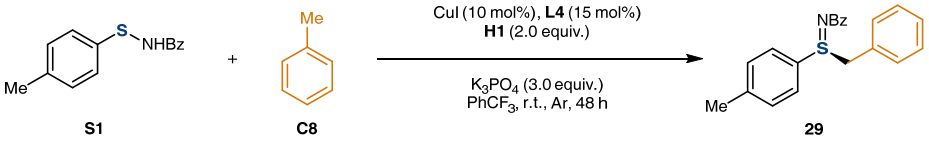
Supplementary Table 6 | Screening of HAT reagents and copper salts with S1 and C8: [a]



Entry	HAT reagent	[Cu]	Yield of 29 (%)	E.e. of 29 (%)
1	**H2**	Cu-TMEDA	41	95
2	**H1**	Cu-TMEDA	84	50
3	TBPB	Cu-TMEDA	38	97
4	DTBP	Cu-TMEDA	0	ND
5	NFSI	Cu-TMEDA	0	ND
6	**H1**	$Cu(OAc)_2$	83	91
7	**H1**	$Cu(CH_3CN)_4PF_6$	81	85
8	**H1**	CuOAc	86	92
9	**H1**	CuI	81	97
10[b]	**H1**	CuI	84	97
11[b,c]	**H1**	CuI	81	97
12[b,d]	**H1**	CuI	52	86

[a]Reaction conditions: **S1** (0.20 mmol), **C8** (40 equiv.), [Cu] (10 mol%), **L4** (15 mol%), HAT reagent (2.0 equiv.), and K_3PO_4 (2.0 equiv.) in $PhCF_3$ (2.0 mL) at r.t. for 48 h under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. values were based on chiral HPLC analysis. [b]With K_3PO_4 (3.0 equiv.). [c]With **C8** (20 equiv.). [d]With **C8** (10 equiv.). TBPB, *tert*-butyl peroxybenzoate; DTBP, di-*tert*-butyl peroxide; NFSI, *N*-fluorobenzenesulfonimide; ND, not determined.

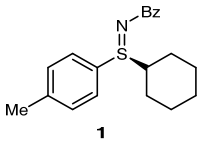
Supplementary Table 7 | Control experiments with S1 and C8[a]



Entry	CuI	L4	K_3PO_4	Yield (%)	E.e. (%)
1	√	√	√	81	97
2	×	√	√	36	2
3	√	×	√	53	0
4	×	×	√	44	0
5	√	√	×	trace	–

[a]Reaction conditions: **S1** (0.20 mmol), **C8** (20 equiv.), CuI (10 mol%), **L4** (15 mol%), **H1** (2.0 equiv.), and K_3PO_4 (3.0 equiv.) in $PhCF_3$ (2.0 mL) at r.t. for 48 h under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. values were based on chiral HPLC analysis.

2. Supplementary figures for experiments



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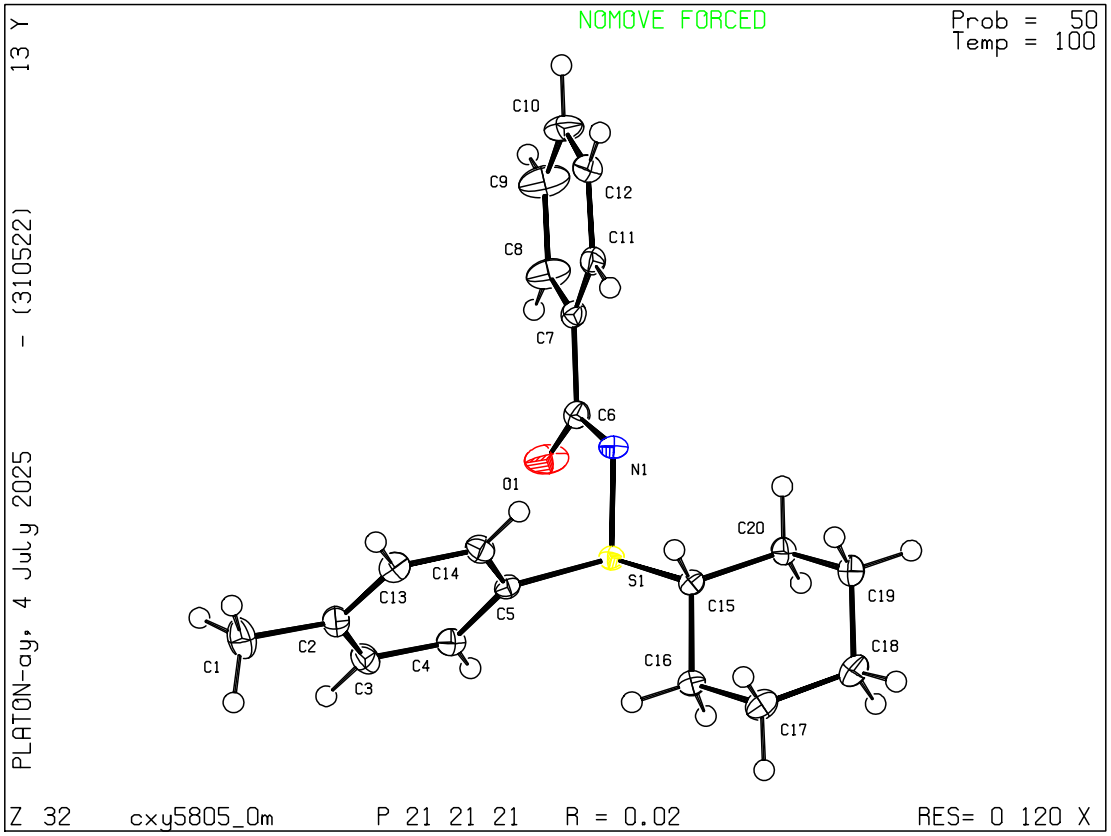
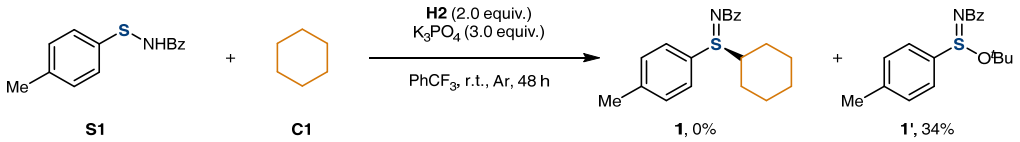
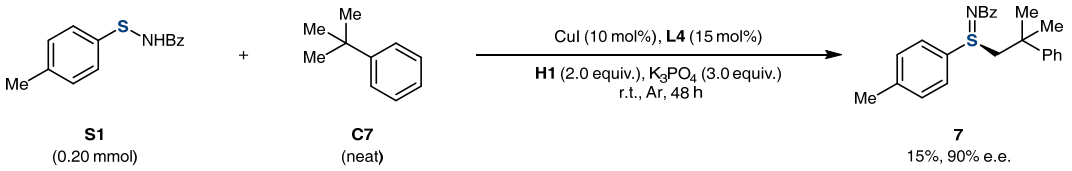


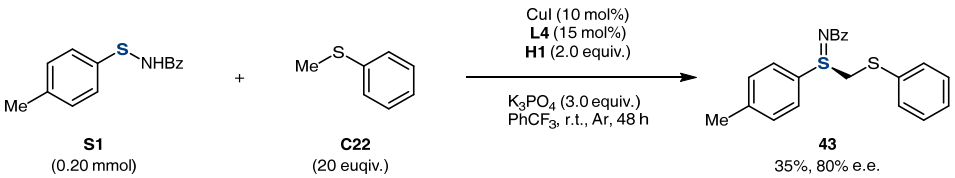
Supplementary Fig. 1 | The X-ray structure of 1 (CCDC 2467538, 50% probability ellipsoids).



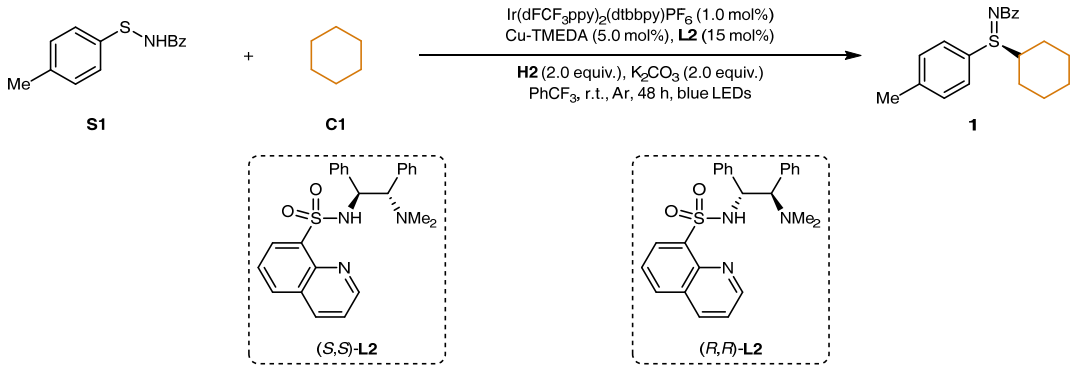
Supplementary Fig. 2 | Control experiments for 1'. Conditions: **S1** (0.20 mmol, 1.0 equiv.), **C1** (8.0 mmol, 40 equiv.), **H2** (0.40 mmol, 2.0 equiv.), and K_3PO_4 (0.60 mmol, 3.0 equiv.) in $PhCF_3$ (2.0 mL) at r.t. for 48 h under argon.



Supplementary Fig. 3 | Asymmetric synthesis of 7 with H1. Conditions: **S1** (0.20 mmol), *tert*-butylbenzene **C7** (2.0 mL), CuI (10 mol%), **L4** (15 mol%), and K_3PO_4 (3.0 equiv.) at r.t. under argon for 48 h.



Supplementary Fig. 4 | Asymmetric synthesis of 43 with H1. Conditions: **S1** (0.20 mmol), (4-methylthio)toluene **C22** (20 equiv.), CuI (10 mol%), **L4** (15 mol%), **H1** (2.0 equiv.), and K_3PO_4 (3.0 equiv.) in $PhCF_3$ (2.0 mL) at r.t. under argon for 48 h.



Entry	Catalyst e.e. (%)	Product e.e. (%)
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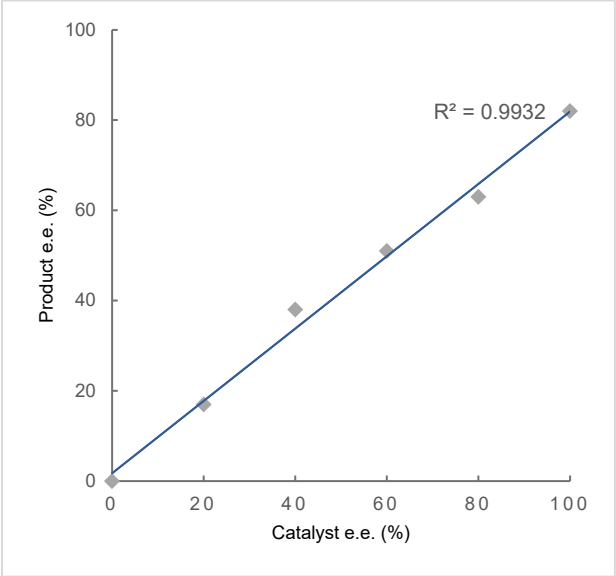
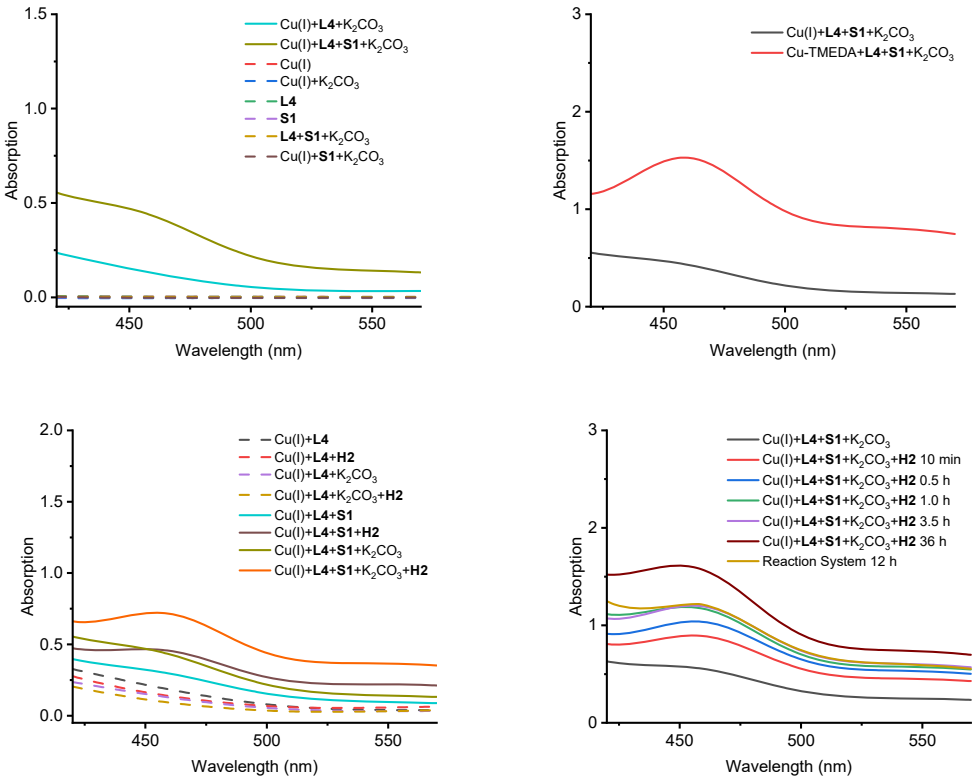
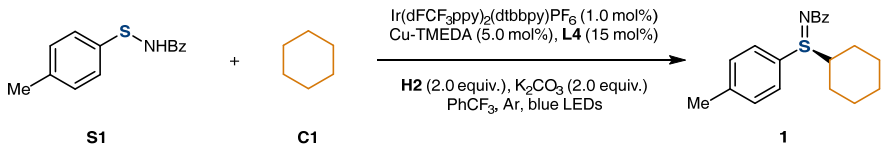
2	80	63
3	60	51
4	40	38
5	20	17
6	0	0

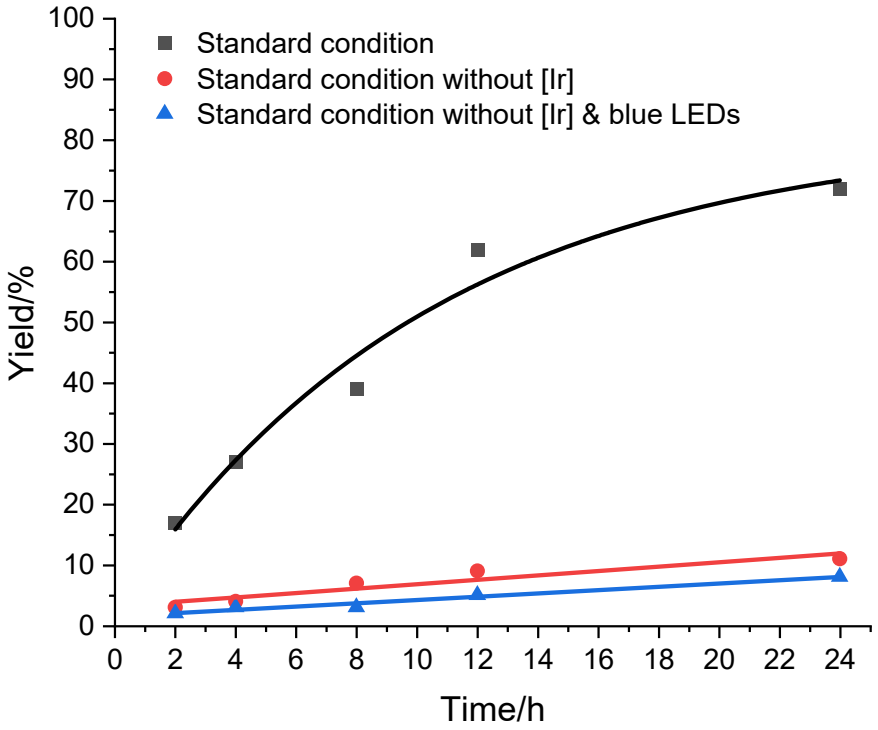


Supplementary Fig. 5 | The non-linear effect. The control experiments indicated a linear relationship between e.e. values of products and corresponding catalysts. Each data point represents a single measurement. The solid line is a least-squares linear fit shown for visualization ($R^2 = 0.9932$; coefficient of determination).

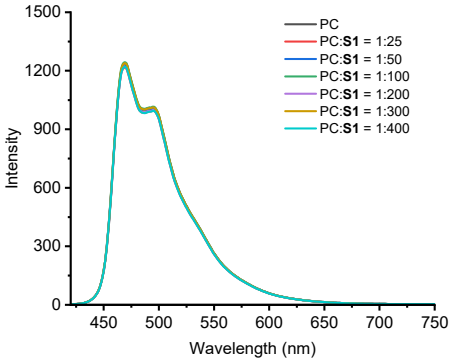


Supplementary Fig. 6 | UV–visible spectroscopic studies of the reaction components. All samples were prepared at ca. 1.0 mM. Each spectrum represents a single measurement.





Supplementary Fig. 7 | The time-course experiments. Each point represents a single measurement. The black solid line represents an exponential fit, and the red and blue solid lines represent linear fits, shown to illustrate the overall trends.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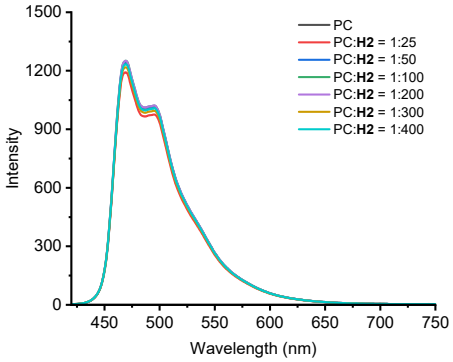
Intensity
Wavelength (nm)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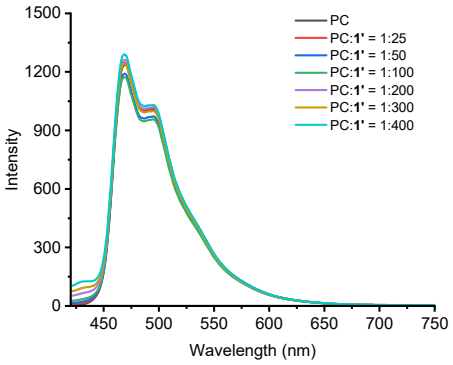
Intensity
Wavelength (nm)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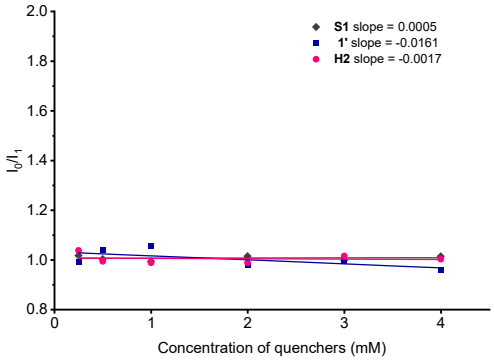
Intensity
Wavelength (nm)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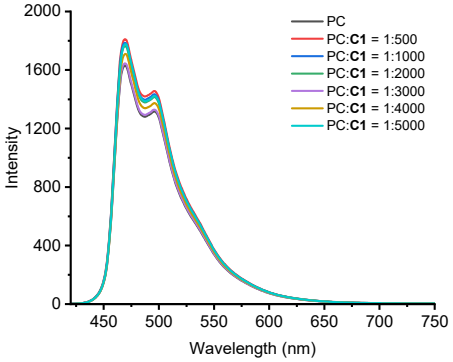
H2 slope = -0.0017
I0/I1
Concentration of quenchers (mM)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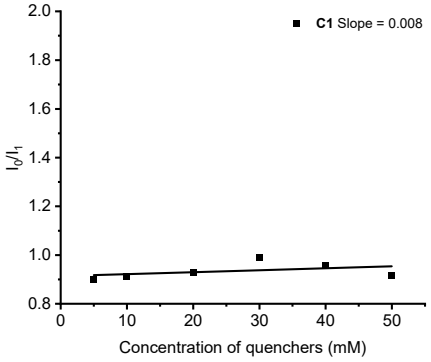
Intensity
Wavelength (nm)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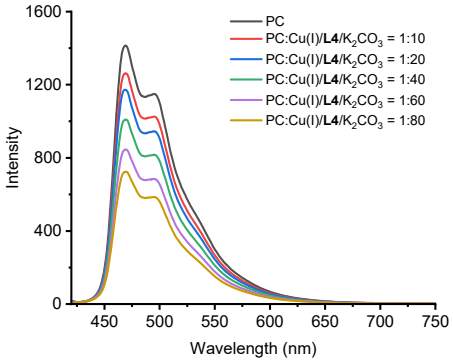
I0/I1
Concentration of quenchers (mM)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PC:Cu(I)/L4/K2CO3 = 1:40
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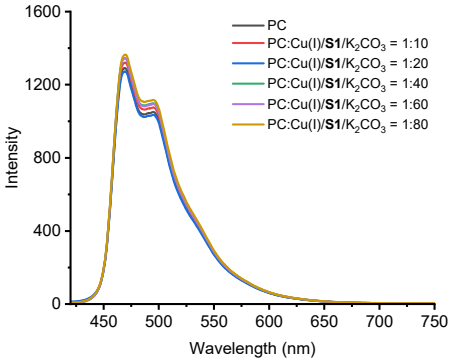
Intensity
Wavelength (nm)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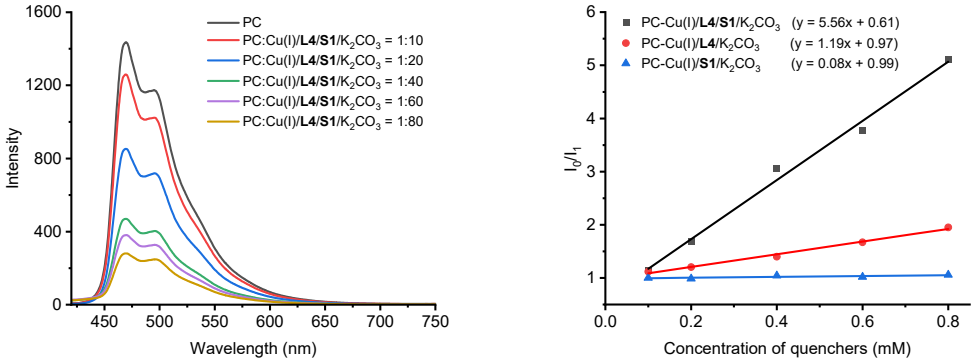
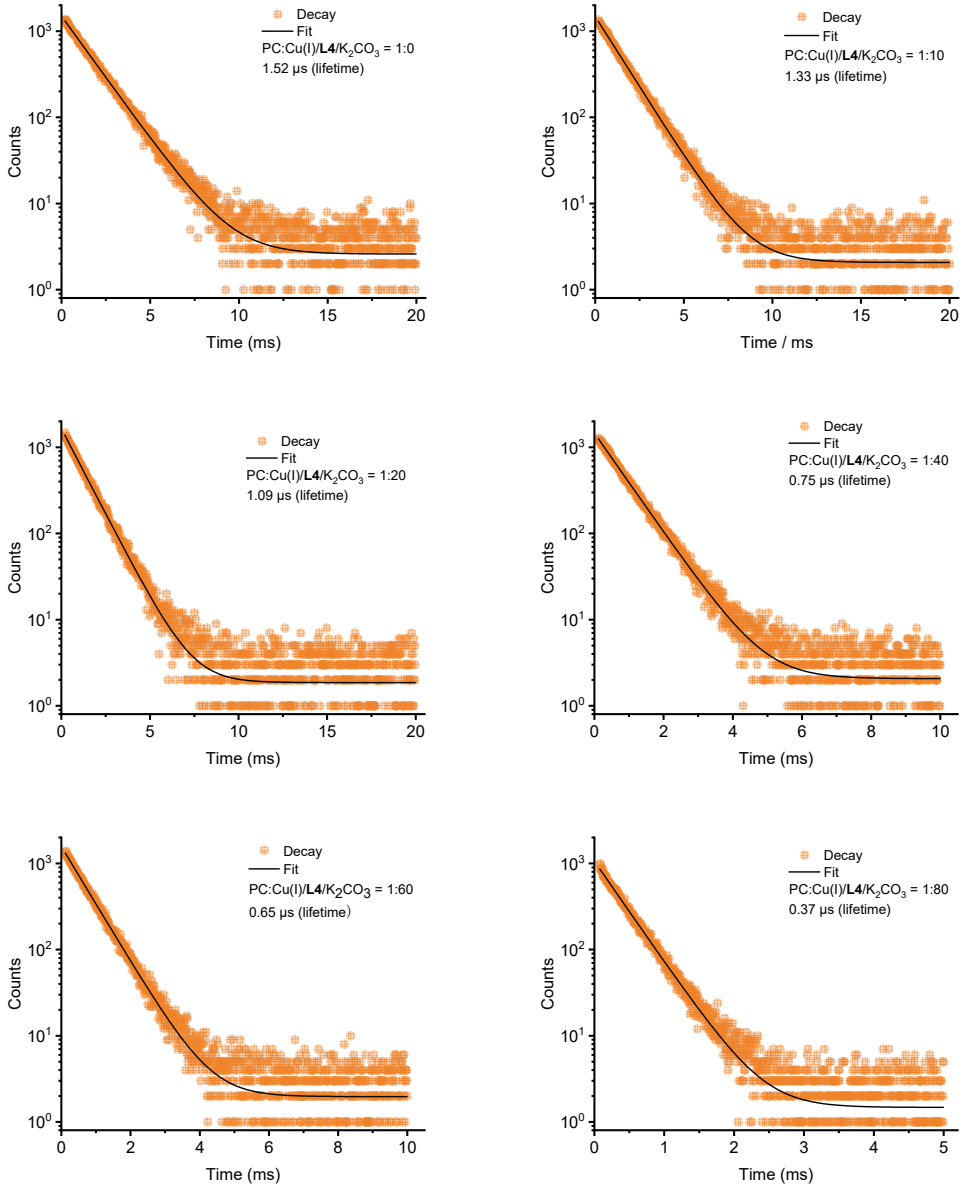
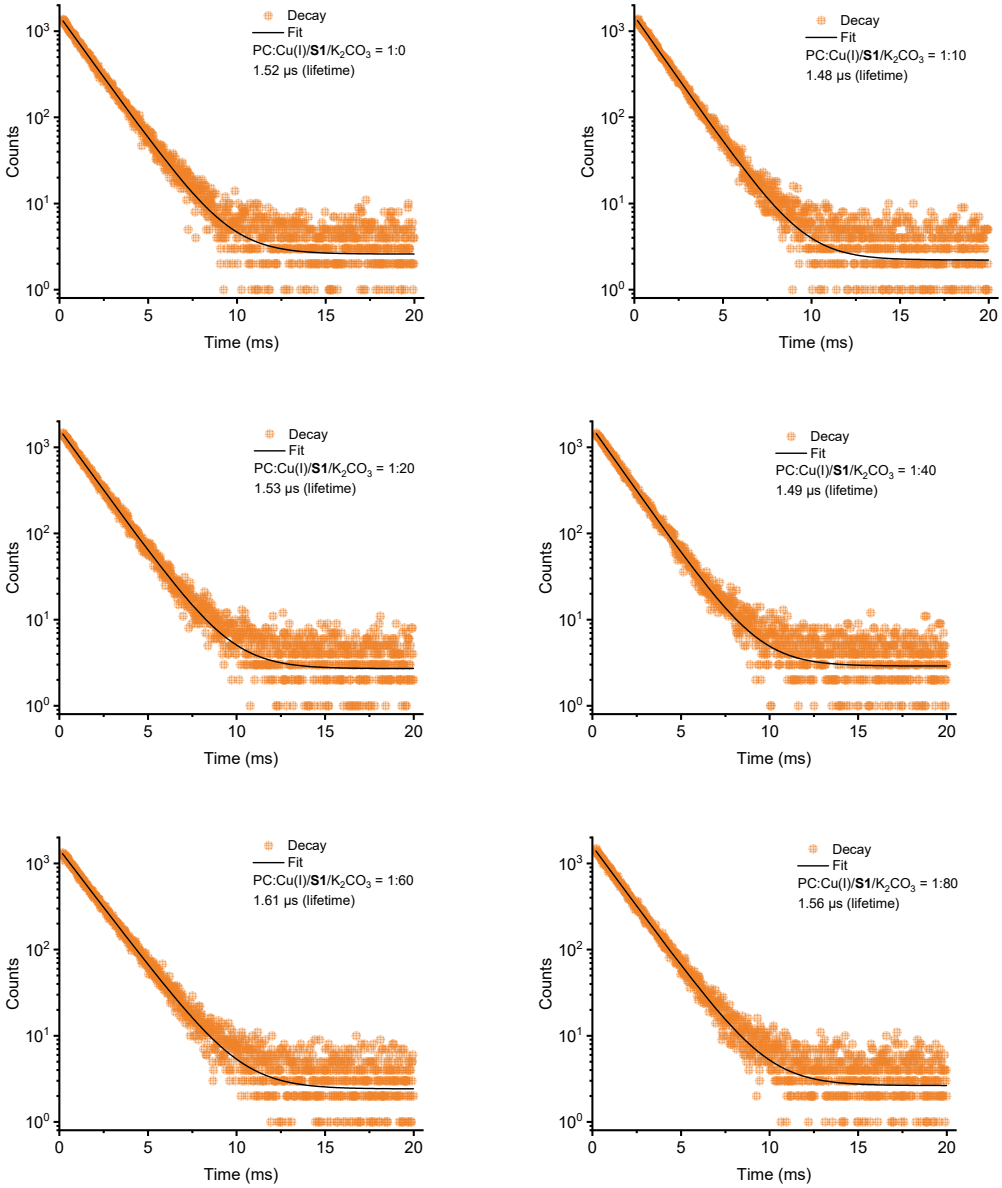
Intensity
Wavelength (nm)



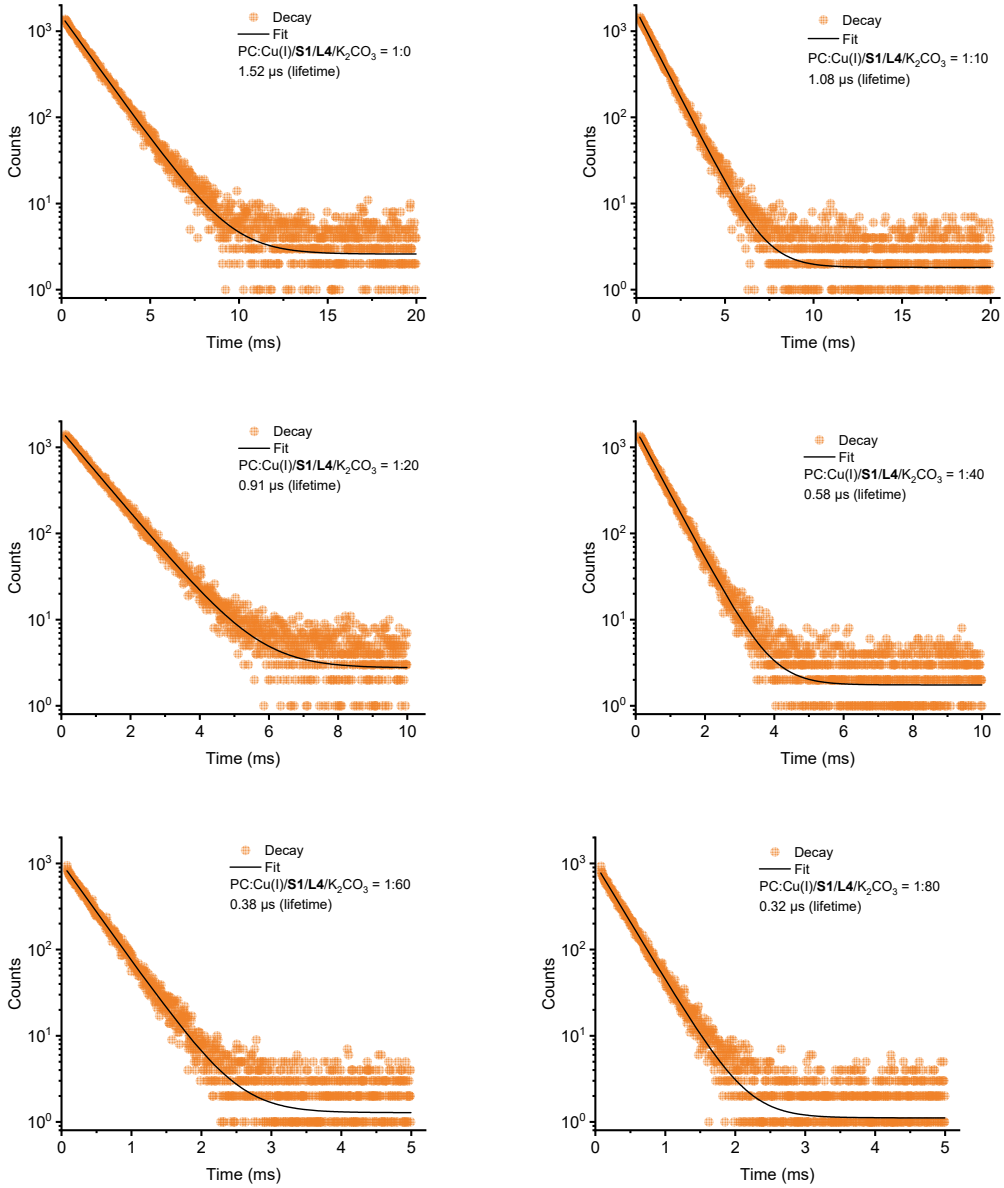
Supplementary Fig. 8 | Stern–Volmer fluorescence-quenching experiments. I_0 is the fluorescence intensity in the absence of quencher and I_1 is the intensity at the indicated quencher concentration. Each point represents a single measurement. The slopes of the linear fits correspond to the apparent Stern–Volmer constants and were used to evaluate the relative quenching efficiencies of the quenchers.



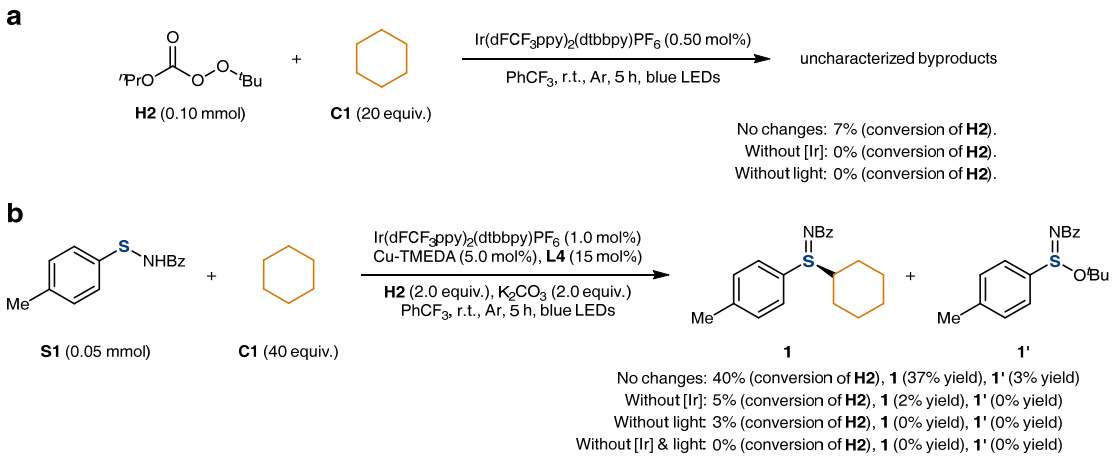
Supplementary Fig. 9 | The time-correlated single photon counting (TCSPC) measurements of photocatalyst with $Cu(CH_3CN)_4BF_4$/L4/K_2CO_3. Fluorescence decay (yellow) at 470 nm for $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in the presence of $Cu(CH_3CN)_4BF_4$/**L4**/K_2CO_3 were recorded and well described by a monoexponential fit (black). Each panel represents one independent TCSPC measurement. The y-axis shows photon counts on a logarithmic scale.



Supplementary Fig. 10 | The time-correlated single photon counting (TCSPC) measurements of photocatalyst with $Cu(CH_3CN)_4BF_4$/S1/K_2CO_3. Fluorescence decay (yellow) at 470 nm for $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in the presence of $Cu(CH_3CN)_4BF_4$/**S1**/K_2CO_3 were recorded and well described by a monoexponential fit (black). Each panel represents one independent TCSPC measurement. The y-axis shows photon counts on a logarithmic scale.

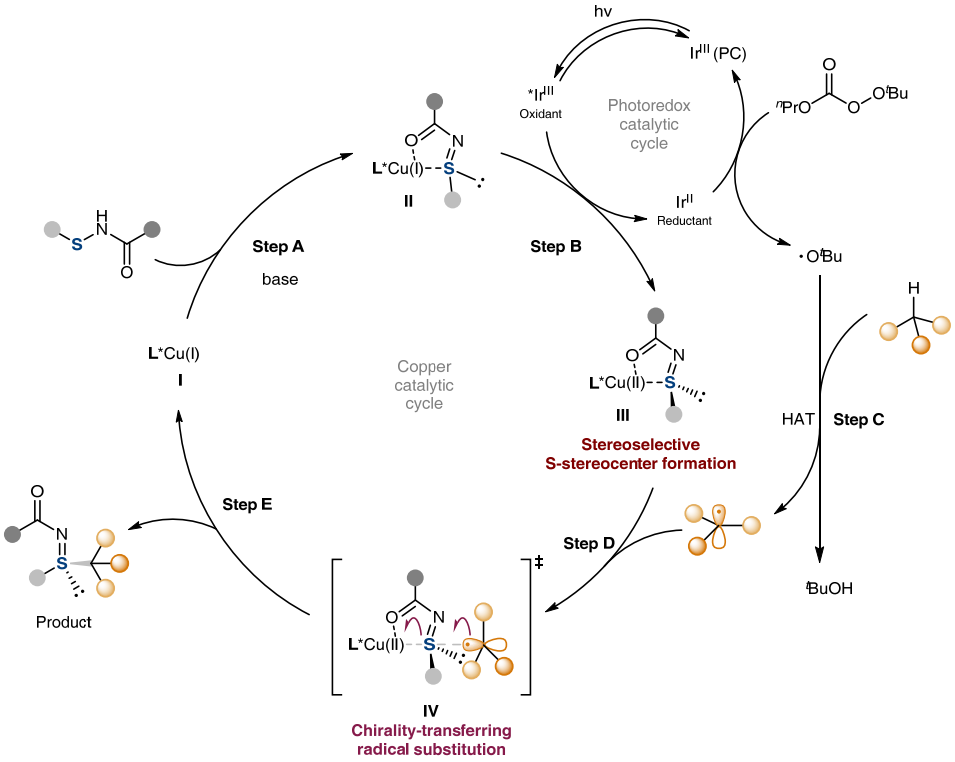


Supplementary Fig. 11 | The time-correlated single photon counting (TCSPC) measurements of photocatalyst with $Cu(CH_3CN)_4BF_4$/S1/L4/K_2CO_3. Fluorescence decay (yellow) at 470 nm for $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in the presence of $Cu(CH_3CN)_4BF_4$/**S1**/**L4**/K_2CO_3 were recorded and well described by a monoexponential fit (black). Each panel represents one independent TCSPC measurement. The y-axis shows photon counts on a logarithmic scale.

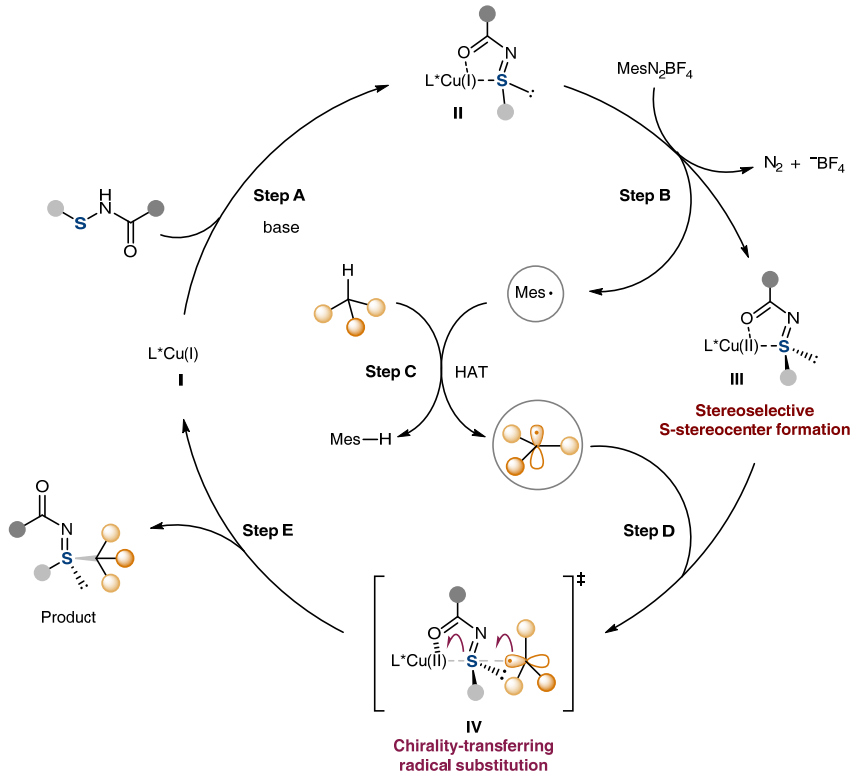


Supplementary Fig. 12 | Control experiments on H2 consumption: Identifying the direct activator. [a]Reaction Conditions: **H2** (0.10 mmol), **C1** (20 equiv.), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (0 or 0.50 mol%) in $PhCF_3$ (0.50 mL) at r.t. under blue LED irradiation or in the absence of light for 5 h under argon. Conversion was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. [b]Reaction Conditions: **S1** (0.050 mmol), **C1** (40 equiv.), Cu-TMEDA (5.0 mol%), **L4** (15 mol%), **H2** (2.0 equiv.), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (0 or 1.0 mol%), and K_2CO_3 (2.0 equiv.) in $PhCF_3$ (0.50 mL) at r.t. under blue LED irradiation or in the absence of light for 5 h under argon. Yield and conversion were based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

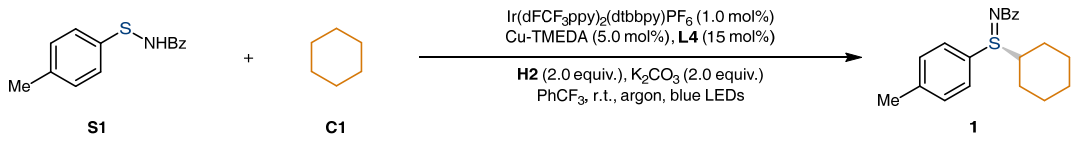
Photocatalytic mechanism (major pathway):



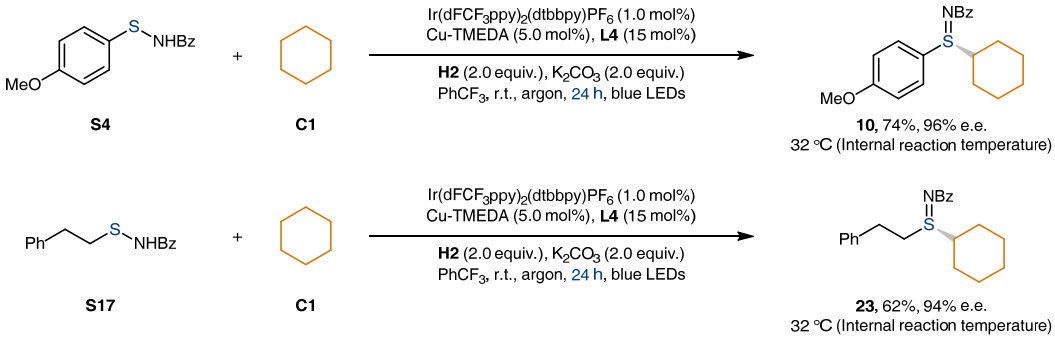
Thermal mechanism:



Supplementary Fig. 13 | Proposed mechanisms.



Entry	Time (h)	Internal reaction temperature	Yield of 1 (%)	e.e. of 1 (%)
1[a]	6	30	28	97
2[a]	12	33	47	97
3	24	33	58	97
4	36	30	71	97
5	48	30	82	97



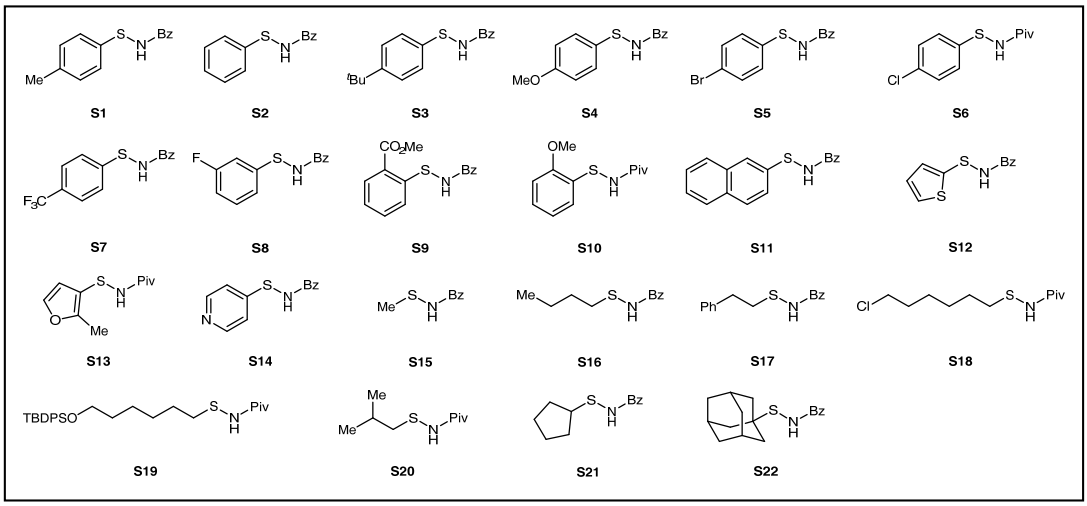
Supplementary Fig. 14 | Evaluation of the internal reaction temperature under the photocatalytic conditions. The reaction mixtures were stirred under the standard conditions for the indicated time points. At each time point, the reaction vessel was briefly opened under irradiation, and the internal temperature was measured by inserting a temperature probe attached to an IKA RCT B S025 magnetic stirrer directly into the reaction mixture and holding it in place for approximately 30 s until the reading stabilized, at which point the internal reaction temperature was recorded. [a]For comparison, the reaction temperature was also measured using a conventional kerosene-filled glass thermometer, which gave comparable values within experimental error.

3. General information

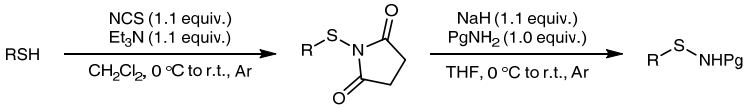
Most of the reactions were carried out under an argon atmosphere using Schlenk techniques. Reagents were purchased at the highest available commercial quality and used without further purification, unless otherwise stated. Cu-TMEDA and K_3PO_4 were purchased from Bide Pharmatech Ltd. and used directly without further treatment. Other reagents were purchased from J&K, Energy, etc. Anhydrous $PhCF_3$ was purchased from J&K. 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 eluents, 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. The blue LED lamp was purchased from Taobao (see Supplementary Fig. 6). Visualization on TLC was achieved by UV light (254 nm), iodine, 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 and at 100 or 150 MHz for ^{13}C NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed in ppm, and coupling constants are given in Hz. Data for ^1H NMR are reported as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; dd, doublet of doublets; dt, doublet of triplets; ddd, doublet of doublet of doublets; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectrometry (HRMS) was performed on a Thermo Scientific Q Exactive mass spectrometer using an ESI ion source. Enantiomeric excess (e.e.) was determined using a SHIMADZU LC-20AD with an SPD-20AV detector. Column conditions are reported in the experimental section below. X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer with Cu–Kα radiation.

4. The preparation of substrates

General procedure for the synthesis of sulfenamides



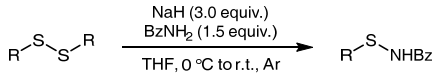
S1–**S13** and **S16**–**S22** were synthesized according to **General Procedure 1**. **S14** and **S15** were synthesized according to **General Procedure 2**. All the characterization data are consistent with those reported in the literature.[1,2]



General Procedure 1:

According to a previously reported procedure[3] with slight modification, the following synthesis was performed: Under an argon atmosphere and in an ice bath, *N*-chlorosuccinimide (NCS, 11 mmol, 1.1 equiv.) was slowly added to a solution of thiol (10 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.2 M, 50 mL). The mixture was stirred at r.t. for 0.5 h. Triethylamine (11 mmol, 1.1 equiv.) was then added slowly under an ice bath, and the reaction mixture was stirred at r.t. overnight. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was used directly in the next step without further purification.

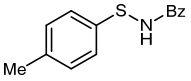
In the subsequent step, under an argon atmosphere and in an ice bath, sodium hydride (60% in mineral oil, 1.1 equiv.) was slowly added to a solution of amide (1.0 equiv.) in anhydrous THF (0.33 M). The reaction mixture was stirred at r.t. for 0.5 h, after which the intermediate product (1.0 equiv.) was added slowly under an ice bath. The reaction mixture was then stirred at r.t. overnight. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel to afford the desired product.



General Procedure 2:

According to a previously reported procedure[4] with slight modification, the following synthesis was performed: Under an argon atmosphere and in an ice bath, sodium hydride (60% in mineral oil, 1.20 g, 30 mmol, 3.0 equiv.) was slowly added to a solution of benzamide (15.0 mmol, 1.5 equiv.) in anhydrous THF (100 mL). The reaction mixture was stirred at r.t. for 0.5 h. Disulfide (10 mmol, 1.0 equiv.) was then added slowly under an ice bath, and the reaction mixture was stirred at r.t. overnight. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel to afford the desired product.

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

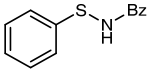


M.P.: 126–129 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.43 (m, 2H), 7.37 – 7.28 (m, 3H), 7.16 – 7.10 (m, 2H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 137.3, 135.1, 133.3, 132.3, 129.8, 128.6, 127.8, 127.0, 21.1.

***N*-(Phenylthio)benzamide (S2)**

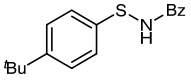


M.P.: 120–122 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 2H), 7.60 – 7.53 (m, 1H), 7.51 – 7.44 (m, 2H), 7.40 – 7.28 (m, 5H), 7.25 – 7.18 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 138.7, 133.0, 132.3, 128.9, 128.7, 128.6, 127.9, 126.6, 126.6, 125.1, 125.1.

***N*-((4-(*t*ert-Butyl)phenyl)thio)benzamide (S3)**

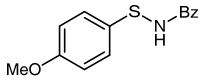


M.P.: 137–139 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.58 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.31 (m, 5H), 1.29 (s, 9H).

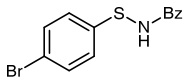
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 150.5, 135.1, 133.3, 132.3, 128.7, 127.8, 126.6, 126.1, 34.6, 31.3.

***N*-((4-Methoxyphenyl)thio)benzamide (S4)**



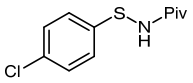
M.P.: 112–115 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.59 – 7.49 (m, 3H), 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 1H), 6.90 – 6.82 (m, 2H), 3.79 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 160.2, 133.6, 132.4, 132.3, 129.0, 128.8, 127.7, 114.7, 55.5.

***N*-((4-Bromophenyl)thio)benzamide (S5)**



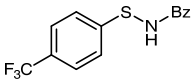
M.P.: 145–149 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 2H), 7.60 – 7.55 (m, 1H), 7.55 – 7.50 (m, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.35 (m, 2H), 7.24 – 7.11 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 137.8, 133.0, 132.8, 132.2, 129.0, 127.8, 127.4, 121.0.

***N*-((4-Chlorophenyl)thio)pivalamide (S6)**



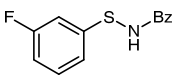
M.P.: 114–116 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.21 – 7.16 (m, 2H), 6.86 (s, 1H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 137.6, 133.0, 129.3, 127.1, 40.1, 27.9.

***N*-((4-(Trifluoromethyl)phenyl)thio)benzamide (S7)**



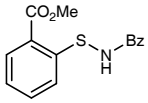
M.P.: 144–146 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.77 (m, 2H), 7.73 – 7.39 (m, 6H), 7.38 – 7.29 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 143.8, 143.8, 133.0, 132.7, 129.0, 128.5 (q, J = 32.7 Hz), 127.8, 126. (q, J = 3.8 Hz), 124.1 (q, J = 271.8 Hz), 123.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.47.

***N*-((3-Fluorophenyl)thio)benzamide (S8)**



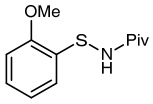
M.P.: 102–104 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 2H), 7.63 – 7.55 (m, 1H), 7.54 – 7.45 (m, 2H), 7.40 (s, 1H), 7.33 – 7.26 (m, 1H), 7.10 – 7.03 (m, 1H), 7.02 – 6.96 (m, 1H), 6.92 – 6.83 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 163.1 (d, J = 248.8 Hz), 141.3 (d, J = 7.3 Hz), 132.8(2), 132.7(5), 130.5 (d, J = 8.4 Hz), 128.9, 127.8, 119.9 (d, J = 3.1 Hz), 113.6 (d, J = 21.4 Hz), 111.5 (d, J = 24.1 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ –111.50.

Methyl 2-(benzamidothio)benzoate (S9)



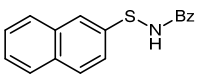
M.P.: 160–162 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 1H), 7.95 – 7.89 (m, 2H), 7.61 – 7.55 (m, 1H), 7.53 – 7.43 (m, 3H), 7.38 – 7.29 (m, 2H), 7.22 – 7.16 (m, 1H), 3.95 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 167.2, 145.0, 133.3, 133.2, 132.6, 131.3, 128.9, 127.8, 124.7, 124.4, 122.2, 52.5.

***N*-((2-Methoxyphenyl)thio)pivalamide (S10)**



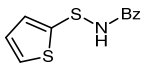
M.P.: 130–132 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 1H), 7.12 – 7.04 (m, 1H), 6.96 – 6.89 (m, 1H), 6.87 – 6.80 (m, 1H), 6.72 (s, 1H), 3.88 (s, 3H), 1.28 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 155.4, 127.7, 126.8, 125.4, 121.4, 110.7, 55.9, 40.1, 27.9.

***N*-(Naphthalen-2-ylthio)benzamide (S11)**



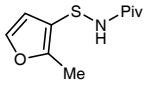
M.P.: 178–181 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.38 (s, 1H), 8.11 – 8.02 (m, 2H), 7.97 – 7.77 (m, 3H), 7.77 – 7.71 (m, 1H), 7.68 – 7.61 (m, 1H), 7.59 – 7.53 (m, 2H), 7.53 – 7.39 (m, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 137.3, 133.2, 133.2, 132.4, 131.4, 128.9, 128.7, 128.1, 127.8, 127.1, 127.0, 125.8, 122.0, 121.0.

***N*-(Thiophen-2-ylthio)benzamide (S12)**



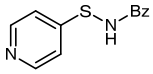
M.P.: 166–170 ℃.
^{1}H NMR 400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 7.89 (d, J = 7.7 Hz, 2H), 7.74 (d, J = 5.3 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.53 – 7.45 (m, 2H), 7.42 (d, J = 3.6 Hz, 1H), 7.12 – 7.03 (m, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 168.1, 136.7, 134.6, 133.1, 132.6, 132.3, 128.6, 127.9, 127.6.

***N*-((2-Methylfuran-3-yl)thio)pivalamide (S13)**



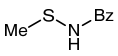
M.P.: 104–106 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J=2.0, 1H), 6.59 (s, 1H), 6.48 (d, J=2.0, 1H), 2.49 (s, 3H), 1.18 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 157.0, 140.9, 114.6, 114.4, 39.8, 27.7, 12.2.

***N*-(Pyridin-4-ylthio)benzamide (S14)**



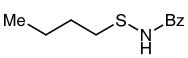
M.P.: 140–143 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.33 (m, 2H), 8.00 (s, 1H), 7.97 – 7.89 (m, 2H), 7.66 – 7.57 (m, 1H), 7.54 – 7.47 (m, 2H), 7.11 – 7.01 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 151.5, 149.1, 133.0, 132.6, 128.9, 128.1, 117.0.

***N*-(Methylthio)benzamide (S15)**



M.P.: 79–82 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.56 – 7.50 (m, 1H), 7.47 – 7.41 (m, 2H), 7.11 (s, 1H), 2.52 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 133.8, 132.3, 128.8, 127.5, 23.3.

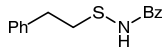
***N*-(Butylthio)benzamide (S16)**



M.P.: 51–54 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 2H), 7.56 – 7.49 (m, 1H), 7.47 – 7.40 (m, 2H), 7.08 (s, 1H), 2.87 – 2.82 (m, 2H), 1.67 – 1.55 (m, 2H), 1.49 – 1.38 (m, 2H),

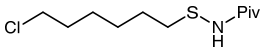
0.91 (t, *J*=7.3, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 133.9, 132.2, 128.8, 127.5, 38.7, 30.0, 21.9, 13.8.

***N*-(Phenethylthio)benzamide (S17)**



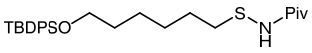
M.P.: 71–75 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.57 – 7.48 (m, 1H), 7.46 – 7.38 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.18 (m, 3H), 6.69 (s, 1H), 3.13 (t, *J*=7.6, 2H), 3.00 (t, *J*=7.3, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 140.0, 133.6, 132.2, 128.6, 128.6, 128.6, 127.5, 126.5, 40.2, 35.1.

***N*-((6-Chlorohexyl)thio)pivalamide (S18)**



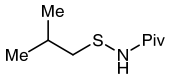
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 1H), 3.54 (t, *J*=6.7, 2H), 2.74 (t, *J*=7.3, 2H), 1.82 – 1.73 (m, 2H), 1.63 – 1.54 (m, 2H), 1.47 – 1.41 (m, 4H), 1.24 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 45.0, 39.7, 38.3, 32.3, 27.7, 27.7, 27.4, 26.4.

***N*-((6-((*tert*-Butyldiphenylsilyl)oxy)hexyl)thio)pivalamide (S19)**



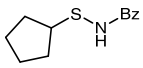
M.P.: 57–60 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 4H), 7.45 – 7.35 (m, 6H), 6.34 (s, 1H), 3.70 – 3.59 (m, 2H), 2.75 – 2.67 (m, 2H), 1.58 – 1.50 (m, 4H), 1.40 – 1.33 (m, 4H), 1.22 (s, 9H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 135.7, 134.2, 129.7, 127.7, 63.9, 39.9, 38.5, 32.5, 28.5, 27.9, 27.8, 27.0, 25.6, 19.4.

***N*-(Isobutylthio)pivalamide (S20)**



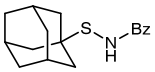
M.P.: 74–76 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1H), 2.62 (d, *J* = 6.9 Hz, 2H), 1.80 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.22 (s, 8H), 1.01 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 47.8, 39.9, 27.9, 27.5, 22.1.

***N*-(Cyclopentylthio)benzamide (S21)**



M.P.: 132–135 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.41 (m, 2H), 7.03 (s, 1H), 3.69 (tt, *J* = 7.3, 5.1 Hz, 1H), 2.05 – 1.86 (m, 2H), 1.86 – 1.71 (m, 2H), 1.68 – 1.51 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 133.9, 132.1, 128.7, 127.5, 49.4, 30.9, 24.9.

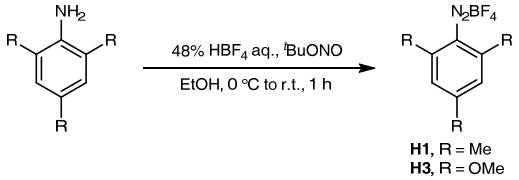
***N*-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)thio)benzamid (S22)**



M.P.: 179–181 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.71 (m, 2H), 7.62 – 7.50 (m, 1H), 7.50 – 7.42 (m, 2H), 6.86 (s, 1H), 2.14 – 2.03 (m, 3H), 1.96 – 1.82 (m, 6H), 1.78 – 1.63 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 134.1, 132.2, 128.8, 127.6, 51.3, 41.4, 36.3, 29.5.

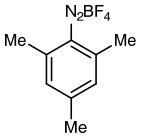
General procedure for the synthesis of HAT reagents

General procedure for the synthesis of diazonium salts



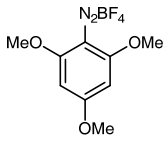
According to a previously reported procedure[5] with slight modification, the following synthesis was performed: In a 50 mL round-bottom flask, aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3.0 mL) and aqueous HBF_4 solution (48%, 2.5 mL), followed by the dropwise addition of ^{t}BuONO (2.7 mL) at 0 °C. The reaction mixture was stirred at r.t. for 1 h, after which diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate. The precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL), dried in vacuo for 10 min, and stored in a refrigerator under an argon atmosphere.

1-Mesityl-2-(tetrafluoro-λ^5-boraneyl)diazene (H1)



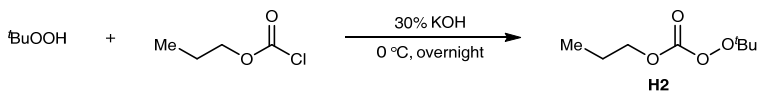
M.P.: 84–86 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 (s, 2H), 2.67 (s, 6H), 2.49 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 153.9, 144.2, 131.2, 112.5, 22.6, 18.6.
^{19}F NMR (376 MHz, DMSO-d_6) δ –148.75 (s, 1F), –148.80 (s, 3F).

1-(Tetrafluoro-λ^5-boraneyl)-2-(2,4,6-trimethoxyphenyl)diazene (H3)



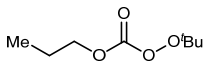
M.P.: 182–184 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 6.69 (s, 2H), 4.14 (s, 6H), 4.10 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 163.5, 93.8, 82.6, 59.0, 58.3.
^{19}F NMR (376 MHz, DMSO-d_6) δ –148.26 (s, 1F), –148.31 (s, 3F).

Procedure for the synthesis of *O*-centered radical precursor H2



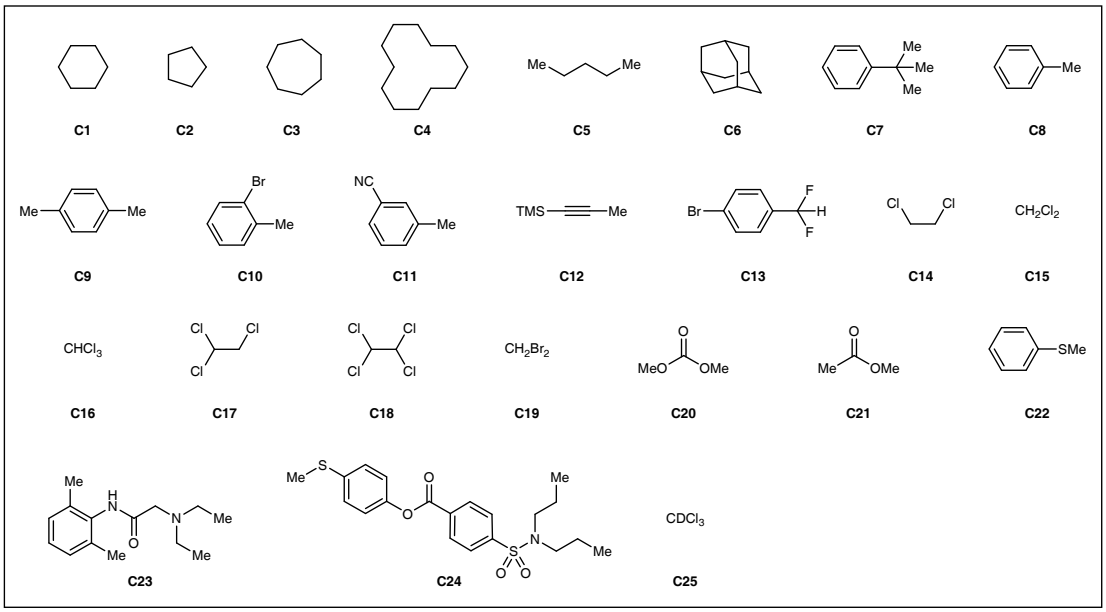
The synthesis of the *O*-centered radical precursor **H2** was performed according to a literature-reported procedure[6]. To a solution of 2-hydroperoxy-2-methylpropane (5.5 mmol, 1.1 equiv.) at 0 °C was added *n*-propyl carbonochloridate (5.0 mmol, 1.0 equiv.) dropwise. The reaction mixture was stirred for 0.5 h. A solution of KOH (30% in water, 6.5 mmol, 1.3 equiv.) was then added dropwise to the resulting mixture. The reaction mixture was stirred overnight at 0 °C. Upon completion (monitored by TLC), the reaction mixture was quenched with water (20 mL), and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated to afford the crude product, which was purified by flash chromatography (PE/EtOAc = 20/1) to yield the desired product **H2**.

***tert*-Butyl propyl carbonoperoxoate (H2)**

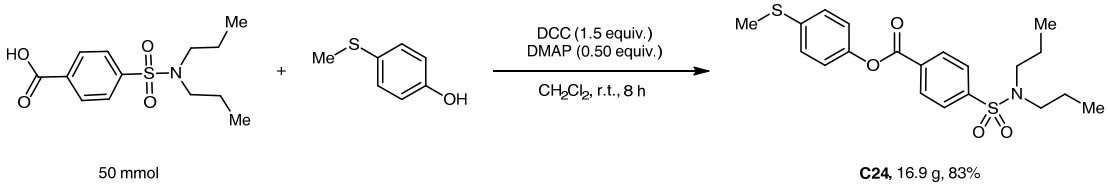


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (t, *J* = 6.7 Hz, 2H), 1.73 (q, *J* = 7.1 Hz, 2H), 1.34 (s, 9H), 0.97 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 84.1, 70.7, 25.9, 22.1, 10.1.

Summary of the C–H substrates

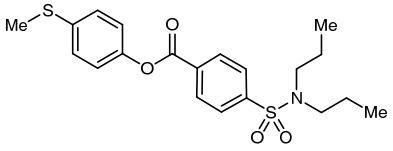


C1–**C23** and **C25** were all purchased from commercial sources.
C24 was synthesized as follows.



According to a previously reported procedure[7] with slight modification, the following synthesis was performed: To 1-(4-methylthio)phenol (7.0 g, 50 mmol, 1.0 equiv.) were added probenecid (14.3 g, 50 mmol, 1.0 equiv.), *N*,*N*′-dicyclohexylcarbodiimide (15.5 g, 75 mmol, 1.5 equiv.), *N*,*N*-dimethyl-4-aminopyridine (3.1 g, 25 mmol, 0.50 equiv.), and finally CH_2Cl_2 (200 mL). The mixture was stirred at r.t. for 8 h and then quenched by saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography (PE/EtOAc = 5/1) to afford **C24** (16.9 g, 83%).

4-(Methylthio)phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (C24)

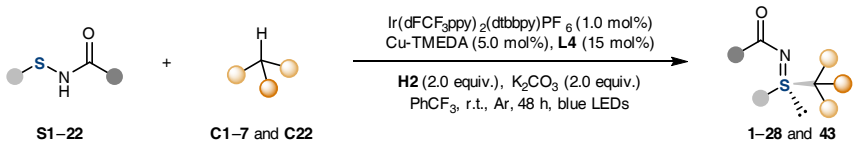


M.P.: 56–58 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.24 (m, 2H), 8.02 – 7.87 (m, 2H), 7.43 – 7.30 (m, 2H), 7.22 – 7.07 (m, 2H), 3.25 – 2.97 (m, 4H), 2.51 (s, 3H), 1.69 – 1.42 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 148.4, 145.1, 136.5, 132.8, 130.9, 128.1, 127.3, 122.1, 50.0, 22.1, 16.5, 11.3.

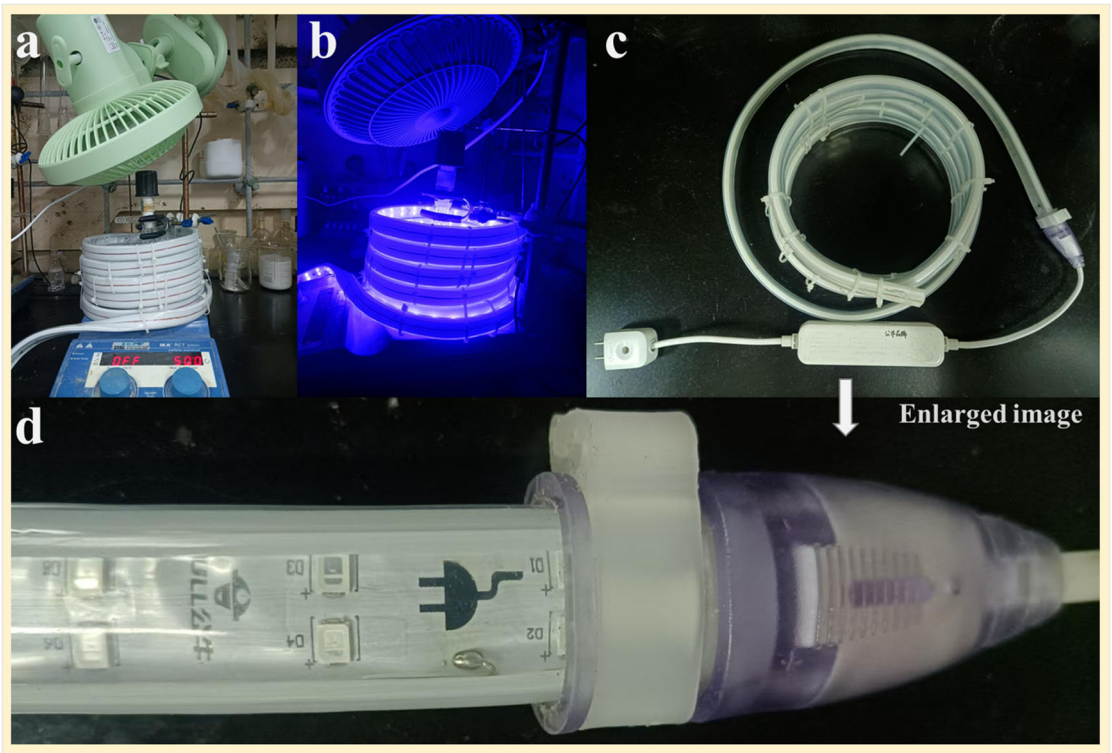
5. General procedure for the synthesis of sulfilimines

General Procedure A:

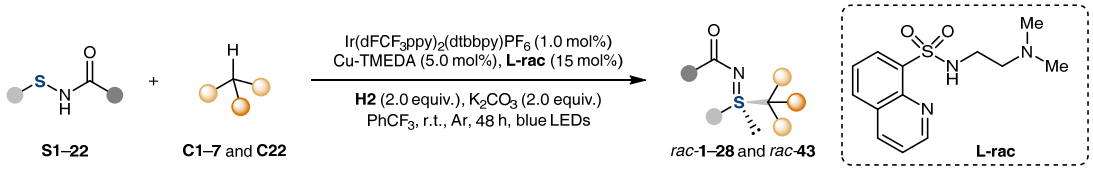


Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S** (0.20 mmol, 1.0 equiv.), alkane **C** (8.0 mmol, 40 equiv.), Cu-TMEDA (4.64 mg, 0.01 mmol, 5.0 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.29 mg, 0.002 mmol, 1.0 mol%), **H2** (70.5 mg, 0.40 mmol, 2.0 equiv.), K_2CO_3 (55.3 mg, 0.40 mmol, 2.0 equiv.), and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at r.t. under blue LED irradiation for 48 h under argon. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was evaporated, and the residue was purified by column chromatography on silica gel to afford the desired product.

Note: All photoreactions were conducted in a ventilated setup with fan-assisted cooling. Although performed at room temperature, the internal reaction temperature under the standard irradiation conditions was approximately 30–33 °C (see Supplementary Fig. 14 for details).



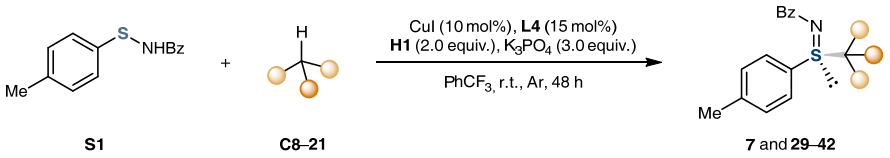
Supplementary Fig. 6 | Assembly of the setup for the photochemical reaction.



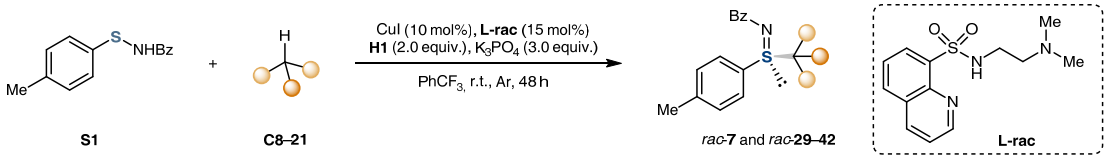
Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S** (0.20 mmol, 1.0 equiv.), alkane **C** (8.0 mmol, 40 equiv.), Cu-TMEDA (4.64 mg, 0.01 mmol, 5.0 mol%), **L-rac** (8.38 mg, 0.03 mmol, 15 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.29 mg, 0.0020 mmol, 1.0 mol%), **H2** (70.5 mg, 0.40 mmol, 2.0 equiv.), K_2CO_3 (55.3 mg, 0.40 mmol, 2.0 equiv.), and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at r.t. under blue LED irradiation for 48 h under argon. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was evaporated, and the residue was purified by column chromatography on silica gel to afford the desired product.

Note: All photoreactions were carried out in a ventilated setup with fan-assisted cooling. Accordingly, although the reactions are described as being conducted at room temperature, the actual reaction temperature may have been slightly above room temperature. Control experiments using water-bath temperature regulation (Supplementary Table 4, entry 2) indicated that this temperature difference had no significant impact on either the reaction efficiency or the enantioselectivity.

General Procedure B:



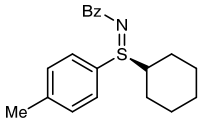
To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (3.80 mg, 0.020 mmol, 10 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), sulfenamide **S1** (48.7 mg, 0.20 mmol, 1.0 equiv.), alkane **C** (4.0 mmol, 20 equiv.), **H1** (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous $PhCF_3$ (2.0 mL). The reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.



To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (3.80

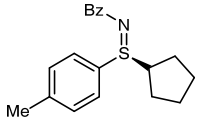
mg, 0.02 mmol, 10 mol%), **L-rac** (8.38 mg, 0.03 mmol, 15 mol%), sulfenamide **S** (0.20 mmol, 1.0 equiv.), alkane **C** (20 equiv.), **H1** (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous $PhCF_3$ (2.0 mL). The reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(*S*)-*N*-(Cyclohexyl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (1)



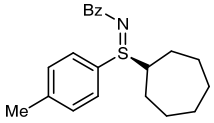
According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **1** as a white solid (54.7 mg, 84% yield, 97% e.e.).
M.P.: 122–127 ℃.
$[\alpha]_D^{25}$ = –145.91 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 9.93 min, t_R (major) = 15.90 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.17 (m, 2H), 7.65 (d, *J* = 8.3, 2H), 7.45 – 7.34 (m, 3H), 7.31 (d, *J* = 8.0, 2H), 3.29 – 3.15 (m, 1H), 2.40 (s, 3H), 2.22 – 2.14 (m, 1H), 1.91 – 1.77 (m, 3H), 1.69 – 1.61 (m, 1H), 1.57 – 1.46 (m, 1H), 1.39 – 1.17 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 142.8, 137.2, 130.6, 130.3, 128.9(3), 128.8(5), 128.2, 127.8, 58.7, 27.2, 26.6, 25.5(2), 25.4(5), 21.6.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NOS$ $[M + H]^+$ 326.1573, found 326.1572.

(*S*)-*N*-(Cyclopentyl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (2)



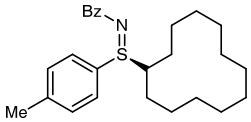
According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and cyclopentane **C2** (0.75 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **2** as a light yellow oil (42.9 mg, 69% yield, 97% e.e.).
$[\alpha]_D^{25}$ = –127.92 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 10.14 min, t_R (major) = 16.38 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.14 (m, 2H), 7.68 (d, *J* = 8.3, 2H), 7.44 – 7.34 (m, 3H), 7.29 (d, *J* = 8.1, 2H), 3.70 – 3.59 (m, 1H), 2.39 (s, 3H), 2.25 – 2.13 (m, 1H), 2.06 – 1.96 (m, 1H), 1.83 – 1.72 (m, 4H), 1.71 – 1.58 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 142.8, 137.2, 131.5, 130.6, 130.4, 128.9, 127.8, 127.7, 59.9, 28.4(4), 28.3(7), 25.6, 25.4, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}NOS$ $[M + H]^+$ 312.1417, found 312.1416.

(*S*)-*N*-(Cycloheptyl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (3)



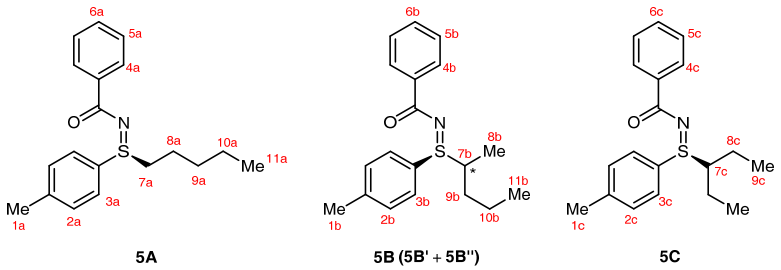
According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and cycloheptane **C3** (0.97 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **3** as a white solid (32.6 mg, 48% yield, 96% e.e.).
M.P.: 126–128 ℃.
$[\alpha]_D^{25}$ = –6.00 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 11.13 min, t_R (major) = 17.72 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.15 (m, 2H), 7.68 (d, *J* = 8.3, 2H), 7.45 – 7.34 (m, 3H), 7.30 (d, *J* = 8.0, 2H), 3.47 – 3.34 (m, 1H), 2.40 (s, 3H), 2.25 – 2.15 (m, 1H), 2.06 – 1.97 (m, 1H), 1.82 – 1.64 (m, 3H), 1.61 – 1.37 (m, 7H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 142.9, 137.2, 130.6, 130.2, 129.1, 128.9, 128.5, 127.8, 59.9, 28.9, 28.1, 28.0, 25.9, 25.8, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{26}NOS$ $[M + H]^+$ 340.1730, found 340.1730.

(*S*)-*N*-(Cyclododecyl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (4)



According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and cyclododecane **C4** (1.70 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **4** as a white solid (41.8 mg, 51% yield, 97% e.e.).
M.P.: 123–125 ℃.
$[\alpha]_D^{25}$ = –49.97 (c 0.5, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 12.82 min, t_R (major) = 21.80 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.16 (m, 2H), 7.65 (d, *J* = 8.2, 2H), 7.46 – 7.35 (m, 3H), 7.31 (d, *J* = 8.0, 2H), 3.43 – 3.32 (m, 1H), 2.40 (s, 3H), 1.95 – 1.85 (m, 1H), 1.84 – 1.68 (m, 3H), 1.66 – 1.55 (m, 1H), 1.53 – 1.27 (m, 17H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 142.8, 137.4, 130.6, 130.3, 129.4, 128.9, 128.3, 127.8, 57.7, 24.5, 24.2, 24.1, 23.7, 23.6(8), 23.6(5), 23.6, 23.5, 22.2, 22.1, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{36}NOS$ $[M + H]^+$ 410.2512, found 410.2512.

***N*-((*S*)-Pentan-1-yl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (5A), *N*-((*S*)-Pentan-2-yl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (5B), and *N*-((*S*)-Pentan-2-yl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (5C)**



5A **5B (5B' + 5B'')** **5C**

According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and *n*-pentane **C5** (0.92 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **5** as a light yellow oil; **5** was obtained as a mixture of regioisomers (**5A**:**5B**:**5C** = 1:10:4). The enantioselectivity and diastereoselectivity were determined where possible: **5A** (97% e.e.), **5B** (dr = 1.1:1.0), **5B′** (>93% e.e.), and the combined **5B″** & **5C** fraction (>94% e.e.). The presence of all three isomers was unequivocally confirmed by ^{1}H NMR spectroscopy. Owing to the highly similar structures of **5A**, **5B**, and **5C**, complete resolution of these compounds could not be achieved by either silica gel column chromatography or HPLC. Consequently, the e.e. values of **5A** and **5B′**, as well as that of the combined **5B″** & **5C** fraction, were estimated from the chiral HPLC chromatograms.

HPLC analysis of **5A**: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 25.05 min, t_R (major) = 50.38 min.

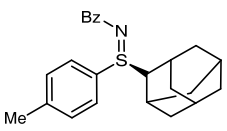
HPLC analysis of **5B** and **5C**: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), $t_{R\ (\mathbf{5B'}\text{ and }\mathbf{5C})}$ (minor) = 22.65 min, $t_{R\ (\mathbf{5B''})}$ (minor) = 26.16 min, $t_{R\ (\mathbf{5B''}\text{ and }\mathbf{5C})}$ (major) = 47.82 min, $t_{R\ (\mathbf{5B'})}$ (major) = 55.92 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.14 (m, H^{4a}, H^{4b}, H^{4c}), 7.69 – 7.57 (m, H^{3a}, H^{3b}, H^{3c}), 7.46 – 7.32 (m, H^{5a}, H^{6a}, H^{5b}, H^{6b}, H^{5c}, H^{6c}), 7.32 – 7.26 (m, H^{2a}, H^{2b}, H^{2c}), 3.52 – 3.42 (m, H^{7b}), 3.31 – 3.17 (m, H^{7a}, H^{7b}), 3.15 – 3.05 (m, H^{7c}), 3.05 – 2.99 (m, H^{7a}), 2.39 (s, H^{1a}, H^{1b}, H^{1c}), 1.69 – 1.21 (m, H^{8a}, H^{9a}, H^{10a}, H^{9b}, H^{10b}, H^{8c}), 1.31 (d, J = 6.8 Hz, H^{8b}), 1.16 (d, J = 6.8 Hz, H^{8b}), 1.07 (t, J = 7.4 Hz, H^{9c}), 1.00 (t, J = 7.4 Hz, H^{9c}), 0.95 (t, J = 6.9 Hz, H^{11b}), 0.93 – 0.81 (m, H^{11a}, H^{11b}).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 176.5, 176.3, 142.9, 142.7, 142.5, 137.1(2), 137.0(5), 130.6(2), 130.5(5), 130.5(3), 130.5(0), 130.3, 130.2, 130.1, 129.0, 128.9, 128.8(4), 128.8(0), 128.7(6), 128.6, 128.1, 127.8(0), 127.7(7), 127.7, 127.6, 127.3, 63.6, 55.5, 54.5, 49.8, 33.1, 32.6, 30.5, 29.7, 23.0, 22.1, 21.5, 20.6, 20.4, 13.9, 13.8, 13.6, 13.1, 11.0, 10.9.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{24}NOS$ $[M + H]^+$ 314.1573, found 314.1571.

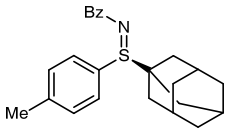
(*S*)-*N*-(Adamantan-2-yl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (6A)



According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and adamantane **C6** (1.09 g, 8.0 mmol, 40 equiv.), the reaction mixture was purified by

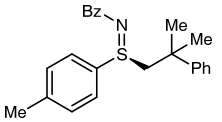
column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **6A** as a yellow solid (18.9 mg, 25% yield, 95% e.e.).
M.P.: 153–156 ℃.
$[\alpha]_D^{25}$ = –116.93 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 14.43 min, t_R (major) = 20.55 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.12 (m, 2H), 7.73 – 7.65 (m, 2H), 7.43 – 7.38 (m, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 3.46 (s, 1H), 2.79 – 2.73 (m, 1H), 2.38 (s, 3H), 2.34 – 2.28 (m, 1H), 2.22 – 2.16 (m, 1H), 2.07 – 2.00 (m, 2H), 1.95 – 1.91 (m, 1H), 1.86 – 1.70 (m, 5H), 1.68 – 1.57 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 142.9, 137.2, 130.7, 130.5, 130.4, 128.8, 128.0, 127.7, 68.7, 37.9, 37.8, 37.1, 32.4, 31.8, 28.4, 28.2, 27.3, 27.1, 21.5.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{28}NOS$ $[M + H]^+$ 378.1886, found 378.1882.

(*S*)-*N*-(Adamantan-1-yl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (6B)



According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and adamantane **C6** (1.09 g, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **6B** as a yellow solid (24.9 mg, 33% yield, 96% e.e.).
M.P.: 168–171 ℃.
$[\alpha]_D^{25}$ = –19.9 (c 0.5, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 12.50 min, t_R (major) = 21.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.22 (m, 2H), 7.61 – 7.55 (m, 2H), 7.46 – 7.41 (m, 1H), 7.41 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 2.40 (s, 3H), 2.17 – 2.12 (m, 3H), 1.99 – 1.87 (m, 6H), 1.72 – 1.62 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 142.7, 137.7, 130.6, 129.8, 129.2, 129.0, 127.8 126.1, 58.0, 36.6, 36.1, 29.3, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{28}NOS$ $[M + H]^+$ 378.1886, found 378.1881.

(*S*)-*N*-((2-Methyl-2-phenylpropyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (7)



According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and neat *tert*-butylbenzene **C7** (2.0 mL) in the absence of $PhCF_3$, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **7** as a white solid (18.8 mg, 25% yield, 65% e.e.).
According to **General Procedure B** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and

neat *tert*-butylbenzene **C7** (2.0 mL) in the absence of $PhCF_3$, **H3** (282.0 mg, 1.0 mmol, 5.0 equiv.) was used as the HAT reagent instead of **H1**, and the reaction mixture was stirred at r.t. for 72 h. Upon completion, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **7** as a white solid (36.1 mg, 48% yield, 93% e.e.).

M.P.: 90–97 ℃.

$[\alpha]_D^{25}$ = –44.97 (c 1.0, $CHCl_3$).

HPLC analysis with **General Procedure A**: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 9.45 min, t_R (major) = 17.07 min.

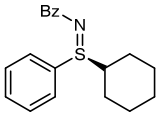
HPLC analysis with **General Procedure B**: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 8.94 min, t_R (major) = 17.02 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.08 (m, 2H), 7.44 – 7.27 (m, 9H), 7.24 – 7.15 (m, 3H), 3.80 (d, *J* = 13.2 Hz, 1H), 3.35 (d, *J* = 13.2 Hz, 1H), 2.35 (s, 3H), 1.69 (s, 3H), 1.51 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 145.7, 142.6, 136.8, 133.1, 130.7, 130.5, 128.8, 128.7, 127.9, 127.1, 127.0, 125.9, 66.3, 38.4, 29.8, 27.7, 21.6.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}NOS$ $[M + H]^+$ 376.1730, found 376.1726.

(*S*)-*N*-(Cyclohexyl(phenyl)-λ^4-sulfaneylidene)benzamide (8)



According to **General Procedure A** with sulfenamide **S2** (45.9 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **8** as a light yellow oil (51.7 mg, 83% yield, 98% e.e.).

$[\alpha]_D^{25}$ = –132.92 (c 1.0, $CHCl_3$).

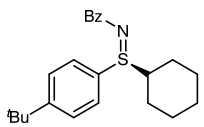
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 9.92 min, t_R (major) = 13.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 2H), 7.79 – 7.73 (m, 2H), 7.57 – 7.48 (m, 3H), 7.45 – 7.34 (m, 3H), 3.27 – 3.17 (m, 1H), 2.20 – 2.11 (m, 1H), 1.92 – 1.77 (m, 3H), 1.69 – 1.61 (m, 1H), 1.60 – 1.49 (m, 1H), 1.39 – 1.17 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 137.1, 132.4, 132.1, 130.6, 129.6, 128.9, 128.2, 127.8, 58.9, 27.1, 26.8, 25.5(5), 25.5(2), 25.4.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}NOS$ $[M + H]^+$ 312.1417, found 312.1415.

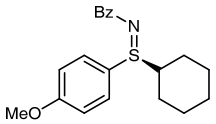
(*S*)-*N*-((4-(*tert*-Butyl)phenyl)(cyclohexyl)-λ^4-sulfaneylidene)benzamide (9)



According to **General Procedure A** with sulfenamide **S3** (57.1 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by

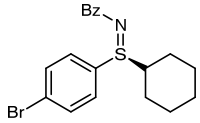
column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **9** as a light yellow oil (55.9 mg, 76% yield, 97% e.e.).
$[\alpha]_D^{25}$ = –116.93 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 7.39 min, t_R (major) = 11.54 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.16 (m, 2H), 7.69 (d, *J* = 8.6, 2H), 7.52 (d, *J* = 8.5, 2H), 7.45 – 7.33 (m, 3H), 3.28 – 3.17 (m, 1H), 2.24 – 2.15 (m, 1H), 1.92 – 1.79 (m, 3H), 1.69 – 1.62 (m, 1H), 1.61 – 1.49 (m, 1H), 1.41 – 1.19 (m, 13H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 155.8, 137.3, 130.6, 129.0, 128.9, 128.1, 127.8, 126.7, 58.8, 35.2, 31.2, 27.2, 26.8, 25.5(3), 25.5(0).
HRMS (ESI) *m/z* calcd. for $C_{23}H_{30}NOS$ $[M + H]^+$ 368.2043, found 368.2042.

(*S*)-*N*-(Cyclohexyl(4-methoxyphenyl)-λ^4-sulfaneylidene)benzamide (10)



According to **General Procedure A** with sulfenamide **S4** (51.9 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **10** as a white solid (59.4 mg, 87% yield, 97% e.e.).
M.P.: 142–144 °C.
$[\alpha]_D^{25}$ = –131.92 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 11.01 min, t_R (major) = 20.51 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 2H), 7.70 (d, *J* = 8.9, 2H), 7.44 – 7.33 (m, 3H), 7.01 (d, *J* = 9.0, 2H), 3.83 (s, 3H), 3.26 – 3.16 (m, 1H), 2.24 – 2.15 (m, 1H), 1.91 – 1.77 (m, 3H), 1.70 – 1.60 (m, 1H), 1.54 – 1.43 (m, 1H), 1.40 – 1.16 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 162.8, 137.3, 130.5, 130.1, 128.8, 127.8, 122.9, 115.1, 58.9, 55.6, 27.3, 26.5, 25.5, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NO_2S$ $[M + H]^+$ 342.1522, found 342.1521.

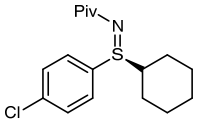
(*S*)-*N*-((4-Bromophenyl)(cyclohexyl)-λ^4-sulfaneylidene)benzamide (11)



According to **General Procedure A** with sulfenamide **S5** (61.6 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **11** as a white solid (63.2 mg, 81% yield, 97% e.e.).
M.P.: 159–161 °C.
$[\alpha]_D^{25}$ = –154.91 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ =

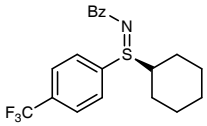
254 nm), t_R (minor) = 10.12 min, t_R (major) = 23.71 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.15 (m, 2H), 7.70 – 7.60 (m, 4H), 7.47 – 7.34 (m, 3H), 3.26 – 3.14 (m, 1H), 2.20 – 2.10 (m, 1H), 1.92 – 1.81 (m, 3H), 1.72 – 1.62 (m, 1H), 1.59 – 1.44 (m, 1H), 1.41 – 1.17 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 136.8, 132.9, 131.7, 130.8, 129.7, 128.9, 127.9, 126.9, 58.9, 27.1, 26.8, 25.6, 25.5, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}BrNOS$ $[M + H]^+$ 390.0522, found 390.0516.

(*S*)-*N*-((4-Chlorophenyl)(cyclohexyl)-λ^4-sulfaneylidene)pivalamide (12)



According to **General Procedure A** with sulfenamide **S6** (48.8 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford product **12** as a white solid (58.7 mg, 90% yield, 96% e.e.).
M.P.: 98–101 ℃.
$[\alpha]_D^{25}$ = –252.85 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 11.69 min, t_R (major) = 24.66 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5, 2H), 7.48 (d, *J* = 8.6, 2H), 3.15 – 3.00 (m, 1H), 2.09 – 1.99 (m, 1H), 1.89 – 1.74 (m, 3H), 1.69 – 1.60 (m, 1H), 1.48 – 1.36 (m, 1H), 1.33 – 1.14 (m, 13H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 138.2, 131.5, 129.7, 129.3, 58.2, 40.3, 28.7, 26.9, 26.6, 25.5, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}ClNOS$ $[M + H]^+$ 326.1340, found 326.1339.

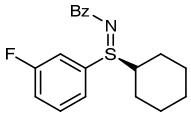
(*S*)-*N*-(Cyclohexyl(4-(trifluoromethyl)phenyl)-λ^4-sulfaneylidene)benzamide (13)



According to **General Procedure A** with sulfenamide **S7** (59.5 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **13** as a white solid (66.8 mg, 88% yield, 96% e.e.).
M.P.: 129–131 ℃.
$[\alpha]_D^{25}$ = –163.90 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 43.63 min, t_R (major) = 33.55 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.15 (m, 2H), 7.89 (d, *J* = 8.2, 2H), 7.78 (d, *J* = 8.2, 2H), 7.50 – 7.35 (m, 3H), 3.34 – 3.16 (m, 1H), 2.20 – 2.09 (m, 1H), 1.96 – 1.81 (m, 3H), 1.74 – 1.65 (m, 1H), 1.65 – 1.53 (m, 1H), 1.41 – 1.21 (m, 4H).

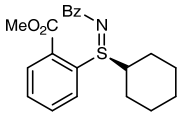
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 137.2, 136.7, 134.1 (q, *J* = 33.1), 131.0, 129.0, 128.6, 127.9, 126.6 (q, *J* = 3.7), 123.4 (q, *J* = 272.9), 59.0, 27.0, 25.6, 25.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ –63.02.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}F_3NOS$ $[M + H]^+$ 380.1290, found 380.1289.

(*S*)-*N*-(Cyclohexyl(3-fluorophenyl)-λ^4-sulfaneylidene)benzamide (14)



According to **General Procedure A** with sulfenamide **S8** (49.5 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **14** as a white solid (56.0 mg, 85% yield, 97% e.e.).
M.P.: 82–85 ℃.
$[\alpha]_D^{25}$ = –168.90 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 10.50 min, t_R (major) = 13.93 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.15 (m, 2H), 7.57 – 7.34 (m, 6H), 7.29 – 7.20 (m, 1H), 3.26 – 3.17 (m, 1H), 2.18 – 2.09 (m, 1H), 1.95 – 1.81 (m, 3H), 1.71 – 1.63 (m, 1H), 1.62 – 1.50 (m, 1H), 1.41 – 1.18 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 163.0 (d, *J* = 252.2), 136.7, 134.8 (d, *J* = 6.6), 131.1 (d, *J* = 8.0), 130.9, 128.9, 127.9, 124.1 (d, *J* = 3.4), 119.5 (d, *J* = 21.5), 115.1 (d, *J* = 24.3), 59.1, 27.0, 26.8, 25.5, 25.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ –108.92.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}FNOS$ $[M + H]^+$ 330.1322, found 330.1321.

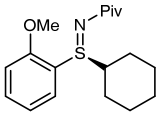
Methyl (*S*)-2-(*N*-benzoyl-cyclohexylsulfinimidoyl)benzoate (15)



According to **General Procedure A** with sulfenamide **S9** (57.5 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **15** as a white solid (54.7 mg, 74% yield, 91% e.e.).
M.P.: 153–164 ℃.
$[\alpha]_D^{25}$ = –181.89 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 24.25 min, t_R (major) = 17.20 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.23 (m, 2H), 8.18 – 8.08 (m, 1H), 8.02 – 7.94 (m, 1H), 7.68 – 7.61 (m, 1H), 7.59 – 7.52 (m, 1H), 7.48 – 7.37 (m, 3H), 3.99 (s, 3H), 3.44 – 3.32 (m, 1H), 2.22 – 2.13 (m, 1H), 2.08 – 1.97 (m, 1H), 1.97 – 1.82 (m, 3H), 1.73 – 1.64 (m, 1H), 1.57 – 1.50 (m, 1H), 1.45 – 1.16 (m, 3H).

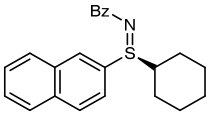
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 165.7, 137.3, 135.9, 133.3, 131.7, 130.9, 130.6, 129.5, 128.9, 127.8, 127.7, 57.8, 53.0, 28.9, 26.5, 26.0, 25.4, 24.7.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}NO_3S$ $[M + H]^+$ 370.1471, found 370.1471.

(*S*)-*N*-(Cyclohexyl(2-methoxyphenyl)-λ^4-sulfaneylidene)pivalamide (16)



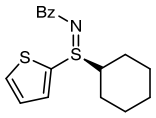
According to **General Procedure A** with sulfenamide **S10** (47.9 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **16** as a yellow solid (59.8 mg, 93% yield, 90% e.e.).
M.P.: 99–104 °C.
$[\alpha]_D^{25}$ = –295.82 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 14.49 min, t_R (major) = 12.19 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 1H), 7.50 – 7.40 (m, 1H), 7.14 – 7.05 (m, 1H), 7.00 – 6.92 (m, 1H), 3.90 (s, 3H), 3.18 – 3.04 (m, 1H), 1.96 – 1.88 (m, 1H), 1.87 – 1.76 (m, 2H), 1.76 – 1.68 (m, 1H), 1.66 – 1.56 (m, 2H), 1.55 – 1.44 (m, 1H), 1.31 – 1.18 (m, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 157.6, 132.6, 127.9, 121.6, 120.7, 111.5, 56.8, 56.2, 40.5, 28.8, 27.3, 25.9, 25.6, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{28}NO_2S$ $[M + H]^+$ 322.1835, found 322.1834.

(*S*)-*N*-(Cyclohexyl(naphthalen-2-yl)-λ^4-sulfaneylidene)benzamide (17)



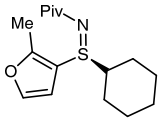
According to **General Procedure A** with sulfenamide **S11** (55.9 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **17** as a white solid (51.3 mg, 71% yield, 97% e.e.).
M.P.: 145–148 °C.
$[\alpha]_D^{25}$ = –127.92 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 13.35 min, t_R (major) = 21.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.19 (m, 3H), 8.00 – 7.77 (m, 4H), 7.63 – 7.54 (m, 2H), 7.48 – 7.35 (m, 3H), 3.43 – 3.25 (m, 1H), 2.28 – 2.18 (m, 1H), 1.93 – 1.76 (m, 3H), 1.69 – 1.53 (m, 2H), 1.40 – 1.17 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 137.1, 134.9, 132.8, 130.7, 129.9, 129.7, 129.4, 128.9, 128.7, 128.4, 128.1, 127.8, 127.5, 123.0, 58.8, 27.2, 26.9, 25.5(2), 25.4(8), 25.4.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}NOS$ $[M + H]^+$ 362.1573, found 362.1572.

(*S*)-*N*-(Cyclohexyl(thiophen-2-yl)-λ^4-sulfaneylidene)benzamide (18)



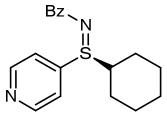
According to **General Procedure A** with sulfenamide **S12** (47.1 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **18** as a light yellow solid (34.3 mg, 54% yield, 96% e.e.).
M.P.: 137–142 ℃.
$[\alpha]_D^{25}$ = –37.98 (c 0.5, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 23.85 min, t_R (major) = 29.68 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.14 (m, 2H), 7.74 – 7.67 (m, 1H), 7.59 – 7.53 (m, 1H), 7.47 – 7.34 (m, 3H), 7.18 – 7.11 (m, 1H), 3.57 – 3.43 (m, 1H), 2.29 – 2.19 (m, 1H), 1.94 – 1.78 (m, 3H), 1.71 – 1.62 (m, 1H), 1.53 – 1.42 (m, 1H), 1.40 – 1.17 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 136.8, 133.2, 133.1, 132.5, 130.8, 128.9, 127.9, 127.5, 60.6, 27.5, 26.4, 25.5, 25.4(6), 25.3(7).
HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}NOS_2$ $[M + H]^+$ 318.0981, found 318.0980.

(*S*)-*N*-(Cyclohexyl(2-methylfuran-3-yl)-λ^4-sulfaneylidene)pivalamide (19)



According to **General Procedure A** with sulfenamide **S13** (42.7 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford product **19** as a white solid (43.1 mg, 73% yield, 96% e.e.).
M.P.: 141–148 ℃.
$[\alpha]_D^{25}$ = –66.96 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 25.61 min, t_R (major) = 34.24 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.1, 1H), 6.62 (d, *J* = 2.1, 1H), 3.41 – 3.30 (m, 1H), 2.49 (s, 3H), 2.20 – 2.14 (m, 1H), 1.89 – 1.77 (m, 3H), 1.71 – 1.63 (m, 1H), 1.39 – 1.21 (m, 5H), 1.19 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 157.1, 142.4, 111.2, 108.9, 56.5, 40.1, 28.7, 27.5, 26.2, 25.5, 25.2(4), 25.2(1), 12.7.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{26}NO_2S$ $[M + H]^+$ 296.1679, found 296.1679.

(*S*)-*N*-(Cyclohexyl(pyridin-4-yl)-λ^4-sulfaneylidene)benzamide (20)



According to **General Procedure A** with sulfenamide **S14** (46.1 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 1/1) to afford product **20** as a white solid (36.2 mg, 58% yield, 89% e.e.).

M.P.: 123–127 ℃.

[α]$_D^{25}$ = –79.95 (c 0.5, $CHCl_3$).

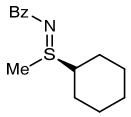
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 10.11 min, t_R (major) = 17.25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 – 8.74 (m, 2H), 8.25 – 8.17 (m, 2H), 7.71 – 7.61 (m, 2H), 7.51 – 7.37 (m, 3H), 3.30 – 3.18 (m, 1H), 2.10 – 2.03 (m, 1H), 2.02 – 1.96 (m, 1H), 1.92 – 1.83 (m, 2H), 1.73 – 1.57 (m, 2H), 1.48 – 1.20 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 150.8, 143.0, 136.4, 131.1, 129.0, 128.0, 122.0, 58.9, 27.1, 26.7, 25.7, 25.6, 25.3.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}N_2OS$ $[M + H]^+$ 313.1369, found 313.1368.

(*R*)-*N*-(Cyclohexyl(methyl)-λ^4-sulfaneylidene)benzamide (21)



According to **General Procedure A** with sulfenamide **S15** (33.5 mg, 0.20 mmol), cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), and **L5** (17.5 mg, 0.030 mmol, 15 mol%) as the ligand, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **21** as a colorless oil (28.9 mg, 58% yield, 84% e.e.).

[α]$_D^{25}$ = –83.95 (c 1.0, $CHCl_3$).

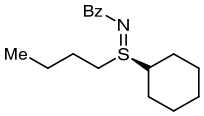
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 10.48 min, t_R (major) = 8.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 2H), 7.45 – 7.33 (m, 3H), 3.23 – 3.12 (m, 1H), 2.66 (s, 3H), 2.27 – 2.19 (m, 1H), 2.12 – 2.03 (m, 1H), 1.96 – 1.86 (m, 2H), 1.76 – 1.67 (m, 1H), 1.59 – 1.47 (m, 2H), 1.45 – 1.22 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 137.0, 130.6, 128.6, 127.8, 55.7, 27.0, 26.7, 26.4, 25.5, 25.4.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{20}NOS$ $[M + H]^+$ 250.1260, found 250.1259.

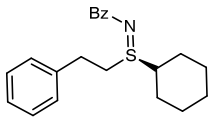
(*R*)-*N*-(Butyl(cyclohexyl)-λ^4-sulfaneylidene)benzamide (22)



According to **General Procedure A** with sulfenamide **S16** (41.9 mg, 0.20 mmol) and

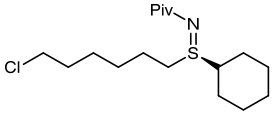
cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **22** as a light yellow solid (45.5 mg, 78% yield, 93% e.e.).
M.P.: 66–70 ℃.
$[\alpha]_D^{25}$ = 46.97 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 34.37 min, t_R (major) = 28.03 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 2H), 7.44 – 7.33 (m, 3H), 3.16 (tt, *J* = 11.5, 3.6, 1H), 3.06 – 2.88 (m, 2H), 2.19 – 2.11 (m, 1H), 2.07 – 2.02 (m, 1H), 1.95 – 1.86 (m, 2H), 1.83 – 1.67 (m, 3H), 1.64 – 1.44 (m, 4H), 1.42 – 1.25 (m, 3H), 0.95 (t, *J* = 7.4, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 137.4, 130.5, 128.8, 127.8, 55.3, 41.9, 27.3, 26.8, 25.7, 25.6, 25.5, 22.0, 13.7.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{26}NOS$ $[M + H]^+$ 292.1730, found 292.1729.

(*R*)-*N*-(Cyclohexyl(phenethyl)-λ^4-sulfaneylidene)benzamide (23)



According to **General Procedure A** with sulfenamide **S17** (51.5 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **23** as a white solid (50.2 mg, 74% yield, 91% e.e.).
M.P.: 70–73 ℃.
$[\alpha]_D^{25}$ = 30.98 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 11.21 min, t_R (major) = 8.71 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 2H), 7.46 – 7.34 (m, 3H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 3H), 3.34 – 3.24 (m, 1H), 3.22 – 3.04 (m, 4H), 2.19 – 2.07 (m, 1H), 2.06 – 1.97 (m, 1H), 1.94 – 1.82 (m, 2H), 1.73 – 1.64 (m, 1H), 1.61 – 1.47 (m, 2H), 1.39 – 1.22 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 138.5, 137.3, 130.6, 128.9, 128.8, 128.7, 127.8, 127.1, 55.5, 43.6, 29.9, 27.2, 26.9, 25.5, 25.4(8), 25.4(5).
HRMS (ESI) *m/z* calcd. for $C_{21}H_{26}NOS$ $[M + H]^+$ 340.1730, found 340.1730.

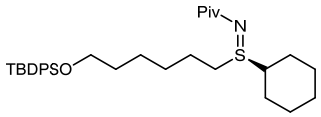
(*R*)-*N*-((6-Chlorohexyl)(cyclohexyl)-λ^4-sulfaneylidene)pivalamide (24)



According to **General Procedure A** with sulfenamide **S18** (50.4 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford product **24** as a

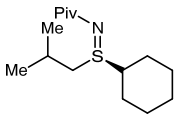
colorless oil (52.1 mg, 78% yield, 92% e.e.).
$[\alpha]_D^{25}$ = 40.98 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 238 nm), t_R (minor) = 17.63 min, t_R (major) = 21.72 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (t, *J* = 6.6, 2H), 3.08 (tt, *J* = 11.4, 3.6, 1H), 2.97 – 2.88 (m, 1H), 2.85 – 2.77 (m, 1H), 2.09 – 2.01 (m, 1H), 2.01 – 1.93 (m, 1H), 1.91 – 1.83 (m, 2H), 1.81 – 1.65 (m, 5H), 1.53 – 1.41 (m, 6H), 1.40 – 1.26 (m, 3H), 1.20 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 54.8, 44.9, 41.6, 40.4, 32.3, 28.8, 27.9, 27.3, 26.8, 26.4, 25.5, 25.4, 23.4.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{33}ClNOS$ $[M + H]^+$ 334.1966, found 334.1967.

(*R*)-*N*-((6-((*tert*-Butyldiphenylsilyl)oxy)hexyl)(cyclohexyl)-λ^4-sulfaneylidene) pivalamide (25)



According to **General Procedure A** with sulfenamide **S19** (94.4 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford product **25** as a colorless oil (94.2 mg, 85% yield, 86% e.e.).
$[\alpha]_D^{25}$ = 27.98 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 94/6, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 14.14 min, t_R (major) = 14.81 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 4H), 7.45 – 7.29 (m, 6H), 3.63 (t, *J* = 6.3 Hz, 1H), 3.10 – 2.99 (m, 1H), 2.95 – 2.83 (m, 1H), 2.81 – 2.69 (m, 1H), 2.02 (d, *J* = 14.0 Hz, 1H), 1.93 (d, *J* = 14.3 Hz, 1H), 1.90 – 1.76 (m, 2H), 1.73 – 1.61 (m, 3H), 1.53 (t, *J* = 6.3 Hz, 2H), 1.48 – 1.22 (m, 9H), 1.19 (s, 9H), 1.03 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 135.5, 133.9, 129.5, 127.6, 63.6, 54.6, 41.4, 40.3, 32.2, 28.8, 27.2, 26.9, 26.6, 25.4, 25.3(2), 25.3(0), 23.3, 19.2.
HRMS (ESI) *m/z* calcd. for $C_{33}H_{52}NO_2SSi$ $[M + H]^+$ 554.3483, found 554.3481.

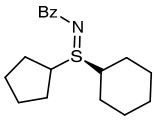
(*R*)-*N*-(Cyclohexyl(isobutyl)-l4-sulfaneylidene)pivalamide (26)



According to **General Procedure A** with sulfenamide **S20** (37.9 mg, 0.20 mmol) and cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford product **26** as a colorless oil (45.1 mg, 83% yield, 95% e.e.).
$[\alpha]_D^{25}$ = 131.92 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254

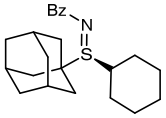
nm), t_R (minor) = 45.01 min, t_R (major) = 39.28 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02 (tt, *J* = 11.5, 3.7 Hz, 1H), 2.86 (dd, *J* = 12.4, 5.2 Hz, 1H), 2.45 (dd, *J* = 12.4, 9.0 Hz, 1H), 2.04 – 1.98 (m, 1H), 1.99 – 1.87 (m, 2H), 1.86 – 1.73 (m, 2H), 1.62 (d, *J* = 11.9 Hz, 1H), 1.46 – 1.33 (m, 2H), 1.33 – 1.14 (m, 5H), 1.12 (s, 9H), 1.00 (t, *J* = 6.0 Hz, 6H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 55.3, 51.0, 40.3, 28.7, 27.2, 26.5, 25.5, 25.4(7), 25.4(6), 24.7, 22.6, 21.7.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{30}NOS$ $[M + H]^+$ 272.2043, found 272.2041.

(*R*)-*N*-(Cyclohexyl(cyclopentyl)-λ^4-sulfaneylidene)benzamide (27)



According to **General Procedure A** with sulfenamide **S21** (44.3 mg, 0.20 mmol), cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), and K_3PO_4 (84.9 mg, 0.40 mmol, 2.0 equiv.) as base, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **27** as a colorless oil (48.4 mg, 80% yield, 91% e.e.).
$[\alpha]_D^{25}$ = 21.99 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 45.19 min, t_R (major) = 39.86 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.07 (m, 2H), 7.45 – 7.32 (m, 3H), 3.57 – 3.45 (m, 1H), 3.08 – 2.96 (m, 1H), 2.33 – 2.20 (m, 1H), 2.10 – 1.97 (m, 3H), 1.94 – 1.73 (m, 6H), 1.73 – 1.57 (m, 5H), 1.41 – 1.23 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 137.7, 130.5, 128.9, 127.8, 55.8, 52.8, 29.3, 28.4, 27.2, 26.4, 26.1, 25.9, 25.6, 25.5, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{26}NOS$ $[M + H]^+$ 304.1730, found 304.1729.

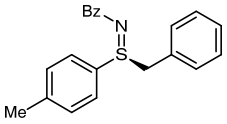
***N*-((*S*)-(Adamantan-1-yl)(cyclohexyl)-λ^4-sulfaneylidene)benzamide (28)**



According to **General Procedure A** with sulfenamide **S22** (57.5 mg, 0.20 mmol), cyclohexane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), and K_3PO_4 (84.9 mg, 0.40 mmol, 2.0 equiv.) as base, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **28** as a white solid (61.3 mg, 83% yield, 82% e.e.).
M.P.: 142–147 °C.
$[\alpha]_D^{25}$ = 66.96 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 230 nm), t_R (minor) = 32.88 min, t_R (major) = 42.56 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.15 (m, 2H), 7.43 – 7.33 (m, 3H), 3.13 – 2.99

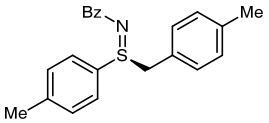
(m, 1H), 2.23 – 2.15 (m, 3H), 2.12 – 1.98 (m, 8H), 1.97 – 1.91 (m, 1H), 1.90 – 1.71 (m, 8H), 1.67 – 1.60 (m, 1H), 1.59 – 1.48 (m, 1H), 1.42 – 1.23 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 137.8, 130.3, 128.8, 127.7, 56.4, 50.5, 37.1, 36.2, 31.8, 29.1, 26.8, 26.3, 25.7, 25.2.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{32}NOS$ $[M + H]^+$ 370.2199, found 370.2199.

(*S*)-*N*-(Benzyl(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (29)



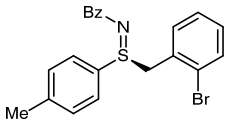
According to **General Procedure B** with toluene **C8** (0.43 mL, 4.0 mmol, 20 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **29** as a white solid (53.4 mg, 80% yield, 98% e.e.).
M.P.: 99–105 ℃.
$[\alpha]_D^{25}$ = 203.88 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 11.69 min, t_R (major) = 24.84 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.15 (m, 2H), 7.49 – 7.36 (m, 5H), 7.31 – 7.18 (m, 5H), 7.01 – 6.93 (m, 2H), 4.64 (d, *J* = 12.3, 1H), 4.23 (d, *J* = 12.3, 1H), 2.39 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.1, 136.8, 130.9, 130.8, 130.2, 128.9(1), 128.8(9), 128.8, 128.6(3), 128.6(1), 128.2, 127.9, 56.1, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}NOS$ $[M + H]^+$ 334.1260, found 334.1256.

(*S*)-*N*-((4-Methylbenzyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (30)



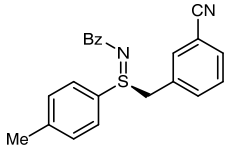
According to **General Procedure B** with *p*-xylene **C9** (0.49 mL, 4.0 mmol, 20 equiv.), the reaction mixture was stirred at −10 ℃ for 72 h. The reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **30** as a white solid (46.6 mg, 67% yield, 92% e.e.).
M.P.: 135–137 ℃.
$[\alpha]_D^{25}$ = 147.91 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 20.13 min, t_R (major) = 40.13 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.16 (m, 2H), 7.45 (d, *J* = 8.4, 2H), 7.43 – 7.34 (m, 3H), 7.22 (d, *J* = 8.0, 2H), 7.02 (d, *J* = 7.8, 2H), 6.86 (d, *J* = 7.9, 2H), 4.60 (d, *J* = 12.4, 1H), 4.19 (d, *J* = 12.3, 1H), 2.39 (s, 3H), 2.30 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.0, 138.9, 136.8, 130.8, 130.7, 130.1, 129.3, 129.0, 128.8, 128.2, 127.9, 125.4, 55.9, 21.6, 21.3.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}NOS$ $[M + H]^+$ 348.1417, found 348.1415.

(*S*)-*N*-((2-Bromobenzyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (31)



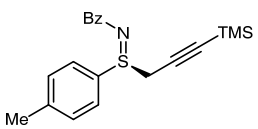
According to **General Procedure B** with 2-bromotoluene **C10** (0.48 mL, 4.0 mmol, 20 equiv.), the reaction mixture was stirred at −10 ℃ for 72 h. The reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **31** as a white solid (53.6 mg, 65% yield, 99% e.e.).
M.P.: 128–130 ℃.
[α]$_D^{25}$ = 32.98 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 13.12 min, t_R (major) = 21.59 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.17 (m, 2H), 7.57 – 7.33 (m, 6H), 7.25 – 7.05 (m, 5H), 4.86 (d, *J* = 12.3, 1H), 4.32 (d, *J* = 12.3, 1H), 2.37 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.2, 136.6, 133.2, 133.0, 130.8, 130.6, 130.2, 129.4, 129.2, 128.8, 127.8(2), 127.7(6), 127.5, 125.8, 56.1, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{19}BrNOS$ $[M + H]^+$ 412.0365, found 412.0364.

(*S*)-*N*-((3-Cyanobenzyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (32)



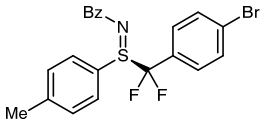
According to **General Procedure B** with *m*-tolunitrile **C11** (0.48 mL, 4.0 mmol, 20 equiv.), the reaction mixture was stirred at −10 ℃ for 72 h. The reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **32** as a white solid (42.3 mg, 59% yield, 99% e.e.).
M.P.: 135–137 ℃.
[α]$_D^{25}$ = 99.94 (c 0.5, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 16.95 min, t_R (major) = 28.57 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.11 (m, 2H), 7.62 – 7.54 (m, 1H), 7.50 – 7.31 (m, 6H), 7.31 – 7.21 (m, 3H), 7.04 (s, 1H), 4.51 – 4.36 (m, 2H), 2.42 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.8, 136.3, 135.4, 134.2, 132.3, 131.1, 130.4, 129.9, 129.3, 128.7, 128.0(0), 128.7(9), 127.8, 118.0, 112.5, 54.4, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{19}N_2OS$ $[M + H]^+$ 359.1213, found 359.1212.

(*S*)-*N*-(*p*-Tolyl(3-(trimethylsilyl)prop-2-yn-1-yl)-λ^4-sulfaneylidene)benzamide (33)



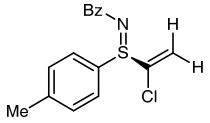
According to **General Procedure B** with 1-(trimethylsilyl)-1-propyne **C12** (1.19 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **33** as a yellow oil (49.5 mg, 70% yield, 98% e.e.).
$[\alpha]_D^{25}$ = 229.86 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 13.35 min, t_R (major) = 24.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.03 (m, 2H), 7.77 – 7.66 (m, 2H), 7.38 – 7.20 (m, 5H), 4.16 (d, *J* = 15.6, 1H), 3.73 (d, *J* = 15.6, 1H), 2.33 (s, 3H), 0.00 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.6, 136.3, 130.9, 130.1, 129.0, 128.8, 128.4, 127.8, 95.4, 93.3, 42.5, 21.6, –0.5.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NOSSi$ $[M + H]^+$ 354.1342, found 354.1342.

(*R*)-*N*-(((4-Bromophenyl)difluoromethyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (34)



According to **General Procedure B** with 1-bromo-4-(difluoromethyl)benzene **C13** (1.03 mL, 8.0 mmol, 40 equiv.), **H3** (112.8 mg, 0.40 mmol, 2.0 equiv.) was used as HAT reagent instead of **H1**. The reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 4/1) to afford product **34** as a yellow oil (53.8 mg, 60% yield, 97% e.e.).
$[\alpha]_D^{25}$ = –56.97 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 18.60 min, t_R (major) = 29.34 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.03 (m, 2H), 7.56 – 7.44 (m, 5H), 7.43 – 7.37 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 2.42 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 144.7, 135.9, 131.4, 131.3, 130.4, 129.1, 129.0 (t, *J* = 6.1 Hz), 128.7, 128.0, 127.4 – 127.3 (m), 124.08 (d, *J* = 265.9 Hz), 21.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ –89.02 (d, *J* = 213.5 Hz), –93.74 (d, *J* = 213.5 Hz).
HRMS (ESI) *m/z* calcd. for $C_{21}H_{17}BrF_2NOS$ $[M + H]^+$ 448.0177, found 448.0176.

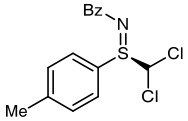
(*R*)-*N*-((1-Chlorovinyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (35)



According to **General Procedure B** with 1,2-dichloroethane **C14** (0.32 mL, 4.0 mmol, 20 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford product **35** as a colorless oil (33.4 mg, 55% yield, 98% e.e.).
$[\alpha]_D^{25}$ = –21.99 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ =

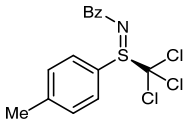
254 nm), t_R (minor) = 22.96 min, t_R (major) = 28.57 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.18 (m, 2H), 7.85 – 7.79 (m, 2H), 7.51 – 7.43 (m, 1H), 7.43 – 7.34 (m, 4H), 6.59 (d, *J* = 3.2, 1H), 6.09 (d, *J* = 3.2, 1H), 2.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 144.1, 137.0, 136.0, 131.3, 130.7, 129.1, 128.9, 128.6, 128.0, 122.2, 21.7.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}ClNOS$ $[M + H]^+$ 304.0557, found 304.0557.

(*R*)-*N*-((Dichloromethyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (36)



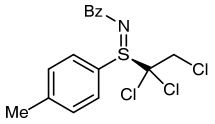
According to **General Procedure B** with dichloromethane **C15** (0.26 mL, 4.0 mmol, 20 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford product **36** as a white solid (58.7 mg, 90% yield, 96% e.e.).
M.P.: 73–78 ℃.
$[\alpha]_D^{25}$ = 78.95 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 15.68 min, t_R (major) = 22.56 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.16 (m, 2H), 8.03 – 7.94 (m, 2H), 7.53 – 7.38 (m, 5H), 7.34 (s, 1H), 2.49 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 145.6, 135.6, 131.6, 131.3, 130.1, 129.1, 128.1, 122.5, 78.6, 21.9.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{14}Cl_2NOS$ $[M + H]^+$ 326.0168, found 326.0168.

(*R*)-*N*-(*p*-Tolyl(trichloromethyl)-λ^4-sulfaneylidene)benzamide (37)



According to **General Procedure B** with chloroform **C16** (0.32 mL, 4.0 mmol, 20 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford product **37** as a white solid (62.0 mg, 86% yield, 93% e.e.).
M.P.: 169–177 ℃.
$[\alpha]_D^{25}$ = 54.97 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 18.86 min, t_R (major) = 28.08 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.27 (m, 2H), 8.09 – 8.00 (m, 2H), 7.54 – 7.36 (m, 5H), 2.46 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 146.0, 136.1, 131.7, 130.6, 130.1, 129.6, 128.0, 127.5, 107.7, 21.9.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{13}Cl_3NOS$ $[M + H]^+$ 359.9778, found 359.9778.

(*R*)-*N*-(*p*-Tolyl(1,1,2-trichloroethyl)-λ^4-sulfaneylidene)benzamide (38)



According to **General Procedure B** with 1,1,2-trichloroethane **C17** (0.74 mL, 8.0 mmol, 40 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford product **38** as a white solid (45.0 mg, 60% yield, 96% e.e.).

M.P.: 125–127 ℃.

$[\alpha]_D^{25}$ = 199.85 (c 0.5, $CHCl_3$).

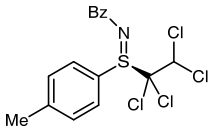
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 17.91 min, t_R (major) = 33.07 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.20 (m, 2H), 7.95 – 7.90 (m, 2H), 7.53 – 7.46 (m, 1H), 7.45 – 7.37 (m, 4H), 4.64 (d, *J* = 12.5, 1H), 4.24 (d, *J* = 12.5, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 145.5, 135.8, 131.7, 130.7, 130.1, 129.3, 128.1, 125.6, 100.3, 52.4, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}Cl_3NOS$ $[M + H]^+$ 373.9934, found 373.9935.

(*R*)-*N*-((1,1,2,2-Tetrachloroethyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (39)



According to **General Procedure B** with 1,1,2,2-tetrachloroethane **C18** (0.42 mL, 4.0 mmol, 20 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford product **39** as a yellow solid (67.9 mg, 83% yield, 94% e.e.).

M.P.: 58–62 ℃.

$[\alpha]_D^{25}$ = 28.98 (c 1.0, $CHCl_3$).

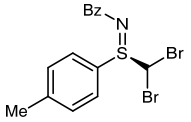
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 7.67 min, t_R (major) = 13.10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.16 (m, 2H), 7.94 – 7.86 (m, 2H), 7.55 – 7.48 (m, 1H), 7.46 – 7.38 (m, 4H), 6.72 (s, 1H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 145.9, 135.4, 131.8, 130.7, 130.2, 129.3, 128.1, 126.3, 105.1, 76.4, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}Cl_4NOS$ $[M + H]^+$ 407.9545, found 407.9544.

(*R*)-*N*-((Dibromomethyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (40)



According to **General Procedure B** with neat dibromomethane **C19** (2.0 mL) in the

absence of $PhCF_3$, **H3** (112.8 mg, 0.40 mmol, 2.0 equiv.) was used as HAT reagent instead of **H1**. Upon completion, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford product **40** as a white solid (49.0 mg, 59% yield, 98% e.e.).

M.P.: 97–101 ℃.

$[\alpha]_D^{25}$ = 99.98 (c 1.0, $CHCl_3$).

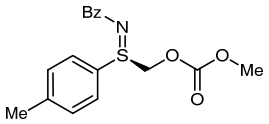
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 9.45 min, t_R (major) = 13.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.16 (m, 2H), 8.06 – 7.98 (m, 2H), 7.52 – 7.37 (m, 5H), 7.27 (s, 1H), 2.49 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 145.6, 135.7, 131.6, 131.3, 129.9, 129.1, 128.1, 123.6, 51.9, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{14}Br_2NOS$ $[M + Na]^+$413.9157, found 413.9160.

(*R*)-(*N*-Benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)methyl methyl carbonate (41)



According to **General Procedure B** with and neat dimethyl carbonate **C20** (2.0 mL) in the absence of $PhCF_3$, **H3** (112.8 mg, 0.40 mmol, 2.0 equiv.) was used as HAT reagent instead of **H1**. Upon completion, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **41** as a yellow solid (33.1 mg, 50% yield, 98% e.e.).

M.P.: 61–64 ℃.

$[\alpha]_D^{25}$ = –62.96 (c 1.0, $CHCl_3$).

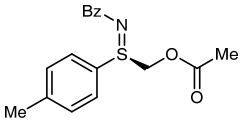
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 16.75 min, t_R (major) = 39.17 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.14 (m, 2H), 7.78 – 7.69 (m, 2H), 7.48 – 7.31 (m, 5H), 5.47 (d, *J* = 9.7, 1H), 5.36 (d, *J* = 9.7, 1H), 3.79 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 154.3, 143.9, 136.0, 131.1, 130.7, 128.9, 127.9, 127.8, 127.7, 78.2, 56.1, 21.6.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}NO_4S$ $[M + H]^+$ 332.0951, found 332.0951.

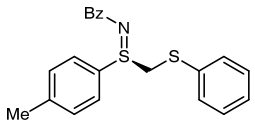
(*R*)-(*N*-Benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)methyl acetate (42)



According to **General Procedure B** with neat methyl acetate **C21** (2.0 mL) in the absence of $PhCF_3$, **H3** (282.0 mg, 1.0 mmol, 5.0 equiv.) was used as HAT reagent instead of **H1**. Upon completion, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **42** as a light yellow oil (49.0 mg, 43% yield, 95% e.e.).

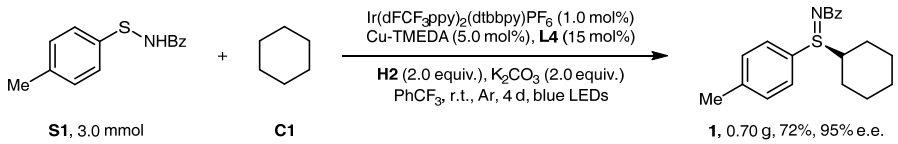
$[\alpha]_D^{25}$ = –79.95 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 14.06 min, t_R (major) = 28.48 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.12 (m, 2H), 7.79 – 7.69 (m, 2H), 7.49 – 7.33 (m, 5H), 5.44 (d, *J* = 9.6, 1H), 5.36 (d, *J* = 9.5, 1H), 2.43 (s, 3H), 2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 169.1, 143.8, 136.1, 131.1, 130.7, 128.9, 128.0, 127.9, 127.8, 75.5, 21.7, 20.4.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}NO_3SNa$ $[M + Na]^+$ 338.0821, found 338.0818.

(*R*)-*N*-(((Phenylthio)methyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (43)



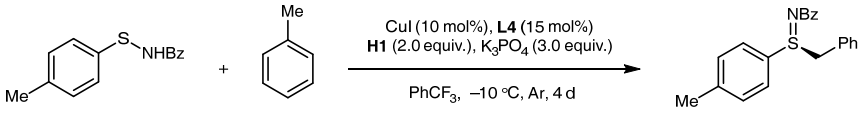
According to **General Procedure A** with sulfenamide **S1** (48.7 mg, 0.20 mmol) and methyl phenyl thioether **C22** (0.47 mL, 4.0 mmol, 20 equiv.), the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 3/1) to afford product **43** as a white solid (43.9 mg, 60% yield, 94% e.e.).
M.P.: 107–113 °C.
$[\alpha]_D^{25}$ = 74.95 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 11.73 min, t_R (major) = 19.48 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.11 (m, 2H), 7.83 – 7.77 (m, 2H), 7.51 – 7.41 (m, 3H), 7.41 – 7.26 (m, 7H), 5.01 (d, *J* = 13.2, 1H), 4.16 (d, *J* = 13.3, 1H), 2.42 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 143.8, 136.4, 132.8, 131.0, 130.4(4), 130.3(6), 129.6, 129.0, 128.9, 128.8, 127.9(3), 127.8(5), 55.1, 21.7.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}NOS_2$ $[M + H]^+$ 366.0981, found 366.0981.

6. Gram-scale reactions



S1, 3.0 mmol **C1** **1**, 0.70 g, 72%, 95% e.e.

Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S1** (729.9 mg, 3.0 mmol, 1.0 equiv.), cyclohexane **C1** (12.9 mL, 120 mmol, 40 equiv.), Cu-TMEDA (69.6 mg, 0.15 mmol, 5.0 mol%), **L4** (237 mg, 0.45 mmol, 15 mol%), Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (34.4 mg, 0.03 mmol, 1.0 mol%), **H2** (1.06 g, 6.0 mmol, 2.0 equiv.), K_2CO_3 (0.83 g, 6.0 mmol, 2.0 equiv.), and $PhCF_3$ (30 mL). The reaction mixture was stirred at r.t. under blue LED irradiation for 4 d under argon. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **1** as a white solid (0.70 g, 72% yield, 95% e.e.).

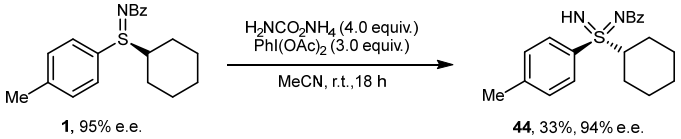


S1, 5.0 mmol **C8** **29**, 1.20 g, 72%, 97% e.e.

To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (95.2 mg, 0.50 mmol, 10 mol%), **L4** (395.0 mg, 0.75 mmol, 15 mol%), sulfenamide **S1** (1.22 g, 5.0 mmol, 1.0 equiv.), toluene **C8** (10.5 mL, 100 mmol, 20 equiv.), **H1** (2.34 g, 10 mmol, 2.0 equiv.), and K_3PO_4 (3.19 g, 15 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous $PhCF_3$ (50 mL). The reaction mixture was stirred at –10 °C for 4 d. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **29** as a white solid (1.20 g, 72% yield, 97% e.e.).

7. Transformation

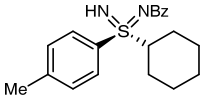
The synthesis of sulfondiimine from sulfilimine:



1, 95% e.e. **44**, 33%, 94% e.e.

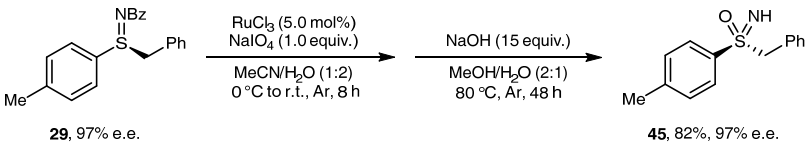
According to a literature procedure[8] with slight modification, the following synthesis was performed: To sulfinamide **1** (97.6 mg, 0.30 mmol, 1.0 equiv.) were added $PhI(OAc)_2$ (290 mg, 0.90 mmol, 3.0 equiv.), ammonium carbamate (93.7 mg, 1.2 mmol, 4.0 equiv.), and MeCN (1.2 mL). The mixture was stirred in an open flask at r.t. for 18 h, then quenched with saturated aqueous $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography on silica gel afforded product **44**.

(*S*)-*N*-(Cyclohexyl(imino)(*p*-tolyl)-λ^6-sulfaneylidene)benzamide (44)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 2/1) to afford **44** as a white solid (33.7 mg, 33% yield, 94% e.e.).
M.P.: 126–130 °C.
$[\alpha]_D^{25}$ = –5.00 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 230 nm), t_R (minor) = 11.51 min, t_R (major) = 13.13 min.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 2H), 7.82 – 7.76 (m, 2H), 7.51 – 7.45 (m, 1H), 7.43 – 7.36 (m, 2H), 7.35 – 7.29 (m, 2H), 3.23 (tt, *J* = 12.1, 3.3, 1H), 2.41 (s, 3H), 2.39 – 2.34 (m, 1H), 2.19 – 2.10 (m, 1H), 1.97 – 1.85 (m, 2H), 1.74 – 1.64 (m, 1H), 1.60 – 1.44 (m, 2H), 1.37 – 1.13 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 144.0, 136.6, 135.3, 131.6, 130.1, 129.1, 128.7, 128.0, 64.3, 25.5(4), 25.5(0), 25.3, 25.2(4), 25.1(9), 21.6.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{25}N_2OS$ $[M + H]^+$ 341.1682, found 341.1679.

The synthesis of sulfoximine from sulfilimine:

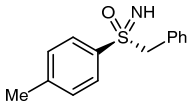


29, 97% e.e. **45**, 82%, 97% e.e.

According to a literature procedure[3] with slight modification, the following synthesis was performed: To a solution of sulfilimine **29** (66.6 mg, 0.20 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added a predissolved solution of $NaIO_4$ (43.2 mg, 0.20 mmol, 1.0

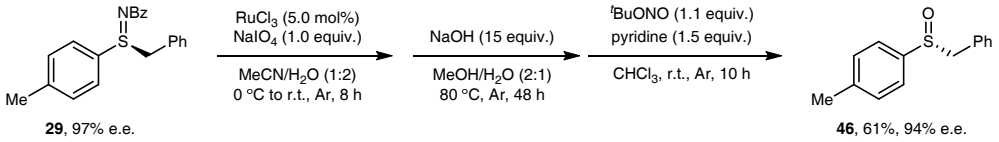
equiv.) in H_2O (4.0 mL). The solution was cooled to 0 °C, and $RuCl_3$ hydrate (2.0 mg, 0.010 mmol, 5.0 mol%) was added under argon. After stirring at 0 °C to r.t. for 8 h, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo.
The resulting residue was dissolved in MeOH (2.0 mL) and H_2O (1.0 mL), and NaOH (120 mg, 3.0 mmol, 15 equiv.) was added under argon. The reaction mixture was heated to 80 °C for 48 h. After cooling to r.t., the mixture was extracted with CH_2Cl_2, and the organic layers were combined and concentrated. Purification by column chromatography on silica gel afforded product **45**.

(*R*)-Benzyl(imino)(*p*-tolyl)-λ^6-sulfanone (45)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 2/1) to afford **45** as a white solid (40.3 mg, 82% yield, 97% e.e.).
M.P.: 111–120 ℃.
$[\alpha]_D^{25}$ = 12.99 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 34.87 min, t_R (major) = 36.97 min.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.56 (m, 2H), 7.37 – 7.20 (m, 5H), 7.16 – 7.06 (m, 2H), 4.43 – 4.24 (m, 2H), 2.66 (s, 1H), 2.42 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 144.1, 137.4, 131.1, 129.6, 128.9, 128.7(9), 128.7(7), 128.5, 64.7, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{16}NOS$ $[M + H]^+$ 246.0947, found 246.0947.

The synthesis of sulfoxide from sulfilimine:

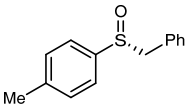


29, 97% e.e. **46**, 61%, 94% e.e.

According to a literature procedure[3] with slight modification, to a solution of sulfilimine **29** (66.6 mg, 0.20 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added a predissolved solution of $NaIO_4$ (43.2 mg, 0.20 mmol, 1.0 equiv.) in H_2O (4.0 mL). The solution was cooled to 0 °C, and $RuCl_3$ hydrate (2.0 mg, 0.010 mmol, 5.0 mol%) was added under argon. After stirring at 0 °C to r.t. for 8 h, the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated.
The resulting residue was dissolved in MeOH (2.0 mL) and H_2O (1.0 mL), and NaOH (120 mg, 3.0 mmol, 15 equiv.) was added under argon. The reaction mixture was heated to 80 °C for 48 h. After cooling to r.t., the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated.

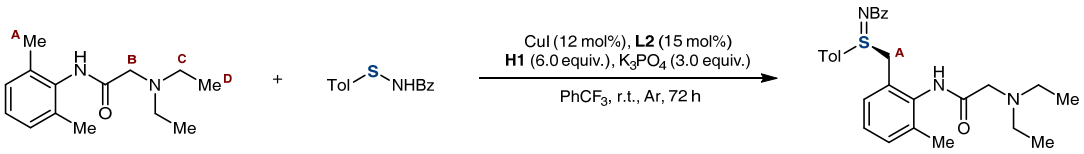
Subsequently, according to a literature procedure[9] with slight modification, the resulting residue was dissolved in MeCN (4.0 mL) and ^{t}BuONO (26.0 μL, 0.22 mmol, 1.1 equiv.) and pyridine (25.0 μL, 0.30 mmol, 1.5 equiv.) were added under argon. The reaction mixture was stirred at r.t. for 10 h, then concentrated. Purification by column chromatography on silica gel afforded product **46**.

(*R*)-1-(Benzylsulfinyl)-4-methylbenzene (46)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 4/1) to afford **46** as a white solid (28.1 mg, 61% yield, 94% e.e.).
M.P.: 137–142 ℃.
[α]$_D^{25}$ = 58.96 (c 1.0, $CHCl_3$).
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 238 nm), t_R (minor) = 16.98 min, t_R (major) = 21.90 min.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 7H), 7.05 – 6.94 (m, 2H), 4.14 – 3.93 (m, 2H), 2.39 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 141.7, 139.6, 130.5, 129.7, 129.4, 128.5, 128.3, 124.5, 63.8, 21.6.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{15}OS$ $[M + H]^+$ 231.0838, found 231.0838.

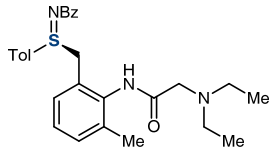
Late-stage benzylic S–C coupling of lidocaine



C23 (**lidocaine**, 20 equiv.) (**S1**, 0.20 mmol) **47**, 54%, 95% e.e. 88% recovery of **C23**

To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (4.57 mg, 0.024 mmol, 12 mol%), **L2** (12.9 mg, 0.030 mmol, 15 mol%), sulfenamide **S1** (48.7 mg, 0.20 mmol, 1.0 equiv.), lidocaine **C23** (0.97 g, 4.0 mmol, 20 equiv.), **H1** (281 mg, 1.20 mmol, 6.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous $PhCF_3$ (4.0 mL). The reaction mixture was stirred at r.t. for 72 h. Upon completion, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc/Et_3N = 2/1/0.02) to afford product **47** as a light red oil (51.4 mg, 54% yield, 95% e.e.). In addition, alkane **C23** was recovered in up to 88% yield (0.82 g).

(*S*)-*N*-((2-(2-(Diethylamino)acetamido)-3-methylbenzyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (47)



$[\alpha]_D^{25}$ = –58.96 (c 1.0, $CHCl_3$).

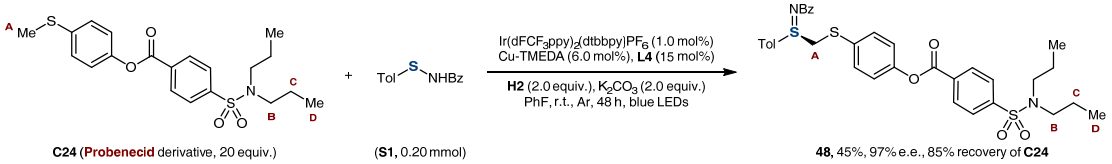
HPLC analysis: Chiralpak IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 15.32 min, t_R (major) = 48.00 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.14 – 8.07 (m, 2H), 7.46 – 7.40 (m, 3H), 7.39 – 7.33 (m, 2H), 7.28 – 7.19 (m, 3H), 7.06 – 6.99 (m, 1H), 6.71 – 6.64 (m, 1H), 4.48 (d, *J* = 12.8, 1H), 4.19 (d, *J* = 12.7, 1H), 3.27 (s, 2H), 2.64 (q, *J* = 7.1, 4H), 2.38 (s, 3H), 2.28 (s, 3H), 1.06 (t, *J* = 7.1, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 171.4, 143.0, 136.6, 136.5, 136.2, 131.9, 130.8, 130.3, 130.2, 129.7, 128.8, 127.8, 127.3, 127.0, 126.1, 57.5, 52.1, 48.7, 21.6, 18.8, 12.0.

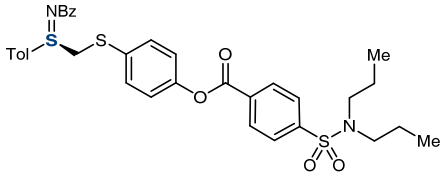
HRMS (ESI) *m/z* calcd. for $C_{28}H_{34}N_3O_2S$ $[M + H]^+$ 476.2366, found 476.2367.

Late-stage regioselective S–C coupling of a probenecid derivative at the α-C(sp^3)–H site



Under an argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S1** (48.7 mg, 0.20 mmol, 1.0 equiv.), alkane **C24** (1.63 g, 4.0 mmol, 20 equiv.), Cu-TMEDA (5.57 mg, 0.0120 mmol, 6.0 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.29 mg, 0.0020 mmol, 1.0 mol%), **H2** (70.5 mg, 0.40 mmol, 2.0 equiv.), K_2CO_3 (55.3 mg, 0.40 mmol, 2.0 equiv.), and PhF (2.0 mL). The reaction mixture was stirred at r.t. under blue LED irradiation for 48 h under argon. Upon completion, the reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 2/1) to afford product **48** as a yellow oil (58.4 mg, 45% yield, 97% e.e.). In addition, alkane **C24** was recovered in up to 85% yield (1.38 g).

(*R*)-4-(((*N*-Benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)methyl)thio)phenyl 4-(*N*,*N*-dipropyl sulfamoyl)benzoate (48)



M.P.: 54–58 ℃.

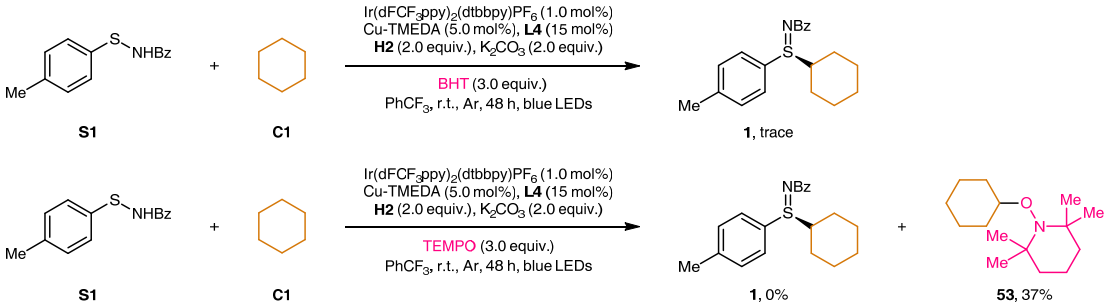
$[\alpha]_D^{25}$ = 29.98 (c 1.0, $CHCl_3$).

HPLC analysis: Chiralpak IB (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ =

254 nm), t_R (minor) = 25.47 min, t_R (major) = 29.29 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.27 (m, 2H), 8.19 – 8.11 (m, 2H), 8.00 – 7.92 (m, 2H), 7.85 – 7.77 (m, 2H), 7.59 – 7.53 (m, 2H), 7.47 – 7.41 (m, 1H), 7.41 – 7.31 (m, 4H), 7.22 – 7.15 (m, 2H), 4.99 (d, *J* = 13.3 Hz, 1H), 4.20 (d, *J* = 13.3 Hz, 1H), 3.21 – 3.05 (m, 4H), 2.44 (s, 3H), 1.61 – 1.53 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 163.6, 150.4, 145.2, 144.0, 136.3, 132.6, 131.9, 131.0(3), 130.9(7), 130.6, 130.5, 129.0, 128.9, 128.6, 128.0, 127.3, 122.8, 55.2, 50.1, 22.1, 21.7, 11.3.
HRMS (ESI) *m/z* calcd. for $C_{34}H_{36}N_2O_5S_3Na$ $[M + Na]^+$ 671.1679, found 671.1677.

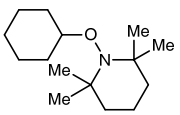
8. Mechanistic investigation

Radical inhibition experiments

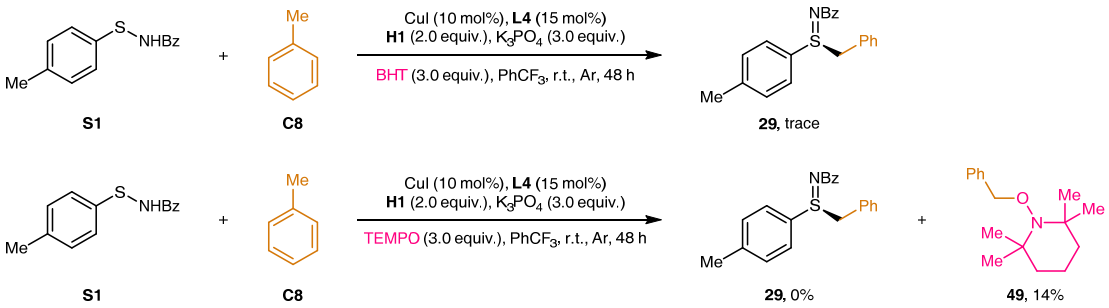


To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (3.80 mg, 0.020 mmol, 10 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), sulfenamide **S1** (48.7 mg, 0.20 mmol, 1.0 equiv.), alkane **C8** (0.43 mL, 4.0 mmol, 20 equiv.), **H1** (93.6 mg, 0.40 mmol, 2.0 equiv.), BHT (132 mg, 0.60 mmol, 3.0 equiv.) or TEMPO (93.8 mg, 0.60 mmol, 3.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous $PhCF_3$ (2.0 mL). The reaction mixture was stirred at r.t. for 48 h. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The yield was determined by ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The yield of **53** was calculated based on **S1**, and the characterization data for **53** were consistent with those reported in the literature[10].

1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (53)



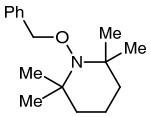
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 – 3.54 (m, 1H), 2.10 – 1.98 (m, 2H), 1.80 – 1.66 (m, 2H), 1.60 – 1.39 (m, 6H), 1.29 – 1.04 (m, 18H).
^{13}C NMR (100 MHz, CDCl) δ 81.9, 59.7, 40.4, 34.6, 33.0, 26.1, 25.2, 20.4, 17.5.
The characterization data of **53** were consistent with those reported in the literature[10].



Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a

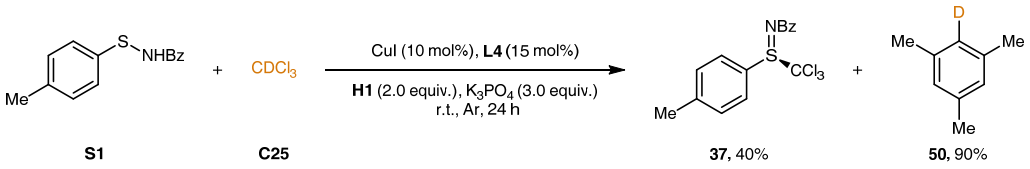
magnetic stir bar was charged with sulfenamide **S1** (48.7 mg, 0.20 mmol, 1.0 equiv.), alkane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), Cu-TMEDA (4.64 mg, 0.010 mmol, 5.0 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), BHT (butylated hydroxytoluene, 132 mg, 0.60 mmol, 3.0 equiv.) or TEMPO (2,2,6,6-tetramethylpiperidinooxy, 93.8 mg, 0.60 mmol, 3.0 equiv.), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.29 mg, 0.0020 mmol, 1.0 mol%), **H2** (70.5 mg, 0.40 mmol, 2.0 equiv.), K_2CO_3 (55.3 mg, 0.40 mmol, 2.0 equiv.), and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at r.t. under blue LED irradiation for 48 h under argon. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The yield was determined by ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The yield of **49** was calculated based on **S1**, and the characterization data for **49** were consistent with those reported in the literature[11].

1-(Benzyloxy)-2,2,6,6-tetramethylpiperidine (49)



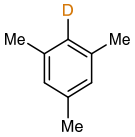
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 3H), 7.29 – 7.23 (m, 1H), 4.83 (s, 2H), 1.72 – 1.40 (m, 5H), 1.40 – 1.30 (m, 1H), 1.26 (s, 6H), 1.15 (s, 6H).
^{13}C NMR (100 MHz, CDCl) δ 138.4, 128.3, 127.6, 127.4, 78.9, 60.1, 39.8, 33.2, 20.4, 17.2.
The characterization data of **49** were consistent with those reported in the literature[11].

Radical deuterium abstraction experiment



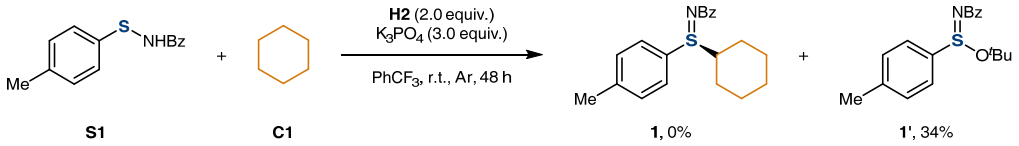
To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (3.80 mg, 0.020 mmol, 10 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), sulfenamide **S1** (48.7 mg, 0.20 mmol, 1.0 equiv.), **H1** (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous $CDCl_3$ (2.0 mL). The reaction mixture was stirred at r.t. for 24 h. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The yield was determined by ^1H NMR analysis of the crude product using dibromomethane as an internal standard. The yield of **50** was calculated based on **S1**.

***d*^{1}-Mesitylene (50)**



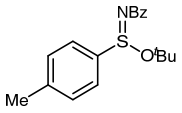
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 2.27 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.8, 127.0, 126.7 (t, J = 23.8 Hz), 21.3(4), 21.2(8).
HRMS (ESI) *m/z* calcd. for $C_9H_{12}D$ $[M + H]^+$ 122.1075, found 122.1074.
The characterization data of **50** were consistent with those reported in the literature[12].

Control experiments for 1':



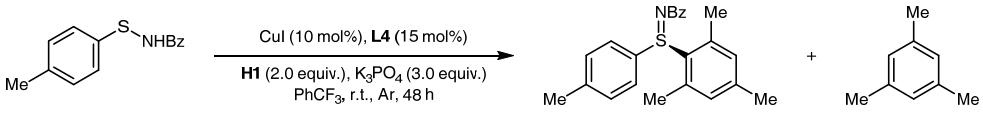
To a flame-dried Schlenk tube equipped with a magnetic stir bar were added sulfenamide **S1** (48.7 mg, 0.20 mmol, 1.0 equiv.), **C1** (0.86 mL, 8.0 mmol, 40 equiv.), **H2** (70.5 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127 mg, 0.60 mmol, 3.0 equiv.) in $PhCF_3$ (2.0 mL). The resulting mixture was stirred at r.t. for 48 h under argon. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The yield was determined by ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard. The yield of **1′** was calculated based on **S1.**

***tert*-Butyl *N*–(pivaloyl)-4-methylphenylsulfinimidate (1')**



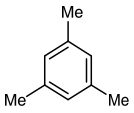
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 2H), 7.84 – 7.79 (m, 2H), 7.51 – 7.45 (m, 1H), 7.43 – 7.39 (m, 2H), 7.36 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H), 1.60 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 143.0, 136.7, 136.4, 131.6, 130.1, 129.6, 128.0, 127.2, 85.5, 29.6, 21.7.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NO_2S$ $[M + H]^+$ 316.1366, found 316.1367.

Control experiments with H1 in the absence of α-functionalized alkanes.



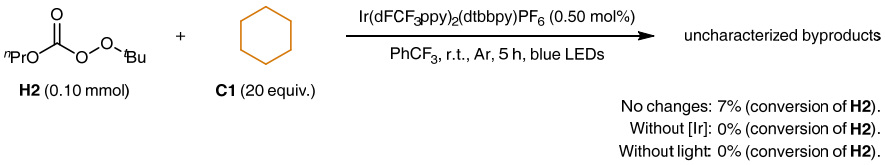
To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (3.80 mg, 0.020 mmol, 10 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), sulfenamide **S1** (48.7 mg, 0.20 mmol, 1.0 equiv.), **H1** (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous $PhCF_3$ (2.0 mL). The resulting mixture was stirred at r.t. for 48 h under argon. Upon completion, the precipitate was filtered off and washed with CH_2Cl_2. The yield was determined by ^{1}H NMR analysis of the crude product using dibromomethane as an internal standard. The yield of **52** was calculated based on **S1.**

Mesitylene (52)

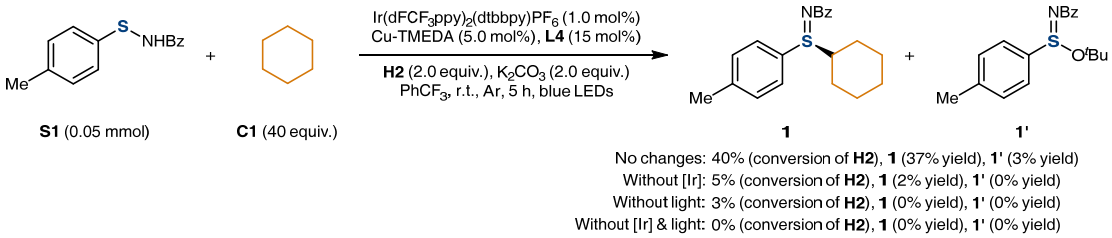


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 3H), 2.27 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 127.0, 21.3.

Control experiments on H2 consumption: Identifying the direct activator.

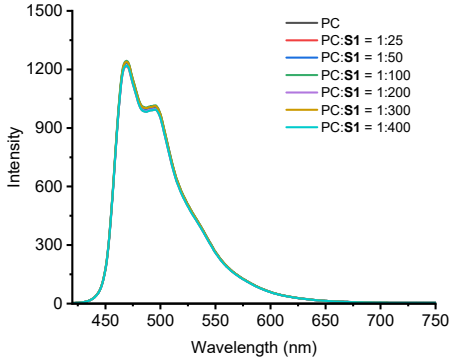


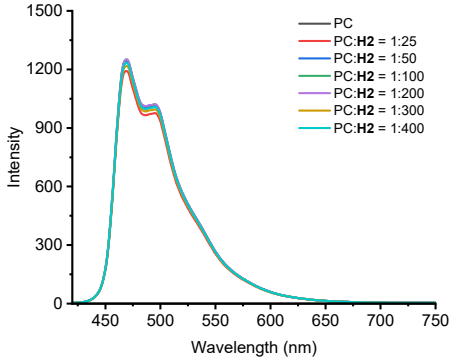
To a flame-dried Schlenk tube equipped with a magnetic stir bar were added **H2** (17.6 mg, 0.10 mmol, 1.0 equiv.), **C1** (0.22 mL, 2.0 mmol, 20 equiv.), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (0 or 0.50 mol%) in $PhCF_3$ (0.50 mL). The resulting mixture was stirred at r.t. under blue LED irradiation or in the absence of light for 5 h under argon. The conversion was determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

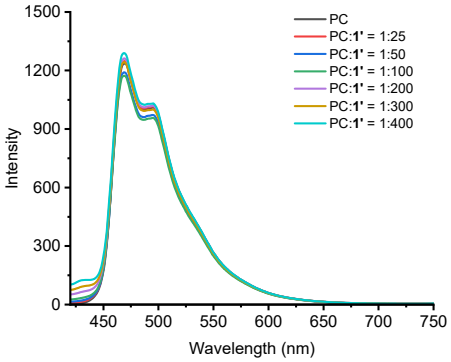


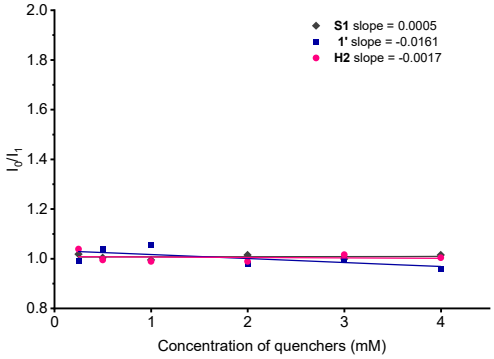
Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S1** (12.2 mg, 0.050 mmol, 1.0 equiv.), alkane **C1** (0.22 mL, 2.0 mmol, 40 equiv.), Cu-TMEDA (1.16 mg, 0.0025 mmol, 5.0 mol%), **L4** (3.95 mg, 0.0075 mmol, 15 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (0 or 1.0 mol%), **H2** (17.6 mg, 0.10 mmol, 2.0 equiv.), K_2CO_3 (13.8 mg, 0.10 mmol, 2.0 equiv.), and $PhCF_3$ (0.50 mL). The reaction mixture was stirred at r.t. under blue LED irradiation or in the absence of light for 5 h under argon. The yield and conversion were based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

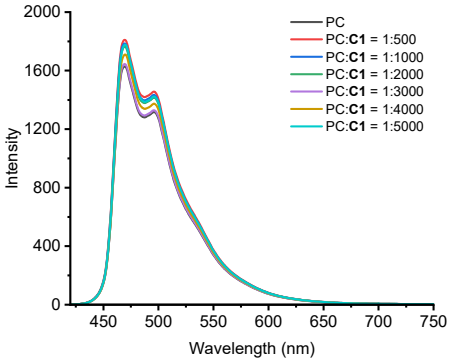
Stern-Volmer fluorescence quenching experiments.

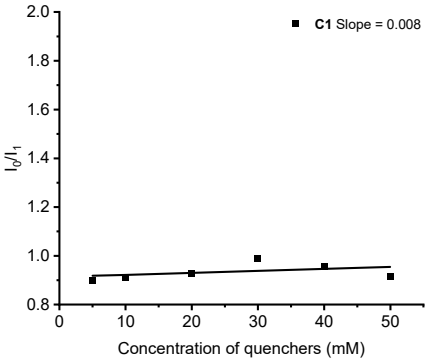


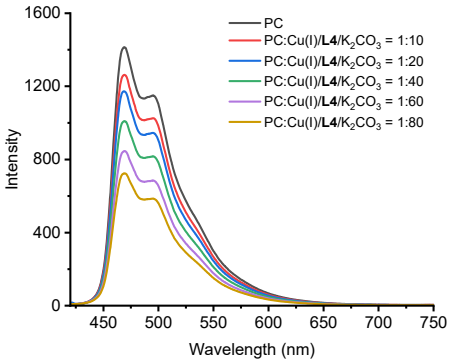


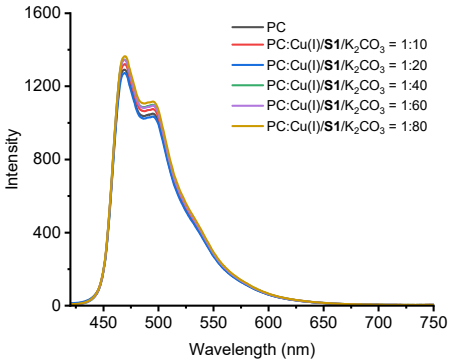


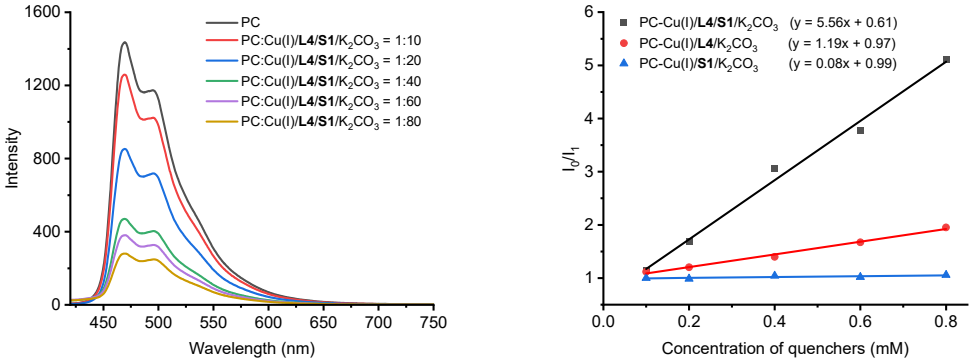












Supplementary Fig. 8 | Stern–Volmer fluorescence-quenching experiments.

Emission intensities were recorded on a HITACHI F-4700 fluorescence spectrometer for all quenching experiments. Solutions of $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ were excited at 400 nm, and the emission intensity was monitored at 470 nm.

In a typical experiment, a 1×10^{-5} M solution of $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ in $PhCF_3$ was placed in a screw-top 4.0 cm quartz cuvette, and the indicated quencher was added. After degassing with argon for 10 min, the emission spectra were recorded.

For in situ–generated Cu-based quenchers, the mixtures were assembled using the same component ratio employed in the mechanistic studies, namely Cu(I):**L4**:**S1**:K_2CO_3 = **1:1.5:5:3**, with omitted components set to 0 equiv. in the corresponding control experiments (e.g., Cu(I)/**S1**/K_2CO_3 = 1:5:3; Cu(I)/**L4**/K_2CO_3 = 1:1.5:3; Cu(I):**L4**:**S1**:K_2CO_3 = **1:1.5:5:3**).

I_0/I_1 was plotted against the concentration of the indicated quencher in Supplementary Fig. 5 (Stern–Volmer plots), where I_0 is the fluorescence intensity in the absence of quencher and I_1 is the fluorescence intensity in the presence of quencher. As shown in Supplementary Fig. 5, substrates **S1**, **C1**, **H2**, **1′**, and the in situ–generated mixture from $Cu(CH_3CN)_4BF_4$/**S1**/K_2CO_3 did not measurably quench the excited state of $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$. In contrast, the in situ–generated mixtures from $Cu(CH_3CN)_4BF_4$/**L4**/K_2CO_3 and $Cu(CH_3CN)_4BF_4$/**L4**/**S1**/K_2CO_3 efficiently quenched the excited state of $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$. Moreover, the quenching rate constant for the in situ–generated mixture from $Cu(CH_3CN)_4BF_4$/**L4**/**S1**/K_2CO_3 was substantially higher than that for the mixture from $Cu(CH_3CN)_4BF_4$/**L4**/K_2CO_3.

UV–visible spectroscopic studies of the reaction components

The UV–vis spectra of the individual reagents were measured directly in $PhCF_3$. For in situ generated complexes, mixtures of the precursor reagents were stirred for 3 h before their spectra were recorded. The concentrations of all tested samples were set at ~1×10^{-3} M.

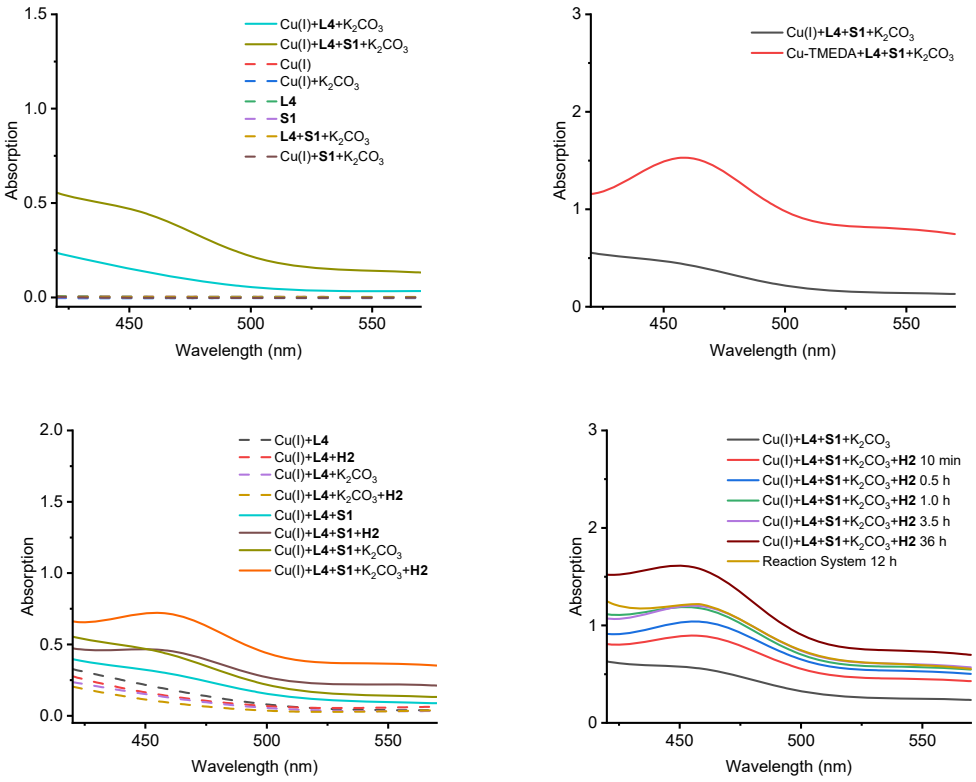
UV–vis studies were performed on in situ–generated Cu complexes assembled from the indicated components. Unless otherwise noted, mixtures were prepared using a fixed molar ratio of Cu:**L4**:**S1**:**H2**:K_2CO_3 = 1:1.5:5:1:3 (with omitted components set to 0 equiv in the corresponding control experiments). For experiments involving **H2**, all other components were first premixed, after which **H2** was added last; the resulting mixture was stirred for 5 min before the UV–vis spectrum was recorded. In the 420–

500 nm region, pronounced absorption was observed for the in situ–generated Cu complexes assembled from (i) $Cu(OAc)_2$/**S1**/**L4**/K_2CO_3, (ii) Cu-TMEDA/**S1**/**L4**/K_2CO_3, (iii) $Cu(CH_3CN)_4BF_4$/**S1**/**L4**/K_2CO_3/**H2**, consistent with assignment of this band to a chiral Cu(II)–S complex.

The UV–vis spectrum of the catalytic reaction mixture after 12 h further indicates that a substantial fraction of Cu(I) species persists under the reaction conditions. Control UV–vis experiments conducted in the presence and absence of **H2** revealed a measurable spectral change only for the species generated from $Cu(CH_3CN)_4BF_4$/**S1**/**L4** and $Cu(CH_3CN)_4BF_4$/**S1**/**L4**/K_2CO_3, supporting the conclusion that the diagnostic absorption of the chiral Cu(II)–S complex arises specifically from **H2**-mediated oxidation of the $Cu(CH_3CN)_4BF_4$/**S1**/**L4**-containing complex.

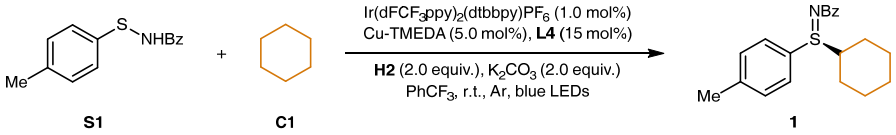
Analogous control experiments performed in the presence versus absence of K_2CO_3 gave broadly similar spectral profiles; however, the complex generated from $Cu(CH_3CN)_4BF_4$/**S1**/**L4**/**H2** displayed a distinct absorption intensity. This observation implies that **L4** can partially act as a base to facilitate formation of the Cu(II) species associated with the characteristic band, albeit less effectively than externally added K_2CO_3.

Upon addition of **H2** to the in situ–generated Cu complex derived from $Cu(CH_3CN)_4BF_4$/**S1**/**L4**/K_2CO_3, time-course UV–vis monitoring showed an initially rapid growth of the Cu(II)-associated band, followed by a plateau and a further increase over extended reaction times. These data indicate that conversion of the Cu(I) complex to the corresponding Cu(II) species by **H2** is not a fast process under the examined conditions.



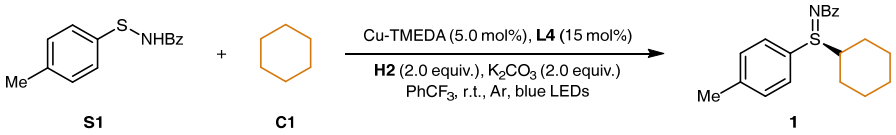
Supplementary Fig. 6 | UV–visible spectroscopic studies of the reaction components.

The time-course experiments:



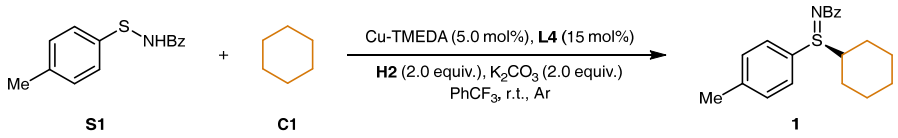
Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S1** (12.2 mg, 0.050 mmol, 1.0 equiv.), alkane **C1** (0.22 mL, 2.0 mmol, 40 equiv.), Cu-TMEDA (1.18 mg, 0.0025 mmol, 5.0 mol%), **L4** (4.0 mg, 0.0075 mmol, 15 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (0.56 mg, 0.00050 mmol, 1.0 mol%), **H2** (17.6 mg, 0.10 mmol, 2.0 equiv.), K_2CO_3 (13.8 mg, 0.10 mmol, 2.0 equiv.), and $PhCF_3$ (0.50 mL). The reaction mixture was stirred at r.t. under blue LED irradiation under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

Entry	Time/h	Yield (%)
1	2 h	17
2	4 h	27
3	8 h	39
4	12 h	62
5	24 h	72



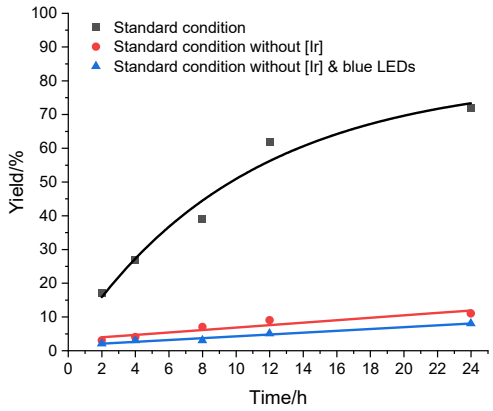
Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S1** (12.2 mg, 0.050 mmol, 1.0 equiv.), alkane **C1** (0.22 mL, 2.0 mmol, 40 equiv.), Cu-TMEDA (1.18 mg, 0.0025 mmol, 5.0 mol%), **L4** (4.0 mg, 0.0075 mmol, 15 mol%), **H2** (17.6 mg, 0.10 mmol, 2.0 equiv.), K_2CO_3 (13.8 mg, 0.10 mmol, 2.0 equiv.), and $PhCF_3$ (0.50 mL). The reaction mixture was stirred at r.t. under blue LED irradiation under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

Entry	Time/h	Yield (%)
1	2 h	3
2	4 h	4
3	8 h	7
4	12 h	9
5	24 h	11



Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S1** (12.2 mg, 0.050 mmol, 1.0 equiv.), alkane **C1** (0.22 mL, 2.0 mmol, 40 equiv.), Cu-TMEDA (1.18 mg, 0.0025 mmol, 5.0 mol%), **L4** (4.0 mg, 0.0075 mmol, 15 mol%), **H2** (17.6 mg, 0.10 mmol, 2.0 equiv.), K_2CO_3 (13.8 mg, 0.10 mmol, 2.0 equiv.), and $PhCF_3$ (0.50 mL). The reaction mixture was stirred at r.t. under argon. Yield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

Entry	Time/h	Yield (%)
1	2 h	2
2	4 h	3
3	8 h	3
4	12 h	5
5	24 h	8

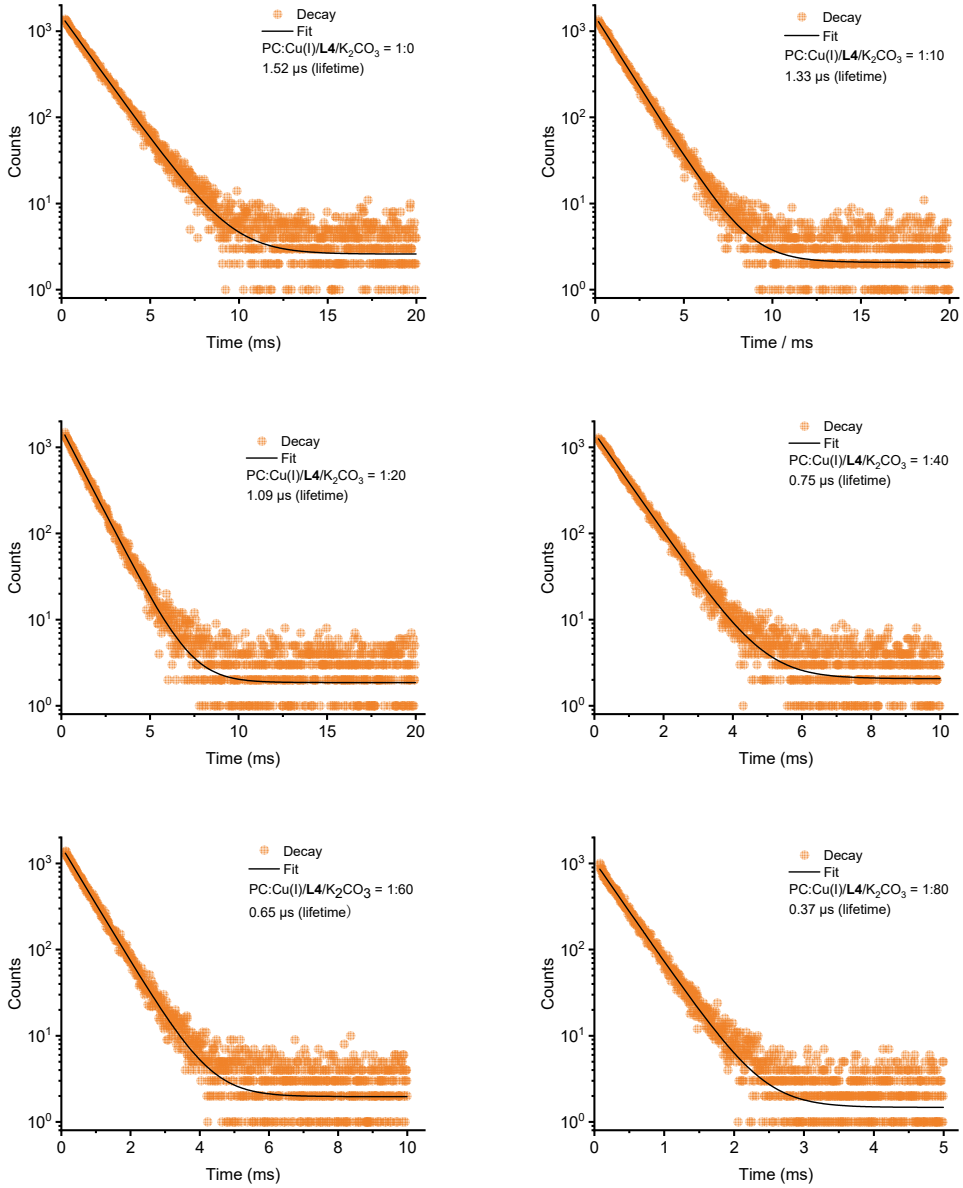


Supplementary Fig. 8 | The time-close experiments.

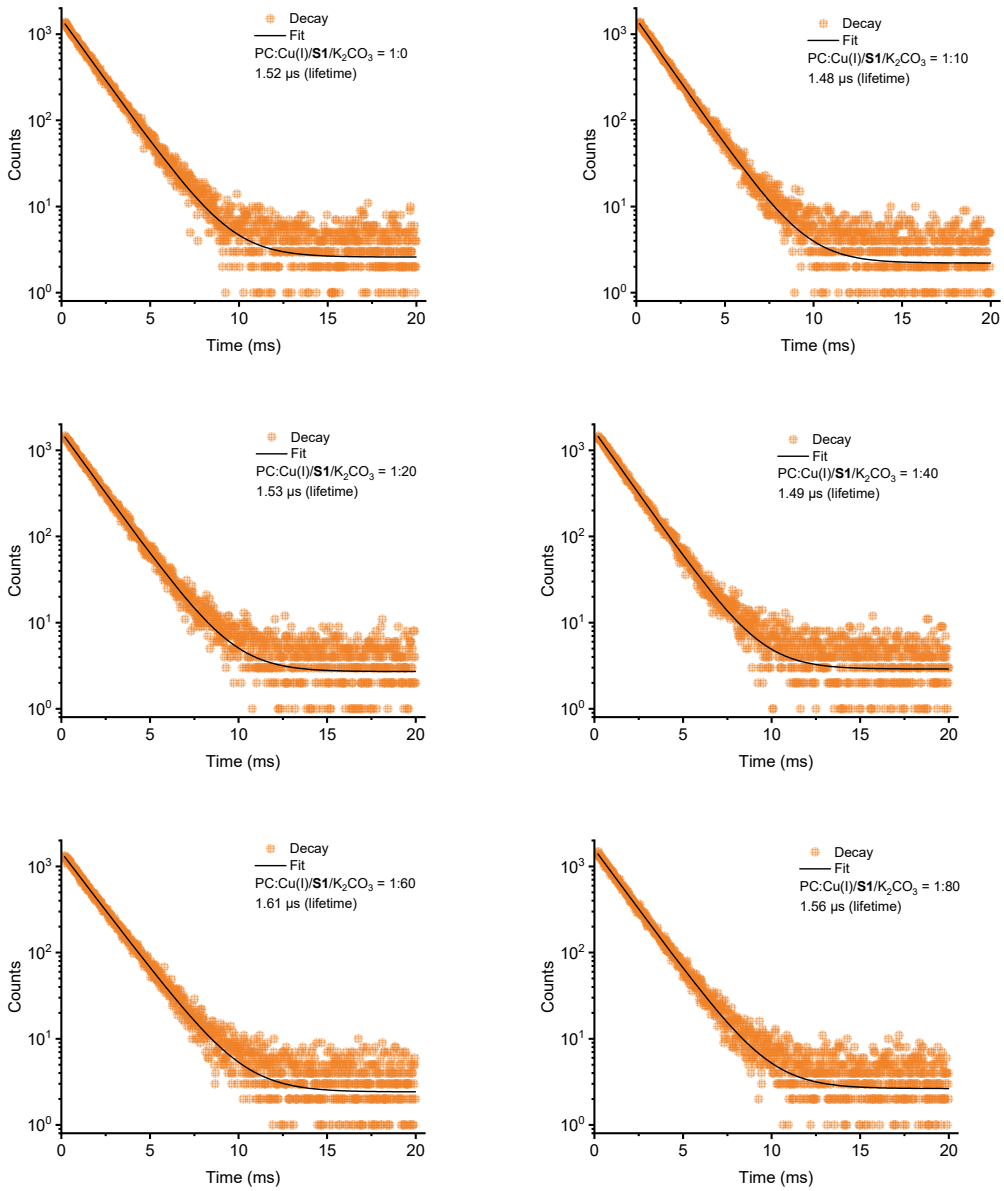
The time-correlated single photon counting (TCSPC) measurements of photocatalyst:

For TCSPC measurements, an Edinburgh instruments EPL-375 (375 nm) was used for the excitation pulse and emission was measured at 470 nm. Instrument parameters were adjusted so the detection rate was less than 2% and measurements acquired until the maximum intensity reached at least 1500 counts. Decays were fit to mono-exponentials using an Edinburgh FLS1000 photoluminescence spectrometer to obtain lifetimes.

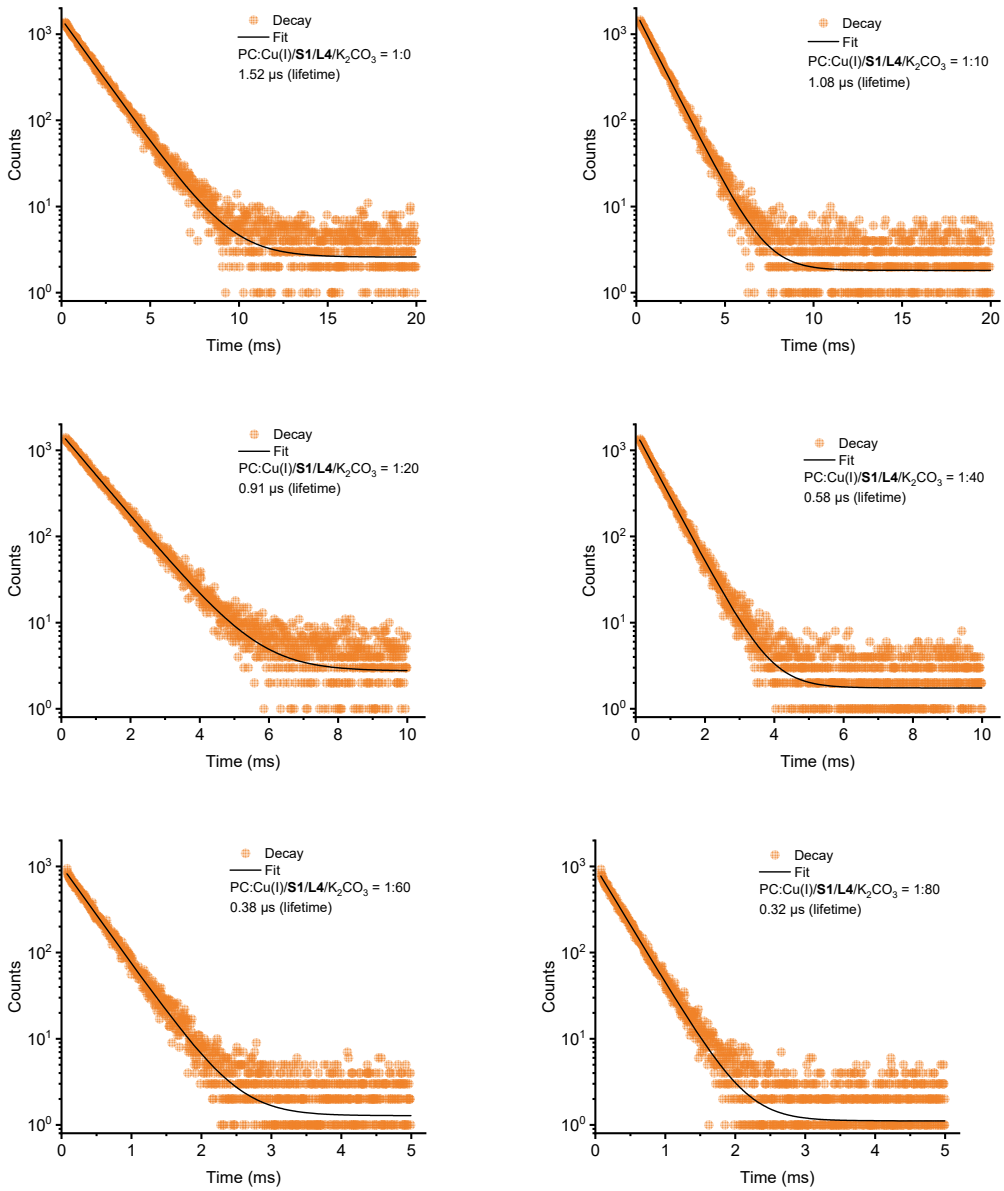
In a typical experiment, a 1×10^{-5} M solution of $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ in $PhCF_3$ was placed in a screw-top 4.0 cm quartz cuvette, and the indicated in situ–generated Cu(I)-based complex (quencher) was added. For Cu-containing quenchers, mixtures were assembled using the standard mechanistic-study component ratio of $Cu(CH_3CN)_4BF_4$:**L4**:**S1**:**H2**:K_2CO_3 = **1:1.5:5:1:3**, with omitted components set to 0 equiv. in the corresponding control experiments. After degassing with argon for 10 min, TCSPC traces were collected.



Supplementary Fig. 9 | The time-correlated single photon counting (TCSPC) measurements of photocatalyst with $Cu(CH_3CN)_4BF_4$/L4/K_2CO_3. Fluorescence decay (yellow) at 470 nm for $Ir[dF(CF_3)ppy]_2(dtbbpy))PF_6$ in the presence of $Cu(CH_3CN)_4BF_4$/**L4**/K_2CO_3 were recorded and well described by a monoexponential fit (black).

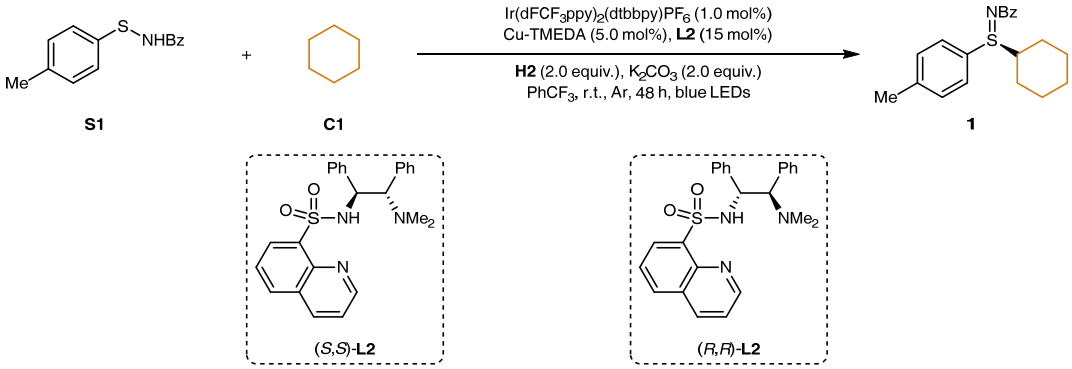


Supplementary Fig. 10 | The time-correlated single photon counting (TCSPC) measurements of photocatalyst with $Cu(CH_3CN)_4BF_4$/S1/K_2CO_3. Fluorescence decay (yellow) at 470 nm for $Ir[dF(CF_3)ppy]_2(dtbbpy))PF_6$ in the presence of $Cu(CH_3CN)_4BF_4$/**S1**/K_2CO_3 were recorded and well described by a monoexponential fit (black).



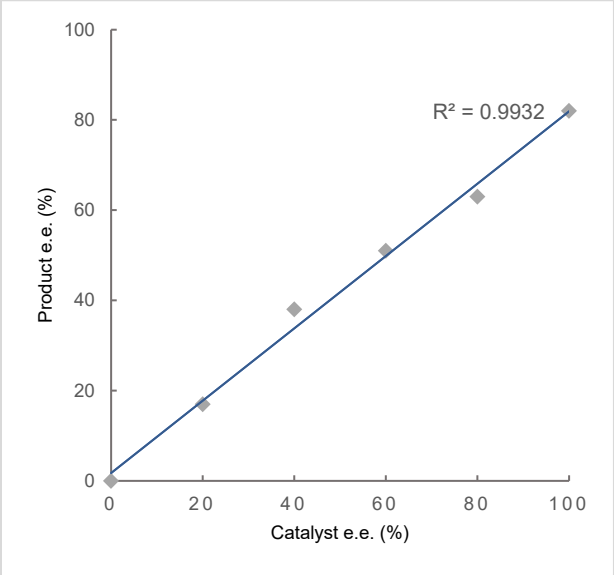
Supplementary Fig. 11 | The time-correlated single photon counting (TCSPC) measurements of photocatalyst with $Cu(CH_3CN)_4BF_4$/S1/L4/K_2CO_3. Fluorescence decay (yellow) at 470 nm for $Ir[dF(CF_3)ppy]_2(dtbbpy))PF_6$ in the presence of $Cu(CH_3CN)_4BF_4$/**S1**/**L4**/K_2CO_3 were recorded and well described by a monoexponential fit (black).

The non-linear effect of catalysts:



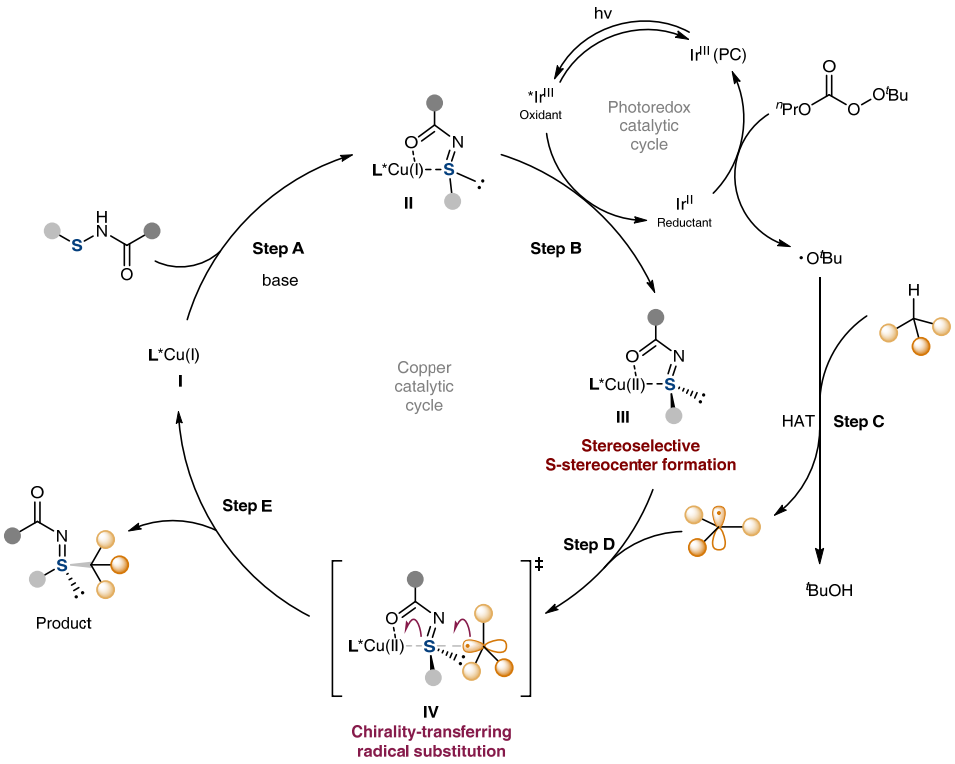
Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S1** (48.6 mg, 0.20 mmol, 1.0 equiv.), alkane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), Cu-TMEDA (4.64 mg, 0.010 mmol, 5.0 mol%), **L2** (12.9 mg, 0.030 mmol, 15 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.29 mg, 0.0020 mmol, 1.0 mol%), **H2** (70.5 mg, 0.40 mmol, 2.0 equiv.), K_2CO_3 (55.3 mg, 0.40 mmol, 2.0 equiv.), and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at r.t. under blue LED irradiation for 48 h under argon. Upon completion (monitored by TLC), product **1** was isolated by preparative TLC on silica gel. The e.e. value of product **1** was determined by HPLC, which indicated a linear relationship between the e.e. values of product **1** and those of the corresponding catalysts. Catalysts **L2** with different e.e. values were prepared by mixing (*S*,*S*)-**L2** (99% e.e.) and (*R*,*R*)-**L2** (99% e.e.) in appropriate ratios.

Entry	Catalyst e.e. (%)	Product e.e. (%)
1	99	82
2	80	63
3	60	51
4	40	38
5	20	17
6	0	0

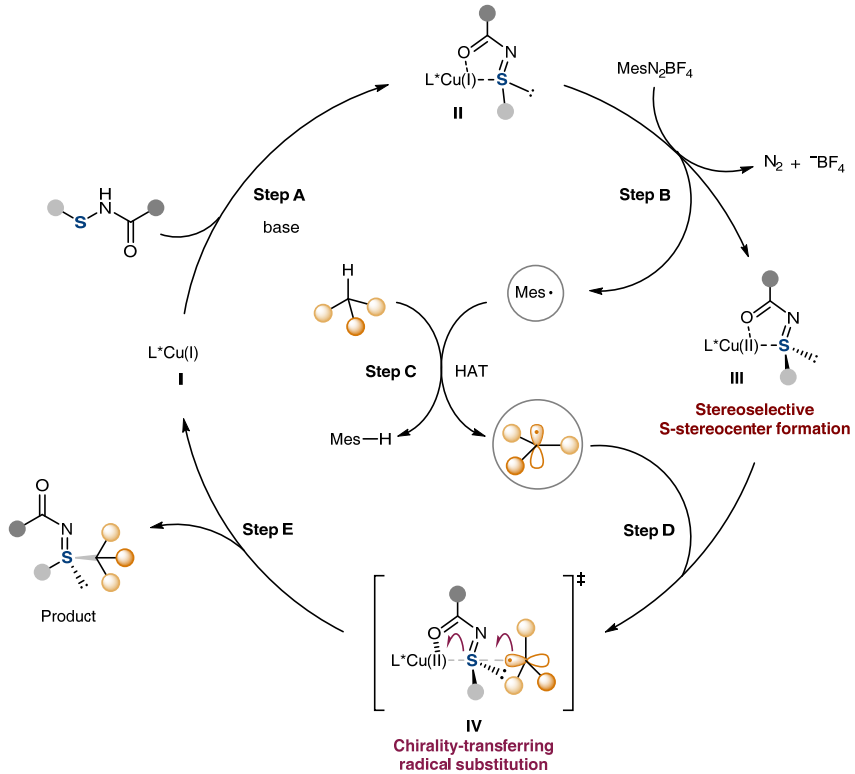

100
80
60
40
20
0
Product e.e. (%)
R² = 0.9932
0
20
40
60
80
100
Catalyst e.e. (%)

Proposed mechanism:

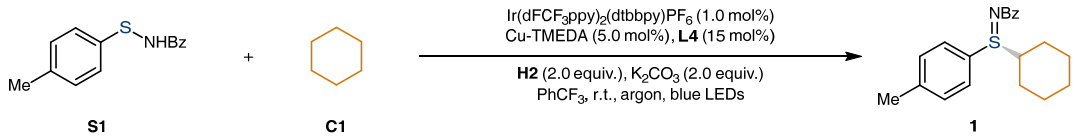
Photocatalytic mechanism:



Thermal mechanism:

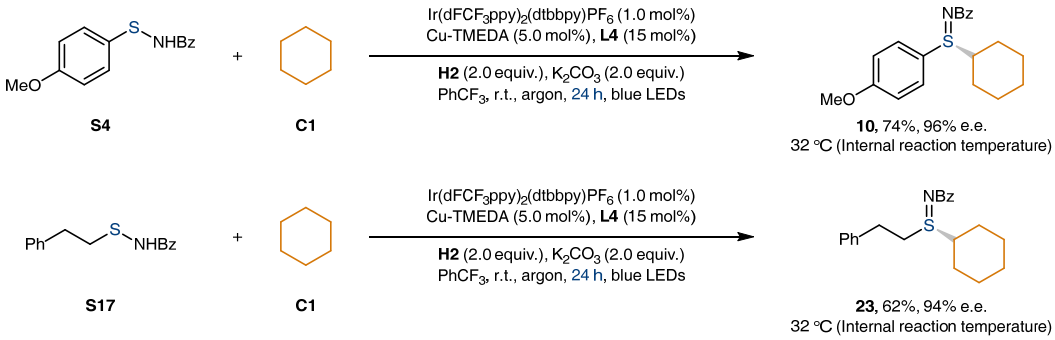


Evaluation of the internal reaction temperature under the photocatalytic conditions.



Entry	Time (h)	Internal reaction temperature	yield of 1 (%)	e.e. of 1 (%)
1[a]	6	30	28	97
2[a]	12	33	47	97
3	24	33	58	97
4	36	30	71	97
5	48	30	82	97

Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S1** (48.6 mg, 0.20 mmol, 1.0 equiv.), alkane **C1** (0.86 mL, 8.0 mmol, 40 equiv.), Cu-TMEDA (4.64 mg, 0.010 mmol, 5.0 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.29 mg, 0.0020 mmol, 1.0 mol%), **H2** (70.5 mg, 0.40 mmol, 2.0 equiv.), K_2CO_3 (55.3 mg, 0.40 mmol, 2.0 equiv.), and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at room temperature under blue LED irradiation in an argon atmosphere. Parallel reactions were performed, and at the indicated time points each reaction vessel was briefly opened under irradiation; a temperature probe attached to an IKA RCT B S025 magnetic stirrer was inserted directly into the reaction mixture and held for approximately 30 s until the reading stabilized, at which point the internal reaction temperature was recorded. Yield was then determined by ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. The e.e. values were determined by chiral HPLC analysis. [a]For comparison, the reaction temperature was also measured using a conventional kerosene-filled glass thermometer, which gave comparable values within experimental error.



Under an argon atmosphere, an oven-dried, resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfenamide **S4** (51.9 mg, 0.20 mmol, 1.0 equiv.), or **S17** (51.5 mg, 0.20 mmol, 1.0 equiv.), alkane **C1** (0.86 mL, 8.0 mmol, 40 equiv.),

Cu-TMEDA (4.64 mg, 0.010 mmol, 5.0 mol%), **L4** (15.8 mg, 0.030 mmol, 15 mol%), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.29 mg, 0.0020 mmol, 1.0 mol%), **H2** (70.5 mg, 0.40 mmol, 2.0 equiv.), K_2CO_3 (55.3 mg, 0.40 mmol, 2.0 equiv.), and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at r.t. under blue LED irradiation under argon. After 24 h of irradiation, the reaction vessel was briefly opened under irradiation; a temperature probe attached to an IKA RCT B S025 magnetic stirrer was inserted directly into the reaction mixture and held for approximately 30 s until the reading stabilized, at which point the internal reaction temperature was recorded. Yield was then determined by 1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. The e.e. values were determined by chiral HPLC analysis.

These control experiments showed that the internal reaction temperatures under the photocatalytic conditions were comparable, remaining within approximately 30–33 °C.

9. References

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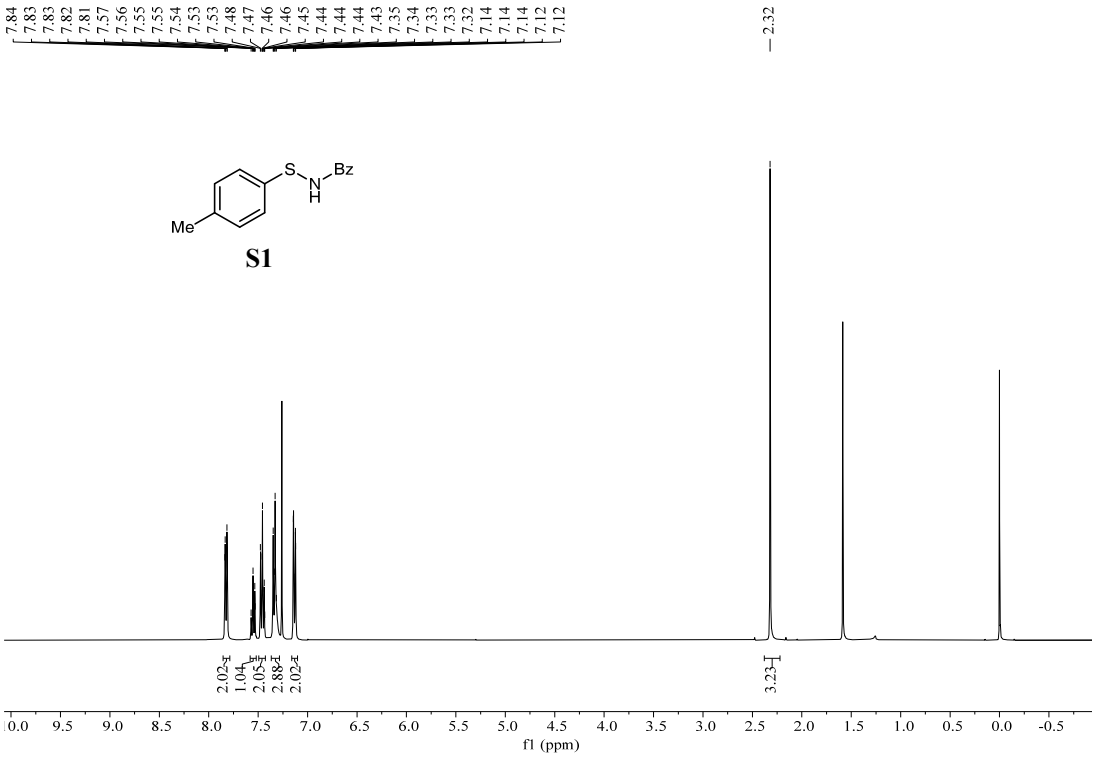
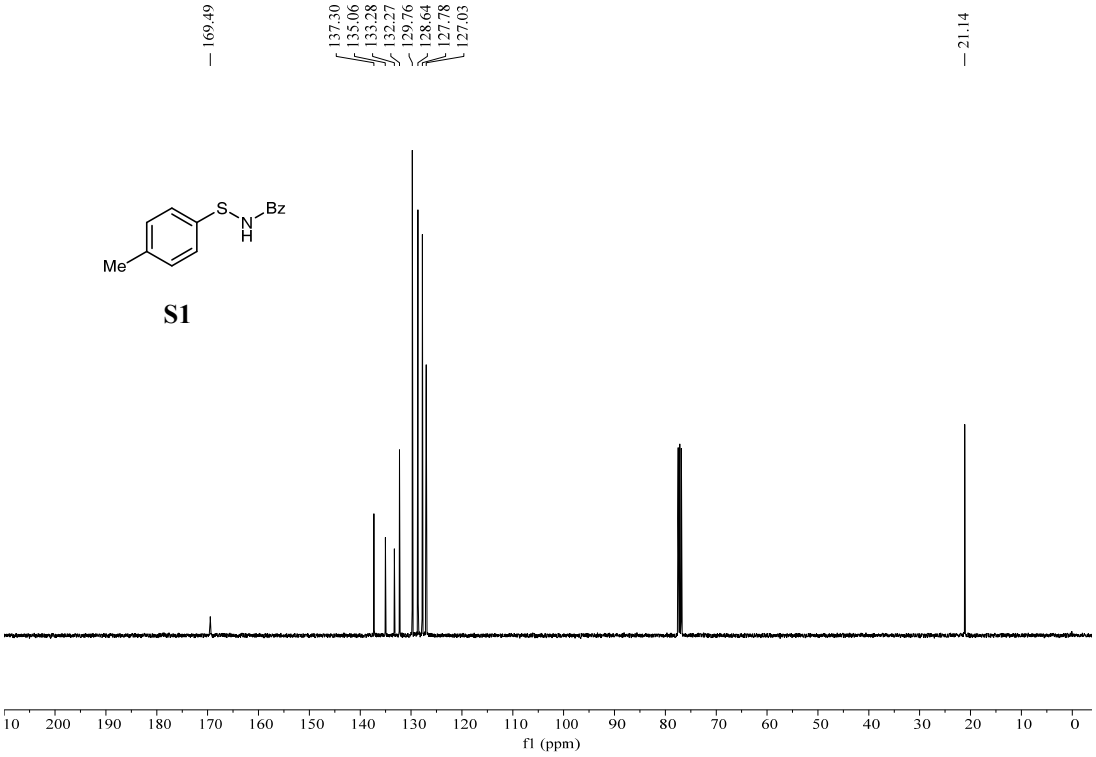
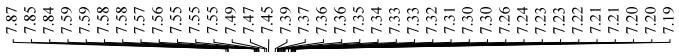
10. NMR spectra



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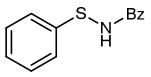
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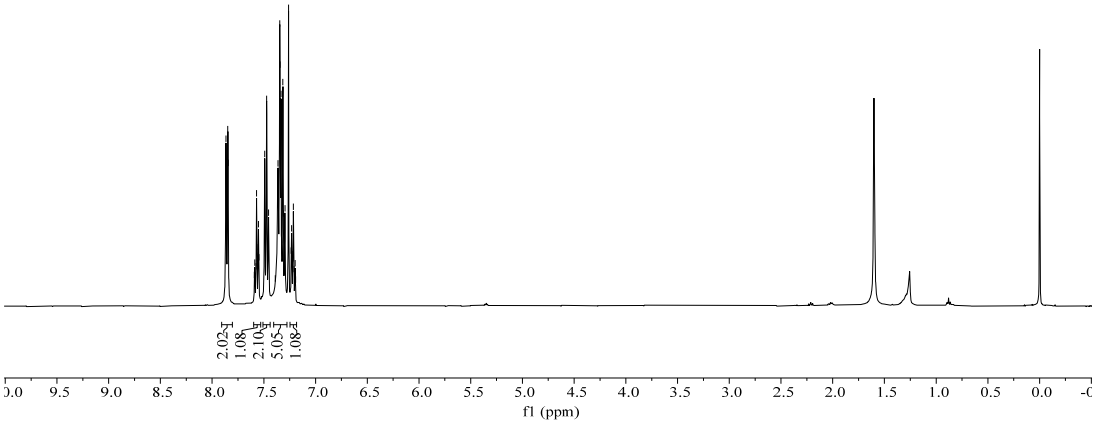
H
Bz

S2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f1 (ppm)


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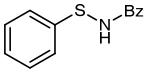
S
N
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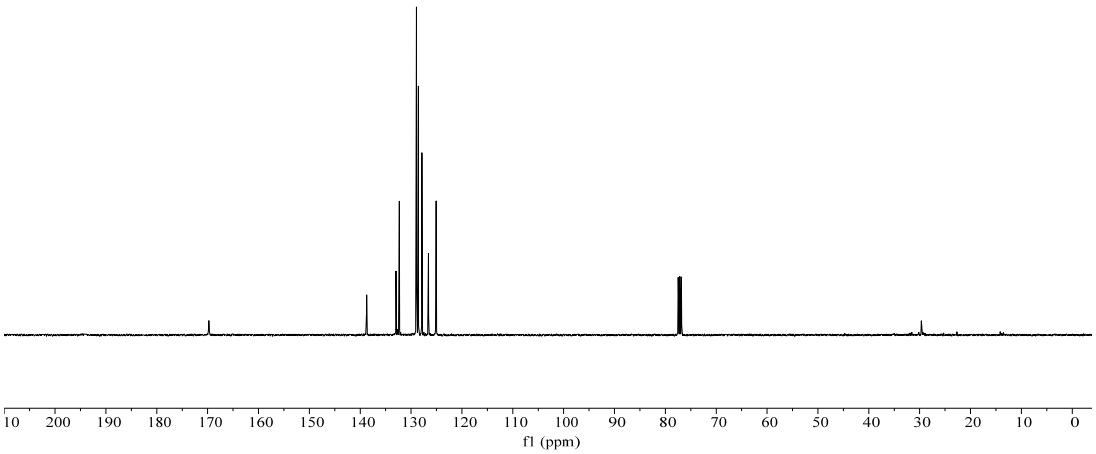
S2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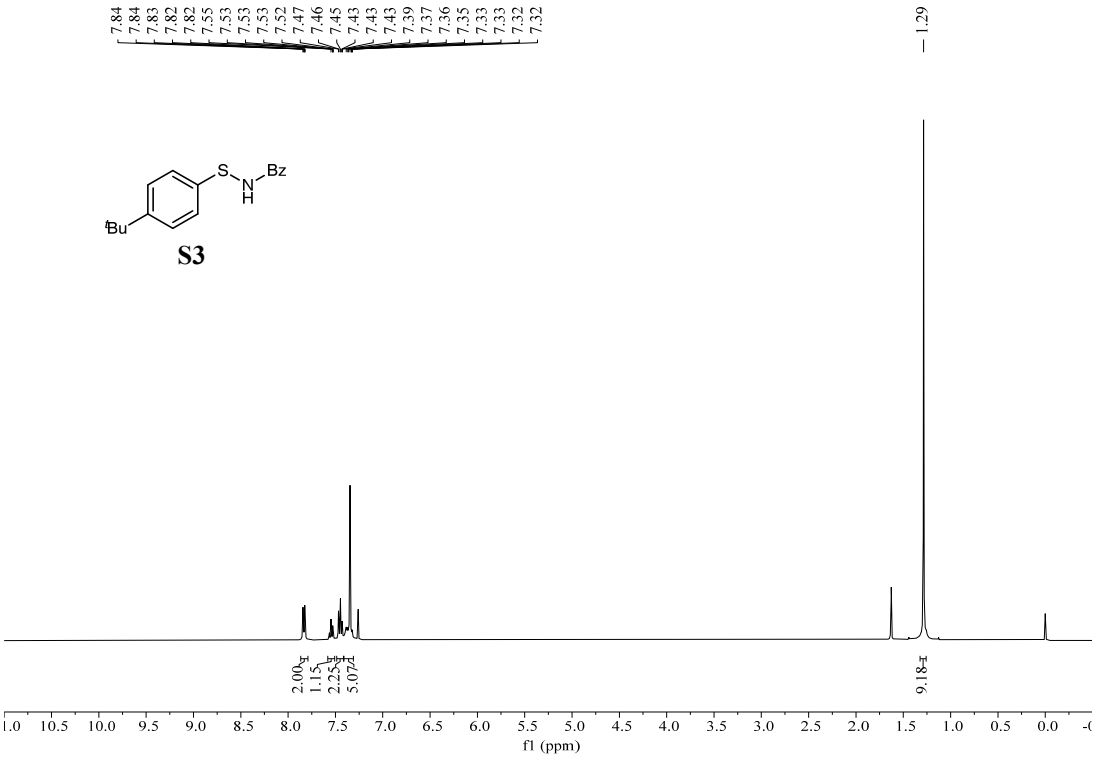
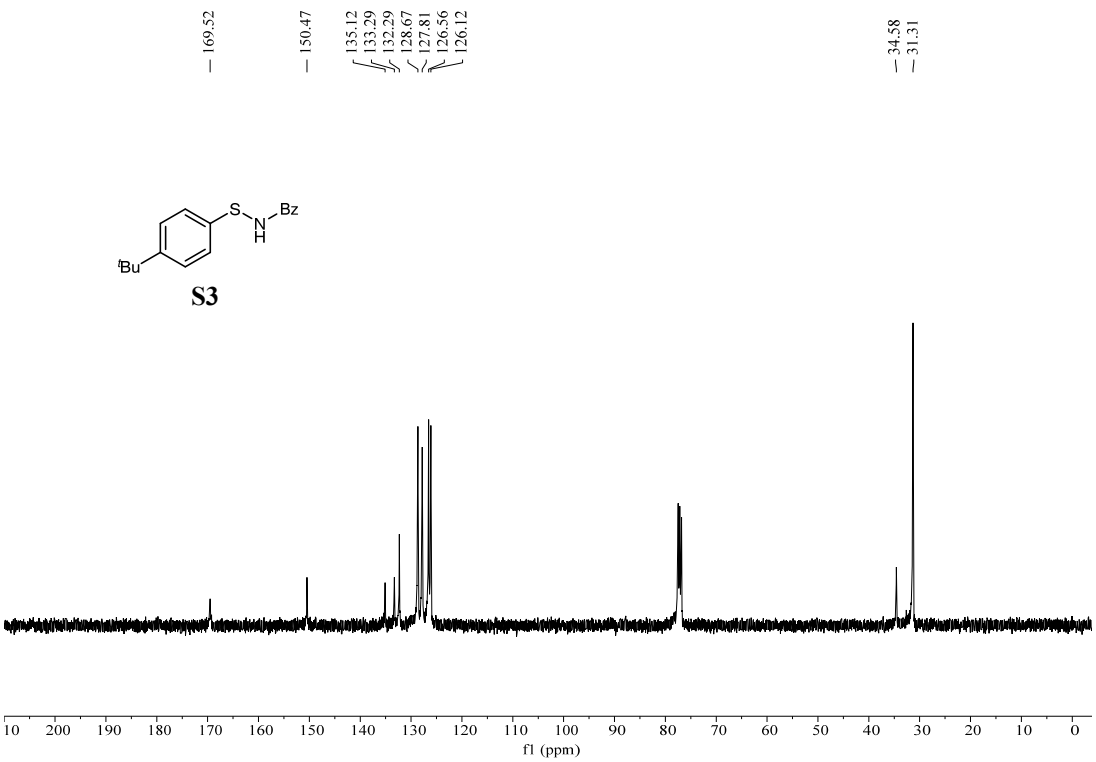
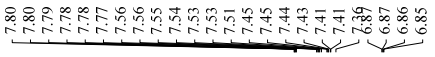
0
f1 (ppm)

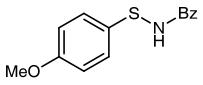

7.84
7.84
7.83
7.82
7.82
7.55
7.53
7.53
7.52
7.47
7.46
7.45
7.43
7.43
7.43
7.39
7.37
7.36
7.35
7.33
7.33
7.32
7.32
1.29
S
N
H
Bz
tBu
2.00
1.15
2.25
5.07
9.18
fl (ppm)

S3

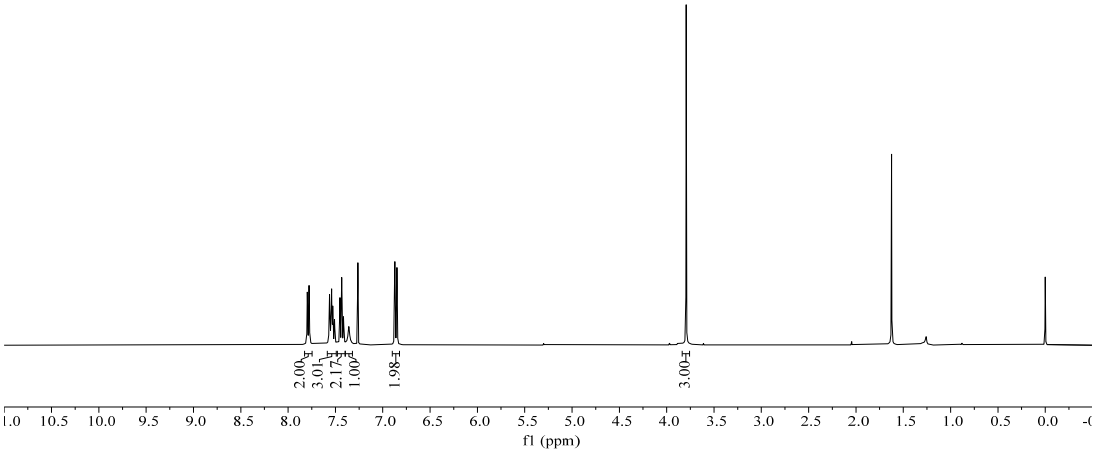

169.52
150.47
135.12
133.29
132.29
128.67
127.81
126.56
126.12
34.58
31.31
S
N
H
Bz
tBu
fl (ppm)

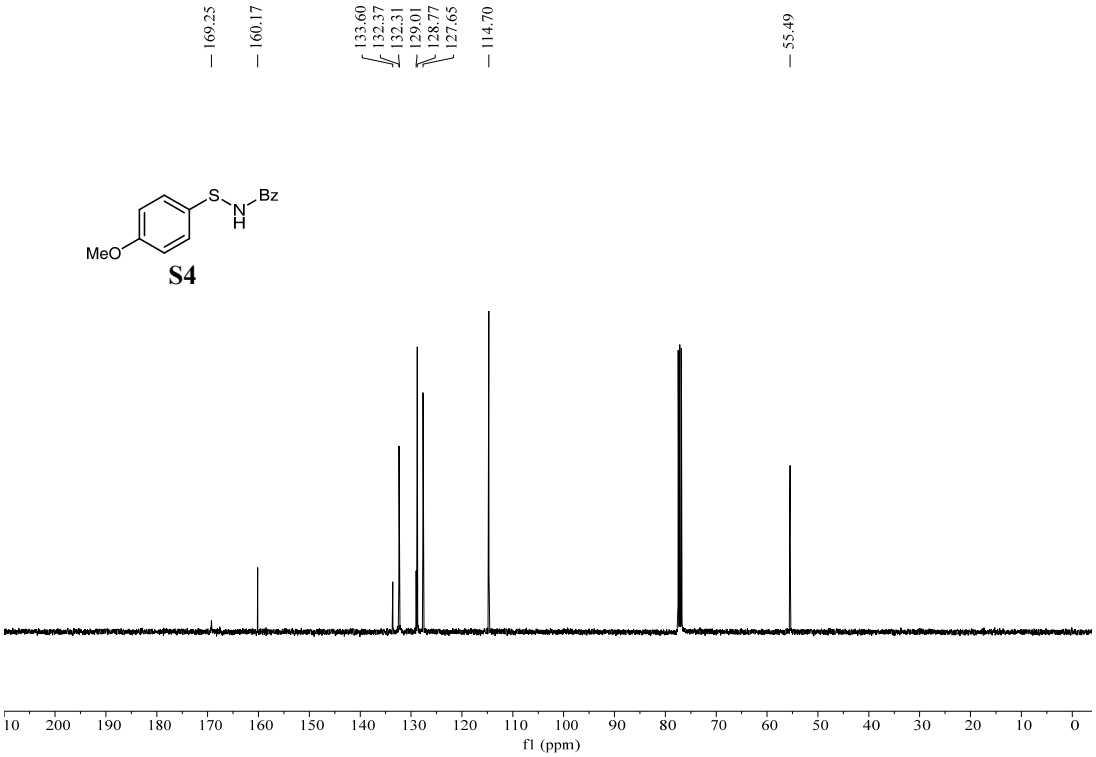
S3


7.80
7.80
7.79
7.78
7.78
7.77
7.56
7.56
7.55
7.54
7.53
7.53
7.51
7.45
7.45
7.44
7.43
7.41
7.41
7.39
6.87
6.86
6.85
3.79


S
N
H
Bz
MeO

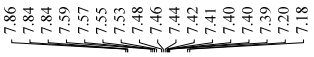
S4

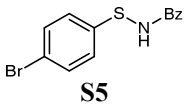

2.00
3.01
2.17
1.00
1.98
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.25
160.17
133.60
132.37
132.31
129.01
128.77
127.65
114.70
55.49
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

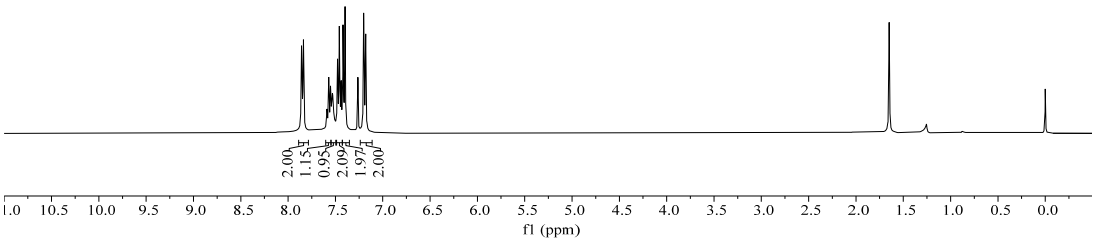
S
N
H
Bz
MeO

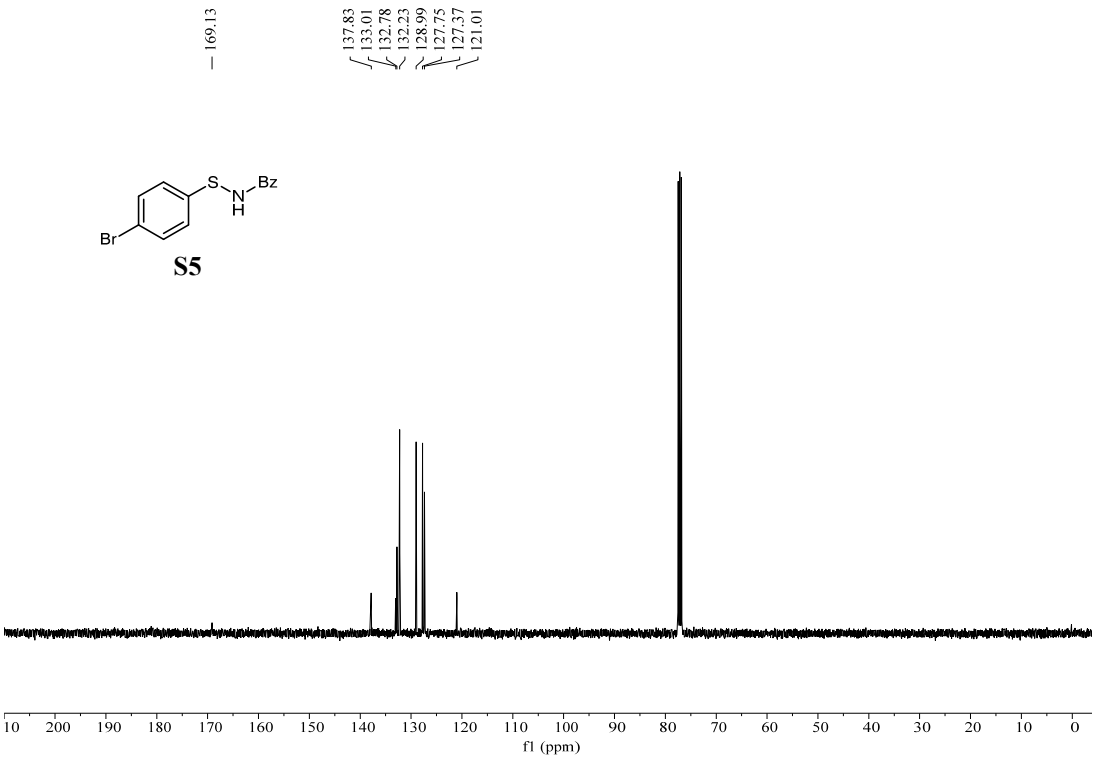
S4


7.86
7.84
7.84
7.59
7.57
7.55
7.53
7.48
7.46
7.44
7.42
7.41
7.40
7.40
7.39
7.20
7.18


S
N
H
Bz
Br

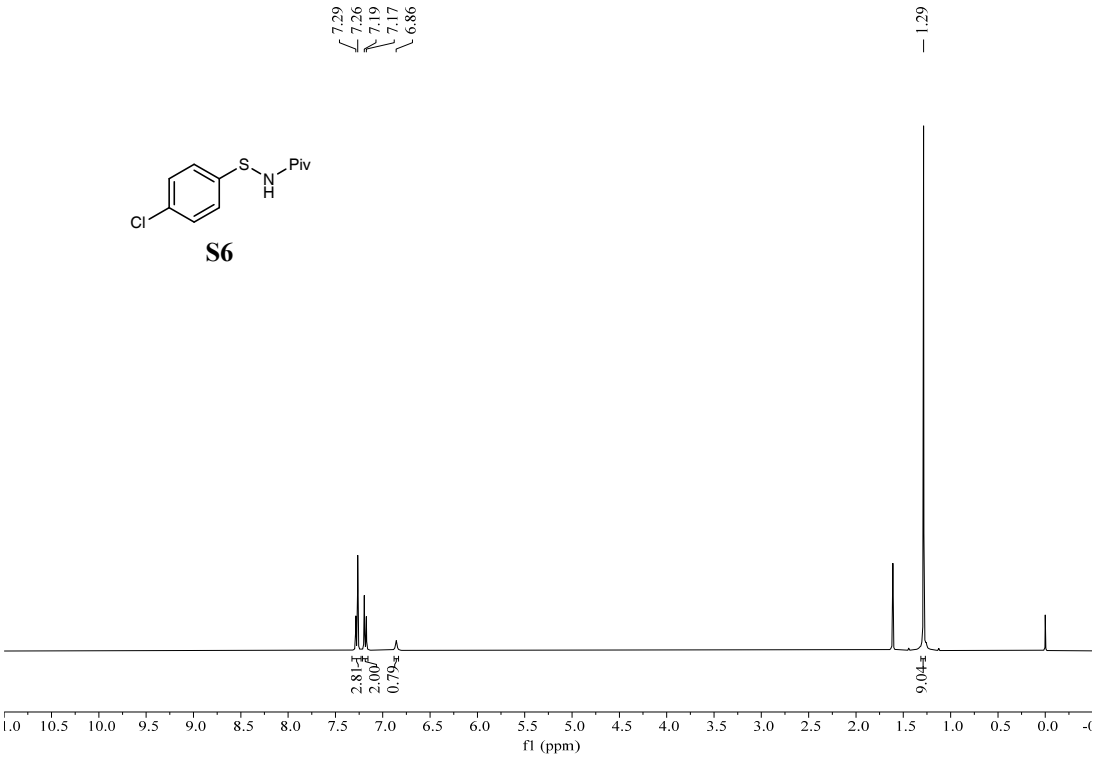
S5


2.00
1.15
0.95
2.09
1.97
2.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

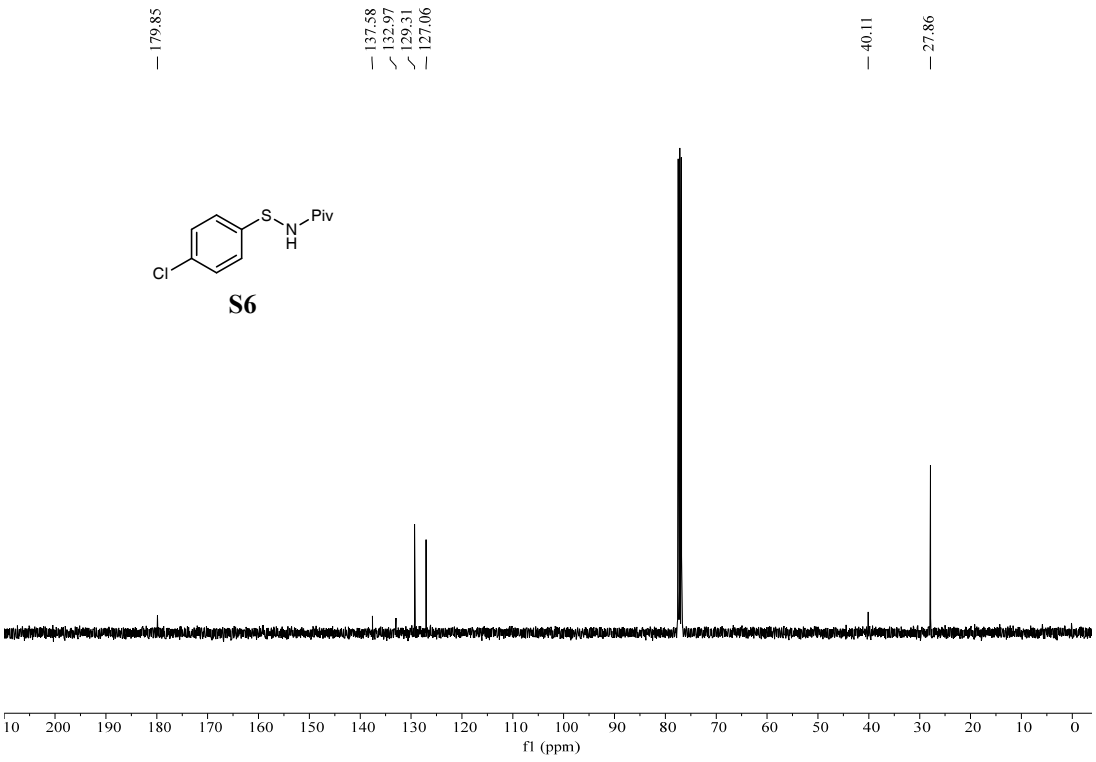

169.13
137.83
133.01
132.78
132.23
128.99
127.75
127.37
121.01
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S
N
H
Bz
Br

S5

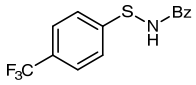

7.29
7.26
7.19
7.17
6.86
1.29
S
N
H
Piv
Cl
2.81
2.00
0.79
9.04
f1 (ppm)

S6

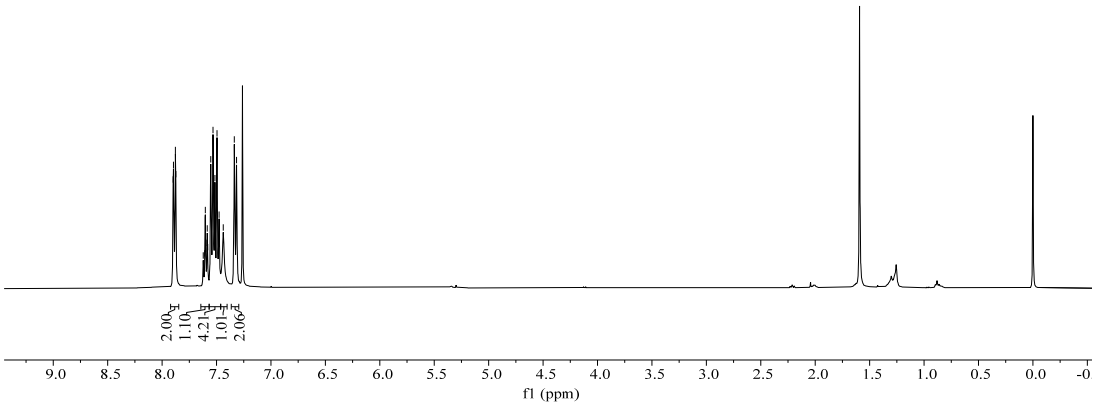

179.85
137.58
132.97
129.31
127.06
40.11
27.86
S
N
H
Piv
Cl
f1 (ppm)

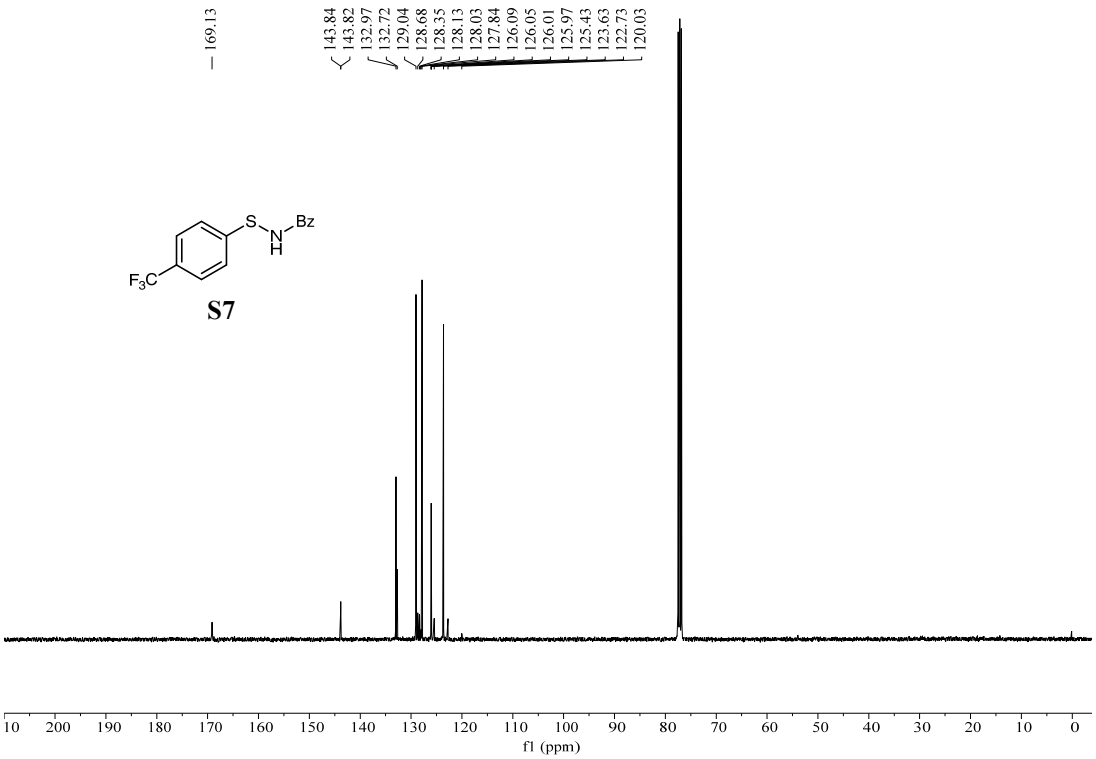
S6


7.90
7.90
7.88
7.87
7.62
7.61
7.60
7.60
7.59
7.58
7.58
7.55
7.53
7.52
7.51
7.50
7.50
7.48
7.44
7.34
7.32

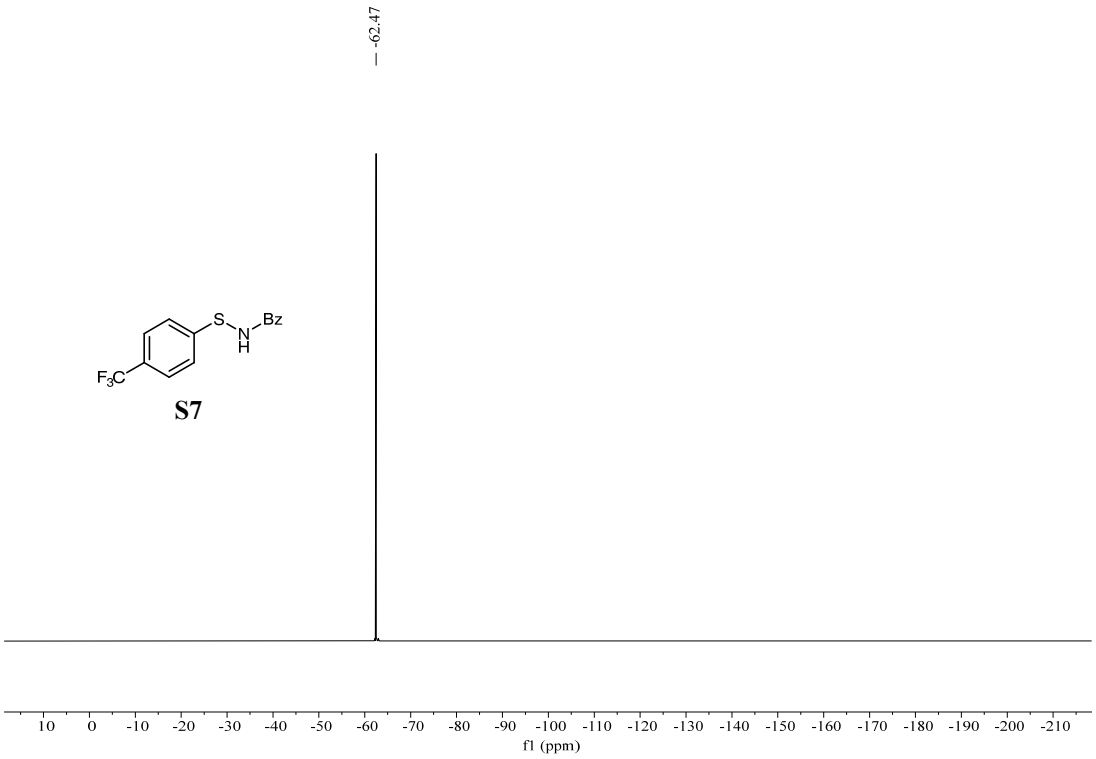

S
N
H
Bz
F3C

S7

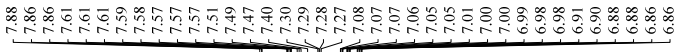

2.00
1.10
4.21
1.01
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

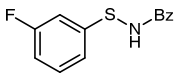

169.13
143.84
143.82
132.97
132.72
129.04
128.68
128.35
128.13
128.03
127.84
126.09
126.05
126.01
125.97
125.43
123.63
122.73
120.03
S
N
H
Bz
F3C
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S7

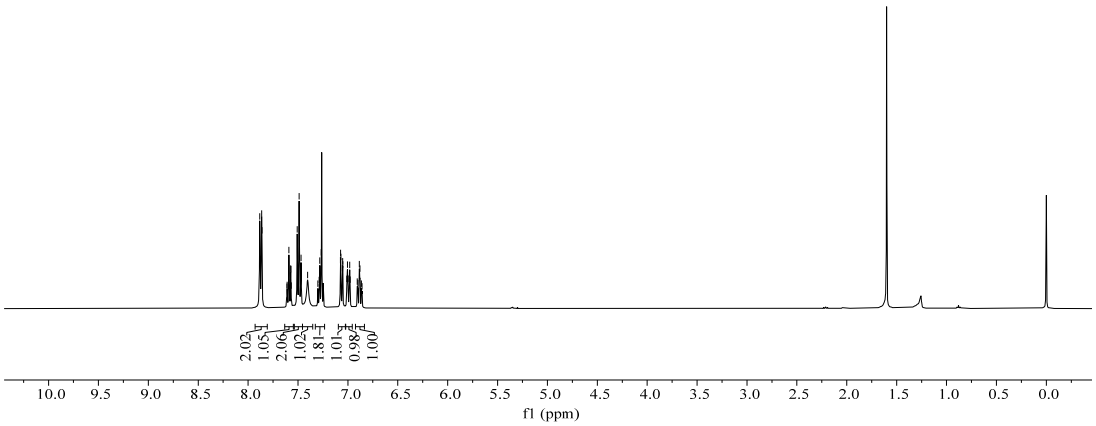

-62.47
S
N
H
Bz
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

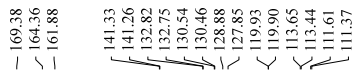
S7

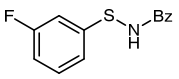

7.88
7.86
7.86
7.61
7.61
7.61
7.59
7.58
7.57
7.57
7.57
7.51
7.49
7.47
7.40
7.30
7.29
7.28
7.27
7.08
7.07
7.07
7.06
7.05
7.05
7.01
7.00
7.00
6.99
6.98
6.98
6.91
6.90
6.88
6.88
6.86
6.86


F
S
N
H
Bz

S8

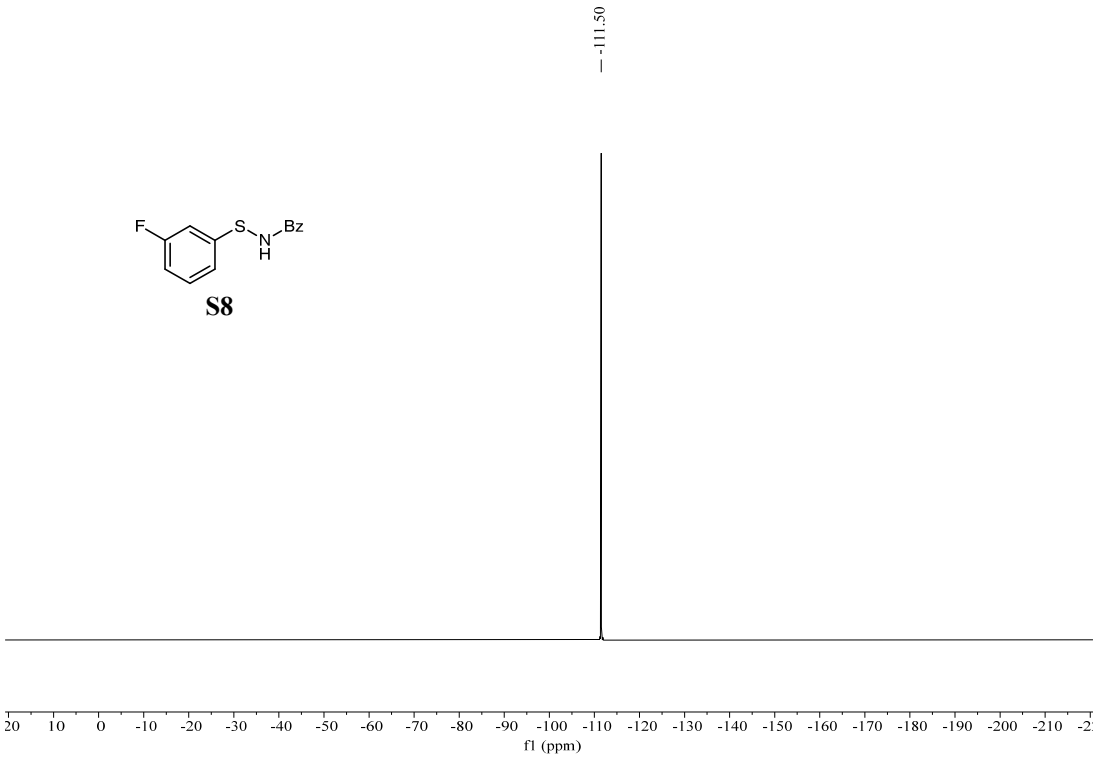

2.02
1.05
2.06
1.02
1.81
1.01
0.98
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.38
164.36
161.88
141.33
141.26
132.82
132.75
130.54
130.46
128.88
127.85
119.93
119.90
113.65
113.44
111.61
111.37

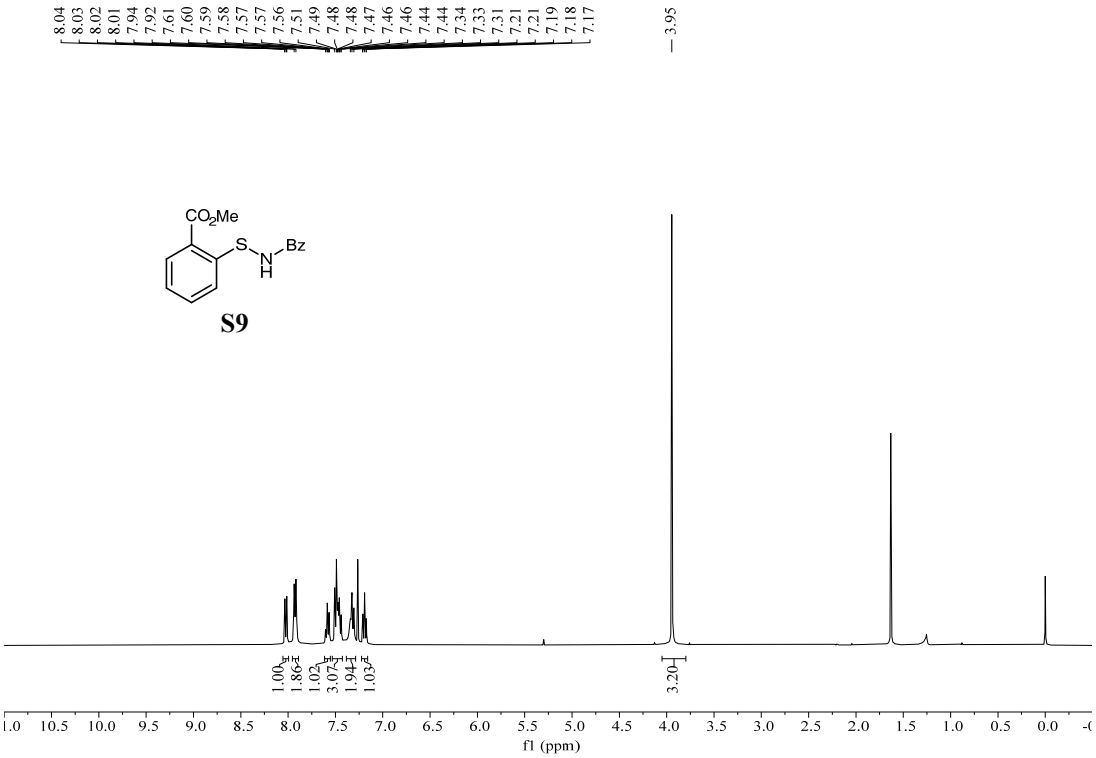

F
S
N
H
Bz

S8

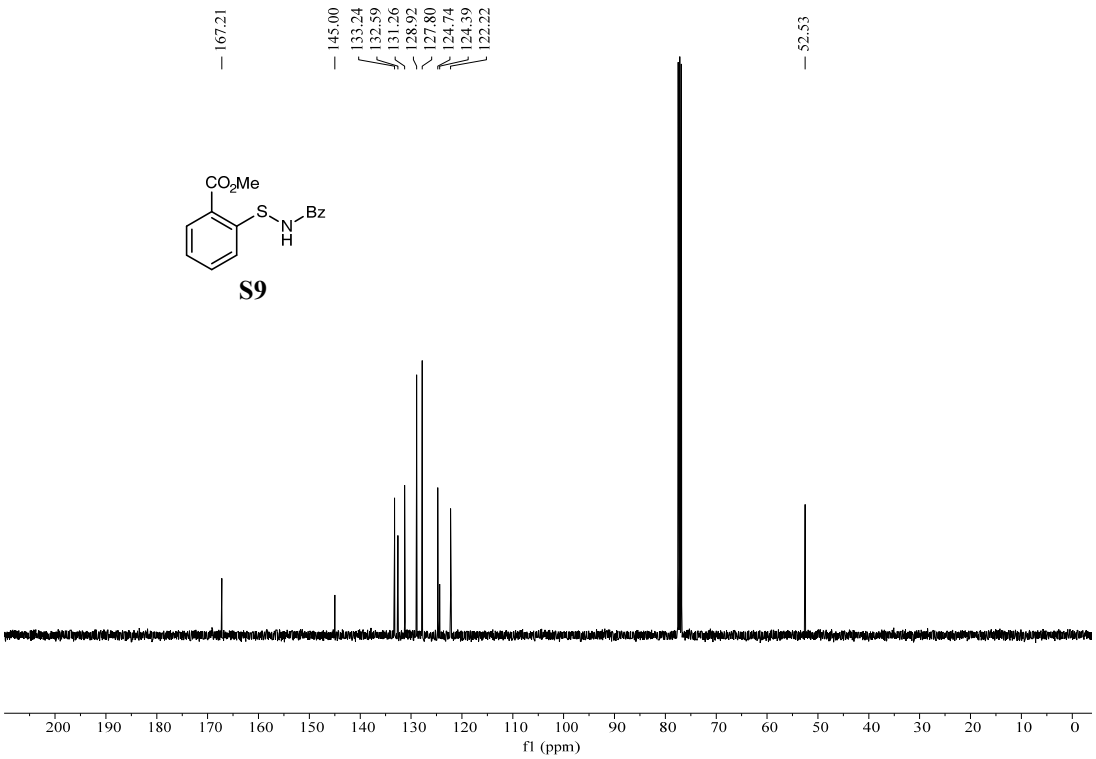
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-111.50
F
S
N
H
Bz
20 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)

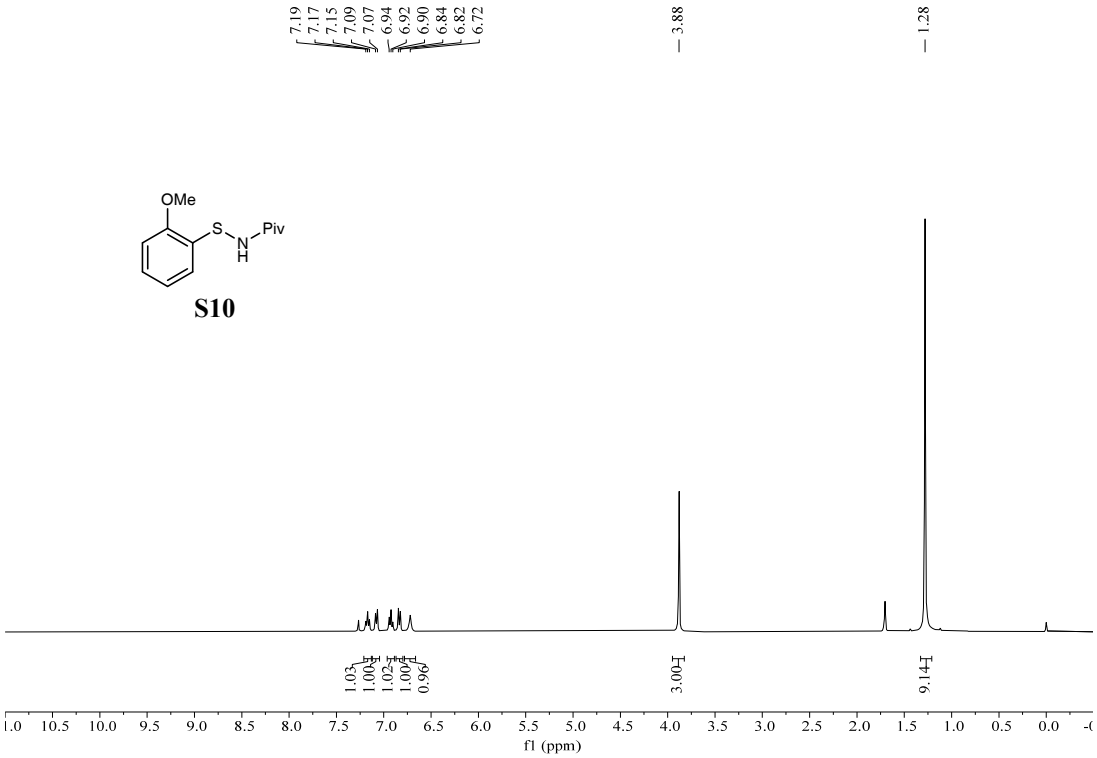
S8


8.04
8.03
8.02
8.01
7.94
7.92
7.61
7.60
7.59
7.58
7.57
7.57
7.56
7.51
7.49
7.48
7.48
7.47
7.46
7.46
7.44
7.44
7.34
7.33
7.31
7.21
7.21
7.19
7.18
7.17
3.95
CO2Me
S
N
H
Bz
1.00
1.86
1.02
3.07
1.94
1.03
3.20
f1 (ppm)

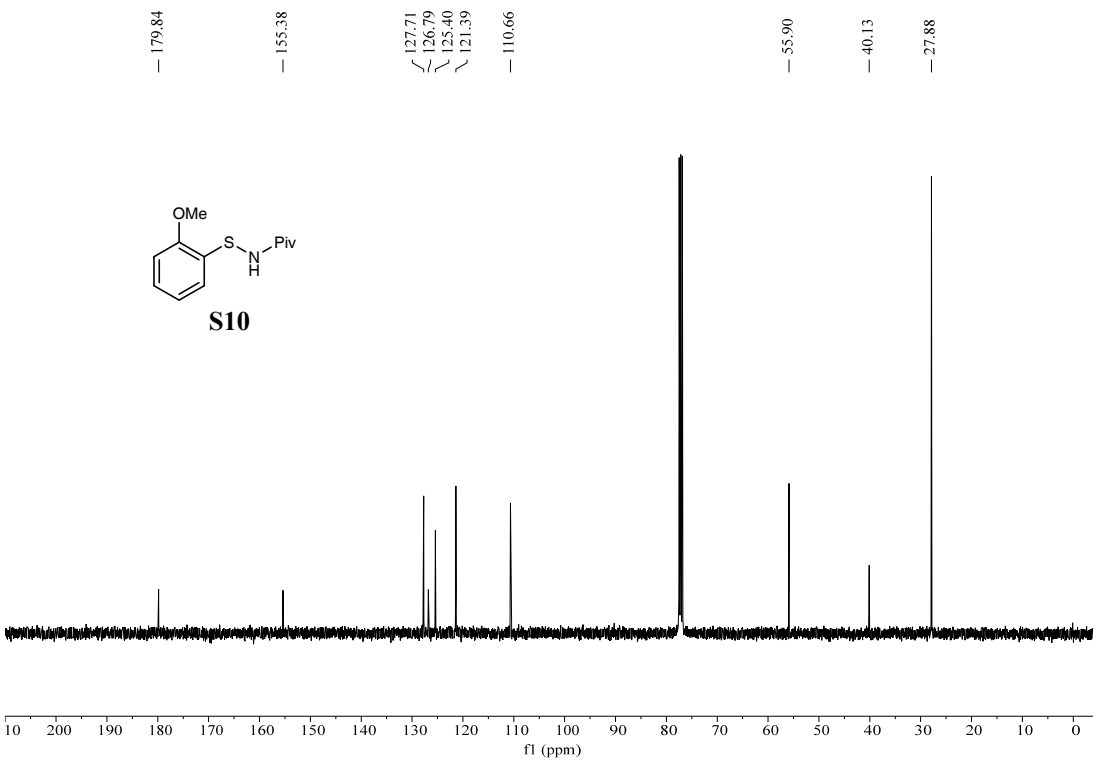
S9


167.21
145.00
133.24
132.59
131.26
128.92
127.80
124.74
124.39
122.22
52.53
CO2Me
S
N
H
Bz
f1 (ppm)

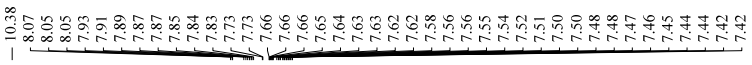
S9


7.19
7.17
7.15
7.09
7.07
6.94
6.92
6.90
6.84
6.82
6.72
3.88
1.28
OMe
S
N
H
Piv
1.03
1.00
1.02
1.00
0.96
3.00
9.14
fl (ppm)

S10


179.84
155.38
127.71
126.79
125.40
121.39
110.66
55.90
40.13
27.88
OMe
S
N
H
Piv
fl (ppm)

S10


10.38
8.07
8.05
8.05
7.93
7.91
7.89
7.87
7.87
7.85
7.84
7.83
7.73
7.73
7.66
7.66
7.66
7.65
7.64
7.63
7.63
7.62
7.62
7.58
7.56
7.56
7.55
7.54
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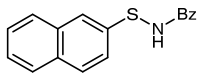
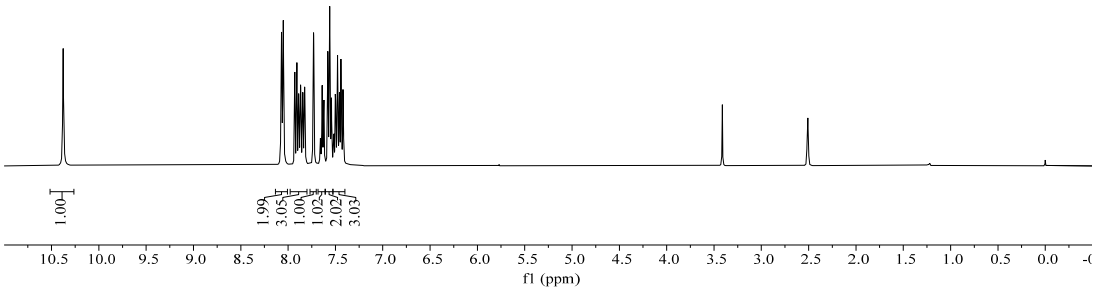
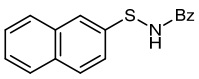
7.46
7.45
7.44
7.44
7.42
7.42


S
N
H
Bz

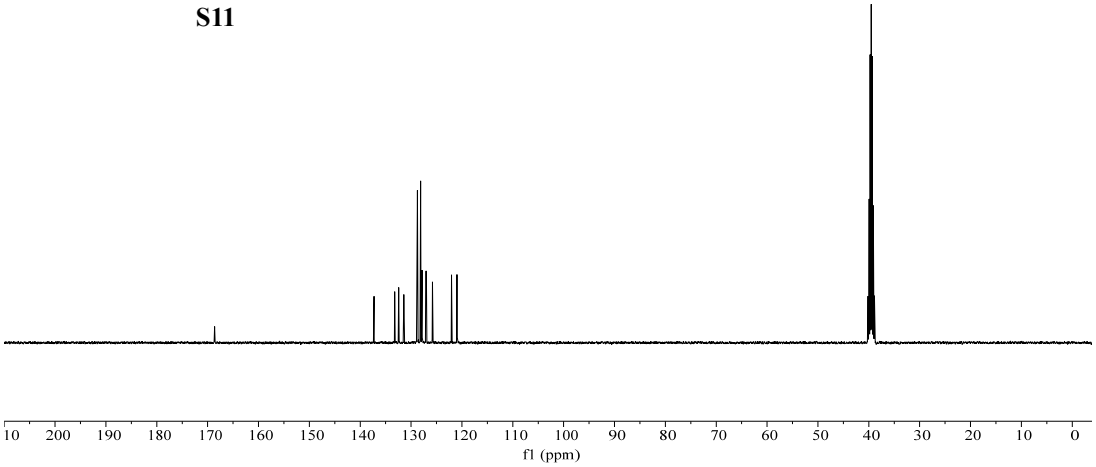
S11

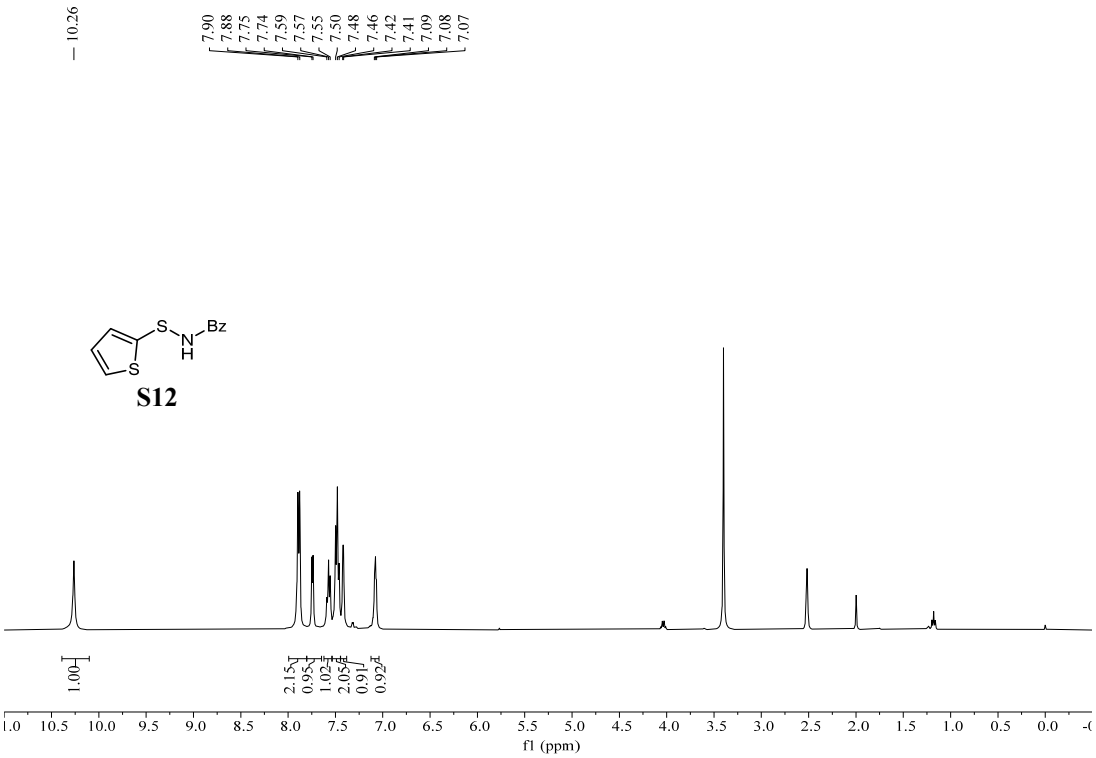

1.00
1.99
3.05
1.00
1.02
2.02
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.62
137.29
133.21
133.16
132.44
131.43
128.85
128.74
128.11
127.84
127.10
126.99
125.80
122.03
120.96

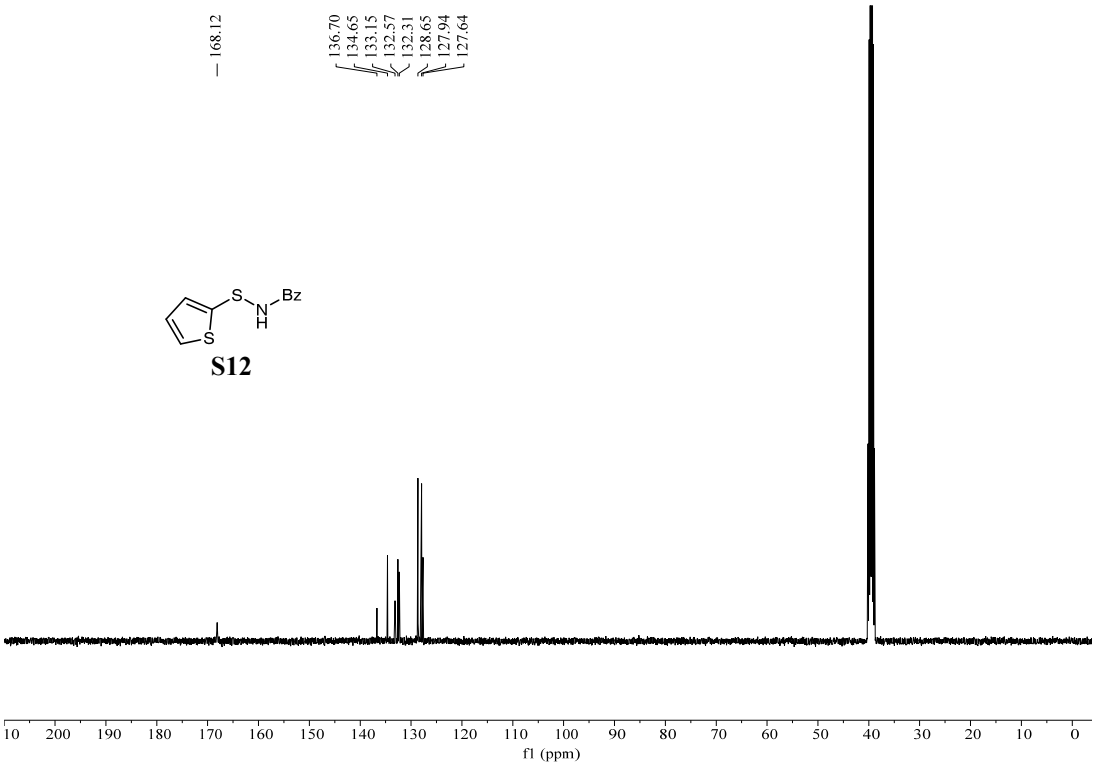

S
N
H
Bz

S11

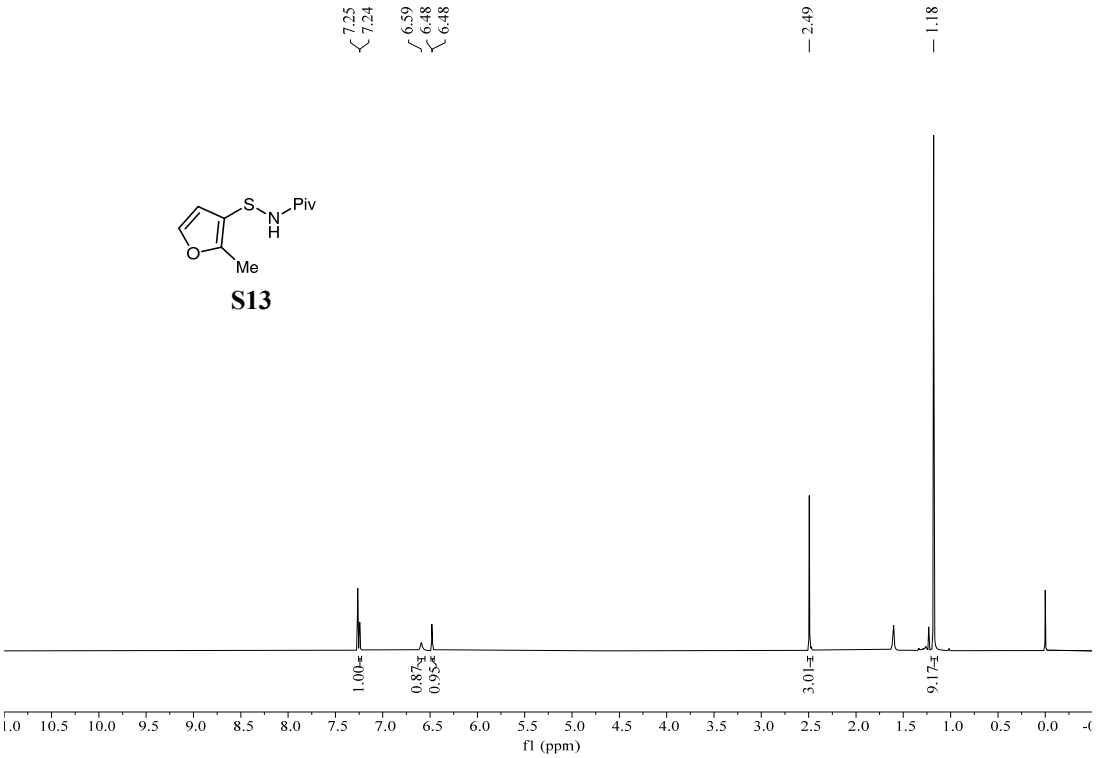

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.26
7.90
7.88
7.75
7.74
7.59
7.57
7.55
7.50
7.48
7.46
7.42
7.41
7.09
7.08
7.07
S
N
H
Bz
S
1.00
2.15
0.95
1.02
2.05
0.91
0.92
f1 (ppm)

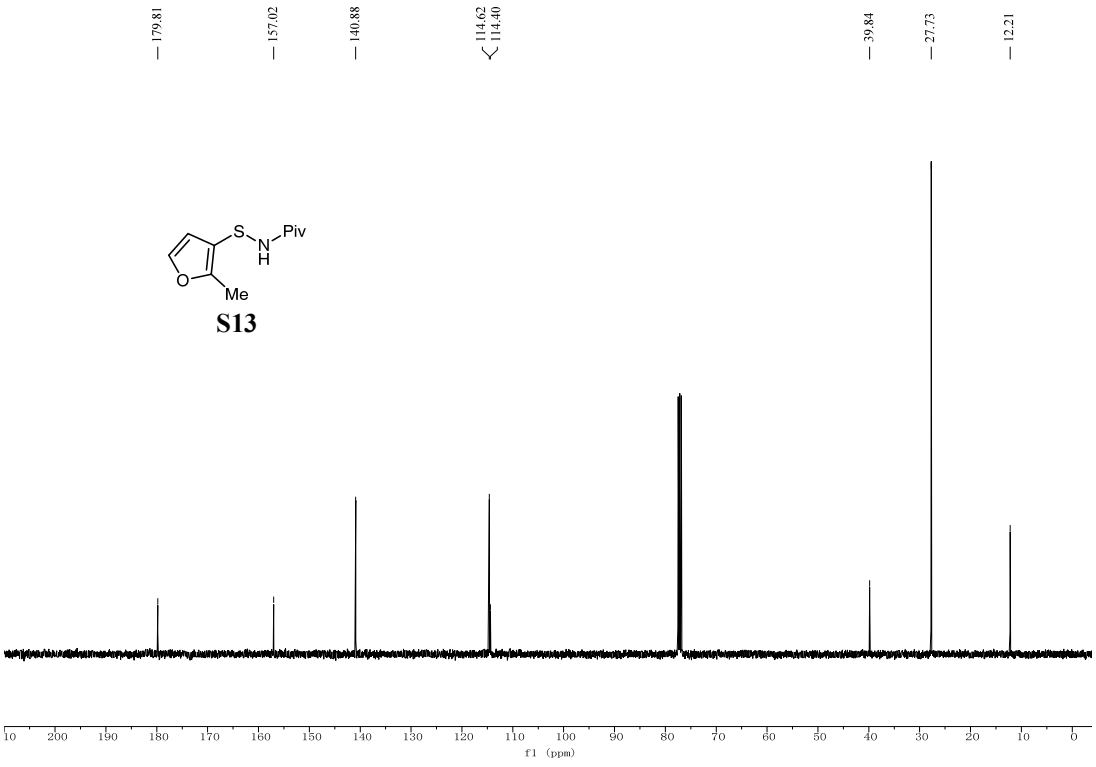
S12


168.12
136.70
134.65
133.15
132.57
132.31
128.65
127.94
127.64
S
N
H
Bz
S
f1 (ppm)

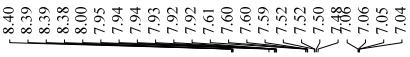
S12

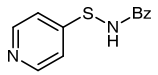

7.25
7.24
6.59
6.48
6.48
2.49
1.18
S
N
H
Piv
O
Me
1.00
0.87
0.95
3.01
9.17
f1 (ppm)

S13

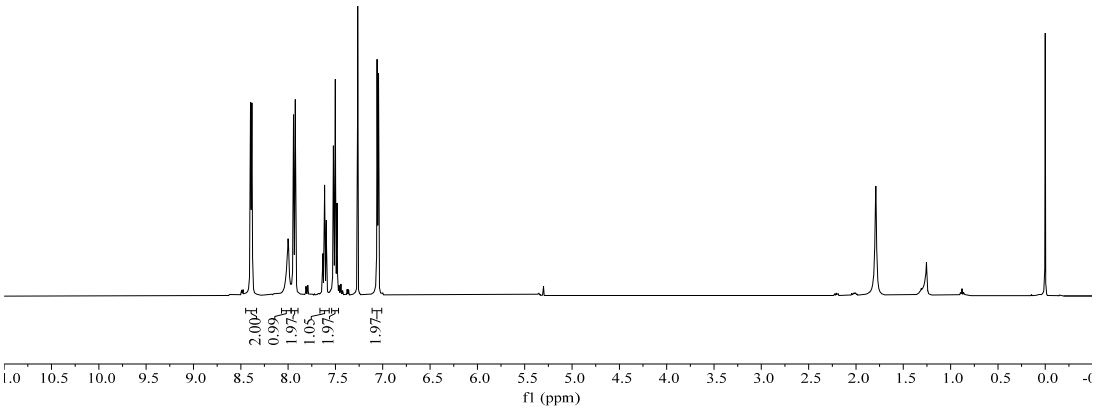

179.81
157.02
140.88
114.62
114.40
39.84
27.73
12.21
S
N
H
Piv
O
Me
f1 (ppm)

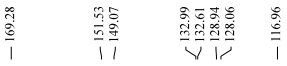
S13

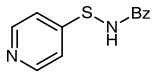

8.40
8.39
8.39
8.38
8.00
7.95
7.94
7.94
7.93
7.92
7.92
7.61
7.60
7.60
7.59
7.52
7.52
7.50
7.48
7.06
7.05
7.04


S
N
H
Bz
N

S14

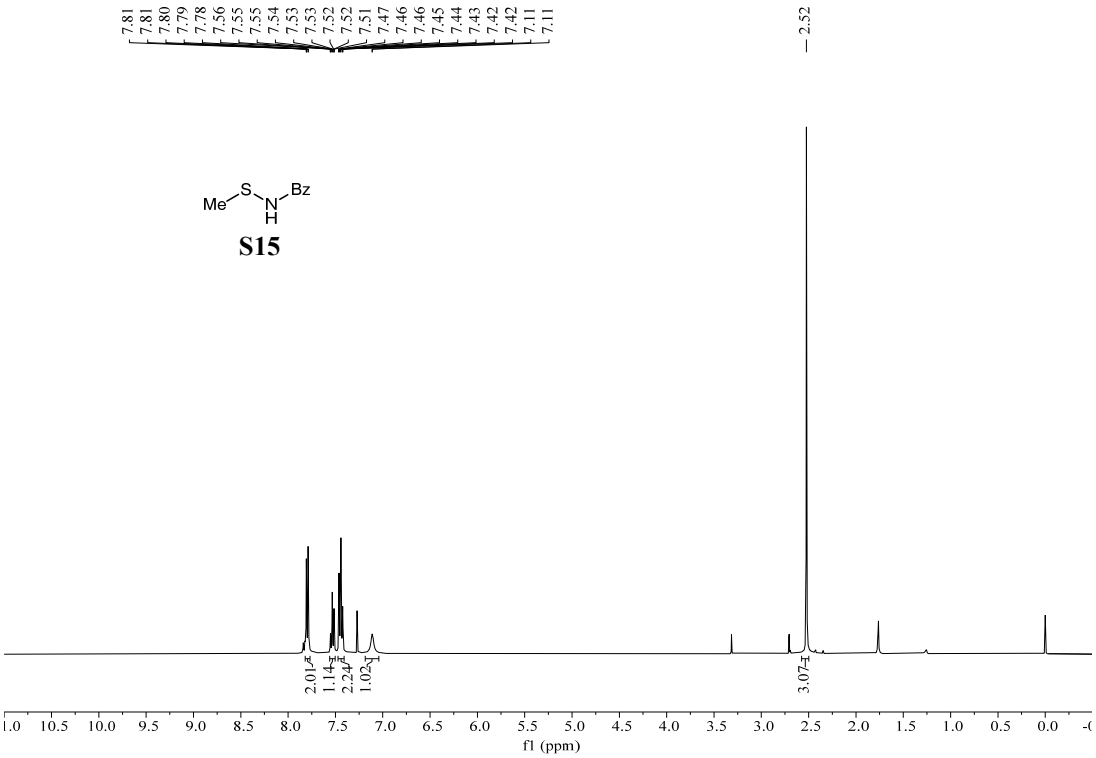

2.00
0.99
1.97
1.05
1.97
1.97
f1 (ppm)


169.28
151.53
149.07
132.99
132.61
128.94
128.06
116.96

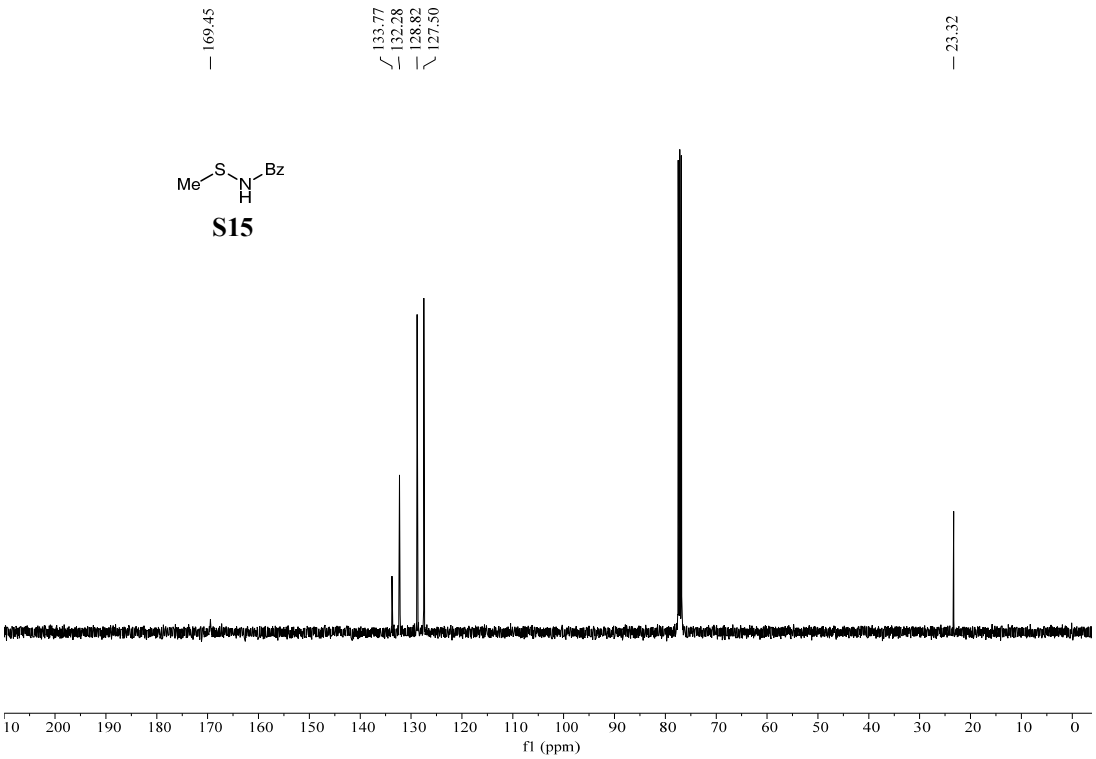

S
N
H
Bz
N

S14

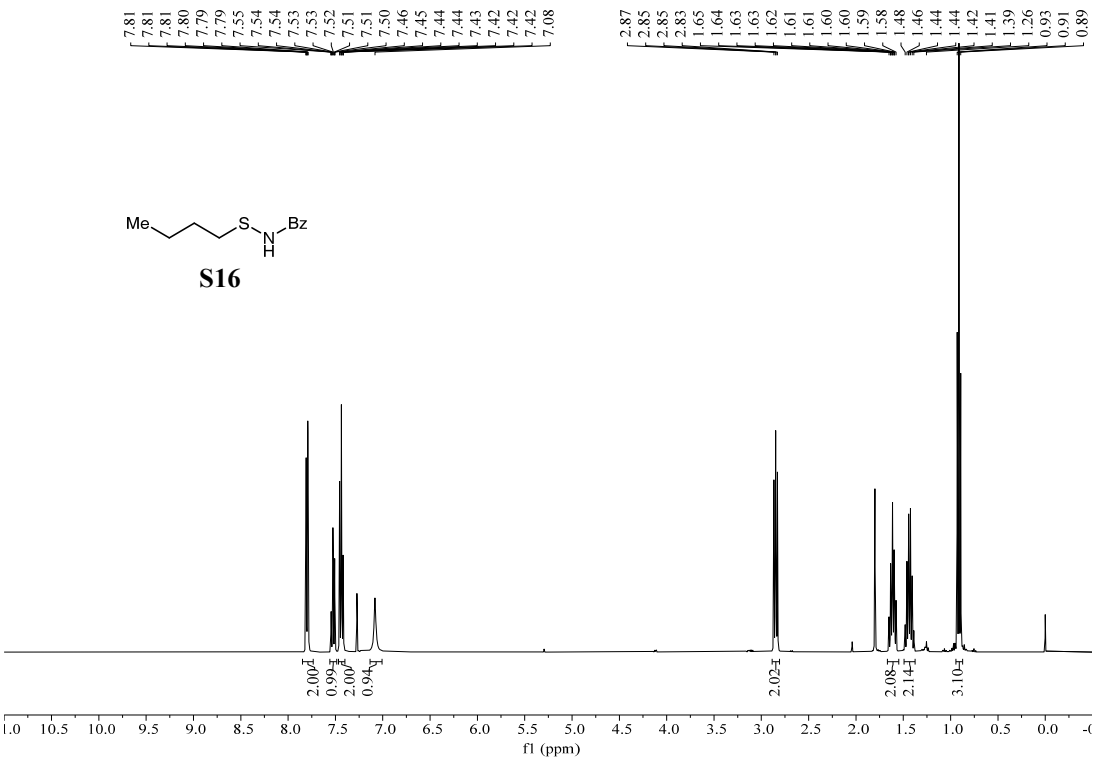
f1 (ppm)

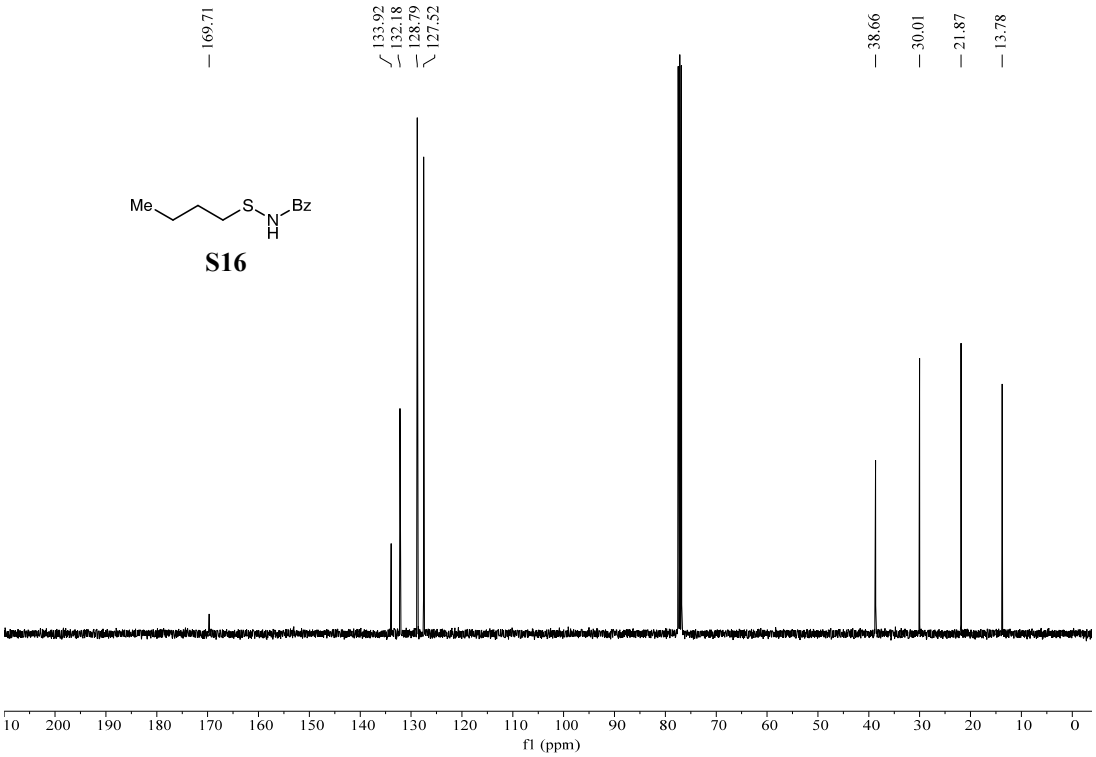

7.81
7.81
7.80
7.79
7.78
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.47
7.46
7.46
7.45
7.44
7.43
7.42
7.42
7.11
7.11
2.52
Me
S
N
H
Bz
2.01
1.14
2.24
1.02
3.07
f1 (ppm)

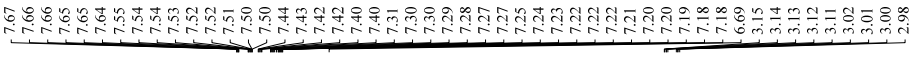
S15

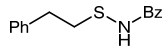

169.45
133.77
132.28
128.82
127.50
23.32
Me
S
N
H
Bz
f1 (ppm)

S15

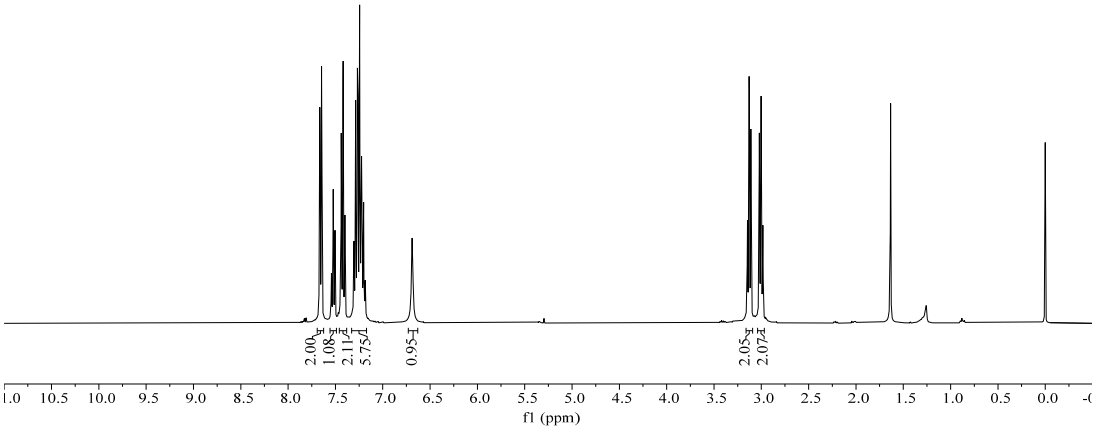

7.81
7.81
7.81
7.80
7.79
7.79
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.42
7.08
2.87
2.85
2.85
2.83
1.65
1.64
1.63
1.63
1.62
1.61
1.61
1.60
1.60
1.59
1.58
1.48
1.46
1.44
1.44
1.42
1.41
1.39
1.26
0.93
0.91
0.89
Me
S
N
H
Bz
S16
2.00
0.99
2.00
0.94
2.02
2.08
2.14
3.10
f1 (ppm)

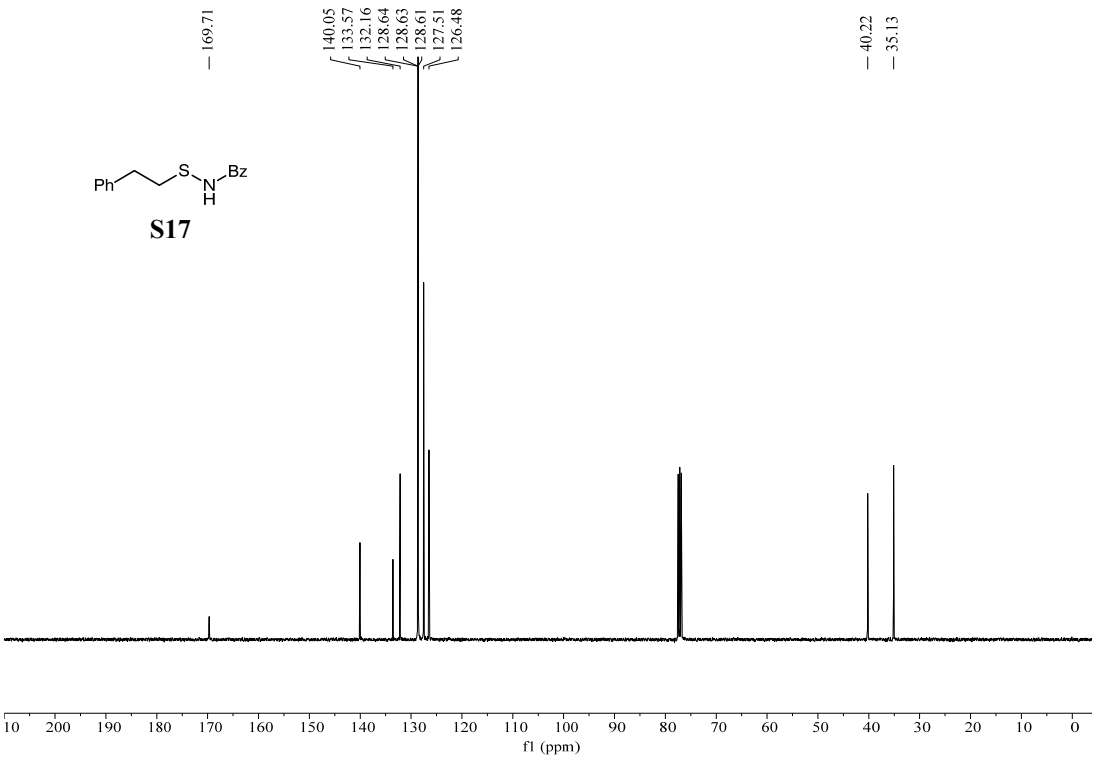

169.71
133.92
132.18
128.79
127.52
38.66
30.01
21.87
13.78
Me
S
N
H
Bz
S16
f1 (ppm)


7.67
7.66
7.66
7.65
7.65
7.64
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.44
7.43
7.42
7.42
7.40
7.40
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.25
7.24
7.23
7.22
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.18
6.69
3.15
3.14
3.13
3.12
3.11
3.02
3.01
3.00
2.98


Ph
S
N
H
Bz

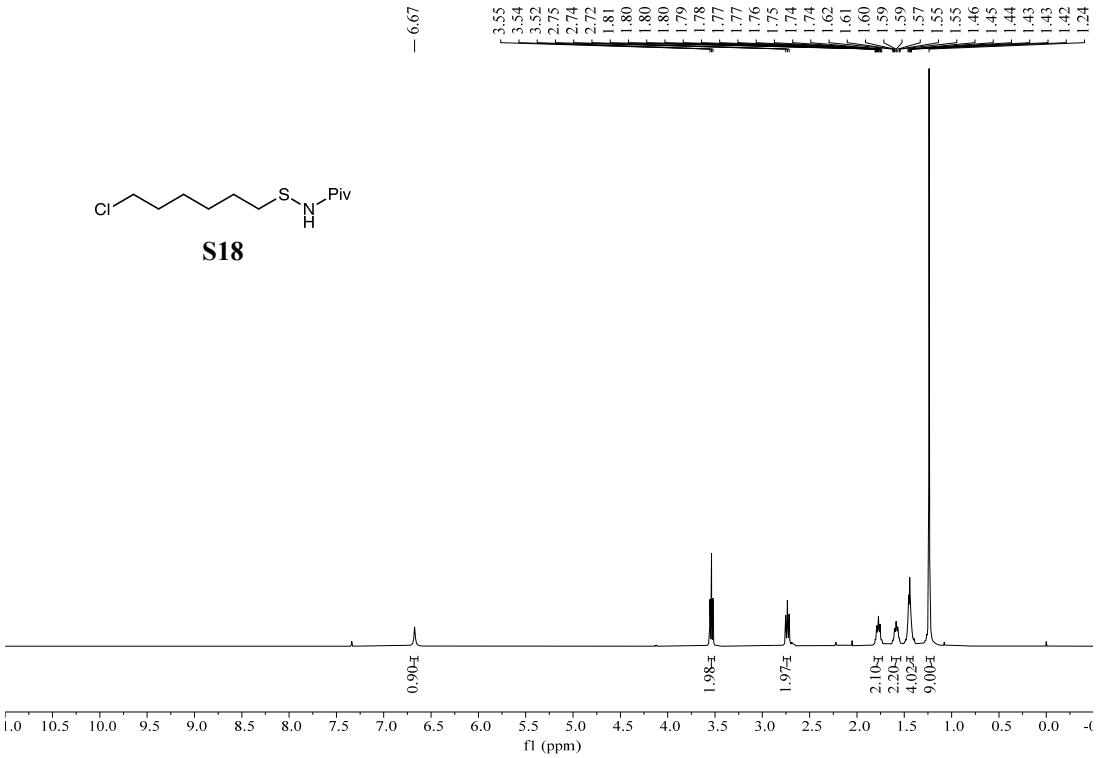
S17


2.00
1.08
2.11
5.75
0.95
2.05
2.07
f1 (ppm)

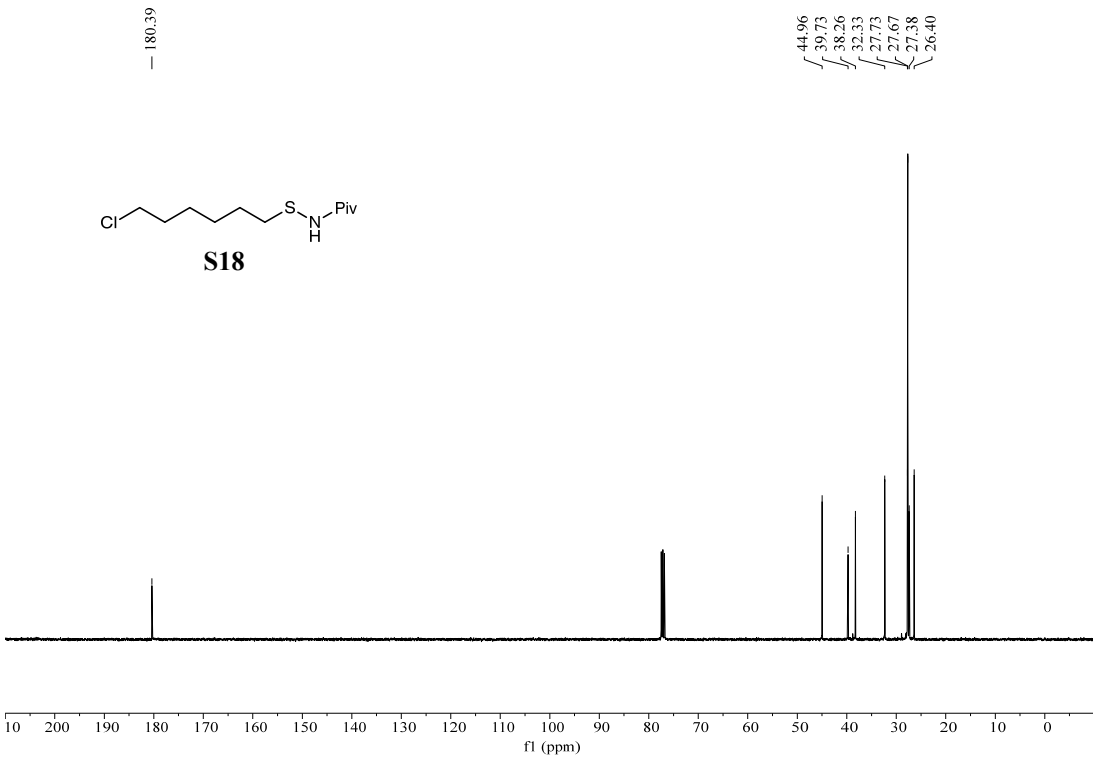

169.71
140.05
133.57
132.16
128.64
128.63
128.61
127.51
126.48
40.22
35.13
f1 (ppm)

Ph
S
N
H
Bz

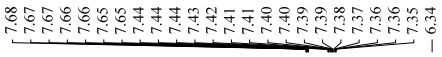
S17

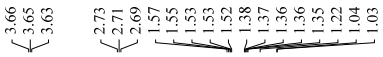

6.67
3.55
3.54
3.52
2.75
2.74
2.72
1.81
1.80
1.80
1.80
1.79
1.78
1.77
1.77
1.76
1.75
1.74
1.74
1.62
1.61
1.60
1.59
1.59
1.57
1.55
1.55
1.46
1.45
1.44
1.43
1.43
1.42
1.24
Cl
S
N
H
Piv
0.90
1.98
1.97
2.10
2.20
4.02
9.00
f1 (ppm)

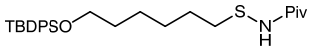
S18


180.39
44.96
39.73
38.26
32.33
27.73
27.67
27.38
26.40
Cl
S
N
H
Piv
f1 (ppm)

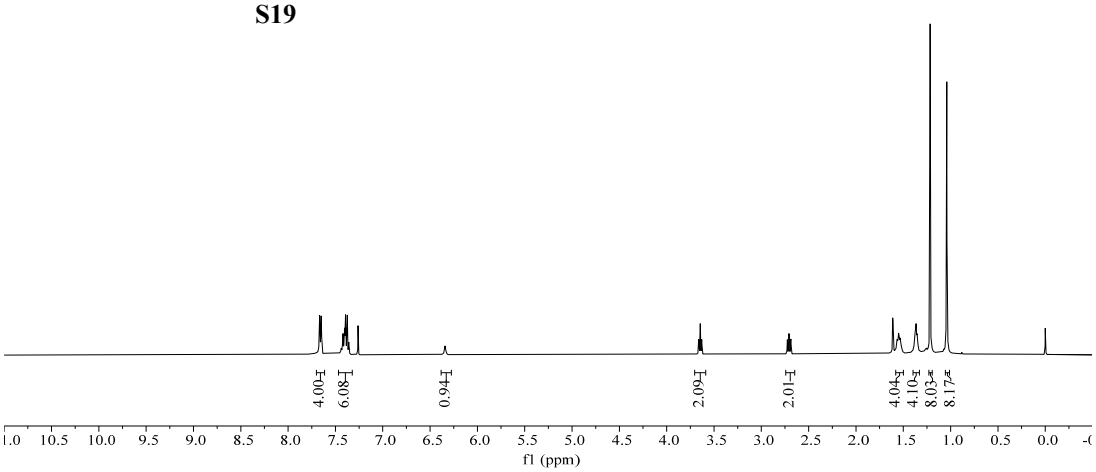
S18


7.68
7.67
7.67
7.66
7.66
7.65
7.44
7.44
7.43
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.35
6.34

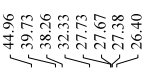

3.66
3.65
3.63
2.73
2.71
2.69
1.57
1.55
1.53
1.53
1.52
1.38
1.37
1.36
1.36
1.35
1.22
1.04
1.03

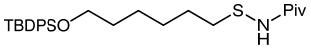

TBDPSO
S
N
H
Piv

S19


4.00
6.08
0.94
2.09
2.01
4.04
4.10
8.03
8.17
f1 (ppm)

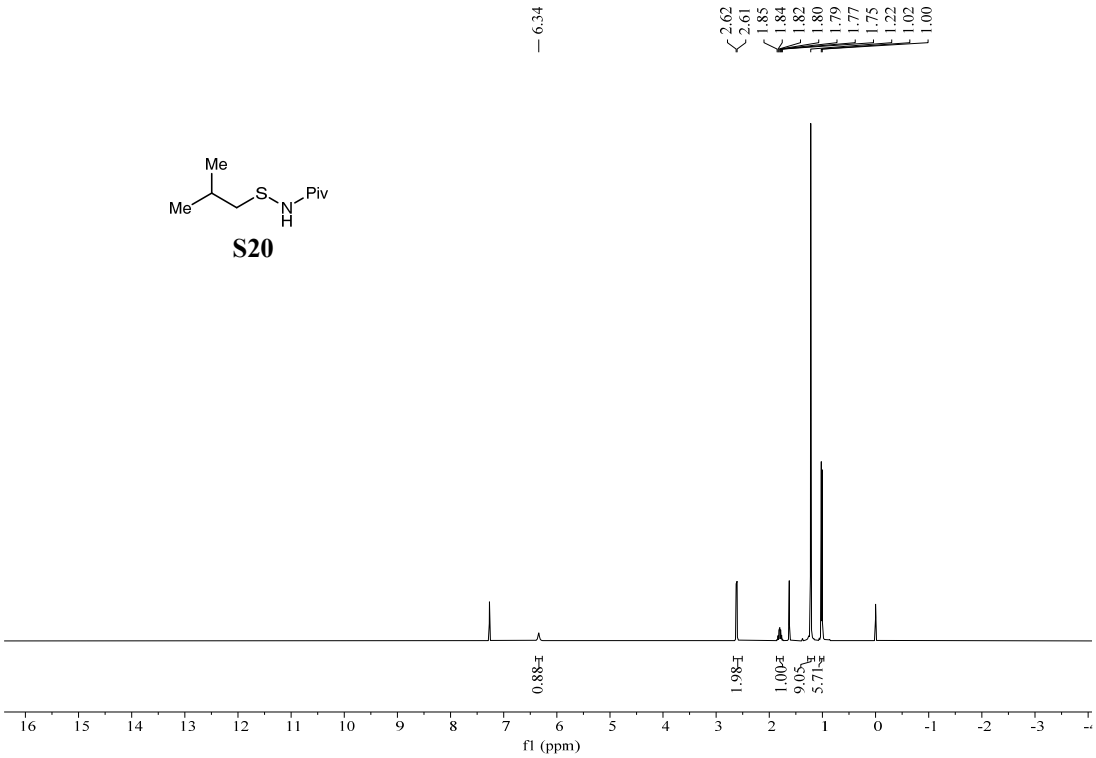

180.39


44.96
39.73
38.26
32.33
27.73
27.67
27.38
26.40

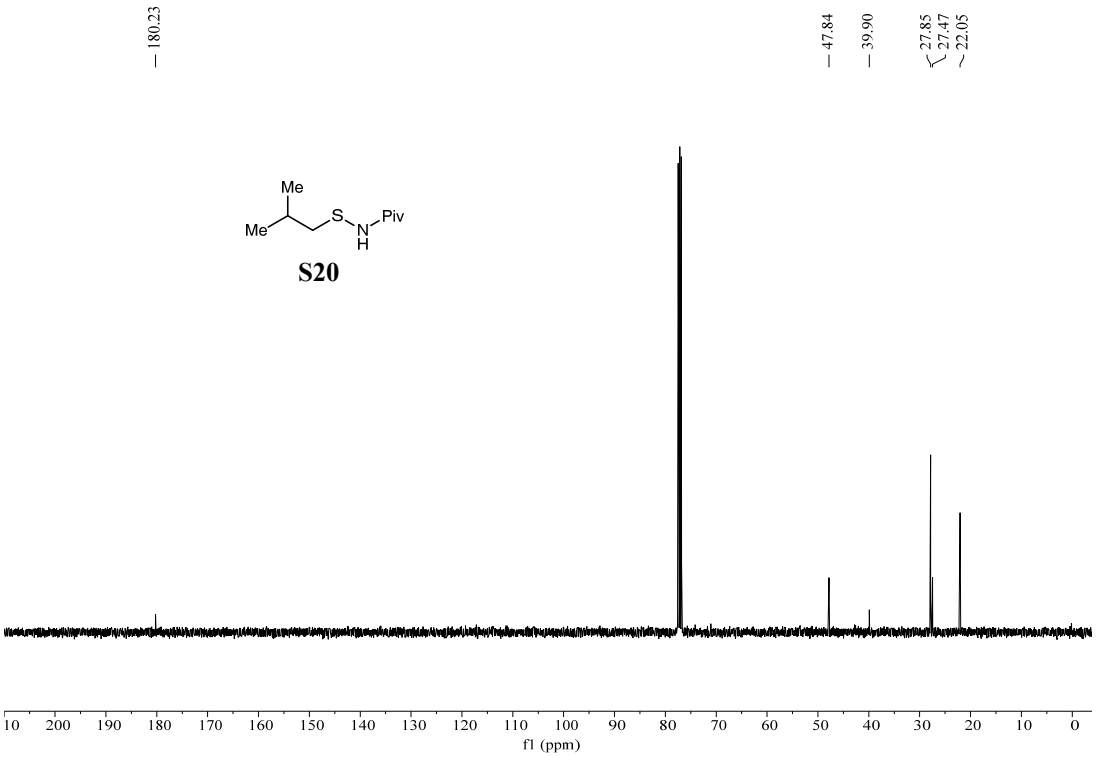

TBDPSO
S
N
H
Piv

S19

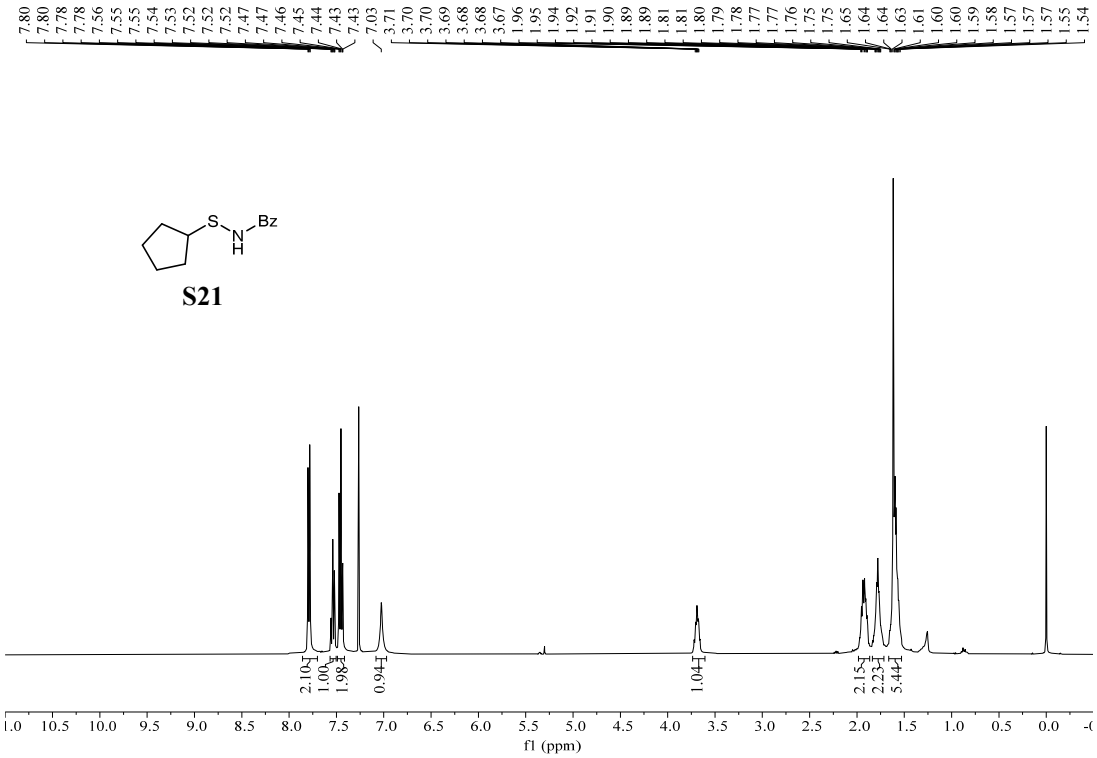
f1 (ppm)

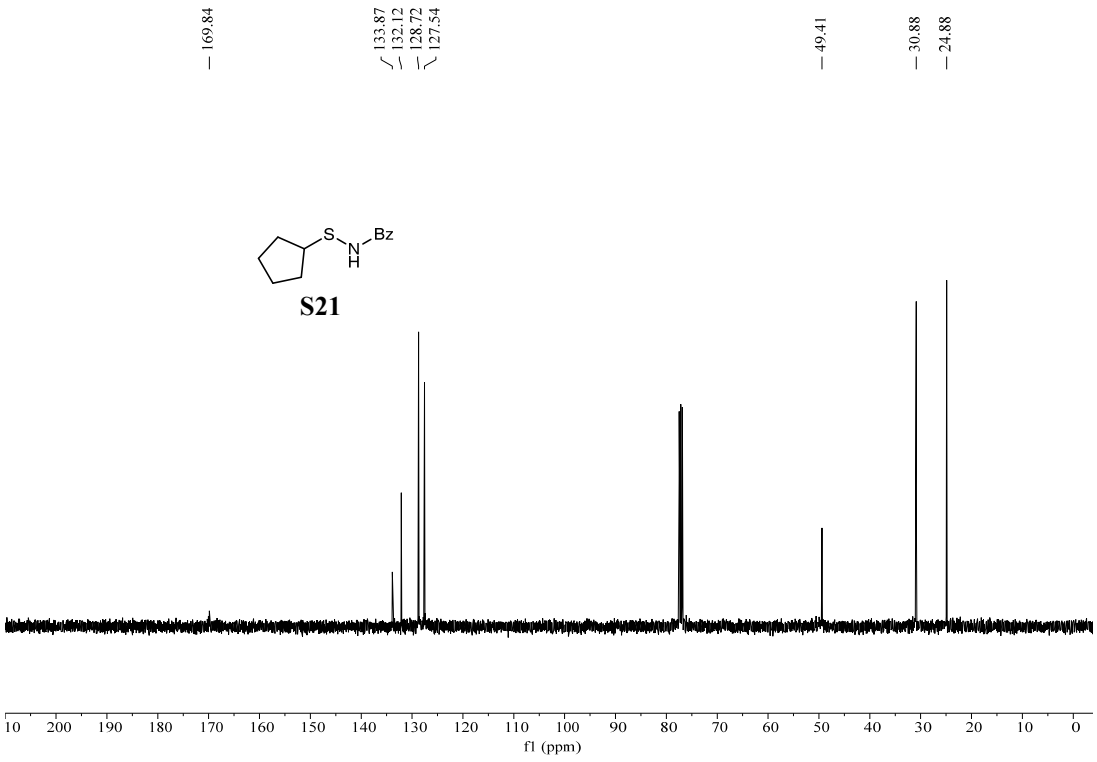

6.34
2.62
2.61
1.85
1.84
1.82
1.80
1.79
1.77
1.75
1.22
1.02
1.00
Me
Me
S
N
H
Piv
0.88
1.98
1.00
9.05
5.71
f1 (ppm)

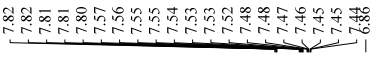
S20

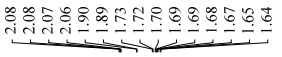

180.23
47.84
39.90
27.85
27.47
22.05
Me
Me
S
N
H
Piv
f1 (ppm)

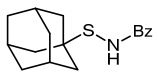
S20


7.80
7.80
7.78
7.78
7.56
7.55
7.54
7.53
7.52
7.52
7.52
7.47
7.46
7.45
7.44
7.43
7.43
7.03
3.71
3.70
3.70
3.69
3.68
3.68
3.67
1.96
1.95
1.94
1.92
1.91
1.90
1.89
1.89
1.81
1.81
1.80
1.79
1.78
1.77
1.77
1.76
1.75
1.75
1.65
1.64
1.64
1.63
1.61
1.60
1.60
1.59
1.58
1.57
1.57
1.57
1.55
1.54
S
N
H
Bz
S21
2.10
1.00
1.98
0.94
1.04
2.15
2.23
5.44
f1 (ppm)


169.84
133.87
132.12
128.72
127.54
49.41
30.88
24.88
S
N
H
Bz
S21
f1 (ppm)


7.82
7.82
7.81
7.81
7.80
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.48
7.48
7.47
7.46
7.45
7.45
7.44
6.86

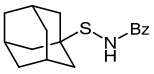

2.08
2.08
2.07
2.06
1.90
1.89
1.73
1.72
1.70
1.69
1.69
1.68
1.67
1.65
1.64


S
N
H
Bz

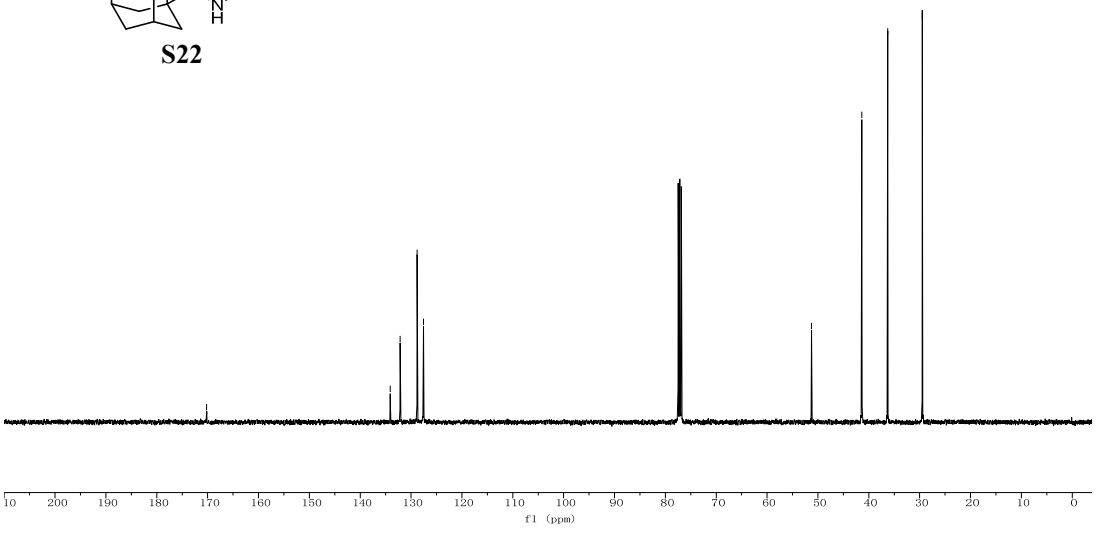
S22

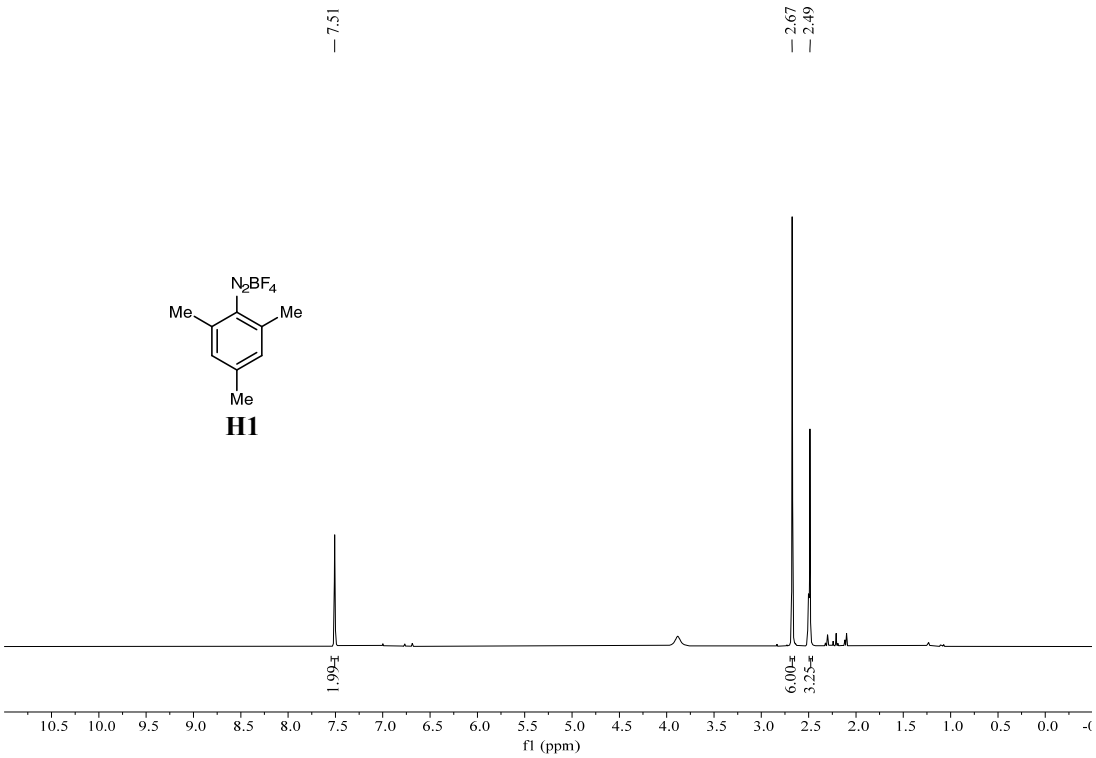
2.00
1.00
2.02
0.99
3.06
6.00
6.34
f1 (ppm)

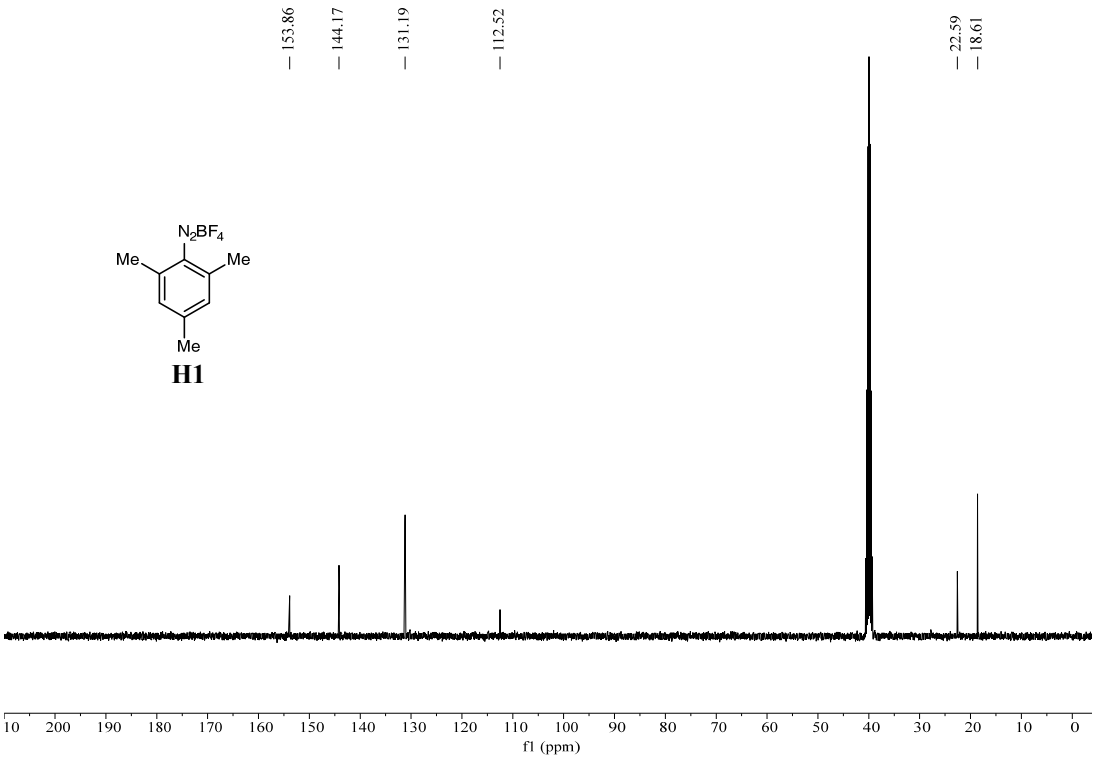

170.19
134.10
132.16
128.81
127.55
51.26
41.37
36.27
29.48

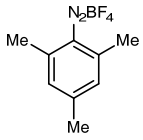

S
N
H
Bz

S22


f1 (ppm)

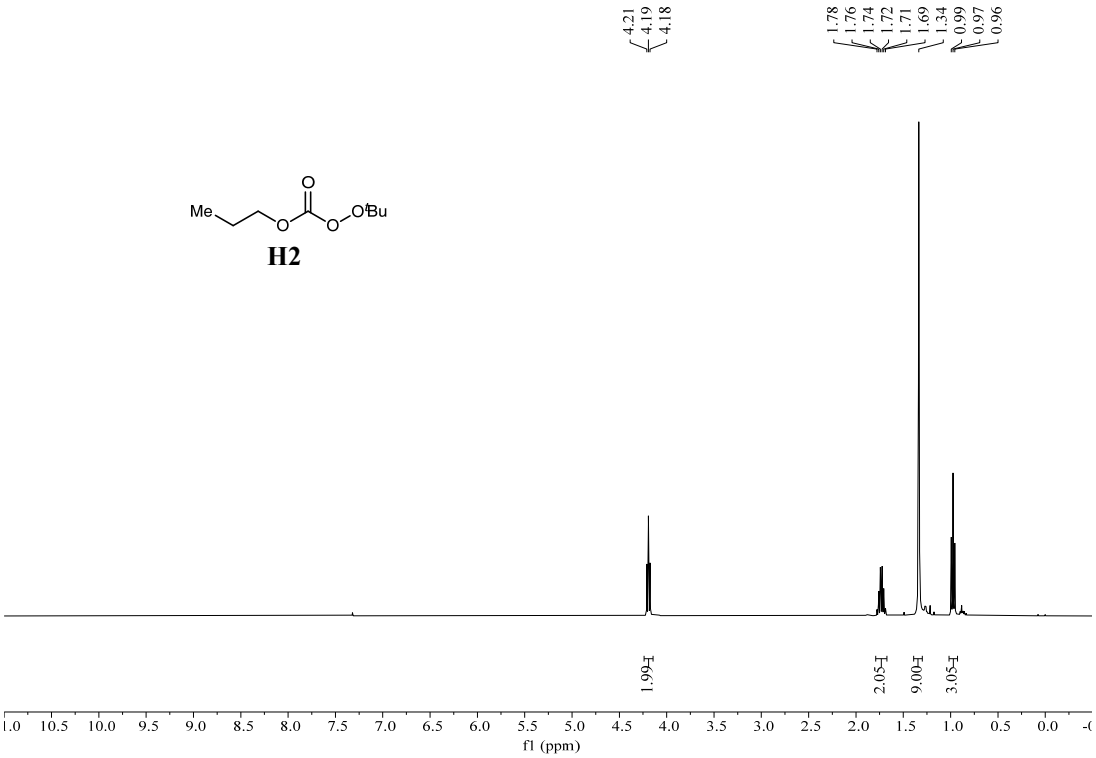

7.51
2.67
2.49
N2BF4
Me
Me
Me
H1
1.99
6.00
3.25
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

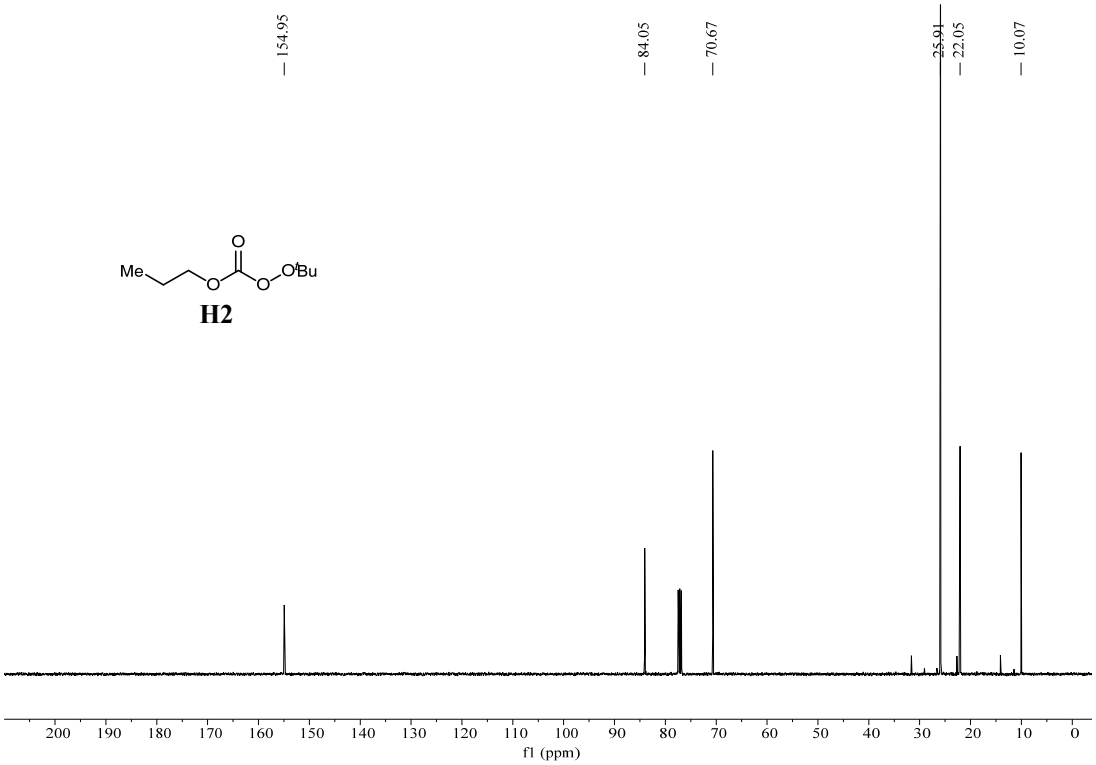

153.86
144.17
131.19
112.52
22.59
18.61
N2BF4
Me
Me
Me
H1
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

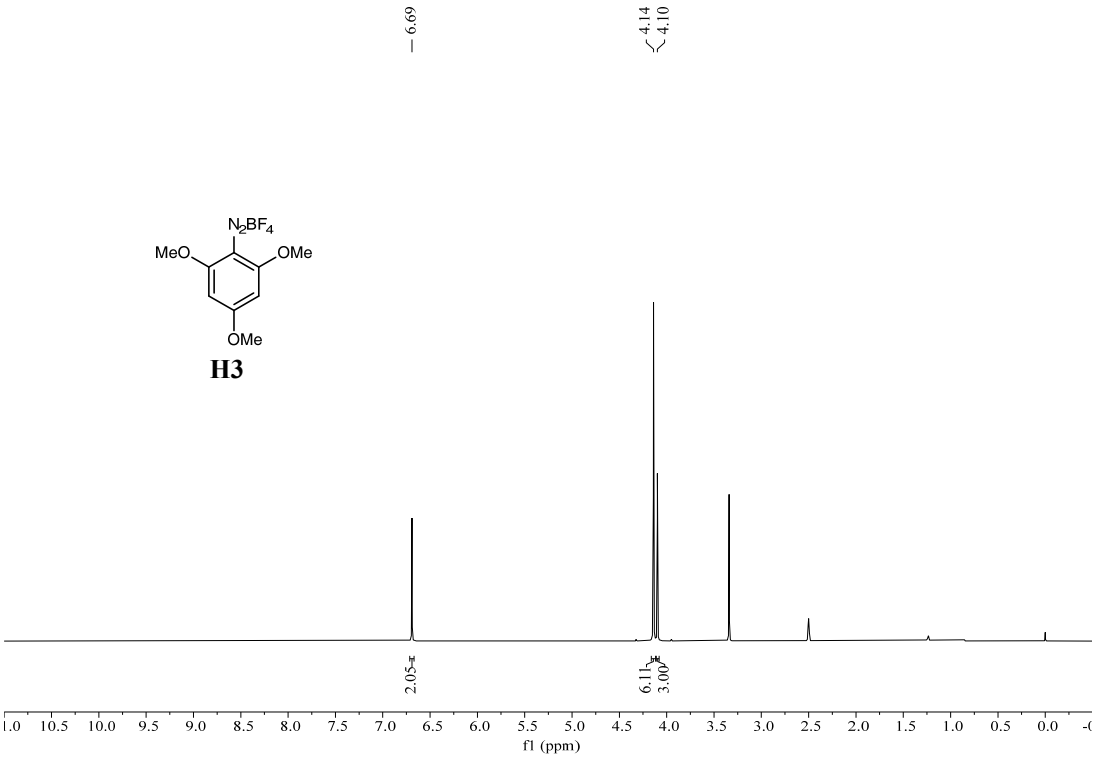

N_2BF_4
Me
Me
Me

H1

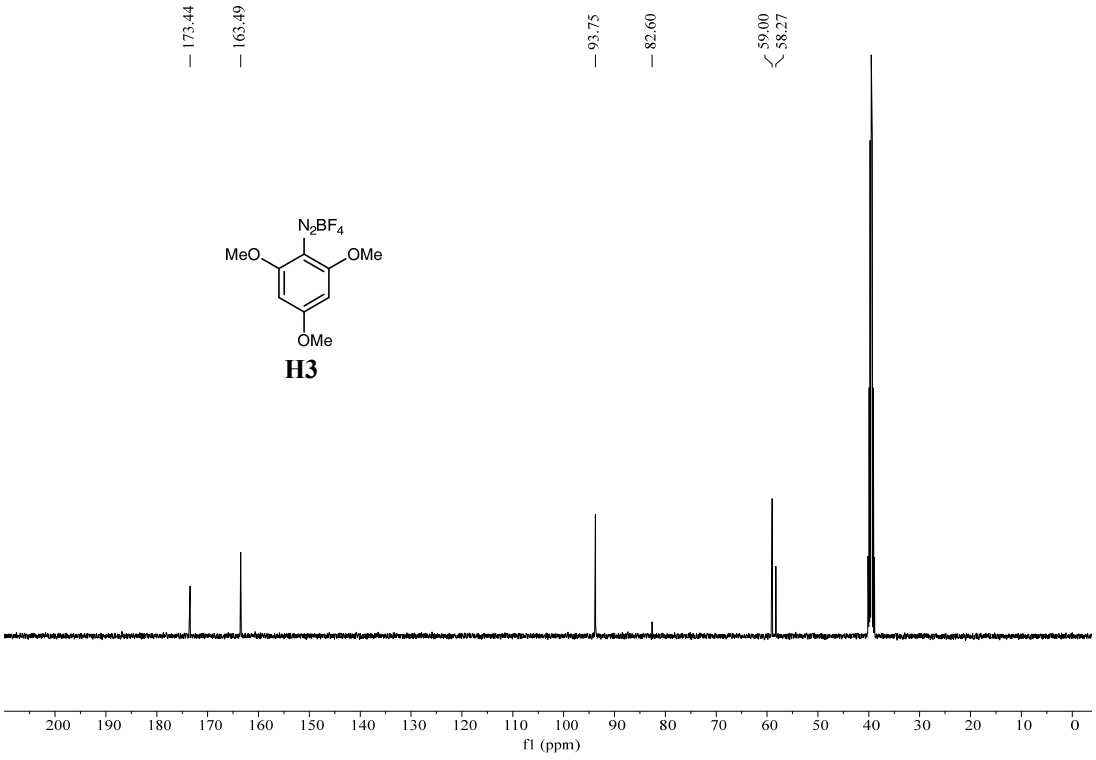
-148.75
-148.80
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


4.21
4.19
4.18
1.78
1.76
1.74
1.72
1.71
1.69
1.34
0.99
0.97
0.96
Me
O
O
O
O
tBu
H2
1.99
2.05
9.00
3.05
f1 (ppm)

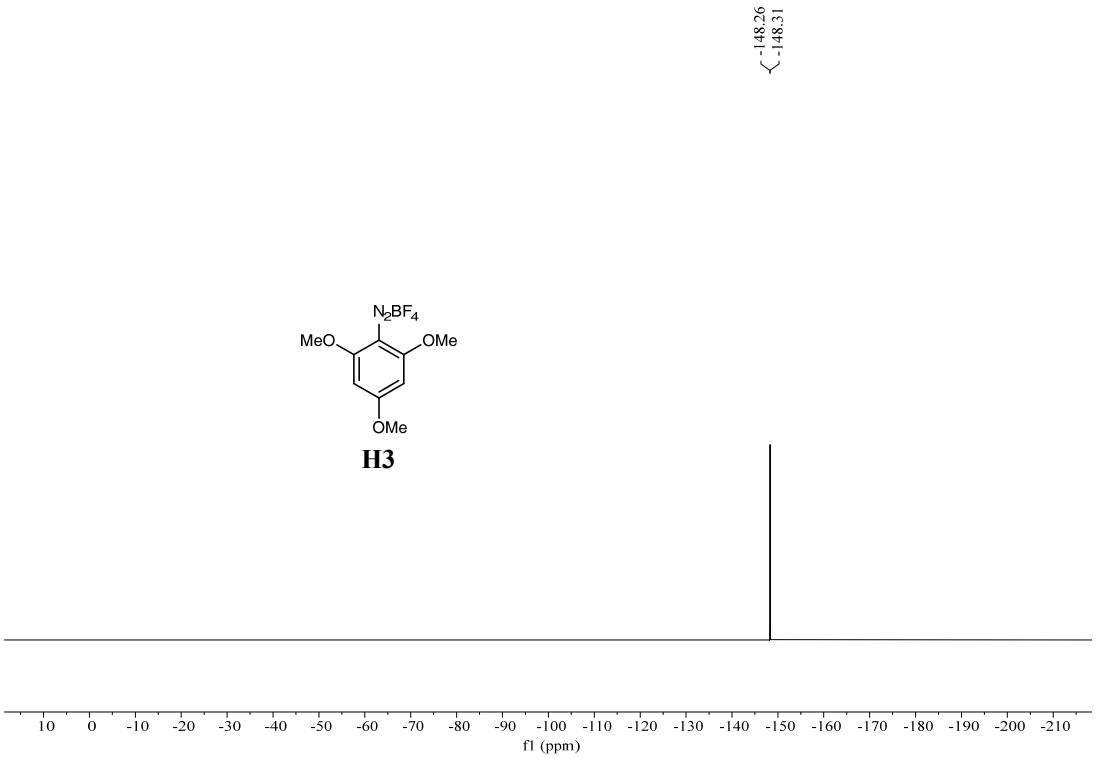

154.95
84.05
70.67
25.91
22.05
10.07
Me
O
O
O
O
tBu
H2
f1 (ppm)


6.69
4.14
4.10
N2BF4
MeO
OMe
OMe
2.05
6.11
3.00
fl (ppm)

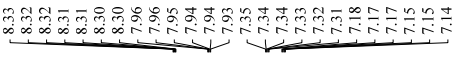
H3


173.44
163.49
93.75
82.60
59.00
58.27
N2BF4
MeO
OMe
OMe
fl (ppm)

H3


-148.26
-148.31
N2BF4
MeO
OMe
OMe
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)

H3


8.33
8.32
8.32
8.31
8.31
8.30
8.30
7.96
7.96
7.95
7.94
7.94
7.93
7.35
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7.33
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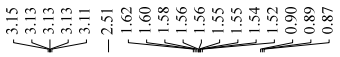
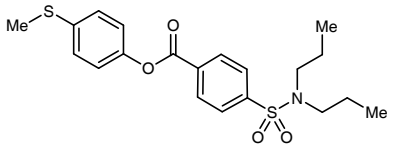
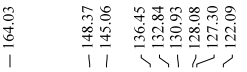
7.18
7.17
7.17
7.15
7.15
7.14

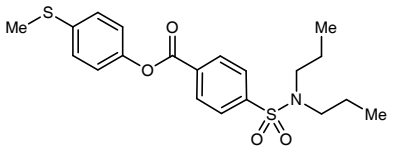

3.15
3.13
3.13
3.13
3.11
2.51
1.62
1.60
1.58
1.56
1.56
1.55
1.55
1.54
1.52
0.90
0.89
0.87


Me
S
O
O
Me
N
Me
S
O
O

C24

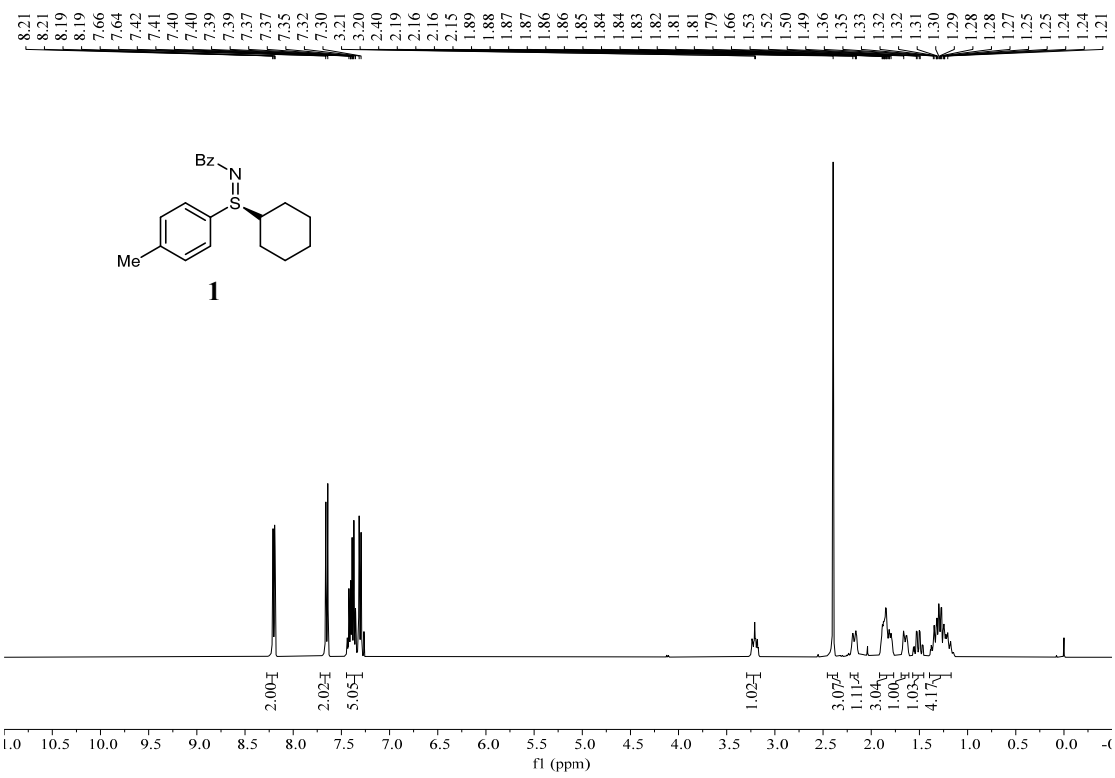
2.00
2.02
2.04
2.04
4.12
3.05
4.10
6.20
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

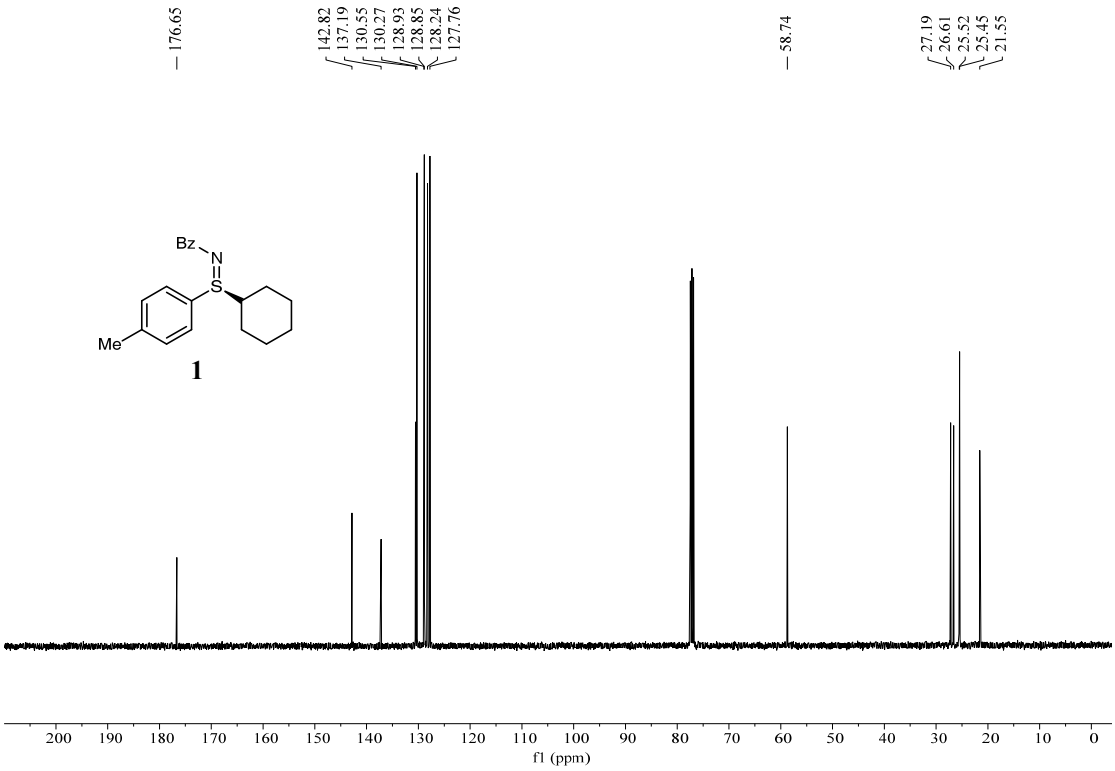

164.03
148.37
145.06
136.45
132.84
130.93
128.08
127.30
122.09
50.04
22.06
16.51
11.30

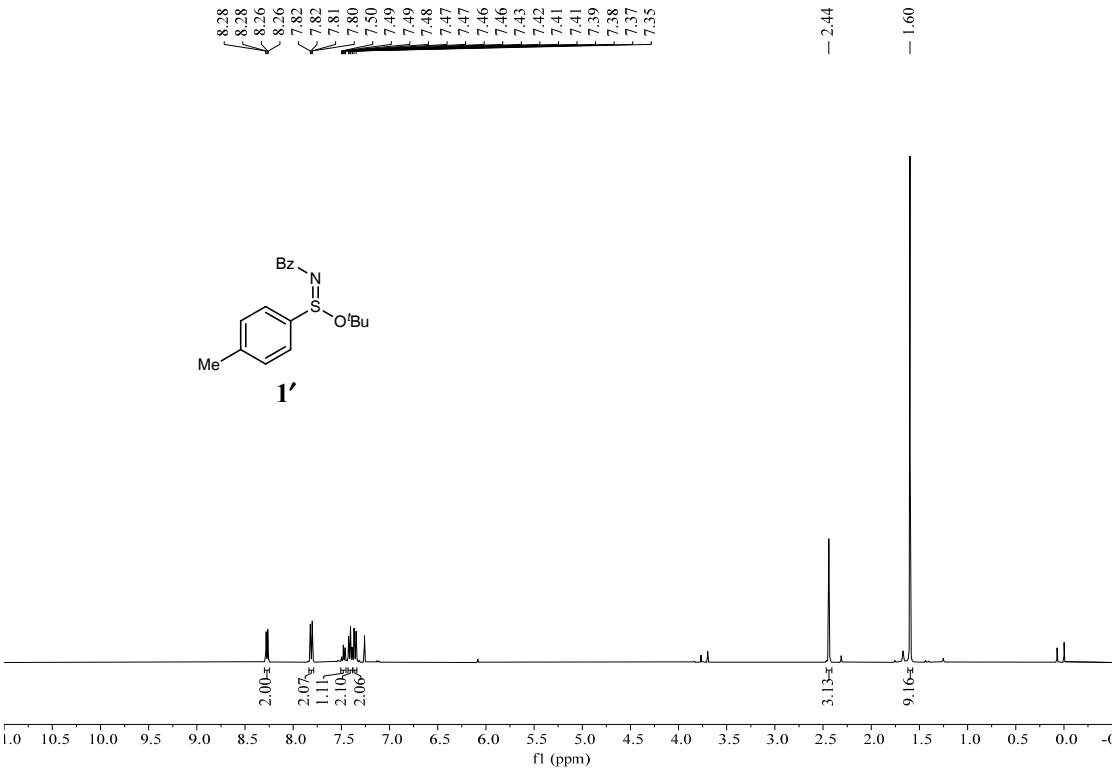

Me
S
O
O
Me
N
Me
S
O
O

C24

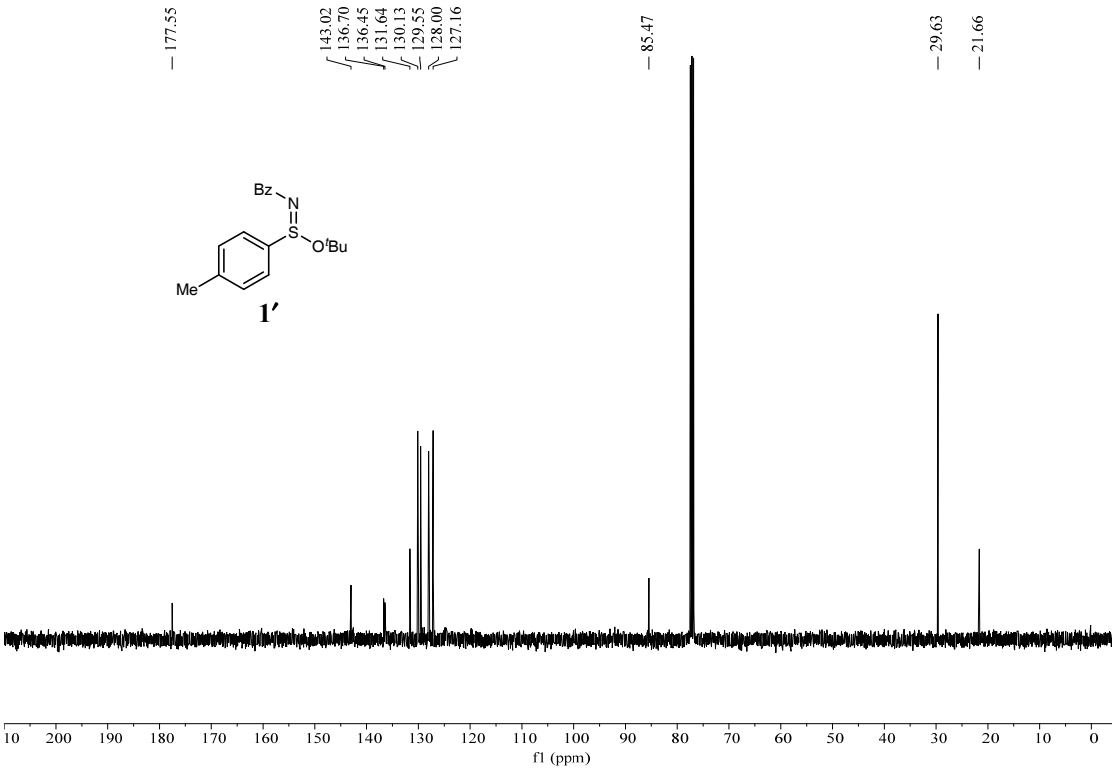
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.21
8.21
8.19
8.19
7.66
7.64
7.42
7.41
7.40
7.40
7.39
7.39
7.37
7.37
7.35
7.32
7.30
3.21
3.20
2.40
2.19
2.16
2.16
2.15
1.89
1.88
1.87
1.87
1.86
1.86
1.85
1.84
1.84
1.83
1.82
1.81
1.81
1.79
1.66
1.53
1.52
1.50
1.49
1.36
1.35
1.33
1.32
1.32
1.31
1.30
1.29
1.28
1.28
1.27
1.25
1.25
1.24
1.24
1.21
Bz
N
S
Me
1
2.00
2.02
5.05
1.02
3.07
1.11
3.04
1.00
1.03
4.17
f1 (ppm)

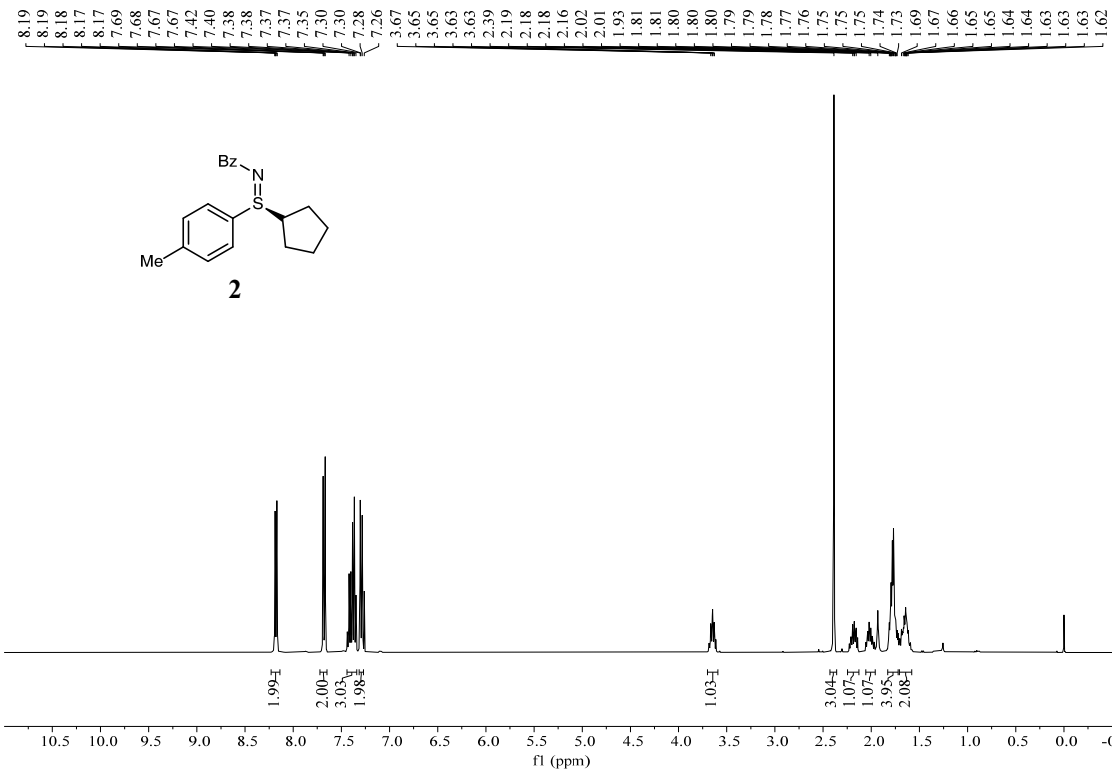

176.65
142.82
137.19
130.55
130.27
128.93
128.85
128.24
127.76
58.74
27.19
26.61
25.52
25.45
21.55
Bz
N
S
Me
1
f1 (ppm)

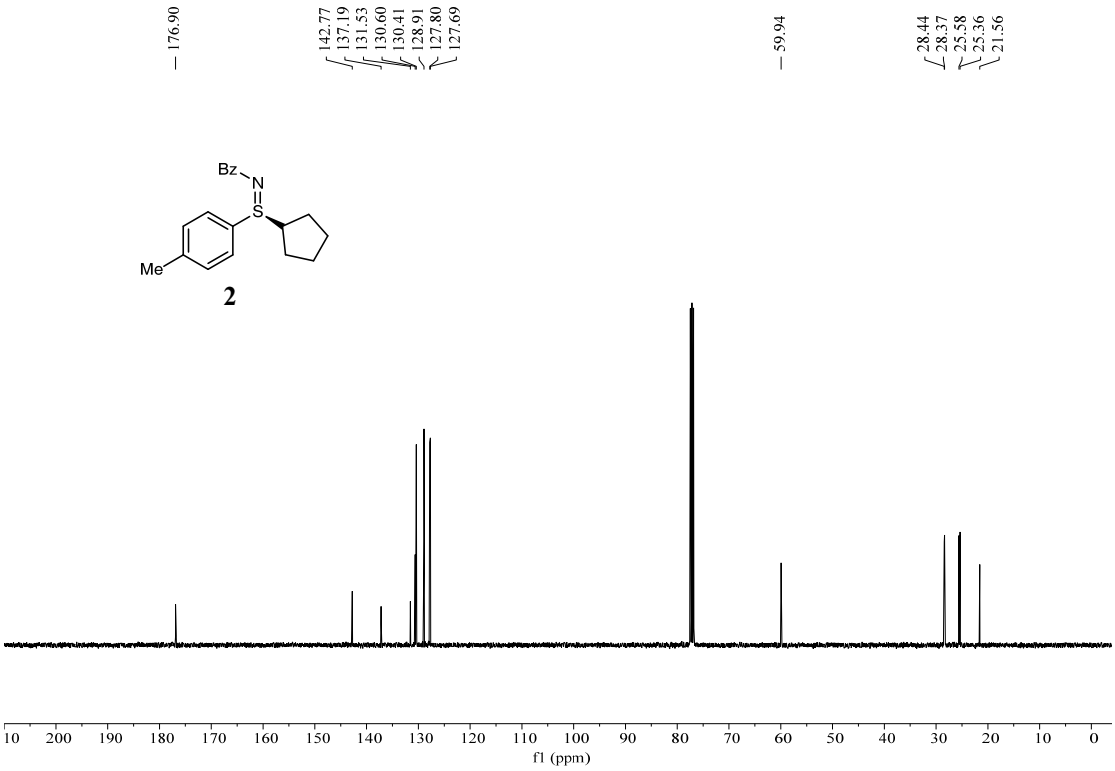

8.28
8.28
8.26
8.26
7.82
7.82
7.81
7.80
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.43
7.42
7.41
7.41
7.39
7.38
7.37
7.35
2.44
1.60
Bz
N
S
O^{t}Bu
Me
2.00
2.07
1.11
2.10
2.06
3.13
9.16
f1 (ppm)

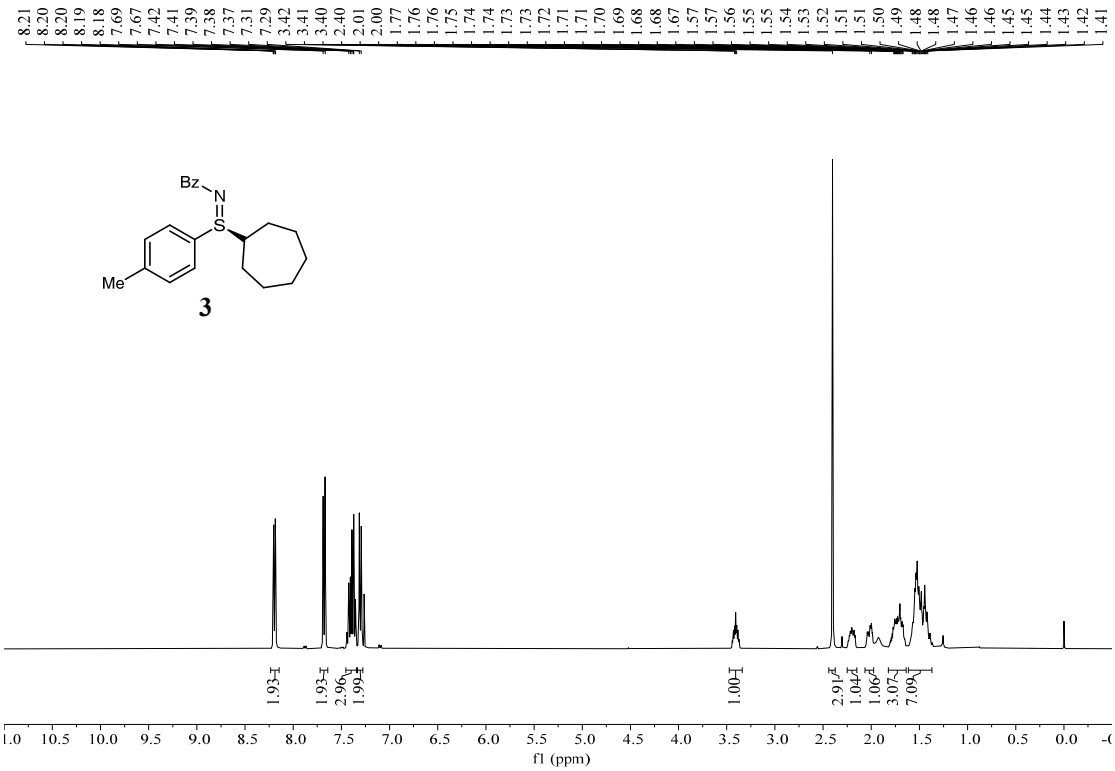
1′

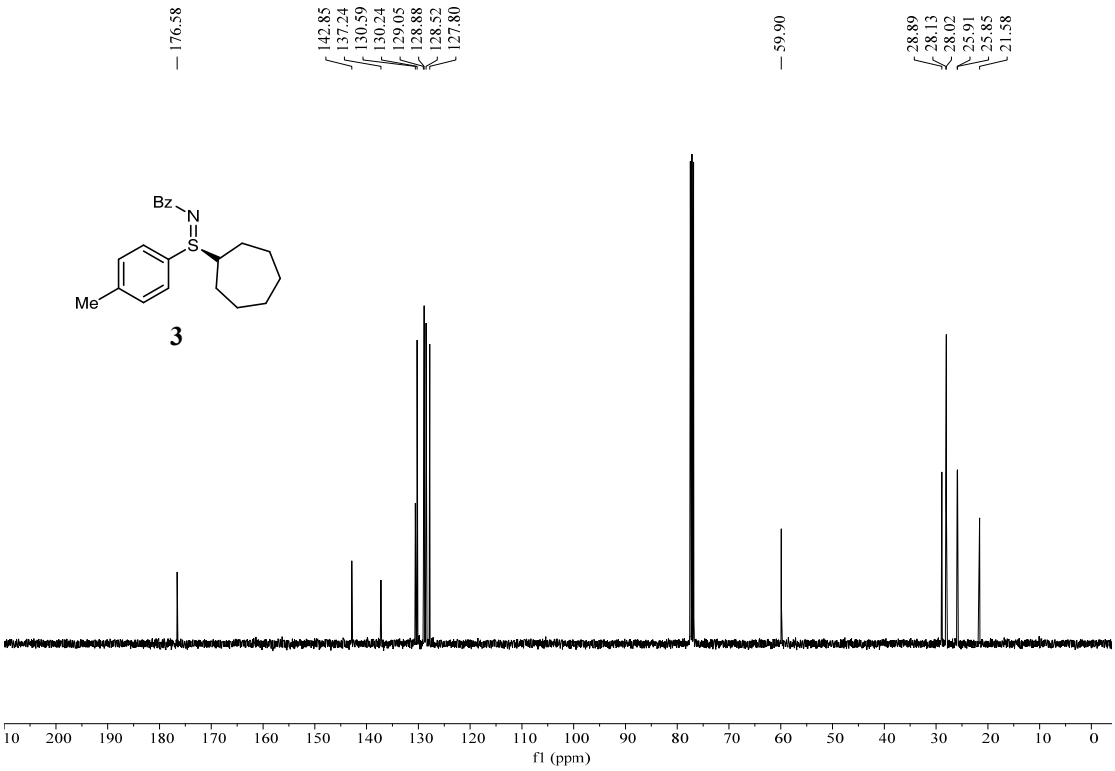

177.55
143.02
136.70
136.45
131.64
130.13
129.55
128.00
127.16
85.47
29.63
21.66
Bz
N
S
O^{t}Bu
Me
f1 (ppm)

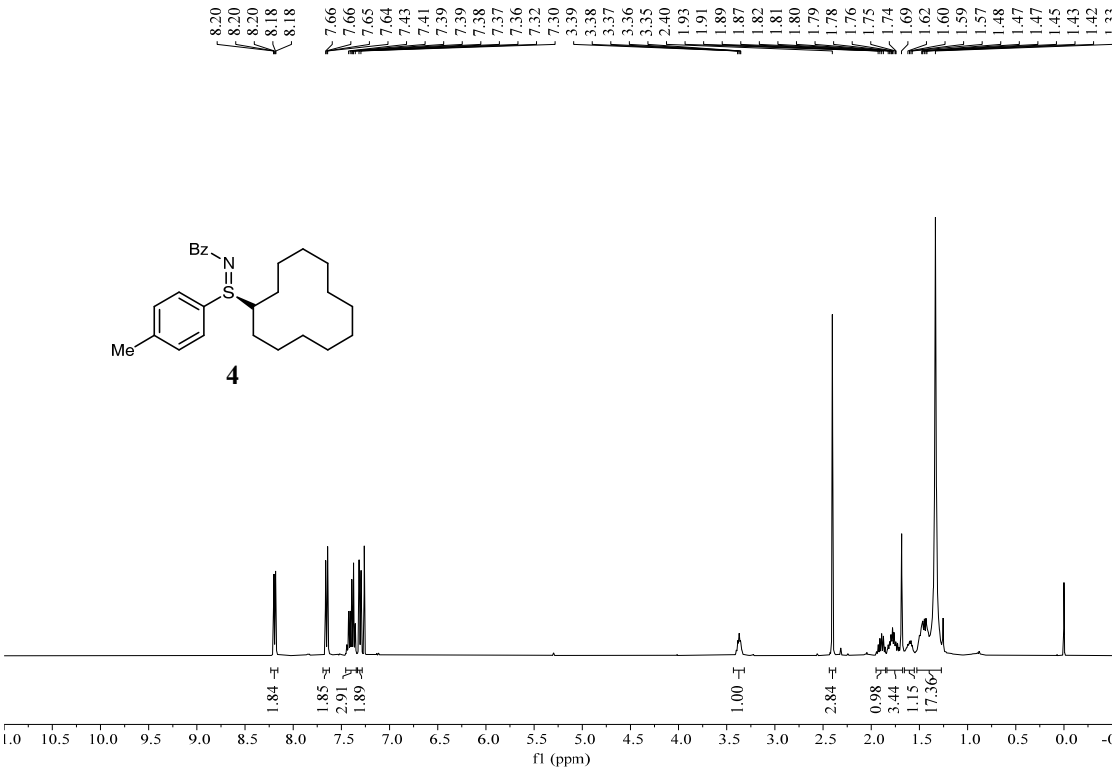
1′

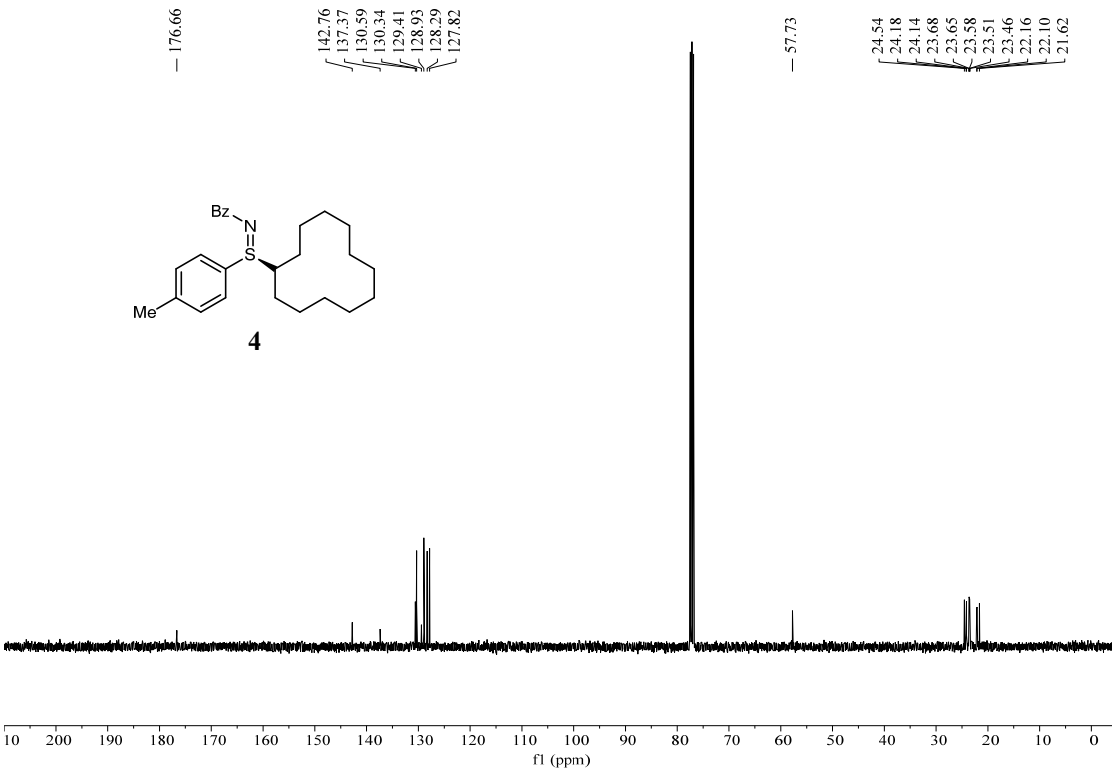

8.19
8.19
8.18
8.17
8.17
7.69
7.68
7.67
7.67
7.42
7.40
7.38
7.38
7.37
7.37
7.35
7.30
7.30
7.28
7.26
3.67
3.65
3.65
3.63
3.63
2.39
2.19
2.18
2.18
2.16
2.02
2.01
1.93
1.81
1.81
1.80
1.80
1.80
1.79
1.79
1.78
1.77
1.76
1.75
1.75
1.75
1.74
1.73
1.69
1.67
1.66
1.65
1.65
1.64
1.64
1.63
1.63
1.63
1.62
Bz
N
S
Me
2
1.99
2.00
3.03
1.98
1.03
3.04
1.07
1.07
3.95
2.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

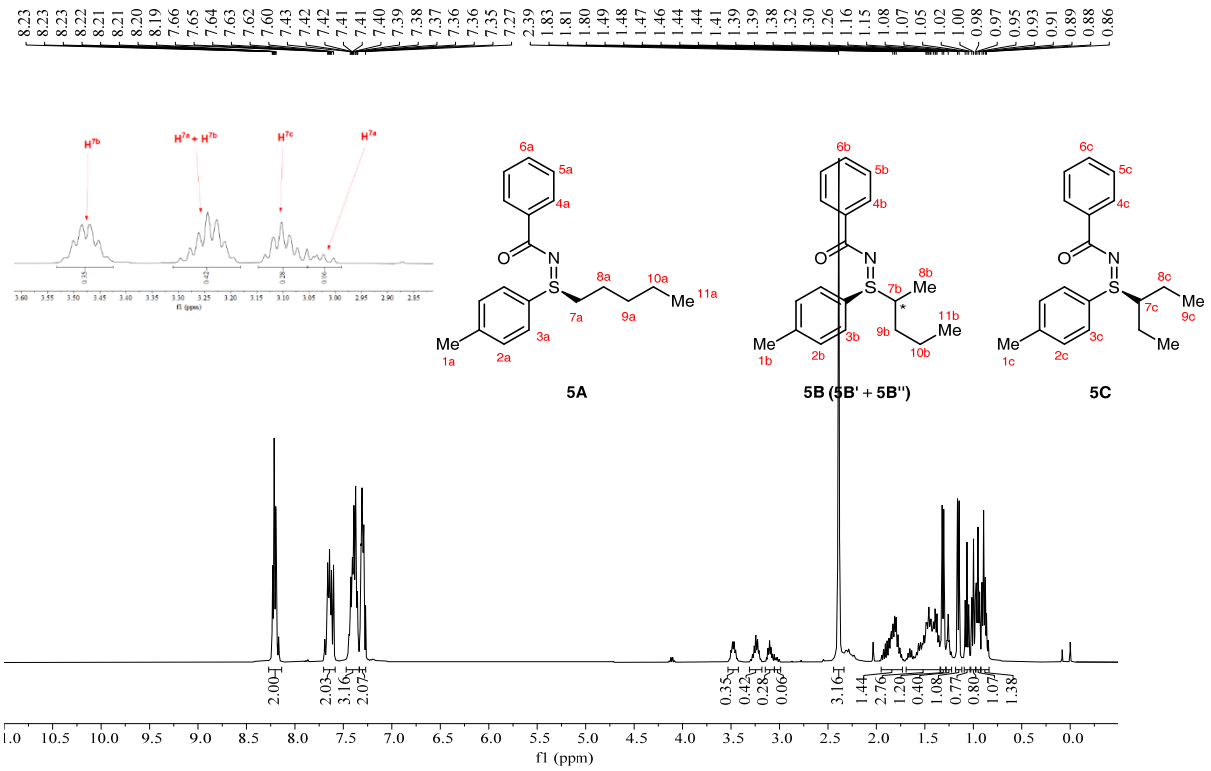

176.90
142.77
137.19
131.53
130.60
130.41
128.91
127.80
127.69
59.94
28.44
28.37
25.58
25.36
21.56
Bz
N
S
Me
2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

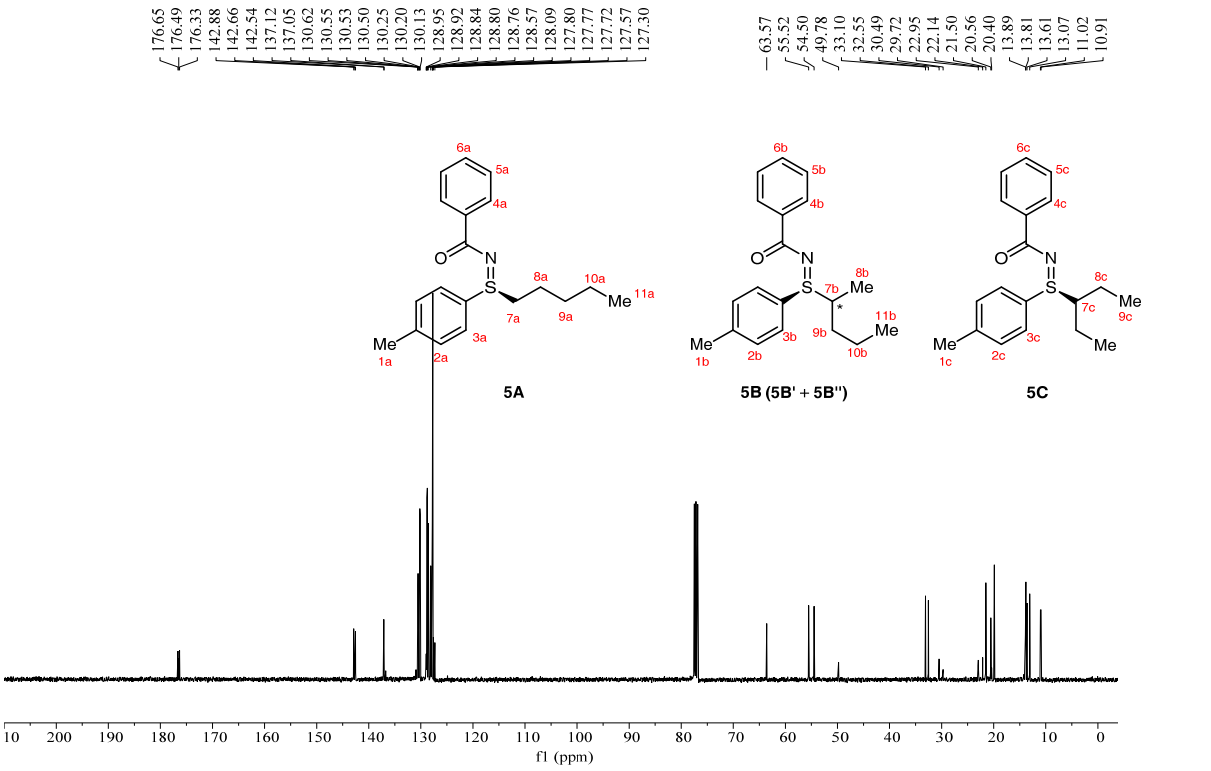

8.21
8.20
8.20
8.19
8.18
7.69
7.67
7.42
7.41
7.39
7.38
7.37
7.31
7.29
3.42
3.41
3.40
2.40
2.01
2.00
1.77
1.76
1.76
1.75
1.74
1.74
1.73
1.73
1.72
1.71
1.71
1.70
1.69
1.68
1.68
1.67
1.57
1.57
1.56
1.55
1.55
1.54
1.53
1.52
1.51
1.51
1.50
1.49
1.48
1.48
1.47
1.46
1.46
1.45
1.44
1.43
1.42
1.41
Bz
N
S
Me
3
1.93
1.93
2.96
1.99
1.00
2.91
1.04
1.06
3.07
7.09
f1 (ppm)

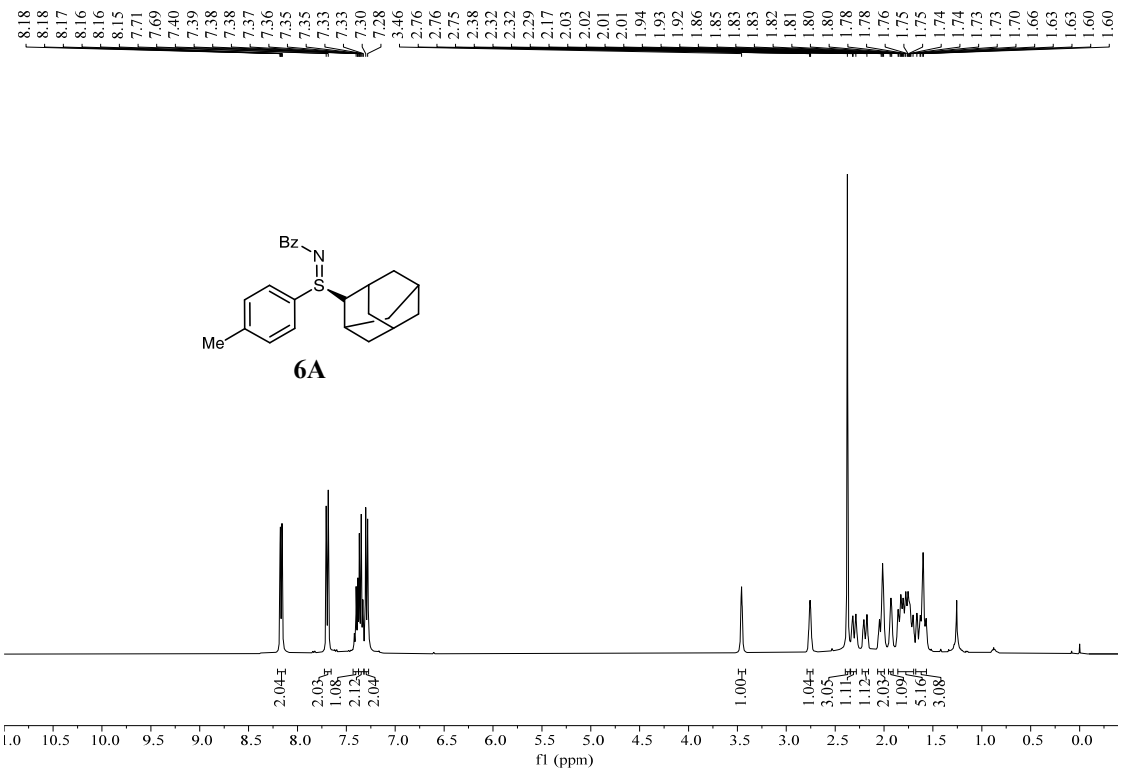

176.58
142.85
137.24
130.59
130.24
129.05
128.88
128.52
127.80
59.90
28.89
28.13
28.02
25.91
25.85
21.58
Bz
N
S
Me
3
f1 (ppm)


8.20
8.20
8.20
8.18
8.18
7.66
7.66
7.65
7.64
7.43
7.41
7.39
7.39
7.38
7.37
7.36
7.32
7.30
3.39
3.38
3.37
3.36
3.35
2.40
1.93
1.91
1.89
1.87
1.82
1.81
1.80
1.79
1.78
1.76
1.75
1.74
1.69
1.62
1.60
1.59
1.57
1.48
1.47
1.47
1.45
1.43
1.42
Bz
N
S
Me
4
1.84
1.85
2.91
1.89
1.00
2.84
0.98
3.44
1.15
17.36
f1 (ppm)

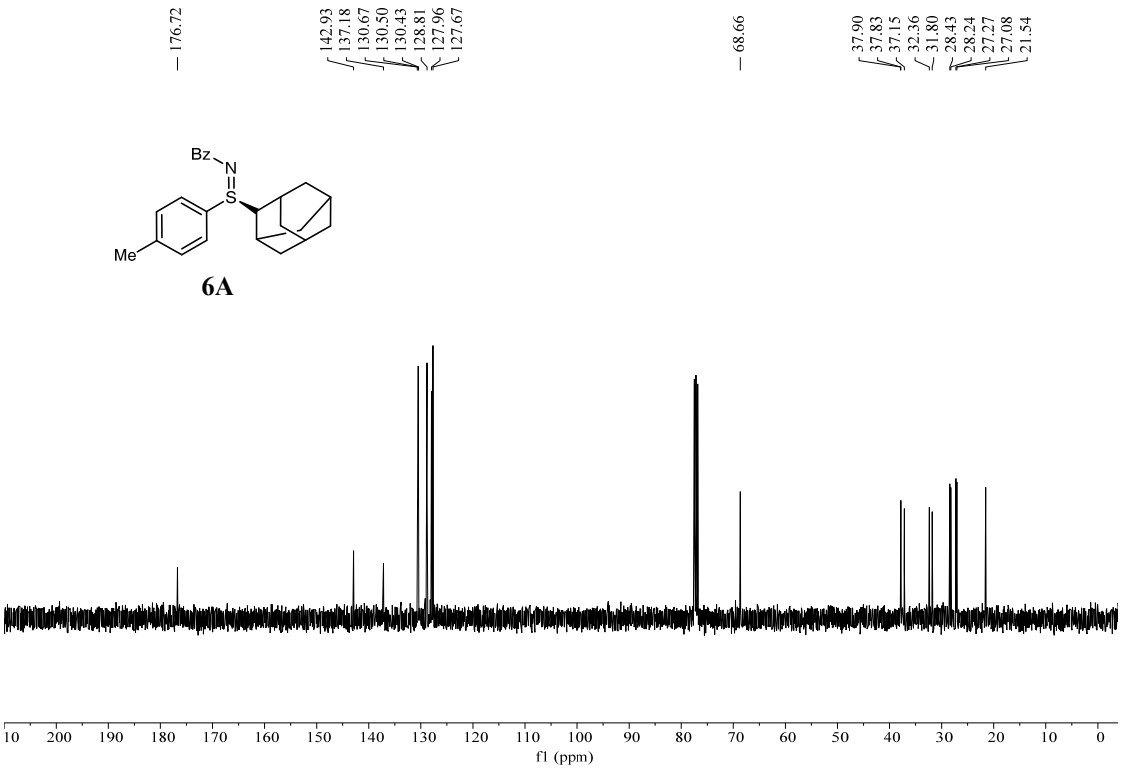

176.66
142.76
137.37
130.59
130.34
129.41
128.93
128.29
127.82
57.73
24.54
24.18
24.14
23.68
23.65
23.58
23.51
23.46
22.16
22.10
21.62
Bz
N
S
Me
4
f1 (ppm)


5A
5B (5B' + 5B'')
5C
f1 (ppm)

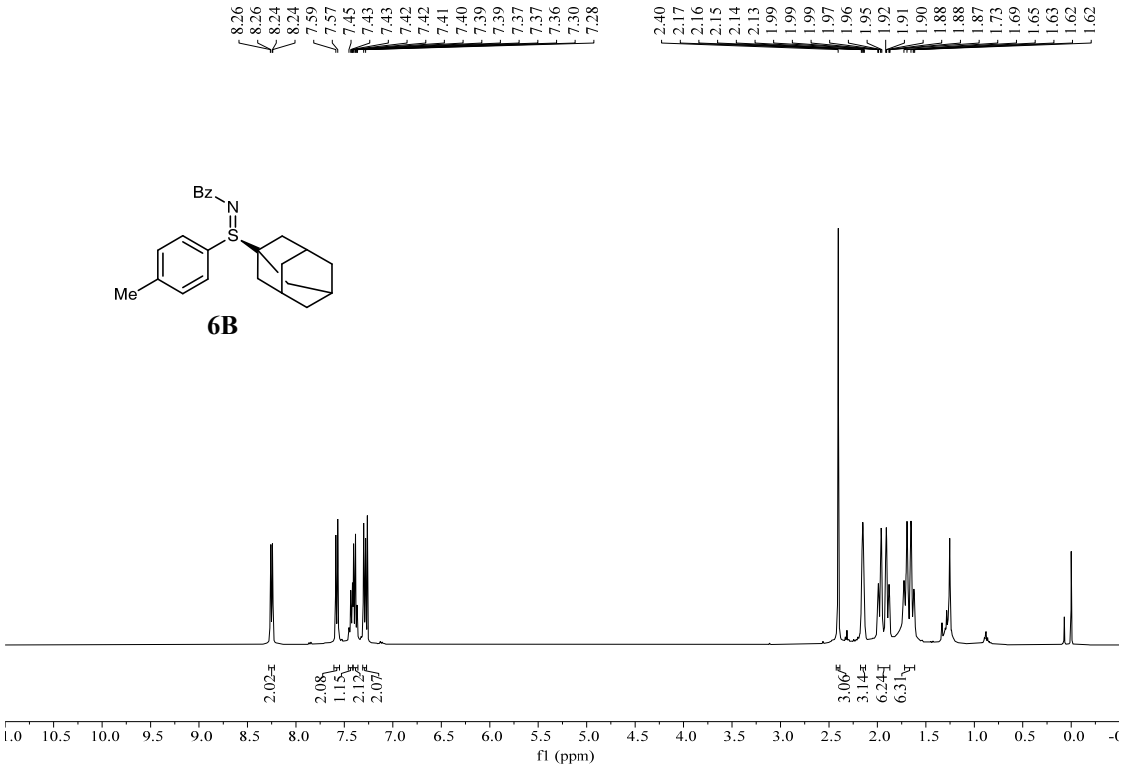

5A
5B (5B' + 5B'')
5C
f1 (ppm)


8.18 8.18 8.17 8.16 8.16 8.15 7.71 7.69 7.40 7.39 7.38 7.38 7.37 7.36 7.35 7.35 7.33 7.33 7.30 7.28 3.46 2.76 2.76 2.75 2.38 2.32 2.32 2.29 2.17 2.03 2.02 2.01 2.01 1.94 1.93 1.92 1.86 1.85 1.83 1.83 1.82 1.81 1.80 1.80 1.78 1.78 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.70 1.66 1.63 1.63 1.60 1.60
Bz
N
S
Me
2.04 2.03 1.08 2.12 2.04 1.00 1.04 3.05 1.11 1.12 2.03 1.09 5.16 3.08
fl (ppm)

6A


176.72
142.93 137.18 130.67 130.50 130.43 128.81 127.96 127.67
68.66
37.90 37.83 37.15 32.36 31.80 28.43 28.24 27.27 27.08 21.54
Bz
N
S
Me
fl (ppm)

6A


8.26
8.26
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8.24
7.59
7.57
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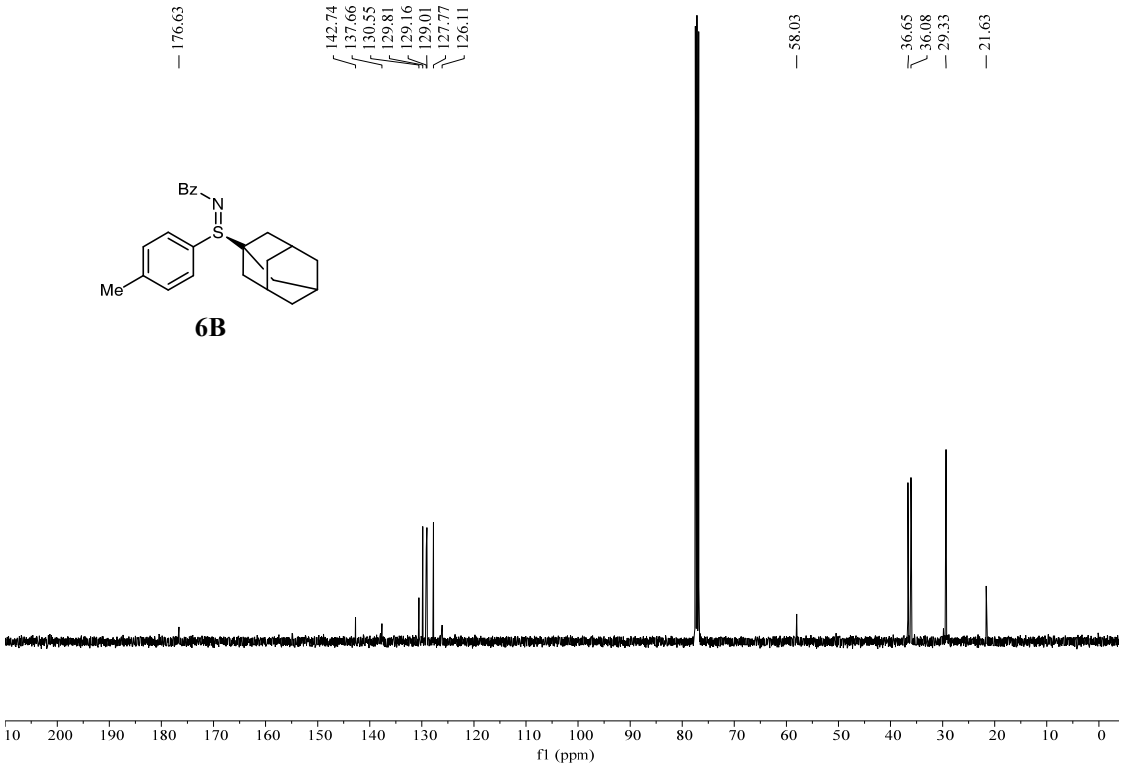
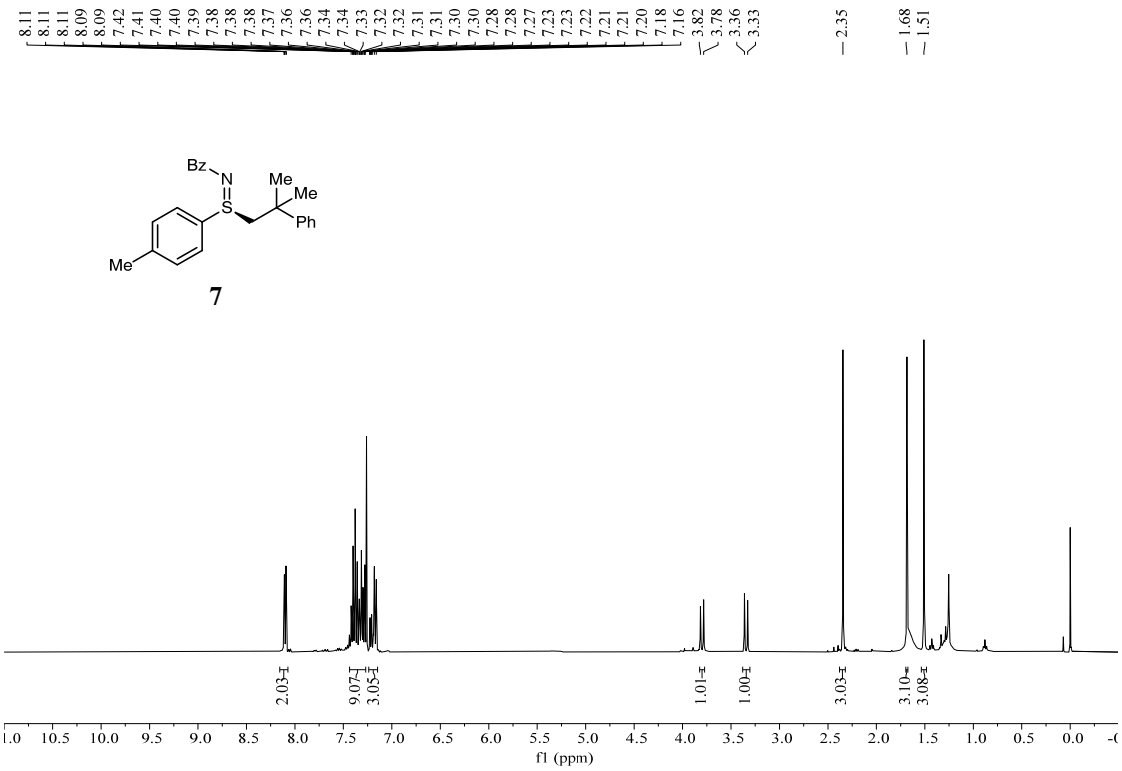
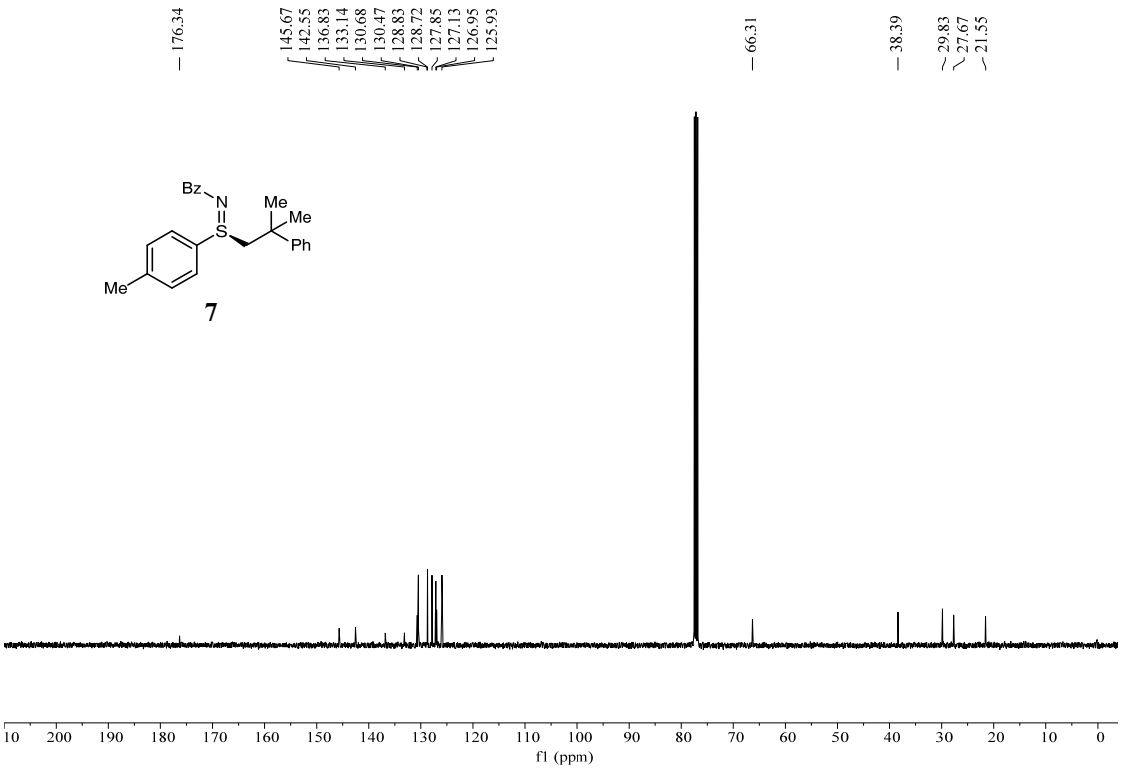
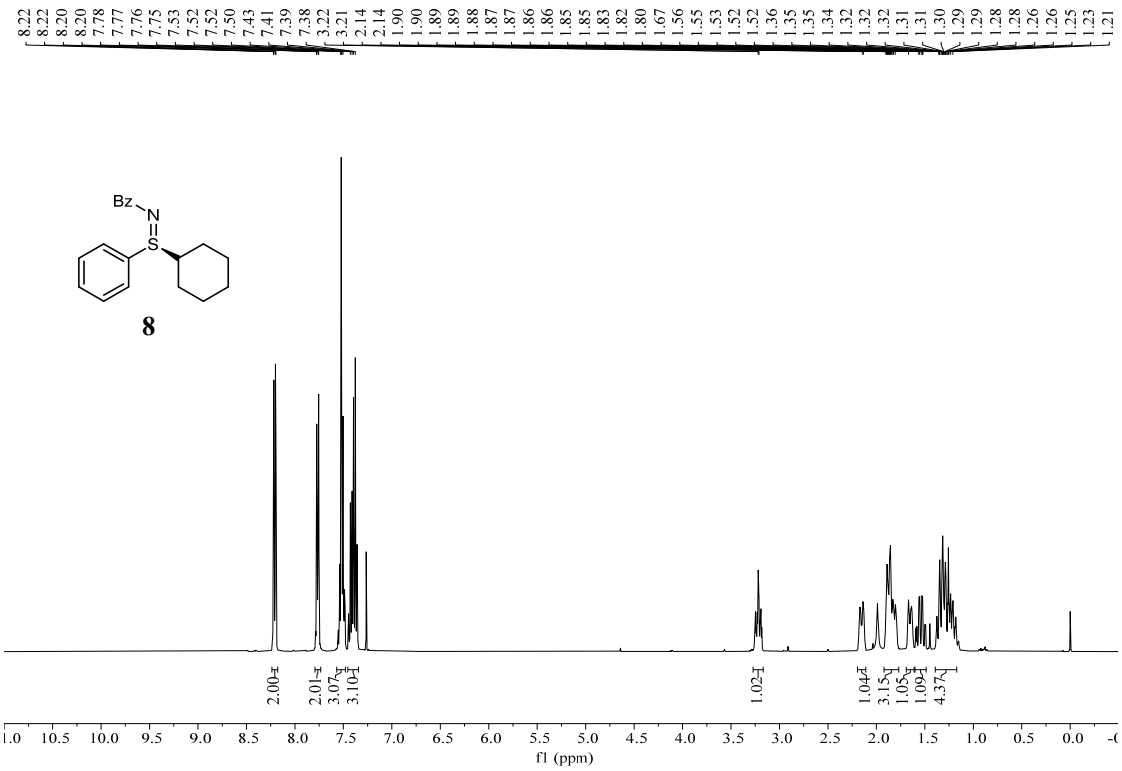
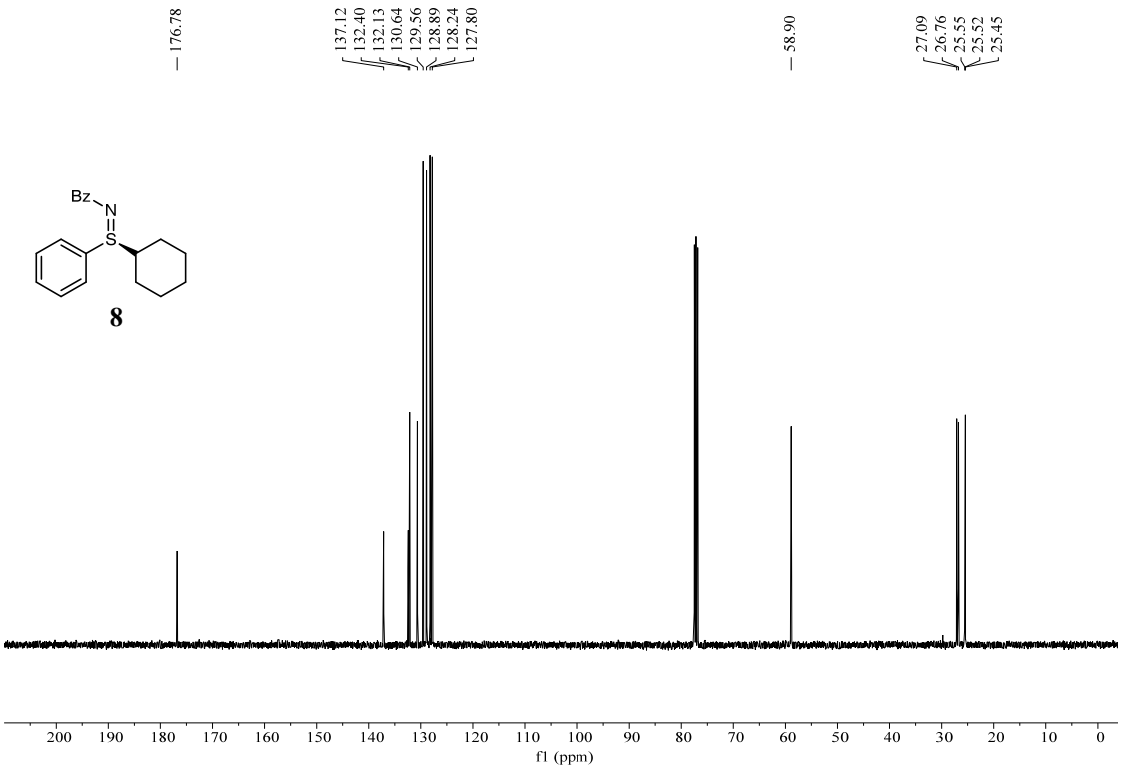
7.43
7.43
7.42
7.42
7.41
7.40
7.39
7.39
7.37
7.37
7.36
7.30
7.28
2.40
2.17
2.16
2.15
2.14
2.13
1.99
1.99
1.99
1.97
1.96
1.95
1.92
1.91
1.90
1.88
1.88
1.87
1.73
1.69
1.65
1.63
1.62
1.62
Bz
N
S
Me
6B
2.02
2.08
1.15
2.12
2.07
3.06
3.14
6.24
6.31
f1 (ppm)

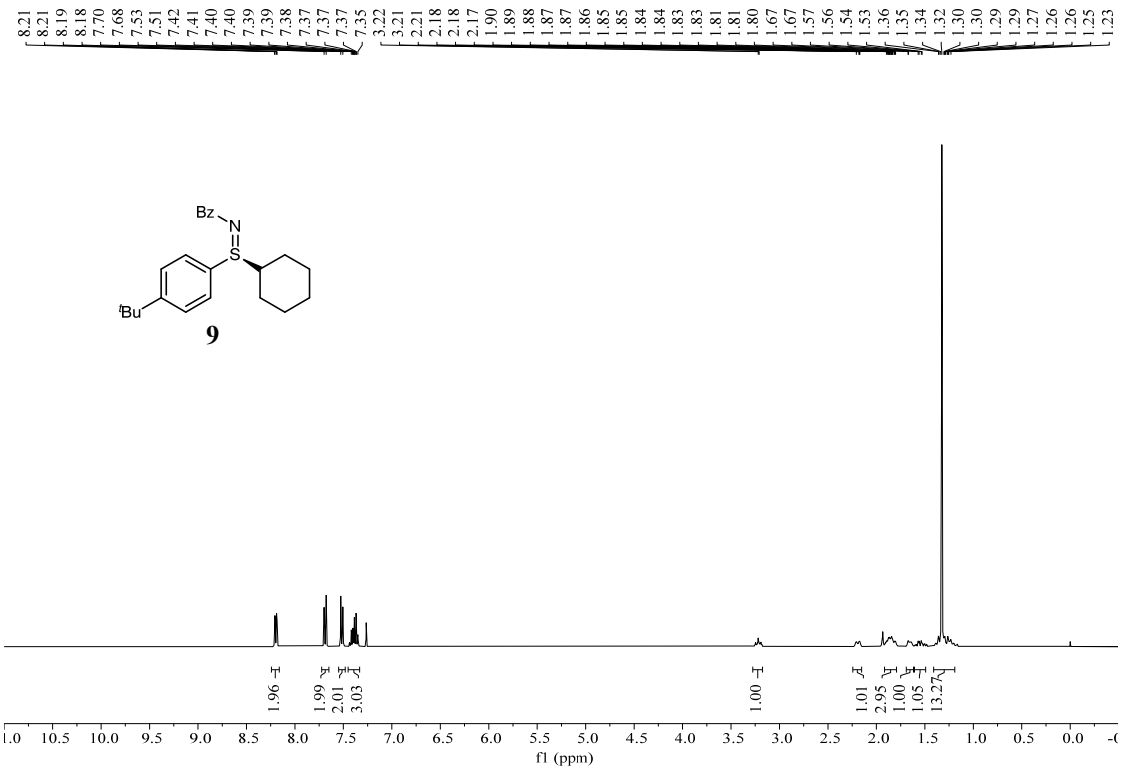

176.63
142.74
137.66
130.55
129.81
129.16
129.01
127.77
126.11
58.03
36.65
36.08
29.33
21.63
Bz
N
S
Me
6B
f1 (ppm)


8.11
8.11
8.11
8.09
8.09
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.36
7.36
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.28
7.28
7.27
7.23
7.23
7.22
7.21
7.21
7.20
7.18
7.16
3.82
3.78
3.36
3.33
2.35
1.68
1.51
Bz
N
S
Me
Me
Ph
Me
7
2.03
9.07
3.05
1.01
1.00
3.03
3.10
3.08
fl (ppm)


176.34
145.67
142.55
136.83
133.14
130.68
130.47
128.83
128.72
127.85
127.13
126.95
125.93
66.31
38.39
29.83
27.67
21.55
Bz
N
S
Me
Me
Ph
Me
7
fl (ppm)


8.22 8.22 8.20 8.20 7.78 7.77 7.76 7.75 7.53 7.52 7.52 7.50 7.43 7.41 7.39 7.38 3.22 3.21 2.14 2.14 1.90 1.90 1.89 1.89 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.83 1.82 1.80 1.67 1.56 1.55 1.53 1.52 1.52 1.36 1.35 1.35 1.34 1.32 1.32 1.32 1.31 1.31 1.30 1.29 1.29 1.28 1.28 1.26 1.26 1.25 1.23 1.21
Bz
N
S
8
2.00
2.01
3.07
3.10
1.02
1.04
3.15
1.05
1.09
4.37
f1 (ppm)


176.78
137.12 132.40 132.13 130.64 129.56 128.89 128.24 127.80
58.90
27.09 26.76 25.55 25.52 25.45
Bz
N
S
8
f1 (ppm)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Bz
N
S
tBu
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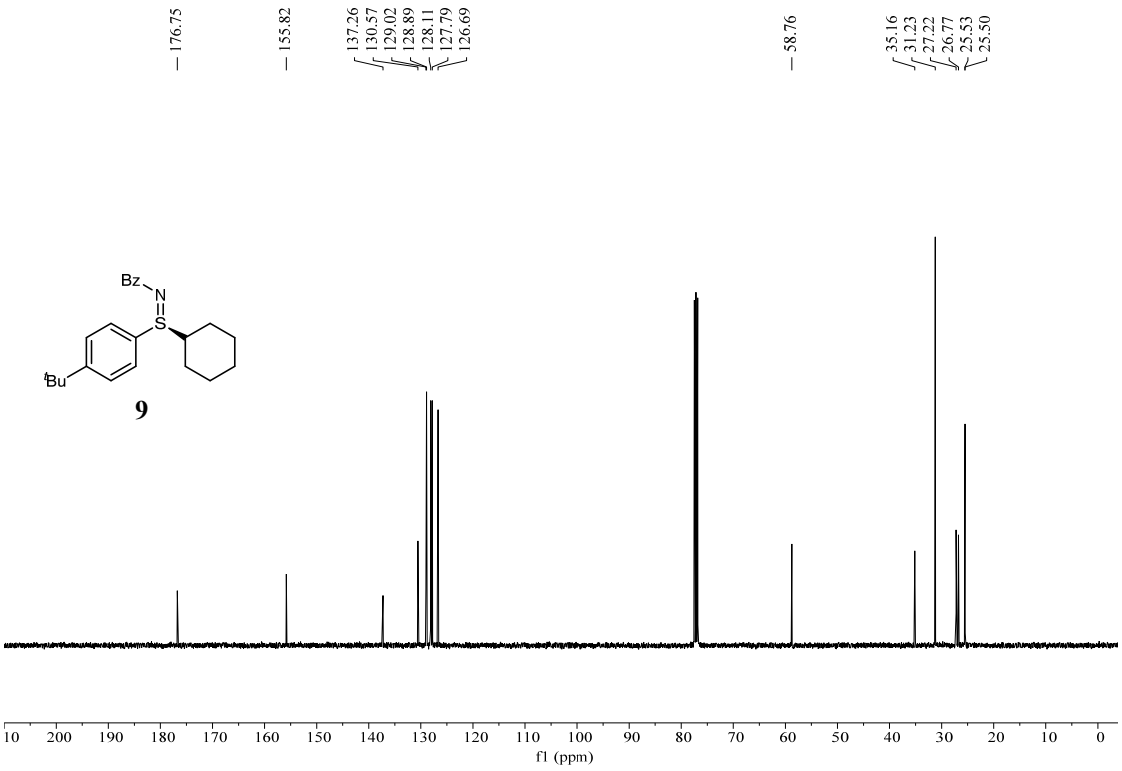
1.01
2.95
1.00
1.05
13.27
f1 (ppm)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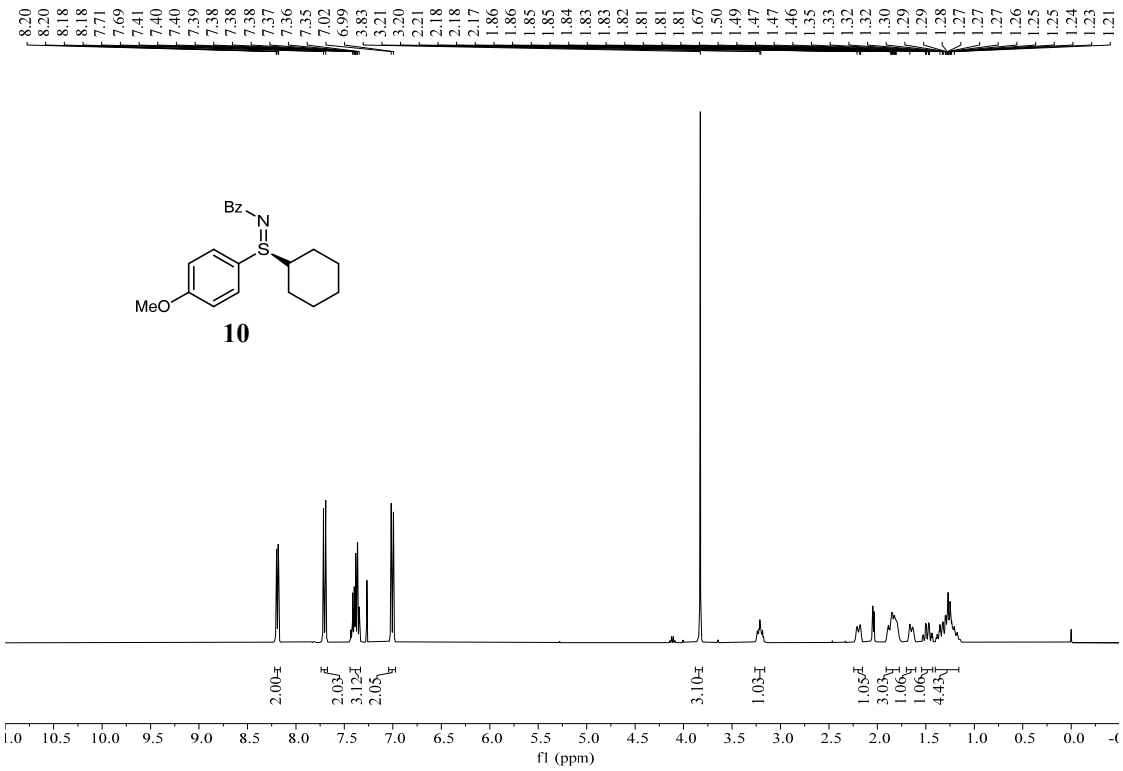
25.50
Bz
N
S
tBu
9
f1 (ppm)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7.35
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3.21
3.20
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2.18
2.18
2.17
1.86
1.86
1.85
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1.29
1.28
1.27
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1.27
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1.25
1.25
1.24
1.23
1.21
Bz
N
S
MeO
10
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1.05
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1.06
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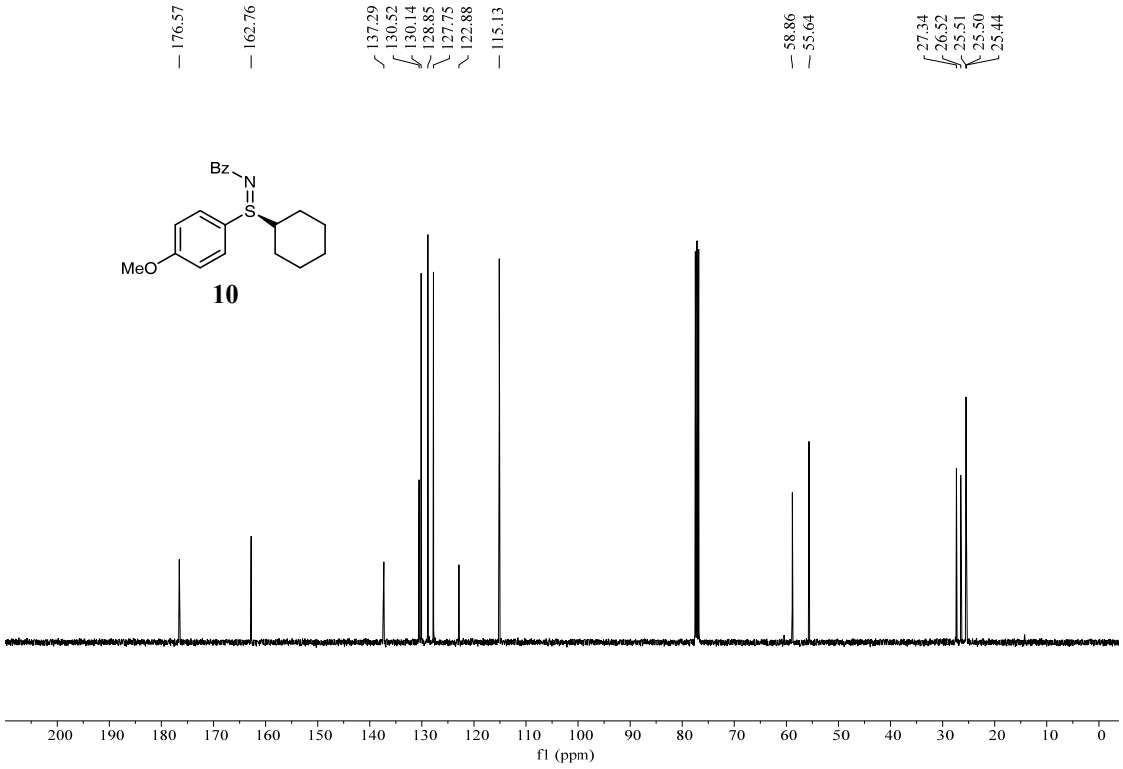
4.43
f1 (ppm)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25.50
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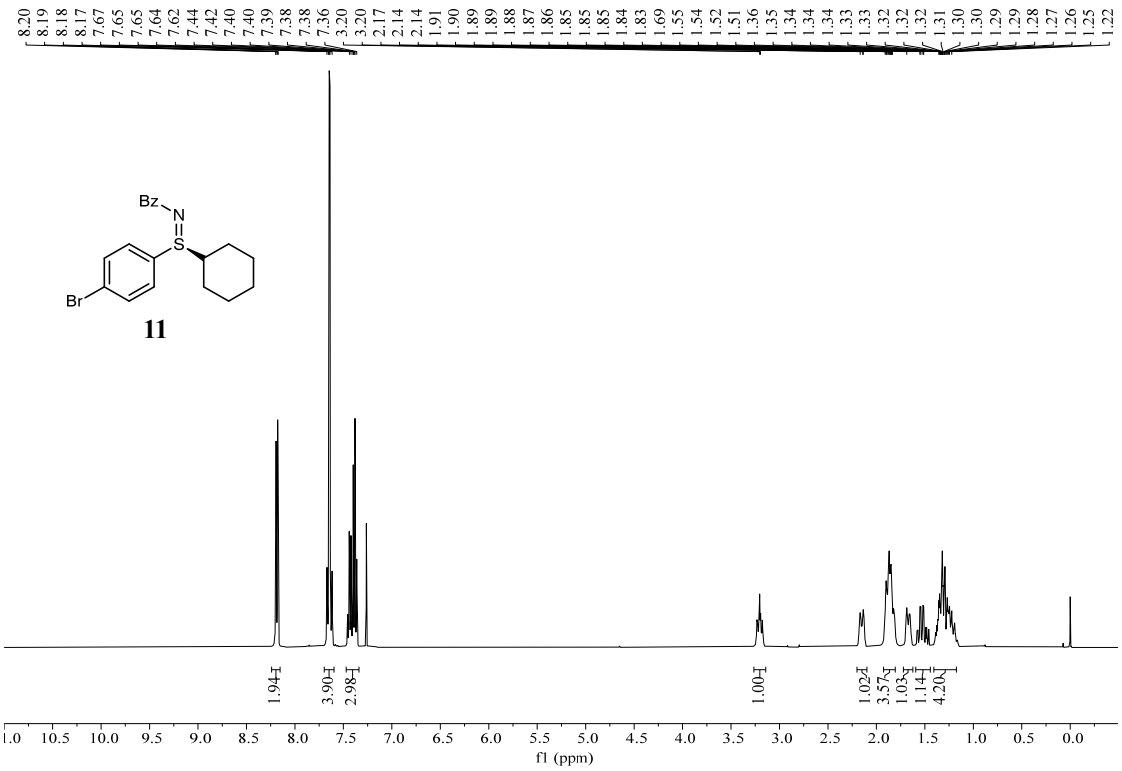
Bz
N
S
MeO
10
f1 (ppm)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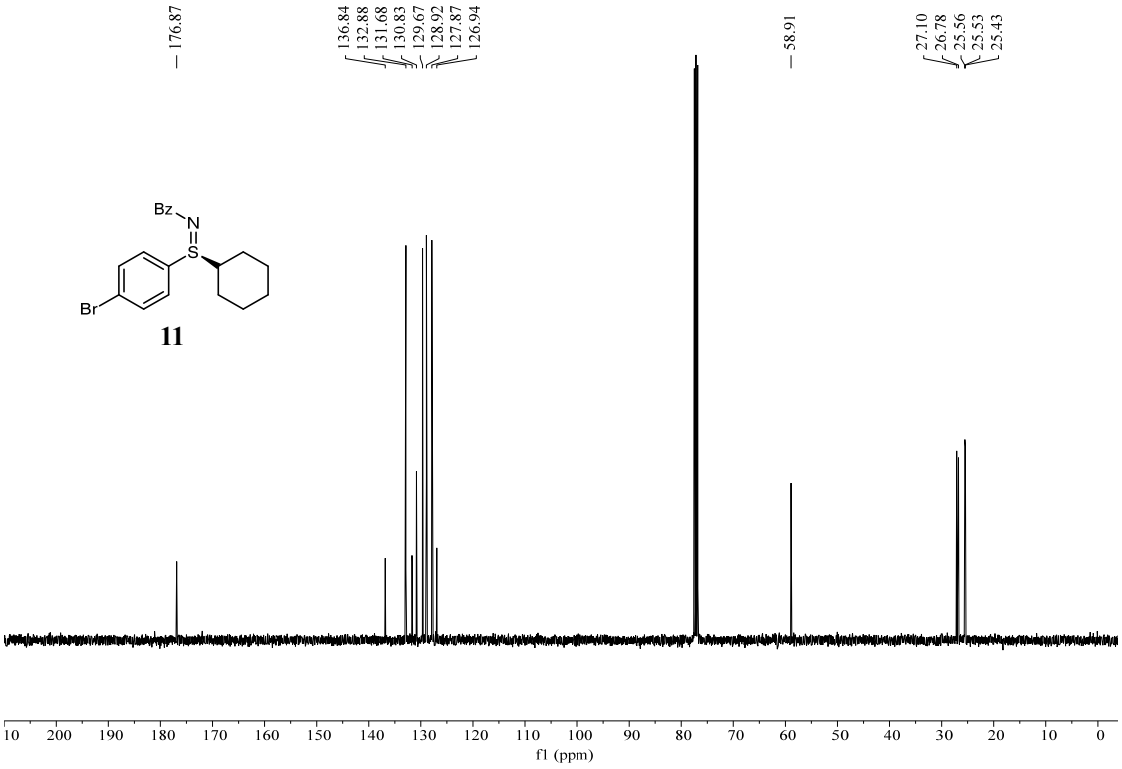
N
S
Br
11
1.94 3.90 2.98 1.00 1.02 3.57 1.03 1.14 4.20
f1 (ppm)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Bz
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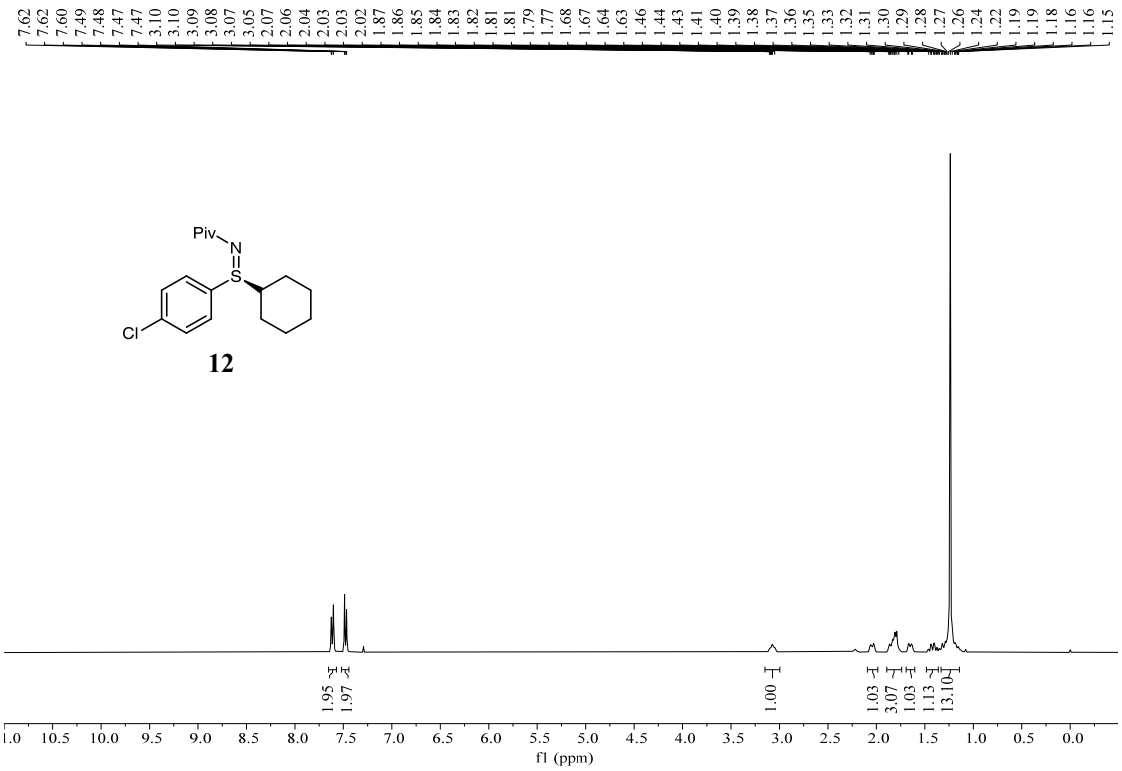
Br
11
f1 (ppm)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S
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12
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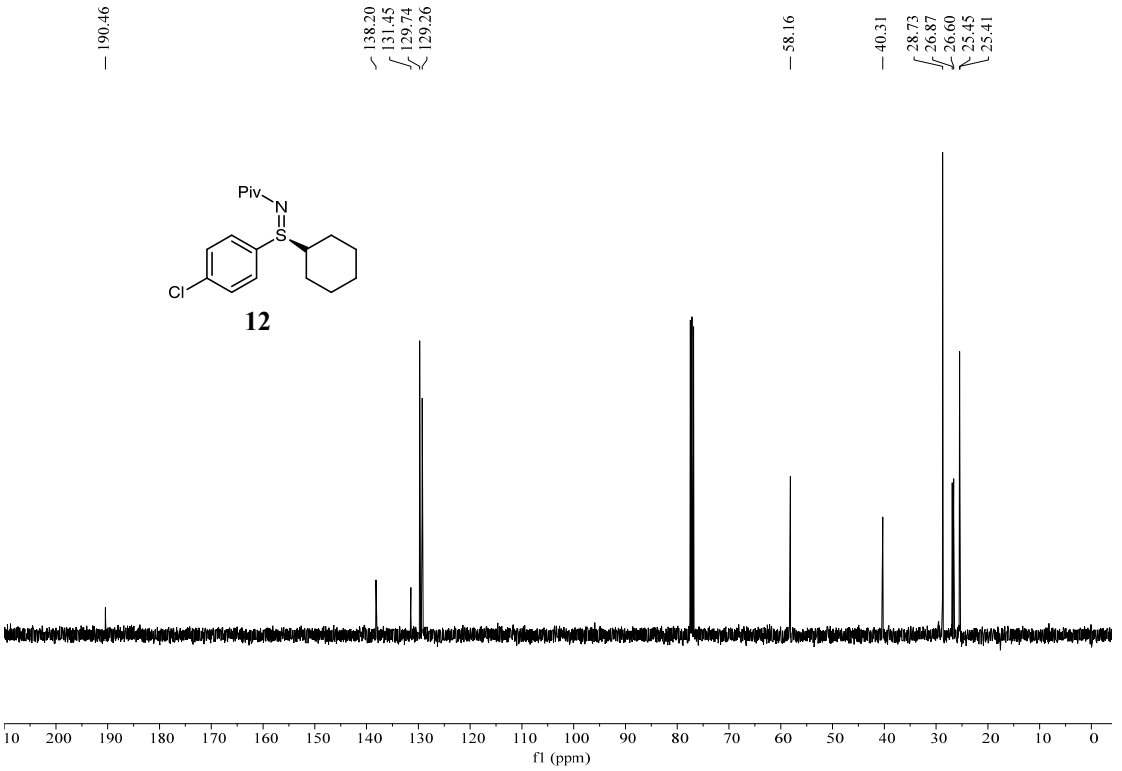
1.97
1.00
1.03
3.07
1.03
1.13
13.10
f1 (ppm)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Piv
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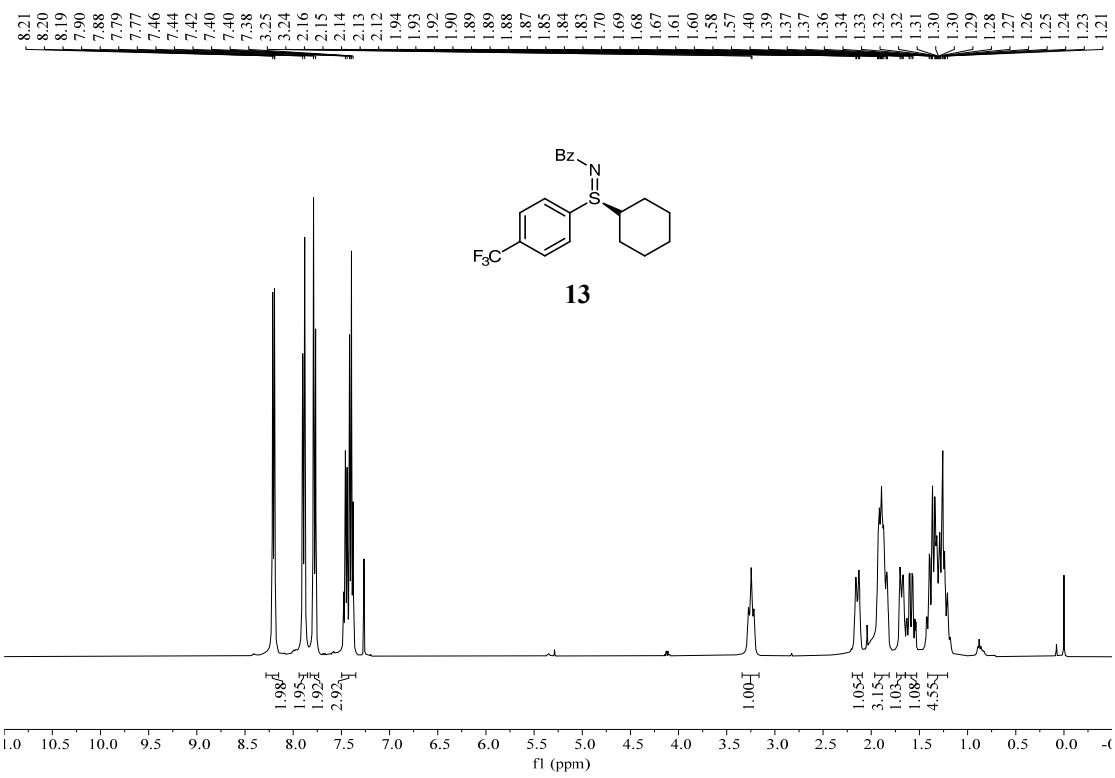
S
Cl
12
f1 (ppm)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1.33
1.32
1.32
1.31
1.30
1.30
1.29
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1.27
1.26
1.25
1.24
1.23
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Bz
N
S
F3C
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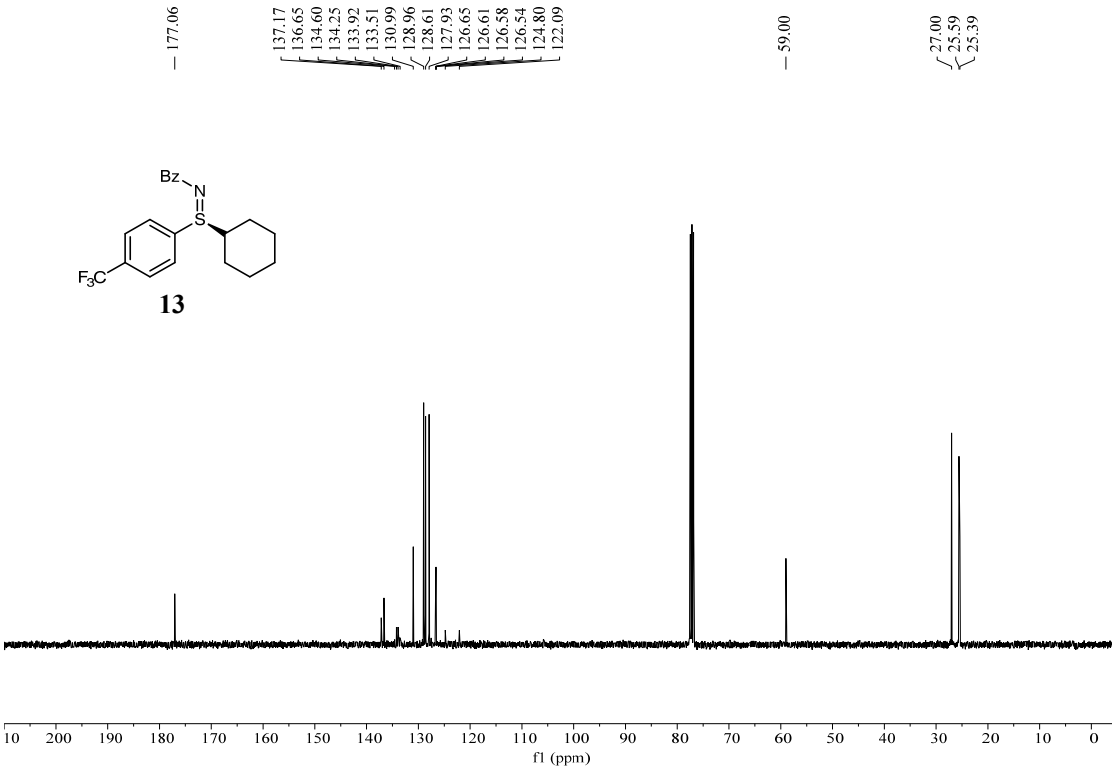
1.05
3.15
1.03
1.08
4.55
f1 (ppm)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126.58
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122.09
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27.00
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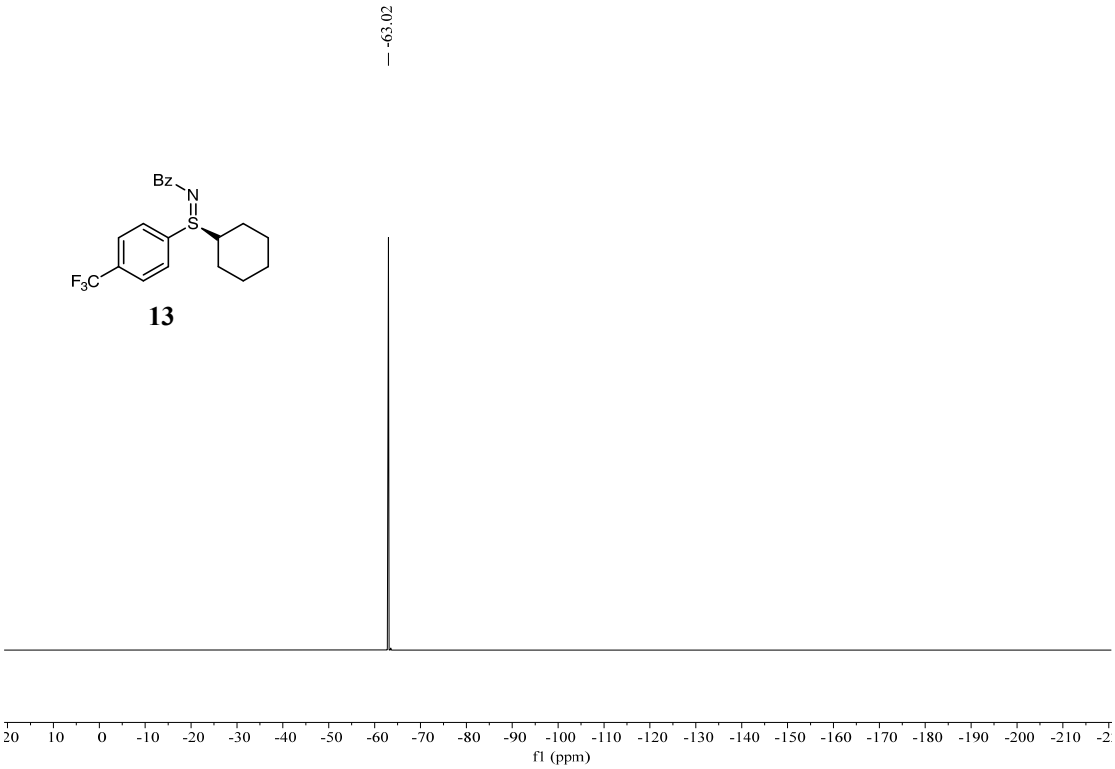
25.39
Bz
N
S
F3C
13
f1 (ppm)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Bz
N
S
F3C
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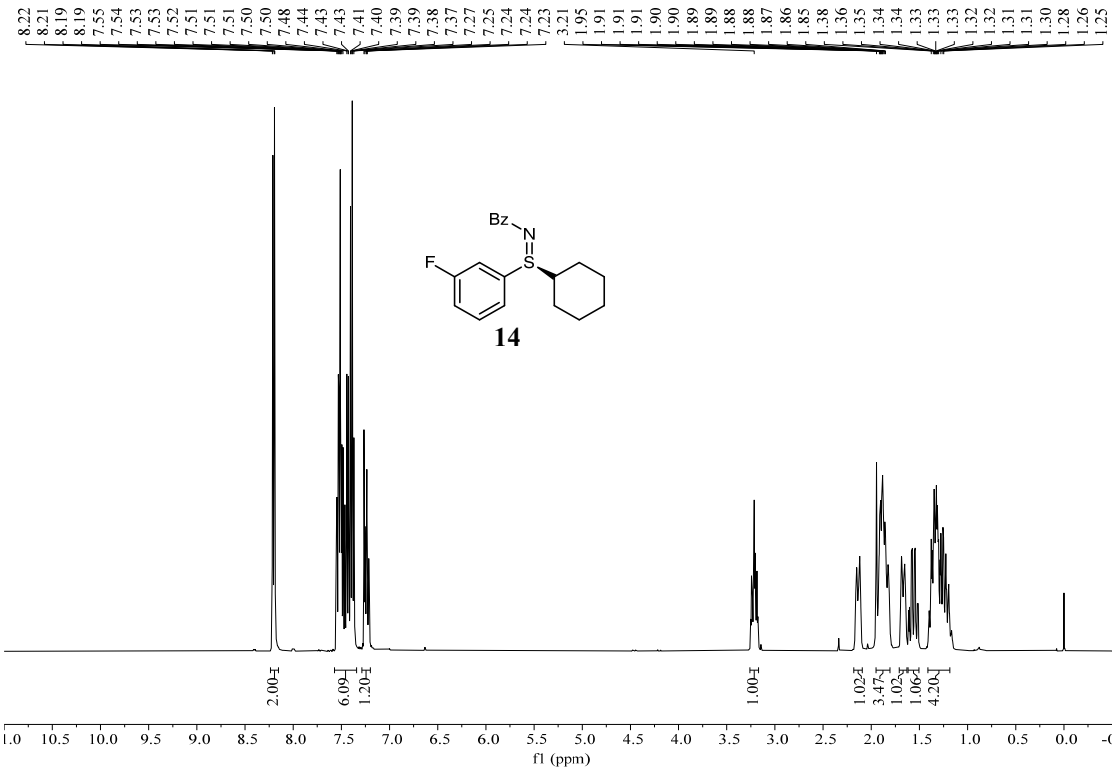
f1 (ppm)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1.32
1.31
1.31
1.30
1.28
1.26
1.25
Bz
N
S
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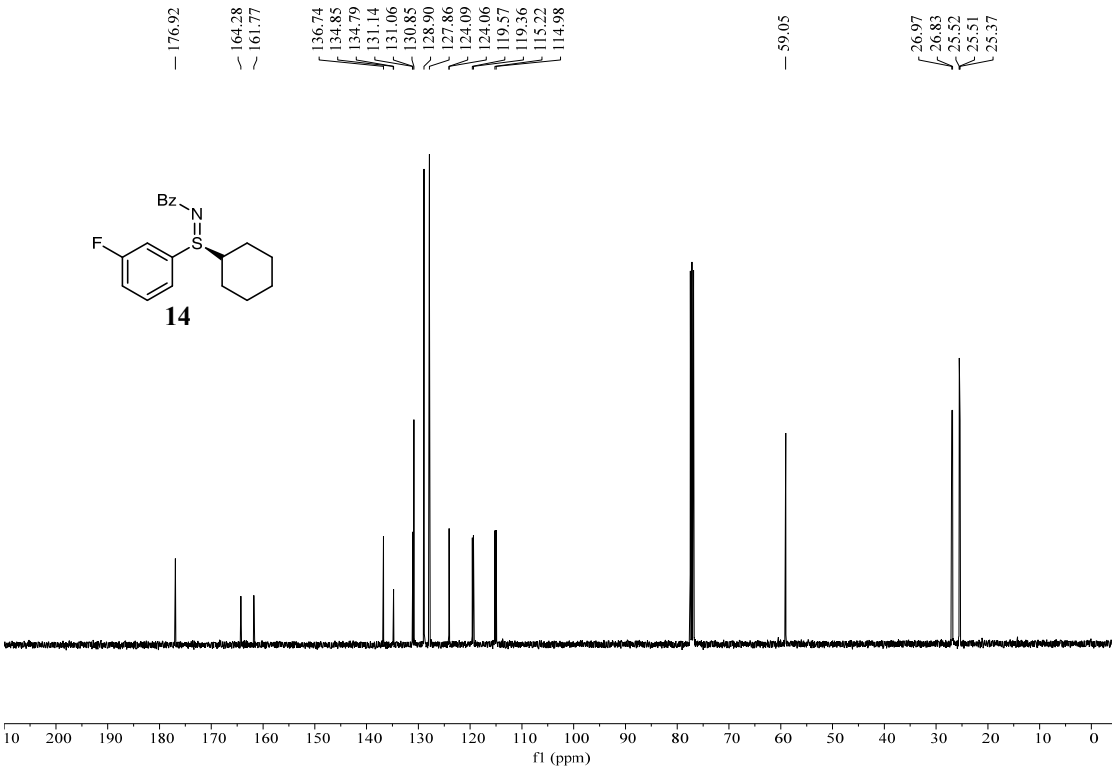
1.00
1.02
3.47
1.02
1.06
4.20
f1 (ppm)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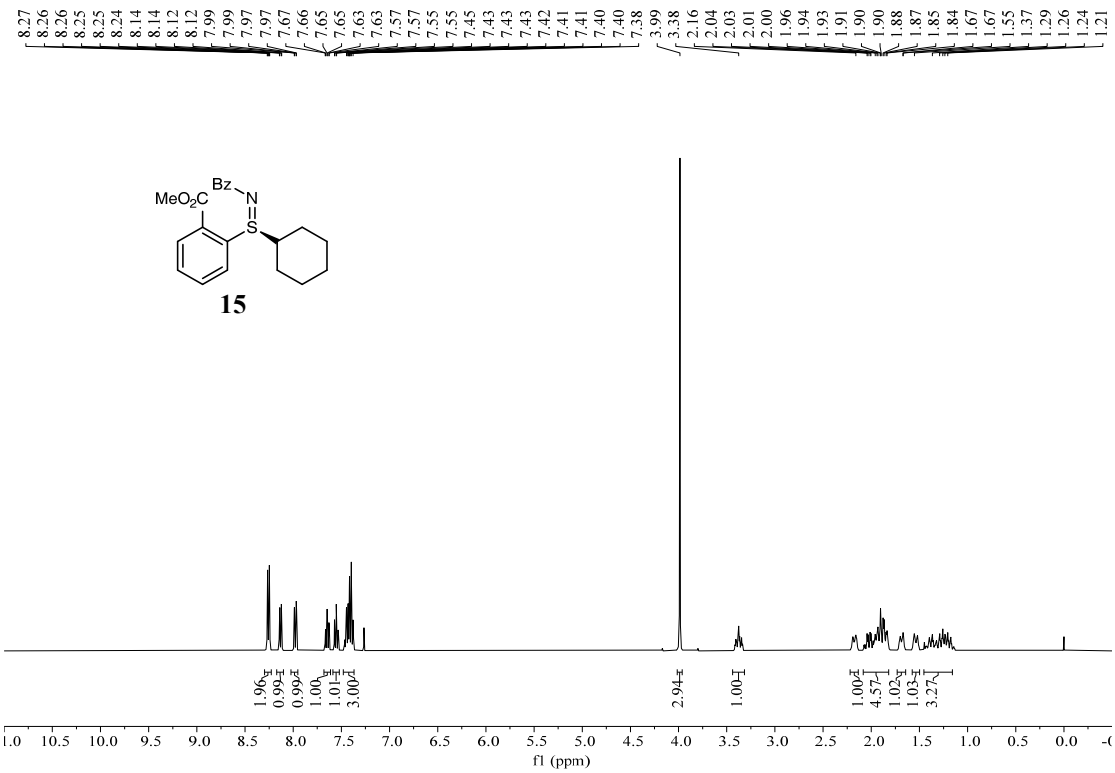
119.57
119.36
115.22
114.98
59.05
26.97
26.83
25.52
25.51
25.37
Bz
N
S
F
14
f1 (ppm)


-108.92
Bz
N
S
F
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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MeO2C
Bz
N
S
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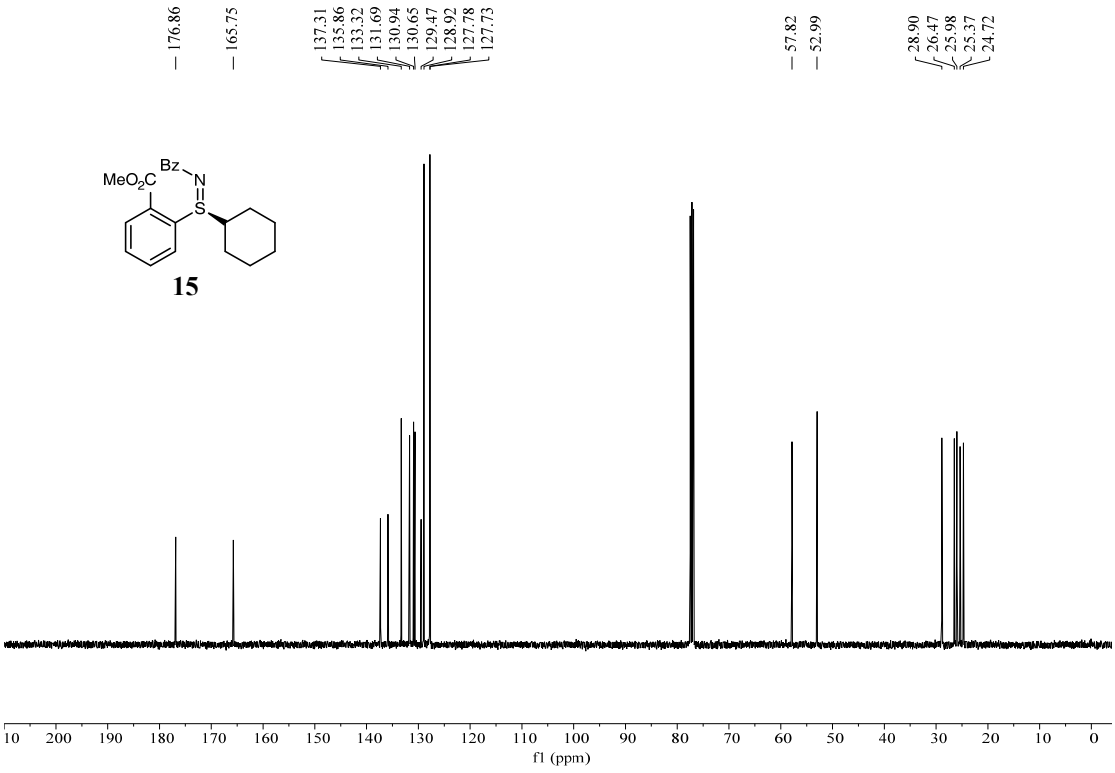
1.96 0.99 0.99 1.00 1.01 3.00 2.94 1.00 1.00 4.57 1.02 1.03 3.27
f1 (ppm)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MeO2C
Bz
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S
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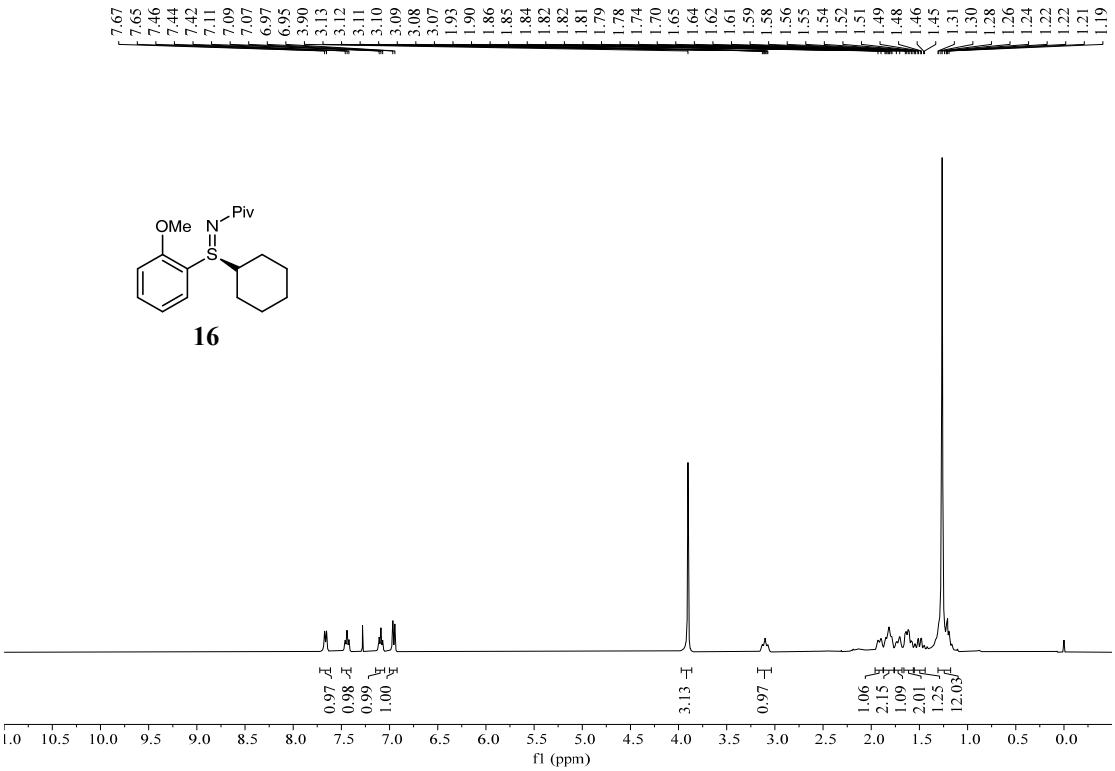
f1 (ppm)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3.11
3.10
3.09
3.08
3.07
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1.28
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1.21
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OMe
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Piv
S
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1.09
2.01
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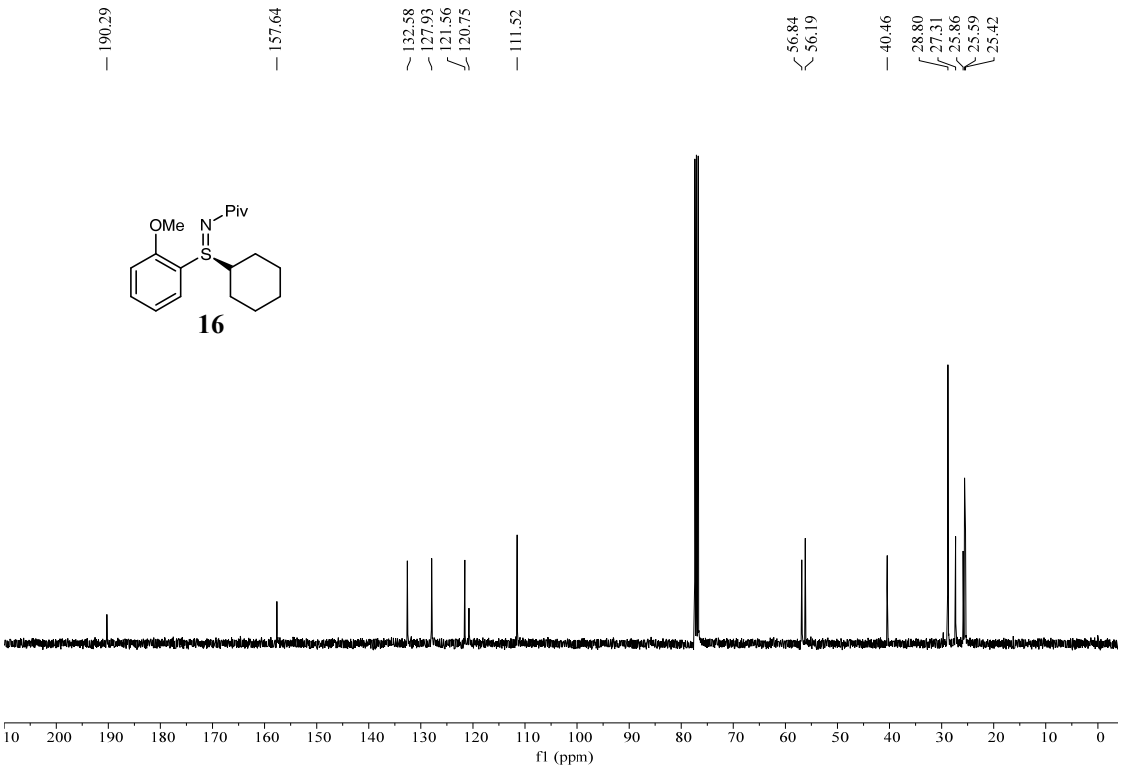
12.03
f1 (ppm)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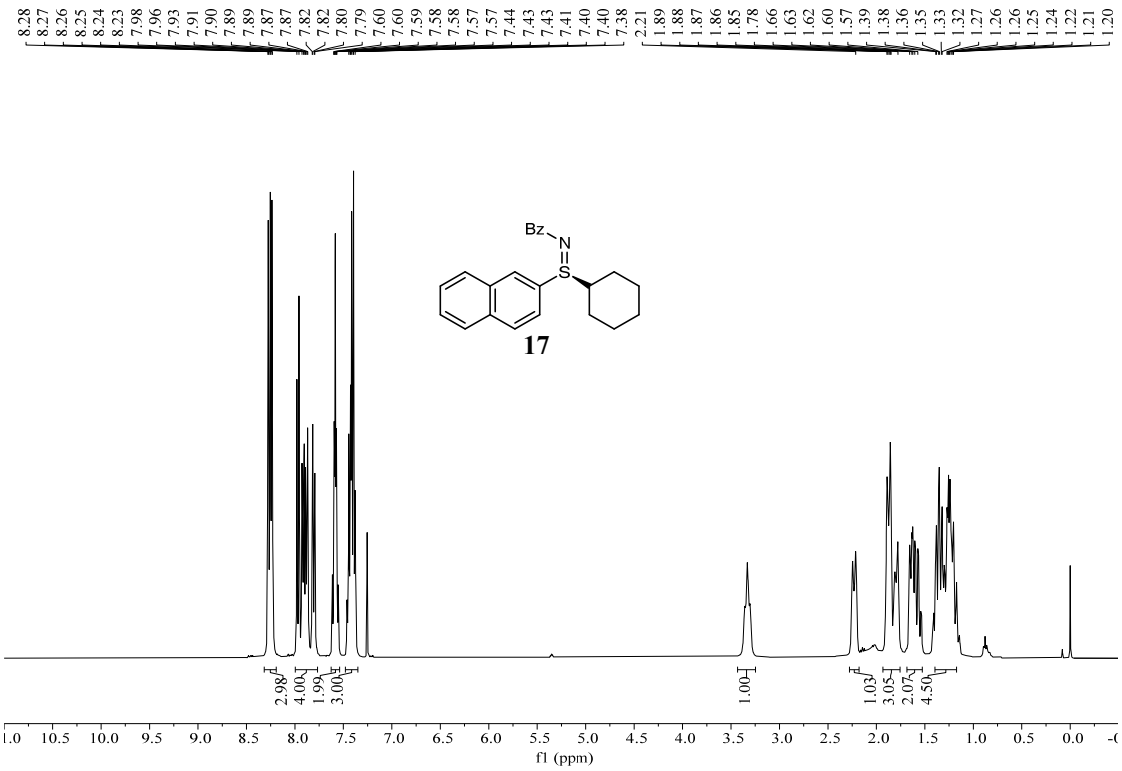
OMe
N
Piv
S
16
f1 (ppm)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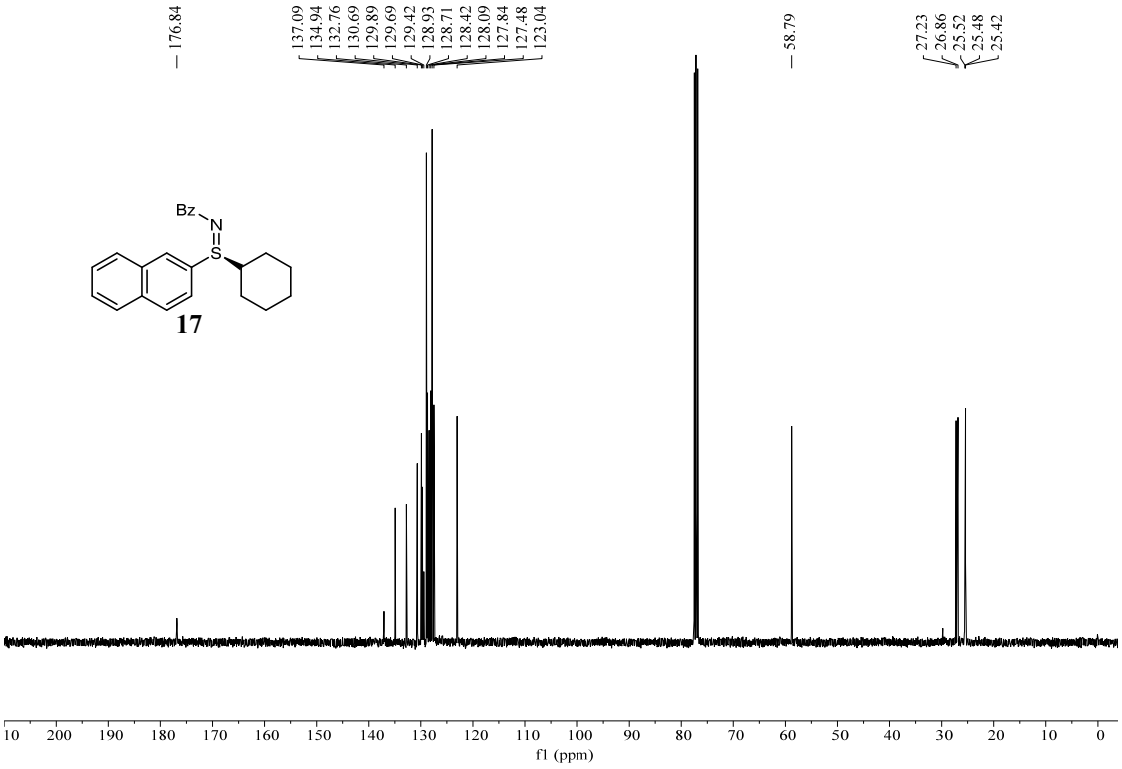
Bz
N
S
17
2.98 4.00 1.99 3.00 1.00 1.03 3.05 2.07 4.50
f1 (ppm)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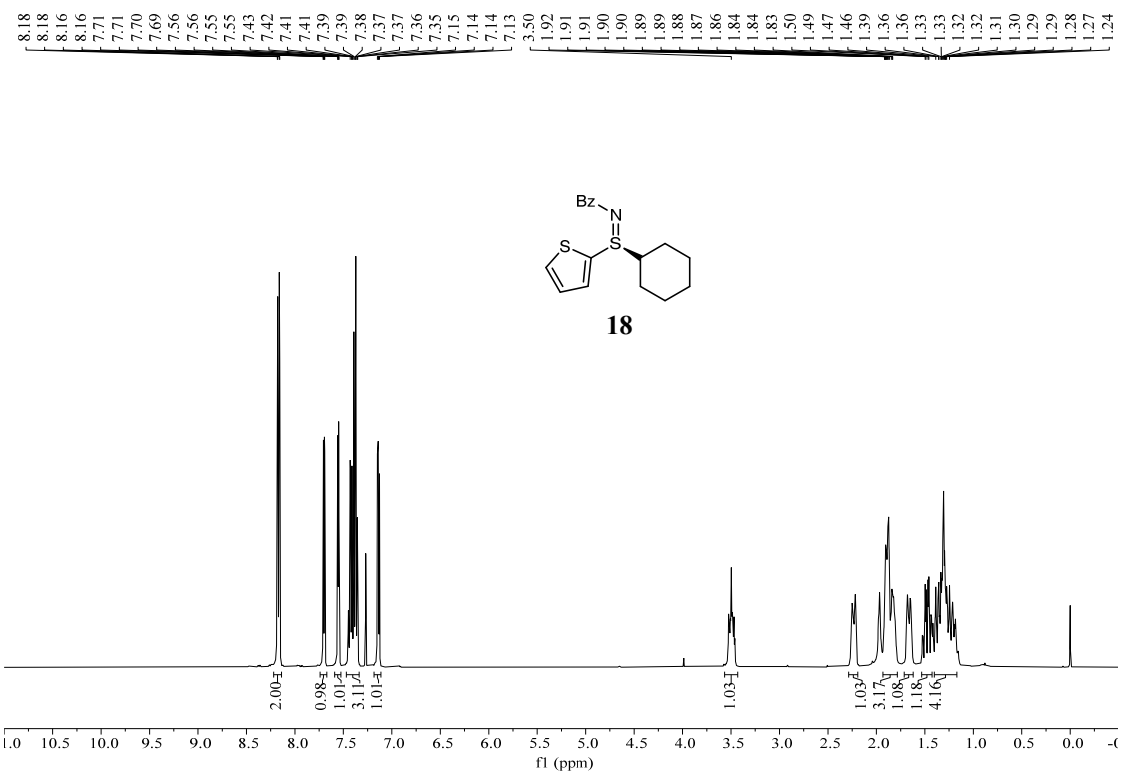
58.79
27.23 26.86 25.52 25.48 25.42
Bz
N
S
17
f1 (ppm)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1.29
1.28
1.27
1.24
Bz
N
S
S
18
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1.08
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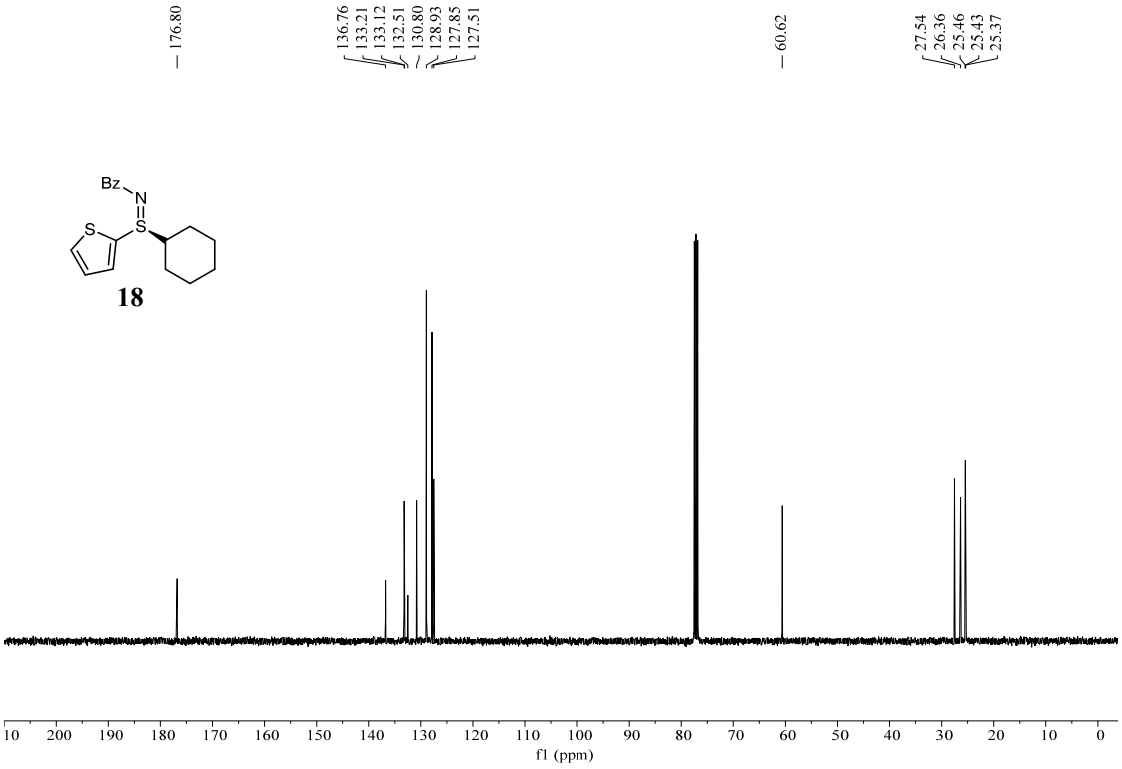
4.16
f1 (ppm)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Bz
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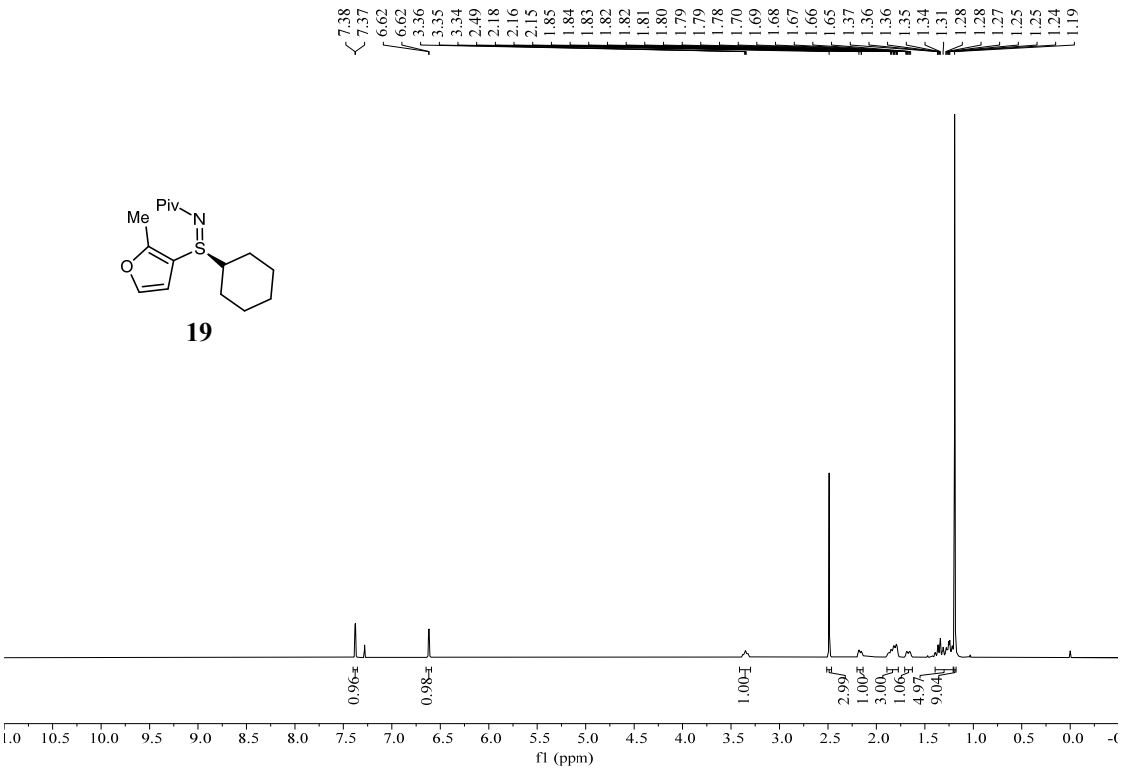
S
S
18
f1 (ppm)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1.28
1.28
1.27
1.25
1.25
1.24
1.19
Me
Piv
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O
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1.00
2.99
1.00
3.00
1.06
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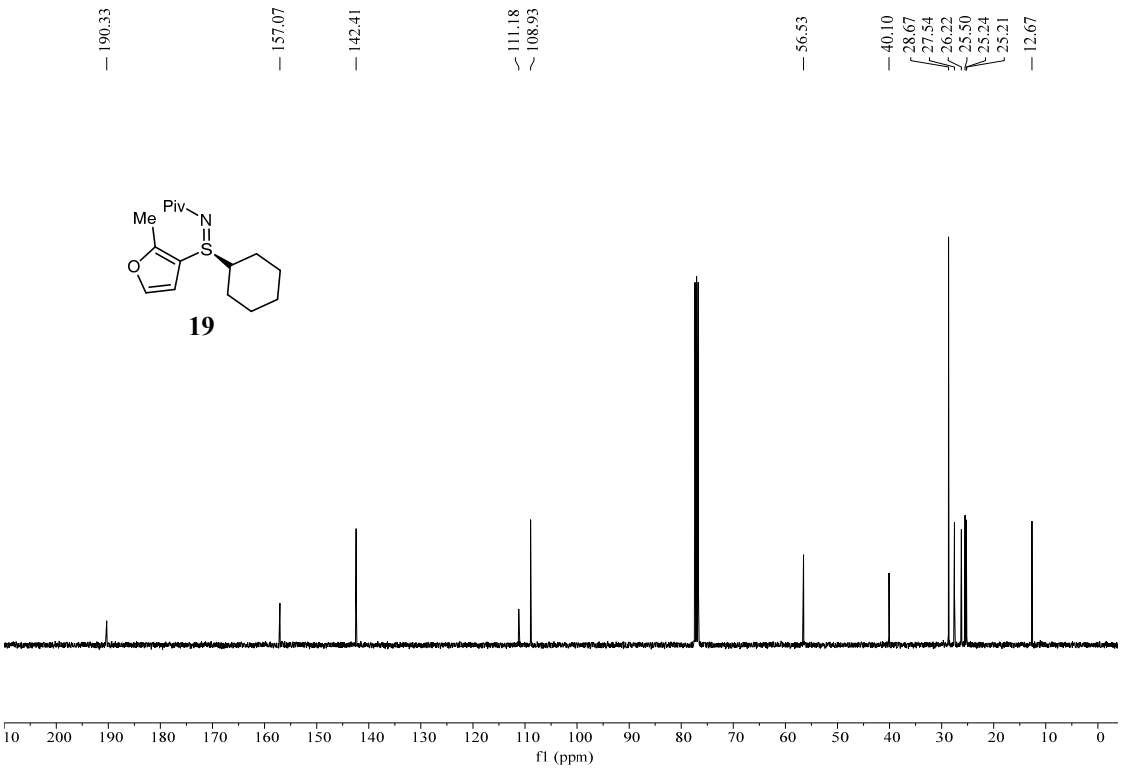
9.04
f1 (ppm)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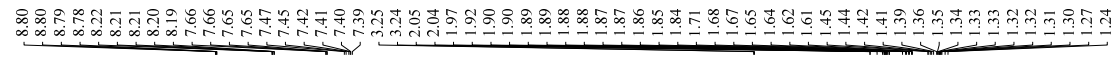
12.67
Me
Piv
N
S
O
19
f1 (ppm)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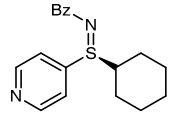
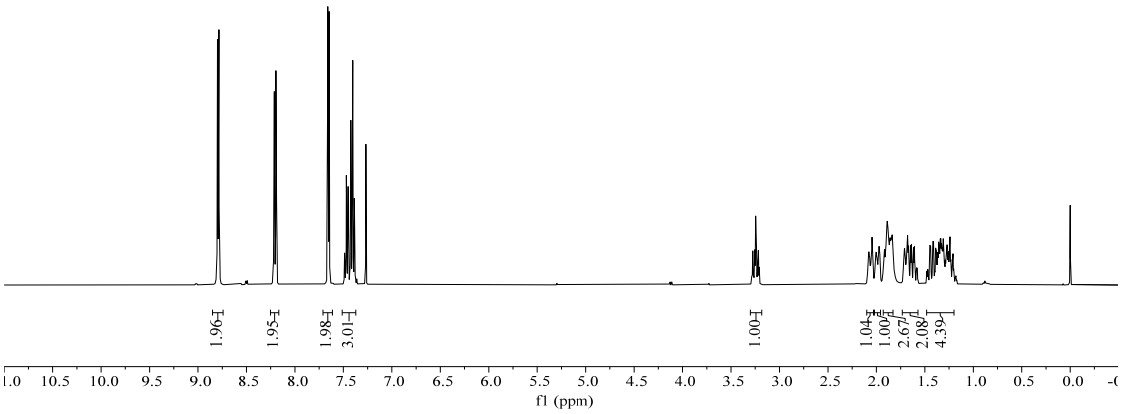

Bz
N
S
N

20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1.00
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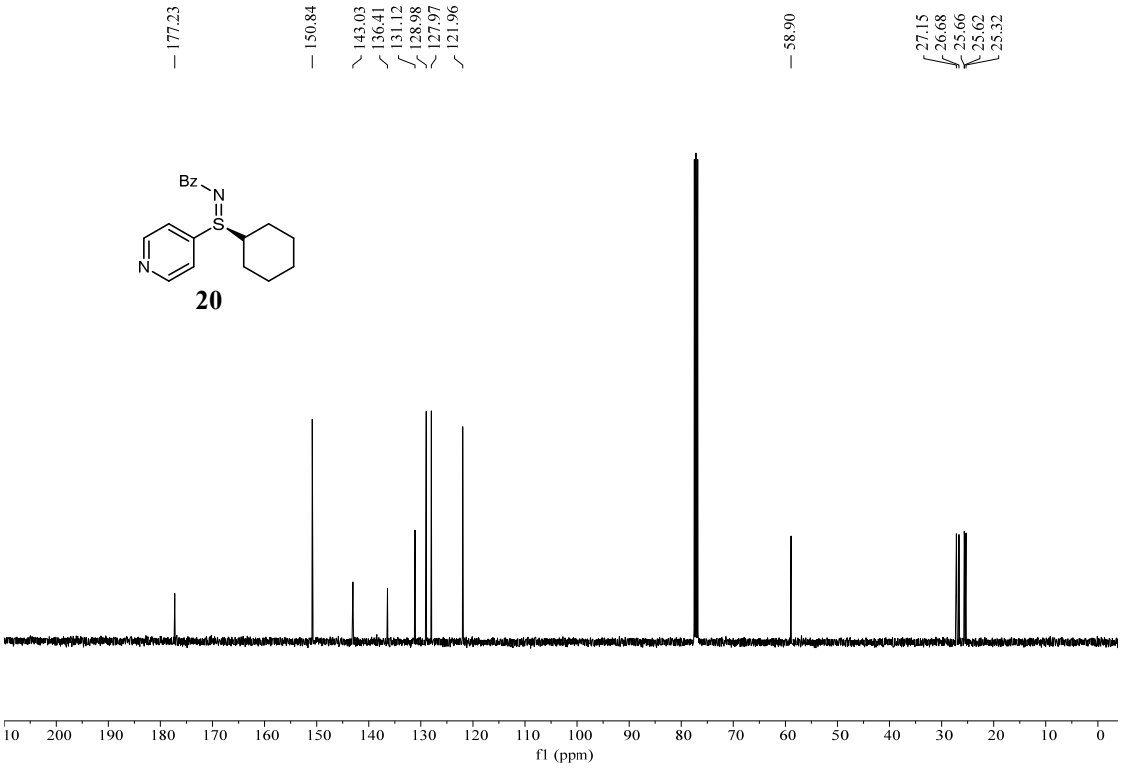
2.08
4.39
f1 (ppm)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25.66
25.62
25.32
Bz
N
S
N
f1 (ppm)

20


8.11
8.11
8.09
8.09
7.41
7.40
7.38
7.38
7.37
7.36
7.36
7.36
7.34
3.21
3.19
3.18
3.17
3.15
2.66
2.24
2.22
2.21
2.09
2.07
2.06
2.06
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1.93
1.93
1.92
1.92
1.90
1.89
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1.72
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1.54
1.53
1.52
1.51
1.51
1.50
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1.41
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1.39
1.38
1.38
1.37
1.37
1.36
1.34
1.34
1.33
1.33
1.30
1.27
Bz
N
S
Me
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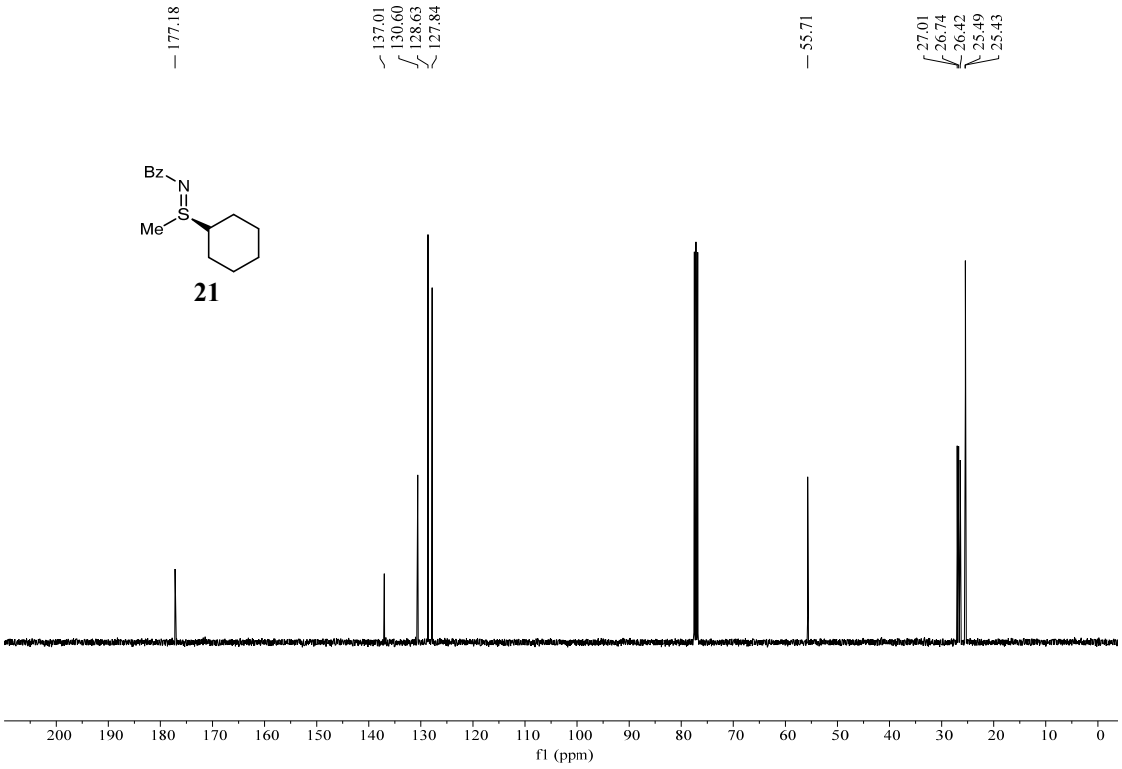
1.07
1.09
2.10
1.05
2.11
3.35
f1 (ppm)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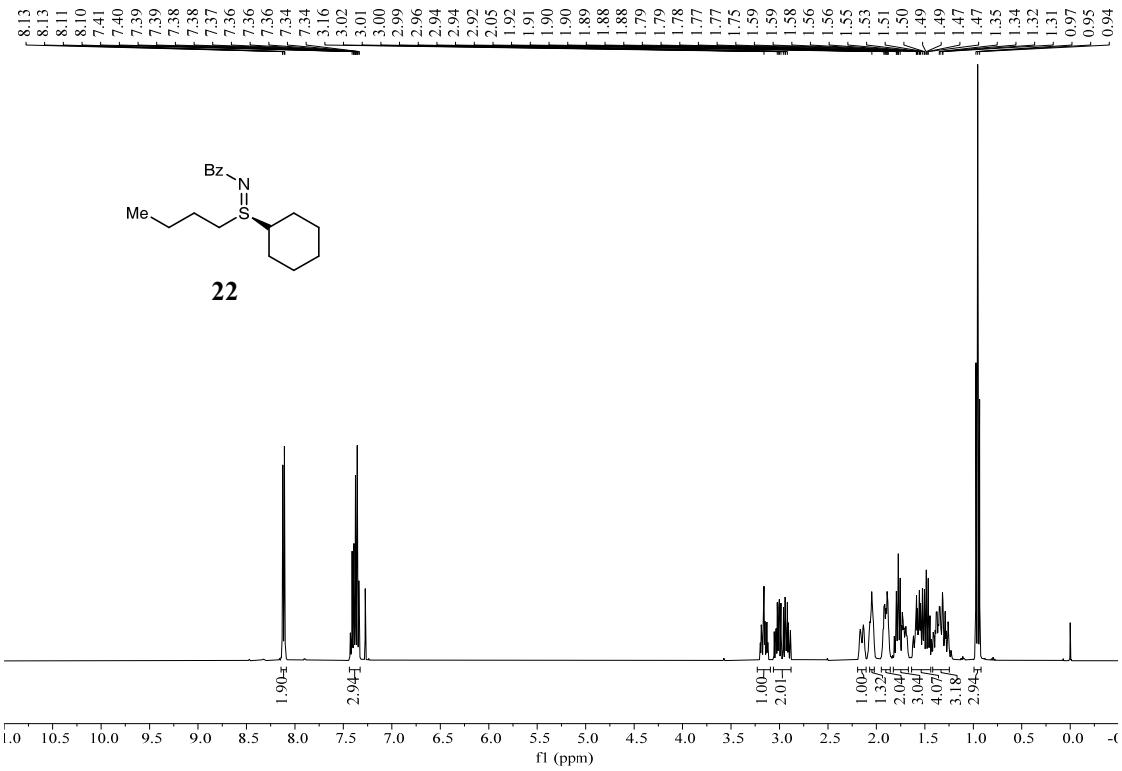
Bz
N
S
Me
21
f1 (ppm)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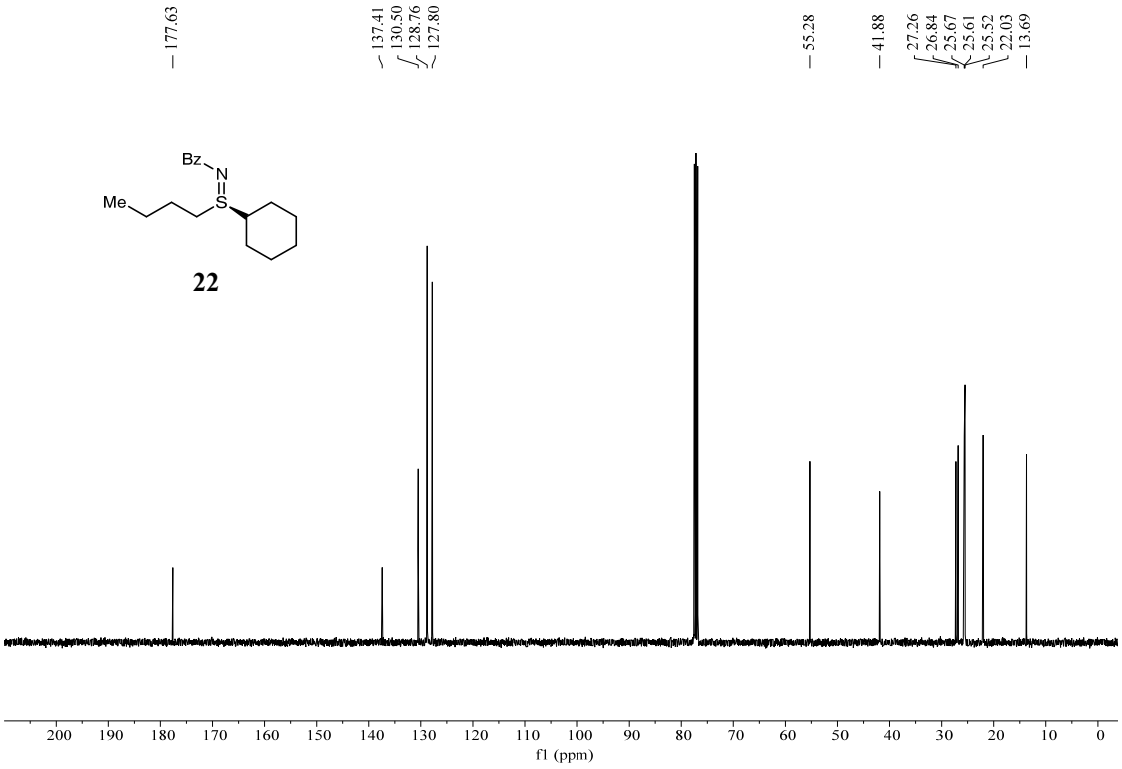
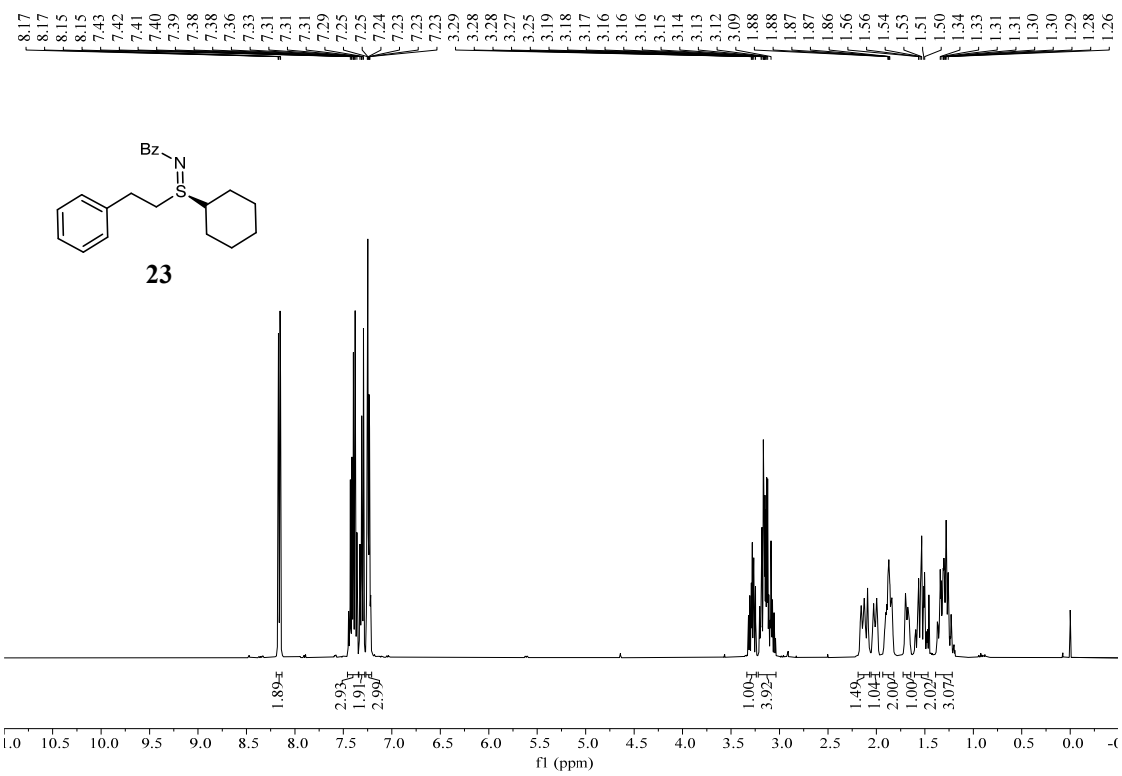
S
Me
22
fl (ppm)


Bz
N
S
Me
22
fl (ppm)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7.31
7.31
7.31
7.29
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7.24
7.23
7.23
7.23
3.29
3.28
3.28
3.27
3.25
3.19
3.18
3.17
3.16
3.16
3.16
3.15
3.14
3.13
3.12
3.09
1.88
1.88
1.87
1.87
1.86
1.56
1.56
1.54
1.53
1.51
1.50
1.34
1.33
1.31
1.31
1.30
1.30
1.29
1.28
1.26
Bz
N
S
23
1.89
2.93
1.91
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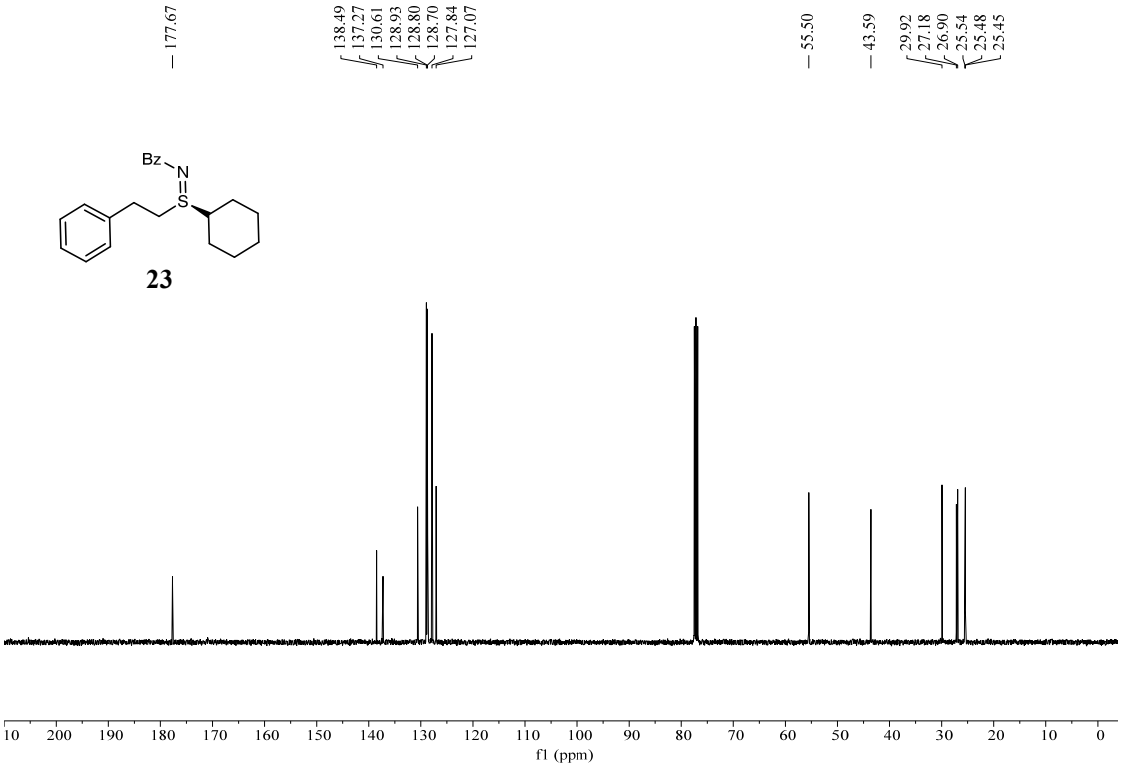
1.00
3.92
1.49
1.04
2.00
1.00
2.02
3.07
f1 (ppm)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137.27
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128.70
127.84
127.07
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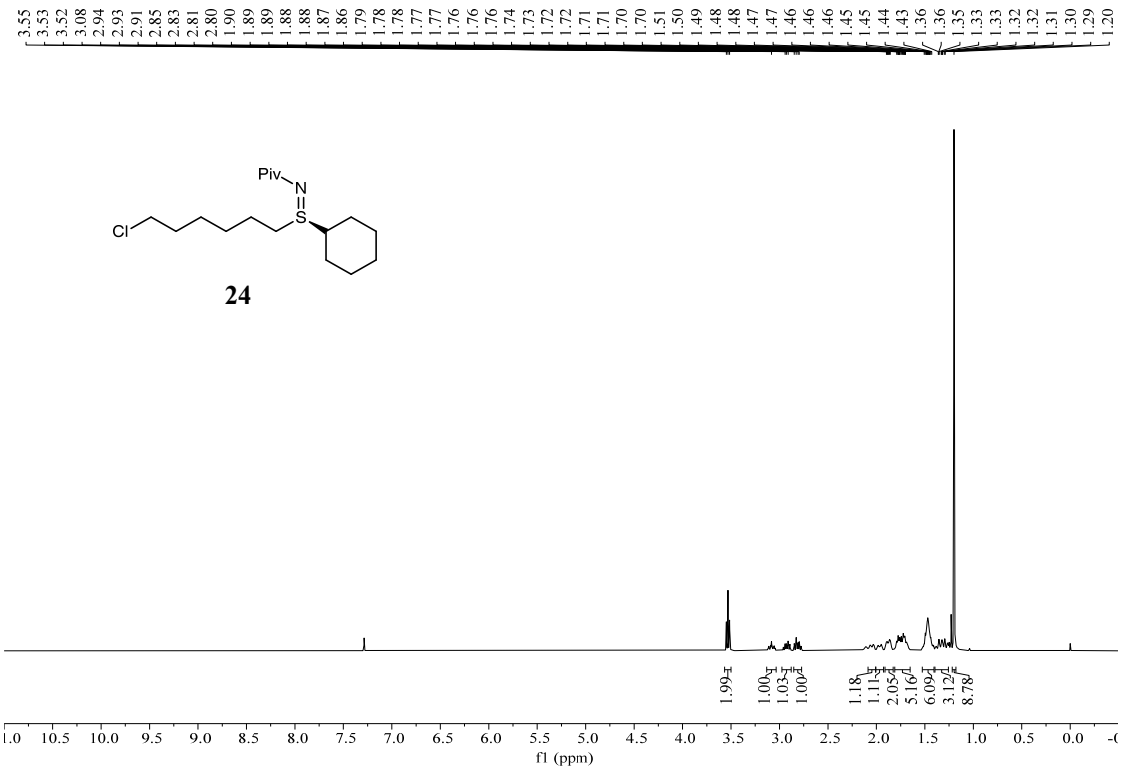
29.92
27.18
26.90
25.54
25.48
25.45
Bz
N
S
23
f1 (ppm)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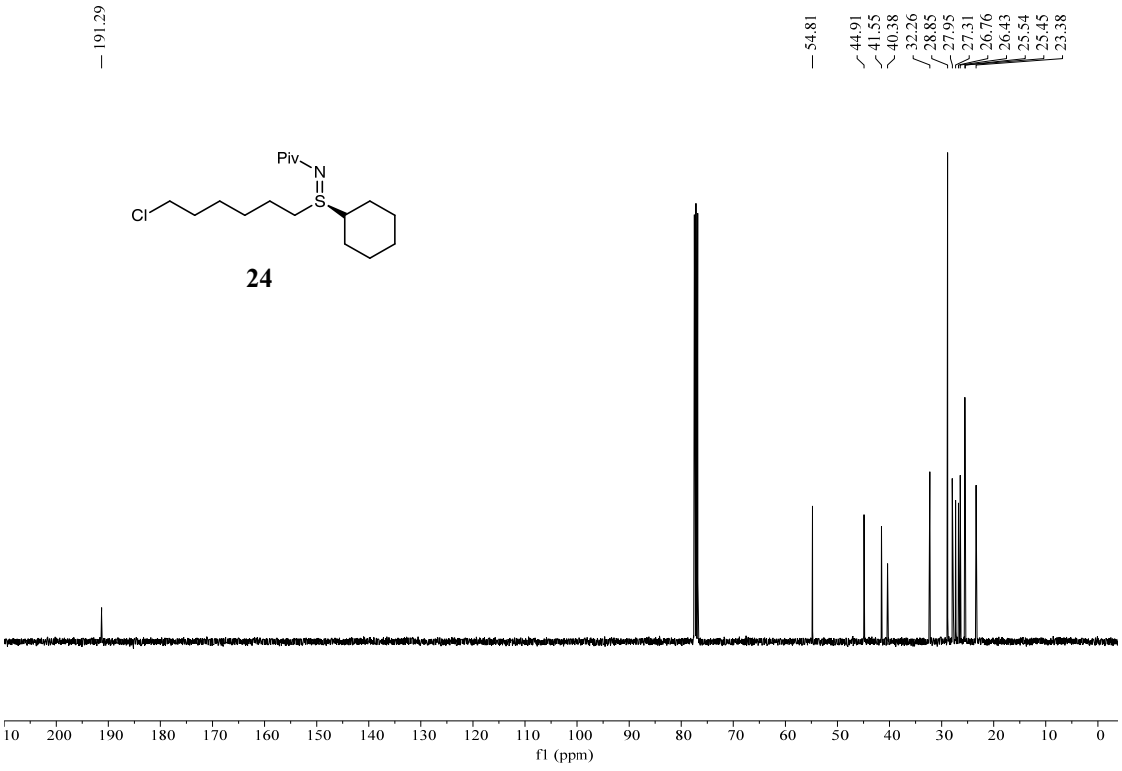
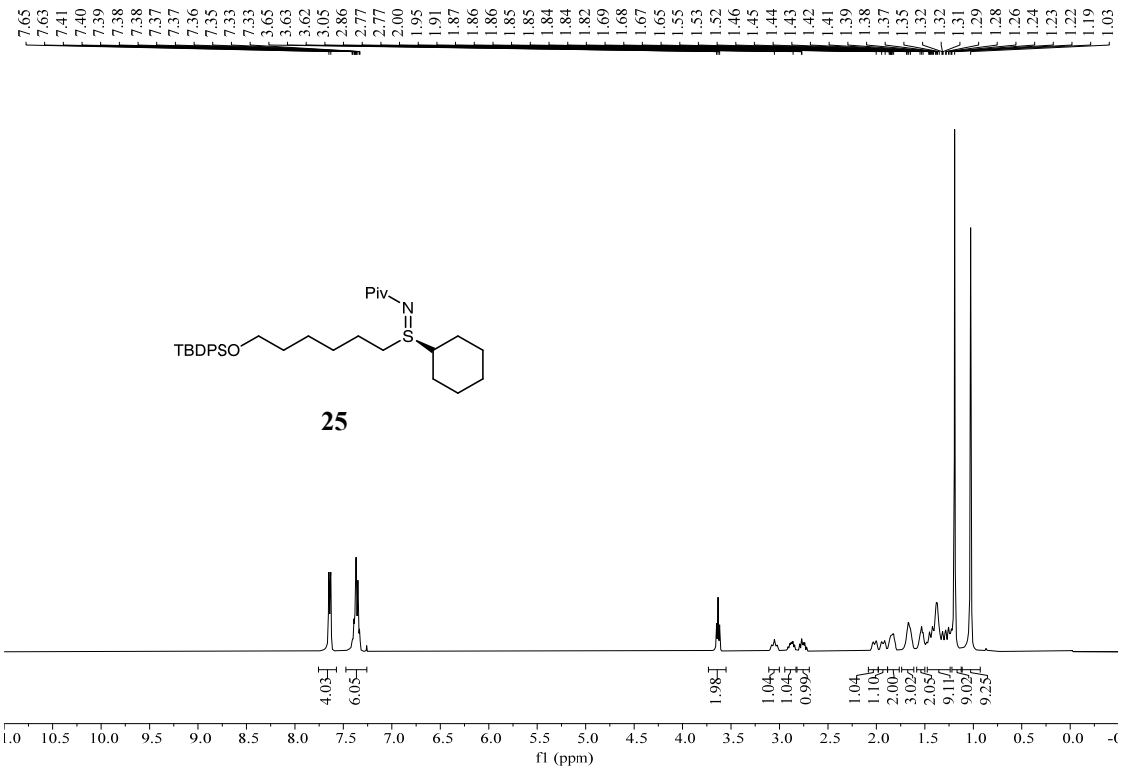
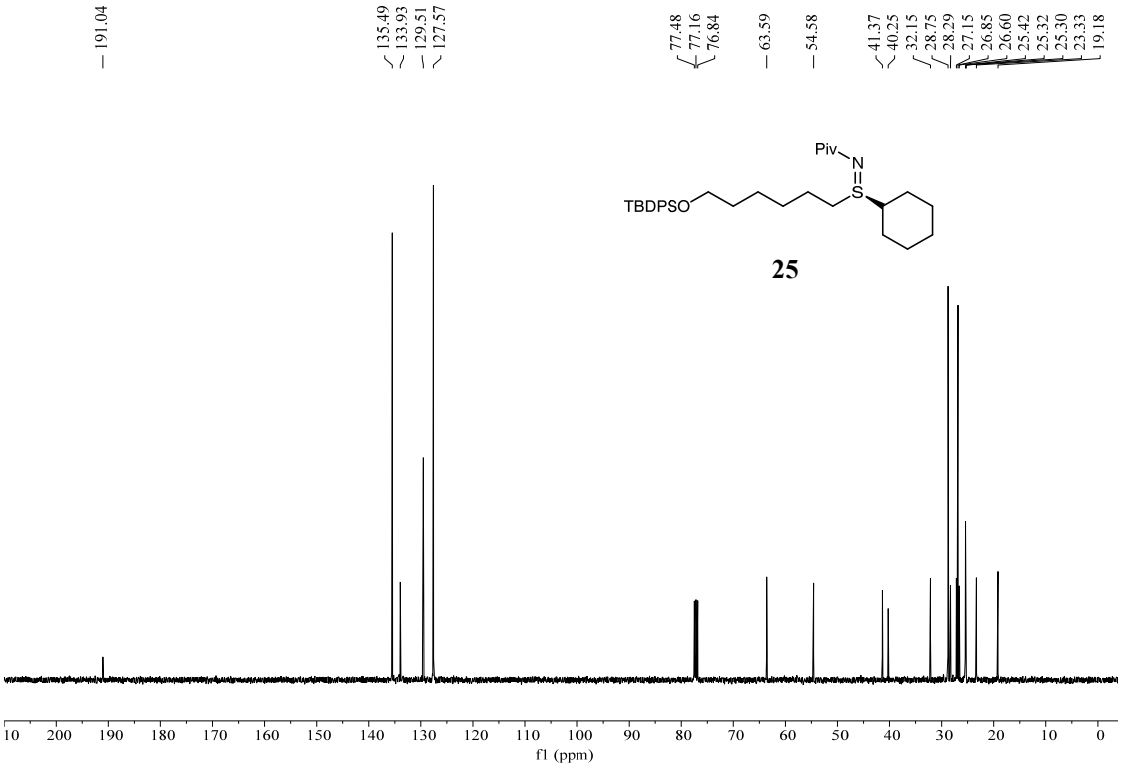
3.52
3.08
2.94
2.93
2.91
2.85
2.83
2.81
2.80
1.90
1.89
1.89
1.88
1.88
1.87
1.86
1.79
1.78
1.78
1.77
1.77
1.76
1.76
1.76
1.74
1.73
1.72
1.72
1.71
1.71
1.70
1.70
1.51
1.50
1.49
1.48
1.48
1.47
1.47
1.46
1.46
1.45
1.45
1.44
1.43
1.36
1.36
1.35
1.33
1.33
1.32
1.31
1.30
1.29
1.20
Piv
N
S
Cl
1.99
1.00
1.03
1.00
1.18
1.11
2.05
5.16
6.09
3.12
8.78
f1 (ppm)

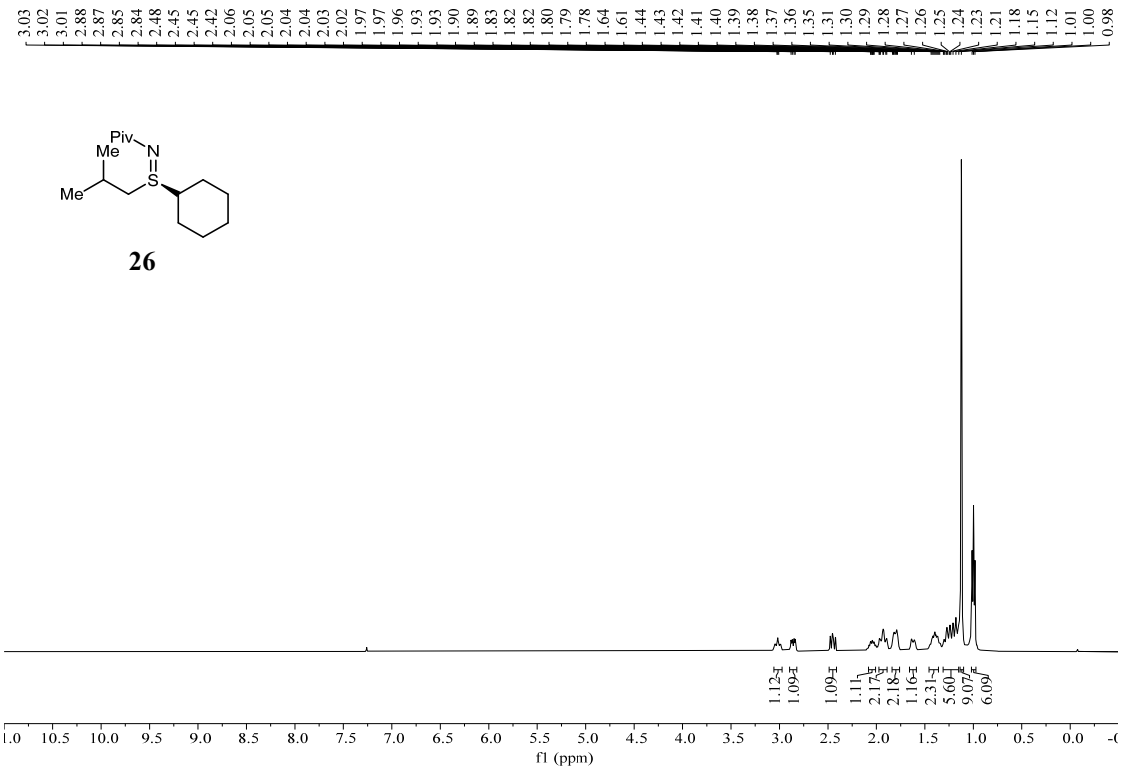
24


191.29
54.81
44.91
41.55
40.38
32.26
28.85
27.95
27.31
26.76
26.43
25.54
25.45
23.38
Piv
N
S
Cl
f1 (ppm)

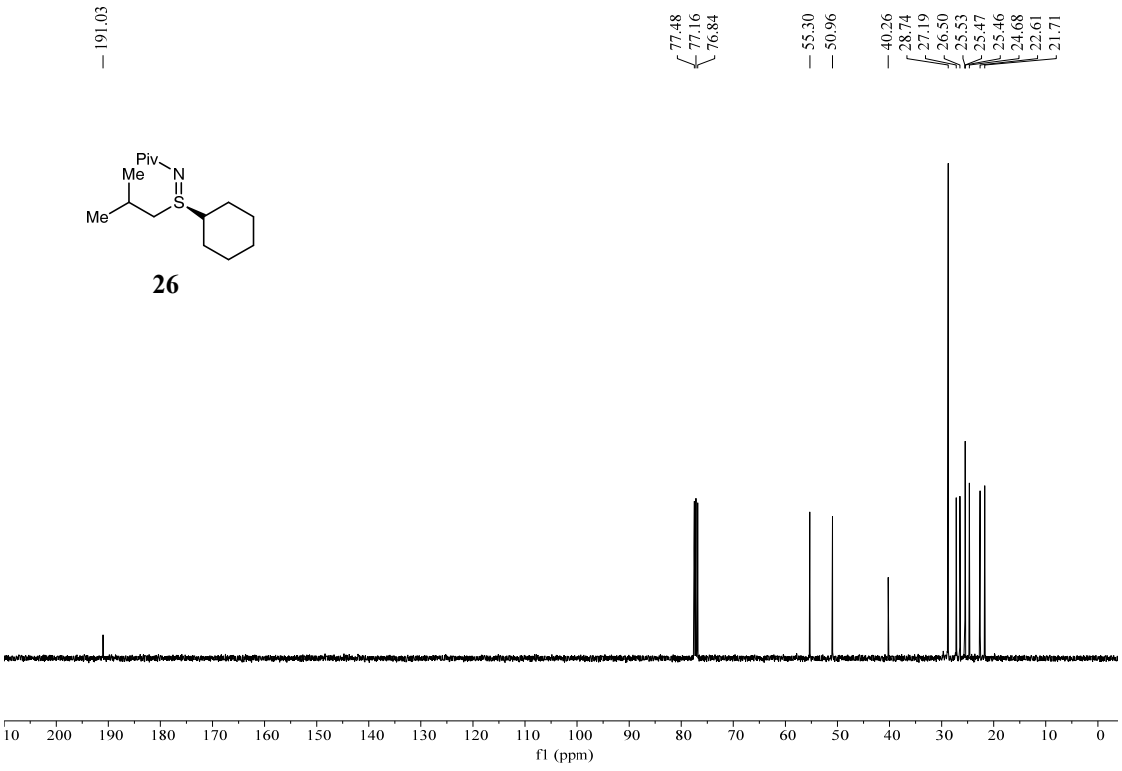
24


Piv
N
S
TBDPSO
25
fl (ppm)

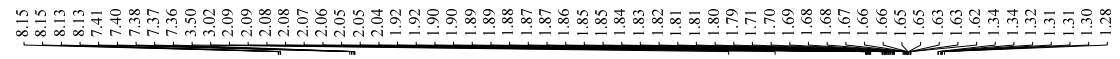

Piv
N
S
TBDPSO
25
fl (ppm)


3.03 3.02 3.01 2.88 2.87 2.85 2.84 2.48 2.45 2.45 2.42 2.06 2.05 2.05 2.04 2.04 2.03 2.02 1.97 1.97 1.96 1.93 1.93 1.90 1.89 1.83 1.82 1.82 1.80 1.79 1.78 1.64 1.61 1.44 1.43 1.42 1.41 1.40 1.39 1.38 1.37 1.36 1.35 1.31 1.30 1.29 1.28 1.27 1.26 1.25 1.24 1.23 1.21 1.18 1.15 1.12 1.01 1.00 0.98
Piv
Me
N
S
Me
1.12
1.09
1.09
1.11
2.17
2.18
1.16
2.31
5.60
9.07
6.09
f1 (ppm)

26


191.03
77.48
77.16
76.84
55.30
50.96
40.26
28.74
27.19
26.50
25.53
25.47
25.46
24.68
22.61
21.71
Piv
Me
N
S
Me
f1 (ppm)

26


8.15
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7.38
7.37
7.36
3.50
3.02
2.09
2.09
2.08
2.08
2.07
2.06
2.05
2.05
2.04
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1.86
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1.84
1.83
1.82
1.81
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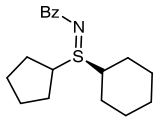
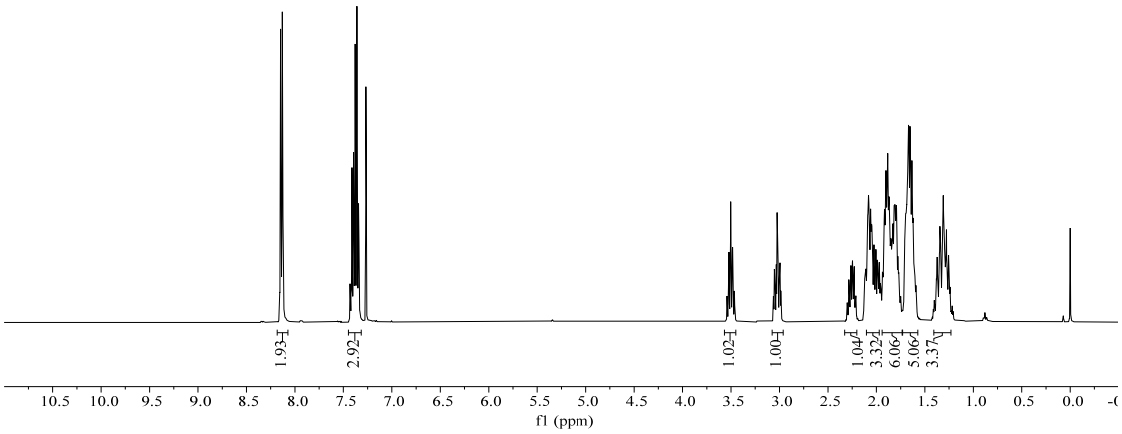
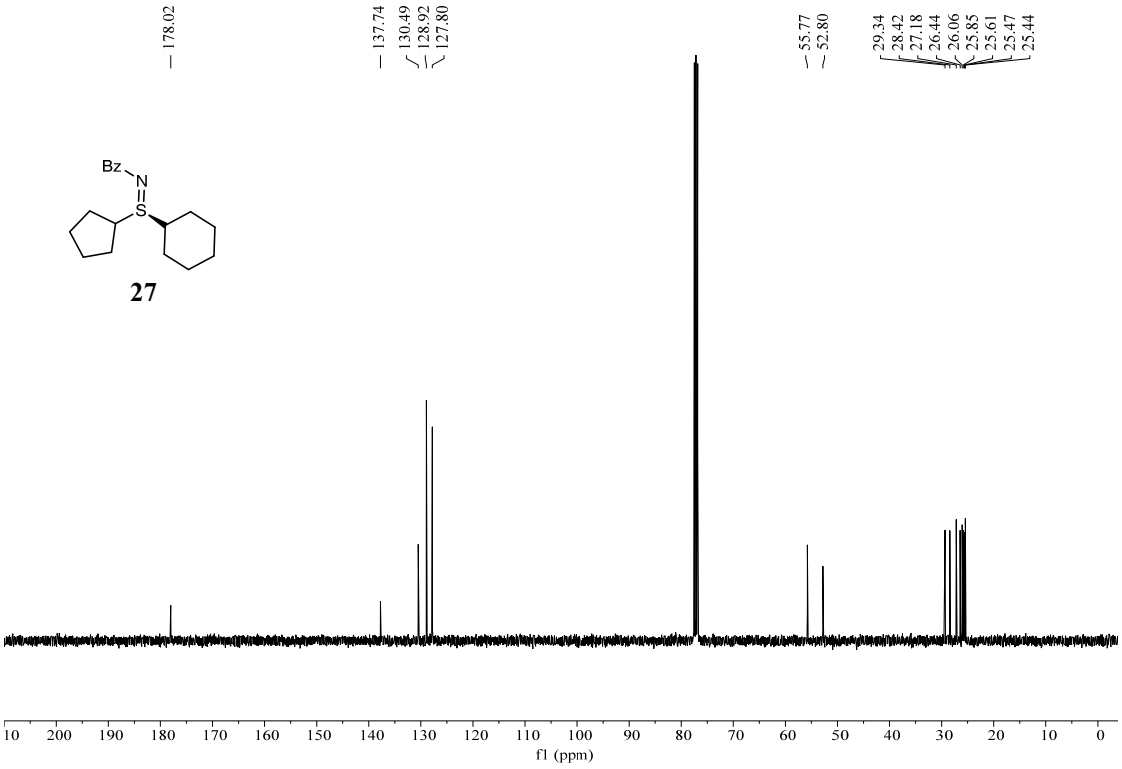
1.32
1.31
1.31
1.30
1.28


Bz
N
S

27


1.93
2.92
1.02
1.00
1.04
3.32
6.06
5.06
3.37
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.49
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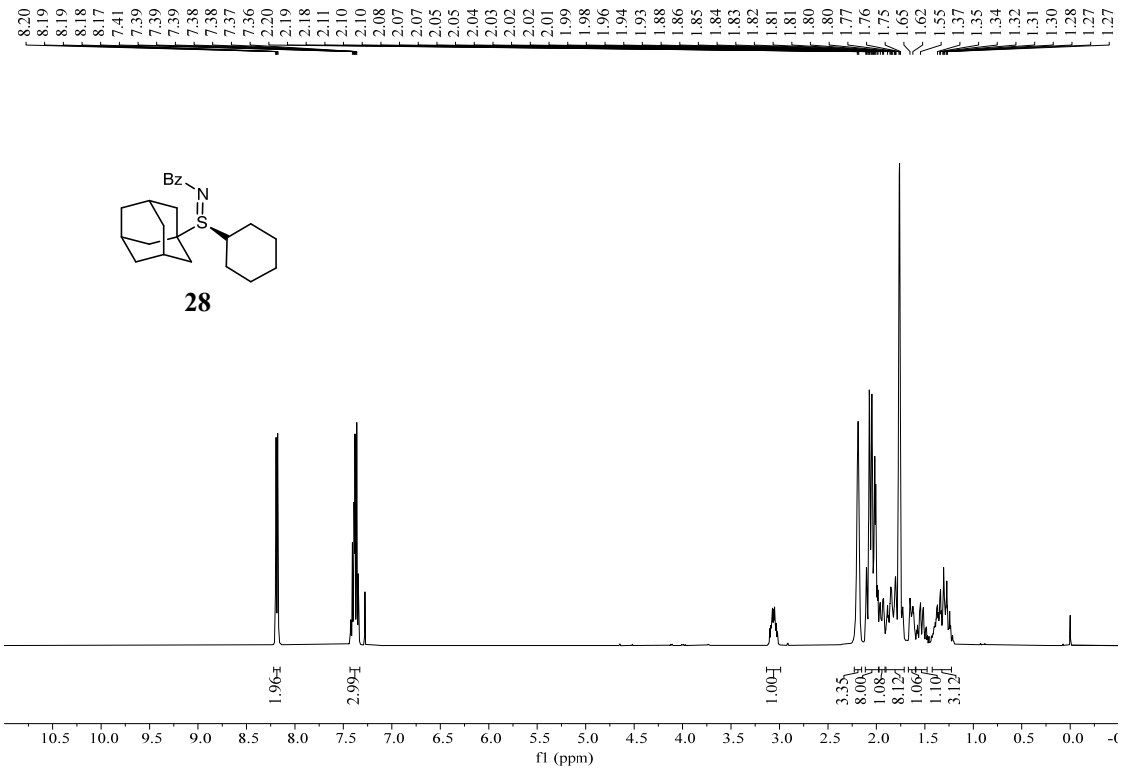
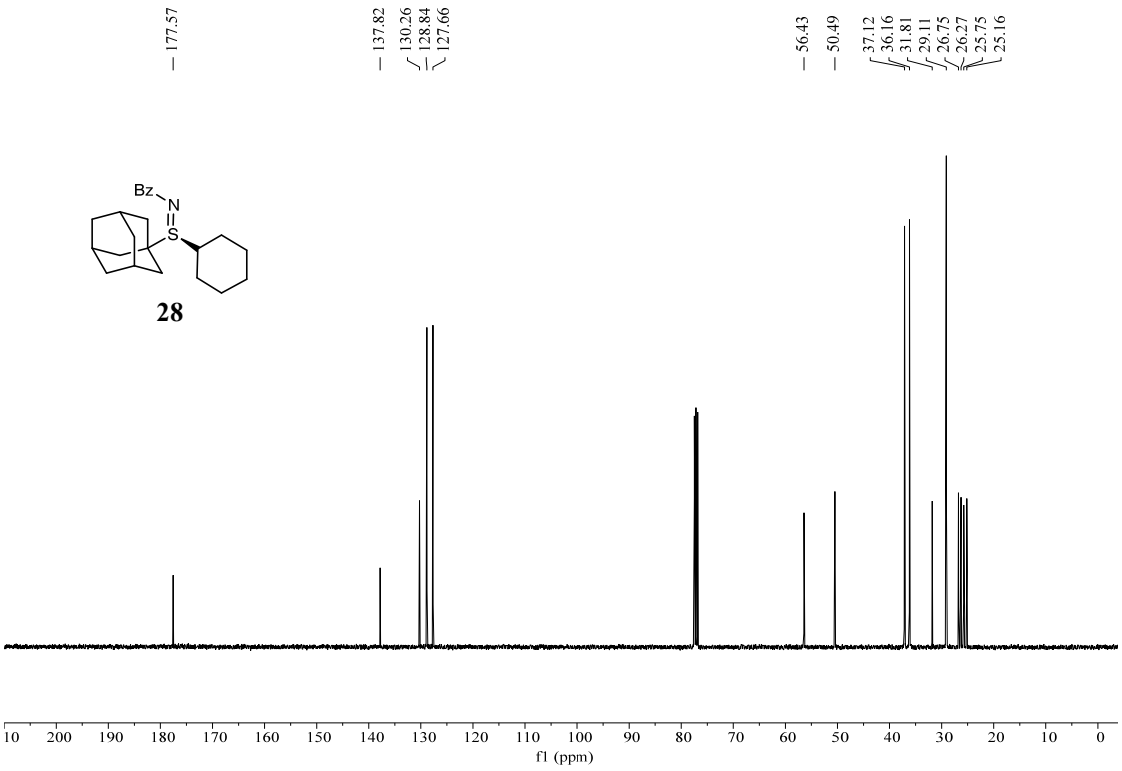
127.80
55.77
52.80
29.34
28.42
27.18
26.44
26.06
25.85
25.61
25.47
25.44
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Bz
N
S

27


8.20 8.19 8.19 8.18 8.17 7.41 7.39 7.39 7.39 7.38 7.38 7.37 7.36 2.20 2.19 2.18 2.11 2.10 2.10 2.08 2.07 2.07 2.05 2.05 2.04 2.03 2.02 2.02 2.01 1.99 1.98 1.96 1.94 1.93 1.88 1.86 1.85 1.84 1.83 1.82 1.81 1.81 1.80 1.80 1.77 1.76 1.75 1.65 1.62 1.55 1.37 1.35 1.34 1.32 1.31 1.30 1.28 1.27 1.27
Bz
N
S
28
1.96 2.99 1.00 3.35 8.00 1.08 8.12 1.06 1.10 3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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56.43
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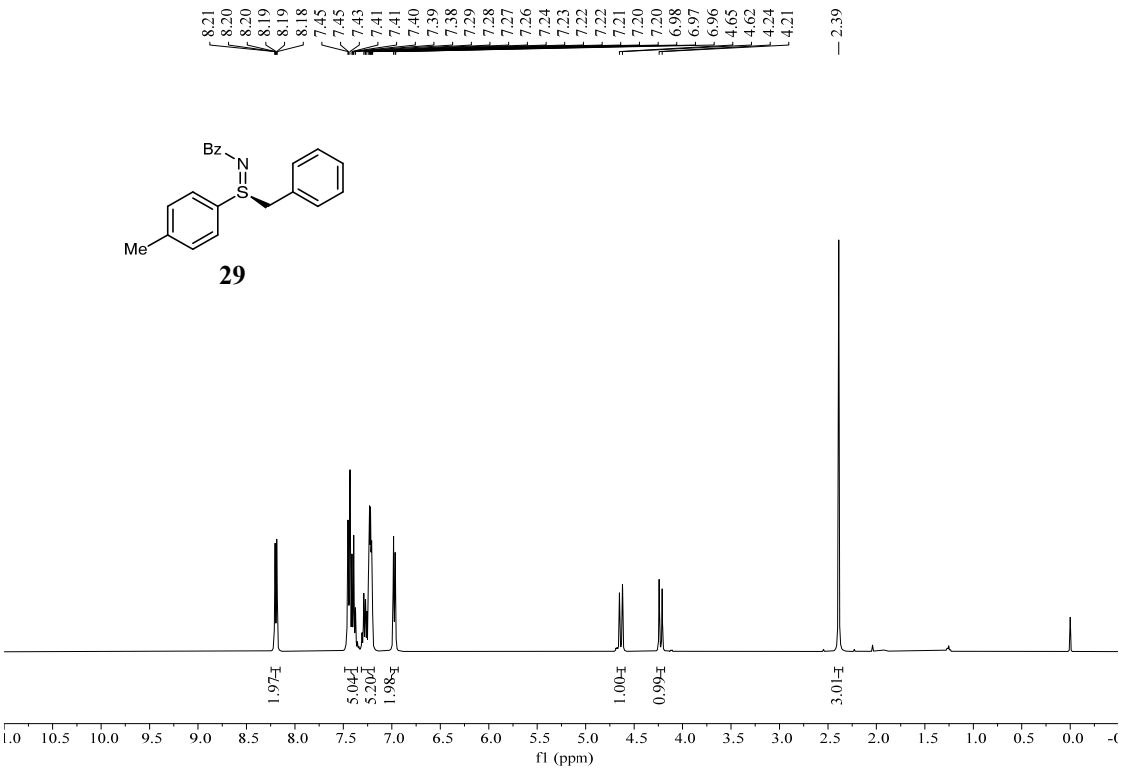
37.12
36.16
31.81
29.11
26.75
26.27
25.75
25.16
Bz
N
S
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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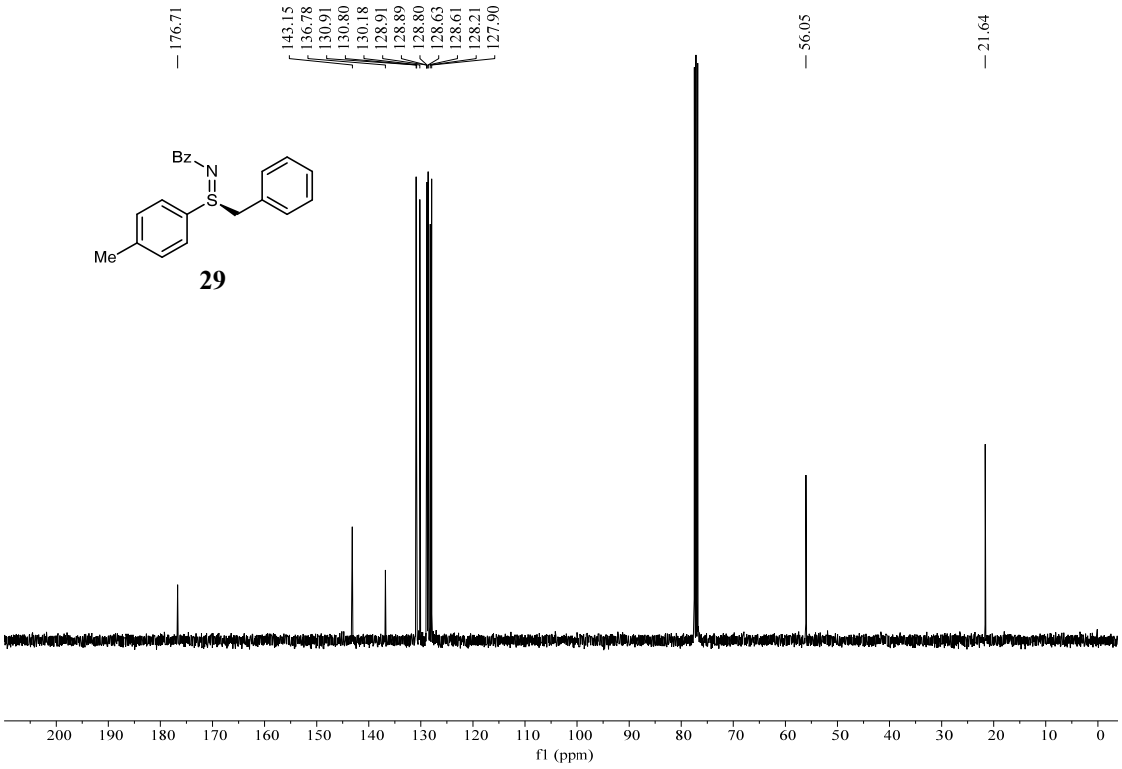
7.45
7.43
7.41
7.41
7.40
7.39
7.38
7.29
7.28
7.27
7.26
7.24
7.23
7.22
7.22
7.21
7.20
7.20
6.98
6.97
6.96
4.65
4.62
4.24
4.21
2.39
Bz
N
S
Me
29
1.97
5.04
5.20
1.98
1.00
0.99
3.01
f1 (ppm)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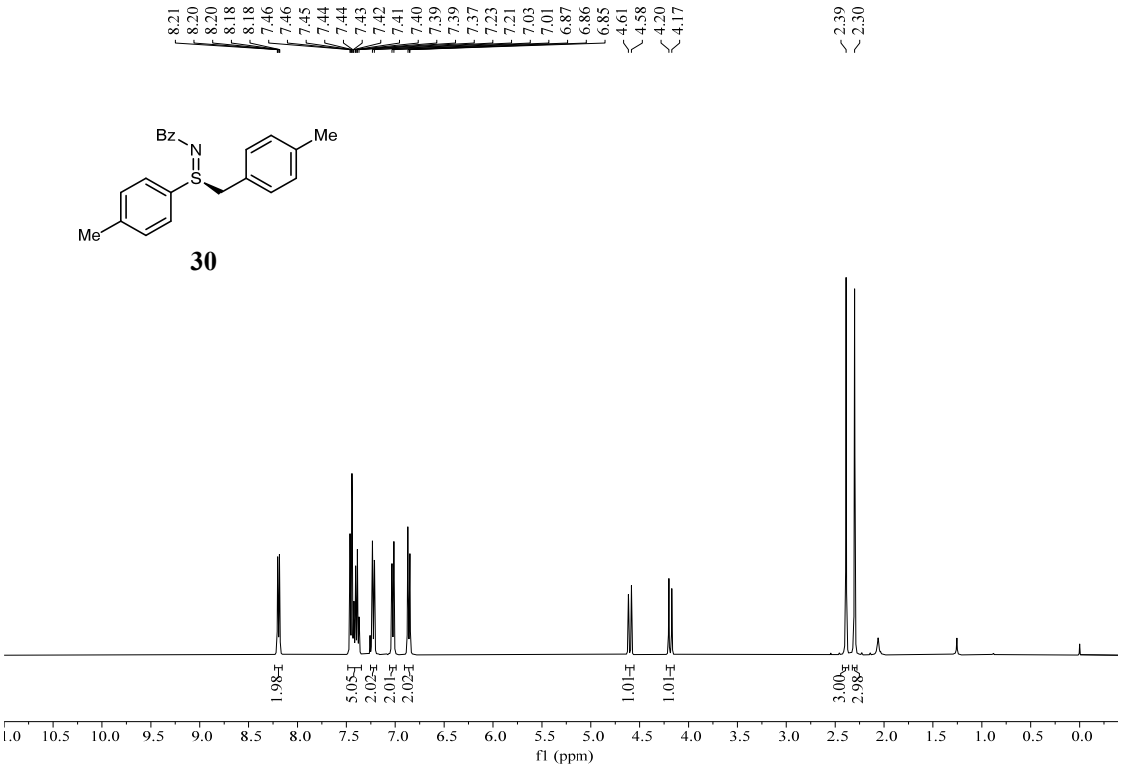
128.21
127.90
56.05
21.64
Bz
N
S
Me
29
f1 (ppm)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7.45
7.44
7.44
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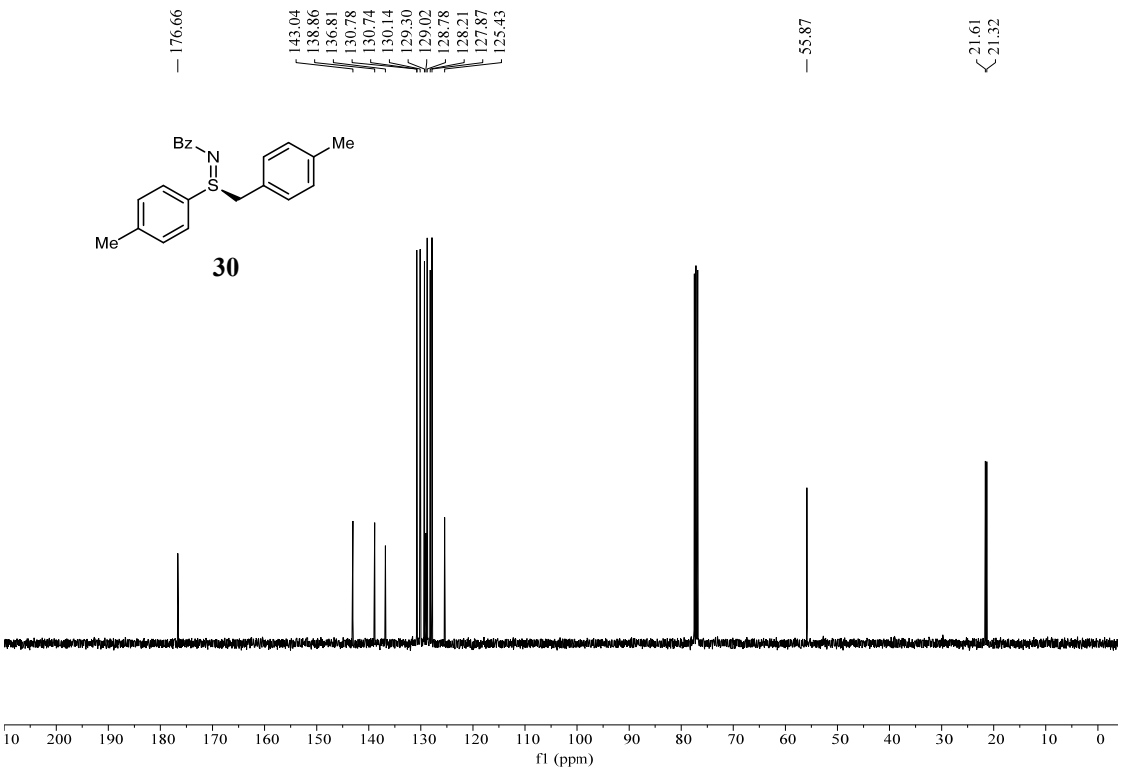
7.42
7.41
7.40
7.39
7.39
7.37
7.23
7.21
7.03
7.01
6.87
6.86
6.85
4.61
4.58
4.20
4.17
2.39
2.30
Bz
N
S
Me
Me
30
1.98
5.05
2.02
2.01
2.02
1.01
1.01
3.00
2.98
fl (ppm)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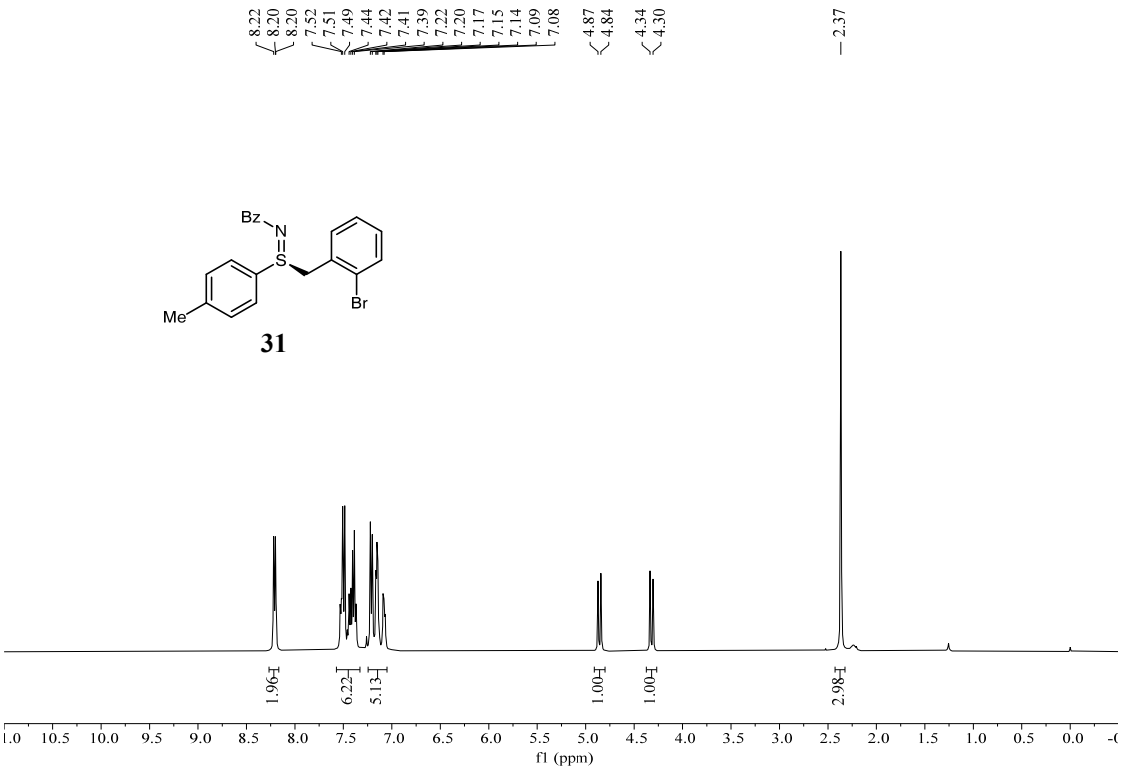
125.43
55.87
21.61
21.32
Bz
N
S
Me
Me
30
fl (ppm)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7.52
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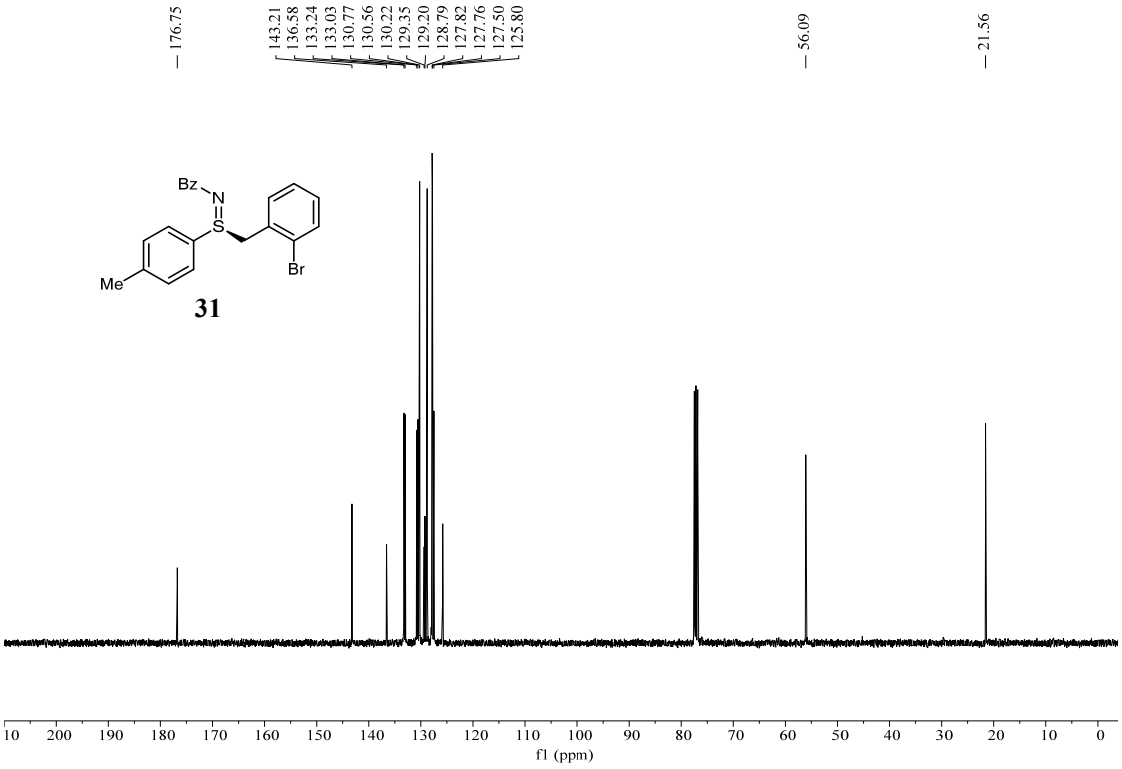
7.44
7.42
7.41
7.39
7.22
7.20
7.17
7.15
7.14
7.09
7.08
4.87
4.84
4.34
4.30
2.37
Bz
N
S
Me
Br
31
1.96
6.22
5.13
1.00
1.00
2.98
f1 (ppm)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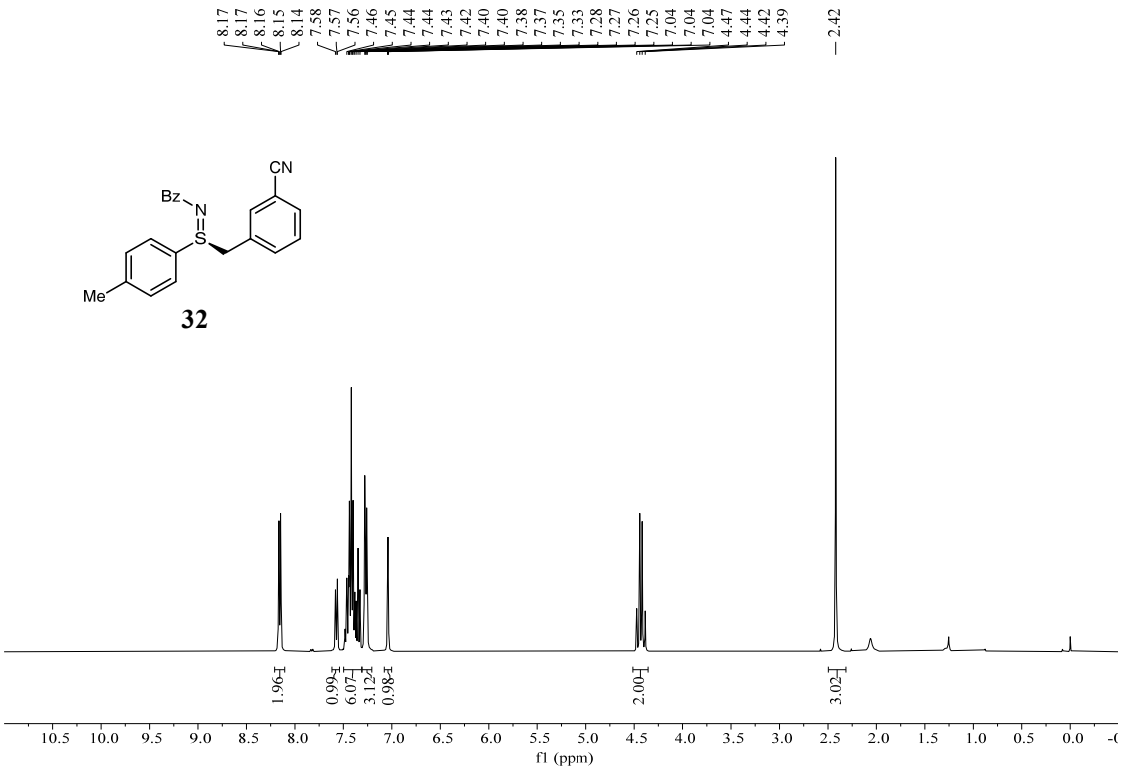
130.77
130.56
130.22
129.35
129.20
128.79
127.82
127.76
127.50
125.80
56.09
21.56
Bz
N
S
Me
Br
31
f1 (ppm)


8.17
8.17
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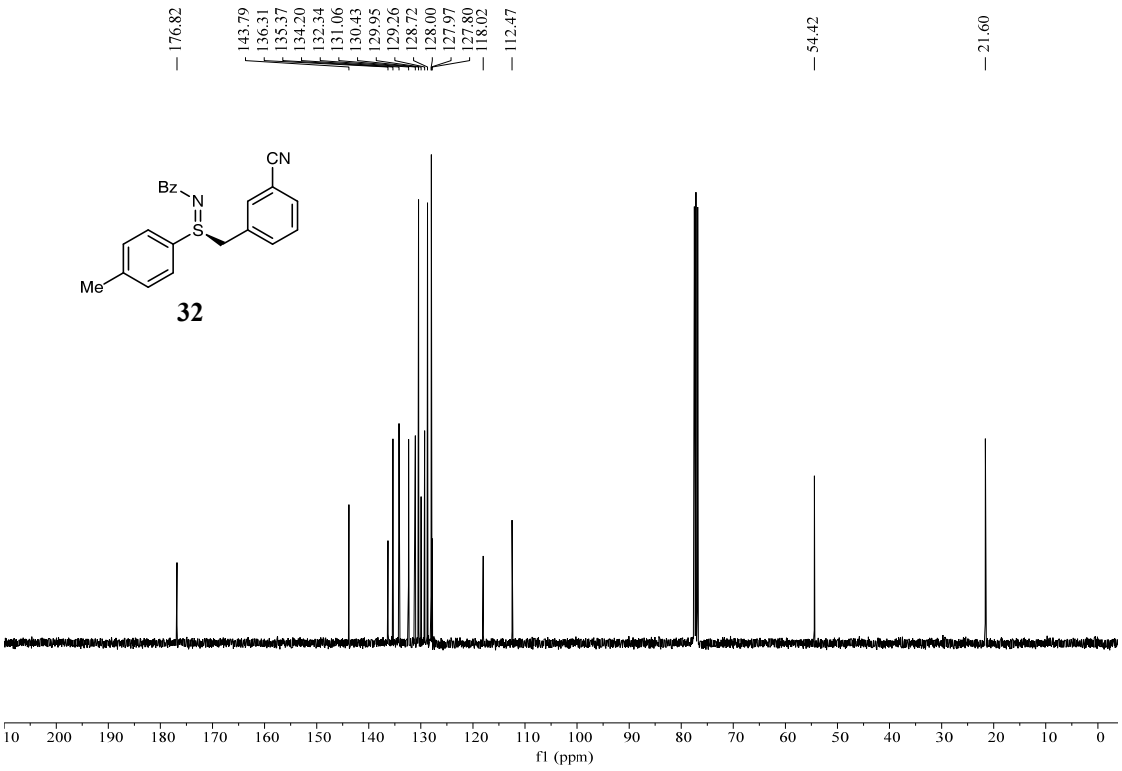
8.14
7.58
7.57
7.56
7.46
7.45
7.44
7.44
7.43
7.42
7.40
7.40
7.38
7.37
7.35
7.33
7.28
7.27
7.26
7.25
7.04
7.04
4.47
4.44
4.42
4.39
2.42
CN
Bz
N
S
Me
32
1.96
0.99
6.07
3.12
0.98
2.00
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.82
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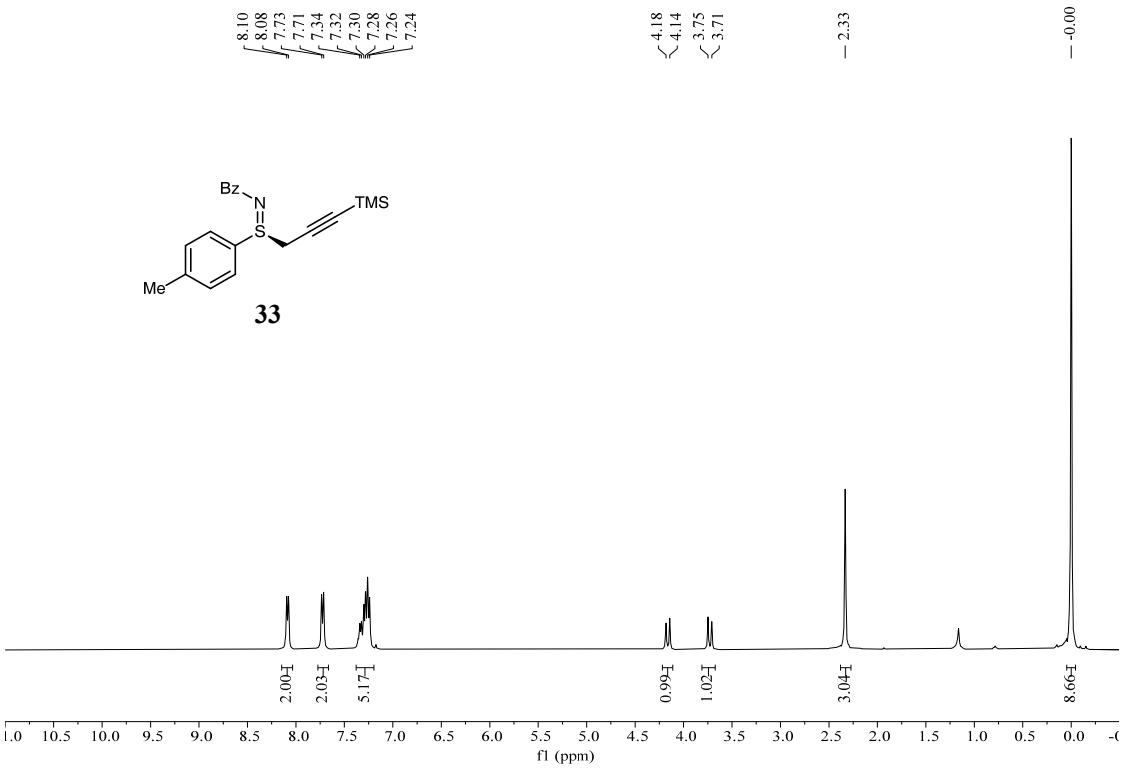
135.37
134.20
132.34
131.06
130.43
129.95
129.26
128.72
128.00
127.97
127.80
118.02
112.47
54.42
21.60
CN
Bz
N
S
Me
32
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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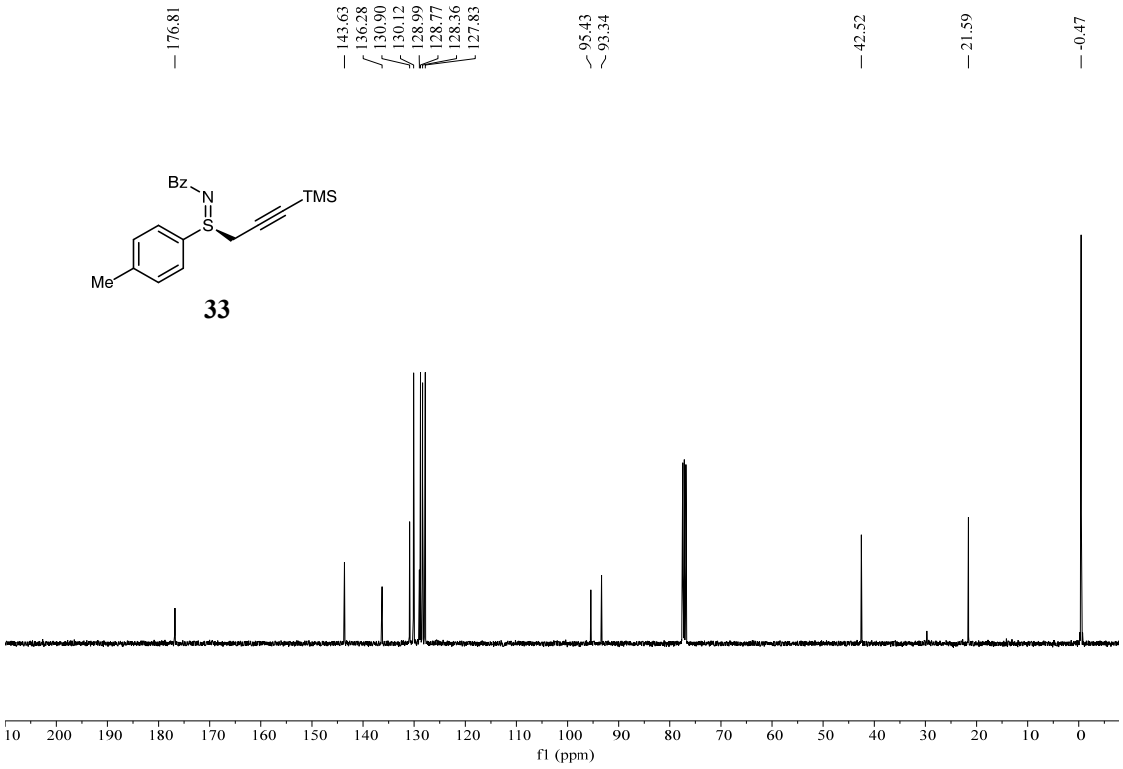
7.71
7.34
7.32
7.30
7.28
7.26
7.24
4.18
4.14
3.75
3.71
2.33
-0.00
Bz
N
S
TMS
Me
2.00
2.03
5.17
0.99
1.02
3.04
8.66
f1 (ppm)

33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128.77
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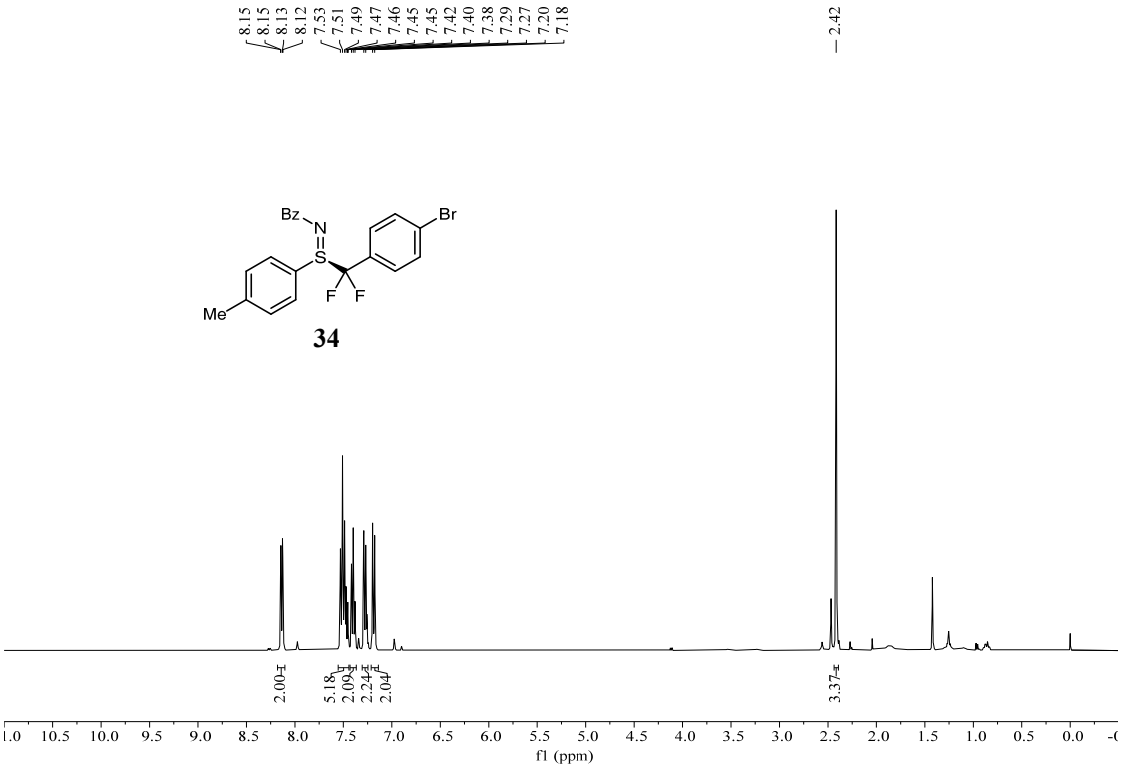
93.34
42.52
21.59
-0.47
Bz
N
S
TMS
Me
f1 (ppm)

33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7.45
7.42
7.40
7.38
7.29
7.27
7.20
7.18
2.42
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Br
F
F
Me
34
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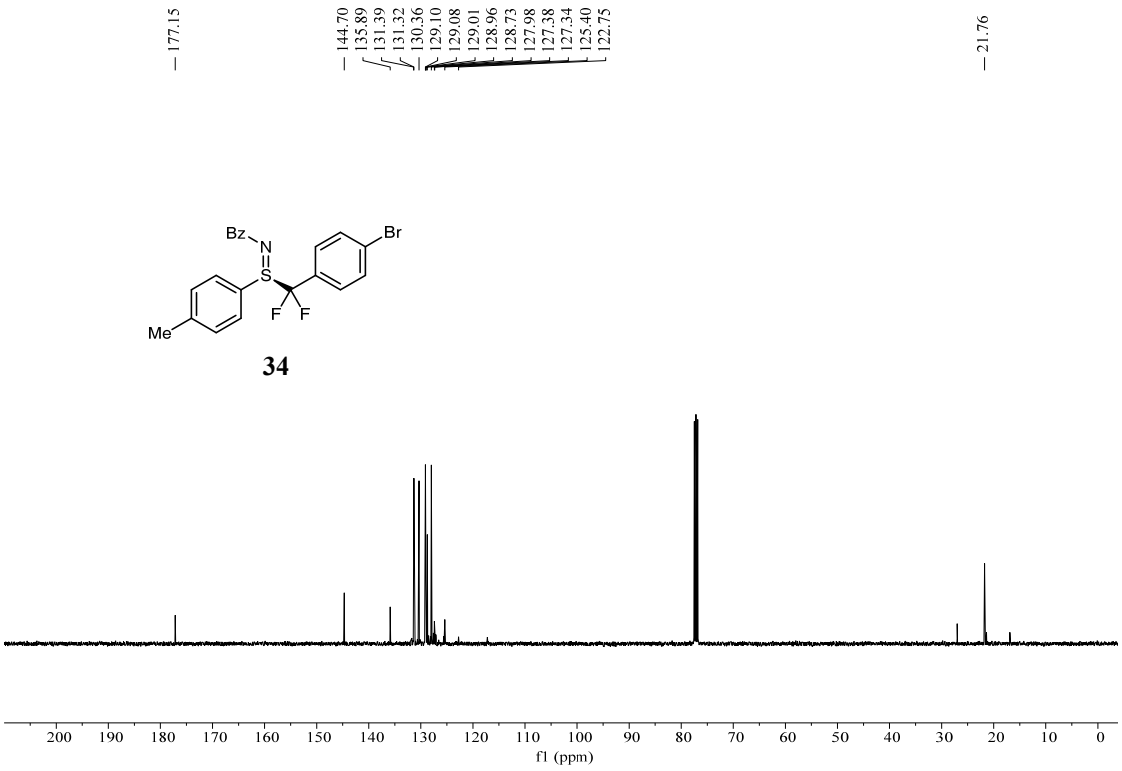
5.18
2.09
2.24
2.04
3.37
fl (ppm)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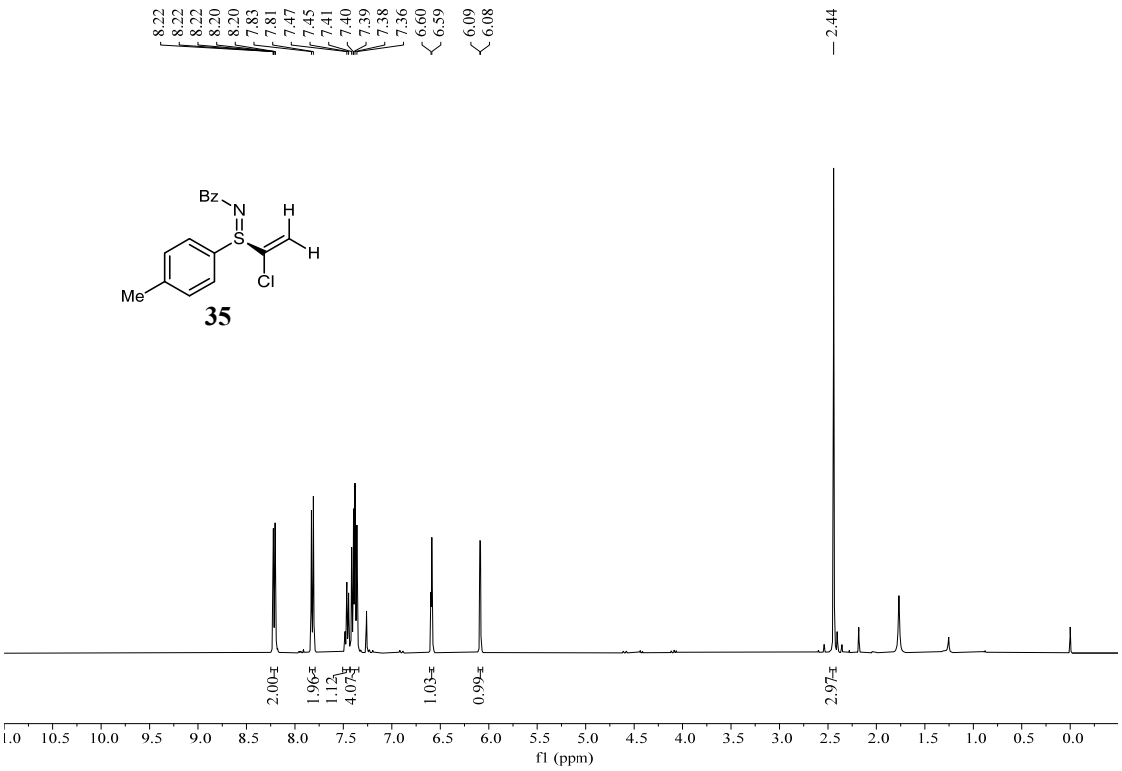
129.08
129.01
128.96
128.73
127.98
127.38
127.34
125.40
122.75
21.76
Bz
N
S
Br
F
F
Me
34
fl (ppm)


-88.73
-89.30
-93.46
-94.03
Bz
N
S
F
F
Br
Me
34
20 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)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7.47
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7.41
7.40
7.39
7.38
7.36
6.60
6.59
6.09
6.08
2.44
Bz
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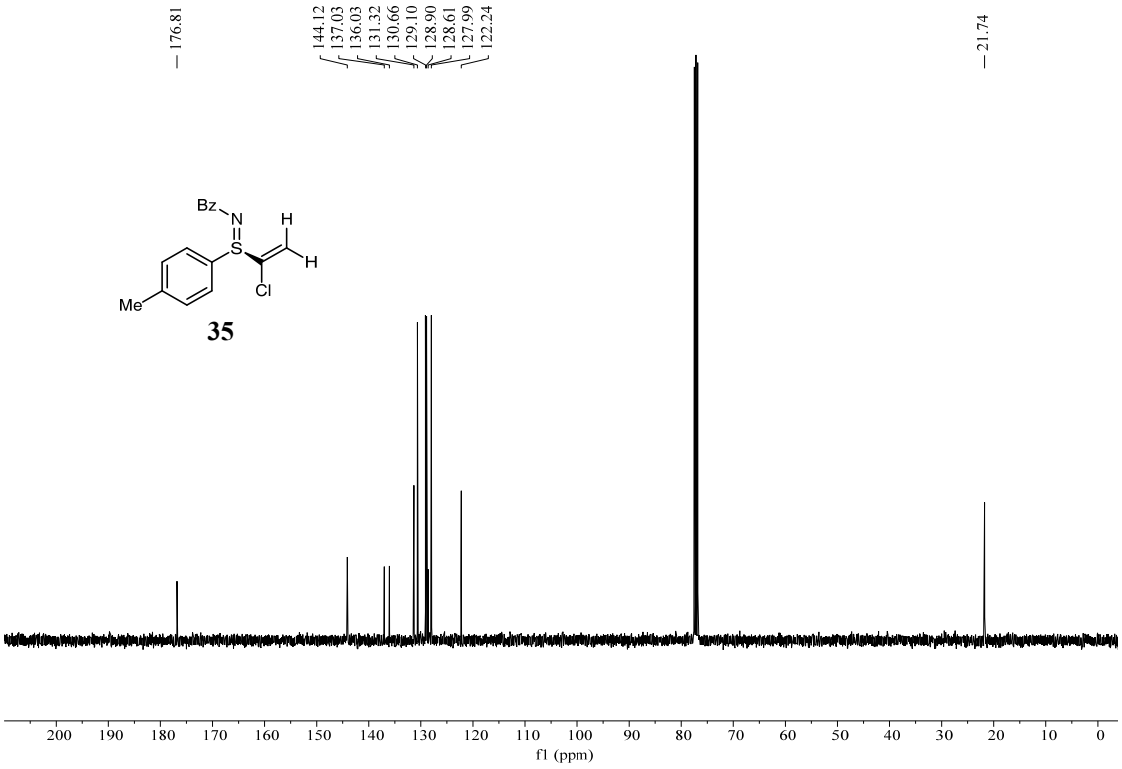
S
H
Cl
Me
35
2.00
1.96
1.12
4.07
1.03
0.99
2.97
fl (ppm)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127.99
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Bz
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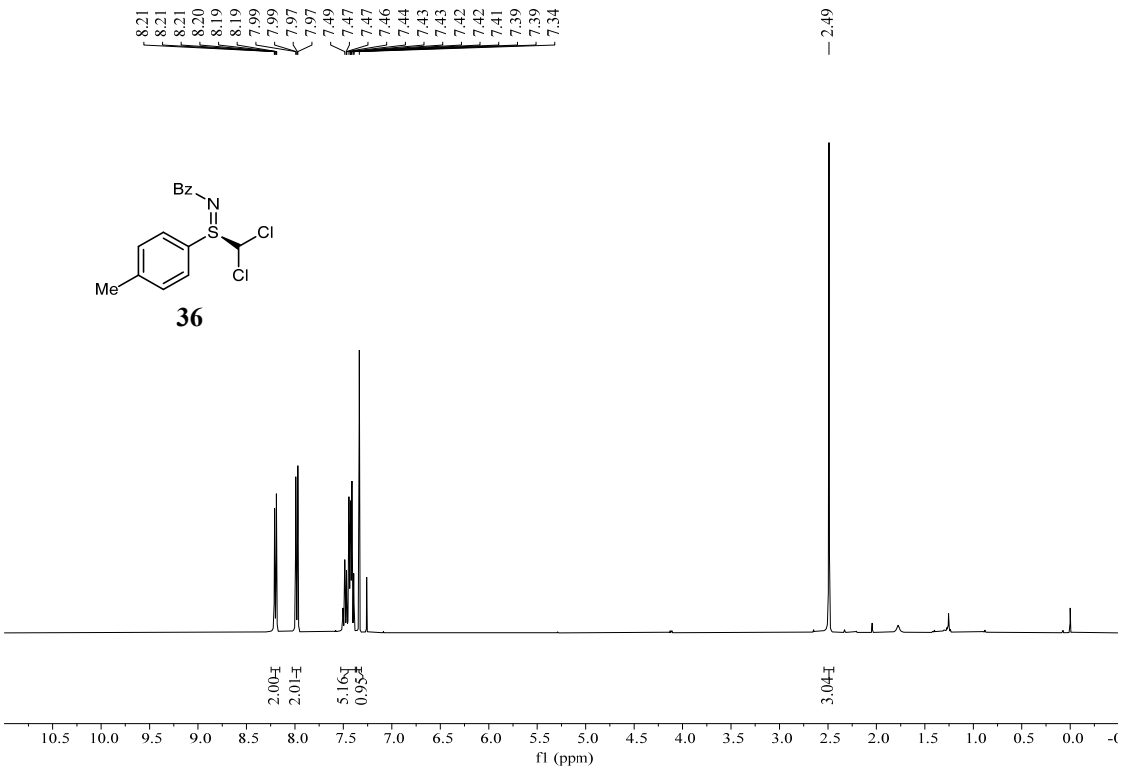
H
S
H
Cl
Me
35
fl (ppm)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7.99
7.97
7.97
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7.47
7.47
7.46
7.44
7.43
7.43
7.42
7.42
7.41
7.39
7.39
7.34
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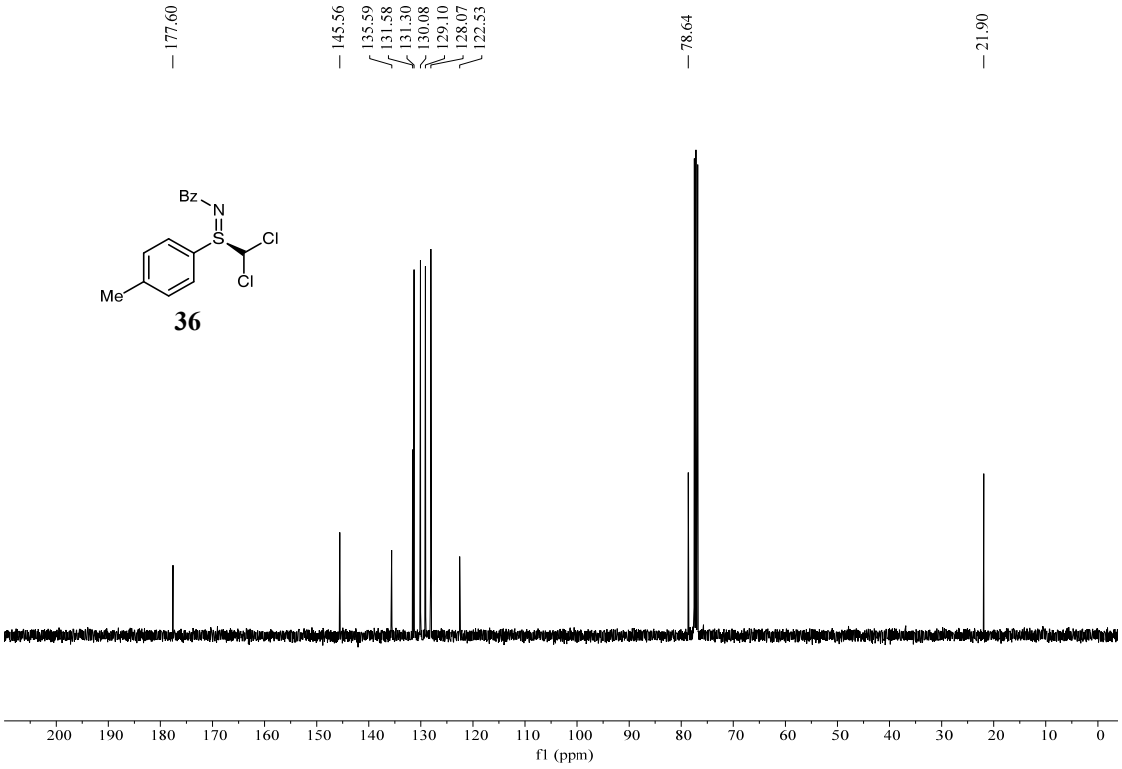
Bz
N
S
Cl
Cl
Me
2.00
2.01
5.16
0.95
3.04
f1 (ppm)

36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145.56
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122.53
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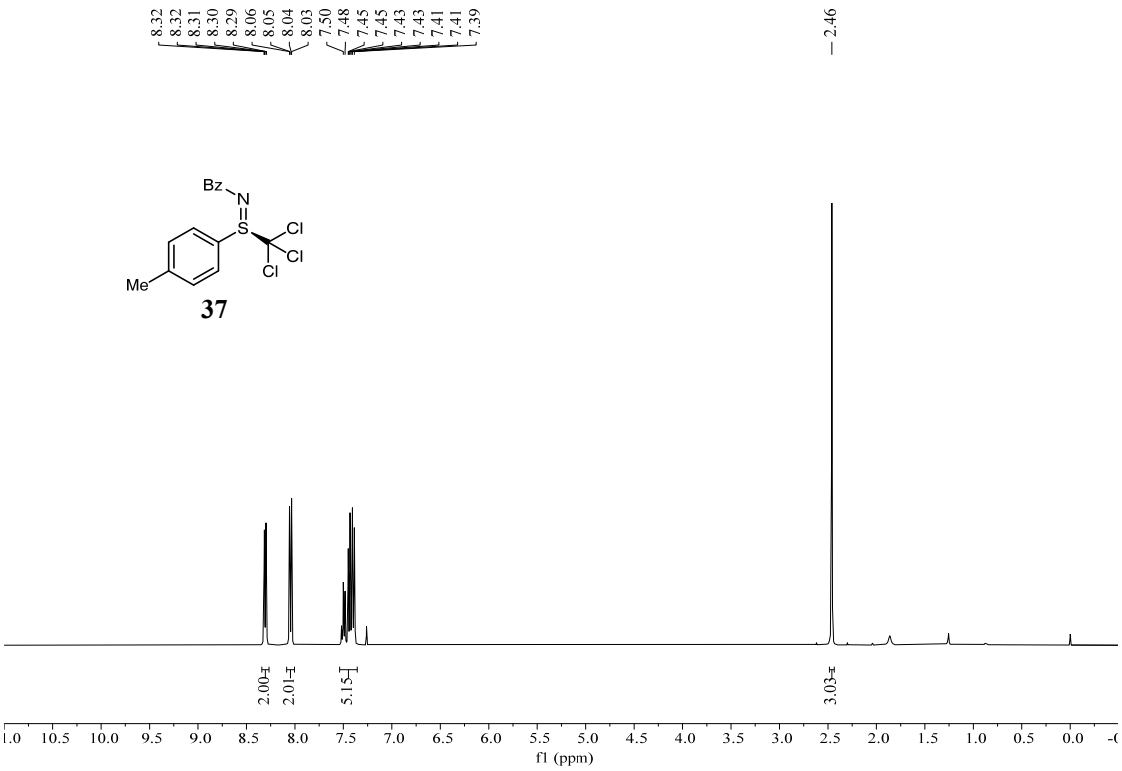
21.90
Bz
N
S
Cl
Cl
Me
f1 (ppm)

36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8.04
8.03
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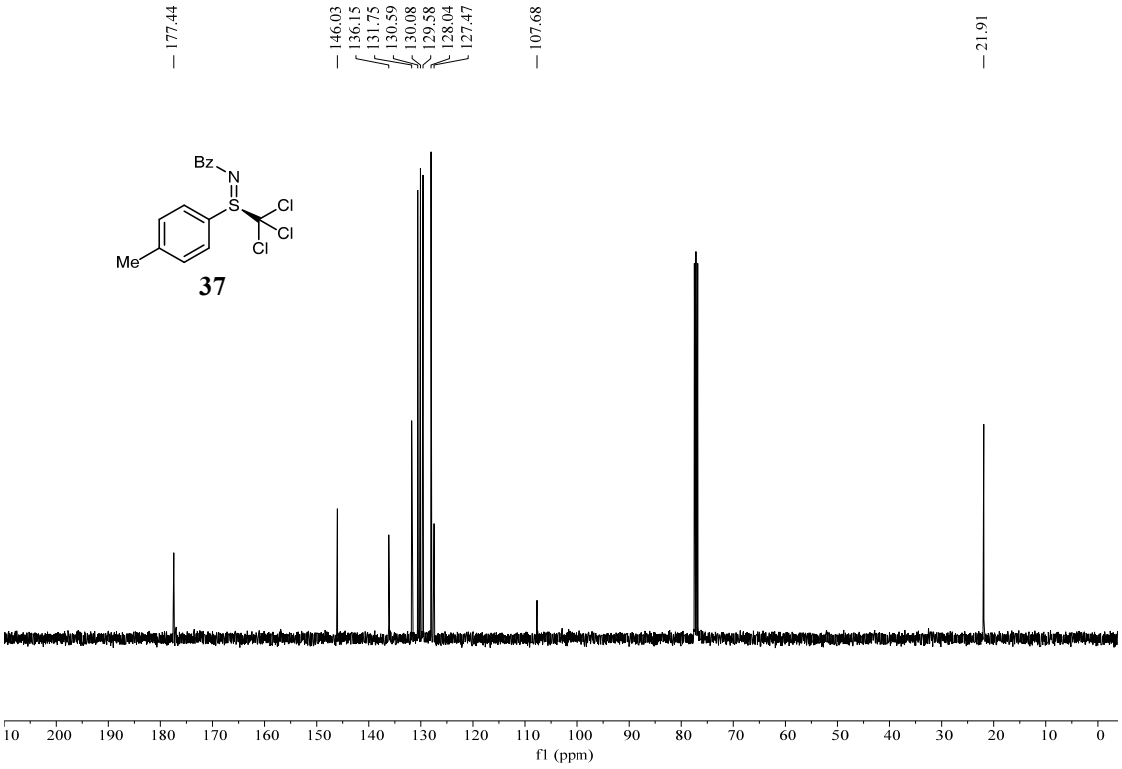
7.48
7.45
7.45
7.43
7.43
7.41
7.41
7.39
2.46
Bz
N
S
Cl
Cl
Cl
Me
37
2.00
2.01
5.15
3.03
f1 (ppm)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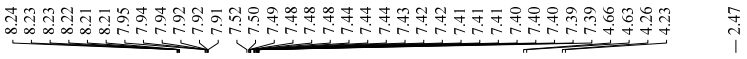
131.75
130.59
130.08
129.58
128.04
127.47
107.68
21.91
Bz
N
S
Cl
Cl
Cl
Me
37
f1 (ppm)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7.94
7.94
7.92
7.92
7.91
7.52
7.50
7.49
7.48
7.48
7.48
7.44
7.44
7.44
7.43
7.42
7.42
7.41
7.41
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7.40
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7.39
7.39
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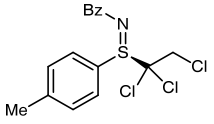
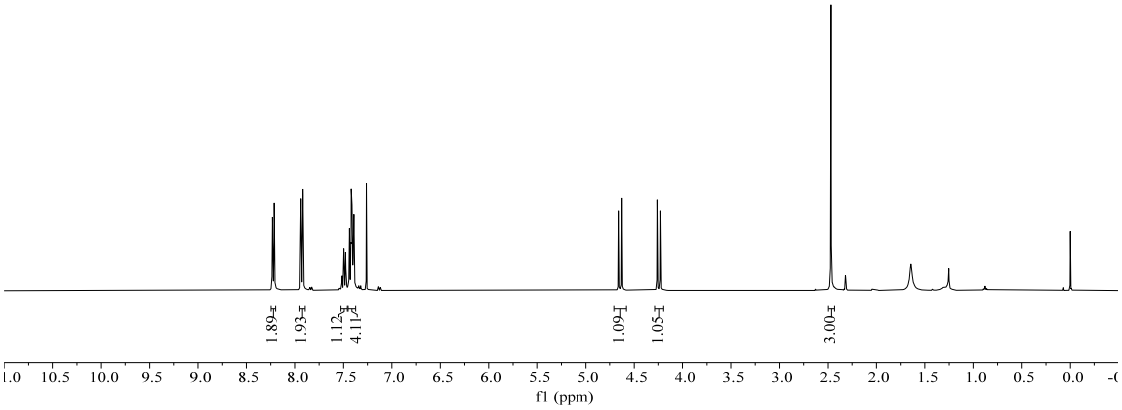
4.63
4.26
4.23
2.47


Bz
N
S
Cl
Cl
Cl
Me

38


1.89
1.93
1.12
4.11
1.09
1.05
3.00
f1 (ppm)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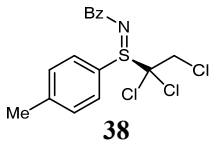
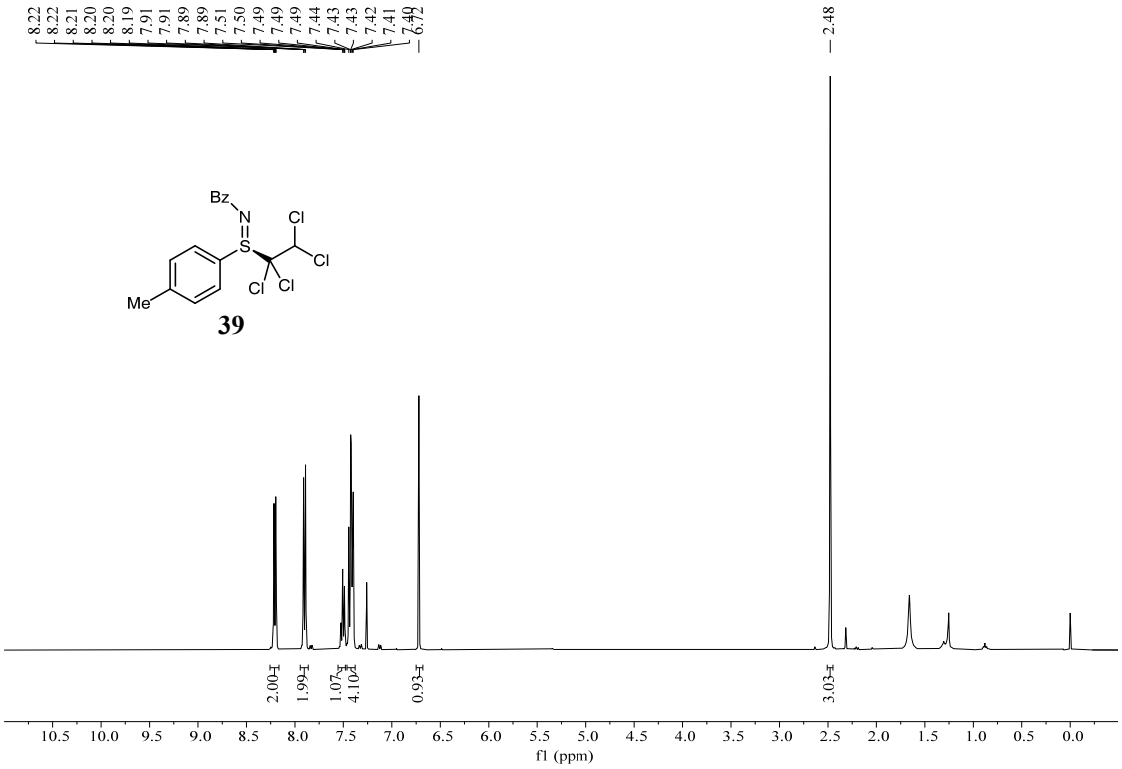
130.12
129.34
128.08
125.63
100.35
52.37
21.88


Bz
N
S
Cl
Cl
Cl
Me

38

f1 (ppm)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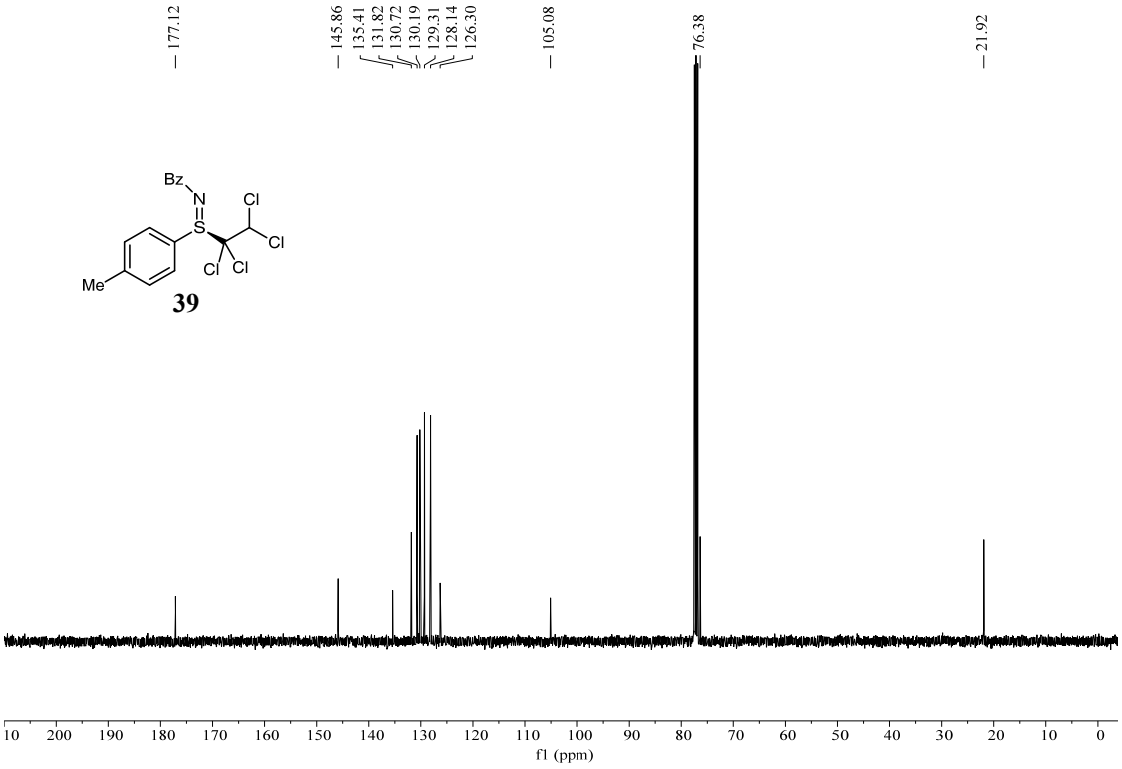
7.49
7.49
7.49
7.44
7.43
7.43
7.42
7.41
7.40
6.92
2.48
Bz
N
S
Cl
Cl
Cl
Cl
Me
39
2.00
1.99
1.07
4.10
0.93
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.41
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130.72
130.19
129.31
128.14
126.30
105.08
76.38
21.92
Bz
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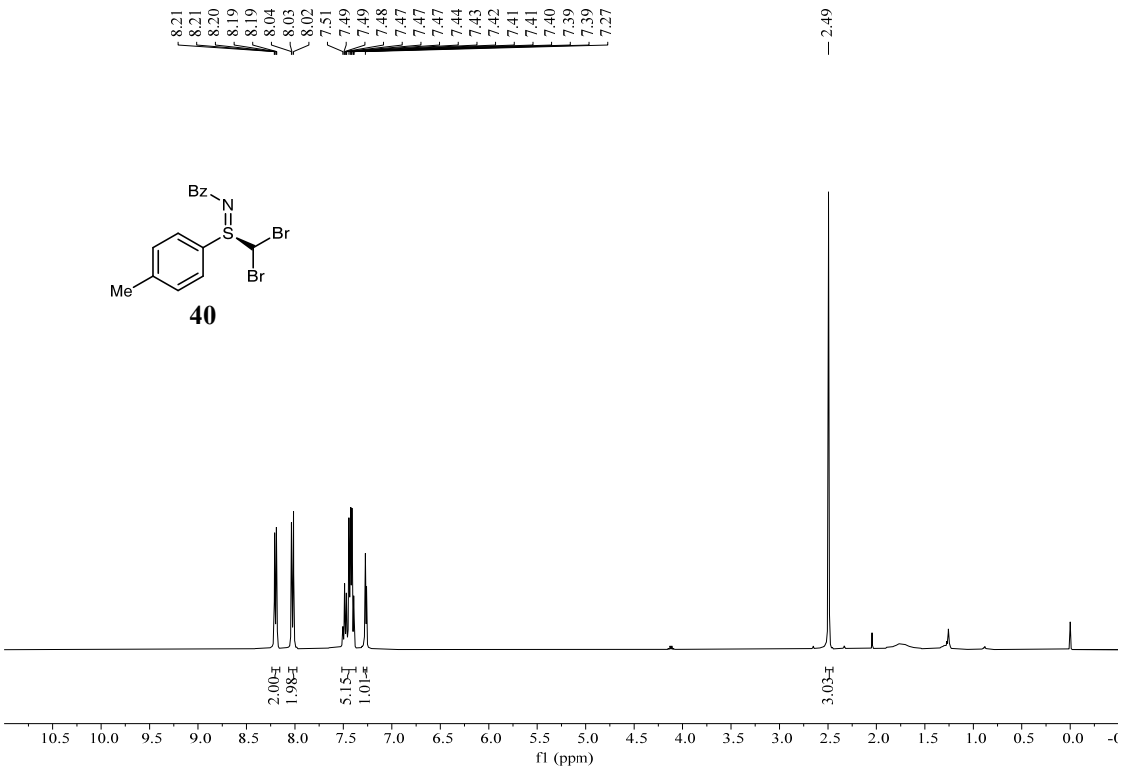
S
Cl
Cl
Cl
Cl
Me
39
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.19
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8.02
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7.49
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7.44
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.27
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Bz
N
S
Br
Br
Me
40
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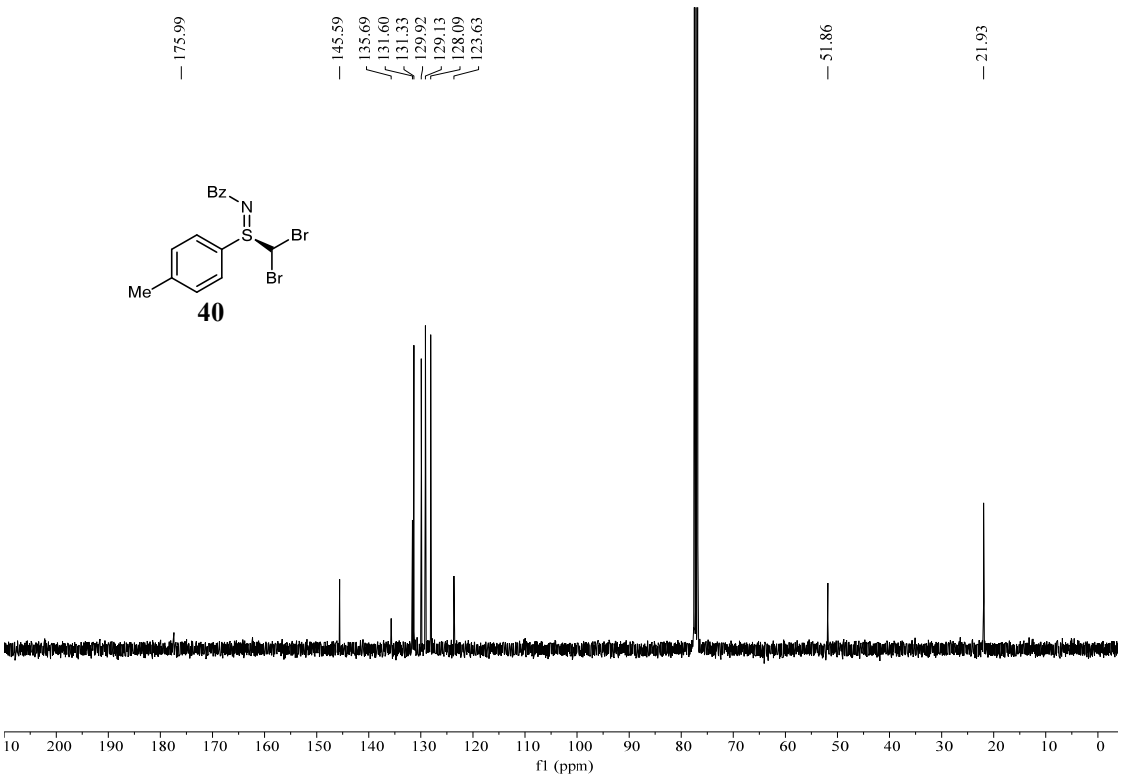
1.98
5.15
1.01
3.03
fl (ppm)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128.09
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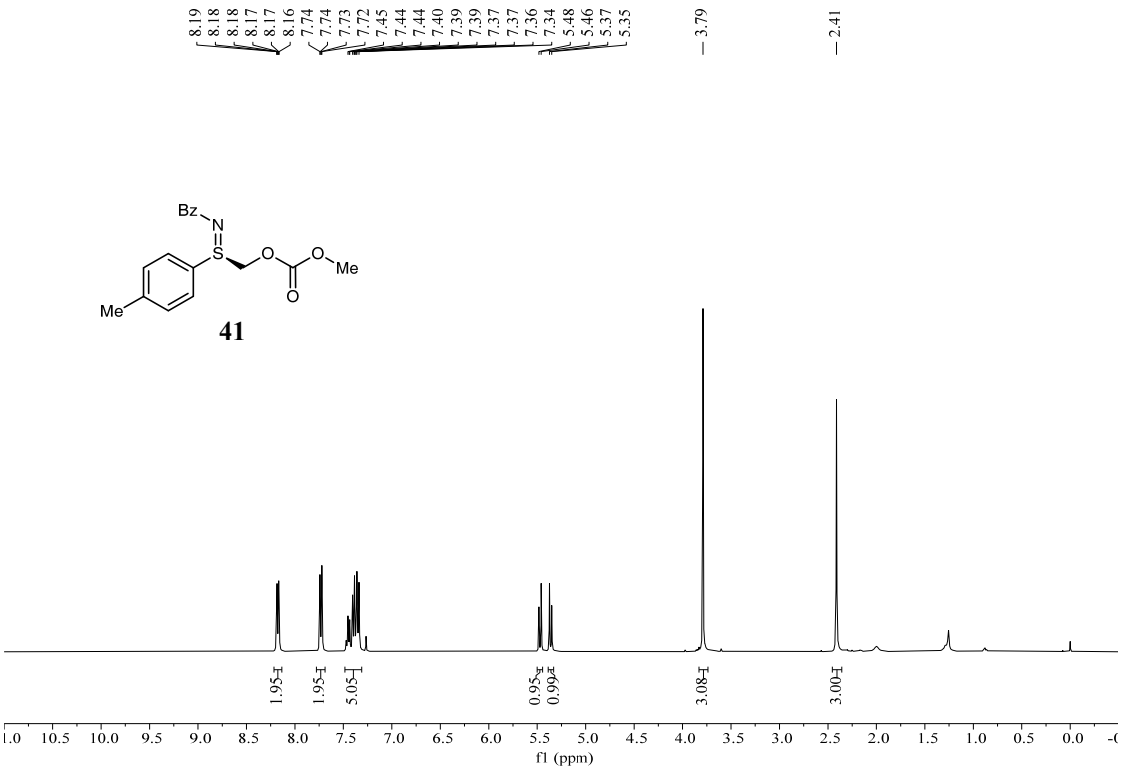
51.86
21.93
Bz
N
S
Br
Br
Me
40
fl (ppm)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8.16
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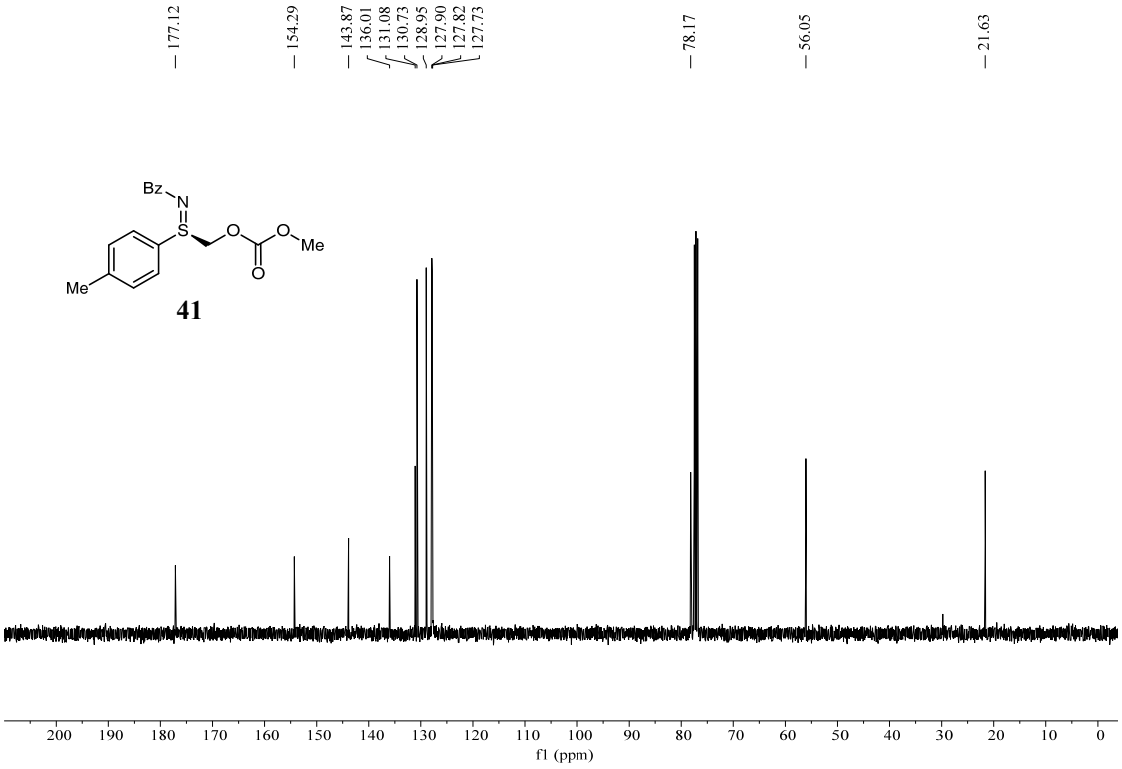
7.73
7.72
7.45
7.44
7.44
7.40
7.39
7.39
7.37
7.37
7.36
7.34
5.48
5.46
5.37
5.35
3.79
2.41
Bz
N
S
O
O
O
Me
Me
41
1.95
1.95
5.05
0.95
0.99
3.08
3.00
f1 (ppm)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154.29
143.87
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128.95
127.90
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127.73
78.17
56.05
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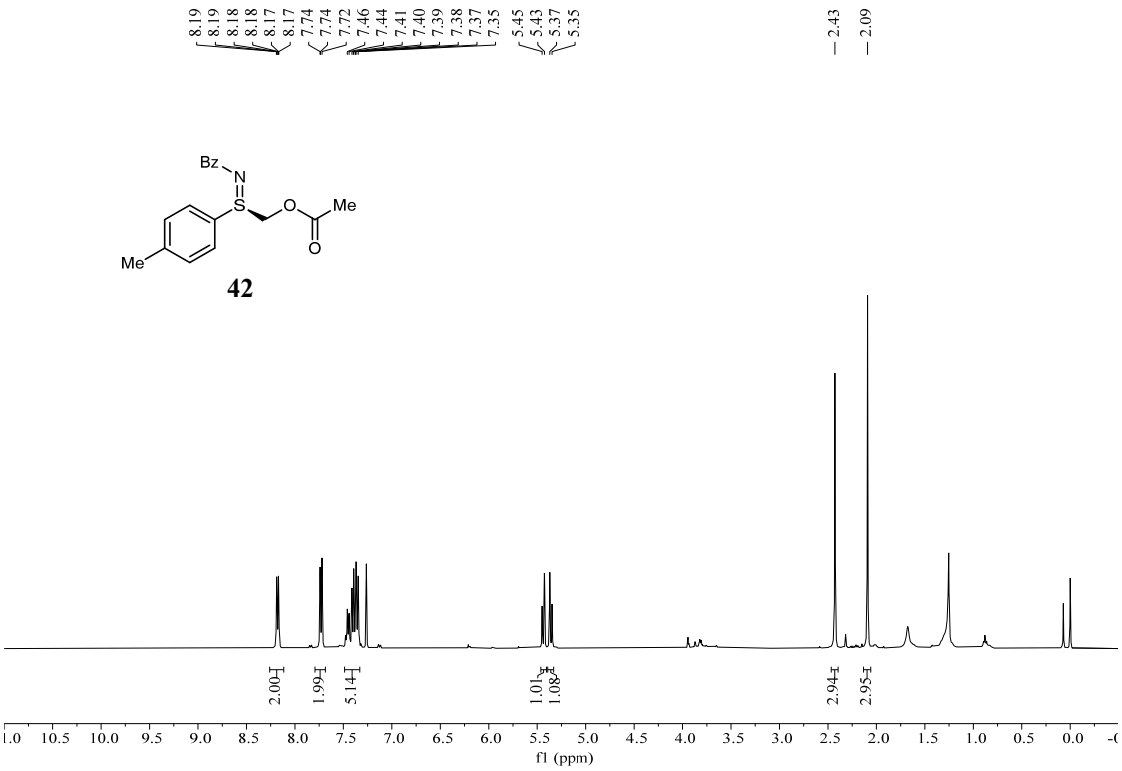
Bz
N
S
O
O
O
Me
Me
41
f1 (ppm)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7.41
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7.39
7.38
7.37
7.35
5.45
5.43
5.37
5.35
2.43
2.09
Bz
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O
Me
O
Me
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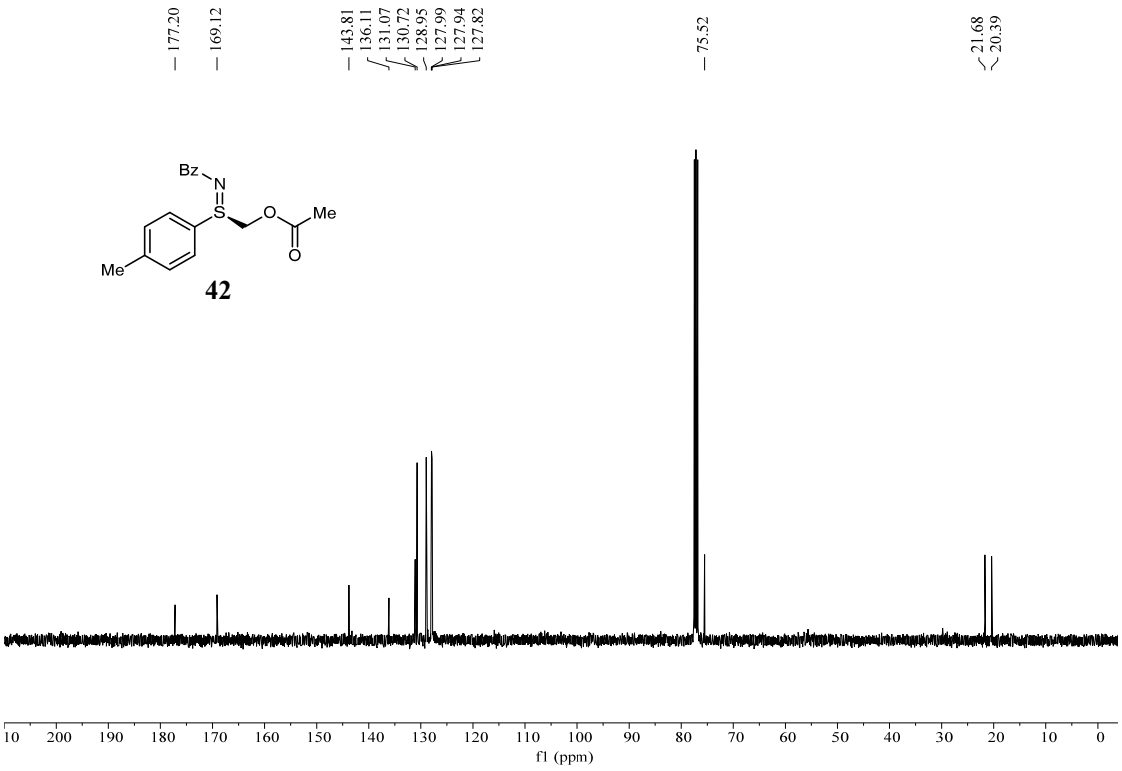
1.99
5.14
1.01
1.08
2.94
2.95
f1 (ppm)

42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127.94
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75.52
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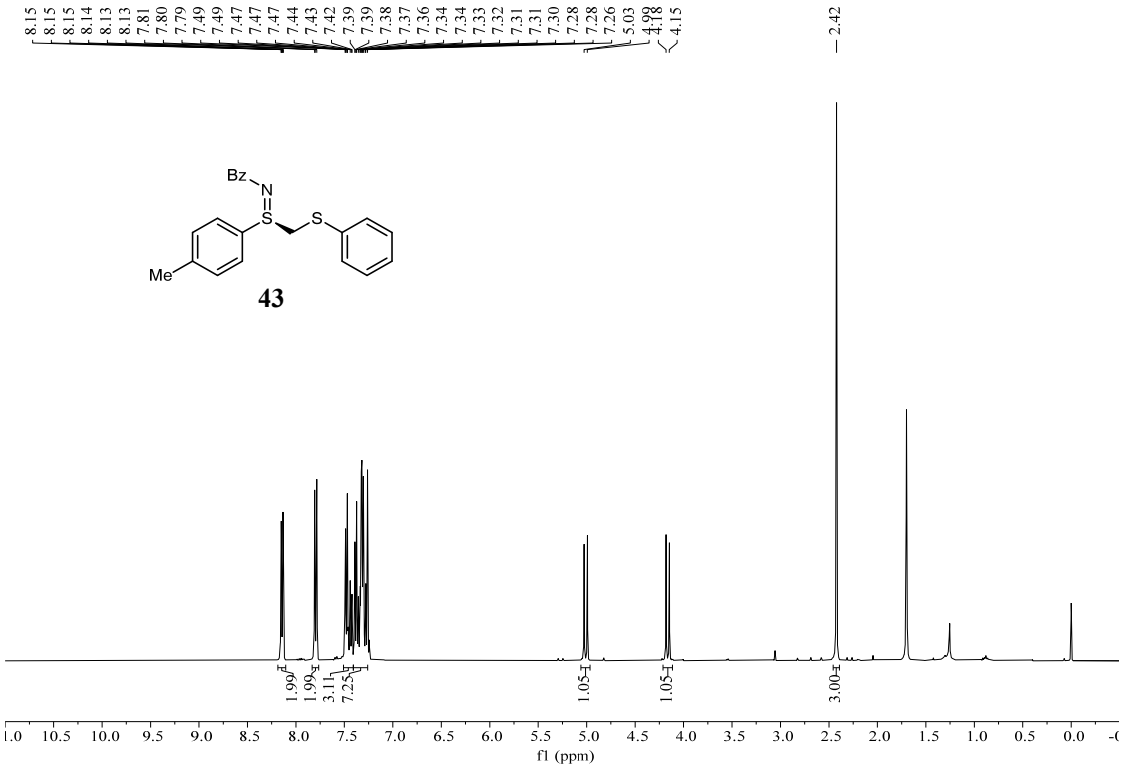
20.39
Bz
N
S
O
Me
O
Me
f1 (ppm)

42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7.39
7.39
7.38
7.37
7.36
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.28
7.28
7.26
5.03
4.99
4.18
4.15
2.42
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Me
43
1.99
1.99
3.11
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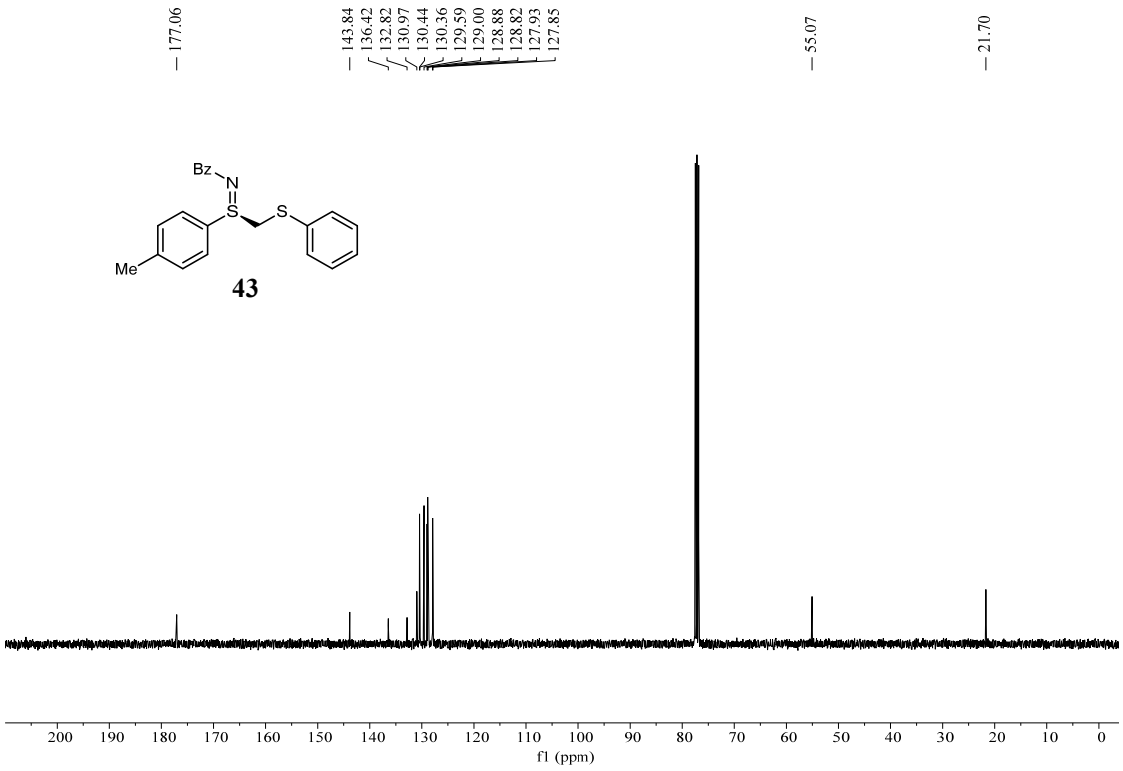
1.05
1.05
3.00
f1 (ppm)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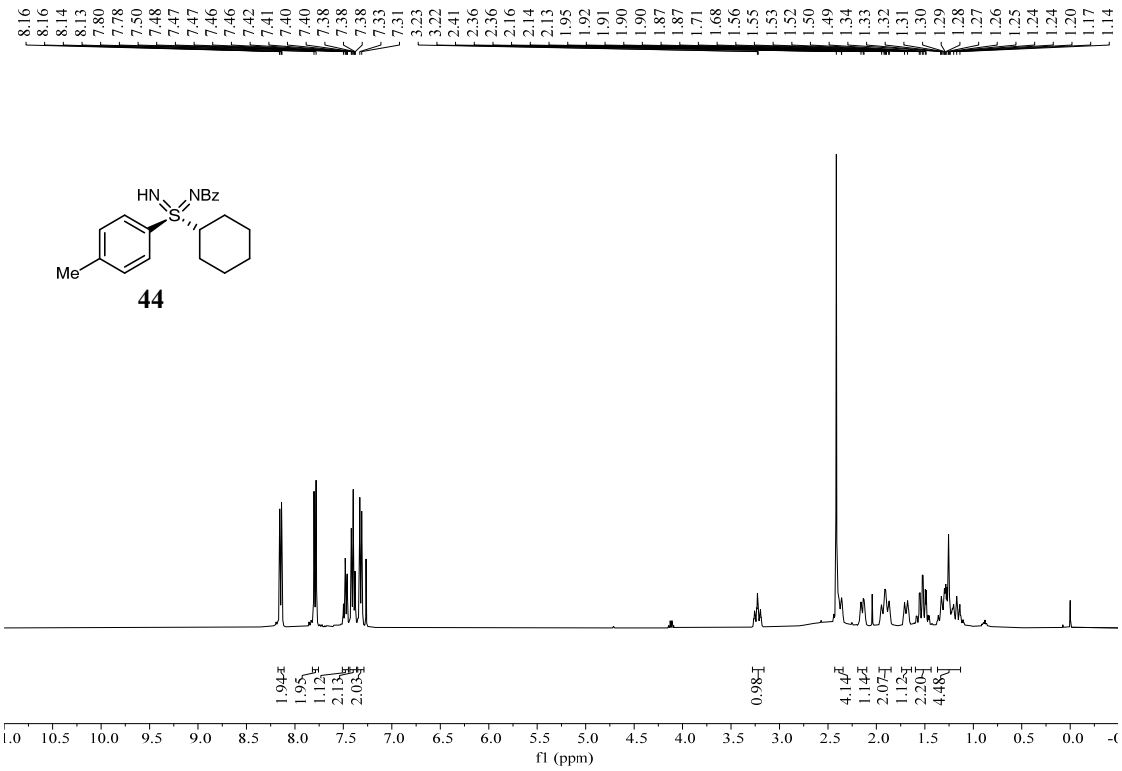
127.93
127.85
55.07
21.70
Bz
N
S
S
Me
43
f1 (ppm)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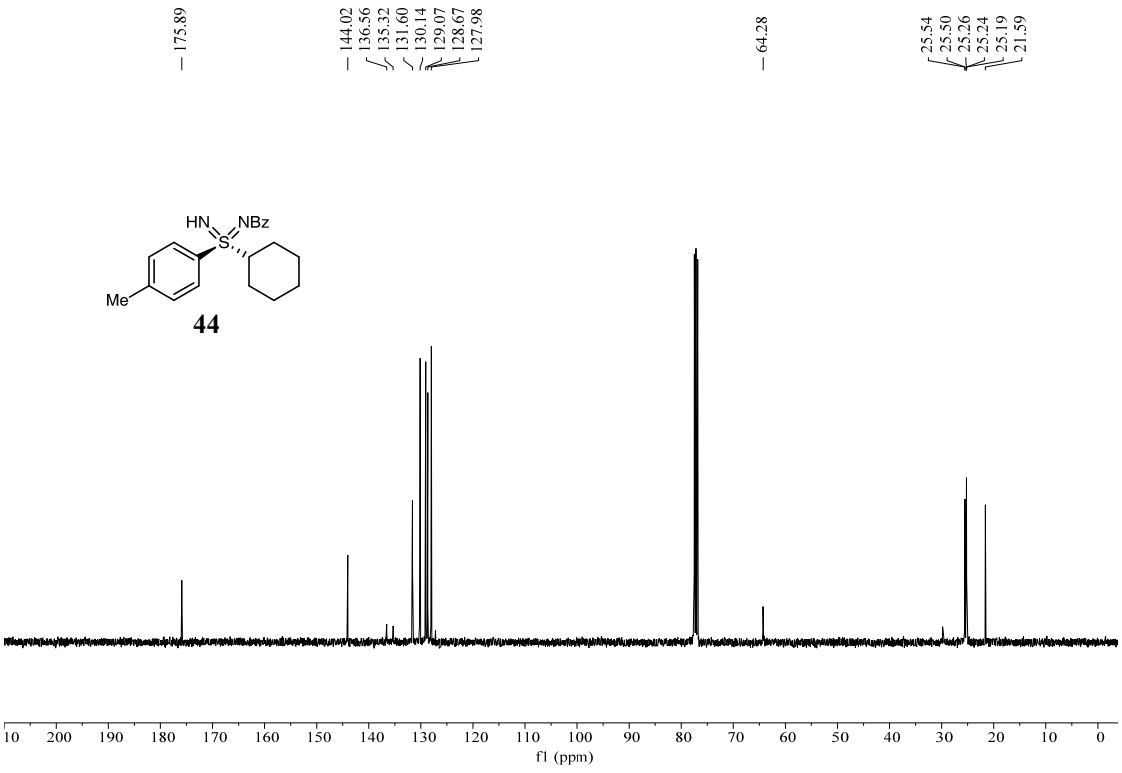
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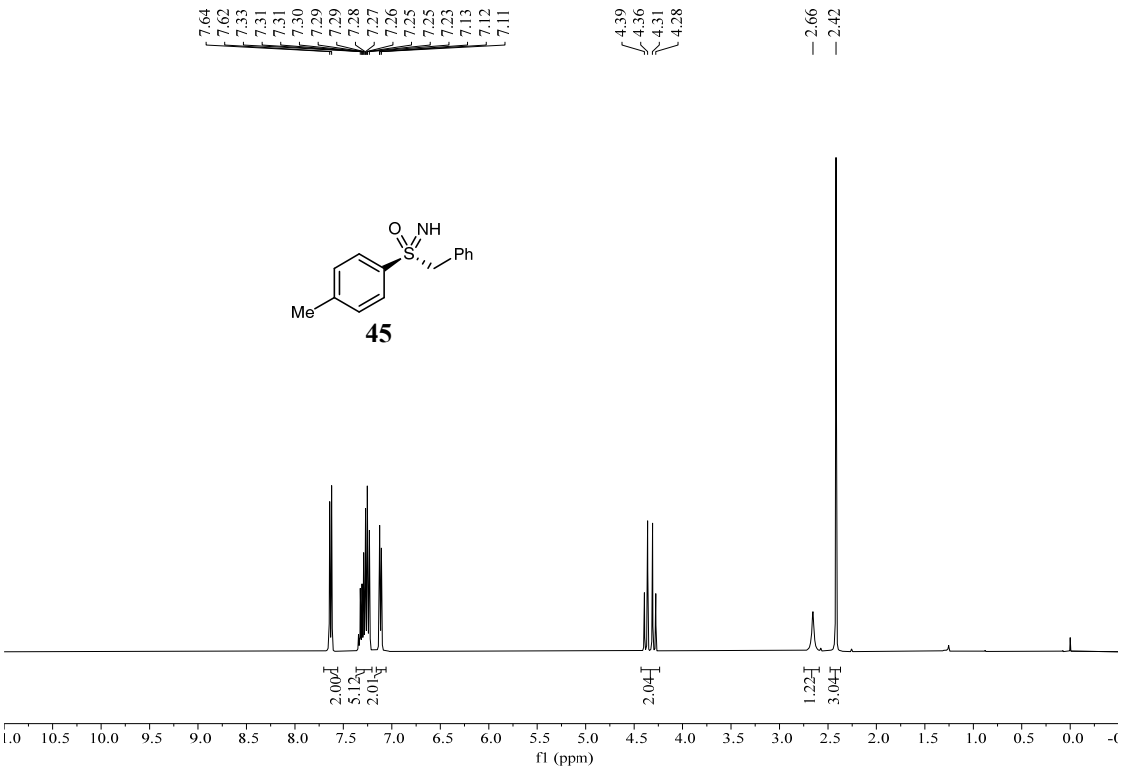
f1 (ppm)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7.23
7.13
7.12
7.11
4.39
4.36
4.31
4.28
2.66
2.42
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S
Ph
Me
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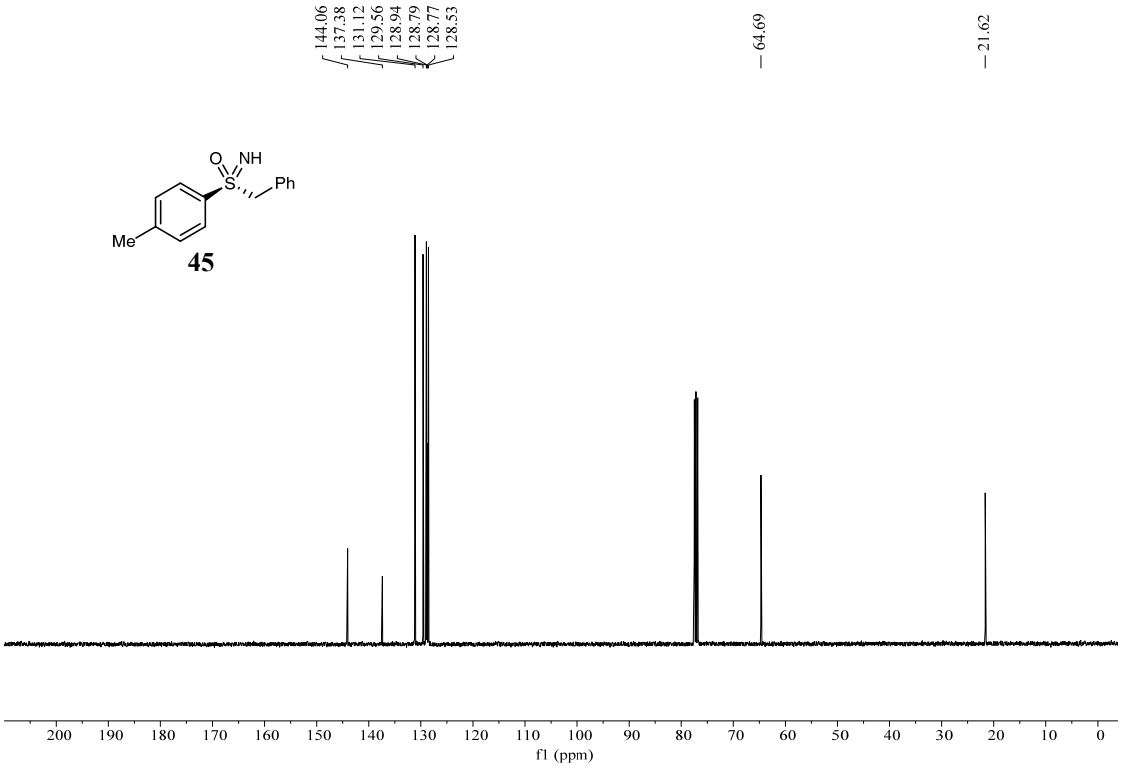
5.12
2.01
2.04
1.22
3.04
f1 (ppm)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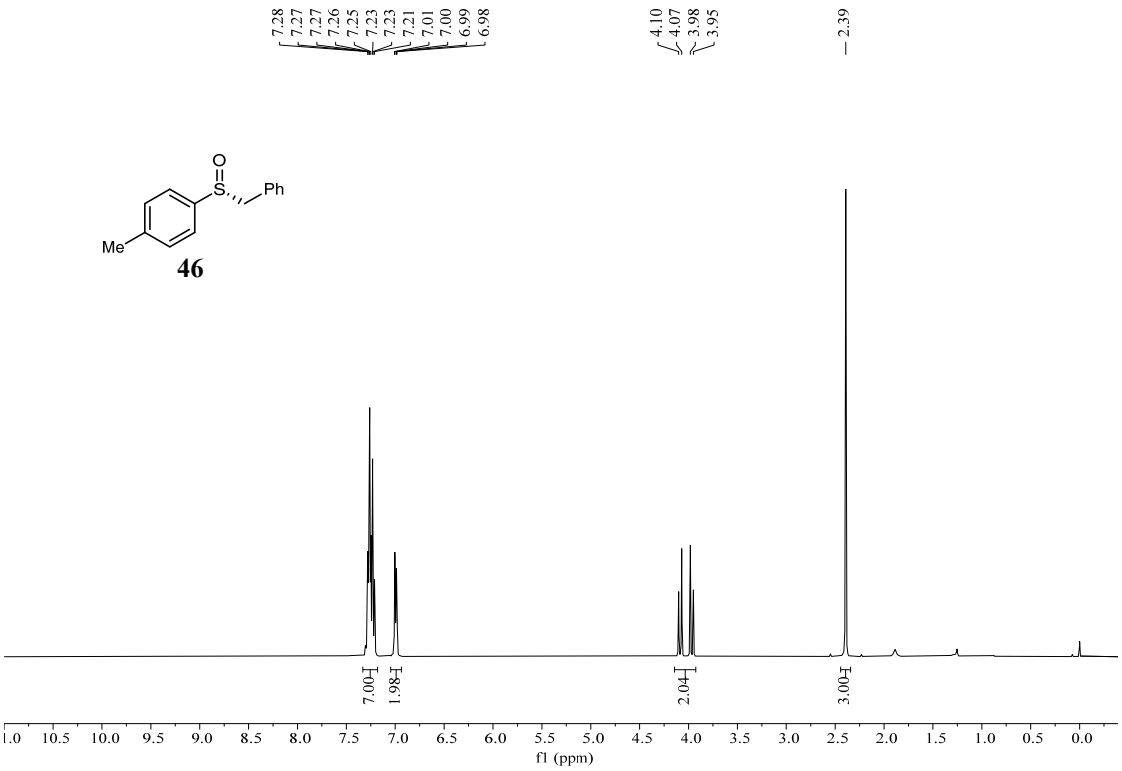
128.79
128.77
128.53
64.69
21.62
O
NH
S
Ph
Me
45
f1 (ppm)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7.23
7.21
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7.00
6.99
6.98
4.10
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2.39
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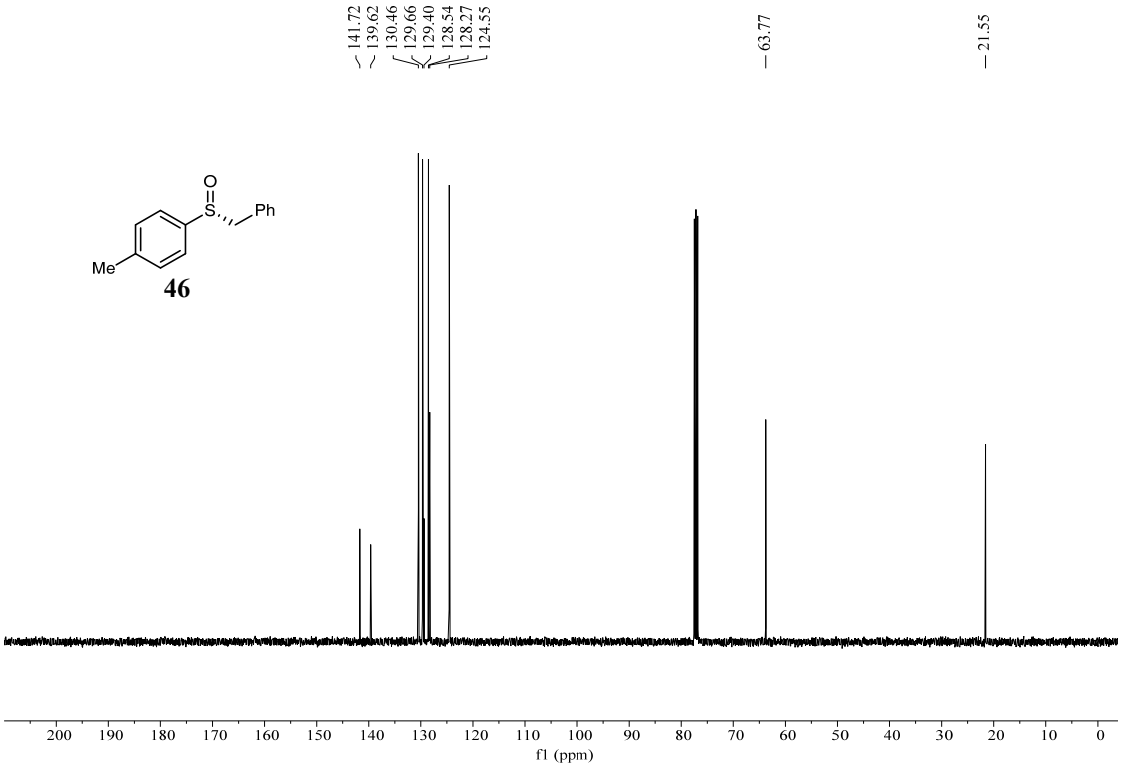
S
Ph
Me
46
7.00
1.98
2.04
3.00
f1 (ppm)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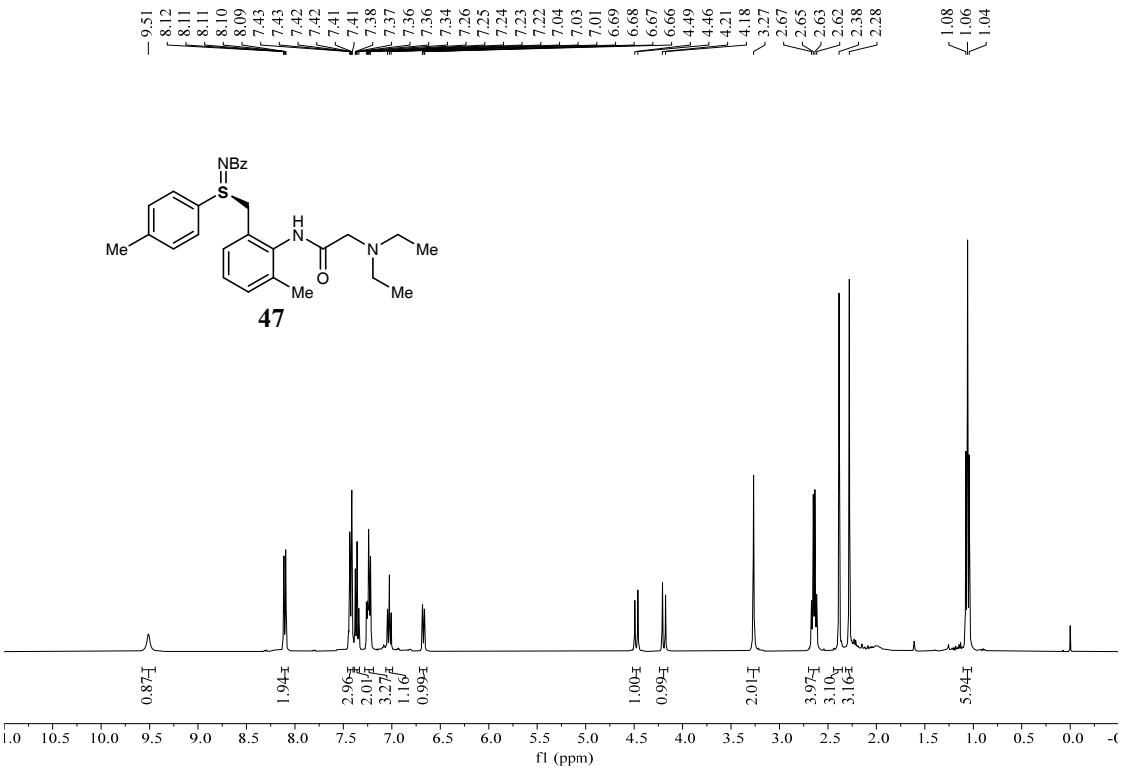
128.27
124.55
63.77
21.55
O
S
Ph
Me
46
f1 (ppm)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7.41
7.41
7.38
7.37
7.36
7.36
7.34
7.26
7.25
7.24
7.23
7.22
7.04
7.03
7.01
6.69
6.68
6.67
6.66
4.49
4.46
4.21
4.18
3.27
2.67
2.65
2.63
2.62
2.38
2.28
1.08
1.06
1.04
NBz
S
H
N
O
Me
Me
Me
Me
Me
47
0.87
1.94
2.96
2.01
3.27
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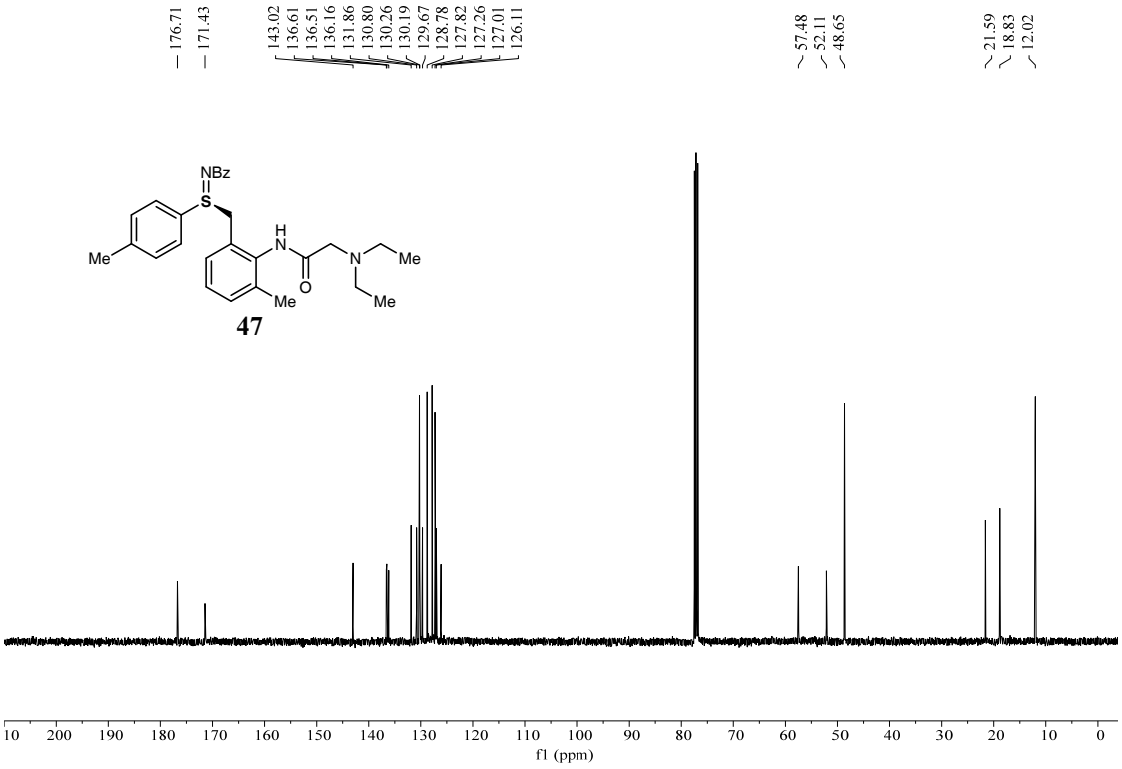
0.99
1.00
0.99
2.01
3.97
3.10
3.16
5.94
f1 (ppm)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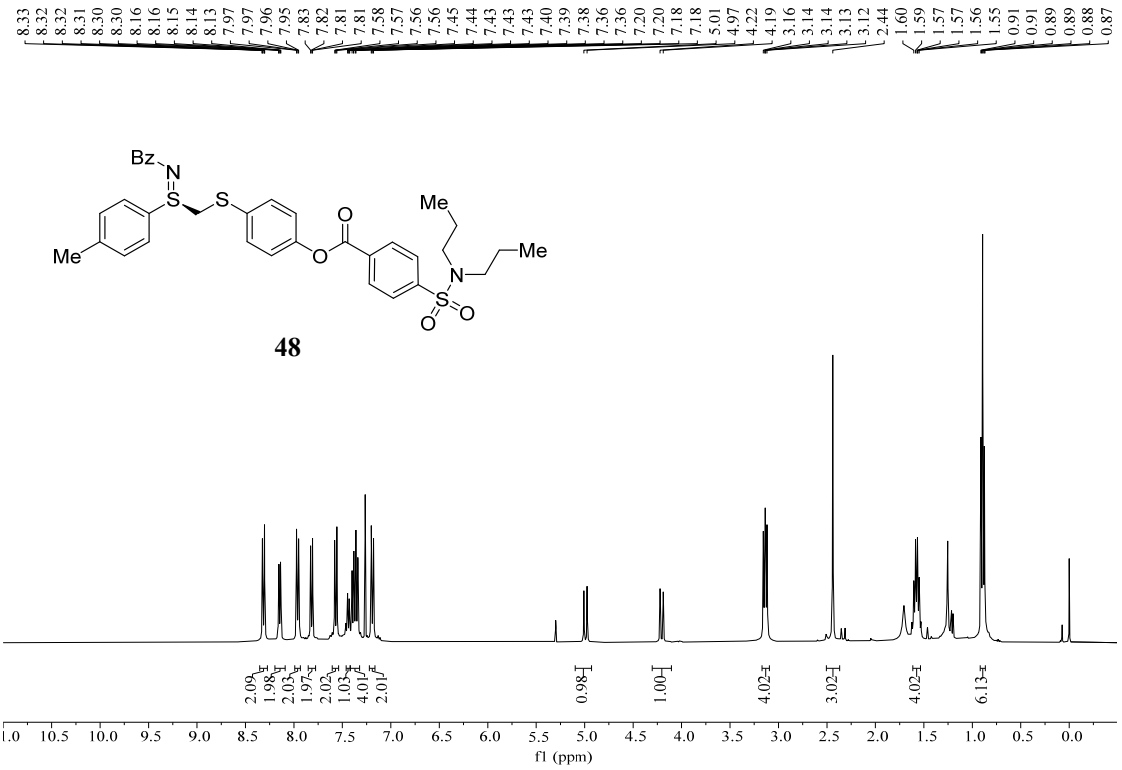
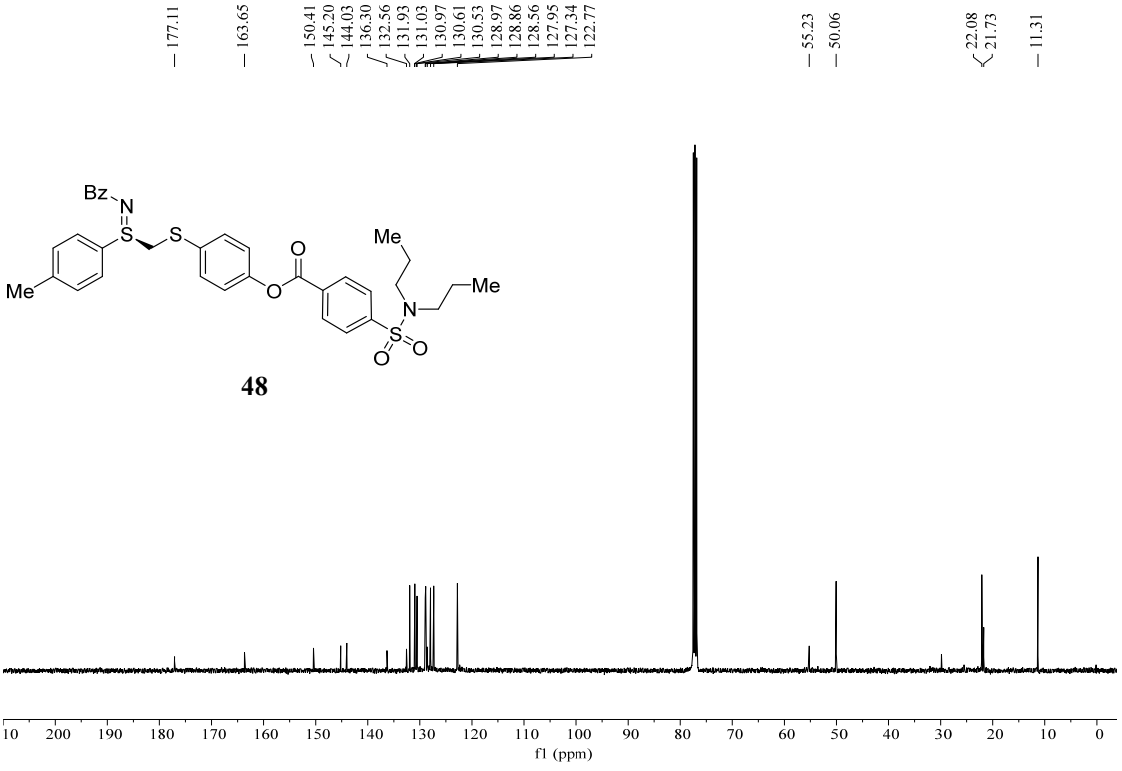
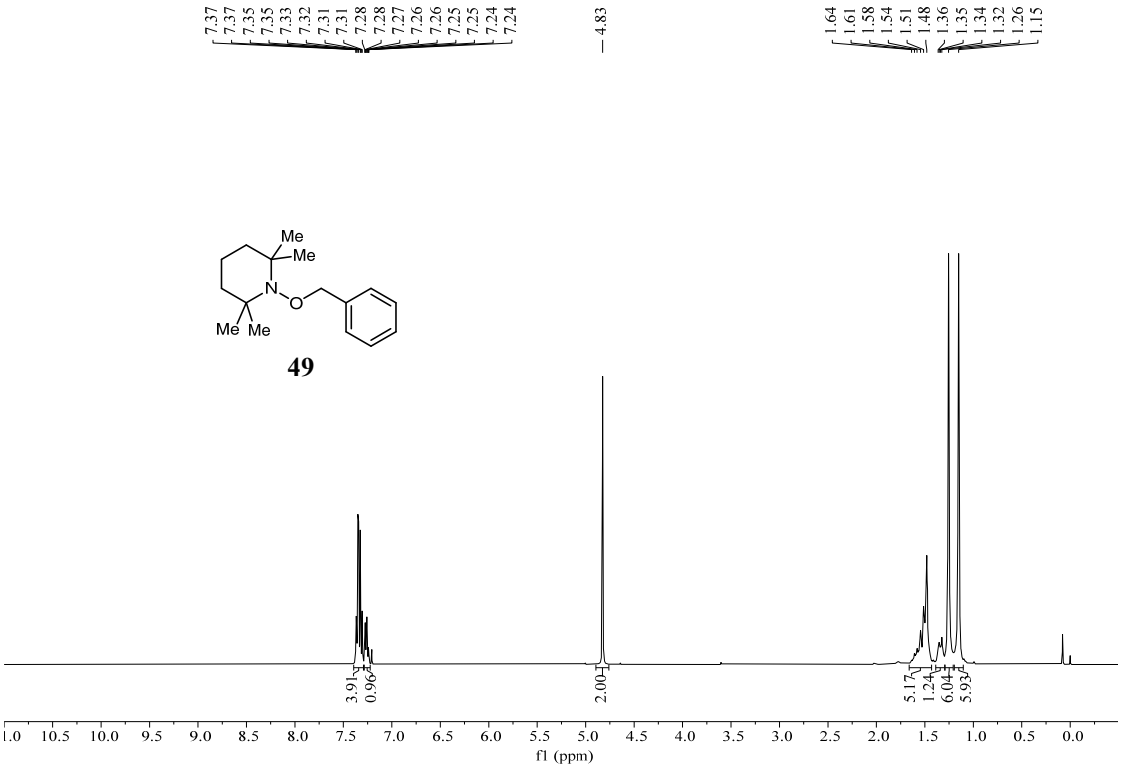
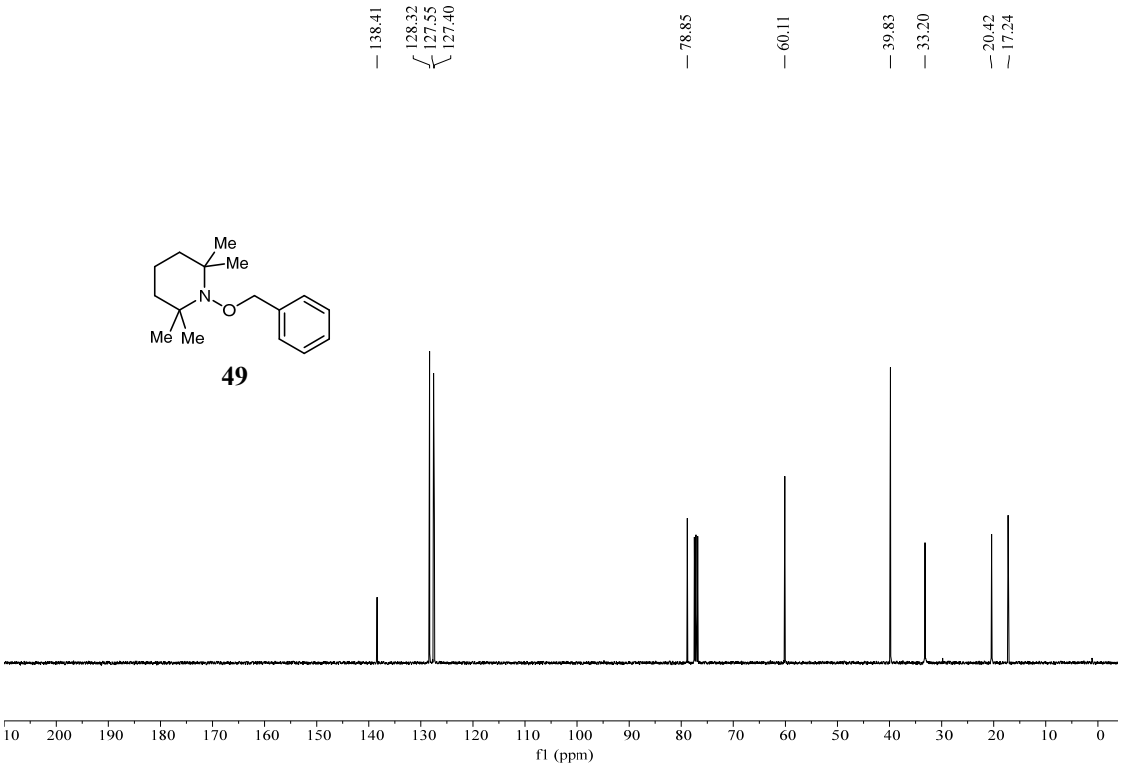
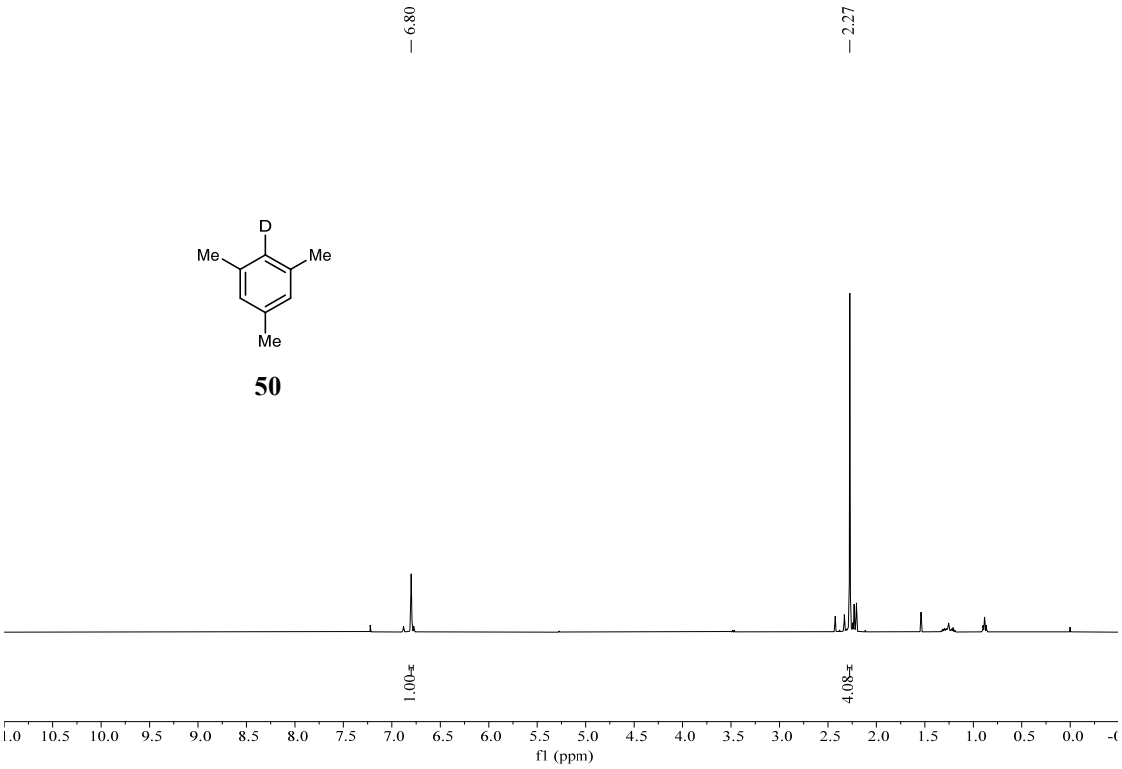
127.82
127.26
127.01
126.11
57.48
52.11
48.65
21.59
18.83
12.02
NBz
S
H
N
O
Me
Me
Me
Me
47
f1 (ppm)


8.33 8.32 8.32 8.31 8.30 8.30 8.16 8.16 8.15 8.14 8.13 7.97 7.97 7.96 7.95 7.83 7.82 7.81 7.81 7.58 7.57 7.56 7.56 7.45 7.44 7.43 7.43 7.43 7.40 7.39 7.38 7.36 7.36 7.20 7.20 7.18 7.18 5.01 4.97 4.22 4.19 3.16 3.14 3.14 3.13 3.12 2.44 1.60 1.59 1.57 1.57 1.56 1.55 0.91 0.91 0.89 0.89 0.88 0.87
Bz
N
S
S
Me
O
O
Me
N
Me
S
O
O
48
2.09 1.98 2.03 1.97 2.02 1.03 4.01 2.01 0.98 1.00 4.02 3.02 4.02 6.13
f1 (ppm)

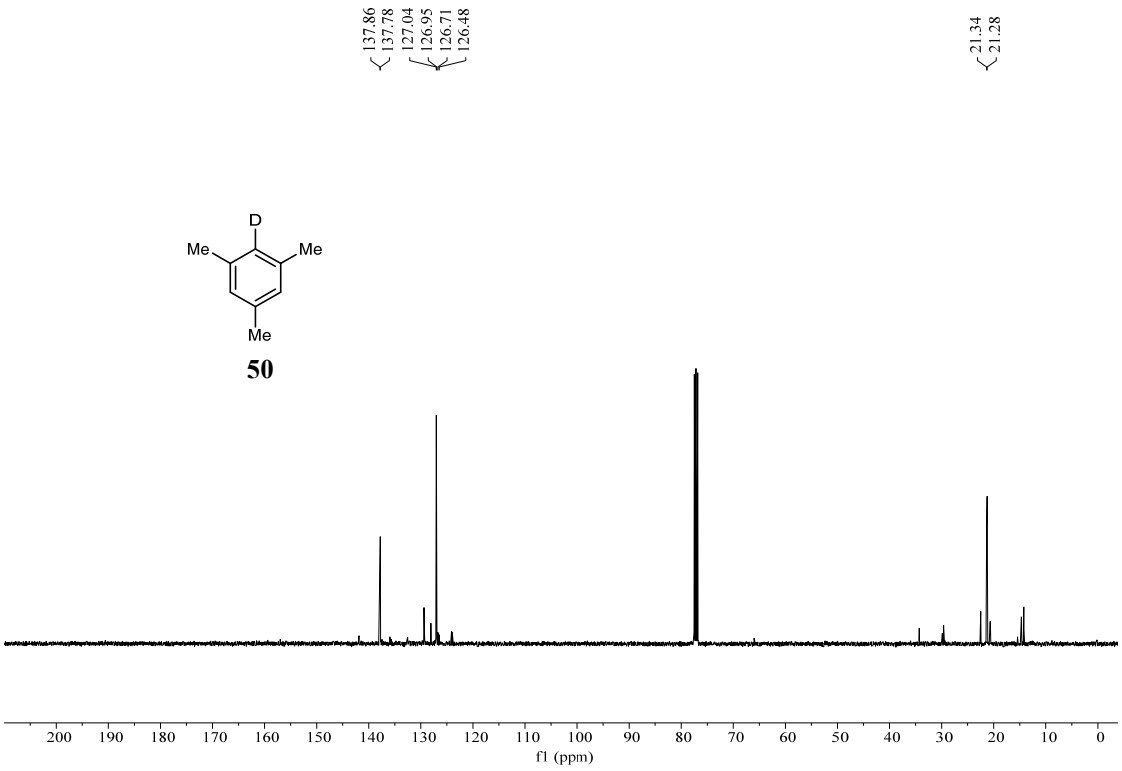

177.11 163.65 150.41 145.20 144.03 136.30 132.56 131.93 131.03 130.97 130.61 130.53 128.97 128.86 128.56 127.95 127.34 122.77 55.23 50.06 22.08 21.73 11.31
Bz
N
S
S
Me
O
O
Me
N
Me
S
O
O
48
f1 (ppm)


7.37
7.37
7.35
7.35
7.33
7.32
7.31
7.31
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
4.83
1.64
1.61
1.58
1.54
1.51
1.48
1.36
1.35
1.34
1.32
1.26
1.15
Me
Me
N
O
Me
Me
49
3.91
0.96
2.00
5.17
1.24
6.04
5.93
f1 (ppm)

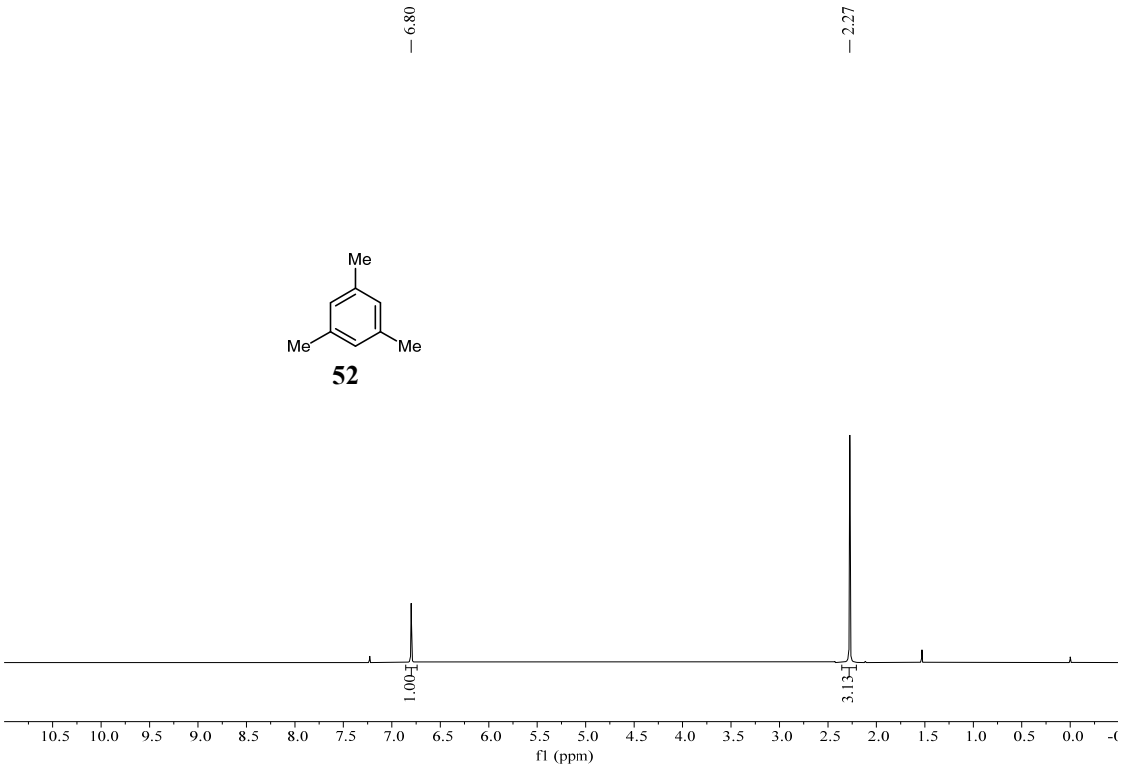

138.41
128.32
127.55
127.40
78.85
60.11
39.83
33.20
20.42
17.24
Me
Me
N
O
Me
Me
49
f1 (ppm)

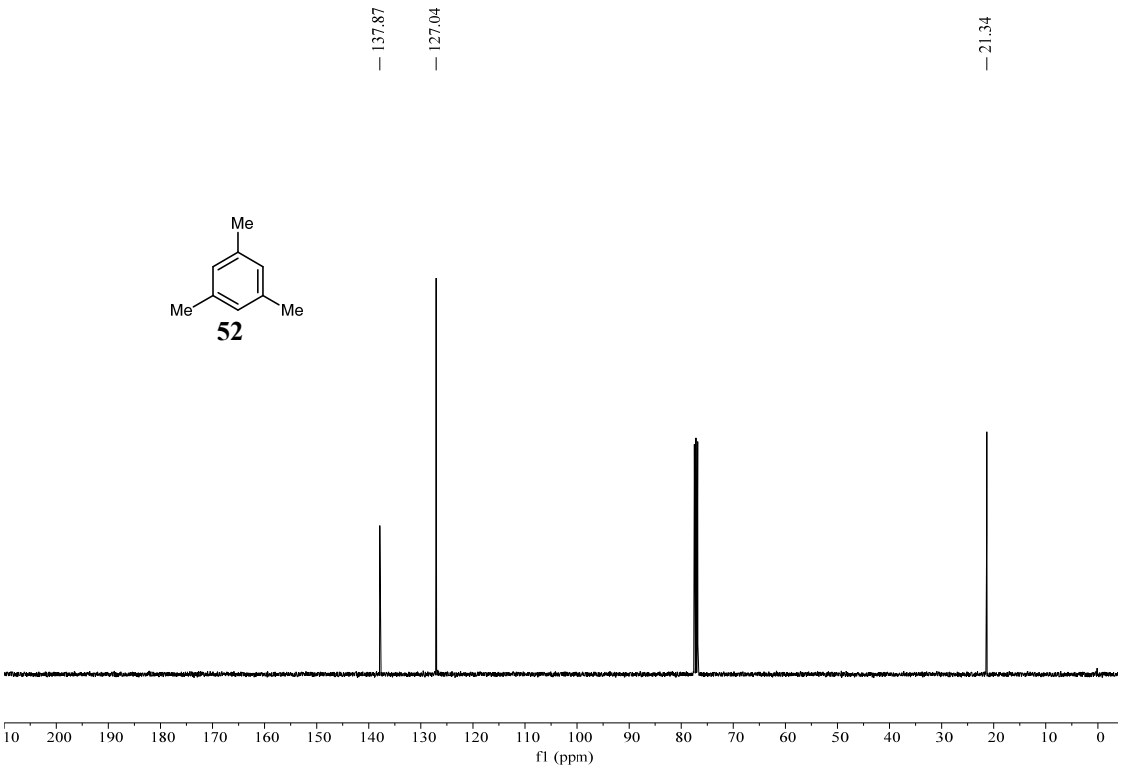

6.80
2.27
D
Me
Me
Me
1.00
4.08
f1 (ppm)

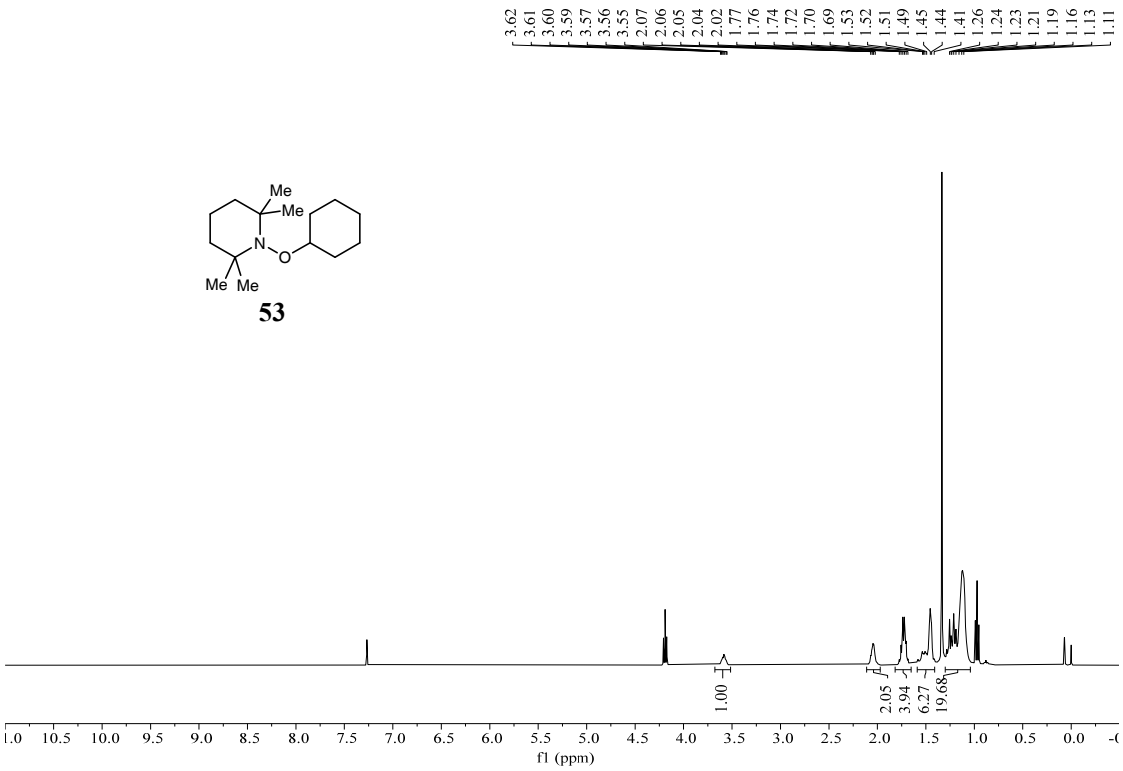
50


137.86
137.78
127.04
126.95
126.71
126.48
21.34
21.28
D
Me
Me
Me
f1 (ppm)

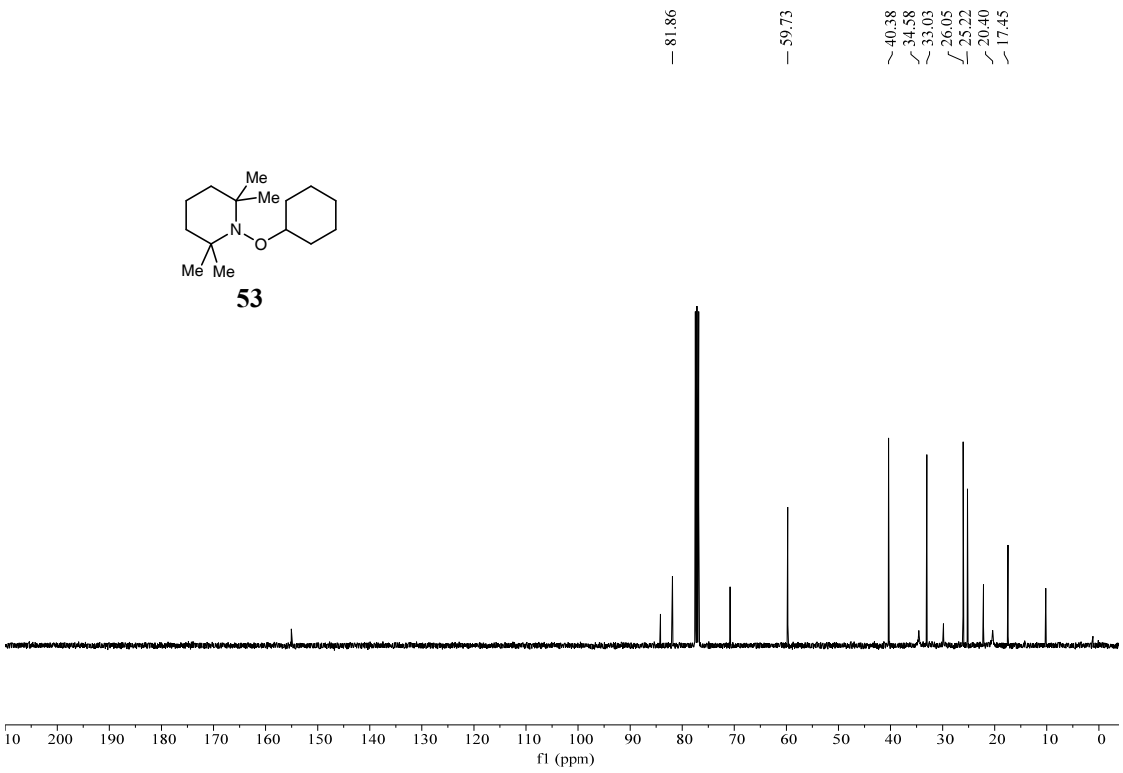
50


6.80
2.27
Me
Me
Me
52
1.00
3.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


137.87
127.04
21.34
Me
Me
Me
52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

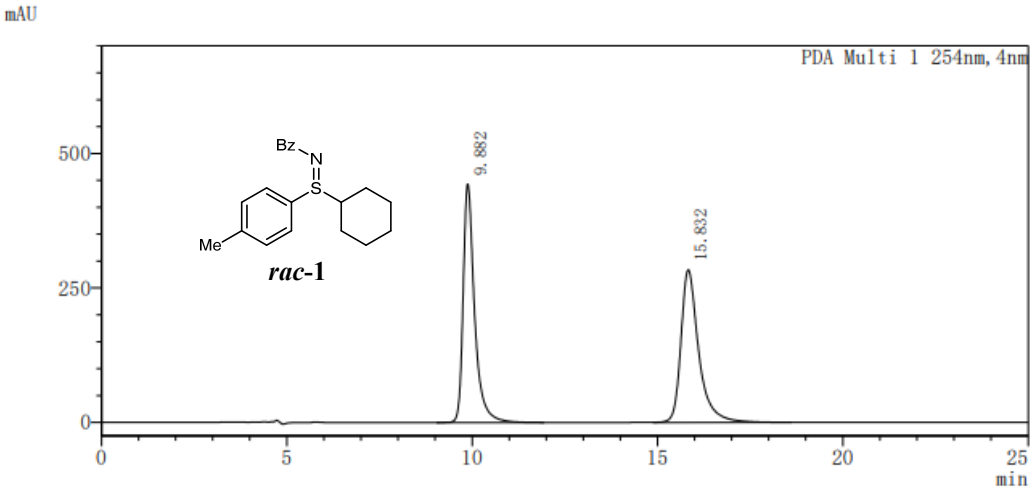

3.62
3.61
3.60
3.59
3.57
3.56
3.55
2.07
2.06
2.05
2.04
2.02
1.77
1.76
1.74
1.72
1.70
1.69
1.53
1.52
1.51
1.49
1.45
1.44
1.41
1.26
1.24
1.23
1.21
1.19
1.16
1.13
1.11
Me
Me
N
O
Me Me
1.00
2.05
3.94
6.27
19.68
f1 (ppm)

53


81.86
59.73
40.38
34.58
33.03
26.05
25.22
20.40
17.45
Me
Me
N
O
Me Me
f1 (ppm)

53

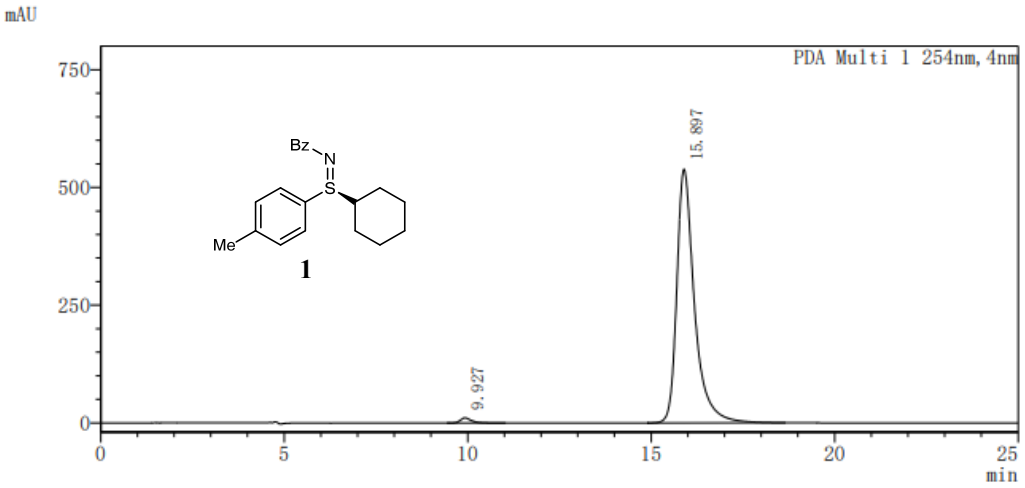
11. HPLC spectra



Peak Table

PDA Ch1 254nm

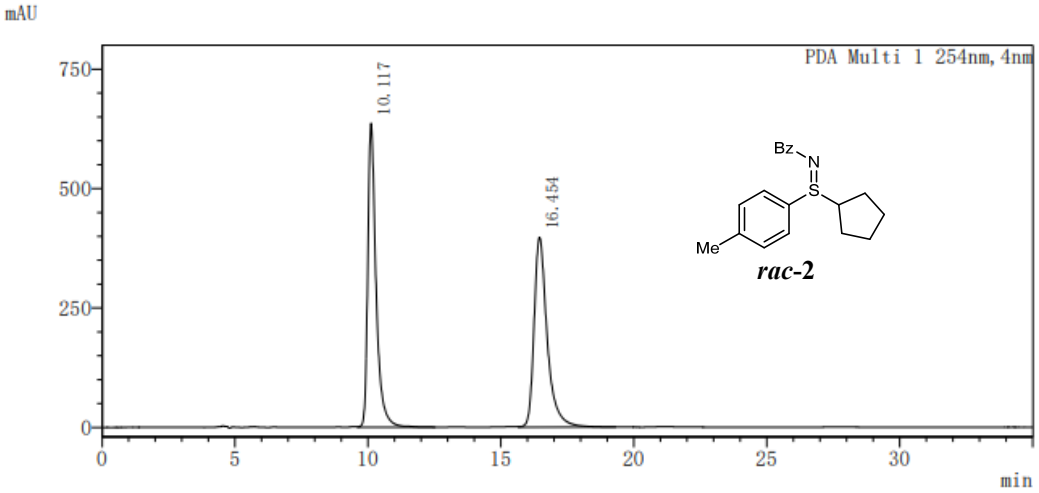
Peak#	Ret. Time	Area	Area%
1	9.882	9527648	50.070
2	15.832	9500892	49.930



Peak Table

PDA Ch1 254nm

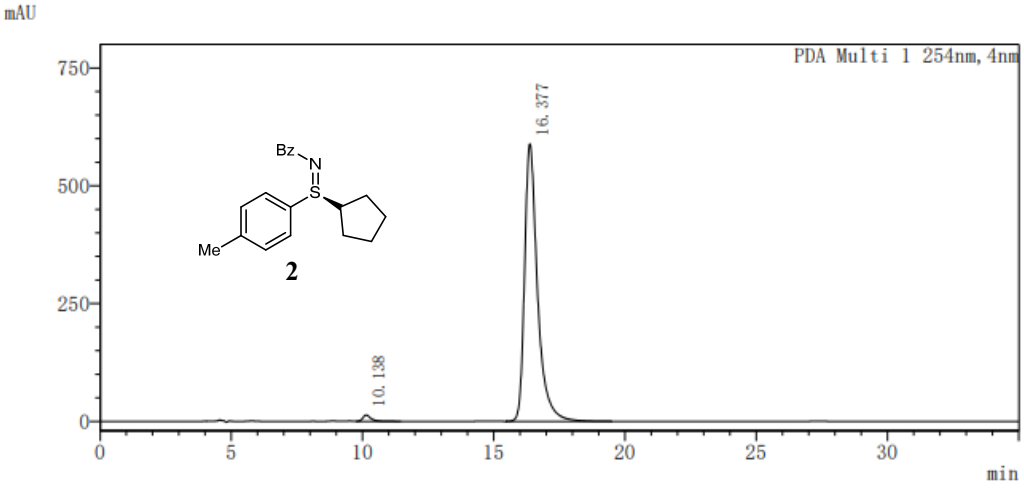
Peak#	Ret. Time	Area	Area%
1	9.927	231740	1.267
2	15.897	18052565	98.733



Peak Table

PDA Ch1 254nm

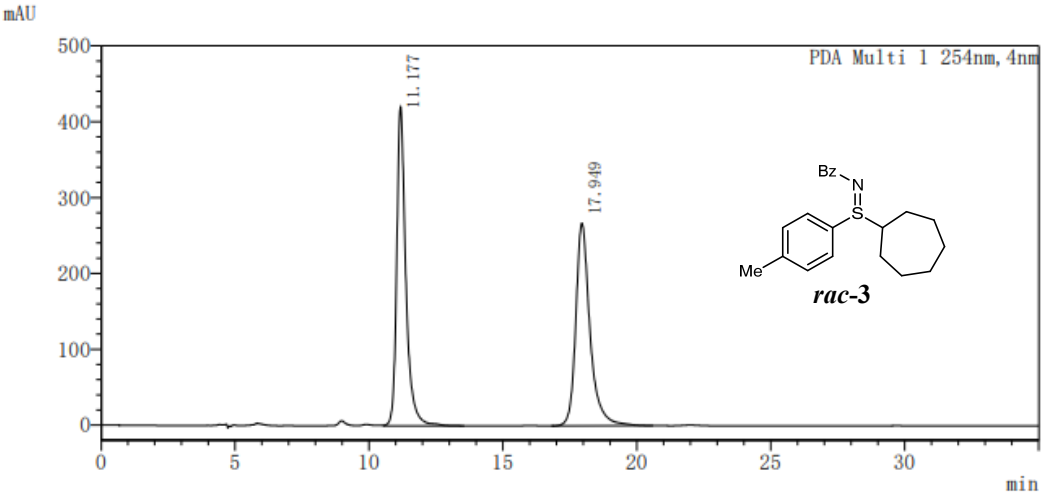
Peak#	Ret. Time	Area	Area%
1	10.117	13786376	50.196
2	16.454	13678469	49.804



Peak Table

PDA Ch1 254nm

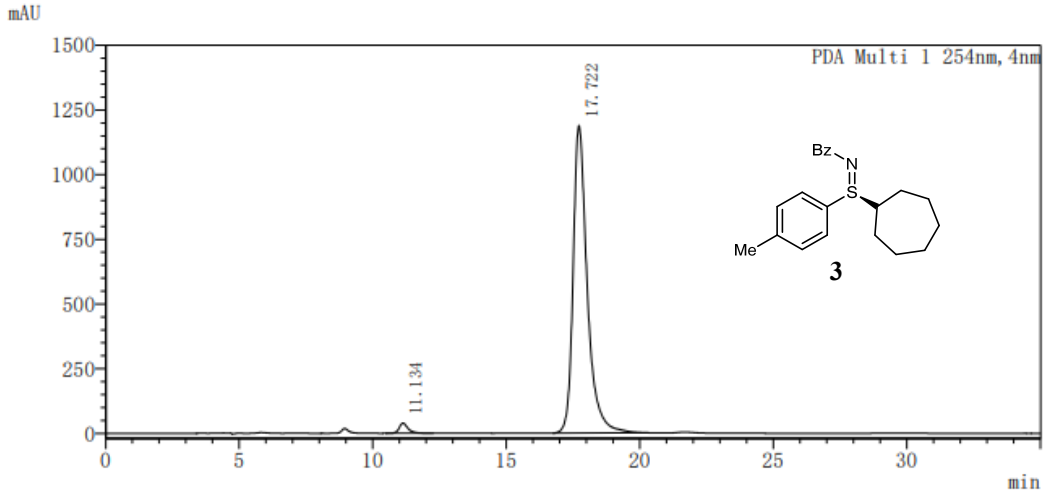
Peak#	Ret. Time	Area	Area%
1	10.138	294083	1.433
2	16.377	20221351	98.567



Peak Table

PDA Ch1 254nm

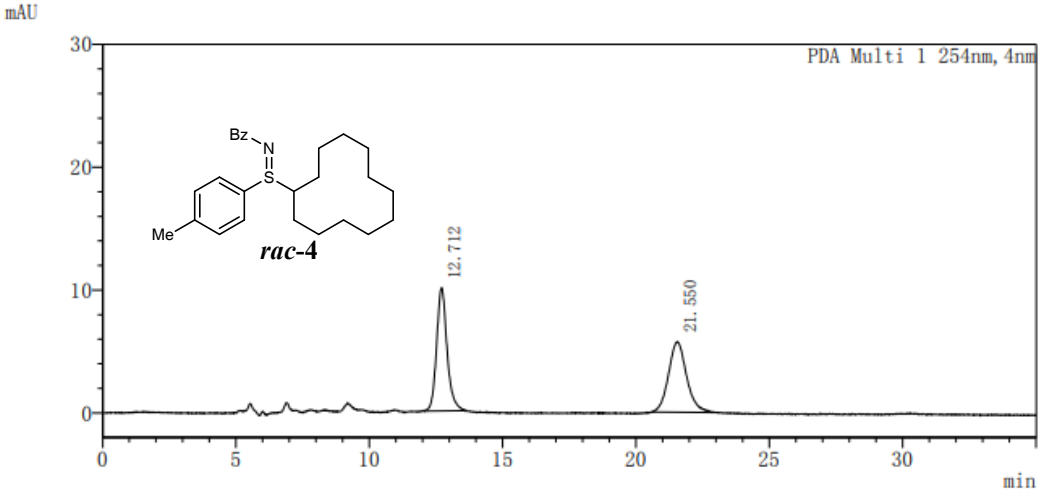
Peak#	Ret. Time	Area	Area%
1	11.177	9997233	50.279
2	17.949	9886261	49.721



Peak Table

PDA Ch1 254nm

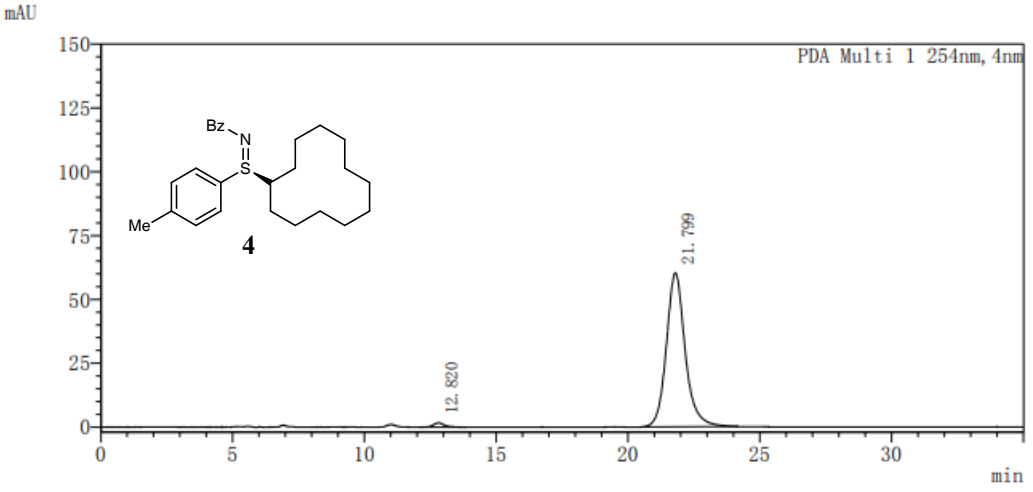
Peak#	Ret. Time	Area	Area%
1	11.134	913914	2.045
2	17.722	43780909	97.955



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.712	274648	50.546
2	21.550	268715	49.454

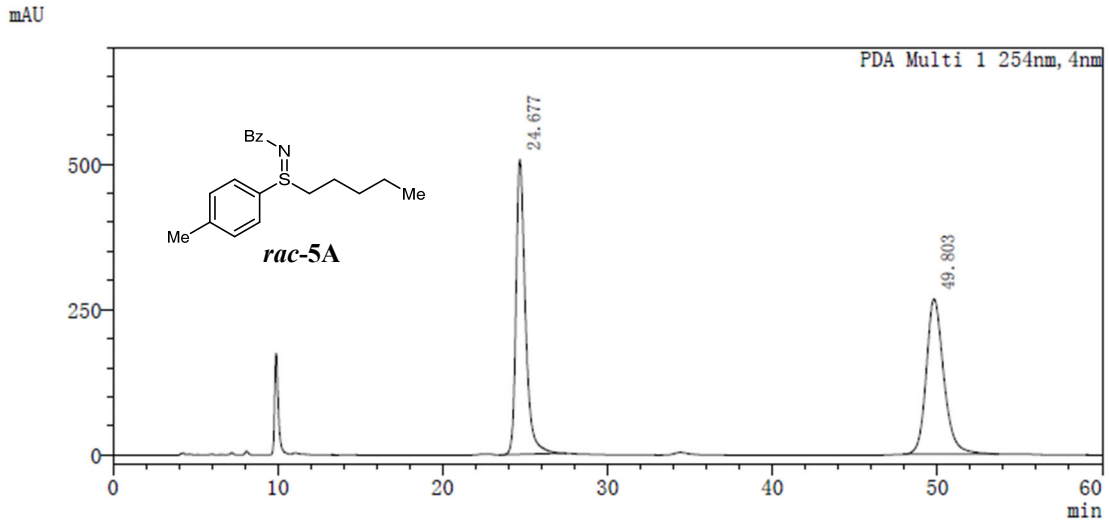


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.820	47153	1.547
2	21.799	3000057	98.453

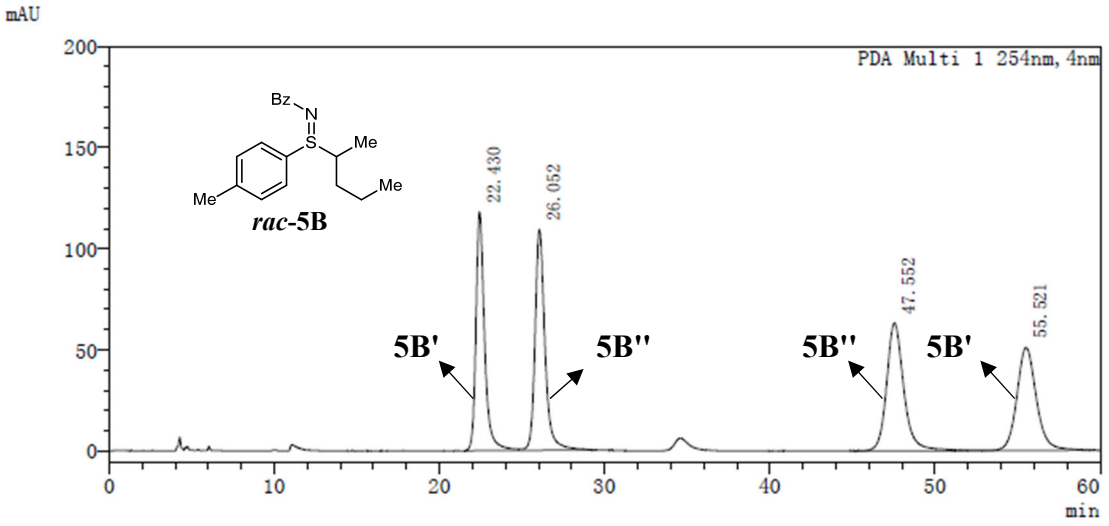
Owing to the highly analogous structures of **5A**, **5B**, and **5C**, these isomers could not be separated by column chromatography, precluding isolation of the pure compounds and affording only mixed fractions containing pairwise combinations (**5A**/**5B** or **5B**/**5C**). Accordingly, we employed chiral HPLC to determine the e.e. values. This approach inevitably results in minor contributions from the co-eluting/configurationally related component (i.e., the secondary component in each pair) being detectable in the corresponding chromatograms. Consequently, the e.e. values of **5A** and **5B′**, as well as that of the combined **5B″** & **5C** fraction, were estimated from the chiral HPLC chromatograms.



Peak Table

PDA Ch1 254nm

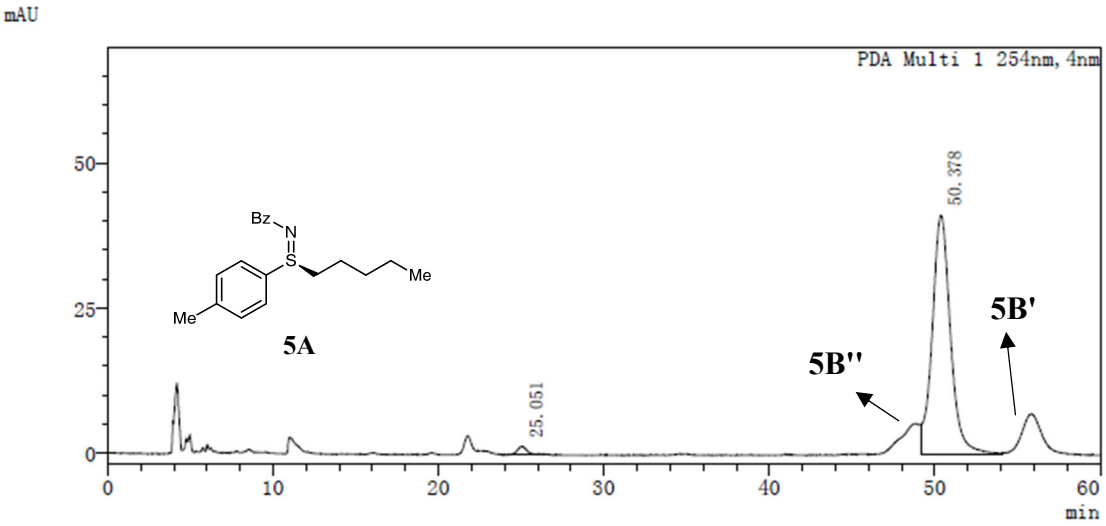
Peak#	Ret. Time	Area	Area%
1	24.677	20007352	50.312
2	49.803	19759485	49.688



Peak Table

PDA Ch1 254nm

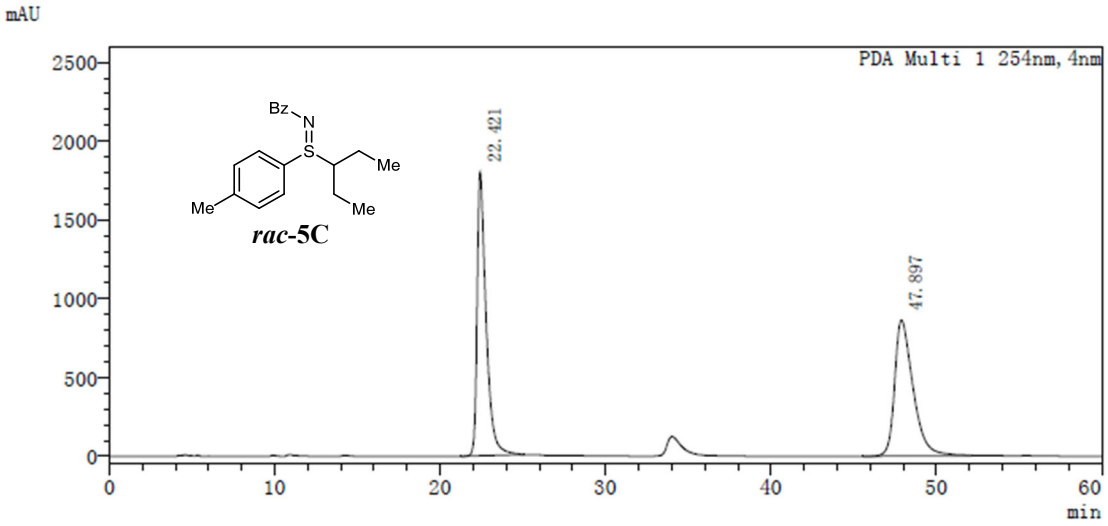
Peak#	Ret. Time	Area	Area%
1	22.430	4282979	24.349
2	26.052	4558721	25.916
3	47.552	4558118	25.913
4	55.521	4190301	23.822



Peak Table

PDA Ch1 254nm

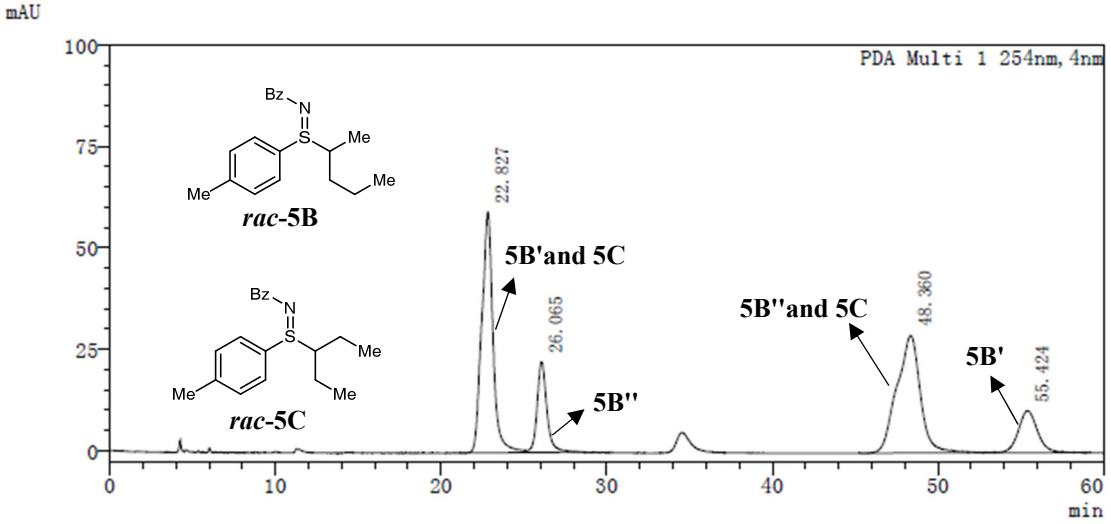
Peak#	Ret. Time	Area	Area%
1	25.051	52273	1.614
2	50.378	3187343	98.386



Peak Table

PDA Ch1 254nm

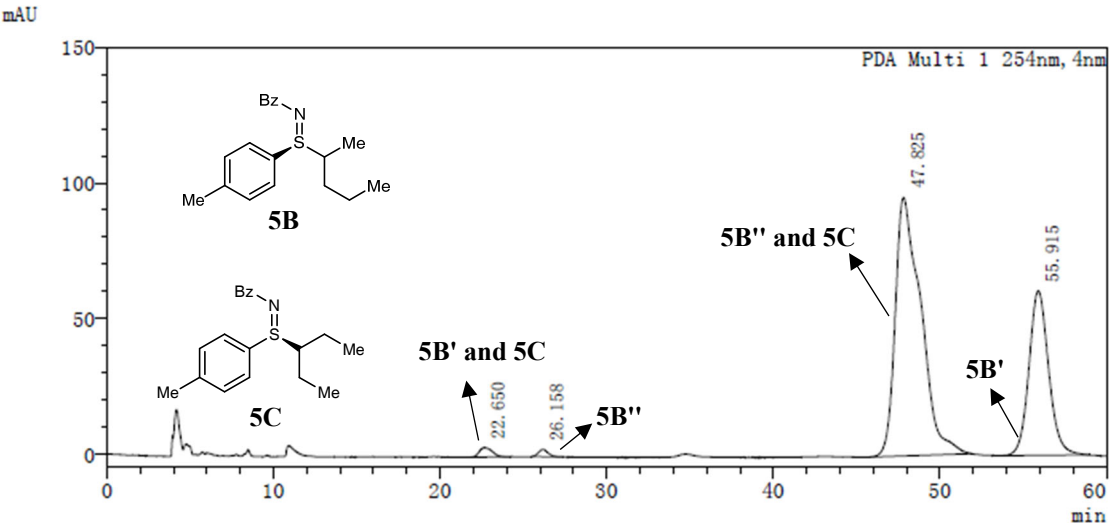
Peak#	Ret. Time	Area	Area%
1	22.421	67755178	50.250
2	47.897	67080324	49.750



Peak Table

PDA Ch1 254nm

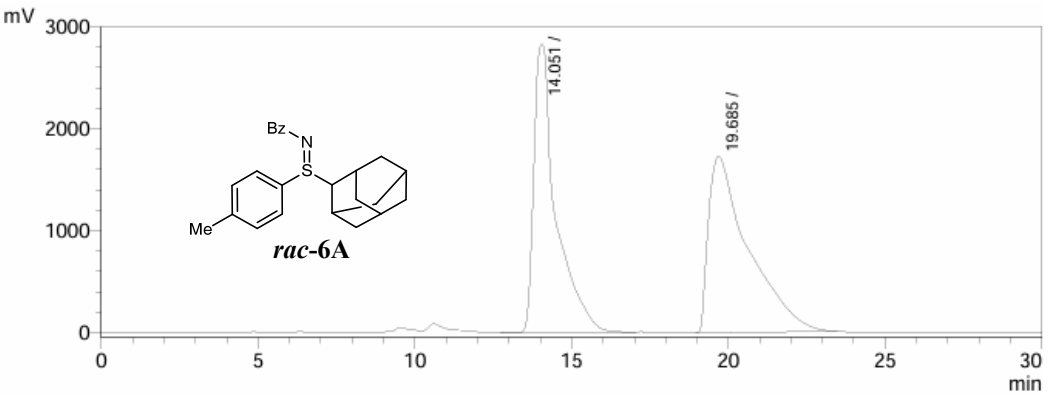
Peak#	Ret. Time	Area	Area%
1	22.827	2799681	37.724
2	26.065	919206	12.386
3	48.360	2854852	38.467
4	55.424	847820	11.424



Peak Table

PDA Ch1 254nm

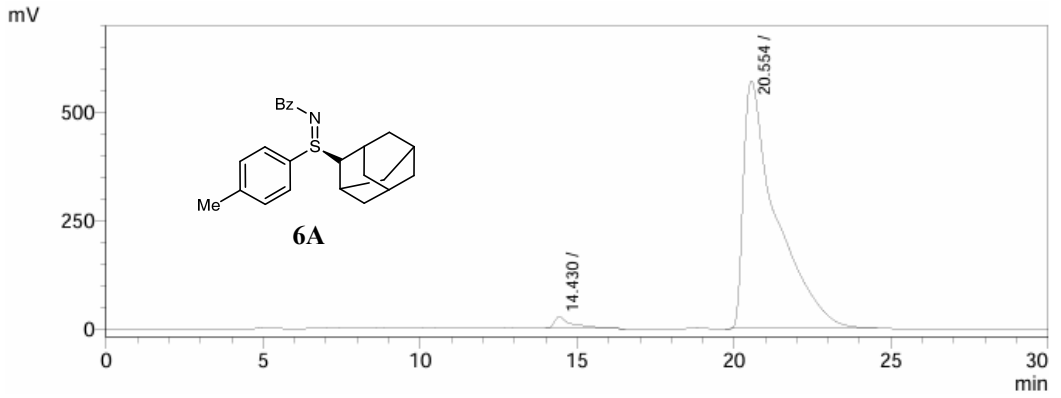
Peak#	Ret. Time	Area	Area%
1	22.650	187875	1.211
2	26.158	110120	0.710
3	47.825	10217361	65.856
4	55.915	4999436	32.224



***rac*-6A**

检测器A 254nm

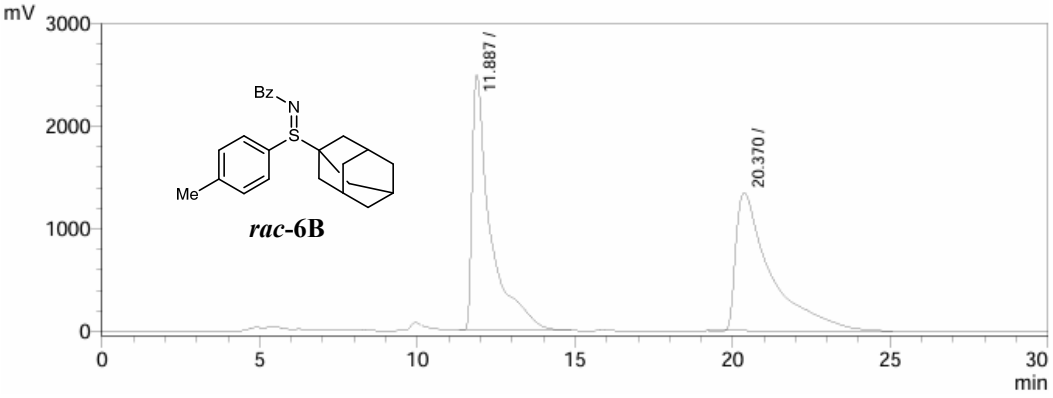
Peak#	Ret. Time	Area	Area%
1	14.051	137758658	47.388
2	19.685	152944379	52.612



6A

检测器A 254nm

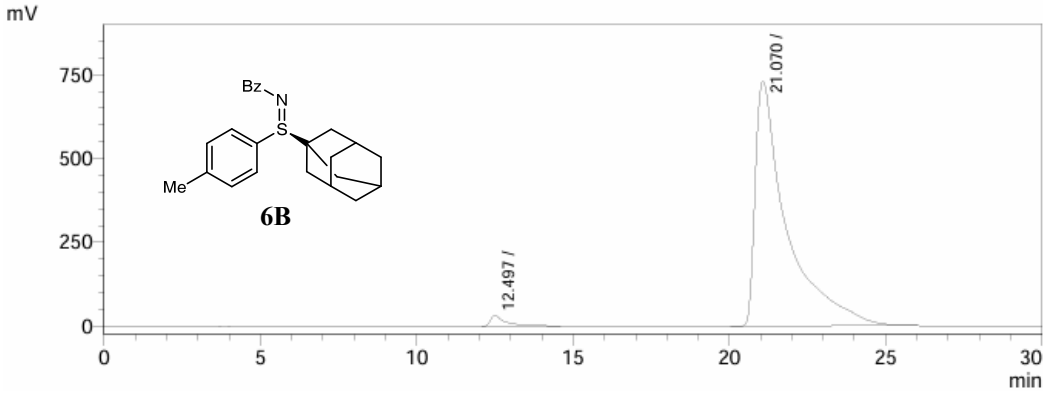
Peak#	Ret. Time	Area	Area%
1	14.430	1082515	2.518
2	20.554	41909388	97.482



***rac*-6B**

检测器A 254nm

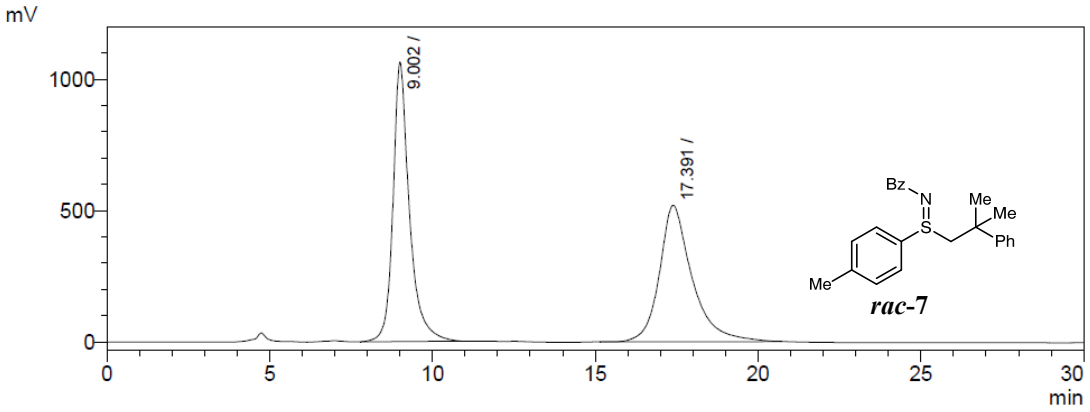
Peak#	Ret. Time	Area	Area%
1	11.887	100828924	49.162
2	20.370	104267475	50.838



6B

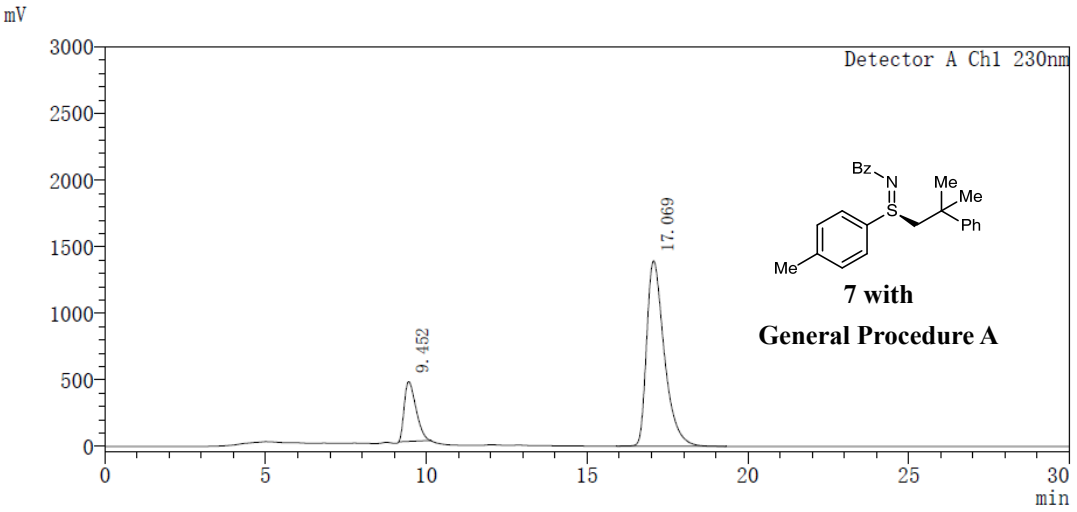
检测器A 254nm

Peak#	Ret. Time	Area	Area%
1	12.497	1070502	2.041
2	21.070	51376869	97.959



检测器A 230nm

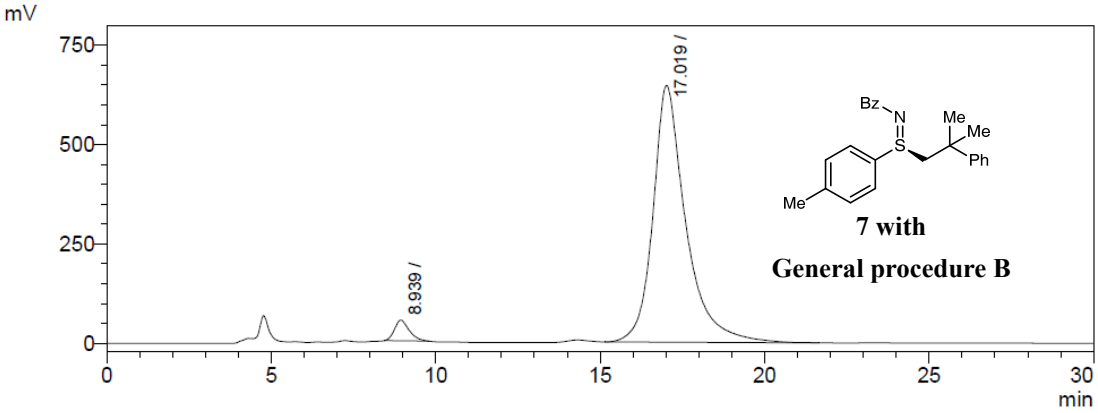
Peak#	Ret. Time	Area	Area%
1	9.002	37289051	50.691
2	17.391	36273027	49.309



Peak Table

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	9.452	11429588	17.714
2	17.069	53094919	82.286

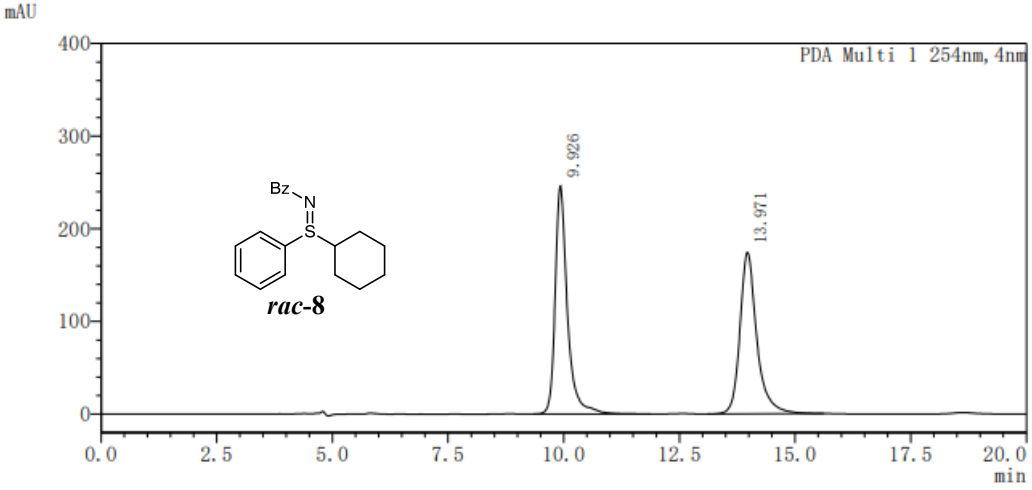


7 with

General procedure B

检测器A 230nm

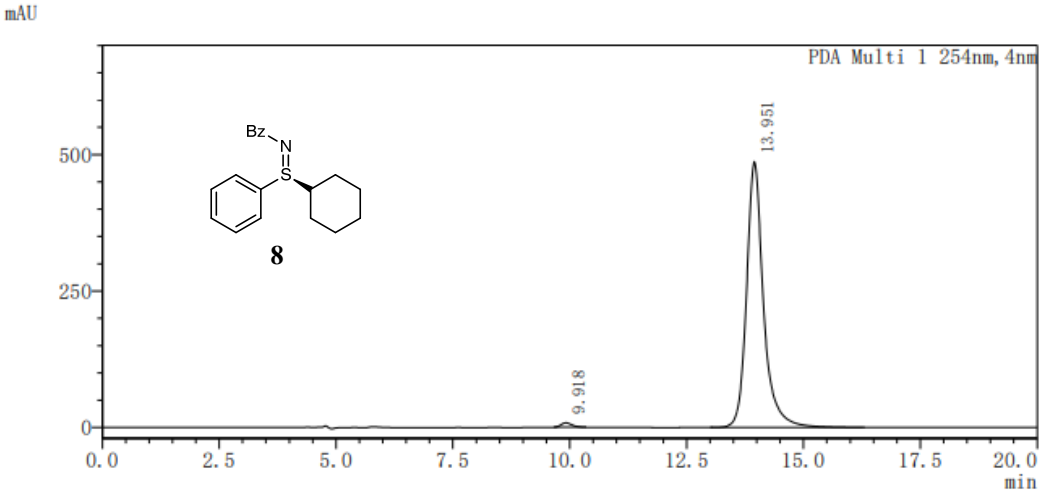
Peak#	Ret. Time	Area	Area%
1	8.939	1610734	3.465
2	17.019	44875677	96.535



Peak Table

PDA Ch1 254nm

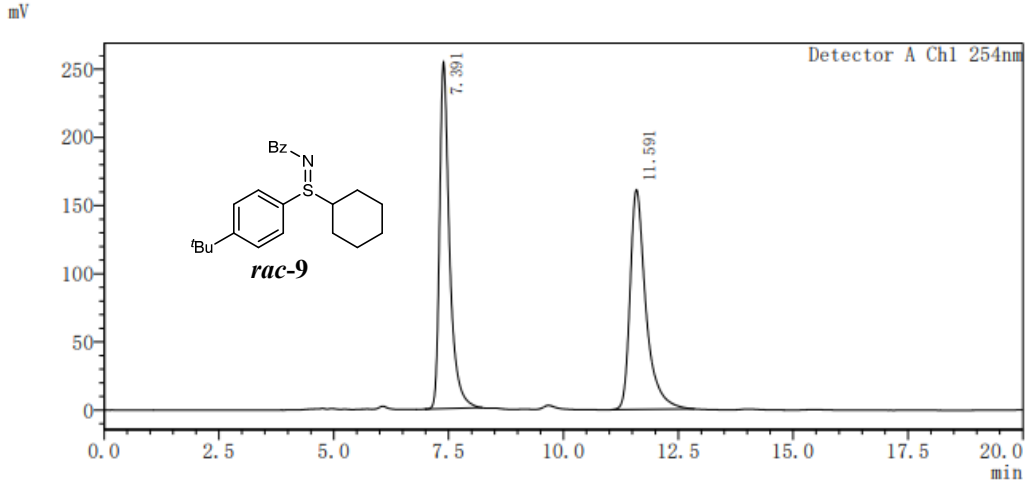
Peak#	Ret. Time	Area	Area%
1	9.926	4527812	50.500
2	13.971	4438173	49.500



Peak Table

PDA Ch1 254nm

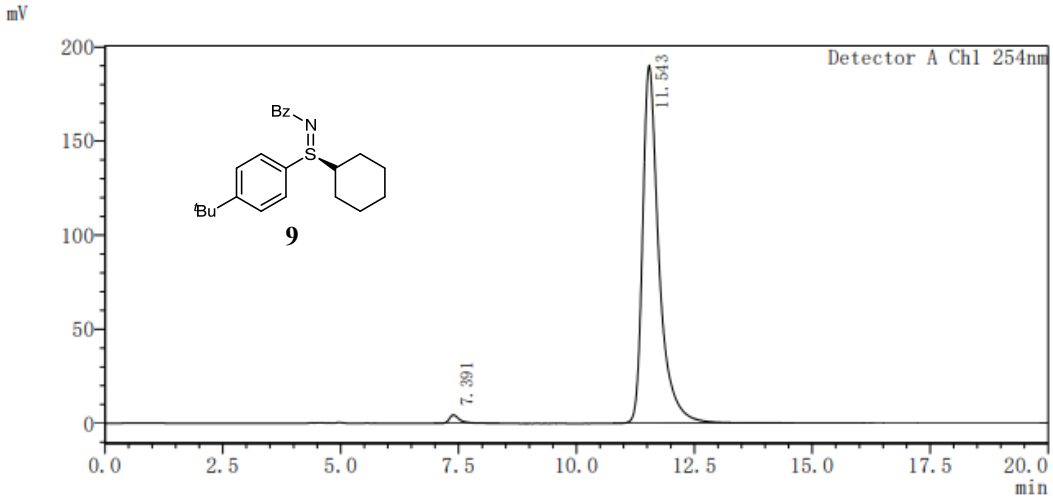
Peak#	Ret. Time	Area	Area%
1	9.918	128634	1.033
2	13.951	12317907	98.967



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.391	3843195	49.886
2	11.591	3860822	50.114

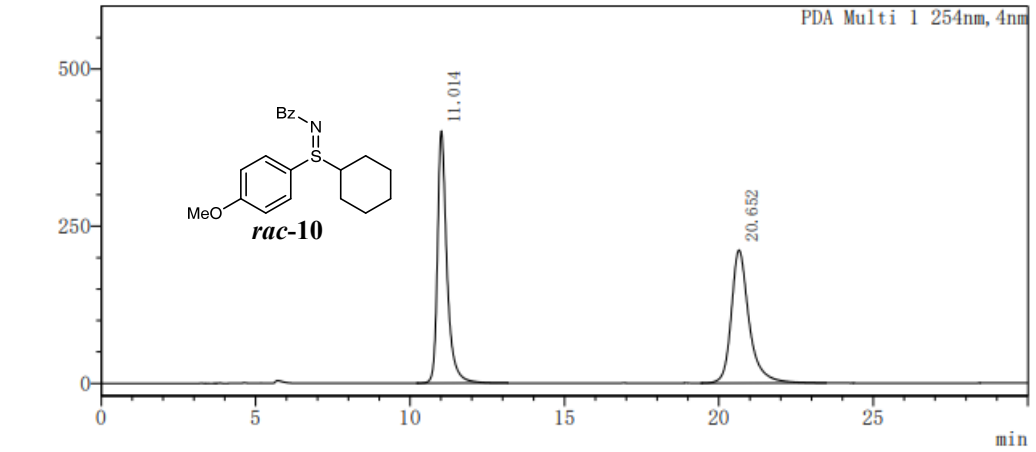


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.391	72251	1.549
2	11.543	4591885	98.451

mAU

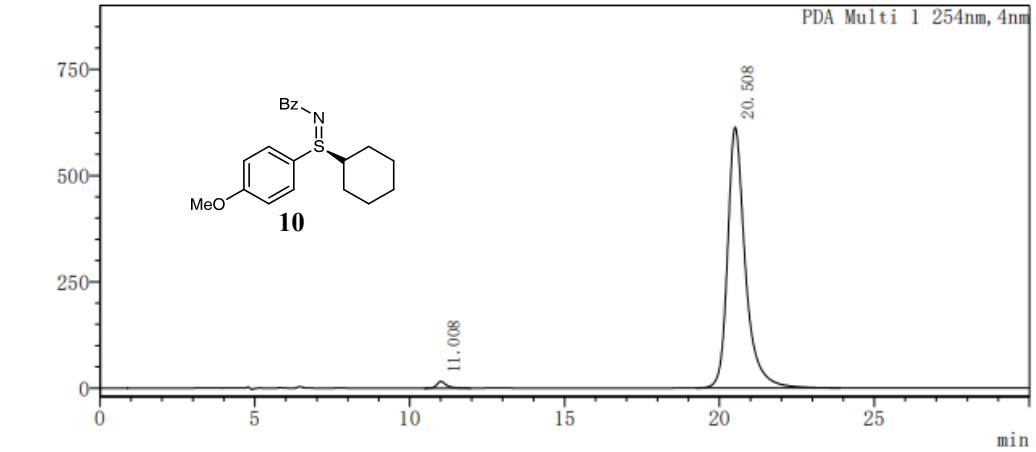


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.014	8564548	50.190
2	20.652	8499555	49.810

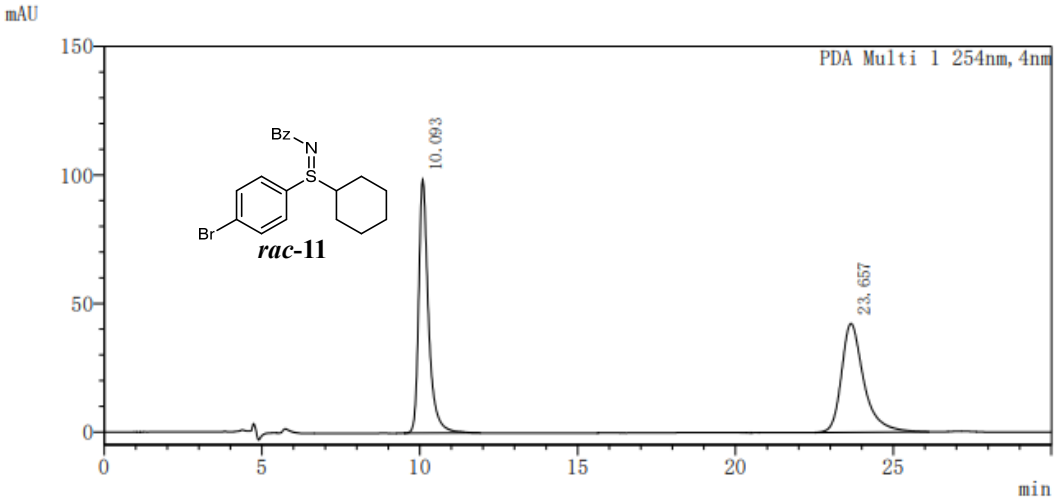
mAU



Peak Table

PDA Ch1 254nm

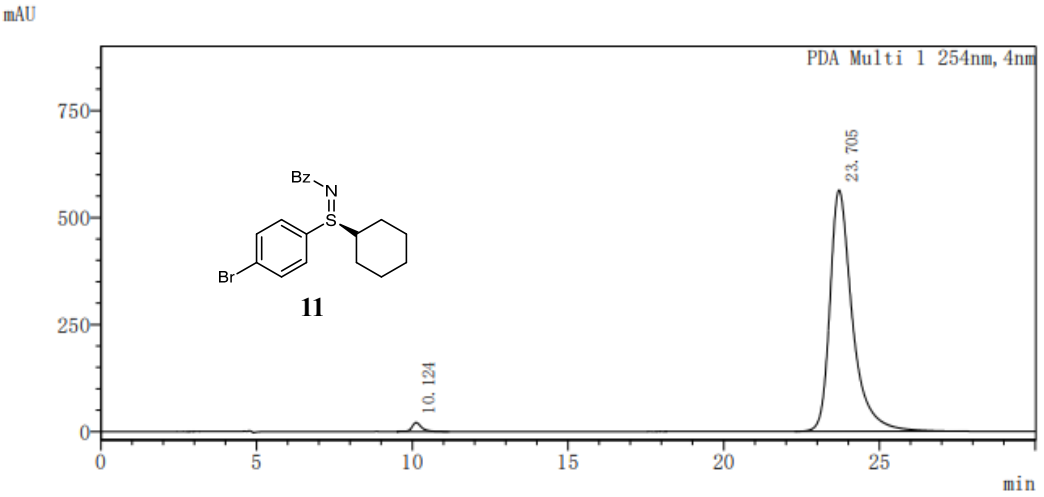
Peak#	Ret. Time	Area	Area%
1	11.008	338651	1.366
2	20.508	24461156	98.634



Peak Table

PDA Ch1 254nm

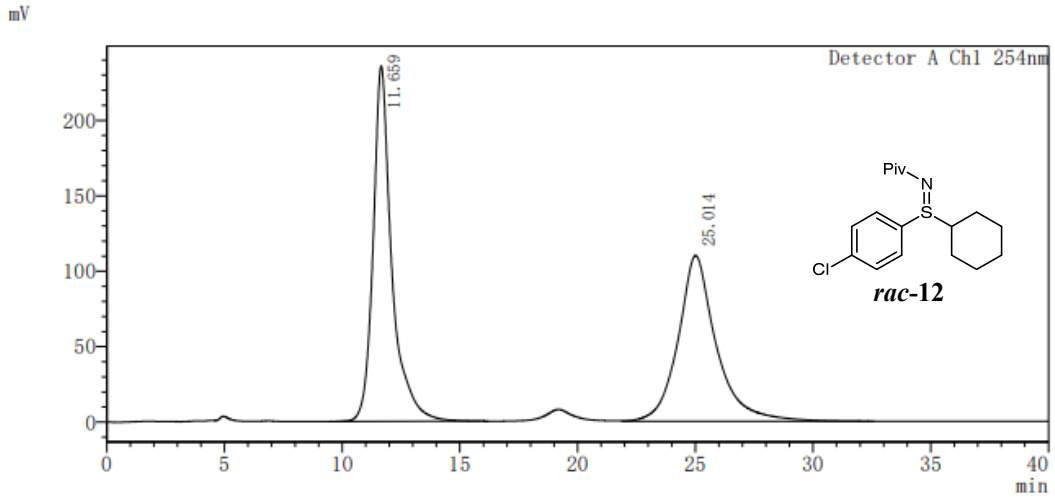
Peak#	Ret. Time	Area	Area%
1	10.093	2127600	50.501
2	23.657	2085405	49.499



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.124	455125	1.580
2	23.705	28348893	98.420

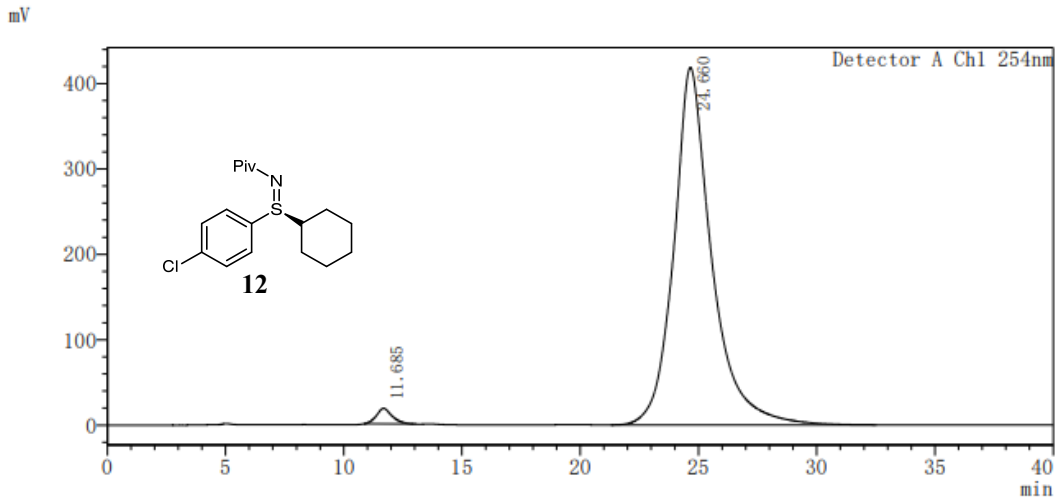


***rac*-12**

Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.659	13047139	51.296
2	25.014	12387806	48.704

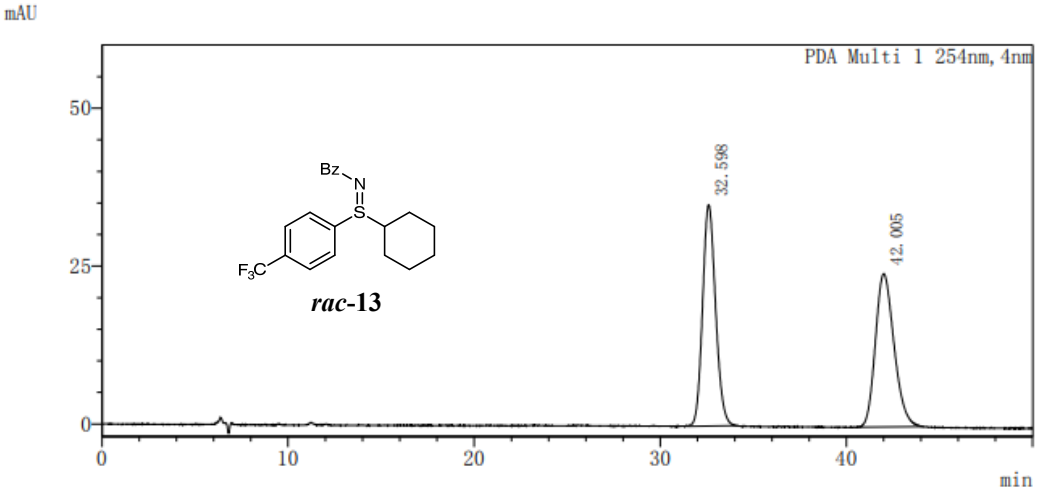


12

Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.685	841378	1.766
2	24.660	46802127	98.234

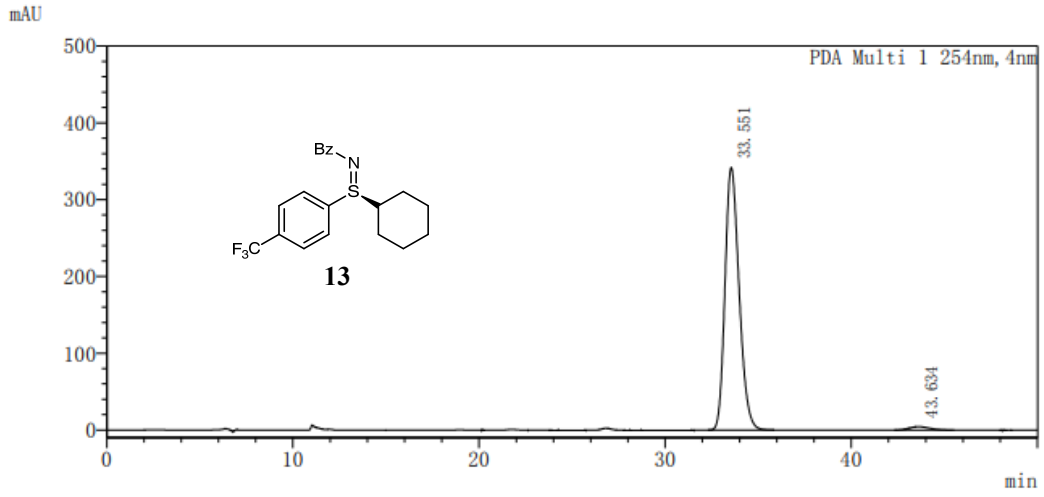


rac-13

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	32.598	1702154	50.177
2	42.005	1690123	49.823



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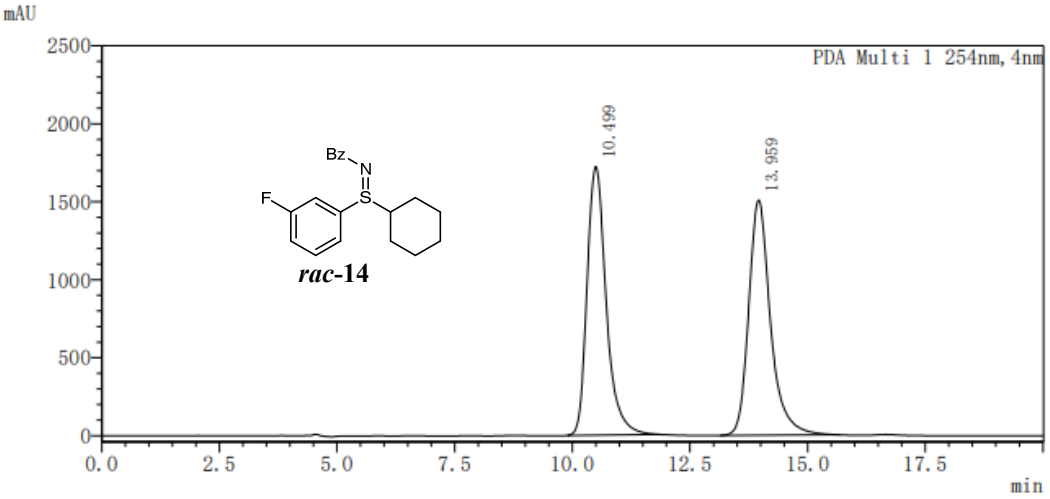
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	33.551	18029205	98.193
2	43.634	331793	1.807

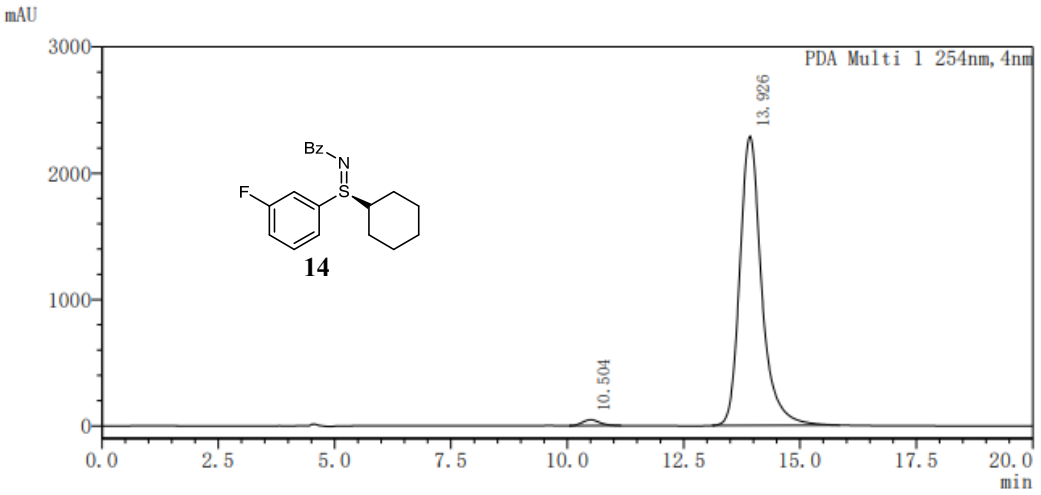


rac-**14**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.499	48636303	50.029
2	13.959	48579487	49.971



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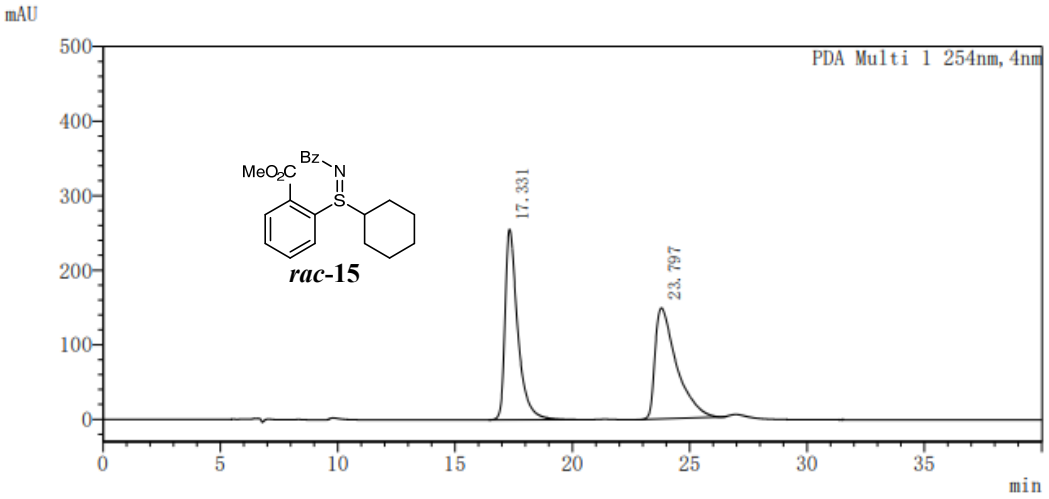
Peak Table

PDA Ch1 254nm

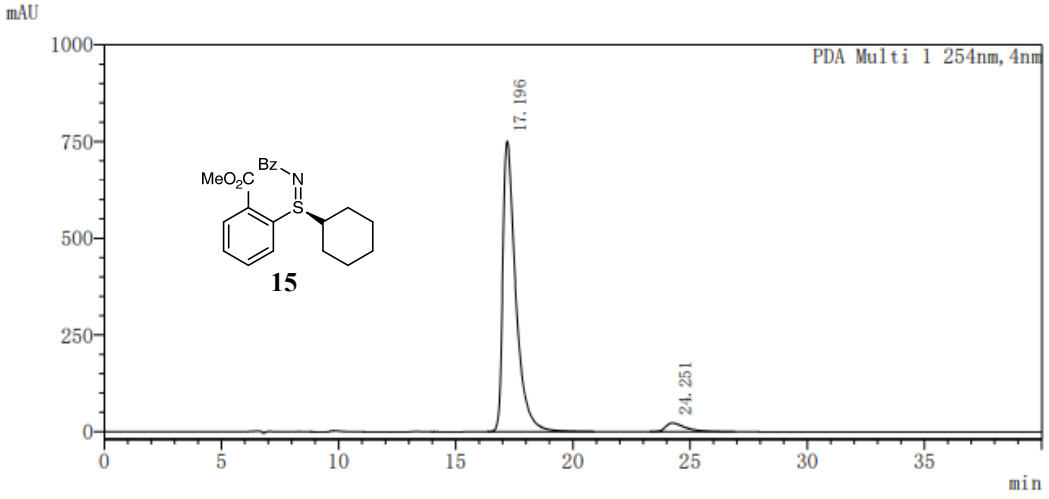
Peak#	Ret. Time	Area	Area%
1	10.504	1190236	1.570
2	13.926	74638717	98.430



Peak Table

PDA Ch1 254nm

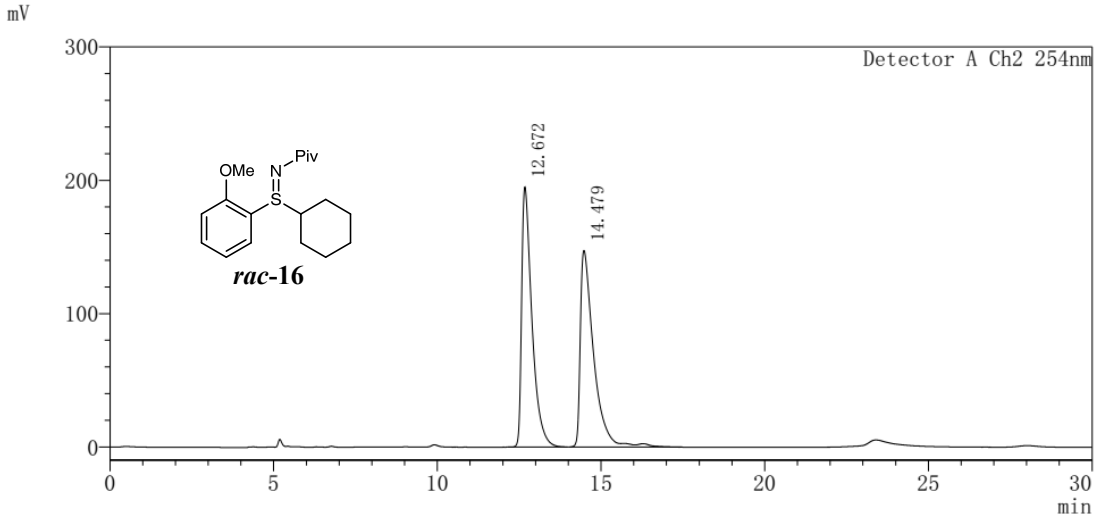
Peak#	Ret. Time	Area	Area%
1	17.331	9607476	50.369
2	23.797	9466729	49.631



Peak Table

PDA Ch1 254nm

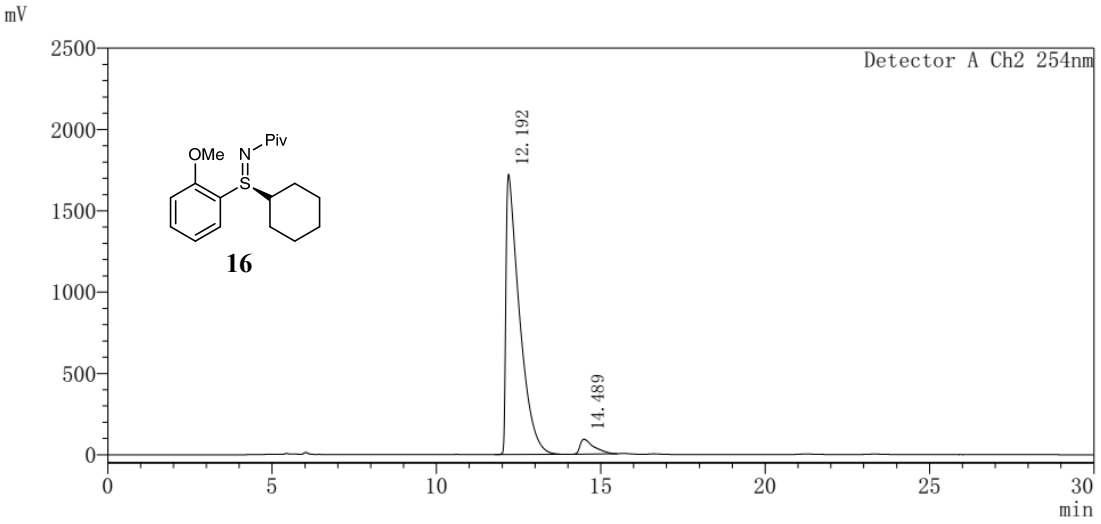
Peak#	Ret. Time	Area	Area%
1	17.196	28965827	95.630
2	24.251	1323700	4.370



Peak Table

Detector A Ch2 254nm

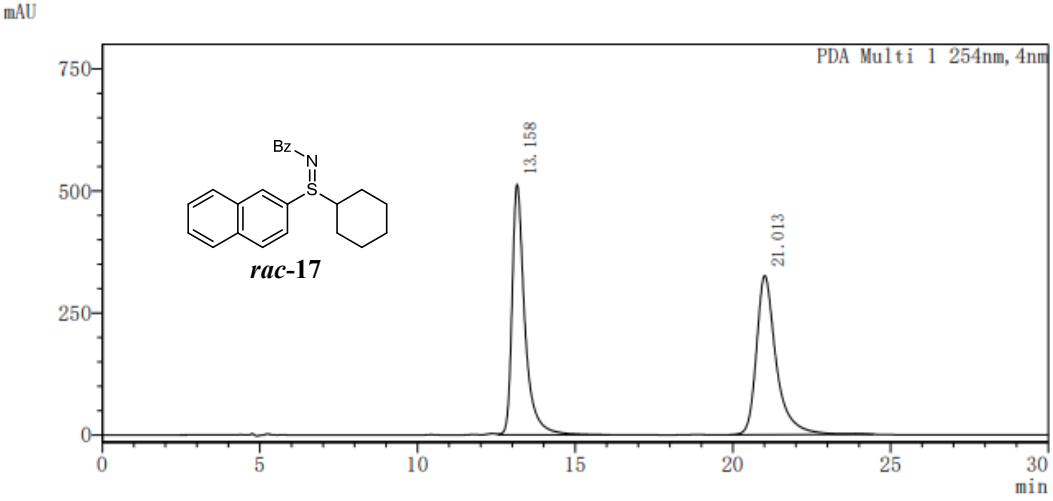
Peak#	Ret. Time	Area	Area%
1	12.672	4267089	50.347
2	14.479	4208312	49.653



Peak Table

Detector A Ch2 254nm

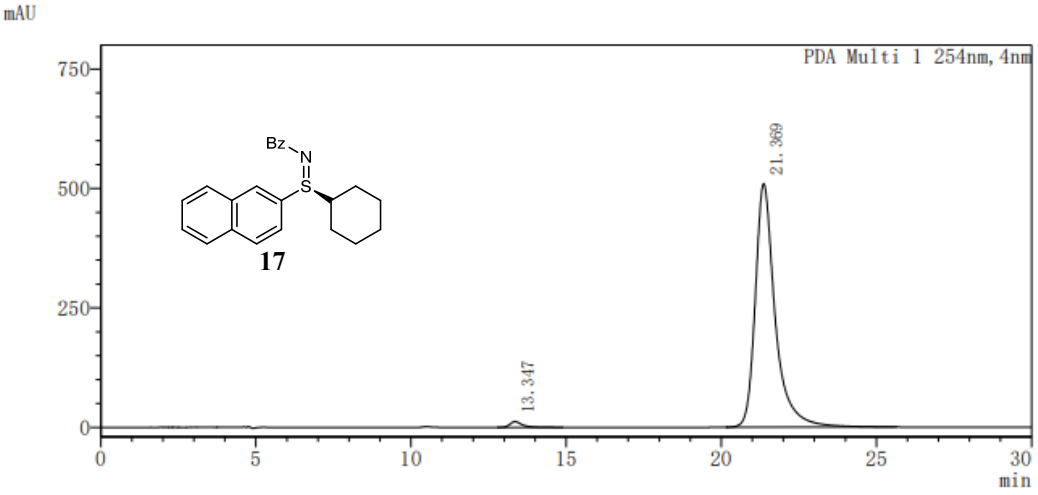
Peak#	Ret. Time	Area	Area%
1	12.192	49446410	94.840
2	14.489	2689993	5.160



Peak Table

PDA Ch1 254nm

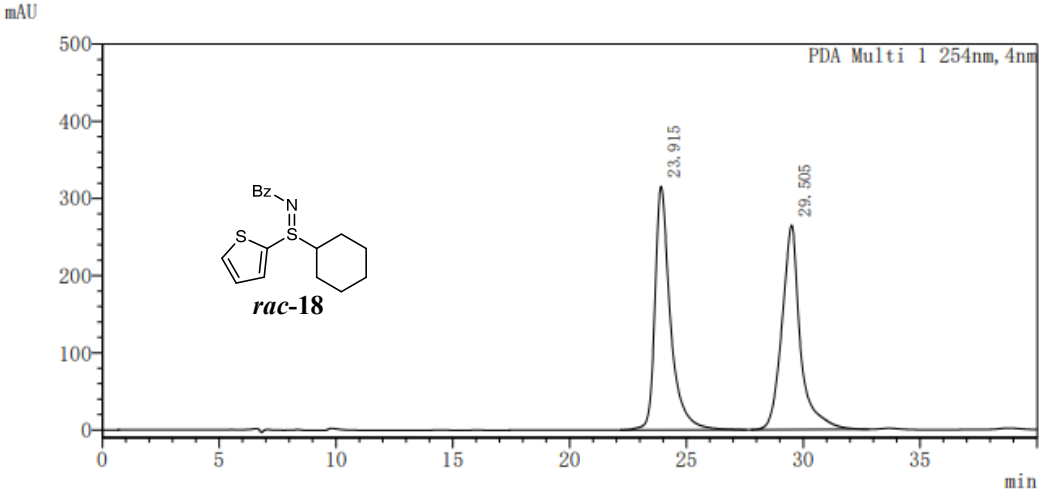
Peak#	Ret. Time	Area	Area%
1	13.158	14443797	50.271
2	21.013	14287794	49.729



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.347	344991	1.488
2	21.369	22839322	98.512

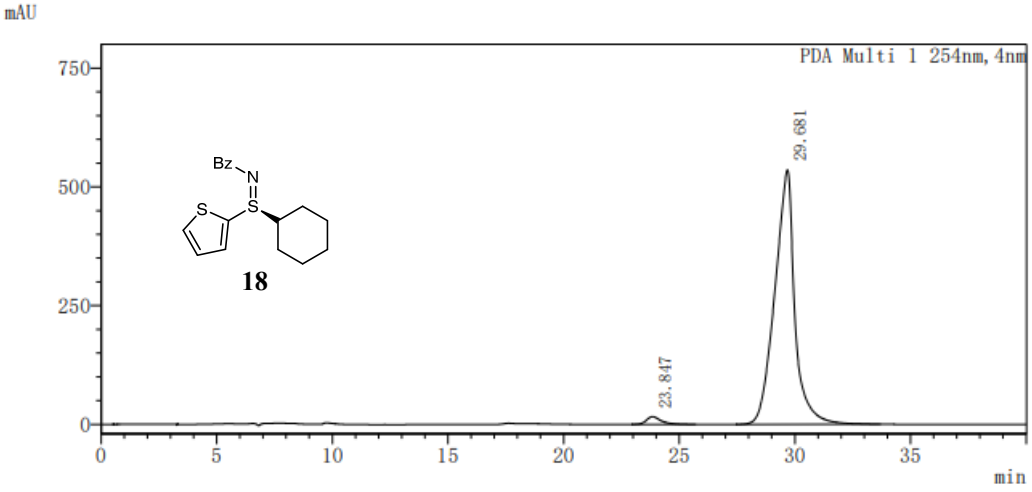


***rac*-18**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.915	14517418	50.018
2	29.505	14506684	49.982



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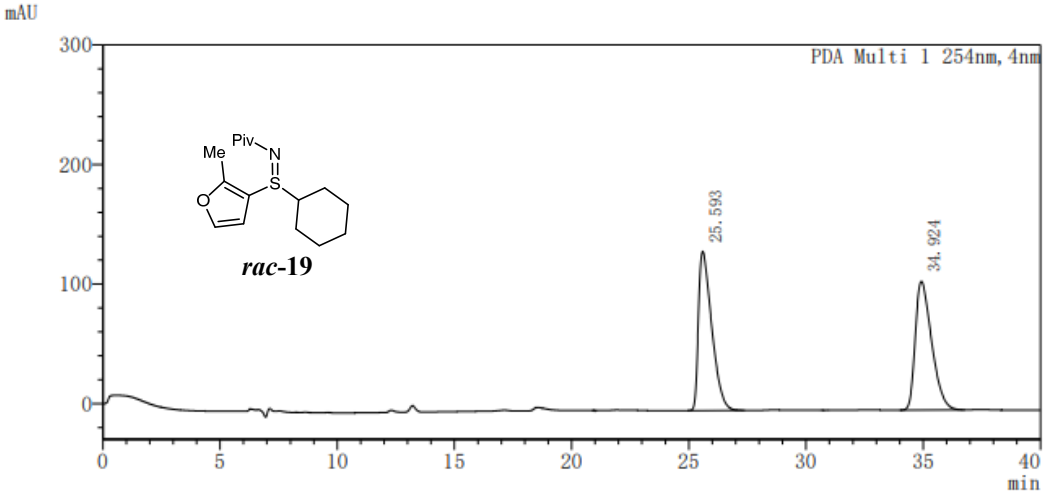
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.847	725568	2.199
2	29.681	32262545	97.801

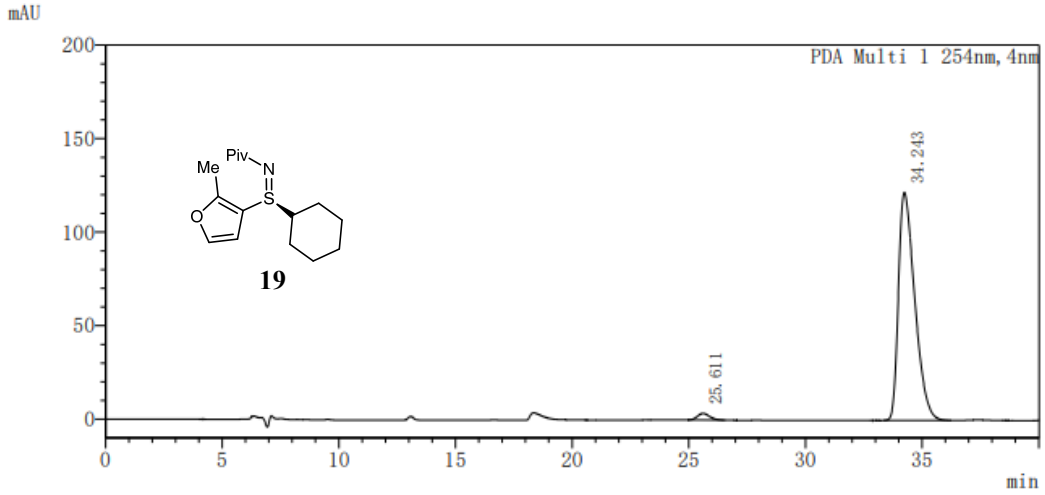


***rac*-19**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.593	5234026	50.038
2	34.924	5226021	49.962



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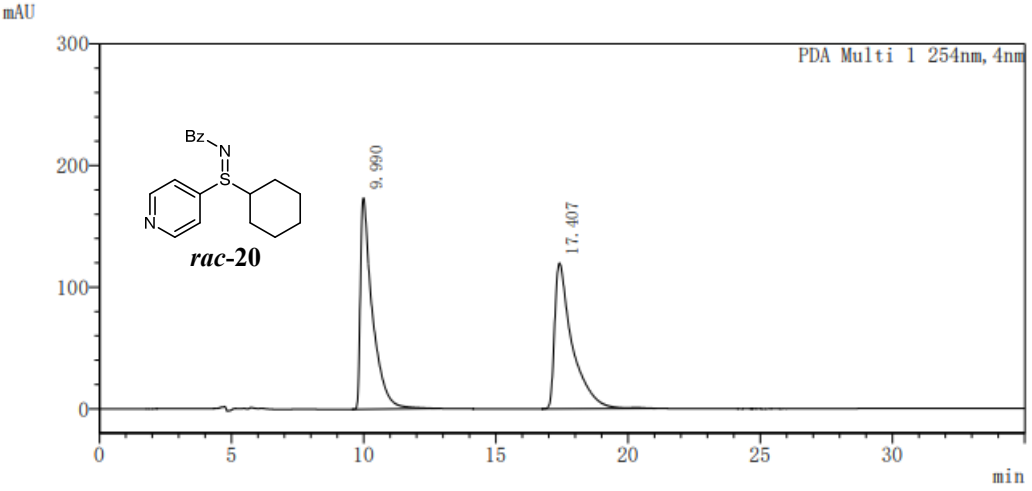
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.611	126591	2.095
2	34.243	5916825	97.905

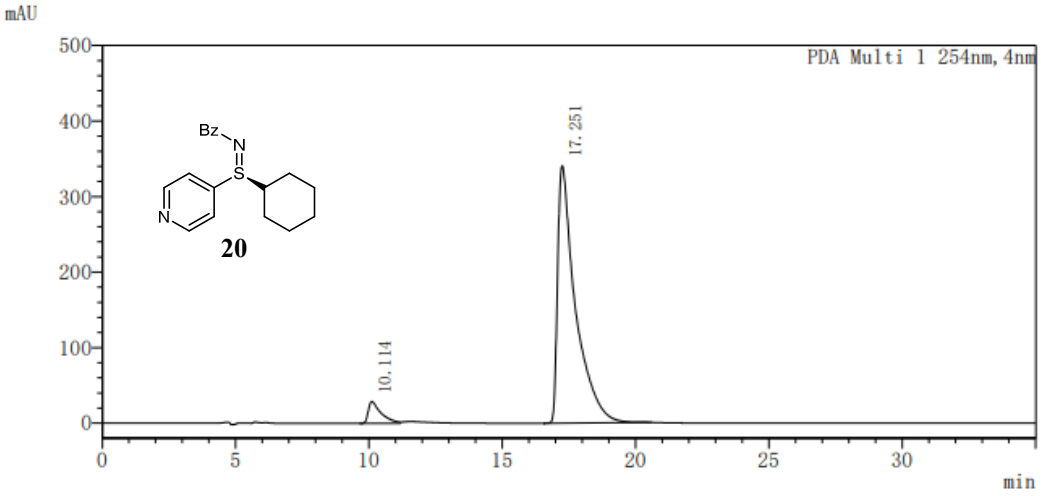


rac-**20**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.990	5495945	49.833
2	17.407	5532806	50.167



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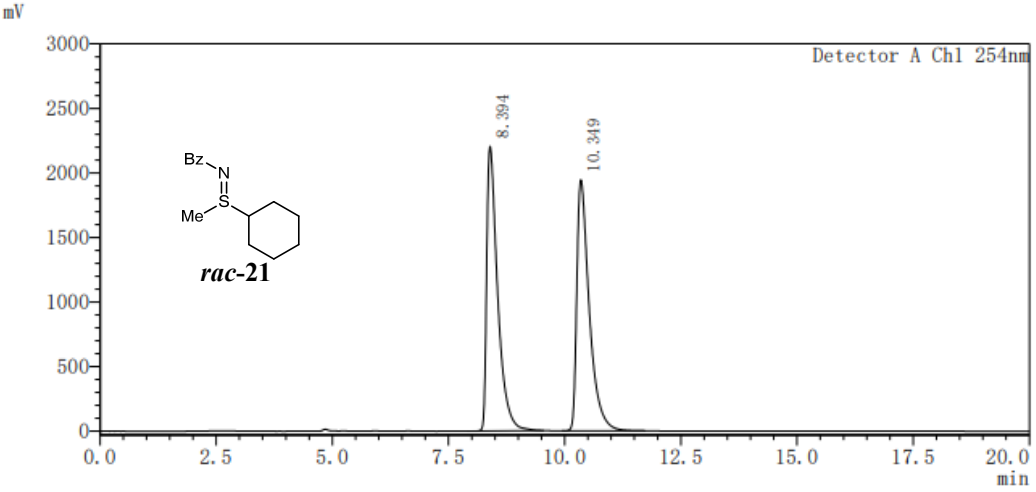
Peak Table

PDA Ch1 254nm

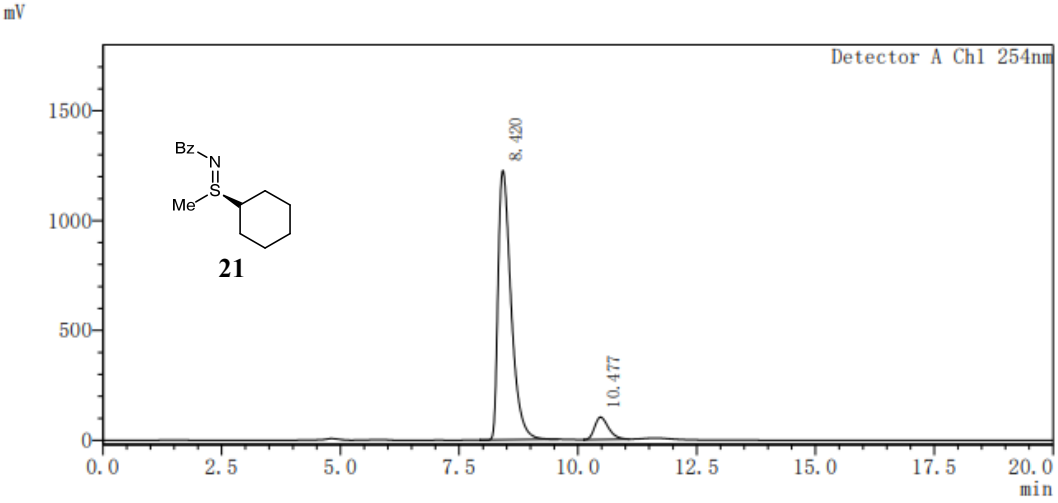
Peak#	Ret. Time	Area	Area%
1	10.114	961069	5.725
2	17.251	15824779	94.275



Peak Table

Detector A Ch1 254nm

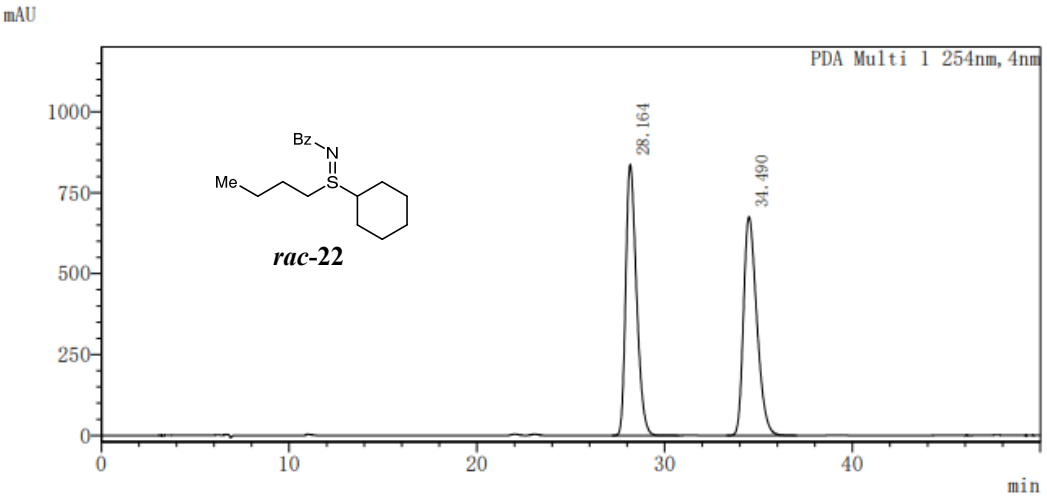
Peak#	Ret. Time	Area	Area%
1	8.394	36140962	49.892
2	10.349	36296858	50.108



Peak Table

Detector A Ch1 254nm

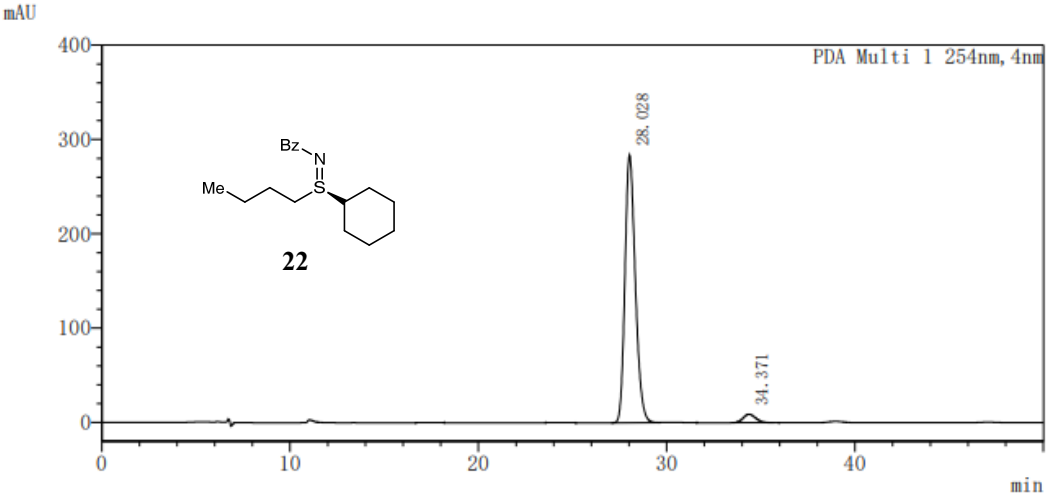
Peak#	Ret. Time	Area	Area%
1	8.420	23374990	91.949
2	10.477	2046638	8.051



Peak Table

PDA Ch1 254nm

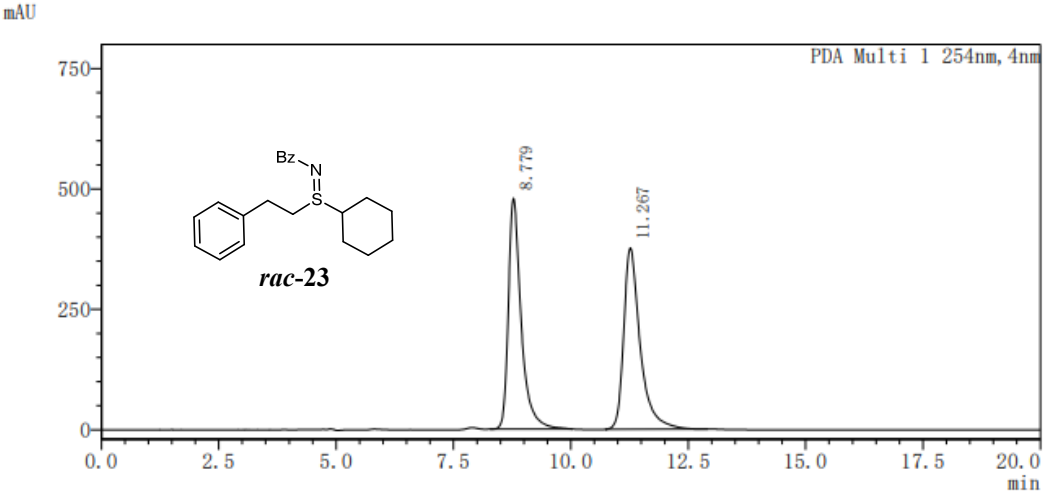
Peak#	Ret. Time	Area	Area%
1	28.164	33329425	49.981
2	34.490	33355147	50.019



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.028	10853585	96.259
2	34.371	421754	3.741

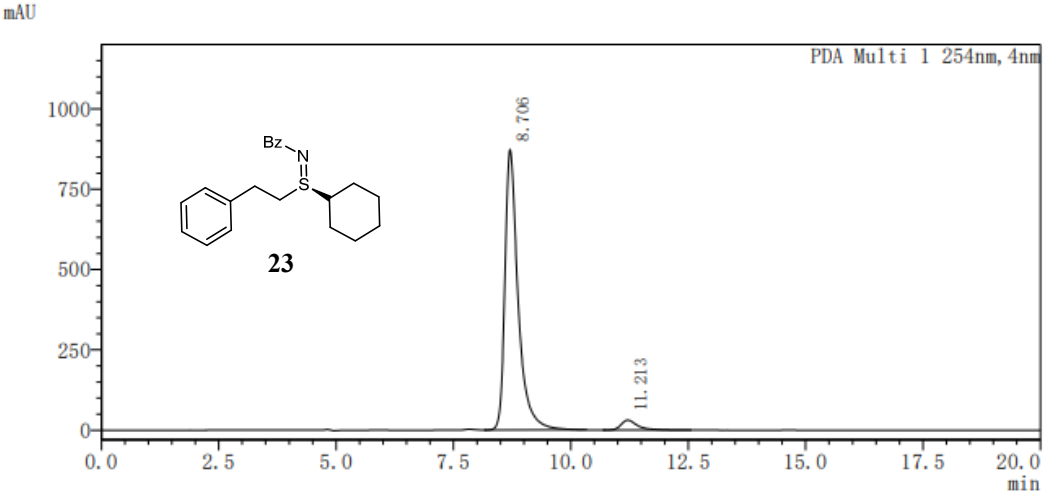


***rac*-23**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.779	9094992	49.646
2	11.267	9224734	50.354



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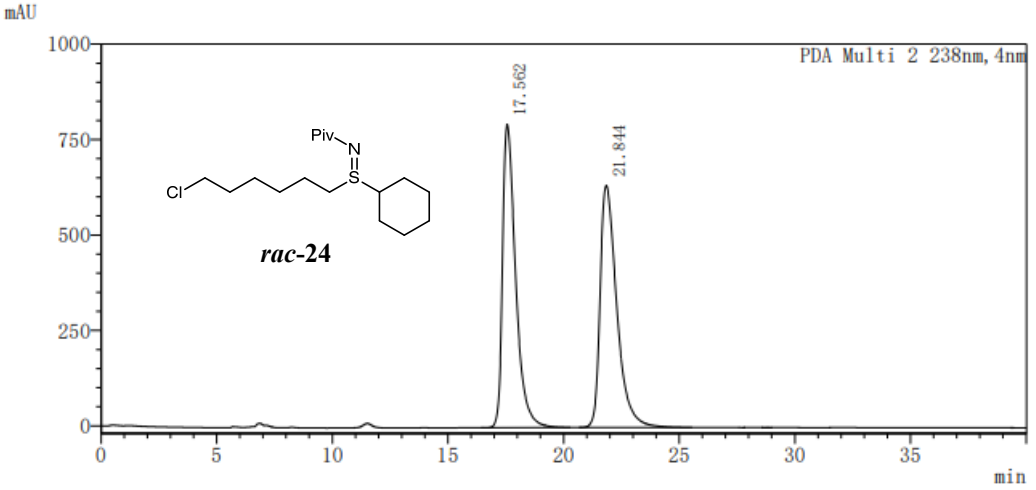
Peak Table

PDA Ch1 254nm

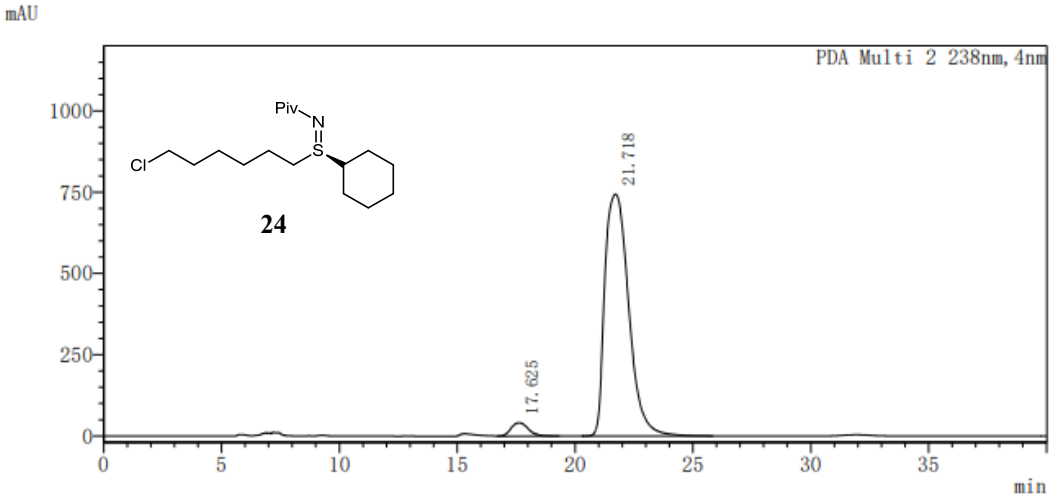
Peak#	Ret. Time	Area	Area%
1	8.706	17103088	95.638
2	11.213	780102	4.362



Peak Table

PDA Ch2 238nm

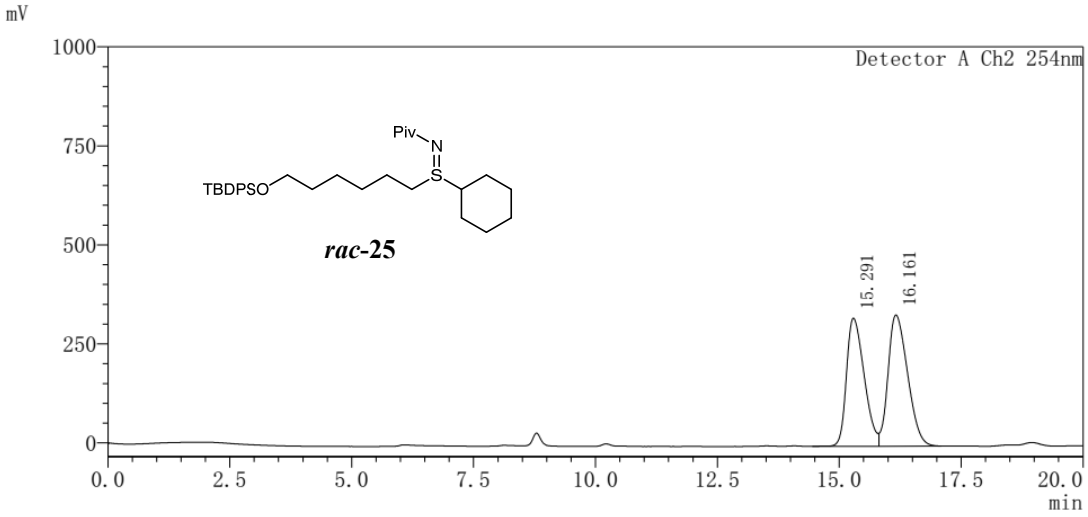
Peak#	Ret. Time	Area	Area%
1	17.562	31316570	49.641
2	21.844	31769829	50.359



Peak Table

PDA Ch2 238nm

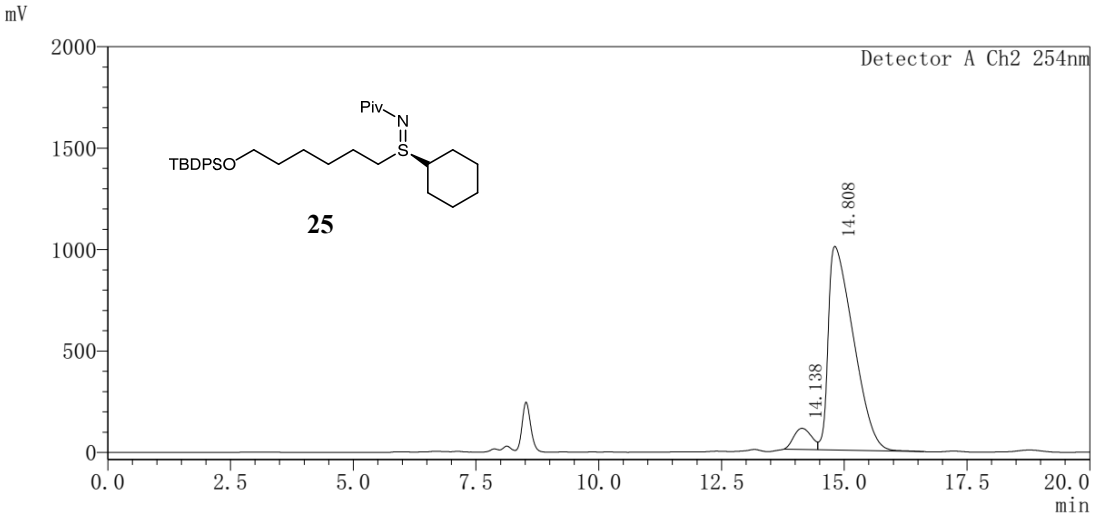
Peak#	Ret. Time	Area	Area%
1	17.625	2091727	3.837
2	21.718	52426408	96.163



Peak Table

Detector A Ch2 254nm

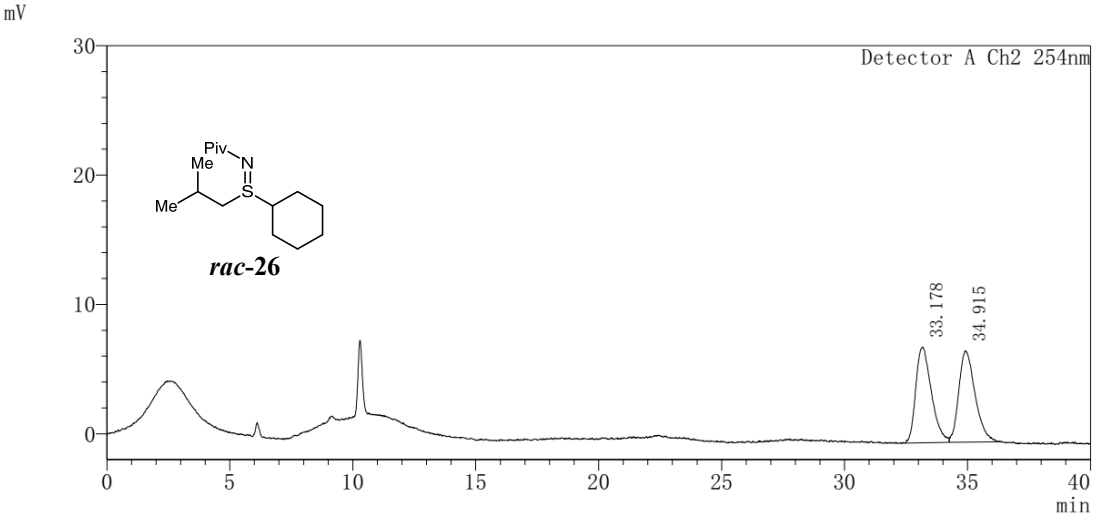
Peak#	Ret. Time	Area	Area%
1	15.291	8198633	47.084
2	16.161	9214132	52.916



Peak Table

Detector A Ch2 254nm

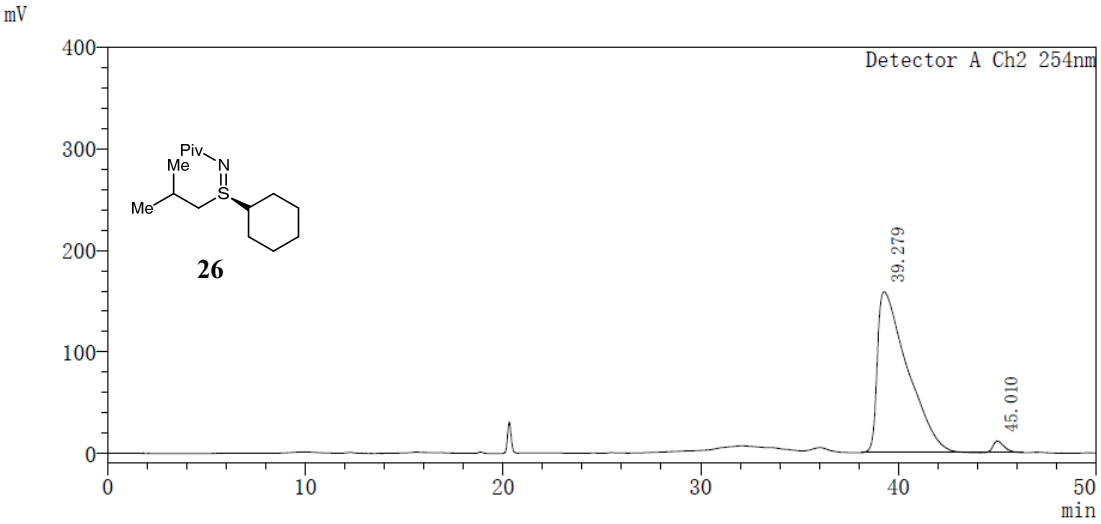
Peak#	Ret. Time	Area	Area%
1	14.138	2621749	6.791
2	14.808	35984920	93.209



Peak Table

Detector A Ch2 254nm

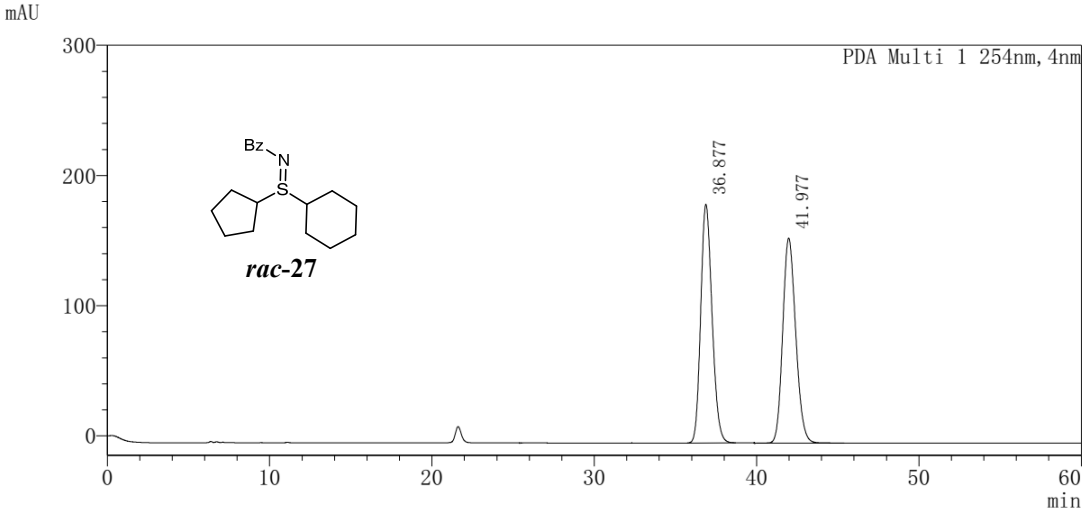
Peak#	Ret. Time	Area	Area%
1	33.178	327774	50.045
2	34.915	327179	49.955



Peak Table

Detector A Ch2 254nm

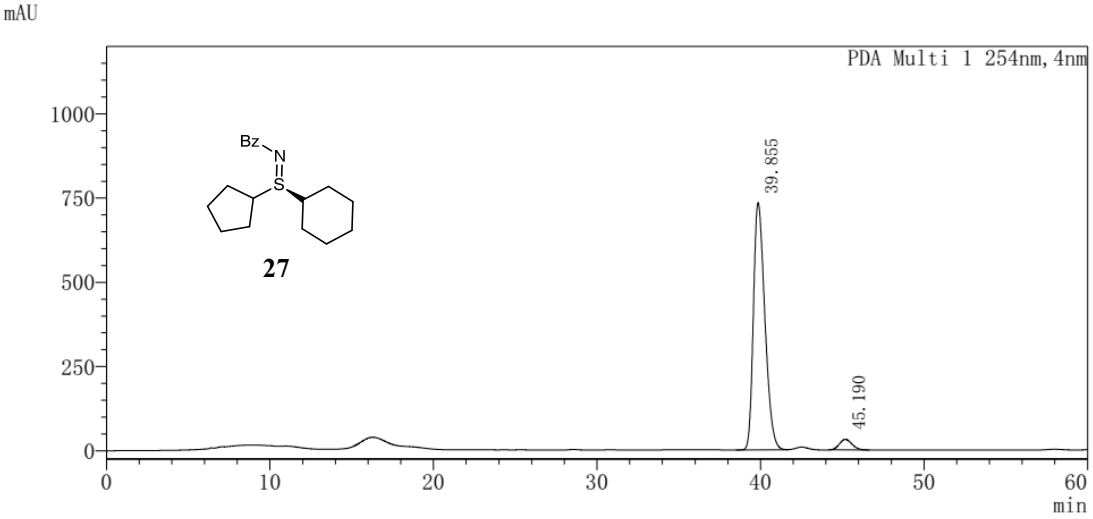
Peak#	Ret. Time	Area	Area%
1	39.279	16842846	97.395
2	45.010	450434	2.605



Peak Table

PDA Ch1 254nm

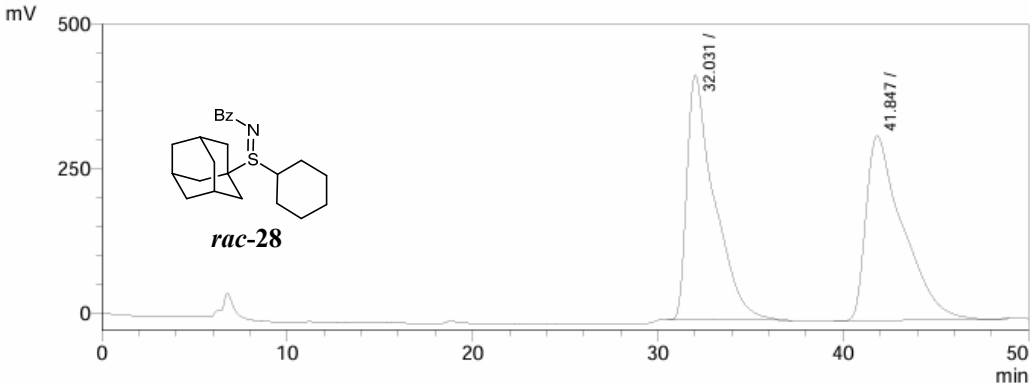
Peak#	Ret. Time	Area	Area%
1	36.877	8891528	50.405
2	41.977	8748674	49.595



Peak Table

PDA Ch1 254nm

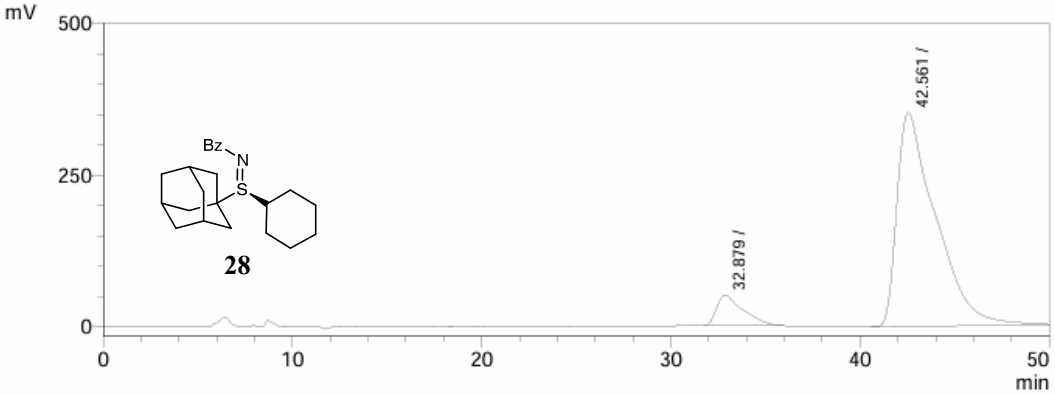
Peak#	Ret. Time	Area	Area%
1	39.855	35766947	95.518
2	45.190	1678172	4.482



***rac*-28**

检测器A 230nm

Peak#	Ret. Time	Area	Area%
1	32.031	43811763	49.752
2	41.847	44248764	50.248



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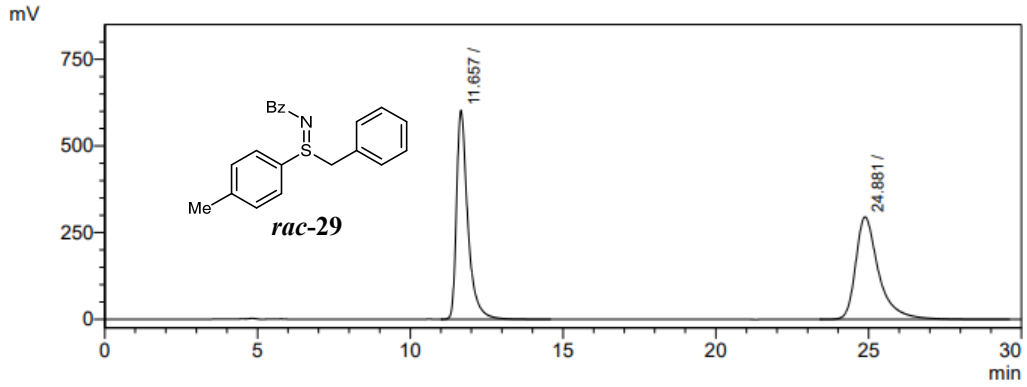
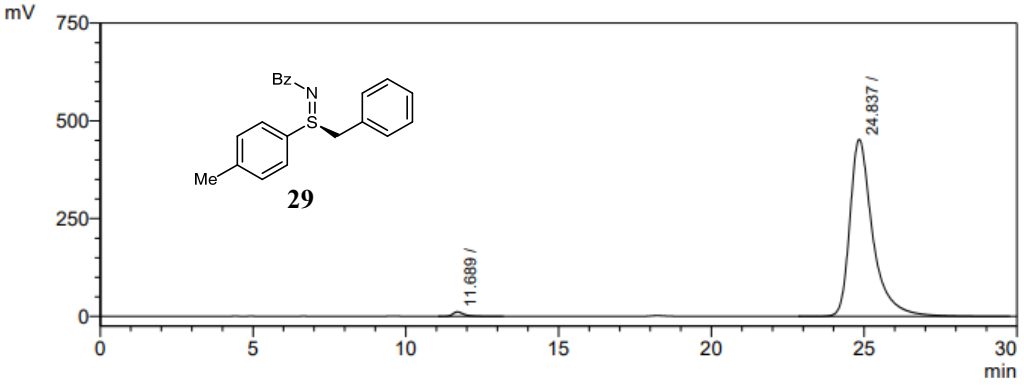
检测器A 230nm

Peak#	Ret. Time	Area	Area%
1	32.879	4851125	8.788
2	42.561	50347469	91.212



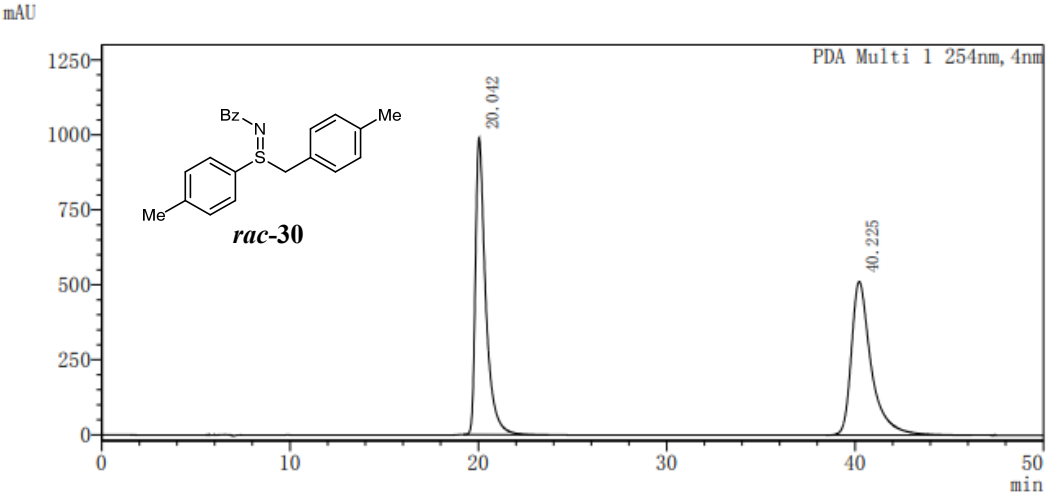
检测器A 254nm

Peak#	Ret. Time	Area	Area%
1	11.657	15501526	49.932
2	24.881	15543969	50.068



检测器A 254nm

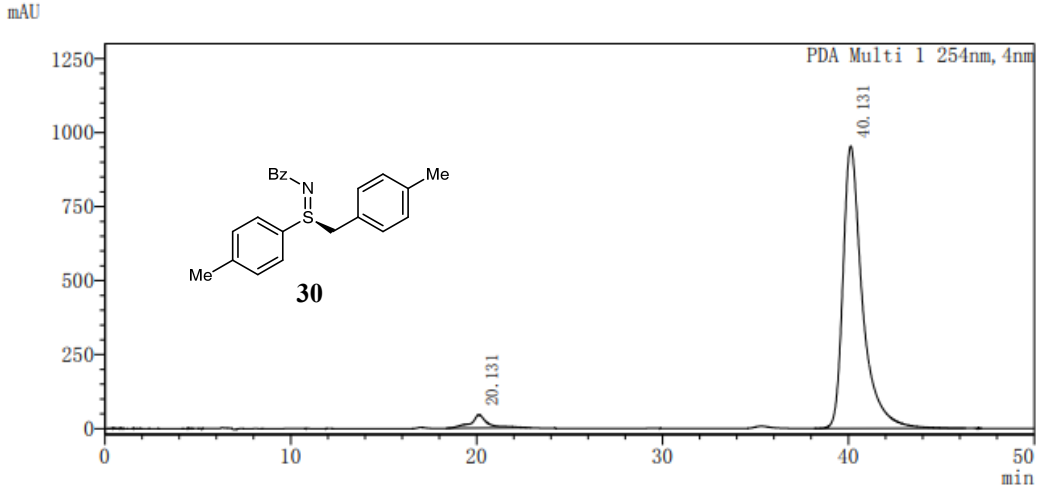
Peak#	Ret. Time	Area	Area%
1	11.689	291585	1.219
2	24.837	23628247	98.781



Peak Table

PDA Ch1 254nm

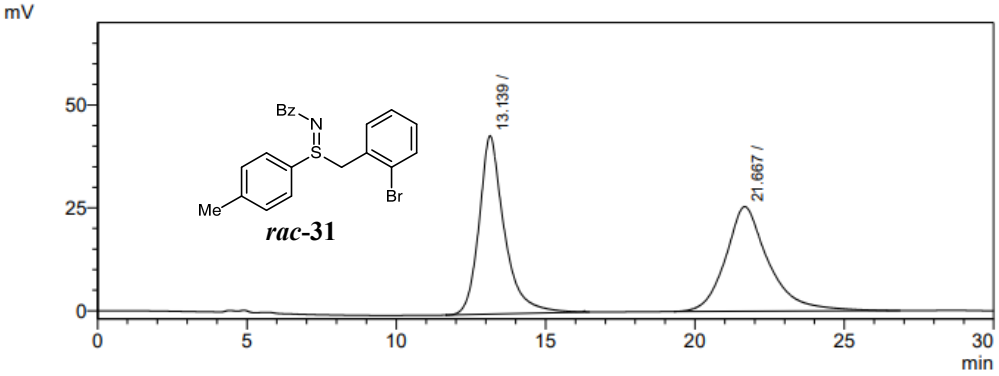
Peak#	Ret. Time	Area	Area%
1	20.042	37495243	49.925
2	40.225	37608142	50.075



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.131	2803084	3.882
2	40.131	69397870	96.118



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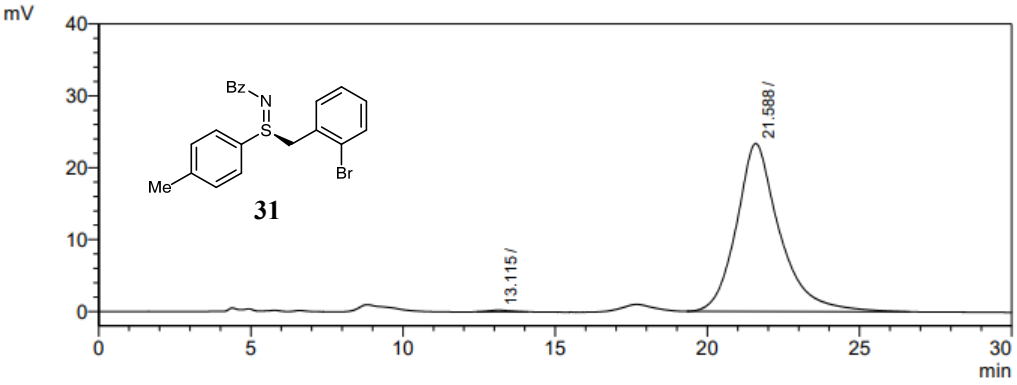
检测器A 254nm

Peak#	Ret. Time	Area	Area%
1	13.139	2547664	50.027
2	21.667	2544894	49.973



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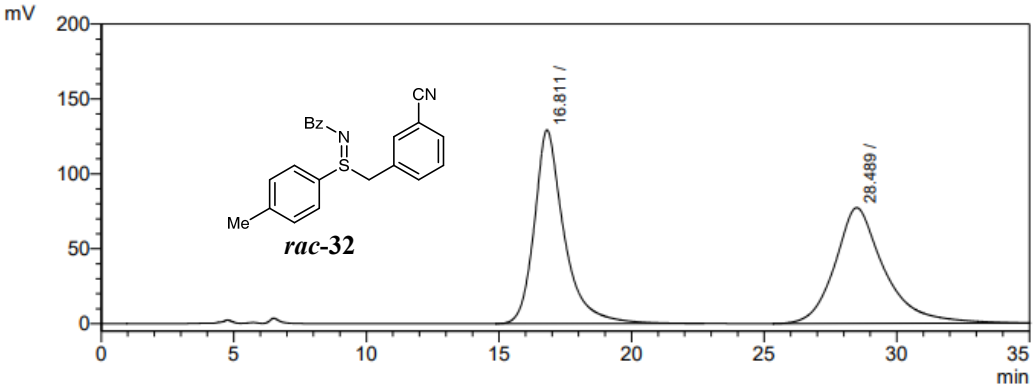
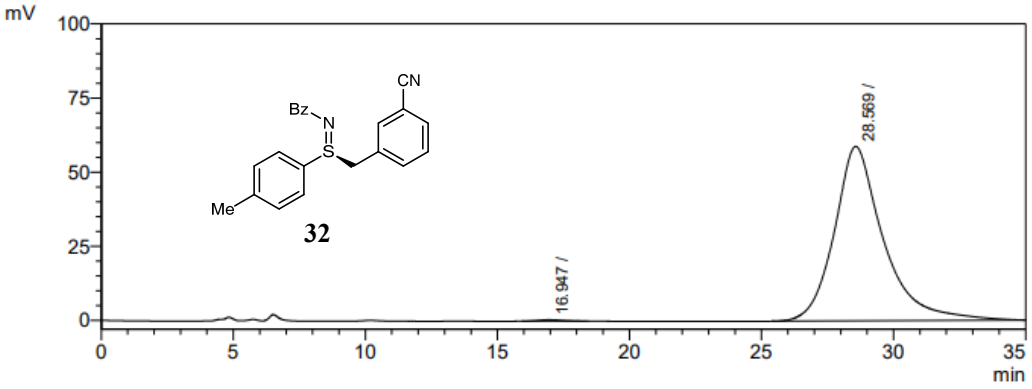
检测器A 254nm

Peak#	Ret. Time	Area	Area%
1	13.115	10635	0.459
2	21.588	2308256	99.541



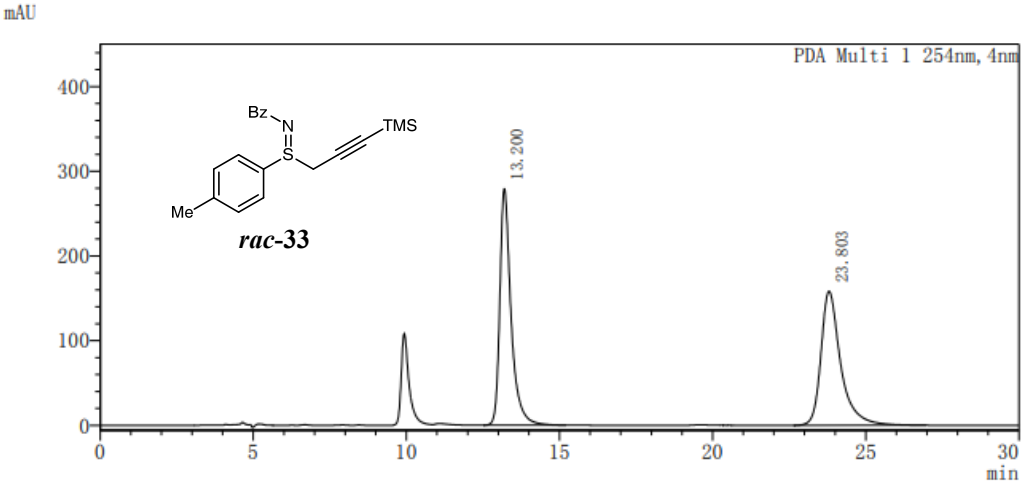
检测器A 254nm

Peak#	Ret. Time	Area	Area%
1	16.811	10098428	50.242
2	28.489	10000961	49.758



检测器A 254nm

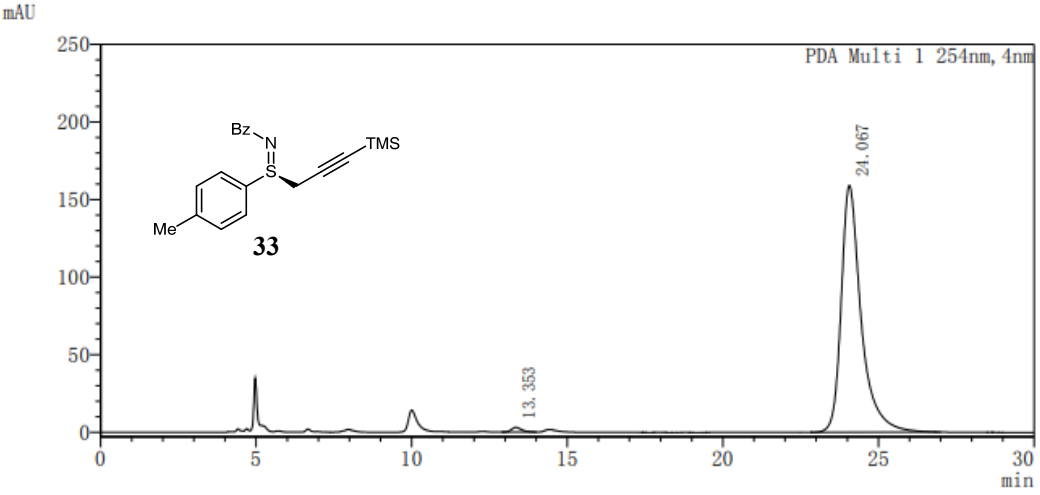
Peak#	Ret. Time	Area	Area%
1	16.947	31762	0.415
2	28.569	7626173	99.585



Peak Table

PDA Ch1 254nm

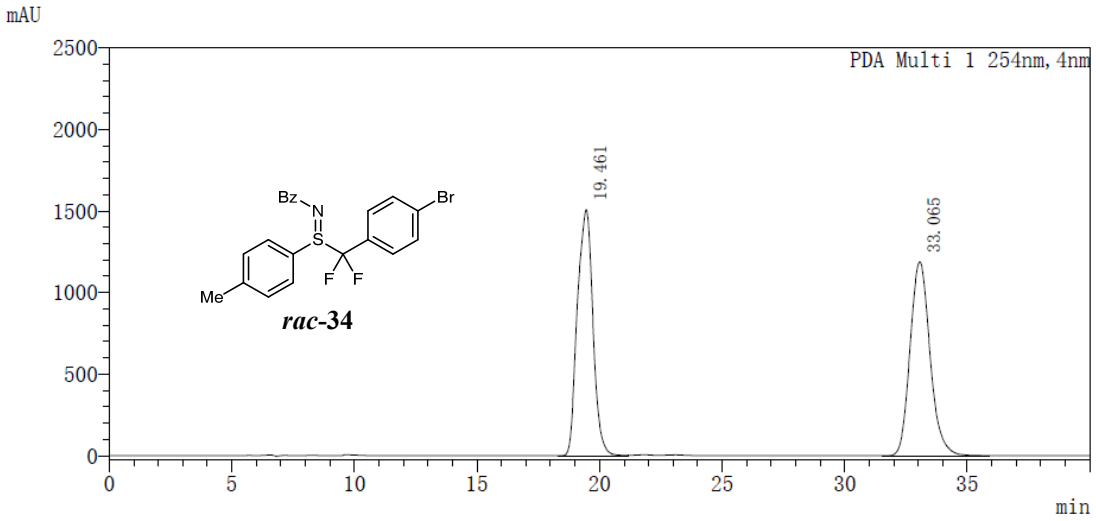
Peak#	Ret. Time	Area	Area%
1	13.200	7126617	50.020
2	23.803	7120979	49.980



Peak Table

PDA Ch1 254nm

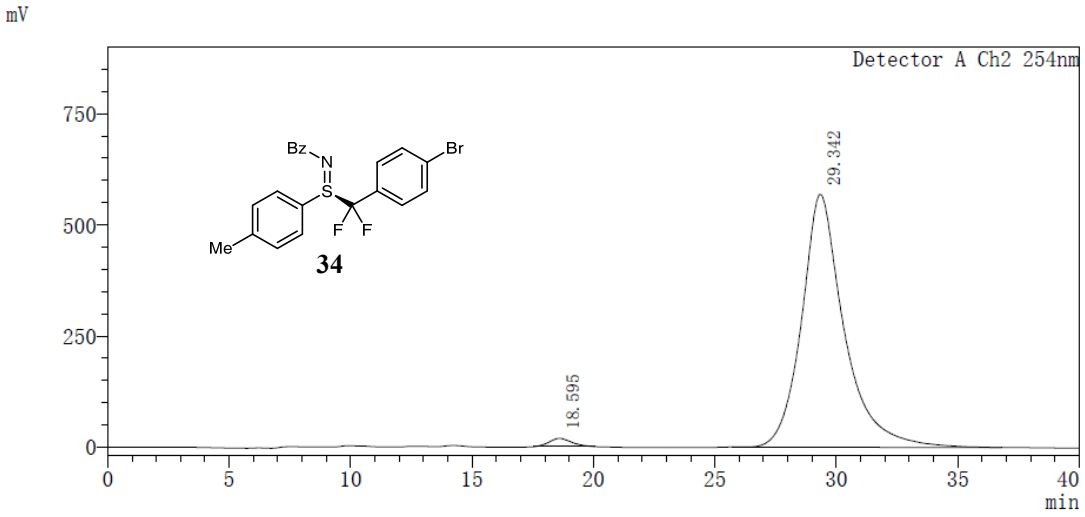
Peak#	Ret. Time	Area	Area%
1	13.353	68193	0.950
2	24.067	7109596	99.050



Peak Table

PDA Ch1 254nm

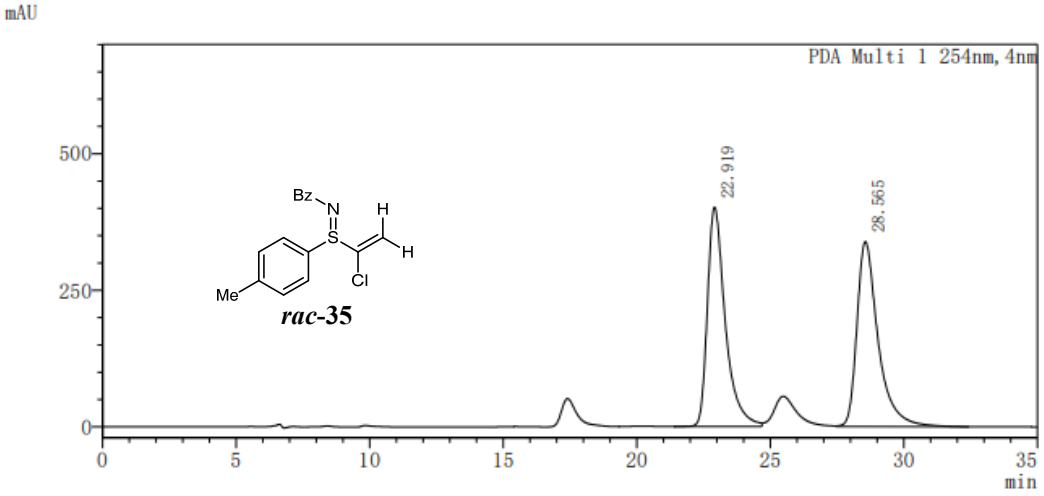
Peak#	Ret. Time	Area	Area%
1	19.461	66744908	49.797
2	33.065	67288233	50.203



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	18.595	1182770	1.673
2	29.342	69524393	98.327

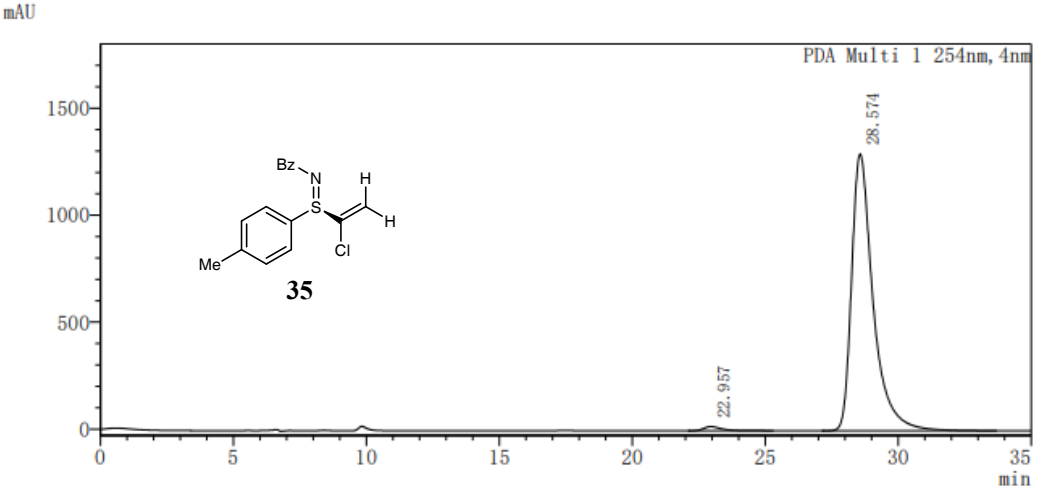


***rac*-35**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.919	18677442	49.894
2	28.565	18756743	50.106



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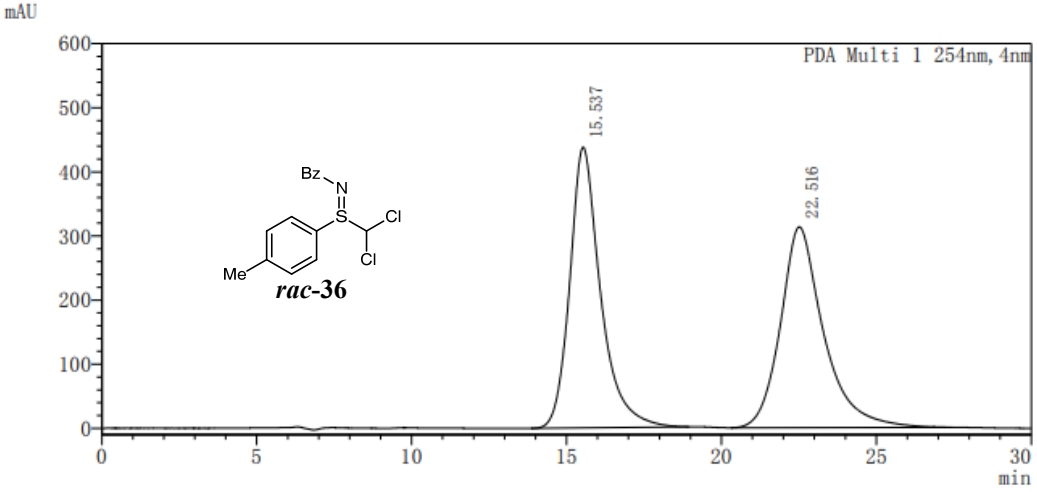
Peak Table

PDA Ch1 254nm

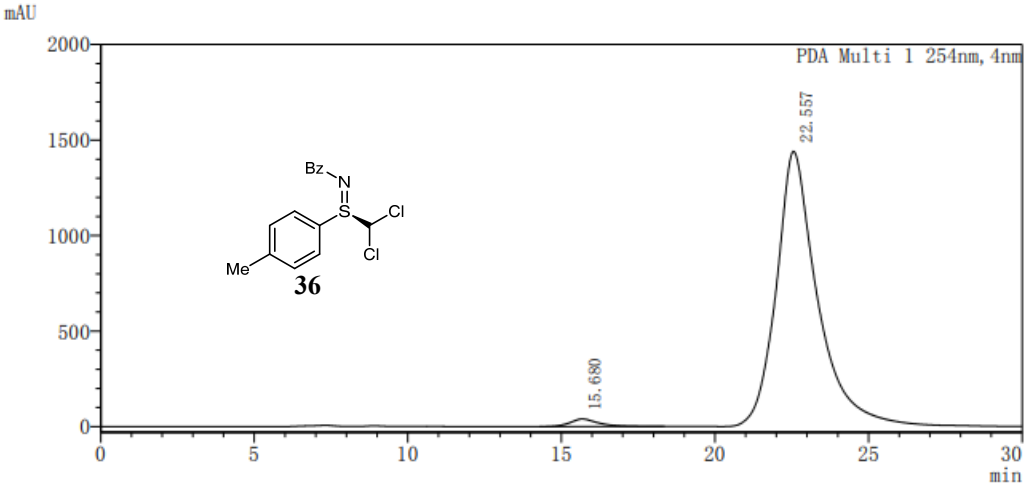
Peak#	Ret. Time	Area	Area%
1	22.957	889767	1.207
2	28.574	72807161	98.793



Peak Table

PDA Ch1 254nm

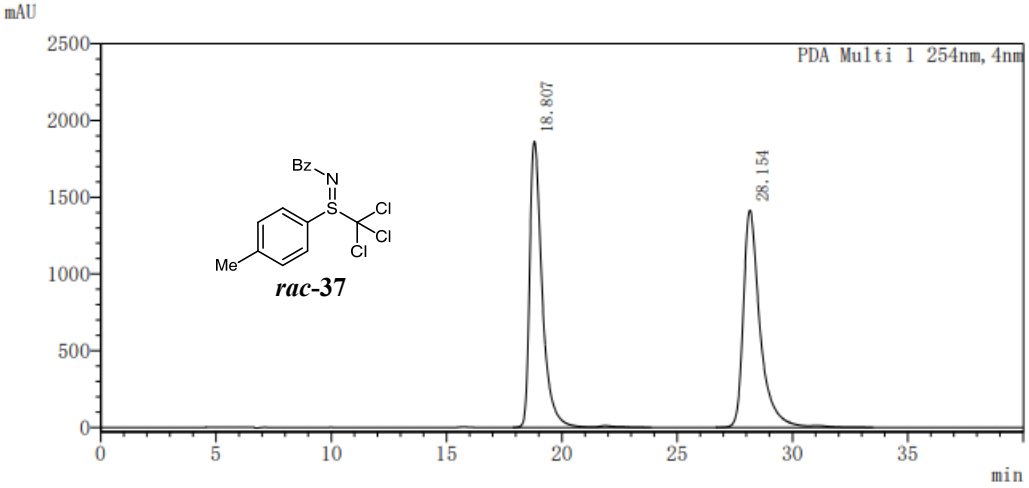
Peak#	Ret. Time	Area	Area%
1	15.537	30262358	49.956
2	22.516	30315464	50.044



Peak Table

PDA Ch1 254nm

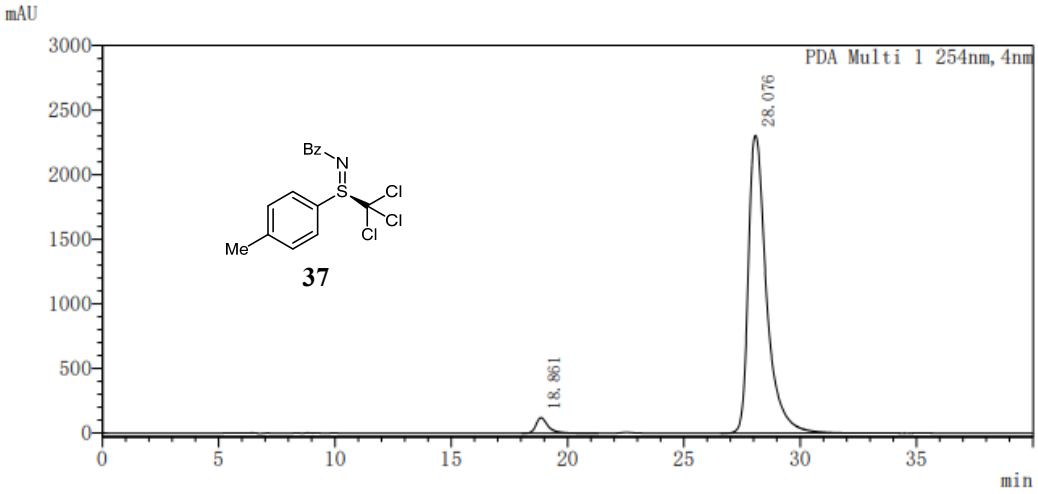
Peak#	Ret. Time	Area	Area%
1	15.680	2504607	1.814
2	22.557	135534624	98.186



Peak Table

PDA Ch1 254nm

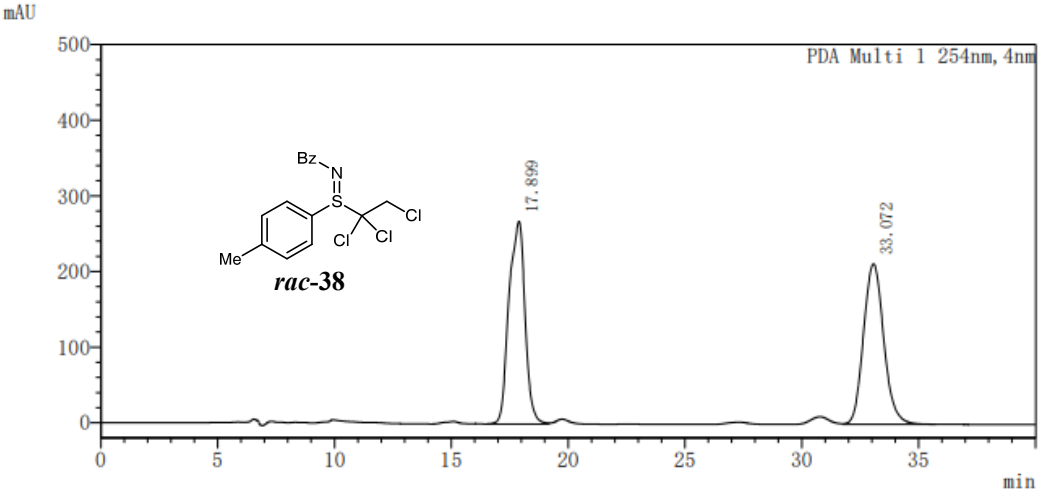
Peak#	Ret. Time	Area	Area%
1	18.807	70739037	49.635
2	28.154	71779381	50.365



Peak Table

PDA Ch1 254nm

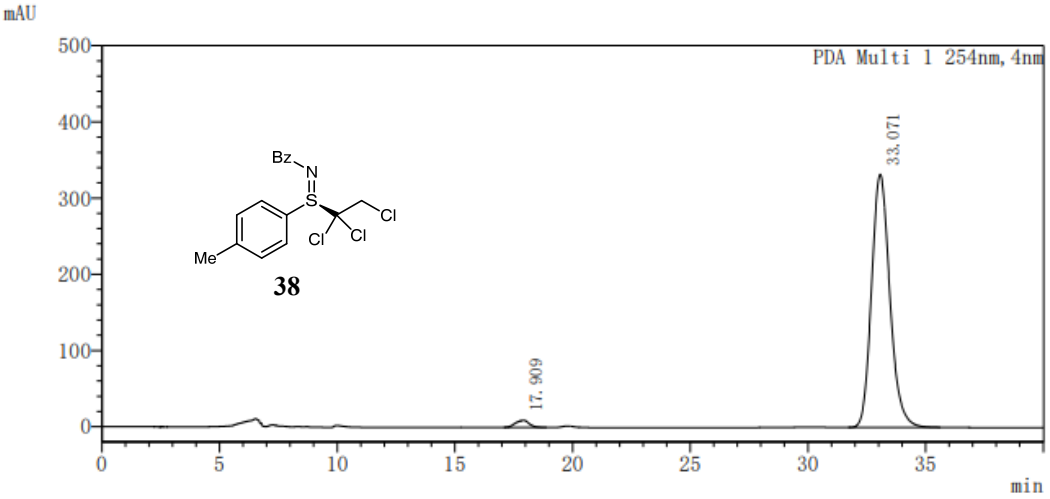
Peak#	Ret. Time	Area	Area%
1	18.861	4379181	3.378
2	28.076	125242994	96.622



Peak Table

PDA Ch1 254nm

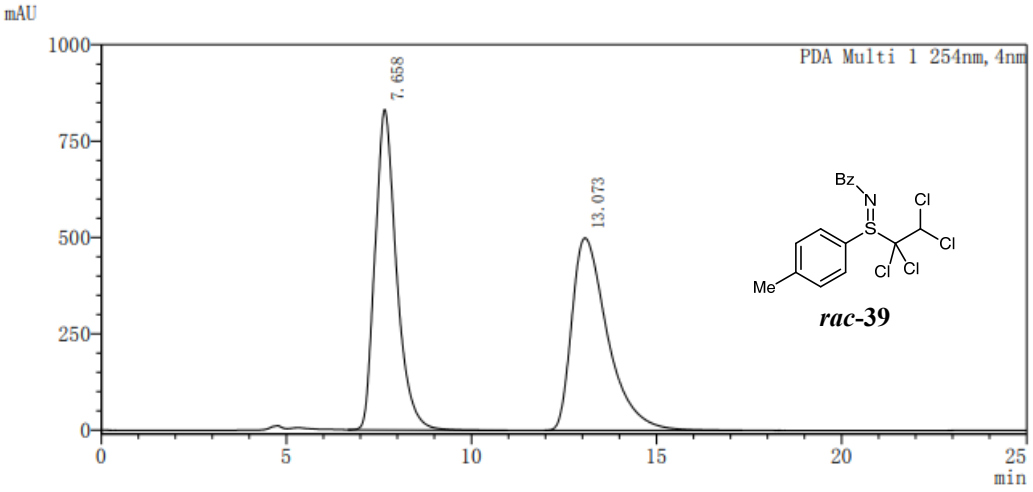
Peak#	Ret. Time	Area	Area%
1	17.899	12816363	50.043
2	33.072	12794556	49.957



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.909	382200	2.080
2	33.071	17993458	97.920

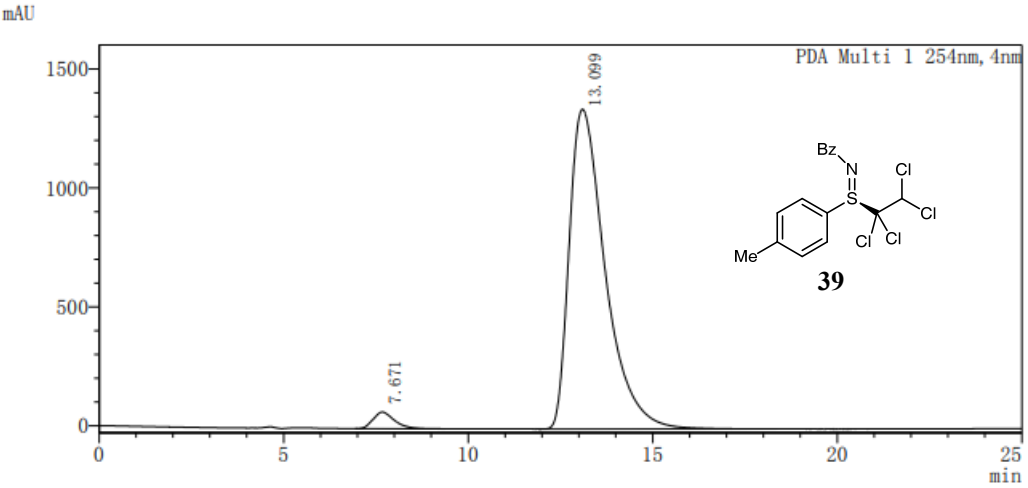


***rac*-39**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.658	33431782	49.934
2	13.073	33519640	50.066



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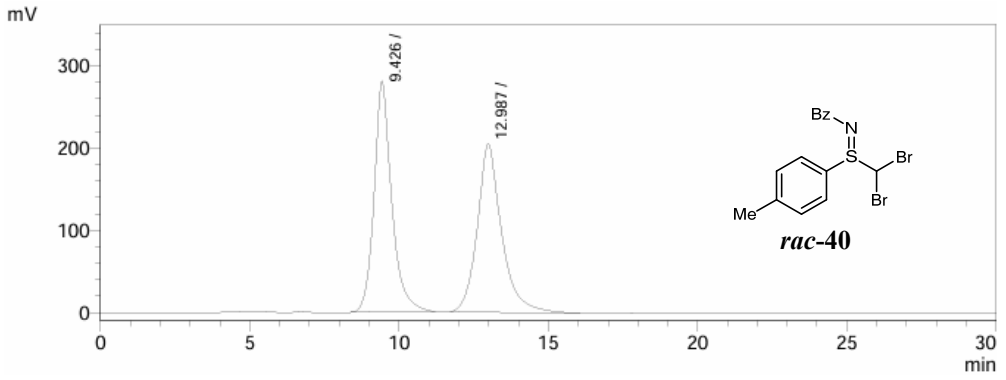
Peak Table

PDA Ch1 254nm

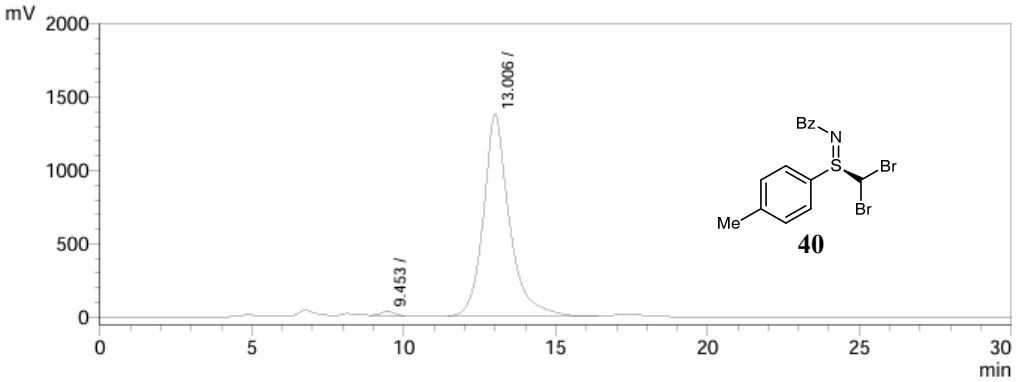
Peak#	Ret. Time	Area	Area%
1	7.671	2803086	2.982
2	13.099	91189665	97.018



***rac*-40**

检测器A 254nm

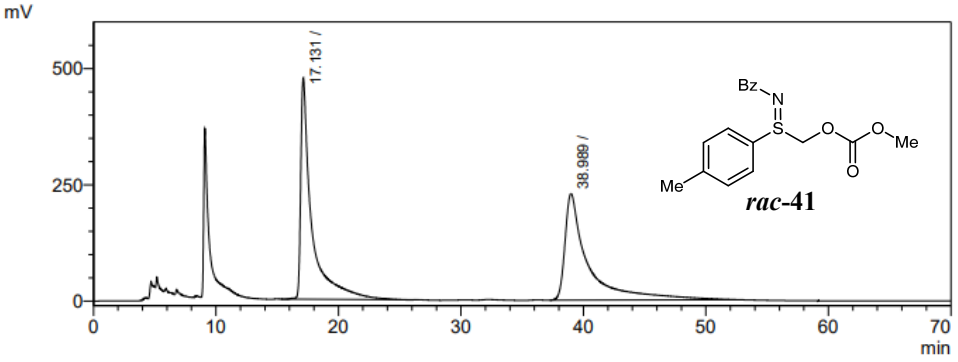
Peak#	Ret. Time	Area	Area%
1	9.426	11514002	49.833
2	12.987	11591331	50.167



40

检测器A 254nm

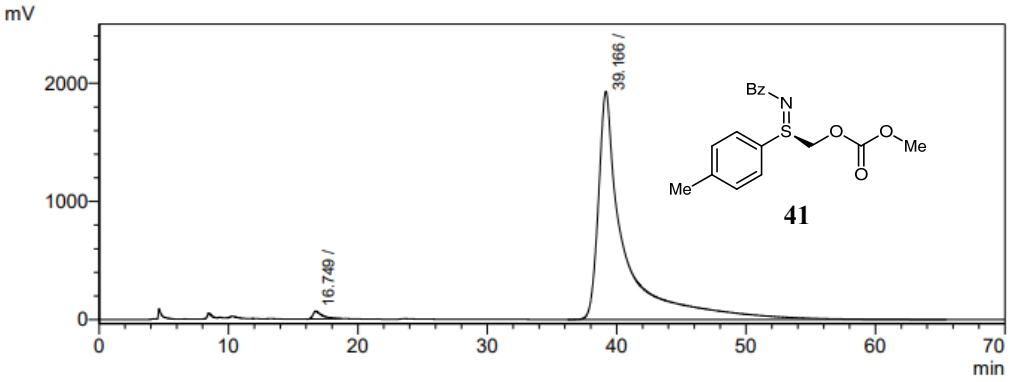
Peak#	Ret. Time	Area	Area%
1	9.453	867826	1.051
2	13.006	81672955	98.949



rac-**41**

检测器A 230nm

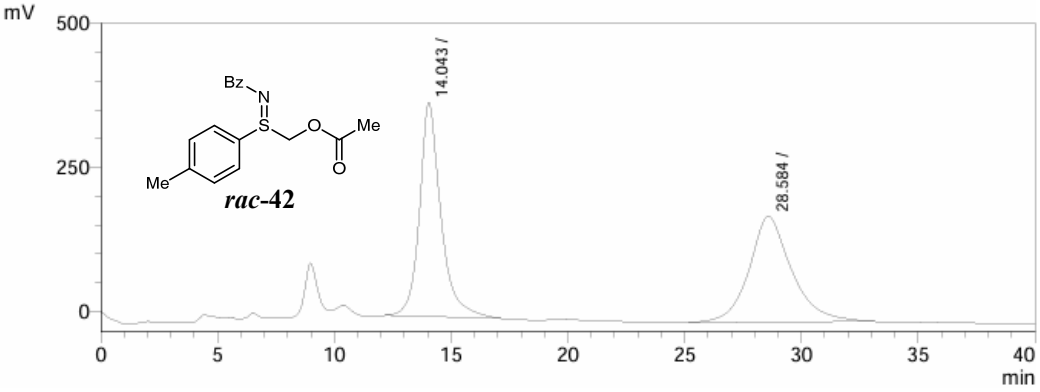
Peak#	Ret. Time	Area	Area%
1	17.131	29754762	49.714
2	38.989	30096788	50.286



41

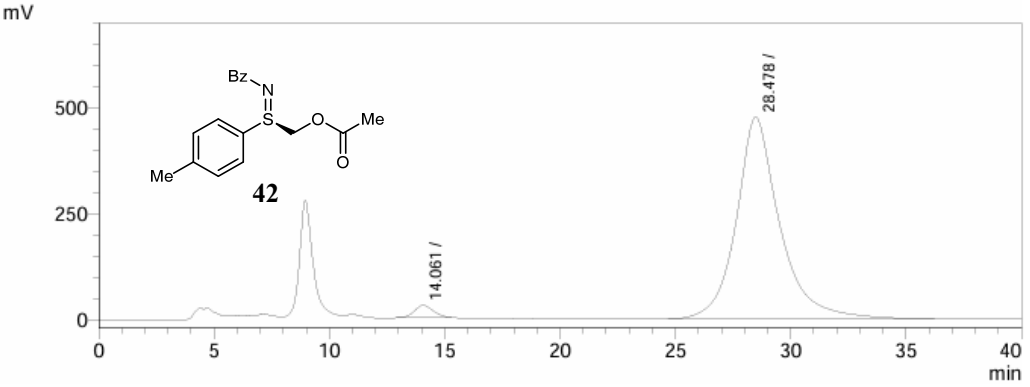
检测器A 230nm

Peak#	Ret. Time	Area	Area%
1	16.749	3040534	1.112
2	39.166	270279419	98.888



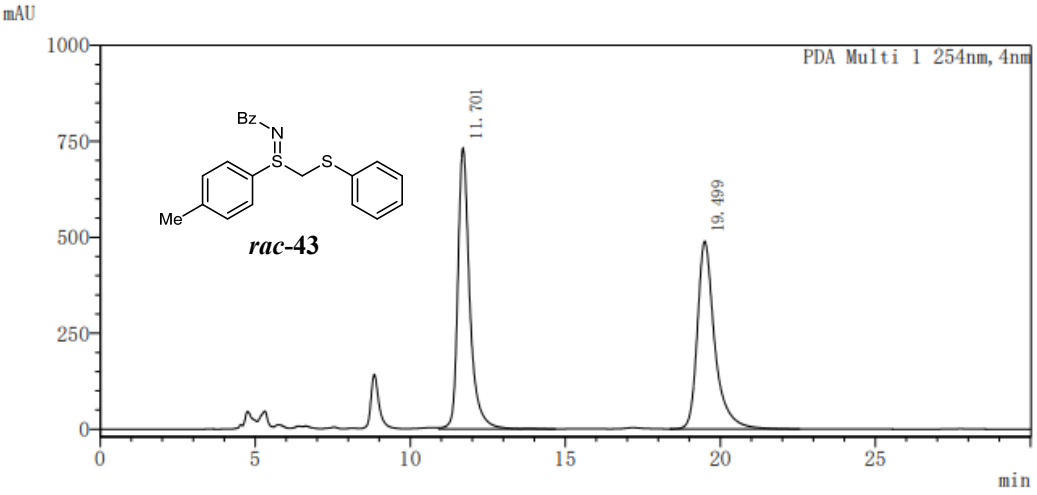
检测器A 230nm

Peak#	Ret. Time	Area	Area%
1	14.043	23669827	50.598
2	28.584	23110129	49.402



检测器A 230nm

Peak#	Ret. Time	Area	Area%
1	14.061	1641219	2.556
2	28.478	62561281	97.444

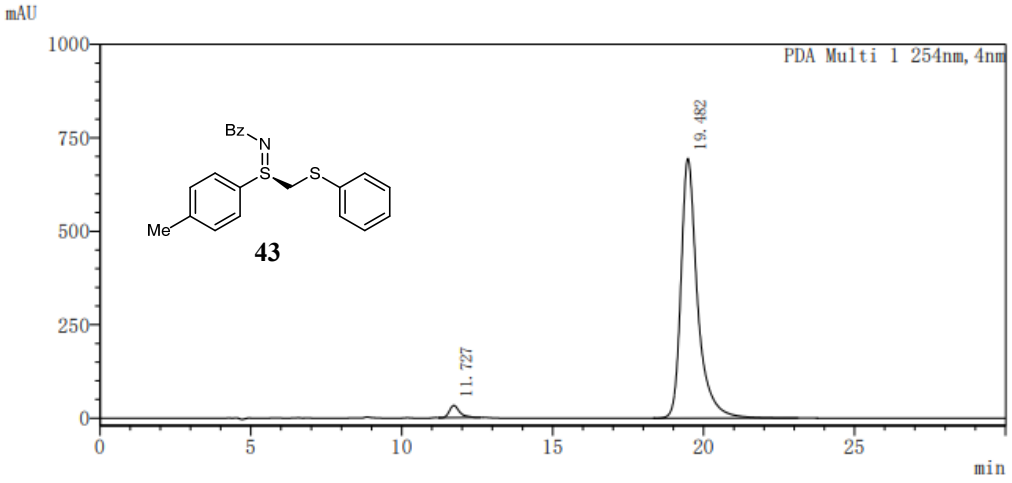


rac-**43**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.701	19511950	50.598
2	19.499	19050501	49.402



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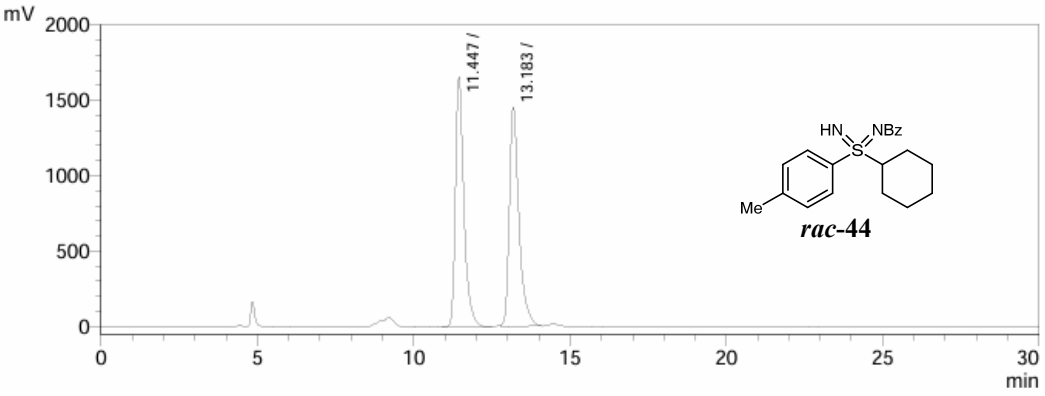
Peak Table

PDA Ch1 254nm

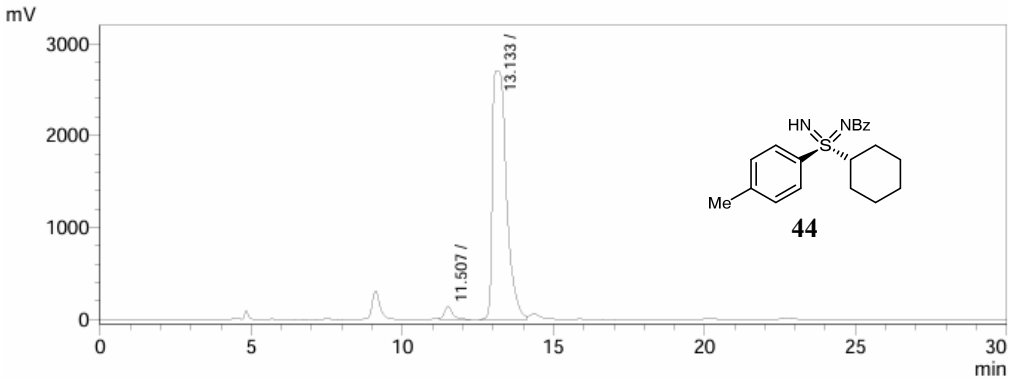
Peak#	Ret. Time	Area	Area%
1	11.727	752240	2.760
2	19.482	26503657	97.240



***rac*-44**

检测器A 230nm

Peak#	Ret. Time	Area	Area%
1	11.447	31054610	49.877
2	13.183	31207439	50.123



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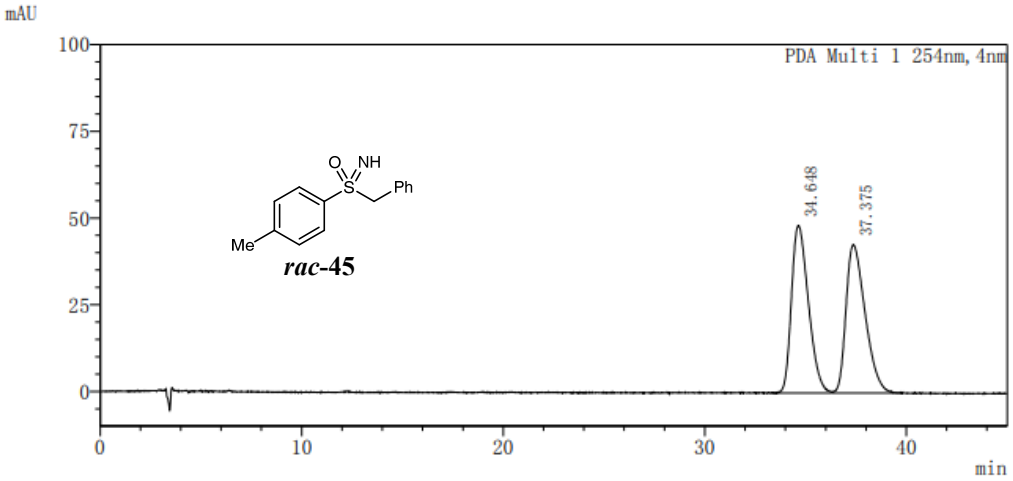
检测器A 230nm

Peak#	Ret. Time	Area	Area%
1	11.507	2547382	2.860
2	13.133	86522981	97.140

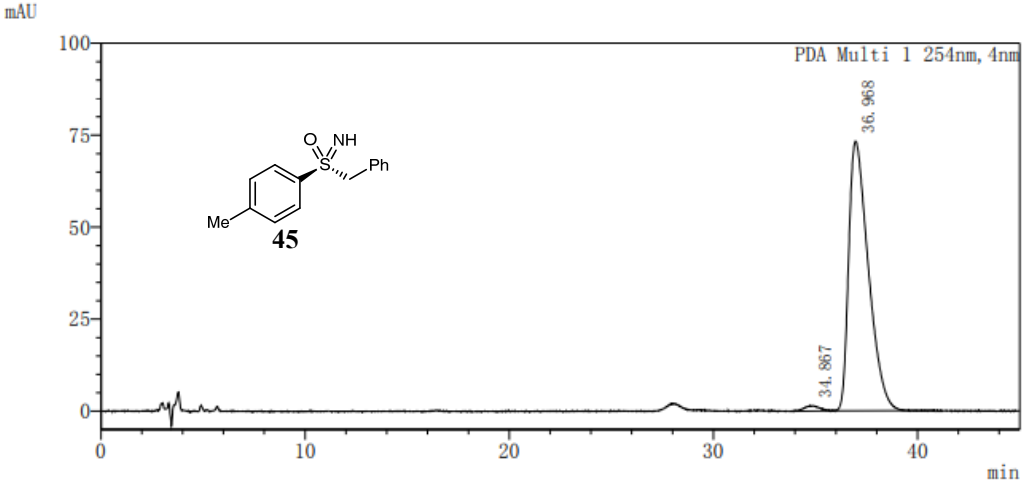


***rac*-45**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	34.648	2822372	49.987
2	37.375	2823835	50.013



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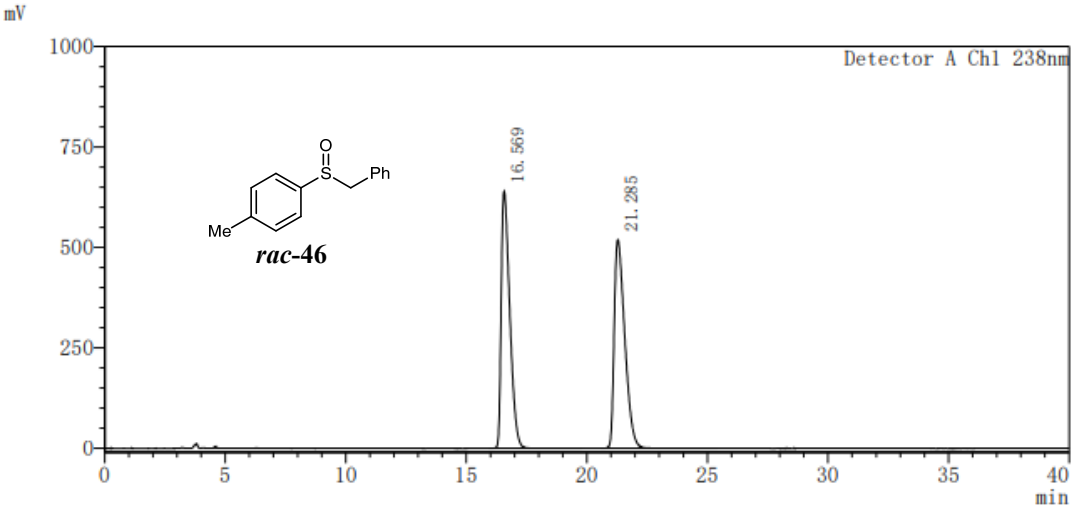
Peak Table

PDA Ch1 254nm

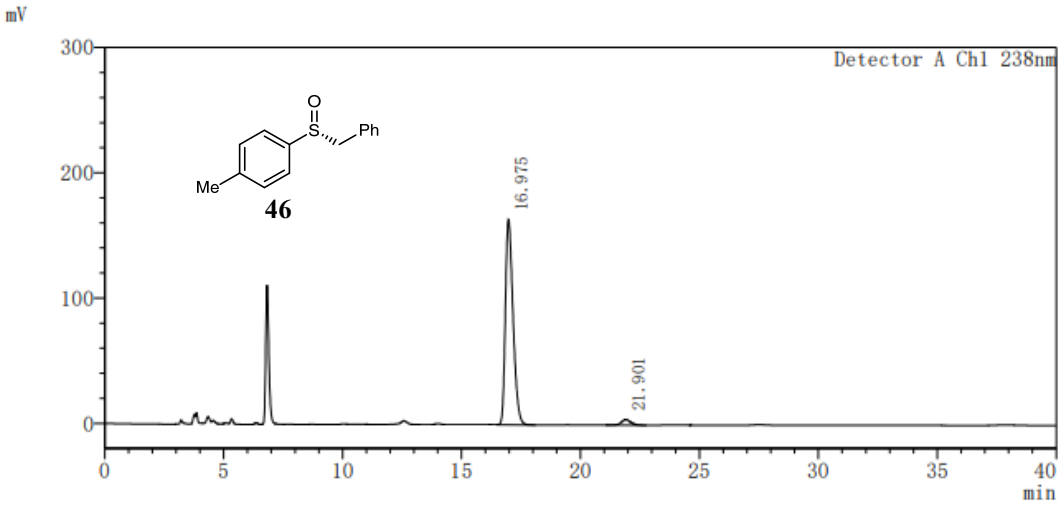
Peak#	Ret. Time	Area	Area%
1	34.867	74976	1.509
2	36.968	4894728	98.491



Peak Table

Detector A Ch1 238nm

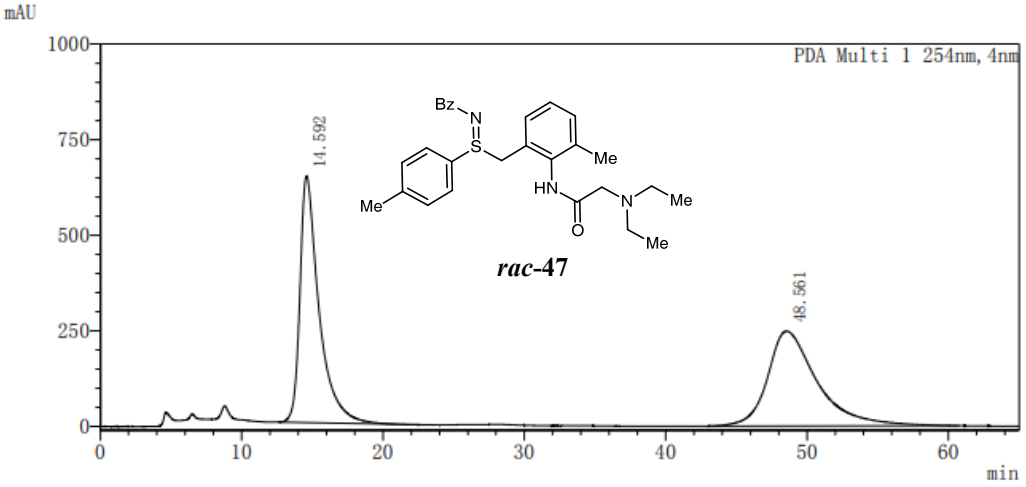
Peak#	Ret. Time	Area	Area%
1	16.569	15785985	49.901
2	21.285	15848920	50.099



Peak Table

Detector A Ch1 238nm

Peak#	Ret. Time	Area	Area%
1	16.975	3669924	96.804
2	21.901	121152	3.196

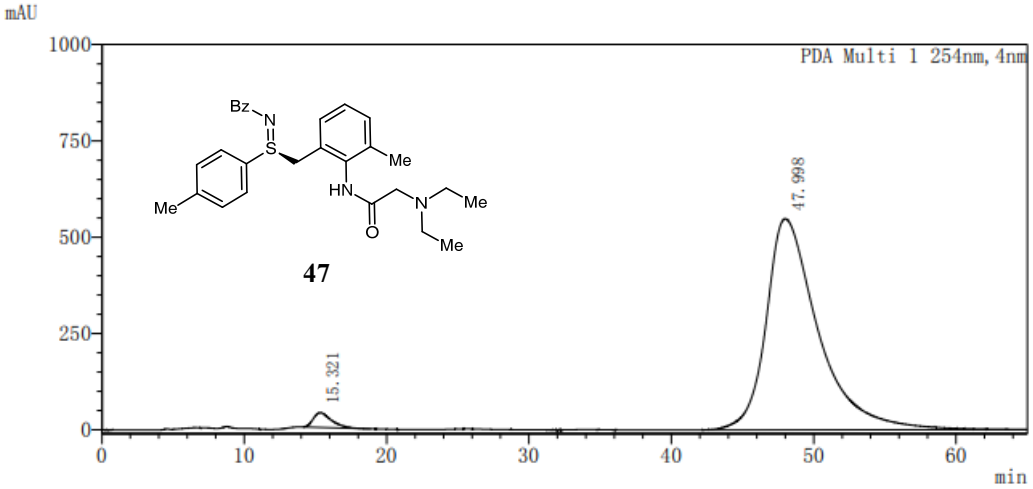


***rac*-47**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.592	60497281	49.965
2	48.561	60582008	50.035



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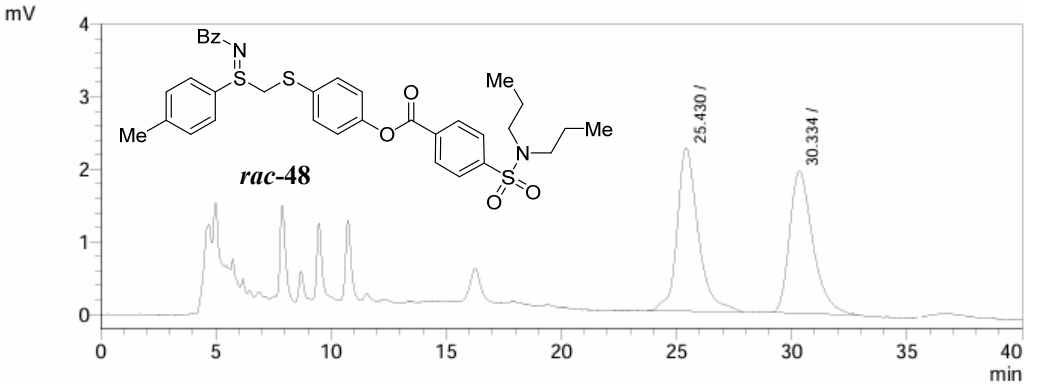
Peak Table

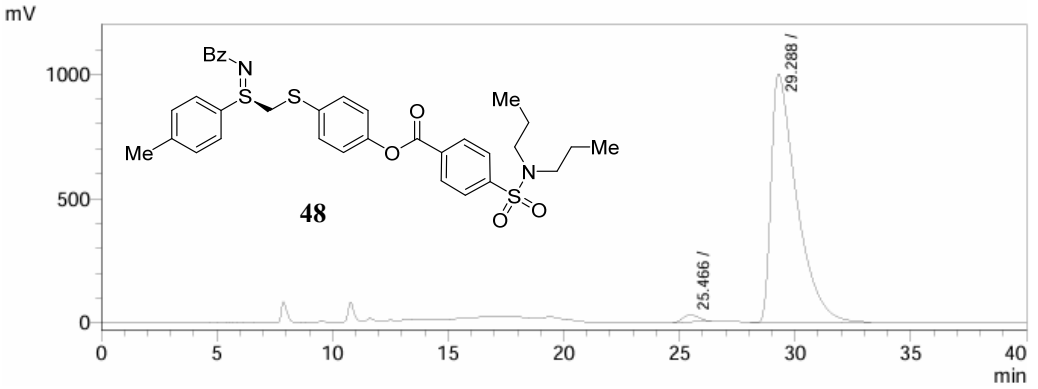
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.321	3393959	2.371
2	47.998	139733755	97.629



检测器A 254nm

Peak#	Ret. Time	Area	Area%
1	25.430	142788	50.790
2	30.334	138346	49.210



检测器A 254nm

Peak#	Ret. Time	Area	Area%
1	25.466	1342678	1.724
2	29.288	76526139	98.276