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Supporting Information

Enantioselective Addition of Selenosulfonates to α,β-unsaturated Ketones

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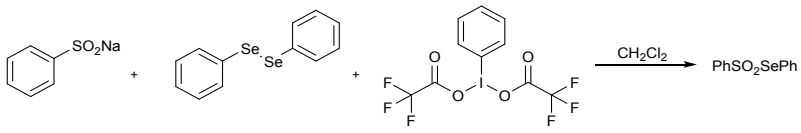
Contents

I. General information

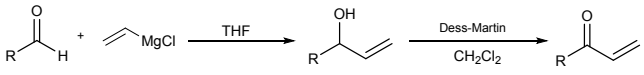
^{1}H and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer and Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual solvent peak was used as an internal reference: ^{1}H (tetramethylsilane δ 0.00), ^{13}C (chloroform δ 77.00). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Enantiomeric excesses (ee) were determined by HPLC analysis on Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6 mm Φ × 250 mmL, DAICEL CHIRALCEL OD-H, 4.6 mm Φ × 250 mmL and DAICEL CHIRALCEL OJ-H, 4.6 mm Φ × 250 mmL. High resolution mass spectra (HRMS) were performed on Bruker Solarix 7.0 T. X-ray crystallography analysis of single crystal was performed on a Agilent SuperNova-CCD X-Ray diffractometer. Optical Rotation was measured on a Rudolph Autopol I polarimeter. Melting points were measured using SGWX-4A Microscopic melting point meter and are uncorrected. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

II. General procedure for the preparation of selenosulfonates



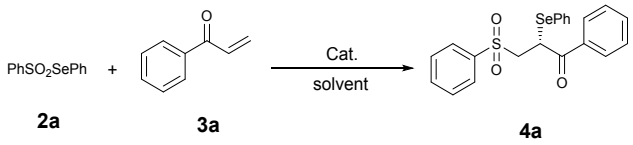
This reaction was carried out according to a literature method.[1] A suspension of $PhSO_2Na$ (657 mg, 4.0 mmol) in CH_2Cl_2 (10 mL) containing diphenyl diselenide (312 mg, 1.0 mmol) was cooled at 0 °C and [bis(trifluoroacetoxy)iodo]benzene (473 mg, 1.1 mmol) in CH_2Cl_2 (4 mL) was added dropwise. The mixture was stirred at room temperature for 3 h. Then, the reaction mixture was washed with H_2O, dried over anhydrous Na_2SO_4. The solvent CH_2Cl_2 was removed under reduced pressure and the residue was purified by a flash chromatography (SiO_2, PE/EA = 6:1) to yield the desired product (404 mg, 68%) as a yellow solid.

III. General procedure for the preparation of vinyl ketones



This reaction was carried out according to a literature method.[2] The mixture of aldehyde (3 mmol) in dry THF (5 mL) was cooled to 0 °C in an ice-water bath and vinylmagnesium chloride (2.0 M solution in THF, 3.6 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for overnight. Saturated NH_4Cl solution (20 mL) was added to quench the reaction and the aqueous layer was extracted with EA (15 mL × 3). The combined organic layers were washed with brine (20 mL × 1), dried over anhydrous Na_2SO_4 and concentrated. The residue was dissolved in CH_2Cl_2 (10 mL) and Dess-Martin periodinane (4.0 mmol) was added. The mixture was stirred at room temperature for overnight. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (PE/EA = 15:1) to get the desired product (75-88% yield for 2 steps). 3-Pridyl vinyl ketone and 2-furanyl vinyl ketone were prepared according to a literature method.[3] The beta-substituted vinyl ketones were prepared according to the known method.[4]

IV. Screening of the reaction conditions



2a **3a** **4a**

Table 1. Equivalent of 2a screening

entry	**2a** (equiv.)	**3a** (equiv.)	Cat. (equiv.)	solvent (1 mL)	time (h)	**4a** yield (%)	**4a** ee (%)	temp. (°C)
1	1.0	1.0	0.1	*o*-xylene	1	65	74	25
2	1.5	1.0	0.1	*o*-xylene	1	68	75	25
3	2.0	1.0	0.1	*o*-xylene	1	72	76	25
4	2.5	1.0	0.1	*o*-xylene	1	75	74	25

Table 2. Catalyst and solvent screening

entry	**2a** (equiv.)	**3a** (equiv.)	Cat. (10 mol%)	solvent (1 mL)	time (h)	**4a** yield (%)	**4a** ee (%)	temp. (°C)
1	2.0	1.0	**1a**	*o*-xylene	1	65	-3	25
2	2.0	1.0	**1b**	*o*-xylene	1	68	-28	25
3	2.0	1.0	**1c**	*o*-xylene	1	66	-18	25
4	2.0	1.0	**1d**	*o*-xylene	1	69	13	25
5	2.0	1.0	**1e**	*o*-xylene	1	72	76	25
6	2.0	1.0	**1e**	*m*-xylene	1	70	71	25
7	2.0	1.0	**1e**	toulene	1	67	63	25
8	2.0	1.0	**1e**	mesitylene	1	65	70	25
9	2.0	1.0	**1e**	CH_2Cl_2	1	75	80	25
10	2.0	1.0	**1e**	$CHCl_3$	1	71	60	25
11	2.0	1.0	**1e**	$ClCH_2CH_2Cl$	1	65	73	25
12	2.0	1.0	**1e**	THF	1	80	24	25
13	2.0	1.0	**1e**	1,4-dioxane	1	61	47	25
14	2.0	1.0	**1e**	butyl ether	1	45	52	25
15	2.0	1.0	**1e**	MeCN	1	55	45	25
16	2.0	1.0	**1e**	EA	1	63	43	25

Table 3. Concentration screening

entry	**2a** (equiv.)	**3a** (equiv.)	Cat-**1e** (equiv.)	CH_2Cl_2 (mL)	time (h)	**4a** Yield (%)	**4a** ee (%)	temp. (°C)
1	2.0	1.0	0.1	0.5	1	79	77	25
2	2.0	1.0	0.1	0.75	1	77	75	25
3	2.0	1.0	0.1	1.0	1	75	80	25
4	2.0	1.0	0.1	1.5	1	70	75	25
5	2.0	1.0	0.1	2.0	1	66	72	25

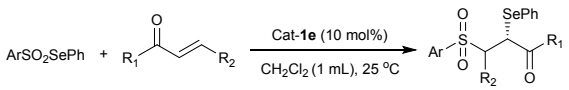
Table 4. Equivalent of catalyst screening

entry	**2a** (equiv.)	**3a** (equiv.)	Cat-**1e** (equiv.)	CH_2Cl_2 (mL)	time (h)	**4a** yield (%)	**4a** ee (%)	temp. (°C)
1	2.0	1.0	0.01	1.0	1	22	25	25
2	2.0	1.0	0.05	1.0	1	42	57	25
3	2.0	1.0	0.1	1.0	1	75	80	25
4	2.0	1.0	0.2	1.0	1	82	80	25

Table 5. Temperature screening

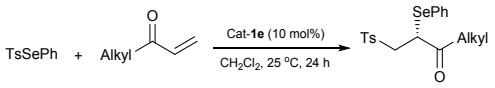
entry	**2a** (equiv.)	**3a** (equiv.)	Cat-**1e** (equiv.)	CH_2Cl_2 (mL)	time (h)	**4a** yield (%)	**4a** ee (%)	temp. (°C)
1	2.0	1.0	0.1	1.0	1	60	34	-78
2	2.0	1.0	0.1	1.0	1	66	69	-10
3	2.0	1.0	0.1	1.0	1	75	80	25
4	2.0	1.0	0.1	1.0	1	78	75	35
5	2.0	1.0	0.1	1.0	1	80	76	40

V. General procedure for the catalytic enantioselective addition



2 **3** **4**

A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with Se-phenyl benzeneselenosulfonate **2** (0.20 mmol) and the catalyst **1e** (6.30 mg, 10 mol%). Vinyl ketones **3** (0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL), and the solution was injected into the tube at 25 °C. After stirring for 1 hour, the mixture was purified by silica gel chromatography (PE/EA = 8/1) to afford the product **4**. Racemic samples were prepared by using the same procedure with DABCO as catalyst.

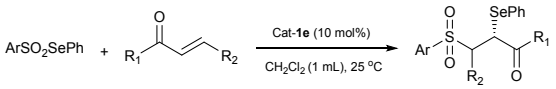


2b **5** **6**

A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with Se-phenyl 4-methyl benzeneselenosulfonate **2b** (0.20 mmol) and the catalyst **1e** (6.30 mg, 10 mol%). Vinyl ketones **5** (0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL), and the solution was injected into the tube at 25 °C. After stirring for 24 h, the mixture was purified by silica gel chromatography (PE/EA = 10/1) to afford the product **6**. Racemic samples were prepared by using the same procedure with DABCO as catalyst.

VI. Substrate scope

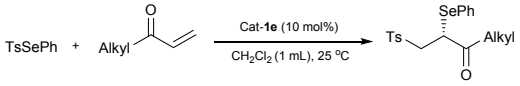
Table 6. Substrate scope 1



2 **3** **4**

entry	Ar	R_1	R_2	time (h)	**4**	
					yield (%)	ee (%)
1	Ph	Ph	H	1	75	80
2	4-ClC_6H_4	Ph	H	1	79	73
3	4-MeC_6H_4	Ph	H	1	80	84
4	4-MeC_6H_4	3-MeC_6H_4	H	1	66	80
5	4-MeC_6H_4	4-MeC_6H_4	H	1	57	82
6	4-MeC_6H_4	4-^{i}PrC_6H_4	H	1	76	89
7	4-MeC_6H_4	4-^{t}BuC_6H_4	H	1	78	88
8	4-MeC_6H_4	4-BrC_6H_4	H	1	71	62
9	4-MeC_6H_4	2-BrC_6H_4	H	1	75	52
10	4-MeC_6H_4	4-FC_6H_4	H	1	73	77
11	4-MeC_6H_4	4-ClC_6H_4	H	1	67	74
12	4-MeC_6H_4	2-$OMeC_6H_4$	H	1	66	71
13	4-MeC_6H_4	3-$OMeC_6H_4$	H	1	87	82
14	4-MeC_6H_4	4-$OMeC_6H_4$	H	1	78	85
16	4-MeC_6H_4	3-pyridinyl	H	1	70	68
17	4-MeC_6H_4	2-furanyl	H	1	81	87
18	4-MeC_6H_4	Ph	Ph	24	trace	-
19	4-MeC_6H_4	Ph	4-^{t}BuC_6H_4	24	trace	-
20	4-MeC_6H_4	Ph	4-BrC_6H_4	24	trace	-

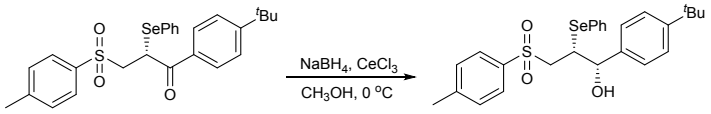
Table 7. Substrate scope 2



2b **5** **6**

entry	Alkyl	time (h)	**6** yield (%)	ee (%)
1	*n*-Pr	24	52	75
2	*n*-Bu	24	57	77
3	*n*-pentyl	24	73	72
4	*n*-hexyl	24	69	68
5	*n*-heptyl	24	61	77
6	*n*-octyl	24	58	78
7	*n*-nonyl	24	59	78
8	cyclohexyl	24	67	72
9	$(CH_2)_2Ph$	24	75	63

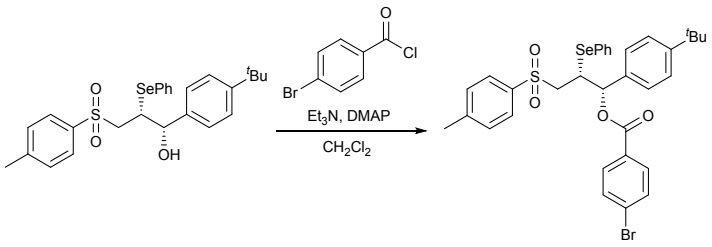
VII. Synthetic transformations



4h: 65% yield, 96% ee
after recrystallization
$[a]_D^{20}$ = -22.6

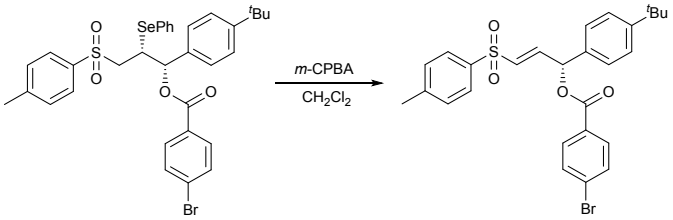
7: 90% yield, 98% ee
d.r. > 20:1

This reaction was carried out according to a literature method.[5] **4h** (50 mg, 0.1 mmol, 1.0 equiv.) and $CeCl_3$ (49.3 mg, 0.2 mmol, 2.0 equiv.) were weighed and added into an oven dried flask, evacuated and backfilled with nitrogen (3 times). Freshly distilled CH_3OH (1 mL) was introduced, and the resulting mixture was cooled down to 0 °C. $NaBH_4$ (7.6 mg, 0.2 mmol, 2.0 equiv.) solved in CH_3OH (0.5 mL) was added dropwise. The mixture was kept stirring for 5 minutes at 0 °C, quenched with H_2O, extracted with EA, concentrated under reduced pressure and purified by flash column chromatography (SiO_2, PE/EA = 6:1) to afford the product **7** as a white solid (45 mg, 0.09 mmol, 90%).



7: 98% ee, d.r. > 20:1 **8**: 91% yield, 92% ee

This reaction was carried out according to a literature method.[6] To a stirred solution of **7** (50 mg, 0.1 mmol, 1.0 equiv.) in CH_2Cl_2 was added 4-bromobenzoyl chloride (32.9 mg, 0.15 mmol, 1.5 equiv.) and DMAP (24.4 mg, 0.2 mmol, 2.0 equiv.) at 0 °C, Et_3N (20.2 mg, 0.2 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to r.t. and stirred for another 4 h. Diluted with EA, quenched with sat. $NaHCO_3$ aq. solution, extracted with EA, washed with brine dried over Na_2SO_4 and filtered, concentrated under reduced pressure and purified by flash column chromatography (SiO_2, PE/EA = 8:1) to afford the desired product **8** as a white solid (62.3 mg, 0.09 mmol, 91%).



8: 92% ee **9**: 95% yield, 88% ee

This reaction was carried out according to a literature method.[7] To a stirred solution of **8** (68.5 mg, 0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added *m*-CPBA (85% purity; 40.6 mg, 0.2 mmol, 2.0 equiv.) at r.t. and with stirring. The resulting solution was stirred for 1 h and then ca. 0.5M-$Na_2S_2O_3$ (3 mL) was added followed by saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with CH_2Cl_2, washed with brine dried over Na_2SO_4 and filtered, concentrated under reduced pressure and purified by flash column chromatography (SiO_2, PE/EA = 15:1) to afford the desired product **9** as a white solid (50.1 mg, 0.095 mmol, 95%).

VIII. References

[1]. Y.-L. Shi and M. Shi, *Org. Biomol. Chem.*, 2005, **3**, 1620.

[2]. Q. Xiao, Q. He, J. Li and J. Wang, *Org. Lett.*, 2015, **17**, 6090.

[3]. G. Zhang, T. Kumamoto, T. Heima and T. Ishikawa, *Tetrahedron Lett.,* 2010, **51**, 3927.

[4]. R. Khan, F. Shah, M. Salman, Z. Khan and A. Tavman, *ChemistrySelect*, 2017, **2**, 9364.

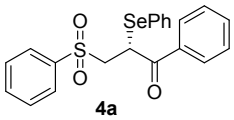
[5]. I. Aoki, Y. Nishibayashi and S. Uemura, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 337.

[6]. Y. Tan, S. Luo, D. Li, N. Zhang, S. Jia, Y. Liu, W. Qin, C. E. Song and H. Yan, *J. Am. Chem. Soc.*, 2017, **139**, 6431.

[7]. S. Uemura and S. Fukuzawa, *J. Chem. Soc., Perkin Trans. 1*, 1985, 471.

IX. ^{1}H, ^{13}C NMR, HRMS data and HPLC traces of compounds (4a-4p, 6a-6i, 7, 8, 9)

(*R*)-1-phenyl-2-(phenylselanyl)-3-(phenylsulfonyl)propan-1-one (4a)



4a

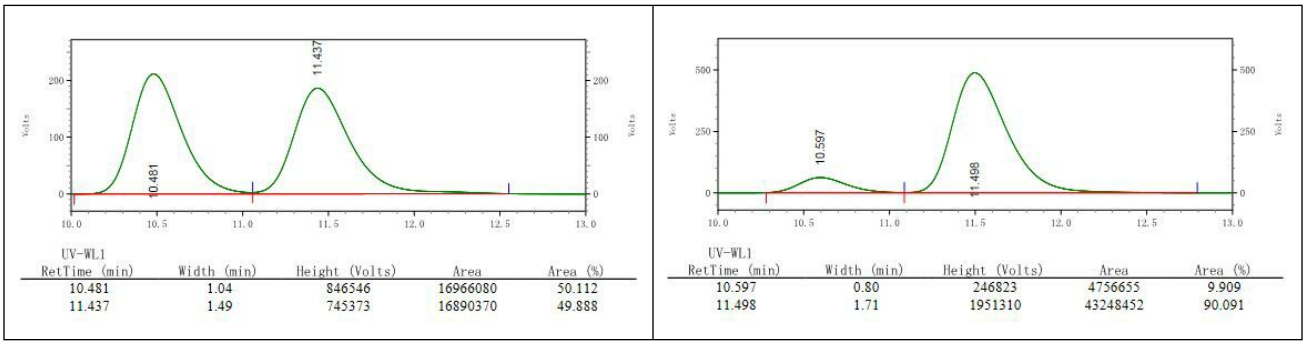
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.816 (d, *J* = 7.8 Hz, 2H), 7.751 (d, *J* = 7.8 Hz, 2H), 7.585 – 7.510 (m, 2H), 7.431 (t, *J* = 7.5 Hz, 2H), 7.411 – 7.336 (m, 5H), 7.288 – 7.238 (m, 2H), 5.046 (dd, *J* = 10.5, 2.1 Hz, 1H), 4.209 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.685 (dd, *J* = 14.1, 2.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 191.722, 138.762, 136.439, 134.790, 133.823, 133.343, 129.735, 129.411, 129.156, 128.566, 128.390, 128.110, 125.481, 58.157, 36.506.

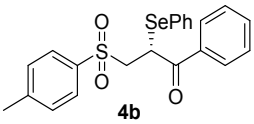
HRMS (ESI) m/z Calcd for $[C_{21}H_{18}O_3SSeNa, M + Na]^+$: 453.00344, Found: 453.00354.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 10.597 min (minor), t_R = 11.498 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -5.7 (c = 1.0, $CHCl_3$); **physical properties**: colorless liquid; **Yield**: 75%, 32.2 mg.



(*R*)-1-phenyl-2-(phenylselanyl)-3-tosylpropan-1-one (4b)



4b

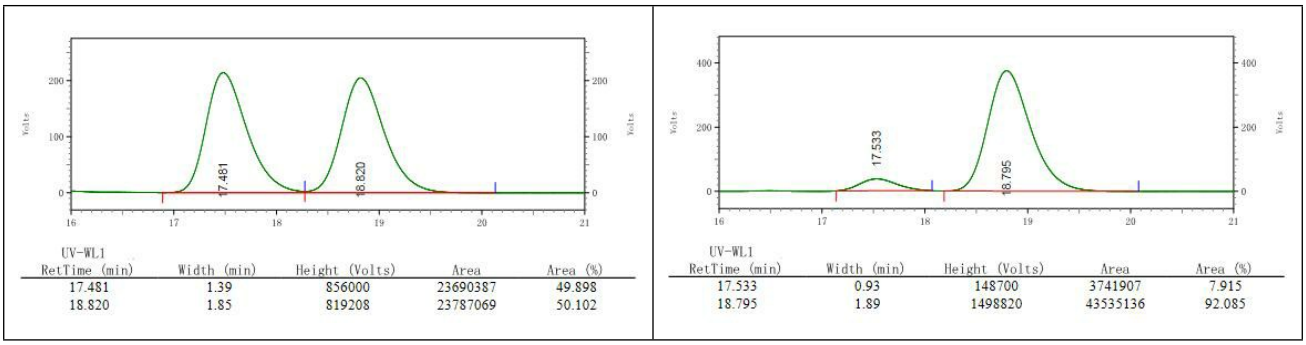
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.806 (d, *J* = 7.2 Hz, 2H), 7.614 (d, *J* = 8.0 Hz, 2H), 7.563 (t, *J* = 7.4 Hz, 1H), 7.428 (t, *J* = 7.6 Hz, 2H), 7.440 – 7.330 (m, 3H), 7.265 (t, *J* = 7.6 Hz, 2H), 7.164 (d, *J* = 8.0 Hz, 2H), 5.023 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.188 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.663 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.349 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.759, 144.864, 136.440, 135.769, 134.856, 133.304, 129.774, 129.702, 129.400, 128.515, 128.390, 128.187, 125.575, 58.309, 36.588, 21.542.

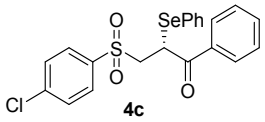
HRMS (ESI) m/z Calcd for $[C_{22}H_{20}O_3SSeNa, M + Na]^+$: 467.01909, Found: 467.01922.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 17.533 min (minor), t_R = 18.795 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -15.8 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 97–98 °C; **yield**: 80%, 35.5 mg.



(*R*)-3-((4-chlorophenyl)sulfonyl)-1-phenyl-2-(phenylselanyl) propan-1-one (4c)



4c

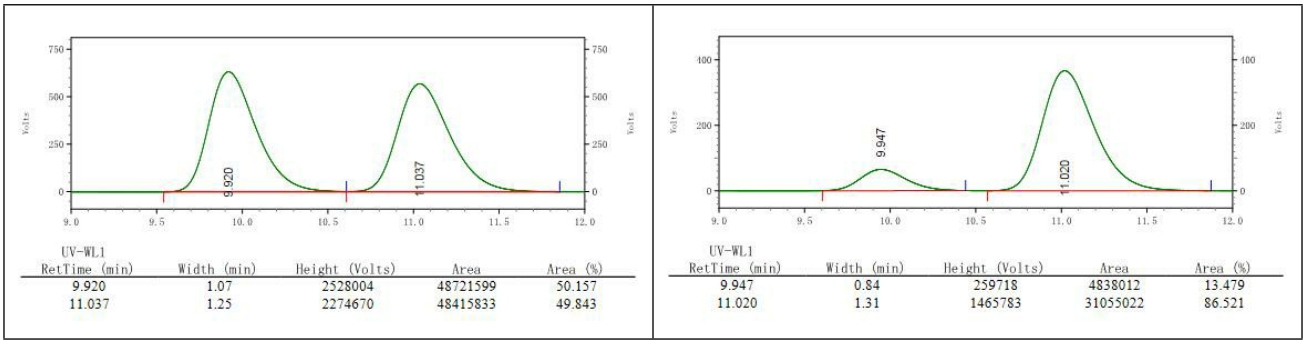
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.814 (d, *J* = 7.2 Hz, 2H), 7.653 (d, *J* = 8.4 Hz, 2H), 7.577 (t, *J* = 7.4 Hz, 1H), 7.443 (t, *J* = 7.6 Hz, 2H), 7.410 – 7.302 (m, 5H), 7.301 – 7.233 (m, 2H), 5.019 (dd, *J* = 10.8, 2.0 Hz, 1H), 4.194 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.689 (dd, *J* = 14.2, 2.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.656, 140.614, 137.211, 136.510, 134.663, 133.488, 129.836, 129.636, 129.439, 128.627, 128.344, 125.327, 58.328, 36.437.

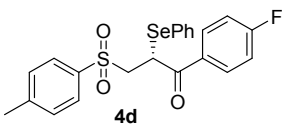
HRMS (ESI) m/z Calcd for $[C_{21}H_{17}ClO_3SSeNa, M + Na]^+$: 486.96422, Found: 486.96433.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 9.947 min (minor), t_R = 11.020 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -15.0 (c = 1.0, $CHCl_3$). **Physical properties**: colorless liquid; **Yield**: 79%, 36.6 mg.



(*R*)-1-(4-fluorophenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4d)



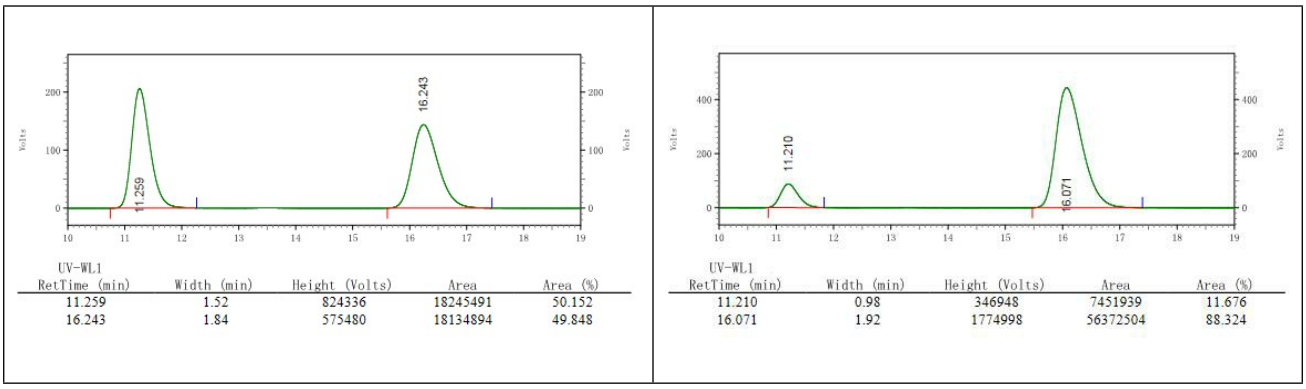
4d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.834 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.622 (d, *J* = 8.0 Hz, 2H), 7.414 – 7.322 (m, 3H), 7.300 – 7.235 (m, 2H), 7.194 (d, *J* = 8.0 Hz, 2H), 7.099 (t, *J* = 8.6 Hz, 2H), 4.981 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.184 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.659 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.368 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 190.471, 165.813 (d, $J_{C\text{-}F}$ = 254.0 Hz), 144.944, 136.408, 135.847, 131.285 (d, $J_{C\text{-}F}$ = 2.9 Hz), 131.072 (d, $J_{C\text{-}F}$ = 9.3 Hz), 129.806, 129.782, 129.461, 128.167, 125.576, 115.693 (d, $J_{C\text{-}F}$ = 21.8 Hz), 58.320, 36.571, 21.561.

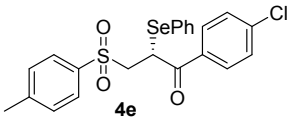
HRMS (ESI) m/z Calcd for $[C_{22}H_{19}FO_3SSeNa, M + Na]^+$: 485.00967, Found: 485.00953.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 11.210 min (minor), t_R = 16.071 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -33.2 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 91–92 °C; **yield**: 73%, 33.7 mg.



(*R*)-1-(4-chlorophenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4e)



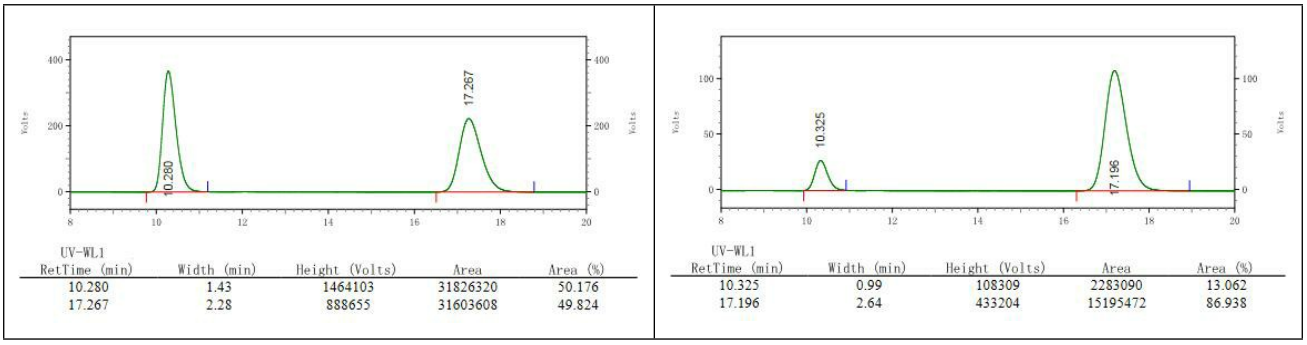
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.749 (d, *J* = 8.4 Hz, 2H), 7.621 (d, *J* = 8.0 Hz, 2H), 7.439 – 7.365 (m, 3H), 7.350 (d, *J* = 8.0 Hz, 2H), 7.268 (t, *J* = 7.6 Hz, 2H), 7.195 (d, *J* = 8.0 Hz, 2H), 4.963 (dd, *J* = 10.6, 1.8 Hz, 1H), 4.165 (dd, *J* = 13.8, 11.0 Hz, 1H), 3.667 (dd, *J* = 14.0, 1.6 Hz, 1H), 2.365 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.653, 144.956, 139.733, 136.430, 135.805, 133.253, 129.816, 129.784, 129.460, 128.844, 128.131, 125.434, 58.236, 36.605, 21.549.

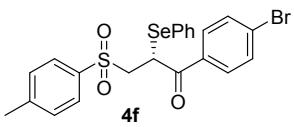
HRMS (ESI) m/z Calcd for $[C_{22}H_{19}ClO_3SSeNa, M + Na]^+$: 500.97988, Found: 500.97973.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 10.325 min (minor), t_R = 17.196 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -16.3 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 92–93 °C; **yield**: 67%, 32 mg.



(*R*)-1-(4-bromophenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4f)



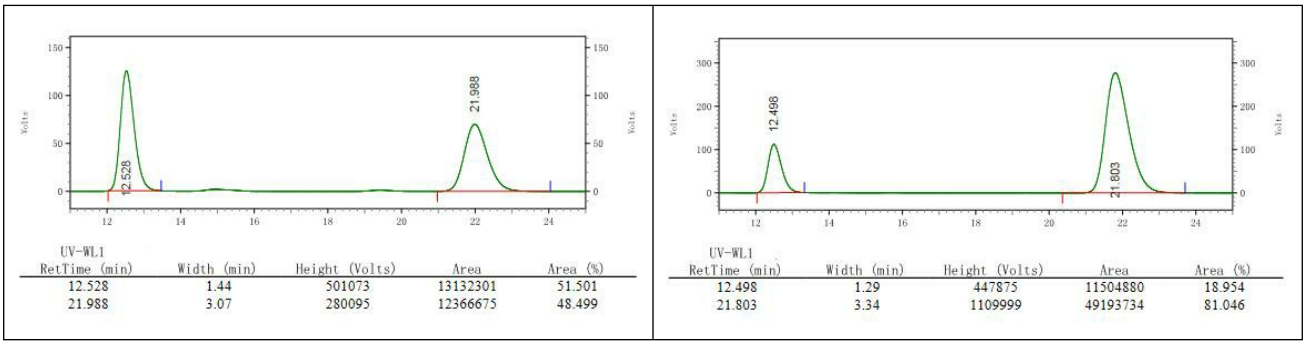
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.670 (d, *J* = 8.4 Hz, 2H), 7.620 (d, *J* = 8.0 Hz, 2H), 7.570 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.320 (m, 3H), 7.300 – 7.245 (m, 2H), 7.198 (d, *J* = 8.0 Hz, 2H), 4.953 (dd, *J* = 10.6, 2.0 Hz, 1H), 4.163 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.662 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.370 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.842, 144.973, 136.442, 135.815, 133.690, 131.848, 129.877, 129.833, 129.476, 128.474, 128.138, 125.432, 58.237, 36.607, 21.564.

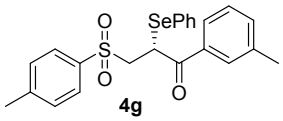
HRMS (ESI) m/z Calcd for $[C_{22}H_{19}BrO_3SSeNa, M + Na]^+$: 544.92933, Found: 544.92945.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 12.498 min (minor), t_R = 21.803 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -10.7 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 99–101 °C; **yield**: 71%, 37.2 mg.



(*R*)-2-(phenylselanyl)-1-(*m*-tolyl)-3-tosylpropan-1-one (4g)



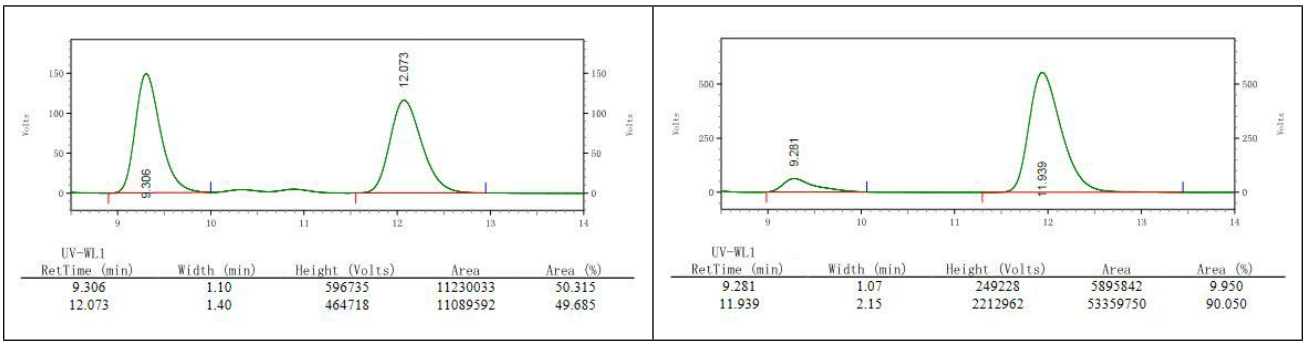
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.618 (d, *J* = 8.0 Hz, 3H), 7.571 (s, 1H), 7.433 – 7.349 (m, 4H), 7.328 (d, *J* = 7.6 Hz, 1H), 7.306 – 7.260 (m, 2H), 7.177 (d, *J* = 8.0 Hz, 2H), 5.008 (d, *J* = 10.4 Hz, 1H), 4.174 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.661 (d, *J* = 14.0 Hz, 1H), 2.382 (s, 3H), 2.362 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.982, 144.851, 138.326, 136.485, 135.795, 134.837, 134.126, 129.772, 129.689, 129.381, 128.981, 128.395, 128.196, 125.700, 125.592, 58.292, 36.638, 21.566, 21.335.

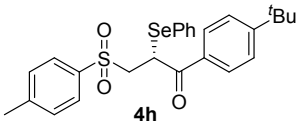
HRMS (ESI) m/z Calcd for $[C_{23}H_{22}O_3SSeNa, M + Na]^+$: 481.03475, Found: 481.03463.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 9.281 min (minor), t_R = 11.939 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -25.4 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 92–93 °C; **yield**: 66%, 30.2 mg.



(*R*)-1-(4-(*tert*-butyl)phenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4h).



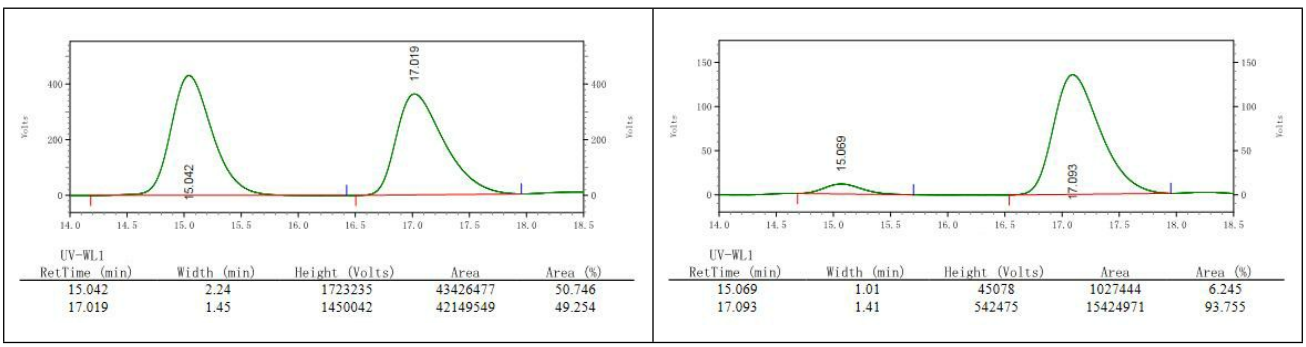
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.749 (d, *J* = 8.0 Hz, 2H), 7.610 (d, *J* = 8.0 Hz, 2H), 7.434 (d, *J* = 8.4 Hz, 2H), 7.368 (t, *J* = 8.0 Hz, 3H), 7.261 (t, *J* = 7.6 Hz, 2H), 7.155 (d, *J* = 8.0 Hz, 2H), 5.015 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.191 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.640 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.348 (s, 3H), 1.355 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.524, 157.159, 144.759, 136.362, 135.821, 132.136, 129.712, 129.584, 129.357, 128.367, 128.213, 125.750, 125.464, 58.336, 36.471, 35.117, 31.050, 21.551.

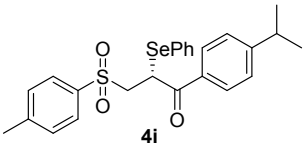
HRMS (ESI) m/z Calcd for $[C_{26}H_{28}O_3SSeNa, M + Na]^+$: 523.08174, Found: 523.08188.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 15.069 min (minor), t_R = 17.093 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -15.5 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 137–138 °C; **yield**: 78%, 38.9 mg.



(*R*)-1-(4-isopropylphenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4i)



4i

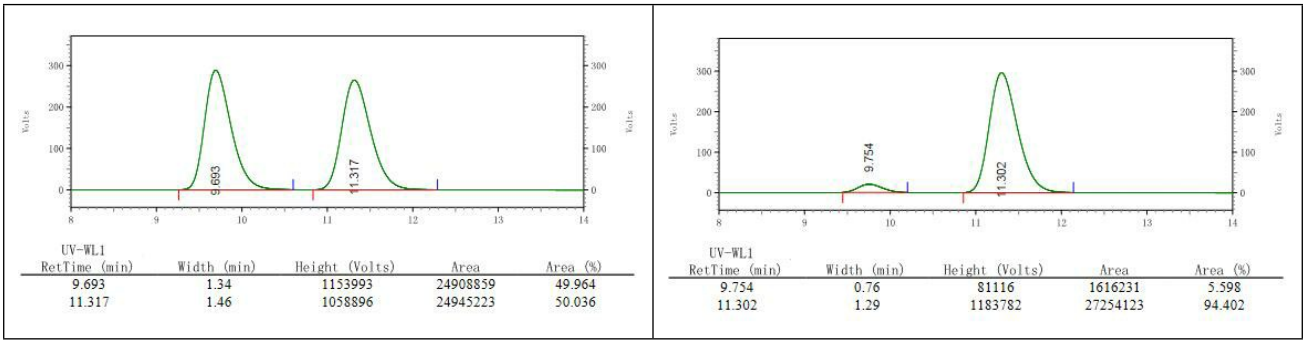
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.742 (d, *J* = 8.0 Hz, 2H), 7.607 (d, *J* = 8.4 Hz, 2H), 7.415 – 7.315 (m, 3H), 7.305 – 7.224 (m, 4H), 7.153 (d, *J* = 8.0 Hz, 2H), 5.008 (dd, *J* = 10.6, 2.2 Hz, 1H), 4.185 (dd, *J* = 14.2, 10.6 Hz, 1H), 3.645 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.972 (dp, *J* = 13.6, 7.0 Hz, 1H), 2.343 (s, 3H), 1.290 (s, 3H), 1.273 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.485, 154.889, 144.738, 136.324, 135.767, 132.543, 129.684, 129.553, 129.321, 128.617, 128.168, 126.570, 125.716, 58.305, 36.452, 34.183, 23.598, 23.583, 21.509.

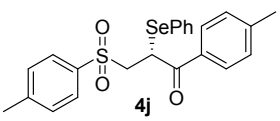
HRMS (ESI) m/z Calcd for $[C_{25}H_{26}O_3SSeNa, M + Na]^+$: 509.06608, Found: 509.06627.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 9.754 min (minor), t_R = 11.302 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -7.6 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 102–103 °C; **yield**: 76%, 36.7 mg.



(*R*)-2-(phenylselanyl)-1-(*p*-tolyl)-3-tosylpropan-1-one (4j)



4j

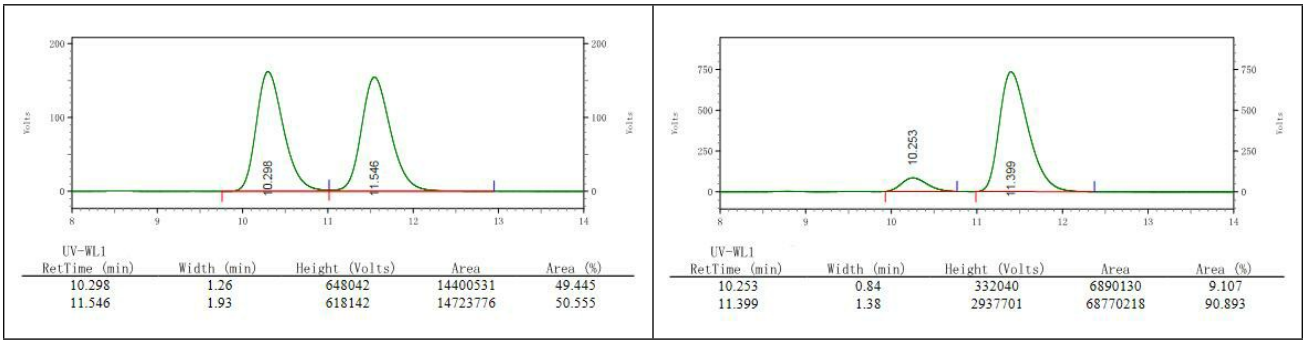
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.710 (d, *J* = 8.0 Hz, 2H), 7.607 (d, *J* = 8.0 Hz, 2H), 7.408 – 7.321 (m, 3H), 7.273 (d, *J* = 7.6 Hz, 2H), 7.229 (d, *J* = 8.2 Hz, 2H), 7.166 (d, *J* = 8.4 Hz, 2H), 5.003 (dd, *J* = 10.6, 2.2 Hz, 1H), 4.185 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.640 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.426 (s, 3H), 2.353 (s, 3H).

^{13}C NMR (100 MHz, CDCl3): δ 191.387, 144.797, 144.252, 136.391, 135.740, 132.210, 129.738, 129.622, 129.356, 129.219, 128.493, 128.160, 125.618, 58.265, 36.445, 21.659, 21.542.

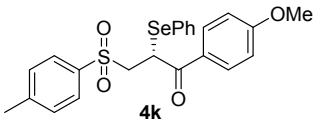
HRMS (ESI) m/z Calcd for $[C_{23}H_{22}O_3SSeNa, M + Na]^+$: 481.03475, Found: 481.03486.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 10.253 min (minor), t_R = 11.399 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -17.8 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 115–116 °C; **yield**: 57%, 26.0 mg.



(*R*)-1-(4-methoxyphenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4k)



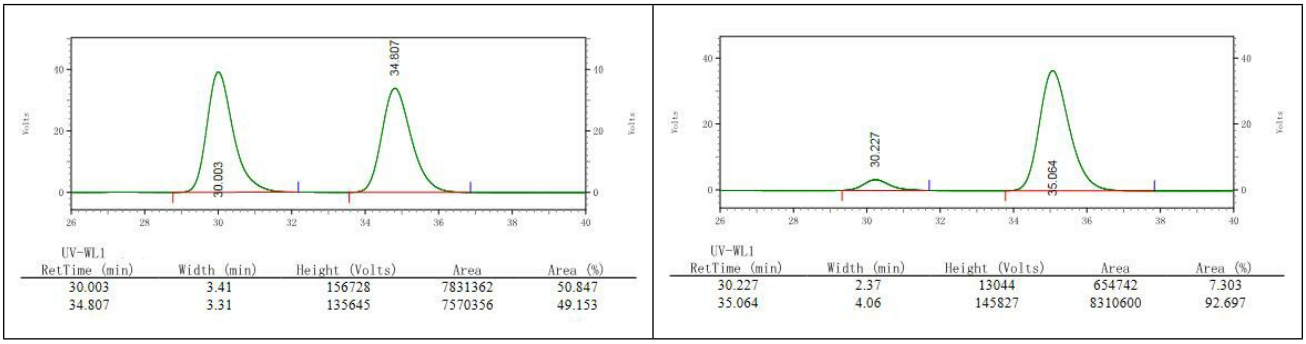
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.782 (d, *J* = 8.8 Hz, 2H), 7.602 (d, *J* = 8.0 Hz, 2H), 7.416 – 7.319 (m, 3H), 7.262 (t, *J* = 7.6 Hz, 2H), 7.164 (d, *J* = 8.0 Hz, 2H), 6.898 (d, *J* = 8.8 Hz, 2H), 4.991 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.212 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.876 (s, 3H), 3.629 (dd, *J* = 14.2, 2.2 Hz, 1H), 2.352 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.552, 163.720, 144.765, 136.277, 135.799, 130.716, 129.702, 129.543, 129.357, 128.186, 127.654, 125.890, 113.721, 58.370, 55.487, 36.346, 21.537.

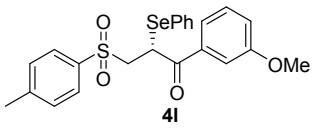
HRMS (ESI) m/z Calcd for $[C_{23}H_{22}O_4SSeNa, M + Na]^+$: 497.02967, Found: 497.02951.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 30.227 min (minor), t_R = 35.064 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = +32 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 95–96 °C; **yield**: 78%, 36.9 mg.



(*R*)-1-(3-methoxyphenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4l)



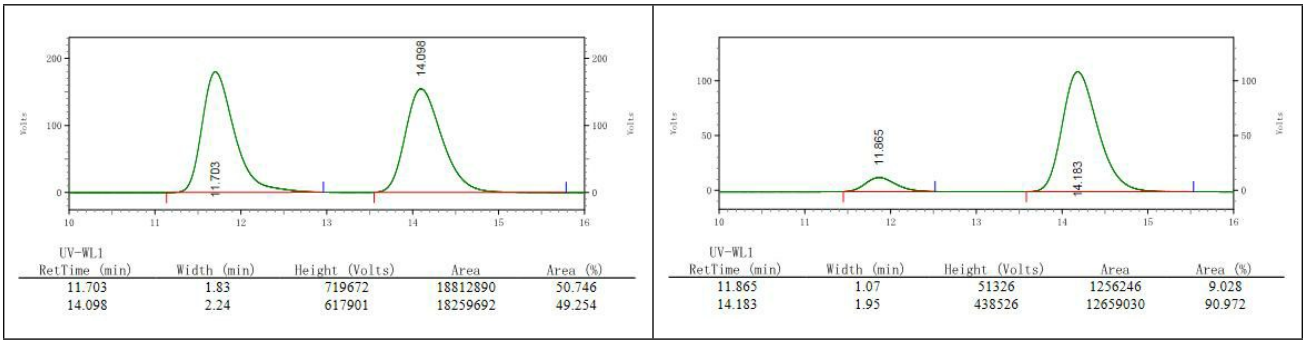
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.617 (d, *J* = 8.0 Hz, 2H), 7.432 – 7.345 (m, 4H), 7.318 (d, *J* = 8.0 Hz, 2H), 7.290 – 7.230 (m, 2H), 7.172 (d, *J* = 8.0 Hz, 2H), 7.132 – 7.073 (m, 1H), 4.987 (dd, *J* = 10.8, 2.0 Hz, 1H), 4.180 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.805 (s, 3H), 3.661 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.349 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.556, 159.696, 144.819, 136.360, 136.178, 135.719, 129.741, 129.640, 129.458, 129.352, 128.135, 125.636, 120.751, 119.768, 112.837, 58.282, 55.329, 36.712, 21.492.

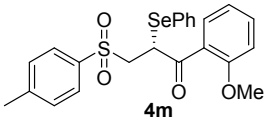
HRMS (ESI) m/z Calcd for $[C_{23}H_{22}O_4SSeNa, M + Na]^+$: 497.02967, Found: 497.02985.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 11.865 min (minor), t_R = 14.183 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -10 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 99–100 °C; **yield**: 87%, 41.3 mg.



(*R*)-1-(2-methoxyphenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4m)



4m

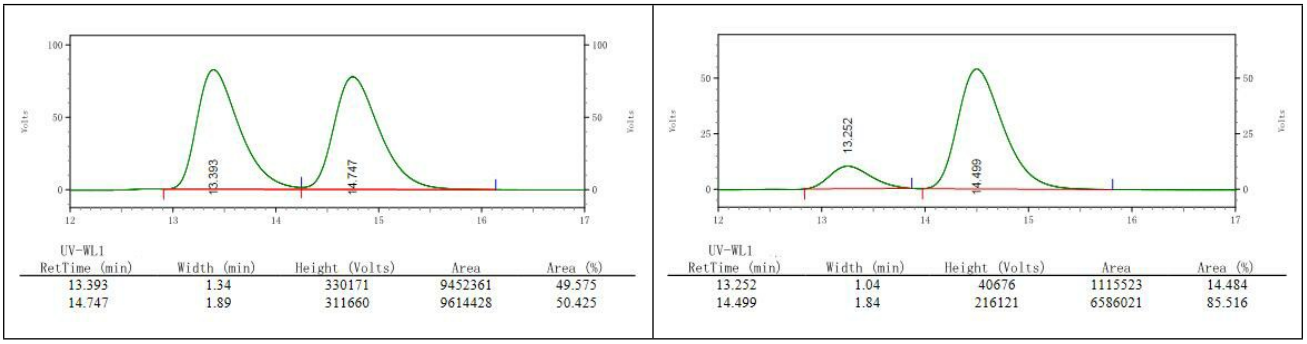
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.699 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.665 (d, *J* = 8.0 Hz, 2H), 7.519 – 7.451 (m, 1H), 7.396 – 7.300 (m, 3H), 7.266 – 7.217 (m, 2H), 7.185 (d, *J* = 8.0 Hz, 2H), 6.999 (t, *J* = 7.4 Hz, 1H), 6.945 (d, *J* = 8.4 Hz, 1H), 5.387 (dd, *J* = 10.2, 2.6 Hz, 1H), 4.072 (dd, *J* = 14.2, 10.2 Hz, 1H), 3.871 (s, 3H), 3.559 (dd, *J* = 14.2, 2.6 Hz, 1H), 2.354 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.406, 158.449, 144.635, 136.442, 136.001, 134.248, 132.012, 129.641, 129.330, 129.115, 128.265, 125.483, 124.674, 120.727, 111.623, 57.726, 55.595, 41.118, 21.547.

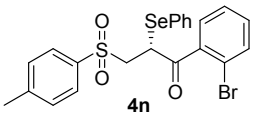
HRMS (ESI) m/z Calcd for $[C_{23}H_{22}O_4SSeNa, M + Na]^+$: 497.02967, Found: 497.02977.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 13.252 min (minor), t_R = 14.499 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = +45 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 106–108 °C; **yield**: 66%, 31.2 mg.



(*R*)-1-(2-bromophenyl)-2-(phenylselanyl)-3-tosylpropan-1-one (4n)



4n

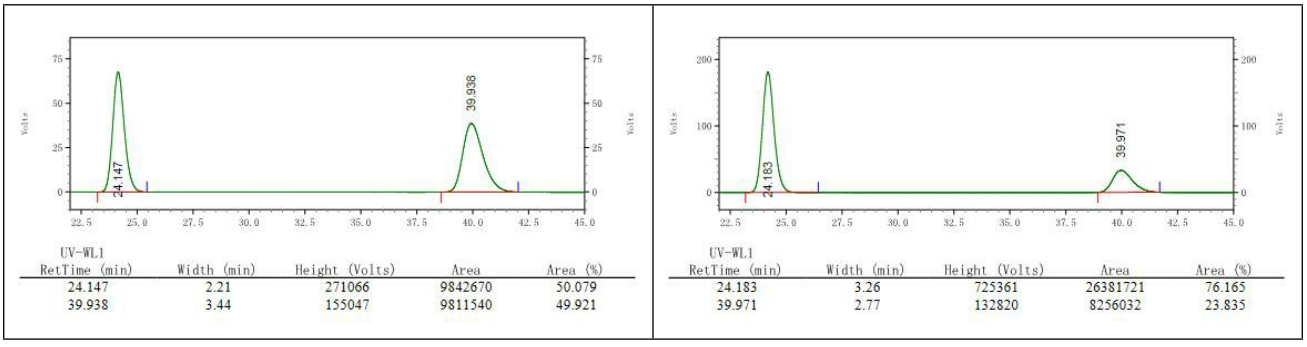
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.747 (d, *J* = 8.4 Hz, 2H), 7.661 – 7.579 (m, 2H), 7.410 (d, *J* = 7.6 Hz, 2H), 7.365 – 7.258 (m, 5H), 7.216 (t, *J* = 7.4 Hz, 2H), 4.990 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.113 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.612 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.399 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 193.081, 144.960, 138.268, 136.408, 136.084, 134.073, 132.235, 129.981, 129.882, 129.445, 129.277, 127.919, 127.113, 125.643, 121.057, 57.028, 40.723, 21.576.

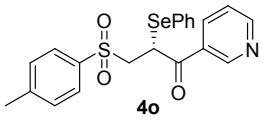
HRMS (ESI) m/z Calcd for $[C_{22}H_{19}BrO_3SSeNa, M + Na]^+$: 544.92933, Found: 544.92954.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 24.183 min (major), t_R = 39.971 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = -25.2 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 97–98 °C; **yield**: 75%, 39.3 mg.



(*R*)-2-(phenylselanyl)-1-(pyridin-3-yl)-3-tosylpropan-1-one (4o)



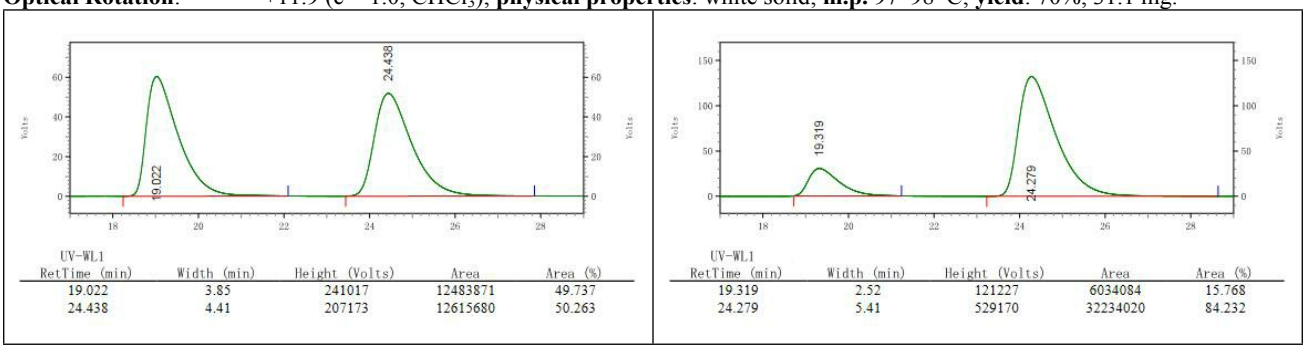
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.016 (s, 1H), 8.772 (d, *J* = 4.8 Hz, 1H), 8.095 (d, *J* = 8.0 Hz, 1H), 7.642 (d, *J* = 8.4 Hz, 2H), 7.427 – 7.318 (m, 4H), 7.272 (t, *J* = 7.4 Hz, 2H), 7.216 (d, *J* = 8.0 Hz, 2H), 4.952 (d, *J* = 10.8 Hz, 1H), 4.191 (dd, *J* = 13.8, 11.0 Hz, 1H), 3.694 (dd, *J* = 10.0, 1.6 Hz, 1H), 2.375 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.609, 153.463, 149.605, 145.087, 136.437, 135.701, 130.399, 129.945, 129.870, 129.531, 128.109, 125.139, 123.404, 57.999, 36.967, 21.534.

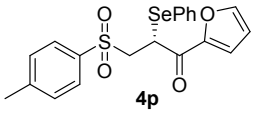
HRMS (ESI) m/z Calcd for $[C_{21}H_{19}NO_3SSeNa, M + Na]^+$: 468.01433, Found: 468.01421.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 19.319 min (minor), t_R = 24.279 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = +11.9 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 97–98 °C; **yield**: 70%, 31.1 mg.



(*R*)-1-(furan-2-yl)-2-(phenylselanyl)-3-tosylpropan-1-one (4p)



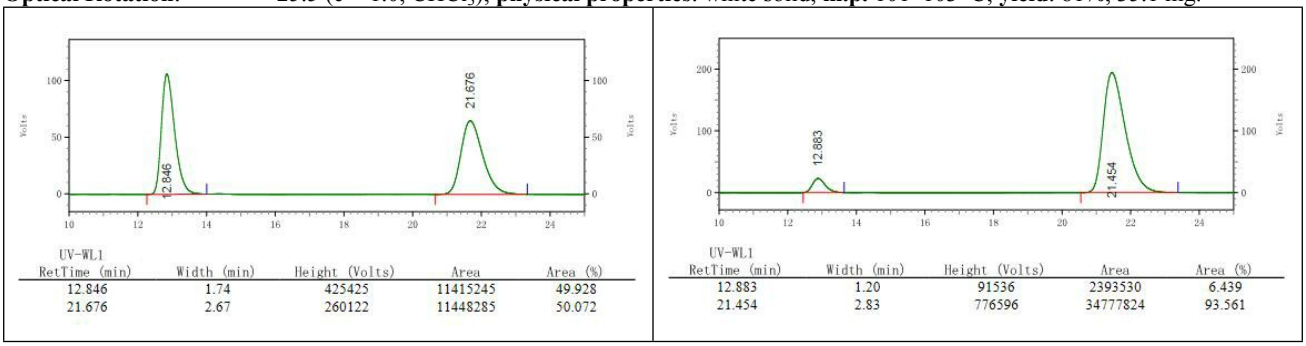
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.630 (d, *J* = 8.0 Hz, 2H), 7.541 (s, 1H), 7.410 (d, *J* = 7.2 Hz, 2H), 7.361 (t, *J* = 7.2 Hz, 1H), 7.258 (t, *J* = 7.4 Hz, 2H), 7.198 (d, *J* = 7.6 Hz, 2H), 7.087 (d, *J* = 2.8 Hz, 1H), 6.522 (s, 1H), 4.852 (d, *J* = 10.4 Hz, 1H), 4.071 (dd, *J* = 13.8, 11.4 Hz, 1H), 3.570 (d, *J* = 14.0 Hz, 1H), 2.360 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 181.112, 150.677, 146.321, 144.867, 136.458, 135.491, 129.616, 129.568, 129.253, 128.147, 125.372, 117.857, 112.566, 57.295, 36.494, 21.492.

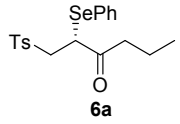
HRMS (ESI) m/z Calcd for $[C_{20}H_{18}O_4SSeNa, M + Na]^+$: 456.99835, Found: 456.99817.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20 flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 12.883 min (minor), t_R = 21.454 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = +25.5 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 101–103 °C; **yield**: 81%, 35.1 mg.



(*R*)-2-(phenylselanyl)-1-tosylhexan-3-one (6a)



6a

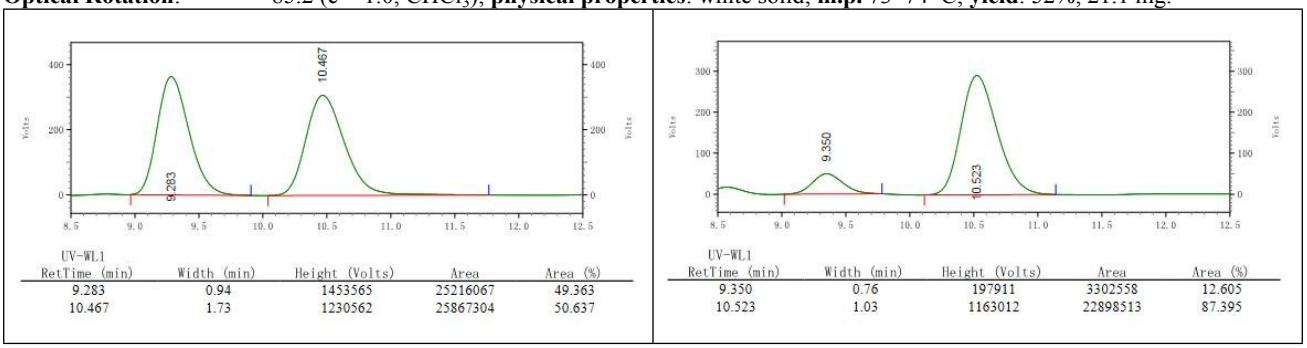
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.688 (d, *J* = 8.0 Hz, 2H), 7.450 – 7.378 (m, 2H), 7.361 (d, *J* = 7.6 Hz, 1H), 7.335 – 7.255 (m, 4H), 4.124 (d, *J* = 10.8 Hz, 1H), 3.960 (dd, *J* = 13.6, 10.8 Hz, 1H), 3.449 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.833 – 2.727 (m, 1H), 2.540 – 2.455 (m, 1H), 2.431 (s, 3H), 1.640 – 1.530 (m, 2H), 0.916 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.203, 144.966, 136.256, 136.051, 129.899, 129.533, 129.463, 128.045, 125.548, 57.651, 42.682, 41.131, 21.627, 17.283, 13.654.

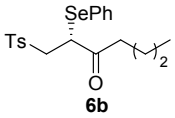
HRMS (ESI) m/z Calcd for $[C_{19}H_{22}O_3SSeNa, M + Na]^+$: 433.03472, Found: 433.03451.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15 flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 9.350 min (minor), t_R = 10.523 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -85.2 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 73–74 °C; **yield**: 52%, 21.1 mg.



(*R*)-2-(phenylselanyl)-1-tosylheptan-3-one（6b）



6b

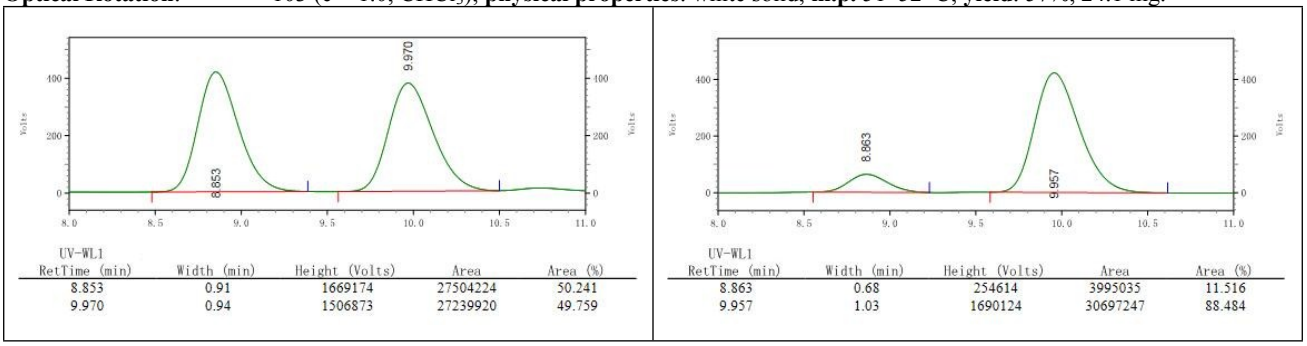
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.688 (d, *J* = 8.0 Hz, 2H), 7.440 – 7.391 (m, 2H), 7.390 – 7.345 (m, 1H), 7.344 – 7.265 (m, 4H), 4.123 (dd, *J* = 10.6, 2.2 Hz, 1H), 3.946 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.453 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.865 – 2.765 (m, 1H), 2.528 – 2.456 (m, 1H), 2.434 (s, 3H), 1.564 – 1.465 (m, 2H), 1.360 – 1.265 (m, 2H), 0.906 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.268, 144.984, 136.129, 136.025, 129.885, 129.570, 129.441, 128.030, 125.320, 57.517, 40.978, 40.449, 25.852, 22.171, 21.646, 13.861.

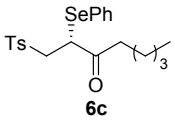
HRMS (ESI) m/z Calcd for $[C_{20}H_{24}O_3SSeNa, M + Na]^+$: 447.05038, Found: 447.05049.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15 flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 8.863 min (minor), t_R = 9.957 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -103 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 51–52 °C; **yield**: 57%, 24.1 mg.



(*R*)-2-(phenylselanyl)-1-tosyloctan-3-one (6c)



6c

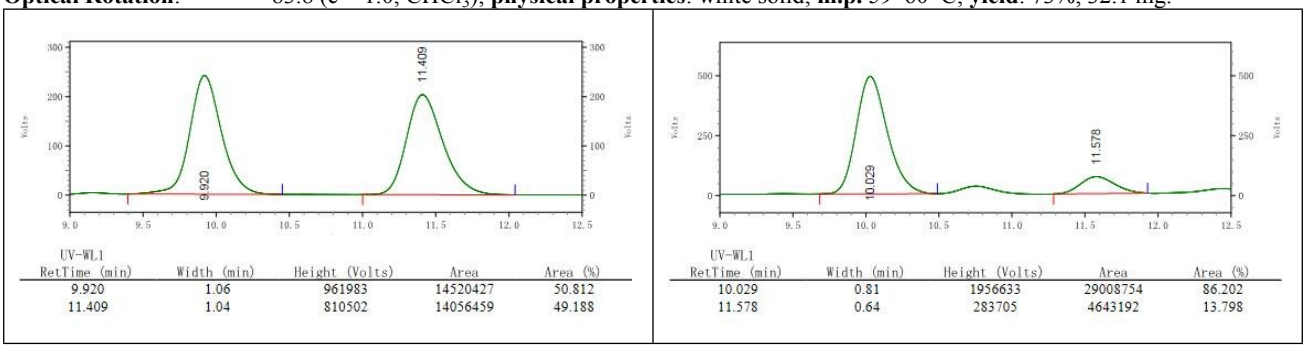
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.686 (d, *J* = 8.0 Hz, 2H), 7.450 – 7.385 (m, 2H), 7.360 (d, *J* = 7.6 Hz, 1H), 7.337 – 7.262 (m, 4H), 4.128 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.962 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.449 (dd, *J* = 14.0, 1.6 Hz, 1H), 2.846 – 2.739 (m, 1H), 2.529 – 2.448 (m, 1H), 2.428 (s, 3H), 1.581 – 1.477 (m, 2H), 1.347 – 1.223 (m, 4H), 0.896 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.328, 144.938, 136.201, 136.035, 129.880, 129.519, 129.446, 128.041, 125.531, 57.611, 41.133, 40.746, 31.210, 23.465, 22.386, 21.613, 13.901.

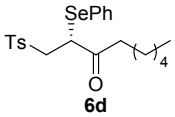
HRMS (ESI) m/z Calcd for $[C_{21}H_{26}O_3SSeNa, M + Na]^+$: 461.06604, Found: 461.06619.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20 flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 10.029 min (major), t_R = 11.578 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = -83.8 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 59–60 °C; **yield**: 73%, 32.1 mg.



(*R*)-2-(phenylselanyl)-1-tosylnonan-3-one (6d)



6d

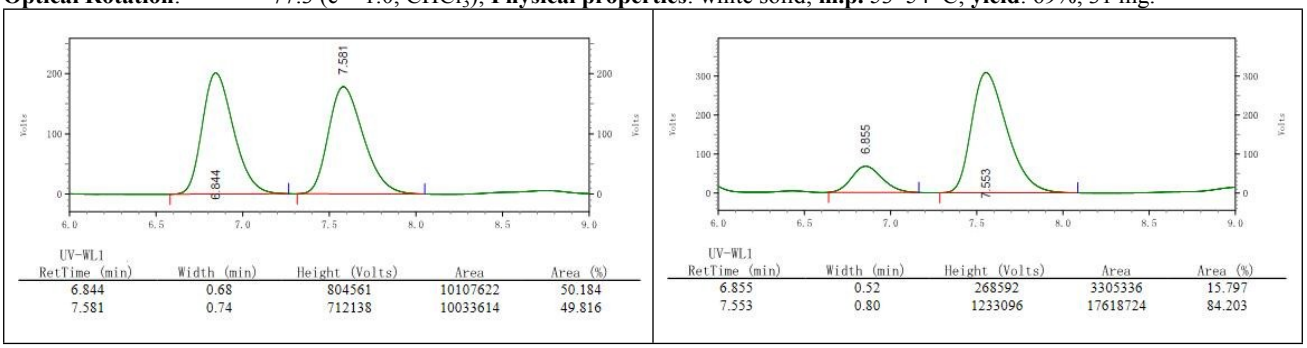
^{1}H NMR (400 MHz, $CDCl_3$): δ7.685 (d, *J* = 8.0 Hz, 2H), 7.443 – 7.380 (m, 2H), 7.359 (d, *J* = 7.6 Hz, 1H), 7.335 – 7.262 (m, 4H), 4.127 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.959 (dd, *J* = 13.8, 10.6 Hz, 1H), 3.447 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.843 – 2.738 (m, 1H), 2.531 – 2.445 (m, 1H), 2.428 (s, 3H), 1.575 – 1.475 (m, 2H), 1.331 – 1.235 (m, 6H), 0.891 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.305, 144.920, 136.189, 136.023, 129.864, 129.502, 129.429, 128.025, 125.515, 57.592, 41.119, 40.778, 31.516, 28.702, 23.739, 22.449, 21.598, 14.012.

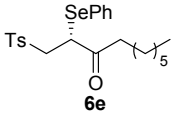
HRMS (ESI) m/z Calcd for $[C_{22}H_{28}O_3SSeNa, M + Na]^+$: 475.08169, Found: 475.08143.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20 flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 6.855 min (minor), t_R = 7.553 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -77.3 (c = 1.0, $CHCl_3$); **Physical properties**: white solid; **m.p.** 53–54 °C; **yield**: 69%, 31 mg.



(*R*)-2-(phenylselanyl)-1-tosyldecan-3-one (6e)



6e

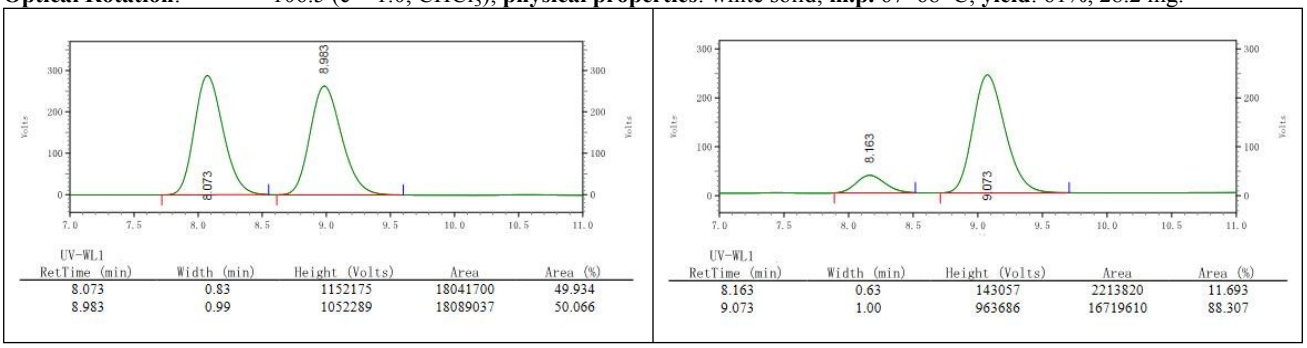
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.688 (d, *J* = 8.4 Hz, 2H), 7.445 – 7.388 (m, 2H), 7.368 (d, *J* = 7.2 Hz, 1H), 7.344 – 7.265 (m, 4H), 4.122 (dd, *J* = 10.6, 2.2 Hz, 1H), 3.948 (dd, *J* = 13.6, 10.8 Hz, 1H), 3.454 (dd, *J* = 14.0, 2.4 Hz, 1H), 2.853 – 2.752 (m, 1H), 2.530 – 2.450 (m, 1H), 2.434 (s, 3H), 1.570 – 1.475 (m, 2H), 1.333 – 1.210 (m, 8H), 0.891 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.321, 144.925, 136.222, 136.033, 129.875, 129.513, 129.442, 128.043, 125.543, 57.612, 41.140, 40.800, 31.655, 29.015, 23.801, 22.591, 21.613, 14.058.

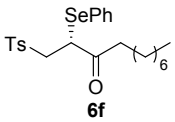
HRMS (ESI) m/z Calcd for $[C_{23}H_{30}O_3SSeNa, M + Na]^+$: 489.09735, Found: 489.09756.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15 flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 8.163 min (minor), t_R = 9.073 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -106.5 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 67–68 °C; **yield**: 61%, 28.2 mg.



(*R*)-2-(phenylselanyl)-1-tosylundecan-3-one (6f)



6f

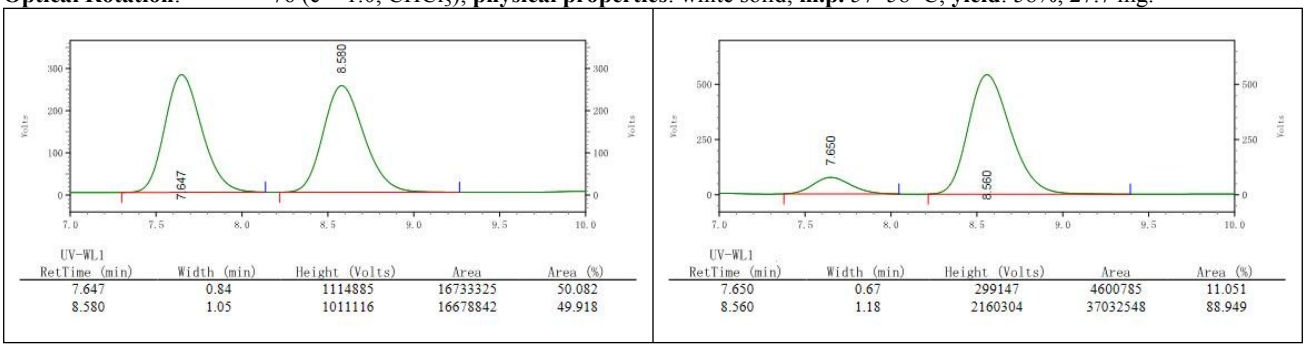
^{1}H NMR (400 MHz, $CDCl_3$): 7.687 (d, *J* = 8.0 Hz, 2H), 7.447 – 7.388 (m, 2H), 7.392 – 7.346 (m, 1H), 7.345 – 7.264 (m, 4H), 4.121 (dd, *J* = 10.6, 2.2 Hz, 1H), 3.946 (dd, *J* = 13.8, 10.6 Hz, 1H), 3.453 (dd, *J* = 14.0, 2.4 Hz, 1H), 2.855 – 2.755 (m, 1H), 2.528 – 2.445 (m, 1H), 2.435 (s, 3H), 1.564 – 1.468 (m, 2H), 1.335 – 1.216 (m, 10H), 0.888 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.338, 144.936, 136.237, 136.048, 129.887, 129.526, 129.454, 128.057, 125.553, 57.626, 41.148, 40.816, 31.822, 29.323, 29.130, 29.083, 23.813, 22.637, 21.627, 14.087.

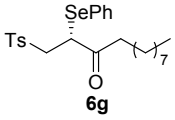
HRMS (ESI) m/z Calcd for $[C_{24}H_{32}O_3SSeNa, M + Na]^+$: 503.11301, Found: 503.11296.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15 flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 7.650 min (minor), t_R = 8.560 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -76 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 57–58 °C; **yield**: 58%, 27.7 mg.



(*R*)-2-(phenylselanyl)-1-tosyldodecan-3-one (6g)



6g

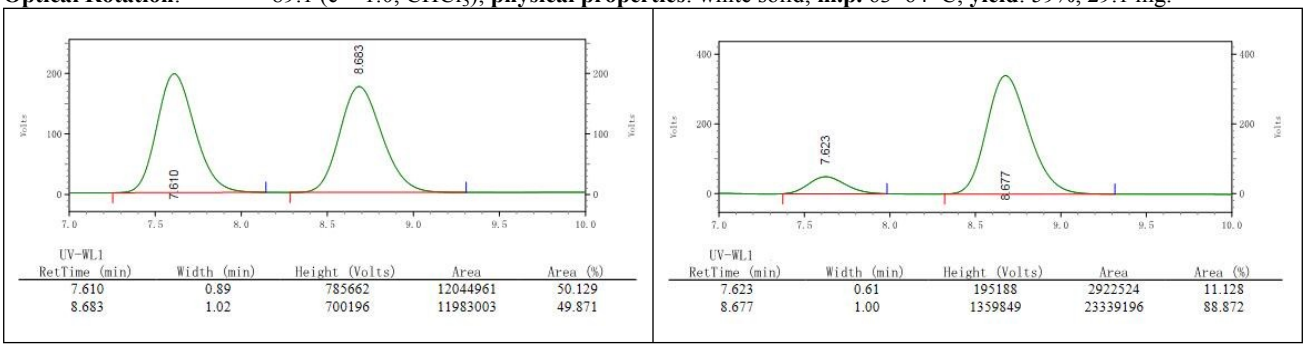
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.687 (d, *J* = 8.2 Hz, 2H), 7.443 – 7.389 (m, 2H), 7.390 – 7.342 (m, 1H), 7.340 – 7.262 (m, 4H), 4.121 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.946 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.453 (dd, *J* = 14.0, 2.4 Hz, 1H), 2.850 – 2.755 (m, 1H), 2.525 – 2.447 (m, 1H), 2.434 (s, 3H), 1.569 – 1.468 (m, 2H), 1.335 – 1.220 (m, 12H), 0.886 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.331, 144.928, 136.232, 136.041, 129.881, 129.519, 129.447, 128.051, 125.548, 57.620, 41.145, 40.810, 31.852, 29.423, 29.362, 29.263, 29.076, 23.811, 22.652, 21.620, 14.089.

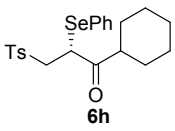
HRMS (ESI) m/z Calcd for $[C_{25}H_{34}O_3SSeNa, M + Na]^+$: 517.12868, Found: 517.12853.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15 flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 7.623 min (minor), t_R = 8.677 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = -89.1 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 63–64 °C; **yield**: 59%, 29.1 mg.



(*R*)-1-cyclohexyl-2-(phenylselanyl)-3-tosylpropan-1-one (6h)



6h

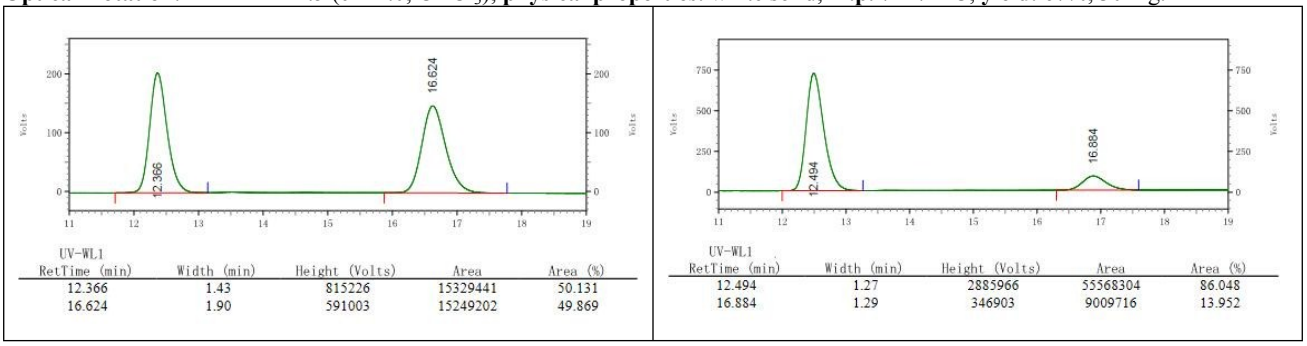
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.691 (d, *J* = 8.2 Hz, 2H), 7.403 (d, *J* = 7.6 Hz, 2H), 7.378 – 7.336 (m, 1H), 7.338 – 7.260 (m, 4H), 4.289 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.952 (dd, *J* = 14.0, 10.4 Hz, 1H), 3.428 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.771 – 2.673 (m, 1H), 2.430 (s, 3H), 1.992 – 1.847 (m, 2H), 1.841 – 1.756 (m, 2H), 1.710 – 1.632 (m, 1H), 1.590 – 1.500 (m, 1H), 1.301 – 1.190 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 204.543, 144.811, 136.488, 136.089, 129.819, 129.483, 129.407, 127.920, 125.355, 57.337, 48.986, 39.713, 29.877, 28.723, 25.980, 25.666, 25.368, 21.603.

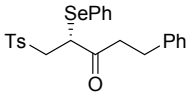
HRMS (ESI) m/z Calcd for $[C_{22}H_{26}O_3SSeNa, M + Na]^+$: 473.06604, Found: 473.06615.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20 flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 12.494 min (major), t_R = 16.884 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = -124.5 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 71–72 °C; **yield**: 67%, 30 mg.



(R)-5-phenyl-2-(phenylselanyl)-1-tosylpentan-3-one (6i)



6i

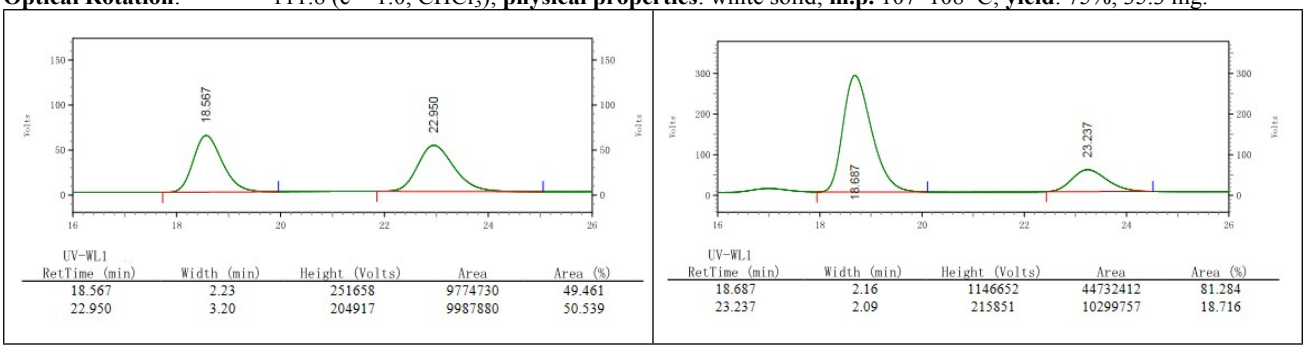
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.682 (d, *J* = 8.0 Hz, 2H), 7.376 – 7.167 (m, 12H), 4.112 (d, *J* = 10.4 Hz, 1H), 3.929 (dd, *J* = 13.6, 11.2 Hz, 1H), 3.459 (d, *J* = 13.6 Hz, 1H), 3.242 – 3.141 (m, 1H), 2.902 – 2.825 (m, 2H), 2.820 – 2.729 (m, 1H), 2.430 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.990, 144.998, 140.639, 136.259, 136.152, 129.912, 129.580, 129.404, 128.415, 128.039, 126.122, 125.126, 57.569, 42.133, 40.987, 29.697, 21.624.

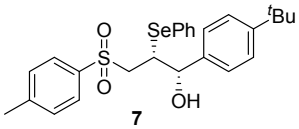
HRMS (ESI) m/z Calcd for $[C_{24}H_{24}O_3SSeNa, M + Na]^+$: 495.05041, Found: 495.05032.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 18.687 min (major), t_R = 23.237 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = -111.8 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 107–108 °C; **yield**: 75%, 35.3 mg.



(*1S*,*2R*)-1-(4-(*tert*-butyl)phenyl)-2-(phenylselanyl)-3-tosylpropan-1-ol (7)



7

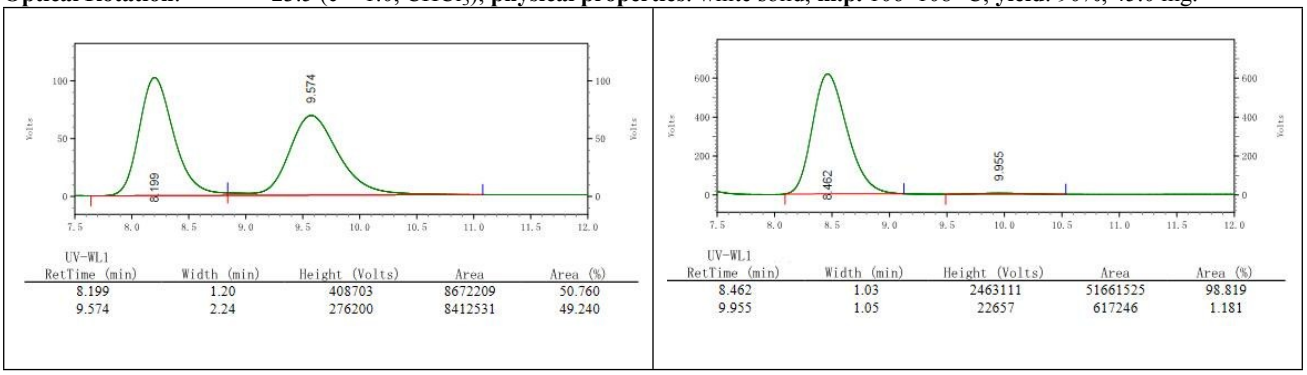
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.656 (d, *J* = 8.4 Hz, 2H), 7.364 – 7.318 (m, 2H), 7.317 – 7.257 (m, 4H), 7.200 (t, *J* = 7.0 Hz, 1H), 7.154 – 7.040 (m, 4H), 5.296 (s, 1H), 3.851 (dd, *J* = 14.4, 9.2 Hz, 1H), 3.714 – 3.644 (m, 1H), 3.439 (dd, *J* = 14.6, 3.8 Hz, 1H), 2.894 (d, *J* = 4.8 Hz, 1H), 2.439 (s, 3H), 1.319 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.800, 144.777, 138.157, 136.103, 134.584, 129.936, 129.063, 127.912, 127.856, 127.781, 125.759, 125.165, 73.007, 58.731, 47.161, 34.528, 31.334, 21.635.

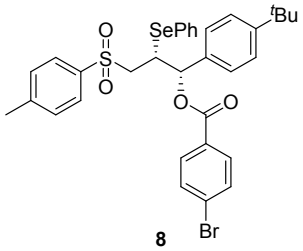
HRMS (ESI) m/z Calcd for $[C_{26}H_{30}O_3SSeNa, M + Na]^+$: 525.09739, Found: 525.09761.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 210 nm), t_R = 8.462 min (major), t_R = 9.955 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = -23.5 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 106–108 °C; **yield**: 90%, 45.0 mg.



(*1S,2R*)-1-(4-(*tert*-butyl)phenyl)-2-(phenylselanyl)-3-tosylpropyl 4-bromobenzoate (8)



8

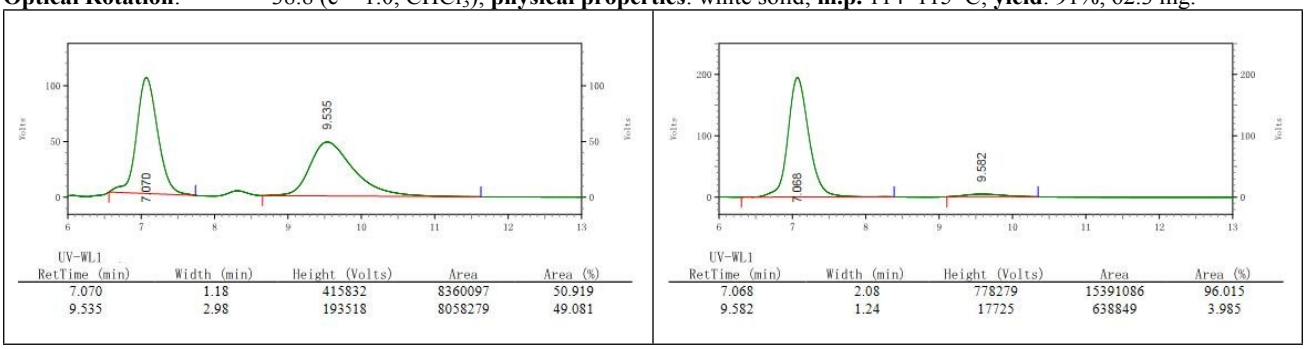
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.914 (d, *J* = 8.0 Hz, 2H), 7.618 (dd, *J* = 15.8, 8.2 Hz, 4H), 7.351 (s, 4H), 7.273 – 7.207 (m, 3H), 7.187 (d, *J* = 7.2 Hz, 2H), 7.124 (t, *J* = 7.4 Hz, 2H), 6.527 (d, *J* = 2.4 Hz, 1H), 3.889 – 3.816 (m, 1H), 3.753 (dd, *J* = 14.6, 8.6 Hz, 1H), 3.484 (dd, *J* = 14.6, 3.8 Hz, 1H), 2.406 (s, 3H), 1.305 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.325, 151.326, 144.769, 136.132, 134.654, 134.292, 131.827, 131.343, 129.912, 129.202, 128.497, 128.025, 127.975, 127.923, 126.043, 125.359, 76.364, 58.965, 44.201, 34.562, 31.264, 21.607.

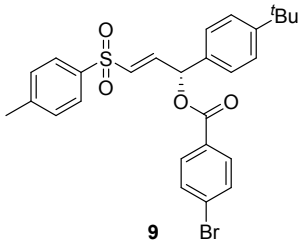
HRMS (ESI) m/z Calcd for $[C_{33}H_{33}BrO_4SSeNa, M + Na]^+$: 707.03398, Found: 707.03383.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 7.068 min (major), t_R = 9.582 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = -38.8 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 114–115 °C; **yield**: 91%, 62.3 mg.



(*R,E*)-1-(4-(*tert*-butyl)phenyl)-3-tosylallyl 4-bromobenzoate (9)



9

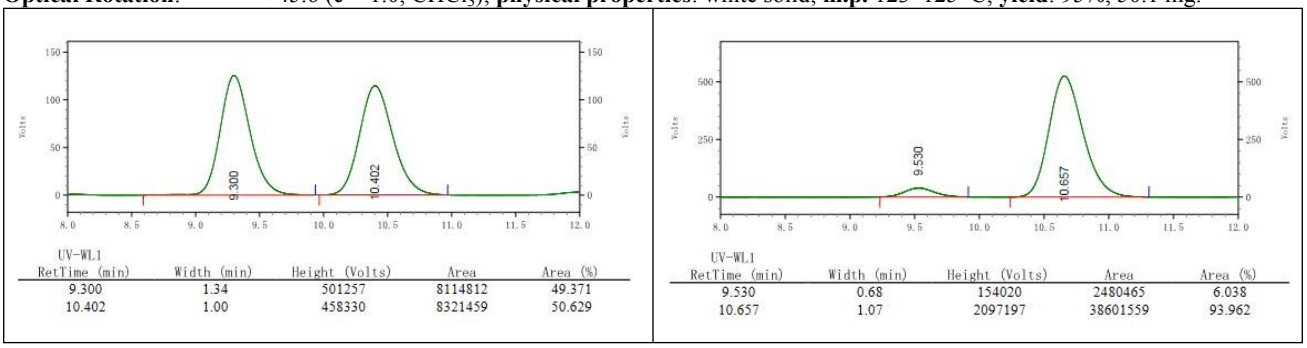
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.879 (d, *J* = 8.0 Hz, 2H), 7.761 (d, *J* = 7.2 Hz, 2H), 7.567 (d, *J* = 8.0 Hz, 2H), 7.399 (d, *J* = 7.6 Hz, 2H), 7.321 (t, *J* = 8.8 Hz, 4H), 7.130 (dd, *J* = 14.8, 3.2 Hz, 1H), 6.648 (s, broad, 1H), 6.604 (d, *J* = 15.6 Hz, 1H), 2.433 (s, 3H), 1.305 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.242, 152.453, 144.710, 142.253, 136.838, 132.892, 131.856, 131.217, 130.009, 128.684, 128.266, 127.852, 127.329, 126.000, 73.790, 34.681, 31.200, 21.623.

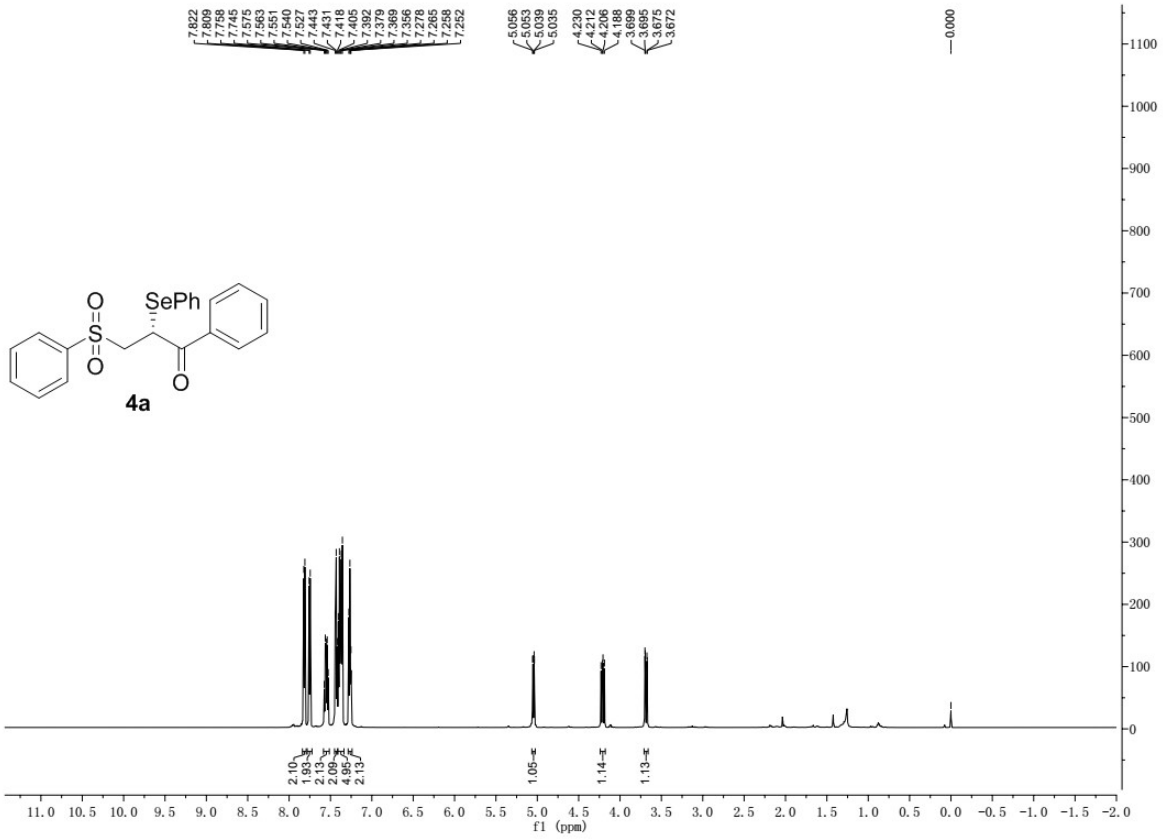
HRMS (ESI) m/z Calcd for $[C_{27}H_{27}BrO_4SNa, M + Na]^+$: 551.06862, Found: 551.06836.

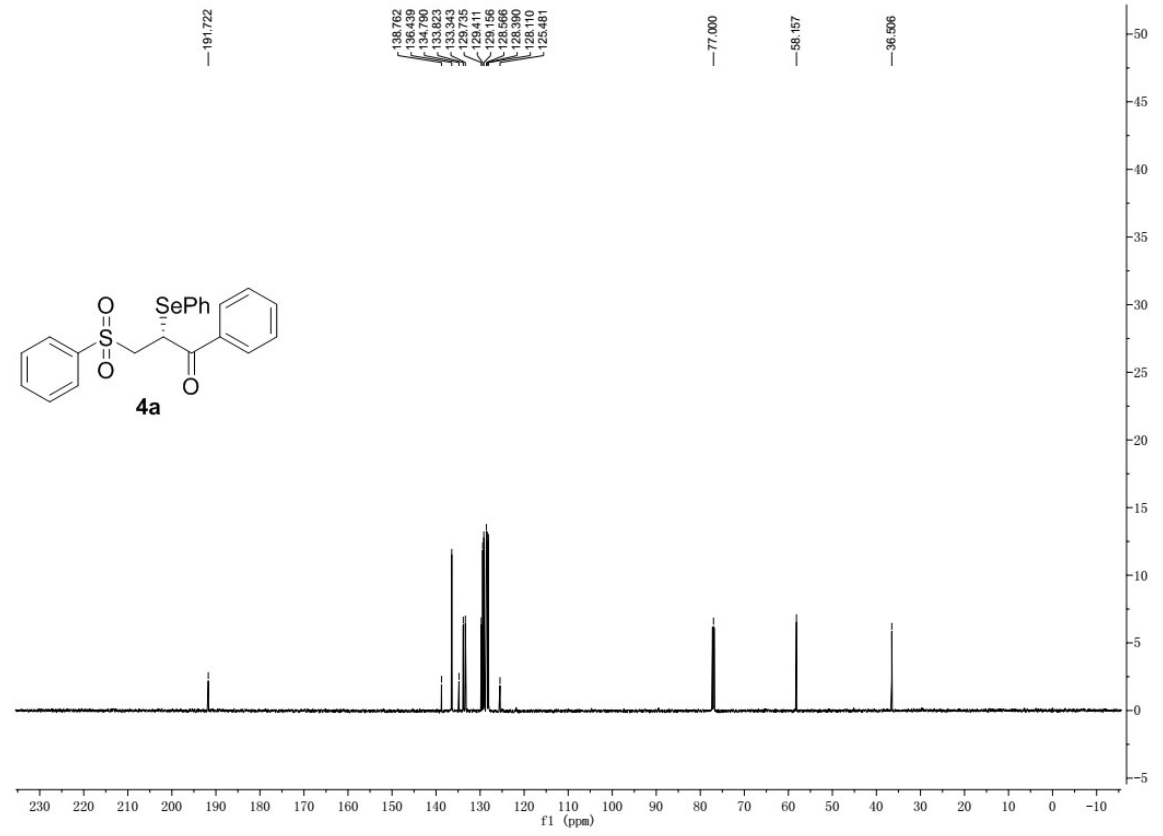
HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 75:25, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 9.530 min (minor), t_R = 10.657 min (major).

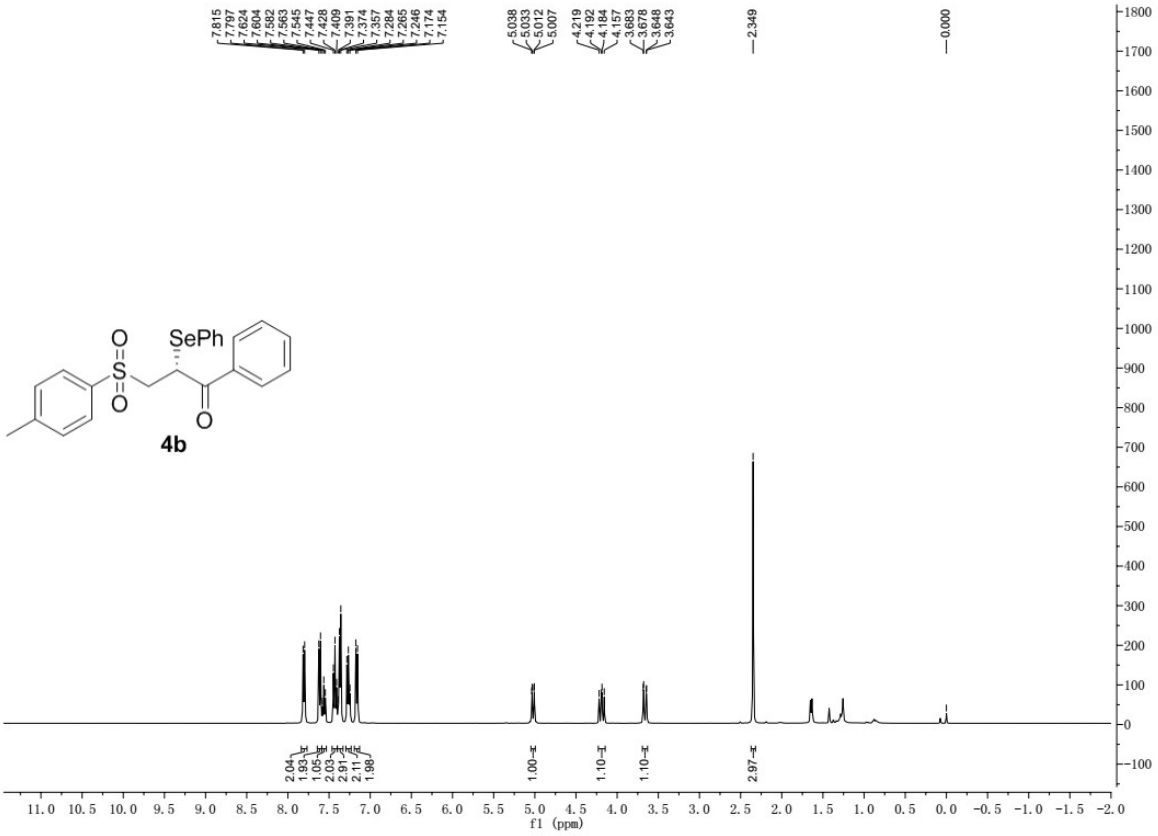
Optical Rotation: $[\alpha]_D^{20}$ = +45.6 (c = 1.0, $CHCl_3$); **physical properties**: white solid; **m.p.** 123–125 °C; **yield**: 95%, 50.1 mg.



X. ^{1}H and ^{13}C NMR spectra of compounds (4a-4p, 6a-6i, 7, 8, 9)



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7.447
7.428
7.409
7.391
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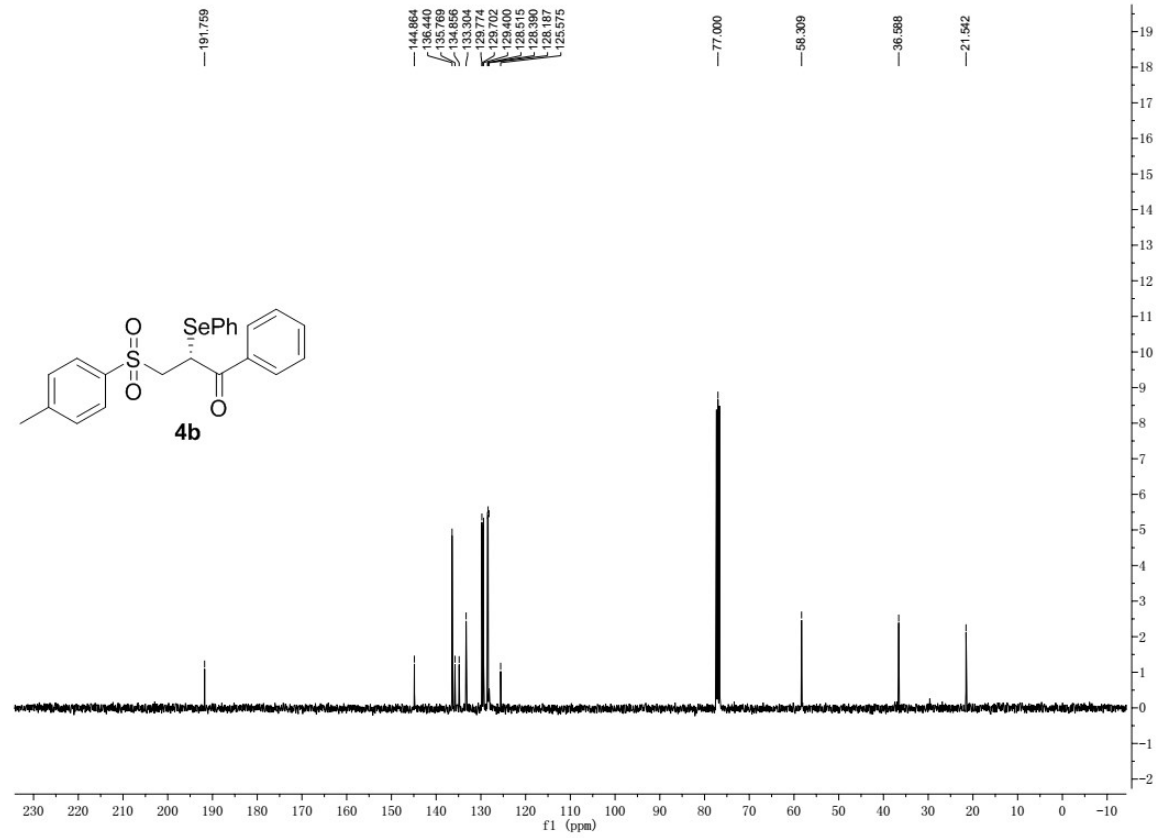
7.357
7.284
7.265
7.246
7.174
7.154
5.038
5.033
5.012
5.007
4.219
4.192
4.184
4.157
3.683
3.678
3.648
3.643
2.349
0.000
SePh
O
S
O
O
4b
2.04
1.93
1.05
2.03
2.91
2.11
1.98
1.00
1.10
1.10
2.97
f1 (ppm)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133.304
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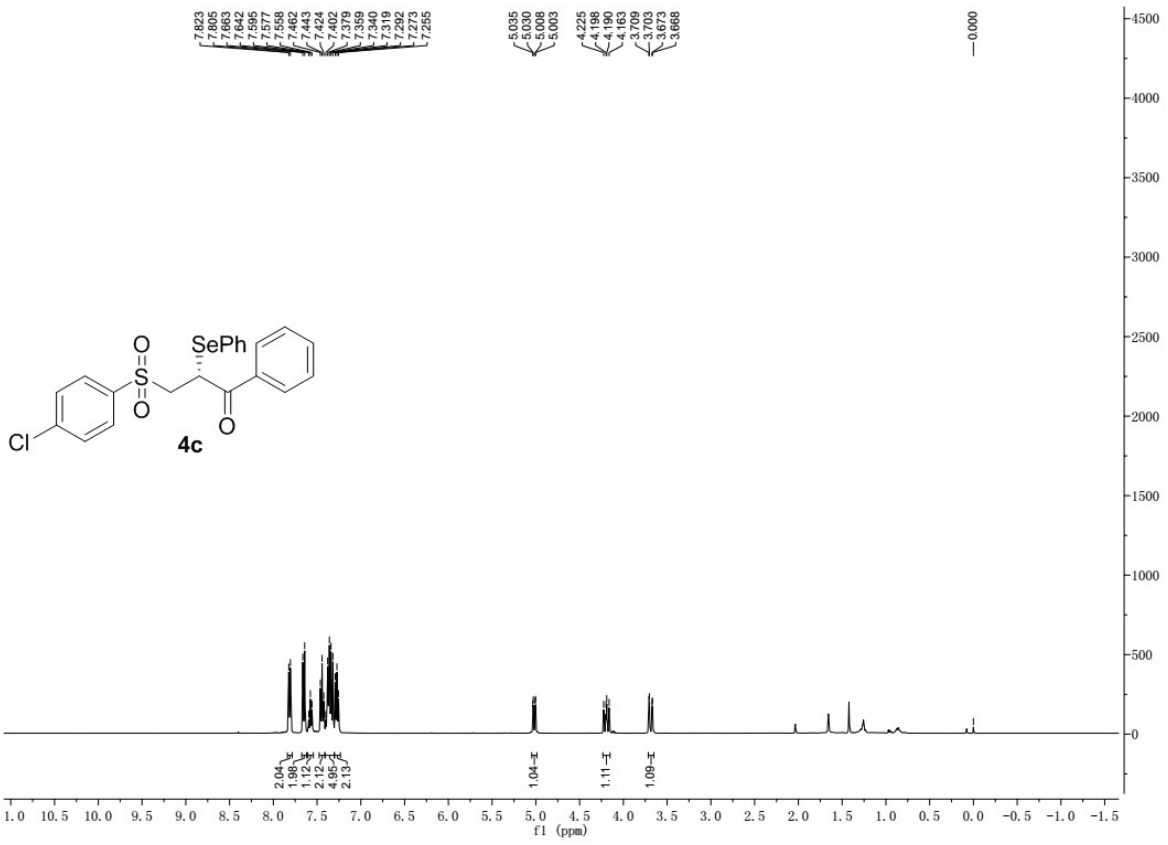
77.000
58.309
36.588
21.542
SePh
O
S
O
O
4b
f1 (ppm)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7.462
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7.424
7.402
7.379
7.359
7.340
7.319
7.292
7.273
7.255
5.035
5.030
5.008
5.003
4.225
4.198
4.190
4.163
3.709
3.703
3.673
3.668
0.000
SePh
O
S
O
O
Cl
4c
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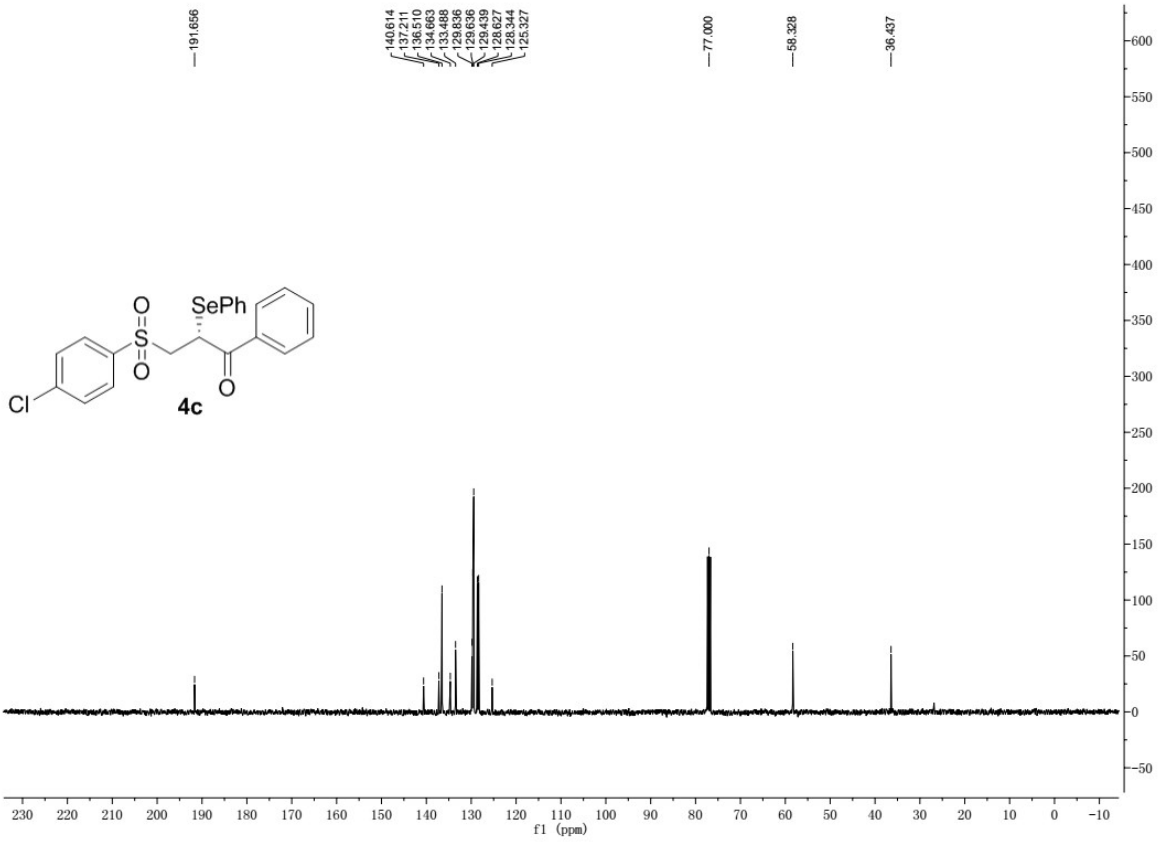
1.98
1.12
2.12
4.95
2.13
1.04
1.11
1.09
f1 (ppm)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134.663
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129.836
129.636
129.439
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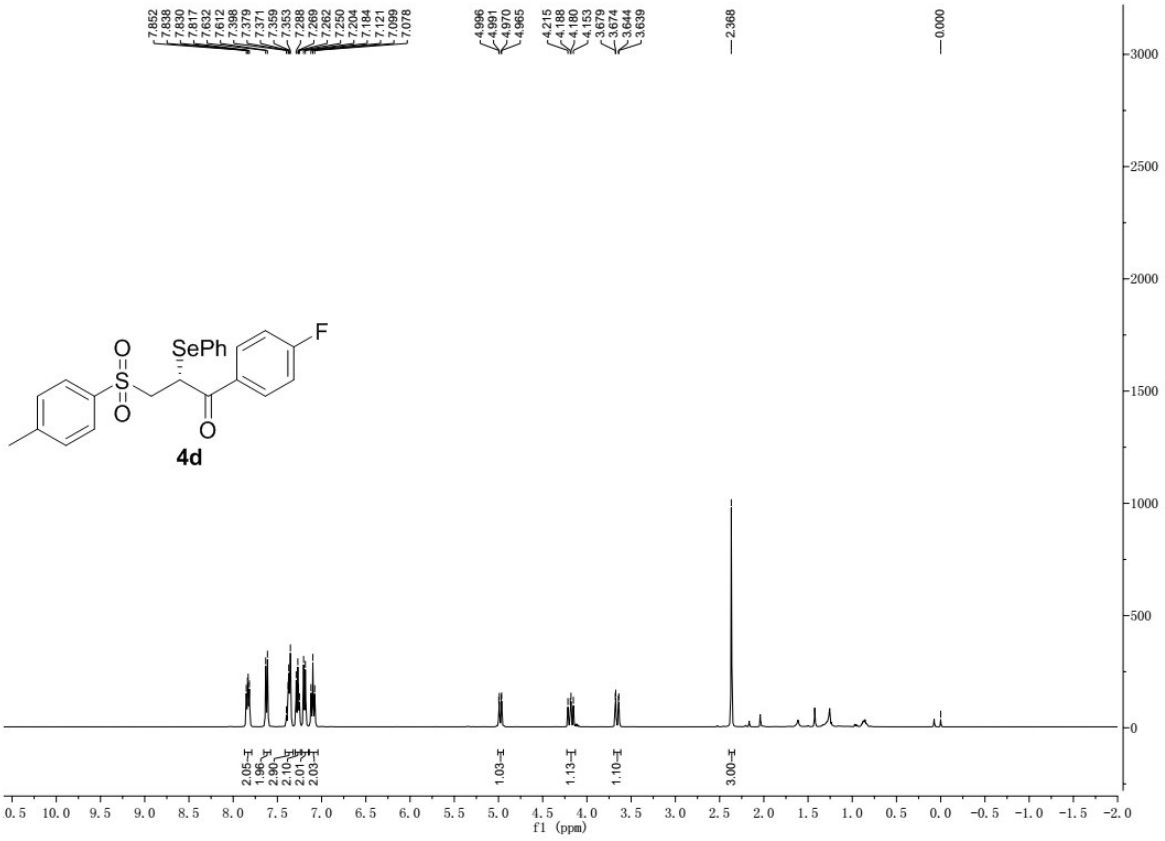
128.344
125.327
77.000
58.328
36.437
SePh
O
S
O
O
Cl
4c
f1 (ppm)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7.830
7.817
7.632
7.612
7.398
7.379
7.371
7.359
7.353
7.288
7.269
7.262
7.250
7.204
7.184
7.121
7.099
7.078
4.996
4.991
4.970
4.965
4.215
4.188
4.180
4.153
3.679
3.674
3.644
3.639
2.368
0.000
SePh
F
O
S
O
O
4d
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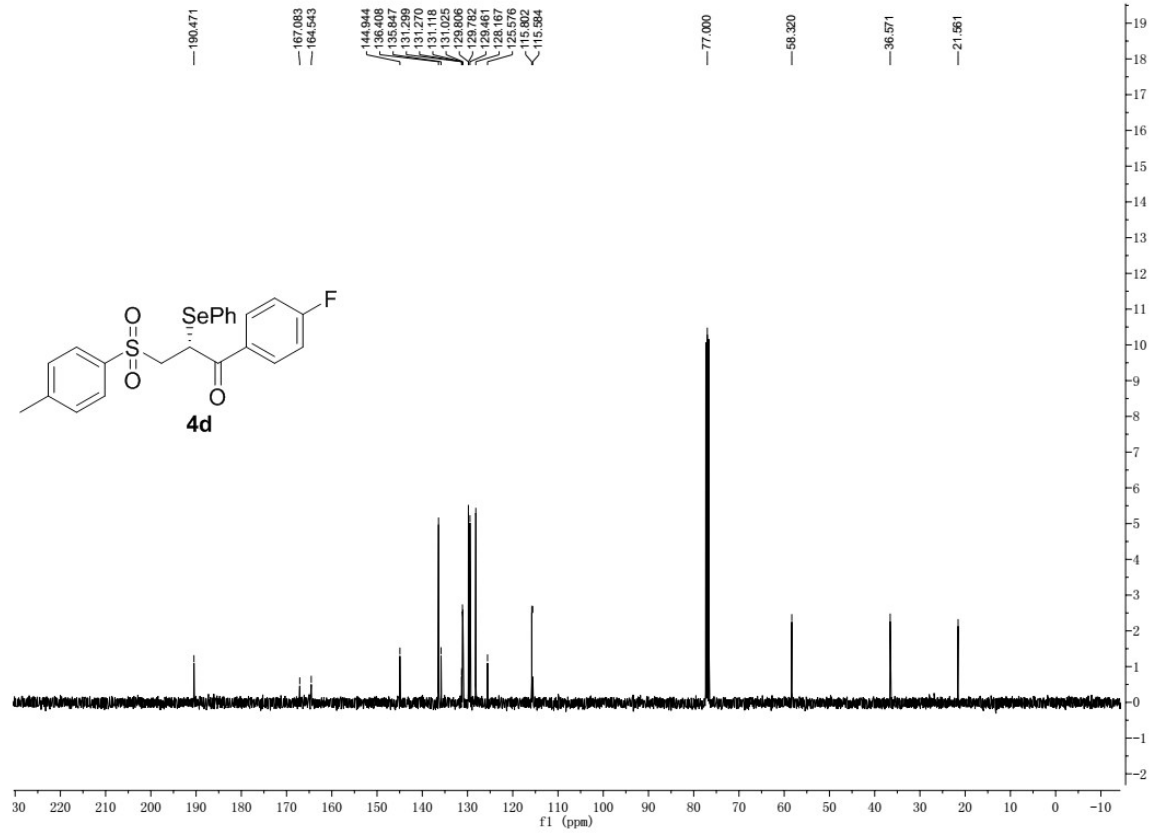
2.90
2.10
2.01
2.03
1.03
1.13
1.10
3.00
f1 (ppm)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135.847
131.299
131.270
131.118
131.025
129.866
129.732
129.461
128.167
125.576
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115.584
77.000
58.320
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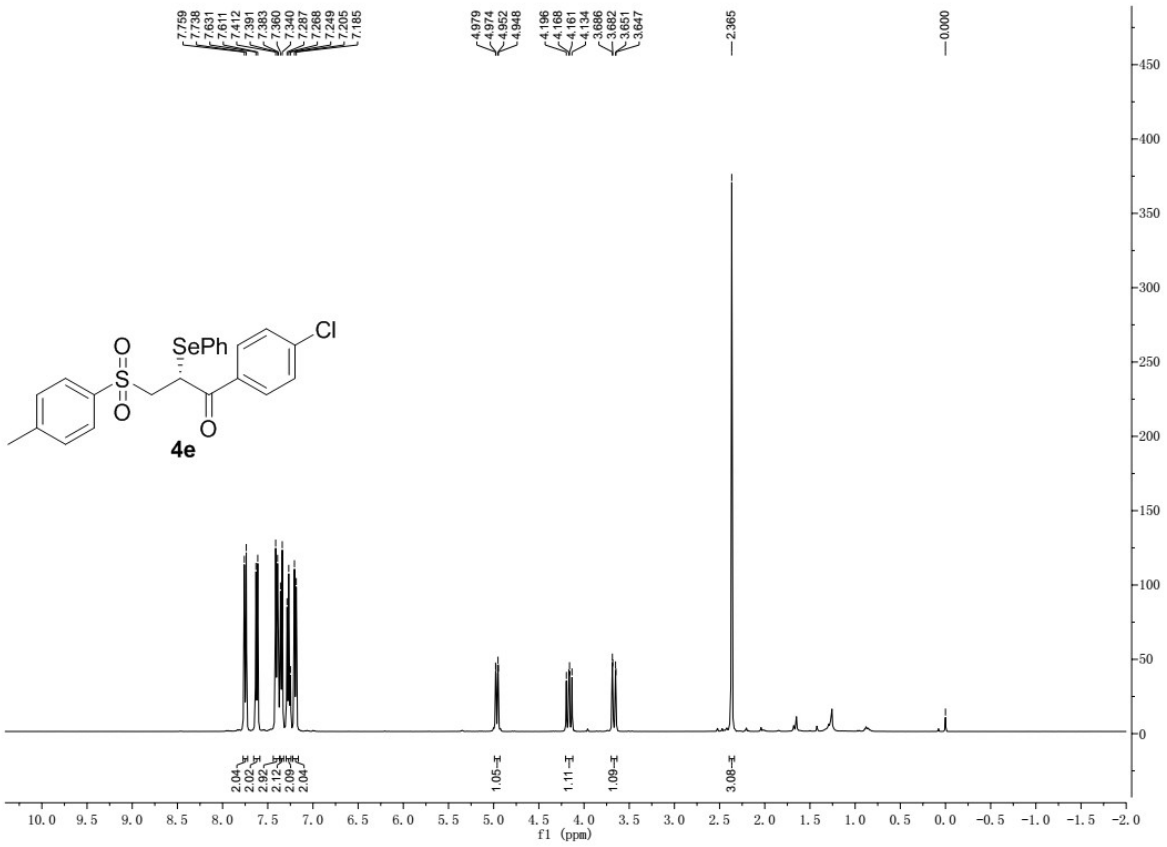
21.561
SePh
F
O
S
O
O
4d
f1 (ppm)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7.205
7.185
4.979
4.974
4.952
4.948
4.196
4.168
4.161
4.134
3.886
3.882
3.851
3.847
2.365
0.000
SePh
Cl
O
S
O
O
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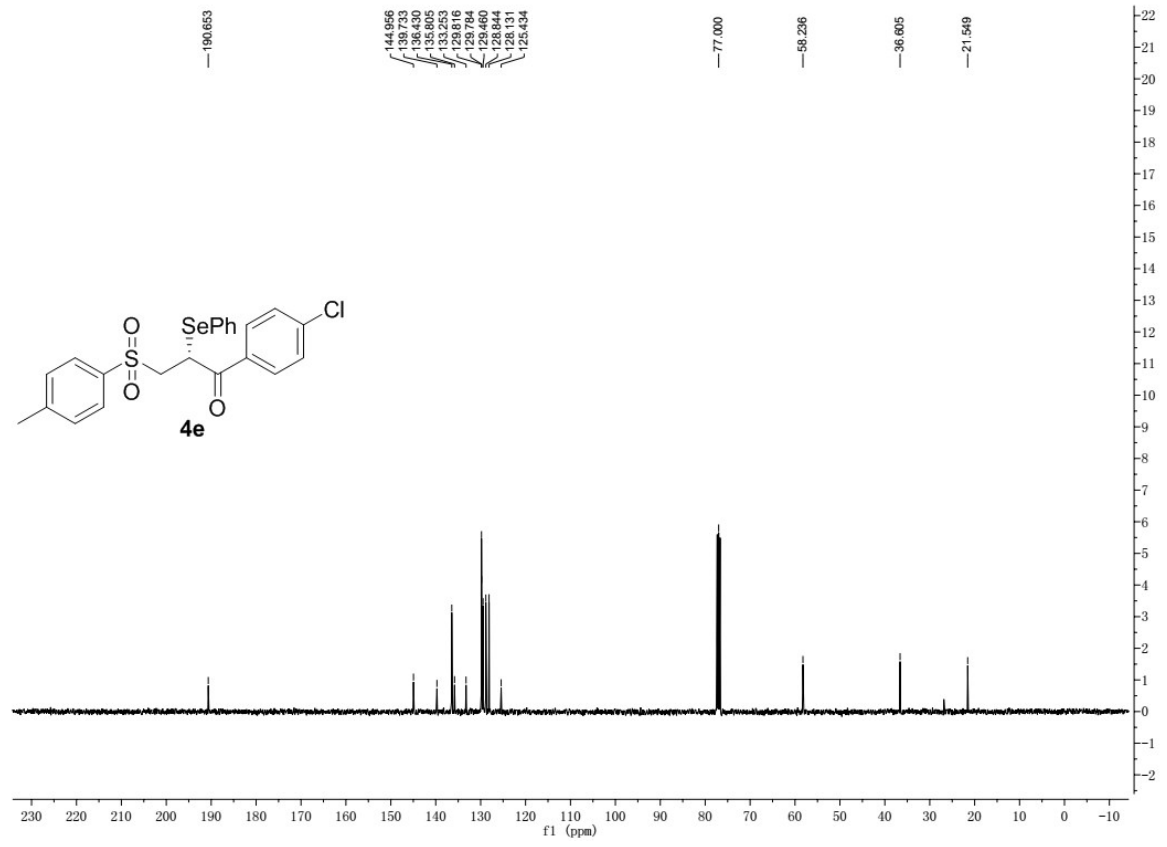
2.02
2.92
2.12
2.09
2.04
1.05
1.11
1.09
3.08
f1 (ppm)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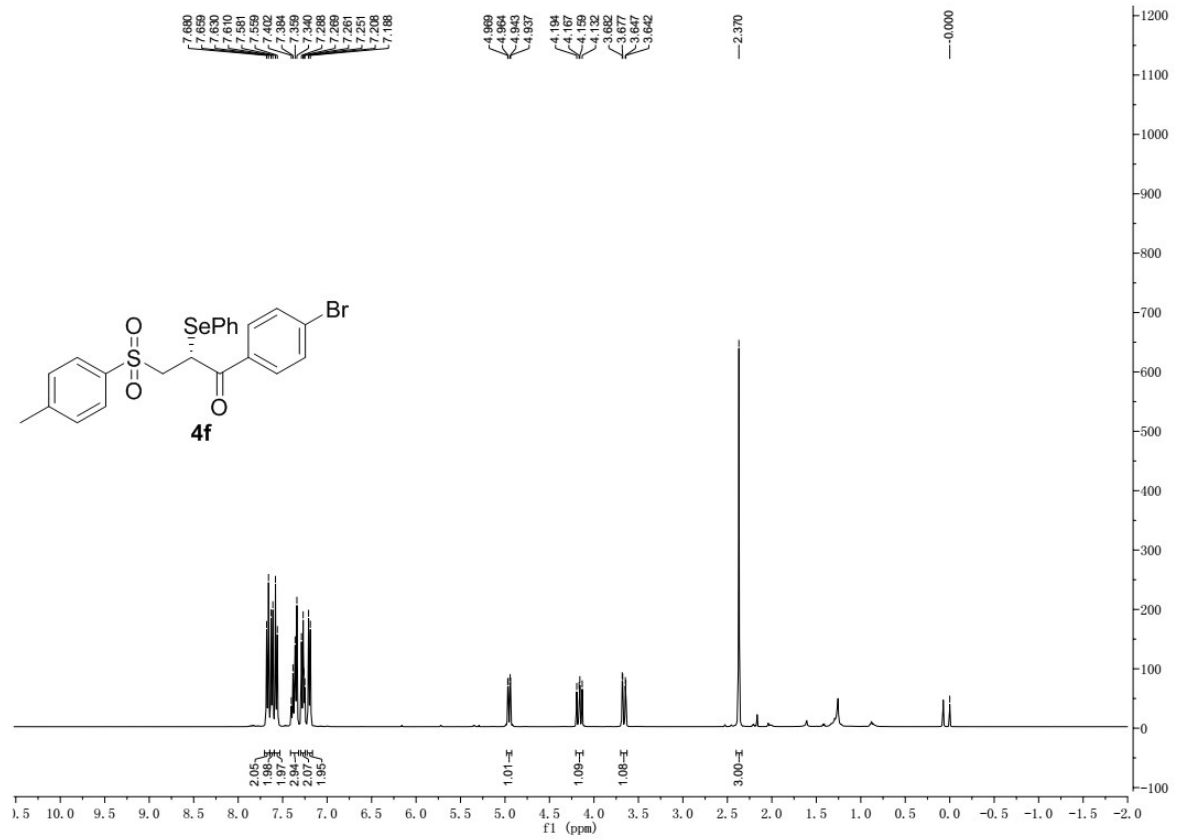
SePh
Cl
O
S
O
O
4e
f1 (ppm)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7.340
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7.269
7.261
7.251
7.208
7.188
4.969
4.964
4.943
4.937
4.194
4.167
4.159
4.132
3.682
3.677
3.647
3.642
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SePh
Br
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S
O
O
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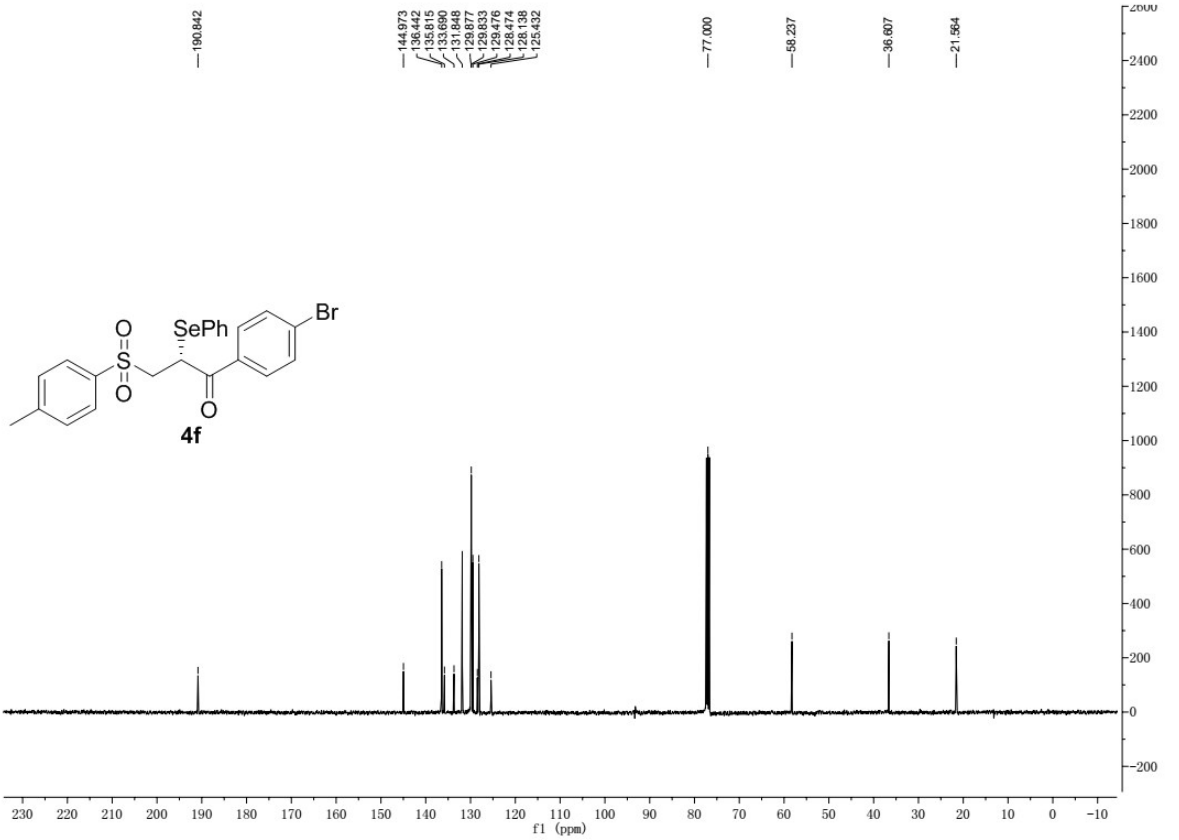
1.09
1.08
3.00
f1 (ppm)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128.474
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21.564
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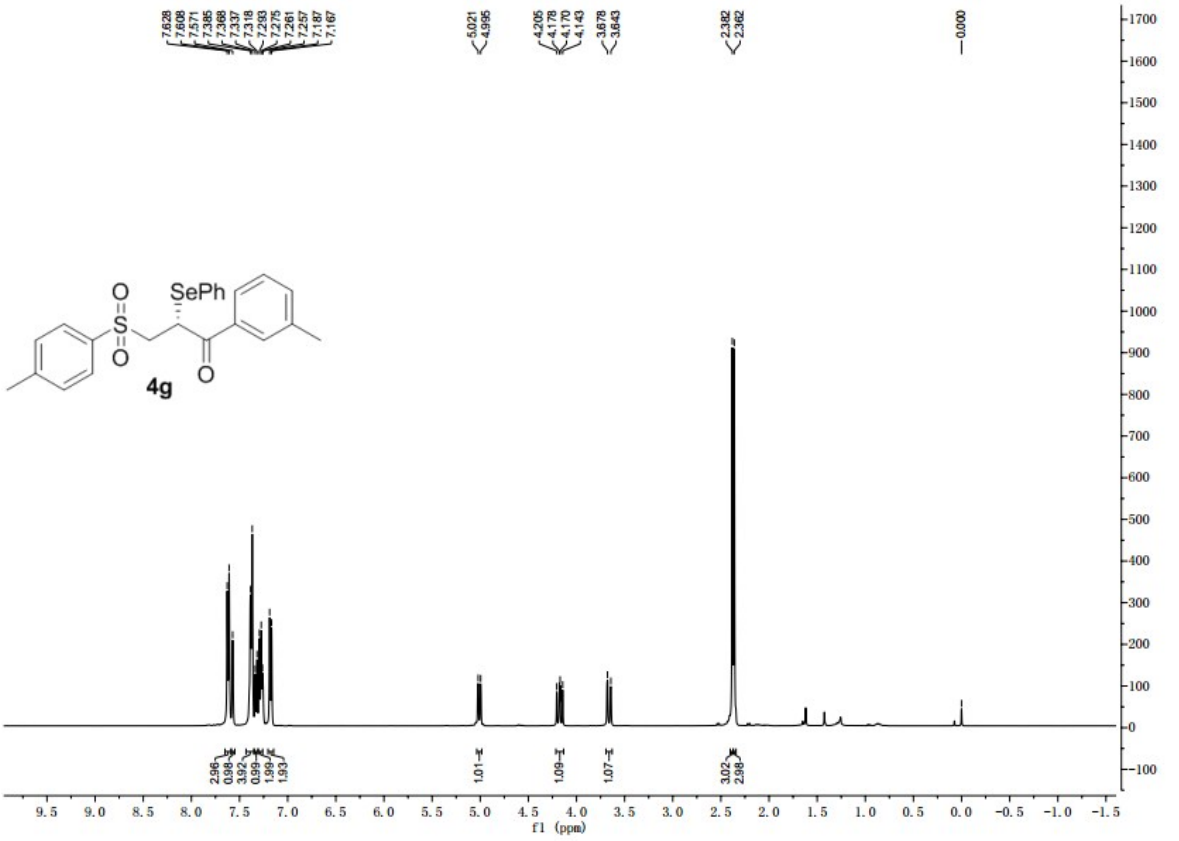
Br
O
S
O
O
4f
f1 (ppm)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7.293
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7.257
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4.170
4.143
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3.643
2.382
2.362
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SePh
O
S
O
O
4g
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0.99
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1.93
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1.07
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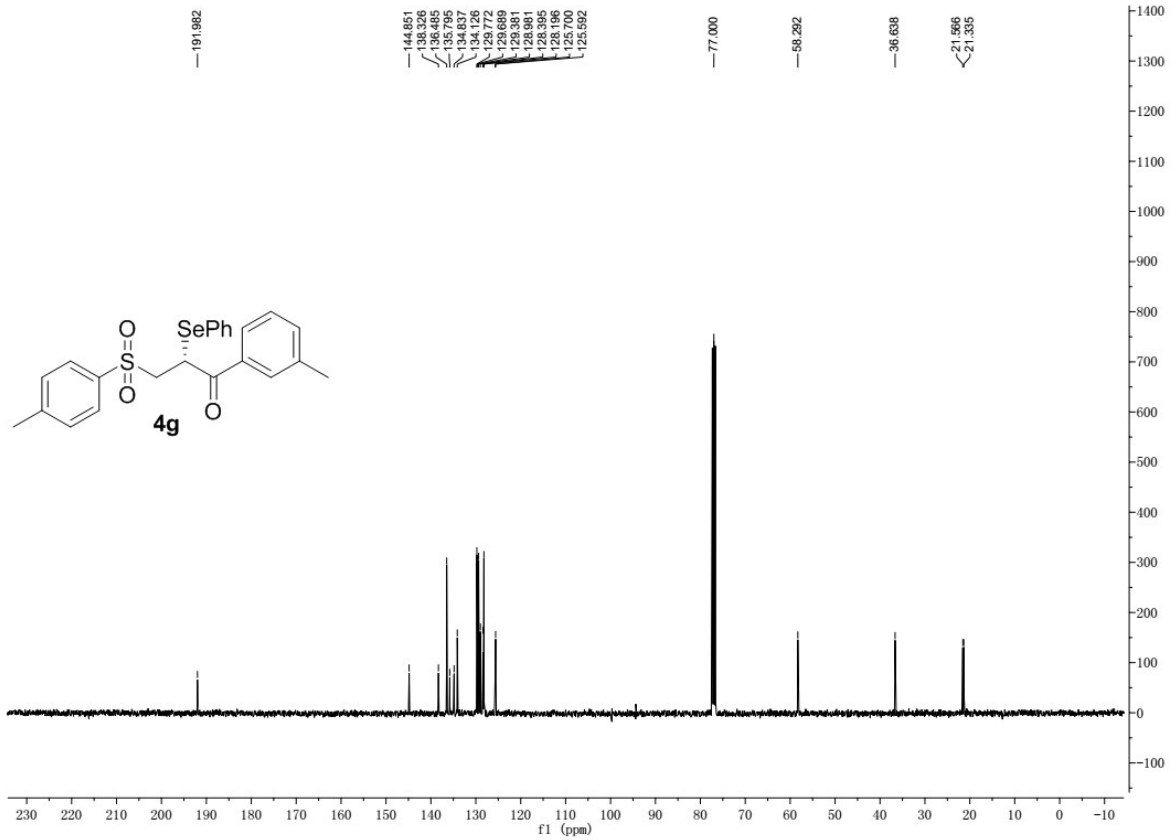
2.98
f1 (ppm)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128.395
128.196
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125.592
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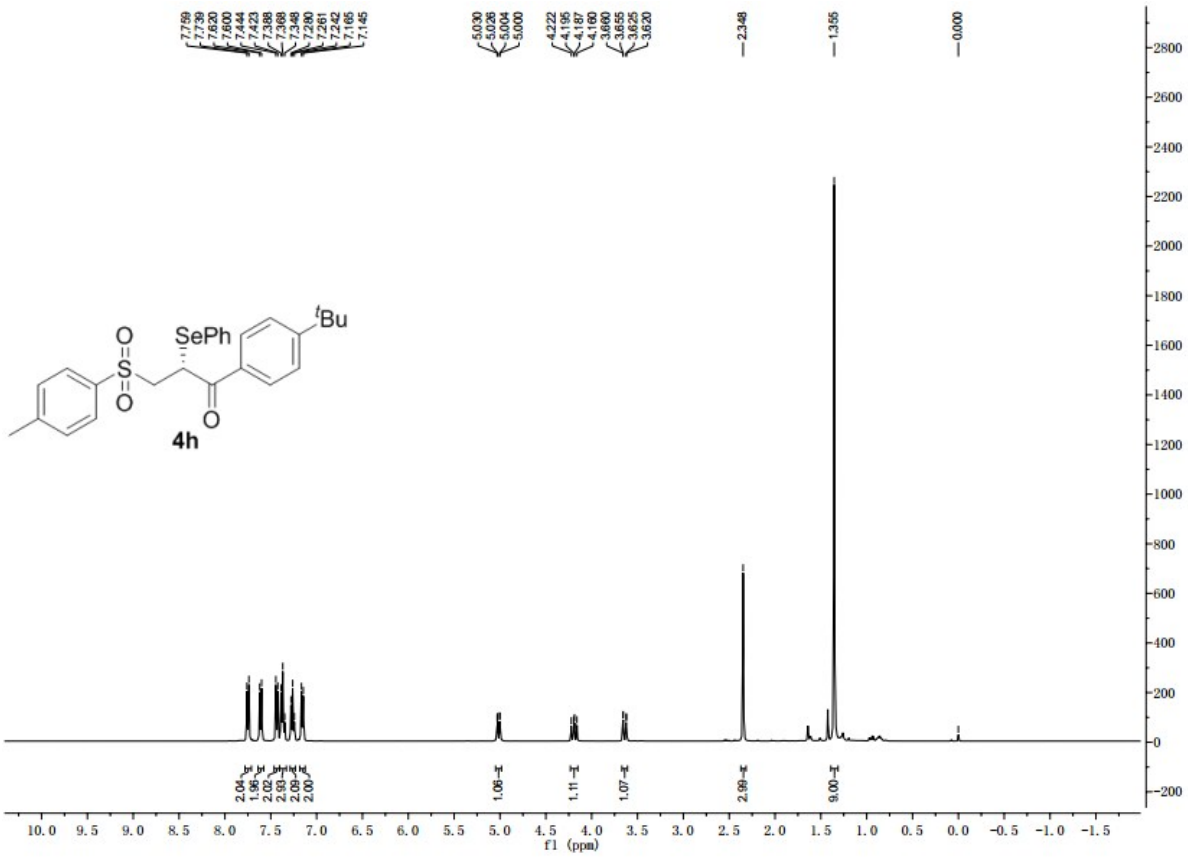
SePh
O
S
O
O
4g
f1 (ppm)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7.145
5.030
5.026
5.004
5.000
4.222
4.195
4.187
4.160
3.680
3.655
3.625
3.620
2.348
1.355
0.000
SePh
tBu
O
S
O
O
4h
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1.96
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2.93
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2.00
1.06
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1.07
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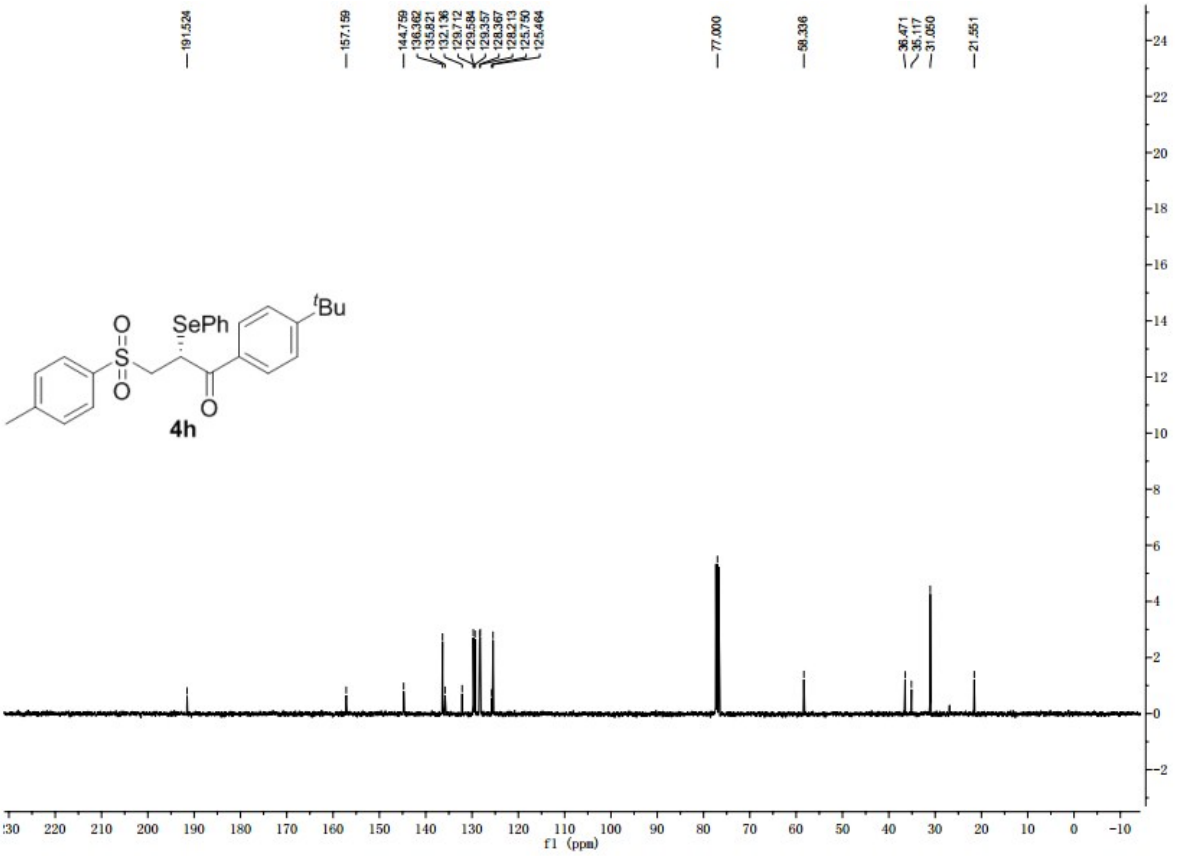
9.00
f1 (ppm)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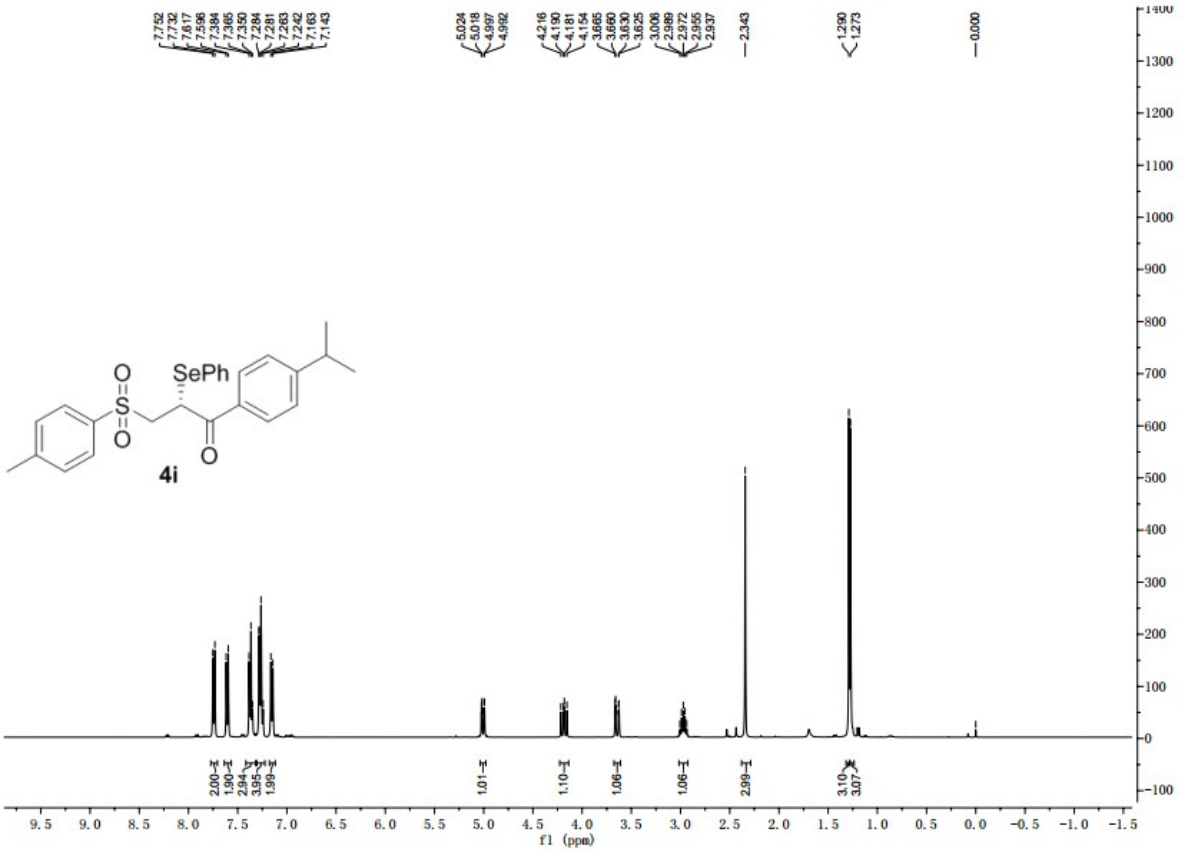
S
O
O
4h
f1 (ppm)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4.992
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4.190
4.181
4.154
3.665
3.660
3.630
3.625
3.006
2.989
2.972
2.955
2.937
2.343
1.290
1.273
0.000
SePh
O
S
O
O
4i
2.00
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2.94
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1.99
1.01
1.10
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1.06
2.99
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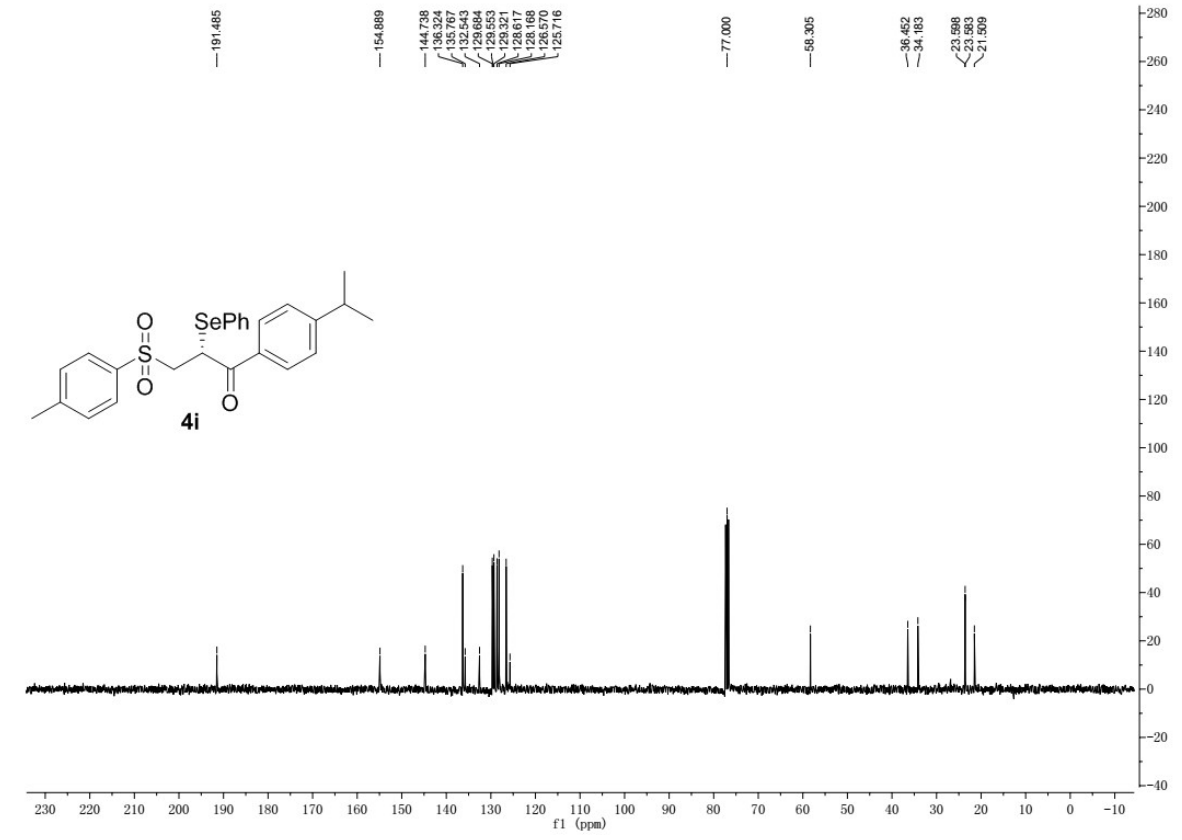
3.07
f1 (ppm)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132.543
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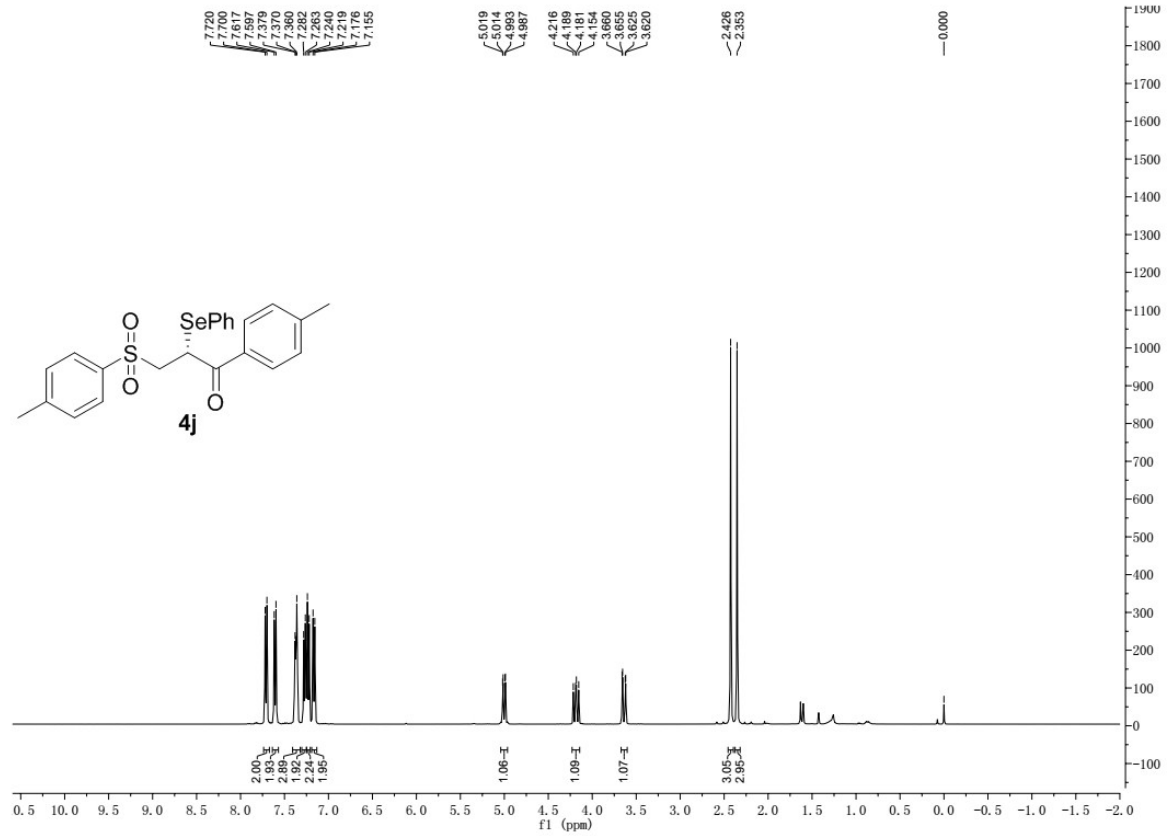
77.000
58.305
36.452
34.183
23.598
23.583
21.509
SePh
O
S
O
O
4i
f1 (ppm)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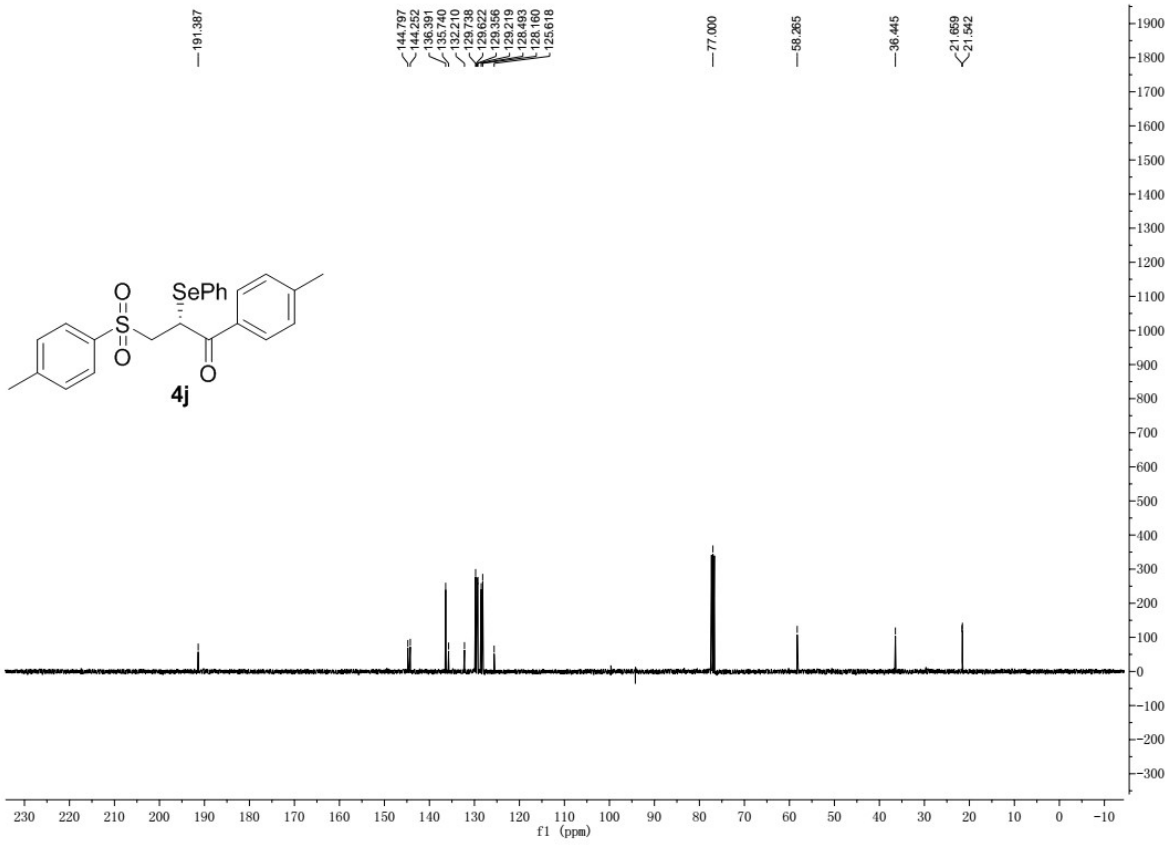
7.597
7.379
7.370
7.360
7.282
7.263
7.240
7.219
7.176
7.155
5.019
5.014
4.993
4.987
4.216
4.189
4.181
4.154
3.660
3.655
3.625
3.620
2.426
2.353
0.000
SePh
O
S
O
O
4j
2.00
1.93
2.89
1.92
2.24
1.95
1.06
1.09
1.07
3.05
2.95
f1 (ppm)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144.252
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135.740
132.210
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129.622
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129.219
128.493
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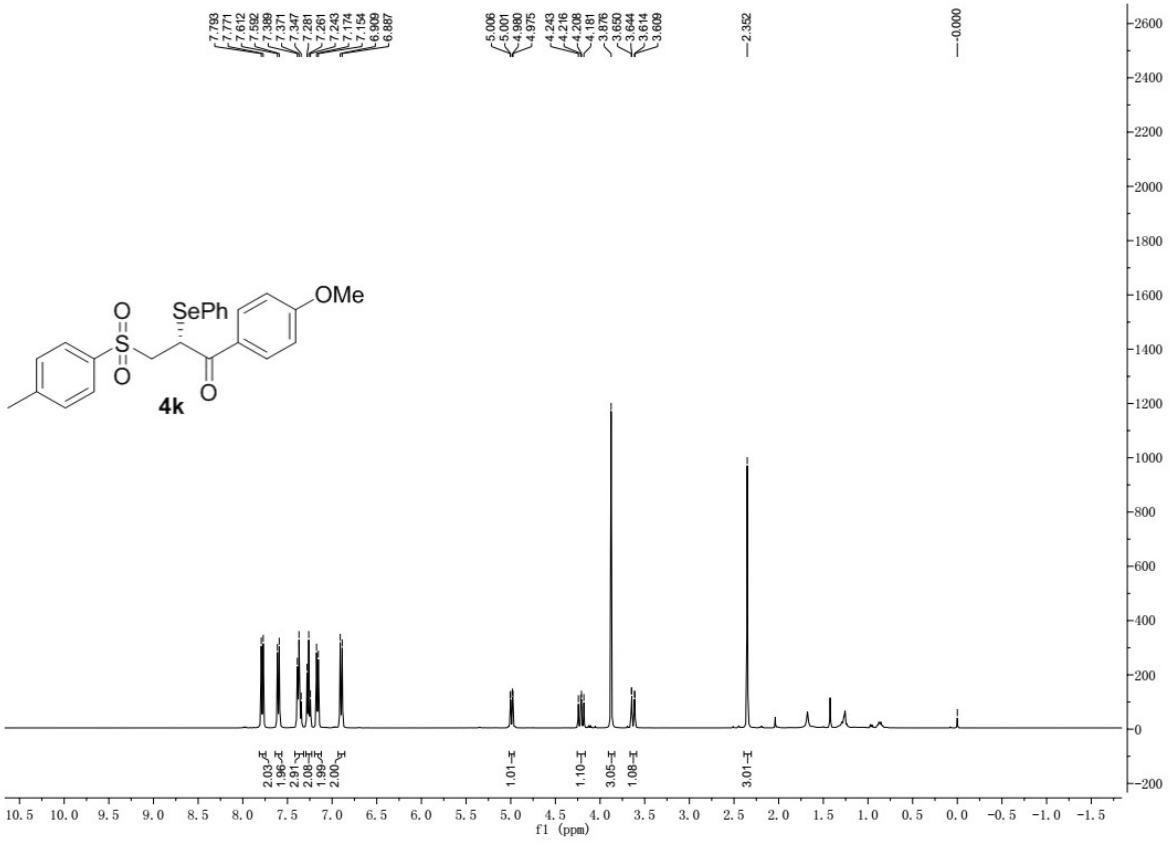
125.618
77.000
58.265
36.445
21.659
21.542
SePh
O
S
O
O
4j
f1 (ppm)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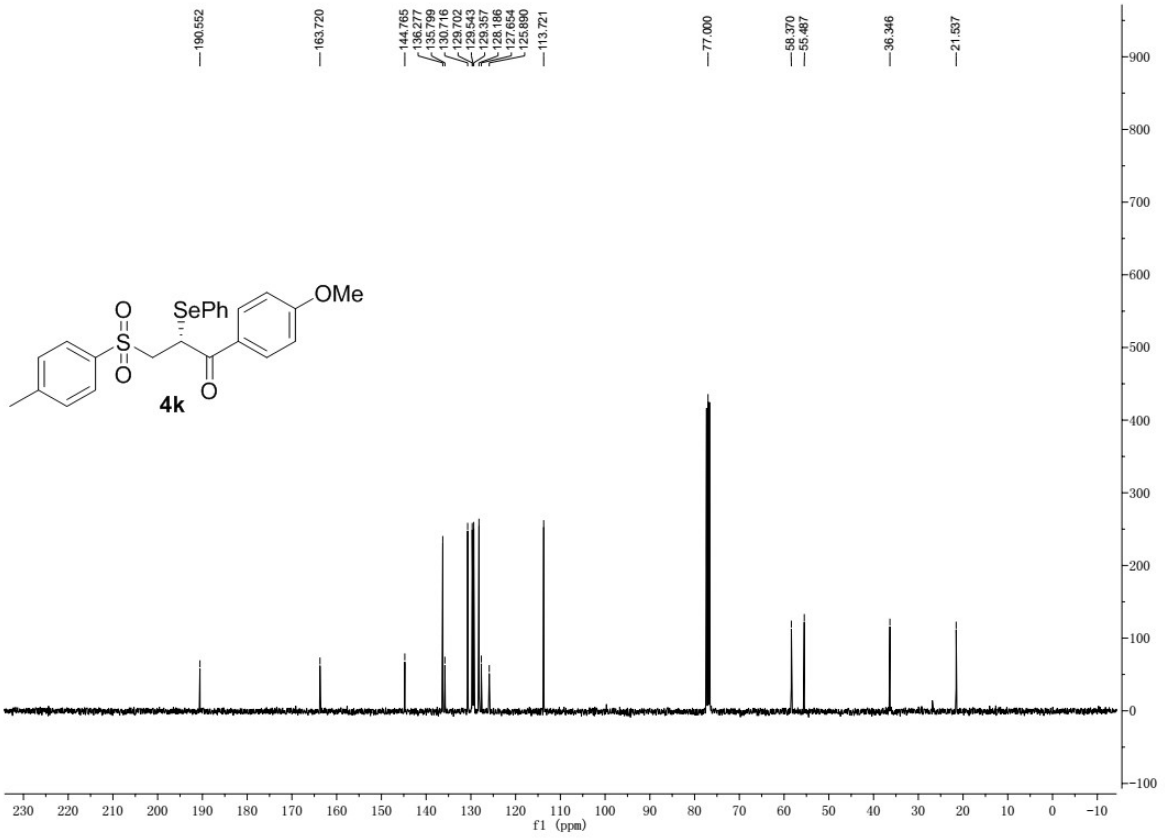
7.261
7.243
7.174
7.154
6.909
6.887
5.006
5.001
4.980
4.975
4.243
4.216
4.208
4.181
3.876
3.650
3.644
3.614
3.609
2.352
0.000
SePh
OMe
O
S
O
O
4k
2.03
1.96
2.91
2.08
1.99
2.00
1.01
1.10
3.05
1.08
3.01
f1 (ppm)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129.543
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77.000
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55.487
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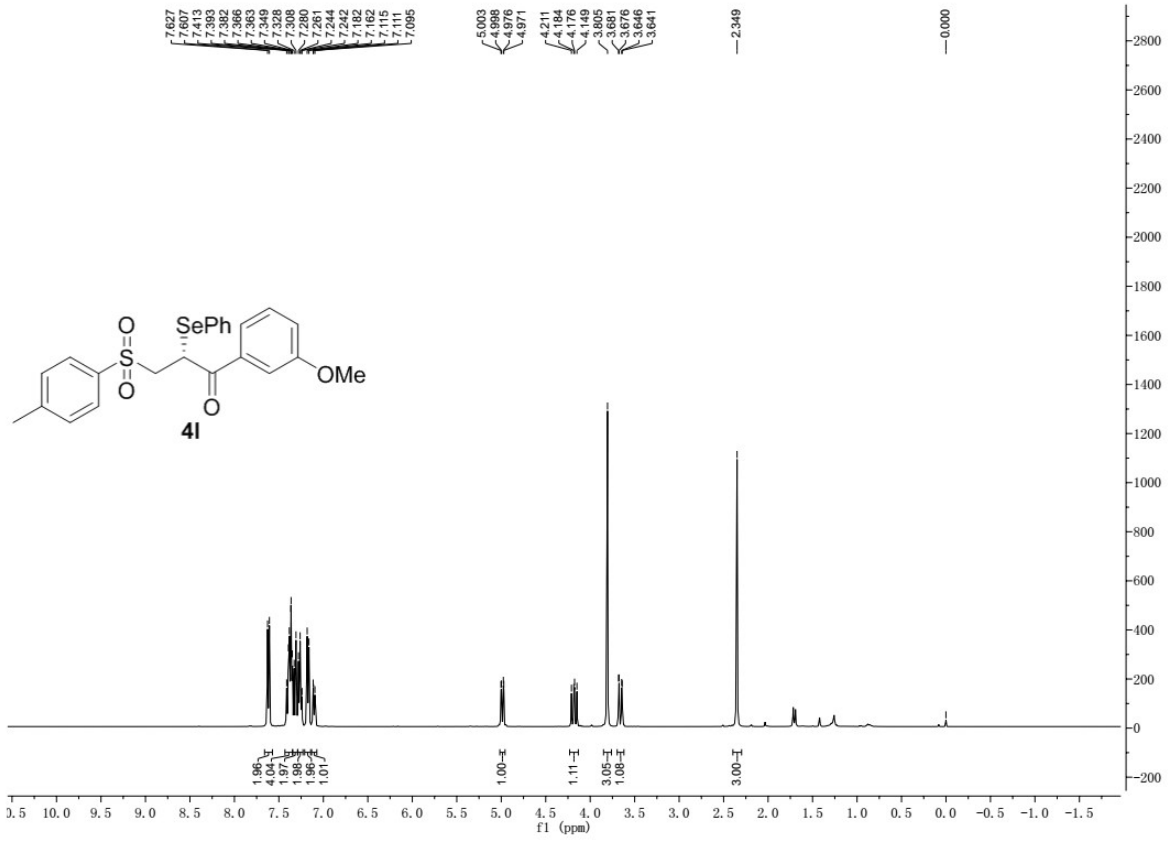
21.537
SePh
OMe
O
S
O
O
4k
f1 (ppm)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7.363
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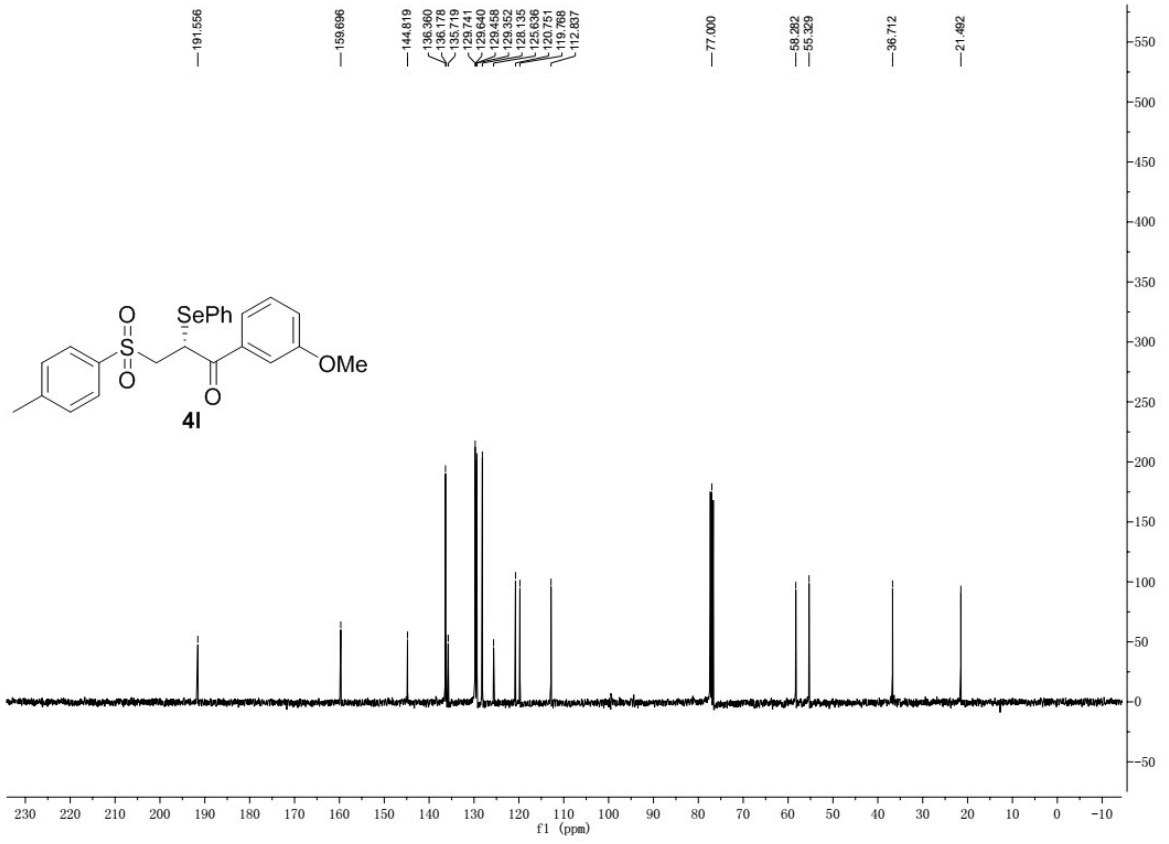
7.328
7.308
7.280
7.261
7.244
7.242
7.182
7.162
7.115
7.111
7.095
5.003
4.998
4.976
4.971
4.211
4.184
4.176
4.149
3.805
3.681
3.676
3.646
3.641
2.349
0.000
SePh
O
S
O
O
OMe
O
4l
1.96
4.04
1.97
1.98
1.96
1.01
1.00
1.11
3.05
1.08
3.00
f1 (ppm)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129.458
129.352
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125.636
120.751
119.768
112.857
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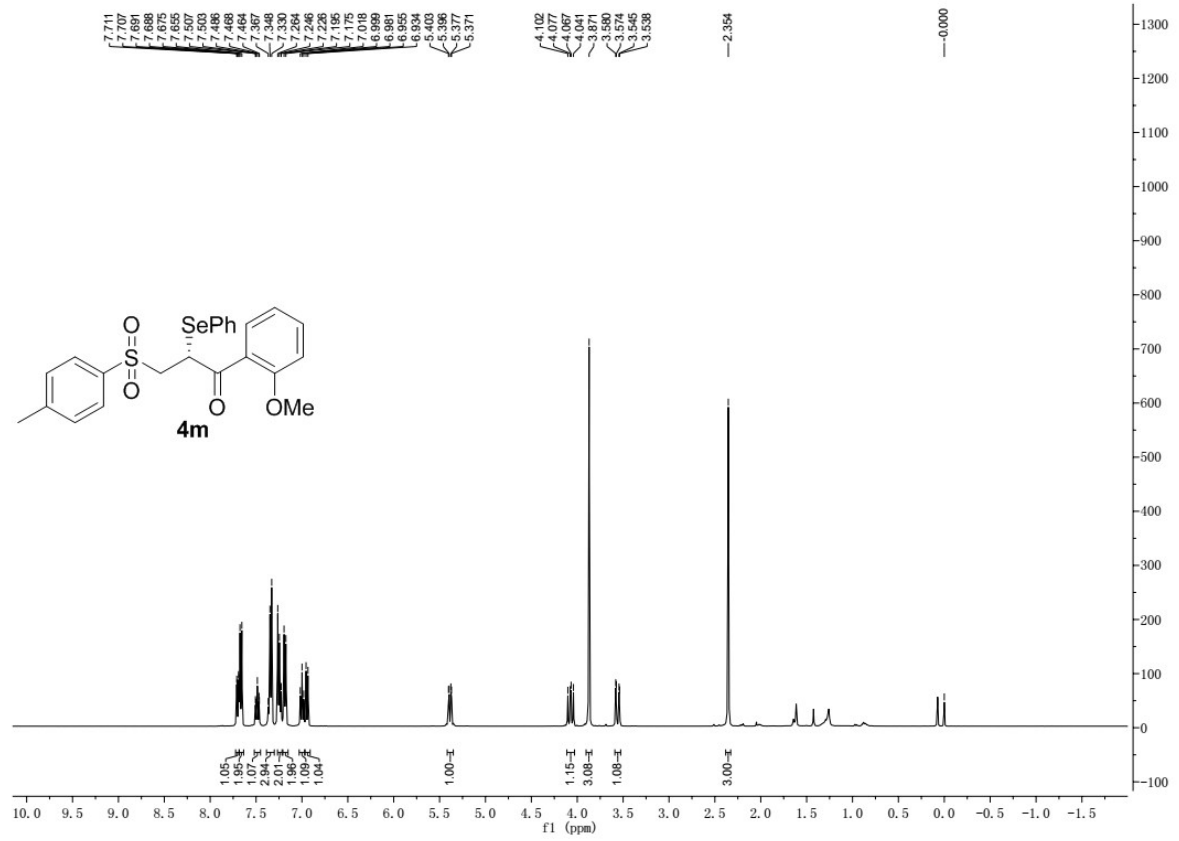
55.329
36.712
21.492
SePh
O
S
O
O
OMe
O
4l
f1 (ppm)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7.691
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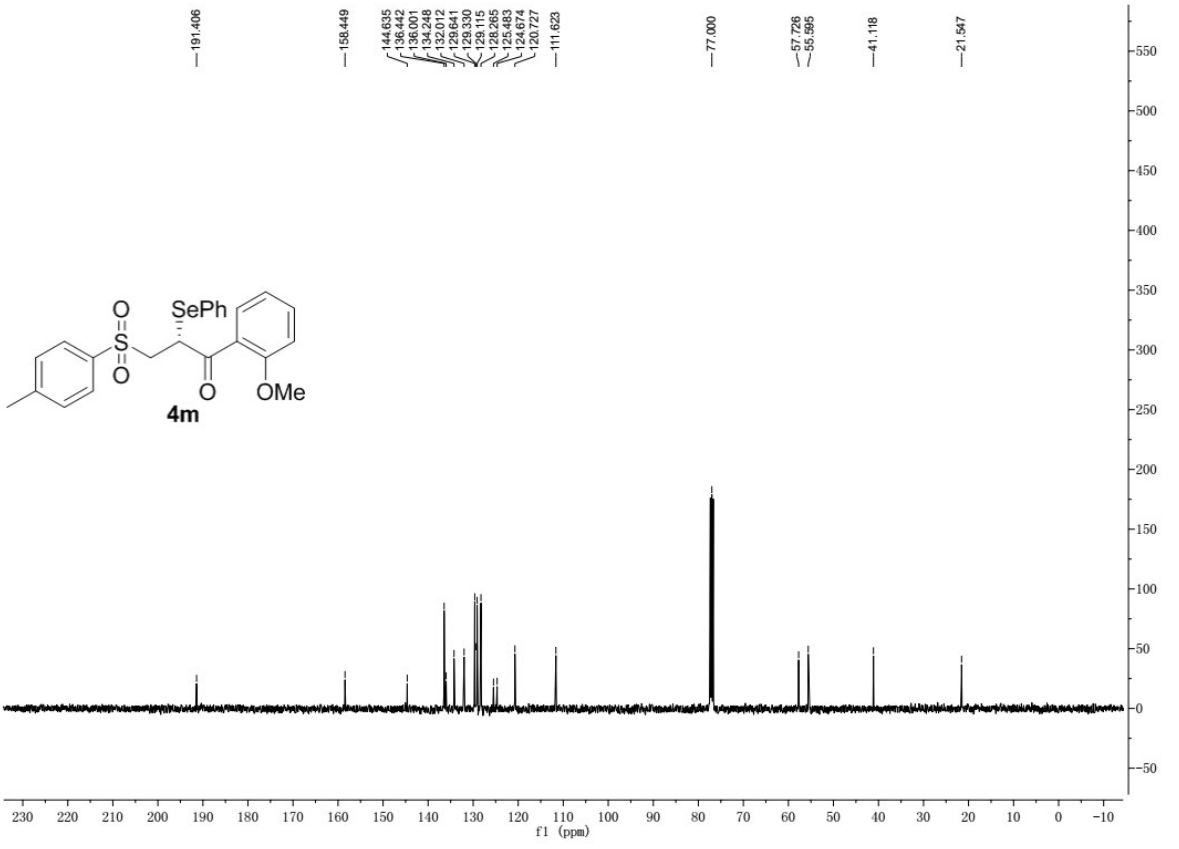
7.675
7.655
7.507
7.505
7.486
7.468
7.464
7.367
7.348
7.330
7.264
7.246
7.226
7.195
7.175
7.018
6.999
6.981
6.955
6.934
5.403
5.396
5.377
5.371
4.102
4.077
4.067
4.041
3.871
3.580
3.574
3.545
3.538
2.354
0.000
SePh
O
S
O
O
OMe
4m
1.05
1.95
1.07
2.94
2.01
1.96
1.09
1.04
1.00
1.15
3.08
1.08
3.00
f1 (ppm)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144.635
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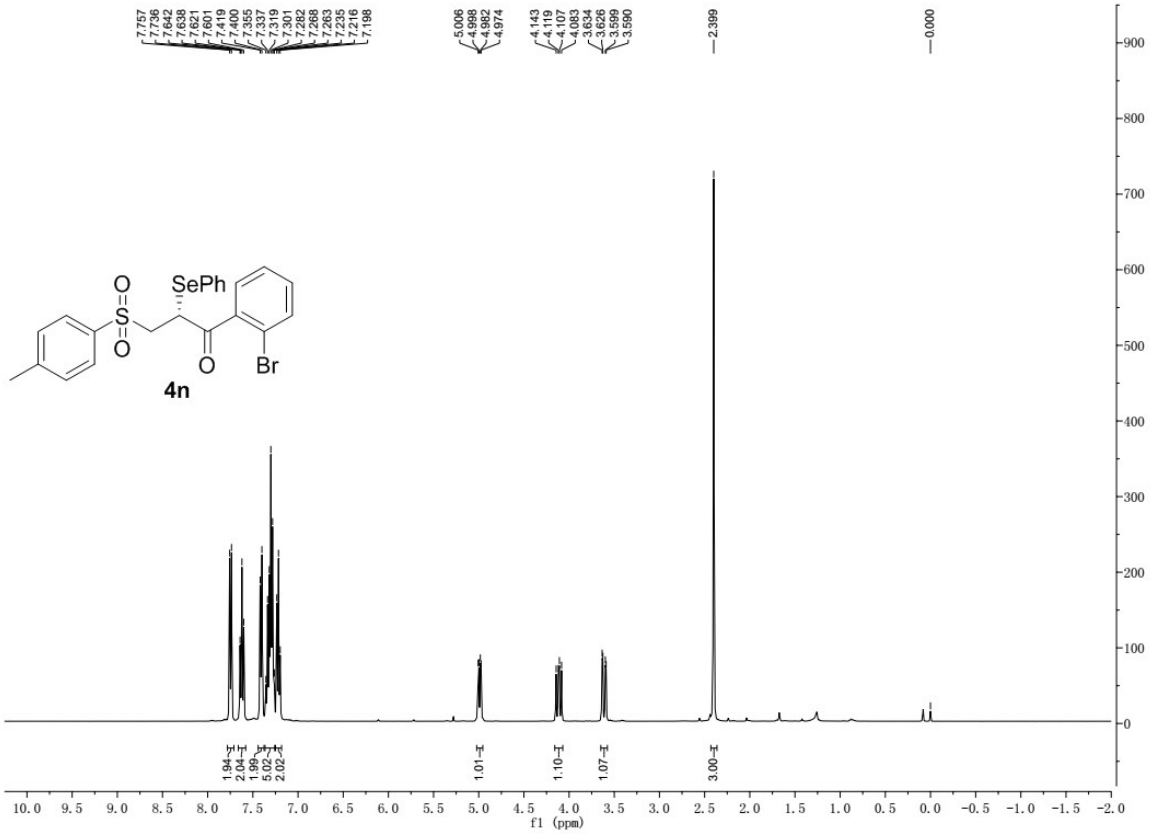
136.001
134.248
132.012
129.641
129.330
129.115
128.265
125.483
124.674
120.727
111.623
77.000
57.726
55.595
41.118
21.547
SePh
O
S
O
O
OMe
4m
f1 (ppm)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7.642
7.638
7.621
7.601
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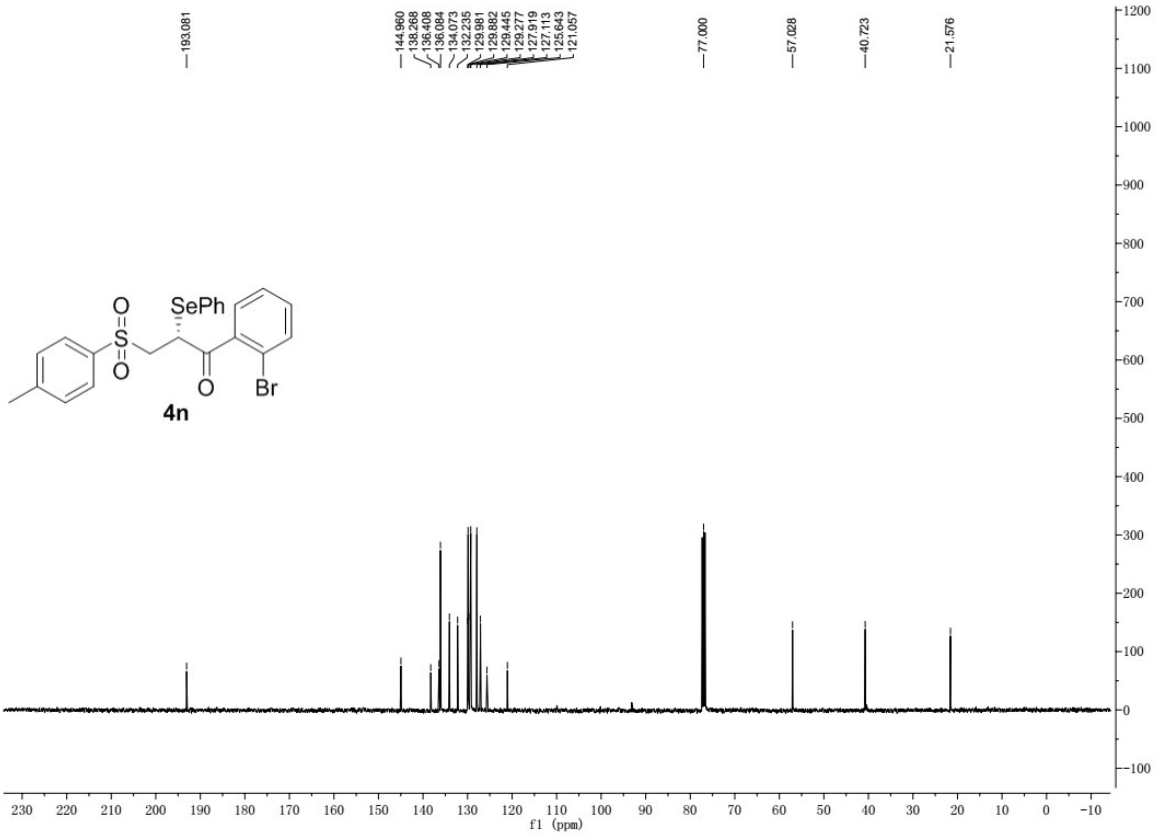
7.400
7.355
7.337
7.319
7.301
7.282
7.268
7.263
7.235
7.216
7.198
5.006
4.998
4.982
4.974
4.143
4.119
4.107
4.083
3.634
3.626
3.599
3.590
2.399
0.000
SePh
O
S
O
O
Br
4n
1.94
2.04
1.92
5.02
2.02
1.01
1.10
1.07
3.00
f1 (ppm)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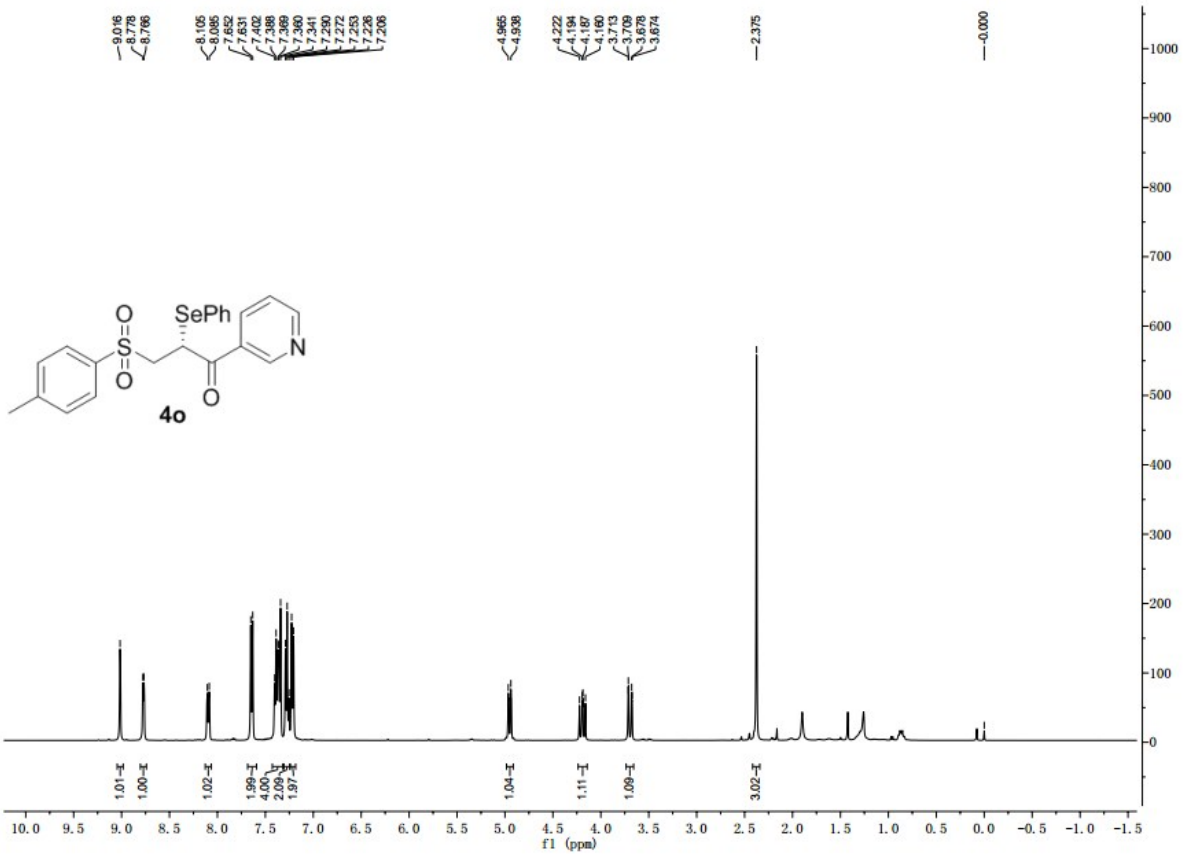
144.960
138.268
136.408
136.084
134.073
132.235
129.981
129.882
129.445
129.277
127.919
127.113
125.643
121.057
77.000
57.028
40.723
21.576
SePh
O
S
O
O
Br
4n
f1 (ppm)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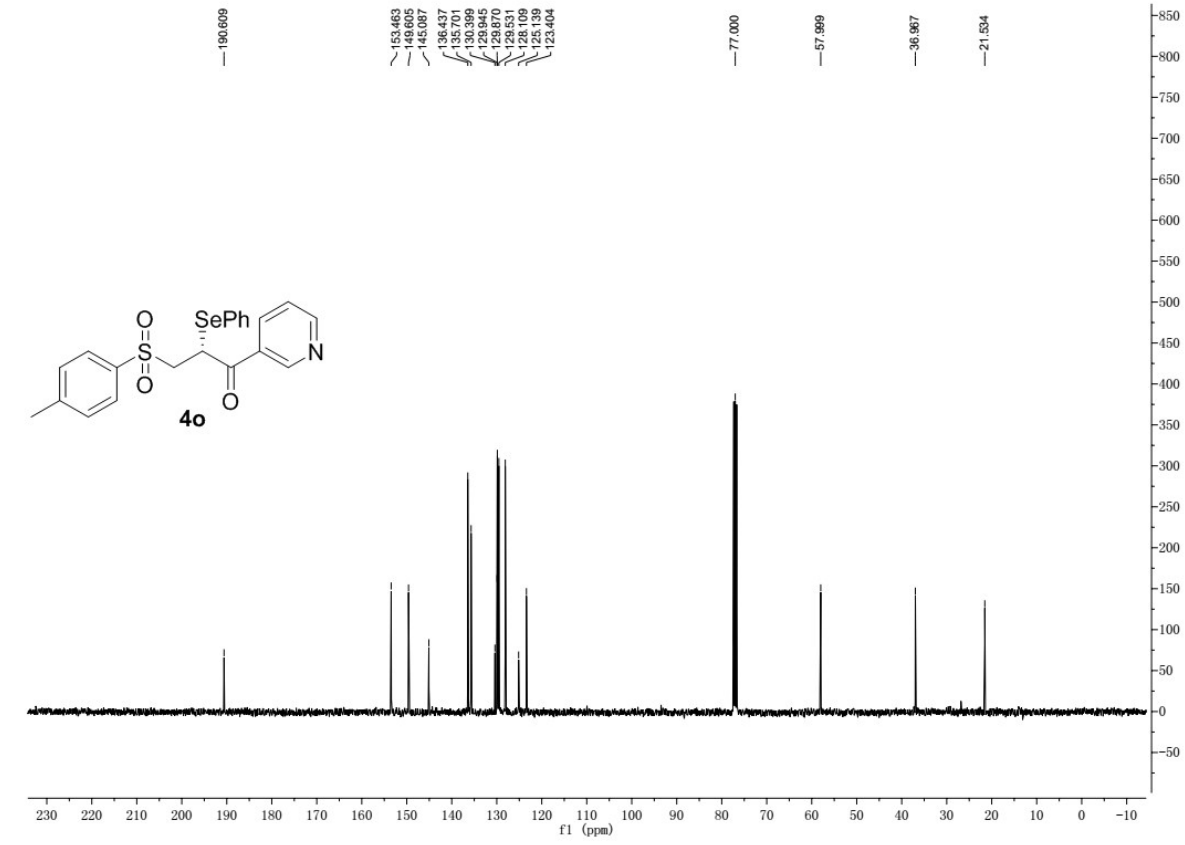
8.778
8.766
8.105
8.095
7.652
7.631
7.402
7.388
7.369
7.360
7.341
7.290
7.272
7.253
7.226
7.206
4.965
4.938
4.222
4.194
4.187
4.160
3.713
3.709
3.678
3.674
2.375
-0.000
SePh
O
S
O
O
N
4o
1.01
1.00
1.02
1.99
4.00
2.09
1.97
1.04
1.11
1.09
3.02
f1 (ppm)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145.087
136.437
135.701
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129.945
129.670
129.511
128.109
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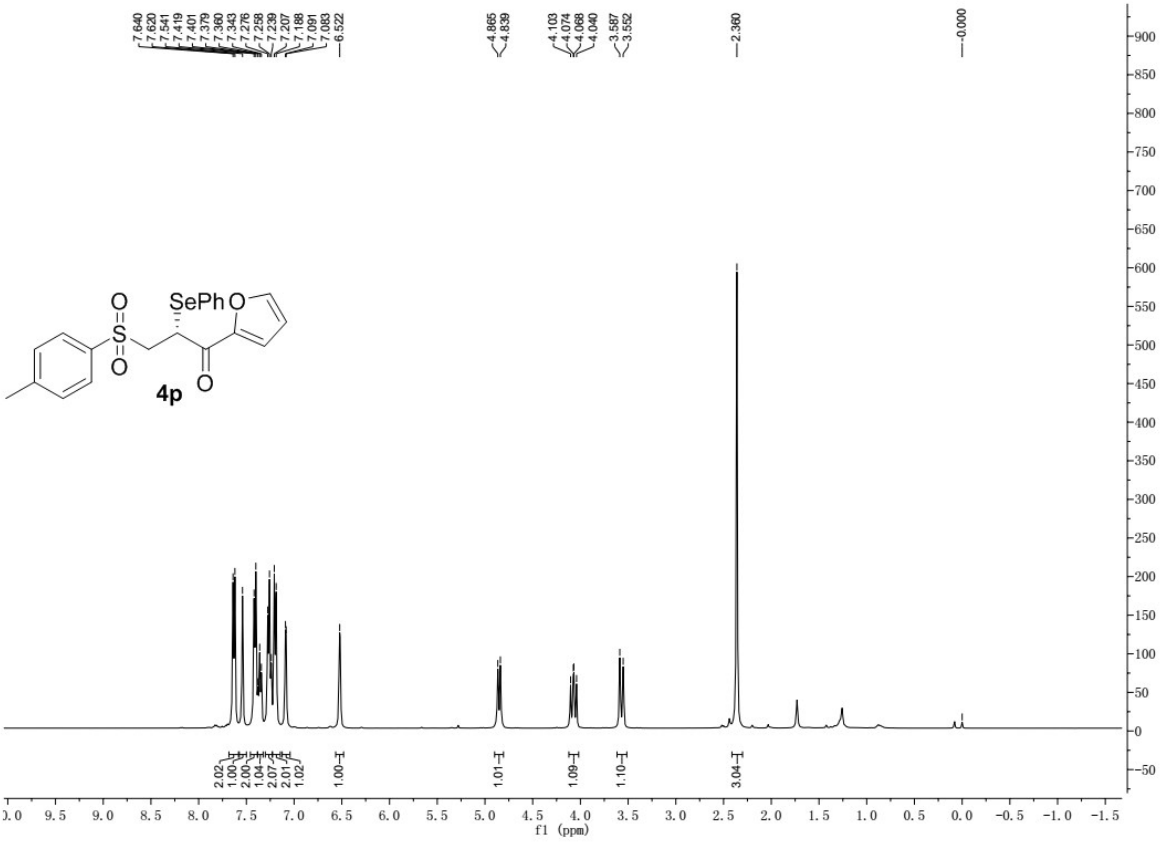
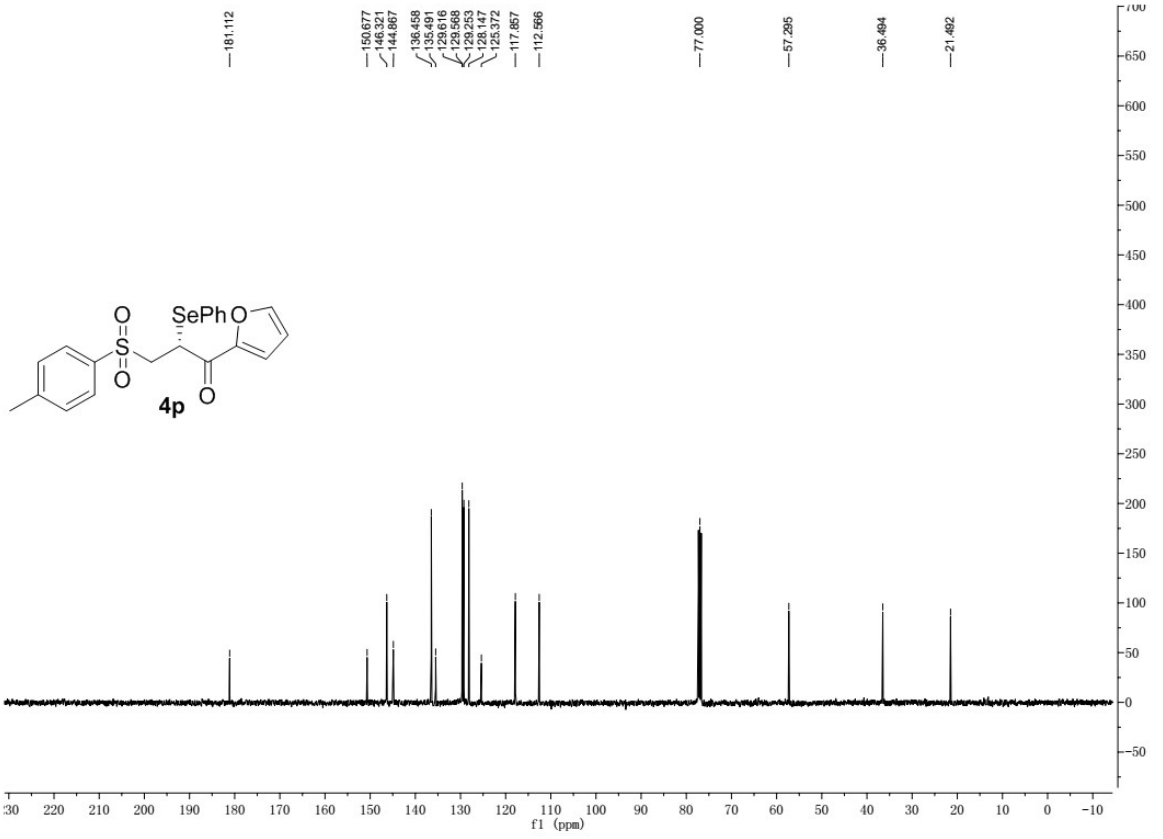
123.404
77.000
57.999
36.967
21.534
SePh
O
S
O
O
N
4o
f1 (ppm)


7.640
7.620
7.541
7.419
7.401
7.379
7.360
7.343
7.276
7.258
7.239
7.207
7.188
7.091
7.083
6.522
4.865
4.839
4.103
4.074
4.068
4.040
3.587
3.552
2.360
0.000
SePh
O
O
O
O
S
4p
f1 (ppm)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129.568
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128.147
125.372
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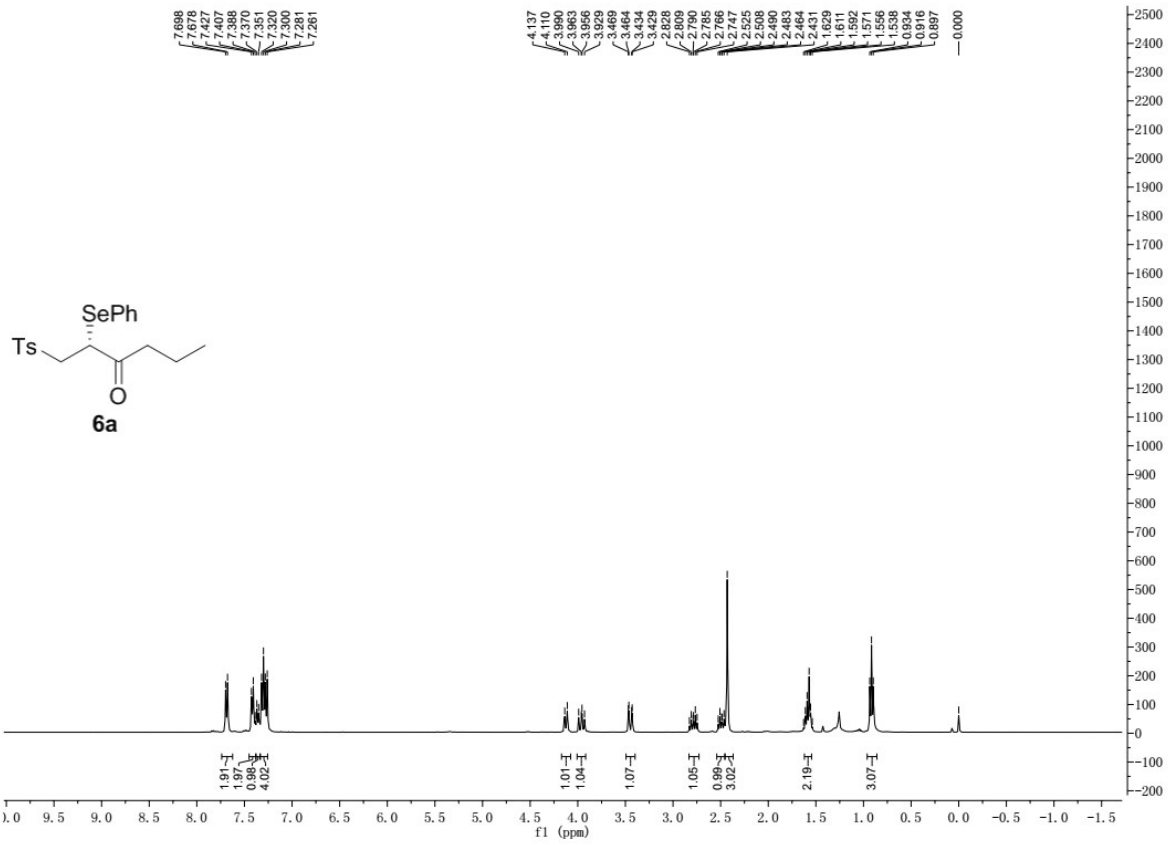
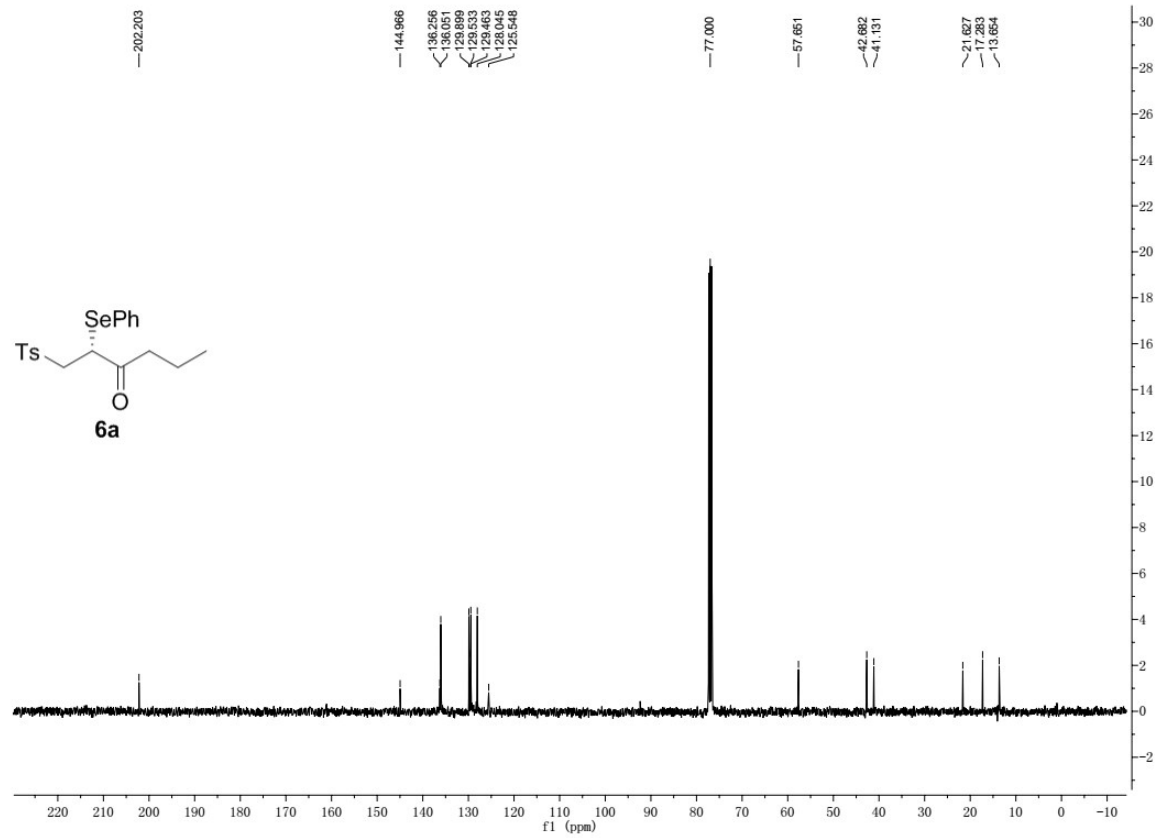
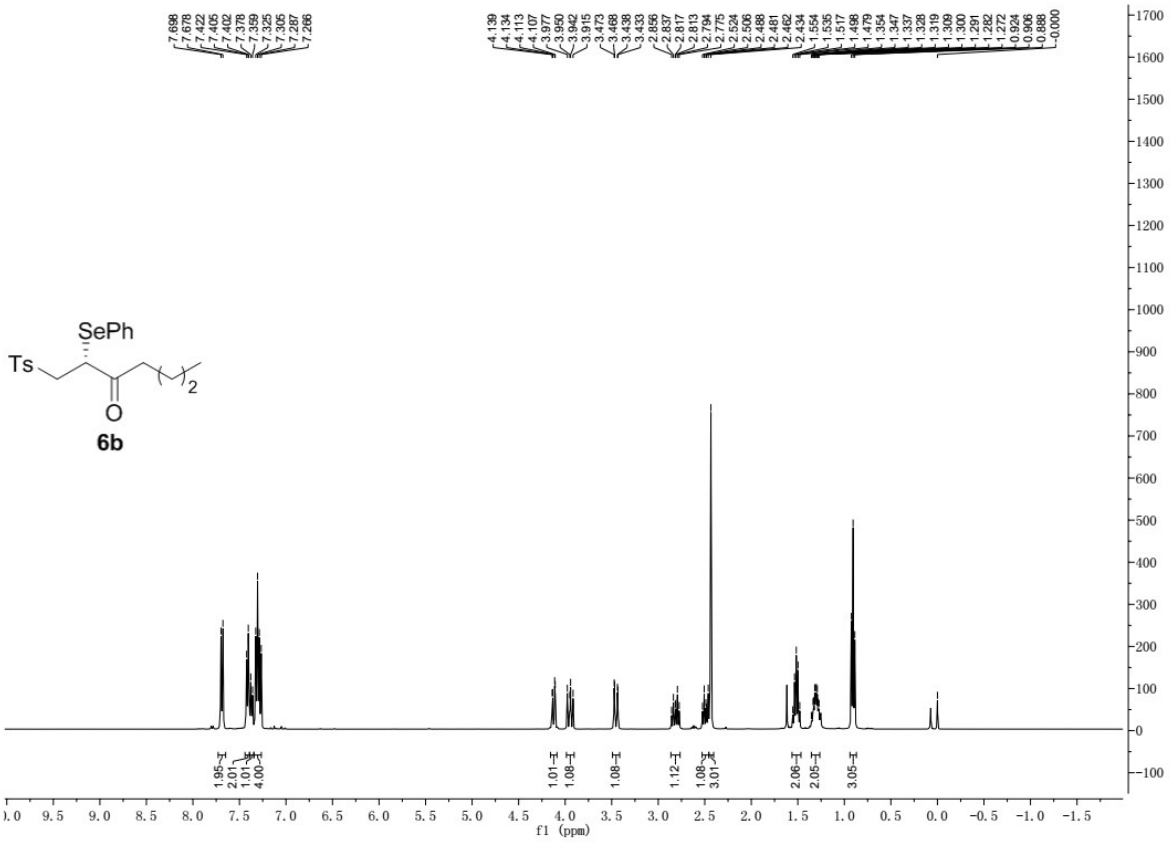
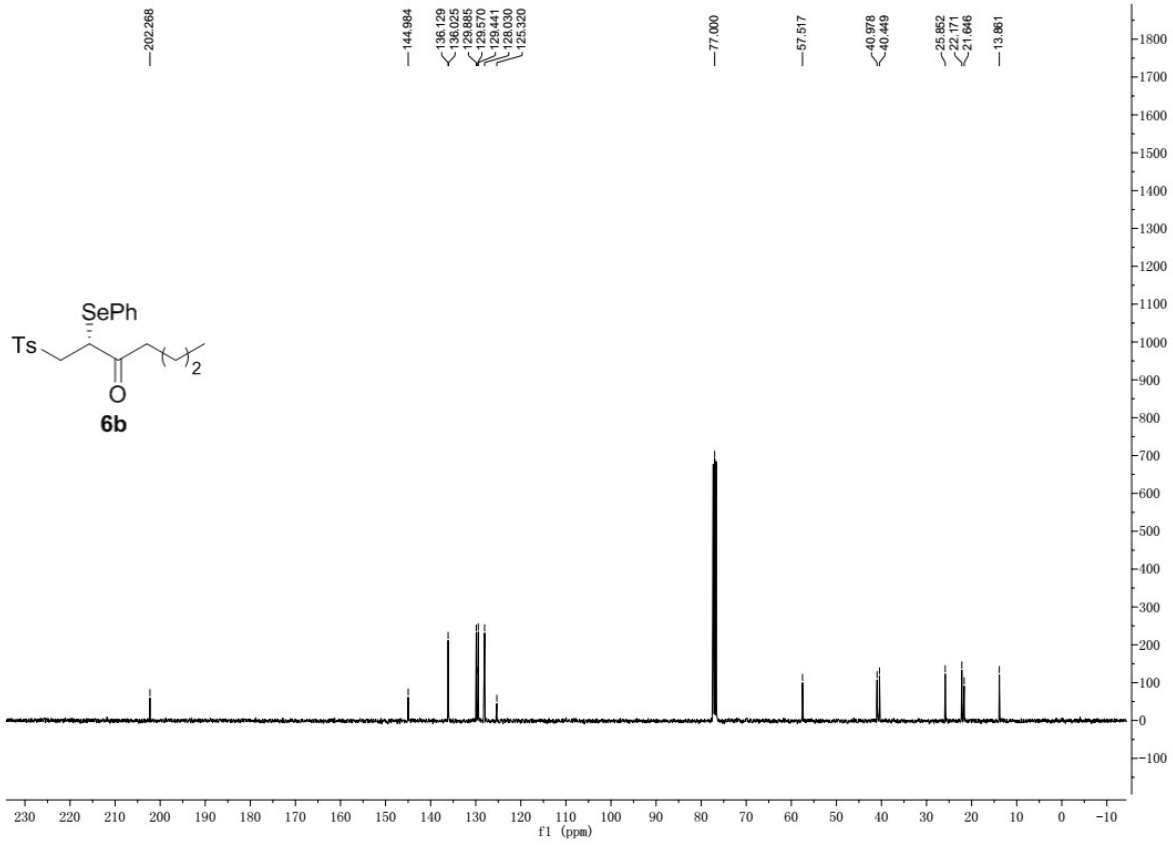
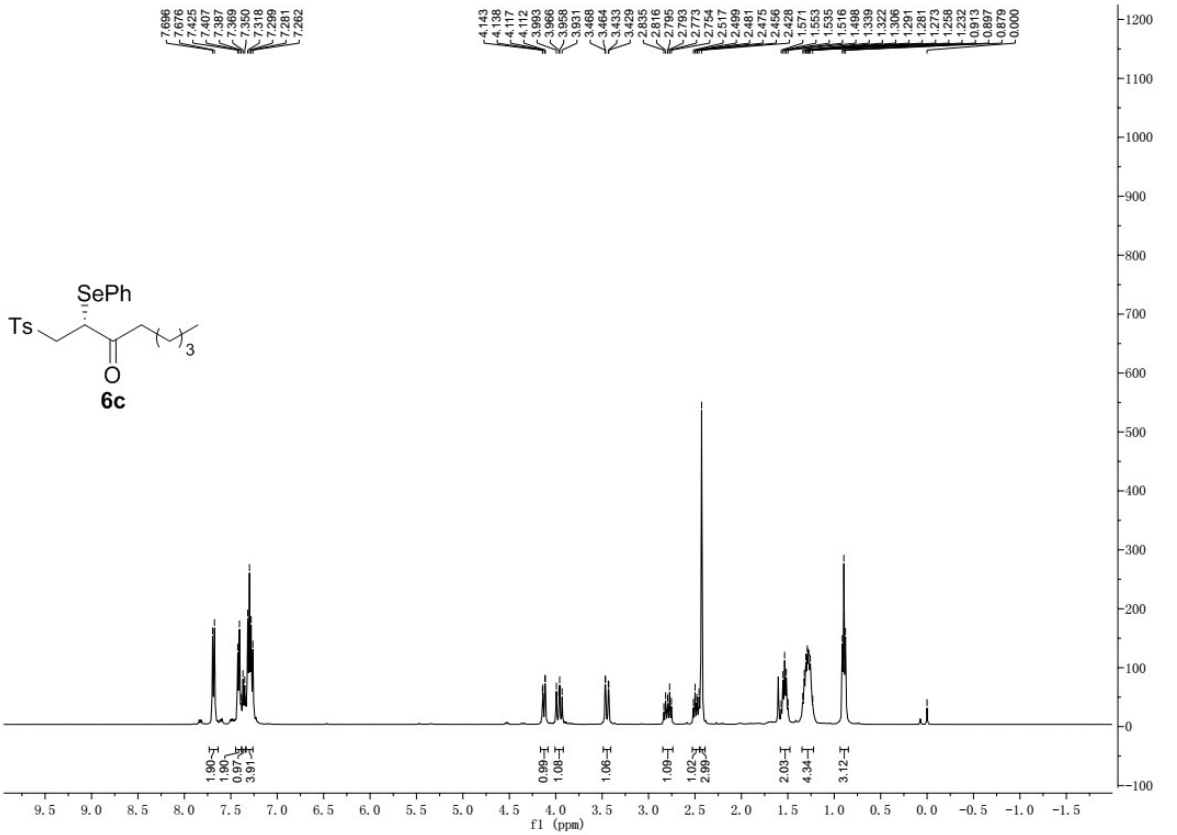
77.000
57.295
36.494
21.492
SePh
O
O
O
O
S
4p
f1 (ppm)

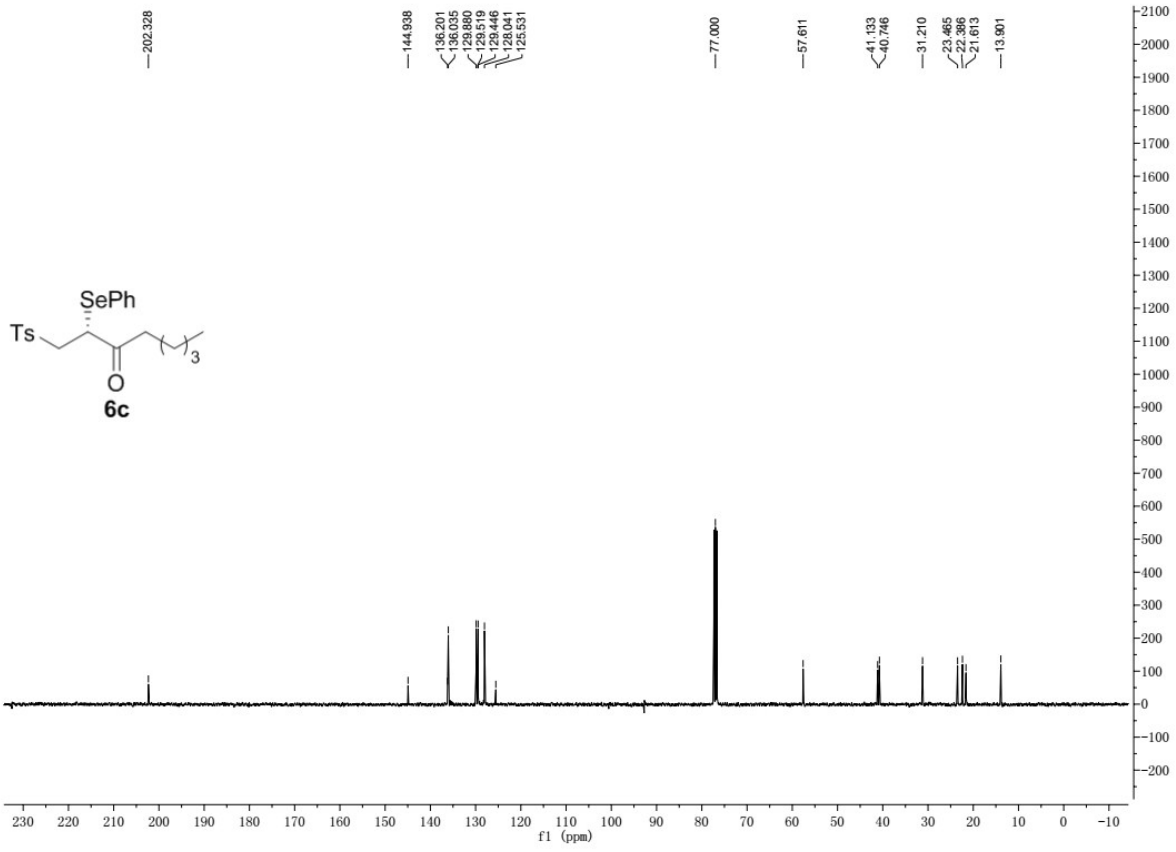

SePh
Ts
O
6a
f1 (ppm)

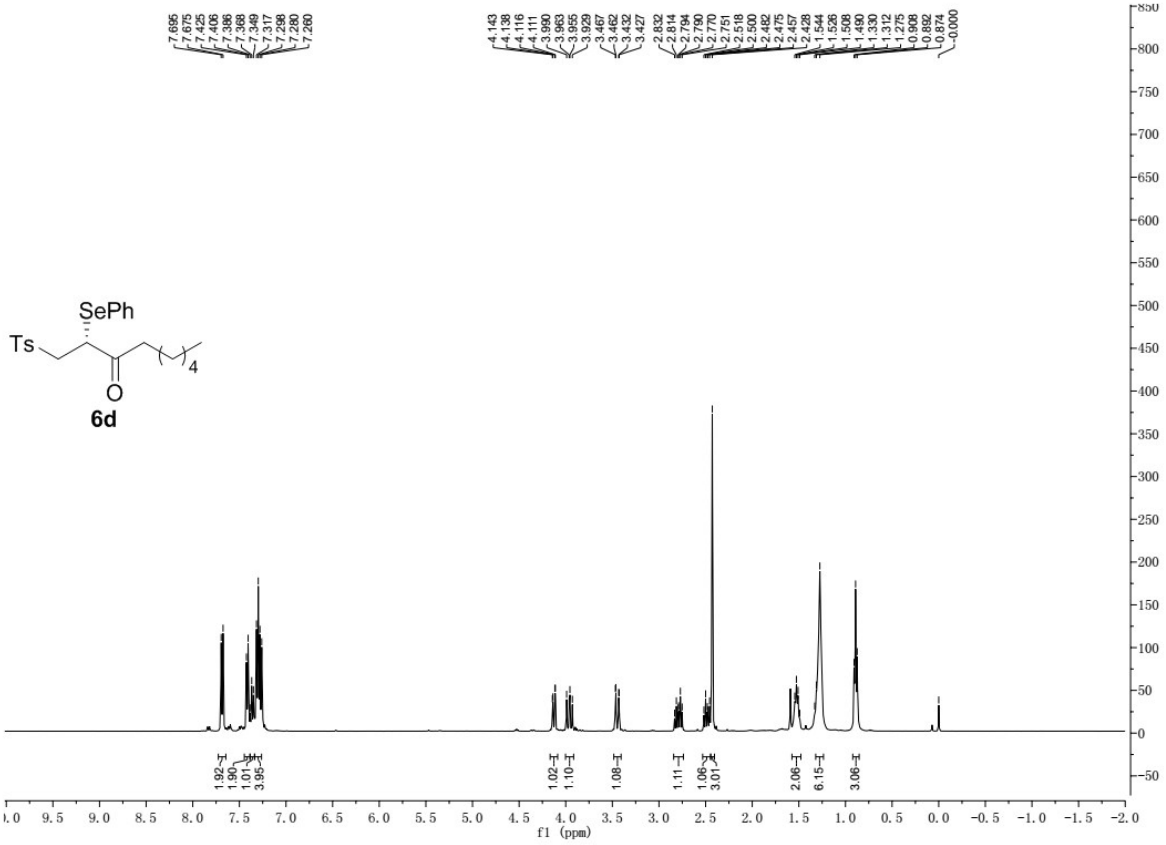

SePh
Ts
O
6a
f1 (ppm)

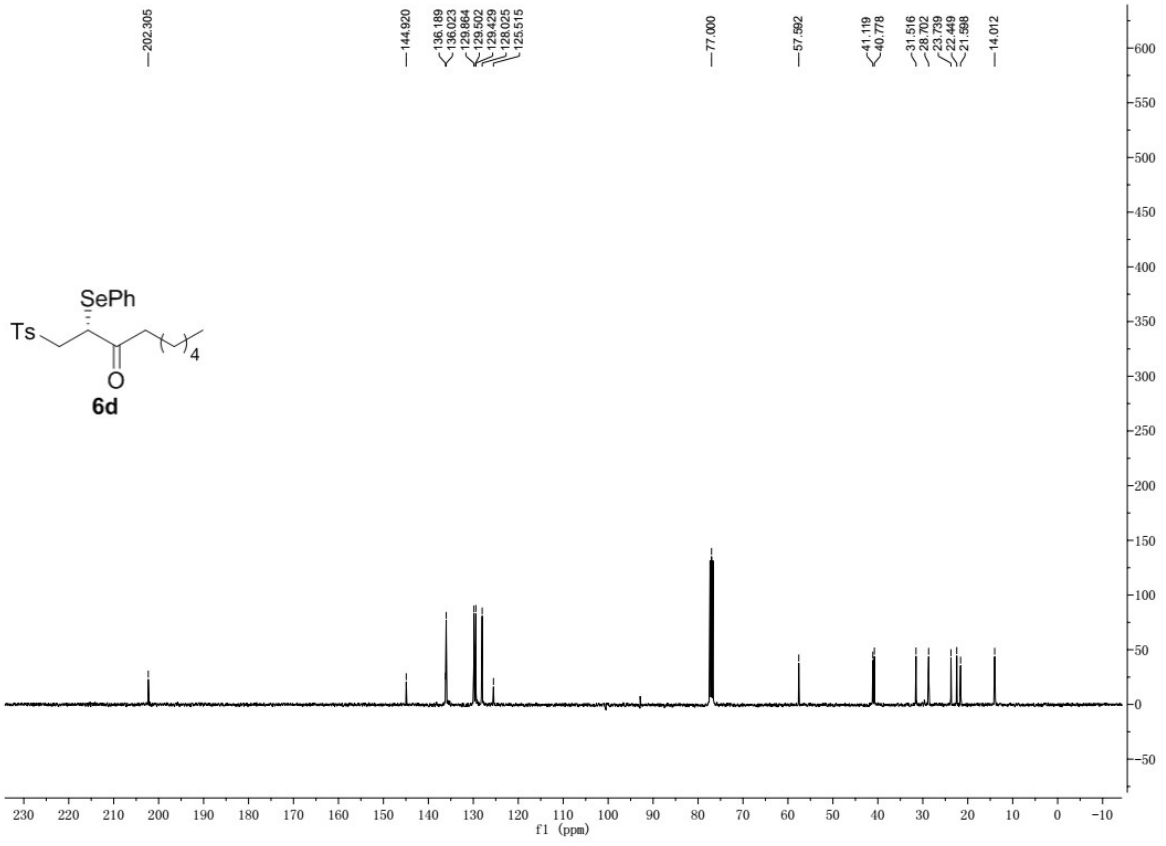

SePh
Ts
O
6b
f1 (ppm)

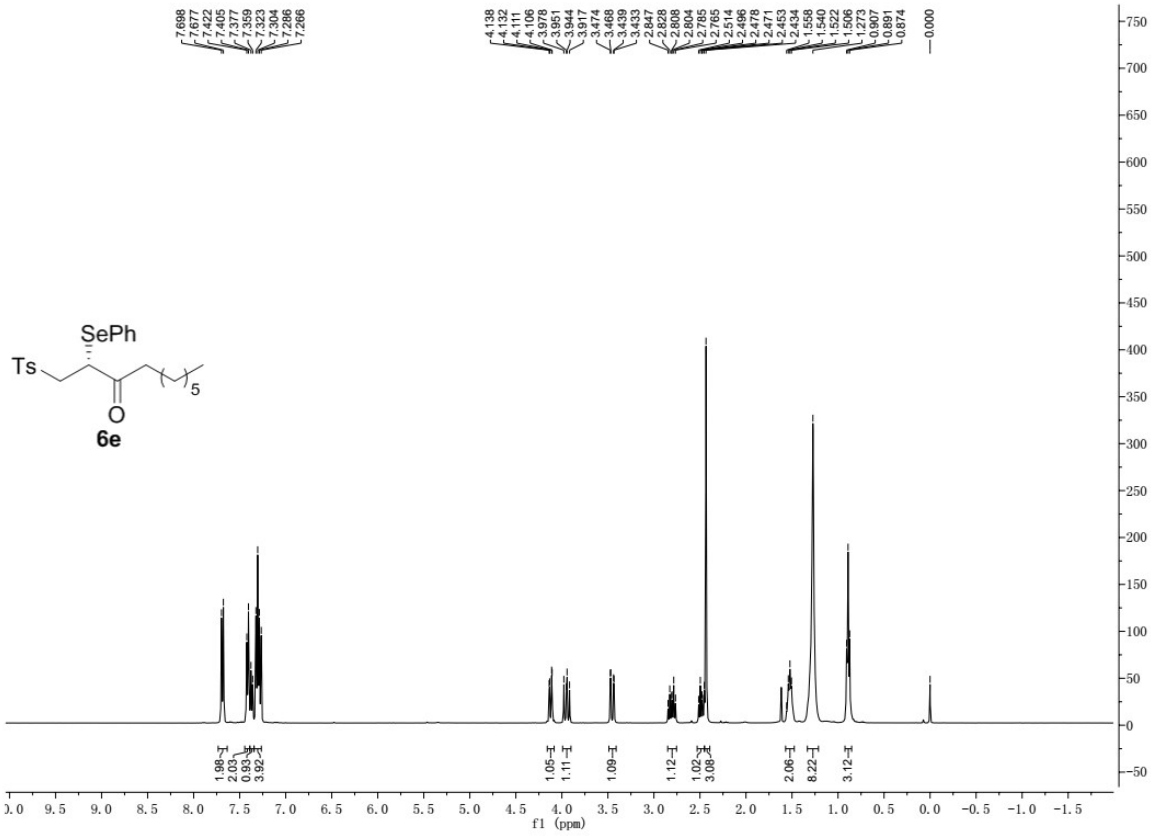

SePh
Ts
O
6b
f1 (ppm)


SePh
Ts
3
O
6c
f1 (ppm)


SePh
Ts
3
O
6c
f1 (ppm)


SePh
Ts
O
4
6d
f1 (ppm)


SePh
Ts
O
4
6d
f1 (ppm)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7.405
7.377
7.359
7.323
7.304
7.286
7.266
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4.132
4.111
4.106
3.978
3.951
3.944
3.917
3.474
3.468
3.439
3.433
2.847
2.828
2.808
2.804
2.785
2.765
2.514
2.496
2.478
2.471
2.453
2.434
1.558
1.540
1.522
1.506
1.273
0.907
0.891
0.874
0.000
SePh
Ts
O
5
6e
1.98
2.03
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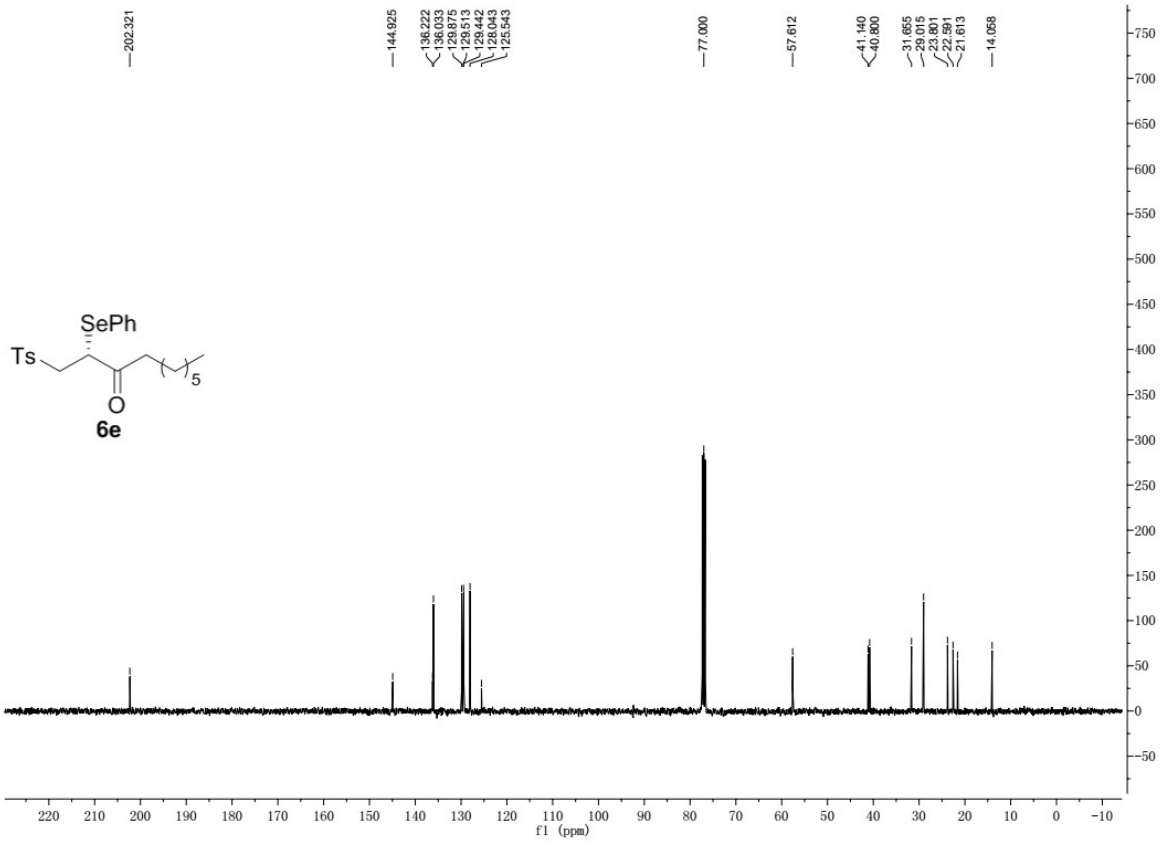
3.92
1.05
1.11
1.09
1.12
1.02
3.08
2.06
8.22
3.12
f1 (ppm)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129.513
129.442
128.043
125.543
77.000
57.612
41.140
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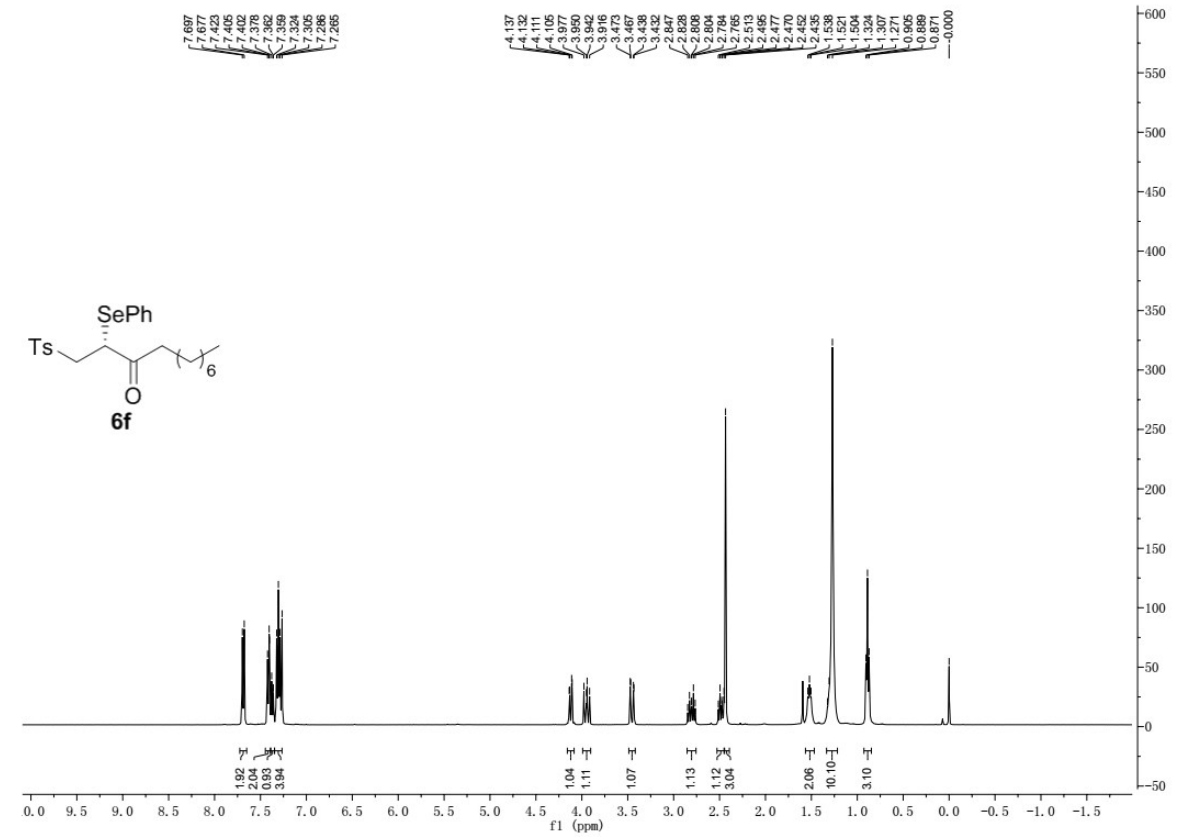
29.015
23.801
22.991
21.613
14.058
SePh
Ts
O
5
6e
f1 (ppm)


7.697
7.677
7.423
7.405
7.402
7.378
7.362
7.359
7.324
7.305
7.286
7.265
4.137
4.132
4.111
4.105
3.977
3.950
3.942
3.916
3.473
3.467
3.438
3.432
2.847
2.828
2.808
2.804
2.784
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2.513
2.496
2.477
2.470
2.452
2.435
1.538
1.521
1.504
1.324
1.307
1.271
0.905
0.889
0.871
-0.000
SePh
Ts
6
O
6f
1.92
2.04
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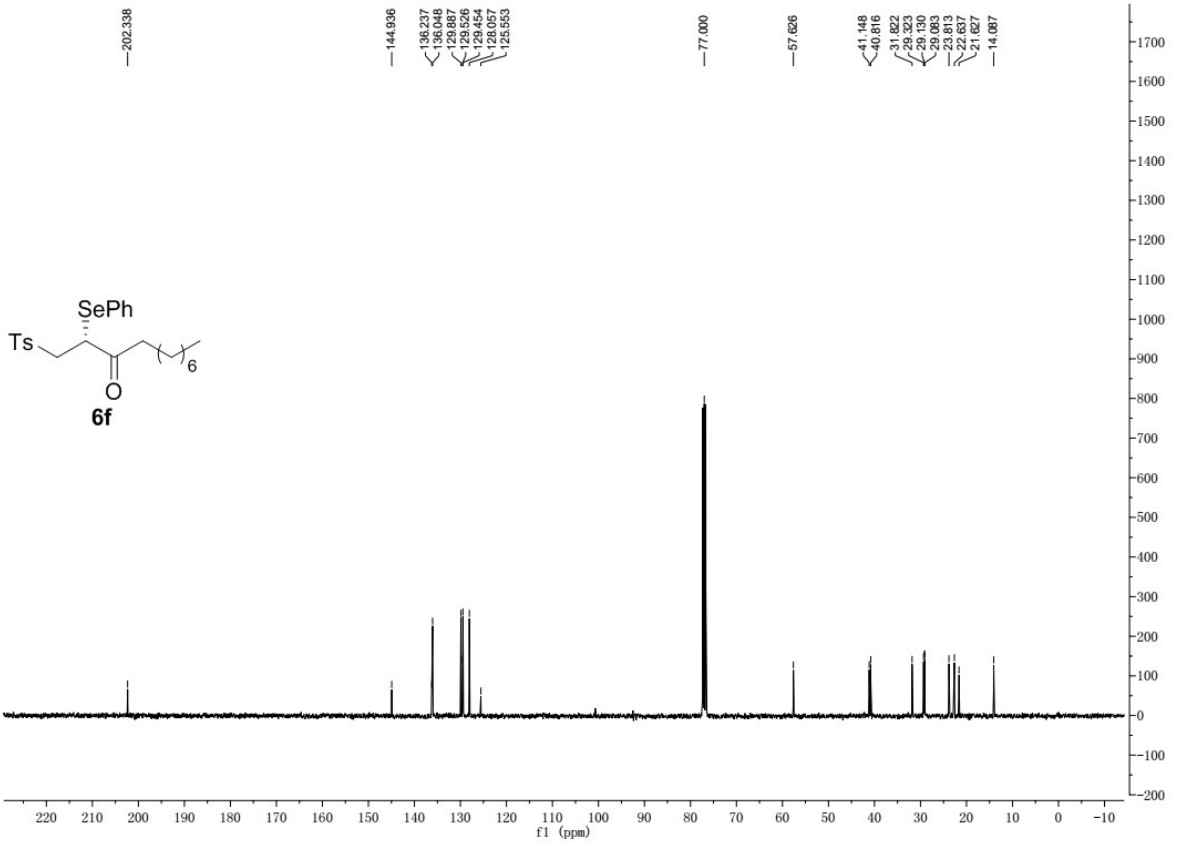
1.11
1.07
1.13
1.12
3.04
2.06
10.10
3.10
f1 (ppm)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128.057
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41.148
40.816
31.822
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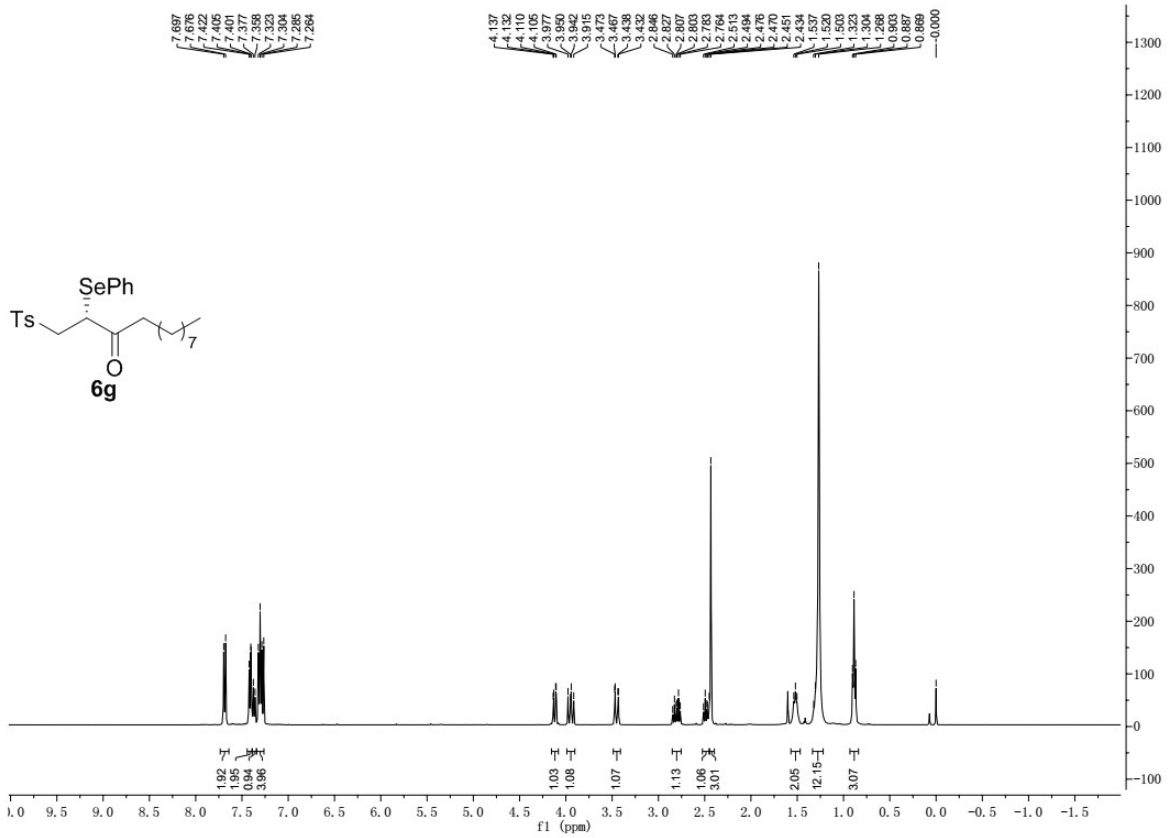
29.083
23.813
22.637
21.627
14.087
SePh
Ts
6
O
6f
f1 (ppm)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7.304
7.285
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4.110
4.105
3.977
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3.942
3.915
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3.432
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2.827
2.807
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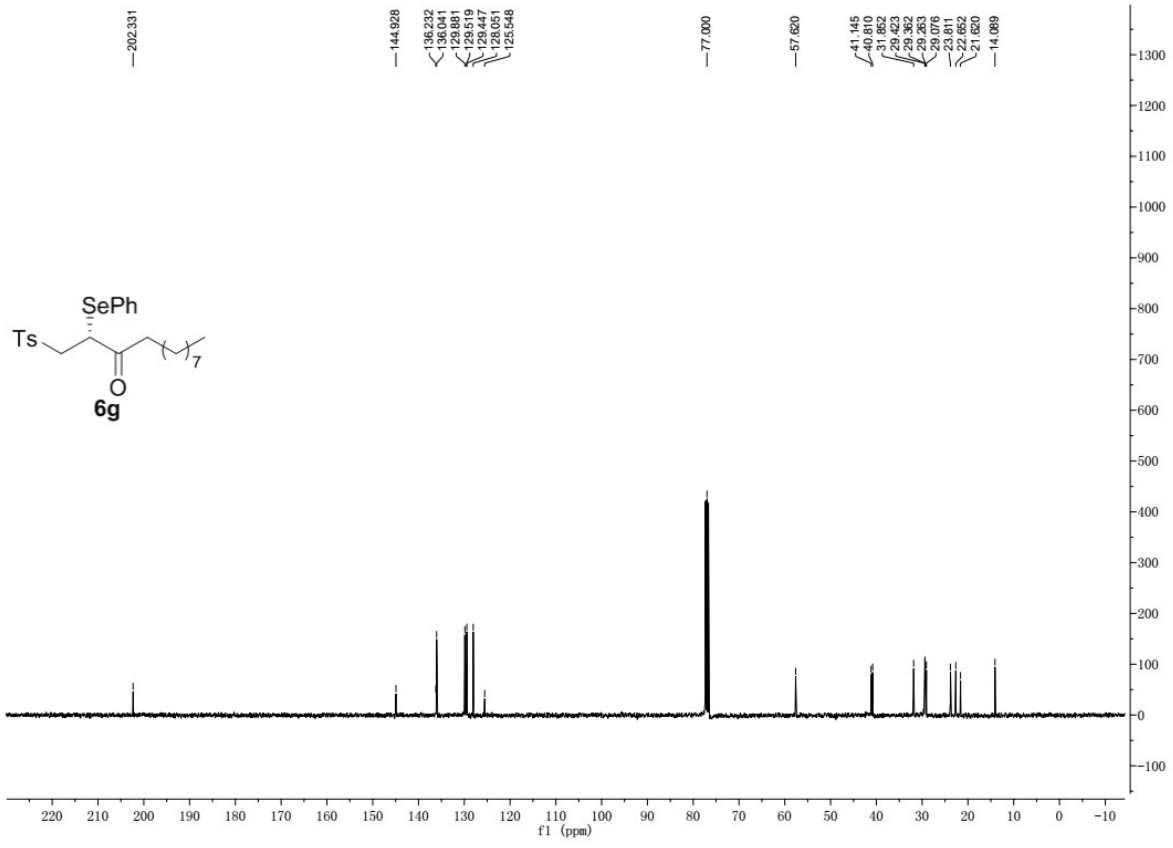
2.513
2.494
2.476
2.470
2.451
2.434
1.537
1.520
1.503
1.323
1.304
1.268
0.903
0.887
0.869
0.000
SePh
Ts
O
6g
1.92
1.95
0.94
3.96
1.03
1.08
1.07
1.13
1.06
3.01
2.05
12.15
3.07
f1 (ppm)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136.041
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129.447
128.051
125.548
77.000
57.620
41.145
40.810
31.852
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29.362
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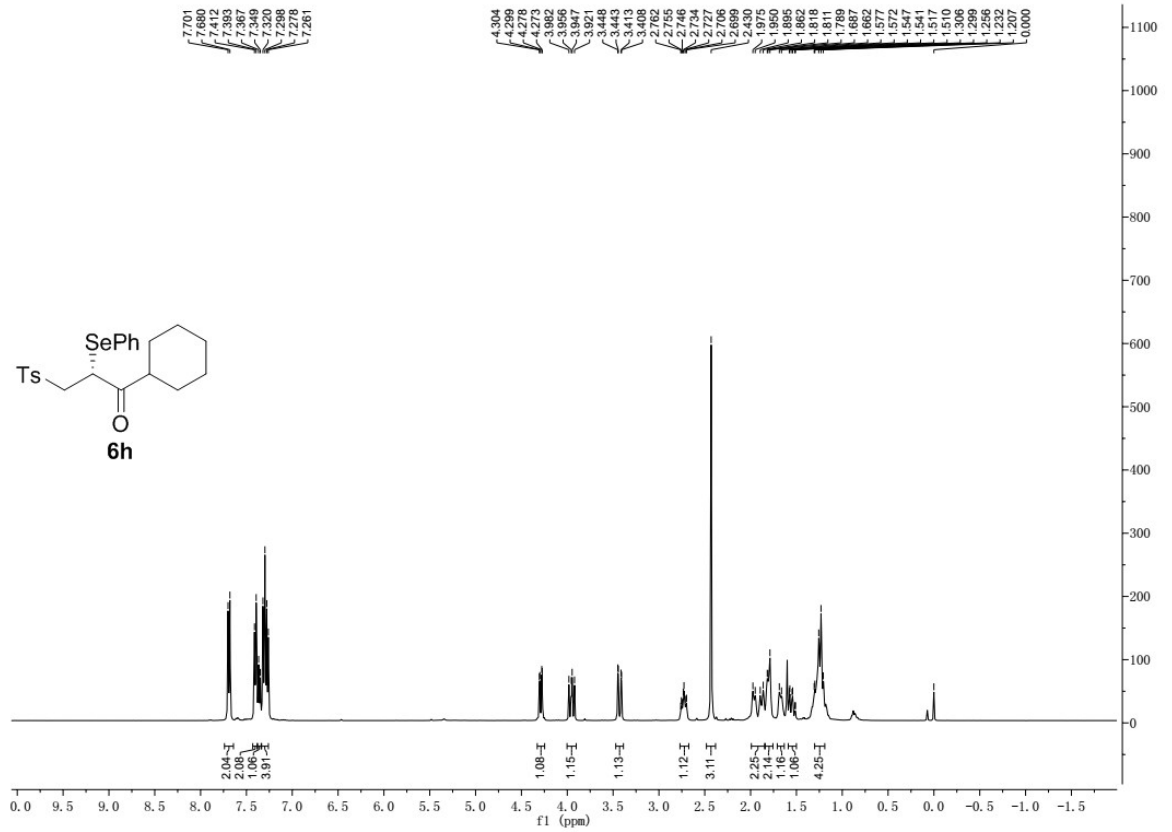
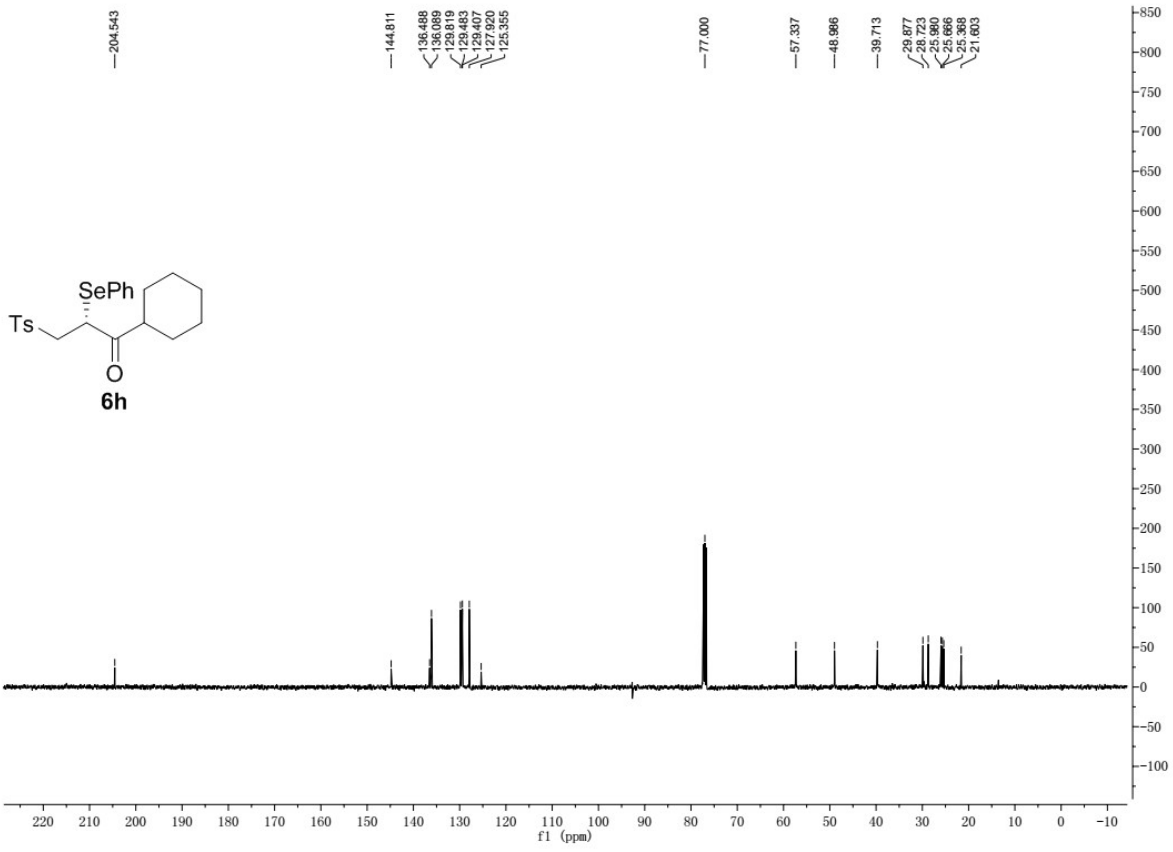
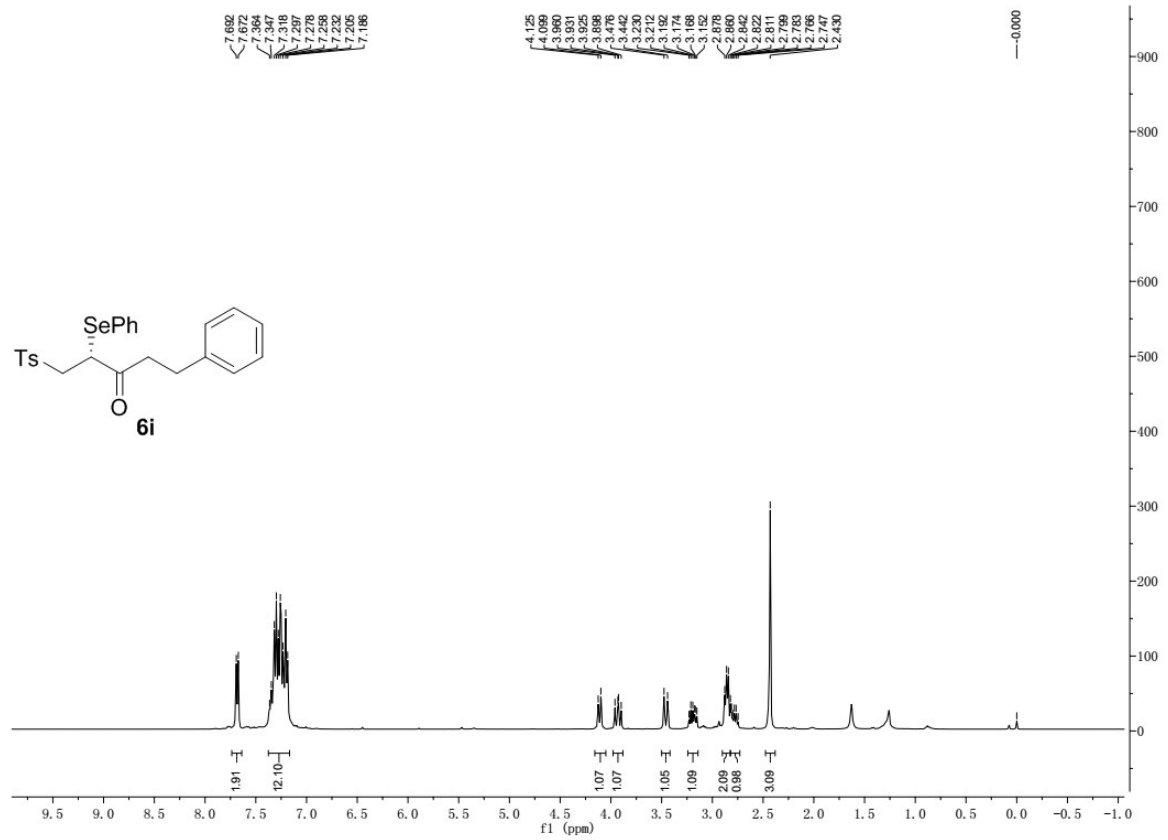
29.076
23.811
22.652
21.620
14.089
SePh
Ts
O
6g
f1 (ppm)


SePh
Ts
O
6h
f1 (ppm)


SePh
Ts
O
6h
f1 (ppm)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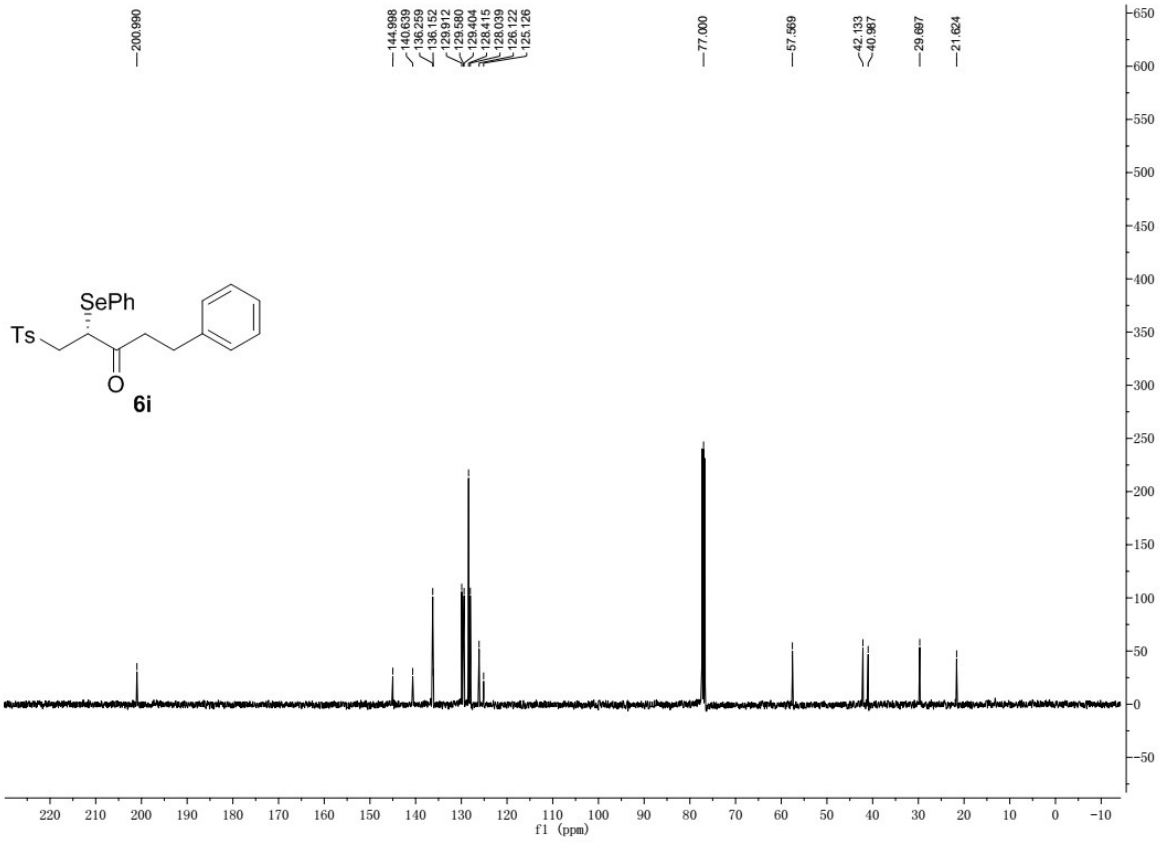
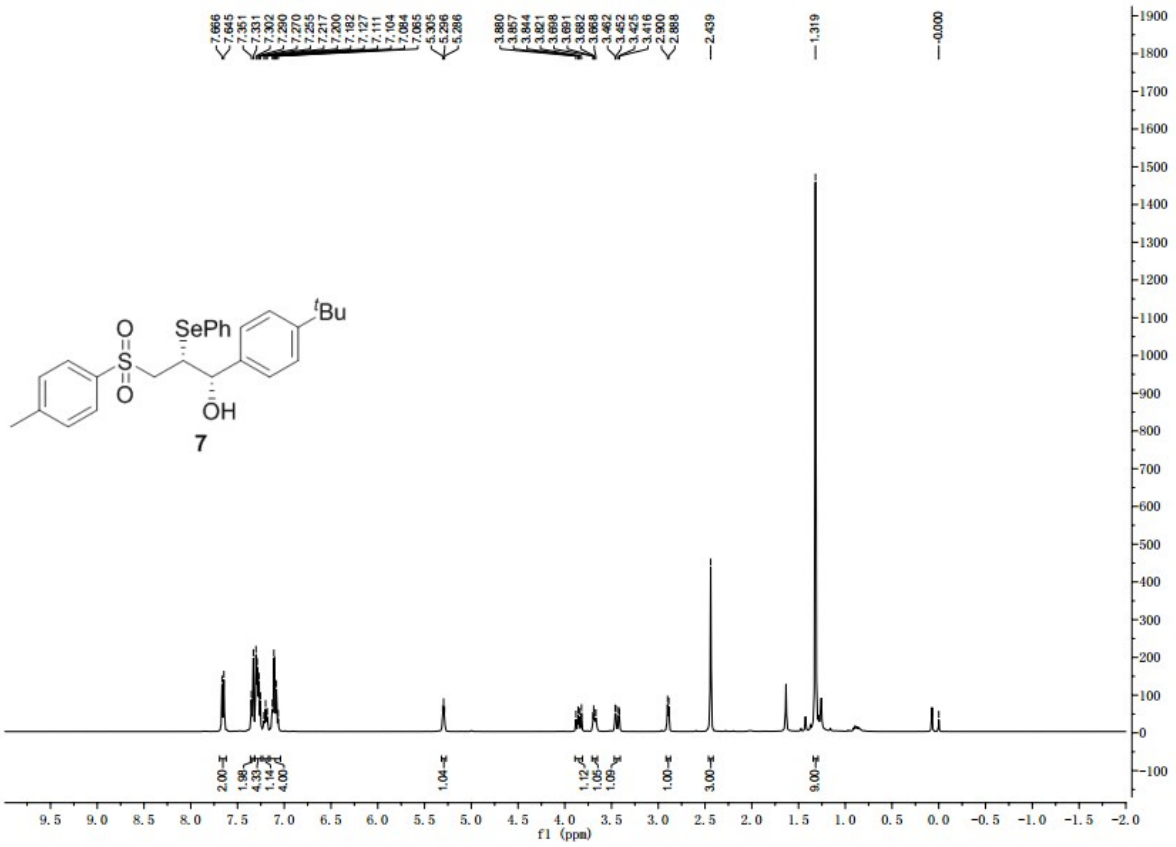
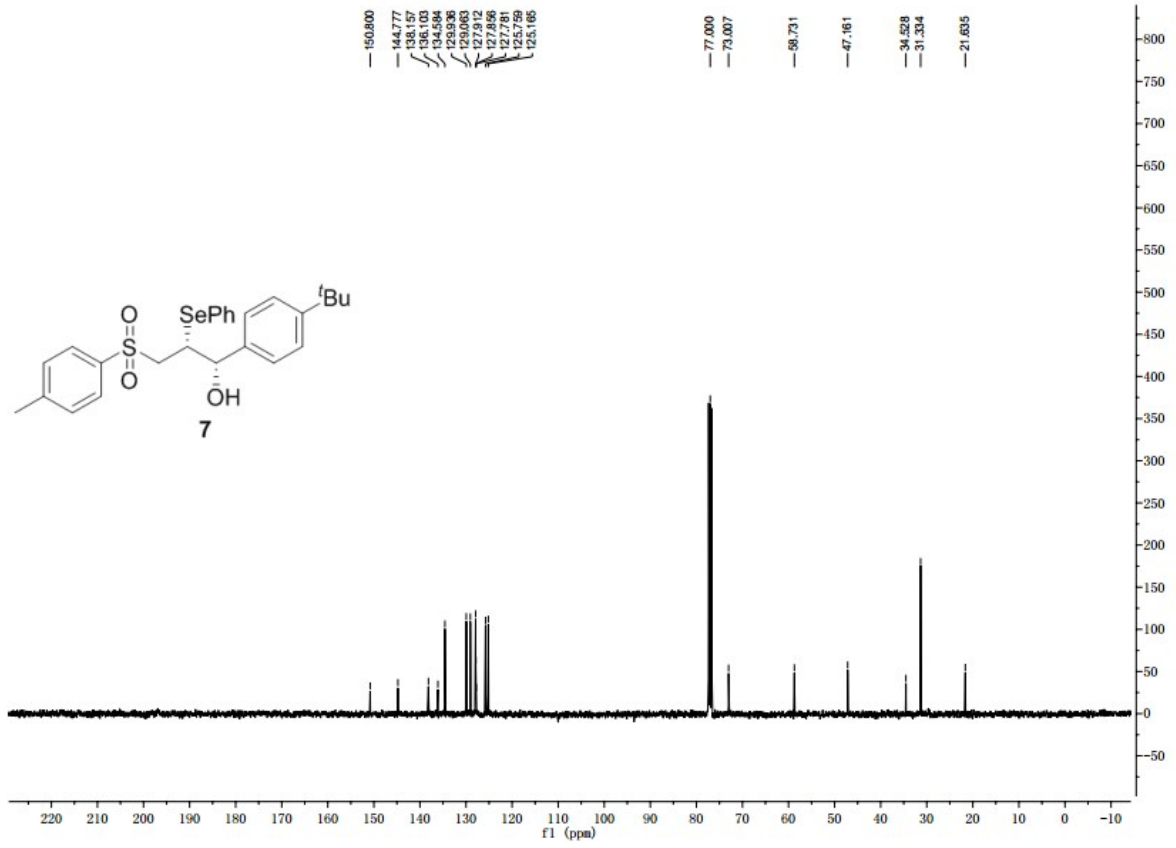
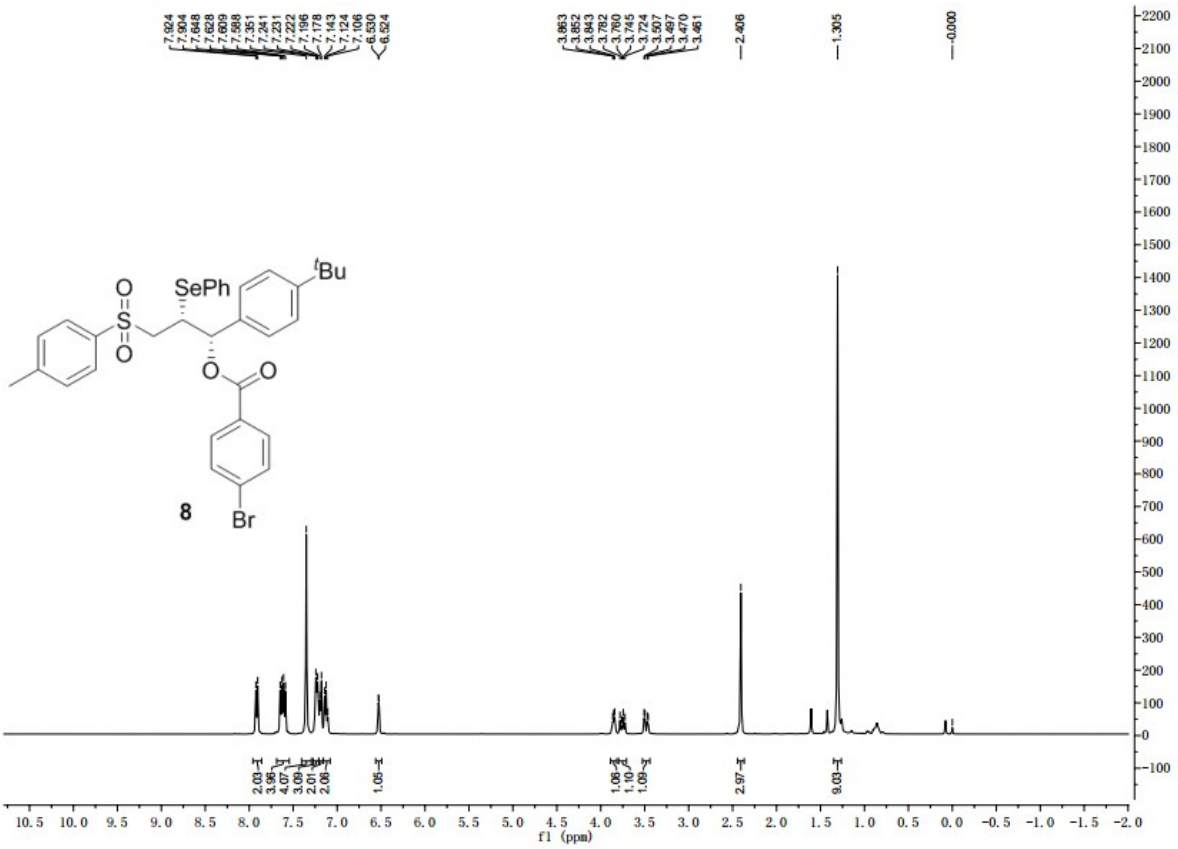
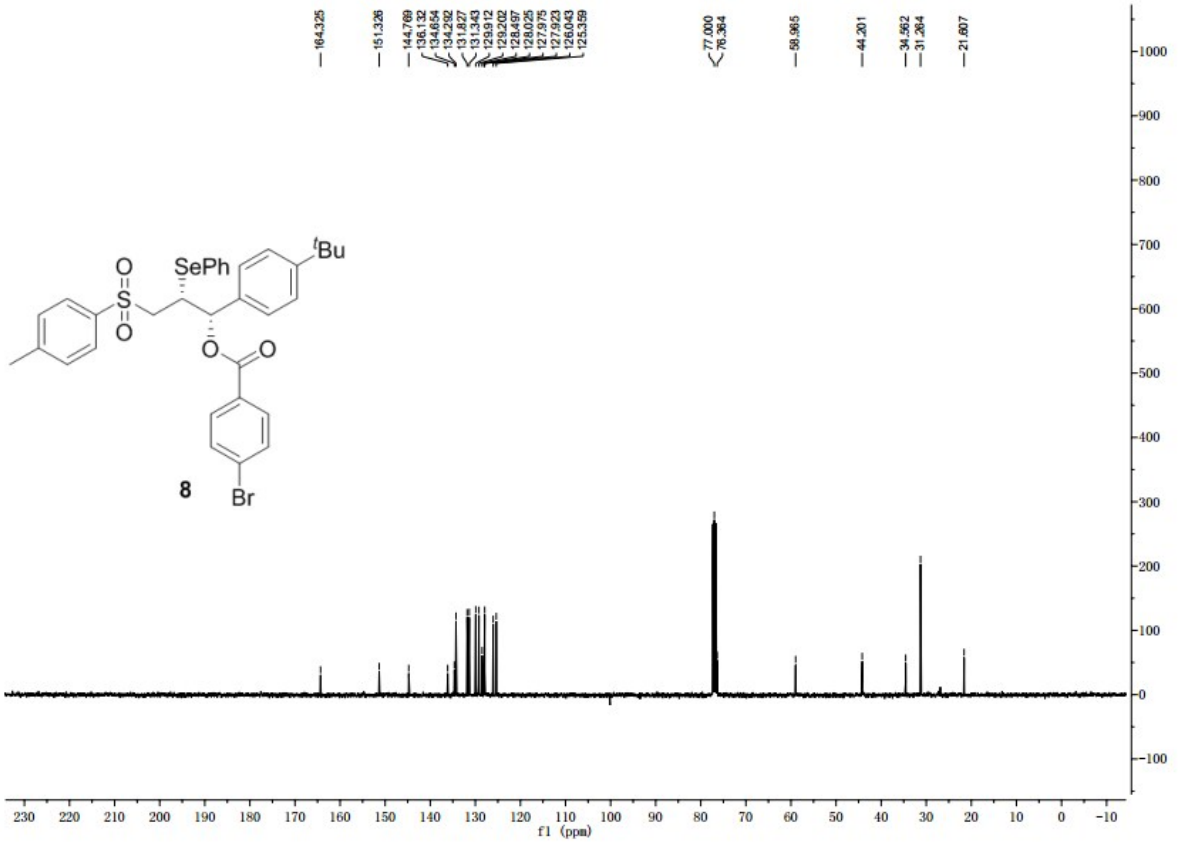
7.258
7.232
7.205
7.186
4.125
4.089
3.960
3.921
3.898
3.476
3.442
3.230
3.212
3.192
3.174
3.168
3.152
2.878
2.860
2.842
2.822
2.811
2.799
2.783
2.766
2.747
2.430
0.000
SePh
Ts
O
6i
1.91
12.10
1.07
1.07
1.05
1.09
2.09
0.98
3.09
f1 (ppm)

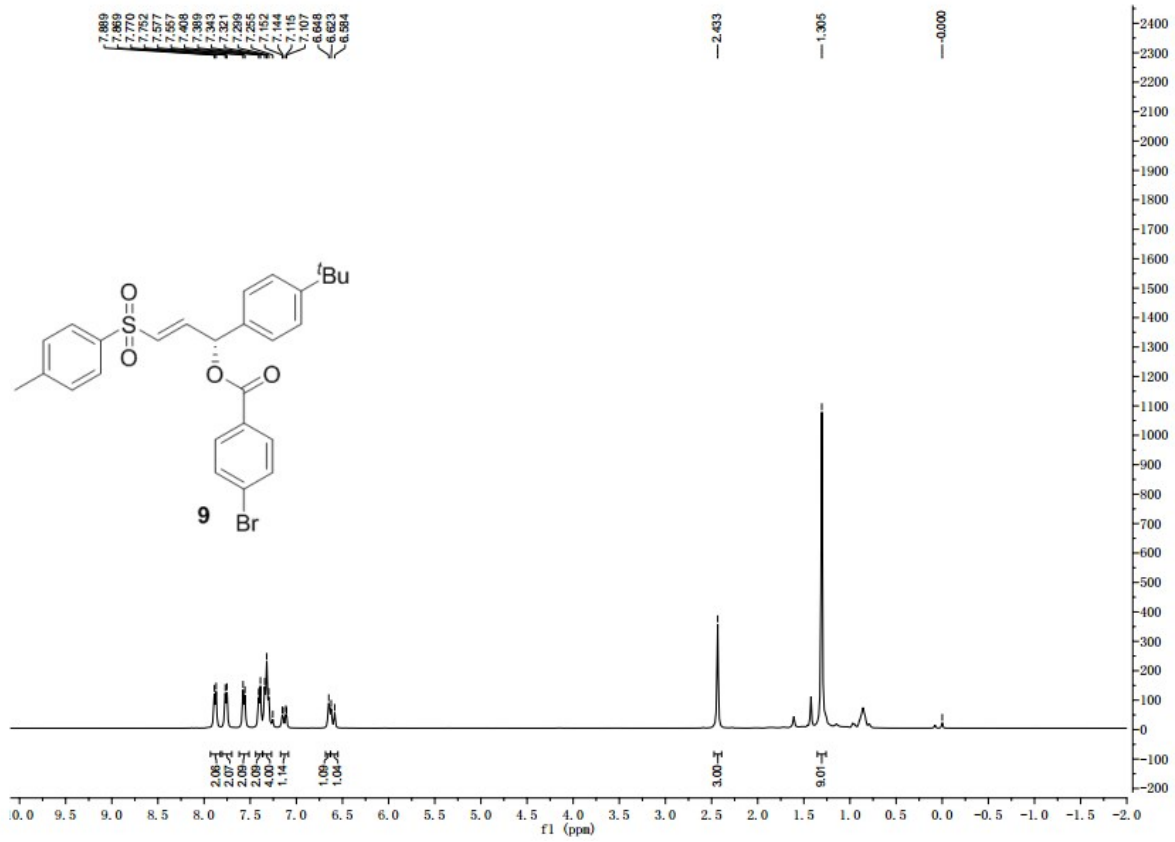

200.990
144.998
140.639
136.259
136.152
129.912
129.580
129.404
128.415
128.039
126.122
125.126
77.000
57.569
42.133
40.987
29.697
21.624
SePh
Ts
O
6i
f1 (ppm)

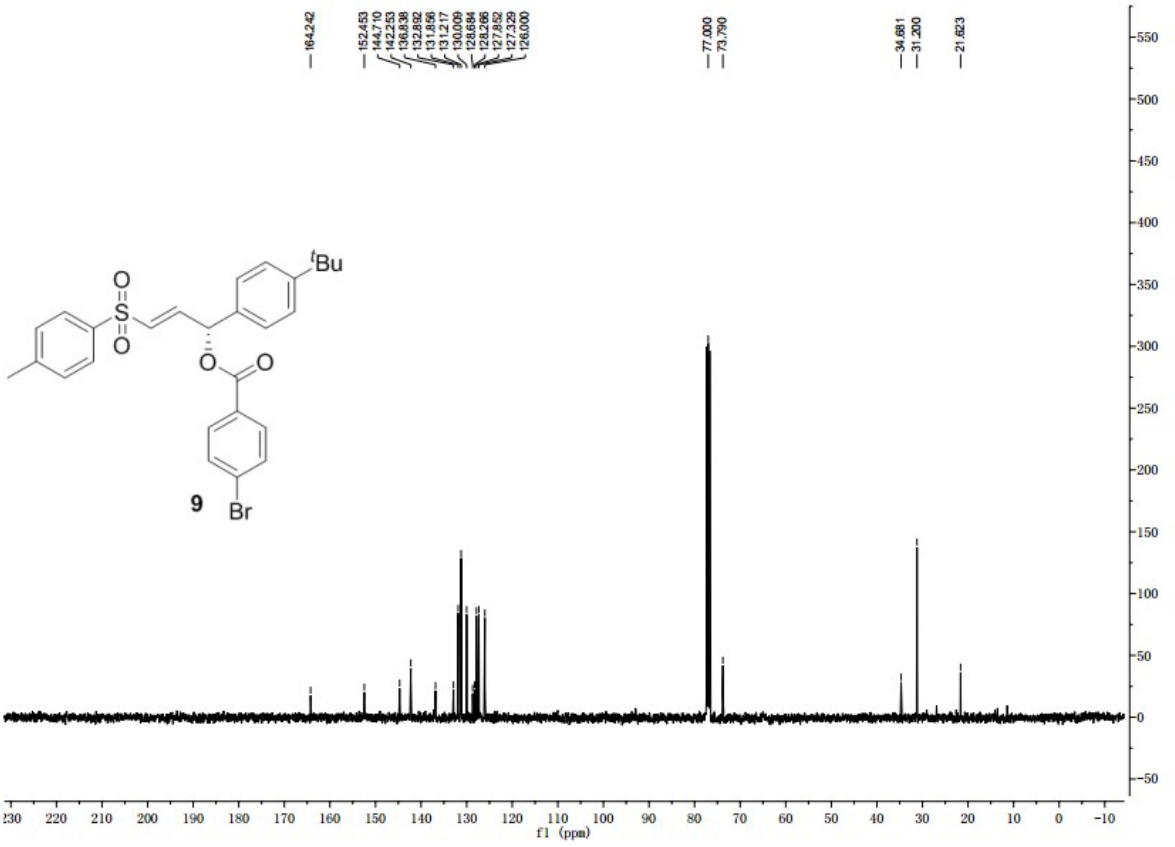

7.666
7.645
7.351
7.331
7.302
7.290
7.270
7.255
7.217
7.200
7.182
7.127
7.111
7.094
7.084
7.065
5.305
5.296
5.286
3.880
3.857
3.844
3.821
3.698
3.691
3.682
3.668
3.462
3.452
3.425
3.416
2.900
2.888
2.439
1.319
0.000
SePh
tBu
O
S
O
OH
7
f1 (ppm)


150.800
144.777
138.157
136.103
134.584
129.936
129.063
127.912
127.856
127.781
125.759
125.165
77.000
73.007
58.731
47.161
34.528
31.334
21.635
SePh
tBu
O
S
O
OH
7
f1 (ppm)

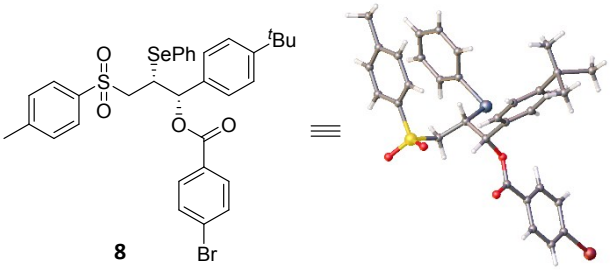

7.924
7.904
7.648
7.628
7.609
7.588
7.351
7.241
7.231
7.222
7.196
7.178
7.143
7.124
7.106
6.530
6.524
3.863
3.852
3.843
3.782
3.760
3.745
3.724
3.507
3.497
3.470
3.461
2.406
1.305
0.000
SePh
tBu
O
S
O
O
O
8
Br
2.03
3.95
4.07
3.09
2.01
2.06
1.05
1.08
1.10
1.09
2.97
9.03
f1 (ppm)


164.325
151.326
144.769
136.132
134.654
134.292
131.827
131.343
129.912
129.202
128.497
128.023
127.975
127.873
126.043
125.359
77.000
76.364
58.965
44.201
34.562
31.264
21.607
SePh
tBu
O
S
O
O
O
8
Br
f1 (ppm)


7.889
7.869
7.770
7.752
7.577
7.557
7.408
7.389
7.343
7.321
7.259
7.255
7.152
7.144
7.115
7.107
6.648
6.623
6.584
2.433
1.305
0.000
tBu
O
S
O
O
O
O
9
Br
2.08
2.07
2.09
2.09
4.00
1.14
1.09
1.04
3.00
9.01
f1 (ppm)


164.242
152.453
144.710
142.253
136.838
132.892
131.856
131.217
130.009
128.684
128.266
127.852
127.329
126.000
77.000
73.790
34.681
31.200
21.623
tBu
O
S
O
O
O
O
9
Br
f1 (ppm)

XI. X-Ray Crystallographic Information (8)



8

Bond precision:	C-C = 0.0246 A		Wavelength=0.71073
Cell:	a=7.9327(4)	b=18.8397(9)	c=22.3499(16)
	alpha=90	beta=100.199(5)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	3287.4(3)	3287.4(3)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C33 H33 Br O4 S Se	C33 H33 Br O4 S Se	
Sum formula	C33 H33 Br O4 S Se	C33 H33 Br O4 S Se	
Mr	684.51	684.52	
Dx,g cm-3	1.383	1.383	
Z	4	4	
Mu (mm-1)	2.454	2.454	
F000	1392.0	1392.0	
F000'	1391.51		
h,k,lmax	9,23,27	9,23,27	
Nref	13419 [6921]	10418	
Tmin,Tmax	0.428,0.541	0.467,1.000	
Tmin'	0.419		

Correction method= # Reported T Limits: Tmin=0.467 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.51/0.78	Theta(max)= 26.371
R(reflections)= 0.0676(6712)	wR2(reflections)= 0.1658(10418)
S = 1.054	Npar= 699

The Flack parameter is 0.046(6) for **8**, CCDC 1820345 contain the supplementary crystallographic data of adducts for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Explaination of B errors: the thermal vibration due to the structure disorder of the *tert*-butyl groups is violent that include the rotation around the C-C bonds and the stretching from the center carbon atoms. If we use splitting treatment on the *tert*-butyl groups, the whole system could not converge to near zero because the hydrogen atoms on the tert-butyl carbon could not be fixed on their positions. So we have to adopt a EADP treatment on the *tert*-butyl carbon atoms to restrain the linked hydrogen atoms, which inevitably leads to some B errors when the checking cif file.