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Supporting Information

Metal-free Difunctionalization of Alkynes to Access Tetrasubstituted Olefins through Spontaneous Selenosulfonylation of Vinylidene *ortho*-Quinone Methide (VQM)

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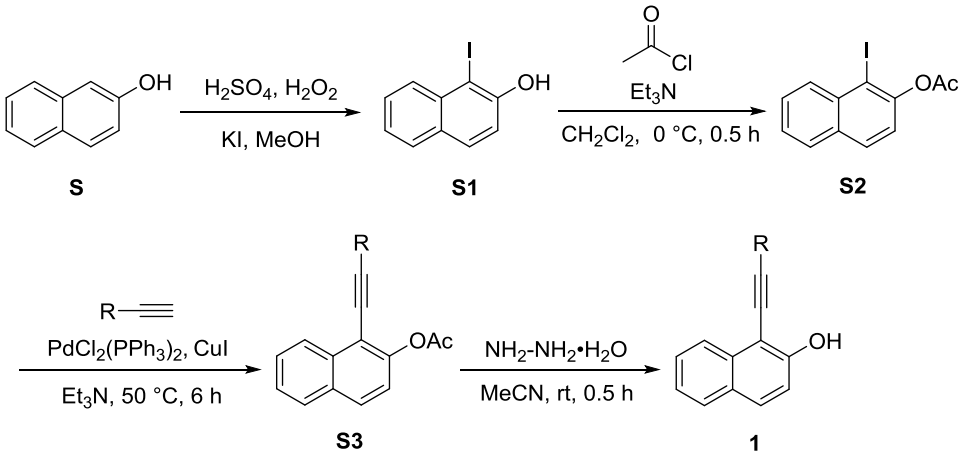
I. General information

^{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: $CDCl_3$ (^{1}H NMR δ 0.00, ^{13}C NMR 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. High resolution mass spectra (HRMS) were performed on Bruker Solarix 7.0T. X-ray crystallography analysis of single crystal was performed on an Agilent SuperNova-CCD X-Ray diffractometer. Melting points were measured using SGWX-4A Microscopic melting point meter and are uncorrected. Enantiomeric excesses (ee) were determined by HPLC analysis on Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6 mm Φ × 250 mmL. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

II. General procedure for the synthesis of *o*-alkynylnaphthols

The preparation of *o*-alkynylnaphthols were followed the literature procedure.[1, 2]

Method A: (**1a, 1b, 1c, 1e, 1f, 1p, 1q, 1r, 1s**)



Sulfuric acid (208.0 mmol) was added to a solution of 2-naphthol **S** (20.0 g, 138.8 mmol) and potassium iodide (23.04 g, 138.8 mmol) in methanol (400 mL) at 0 ^{o}C. A precipitate formed, and hydrogen peroxide (30% aqueous solution, 277.6 mmol) was added. After 1.5 h of warming slowly to room temperature, the mixture was filtered, and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2 (300 mL), washed with 25% sat.aq. $Na_2S_2O_3$ (250 mL) and water (200 mL), dried over Na_2SO_4, and concentrated to provide a solid (26.32 g). This material was purified by column chromatography on silica gel (PE:EA = 20:1) to provide an orange solid **S1** (34.0 g, 91%).

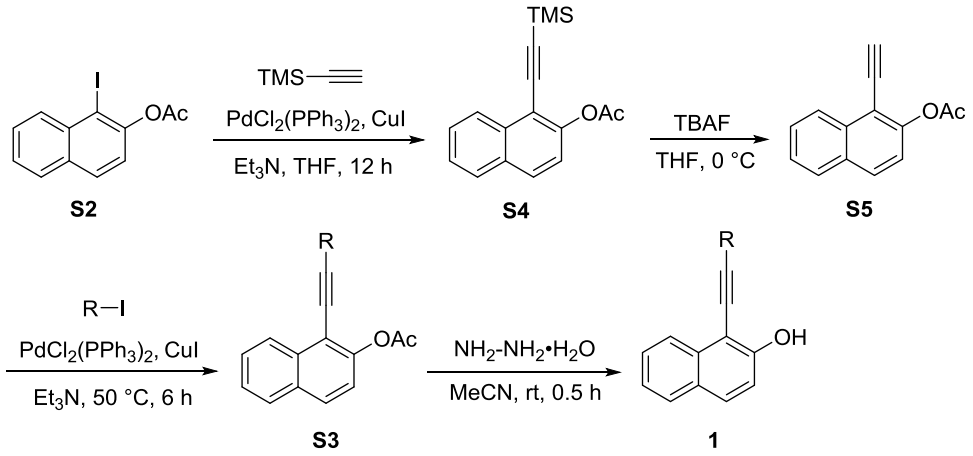
Acetyl chloride (1.5 equiv.) was dropwise added to a solution of **S1** (21.8 g, 80.7 mmol) and Et_3N (22.4 mL, 161.4 mmol) in CH_2Cl_2 (200 mL) at 0 ℃ under N_2. The reaction mixture was

stirred at 0 ℃ for 30 min and then quenched with sat. aq. NH_4Cl followed by extraction with CH_2Cl_2. The organic phase was washed with brine and dried over Na_2SO_4, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel to afford **S2** (23.9 g, 95%).

To a dry flask under N_2 containing **S2** (5 mmol) was sequentially added Et_3N (10 mL), appropriate alkynes (5 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), CuI (47.6 mg, 0.25 mmol). The mixture was stirred for 6 h at 50 °C. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel to afford **S3**.

Hydrazine monohydrate (10 mmol) was dropwise added to a solution of **S3** (2 mmol) in CH_3CN (10 mL). After the resulted mixture was stirred at room temperature for 0.5 h, the mixture was treated with sat. aq. NH_4Cl and extracted with CH_2Cl_2 and dried over Na_2SO_4. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel to afford the compound **1**.

Method B: (**1d, 1g-1o**)



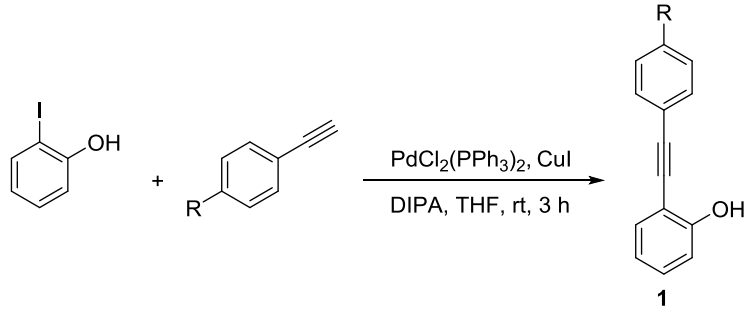
Trimethylsilylacetylene (5.9 mL, 41.7 mmol) was dropwise added to a solution of **S2** (10 g, 32.1 mmol), $PdCl_2(PPh_3)_2$ (1.1 g, 1.6 mmol), CuI (609 mg, 3.2 mmol) and Et_3N (13.4 mL, 96.1 mmol) in THF (50 mL) at room temperature under N_2. Then, the mixture was stirred for 12 h. The reaction mixture was treated with sat. aq. NH_4Cl followed by extraction with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (PE:EA = 30:1) to afford **S4** (7.3 g, 80% yield).

To a solution of **S4** (7.0 g, 24.8 mmol) in THF (75 mL) was added TBAF in THF (1 M, 12.4 mL, 12.4 mmol) dropwise at 0 °C under N_2. Then the mixture was stirred for 1 h. The reaction mixture was treated with sat. aq. NH_4Cl followed by extraction with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (PE:EA = 100:1) to afford **S5** (3.9 g, 75% yield).

To a dry flask under N_2 containing the appropriate iodebenzenes (2.4 mmol) was sequentially added Et_3N (5.0 mL), **S5** (500 mg, 2.4 mmol), $PdCl_2(PPh_3)_2$ (33.7 mg, 0.048 mmol) and CuI (22.9 mg, 0.12 mmol). The mixture was stirred for 6 h at 50 °C. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel to afford **S3**.

Hydrazine monohydrate (10 mmol) was dropwise added to a solution of **S3** (2 mmol) in CH_3CN (10 mL). After the resulted mixture was stirred at room temperature for 0.5 h, the mixture was treated with sat. aq. NH_4Cl and extracted with CH_2Cl_2, and dried over Na_2SO_4. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel afford the compound **1**.

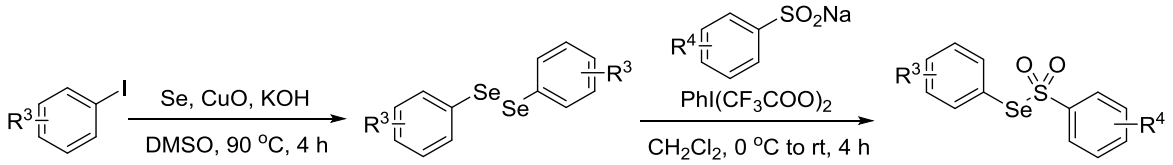
III. General procedure for the synthesis of *o*-alkynylphenols



1

To a dry flask under N_2 containing 2-iodophenol (10.0 mmol) was sequentially added THF (25 mL), diisopropylamine (10.0 mmol), appropriate alkynes (12.0 mmol), $PdCl_2(PPh_3)_2$ (0.3 mmol), CuI (0.9 mmol). The resulting solution was stirred at room temperature for 3 h. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel to afford appropriate *o*-alkynylphenols.

IV. General procedure for the synthesis of selenosulfonates

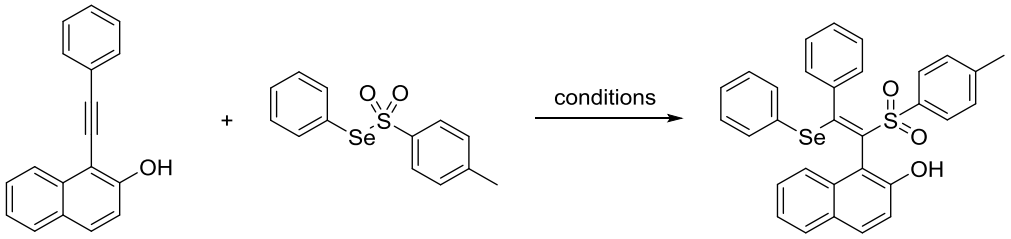


S6 **2**

The preparation of compound **S6** were followed the literature procedure.[3] To a stirred solution of Se^0 metal (10 mmol, 2.0 equiv.) and halides (5 mmol, 1.0 equiv.) in DMSO (10 mL) was added CuO nanoparticles (0.5 mmol, 0.1 equiv.) followed by KOH (10 mmol, 2.0 equiv.) under nitrogen atmosphere. The resulting reaction mixture was stirred at 90 °C for 6 h. After the reaction was complete, the reaction mixture was allowed to cool, extraction with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (PE:EA = 100:1) to afford **S6**.

The preparation of compound **2** were followed the literature procedure.[4] A suspension of appropriate sodium benzenesulfinates (20 mmol, 4.0 equiv.) in CH_2Cl_2 (50 mL) containing **S6** (5 mmol, 1.0 equiv.) was cooled at 0 °C and [bis(trifluoroacetoxy)iodo]benzene (5.5 mmol, 1.1 equiv.) in CH_2Cl_2 (20 mL) was added dropwise. Then the mixture was stirred at room temperature for 3 h. 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 column chromatography on silica gel (PE:EA = 6:1) to afford compound **2**.

V. Optimization of the reaction conditions



1a **2a** **3a**

Table 1. Screening of solvent[a]

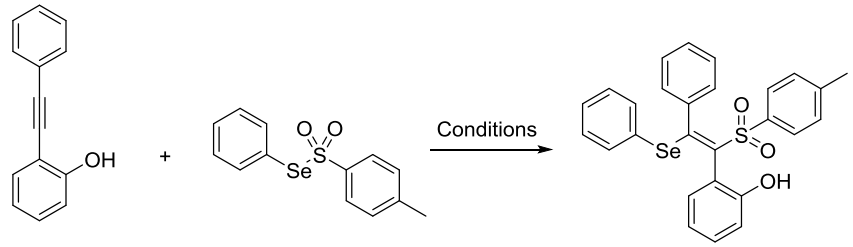
entry	solvent	additive	yield (%)[b]	*E:Z*[c]
1	CH_2Cl_2	-	73	>99:1
2	CH_3OH	-	69	>99:1
3	DCE	-	85	>99:1
4	*m*-xylene	-	60	>99:1
5	toluene	-	63	>99:1
6[d]	toluene	-	64	>99:1
7	CH_3CN	-	54	>99:1
8	$CHCl_3$	-	52	>99:1
9	THF	-	<5	>99:1

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol) in solvent (1.0 mL) at room temperature for 10 h. [b]Yield ratio was determined by column chromatography. [c]Determined by ^{1}H NMR analysis. [d]The reaction were carried out at 80 ℃.

Table 2. Screening of additive[a]

entry	solvent	additive	yield (%)[b]	*E:Z*[c]
1	DCE	Et_3N	67	>99:1
2	DCE	K_2CO_3	69	>99:1
3	DCE	KF	73	>99:1
4	DCE	DABCO	70	>99:1
5	DCE	malonic acid	72	>99:1
6	DCE	benzoic acid	54	>99:1
7	DCE	citric acid	57	>99:1
8	DCE	cinnamic acid	49	>99:1
9	DCE	boric acid	<5	>99:1
10	DCE	AIBN	48	>99:1

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), additive (0.1 mmol) in DCE (1.0 mL) at room temperature for 10 h. [b]Yield ratio was determined by column chromatography. [c]Determined by ^{1}H NMR analysis.



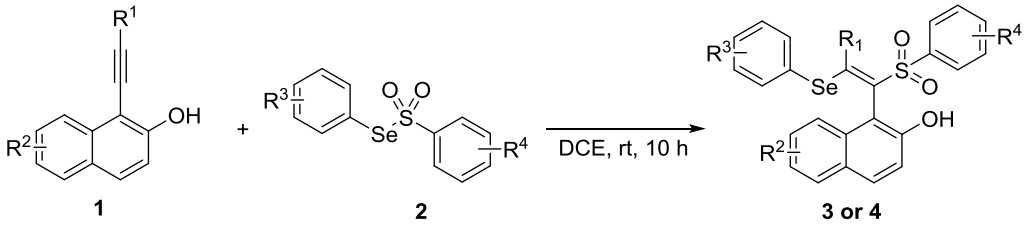
1t **2a** **3t**

Table 3. Screening of conditions for phenol derivatives[a]

entry	solvent	base	*T* (℃)	time (h)	yield (%)[b]
1	DCE	-	r.t	96	0
2	DCE	-	reflux	48	0
3	toluene	-	reflux	48	0
4	DMF	-	reflux	48	0
5	DMSO	-	reflux	48	0
6	DCE	K_2CO_3	r.t	48	0
7	DCE	KF	r.t	24	0
8	DCE	Na_2CO_3	r.t	24	0
9	DCE	KOH	r.t	24	0
10	DCE	NaOH	r.t	24	0
11	DCE	*t*-BuOK	r.t	24	0
12	DCE	EtONa	r.t	24	0
13	DCE	MeONa	r.t	24	0
14	DCE	NaOAc	r.t	24	0
15	DCE	DABCO	r.t	24	0
16	DCE	DBU	r.t	24	0
17	DCE	Et_3N	r.t	24	trace
18	toluene	Et_3N	reflux	16	20

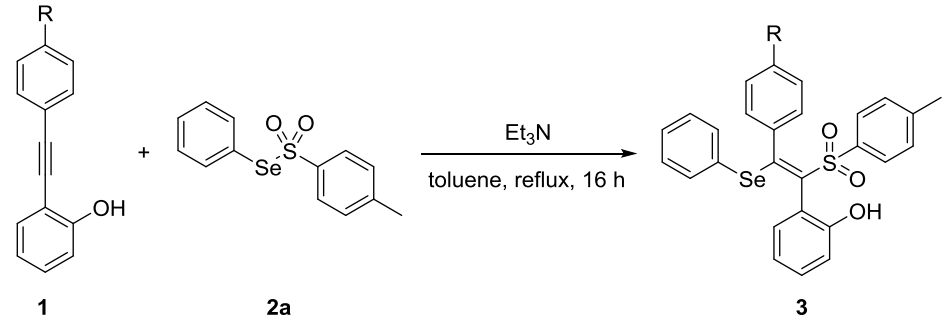
[a]Unless otherwise noted, all reactions were carried out with **1t** (0.2 mmol) and **2a** (0.2 mmol) in 2.0 mL solvents loading at corresponding temperature and reaction time. [b]Isolated yield of **3t**.

VI. General procedure for the synthesis of compounds 3 or 4



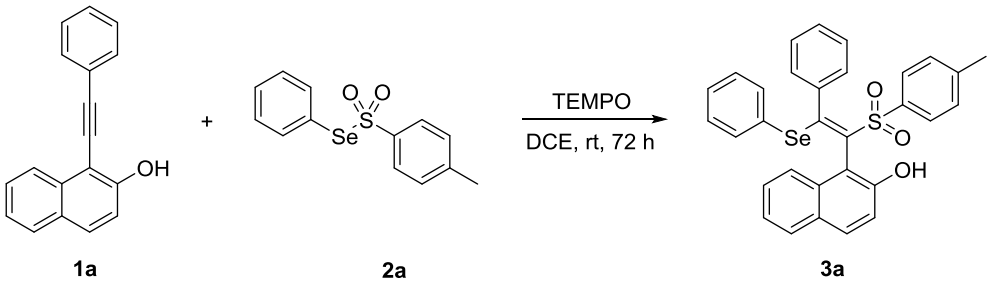
The substrate **1** (0.2 mmol) and selenosulfonate **2** (0.2 mmol) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. DCE (2.0 mL) was injected into the tube. After stirring at room temperature for 10 h, the mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the products **3** or **4**.

VII. General procedure for the synthesis of compounds 3t and 3u

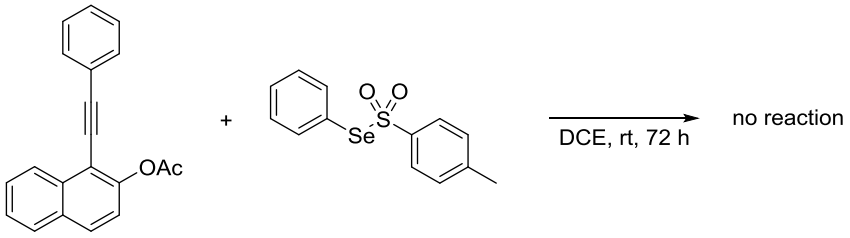


The Et_3N (1.0 mmol) was added to a solution of substrate **1t** or **1u** (1.0 mmol) and selenosulfonate **2a** (1.0 mmol) in toluene (10 mL). After reflux for 16 h, The mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the products **3t** or **3u**.

VIII. Mechanistic studies

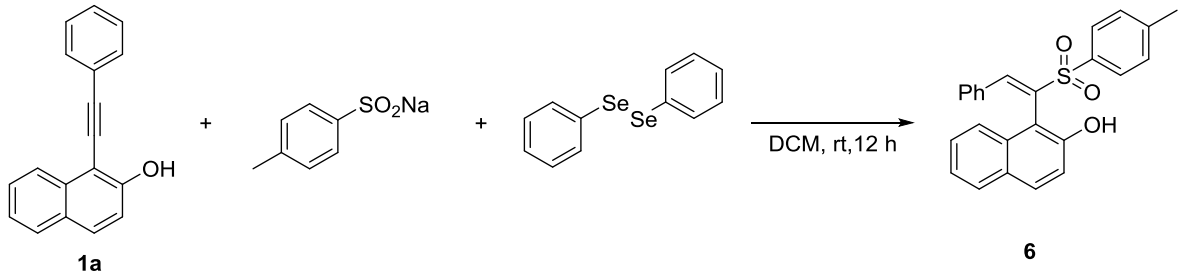


The substrate **1a** (0.1 mmol), selenosulfonate **2a** (0.1 mmol) and (2,2,6,6-tetramethyl-1-piperidinyl)oxyl (TEMPO) (0.1 mmol) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. DCE (1.0 mL) was injected into the tube. After stirring at room temperature for 72 h, The mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the product **3a**.



5 **2a**

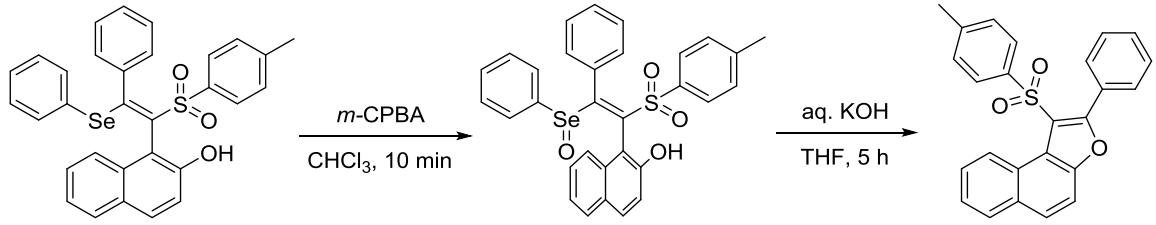
The substrate **5** (0.1 mmol) and selenosulfonate **2a** (0.1 mmol) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. DCE (1.0 mL) was injected into the tube. Then the mixture was stirring at room temperature for 72 h.



1a **6**

The substrate **1a** (0.2 mmol), sodium 4-methy-benzenesulfinate (0.2 mmol) and diphenyl diselenide (0.2 mmol) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. CH_2Cl_2 (2.0 mL) was injected into the tube. After stirring at room temperature for 12 h, The mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the compound **6** (20% yield).

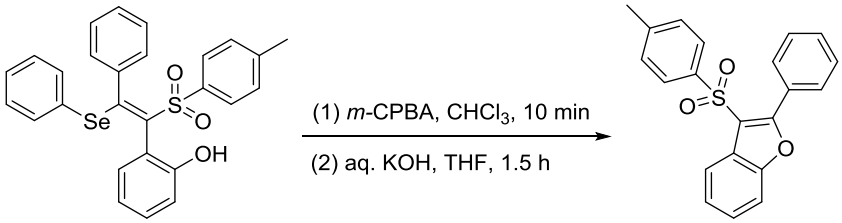
IX. Synthetic transformations



3a **7** 89% yield **8** 95% yield

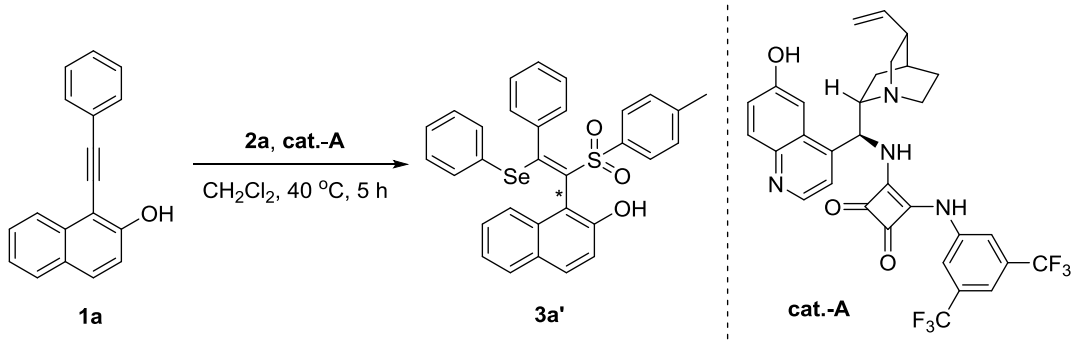
The preparation of compound **7** were followed the literature procedure.[5] *m*-CPBA (0.6 mmol, 1.2 equiv.) was dissolved in 5 mL of $CHCl_3$ and added to a solution of **3a** (0.5 mmol, 1 equiv.) in 20 mL of $CHCl_3$. After standing for 10 min at room temperature, the solvent $CHCl_3$ was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EA = 1:10) to afford compound **7** (254.0 mg, 89%).

A solution of KOH (6.34 mmol) in 5 mL of water was added dropwise to **7** (0.2 mmol) in 10 mL of THF. After 5 h at room temperature, the mixture was extracted with EA. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (PE:EA = 4:1) to afford **8**.



3t **9**

m-CPBA (1.2 mmol, 2.4 equiv.) was dissolved in 5 mL of $CHCl_3$ and added to a solution of **3t** (0.5 mmol, 1 equiv.) in 20 mL of $CHCl_3$. After standing for 10 min at room temperature, the solvent was removed under reduced pressure to afford a residue. Then the residue was dissolved by 20 mL of THF and 5 mL of **1** M aqueous KOH solution was added dropwise. After 1.5 h at room temperature, the mixture was extracted with EA. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (PE:EA = 15:1) to afford **9** (132.0 mg, 76%).

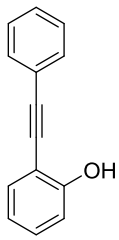


1a **3a'** **cat.-A**

84% ee; 43% yield

The substrate **1a** (0.1 mmol), selenosulfonate **2a** (0.1 mmol) and **cat.-A** (10 mol%) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. CH_2Cl_2 (1.0 mL) was injected into the tube. After stirring at 40 °C for 5 h, the mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the product **3a'**.

X. ^{1}H, ^{13}C NMR and HRMS data of compounds (1t, 1u, 3a-3u, 4a-4n, 7, 8, 9)



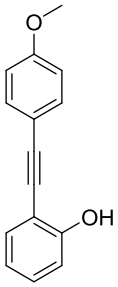
1t

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 – 7.51 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.34 (m, 3H), 7.26 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 5.86 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.44, 131.63, 131.54, 130.43, 128.75, 128.43, 122.32, 120.38, 114.70, 109.54, 96.31, 83.01.

HRMS (ESI) m/z Calcd for $[C_{14}H_{10}NaO, M + Na]^+$: 217.0624, Found: 217.0620.

Physical properties: yellow solid; **Yield:** 95%, 1.84 g; **M. p.** 70–71 ℃



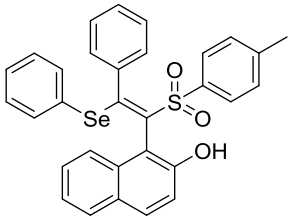
1u

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.89 – 6.83 (m, 3H), 5.93 (s, 1H), 3.78 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.92, 156.30, 133.02, 131.48, 130.06, 120.29, 114.58, 114.33, 114.05, 109.87, 96.32, 81.66, 55.21.

HRMS (ESI) m/z Calcd for $[C_{15}H_{12}NaO_2, M + Na]^+$: 247.0730, Found: 247.0724.

Physical properties: yellow solid; **Yield:** 90%, 1.75 g; **M. p.** 67–68 ℃



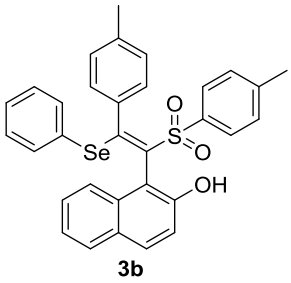
3a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 8.3 Hz, 1H), 7.38 – 7.24 (m, 6H), 7.14 – 6.96 (m, 8H), 6.93 – 6.84 (m, 4H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 160.15, 153.19, 144.00, 137.11, 135.87, 135.77, 135.11, 132.19, 132.12, 130.41, 130.27, 128.96, 128.87, 128.58, 128.49, 128.30, 127.86, 127.14, 127.01, 123.55, 122.95, 119.32, 114.29, 21.38.

HRMS (ESI) m/z Calcd for $[C_{31}H_{24}NaO_3SSe, M + Na]^+$: 579.0504, Found: 579.0508.

Physical properties: white solid; **Yield:** 85%, 94.4 mg; **M. p.** 171–173 ℃



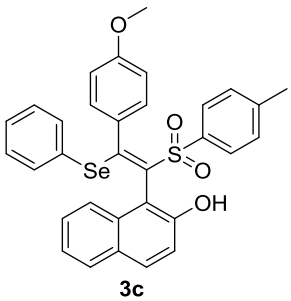
3b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.23 (m, 6H), 7.09 – 6.97 (m, 5H), 6.94 – 6.83 (m, 6H), 2.23 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.55, 153.12, 143.95, 137.82, 136.99, 135.79, 132.22, 132.06, 130.11, 128.92, 128.78, 128.50, 128.45, 128.26, 127.81, 127.18, 126.95, 123.52, 123.00, 119.28, 114.43, 21.37, 21.28.

HRMS (ESI) m/z Calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, Found: 593.0658.

Physical properties: white solid; **Yield:** 44%, 50.1 mg; **M. p.** 188–190 ℃



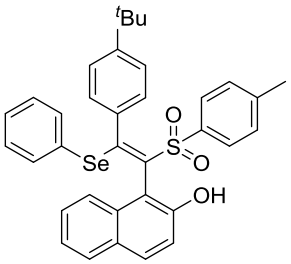
3c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.24 (m, 6H), 7.12 – 6.97 (m, 5H), 6.97 – 6.85 (m, 4H), 6.62 (d, *J* = 8.5 Hz, 2H), 3.73 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.23, 159.35, 153.04, 143.89, 136.91, 136.01, 132.29, 132.04, 130.53, 130.22, 128.94, 128.79, 128.47, 128.44, 128.34, 128.27, 127.48, 127.38, 126.99, 123.55, 123.08, 119.20, 114.61, 112.66, 55.18, 21.37.

HRMS (ESI) m/z Calcd for $[C_{32}H_{26}NaO_4SSe, M + Na]^+$: 609.0609, Found: 609.0613.

Physical properties: white solid; **Yield:** 76%, 89.0 mg; **M. p.** 189–190 ℃



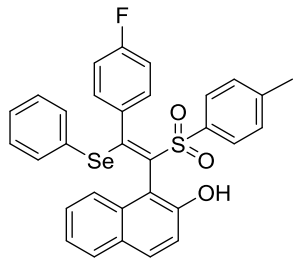
3d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.23 (m, 6H), 7.02 (t, 3H), 6.98 – 6.89 (m, 4H), 6.85 (q, 4H), 2.20 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.70, 153.11, 150.88, 143.75, 137.15, 136.19, 132.27, 132.07, 131.93, 130.17, 129.02, 128.81, 128.47, 128.31, 128.29, 128.12, 127.34, 127.06, 123.98, 123.59, 123.14, 119.20, 114.25, 34.39, 31.20, 21.39.

HRMS (ESI) m/z Calcd for $[C_{35}H_{32}NaO_3SSe, M + Na]^+$: 635.1130, Found: 635.1126.

Physical properties: white solid; **Yield:** 53%, 61.4 mg; **M. p.** 212–213 ℃



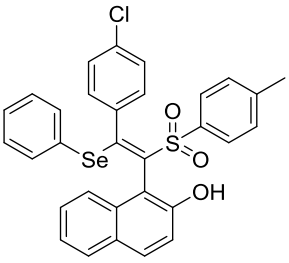
3e

^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.26 (m, 6H), 7.12 – 7.05 (m, 3H), 7.02 (d, *J* = 7.1 Hz, 2H), 6.98 – 6.86 (m, 4H), 6.78 (t, *J* = 8.3 Hz, 2H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.20 (d, *J* = 258.0 Hz), 158.78, 153.13, 144.17, 137.09, 135.74, 132.20, 132.10, 131.21, 131.18, 128.95, 128.90, 128.82, 128.51, 128.43, 128.34, 127.07, 126.90, 123.61, 122.86, 119.28, 114.40, 114.18, 21.39.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}FNaO_3SSe, M + Na]^+$: 597.0409, Found: 597.0412.

Physical properties: white solid; **Yield:** 81%, 92.9 mg; **M. p.** 182–184 ℃



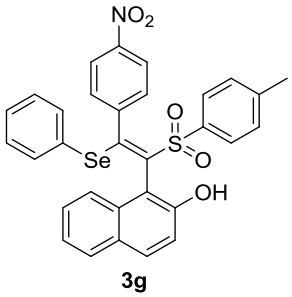
3f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.73 (q, *J* = 9.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.20 (m, 7H), 7.16 – 7.00 (m, 6H), 6.99 – 6.84 (m, 4H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.40, 158.40, 153.13, 144.75, 144.29, 137.11, 135.52, 133.93, 133.75, 132.26, 132.06, 131.15, 128.94, 128.58, 128.49, 128.35, 128.26, 127.41, 127.08, 126.69, 123.63, 122.78, 119.34, 118.98, 114.09, 21.42.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}ClNaO_3SSe, M + Na]^+$: 613.0114, Found: 613.0118.

Physical properties: white solid; **Yield:** 47%, 55.5 mg; **M. p.** 171–172 ℃



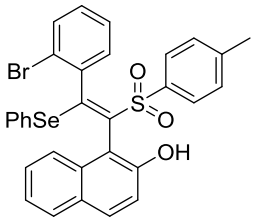
3g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 2H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.40 (s, 1H), 7.36 – 7.22 (m, 8H), 7.14 – 7.00 (m, 3H), 6.99 – 6.84 (m, 4H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.40, 153.25, 146.83, 144.79, 142.40, 137.25, 134.74, 132.54, 131.83, 131.57, 129.42, 129.11, 128.95, 128.84, 128.56, 128.44, 127.18, 125.95, 123.74, 122.43, 119.53, 113.54, 21.43.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}NNaO_5SSe, M + Na]^+$: 624.0354, Found: 624.0355.

Physical properties: yellow solid; **Yield:** 61%, 73.3 mg; **M. p.** 120–123 ℃



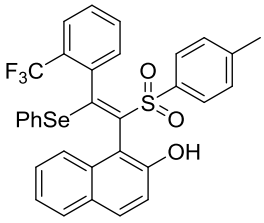
3h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.9 Hz, 1H), 7.73 – 7.61 (m, 3H), 7.43 – 7.28 (m, 4H), 7.26 – 7.15 (m, 5H), 7.15 – 7.07 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 3H), 6.87 (d, *J* = 8.0 Hz, 2H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.79, 153.18, 144.45, 137.58, 136.00, 134.24, 132.40, 132.33, 131.90, 131.10, 129.62, 129.28, 129.07, 128.97, 128.80, 128.24, 127.97, 126.72, 126.45, 125.86, 123.62, 123.58, 121.32, 119.71, 113.73, 21.38.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}BrNaO_3SSe, M + Na]^+$: 656.9609, Found: 656.9614.

Physical properties: white solid; **Yield:** 47%, 59.6 mg; **M. p.** 175–177 ℃



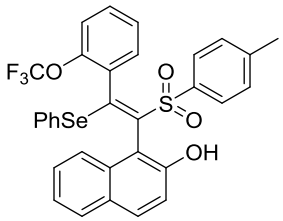
3i

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 9.4 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 8.9 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.26 – 7.15 (m, 3H), 7.09 (t, *J* = 8.3 Hz, 3H), 6.93 (t, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.55, 153.12, 144.52, 137.77, 133.98, 133.25, 132.53, 132.47, 131.27, 130.84, 129.95, 129.11, 129.01, 128.83, 128.76, 128.34, 128.22, 127.93, 126.93, 126.18 (q, *J* = 30.0 Hz), 126.15 (q, *J* = 5.0 Hz), 125.90, 124.06 (q, *J* = 272.0 Hz), 123.64, 122.78, 122.77, 119.80, 113.90, 21.34.

HRMS (ESI) m/z Calcd for $[C_{32}H_{23}F_3NaO_3SSe, M + Na]^+$: 647.0377, Found: 647.0374.

Physical properties: white solid; **Yield:** 30%, 37.4 mg; **M. p.** 201–204 ℃



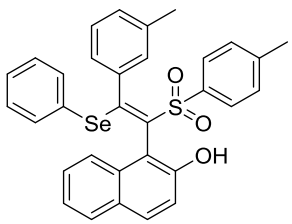
3j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 10.0 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.06 (m, 6H), 7.05 – 6.98 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 2H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.24, 153.36, 144.79, 144.53, 137.35, 134.12, 132.41, 132.04, 131.26, 130.69, 129.51, 129.09, 128.85, 128.82, 128.75, 128.41, 127.94, 126.75, 126.39, 126.08, 124.56, 123.60, 123.16, 120.56 (q, *J* = 258.0 Hz), 119.62, 115.77, 113.71, 21.35.

HRMS (ESI) m/z Calcd for $[C_{32}H_{23}F_3NaO_4SSe, M + Na]^+$: 663.0327, Found: 663.0330.

Physical properties: white solid; **Yield:** 55%, 70.4 mg; **M. p.** 161–163 ℃



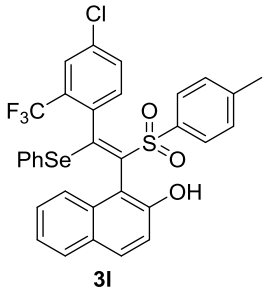
3k

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.39 – 7.25 (m, 6H), 7.09 – 6.93 (m, 5H), 6.93 – 6.79 (m, 5H), 6.67 (s, 1H), 2.20 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.21, 153.21, 143.80, 137.11, 136.55, 136.20, 134.73, 132.04, 130.34, 128.97, 128.82, 128.55, 128.46, 128.29, 128.08, 127.17, 127.04, 123.54, 123.08, 119.20, 114.21, 21.37, 21.02.

HRMS (ESI) m/z Calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, Found: 593.0657.

Physical properties: white solid; **Yield:** 51%, 56.7 mg; **M. p.** 175–178 ℃



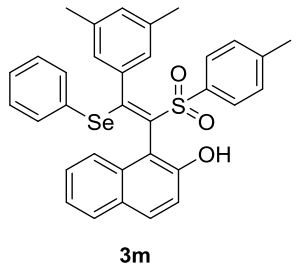
3l

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.79 (m, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.43 (s, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.07 (m, 9H), 6.97 (t, *J* = 7.4 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 2H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.00, 153.04, 144.72, 137.74, 134.31, 133.74, 132.63, 132.55, 132.37, 131.97, 130.94, 130.79, 129.44, 128.99, 128.90, 128.75, 128.60, 127.99, 127.63 (q, *J* = 31.0 Hz), 126.99, 126.48 (q, *J* = 5.0 Hz), 125.62, 123.70, 123.20 (q, *J* = 273.0 Hz) 122.59, 119.82, 113.73, 21.35.

HRMS (ESI) m/z Calcd for $[C_{32}H_{22}ClF_3NaO_3SSe, M + Na]^+$: 680.9988, Found: 680.9989.

Physical properties: white solid; **Yield:** 31%, 40.8 mg; **M. p.** 182–184 ℃



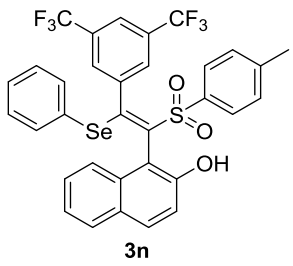
3m

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.36 – 7.24 (m, 5H), 7.04 (t, *J* = 7.3 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.91 (d, *J* = 7.8 Hz, 4H), 6.63 (s, 1H), 6.57 (s, 2H), 2.22 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 160.28, 153.24, 143.62, 137.11, 136.57, 136.40, 134.46, 132.36, 131.94, 130.42, 129.17, 128.97, 128.75, 128.50, 128.45, 128.29, 127.87, 127.29, 127.06, 125.90, 123.52, 123.19, 119.12, 114.17, 21.35, 20.92.

HRMS (ESI) m/z Calcd for $[C_{33}H_{28}NaO_3SSe, M + Na]^+$: 607.0817, Found: 607.0818.

Physical properties: white solid; **Yield:** 43%, 50.2 mg; **M. p.** 192–193 ℃



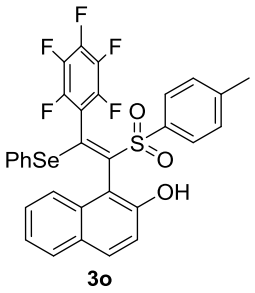
3n

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (t, *J* = 7.8 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.00 – 6.89 (m, 6H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.88, 153.39, 144.80, 137.39, 137.27, 135.91, 133.70, 132.44, 131.96, 130.46 (q, *J* = 33.0 Hz), 129.36, 129.29, 129.03, 128.88, 128.55, 128.26, 127.48, 126.18, 123.82, 123.29 (q, *J* = 270.0 Hz), 122.71, 121.13 (t, *J* = 4.0 Hz), 118.75, 113.32, 21.39.

HRMS (ESI) m/z Calcd for $[C_{33}H_{22}F_6NaO_3SSe, M + Na]^+$: 715.0251, Found: 715.0249.

Physical properties: white solid; **Yield:** 46%, 63.6 mg; **M. p.** 179–182 ℃



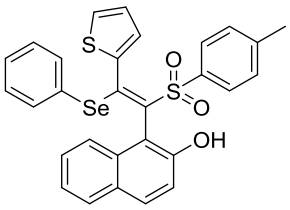
3o

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.9 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.14 (m, 10H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.23, 145.19, 143.37, 137.00, 134.15, 133.54, 132.88, 131.26, 130.16, 129.20, 128.99, 128.83, 128.21, 127.23, 125.57, 123.74, 122.53, 119.49, 112.45, 21.43.

HRMS (ESI) m/z Calcd for $[C_{31}H_{19}F_5NaO_3SSe, M + Na]^+$: 669.0032, Found:669.0030.

Physical properties: white solid; **Yield:** 61%, 78.8 mg; **M. p.** 211–213 ℃



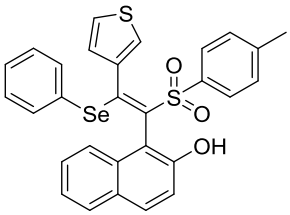
3p

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.33 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 7.16 (d, *J* = 4.5 Hz, 1H), 7.15 – 7.06 (m, 3H), 7.03 – 6.93 (m, 3H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.77 – 6.70 (m, 1H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.99, 150.76, 143.93, 136.39, 135.89, 135.38, 134.57, 132.29, 132.04, 130.64, 128.83, 128.58, 128.44, 128.42, 128.29, 128.05, 127.73, 127.18, 126.16, 123.61, 123.16, 119.02, 114.63, 21.40.

HRMS (ESI) m/z Calcd for $[C_{29}H_{22}NaO_3SSe, M + Na]^+$: 585.0068, Found: 585.0070.

Physical properties: white solid; **Yield:** 46%, 51.7 mg; **M. p.** 97–99 ℃



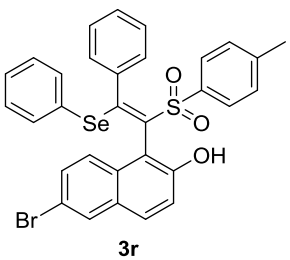
3q

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 8.1, 4.6 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 6.3 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.16 – 7.00 (m, 4H), 7.01 – 6.84 (m, 5H), 6.67 (d, *J* = 4.8 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.16, 153.04, 143.73, 136.56, 136.51, 134.52, 132.63, 132.27, 131.97, 128.93, 128.84, 128.49, 128.42, 128.38, 128.32, 128.17, 127.45, 127.15, 125.97, 124.15, 123.59, 123.25, 118.96, 114.31, 21.40.

HRMS (ESI) m/z Calcd for $[C_{29}H_{22}NaO_3SSe, M + Na]^+$: 585.0068, Found: 585.0071.

Physical properties: white solid; **Yield:** 62%, 69.6 mg; **M. p.** 188–189 ℃



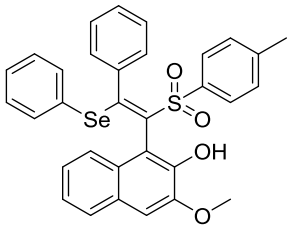
3r

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.52 (s, 1H), 7.46 – 7.38 (m, 2H), 7.32 – 7.23 (m, 3H), 7.15 – 7.00 (m, 6H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.95 – 6.80 (m, 4H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.42, 153.67, 144.17, 137.04, 135.91, 134.80, 131.04, 130.84, 130.25, 130.22, 130.11, 130.04, 129.01, 128.66, 128.38, 128.35, 127.91, 127.13, 126.80, 124.86, 120.48, 117.22, 114.41, 21.45.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}BrNaO_3SSe, M + Na]^+$: 656.9609, Found: 656.9607.

Physical properties: white solid; **Yield:** 76%, 94.4 mg; **M. p.** 172–175 ℃



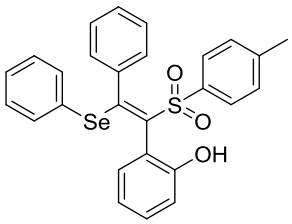
3s

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.47 (t, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.25 (s, 2H), 7.07 – 6.94 (m, 5H), 6.94 – 6.78 (m, 6H), 6.56 (s, 1H), 4.06 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.06, 146.81, 144.91, 142.92, 138.53, 136.94, 134.93, 133.52, 129.46, 129.00, 128.54, 128.33, 128.23, 128.21, 127.80, 127.52, 127.35, 127.08, 126.81, 125.34, 124.40, 123.94, 114.54, 107.61, 55.99, 21.46.

HRMS (ESI) m/z Calcd for $[C_{32}H_{26}NaO_4SSe, M + Na]^+$: 609.0609, Found: 609.0605.

Physical properties: white solid; **Yield:** 72%, 84.3 mg; **M. p.** 171–172 ℃



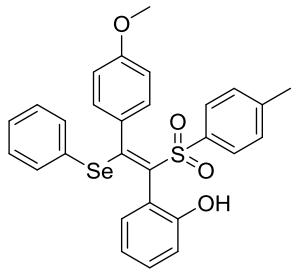
3t

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (s, 4H), 7.40 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.10 – 7.05 (m, 3H), 6.95 – 6.88 (m, 3H), 6.58 (d, *J* = 8.1 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.50 (t, *J* = 7.4 Hz, 1H), 5.62 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 151.88, 151.78, 143.78, 139.38, 137.47, 136.91, 134.33, 129.88, 129.79, 129.59, 129.11, 128.86, 128.77, 128.30, 128.12, 127.13, 123.62, 119.96, 116.95, 21.55.

HRMS (ESI) m/z Calcd for $[C_{27}H_{22}NaO_3SSe, M + Na]^+$: 529.0347, Found: 529.0351.

Physical properties: white solid; **Yield:** 20%, 101.2 mg; **M. p.** 76–78 ℃



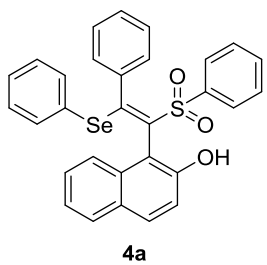
3u

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 3H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.92 (dt, *J* = 18.7, 7.1 Hz, 3H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.50 (q, *J* = 7.7 Hz, 2H), 5.52 (s, 1H), 3.88 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 160.54, 151.99, 151.75, 143.68, 139.20, 137.59, 136.92, 131.83, 129.86, 129.79, 129.10, 128.75, 128.30, 128.07, 127.27, 126.30, 123.78, 120.01, 116.99, 114.32, 55.30, 21.56.

HRMS (ESI) m/z Calcd for $[C_{28}H_{24}NaO_4SSe, M + Na]^+$: 559.0453, Found: 559.0449.

Physical properties: white solid; **Yield:** 26%, 139.3 mg; **M. p.** 183–184 ℃



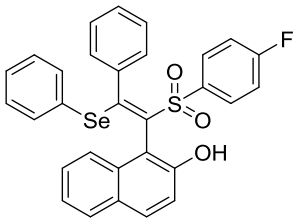
4a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.38 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.18 – 6.94 (m, 10H), 6.89 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 160.49, 153.27, 138.97, 137.06, 134.97, 132.92, 132.16, 130.32, 128.93, 128.58, 128.38, 128.31, 128.22, 127.89, 127.17, 127.11, 126.96, 123.60, 122.89, 119.21, 114.02.

HRMS (ESI) m/z Calcd for $[C_{30}H_{22}NaO_3SSe, M + Na]^+$: 565.0347, Found: 565.0349.

Physical properties: white solid; **Yield:** 59%, 63.9 mg; **M. p.** 121–123 ℃



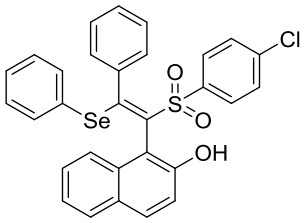
4b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.48 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.18 – 6.95 (m, 8H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.75 (t, *J* = 8.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 165.20 (d, *J* = 254.0 Hz), 160.49, 153.24, 137.04, 135.32 (d, *J* = 2.0 Hz), 134.89, 132.24, 132.11, 131.21, 131.11, 130.51, 128.95, 128.63, 128.48, 128.34, 127.98, 127.32, 127.20, 126.90, 123.76, 122.84, 119.06, 115.43 (d, *J* = 22.0 Hz), 113.81.

HRMS (ESI) m/z Calcd for $[C_{30}H_{21}FNaO_3SSe, M + Na]^+$: 583.0253, Found: 583.0250.

Physical properties: white solid; **Yield:** 64%, 71.6 mg; **M. p.** 158–159 ℃



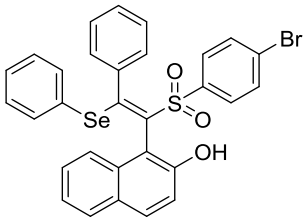
4c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.27 – 7.23 (m, 1H), 7.18 (s, 1H), 7.13 – 7.03 (m, 7H), 7.01 (d, *J* = 7.7 Hz, 3H), 6.90 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 161.00, 153.20, 139.58, 137.82, 137.07, 134.85, 132.33, 132.10, 130.27, 129.79, 129.01, 128.68, 128.52, 128.46, 128.38, 128.05, 127.38, 127.22, 126.88, 123.82, 122.84, 119.07, 113.75.

HRMS (ESI) m/z Calcd for $[C_{30}H_{21}ClNaO_3SSe, M + Na]^+$: 598.9957, Found: 598.9960.

Physical properties: white solid; **Yield:** 76%, 87.6 mg; **M. p.** 166–169 ℃



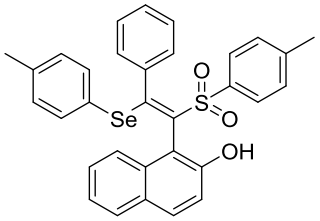
4d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (t, *J* = 7.7 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.25 – 7.19 (m, 3H), 7.13 – 6.92 (m, 8H), 6.88 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 160.78, 153.31, 138.66, 137.03, 134.78, 132.24, 132.17, 131.43, 130.64, 129.79, 128.97, 128.63, 128.51, 128.34, 128.10, 127.99, 127.41, 127.17, 126.90, 123.77, 122.91, 118.98, 113.63.

HRMS (ESI) m/z Calcd for $[C_{30}H_{21}BrNaO_3SSe, M + Na]^+$: 642.9452, Found: 642.9449.

Physical properties: white solid; **Yield:** 70%, 86.9 mg; **M. p.** 110–111 ℃



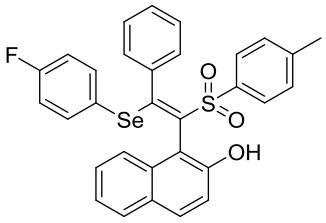
4e

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.45 (s, 1H), 7.36 – 7.23 (m, 5H), 7.07 (s, 5H), 6.86 (d, *J* = 7.6 Hz, 4H), 6.68 (d, *J* = 7.7 Hz, 2H), 2.18 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.30, 153.22, 143.84, 138.68, 136.93, 136.03, 135.15, 132.22, 131.98, 130.30, 129.07, 129.07, 128.89, 128.82, 128.40, 128.40, 128.24, 127.74, 127.05, 126.97, 123.48, 123.41, 123.02, 119.19, 114.21, 21.36, 21.04.

HRMS (ESI) m/z Calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, Found: 593.0659.

Physical properties: white solid; **Yield:** 56%, 63.8 mg; **M. p.** 179–181 ℃



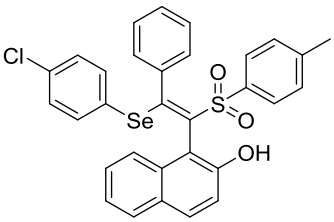
4f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.48 (s, 1H), 7.38 – 7.26 (m, 4H), 7.24 (s, 1H), 7.19 – 6.99 (m, 5H), 6.99 – 6.92 (m, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.57 (t, *J* = 8.5 Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.91 (d, *J* = 248.0 Hz), 159.30, 153.29, 143.93, 139.13, 139.05, 136.01, 134.91, 132.16, 132.07, 131.01, 128.87, 128.39, 128.30, 127.94, 127.21, 127.06, 123.53, 122.91, 121.95 (d, *J* = 3.0 Hz), 119.18, 115.49 (d, *J* = 22.0 Hz), 115.38, 113.97, 21.36.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}FNaO_3SSe, M + Na]^+$: 597.0409, Found: 597.0411.

Physical properties: white solid; **Yield:** 65%, 74.6 mg; **M. p.** 159–161 ℃



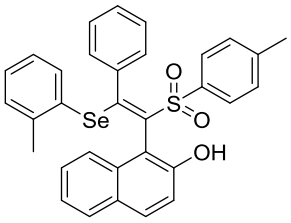
4g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.37 – 7.22 (m, 5H), 7.18 – 7.00 (m, 5H), 6.99 – 6.78 (m, 6H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.98, 153.28, 144.02, 138.22, 135.89, 135.19, 134.94, 132.16, 132.14, 131.17, 128.89, 128.48, 128.45, 128.32, 128.12, 127.30, 127.08, 125.22, 123.57, 122.87, 119.24, 114.03, 21.38.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}ClNaO_3SSe, M + Na]^+$: 613.0114, Found: 613.0115.

Physical properties: white solid; **Yield:** 75%, 88.5 mg; **M. p.** 158–160 ℃



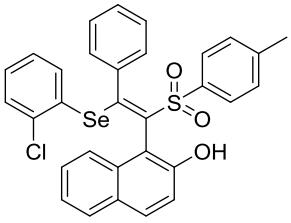
4h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.40 (s, 1H), 7.34 – 7.22 (m, 5H), 7.15 – 7.01 (m, 6H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 3H), 6.71 (t, *J* = 7.6 Hz, 1H), 2.18 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.95, 153.16, 143.91, 142.74, 138.89, 135.88, 135.28, 132.37, 131.97, 130.95, 129.48, 128.89, 128.83, 128.43, 128.27, 128.03, 127.94, 126.98, 126.93, 125.79, 123.52, 123.02, 119.27, 114.54, 23.21, 21.37.

HRMS (ESI) m/z Calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, Found: 593.0662.

Physical properties: white solid; **Yield:** 61%, 69.5 mg; **M. p.** 188–191 ℃



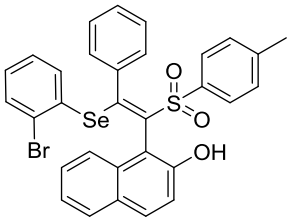
4i

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.17 (m, 7H), 7.17 – 7.01 (m, 5H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.25, 153.23, 143.97, 140.06, 139.59, 135.82, 134.96, 132.25, 132.12, 131.43, 130.57, 129.04, 128.84, 128.44, 128.23, 128.15, 127.79, 127.02, 126.48, 123.60, 123.13, 119.17, 114.11, 21.38.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}ClNaO_3SSe, M + Na]^+$: 613.0114, Found: 613.0113

Physical properties: white solid; **Yield:** 66%, 77.9 mg; **M. p.** 197–199 ℃



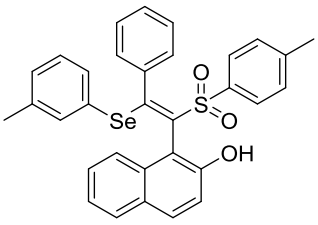
4j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.23 (m, 9H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.05 (m, 3H), 6.87 (d, *J* = 7.9 Hz, 3H), 6.82 (t, *J* = 7.5 Hz, 1H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.42, 153.18, 144.03, 139.59, 135.75, 134.97, 132.42, 132.29, 132.16, 131.72, 131.32, 130.51, 130.28, 128.90, 128.85, 128.49, 128.25, 128.21, 127.12, 127.06, 127.00, 123.61, 123.19, 119.23, 114.12, 21.38.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}BrNaO_3SSe, M + Na]^+$: 656.9609, Found: 656.9610.

Physical properties: white solid; **Yield:** 54%, 68.5 mg; **M. p.** 189–191 ℃



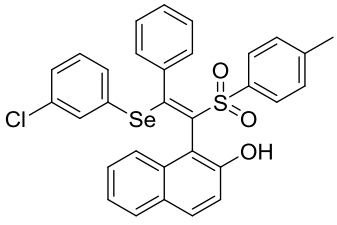
4k

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.39 (s, 1H), 7.36 – 7.22 (m, 5H), 7.07 (s, 5H), 6.92 – 6.71 (m, 6H), 2.18 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.27, 153.20, 143.90, 137.99, 137.73, 135.94, 135.04, 133.87, 132.18, 132.04, 130.25, 129.25, 128.92, 128.84, 128.44, 128.25, 128.05, 127.77, 126.97, 126.94, 126.73, 123.51, 123.00, 119.23, 114.18, 21.36, 20.79.

HRMS (ESI) m/z Calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, Found: 593.0663.

Physical properties: white solid; **Yield:** 79%, 90.0 mg; **M. p.** 187–189 ℃



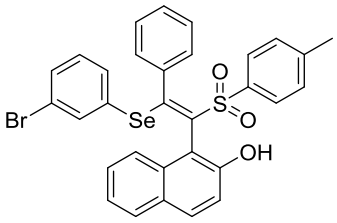
4l

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 6.8 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.35 – 7.25 (m, 5H), 7.18 – 7.07 (m, 5H), 7.02 (d, 1H), 6.96 (s, 1H), 6.89 (t, *J* = 8.4 Hz, 3H), 6.83 (t, *J* = 7.8 Hz, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 159.03, 153.28, 144.11, 136.68, 135.74, 134.97, 134.72, 133.54, 132.24, 132.08, 131.02, 129.29, 128.93, 128.76, 128.49, 128.37, 128.34, 128.17, 127.26, 127.12, 123.62, 122.82, 119.29, 113.95, 21.40.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}ClNaO_3SSe, M + Na]^+$: 613.0114, Found: 613.0113

Physical properties: white solid; **Yield:** 61%, 72.0 mg; **M. p.** 183–185 ℃



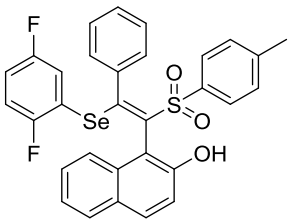
4m

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 6.9 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.38 (s, 1H), 7.34 – 7.25 (m, 5H), 7.24 – 7.05 (m, 7H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 7.8 Hz, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 159.13, 153.26, 144.15, 139.48, 135.65, 135.36, 134.71, 132.27, 132.06, 131.63, 130.87, 129.60, 128.94, 128.66, 128.52, 128.34, 128.22, 127.28, 127.11, 123.63, 122.80, 121.67, 119.34, 113.97, 21.41.

HRMS (ESI) m/z Calcd for $[C_{31}H_{23}BrNaO_3SSe, M + Na]^+$: 656.9609, Found: 656.9610.

Physical properties: white solid; **Yield:** 76%, 96.4 mg; **M. p.** 189–191 ℃



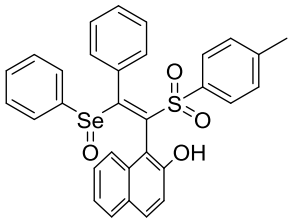
4n

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.24 (m, 6H), 7.24 – 7.07 (m, 5H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.82 – 6.69 (m, 2H), 6.69 – 6.60 (m, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 158.58 (d, *J* = 241.0 Hz), 158.30, 157.28 (d, *J* = 244.0 Hz), 153.34, 144.21, 135.52, 134.77, 132.37, 132.01, 131.55, 128.94, 128.54, 128.39, 128.30, 124.98, 124.74, 123.70, 122.83, 119.31, 118.31 (d, *J* = 8.0 Hz), 118.08 (d, *J* = 7.0 Hz), 115.97 (d, *J* = 8.0 Hz), 115.70 (d, *J* = 8.0 Hz), 113.86, 21.41.

HRMS (ESI) m/z Calcd for $[C_{31}H_{22}F_2NaO_3SSe, M + Na]^+$: 615.0315, Found: 615.0313.

Physical properties: white solid; **Yield:** 64%, 75.7 mg; **M. p.** 203–204 ℃



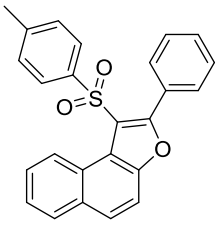
7

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.30 (m, 7H), 7.30 – 7.20 (m, 5H), 6.94 (d, *J* = 8.0 Hz, 3H), 6.80 (d, *J* = 7.7 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$)**:** δ 155.60, 154.16, 146.43, 143.96, 137.63, 136.64, 134.25, 132.34, 131.66, 130.73, 129.34, 129.13, 128.68, 128.47, 128.32, 127.88, 127.66, 127.14, 126.78, 126.05, 124.35, 123.55, 118.61, 111.07, 21.52.

HRMS (ESI) m/z Calcd for $[C_{31}H_{24}NaO_4SSe, M + Na]^+$: 595.0453, Found: 595.0458.

Physical properties: white solid; **Yield:** 89%, 254.0 mg; **M. p.** 123–126 ℃



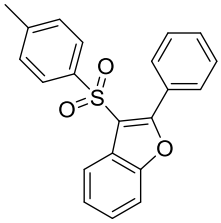
8

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.80 – 7.68 (m, 4H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.35, 151.91, 143.89, 139.45, 131.43, 130.82, 130.41, 129.55, 129.15, 129.01, 128.41, 127.74, 127.07, 126.99, 126.61, 126.11, 125.25, 119.95, 118.93, 111.82, 21.47.

HRMS (ESI) m/z Calcd for $[C_{25}H_{18}NaO_3S, M + Na]^+$: 421.0869, Found: 421.0862.

Physical properties: white solid; **Yield:** 95%, 76.0 mg; **M. p.** 167–168 ℃



9

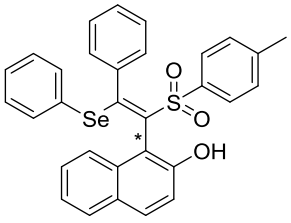
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 – 8.03 (m, 1H), 7.82 (d, *J* = 7.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.37 (m, 4H), 7.29 – 7.25 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 2.21 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.70, 153.16, 144.08, 139.43, 130.78, 130.05, 129.51, 128.14, 128.10, 126.66, 125.87, 125.47, 124.51, 121.62, 118.72, 111.36, 21.44.

HRMS (ESI) m/z Calcd for $[C_{21}H_{16}NaO_3S, M + Na]^+$: 371.0712, Found: 371.0717.

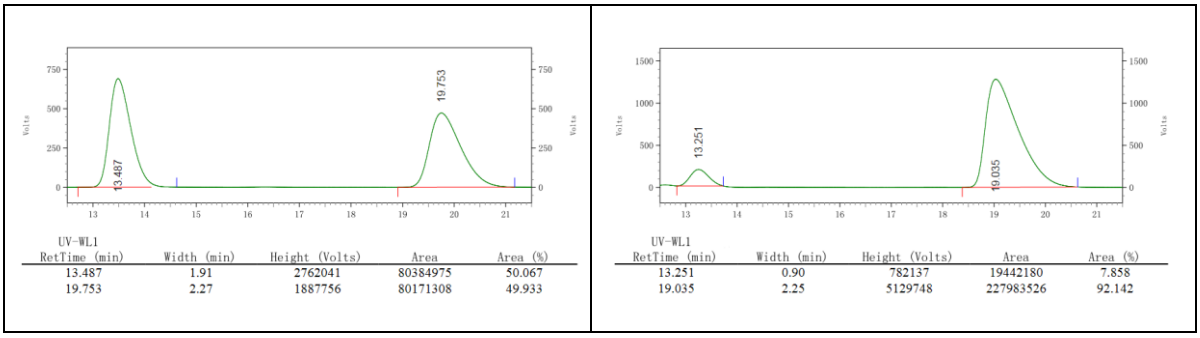
Physical properties: white solid; **Yield:** 76%, 132.0 mg; **M. p.** 112–114 ℃

XI. HPLC traces of compound 3a'

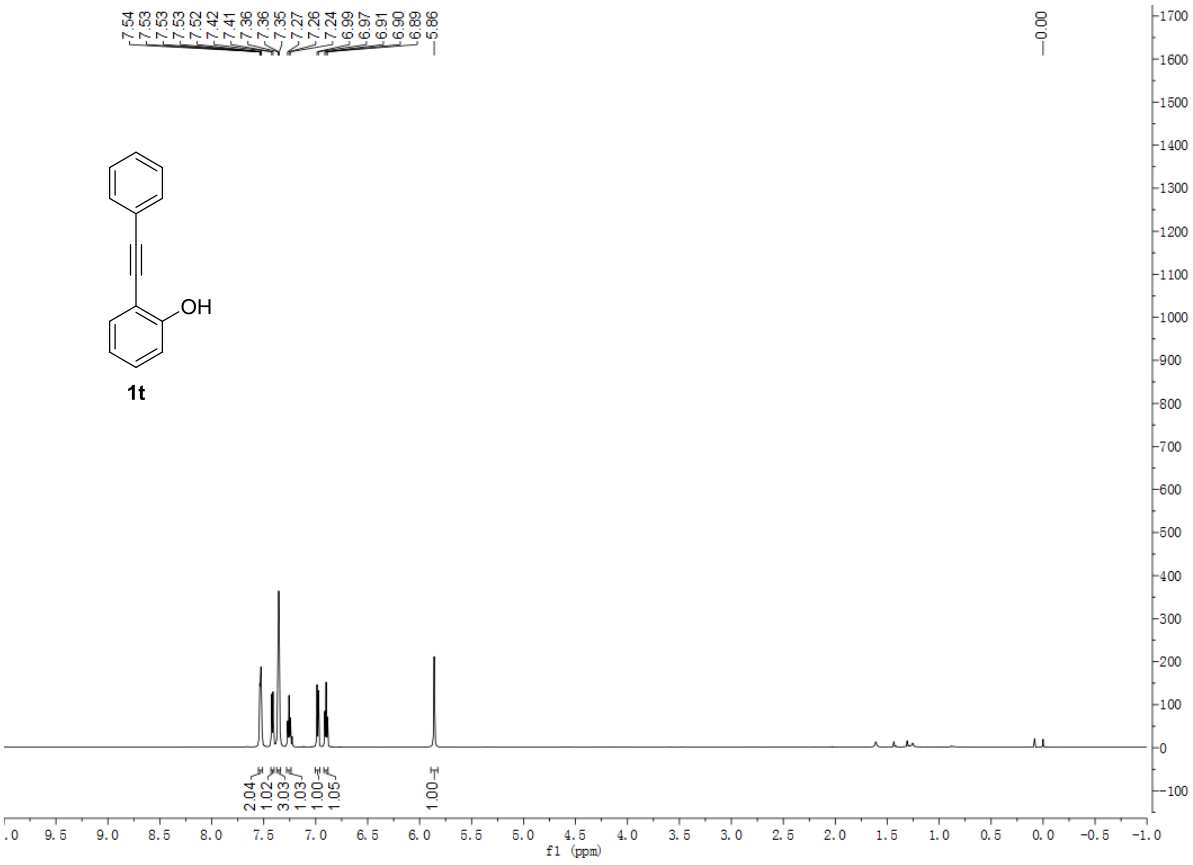


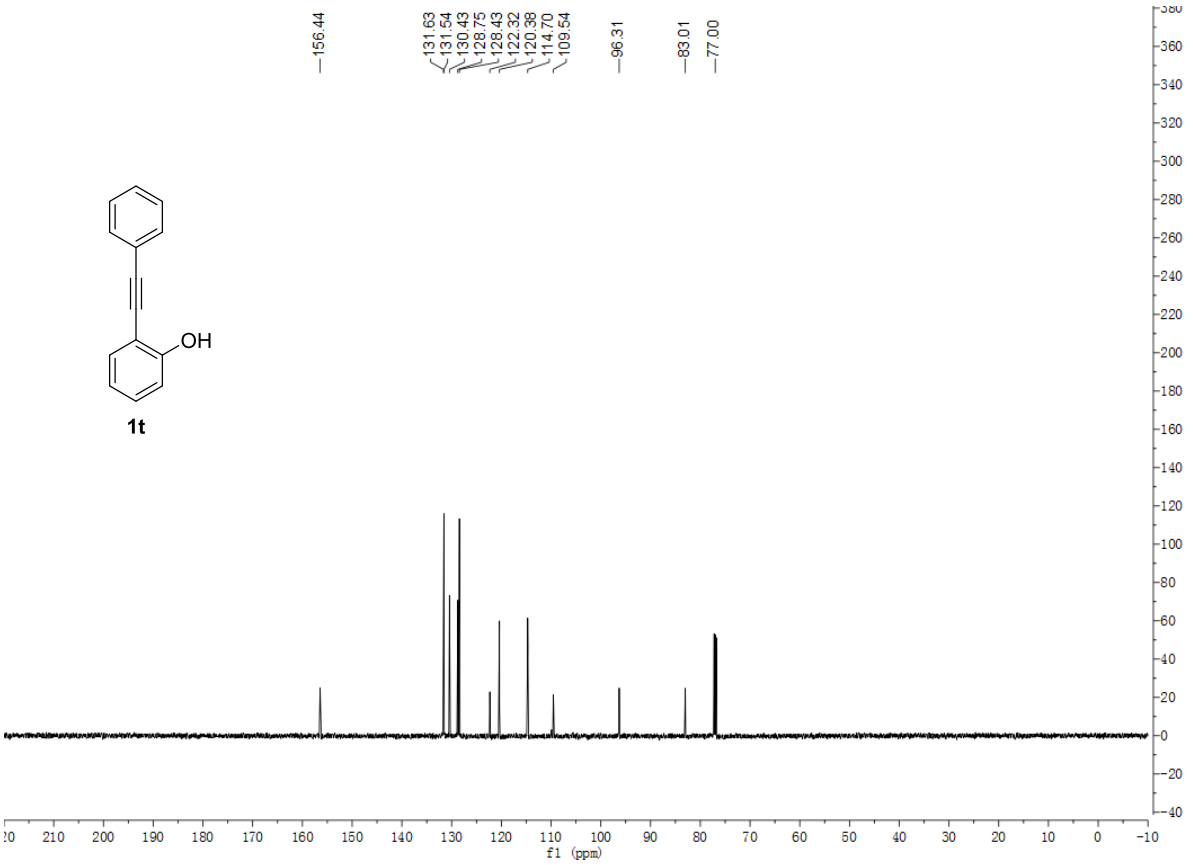
3a'

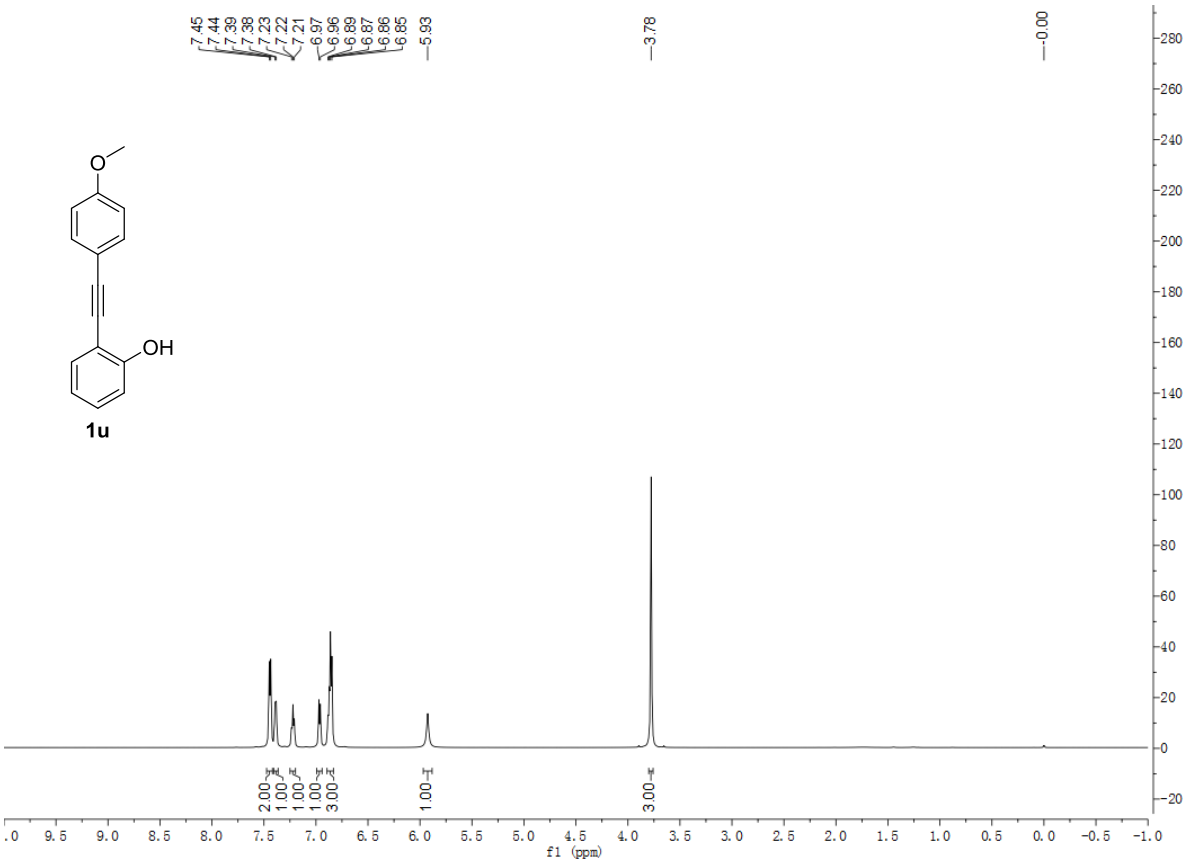
(3a') HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20), flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 13.251 min (minor), t_R = 19.035 min (major).



XII. ^{1}H and ^{13}C NMR spectra of compounds (1t, 1u, 3a-3u, 4a-4n, 7, 8, 9)



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6.85
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OH
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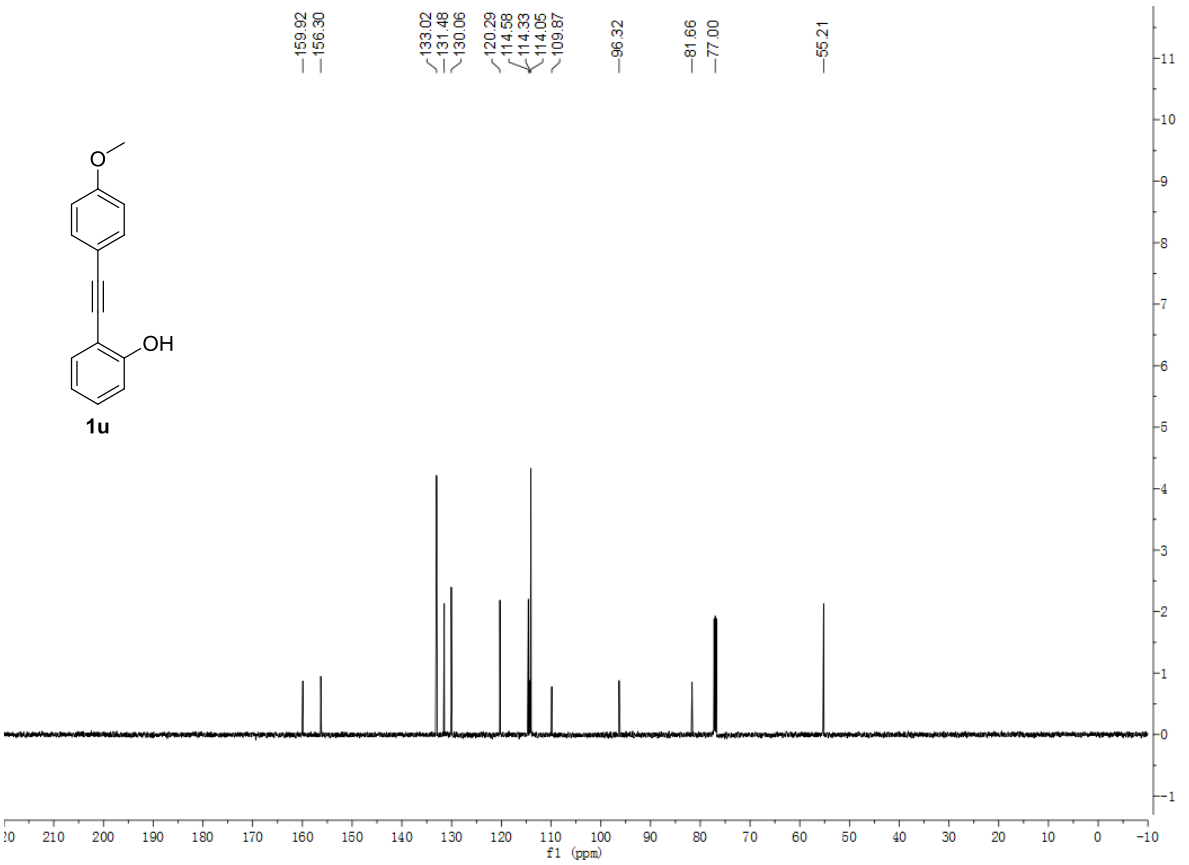
1.00
3.00
1.00
3.00
f1 (ppm)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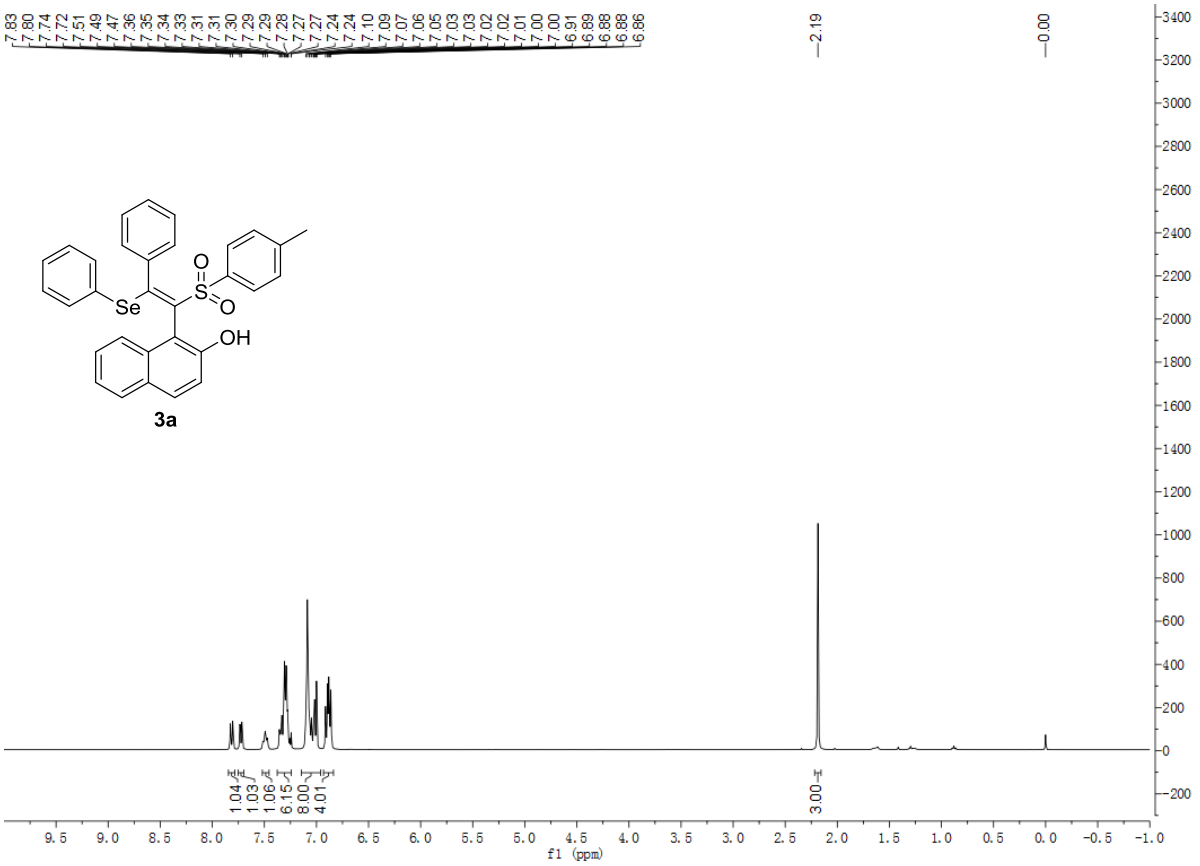
f1 (ppm)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7.01
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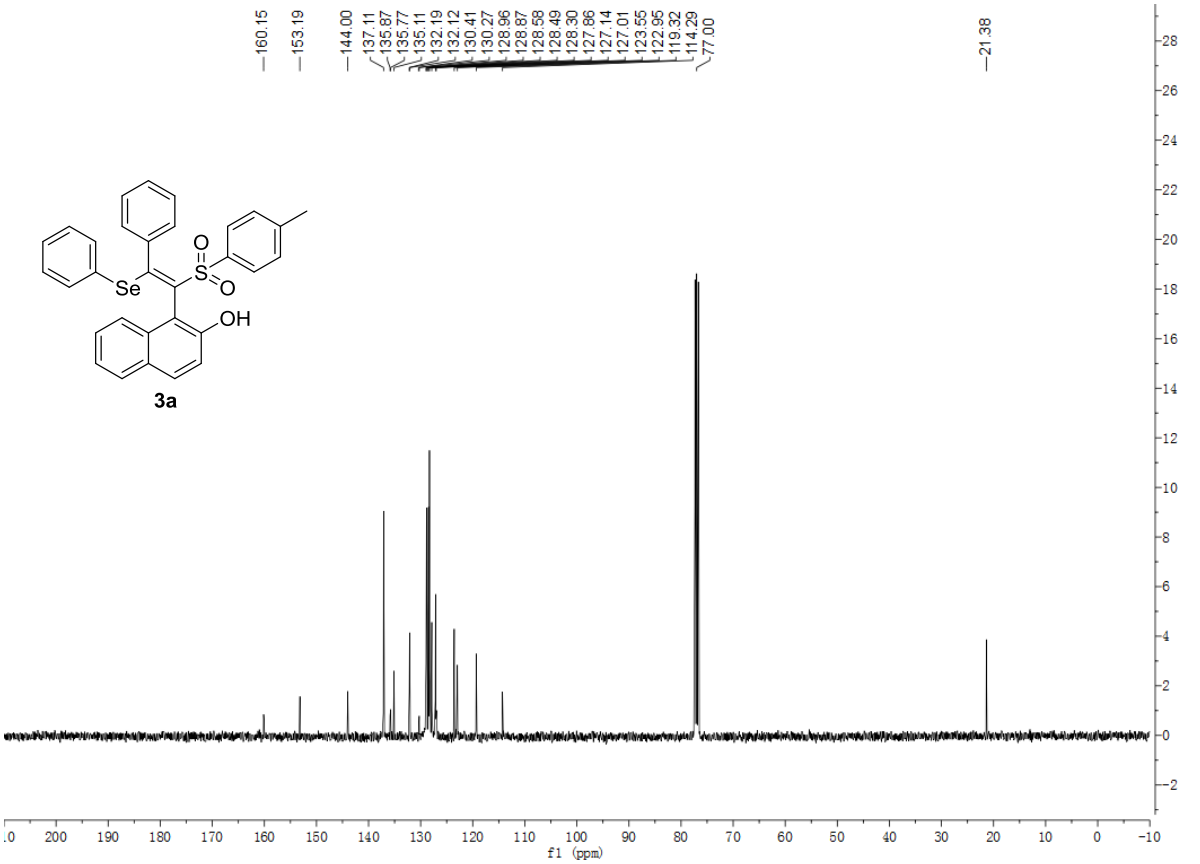
f1 (ppm)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127.86
127.14
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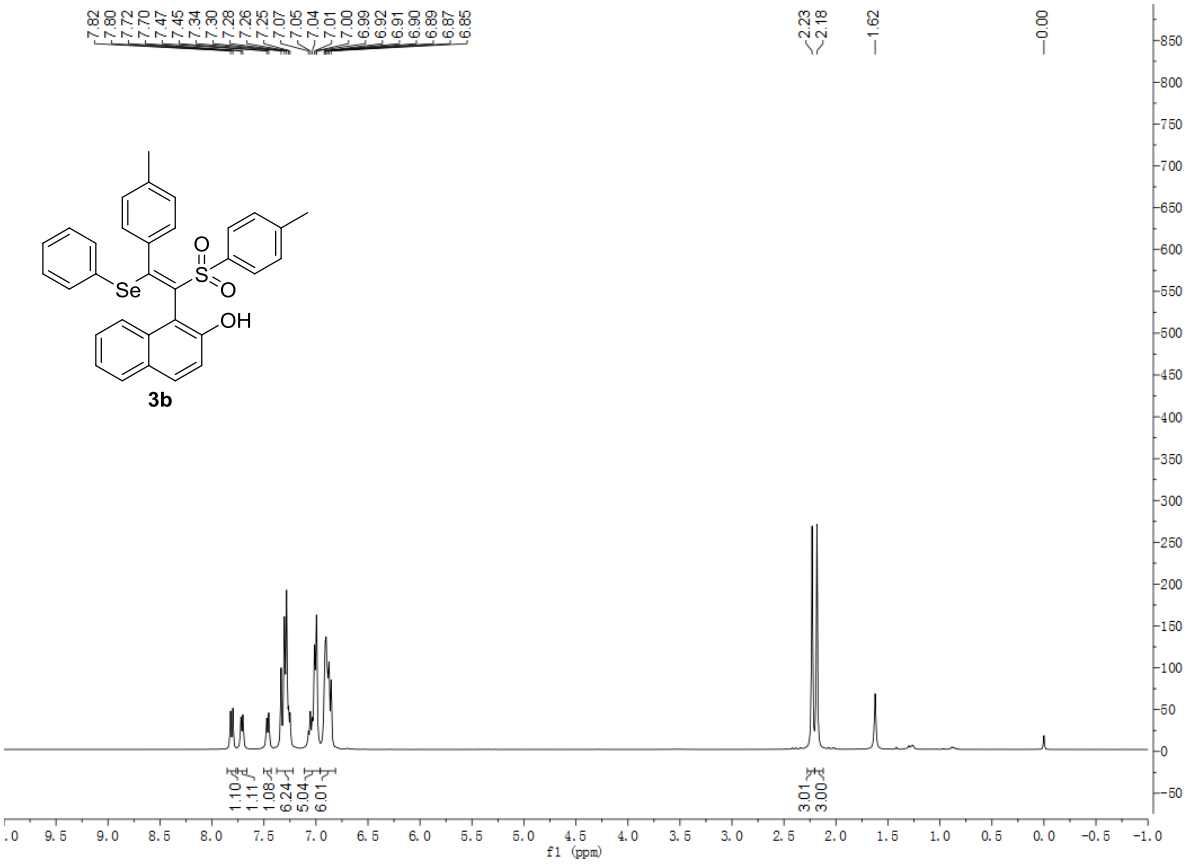
O
OH
3a
f1 (ppm)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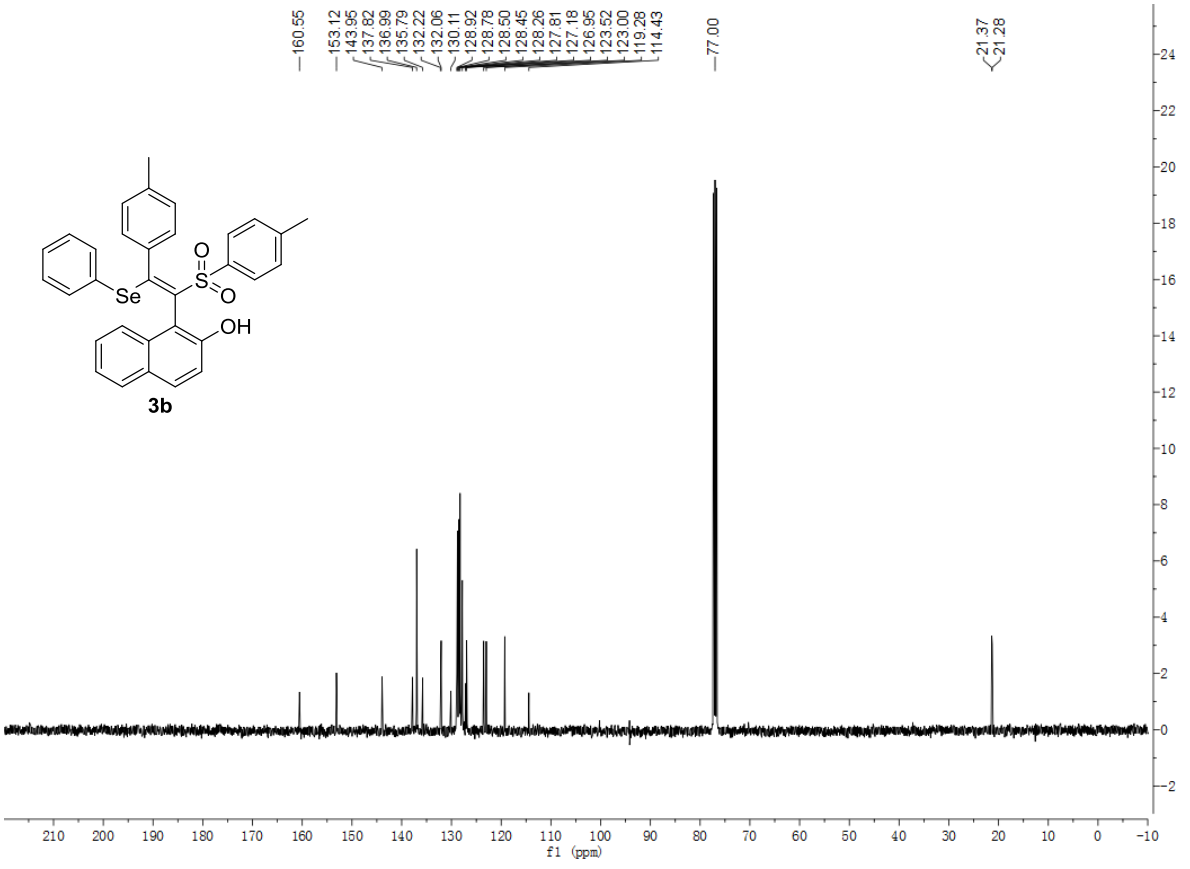
f1 (ppm)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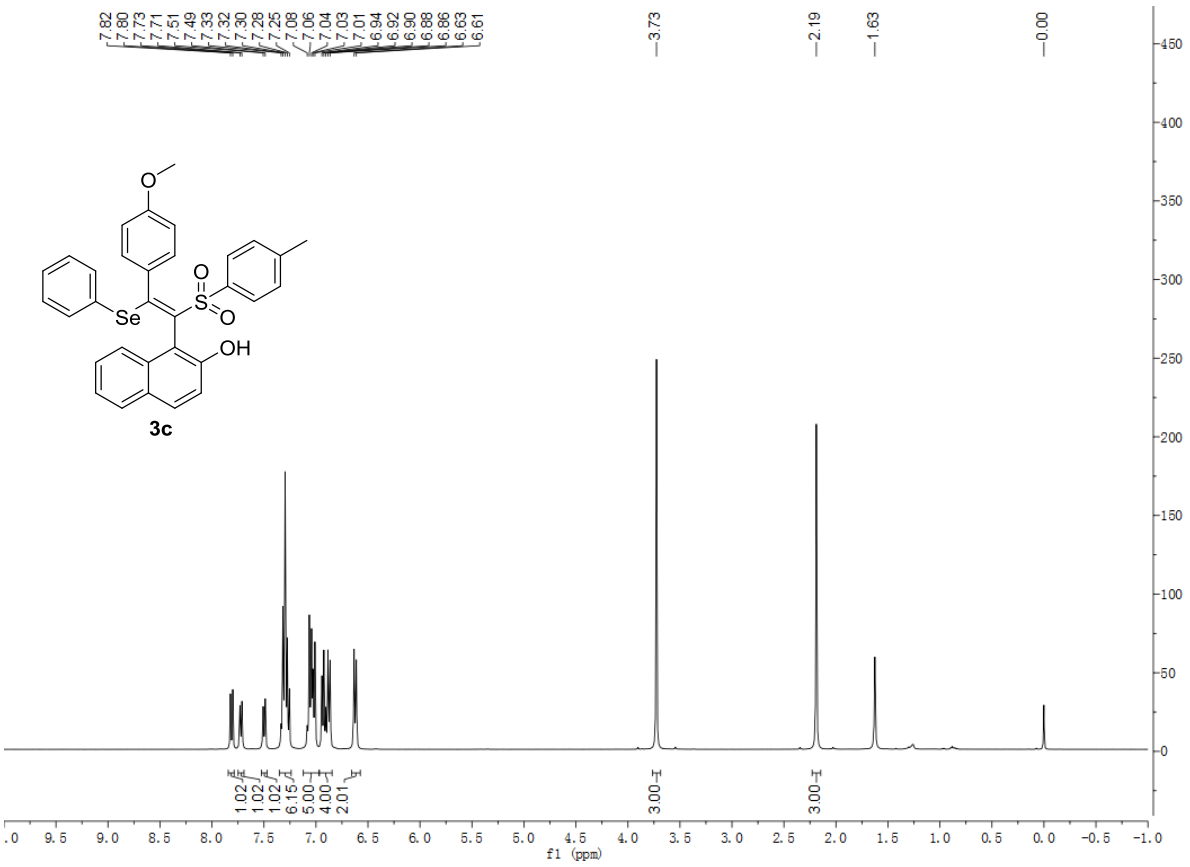
O
OH
3b
f1 (ppm)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S
O
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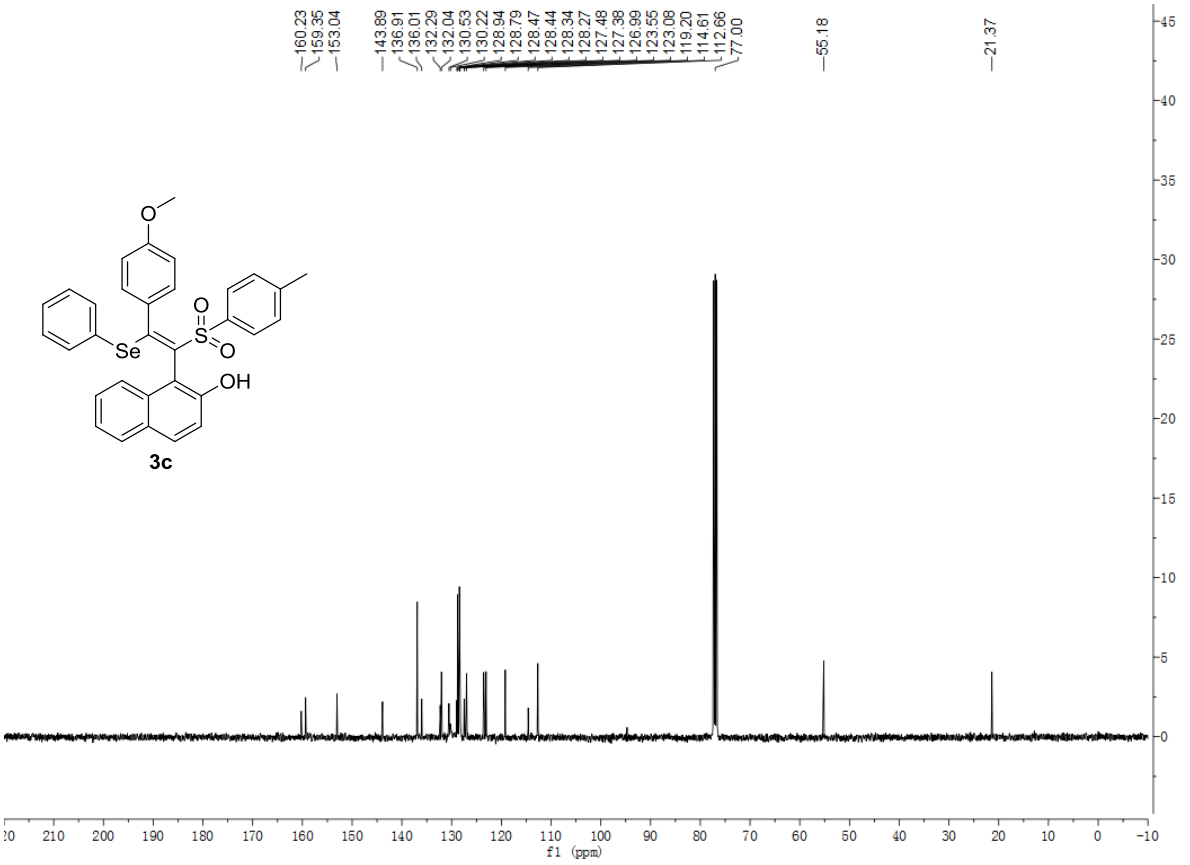
3.00
f1 (ppm)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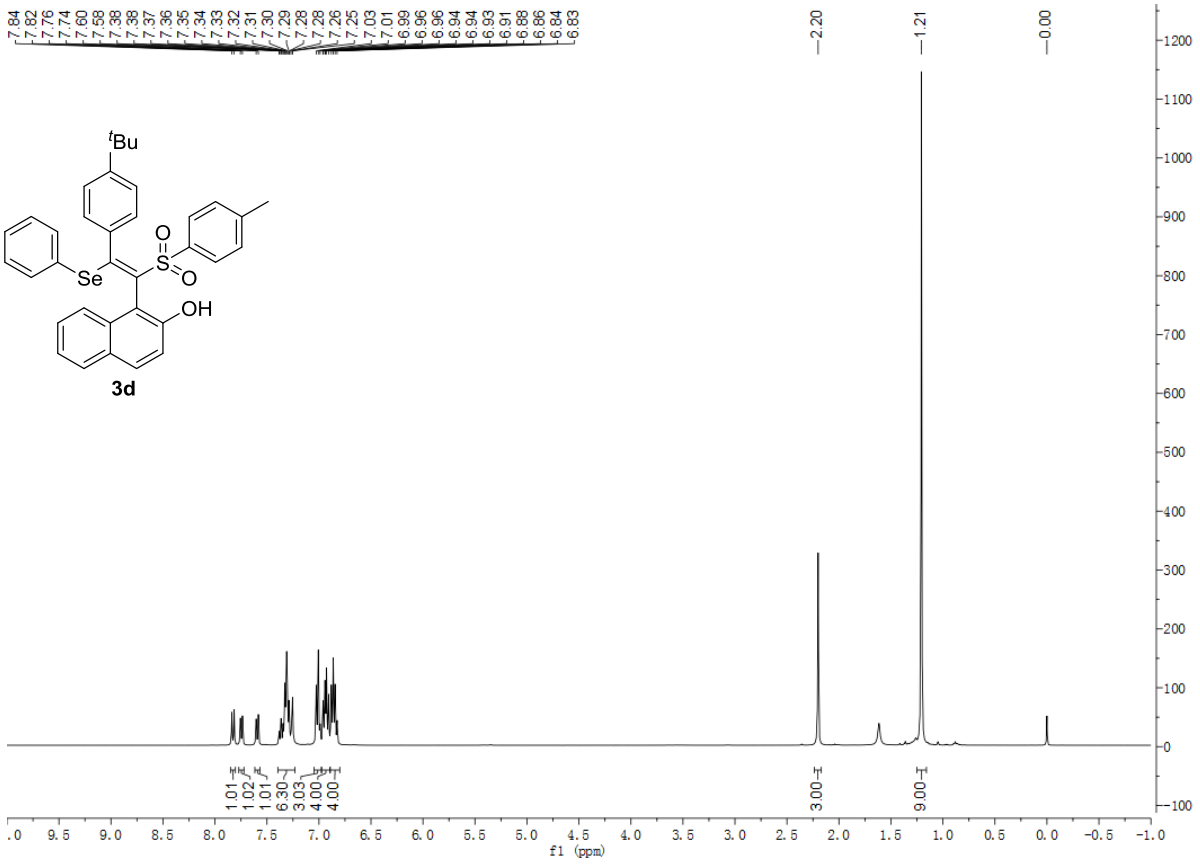
f1 (ppm)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7.25
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7.01
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6.94
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6.91
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6.86
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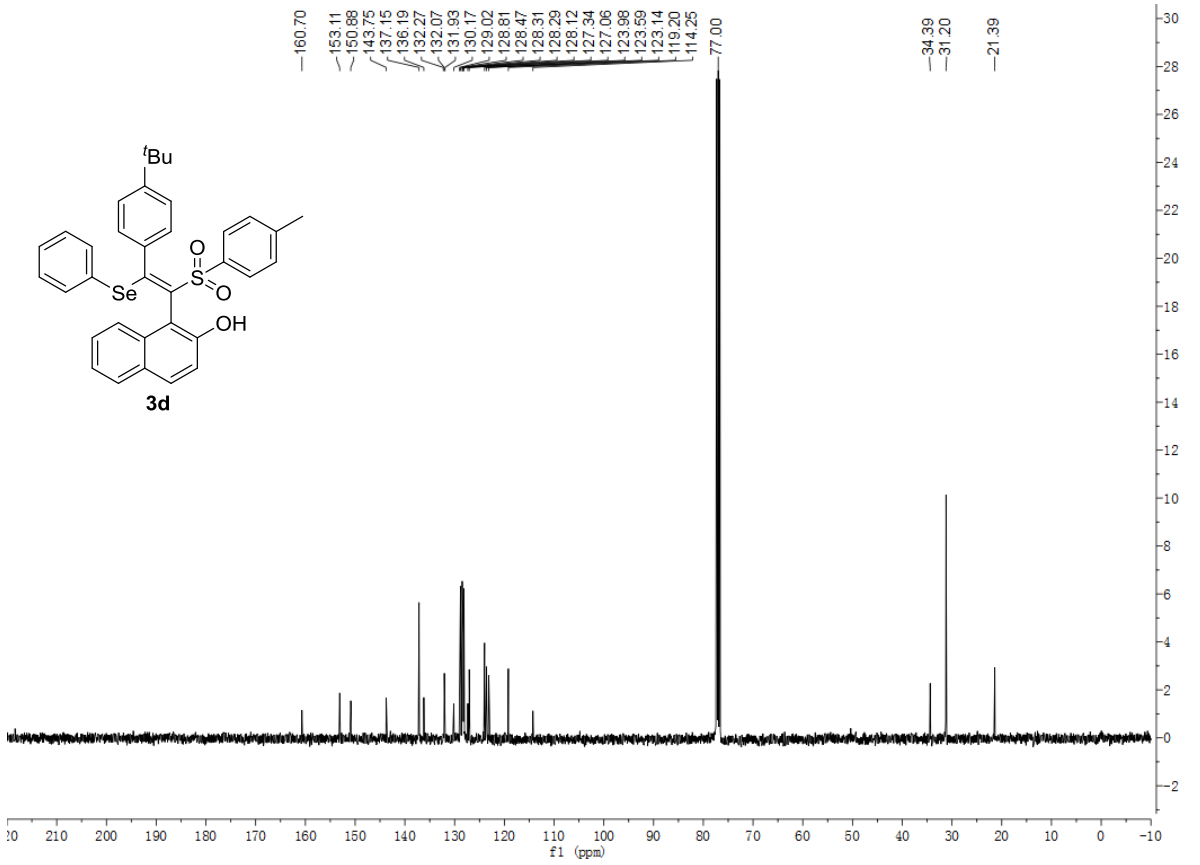
f1 (ppm)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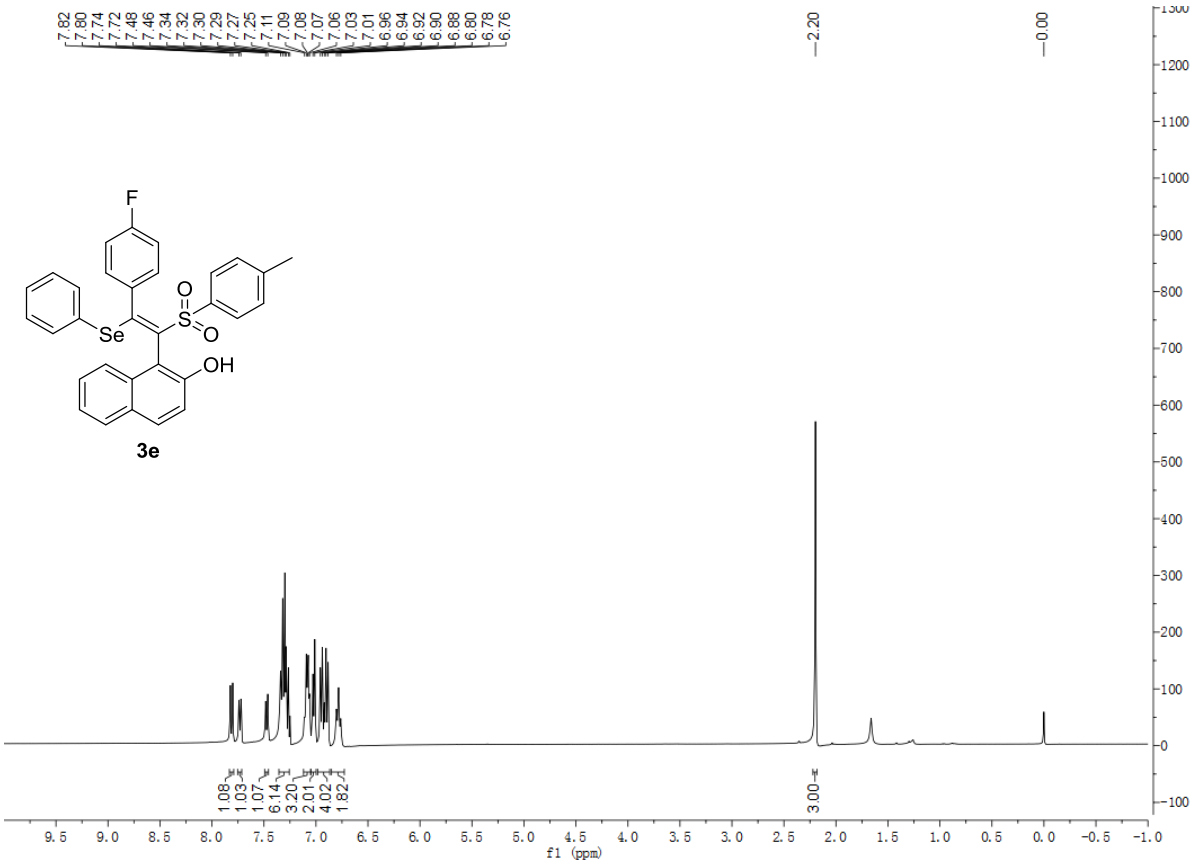
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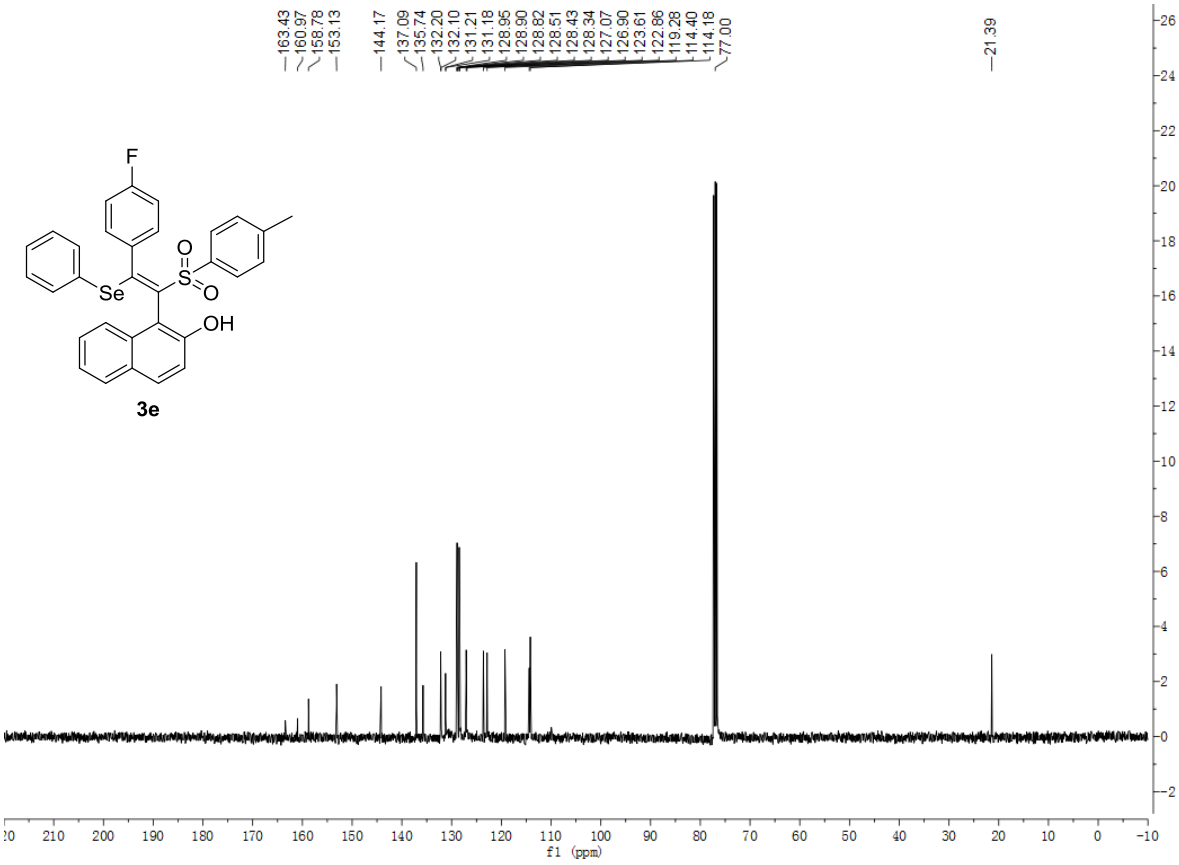
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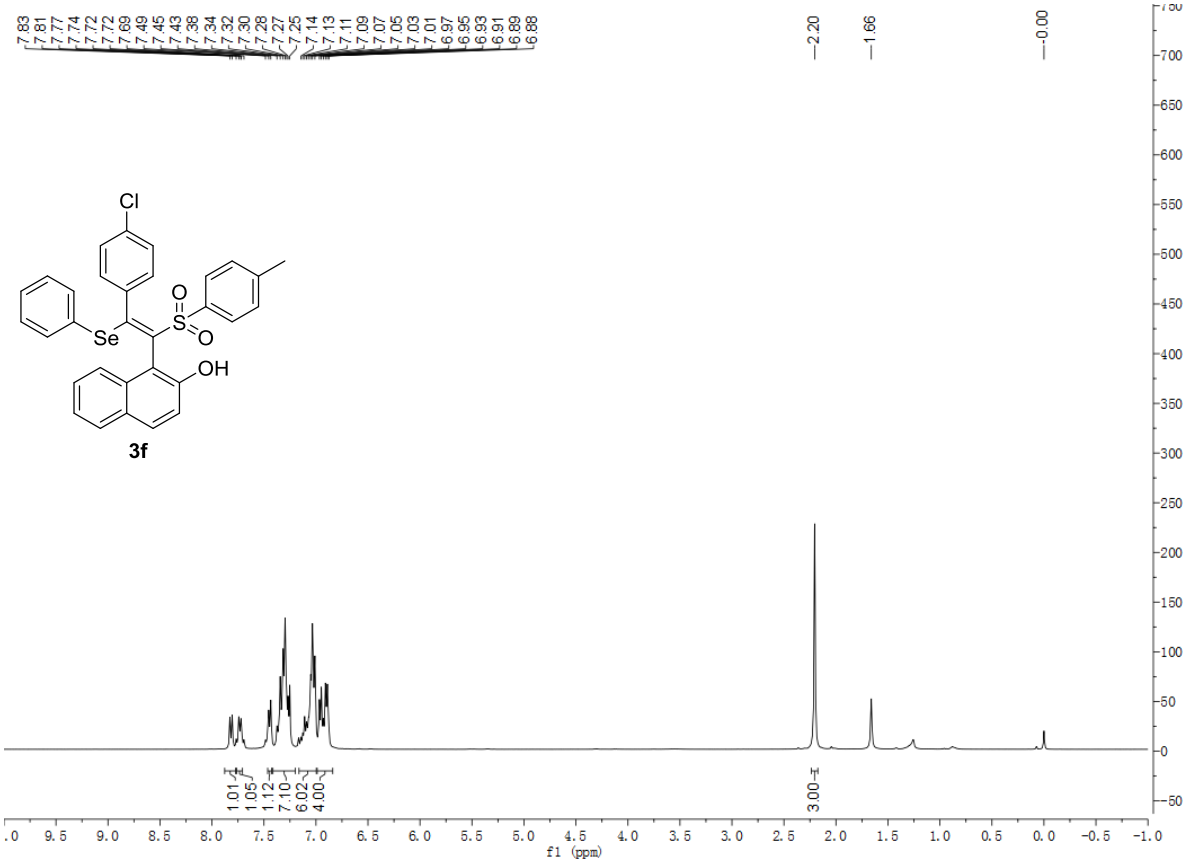
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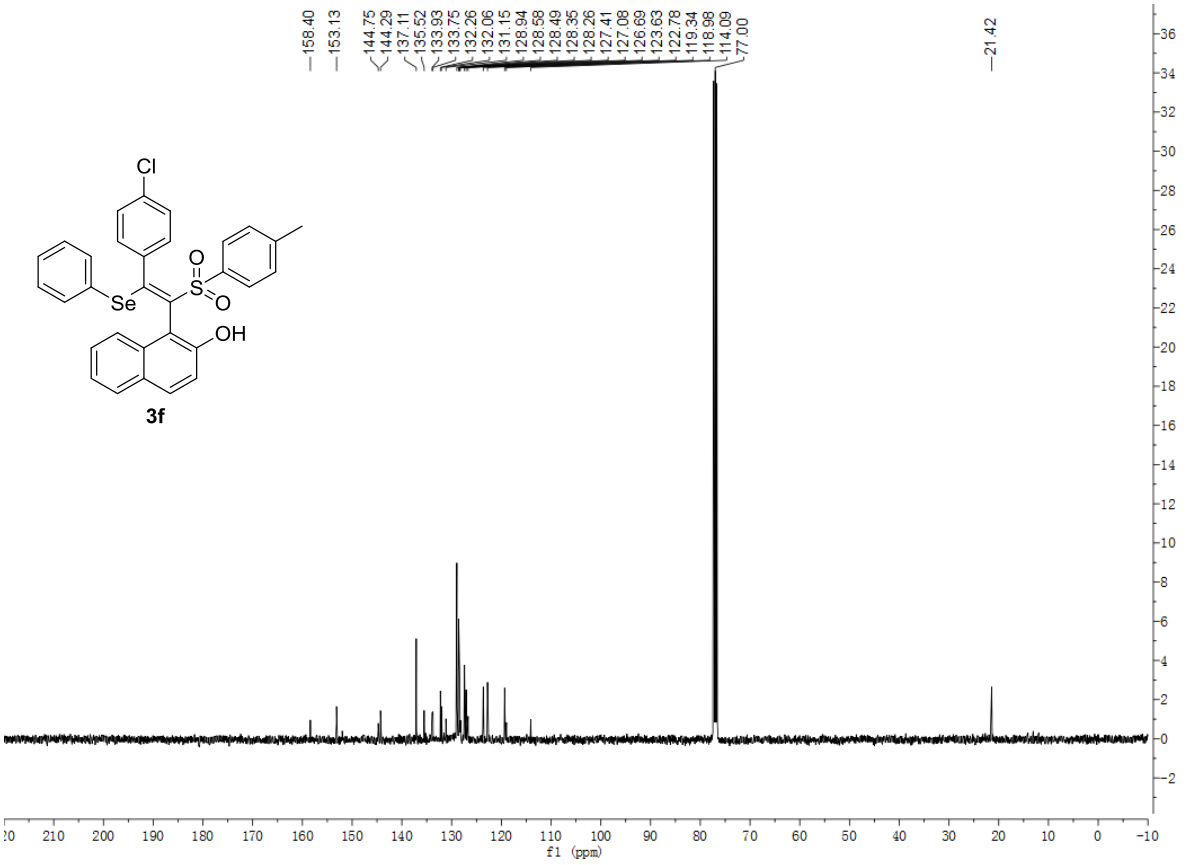
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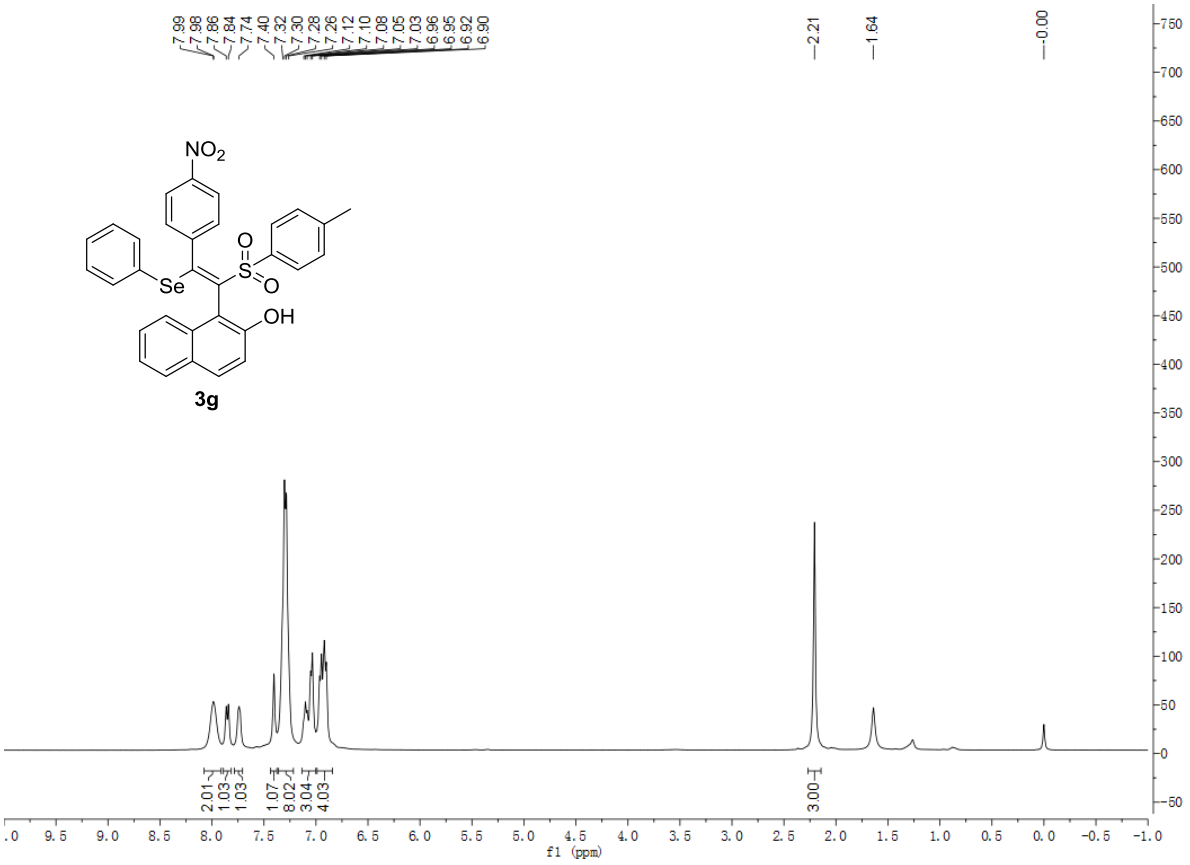
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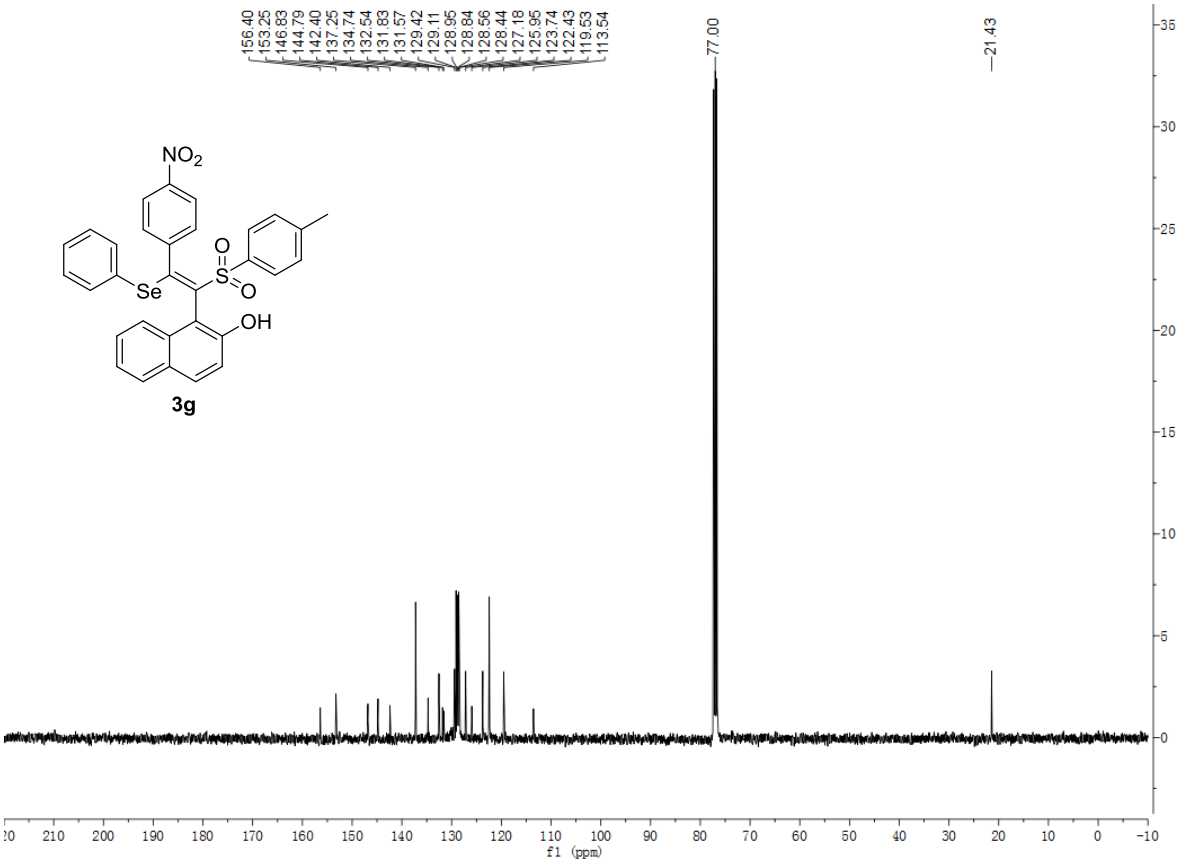
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S
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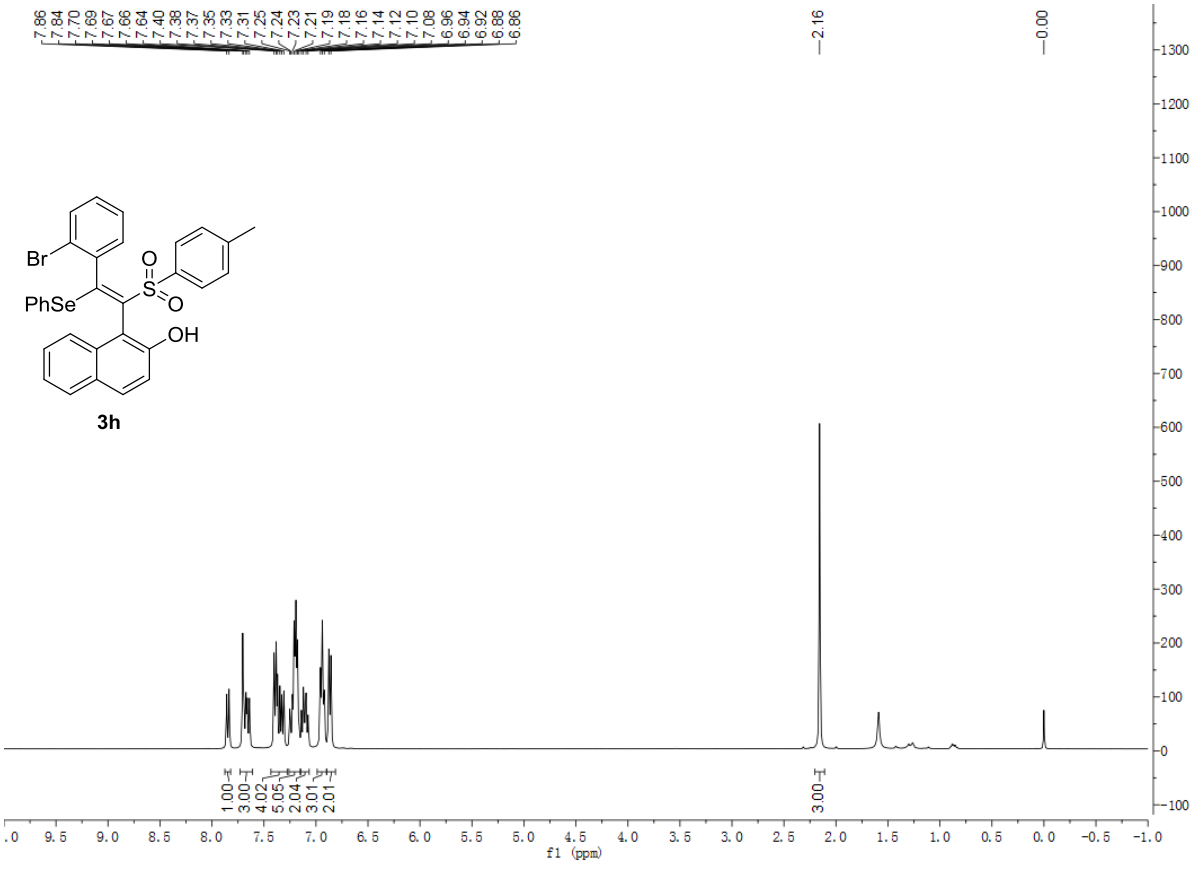
3g
f1 (ppm)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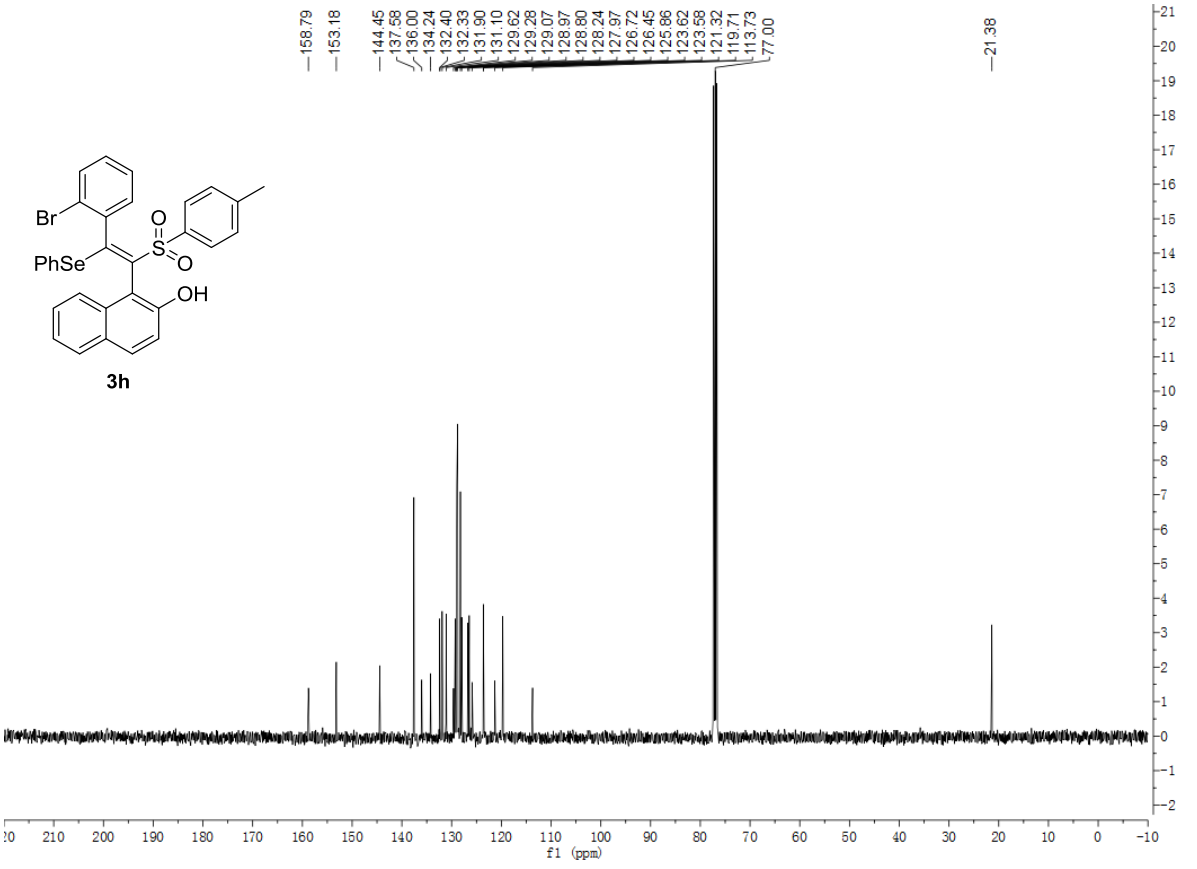
f1 (ppm)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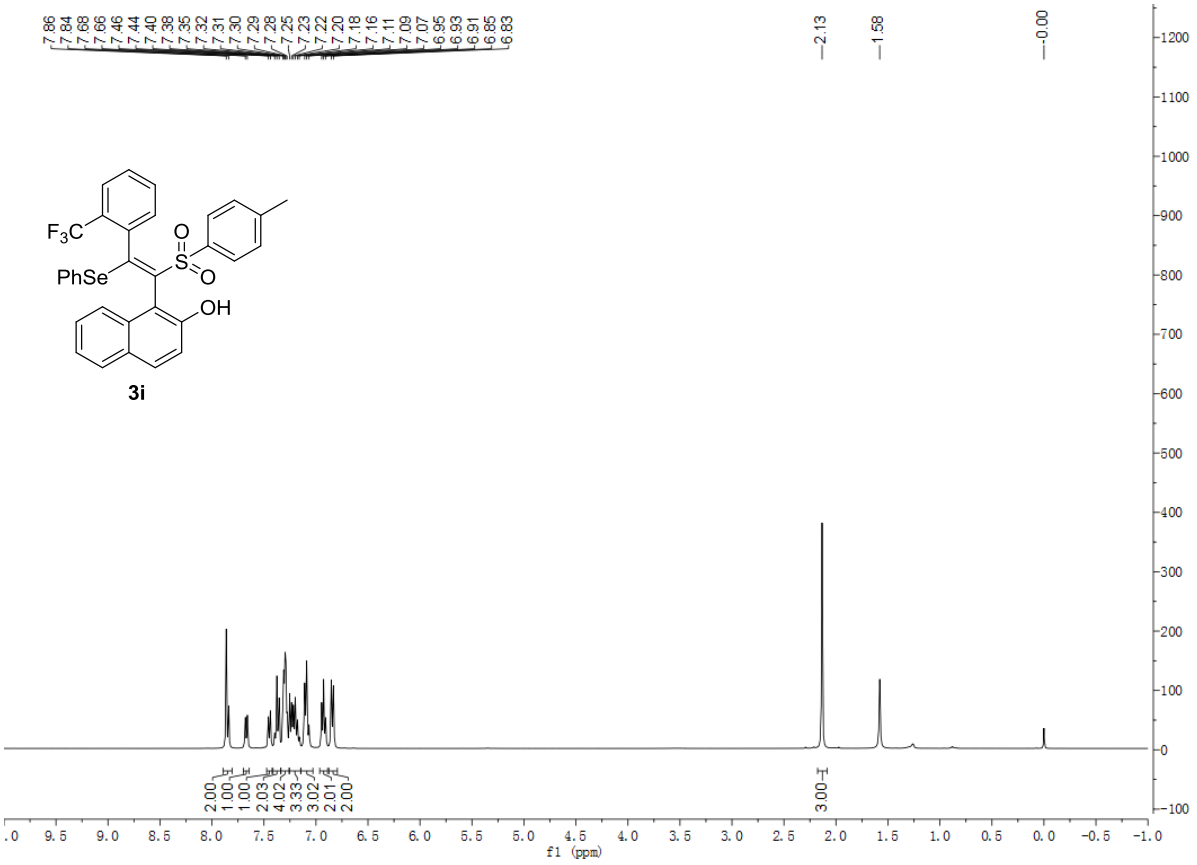
O
OH
3h
f1 (ppm)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7.07
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6.93
6.91
6.85
6.83
2.13
1.58
0.00
F3C
O
S
O
PhSe
OH
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2.01
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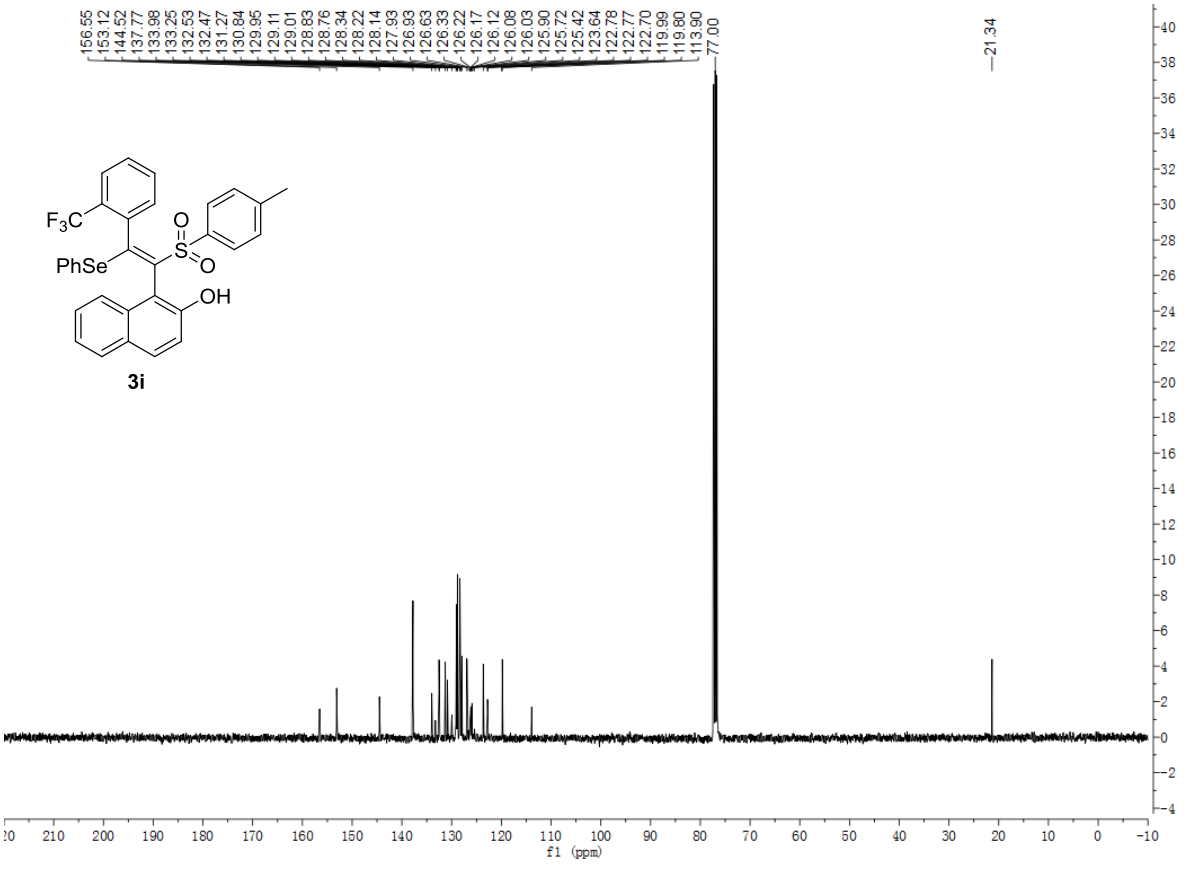
f1 (ppm)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126.12
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125.42
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122.77
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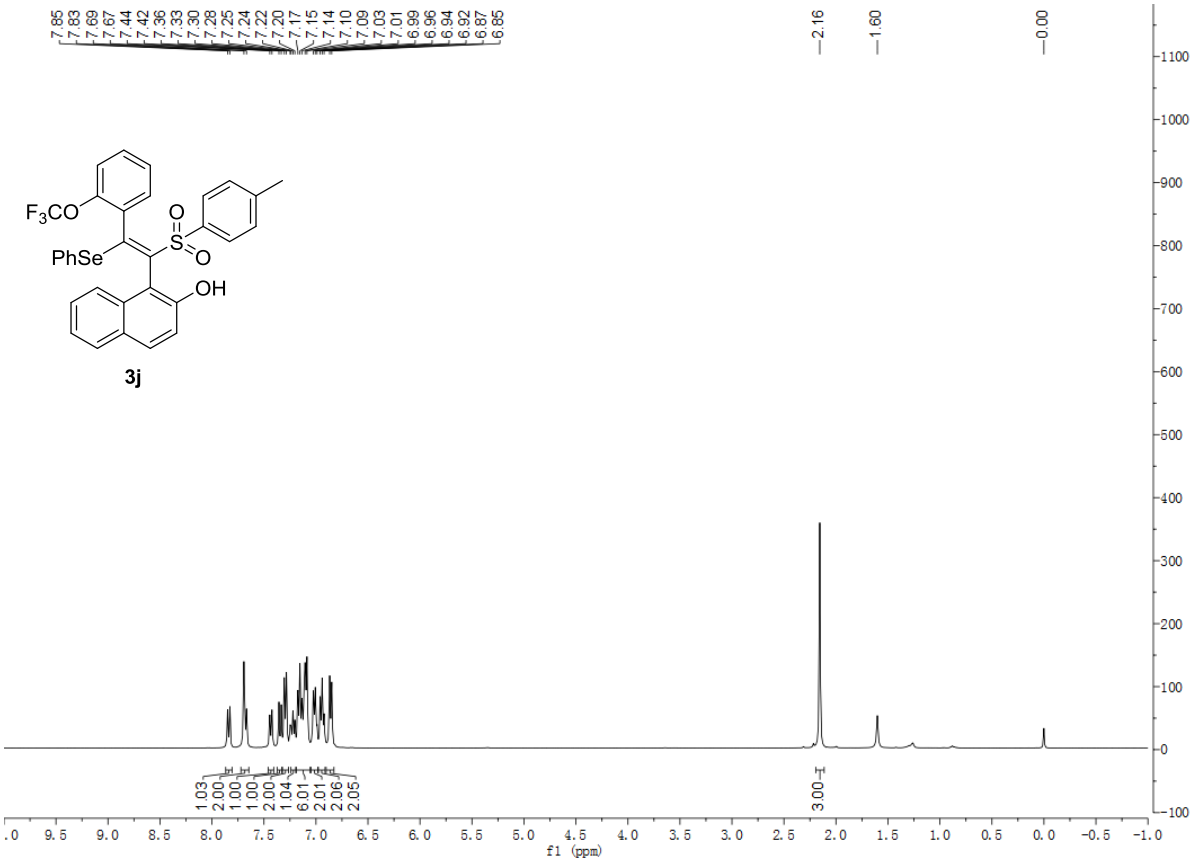
O
S
O
PhSe
OH
3i
f1 (ppm)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7.10
7.09
7.03
7.01
6.99
6.96
6.94
6.92
6.87
6.85
2.16
1.60
0.00
F3CO
PhSe
O
S
O
OH
3j
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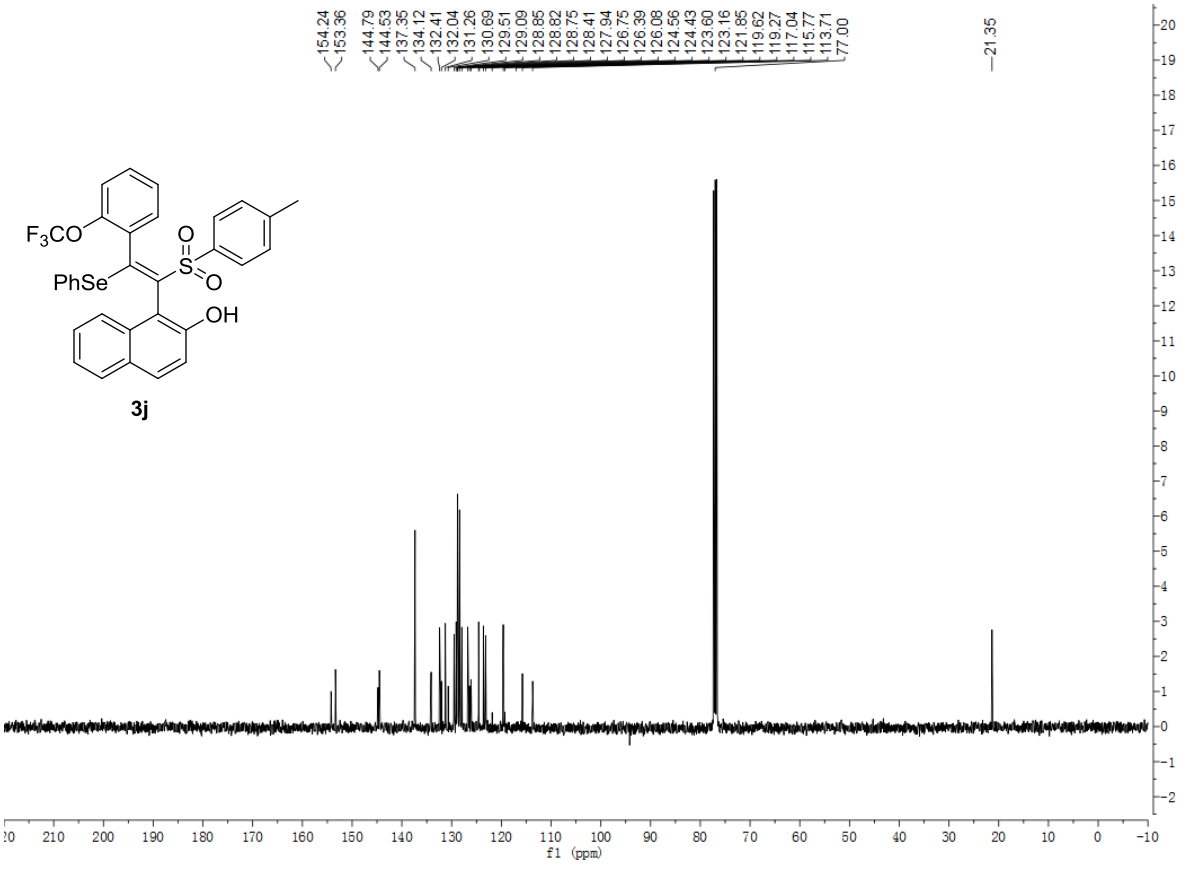
f1 (ppm)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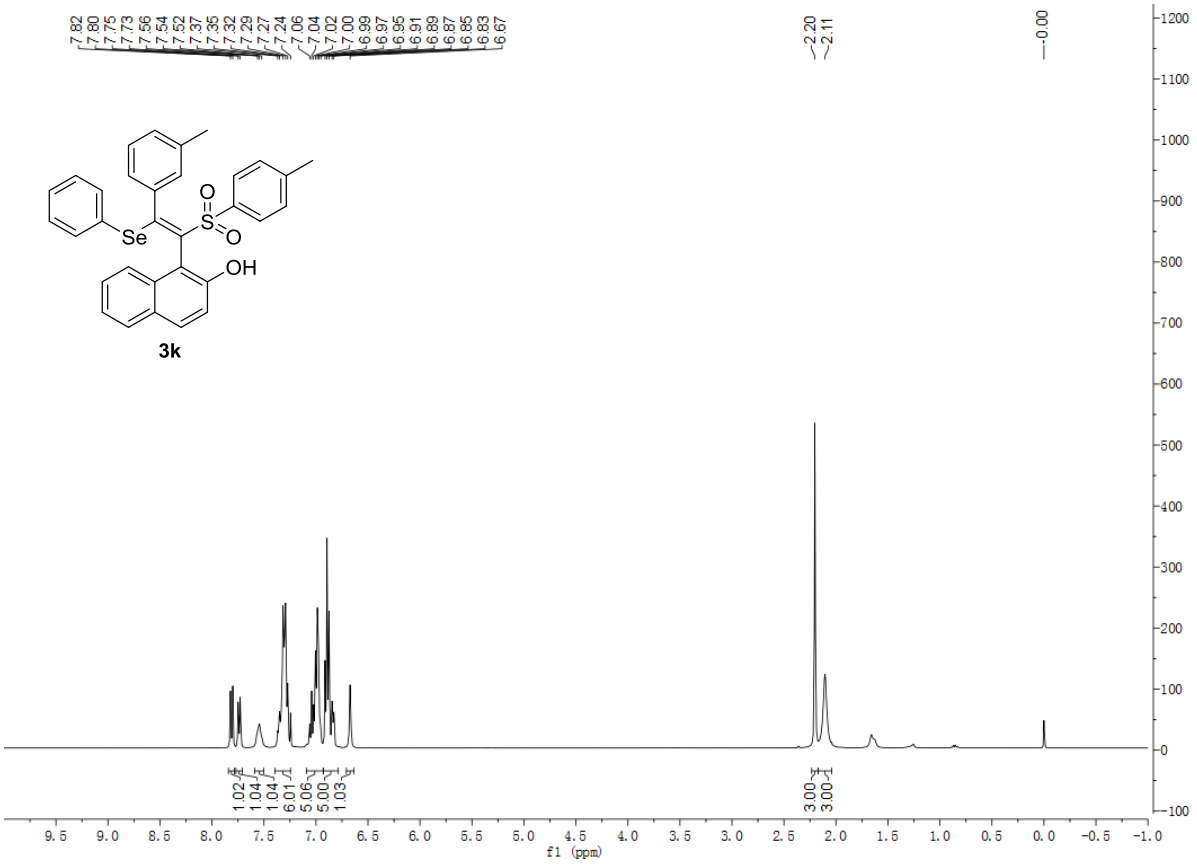
PhSe
O
S
O
OH
3j
f1 (ppm)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7.06
7.04
7.02
7.00
6.99
6.97
6.95
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6.89
6.87
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6.83
6.67
2.20
2.11
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Se
O
S
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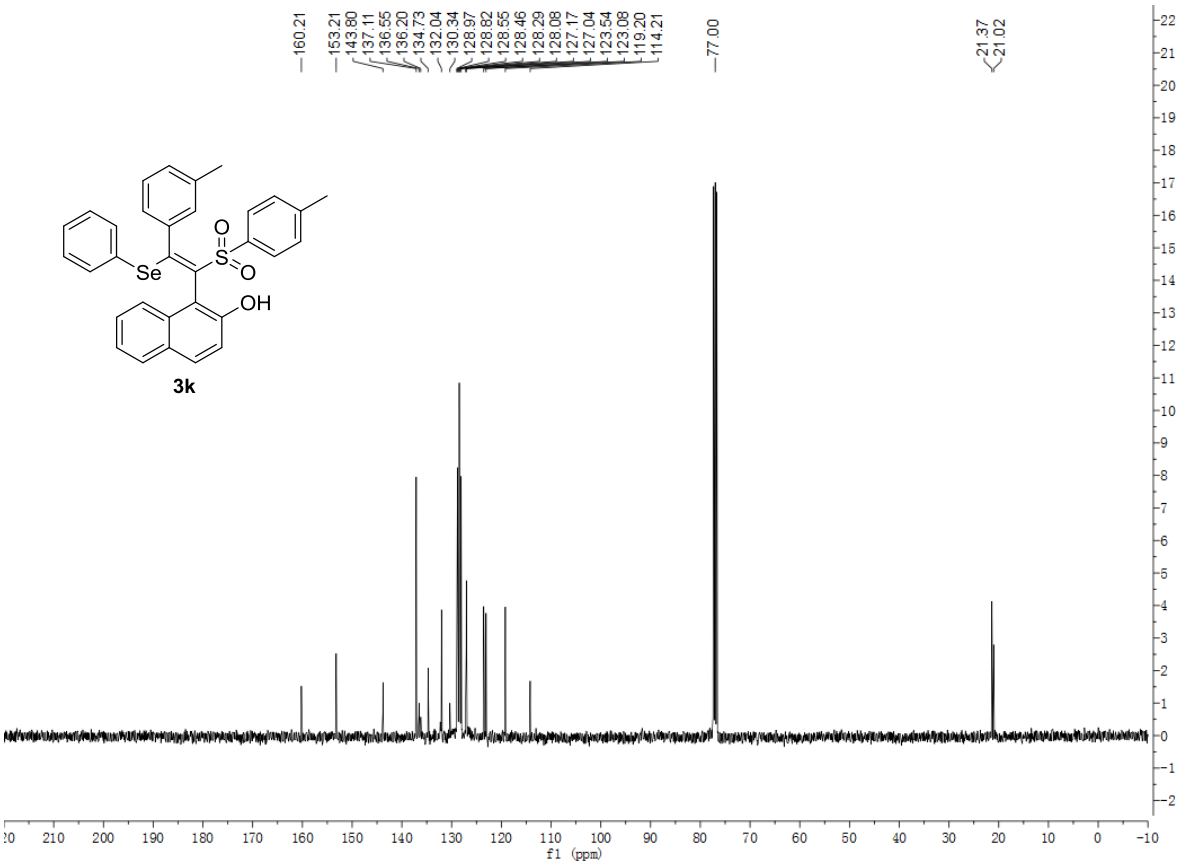
3.00
f1 (ppm)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128.08
127.17
127.04
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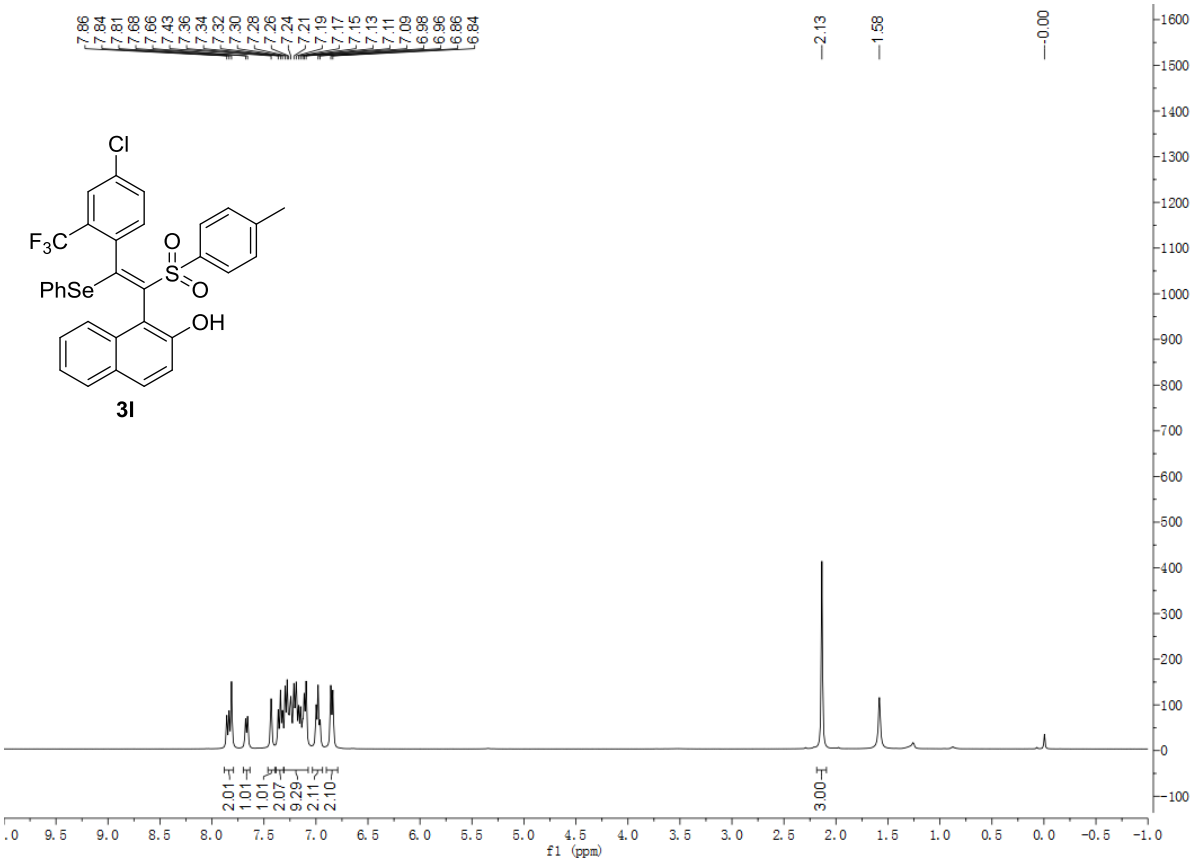
Se
O
S
O
OH
3k
f1 (ppm)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7.19
7.17
7.15
7.13
7.11
7.09
6.98
6.96
6.86
6.84
2.13
1.58
0.00
Cl
F3C
O
S
O
PhSe
OH
3l
2.01
1.01
1.01
2.07
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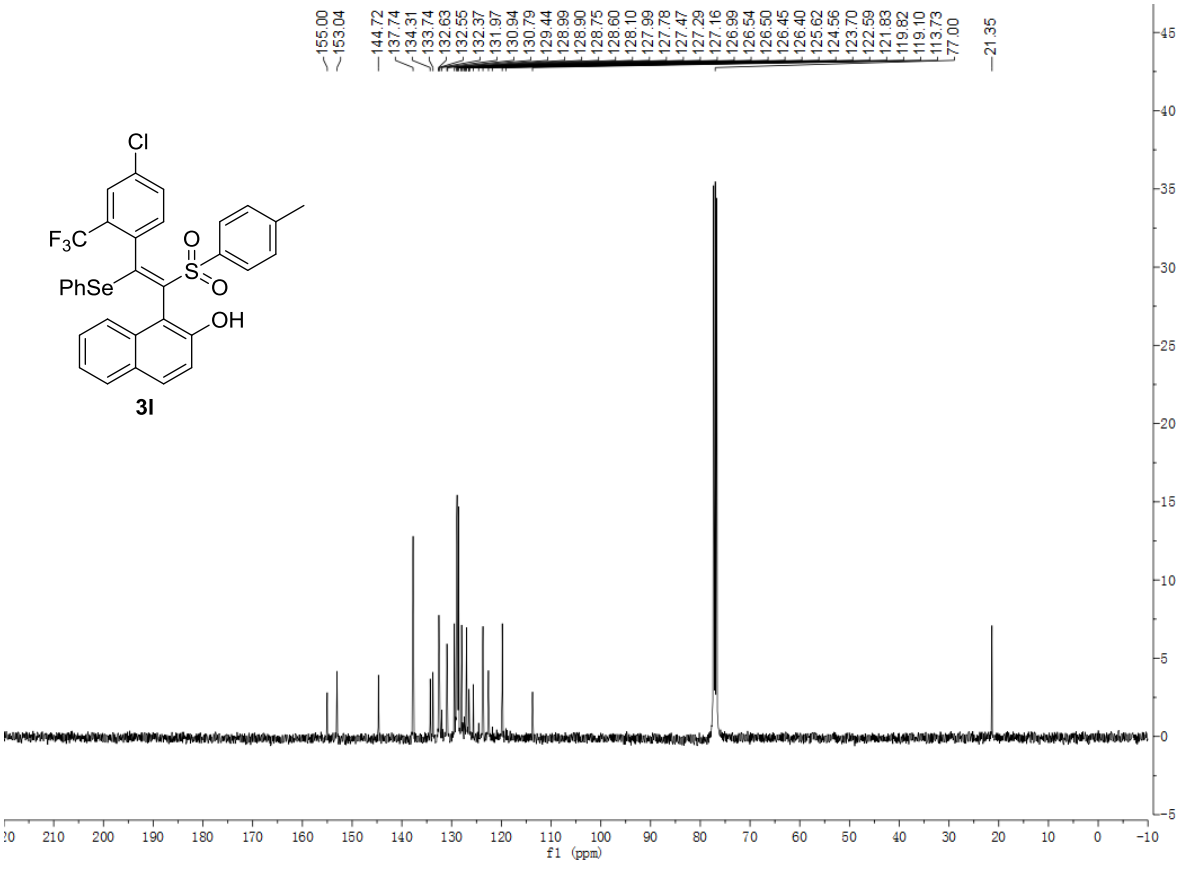
2.11
2.10
3.00
f1 (ppm)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128.75
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128.10
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126.45
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124.56
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122.59
121.83
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77.00
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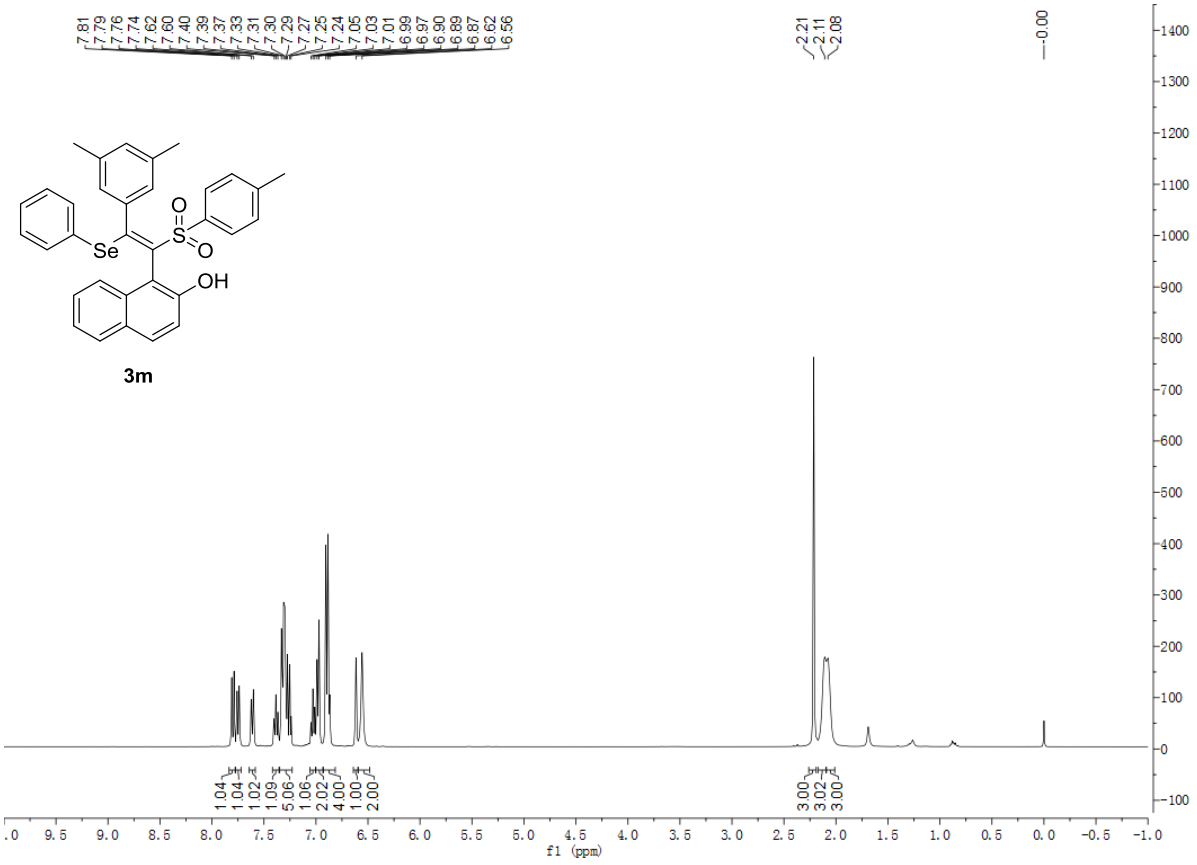
Cl
F3C
O
S
O
PhSe
OH
3l
f1 (ppm)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7.27
7.25
7.24
7.05
7.03
7.01
6.99
6.97
6.90
6.89
6.87
6.62
6.56
2.21
2.11
2.08
0.00
Se
O
S
O
OH
3m
1.04
1.04
1.02
1.09
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1.06
2.02
4.00
1.00
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3.00
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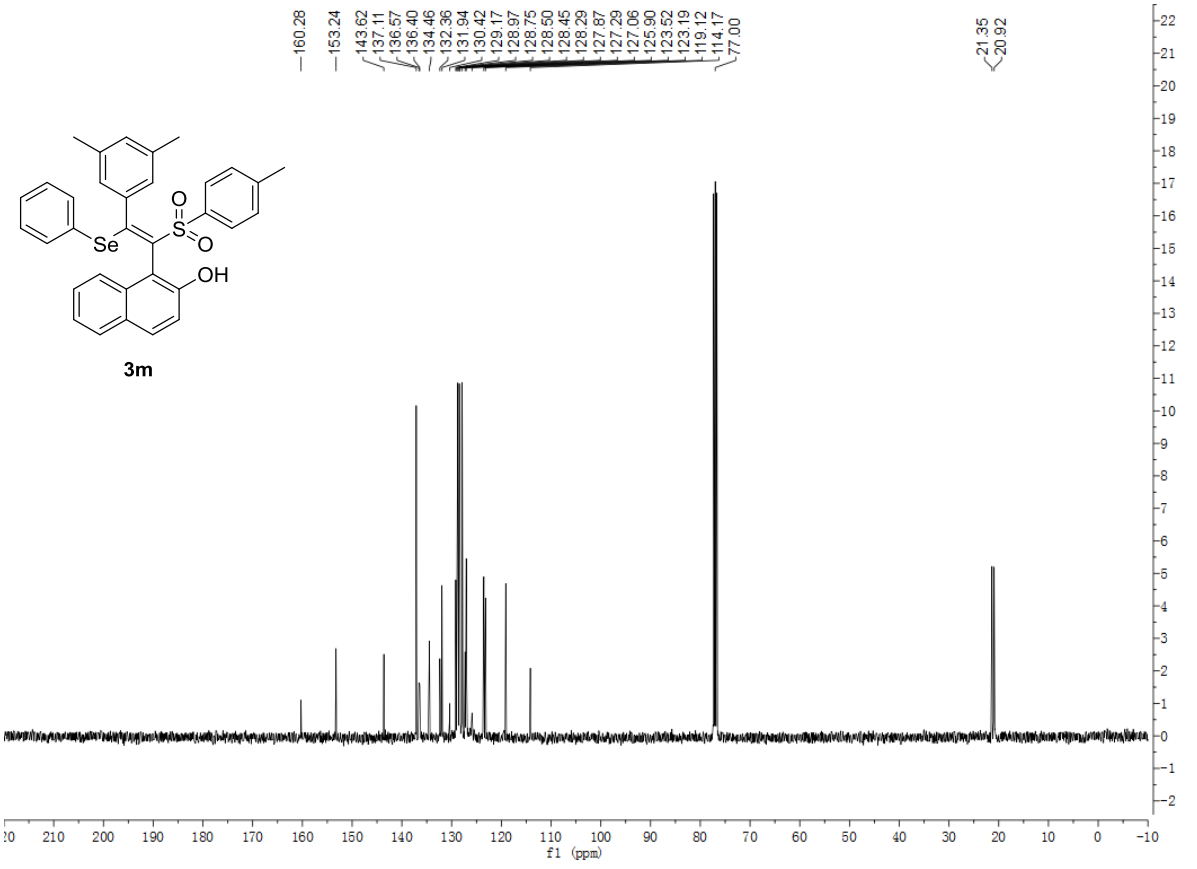
3.00
f1 (ppm)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127.29
127.06
125.90
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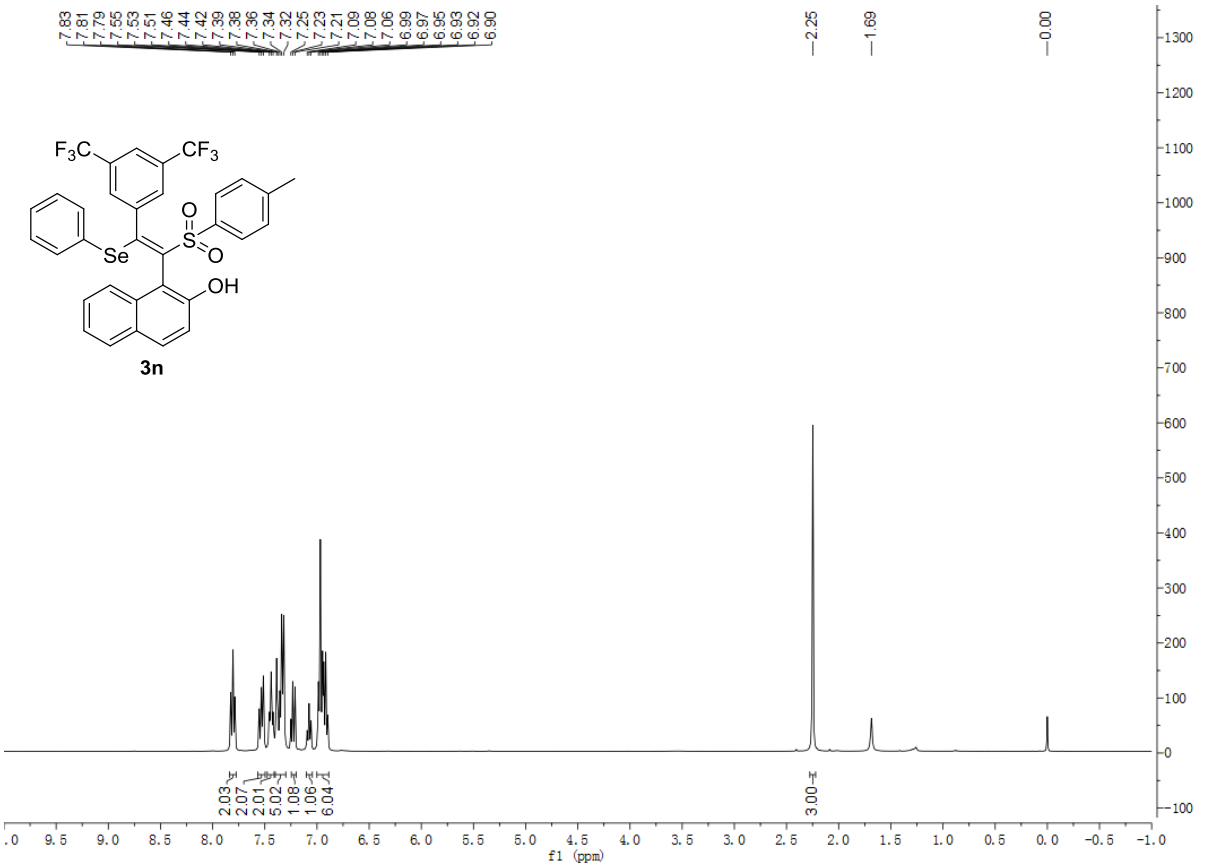
O
S
O
OH
3m
f1 (ppm)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7.25
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7.09
7.08
7.06
6.99
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6.95
6.93
6.92
6.90
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F3C
CF3
O
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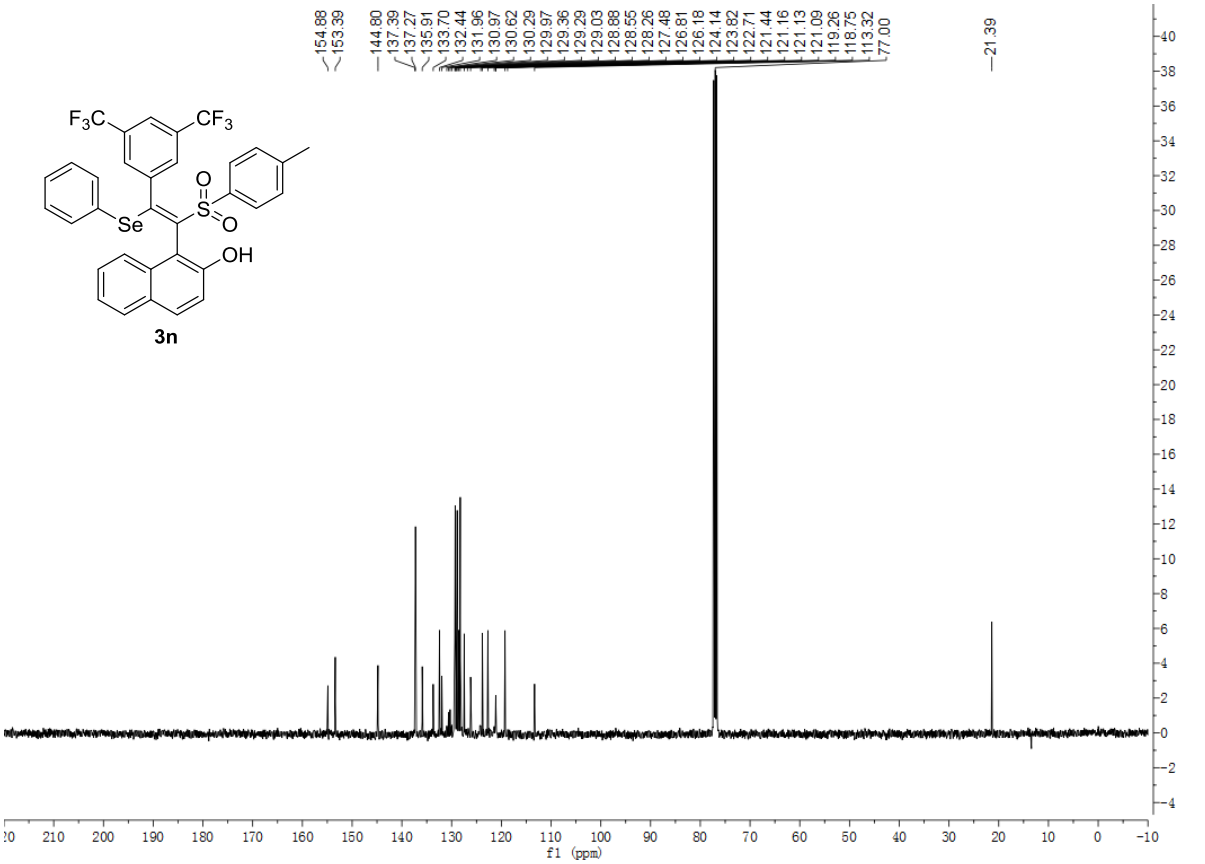
6.04
3.00
f1 (ppm)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121.44
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CF3
O
S
O
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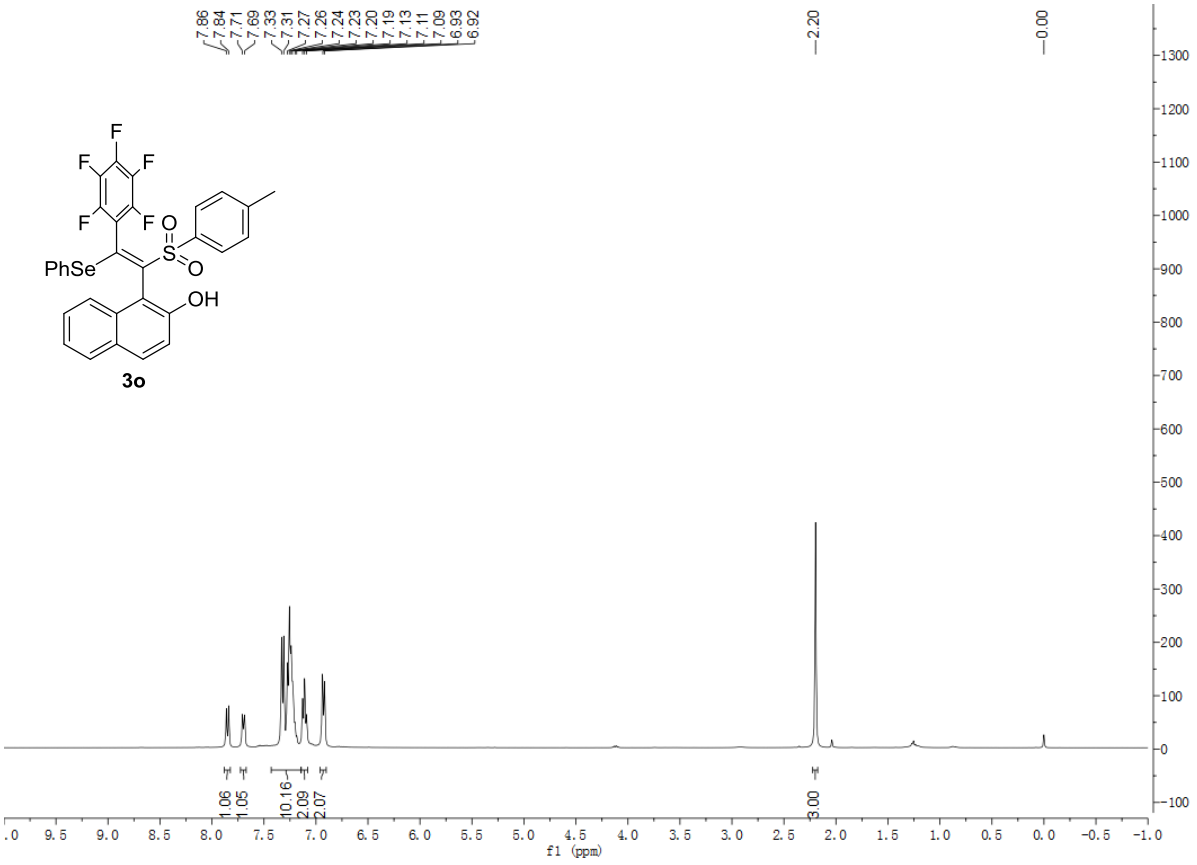
OH
3n
f1 (ppm)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7.11
7.09
6.93
6.92
2.20
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F
F
F
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OH
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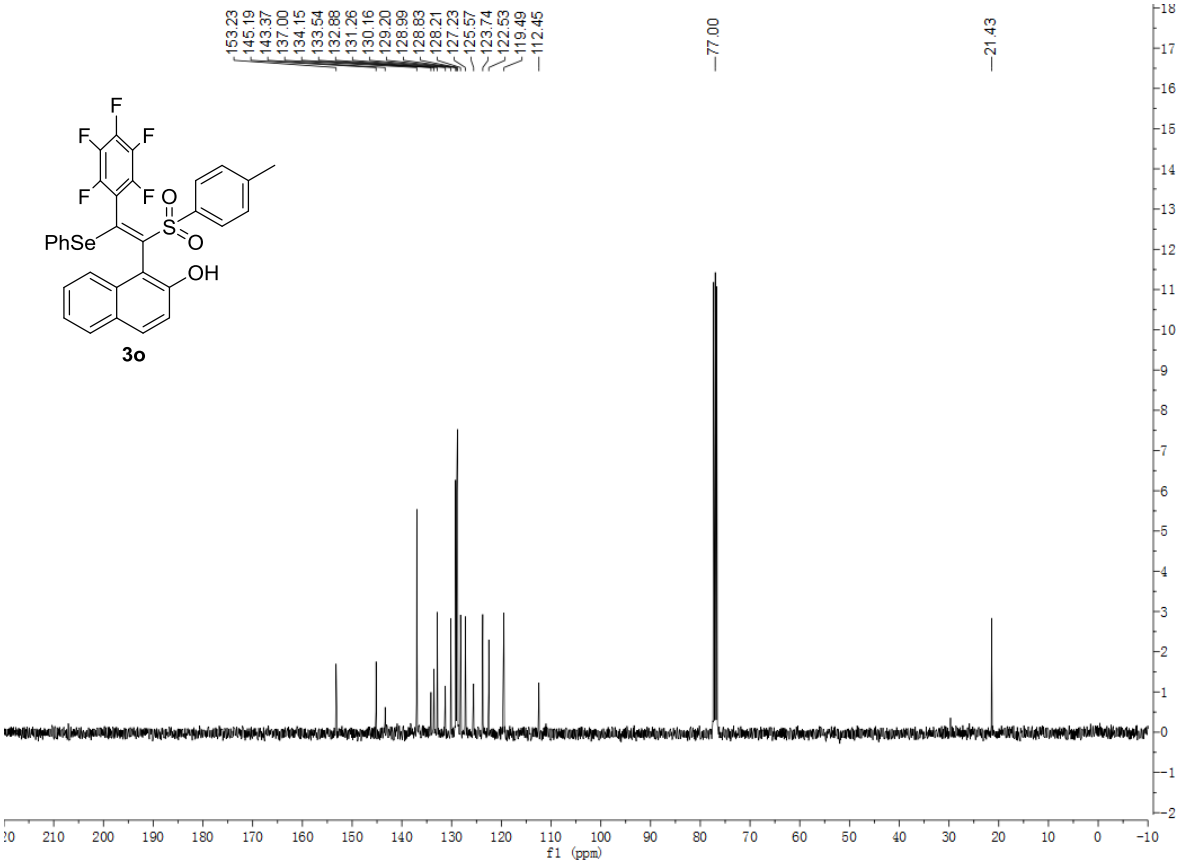
2.09
2.07
3.00
f1 (ppm)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123.74
122.53
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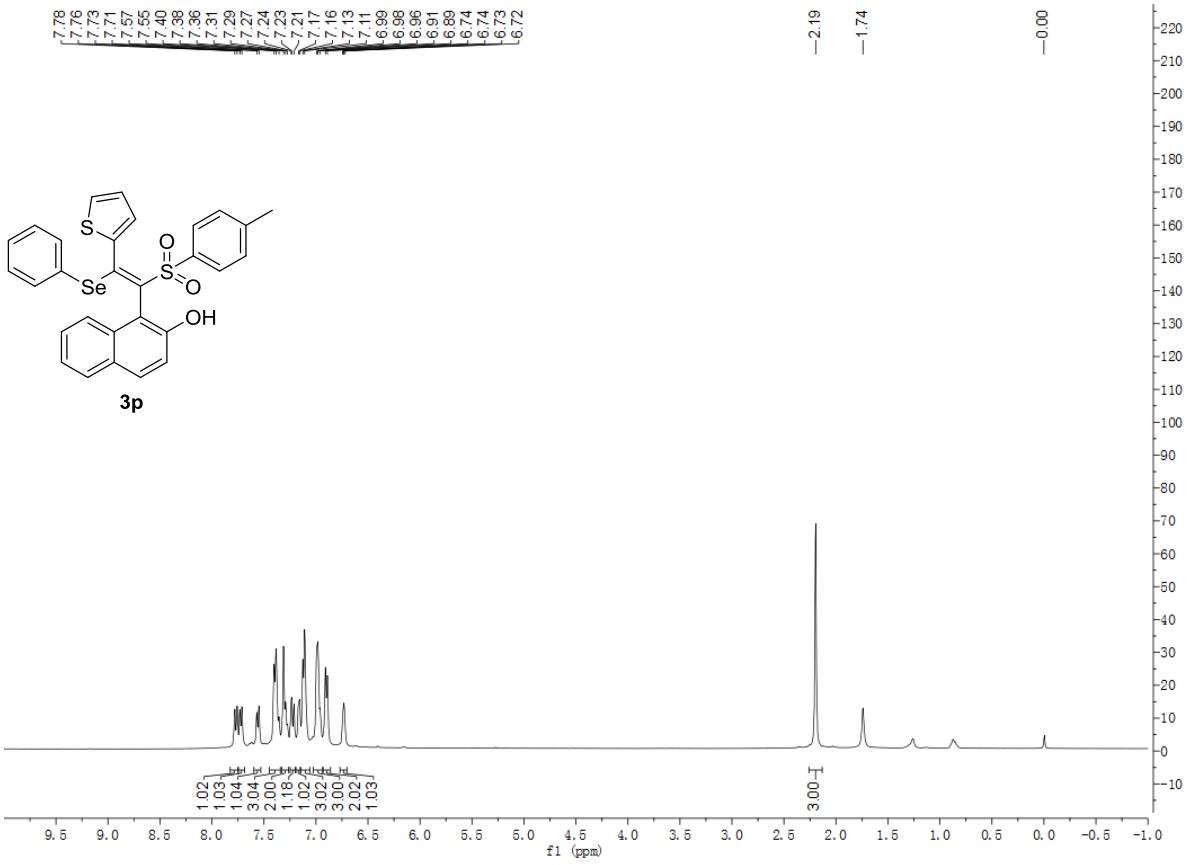
F
F
F
F
O
S
O
PhSe
OH
3o
f1 (ppm)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7.21
7.17
7.16
7.13
7.11
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6.98
6.96
6.91
6.89
6.74
6.74
6.73
6.72
2.19
1.74
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S
Se
O
S
O
OH
3p
1.02
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3.00
2.02
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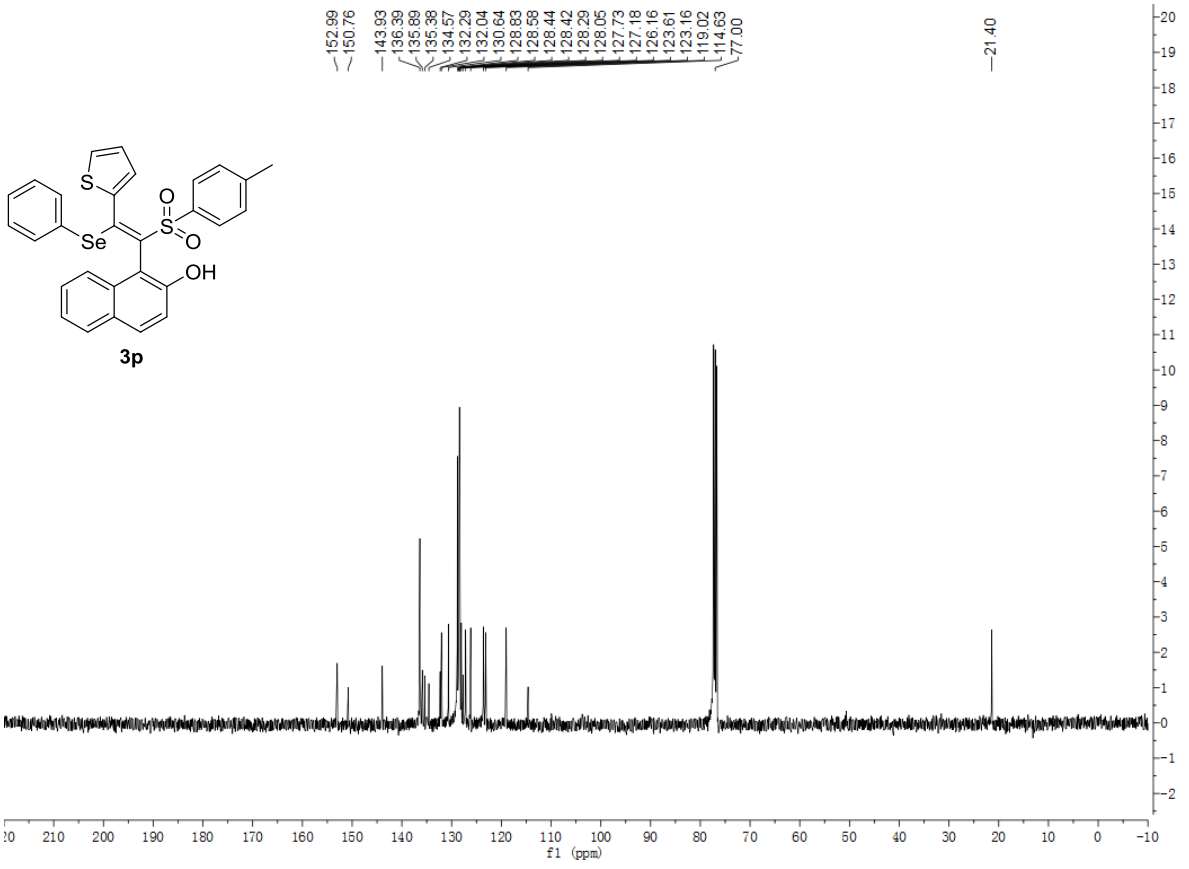
3.00
f1 (ppm)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126.16
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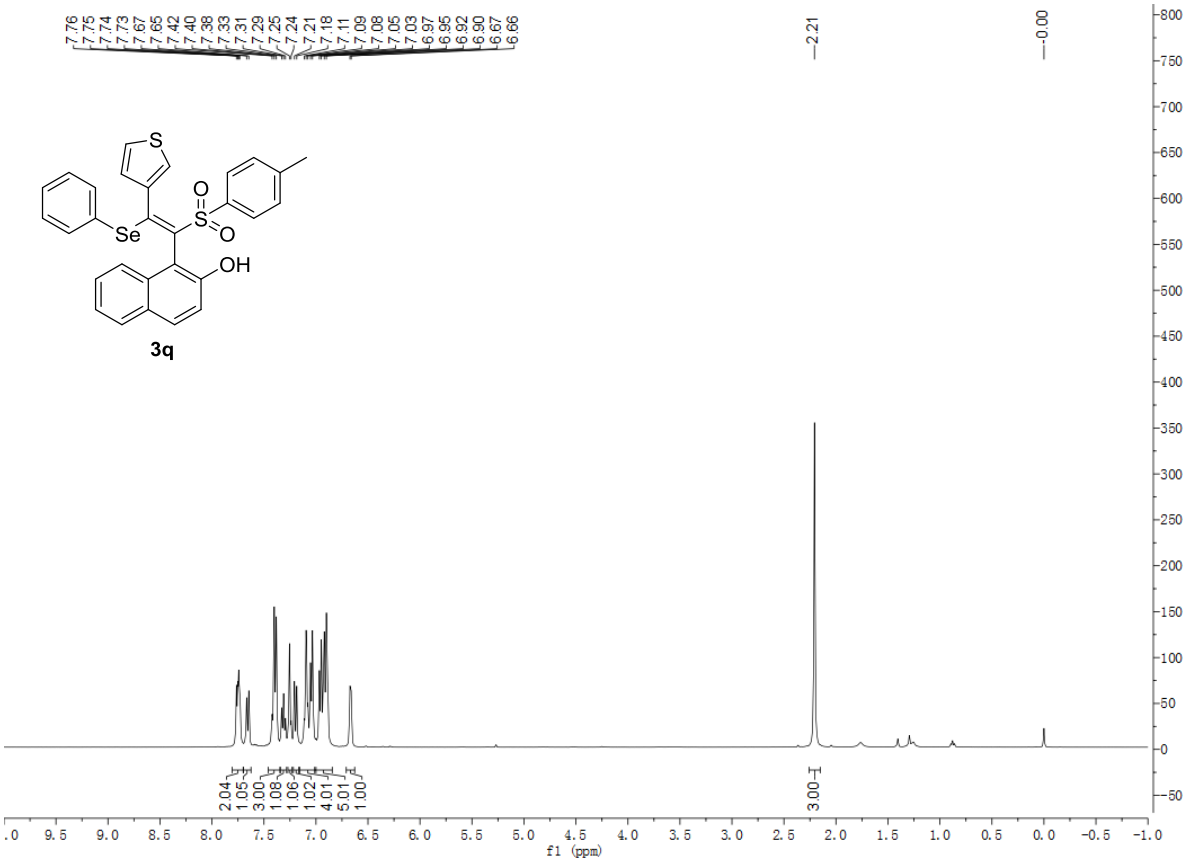
S
Se
O
S
O
OH
3p
f1 (ppm)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7.21
7.18
7.11
7.09
7.08
7.05
7.03
6.97
6.95
6.92
6.90
6.67
6.66
2.21
0.00
S
Se
O
S
O
OH
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3.00
1.08
1.06
1.02
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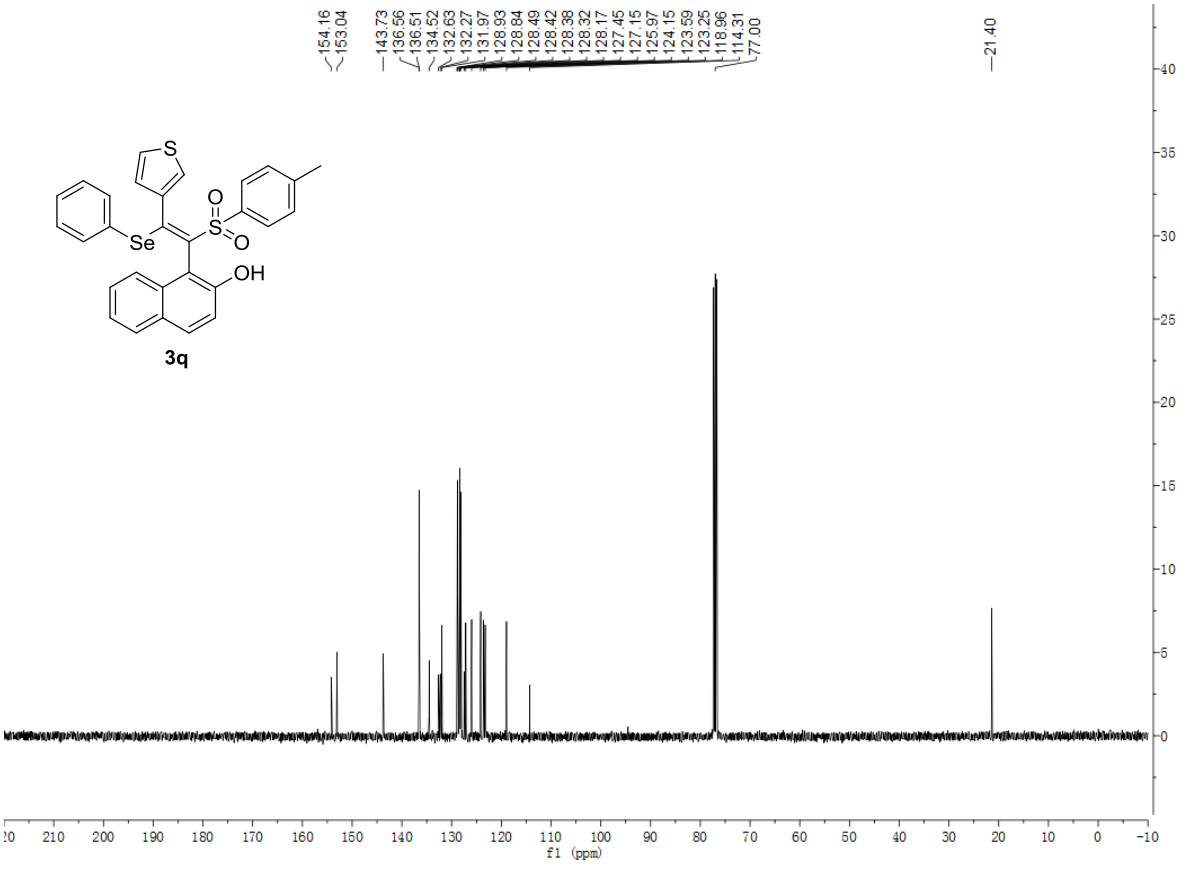
5.01
1.00
3.00
f1 (ppm)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127.45
127.15
125.97
124.15
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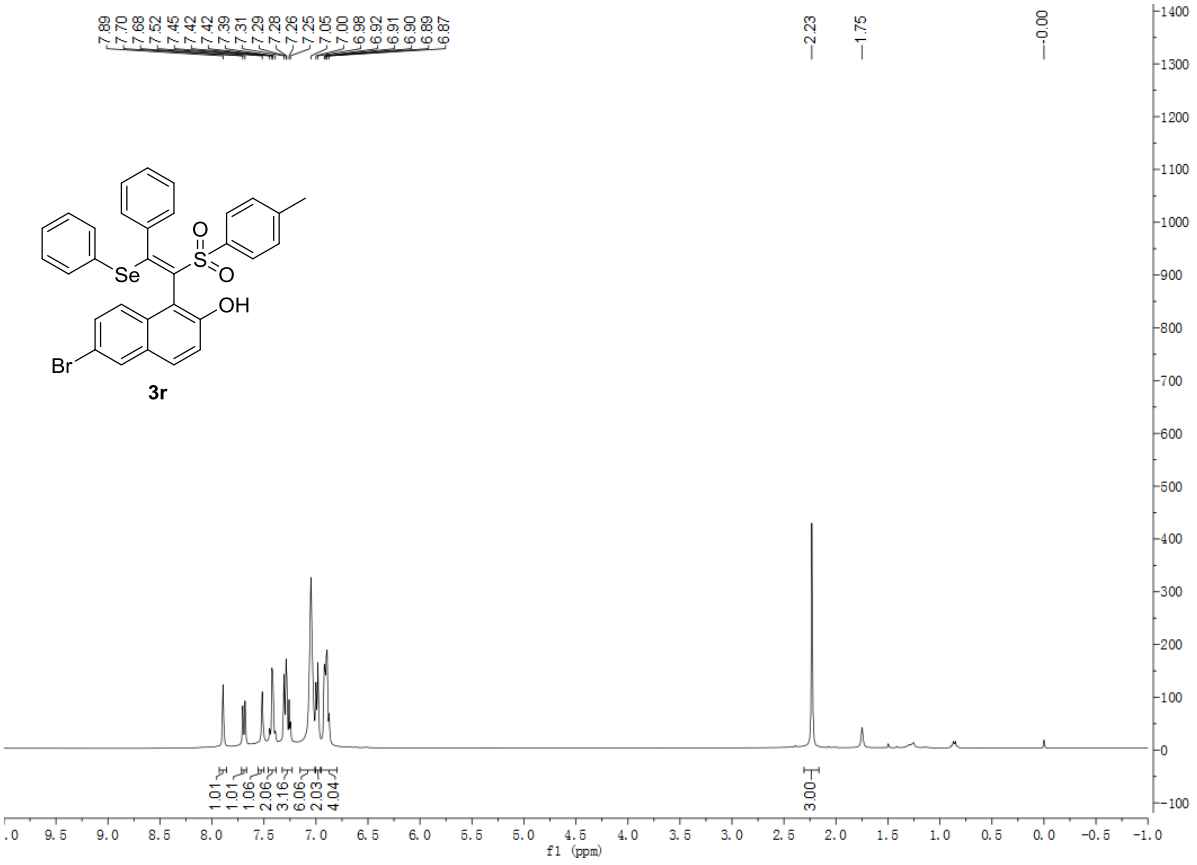
114.31
77.00
21.40
S
Se
O
S
O
OH
3q
f1 (ppm)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7.00
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6.92
6.91
6.90
6.89
6.87
2.23
1.75
0.00
Se
O
S
O
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Br
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2.03
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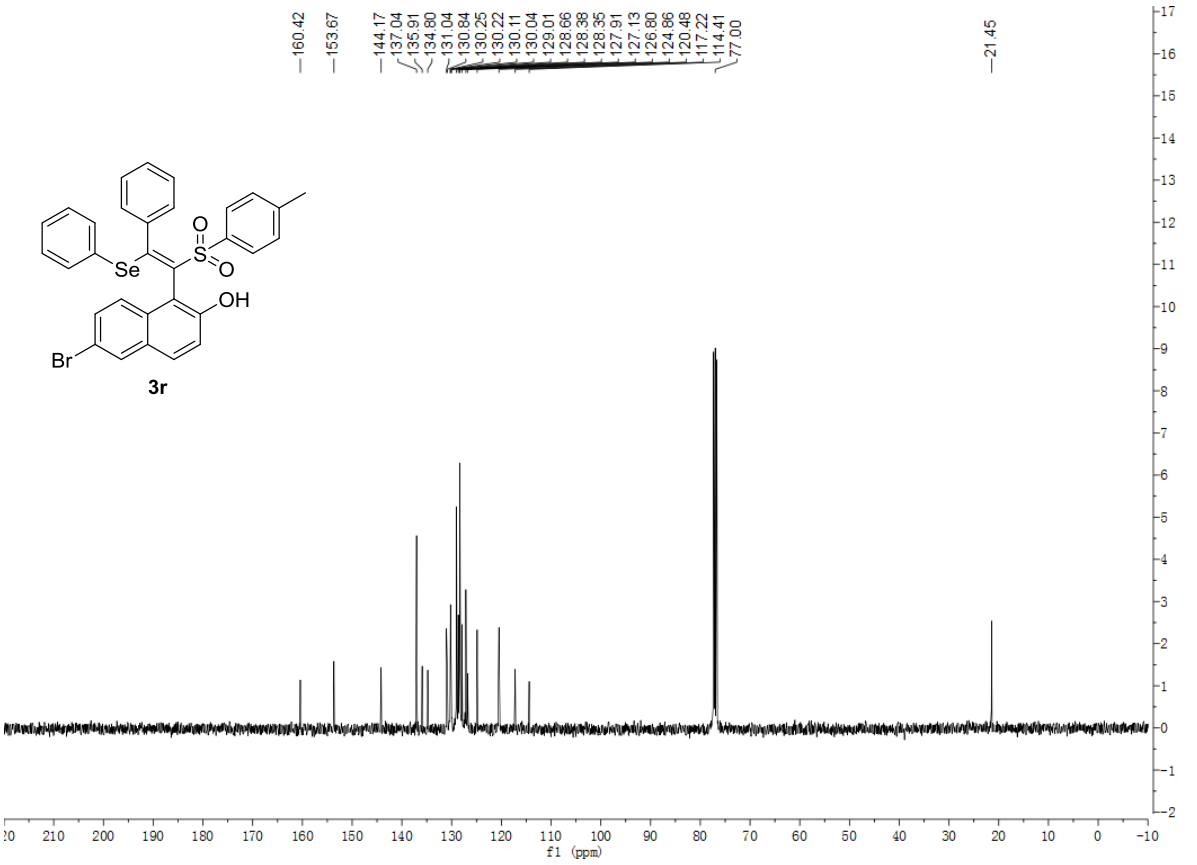
3.00
f1 (ppm)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127.13
126.80
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S
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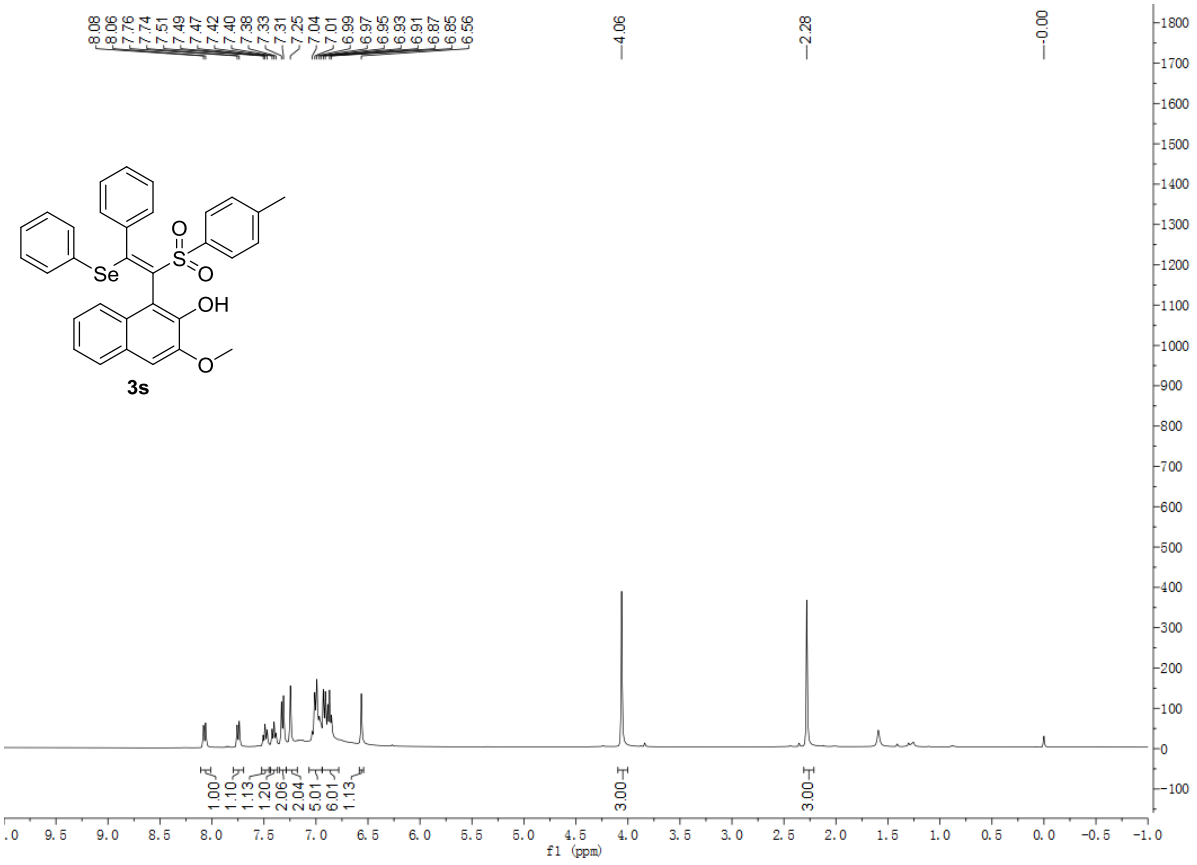
OH
Br
3r
f1 (ppm)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7.04
7.01
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6.97
6.95
6.93
6.91
6.87
6.85
6.56
4.06
2.28
0.00
Se
O
S
O
OH
O
3s
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1.20
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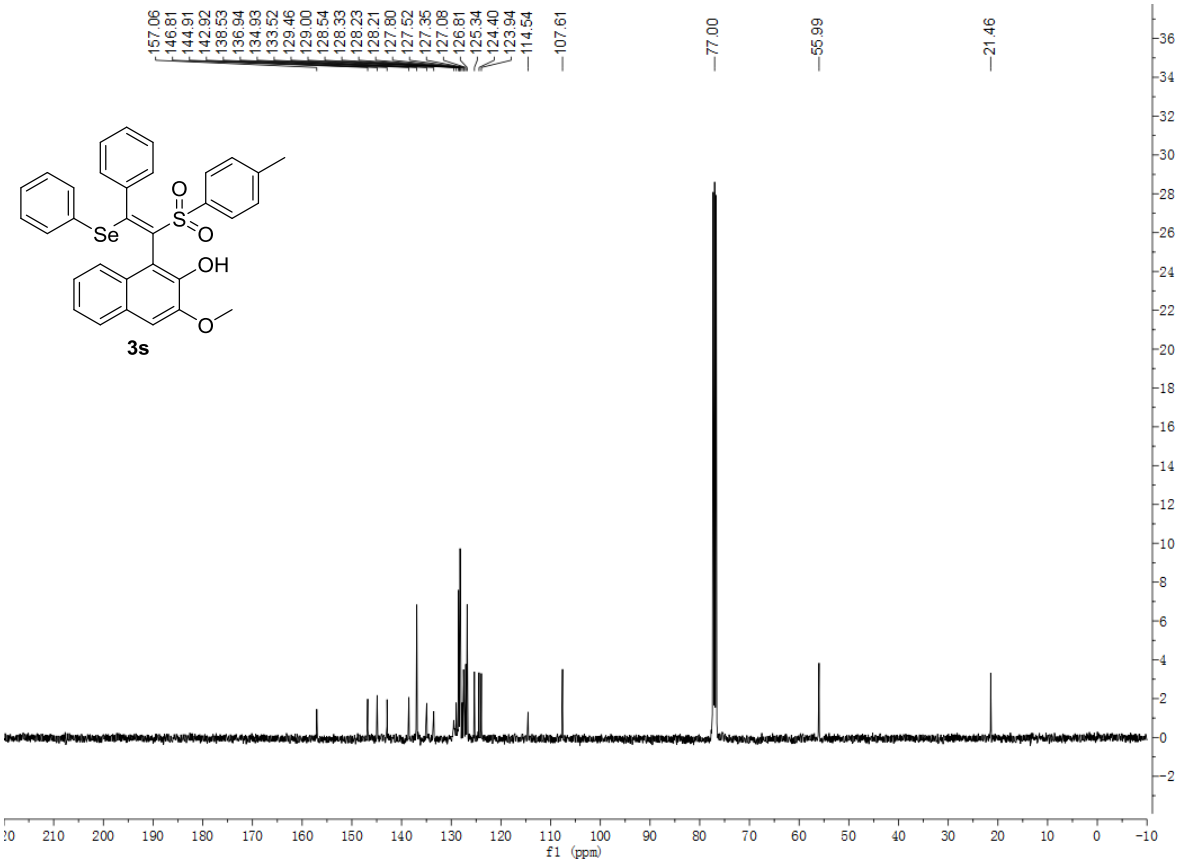
2.04
5.01
6.01
1.13
3.00
3.00
f1 (ppm)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127.08
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Se
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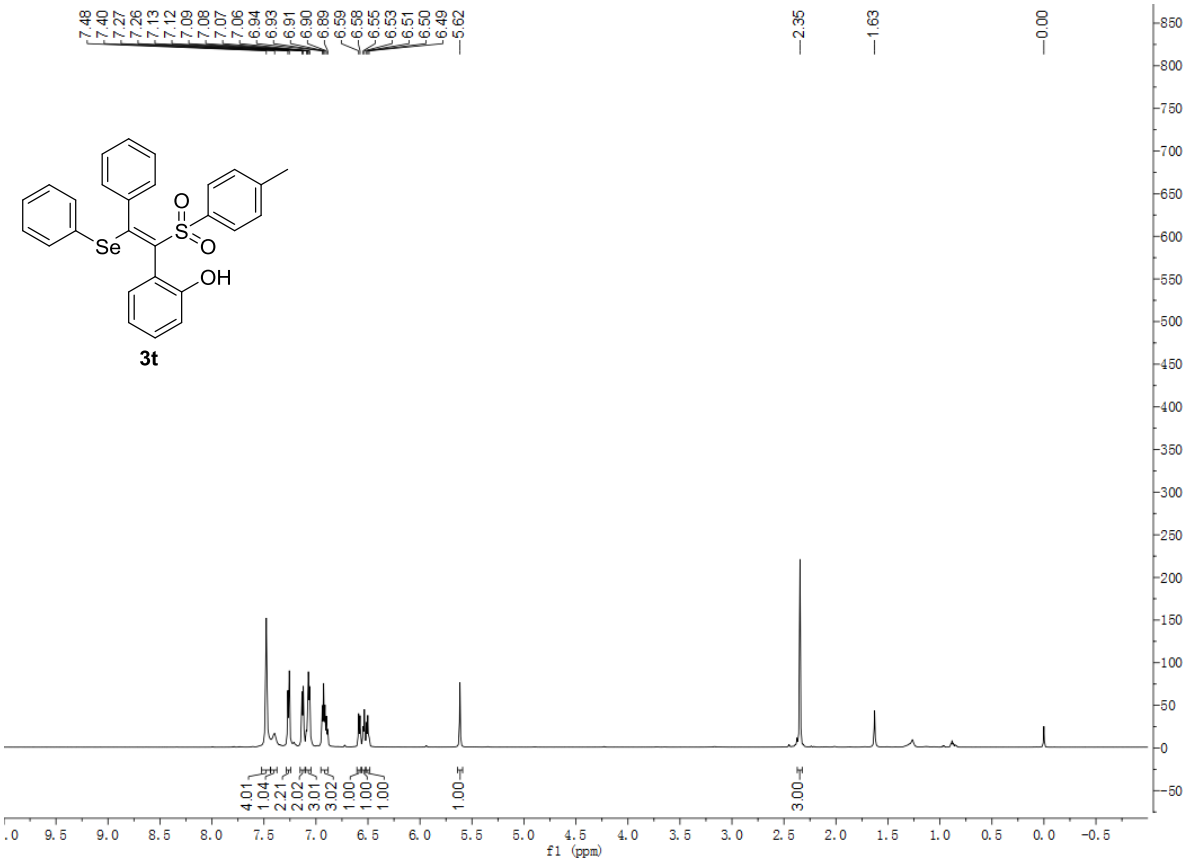
S
O
OH
O
3s
f1 (ppm)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6.58
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6.53
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6.50
6.49
5.62
2.35
1.63
0.00
Se
O
S
O
OH
3t
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3.01
3.02
1.00
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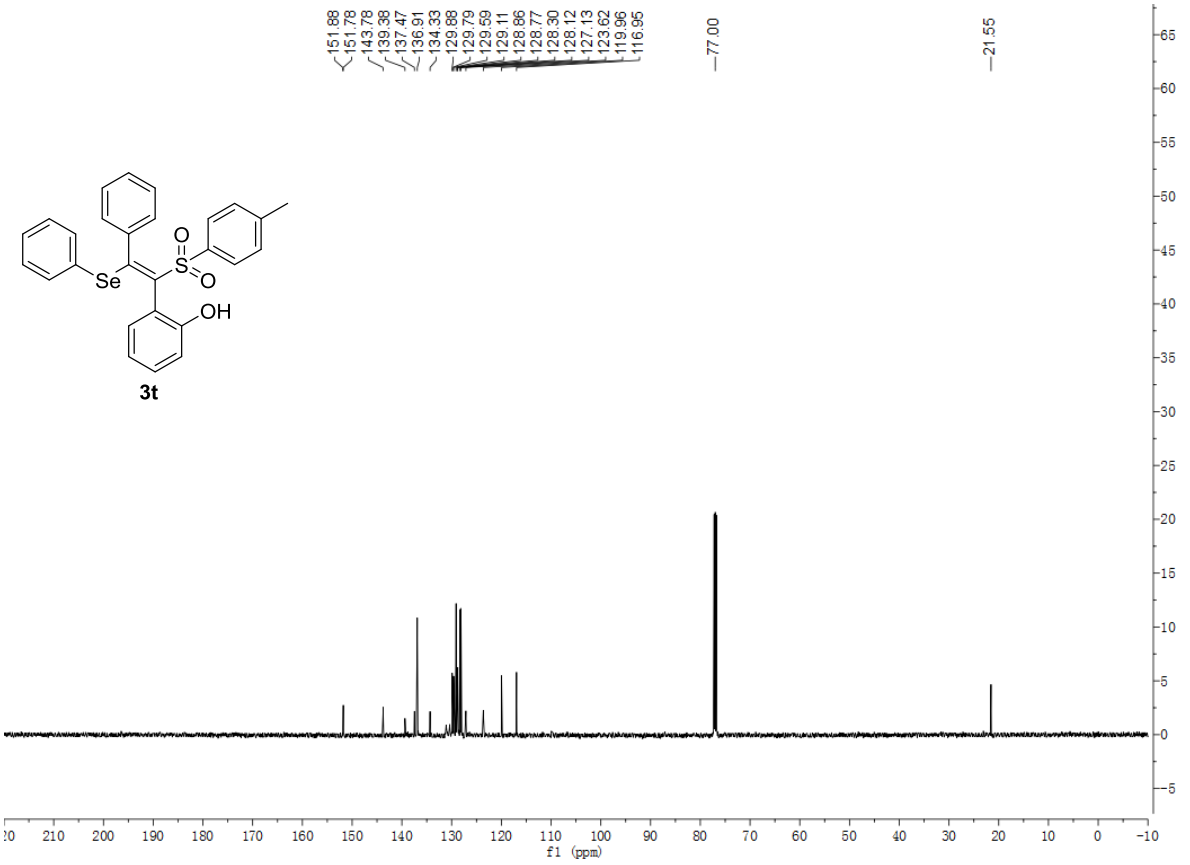
1.00
1.00
3.00
f1 (ppm)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116.95
77.00
21.55
Se
O
S
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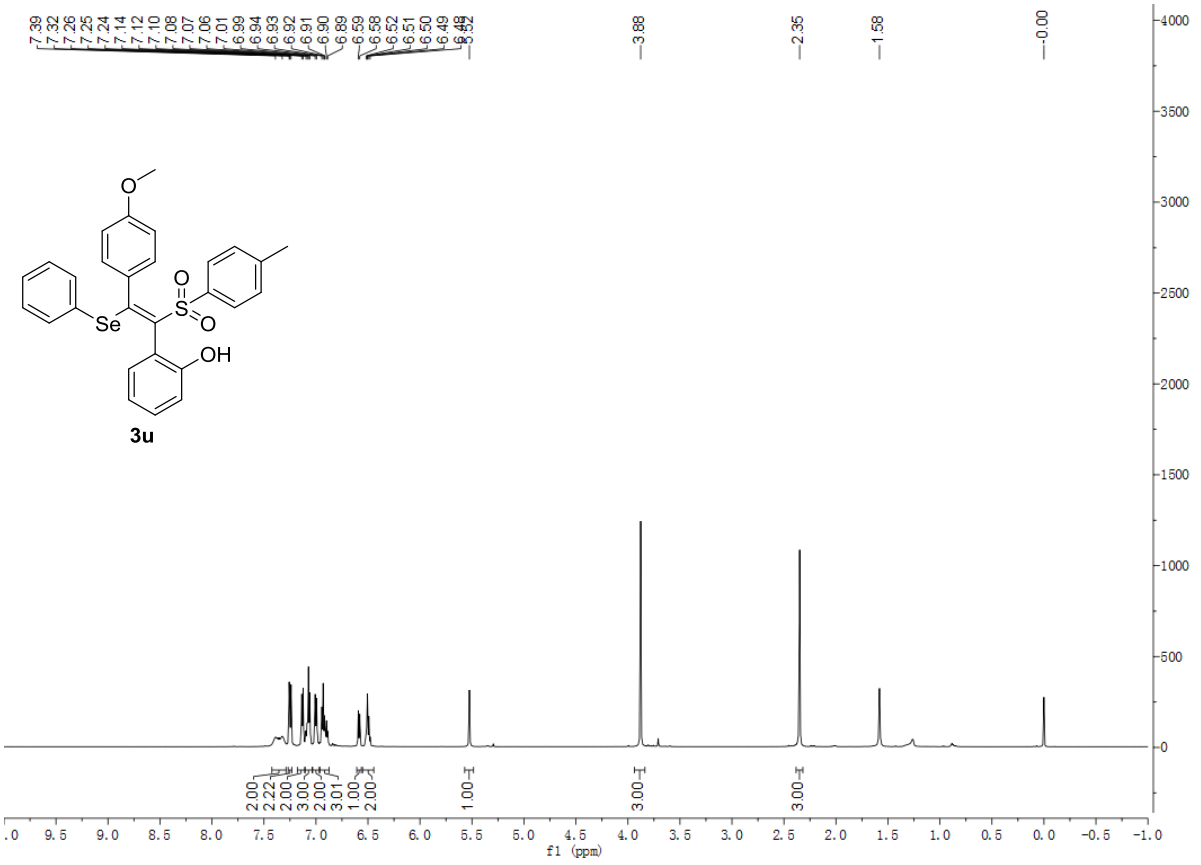
OH
3t
f1 (ppm)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O
Se
S
O
O
OH
3u
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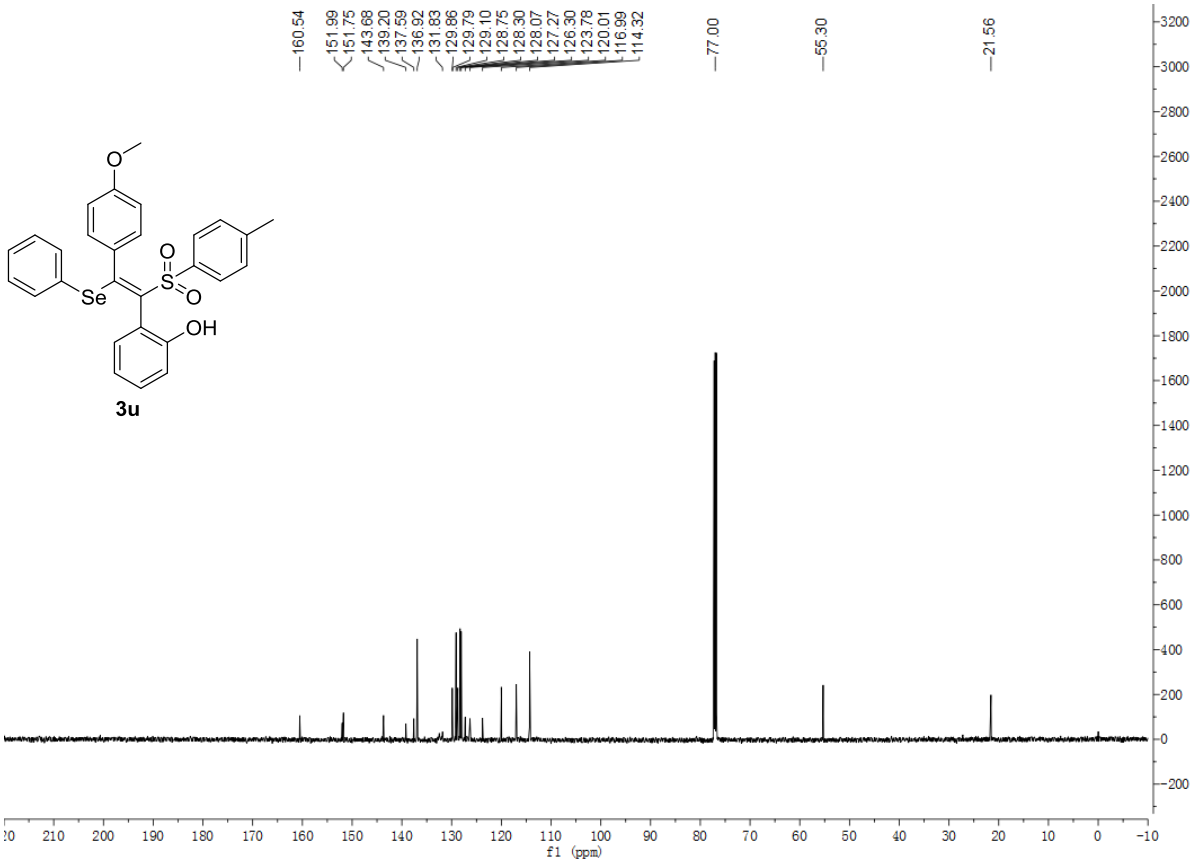
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123.78
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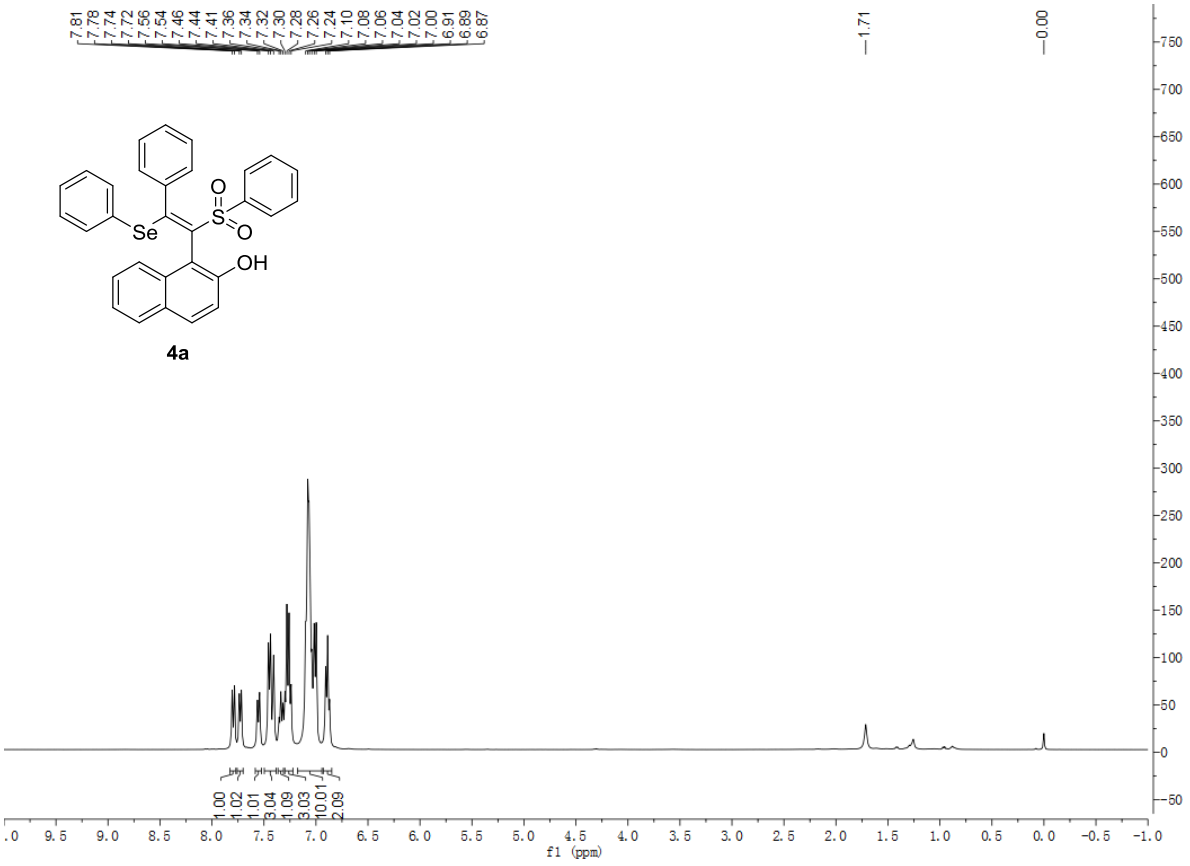
O
OH
3u
f1 (ppm)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7.08
7.06
7.04
7.02
7.00
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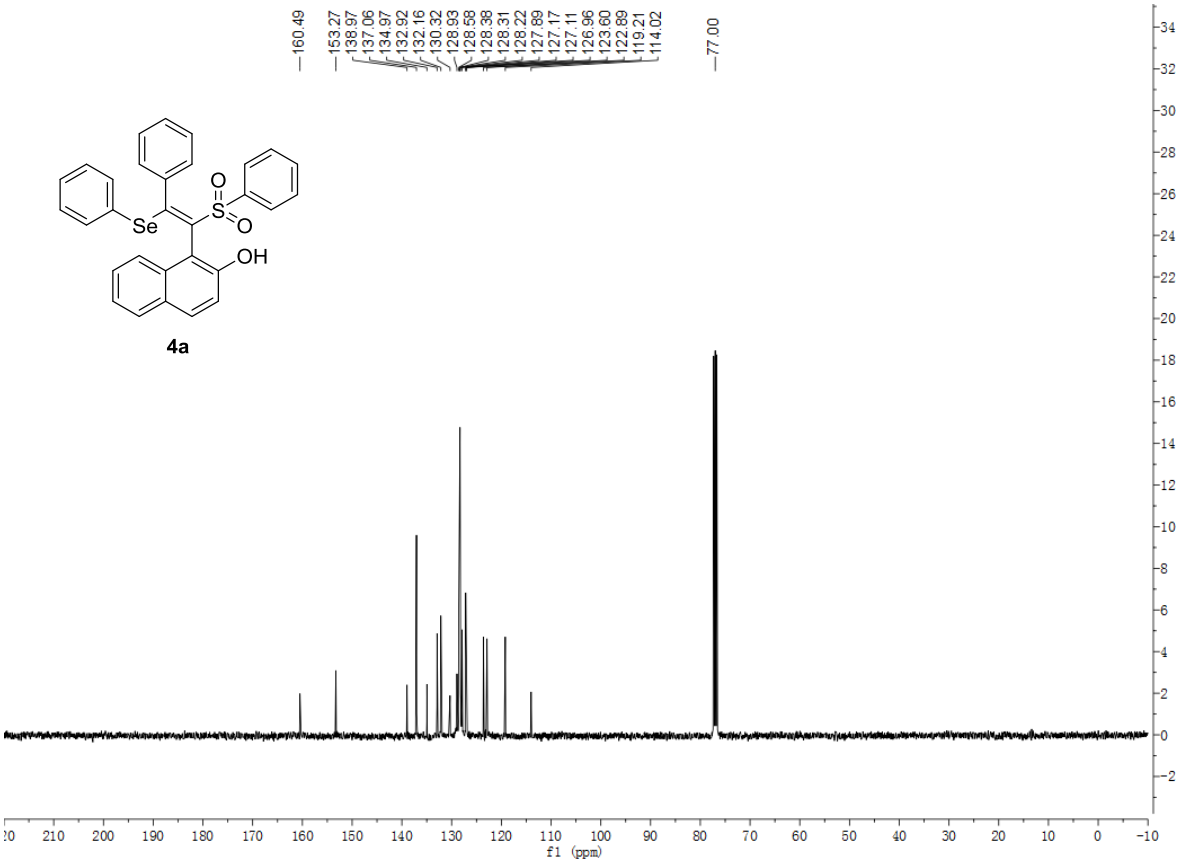
2.09
f1 (ppm)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127.17
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O
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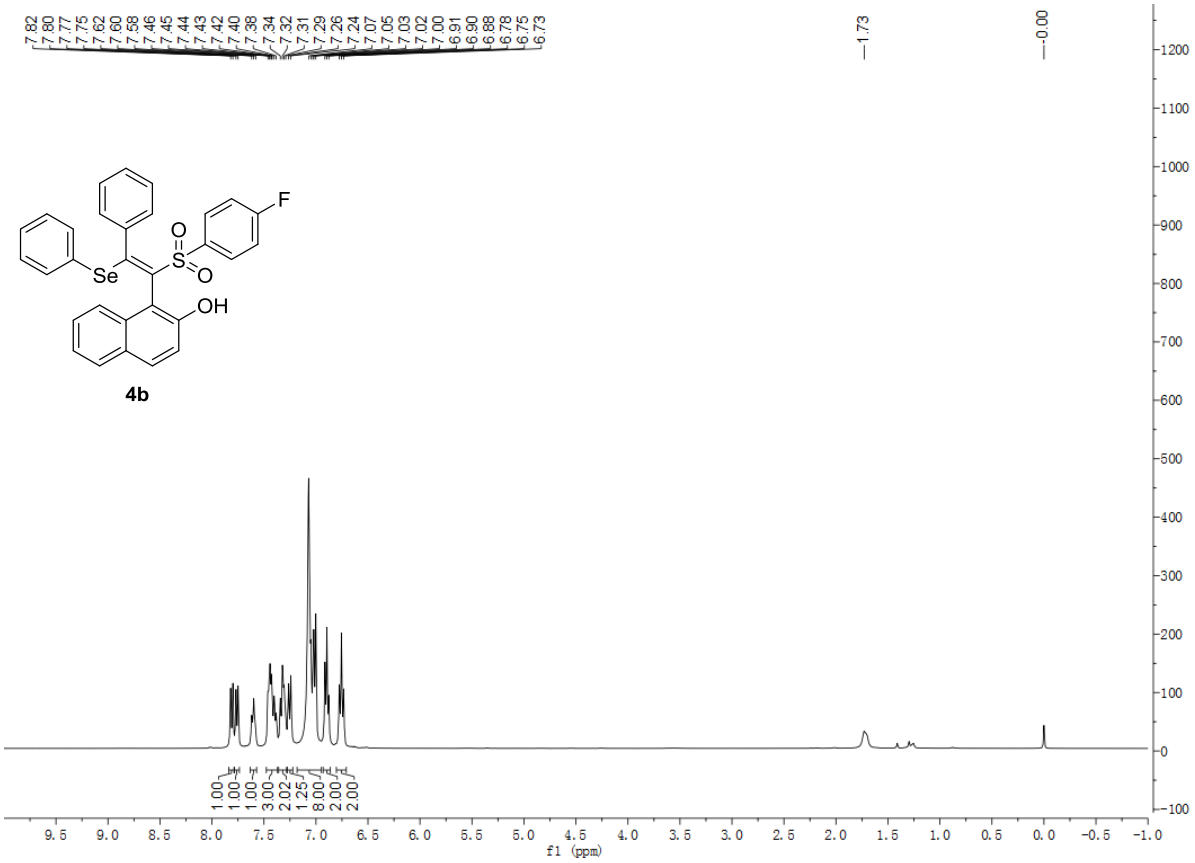
4a
f1 (ppm)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7.07
7.05
7.03
7.02
7.00
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6.90
6.88
6.78
6.75
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1.73
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F
O
S
O
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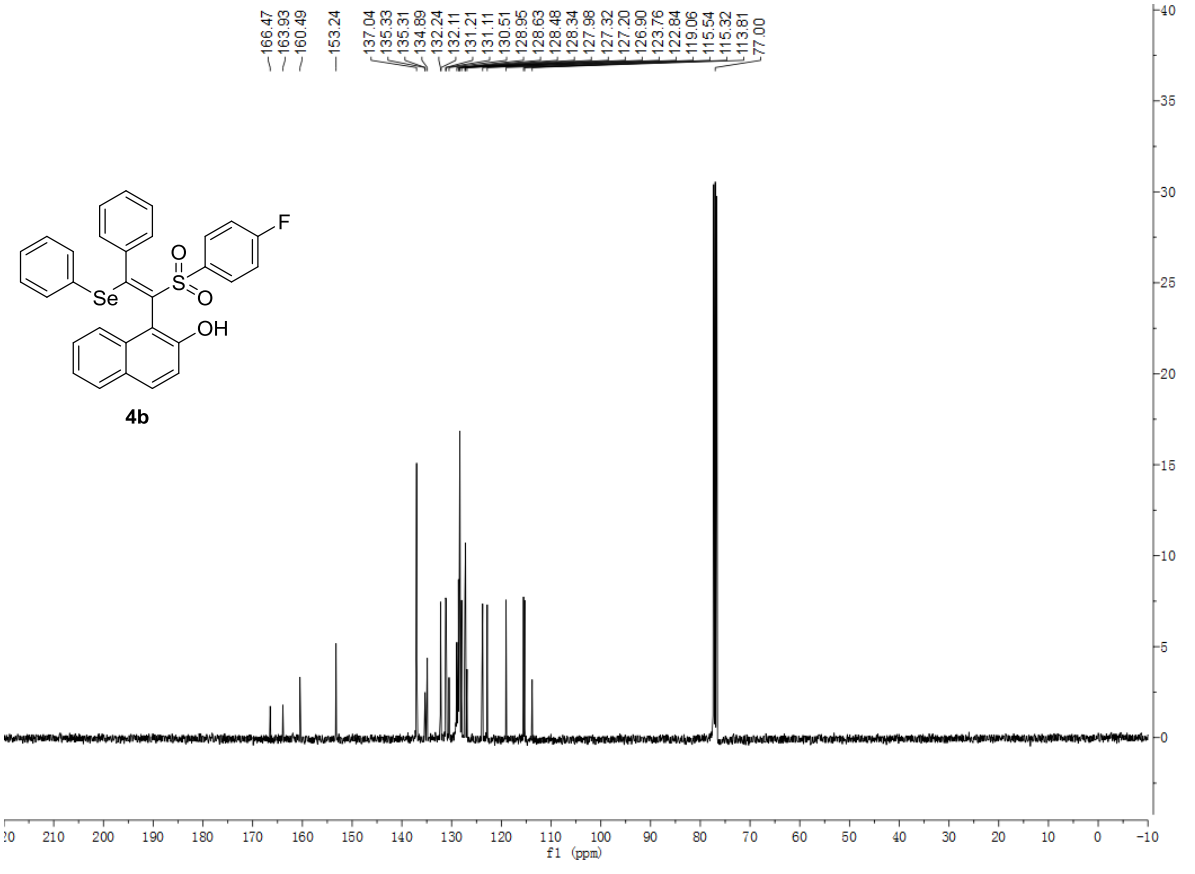
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S
O
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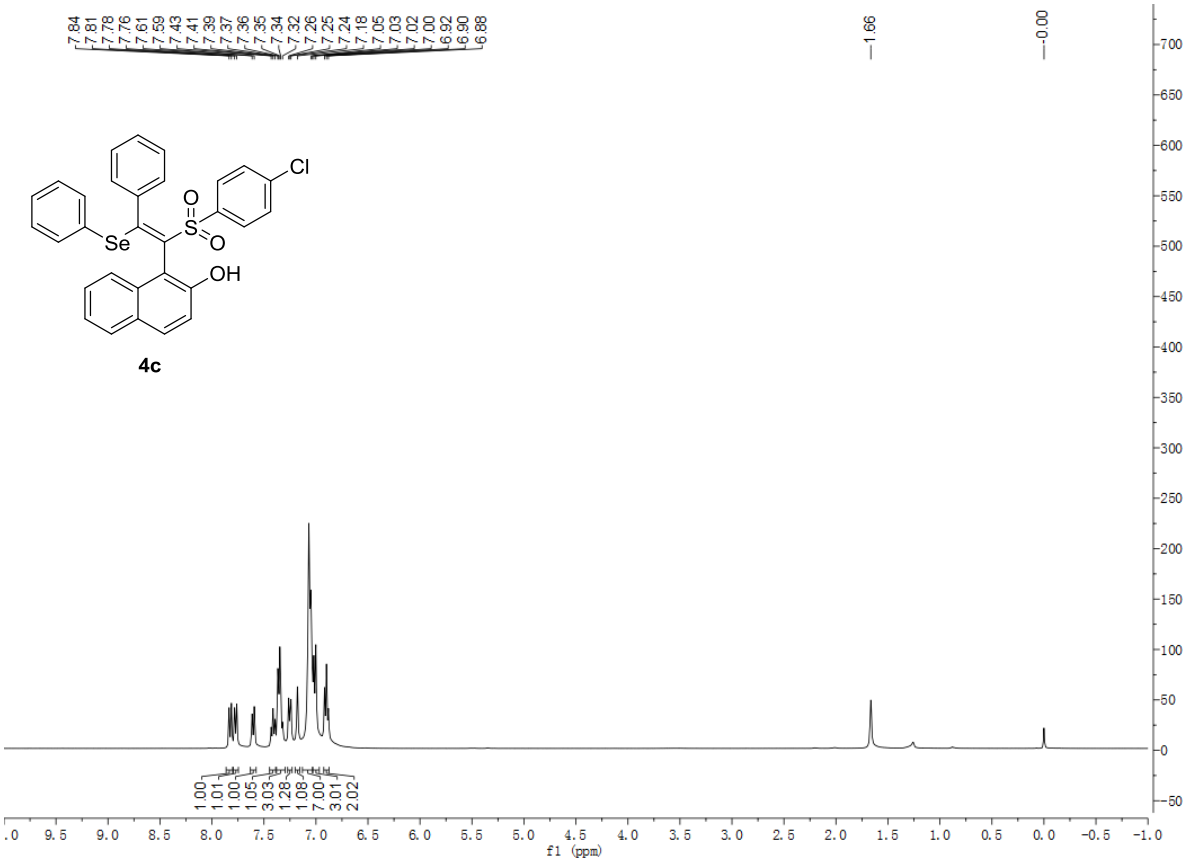
OH
4b
f1 (ppm)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7.25
7.24
7.18
7.05
7.03
7.02
7.00
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6.90
6.88
1.66
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Cl
O
S
O
Se
OH
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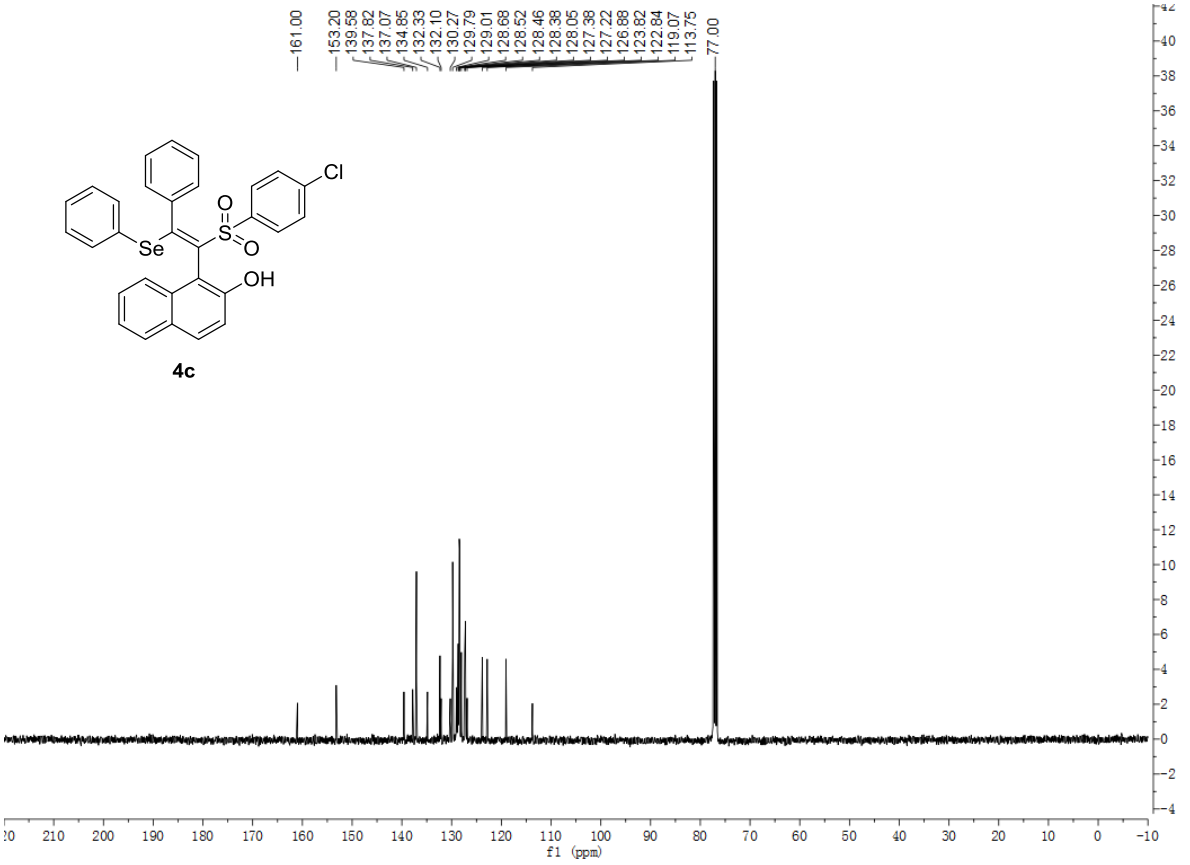
2.02
f1 (ppm)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127.38
127.22
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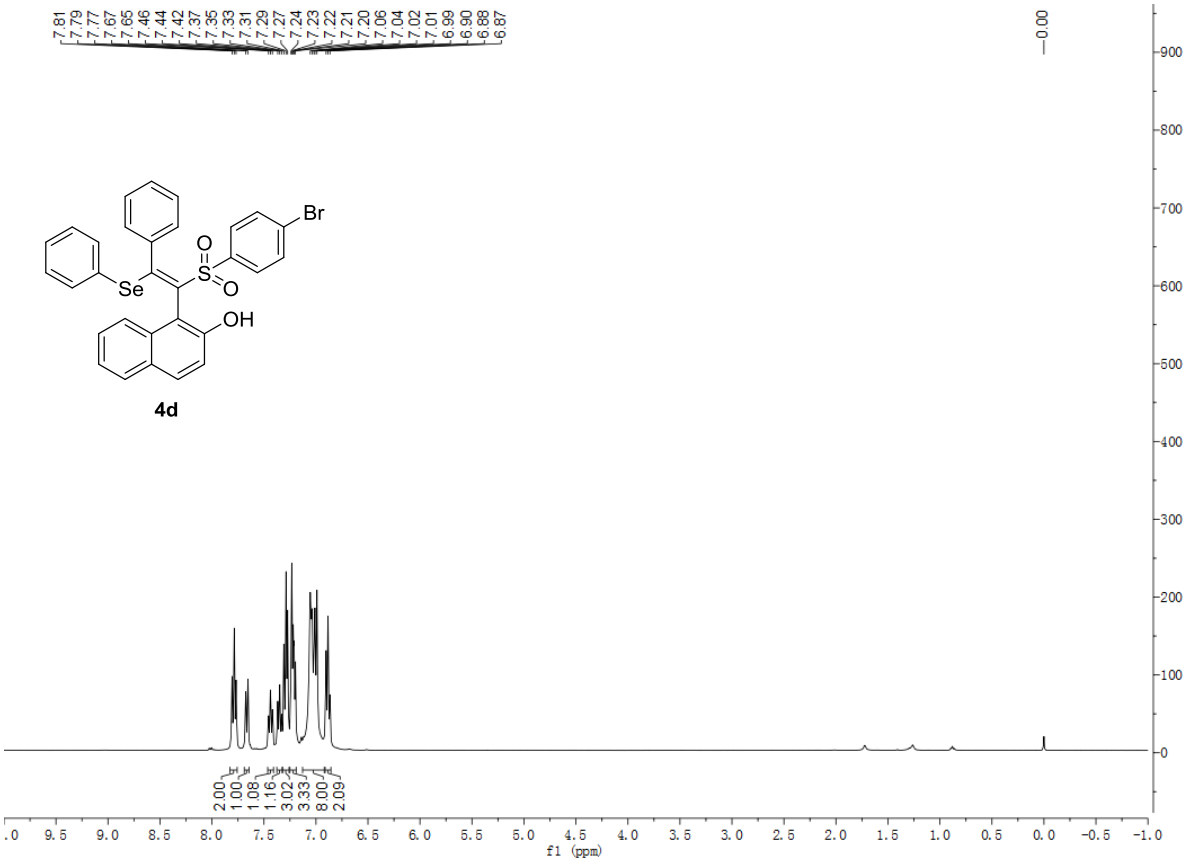
O
S
O
Se
OH
4c
f1 (ppm)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7.06
7.04
7.02
7.01
6.99
6.90
6.88
6.87
0.00
Br
O
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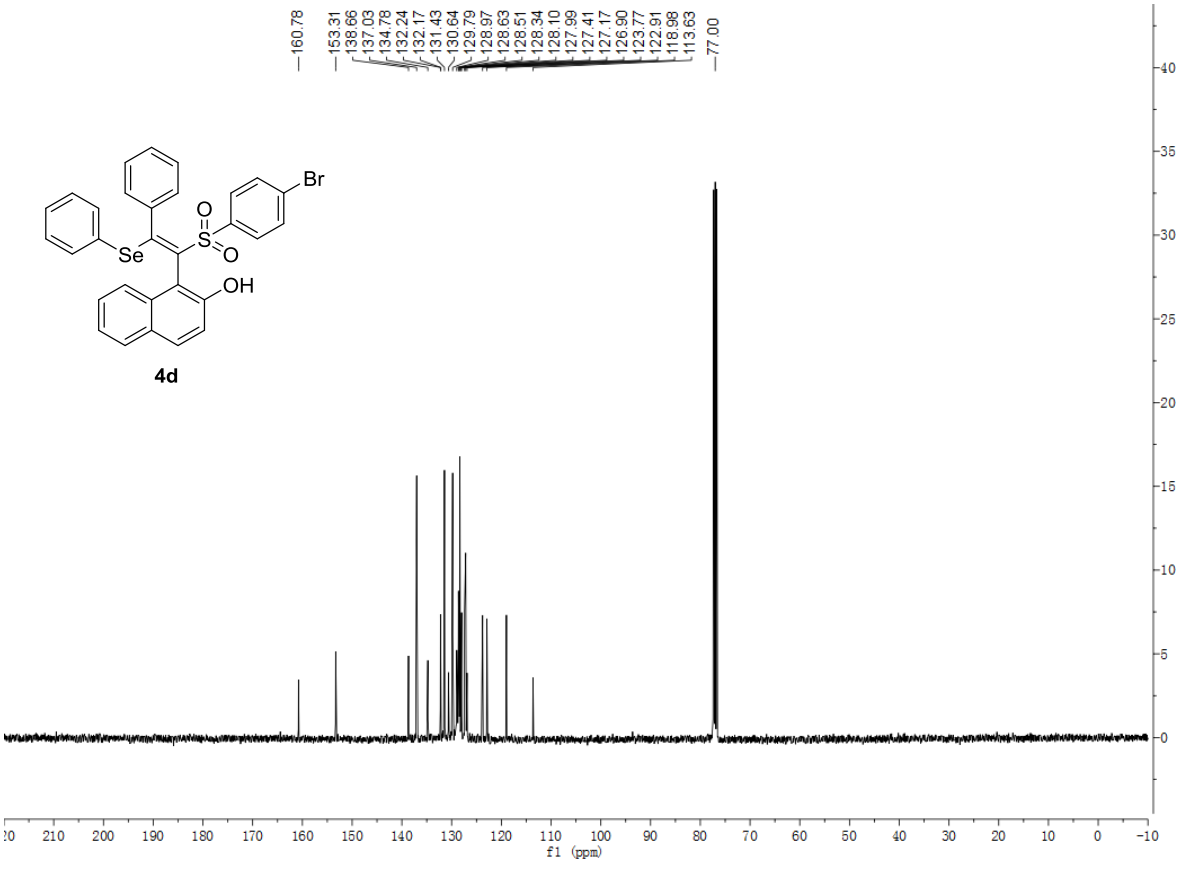
3.33
8.00
2.09
f1 (ppm)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128.10
127.99
127.41
127.17
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118.98
113.63
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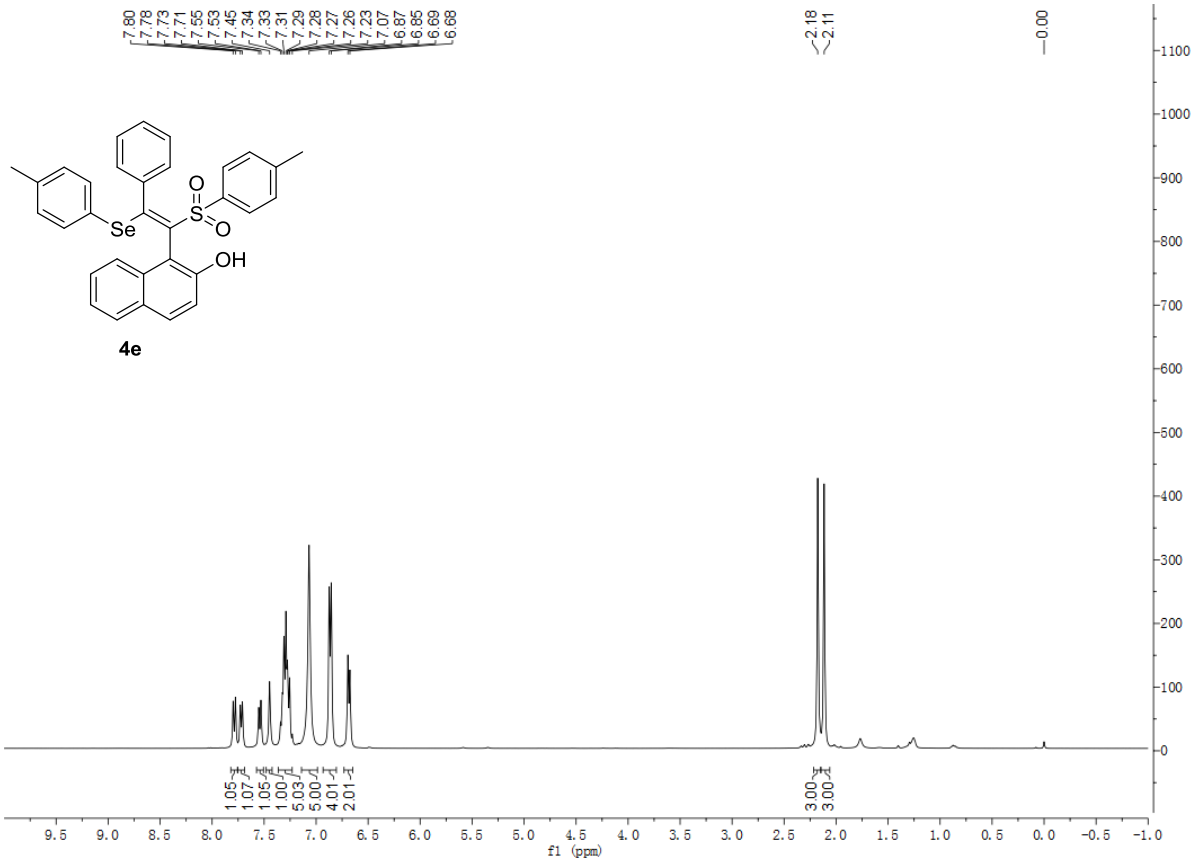
O
S
O
Se
OH
4d
f1 (ppm)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6.69
6.68
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2.11
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O
S
O
OH
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3.00
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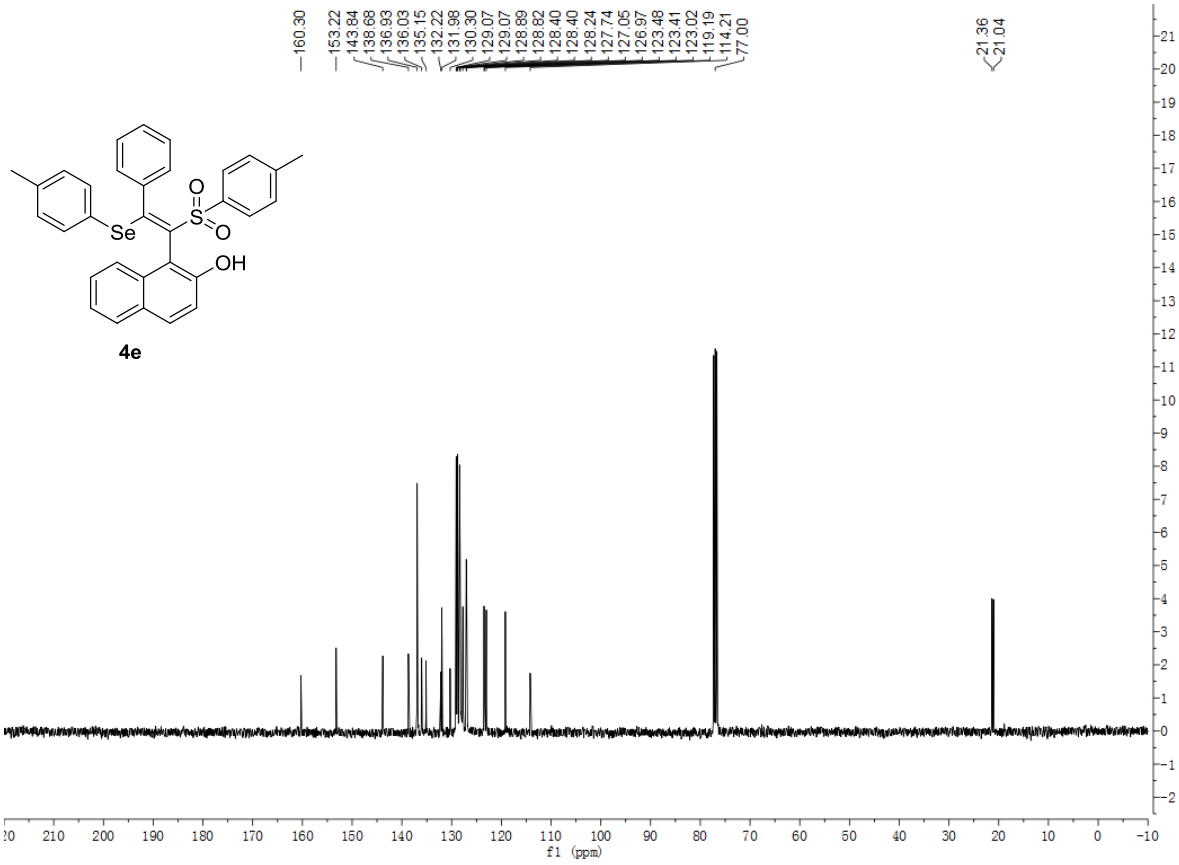
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123.48
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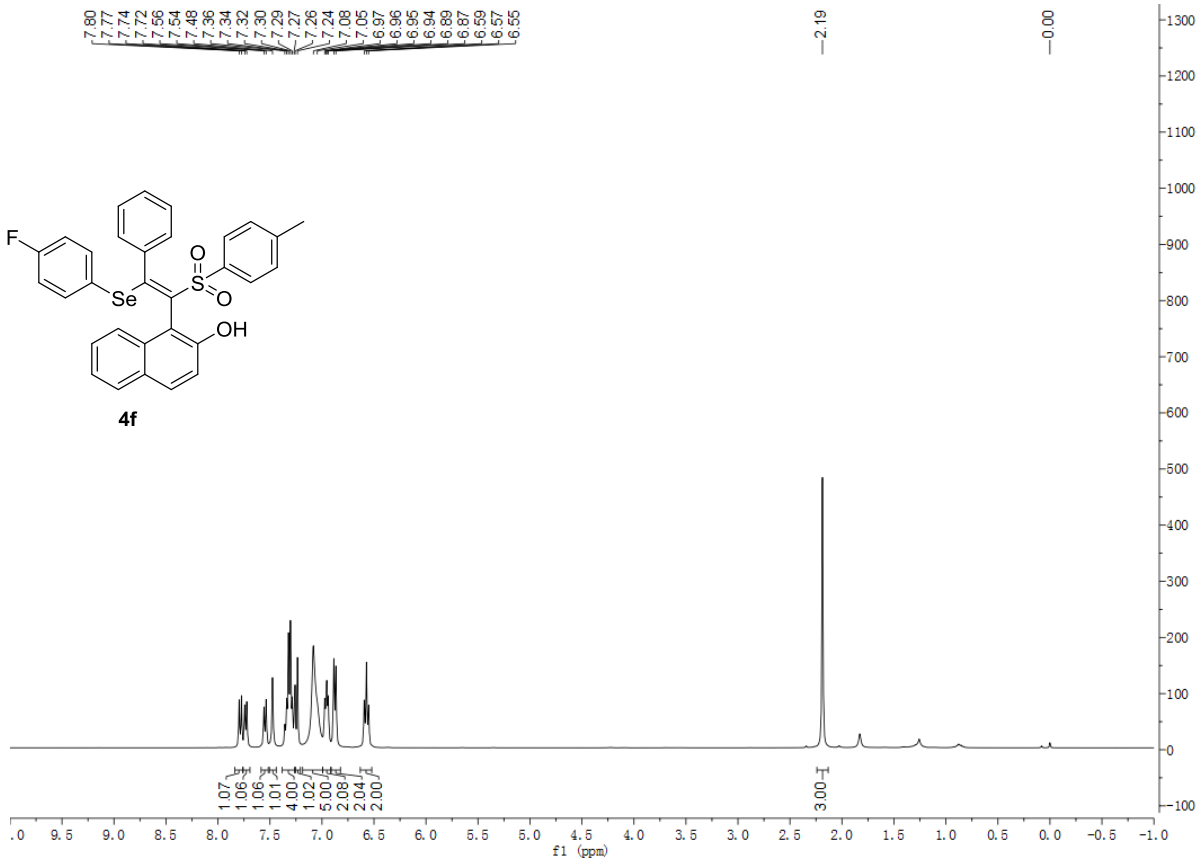
O
S
O
OH
4e
f1 (ppm)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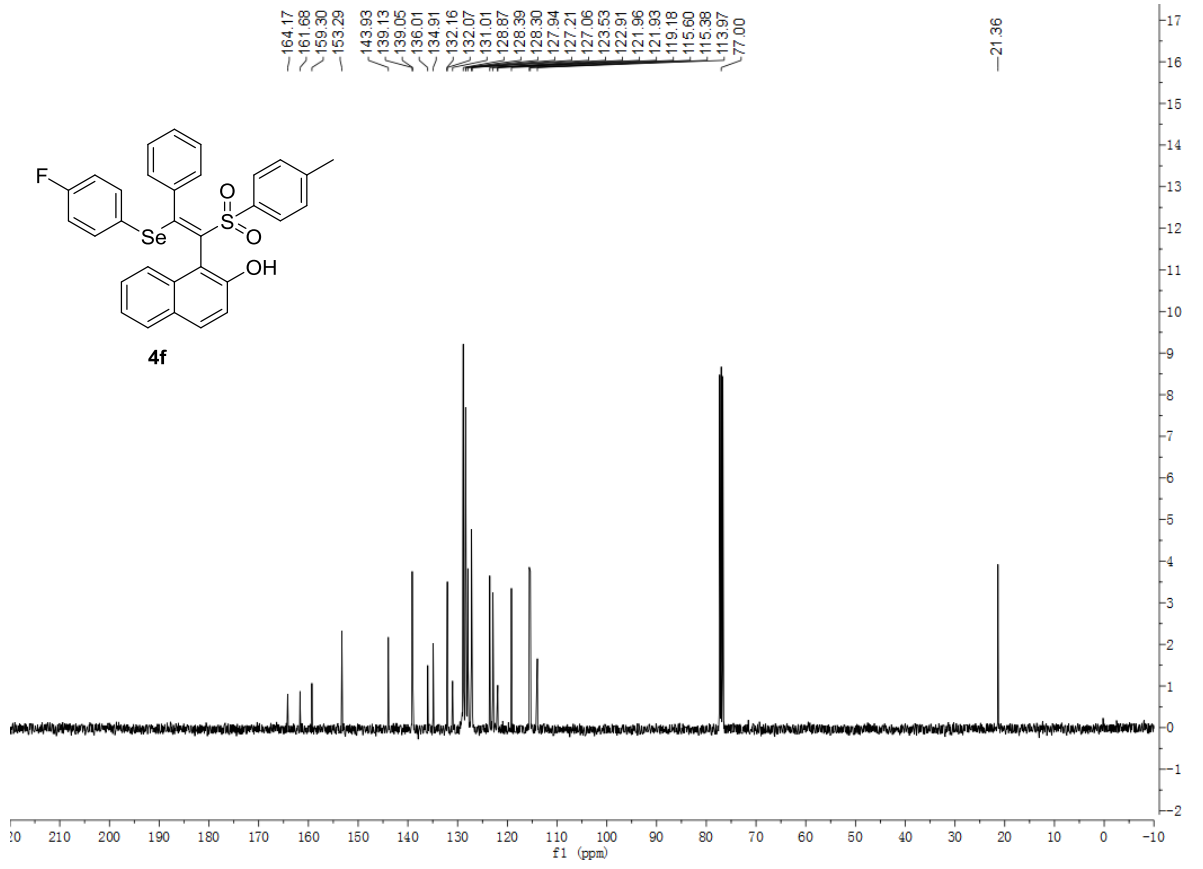
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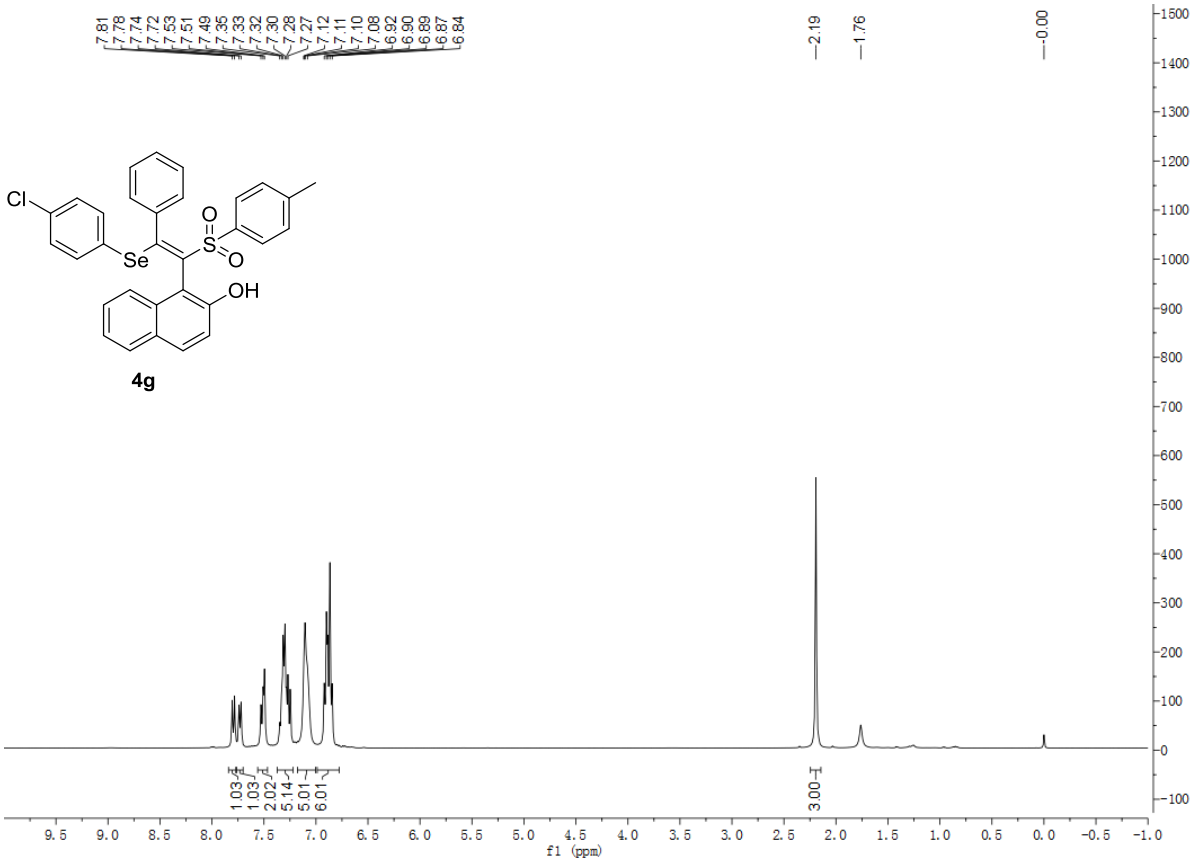
f1 (ppm)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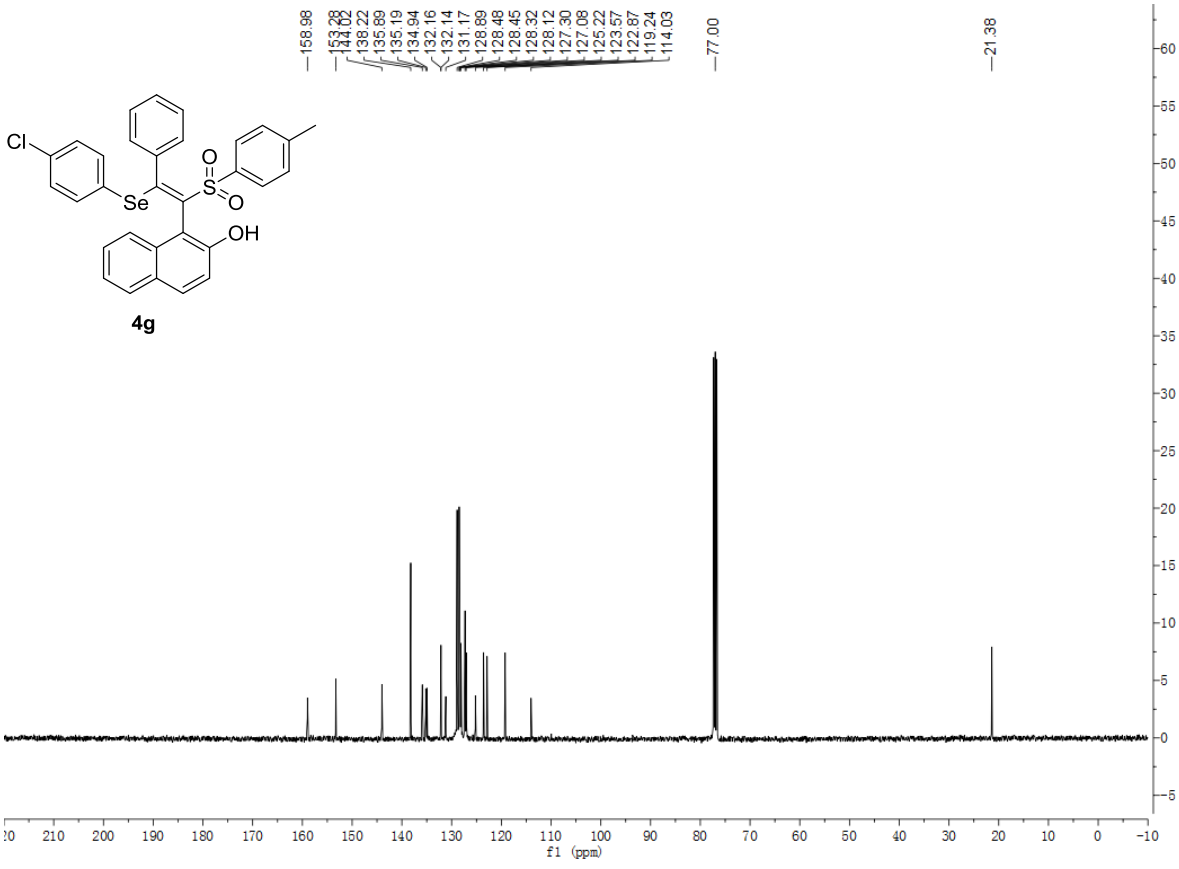
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O
S
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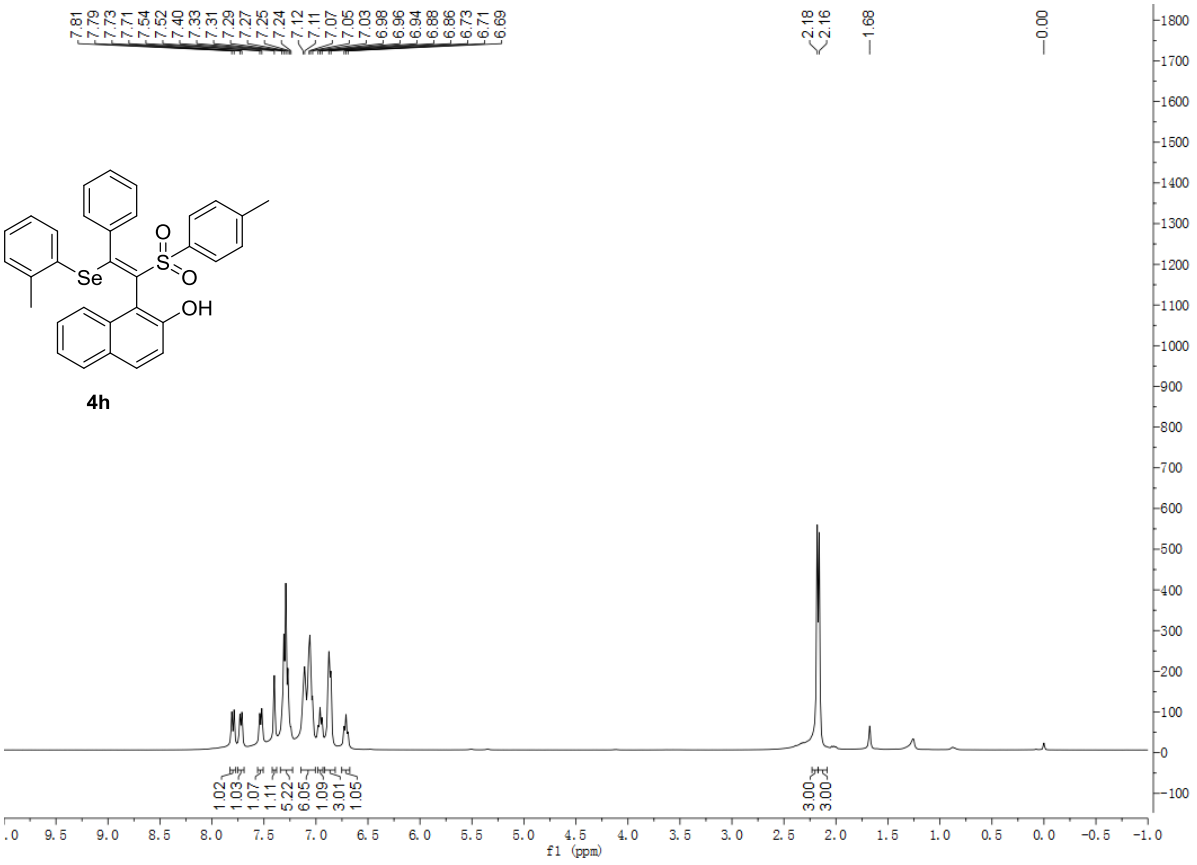
OH
4g
f1 (ppm)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S
O
OH
4h
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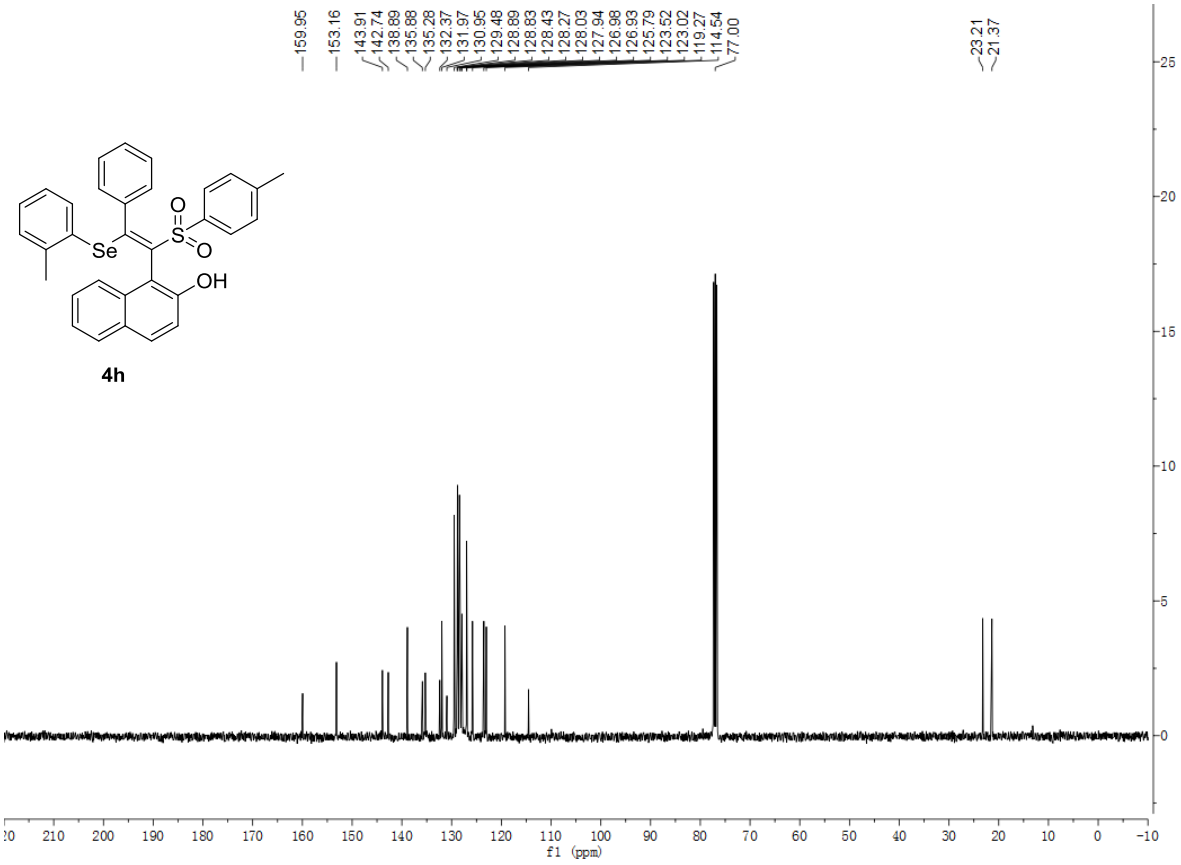
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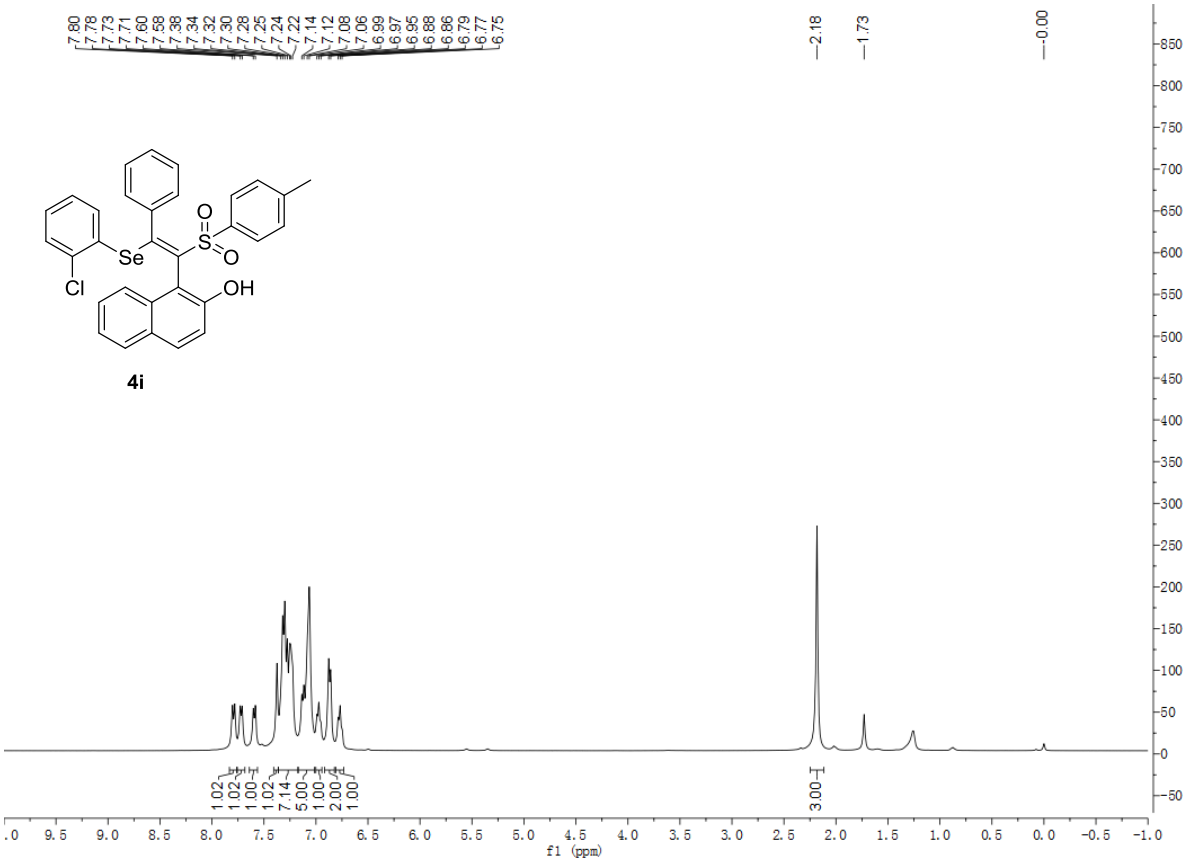
OH
4h
f1 (ppm)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Cl
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S
O
OH
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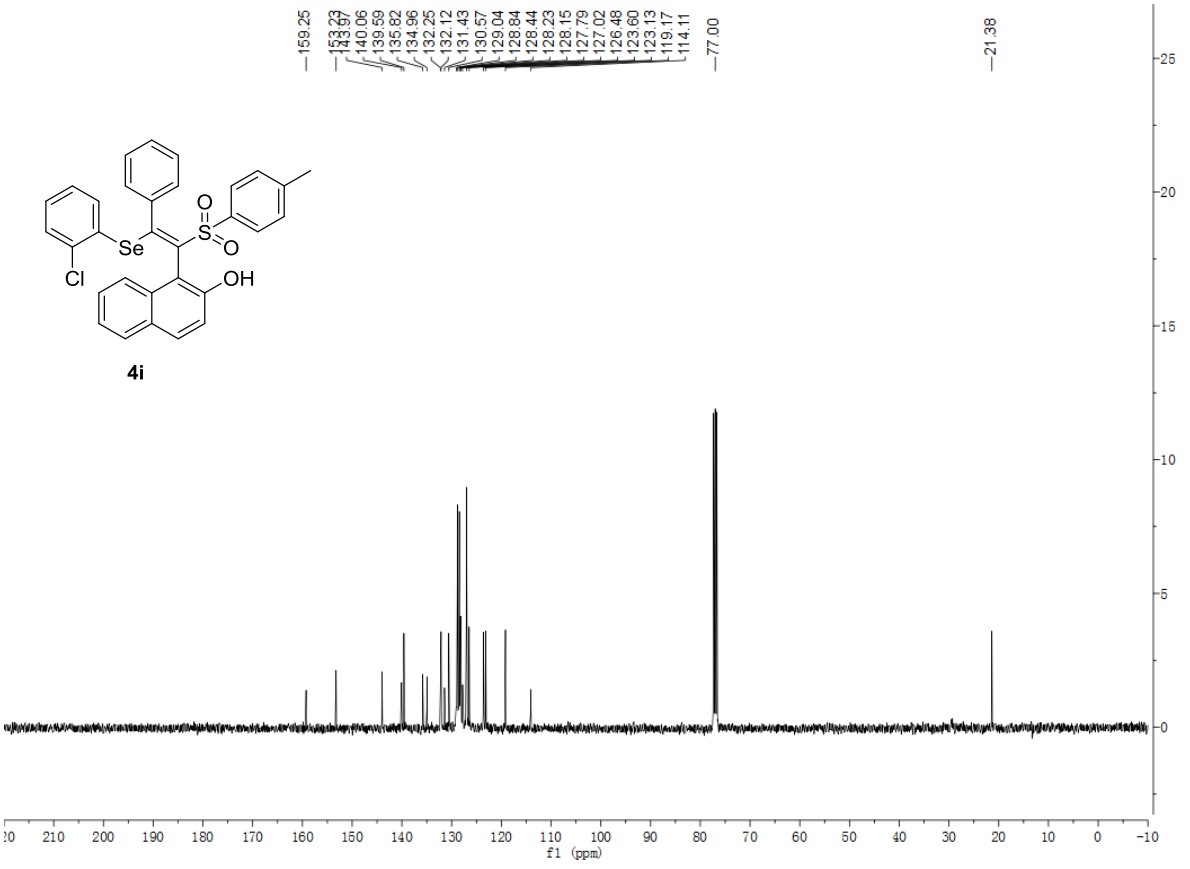
f1 (ppm)

4i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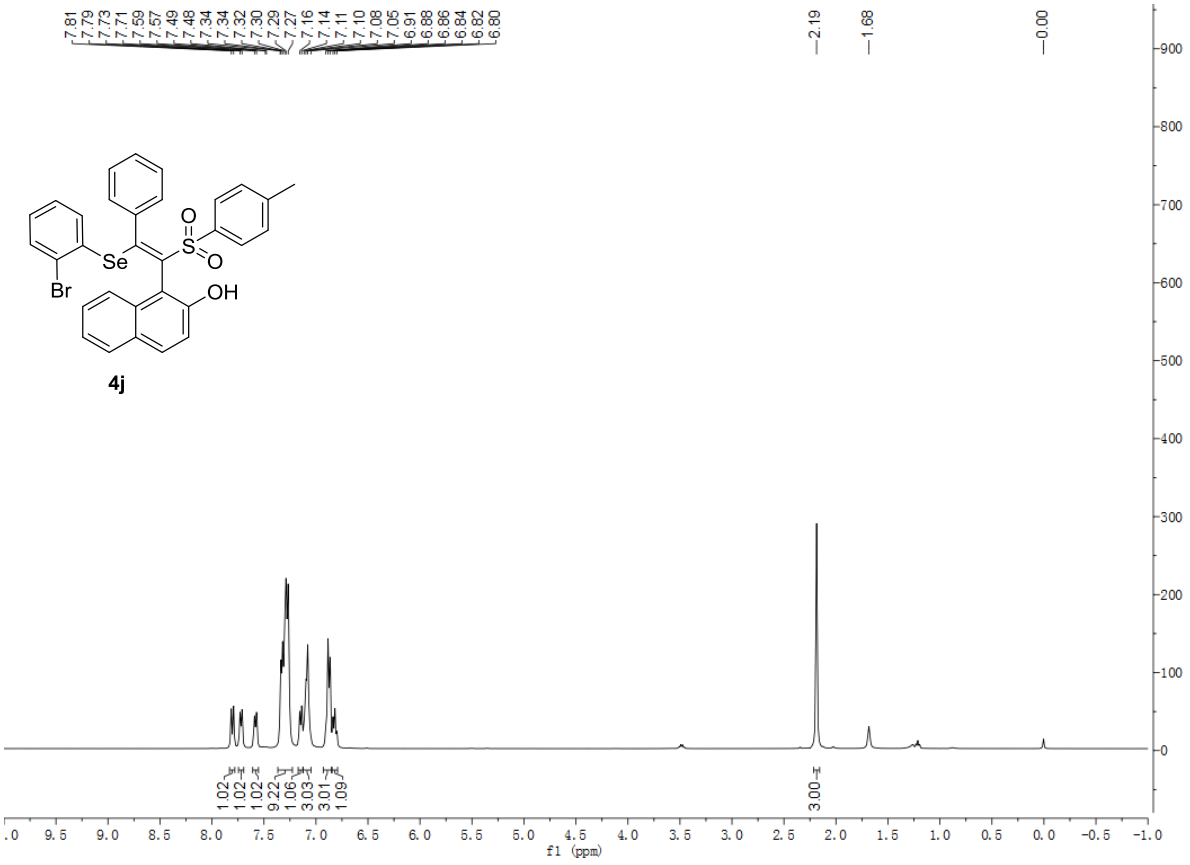
Cl
O
S
O
OH
f1 (ppm)

4i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6.84
6.82
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Br
O
S
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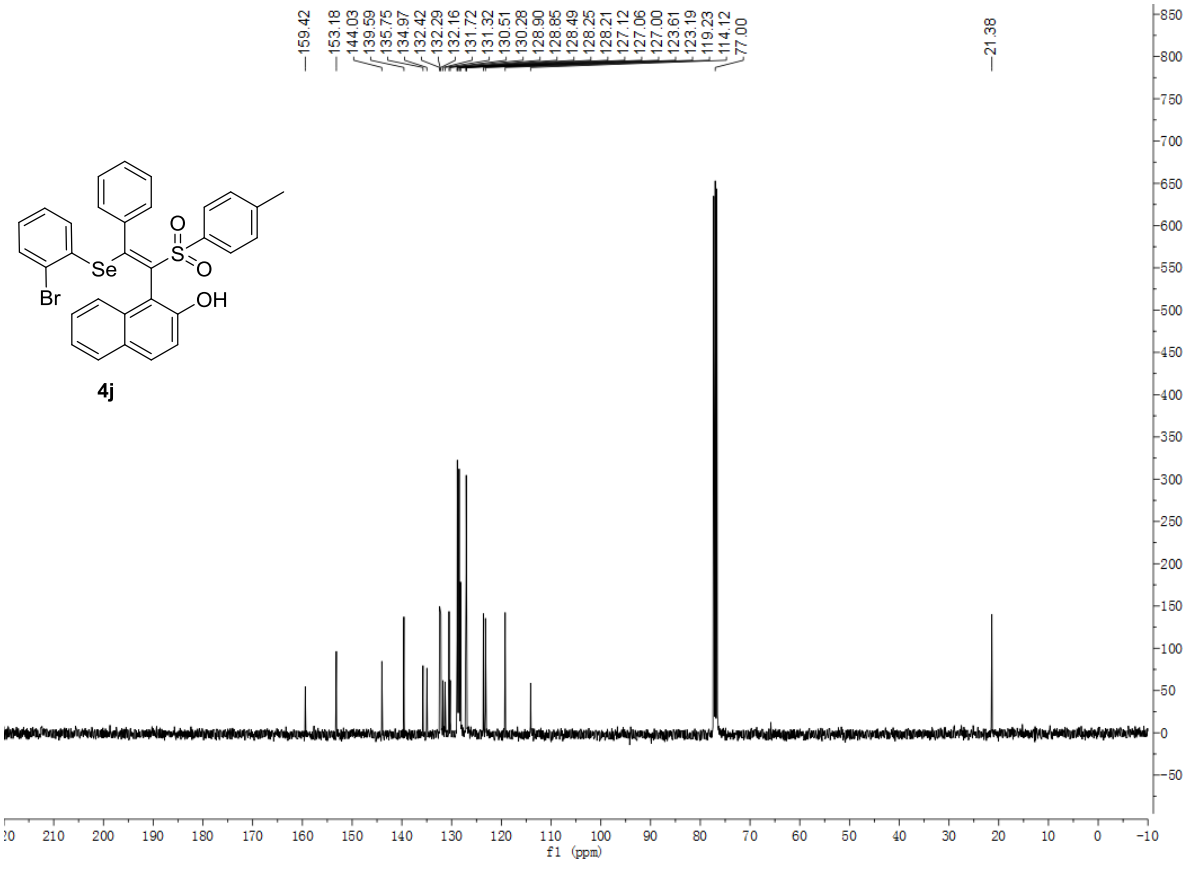
3.00
f1 (ppm)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127.06
127.00
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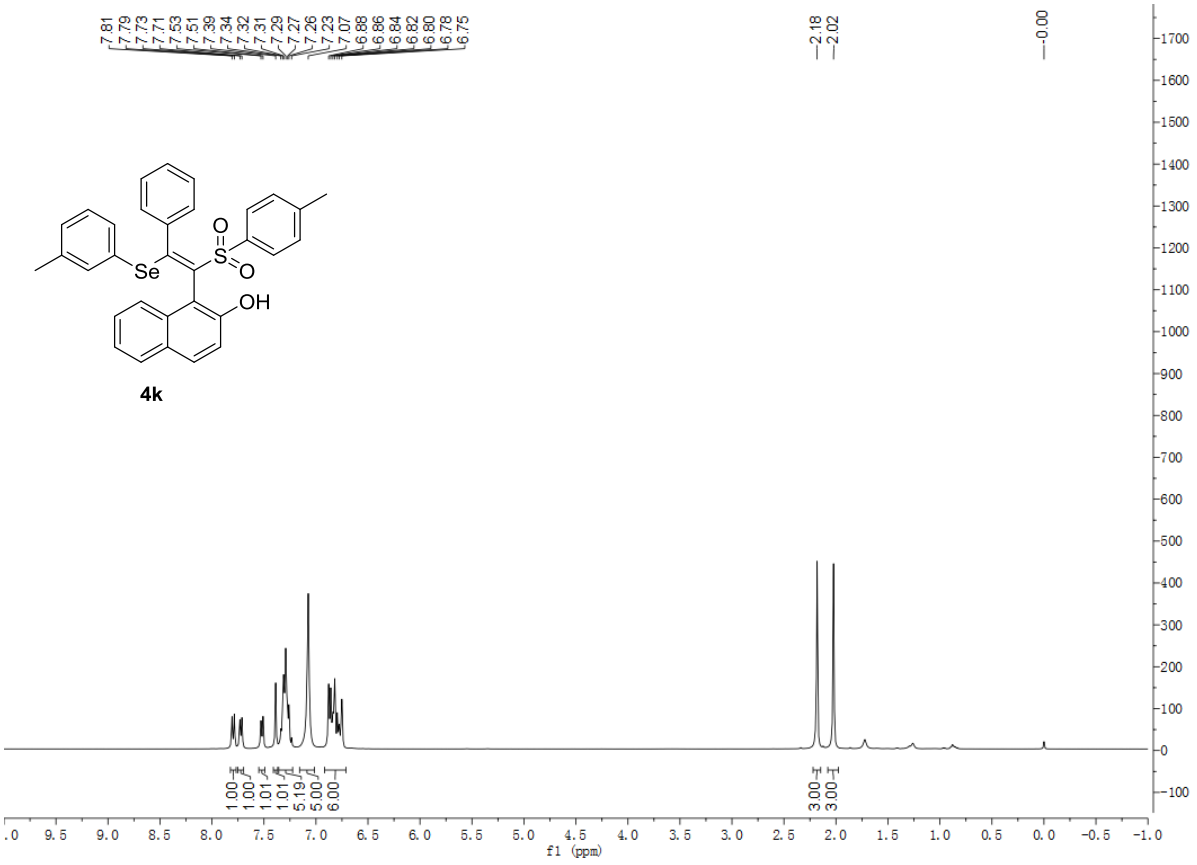
Se
Br
O
S
O
OH
4j
f1 (ppm)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6.78
6.75
2.18
2.02
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O
S
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1.01
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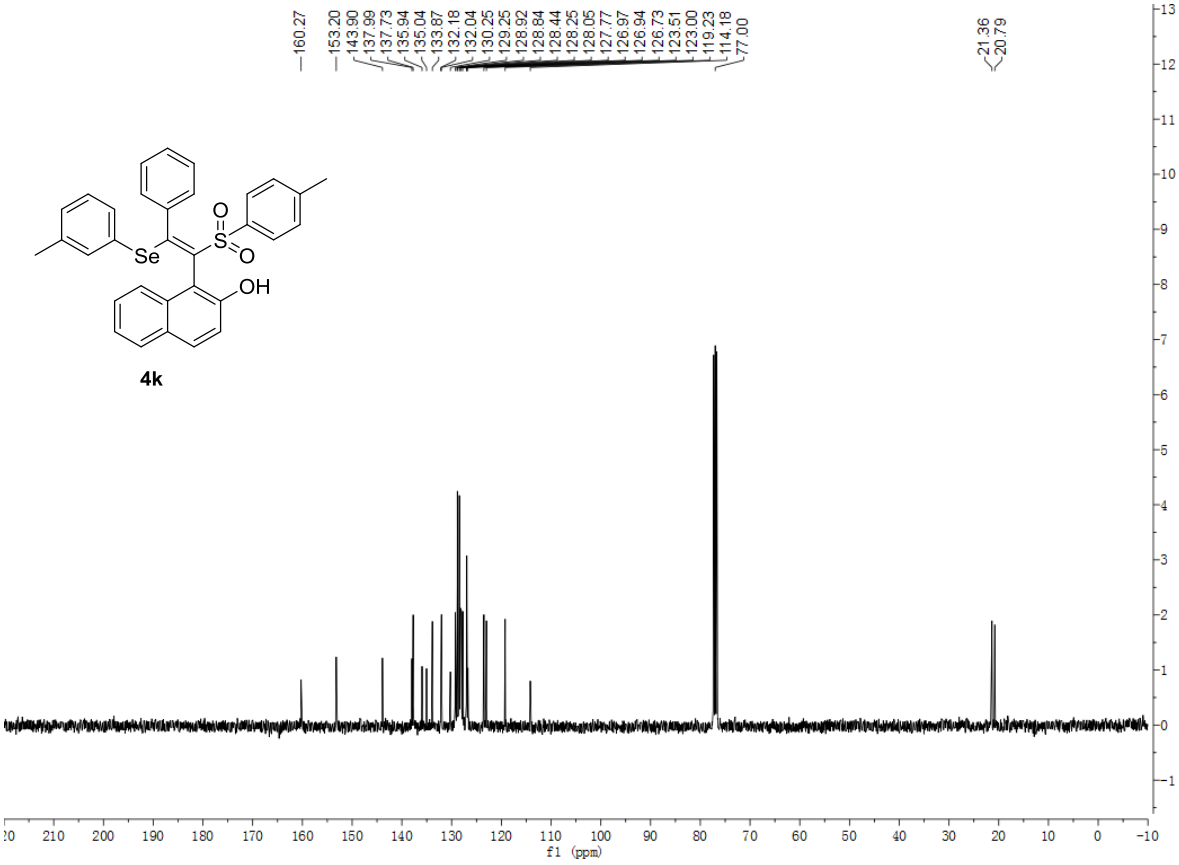
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126.73
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21.36
20.79
Se
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S
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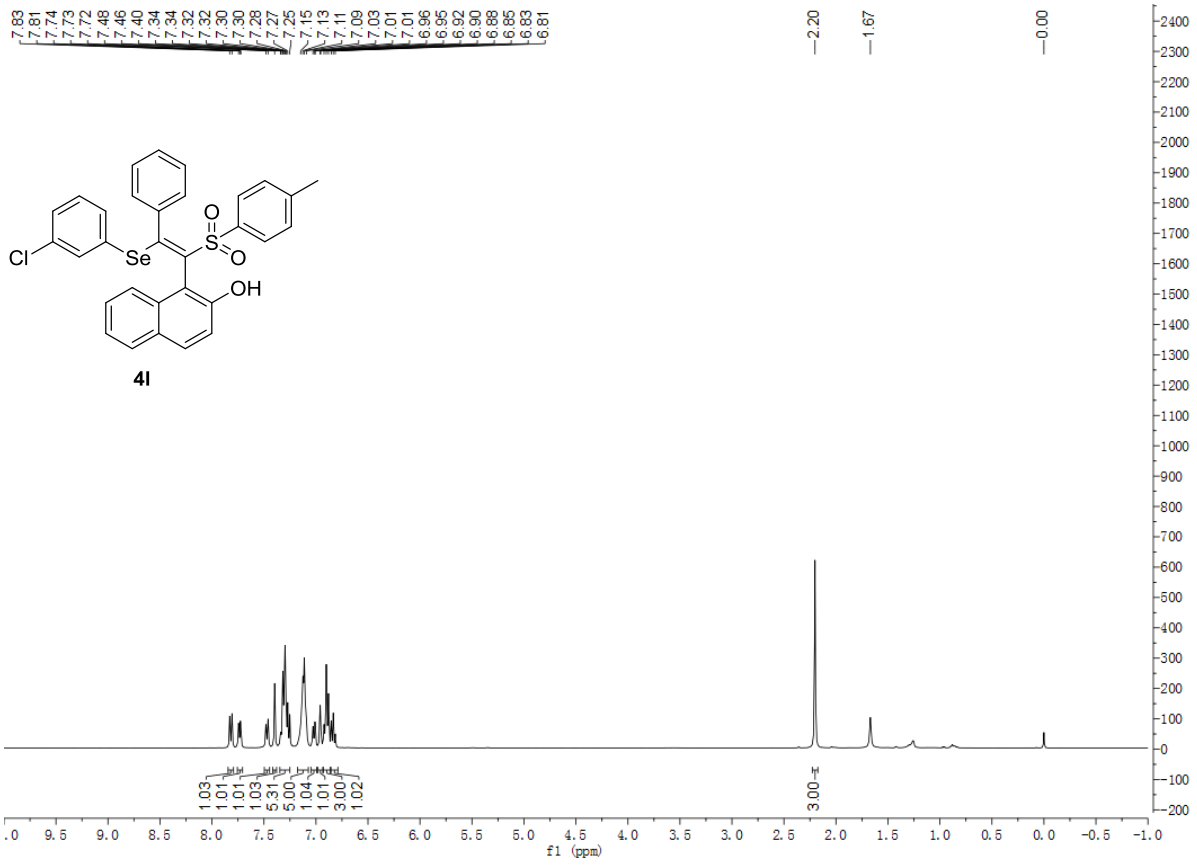
OH
4k
f1 (ppm)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7.13
7.11
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S
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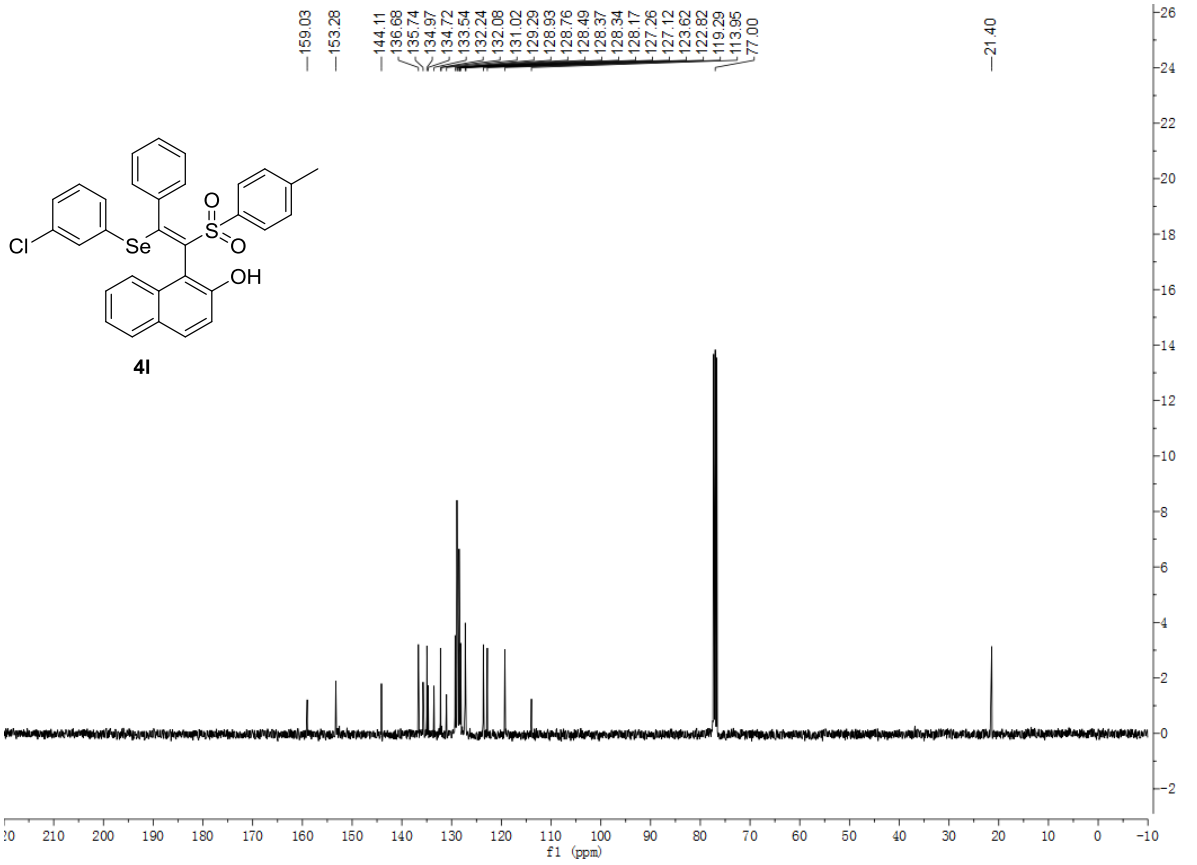
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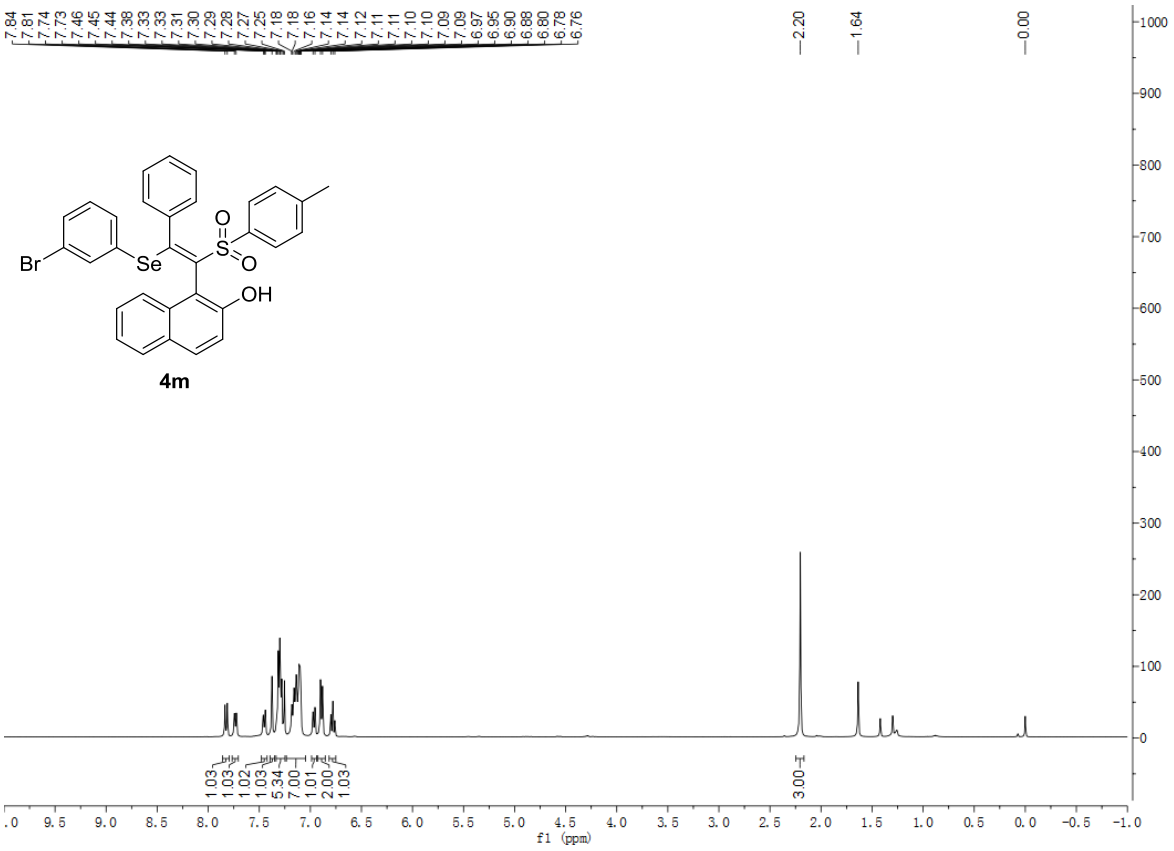
Cl
Se
O
S
O
OH
4l
f1 (ppm)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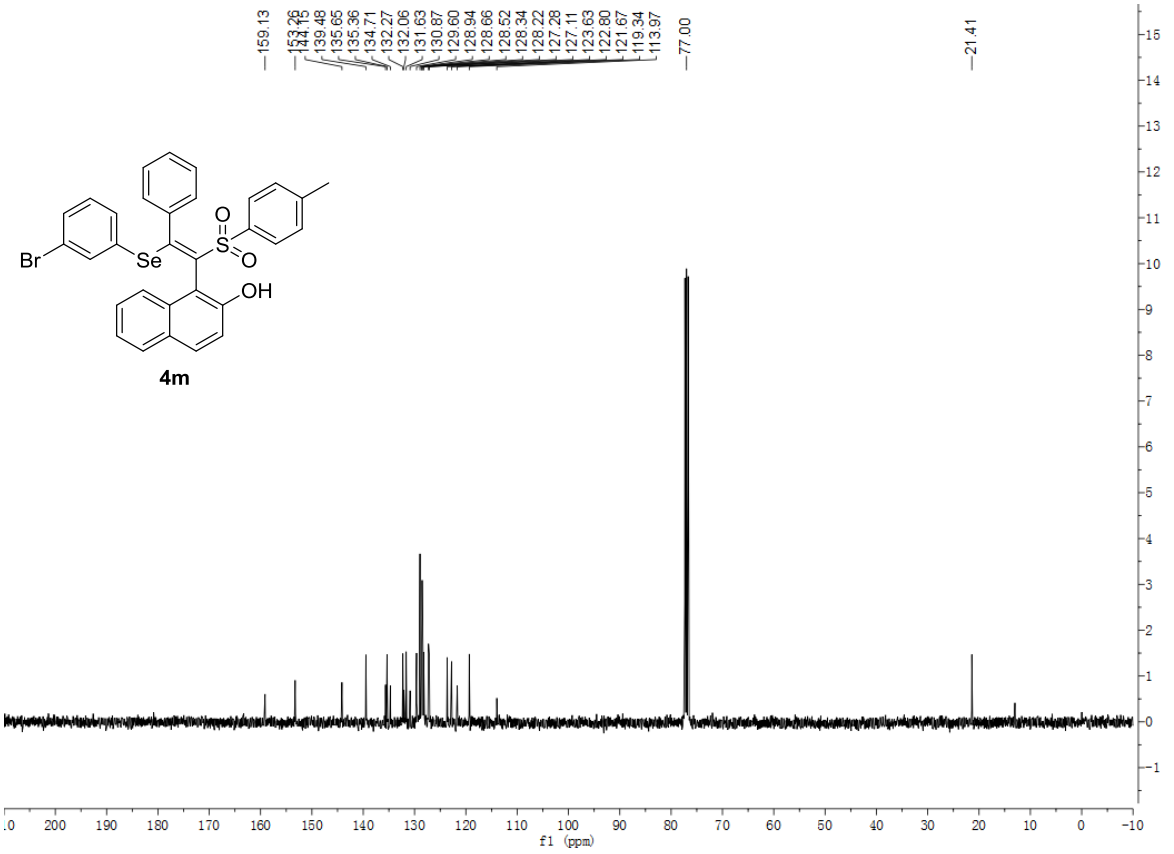
7.30
7.29
7.28
7.27
7.25
7.18
7.18
7.16
7.14
7.14
7.12
7.11
7.11
7.10
7.10
7.09
7.09
6.97
6.95
6.90
6.88
6.80
6.78
6.76
2.20
1.64
0.00
Br
Se
O
S
O
OH
4m
1.03
1.03
1.02
1.03
5.34
7.00
1.01
2.00
1.03
3.00
f1 (ppm)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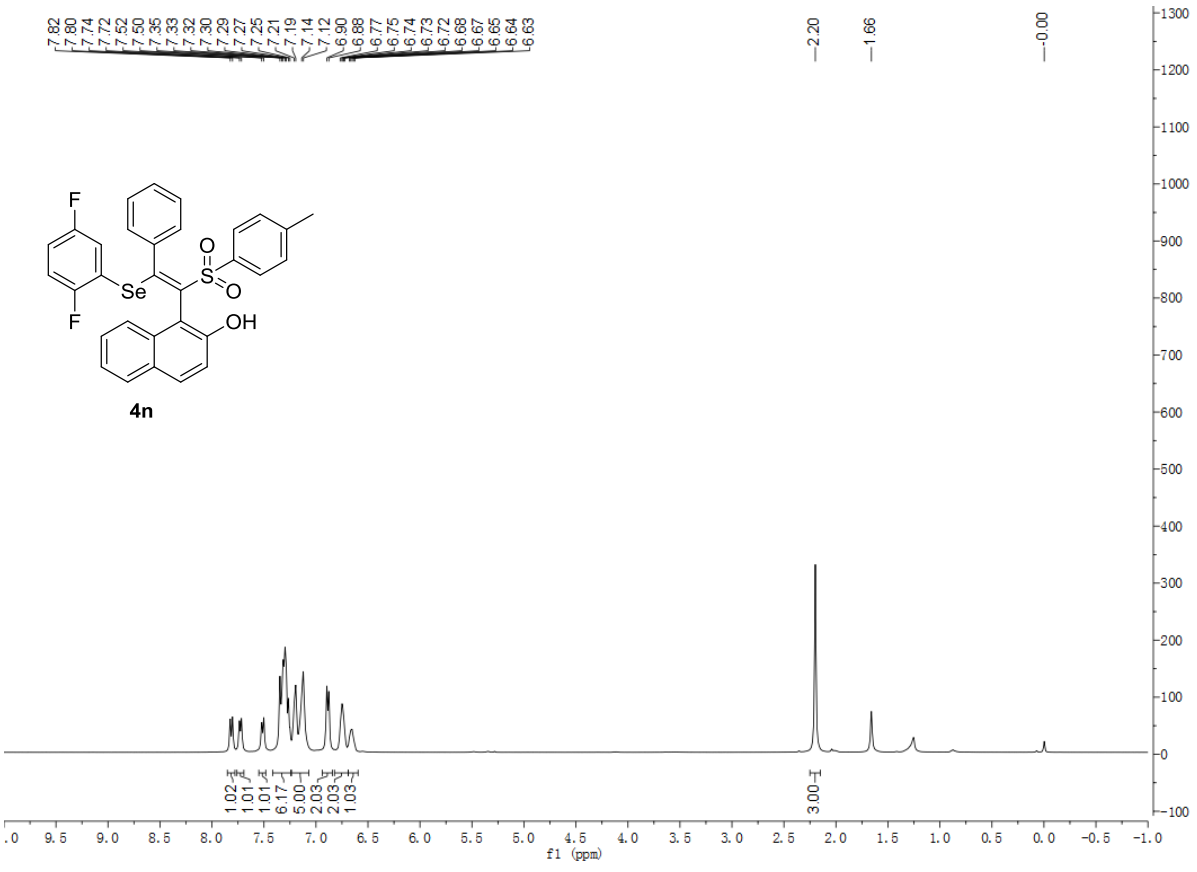
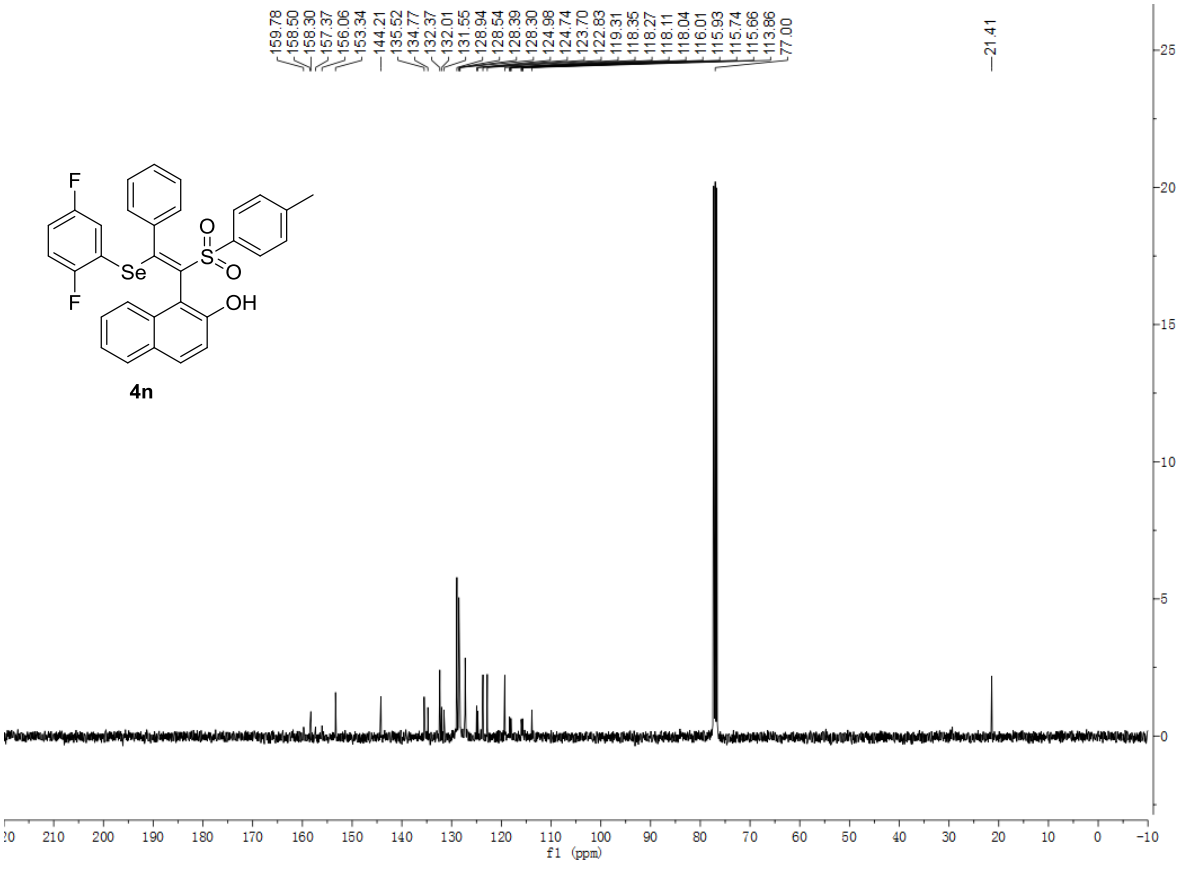
153.26
151.75
139.48
135.65
135.36
134.71
132.27
132.06
131.63
130.87
129.60
128.94
128.66
128.52
128.34
128.22
127.28
127.11
123.63
122.80
121.67
119.34
113.97
77.00
21.41
Br
Se
O
S
O
OH
4m
f1 (ppm)


7.82
7.80
7.74
7.72
7.52
7.50
7.35
7.33
7.32
7.30
7.29
7.27
7.25
7.21
7.19
7.14
7.12
6.90
6.88
6.77
6.75
6.74
6.73
6.72
6.68
6.67
6.65
6.64
6.63
2.20
1.66
0.00
F
Se
F
O
S
O
OH
1.02
1.01
1.01
6.17
5.00
2.03
2.03
1.03
3.00
f1 (ppm)

4n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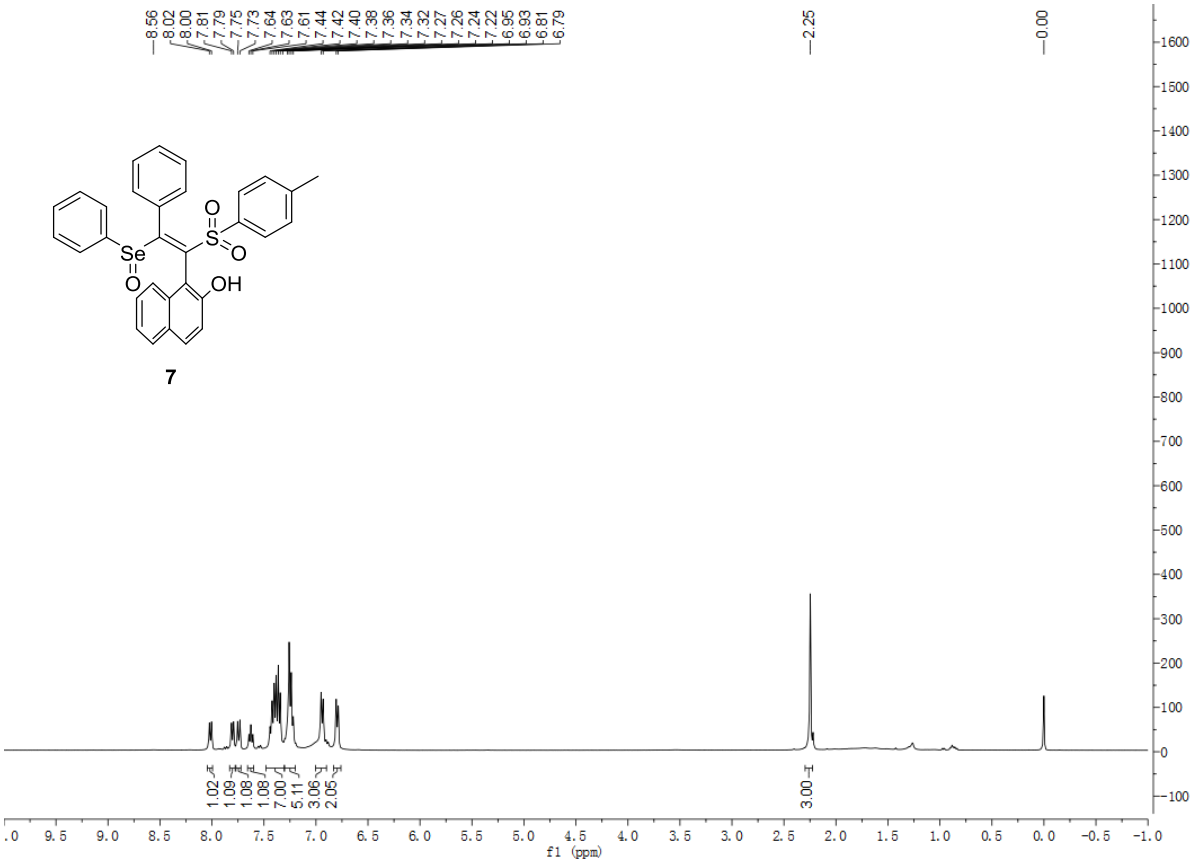
158.50
158.30
157.37
156.06
153.34
144.21
135.52
134.77
132.37
132.01
131.55
128.94
128.54
128.39
128.30
124.98
124.74
123.70
122.83
119.31
118.35
118.27
118.11
118.04
116.01
115.93
115.74
115.66
113.86
77.00
21.41
F
Se
F
O
S
O
OH
f1 (ppm)

4n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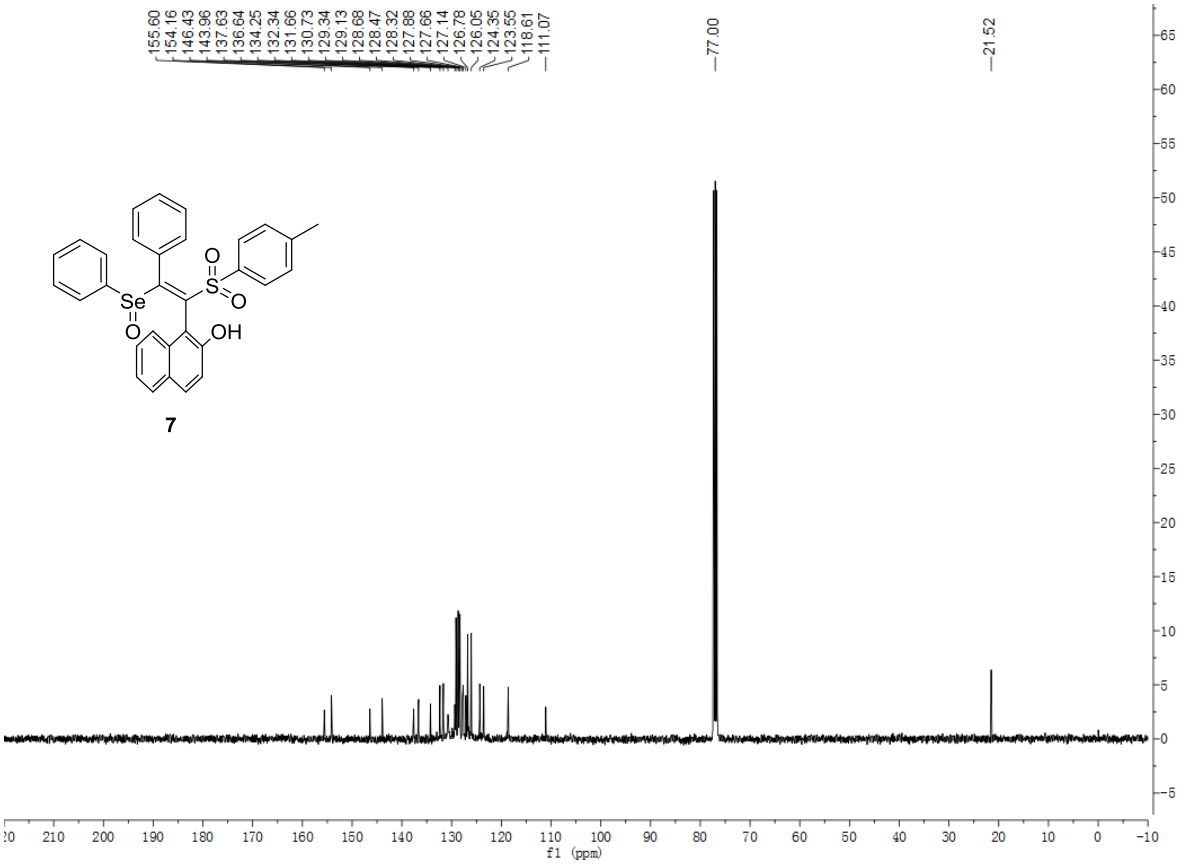
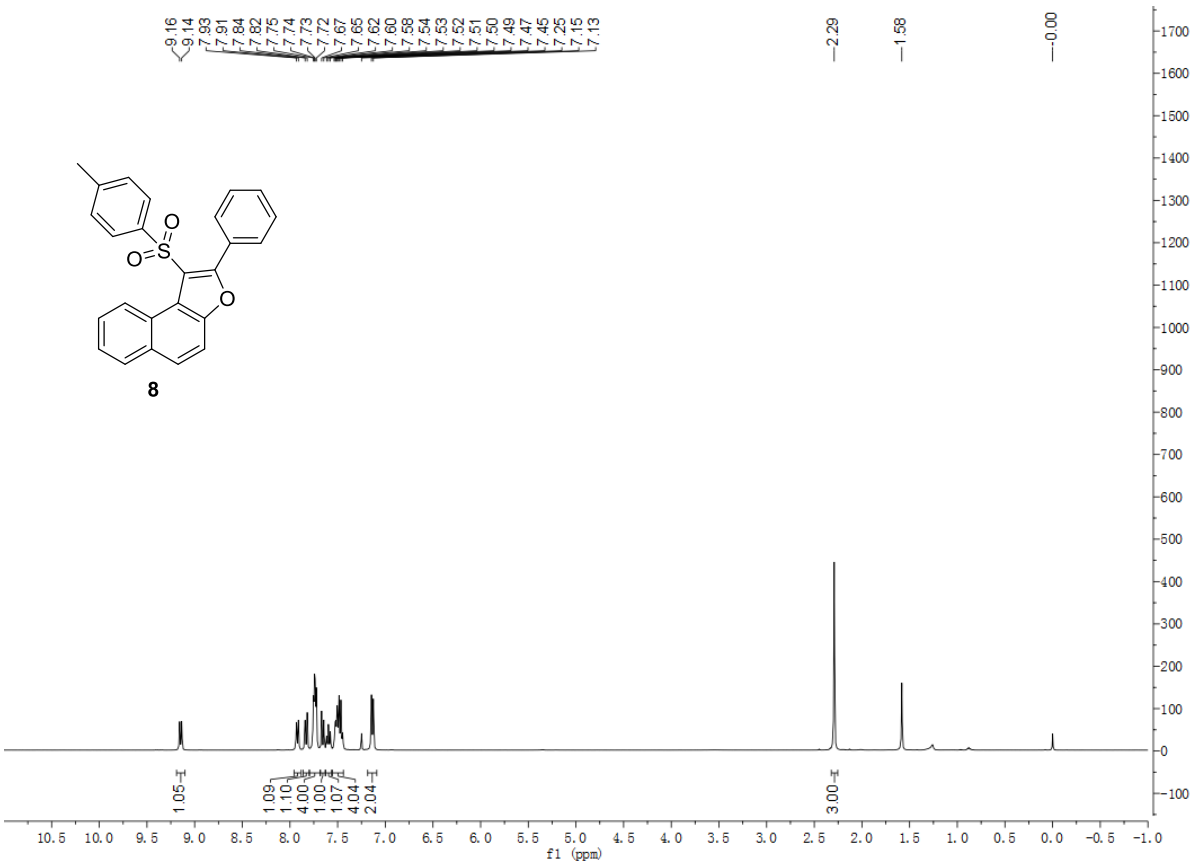
8.02
8.00
7.81
7.79
7.75
7.73
7.64
7.63
7.61
7.44
7.42
7.40
7.38
7.36
7.34
7.32
7.27
7.26
7.24
7.22
6.95
6.93
6.81
6.79
2.25
0.00
1.02
1.09
1.08
1.08
7.00
5.11
3.06
2.05
3.00
f1 (ppm)

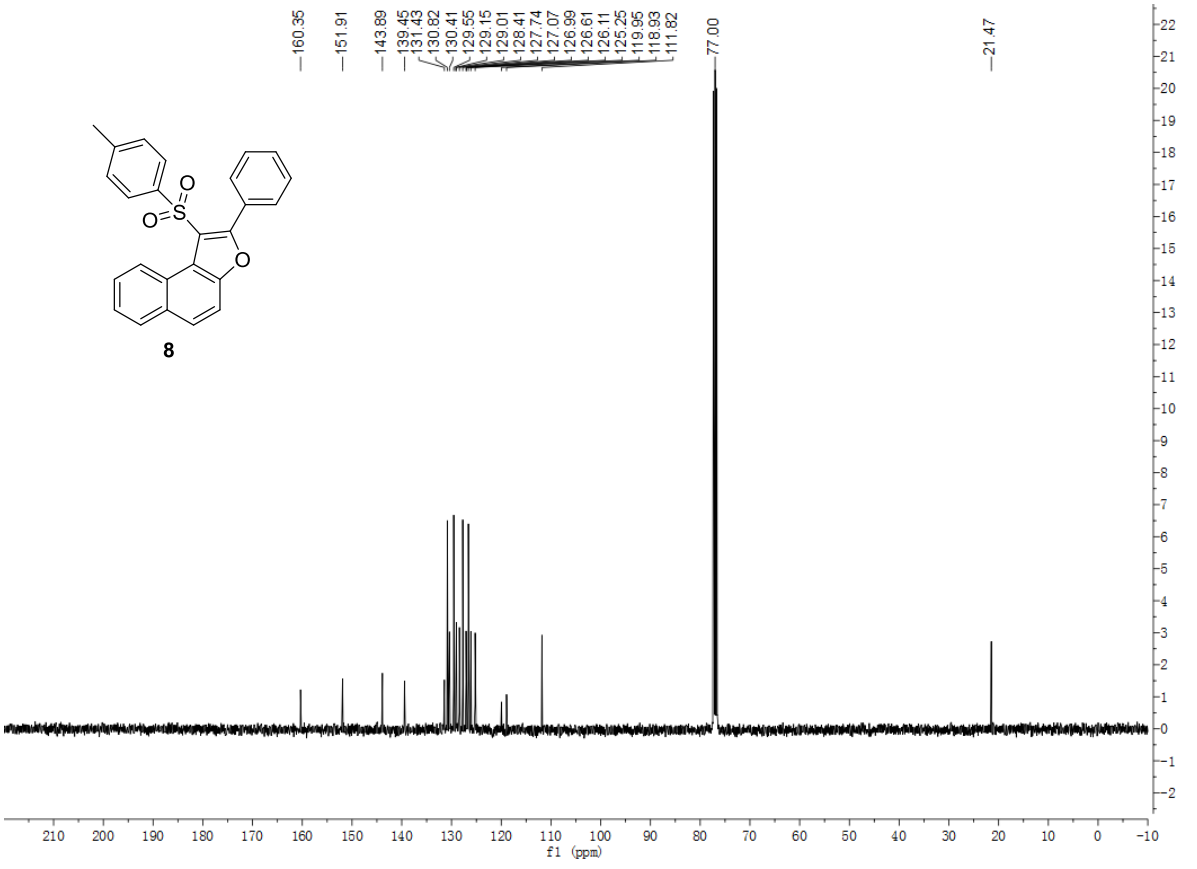
7


155.60
154.16
146.43
143.96
137.63
136.64
134.25
132.34
131.66
130.73
129.34
129.13
128.88
128.47
128.32
127.88
127.66
127.14
126.78
126.05
124.35
123.55
118.61
111.07
77.00
21.52
f1 (ppm)

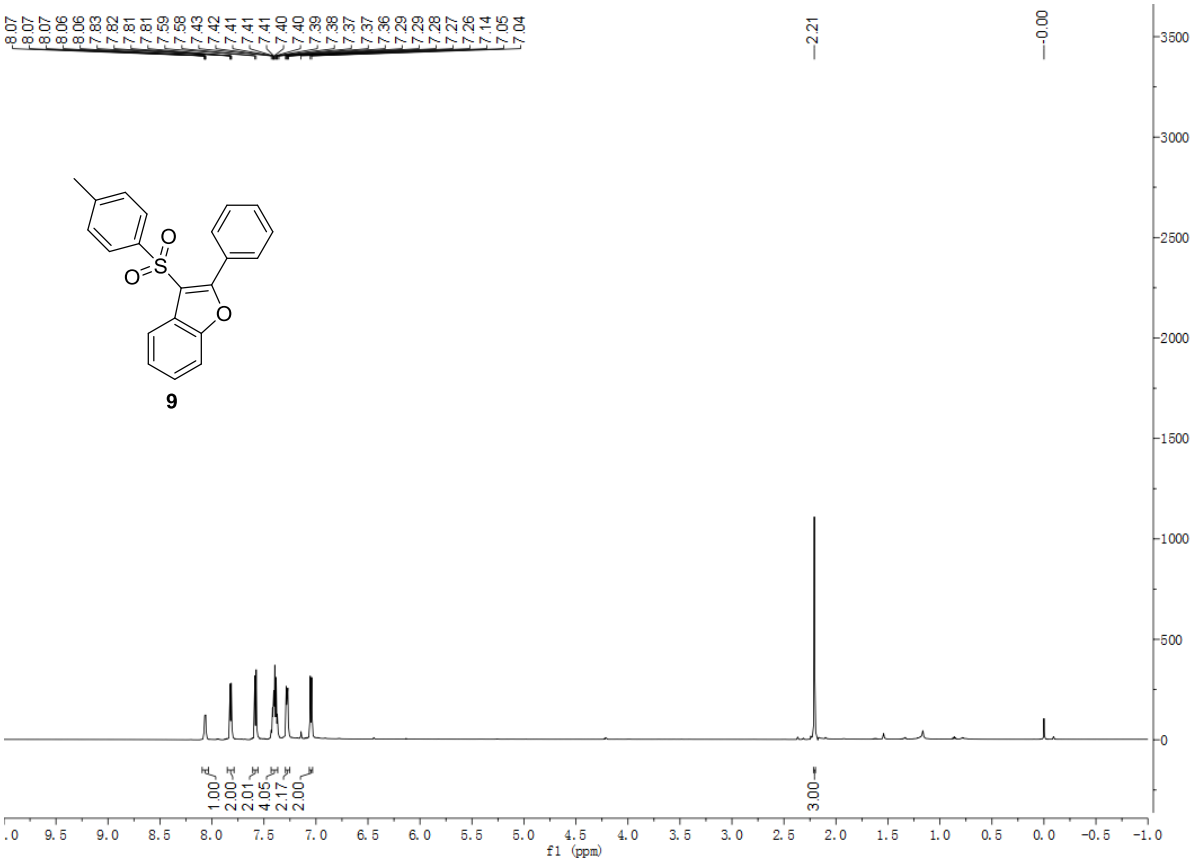
7


9.16
9.14
7.93
7.91
7.84
7.82
7.75
7.74
7.73
7.72
7.67
7.65
7.62
7.60
7.58
7.54
7.53
7.52
7.51
7.50
7.49
7.47
7.45
7.25
7.15
7.13
2.29
1.58
0.00
1.05
1.09
1.10
4.00
1.00
1.07
4.04
2.04
3.00
f1 (ppm)

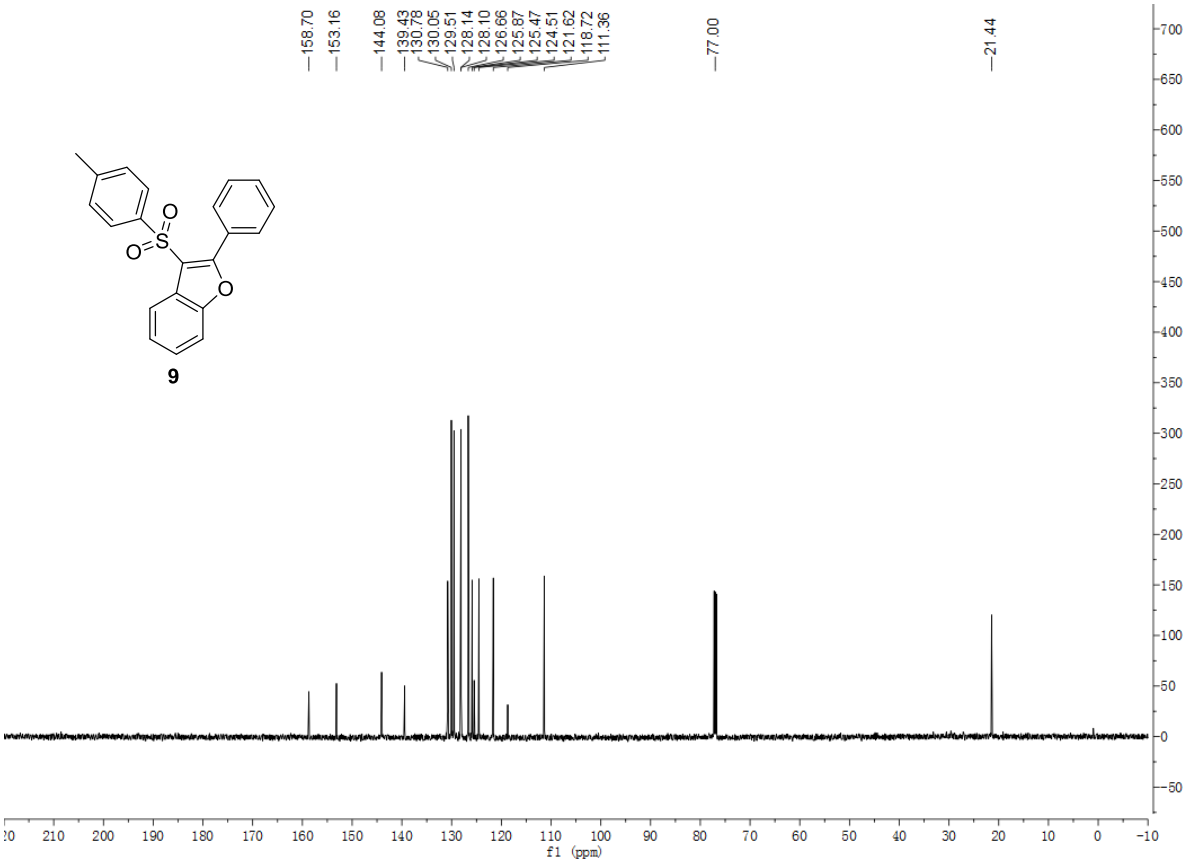
8


160.35
151.91
143.89
139.45
131.43
130.82
130.41
129.55
129.15
129.01
128.41
127.74
127.07
126.99
126.61
126.11
125.25
119.95
118.93
111.82
77.00
21.47
f1 (ppm)

8

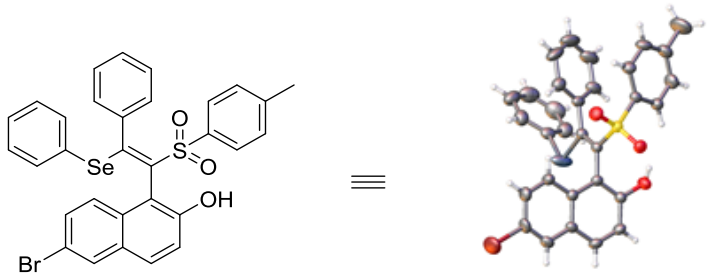

8.07
8.07
8.06
8.06
7.83
7.82
7.81
7.81
7.59
7.58
7.43
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.29
7.29
7.28
7.27
7.26
7.14
7.05
7.04
2.21
0.00
1.00
2.00
2.01
4.05
2.17
2.00
3.00
f1 (ppm)

9


158.70
153.16
144.08
139.43
130.78
130.05
129.51
128.14
128.10
126.66
125.87
125.47
124.51
121.62
118.72
111.36
77.00
21.44
f1 (ppm)

9

XIII. X-Ray Crystallographic information



3r ≡ CCDC 1877497

Bond precision:	C-C = 0.0049 A		Wavelength = 0.71073
Cell:	a = 14.8543 (4)	b = 12.8156 (3)	c = 16.9743 (5)
	alpha = 90	beta = 105.-20(3)	gamma = 90
Temperature:	295 K		
	Calculated		Reported
Volume	3120.95(15)		3120.94 (15)
Space group	P 21/c		P 1 21/c 1
Hall group	: -P 2ybc		-P 2ybc
Moiety formula	C31 H23 Br O3 S Se [+ solvent]		C31 H23 Br O3 S Se
Sum formula	C31 H23 Br O3 S Se [+ solvent]		C24 H17 Br O3 S Se
Mr	634.41		634.42
Dx,g cm-3	1.350		1.350
Z	4		4
Mu (mm-1)	2.577		2.577
F000	1272.0		1272.0
F000’	1271.47		
h, k, lmax	18, 16, 21		18, 16, 21
Nref	6391		6378
Tmin, Tmax	0.352, 0.366		0.691, 1.000
Tmin’	0.326		

Correction method= # Reported T Limits: Tmin=0.691 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness = 0.998	Theta(max) = 26.372
R(reflections) = 0.0435 (4724)	wR2(reflections) = 0.1184(6378)
S = 1.048	Npar = 336

XIV. Reference

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2 D. Li, Y. Tan, L. Peng, S. Li, N. Zhang, Y. Liu and H. Yan, *Org. Lett.*, 2018, **20**, 4959–4963.

3 D. Singh, A. M. Deobald, L. R. S. Camargo, G. Tabarelli, O. E. D. Rodrigues and A. L. Braga, *Org. Lett.*, 2010, **12**, 3288–3291.

4 S. Luo, N. Zhang, Z. Wang and H. Yan, *Org. Biomol. Chem.*, 2018, **16**, 2893–2901.

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