Supporting Information

Catalyst-Free and Rapid Access to *α*-Selenomethyl Ketones: A Direct One-Pot Synthesis from Sulfoxonium Ylides and Benzeneselenol

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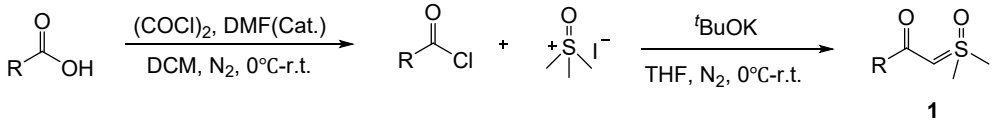
1. General Considerations

1.1. General information

All reagents, were purchased from commercial suppliers (e.g., Bide Pharmatech, Energy Chemical, and Leyan) and used directly without further purification. All heating reactions were carried out using an oil bath. Reaction progress was monitored by thin-layer chromatography (TLC) using pre-coated silica gel plates (GF254). Flash column chromatography was performed using Qingdao Haiyang Chemical silica gel (200-300 mesh) with PE/EA as the eluent.NMR spectra were recorded on a Bruker Avance III spectrometer (400 MHz). ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were obtained using $CDCl_3$ as the deuterated solvent. Chemical shifts (δ) are reported in ppm, with the residual solvent peaks of $CDCl_3$ referenced at 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR. Coupling constants (J) are reported in Hz. High-resolution mass spectra (HRMS) were acquired on a Bruker micro TOF Q III instrument. Experimental Details

2. Experimental Details

2.1 Synthetic Methods for α-Carbonyl Sulfur Ylides (1a-1r, 1v,1w)[1, 2]

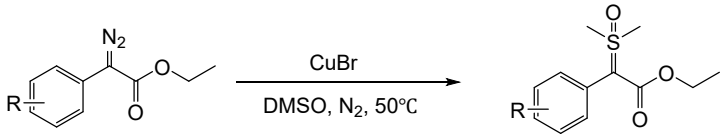


Step 1: A solution of the carboxylic acid (5 mmol, 1.0 equiv) in DCM (30 mL) was treated dropwise with $(COCl)_2$ (10 mmol, 2.0 equiv) and a catalytic amount of DMF (2 drops) at 0°C under a nitrogen atmosphere. The reaction mixture was then allowed to warm to room temperature and stirred for 2 h. After removal of the solvent under reduced pressure, the corresponding acyl chloride was obtained as a crude product.

Step 2: To a 100 mL three-necked flask were added potassium tert-butoxide (4.5 mmol, 3.0 equiv) and trimethyl sulfoxonium iodide (3.0 mmol, 2.0 equiv), followed by the addition of 20 mL THF. The system was purged with nitrogen and then heated under reflux in an oil bath for 2 hours. Subsequently, the mixture was cooled to 0°C, and a THF solution of the crude acyl chloride (10 mL, 0.15 mmol/mL) was added dropwise. After complete addition, the reaction was allowed to warm to room temperature and stirred for an additional 3 h. The reaction progress was monitored by TLC. Once the starting acyl chloride had been consumed, the solvent was removed under reduced pressure. Water was added, and the mixture was extracted with ethyl acetate (EA). The

combined organic layers were washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (eluent: EA/MeOH = 10:1) yielded pure compound **1**.

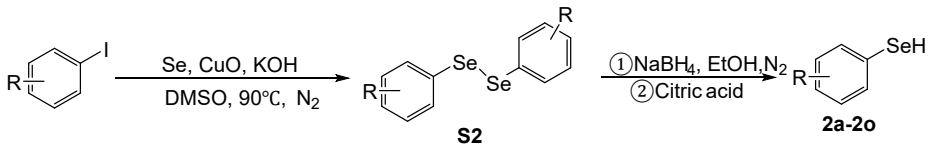
2.2 Synthetic Methods for *α*-Aryl Sulfur Ylide Esters (1s-1u)[1, 2]



1'

A 20 mL reaction tube was charged with copper(I) bromide (CuBr, 10 mol%) and the corresponding diazo compound (0.5 mmol) under a nitrogen atmosphere. Dimethyl sulfoxide (DMSO, 5 mL) was added as the solvent. After purging with nitrogen three times, the tube was placed in an oil bath and stirred at 50°C for 3 hours. The reaction progress was monitored by thin-layer chromatography (TLC). Upon complete consumption of the starting diazo compound, the reaction mixture was cooled to room temperature. Water was added, and the mixture was extracted with ethyl acetate (EA) three times. The combined organic layers were washed with water (10 mL × 3), followed by saturated brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford the crude product. Purification by silica gel column chromatography (eluent: EA/MeOH = 10:1) yielded pure compound **1'**.

2.3 General Procedure for the Synthesis of Benzeneselenol Compounds (2a-2l)[3]



S2 **2a-2o**

Step 1：In a 100 mL round-bottom flask, the aryl iodide compound (5 mmol, 1.0 equiv.) was dissolved in DMSO (10.00 mL), followed by the sequential addition of selenium powder (1.10 mmol, 2.2 equiv.), CuO (0.50 mmol, 0.1 equiv.), and KOH (10.00 mmol, 2.0 equiv.). The reaction mixture was stirred at 80°C for 6 h, and the progress was monitored by TLC.After completion, the reaction mixture was diluted with ethyl acetate (EA, 10.00 mL) and washed with water (10.00 mL × 3), followed by saturated brine (15.00 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), concentrated under reduced pressure, and the crude product was purified by column chromatography using petroleum ether (PE) as the eluent to afford **S2**.

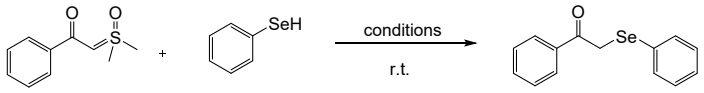
Step 2：In a 50 mL three-necked flask, **S2** (1.50 mmol) was dissolved in EtOH (5.00 mL), and the system was purged with N_2. At 0°C, $NaBH_4$ (4.50 mmol, 3.0 equiv.) was added, and the reaction was stirred for 15 min. Subsequently, citric acid (7.50 mmol, 5.0 equiv.) was added, and the mixture was stirred for an additional 5 min.Upon completion, the reaction was quenched with ethyl acetate (EA, 10.00 mL) and washed sequentially with:Saturated $NaHCO_3$ solution (8.00 mL), Saturated NH_4Cl solution (8.00 mL), Saturated NaCl solution (15.00 mL).The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the crude product was obtained as the corresponding aryl selenol derivatives **(2a-2l)**.

2.4 General Procedure for the Synthesis of 3

1 2 3

A dry 8 mL reaction vial was charged with sulfoxonium ylide 1 (0.15 mmol, 1.5 equiv) and dissolved in dichloromethane (DCM, 1 mL). To this solution, benzeneselenol 2 (0.1 mmol, 1.0 equiv) was added. The mixture was stirred at room temperature, and the reaction progress was monitored by TLC. Upon completion, the solvent was removed under reduced pressure. The resulting crude material was purified by silica gel column chromatography to afford the desired product 3.

2.5 Optimization of the Reaction Conditions[a]



1a 2a 3aa

Entry	Solvent	Temp.(°C)	**1a** (equiv)	**2a** (equiv)	Yeild(%)
1	DCM	r.t.(20)	1.0	1.0	71
2	DCE	r.t.(20)	1.0	1.0	66
3	MeOH	r.t.(20)	1.0	1.0	-
3	CH_3CN	r.t.(20)	1.0	1.0	57
4	Toluene	r.t.(20)	1.0	1.0	65
5	EA	r.t.(20)	1.0	1.0	48
6	H_2O	r.t.(20)	1.0	1.0	-
7	Acetone	r.t.(20)	1.0	1.0	65
8	DCM	50	1.0	1.0	72
9	**DCM**	**r.t.(20)**	**1.5**	**1.0**	**85[b](82[c])**
10	DCM	r.t.(20)	2.0	1.0	60
11	DCM	r.t.(20)	3.0	1.0	57
12	DCM	r.t.(20)	1.0	1.5	60
13	DCM	r.t.(20)	1.0	2.0	12
14	DCM	r.t.(20)	1.0	3.0	-

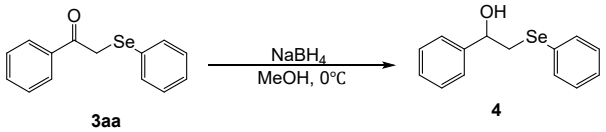
[a]Reaction conditions: a solution of α-benzoyl sulfoxonium ylide **1a**, phenylselenol **2a** in indicated solvent (1.0 mL) was stirred at room temperature for 5 minutes. [b]The NMR yield was determined using 1,3,5-trimethylbenzene as the internal standard. [c]Isolated yield.

2.6 Gram-scale reaction

1a 2a 3aa

In a 100 mL round-bottom flask, compound **1a** (1.00 g, 5.10 mmol, 1.5 equiv) was dissolved in dichloromethane (DCM, 30 mL). At room temperature, 2a (0.52 g, 3.40 mmol, 1.0 equiv) was added to the solution, and the reaction was stirred for 30 minutes. Upon completion, the solvent was removed under reduced pressure. The resulting crude product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 30:1) to afford 3aa (0.64 g, 70% yield).

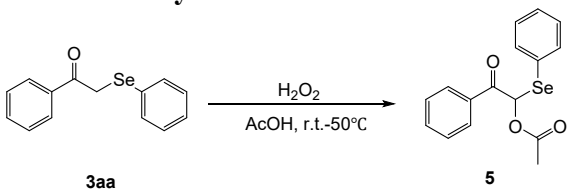
2.7 General Procedure for the Synthesis of 4



3aa 4

In a 10 mL reaction tube, **3aa** (0.028g, 0.1 mmol, 1.0 equiv.) was dissolved in MeOH (1.00 mL). At 0°C, $NaBH_4$ (0.008 g, 0.2 mmol, 2.0 equiv.) was added slowly, and the mixture was stirred for 1 hour.After completion of the reaction, water (1.00 mL) was added, followed by extraction with ethyl acetate (EA, 5.00 mL × 3). The combined organic layers were washed successively with:Saturated NH_4Cl solution (5.00 mL)Saturated NaCl solution (5.00 mL).The organic phase was dried over anhydrous Na_2SO_4, and the crude product was purified by column chromatography using PE/EA (10:1, petroleum ether/ethyl acetate) as the eluent to afford the desired product **4** (0.018 g, 64% yield).

2.8 General Procedure for the Synthesis of 5

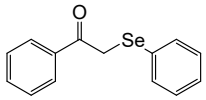


3aa 5

In a 10 mL reaction tube, **3aa** (0.028 g, 0.10 mmol, 1.0 equiv.) was dissolved in acetic acid (AcOH, 2.00 mL). At room temperature, 30% H_2O_2 solution (0.017 g,0.15 mmol, 1.5 equiv.) was added, and the reaction mixture was stirred at 50°C for 2 hours.Upon completion of the reaction, water (1.00 mL) was added, followed by extraction with ethyl acetate (EA, 5.00 mL × 3). The combined organic layers were washed successively with:Saturated $NaHCO_3$ solution (5.00 mL), Saturated NaCl solution (5.00 mL).The organic phase was dried over anhydrous Na_2SO_4, and the crude product was purified by column chromatography using PE/EA (10:1, petroleum ether/ethyl acetate) as the eluent to afford the desired product 4 (0.020 g, 62% yield).

3. Characterization Data of Products

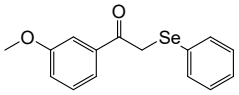
1-phenyl-2-(phenylselanyl)ethan-1-one (3aa)[4]



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 23 mg (82%).

^{1}H NMR (400 MHz, CDCl3) δ 7.92 – 7.83 (m, 2H), 7.54 (ddd, J = 9.6, 5.6, 1.8 Hz, 3H), 7.42 (t, J = 7.7 Hz, 2H), 7.30 – 7.24 (m, 3H), 4.17 (s, 2H).

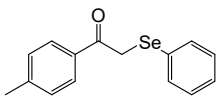
1-phenyl-2-(phenylselanyl)ethan-1-one (3ba)[4]



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 21 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dq, J = 8.1, 2.6 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.35 – 7.26 (m, 4H), 7.10 (dd, J = 8.3, 2.7 Hz, 1H), 4.16 (s, 2H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8, 158.9, 135.9, 133.0, 133.0, 128.5, 128.2, 127.0, 120.3, 118.9, 111.9, 54.4, 31.8. **HRMS (ESI)** : *m/z*[M+Na]$^+$ calcd for $C_{15}H_{14}O_2SeNa^+$: 329.0051; found: 329.0053.

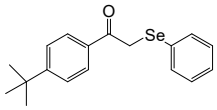
2-(phenylselanyl)-1-(p-tolyl)ethan-1-one (3ca)[4]



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 15 mg (52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.56 – 7.52 (m, 2H), 7.29 – 7.26 (m, 3H), 7.23 (d, J = 8.0 Hz, 2H), 4.16 (s, 2H), 2.41 (s, 3H).

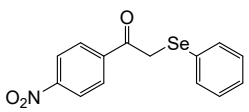
1-(4-(*tert*-butyl)phenyl)-2-(phenylselanyl)ethan-1-one (3da)[4]



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1); yield: 31 mg (94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.56 – 7.52 (m, 2H), 7.46 – 7.42 (m, 2H), 7.29 – 7.25 (m, 3H), 4.17 (s, 2H), 1.34 (s, 9H).

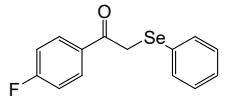
1-(4-nitrophenyl)-2-(phenylselanyl)ethan-1-one (3ea)[4]



Yellow solid; eluent: petroleum ether/ethyl acetate (5:1), yield: 23 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 8.6 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.33 – 7.27 (m, 3H), 4.15 (s, 2H).

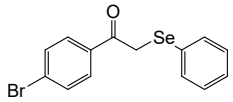
1-(4-fluorophenyl)-2-(phenylselanyl)ethan-1-one (3fa)[4]



Brownish-yellow oil; eluent: petroleum ether/ethyl acetate (10:1), yield: 6 mg (21%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 2H), 7.54 – 7.50 (m, 2H), 7.31 – 7.24 (m, 3H), 7.09 (t, J = 8.6 Hz, 2H), 4.13 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.72.

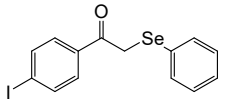
1-(4-bromophenyl)-2-(phenylselanyl)ethan-1-one (3ga)[4]



Brownish-yellow oil; eluent: petroleum ether/ethyl acetate (20:1), yield: 31 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.57 – 7.53 (m, 2H), 7.51 (dt, J = 6.4, 1.7 Hz, 2H), 7.32 – 7.25 (m, 3H), 4.11 (s, 2H).

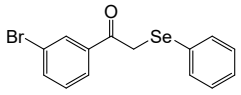
1-(4-iodophenyl)-2-(phenylselanyl)ethan-1-one (3ha)[4]



Yellow solid; eluent: petroleum ether/ethyl acetate (30:1), yield: 32 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.58 – 7.54 (m, 2H), 7.51 (dt, J = 6.5, 1.7 Hz, 2H), 7.31 – 7.26 (m, 3H), 4.10 (s, 2H).

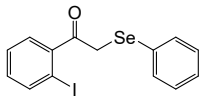
1-(3-bromophenyl)-2-(phenylselanyl)ethan-1-one (3ia)[5]



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 27 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, J = 1.8 Hz, 1H), 7.77 (dt, J = 7.8, 1.3 Hz, 1H), 7.66 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.32 – 7.25 (m, 4H), 4.11 (s, 2H).

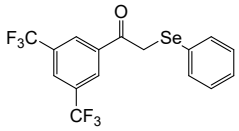
1-(2-iodophenyl)-2-(phenylselanyl)ethan-1-one (3ja)



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 31 mg (78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.9 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.33 – 7.31 (m, 2H), 7.26 – 7.23 (m, 3H), 7.11 – 7.06 (m, 1H), 4.17 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.5, 142.2, 139.4, 132.7, 130.7, 128.2, 128.2, 127.8, 127.0, 126.8, 91.0, 34.2. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{14}H_{12}IOSe^+$: 402.9093; found: 402.9085.

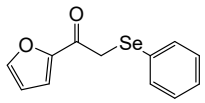
1-(3,5-bis(trifluoromethyl)phenyl)-2-(phenylselanyl)ethan-1-one (3ka)



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 10 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 8.02 (s, 1H), 7.51 – 7.47 (m, 2H), 7.36 – 7.26 (m, 3H), 4.15 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.9, 136.2, 133.6, 131.5, 131.1, 128.5, 127.9, 127.6, 126.8, 125.3, 120.4, 31.0. **HRMS (ESI)** : m/z[M+K]$^+$ calcd for $C_{16}H_{10}F_6OSeK^+$: 450.9433; found: 450.9442.

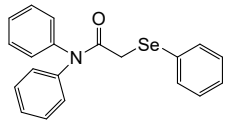
1-(furan-2-yl)-2-(phenylselanyl)ethan-1-one (3la)



Yellow oil; eluent: petroleum ether/ethyl acetate (10:1), yield: 20 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 4H), 7.28 (s, 2H), 7.11 (d, J = 3.6 Hz, 1H), 6.50 (dd, J = 3.7, 1.7 Hz, 1H), 3.98 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.3, 150.6, 145.5, 133.1, 128.2, 128.0, 127.1, 116.8, 111.5, 31.0. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{12}H_{11}O_2Se^+$: 266.9919; found: 266.9916.

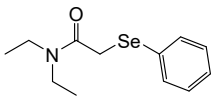
N,N-diphenyl-2-(phenylselanyl)acetamide (3ma)



Yellow solid; m.p.: 104-105℃; eluent: petroleum ether/ethyl acetate (20:1), yield: 29 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.34 (s, 5H), 7.27 – 7.21 (m, 8H), 3.65 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 141.6, 132.6, 128.6, 128.3, 128.1, 126.7, 28.7. **HRMS (ESI)** : m/z[M+Na]$^+$ calcd for $C_{20}H_{17}NOSeNa^+$: 390.0368; found: 390.0367.

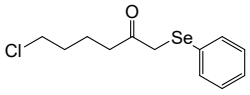
N,N-diethyl-2-(phenylselanyl)acetamide (3na)



Yellow oil; eluent: petroleum ether/ethyl acetate (5:1), yield: 20 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.29 – 7.26 (m, 3H), 3.69 (s, 2H), 3.36 (d, J = 7.1 Hz, 2H), 3.25 (d, J = 7.1 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 132.8, 128.4, 128.1, 126.7, 41.8, 39.4, 27.5, 13.4, 11.8. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{12}H_{18}NOSe^+$: 272.0548; found: 272.0547.

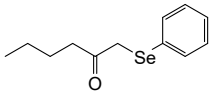
6-chloro-1-(phenylselanyl)hexan-2-one (3oa)



Yellow oil; eluent: petroleum ether/ethyl acetate (20:1), yield: 21 mg (72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (ddd, J = 6.6, 3.2, 1.5 Hz, 2H), 7.31 – 7.27 (m, 3H), 3.58 (s, 2H), 3.52 – 3.47 (m, 2H), 2.63 – 2.59 (m, 2H), 1.72 (dq, J = 6.5, 2.0 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.0, 132.3, 128.4, 127.8, 127.0, 43.5, 38.6, 34.9, 30.8, 20.2. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{12}H_{16}ClOSe^+$: 291.0049; found: 291.0036.

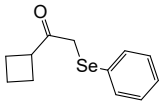
1-(phenylselanyl)hexan-2-one (3pa)



Yellow oil; eluent: petroleum ether/ethyl acetate (20:1), yield: 20 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.30 – 7.25 (m, 3H), 3.59 (s, 2H), 2.56 (t, J = 7.4 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.31 – 1.25 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.9, 132.3, 128.3, 128.0, 126.9, 39.5, 35.0, 25.1, 21.2, 12.8. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{12}H_{17}OSe^+$: 257.0439; found: 257.0431.

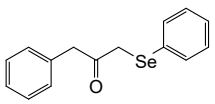
1-cyclobutyl-2-(phenylselanyl)ethan-1-one (3qa)



Brown Oil; eluent: petroleum ether/ethyl acetate (20:1), yield: 14 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.29 – 7.26 (m, 3H), 3.58 (s, 2H), 3.52 (qd, J = 8.6, 1.1 Hz, 1H), 2.27 – 2.16 (m, 2H), 2.10 (tdd, J = 12.1, 8.0, 2.5 Hz, 2H), 2.00 – 1.90 (m, 1H), 1.85 – 1.76 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.7, 132.1, 128.2, 128.0, 126.7, 42.6, 33.1, 23.9, 16.8. **HRMS (ESI)** : m/z[M+Na]$^+$ calcd for $C_{12}H_{14}OSeNa^+$: 277.0102; found: 277.0098.

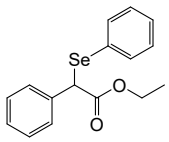
1-phenyl-3-(phenylselanyl)propan-2-one (3ra)



Yellow oil; eluent: petroleum ether/ethyl acetate (20:1), yield: 27 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.29 (td, J = 5.5, 2.0 Hz, 6H), 7.17 – 7.13 (m, 2H), 3.87 (s, 2H), 3.61 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.8, 133.0, 132.5, 128.5, 128.4, 128.4, 127.7, 127.0, 126.1, 46.7, 34.2. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{15}H_{15}OSe^+$: 291.0283; found: 291.0277.

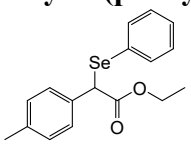
ethyl 2-phenyl-2-(phenylselanyl)acetate (3sa)



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 25 mg (78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.44 – 7.41 (m, 2H), 7.32 – 7.24 (m, 6H), 4.90 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 135.2, 134.6, 127.9, 127.8, 127.7, 127.6, 127.5, 126.9, 60.5, 47.2, 12.9. **HRMS (ESI)** : m/z[M+Na]$^+$ calcd for $C_{16}H_{16}O_2SeNa^+$: 343.0208; found: 343.0206.

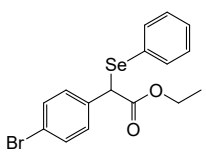
ethyl 2-(phenylselanyl)-2-(p-tolyl)acetate (3ta)



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 25 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, J = 6.9, 1.5 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.31 – 7.26 (m, 2H), 7.13 (d, J = 7.9 Hz, 2H), 4.91 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 136.7, 134.5, 132.1, 128.2, 128.1, 127.9, 127.5, 127.5, 60.4, 47.1, 20.1, 12.9. **HRMS (ESI)** : m/z[M+Na]$^+$ calcd for $C_{17}H_{19}O_2SeNa^+$: 357.0364; found: 357.0349.

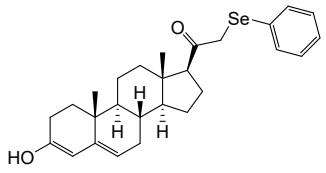
ethyl 2-(4-bromophenyl)-2-(phenylselanyl)acetate (3ua)



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1), yield: 10 mg (26%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.41 – 7.38 (m, 2H), 7.35 – 7.30 (m, 1H), 7.27 (dd, J = 7.0, 1.5 Hz, 4H), 4.82 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 134.9, 134.4, 130.5, 129.3, 128.1, 127.8, 127.3, 120.9, 60.7, 46.3, 12.9. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{16}H_{16}O_2BrSe^+$: 398.9493; found: 398.9486.

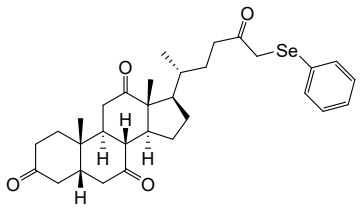
1-((8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(phenylselanyl)ethan-1-one (3va)



Yellow oil; eluent: petroleum ether/ethyl acetate (5:1), yield: 12 mg (26%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 6.7, 3.0 Hz, 2H), 7.30 – 7.26 (m, 3H), 6.05 (d, J = 2.5 Hz, 1H), 5.40 – 5.37 (m, 1H), 3.66 – 3.56 (m, 2H), 2.83 (t, J = 8.9 Hz, 1H), 2.48 (d, J = 14.4 Hz, 1H), 2.32 (dd, J = 18.0, 5.7 Hz, 1H), 2.17 – 2.12 (m, 1H), 1.97 – 1.90 (m, 1H), 1.89 – 1.79 (m, 1H), 1.69 (dd, J = 10.2, 5.2 Hz, 3H), 1.64 (d, J = 8.3 Hz, 2H), 1.60 – 1.55 (m, 2H), 1.48 – 1.43 (m, 1H), 1.40 (d, J = 8.3 Hz, 1H), 1.36 (d, J = 2.8 Hz, 1H), 1.32 (d, J = 5.9 Hz, 1H), 1.30 – 1.27 (m, 2H), 0.95 (s, 3H), 0.66 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.9, 139.5, 132.6, 129.4, 128.2, 128.0, 126.8, 125.9, 122.8, 59.9, 55.9, 46.8 43.7, 37.7, 36.7, 33.8, 33.5, 30.7, 30.6, 29.6, 23.5, 22.8, 20.1, 17.8, 12.6. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{27}H_{35}O_2Se^+$: 471.1797; found: 471.1811. **[α]13 D**: -19.04 (c = 10.00, $CHCl_3$).

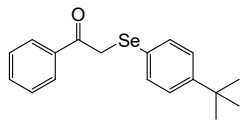
(5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-5-oxo-6-(phenylselanyl)hexan-2-yl)dodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (3wa)



White Solid; m.p.: 153-154℃; eluent: petroleum ether/ethyl acetate (30:1), yield: 31 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.27 (d, J = 3.1 Hz, 3H), 3.59 (s, 2H), 2.92 (dd, J = 12.9, 6.0 Hz, 1H), 2.85 – 2.71 (m, 2H), 2.60 (q, J = 4.4 Hz, 3H), 2.30 – 2.20 (m, 3H), 2.07 (dd, J = 12.2, 5.1 Hz, 1H), 1.95 (dt, J = 9.4, 2.2 Hz, 3H), 1.80 – 1.73 (m, 3H), 1.68 – 1.60 (m, 3H), 1.35 (s, 3H), 1.31 – 1.20 (m, 5H), 1.01 (s, 3H), 0.78 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.6, 208.7, 205.0, 132.3, 128.3, 127.9, 126.9, 56.8, 55.9, 52.3, 50.9, 48.0, 44.5, 44.3, 44.0, 43.1, 37.6, 36.8, 35.1, 34.9, 34.3, 32.0, 28.5, 26.6, 24.2, 21.6, 17.8, 10.8. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{31}H_{41}O_4Se^+$: 557.2165; found: 557.2176. **[α]13 D**: +20.27 (c = 10.00, $CHCl_3$).

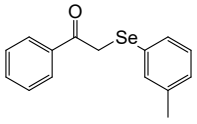
2-((4-(tert-butyl)phenyl)selanyl)-1-phenylethan-1-one (3ab)[4]



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1); yield: 21mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.57 – 7.52 (m, 1H), 7.48 – 7.45 (m, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.30 – 7.27 (m, 2H), 4.14 (s, 2H), 1.30 (s, 9H).

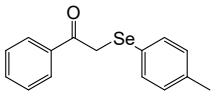
1-phenyl-2-(*m*-tolylselanyl)ethan-1-one (3ac)[4]



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1); yield: 20 mg (69%).

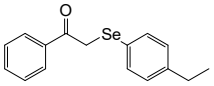
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.58 – 7.53 (m, 1H), 7.43 (dd, J = 8.4, 7.1 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 4.17 (s, 2H), 2.31 (s, 3H).

1-phenyl-2-(*p*-tolylselanyl)ethan-1-one (3ad)[4]



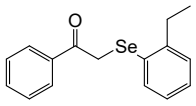
Yellow oil; eluent: petroleum ether/ethyl acetate (20:1); yield: 21 mg (72%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.58 – 7.53 (m, 1H), 7.43 (t, J = 7.6 Hz, 4H), 7.08 (d, J = 7.9 Hz, 2H), 4.12 (s, 2H), 2.33 (s, 3H).

2-((4-ethylphenyl)selanyl)-1-phenylethan-1-one (3ae)[4]



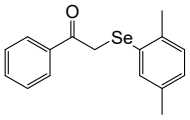
Yellow solid; eluent: petroleum ether/ethyl acetate (30:1); yield: 7 mg (23%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.50 (d, J = 6.3 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.10 (d, J = 7.9 Hz, 2H), 4.13 (s, 2H), 2.63 (q, J = 7.6 Hz, 2H), 1.21 (d, J = 7.6 Hz, 3H).

2-((2-ethylphenyl)selanyl)-1-phenylethan-1-one (3af)[4]



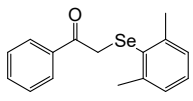
Yellow oil; eluent: petroleum ether/ethyl acetate (30:1); yield: 25 mg (83%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.58 – 7.52 (m, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.12 (td, J = 7.4, 2.0 Hz, 1H), 4.15 (d, J = 0.8 Hz, 2H), 2.74 (q, J = 7.5 Hz, 2H), 1.16 (td, J = 7.5, 0.9 Hz, 3H).

2-((2,5-dimethylphenyl)selanyl)-1-phenylethan-1-one (3ag)



Yellow oil; eluent: petroleum ether/ethyl acetate (30:1); yield: 20 mg (63%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.55 (td, J = 7.2, 1.3 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 1.8 Hz, 1H), 7.08 (d, J = 7.7 Hz, 1H), 7.01 (dd, J = 7.7, 1.8 Hz, 1H), 4.12 (s, 2H), 2.34 (s, 3H), 2.27 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 136.5, 135.3, 134.6, 134.1, 132.2, 128.9, 128.7, 128.2, 127.7, 127.5, 30.9, 21.0, 19.7. **HRMS (ESI)** : *m/z*$[M+H]^+$ calcd for $C_{16}H_{17}OSe^+$: 305.0439 found: 305.0437.

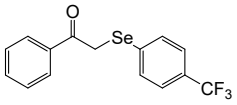
2-((2,6-dimethylphenyl)selanyl)-1-phenylethan-1-one (3ah)[4]



Yellow solid; mp 86-88 °C; eluent: petroleum ether/ethyl acetate (40:1); yield: 14mg (48%).

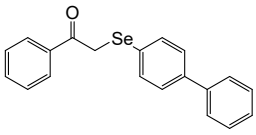
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.55 – 7.50 (m, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.14 (dd, J = 8.5, 6.3 Hz, 1H), 7.07 (d, J = 7.3 Hz, 2H), 3.93 (s, 2H), 2.44 (s, 6H).

1-phenyl-2-((4-(trifluoromethyl)phenyl)selanyl)ethan-1-one (3ai)



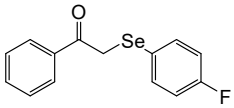
Yellow oil; eluent: petroleum ether/ethyl acetate (20:1); yield: 7 mg (20%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.59 – 7.56 (m, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.9 Hz, 2H), 4.26 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.5, 134.1, 132.6, 131.8, 127.7, 127.6, 125.0, 124.9, 124.9, 124.9, 31.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.73. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{15}H_{12}OSe^+$: 345.0000 found: 345.0010.

2-([1,1'-biphenyl]-4-ylselanyl)-1-phenylethan-1-one (3aj)



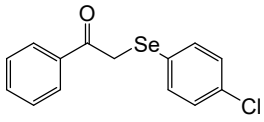
Yellow oil; eluent: petroleum ether/ethyl acetate (30:1); yield: 7 mg (20%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.61 – 7.55 (m, 3H), 7.50 (t, J = 7.6 Hz, 3H), 7.46 – 7.42 (m, 5H), 7.37 (d, J = 7.2 Hz, 1H), 4.21 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0, 140.0, 134.4, 133.4, 132.3, 131.2, 127.8, 127.7, 127.6, 126.9, 126.6, 126.0, 126.0, 31.7. **HRMS (ESI)** : m/z[M+H]$^+$ calcd for $C_{20}H_{17}OSe^+$: 353.0439 found: 353.0433.

2-((4-fluorophenyl)selanyl)-1-phenylethan-1-one (3ak)[4]



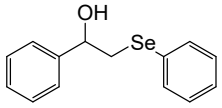
Yellow-brown oil; eluent: petroleum ether/ethyl acetate (15:1); yield: 20 mg (69%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.59 – 7.54 (m, 1H), 7.52 – 7.48 (m, 2H), 7.44 (t, J = 7.7 Hz, 2H), 6.99 – 6.93 (m, 2H), 4.12 (s, 2H).

2-((4-chlorophenyl)selanyl)-1-phenylethan-1-one (3al)[4]



Yellow oil; eluent: petroleum ether/ethyl acetate (10:1); yield: 20 mg (65%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 – 7.43 (m, 4H), 7.25 – 7.22 (m, 2H), 4.15 (s, 2H).

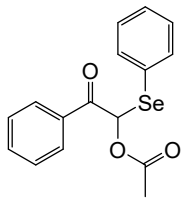
1-phenyl-2-(phenylselanyl)ethan-1-ol (4)[4]



Yellow oil; eluent: petroleum ether/ethyl acetate (10:1); yield: 18 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 5.7 Hz, 2H), 7.34 (d, J = 4.4 Hz, 4H), 7.30 – 7.26 (m, 4H), 4.79 – 4.73 (m, 1H), 3.31 (dd, J = 12.8, 3.7 Hz, 1H), 3.14 (t, J = 11.2 Hz, 1H), 2.81 (s, 1H).

2-oxo-2-phenyl-1-(phenylselanyl)ethyl acetate (5)[4]



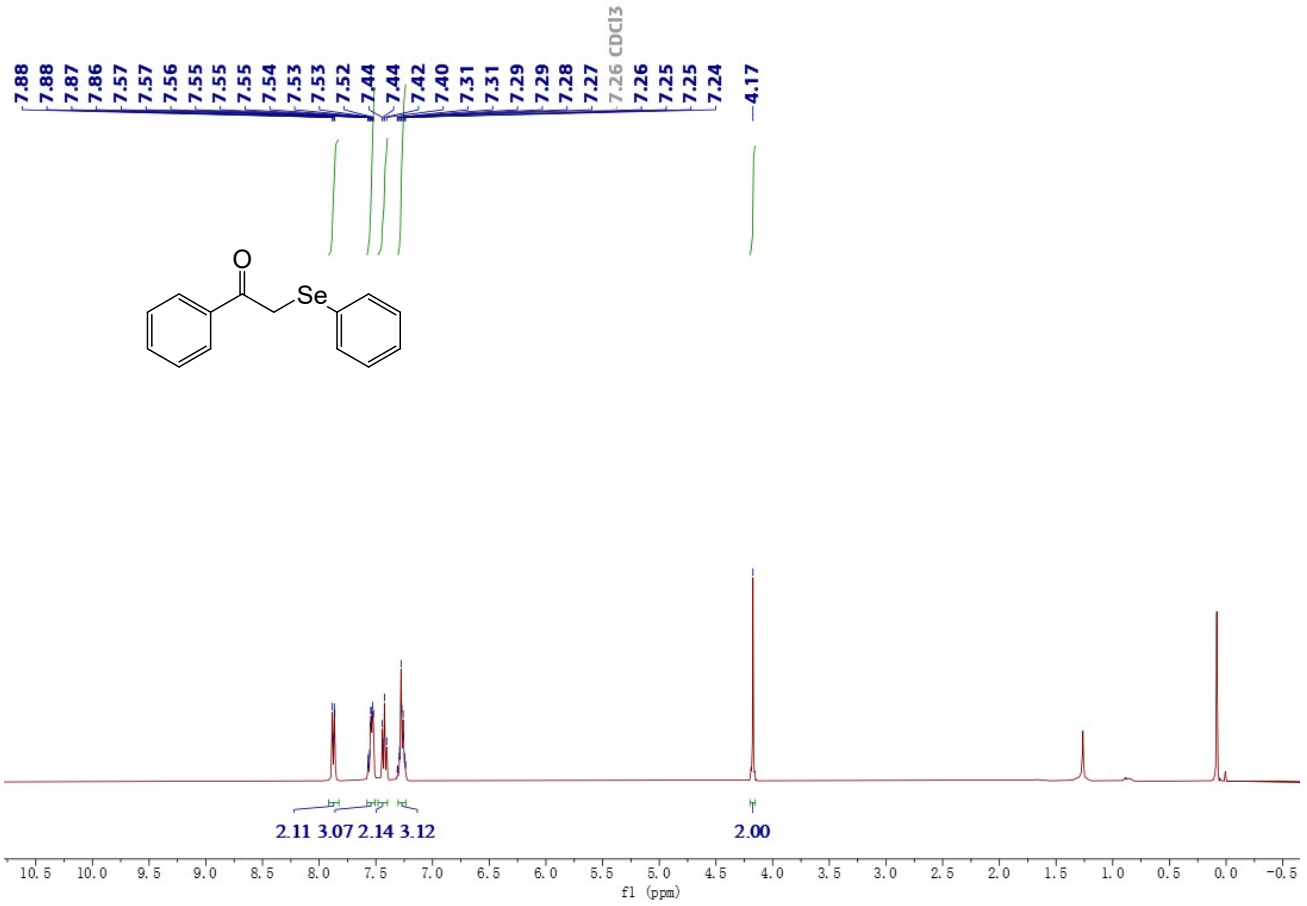
Yellow oil; eluent: petroleum ether/ethyl acetate (10:1); yield: 21 mg (62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.7 Hz, 2H), 7.56 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.36 (d, J = 7.3 Hz, 1H), 7.31 – 7.26 (m, 3H), 2.22 (s, 3H).

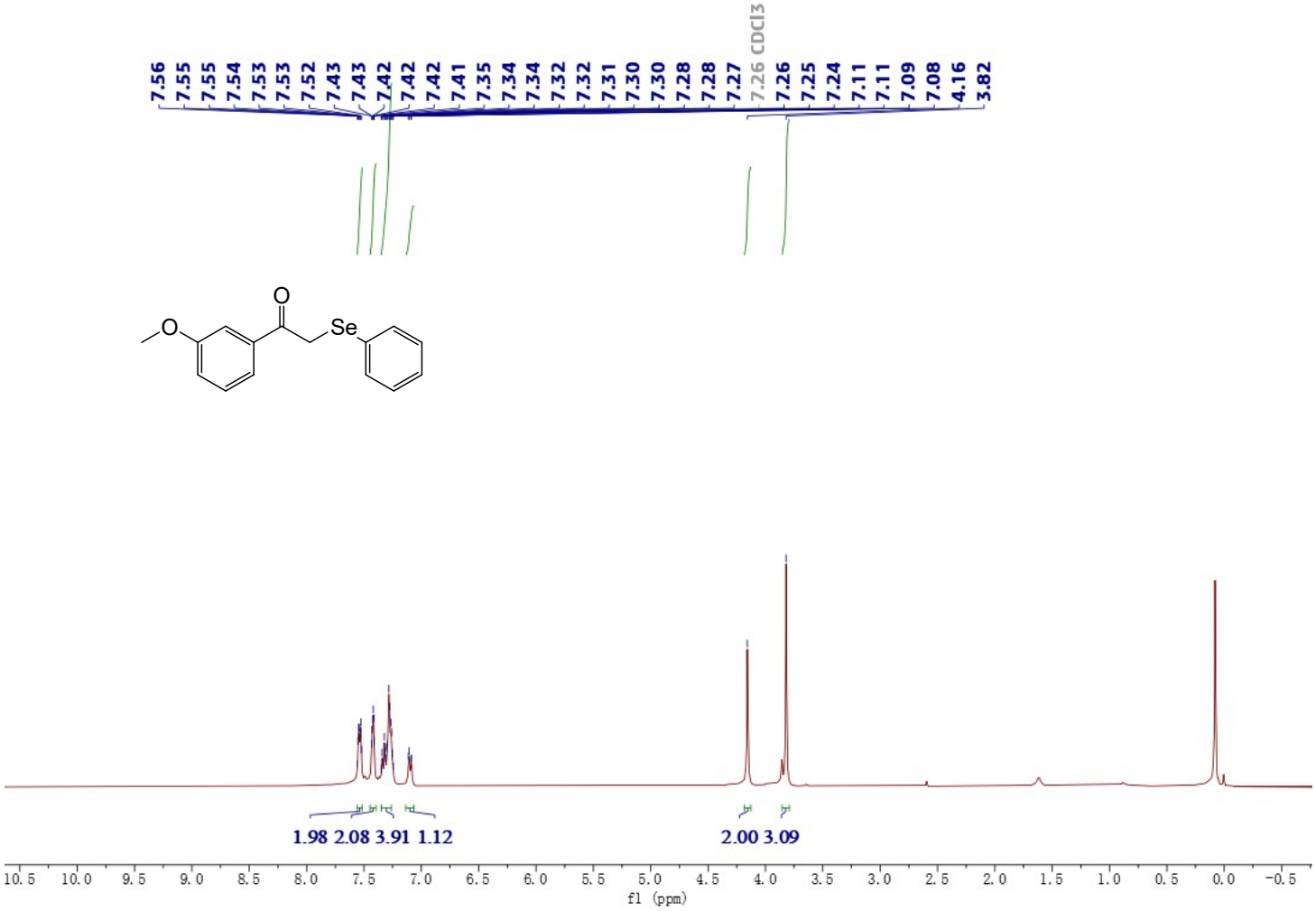
4. Copies of NMR Spectra for Products

The ^{13C} NMR data for all known compounds can be found in the literature.[4,5]

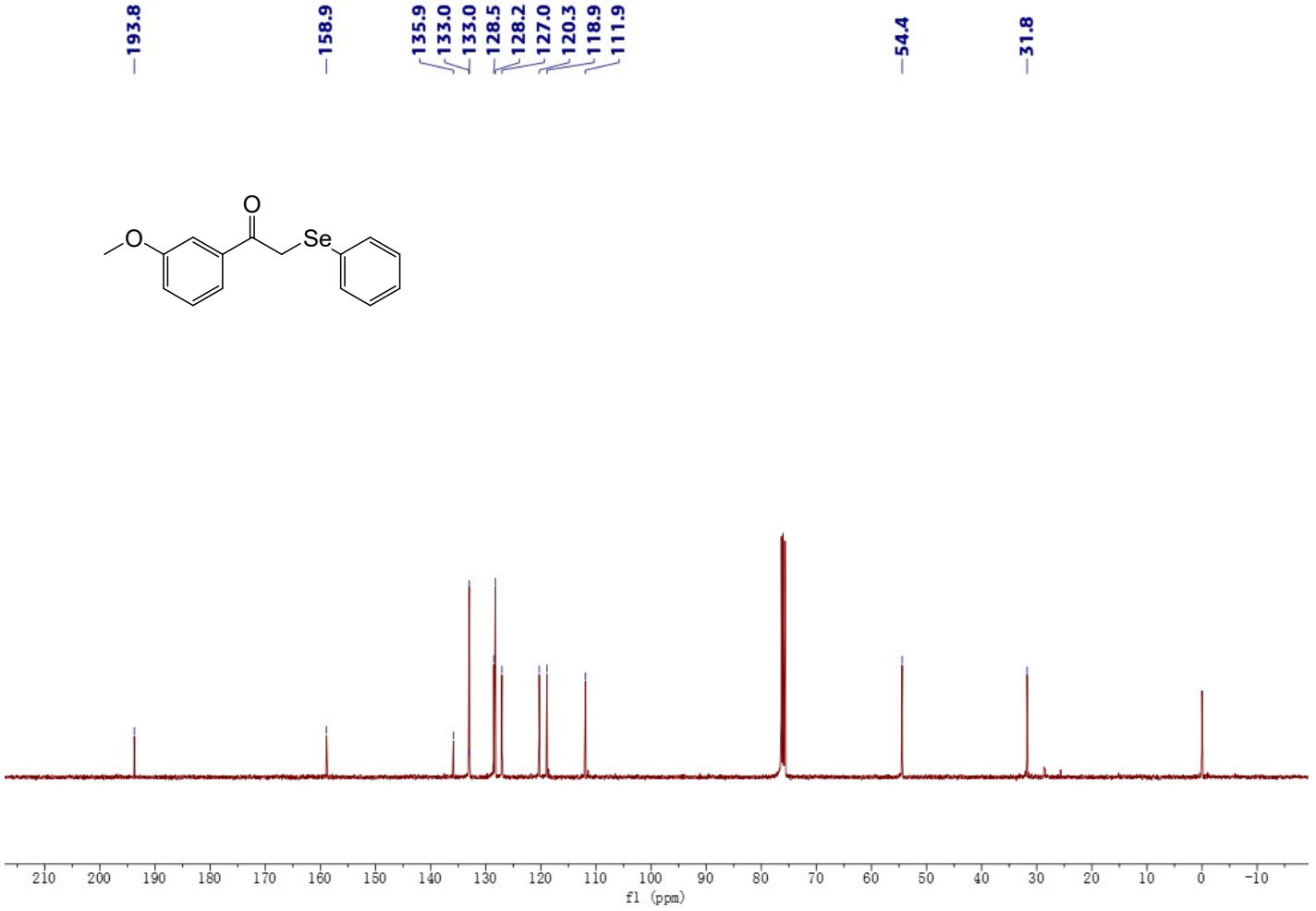
3aa: ^{1}H NMR (400 MHz, $CDCl_3$)



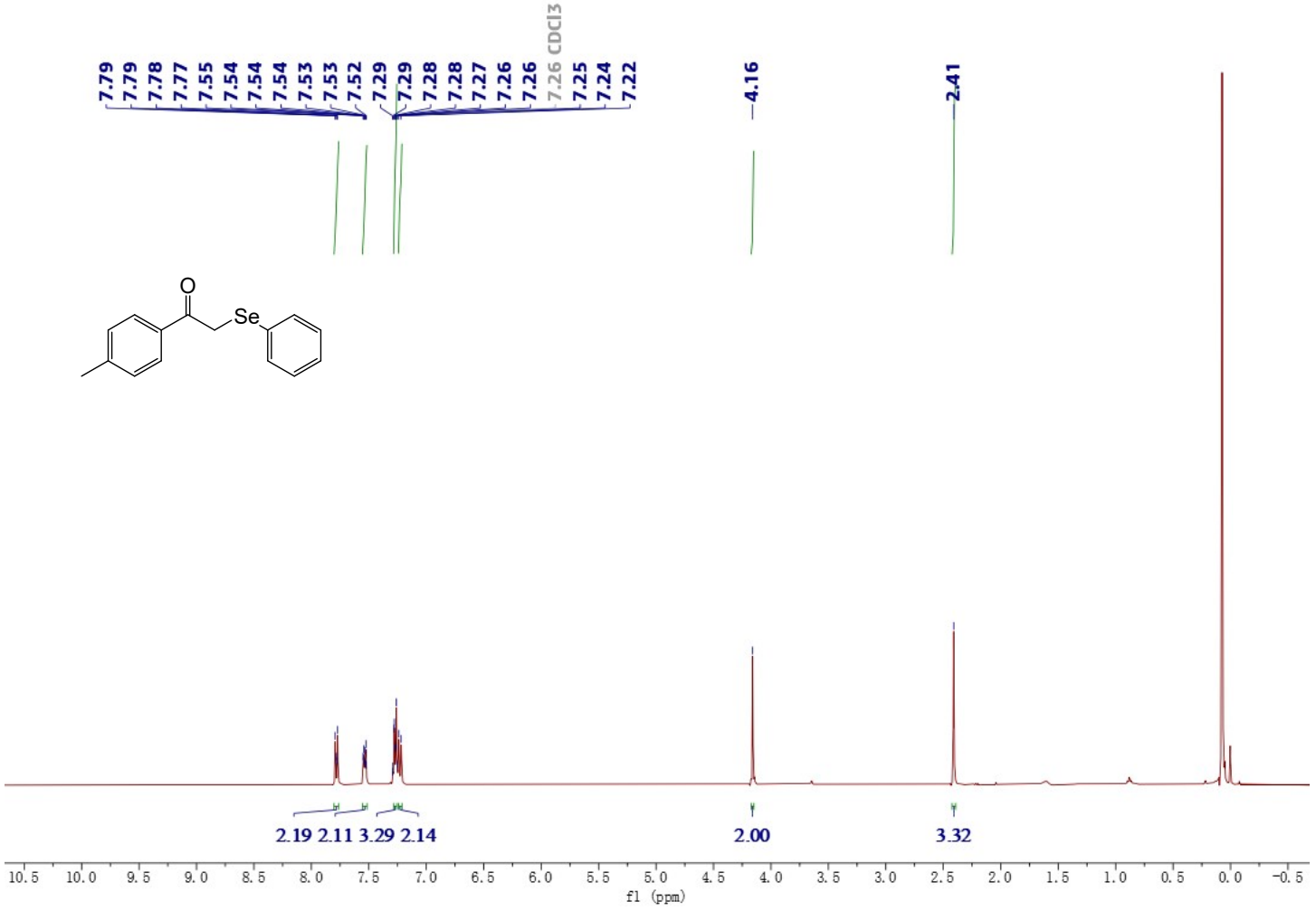
3ba: ^{1}H NMR (400 MHz, $CDCl_3$)



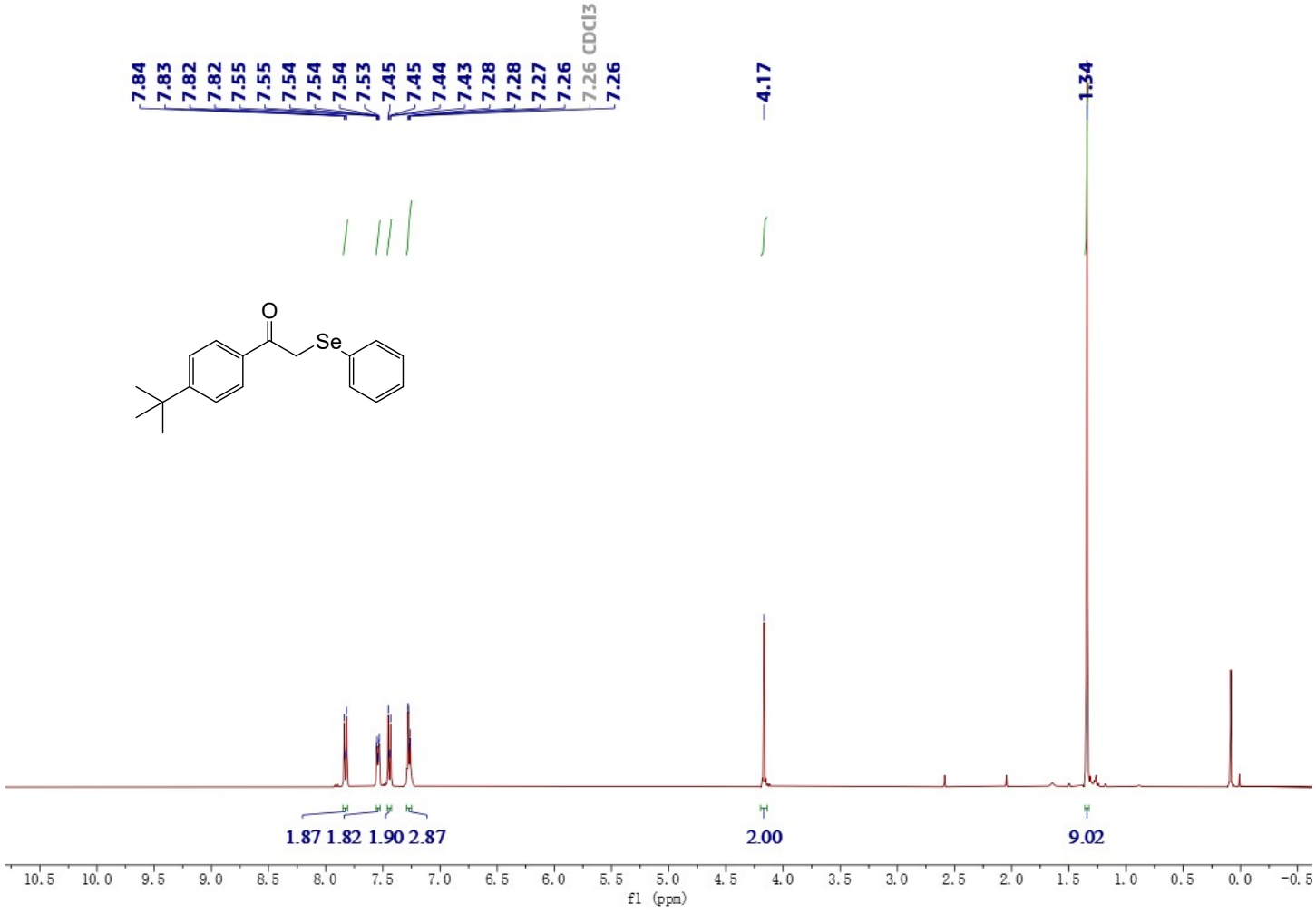
3ba: ^{13}C NMR (100 MHz, $CDCl_3$)



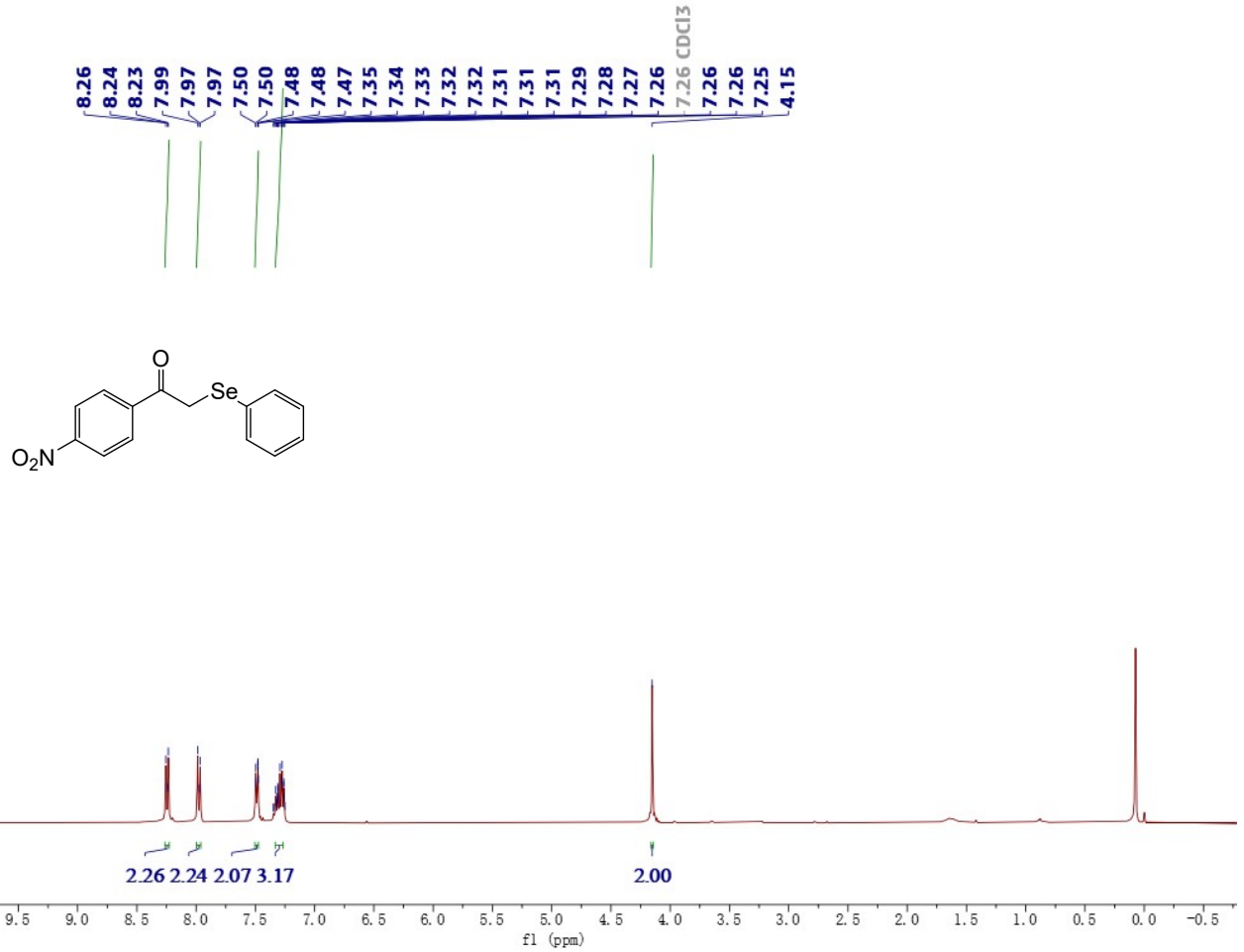
3ca: ^{1}H NMR (400 MHz, $CDCl_3$)



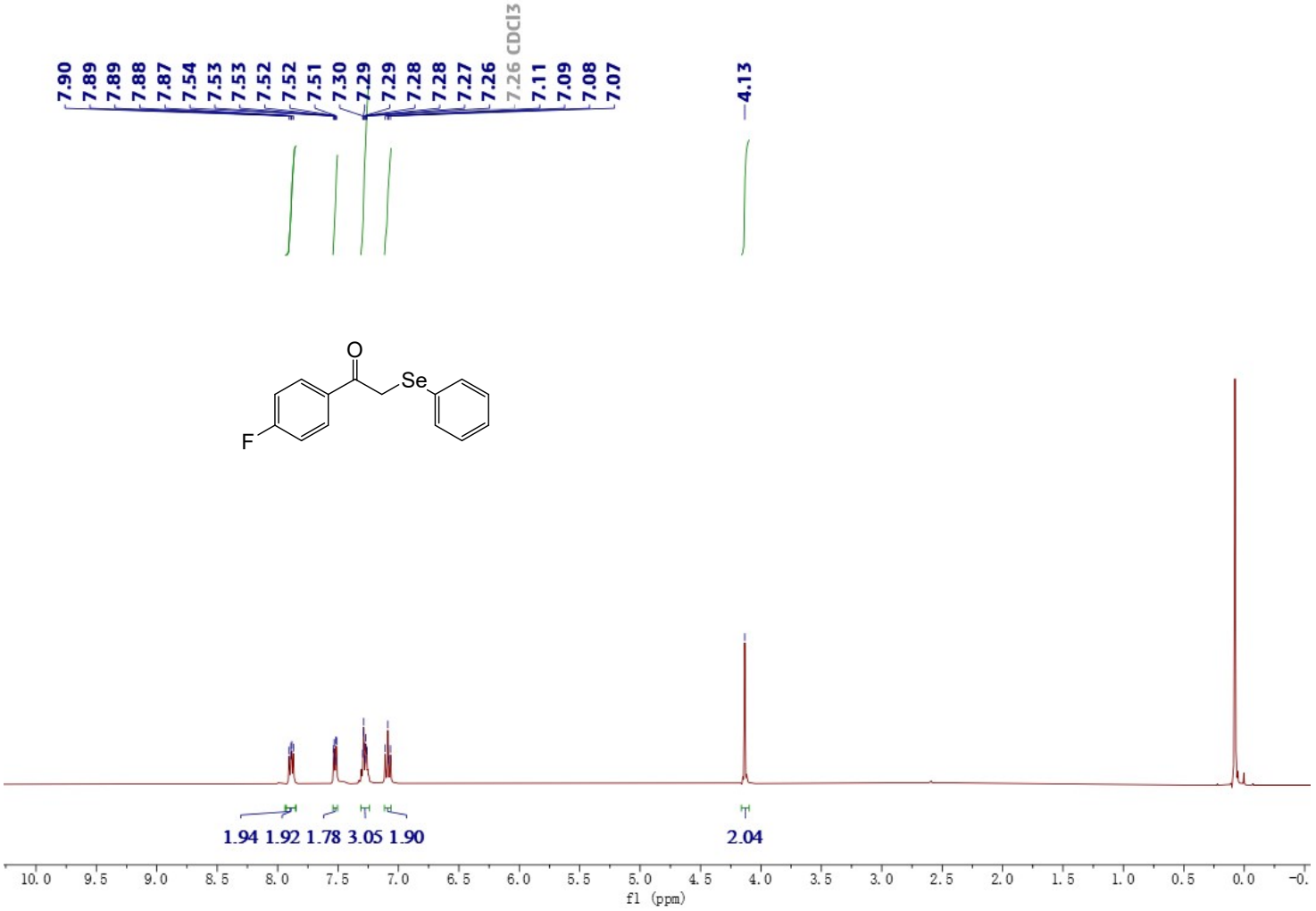
3da: ^{1}H NMR (400 MHz, $CDCl_3$)



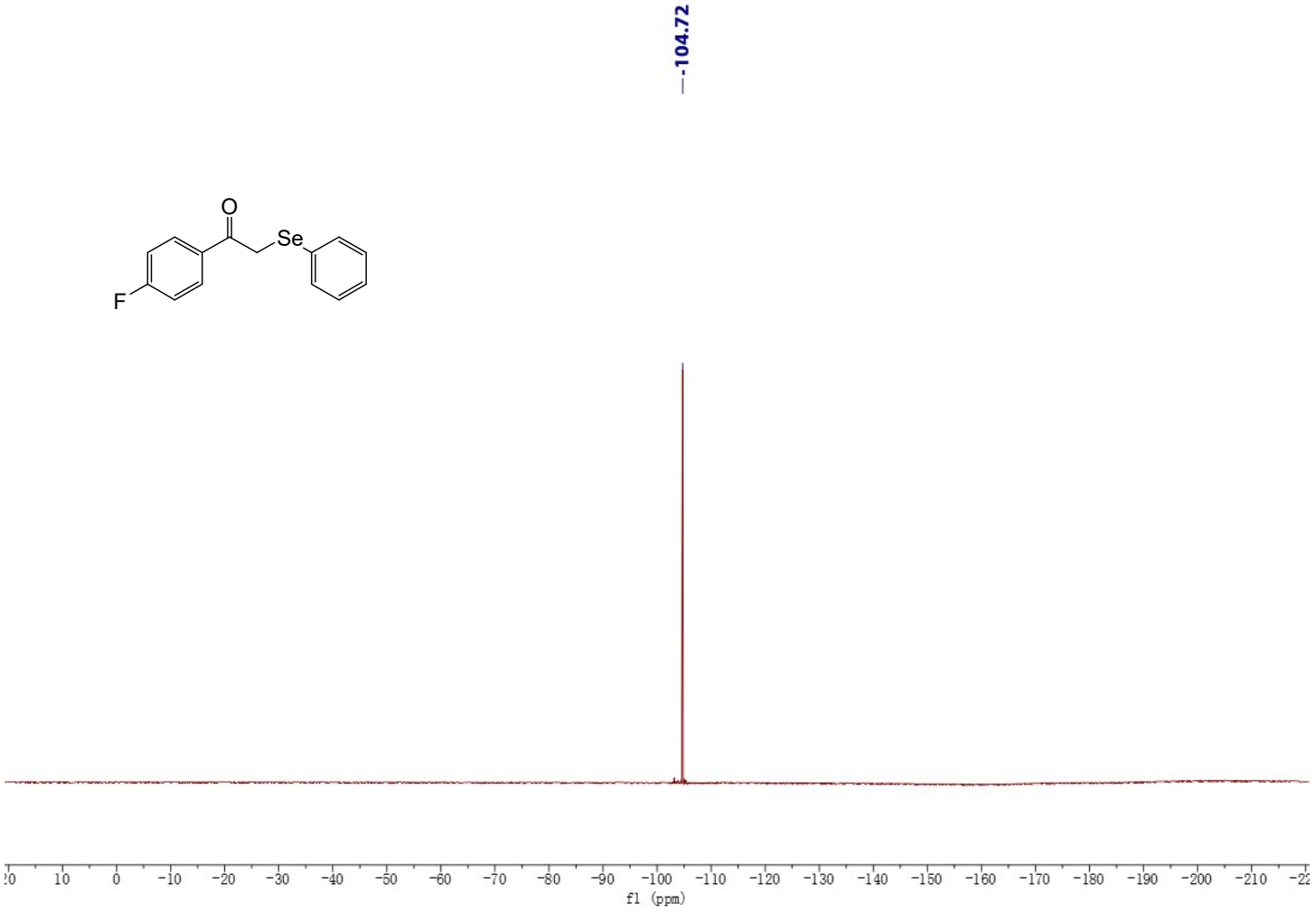
3ea: ^{1}H NMR (400 MHz, $CDCl_3$)



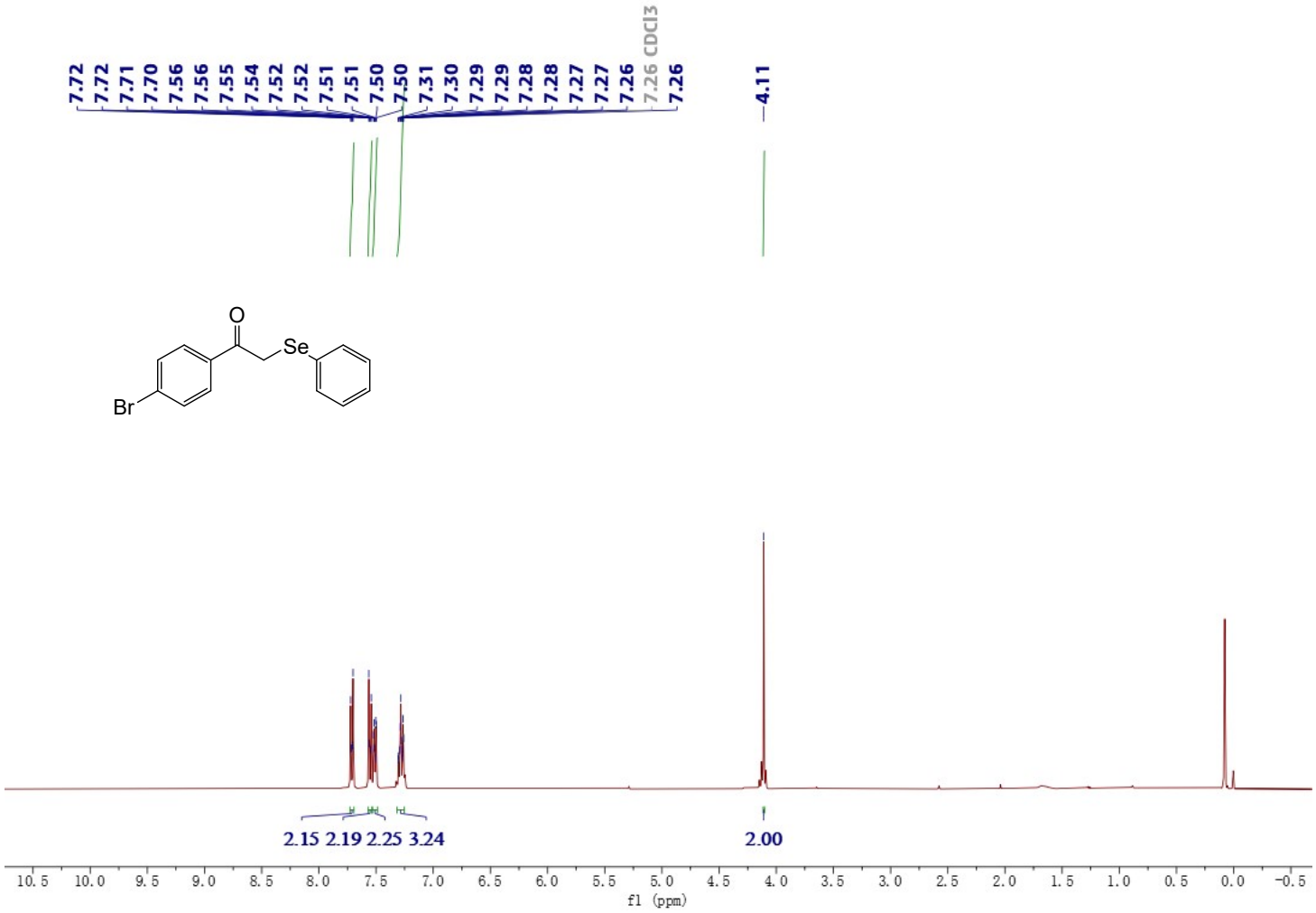
3fa: ^{1}H NMR (400 MHz, $CDCl_3$)



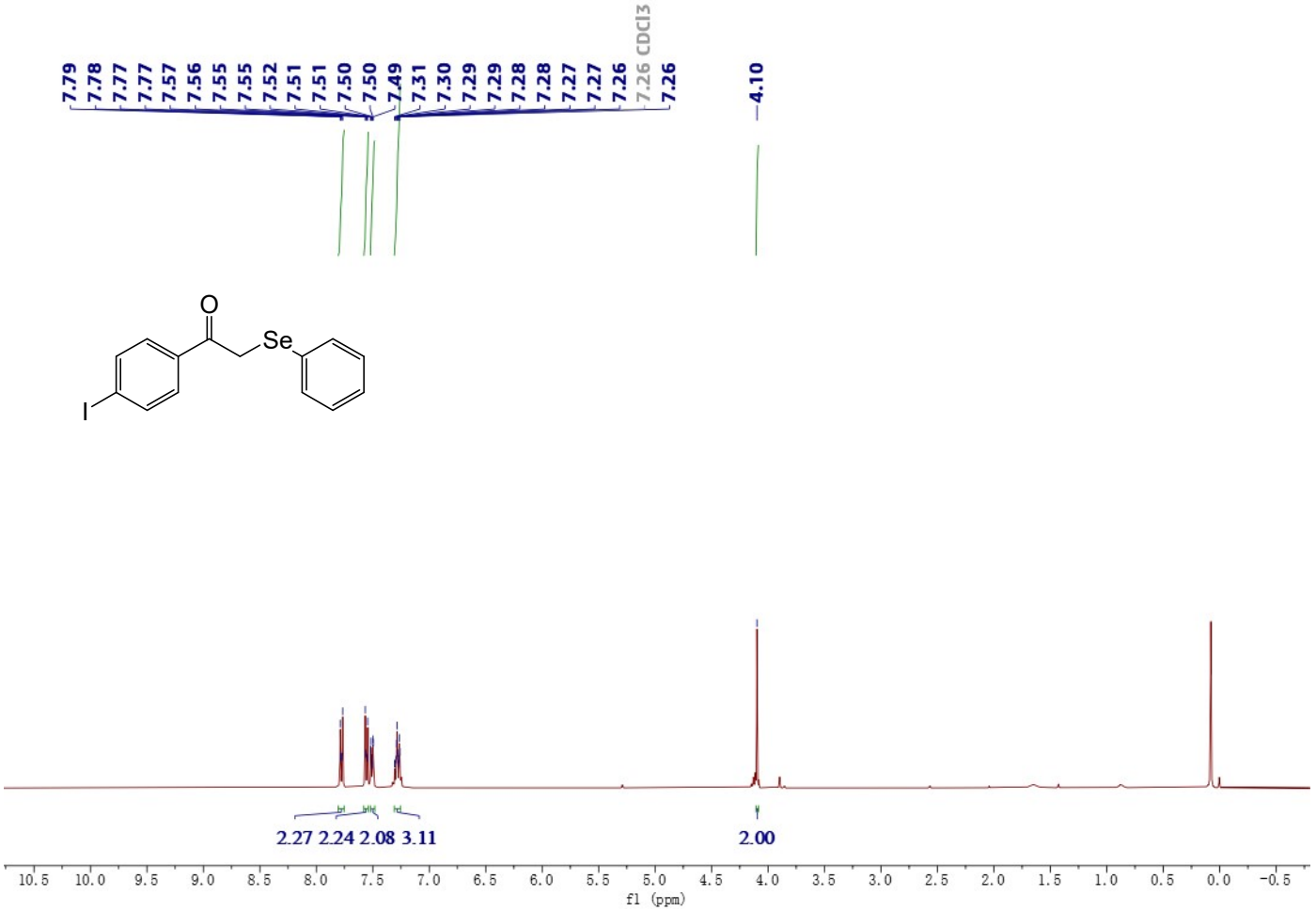
3fa: ^{19}F NMR (376 MHz, $CDCl_3$)



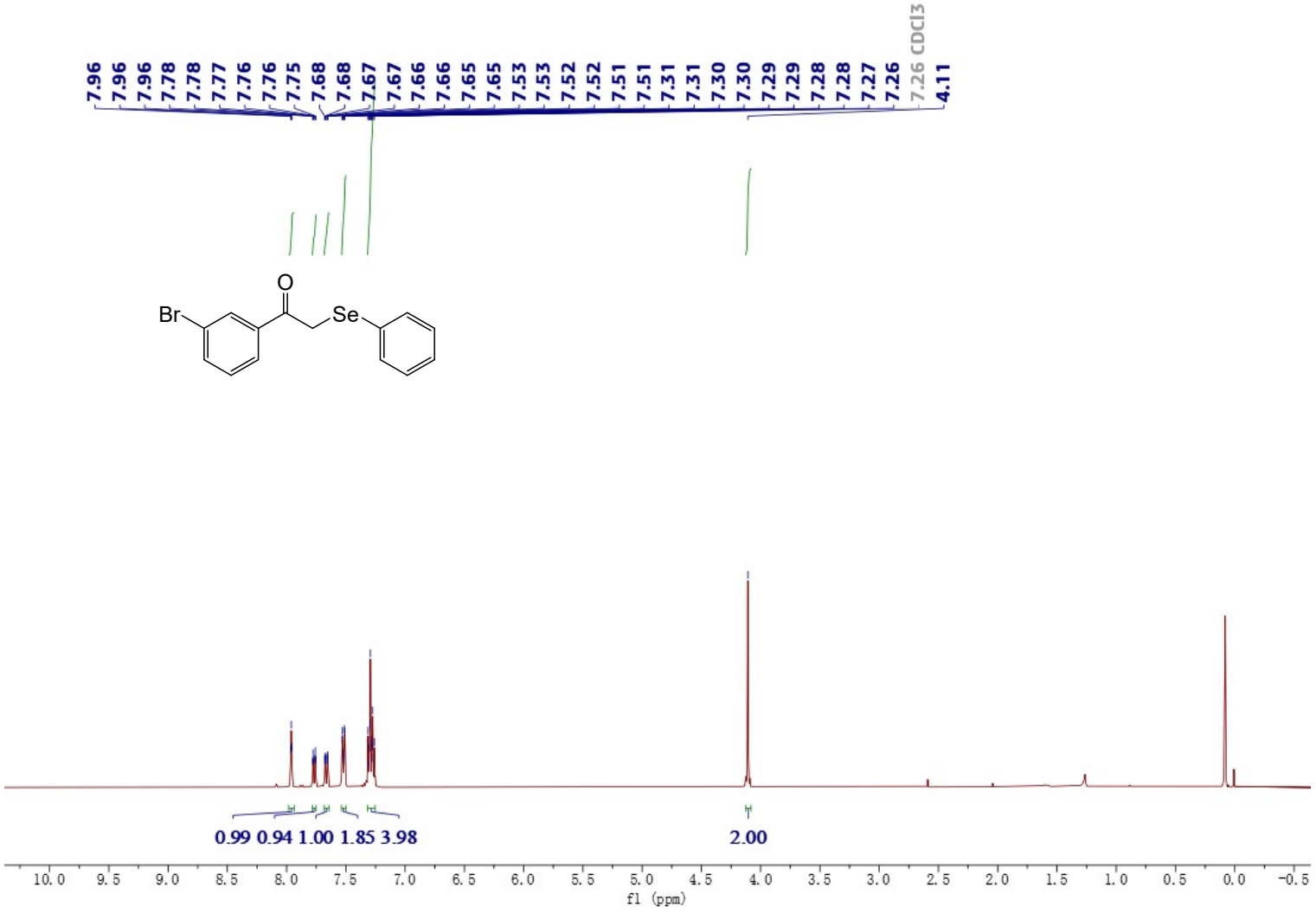
3ga: ^{1}H NMR (400 MHz, $CDCl_3$)



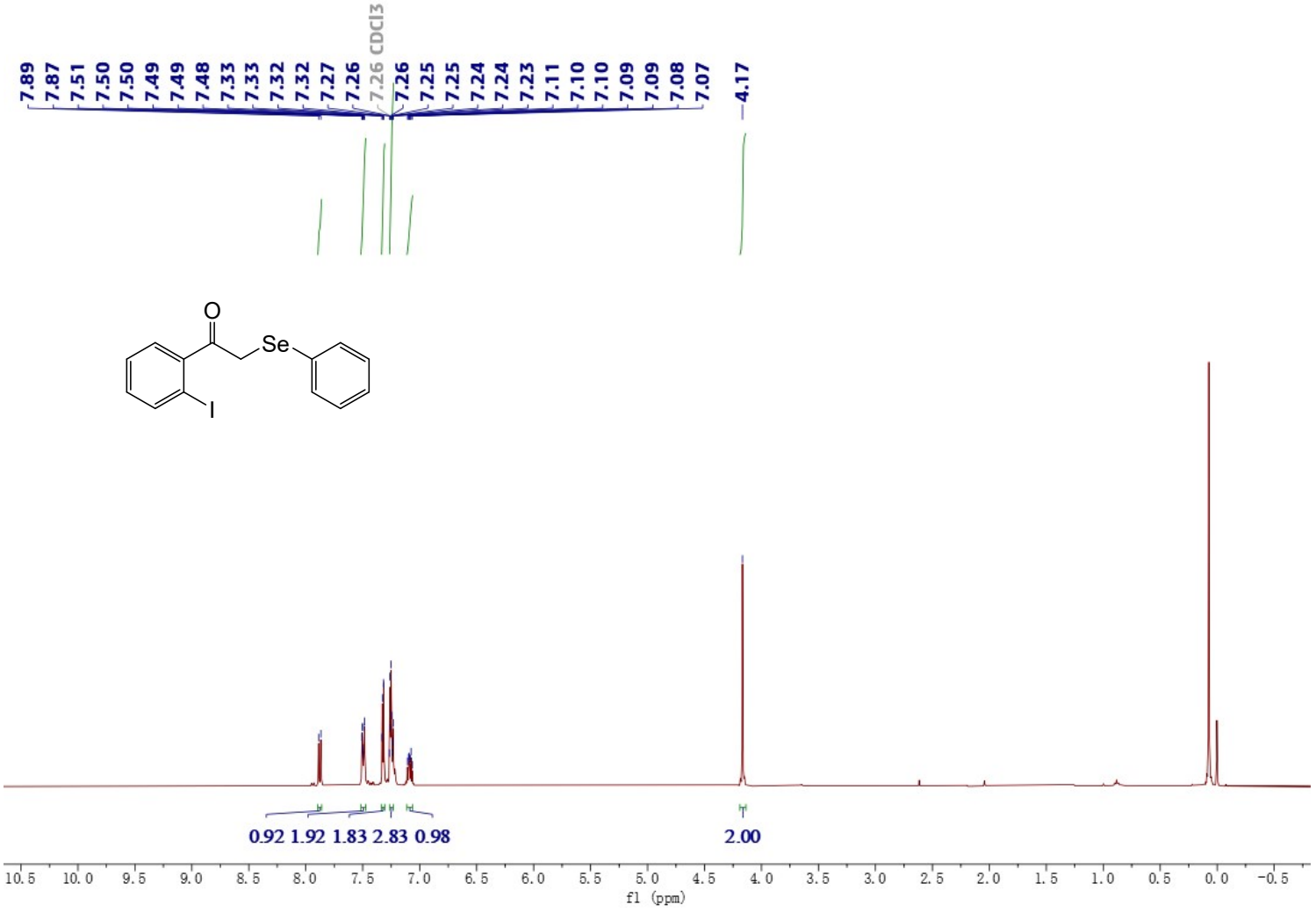
3ha: ^{1}H NMR (400 MHz, $CDCl_3$)



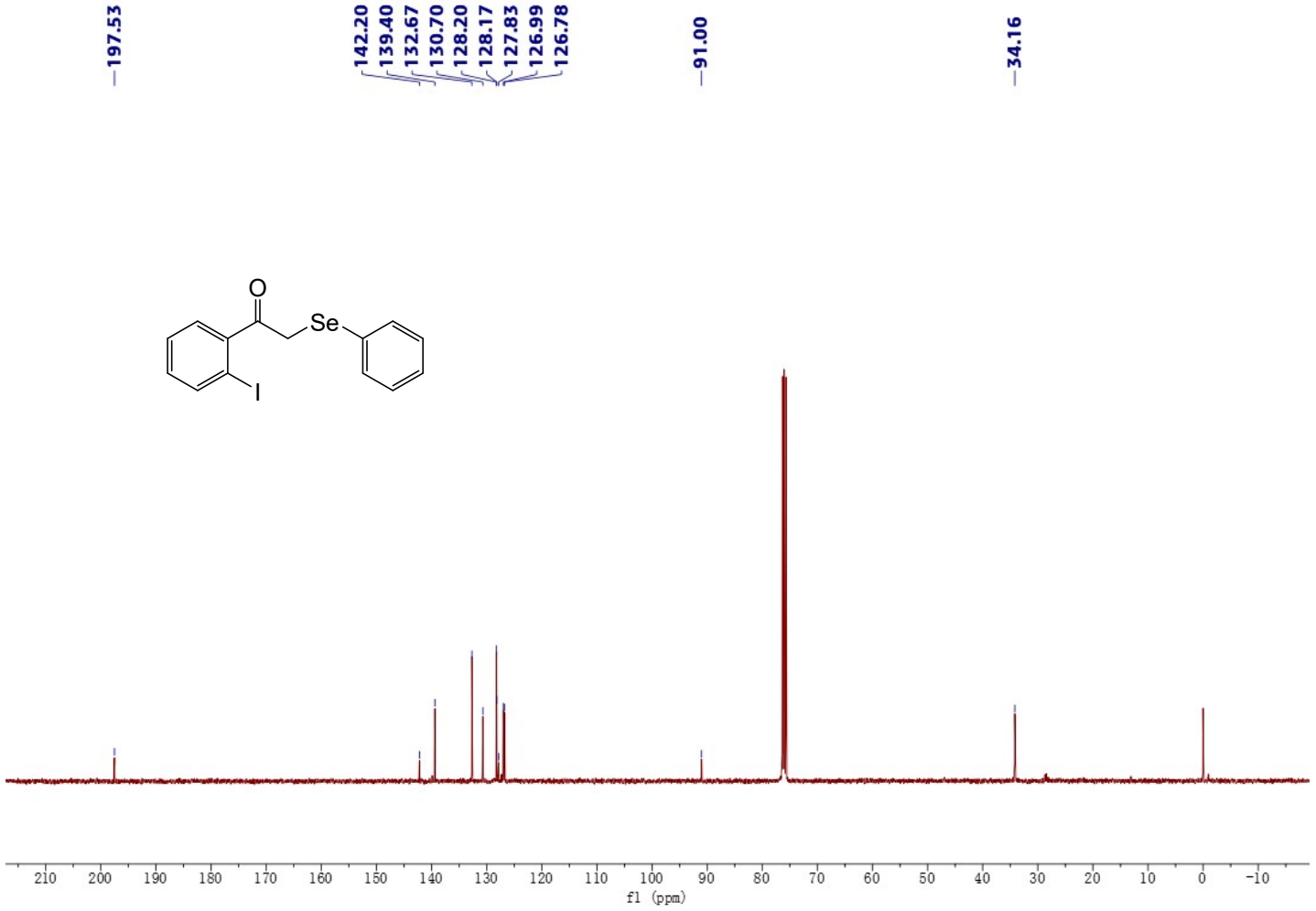
3ia: ^{1}H NMR (400 MHz, $CDCl_3$)



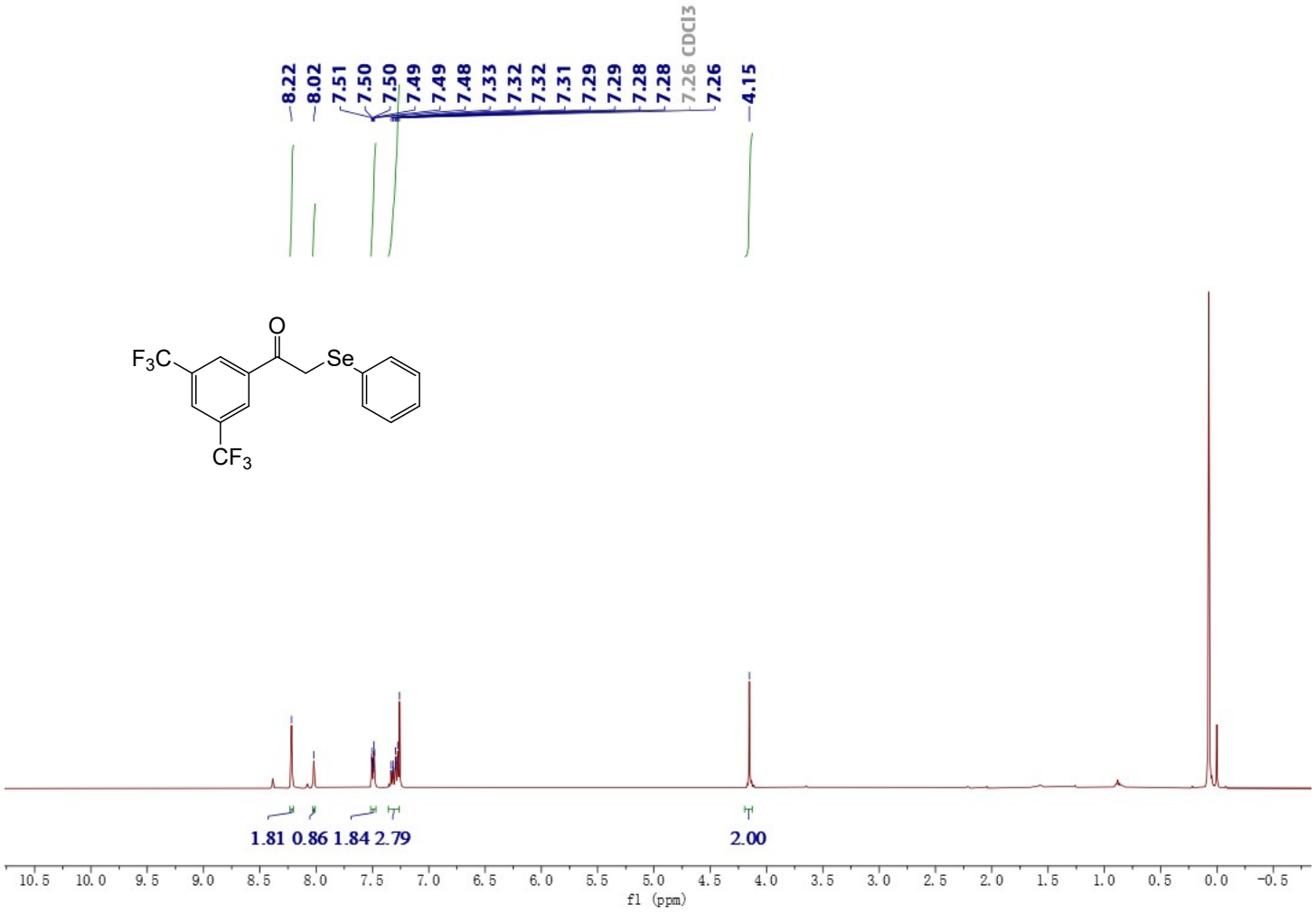
3ja: ^{1}H NMR (400 MHz, $CDCl_3$)



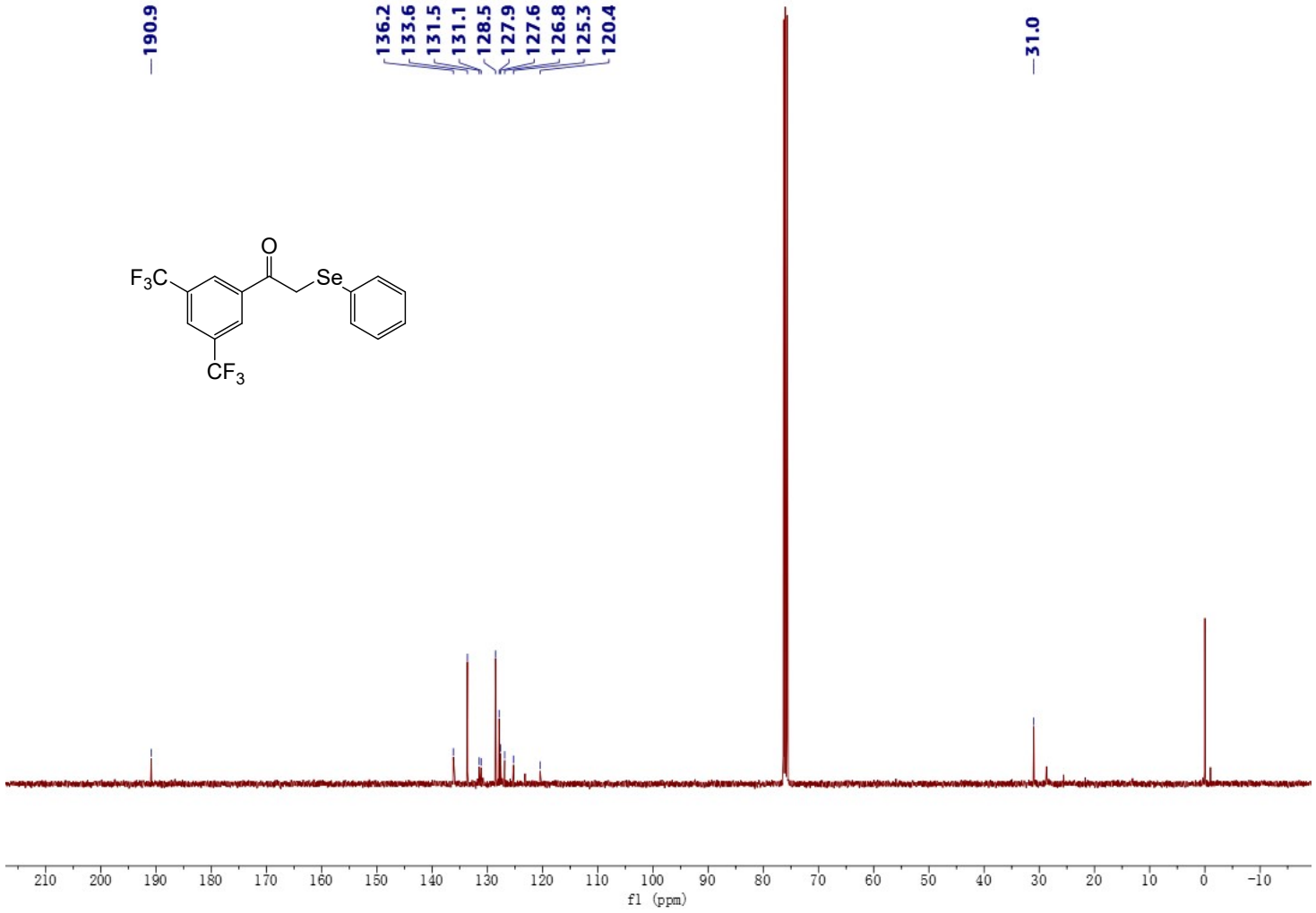
3ja: ^{13}C NMR (100 MHz, $CDCl_3$)



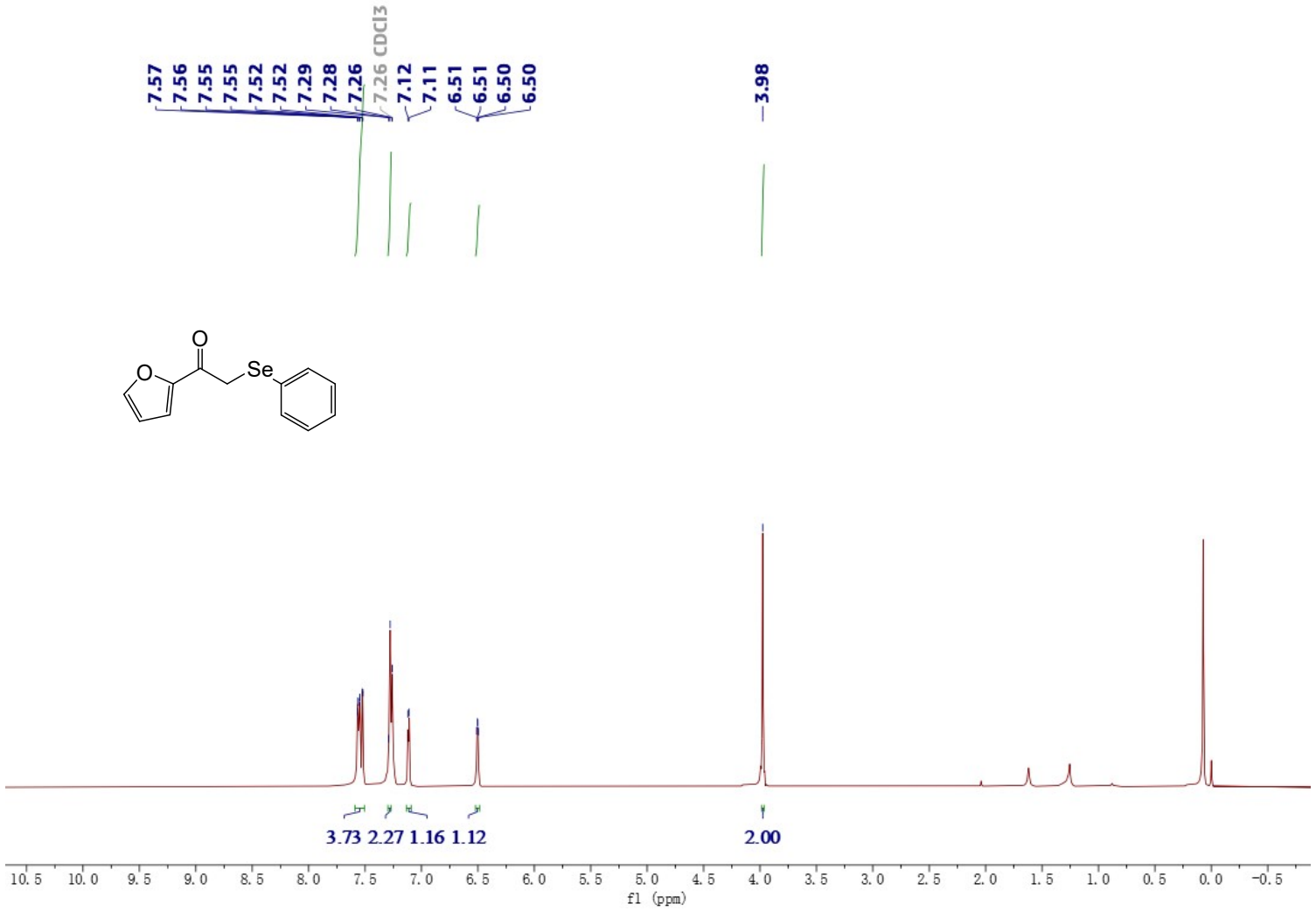
3ka: ^{1}H NMR (400 MHz, $CDCl_3$)



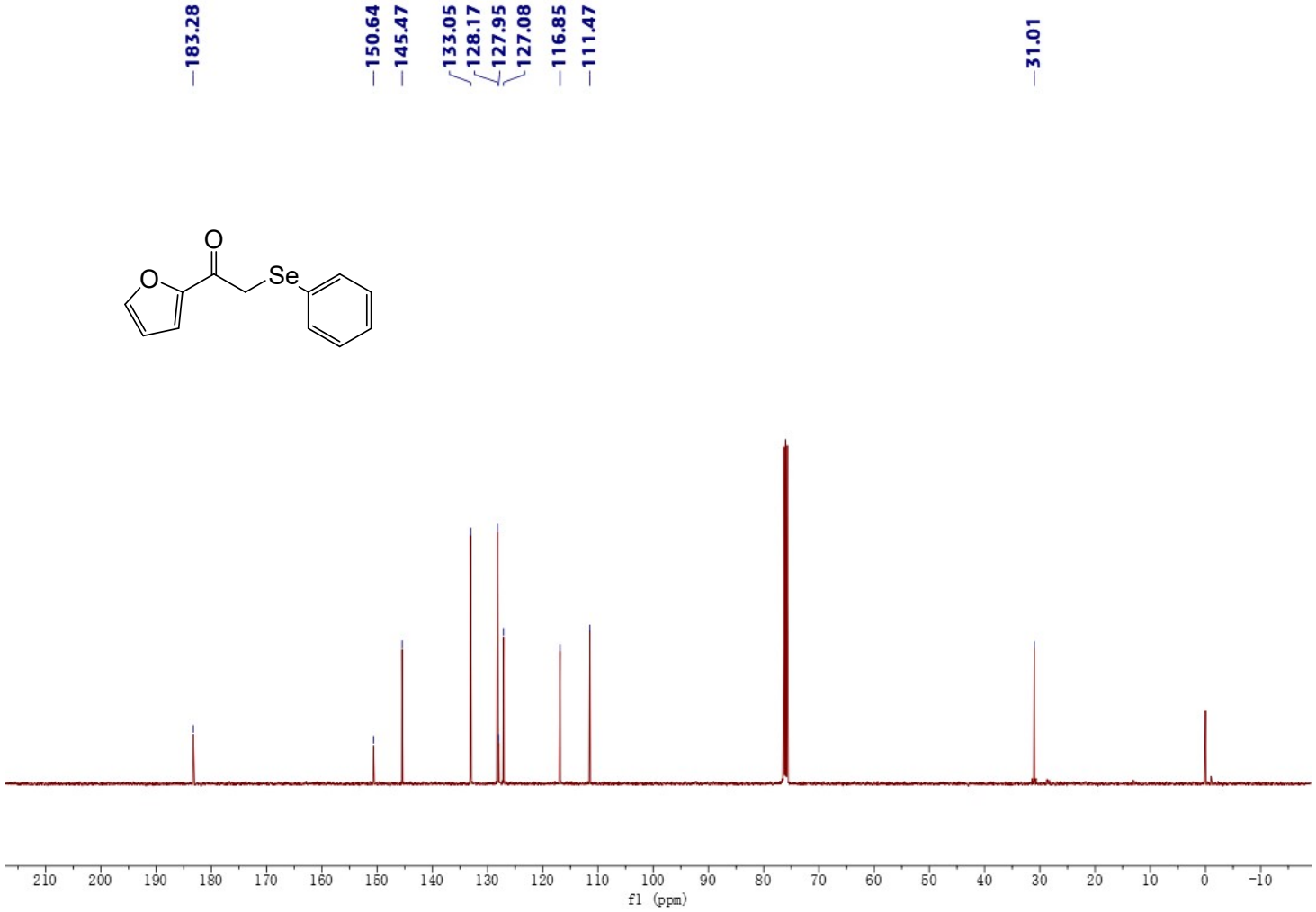
3ka: ^{13}C NMR (100 MHz, $CDCl_3$)



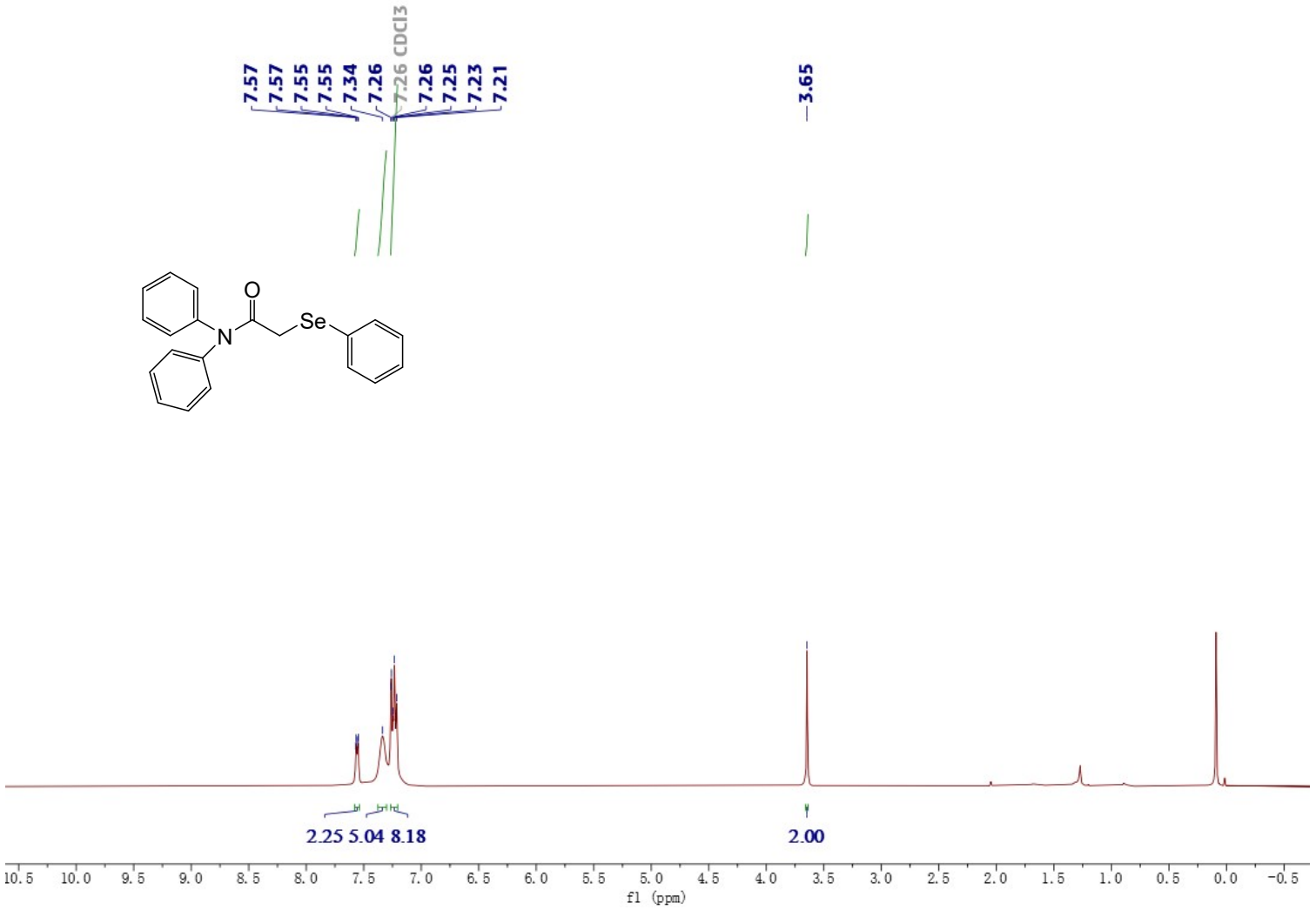
3la: ^{1}H NMR (400 MHz, $CDCl_3$)



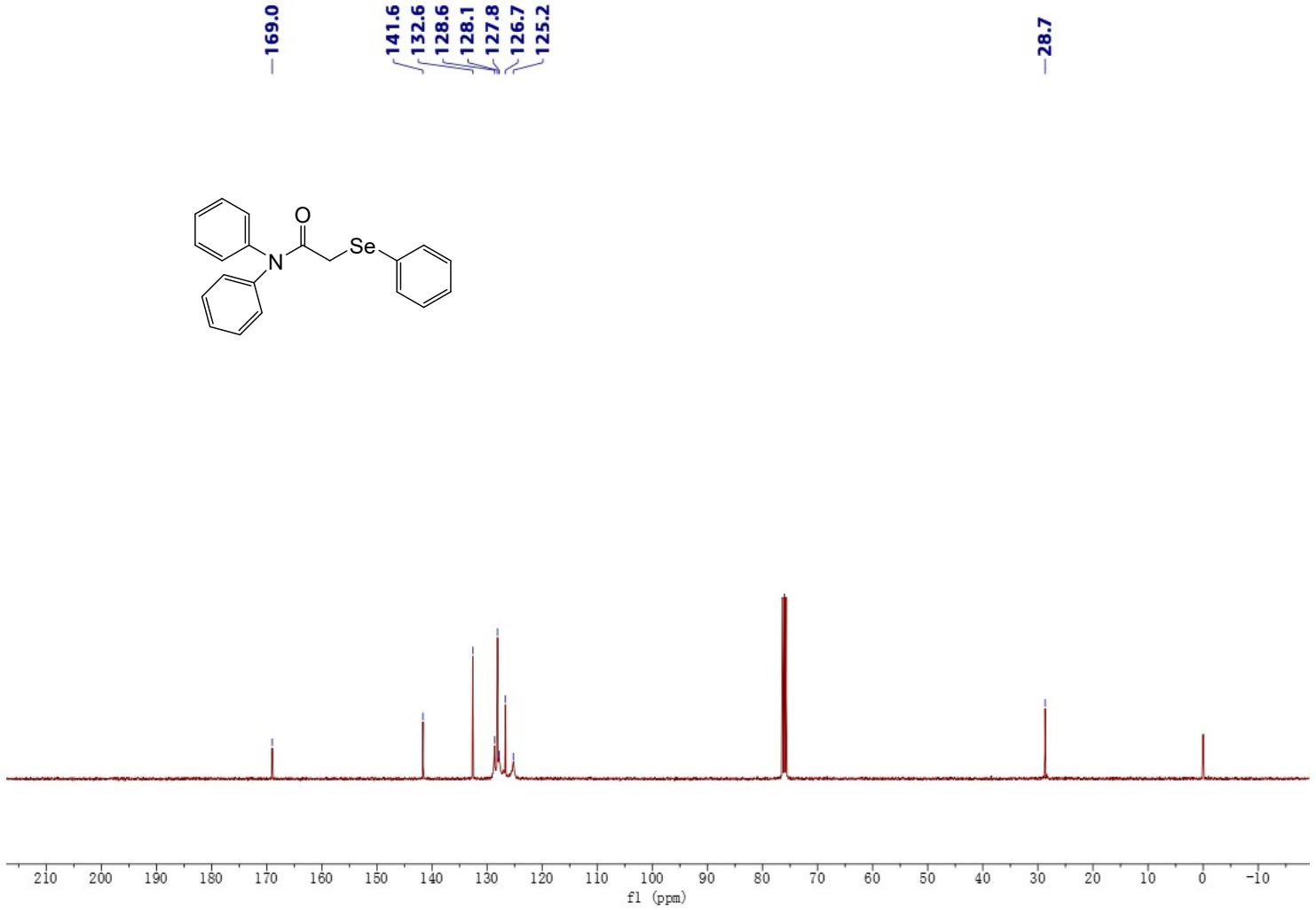
3la: ^{13}C NMR (100 MHz, $CDCl_3$)



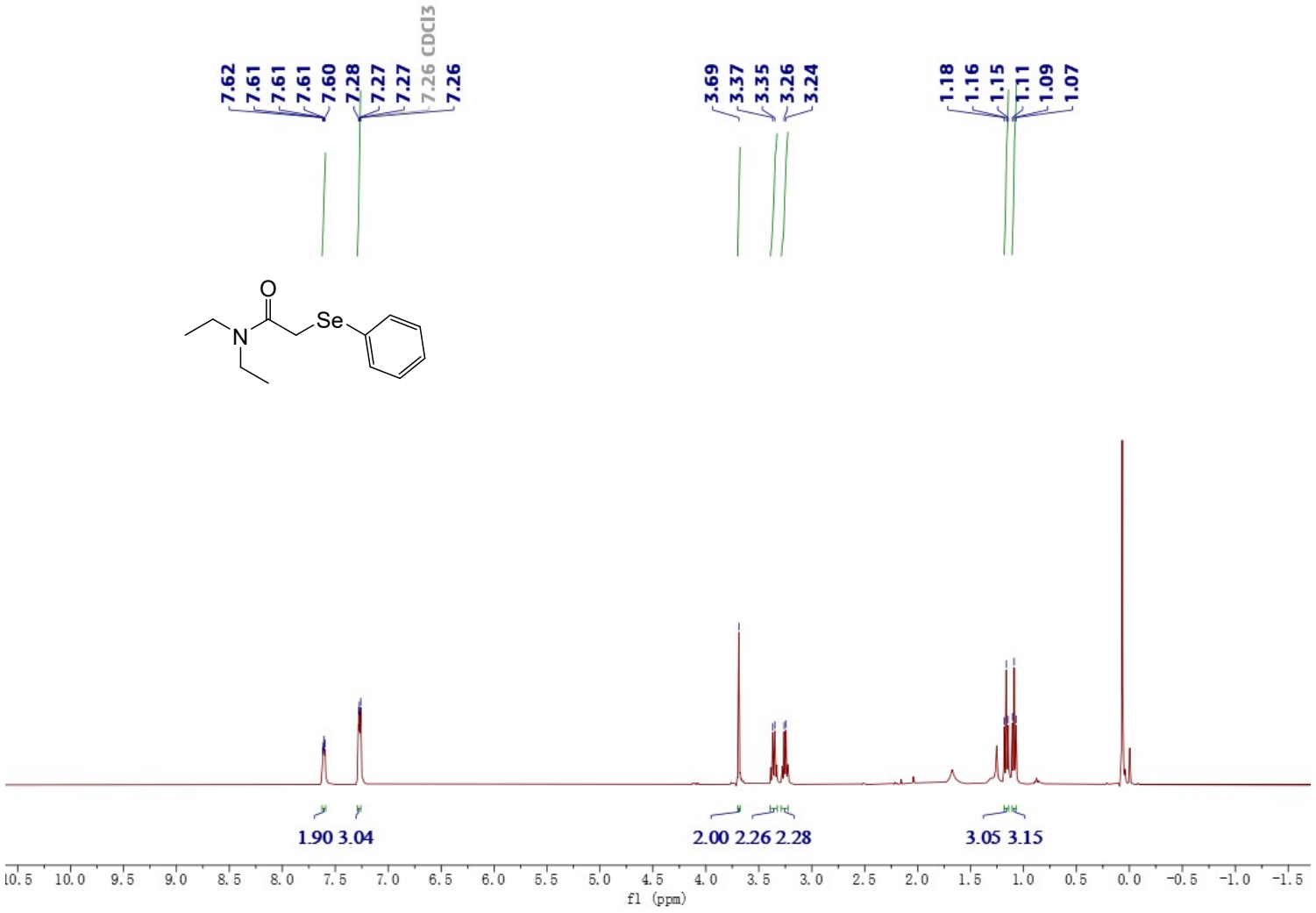
3ma: ^{1}H NMR (400 MHz, $CDCl_3$)



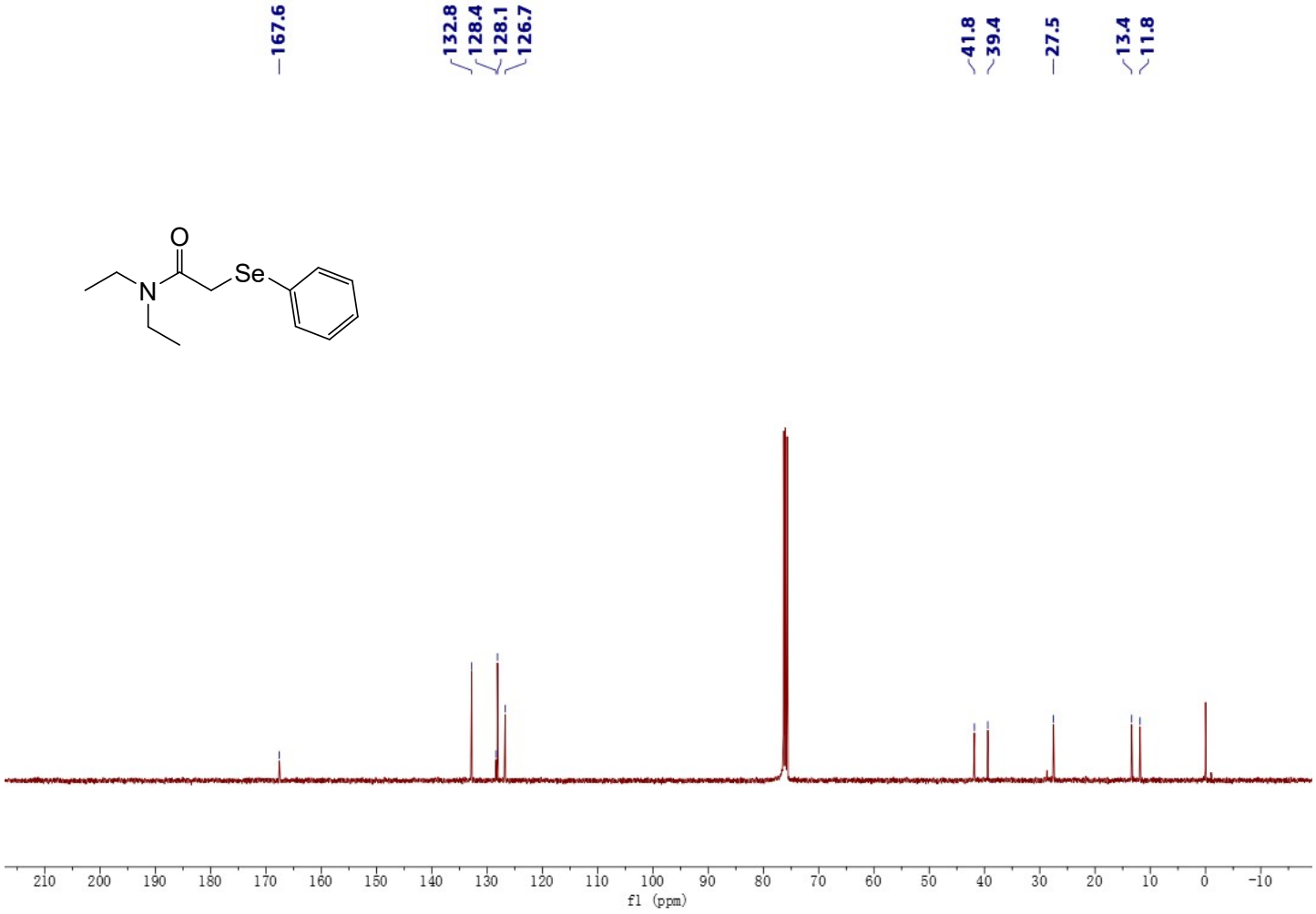
3ma: ^{13}C NMR (100 MHz, $CDCl_3$)



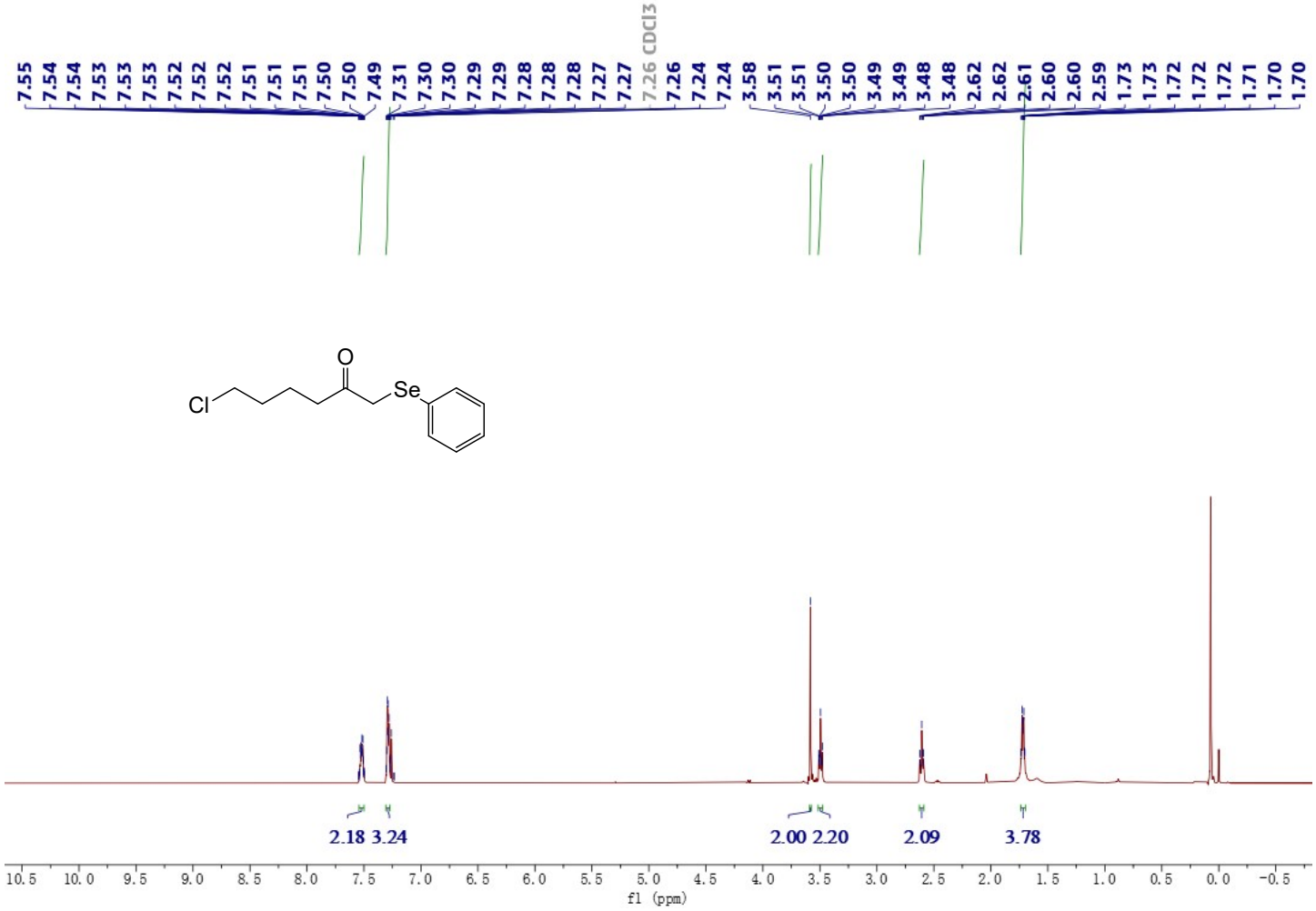
3na: ^{1}H NMR (400 MHz, $CDCl_3$)



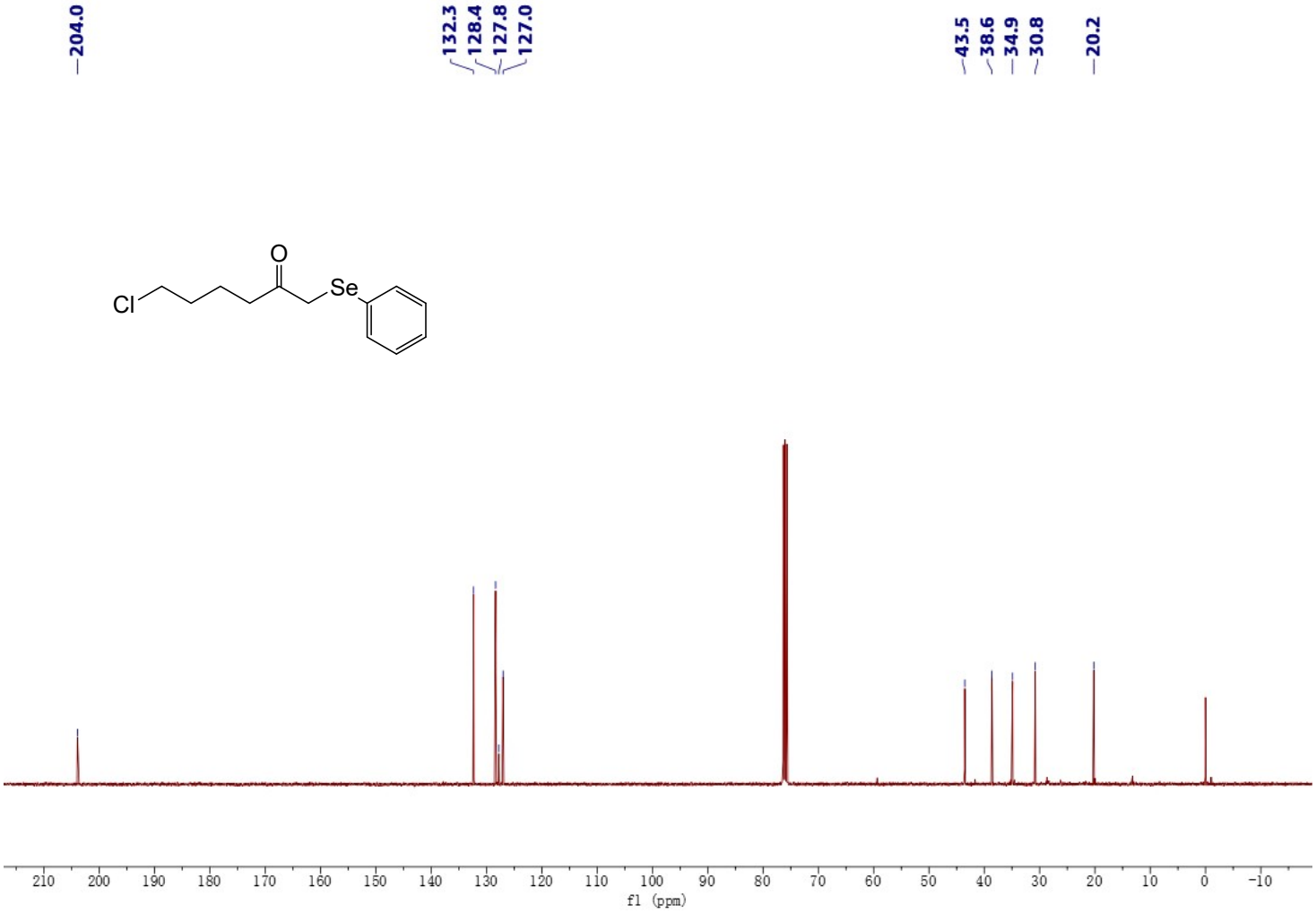
3na: ^{13}C NMR (100 MHz, $CDCl_3$)



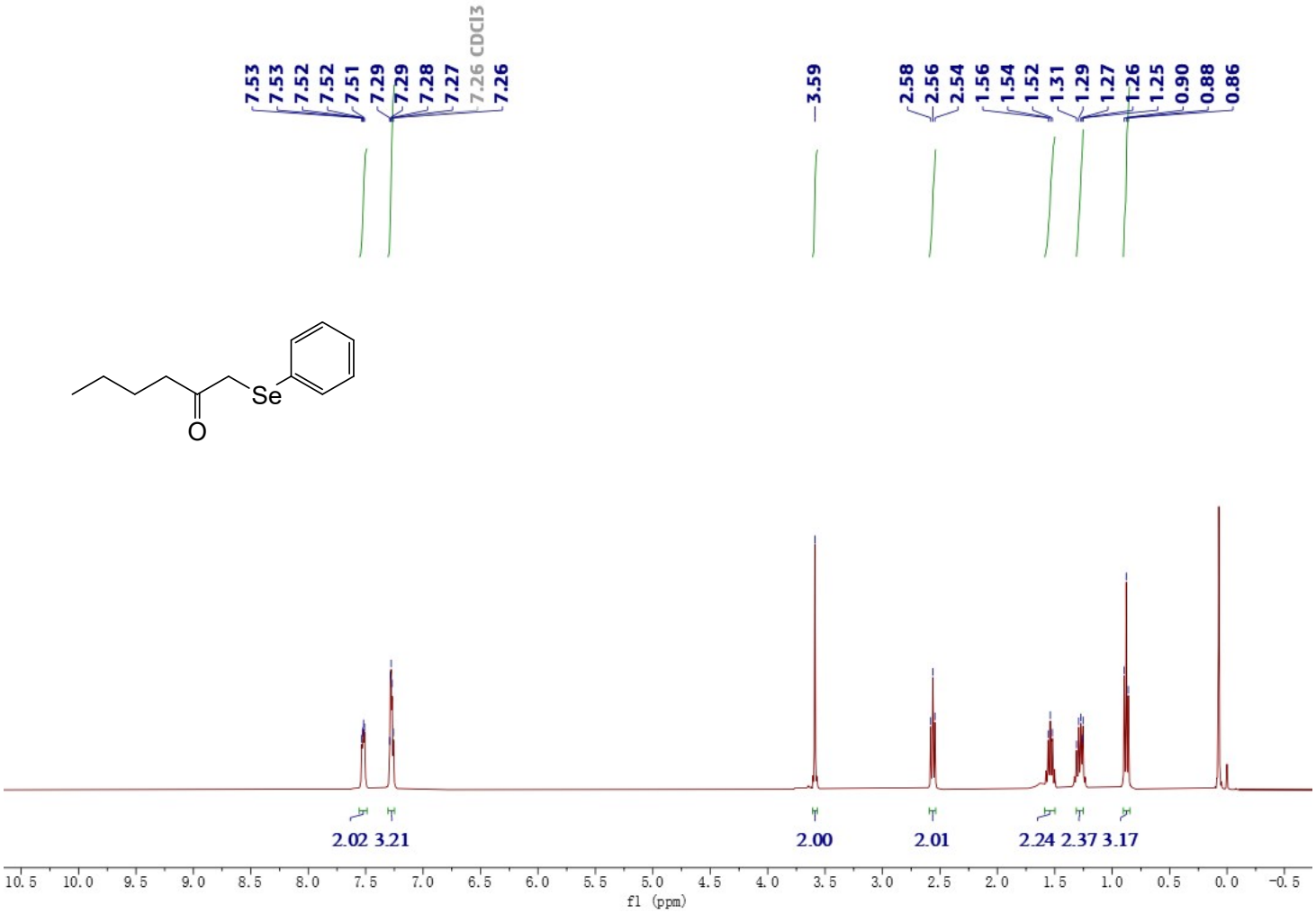
3oa: ^{1}H NMR (400 MHz, $CDCl_3$)



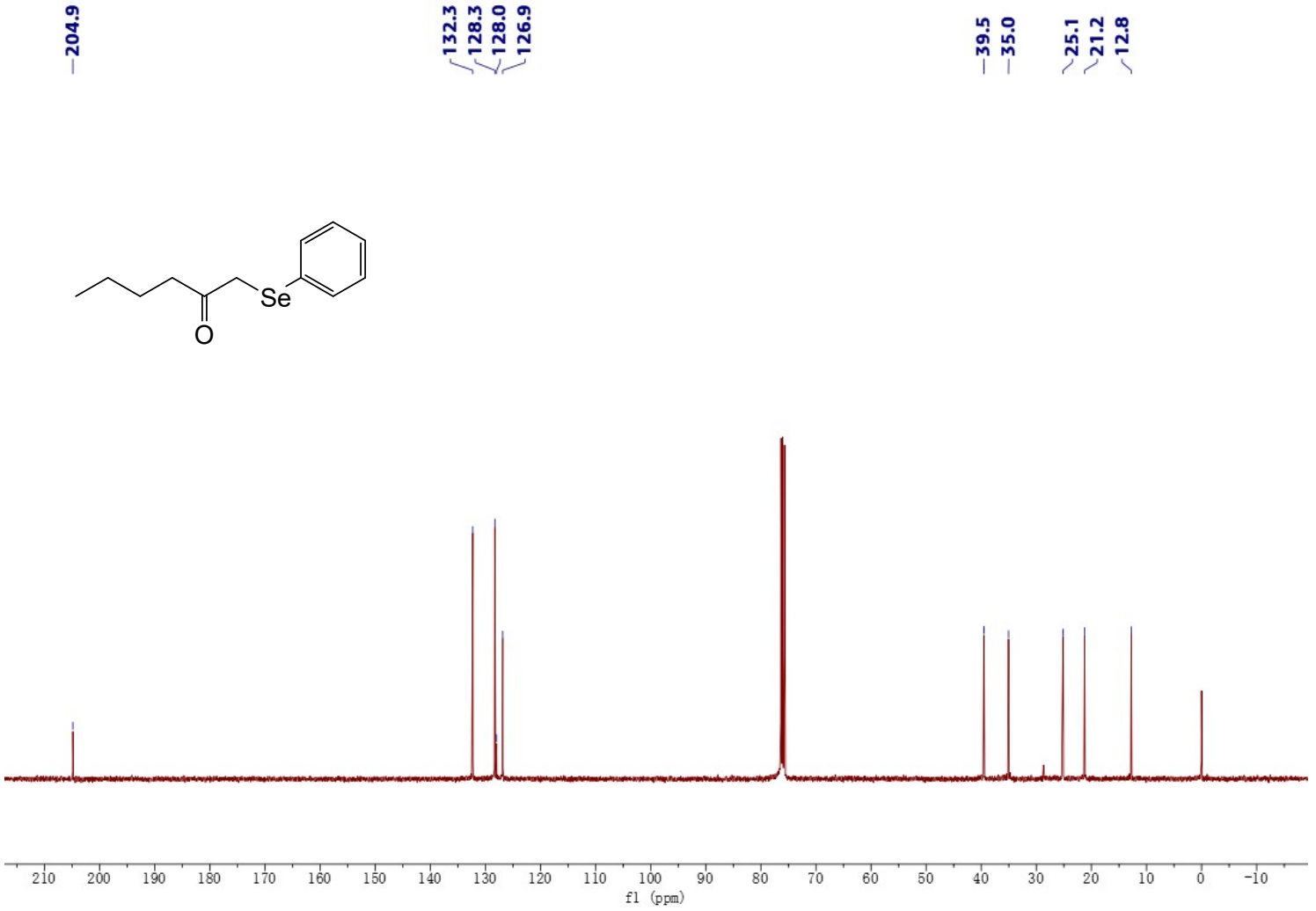
3oa: ^{13}C NMR (100 MHz, $CDCl_3$)



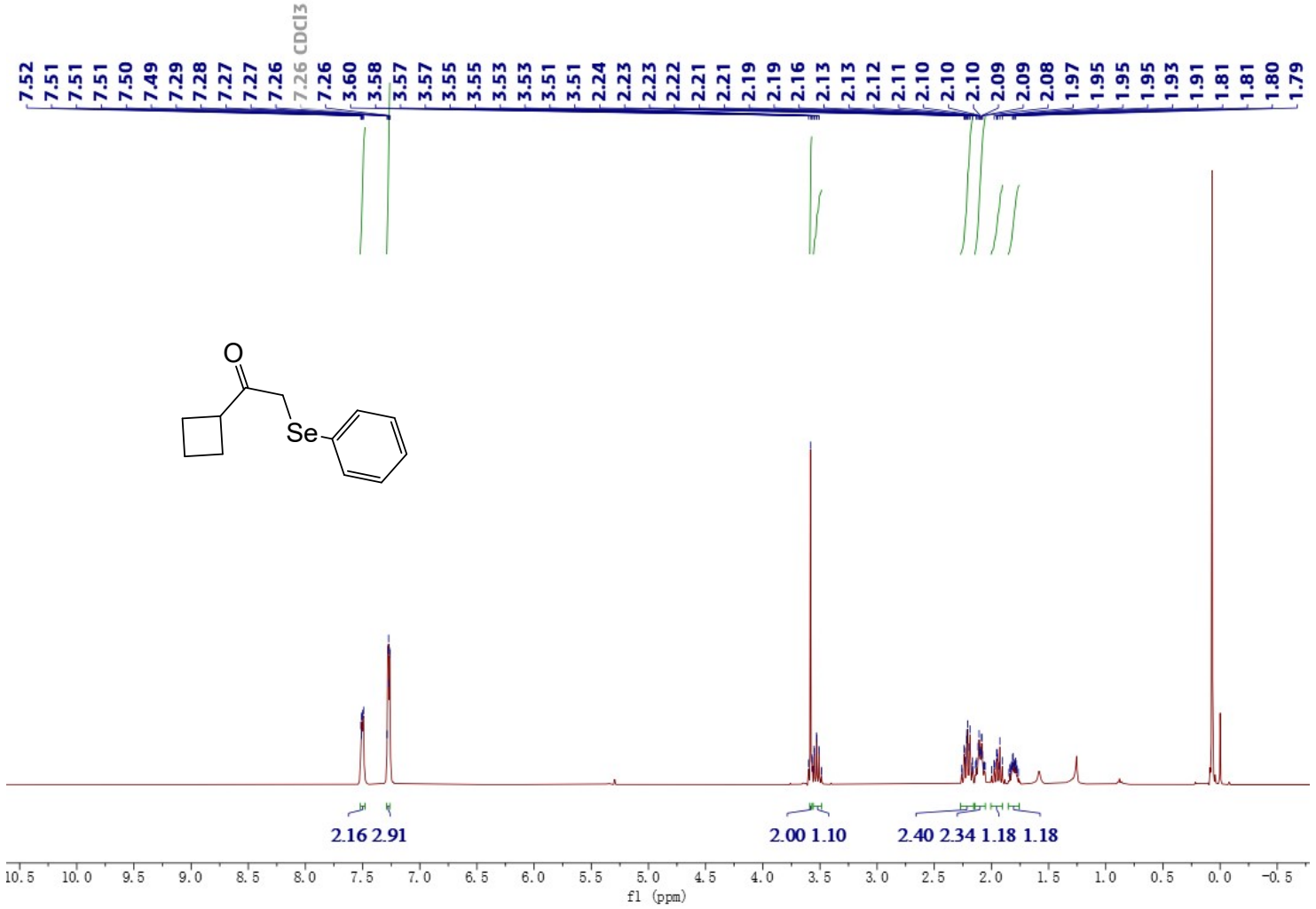
3pa: ^{1}H NMR (400 MHz, $CDCl_3$)



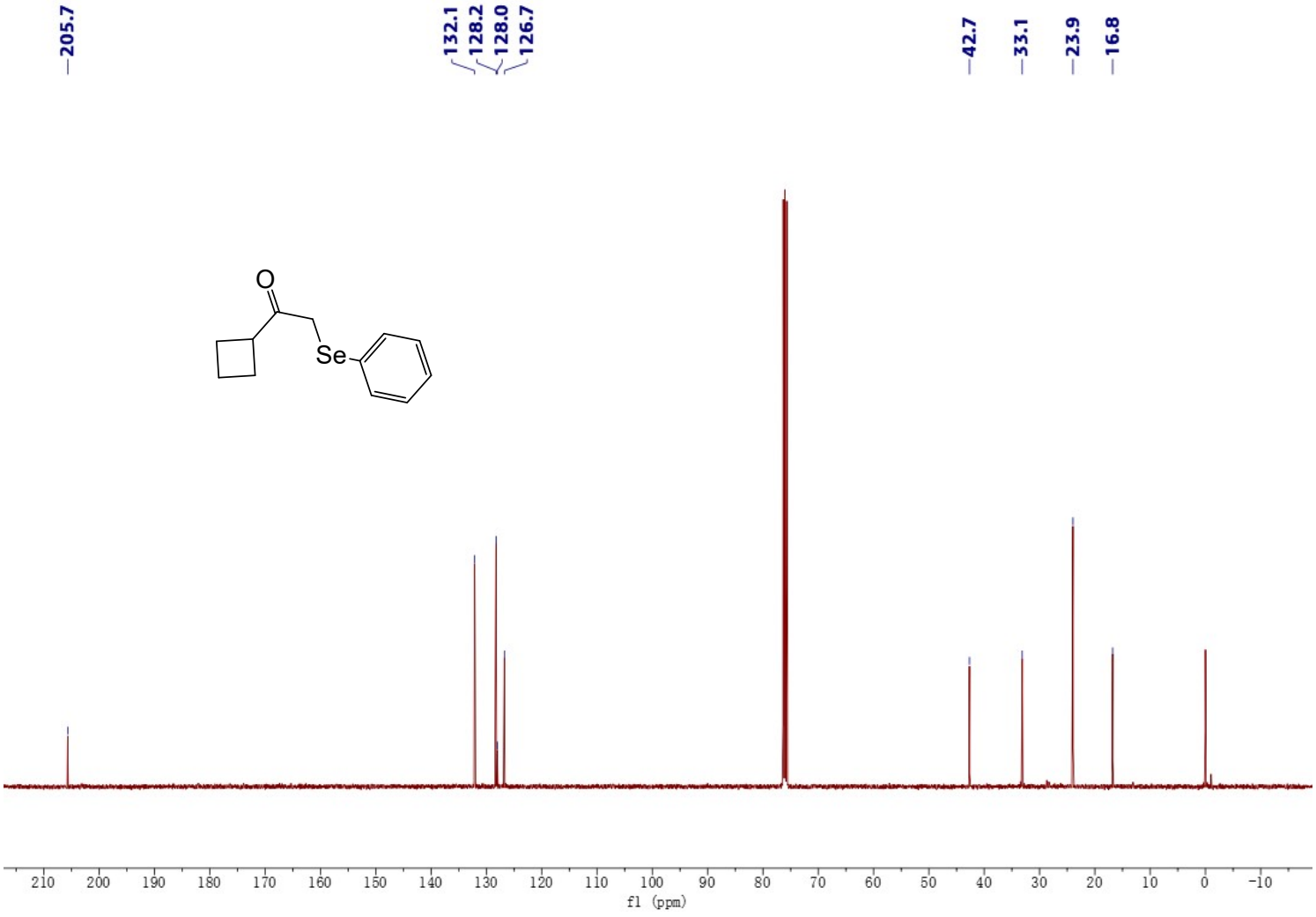
3pa: ^{13}C NMR (100 MHz, $CDCl_3$)



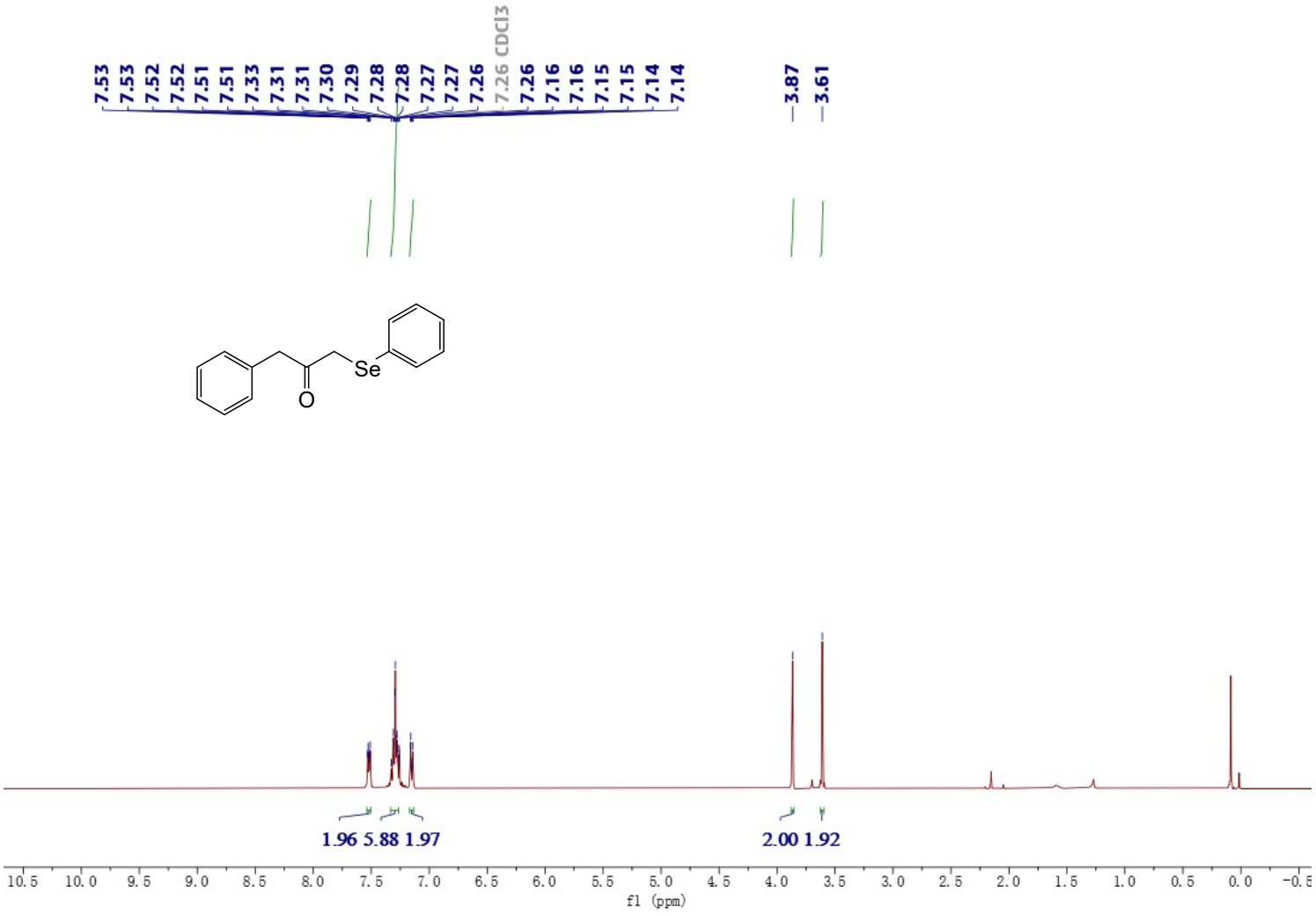
3qa: ^{1}H NMR (400 MHz, $CDCl_3$)



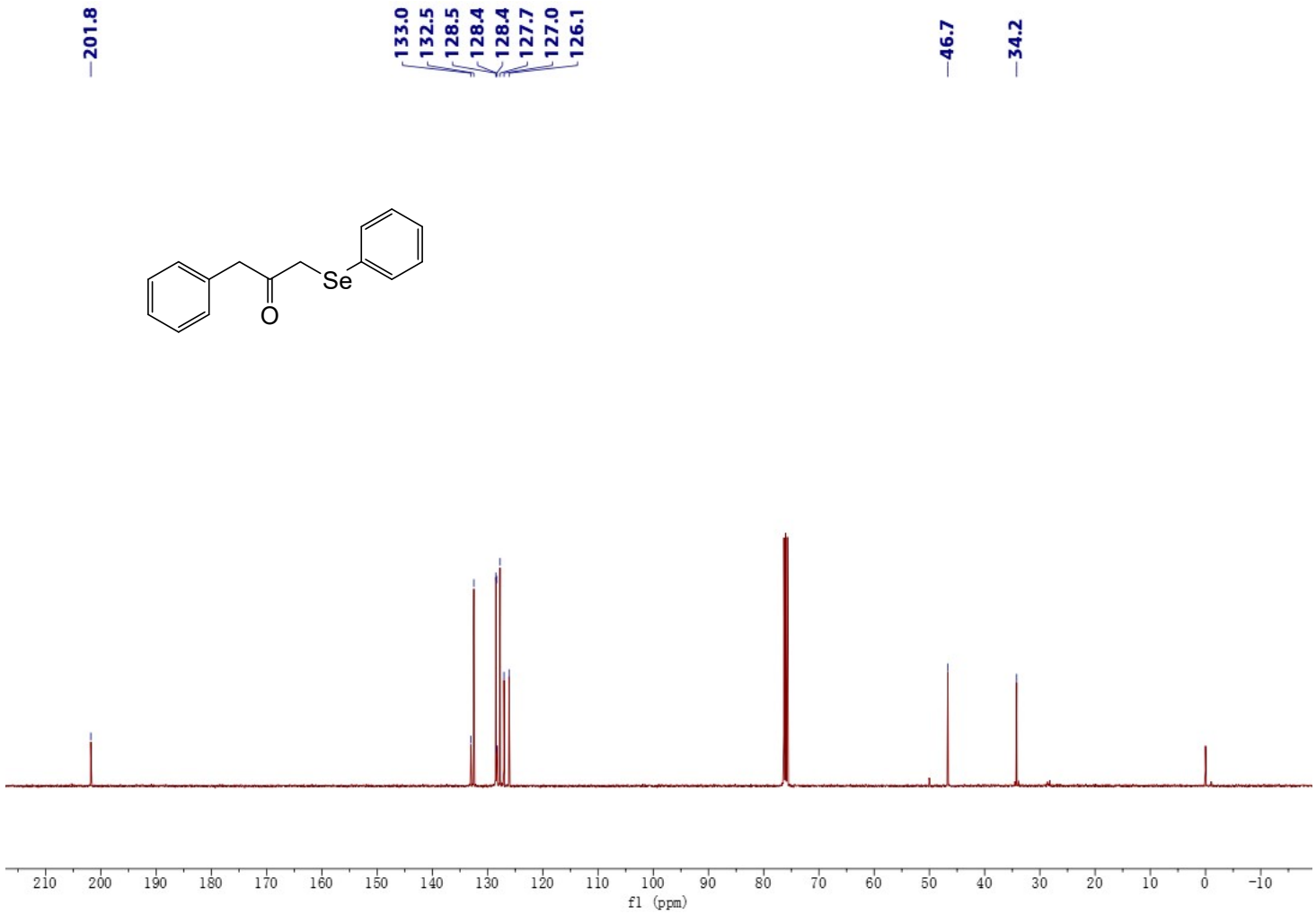
3qa: ^{13}C NMR (100 MHz, $CDCl_3$)



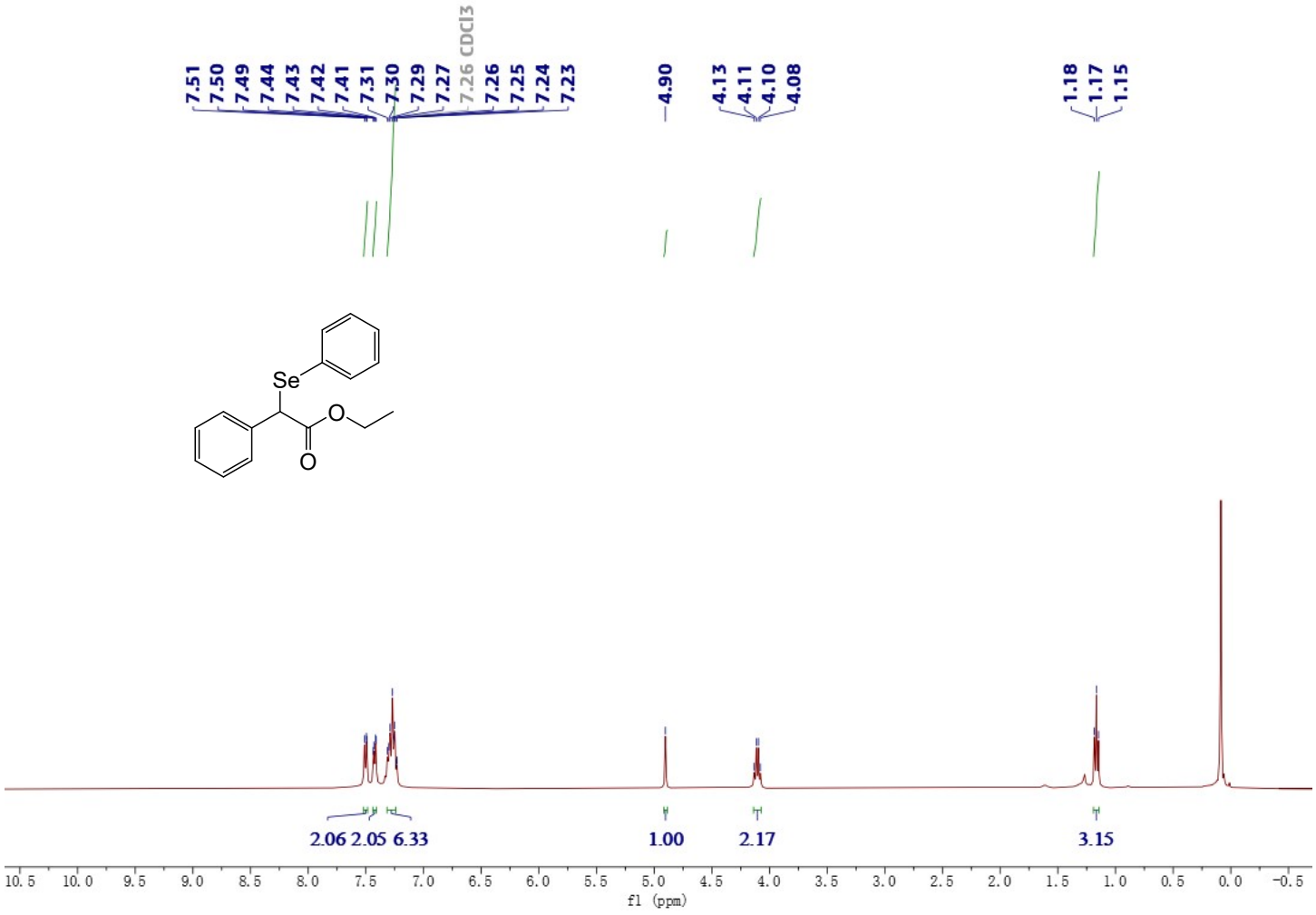
3ra: ^{1}H NMR (400 MHz, $CDCl_3$)



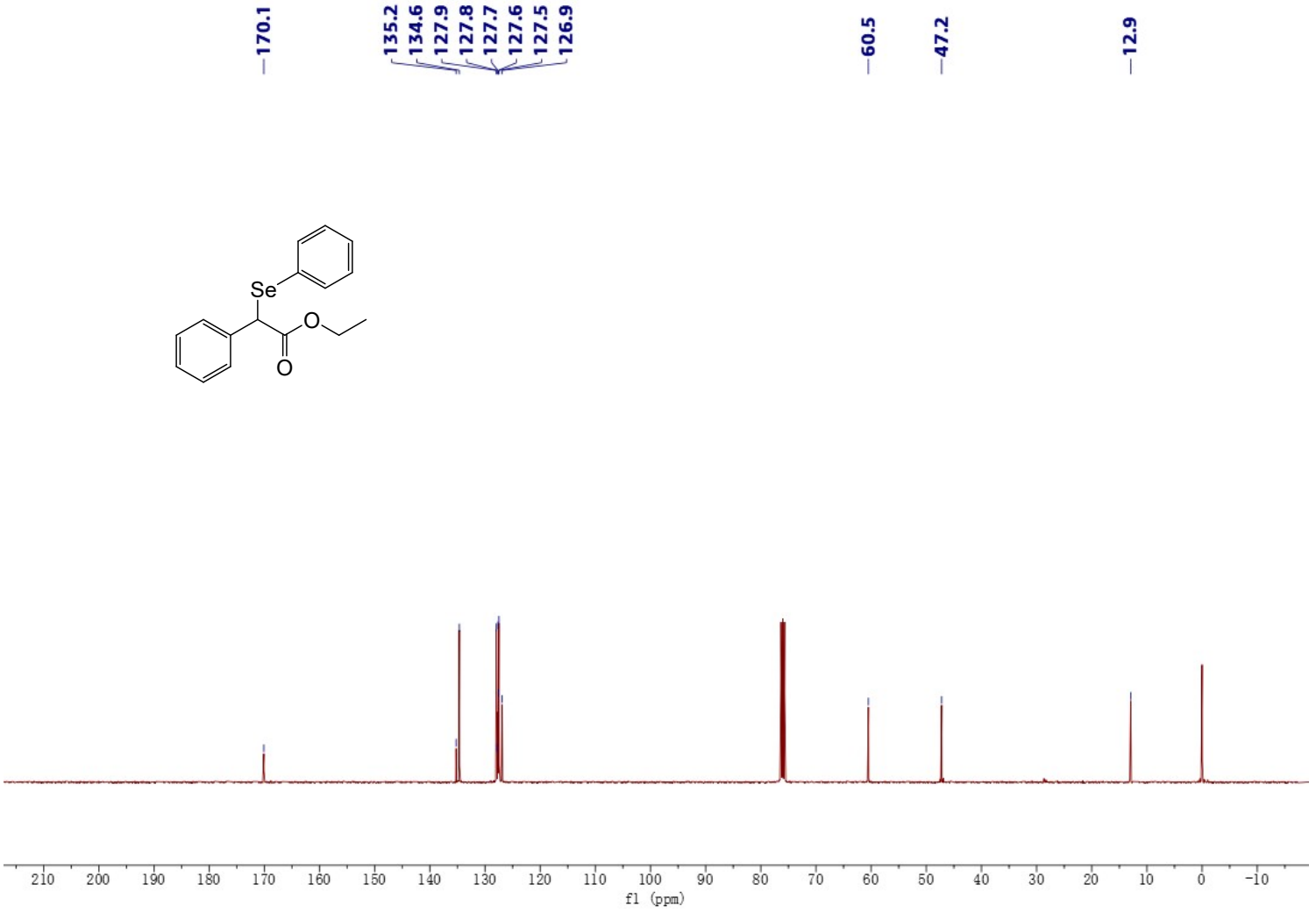
3ra: ^{13}C NMR (100 MHz, $CDCl_3$)



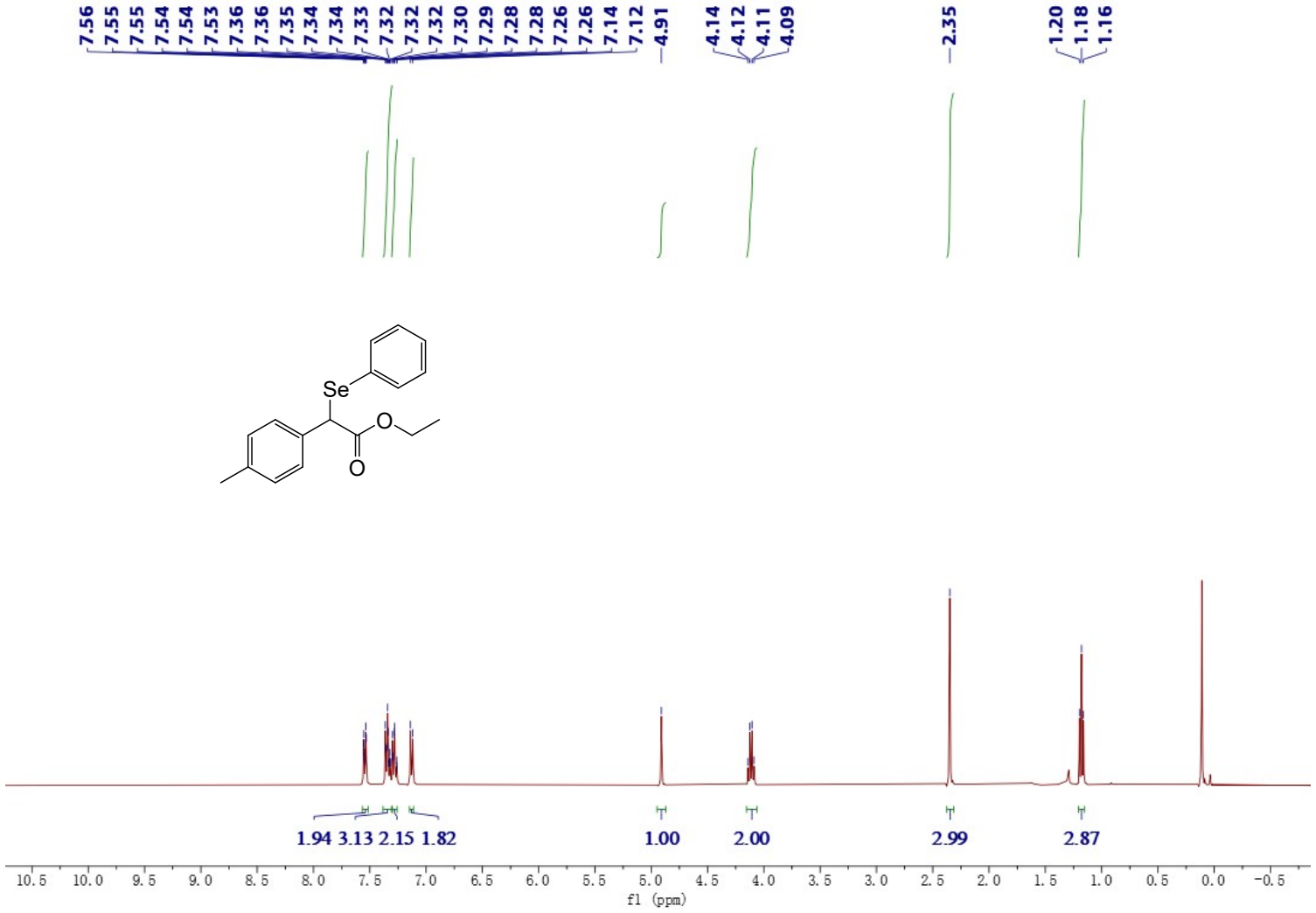
3sa: ^{1}H NMR (400 MHz, $CDCl_3$)



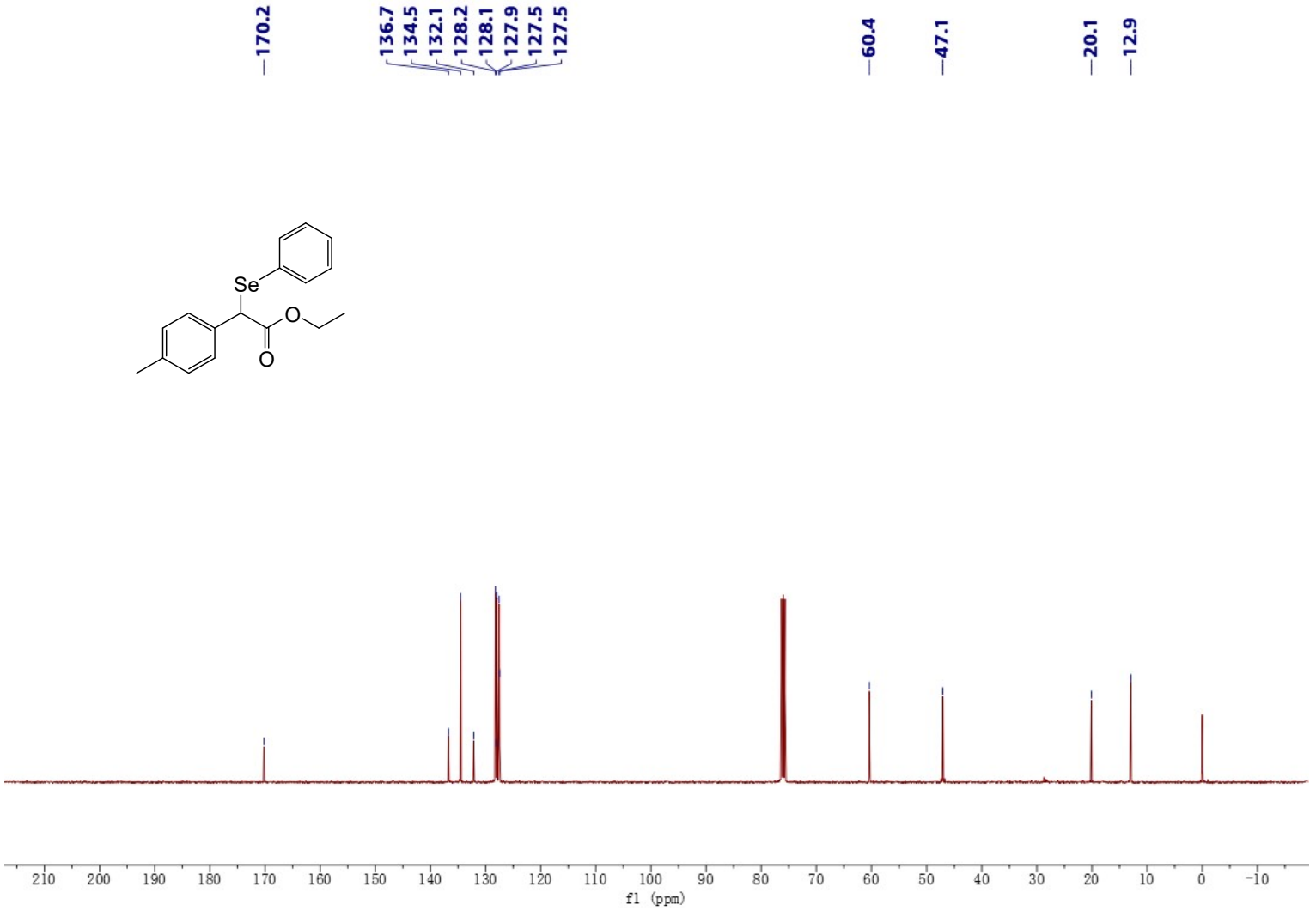
3sa: ^{13}C NMR (100 MHz, $CDCl_3$)



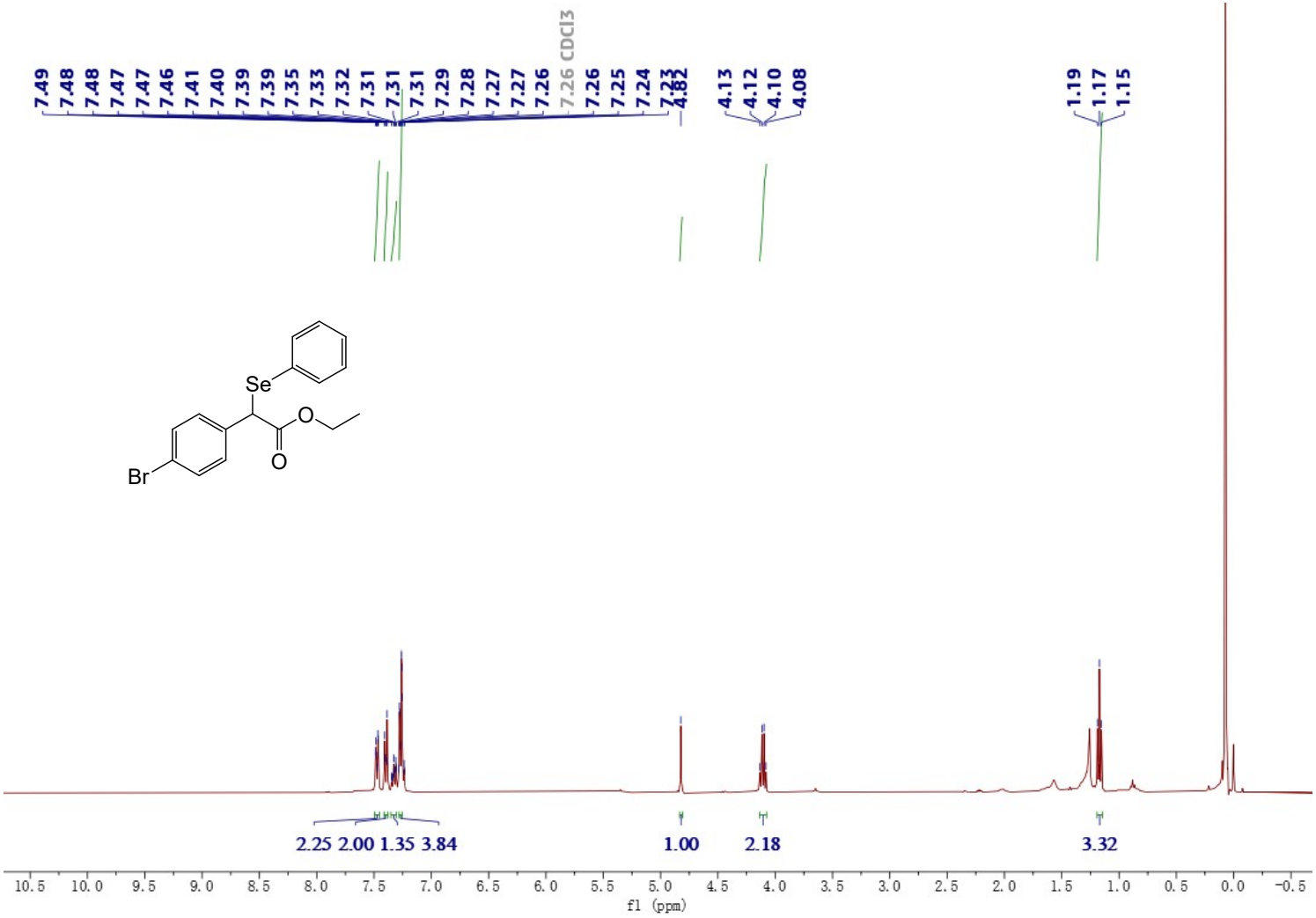
3ta: ^{1}H NMR (400 MHz, $CDCl_3$)



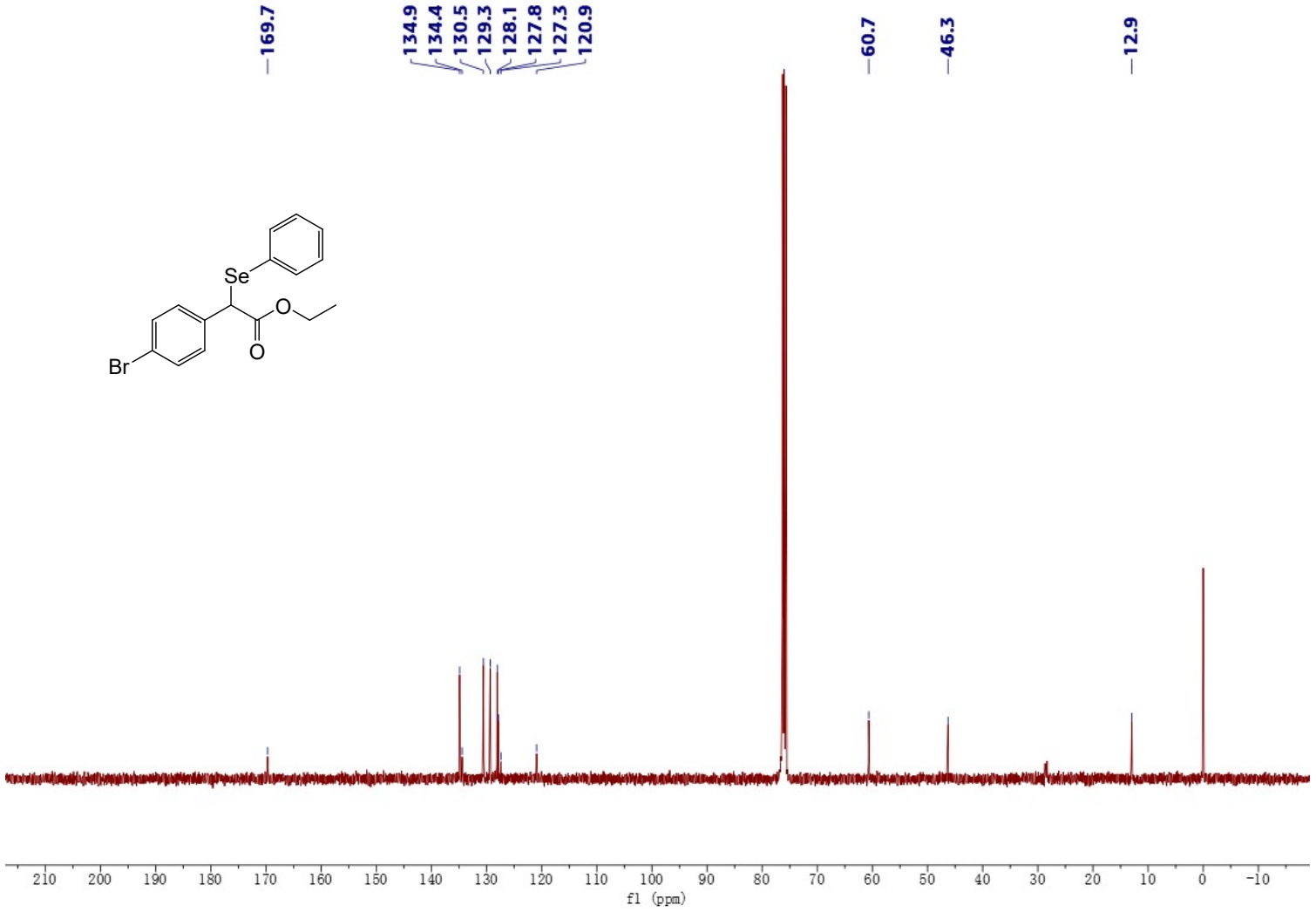
3ta: ^{13}C NMR (100 MHz, $CDCl_3$)



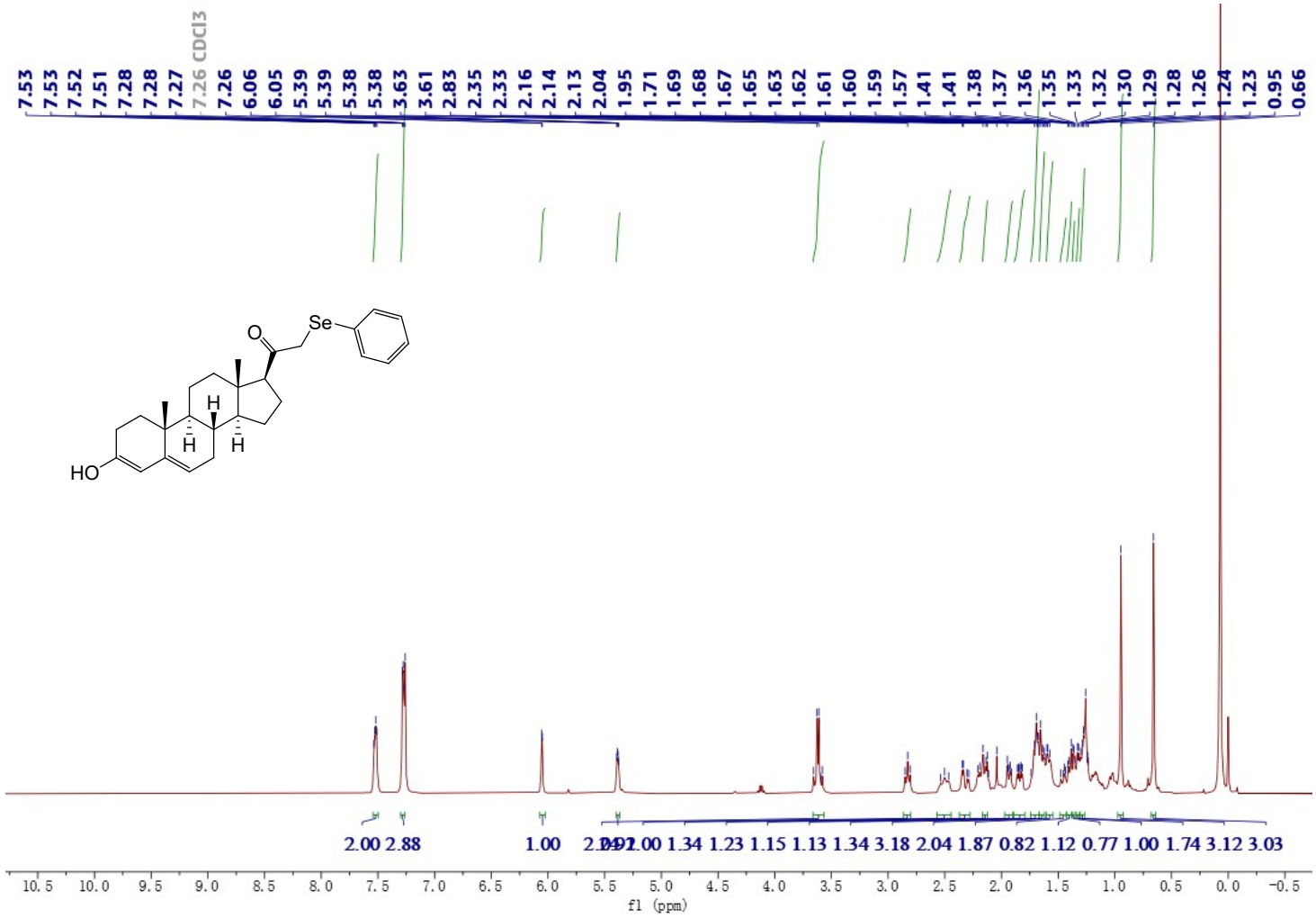
3ua: ^{1}H NMR (400 MHz, $CDCl_3$)



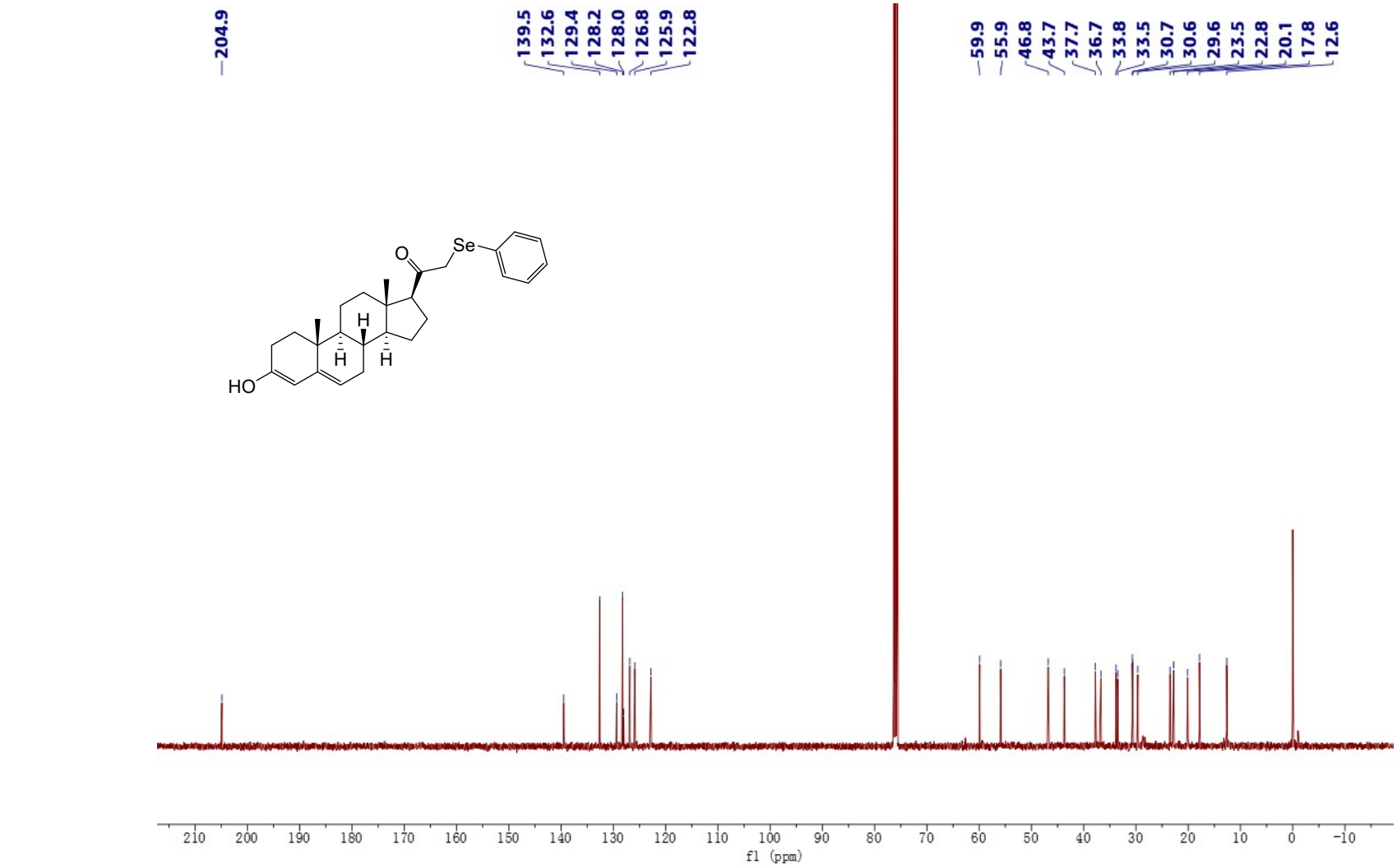
3ua: ^{13}C NMR (100 MHz, $CDCl_3$)



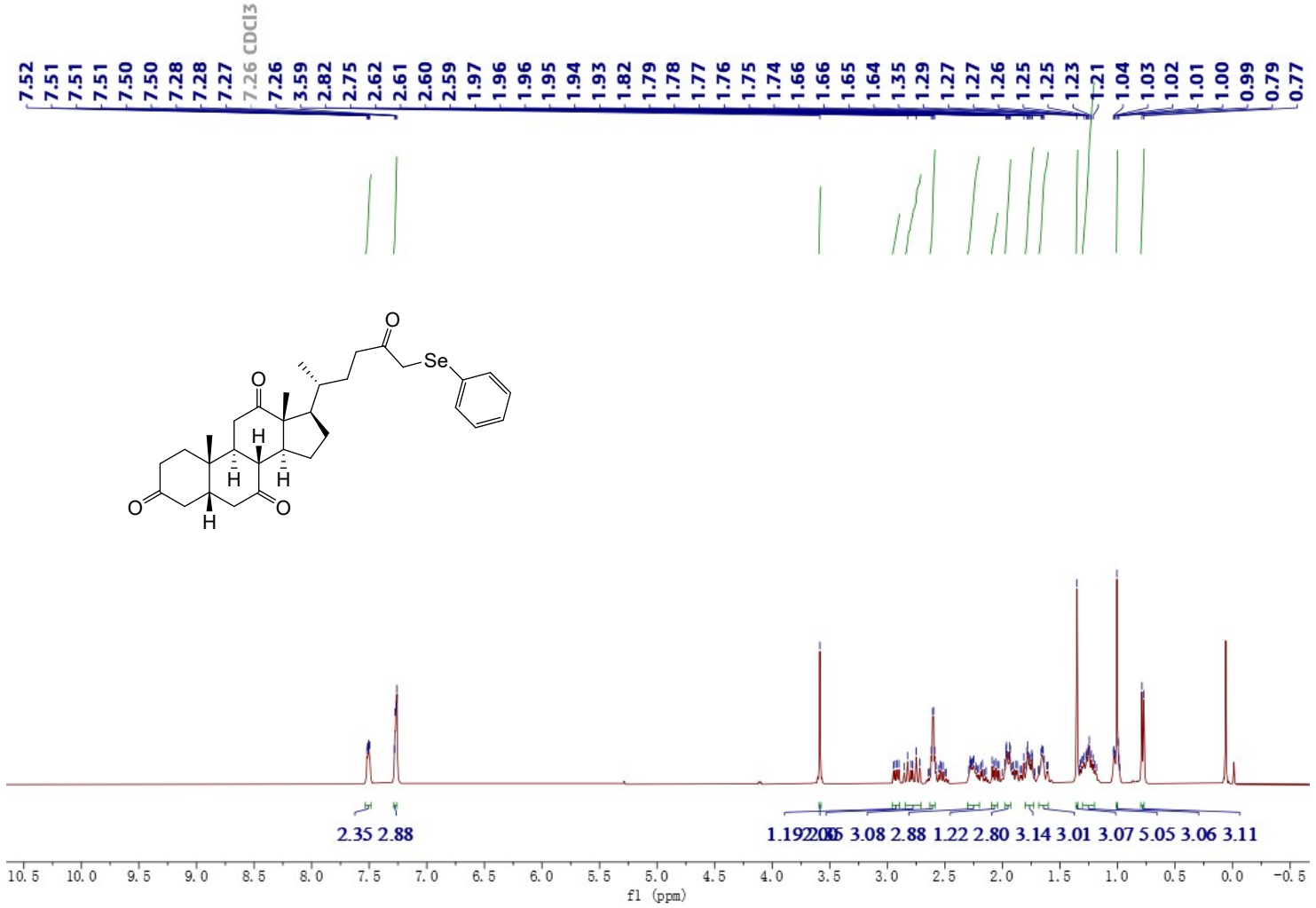
3va: ^{1}H NMR (400 MHz, $CDCl_3$)



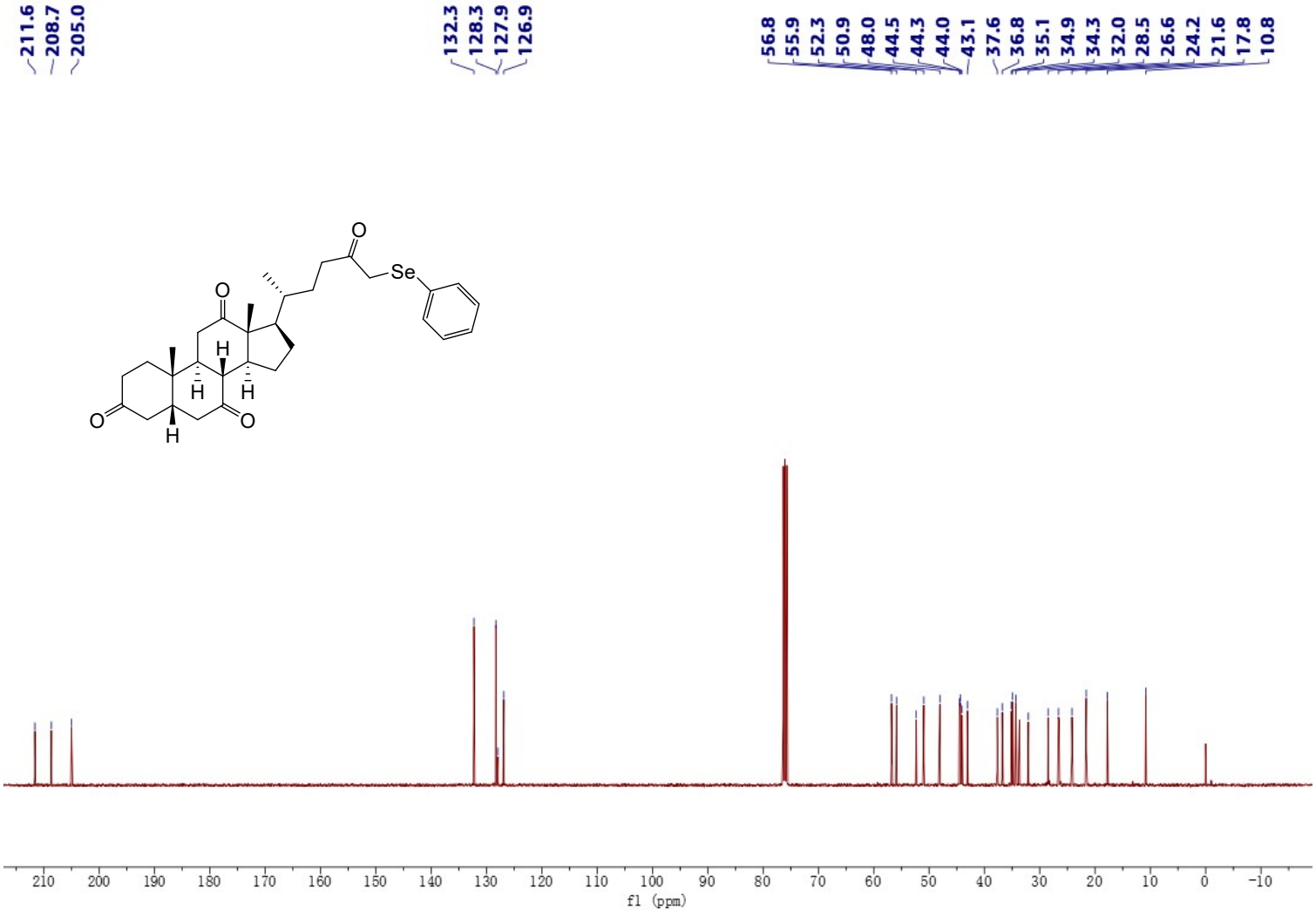
3va: ^{13}C NMR (100 MHz, $CDCl_3$)



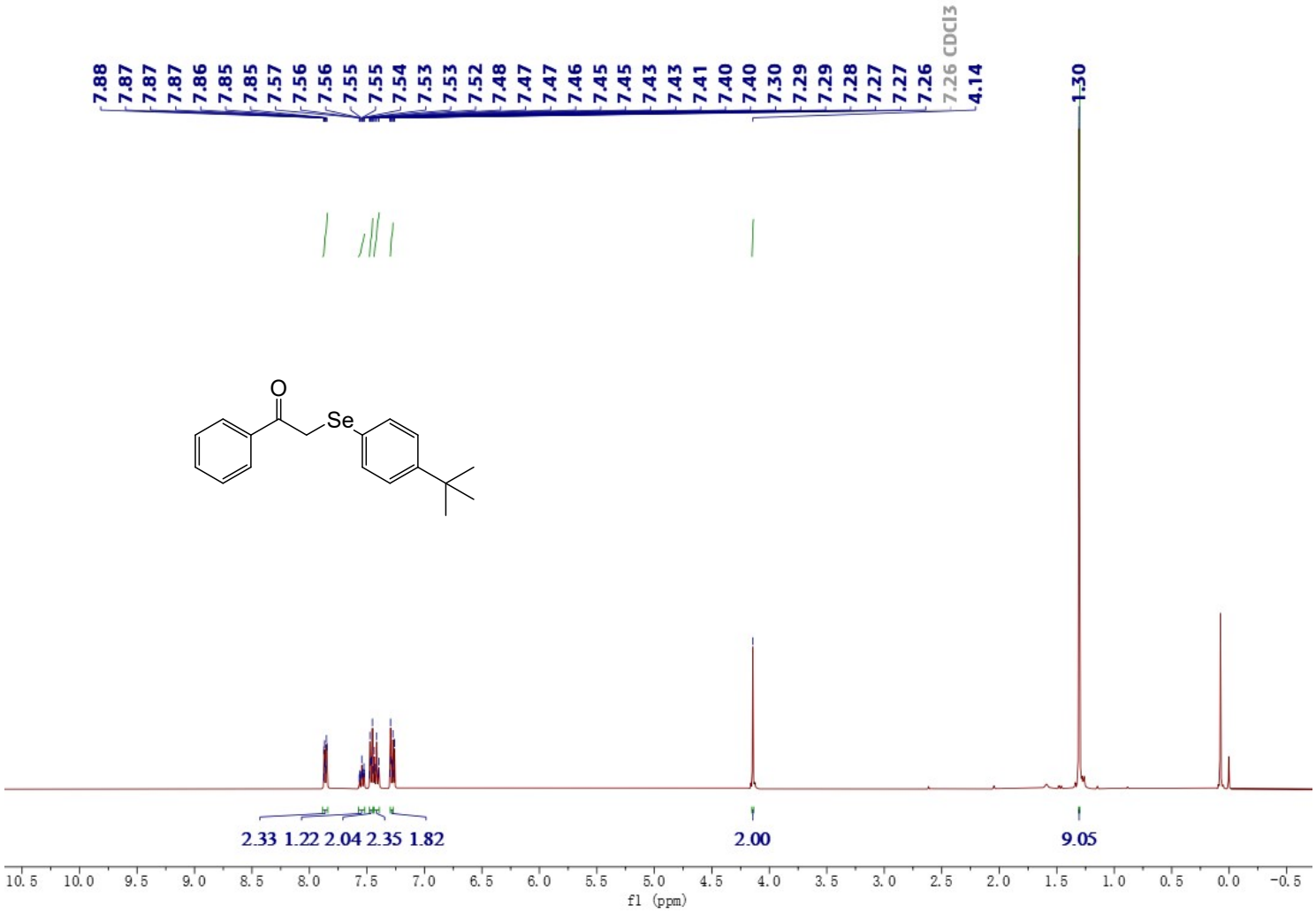
3wa: ^{1}H NMR (400 MHz, $CDCl_3$)



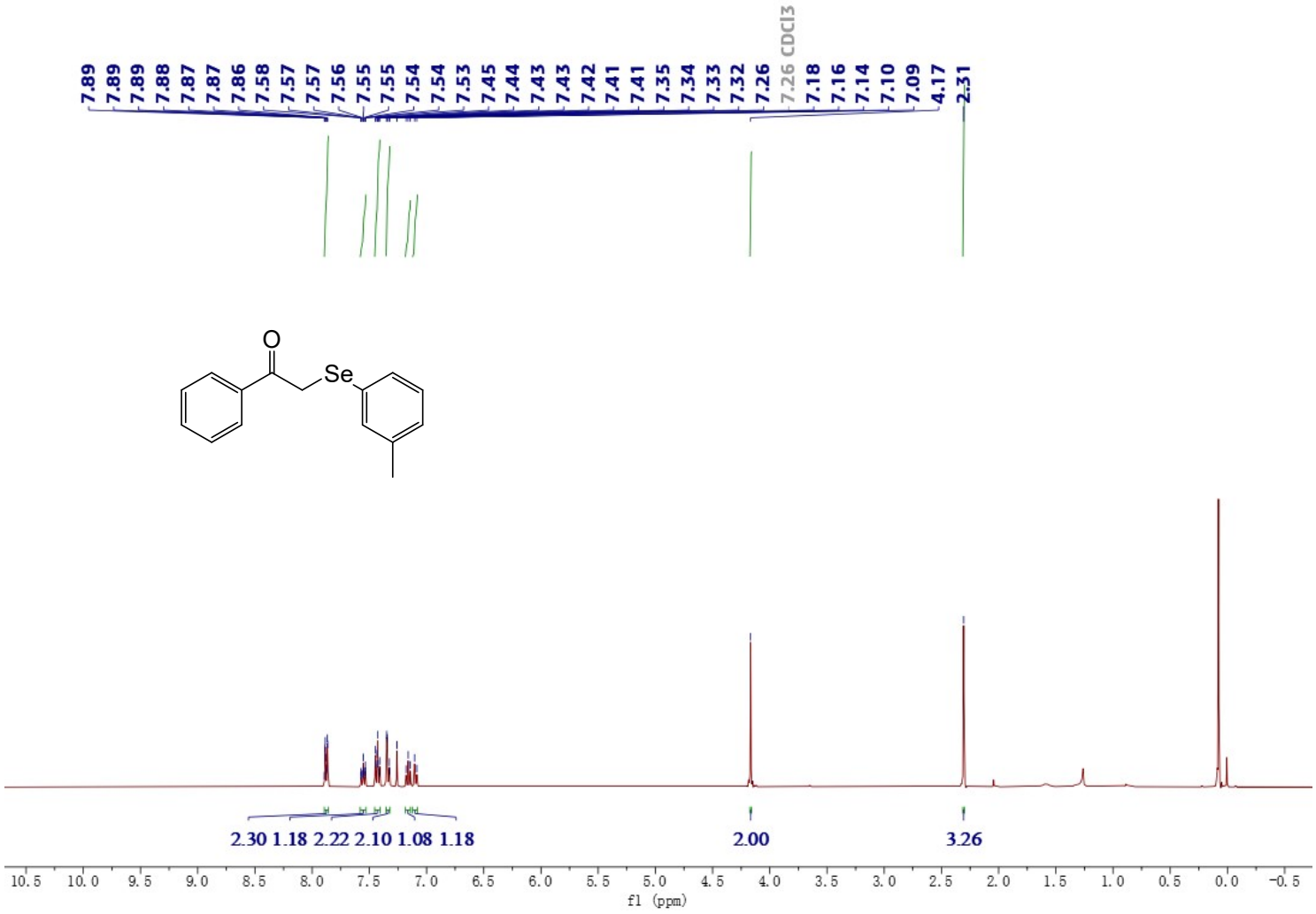
3wa: ^{13}C NMR (100 MHz, $CDCl_3$)



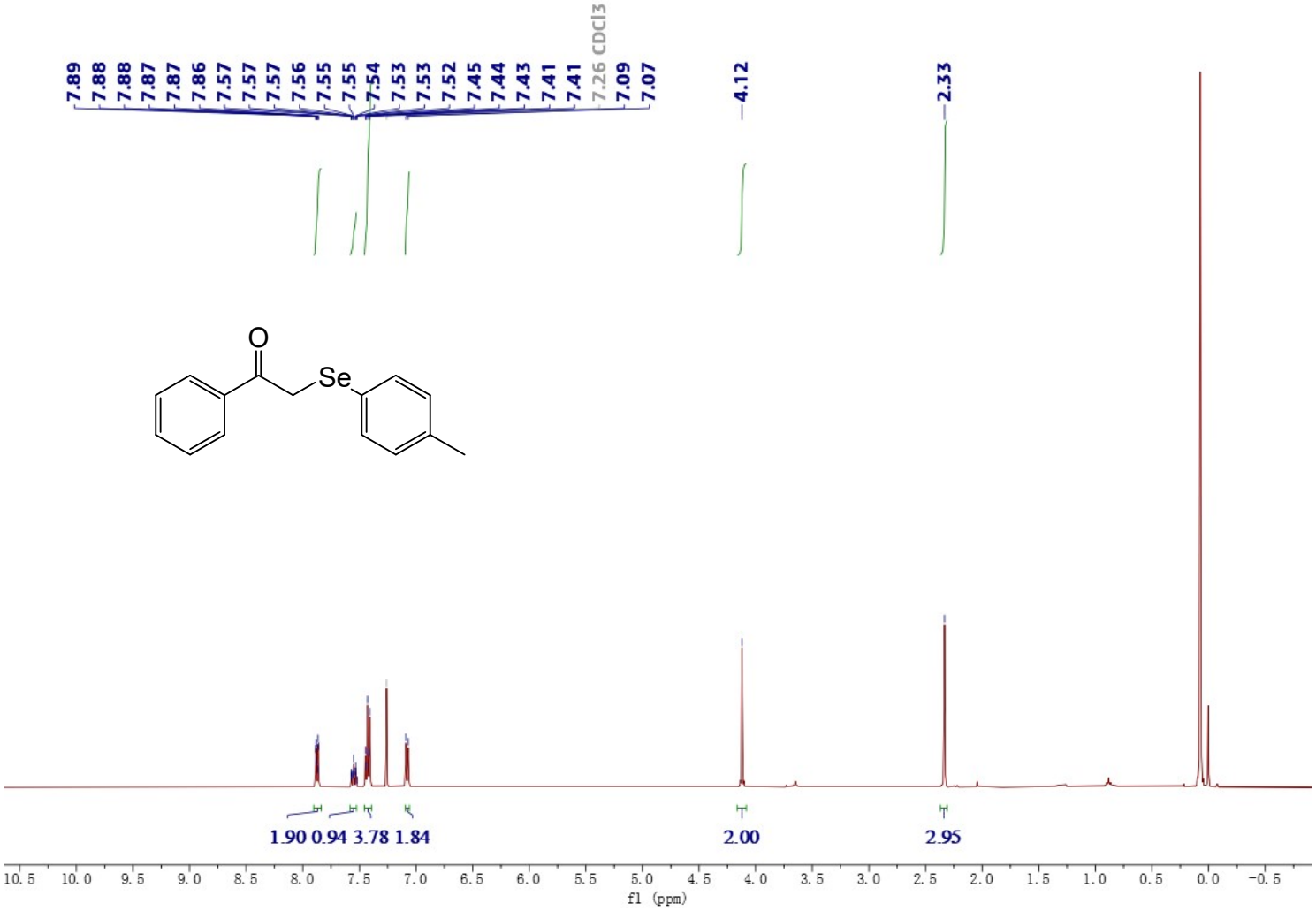
3ab: ^{1}H NMR (400 MHz, $CDCl_3$)



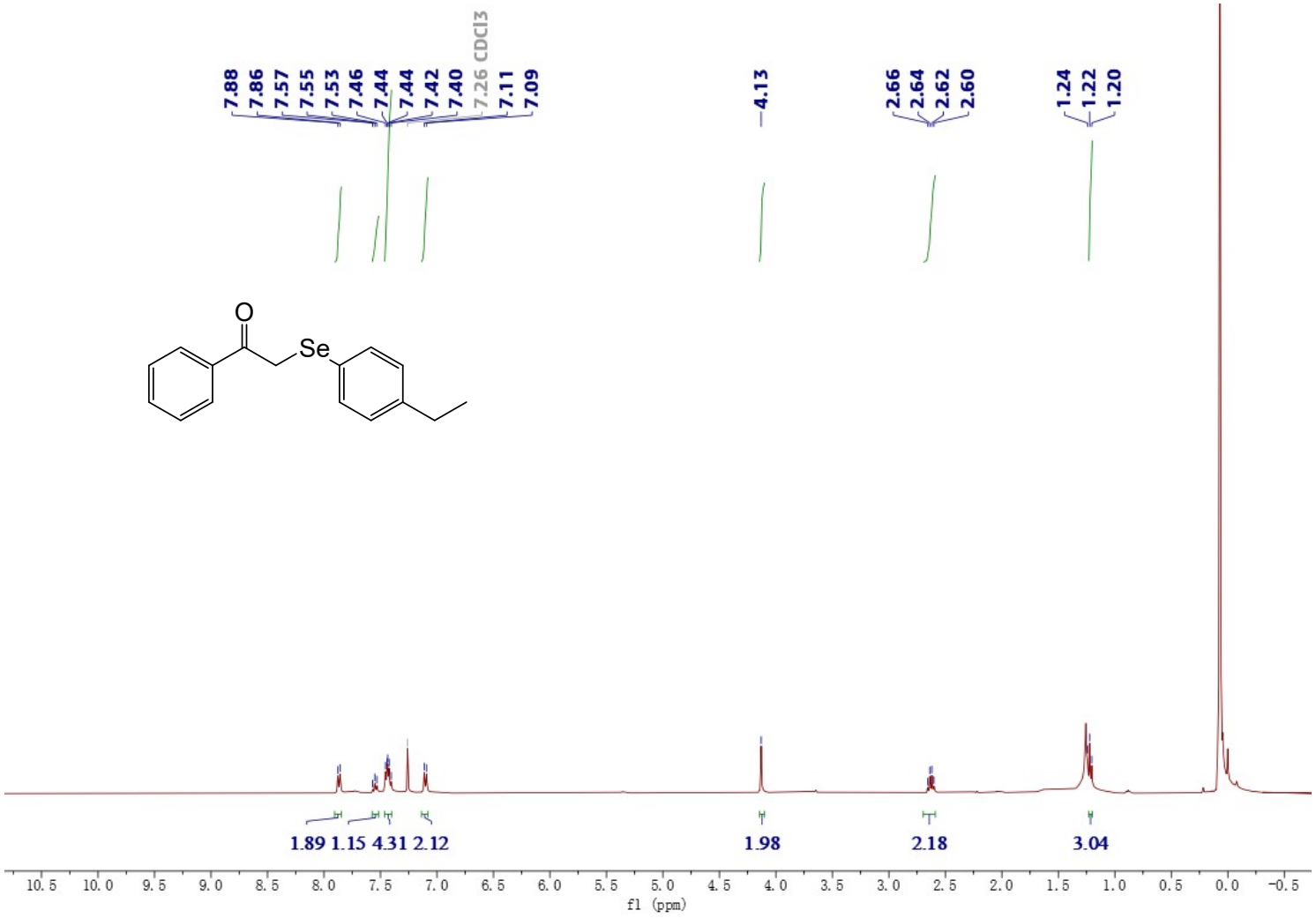
3ac: ^{1}H NMR (400 MHz, $CDCl_3$)



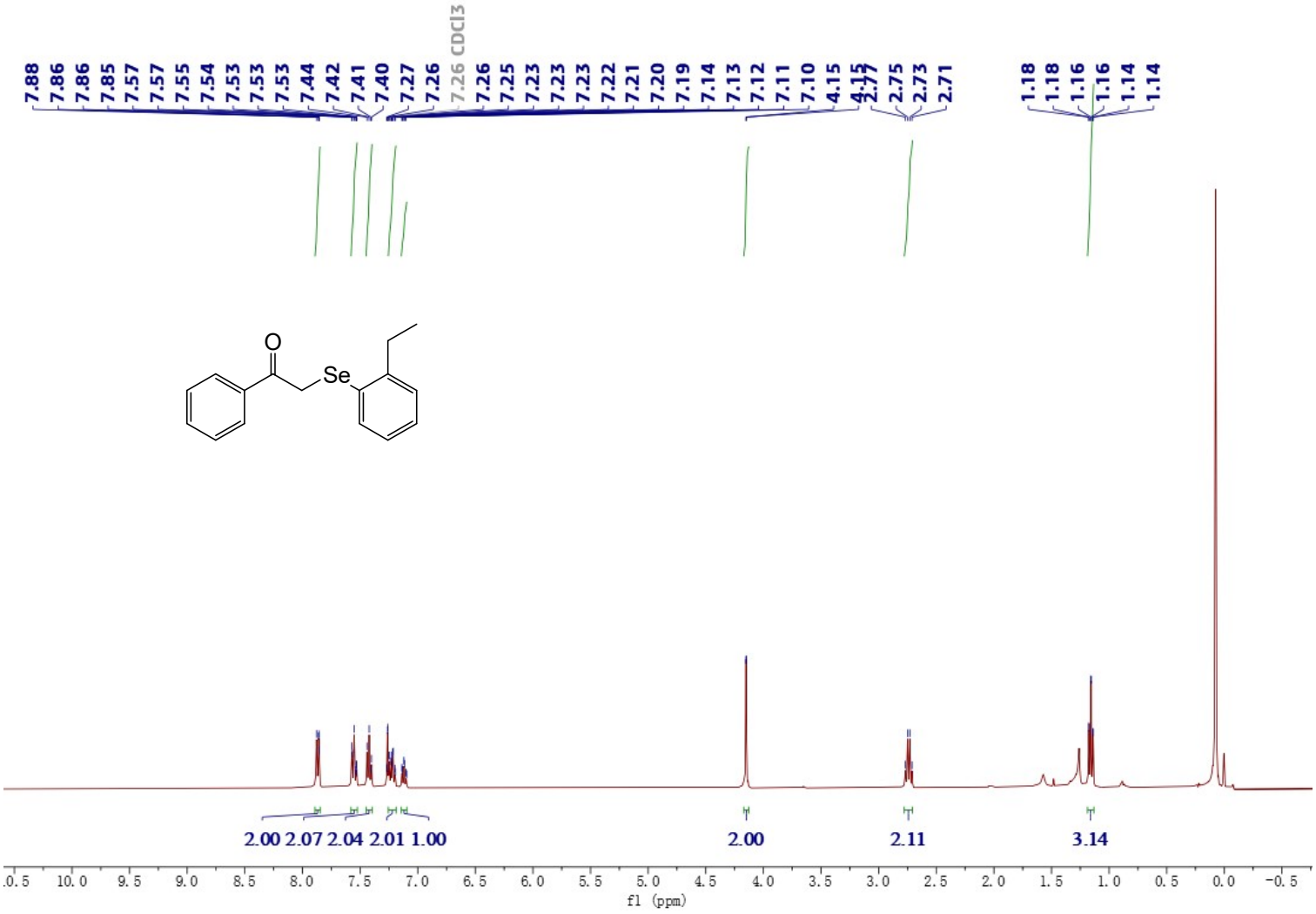
3ad: ^{1}H NMR (400 MHz, $CDCl_3$)



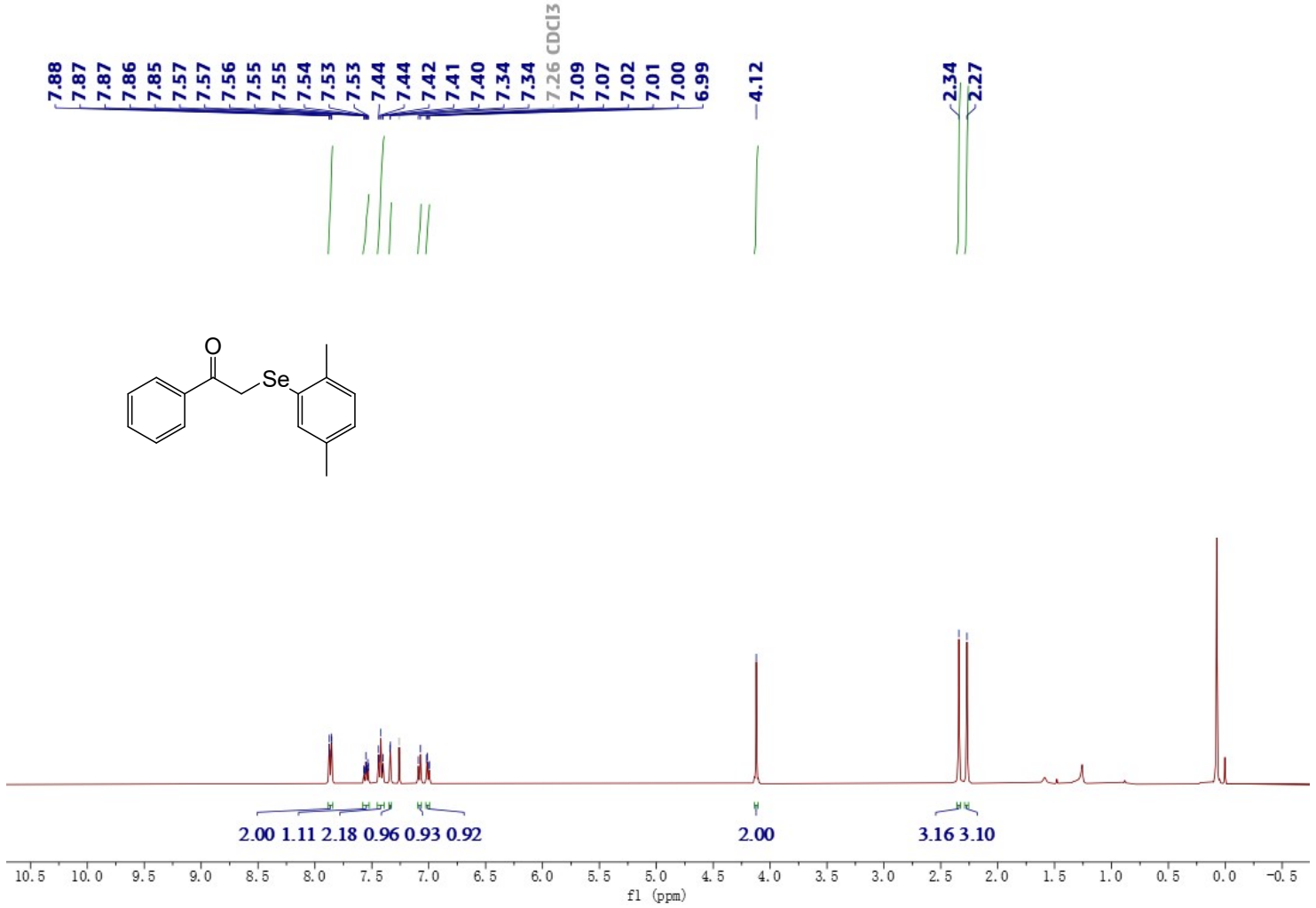
3ae: ^{1}H NMR (400 MHz, $CDCl_3$)



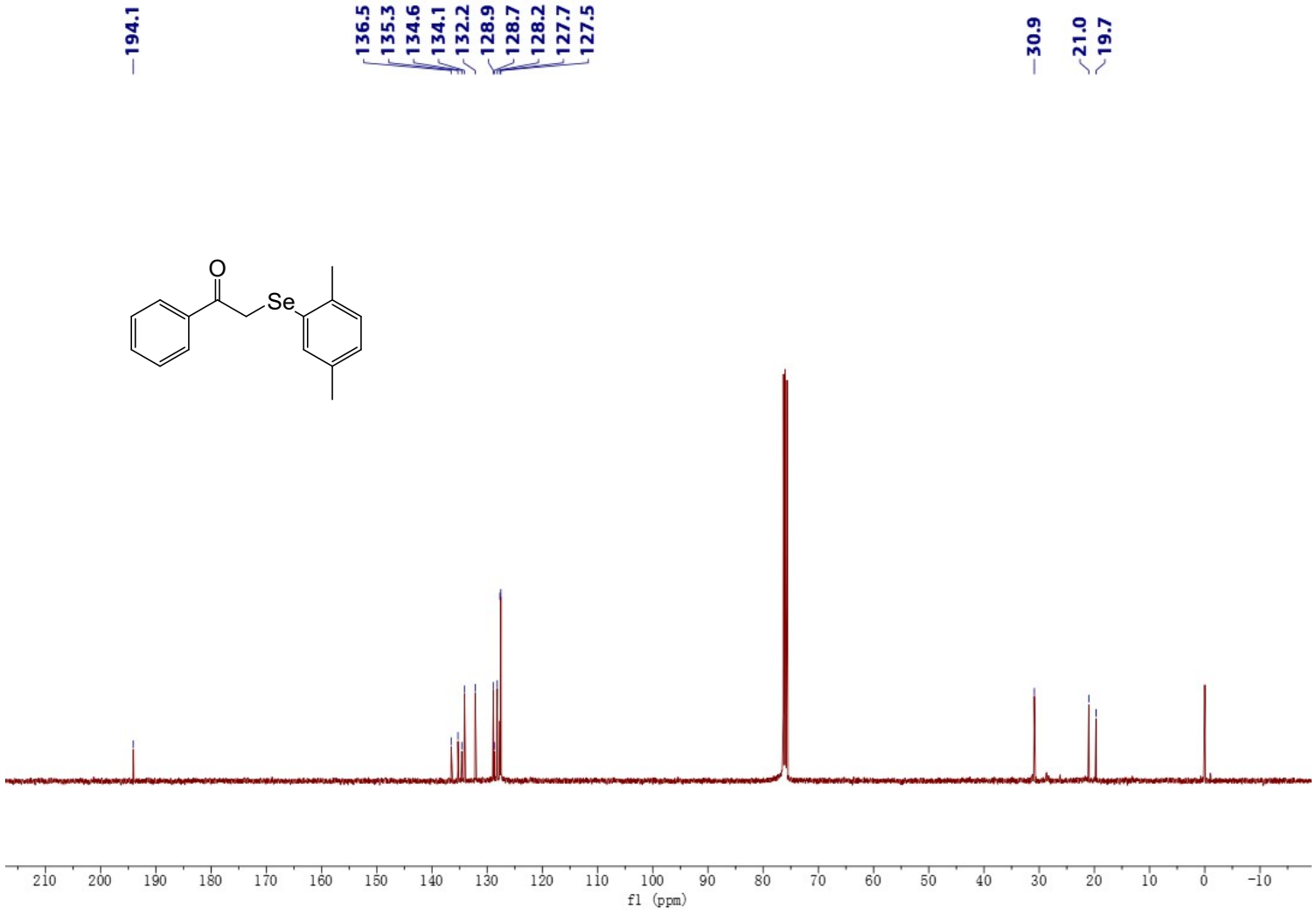
3af: ^{1}H NMR (400 MHz, $CDCl_3$)



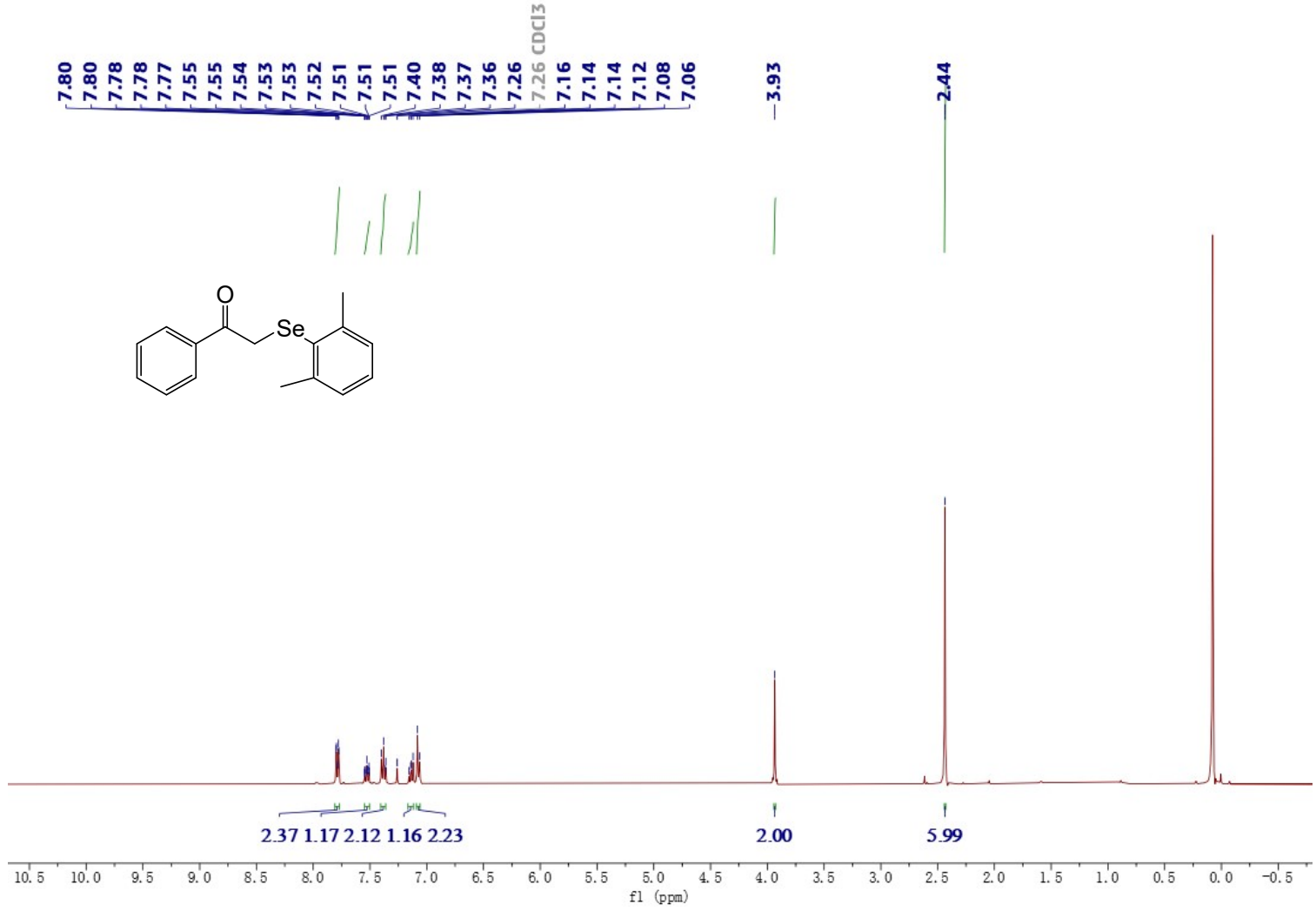
3ag: ^{1}H NMR (400 MHz, $CDCl_3$)



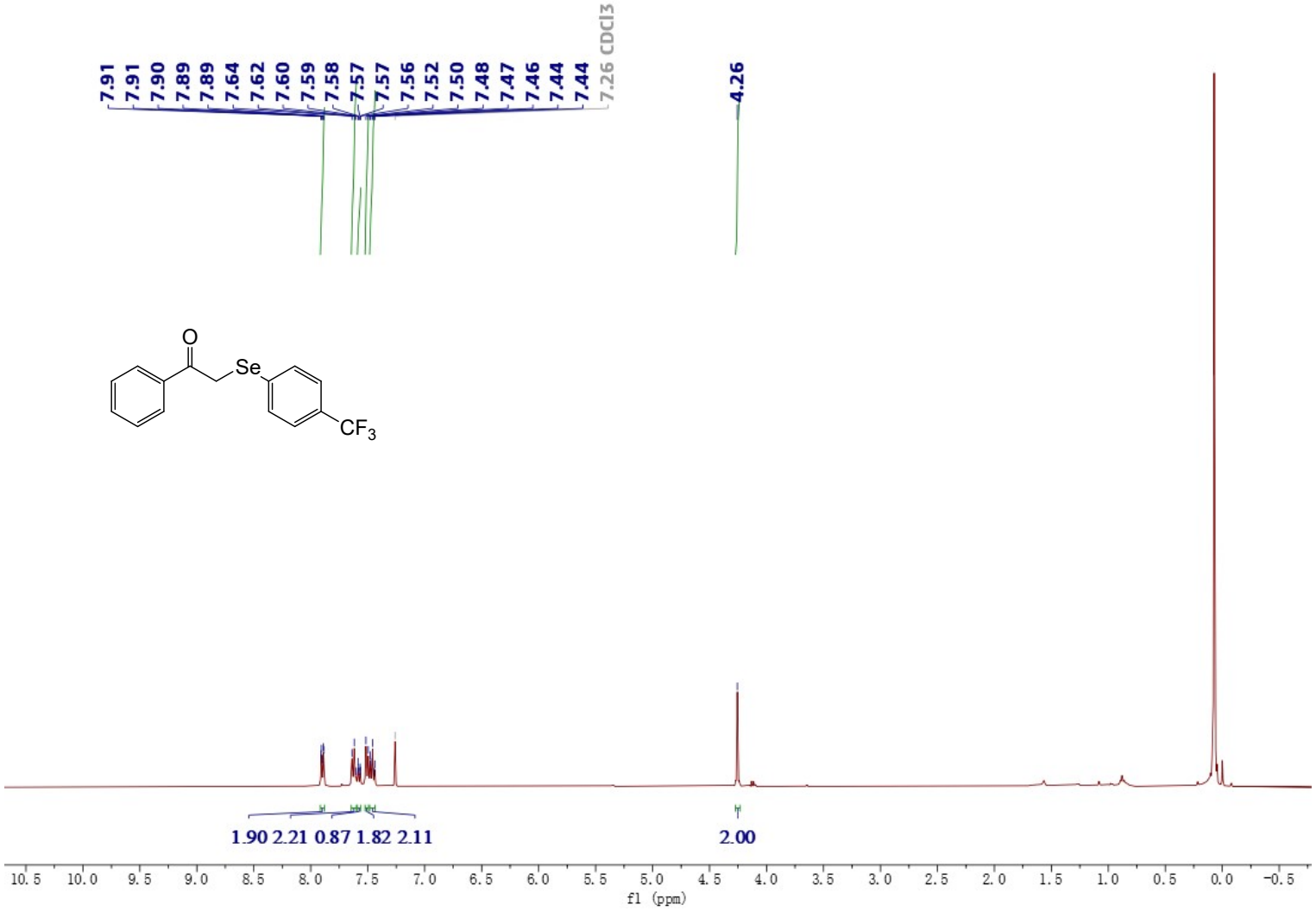
3ag: ^{13}C NMR (100 MHz, $CDCl_3$)



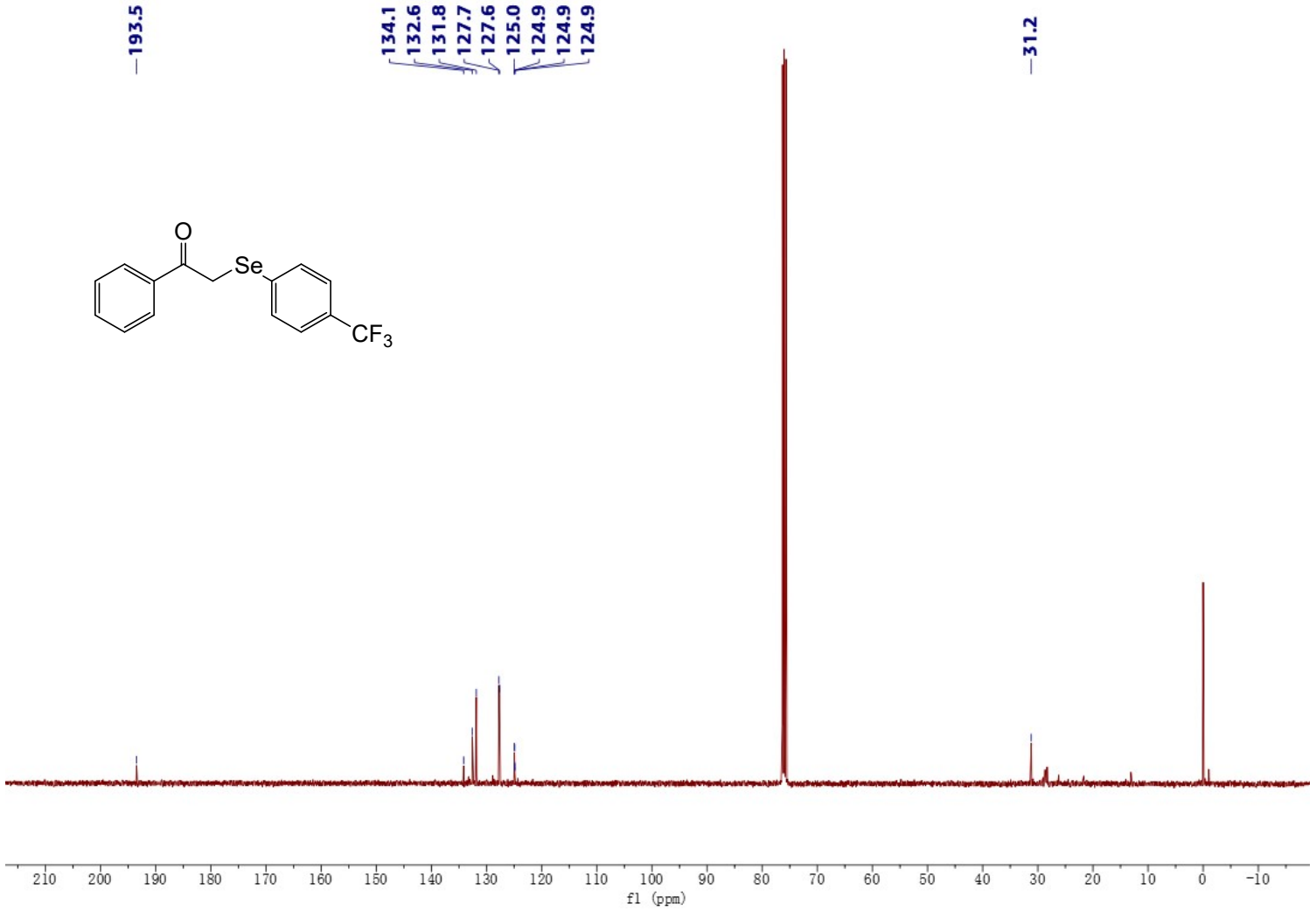
3ah: ^{1}H NMR (400 MHz, $CDCl_3$)



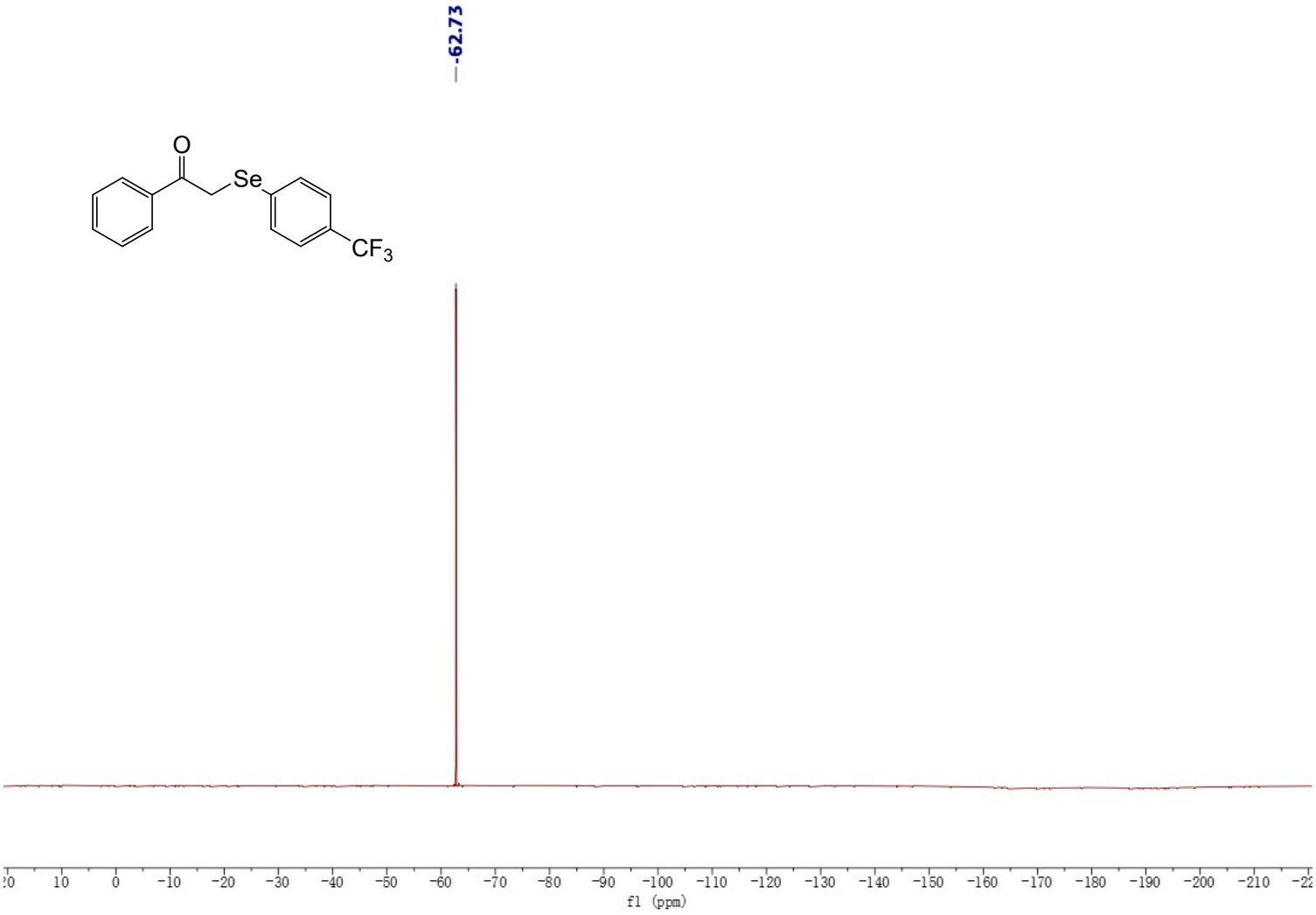
3ai: ^{1}H NMR (400 MHz, $CDCl_3$)



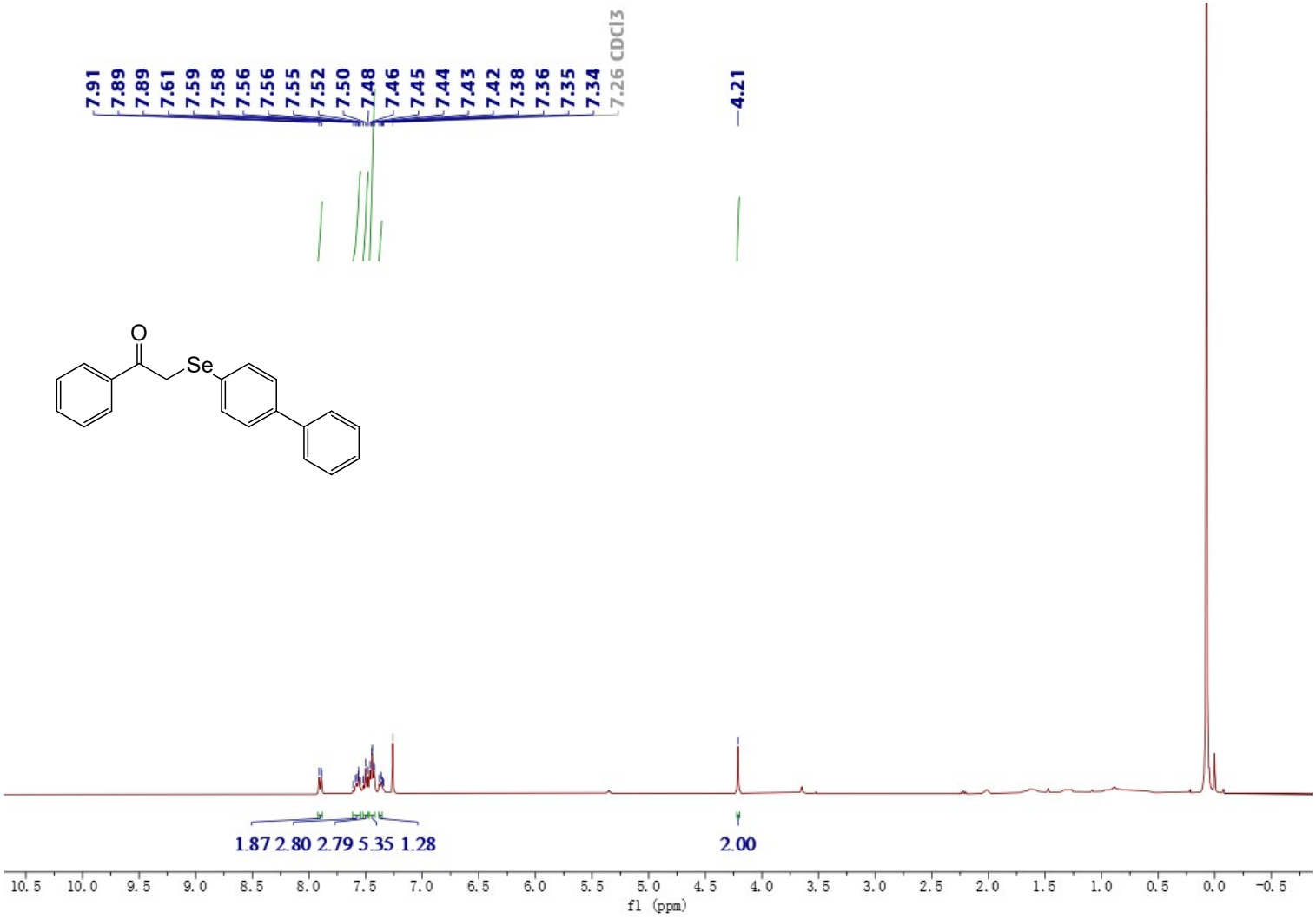
3ai: ^{13}C NMR (100 MHz, $CDCl_3$)



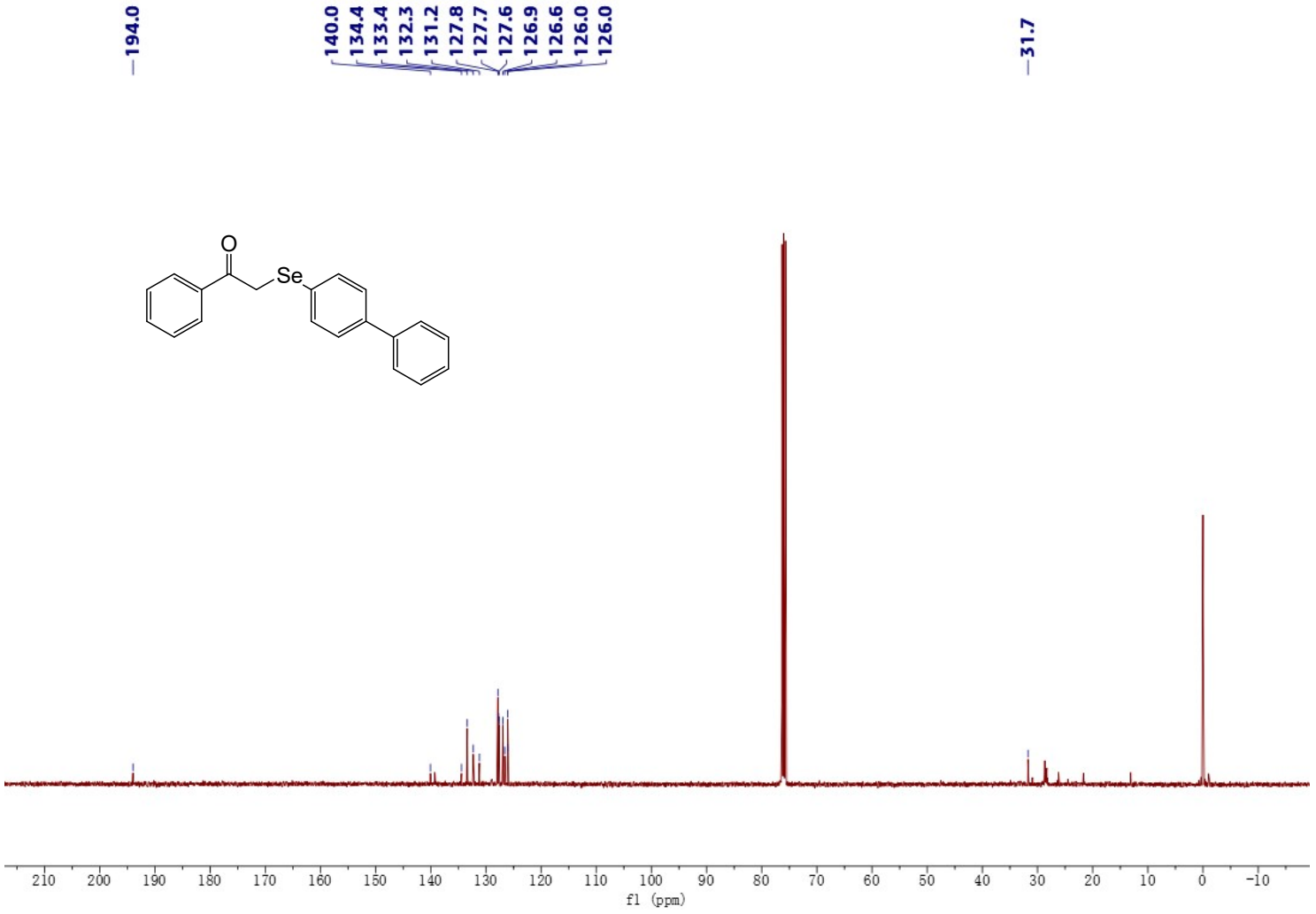
3ai: ^{19}F NMR (376 MHz, $CDCl_3$)



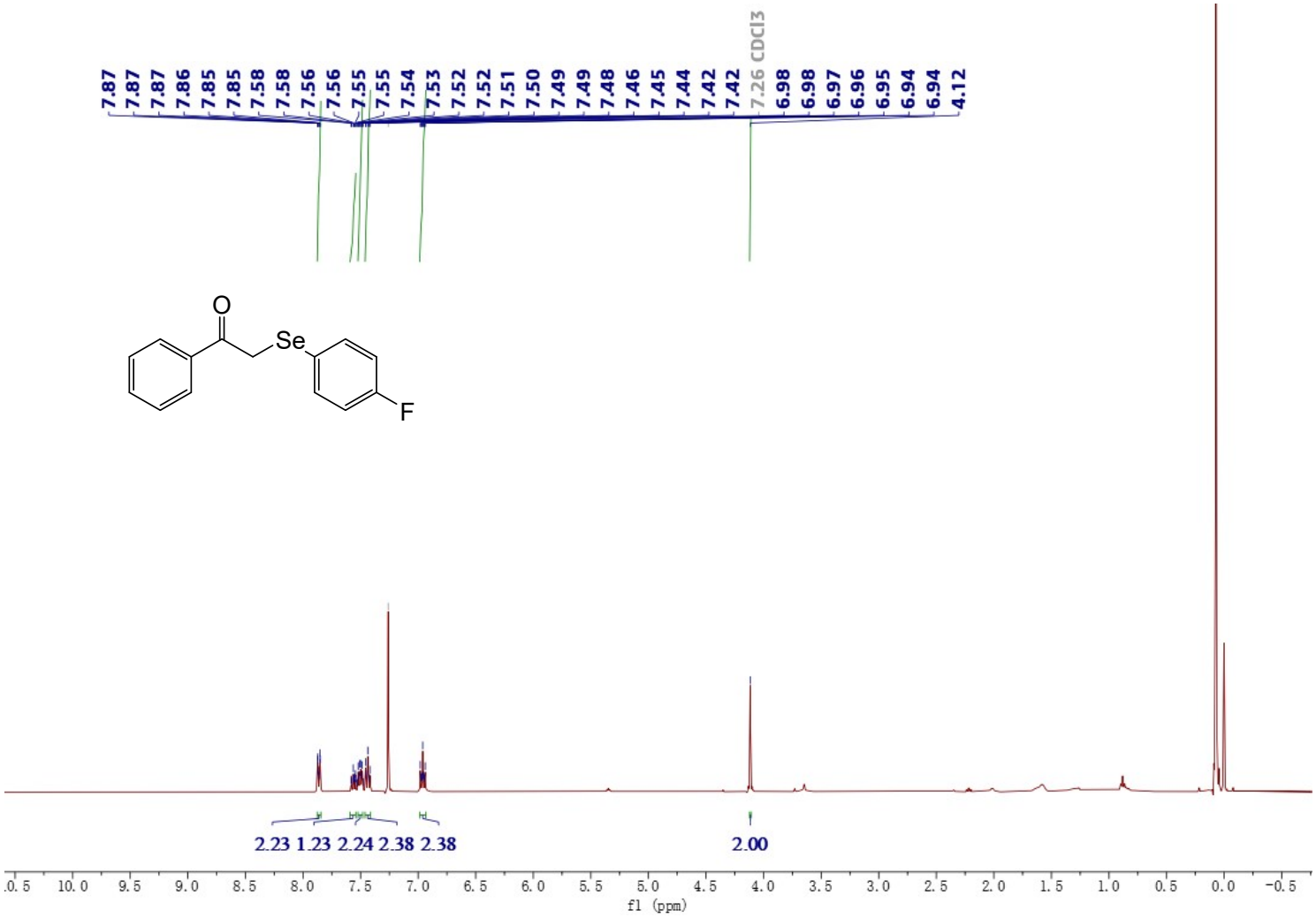
3aj: ^{1}H NMR (400 MHz, $CDCl_3$)



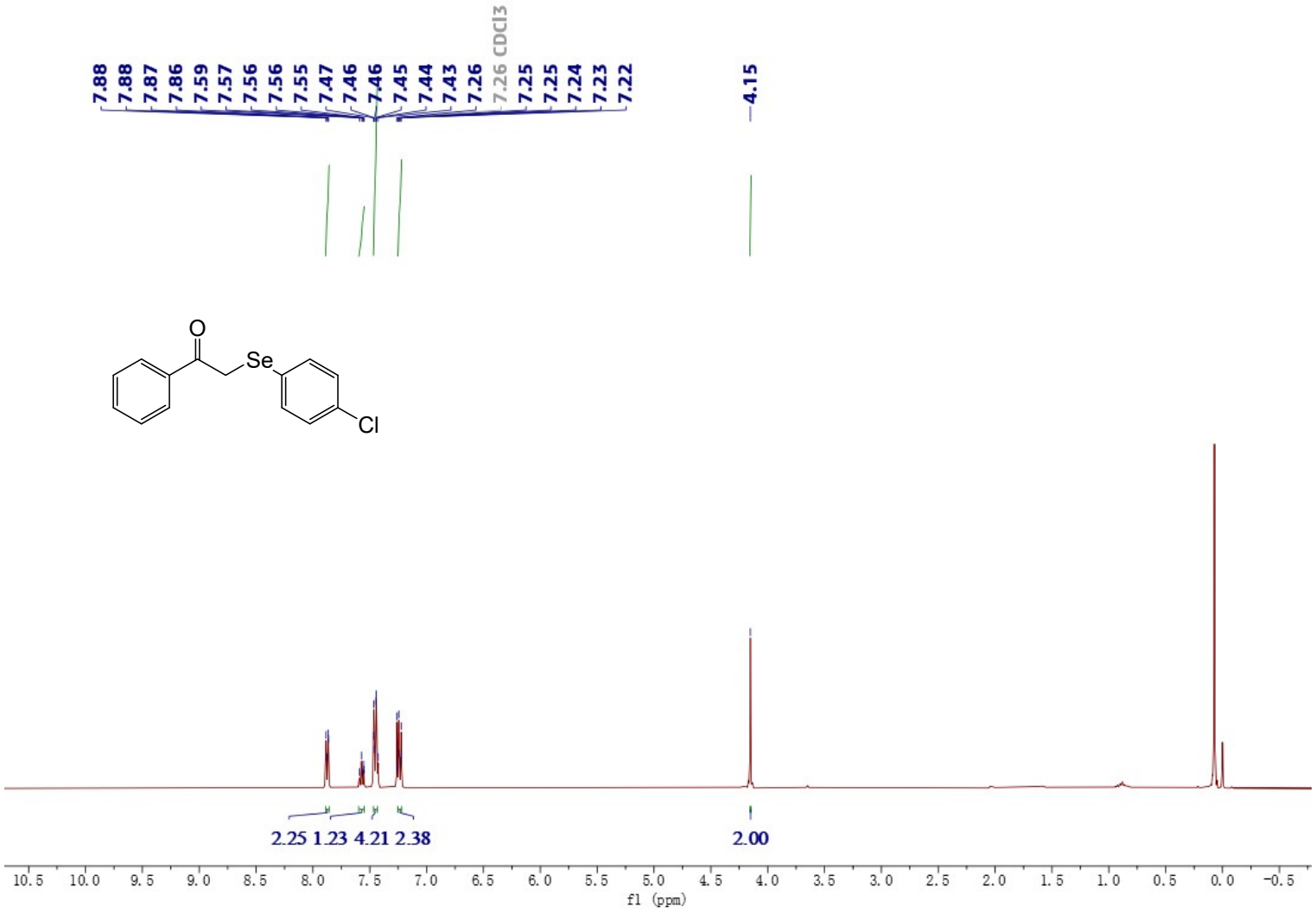
3aj: ^{13}C NMR (100 MHz, $CDCl_3$)



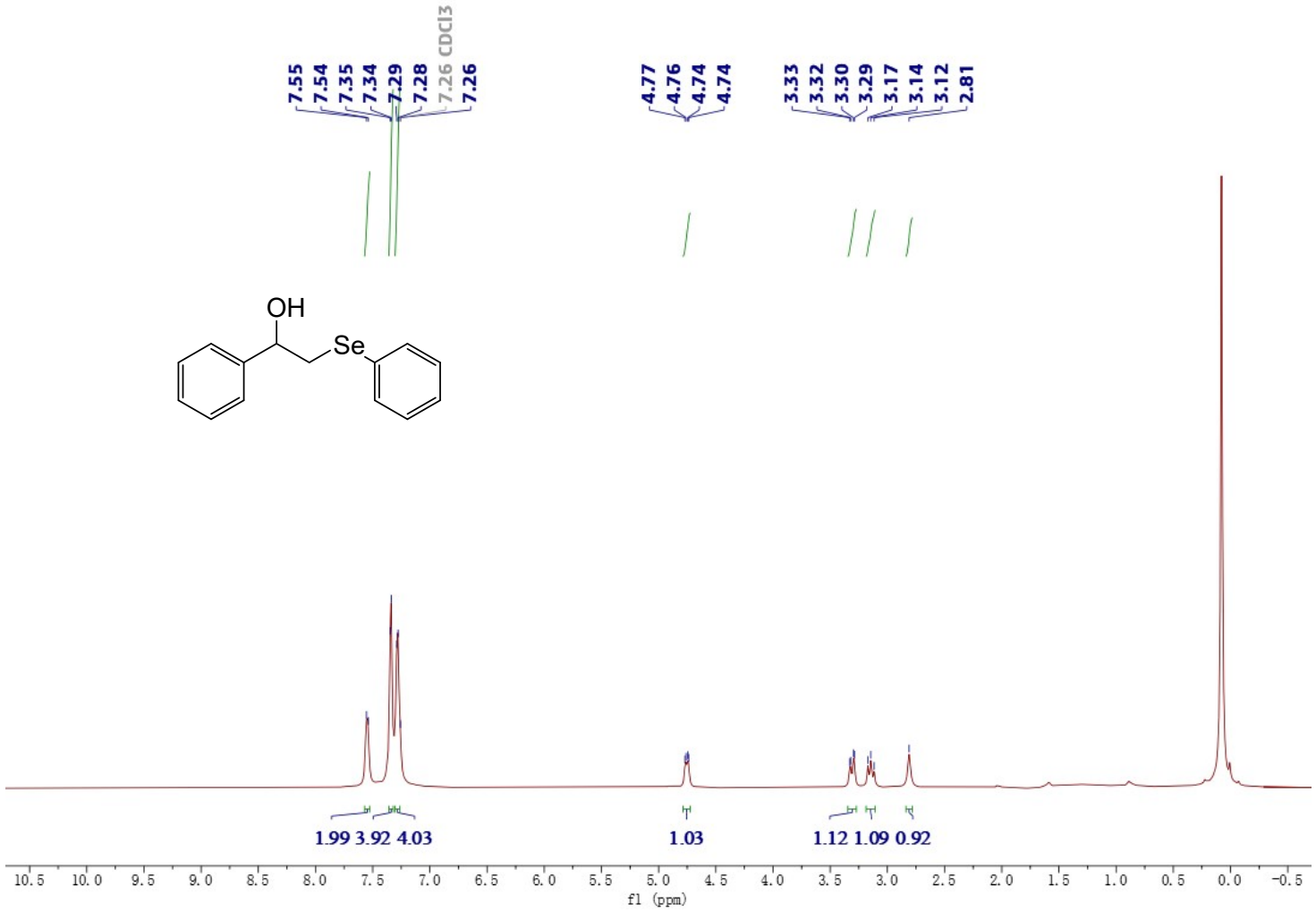
3ak: ^{1}H NMR (400 MHz, $CDCl_3$)



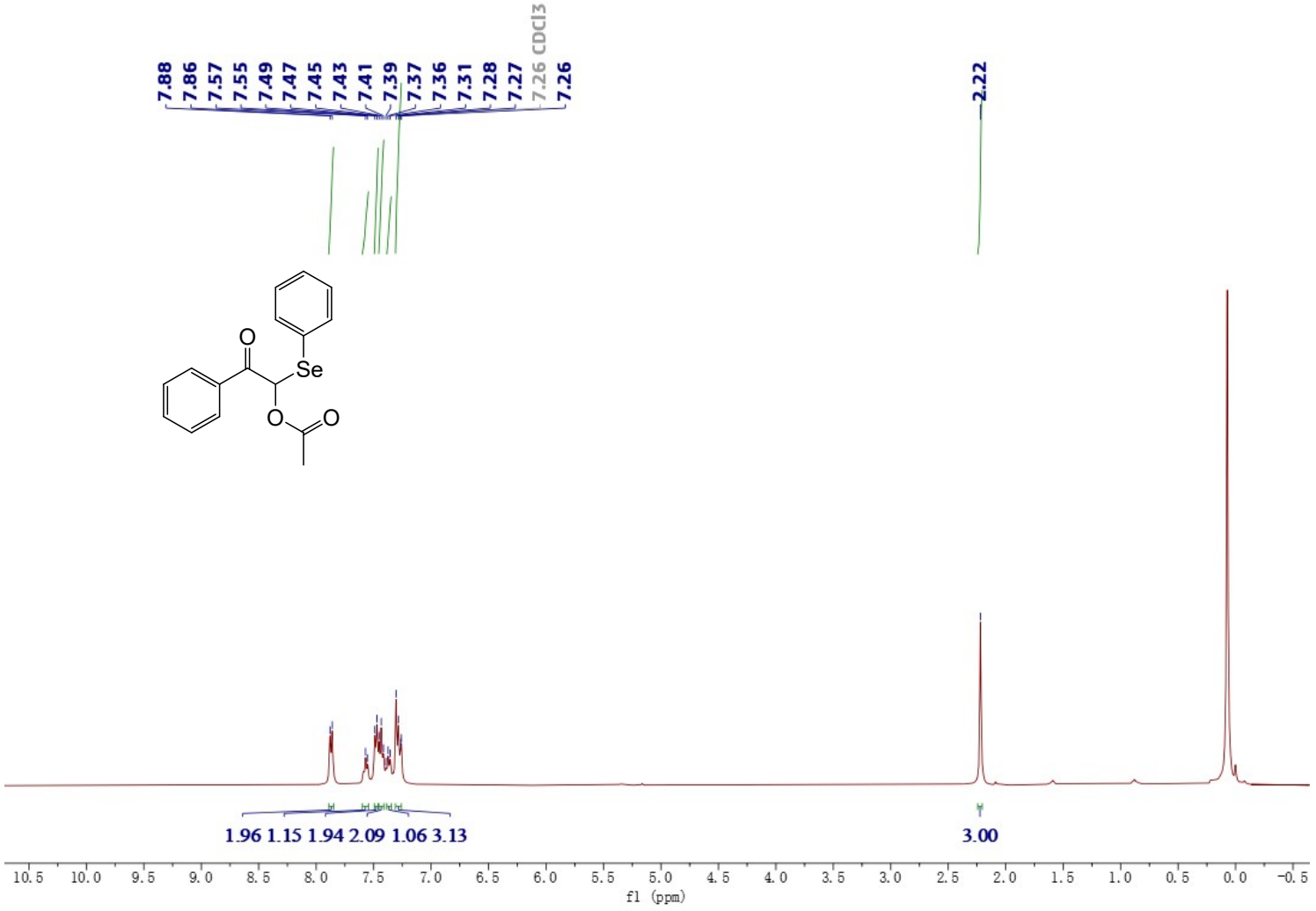
3al: ^{1}H NMR (400 MHz, $CDCl_3$)



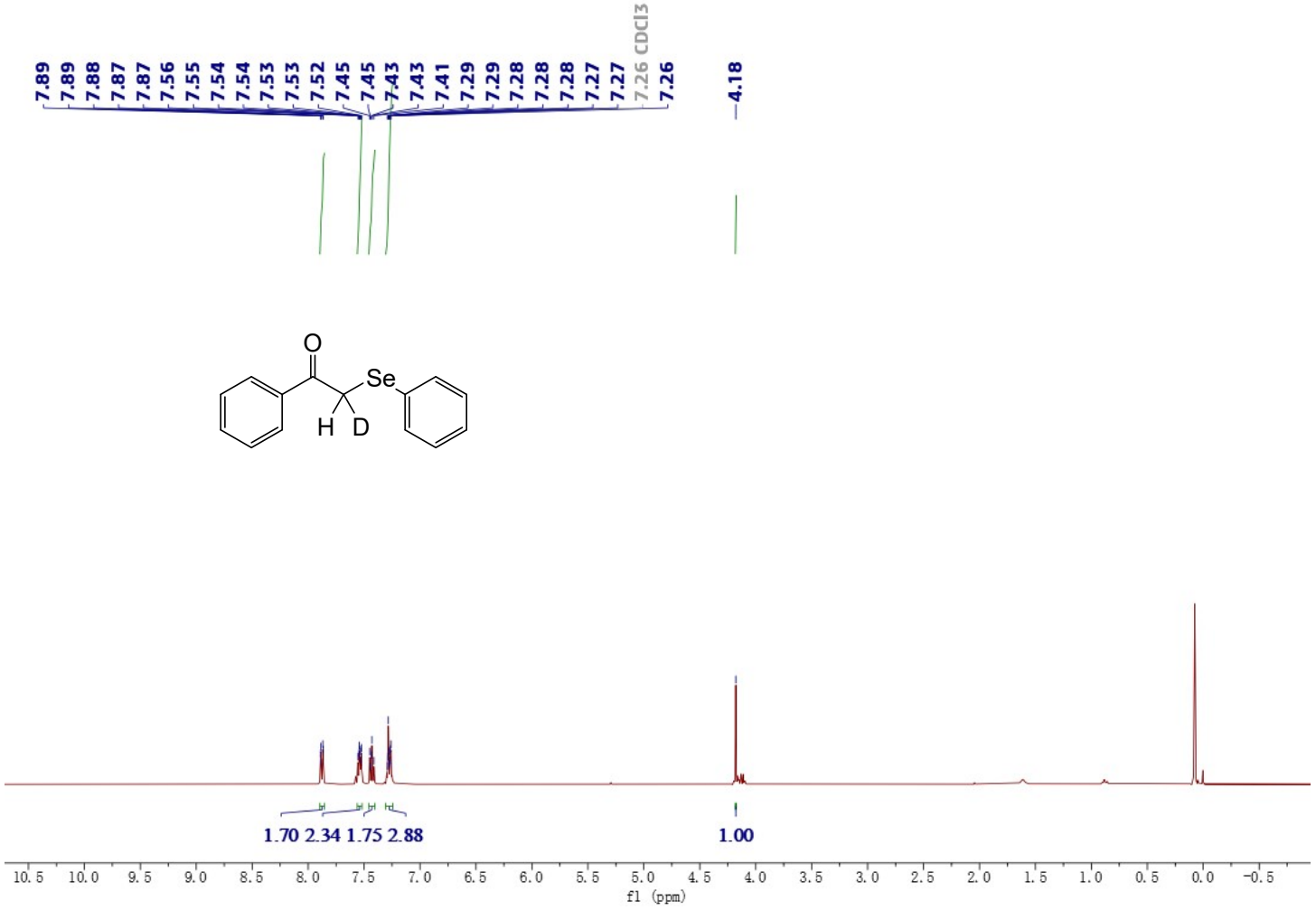
4: ^{1}H NMR (400 MHz, $CDCl_3$)



5: ^{1}H NMR (400 MHz, $CDCl_3$)



3aa-D: ^{1}H NMR (400 MHz, $CDCl_3$)



5. References

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