Supporting Information

Metal−Free Radical Selenothiocyanation of Terminal and Internal Alkynes

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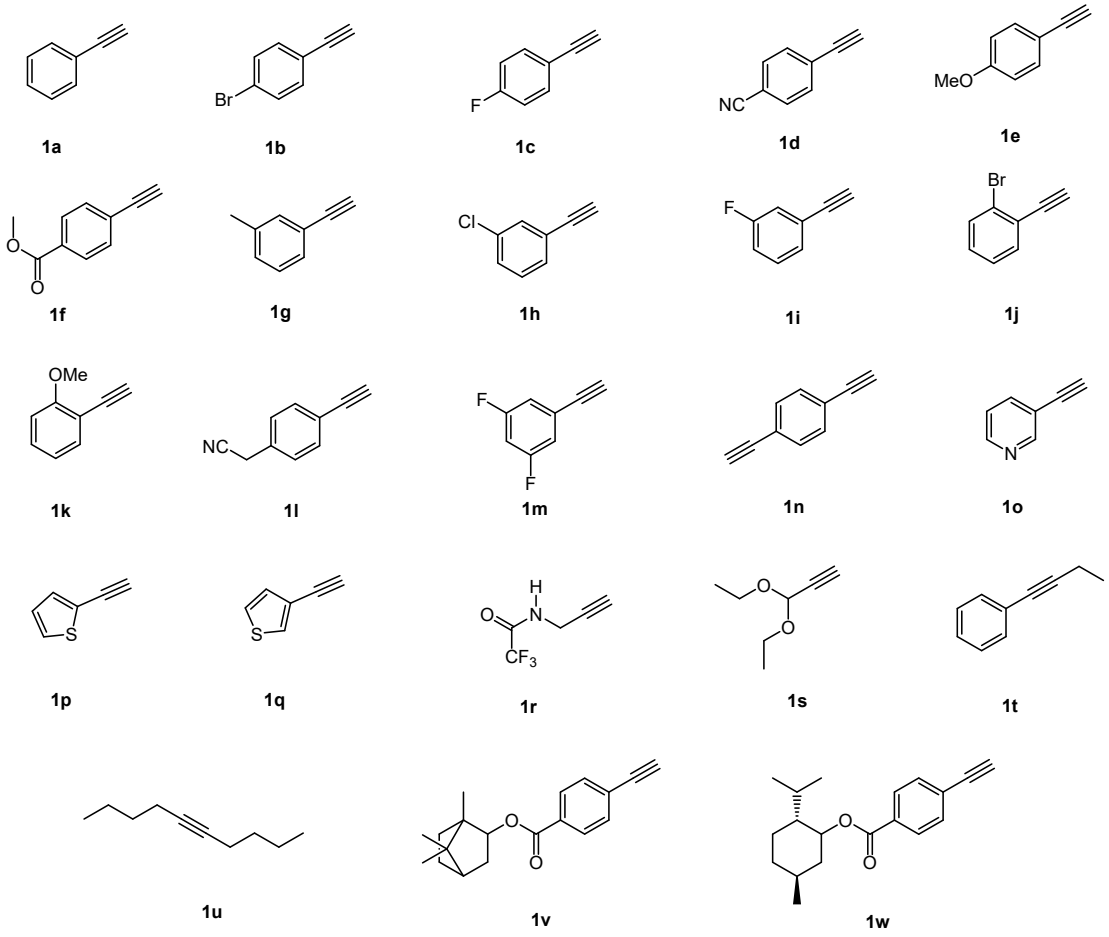
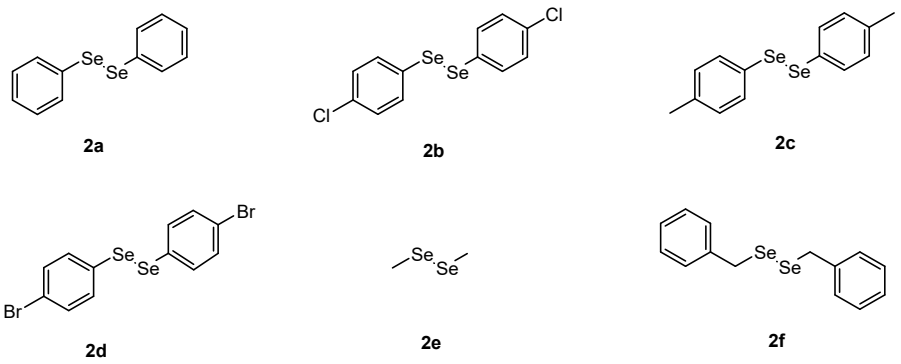
General information

Chemicals and solvents were purchased from commercial sources (Energy Chemical, J&KChemic, TCI, Fluka, Acros, SCRC) and used without further purification unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products. ^{1}H, ^{13}C and ^{19}F Nuclear Magnetic Resonance spectra were recorded on Bruker 500 MHz NMR spectrometer using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal standard. ^{1}H NMR and ^{13}C NMR spectra were recorded on 500MHz MHz Bruker spectrometers. Chemical shifts of ^{1}H were reported in part per million relative to the $CDCl_3$ residual peak (δ 7.280). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.00). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint (quintet), m (multiplet). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (virt.). High resolution mass spectra (HRMS) data were measured by ESI-microTOF II. Melting points were measured by SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Reaction solvent and eluent without further purification: Ethyl acetate (AR, ≥99.5%), Petroleum ether (60-90 °C) (AR, ≥99.9%), Dichloromethane (AR, ≥99.9%), Hexane (AR, ≥97%). The starting material is labeled as **1a-1w, 2a-2f**.

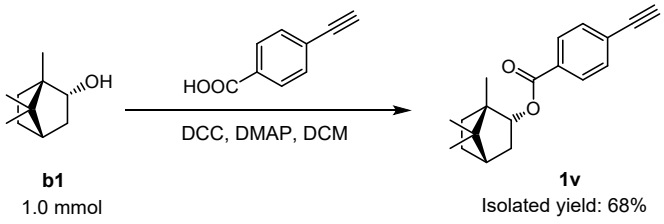




Scheme S1. Substrates employed for the reaction

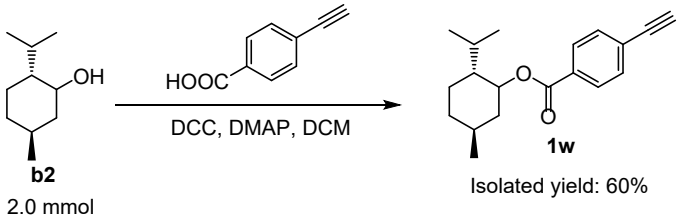
Substrate preparation

Synthesis of compound 1v [1]: In a 25 mL round-bottom flask, L(-)-Borneol **b1** (1.0 mmol, 154.2 mg), 4-ethynyl-benzoic acid (1.2 mmol, 197.0 mg), DMAP (0.1 mmol, 12.2 mg), CH_2Cl_2 (10.0 mL) and dicyclohexylcarbodiimide (2.0 mmol, 412.6 mg) were successively added. The mixture was stirred at room temperature overnight. The reaction was quenched with aqueous NH_4Cl (10 mL), extracted with EtOAc (3 × 30 mL). The combined ethyl acetate layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = 10/1) on silica gel to afford product **1v** (191.9 mg, 68% isolated yield) as a white solid.



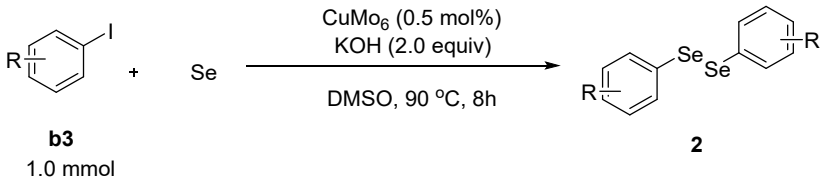
Scheme S2. The general procedure synthesis experiment of **1v**

Synthesis of compound 1w [1]: In a 25 mL round-bottom flask, L-Menthol **b2** (2.0 mmol, 312.5 mg), 4-ethynyl-benzoic acid (2.4 mmol, 394.0 mg), DMAP (0.2 mmol, 24.4 mg), CH_2Cl_2 (10.0 mL) and dicyclohexylcarbodiimide (4.0 mmol, 825.3 mg) were successively added. The mixture was stirred at room temperature overnight. The reaction was quenched with aqueous NH_4Cl, extracted with EtOAc (3 × 30 mL). The combined ethyl acetate layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = 10/1) on silica gel to afford product **1w** (341.3 mg, 60% yield) with light yellow liquid.



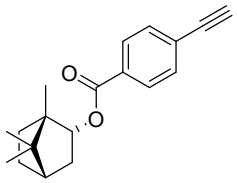
Scheme S3. The general procedure synthesis experiment of **1w**

Synthesis of compound 2 [2]: To a stirred solution of Se powder (2.0 mmol, 162.0 mg) and halides **b3** (1.0 mmol) in DMSO (4.0 mL) was added by using $CuMo_6$ catalyst (0.5 mol%) followed by KOH (2.0 equiv) at 90 °C for 8 h under air atmosphere. After completion of the reaction, 3.0 mL of water was added and the mixture was extracted three times with ethyl acetate (3 × 3.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the product **2** was obtained by flash column chromatography on silica gel.



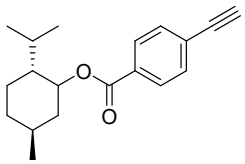
Scheme S4. The general procedure synthesis experiment of **2**

(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo [2.2.1] heptan-2-yl 4-ethynylbenzoate (**1v**)[1]



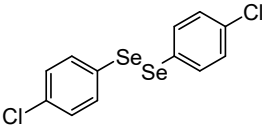
White solid (191.9 mg, 68%, mp: 100-103 °C). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 5.15-5.12 (m, 1H), 3.25 (s, 1H), 2.50 (d, *J* = 4.4 Hz, 1H), 2.14 (d, *J* = 13.5 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.77 (t, *J* = 4.5 Hz, 1H), 1.43 (t, *J* = 12.5 Hz, 1H), 1.36 – 1.30 (m, 1H), 1.14 (dd, *J* = 13.9, 3.5 Hz, 1H), 0.99 (s, 3H), 0.94 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 132.1, 130.9, 129.4, 126.6, 82.9, 80.9, 80.0, 49.1, 47.9, 45.0, 36.9, 28.1, 27.4, 19.7, 18.9, 13.6.

(2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-ethynylbenzoate (**1w**)[1]



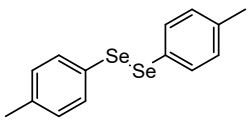
Light yellow oil (341.3 mg, 60%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 4.95 (td, *J* = 10.9, 4.4 Hz, 1H), 3.25 (s, 1H), 2.14 (d, *J* = 12.5 Hz, 1H), 1.96 (ddd, *J* = 11.3, 7.0, 3.5 Hz, 1H), 1.78 – 1.73 (m, 2H), 1.62 – 1.55 (m, 2H), 1.17 – 1.10 (m, 2H), 0.94 (t, *J* = 6.5 Hz, 7H), 0.81 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 132.0, 130.8, 129.4, 126.5, 82.9, 79.9, 75.1, 47.2, 40.9, 34.3, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5.

1,2-bis(4-chlorophenyl)diselenide (**2b**)[2]



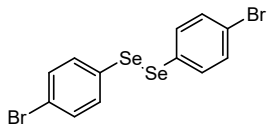
Orange oil (342.9 mg, 90%). TLC (petroleum ether), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 4H), 7.28 – 7.25 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.3, 133.3, 129.4, 128.8.

1, 2-di-p-tolyldiselenide (**2c**)[2]



Light yellow oil (289.2 mg, 85%). TLC (petroleum ether), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 4H), 7.11 (d, *J* = 7.9 Hz, 4H), 2.38 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 132.3, 129.9, 127.6, 21.1.

1,2-bis(4-bromophenyl)diselenide (**2d**)[2]

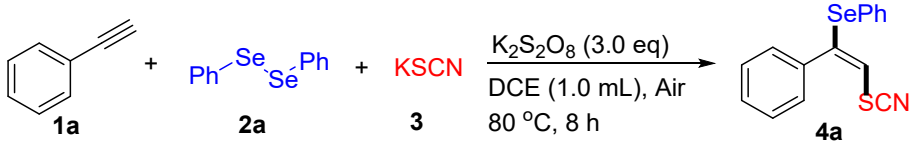


Dark orange oil (329.0 mg, 70%). TLC (petroleum ether), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 4H), 7.43 – 7.39 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.4, 132.3, 129.4, 122.4.

General procedure for (*E*)-phenyl(1-phenyl-2-thiocyanatovinyl)selane

Procedure A

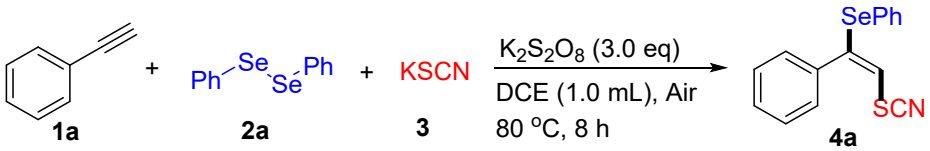
A mixture of alkynes **1a** (0.5 mmol), **2a** (0.3 mmol, 0.6 equiv, 93.6 mg), **3** (0.6 mmol, 1.2 equiv, 58.3 mg), $K_2S_2O_8$ (1.5 mmol, 3.0 equiv, 405.5 mg) and DCE (1.0 mL) was added successively in a 15.0 mL thick-wall Schlenk tube under air atmosphere. The sealed Schlenk tube was then immersed in an oil bath at 80 °C stirring for 8 h. After completion of the reaction, 3.0 mL of water was added and the mixture was extracted three times with ethyl acetate (3 × 3.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the product **4a** was obtained by flash column chromatography on silica gel (The ratio of eluent is configured according to the TLC developing solvent).



Scheme S5. Synthesis of (*E*)-phenyl(1-phenyl-2-thiocyanatovinyl)selane

Reaction on 1 mmol Scale

A mixture of alkynes **1a** (1.0 mmol), **2a** (0.6 mmol, 0.6 equiv, 187.2 mg), **3** (1.2 mmol, 1.2 equiv, 116.6 mg), $K_2S_2O_8$ (3.0 mmol, 3.0 equiv, 811.0 mg), and DCE (1.0 mL) was added successively in a 15.0 mL thick-wall Schlenk tube under air atmosphere. The sealed Schlenk tube was then immersed in an oil bath at 80 °C stirring for 8 h. After completion of the reaction, 3.0 mL of water was added and the mixture was extracted three times with ethyl acetate (3 × 3.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the products **4a** were obtained (244.1 mg, 77%) by flash column chromatography on silica gel (The ratio of eluent is configured according to the TLC developing solvent).



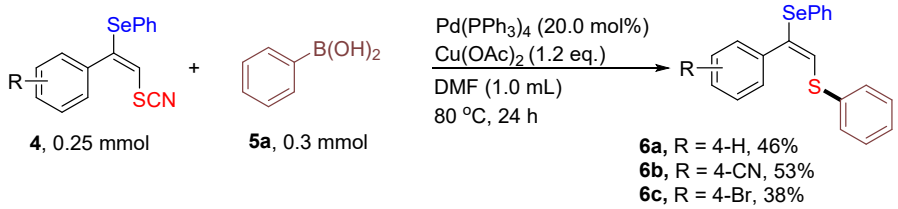
Scheme S5. Synthesis of (*E*)-phenyl(1-phenyl-2-thiocyanatovinyl)selane

Application:

Reaction on 0.25 mmol Scale [3]

To a stirred solution of phenylboronic acid (0.3 mmol, 1.2 equiv, 32.7 mg) and **4** (0.25 mmol) in DMF (1.0 mL) was added $Pd(PPh_3)_4$ (20.0 mol%) followed by $Cu(OAc)_2$ (1.2 equiv) under air atmosphere at 80 °C for 24 h. After completion of the reaction, 3.0 mL of water was added and the mixture was extracted three times with ethyl acetate (3 × 3.0 mL). The combined organic layer

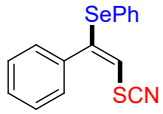
was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the product **6** was obtained by flash column chromatography on silica gel.



Scheme S6. Application of (*E*)-vinyl thiocyanates

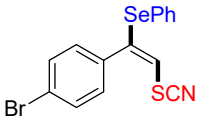
Analytic data of the obtained compounds

(1) (*E*)-phenyl(1-phenyl-2-thiocyanatovinyl)selane (**4a**)



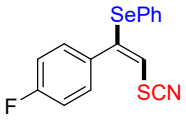
Light yellow oil (144.2 mg, 91%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.41 – 7.37 (m, 6H), 7.33 (dd, *J* = 7.7, 1.9 Hz, 2H), 5.99 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 135.9, 135.6, 129.8, 129.5, 129.3, 128.8, 128.4, 127.2, 110.8, 107.6. HRMS (ESI): Calcd. for $C_{15}H_{12}NSSe$ $[M+H]^+$: 317.9846; found: 317.9850.

(2) (*E*)-(1-(4-bromophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4b**)



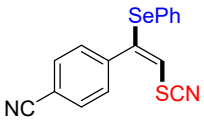
Light yellow oil (181.6 mg, 92%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dt, *J* = 6.7, 1.6 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.21 – 7.19 (m, 2H), 6.05 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 135.5, 134.7, 132.0, 130.0, 129.9, 129.5, 126.9, 123.8, 110.3, 108.5. HRMS (ESI): Calcd. for $C_{15}H_{11}BrNSSe$ $[M+H]^+$: 395.8945; found: 395.8955.

(3) (*E*)-(1-(4-fluorophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4c**)



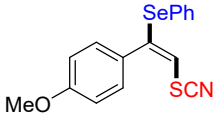
Light yellow oil (120.6 mg, 72%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.41 – 7.36 (m, 3H), 7.33 – 7.30 (m, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.03 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (d, J_{C-F} = 250.0 Hz), 142.9, 135.5, 131.8 (d, J_{C-F} = 2.5 Hz), 130.4 (d, J_{C-F} = 8.8 Hz), 129.8, 129.4, 127.1, 116.0 (d, J_{C-F} = 21.3 Hz), 110.5, 108.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.47. HRMS (ESI): Calcd. for $C_{15}H_{11}FNSSe$ $[M+H]^+$: 335.9750; found: 335.9756.

(4) (*E*)-4-(1-(phenylselanyl)-2-thiocyanatovinyl)benzonitrile (**4d**)



Light yellow oil (159.0 mg, 93%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.53 (dt, *J* = 6.9, 1.5 Hz, 2H), 7.43 – 7.39 (m, 3H), 7.35 (dd, *J* = 8.2, 6.6 Hz, 2H), 6.20 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 140.6, 135.6, 132.5, 120.0, 129.7, 129.2, 126.5, 118.0, 113.2, 110.0, 109.7. HRMS (ESI): Calcd. for $C_{16}H_{11}N_2SSe$ $[M+H]^+$: 342.9800; found: 342.9803.

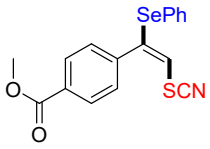
(5) (*E*)-(1-(4-methoxyphenyl)-2-thiocyanatovinyl)(phenyl)selane (**4e**)



Brown oil (161.4 mg, 93%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.28 (dd, *J* = 9.1, 5.7 Hz,

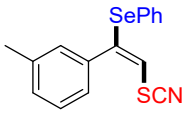
3H), 7.22 – 7.19 (m, 2H), 6.84 – 6.81 (m, 2H), 5.87 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 143.6, 135.4, 129.9, 129.8, 129.1, 127.9, 127.6, 114.1, 110.9, 106.9, 55.3. HRMS (ESI): Calcd. for $C_{16}H_{14}NOSSe$ $[M+H]^+$: 347.9950; found: 347.9956.

(6) methyl (*E*)-4-(1-(phenylselanyl)-2-thiocyanatovinyl)benzoate (**4f**)



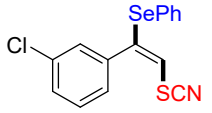
White solid (178.1 mg, 95%, mp: 105-108 °C). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.54 (m, 2H), 7.40 – 7.34 (m, 5H), 6.13 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 142.6, 140.4, 135.5, 130.9, 130.0, 129.9, 129.5, 128.5, 126.8, 110.2, 109.2, 52.3. HRMS (ESI): Calcd. for $C_{17}H_{14}NO_2SSe$ $[M+H]^+$: 375.9907; found: 375.9905.

(7) (*E*)-2-bromo-1-(4-(trifluoromethyl)phenyl)vinyl trifluoromethanesulfonat (**4g**)



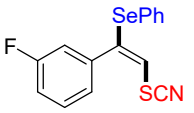
Light yellow oil (155.6 mg, 94%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.41 – 7.37 (m, 3H), 7.29 (s, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 9.9 Hz, 2H), 5.90 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 138.7, 135.8, 135.7, 130.3, 129.9, 129.4, 128.8, 128.7, 127.3, 125.4, 111.0, 107.0, 21.4. HRMS (ESI): Calcd. for $C_{16}H_{14}NSSe$ $[M+H]^+$: 332.0000; found: 332.0007.

(8) (*E*)-(1-(3-chlorophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4h**)



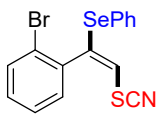
Light yellow oil (143.9 mg, 82%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dt, *J* = 6.7, 1.6 Hz, 2H), 7.39 (dd, *J* = 12.1, 7.3 Hz, 3H), 7.33 (dd, *J* = 5.9, 2.3 Hz, 3H), 7.19 (dt, *J* = 6.8, 1.8 Hz, 1H), 6.04 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 137.5, 135.6, 134.7, 130.1, 129.9, 129.6, 129.5, 128.4, 126.8, 126.5, 110.3, 108.7. HRMS (ESI): Calcd. for $C_{15}H_{11}ClNSSe$ $[M+H]^+$: 351.9453; found: 351.9460.

(9) (*E*)-(1-(3-fluorophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4i**)



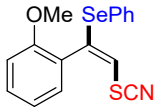
Light yellow oil (77.0 mg, 46%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dt, *J* = 6.7, 1.6 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.07 (ddd, *J* = 17.2, 8.2, 1.3 Hz, 3H), 6.07 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$)) δ 162.6 (d, J_{C-F} = 247.5 Hz), 142.0, 137.9 (d, J_{C-F} = 7.5 Hz), 135.6, 130.5 (d, J_{C-F} = 8.8 Hz), 129.9, 129.5, 126.9, 124.2 (d, J_{C-F} = 3.8 Hz), 116.5 (d, J_{C-F} = 21.3 Hz), 115.5 (d, J_{C-F} = 22.5 Hz), 110.3, 108.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.27. HRMS (ESI): Calcd. for $C_{15}H_{11}FNSSe$ $[M+H]^+$: 335.9751; found: 335.9756.

(10) (*E*)-(1-(2-bromophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4j**)



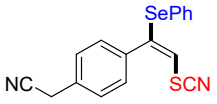
Light yellow oil (77.0 mg, 39%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 3H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 15.0 Hz, 1H), 7.20 – 7.17 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.01 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 136.4, 136.4, 133.3, 130.6, 130.0, 129.8, 129.7, 127.7, 126.4, 122.3, 110.3, 109.7. HRMS (ESI): Calcd. for $C_{15}H_{11}BrNSSe$ $[M+H]^+$: 395.8950; found: 395.8955.

(11) (*E*)-(1-(2-methoxyphenyl)-2-thiocyanatovinyl)(phenyl)selane (**4k**)



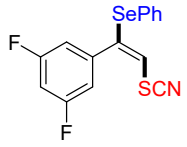
Light yellow oil (140.5 mg, 81%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.22 (d, *J* = 7.3 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 2H), 6.78 (s, 1H), 5.89 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 143.2, 137.1, 135.6, 129.9, 129.8, 129.3, 127.3, 120.6, 115.4, 113.6, 110.8, 107.8, 55.3. HRMS (ESI): Calcd. for $C_{16}H_{14}NOSSe$ $[M+H]^+$: 347.9952; found: 347.9956.

(12) (*E*)-2-(4-(1-(phenylselanyl)-2-thiocyanatovinyl)phenyl)acetonitrile (**4l**)



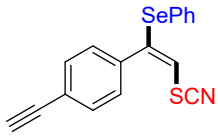
Light yellow oil (133.5 mg, 75%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.40 – 7.37 (m, 2H), 7.36 (d, *J* = 3.6 Hz, 5H), 6.05 (s, 1H), 3.78 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 135.9, 135.5, 131.3, 129.9, 129.4, 129.2, 128.4, 127.0, 117.2, 110.4, 108.3, 23.4. HRMS (ESI): Calcd. for $C_{17}H_{13}N_2SSe$ $[M+H]^+$: 356.9952; found: 356.9959.

(13) (*E*)-(1-(3,5-difluorophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4m)**



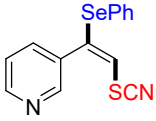
Light yellow oil (98.8 mg, 56%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.42 – 7.36 (m, 3H), 6.87 – 6.80 (m, 3H), 6.11 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 (d, $J_{C\text{-}F}$ = 12.5 Hz), 161.9 (d, $J_{C\text{-}F}$ = 12.5 Hz), 140.7 (t, $J_{C\text{-}F}$ = 2.5 Hz), 138.9 (t, $J_{C\text{-}F}$ = 10.0 Hz), 135.6, 130.0, 129.6, 126.5, 111.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 111.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 109.9, 109.9, 105.0 (t, $J_{C\text{-}F}$ = 25.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.65. HRMS (ESI): Calcd. for $C_{15}H_{10}F_2NSSe$ $[M+H]^+$: 353.9655; found: 353.9662.

(14) (*E*)-(1-(4-ethynylphenyl)-2-thiocyanatovinyl)(phenyl)selane (**4n**)



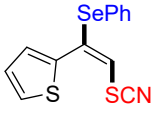
Light yellow oil (59.7 mg, 35%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.44 – 7.41 (m, 2H), 7.30 (td, *J* = 6.3, 5.6, 4.7 Hz, 3H), 7.23 – 7.21 (m, 2H), 6.00 (s, 1H), 3.10 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 136.2, 135.5, 132.5, 129.8, 129.4, 128.4, 127.0, 123.3, 110.4, 108.6, 82.7, 78.8. HRMS (ESI): Calcd. for $C_{17}H_{12}NSSe$ $[M+H]^+$: 341.9839; found: 341.9850.

(15) (*E*)-3-(1-(phenylselanyl)-2-thiocyanatovinyl)pyridine (**4o**)



Light yellow oil (147.9 mg, 93%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 20.1 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 6.7 Hz, 2H), 7.40 – 7.34 (m, 4H), 6.20 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 148.9, 140.7, 136.1, 135.6, 132.2, 130.0, 129.9, 129.6, 126.6, 123.5, 109.9. HRMS (ESI): Calcd. for $C_{14}H_{11}N_2SSe$[M+H]$^+$: 318.9799; found: 318.9803.

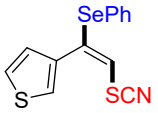
(16) (*E*)-2-(1-(phenylselanyl)-2-thiocyanatovinyl)thiophene (**4p**)



Brown oil (148.5 mg, 92%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.55 (dd, *J* = 5.0, 1.2 Hz,

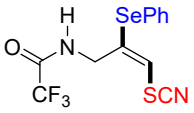
1H), 7.45 (d, J = 5.9 Hz, 3H), 7.32 (d, J = 3.7 Hz, 1H), 7.16 – 7.14 (m, 1H), 6.32 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 134.4, 132.9, 129.8, 129.6, 129.0, 128.8, 128.4, 127.6, 110.5, 110.3. HRMS (ESI): Calcd. for $C_{13}H_{10}NS_2Se$ $[M+H]^+$: 323.9409; found: 323.9414.

(17) (*E*)-3-(1-(phenylselanyl)-2-thiocyanatovinyl)thiophene (**4q**)



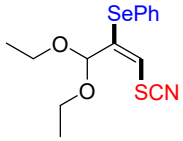
Light yellow oil (145.3 mg, 90%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.40 – 7.35 (m, 5H), 7.18 (dd, J = 5.0, 1.4 Hz, 1H), 6.02 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.0, 136.1, 135.1, 129.8, 129.2, 127.6, 127.4, 126.7, 126.3, 110.7, 108.2. HRMS (ESI): Calcd. for $C_{13}H_{10}NS_2Se$ $[M+H]^+$: 323.9410; found: 323.9414.

(18) (*E*)-2,2,2-trifluoro-N-(2-(phenylselanyl)-3-thiocyanatoallyl)acetamide (**4r**)



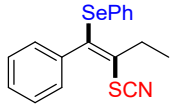
Light yellow oil (144.6 mg, 79%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dt, J = 6.7, 1.6 Hz, 2H), 7.46 – 7.40 (m, 3H), 6.70 (s, 1H), 6.28 (s, 1H), 4.30 (d, J = 5.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3 (q, $J_{C\text{-}F}$ = 37.5 Hz), 140.0, 135.1, 130.2, 129.7, 125.7, 115.4 (q, $J_{C\text{-}F}$ = 285.0 Hz), 113.8, 109.6, 41.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.70. HRMS (ESI): Calcd. for $C_{12}H_{10}F_3N_2OSSe$ $[M+H]^+$: 366.9621; found: 366.9626.

(19) (*E*)-(3,3-diethoxy-1-thiocyanatoprop-1-en-2-yl)(phenyl)selane (**4s**)



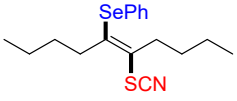
Light yellow oil (42.9 mg, 25%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.45 – 7.38 (m, 3H), 5.80 (s, 1H), 5.21 (s, 1H), 3.70 – 3.63 (m, 2H), 3.62 – 3.55 (m, 2H), 1.26 (t, J = 7.1 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 137.6, 135.8, 129.9, 129.3, 126.6, 112.2, 100.3, 61.9, 15.0. HRMS (ESI): Calcd. for $C_{14}H_{18}NO_2SSe$ $[M+H]^+$: 344.0207; found: 344.0218.

(20) (*E*)-phenyl(1-phenyl-2-thiocyanatobut-1-en-1-yl)selane (**4t**)



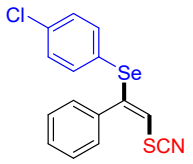
Light yellow oil (163.9 mg, 95%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.1, 1.4 Hz, 2H), 7.22 – 7.18 (m, 4H), 7.13 (t, J = 7.6 Hz, 2H), 7.01 (dd, J = 7.2, 2.4 Hz, 2H), 3.08 (q, J = 7.4 Hz, 2H), 1.43 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.3, 135.4, 129.0, 128.8, 128.3, 128.2, 128.1, 128.0, 126.3, 110.5, 30.6, 13.0. HRMS (ESI): Calcd. for $C_{17}H_{16}NSSe$ $[M+H]^+$: 346.0158; found: 346.0163.

(21) (*E*)-phenyl(6-thiocyanatodec-5-en-5-yl)selane (**4u**)



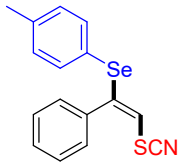
Light yellow oil (158.9 mg, 90%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, J = 7.9, 1.8 Hz, 2H), 7.29 (d, J = 7.1 Hz, 3H), 2.84 – 2.79 (m, 2H), 2.37 – 2.31 (m, 2H), 1.60 (t, J = 7.7 Hz, 2H), 1.41 – 1.34 (m, 4H), 1.18 – 1.10 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H), 0.77 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 134.5, 129.3, 128.4, 128.3, 123.3, 110.4, 37.2, 35.7, 30.8, 30.3, 22.0, 22.0, 13.9, 13.7. HRMS (ESI): Calcd. for $C_{17}H_{24}NSSe$ $[M+H]^+$: 354.0781; found: 354.0789.

(22) (*E*)-(4-chlorophenyl)(1-phenyl-2-thiocyanatovinyl)selane (**4v**)



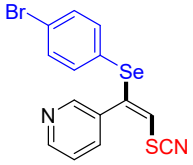
Light yellow oil (66.7 mg, 38%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.40 – 7.38 (m, 3H), 7.31 (dd, *J* = 8.2, 1.7 Hz, 4H), 6.12 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 136.7, 135.7, 135.5, 130.0, 129.7, 128.9, 128.4, 125.5, 110.6, 109.0. HRMS (ESI): Calcd. for $C_{15}H_{11}ClNSSe$ $[M+H]^+$: 351.9452; found: 351.9460.

(23) (*E*)-(1-phenyl-2-thiocyanatovinyl)(p-tolyl)selane (**4w**)



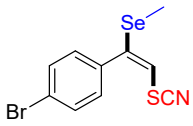
Light yellow oil (153.9 mg, 93%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.1 Hz, 3H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 5.83 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 139.8, 136.0, 135.9, 130.8, 129.5, 128.8, 128.3, 123.4, 111.0, 106.0, 21.3. HRMS (ESI): Calcd. for $C_{16}H_{14}NSSe$ $[M+H]^+$: 332.0001; found: 332.0007.

(24) (*E*)-3-(1-((4-bromophenyl)selanyl)-2-thiocyanatovinyl)pyridine (**4x**)



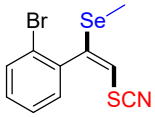
Light yellow oil (51.5 mg, 26%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.55 – 8.48 (m, 1H), 7.75 (dt, *J* = 8.1, 1.9 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.24 (dd, *J* = 8.1, 4.8 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.03 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 148.2, 135.0, 134.1, 133.8, 133.7, 132.8, 126.4, 125.2, 123.4, 122.8, 110.0. HRMS (ESI): Calcd. for $C_{14}H_{10}BrN_2SSe$ $[M+H]^+$: 396.8901; found: 396.8908.

(25) (*E*)-(1-(4-bromophenyl)-2-thiocyanatovinyl)(methyl)selane (**4y**)



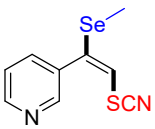
Yellow solid (136.5 mg, 82%, mp: 115-117 °C). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.21 – 7.19 (m, 2H), 6.13 (s, 1H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 135.0, 132.2, 129.9, 123.8, 110.6, 105.2, 7.9. HRMS (ESI): Calcd. for $C_{10}H_9BrNSSe$ $[M+H]^+$: 333.8794; found: 333.8799.

(26) (*E*)-(1-(2-bromophenyl)-2-thiocyanatovinyl)(methyl)selane (**4z**)



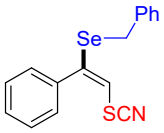
Light yellow oil (111.5 mg, 67%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.27 (ddd, *J* = 18.7, 7.6, 1.7 Hz, 2H), 6.22 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 136.7, 133.3, 130.7, 130.0, 127.9, 122.2, 110.4, 107.5, 7.5. HRMS (ESI): Calcd. for $C_{10}H_9BrNSSe$ $[M+H]^+$: 333.8792; found: 333.8799.

(27) (*E*)-3-(1-(methylselanyl)-2-thiocyanatovinyl)pyridine (**4aa**)



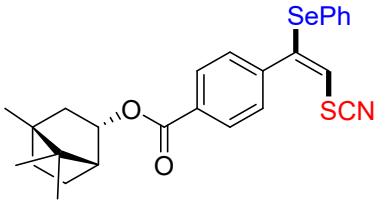
Light yellow oil (34.6 mg, 27%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.57 (s, 1H), 7.68 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.40 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.21 (s, 1H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 148.8, 140.9, 136.0, 132.4, 123.6, 110.2, 106.3, 8.0. HRMS (ESI): Calcd. for $C_9H_9N_2SSe$ $[M+H]^+$: 256.9641; found: 256.9646.

(28) (*E*)-benzyl(1-phenyl-2-thiocyanatovinyl)selane (**4ab**)



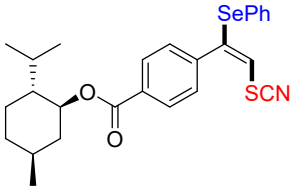
Light yellow oil (41.4 mg, 25%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.45 – 7.39 (m, 3H), 7.38 – 7.34 (m, 2H), 7.34 – 7.29 (m, 3H), 7.28 (s, 1H), 4.05 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 135.9, 130.7, 129.5, 129.0, 128.9, 128.8, 128.5, 127.5, 119.7, 110.4, 31.5. HRMS (ESI): Calcd. for $C_{16}H_{14}NSSe$ $[M+H]^+$: 332.0002; found: 332.0007.

(29) (1*R*,2*S*,4*R*)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((*E*)-1-(phenylselanyl)-2-thiocyanatovinyl)benzoate (**4ac**)



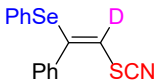
Light yellow oil (161.6 mg, 65%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 2H), 7.57 (dd, *J* = 6.6, 1.7 Hz, 2H), 7.42 – 7.36 (m, 5H), 6.11 (s, 1H), 5.13 (d, *J* = 8.6 Hz, 1H), 2.49 (d, *J* = 4.0 Hz, 1H), 2.12 (t, *J* = 9.0 Hz, 1H), 1.84 – 1.75 (m, 2H), 1.43 (s, 1H), 1.35 (s, 1H), 1.12 (s, 1H), 0.98 (s, 3H), 0.93 (d, *J* = 3.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 142.7, 140.2, 135.5, 131.7, 129.9, 129.9, 129.5, 128.4, 126.9, 110.3, 109.1, 81.0, 49.1, 47.9, 44.9, 36.8, 28.0, 27.3, 19.7, 18.9, 13.6. HRMS (ESI): Calcd. for $C_{26}H_{28}NO_2SSe$ $[M+H]^+$: 498.0994; found: 498.1000.

(30) (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-1-(phenylselanyl)-2-thiocyanatovinyl) benzoate (**4ad**)



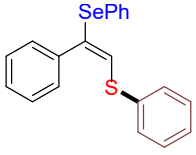
Light yellow oil (132.3 mg, 53%). TLC (petroleum ether/EtOAc = 10:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 6.5 Hz, 2H), 7.39 (dd, *J* = 11.4, 7.9 Hz, 5H), 6.09 (s, 1H), 4.96 (d, *J* = 4.4 Hz, 1H), 2.13 (dd, *J* = 12.0, 3.1 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.76 (d, *J* = 11.9 Hz, 2H), 1.57 (s, 2H), 1.12 (d, *J* = 11.5 Hz, 2H), 0.95 (dd, *J* = 6.8, 3.3 Hz, 7H), 0.82 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 142.7, 140.2, 135.5, 131.6, 130.0, 129.9, 129.5, 128.4, 126.9, 110.3, 109.0, 75.2, 47.2, 40.9, 34.2, 31.4, 26.4, 23.5, 22.0, 20.8, 16.4. HRMS (ESI): Calcd. for $C_{26}H_{30}NO_2SSe$ $[M+H]^+$: 500.1148; found: 500.1157.

(31) (*E*)-phenyl(1-phenyl-2-thiocyanatovinyl-2-d)selane (**4a-D**)



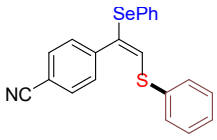
Light yellow oil (111.3 mg, 70%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.42 – 7.36 (m, 6H), 7.34 – 7.32 (m, 2H), 5.98 (s, 0.3H). ^{2}H NMR (77 MHz, DCM) δ 5.98 (s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 135.9, 135.6, 129.8, 129.5, 129.3, 128.8, 128.4, 127.2, 110.8, 107.5.

(32) (*E*)-phenyl(2-phenyl-2-(phenylselanyl)vinyl)sulfane (**6a**) [4]



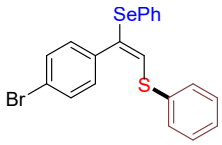
Light yellow oil (42.3 mg, 46%). TLC (petroleum ether/EtOAc = 40:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 20.7, 6.9 Hz, 4H), 7.32 (dd, *J* = 11.9, 7.4 Hz, 6H), 7.27 – 7.22 (m, 5H), 6.88 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 135.8, 132.9, 130.6, 129.7, 129.3, 129.2, 129.2, 129.1, 129.0, 128.2, 128.1, 127.4, 126.9.

(33) (*E*)-4-(1-(phenylselanyl)-2-(phenylthio)vinyl)benzonitrile (**6b**) [4]



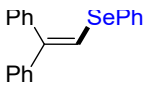
Orange oil (52.1 mg, 53%). TLC (petroleum ether/EtOAc = 30:1), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 4H), 7.44 (s, 3H), 7.36 (d, *J* = 6.4 Hz, 4H), 7.25 – 7.23 (m, 3H), 7.13 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 134.6, 133.3, 132.7, 132.0, 130.0, 129.9, 129.8, 129.3, 129.3, 127.7, 127.6, 126.6, 118.7, 111.3.

(34) (*E*)-(2-(4-bromophenyl)-2-(phenylselanyl)vinyl)(phenyl)sulfane (**6c**) [4]



Light yellow oil (42.4 mg, 38%). TLC (petroleum ether), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.56 (s, 1H), 7.43 (s, 2H), 7.41 – 7.35 (m, 6H), 7.26 (s, 1H), 7.23 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 136.5, 133.9, 133.4, 131.5, 131.1, 130.5, 129.5, 129.0, 128.4, 128.2, 128.1, 126.3, 121.5.

(35) (2,2-diphenylvinyl)(phenyl)selane (**8'**)

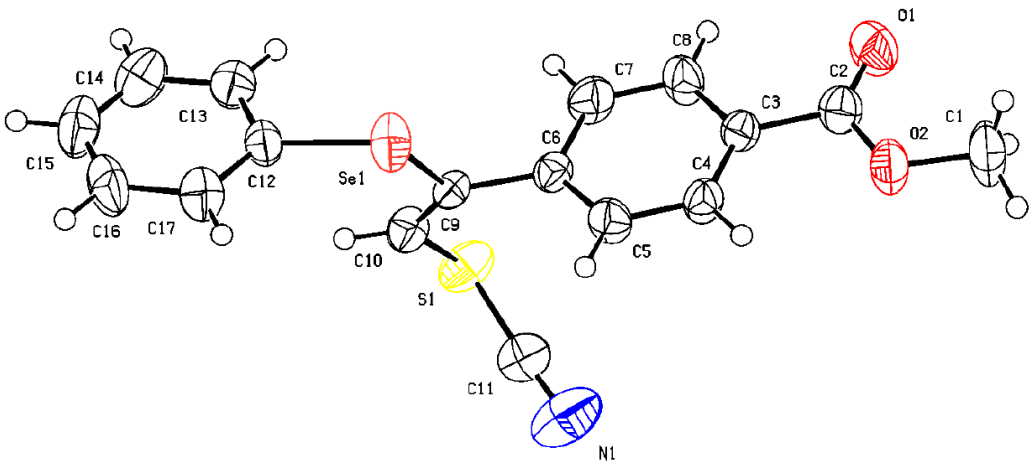


Light yellow oil (64.7 mg, 77%). TLC (petroleum ether), R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 3H), 7.37 (dd, *J* = 16.3, 6.4 Hz, 8H), 7.25 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 141.5, 140.3, 132.4, 131.5, 129.3, 129.2, 128.5, 128.2, 127.9, 127.3, 127.2, 127.1, 122.5.

Crystal data of 4f

Crystallographic data of compound 4f

Experimental: Single crystals of $C_{17}H_{13}NO_2SSe$ (**4f**) were generation in the mixed solution of dichloromethane and n-hexane (1:1). X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 296 K, using the ω - and φ - scans to a maximum θ value of 25.025 °. The data were refined by full-matrix least-squares techniques on F2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. X-ray crystallographic structures for **4f** ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 2341428.



Scheme S7 X-ray crystallographic structures of **4f** with thermal ellipsoids at 50% probability.

Table S1 Crystal data and structure refinement for **4f**

Identification code	**4f**
Empirical formula	$C_{17}H_{13}NO_2SSe$
Formula weight	374.30
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 5.852 Å a= 90°. b = 19.044 Å b= 101.05°. c = 14.544 Å g = 90°.
Volume	1590.7 $Å^3$
Z	4
Density (calculated)	1.563 Mg/m^3
Absorption coefficient	2.497 mm^{-1}
F(000)	752.0
Crystal size	0.22x 0.2 x 0.18 mm^3
Radiation	MoK^{α} (λ = 0.71073)
2^{Θ}range for data collection	4.278 to 50.128°
Index ranges	-6<=h<=6, -22<=k<=22, 0<=l<=17
Reflections collected	5133
Independent reflections	2799 [Rint = 0.0567, Rsigma = 0.0895]
Data / restraints / parameters	2799 / 0 / 200
Goodness-of-fit on F^2	0.989
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.0865
Final R indices (all data)	R1 = 0.0935, wR2 = 0.1214
Largest diff. peak and hole	0.29 and -0.33 e.$Å^{-3}$

NMR spectra of the obtained compounds

Figure S1. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-phenyl(1-phenyl-2-thiocyanatovinyl)selane (**4a**) in $CDCl_3$.

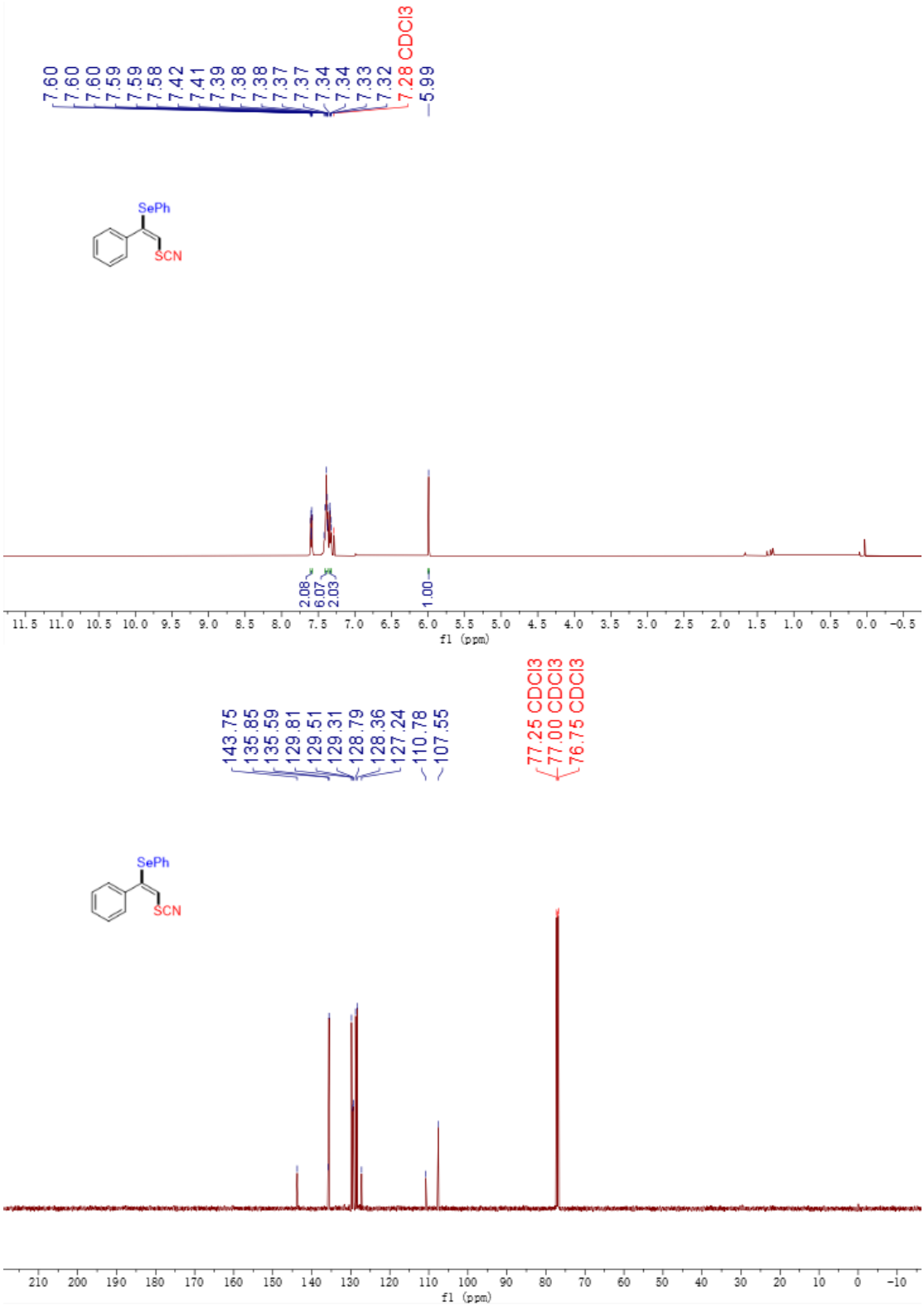


Figure S2. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(1-(4-bromophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4b**) in $CDCl_3$.

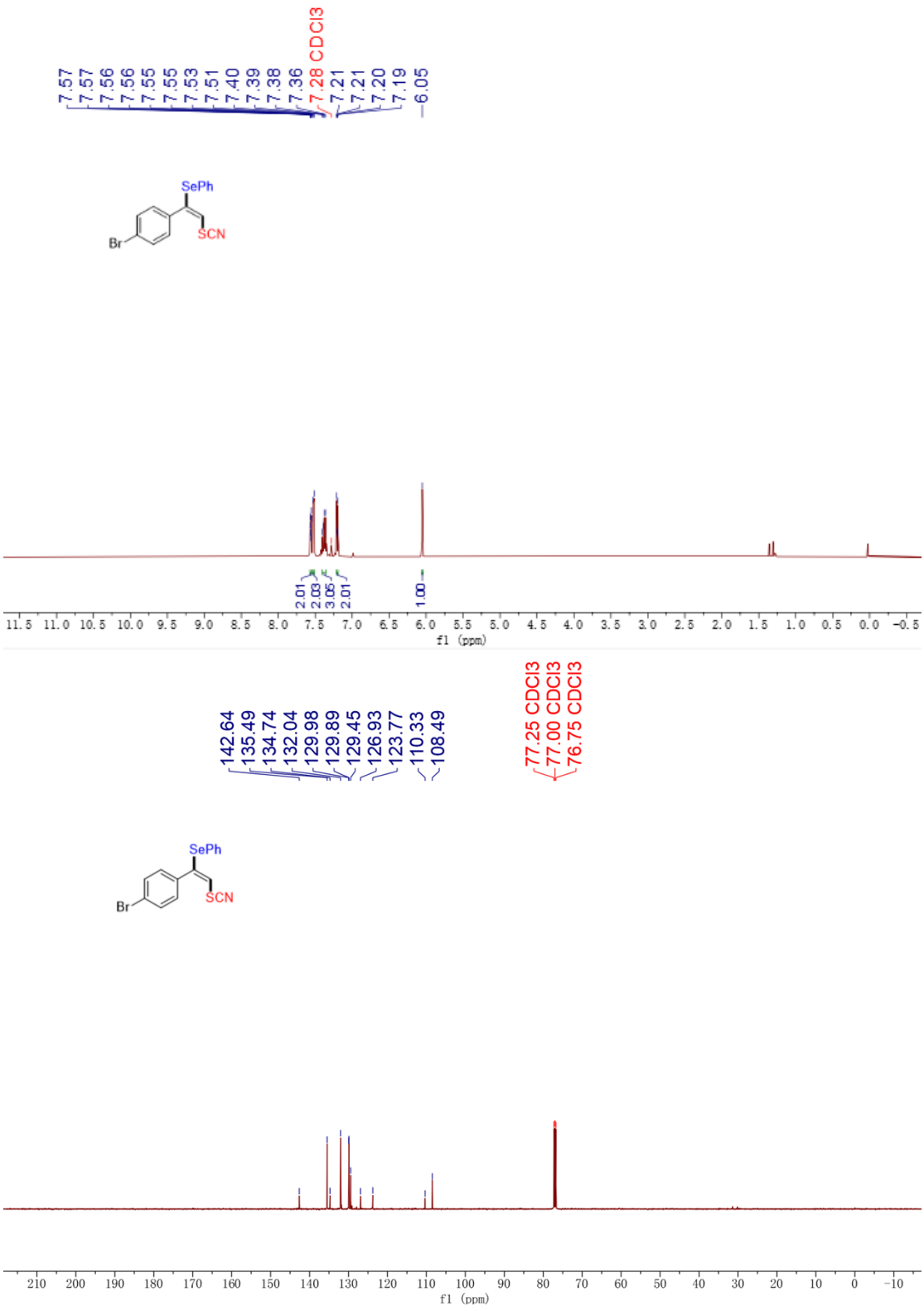
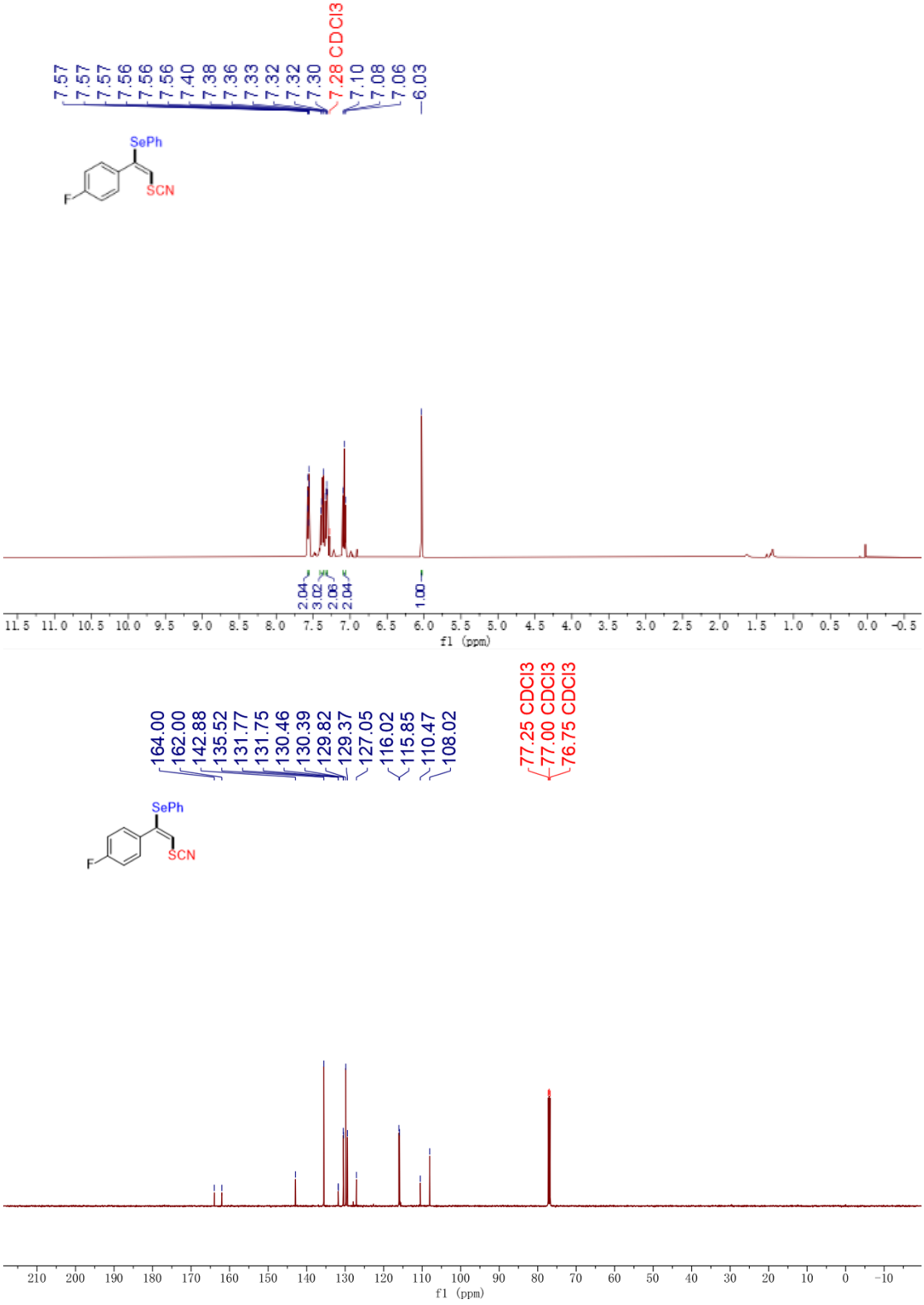


Figure S3. The ^{1}H (500 MHz), ^{13}C (125 MHz) and ^{19}F (471 MHz) NMR spectrum for (*E*)-(1-(4-fluorophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4c**) in $CDCl_3$.



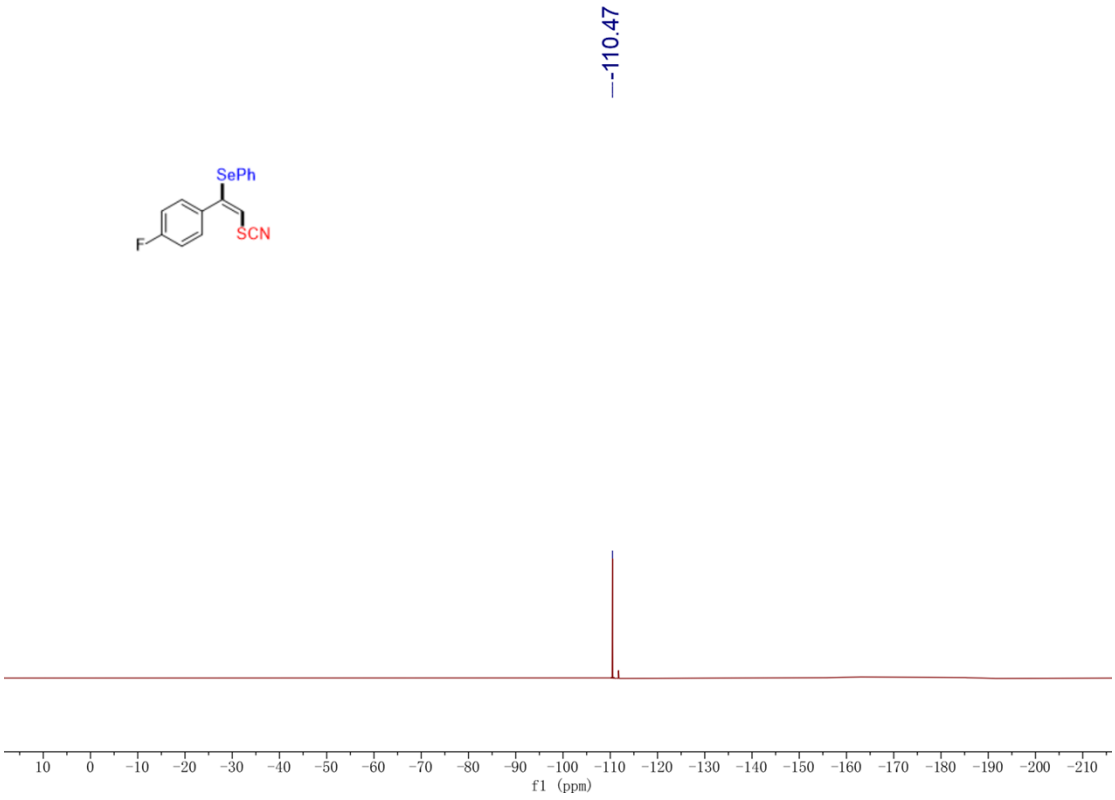
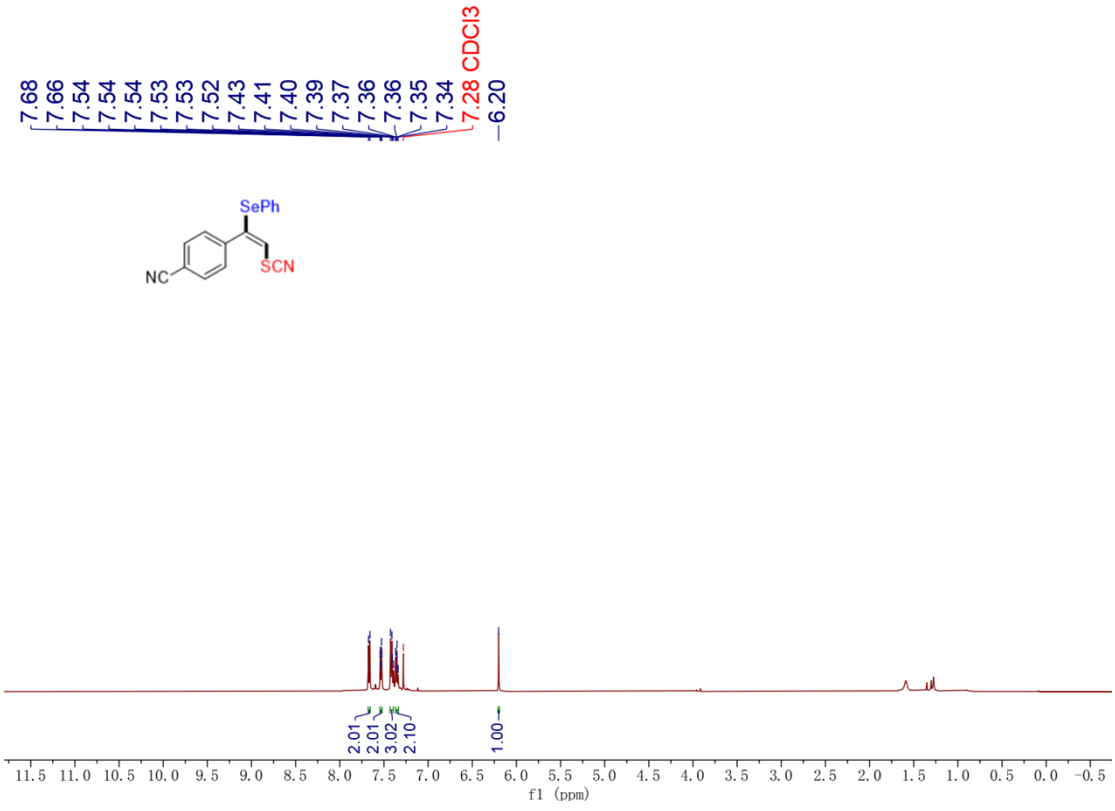


Figure S4. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-4-(1-(phenylselanyl)-2-thiocyanatovinyl)benzonitrile (**4d**) in $CDCl_3$.



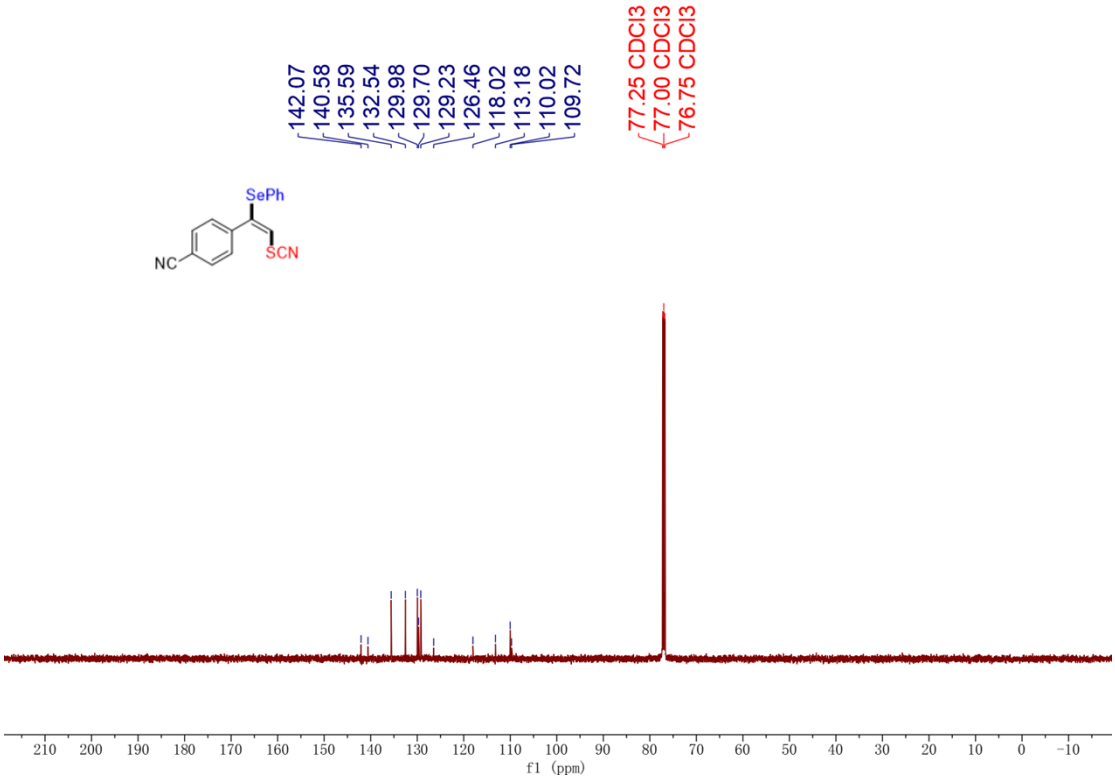
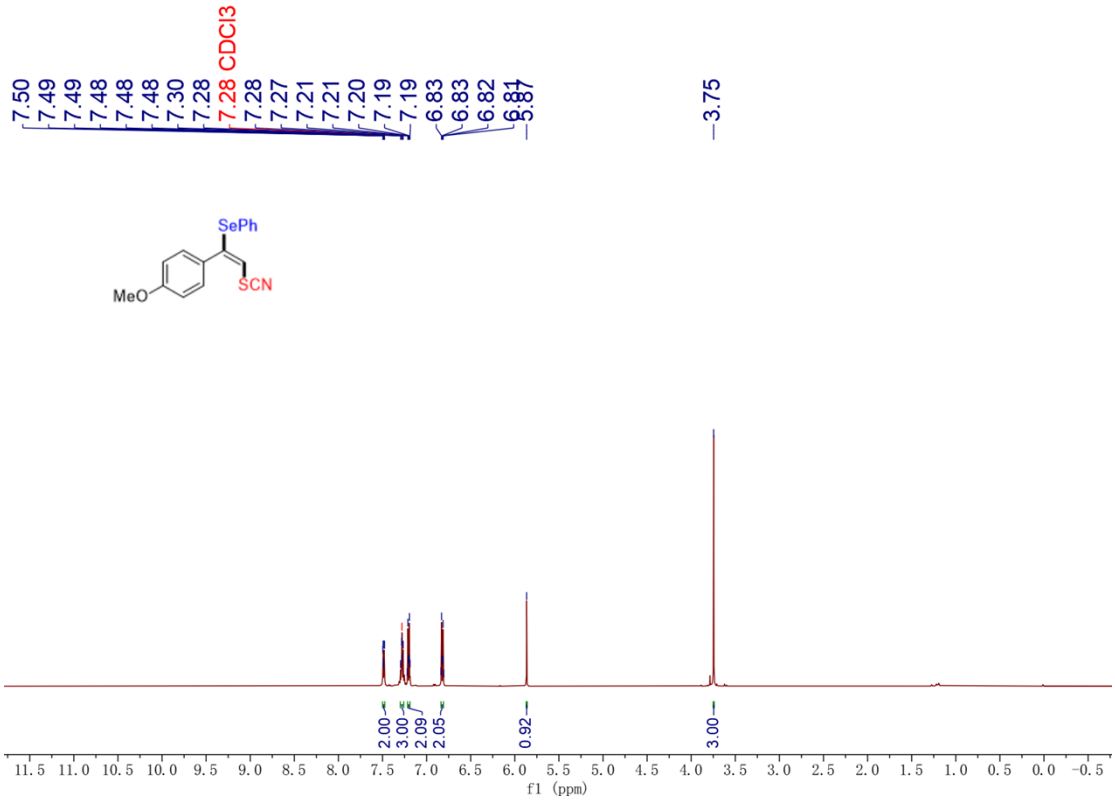


Figure S5. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(1-(4-methoxyphenyl)-2-thiocyanatovinyl)(phenyl)selane (**4e**) in $CDCl_3$.



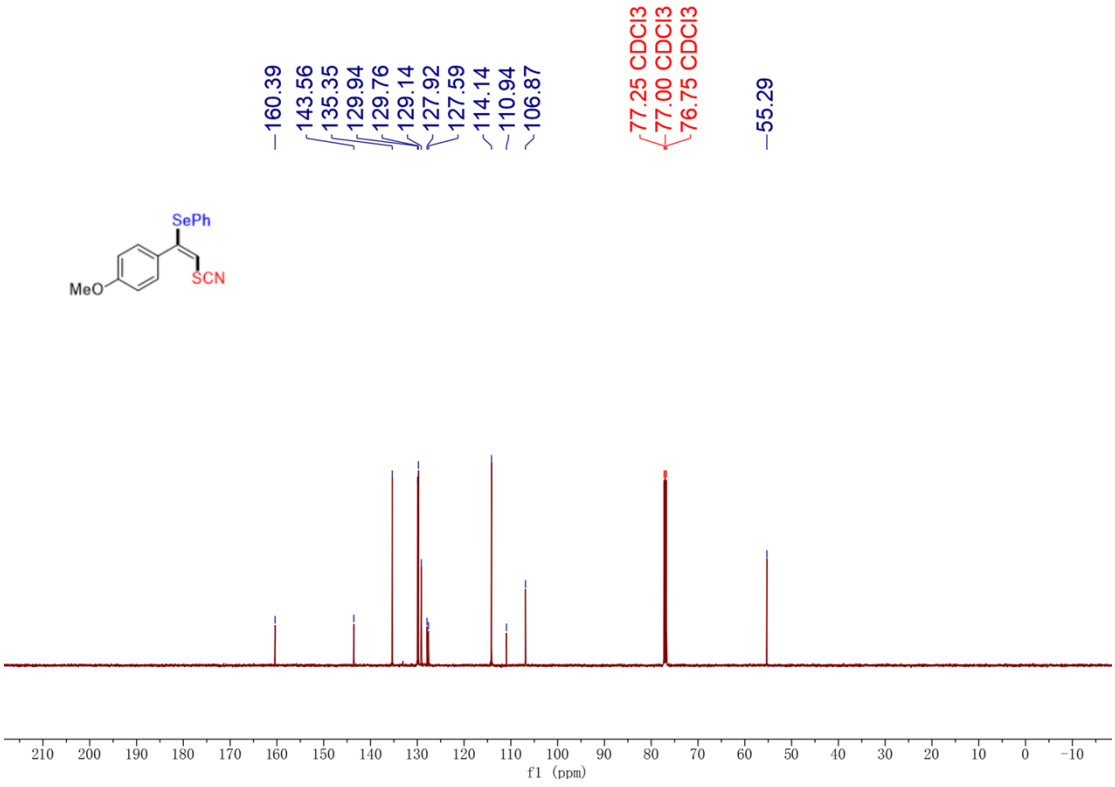
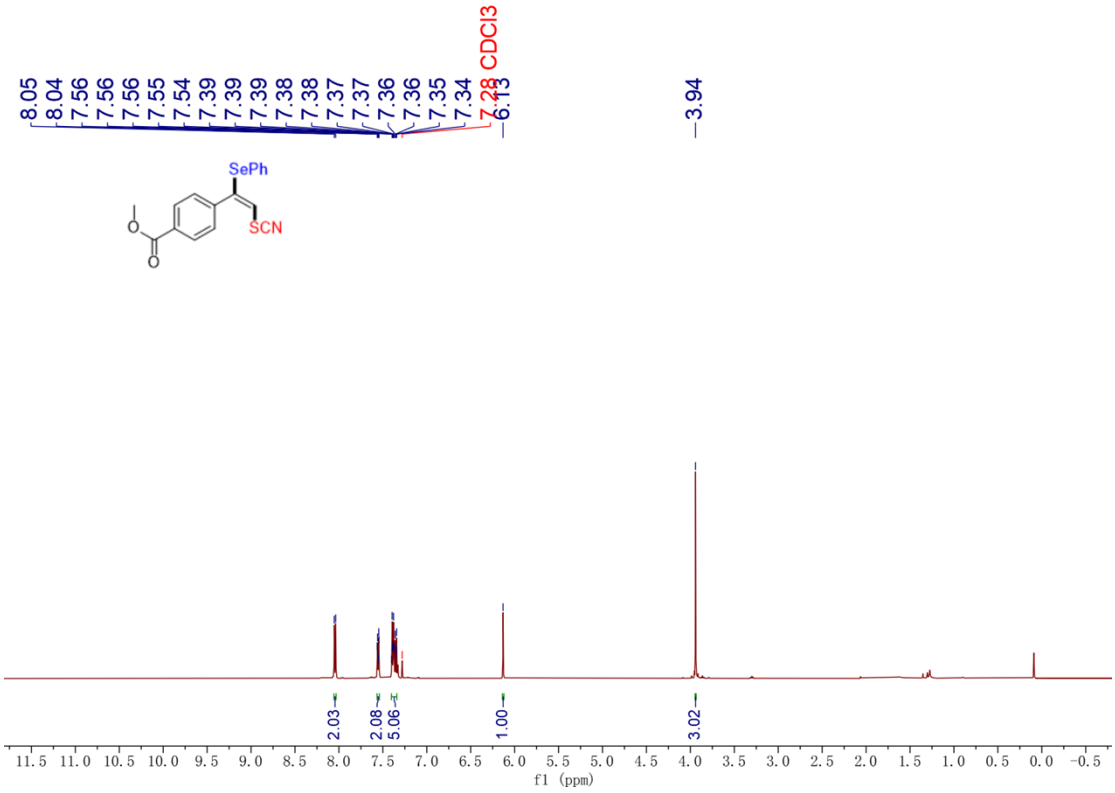


Figure S6. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for methyl (*E*)-4-(1-(phenylselanyl)-2-thiocyanatovinyl)benzoate (**4f**) in $CDCl_3$.



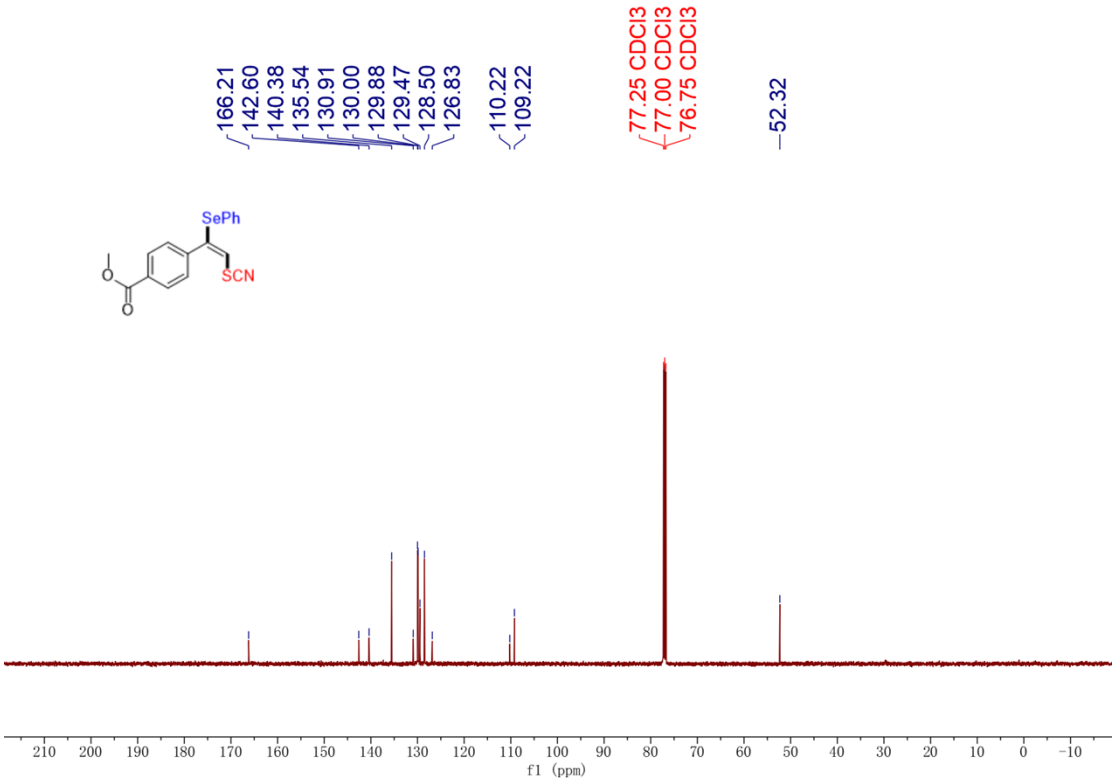
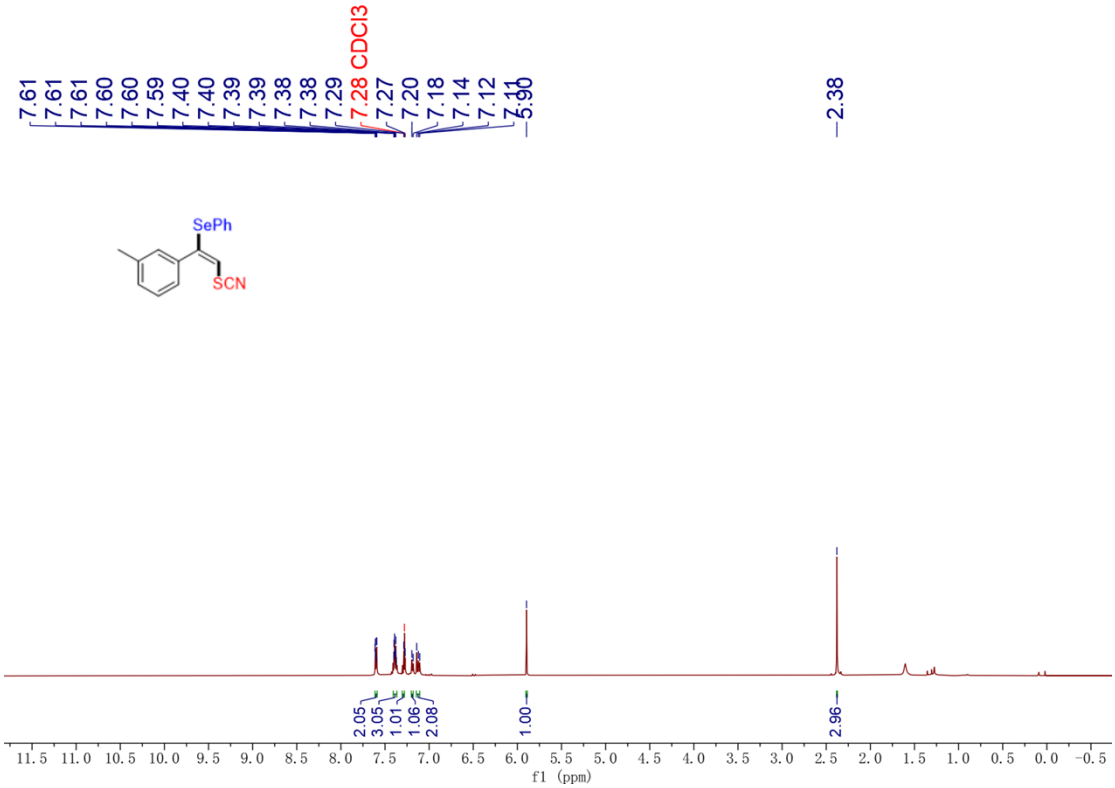


Figure S7. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-2-bromo-1-(4-(trifluoromethyl)phenyl)vinyl trifluoromethanesulfonat (**4g**) in $CDCl_3$.



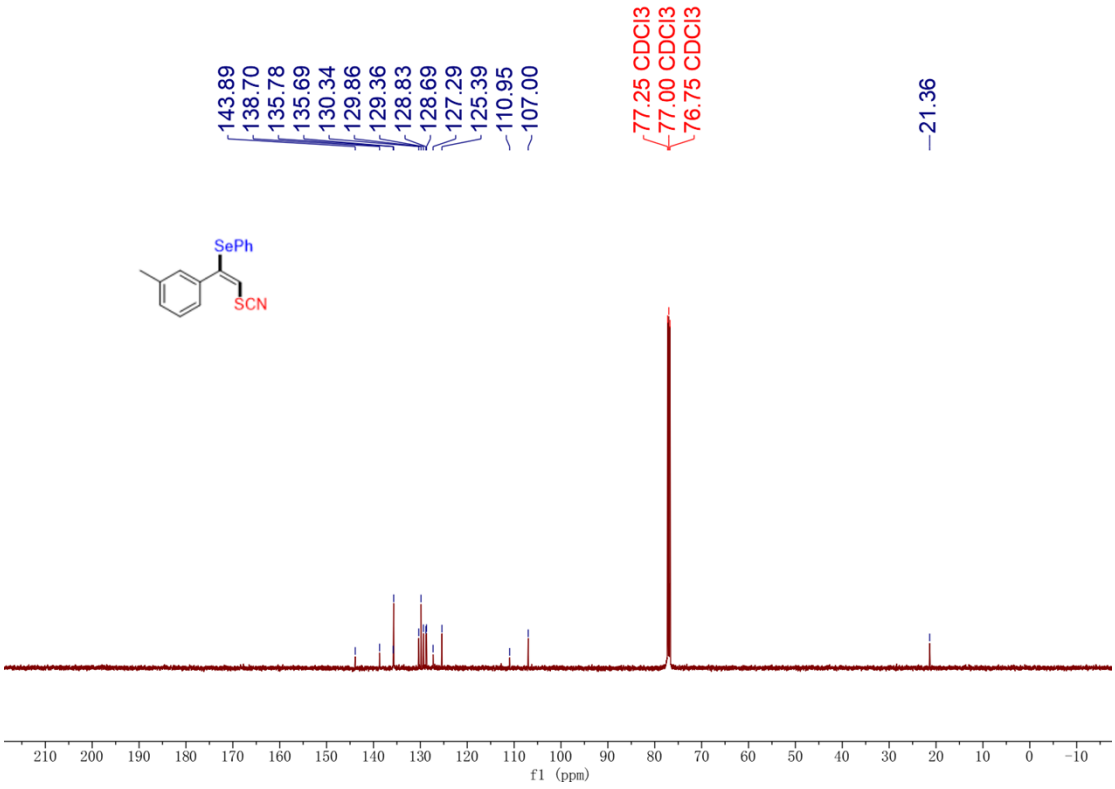
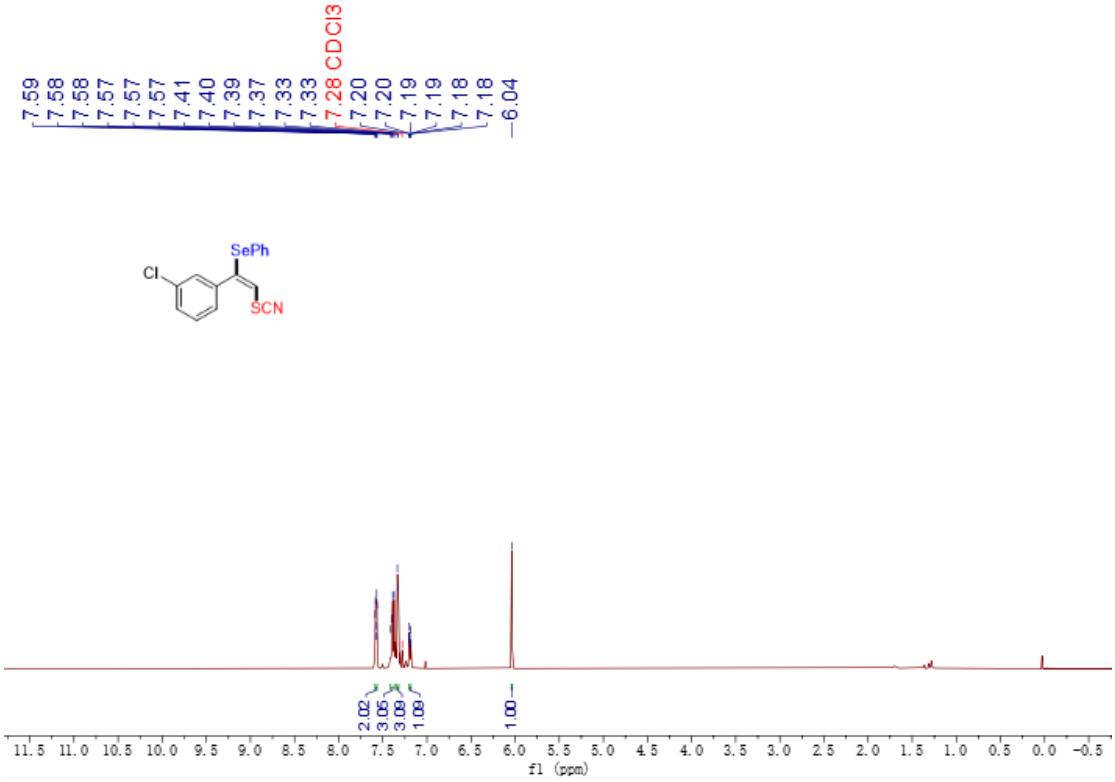


Figure S8. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(1-(3-chlorophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4h**) in $CDCl_3$.



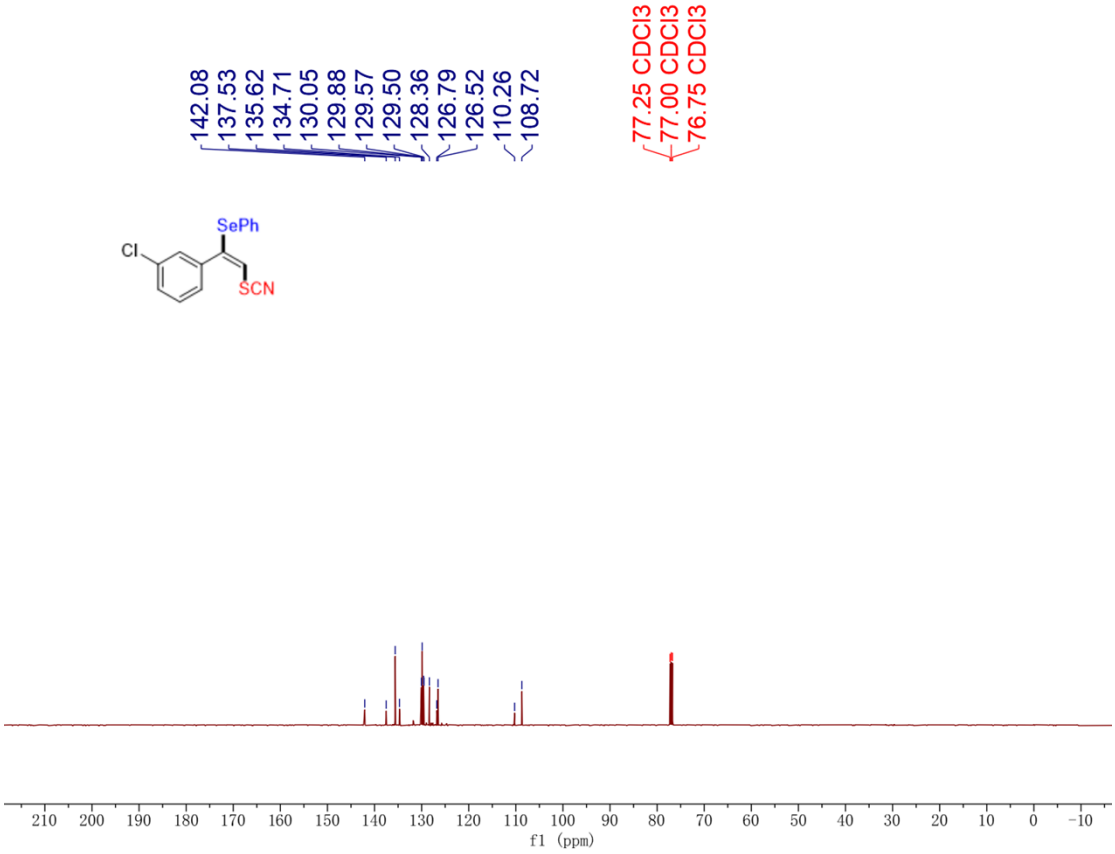
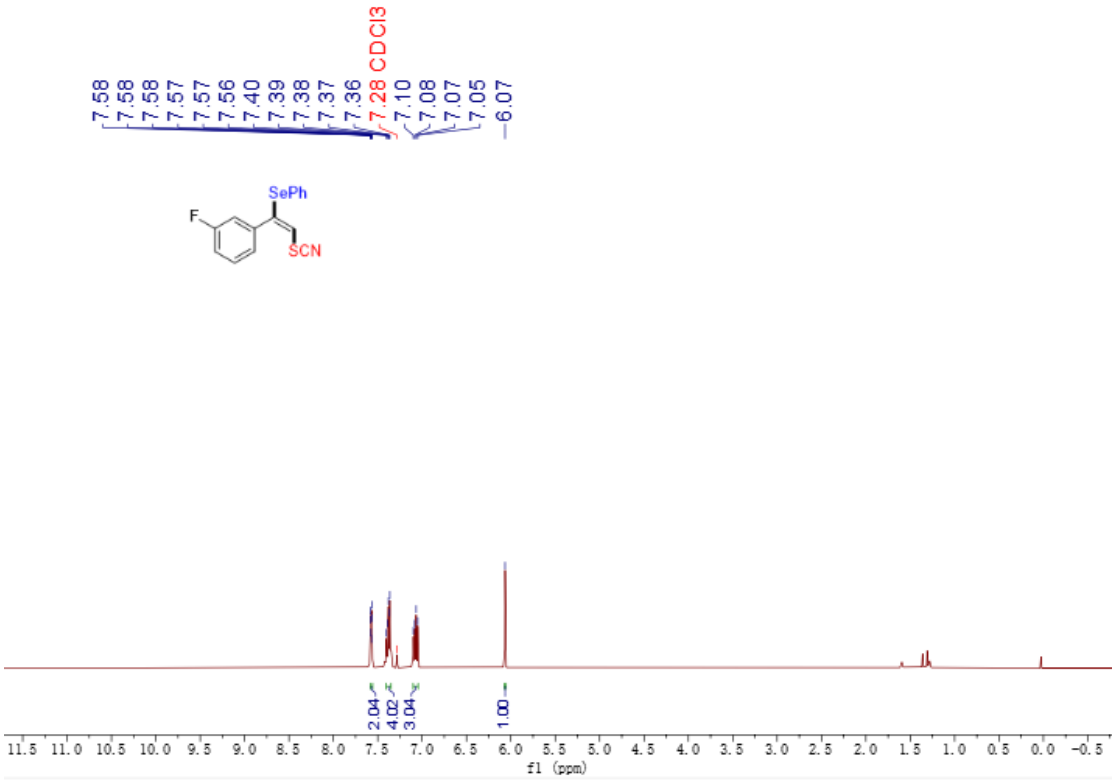


Figure S9. The ^{1}H (500 MHz), ^{13}C (125 MHz) and ^{19}F (471 MHz) NMR spectrum for methyl (*E*)-(1-(3-fluorophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4i**) in $CDCl_3$.



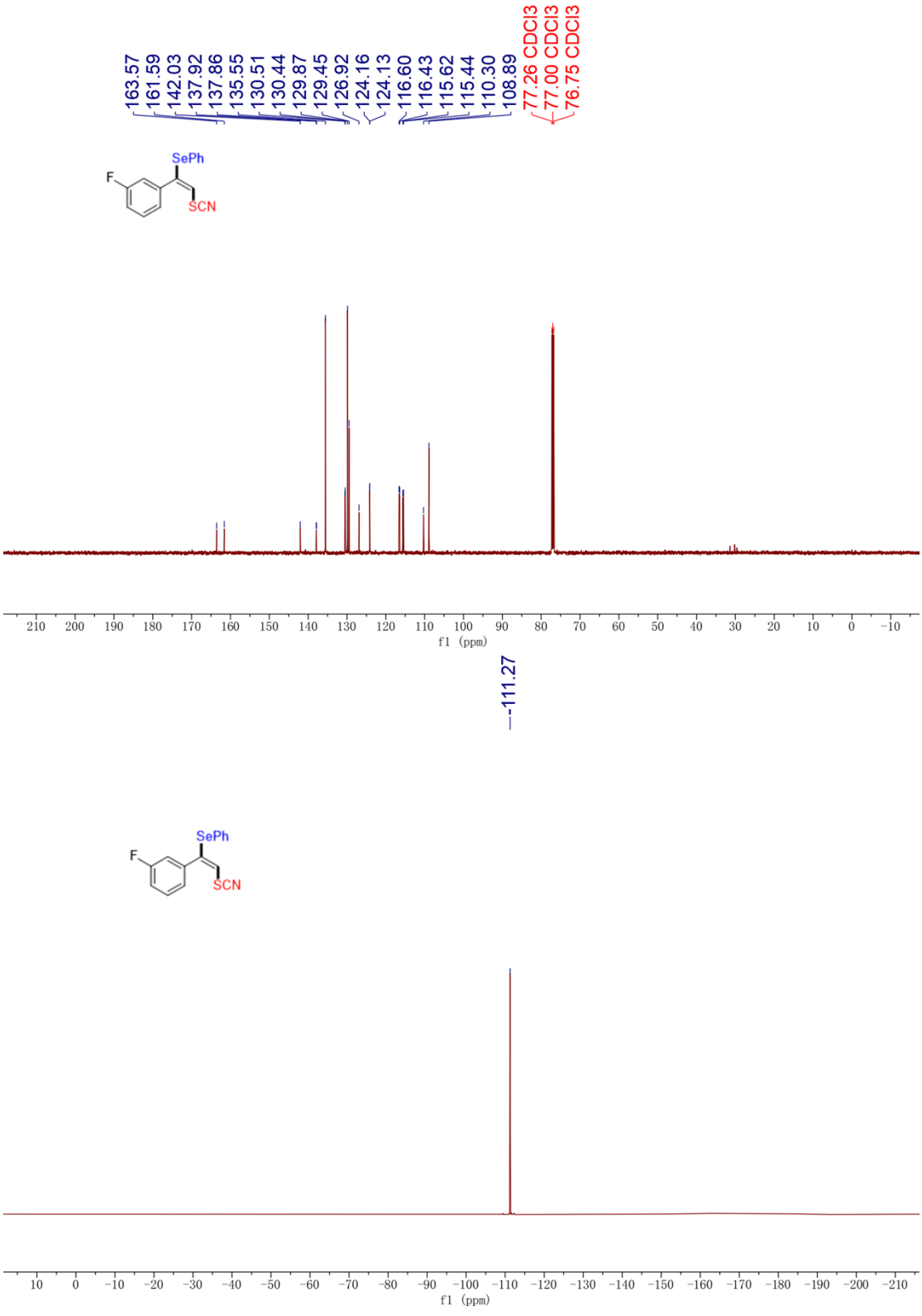


Figure S10. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(1-(2-bromophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4j**) in $CDCl_3$.

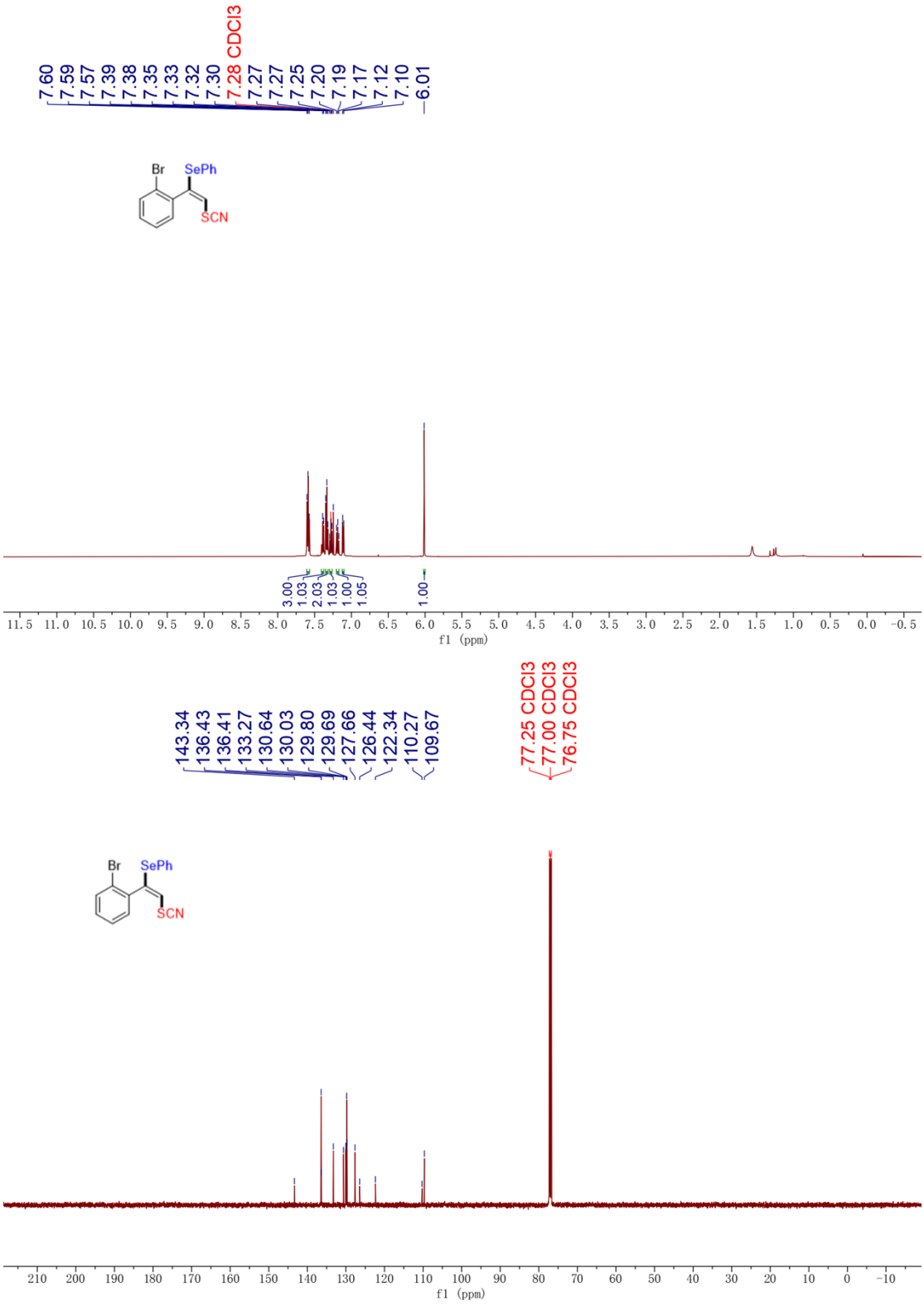


Figure S11. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(1-(2-methoxyphenyl)-2-thiocyanatovinyl)(phenyl)selane (**4k**) in $CDCl_3$.

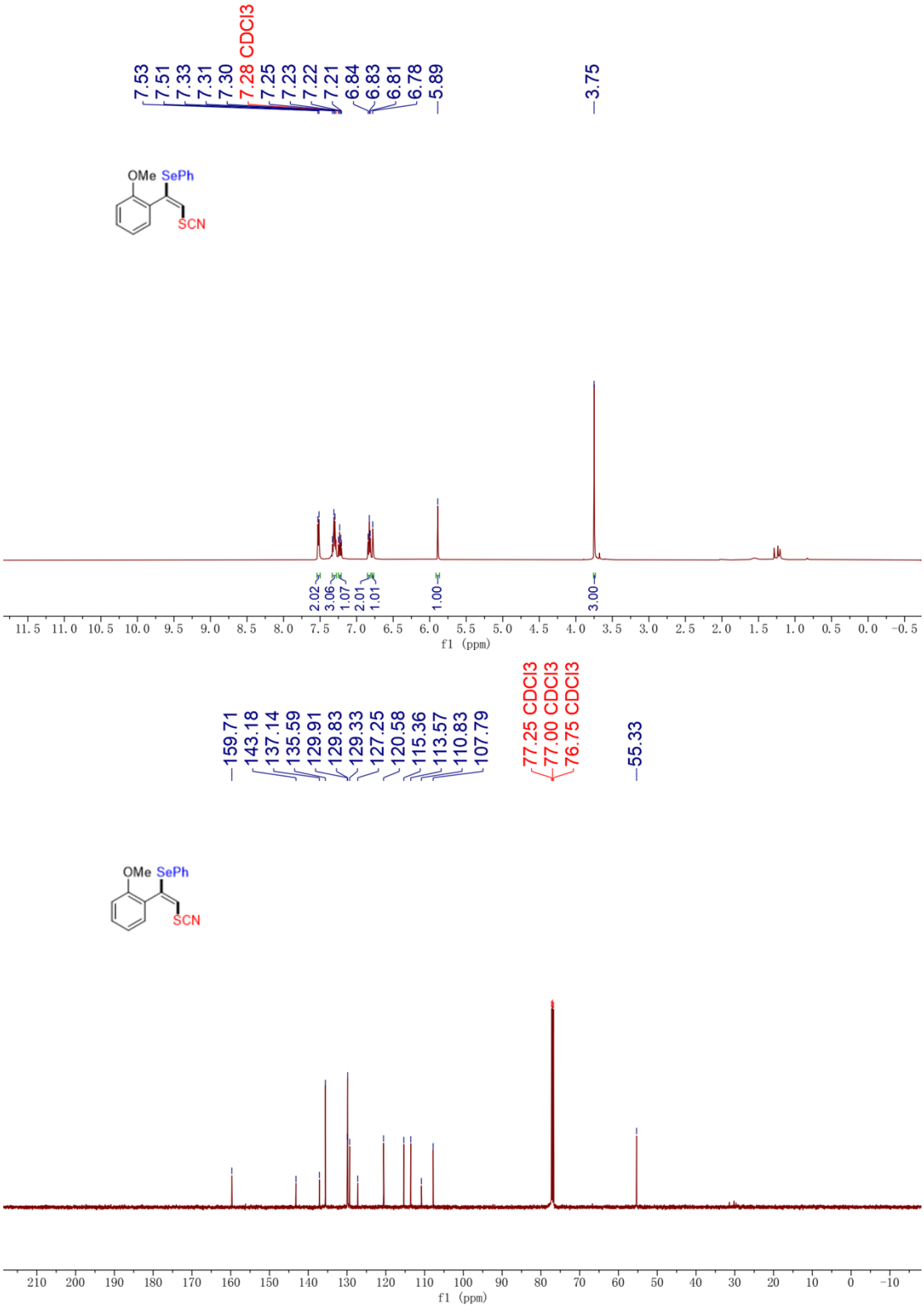


Figure S12. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-2-(4-(1-(phenylselanyl)-2-thiocyanatovinyl)phenyl)acetonitrile (**4l**) in $CDCl_3$.

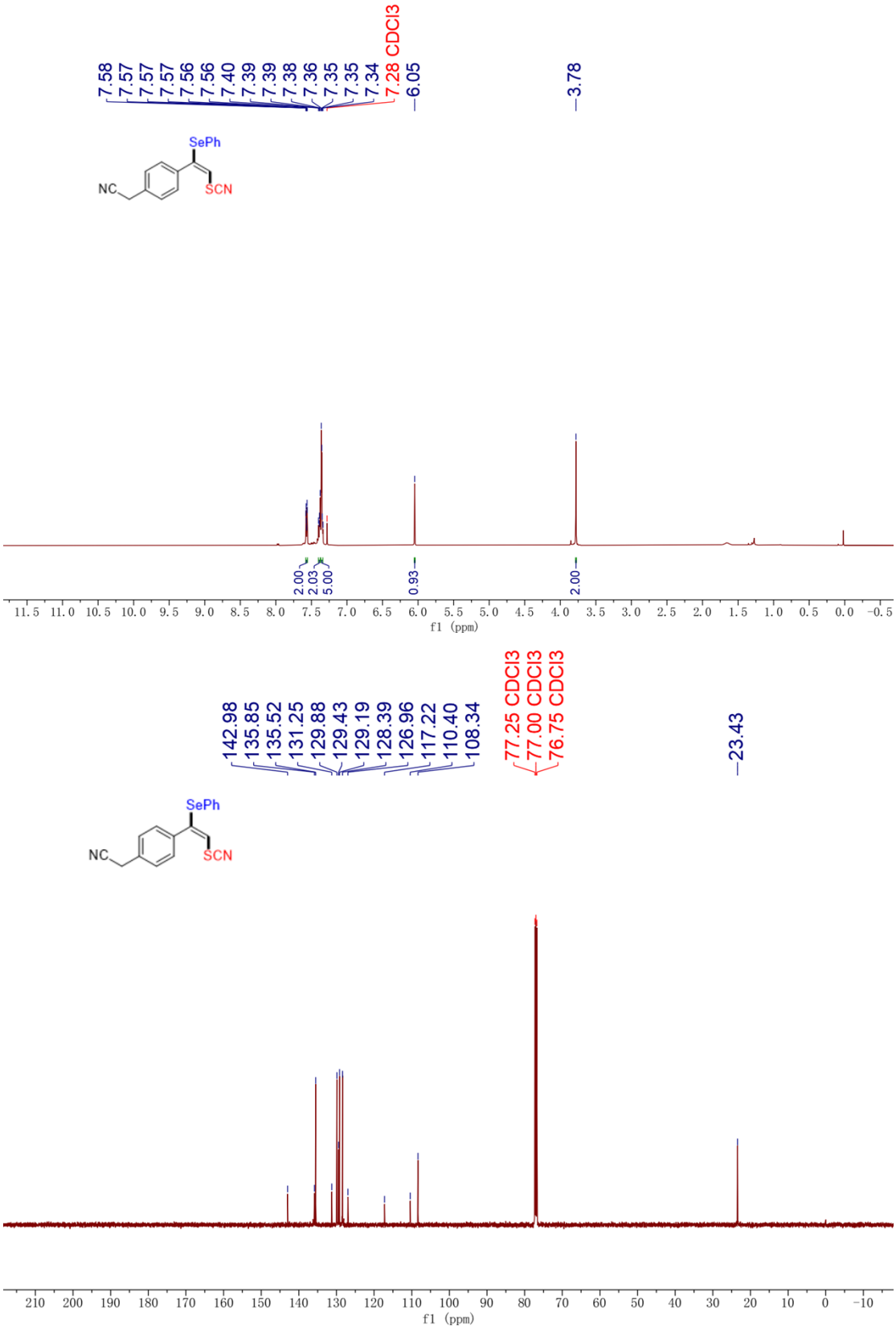
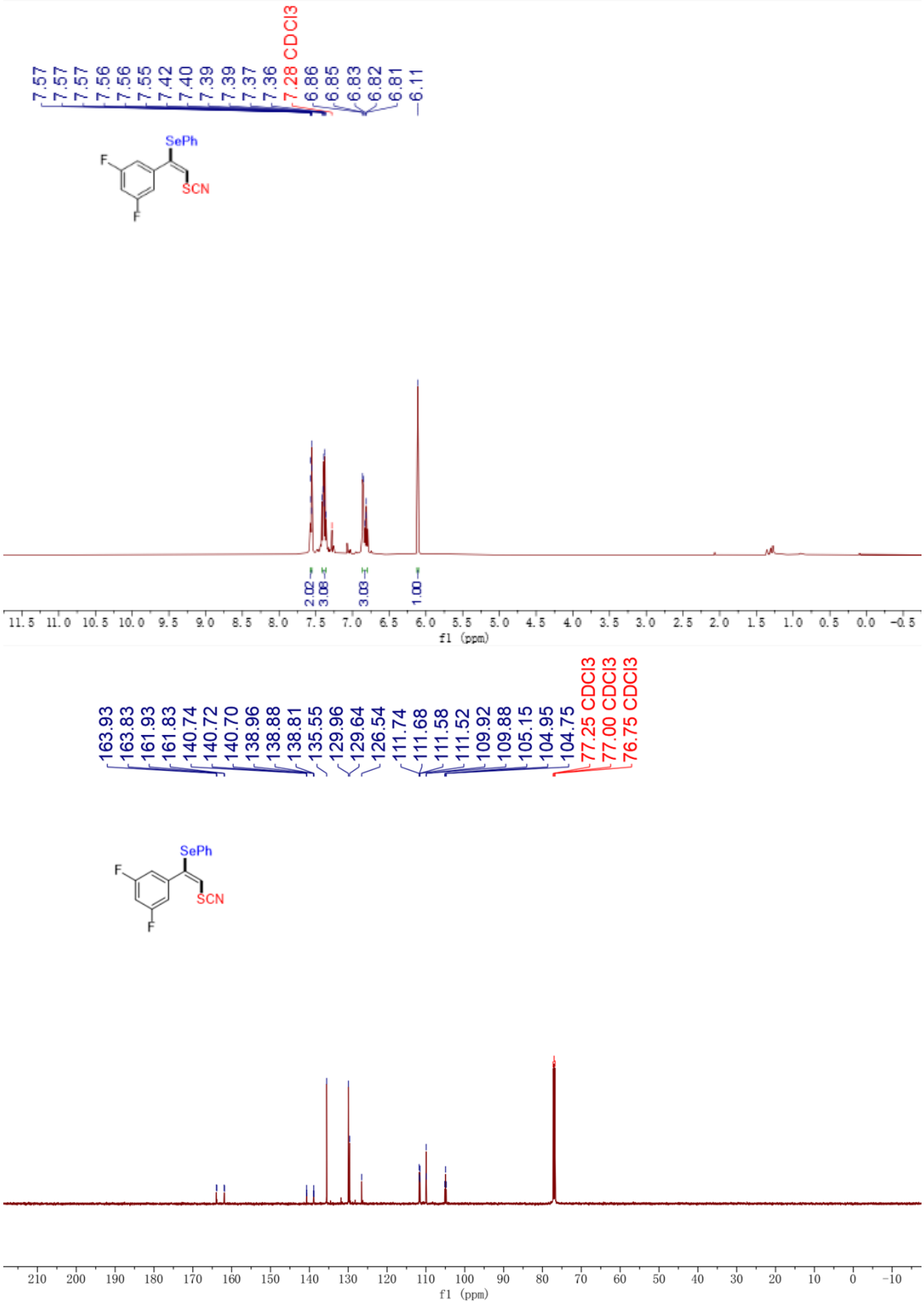

7.58
7.57
7.57
7.57
7.56
7.56
7.40
7.39
7.39
7.38
7.36
7.35
7.35
7.34
7.28 CDCl3
6.05
3.78
SePh
NC
SCN
2.00
2.03
5.00
0.93
2.00
f1 (ppm)
142.98
135.85
135.52
131.25
129.88
129.43
129.19
128.39
126.96
117.22
110.40
108.34
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
23.43
SePh
NC
SCN
f1 (ppm)

Figure S13. The ^{1}H (500 MHz), ^{13}C (125 MHz) and ^{19}F (471 MHz) NMR spectrum for (*E*)-(1-(3,5-difluorophenyl)-2-thiocyanatovinyl)(phenyl)selane (**4m)** in $CDCl_3$.



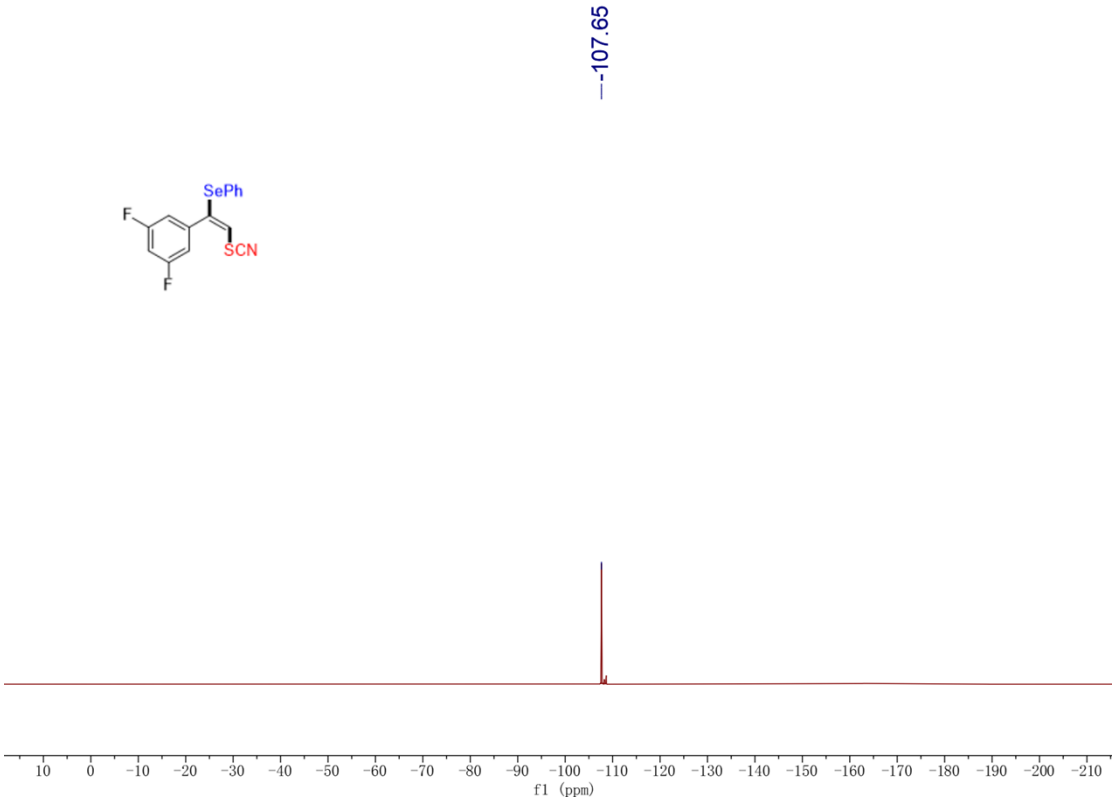
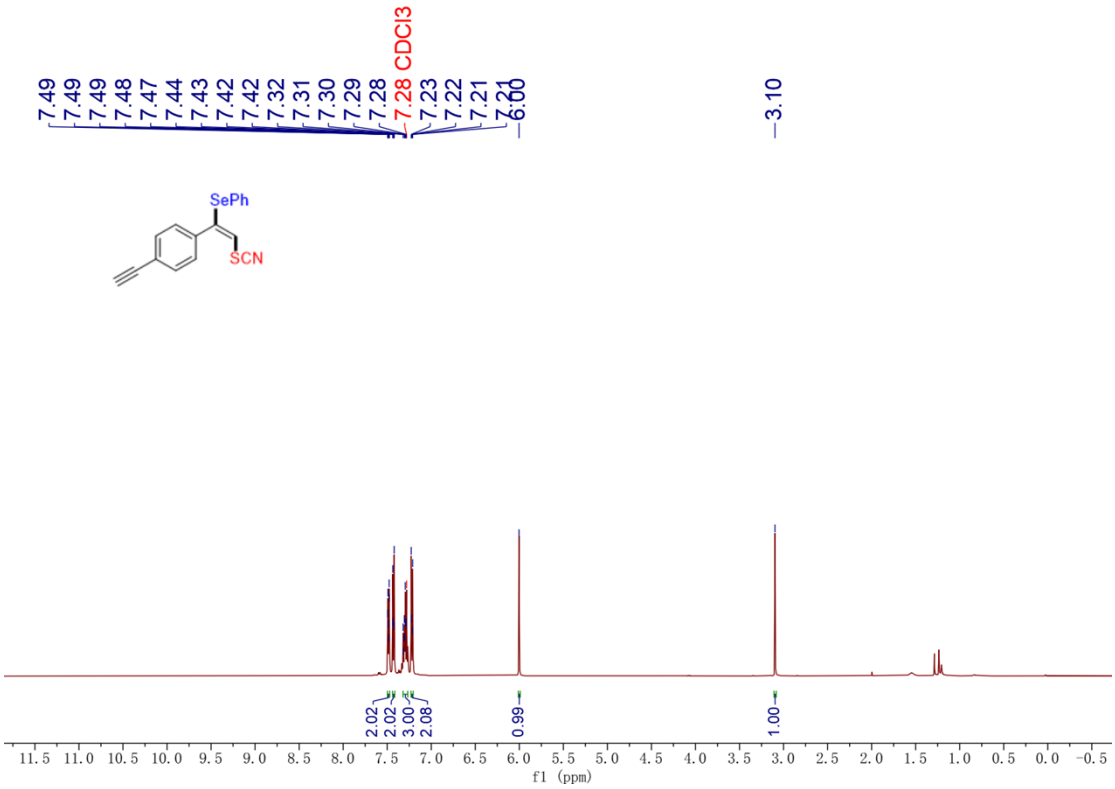


Figure S14. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(1-(4-ethynylphenyl)-2-thiocyanatovinyl)(phenyl)selane (**4n**) in $CDCl_3$.



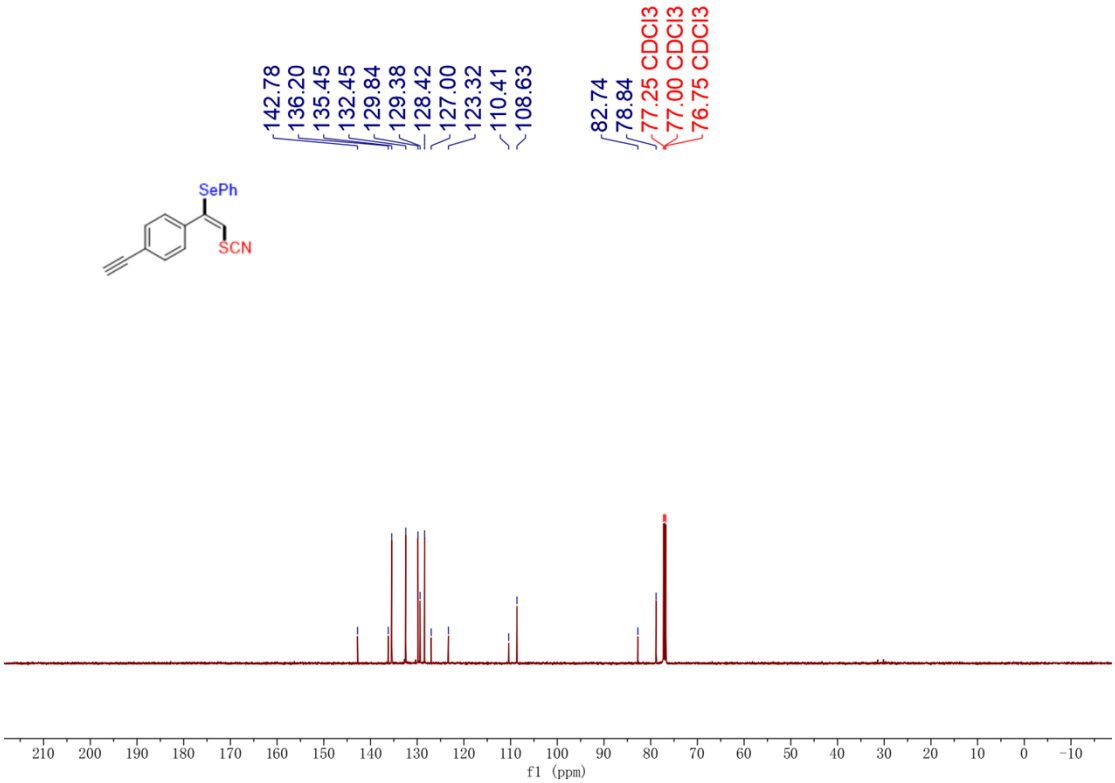
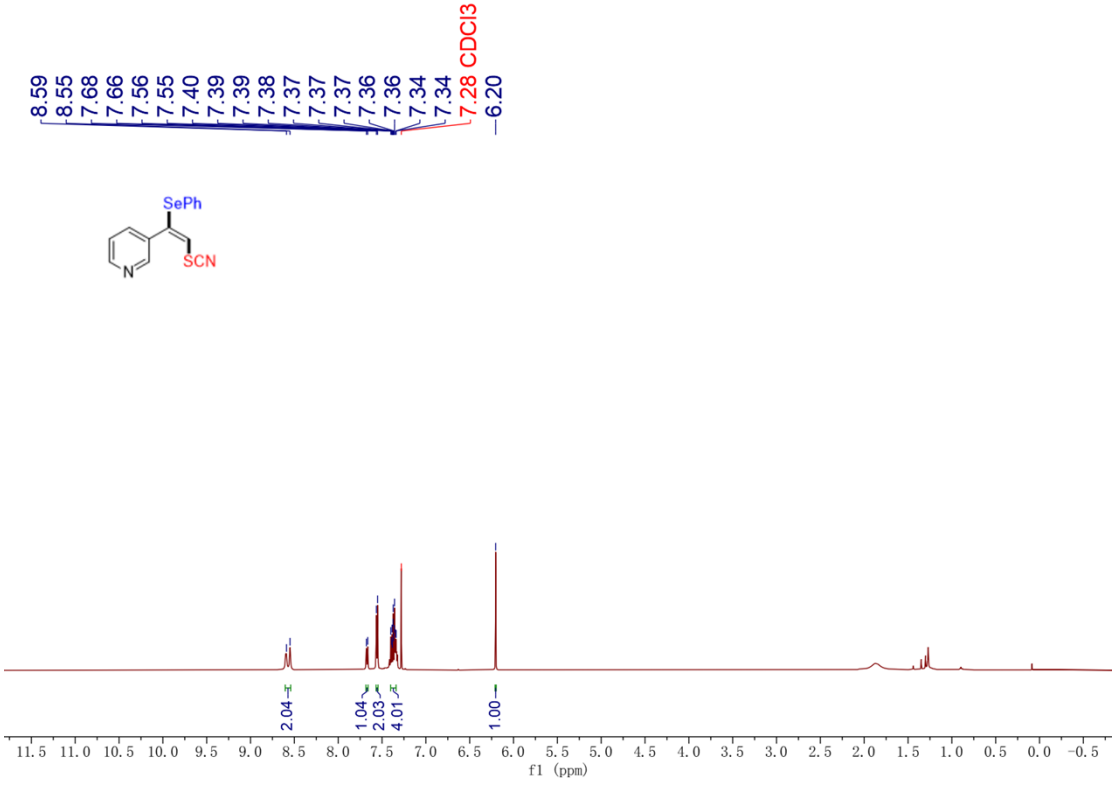


Figure S15. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for methyl (*E*)-3-(1-(phenylselanyl)-2-thiocyanatovinyl)pyridine (**4o**) in $CDCl_3$.



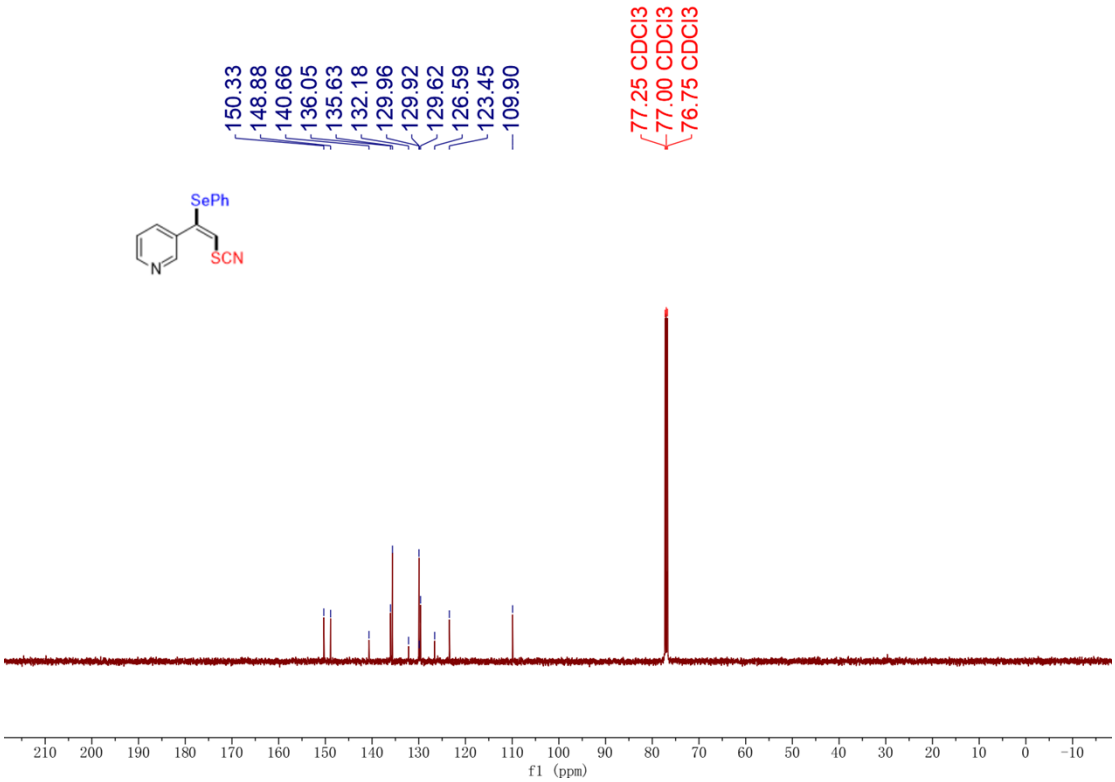
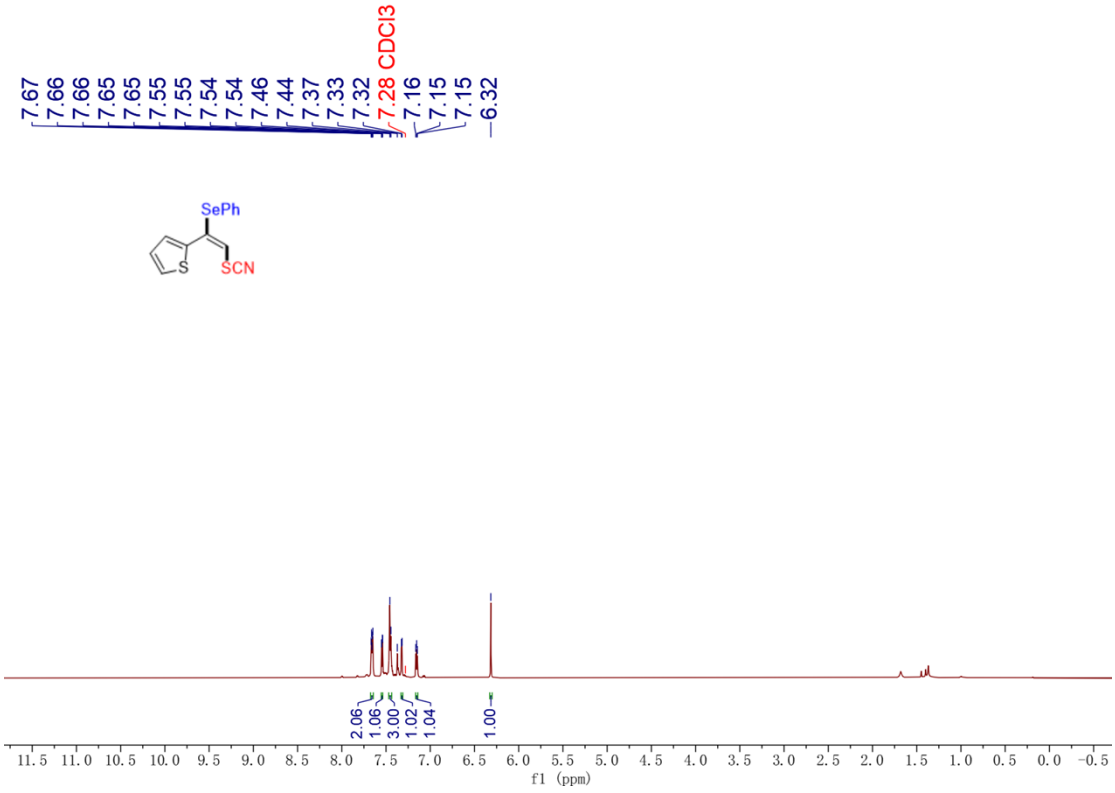


Figure S16. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-2-(1-(phenylselanyl)-2-thiocyanatovinyl)thiophene (**4p**) in $CDCl_3$.



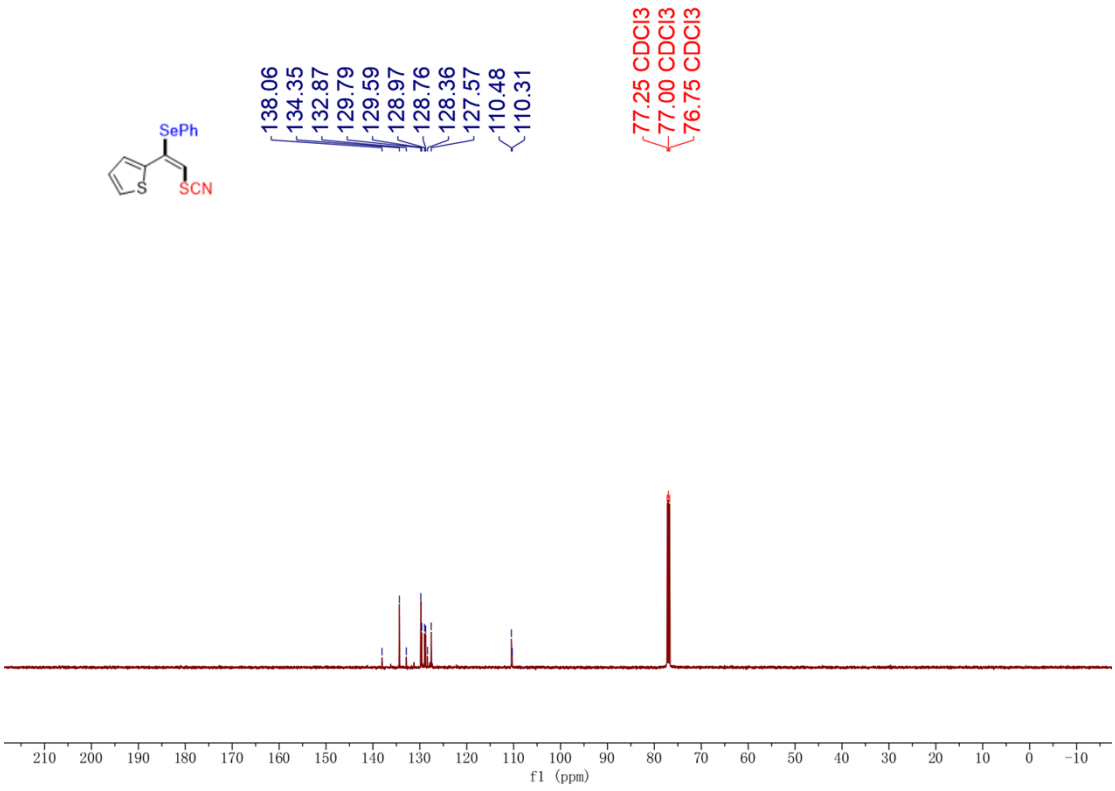
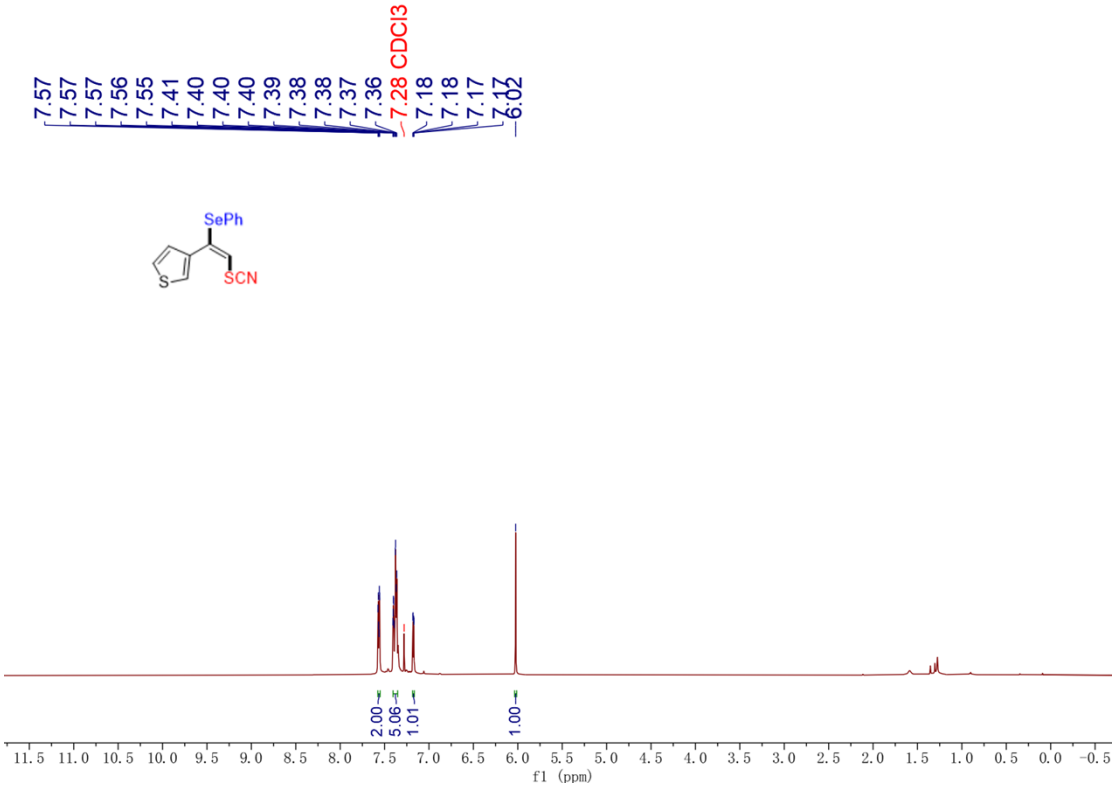


Figure S17. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-3-(1-(phenylselanyl)-2-thiocyanatovinyl)thiophene (**4q**) in $CDCl_3$.



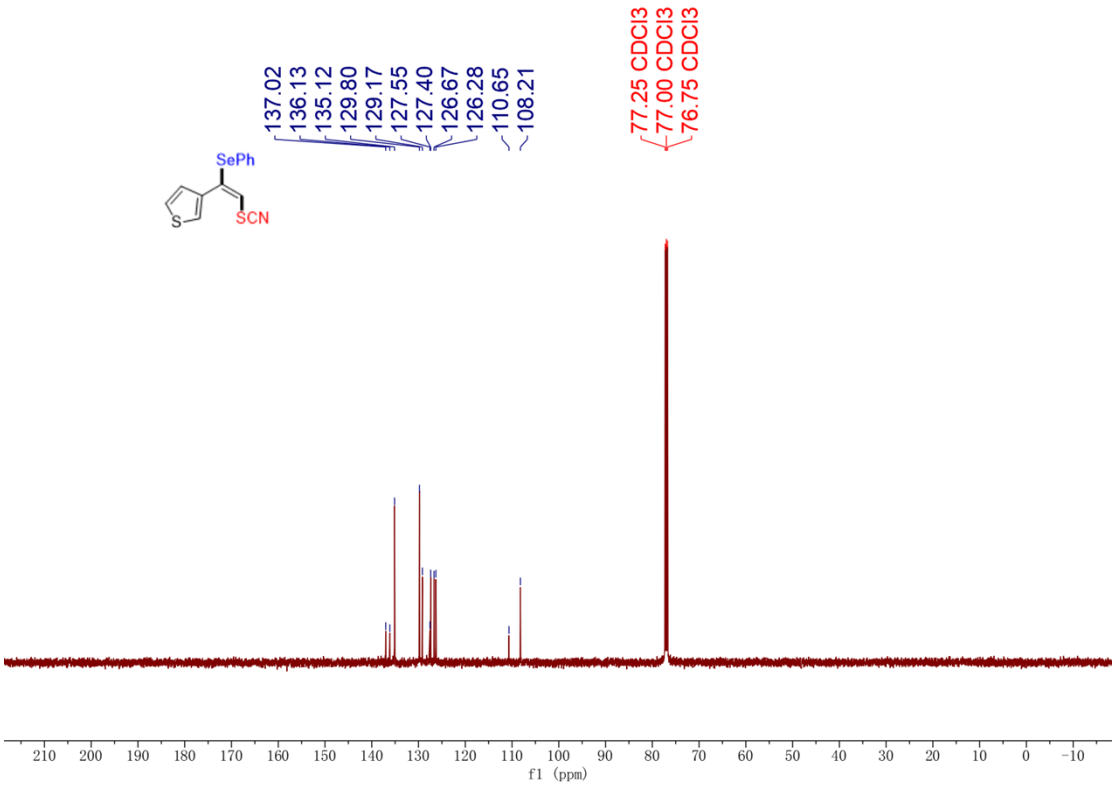
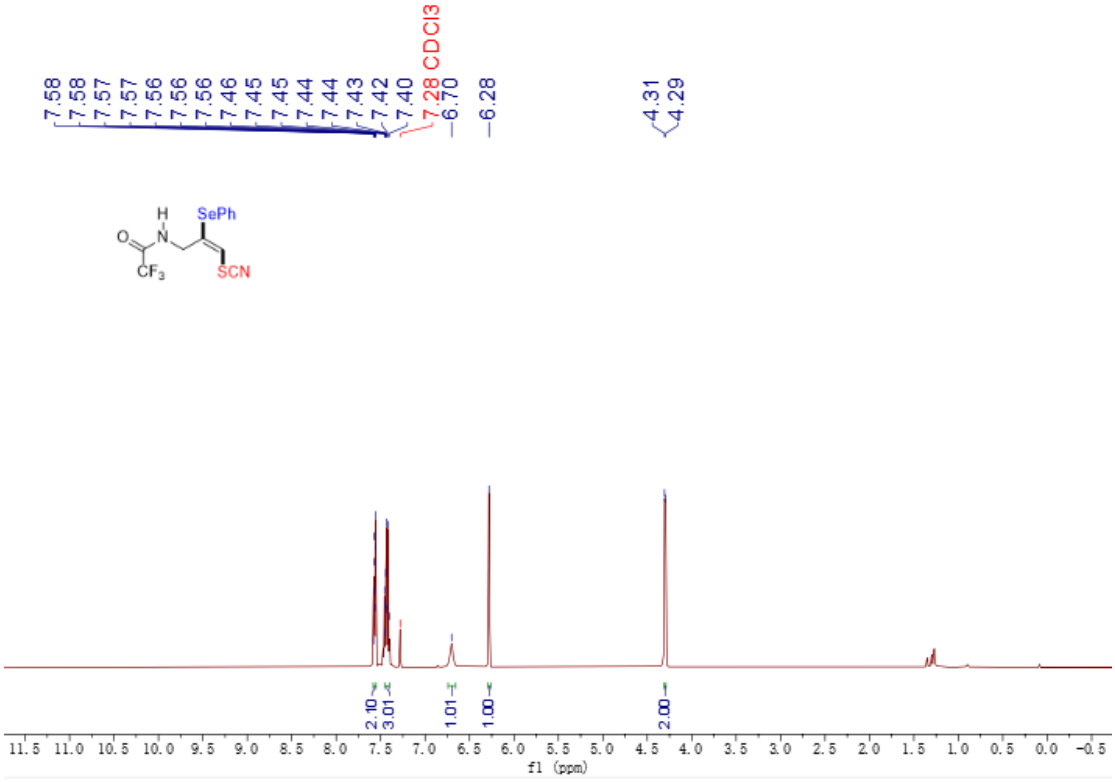


Figure S18. The ^{1}H (500 MHz), ^{13}C (125 MHz) and ^{19}F (471 MHz) NMR spectrum for (*E*)-2,2,2-trifluoro-N-(2-(phenylselanyl)-3-thiocyanatoallyl)acetamide (**4r**) in $CDCl_3$.



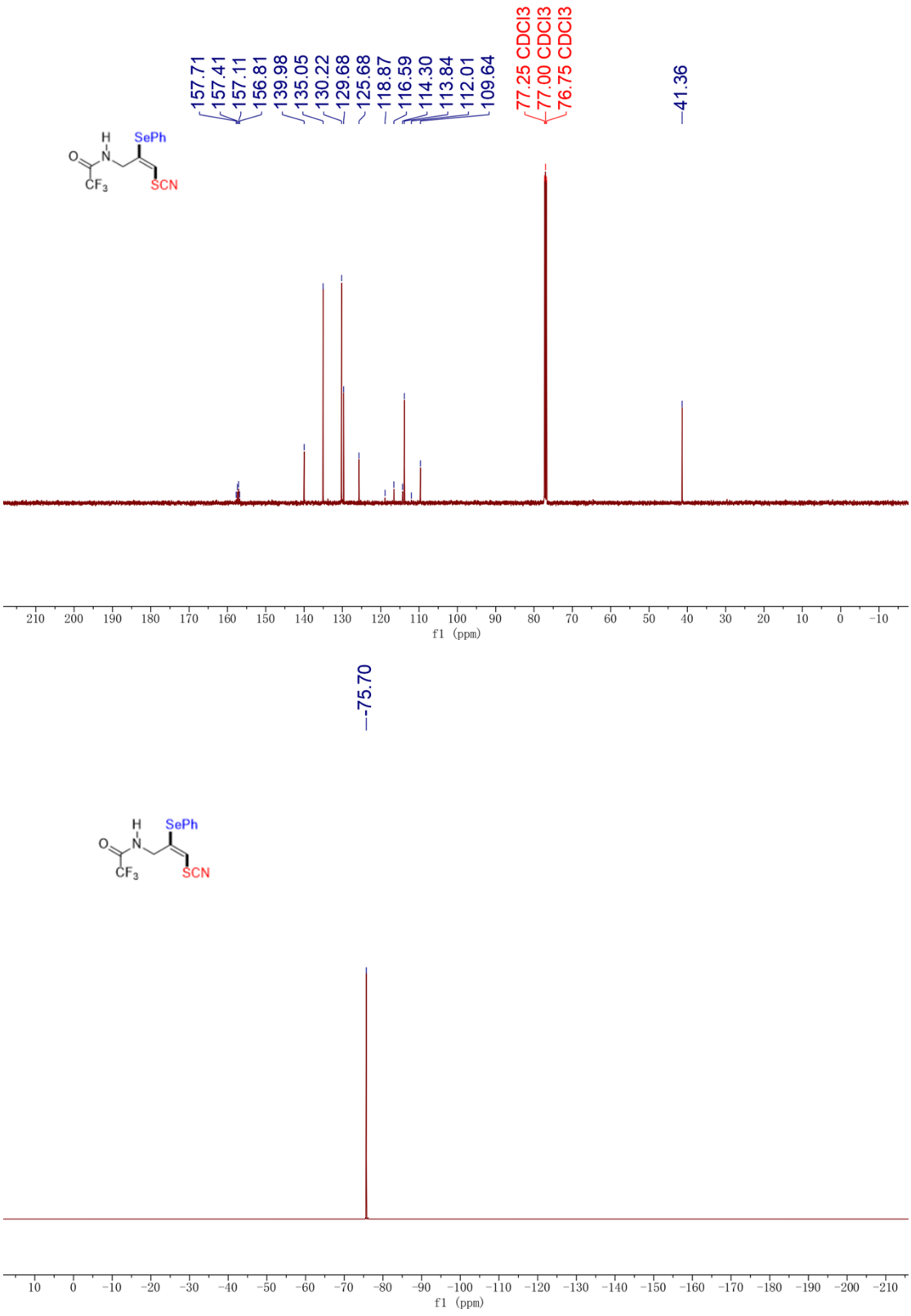


Figure S19. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(3,3-diethoxy-1-thiocyanatoprop-1-en-2-yl)(phenyl)selane (**4s**) in $CDCl_3$.

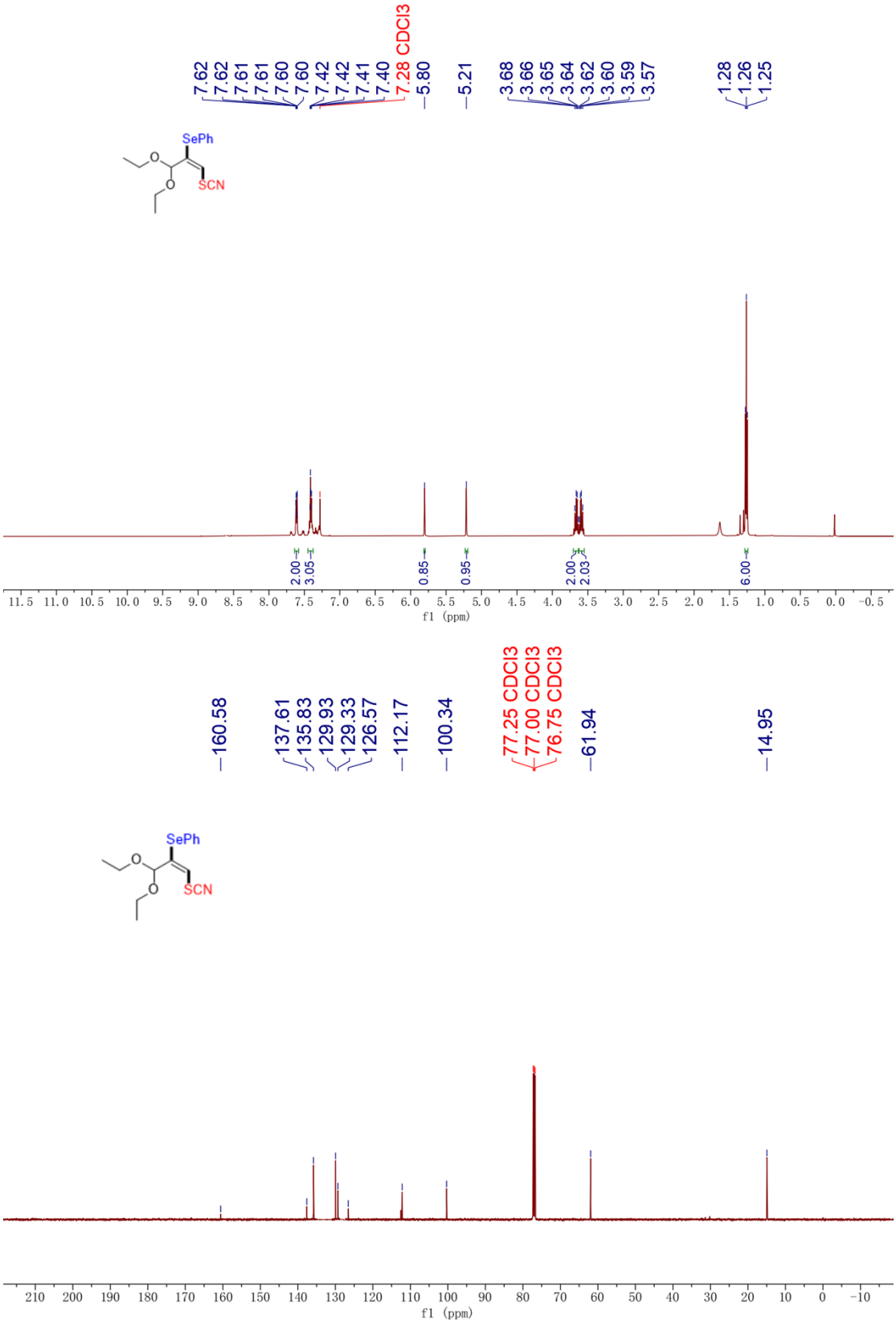


Figure S20. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-phenyl(1-phenyl-2-thiocyanatobut-1-en-1-yl)selane (**4t**) in $CDCl_3$.

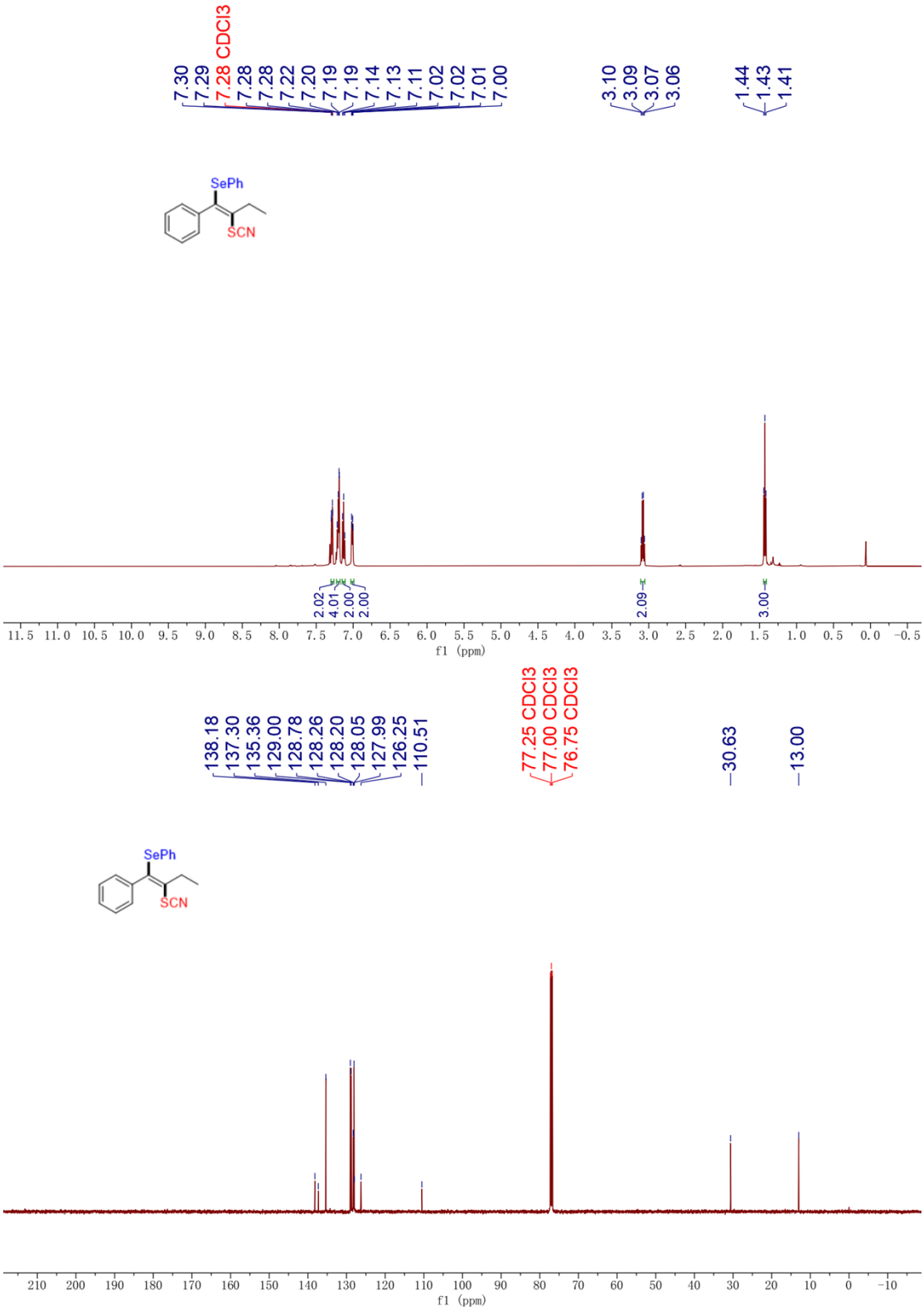
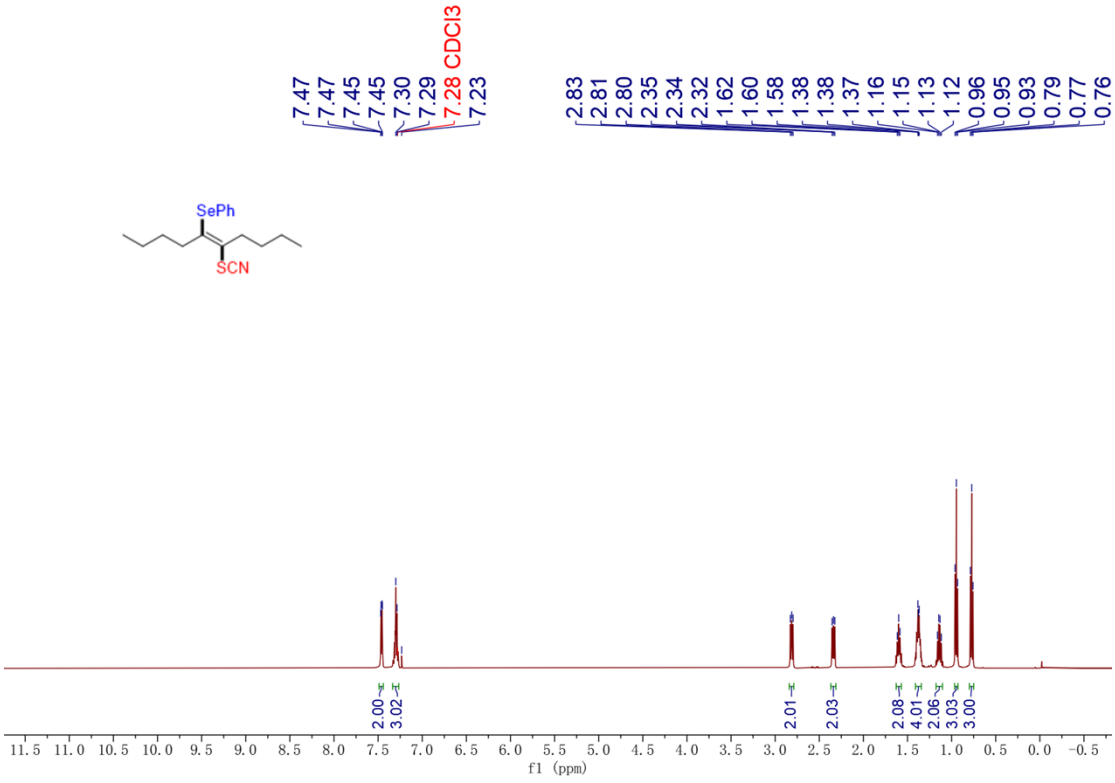


Figure S21. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-phenyl(6-thiocyanatodec-5-en-5-yl)selane (**4u**) in $CDCl_3$.


7.47
7.47
7.45
7.45
7.30
7.29
7.28 CDCl3
7.23
2.83
2.81
2.80
2.35
2.34
2.32
1.62
1.60
1.58
1.38
1.38
1.37
1.16
1.15
1.13
1.12
0.96
0.95
0.93
0.79
0.77
0.76
SePh
SCN
2.00
3.02
2.01
2.03
2.08
4.01
2.06
3.03
3.00
f1 (ppm)

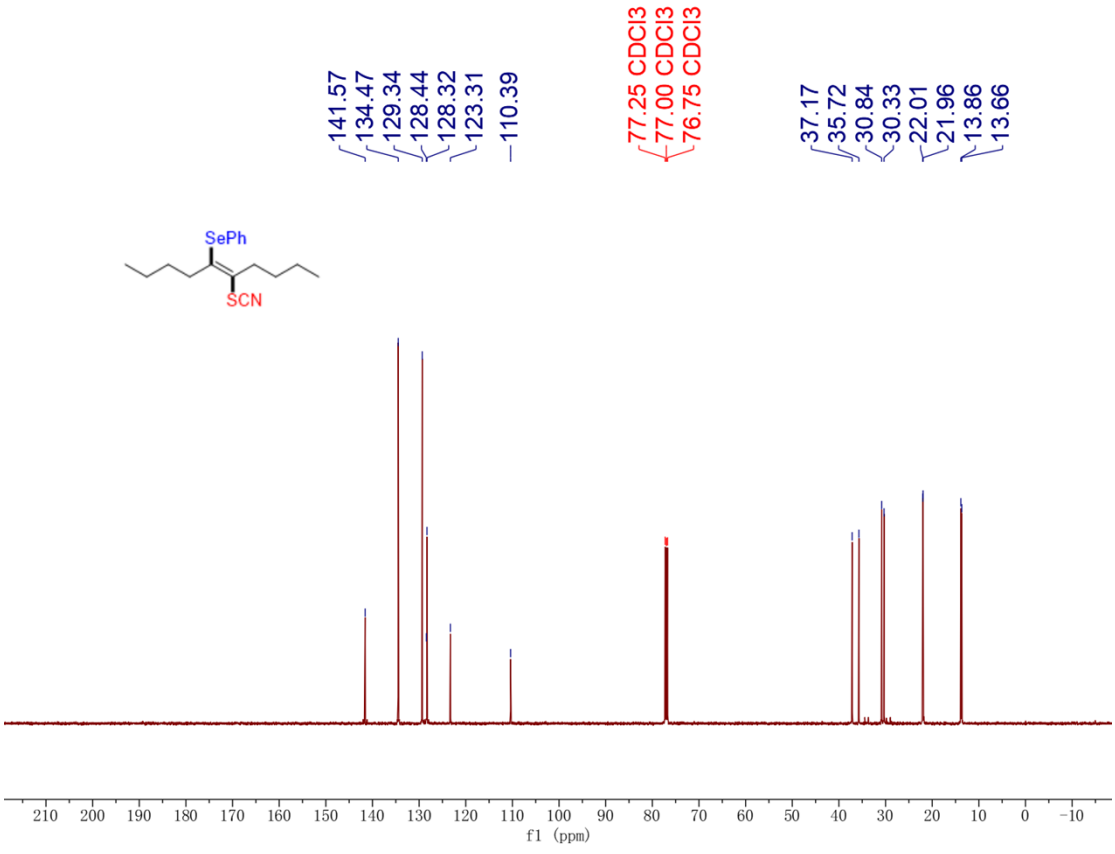

141.57
134.47
129.34
128.44
128.32
123.31
110.39
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
37.17
35.72
30.84
30.33
22.01
21.96
13.86
13.66
SePh
SCN
f1 (ppm)

Figure S22. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(4-chlorophenyl)(1-phenyl-2-thiocyanatovinyl)selane (**4v**) in $CDCl_3$.

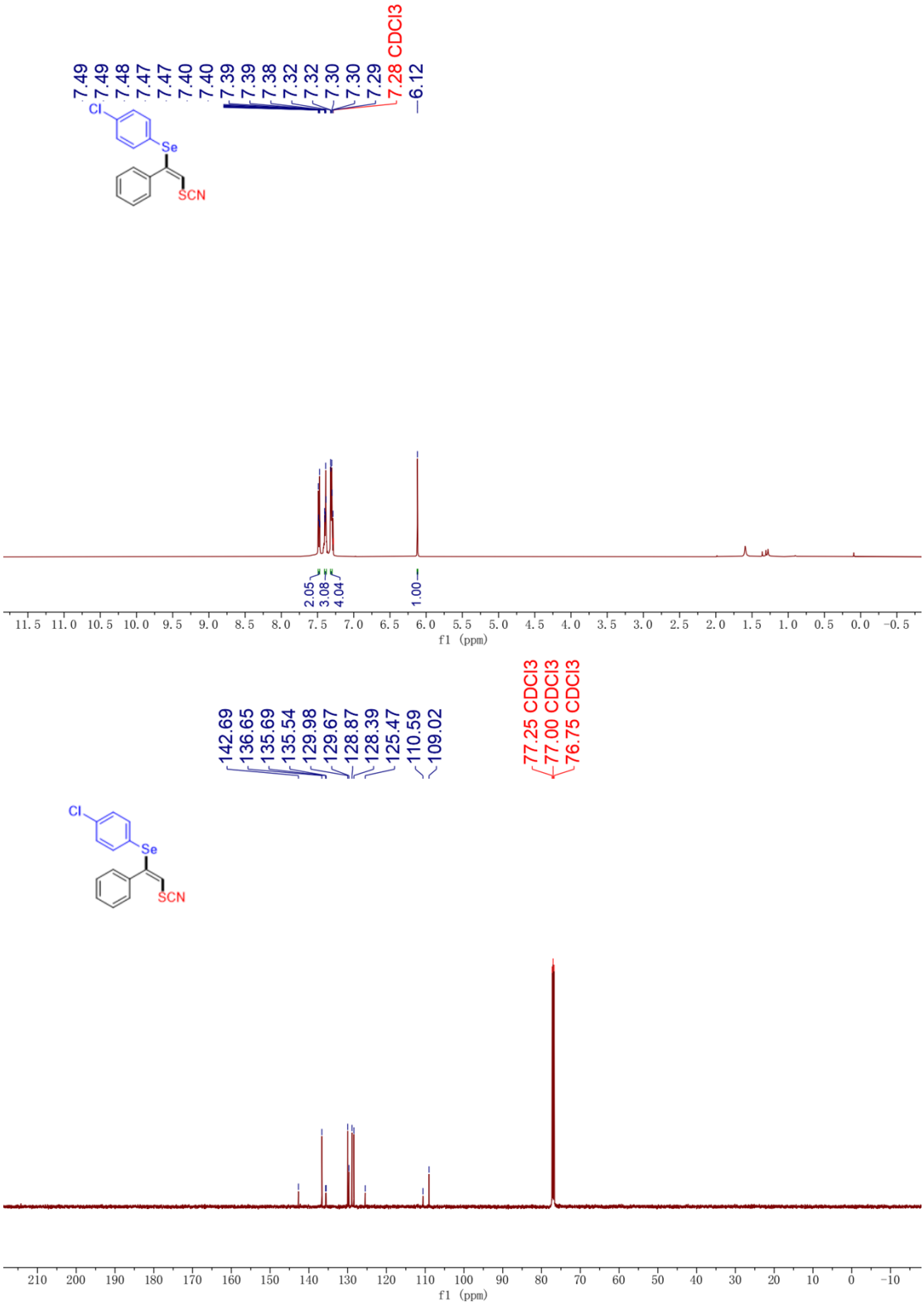


Figure S23. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(1-phenyl-2-thiocyanatovinyl)(p-tolyl)selane (**4w**) in $CDCl_3$.

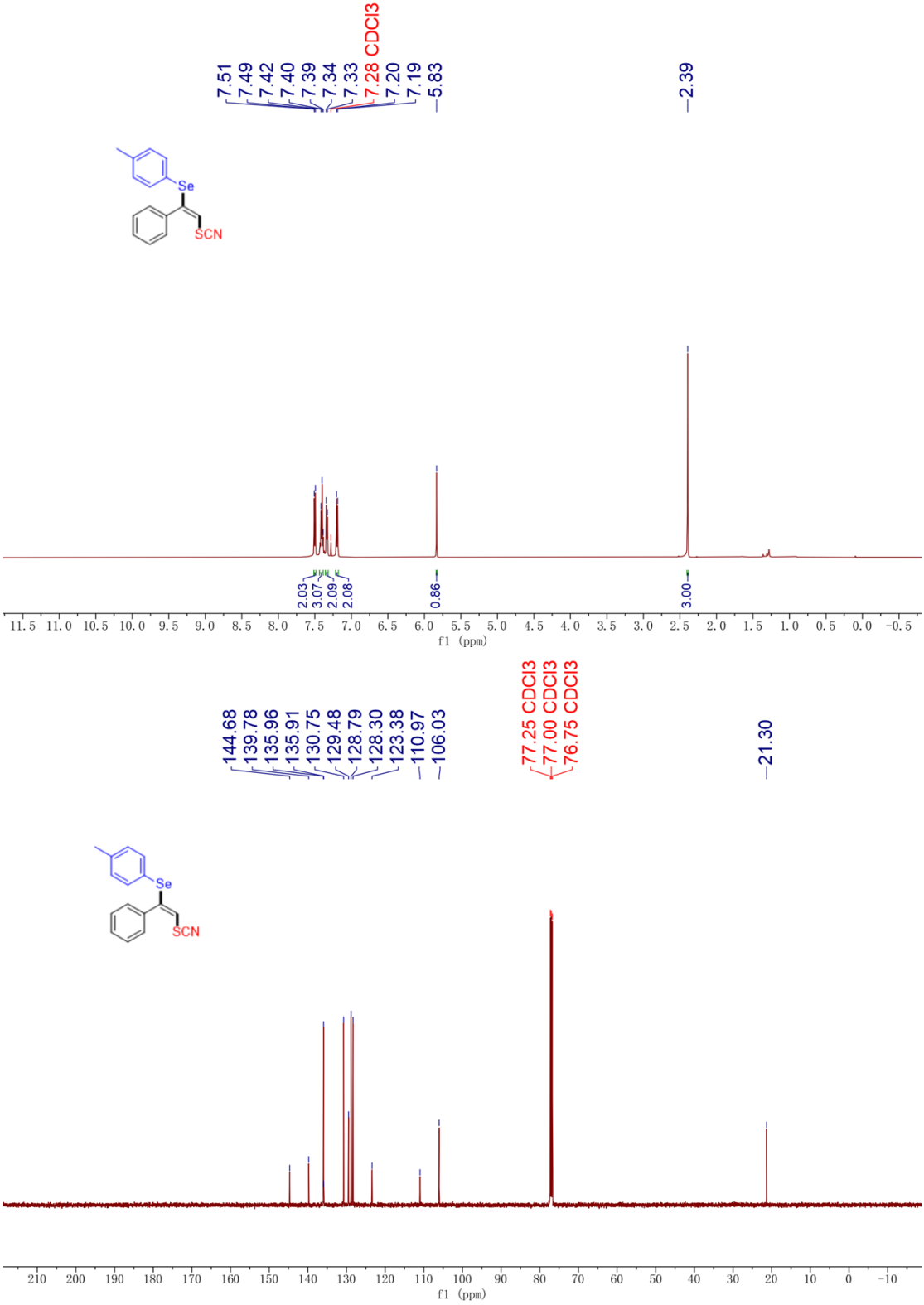


Figure S24. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-3-(1-((4-bromophenyl)selanyl)-2-thiocyanatovinyl)pyridine (**4x**) in $CDCl_3$.

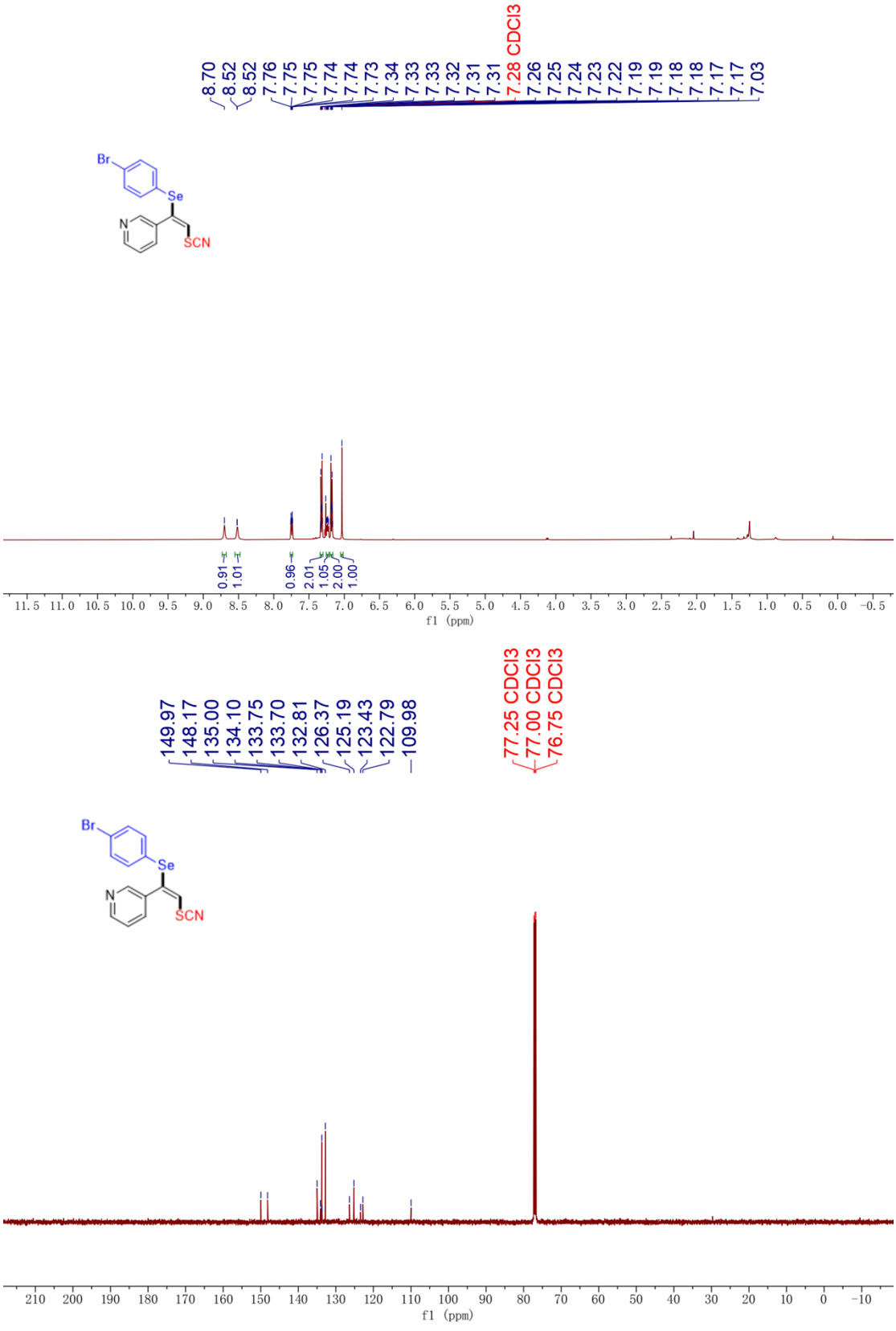


Figure S25. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(1-(4-bromophenyl)-2-thiocyanatovinyl)(methyl)selane (**4y**) in $CDCl_3$.

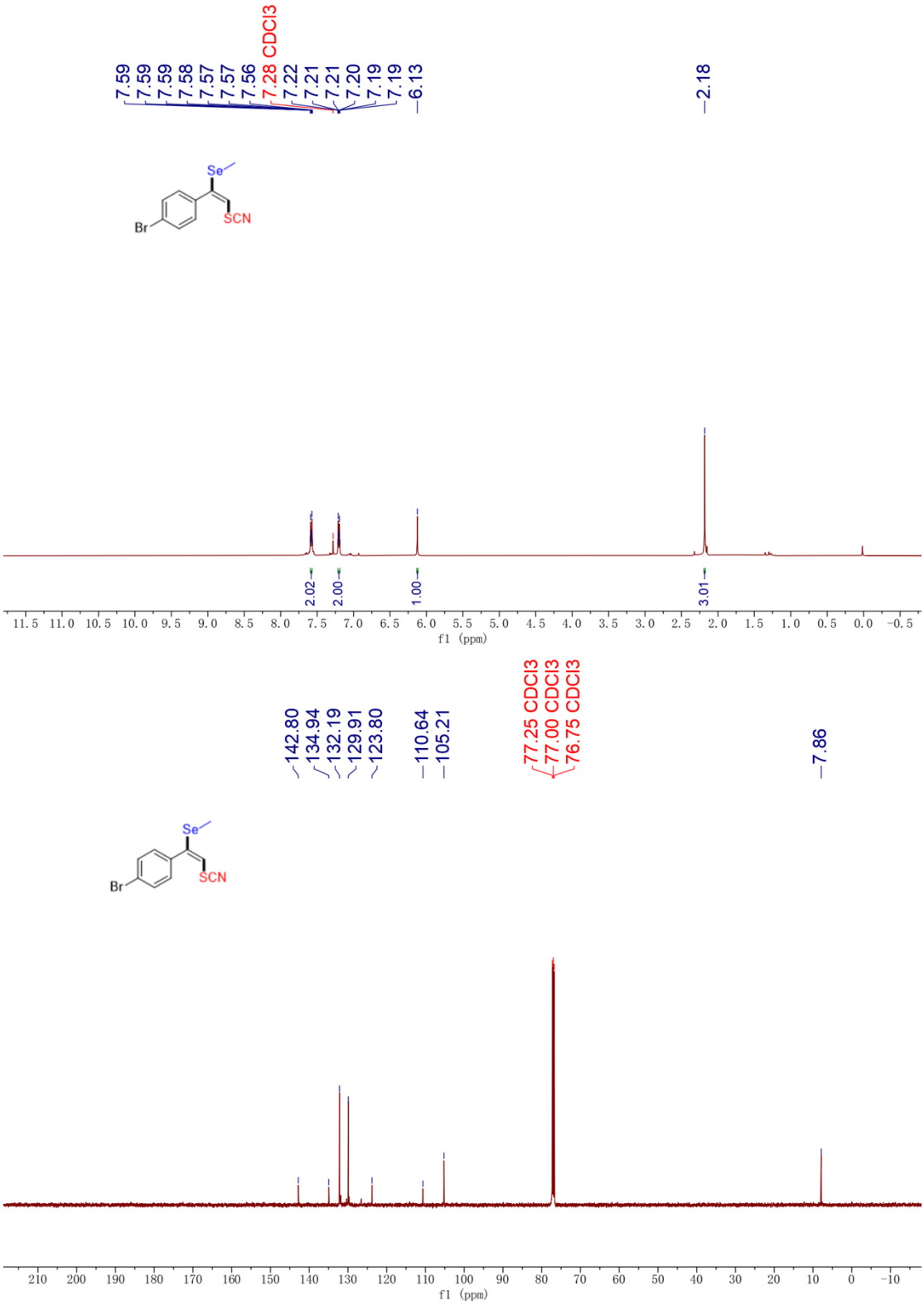


Figure S26. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for ethyl(*E*)-(1-(2-bromophenyl)-2-thiocyanatovinyl)(methyl)selane (**4z**) in $CDCl_3$.

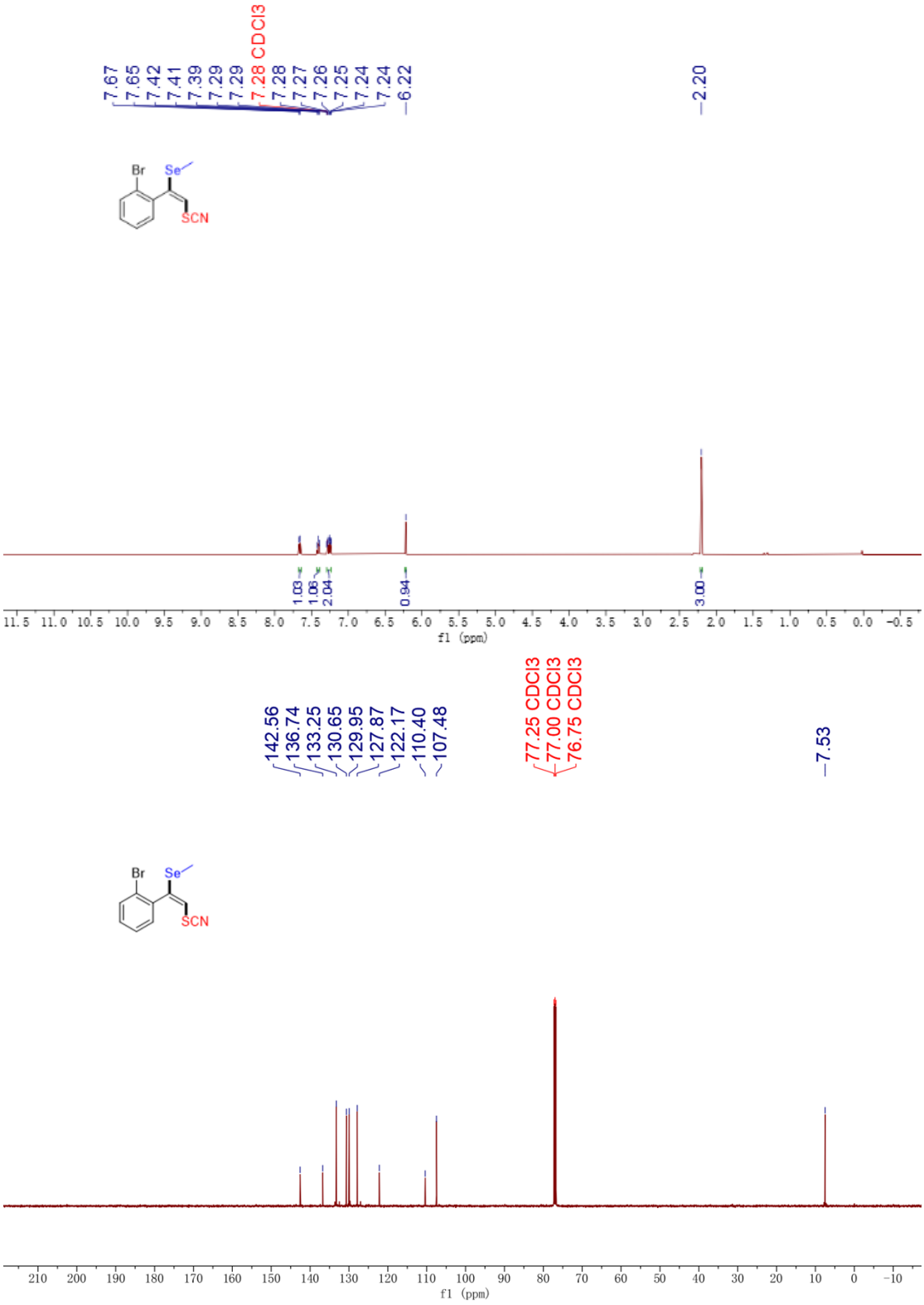
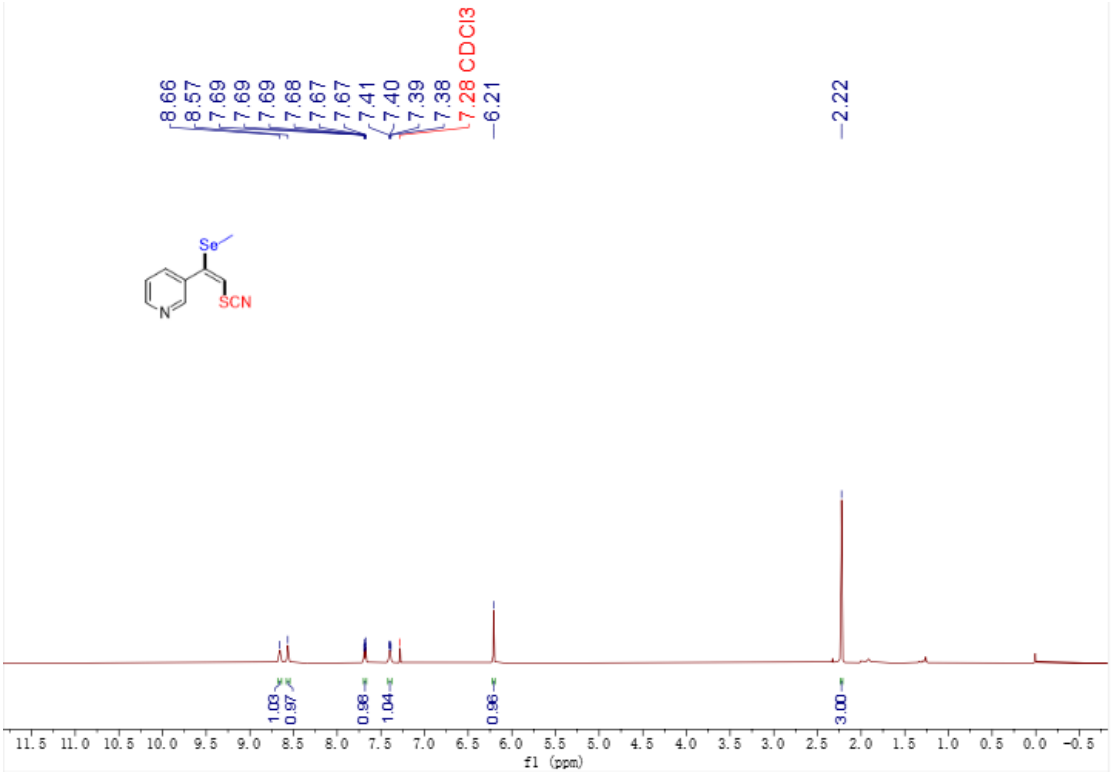


Figure S27. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-3-(1-(methylselanyl)-2-thiocyanatovinyl)pyridine (**4aa**) in $CDCl_3$.



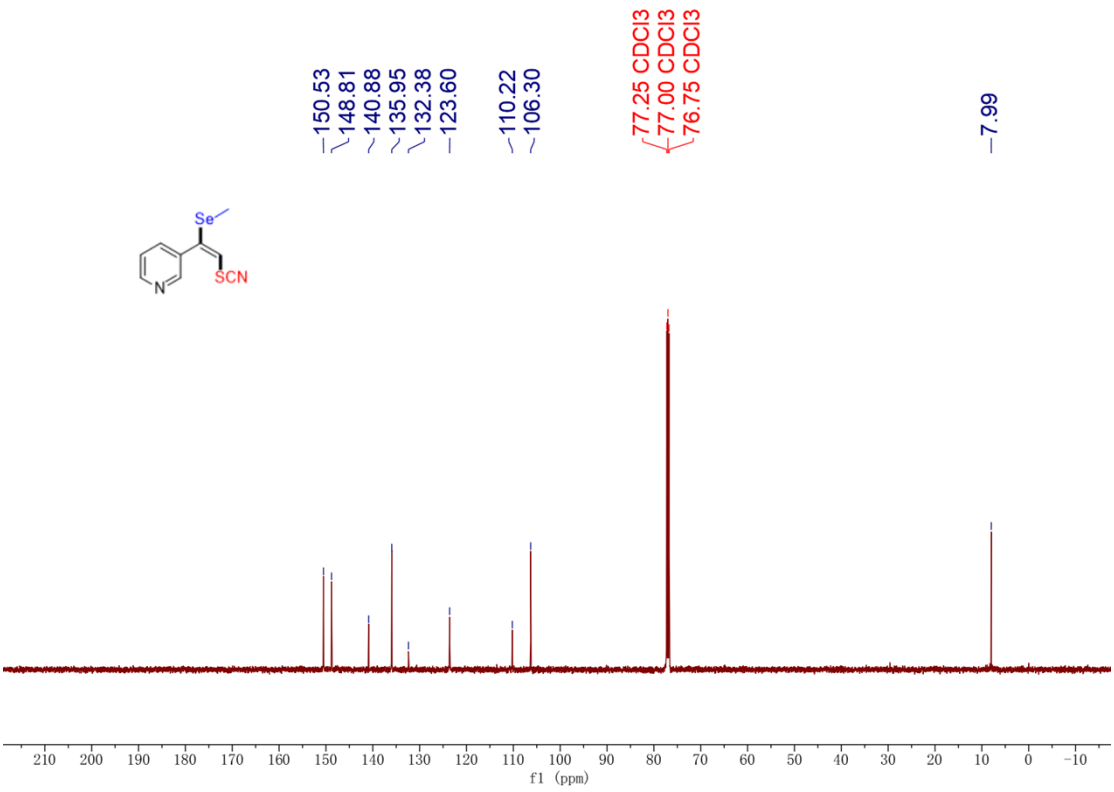


Figure S28. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-benzyl(1-phenyl-2-thiocyanatovinyl)selane (**4ab**) in $CDCl_3$.

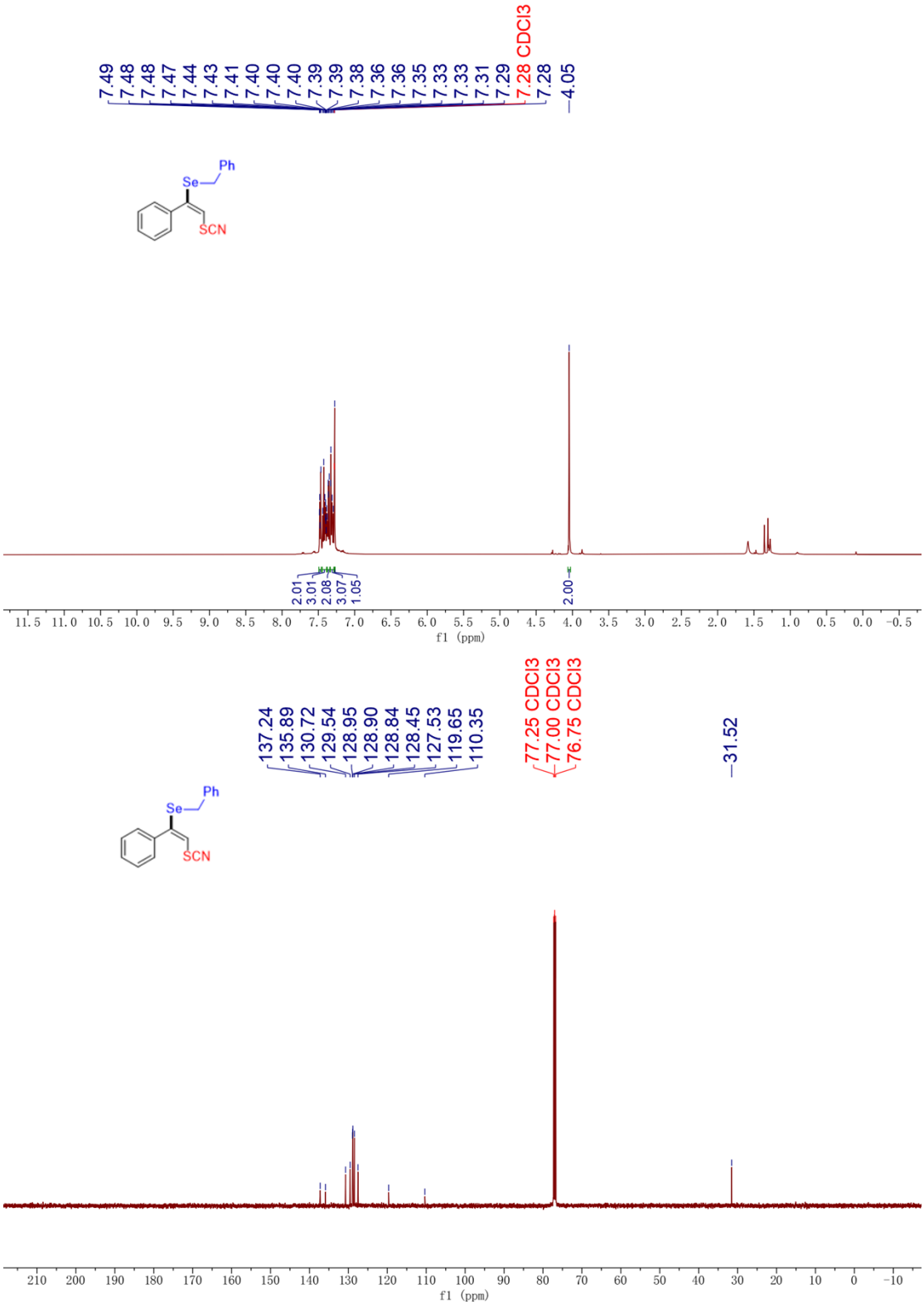


Figure S29. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (1*R*,2*S*,4*R*)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((*E*)-1-(phenylselanyl)-2-thiocyanatovinyl)benzoate (**4ac**) in $CDCl_3$.

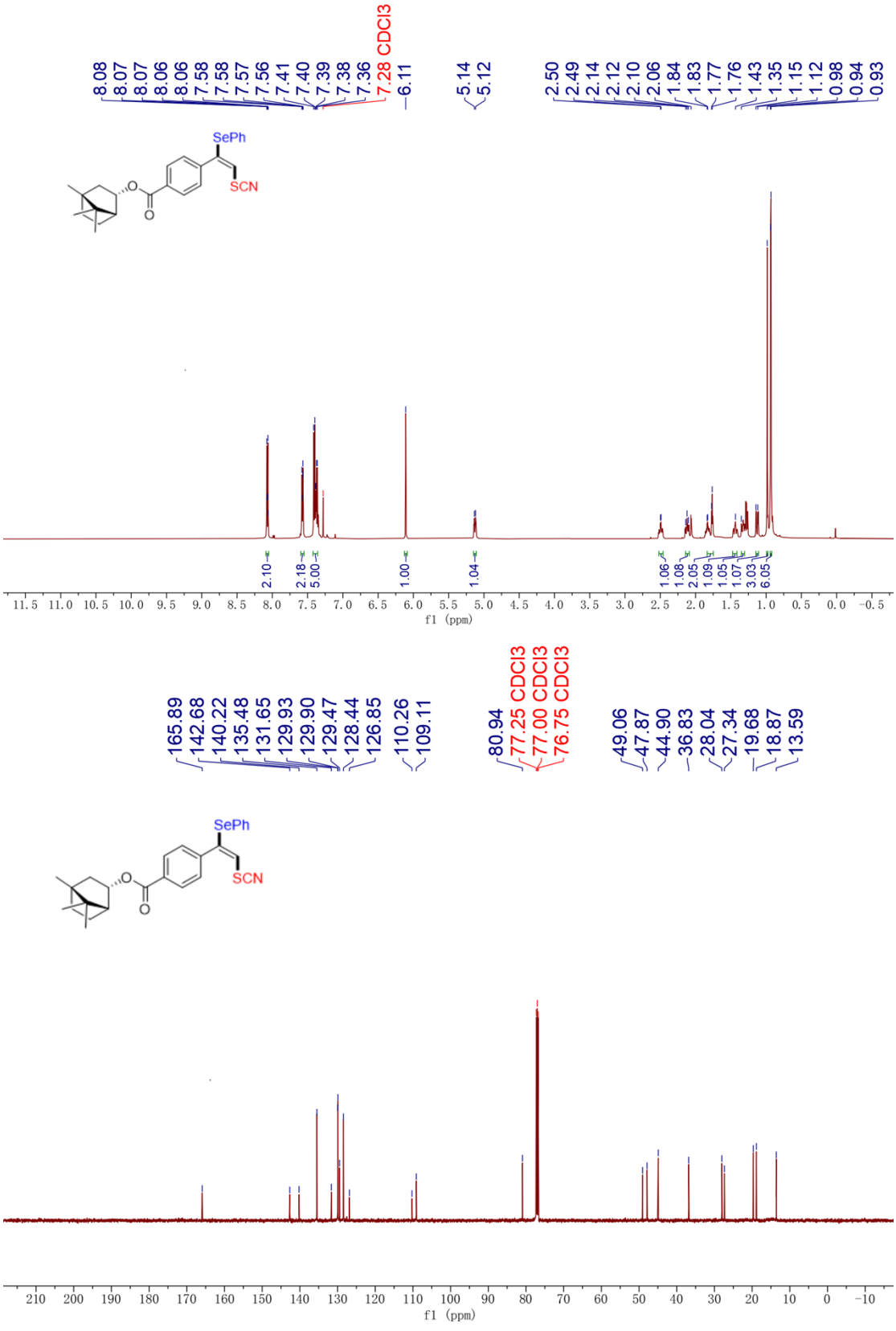


Figure S30. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-1-(phenylselanyl)-2-thiocyanatovinyl) benzoate (**4ad**) in $CDCl_3$.

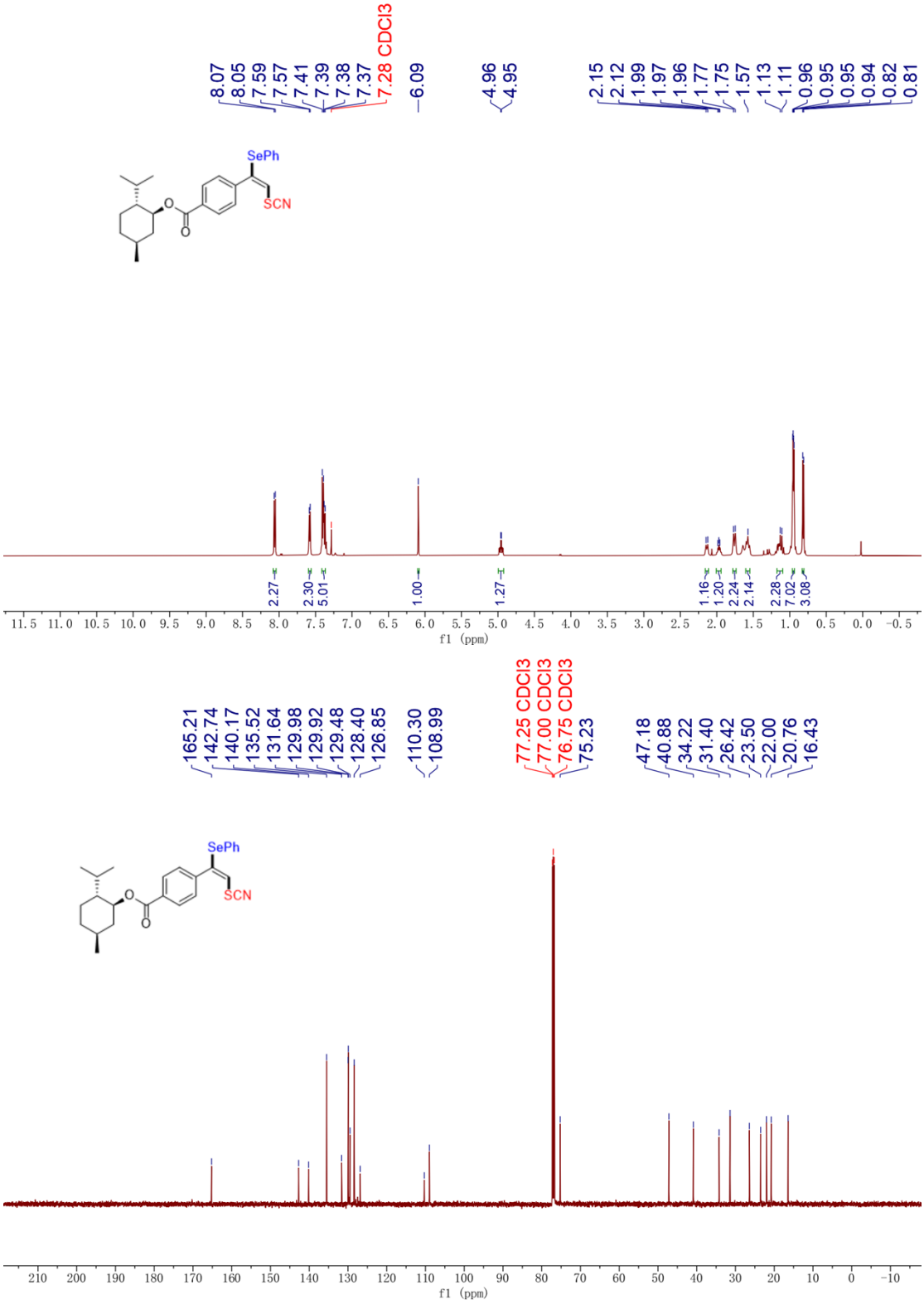
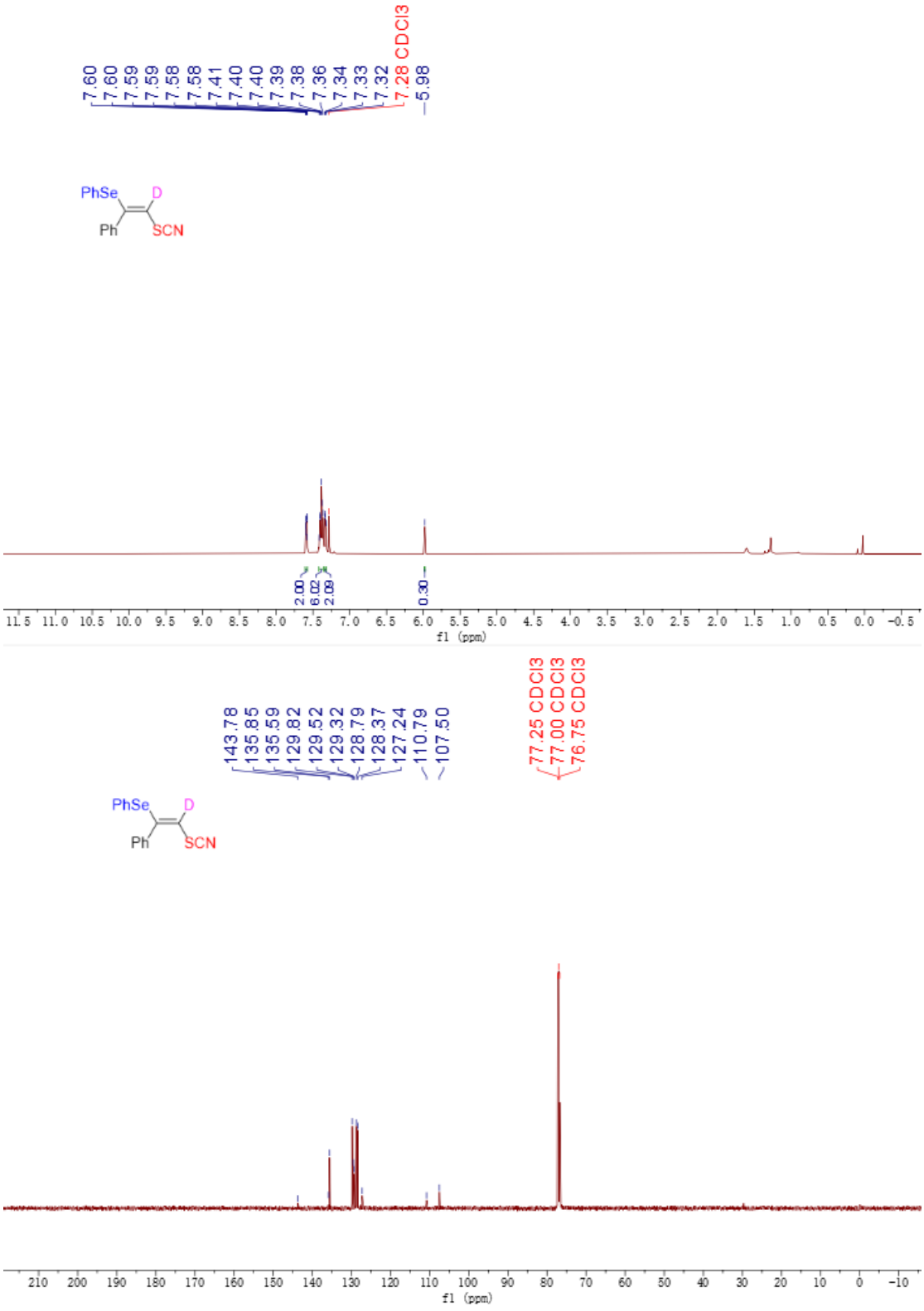


Figure S31. The ^{1}H (500 MHz), ^{2}H (500 MHz) and ^{13}C (125 MHz) NMR spectrum for (*E*)-phenyl(1-phenyl-2-thiocyanatovinyl-2-d)selane (**4a-D**) in $CDCl_3$.



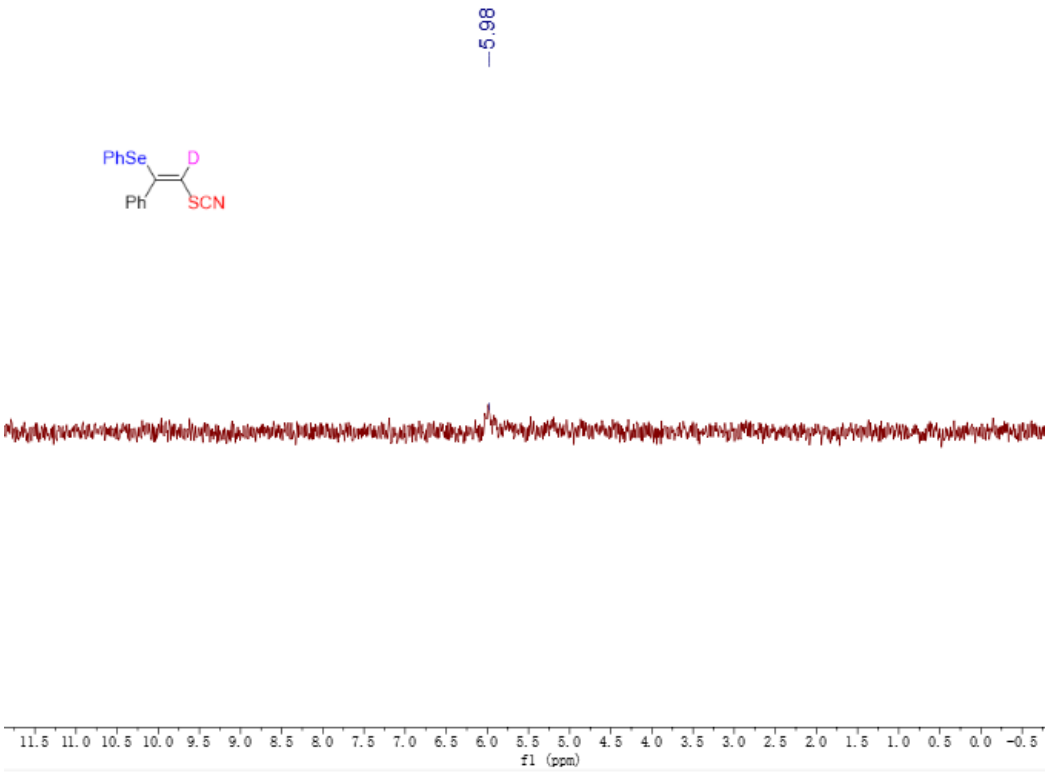
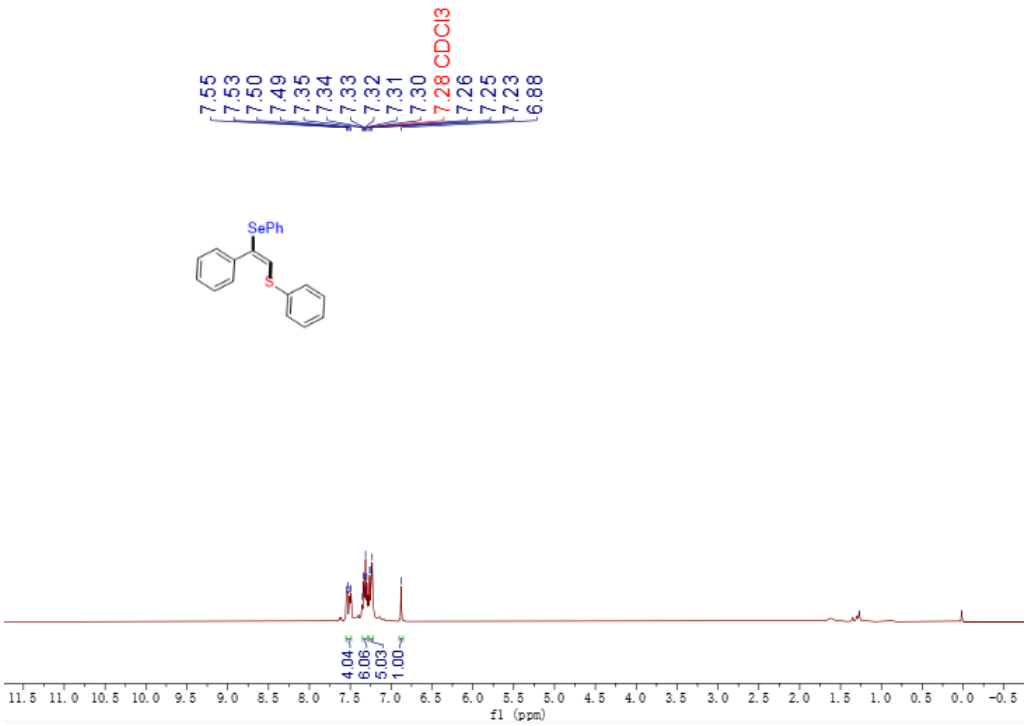


Figure S32. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (E)-phenyl(2-phenyl-2-(phenylselanyl)vinyl)sulfane (**6a**) in $CDCl_3$.



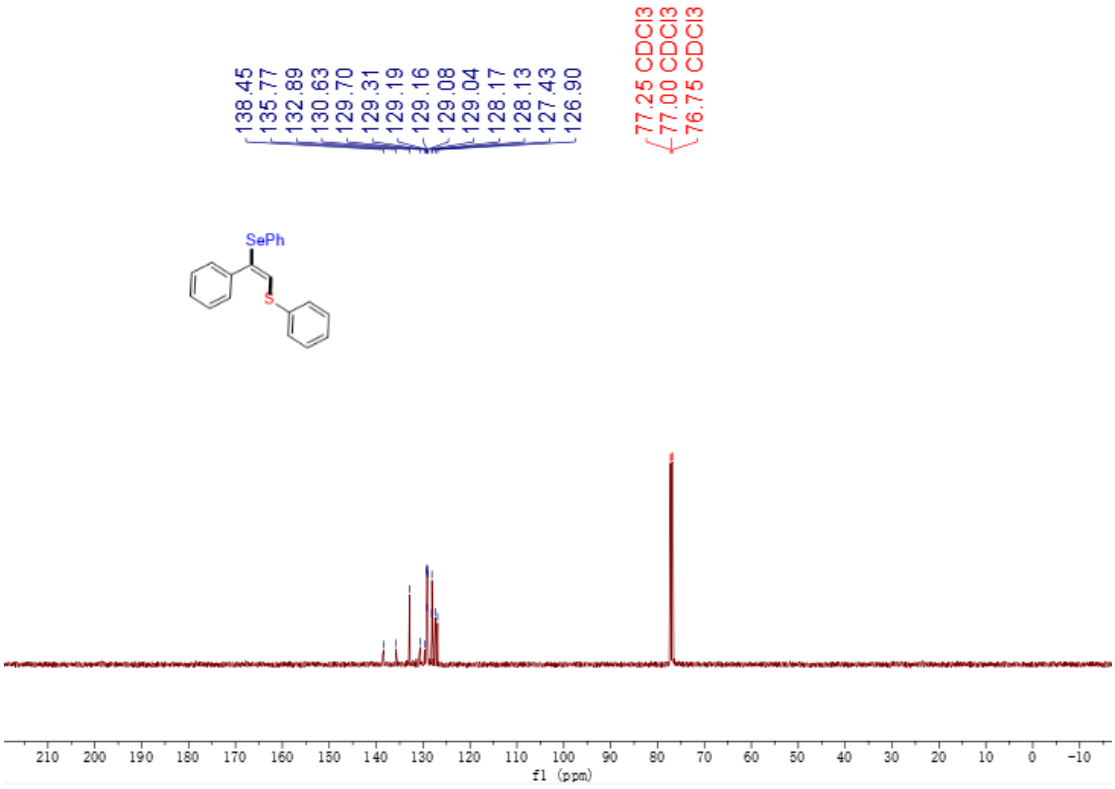
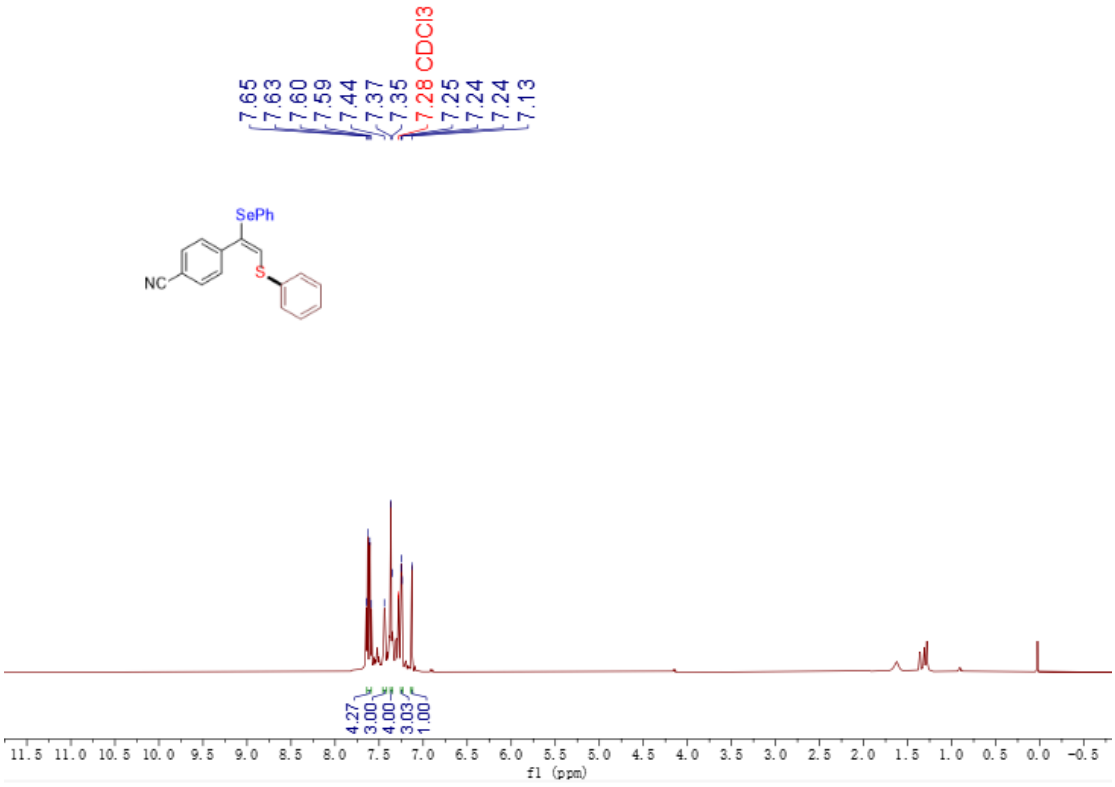


Figure S33. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-4-(1-(phenylselanyl)-2-(phenylthio)vinyl)benzonitrile (**6b**) in $CDCl_3$.



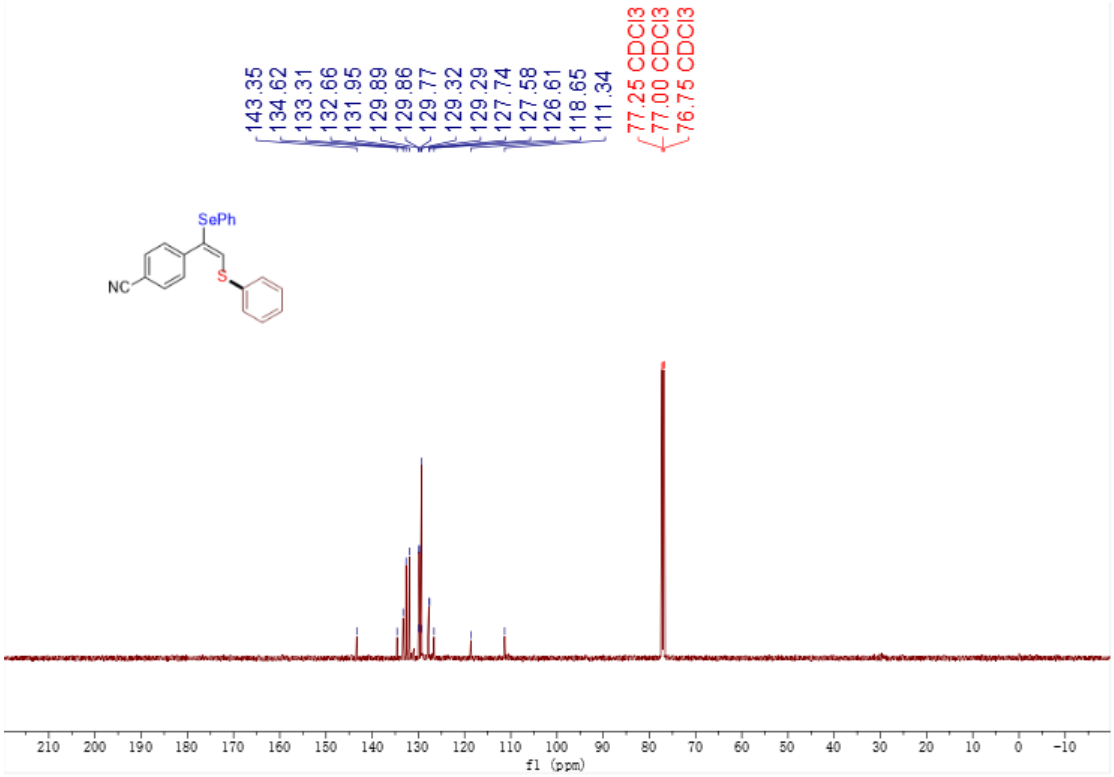
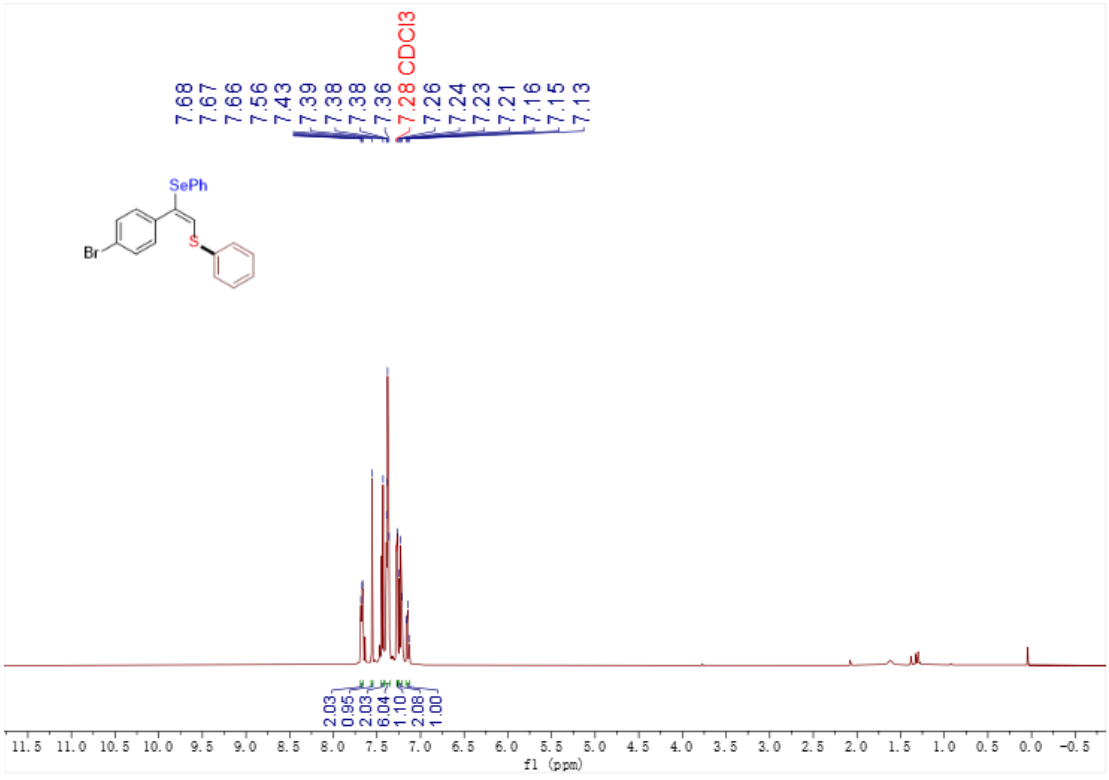


Figure S34. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (*E*)-(2-(4-bromophenyl)-2-(phenylselanyl)vinyl)(phenyl)sulfane (**6c**) in $CDCl_3$.



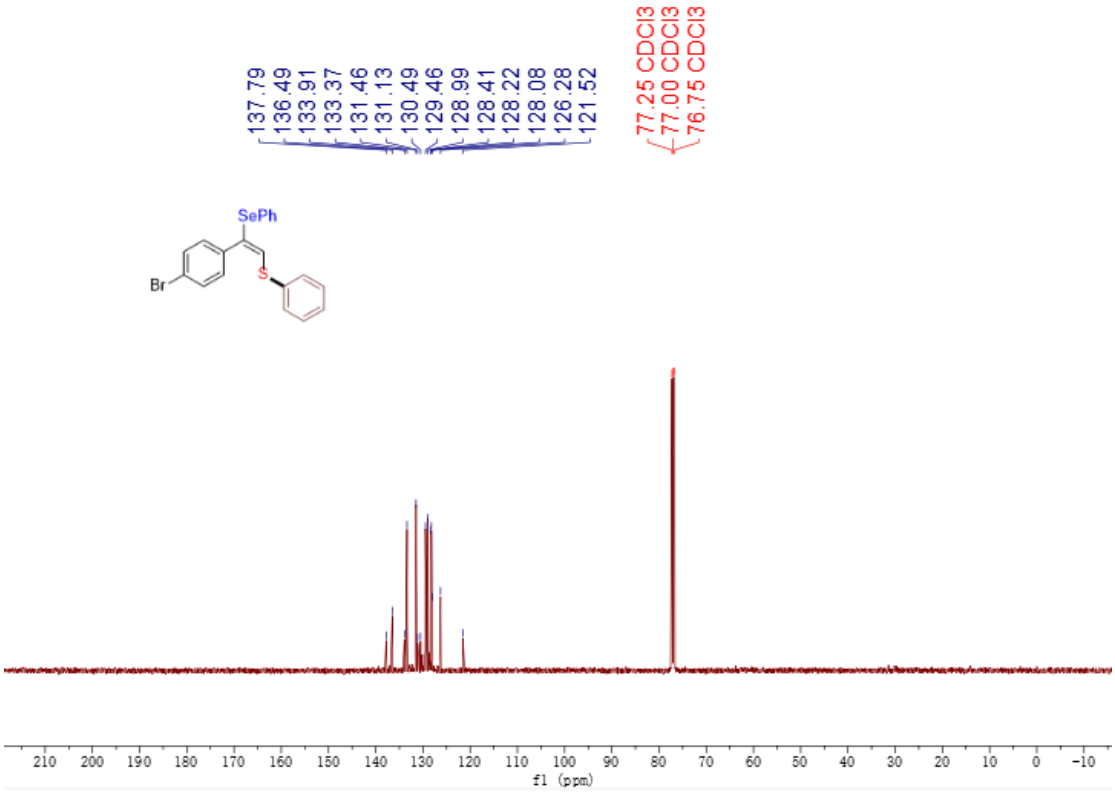
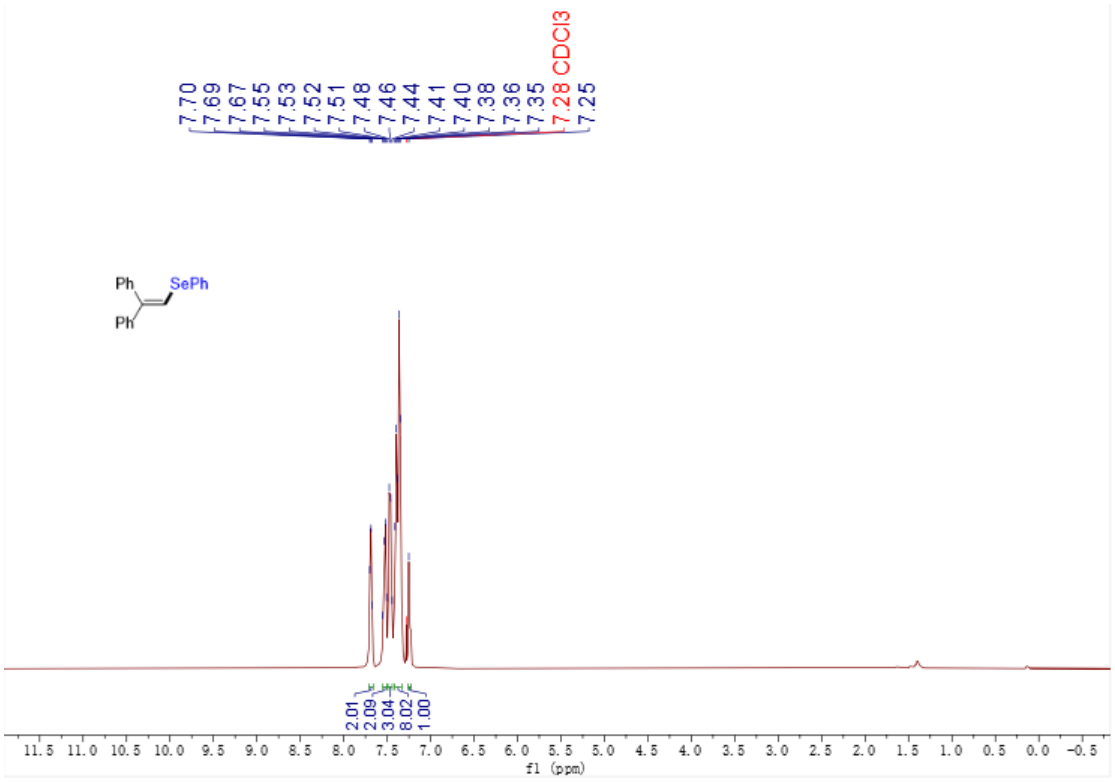


Figure S35. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (2,2-diphenylvinyl) (phenyl)selane (**8'**) in $CDCl_3$.



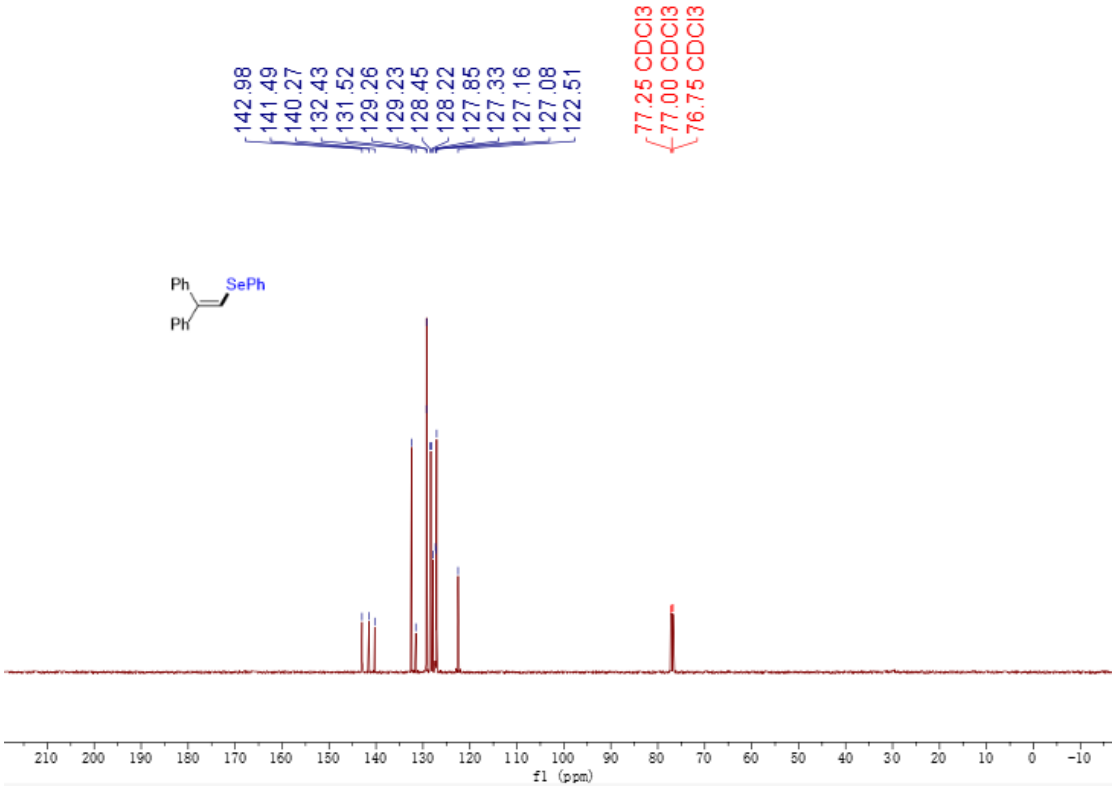
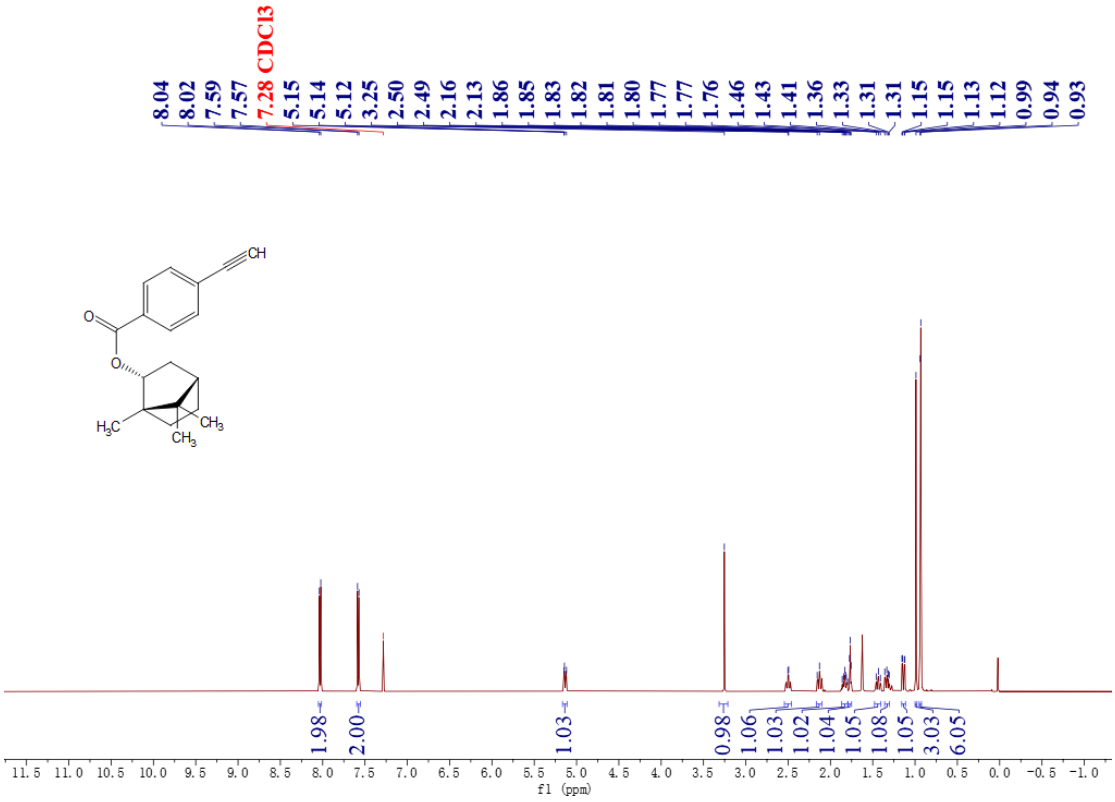


Figure S36. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo [2.2.1] heptan-2-yl 4-ethynylbenzoate (**1v**) in $CDCl_3$.



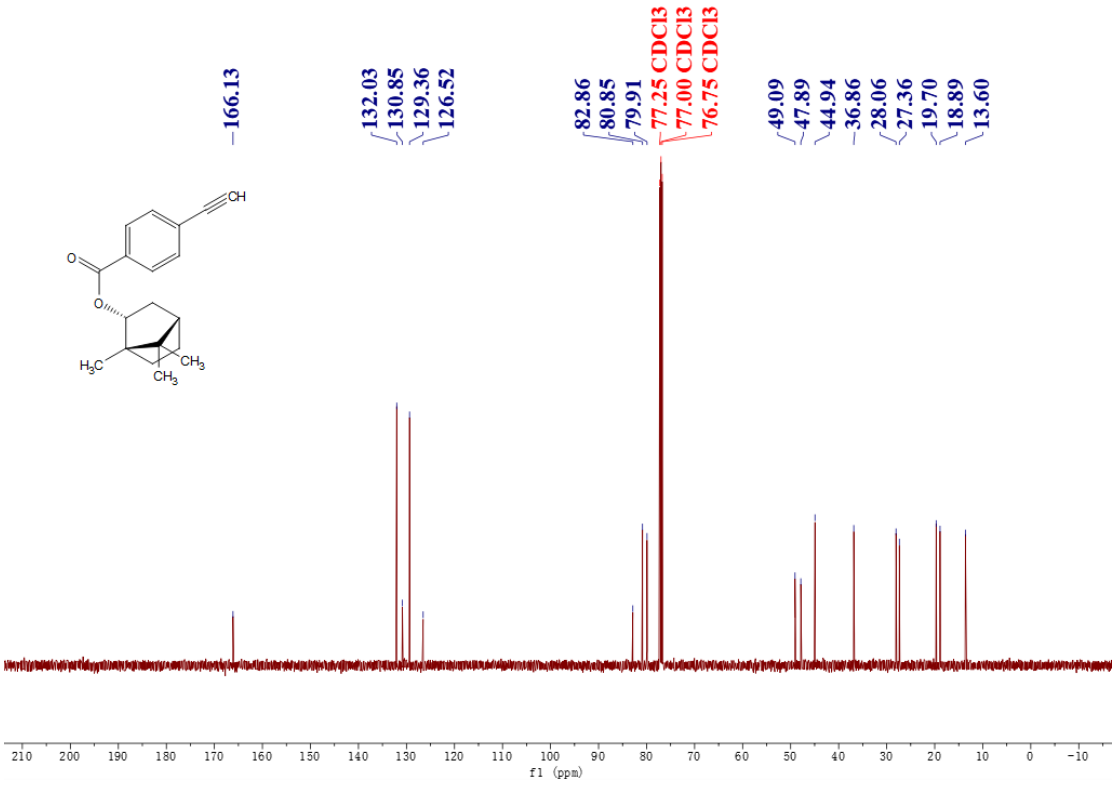


Figure S37. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for (2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-ethynylbenzoate (**1w**) in $CDCl_3$.

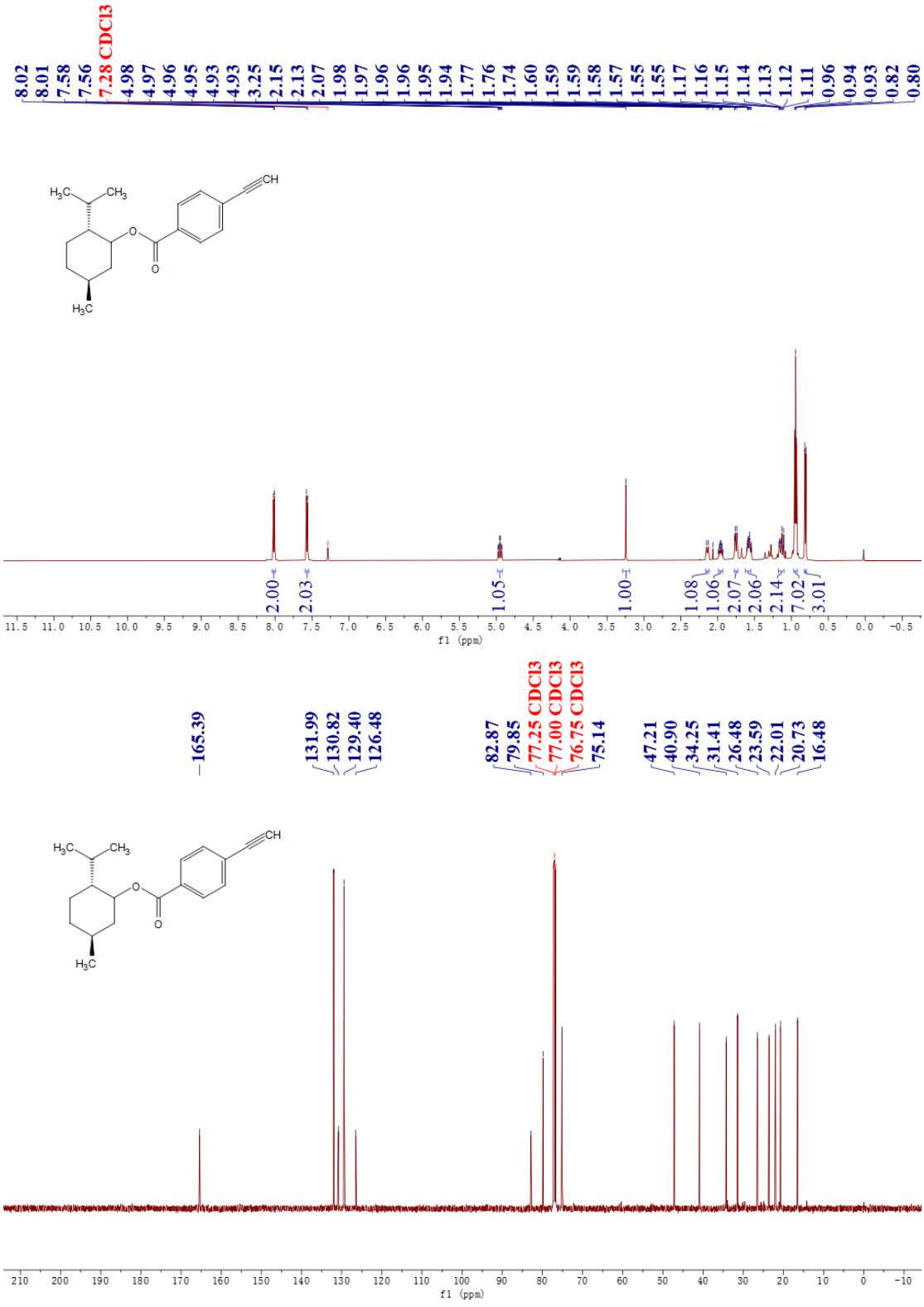


Figure S38. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for 1,2-bis(4-chlorophenyl)disele nide (**2b**) in $CDCl_3$.

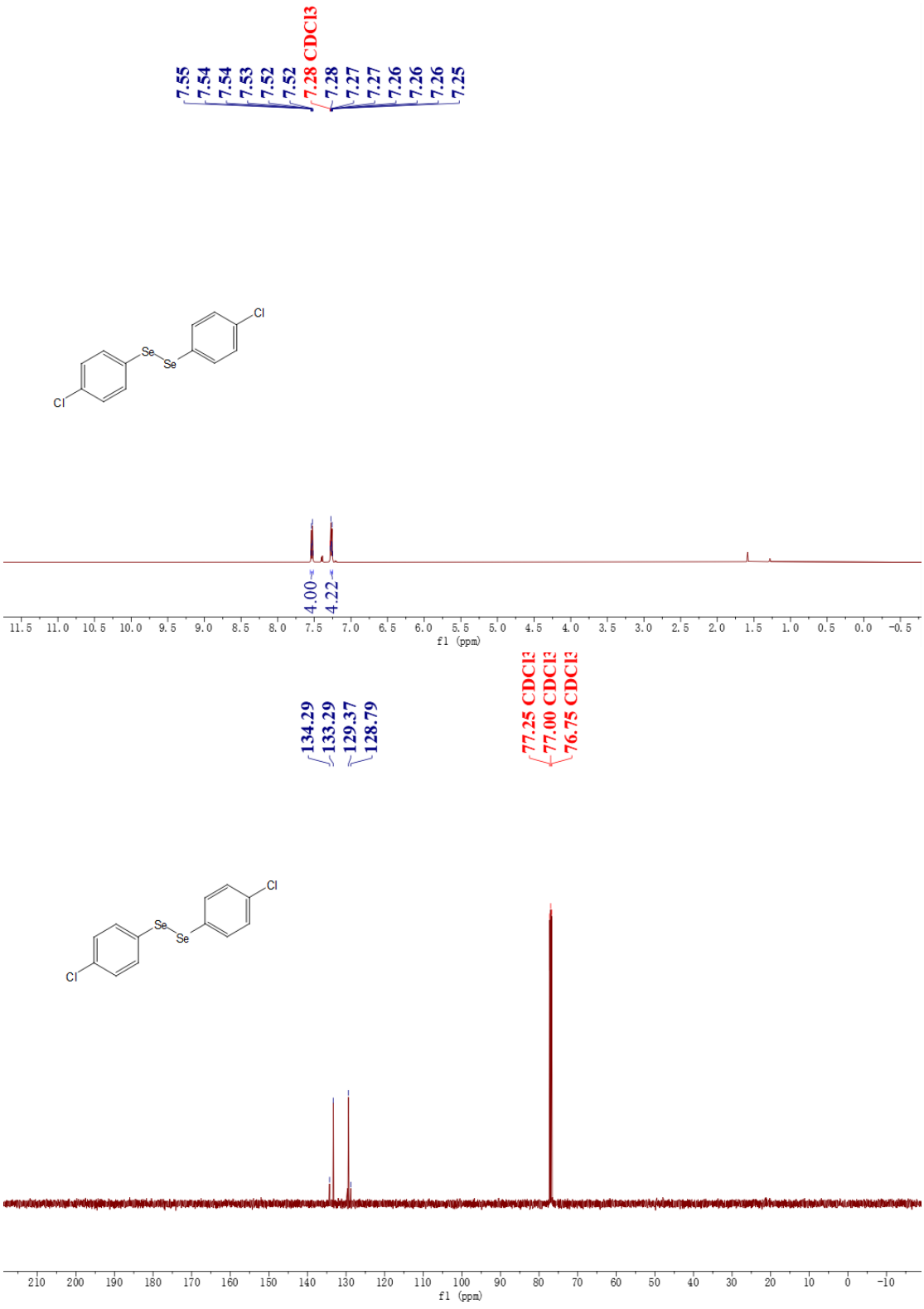
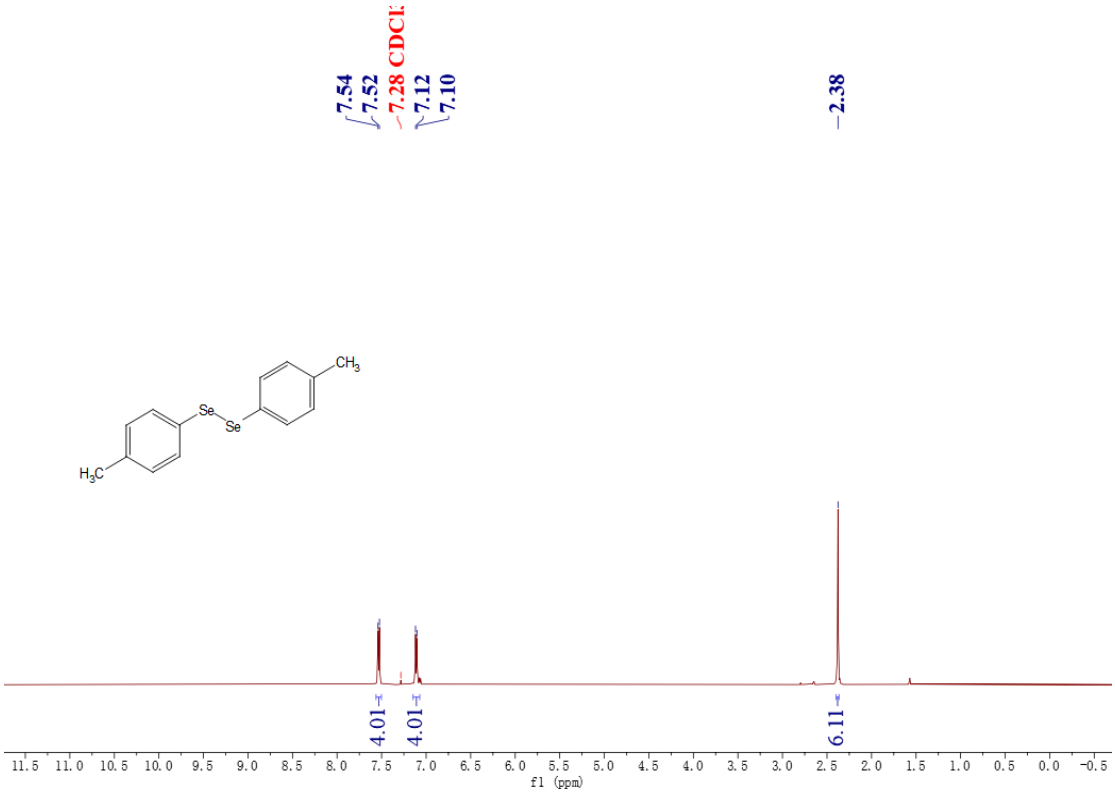


Figure S39. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for 1, 2-di-p-tolyldiselenide (**2c**) in $CDCl_3$.


7.54
7.52
7.28 CDCl3
7.12
7.10
2.38
CH3
Se
Se
H3C
4.01
4.01
6.11
f1 (ppm)

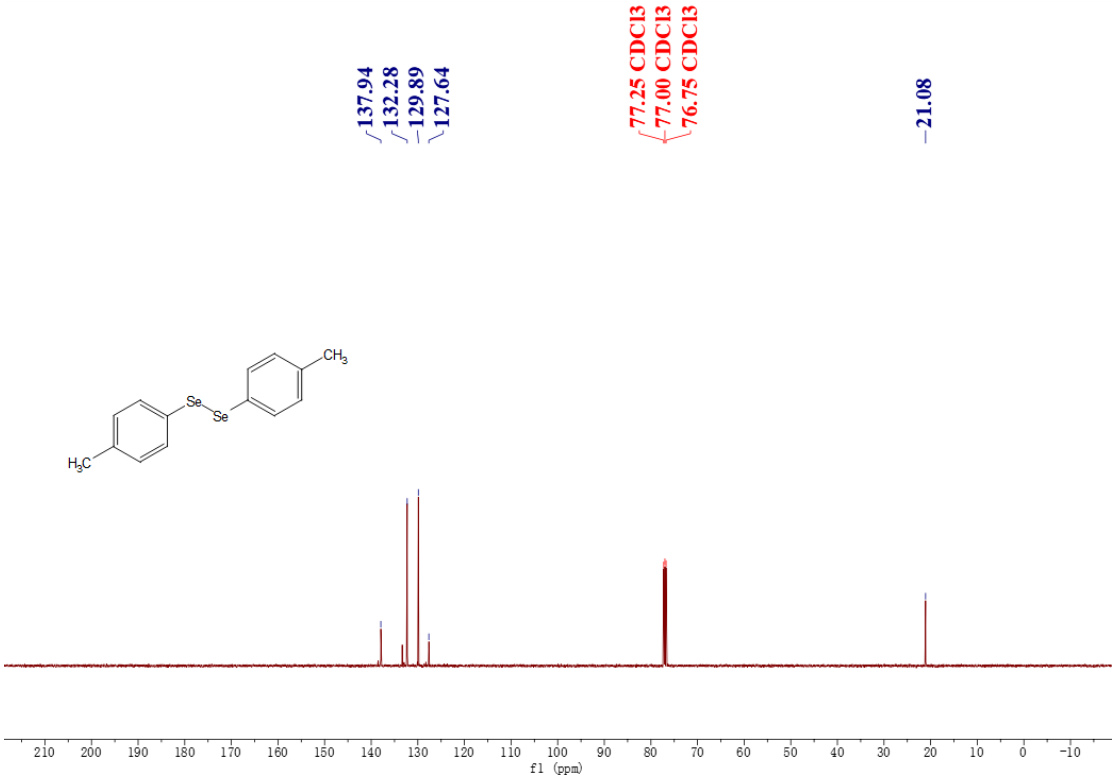
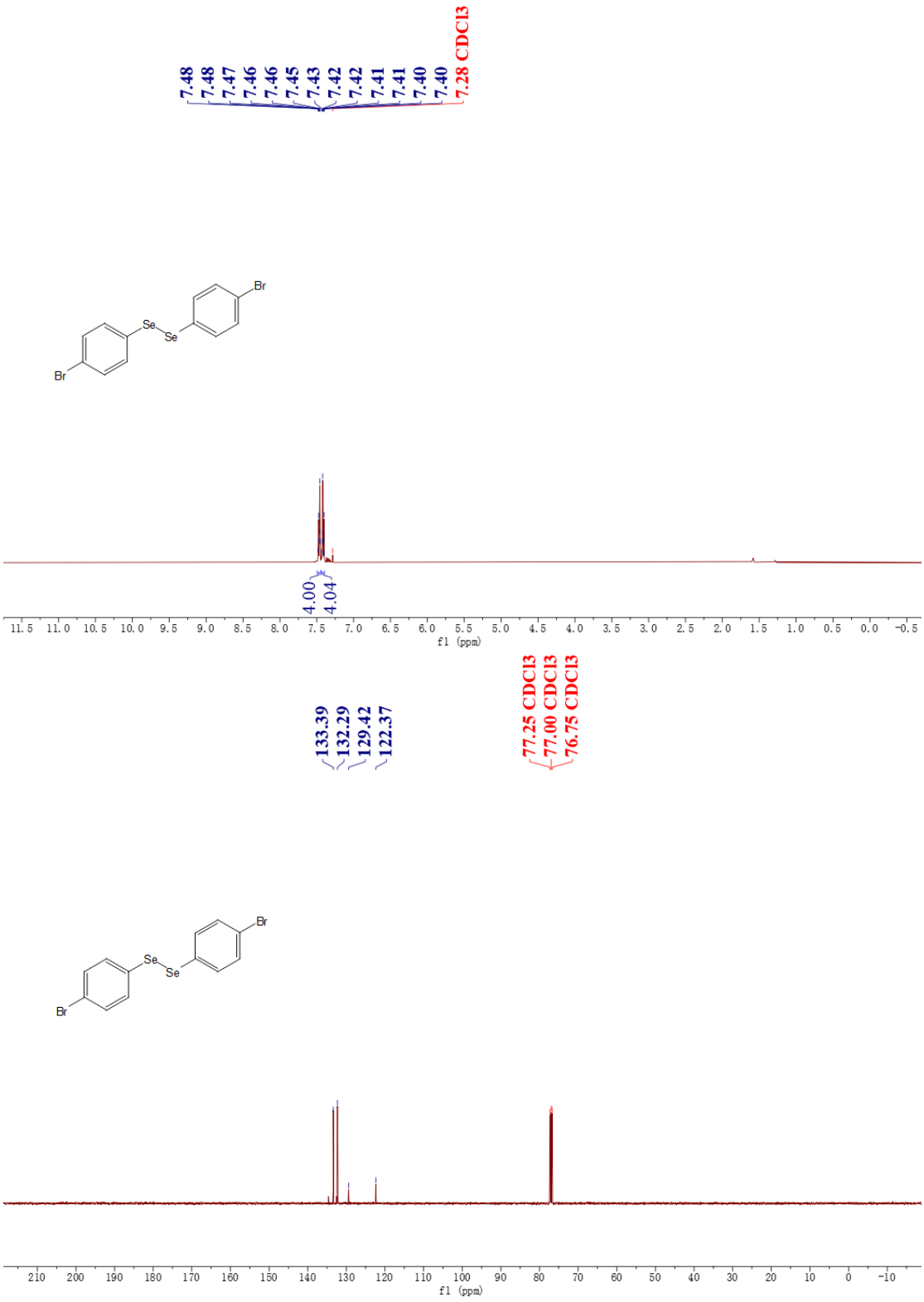

137.94
132.28
129.89
127.64
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
21.08
CH3
Se
Se
H3C
f1 (ppm)

Figure S40. The ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectrum for 1,2-bis(4-bromophenyl)diselenide (**2d**) in $CDCl_3$.



References

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