Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Regio- and stereo-selective electrochemical selenoalkylation of alkynes with 1,3-dicarbonyl compounds and diselenides

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Contents

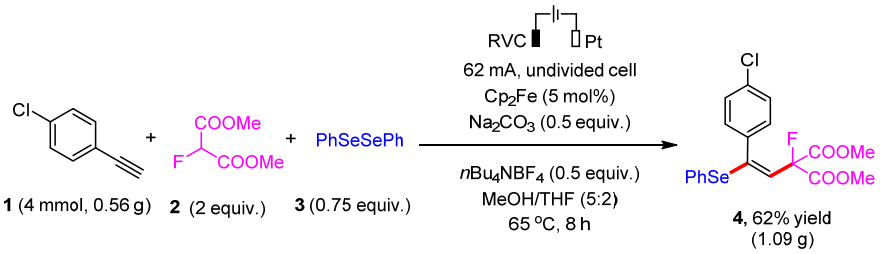
1. General Information

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to the general methods. Flash column chromatography was performed with silica gel (200–300 mesh). NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H NMR and $CDCl_3$ (77.2 ppm) for ^{13}C NMR. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (ESI HRMS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

2. General Procedure for the Electrolysis

General Procedure for the Model Reaction: A 20 mL three-necked beaker-type cell (Figure S1A) was charged with alkyne (0.20 mmol, 1.0 equiv.), diselenide (0.15 mmol, 0.75 equiv.), dimethyl 2-fluoromalonate (0.40 mmol, 2.0 equiv.), Cp_2Fe (5 mol%), Na_2CO_3 (0.10 mmol, 0.5 equiv.) and *n*-Bu_4NBF_4 (0.10 mmol, 0.5 equiv.). The cell was equipped with a reticulated vitreous carbon (RVC, 100 PPI, 1.2 cm x 0.8 cm x 0.8 cm) anode and a platinum plate (1 cm x 1 cm x 0.1 mm) cathode (Figure S1B), MeOH (5.0 mL) and THF (2.0 mL) were added. The electrolysis was carried out at 65 °C (oil bath temperature) using a constant current of 10 mA for 2.5 h. The reaction mixture was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product.

General Procedure for the Gram-Scale Synthesis of 4



The gram-scale electrosynthesis of **4** was conducted in a 100 mL three-necked round-bottomed flask (Figure S1C) with a piece of RVC (2.0 cm x 2.0 cm x 1.2 cm) as the anode, a Pt plate as the cathode (1.5 cm x 1.5 cm x 0.3 mm), and a constant current of 62 mA for 8.0 h at 65 °C. The reaction mixture consisted 4-chlorophenylacetylene (0.56 g, 4.0 mmol, 1.0 equiv.), diselenide (0.94 g, 3.0 mmol, 0.75 equiv.), dimethyl 2-fluoromalonate (1.20 g, 8.0 mmol, 2.0 equiv.), Cp_2Fe (37 mg, 5 mol%), Na_2CO_3 (0.21 g, 2.0 mmol, 0.5 equiv.) and *n*-Bu_4NBF_4 (0.66 g, 2.0 mmol, 0.5 equiv.), MeOH (60 mL) and THF (24 mL). When the reaction was complete, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **4** (1.09 g, 62% yield).

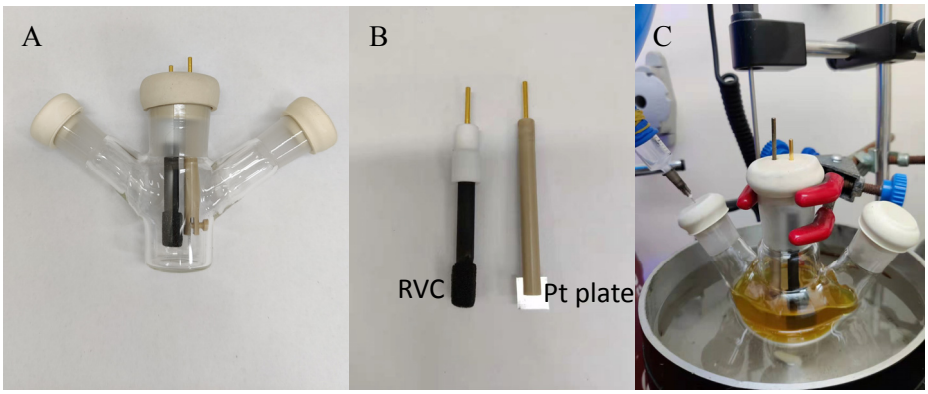


Figure S1. The electrolysis setup.

3. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte of *n*-Bu_4NBF_4 (0.1 M) in MeOH/THF (2:1, 5.0 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate was 100 mV/s.

We have previously reported the cyclic voltammetry experiments to demonstrate the role of ferrocene in the electrochemical generation of 1,3-dicarbonyl radicals [Ref.: *Org. Lett.,* 2021, **23**, 8585−8589]. In this study, we tested cyclic voltammograms (CVs) of 1-chloro-4-ethynylbenzene (**1**) and diphenyldiselenide (**3**) (Figure S2 and S3). These results suggested that effective electron transfer occurred between Cp_2Fe^+ produced through anodic oxidation of Cp_2Fe ($E_{p/2}$ = 0.46 V vs. Ag/AgCl) and the conjugate base ($E_{p/2}$ = 0.45 V vs. Ag/AgCl) of **2** instead of **2** ($E_{p/2}$ = 1.21 V vs. Ag/AgCl), **1** ($E_{p/2}$ = 1.43 V vs. Ag/AgCl) and **3** ($E_{p/2}$ = 1.49 V vs. Ag/AgCl). Cp_2Fe acts as a redox catalyst in the electrochemical process with the assistance of a base.

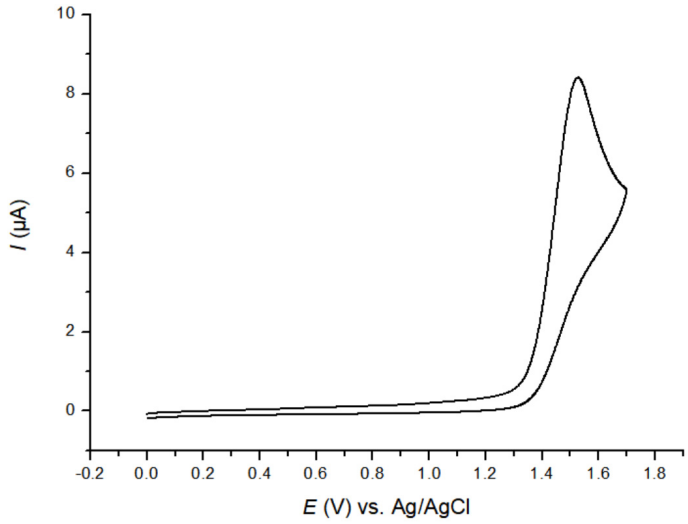


Figure S2. Cyclic voltammogram of 1-chloro-4-ethynylbenzene (**1**, 10 mM) in an electrolyte of *n*-Bu_4NBF_4 (0.1 M) in MeOH/THF (2:1, 5 mL). $E_{p/2}$ = 1.43 V.

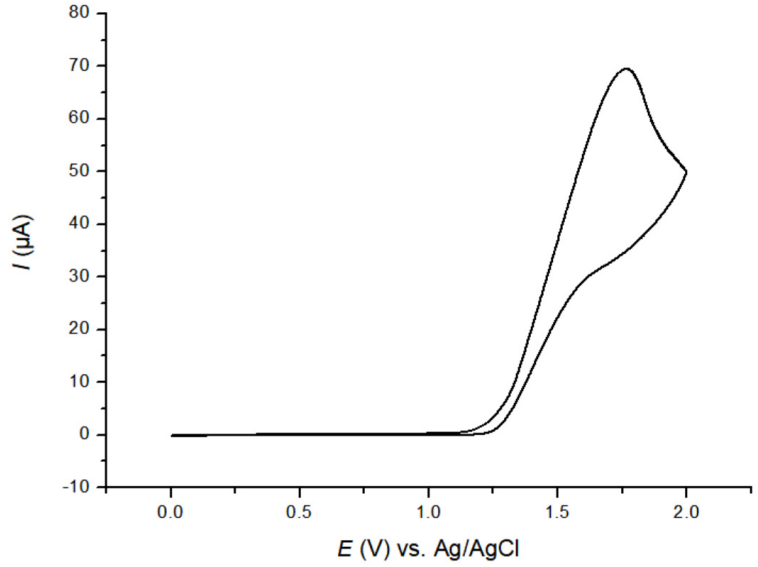
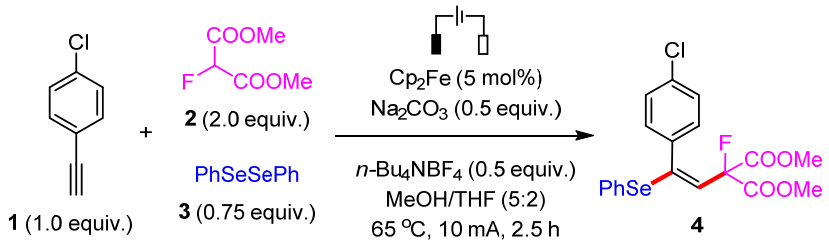


Figure S3. Cyclic voltammogram of diphenyldiselenide (**3**, 10 mM) in an electrolyte of *n*-Bu_4NBF_4 (0.1 M) in MeOH/THF (2:1, 5 mL). $E_{p/2}$ = 1.49 V.

4. Optimization of the Electrode Materials

Table S1 Optimization of the electrode combinations[a]



Entry	Electrode materials	Yield of **4**[b]
1	graphite rod(+)/Pt(-)	46
2	Pt(+)/Pt(-)	32
3	Pt(+)/RVC(-)	18
4	RVC(+)/Ni(-)	39
5	RVC(+)/Zn(-)	Trace
6	RVC(+)/Fe(-)	35

[a]Reaction condition:undivided cell, **1** (0.20 mmol), **2** (0.40 mmol), **3** (0.15 mmol), Cp_2Fe (5 mol%), Na_2CO_3 (0.10 mmol), *n*-Bu_4NBF_4 (0.10 mmol), MeOH/THF (5.0 mL/2.0 mL), 65 ℃, 10 mA, 2.5 h (4.6 F•mol^{-1}). [b]Yield determined by ^{1}H NMR analysis of the crude reaction mixture using coumarin as the internal standard.

5. Unsuccessful Substrates

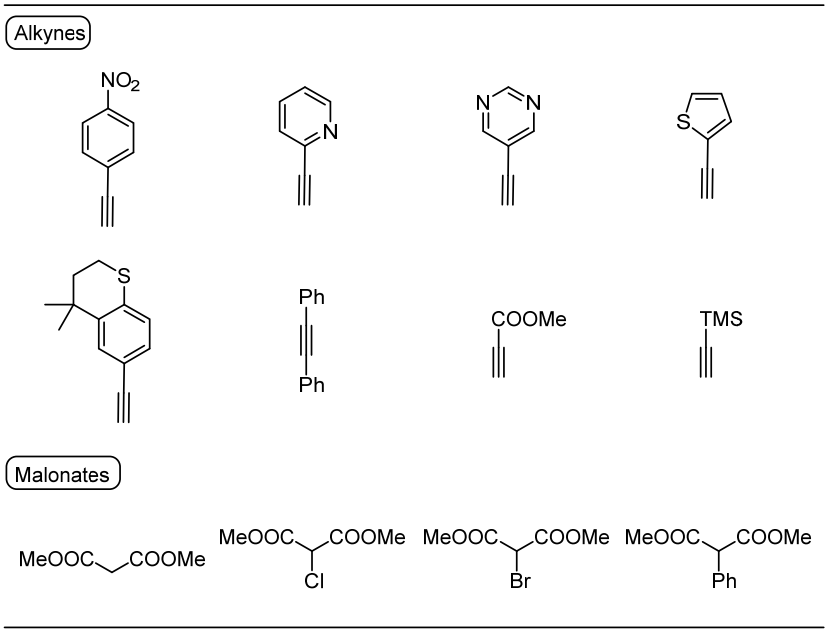
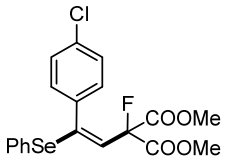
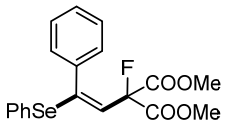


Figure S4. Unsuccessful substrates

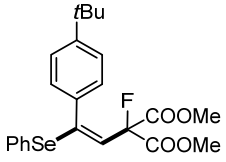
6. Characterization Data for the Electrolysis Products



Dimethyl (*E*)-2-(2-(4-chlorophenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (4). Yield = 78%; White solid; m.p. = 118.8−120.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.51 (m, 2H), 7.35–7.28 (m, 3H), 7.25–7.19 (m, 4H), 6.09 (d, J = 10.6 Hz, 1H), 3.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, $J_{C–F}$ = 27.1 Hz), 146.4 (d, $J_{C–F}$ = 6.7 Hz), 136.2, 135.1, 134.9, 130.6 (d, $J_{C–F}$ = 3.1 Hz), 129.7, 129.3, 128.1, 127.9, 120.3 (d, $J_{C–F}$ = 17.6 Hz), 91.3 (d, $J_{C–F}$ = 200.7 Hz), 53.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −140.7 (d, J = 10.6 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 464.9779, obsd 464.9778.

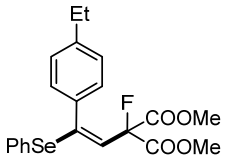


Dimethyl (*E*)-2-fluoro-2-(2-phenyl-2-(phenylselanyl)vinyl)malonate (5). Yield = 75%; White solid; m.p. = 54.8−56.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.54 (m, 2H), 7.35–7.25 (m, 8H), 6.03 (d, J = 9.4 Hz, 1H), 3.54 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, $J_{C–F}$ = 27.5 Hz), 148.4 (d, $J_{C–F}$ = 7.6 Hz), 136.5, 136.3, 129.6, 129.3 (d, $J_{C–F}$ = 3.0 Hz), 129.2, 129.0, 128.1, 127.9, 119.4 (d, $J_{C–F}$ = 17.8 Hz), 91.2 (d, $J_{C–F}$ = 199.6 Hz), 53.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.1 (d, J = 9.4 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 431.0168, obsd 431.0174.

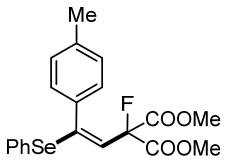


Dimethyl (*E*)-2-(2-(4-(*tert*-butyl)phenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (6). Yield = 82%; White solid; m.p. = 84.5−86.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.57 (m, 2H), 7.36–7.28 (m, 5H), 7.26–7.23 (m, 2H), 5.91 (d, J = 9.0 Hz, 1H), 3.50 (s, 6H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, $J_{C–F}$ = 27.2 Hz), 152.1, 148.9 (d, $J_{C–F}$ = 7.9 Hz),

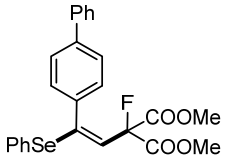
136.4, 133.5 (d, $J_{C–F}$ = 1.8 Hz), 129.7, 129.1, 129.1 (d, $J_{C–F}$ = 3.1 Hz), 128.4, 124.9, 118.8 (d, $J_{C–F}$ = 18.0 Hz), 91.3 (d, $J_{C–F}$ = 199.6 Hz), 53.5, 34.8, 31.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −137.0 (d, J = 9.0 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 487.0794, obsd 487.0796.



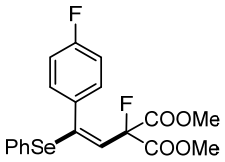
Dimethyl (*E*)-2-(2-(4-ethylphenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (7). Yield = 80%; White solid; m.p. = 86.9−88.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.61–7.55 (m, 2H), 7.37–7.29 (m, 3H), 7.25–7.20 (m, 2H), 7.14–7.09 (m, 2H), 5.95 (d, J = 8.9 Hz, 1H), 3.52 (s, 6H), 2.61 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, $J_{C–F}$ = 27.4 Hz), 148.8 (d, $J_{C–F}$ = 7.7 Hz), 145.3, 136.3, 133.8 (d, $J_{C–F}$ = 1.7 Hz), 129.6, 129.3 (d, $J_{C–F}$ = 3.1 Hz), 129.1, 128.4, 127.5, 119.0 (d, $J_{C–F}$ = 17.8 Hz), 91.2 (d, $J_{C–F}$ = 199.5 Hz), 53.5, 28.8, 15.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −137.3 (d, J = 8.4 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 459.0481, obsd 459.0482.



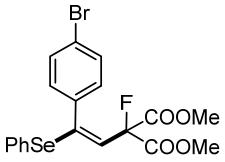
Dimethyl (*E*)-2-fluoro-2-(2-(phenylselanyl)-2-(*p*-tolyl)vinyl)malonate (8). Yield = 77%; White solid; m.p. = 114.5−116.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.55 (m, 2H), 7.36–7.29 (m, 3H), 7.23–7.18 (m, 2H), 7.11–7.06 (m, 2H), 5.97 (d, J = 9.2 Hz, 1H), 3.54 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, $J_{C–F}$ = 27.5 Hz), 148.6 (d, $J_{C–F}$ = 7.4 Hz), 139.0, 136.2, 133.6 (d, $J_{C–F}$ = 1.6 Hz), 129.6, 129.2 (d, $J_{C–F}$ = 3.1 Hz), 129.1, 128.6, 128.4, 119.1 (d, $J_{C–F}$ = 17.7 Hz), 91.2 (d, $J_{C–F}$ = 199.5 Hz), 53.5, 21.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −137.7 (d, J = 9.2 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 445.0325, obsd 445.0329.



Dimethyl (*E*)-2-(2-([1,1'-biphenyl]-4-yl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (9). Yield = 83%; White solid; m.p. = 113.4−115.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 7.55 (m, 4H), 7.53–7.49 (m, 2H), 7.45–7.40 (m, 2H), 7.39–7.29 (m, 6H), 6.05 (d, J = 9.6 Hz, 1H), 3.55 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, $J_{C–F}$ = 27.3 Hz), 147.9 (d, $J_{C–F}$ = 7.4 Hz), 141.6, 140.4, 136.2, 135.5 (d, $J_{C–F}$ = 1.5 Hz), 129.8 (d, $J_{C–F}$ = 3.3 Hz), 129.7, 129.2, 129.0, 128.2, 127.8, 127.2, 126.5, 119.6 (d, $J_{C–F}$ = 17.8 Hz), 91.3 (d, $J_{C–F}$ = 200.2 Hz), 53.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.5 (d, J = 9.6 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 507.0481, obsd 507.0481.

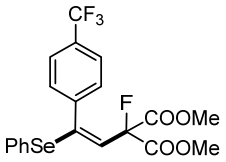


Dimethyl (*E*)-2-fluoro-2-(2-(4-fluorophenyl)-2-(phenylselanyl)vinyl)malonate (10). Yield = 81%; White solid; m.p. = 81.8−83.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.51 (m, 2H), 7.36–7.25 (m, 5H), 6.98–6.91 (m, 2H), 6.09 (d, J = 10.0 Hz, 1H), 3.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (d, $J_{C–F}$ = 27.3 Hz), 162.9 (d, $J_{C–F}$ = 249.1 Hz), 147.0 (d, $J_{C–F}$ = 7.0 Hz), 136.2, 132.6 (dd, $J_{C–F}$ = 3.6, 1.4 Hz), 131.3 (dd, $J_{C–F}$ = 8.4, 3.2 Hz), 129.7, 129.2, 128.0, 120.2 (d, $J_{C–F}$ = 17.7 Hz), 115.0 (d, $J_{C–F}$ = 21.7 Hz), 91.3 (d, $J_{C–F}$ = 200.2 Hz), 53.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −111.9, −139.3 (d, J = 10.0 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 449.0074, obsd 449.0082.

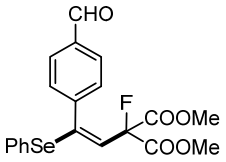


Dimethyl (*E*)-2-(2-(4-bromophenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (11). Yield = 79%; White solid; m.p. = 130.1−131.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.41–7.37 (m, 2H), 7.36–7.28 (m, 3H), 7.17–7.12 (m, 2H), 6.08 (d, J = 11.0 Hz, 1H), 3.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, $J_{C–F}$ = 27.1 Hz), 146.3 (d, $J_{C–F}$ = 6.6 Hz), 136.2, 135.7, 131.1, 130.8 (d, $J_{C–F}$ = 3.1 Hz), 129.7, 129.3, 127.9, 123.1, 120.3 (d, $J_{C–F}$ = 17.6 Hz), 91.4 (d, $J_{C–F}$ = 201.0 Hz), 53.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −140.9 (d, J = 11.0

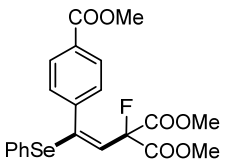
Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 508.9273, obsd 508.9281.



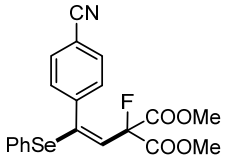
Dimethyl (*E*)-2-fluoro-2-(2-(phenylselanyl)-2-(4-(trifluoromethyl)phenyl)vinyl)malonate (12). Yield = 62%; White solid; m.p. = 105.8−107.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 4H), 7.38–7.27 (m, 5H), 6.13 (d, J = 12.4 Hz, 1H), 3.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, J_{C-F} = 26.9 Hz), 145.3 (d, J_{C-F} = 6.0 Hz), 140.6, 136.3, 130.6 (q, J_{C-F} = 32.5 Hz), 129.8, 129.5 (d, J_{C-F} = 3.1 Hz), 129.4, 127.6, 124.8 (q, J_{C-F} = 3.8 Hz), 124.0 (q, J_{C-F} = 272.3 Hz), 120.8 (d, J_{C-F} = 17.5 Hz), 91.6 (d, J_{C-F} = 202.0 Hz), 53.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.8, −143.5 (d, J = 12.4 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 499.0042, obsd 499.0047.



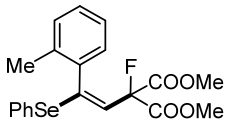
Dimethyl (*E*)-2-fluoro-2-(2-(4-formylphenyl)-2-(phenylselanyl)vinyl)malonate (13). Yield = 45%; White solid; m.p. = 119.5−121.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.78–7.74 (m, 2H), 7.53–7.49 (m, 2H), 7.42–7.37 (m, 2H), 7.35–7.26 (m, 3H), 6.20 (d, J = 12.5 Hz, 1H), 3.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 165.4 (d, J_{C-F} = 27.0 Hz), 145.2 (d, J_{C-F} = 5.9 Hz), 143.1, 136.2, 136.0, 129.8 (d, J_{C-F} = 3.0 Hz), 129.7, 129.4, 129.1, 127.5, 120.9 (d, J_{C-F} = 17.6 Hz), 91.5 (d, J_{C-F} = 201.7 Hz), 53.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −144.0 (d, J = 12.5 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 459.0117, obsd 459.0119.



Dimethyl (*E*)-2-fluoro-2-(2-(4-(methoxycarbonyl)phenyl)-2-(phenylselanyl)vinyl)malonate (14). Yield = 53%; White solid; m.p. = 106.2−108.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.90 (m, 2H), 7.54–7.50 (m, 2H), 7.35–7.26 (m, 5H), 6.16 (d, J = 11.4 Hz, 1H), 3.89 (s, 3H), 3.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 165.5 (d, $J_{C–F}$ = 27.1 Hz), 146.0 (d, $J_{C–F}$ = 6.4 Hz), 141.4, 136.2, 130.2, 129.7, 129.3, 129.2 (d, $J_{C–F}$ = 3.1 Hz),, 129.1, 127.7, 120.6 (d, $J_{C–F}$ = 17.6 Hz), 91.4 (d, $J_{C–F}$ = 201.2 Hz), 53.7, 52.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −142.1 (d, J = 11.4 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 489.0223, obsd 489.0230.

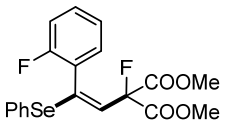


Dimethyl (*E*)-2-(2-(4-cyanophenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (15). Yield = 56%; White solid; m.p. = 125.2−127.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.50–7.46 (m, 2H), 7.36–7.26 (m, 5H), 6.23 (d, J = 13.4 Hz, 1H), 3.66 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, $J_{C–F}$ = 26.8 Hz), 144.0 (d, $J_{C–F}$ = 5.2 Hz), 141.9, 136.2, 131.6, 129.8 (2C), 129.5, 127.4, 121.4 (d, $J_{C–F}$ = 17.3 Hz), 118.6, 112.3, 91.7 (d, $J_{C–F}$ = 202.5 Hz), 53.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −145.9 (d, J = 13.4 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 456.0121, obsd 456.0125.

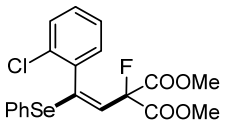


Dimethyl (*E*)-2-fluoro-2-(2-(phenylselanyl)-2-(*o*-tolyl)vinyl)malonate (16). Yield = 76%; White solid; m.p. = 69.5−72.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.54 (m, 2H), 7.39–7.29 (m, 3H), 7.19–7.05 (m, 3H), 7.03–6.99 (m, 1H), 6.00 (d, J = 10.0 Hz, 1H), 3.56 (s, 3H), 3.53 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (d, $J_{C–F}$ = 27.2 Hz), 165.6 (d, $J_{C–F}$ = 27.2 Hz), 147.3, 147.2, 136.8, 136.5 (d, $J_{C–F}$ = 2.4 Hz), 135.2 (d, $J_{C–F}$ = 1.4 Hz), 130.1, 129.6, 129.5 (d, $J_{C–F}$ = 2.8 Hz), 129.4, 128.9, 127.7, 125.1, 119.1 (d, $J_{C–F}$ = 18.0

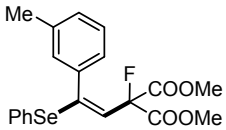
Hz), 91.2 (d, $J_{C–F}$ = 200.0 Hz), 53.5 (2C), 19.6 (2C); ^{19}F NMR (377 MHz, $CDCl_3$) δ −144.1 (d, J = 10.0 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 445.0325, obsd 445.0332.



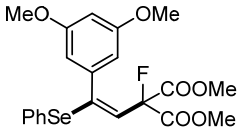
Dimethyl (*E*)-2-fluoro-2-(2-(2-fluorophenyl)-2-(phenylselanyl)vinyl)malonate (17). Yield = 69%; White solid; m.p. = 67.6−69.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.33–7.28 (m, 1H), 7.27–7.17 (m, 3H), 7.11 (td, J = 7.5, 1.6 Hz, 1H), 7.00 (td, J = 7.5, 1.6 Hz, 1H), 6.95–6.90 (m, 1H), 6.33 (d, J = 14.2 Hz, 1H), 3.68 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (d, $J_{C–F}$ = 26.9 Hz), 158.7 (dd, $J_{C–F}$ = 249.0, 2.8 Hz), 138.6 (d, $J_{C–F}$ = 5.3 Hz), 136.3, 131.1 (t, $J_{C–F}$ = 2.6 Hz), 130.6 (d, $J_{C–F}$ = 8.2 Hz), 129.4, 129.1, 127.7, 124.7 (d, $J_{C–F}$ = 15.7 Hz), 123.5 (d, $J_{C–F}$ = 3.7 Hz), 122.5 (d, $J_{C–F}$ = 16.9 Hz), 115.4 (d, $J_{C–F}$ = 21.6 Hz), 91.8 (d, $J_{C–F}$ = 202.9 Hz), 53.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −112.5, −151.0 (d, J = 14.2 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 449.0074, obsd 449.0080.



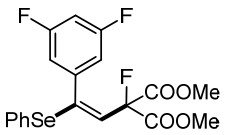
Dimethyl (*E*)-2-(2-(2-chlorophenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (18). Yield = 68%; White solid; m.p. = 91.9−93.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.51 (m, 2H), 7.35–7.24 (m, 4H), 7.16 (td, J = 7.6, 1.6 Hz, 1H), 7.11 (td, J = 7.6, 1.6 Hz, 1H), 7.04 (dd, J = 7.6, 1.6 Hz, 1H), 6.26 (d, J = 14.8 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, $J_{C–F}$ = 26.1 Hz), 165.0 (d, $J_{C–F}$ = 27.5 Hz), 142.1 (d, $J_{C–F}$ = 5.1 Hz), 136.6, 135.5, 132.5 (d, $J_{C–F}$ = 2.9 Hz), 130.9 (d, $J_{C–F}$ = 2.8 Hz), 129.8, 129.4, 129.2, 127.6, 126.1, 121.6 (d, $J_{C–F}$ = 17.0 Hz), 91.9 (d, $J_{C–F}$ = 203.0 Hz), 53.8, 53.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −151.5 (d, J = 14.8 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 464.9779, obsd 464.9778.



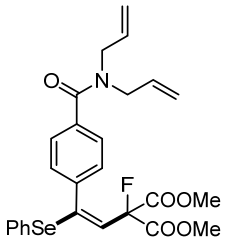
Dimethyl (*E*)-2-fluoro-2-(2-(phenylselanyl)-2-(m-tolyl)vinyl)malonate (19). Yield = 61%; White solid; m.p. = 44.3−45.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.57 (m, 2H), 7.37–7.30 (m, 3H), 7.20–7.07 (m, 4H), 5.94 (d, J = 8.8 Hz, 1H), 3.54 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, $J_{C–F}$ = 27.5 Hz), 148.8 (d, $J_{C–F}$ = 7.7 Hz), 137.6, 136.4, 129.8 (3C), 129.7, 129.2, 128.2, 127.9, 126.3 (d, $J_{C–F}$ = 3.1 Hz), 118.8 (d, $J_{C–F}$ = 17.7 Hz), 91.1 (d, $J_{C–F}$ = 199.2 Hz), 53.5, 21.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −137.4 (d, J = 8.8 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 445.0325, obsd 445.0333.



Dimethyl (*E*)-2-(2-(3,5-dimethoxyphenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (20). Yield = 68%; Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.58 (m, 2H), 7.39–7.31 (m, 3H), 6.50–6.46 (m, 2H), 6.37 (t, J = 2.3 Hz, 1H), 5.92 (d, J = 8.8 Hz, 1H), 3.76 (s, 6H), 3.58 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, $J_{C–F}$ = 27.3 Hz), 160.2, 148.2 (d, $J_{C–F}$ = 7.7 Hz), 138.3 (d, $J_{C–F}$ = 1.7 Hz), 136.3, 129.7, 129.3, 128.1, 118.9 (d, $J_{C–F}$ = 17.9 Hz), 107.1 (d, $J_{C–F}$ = 3.2 Hz), 101.8, 91.2 (d, $J_{C–F}$ = 199.5 Hz), 55.6, 53.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.2 (d, J = 8.8 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 491.0380, obsd 491.0387.

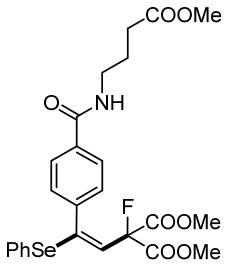


Dimethyl (*E*)-2-(2-(3,5-difluorophenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (21). Yield = 60%; White solid; m.p. = 61.6−63.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.38–7.29 (m, 3H), 6.80–6.74 (m, 2H), 6.72–6.66 (m, 1H), 6.12 (d, J = 12.6 Hz, 1H), 3.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (d, $J_{C–F}$ = 26.8 Hz), 162.2 (dd, $J_{C–F}$ = 249.5, 12.8 Hz), 144.1, 140.0 (t, $J_{C–F}$ = 9.8 Hz), 136.3, 129.8, 129.5, 127.4, 120.9 (d, $J_{C–F}$ = 17.3 Hz), 112.3 (dd, $J_{C–F}$ = 26.3, 3.2 Hz), 104.1 (t, $J_{C–F}$ = 25.2 Hz), 91.5 (d, $J_{C–F}$ = 202.2 Hz), 53.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −109.7 (t, J = 8.0 Hz), −144.6 (d, J = 12.6 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 466.9980, obsd 466.9985.



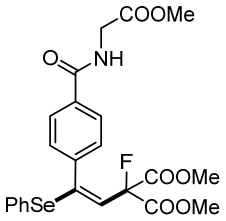
Dimethyl

(*E*)-2-(2-(4-(diallylcarbamoyl)phenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (22). Yield = 49%; White solid; m.p. = 73.5−75.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.55–7.51 (m, 2H), 7.33–7.26 (m, 7H), 6.13 (d, J = 10.6 Hz, 1H), 5.89–5.65 (m, 2H), 5.25–5.15 (m, 4H), 4.15–4.07 (m, 2H), 3.78–3.71 (m, 2H), 3.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 165.6 (d, $J_{C–F}$ = 27.2 Hz), 146.9 (d, $J_{C–F}$ = 6.8 Hz), 138.0, 136.5, 136.3, 133.2, 132.8, 129.6, 129.3 (d, $J_{C–F}$ = 3.1 Hz), 129.2, 127.8, 126.1, 120.2 (d, $J_{C–F}$ = 17.6 Hz), 117.9, 117.8, 91.2 (d, $J_{C–F}$ = 200.6 Hz), 53.6, 50.8, 47.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ −140.0 (d, J = 10.6 Hz); ESI HRMS *m/z* $(M+H)^+$ calcd 532.1033, obsd 532.1035.



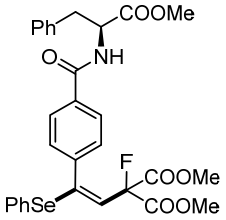
Dimethyl

(*E*)-2-fluoro-2-(2-(4-((4-methoxy-4-oxobutyl)carbamoyl)phenyl)-2-(phenylselanyl)vinyl) malonate (23). Yield = 60%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 2H), 7.56–7.50 (m, 2H), 7.35–7.27 (m, 5H), 6.62 (t, J = 5.6 Hz, 1H), 6.13 (d, J = 11.2 Hz, 1H), 3.67 (s, 3H), 3.60 (s, 6H), 3.49 (q, J = 6.6 Hz, 2H), 2.45 (t, J = 6.6 Hz, 2H), 2.00–1.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 166.8, 165.6 (d, $J_{C–F}$ = 27.2 Hz), 146.2 (d, $J_{C–F}$ = 6.5 Hz), 140.0, 136.2, 134.5, 129.7, 129.4 (d, $J_{C–F}$ = 3.0 Hz), 129.3, 127.8, 126.5, 120.5 (d, $J_{C–F}$ = 17.6 Hz), 91.4 (d, $J_{C–F}$ = 200.9 Hz), 53.7, 52.0, 39.9, 31.9, 24.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −141.7 (d, J = 11.2 Hz); ESI HRMS *m/z* $(M+H)^+$ calcd 552.0931, obsd 552.0931.



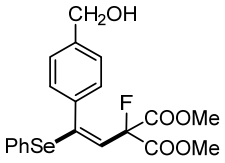
Dimethyl

(*E*)-2-fluoro-2-(2-(4-((2-methoxy-2-oxoethyl)carbamoyl)phenyl)-2-(phenylselanyl)vinyl) malonate (24). Yield = 69%; Yellow solid; m.p. = 79.5−81.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.68 (m, 2H), 7.56–7.49 (m, 2H), 7.37–7.24 (m, 5H), 6.81 (t, J = 5.1 Hz, 1H), 6.15 (d, J = 11.8 Hz, 1H), 4.21 (d, J = 5.1 Hz, 2H), 3.79 (s, 3H), 3.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 166.8, 165.5 (d, $J_{C–F}$ = 27.1 Hz), 145.9 (d, $J_{C–F}$ = 6.2 Hz), 140.4, 136.1, 133.6, 129.7, 129.4 (d, $J_{C–F}$ = 3.1 Hz), 129.3, 127.7, 126.7, 120.5 (d, $J_{C–F}$ = 17.5 Hz), 91.4 (d, $J_{C–F}$ = 201.1 Hz), 53.7, 52.6, 41.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −142.3 (d, J = 11.8 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 546.0438, obsd 546.0441.

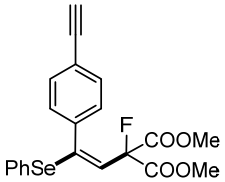


Dimethyl

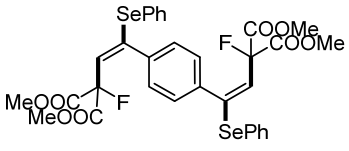
(*S*,*E*)-2-fluoro-2-(2-(4-((1-methoxy-1-oxo-3-phenylpropan-2-yl)carbamoyl)phenyl)-2-(phenylselanyl)vinyl)malonate (25). Yield = 61%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.60 (m, 2H), 7.54–7.51 (m, 2H), 7.34–7.26 (m, 8H), 7.13–7.10 (m, 2H), 6.58 (d, J = 7.6 Hz, 1H), 6.12 (d, J = 11.6 Hz, 1H), 5.08–5.03 (m, 1H), 3.76 (s, 3H), 3.59 (s, 3H), 3.58 (s, 3H), 3.29–3.19 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 166.1, 165.5 (d, $J_{C–F}$ = 27.6 Hz), 145.8 (d, $J_{C–F}$ = 6.3 Hz), 140.4, 136.1, 135.9, 133.8, 129.7, 129.4, 129.4 (d, $J_{C–F}$ = 3.0 Hz), 129.3, 128.8, 127.7, 127.4, 126.6, 120.4 (d, $J_{C–F}$ = 17.5 Hz), 91.4 (d, $J_{C–F}$ = 201.4 Hz), 53.7, 52.6, 38.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ −142.6 (d, J = 11.6 Hz); ESI HRMS *m/z* $(M+H)^+$ calcd 614.1088, obsd 614.1087.



Dimethyl (*E*)-2-fluoro-2-(2-(4-(hydroxymethyl)phenyl)-2-(phenylselanyl)vinyl)malonate (26). Yield = 73%; White solid; m.p. = 69.4.8−71.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.55 (m, 2H), 7.37–7.27 (m, 7H), 6.02 (d, J = 10.0 Hz, 1H), 4.65 (s, 2H), 3.57 (s, 6H), 1.89 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, $J_{C–F}$ = 27.5 Hz), 147.9 (d, $J_{C–F}$ = 7.0 Hz), 141.8, 136.2, 135.9, 129.7, 129.4 (d, $J_{C–F}$ = 3.0 Hz), 129.2, 128.2, 126.4, 119.5 (d, $J_{C–F}$ = 17.6 Hz), 91.3 (d, $J_{C–F}$ = 199.9 Hz), 65.0, 53.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −139.3 (d, J = 10.0 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 461.0274, obsd 461.0279.

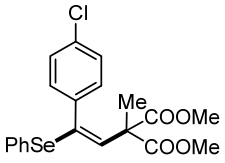


Dimethyl (*E*)-2-(2-(4-ethynylphenyl)-2-(phenylselanyl)vinyl)-2-fluoromalonate (27). Yield = 41%; White solid; m.p. = 115.6−117.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.40–7.36 (m, 2H), 7.34–7.27 (m, 3H), 7.25–7.21 (m, 2H), 6.10 (d, J = 10.8 Hz, 1H), 3.59 (s, 6H), 3.09 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, $J_{C–F}$ = 27.1 Hz), 146.8 (d, $J_{C–F}$ = 6.9 Hz), 137.2 (d, $J_{C–F}$ = 1.3 Hz), 136.2, 131.6, 129.7, 129.3 (d, $J_{C–F}$ = 1.7 Hz), 129.2, 127.9, 122.6, 120.3 (d, $J_{C–F}$ = 17.7 Hz), 91.3 (d, $J_{C–F}$ = 200.7 Hz), 83.3, 78.4, 53.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −140.4 (d, J = 10.8 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 455.0168, obsd 455.0164.

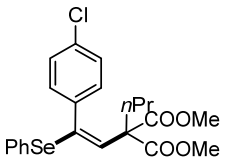


Tetramethyl 2,2'-((1*E*,1'*E*)-1,4-phenylenebis(2-(phenylselanyl)ethene-2,1-diyl))bis(2-fluoromalonate) (28). Yield = 52%; White solid; m.p. = 126.3−128.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.53 (m, 4H), 7.36–7.30 (m, 6H), 7.25–7.21 (m, 4H), 6.01 (d, J = 11.1 Hz, 2H), 3.56 (s,

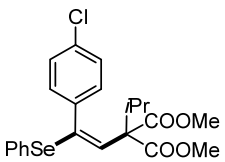
12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (d, $J_{C–F}$ = 27.1 Hz), 146.5 (d, $J_{C–F}$ = 6.6 Hz), 137.2, 136.0, 129.8, 129.2, 128.7 (d, $J_{C–F}$ = 3.0 Hz), 128.1, 120.1 (d, $J_{C–F}$ = 17.6 Hz), 91.4 (d, $J_{C–F}$ = 200.9 Hz), 53.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −141.4 (d, J = 11.1 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 760.9975, obsd 760.9983.



Dimethyl (*E*)-2-(2-(4-chlorophenyl)-2-(phenylselanyl)vinyl)-2-methylmalonate (29). Yield = 70%; White solid; m.p. = 88.5−90.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.27–7.20 (m, 3H), 7.18–7.13 (m, 2H), 7.05–7.00 (m, 2H), 6.45 (s, 1H), 3.50 (s, 6H), 1.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 136.5, 135.2, 134.7, 133.8, 130.8, 130.5, 129.3, 129.0, 128.4, 128.0, 56.5, 52.9, 23.5; ESI HRMS *m/z* $(M+Na)^+$ calcd 461.0029, obsd 461.0035.

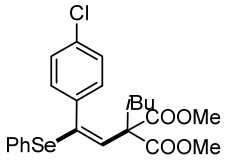


Dimethyl (*E*)-2-(2-(4-chlorophenyl)-2-(phenylselanyl)vinyl)-2-propylmalonate (30). Yield = 67%; White solid; m.p. = 80.6−82.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.29–7.22 (m, 3H), 7.18–7.14 (m, 2H), 6.99–6.95 (m, 2H), 6.54 (s, 1H), 3.50 (s, 6H), 1.86–1.79 (m, 2H), 1.24–1.16 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 136.5, 135.4, 134.6, 133.9, 130.2, 129.5, 129.3, 129.0, 128.5, 128.0, 60.1, 52.7, 38.8, 18.0, 14.4; ESI HRMS *m/z* $(M+Na)^+$ calcd 489.0342, obsd 489.0345.

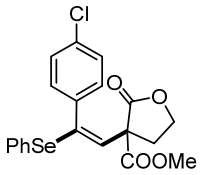


Dimethyl (*E*)-2-(2-(4-chlorophenyl)-2-(phenylselanyl)vinyl)-2-isopropylmalonate (31). Yield = 62%; White solid; m.p. = 88.2−90.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.43 (m,

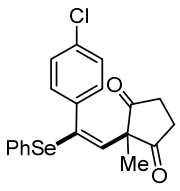
2H), 7.28–7.21 (m, 3H), 7.17–7.12 (m, 2H), 7.04–6.99 (m, 2H), 6.31 (s, 1H), 3.41 (s, 6H), 2.42–2.33 (m, 1H), 0.97 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 136.5, 135.5, 134.3, 133.7, 130.5, 129.3, 129.2, 129.0, 128.5, 127.8, 64.1, 52.2, 35.4, 19.1; ESI HRMS *m/z* $(M+Na)^+$ calcd 489.0342, obsd 489.0349.



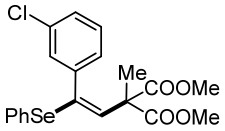
Dimethyl (*E*)-2-(2-(4-chlorophenyl)-2-(phenylselanyl)vinyl)-2-isobutylmalonate (32). Yield = 60%; White solid; m.p. = 83.3−85.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.29–7.22 (m, 3H), 7.18–7.14 (m, 2H), 6.97–6.92 (m, 2H), 6.65 (s, 1H), 3.50 (s, 6H), 1.88 (d, J = 6.6 Hz, 2H), 1.70–1.61 (m, 1H), 0.84 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 136.5, 135.7, 134.4, 133.9, 130.2, 129.6, 129.3, 128.9, 128.6, 128.0, 59.3, 52.8, 45.3, 24.8, 23.7; ESI HRMS *m/z* $(M+Na)^+$ calcd 503.0499, obsd 503.0505.



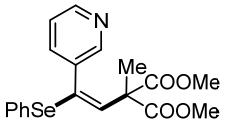
Methyl (*S*,*E*)-3-(2-(4-chlorophenyl)-2-(phenylselanyl)vinyl)-2-oxotetrahydrofuran-3-carboxylate (33). Yield = 64%; White solid; m.p. = 79.7−81.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.28–7.19 (m, 5H), 7.14–7.09 (m, 2H), 6.34 (s, 1H), 4.16–4.10 (m, 2H), 3.68 (s, 3H), 2.35–2.29 (m, 1H), 2.11–2.02 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 168.6, 138.1, 136.6, 135.3, 134.4, 130.4, 129.5, 128.7, 128.5, 128.4, 127.6, 66.5, 56.7, 53.7, 34.2; ESI HRMS *m/z* $(M+Na)^+$ calcd 458.9873, obsd 458.9875.



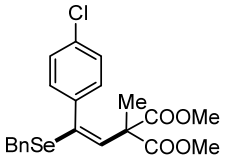
(*E*)-2-(2-(4-Chlorophenyl)-2-(phenylselanyl)vinyl)-2-methylcyclopentane-1,3-dione (34). Yield = 58%; Light yellow solid; m.p. = 65.2−67.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.27–7.20 (m, 3H), 7.17–7.12 (m, 2H), 6.90–6.83 (m, 2H), 5.87 (s, 1H), 2.58–2.49 (m, 2H), 1.91–1.80 (m, 2H), 1.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.1, 137.7, 137.3, 135.5, 134.4, 132.3, 131.1, 129.4, 128.6, 128.4, 128.3, 59.1, 35.0, 23.2; ESI HRMS *m/z* $(M+H)^+$ calcd 405.0155, obsd 405.0160.



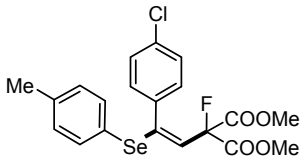
Dimethyl (*E*)-2-(2-(3-chlorophenyl)-2-(phenylselanyl)vinyl)-2-methylmalonate (35). Yield = 58%; White solid; m.p. = 48.6−50.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.30–7.21 (m, 3H), 7.16–7.08 (m, 2H), 7.07–7.05 (m, 1H), 6.96–6.92 (m, 1H), 6.46 (s, 1H), 3.52 (s, 6H), 1.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.7, 135.5, 134.4, 133.5, 130.7, 129.3, 129.2, 129.0, 128.8, 128.5, 128.1, 127.3, 56.4, 52.9, 23.6; ESI HRMS *m/z* $(M+Na)^+$ calcd 461.0029, obsd 461.0034.



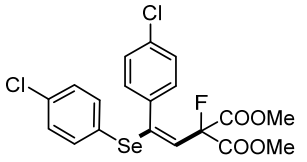
Dimethyl (*E*)-2-methyl-2-(2-(phenylselanyl)-2-(pyridin-3-yl)vinyl)malonate (36). Yield = 60%; White solid; m.p. = 84.8−85.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41–8.34 (m, 1H), 8.30 (s, 1H), 7.45–7.40 (m, 2H), 7.38–7.34 (m, 1H), 7.28–7.19 (m, 3H), 7.09 (dd, J = 7.8, 4.9 Hz, 1H), 6.61 (s, 1H), 3.50 (s, 6H), 1.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 149.6, 148.8, 136.4, 135.4, 134.0, 132.4, 132.1, 129.3, 128.6, 128.5, 122.5, 56.5, 53.0, 23.9; ESI HRMS *m/z* $(M+H)^+$ calcd 406.0552, obsd 406.0554.



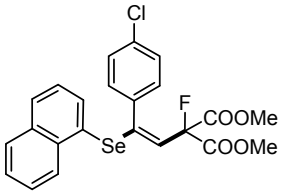
Dimethyl (*E*)-2-(2-(benzylselanyl)-2-(4-chlorophenyl)vinyl)-2-methylmalonate (37). Yield = 63%; Yellow solid; m.p. = 71.3−73.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 4H), 7.21–7.17 (m, 3H), 7.12–7.08 (m, 2H), 6.49 (s, 1H), 3.74 (s, 2H), 3.51 (s, 6H), 1.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 137.9, 136.6, 134.1, 133.7, 130.7, 130.0, 129.1, 128.6, 128.3, 127.0, 56.4, 52.9, 31.0, 23.6; ESI HRMS *m/z* $(M+Na)^+$ calcd 475.0186, obsd 475.0187.



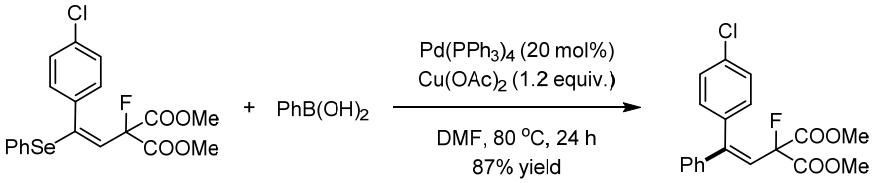
Dimethyl (*E*)-2-(2-(4-chlorophenyl)-2-(*p*-tolylselanyl)vinyl)-2-fluoromalonate (38). Yield = 64%; White solid; m.p. = 121.3−123.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.26–7.20 (m, 4H), 7.15–7.10 (m, 2H), 6.02 (d, J = 10.8 Hz, 1H), 3.59 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (d, $J_{C–F}$ = 27.2 Hz), 146.9 (d, $J_{C–F}$ = 6.8 Hz), 139.6, 136.3, 135.2, 134.9, 130.6, 130.5, 128.2, 124.3, 119.6 (d, $J_{C–F}$ = 17.6 Hz), 91.4 (d, $J_{C–F}$ = 200.5 Hz), 53.7, 21.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −140.2 (d, J = 10.8 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 478.9935, obsd 478.9942.



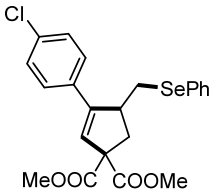
Dimethyl (*E*)-2-(2-(4-chlorophenyl)-2-((4-chlorophenyl)selanyl)vinyl)-2-fluoromalonate (39). Yield = 72%; m.p. = 119.7−121.2 °C; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.29–7.23 (m, 4H), 7.22–7.17 (m, 2H), 6.14 (d, J = 10.9 Hz, 1H), 3.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, $J_{C–F}$ = 27.0 Hz), 145.7 (d, $J_{C–F}$ = 6.5 Hz), 137.3, 135.7, 135.1, 134.9, 130.6 (d, $J_{C–F}$ = 3.1 Hz), 129.9, 128.2, 126.1, 121.0 (d, $J_{C–F}$ = 17.6 Hz), 91.3 (d, $J_{C–F}$ = 201.3 Hz), 53.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −141.3 (d, $J_{C–F}$ = 10.9 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 498.9389, obsd 498.9392.



Dimethyl (*E*)-2-(2-(4-chlorophenyl)-2-(naphthalen-1-ylselanyl)vinyl)-2-fluoromalonate (40). Yield = 75%; White solid; m.p. = 124.2−125.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 7.91–7.82 (m, 3H), 7.61–7.51 (m, 2H), 7.41–7.36 (m, 1H), 7.22–7.17 (m, 4H), 5.84 (d, J = 12.0 Hz, 1H), 3.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, $J_{C–F}$ = 27.2 Hz), 145.3 (d, $J_{C–F}$ = 6.4 Hz), 136.8, 135.1, 134.8, 134.5, 134.3, 131.0, 130.4 (d, $J_{C–F}$ = 3.1 Hz), 128.8, 128.1, 128.0, 127.5, 127.2, 126.6, 126.1, 120.0 (d, $J_{C–F}$ = 17.6 Hz), 91.5 (d, $J_{C–F}$ = 200.8 Hz), 53.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −142.4 (d, J = 12.0 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 514.9935, obsd 514.9938.

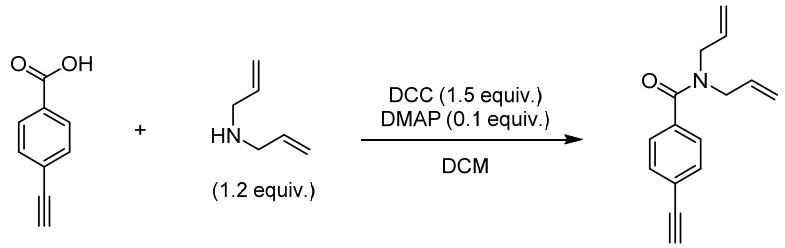


Dimethyl (*Z*)-2-(2-(4-chlorophenyl)-2-phenylvinyl)-2-fluoromalonate (41). To a solution of **4** (88 mg, 0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (46 mg, 20 mol%) and phenylboronic acid (73 mg, 0.6 mmol, 3 equiv.) in DMF (3 mL) was added $Cu(OAc)_2$ (44 mg, 2.4 mmol, 1.2 equiv.). The resulting mixture was stirred at 80 °C for 24 h. After that, the reaction was cooled to room temperature, diluted with ethyl acetate (10 mL) and then washed with saturated solution of NH_4Cl (20 mL). The organic phase was separated, dried over Na_2SO_4 and concentrated under vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding products **41** as a white solid (63 mg, 87% yield). m.p. = 114.7−116.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 5H), 7.27–7.22 (m, 2H), 7.18–7.13 (m, 2H), 6.56 (d, J = 11.2 Hz, 1H), 3.68 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (d, J = 27.0 Hz), 149.9 (d, J = 5.6 Hz), 141.0 (d, J = 2.6 Hz), 136.1 (d, J = 1.7 Hz), 134.6, 131.6 (d, J = 3.8 Hz), 129.1, 128.5, 128.3, 128.0 (d, J = 2.1 Hz), 120.3 (d, J = 16.4 Hz), 91.5 (d, J = 199.4 Hz), 53.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -141.8 (d, J = 11.1 Hz); ESI HRMS *m/z* $(M+Na)^+$ calcd 391.1880, obsd 391.1883.



Dimethyl 3-(4-chlorophenyl)-4-((phenylselanyl)methyl)cyclopent-2-ene-1,1-dicarboxylate (43). Yield = 35%; Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.47 (m, 2H), 7.29–7.23 (m, 5H), 7.17–7.11 (m, 2H), 6.10 (d, J = 1.5 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.52–3.44 (m, 1H), 3.14 (dd, J = 12.2, 3.2 Hz, 1H), 2.87 (dd, J = 14.2, 9.6 Hz, 1H), 2.71 (dd, J = 12.2, 9.6 Hz, 1H), 2.63 (dd, J = 14.2, 3.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 171.5, 148.6, 134.2, 133.9, 132.6, 129.6, 129.2, 128.9, 128.0, 127.5, 125.0, 65.4, 53.2, 53.1, 45.3, 37.6, 32.8; ESI HRMS *m/z* $(M+Na)^+$ calcd 487.0186, obsd 487.0187.

7. Synthesis and Characterization of Substrates



3-(4-Methoxyphenyl)propyl 2-(4-*iso*-butylphenyl)propanoate (S1). To a solution of 4-ethynylbenzoic acid (438 mg, 3.0 mmol, 1.0 equiv.), diallylamine (0.44 mL, 3.6 mmol, 1.2 equiv.) and DMAP (37 mg, 0.3 mmol, 0.1 equiv.) in CH_2Cl_2 (10 mL) was added DCC (0.74 mL, 4.5 mmol, 1.5 equiv.). The reaction mixture was stirred for 12 h at r.t. The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product as a white solid (466 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.42–7.38 (m, 2H), 5.93–5.66 (m, 2H), 5.27–5.16 (m, 4H), 4.20–4.06 (m, 2H), 3.89–3.74 (m, 2H), 3.15 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 136.5, 133.1, 132.7, 132.2, 126.8, 123.7, 118.0, 117.9, 83.0, 78.8, 50.8, 47.2.

8. X-Ray Crystallography

X-Ray single crystal diffraction analysis of compound 4 (CCDC: 2150878)

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of each compound (Petroleum ether/CH_2Cl_2) in a loosely capped vial.

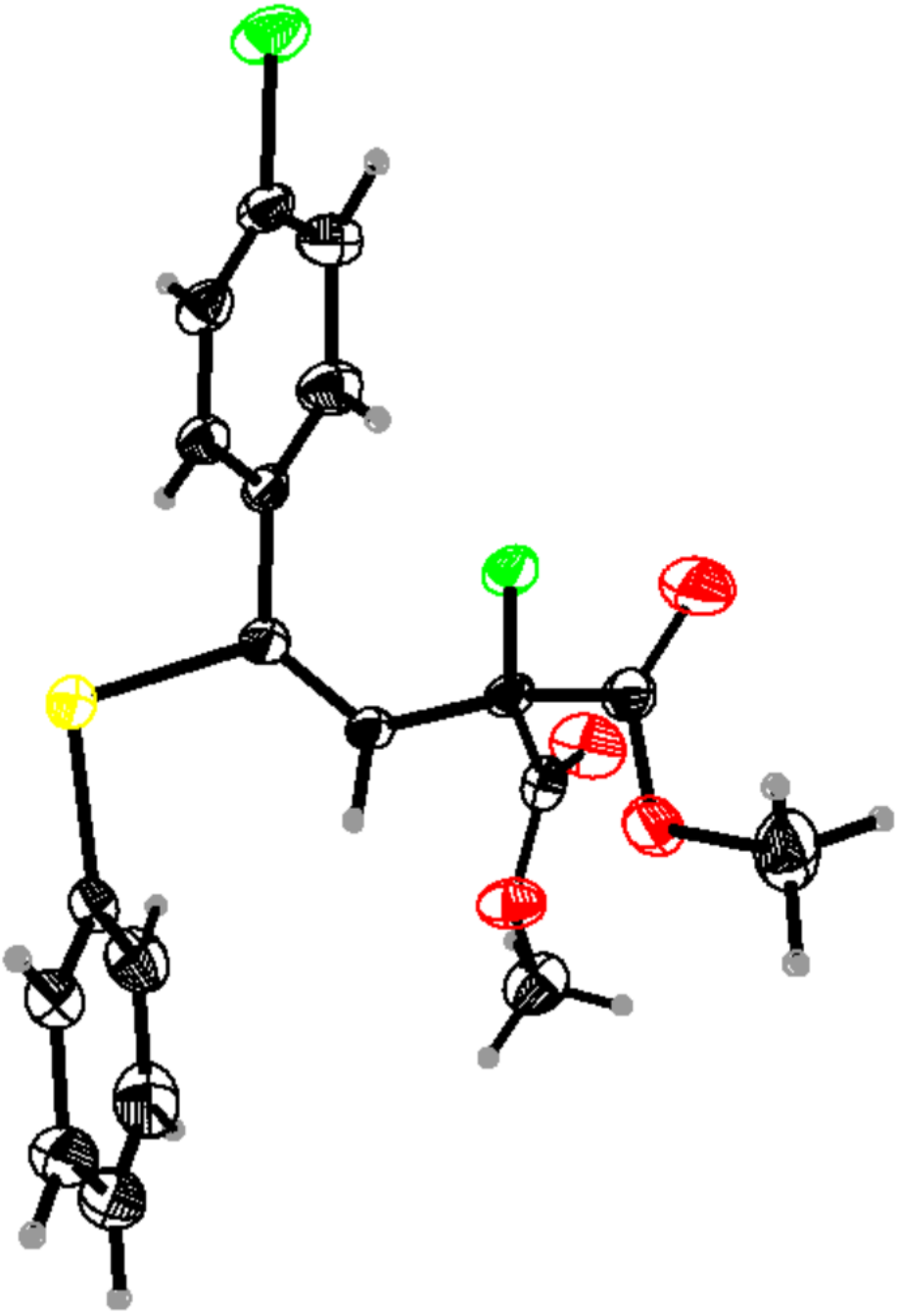


Figure S2. ORTEP diagram of **4** with thermal displacement parameters drawn at 30% probability.

Datablock: 1

Bond precision: C-C = 0.0046 A Wavelength=0.71073

Cell: a=7.4845(8) b=10.2563(12) c=13.5628(15)
alpha=99.603(2) beta=100.338(2) gamma=109.552(2)
Temperature: 273 K

	Calculated	Reported
Volume	935.82(18)	935.81(18)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H16 Cl F O4 Se	?
Sum formula	C19 H16 Cl F O4 Se	C19 H16 Cl F O4 Se
Mr	441.73	441.73
Dx,g cm-3	1.568	1.568
Z	2	2
Mu (mm-1)	2.179	2.179
F000	444.0	444.0
F000'	444.32	
h,k,lmax	8,12,16	8,12,16
Nref	3292	3270
Tmin,Tmax	0.573,0.633	
Tmin'	0.562	

Correction method= Not given

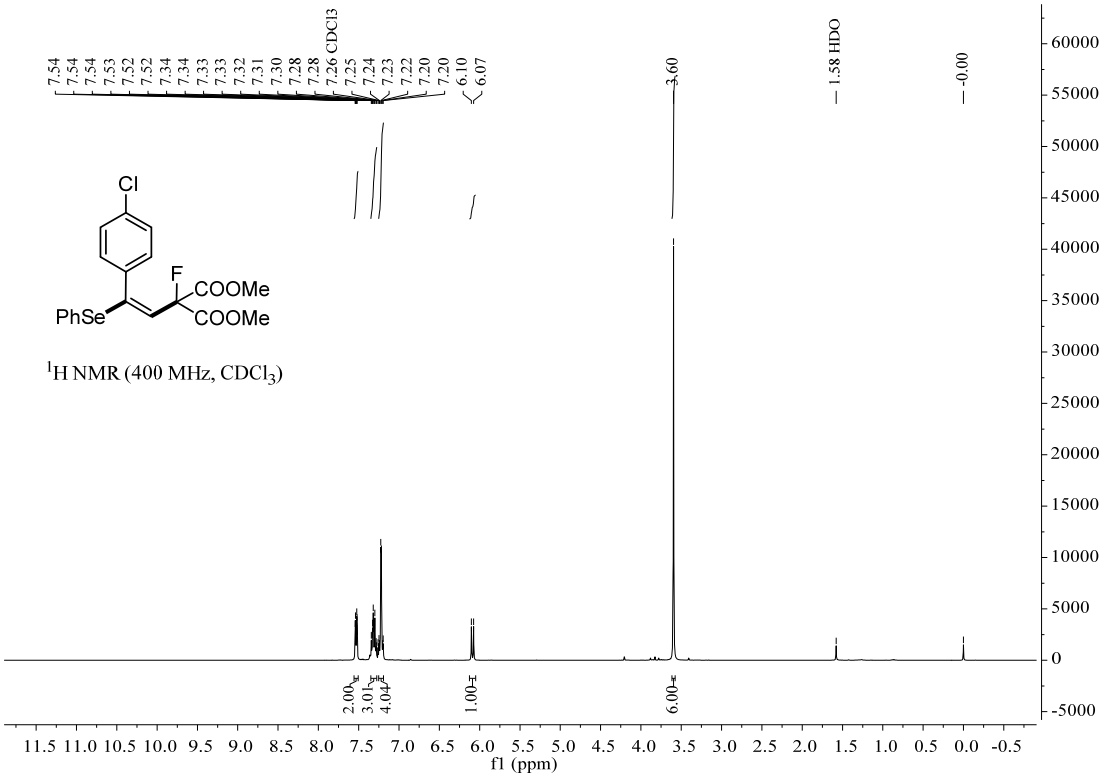
Data completeness= 0.993 Theta(max)= 24.999

R(reflections)= 0.0329(2786) wR2(reflections)= 0.0891(3270)

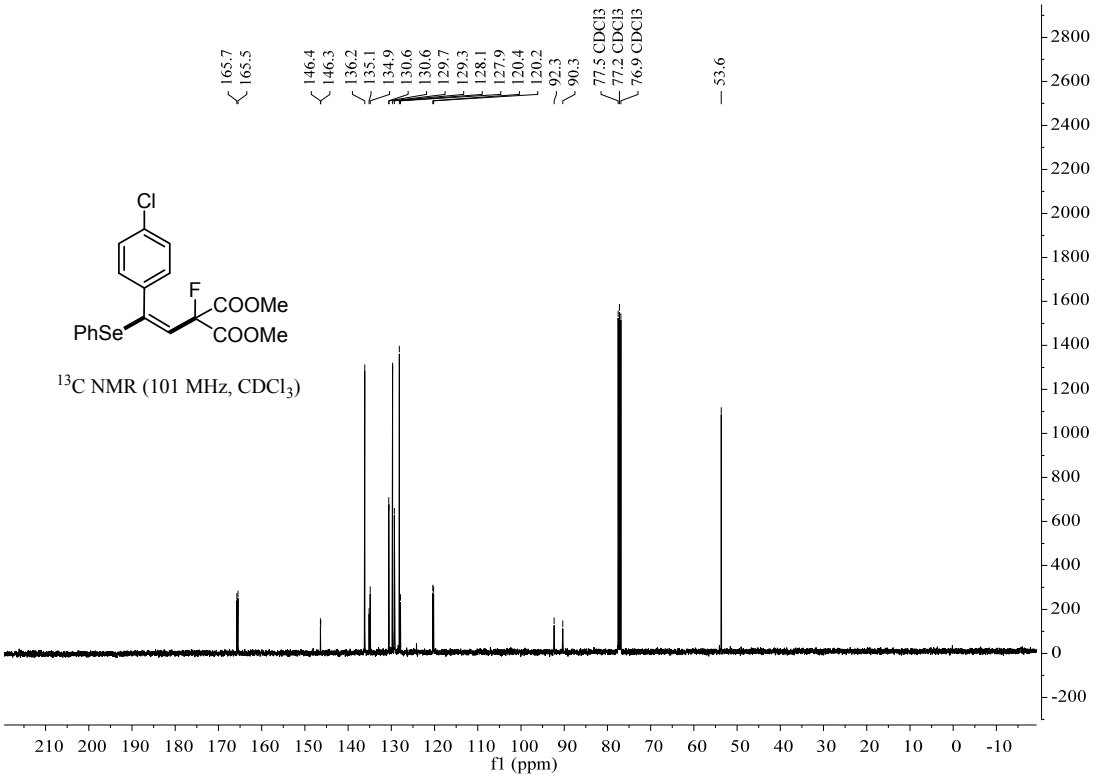
S = 1.056 Npar= 237

9. NMR Spectra for Compounds

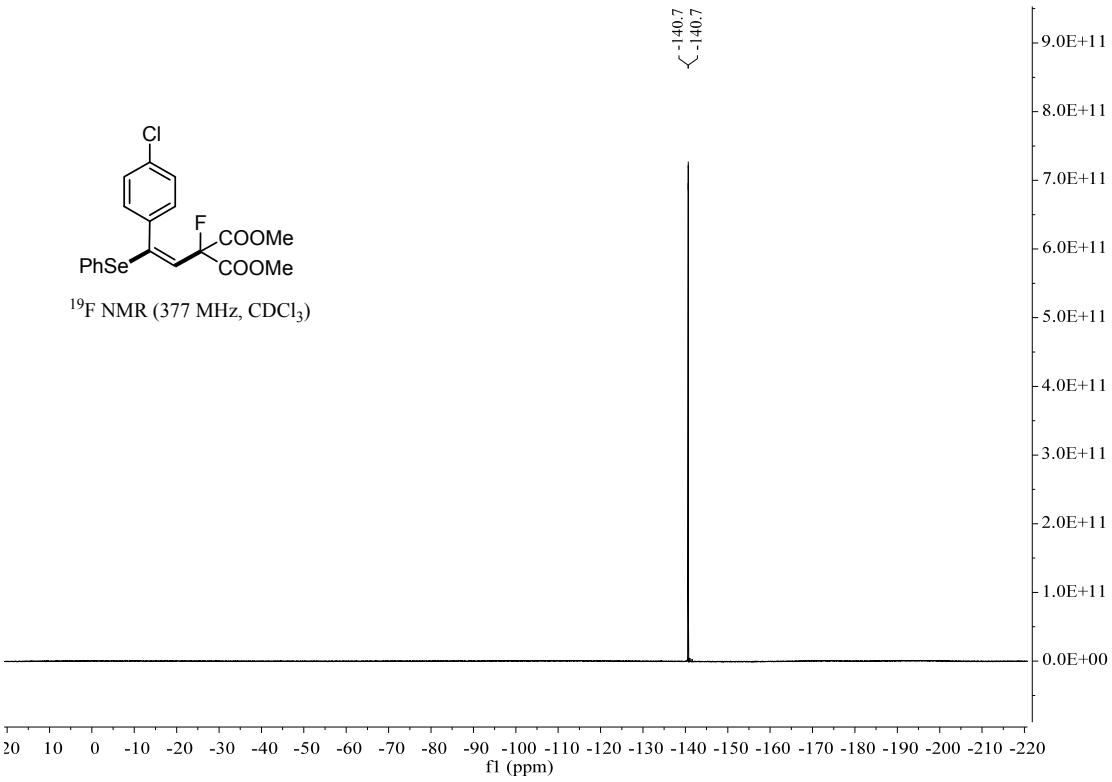
Compound 4



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

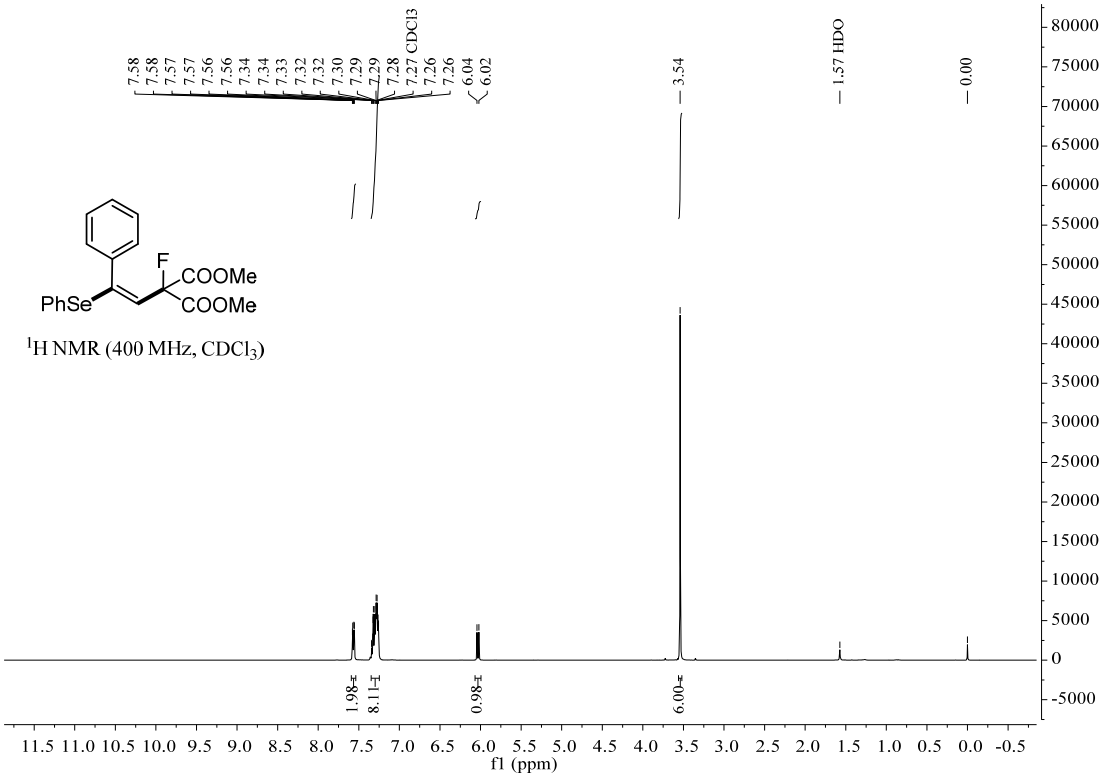


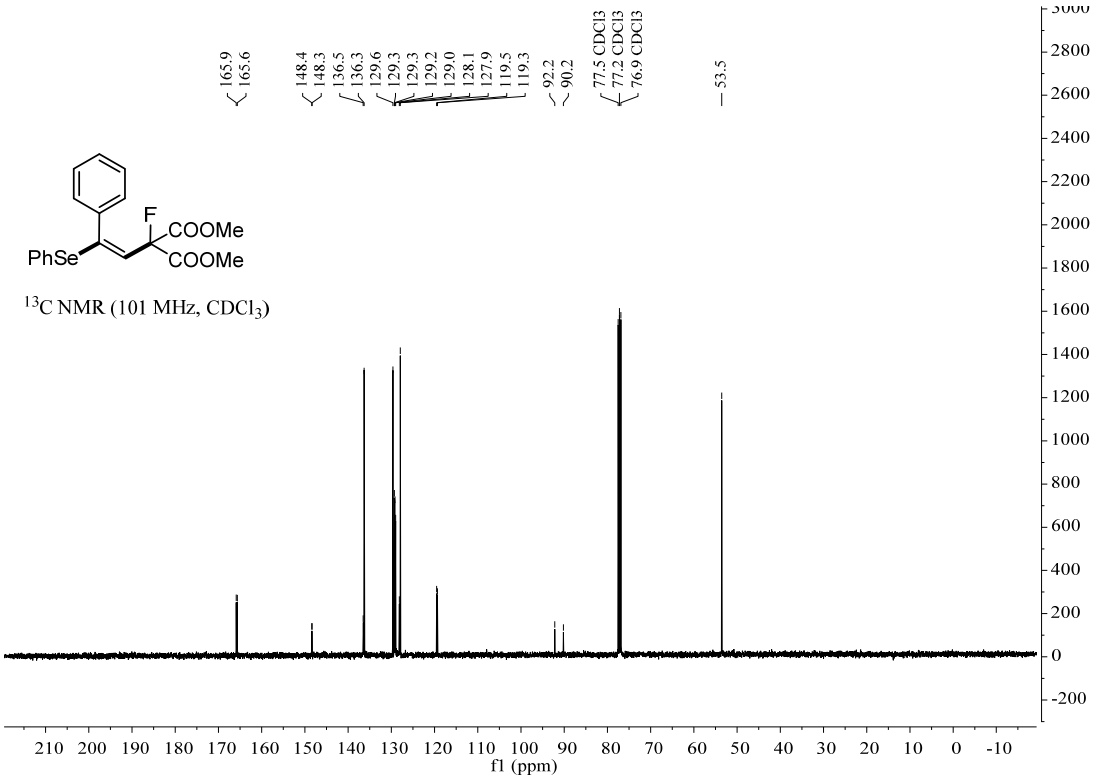
^{13}C NMR (101 MHz, $CDCl_3$)

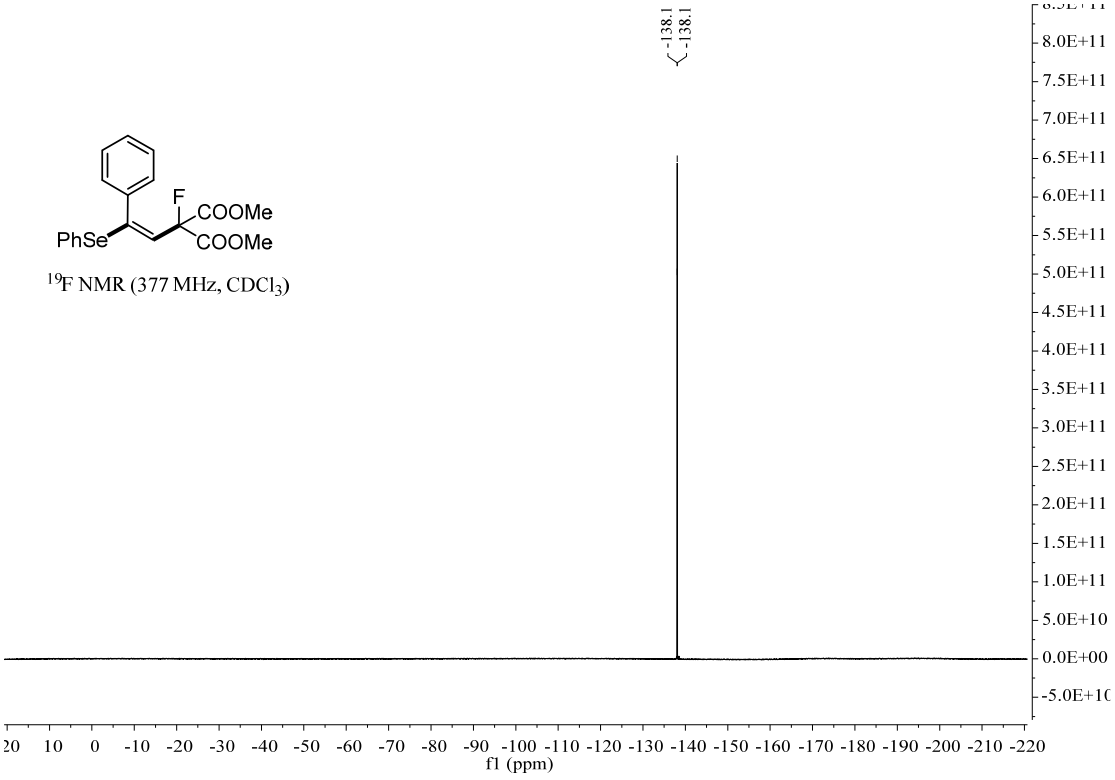


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 5

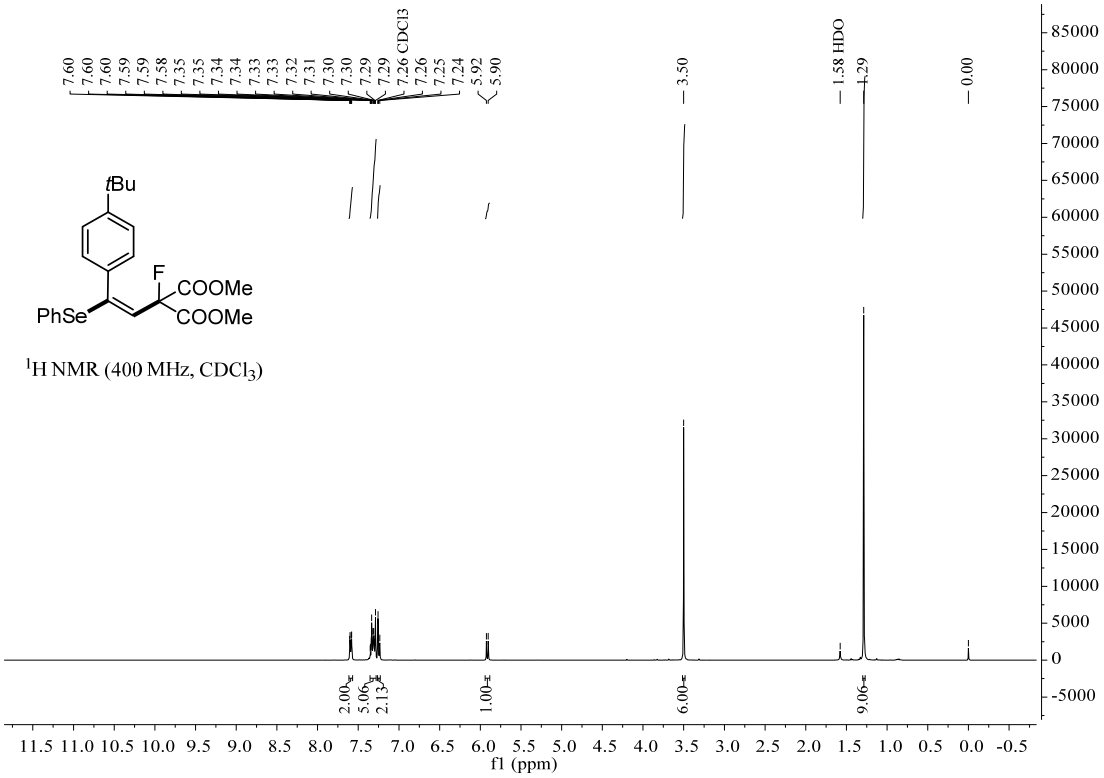

7.58
7.58
7.57
7.57
7.56
7.56
7.34
7.34
7.33
7.32
7.32
7.30
7.29
7.29
7.28
7.27 CDCl3
7.26
7.26
6.04
6.02
3.54
1.57 HDO
0.00
F
COOMe
COOMe
PhSe
1H NMR (400 MHz, CDCl3)
1.98
8.11
0.98
6.00
f1 (ppm)


165.9
165.6
148.4
148.3
136.5
136.3
129.6
129.3
129.3
129.2
129.0
128.1
127.9
119.5
119.3
92.2
90.2
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
53.5
F
COOMe
COOMe
PhSe
13C NMR (101 MHz, CDCl3)
f1 (ppm)

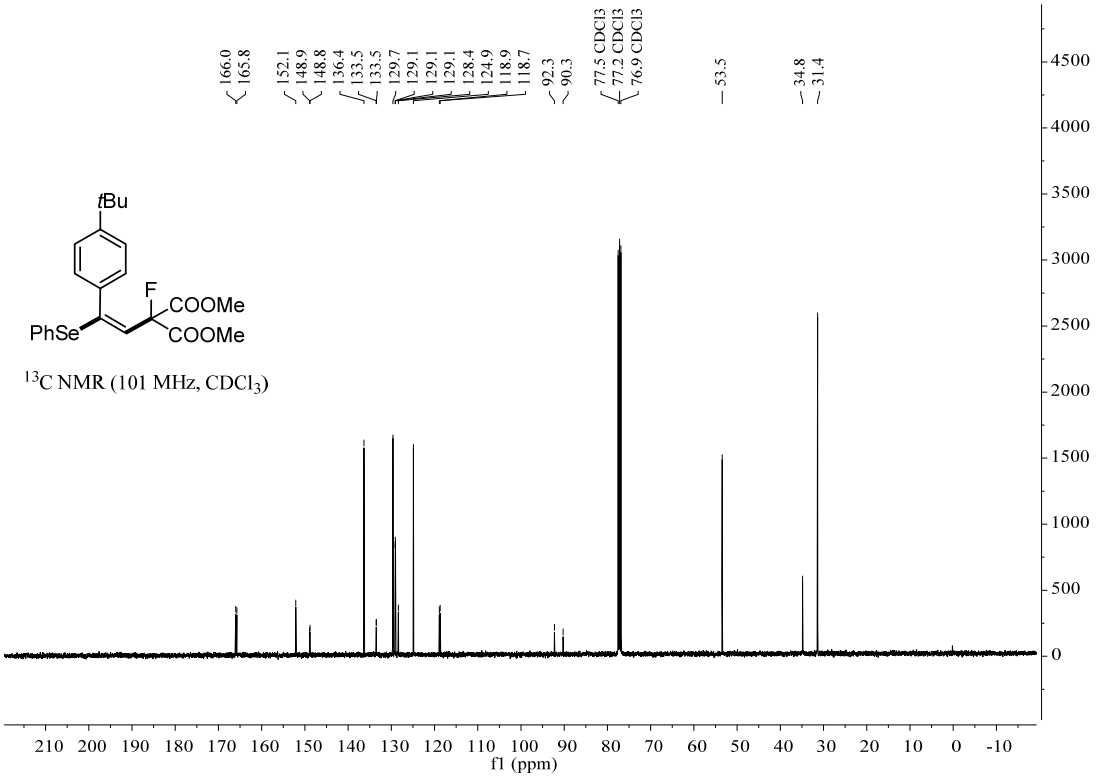


^{19}F NMR (377 MHz, $CDCl_3$)

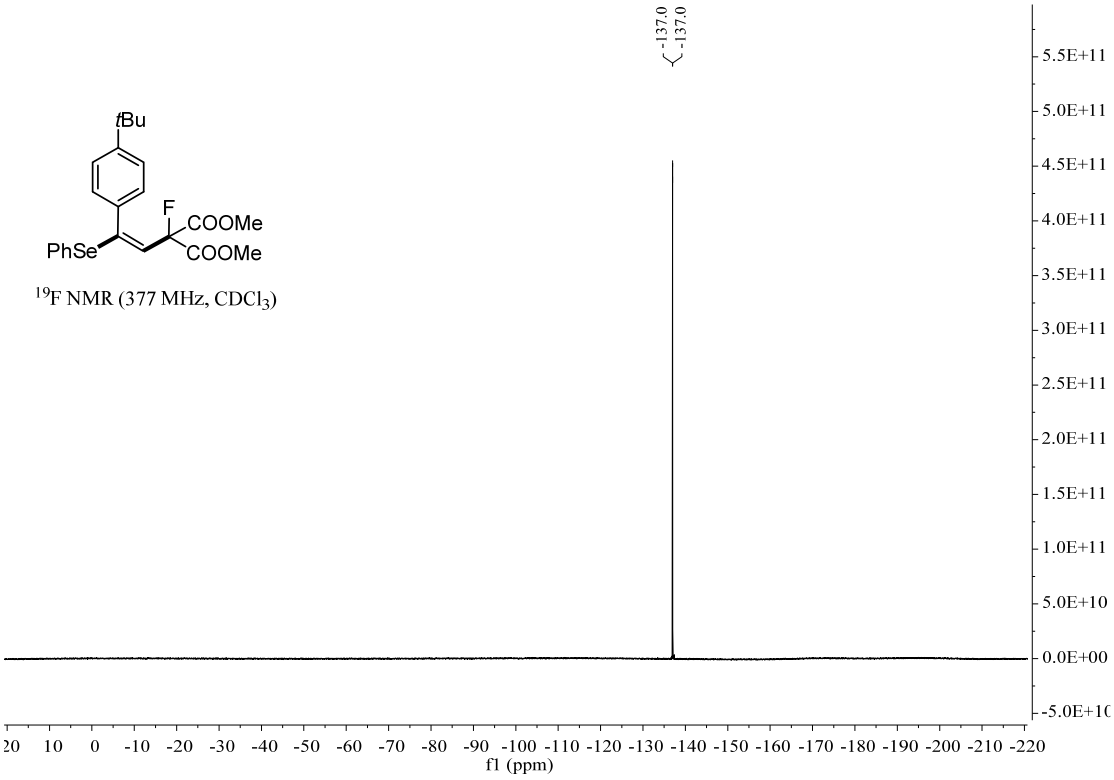
Compound 6



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

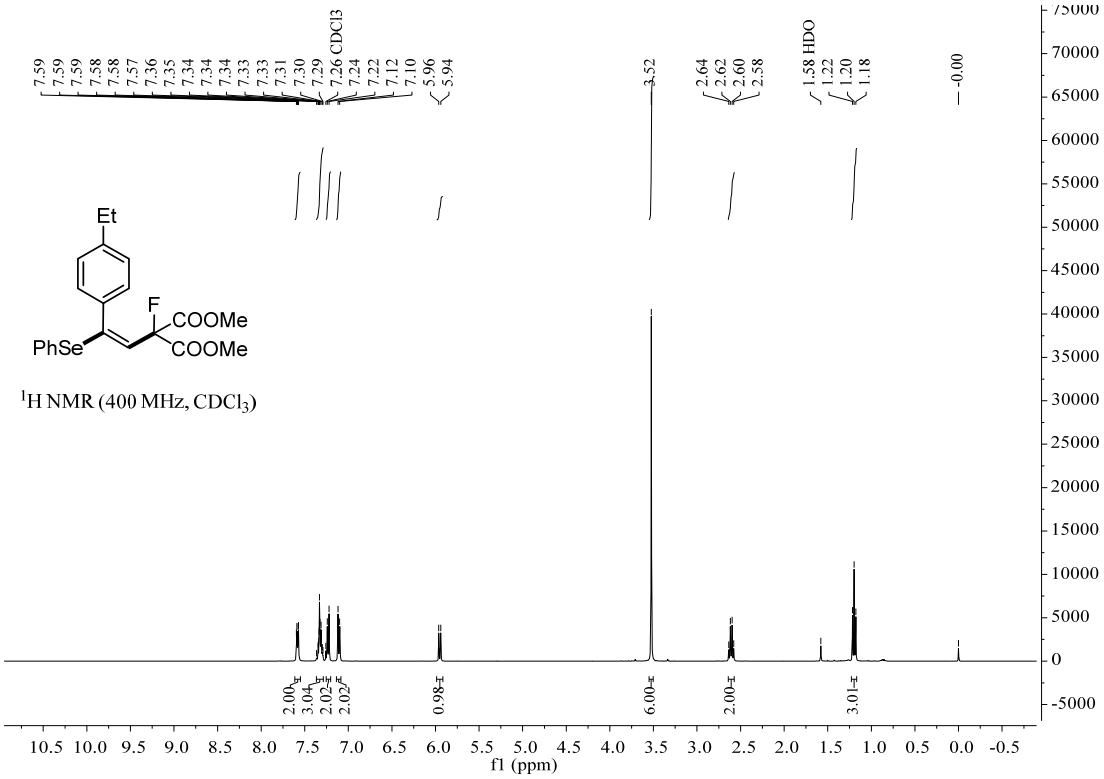


^{13}C NMR (101 MHz, $CDCl_3$)

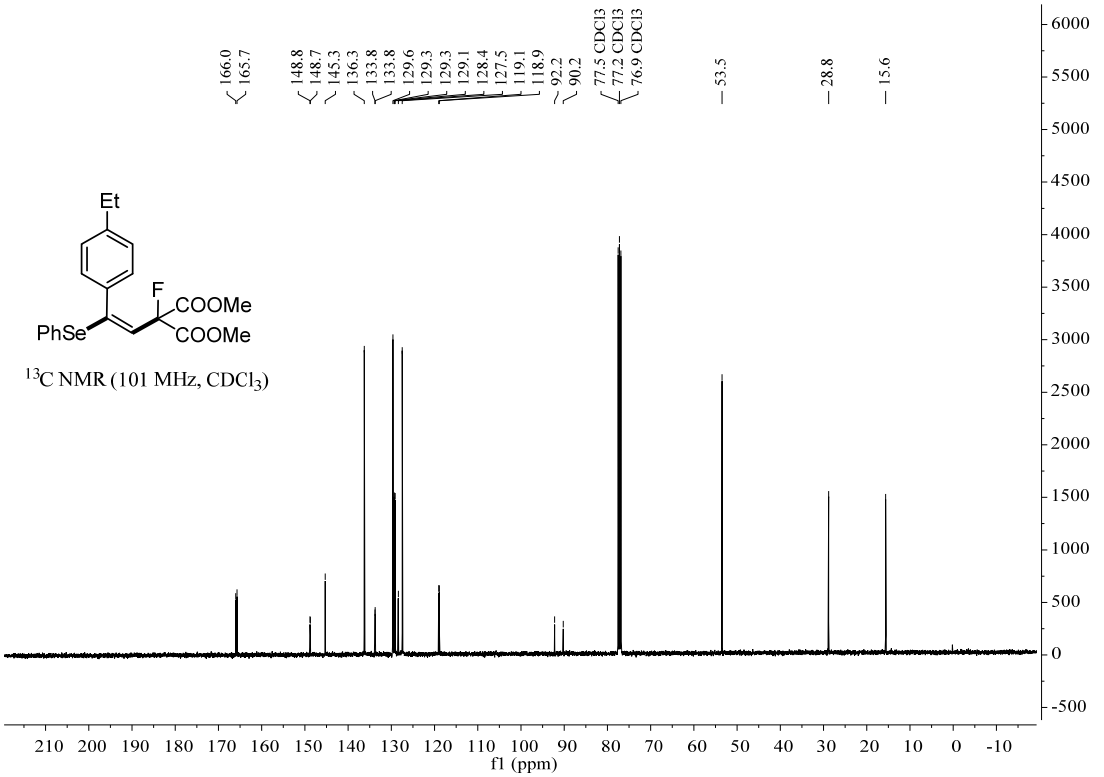


^{19}F NMR (377 MHz, $CDCl_3$)

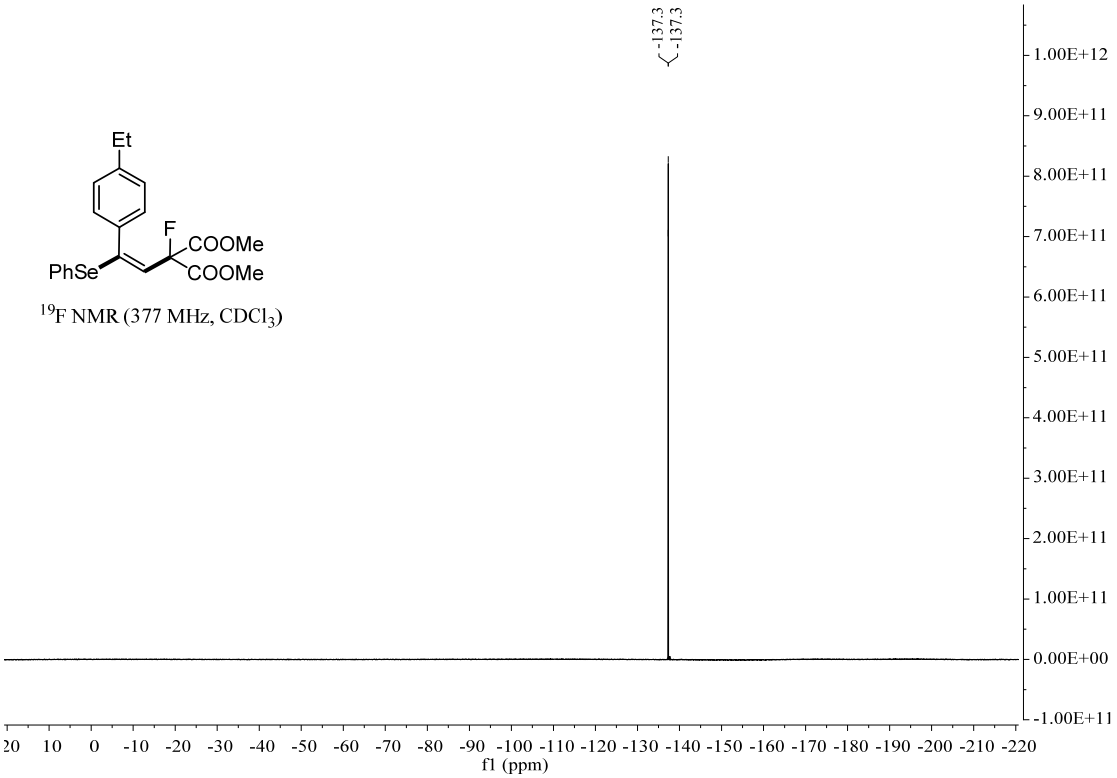
Compound 7



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

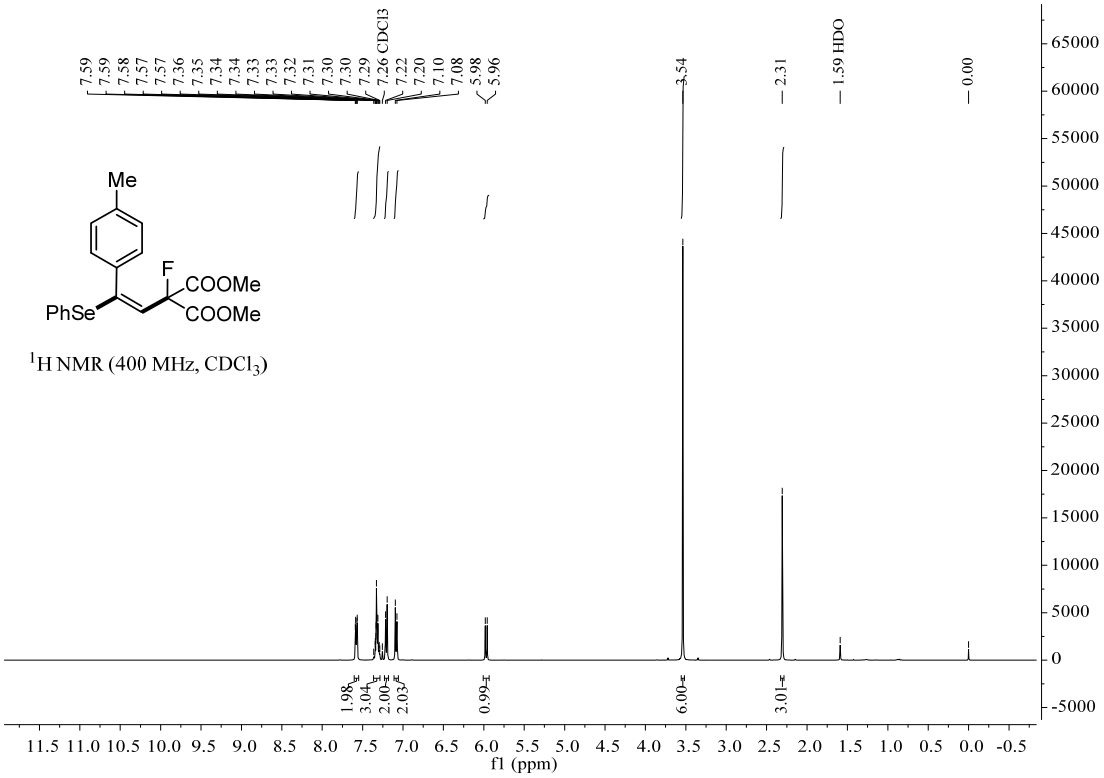


^{13}C NMR (101 MHz, $CDCl_3$)

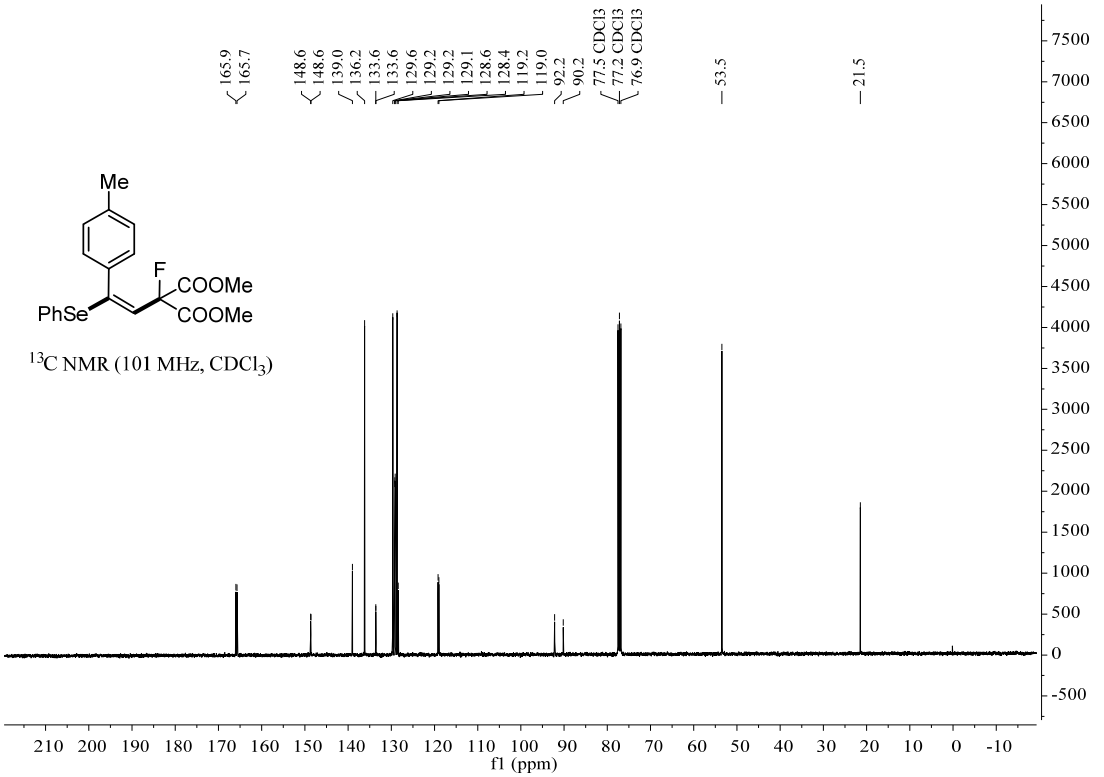


^{19}F NMR (377 MHz, $CDCl_3$)

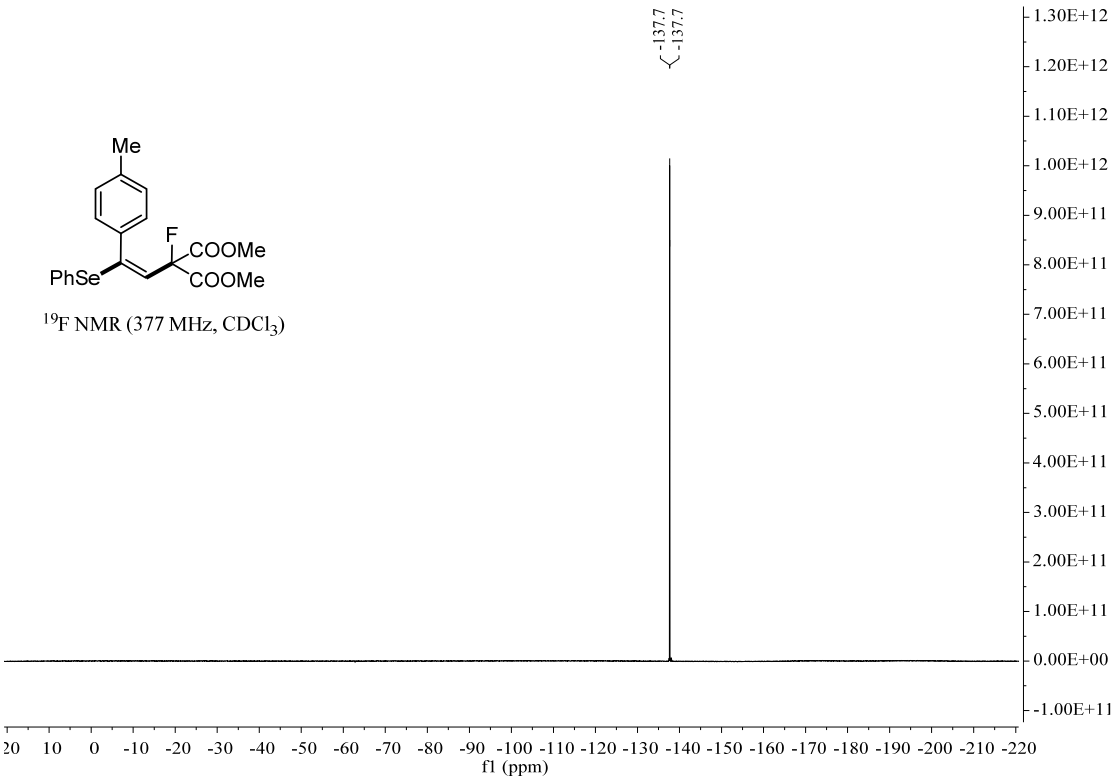
Compound 8



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

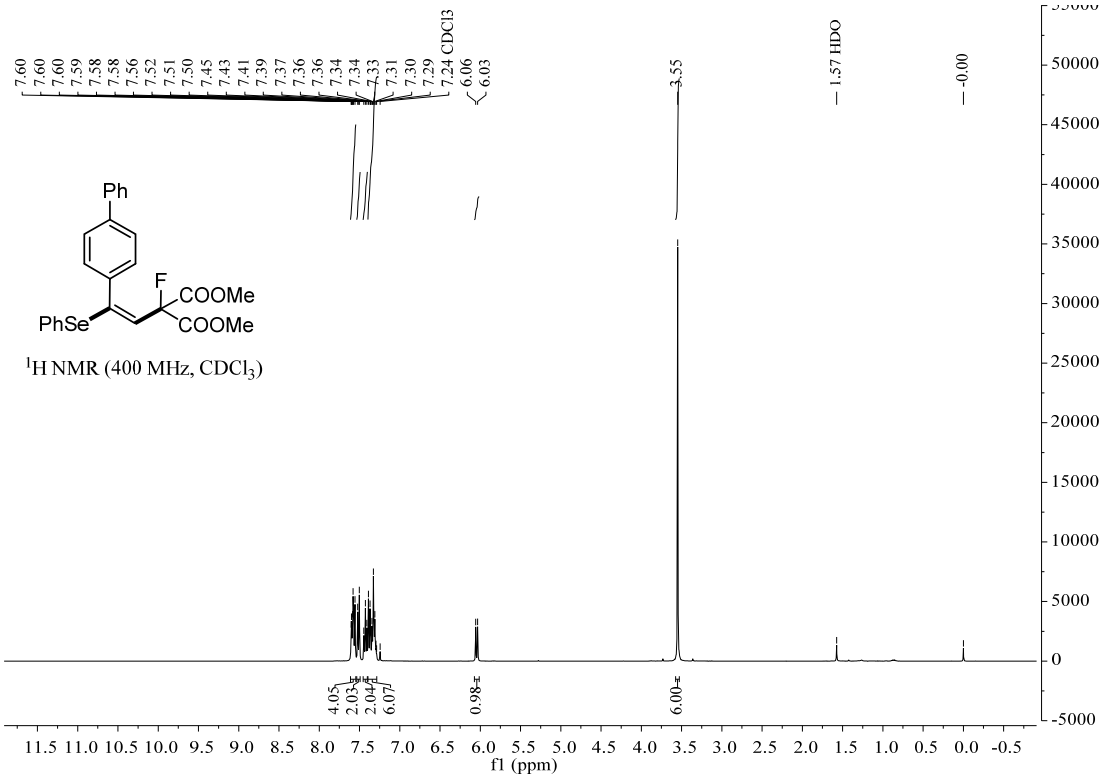


^{13}C NMR (101 MHz, $CDCl_3$)

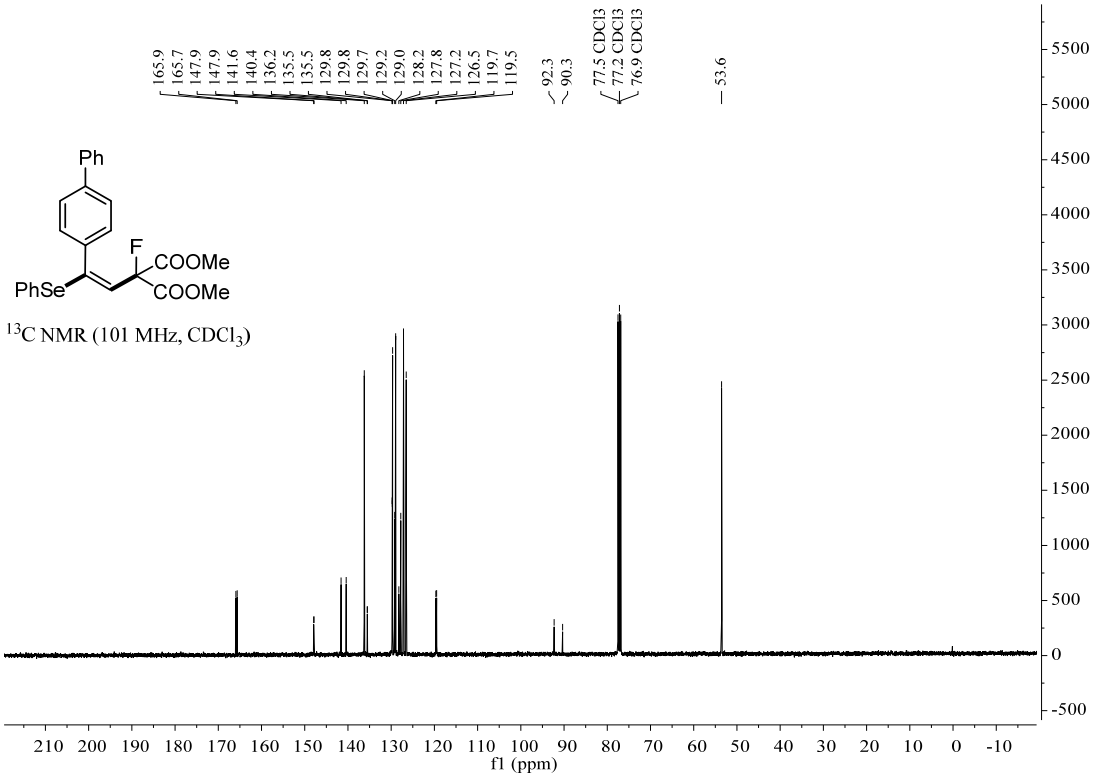


^{19}F NMR (377 MHz, $CDCl_3$)

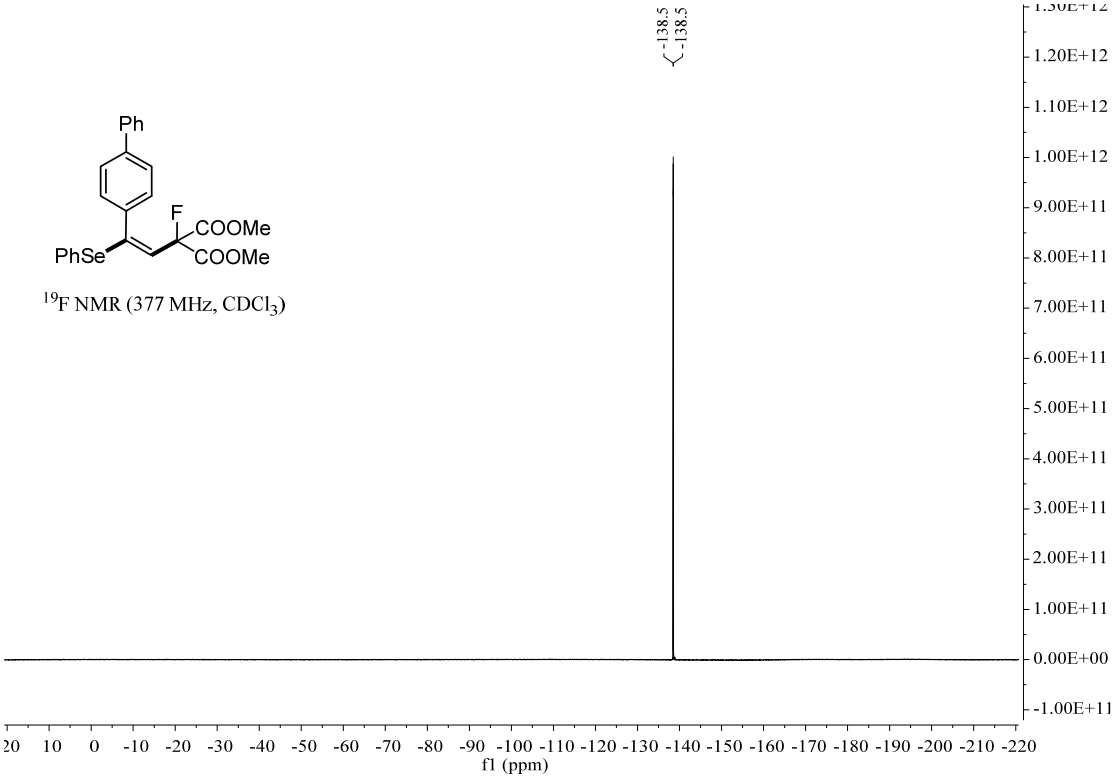
Compound 9



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

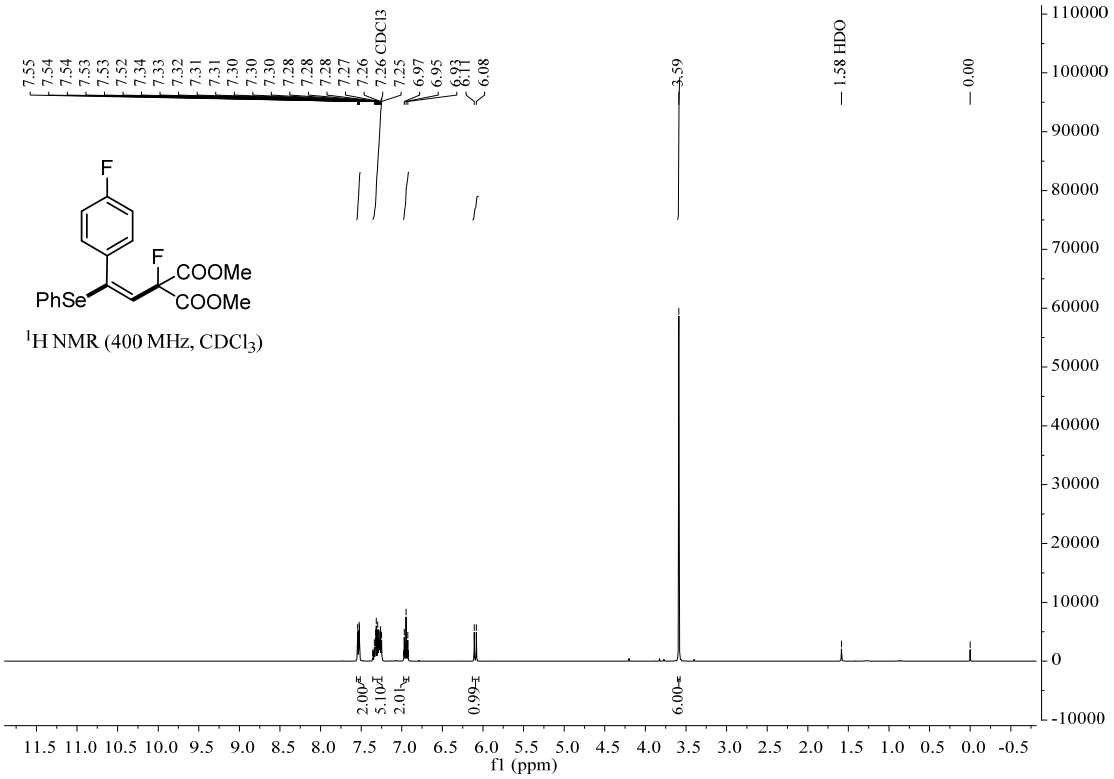


^{13}C NMR (101 MHz, $CDCl_3$)

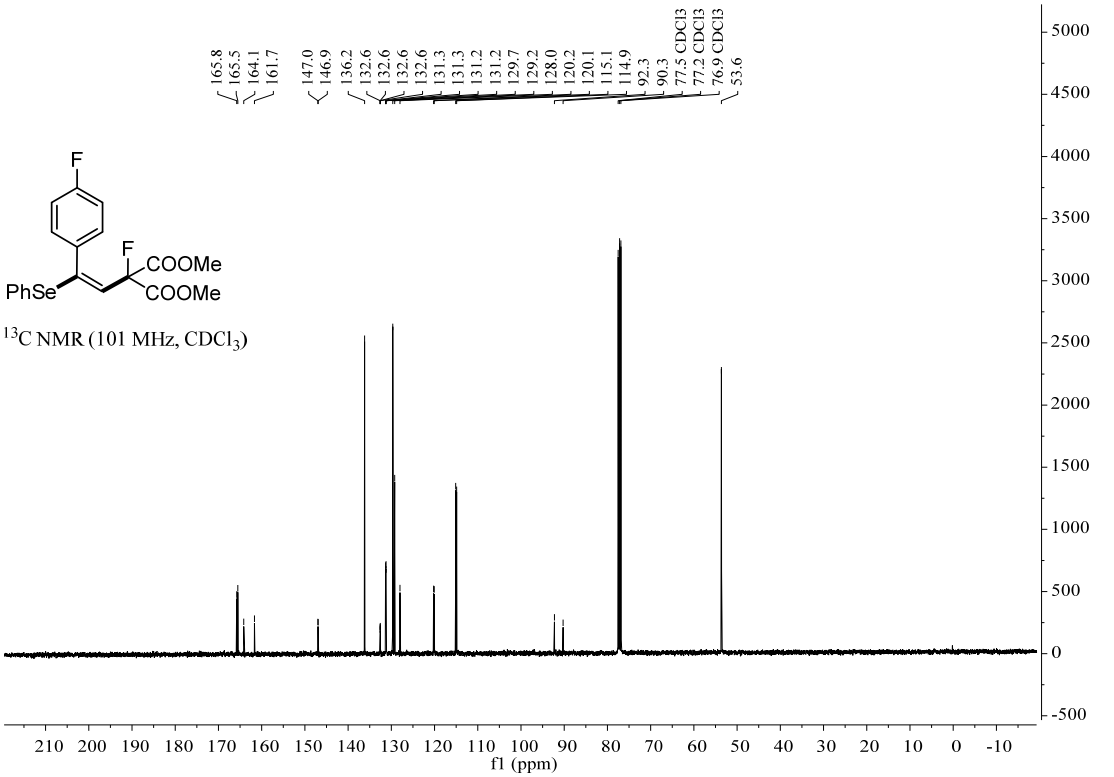


^{19}F NMR (377 MHz, $CDCl_3$)

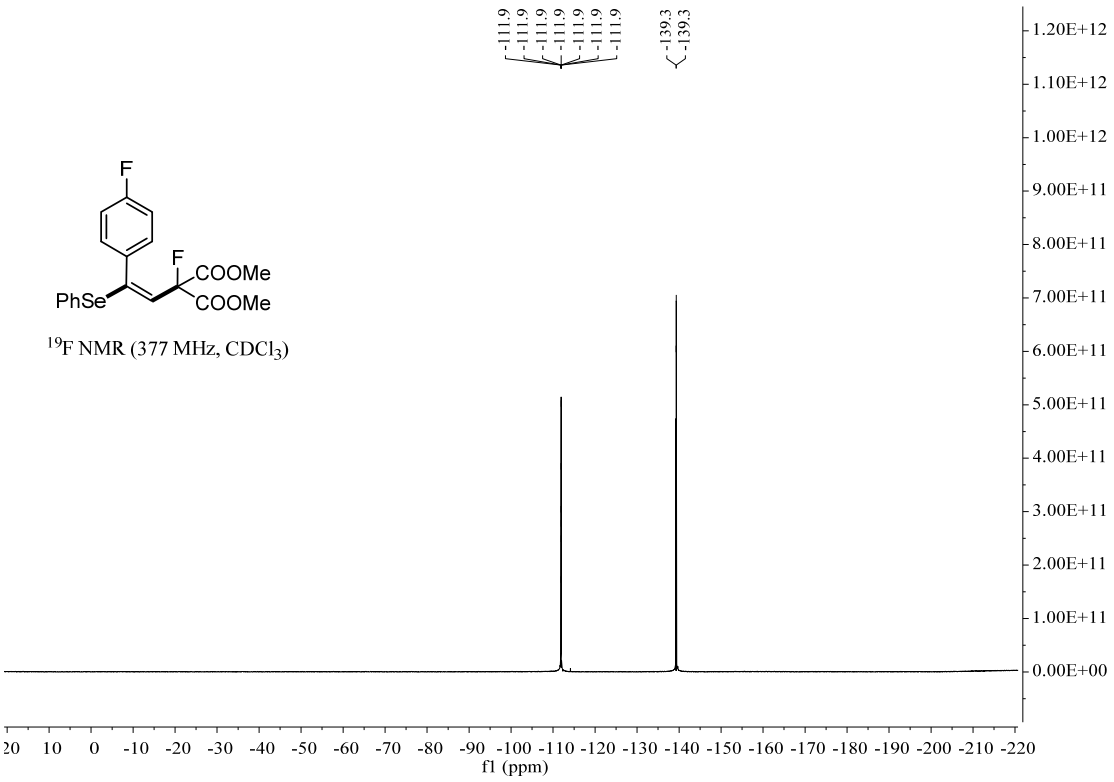
Compound 10



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

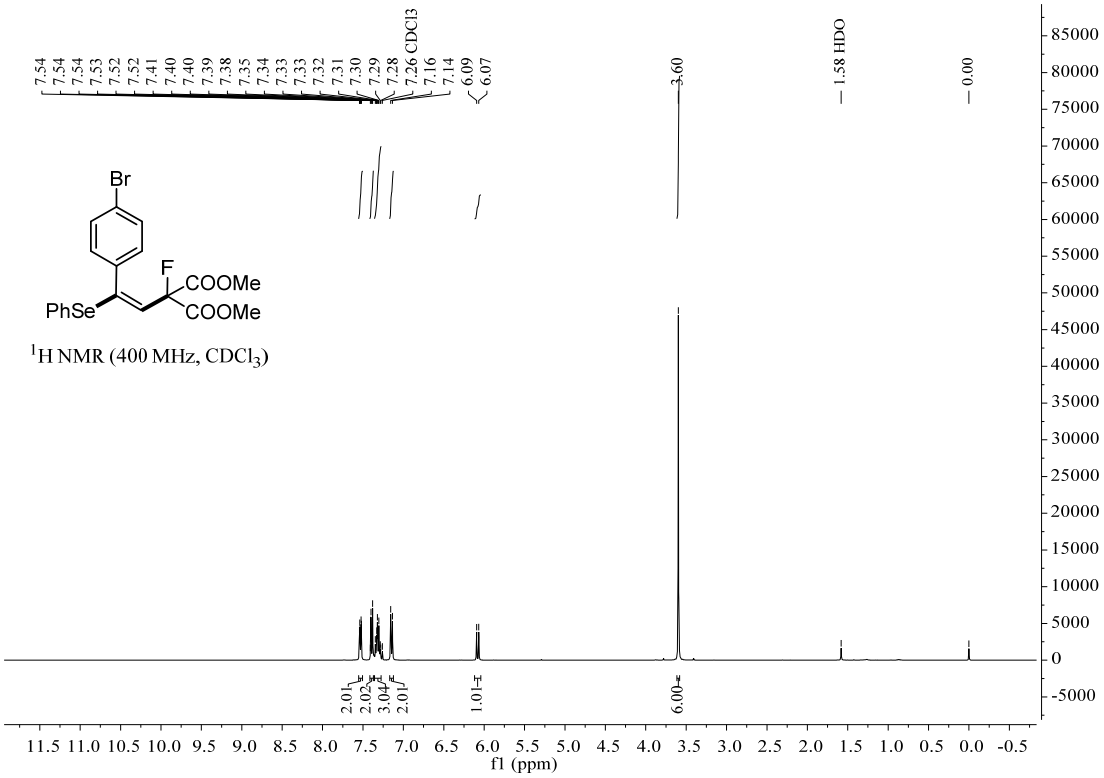


^{13}C NMR (101 MHz, $CDCl_3$)

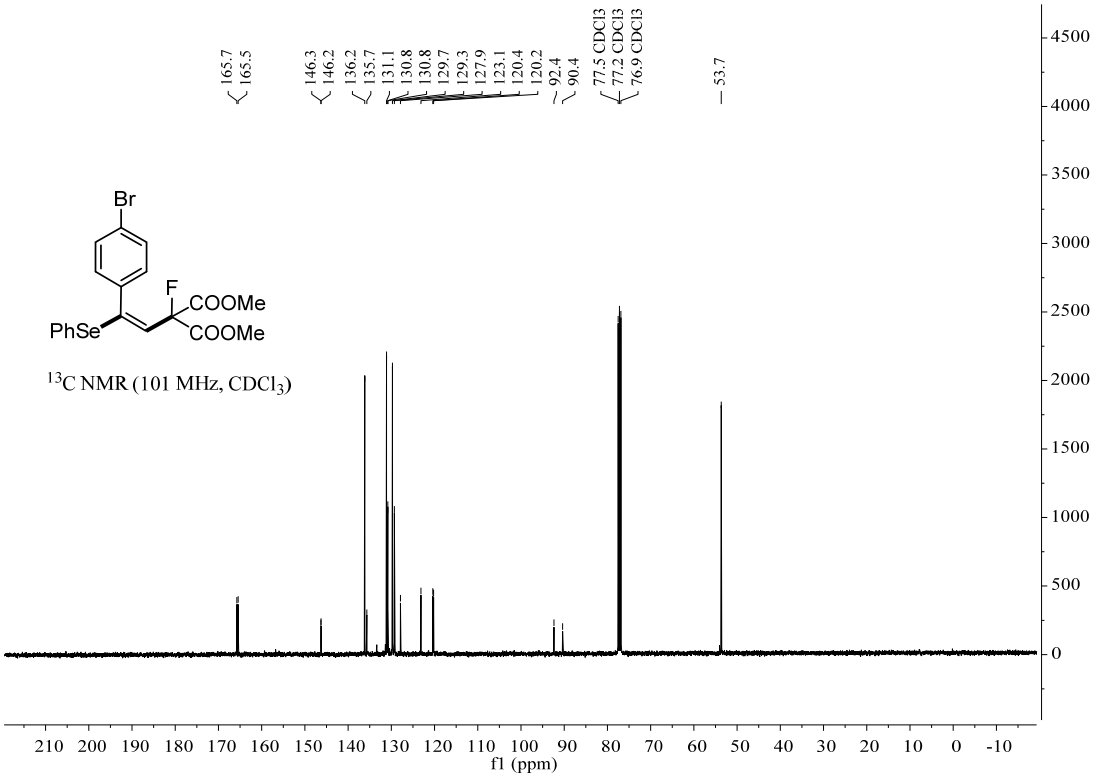


^{19}F NMR (377 MHz, $CDCl_3$)

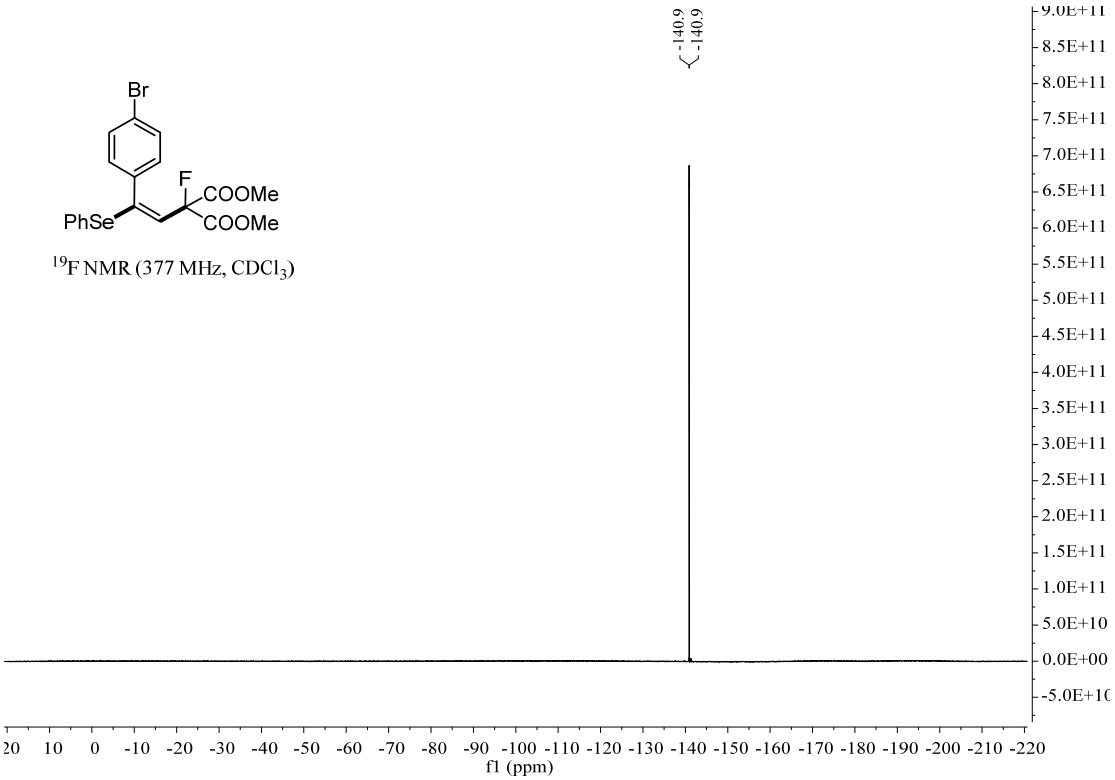
Compound 11



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

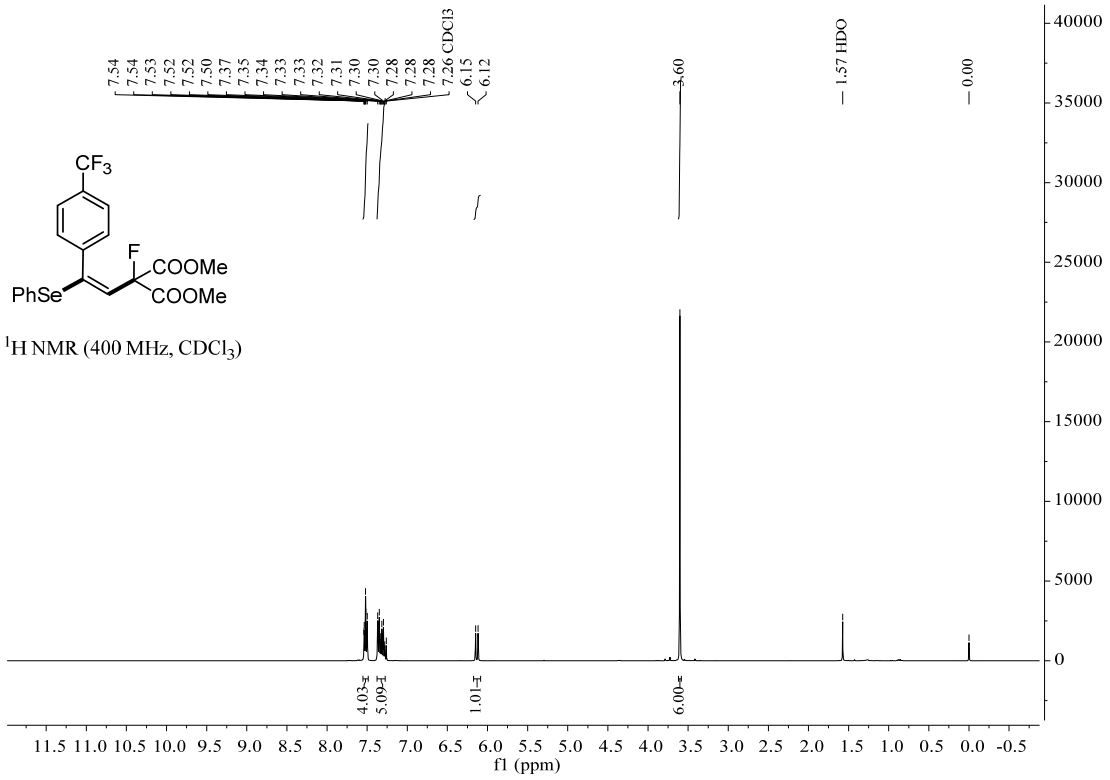


^{13}C NMR (101 MHz, $CDCl_3$)

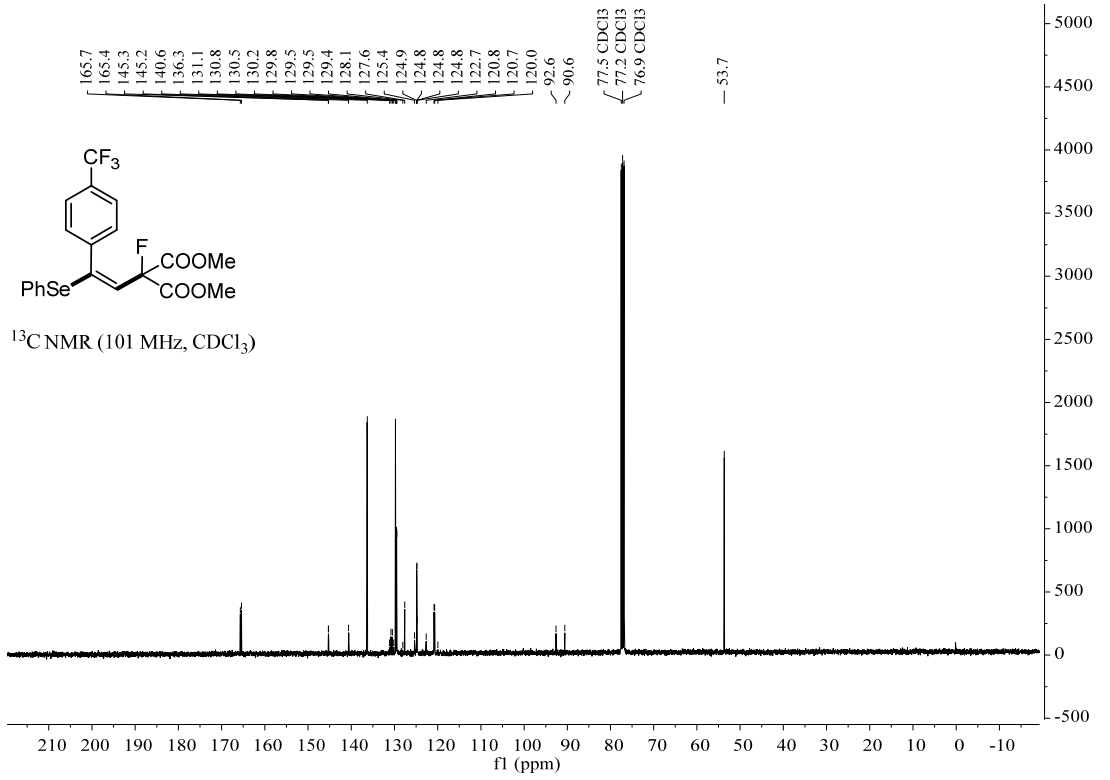


^{19}F NMR (377 MHz, $CDCl_3$)

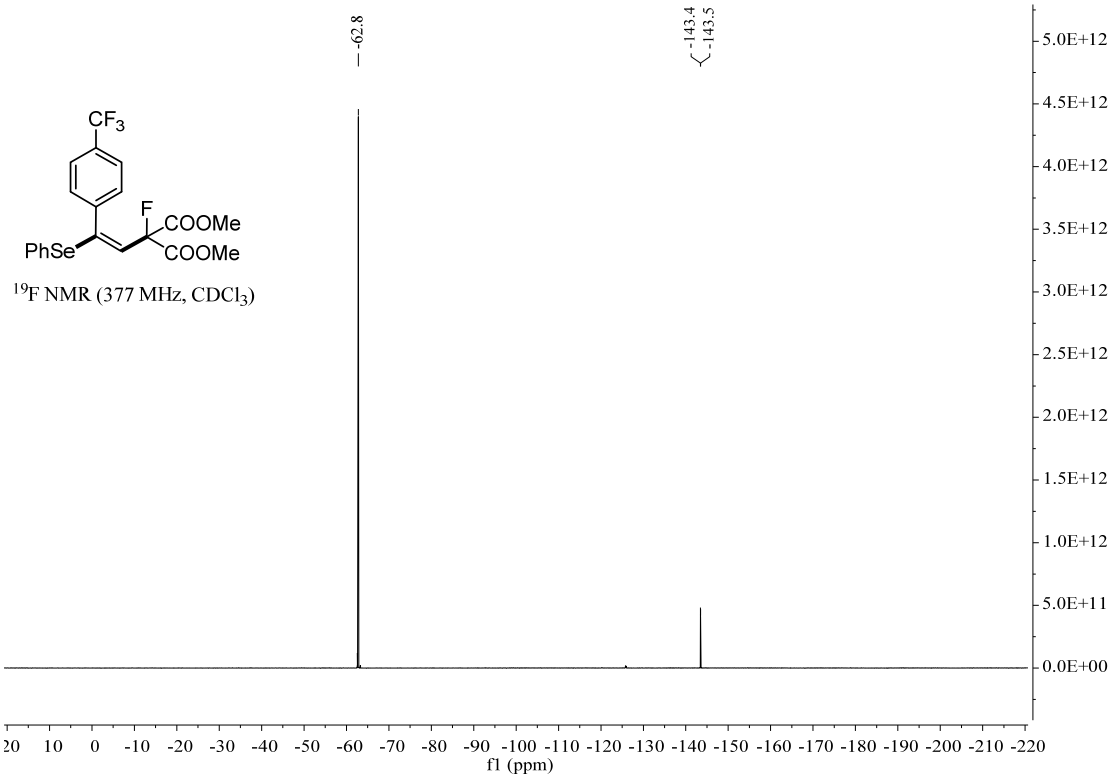
Compound 12



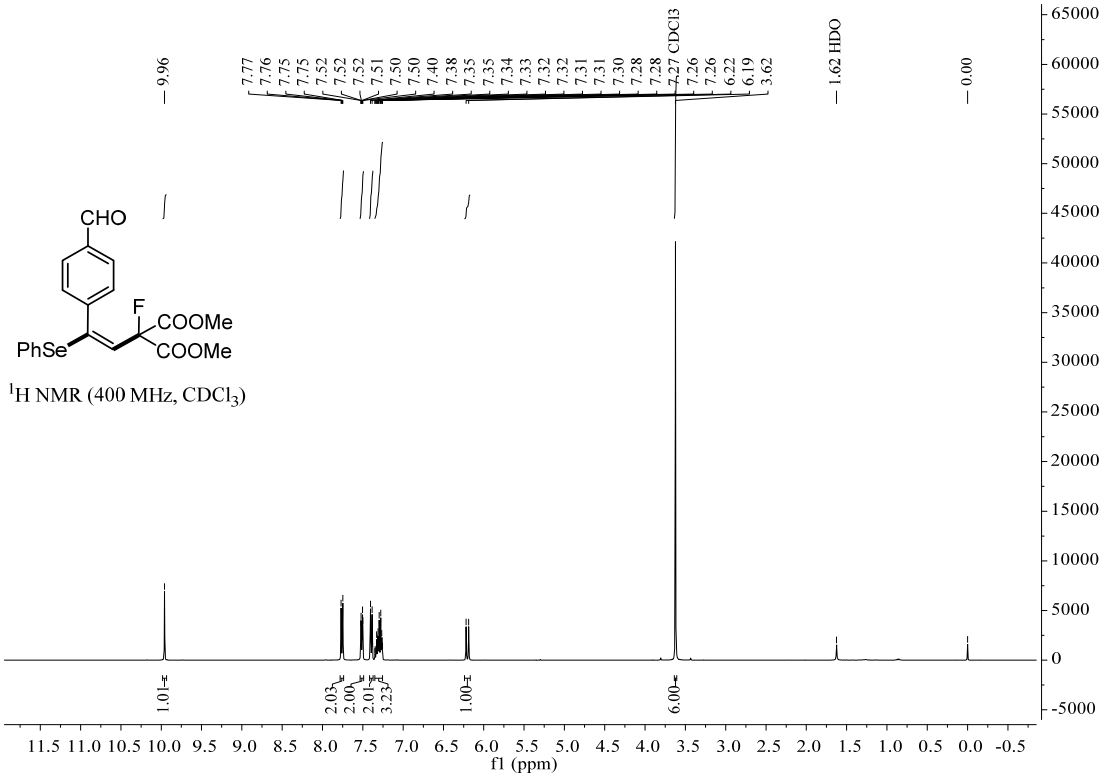
^{1}H NMR (400 MHz, $CDCl_3$)



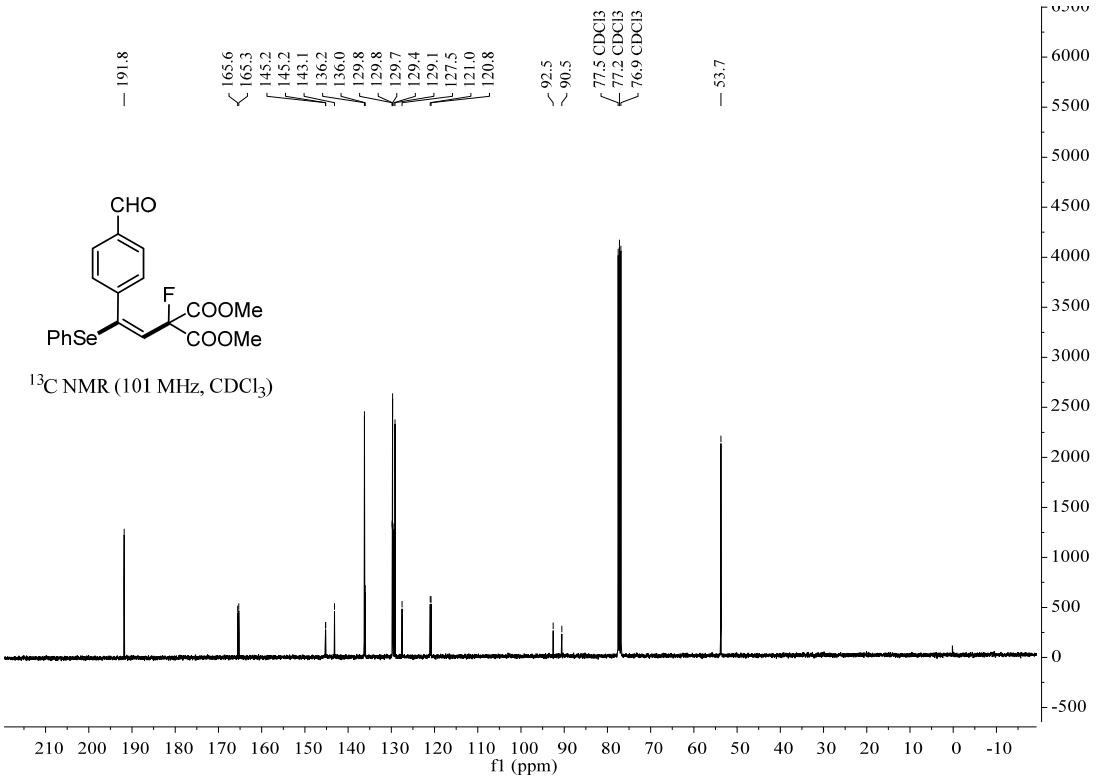
^{13}C NMR (101 MHz, $CDCl_3$)


CF3
F
COOMe
COOMe
PhSe
19F NMR (377 MHz, CDCl3)
-62.8
-143.4
-143.5
5.0E+12
4.5E+12
4.0E+12
3.5E+12
3.0E+12
2.5E+12
2.0E+12
1.5E+12
1.0E+12
5.0E+11
0.0E+00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

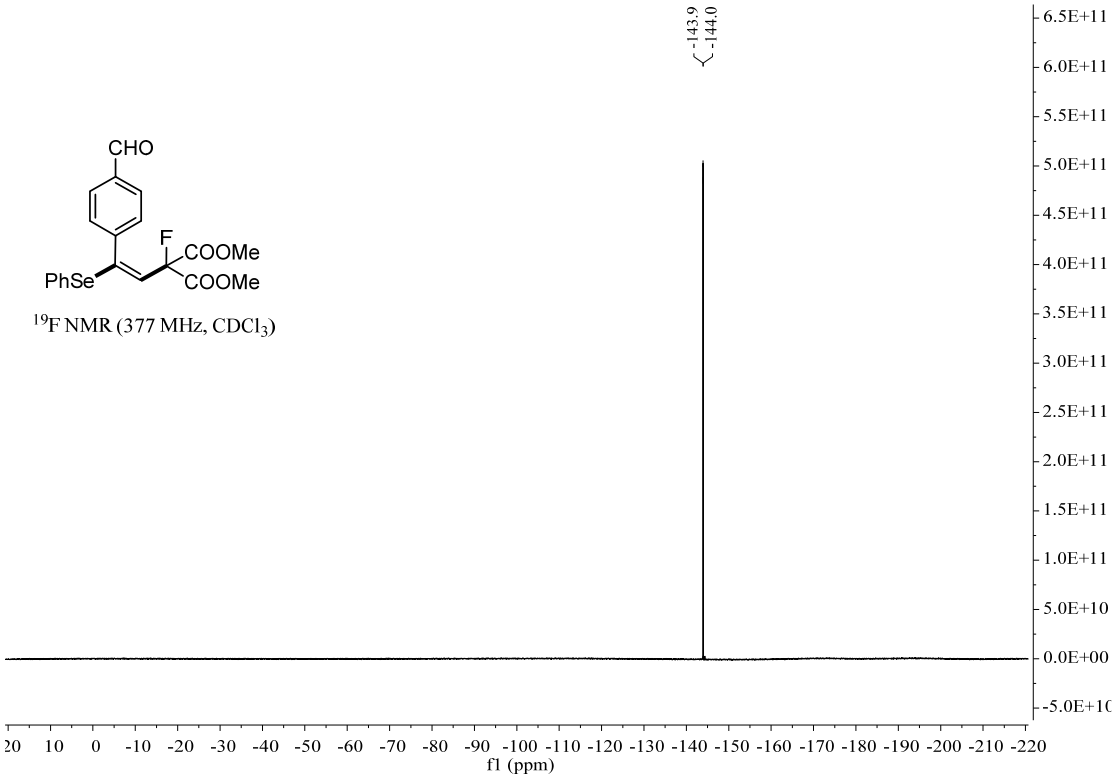
Compound 13



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

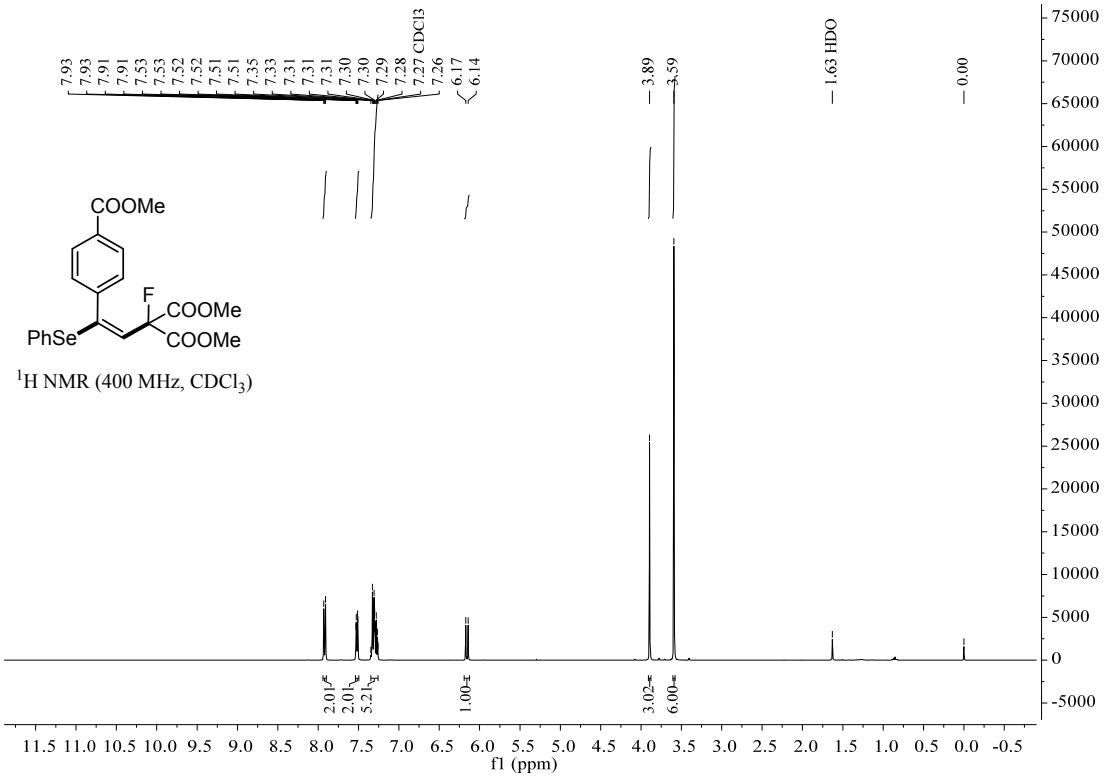


^{13}C NMR (101 MHz, $CDCl_3$)

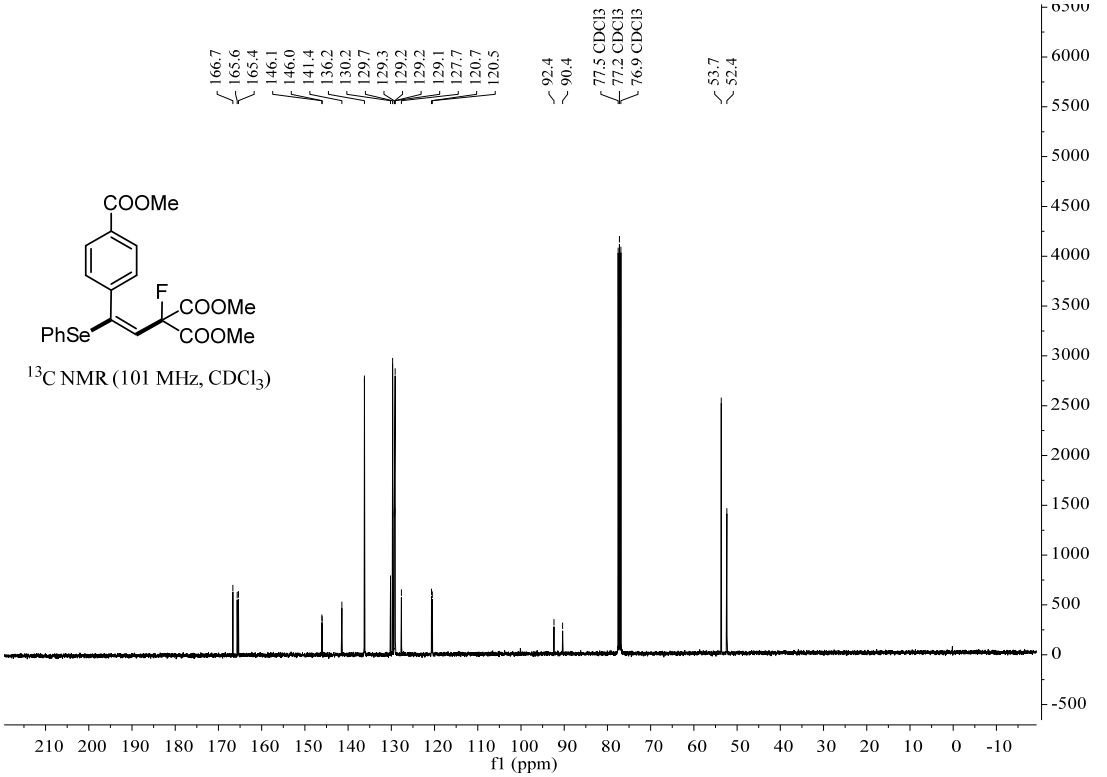


^{19}F NMR (377 MHz, $CDCl_3$)

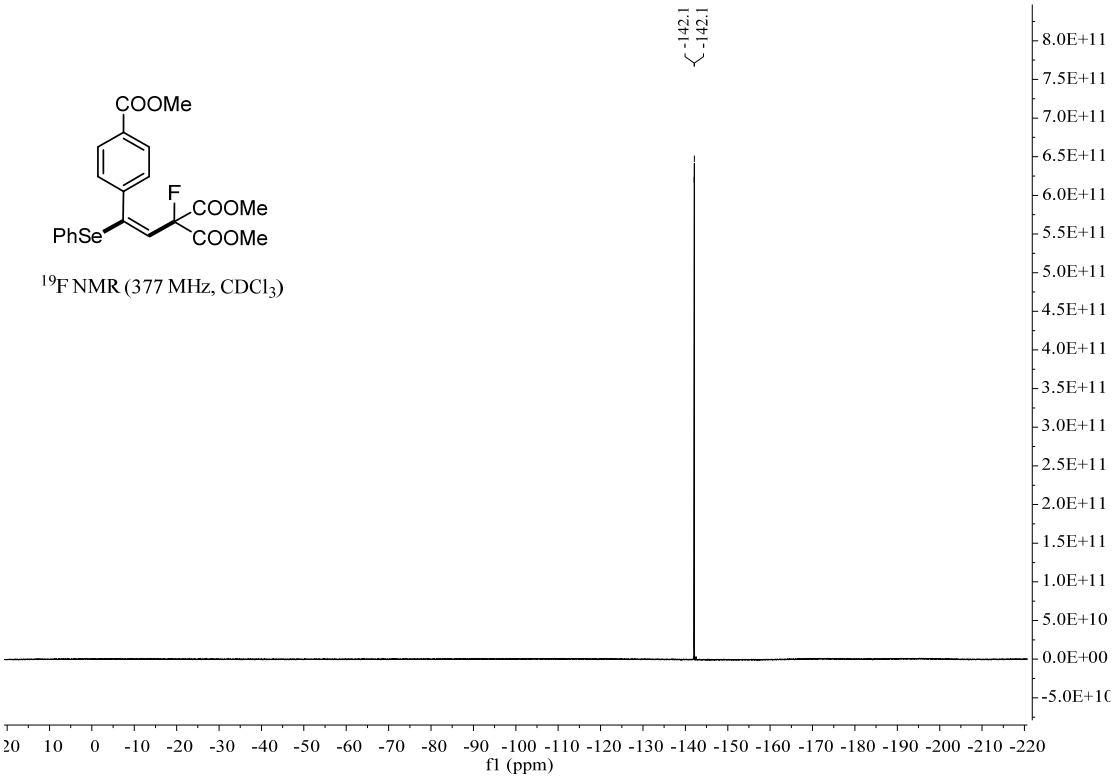
Compound 14



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

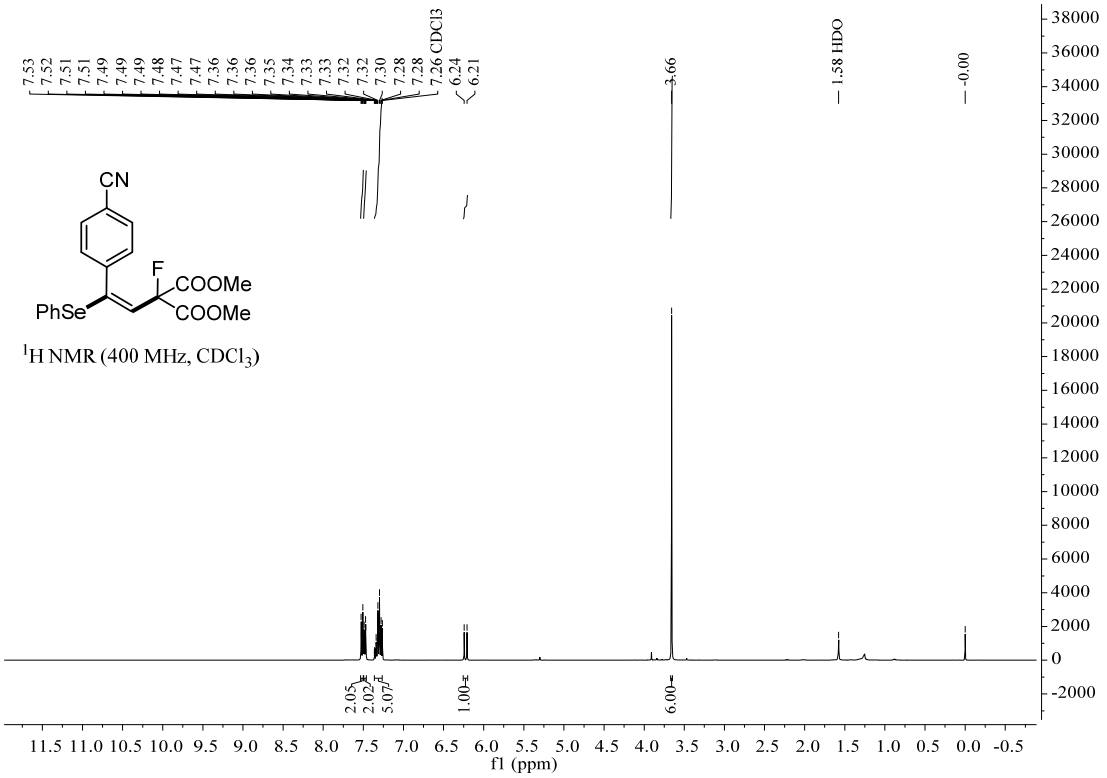


^{13}C NMR (101 MHz, $CDCl_3$)

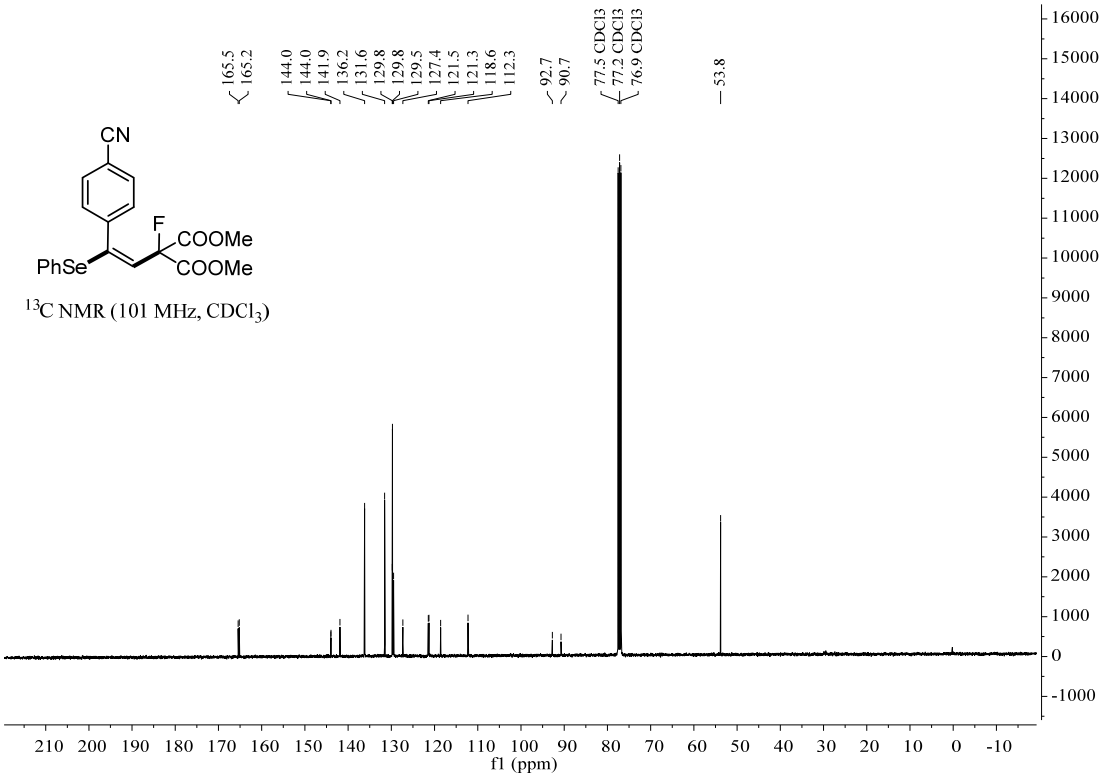


^{19}F NMR (377 MHz, $CDCl_3$)

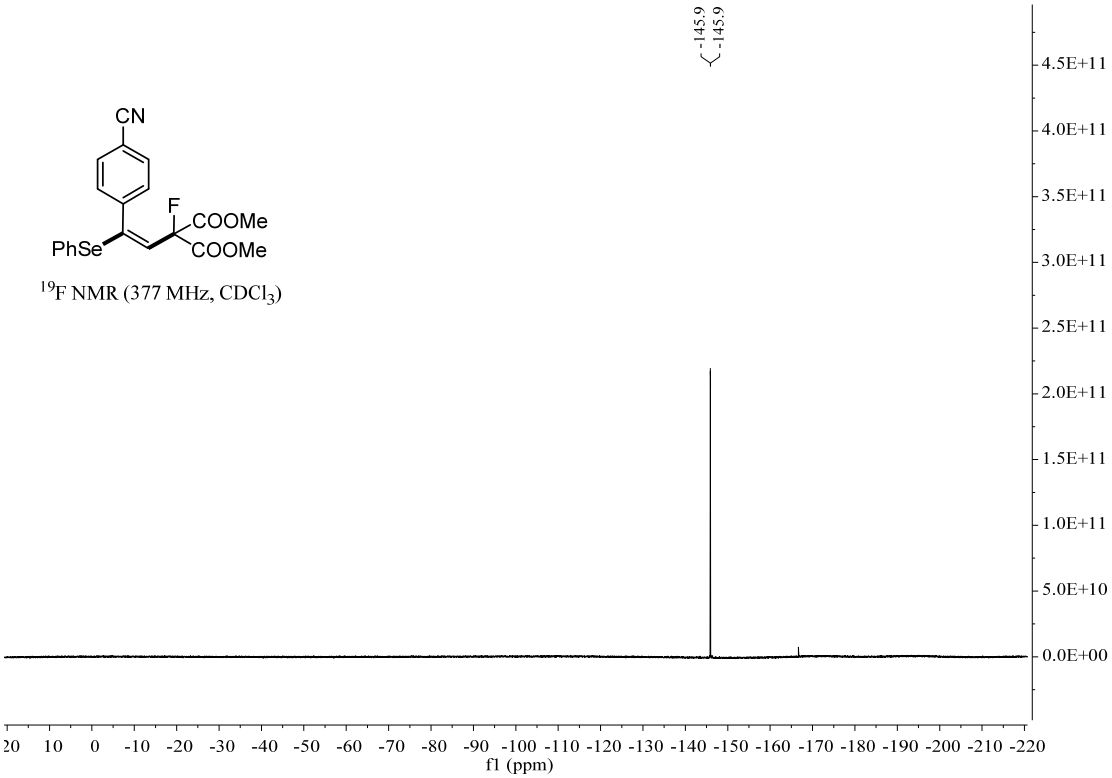
Compound 15



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

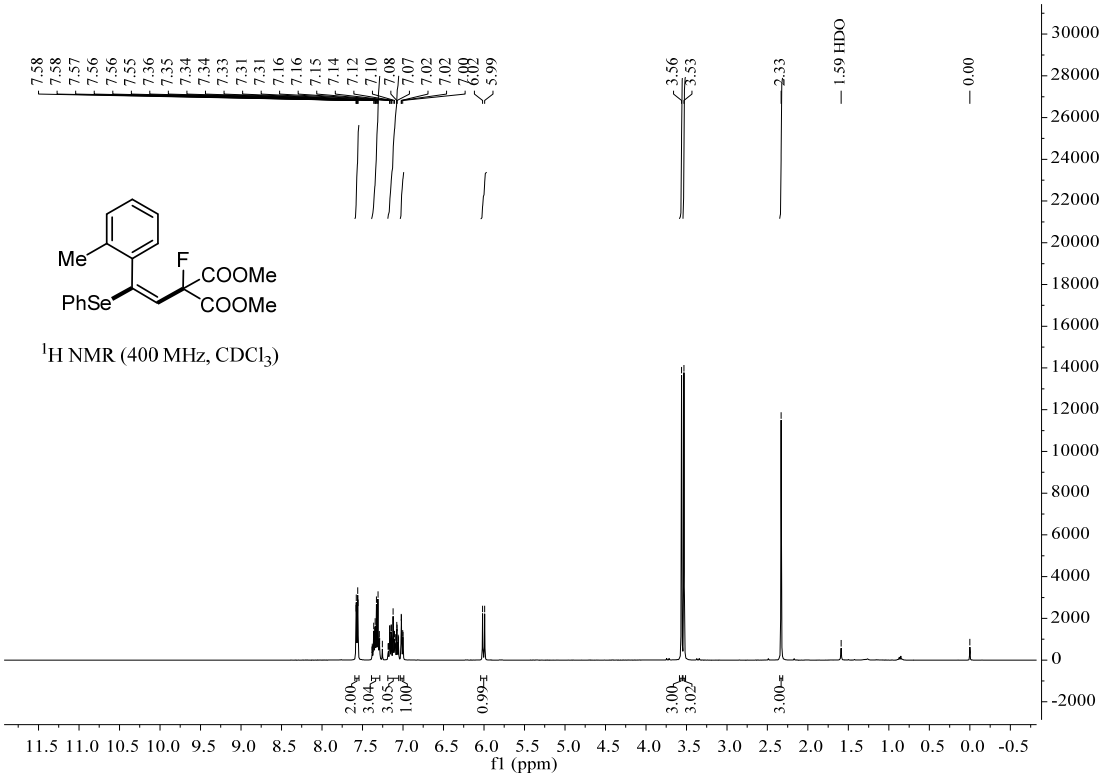


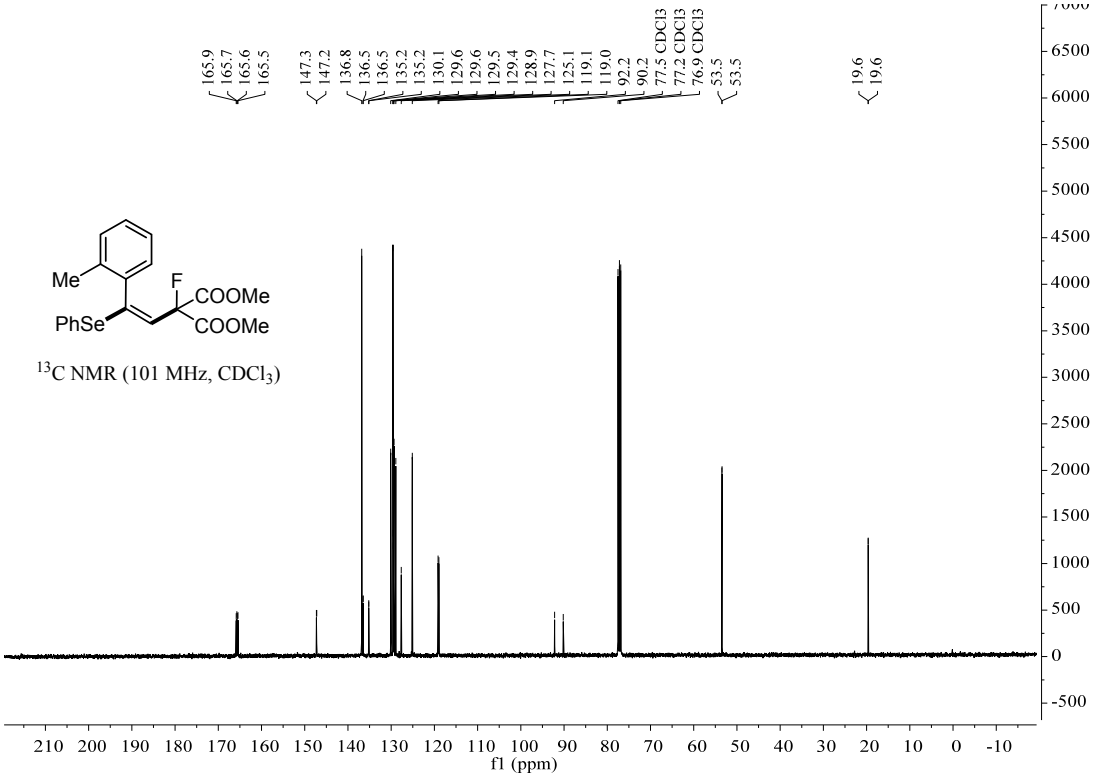
^{13}C NMR (101 MHz, $CDCl_3$)

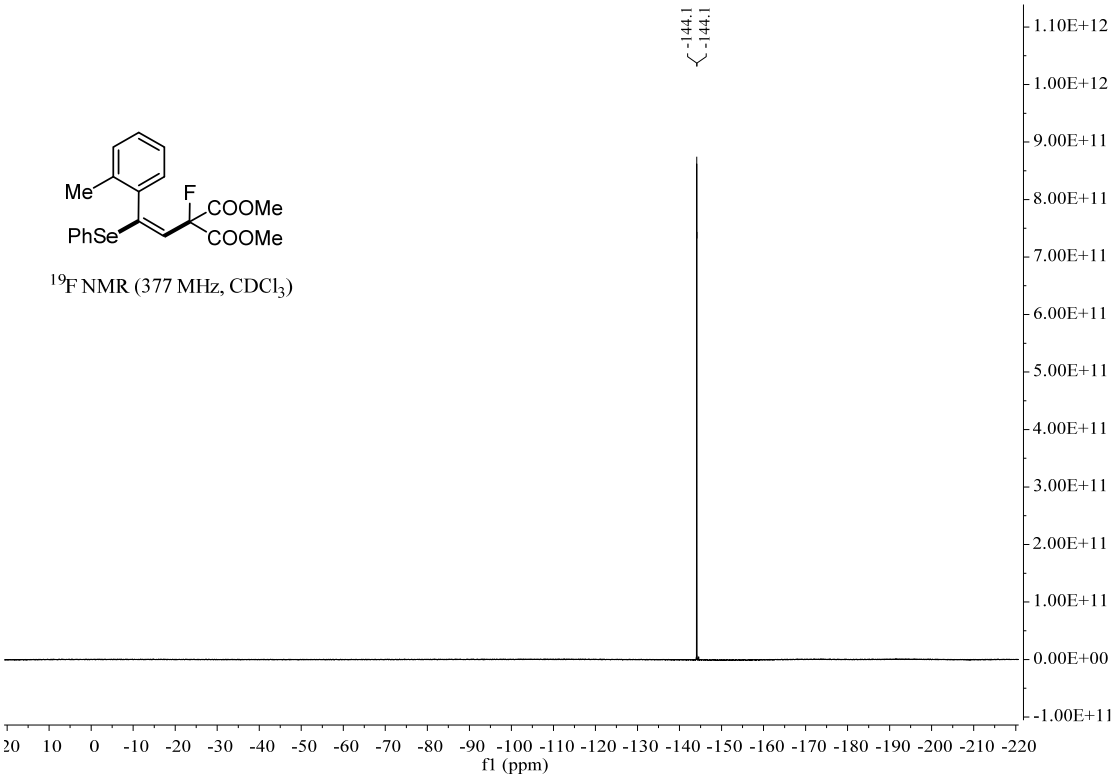


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 16

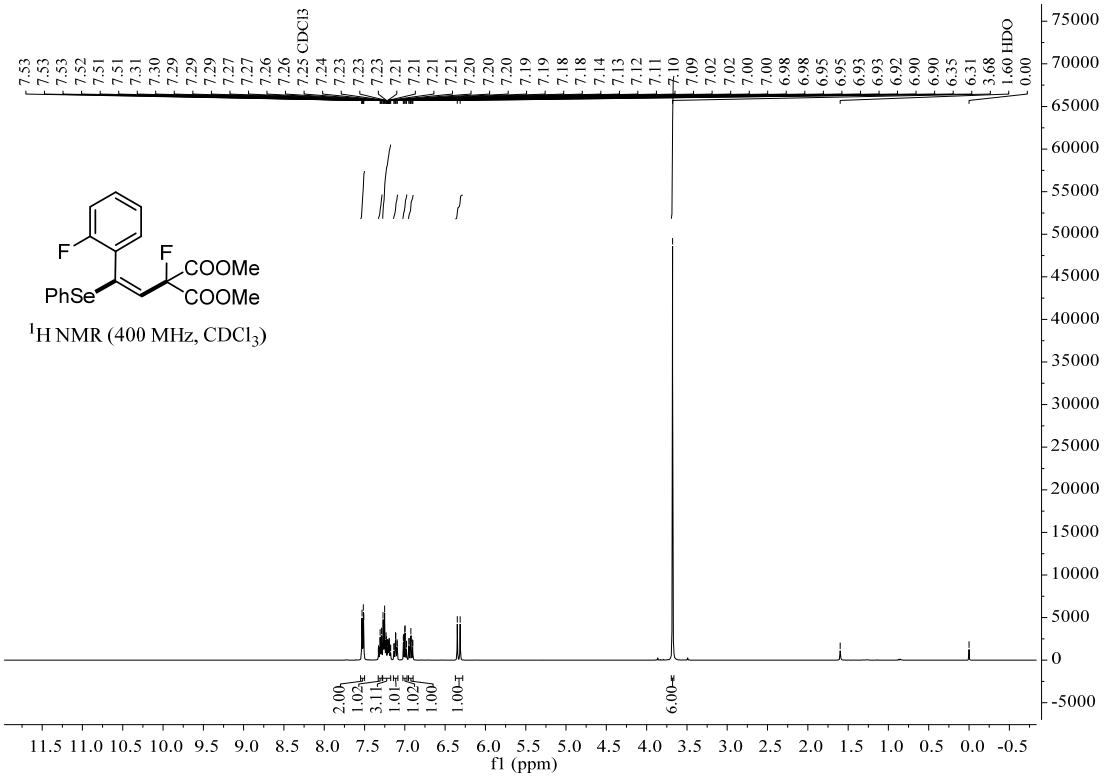

Me
F
COOMe
COOMe
PhSe
1H NMR (400 MHz, CDCl3)
f1 (ppm)

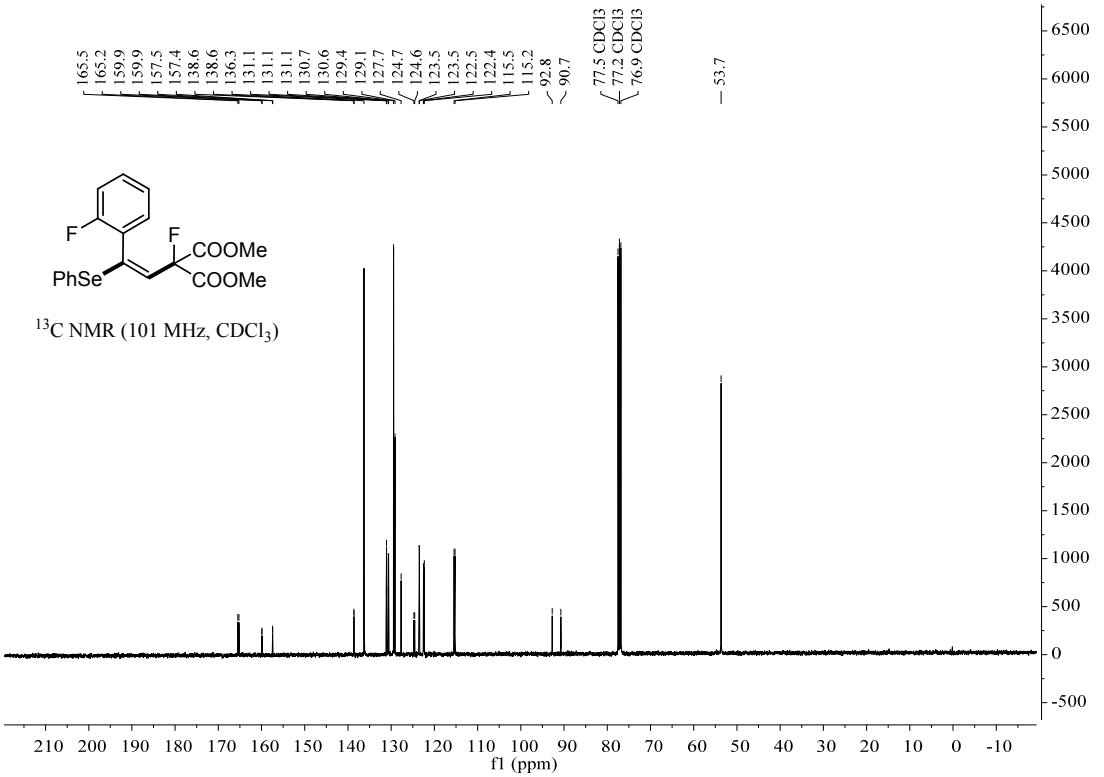

Me
F
COOMe
COOMe
PhSe
13C NMR (101 MHz, CDCl3)
f1 (ppm)

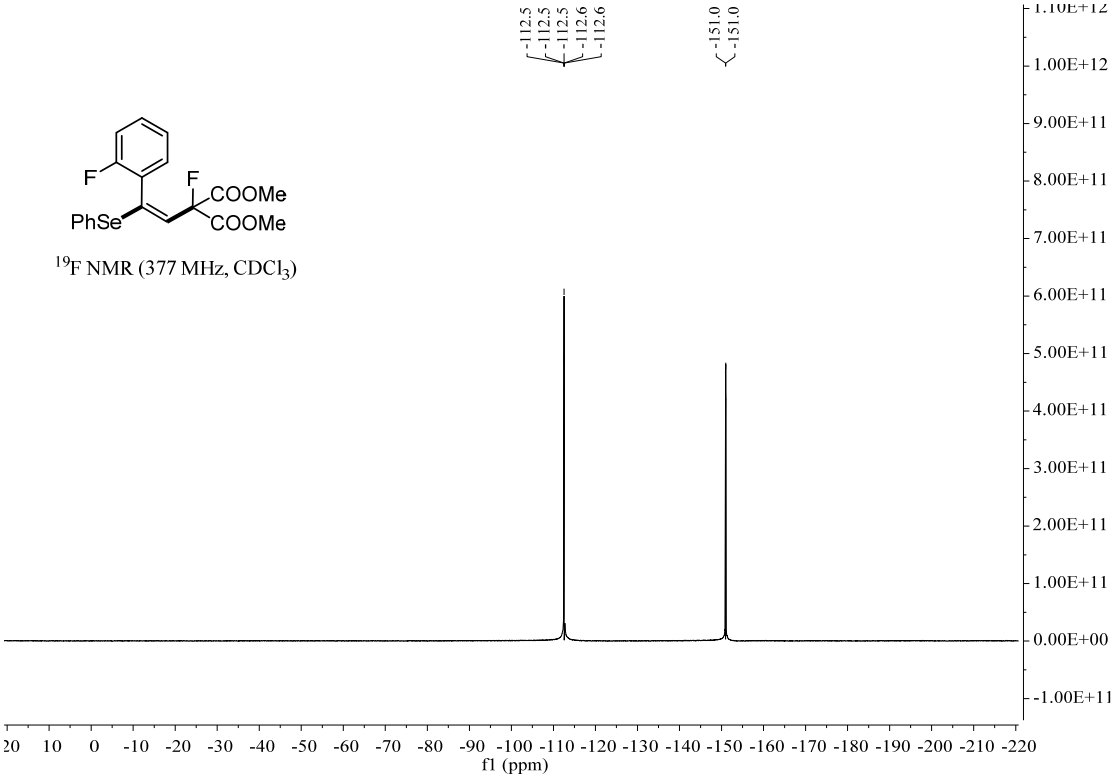


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 17

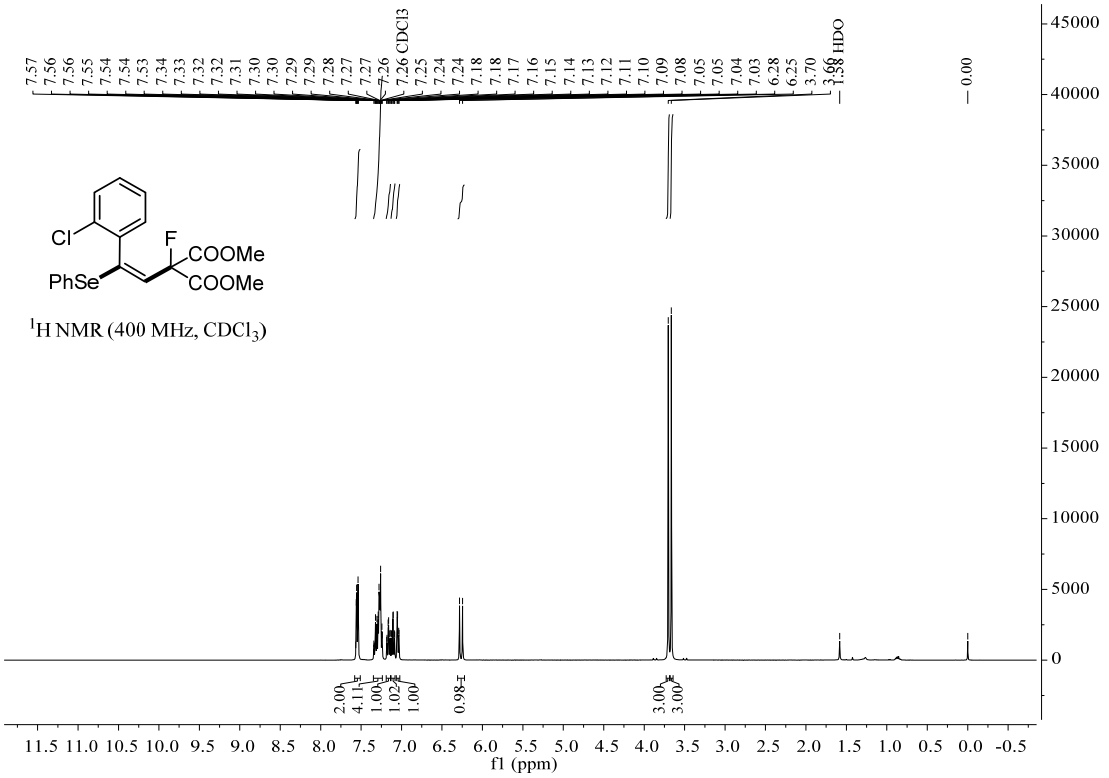

F
F
COOMe
COOMe
PhSe
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

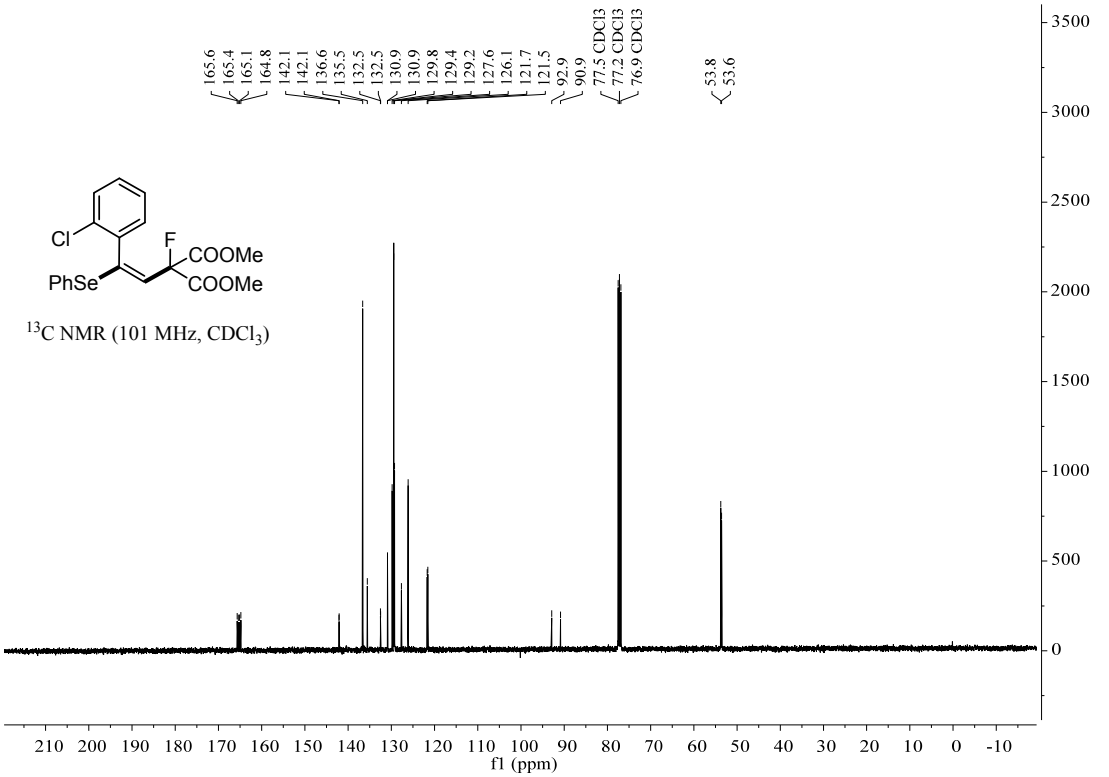

F
F
COOMe
COOMe
PhSe
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

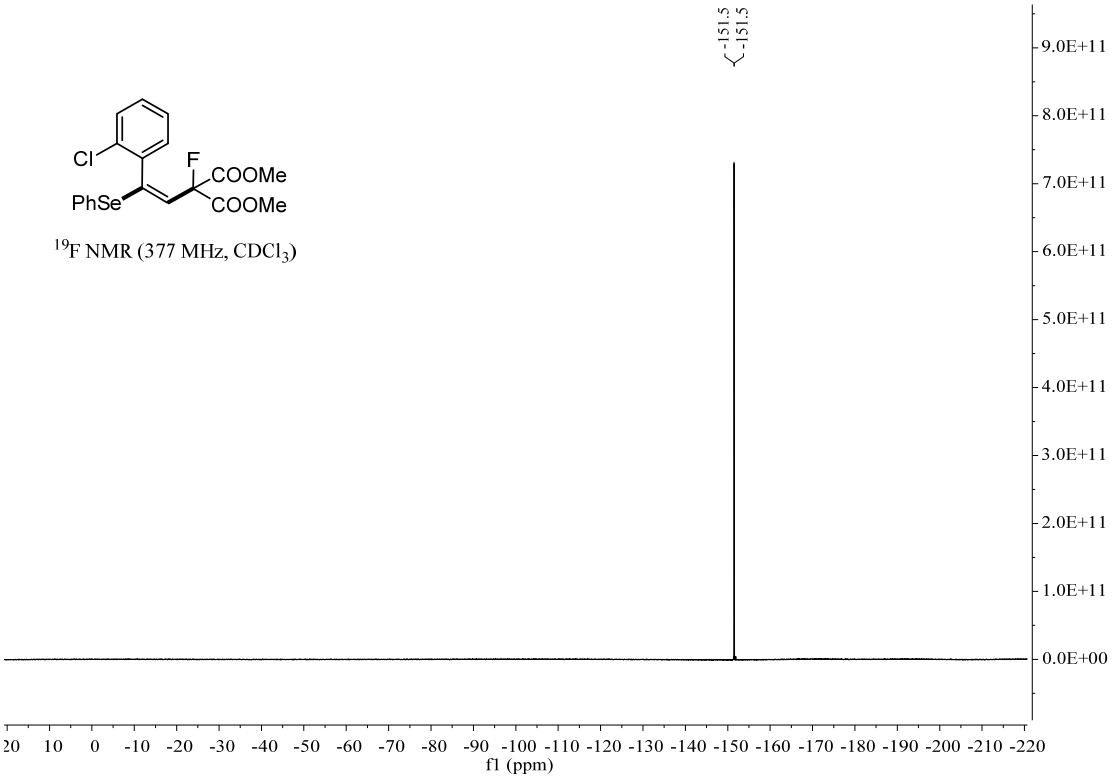


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 18

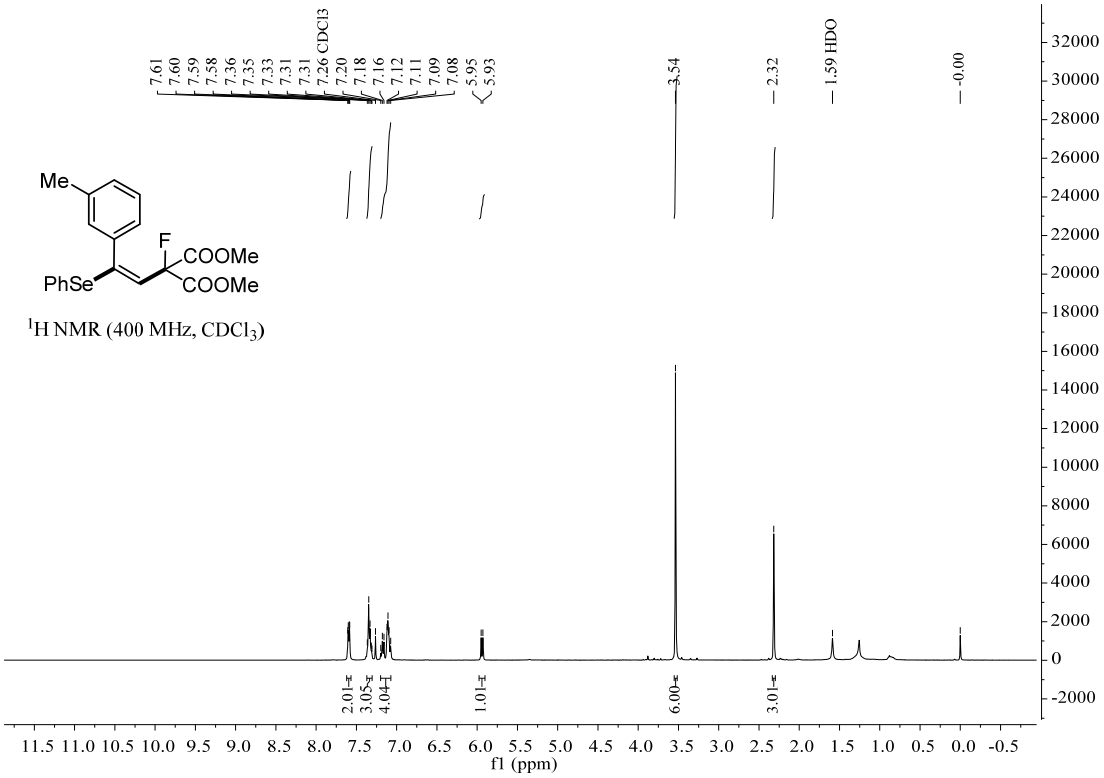

Cl
F
COOMe
COOMe
PhSe
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Cl
F
COOMe
COOMe
PhSe
13C NMR (101 MHz, CDCl3)
f1 (ppm)

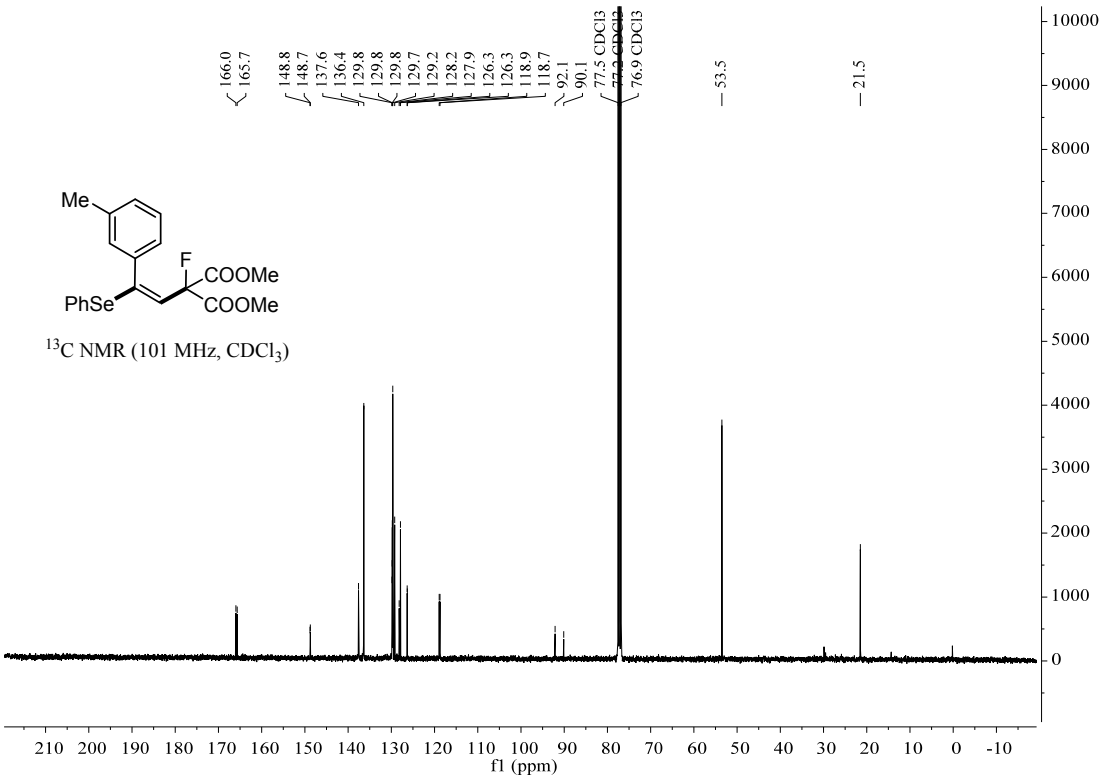


^{19}F NMR (377 MHz, $CDCl_3$)

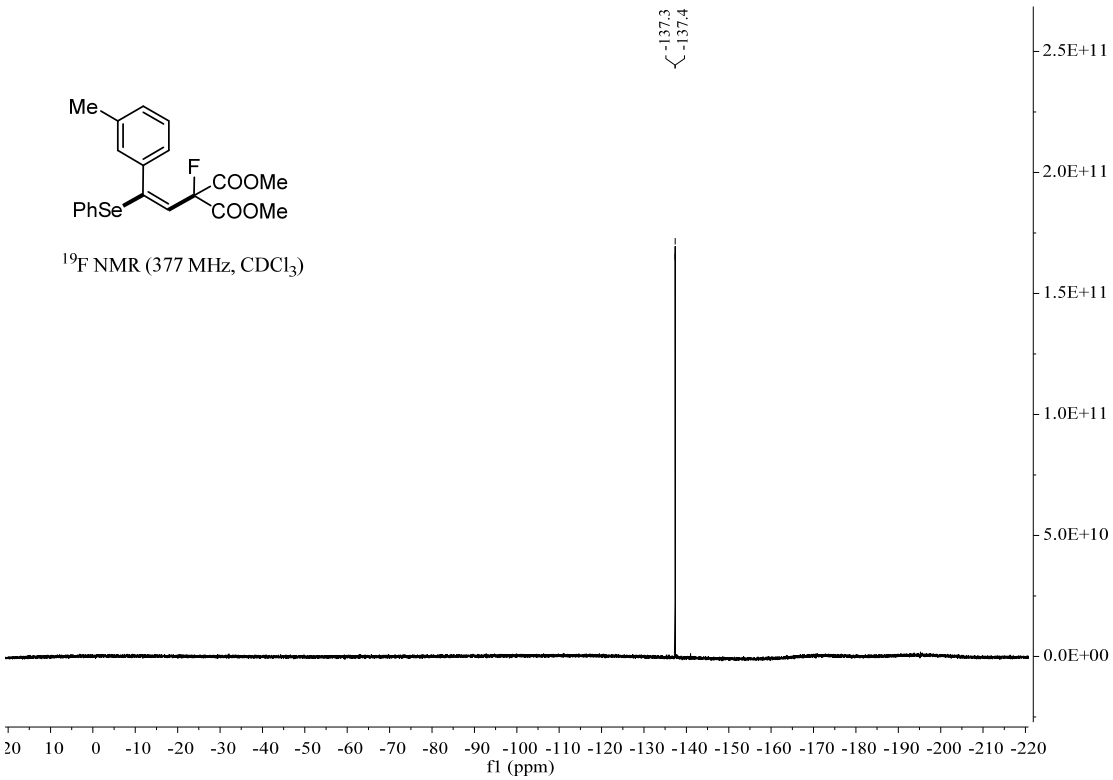
Compound 19



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

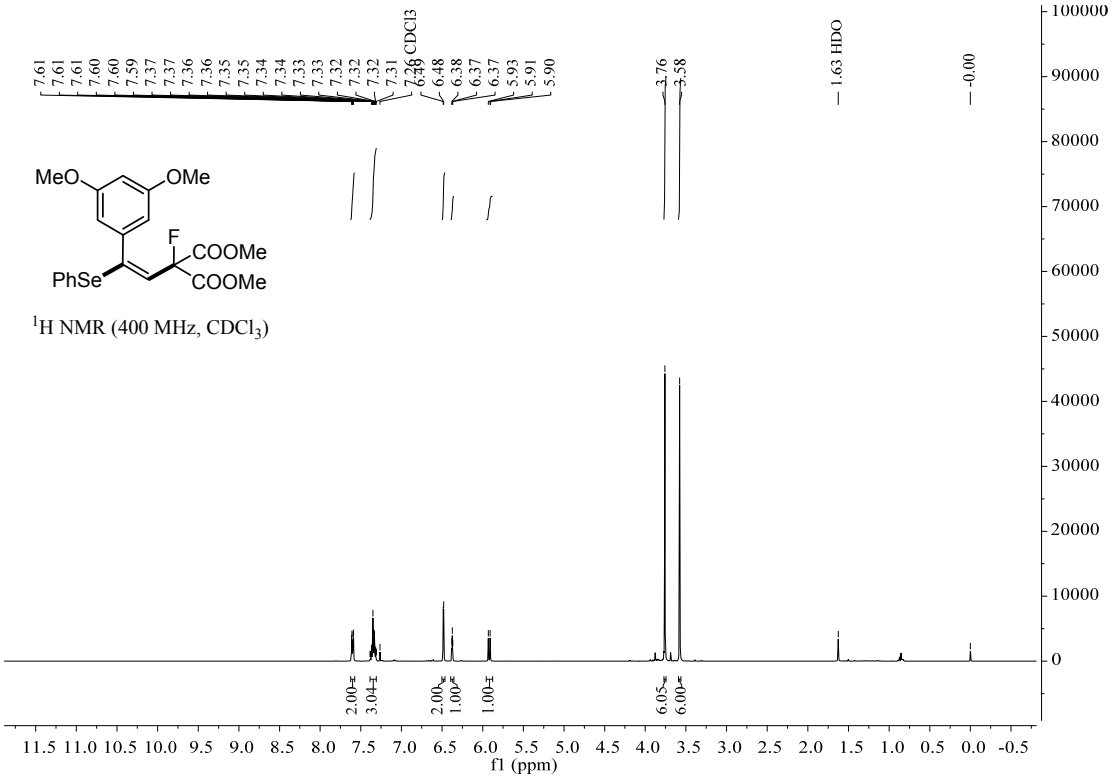


^{13}C NMR (101 MHz, $CDCl_3$)

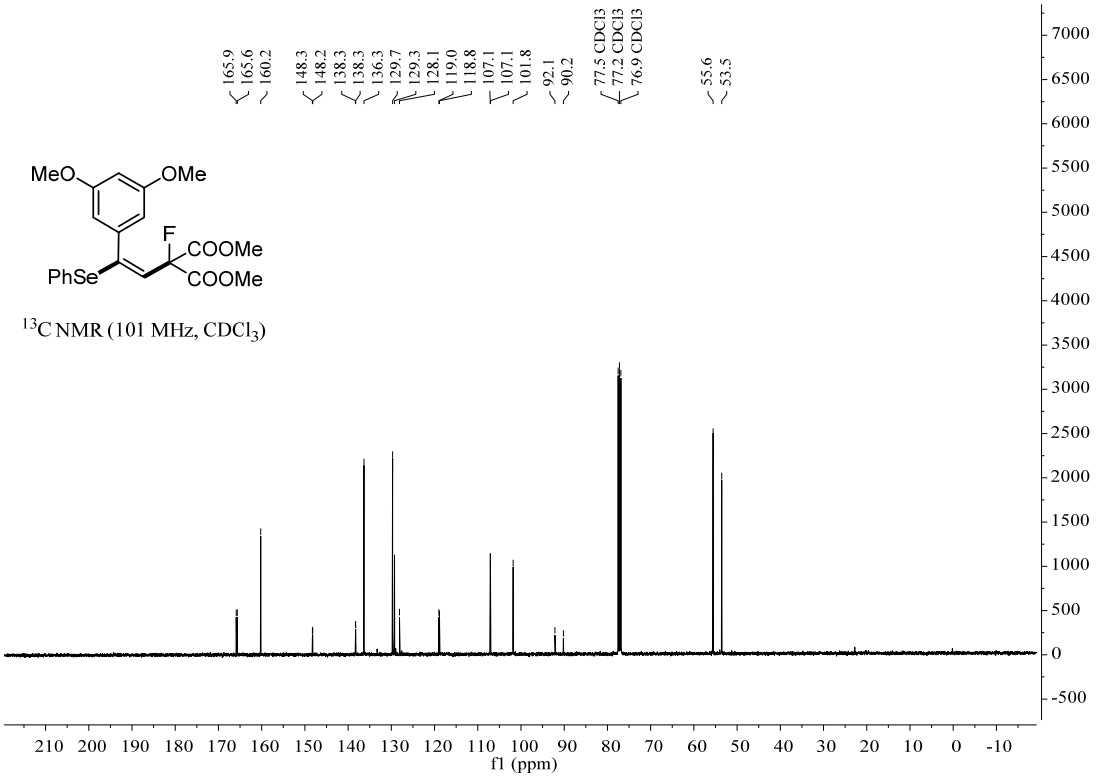


^{19}F NMR (377 MHz, $CDCl_3$)

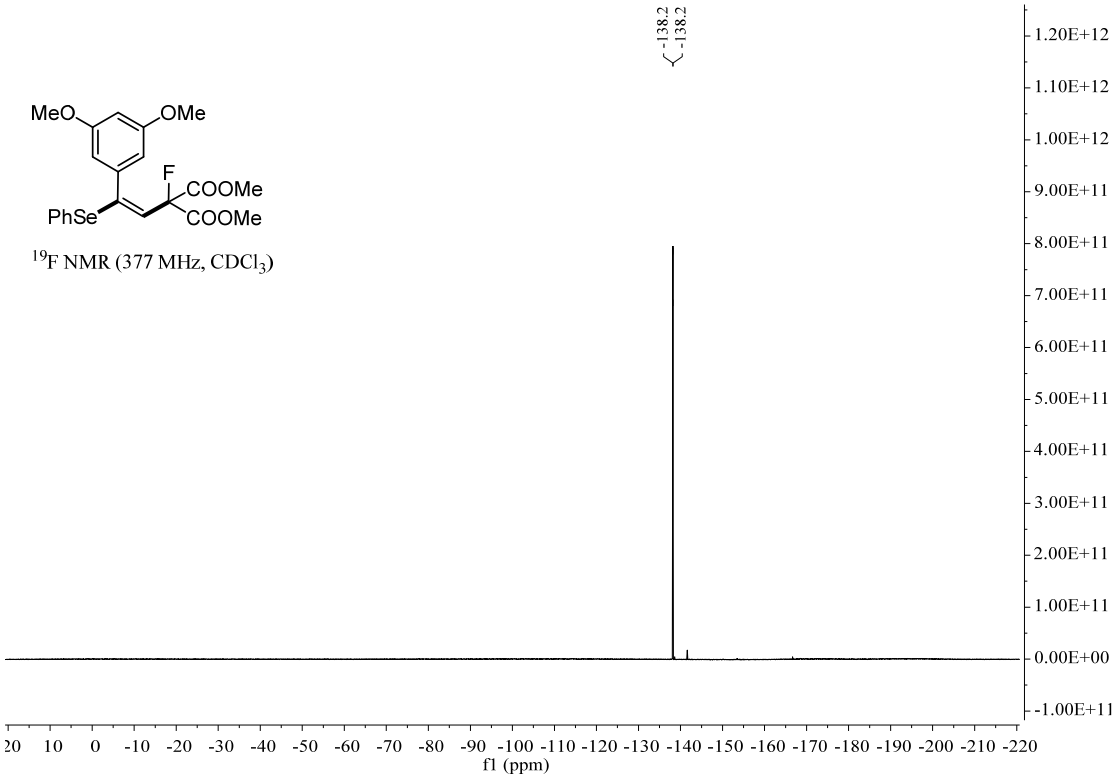
Compound 20



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

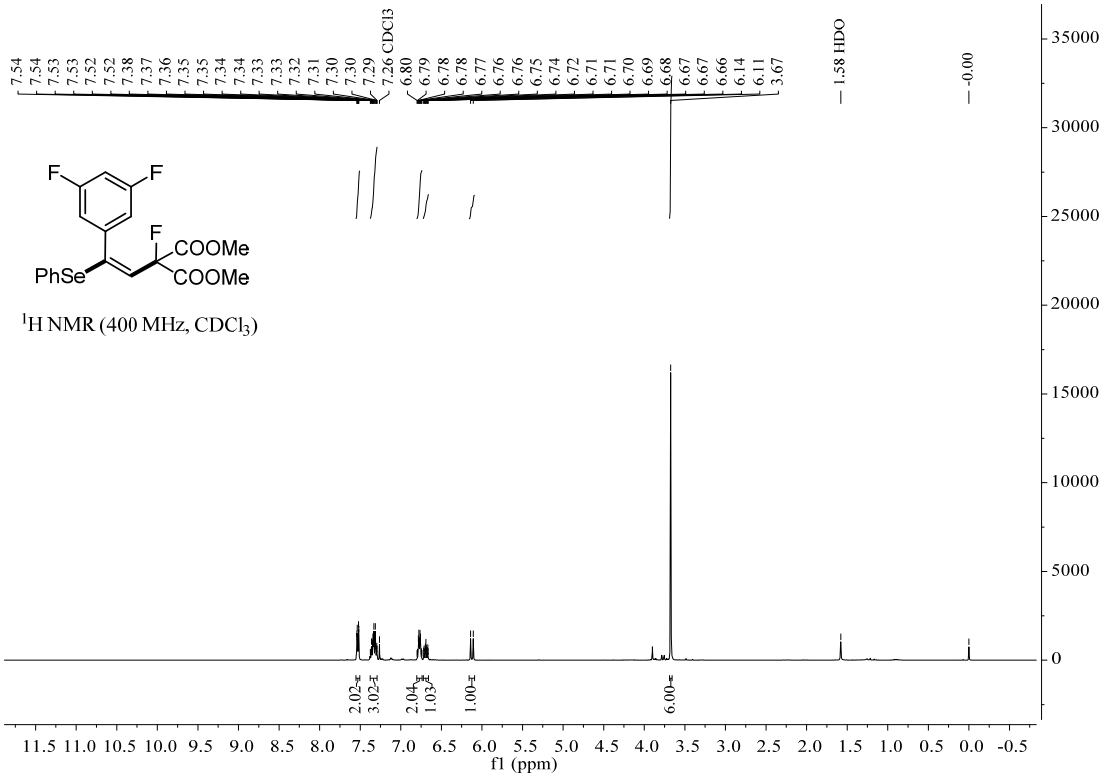


^{13}C NMR (101 MHz, $CDCl_3$)

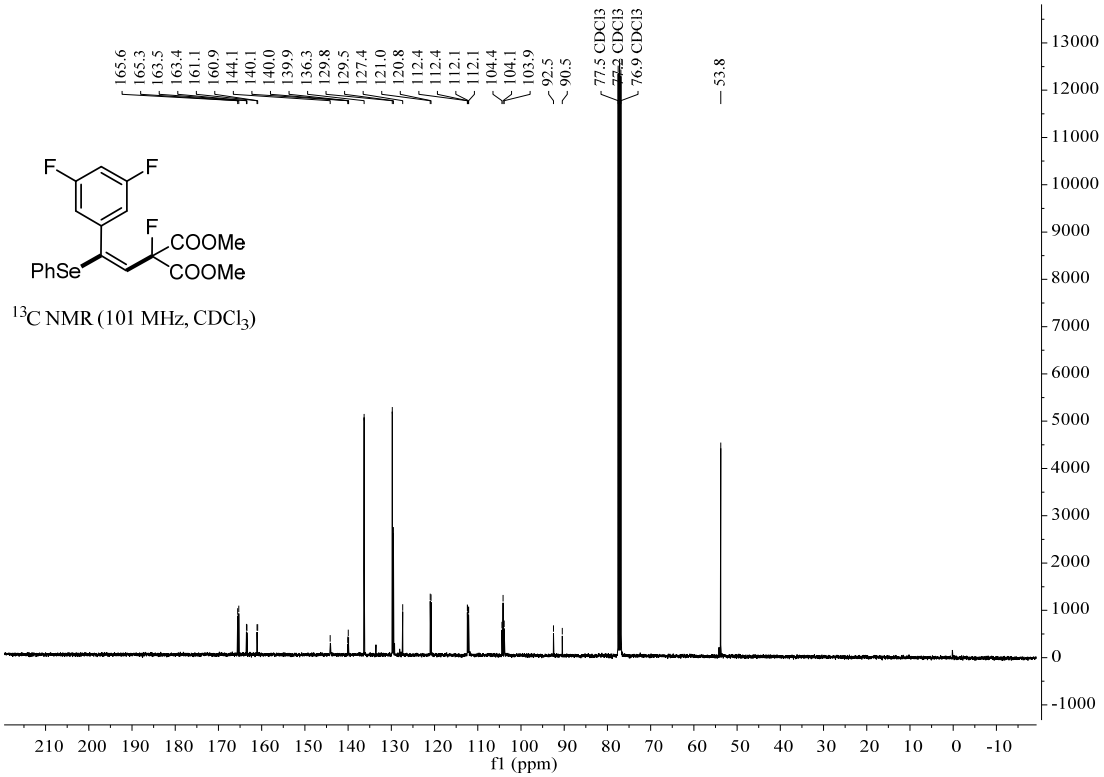


^{19}F NMR (377 MHz, $CDCl_3$)

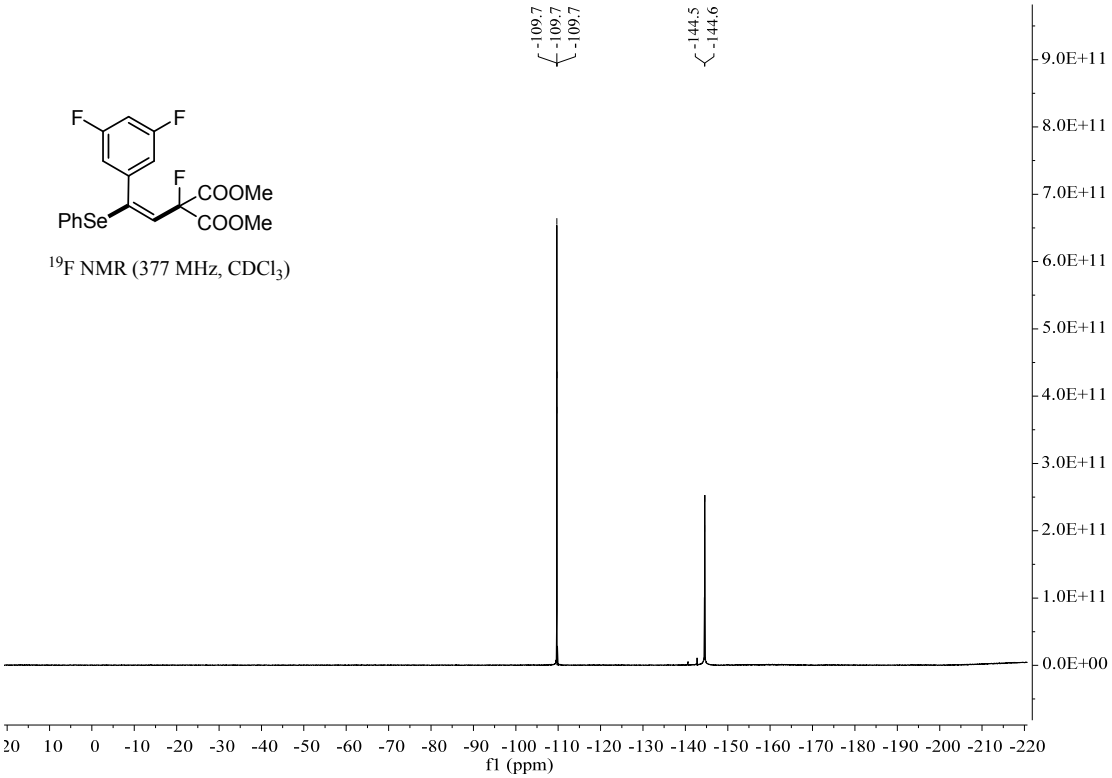
Compound 21



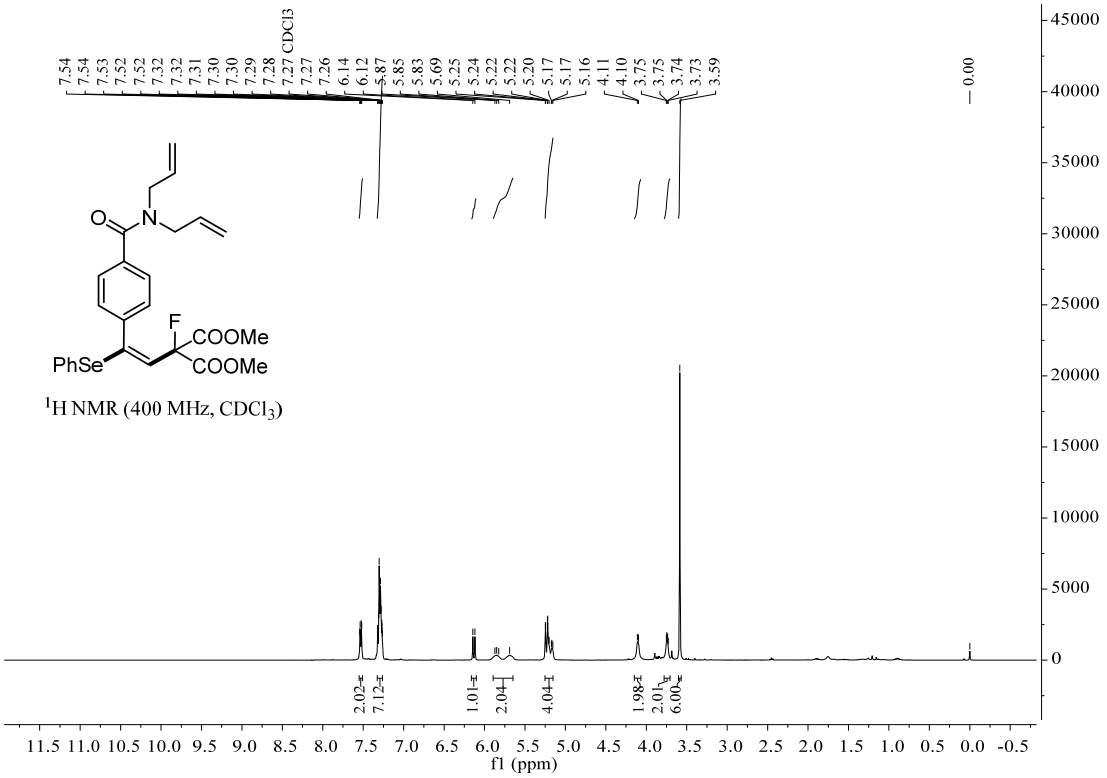
^{1}H NMR (400 MHz, $CDCl_3$)



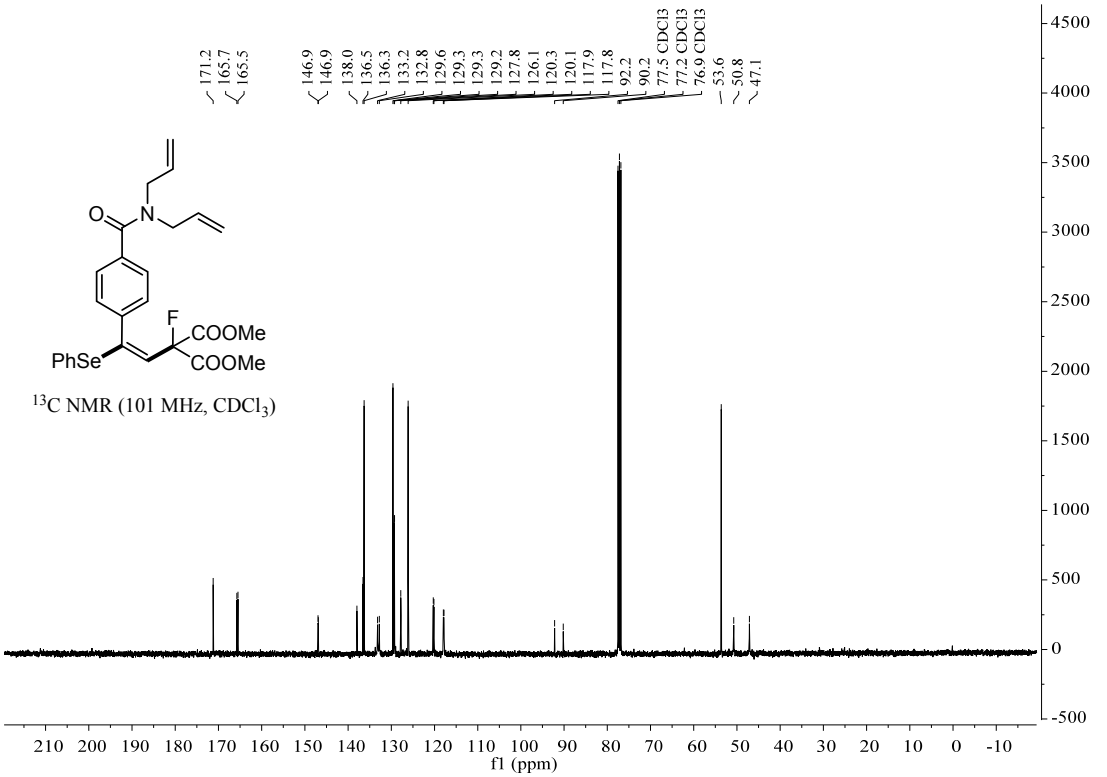
^{13}C NMR (101 MHz, $CDCl_3$)


F
F
F
COOMe
COOMe
PhSe
^{19}F NMR (377 MHz, $CDCl_3$)
-109.7
-109.7
-109.7
-144.5
-144.6
9.0E+11
8.0E+11
7.0E+11
6.0E+11
5.0E+11
4.0E+11
3.0E+11
2.0E+11
1.0E+11
0.0E+00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

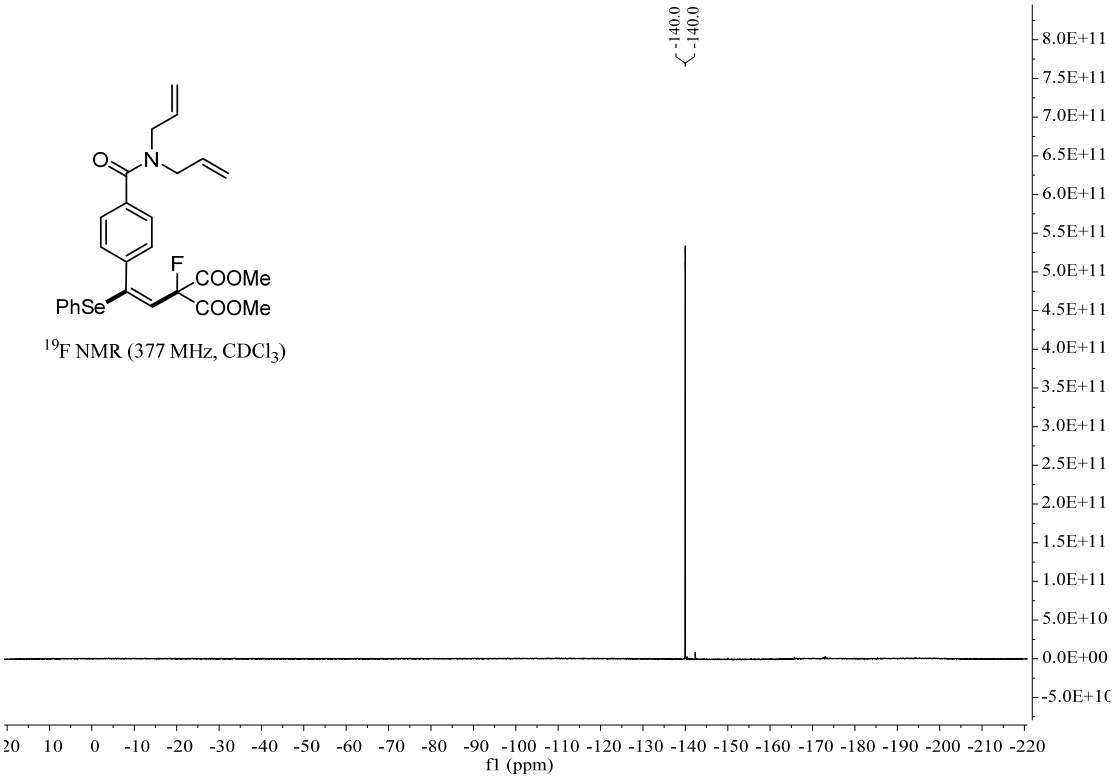
Compound 22



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

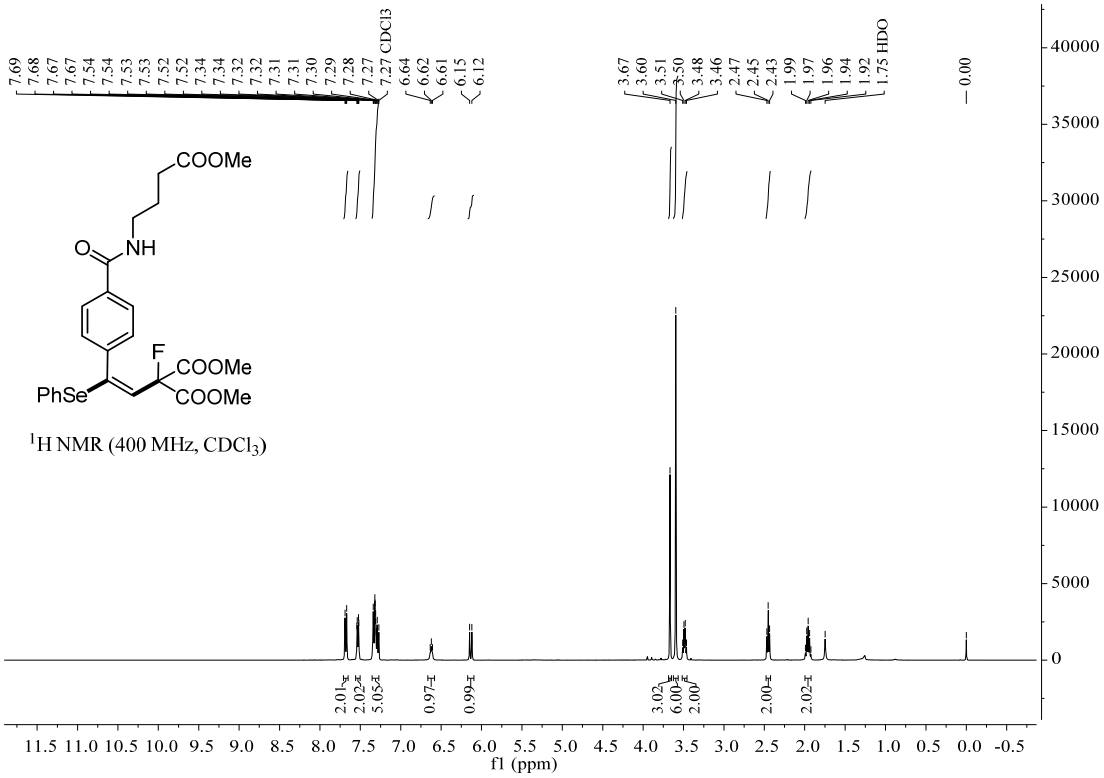


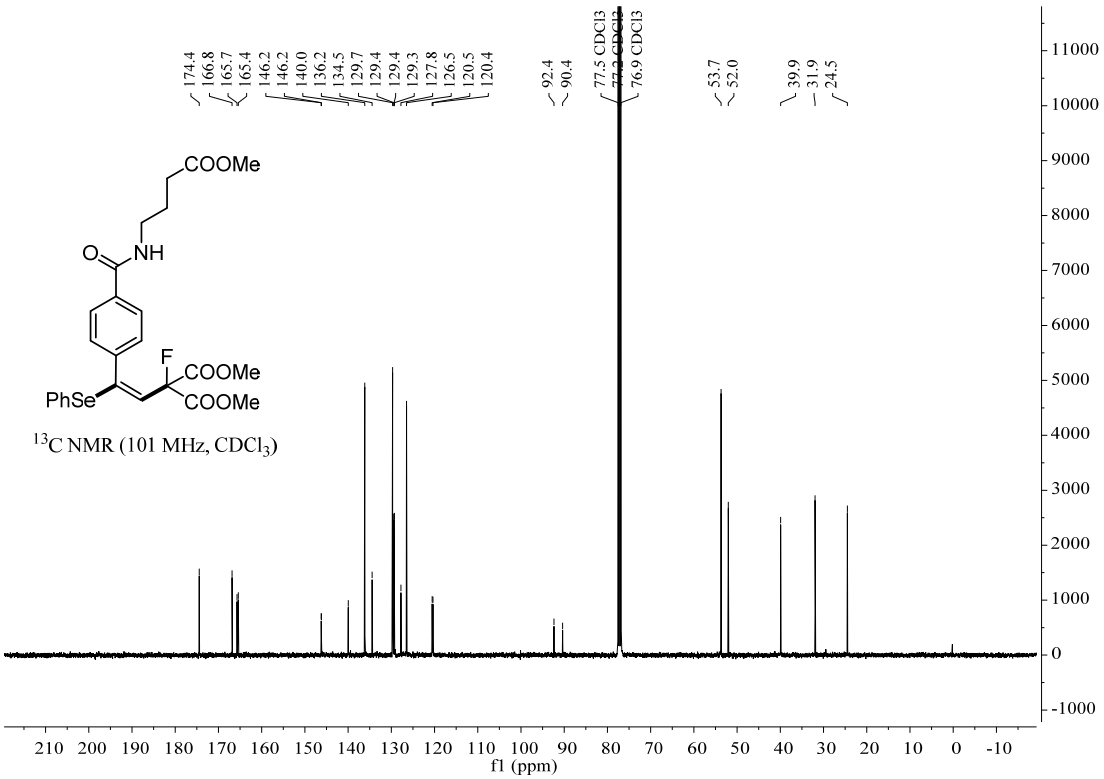
^{13}C NMR (101 MHz, $CDCl_3$)

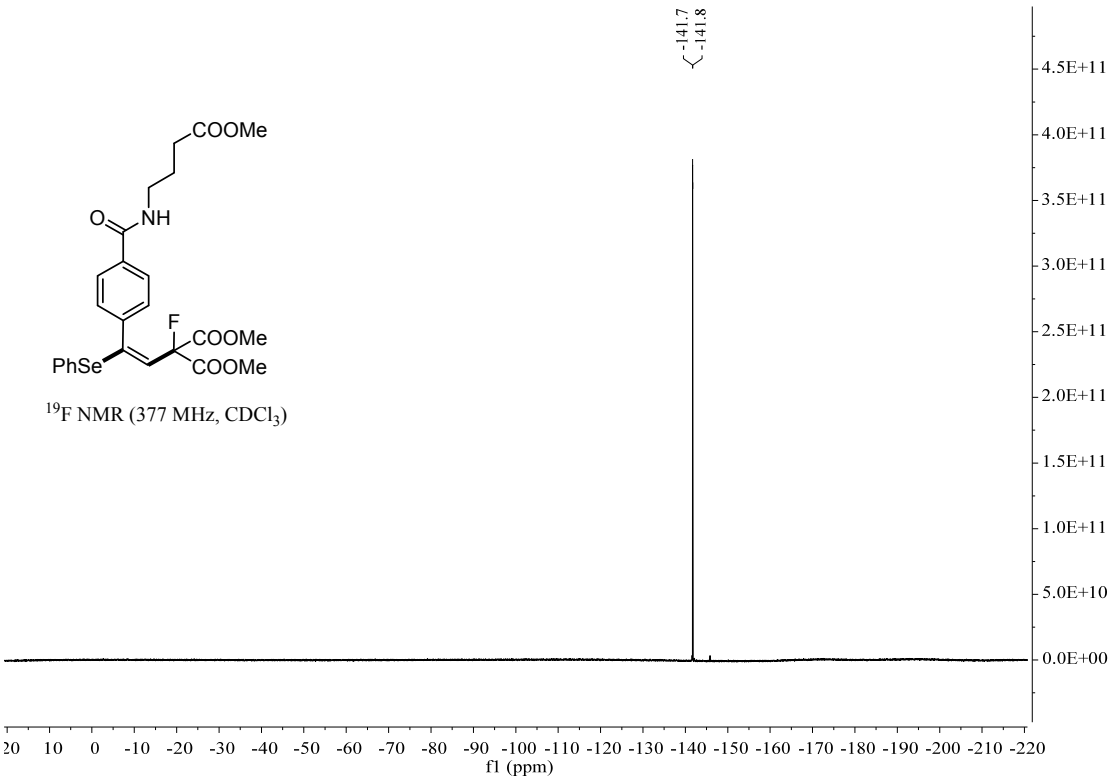


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 23

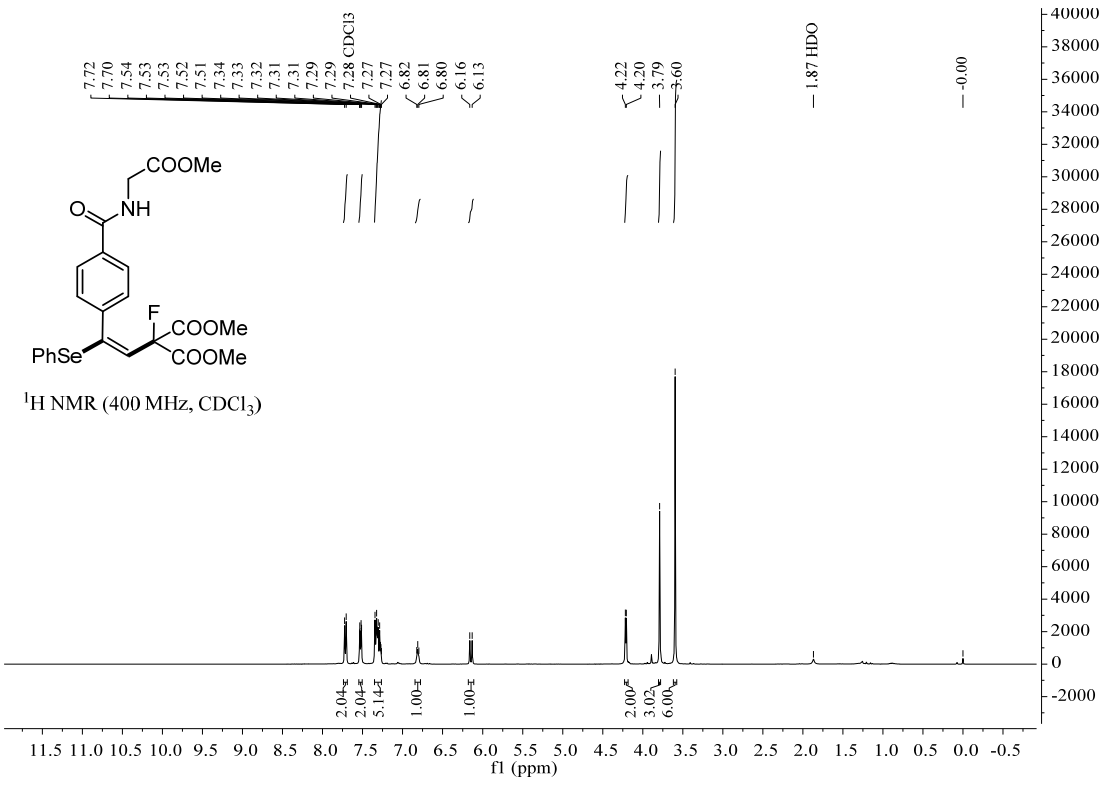

7.69
7.68
7.67
7.67
7.54
7.54
7.53
7.53
7.52
7.52
7.34
7.34
7.32
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.27 CDCl3
6.64
6.62
6.61
6.15
6.12
3.67
3.60
3.51
3.50
3.48
3.46
2.47
2.45
2.43
1.99
1.97
1.96
1.94
1.92
1.75 HDO
0.00
COOMe
NH
O
F
COOMe
COOMe
PhSe
1H NMR (400 MHz, CDCl3)
2.01
2.02
5.05
0.97
0.99
3.02
6.00
2.00
2.00
2.02
f1 (ppm)


174.4
166.8
165.7
165.4
146.2
146.2
140.0
136.2
134.5
129.7
129.4
129.4
129.3
127.8
126.5
120.5
120.4
92.4
90.4
77.5 CDCl3
77.0 CDCl3
76.9 CDCl3
53.7
52.0
39.9
31.9
24.5
COOMe
NH
O
F
COOMe
COOMe
PhSe
13C NMR (101 MHz, CDCl3)
f1 (ppm)

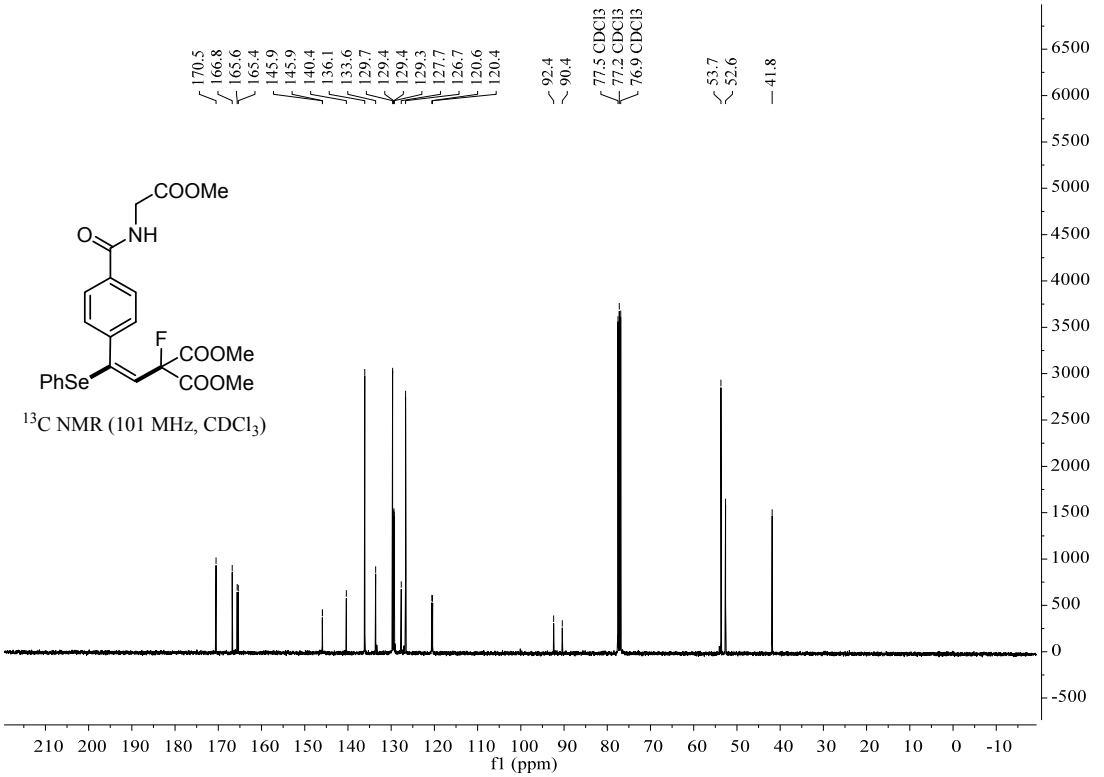


^{19}F NMR (377 MHz, $CDCl_3$)

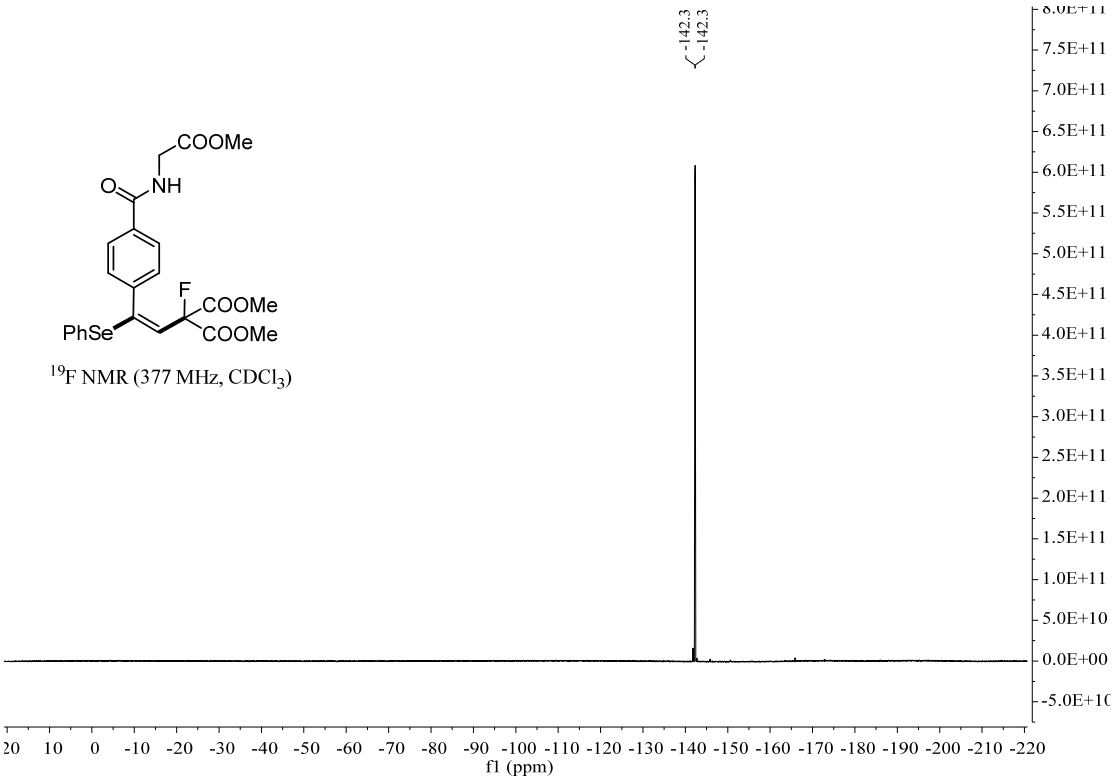
Compound 24



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

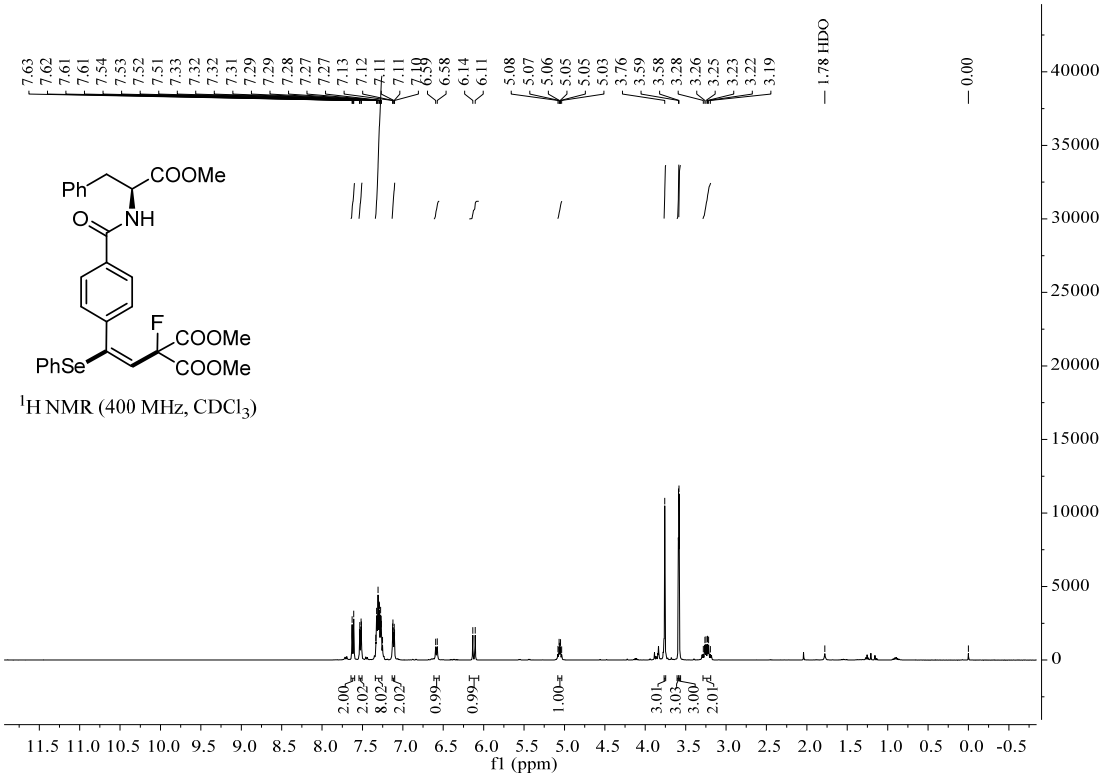


^{13}C NMR (101 MHz, $CDCl_3$)

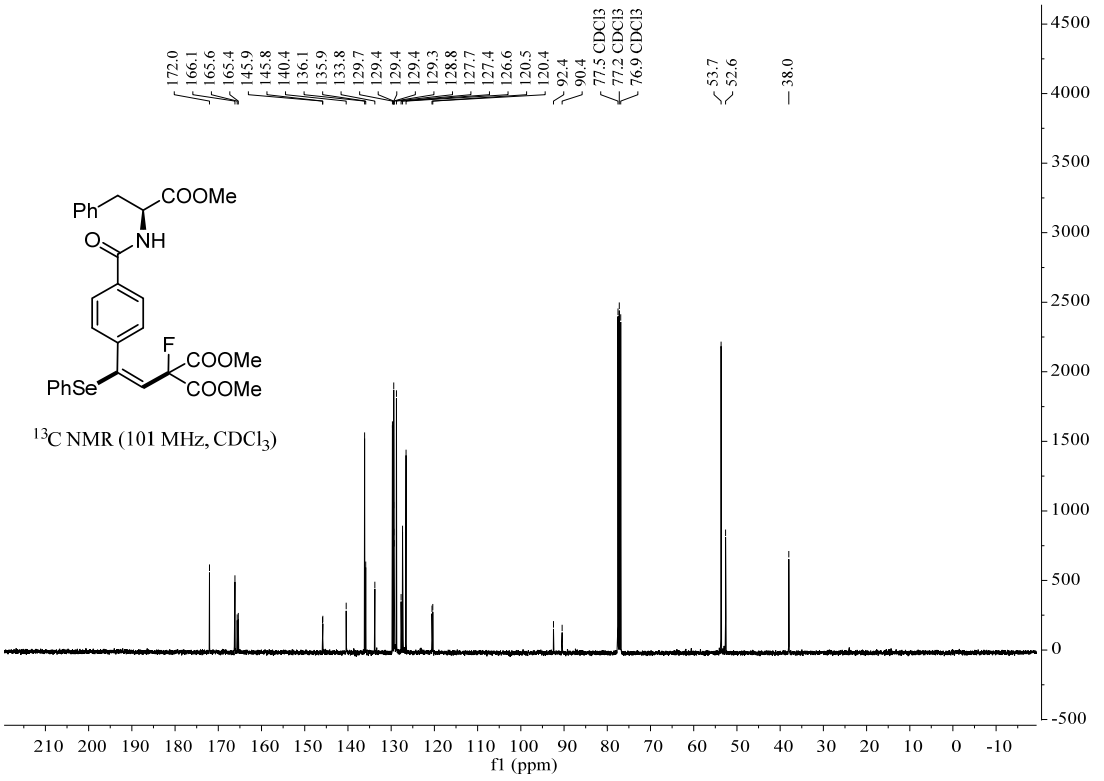


^{19}F NMR (377 MHz, $CDCl_3$)

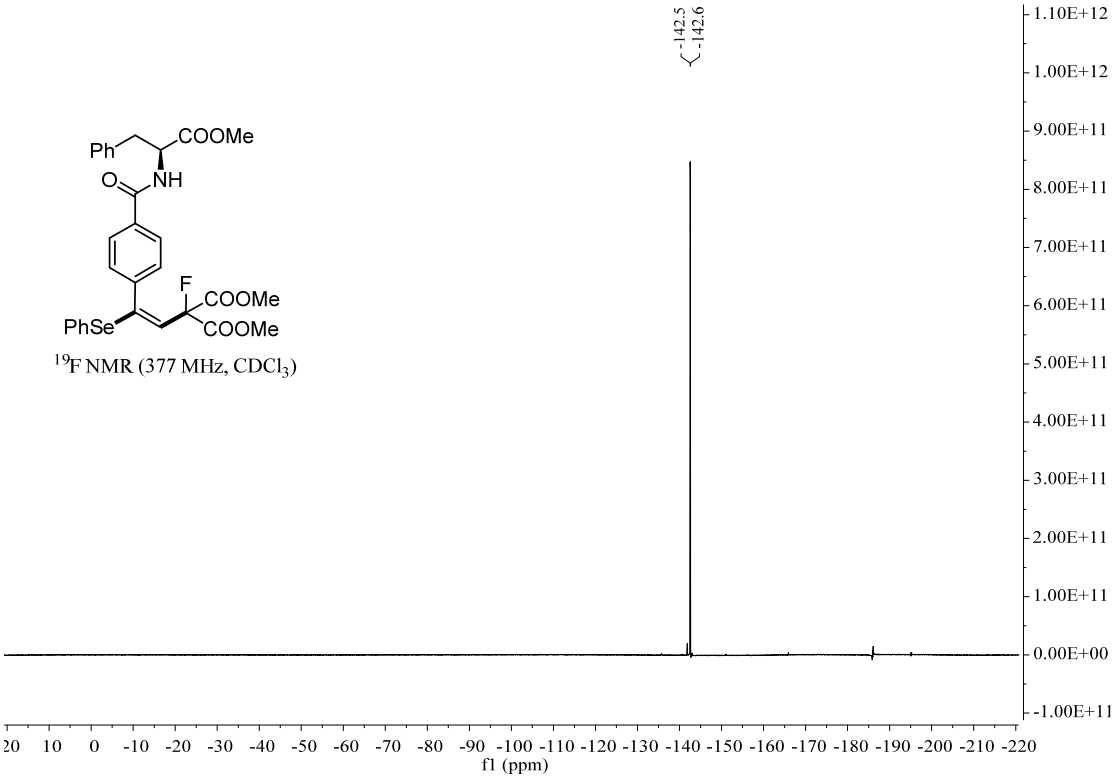
Compound 25



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

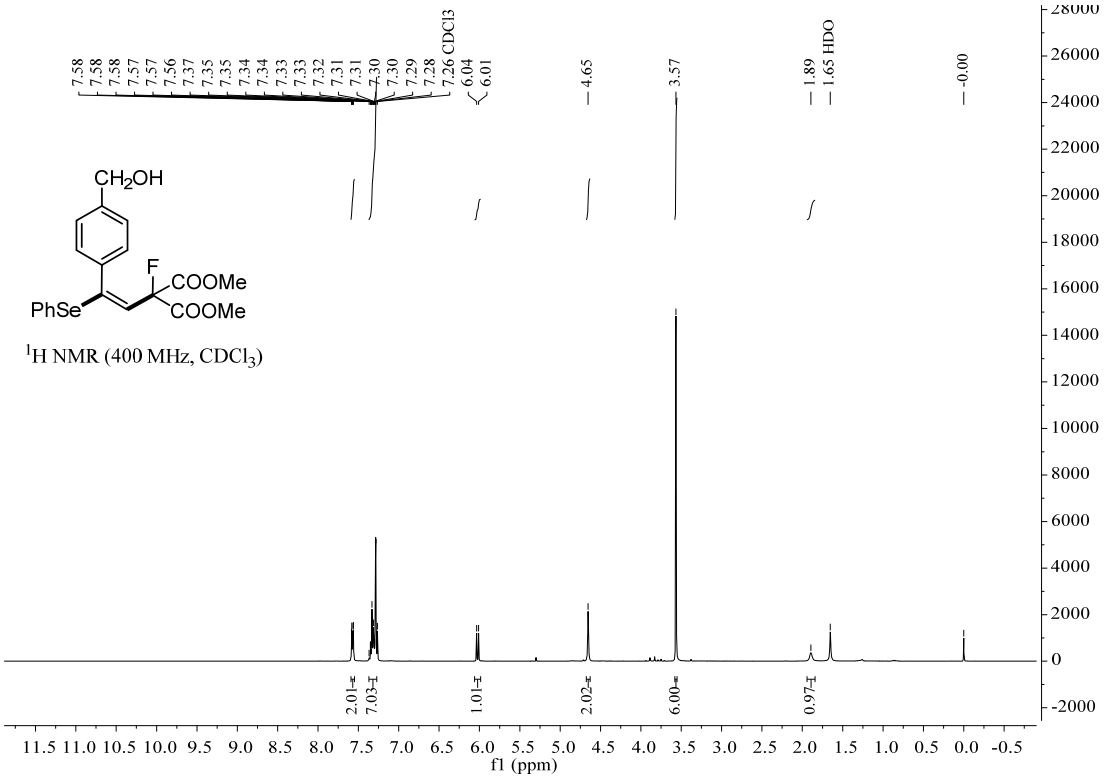


^{13}C NMR (101 MHz, $CDCl_3$)

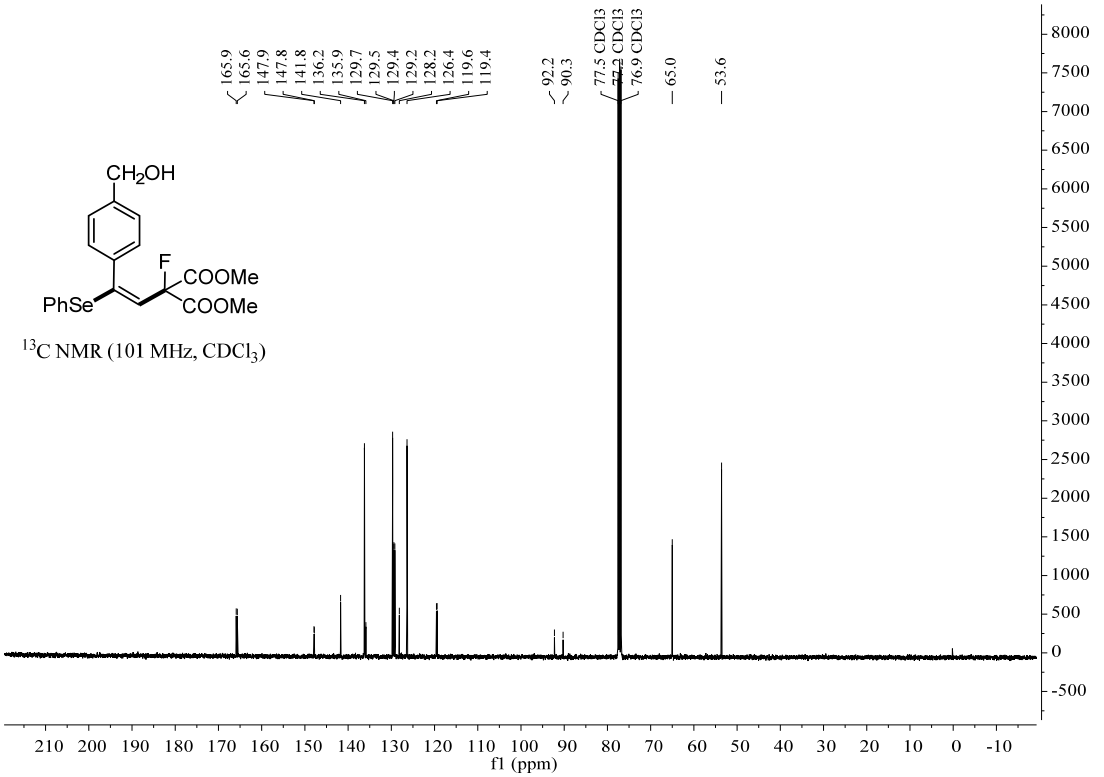


^{19}F NMR (377 MHz, $CDCl_3$)

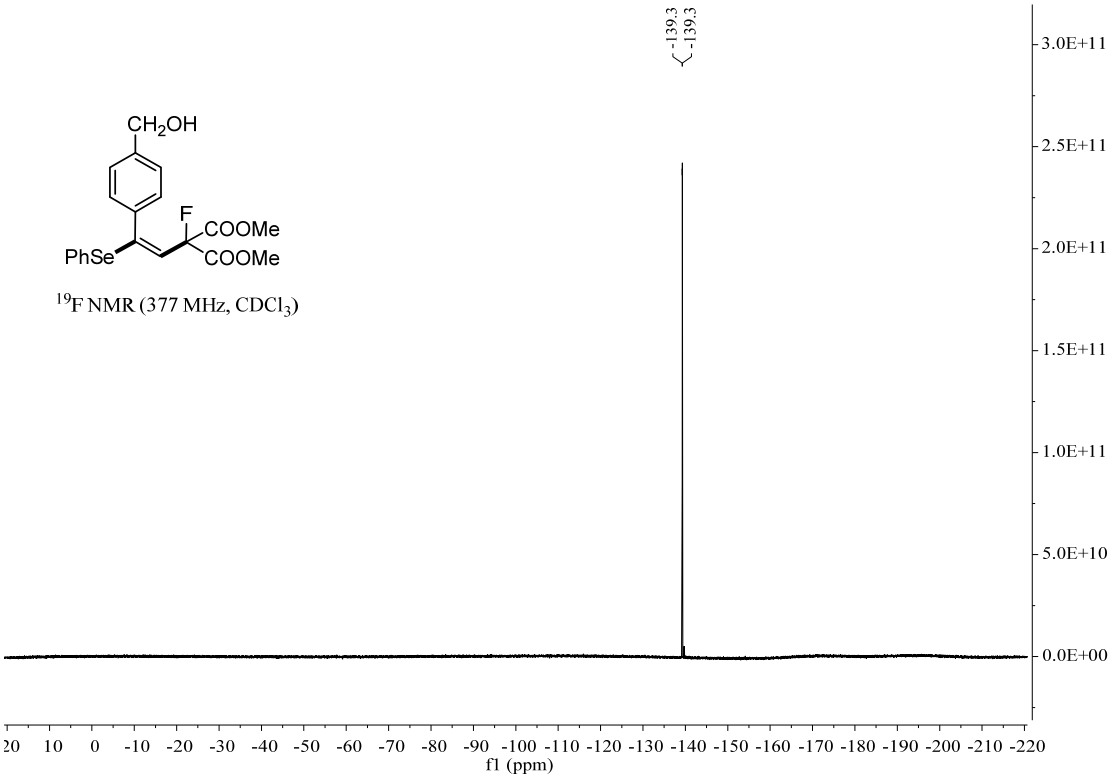
Compound 26



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

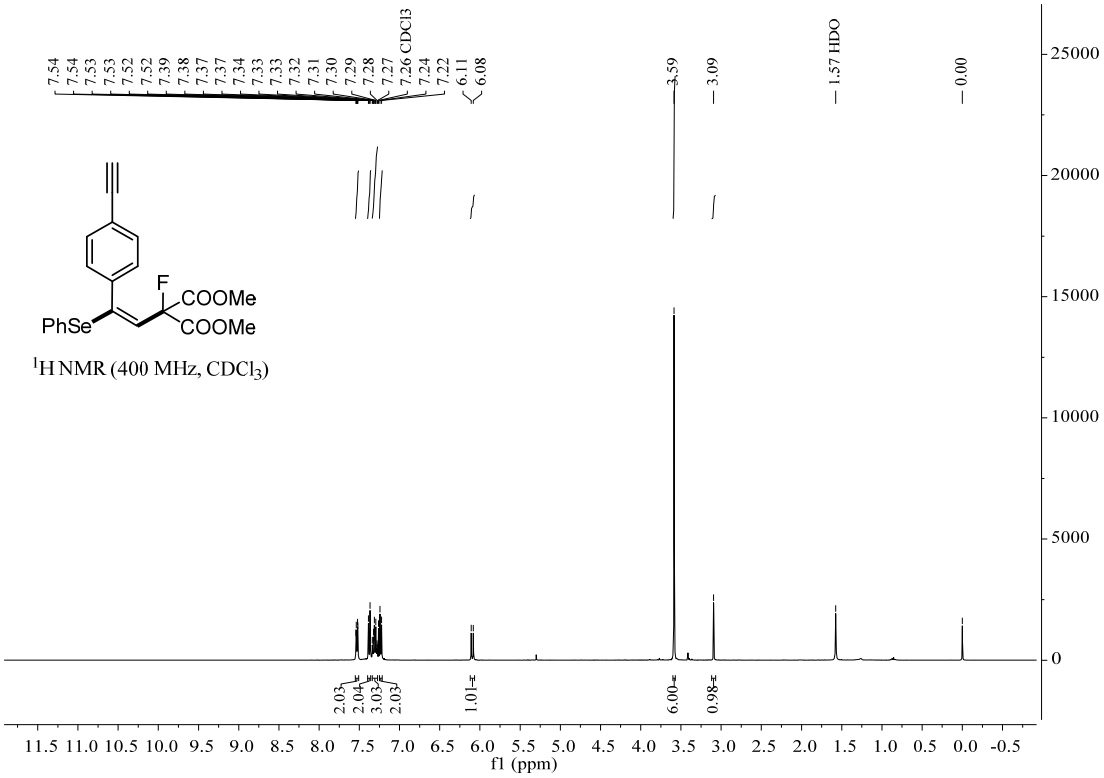


^{13}C NMR (101 MHz, $CDCl_3$)

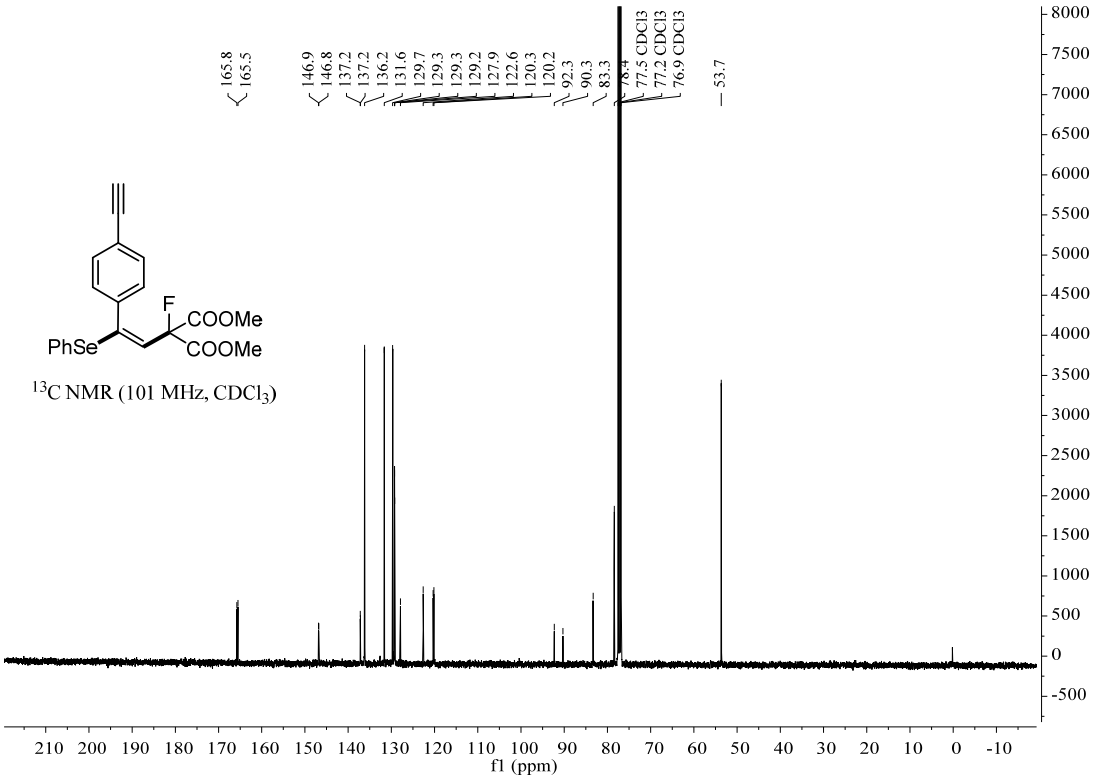


^{19}F NMR (377 MHz, $CDCl_3$)

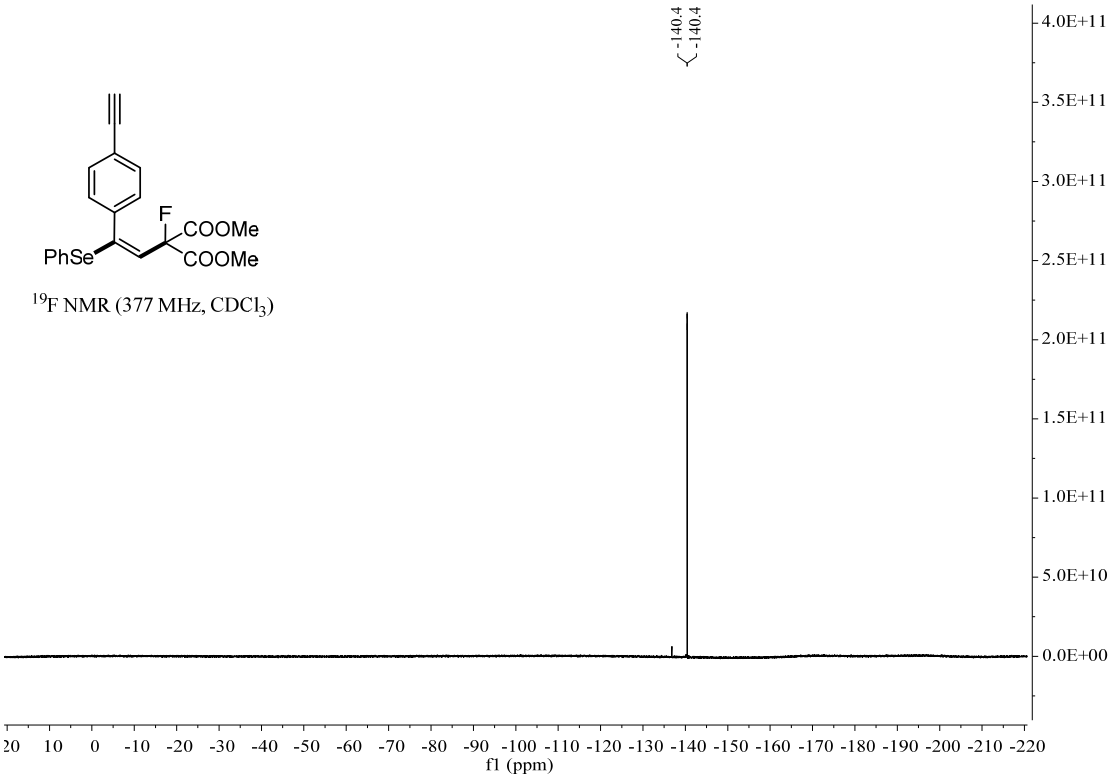
Compound 27



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

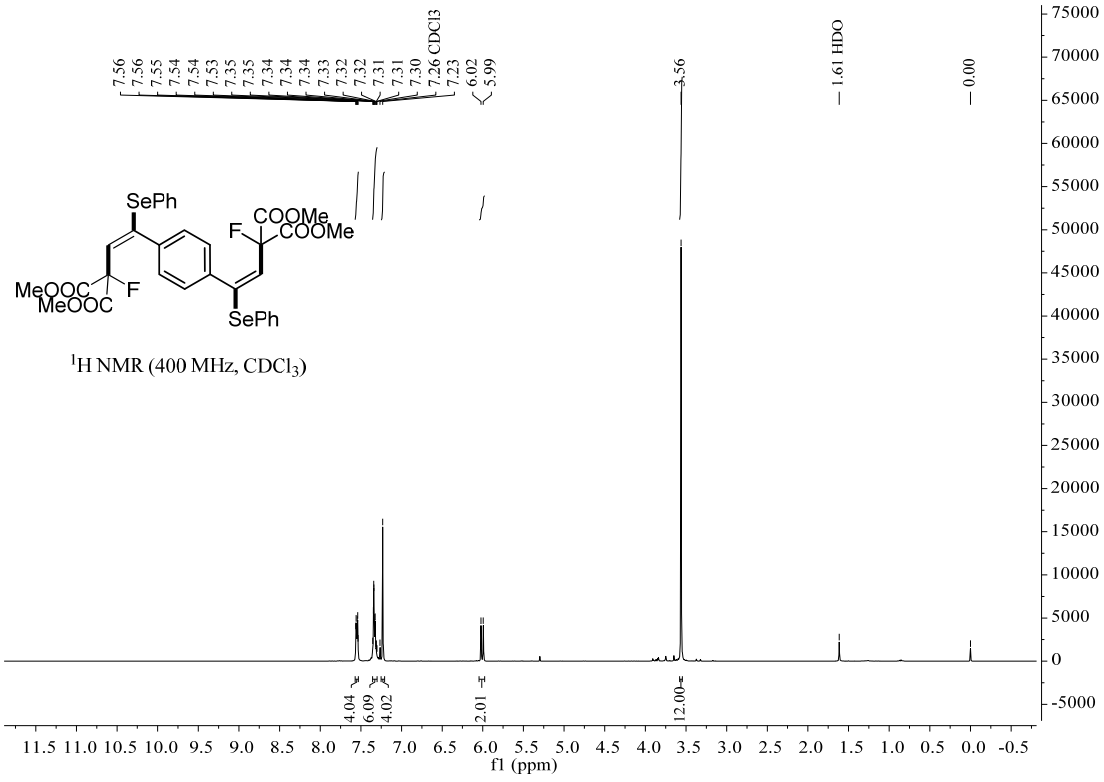


^{13}C NMR (101 MHz, $CDCl_3$)

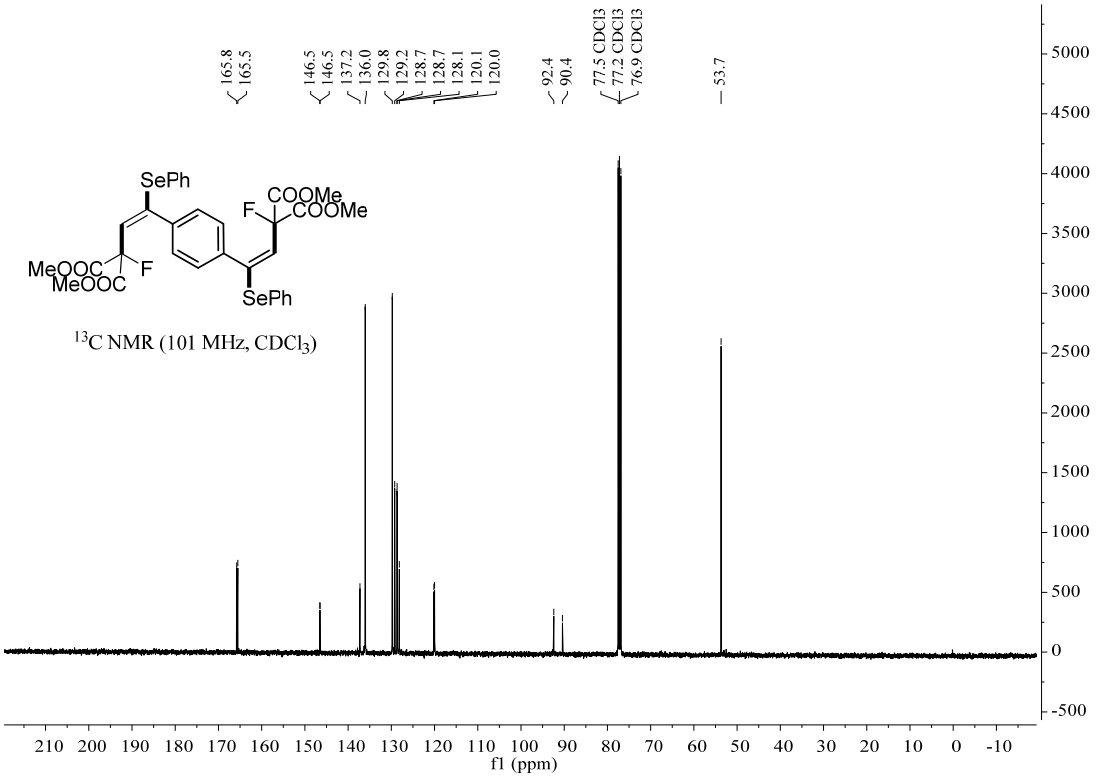


^{19}F NMR (377 MHz, $CDCl_3$)

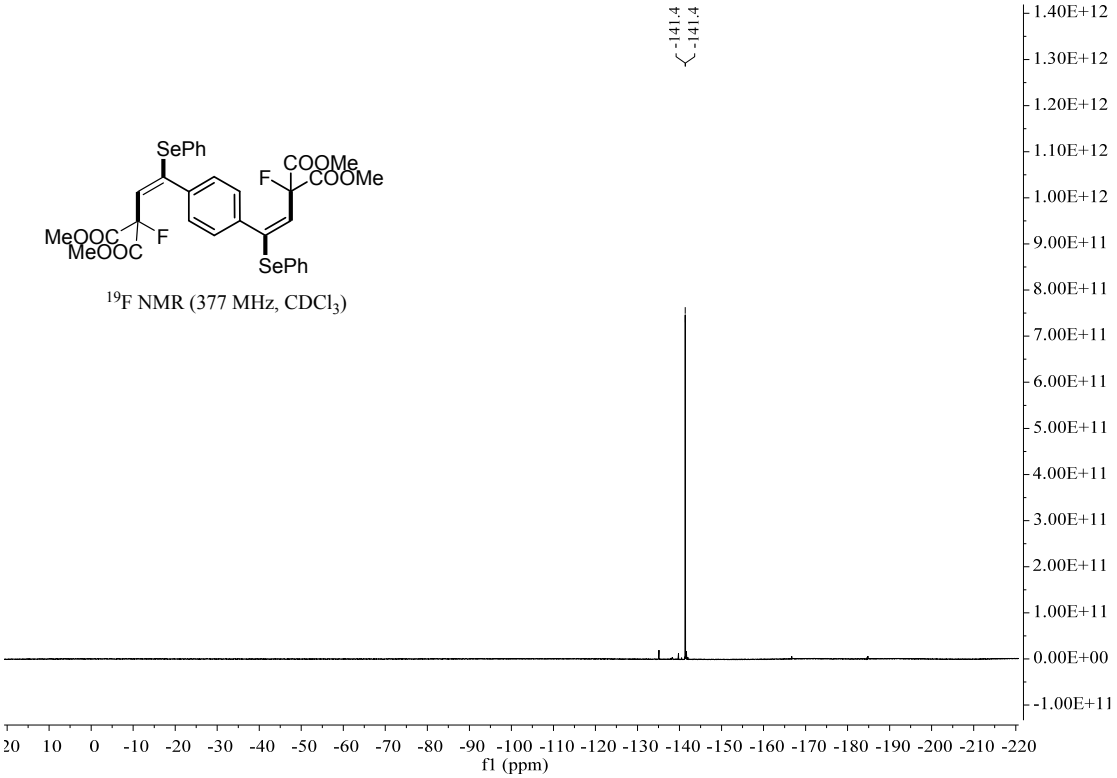
Compound 28



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

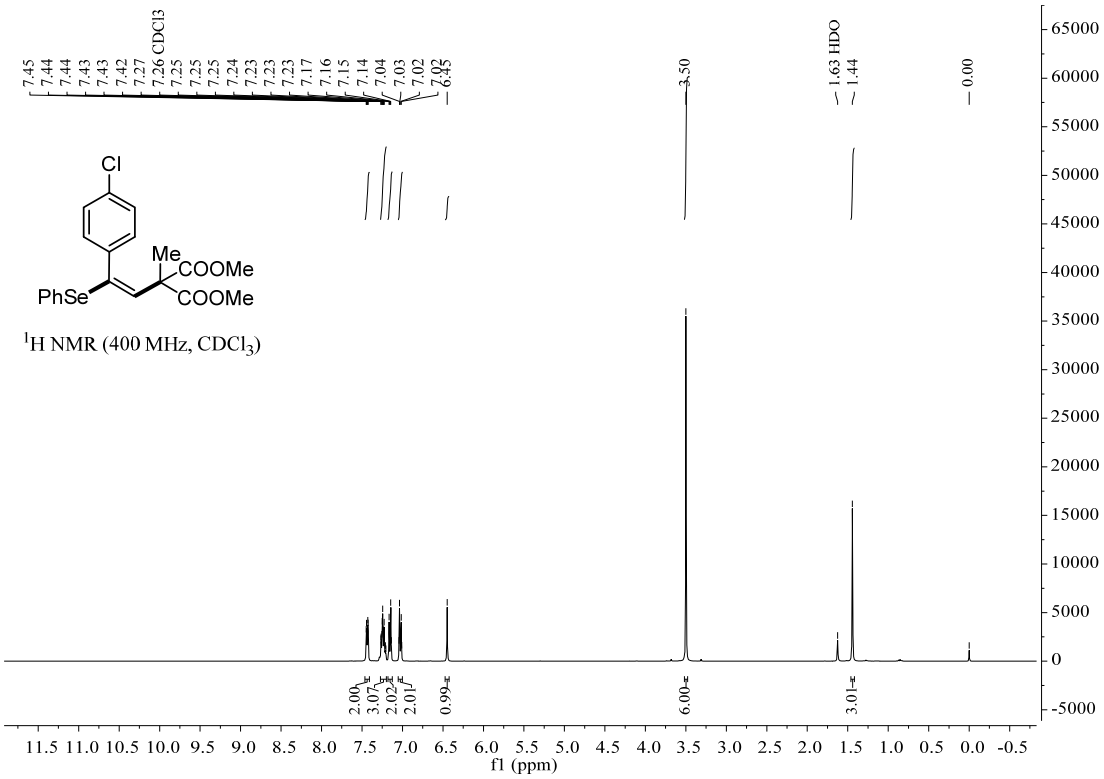


^{13}C NMR (101 MHz, $CDCl_3$)

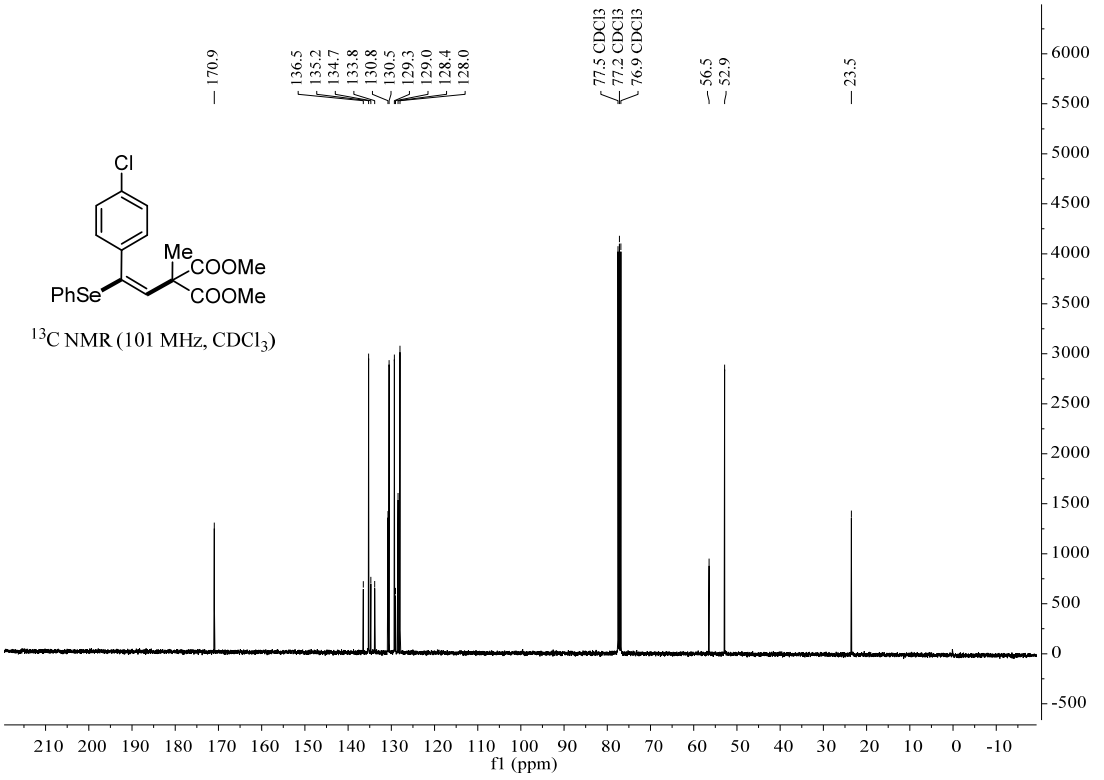


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 29

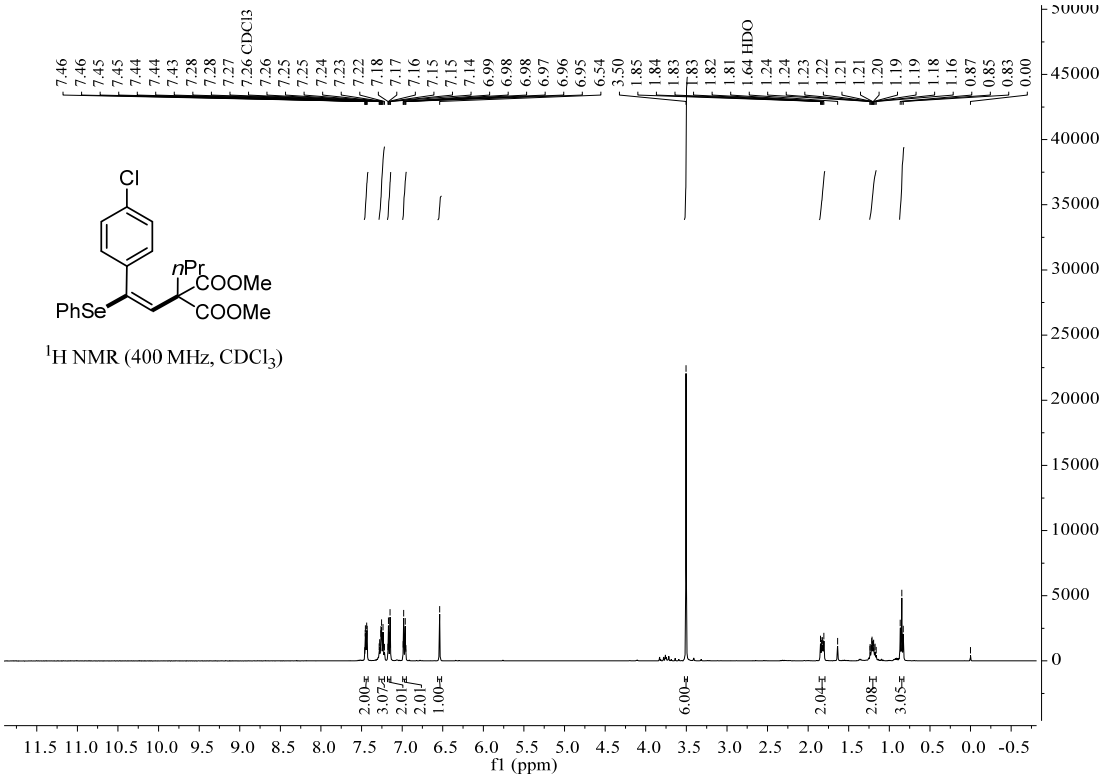


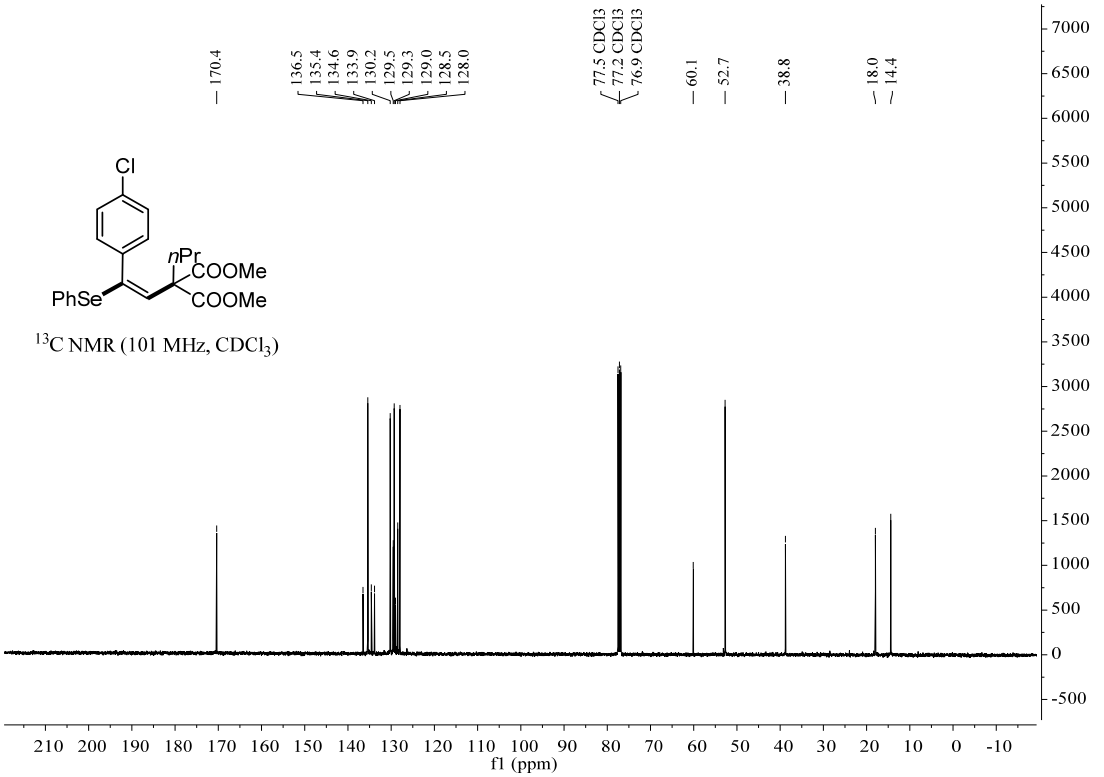
^{1}H NMR (400 MHz, $CDCl_3$)



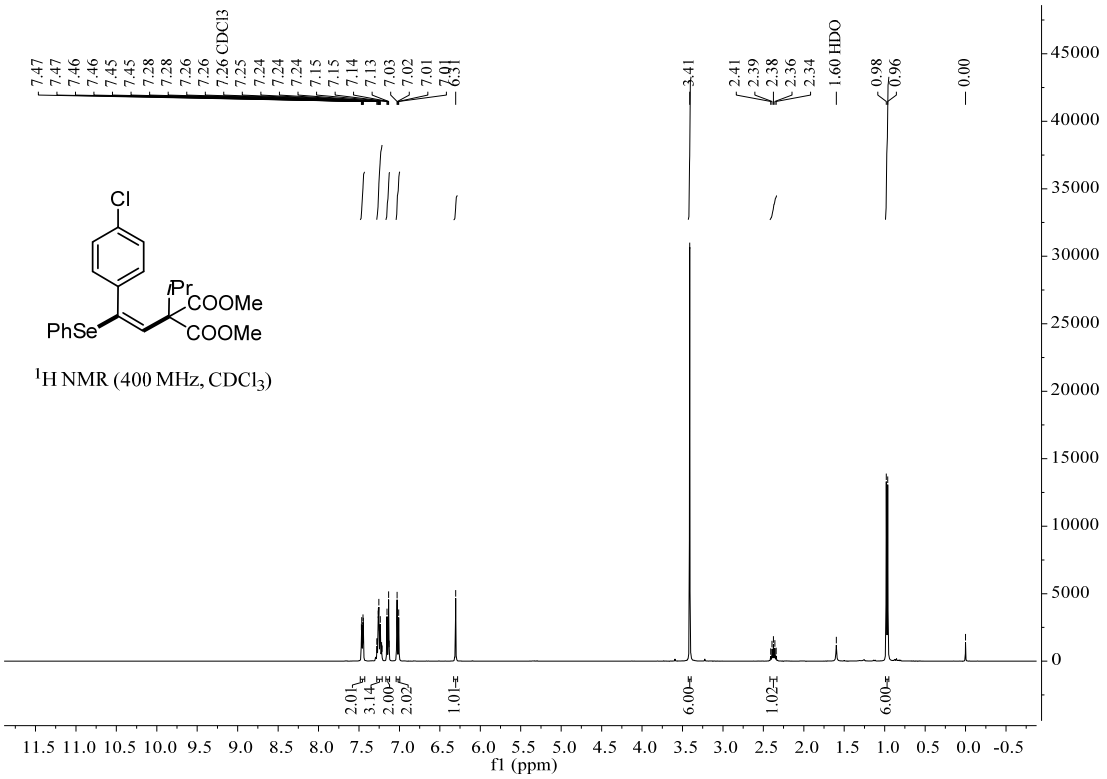
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 30

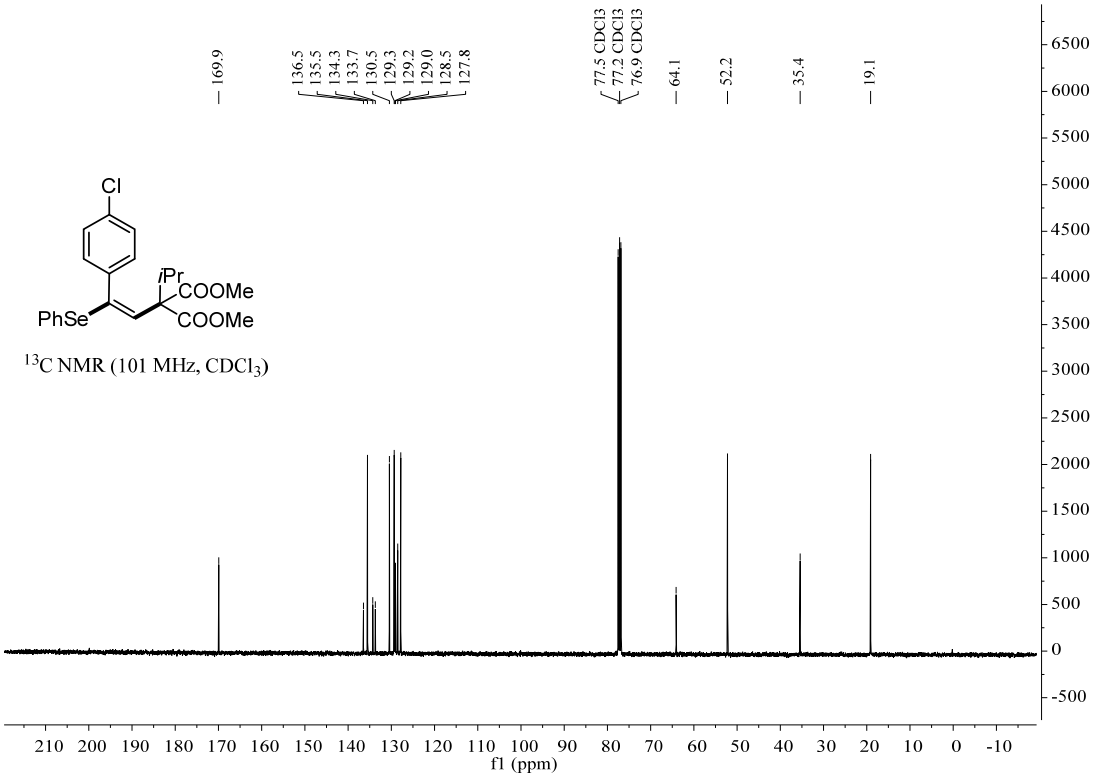

7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.28 7.28 7.27 7.26 CDCl3 7.26 7.25 7.25 7.24 7.23 7.22 7.18 7.17 7.16 7.15 7.15 7.14 6.99 6.98 6.98 6.97 6.96 6.95 6.54 3.50 1.85 1.84 1.83 1.83 1.82 1.81 1.64 HDO 1.24 1.24 1.23 1.22 1.21 1.21 1.20 1.19 1.19 1.18 1.16 0.87 0.85 0.83 0.00
Cl
nPr
COOMe
COOMe
PhSe
1H NMR (400 MHz, CDCl3)
2.00 3.07 2.01 2.01 1.00 6.00 2.04 2.08 3.05
f1 (ppm)


170.4
136.5 135.4 134.6 133.9 130.2 129.5 129.3 129.0 128.5 128.0
77.5 CDCl3 77.2 CDCl3 76.9 CDCl3
60.1
52.7
38.8
18.0
14.4
Cl
nPr
COOMe
COOMe
PhSe
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 31

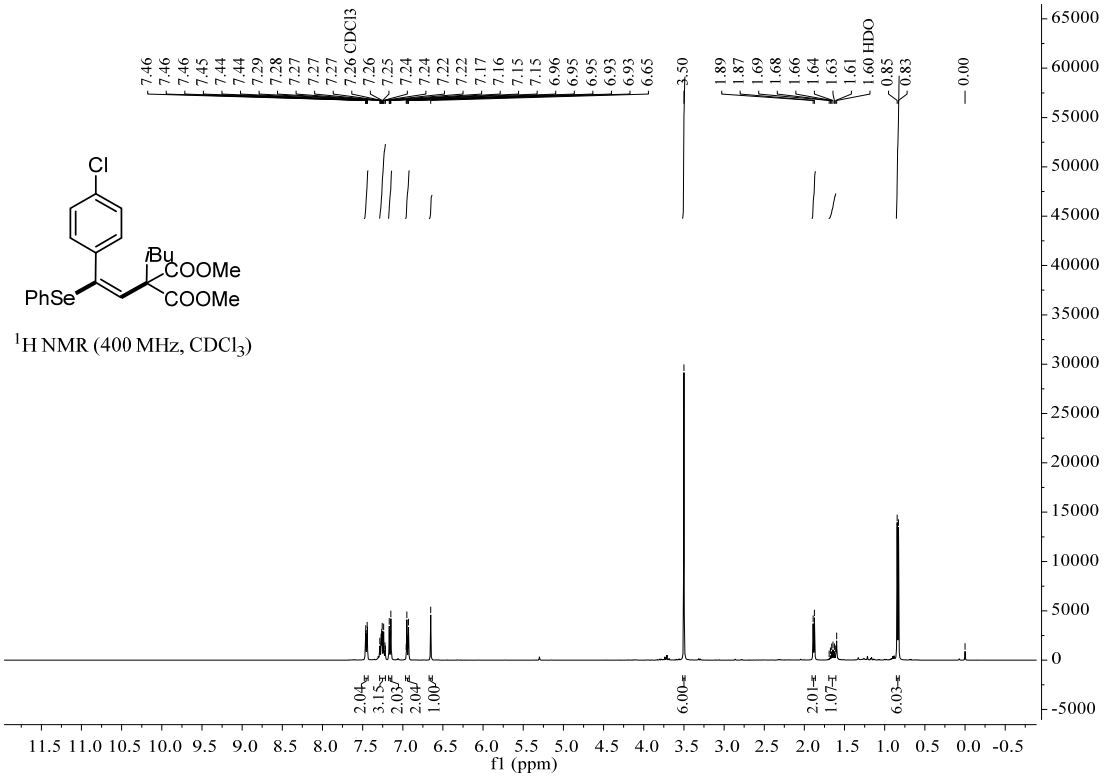


^{1}H NMR (400 MHz, $CDCl_3$)

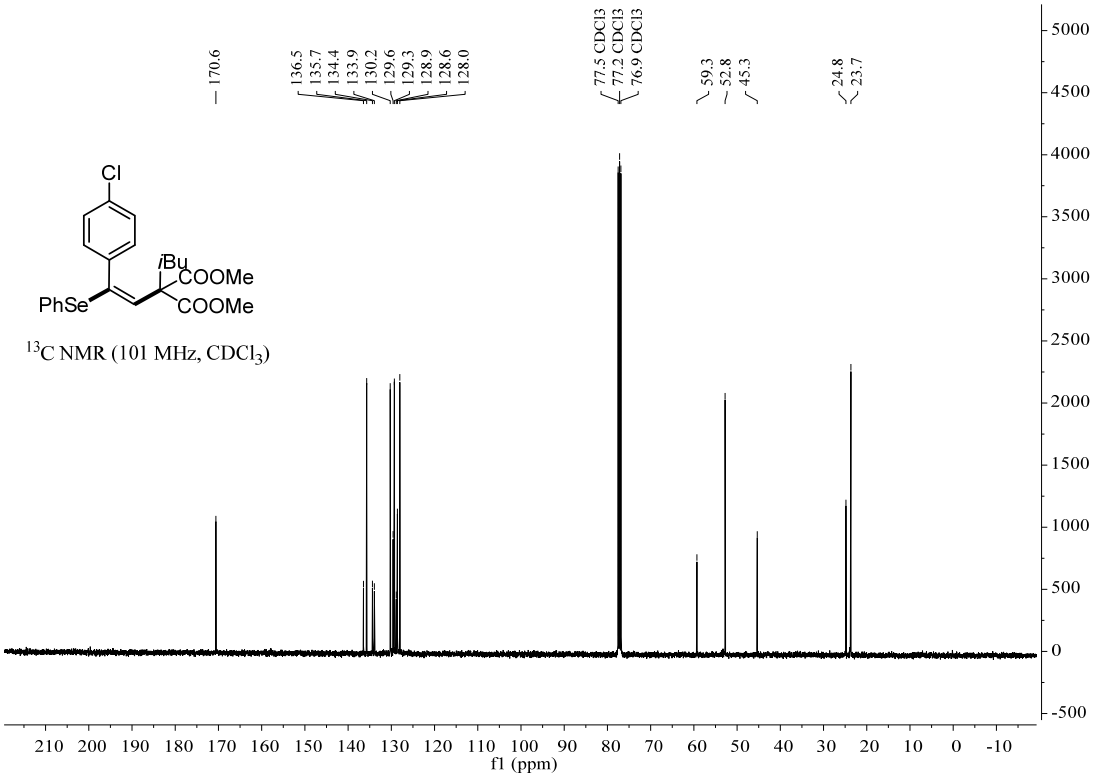


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 32

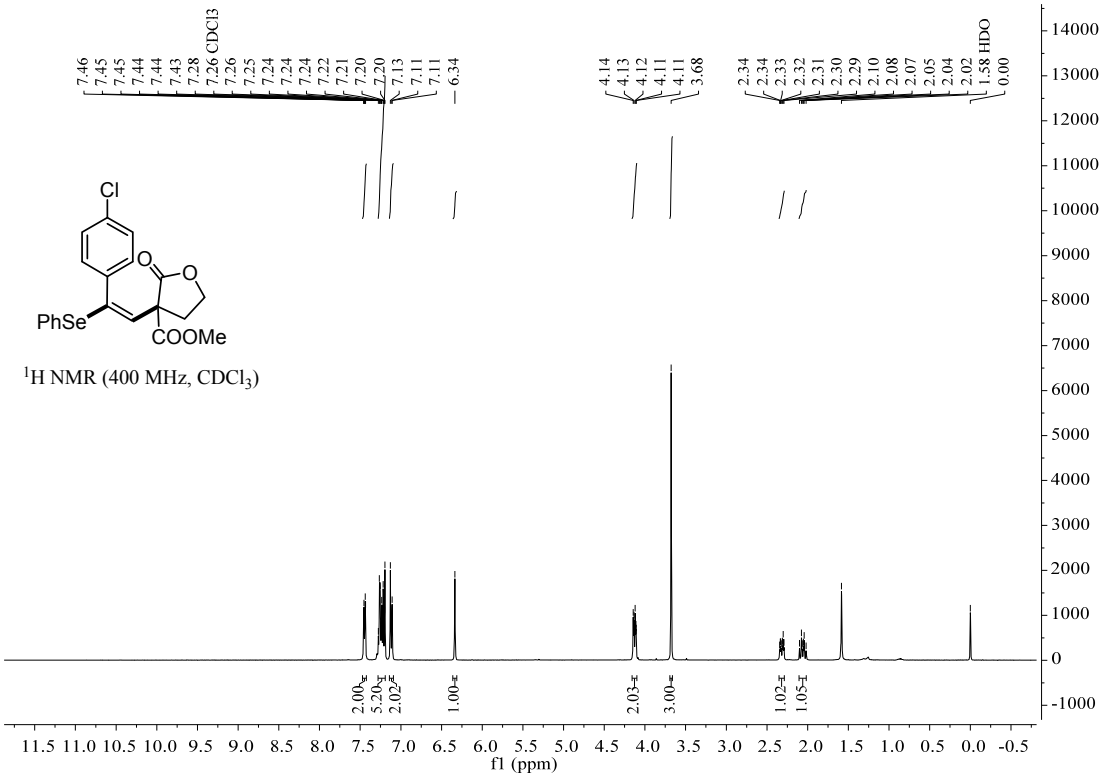


^{1}H NMR (400 MHz, $CDCl_3$)

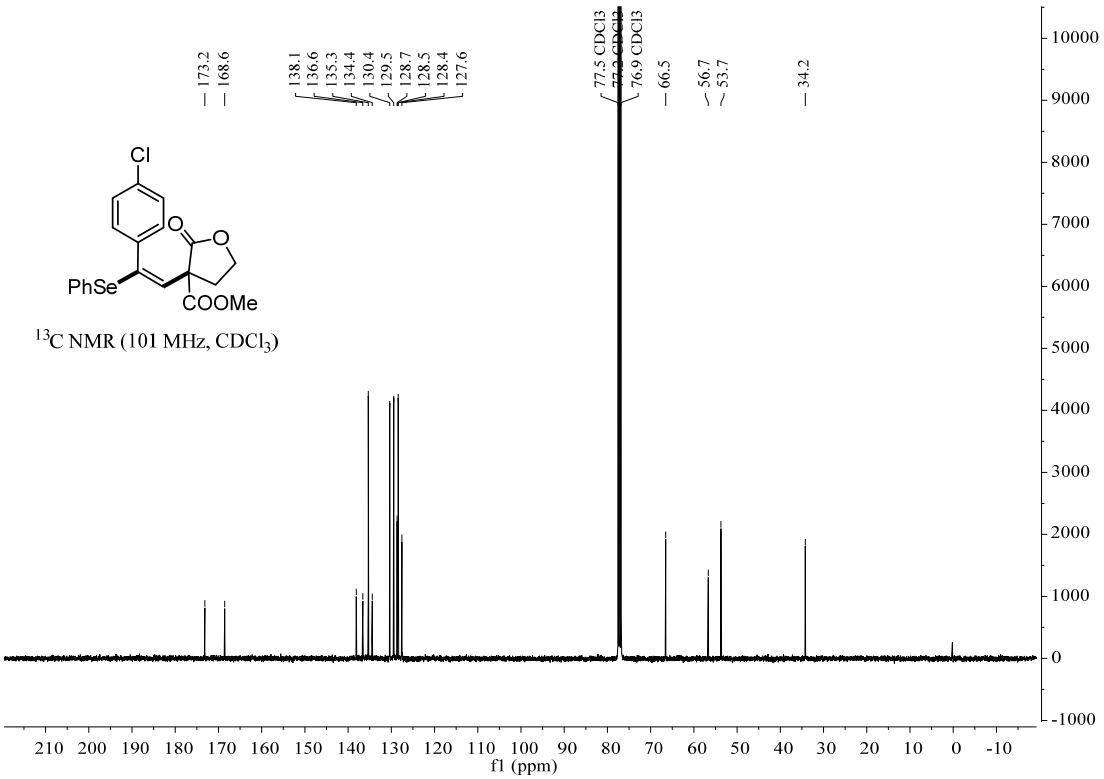


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 33

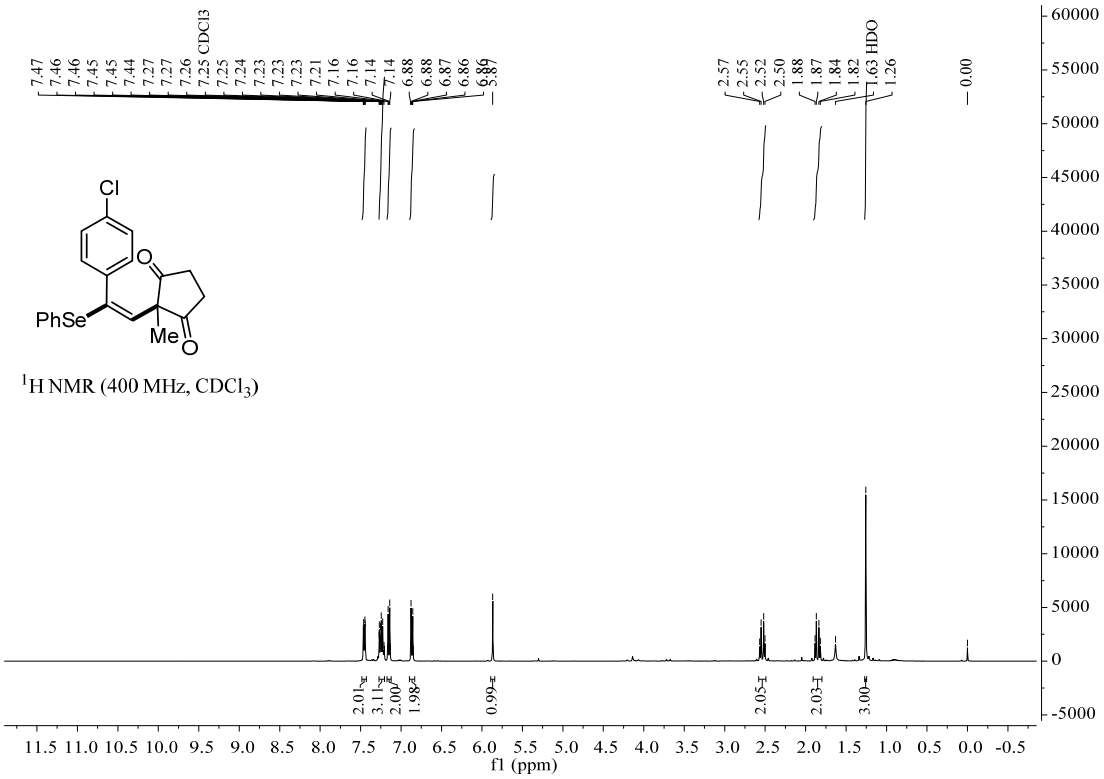


^{1}H NMR (400 MHz, $CDCl_3$)

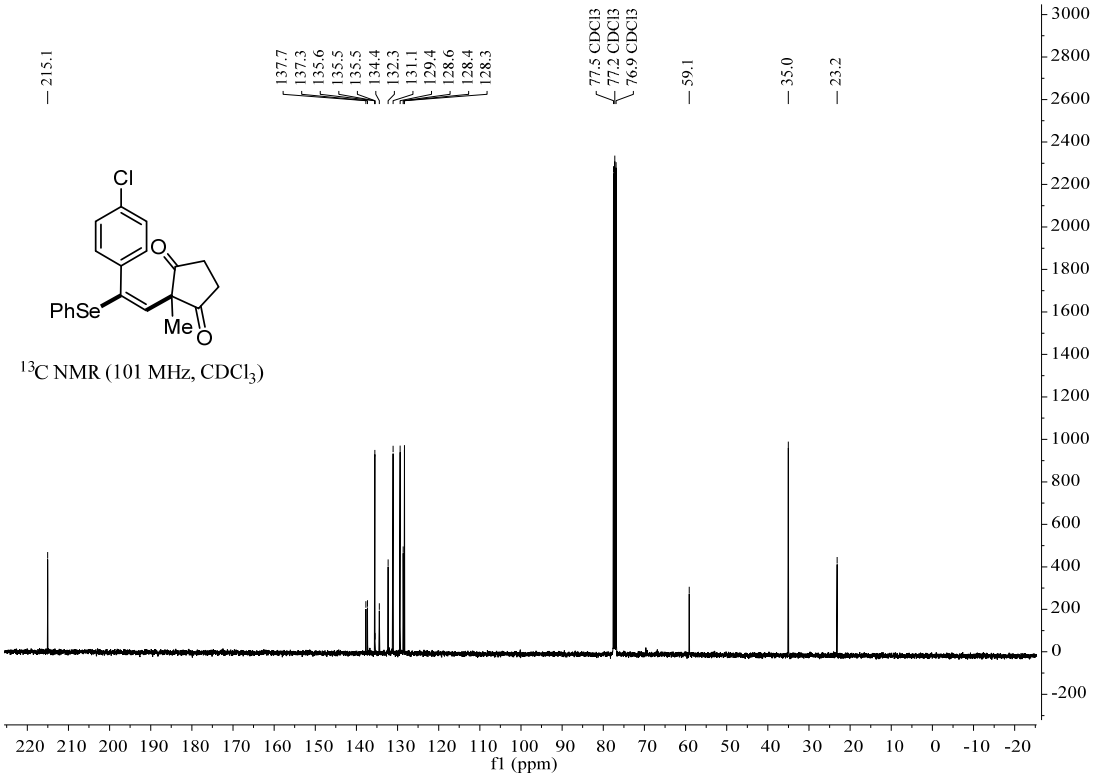


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 34

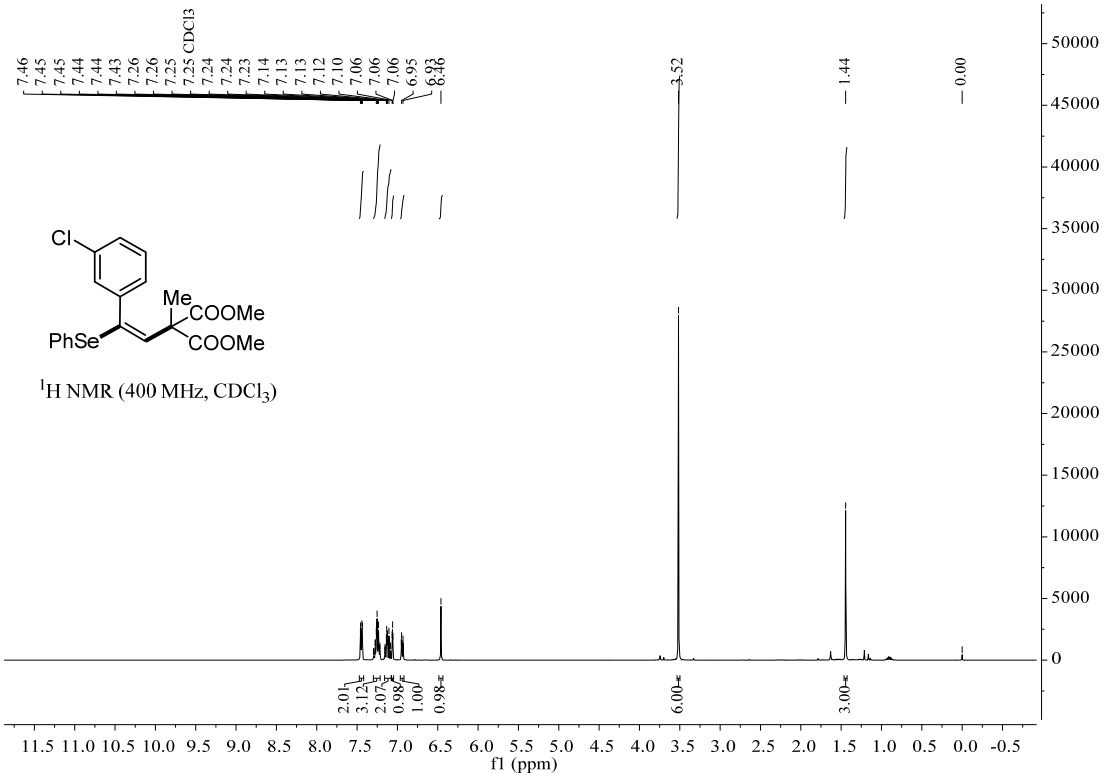


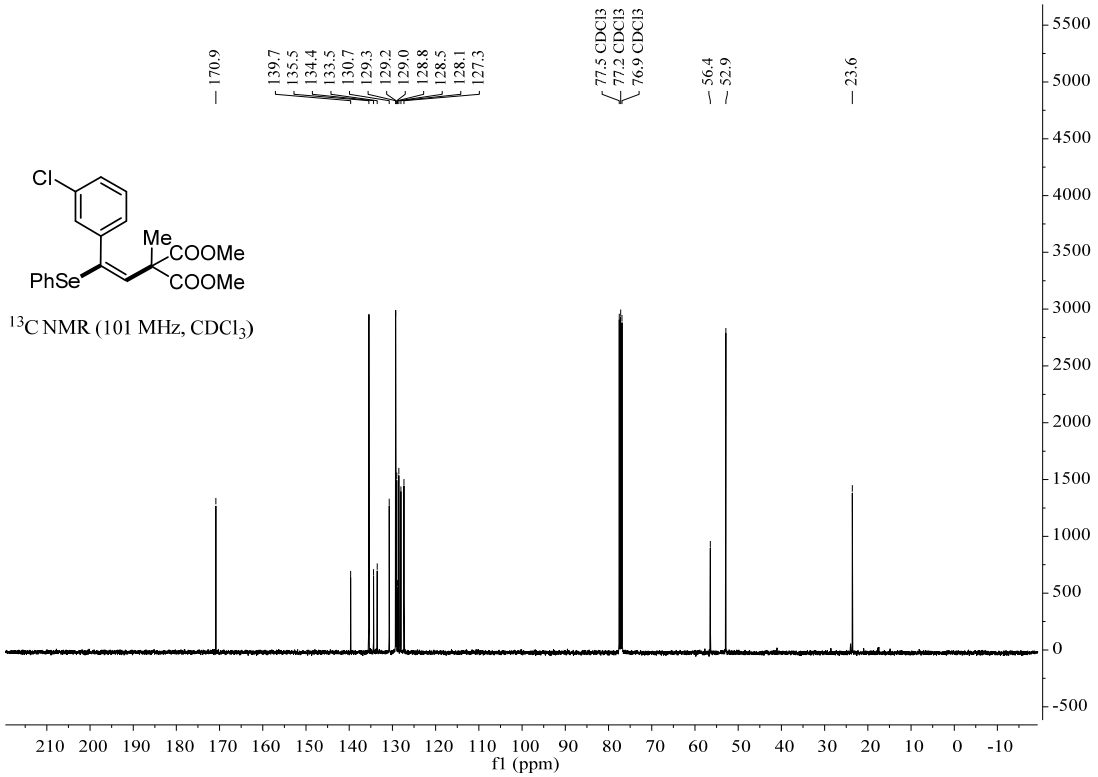
^{1}H NMR (400 MHz, $CDCl_3$)



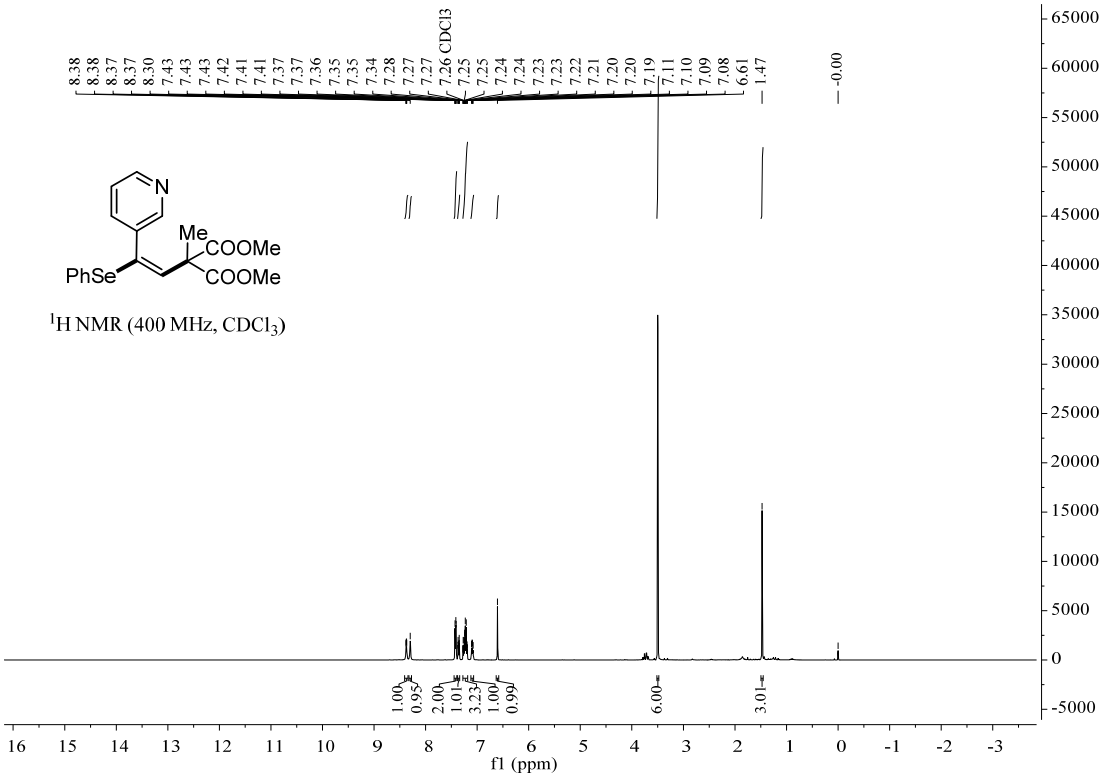
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 35

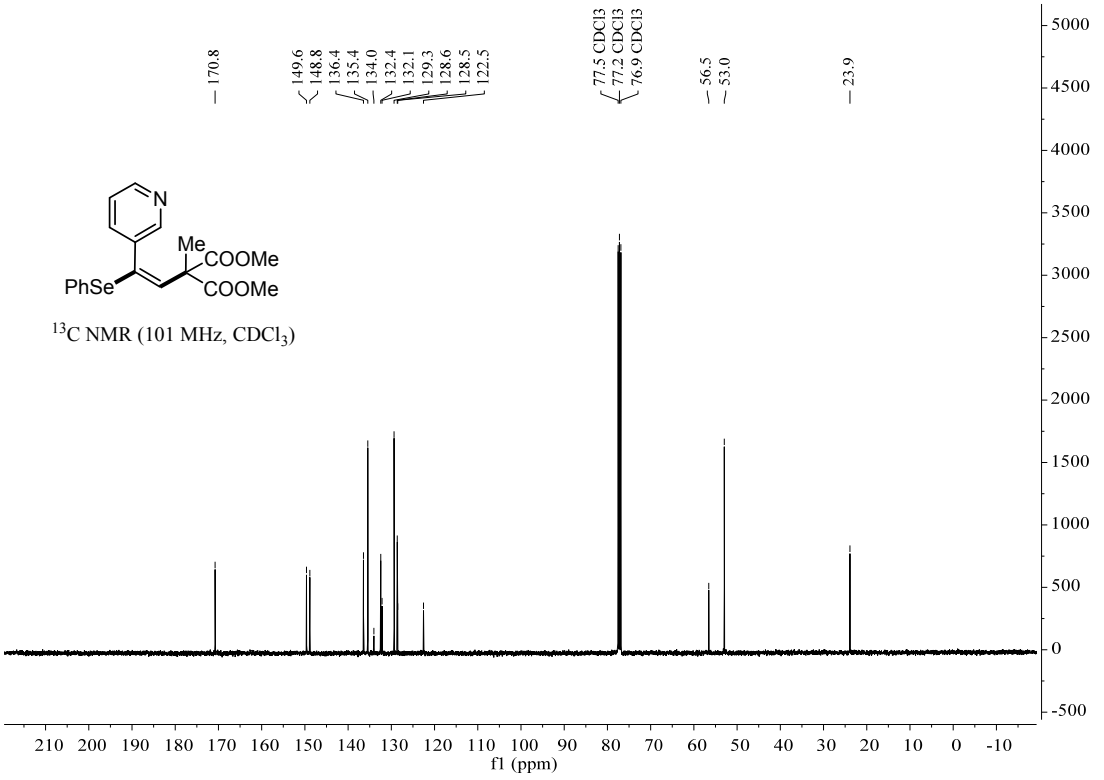

7.46
7.45
7.45
7.44
7.44
7.43
7.26
7.26
7.25
7.25 CDCl3
7.24
7.24
7.23
7.14
7.13
7.13
7.12
7.10
7.06
7.06
7.06
6.95
6.93
6.46
3.52
1.44
0.00
Cl
Me
COOMe
COOMe
PhSe
1H NMR (400 MHz, CDCl3)
2.01
3.12
2.07
0.98
1.00
0.98
6.00
3.00
f1 (ppm)


170.9
139.7
135.5
134.4
133.5
130.7
129.3
129.2
129.0
128.8
128.5
128.1
127.3
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
56.4
52.9
23.6
Cl
Me
COOMe
COOMe
PhSe
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 36

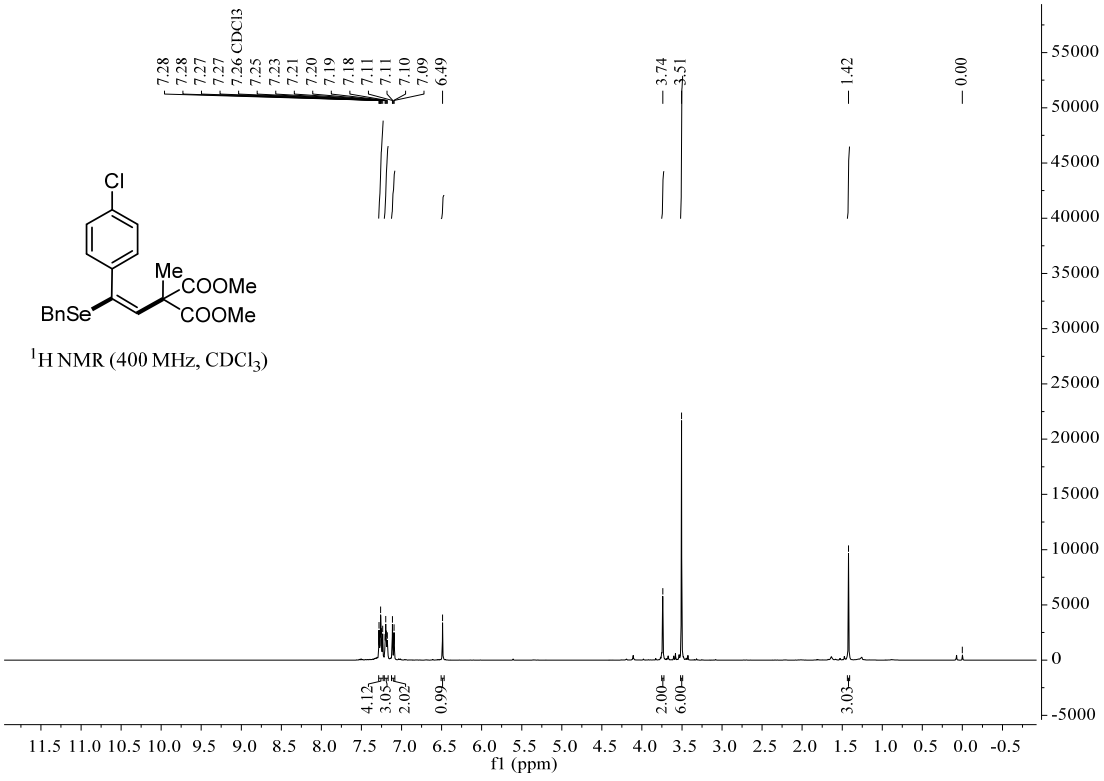


^{1}H NMR (400 MHz, $CDCl_3$)

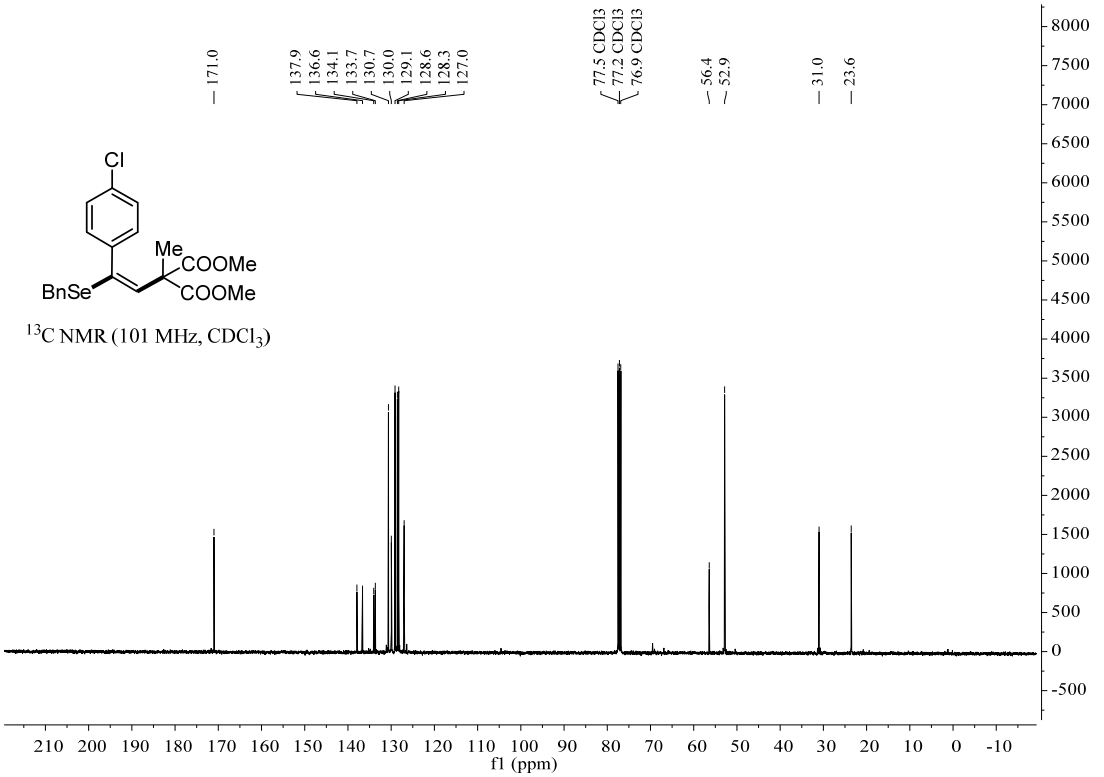


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 37

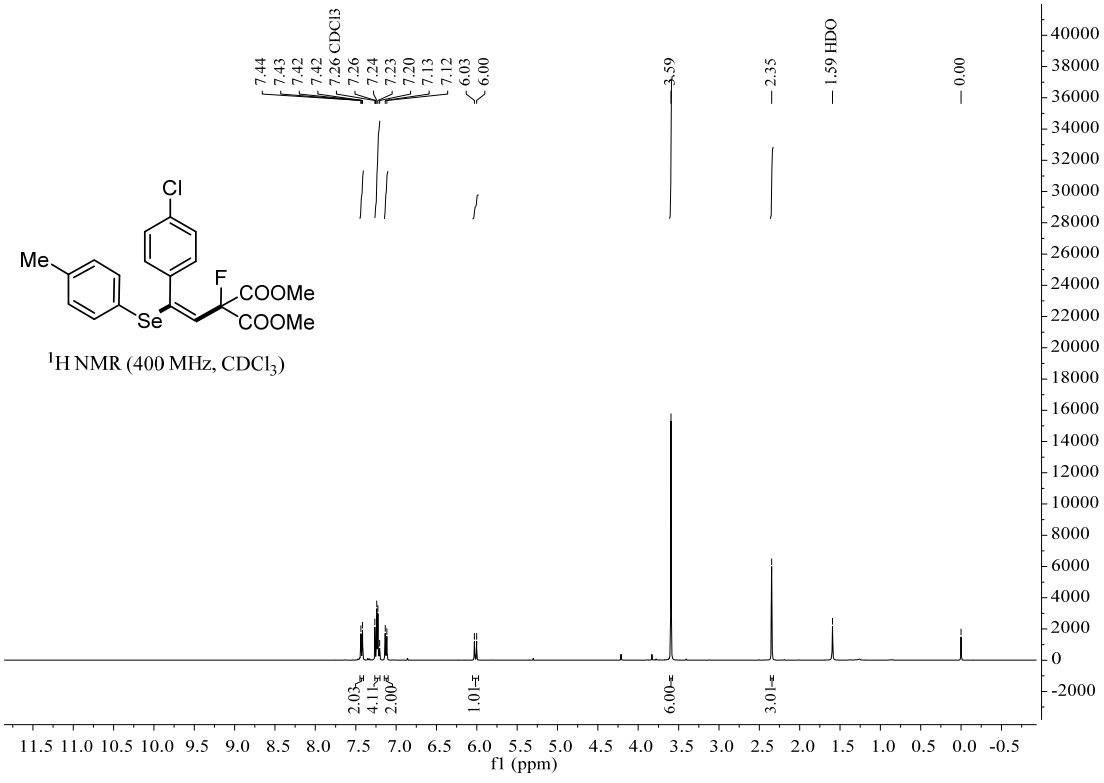


^{1}H NMR (400 MHz, $CDCl_3$)

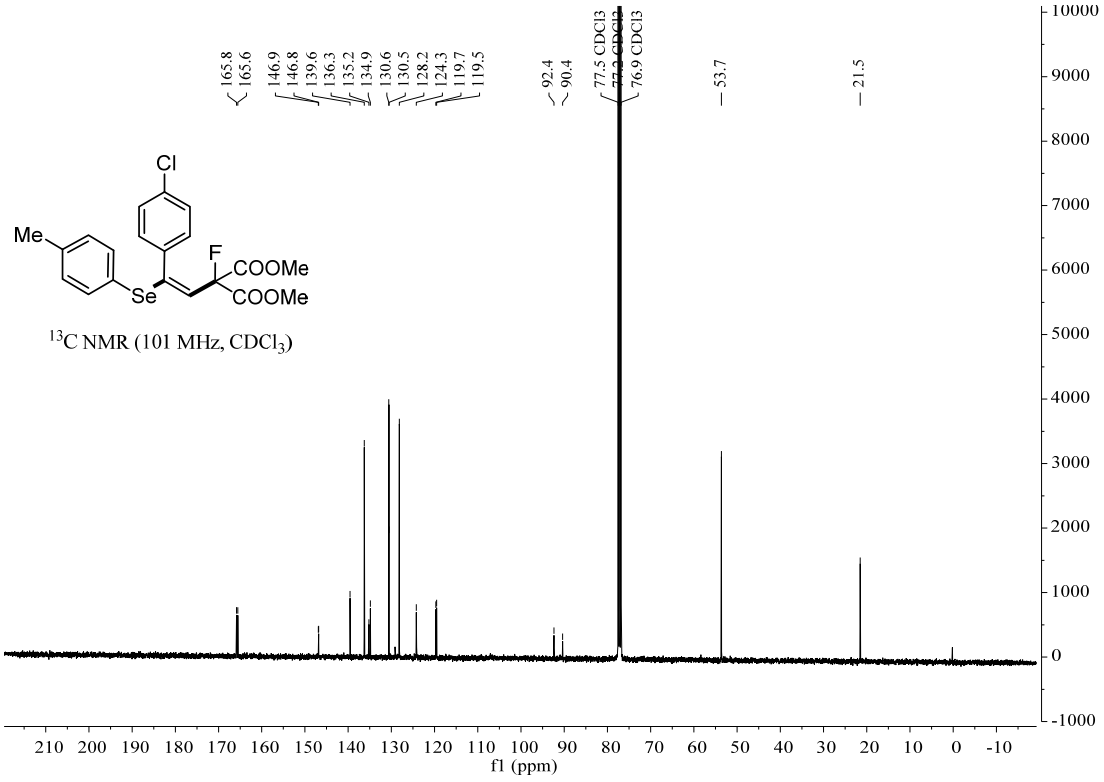


^{13}C NMR (101 MHz, $CDCl_3$)

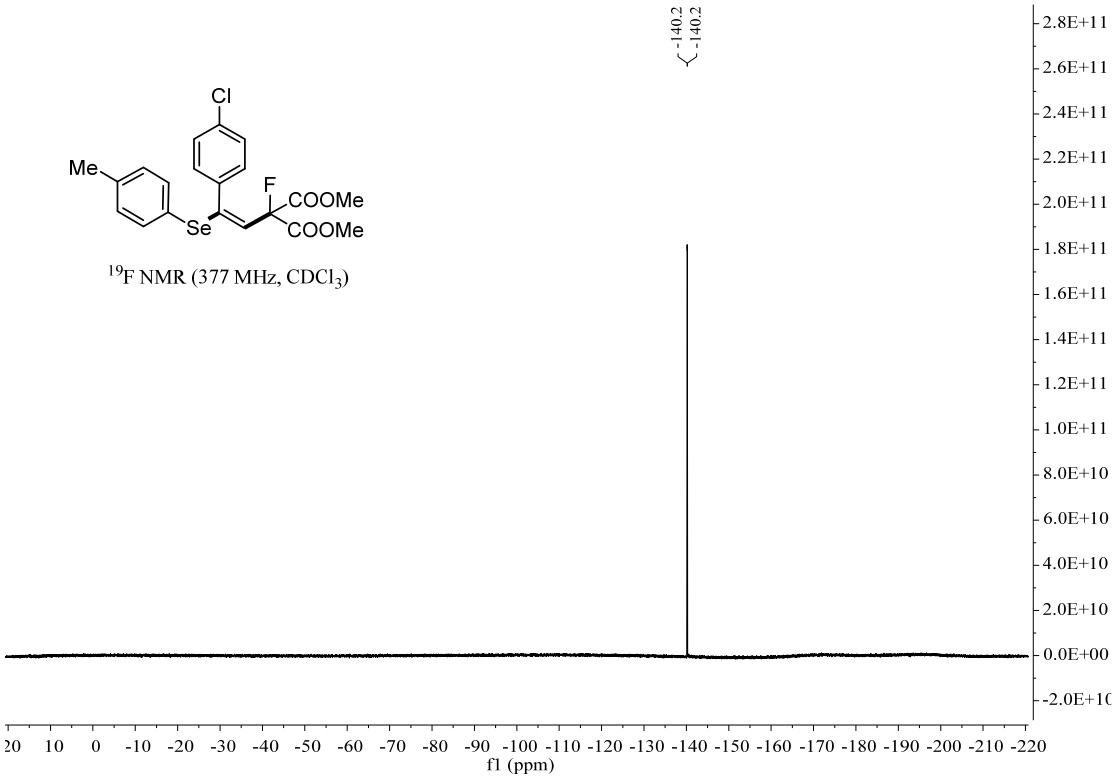
Compound 38



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

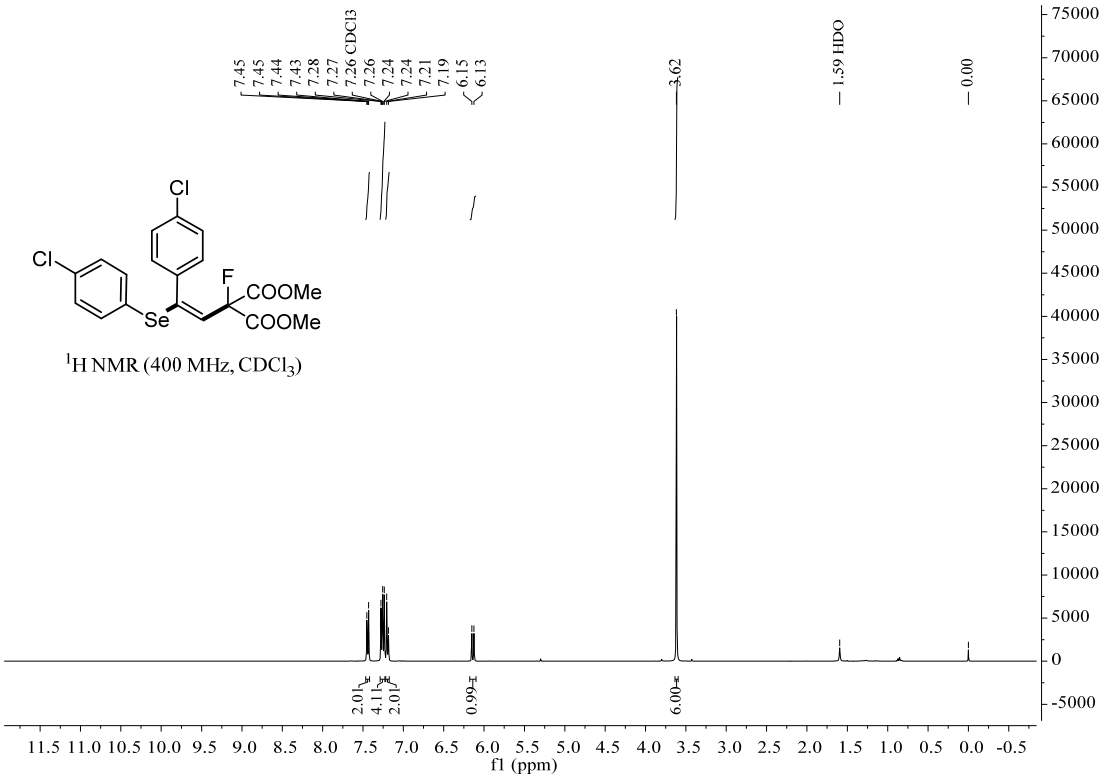


^{13}C NMR (101 MHz, $CDCl_3$)

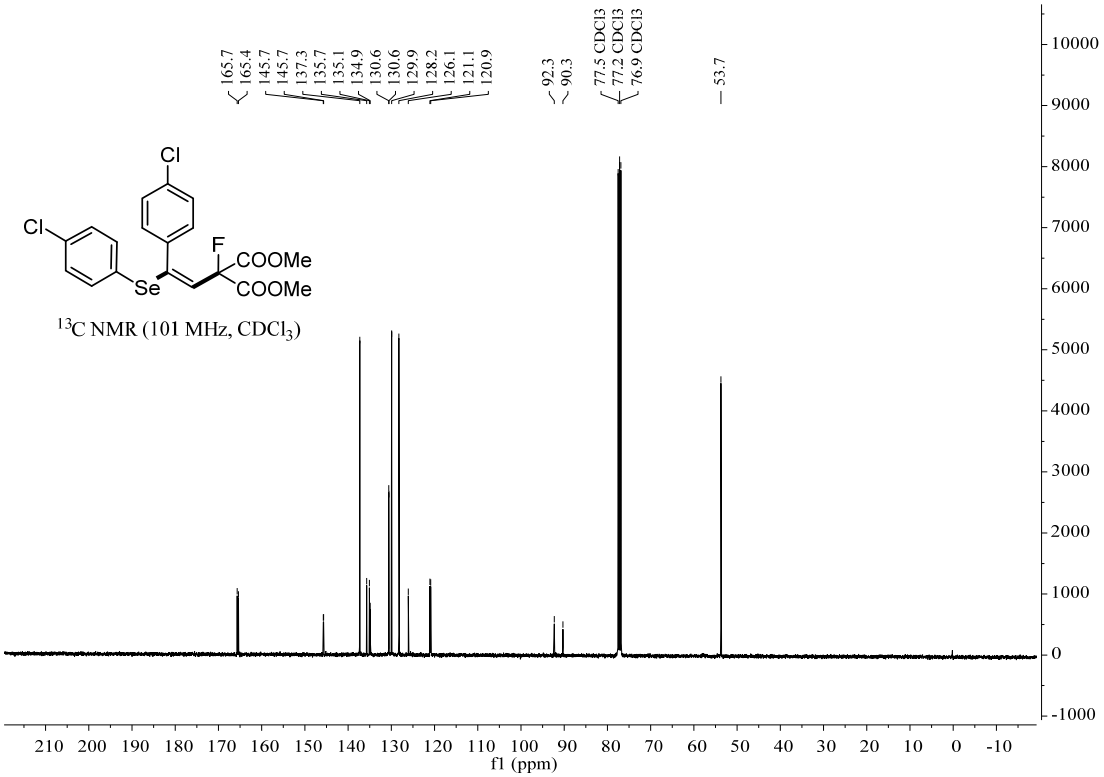


^{19}F NMR (377 MHz, $CDCl_3$)

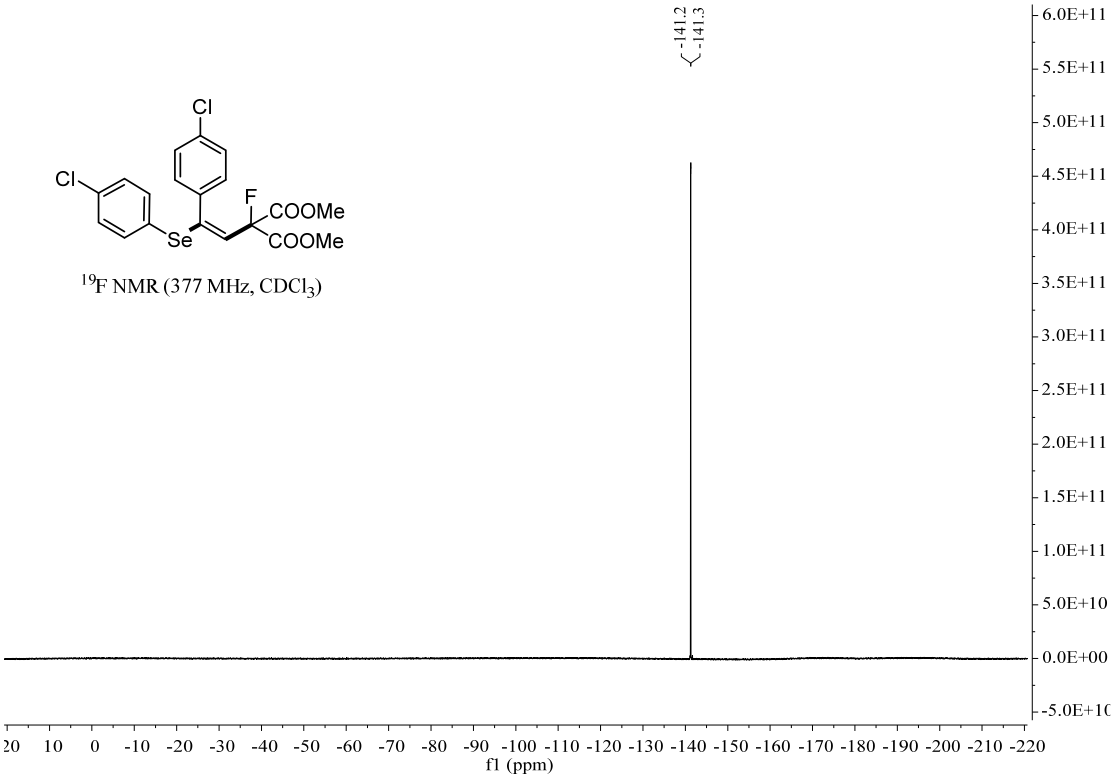
Compound 39



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

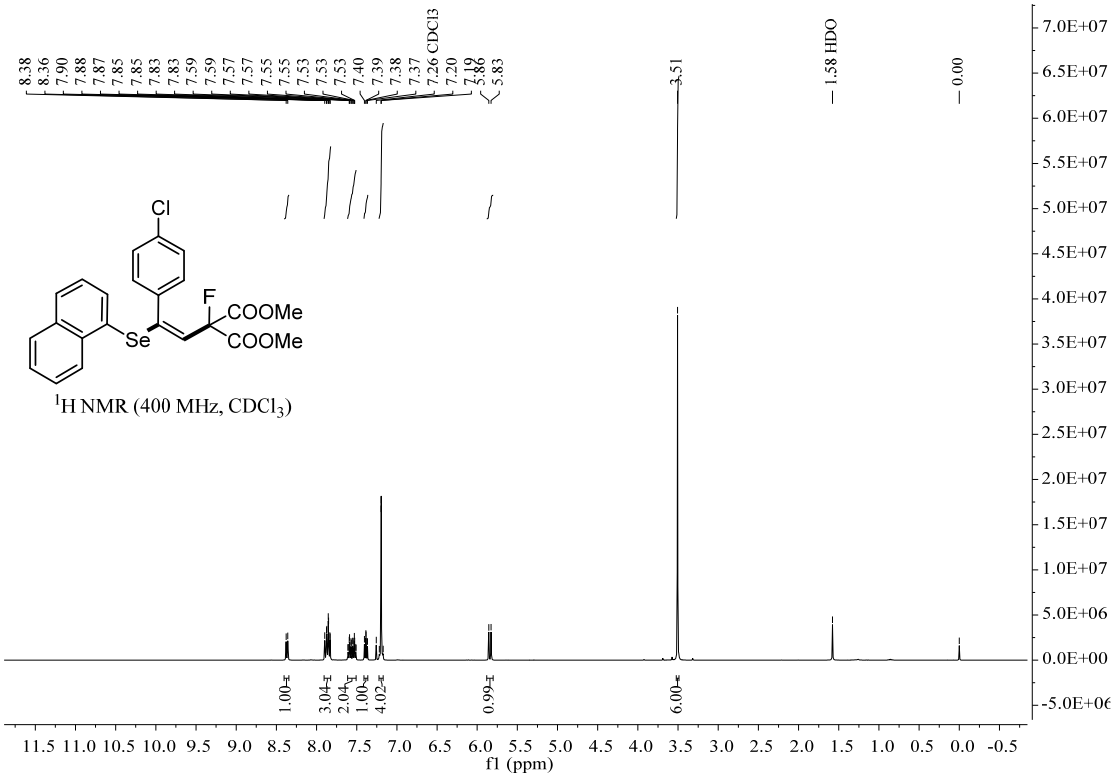


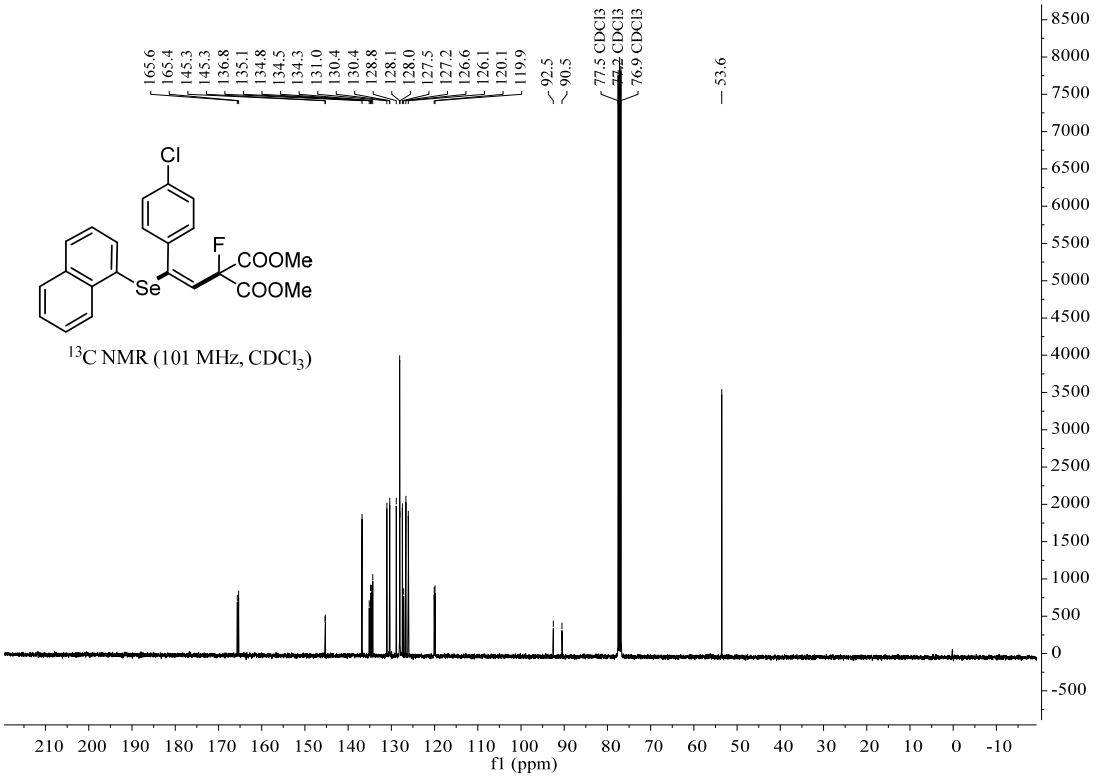
^{13}C NMR (101 MHz, $CDCl_3$)

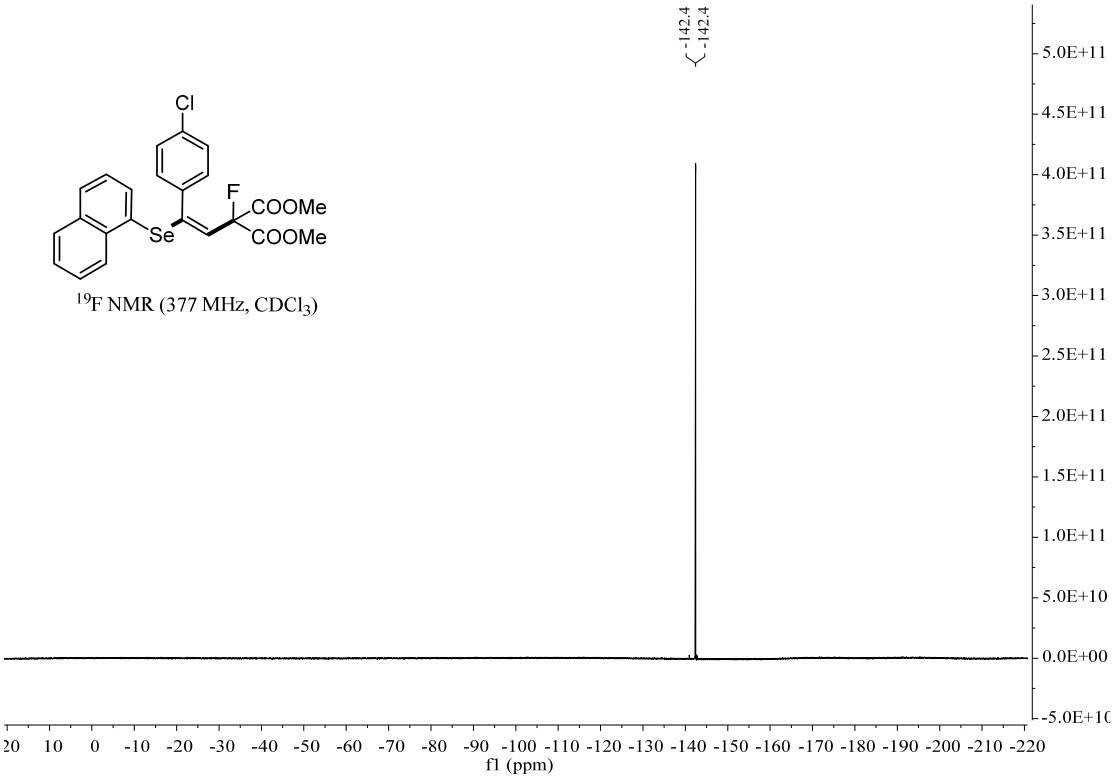


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 40

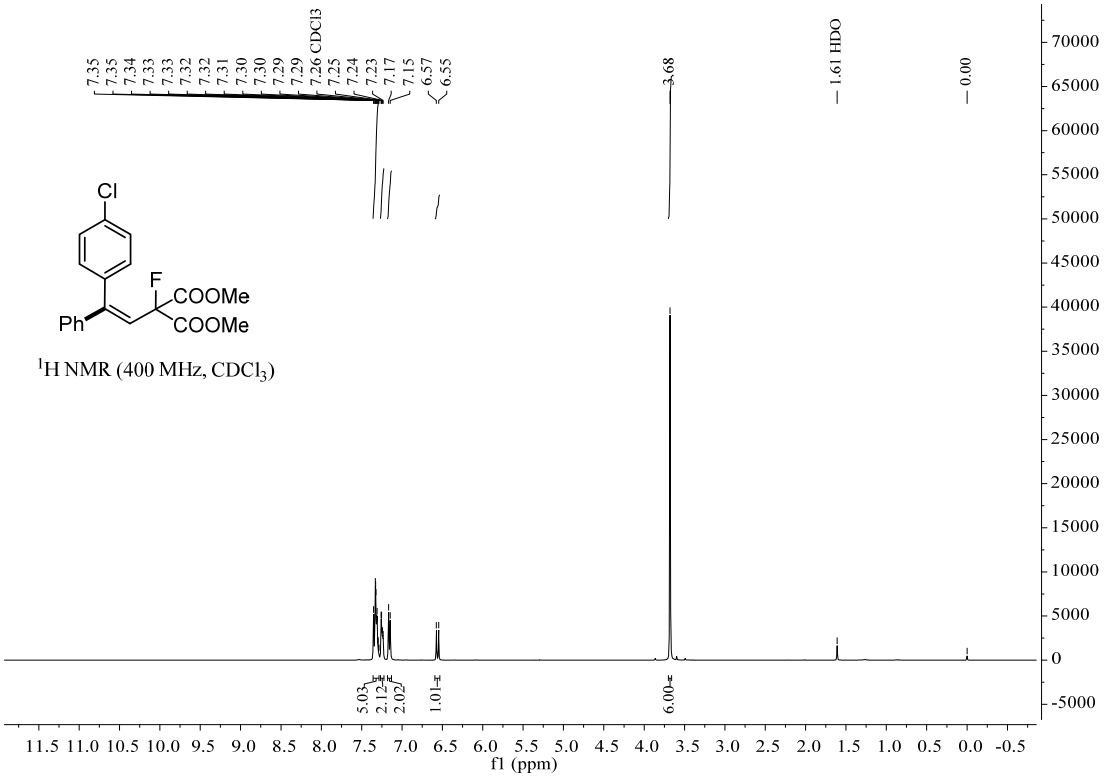

8.38
8.36
7.90
7.88
7.87
7.85
7.85
7.83
7.83
7.59
7.59
7.57
7.57
7.55
7.55
7.53
7.53
7.53
7.40
7.39
7.38
7.37
7.26 CDCl3
7.20
5.86
5.83
3.51
1.58 HDO
0.00
Cl
F
COOMe
COOMe
Se
1H NMR (400 MHz, CDCl3)
1.00
3.04
2.04
1.00
4.02
0.99
6.00
f1 (ppm)


165.6
165.4
145.3
145.3
136.8
135.1
134.8
134.5
134.3
131.0
130.4
130.4
128.8
128.1
128.0
127.5
127.2
126.6
126.1
120.1
119.9
92.5
90.5
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
53.6
Cl
F
COOMe
COOMe
Se
13C NMR (101 MHz, CDCl3)
f1 (ppm)

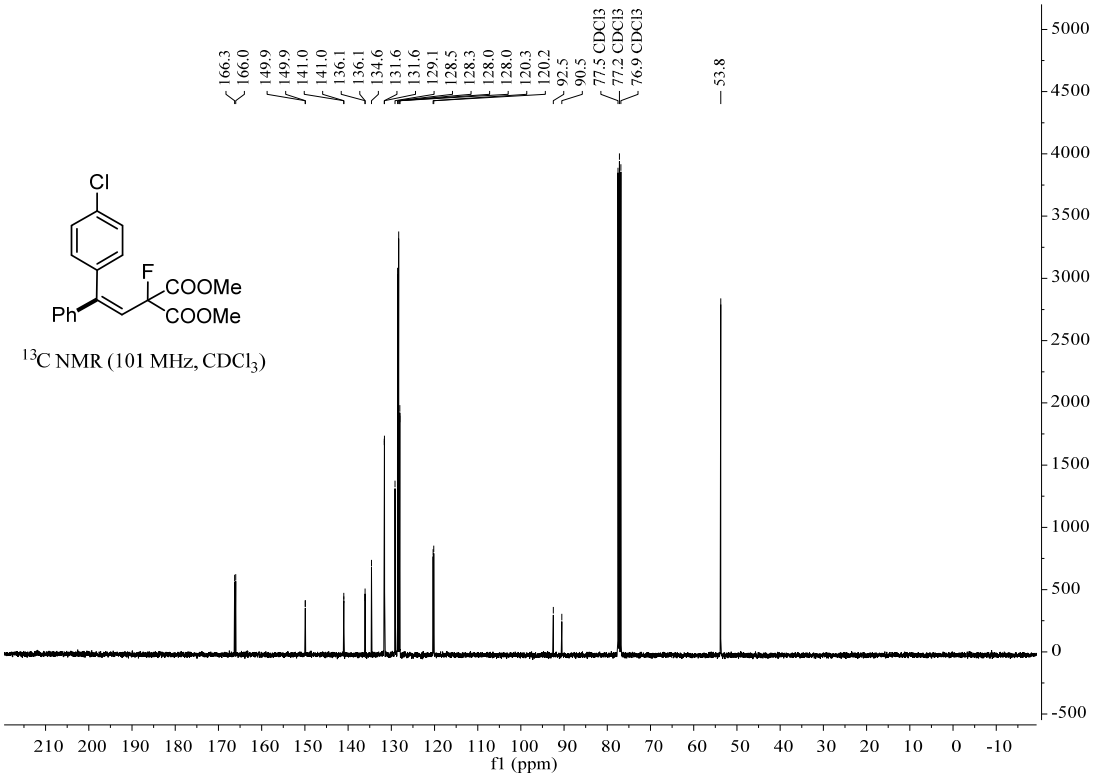


^{19}F NMR (377 MHz, $CDCl_3$)

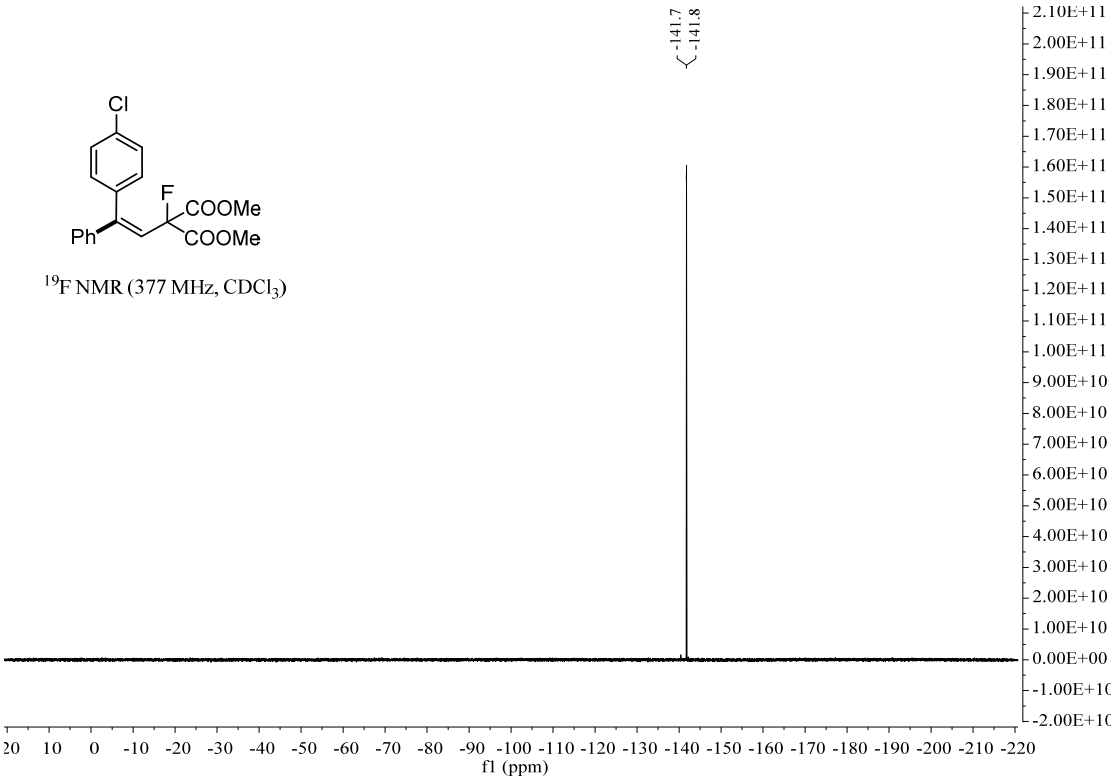
Compound 41



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

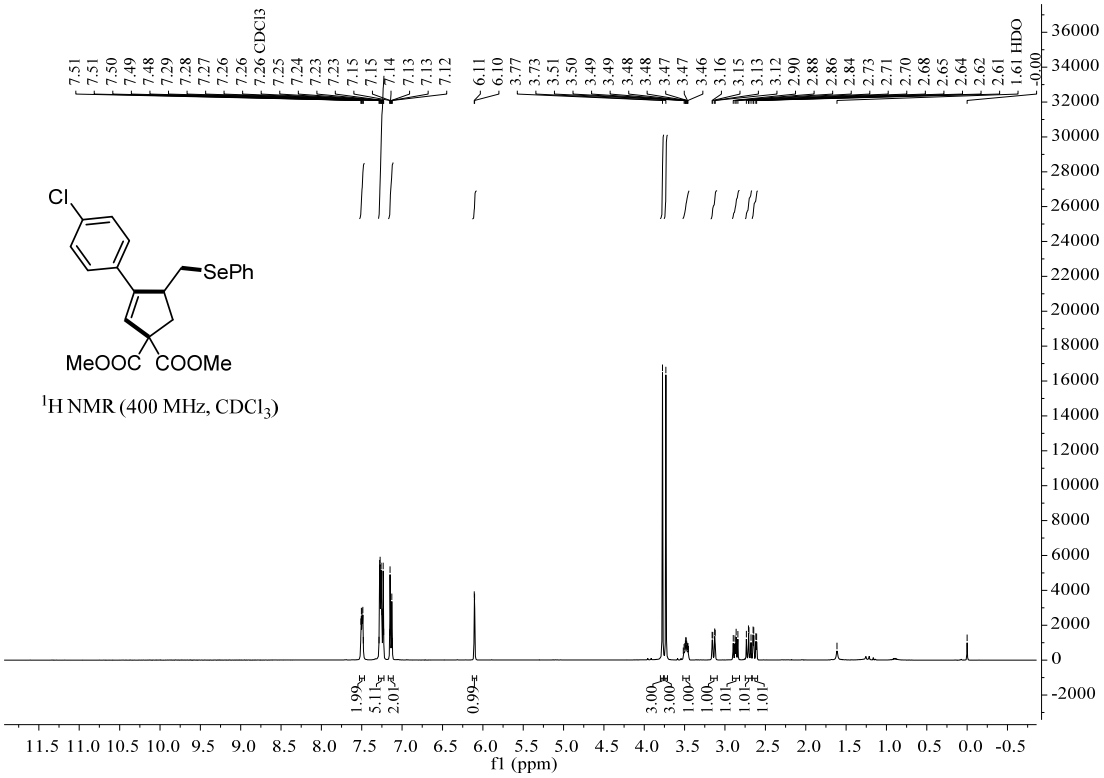


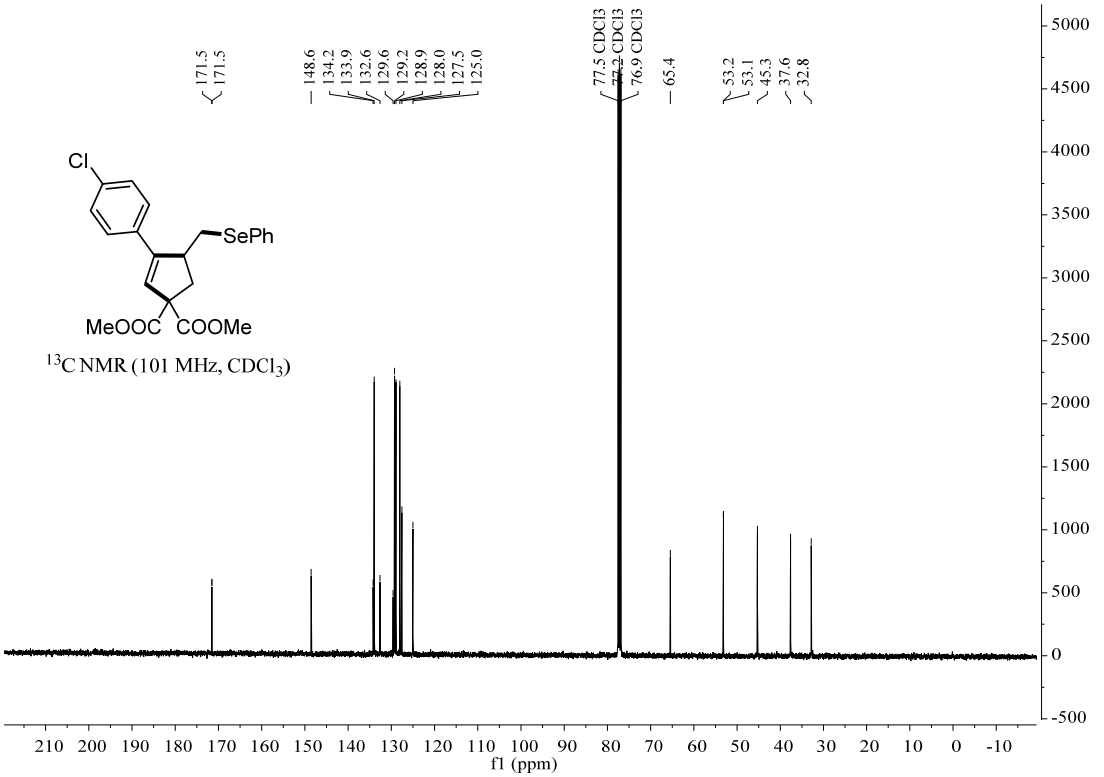
^{13}C NMR (101 MHz, $CDCl_3$)



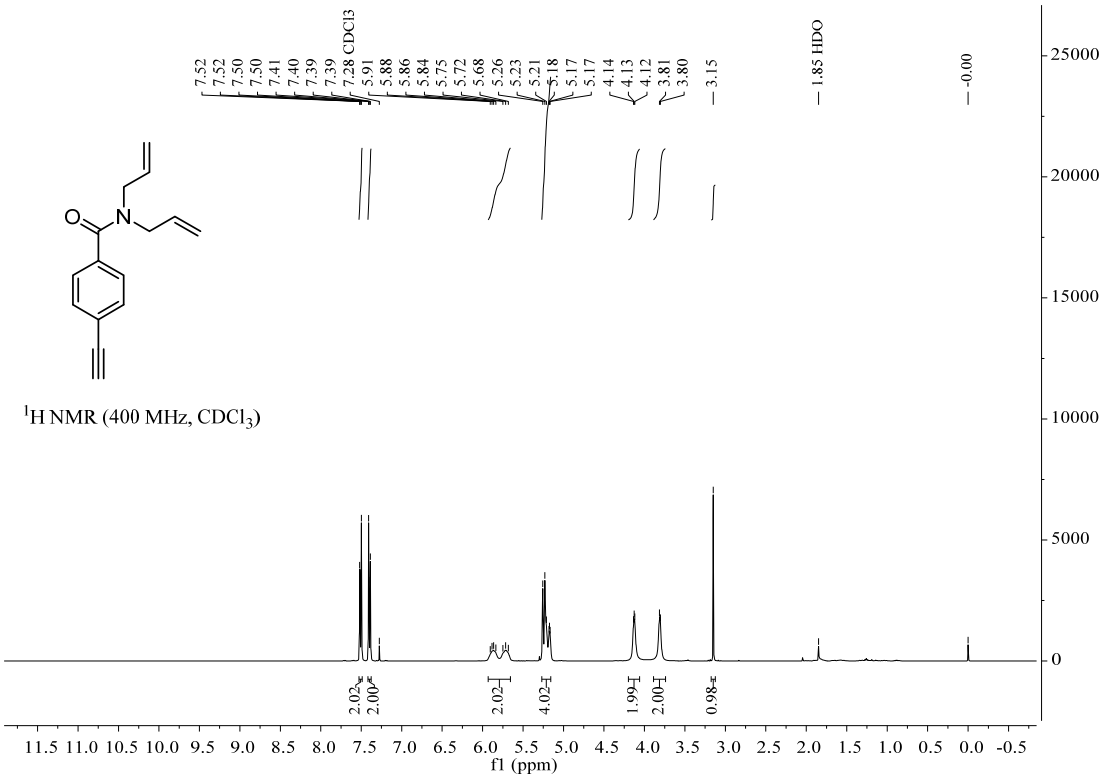
^{19}F NMR (377 MHz, $CDCl_3$)

Compound 43

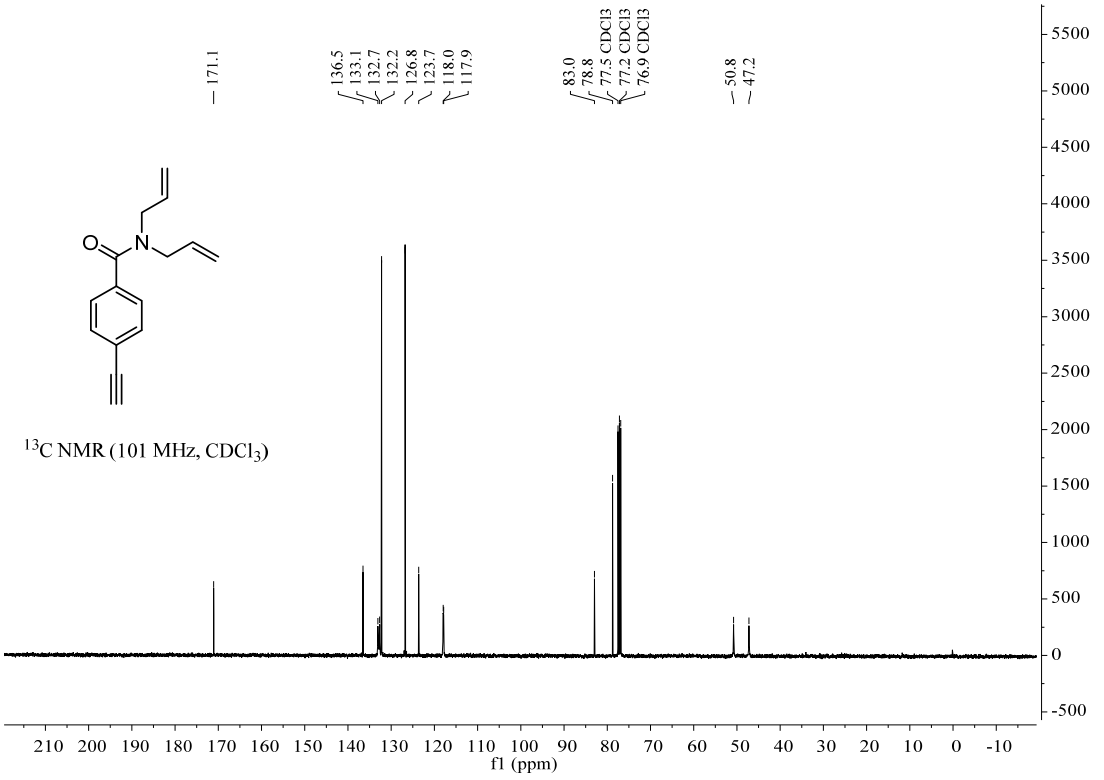

Cl
SePh
MeOOC COOMe
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


Cl
SePh
MeOOC COOMe
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound S1



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



^{13}C NMR (101 MHz, $CDCl_3$)