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Supporting Information

Cascade cyclization/fluoromethylthiolation of alkynes, unsaturated *α*-bromocarbonyls and $PhSO_2SR_F$

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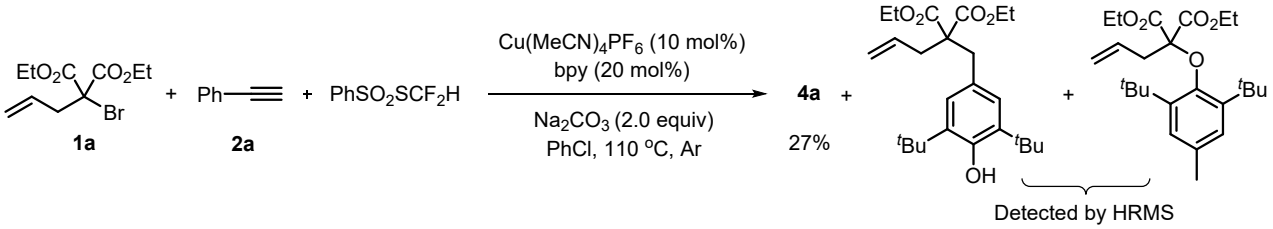
1. General information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker AVANCE III HD 600 (600 MHz for ^{1}H; 151 MHz for ^{13}C) and DRX 500 (500 MHz for ^{1}H; 126 MHz for ^{13}C, 471 MHz for ^{19}F) instruments internally referenced to tetramethylsilane (TMS) signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. $CDCl_3$ was used as the NMR solvent in all cases. High-resolution mass spectra (HRMS) were measured on Agilent 6530 Accurate-Mass Q-TOF LC/MS and Waters G2-XS Qtof spectrometers using electrospray ionization (ESI). Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Column chromatography was carried out on silica gel (particle size 200-300 mesh). α-Bromocarbonyls **1**[1], $PhSO_2SCF_2H$ (**3**)[2] and $PhSO_2SCF_3$ (**5**)[3] were prepared following literature procedures.

2. Mechanistic experiments



In a Schlenk tube, $Cu(MeCN)_4PF_6$ (10 mol%, 7.5 mg), bpy (20 mol%, 6.2 mg), Na_2CO_3 (2.0 equiv, 42.4 mg) and BHT (5.0 equiv, 220 mg) were added and charged with Ar three times. Then 2-allyl-2-bromomalonate **1a** (0.2 mmol, 1.0 equiv, 56 mg), ethynylbenzene **2a** (1.0 mmol, 5.0 equiv, 102 mg), $PhSO_2SCF_2H$ (1.0 mmol, 5.0 equiv, 224 mg) and PhCl (5 mL) were added. The mixture was allowed to stir at 110 °C (oil bath) for 12 hours. After cooling down to room temperature, the mixture was under HRMS (ESI) analysis. The result revealed the formation of BHT adduct (Figure S1). The mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether/1,4-dioxane (30/1) as the eluent to obtain the corresponding product **4a** in 27% yield.

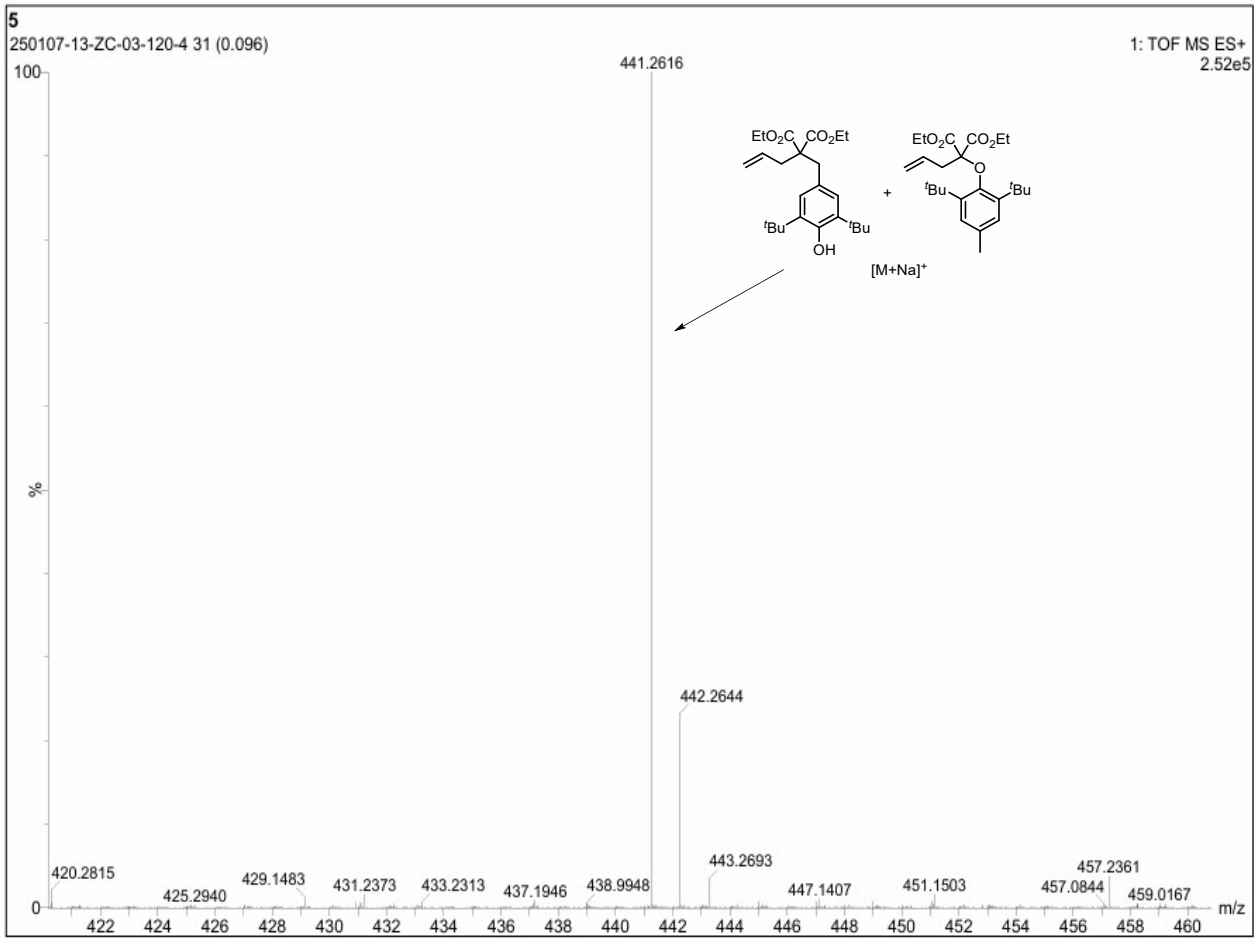
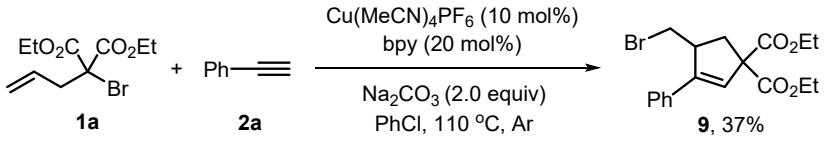
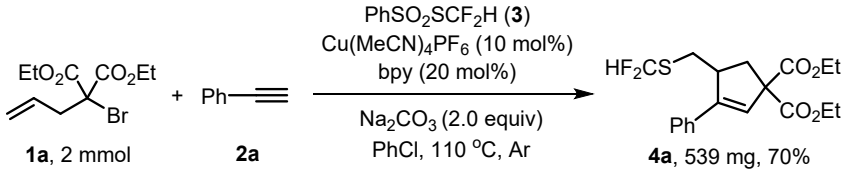


Figure S1. HRMS spectrum of the reaction solution



In a Schlenk tube, $Cu(MeCN)_4PF_6$ (10 mol%, 7.5 mg), bpy (20 mol%, 6.2 mg), Na_2CO_3 (2.0 equiv, 42.4 mg) and BHT (5.0 equiv, 220 mg) were added and charged with Ar three times. Then 2-allyl-2-bromomalonate **1a** (0.2 mmol, 1.0 equiv, 56 mg), ethynylbenzene **2a** (1.0 mmol, 5.0 equiv, 102 mg) and PhCl (5 mL) were added. The mixture was allowed to stir at 110 °C (oil bath) for 12 hours. After cooling down to room temperature, the mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether/1,4-dioxane (30/1) as the eluent to obtain the bromo-substituted cyclopentene **9** in 37% yield (28 mg).

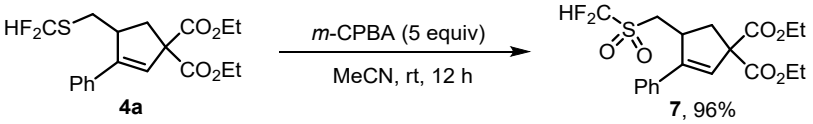
3. Scaled-up synthesis of 4a



In a round-bottom flask, $Cu(MeCN)_4PF_6$ (10 mol%, 75 mg), bpy (20 mol%, 62 mg) and Na_2CO_3 (2.0 equiv, 424 mg) were added and charged with Ar three times. Then 2-allyl-2-bromomalonate **1a** (2 mmol, 1.0 equiv, 558 mg), ethynylbenzene **2a** (10 mmol, 5.0 equiv, 1.02 g), $PhSO_2SCF_2H$ (10 mmol, 5.0 equiv, 2.24 g) and PhCl (50 mL) were added. The mixture was allowed to stir at 110 °C (oil bath) for 12 hours. After cooling down to room temperature, the mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether/1,4-dioxane (30/1) as the eluent to afford the corresponding product **4a** in 70% yield (539 mg).

4. Further transformations of 4a

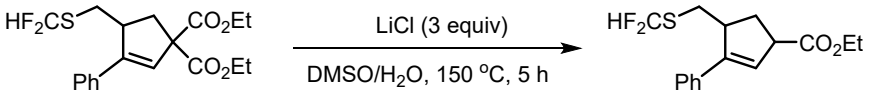
(1) Synthesis of compound 7



In a reaction tube, **4a** (0.1 mmol, 1.0 equiv, 38.4 mg) and MeCN (2 mL) were added. Then *m*-CPBA (80% w/w, 0.5 mmol, 5.0 equiv, 108 mg) was added at 0 °C. The mixture was allowed to stir at 25 °C for 12 hours. Then the mixture was purified by silica gel rapid chromatography using petroleum ether/ethyl acetate (15/1) as eluent to obtain the corresponding product **7** in 96% yield (40 mg).

Diethyl 4-(((difluoromethyl)sulfonyl)methyl)-3-phenylcyclopent-2-ene-1,1-dicarboxylate (7). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (ddd, J = 24.6, 16.4, 7.1 Hz, 5H), 6.29 (s, 1H), 6.11 (t, J = 52.8 Hz, 1H), 4.34 – 4.15 (m, 4H), 4.06 (t, J = 8.8 Hz, 1H), 3.42−3.17 (m, 2H), 3.04−2.71 (m, 2H), 1.31−1.26 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 170.4, 146.7, 132.4, 129.09, 129.06, 126.5, 126.1, 114.9 (t, J = 286.3 Hz), 66.3, 62.2, 61.9, 50.8, 37.6, 36.9, 14.03, 14.00. ^{19}F NMR (471 MHz, $CDCl_3$) δ -122.31 (dd, J = 270.5, 52.8 Hz), -123.10 (dd, J = 270.5, 52.7 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{22}F_2NaO_6S^+$, 439.0997; found, 439.1006.

(2) Synthesis of compound 8



4a **8**, 63%, 1.1/1 dr

In a reaction tube, **4a** (0.3 mmol, 1.0 equiv, 115 mg), LiCl (0.9 mmol, 38 mg), H_2O (0.25 mL) and DMSO (1 mL) were added in a Schlenk tube. The mixture was refluxed at 150 ℃ for 5 h. After cooling to room temperature, the reaction was quenched with water, extracted with ethyl acetate, washed with brine, and dried over anhydrous Na_2SO_4. Then mixture was purified by silica gel rapid chromatography using petroleum ether/ethyl acetate (50/1) as eluent to obtain the corresponding product **8** in 63% yield (59 mg).

Ethyl 4-(((difluoromethyl)thio)methyl)-3-phenylcyclopent-2-ene-1-carboxylate (8).

The major isomer: Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.76 (t, *J* = 56.2 Hz, 1H), 6.15 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.80 (t, *J* = 7.9 Hz, 1H), 3.64 (d, *J* = 8.4 Hz, 1H), 3.15 (dd, *J* = 13.2, 2.7 Hz, 1H), 2.66 (dd, *J* = 13.0, 9.4 Hz, 1H), 2.58 (dt, *J* = 13.7, 8.1 Hz, 1H), 2.27−2.23 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 146.6, 134.2, 128.7, 128.0, 126.2, 125.8, 120.4 (t, *J* = 273.0 Hz), 60.9, 49.6, 45.0, 32.3, 30.9, 14.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.87 (dd, *J* = 241.0, 2.9 Hz), -92.56 (dd, *J* = 241.0, 2.9 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{18}F_2NaO_2S^+$, 335.0888; found, 335.0893.

The minor isomer: Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.80 (t, *J* = 56.4 Hz, 1H), 6.08 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.19 (qd, *J* = 7.1, 2.0 Hz, 2H), 3.72−3.64 (m, 1H), 3.51 (t, *J* = 9.7 Hz, 1H), 3.21 (dd, *J* = 13.3, 2.9 Hz, 1H), 2.72−2.62 (m, 1H), 2.55 (dt, *J* = 13.8, 9.2 Hz, 1H), 2.30 (dt, *J* = 13.8, 4.1 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 147.2, 134.6, 128.7, 128.0, 126.5, 125.5, 120.8 (t, *J* = 272.6 Hz), 60.9, 49.6, 45.8, 31.8, 14.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.51 (d, *J* = 241.9 Hz), -92.50 (d, *J* = 241.9 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{18}F_2NaO_2S^+$, 335.0888; found, 335.0887.

5. General procedure for the synthesis of 4

(1) General procedure for the synthesis of 4a-4f, 4i-4q, 4t-4z

In a Schlenk tube, $Cu(MeCN)_4PF_6$ (10 mol%, 7.5 mg), bpy (20 mol%, 6.2 mg) and Na_2CO_3 (2.0 equiv, 42 mg) were added and charged with Ar three times. Then unsaturated α-bromocarbonyl compound **1** (0.2 mmol, 1.0 equiv), alkyne **2** (1.0 mmol, 5.0 equiv), $PhSO_2SCF_2H$ (1.0 mmol, 5.0 equiv, 224 mg) and PhCl (5.0 mL) were added. The mixture was allowed to stir at 110 °C (oil bath) for 12 hours. After cooling down to room temperature, the mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether/1,4-dioxane as the eluent to afford the corresponding product **4**.

(2) General procedure for the synthesis of 4g, 4h, 4r

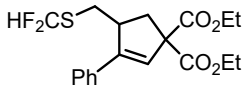
In a Schlenk tube, $Cu(MeCN)_4PF_6$ (10 mol%, 7.5 mg), bpy (20 mol%, 6.2 mg) and Na_2CO_3 (2.0 equiv, 42 mg) were added and charged with Ar three times. Then unsaturated α-bromocarbonyl compound **1** (0.2 mmol, 1.0 equiv), alkyne **2** (1.0 mmol, 5.0 equiv), $PhSO_2SCF_2H$ (1.0 mmol, 5.0 equiv, 224 mg) and PhCl (5.0 mL) were added. The mixture was allowed to stir at 80 °C (oil bath) for 12 hours. After cooling down to room temperature, the mixture

was concentrated under reduced pressure and purified by column chromatography using petroleum ether/1,4-dioxane as the eluent to afford the corresponding product **4**.

6. General procedure for the synthesis of 6

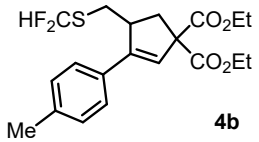
In a Schlenk tube, $Cu(MeCN)_4PF_6$ (10 mol%, 7.5 mg), bpy (20 mol%, 6.2 mg) and AcONa (2.0 equiv, 33 mg) were added and charged with Ar three times. Then unsaturated α-bromocarbonyl compound **1** (0.2 mmol, 1.0 equiv), alkyne **2** (1.0 mmol, 5.0 equiv), $PhSO_2SCF_3$ (0.8 mmol, 4.0 equiv, 194 mg) and PhCl (4.0 mL) were added. The mixture was allowed to stir at 70 °C (oil bath) for 12 hours. After cooling down to room temperature, the mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether/1,4-dioxane as the eluent to afford the corresponding product **6**.

7. Characterization of compounds



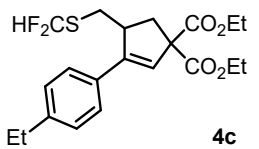
4a

Diethyl 4-(((difluoromethyl)thio)methyl)-3-phenylcyclopent-2-ene-1,1-dicarboxylate (4a). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 59 mg (76%) of **4a**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 6.80 (t, *J* = 56.2 Hz, 1H), 6.17 (s, 1H), 4.23 (m, 4H), 3.64 (t, *J* = 9.2 Hz, 1H), 3.20 (dd, *J* = 13.4, 2.6 Hz, 1H), 2.85 (dd, *J* = 14.1, 8.6 Hz, 1H), 2.73−2.44 (m, 2H), 1.31−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.9, 148.7, 133.8, 128.8, 128.5, 126.6, 125.0, 120.6 (t, *J* = 273.3 Hz), 65.5, 61.84, 61.77, 45.4, 36.3, 31.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.60 (d, *J* = 241.0 Hz), -92.64 (d, *J* = 240.9 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{22}F_2NaO_4S^+$, 407.1099; found, 407.1105.



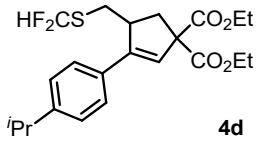
4b

Diethyl 4-(((difluoromethyl)thio)methyl)-3-(*p*-tolyl)cyclopent-2-ene-1,1-dicarboxylate (4b). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 60 mg (75%) of **4b**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.80 (t, *J* = 56.2 Hz, 1H), 6.11 (s, 1H), 4.69−3.96 (m, 4H), 3.61 (t, *J* = 9.4 Hz, 1H), 3.19 (dd, *J* = 13.4, 2.4 Hz, 1H), 2.83 (dd, *J* = 14.1, 8.6 Hz, 1H), 2.75−2.50 (m, 2H), 2.36 (s, 3H), 1.30 – 1.24 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 171.0, 148.5, 138.5, 130.9, 129.4, 126.5, 124.1, 120.6 (t, *J* = 273.3 Hz), 65.5, 61.8, 61.7, 45.4, 36.3, 31.3, 21.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.57 (dd, *J* = 241.3, 2.4 Hz), -92.68 (dd, *J* = 241.2, 2.5 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{24}F_2NaO_4S^+$, 421.1256; found, 421.1257.



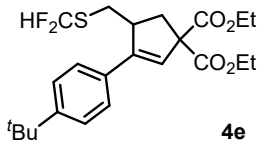
4c

Diethyl 4-(((difluoromethyl)thio)methyl)-3-(4-ethylphenyl)cyclopent-2-ene-1,1-dicarboxylate (4c). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 59 mg (72%) of **4c**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.80 (t, *J* = 56.2 Hz, 1H), 6.12 (s, 1H), 4.56−3.76 (m, 4H), 3.61 (t, *J* = 9.0 Hz, 1H), 3.21 (d, *J* = 13.1 Hz, 1H), 2.83 (dd, *J* = 14.0, 8.7 Hz, 1H), 2.67−2.57 (m, 4H), 1.49−1.13 (m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 171.0, 148.5, 144.8, 131.1, 128.3, 126.6, 124.1, 120.6 (t, *J* = 273.1 Hz), 65.5, 61.8, 61.7, 45.4, 36.3, 31.3, 28.6, 15.5, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.58 (dd, *J* = 241.5, 2.5 Hz), -92.57 (dd, *J* = 241.5, 2.6 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{26}F_2NaO_4S^+$, 435.1412; found, 435.1421.



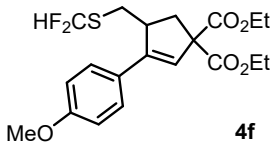
4d

Diethyl 4-(((difluoromethyl)thio)methyl)-3-(4-isopropylphenyl)cyclopent-2-ene-1,1-dicarboxylate (4d). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 65 mg (76%) of **4d**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.81 (t, *J* = 56.2 Hz, 1H), 6.12 (s, 1H), 4.34−4.03 (m, 4H), 3.61 (t, *J* = 9.3 Hz, 1H), 3.22 (d, *J* = 11.9 Hz, 1H), 2.93−2.89 (m, 1H), 2.83 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.70−2.50 (m, 2H), 1.37−1.07 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 171.0, 149.4, 148.5, 131.3, 126.8, 126.5, 124.2, 120.6 (t, *J* = 273.1 Hz), 65.4, 61.8, 61.7, 45.4, 36.3, 33.9, 31.4, 23.9, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.54 (dd, *J* = 241.4, 2.1 Hz), -92.55 (dd, *J* = 241.5, 2.4 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{28}F_2NaO_4S^+$, 449.1569; found, 445.1575.



4e

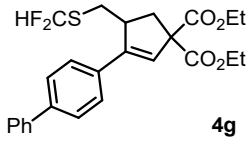
Diethyl 3-(4-(*tert*-butyl)phenyl)-4-(((difluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (4e). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 66 mg (75%) of **4e**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (q, *J* = 8.4 Hz, 4H), 6.81 (t, *J* = 56.2 Hz, 1H), 6.13 (s, 1H), 4.35−3.95 (m, 4H), 3.61 (t, *J* = 9.4 Hz, 1H), 3.23 (dd, *J* = 13.3, 2.0 Hz, 1H), 2.83 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.70−2.50 (m, 2H), 1.32 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 171.0, 151.7, 148.4, 130.8, 126.3, 125.7, 124.2, 120.6 (t, *J* = 273.0 Hz), 65.5, 61.8, 61.7, 45.4, 36.4, 34.7, 31.4, 31.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.52 (dd, *J* = 244.9, 9.4 Hz), -92.52 (dd, *J* = 244.9, 9.4 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{30}F_2NaO_4S^+$, 463.1725; found, 463.1732.



4f

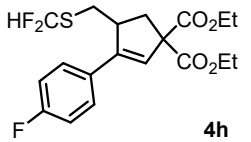
Diethyl 4-(((difluoromethyl)thio)methyl)-3-(4-methoxyphenyl)cyclopent-2-ene-1,1-dicarboxylate (4f). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 53 mg (63%) of **4f**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.83 (dd, *J* = 81.4, 32.2 Hz, 3H), 6.05 (s, 1H), 4.36−4.07 (m, 4H), 3.83 (s, 3H), 3.58 (t, *J* = 9.3 Hz, 1H), 3.19 (dd, *J*

= 13.3, 1.9 Hz, 1H), 2.80 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.71−2.48 (m, 2H), 1.30−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 171.1, 159.7, 148.1, 127.9, 126.3, 122.9, 120.6 (t, *J* = 273.3 Hz), 114.1, 61.8, 61.7, 55.3, 45.5, 36.3, 31.3, 14.04, 14.03. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.55 (d, *J* = 240.9 Hz), -92.63 (d, *J* = 241.4 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{24}F_2NaO_5S^+$, 437.1205; found, 437.1213.



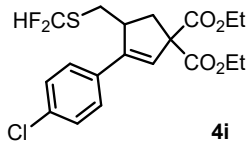
4g

Diethyl 3-([1,1'-biphenyl]-4-yl)-4-(((difluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (4g). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 38 mg (42%) of **4g**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.1 Hz, 4H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.83 (t, *J* = 56.2 Hz, 1H), 6.22 (s, 1H), 4.24 (m, 4H), 3.67 (t, *J* = 9.3 Hz, 1H), 3.25 (dd, *J* = 13.4, 2.5 Hz, 1H), 2.87 (dd, *J* = 14.1, 8.6 Hz, 1H), 2.73−2.56 (m, 2H), 1.31−1.26 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.9, 148.2, 141.2, 140.3, 132.7, 128.8, 127.5, 127.4, 127.01, 126.96, 125.0, 120.6 (t, *J* = 273.3 Hz), 65.5, 61.9, 61.8, 45.4, 36.3, 31.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.49 (d, *J* = 240.8 Hz), -92.61 (d, *J* = 240.8 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{26}F_2NaO_4S^+$, 483.1412; found, 483.1421.



4h

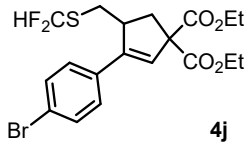
Diethyl 4-(((difluoromethyl)thio)methyl)-3-(4-fluorophenyl)cyclopent-2-ene-1,1-dicarboxylate (4h). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 41 mg (51%) of **4h**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.80 (t, *J* = 56.1 Hz, 1H), 6.11 (s, 1H), 4.79−4.04 (m, 4H), 3.59 (t, *J* = 9.2 Hz, 1H), 3.16 (dd, *J* = 13.4, 2.5 Hz, 1H), 2.83 (dd, *J* = 14.1, 8.6 Hz, 1H), 2.72−2.38 (m, 2H), 1.30−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.93, 170.85, 162.7 (d, *J* = 248.6 Hz), 147.6, 129.9 (d, *J* = 3.3 Hz), 128.3 (d, *J* = 8.2 Hz), 124.9, 120.5 (t, *J* = 273.3 Hz), 115.8 (d, *J* = 21.6 Hz), 65.5, 61.9, 61.8, 45.6, 36.3, 31.0, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.58 (d, *J* = 240.2 Hz), -92.83 (d, *J* = 240.2 Hz), -112.72. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{21}F_3NaO_4S^+$, 425.1005; found, 425.1014.



4i

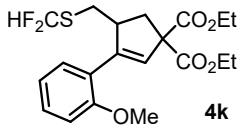
Diethyl 3-(4-chlorophenyl)-4-(((difluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (4i). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 60 mg (72%) of **4i**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43−7.29 (m, 4H), 6.80 (t, *J* = 56.0 Hz, 1H), 6.15 (s, 1H), 4.32−4.14 (m, 4H), 3.59 (t, *J* = 9.4 Hz, 1H), 3.24−3.03 (m, 1H), 2.84 (dd, *J* = 14.1, 8.6 Hz, 1H), 2.69−2.50 (m, 2H), 1.30−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.82, 170.75, 147.6, 134.3, 132.3, 129.0, 127.9, 120.4 (t, *J* = 273.3 Hz), 65.5, 61.9, 61.8, 45.5, 36.3, 31.0, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ

-91.56 (dd, J = 240.5, 2.1 Hz), -92.84 (dd, J = 240.1, 1.7 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{21}ClF_2NaO_4S^+$, 441.0709; found, 441.0717.



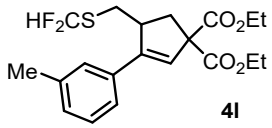
4j

Diethyl 3-(4-bromophenyl)-4-(((difluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (4j). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 57 mg (62%) of **4j**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.80 (t, J = 56.0 Hz, 1H), 6.17 (s, 1H), 4.45−3.95 (m, 4H), 3.59 (t, J = 9.4 Hz, 1H), 3.15 (d, J = 13.4 Hz, 1H), 2.84 (dd, J = 14.1, 8.6 Hz, 1H), 2.72−2.47 (m, 2H), 1.30−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 170.7, 147.6, 132.7, 131.9, 128.2, 125.7, 122.5, 120.4 (t, J = 273.3 Hz), 65.5, 61.92, 61.85, 45.4, 36.3, 30.9, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.55 (dd, J = 240.4, 2.5 Hz), -92.83 (dd, J = 240.4, 2.5 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{21}BrF_2NaO_4S^+$, 485.0204; found, 485.0208.



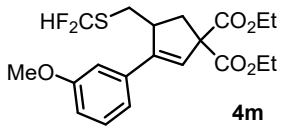
4k

Diethyl 4-(((difluoromethyl)thio)methyl)-3-(2-methoxyphenyl)cyclopent-2-ene-1,1-dicarboxylate (4k). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 56 mg (68%) of **4k**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, J = 9.3, 3.4 Hz, 2H), 6.94 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 6.74 (t, J = 56.4 Hz, 1H), 6.11 (s, 1H), 4.31−4.12 (m, 4H), 3.87 (s, 1H), 3.83 (s, 3H), 3.05 (dd, J = 13.1, 2.9 Hz, 1H), 2.92 (dd, J = 13.8, 8.3 Hz, 1H), 2.59−2.46 (m, 1H), 2.34 (dd, J = 13.8, 5.5 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 170.8, 157.0, 147.7, 130.0, 129.6, 127.4, 123.5, 120.69, 120.65 (t, J = 272.7 Hz), 110.9, 65.2, 61.7, 61.6, 55.2, 46.2, 36.8, 31.5, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.87 (dd, J = 242.1, 2.6 Hz), -92.86 (dd, J = 242.1, 2.5 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{24}F_2NaO_5S^+$, 437.1205; found, 437.1213.



4l

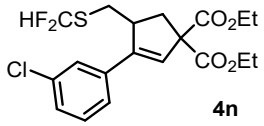
Diethyl 4-(((difluoromethyl)thio)methyl)-3-(*m*-tolyl)cyclopent-2-ene-1,1-dicarboxylate (4l). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 57 mg (72%) of **4l**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, J = 5.8 Hz, 2H), 7.21 (d, J = 7.5 Hz, 1H), 7.13 (d, J = 7.3 Hz, 1H), 6.80 (t, J = 56.2 Hz, 1H), 6.14 (s, 1H), 4.33−4.09 (m, 4H), 3.62 (t, J = 9.1 Hz, 1H), 3.20 (d, J = 13.4 Hz, 1H), 2.84 (dd, J = 14.1, 8.6 Hz, 1H), 2.67−2.51 (m, 2H), 2.36 (s, 3H), 1.31−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 170.9, 148.8, 138.4, 133.7, 129.3, 128.6, 127.3, 124.8, 123.6, 120.6 (t, J = 273.3 Hz), 65.5, 61.8, 61.7, 45.4, 36.3, 31.3, 21.4, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.60 (dd, J = 241.4, 2.1 Hz), -92.60 (dd, J = 241.4, 2.1 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{24}F_2NaO_4S^+$, 421.1256; found, 421.1264.



4m

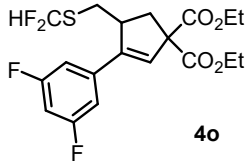
Diethyl 4-(((difluoromethyl)thio)methyl)-3-(3-methoxyphenyl)cyclopent-2-ene-1,1-dicarboxylate (4m). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 50 mg (61%) of **4m**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 14.1, 5.9 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 6.92−6.68 (m, 2H), 6.16 (s, 1H), 4.38−4.09 (m, 4H), 3.82 (s, 3H), 3.61 (d, *J* = 9.1 Hz, 1H), 3.22 (d, *J* = 13.2 Hz, 1H), 2.85 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.77−2.43 (m, 2H), 1.30−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.9, 159.8, 148.6, 135.2, 129.8, 125.3, 120.6 (t, *J* = 273.1 Hz), 119.0, 114.2, 111.9, 65.5, 61.9, 61.8, 55.2, 45.6, 36.3, 31.2, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.49 (dd, *J* = 240.9, 2.7 Hz), -92.63 (dd, *J* = 240.8, 2.9 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{24}F_2NaO_5S^+$, 437.1205; found, 437.1213.

Diethyl 3-(3-chlorophenyl)-4-(((difluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (4n).



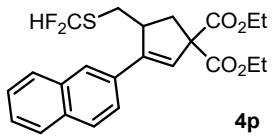
4n

Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 47 mg (56%) of **4n**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.29 (q, *J* = 7.3 Hz, 3H), 6.81 (t, *J* = 56.1 Hz, 1H), 6.19 (s, 1H), 4.61−3.88 (m, 3H), 3.59 (d, *J* = 8.8 Hz, 1H), 3.16 (d, *J* = 13.2 Hz, 1H), 2.85 (dd, *J* = 14.0, 8.7 Hz, 1H), 2.62 (dd, *J* = 23.7, 11.6 Hz, 2H), 1.31−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.74, 170.65, 147.5, 135.7, 134.7, 130.0, 128.5, 126.8, 126.5, 124.6, 120.4 (t, *J* = 273.3 Hz), 65.5, 61.94, 61.86, 45.4, 36.3, 30.9, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.55 (dd, *J* = 240.8, 2.5 Hz), -92.79 (dd, *J* = 240.8, 2.5 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{21}ClF_2NaO_4S^+$, 441.0709; found, 441.0717.



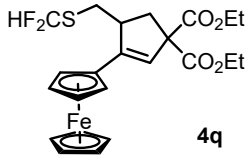
4o

Diethyl 4-(((difluoromethyl)thio)methyl)-3-(3,5-difluorophenyl)cyclopent-2-ene-1,1-dicarboxylate (4o). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 66 mg (78%) of **4o**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94 (d, J = 6.4 Hz, 2H), 6.92−6.71 (m, 2H), 6.21 (s, 1H), 4.38−4.10 (m, 4H), 3.55 (t, *J* = 9.2 Hz, 1H), 3.15 (dd, *J* = 13.5, 2.7 Hz, 1H), 2.85 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.71−2.53 (m, 2H), 1.31−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.53, 170.46, 163.2 (dd, *J* = 248.9, 13.0 Hz), 146.8 (t, *J* = 2.5 Hz), 137.1 (t, *J* = 9.5 Hz), 127.7, 120.4 (t, *J* = 273.3 Hz), 109.5 (dd, *J* = 20.5, 5.3 Hz), 103.8 (t, *J* = 25.4 Hz), 65.5, 62.04, 61.96, 45.5, 36.2, 30.8, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.52 (dd, *J* = 240.3, 2.2 Hz), -92.88 (dd, *J* = 240.2, 2.4 Hz), -109.07. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{20}F_4NaO_4S^+$, 443.0911; found, 443.0912.



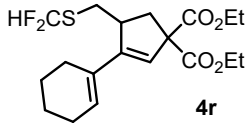
4p

Diethyl 4-(((difluoromethyl)thio)methyl)-3-(naphthalen-2-yl)cyclopent-2-ene-1,1-dicarboxylate (4p). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 61 mg (70%) of **4p**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 4H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.57−7.42 (m, 2H), 6.83 (t, *J* = 56.1 Hz, 1H), 6.31 (s, 1H), 4.60−4.00 (m, 4H), 3.77 (t, *J* = 9.6 Hz, 1H), 3.29 (dd, *J* = 13.6, 2.8 Hz, 1H), 2.89 (dd, *J* = 14.1, 8.6 Hz, 1H), 2.80−2.56 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.9, 148.6, 133.3, 133.1, 131.1, 128.4, 128.3, 127.6, 126.49, 126.47, 125.7, 125.4, 124.5, 120.6 (t, *J* = 273.0 Hz), 65.6, 61.9, 61.8, 45.6, 36.3, 31.3, 14.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.37 (dd, *J* = 240.9, 2.4 Hz), -92.70 (dd, *J* = 240.8, 2.2 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{24}F_2NaO_4S^+$, 457.1256; found, 457.1263.



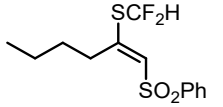
4q

Diethyl 4-(((difluoromethyl)thio)methyl)-3-ferrocenylcyclopent-2-ene-1,1-dicarboxylate (4q). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 42 mg (43%) of **4q**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (t, *J* = 56.0 Hz, 1H), 5.90 (s, 1H), 4.49 (s, 1H), 4.38 (s, 1H), 4.29 (d, *J* = 17.8 Hz, 2H), 4.26−4.17 (m, 4H), 4.11 (s, 4H), 3.59−3.39 (m, 1H), 3.28 (t, *J* = 9.6 Hz, 1H), 2.78−2.64 (m, 2H), 2.61 (dd, *J* = 14.0, 2.2 Hz, 1H), 1.29−1.27 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 171.2, 147.6, 121.3, 120.7 (t, *J* = 273.0 Hz), 69.6, 69.4, 69.1, 67.4, 66.7, 65.5, 61.73, 61.65, 47.1, 36.7, 32.0, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.27 (d, *J* = 239.9 Hz), -92.70 (d, *J* = 240.0 Hz). HRMS (ESI-TOF) *m/z*: $[M]^+$ calcd for $C_{23}H_{26}F_2FeO_4S^+$, 492.0869; found, 492.0872.



4r

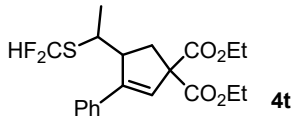
Diethyl 3-(cyclohex-1-en-1-yl)-4-(((difluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (4r). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 70 mg (84%) of **4r**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (t, *J* = 56.3 Hz, 1H), 5.87 (s, 1H), 5.70 (s, 1H), 4.49−4.00 (m, 4H), 3.45−3.05 (m, 2H), 2.73−2.48 (m, 3H), 2.35−2.25 (m, 1H), 2.24−2.08 (m, 3H), 1.68−1.56 (m, 4H), 1.26 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 171.3, 150.1, 131.3, 128.2, 121.8, 120.8 (t, *J* = 273.3 Hz), 65.2, 61.7, 61.6, 44.7, 36.0, 31.7, 26.2, 25.8, 22.4, 22.0, 14.03, 13.98. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.44 (d, *J* = 241.7 Hz), -92.59 (d, *J* = 241.7 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{26}F_2NaO_4S^+$, 411.1412; found, 411.1414.



4s'

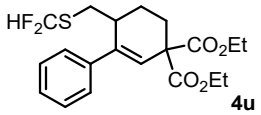
(*E*)-(difluoromethyl)(1-(phenylsulfonyl)hex-1-en-2-yl)sulfane (4s′). Purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 33 mg (11%) of **4s′**. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96−7.87 (m, 2H), 7.67−7.64 (m, 2H), 7.59−7.56 (m, 2H), 6.89 (t, *J* = 55.6 Hz, 1H), 6.39 (s, 1H), 2.87−2.76 (m, 2H), 1.57 (s, 1H), 1.56−1.49 (m, 2H), 1.44−1.32 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

152.3, 141.7, 133.6, 129.4, 127.3, 127.0, 119.0 (t, J = 275.7 Hz), 33.0, 31.1, 22.4, 13.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -93.44. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{13}H_{16}F_2NaO_2S_2^+$, 329.0452; found, 329.0463.



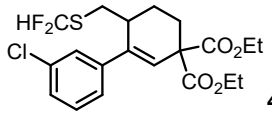
4t

Diethyl 4-(1-((difluoromethyl)thio)ethyl)-3-phenylcyclopent-2-ene-1,1-dicarboxylate (4t). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 38 mg (47%) of **4t**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (dt, J = 15.0, 7.4 Hz, 4H), 7.33 (t, J = 7.0 Hz, 1H), 6.85 (t, J = 56.1 Hz, 1H), 6.14−6.00 (m, 1H), 4.35−4.07 (m, 4H), 4.00−3.85 (m, 1H), 3.73 (dt, J = 10.6, 5.3 Hz, 1H), 2.93 (dd, J = 14.6, 9.3 Hz, 1H), 2.46 (dd, J = 14.7, 5.4 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.9, 148.0, 134.4, 128.8, 128.4, 126.6, 126.3, 120.7 (t, J = 272.9 Hz), 65.5, 61.9, 61.7, 50.0, 38.1, 31.7, 15.2, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.13 (dd, J = 242.8, 3.6 Hz), -91.99 (dd, J = 242.7, 3.6 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{24}F_2NaO_4S^+$, 421.1256; found, 421.1263.



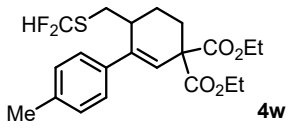
4u

Diethyl 6-(((difluoromethyl)thio)methyl)-5,6-dihydro-[1,1'-biphenyl]-3,3(4*H*)-dicarboxylate (4u). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 34 mg (42%) of **4u**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, J = 4.3 Hz, 4H), 7.32 (m, J = 8.9, 4.3 Hz, 1H), 6.68 (t, J = 56.3 Hz, 1H), 6.16 (s, 1H), 4.28−4.19 (m, 3H), 4.18−4.07 (m, 1H), 3.00 (d, J = 6.6 Hz, 1H), 2.90 (dd, J = 13.6, 2.6 Hz, 1H), 2.57−2.47 (m, 1H), 2.17−1.91 (m, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.3, 143.1, 140.0, 128.6, 127.9, 126.6, 124.1, 120.6 (t, J = 273.0 Hz), 61.7 (d, J = 4.3 Hz), 55.4, 35.9, 29.9, 24.7, 23.1, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.70 (dd, J = 241.8, 2.7 Hz), -92.49 (dd, J = 241.8, 2.8 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{24}F_2NaO_4S^+$, 421.1256; found, 421.1264.



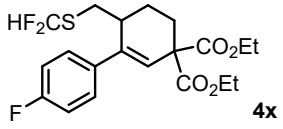
4v

Diethyl 3'-chloro-6-(((difluoromethyl)thio)methyl)-5,6-dihydro-[1,1'-biphenyl]-3,3(4*H*)-dicarboxylate (4v). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 30 mg (35%) of **4v**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.31−7.28 (m, 2H), 7.24 (dd, J = 7.7, 4.9 Hz, 1H), 6.70 (t, J = 56.1 Hz, 1H), 6.17 (s, 1H), 4.30−4.19 (m, 3H), 4.17−4.12 (m, 1H), 2.99−2.92 (m, 1H), 2.88 (dd, J = 13.6, 2.6 Hz, 1H), 2.52 (dd, J = 12.9, 11.4 Hz, 1H), 2.27 (dd, J = 16.0, 9.7 Hz, 1H), 2.14−1.93 (m, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 170.1, 142.0, 141.9, 134.5, 129.8, 128.0, 126.9, 125.3, 124.7, 120.4 (t, J = 273.3 Hz), 61.9, 61.8, 55.4, 35.9, 29.6, 24.7, 23.1, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.71 (dd, J = 241.0, 2.8 Hz), -92.75 (dd, J = 241.0, 2.7 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{23}ClF_2NaO_4S^+$, 455.0866; found, 455.0864.



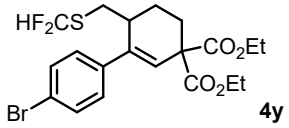
4w

Diethyl 6-(((difluoromethyl)thio)methyl)-4'-methyl-5,6-dihydro-[1,1'-biphenyl]-3,3(4*H*)-dicarboxylate (4w). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 36 mg (43%) of **4w**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 56.3 Hz, 1H), 6.13 (s, 1H), 4.29−4.18 (m, 3H), 4.16−4.06 (m, 1H), 2.98 (d, *J* = 9.0 Hz, 1H), 2.90 (d, *J* = 13.5 Hz, 1H), 2.57−2.47 (m, 1H), 2.36 (s, 3H), 2.32−2.25 (m, 1H), 2.10−1.94 (m, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.3, 142.9, 137.8, 137.0, 129.3, 126.4, 123.4, 120.6 (t, *J* = 273.0 Hz), 61.7, 61.6, 55.4, 35.8, 29.9, 24.6, 23.1, 21.1, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.66 (d, *J* = 242.0 Hz), -92.39 (d, *J* = 242.0 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{26}F_2NaO_4S^+$, 435.1412; found, 435.1419.



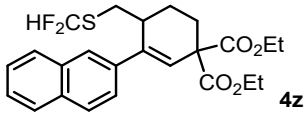
4x

Diethyl 6-(((difluoromethyl)thio)methyl)-4'-fluoro-5,6-dihydro-[1,1'-biphenyl]-3,3(4*H*)-dicarboxylate (4x). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 22 mg (26%) of **4x**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.69 (t, *J* = 56.1 Hz, 1H), 6.11 (s, 1H), 4.32−4.19 (m, 3H), 4.18−4.08 (m, 1H), 2.95 (d, *J* = 9.6 Hz, 1H), 2.88 (dd, *J* = 13.6, 2.5 Hz, 1H), 2.58−2.38 (m, 1H), 2.27 (dd, *J* = 14.8, 8.1 Hz, 1H), 2.09−1.94 (m, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.2, 163.6, 161.6, 142.2, 136.2, 128.33, 128.26, 124.4, 120.5 (t, *J* = 273.4 Hz), 115.6, 115.4, 61.8, 55.5, 36.2, 29.8, 24.7, 23.3, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.73 (d, *J* = 241.1 Hz), -92.76 (d, *J* = 241.1 Hz), -114.26. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{23}F_3NaO_4S^+$, 439.1161; found, 439.1163.



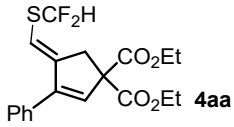
4y

Diethyl 4'-bromo-6-(((difluoromethyl)thio)methyl)-5,6-dihydro-[1,1'-biphenyl]-3,3(4*H*)-dicarboxylate (4y). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 51 mg (53%) of **4y**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.69 (t, *J* = 56.1 Hz, 1H), 6.15 (s, 1H), 4.28−4.19 (m, 4H), 4.18−4.10 (m, 1H), 2.95 (d, *J* = 7.6 Hz, 1H), 2.87 (dd, *J* = 13.6, 2.3 Hz, 1H), 2.56−2.42 (m, 1H), 2.27 (dt, *J* = 14.3, 7.3 Hz, 1H), 2.10−1.96 (m, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 170.1, 142.1, 138.9, 131.7, 128.2, 124.8, 122.0, 120.4 (t, *J* = 273.3 Hz), 61.82, 61.78, 55.4, 35.9, 29.7, 24.6, 23.1, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.67 (dd, *J* = 240.8, 2.9 Hz), -92.70 (dd, *J* = 240.8, 2.9 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{23}BrF_2NaO_4S^+$, 499.0361; found, 499.0363.



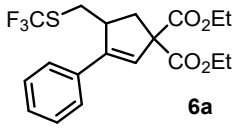
4z

Diethyl 4-(((difluoromethyl)thio)methyl)-3-(naphthalen-2-yl)cyclohex-2-ene-1,1-dicarboxylate (4z). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 42 mg (47%) of **4z**. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89−7.75 (m, 4H), 7.58−7.42 (m, 3H), 6.68 (t, *J* = 56.3 Hz, 1H), 6.30 (s, 1H), 4.32−4.19 (m, 3H), 4.14 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.15 (d, *J* = 6.9 Hz, 1H), 2.95 (dd, *J* = 13.6, 2.7 Hz, 1H), 2.72−2.48 (m, 1H), 2.44−2.28 (m, 1H), 2.17−1.96 (m, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.2, 143.0, 137.3, 133.3, 132.9, 128.2, 128.1, 127.6, 126.4, 126.1, 125.5, 124.7, 124.6, 120.6 (t, *J* = 273.3 Hz), 61.8, 61.7, 55.5, 36.0, 30.0, 24.7, 23.2, 14.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.55 (d, *J* = 241.7 Hz), -92.40 (d, *J* = 241.8 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{26}F_2NaO_4S^+$, 471.1412; found, 471.1415.



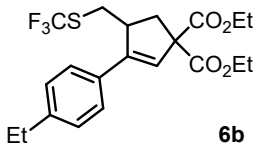
4aa

Diethyl (*E*)-4-(((difluoromethyl)thio)methylene)-3-phenylcyclopent-2-ene-1,1-dicarboxylate (4aa). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 40 mg (52%) of **4aa**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41−7.38 (m, 2H), 7.38−7.34 (m, 3H), 6.82 (t, *J* = 56.4 Hz, 1H), 6.27 (s, 1H), 6.14 (t, *J* = 2.2 Hz, 1H), 4.28−4.21 (m, 4H), 3.34 (d, *J* = 2.2 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 148.0, 147.5, 133.5, 133.4, 128.61, 128.57, 128.2, 119.4 (t, *J* = 275.4 Hz), 105.8, 105.7 (t, *J* = 4.6 Hz), 63.9, 62.1, 37.4, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -93.02 (d, *J* = 2.8 Hz). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{20}F_2NaO_4S^+$, 405.0943; found,405.0949.



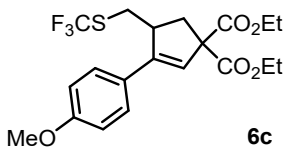
6a

Diethyl 3-phenyl-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6a). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 48 mg (60%) of **6a**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46−7.35 (m, 4H), 7.33 (t, *J* = 7.1 Hz, 1H), 6.18 (s, 1H), 4.49−3.96 (m, 4H), 3.65 (t, *J* = 9.5 Hz, 1H), 3.24 (dd, *J* = 13.4, 2.6 Hz, 1H), 2.85 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.81−2.68 (m, 1H), 2.59 (dd, *J* = 14.2, 3.3 Hz, 1H), 1.31−1.25 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.8, 148.2, 133.5, 131.1 (q, *J* = 306.2 Hz), 128.8, 128.6, 126.5, 125.3, 65.5, 61.9, 61.8, 44.8, 36.2, 34.0, 14.03, 14.01. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.67. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{21}F_3NaO_4S^+$, 425.1005; found, 425.1011.



6b

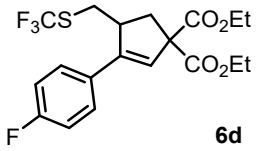
Diethyl 3-(4-ethylphenyl)-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6b). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 44 mg (51%) of **6b**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.14 (s, 1H), 4.32−4.11 (m, 4H), 3.63 (t, *J* = 8.9 Hz, 1H), 3.26 (d, *J* = 13.4 Hz, 1H), 2.83 (dd, *J* = 14.0, 8.7 Hz, 1H), 2.73 (t, *J* = 12.2 Hz, 1H), 2.66 (q, *J* = 7.5 Hz, 2H), 2.59 (d, *J* = 14.2 Hz, 1H), 1.33−1.22



6c

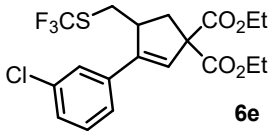
(m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.9, 148.1, 145.0, 131.1 (q, *J* = 306.1 Hz), 130.9, 128.3, 126.5, 124.4, 65.5, 61.9, 61.8, 44.7, 36.2, 34.1, 28.6, 15.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.62. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{25}F_3NaO_4S^+$, 453.1318; found, 453.1325.

Diethyl 3-(4-methoxyphenyl)-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6c). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 51 mg (59%) of **6c**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.07 (s, 1H), 4.39−4.08 (m, 4H), 3.83 (s, 3H), 3.59 (t, *J* = 9.5 Hz, 1H), 3.24 (dd, *J* = 13.4, 2.1 Hz, 1H), 2.80 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.74 (t, *J* = 12.2 Hz, 1H), 2.60 (dd, *J* = 14.2, 2.6 Hz, 1H), 1.32−1.24 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 171.0, 159.8, 147.7, 131.1 (q, *J* = 306.1 Hz), 127.8, 126.0, 123.2, 114.1, 65.4, 61.9, 61.7, 55.3, 44.8, 36.1, 34.0, 14.02, 14.00. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.63. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{23}F_3NaO_5S^+$, 455.1111; found, 455.1104.



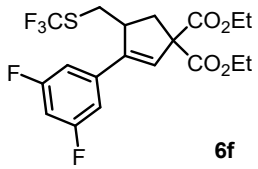
6d

Diethyl 3-(4-fluorophenyl)-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6d). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 45 mg (54%) of **6d**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.8, 5.6 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 6.13 (s, 1H), 4.35−4.13 (m, 4H), 3.60 (t, *J* = 9.5 Hz, 1H), 3.19 (dd, *J* = 13.5, 2.3 Hz, 1H), 2.84 (dd, *J* = 14.2, 8.7 Hz, 1H), 2.76−2.71 (m, 1H), 2.60 (dd, *J* = 14.2, 2.9 Hz, 1H), 1.31−1.24 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 170.7, 162.8 (d, *J* = 248.8 Hz), 147.2, 131.0 (q, *J* = 306.1 Hz), 129.7 (d, *J* = 3.3 Hz), 128.3 (d, *J* = 8.1 Hz), 125.2, 115.8 (d, *J* = 21.6 Hz), 65.5, 62.0, 61.9, 44.9, 36.2, 33.8, 14.01, 14.00. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.67, -112.46. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{20}F_4NaO_4S^+$, 443.0911; found, 443.0916.



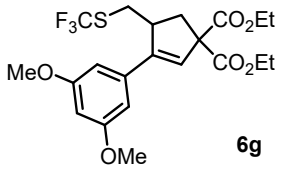
6e

Diethyl 3-(3-chlorophenyl)-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6e). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 39 mg (45%) of **6e**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.36−7.28 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 6.21 (s, 1H), 4.33−4.16 (m, 4H), 3.61 (t, *J* = 9.2 Hz, 1H), 3.20 (dd, *J* = 13.4, 1.8 Hz, 1H), 2.85 (dd, *J* = 14.2, 8.7 Hz, 1H), 2.74 (t, *J* = 12.1 Hz, 1H), 2.60 (dd, *J* = 14.2, 2.7 Hz, 1H), 1.31−1.26 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 170.5, 147.0, 135.4, 134.8, 131.0 (q, *J* = 306.2 Hz), 130.1, 128.6, 126.8, 126.7, 124.5, 65.5, 62.0, 61.9, 44.8, 36.1, 33.8, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.45. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{20}ClF_3NaO_4S^+$, 459.0615; found, 459.0612.



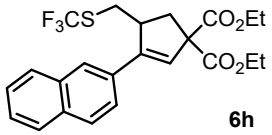
6f

Diethyl 3-(3,5-difluorophenyl)-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6f). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 35 mg (40%) of **6f**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 (d, *J* = 6.4 Hz, 2H), 6.78 (t, *J* = 8.7 Hz, 1H), 6.23 (s, 1H), 4.33−4.16 (m, 4H), 3.56 (t, *J* = 9.4 Hz, 1H), 3.19 (dd, *J* = 13.5, 2.7 Hz, 1H), 2.85 (dd, *J* = 14.3, 8.7 Hz, 1H), 2.79−2.71 (m, 1H), 2.61 (dd, *J* = 14.3, 3.2 Hz, 1H), 1.34−1.22 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 170.3, 163.2 (dd, *J* = 249.1, 13.0 Hz), 146.3, 136.8 (t, *J* = 9.5 Hz), 130.9 (q, *J* = 306.3 Hz), 128.0, 109.5 (dd, *J* = 20.5, 5.4 Hz), 104.0 (t, *J* = 25.4 Hz), 65.5, 62.1, 62.0, 44.8, 36.1, 33.7, 14.01, 13.99. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.53. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{19}F_5NaO_4S^+$,461.0816; found, 461.0824.



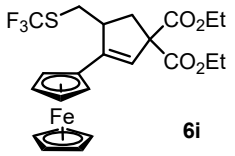
6g

Diethyl 3-(3,5-dimethoxyphenyl)-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6g). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 29 mg (31%) of **6g**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.54 (s, 2H), 6.44 (s, 1H), 6.17 (s, 1H), 4.32−4.14 (m, 4H), 3.80 (s, 6H), 3.60 (t, *J* = 9.5 Hz, 1H), 3.39−3.16 (m, 1H), 2.85 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.72 (t, *J* = 12.3 Hz, 1H), 2.56 (dd, *J* = 14.2, 3.0 Hz, 1H), 1.34−1.23 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.7, 161.0, 148.2, 135.5, 131.2 (q, *J* = 306.2 Hz), 128.8, 125.7, 104.5, 100.8, 65.4, 61.9, 61.8, 55.3, 45.1, 36.2, 34.1, 14.01, 14.00. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.53. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{25}F_3NaO_6S^+$, 485.1216; found, 485.1220.



6h

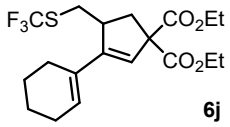
Diethyl 3-(naphthalen-2-yl)-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6h). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 48 mg (53%) of **6h**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (t, *J* = 5.9 Hz, 3H), 7.79 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.50 (dd, *J* = 9.1, 5.3 Hz, 2H), 6.33 (s, 1H), 4.33−4.17 (m, 4H), 3.79 (t, *J* = 9.4 Hz, 1H), 3.33 (d, *J* = 13.6 Hz, 1H), 2.89 (dd, *J* = 14.0, 8.7 Hz, 1H), 2.79 (t, *J* = 12.3 Hz, 1H), 2.66 (dd, *J* = 14.1, 2.4 Hz, 1H), 1.33-1.26 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.8, 148.2, 133.34, 133.26, 131.2 (q, *J* = 306.1 Hz), 131.0, 128.5, 128.3, 127.7, 126.58, 126.56, 125.9, 125.7, 124.4, 65.7, 61.9, 61.8, 45.1, 36.3, 34.1, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.52. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{23}F_3NaO_4S^+$, 475.1161; found, 475.1168.



6i

Diethyl 3-ferrocenyl-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6i). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1)

to afford 42 mg (41%) of **6i**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.91 (s, 1H), 4.46 (s, 1H), 4.35 (s, 1H), 4.31 (s, 1H), 4.29 (s, 1H), 4.22 (qd, *J* = 10.7, 3.5 Hz, 4H), 4.10 (s, 5H), 3.61−3.44 (m, 1H), 3.29 (t, *J* = 9.7 Hz, 1H), 2.81 (t, *J* = 12.6 Hz, 1H), 2.67 (dd, *J* = 14.0, 8.5 Hz, 1H), 2.64−2.56 (m, 1H), 1.28−1.27 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 171.0, 147.2, 131.3 (q, *J* = 306.0 Hz), 121.6, 77.5, 69.6, 69.5, 69.2, 67.3, 66.5, 65.4, 61.8, 61.7, 46.3, 36.5, 34.9, 14.03, 13.99. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.45. HRMS (ESI-TOF) *m/z*: $[M]^+$ calcd for $C_{23}H_{25}F_3FeO_4S^+$, 510.0775; found, 510.0770.



6j

Diethyl 3-(cyclohex-1-en-1-yl)-4-(((trifluoromethyl)thio)methyl)cyclopent-2-ene-1,1-dicarboxylate (6j). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 20 mg (25%) of **6j**. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84 (s, 1H), 5.72 (s, 1H), 4.30−4.10 (m, 4H), 3.29 (t, *J* = 12.5 Hz, 2H), 2.72 (t, *J* = 12.5 Hz, 1H), 2.62 (d, *J* = 14.2 Hz, 1H), 2.56 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.35−2.25 (m, 1H), 2.15 (dt, *J* = 22.6, 17.4 Hz, 3H), 1.68 (d, *J* = 5.1 Hz, 2H), 1.60 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.22, 171.21, 149.7, 131.23, 131.22 (q, *J* = 306.3 Hz), 128.2, 122.1, 65.2, 61.8, 61.7, 44.0, 35.9, 34.4, 26.2, 25.8, 22.4, 22.0, 14.03, 13.97. ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.62. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{25}F_3NaO_4S^+$, 429.1318; found, 429.1316.

References

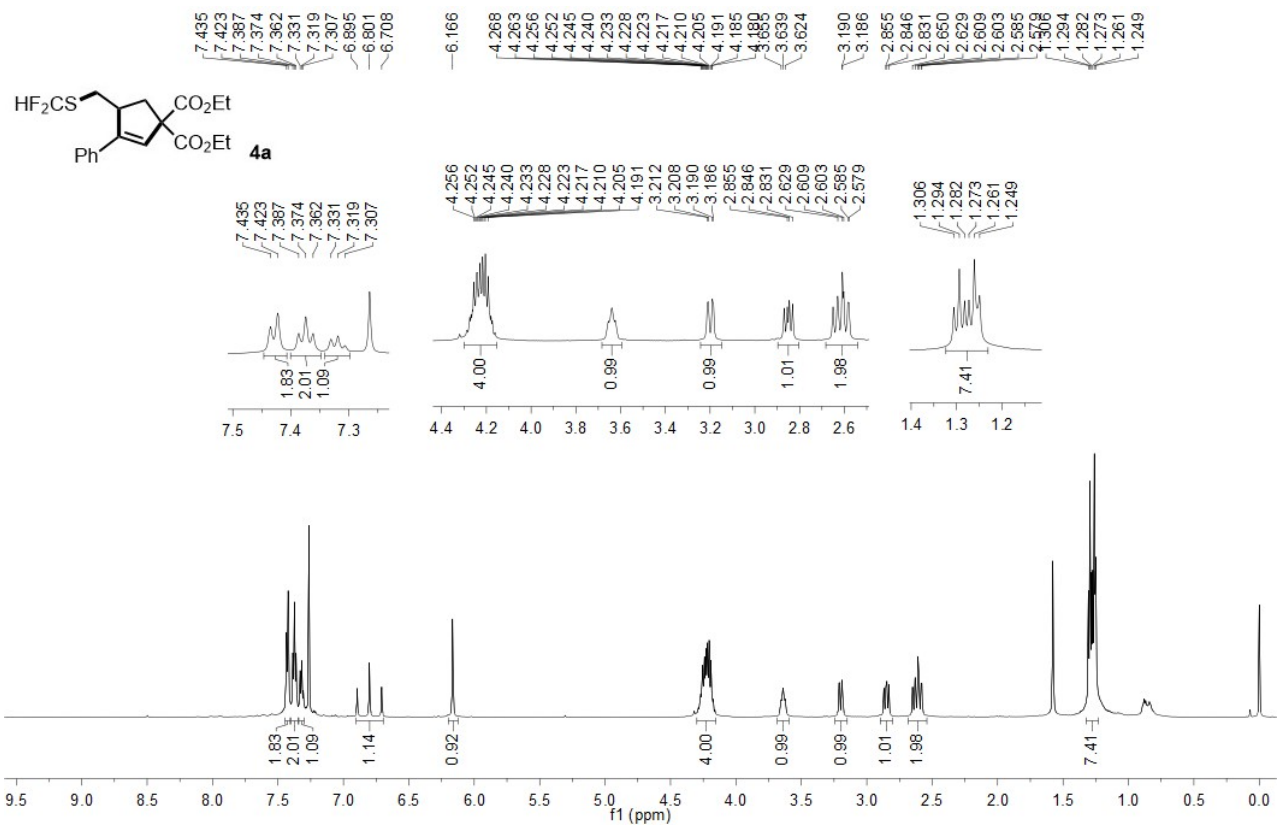
(1) (a) W. Yang, L. Huang, H. Liu, W. Wang, H. Li, Efficient synthesis of highly substituted pyrroles through a $Pd(OCOCF_3)_2$-catalyzed cascade reaction of 2-alkenal-1,3-dicarbonyl compounds with primary amines, *Chem. Commun*., 2013, **49**, 4667−4669; (b) D. Yang, Y. Yan, B. Lui, Mild α-halogenation reactions of 1,3-dicarbonyl compounds catalyzed by Lewis acids, *J. Org. Chem.*, 2002, **67**, 7429−7431; (c) L. Dai, Z. H. Xia, Y. Y. Gao, Z. H. Gao, S. Ye, Visible-light-driven N-heterocyclic carbene catalyzed γ- and ϵ-alkylation with alkyl radicals, *Angew. Chem., Int. Ed.*, 2019, **58**, 18124−18130.

(2) D.-H. Zhu, X.-X. Shao, X. Hong, L. Lu, Q.-L. Shen, $PhSO_2SCF_2H$: a shelf-stable, easily scalable reagent for radical difluoromethylthiolation, *Angew. Chem., Int. Ed.*, 2016, **55**, 15807−15811.

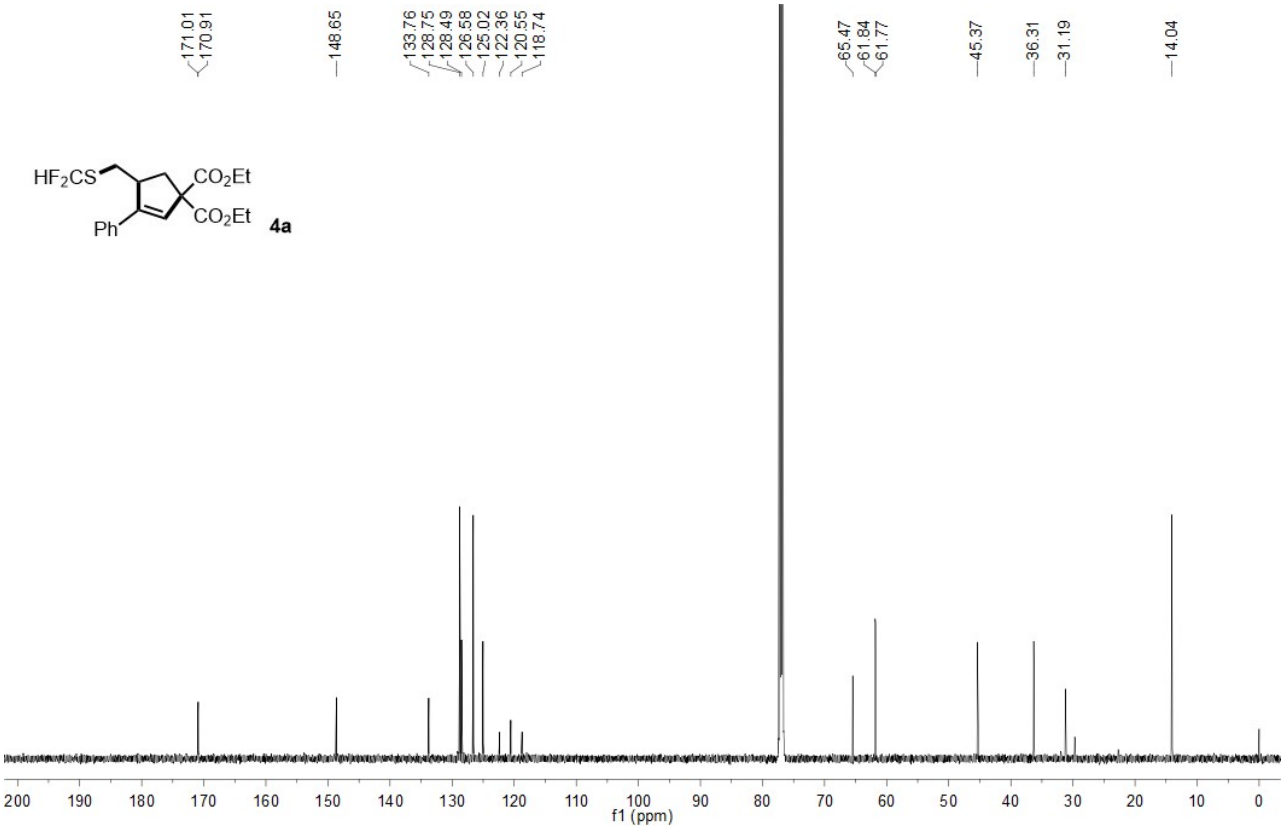
(3) X. Shao, S. Zhou, Z. Hu, Y. Zha, S. Wu, X. Wang, S. Xu, H. Zhou, Metal-catalyzed radical trifluoromethylthiolation of aryl boronic acids in the aqueous phase, *ChemCatChem,* 2022, **14**, e202200546.

8. Charts of compounds

^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 151 MHz, $CDCl_3$



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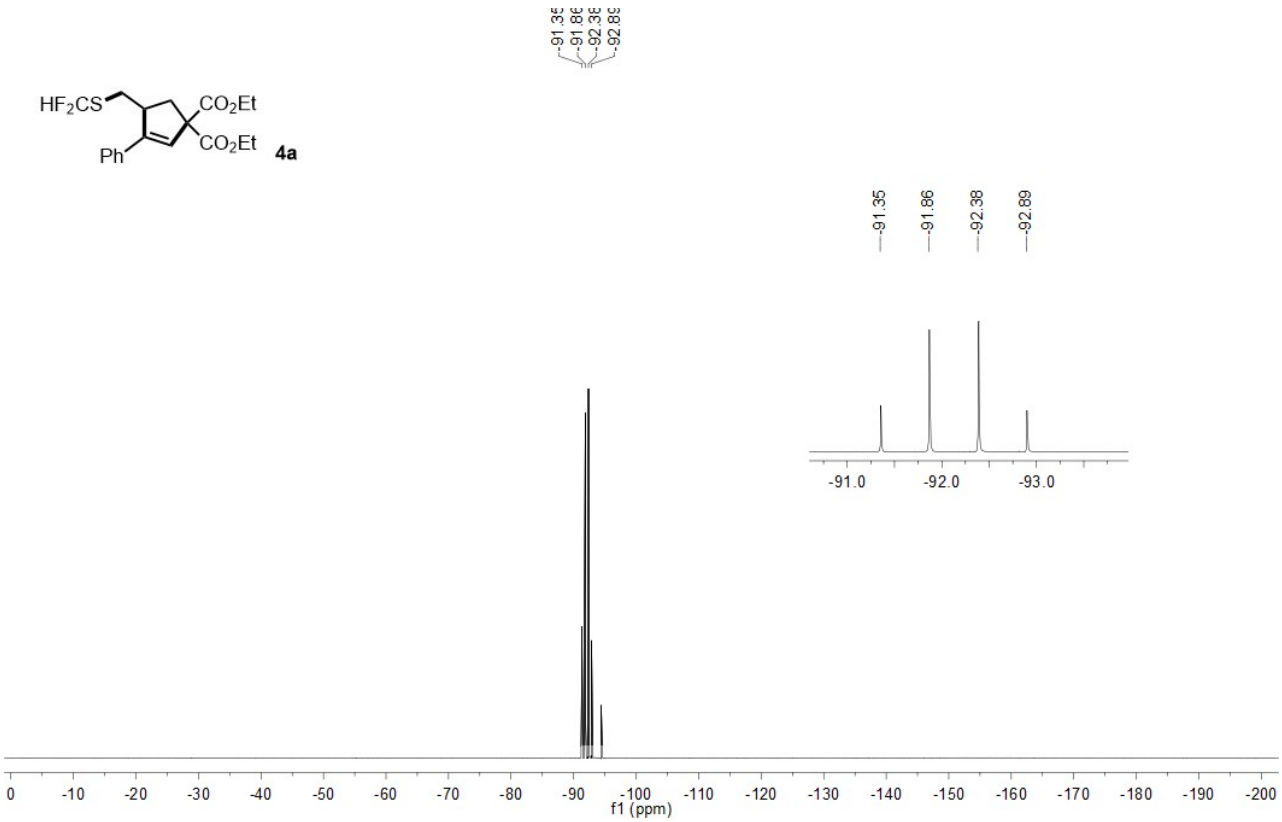

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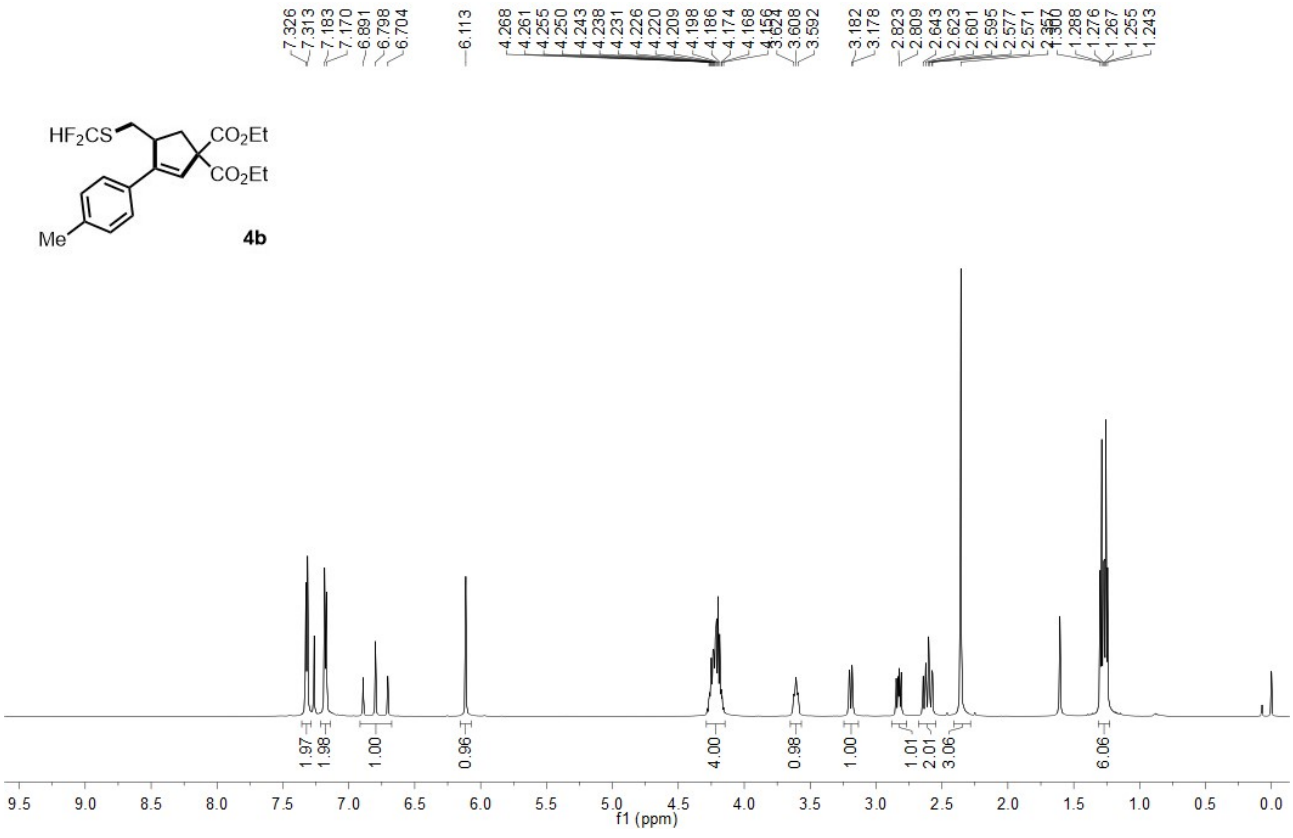

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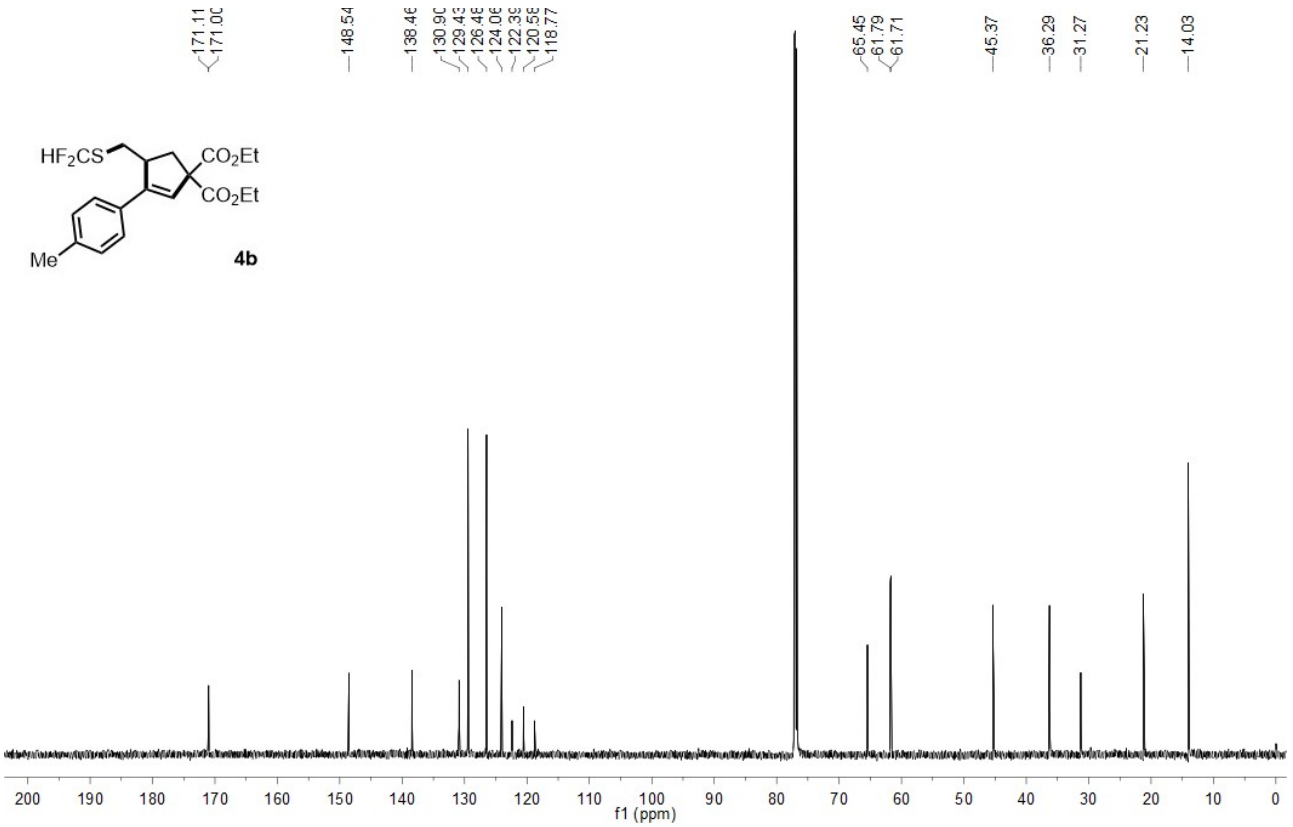

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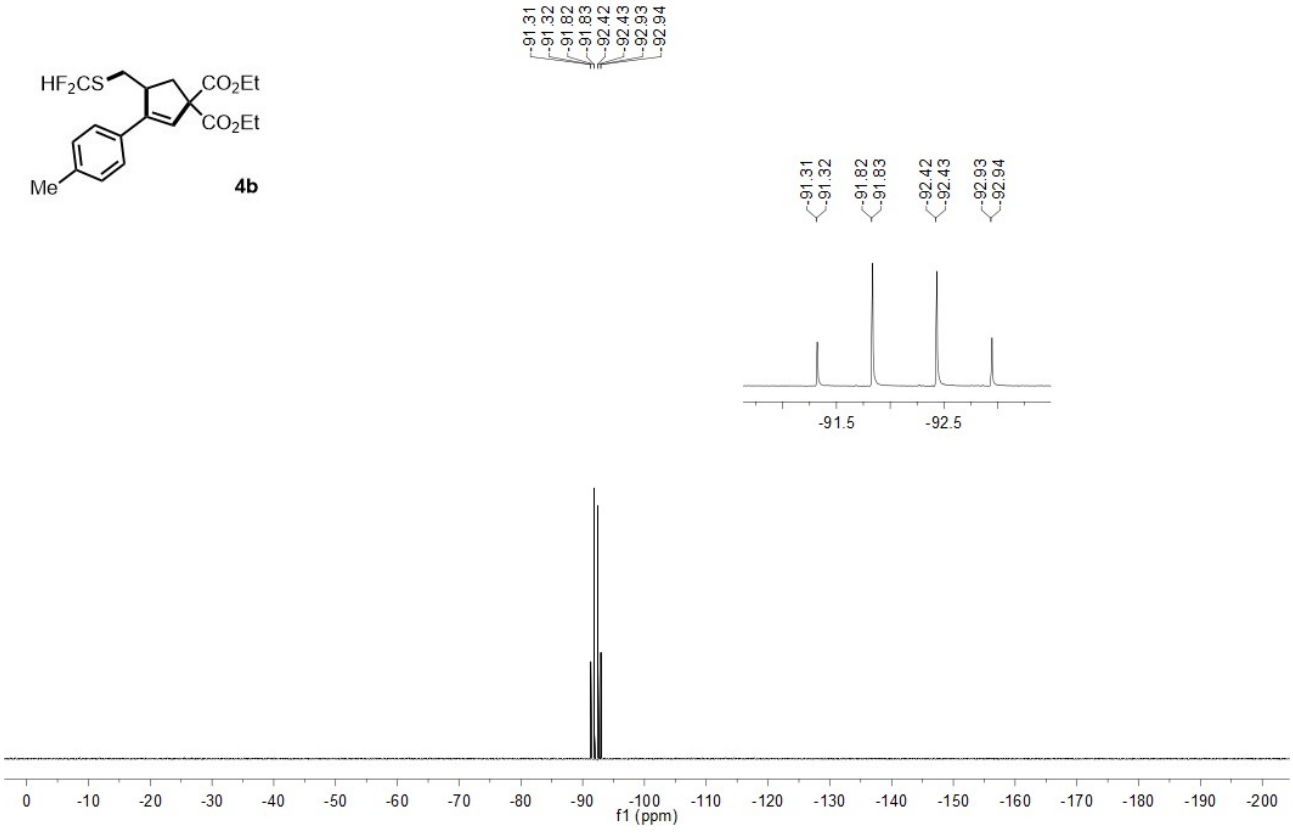

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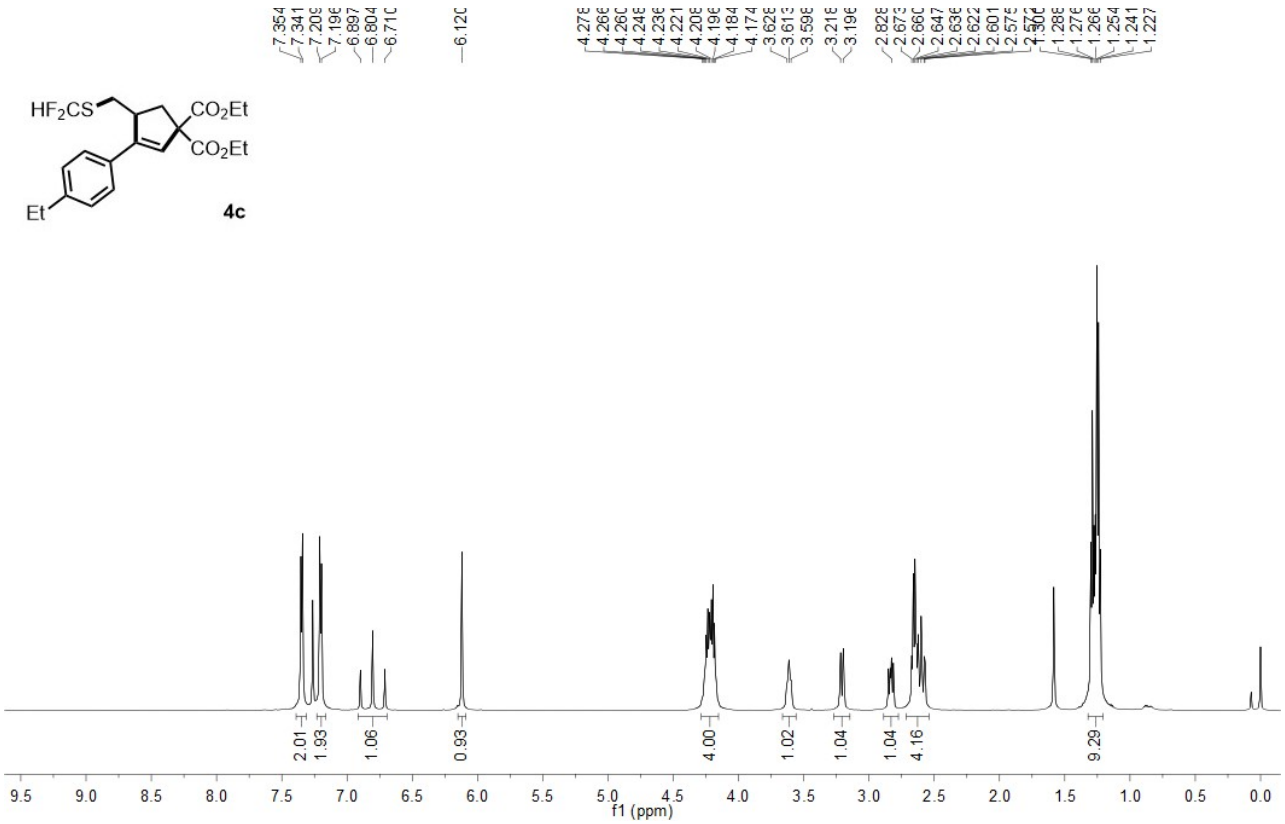

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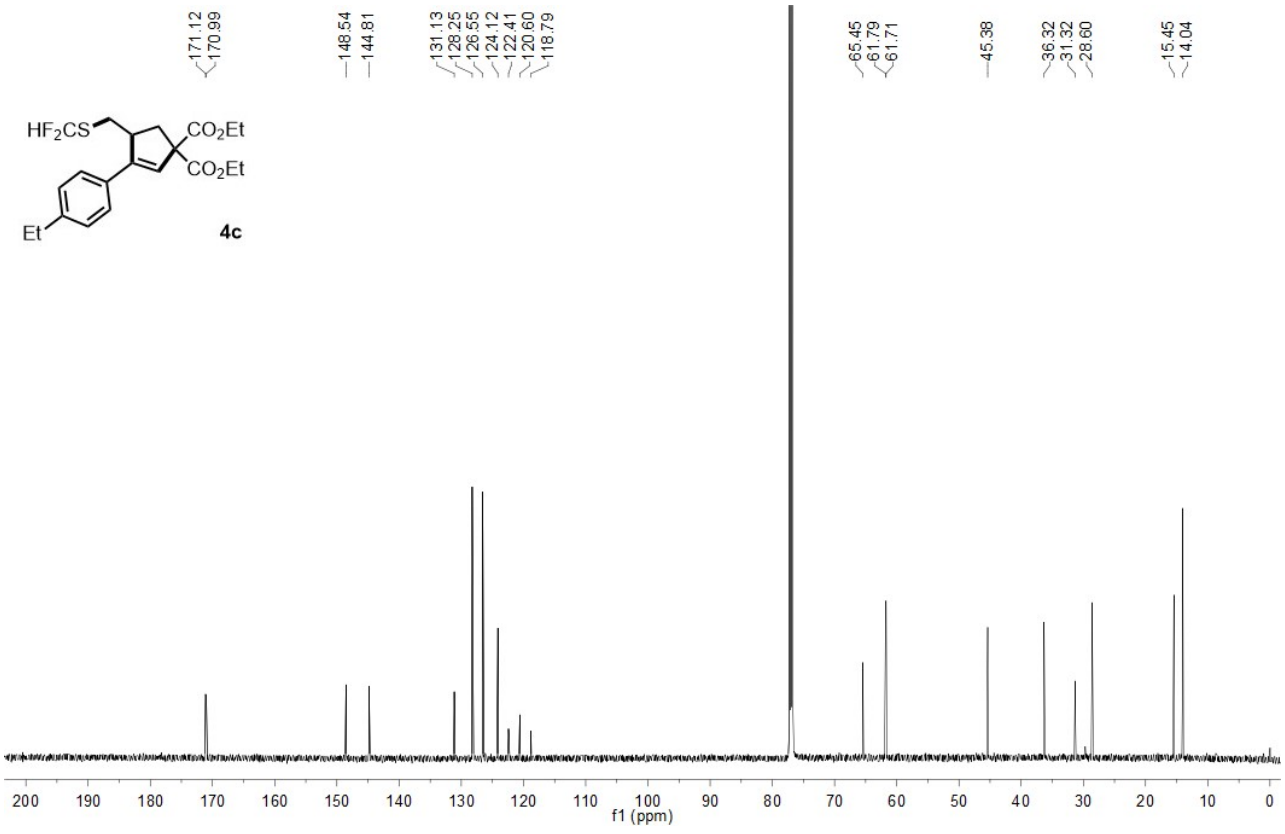

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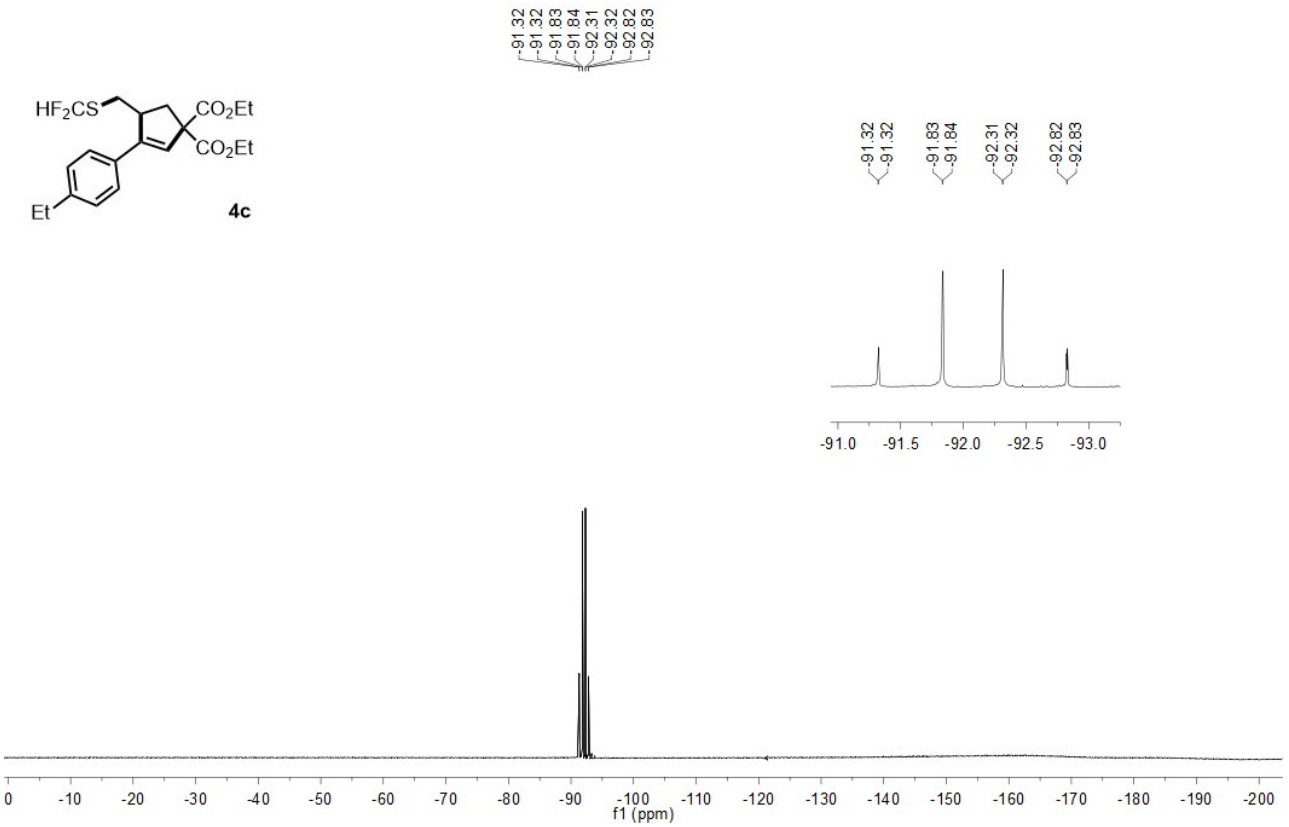

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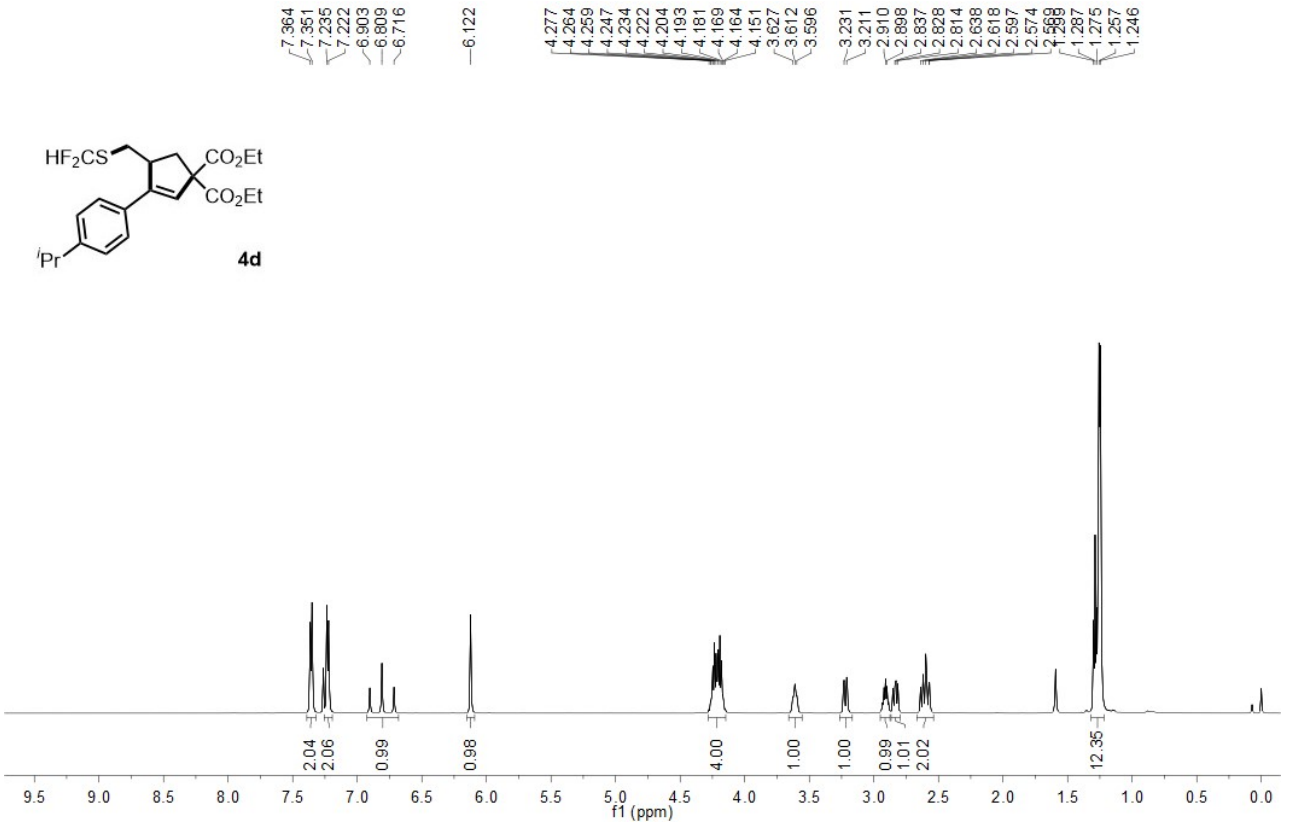

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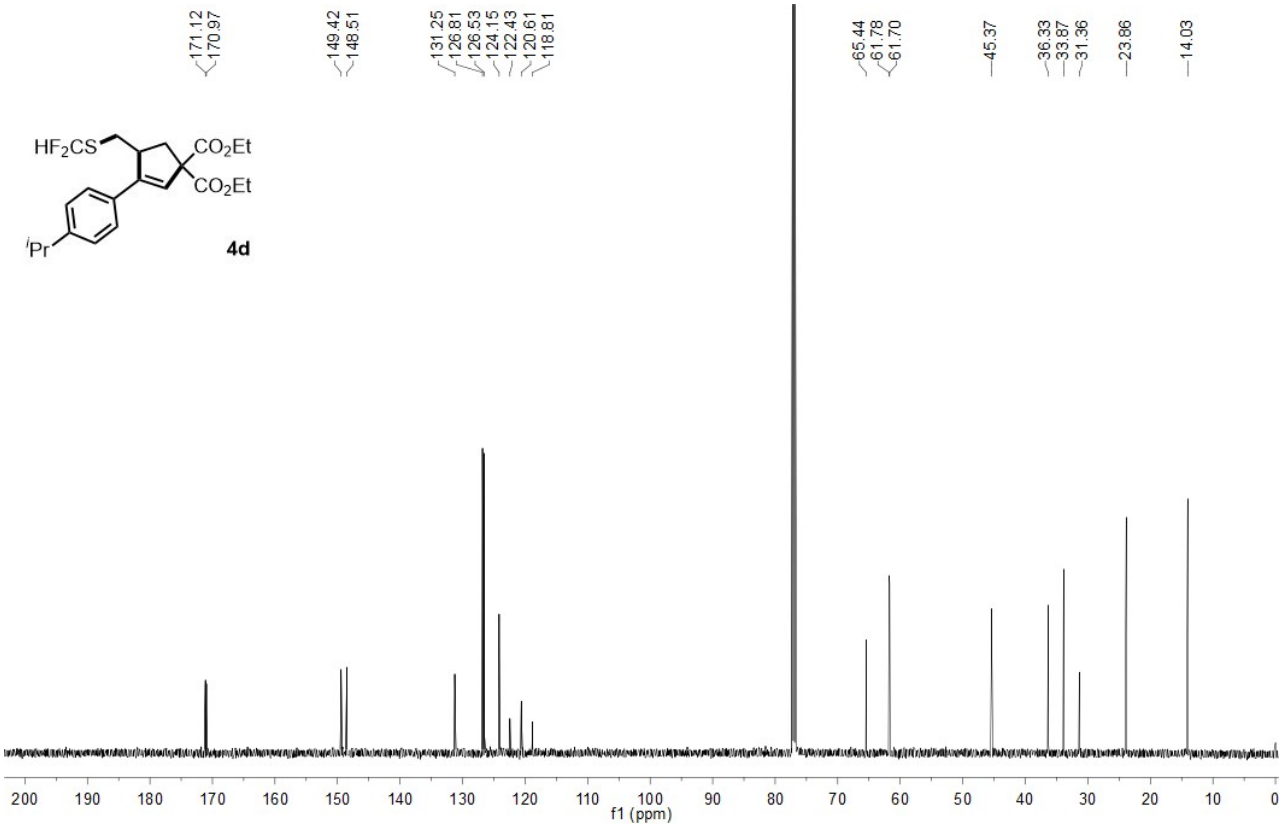

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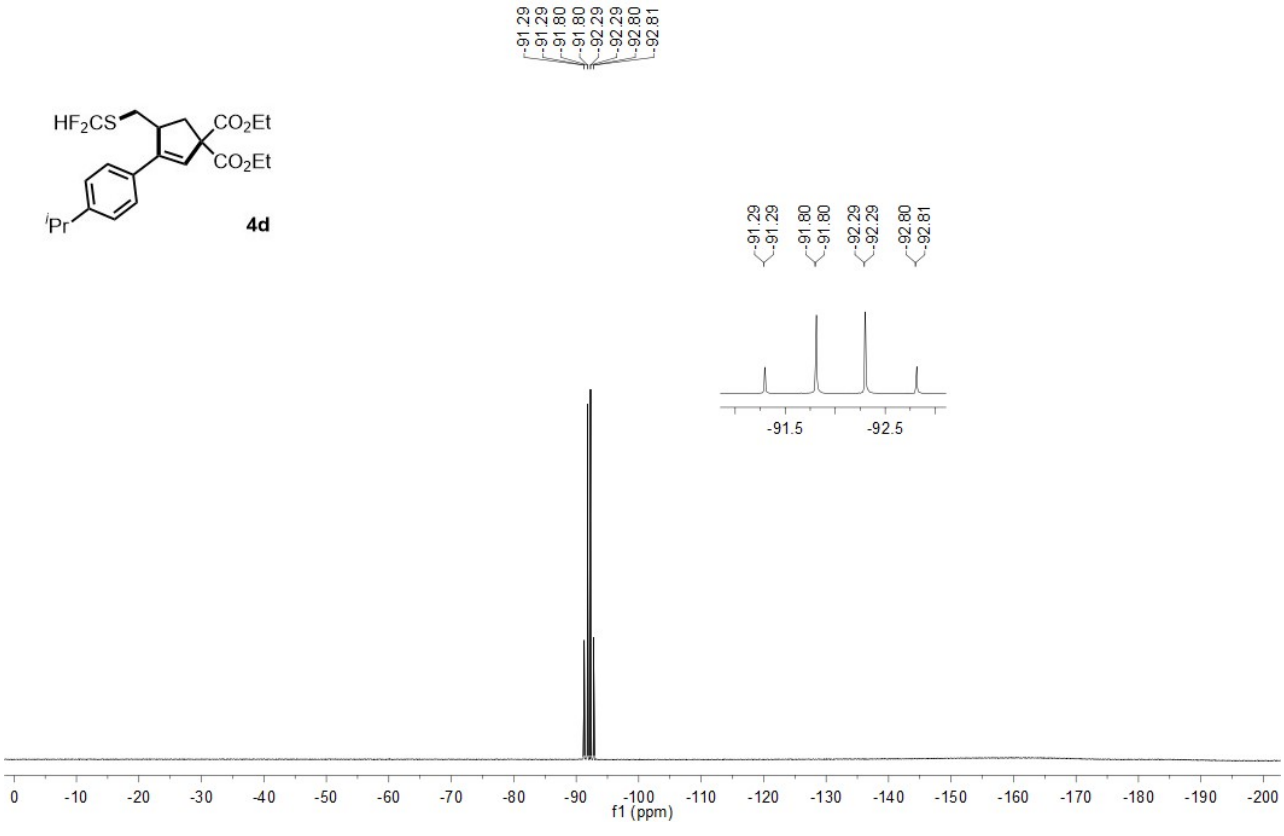

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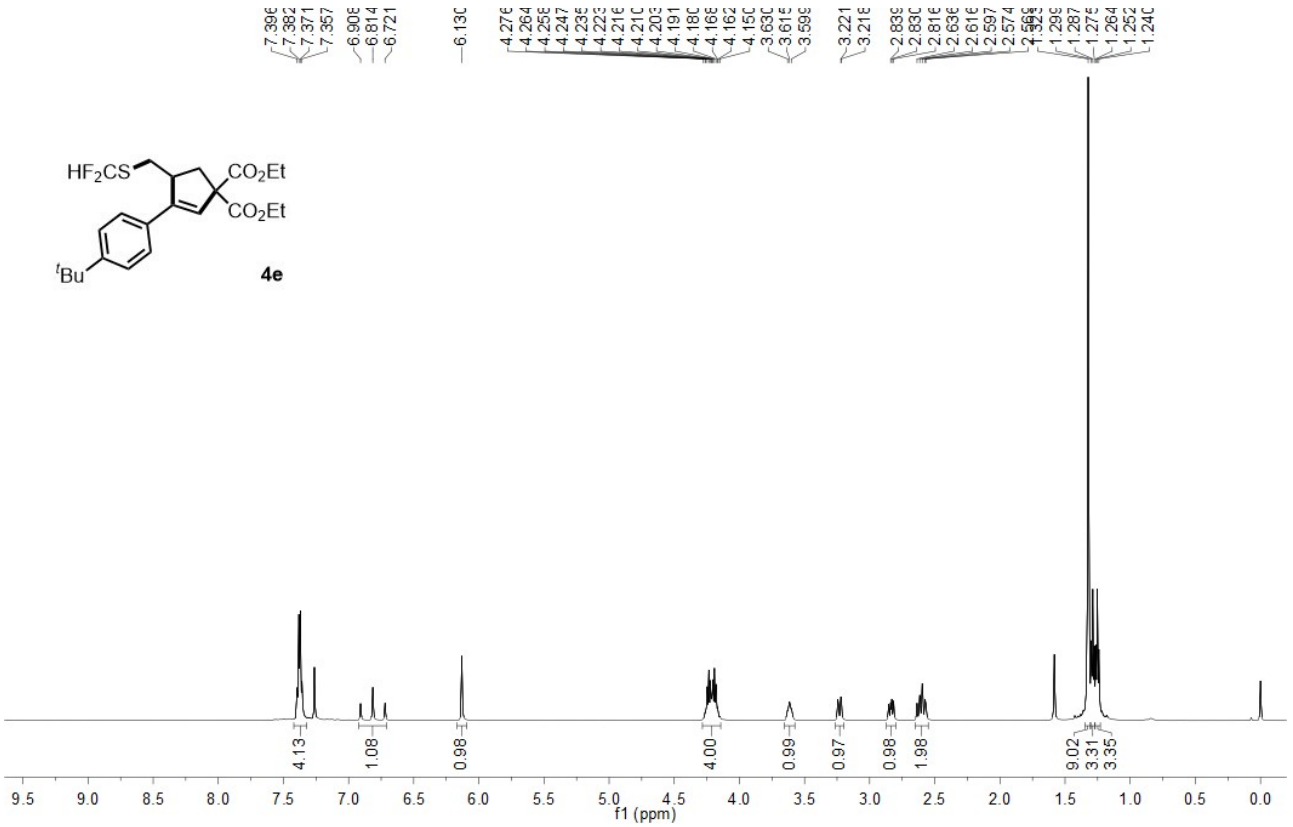

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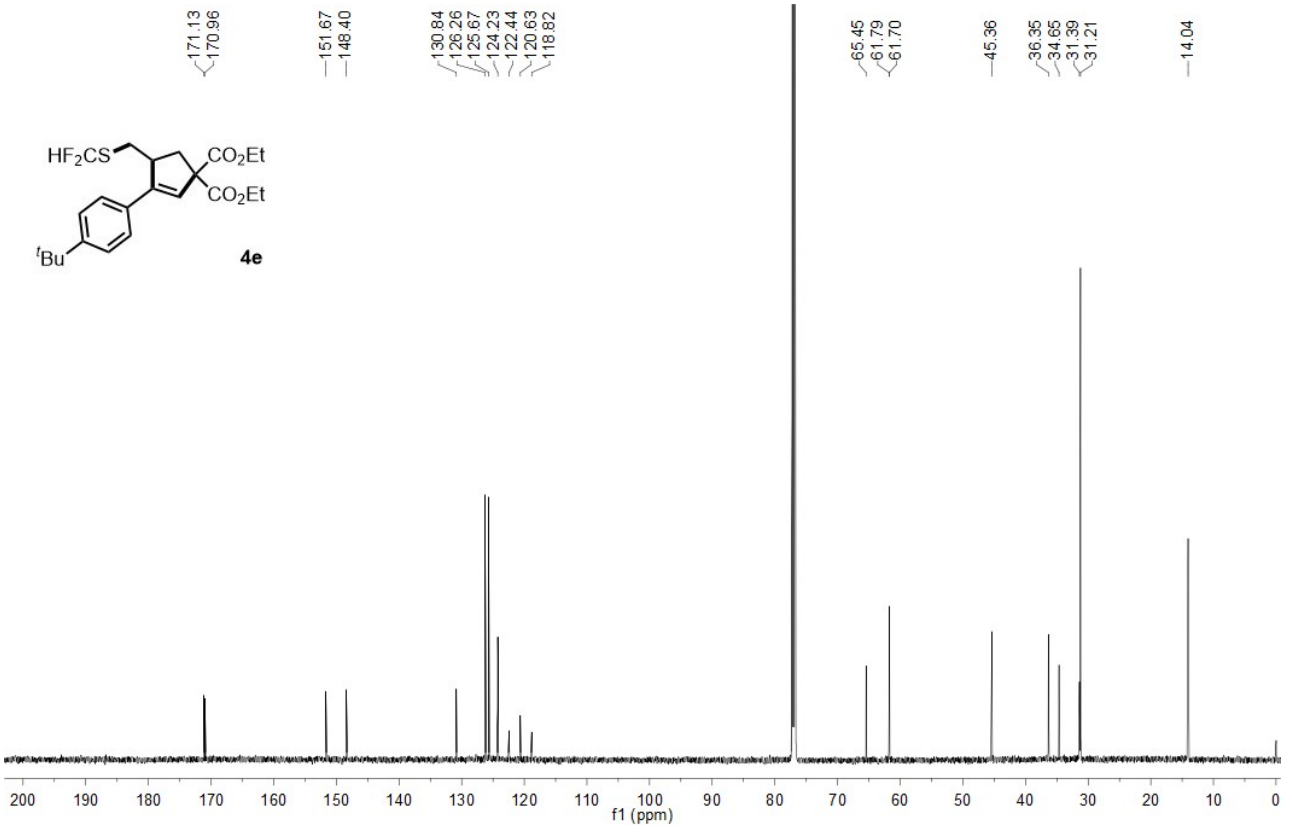

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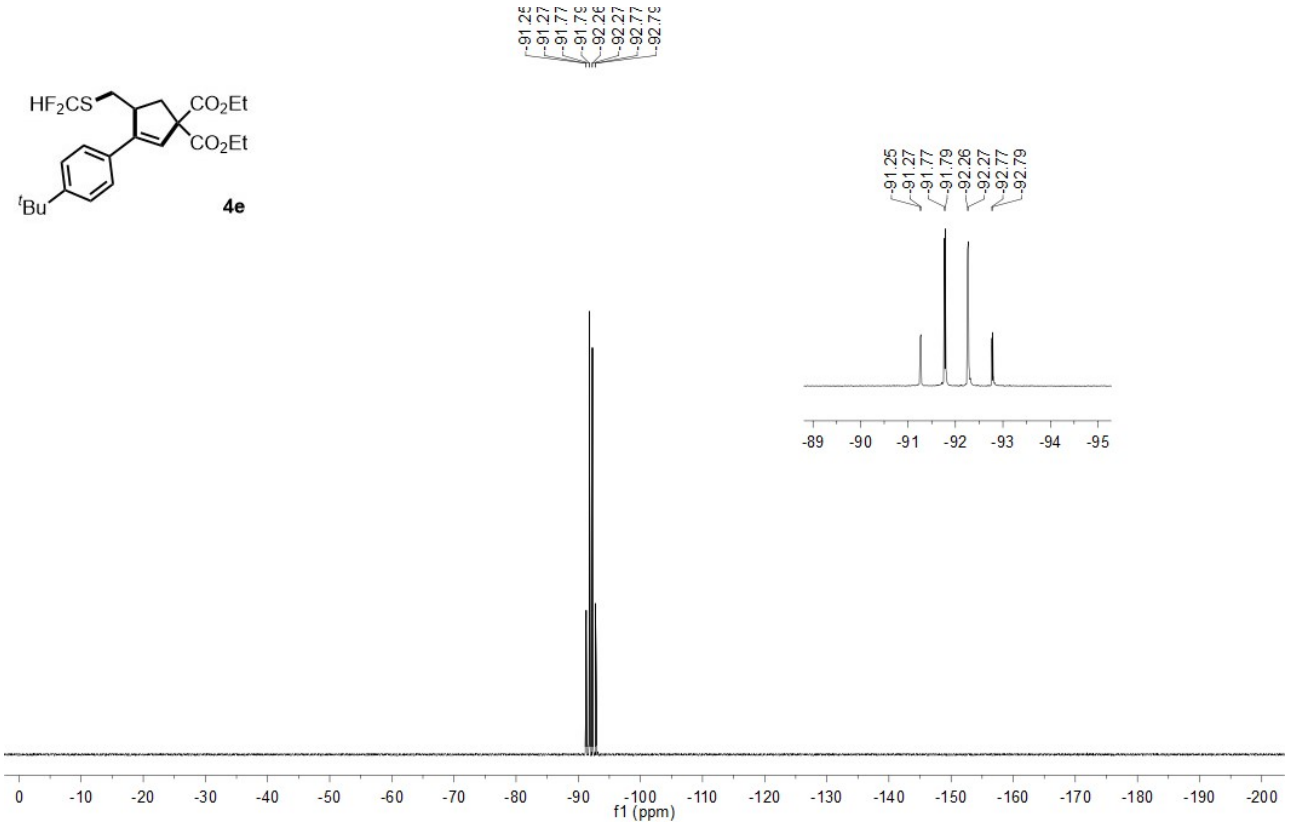

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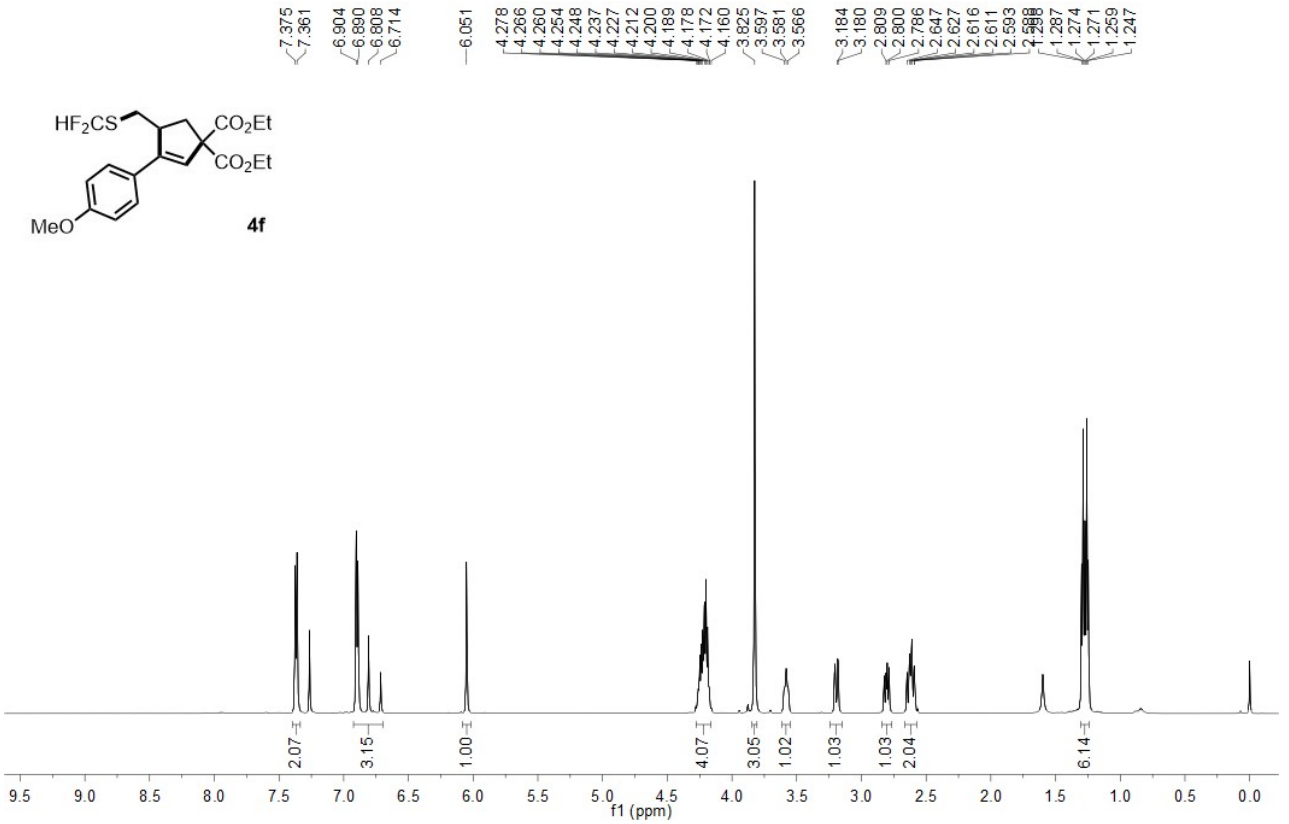

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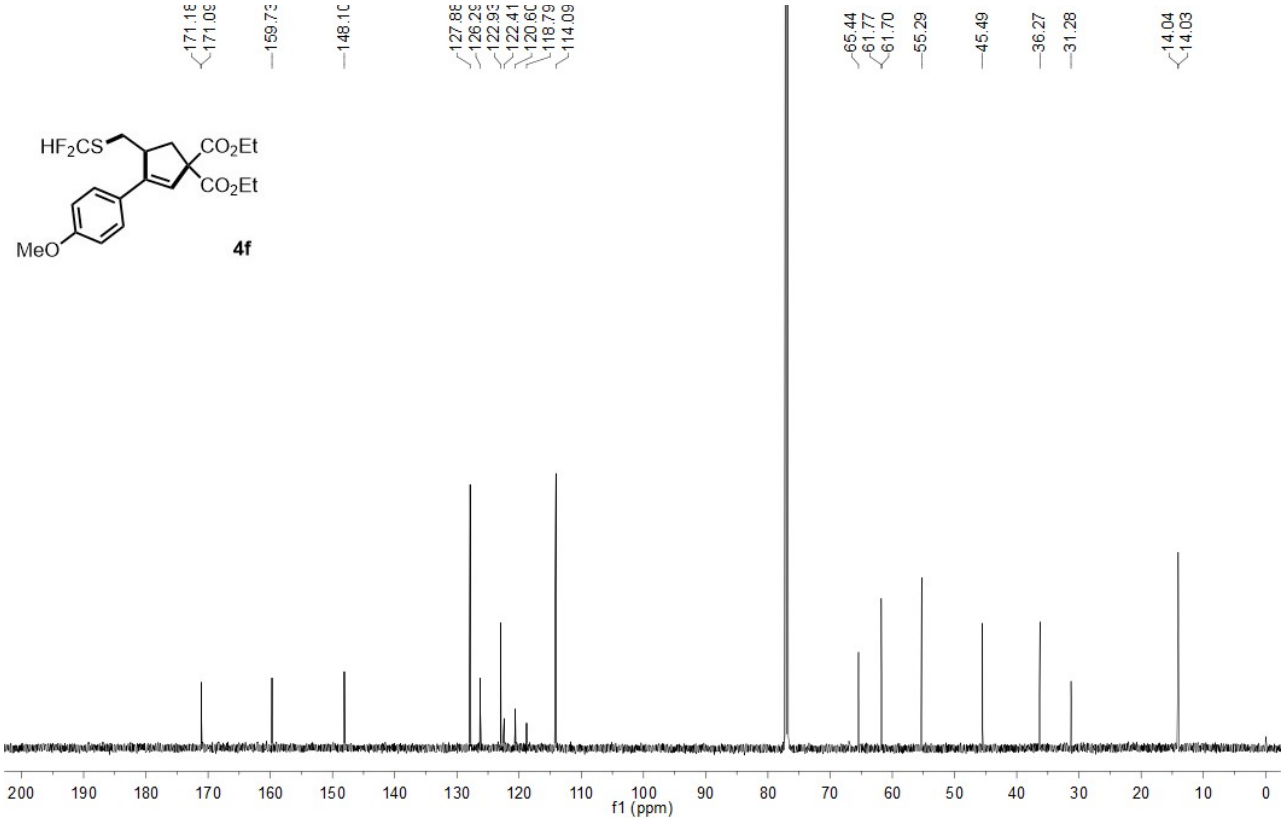

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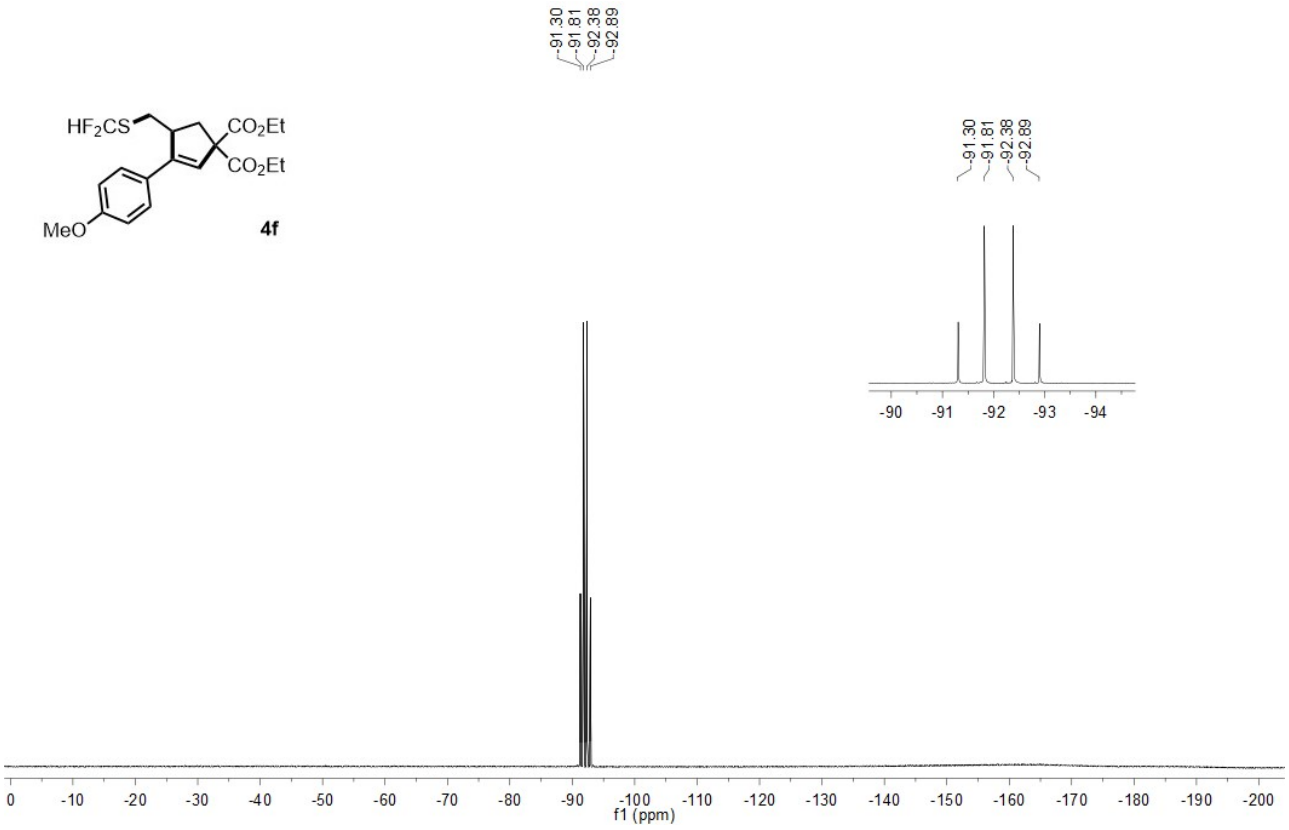

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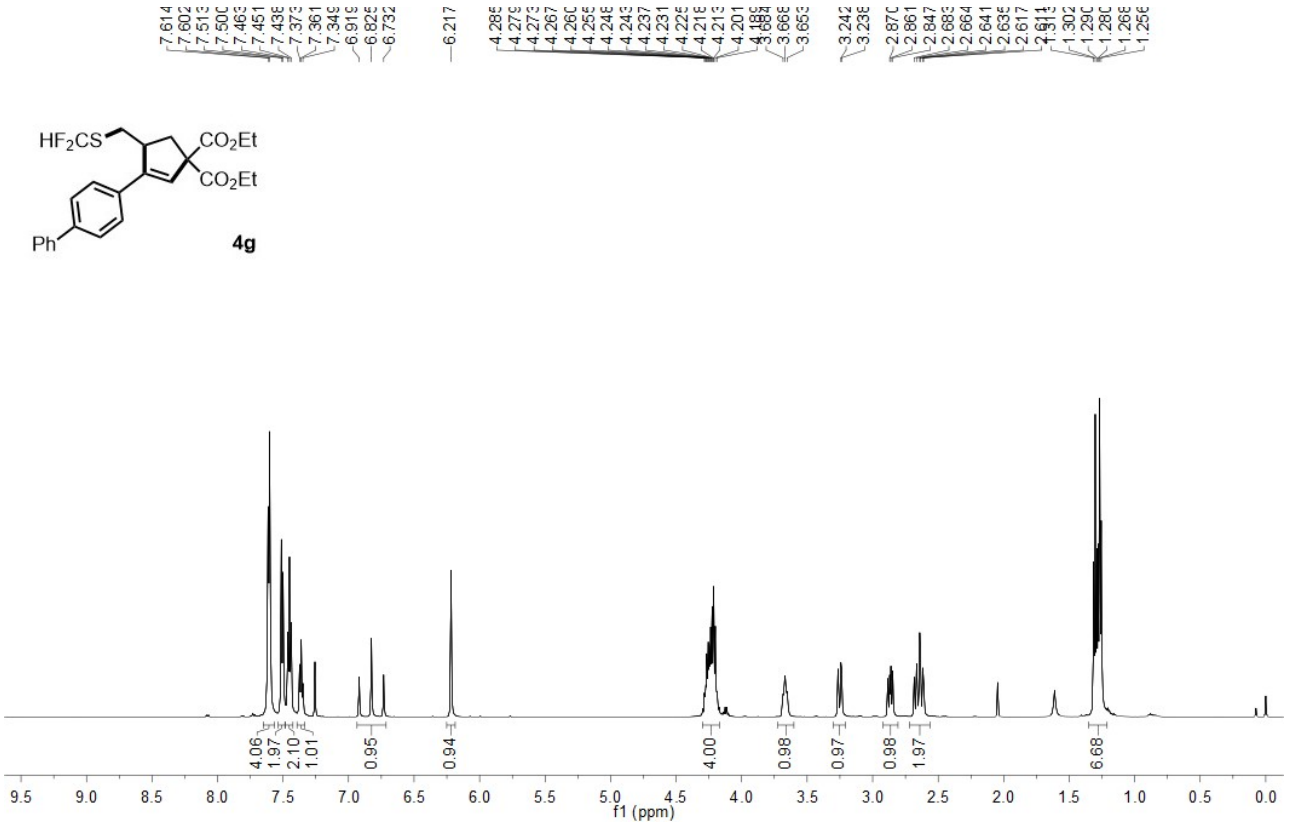

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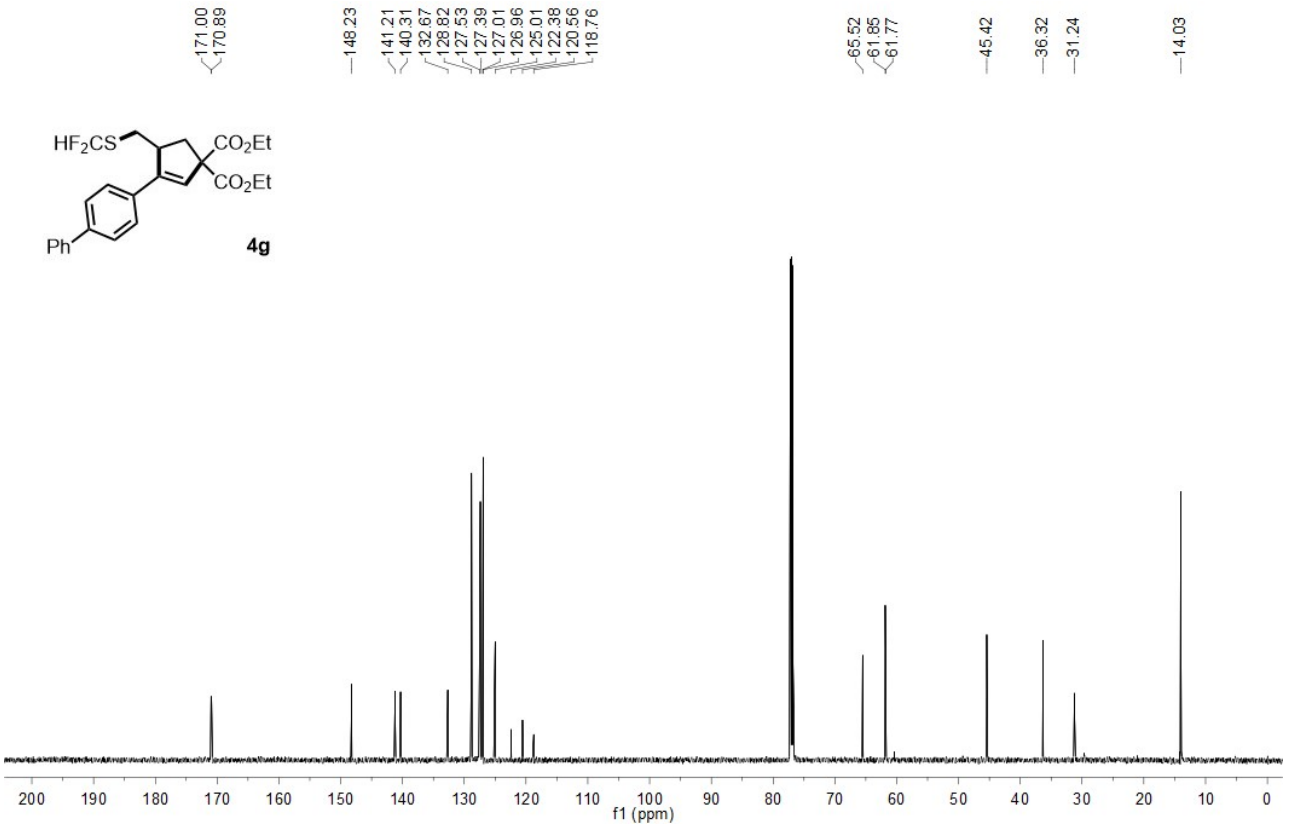

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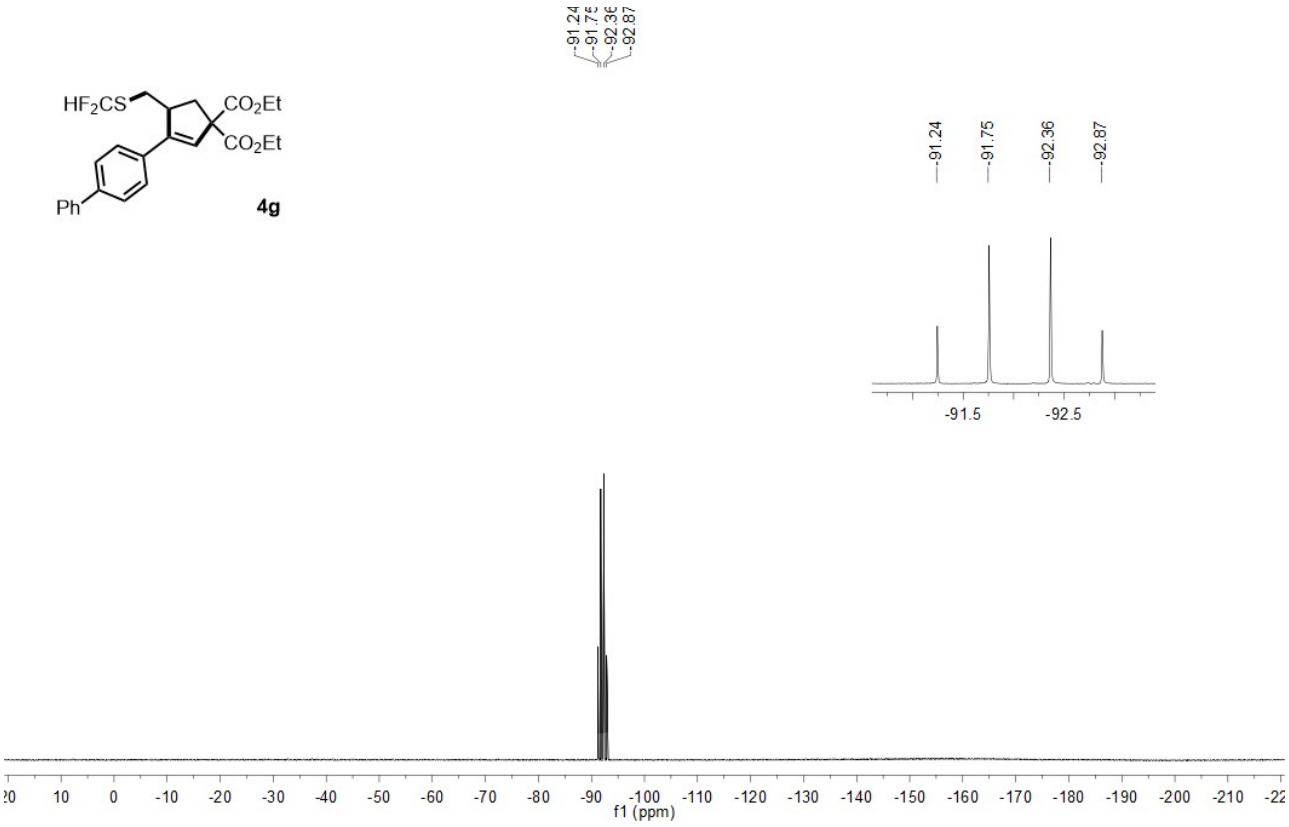

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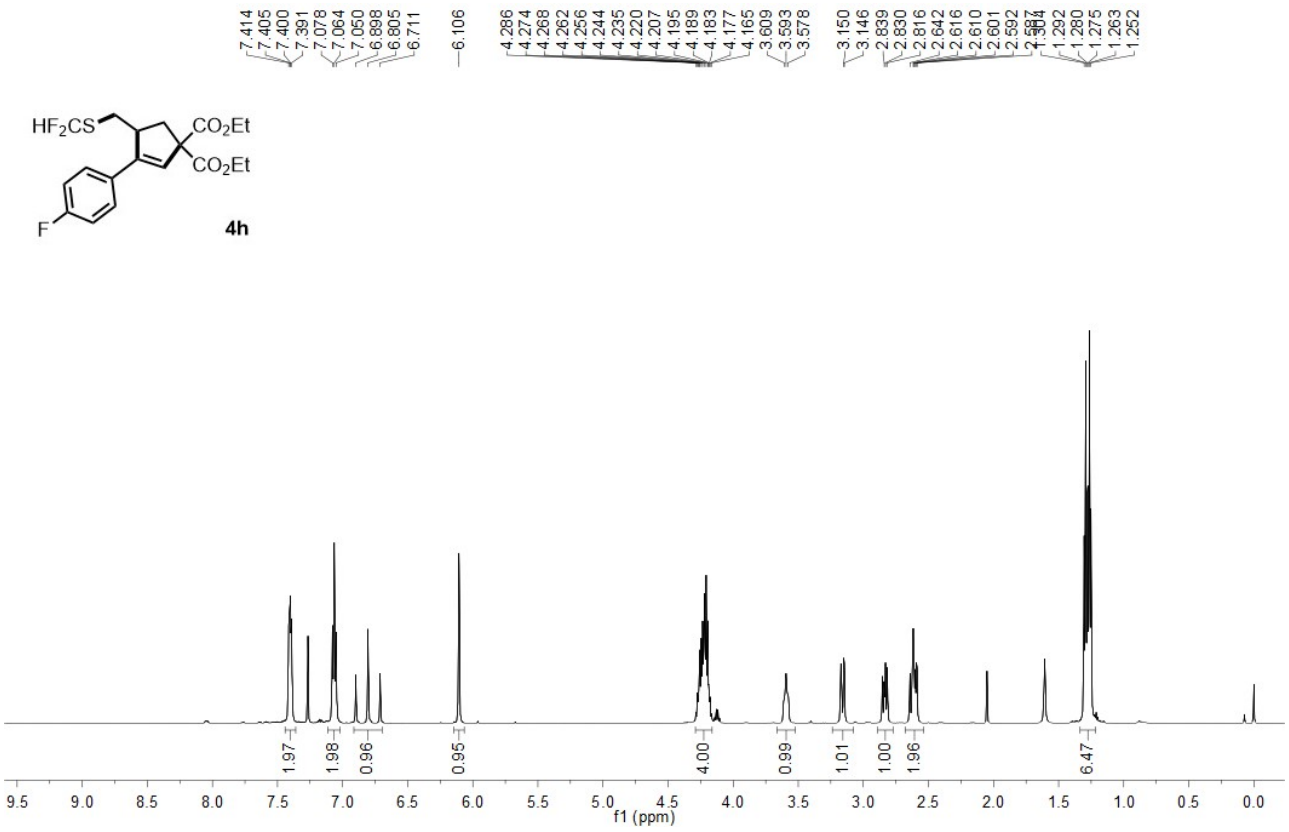

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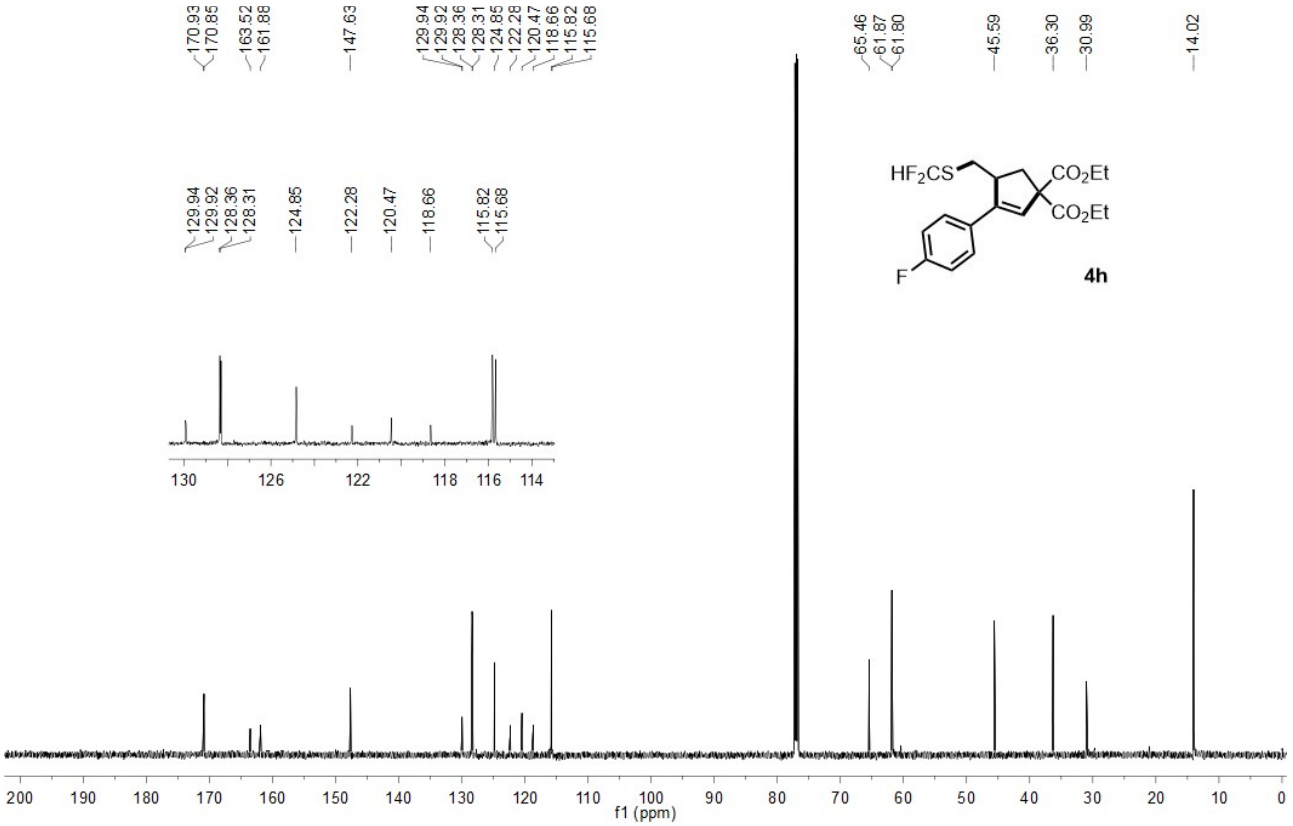

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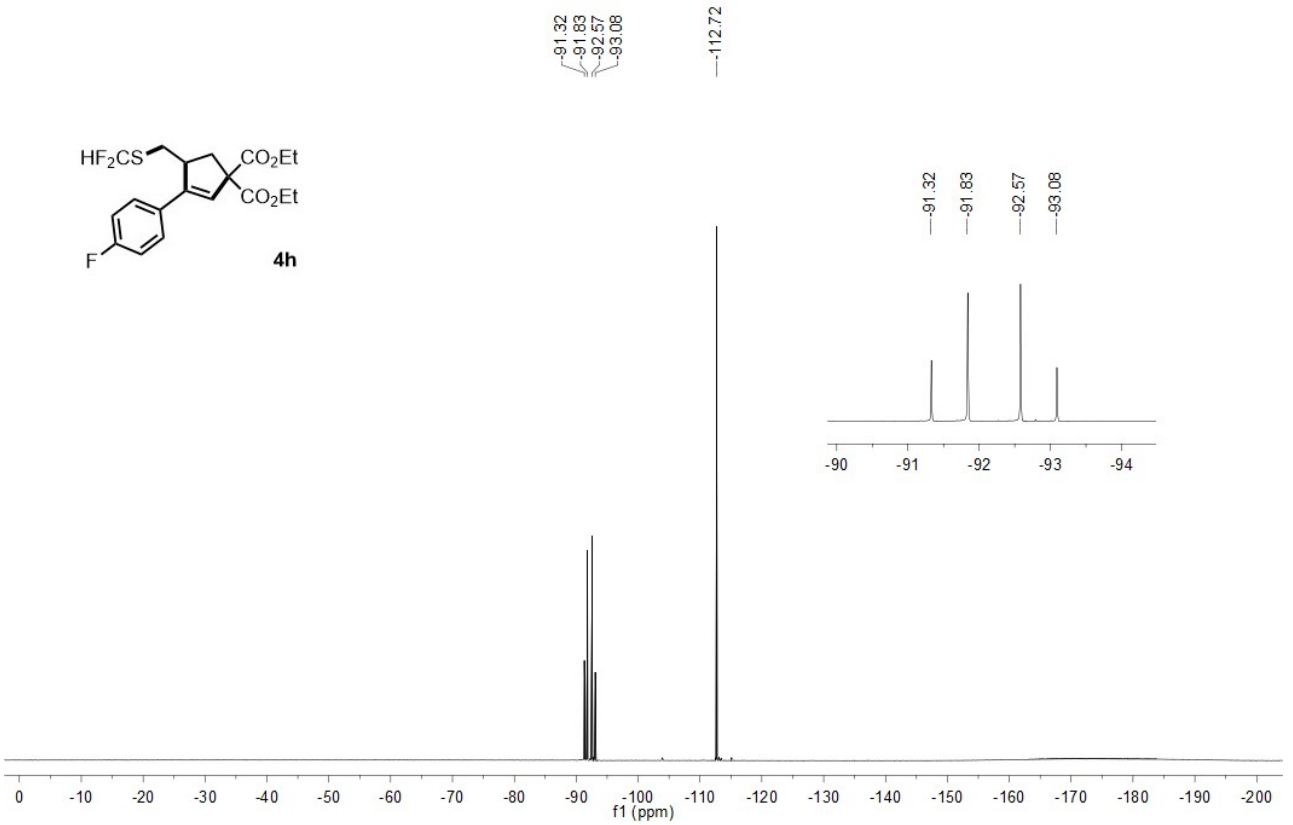

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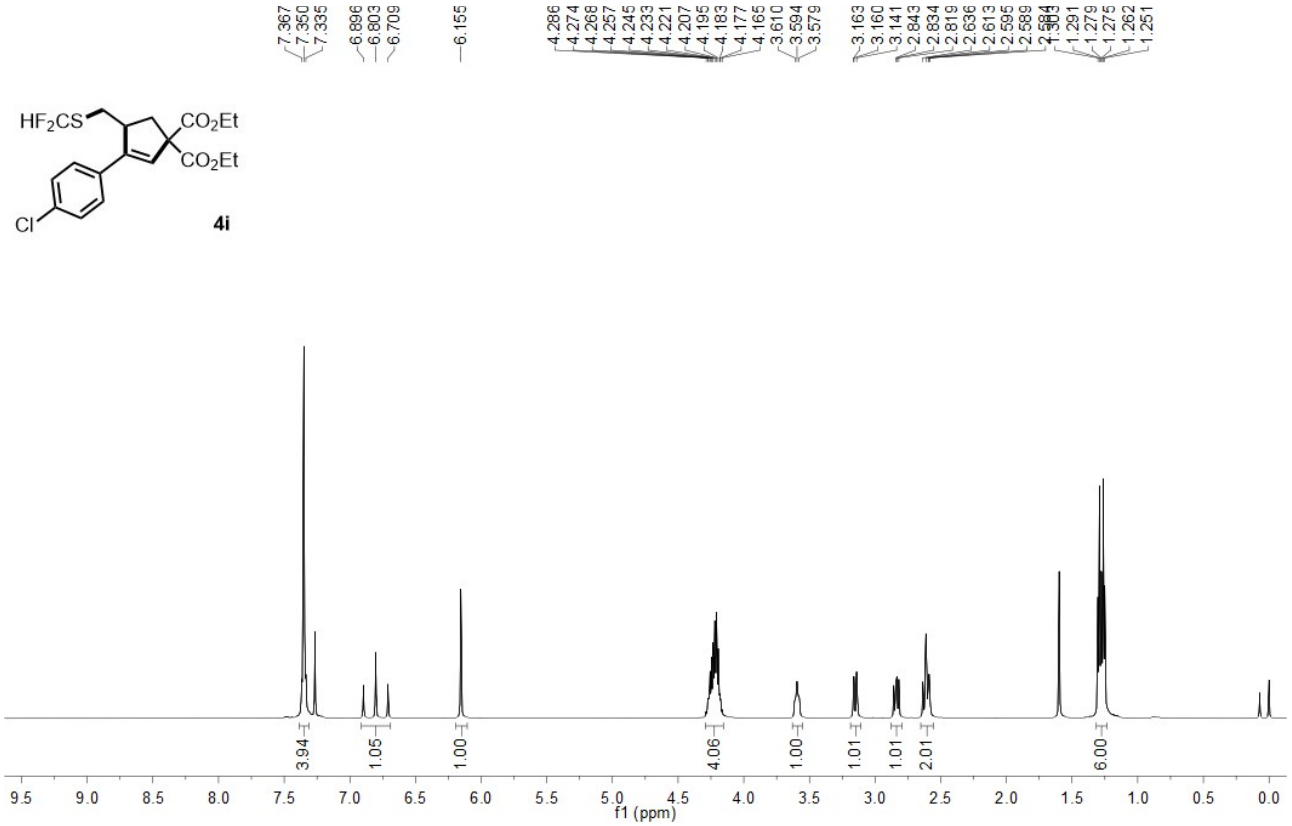

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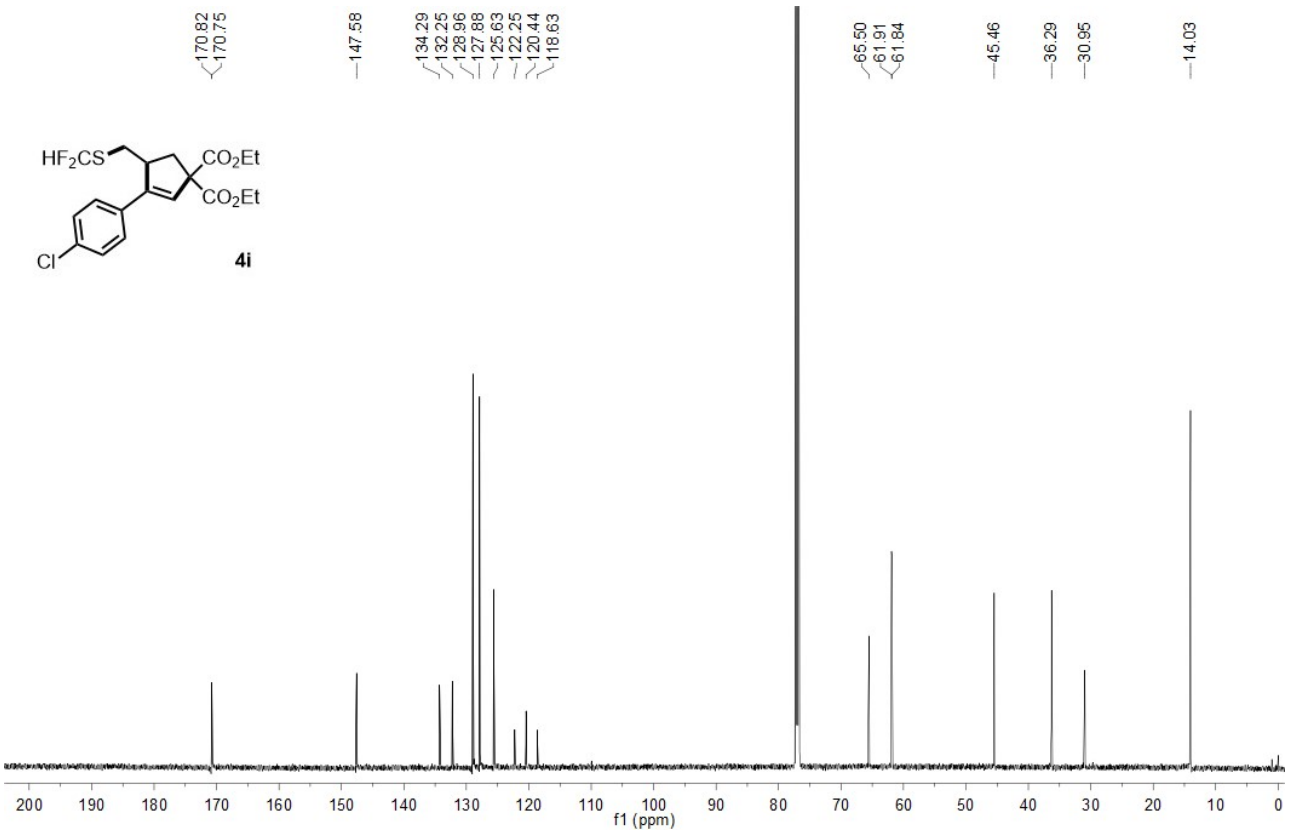

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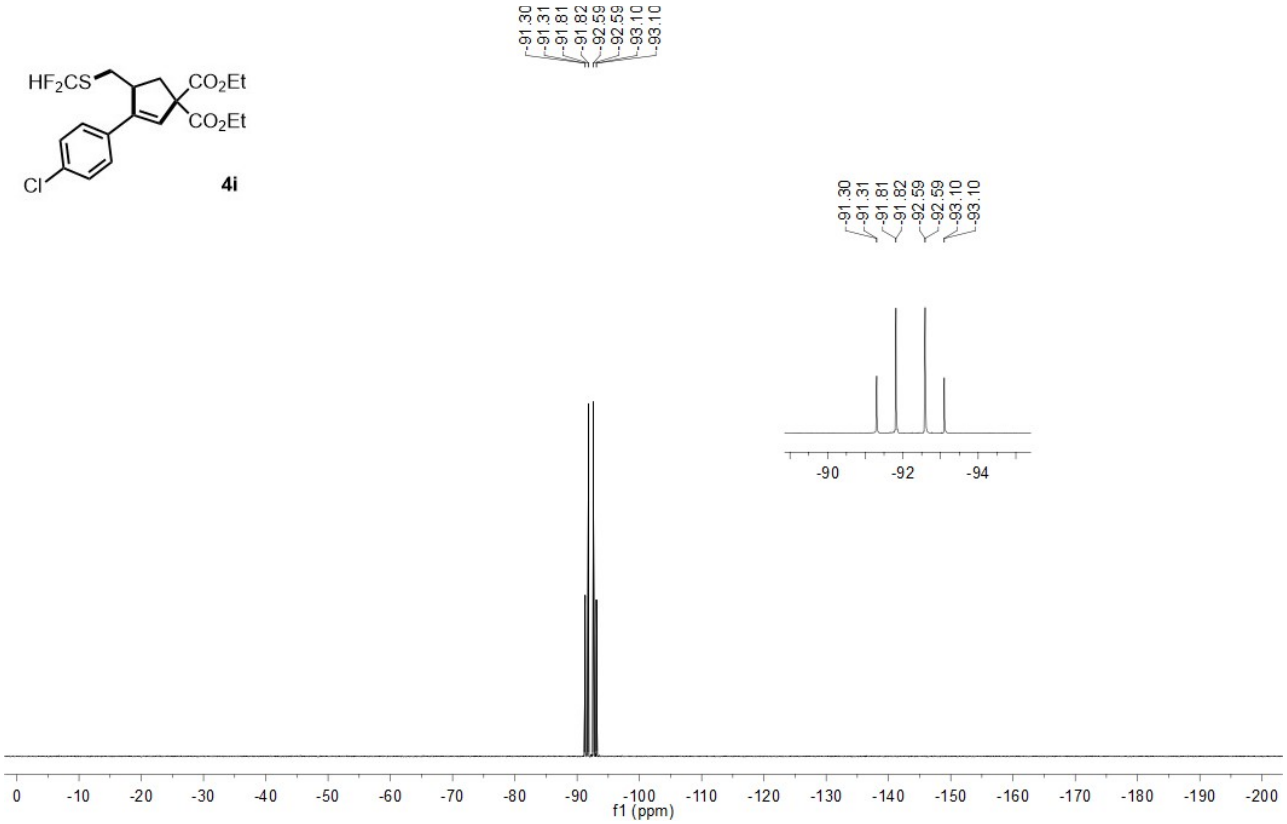

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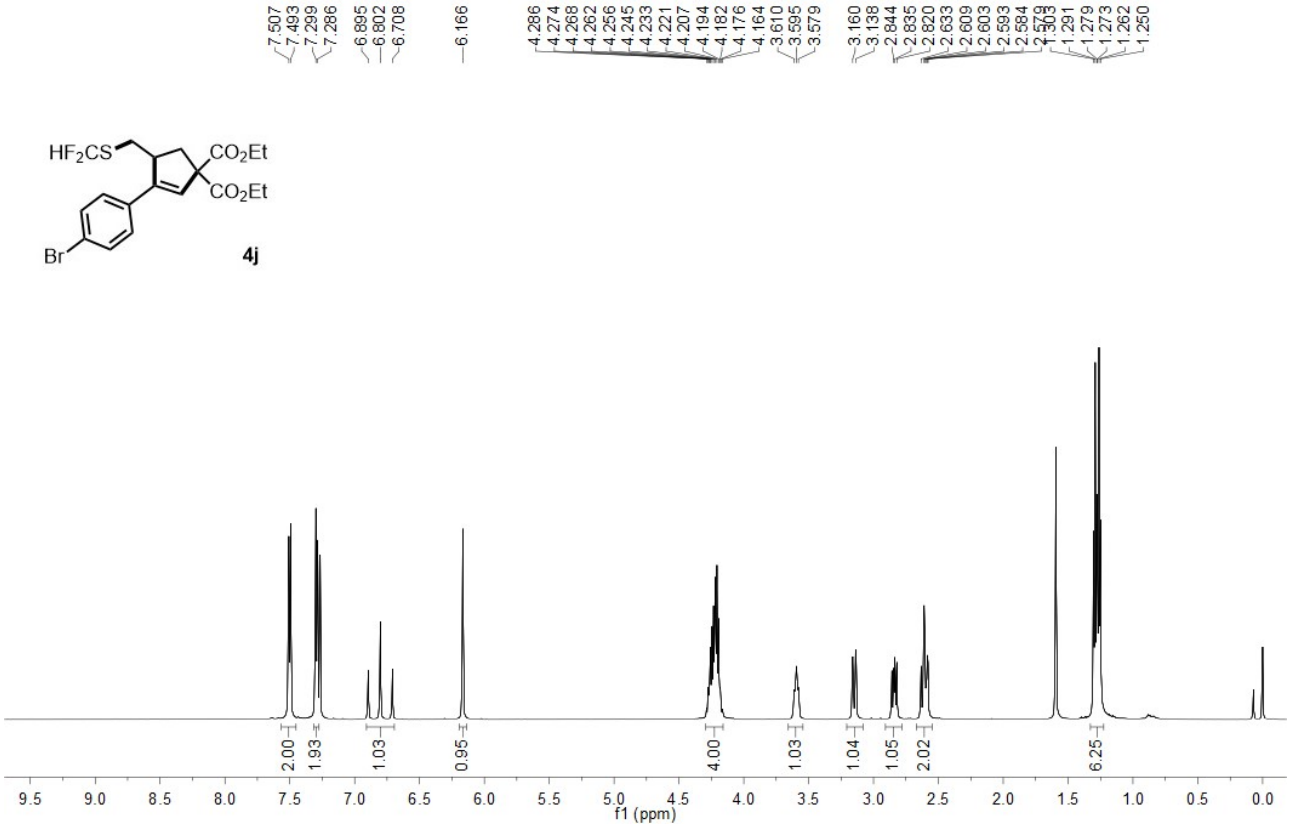
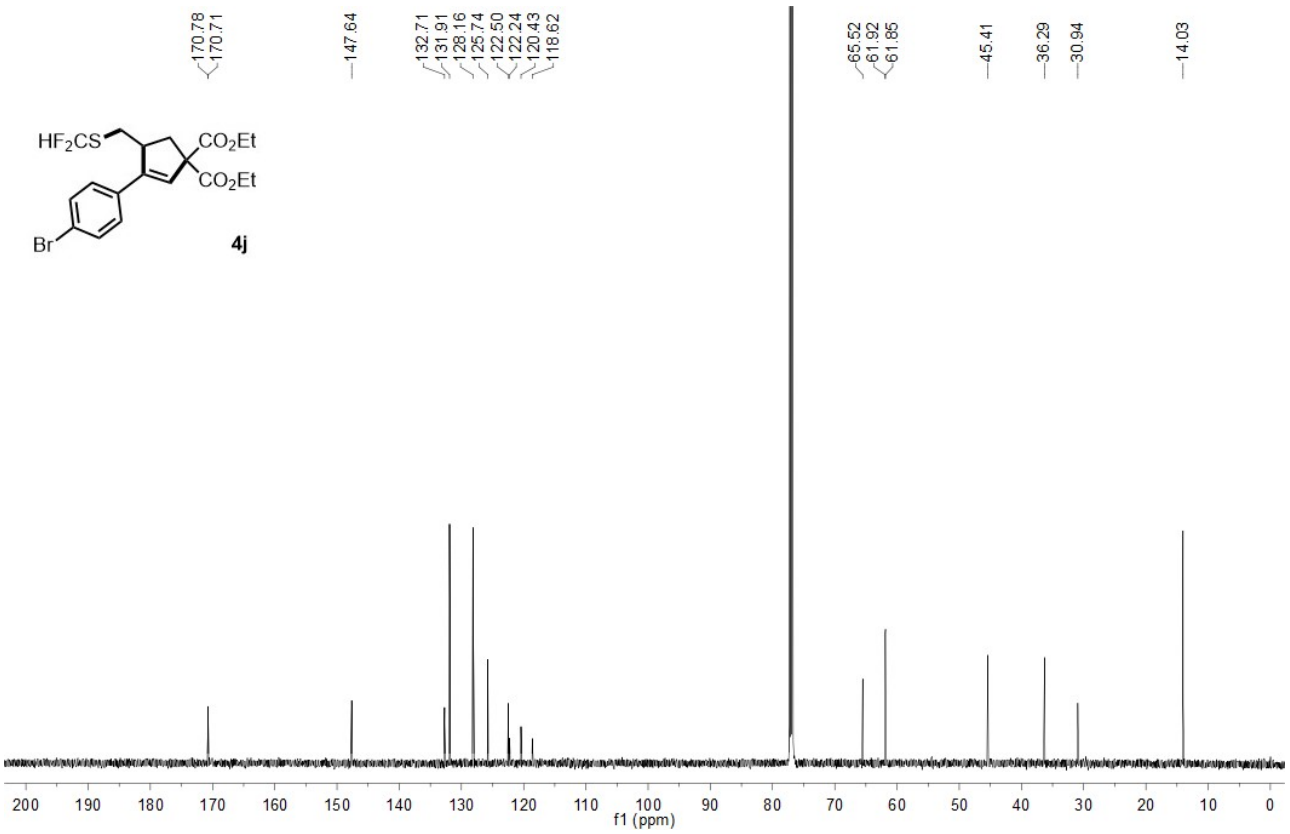
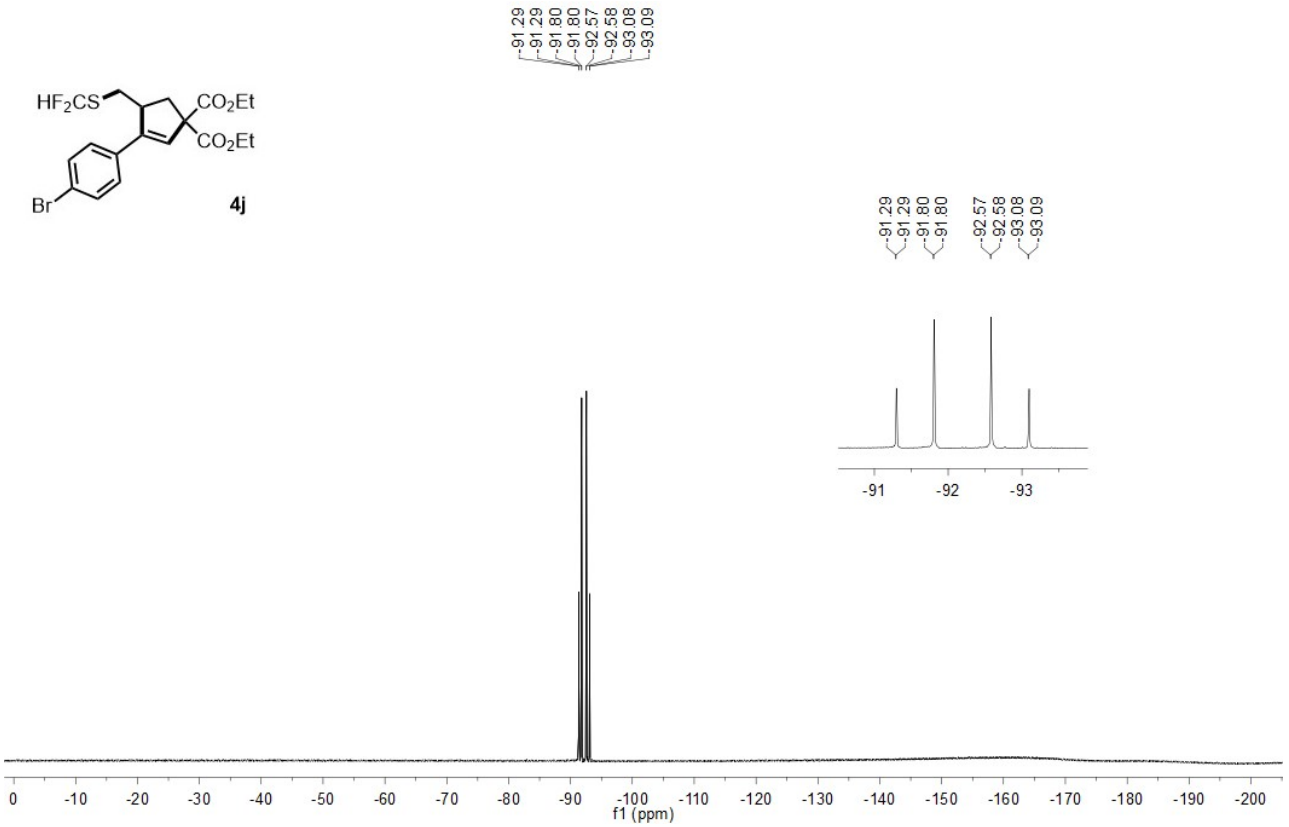


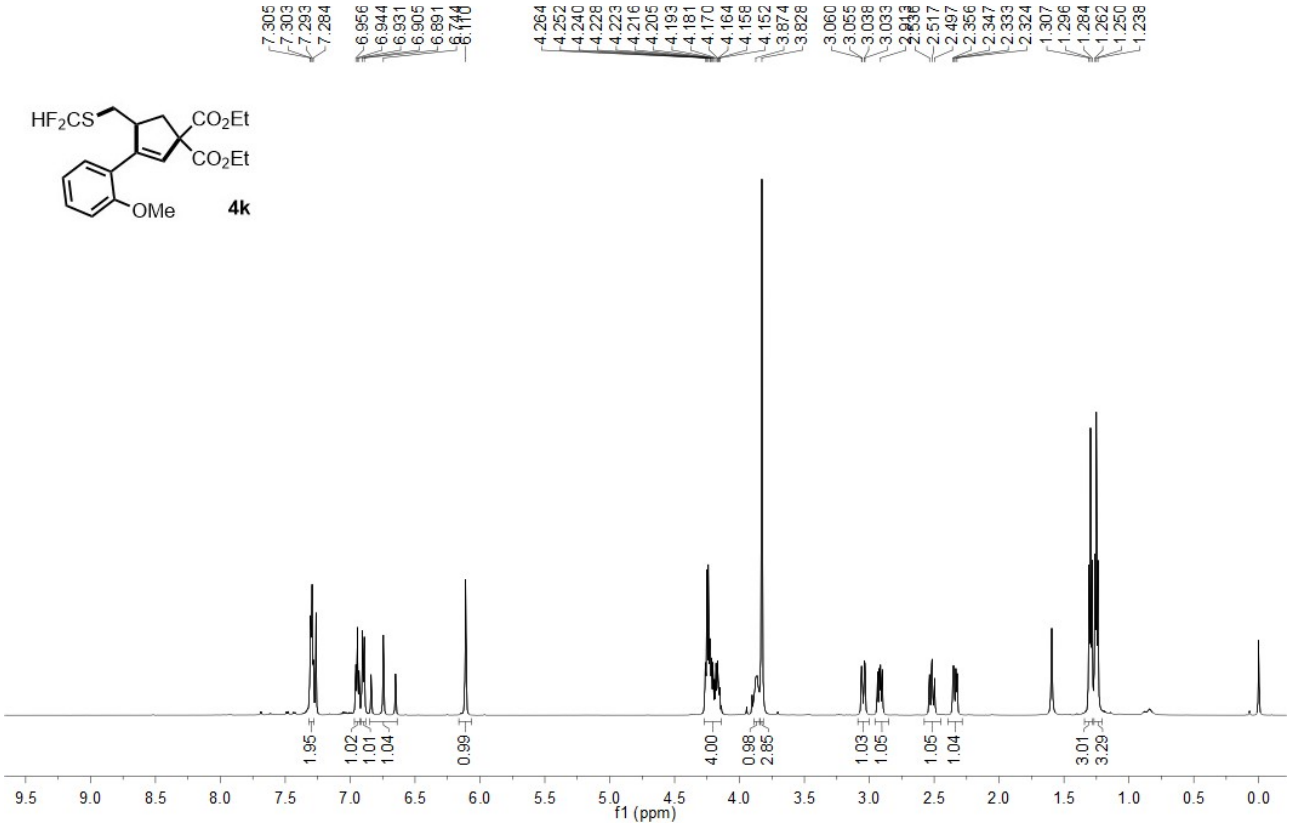
^{13}C NMR, 151 MHz, $CDCl_3$



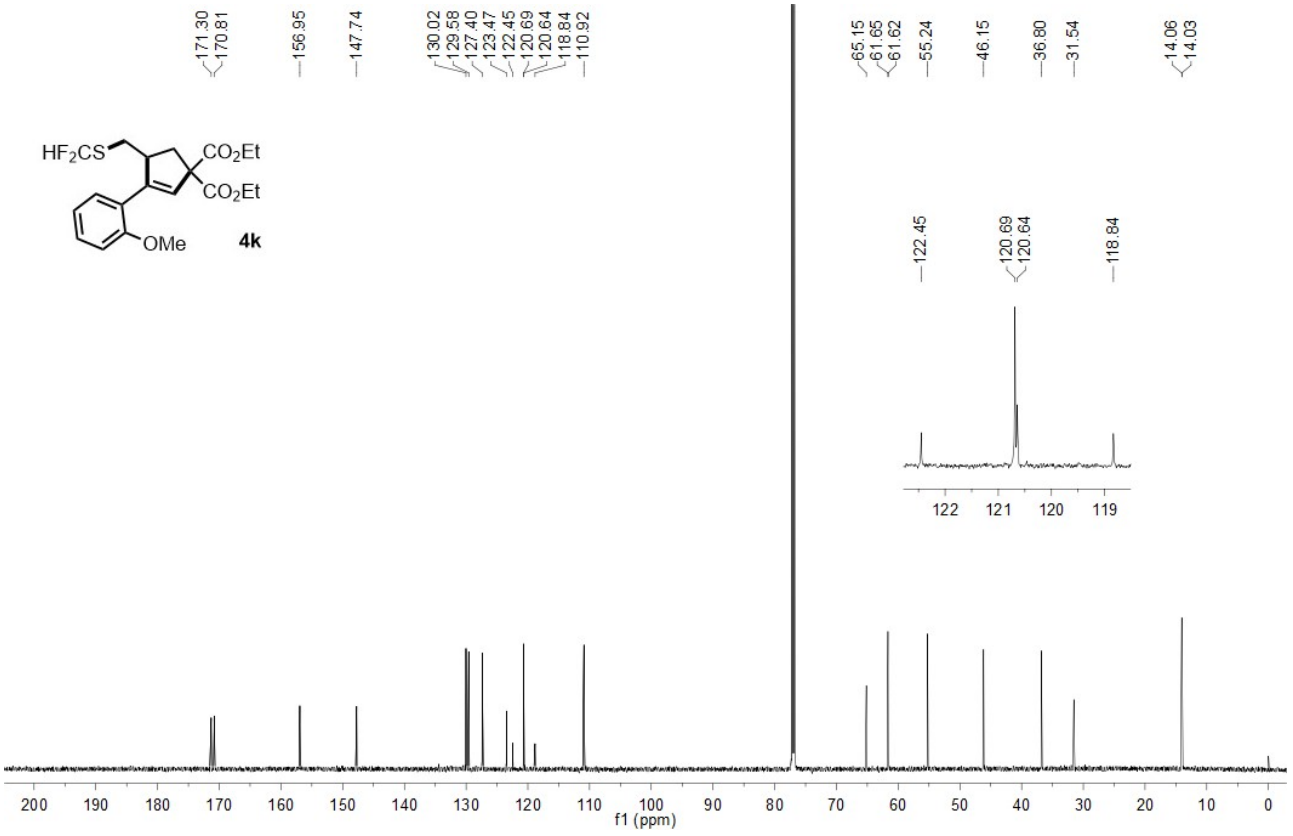
^{19}F NMR, 471 MHz, $CDCl_3$



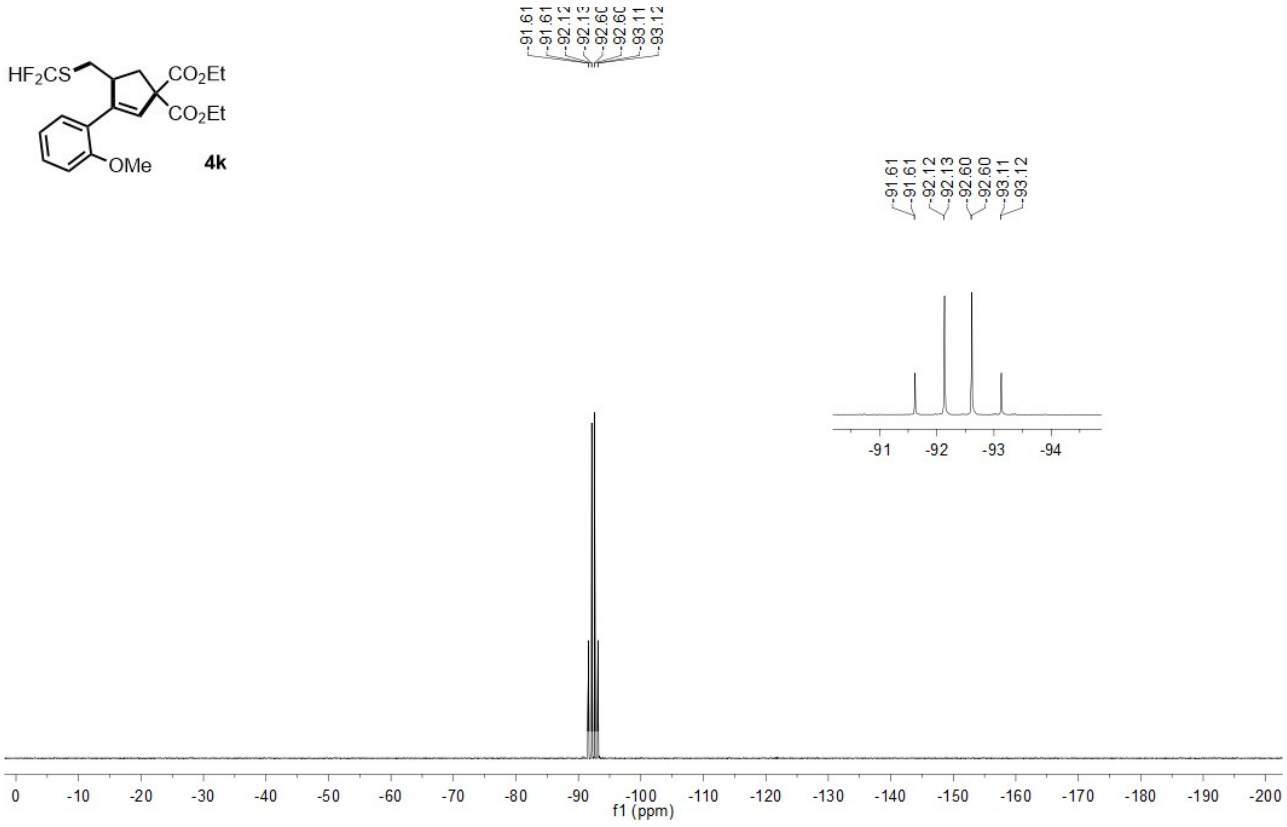
^{1}H NMR, 600 MHz, $CDCl_3$



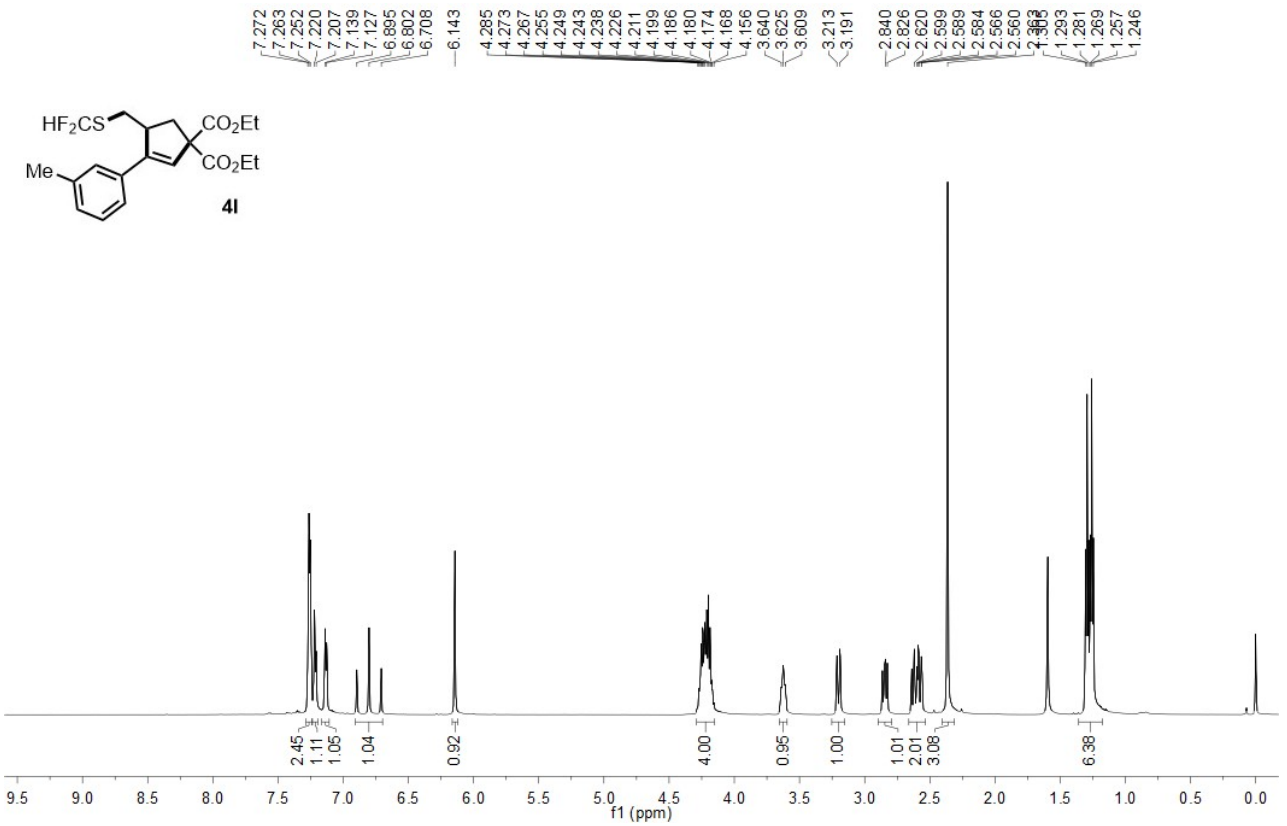
^{13}C NMR, 151 MHz, $CDCl_3$



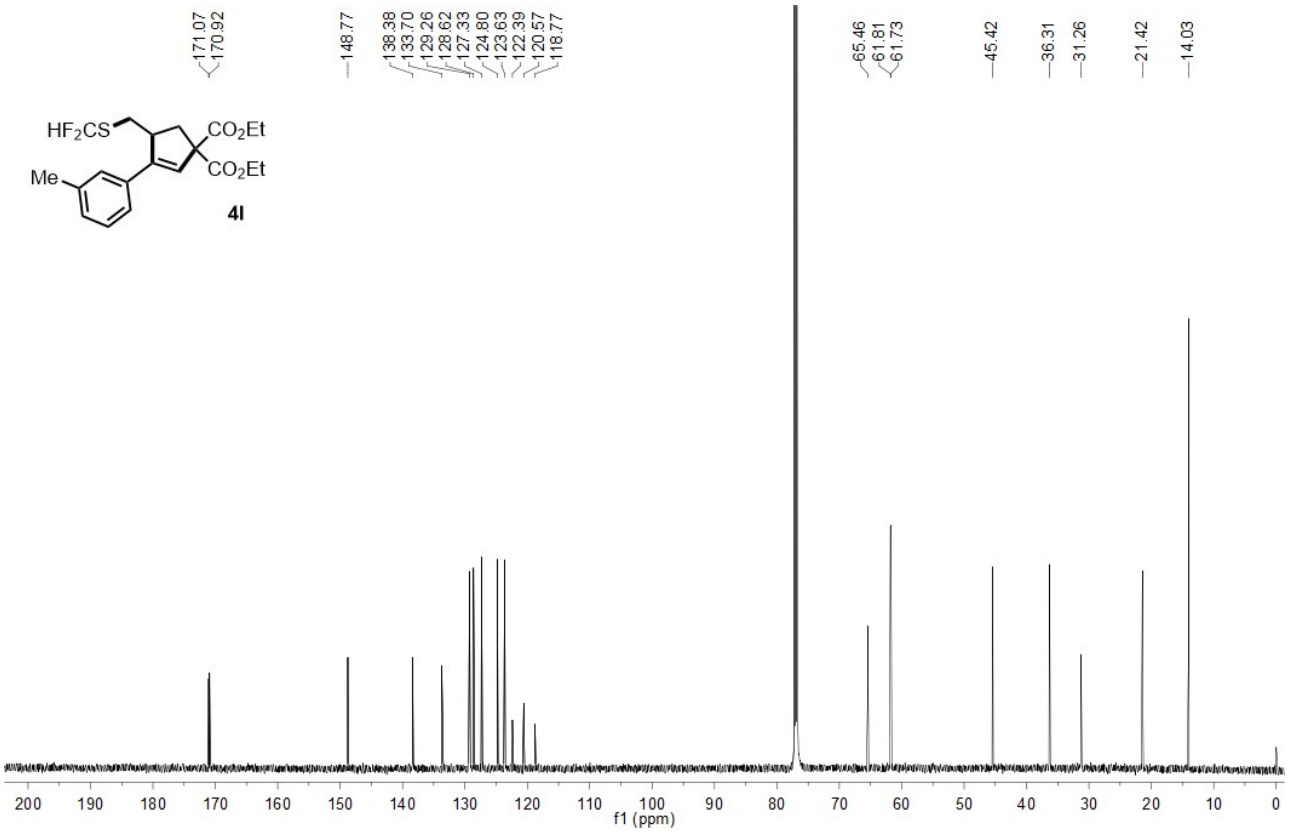
^{19}F NMR, 471 MHz, $CDCl_3$



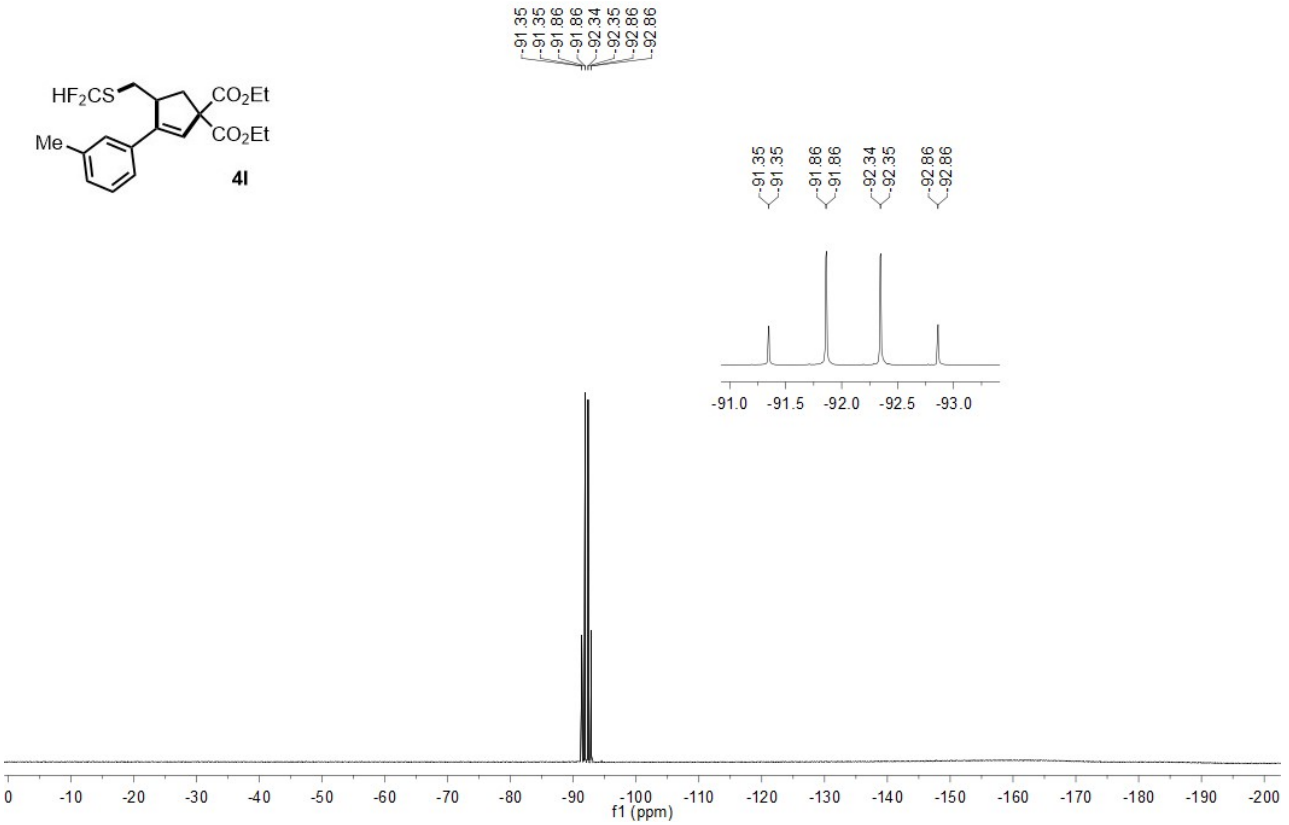
^{1}H NMR, 600 MHz, $CDCl_3$



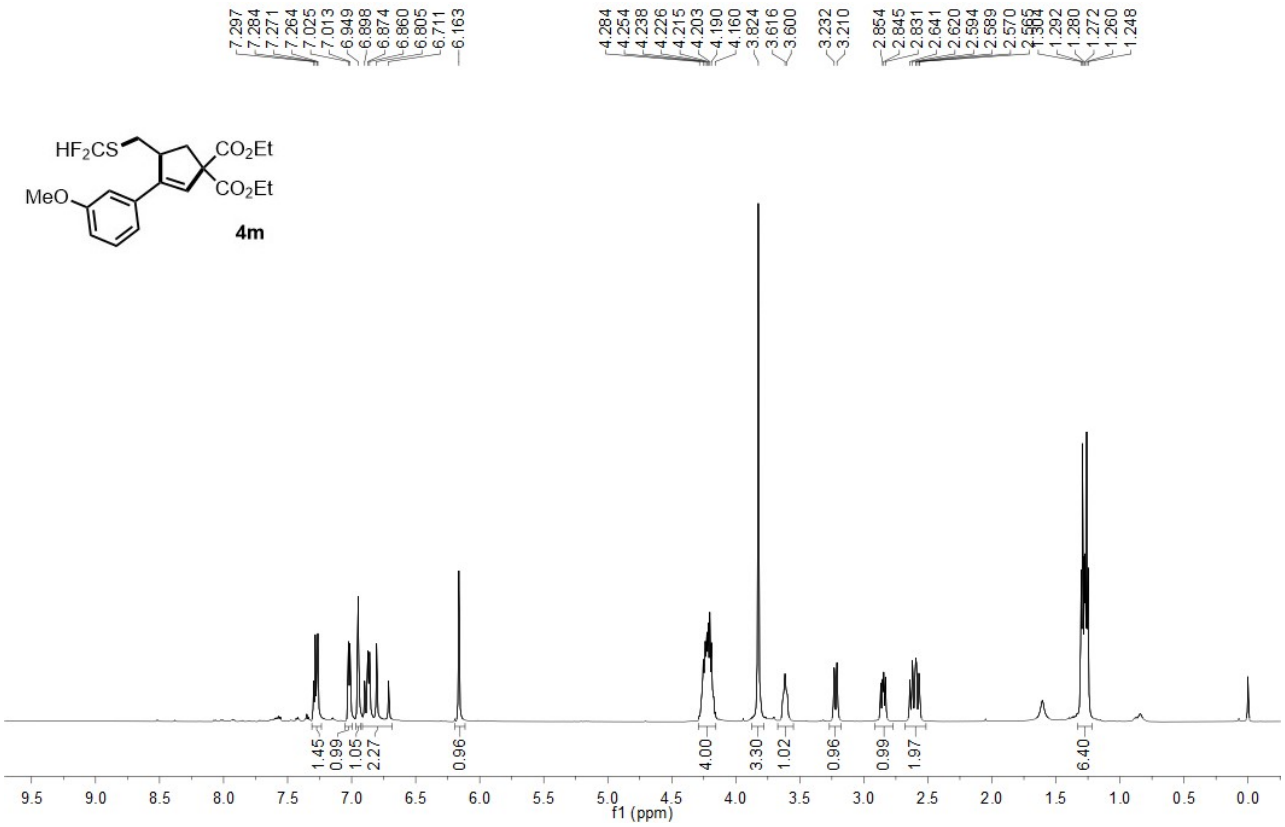
^{13}C NMR, 151 MHz, $CDCl_3$



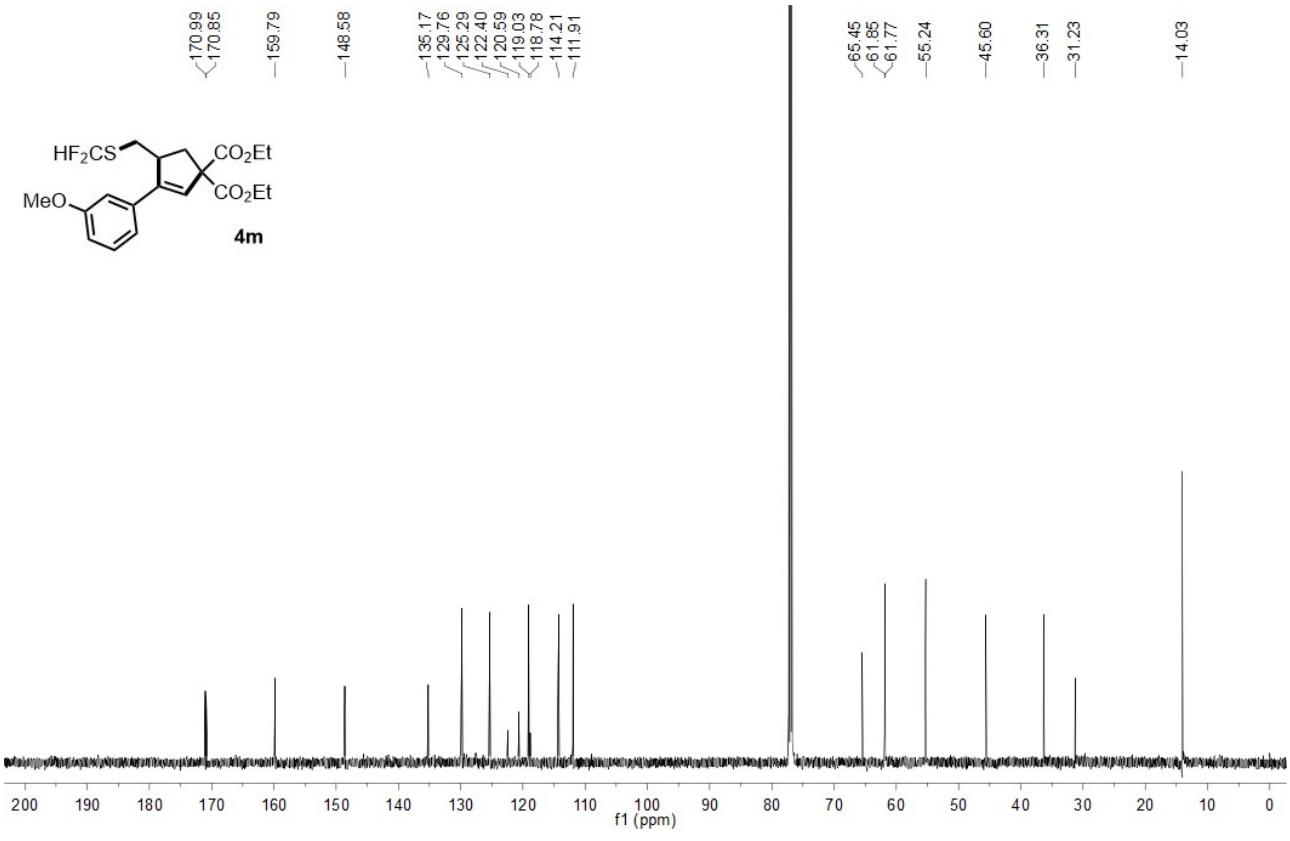
^{19}F NMR, 471 MHz, $CDCl_3$



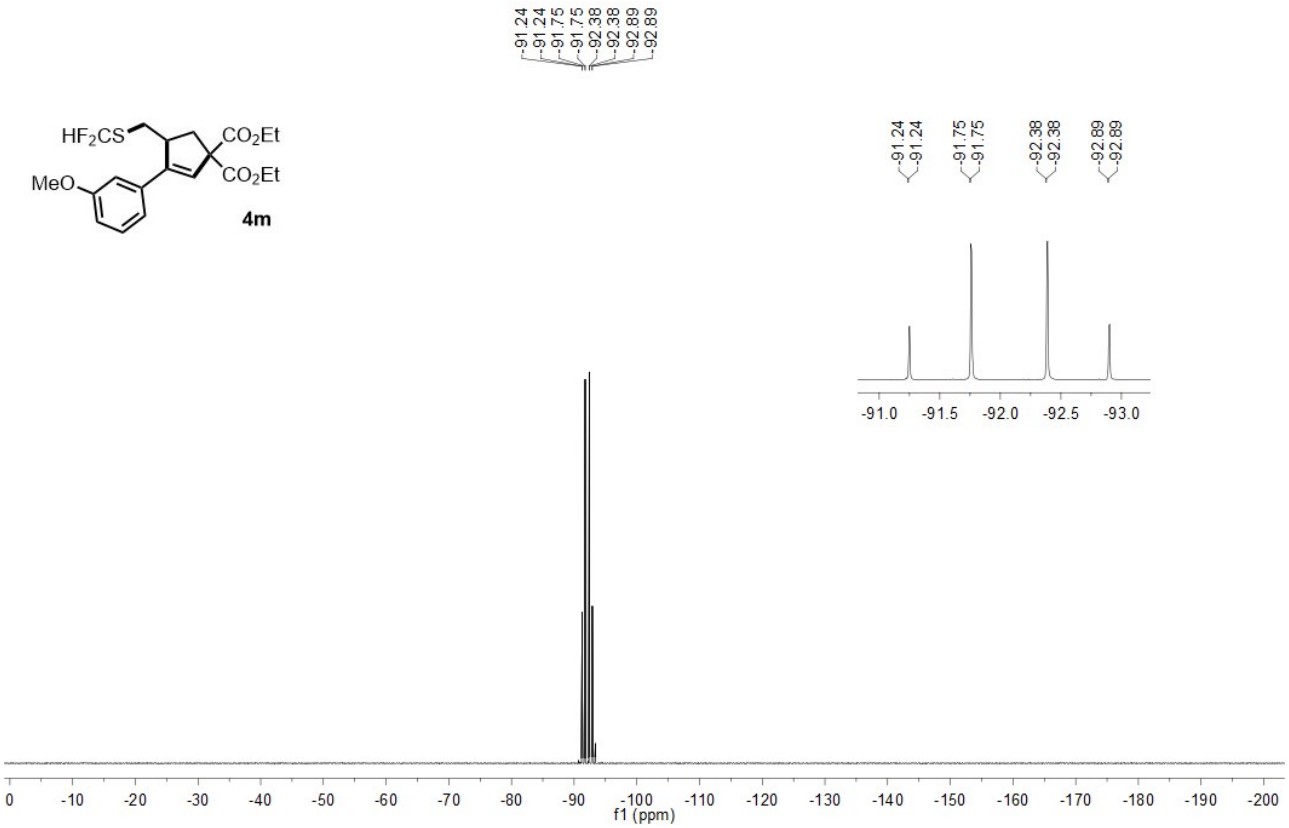
^{1}H NMR, 600 MHz, $CDCl_3$



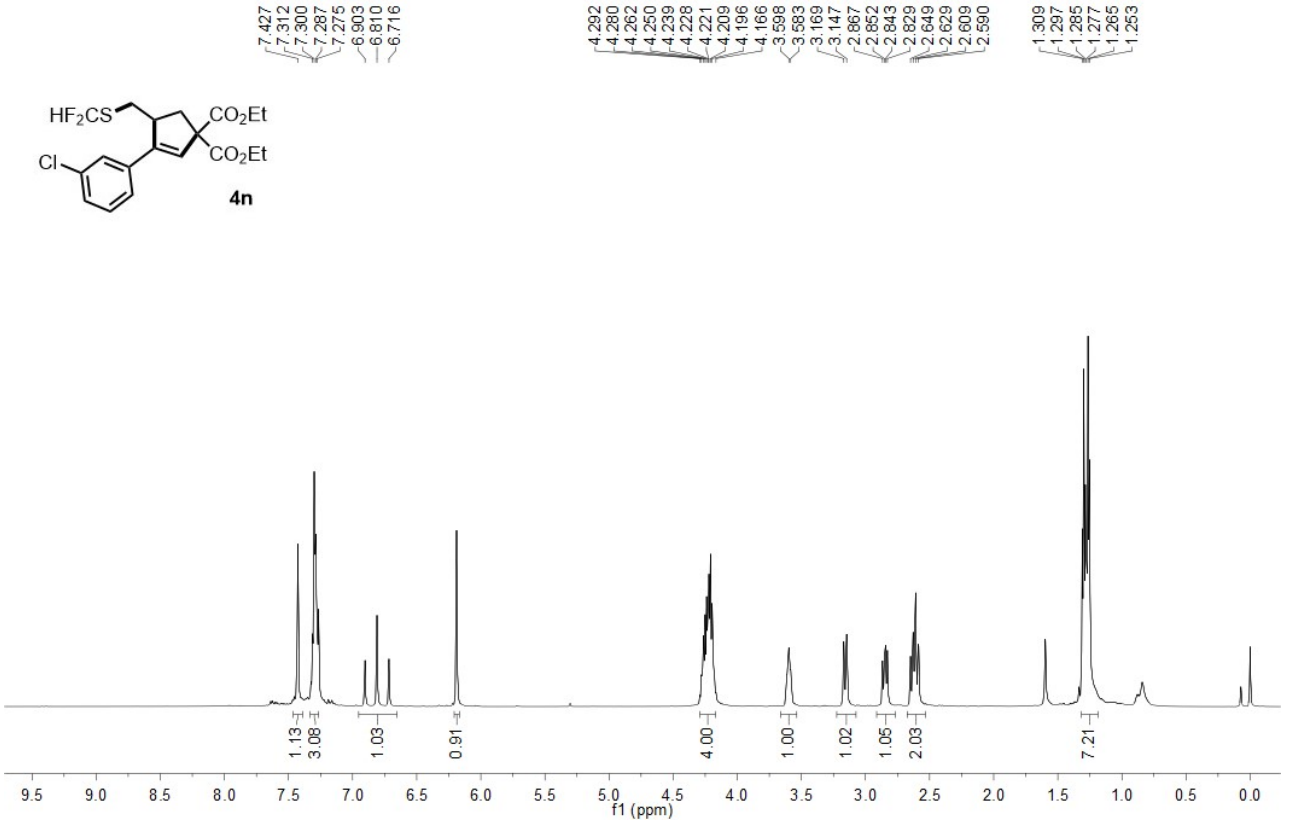
^{13}C NMR, 151 MHz, $CDCl_3$



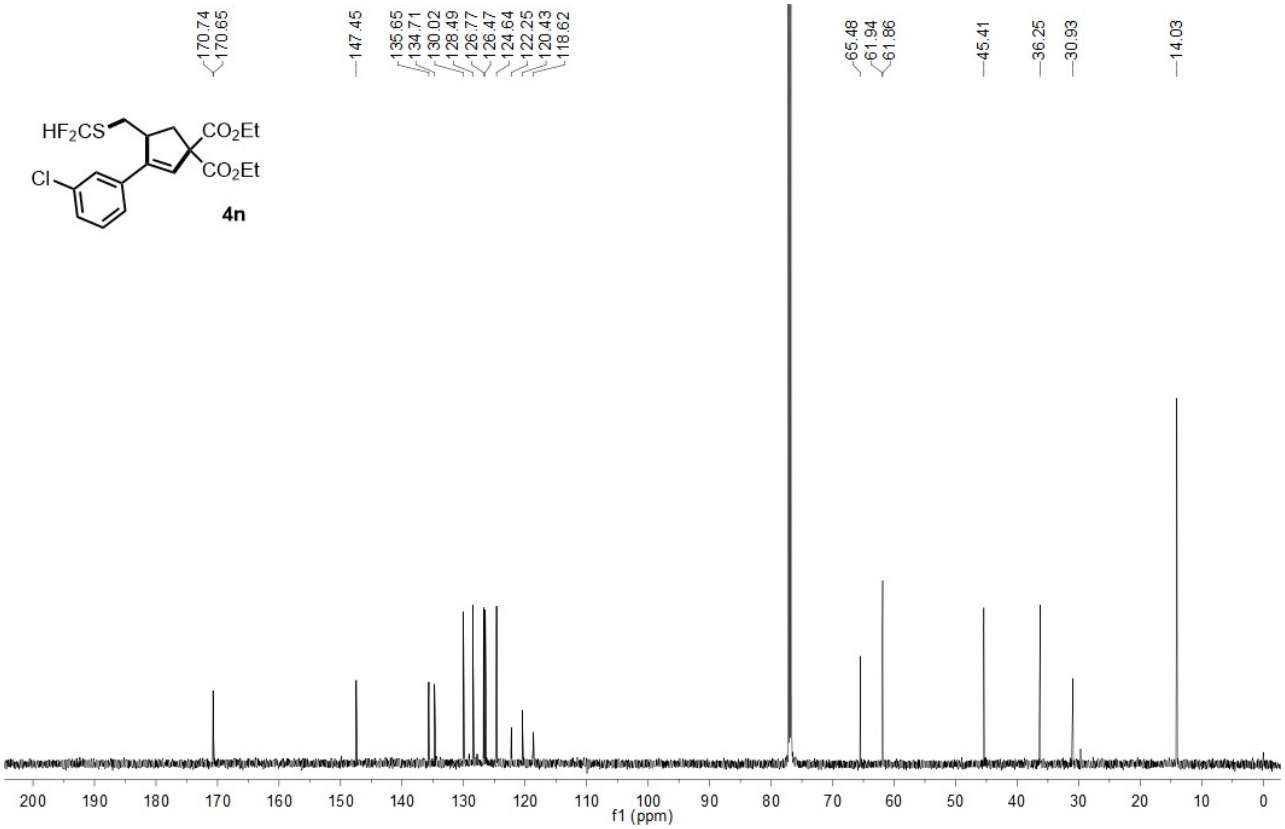
^{19}F NMR, 471 MHz, $CDCl_3$



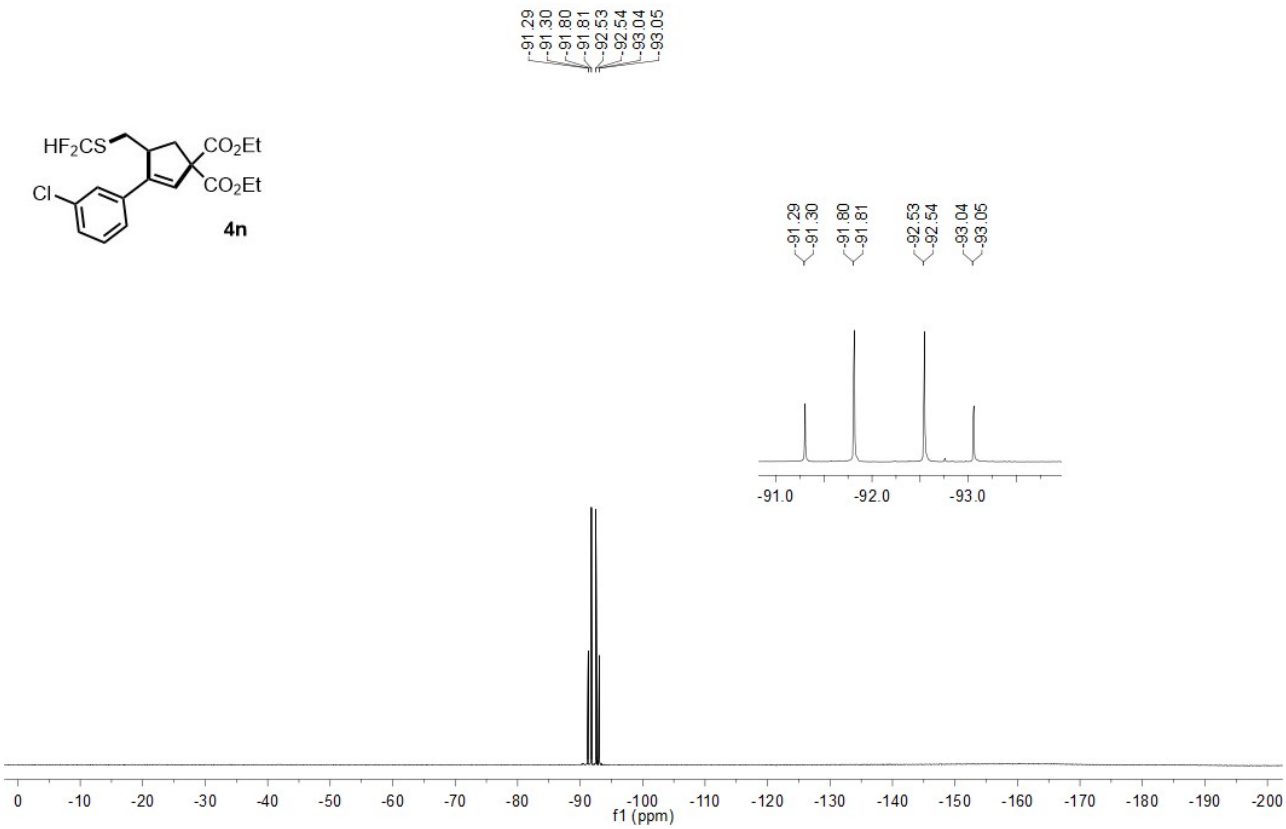
^{1}H NMR, 600 MHz, $CDCl_3$



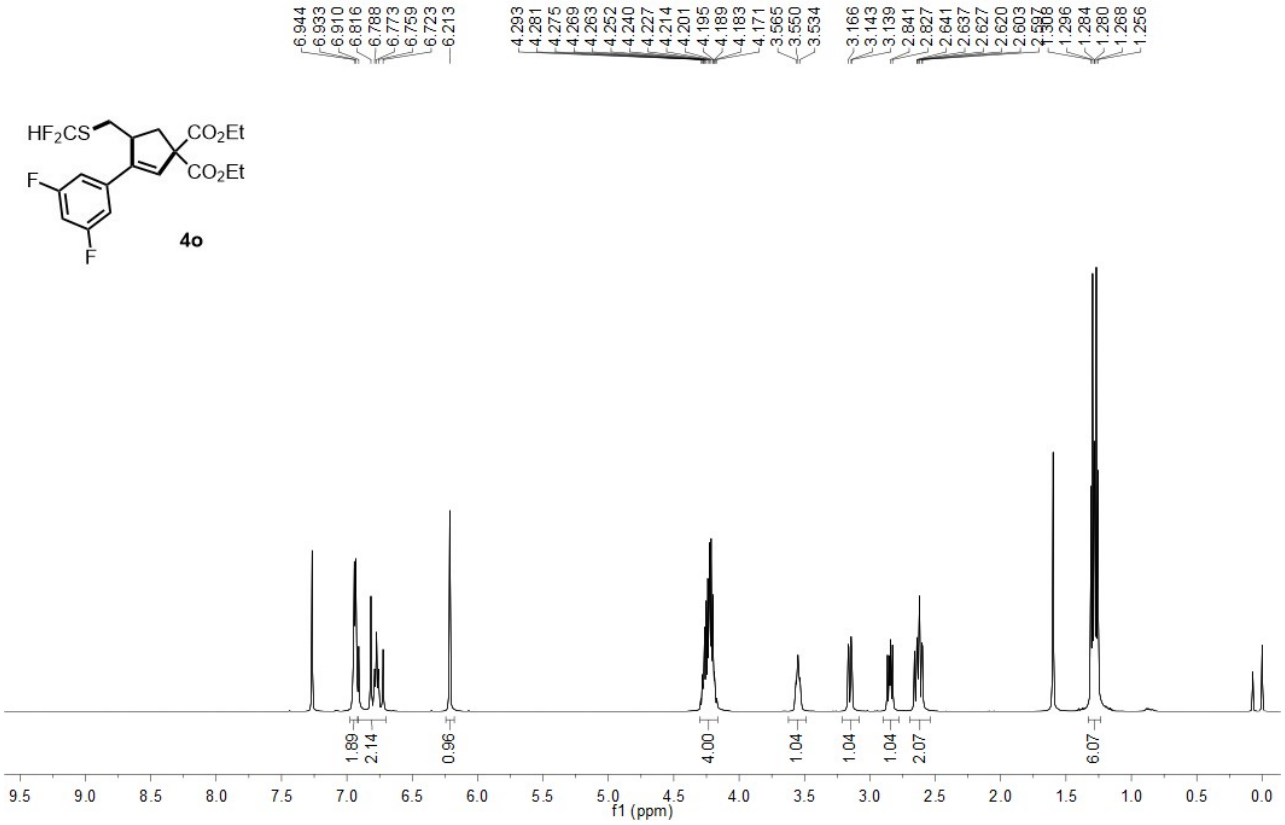
^{13}C NMR, 151 MHz, $CDCl_3$



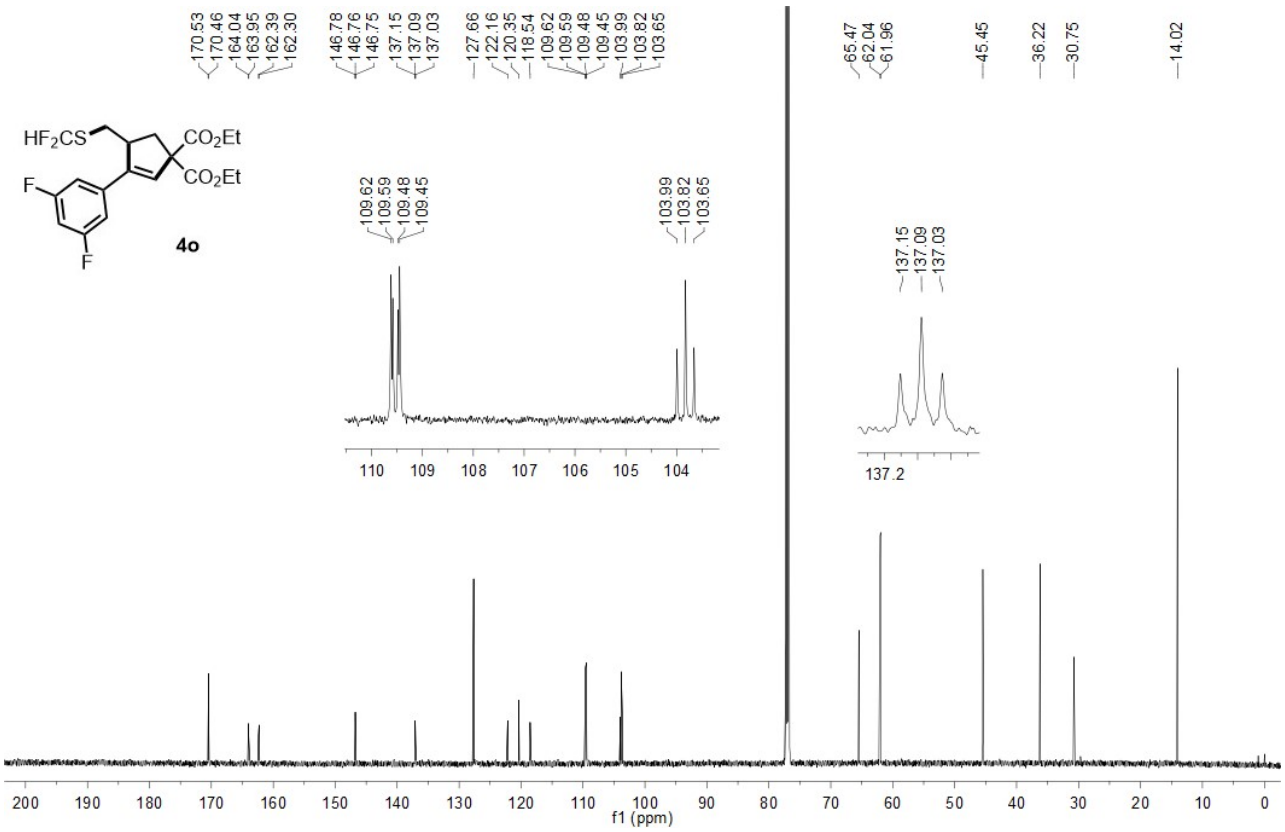
^{19}F NMR, 471 MHz, $CDCl_3$



^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 151 MHz, $CDCl_3$



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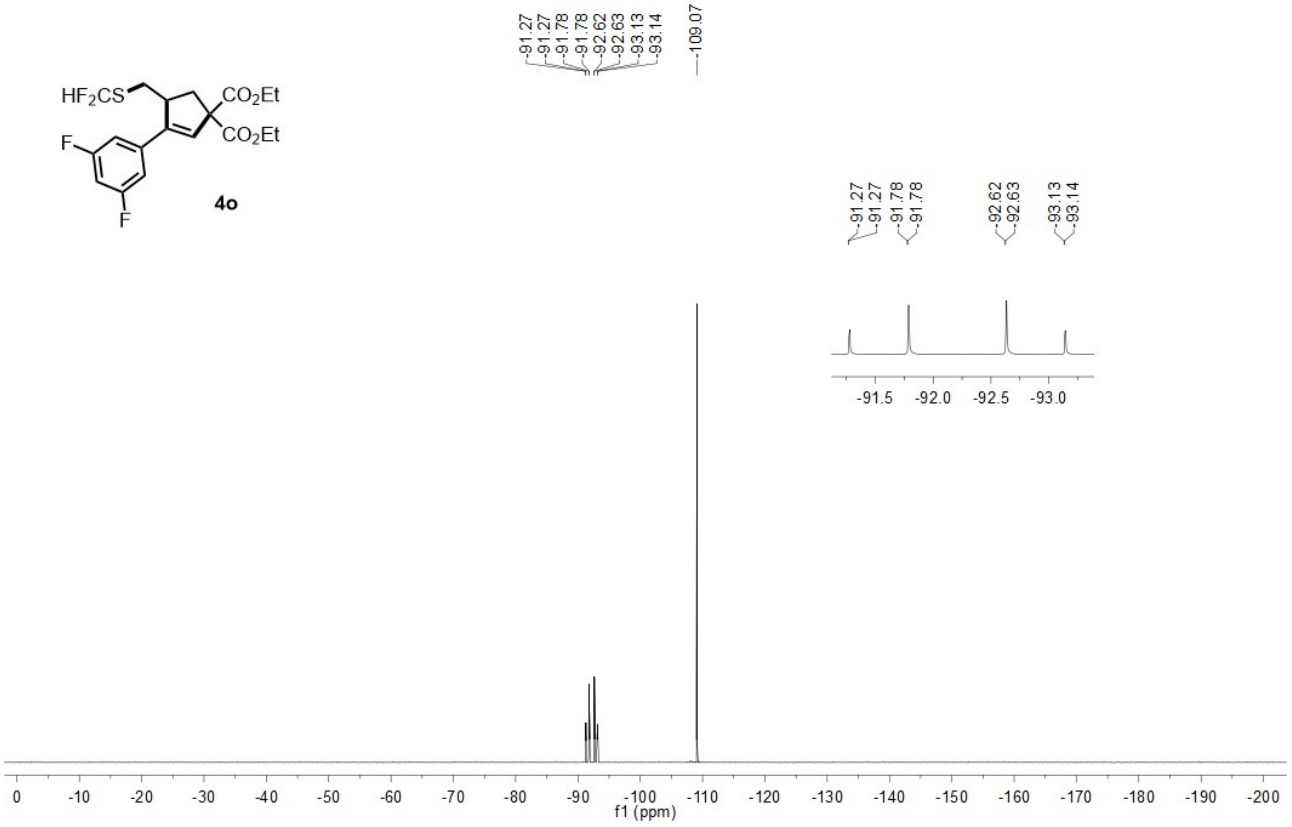
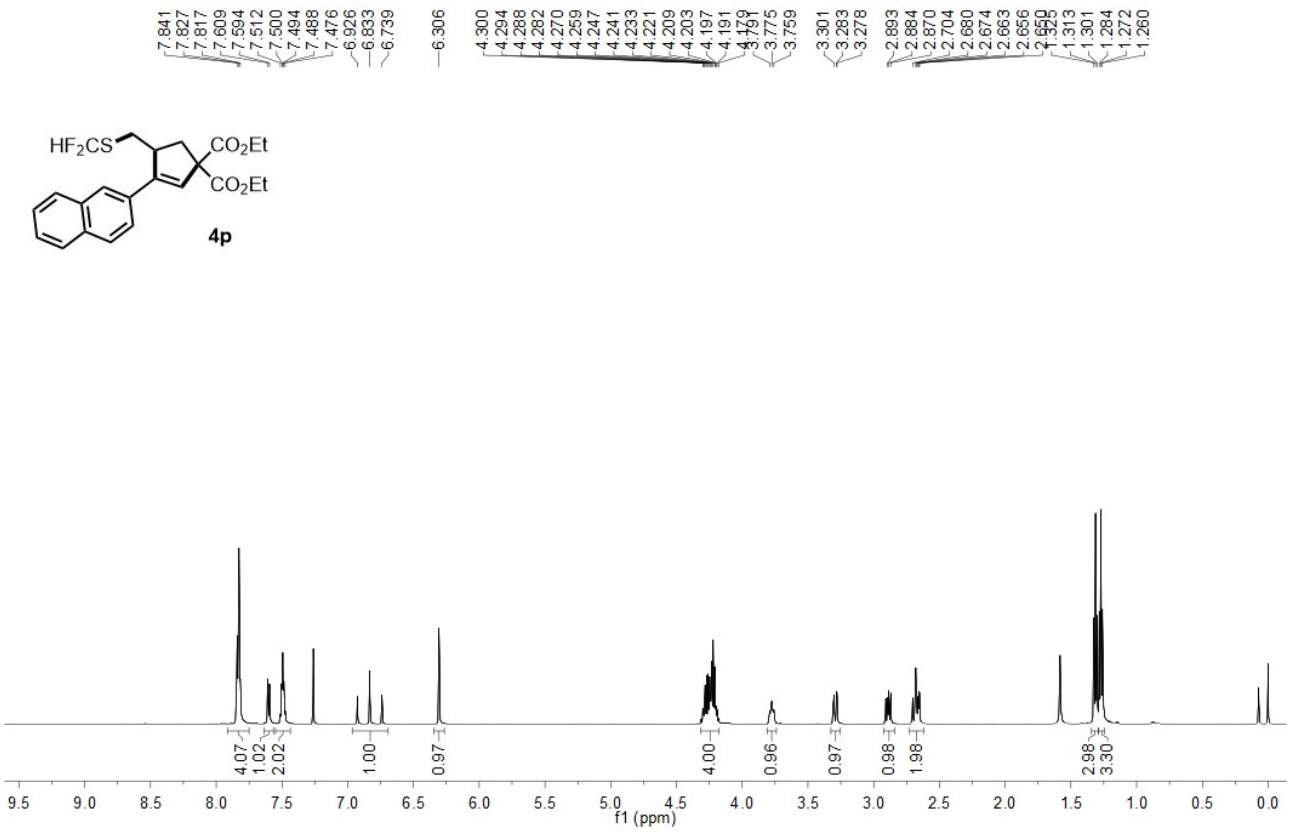
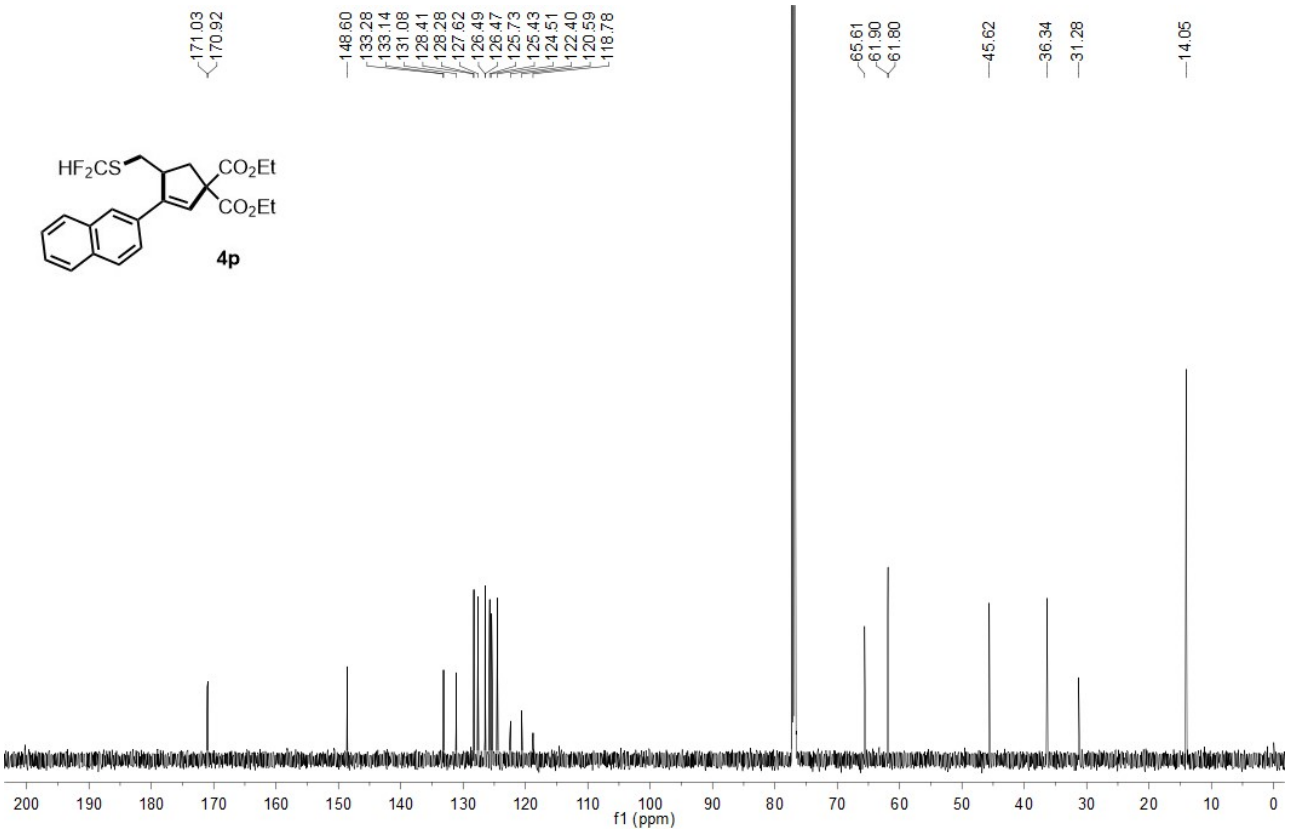


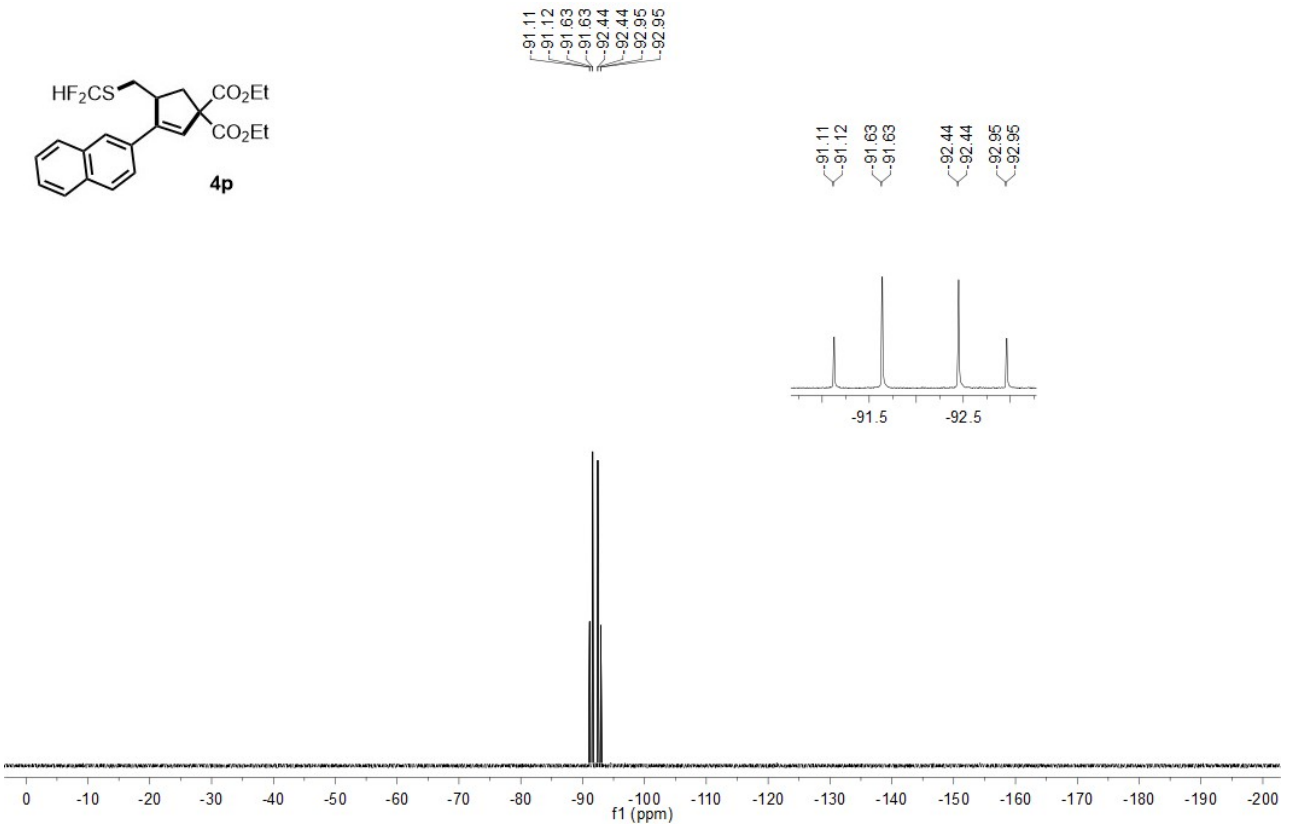
^{1}H NMR, 600 MHz, $CDCl_3$



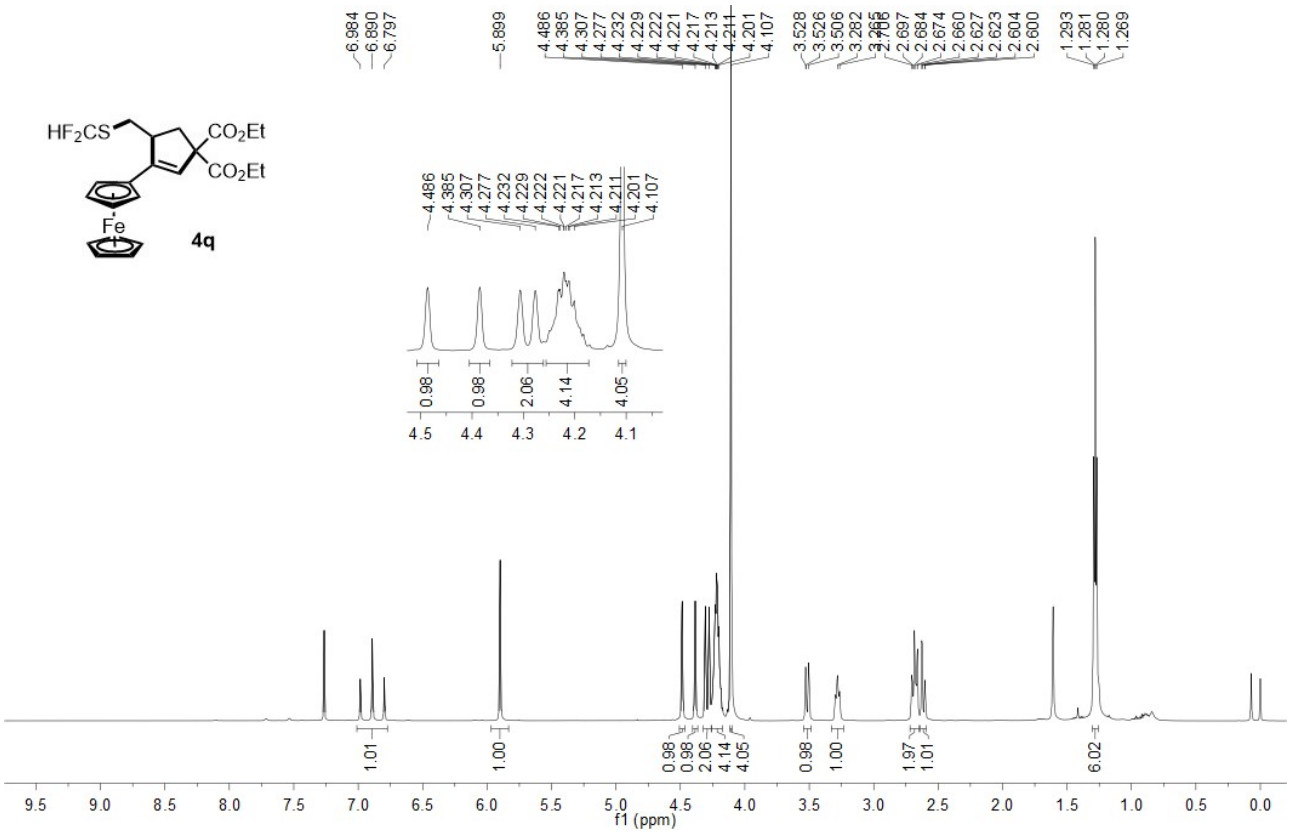
^{13}C NMR, 151 MHz, $CDCl_3$



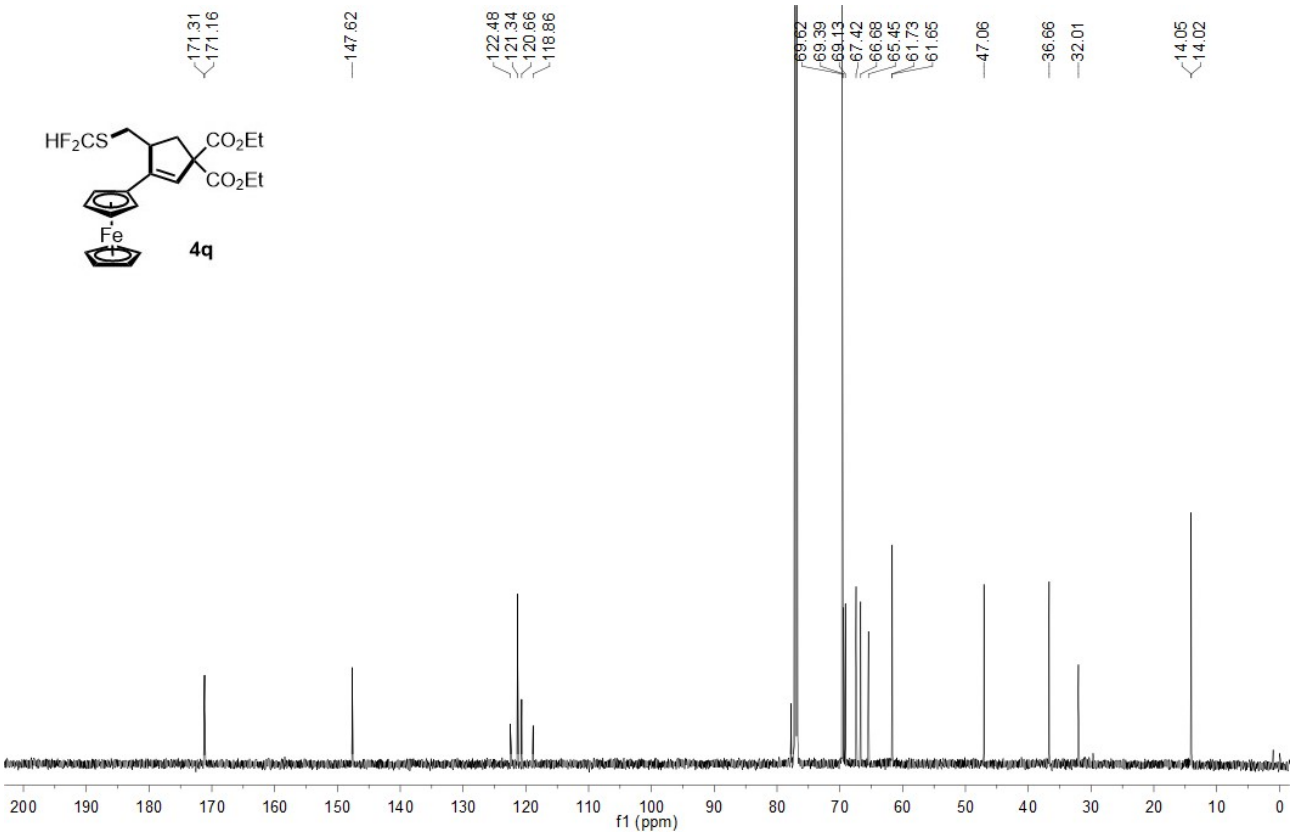
^{19}F NMR, 471 MHz, $CDCl_3$



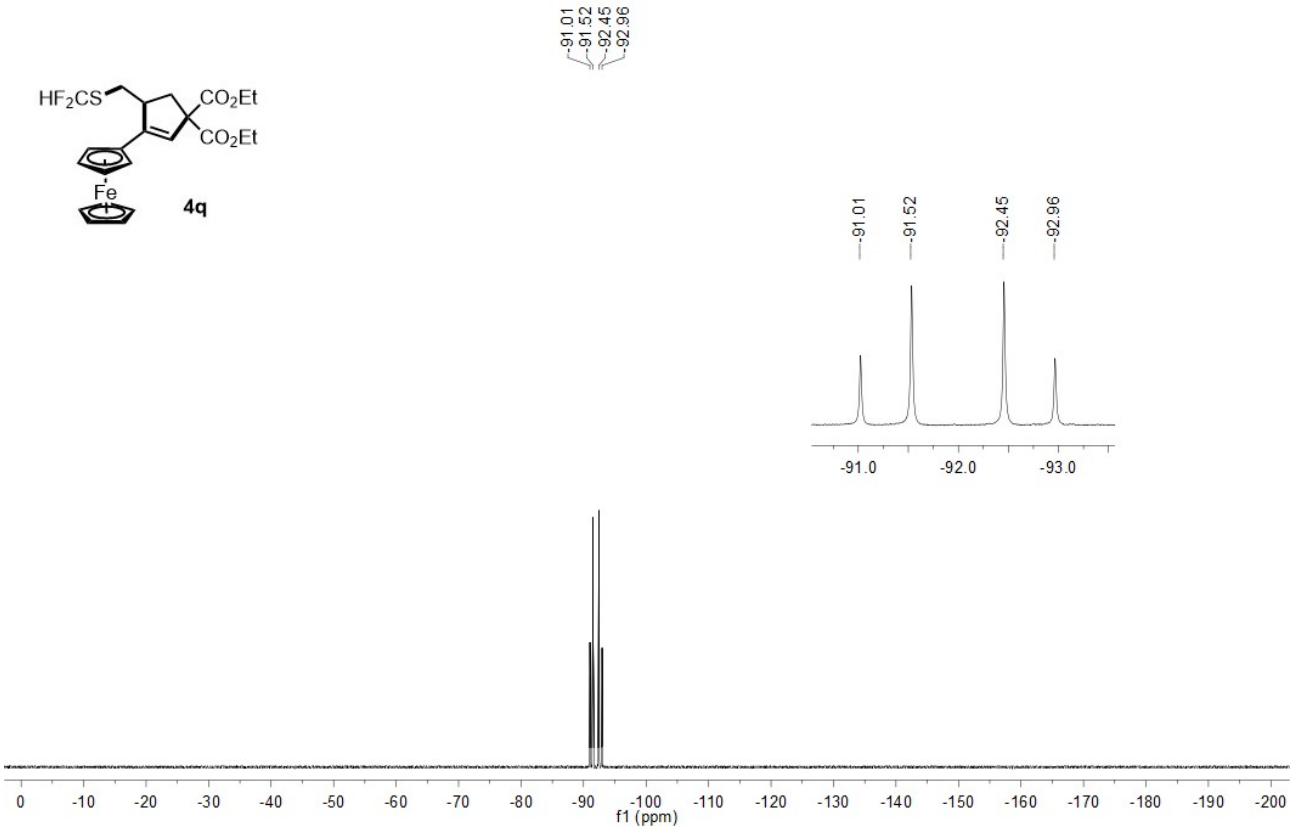
^{1}H NMR, 600 MHz, $CDCl_3$



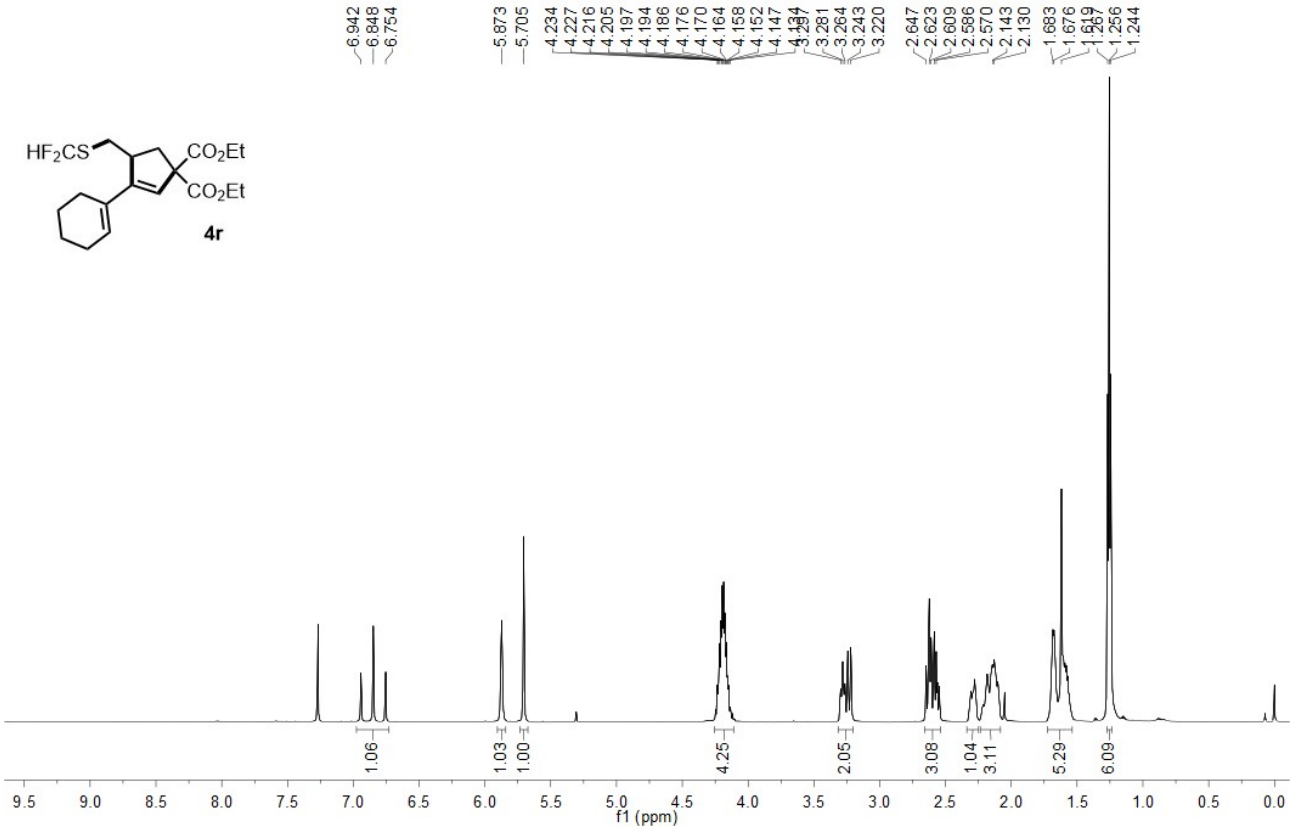
^{13}C NMR, 151 MHz, $CDCl_3$



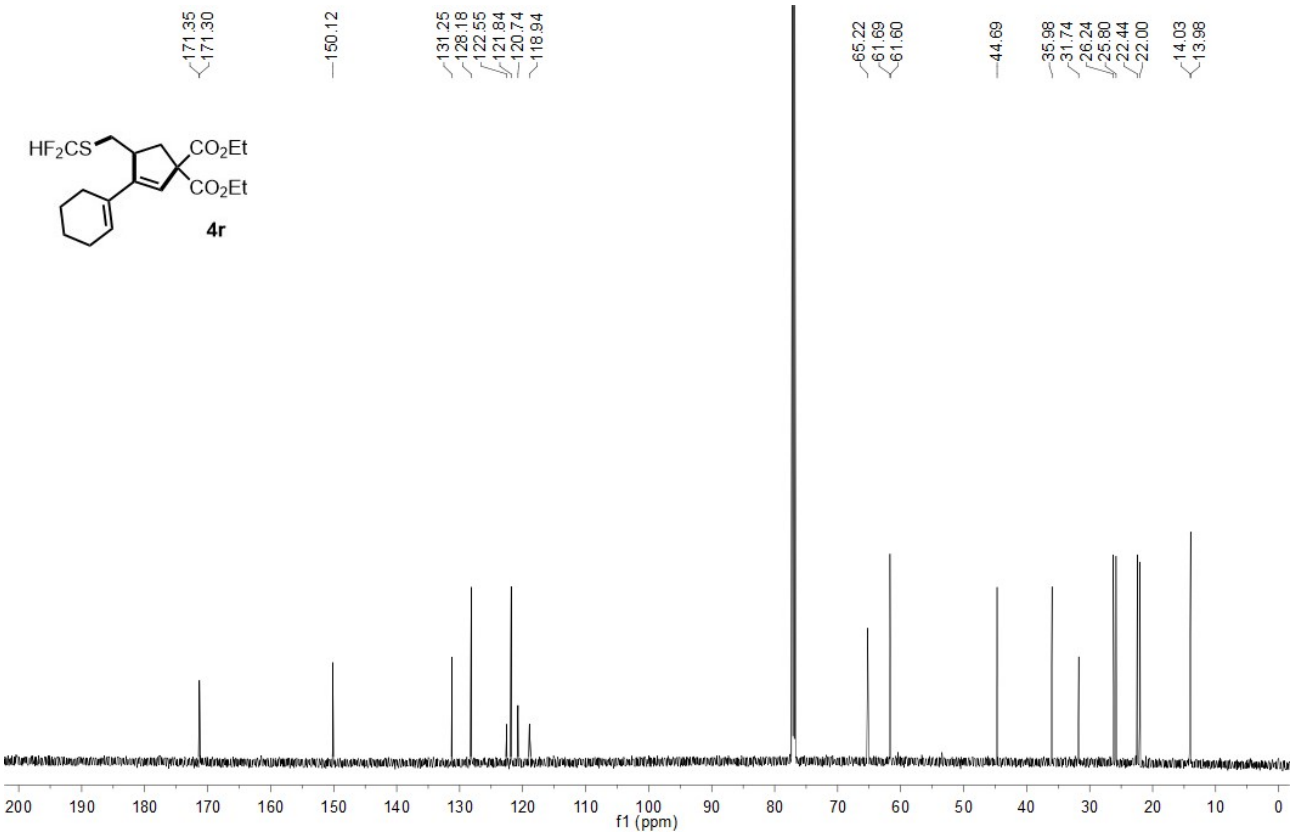
^{19}F NMR, 471 MHz, $CDCl_3$



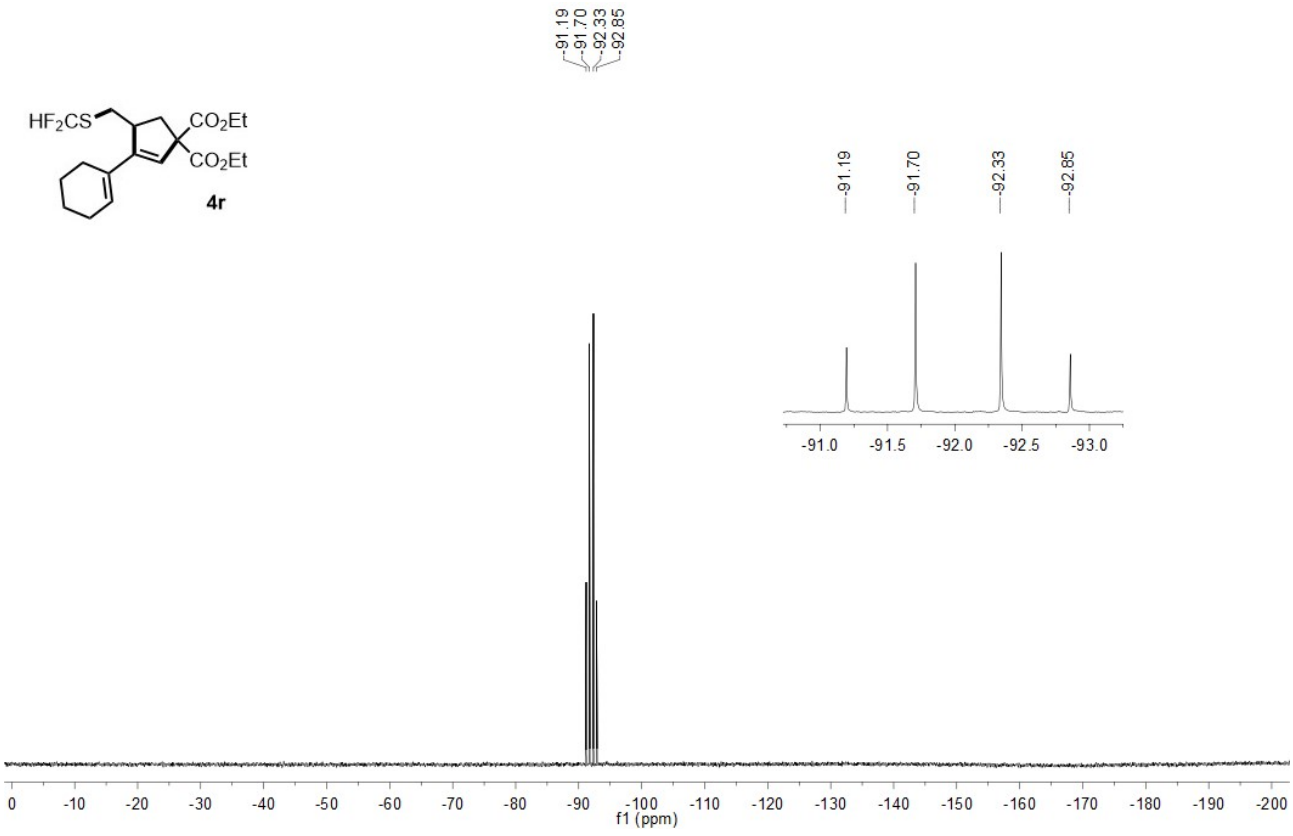
^{1}H NMR, 600 MHz, $CDCl_3$



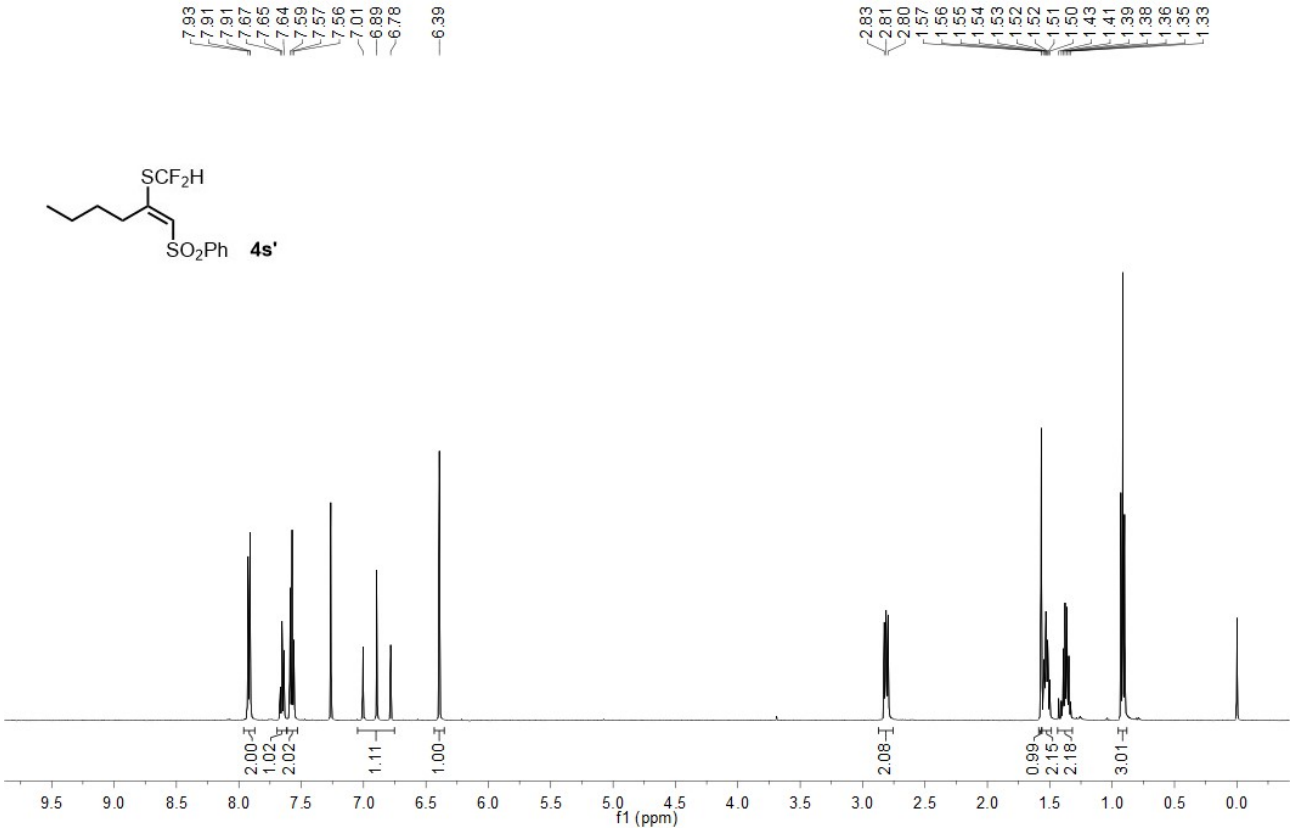
^{13}C NMR, 151 MHz, $CDCl_3$



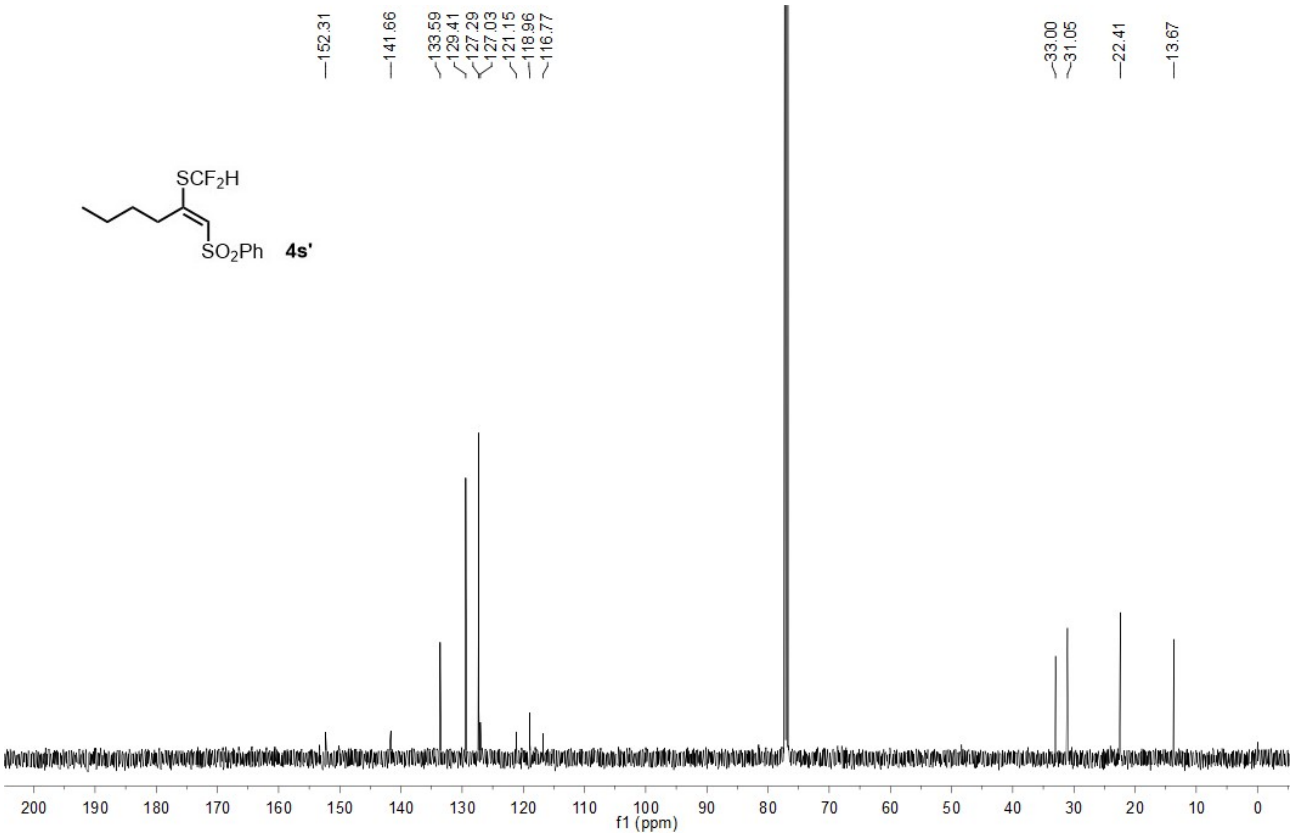
^{19}F NMR, 471 MHz, $CDCl_3$



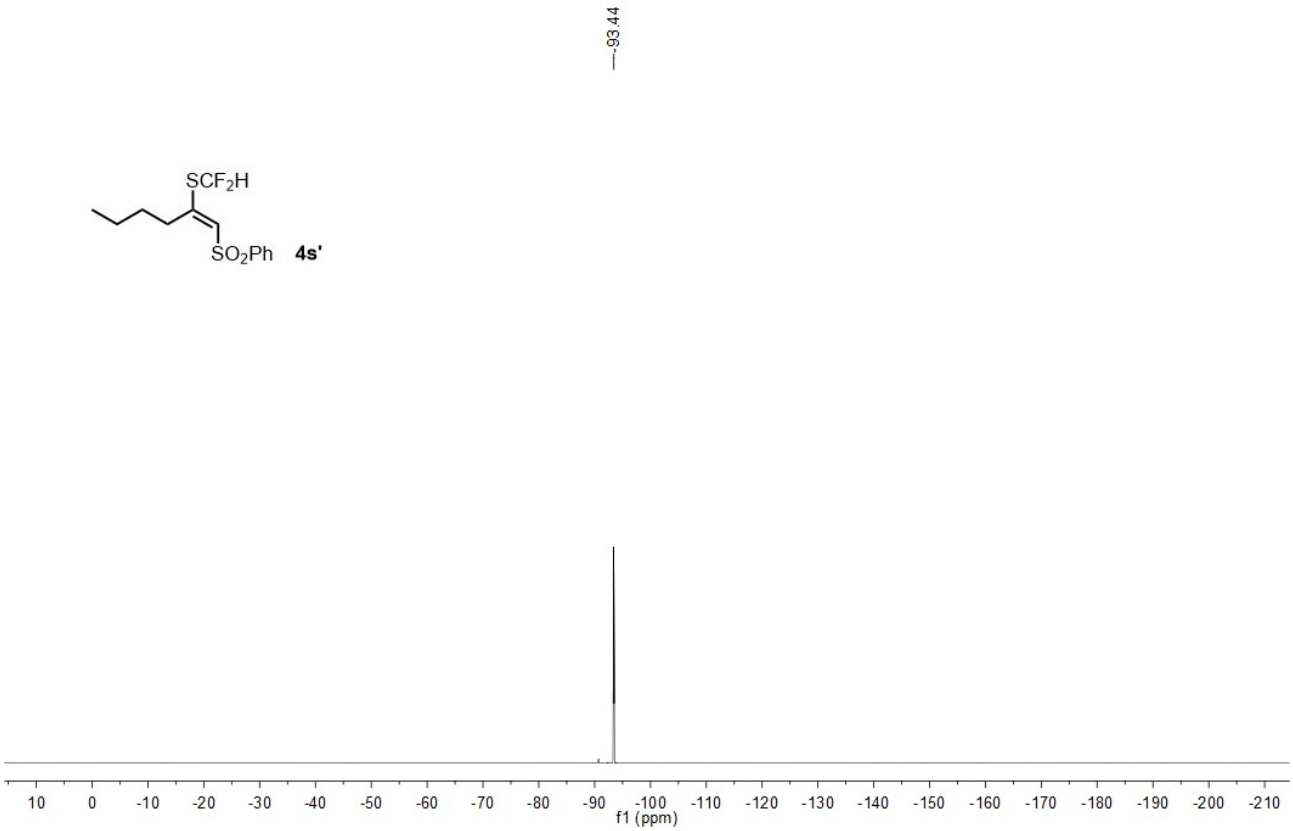
^{1}H NMR, 500 MHz, $CDCl_3$



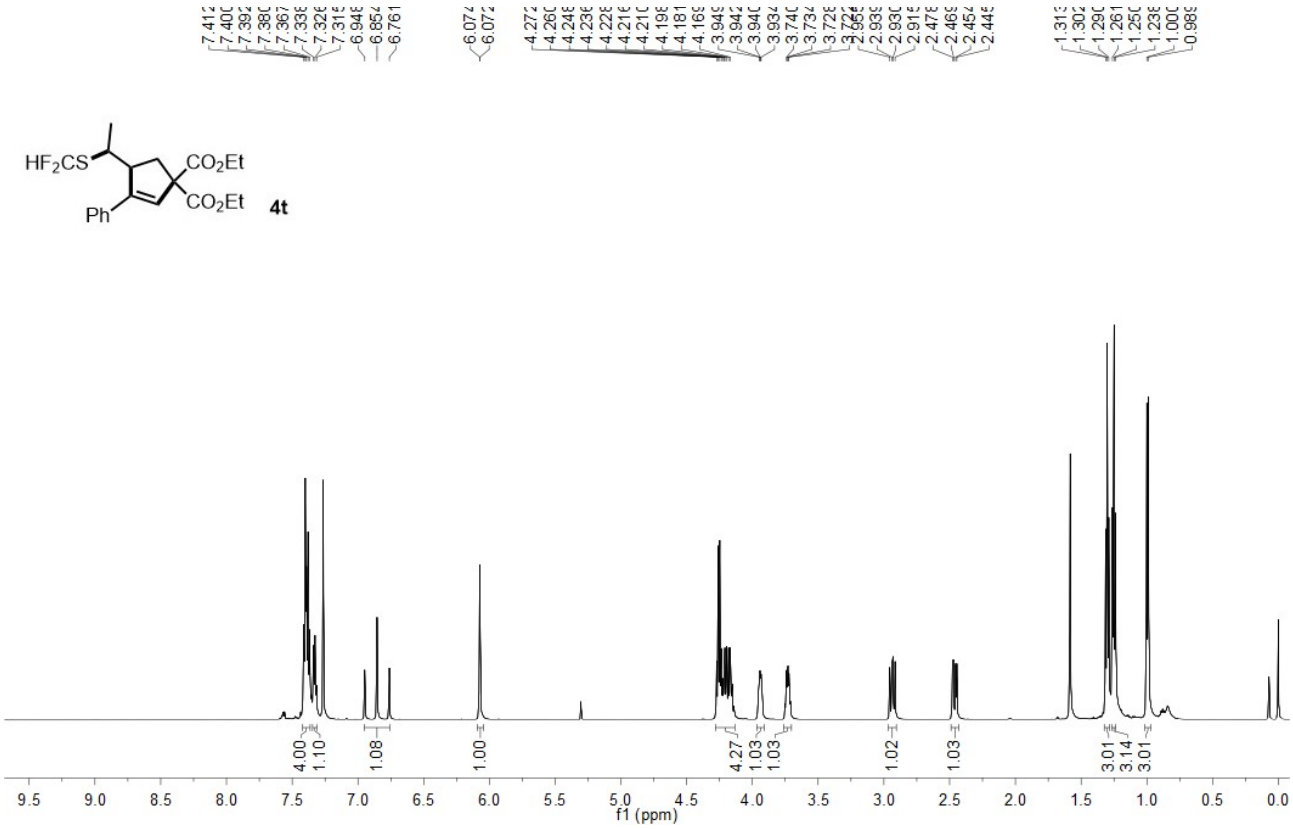
^{13}C NMR, 126 MHz, $CDCl_3$



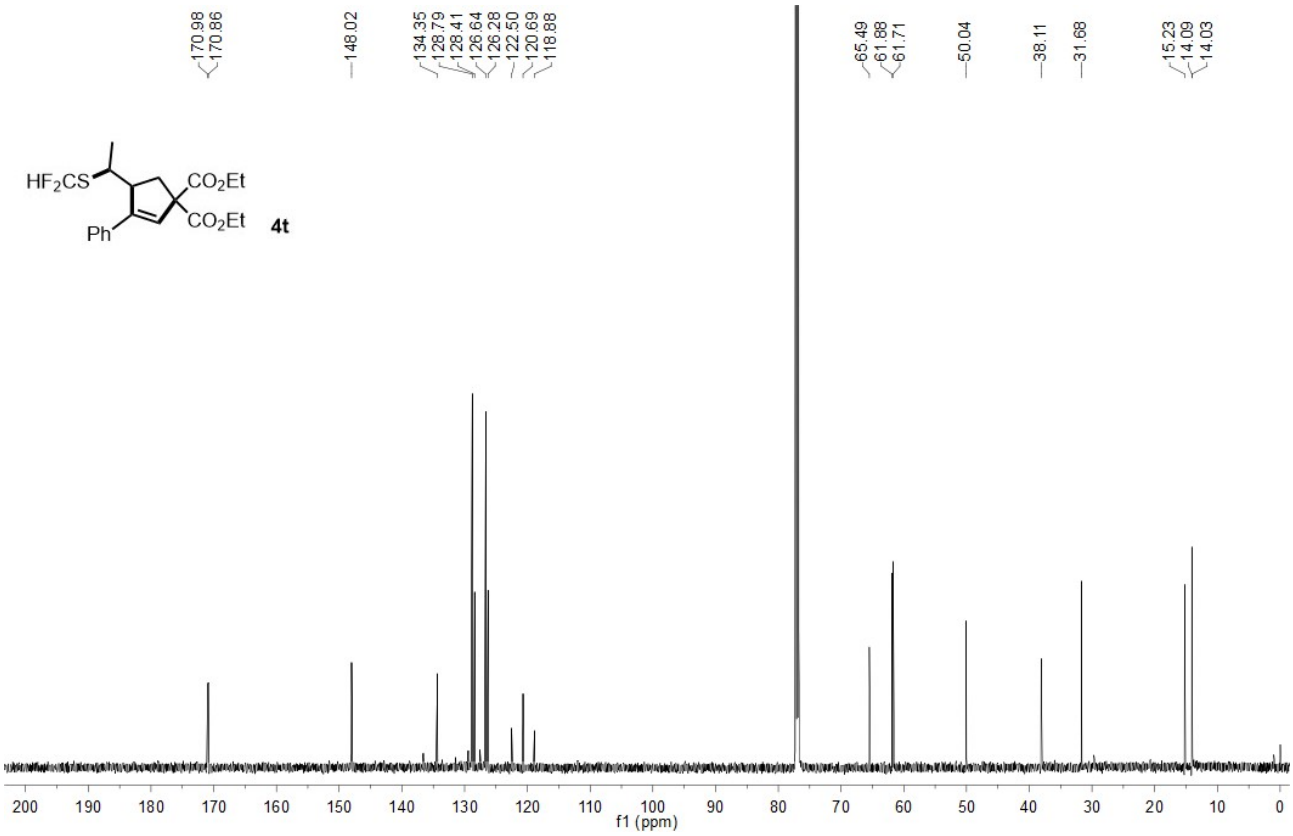
^{19}F NMR, 471 MHz, $CDCl_3$



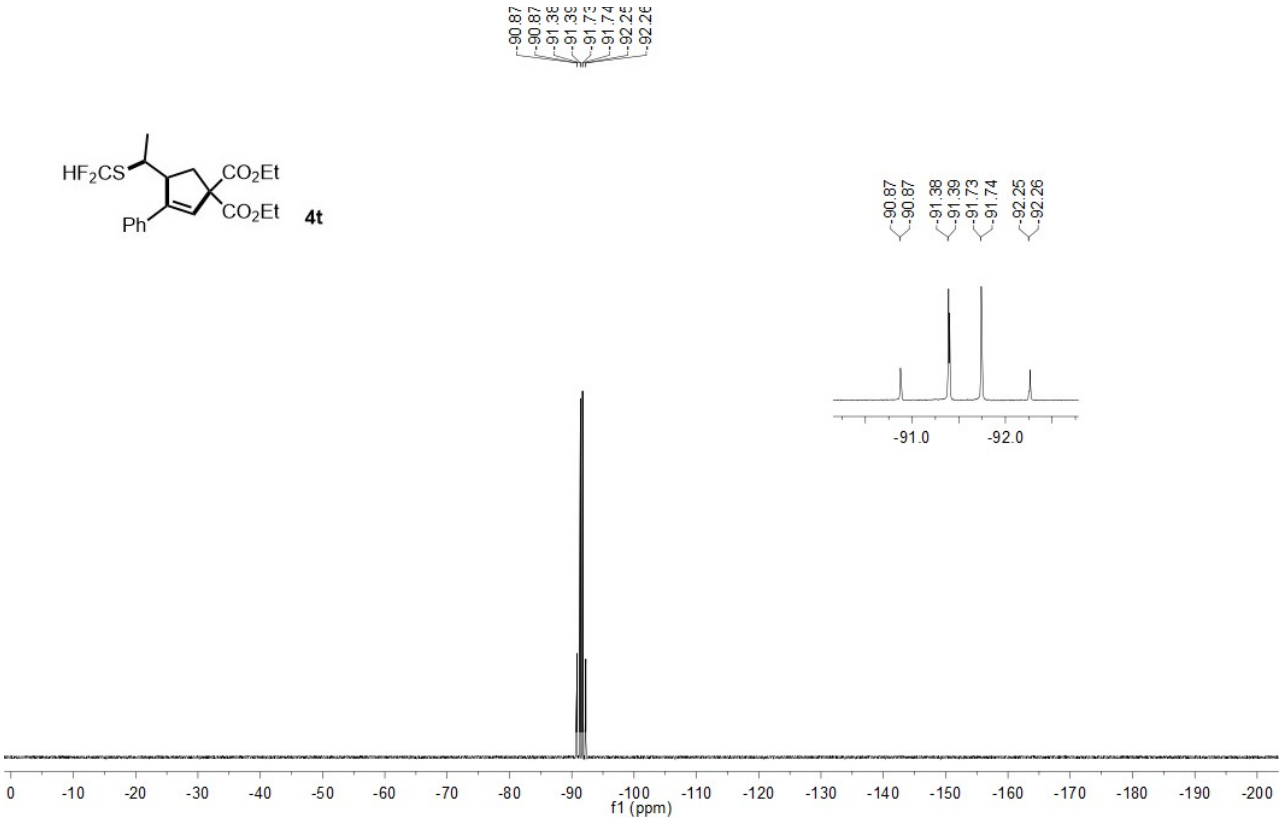
^{1}H NMR, 600 MHz, $CDCl_3$



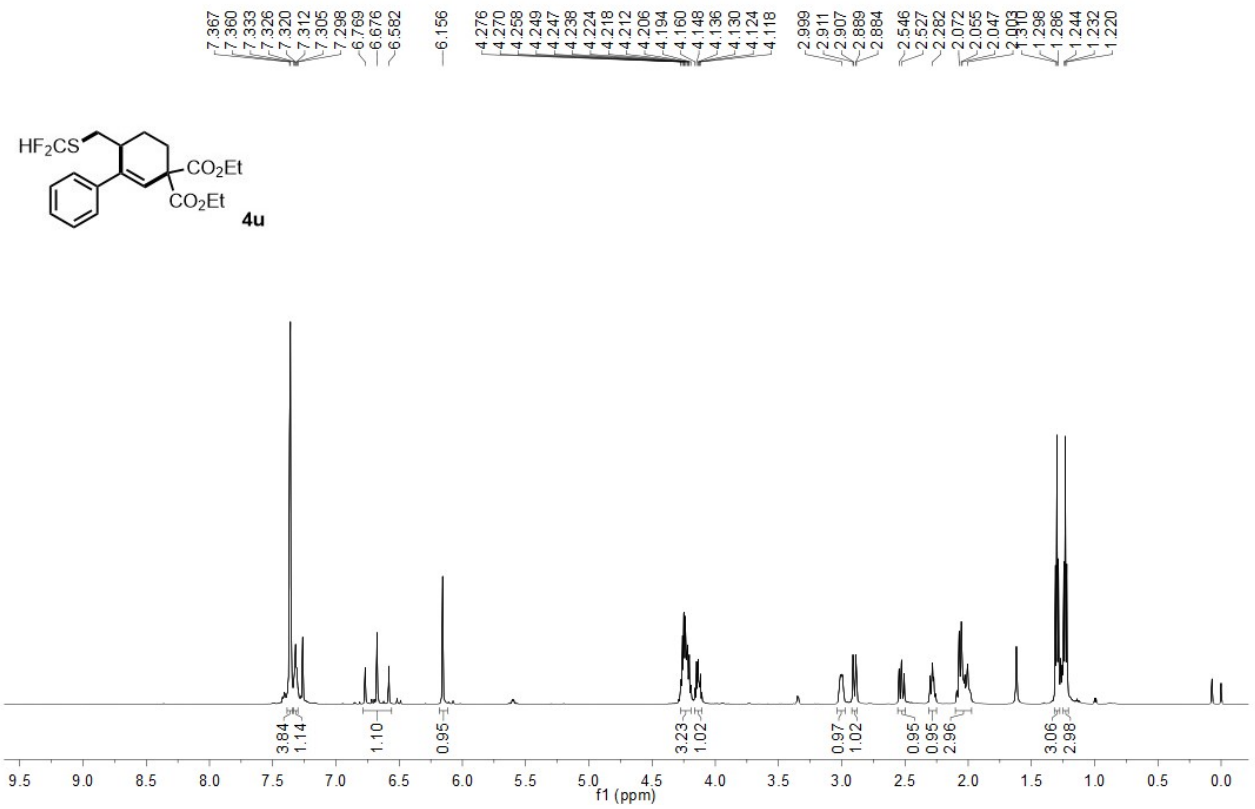
^{13}C NMR, 151 MHz, $CDCl_3$



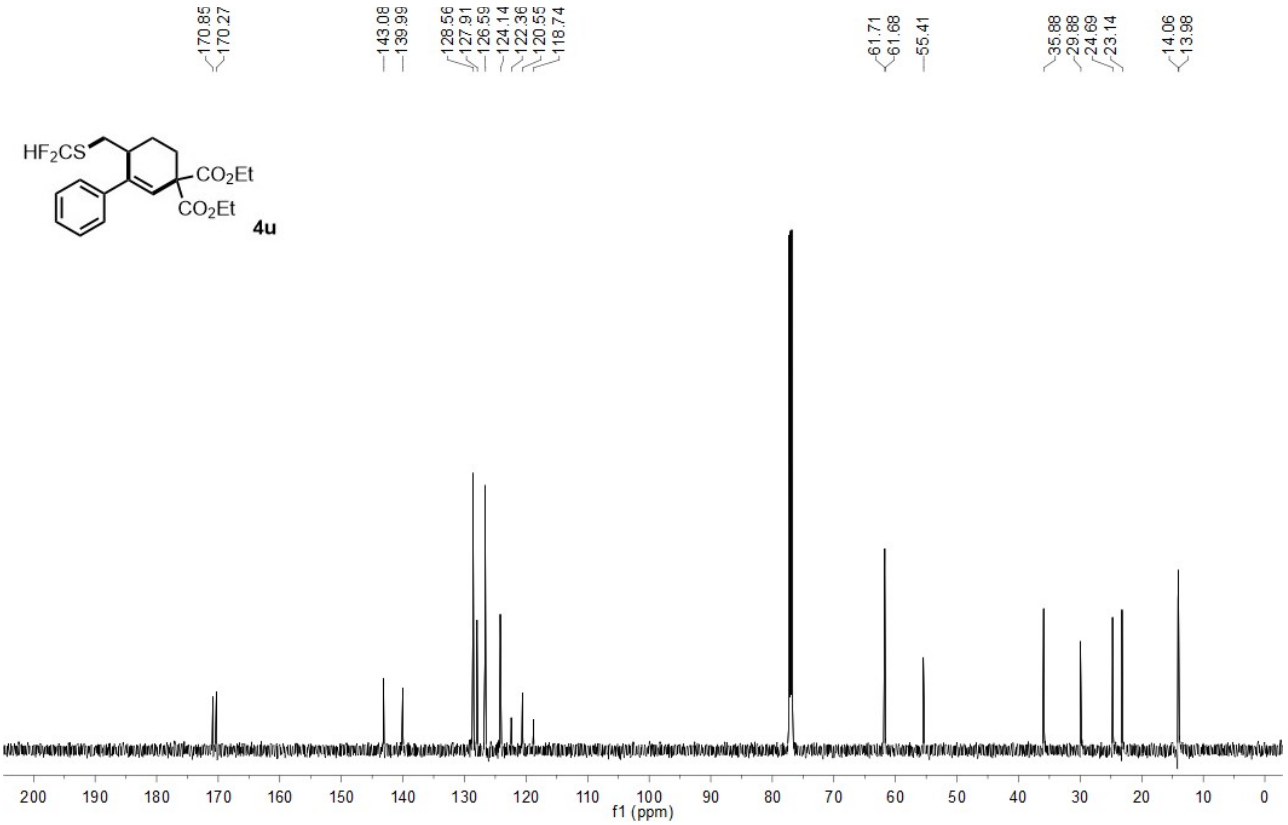
^{19}F NMR, 471 MHz, $CDCl_3$



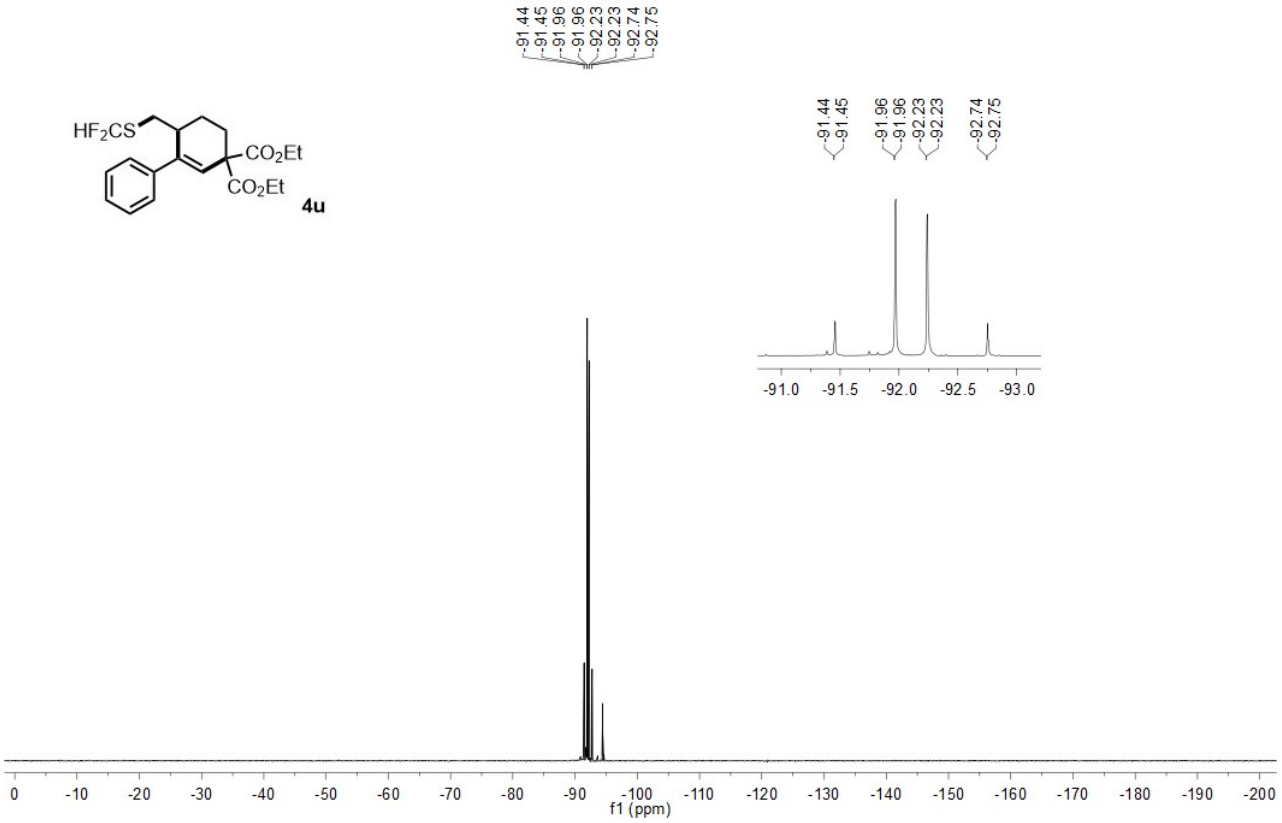
^{1}H NMR, 600 MHz, $CDCl_3$



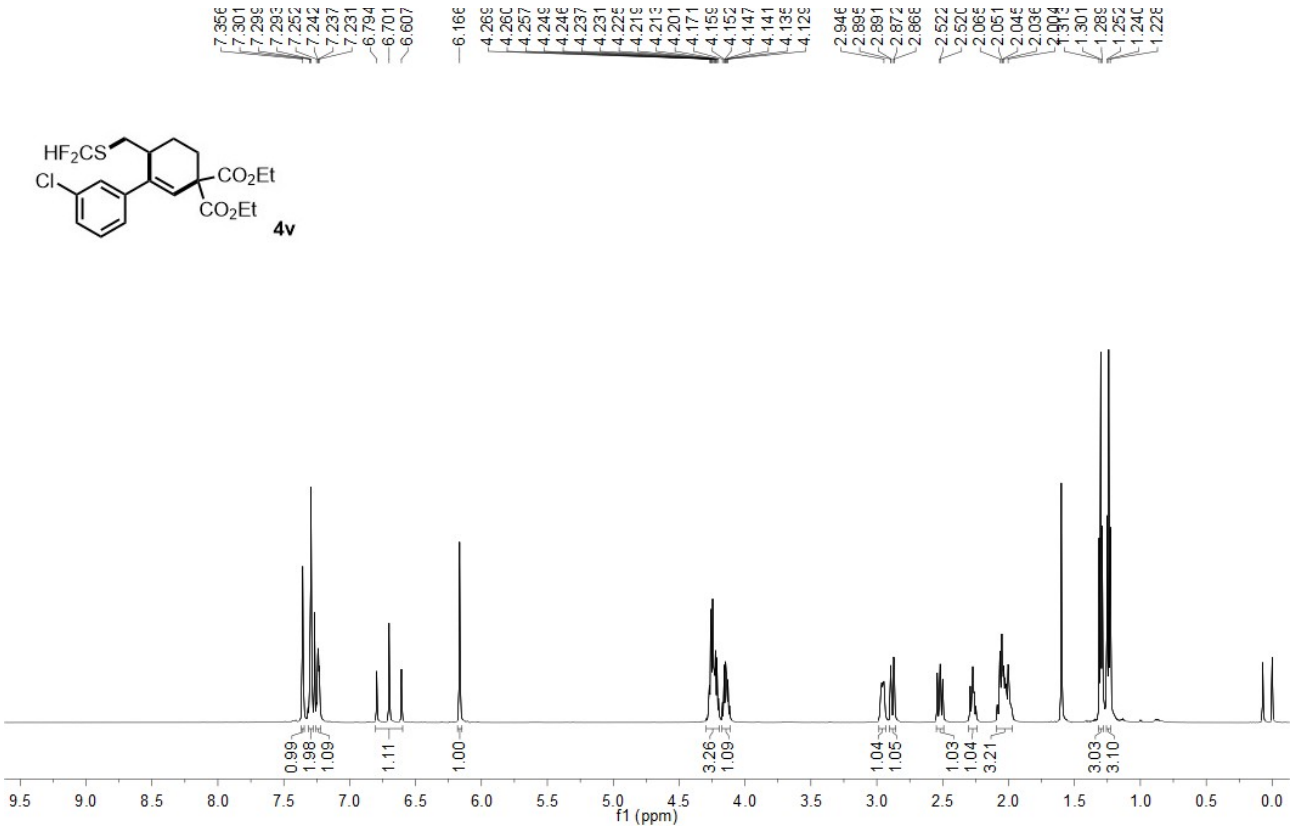
^{13}C NMR, 151 MHz, $CDCl_3$



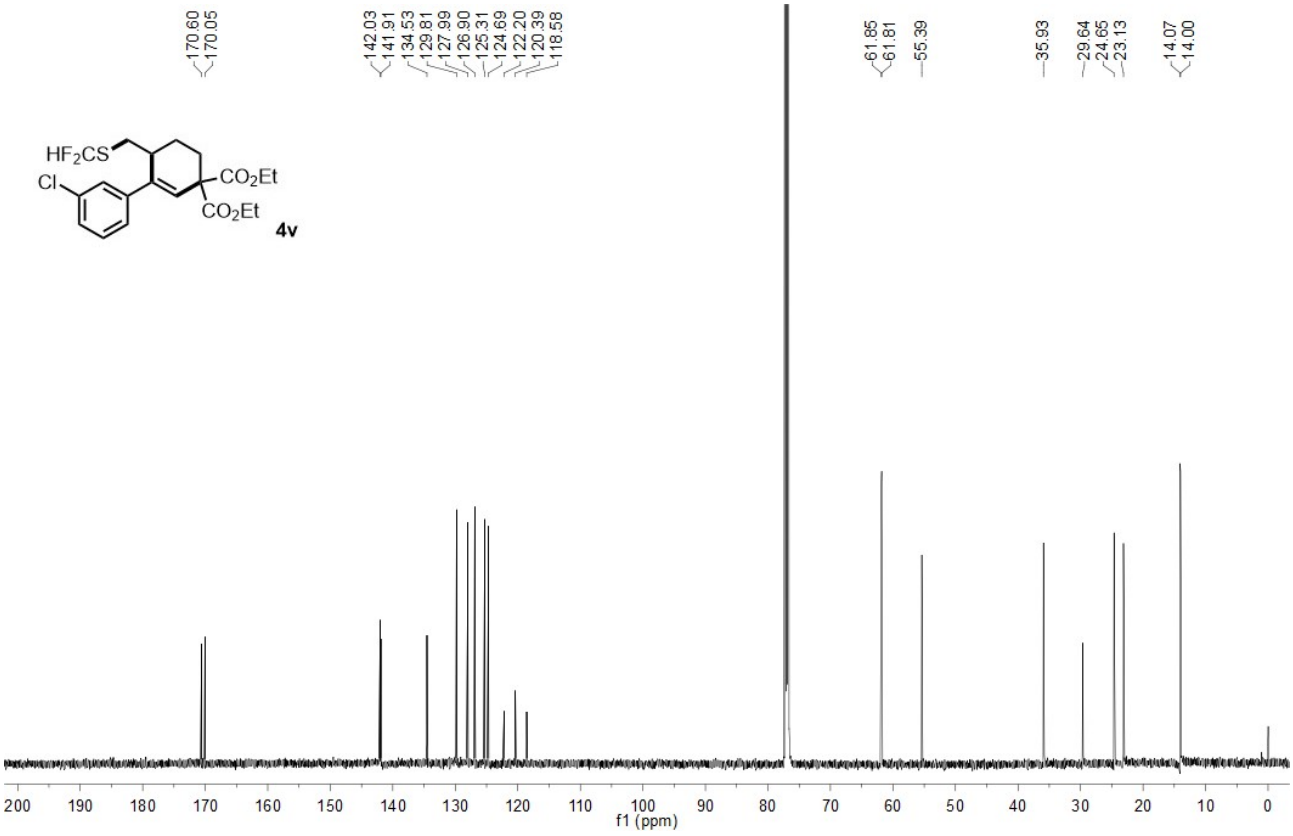
^{19}F NMR, 471 MHz, $CDCl_3$



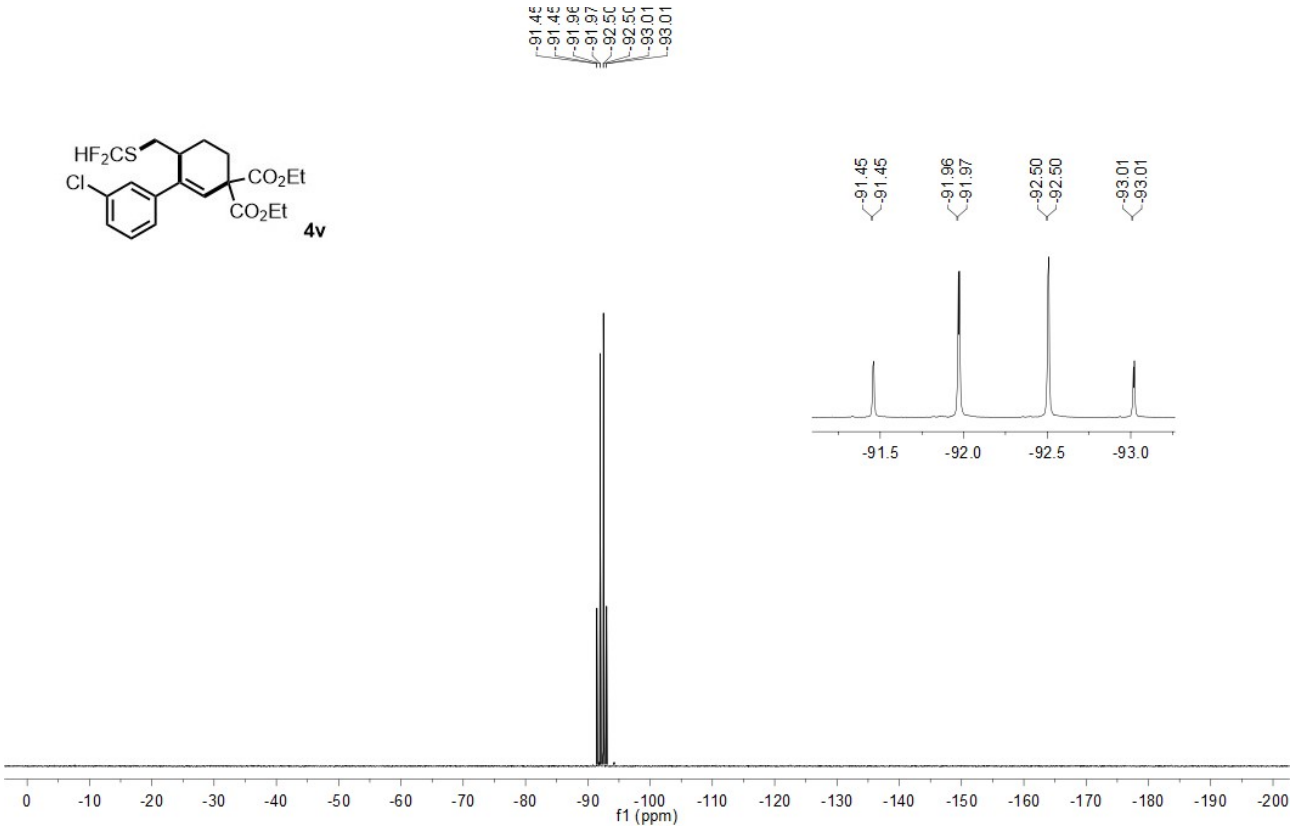
^{1}H NMR, 600 MHz, $CDCl_3$



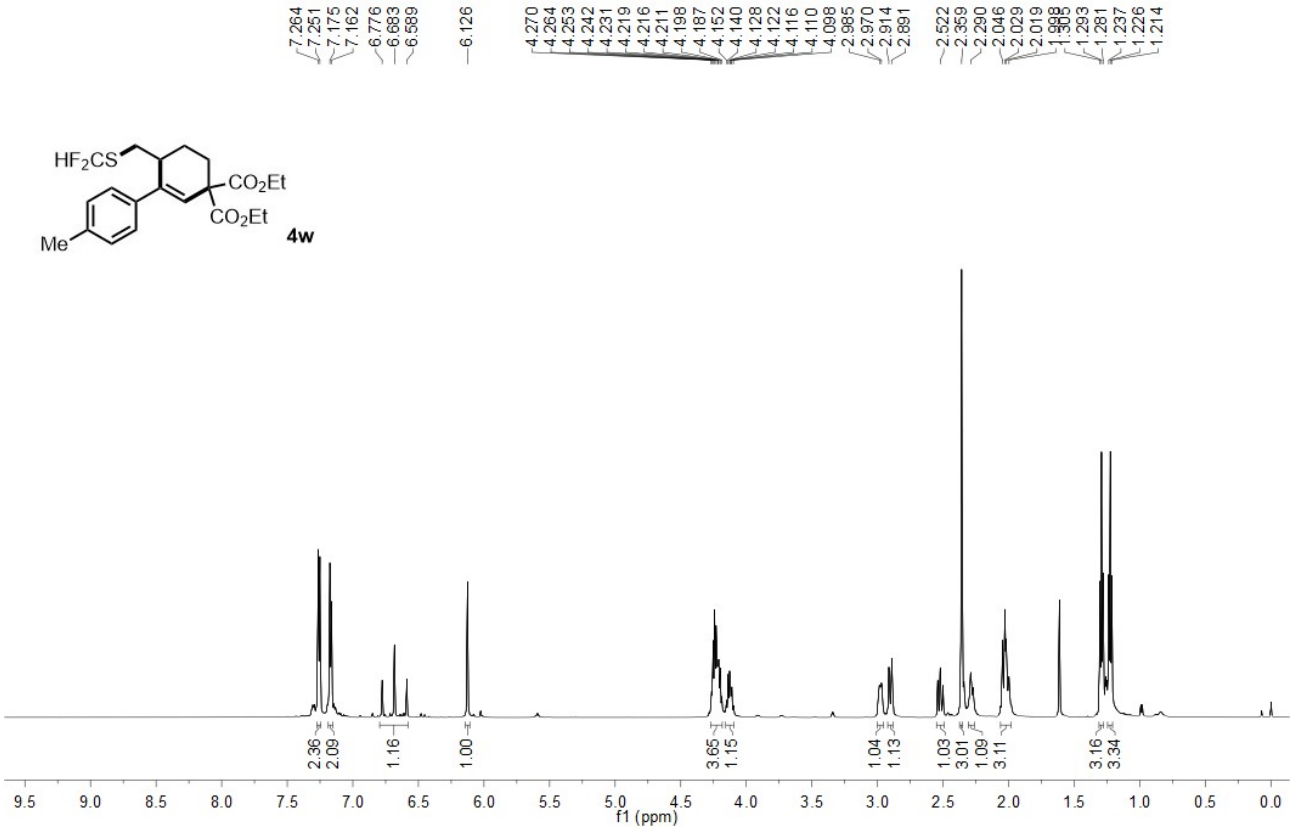
^{13}C NMR, 151 MHz, $CDCl_3$



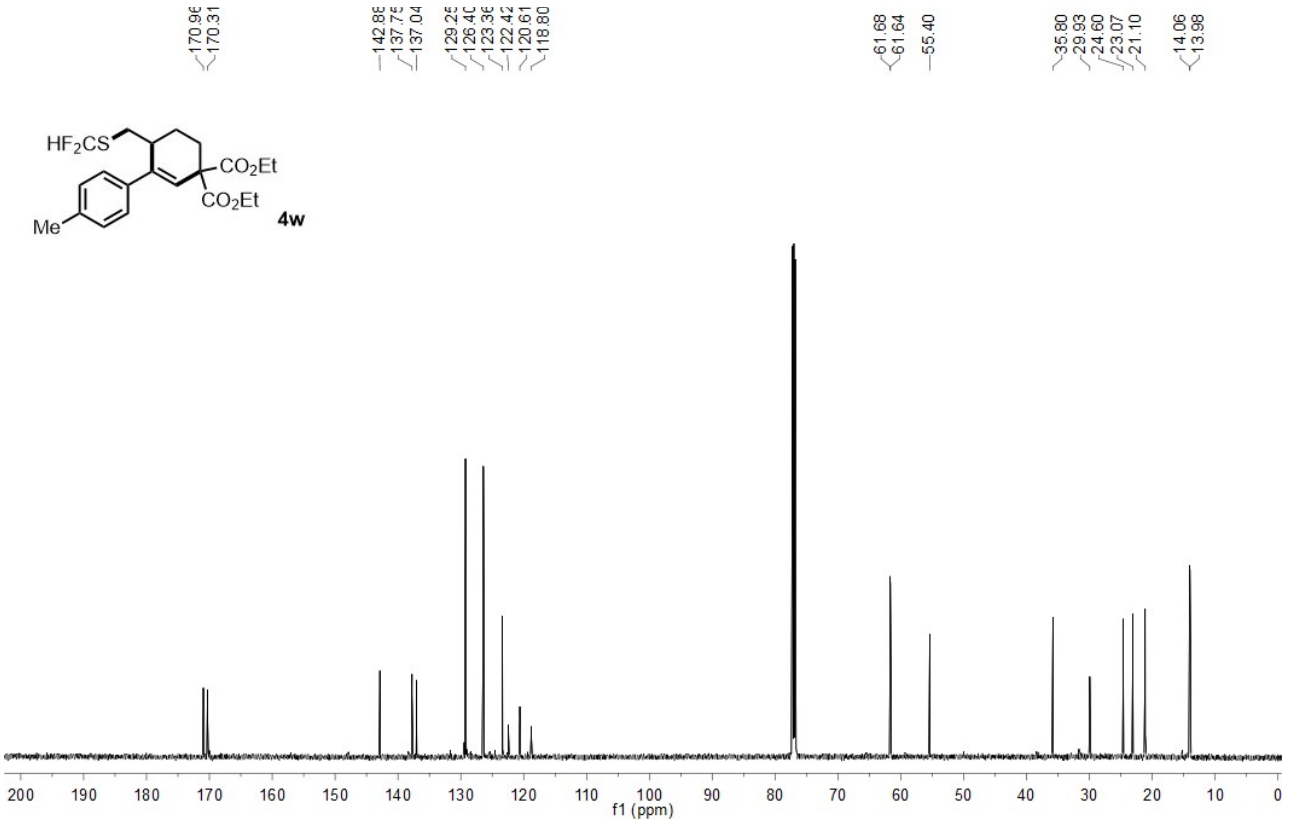
^{19}F NMR, 471 MHz, $CDCl_3$



^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 151 MHz, $CDCl_3$



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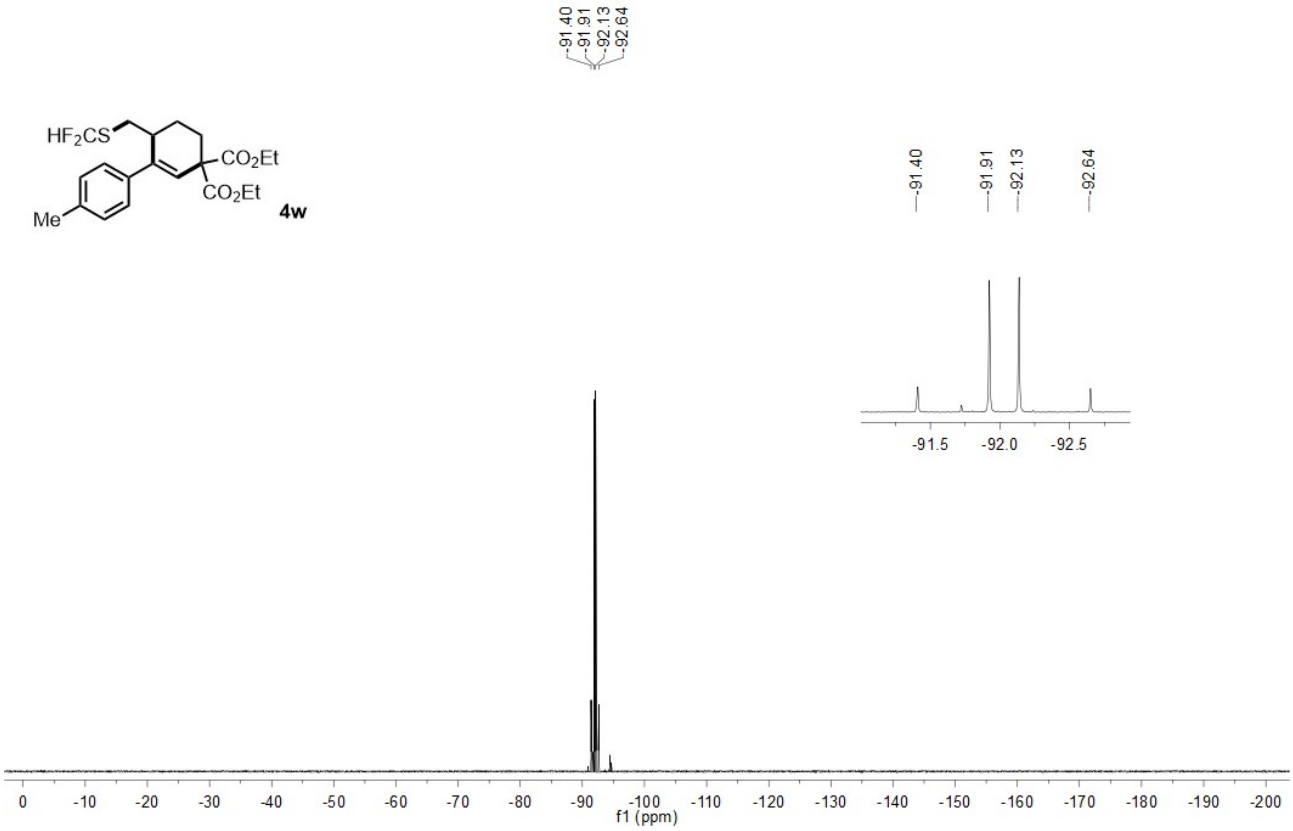
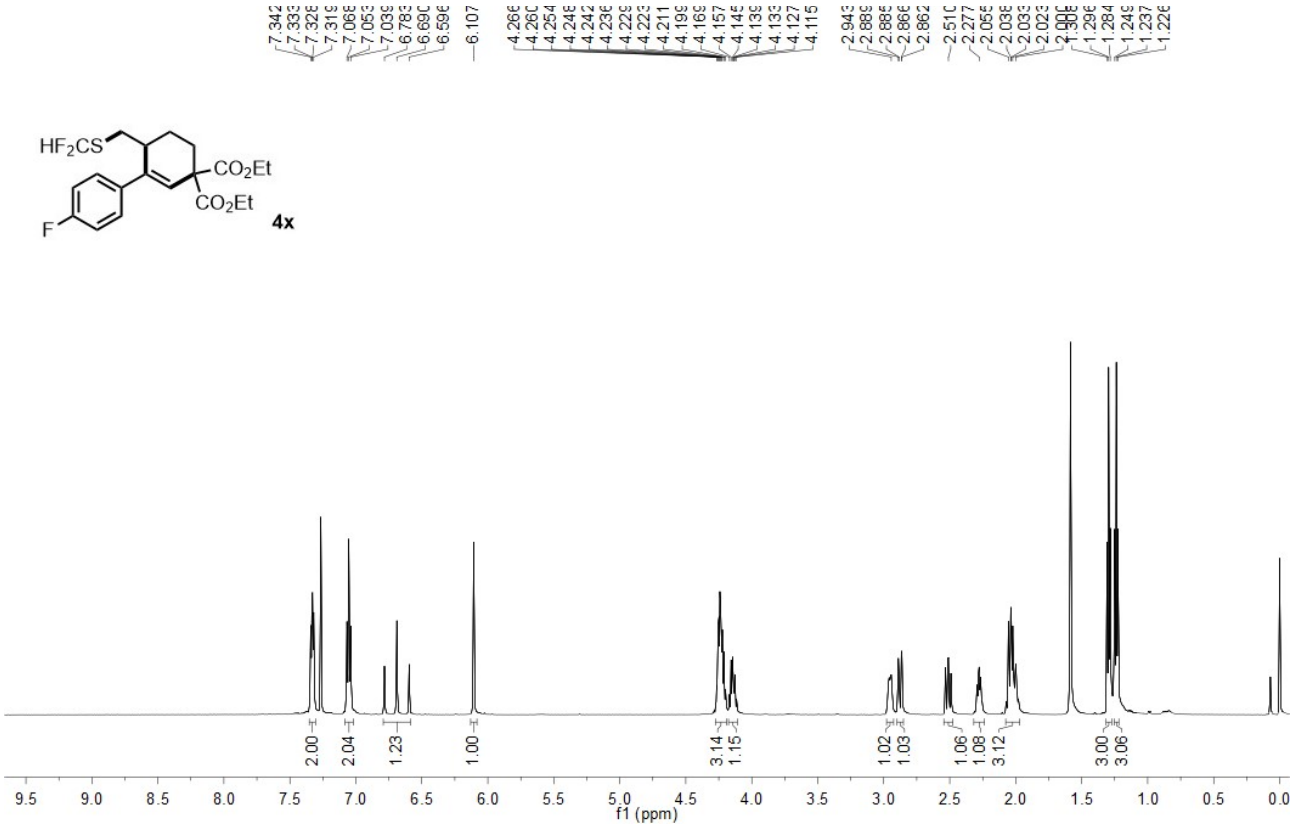
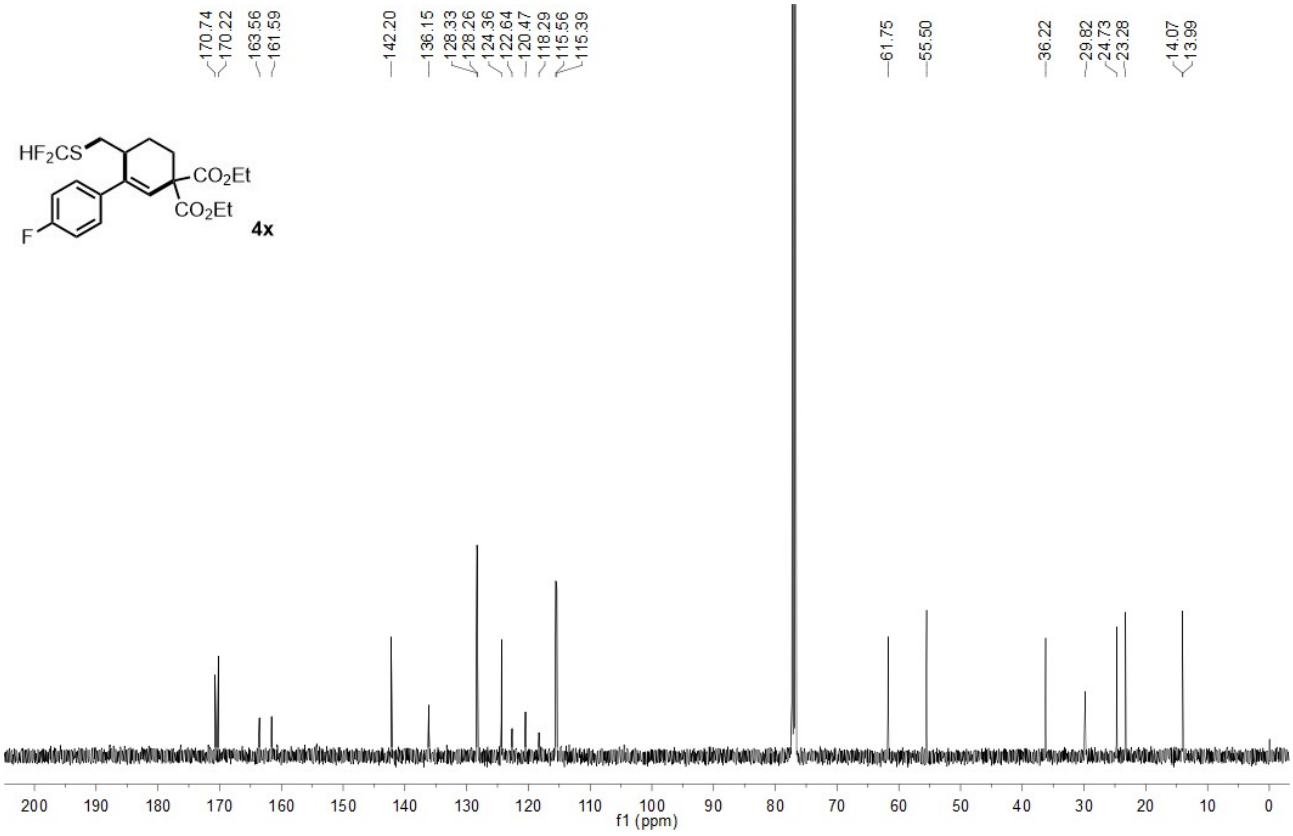


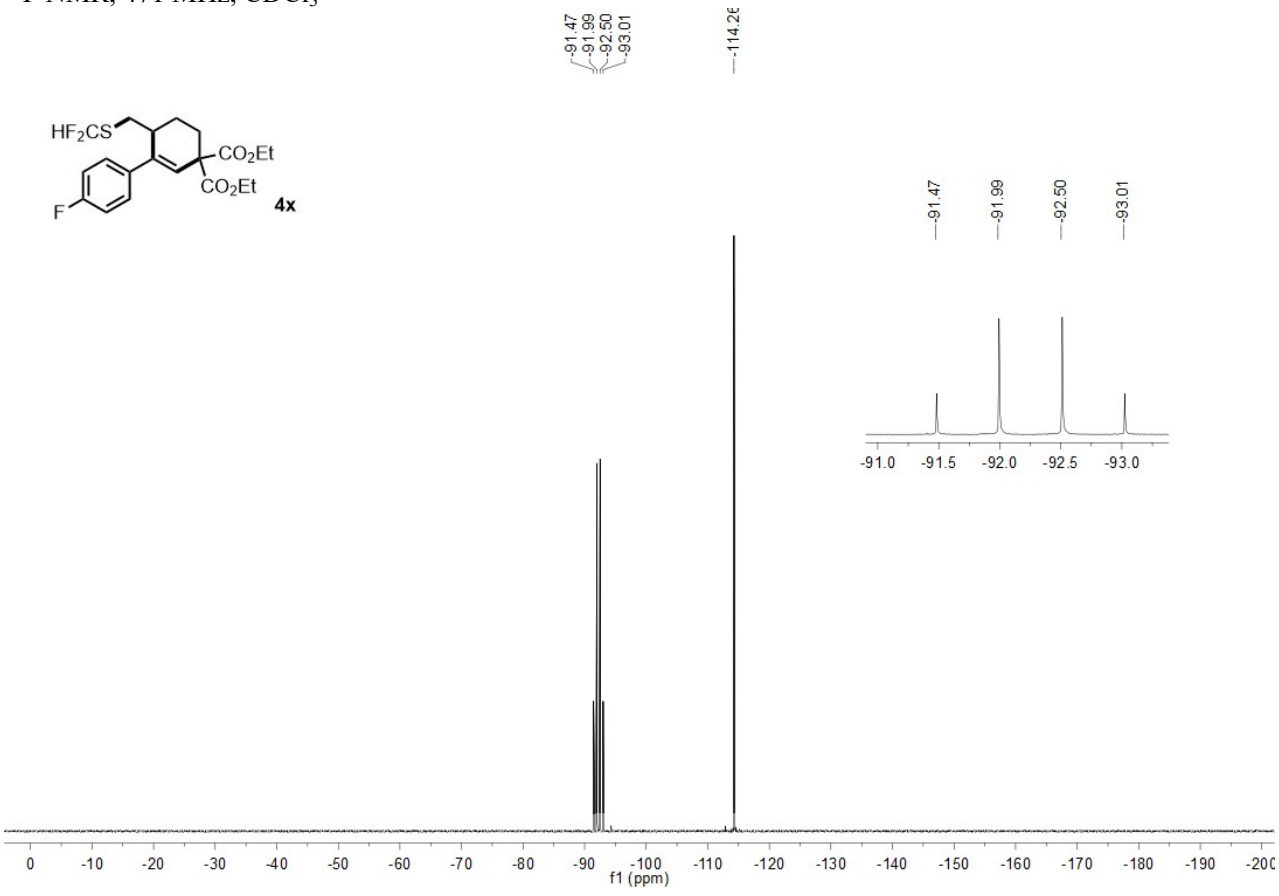
^{1}H NMR, 600 MHz, $CDCl_3$



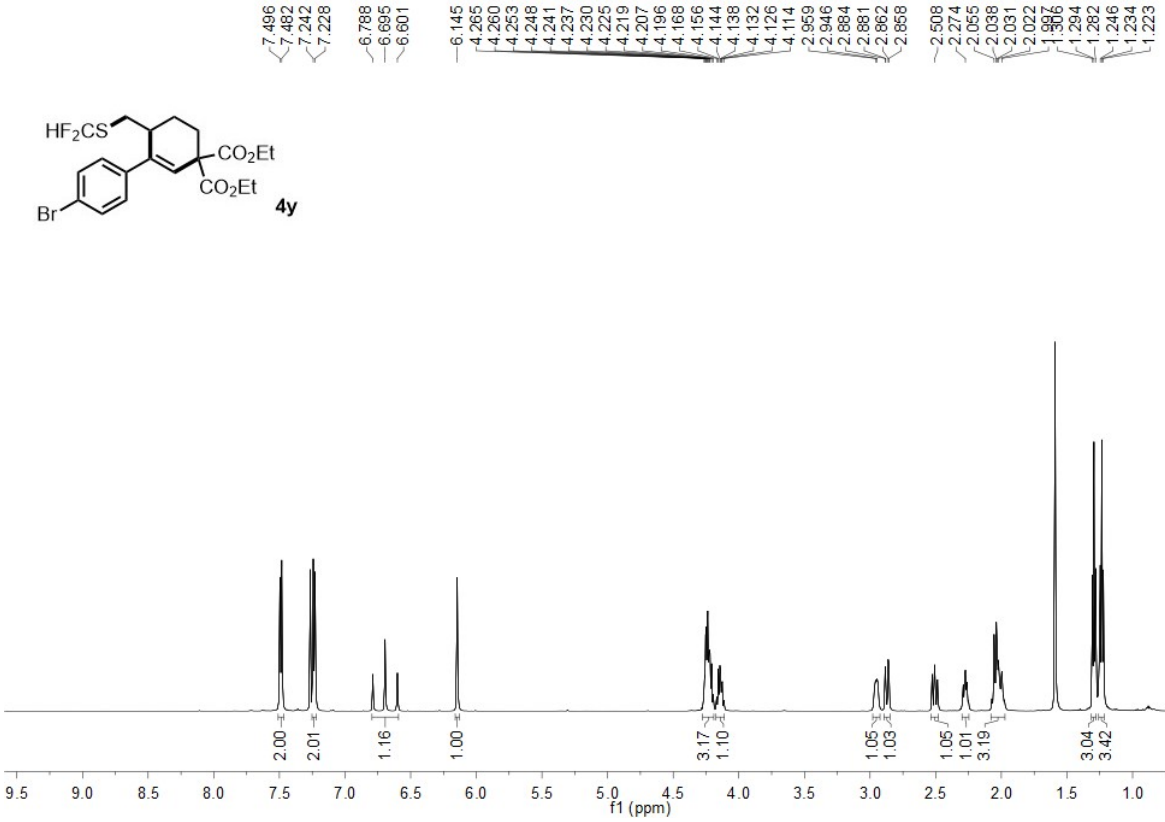
^{13}C NMR, 151 MHz, $CDCl_3$



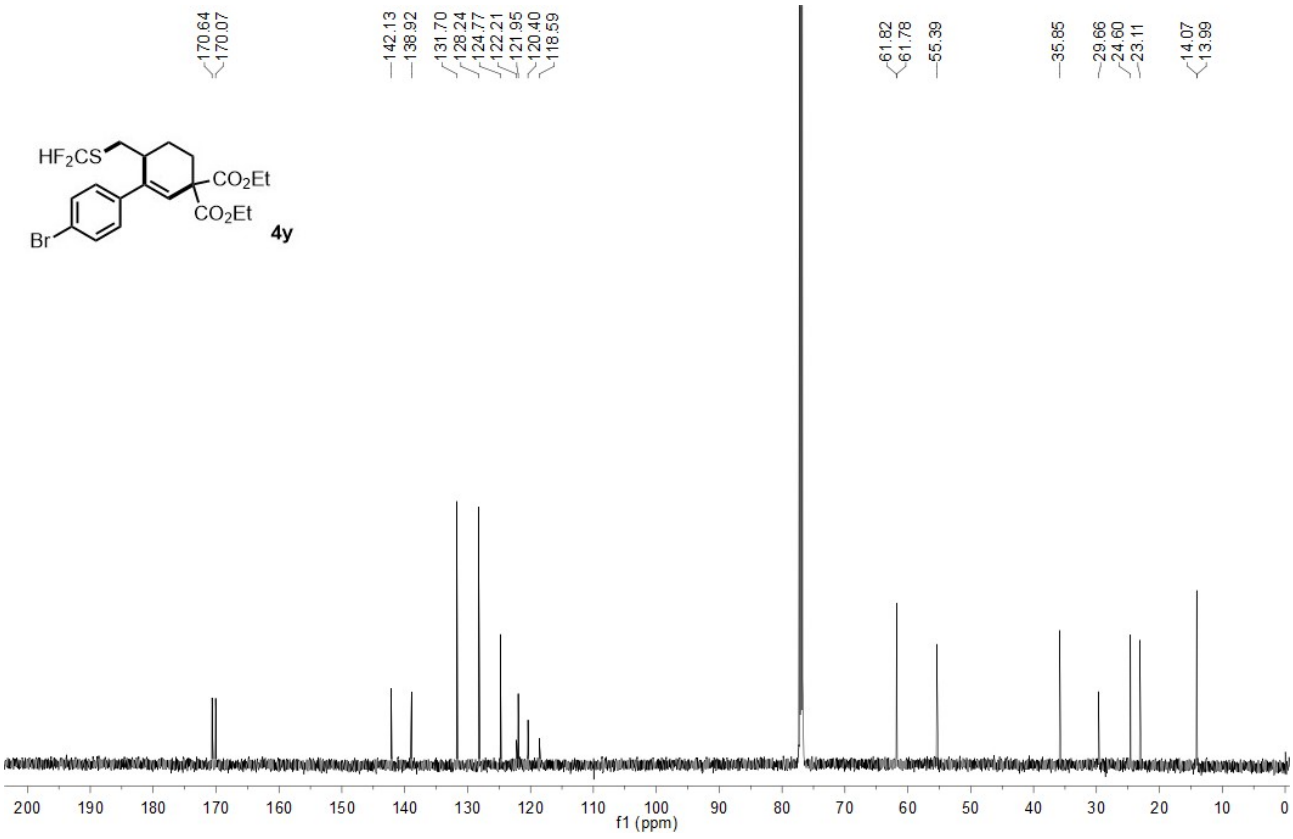
^{19}F NMR, 471 MHz, $CDCl_3$



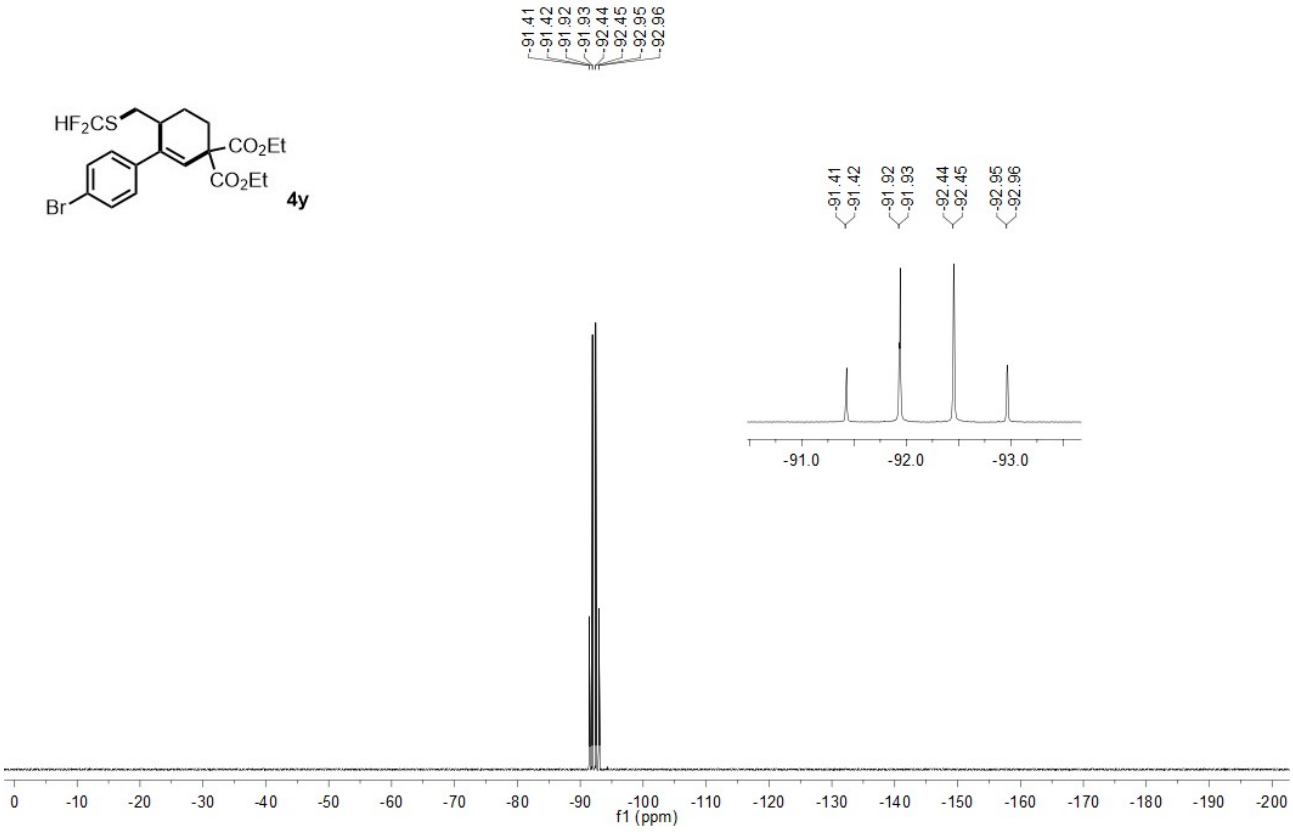
^{1}H NMR, 600 MHz, $CDCl_3$



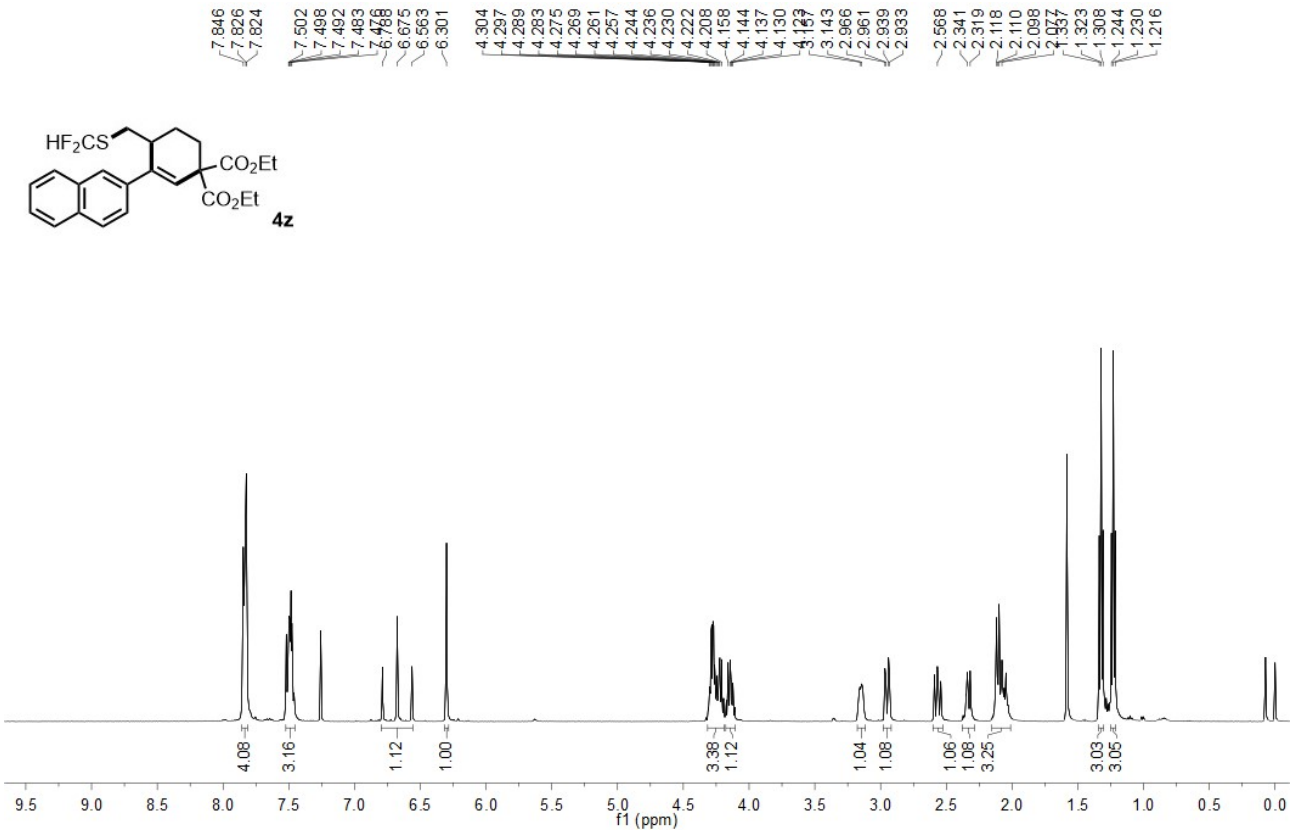
^{13}C NMR, 151 MHz, $CDCl_3$



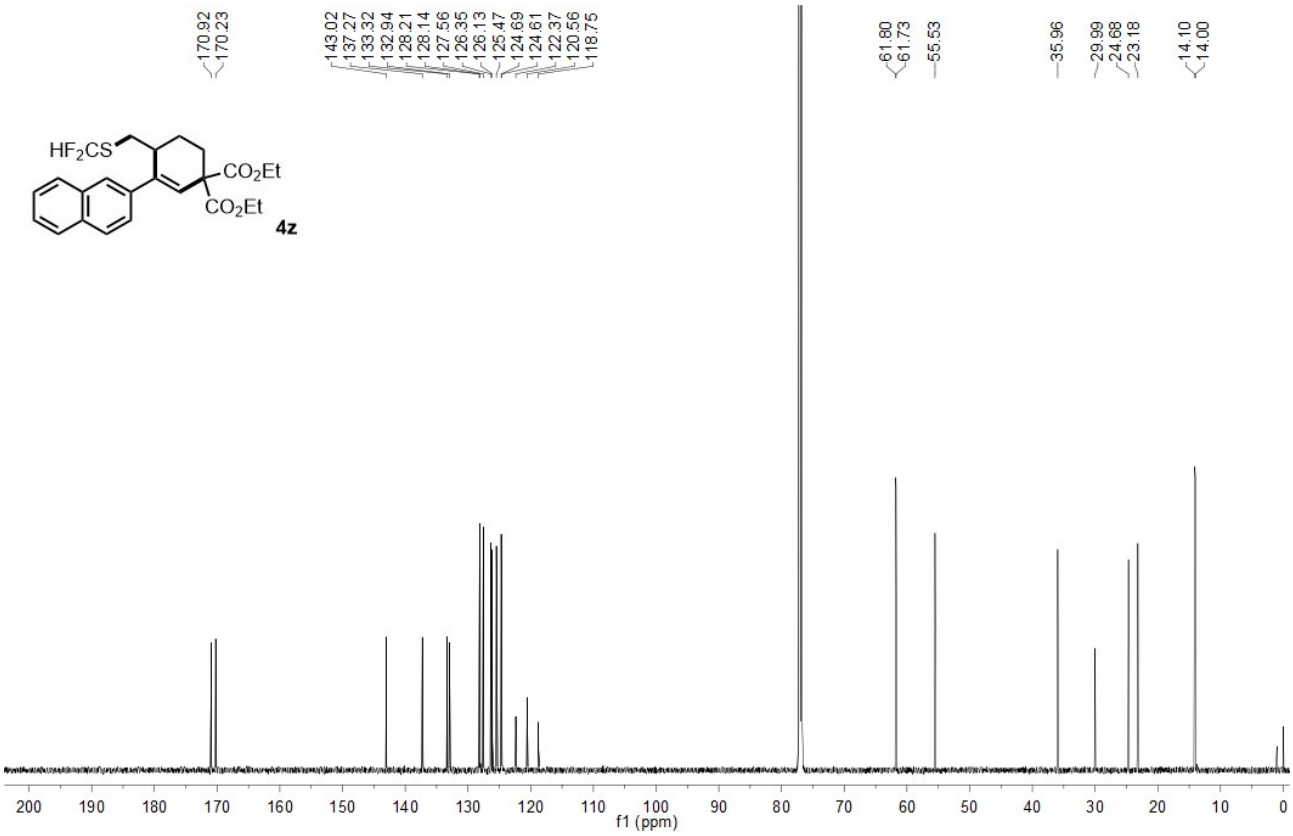
^{19}F NMR, 471 MHz, $CDCl_3$



^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 151 MHz, $CDCl_3$



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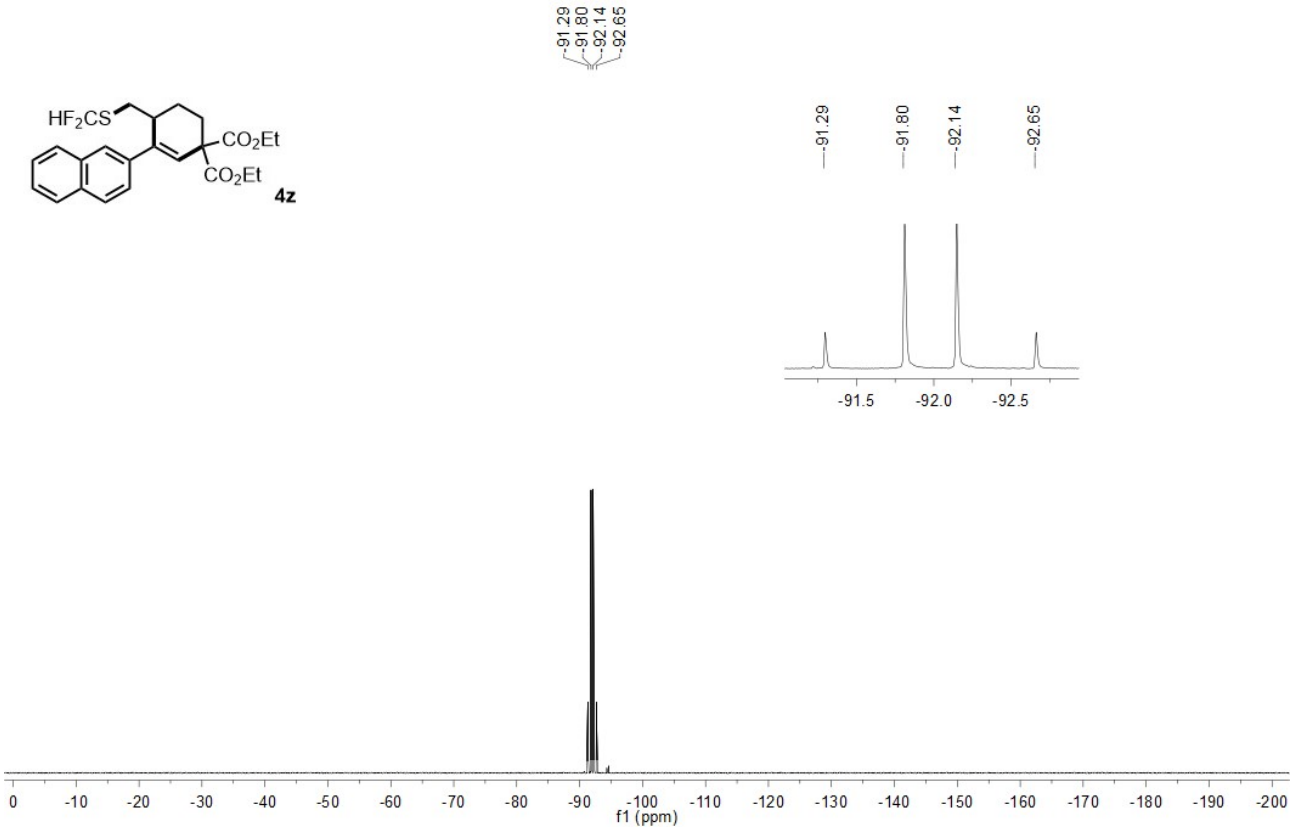

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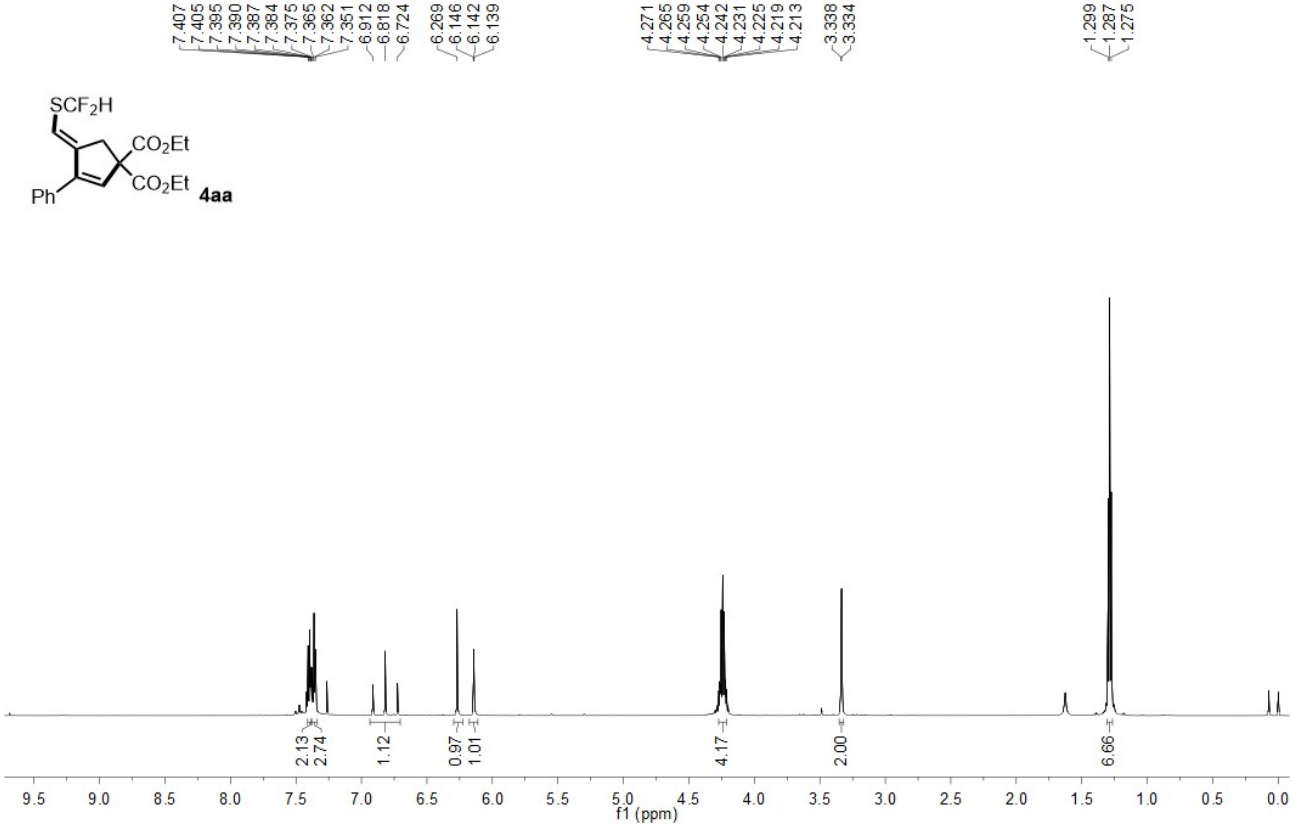
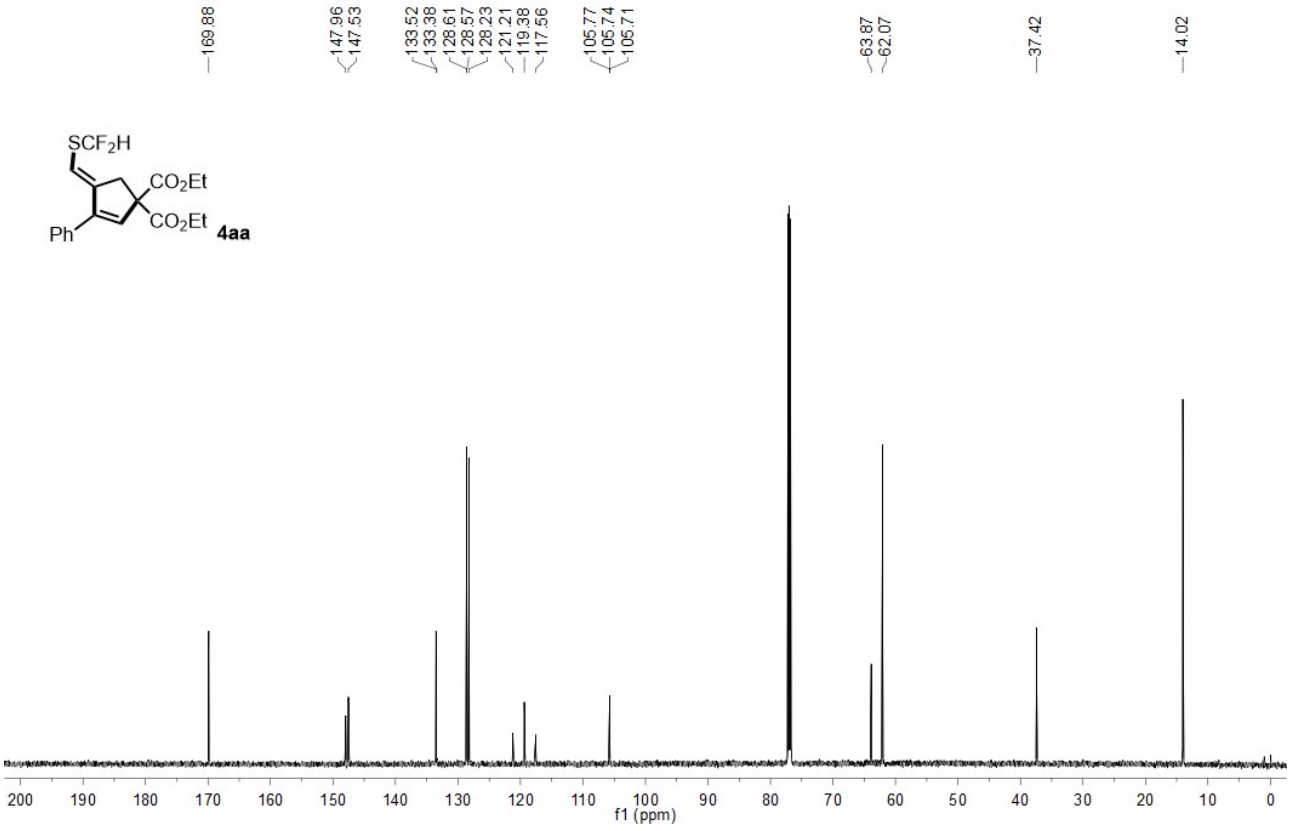
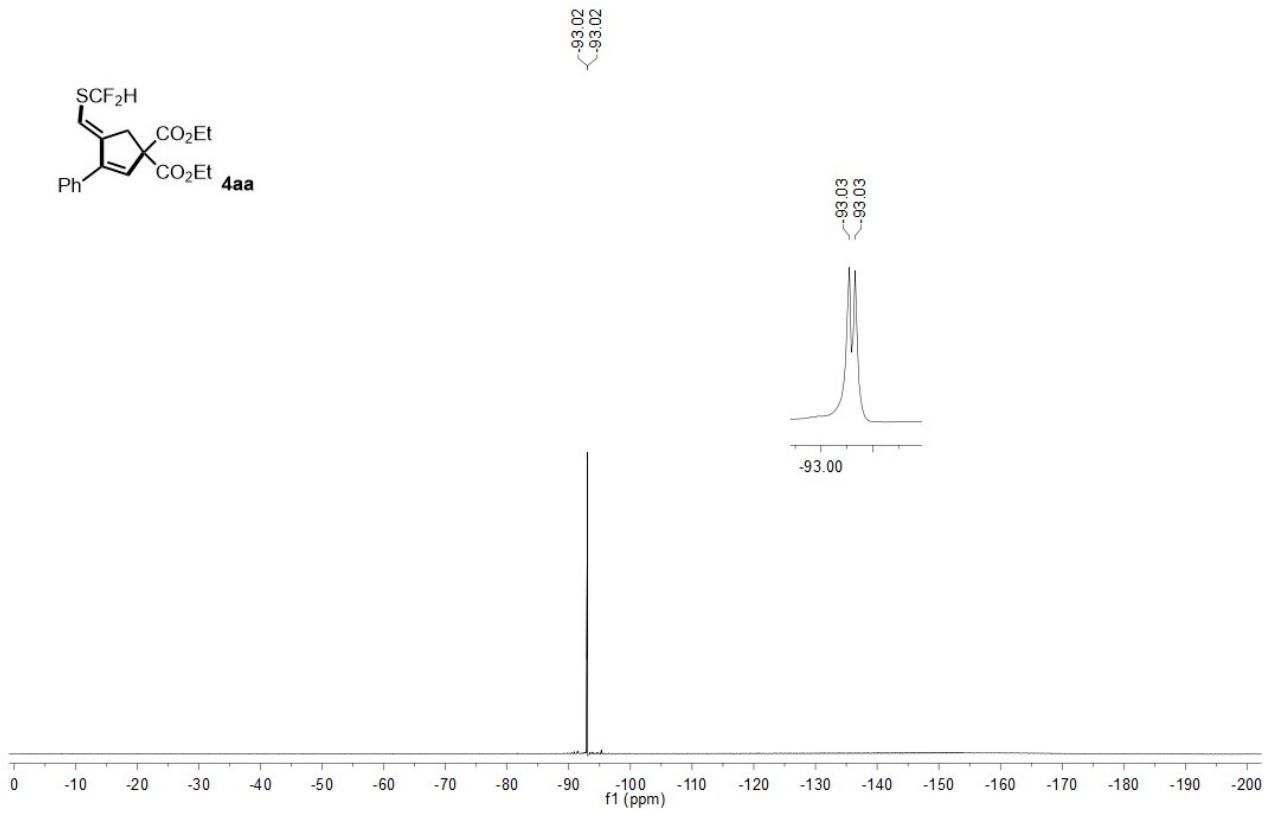


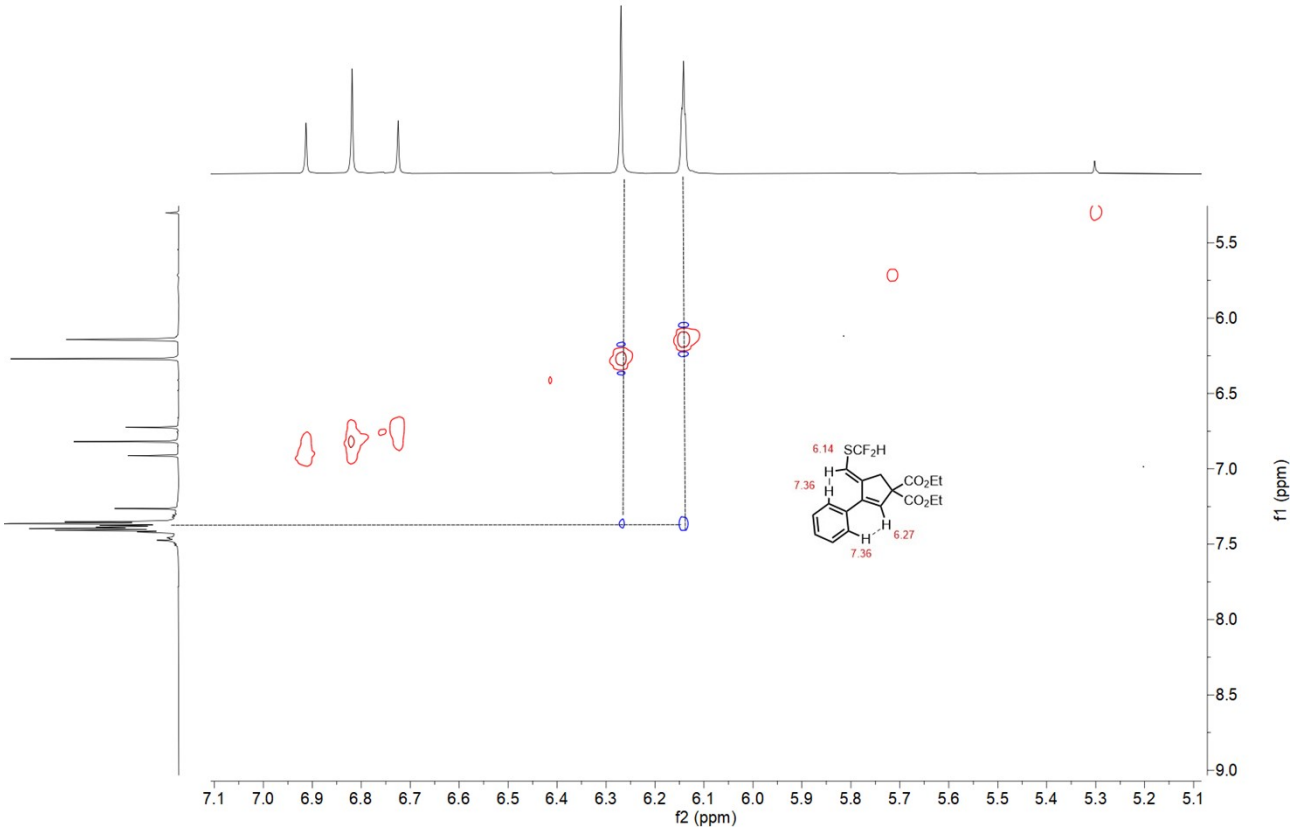
^{13}C NMR, 151 MHz, $CDCl_3$

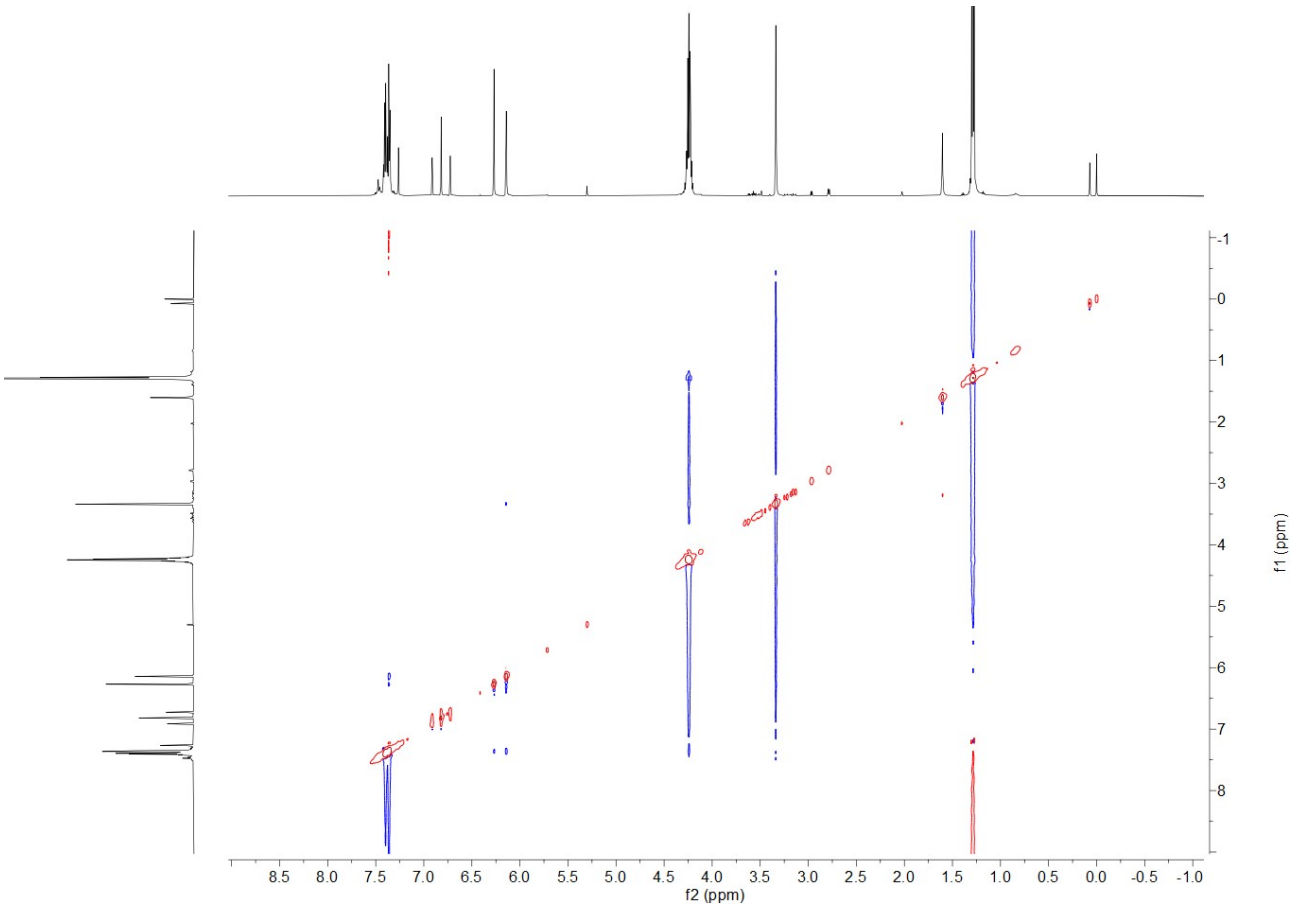


^{19}F NMR, 471 MHz, $CDCl_3$

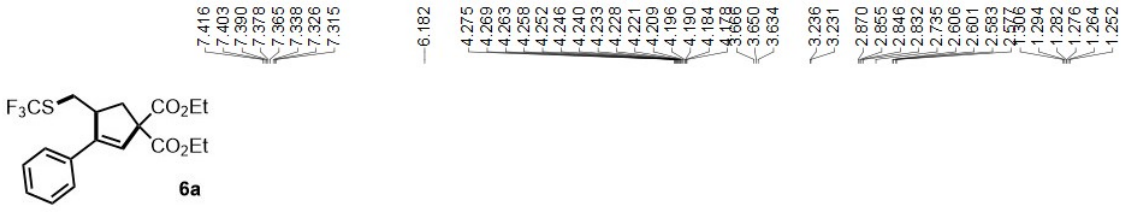


NOESY, 600 MHz, $CDCl_3$

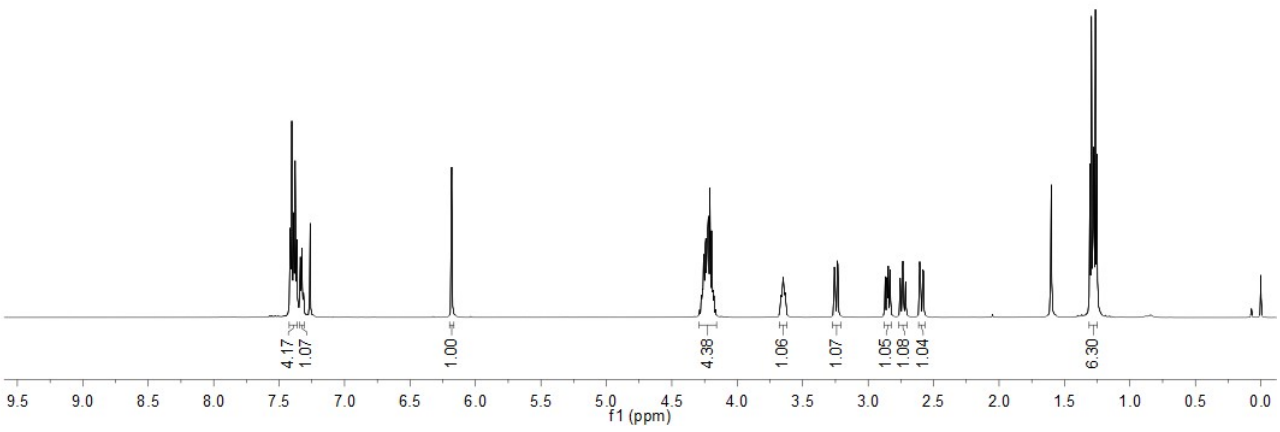




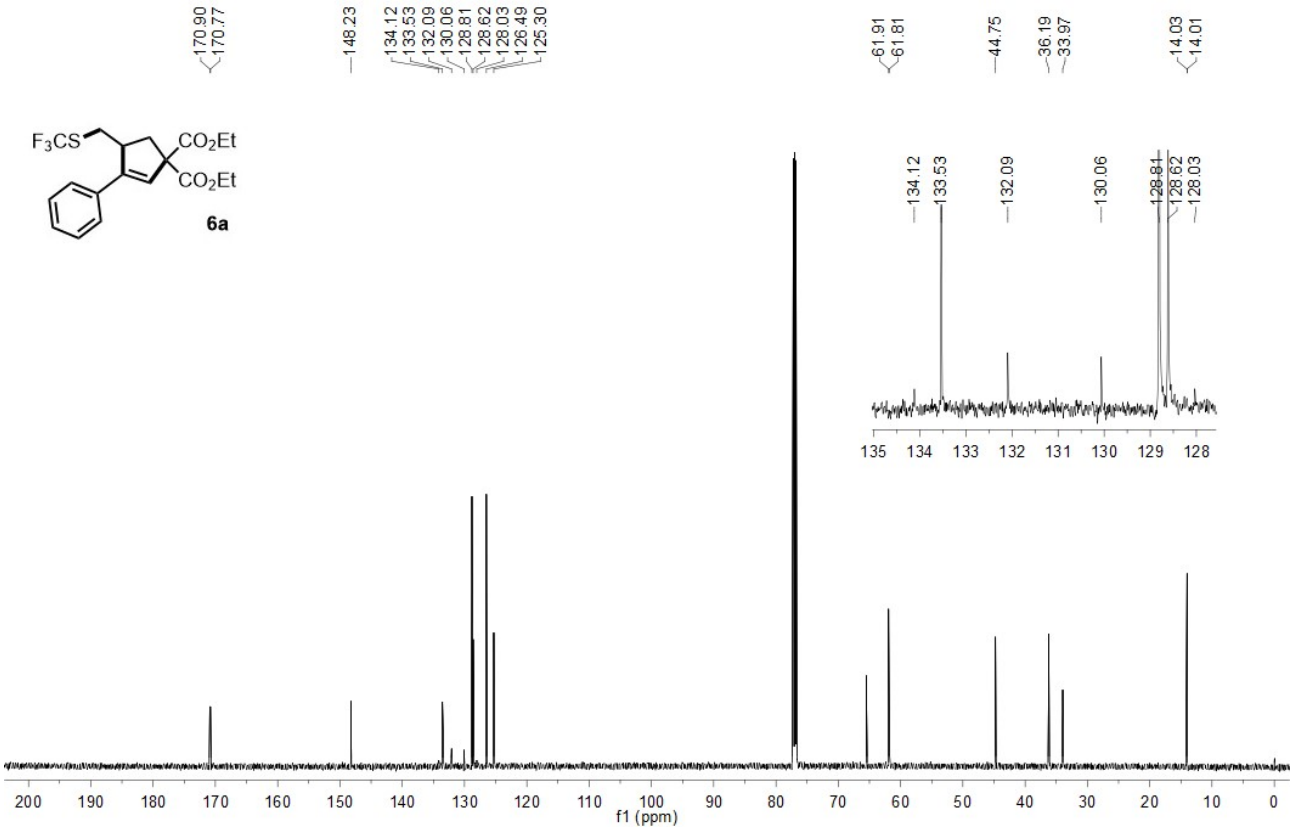
^{1}H NMR, 600 MHz, $CDCl_3$



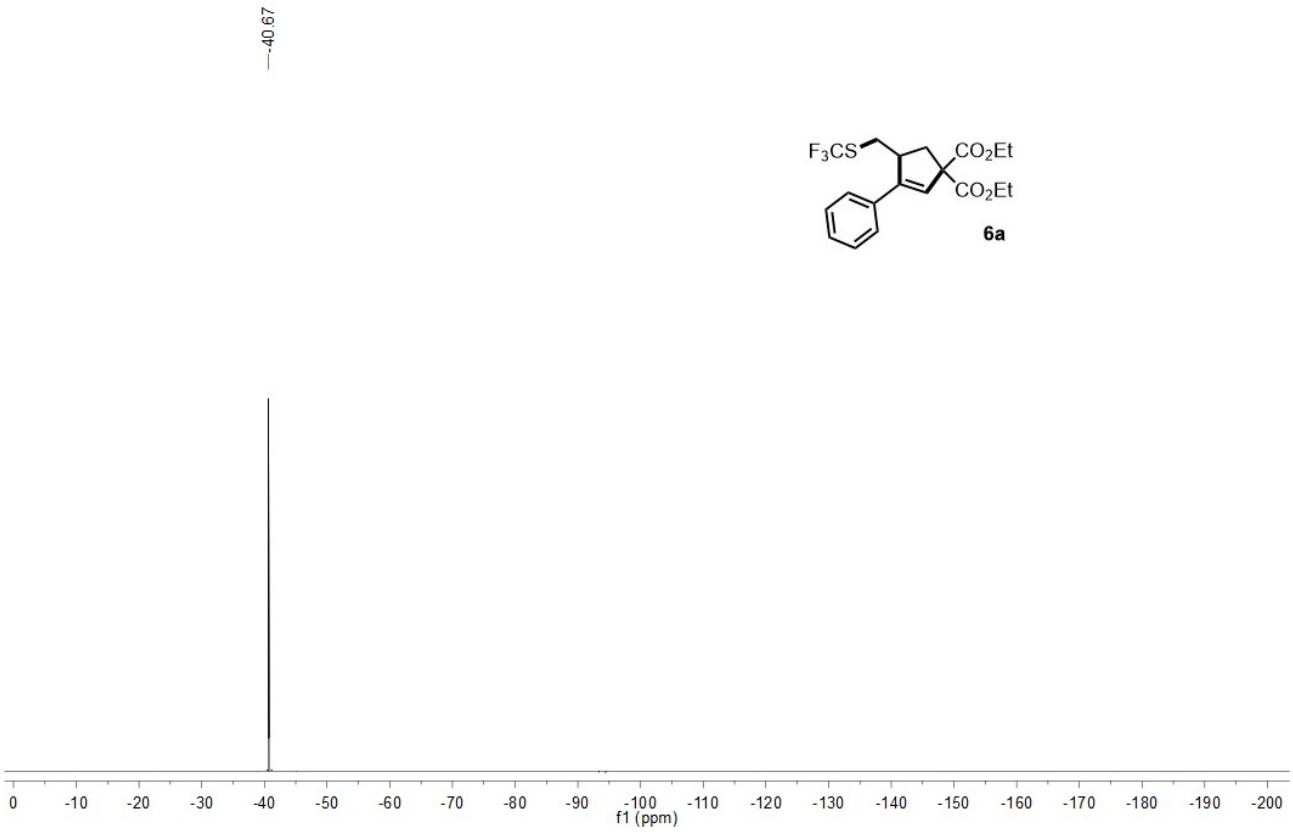
6a



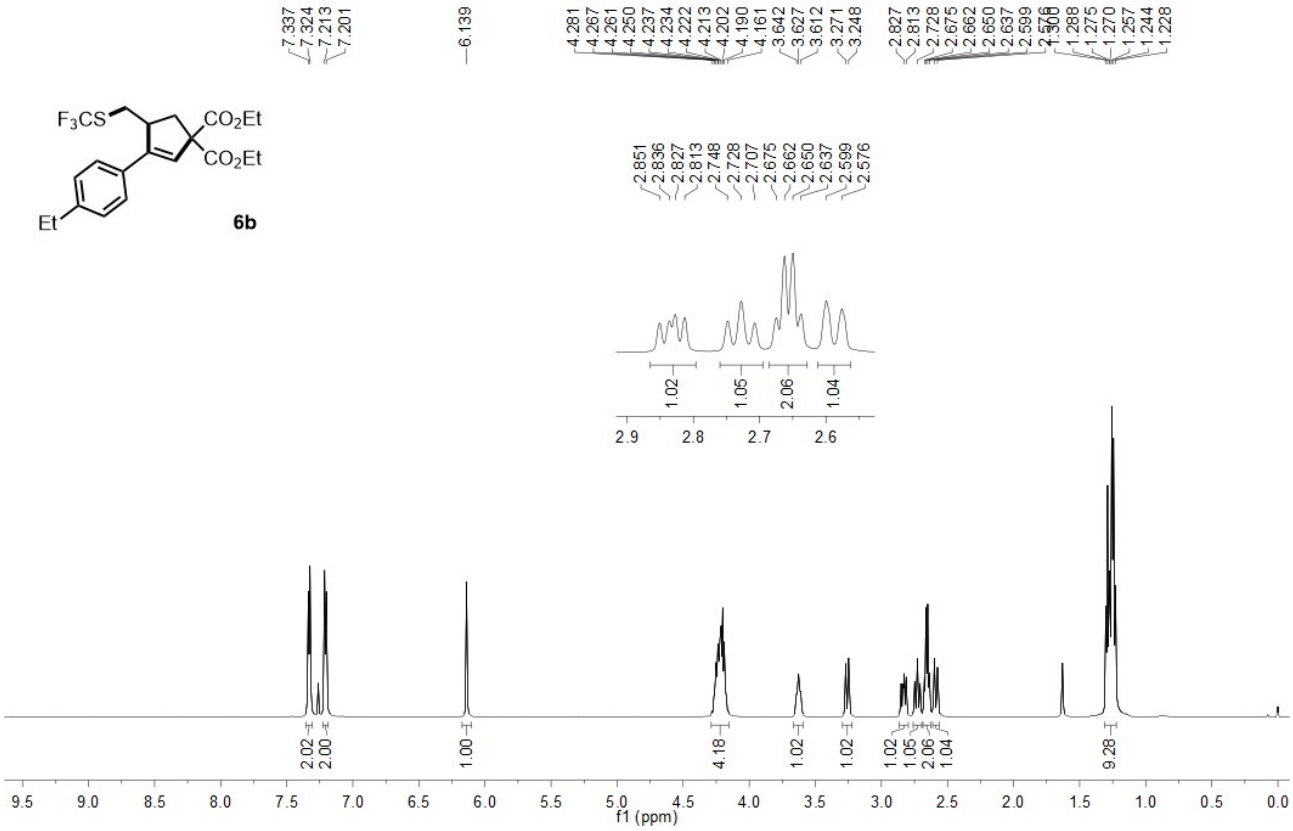
^{13}C NMR, 151 MHz, $CDCl_3$



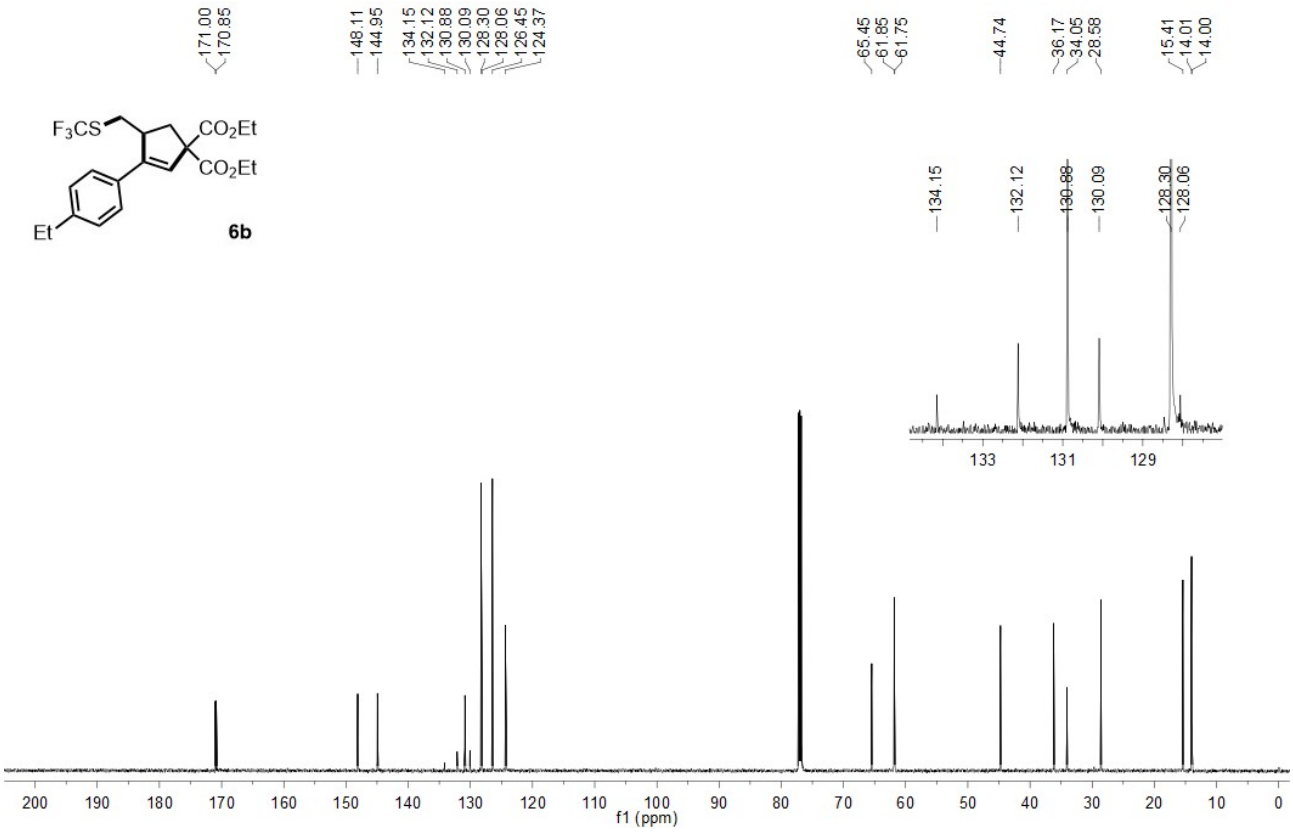
^{19}F NMR, 471 MHz, $CDCl_3$



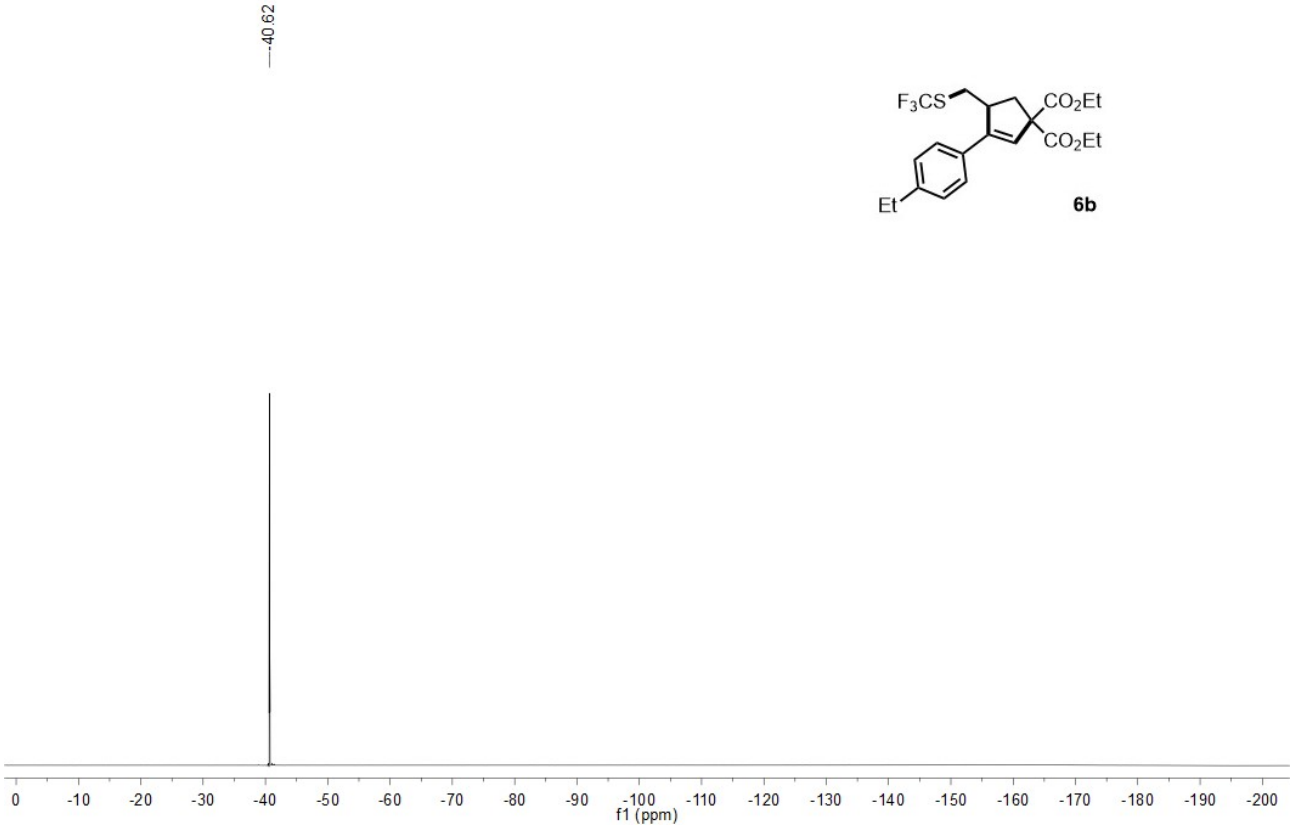
^{1}H NMR, 600 MHz, $CDCl_3$



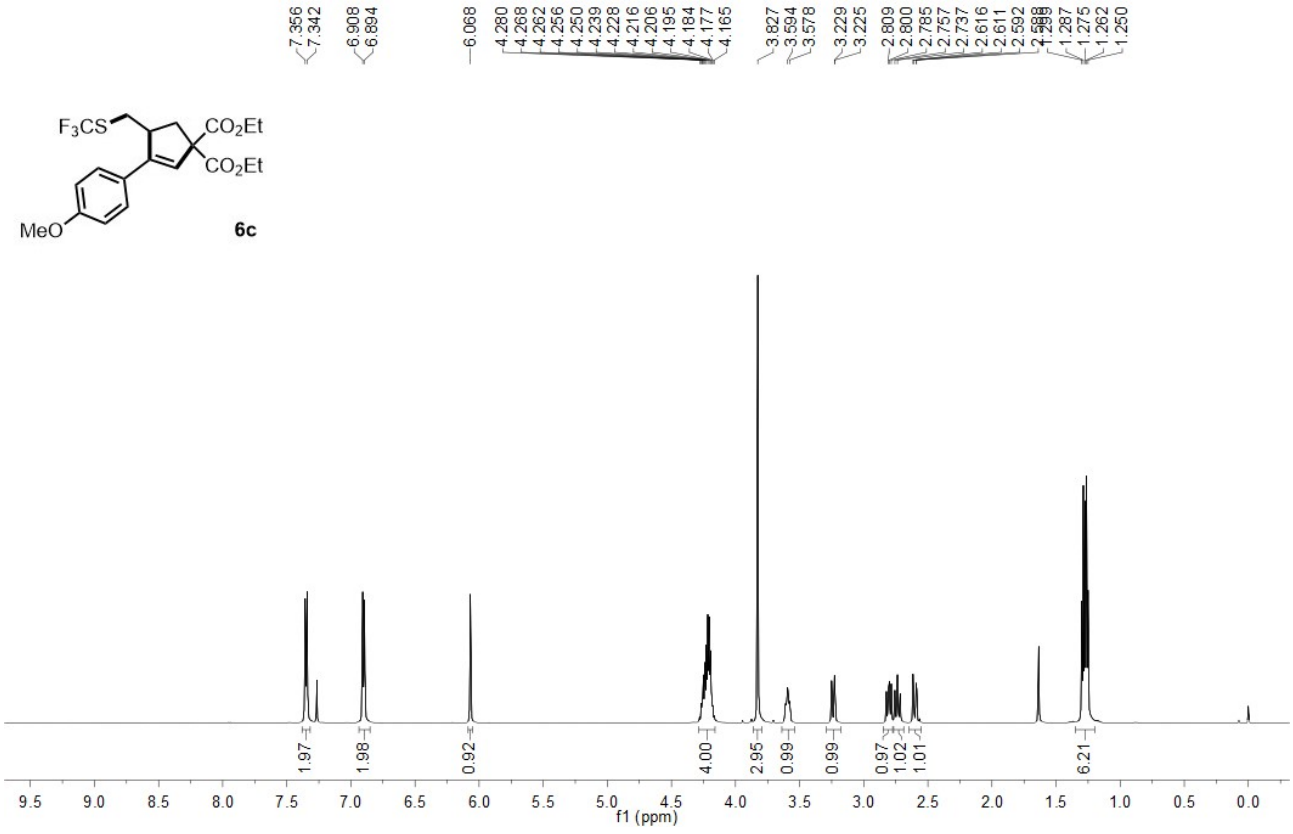
^{13}C NMR, 151 MHz, $CDCl_3$



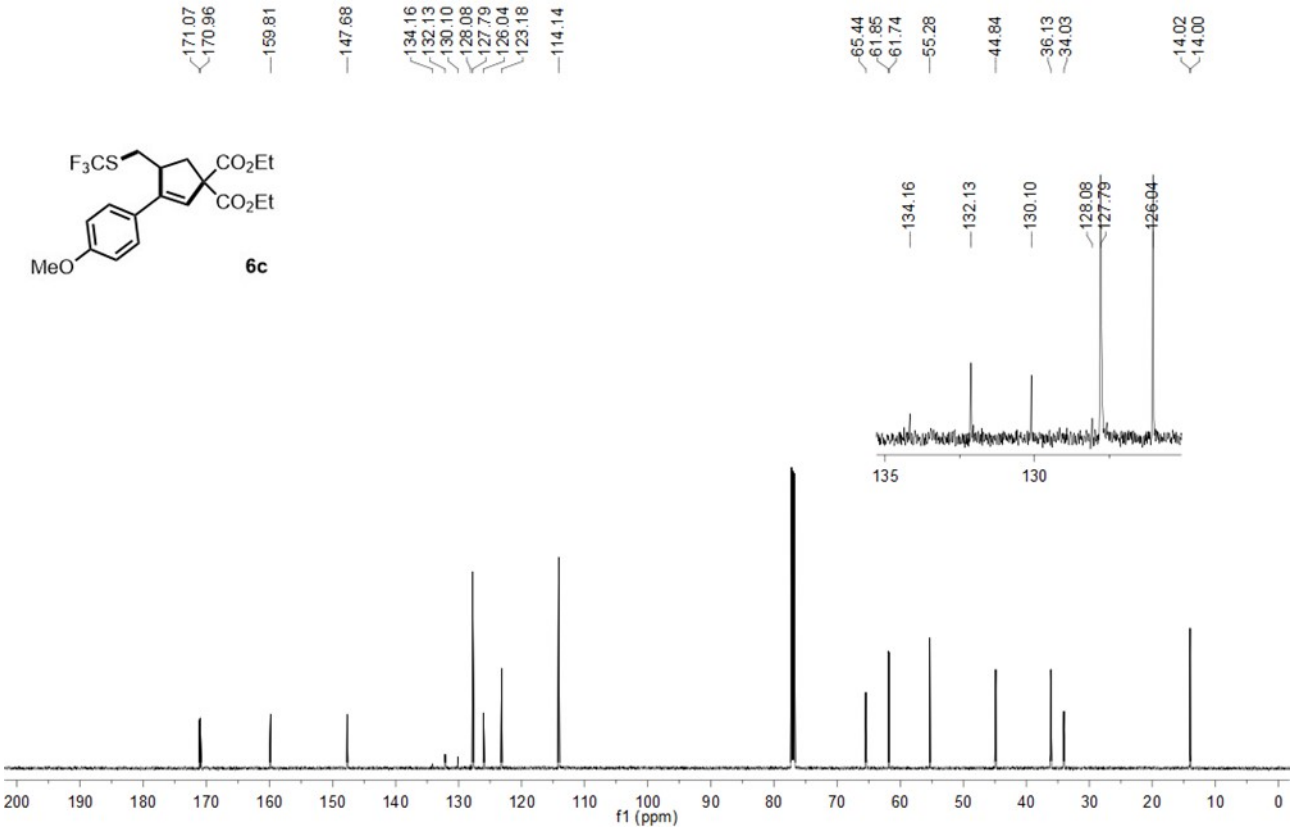
^{19}F NMR, 471 MHz, $CDCl_3$



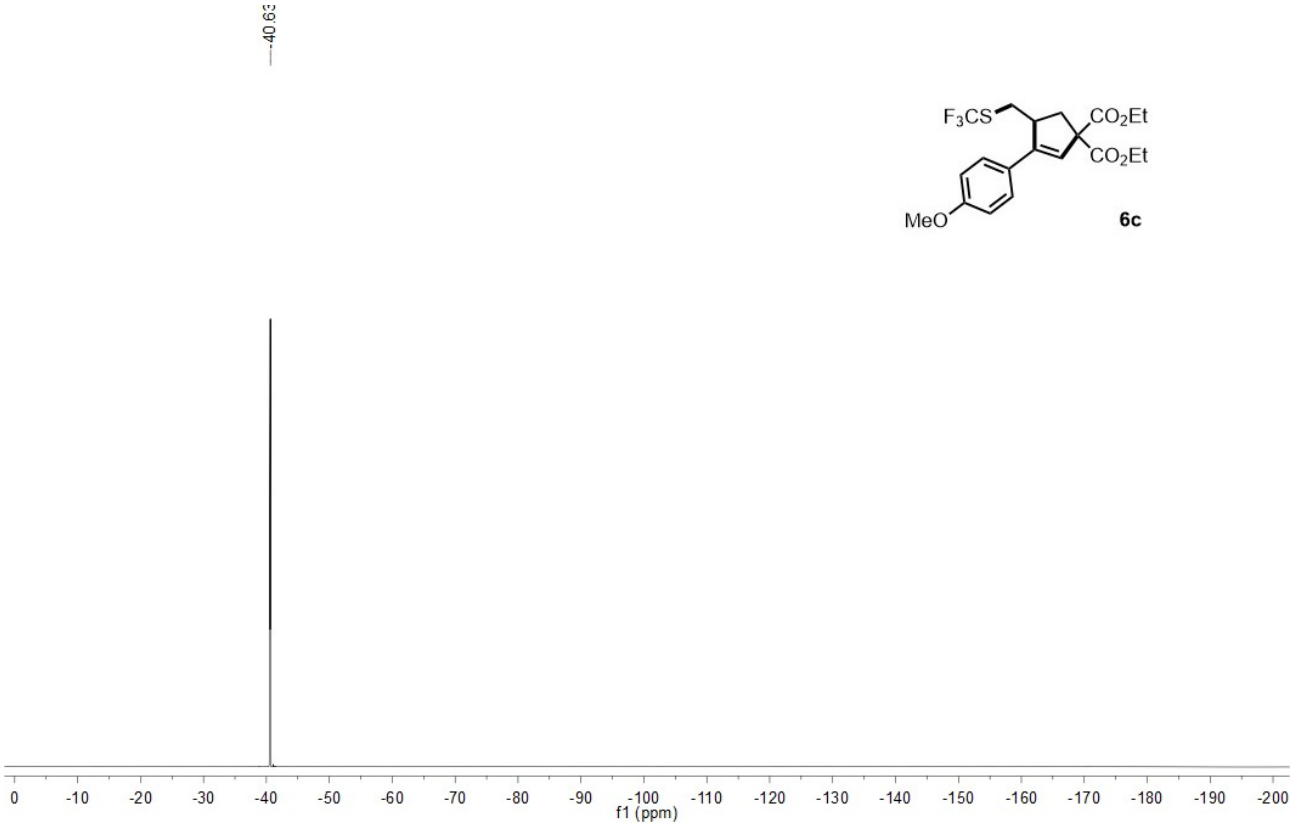
^{1}H NMR, 600 MHz, $CDCl_3$



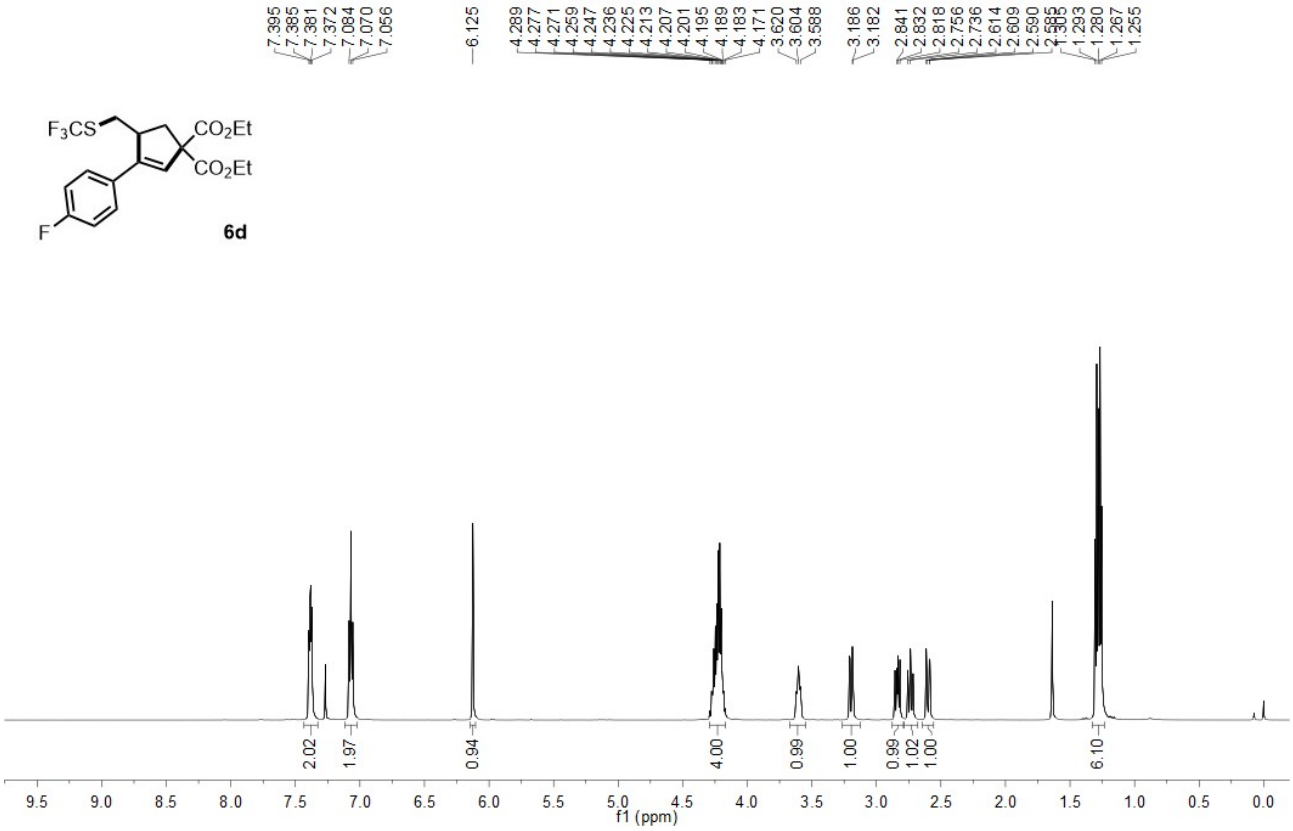
^{13}C NMR, 151 MHz, $CDCl_3$



^{19}F NMR, 471 MHz, $CDCl_3$



^{1}H NMR, 600 MHz, $CDCl_3$



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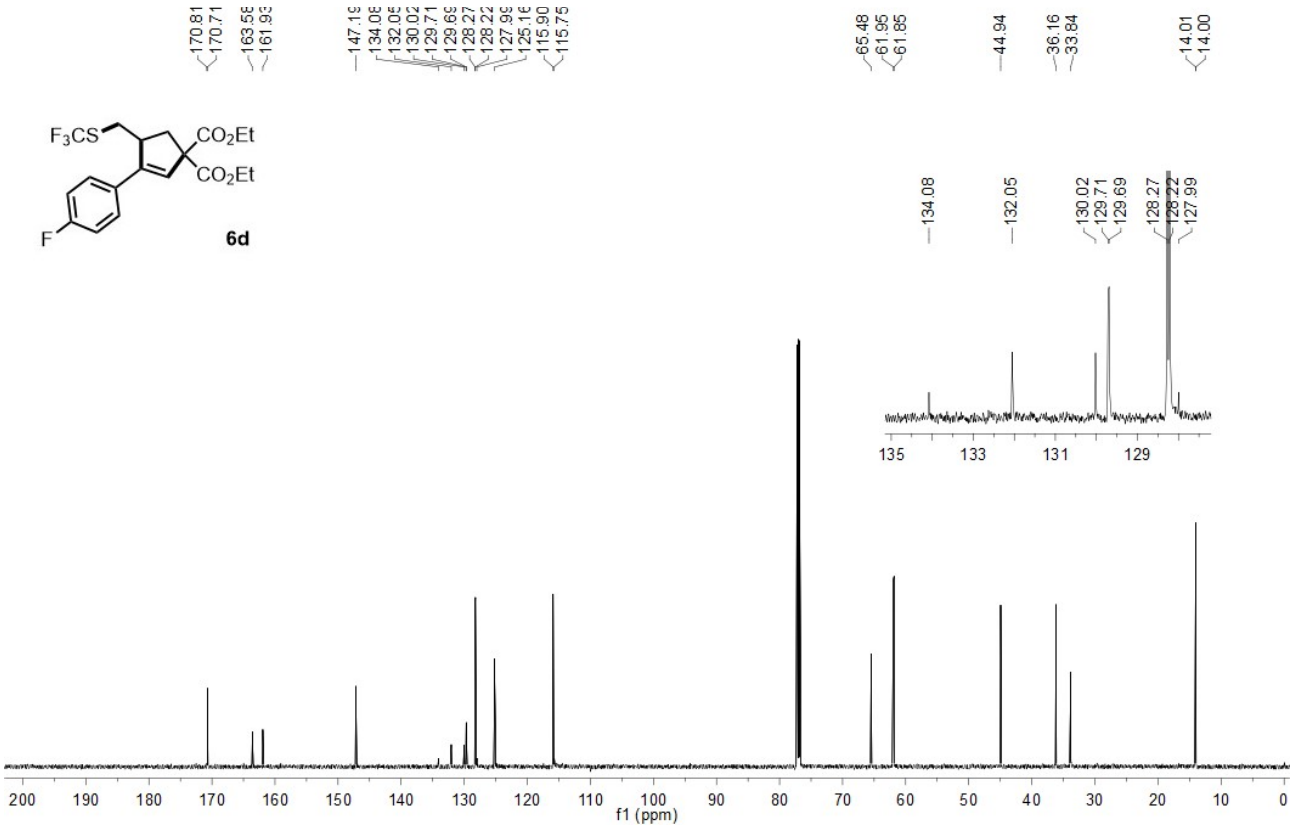
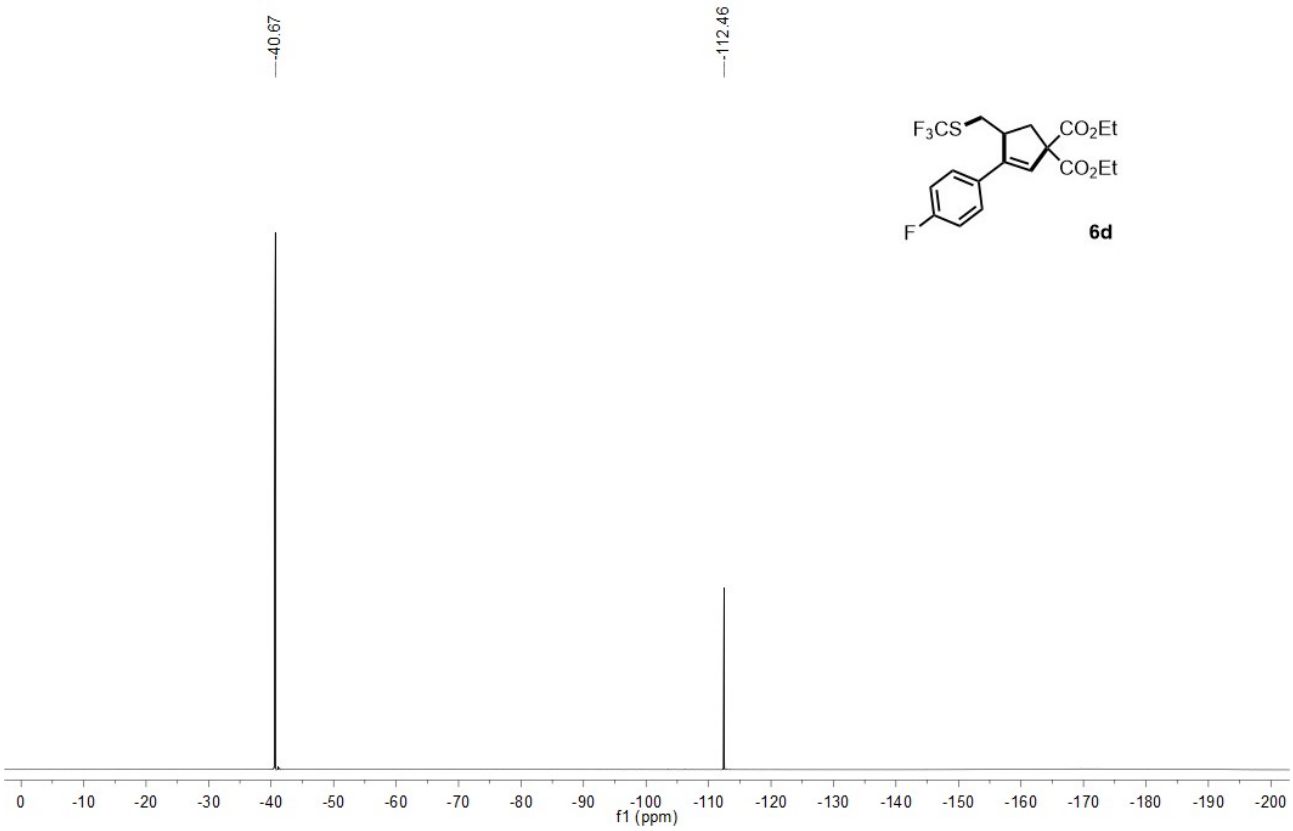
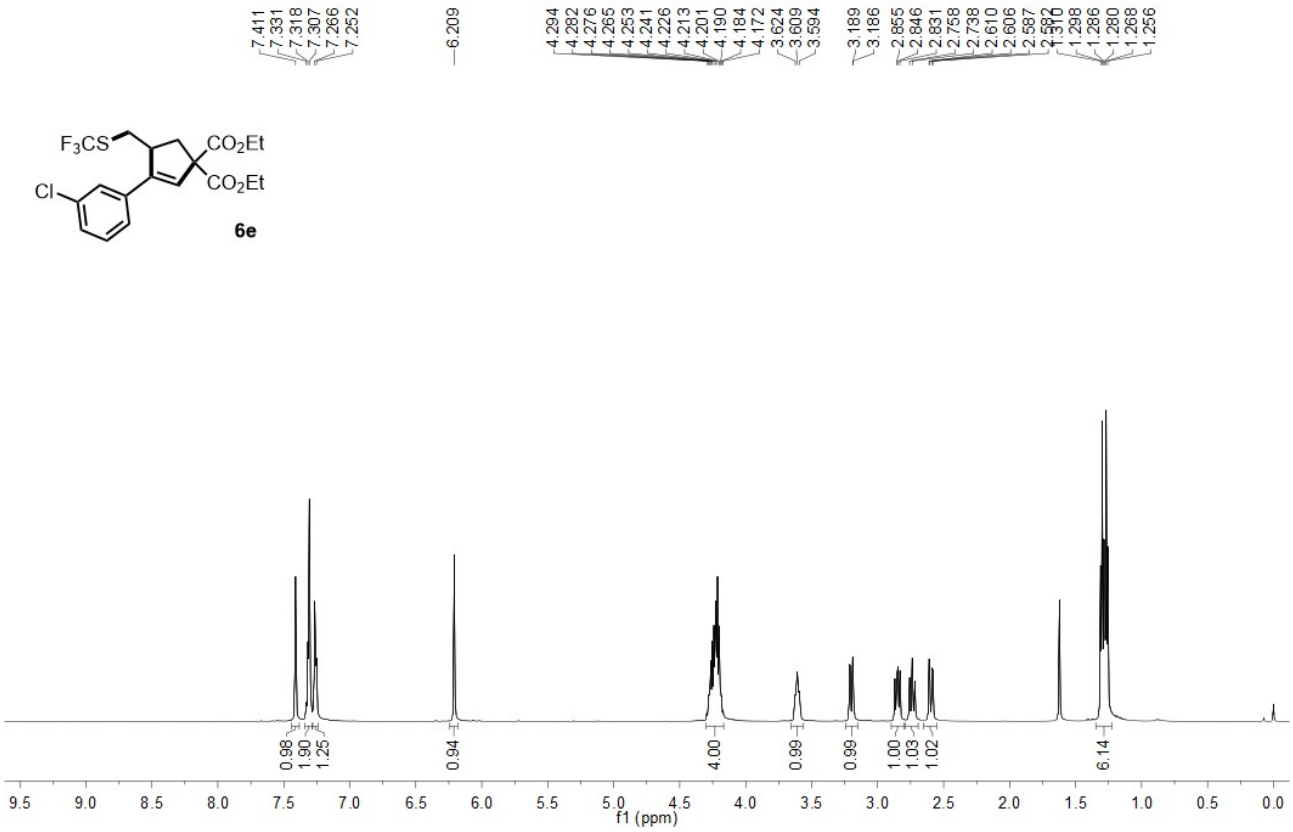


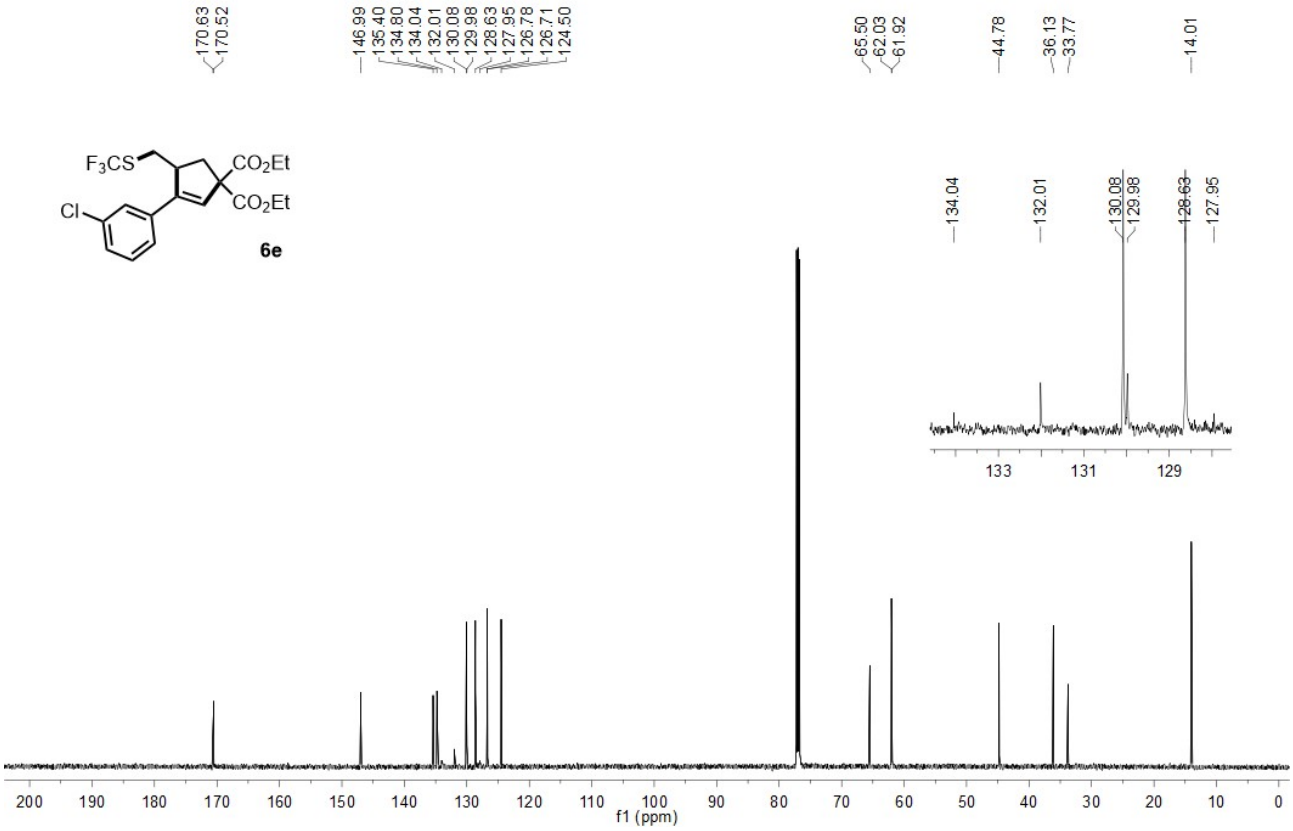
^{19}F NMR, 471 MHz, $CDCl_3$



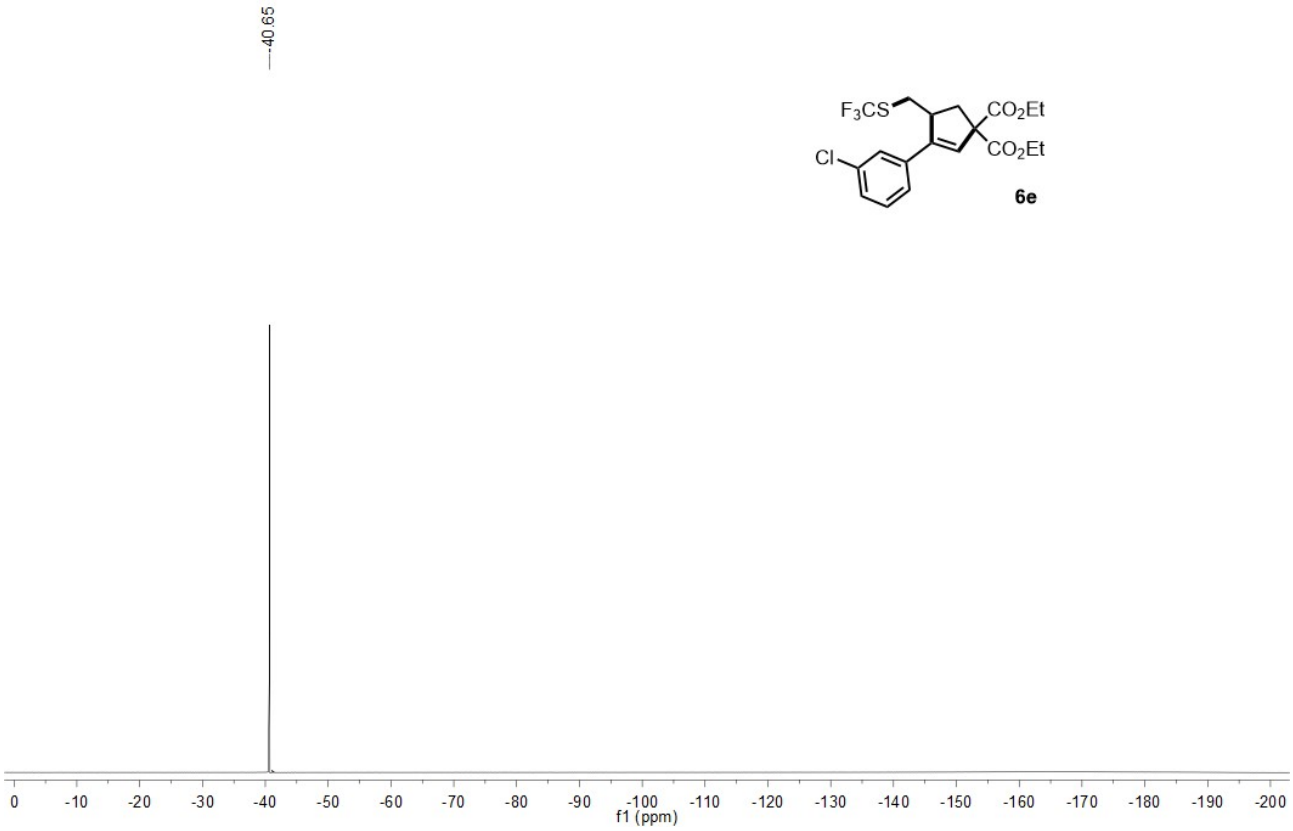
^{1}H NMR, 600 MHz, $CDCl_3$



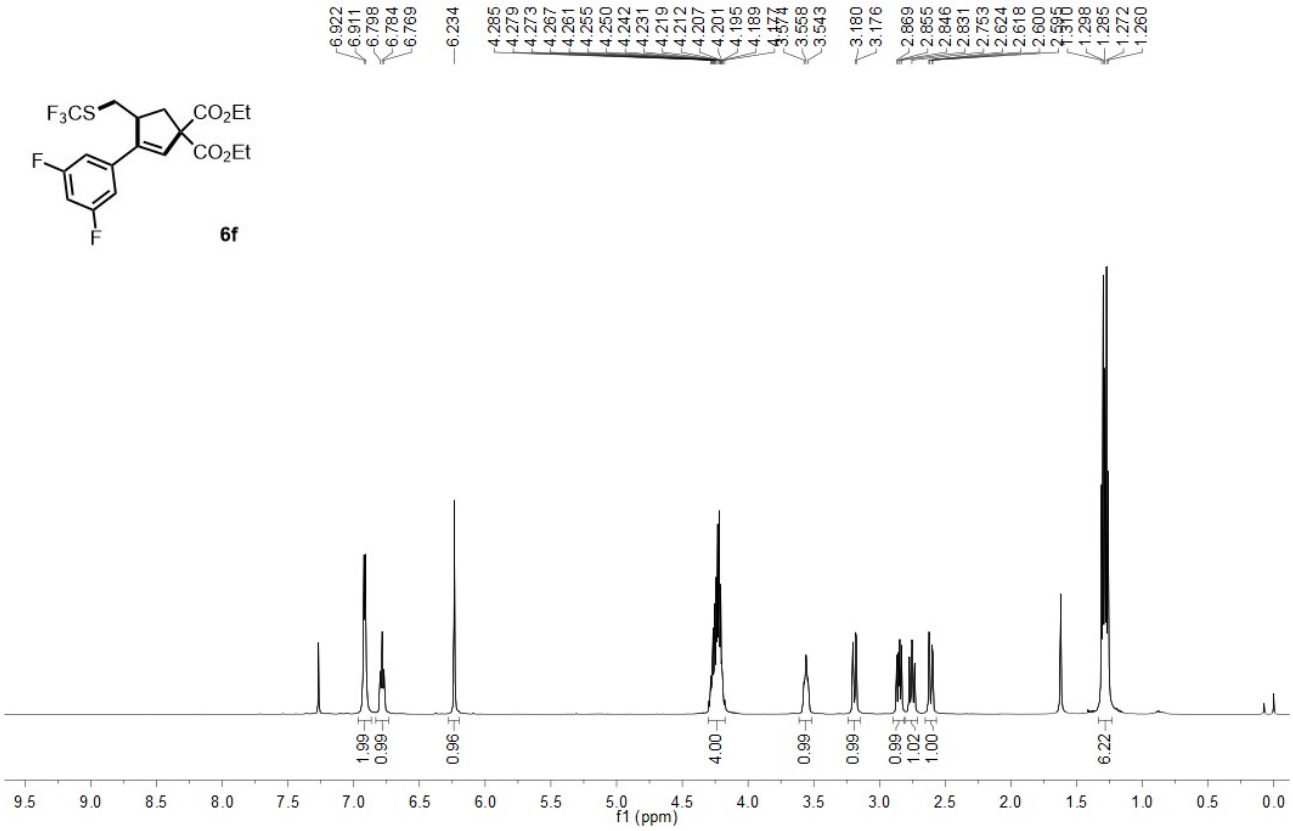
^{13}C NMR, 151 MHz, $CDCl_3$



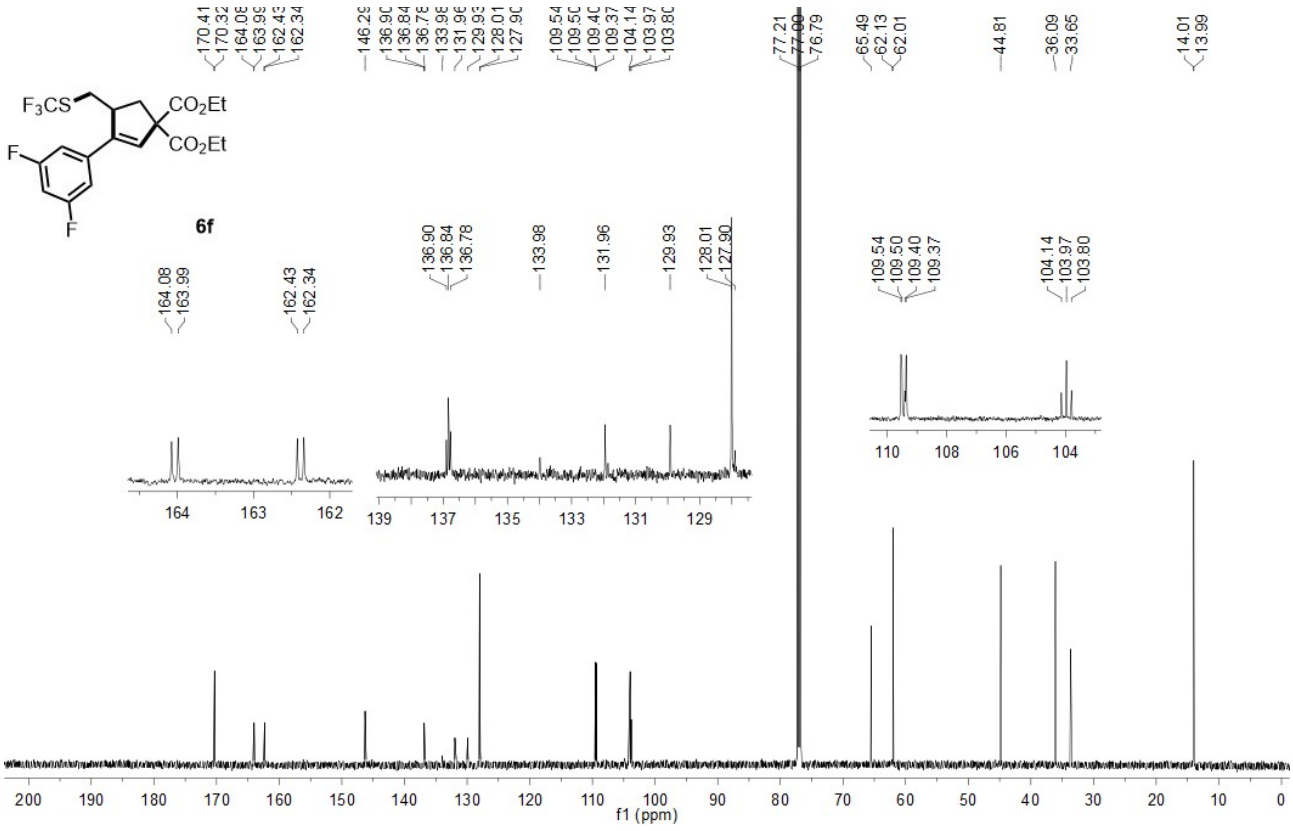
^{19}F NMR, 471 MHz, $CDCl_3$



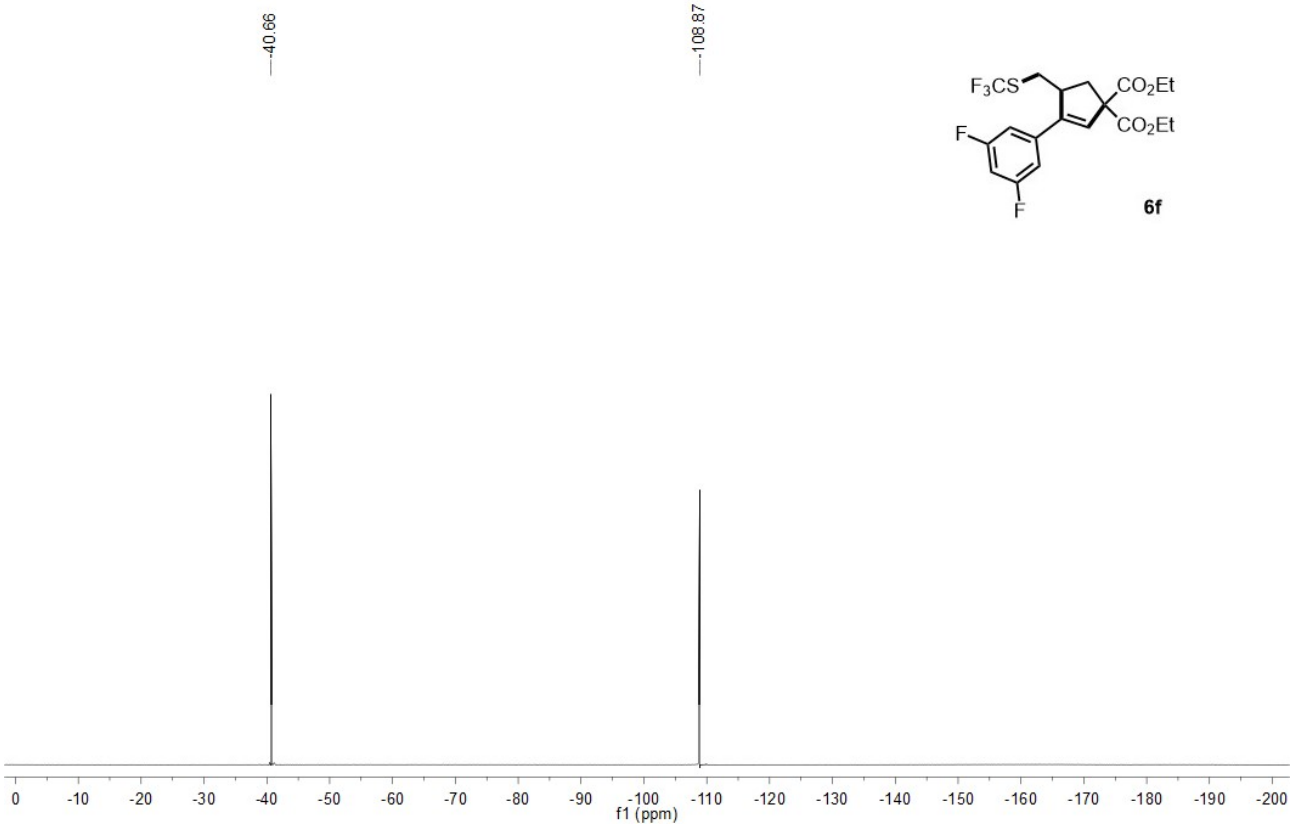
^{1}H NMR, 600 MHz, $CDCl_3$



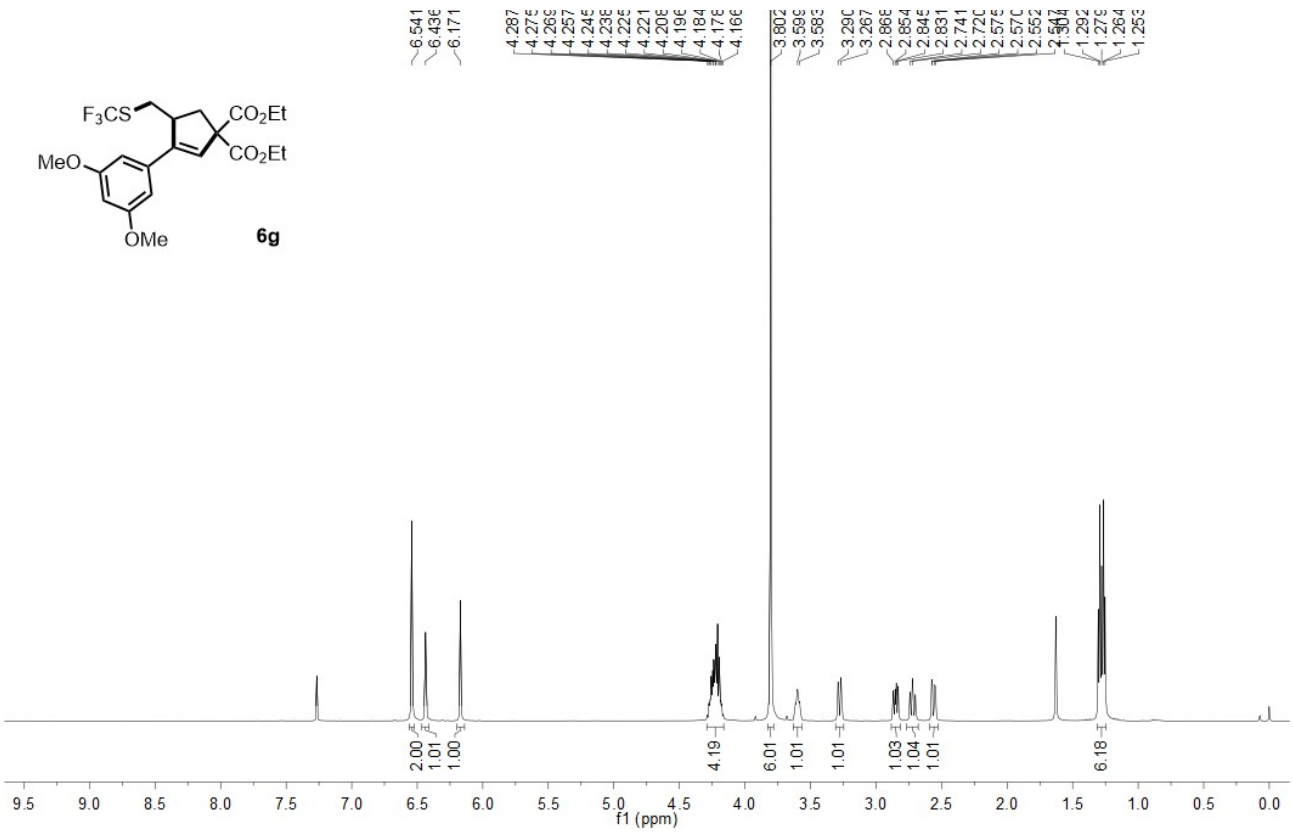
^{13}C NMR, 151 MHz, $CDCl_3$



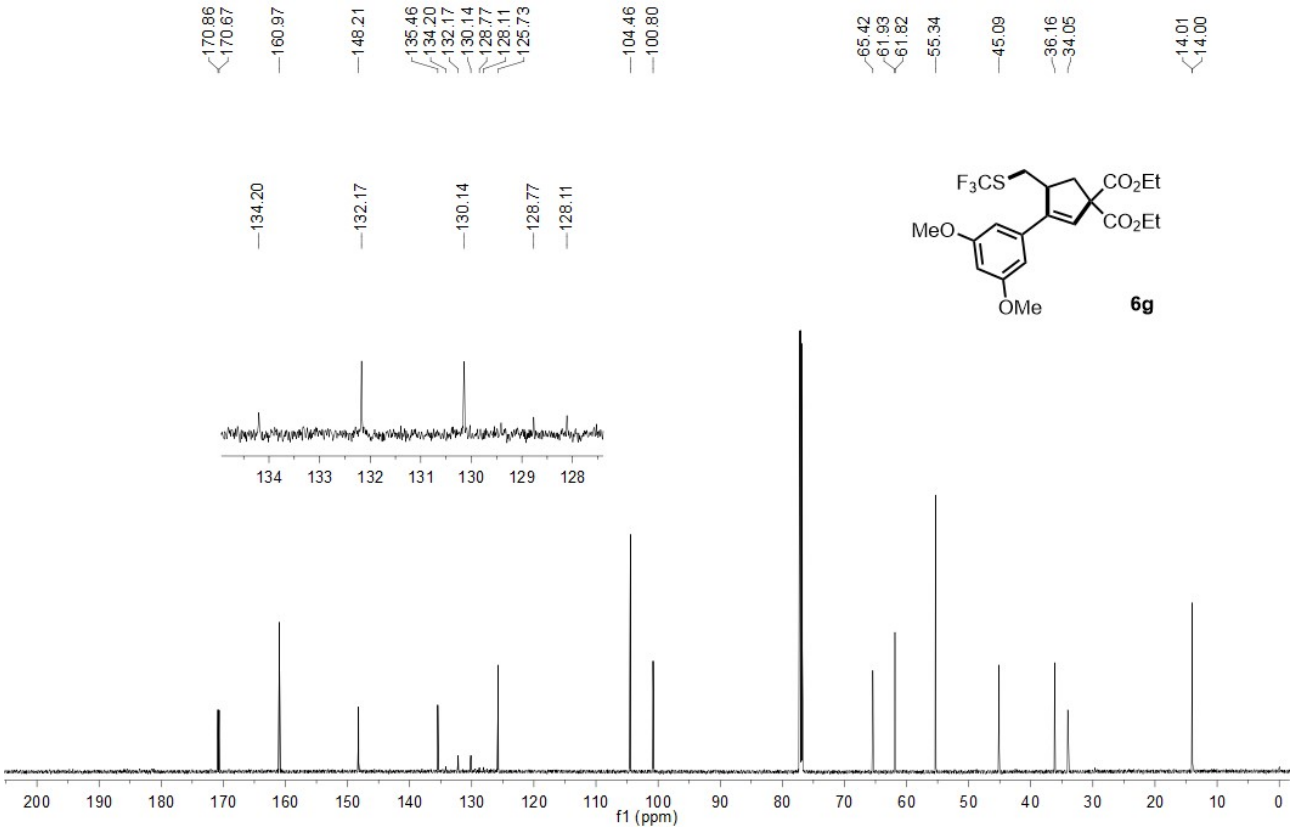
^{19}F NMR, 471 MHz, $CDCl_3$



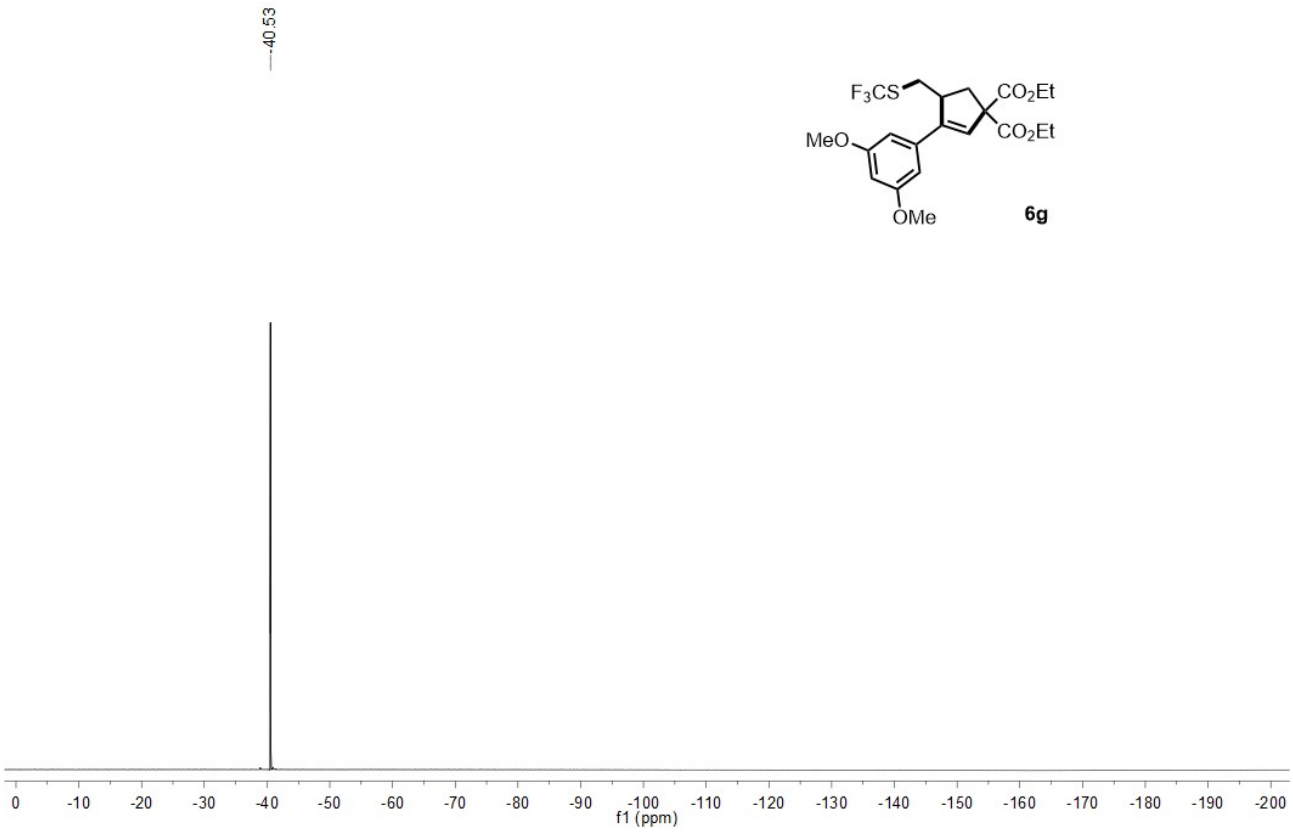
^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 151 MHz, $CDCl_3$



^{19}F NMR, 471 MHz, $CDCl_3$



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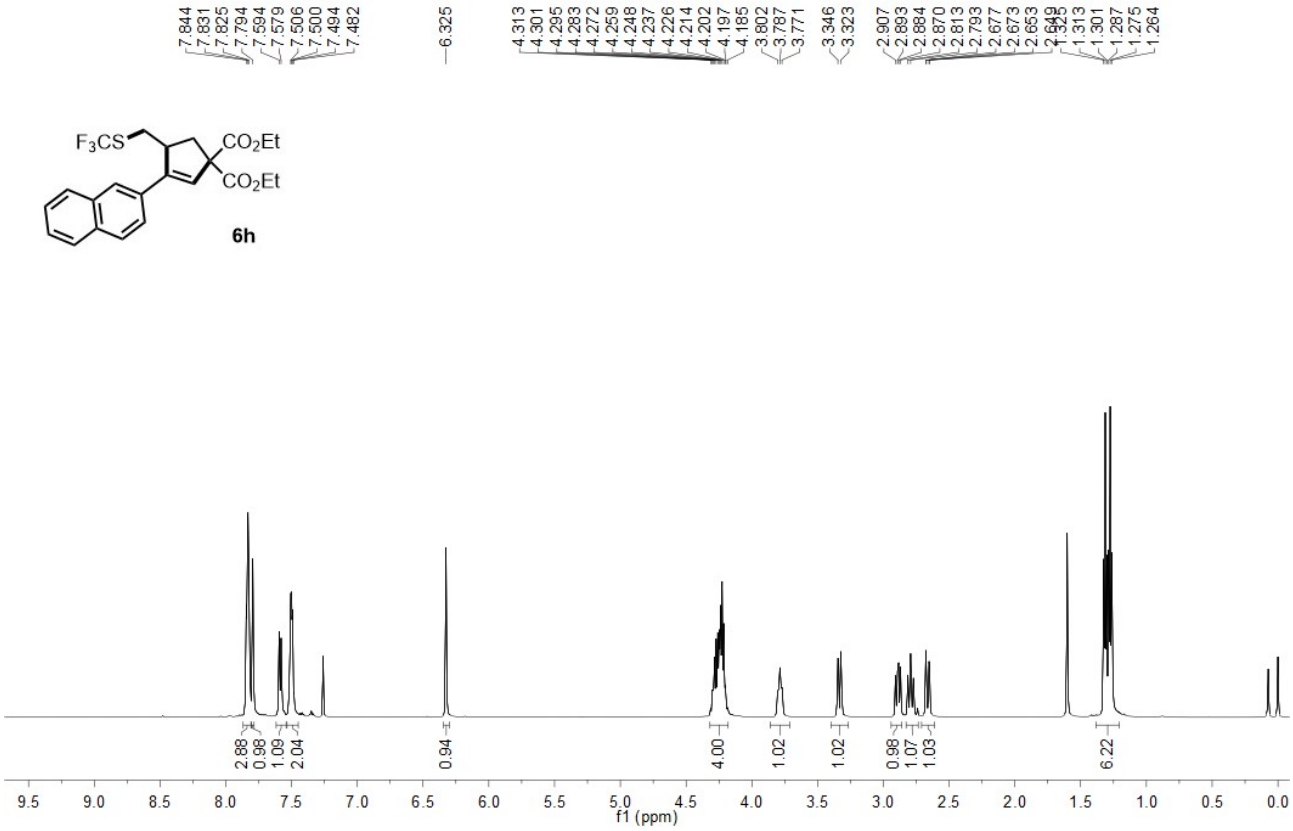
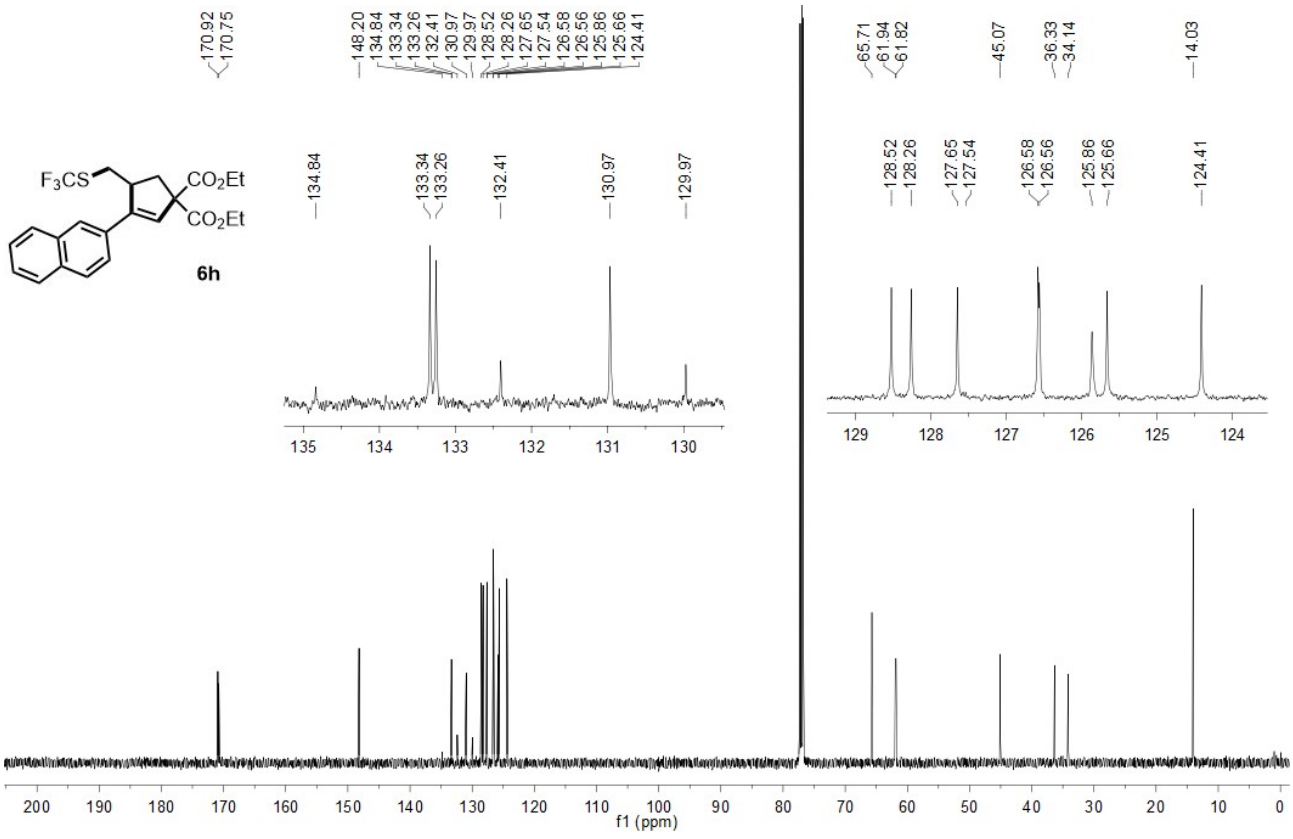
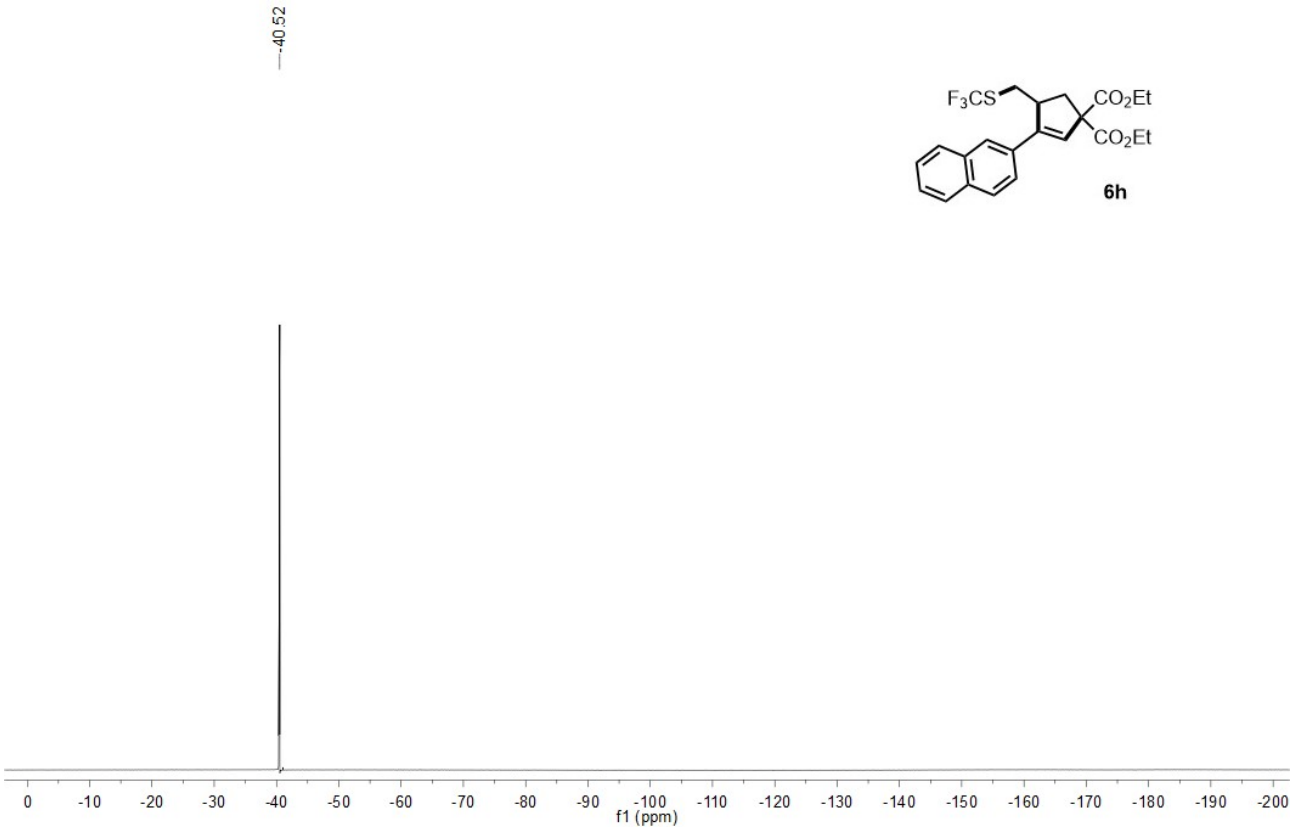


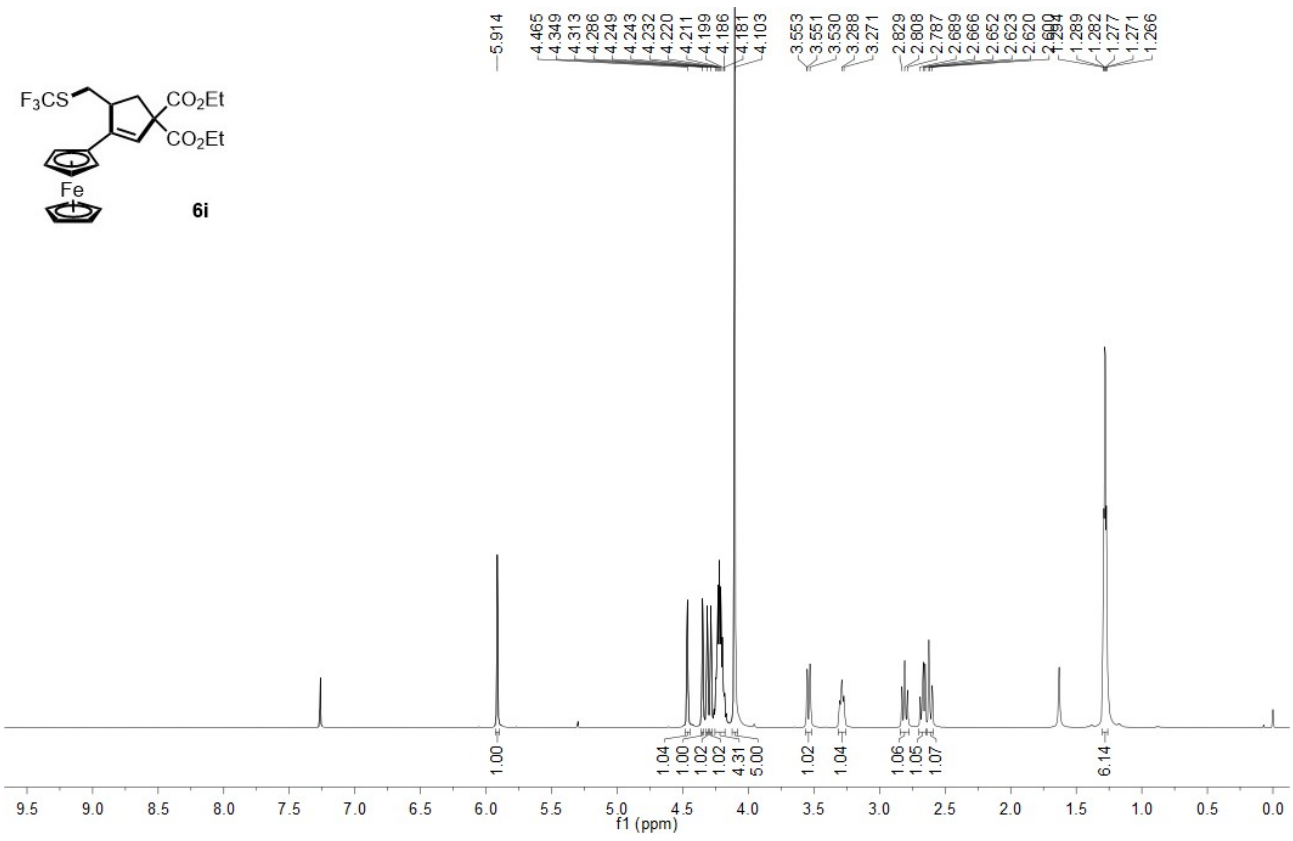
^{13}C NMR, 151 MHz, $CDCl_3$



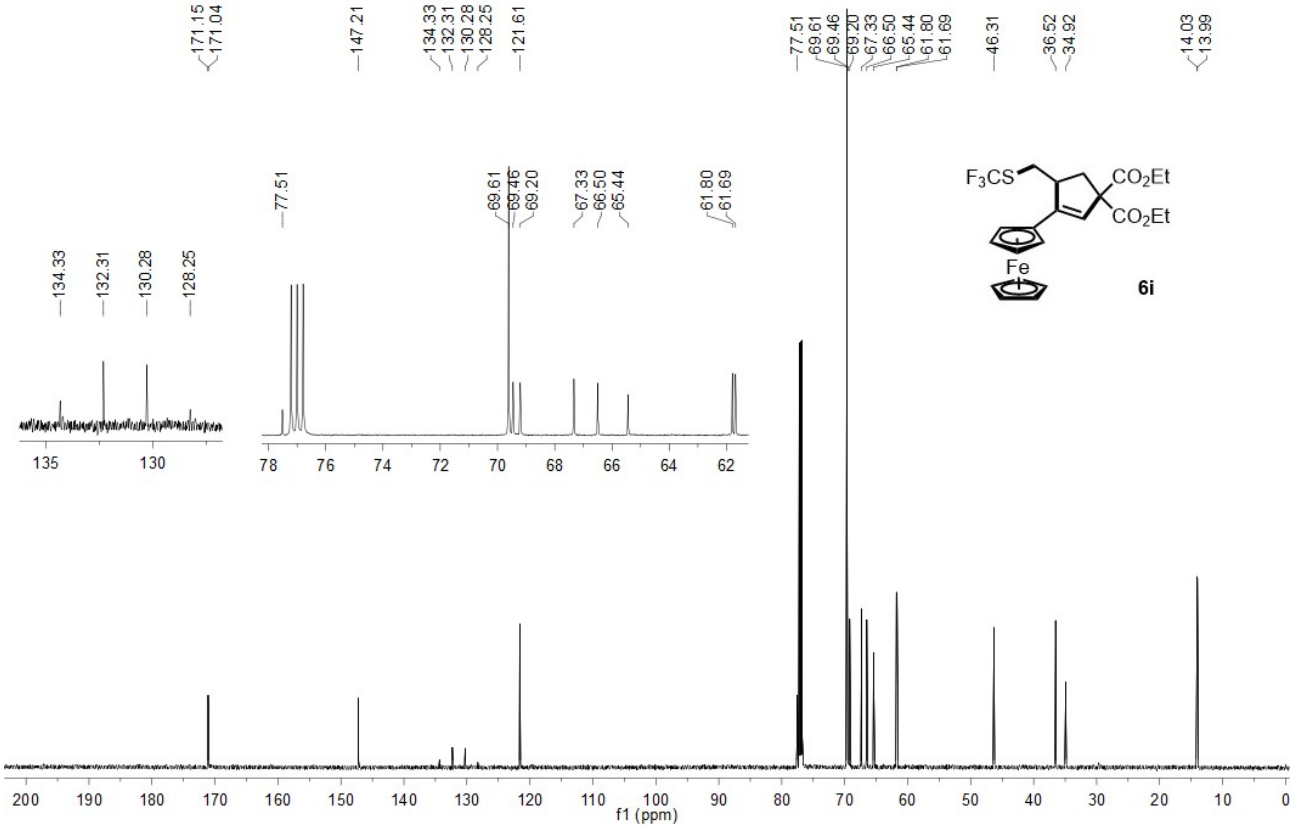
^{19}F NMR, 471 MHz, $CDCl_3$



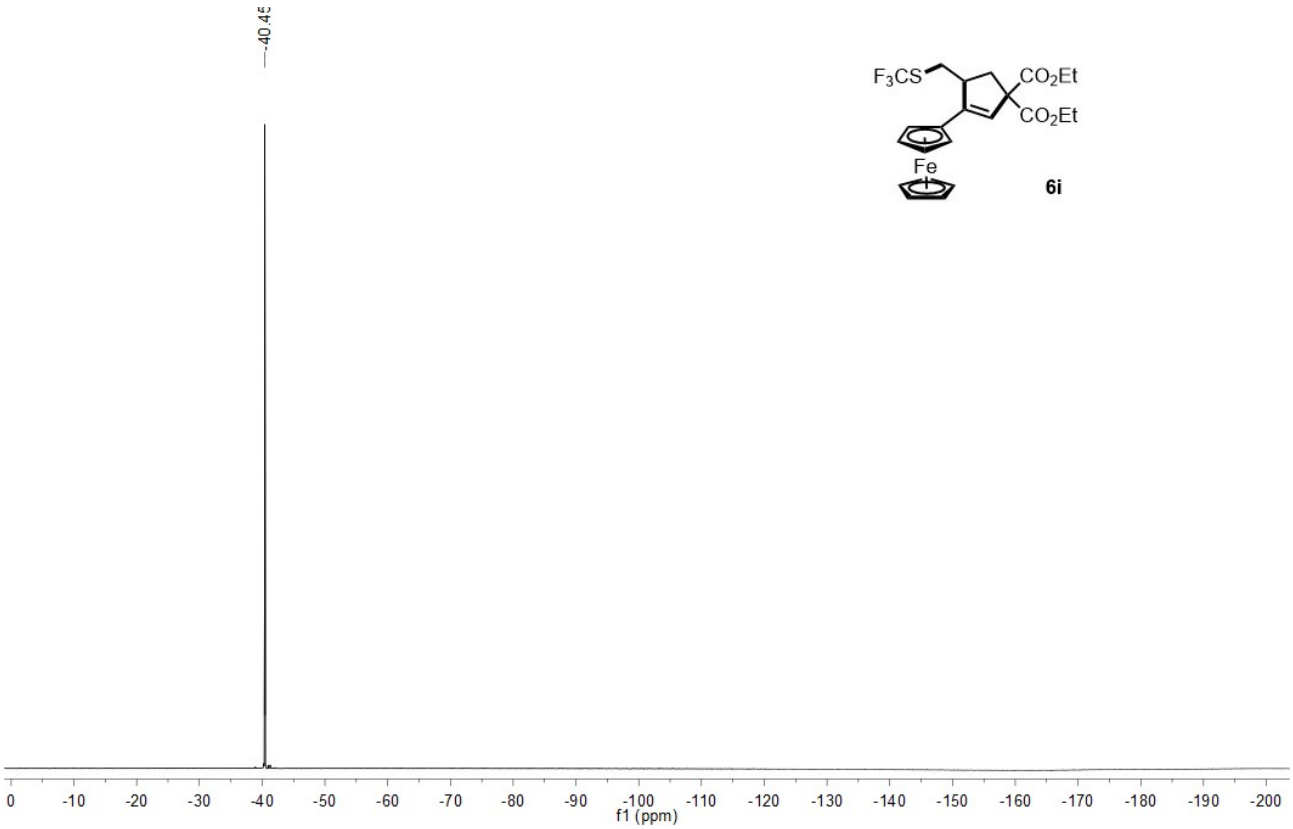
^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 151 MHz, $CDCl_3$



^{19}F NMR, 471 MHz, $CDCl_3$



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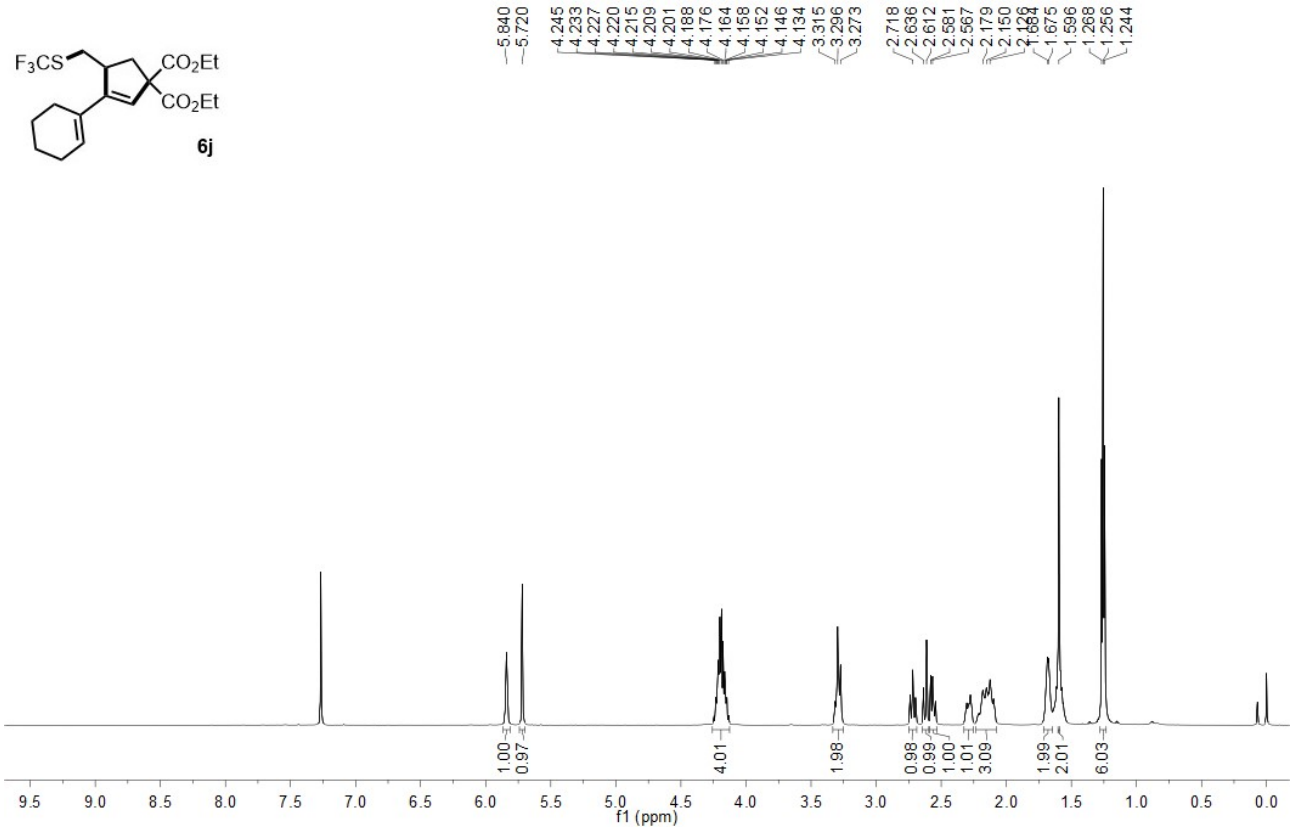

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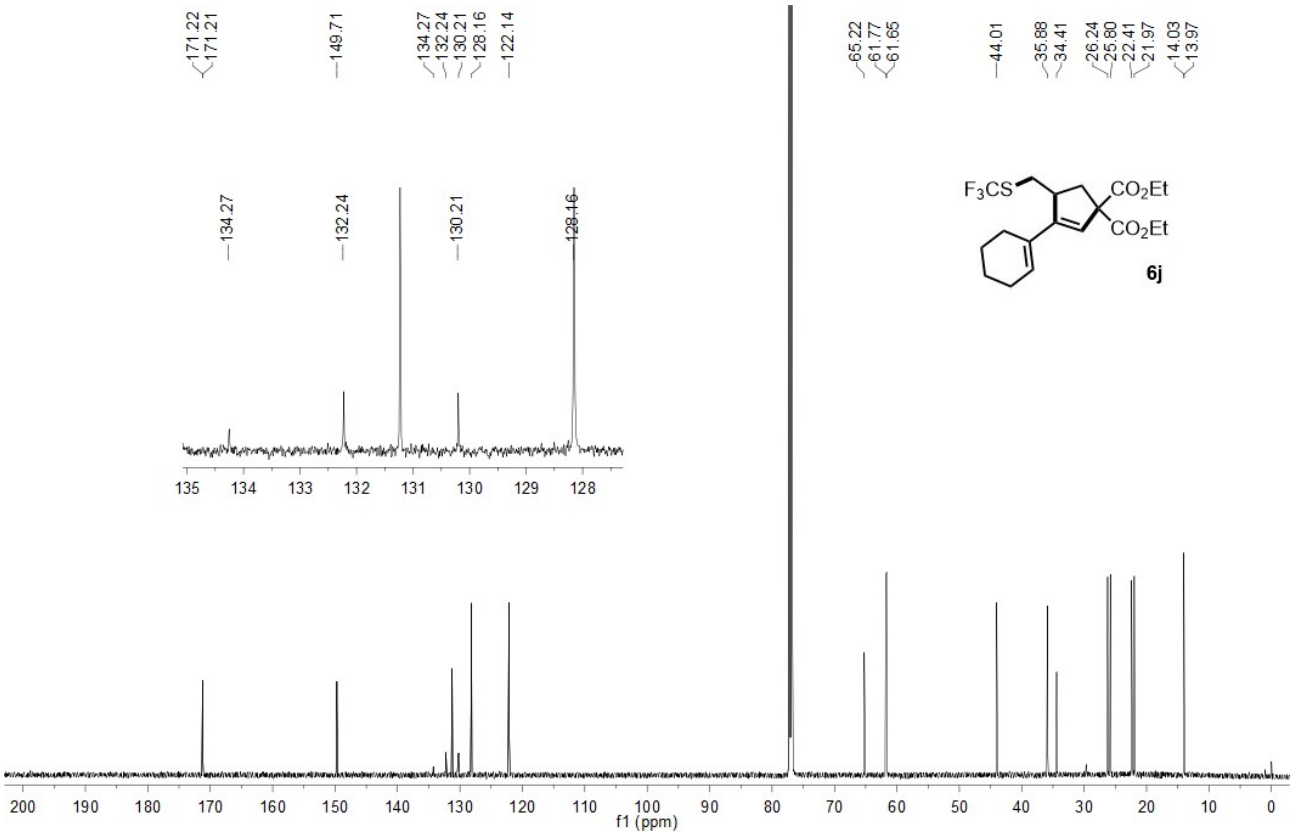
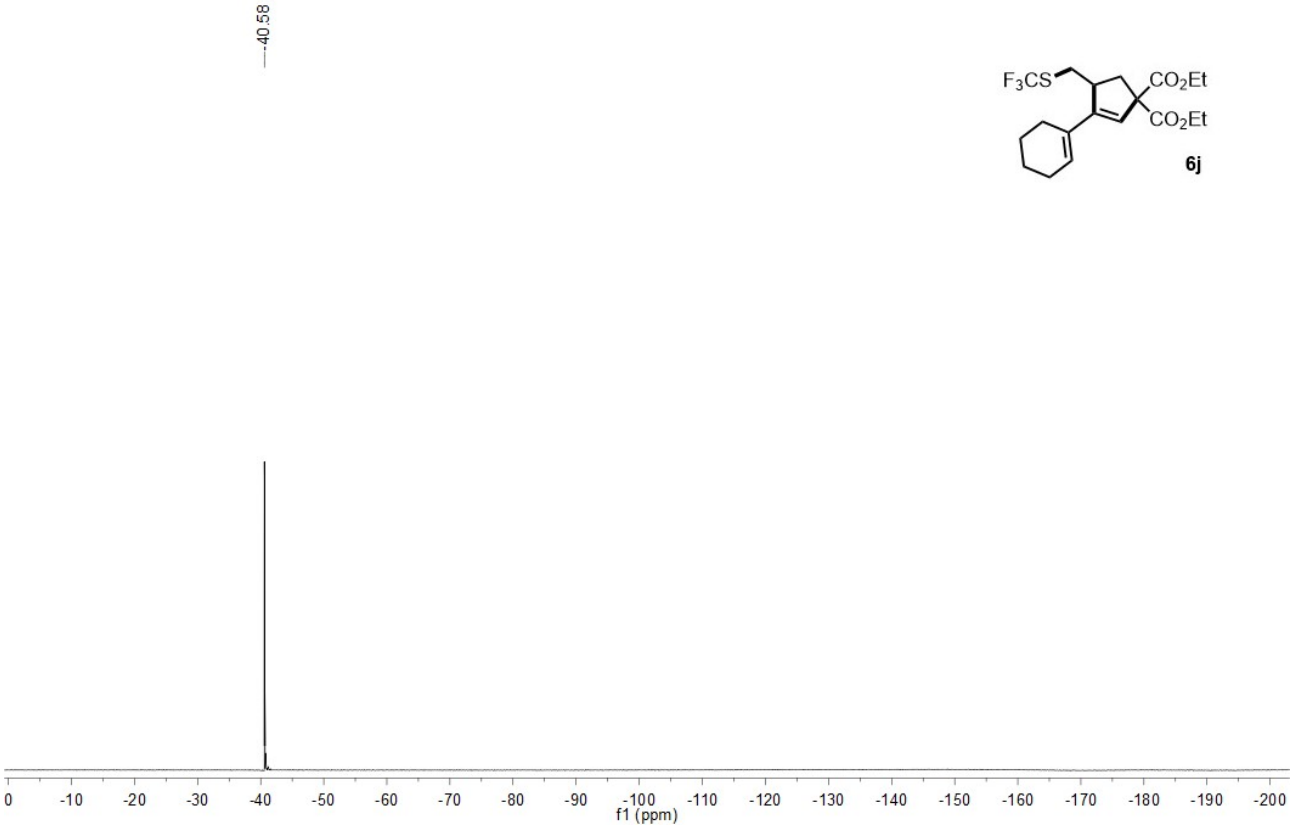
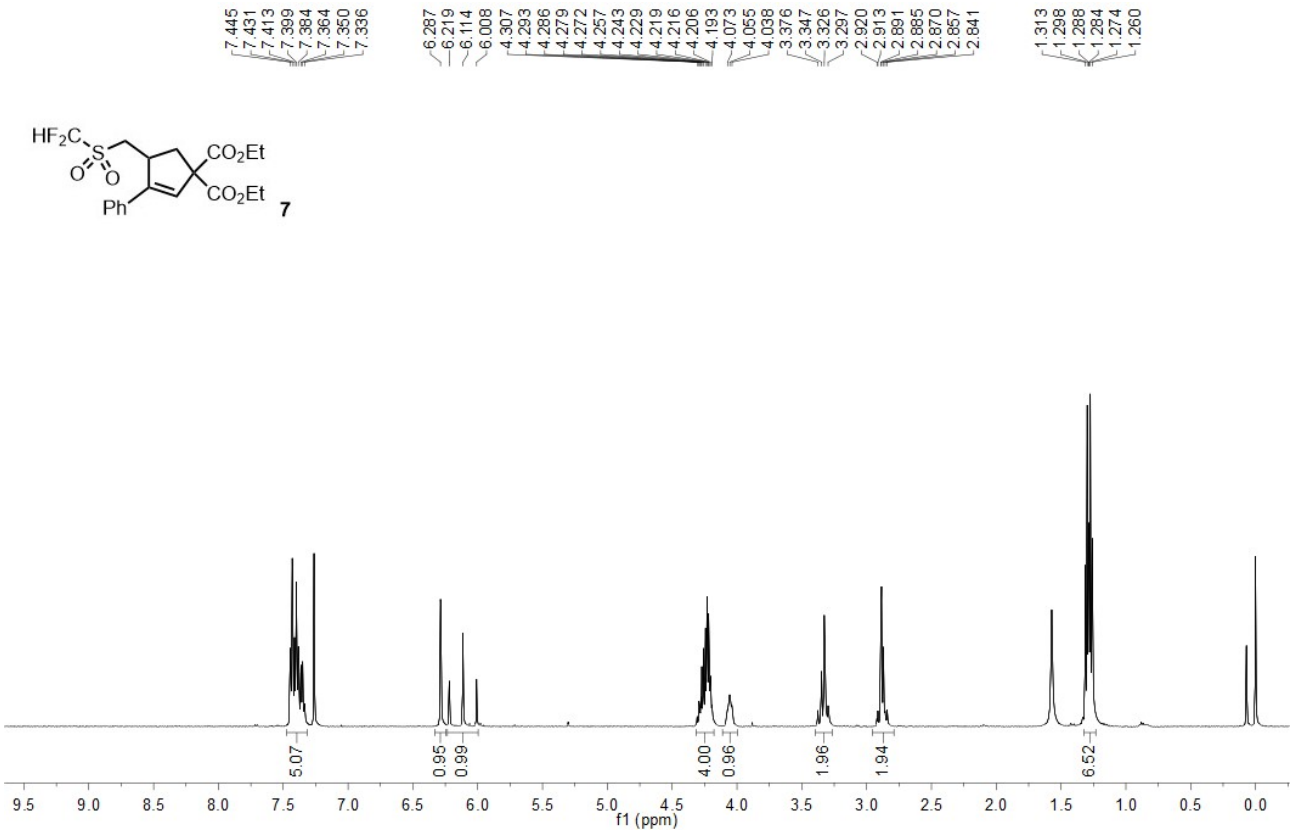


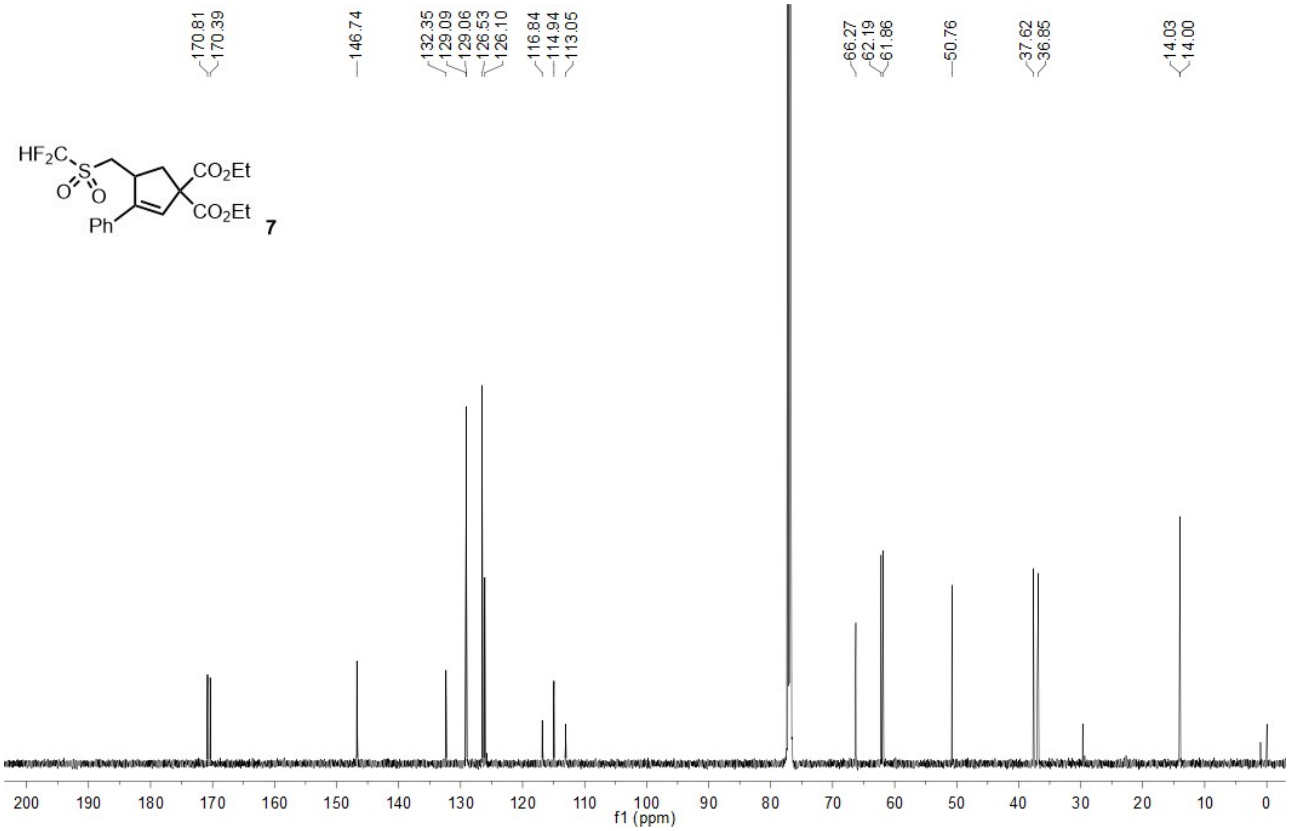
^{19}F NMR, 471 MHz, $CDCl_3$



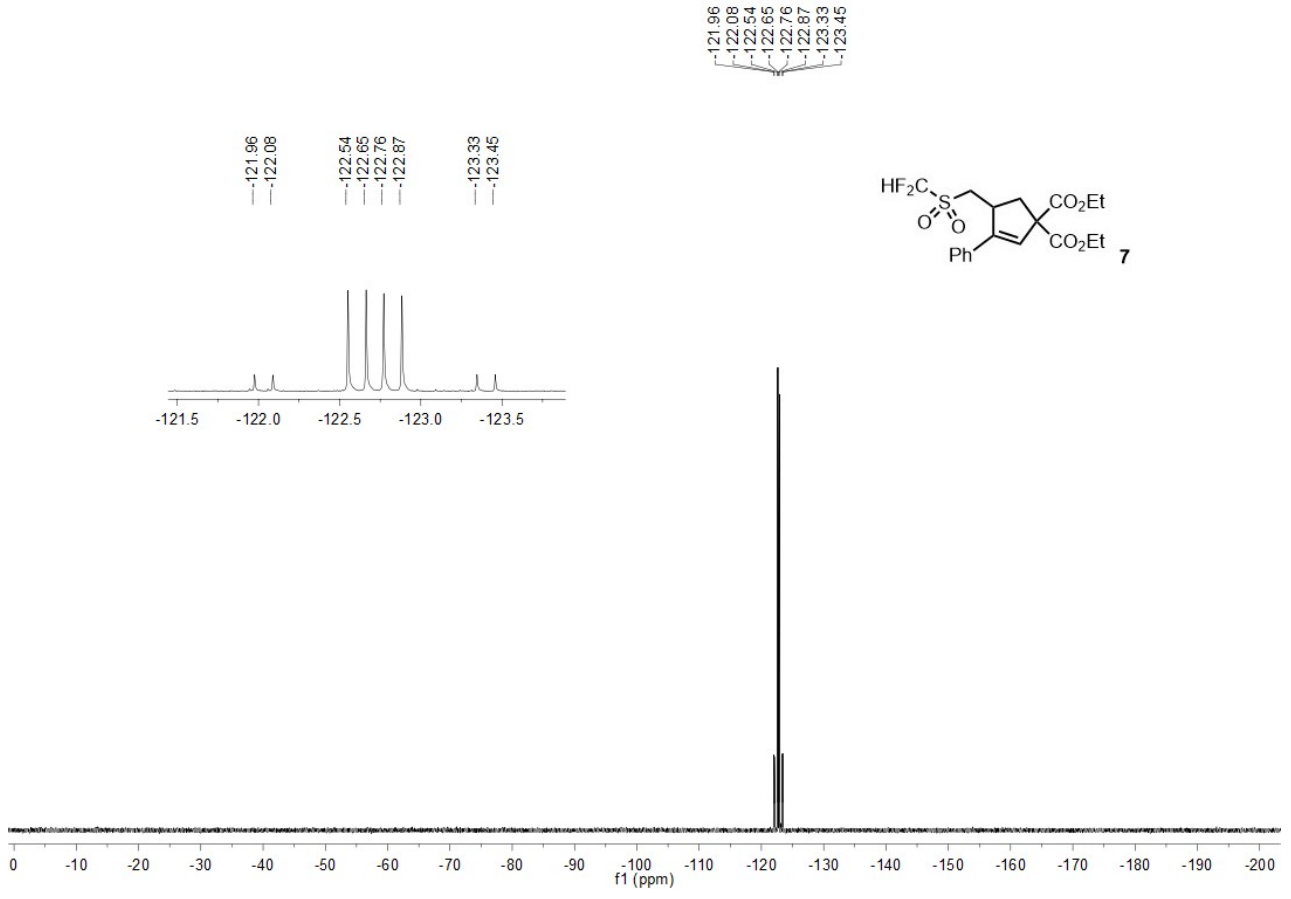
^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 151 MHz, $CDCl_3$



^{19}F NMR, 471 MHz, $CDCl_3$



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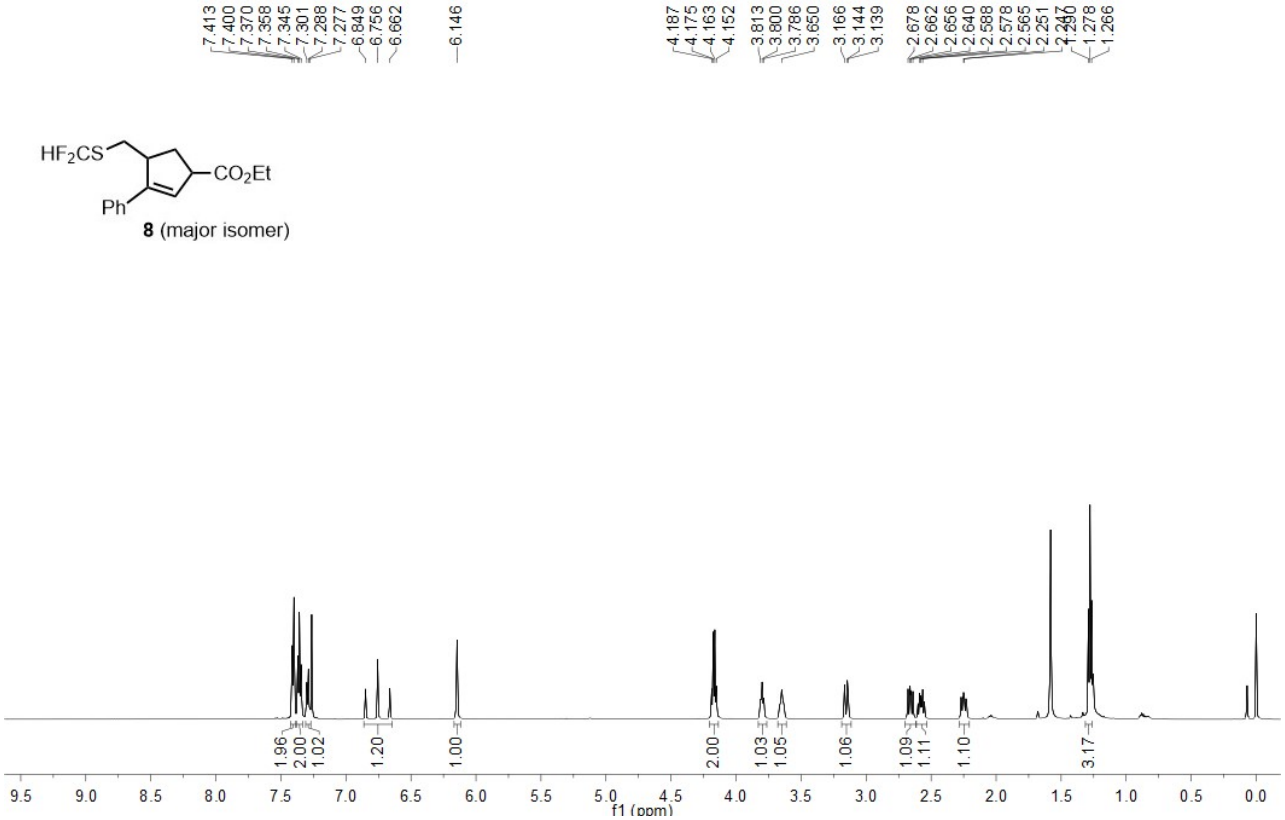

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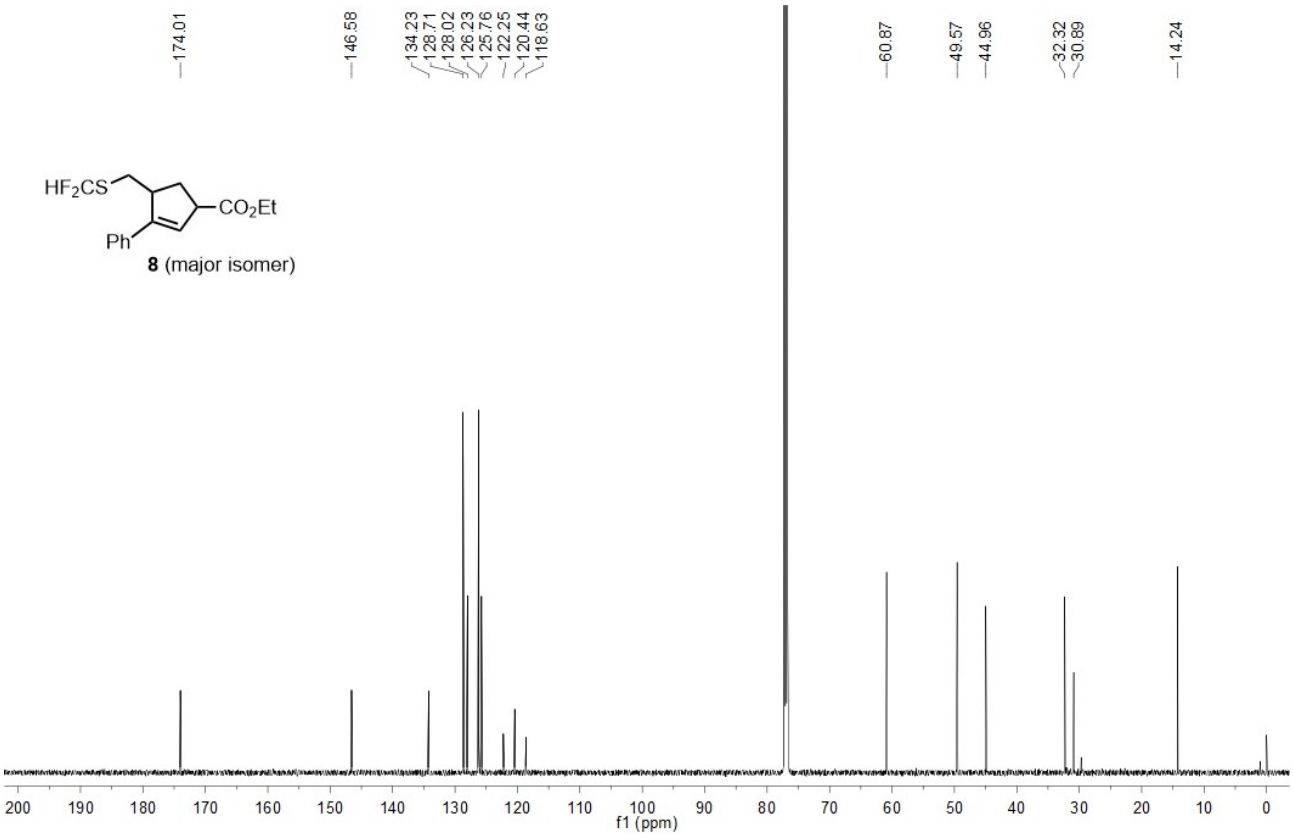

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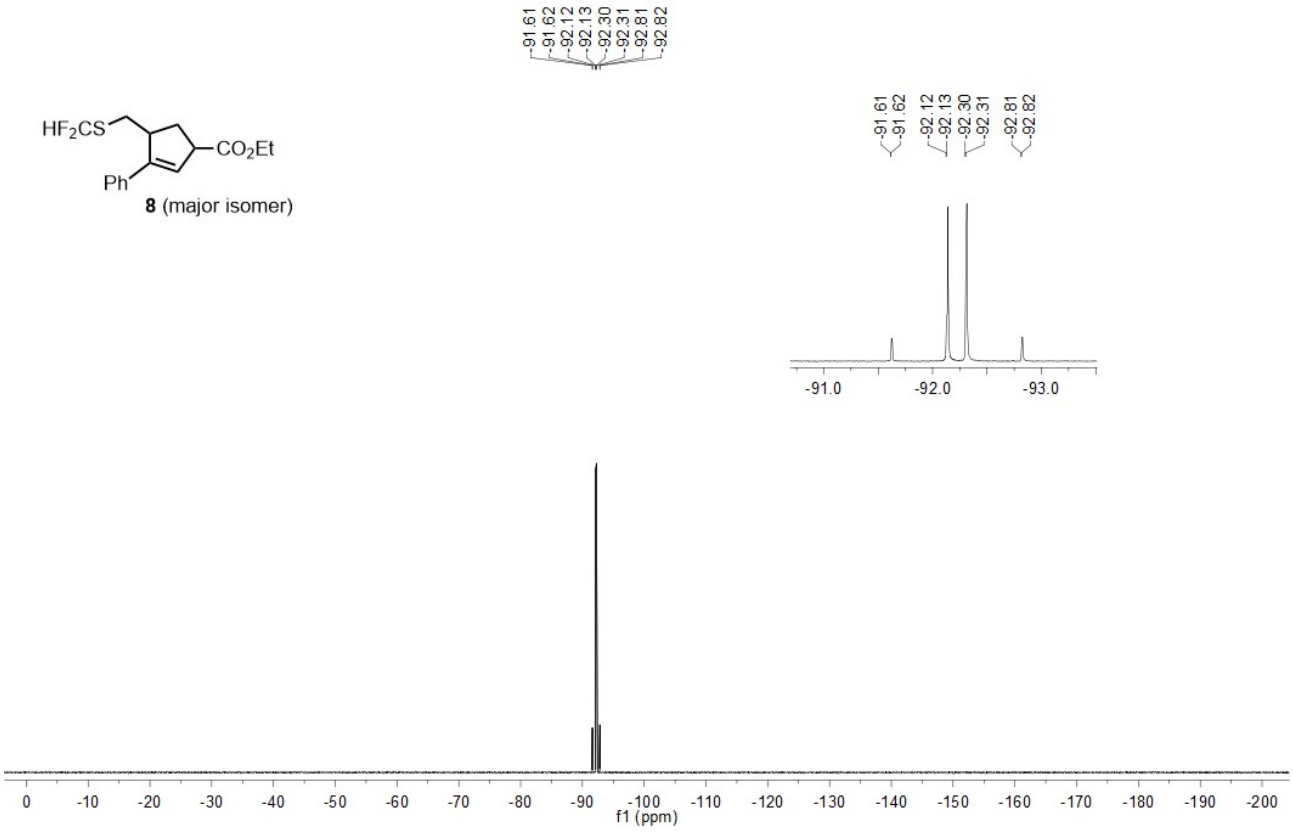

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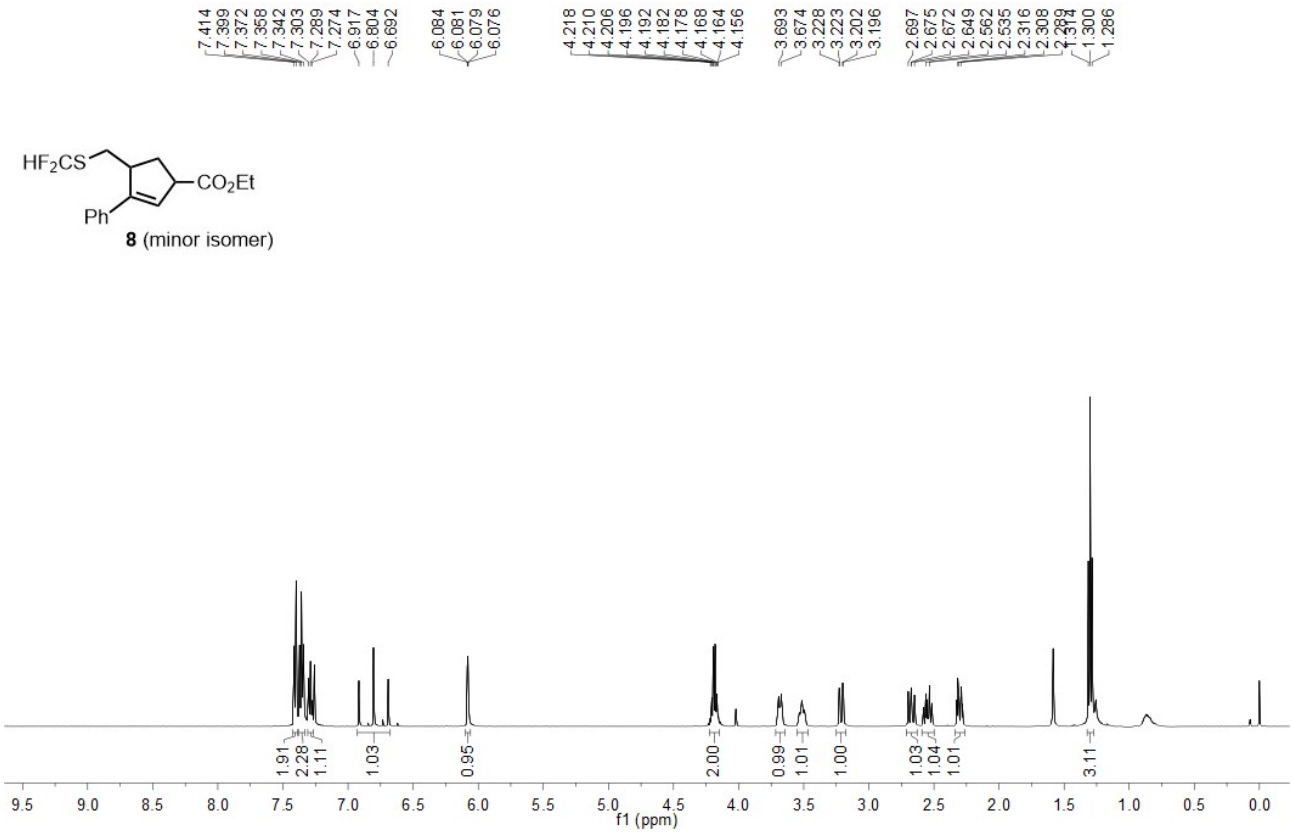
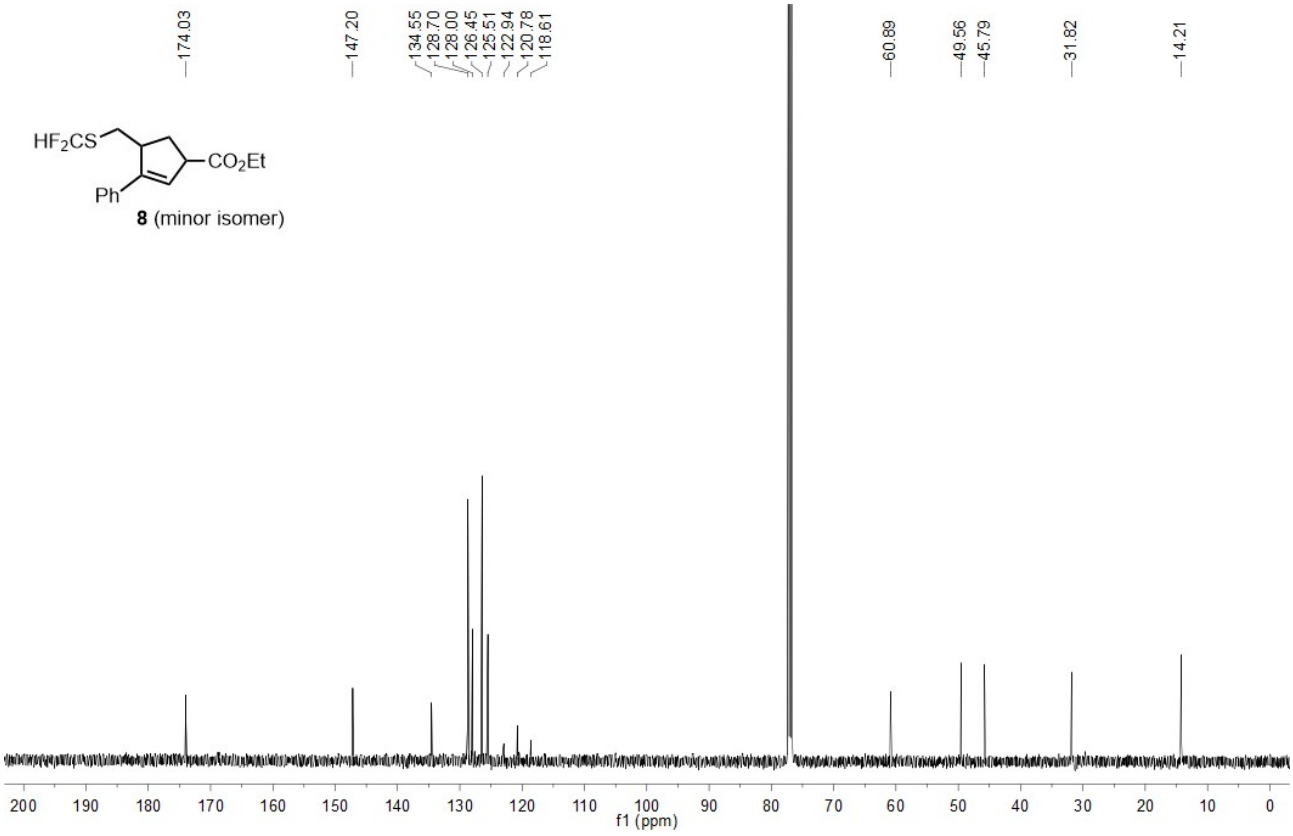


^{13}C NMR, 151 MHz, $CDCl_3$



^{19}F NMR, 471 MHz, $CDCl_3$