

Copper-Catalyzed Cross-Nucleophile Coupling of β -Allenyl Silanes with Tertiary C–H Bonds: A Radical Approach to Branched 1,3-Dienes

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1. General methods

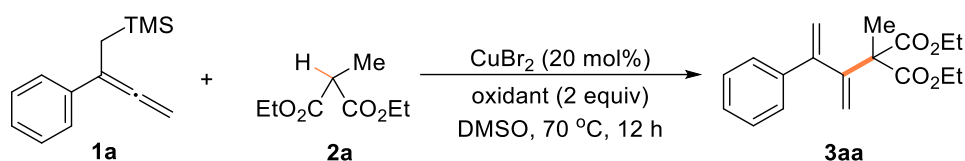
Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware by using Schlenk line techniques with a four-port dual-bank manifold under a nitrogen atmosphere. Commercial solvents and reagents were purchased from Energy-Chemical, Aladdin Bio-Chem Technology, and J&K Scientific, and were used without further purification.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating on a hot plate. Flash chromatography was performed using Nuotai silica gel (200 – 300 mesh) with distilled solvents. Columns were typically packed as slurry and equilibrated with petroleum ether prior to use.

Proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on a Bruker Advance 400 MHz and JEOL 400 MHz spectrometers. Chemical shifts for ^1H NMR spectra are reported as in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-*d* (J = 7.264, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); ddd (doublet of doublets of doublets); dddd (doublet of doublets of doublets of doublets); dt (doublet of triplets); m (multiplet), etc. The number of protons (*n*) for a given resonance is indicated by *n*H. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ = 0.0) and relative to the signal of chloroform-*d* (δ = 77.00, triplet). To clarify the complete signal assignments, “*x* number” indicates the multiple carbons due to the superposition of chemical shifts.

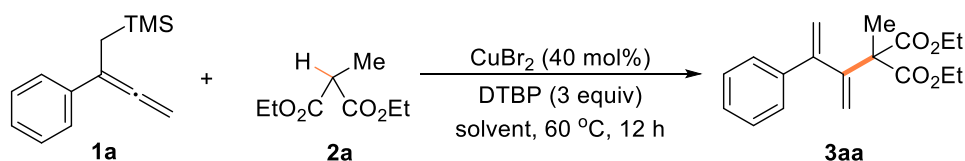
High resolution mass spectral analysis (HRMS) was performed on Water Q-TOF Premier mass spectrometer (Thermo Electron Corporation). Gas chromatography-mass spectrometer (GC-MS) analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Thermo Fisher Scientific GC column TG-5MS (30 m \times 0.25 mm \times 0.25 μm).

2. Optimization of the reaction conditions

Table S1. Effect of Oxidants on the Reaction^a

entry	oxidant	yield (%) ^b
1	DTBP	44
2	TBHP	n.d.
3	TBPP	n.d.
4	BPO	n.d.
5	LPO	n.d.
6	Ag_2CO_3	n.d.

^aReaction conditions: **1a** (0.15 mmol), **2a** (0.225 mmol), CuBr_2 (20 mol%) and oxidant (0.3 mmol) in DMSO (1.5 mL) at 70 °C for 12 h. ^bYield of isolated product. n.d. = not detected; TBHP = *tert*-butyl hydroperoxide; TBPP = *tert*-butyl peroxybenzoate; BPO = benzoyl peroxide; LPO = lauroyl peroxide.

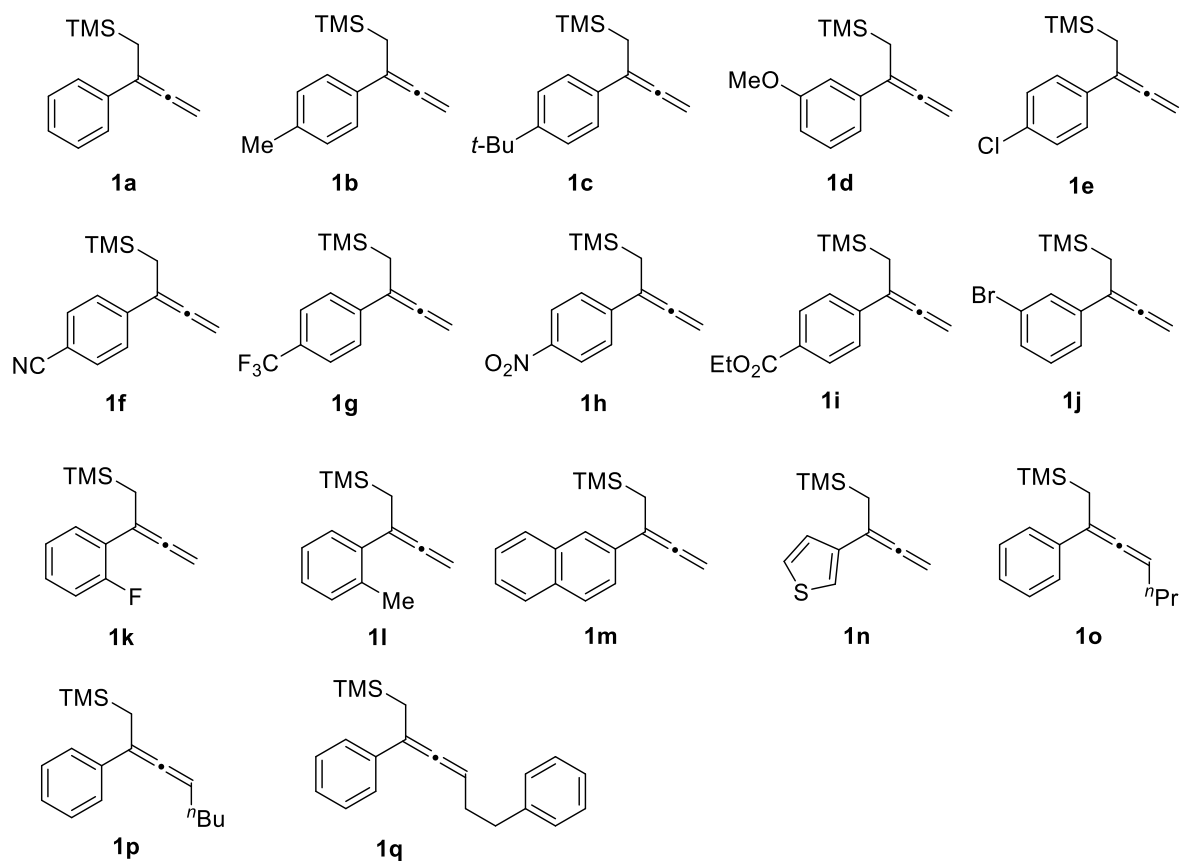
Table S2. Effect of Solvents on the Reaction^a

entry	solvent	yield (%) ^b
1	DMSO	70
2	DMF	n.d.
3	PhCl	n.d.
4	1,2-DCE	n.d.
5	THF	trace
6	toluene	n.d.
7	CH_3CN	13

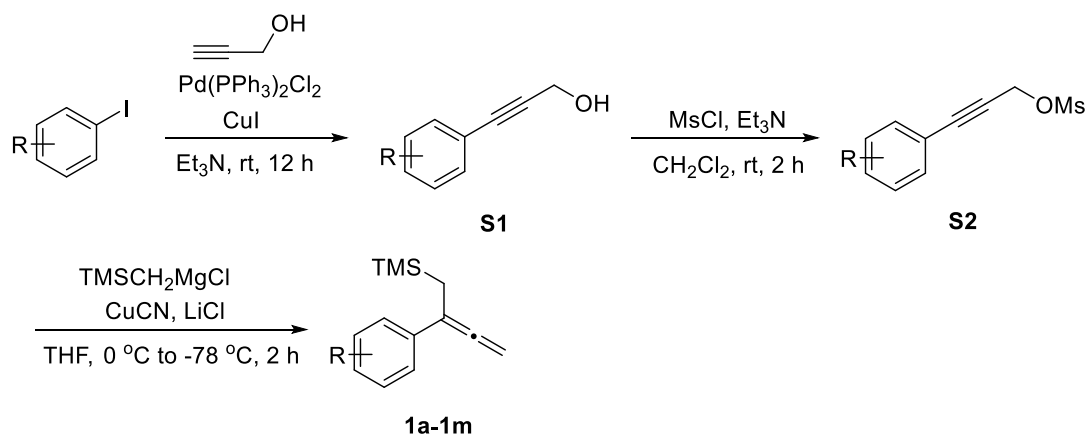
^aReaction conditions: **1a** (0.21 mmol), **2a** (0.15 mmol), CuBr_2 (40 mol%) and DTBP (0.45 mmol) in solvent (1.5 mL) at 60 °C for 12 h. ^bYield of isolated product. n.d. = not detected. 1,2-DCE = 1,2-dichloroethane.

3. Preparation of the starting materials

3.1 Preparation of β -allenyl silanes **1a–1q**



3.1.1 Compounds 1a–1m were prepared according to the general procedure 1 (GP1)^[1]



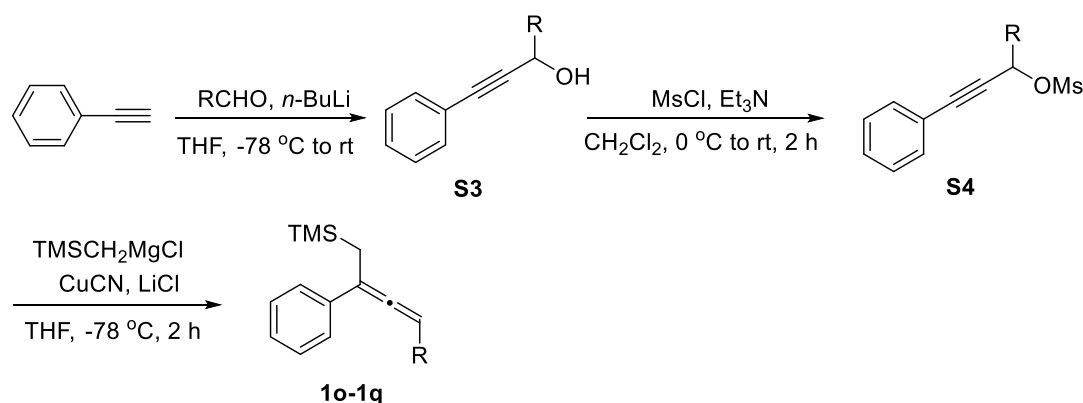
(1) To a solution of aryl iodide (5 mmol, 1.0 equiv) and propargyl alcohol (840.5 mg, 15 mmol, 3.0 equiv) in triethylamine (25 mL, 0.2 M) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (35.1 mg, 0.05 mmol, 1 mol%) and CuI (47.6 mg, 0.25 mmol, 5 mol%) under N_2 atmosphere. The resulting mixture was stirred at ambient temperature for 12 h. After completion of the reaction as monitored by TLC, the reaction mixture was diluted with EtOAc (20 mL) and filtered through a short pad of Celite®. The filtrate was concentrated in vacuo and the crude residue were purified by flash column chromatography (petroleum ether/ EtOAc) on silica gel to afford the propargylic alcohol **S1**.

(2) To a solution of the individual propargylic alcohol **S1** (1.0 equiv) and triethylamine (2.0 equiv) in CH_2Cl_2 (0.2 M) was added methanesulfonyl chloride (1.5 equiv) dropwise at 0 °C under N_2 atmosphere. The reaction

mixture was allowed to warm to room temperature. After full conversion, saturated aqueous NaHCO_3 (10 mL) was added to quench the reaction and the aqueous layer was extracted with CH_2Cl_2 (15 mL x 3). The combined organic extracts were washed with H_2O (20 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude products were purified by flash column chromatography (petroleum ether/EtOAc) to afford **S2**.

(3) To an ice-cooled suspension of CuCN (3.0 equiv) and LiCl (6.0 equiv) in anhydrous THF (0.1 M) was added a solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (1.0 M in Et_2O , 2.5 equiv). After being stirred for 25 min, the mixture was cooled to -78°C and a solution of **S2** (1.0 equiv) in THF (5 mL) was added dropwise. After 2 h, the reaction was quenched with saturated aqueous NH_4Cl (5 mL). The reaction mixture was extracted with Et_2O (20 mL x 3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude products were purified by flash column chromatography (petroleum ether/EtOAc) to afford β -allenyl silanes **1a–1m**.

3.1.2 Compounds **1o–1q** were prepared according to the general procedure 2 (GP2)^[1]



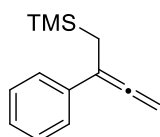
(1) To a 100 mL round bottom flask equipped with a stir bar was added phenylacetylene (1.02 g, 10 mmol, 1.0 equiv) and THF (20 mL) and then cooled to -78°C . $n\text{-BuLi}$ (2.5 M in hexane, 4.0 mL, 1.0 equiv) was added dropwise and the slightly yellow solution was stirred for 30 min. The corresponding aldehyde (10.0 mmol, 1.0 equiv) was added and the mixture was allowed to warm to room temperature and further stirred for 1 h. After completion, the reaction was quenched with aqueous HCl (1.0 M) and then extracted with CH_2Cl_2 (20 mL x 3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 , and concentrated in vacuo. The crude product was purified by flash column chromatography (petroleum ether/EtOAc) to provide the corresponding propargylic alcohol **S3**.

(2) To a solution of the individual propargylic alcohol **S3** (1.0 equiv) and triethylamine (2.0 equiv) in CH_2Cl_2 (0.2 M) was added methanesulfonyl chloride (1.5 equiv) dropwise at 0°C under N_2 atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After completion, saturated aqueous NaHCO_3 (15 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (15 mL x 3). The combined organic extracts were washed with H_2O (20 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (petroleum ether/EtOAc) to afford **S4**.

(3) To an ice-cooled suspension of CuCN (3.0 equiv) and LiCl (6.0 equiv) in anhydrous THF (0.1 M) was added

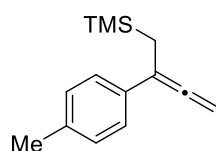
a solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (1.0 M in Et_2O , 2.5 equiv). After being stirred for 25 min, the mixture was cooled to -78°C and a solution of the **S4** (1.0 equiv) in THF (5 mL) was added. After 2 h, the reaction was quenched with saturated aqueous NH_4Cl (5 mL). The reaction mixture was extracted with Et_2O (20 mL x 3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude products were purified by flash column chromatography (petroleum ether/ EtOAc) to afford β -allenyl silanes **1o–1q**.

Trimethyl(2-phenylbuta-2,3-dien-1-yl)silane (**1a**)



The title compound was prepared according to **GP1** and isolated as a colorless oil (647.8 mg, 3.20 mmol, 64%). ^1H NMR (400 MHz, Chloroform- d) δ 7.42 – 7.37 (m, 2H), 7.30 – 7.26 (m, 3H), 4.94 (t, J = 2.5 Hz, 2H), 1.57 (t, J = 2.5 Hz, 2H), 0.12 (s, 9H). The spectral data matched those reported previously.^[1]

Trimethyl(2-(*p*-tolyl)buta-2,3-dien-1-yl)silane (**1b**)

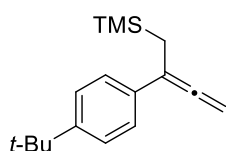


The title compound was prepared according to **GP1** and isolated as a colorless oil (616.7 mg, 2.85 mmol, 57%). ^1H NMR (400 MHz, Chloroform- d) δ 7.30 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.01 (t, J = 2.6 Hz, 2H), 2.34 (s, 3H), 1.79 (t, J = 2.6 Hz, 2H), 0.02 (s, 9H).

^{13}C NMR (101 MHz, Chloroform- d) δ 209.0, 136.0, 134.3, 128.9 \times 2, 126.0 \times 2, 102.1, 77.1,

21.0, 18.5, -1.0×3 . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{21}\text{Si}$ 217.1407; Found: 217.1413.

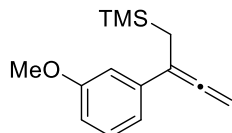
(2-(4-(*tert*-Butyl)phenyl)buta-2,3-dien-1-yl)trimethylsilane (**1c**)



The title compound was prepared according to **GP1** and isolated as a colorless oil (775.4 mg, 3.00 mmol, 60%). ^1H NMR (400 MHz, Chloroform- d) δ 7.25 (s, 4H), 4.92 (t, J = 2.7 Hz, 2H), 1.70 (t, J = 2.6 Hz, 2H), 1.23 (s, 9H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 209.2, 149.3, 134.4, 125.8 \times 2, 125.1 \times 2, 102.0, 77.2, 34.4, 31.3 \times 3, 18.4, -1.0×3 .

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{27}\text{Si}$ 259.1877; Found: 259.1882.

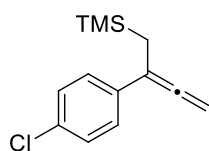
(2-(3-Methoxyphenyl)buta-2,3-dien-1-yl)trimethylsilane (**1d**)



The title compound was prepared according to **GP1** and isolated as a colorless oil (611.2 mg, 2.63 mmol, 53%). ^1H NMR (400 MHz, Chloroform- d) δ 7.26 – 7.21 (m, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.98 (t, J = 2.1 Hz, 1H), 6.75 (ddd, J = 8.2, 2.6, 0.8 Hz, 1H), 5.04 (t, J = 2.6

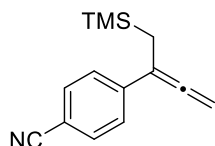
Hz, 2H), 3.82 (s, 3H), 1.80 (t, J = 2.6 Hz, 2H), 0.04 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 209.2, 159.4, 138.9, 129.0, 118.7, 112.0, 111.7, 102.2, 77.3, 55.1, 18.5, -1.1×3 . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{21}\text{OSi}$ 233.1356; Found: 233.1362.

(2-(4-Chlorophenyl)buta-2,3-dien-1-yl)trimethylsilane (**1e**)



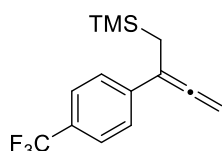
The title compound was prepared according to **GP1** and isolated as a colorless oil (698.6 mg, 2.95 mmol, 59%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 2H), 7.27 (q, *J* = 1.1 Hz, 1H), 7.26 – 7.25 (m, 1H), 5.03 (t, *J* = 2.6 Hz, 2H), 1.76 (t, *J* = 2.6 Hz, 2H), 0.01 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 209.2, 136.0, 132.1, 128.4 \times 2, 127.5 \times 2, 101.7, 77.9, 18.5, -0.9 \times 3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₈ClSi 237.0861; Found: 237.0866.

4-(1-(Trimethylsilyl)buta-2,3-dien-2-yl)benzonitrile (1f)



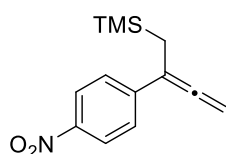
The title compound was prepared according to **GP1** and isolated as a colorless oil (534.3 mg, 2.35 mmol, 47%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 5.12 (t, *J* = 2.6 Hz, 2H), 1.79 (t, *J* = 2.7 Hz, 2H), 0.02 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 210.1, 142.7, 132.0 \times 2, 126.7 \times 2, 119.3, 109.7, 102.0, 78.5, 18.2, -1.0 \times 3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₈NSi 228.1203; Found: 228.1208.

Trimethyl(2-(4-(trifluoromethyl)phenyl)buta-2,3-dien-1-yl)silane (1g)



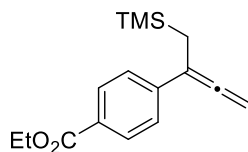
The title compound was prepared according to **GP1** and isolated as a colorless oil (567.8 mg, 2.10 mmol, 42%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.45 (m, 4H), 5.07 (t, *J* = 2.4 Hz, 2H), 1.79 (t, *J* = 2.6 Hz, 2H), 0.00 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 209.7, 141.3, 128.3 (q, *J* = 32.3 Hz), 126.3 \times 2, 125.0 \times 2 (q, *J* = 3.9 Hz), 124.3 (q, *J* = 271.8 Hz), 101.8, 77.9, 18.3, -1.1 \times 3. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -62.18. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₈F₃Si 271.1124; Found: 271.1130.

Trimethyl(2-(4-nitrophenyl)buta-2,3-dien-1-yl)silane (1h)

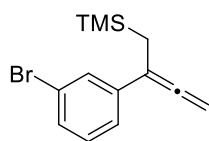


The title compound was prepared according to **GP1** and isolated as a colorless oil (494.7 mg, 2.00 mmol, 40%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 2H), 5.14 (t, *J* = 2.6 Hz, 2H), 1.82 (t, *J* = 2.6 Hz, 2H), 0.03 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 210.3, 146.0, 144.7, 126.6 \times 2, 123.4 \times 2, 101.8, 78.4, 18.2, -1.1 \times 3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₈NO₂Si 248.1101; Found: 248.1107.

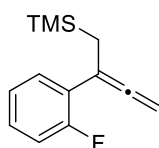
Ethyl 4-(1-(trimethylsilyl)buta-2,3-dien-2-yl)benzoate (1i)



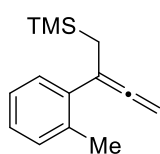
The title compound was prepared according to **GP1** and isolated as a colorless oil (823.3 mg, 3.00 mmol, 60%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 5.08 (t, *J* = 2.6 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.81 (t, *J* = 2.6 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.01 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 209.8, 166.5, 142.2, 129.4 \times 2, 128.2, 125.9 \times 2, 102.1, 77.7, 60.8, 18.2, 14.3, -1.1 \times 3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₂₃O₂Si 275.1462; Found: 275.1467.

(2-(3-Bromophenyl)buta-2,3-dien-1-yl)trimethylsilane (1j)

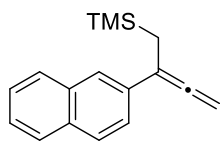
The title compound was prepared according to **GP1** and isolated as a colorless oil (787.6 mg, 2.80 mmol, 56%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 (t, *J* = 2.0 Hz, 1H), 7.31 (ddt, *J* = 8.9, 6.0, 1.3 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 1H), 5.07 (t, *J* = 2.5 Hz, 2H), 1.76 (t, *J* = 2.6 Hz, 2H), 0.02 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 209.2, 139.8, 129.6, 129.3, 129.1, 124.6, 122.4, 101.5, 77.9, 18.3, -1.1 \times 3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₈⁷⁹BrSi 281.0356; Found: 281.0361.

(2-(2-Fluorophenyl)buta-2,3-dien-1-yl)trimethylsilane (1k)

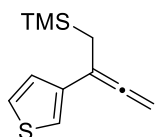
The title compound was prepared according to **GP1** and isolated as a colorless oil (517.8 mg, 2.35 mmol, 47%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.29 (m, 1H), 7.19 (dddd, *J* = 8.1, 7.0, 5.0, 1.8 Hz, 1H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1H), 7.01 (ddd, *J* = 11.1, 8.1, 1.3 Hz, 1H), 4.88 (t, *J* = 2.6 Hz, 2H), 1.84 (td, *J* = 2.6, 0.9 Hz, 2H), -0.04 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 209.4 (d, *J* = 1.4 Hz), 160.0 (d, *J* = 248.4 Hz), 129.7 (d, *J* = 3.9 Hz), 128.3 (d, *J* = 8.3 Hz), 126.5 (d, *J* = 12.5 Hz), 123.8 (d, *J* = 3.8 Hz), 115.9 (d, *J* = 22.7 Hz), 97.8, 75.1 (d, *J* = 1.5 Hz), 21.0 (d, *J* = 2.9 Hz), -1.3 \times 3. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -112.96. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₈FSi 221.1156; Found: 221.1161.

Trimethyl(2-(*o*-tolyl)buta-2,3-dien-1-yl)silane (1l)

The title compound was prepared according to **GP1** and isolated as a colorless oil (586.4 mg, 2.71 mmol, 54%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.23 (m, 1H), 7.21 – 7.13 (m, 3H), 4.78 (t, *J* = 2.7 Hz, 2H), 2.40 (s, 3H), 1.78 (t, *J* = 2.7 Hz, 2H), -0.00 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 207.5, 138.6, 135.5, 130.5, 127.9, 126.7, 125.7, 101.1, 74.6, 23.0, 20.5, -1.2 \times 3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₄H₂₁Si 217.1407; Found: 217.1413.

Trimethyl(2-(naphthalen-2-yl)buta-2,3-dien-1-yl)silane (1m)

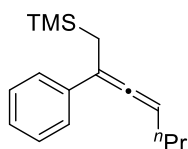
The title compound was prepared according to **GP1** and isolated as a colorless oil (517.5 mg, 2.05 mmol, 41%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (ddd, *J* = 6.9, 4.6, 1.8 Hz, 2H), 7.75 – 7.70 (m, 2H), 7.62 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.48 – 7.37 (m, 2H), 5.10 (t, *J* = 2.6 Hz, 2H), 1.92 (t, *J* = 2.6 Hz, 2H), 0.04 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 209.9, 134.5, 133.4, 132.2, 127.9, 127.5, 127.5, 126.0, 125.5, 125.3, 123.9, 102.6, 77.7, 18.4, -1.0 \times 3. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₇H₂₁Si 253.1407; Found: 253.1413.

Trimethyl(2-(thiophen-3-yl)buta-2,3-dien-1-yl)silane (1n)

The title compound was prepared according to **GP1** and isolated as a colorless oil (427.2 mg, 2.05 mmol, 41%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.12 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.01 (dt, *J* = 3.0, 1.2 Hz, 1H), 5.00 (td, *J* = 2.5, 0.9 Hz, 2H), 1.74 (t, *J* = 2.6 Hz,

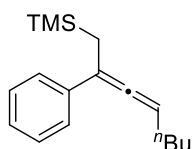
2H), 0.03 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.5, 139.3, 126.9, 125.1, 119.2, 98.6, 77.1, 19.3, -1.1 \times 3. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{17}\text{SSi}$ 209.0815; Found: 209.0820.

Trimethyl(2-phenylhepta-2,3-dien-1-yl)silane (1o)



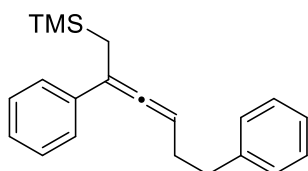
The title compound was prepared according to **GP2** and isolated as a colorless oil (974.5 mg, 3.99 mmol, 40%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dd, J = 8.5, 1.4 Hz, 2H), 7.29 (dd, J = 8.5, 7.0 Hz, 2H), 7.20 – 7.14 (m, 1H), 5.41 (tt, J = 6.9, 2.4 Hz, 1H), 2.09 (dt, J = 7.7, 6.9 Hz, 2H), 1.80 (dd, J = 4.6, 2.4 Hz, 2H), 1.51 (h, J = 7.4 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.2, 138.5, 128.0, 126.1 \times 2, 126.1 \times 2, 102.4, 93.1, 31.6, 22.7, 19.0, 13.9, -1.1 \times 3. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{25}\text{Si}$ 245.1720; Found: 245.1725.

Trimethyl(2-phenylocta-2,3-dien-1-yl)silane (1p)



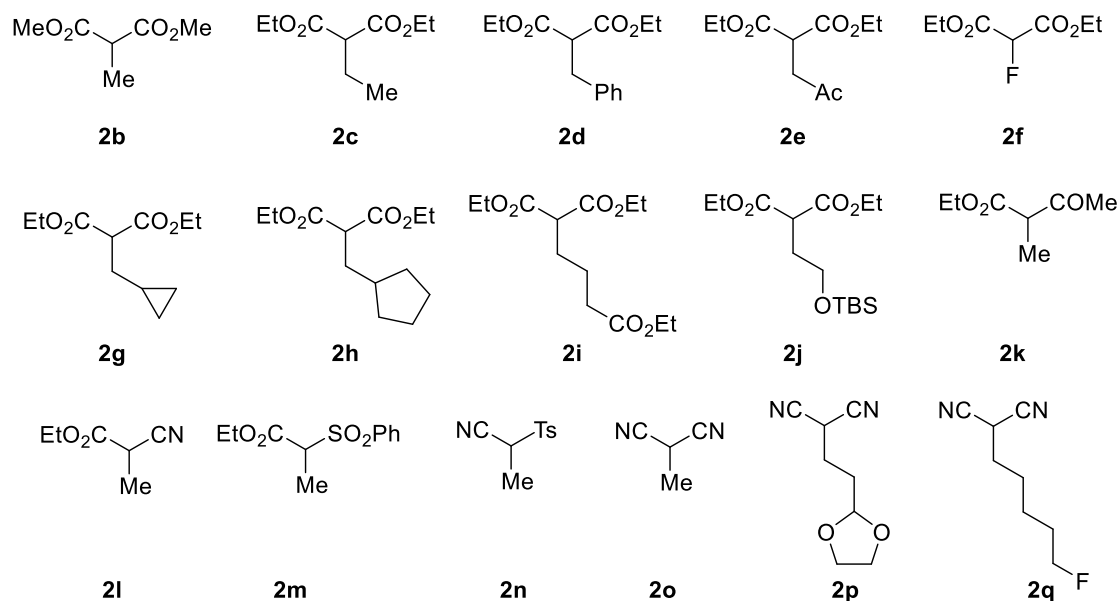
The title compound was prepared according to **GP2** and isolated as a colorless oil (784.7 mg, 3.04 mmol, 30%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 2H), 7.32 – 7.28 (m, 2H), 7.20 – 7.13 (m, 1H), 5.46 – 5.37 (m, 1H), 2.11 (q, J = 7.1 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.49 – 1.36 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.1, 138.5, 128.0 \times 2, 126.1, 126.1 \times 2, 102.5, 93.3, 31.6, 29.2, 22.4, 19.0, 14.0, -1.1 \times 3. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{27}\text{Si}$ 259.1877; Found: 259.1882.

(2,5-Diphenylpenta-2,3-dien-1-yl)trimethylsilane (1q)



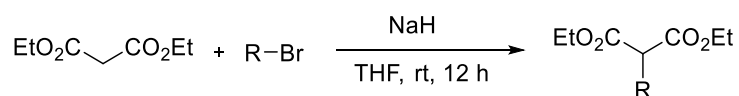
The title compound was prepared according to **GP2** and isolated as a colorless oil (1.26 g, 4.11 mmol, 41%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 6H), 7.31 – 7.21 (m, 4H), 5.51 (tt, J = 6.7, 2.4 Hz, 1H), 2.86 (td, J = 7.5, 2.1 Hz, 2H), 2.56 – 2.44 (m, 2H), 1.82 (d, J = 2.5 Hz, 2H), 0.07 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.3, 141.7, 138.1, 128.6 \times 2, 128.3 \times 2, 128.0 \times 2, 126.2, 126.1 \times 2, 125.8, 103.0, 92.5, 35.7, 31.5, 18.9, -1.1 \times 3. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{27}\text{Si}$ 307.1877; Found: 307.1882.

3.2 Preparation of tertiary hydrocarbons 2b–2q



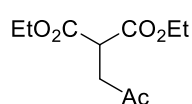
Compounds **2b–2d**, **2f**, **2k**, and **2l** were commercial available. Compounds **2e**, **2g–2j** were prepared according to the general procedure 3.^[2] Compound **2m**^[3], **2n**^[4], and **2o**^[5] were prepared according to the known procedures. Compounds **2p** and **2q** were prepared according to the general procedure 4.^[6]

3.2.1 The general procedure 3 (GP3) for the synthesis of **2e**, **2g–2j**^[2]



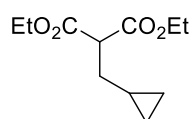
To a stirred solution of diethyl malonate (1.60 g, 10 mmol, 1.0 equiv) in THF (10 mL) was added NaH (60% in mineral oil, 0.42 mg, 10.5 mmol, 1.05 equiv) in several portions at room temperature. The mixture was stirred at this temperature for 10 min. R–Br (1.0 equiv, 10 mmol) was slowly added to the mixture, then the solution was stirred for 12 h at room temperature. After completion of the reaction (as judged by TLC), the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (30 mL \times 3). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 , filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc) to give α -substituted malonates **2e**, **2g–2j**.

Diethyl 2-(2-oxopropyl)malonate (**2e**)



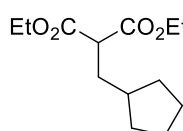
The title compound was prepared according to **GP3** and isolated as a colorless oil (1.54 g, 7.12 mmol, 71%). ^1H NMR (400 MHz, Chloroform-*d*) δ 4.20 (qd, J = 7.1, 2.4 Hz, 4H), 3.85 (t, J = 7.2 Hz, 1H), 3.06 (d, J = 7.1 Hz, 2H), 2.21 (s, 3H), 1.27 (t, J = 7.2 Hz, 6H). The spectral data matched those reported previously.^[7]

Diethyl 2-(cyclopropylmethyl)malonate (**2g**)



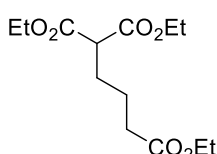
The title compound was prepared according to **GP3** and isolated as a colorless oil (1.61 g, 7.51 mmol, 75%). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.20 (q, J = 7.1 Hz, 4H), 3.44 (t, J = 7.5 Hz, 1H), 1.80 (t, J = 7.3 Hz, 2H), 1.27 (t, J = 7.1 Hz, 6H), 0.79 – 0.68 (m, 1H), 0.49 – 0.41 (m, 2H), 0.12 – 0.06 (m, 2H). The spectral data matched those reported previously.^[2]

Diethyl 2-(cyclopentylmethyl)malonate (2h)



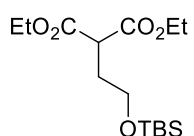
The title compound was prepared according to **GP3** and isolated as a colorless oil (1.52 g, 6.27 mmol, 63%). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.19 (q, J = 7.2 Hz, 4H), 3.44 (t, J = 7.7 Hz, 1H), 1.79 (t, J = 7.3 Hz, 2H), 1.75 – 1.65 (m, 4H), 1.26 (t, J = 7.1 Hz, 6H), 1.22 – 1.10 (m, 3H), 0.91 (dd, J = 12.9, 9.7 Hz, 2H). The spectral data matched those reported previously.^[2]

Triethyl butane-1,1,4-tricarboxylate (2i)



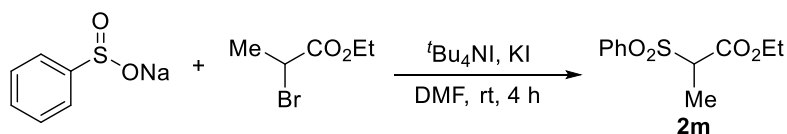
The title compound was prepared according to **GP3** and isolated as a colorless oil (1.46 g, 5.32 mmol, 53%). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.25 – 4.15 (m, 4H), 4.11 (q, J = 7.1 Hz, 2H), 3.33 (t, J = 7.5 Hz, 1H), 2.33 (t, J = 7.5 Hz, 2H), 1.97 – 1.87 (m, 2H), 1.69 – 1.60 (m, 2H), 1.31 – 1.20 (m, 9H). The spectral data matched those reported previously.^[8]

Diethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)malonate (2j)

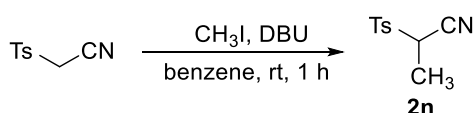


The title compound was prepared according to **GP3** and isolated as a colorless oil (2.32 g, 7.28 mmol, 73%). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.23 – 4.14 (m, 4H), 3.65 (t, J = 5.7 Hz, 2H), 3.58 (t, J = 7.2 Hz, 1H), 2.10 (q, J = 6.2 Hz, 2H), 1.26 (t, J = 7.1 Hz, 6H), 0.87 (s, 9H), 0.02 (s, 6H). The spectral data matched those reported previously.^[9]

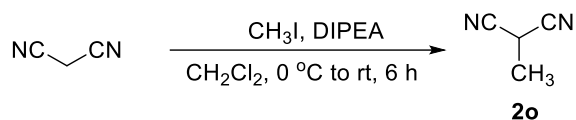
3.2.2 Synthesis of **2m**^[3]



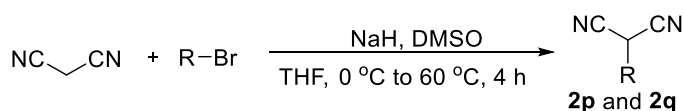
To a solution of sodium benzenesulfonate (0.82 g, 5 mmol, 1.0 equiv) in DMF (30 mL) was added ethyl 2-bromopropionate (1.09 g, 6 mmol, 1.2 equiv), tetrabutylammonium iodide (184.7 mg, 0.5 mmol, 0.1 equiv), potassium iodide (1.00 g, 6 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 4 h and then quenched with saturated aqueous NaHCO₃ (10 mL). The mixture was extracted with CH₂Cl₂ (20 mL \times 3). The combined organic extracts were washed with brine (10 mL), dried over Na₂SO₄. Removal of the solvent in vacuo gave **2m** (831.1 mg, 3.43 mmol, 69%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, J = 8.4, 1.3 Hz, 2H), 7.74 – 7.66 (m, 1H), 7.58 (t, J = 7.7 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 4.05 (q, J = 7.2 Hz, 1H), 1.57 (d, J = 7.1 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H). The spectral data matched those reported previously.^[3]

3.2.3 Synthesis of **2n**^[4]

To a stirred solution of tosylacetonitrile (390.5 mg, 2 mmol, 1.0 equiv) and DBU (334.9 mg, 2 mmol, 1.1 equiv) in benzene (10 mL) was added CH₃I (567.8 mg, 4 mmol, 2.0 equiv) and the solution was stirred at room temperature for 1 h. The precipitated DBU-HI salt was removed by filtration and the residue was concentrated in vacuo to give the crude product. The crude product was purified by flash column chromatography (petroleum ether/EtOAc) to give a colorless liquid **2n** (226.0 mg, 1.08 mmol, 54%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.97 (q, *J* = 7.2 Hz, 1H), 2.48 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H).

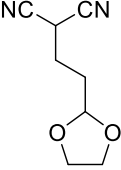
3.2.3 Synthesis of **2o**^[5]

To a solution of malononitrile (330.3 mg, 5 mmol, 1.0 equiv) and *N,N*-diisopropylethylamine (DIPEA, 646.2 mg, 5 mmol, 1.0 equiv) in CH₂Cl₂ (10 mL) was added CH₃I (709.7 mg, 5 mmol, 1.0 equiv) at 0 °C, then the solution was allowed to warm to room temperature and stirred for 4 h. The reaction mixture was concentrated in vacuo to give crude product, which was purified by flash column chromatography (petroleum ether/EtOAc) to afford a colorless liquid **2o** (152.2 mg, 1.9 mmol, 38%) ¹H NMR (400 MHz, Chloroform-*d*) δ 3.79 (q, *J* = 7.3 Hz, 1H), 1.79 (d, *J* = 7.3 Hz, 3H). The spectral data matched those reported previously.^[5]

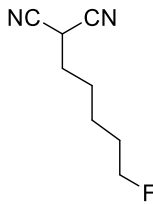
3.2.4 The general procedure 4 (GP4) for the synthesis of **2p** and **2q**^[6]

To a stirred suspension of NaH (60% in mineral oil, 0.40 g, 10 mmol, 1.0 equiv) in THF (30 mL) at 0 °C was added a solution of malononitrile (0.65 g, 10 mmol, 1.0 equiv) in THF (10 mL). After 30 min, DMSO (5 mL) and a solution of alkyl bromide (10 mmol 1.0 equiv) in THF (10 mL) were added, and the mixture was heated to 60 °C and stirred for 4 h. The reaction mixture was quenched with saturated aqueous NH₄Cl (10 mL), and extracted with Et₂O (30 mL × 3). The organic layer was washed with H₂O (10 mL) and brine (10 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc) to give **2p** and **2q**.

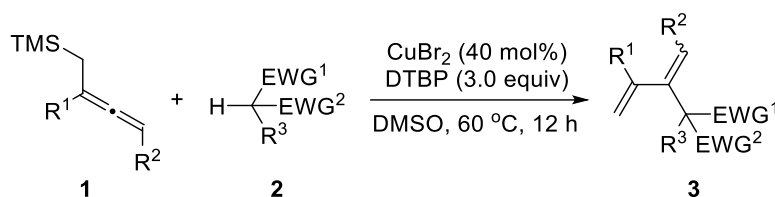
2-(2-(1,3-Dioxolan-2-yl)ethyl)malononitrile (**2p**)


 The title compound was prepared according to **GP4** and isolated as a colorless oil (701.3 mg, 4.22 mmol, 42%). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.93 (t, *J* = 3.8 Hz, 1H), 4.05 (t, *J* = 7.5 Hz, 1H), 4.02 – 3.93 (m, 2H), 3.92 – 3.81 (m, 2H), 2.19 (q, *J* = 7.1 Hz, 2H), 1.99 (td, *J* = 6.9, 3.8 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 112.8 \times 2, 102.7, 65.2 \times 2, 29.4, 25.4, 22.4. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₈H₁₁N₂O₂ 167.0815; Found: 167.0820.

2-(5-Fluoropentyl)malononitrile (2q)

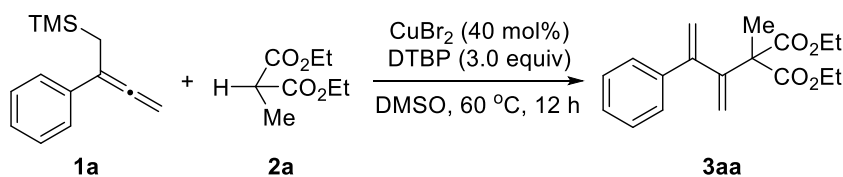

 The title compound was prepared according to **GP4** and isolated as a colorless oil (591.5 mg, 3.84 mmol, 38%). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.46 (dt, *J* = 47.2, 5.8 Hz, 2H), 3.72 (t, *J* = 6.8 Hz, 1H), 2.13 – 1.88 (m, 2H), 1.83 – 1.61 (m, 4H), 1.55 – 1.48 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 112.4 \times 2, 83.5 (d, *J* = 165.2 Hz), 30.7, 29.8 (d, *J* = 19.8 Hz), 26.2, 24.3 (d, *J* = 4.8 Hz), 22.5. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -218.96. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₈H₁₂FN₂ 155.0979; Found: 155.0982.

4. The general procedure 5 (GP5) for the synthesis of 3



An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with CuBr₂ (13.4 mg, 0.06 mmol, 40 mol%) and the tube was evacuated and backfilled with N₂ for 3 times. **1** (0.21 mmol, 1.4 equiv), **2** (0.15 mmol, 1.0 equiv), DTBP (65.8 mg, 0.45 mmol, 3.0 equiv) and DMSO (1.5 mL) were successively added via syringe under N₂ atmosphere. The sealed tube was placed into a preheated oil bath at 60 °C with stirring for 12 h. After cooling to room temperature, the mixture was diluted with water (10 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (10 mL \times 3). The combined organic layers were rinsed with brine (10 mL), dried over Na₂SO₄, and concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc) on silica gel to afford **3**.

5. Scale-up synthesis of product 3aa

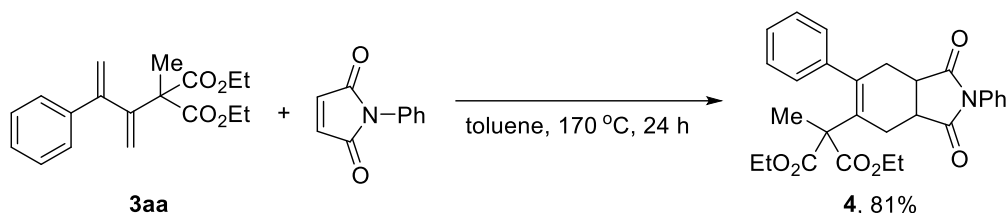


An oven-dried 50 mL Schlenk tube equipped with a stir bar was charged with CuBr₂ (89.3 mg, 0.4 mmol, 40 mol%) and the tube was evacuated and backfilled with N₂ for 3 times. **1a** (283.3 mg, 1.4 mmol, 1.4 equiv), **2a**

(174.2 mg, 1 mmol, 1.0 equiv), DTBP (438.7 mg, 3 mmol, 3.0 equiv) and DMSO (10 mL) were successively added via syringe under N₂ atmosphere. The sealed tube was placed into a preheated oil bath at 60 °C with stirring for 12 h. After cooling to room temperature, the mixture was diluted with water (40 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (30 mL × 3). The combined organic layers were rinsed with brine (10 mL), dried over anhydrous Na₂SO₄, filtered and the filtrate was concentrated in vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/EtOAc) on silica gel to afford the coupling product **3aa** (214.7 mg, 0.71 mmol, 71%).

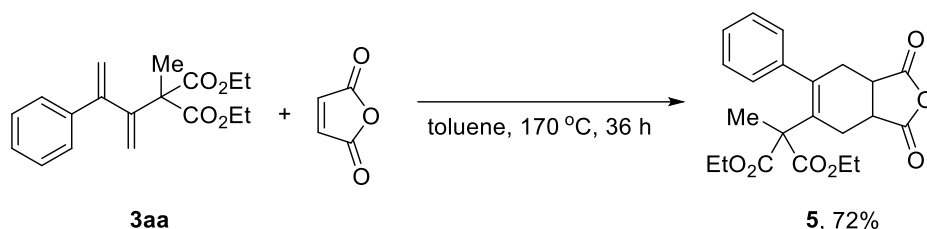
6. Derivatization reactions of product 3aa

6.1 Synthesis of compound 4



To a solution of **3aa** (30.2 mg, 0.10 mmol, 1.0 equiv) in toluene (3.0 mL) was added *N*-phenylmaleimide (34.6 mg, 0.20 mmol, 2.0 equiv), then the mixture was stirred at 170 °C for 24 h. Toluene was removed in vacuo, and the reaction mixture was purified by flash column chromatography (petroleum ether/EtOAc) on silica gel to afford the compound **4** as a colorless oil (38.5 mg, 0.081 mmol, 81%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.43 (m, 2H), 7.42 – 7.36 (m, 1H), 7.35 – 7.29 (m, 2H), 7.27 (t, *J* = 1.6 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.15 – 7.04 (m, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.47 (m, 2H), 3.37 – 3.28 (m, 2H), 2.90 (dd, *J* = 15.0, 3.0 Hz, 1H), 2.73 – 2.66 (m, 2H), 2.61 – 2.49 (m, 1H), 1.43 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 178.6, 178.2, 170.7, 170.5, 141.2, 137.6, 132.1, 131.4, 129.2 × 2, 128.7, 128.3 × 2, 127.9 × 2, 127.2, 126.6 × 2, 62.61, 61.4, 59.9, 40.2, 40.1, 34.1, 29.3, 22.4, 13.8, 13.6. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₈H₃₀NO₆ 476.2068; Found: 476.2073.

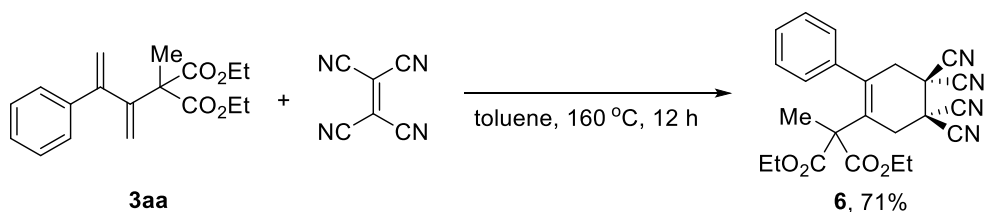
6.2 Synthesis of compound 5



To a solution of **3aa** (30.2 mg, 0.10 mmol, 1.0 equiv) in toluene (3 mL), maleic anhydride (19.6 mg, 0.20 mmol, 2.0 equiv) was added, then the mixture stirred at 170 °C for 36 h. Toluene was removed in vacuo, and the reaction mixture was purified by flash column chromatography (petroleum ether/EtOAc) on silica gel to afford the compound

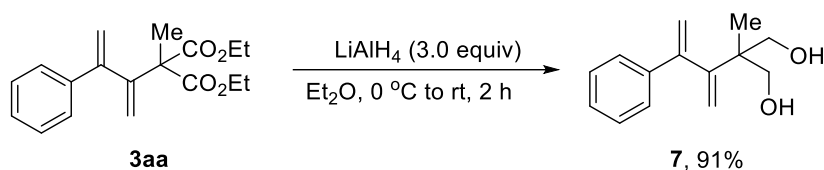
5 as a colorless oil (29.0 mg, 0.072 mmol, 72%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, J = 6.7 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.09 – 6.99 (m, 2H), 3.94 – 3.86 (m, 1H), 3.84 – 3.75 (m, 3H), 3.50 – 3.40 (m, 2H), 2.79 (dd, J = 15.0, 2.4 Hz, 1H), 2.70 – 2.60 (m, 2H), 2.60 – 2.51 (m, 1H), 1.38 (s, 3H), 1.16 (dt, J = 13.9, 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 173.4, 170.6, 170.4, 140.9, 137.8, 131.7, 128.1 \times 2, 128.0 \times 2, 127.5, 61.7, 61.7, 60.0, 40.8, 40.4, 33.4, 29.4, 22.1, 13.7, 13.7. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{25}\text{O}_7$ 401.1595; Found: 401.1600.

6.3 Synthesis of compound 6



To a solution of **3aa** (30.2 mg, 0.10 mmol, 1.0 equiv) in toluene (3 mL) was added tetracyanoethylene (25.6 mg, 0.20 mmol, 2.0 equiv), then the mixture stirred at 160 $^\circ\text{C}$ for 12 h. Toluene was removed in vacuo, and the reaction mixture was purified by flash column chromatography (petroleum ether/EtOAc) on silica gel to afford the compound **6** as a colorless oil (30.5 mg, 0.071 mmol, 71%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 3H), 7.09 (dd, J = 6.6, 2.9 Hz, 2H), 4.21 – 3.89 (m, 4H), 3.31 (s, 2H), 3.27 (s, 2H), 1.28 – 1.22 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6 \times 2, 137.0, 131.9, 129.1, 128.9 \times 2, 128.1 \times 2, 126.2, 110.4 \times 2, 110.2 \times 2, 62.4 \times 2, 59.5, 40.5, 38.0, 37.7, 35.1, 22.1, 13.8 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{23}\text{N}_4\text{O}_4$ 431.1714; Found: 431.1719.

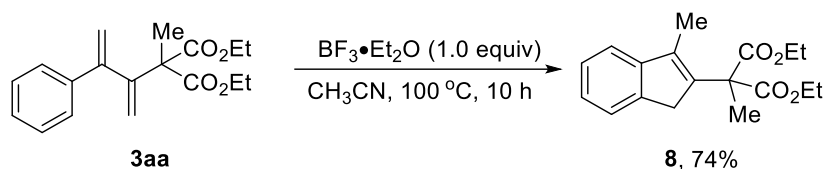
6.4 Synthesis of compound 7



Lithium aluminium hydride (11.4 mg, 0.30 mmol, 3.0 equiv) was taken up in Et_2O (1 mL) and then cooled to 0 $^\circ\text{C}$. To the 0 $^\circ\text{C}$ stirred grey mixture was added dropwise **3aa** (30.2 mg, 0.1 mmol, 1.0 equiv) in a solution of Et_2O (1 mL). The resulting mixture was warmed to room temperature and stirred for 2 h. The mixture was cooled back to 0 $^\circ\text{C}$ and carefully quenched with H_2O (5 mL) to give a white milky mixture, which was then extracted with Et_2O (10 mL \times 3). The combined organic layers were washed with brine (5 mL) and purified by flash column chromatography ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$) on silica gel to afford the compound **7** as a colorless oil (19.9 mg, 0.091 mmol, 91%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 2H), 7.34 – 7.27 (m, 3H), 5.38 (d, J = 1.5 Hz, 1H), 5.36 (d, J = 1.8 Hz, 1H), 5.27 (d, J = 1.6 Hz, 1H), 5.09 (d, J = 1.8 Hz, 1H), 3.59 (d, J = 11.2 Hz, 2H), 3.48 (d, J = 11.0

Hz, 2H), 2.04 (br s, 2H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.5, 150.7, 140.4, 128.5 \times 2, 128.0, 126.3 \times 2, 117.3, 115.8, 68.3 \times 2, 45.8, 19.9. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ 219.1380; Found: 219.1385.

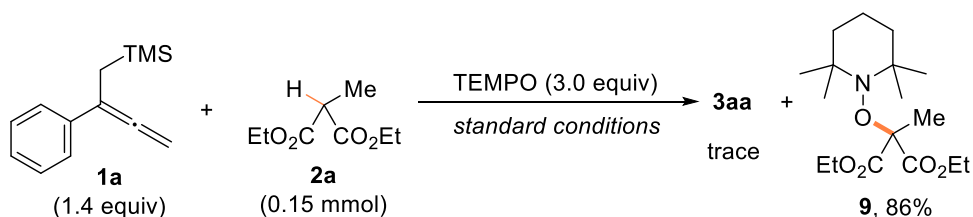
6.5 Synthesis of compound 8



To a solution of **3aa** (30.2 mg, 0.10 mmol, 1.0 equiv) in acetonitrile (2 mL) was added boron trifluoride etherate (14.6 mg, 0.10 mmol, 1.0 equiv, 46.5% in Et_2O). Then, the mixture stirred at 100 °C for 10 h under N_2 atmosphere. Acetonitrile was removed in vacuo and the reaction mixture was purified by flash column chromatography (petroleum ether/ EtOAc) on silica gel to afford the compound **8** as a colorless oil (22.4 mg, 0.074 mmol, 74%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, J = 7.3 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.20 – 7.16 (m, 1H), 4.30 – 4.12 (m, 4H), 3.43 (d, J = 2.3 Hz, 2H), 2.05 (t, J = 2.2 Hz, 3H), 1.77 (s, 3H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5 \times 2, 146.9, 141.7, 137.0, 136.9, 126.2, 124.8, 123.1, 118.8, 61.7 \times 2, 56.0, 39.7, 22.5, 14.0 \times 2, 12.0. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{O}_4$ 303.1591; Found: 303.1596.

7. Mechanistic exploration experiments

7.1 Radical trapping experiments



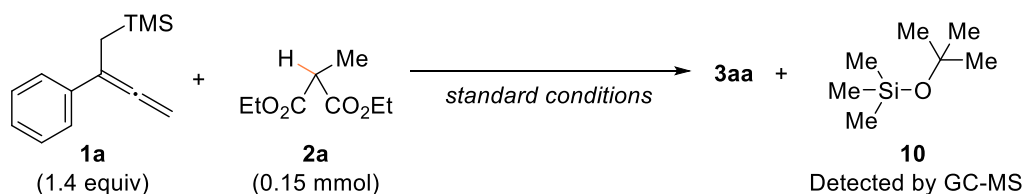
An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with CuBr_2 (13.4 mg, 0.06 mmol, 40 mol%), 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO, 70.3 mg, 0.45 mmol, 3.0 equiv) and the tube was evacuated and backfilled with N_2 for 3 times. **1a** (42.5 mg, 0.21 mmol, 1.4 equiv), **2a** (26.1 mg, 0.15 mmol, 1.0 equiv), DTBP (65.8 mg, 0.45 mmol, 3.0 equiv) and DMSO (1.5 mL) were successively added via syringe under N_2 atmosphere. The mixture was stirred at 60 °C for 12 h under N_2 atmosphere. After cooling to room temperature, the mixture was diluted with water (10 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL \times 3). The combined organic layers were rinsed with brine (10 mL), dried over Na_2SO_4 , and concentrated in vacuo. Traces of the coupling product **3aa** was observed by TLC analysis. The resultant residue was purified by flash column chromatography (petroleum ether/ EtOAc) on silica gel to afford **9** (42.5 mg, 0.129 mmol, 86%). ^1H NMR

(400 MHz, Chloroform-*d*) δ 4.63 – 4.01 (m, 4H), 1.73 (s, 3H), 1.65 – 1.38 (m, 6H), 1.27 (t, $J = 7.2$ Hz, 6H), 1.22 (s, 6H), 1.02 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2 \times 2, 85.3, 61.5 \times 2, 60.1 \times 2, 40.6 \times 2, 32.9 \times 2, 20.5 \times 2, 17.8, 16.8, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{32}\text{NO}_5$ 330.2275; Found: 330.2281.



An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with CuBr_2 (13.4 mg, 0.06 mmol, 40 mol%), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 33.1 mg, 0.15 mmol, 1.0 equiv) and the tube was evacuated and backfilled with N_2 for 3 times. **1a** (42.5 mg, 0.21 mmol, 1.4 equiv), **2a** (26.1 mg, 0.15 mmol, 1.0 equiv), DTBP (65.8 mg, 0.45 mmol, 3.0 equiv) and DMSO (1.5 mL) were successively added via syringe under N_2 atmosphere. The mixture was stirred at 60 °C for 12 h under N_2 atmosphere. After cooling to room temperature, the mixture was diluted with water (10 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL \times 3). The combined organic layers were rinsed with brine (10 mL), dried over Na_2SO_4 , and concentrated in vacuo. Traces of the desired product **3aa** was observed from ^1H NMR spectrometry of the crude mixture.

7.2 By-product tracking experiment



Following the standard conditions for the preparation of **3aa**, by-product **10** in the reaction crude mixture was detected by GC-MS analysis (CH_2Cl_2 as solvent) in comparison with commercial available *tert*-butoxytrimethylsilane.

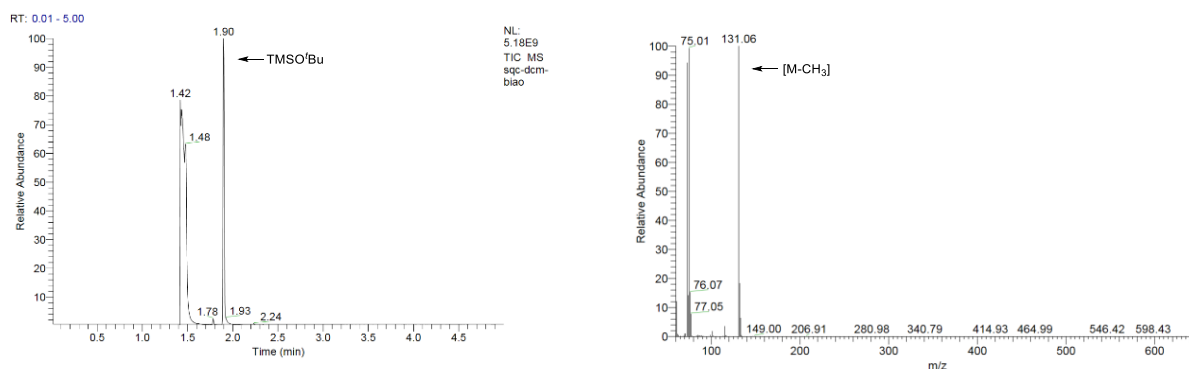


Figure S1. GC-MS spectrum for commercial available *tert*-butoxytrimethylsilane

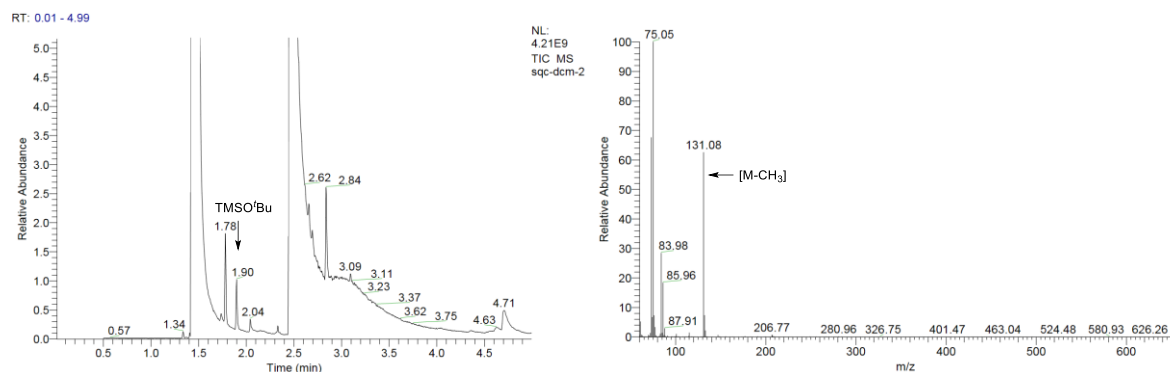
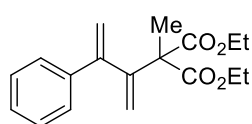


Figure S2. GC-MS spectrum of the reaction mixture

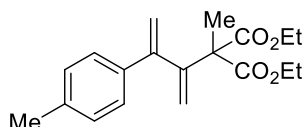
8. NMR data of the products

Diethyl 2-methyl-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3aa)



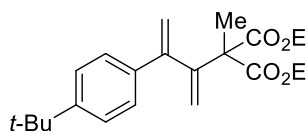
The title compound was prepared according to **GP5** and isolated as a yellow oil (31.8 mg, 0.105 mmol, 70%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.32 – 7.25 (m, 3H), 5.44 (s, 1H), 5.37 (d, J = 1.3 Hz, 1H), 5.32 (s, 1H), 5.22 (d, J = 1.4 Hz, 1H), 4.09 (dddd, J = 17.9, 10.7, 7.1, 3.6 Hz, 4H), 1.52 (s, 3H), 1.21 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1 \times 2, 148.8, 146.4, 140.6, 128.0 \times 2, 127.6, 127.2 \times 2, 120.5, 116.0, 61.5 \times 2, 59.4, 22.0, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{O}_4$ 303.1591; Found: 303.1588.

Diethyl 2-methyl-2-(3-(*p*-tolyl)buta-1,3-dien-2-yl)malonate (3ba)

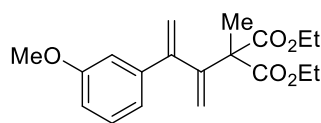


The title compound was prepared according to **GP5** and isolated as a yellow oil (33.5 mg, 0.106 mmol, 71%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 5.44 (d, J = 0.6 Hz, 1H), 5.36 (d, J = 1.5 Hz, 1H), 5.33 (s, 1H), 5.18 (d, J = 1.5 Hz, 1H), 4.20 – 4.03 (m, 4H), 2.33 (s, 3H), 1.53 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2 \times 2, 148.6, 146.4, 137.7, 137.4, 128.7 \times 2, 127.1 \times 2, 120.3, 115.2, 61.5 \times 2, 59.3, 21.9, 21.1, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{25}\text{O}_4$ 317.1747; Found: 317.1753.

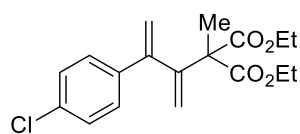
Diethyl 2-(3-(4-(*tert*-butyl)phenyl)buta-1,3-dien-2-yl)-2-methylmalonate (3ca)



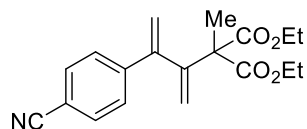
The title compound was prepared according to **GP5** and isolated as a yellow oil (35.1 mg, 0.098 mmol, 65%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 4H), 5.44 (d, J = 0.7 Hz, 1H), 5.38 (d, J = 1.5 Hz, 1H), 5.33 (d, J = 0.8 Hz, 1H), 5.18 (d, J = 1.5 Hz, 1H), 4.09 (qq, J = 10.7, 7.1 Hz, 4H), 1.55 (s, 3H), 1.31 (s, 9H), 1.21 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2 \times 2, 150.6, 148.5, 146.4, 137.6, 126.8 \times 2, 124.9 \times 2, 120.3, 115.3, 61.5 \times 2, 59.4, 34.5, 31.3 \times 3, 22.0, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{31}\text{O}_4$ 359.2217; Found: 359.2222.

Diethyl 2-(3-(3-methoxyphenyl)buta-1,3-dien-2-yl)-2-methylmalonate (3da)

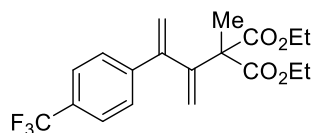
The title compound was prepared according to **GP5** and isolated as a yellow oil (31.3 mg, 0.094 mmol, 63%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.21 (t, J = 7.9 Hz, 1H), 6.99 (dt, J = 7.7, 1.3 Hz, 1H), 6.95 (dd, J = 2.6, 1.7 Hz, 1H), 6.81 (ddd, J = 8.1, 2.6, 0.9 Hz, 1H), 5.45 (s, 1H), 5.40 (d, J = 1.4 Hz, 1H), 5.35 (s, 1H), 5.23 (d, J = 1.5 Hz, 1H), 4.19 – 4.03 (m, 4H), 3.80 (s, 3H), 1.53 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1 \times 2, 159.3, 148.6, 146.2, 142.0, 129.0, 120.6, 119.7, 116.1, 113.1, 112.9, 61.5 \times 2, 59.3, 55.2, 21.9, 13.8 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{25}\text{O}_5$ 333.1697; Found: 333.1702.

Diethyl 2-(3-(4-chlorophenyl)buta-1,3-dien-2-yl)-2-methylmalonate (3ea)

The title compound was prepared according to **GP5** and isolated as a yellow oil (32.3 mg, 0.096 mmol, 64%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 2H), 7.27 – 7.25 (m, 2H), 5.46 (s, 1H), 5.37 (d, J = 1.3 Hz, 1H), 5.32 (s, 1H), 5.24 (d, J = 1.2 Hz, 1H), 4.20 – 3.99 (m, 4H), 1.53 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0 \times 2, 147.7, 146.0, 139.1, 133.5, 128.6 \times 2, 128.2 \times 2, 120.8, 116.5, 61.6 \times 2, 59.3, 22.0, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}\text{ClO}_4$ 337.1201; Found: 337.1207.

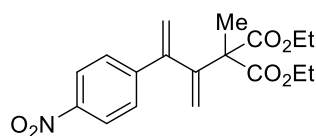
Diethyl 2-(3-(4-cyanophenyl)buta-1,3-dien-2-yl)-2-methylmalonate (3fa)

The title compound was prepared according to **GP5** and isolated as a yellow oil (27.8 mg, 0.085 mmol, 57%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.56 (m, 2H), 7.54 – 7.48 (m, 2H), 5.52 (s, 1H), 5.49 (d, J = 0.9 Hz, 1H), 5.39 (d, J = 1.0 Hz, 1H), 5.32 (s, 1H), 4.11 (qq, J = 10.7, 7.1 Hz, 4H), 1.54 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8 \times 2, 147.4, 145.5, 145.3, 132.0 \times 2, 127.8 \times 2, 121.5, 118.8, 118.7, 111.2, 61.7 \times 2, 59.3, 22.2, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_4$ 328.1543; Found: 328.1549.

Diethyl 2-methyl-2-(3-(4-(trifluoromethyl)phenyl)buta-1,3-dien-2-yl)malonate (3ga)

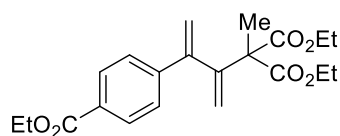
The title compound was prepared according to **GP5** and isolated as a yellow oil (31.2 mg, 0.084 mmol, 56%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.46 (m, 4H), 5.50 (s, 1H), 5.45 (d, J = 1.1 Hz, 1H), 5.34 (d, J = 1.1 Hz, 1H), 5.33 (s, 1H), 4.10 (qq, J = 10.8, 7.1 Hz, 4H), 1.55 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1 \times 2, 147.8, 146.0, 144.4 (q, J = 1.3 Hz), 129.7 (q, J = 32.4 Hz), 127.7 \times 2, 125.2 \times 2 (q, J = 4.1 Hz), 124.3 (q, J = 272.1 Hz), 121.3, 117.9, 61.7 \times 2, 59.4, 22.3, 14.0 \times 2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.38. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{22}\text{F}_3\text{O}_4$ 371.1465; Found: 371.1470.

Diethyl 2-methyl-2-(3-(4-nitrophenyl)buta-1,3-dien-2-yl)malonate (3ha)



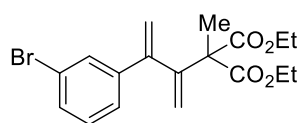
The title compound was prepared according to **GP5** and isolated as a yellow oil (19.9 mg, 0.057 mmol, 38%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.14 (m, 2H), 7.65 – 7.54 (m, 2H), 5.55 – 5.52 (m, 2H), 5.43 (d, J = 0.9 Hz, 1H), 5.34 (s, 1H), 4.20 – 4.00 (m, 4H), 1.56 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8 \times 2, 147.3, 147.1, 147.1, 145.5, 128.0 \times 2, 123.4 \times 2, 121.7, 119.2, 61.7 \times 2, 59.3, 22.2, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_6$ 348.1442; Found: 348.1447.

Diethyl 2-(3-(4-(ethoxycarbonyl)phenyl)buta-1,3-dien-2-yl)-2-methylmalonate (3ia)



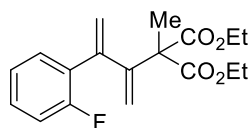
The title compound was prepared according to **GP5** and isolated as a yellow oil (35.9 mg, 0.096 mmol, 64%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 5.51 – 5.46 (m, 2H), 5.34 (s, 2H), 4.37 (q, J = 7.1 Hz, 2H), 4.17 – 4.04 (m, 4H), 1.53 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0 \times 2, 166.4, 148.1, 145.9, 145.1, 129.5, 129.4 \times 2, 127.1 \times 2, 121.0, 117.7, 61.6 \times 2, 60.9, 59.3, 22.0, 14.3, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{27}\text{O}_6$ 375.1802; Found: 375.1808.

Diethyl 2-(3-(3-bromophenyl)buta-1,3-dien-2-yl)-2-methylmalonate (3ja)

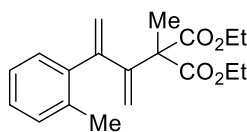


The title compound was prepared according to **GP5** and isolated as a yellow oil (31.9 mg, 0.084 mmol, 56%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.53 (t, J = 1.9 Hz, 1H), 7.39 (ddd, J = 7.9, 2.0, 1.1 Hz, 1H), 7.32 (dt, J = 7.8, 1.3 Hz, 1H), 7.17 (t, J = 7.9 Hz, 1H), 5.47 (s, 1H), 5.39 (d, J = 1.2 Hz, 1H), 5.33 (s, 1H), 5.27 (d, J = 1.2 Hz, 1H), 4.23 – 3.96 (m, 4H), 1.54 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0 \times 2, 147.6, 145.9, 142.8, 130.6, 130.2, 129.6, 125.9, 122.2, 121.0, 117.2, 61.6 \times 2, 59.2, 22.1, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}^{79}\text{BrO}_4$ 381.0696; Found: 381.0702.

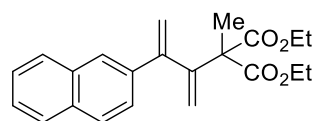
Diethyl 2-(3-(2-fluorophenyl)buta-1,3-dien-2-yl)-2-methylmalonate (3ka)



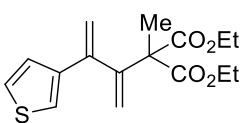
The title compound was prepared according to modified **GP5** as the reaction was carried out at 80 °C and isolated as a yellow oil (29.4 mg, 0.092 mmol, 61%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, J = 1.8 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.07 (dd, J = 7.5, 1.2 Hz, 1H), 7.05 – 6.98 (m, 1H), 5.40 (d, J = 1.0 Hz, 1H), 5.34 (d, J = 1.3 Hz, 1H), 5.31 (s, 1H), 5.23 (s, 1H), 4.21 – 4.05 (m, 4H), 1.62 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1 \times 2, 159.8 (d, J = 248.8 Hz), 146.3, 142.4, 131.0 (d, J = 3.5 Hz), 129.1 (d, J = 8.2 Hz), 128.8 (d, J = 13.6 Hz), 123.6 (d, J = 3.8 Hz), 119.8, 119.6 (d, J = 3.4 Hz), 115.7 (d, J = 22.2 Hz), 61.6 \times 2, 59.1, 21.9, 13.8 \times 2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.05. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}\text{FO}_4$ 321.1497; Found: 321.1502.

Diethyl 2-methyl-2-(3-(*o*-tolyl)buta-1,3-dien-2-yl)malonate (3la)

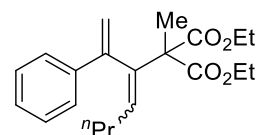
The title compound was prepared according to modified **GP5** as the reaction was carried out at 80 °C and isolated as a yellow oil (16.1 mg, 0.051 mmol, 34%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.00 (m, 4H), 5.30 (s, 1H), 5.18 (d, *J* = 1.1 Hz, 1H), 5.06 (s, 1H), 4.93 (s, 1H), 4.22 – 4.13 (m, 4H), 2.24 (s, 3H), 1.75 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.3 \times 2, 147.1, 146.0, 141.6, 136.1, 129.8, 129.7, 127.2, 125.3, 119.5, 117.1, 61.6 \times 2, 59.1, 22.3, 19.7, 13.9 \times 2. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₅O₄ 317.1747; Found: 317.1753.

Diethyl 2-methyl-2-(3-(naphthalen-2-yl)buta-1,3-dien-2-yl)malonate (3ma)

The title compound was prepared according to **GP5** and isolated as a yellow oil (36.9 mg, 0.105 mmol, 70%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.76 (m, 4H), 7.56 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.49 – 7.43 (m, 2H), 5.53 (s, 2H), 5.42 (s, 1H), 5.34 (d, *J* = 1.2 Hz, 1H), 4.19 – 4.00 (m, 4H), 1.57 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.2 \times 2, 148.7, 146.3, 137.9, 133.1, 132.8, 128.2, 127.7, 127.5, 126.4, 126.1, 126.0, 125.3, 120.8, 116.5, 61.5 \times 2, 59.4, 22.0, 13.8 \times 2. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₅O₄ 353.1747; Found: 353.1753.

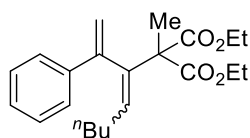
Diethyl 2-methyl-2-(3-(thiophen-3-yl)buta-1,3-dien-2-yl)malonate (3na)

The title compound was prepared according to **GP5** and isolated as a yellow oil (23.2 mg, 0.075 mmol, 50%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.25 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.20 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.18 (dd, *J* = 4.9, 1.4 Hz, 1H), 5.45 – 5.43 (m, 2H), 5.37 (d, *J* = 0.6 Hz, 1H), 5.14 (d, *J* = 1.4 Hz, 1H), 4.19 – 4.08 (m, 4H), 1.56 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.3 \times 2, 146.3, 143.2, 142.4, 126.2, 125.7, 123.0, 120.0, 114.4, 61.7 \times 2, 59.5, 21.8, 14.0 \times 2. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₂₁O₄S 309.1155; Found: 309.1161.

Diethyl 2-methyl-2-(2-phenylhepta-1,3-dien-3-yl)malonate (3oa)

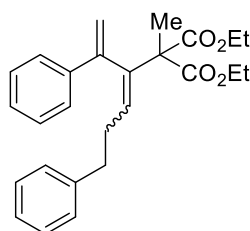
The title compound was prepared according to **GP5** and isolated as a yellow oil (34.8 mg, 0.100 mmol, 67%, *E/Z* = 9.1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.42 (m, 2H), 7.34 – 7.27 (m, 3H), 5.83 (t, *J* = 7.3 Hz, 1H), 5.69 (d, *J* = 1.7 Hz, 1H), 5.12 (d, *J* = 1.6 Hz, 1H), 4.13 – 4.05 (m, 4H), 2.05 – 1.99 (m, 2H), 1.43 (s, 3H), 1.38 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.21 (d, *J* = 7.1 Hz, 6H), 0.87 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.8 \times 2, 145.1, 139.6, 136.4, 134.6, 128.3 \times 2, 127.7, 126.3 \times 2, 116.3, 61.4 \times 2, 59.9, 31.9, 22.7, 21.7, 14.0, 13.9 \times 2. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₉O₄ 345.2060; Found: 345.2066.

Diethyl 2-methyl-2-(2-phenylocta-1,3-dien-3-yl)malonate (3pa)



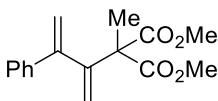
The title compound was prepared according to **GP5** and isolated as a yellow oil (34.1 mg, 0.095 mmol, 63%, *E/Z* = 10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.41 (m, 2H), 7.33 – 7.28 (m, 3H), 5.82 (t, *J* = 7.3 Hz, 1H), 5.69 (d, *J* = 1.6 Hz, 1H), 5.12 (d, *J* = 1.5 Hz, 1H), 4.13 – 4.06 (m, 4H), 2.07 – 2.02 (m, 2H), 1.43 (s, 3H), 1.38 – 1.28 (m, 4H), 1.22 (d, *J* = 7.1 Hz, 6H), 0.84 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.7 \times 2, 144.9, 139.5, 136.0, 134.6, 128.2 \times 2, 127.6, 126.2 \times 2, 116.2, 61.3 \times 2, 59.7, 31.6, 29.5, 22.3, 21.5, 14.0, 13.9 \times 2. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₂H₃₁O₄ 359.2217; Found: 359.2223.

Diethyl 2-(2,5-diphenylpenta-1,3-dien-3-yl)-2-methylmalonate (3qa)



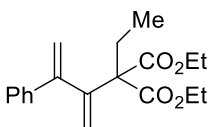
The title compound was prepared according to **GP5** and isolated as a yellow oil (33.7 mg, 0.083 mmol, 55%, *E/Z* = 10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 7.29 (dd, *J* = 2.6, 1.8 Hz, 1H), 7.24 – 7.22 (m, 3H), 7.19 – 7.13 (m, 2H), 7.11 – 7.08 (m, 2H), 5.88 (t, *J* = 7.3 Hz, 1H), 5.65 (d, *J* = 1.6 Hz, 1H), 5.02 (d, *J* = 1.5 Hz, 1H), 4.07 (ddd, *J* = 10.7, 7.1, 3.5 Hz, 4H), 2.67 (dd, *J* = 8.6, 6.8 Hz, 2H), 2.39 – 2.34 (m, 2H), 1.42 (s, 3H), 1.20 (d, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.5 \times 2, 144.7, 141.6, 139.3, 137.0, 133.2, 128.5 \times 2, 128.3, 128.2 \times 2, 128.2 \times 2, 127.6, 126.1 \times 2, 125.8, 61.3 \times 2, 59.6, 35.7, 31.9, 21.5, 13.9 \times 2. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₆H₃₁O₄ 407.2217; Found: 407.2222.

Dimethyl 2-methyl-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3ab)



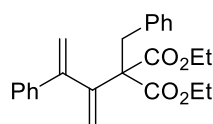
The title compound was prepared according to **GP5** and isolated as a yellow oil (26.4 mg, 0.096 mmol, 64%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 2H), 7.32 – 7.25 (m, 3H), 5.41 (s, 1H), 5.37 (d, *J* = 1.2 Hz, 1H), 5.34 (s, 1H), 5.20 (d, *J* = 1.2 Hz, 1H), 3.62 (s, 6H), 1.54 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.5 \times 2, 148.7, 146.2, 140.4, 128.1 \times 2, 127.7, 127.2 \times 2, 120.5, 116.3, 59.4 \times 2, 52.6, 21.9. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₉O₄ 275.1278; Found: 275.1283.

Diethyl 2-ethyl-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3ac)



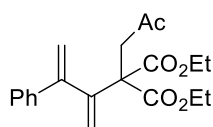
The title compound was prepared according to modified **GP5** as the reaction was carried out at 70 °C and isolated as a yellow oil (31.3 mg, 0.099 mmol, 66%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.34 (m, 2H), 7.31 – 7.25 (m, 3H), 5.60 (d, *J* = 0.9 Hz, 1H), 5.35 (d, *J* = 0.9 Hz, 1H), 5.30 (d, *J* = 1.3 Hz, 1H), 5.19 (d, *J* = 1.4 Hz, 1H), 4.10 – 3.94 (m, 4H), 2.02 (q, *J* = 7.4 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 6H), 0.90 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.1 \times 2, 149.3, 145.0, 140.7, 127.9 \times 2, 127.6, 127.3 \times 2, 121.3, 115.9, 63.3, 61.1 \times 2, 28.4, 13.9 \times 2, 9.6. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₅O₄ 317.1747; Found: 317.1753.

Diethyl 2-benzyl-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3ad)



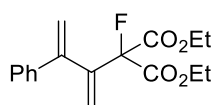
The title compound was prepared according to **GP5** and isolated as a yellow oil (35.1 mg, 0.093 mmol, 62%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 2H), 7.34 – 7.27 (m, 3H), 7.23 – 7.17 (m, 5H), 5.41 (s, 1H), 5.38 (d, J = 1.2 Hz, 1H), 5.34 (s, 1H), 5.25 (d, J = 1.2 Hz, 1H), 4.03 – 3.84 (m, 4H), 3.40 (s, 2H), 1.10 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6 \times 2, 149.4, 144.1, 140.7, 136.6, 130.6 \times 2, 127.9 \times 2, 127.8 \times 2, 127.6, 127.5 \times 2, 126.8, 122.3, 115.9, 64.4, 61.2 \times 2, 41.3, 13.7 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{27}\text{O}_4$ 379.1904; Found: 379.1909.

Diethyl 2-(2-oxopropyl)-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3ae)



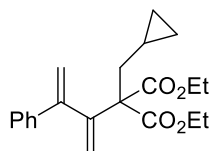
The title compound was prepared according to **GP5** and isolated as a yellow oil (32.1 mg, 0.093 mmol, 62%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.34 – 7.28 (m, 3H), 5.50 (s, 1H), 5.40 (d, J = 1.5 Hz, 1H), 5.35 (s, 1H), 5.17 (d, J = 1.4 Hz, 1H), 4.16 – 4.00 (m, 4H), 3.06 (s, 2H), 2.06 (s, 3H), 1.21 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.8, 169.2 \times 2, 148.7, 145.0, 139.6, 128.2 \times 2, 128.0, 127.0 \times 2, 120.8, 116.7, 61.7 \times 2, 60.6, 48.2, 29.9, 13.8 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{25}\text{O}_5$ 345.1697; Found: 345.1702.

Diethyl 2-fluoro-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3af)



The title compound was prepared according to **GP5** and isolated as a yellow oil (29.4 mg, 0.096 mmol, 64%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.22 (m, 5H), 5.57 (d, J = 3.0 Hz, 1H), 5.48 – 5.40 (m, 2H), 5.35 (d, J = 2.0 Hz, 1H), 4.30 – 4.15 (m, 4H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4 \times 2 (d, J = 26.9 Hz), 146.1, 142.1 (d, J = 19.7 Hz), 140.4, 128.1 \times 2, 127.9 \times 2, 127.8, 123.1 (d, J = 7.2 Hz), 116.8 (d, J = 2.4 Hz), 95.1 (d, J = 199.4 Hz), 62.8 \times 2, 13.8 \times 2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.84. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{20}\text{FO}_4$ 307.1340; Found: 307.1342.

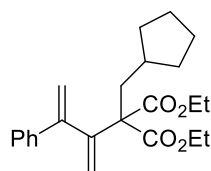
Diethyl 2-(cyclopropylmethyl)-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3ag)



The title compound was prepared according to **GP5** and isolated as a yellow oil (30.5 mg, 0.089 mmol, 59%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.34 (m, 2H), 7.30 – 7.25 (m, 3H), 5.69 (d, J = 0.9 Hz, 1H), 5.36 (d, J = 1.1 Hz, 1H), 5.31 (d, J = 1.4 Hz, 1H), 5.21 (d, J = 1.4 Hz, 1H), 4.13 – 3.89 (m, 4H), 1.94 (d, J = 6.6 Hz, 2H), 1.18 (t, J = 7.1 Hz, 6H), 0.90 – 0.78 (m, 1H), 0.42 – 0.36 (m, 2H), 0.04 – -0.01 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2 \times 2, 149.4, 145.3, 140.7, 127.9 \times 2, 127.6, 127.3 \times 2, 121.4, 115.9, 62.7, 61.1 \times 2, 40.3, 13.8 \times 2, 6.9, 4.6 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{27}\text{O}_4$ 343.1904; Found: 343.1909.

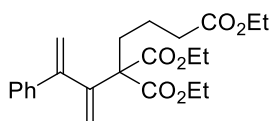
Diethyl 2-(cyclopentylmethyl)-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3ah)

The title compound was prepared according to modified **GP5** as the reaction was carried out at 80 °C and isolated



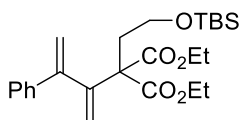
as a yellow oil (36.5 mg, 0.099 mmol, 66%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 2H), 7.30 – 7.22 (m, 3H), 5.73 (d, J = 0.9 Hz, 1H), 5.35 (d, J = 0.9 Hz, 1H), 5.29 (d, J = 1.4 Hz, 1H), 5.19 (d, J = 1.4 Hz, 1H), 4.08 – 3.88 (m, 4H), 1.93 (d, J = 5.5 Hz, 2H), 1.64 – 1.57 (m, 4H), 1.16 (t, J = 7.2 Hz, 6H), 1.13 – 1.02 (m, 1H), 0.94 – 0.85 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4 \times 2, 149.6, 145.3, 140.9, 128.0 \times 2, 127.6, 127.5 \times 2, 121.5, 116.1, 61.8 \times 2, 61.1, 42.3, 34.4 \times 2, 34.3, 26.5, 26.3, 13.9 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{31}\text{O}_4$ 371.2217; Found: 371.2223.

Triethyl 5-methylene-6-phenylhept-6-ene-1,4,4-tricarboxylate (3ai)



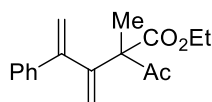
The title compound was prepared according to **GP5** and isolated as a yellow oil (40.0 mg, 0.099 mmol, 66%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 2H), 7.30 – 7.25 (m, 2H), 7.25 – 7.22 (m, 1H), 5.62 (s, 1H), 5.36 (d, J = 0.9 Hz, 1H), 5.30 (d, J = 1.4 Hz, 1H), 5.19 (d, J = 1.4 Hz, 1H), 4.11 – 4.03 (m, 4H), 4.02 – 3.94 (m, 2H), 2.21 (t, J = 7.5 Hz, 2H), 2.03 – 1.91 (m, 2H), 1.68 – 1.60 (m, 2H), 1.23 – 1.16 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1, 169.9 \times 2, 149.2, 144.7, 140.6, 127.9 \times 2, 127.6, 127.3 \times 2, 121.6, 116.1, 62.6, 61.3 \times 2, 60.2, 34.4, 34.4, 20.6, 14.2, 13.8 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{31}\text{O}_6$ 403.2115; Found: 403.2121.

Diethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3aj)



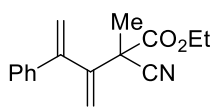
The title compound was prepared according to **GP5** and isolated as a yellow oil (46.7 mg, 0.105 mmol, 70%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 (dd, J = 8.1, 1.6 Hz, 2H), 7.32 – 7.26 (m, 3H), 5.63 (d, J = 0.8 Hz, 1H), 5.38 (d, J = 0.8 Hz, 1H), 5.33 (d, J = 1.3 Hz, 1H), 5.20 (d, J = 1.3 Hz, 1H), 4.09 – 3.96 (m, 4H), 3.73 – 3.65 (m, 2H), 2.34 – 2.23 (m, 2H), 1.18 (t, J = 7.1 Hz, 6H), 0.86 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9 \times 2, 149.2, 144.7, 140.6, 127.9 \times 2, 127.6, 127.4 \times 2, 121.6, 116.0, 61.3 \times 2, 60.9, 59.9, 37.7, 25.9 \times 3, 18.3, 13.8 \times 2, -5.3 \times 2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{39}\text{O}_5\text{Si}$ 447.2561; Found: 447.2566.

Ethyl 2-acetyl-2-methyl-3-methylene-4-phenylpent-4-enoate (3ak)



The title compound was prepared according to **GP5** and isolated as a yellow oil (15.5 mg, 0.057 mmol, 38%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 2H), 7.34 – 7.27 (m, 3H), 5.41 (d, J = 0.6 Hz, 1H), 5.36 (d, J = 1.2 Hz, 1H), 5.33 (d, J = 0.6 Hz, 1H), 5.16 (d, J = 1.2 Hz, 1H), 4.09 (qd, J = 7.1, 1.9 Hz, 2H), 2.29 (s, 3H), 1.44 (s, 3H), 1.25 – 1.18 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.8, 171.4, 149.0, 146.6, 140.4, 128.2 \times 2, 127.8, 127.3 \times 2, 121.3, 116.0, 65.3, 61.5, 26.9, 20.6, 13.9. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{21}\text{O}_3$ 273.1485; Found: 273.1491.

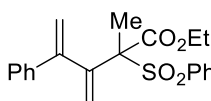
Ethyl 2-cyano-2-methyl-3-methylene-4-phenylpent-4-enoate (3al)



The title compound was prepared according to modified **GP5** as the reaction was carried out at 70 °C and isolated as a yellow oil (23.7 mg, 0.093 mmol, 62%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 5H), 5.77 (s, 1H), 5.43 (d, *J* = 0.9 Hz, 1H), 5.42 (s, 1H), 5.32

(d, *J* = 0.9 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.94 – 3.86 (m, 1H), 1.72 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 167.4, 146.8, 143.7, 139.4, 128.2 × 2, 128.1, 127.3 × 2, 120.4, 119.2, 117.6, 63.0, 48.2, 23.3, 13.7. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₈NO₂ 256.1332; Found: 256.1338.

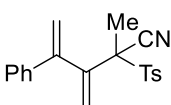
Ethyl 2-methyl-3-methylene-4-phenyl-2-(phenylsulfonyl)pent-4-enoate (3am)



The title compound was prepared according to modified **GP5** as the reaction was carried out at 50 °C and isolated as a yellow oil (34.1 mg, 0.092 mmol, 61%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.69 – 7.62 (m, 1H), 7.53 (dd, *J* = 8.4, 7.1

Hz, 2H), 7.26 (s, 5H), 5.97 (d, *J* = 0.8 Hz, 1H), 5.58 (d, *J* = 0.7 Hz, 1H), 5.32 (d, *J* = 1.4 Hz, 1H), 4.93 (d, *J* = 1.3 Hz, 1H), 4.01 – 3.68 (m, 2H), 1.80 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 167.5, 148.6, 142.4, 139.5, 136.6, 133.8, 132.0 × 2, 128.2 × 2, 128.1 × 2, 127.9, 126.8 × 2, 125.4, 116.4, 76.5, 62.2, 20.5, 13.5. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₃O₄S 371.1312; Found: 371.1317.

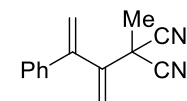
2-Methyl-3-methylene-4-phenyl-2-tosylpent-4-enenitrile (3an)



The title compound was prepared according to **GP5** and isolated as a yellow oil (34.1 mg, 0.100 mmol, 67%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.26 (m, 5H), 5.83 (s, 1H), 5.64 (s, 1H), 5.55 (s, 1H), 5.21 (s, 1H), 2.48 (s, 3H), 1.66

(s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.5, 146.2, 139.2, 139.1, 131.3 × 2, 130.6, 129.7 × 2, 128.6 × 2, 128.3, 126.8, 126.4 × 2, 118.8, 117.7, 65.7, 21.8, 20.8. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₀NO₂S 338.1209; Found: 338.1215.

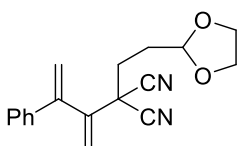
2-Methyl-2-(3-phenylbuta-1,3-dien-2-yl)malononitrile (3ao)



The title compound was prepared according to **GP5** and isolated as a yellow oil (23.5 mg, 0.113 mmol, 75%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.32 (m, 5H), 5.96 (d, *J* = 0.5 Hz, 1H), 5.64 (d, *J* = 0.6 Hz, 1H), 5.58 (s, 1H), 5.49 (s, 1H), 1.84 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 144.8, 140.8, 138.3, 128.8, 128.7 × 2, 127.1 × 2, 121.7, 119.5, 115.1 × 2, 36.3, 26.0. HRMS (ESI)

m/z: [M + H]⁺ Calcd for C₁₄H₁₃N₂ 209.1073; Found: 209.1079.

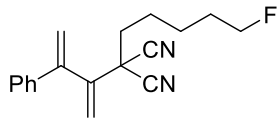
Diethyl 2-(3-(1,3-dioxolan-2-yl)propyl)-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3ap)



The title compound was prepared according to **GP5** and isolated as a yellow oil (26.9 mg, 0.091 mmol, 61%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 5H), 5.93 (s, 1H), 5.59 (s, 2H), 5.45 (s, 1H), 4.87 (t, *J* = 4.0 Hz, 1H), 3.92 – 3.75 (m, 4H), 2.17 – 2.08 (m,

2H), 1.98 – 1.93 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.0, 139.8, 138.3, 128.8, 128.6 \times 2, 127.2 \times 2, 122.4, 119.6, 114.1 \times 2, 102.2, 65.1 \times 2, 41.8, 32.2, 29.7. HRMS (ESI) *m/z*: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2$ 295.1441; Found: 295.1447.

Diethyl 2-(5-fluoropentyl)-2-(3-phenylbuta-1,3-dien-2-yl)malonate (3aq)

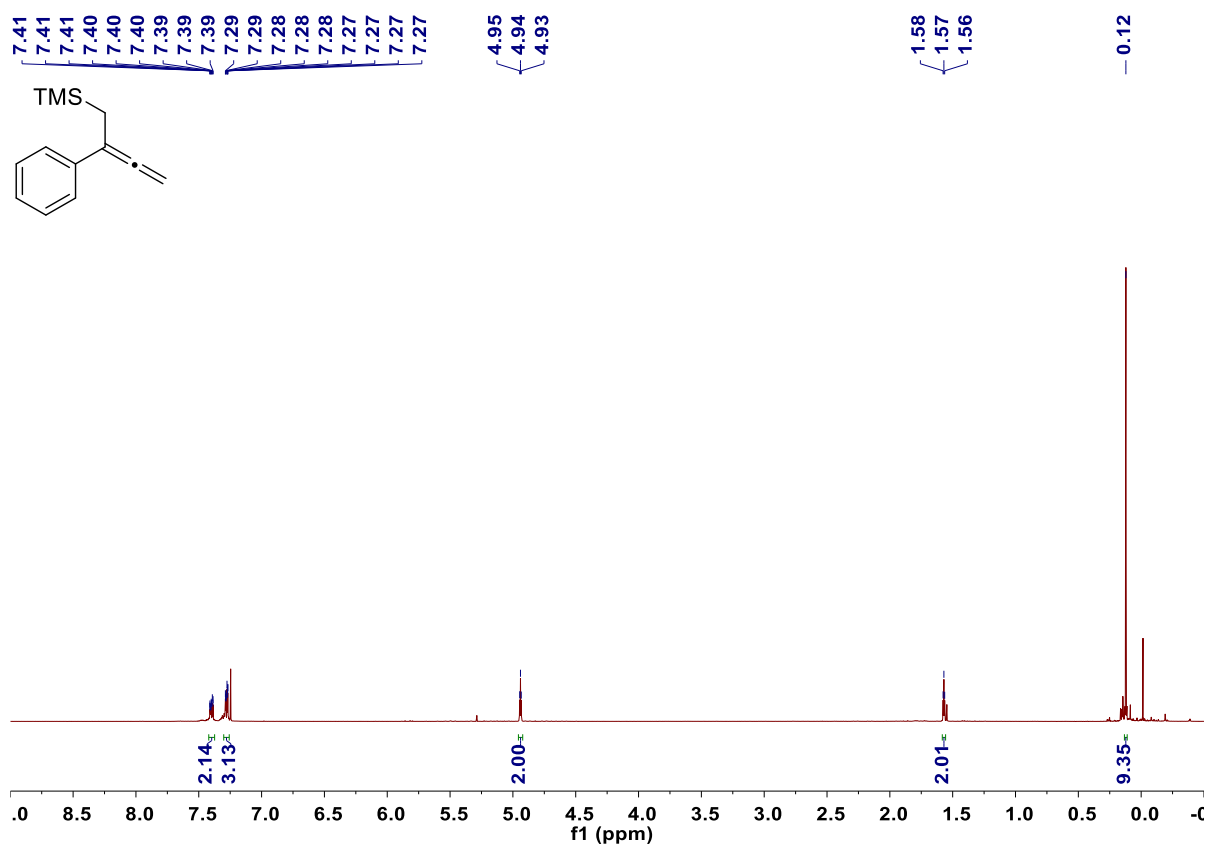
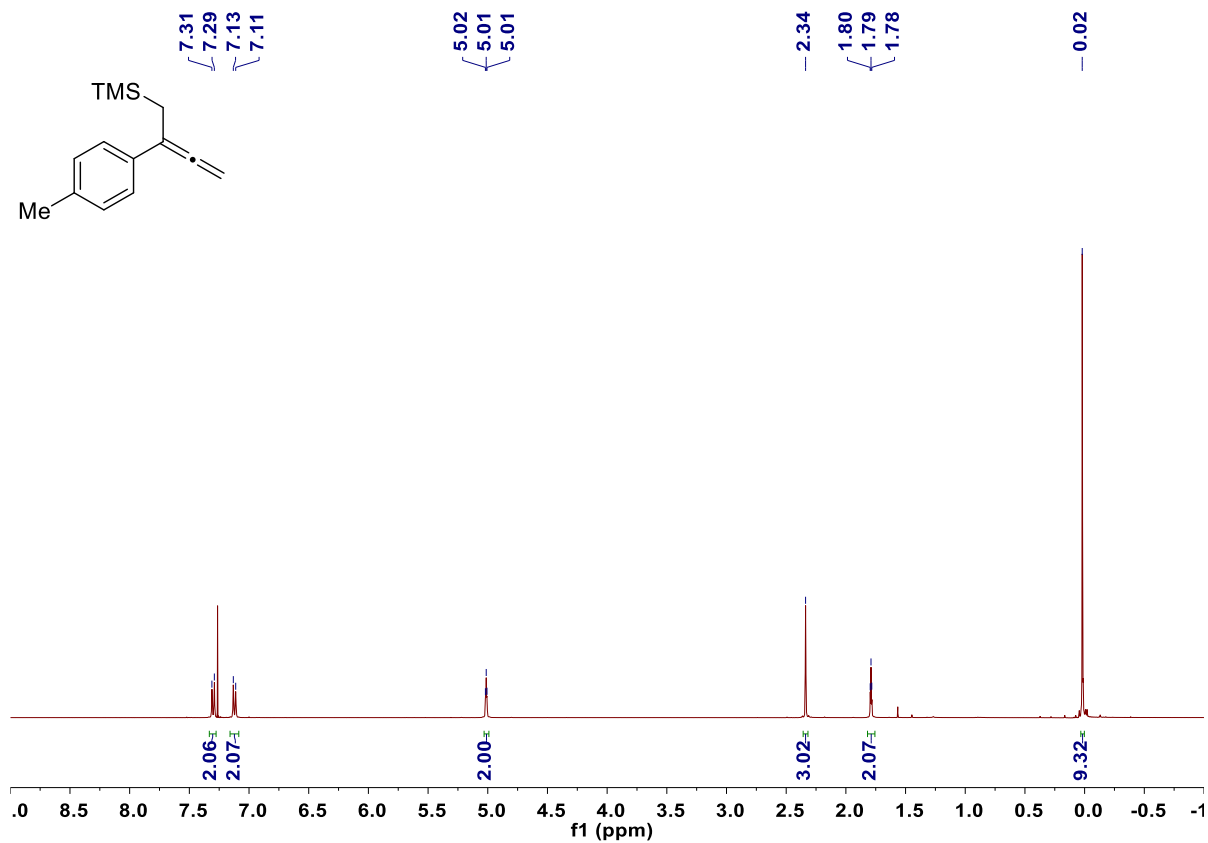


The title compound was prepared according to **GP5** and isolated as a yellow oil (30.2 mg, 0.107 mmol, 71%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 5H), 5.94 (s, 1H), 5.59 (s, 2H), 5.43 (d, J = 0.8 Hz, 1H), 4.40 (dt, J = 47.3, 5.9 Hz, 2H), 2.00 – 1.88 (m, 2H), 1.72 – 1.58 (m, 4H), 1.42 – 1.31 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.1, 139.9, 138.3, 128.8 \times 2, 128.6 \times 2, 127.1, 122.2, 119.7, 114.3 \times 2, 83.5 (d, J = 164.8 Hz), 42.3, 37.9, 29.8 (d, J = 19.9 Hz), 25.1, 24.4 (d, J = 5.0 Hz). HRMS (ESI) *m/z*: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{FN}_2$ 283.1605; Found: 283.1610.

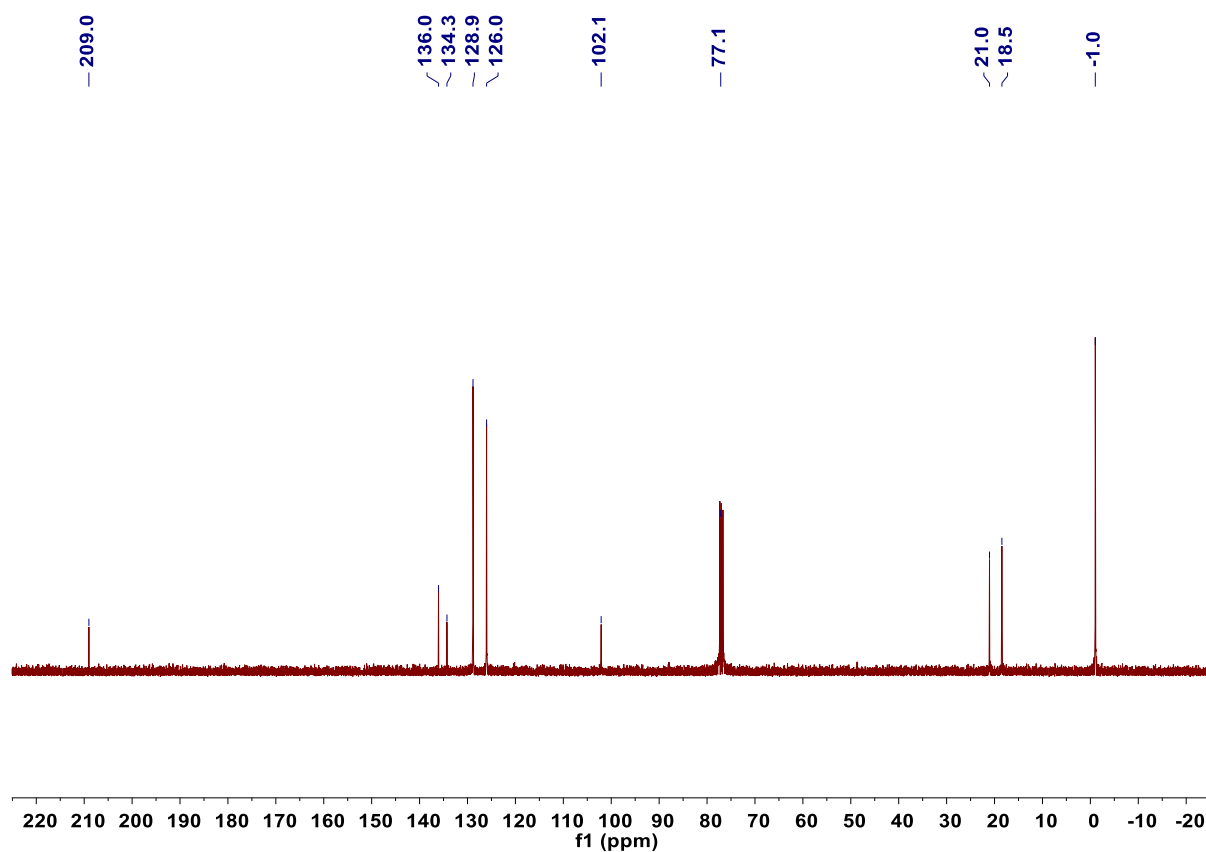
9. References

- [1] Pacheco, M. C.; Gouverneur, V. Electrophilic Fluorodesilylation of Allenylmethylsilanes: A Novel Entry to 2-Fluoro-1,3-dienes. *Org. Lett.* **2005**, *7*, 1267–1270.
- [2] Tian, M.-Q.; Wang, C.; Hu, X.-H.; Loh, T.-P. Divergent C–H Oxidative Radical Functionalization of Olefins to Install Tertiary Alkyl Motifs Enabled by Copper Catalysis. *Org. Lett.* **2019**, *21*, 1607–1611.
- [3] Wang, C.; Liu, R.-H.; Tian, M.-Q.; Hu, X.-H.; Loh, T.-P. Regioselective Copper-Catalyzed Oxidative Coupling of α -Alkylated Styrenes with Tertiary Alkyl Radicals. *Org. Lett.* **2018**, *20*, 4032–4035.
- [4] Ono, N.; Tamura, R.; Tanikaga, R.; Kaji, A. Selective Monoalkylation of Tosylacetoneitrile. *Synthesis* **1977**, *10*, 690–691.
- [5] Ghorai, M. K.; Talukdar, R.; Tiwari, D. P. A Route to Highly Functionalized β -Enaminoesters via a Domino Ring-Opening Cyclization/Decarboxylative Tautomerization Sequence of Donor–Acceptor Cyclopropanes with Substituted Malononitriles. *Org. Lett.* **2014**, *16*, 2204–2207.
- [6] Hu, C.; Hong, G.; Qian, X.; Kim, K. R.; Zhu, X.; Wang, L. AlCl_3 catalyzed coupling of N-benzylic sulfonamides with 2-substituted cyanoacetates through carbon–nitrogen bond cleavage. *Org. Biomol. Chem.* **2017**, *15*, 4984–4971.
- [7] Arceo, E.; Montroni, E.; Melchiorre, P. Photo-Organocatalysis of Atom-Transfer Radical Additions to Alkenes. *Angew. Chem., Int. Ed.* **2014**, *53*, 12064–12068.
- [8] Ma, Y.; Ding, Y.; Cai, Y.; Lei, C.; Zhu, D.; Li, T. Synthesis and neuroprotective effect of nNOS PDZ structural domain inhibitors. *Acta Univ. Med. Nanjing (Natural Science)* **2014**, *34*, 314–322.
- [9] Tian, M.-Q.; Shen, Z.-Y.; Zhao, X.; Walsh, P. J.; Hu, X.-H. Iron-Catalyzed Tertiary Alkylation of Terminal Alkynes with 1,3-Diesters via a Functionalized Alkyl Radical. *Angew. Chem., Int. Ed.* **2021**, *60*, 9706–9711.

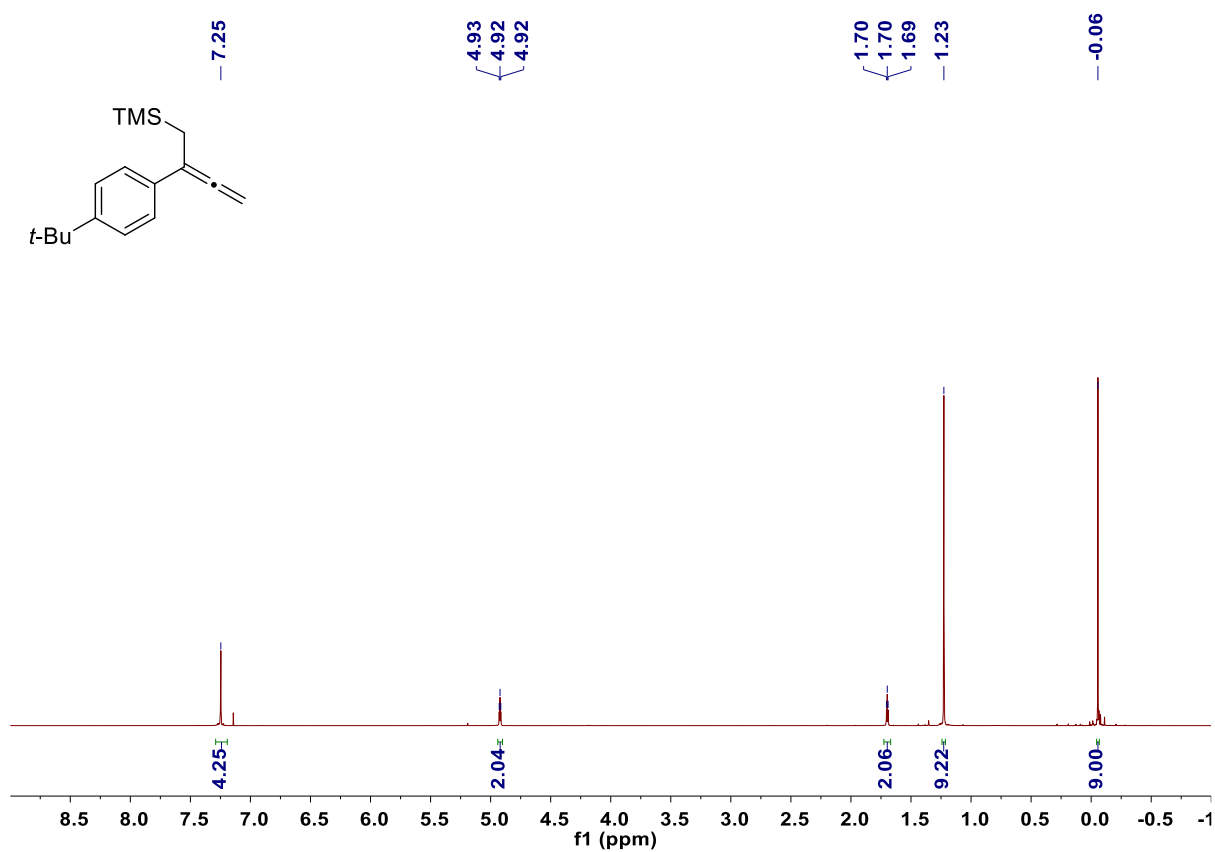
10. NMR spectra of the starting materials

¹H NMR spectrum for compound 1a (400 MHz, CDCl₃)

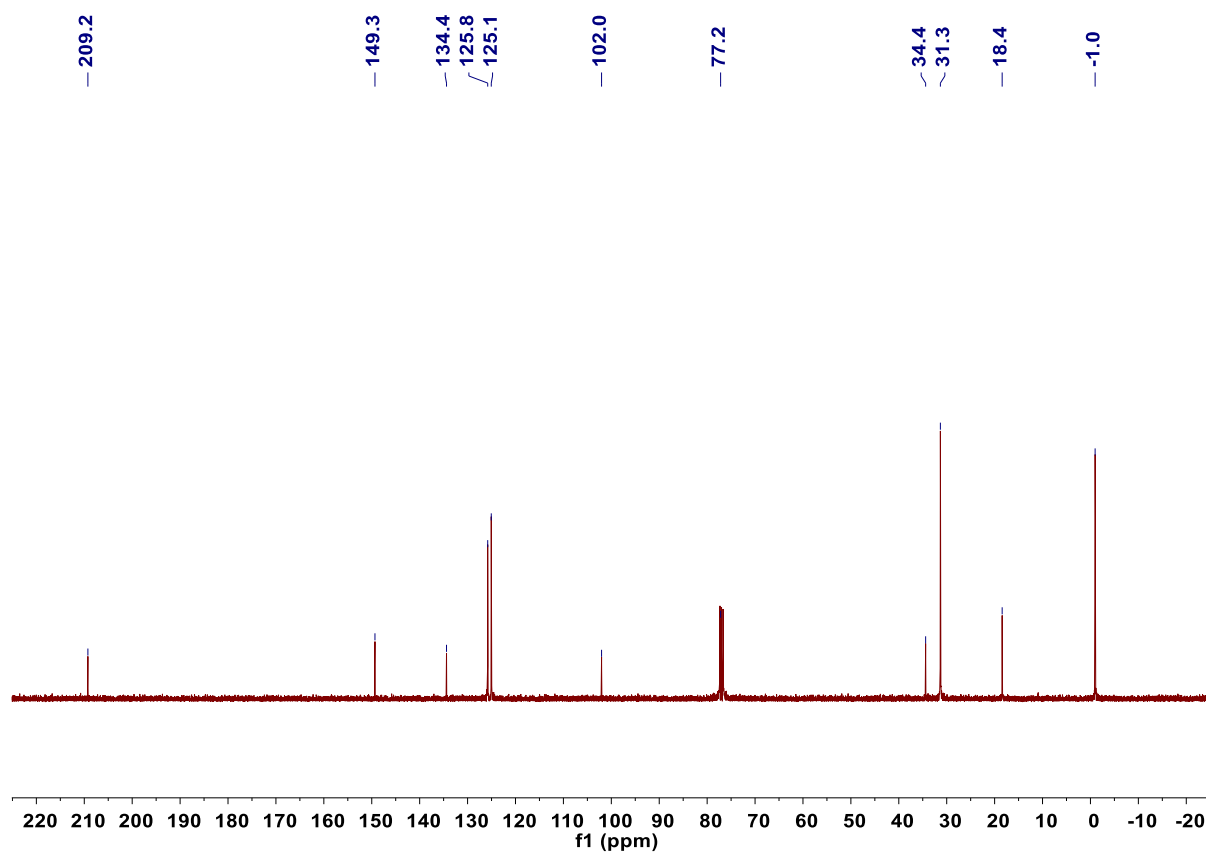
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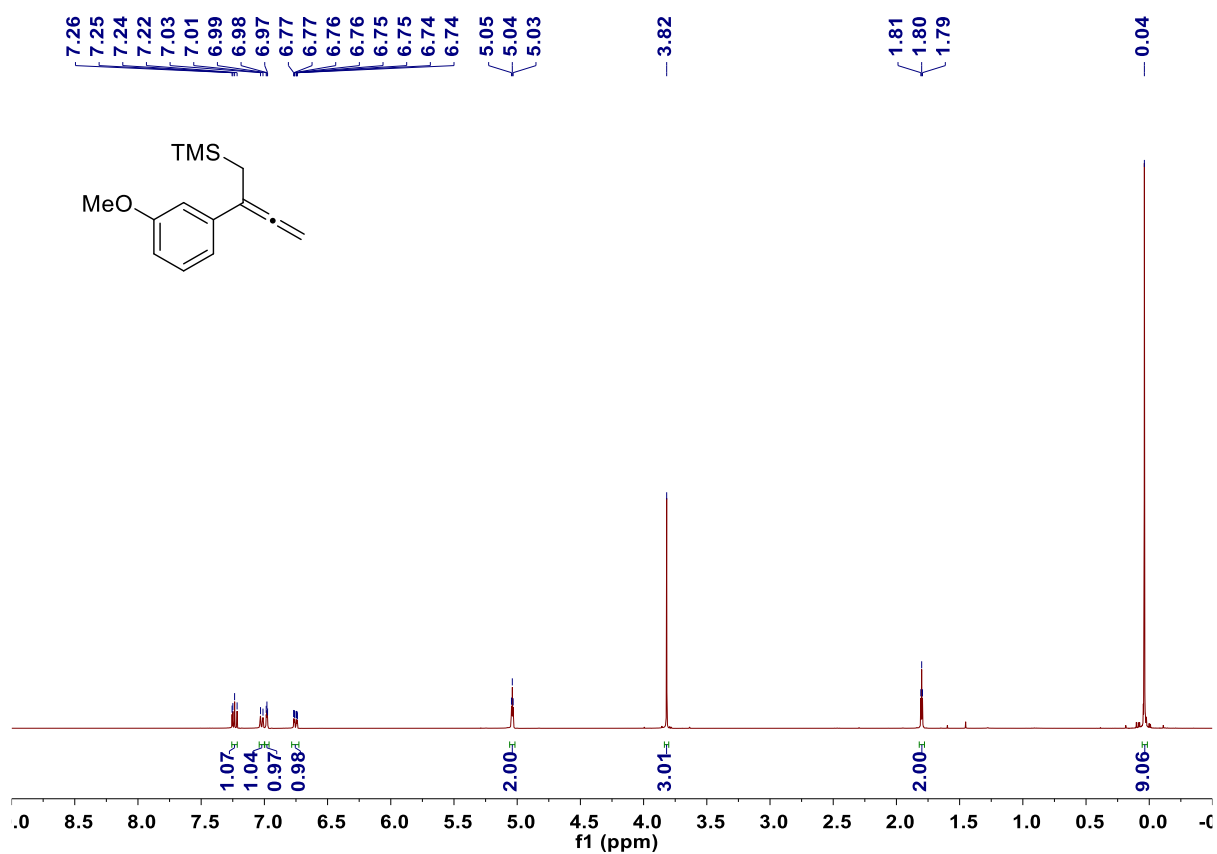
¹H and ¹³C NMR spectra for compound 1b (400 MHz, CDCl₃)



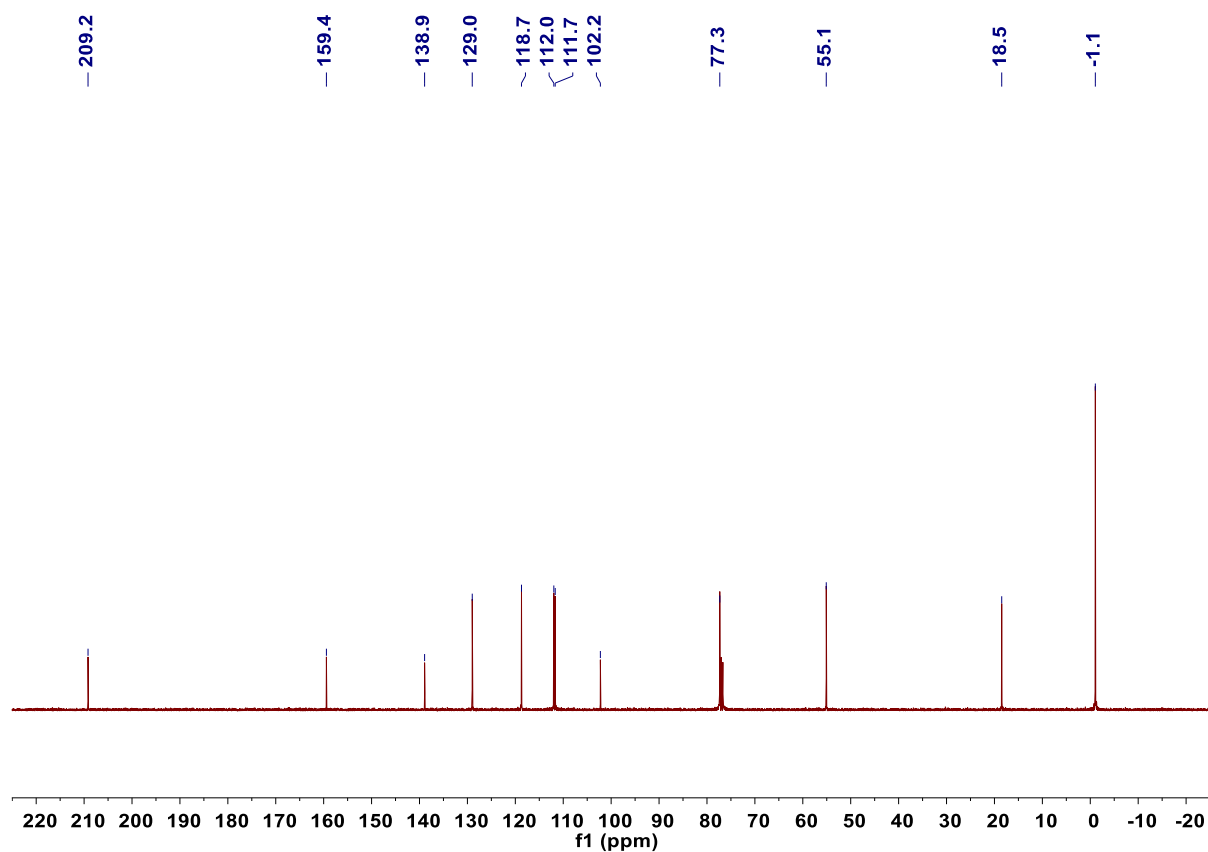
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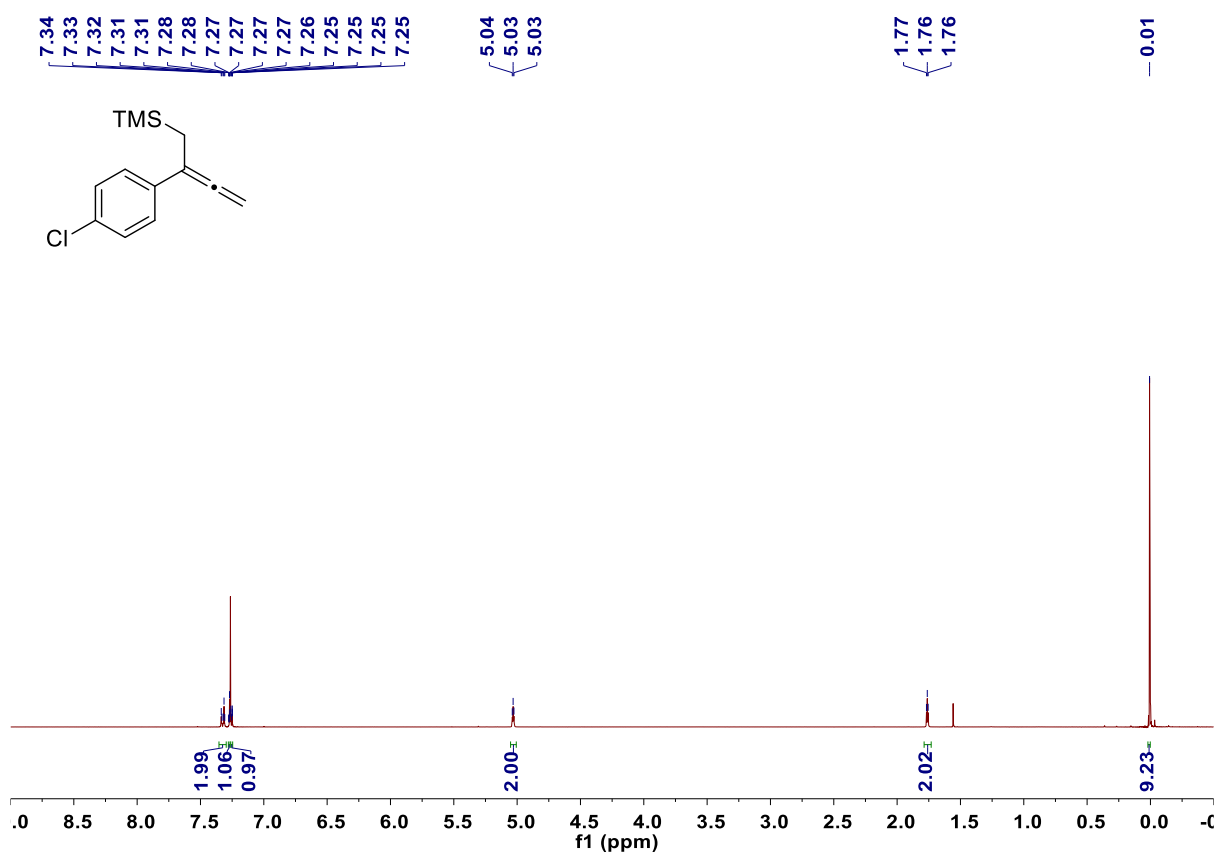
^1H and ^{13}C NMR spectra for compound 1c (400 MHz, CDCl_3)



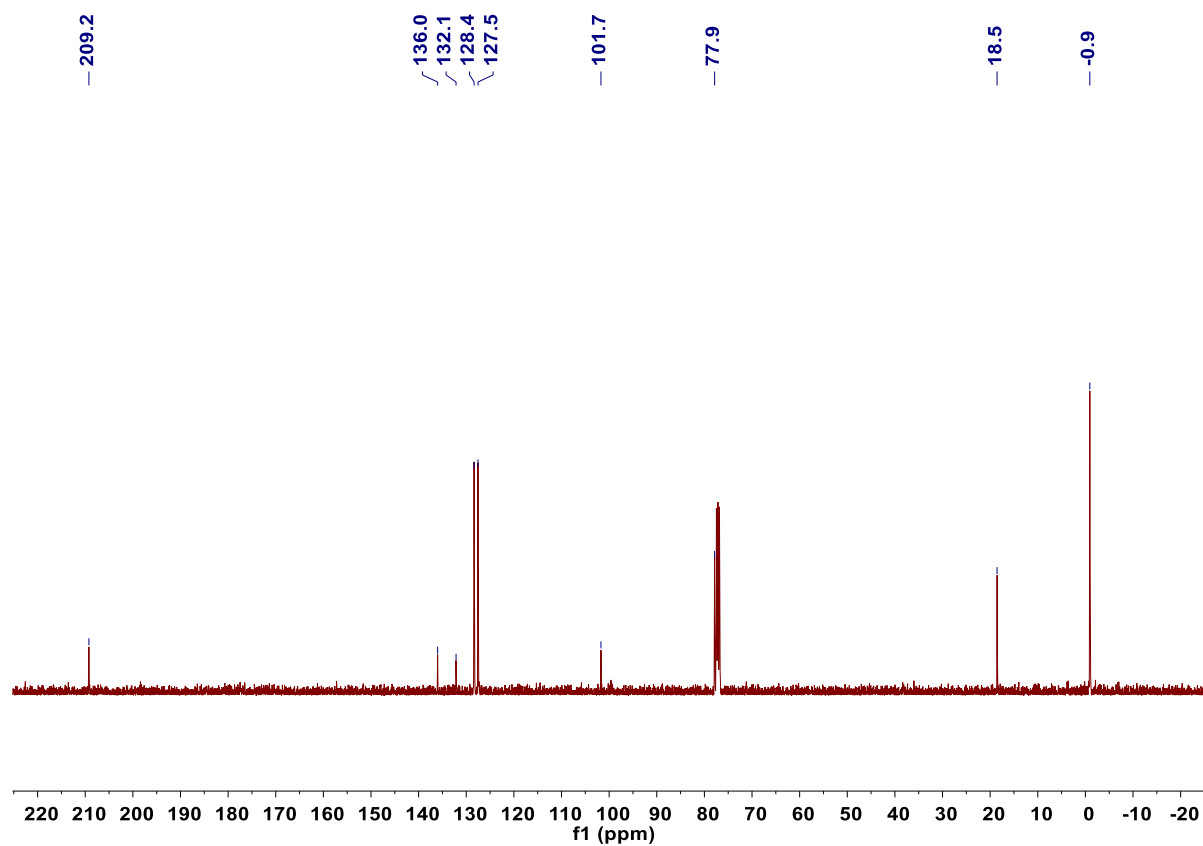
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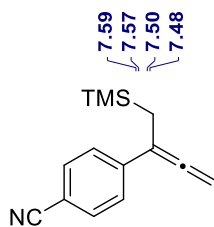
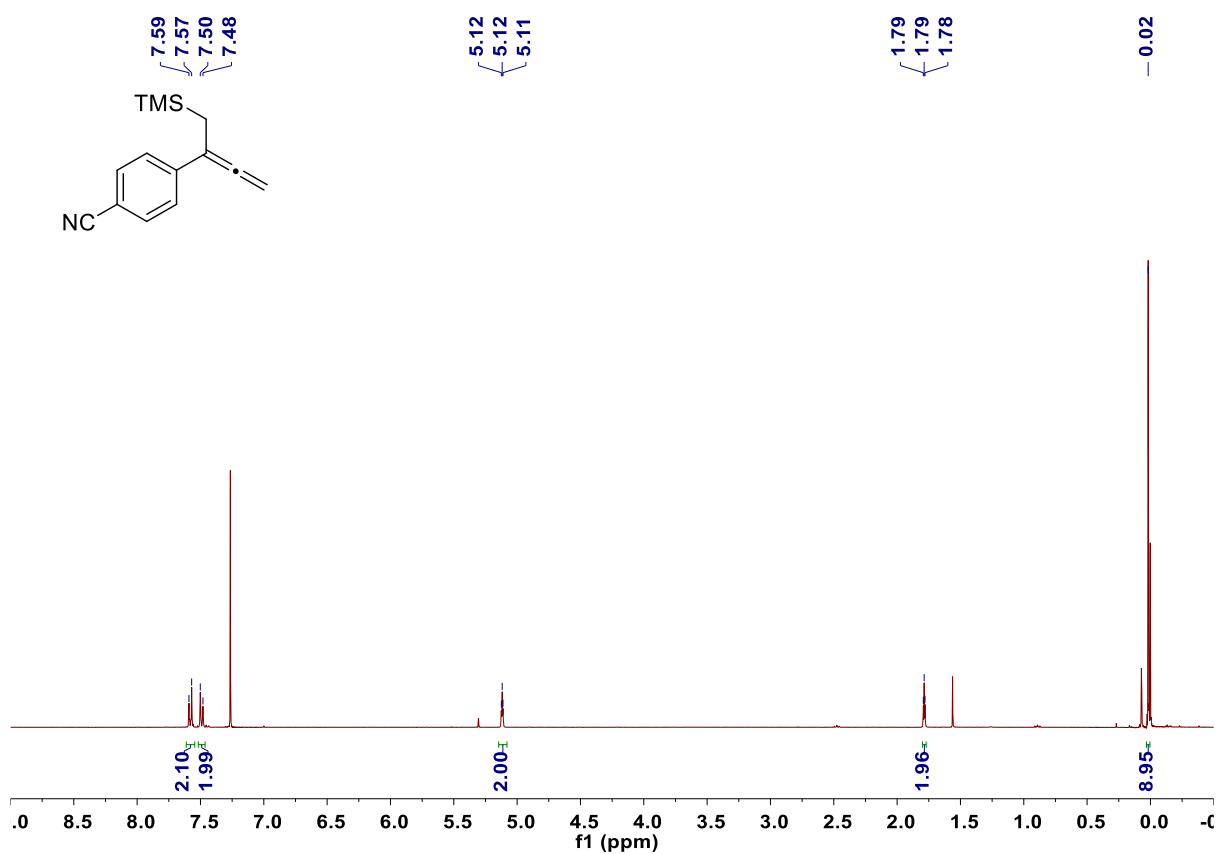
¹H and ¹³C NMR spectra for compound 1d (400 MHz, CDCl₃)



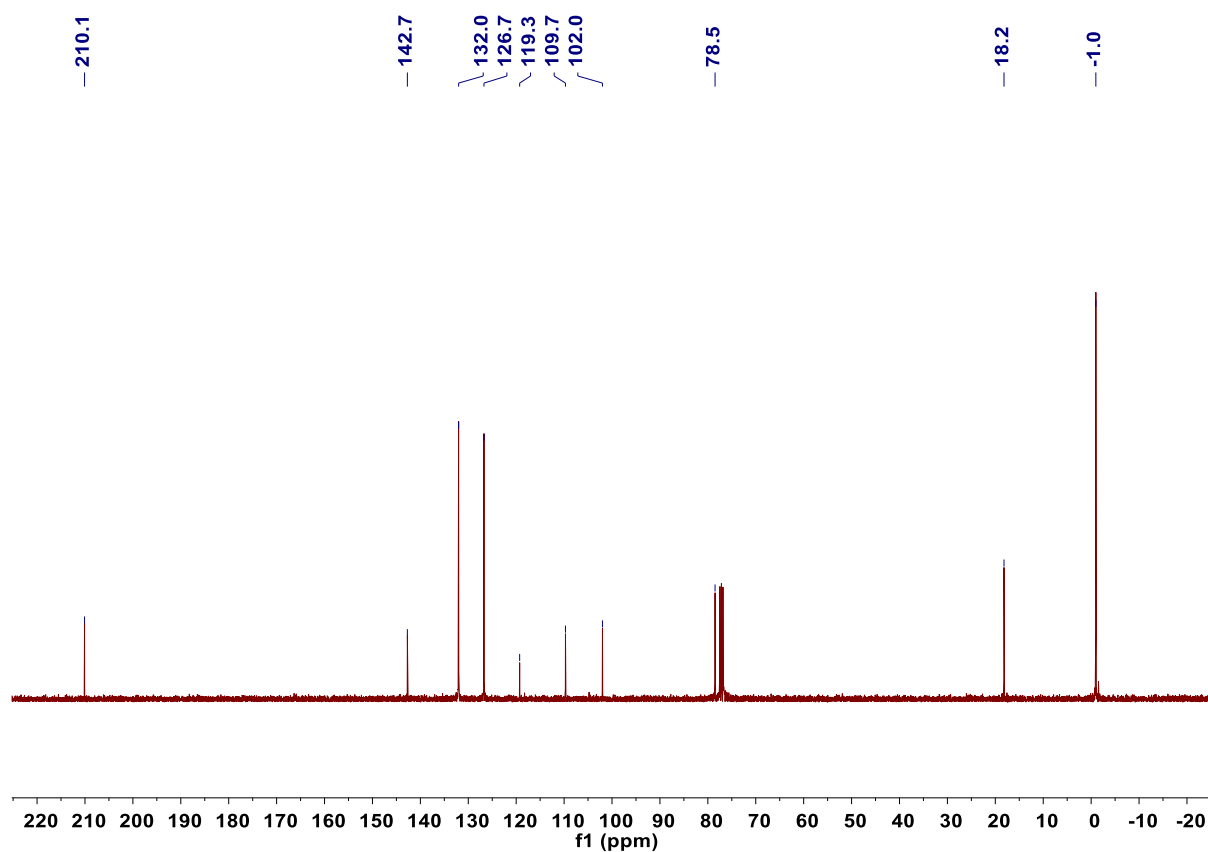
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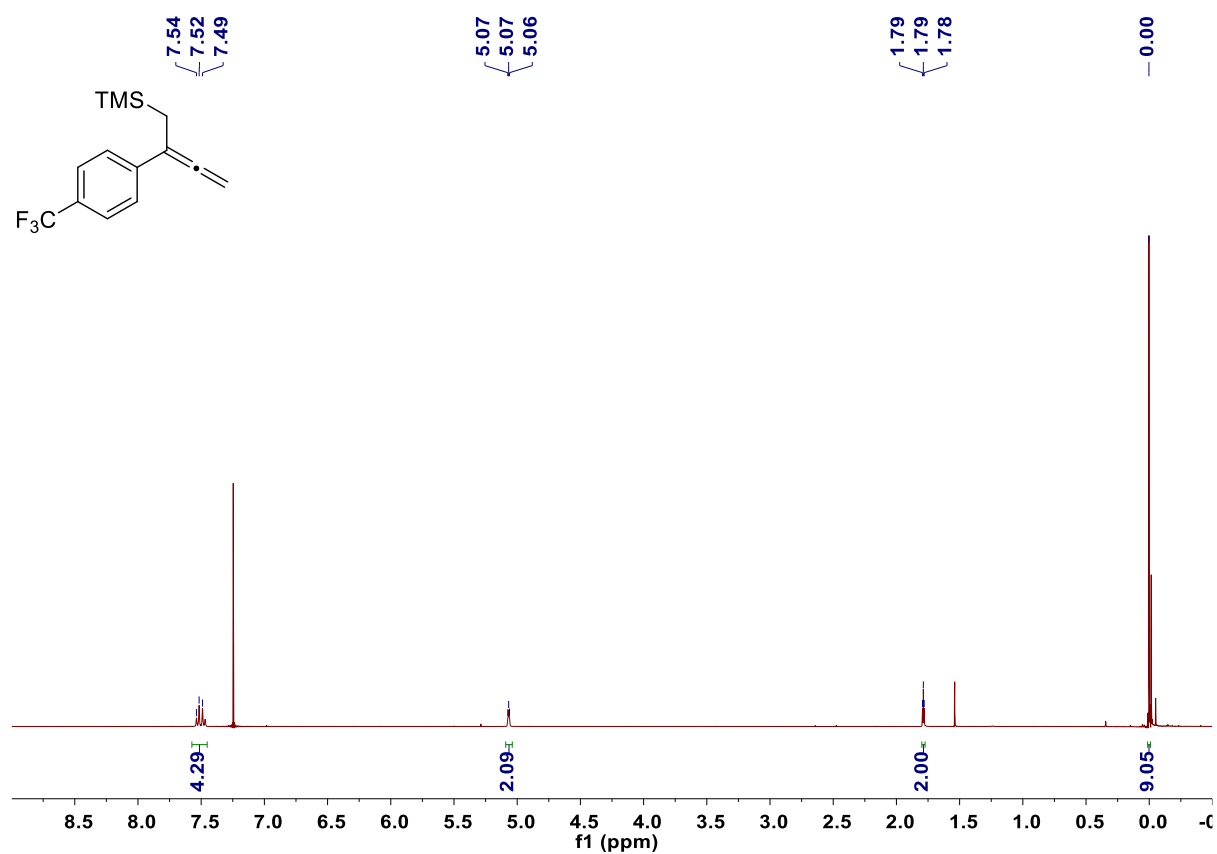
¹H and ¹³C NMR spectra for compound 1e (400 MHz, CDCl₃)

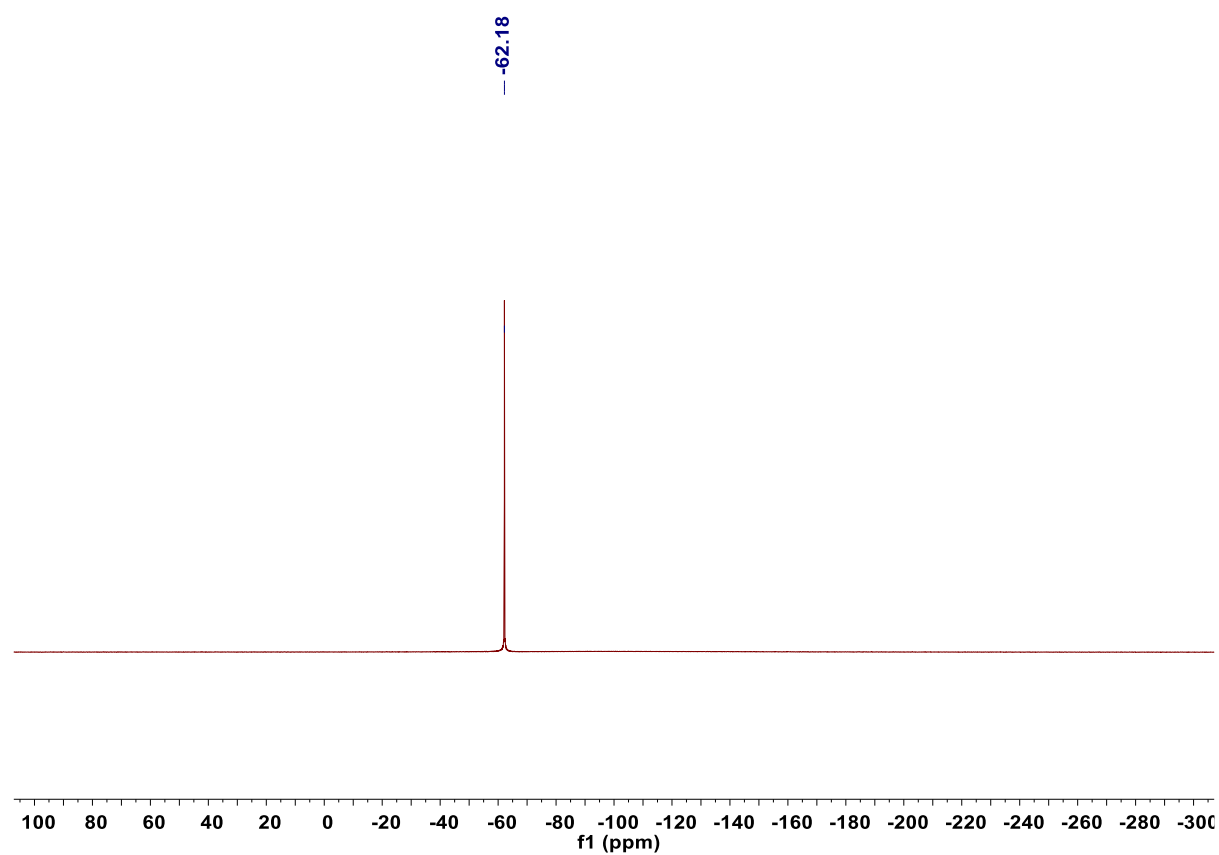
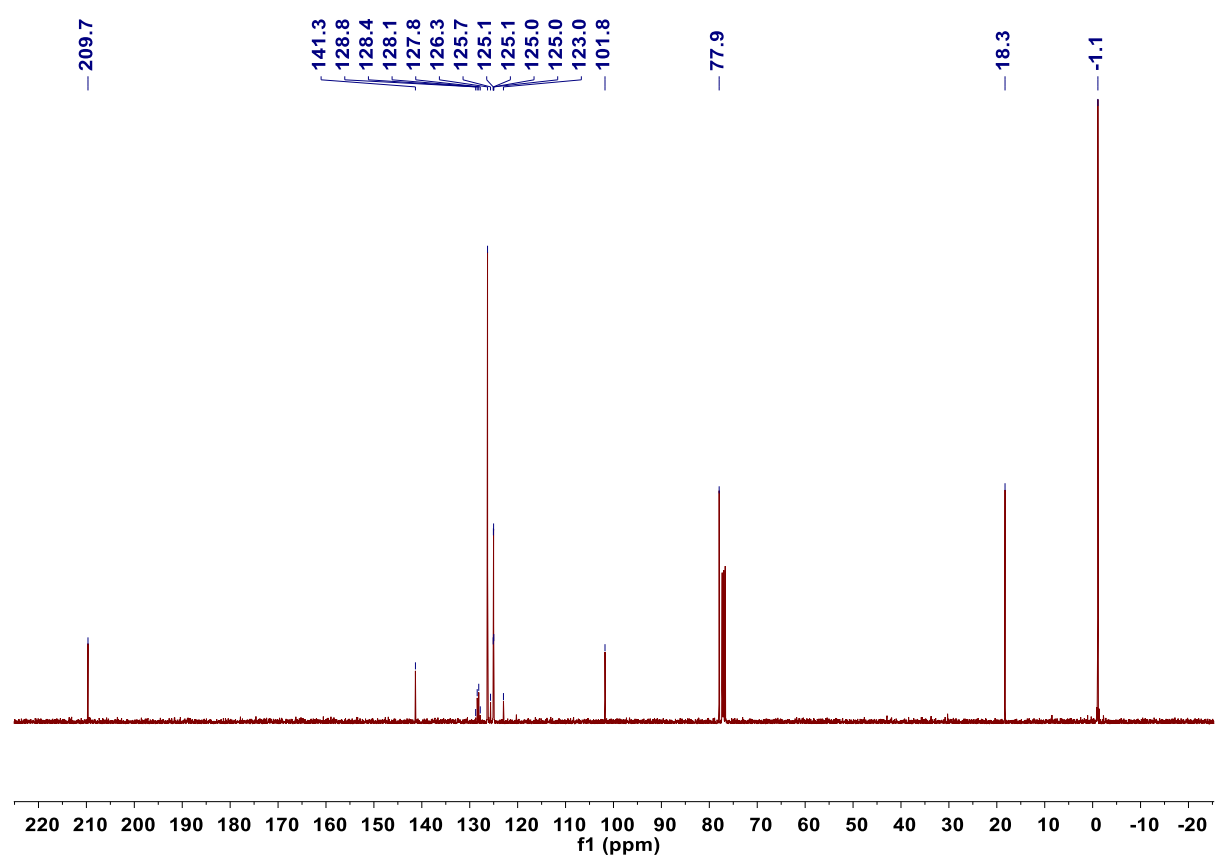


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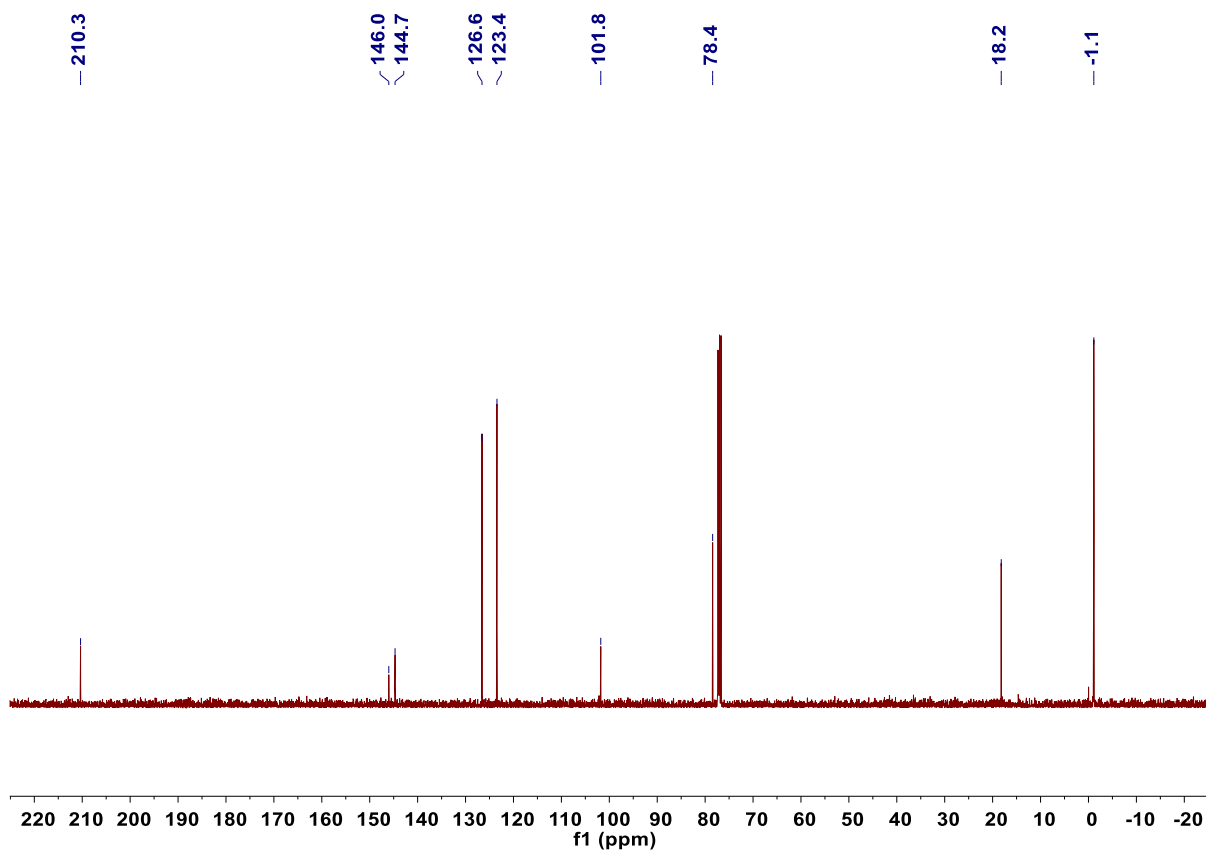
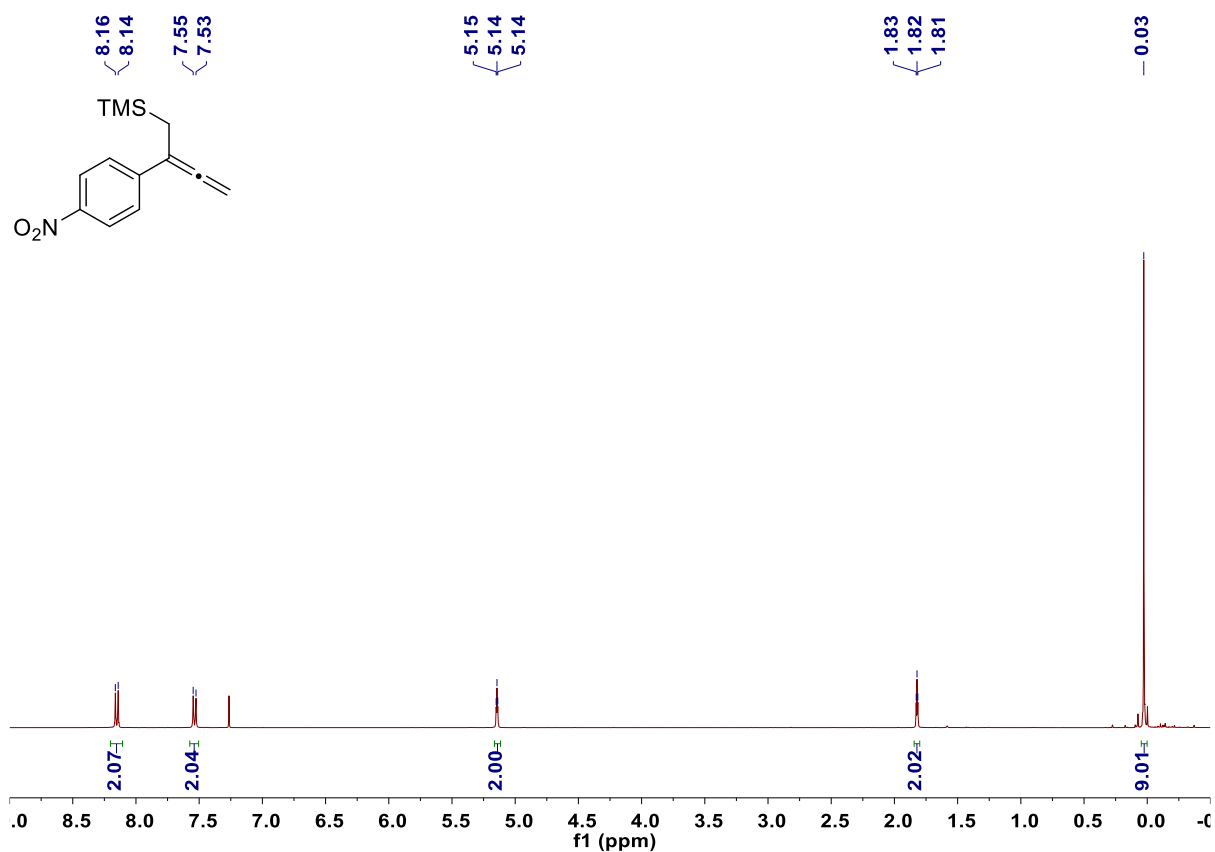
¹H and ¹³C NMR spectra for compound 1f (400 MHz, CDCl₃)





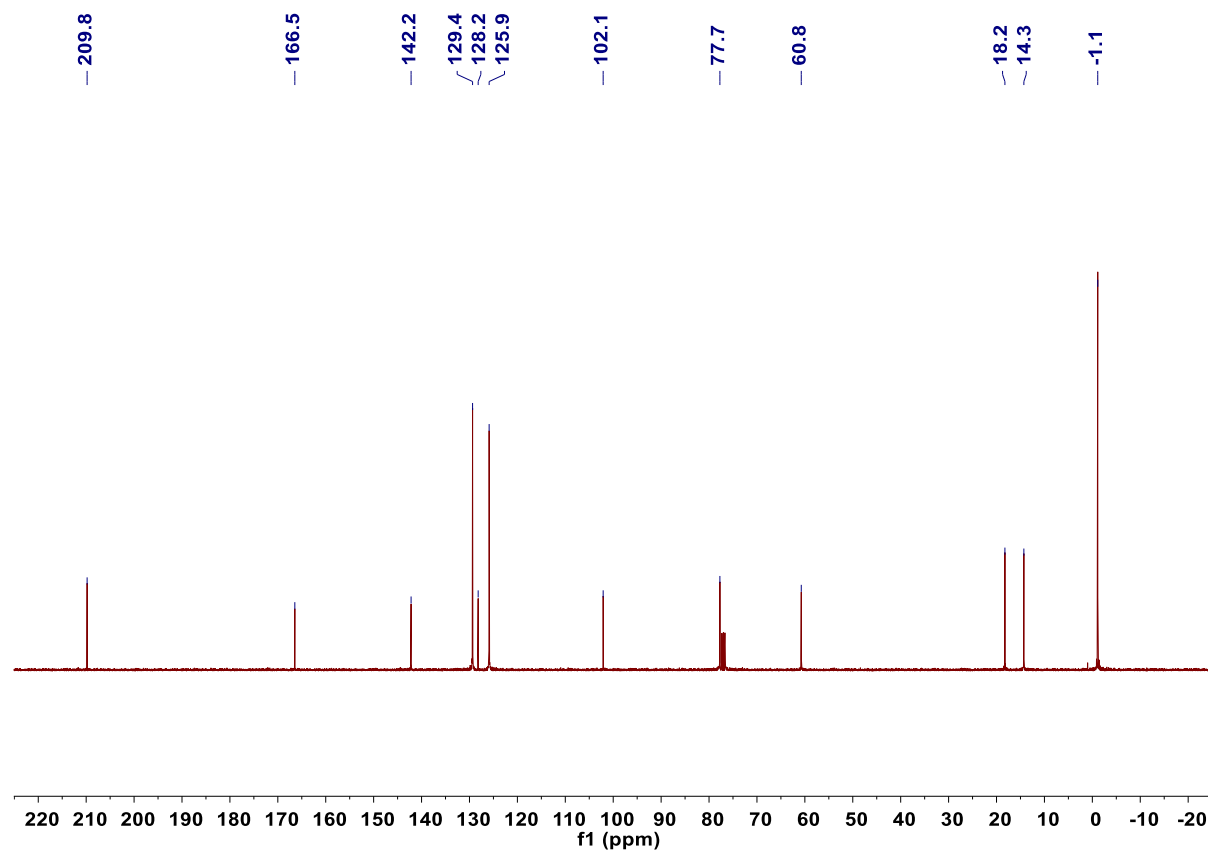
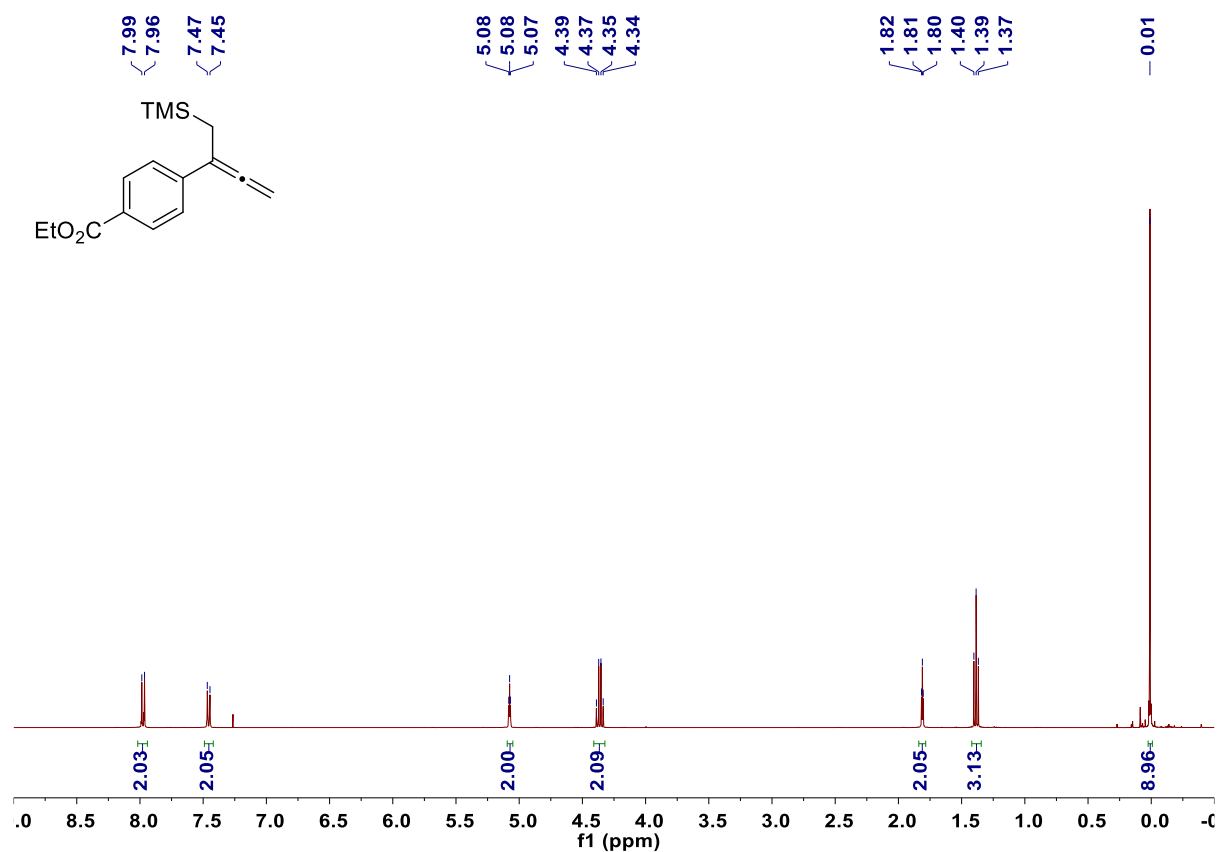
¹H, ¹³C and ¹⁹F NMR spectra for compound 1g (400 MHz, CDCl₃)

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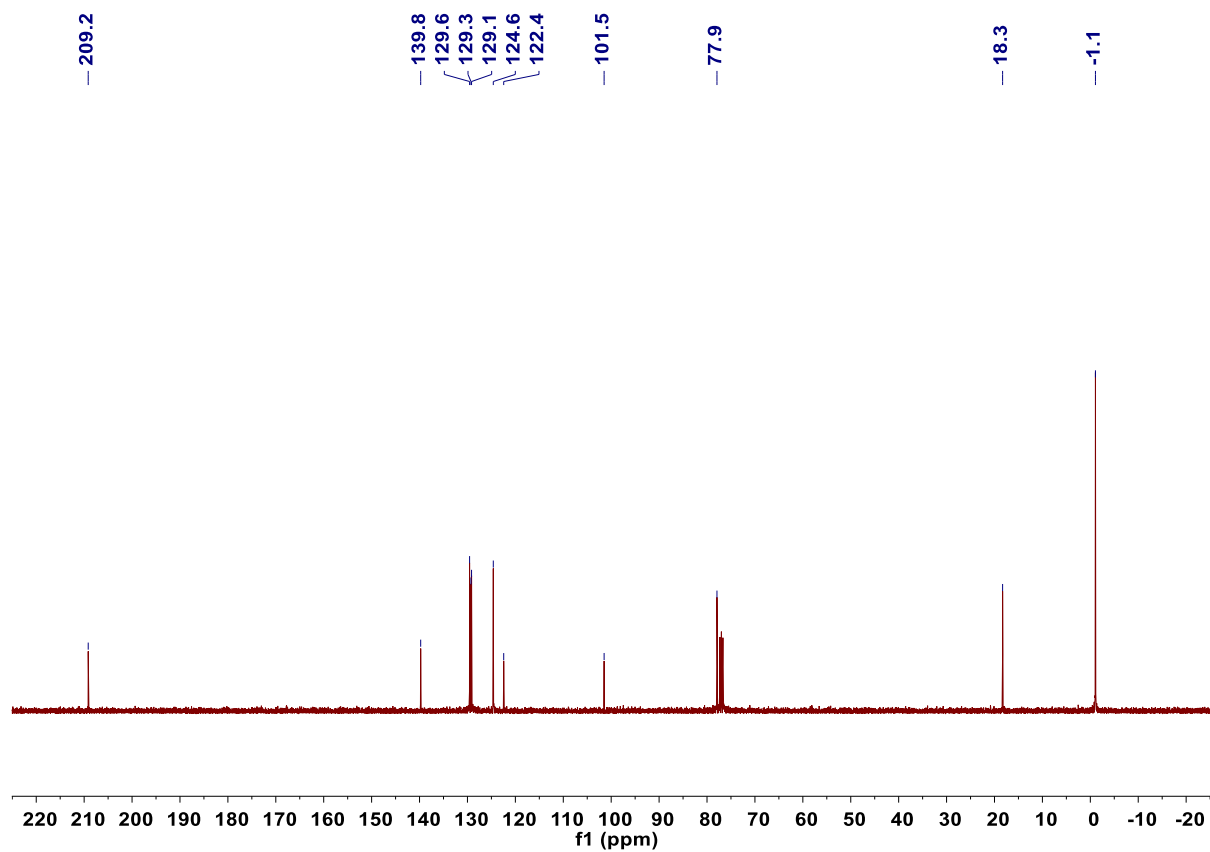
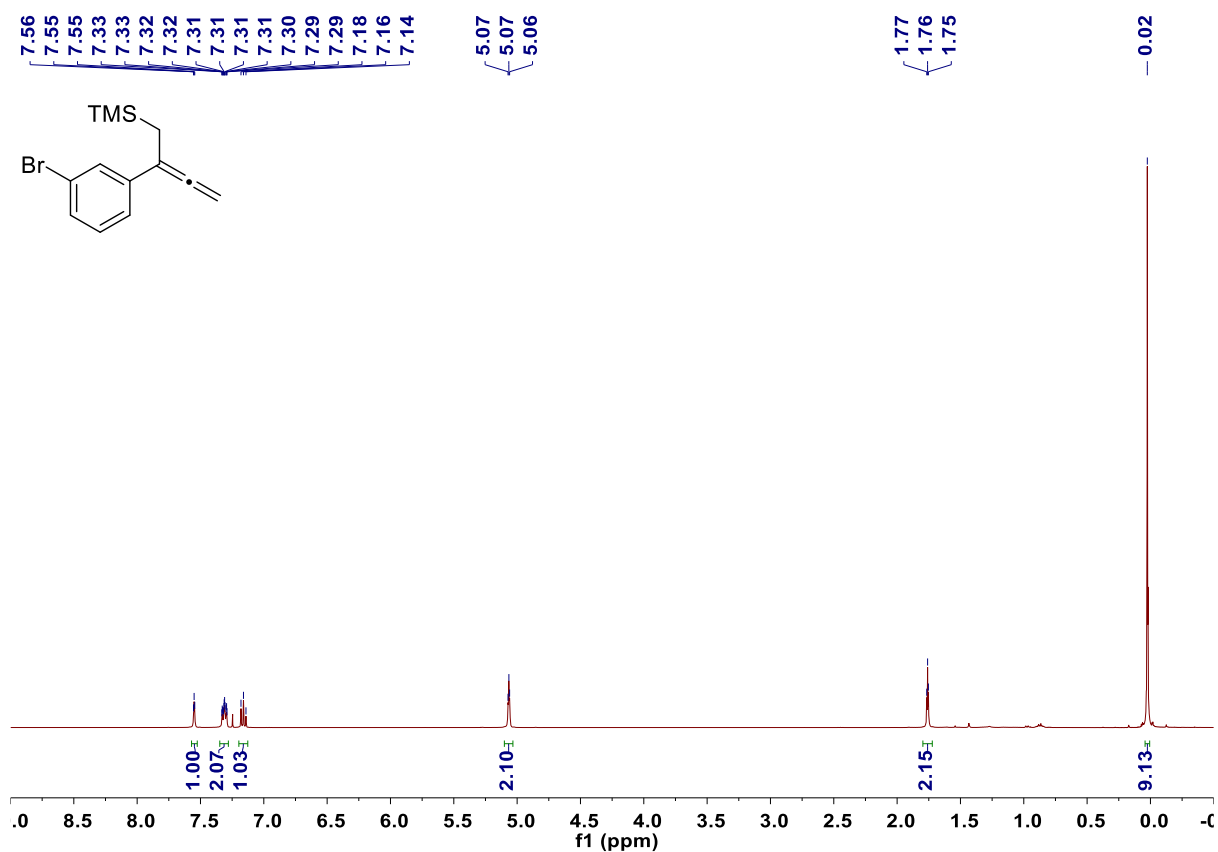
¹H and ¹³C NMR spectra for compound 1h (400 MHz, CDCl₃)

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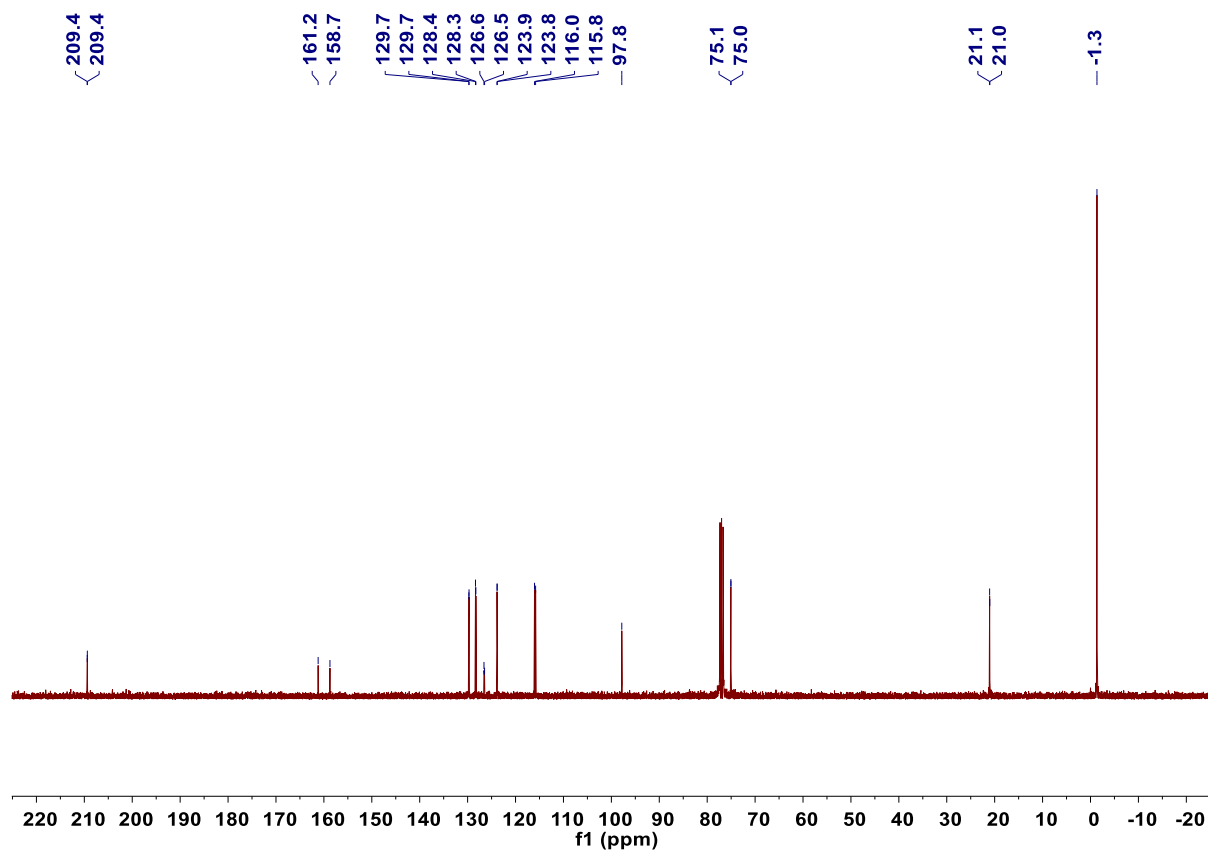
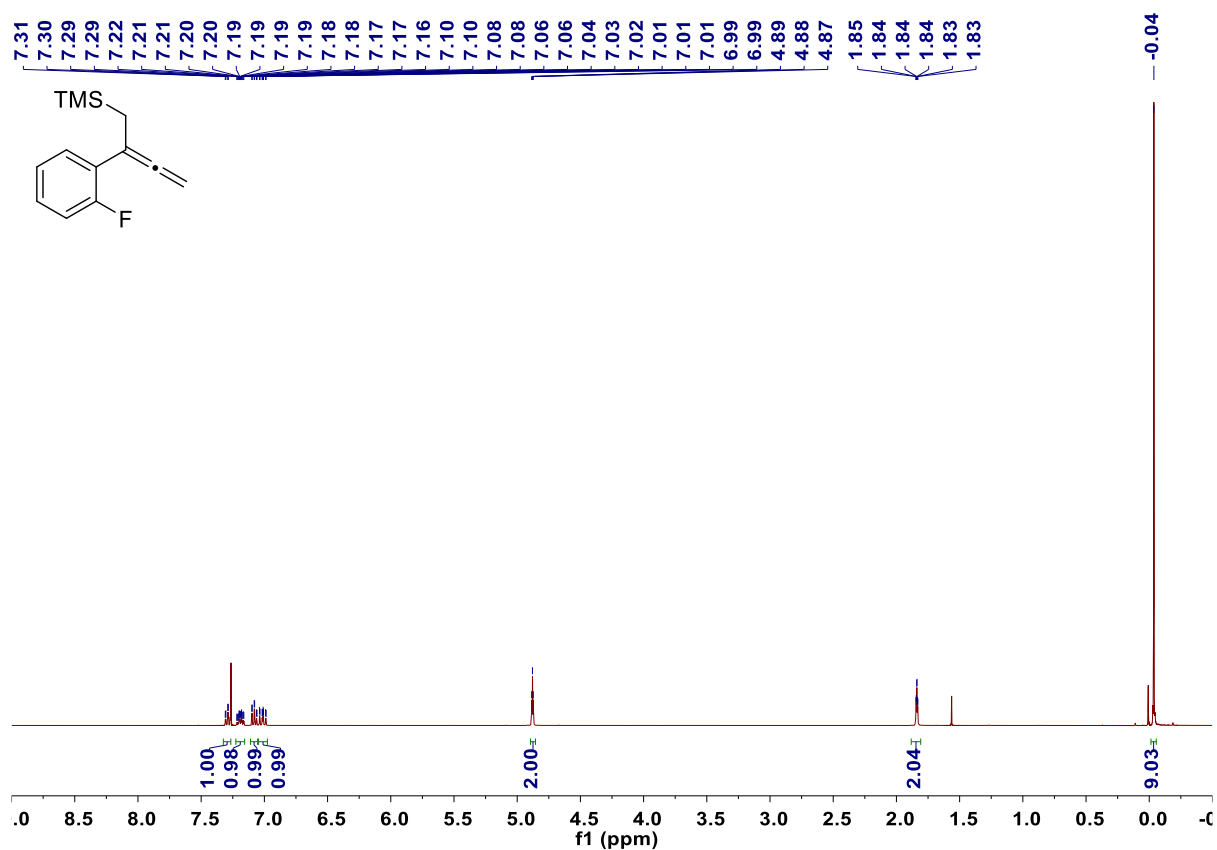
¹H and ¹³C NMR spectra for compound 1i (400 MHz, CDCl₃)

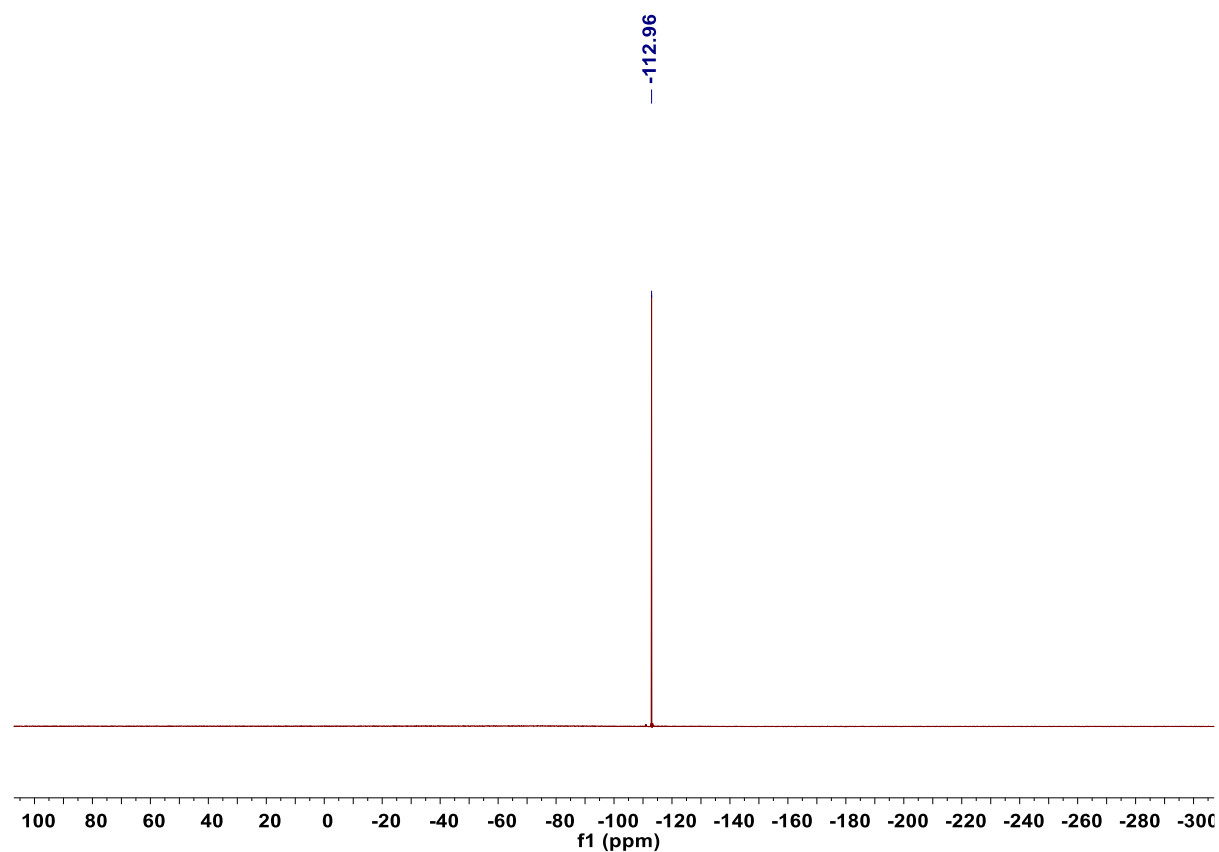
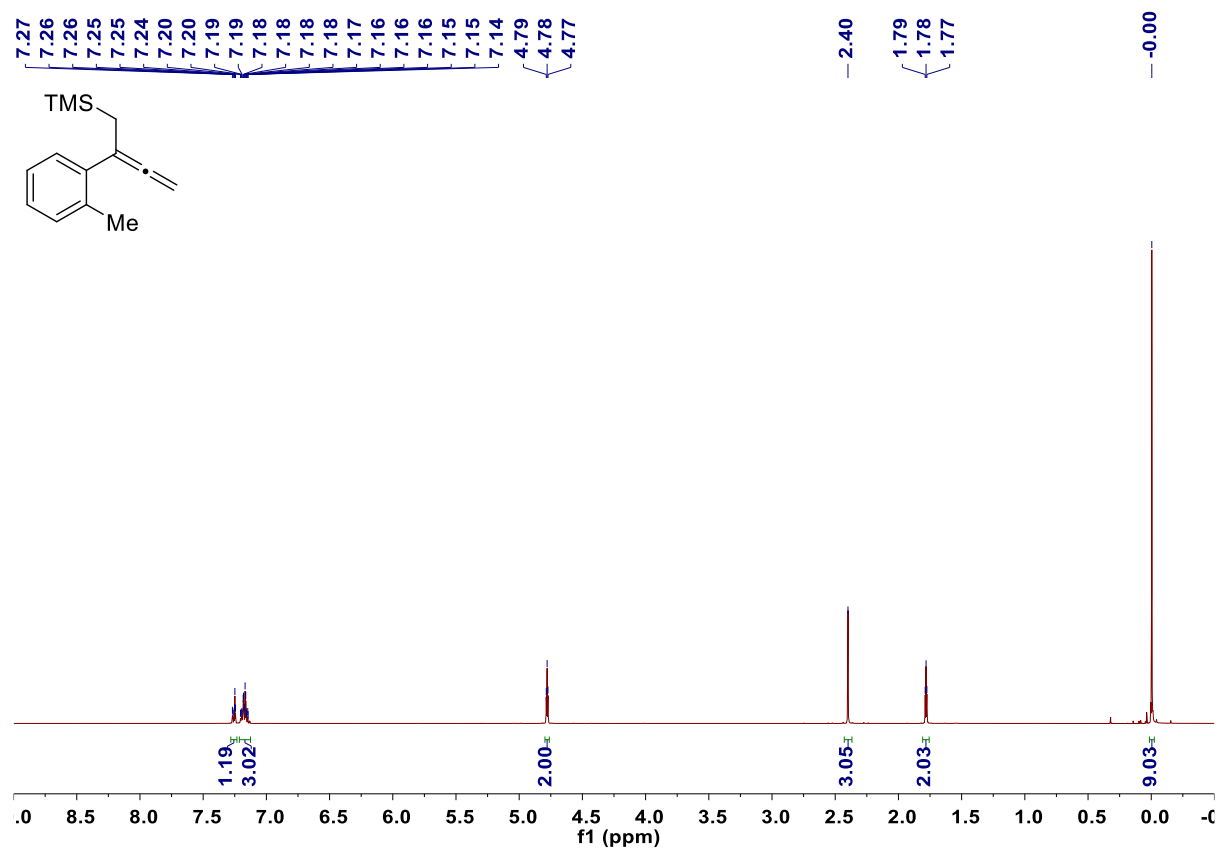
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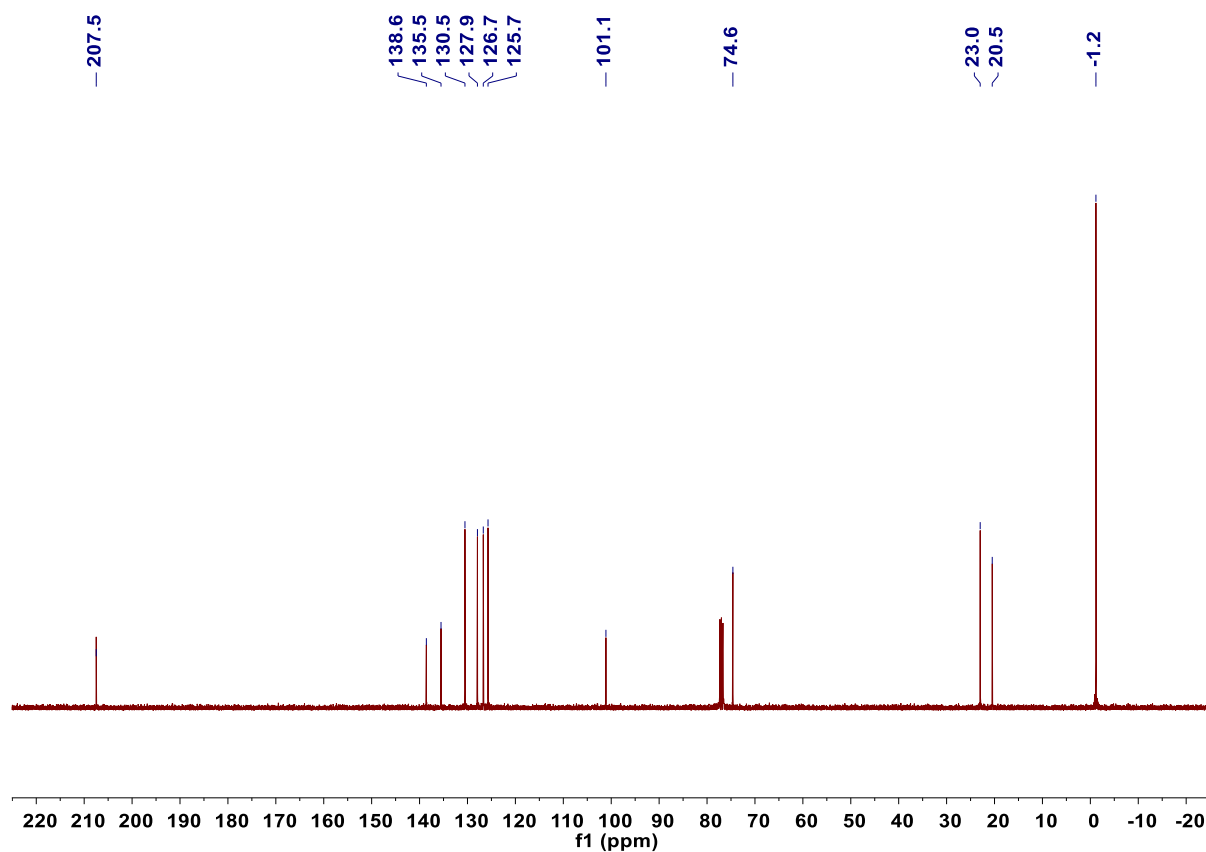
¹H and ¹³C NMR spectra for compound 1j (400 MHz, CDCl₃)

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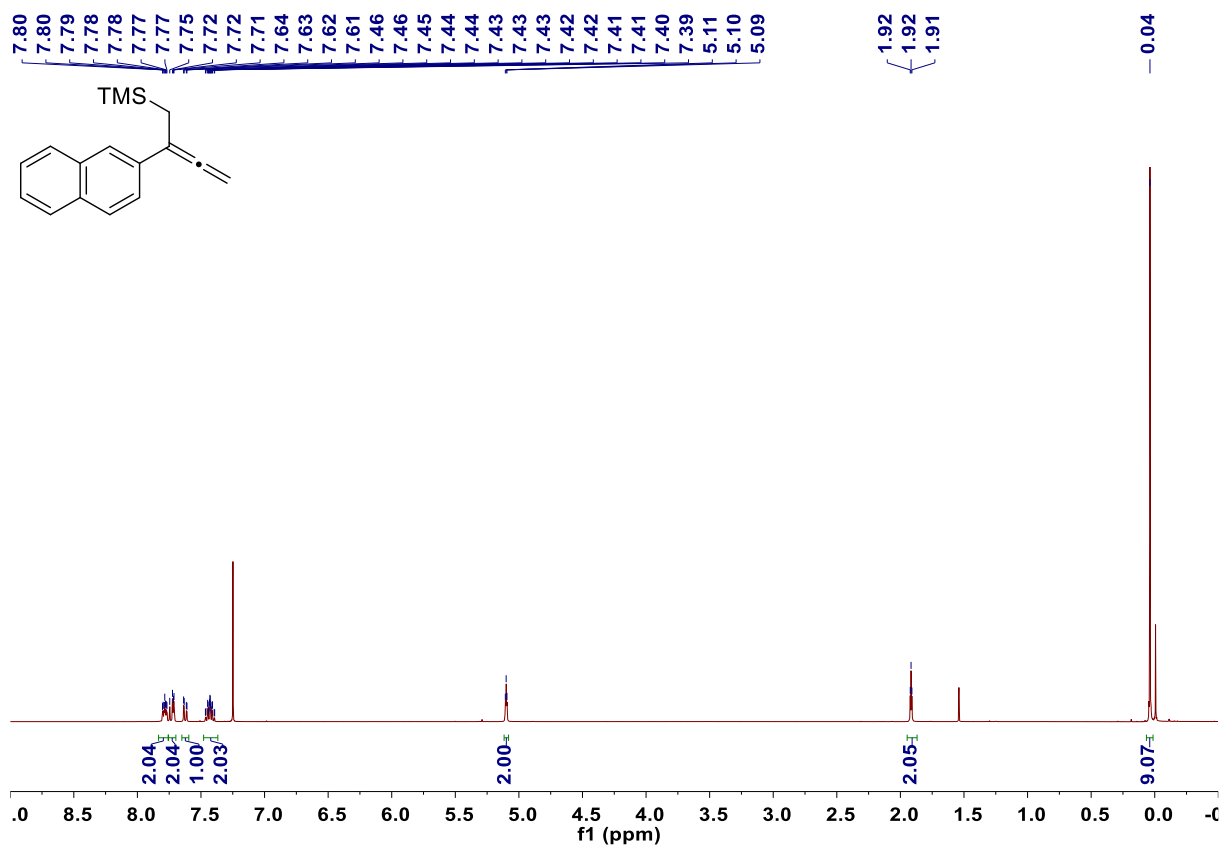


 ^1H , ^{13}C and ^{19}F NMR spectra for compound 1k (400 MHz, CDCl_3)

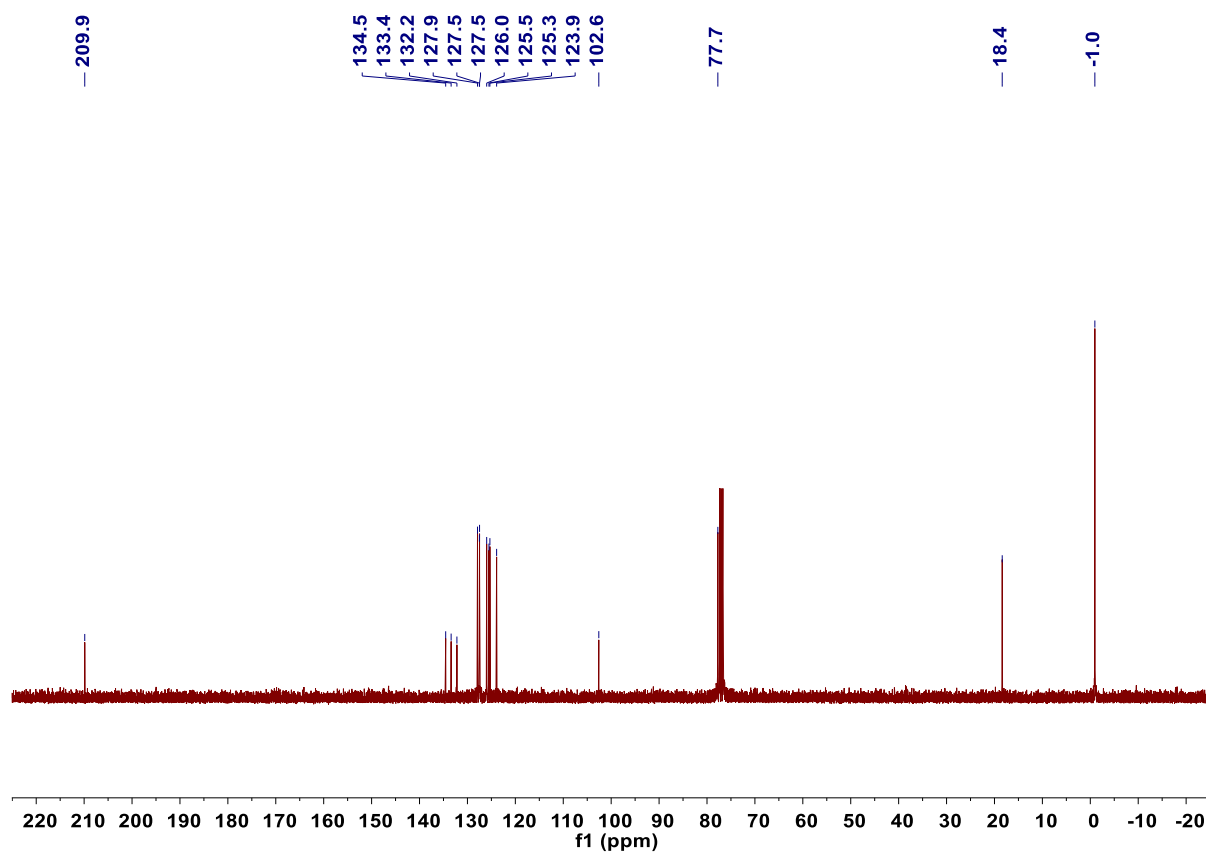
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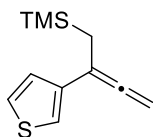
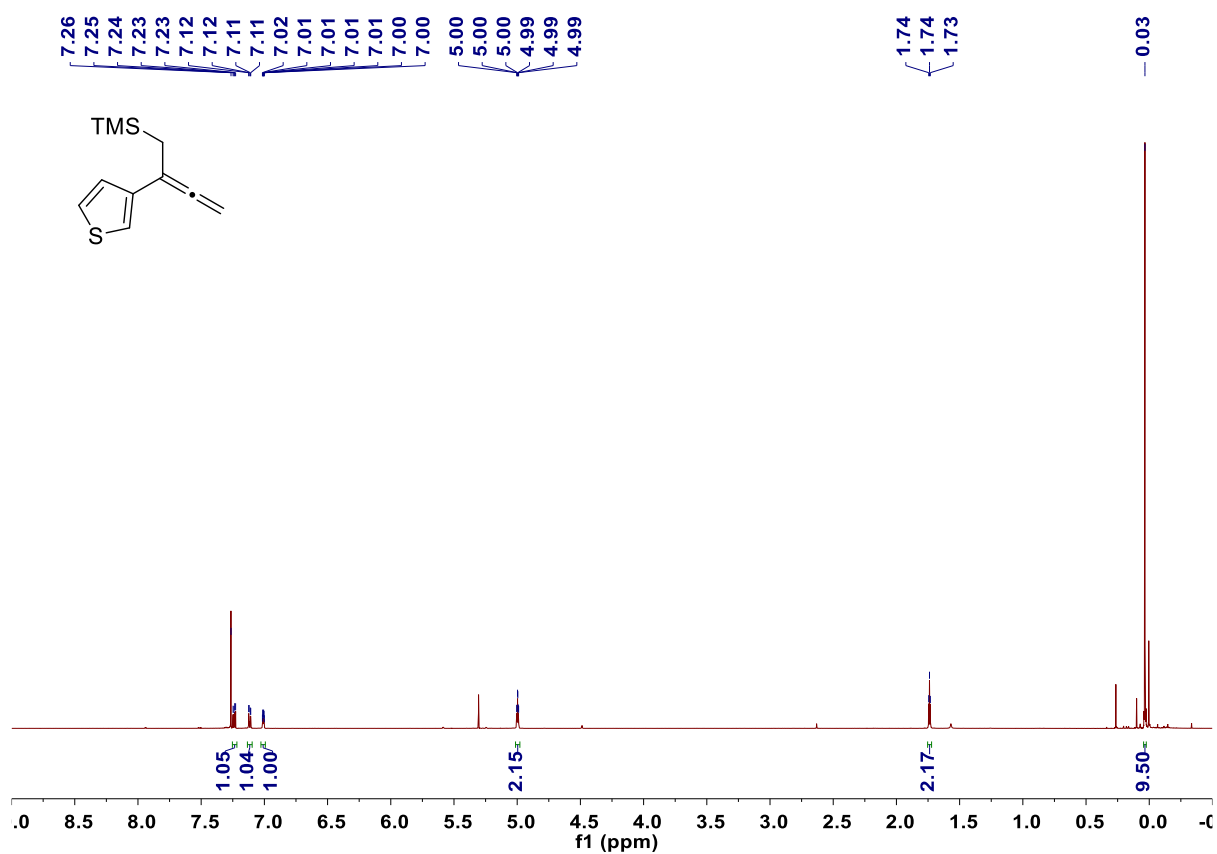
^1H and ^{13}C NMR spectra for compound 11 (400 MHz, CDCl_3)

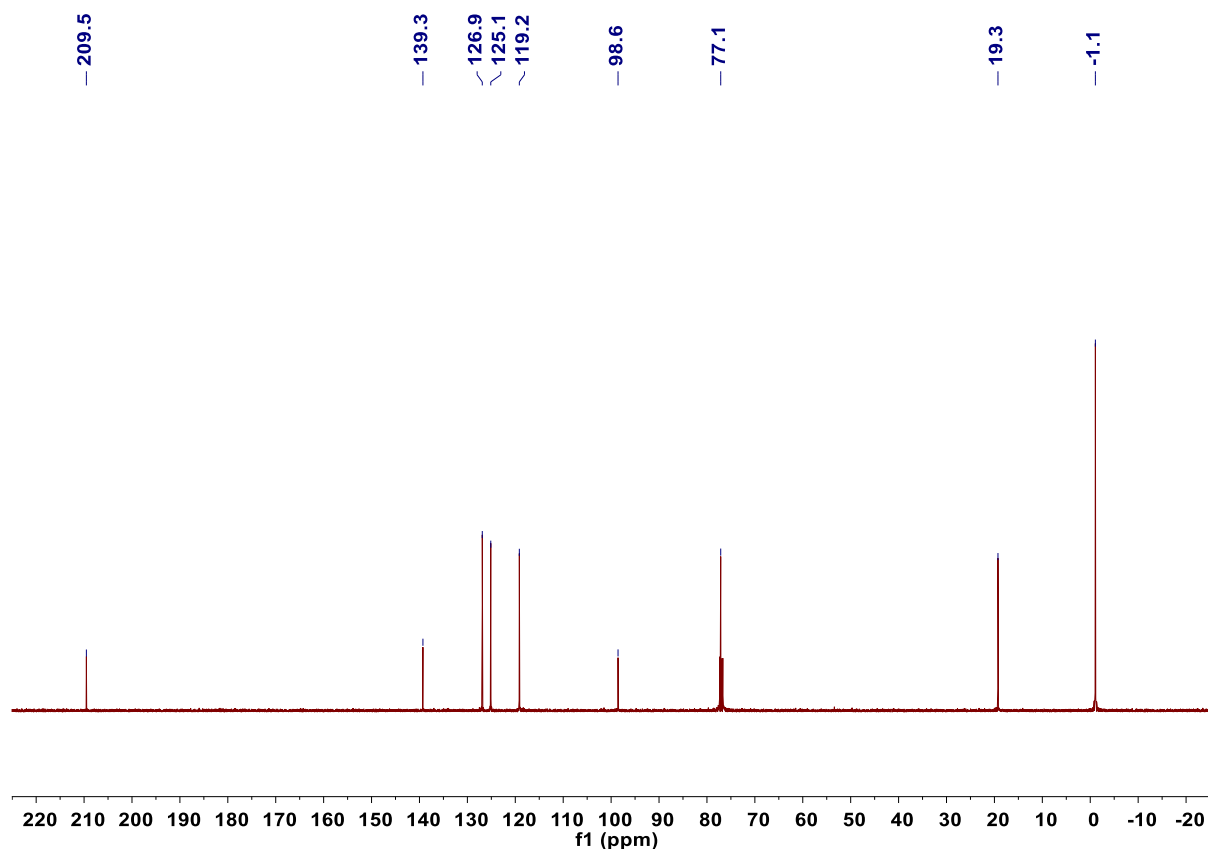


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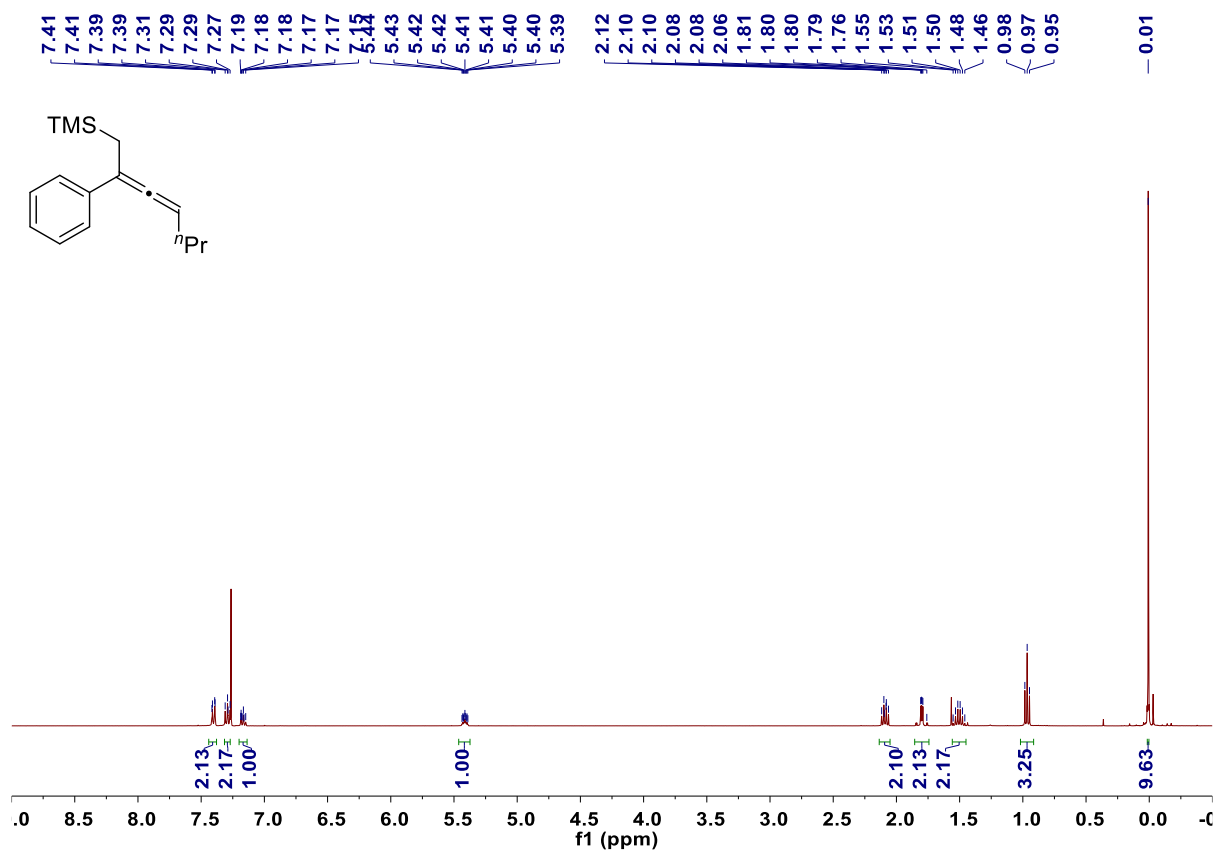


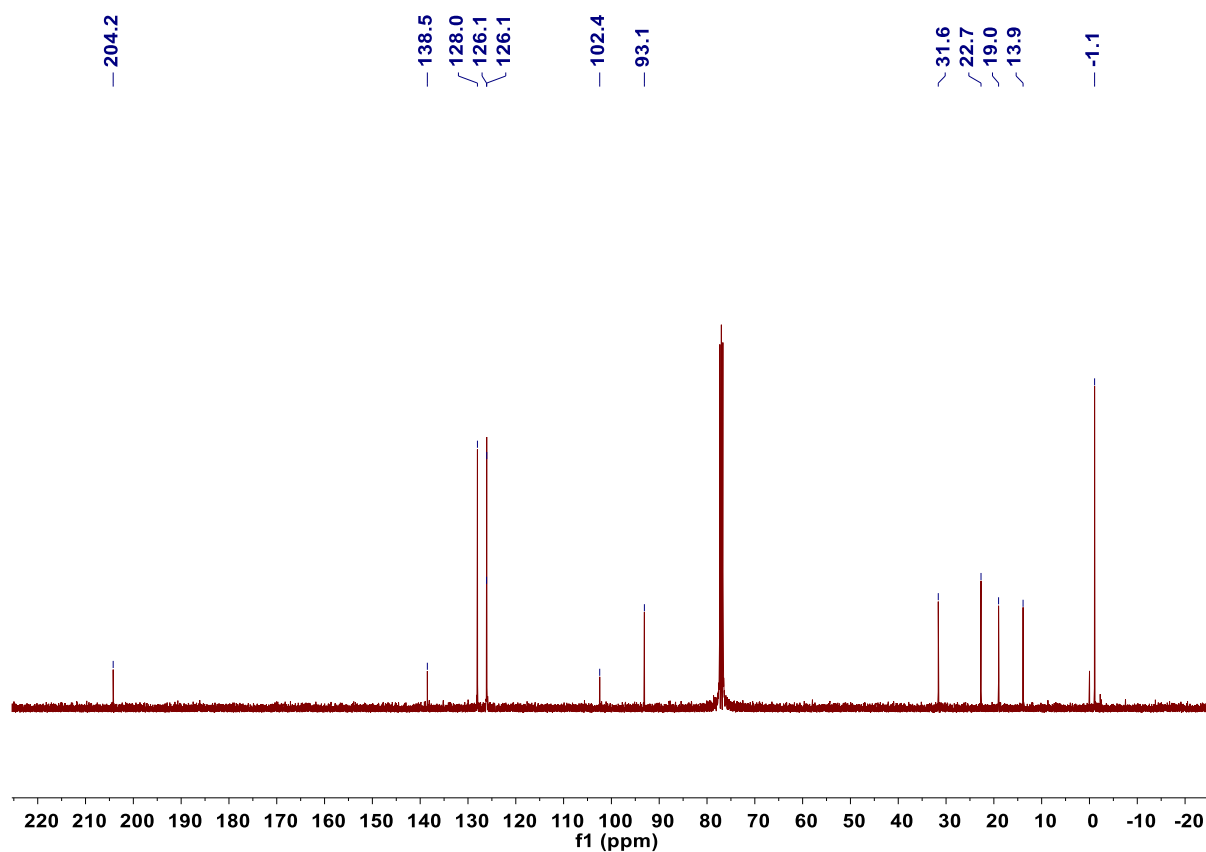
¹H and ¹³C NMR spectra for compound 1m (400 MHz, CDCl₃)



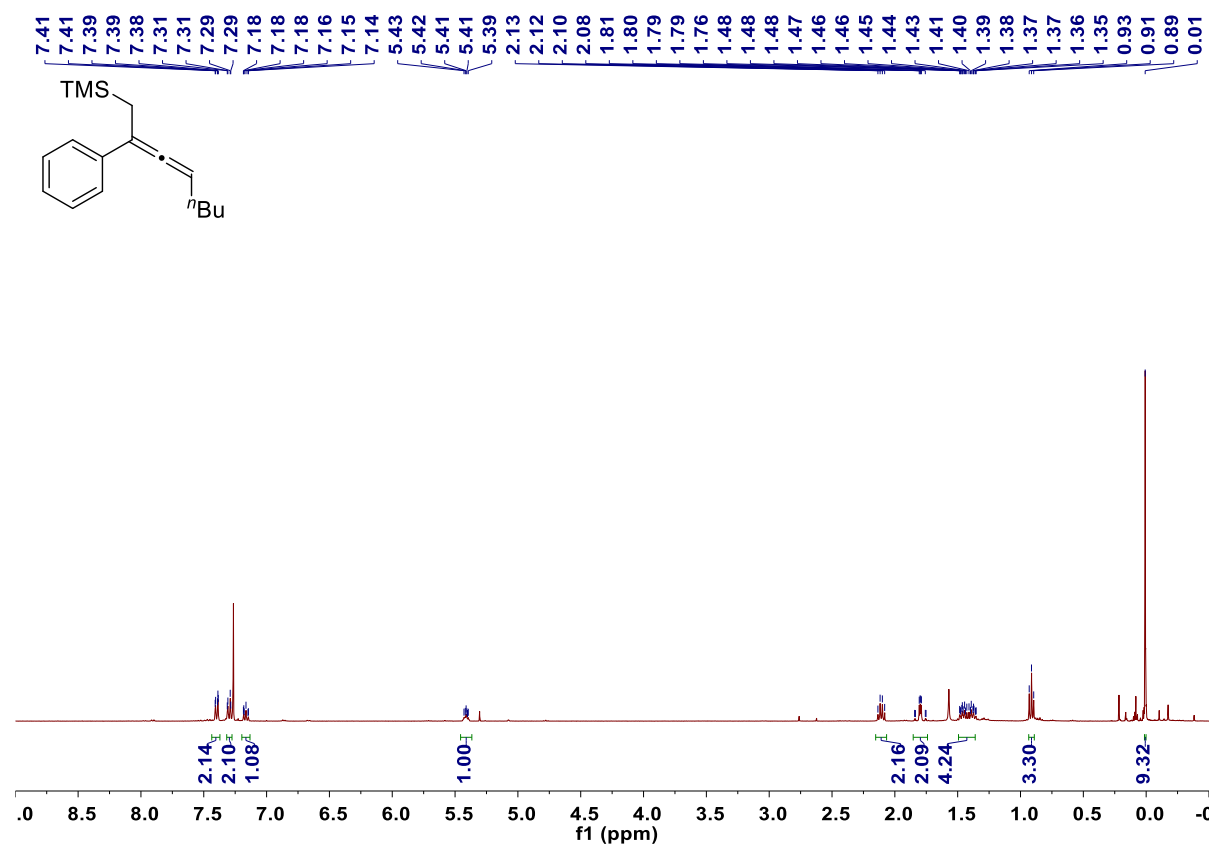


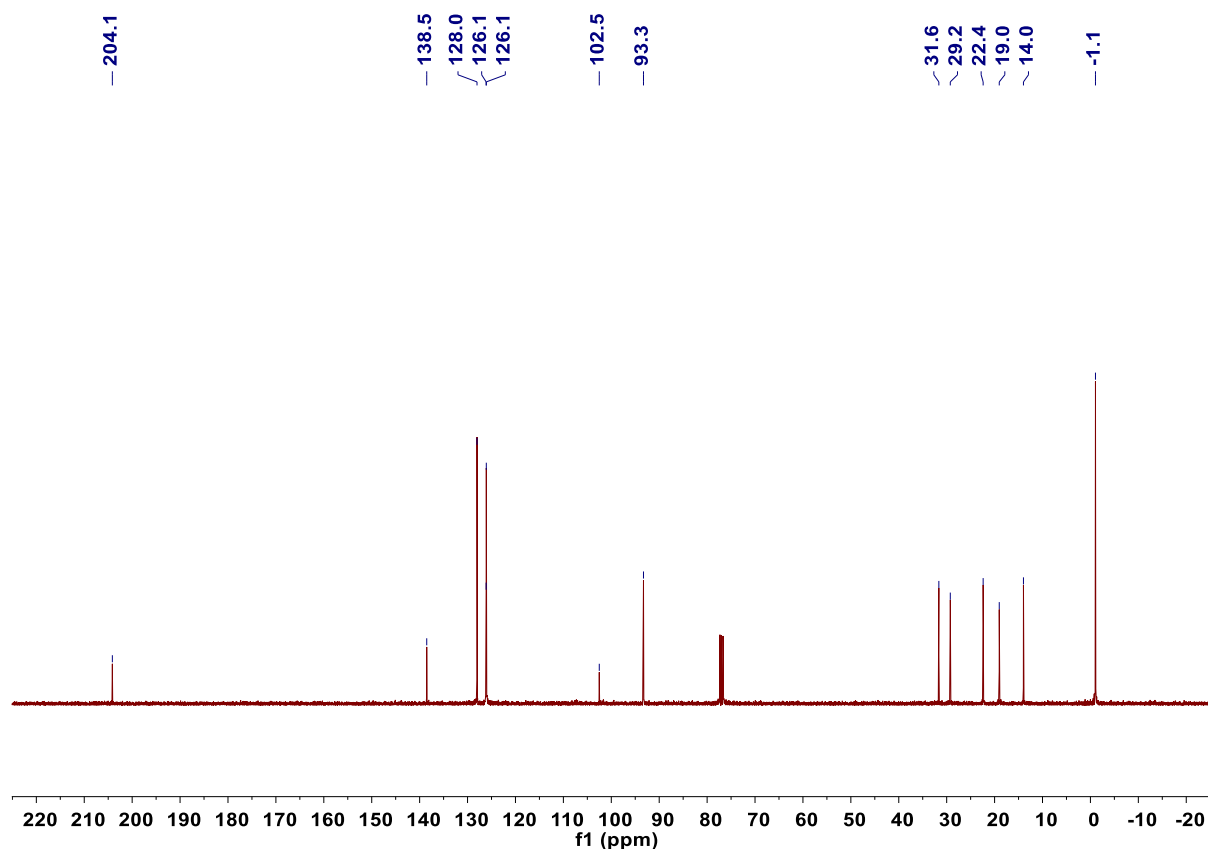
¹H and ¹³C NMR spectra for compound 1n (400 MHz, CDCl₃)



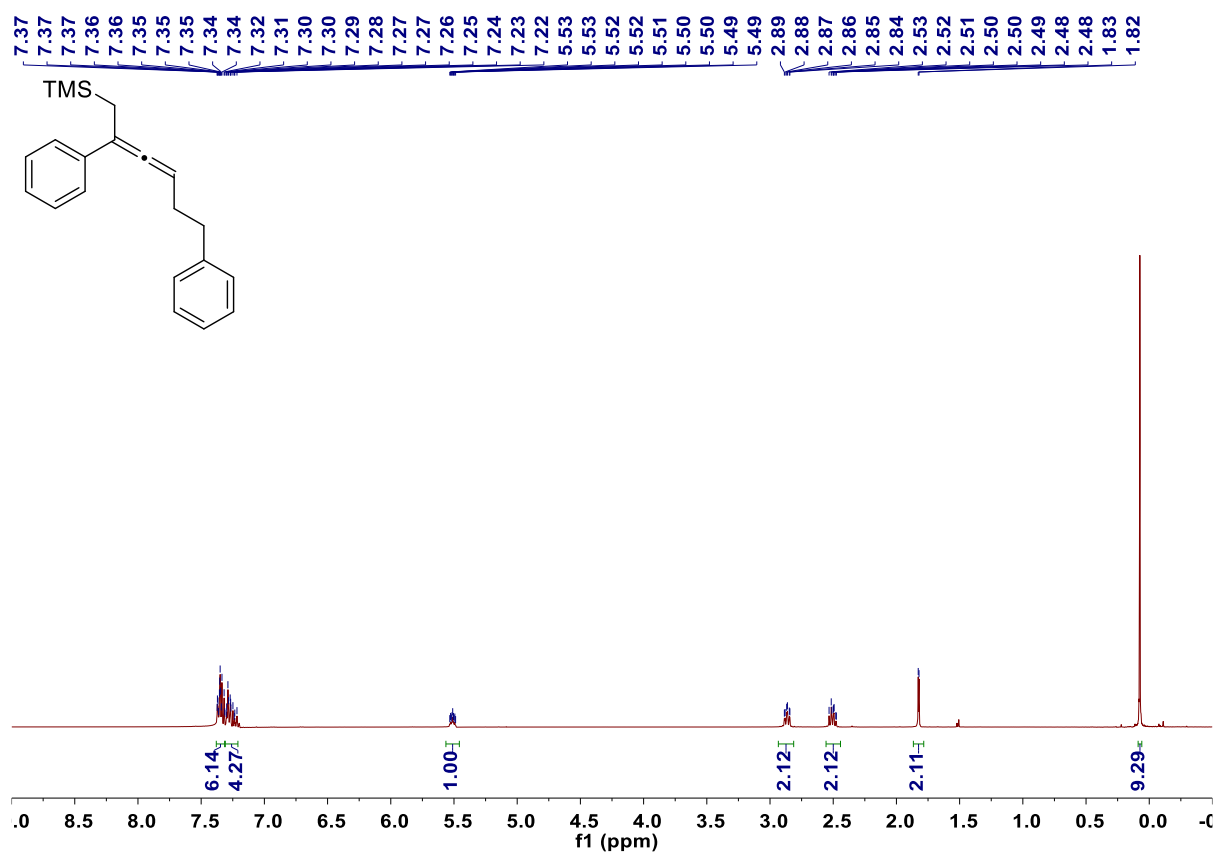


¹H and ¹³C NMR spectra for compound 1o (400 MHz, CDCl₃)

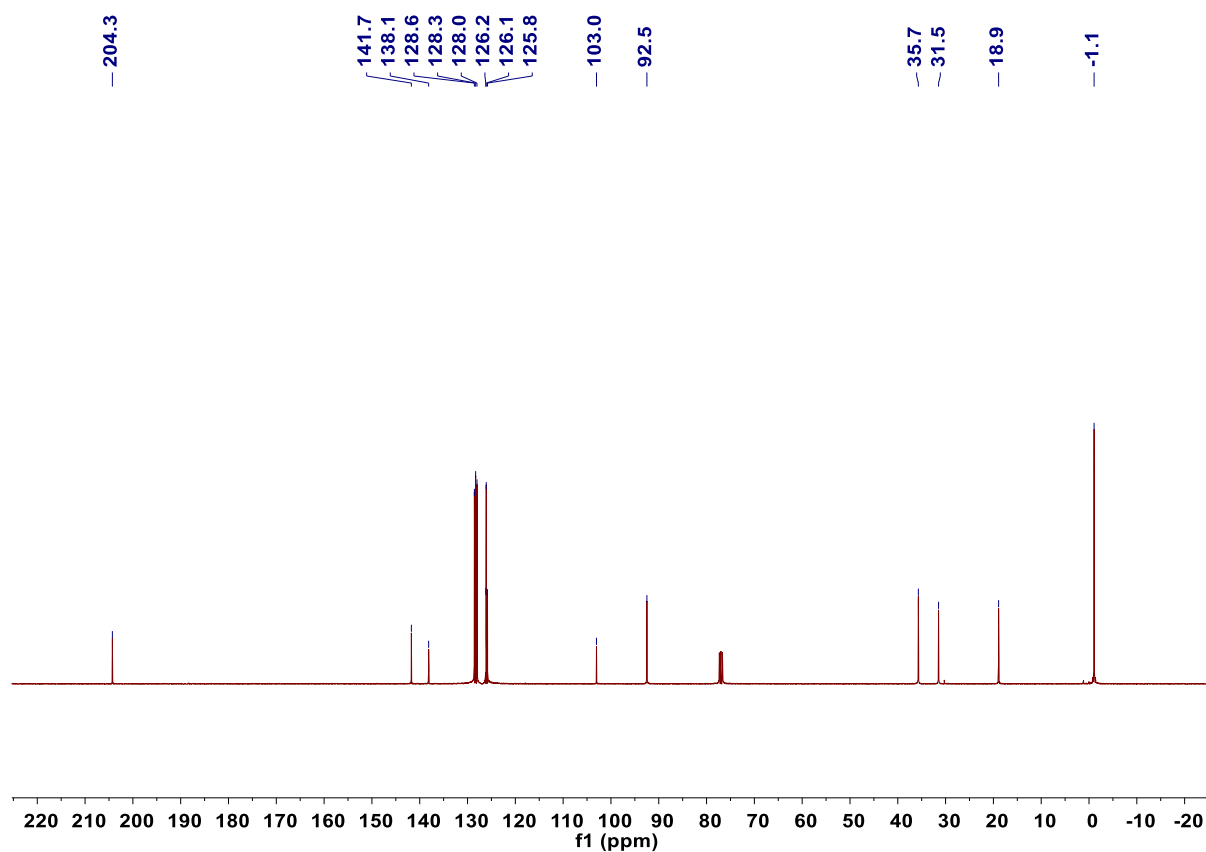




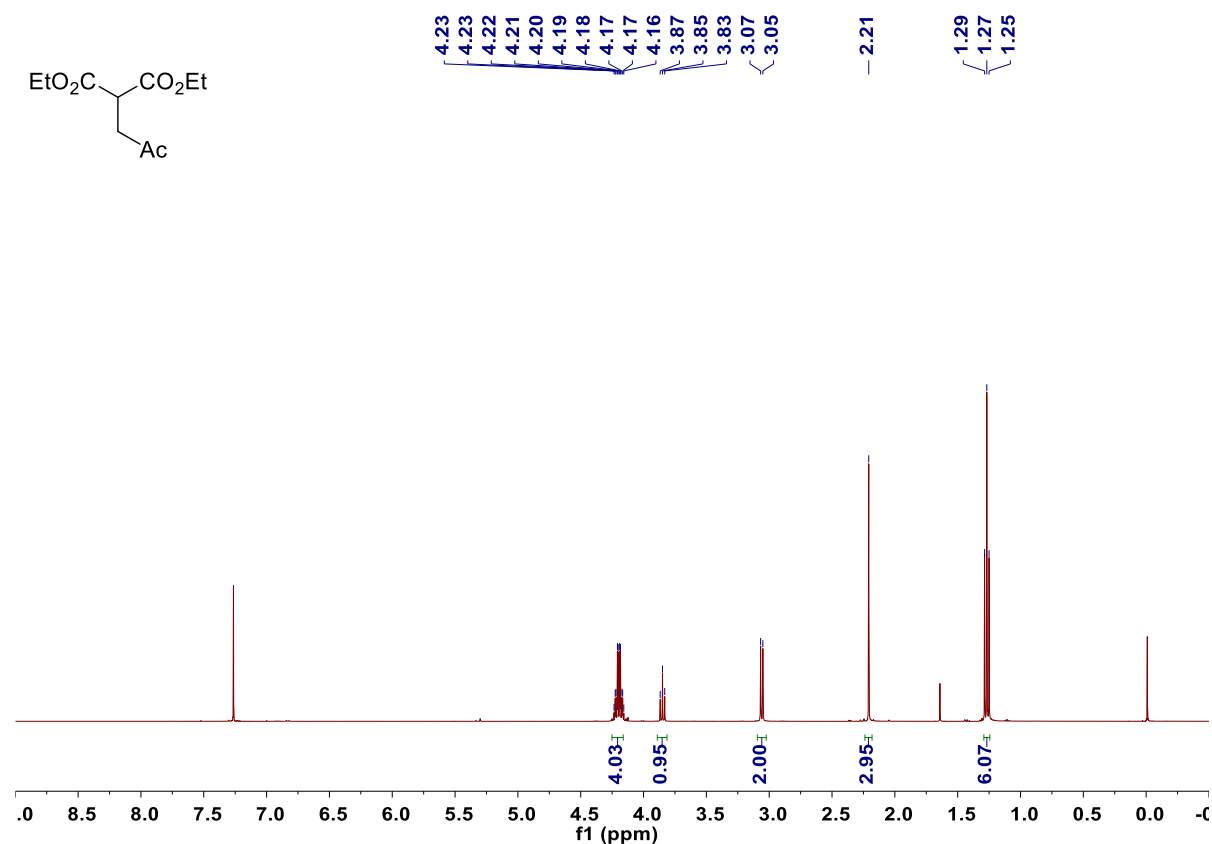
¹H and ¹³C NMR spectra for compound 1p (400 MHz, CDCl₃)



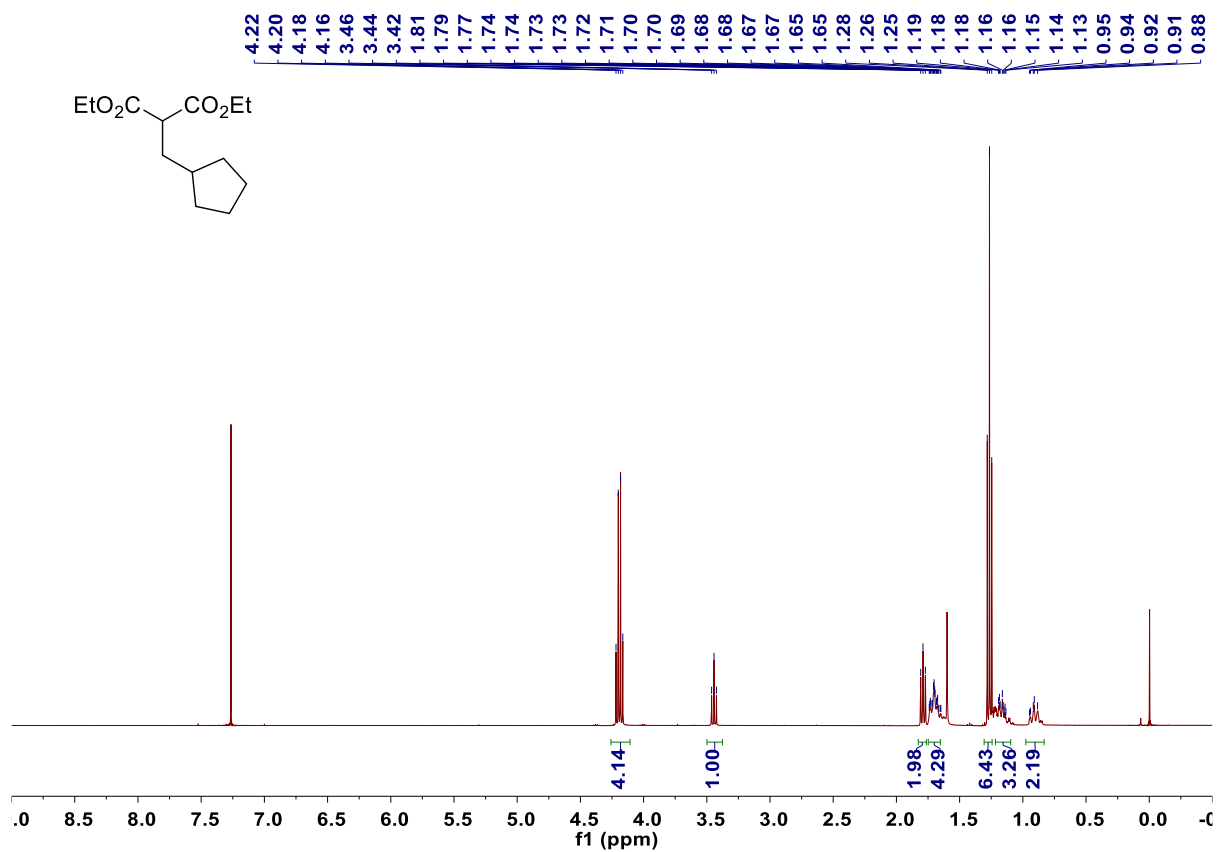
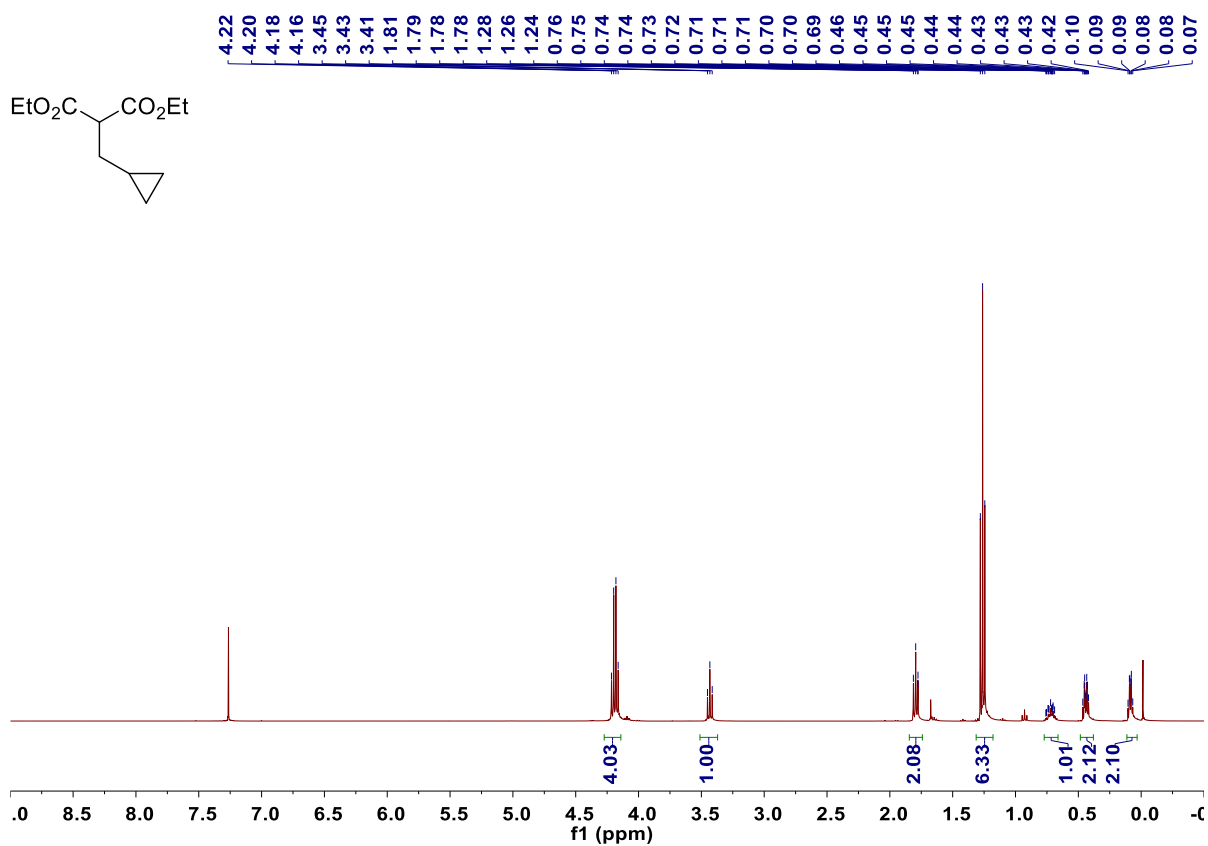
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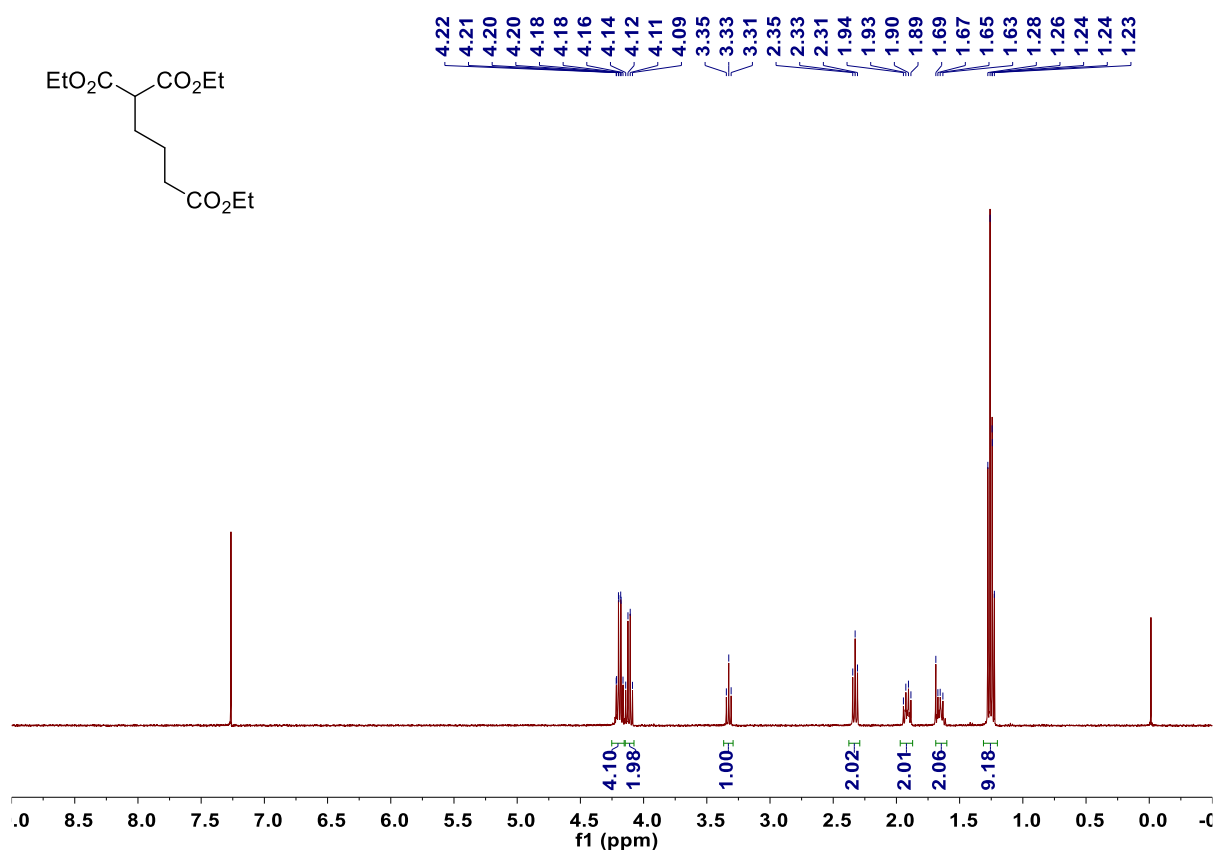


¹H and ¹³C NMR spectra for compound 1q (400 MHz, CDCl₃)

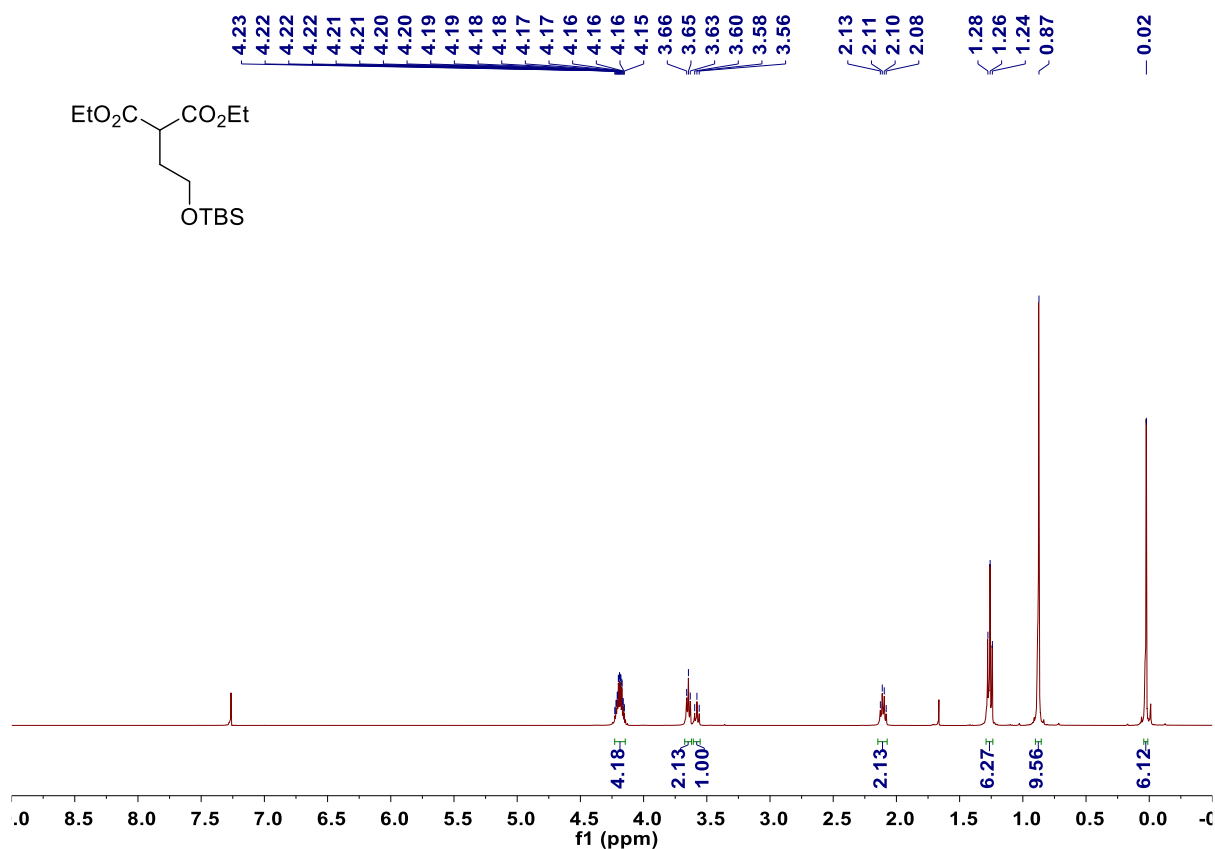


¹H NMR spectrum for compound 2e (400 MHz, CDCl₃)

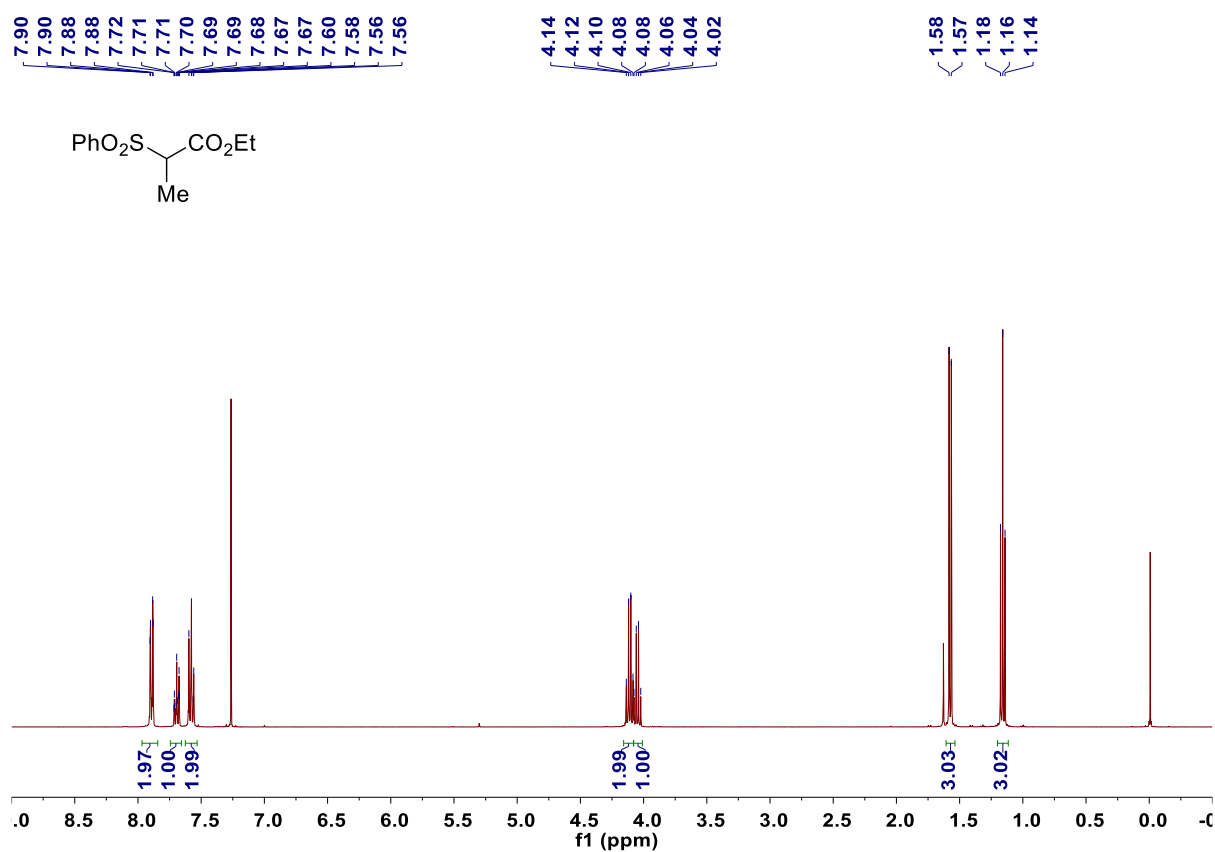




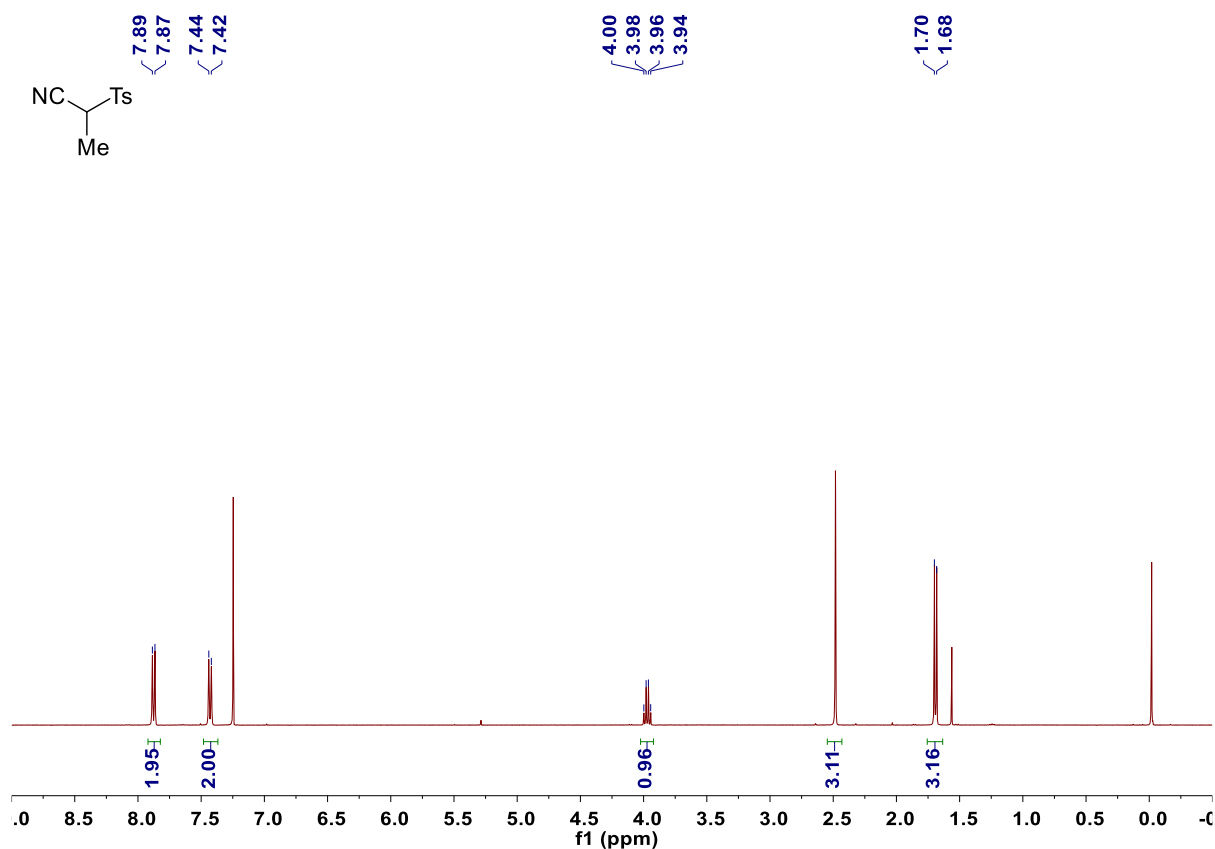
¹H NMR spectrum for compound 2i (400 MHz, CDCl₃)



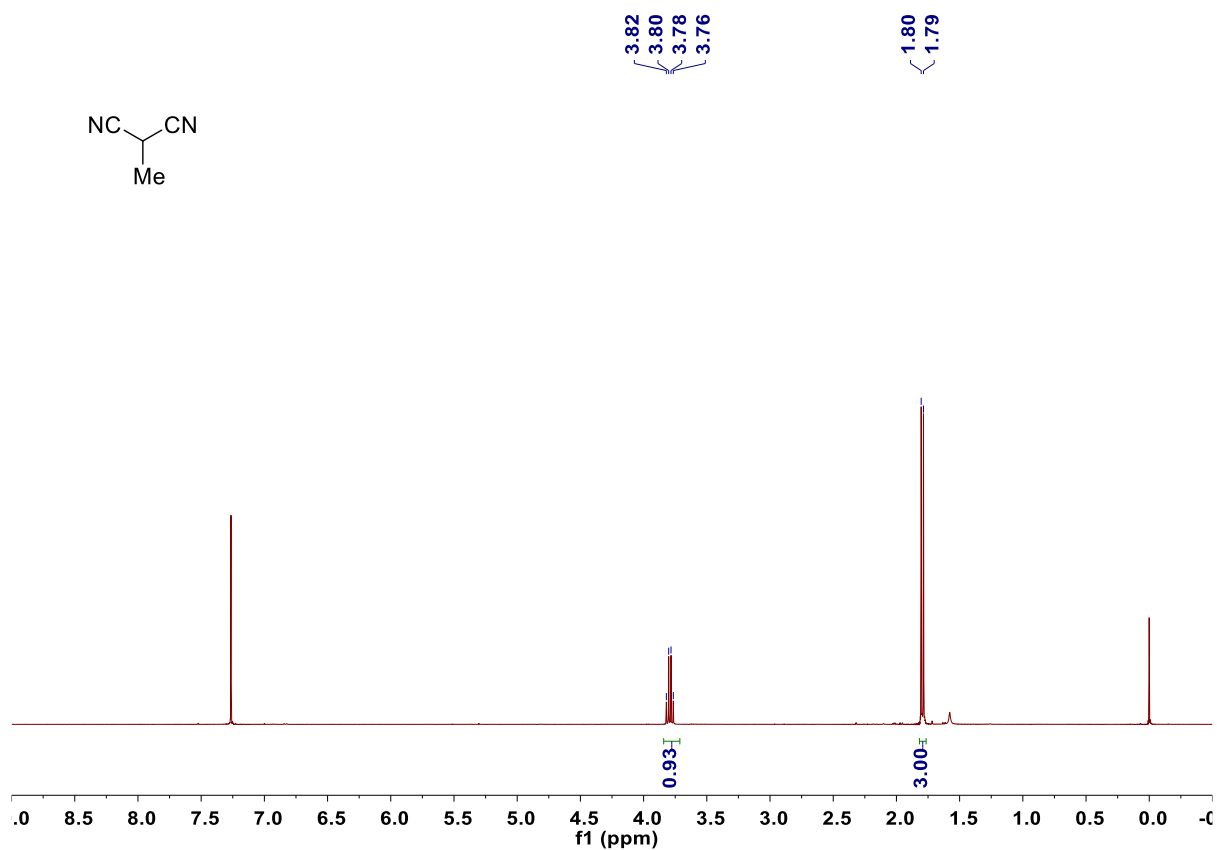
¹H NMR spectrum for compound 2j (400 MHz, CDCl₃)



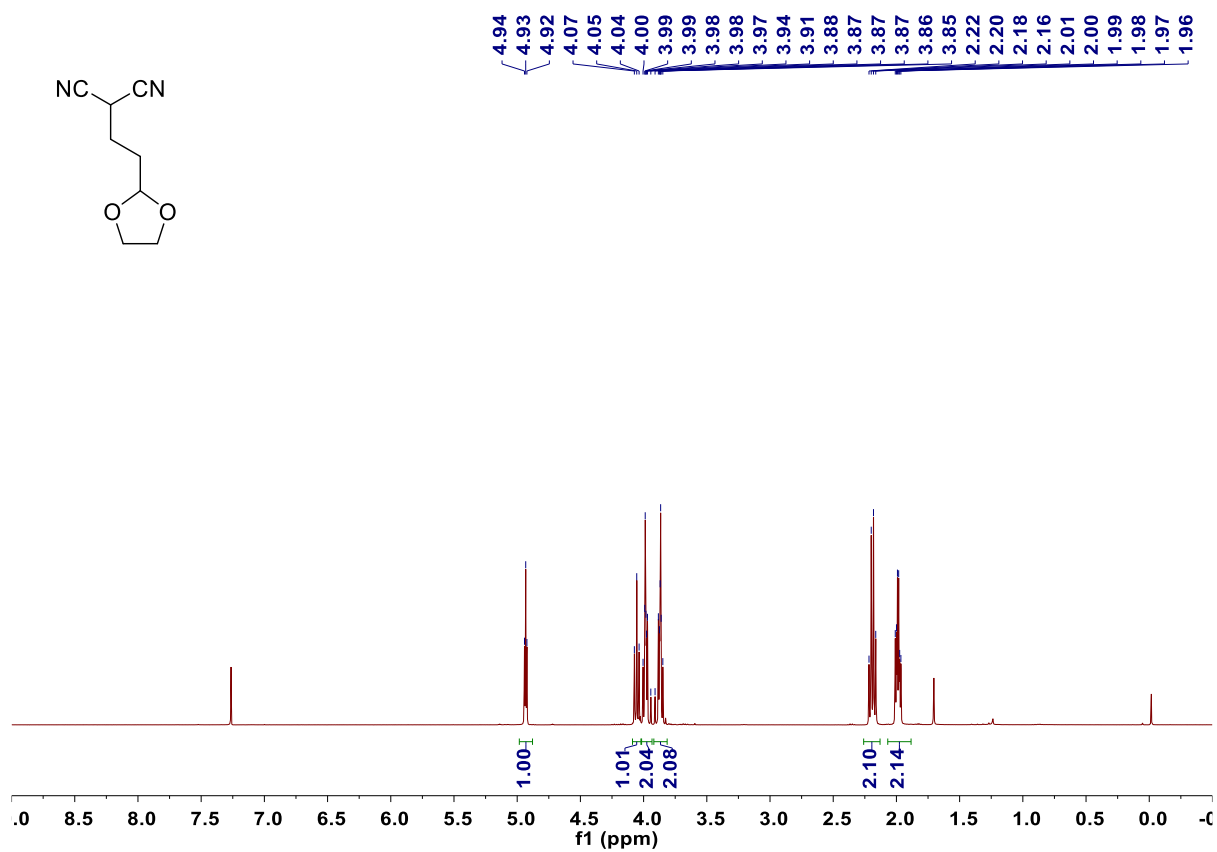
¹H NMR spectrum for compound 2m (400 MHz, CDCl₃)



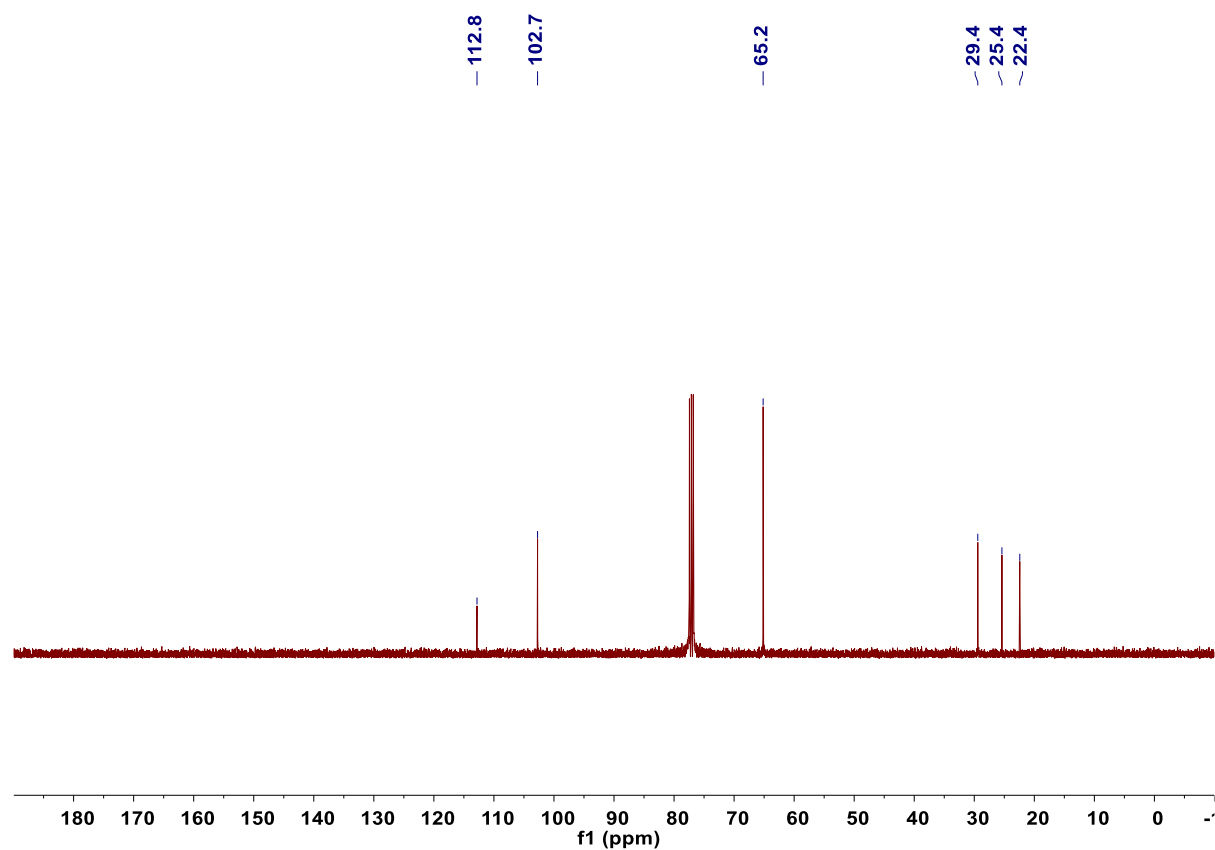
¹H NMR spectrum for compound 2n (400 MHz, CDCl₃)



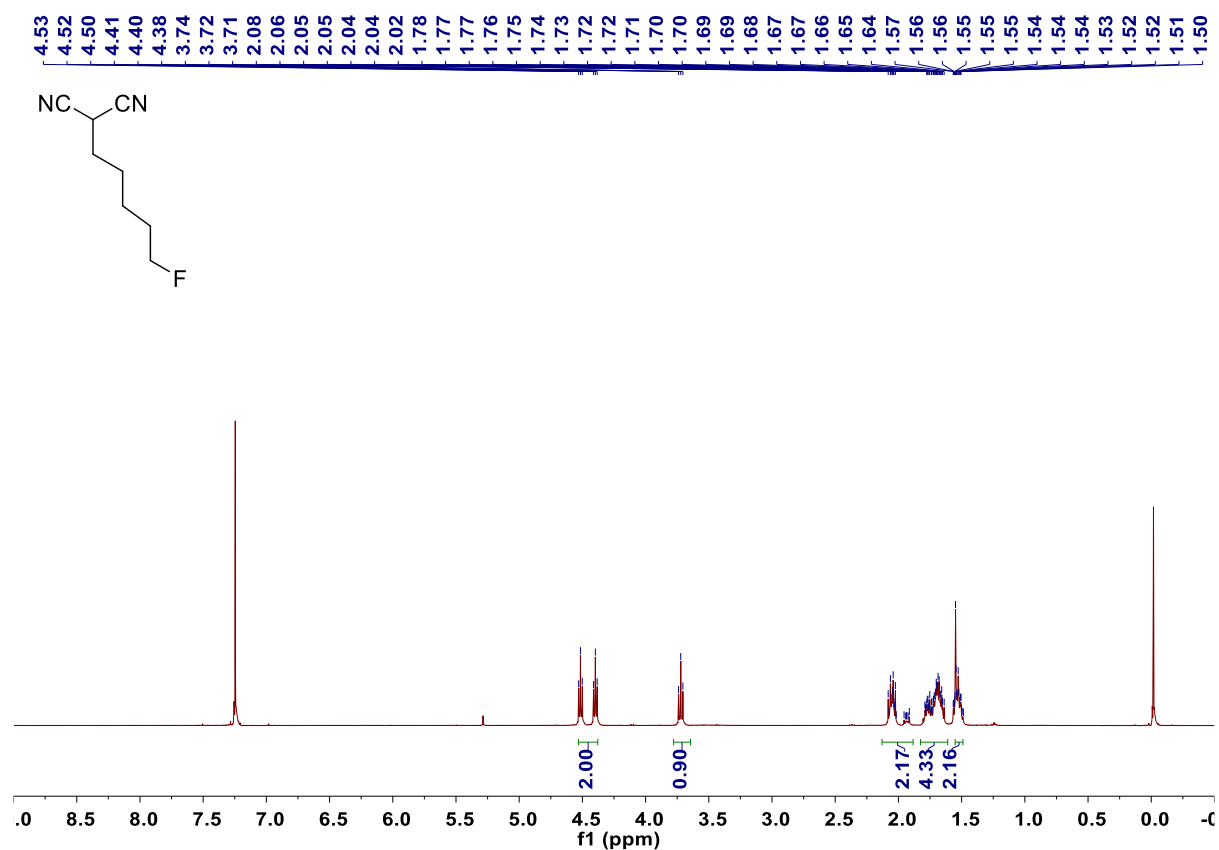
¹H NMR spectrum for compound 2o (400 MHz, CDCl₃)

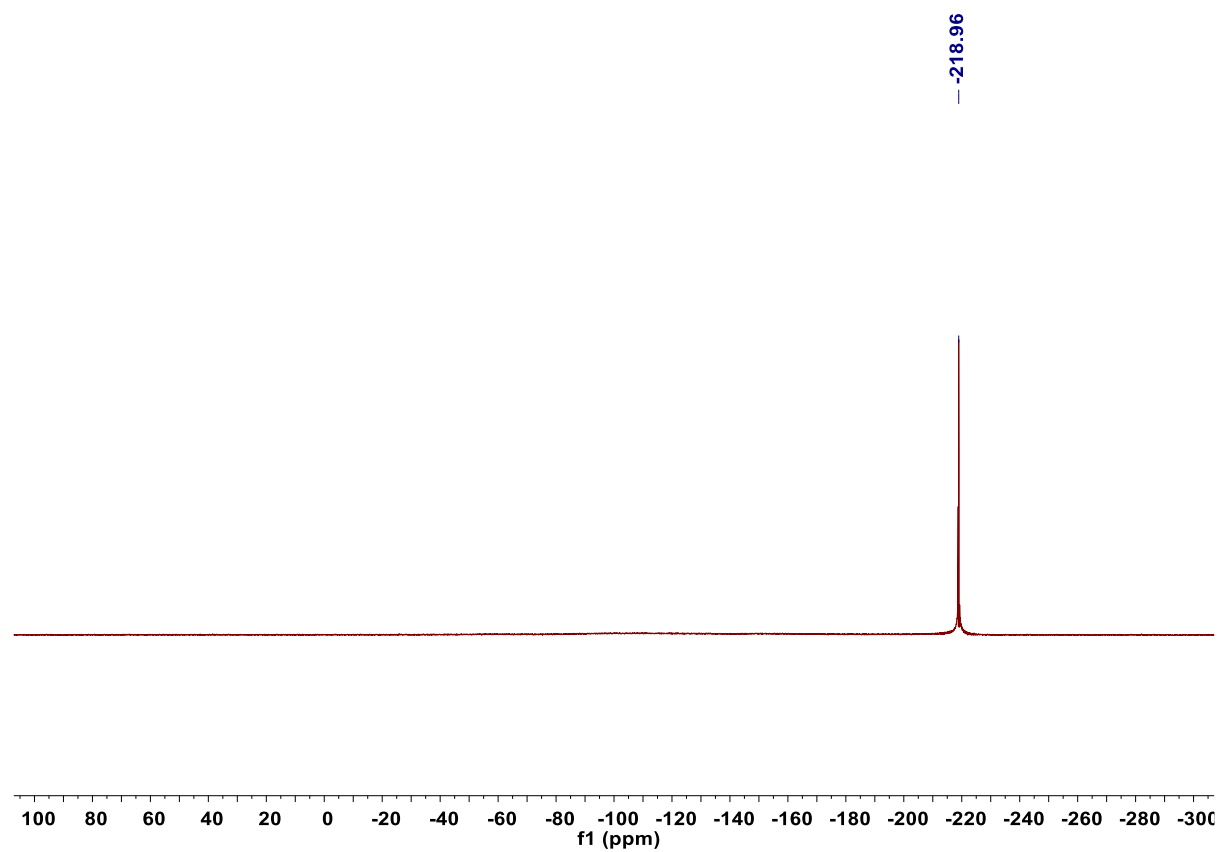
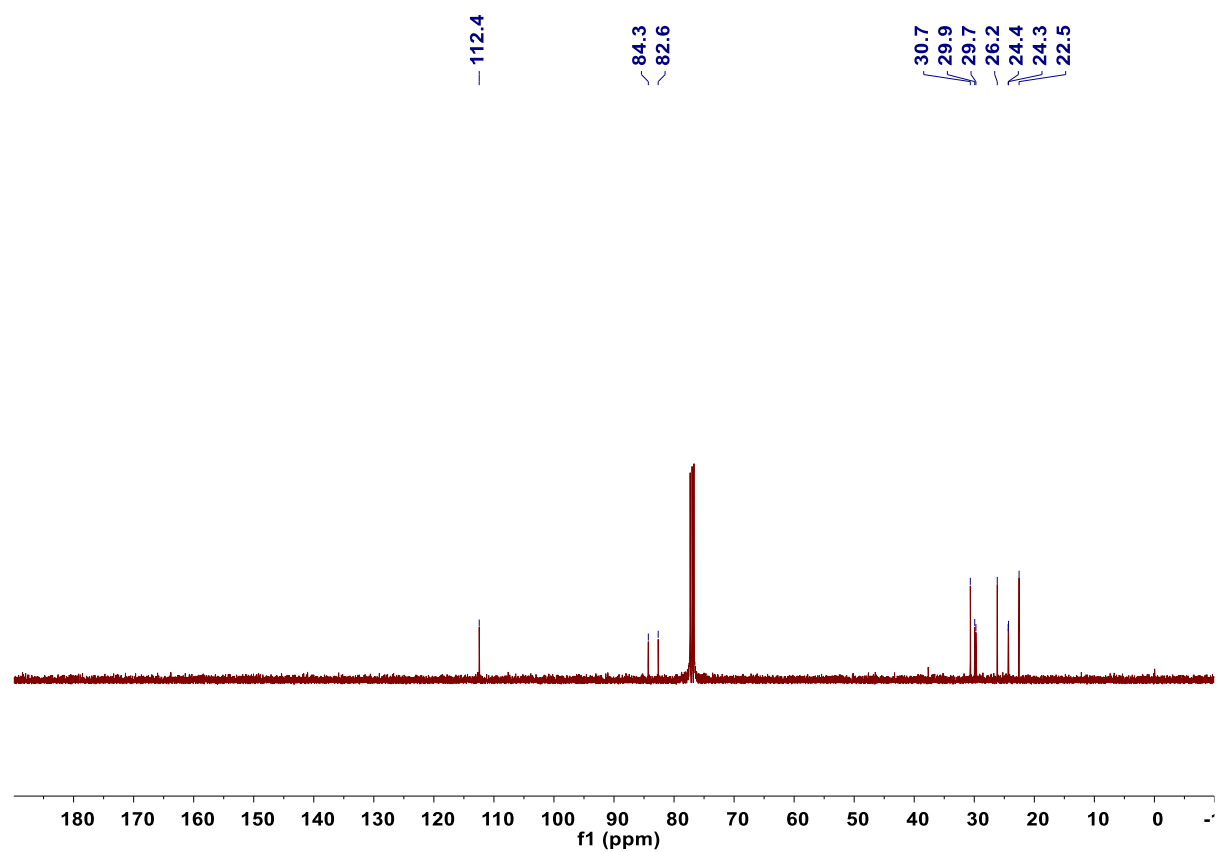


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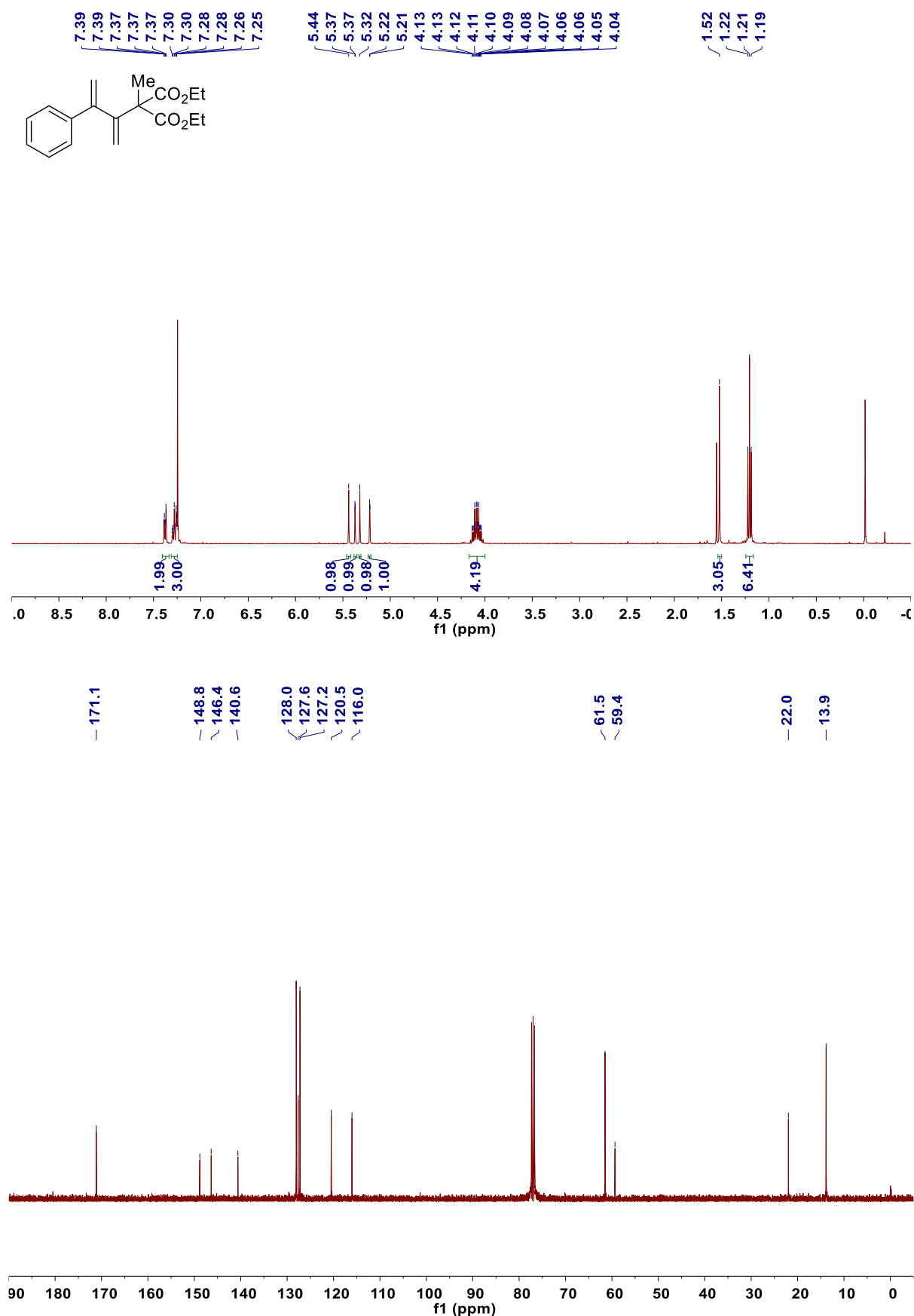
^1H and ^{13}C NMR spectra for compound 2p (400 MHz, CDCl_3)



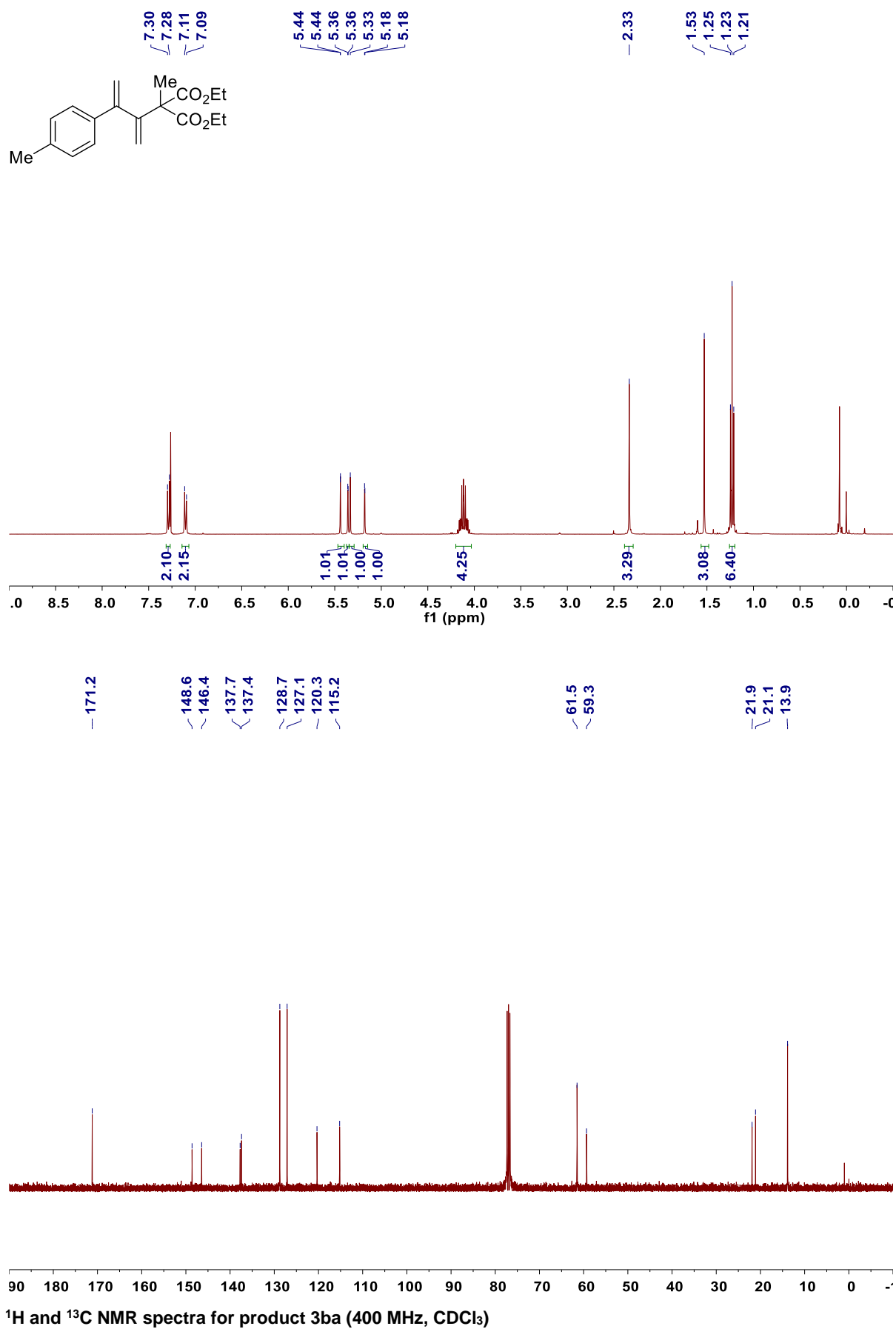


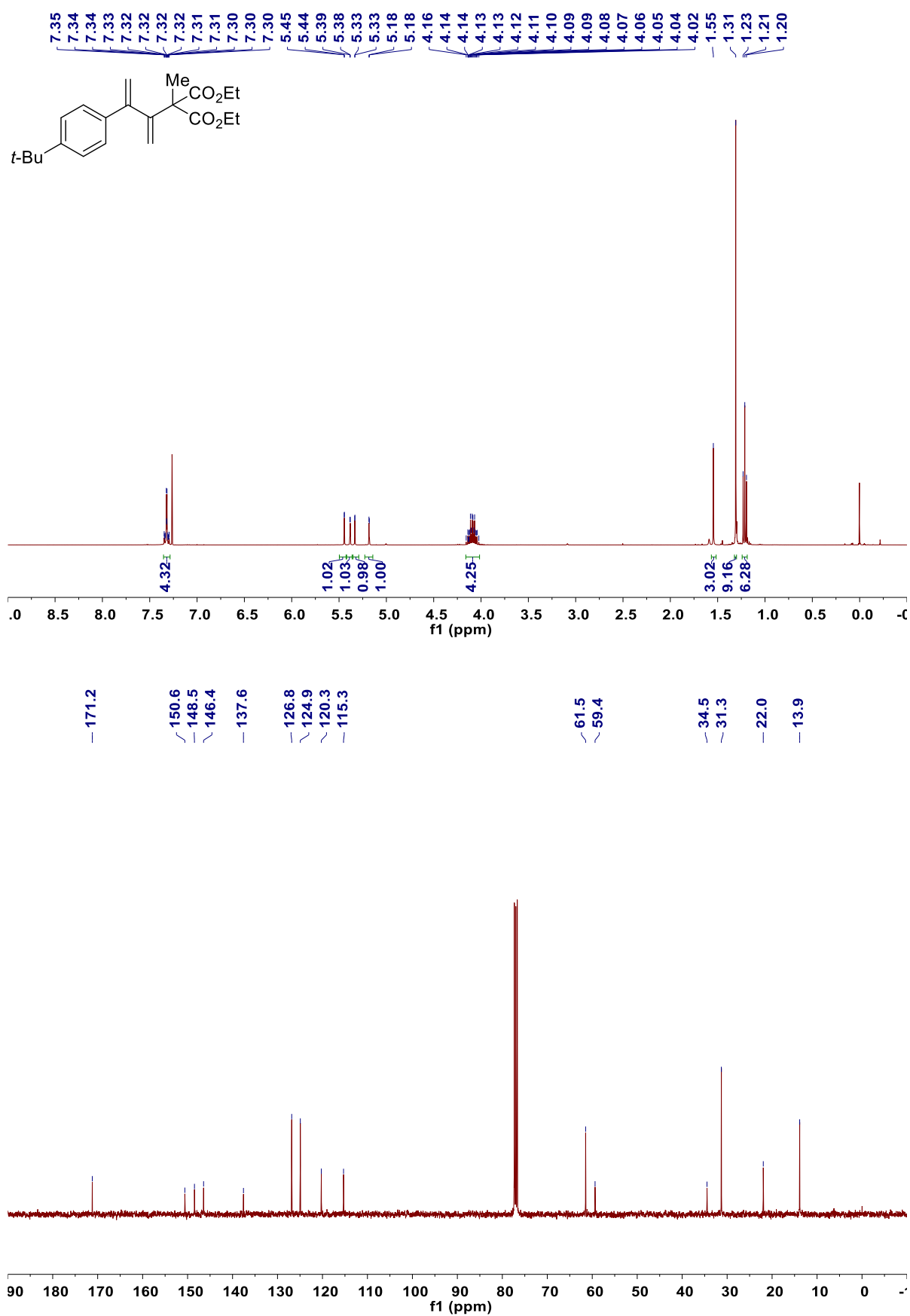
¹H, ¹³C and ¹⁹F NMR spectra for compound 2q (400 MHz, CDCl₃)

11. NMR spectra of all the products

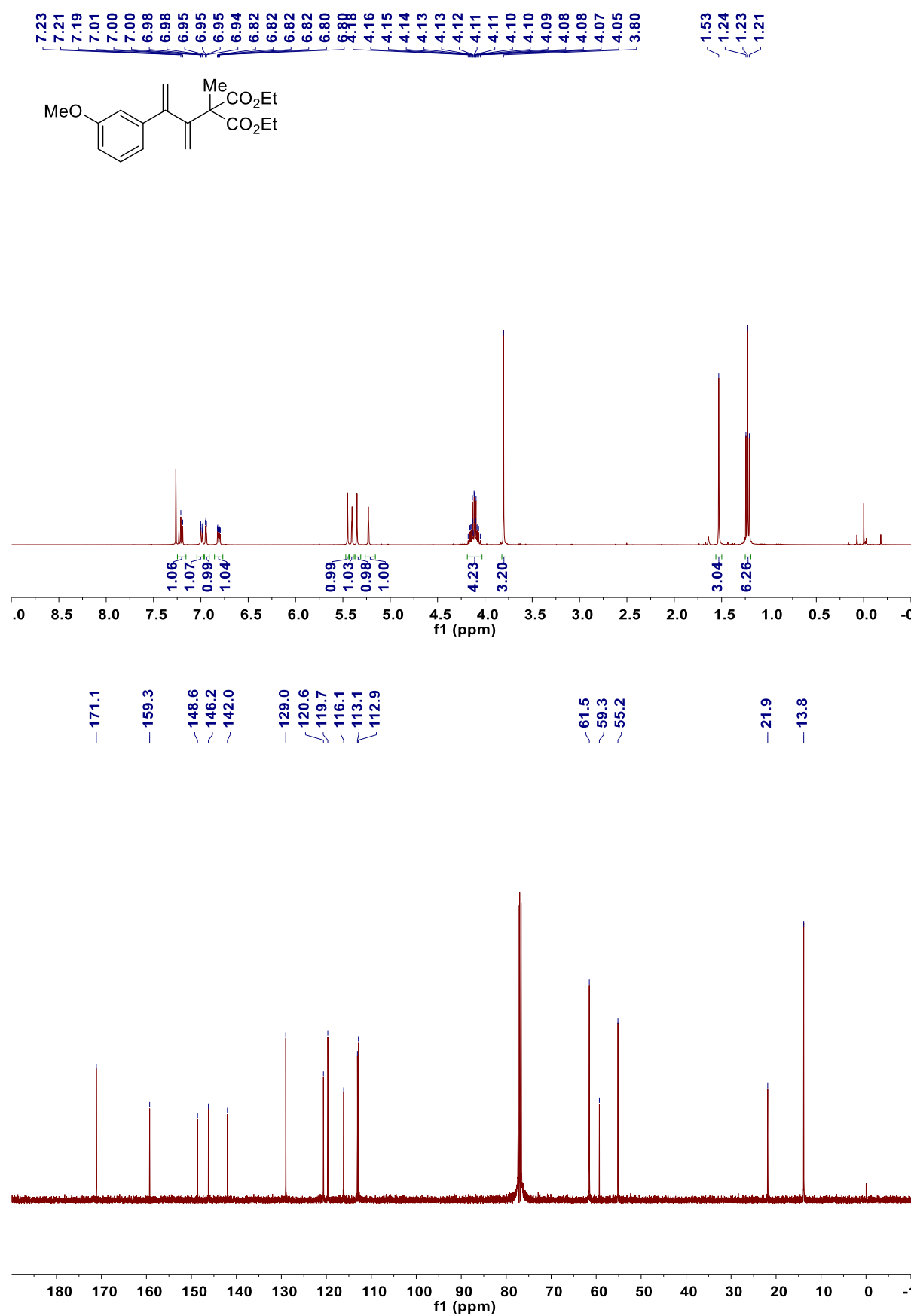
¹H and ¹³C NMR spectra for product 3aa (400 MHz, CDCl₃)

SUPPORTING INFORMATION



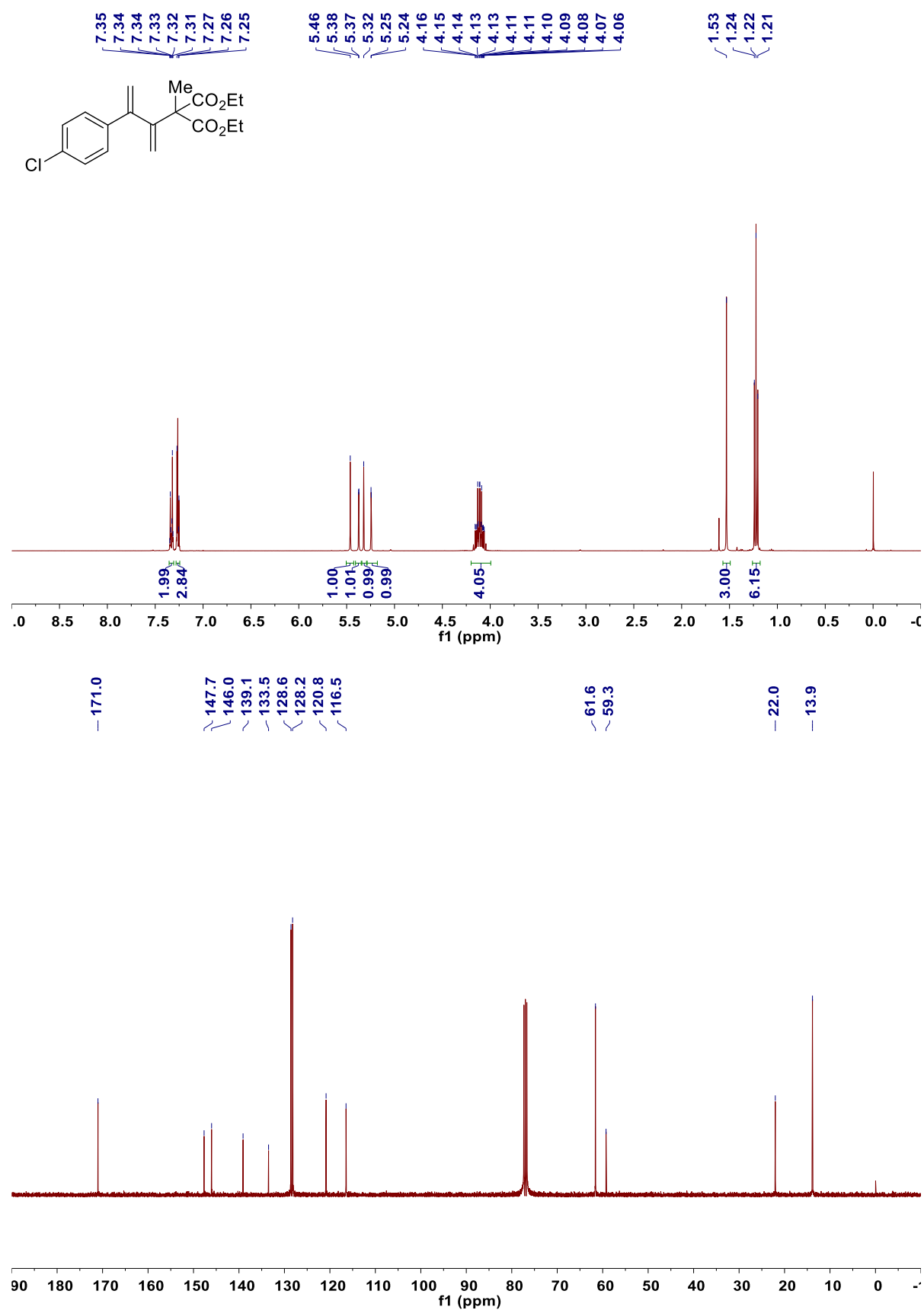
¹H and ¹³C NMR spectra for product 3ca (400 MHz, CDCl₃)

SUPPORTING INFORMATION



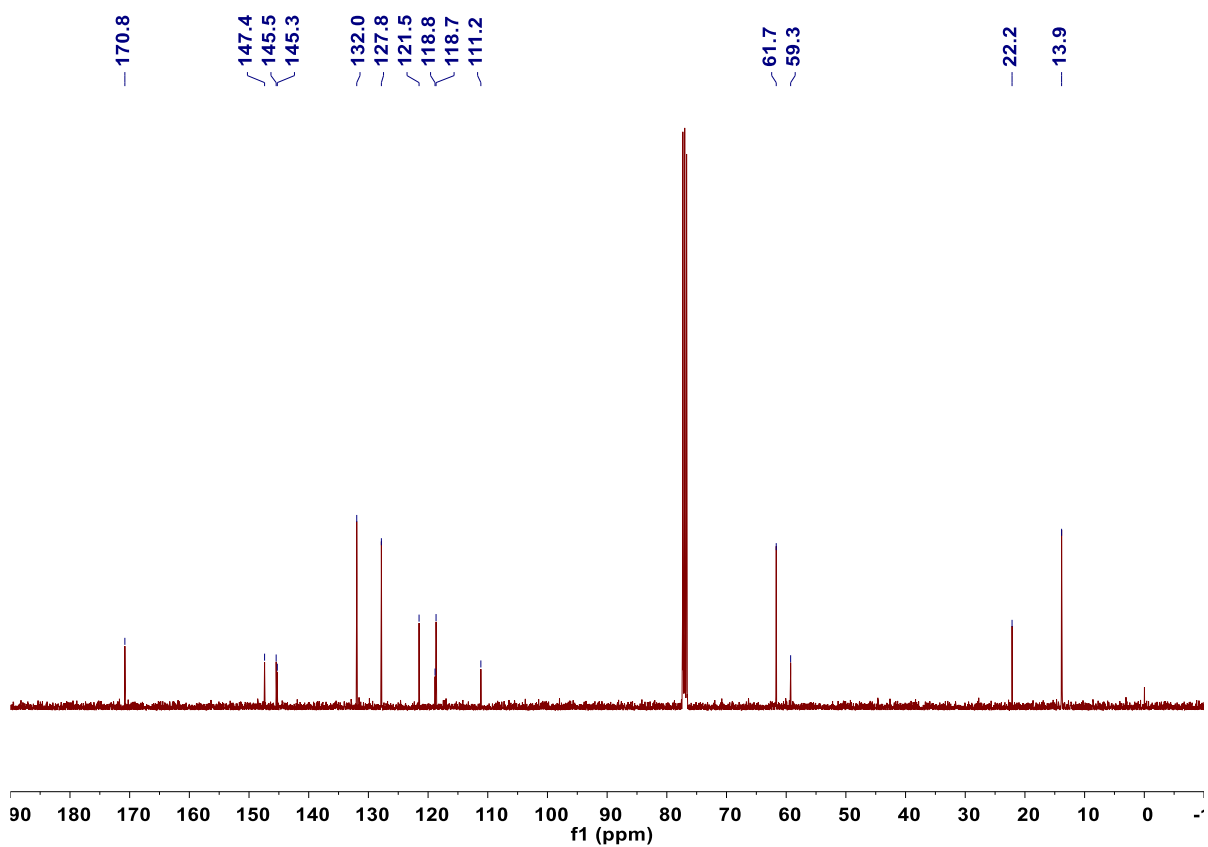
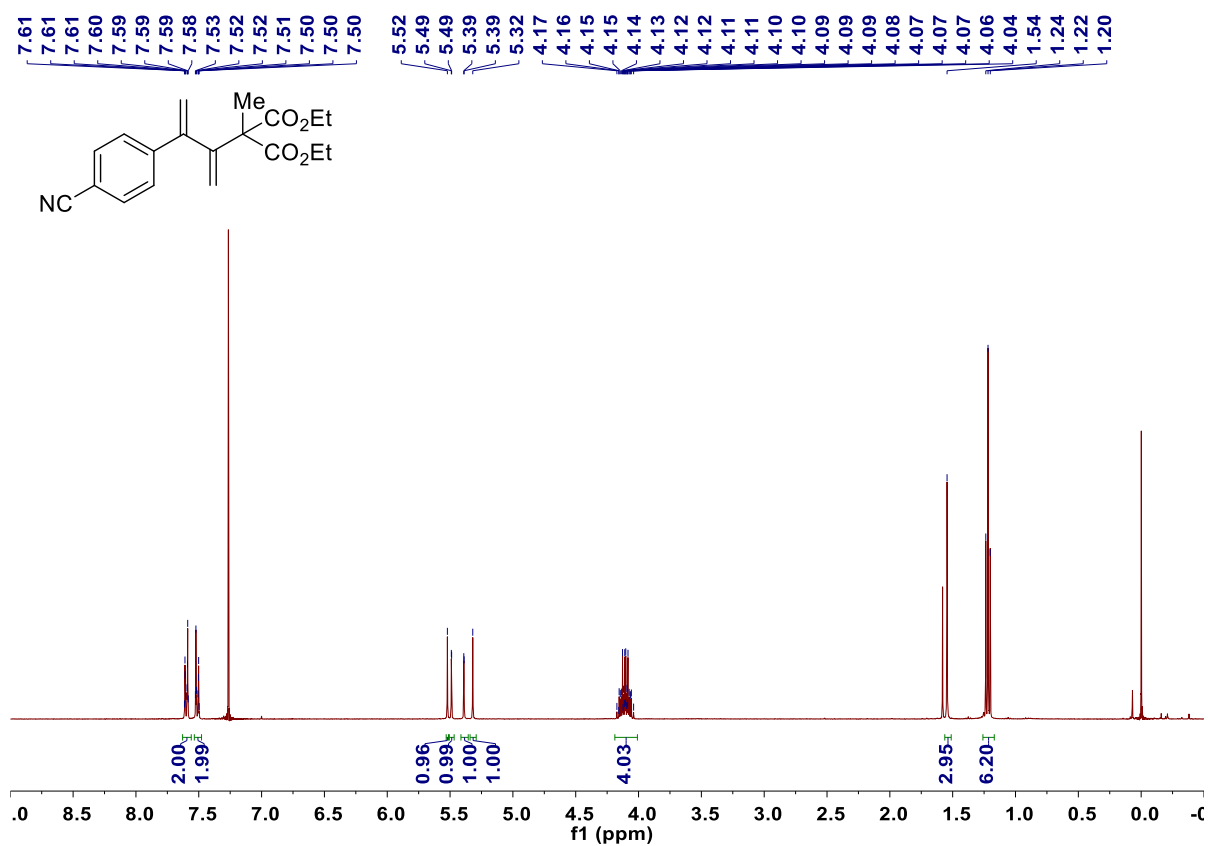
¹H and ¹³C NMR spectra for product 3da (400 MHz, CDCl₃)

SUPPORTING INFORMATION



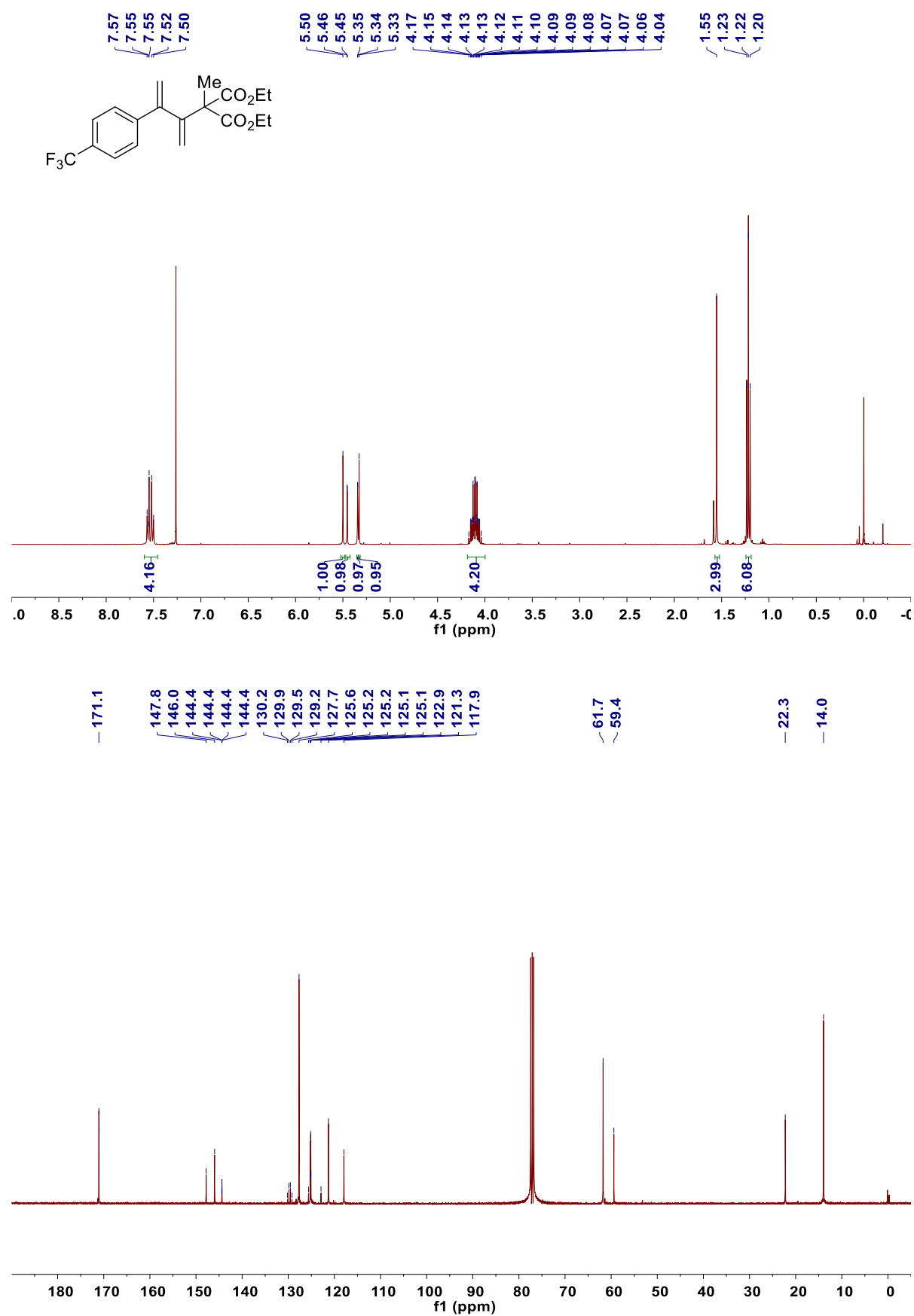
¹H and ¹³C NMR spectra for product 3ea (400 MHz, CDCl₃)

SUPPORTING INFORMATION

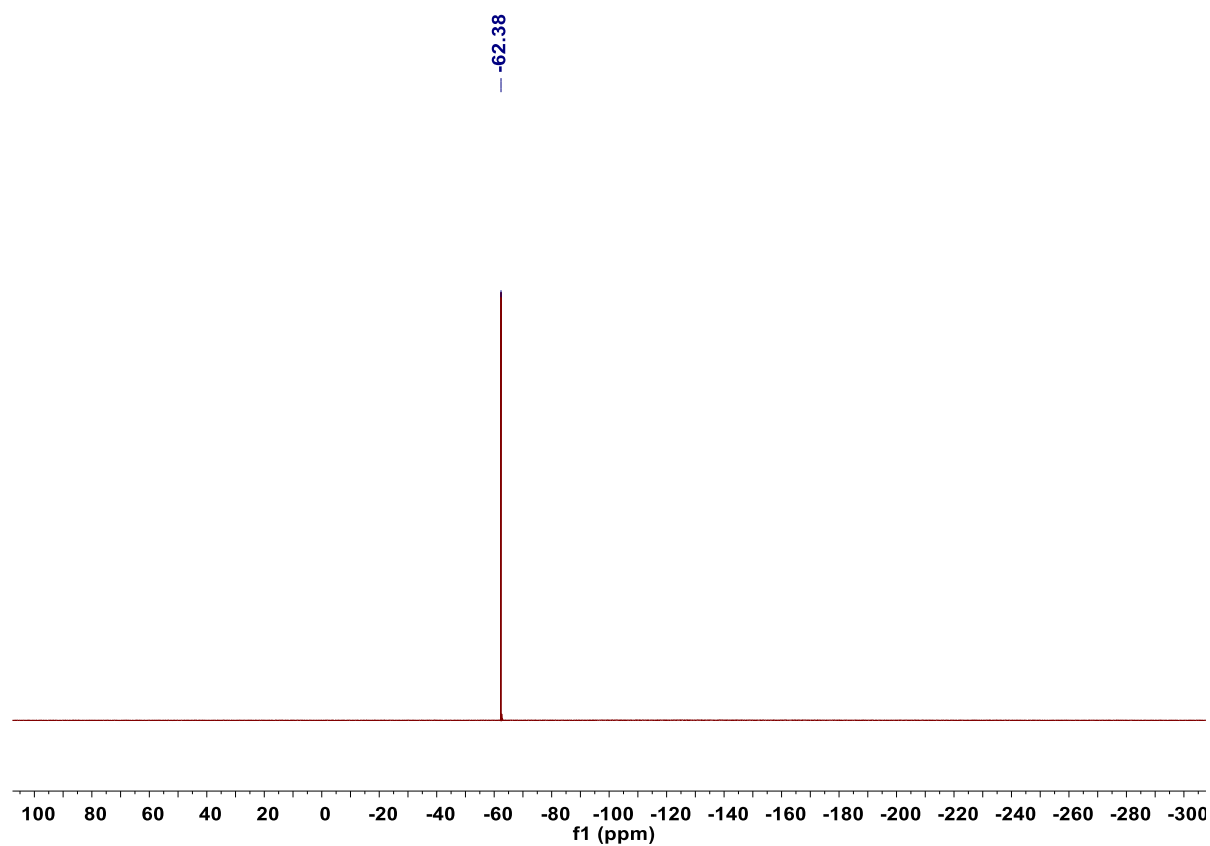


¹H and ¹³C NMR spectra for product 3fa (400 MHz, CDCl₃)

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^1H , ^{13}C and ^{19}F NMR spectra for product 3ga (400 MHz, CDCl_3)

Chemical structure of the compound is shown above the spectra. The structure is a 4-nitrophenyl substituted alkene derivative, specifically 4-nitro-1-(4-methoxycarbonylphenyl)-1,3-butadiene-1,3-diol diethyl ester.

¹H NMR Spectrum (Top): The spectrum shows peaks in the aromatic region (7.55-8.18 ppm) and the aliphatic region (1.21-4.18 ppm). Integration values are provided below the peaks.

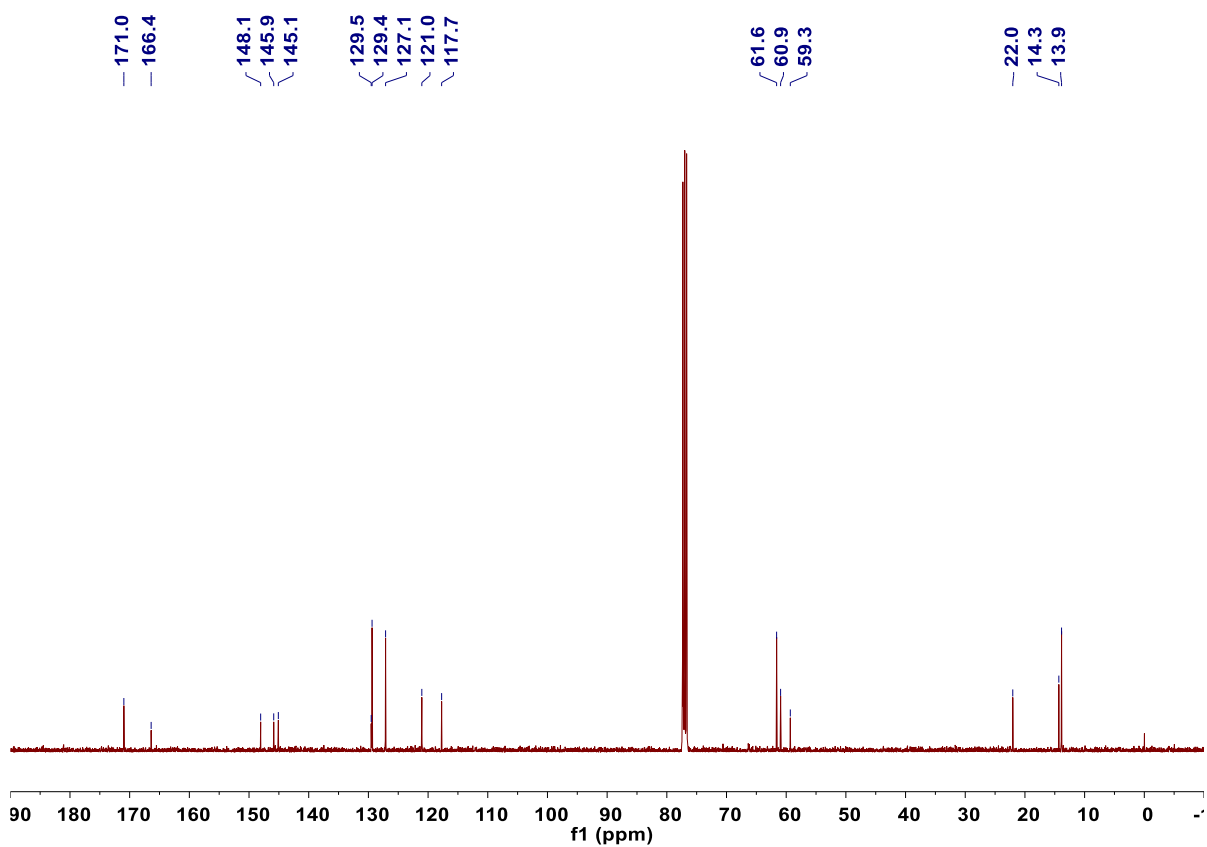
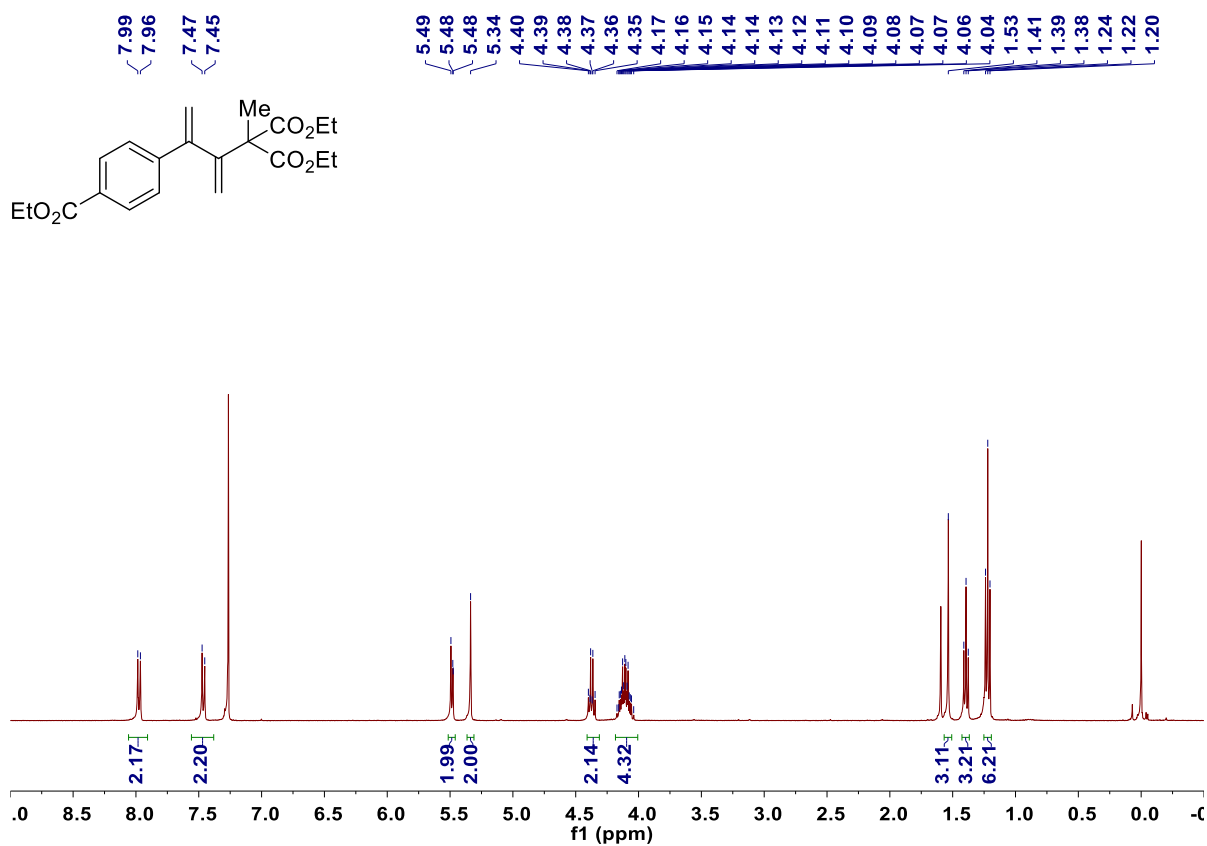
Chemical Shift (ppm)	Integration
8.18, 8.17, 8.16, 8.15	1.96
7.58, 7.57, 7.56, 7.55	2.01
5.54, 5.54, 5.43, 5.43	2.00, 1.00, 1.01
4.18, 4.16, 4.16, 4.15, 4.14, 4.13, 4.13, 4.12, 4.12, 4.11, 4.11, 4.10, 4.10, 4.09, 4.08, 4.07, 4.05	4.06
1.56, 1.24, 1.22, 1.21	3.06, 6.32

¹³C NMR Spectrum (Bottom): The spectrum shows peaks in the aromatic region (119.2-147.3 ppm) and the aliphatic region (13.9-61.7 ppm).

Chemical Shift (ppm)
170.8
147.3, 147.1, 147.1, 145.5
128.0, 123.4, 121.7, 119.2
61.7, 59.3
22.2, 13.9

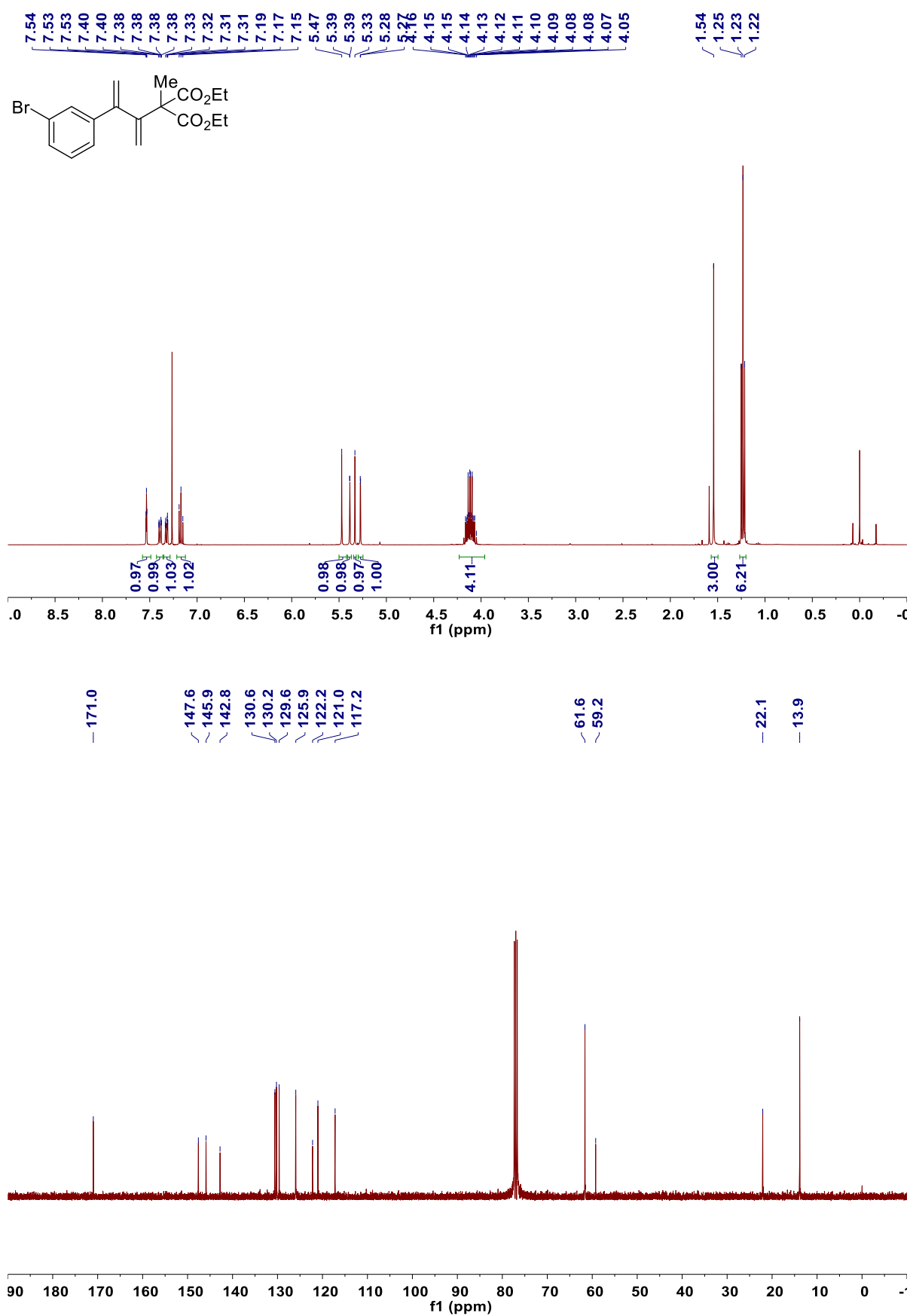
S59

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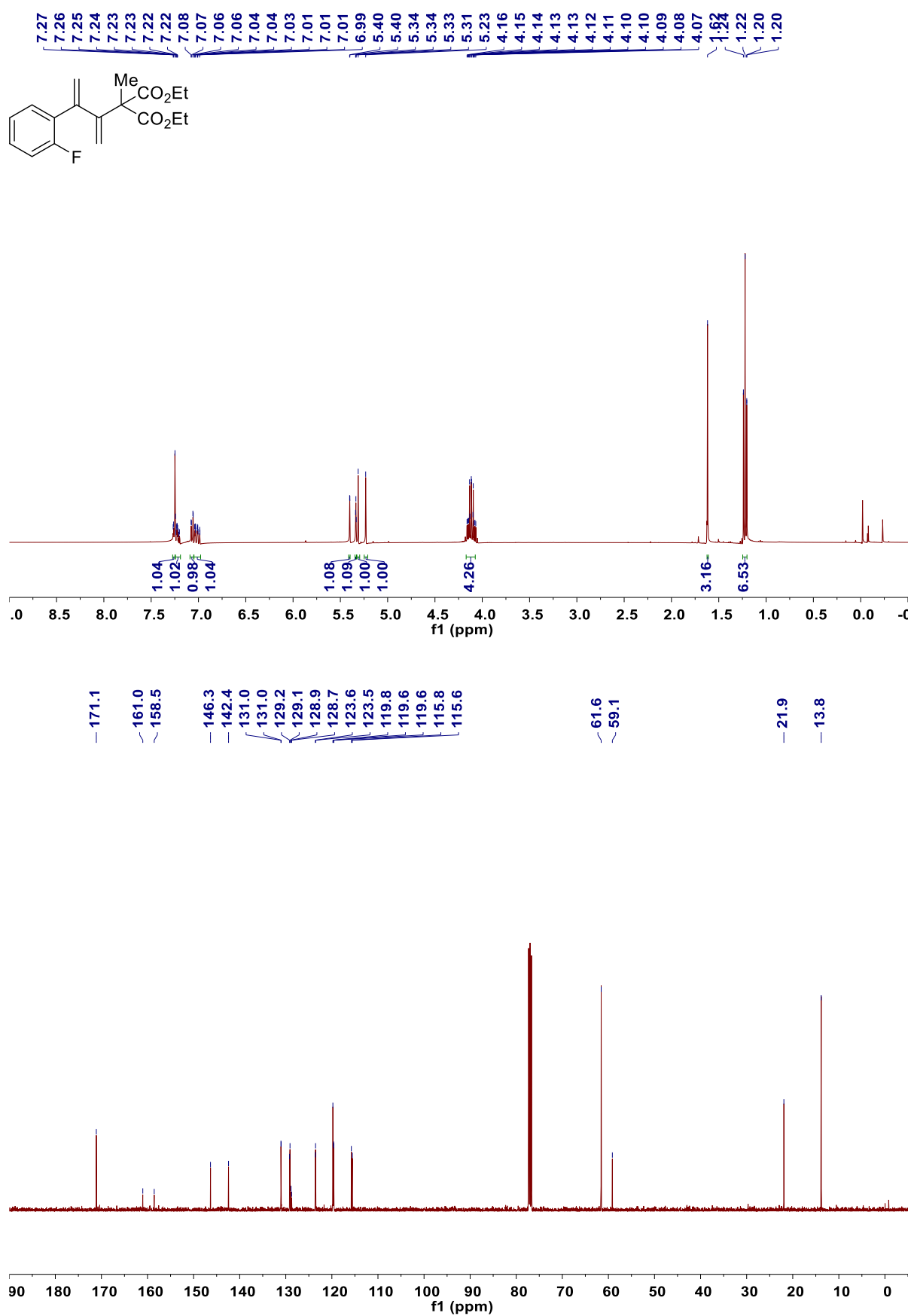
¹H and ¹³C NMR spectra for product 3ia (400 MHz, CDCl₃)

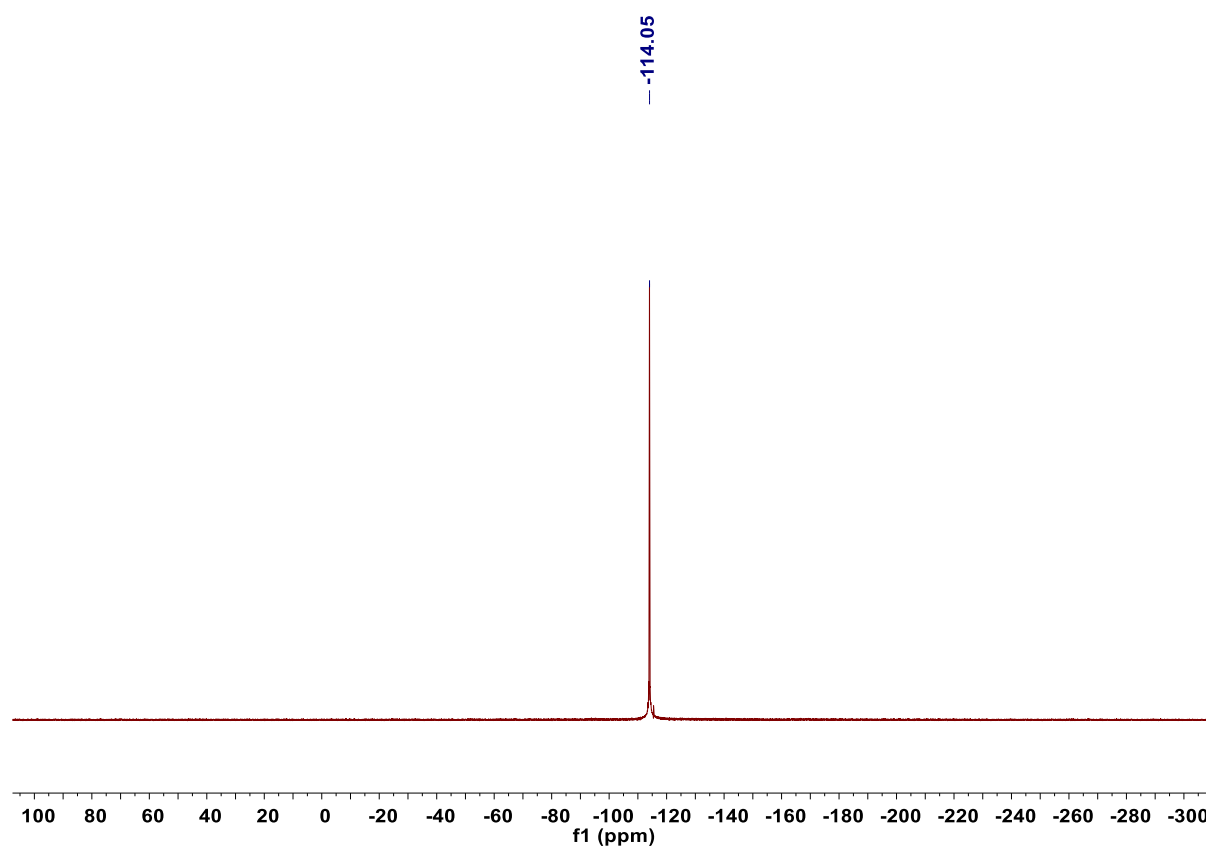
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¹H and ¹³C NMR spectra for product 3ja (400 MHz, CDCl₃)

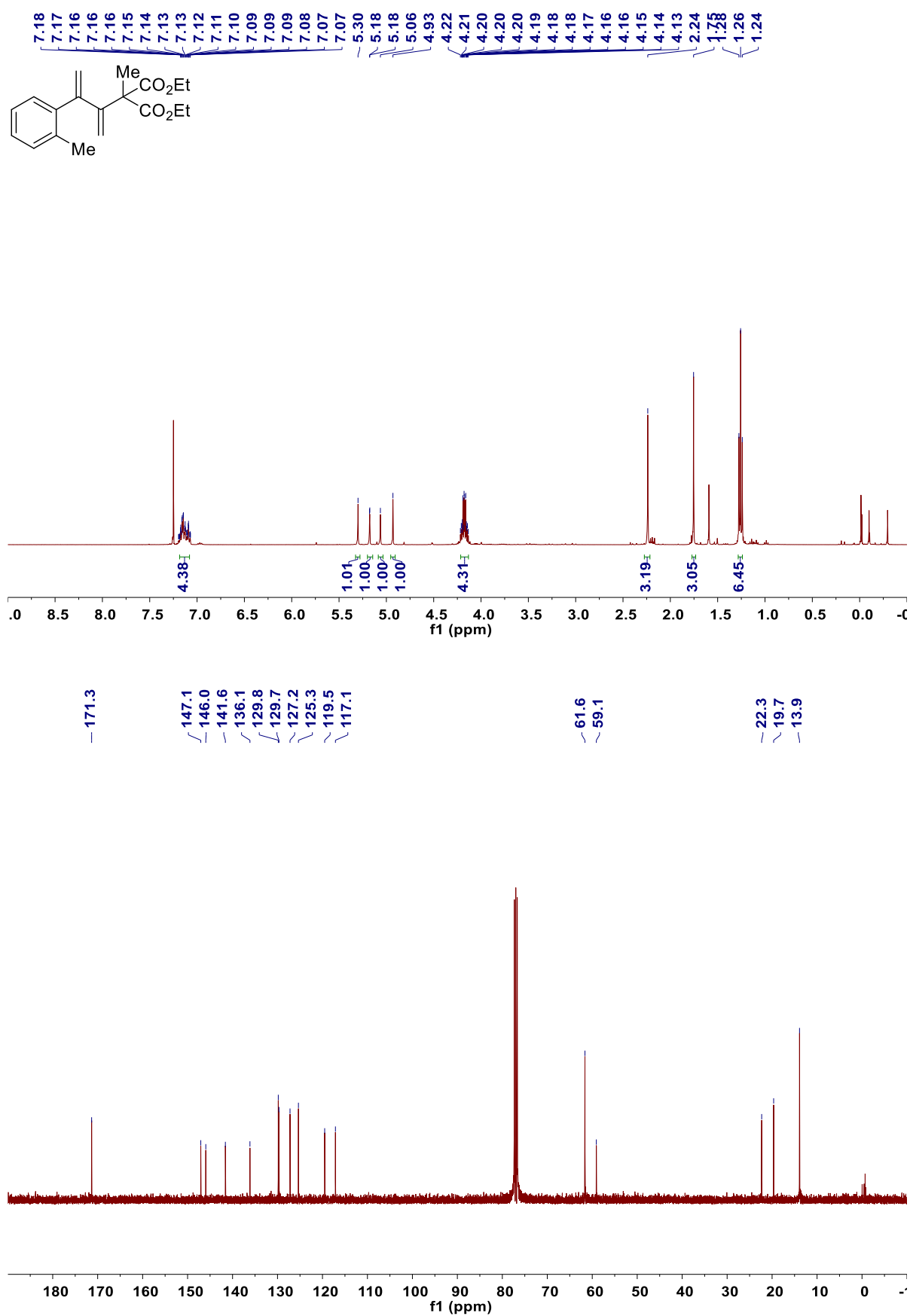
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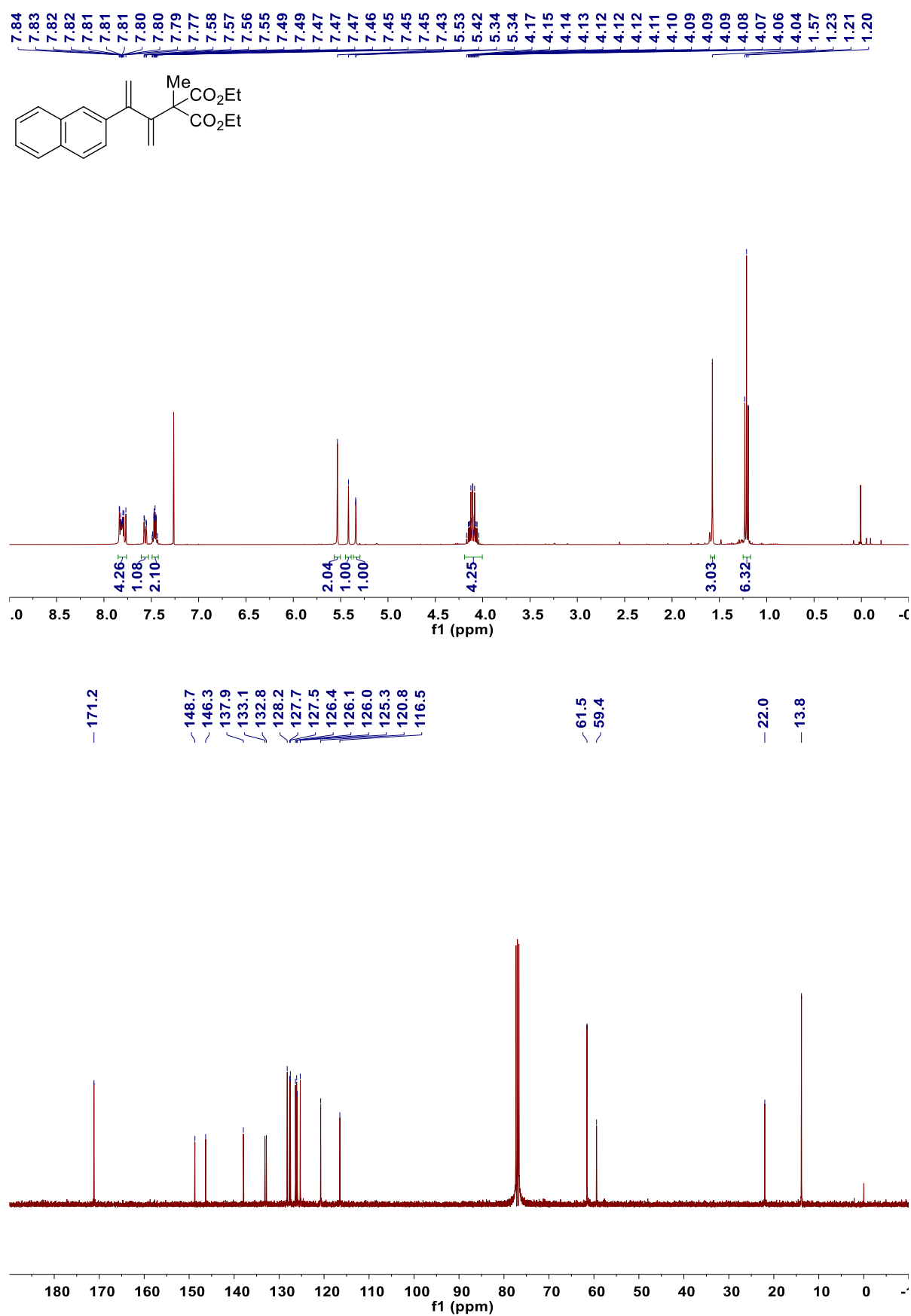




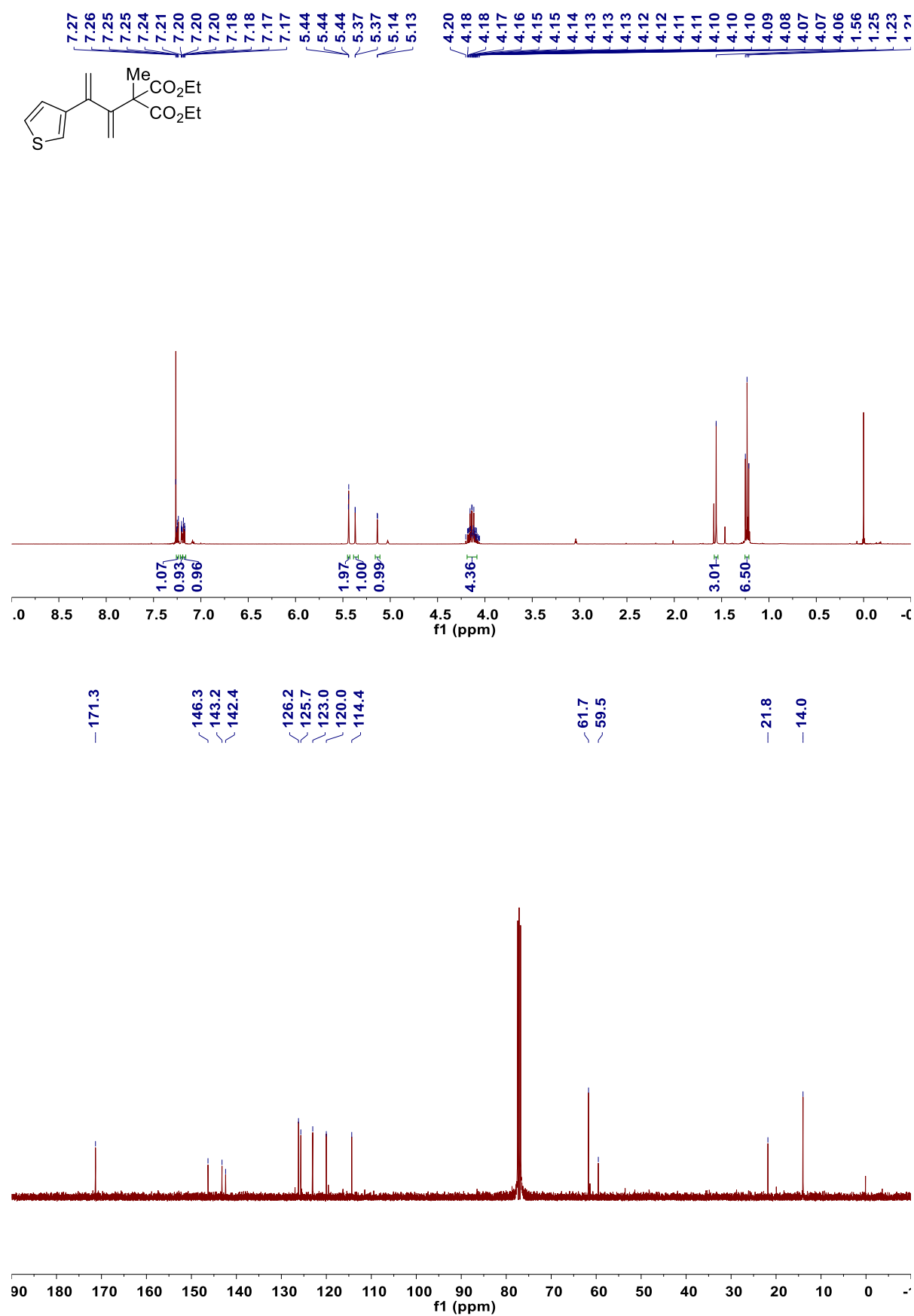
^1H , ^{13}C and ^{19}F NMR spectra for product 3ka (400 MHz, CDCl_3)

SUPPORTING INFORMATION

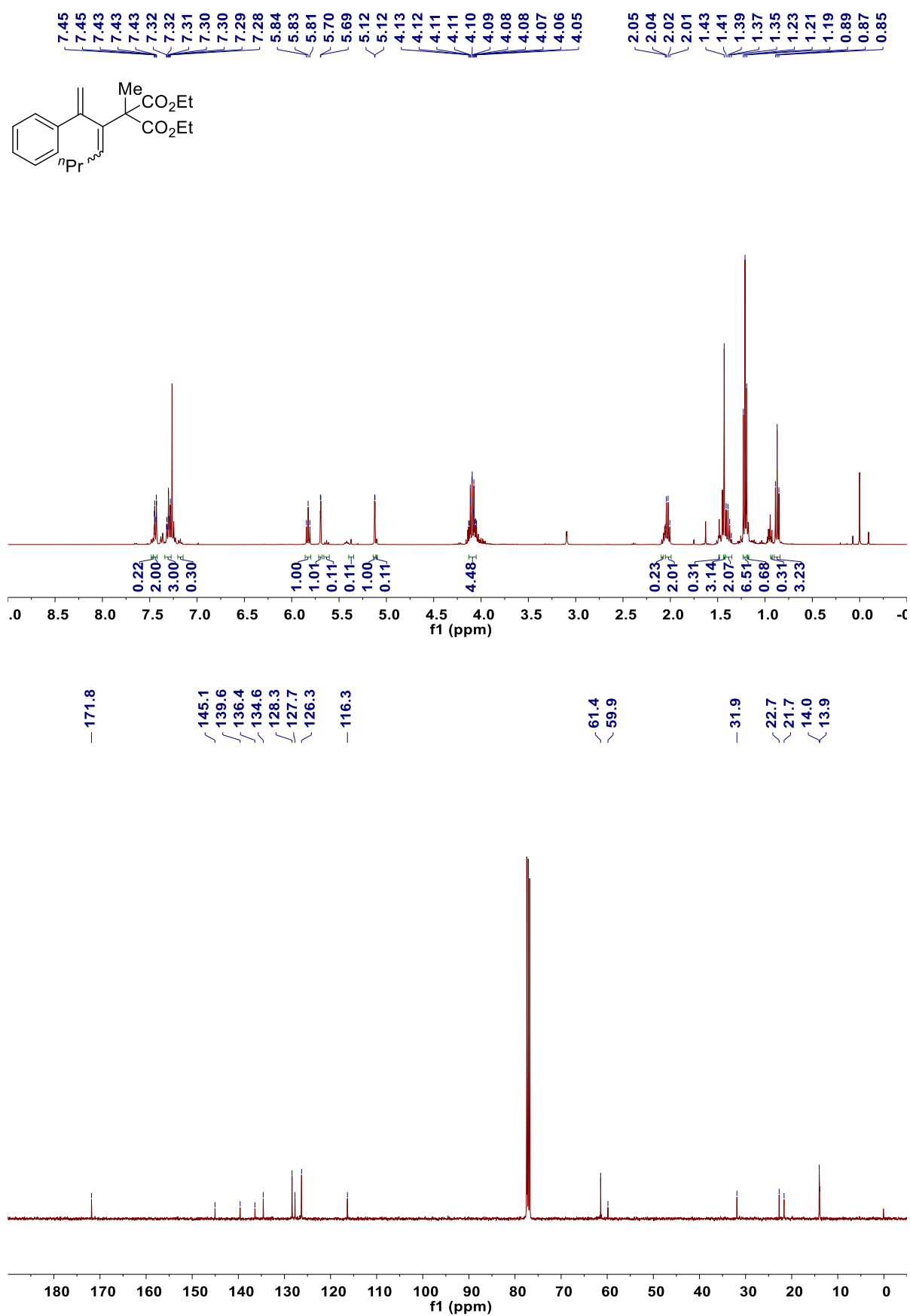




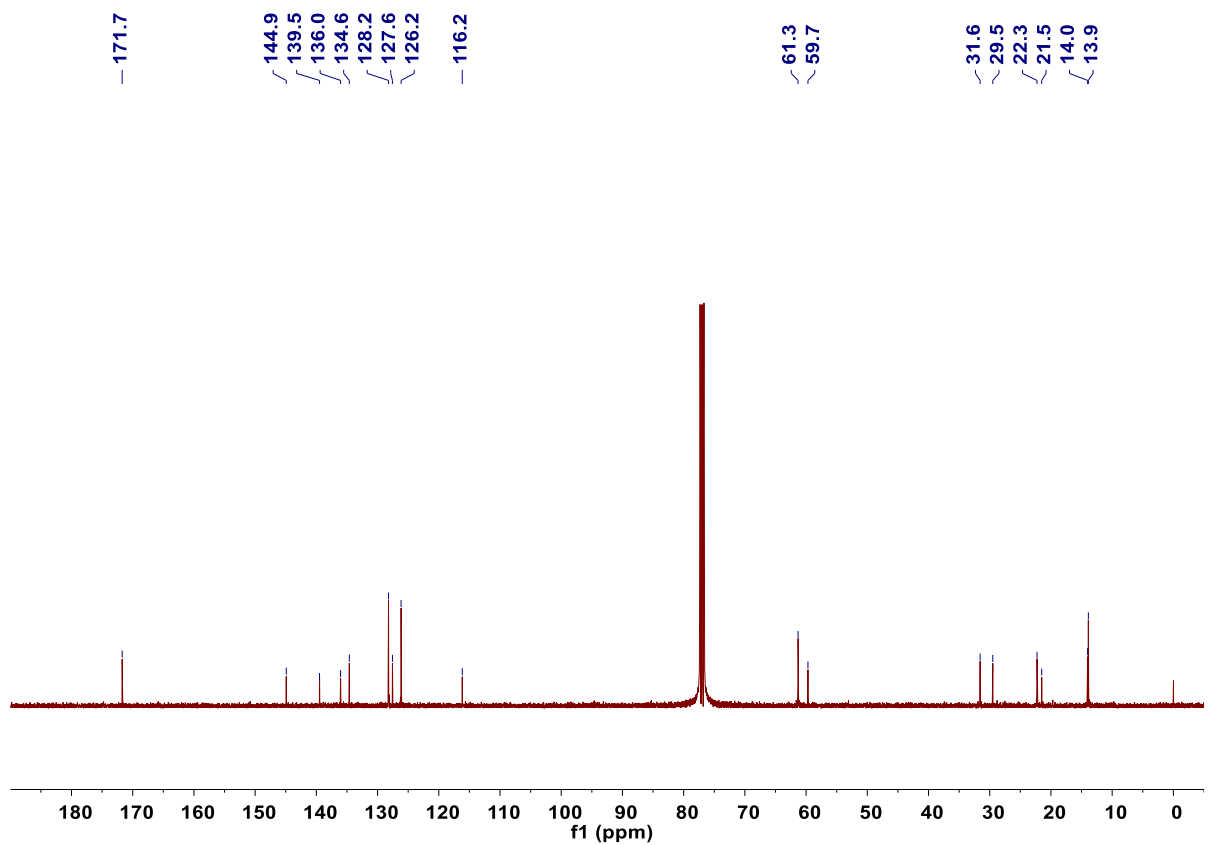
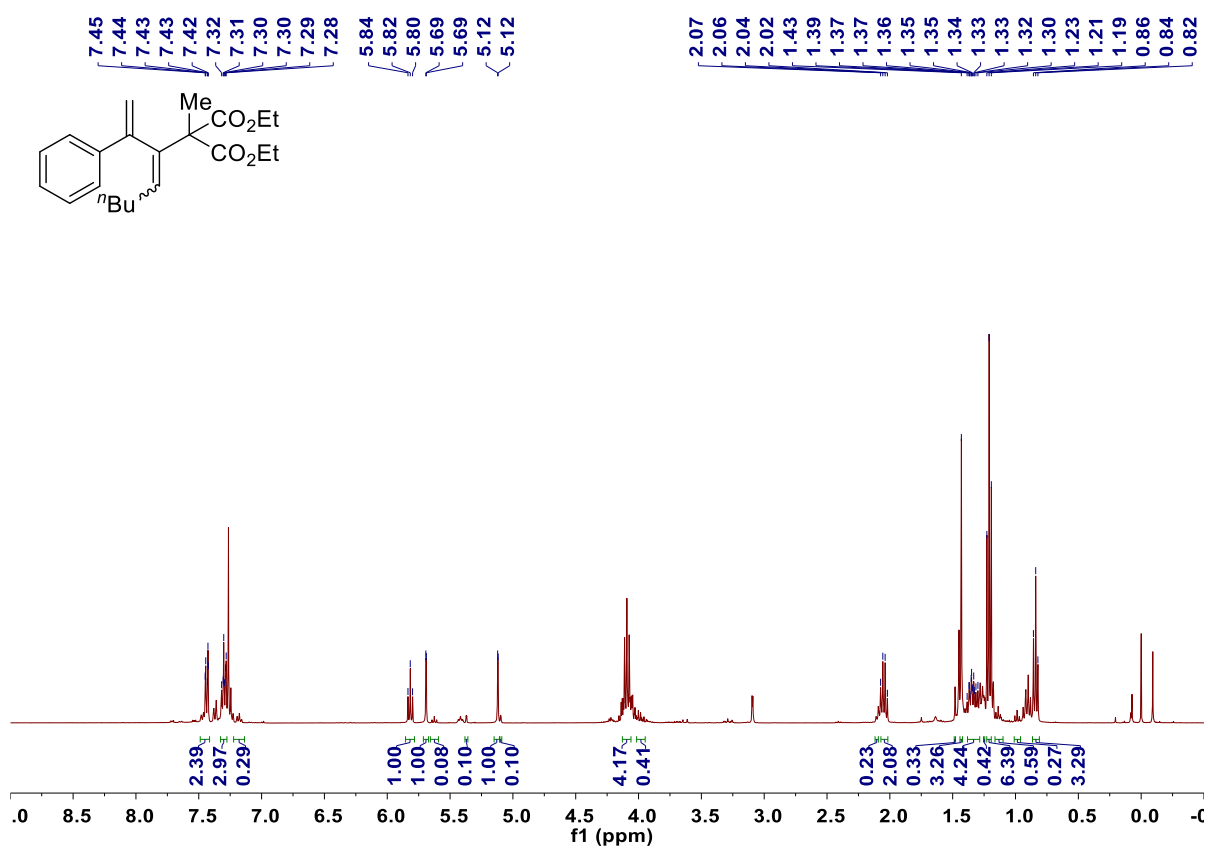
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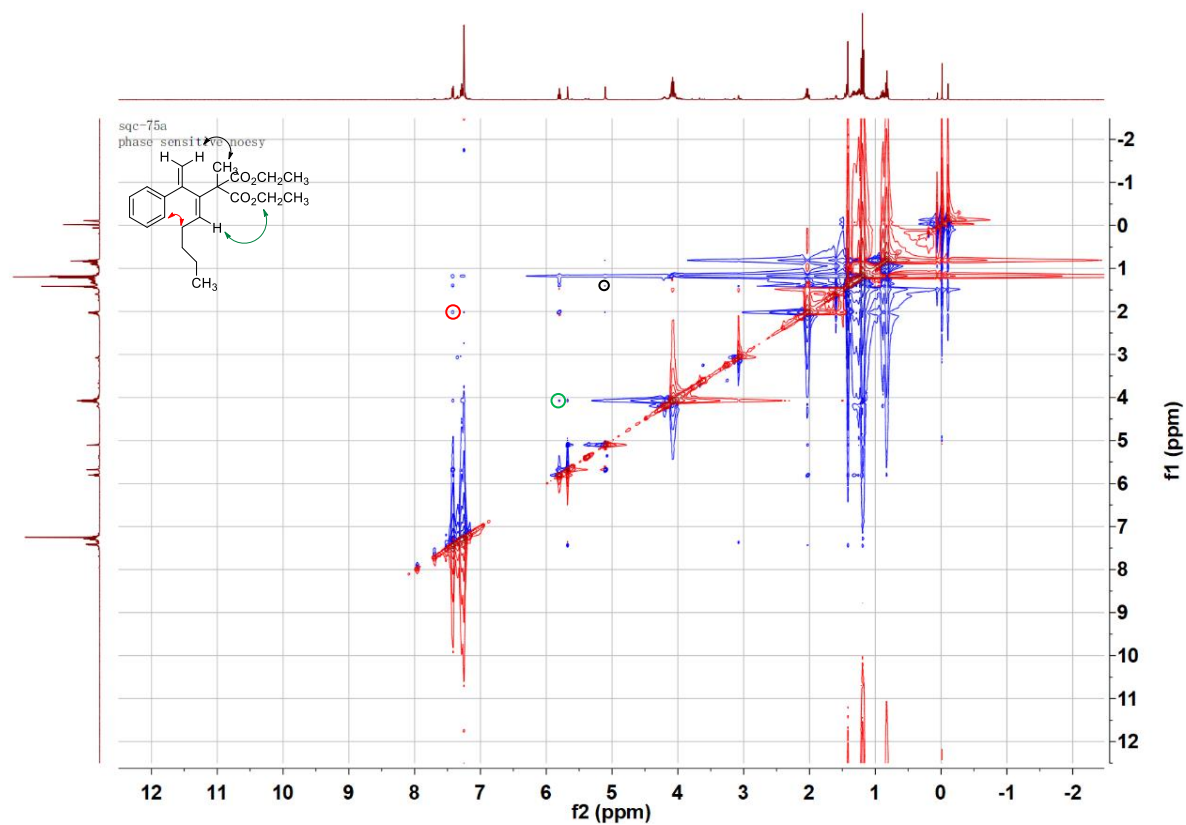


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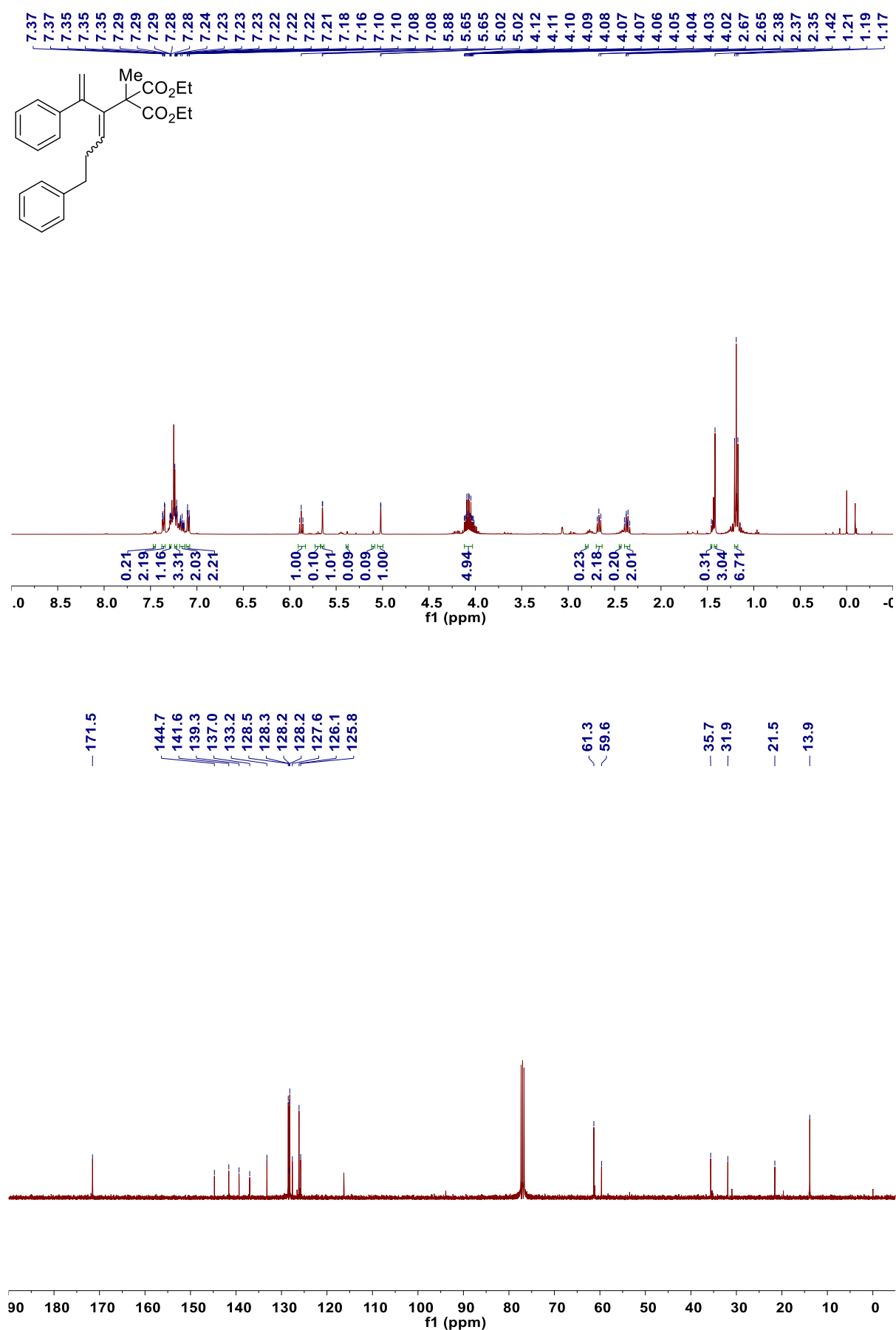


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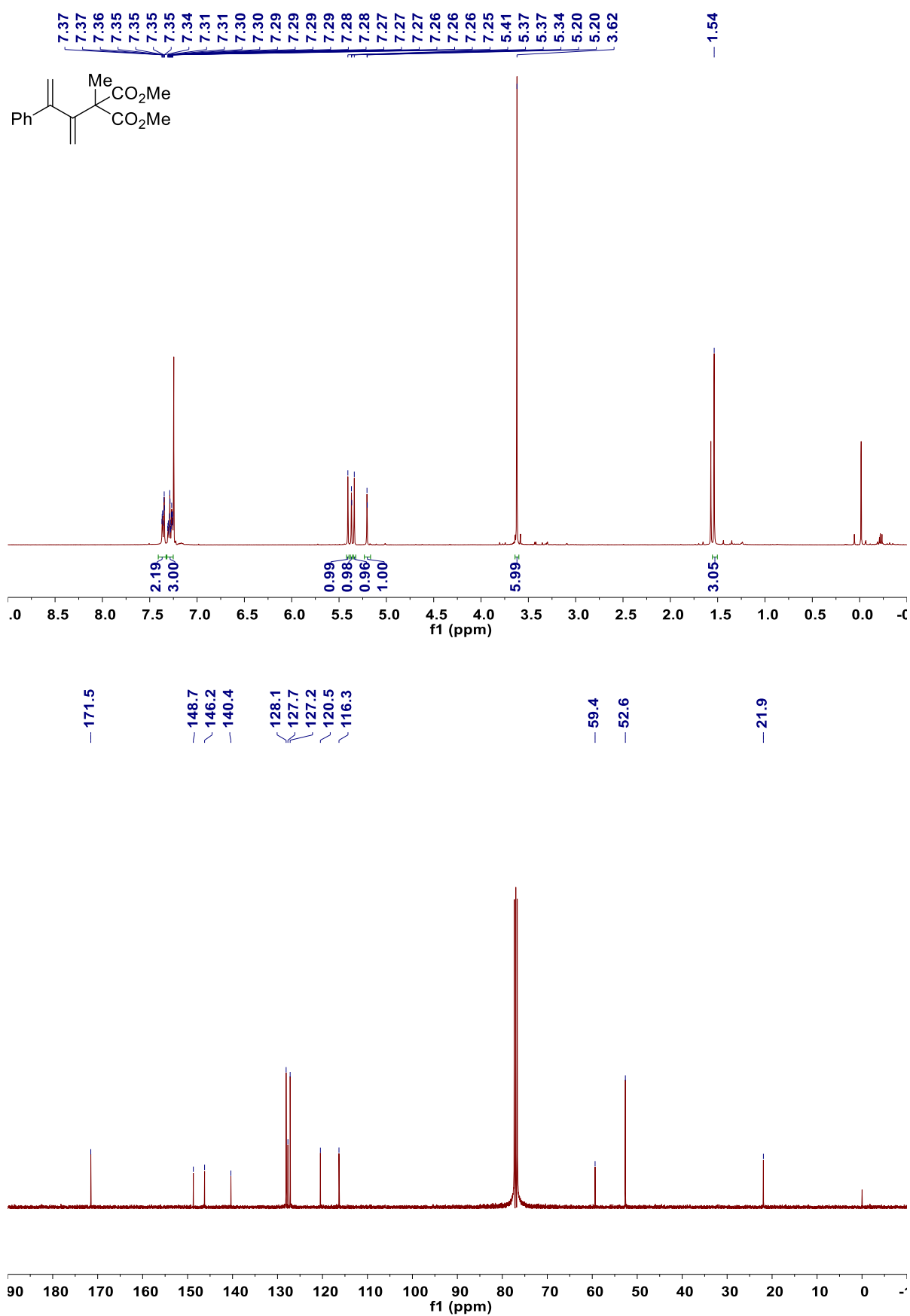




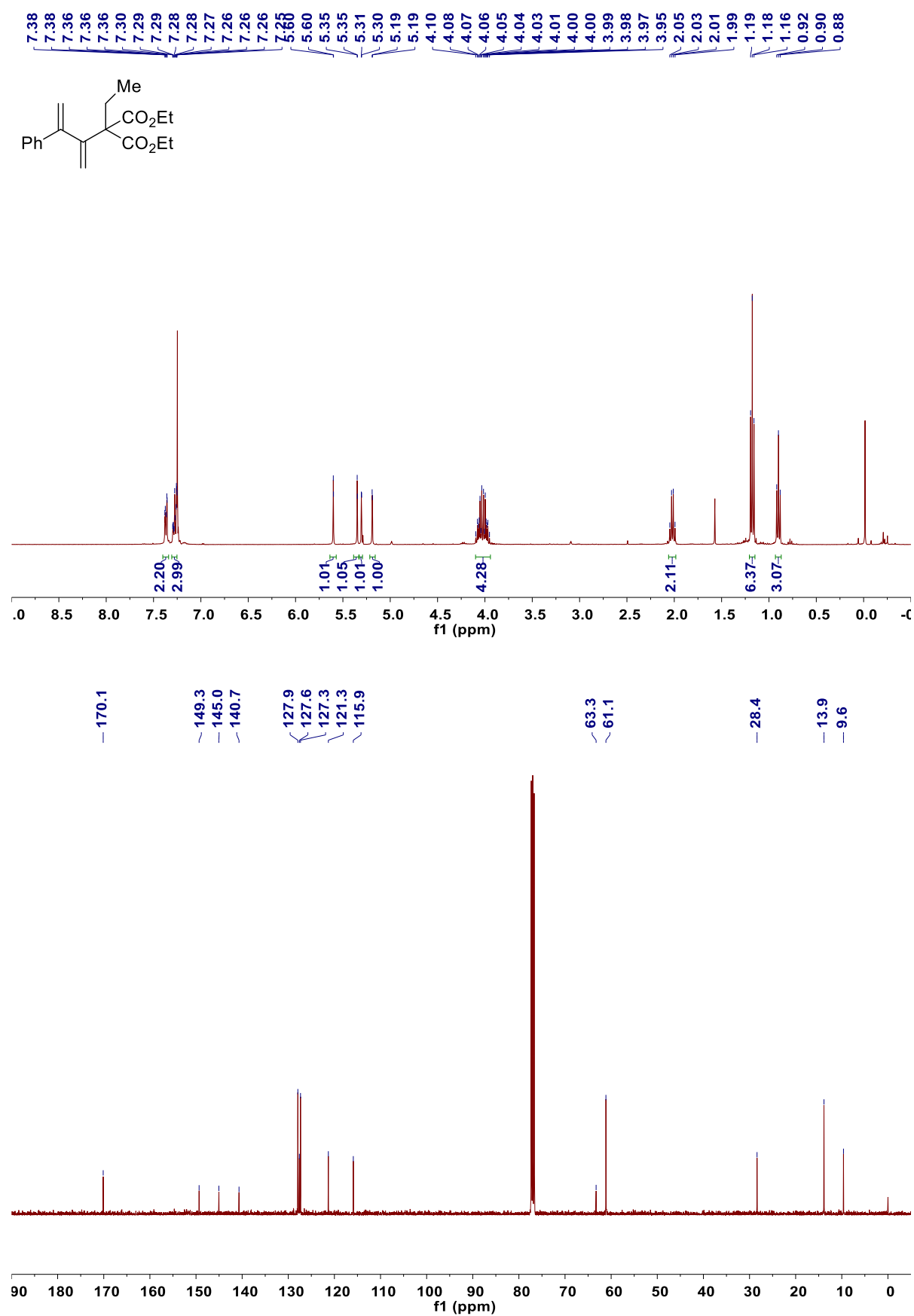
^1H , ^{13}C NMR and NOESY spectra for product 3pa (400 MHz, CDCl_3)

 ^1H and ^{13}C NMR spectra for product 3qa (400 MHz, CDCl_3)

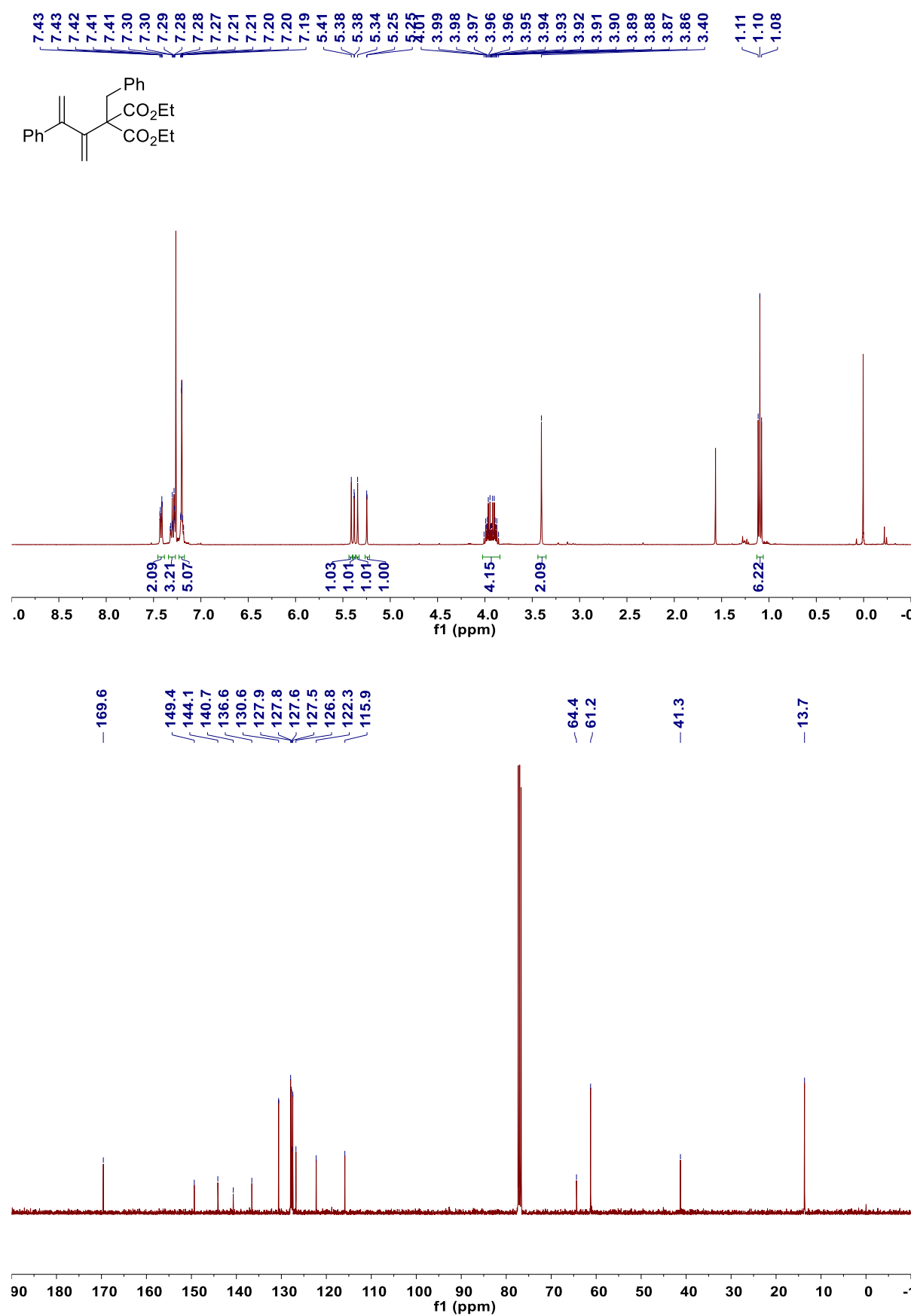
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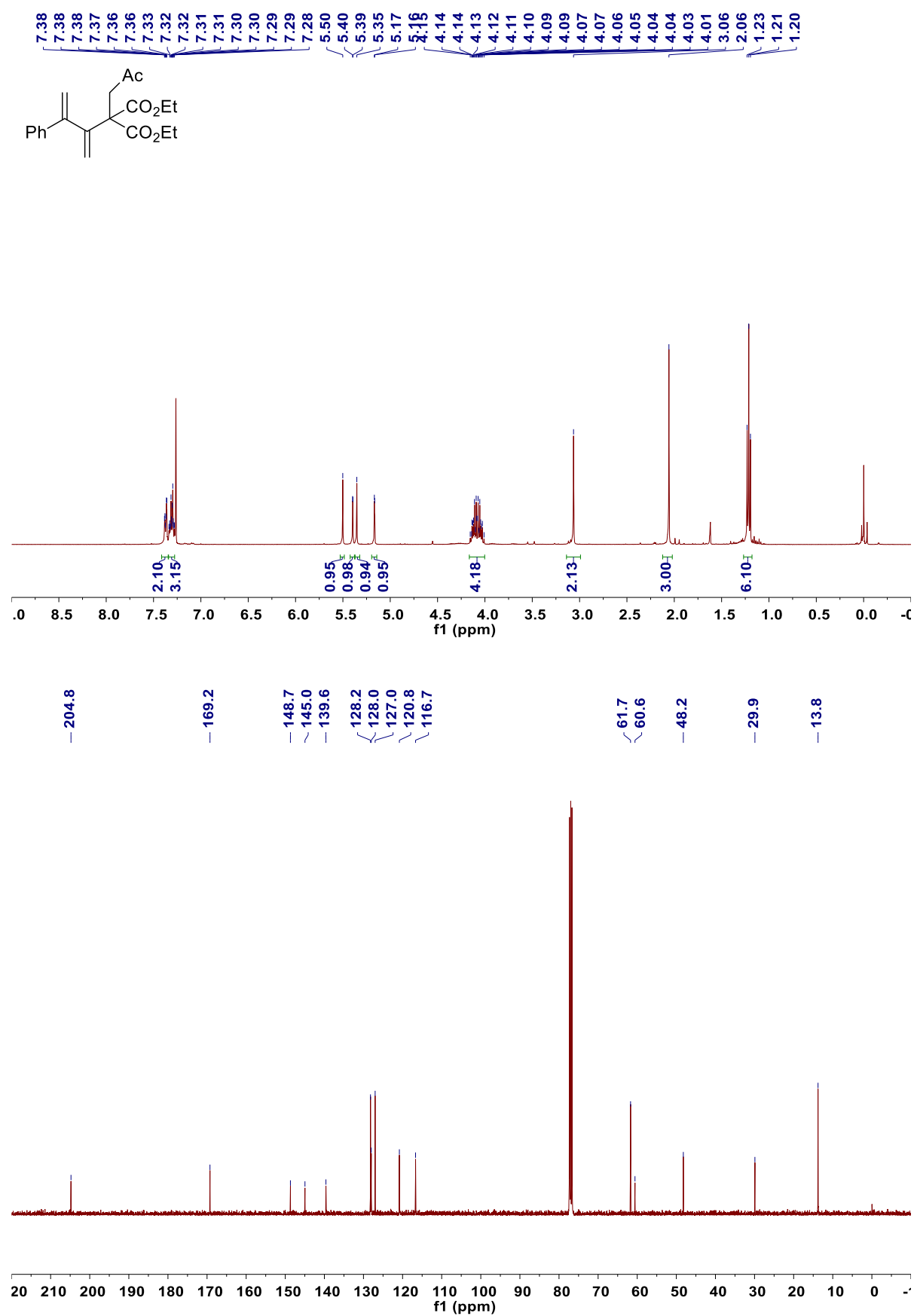
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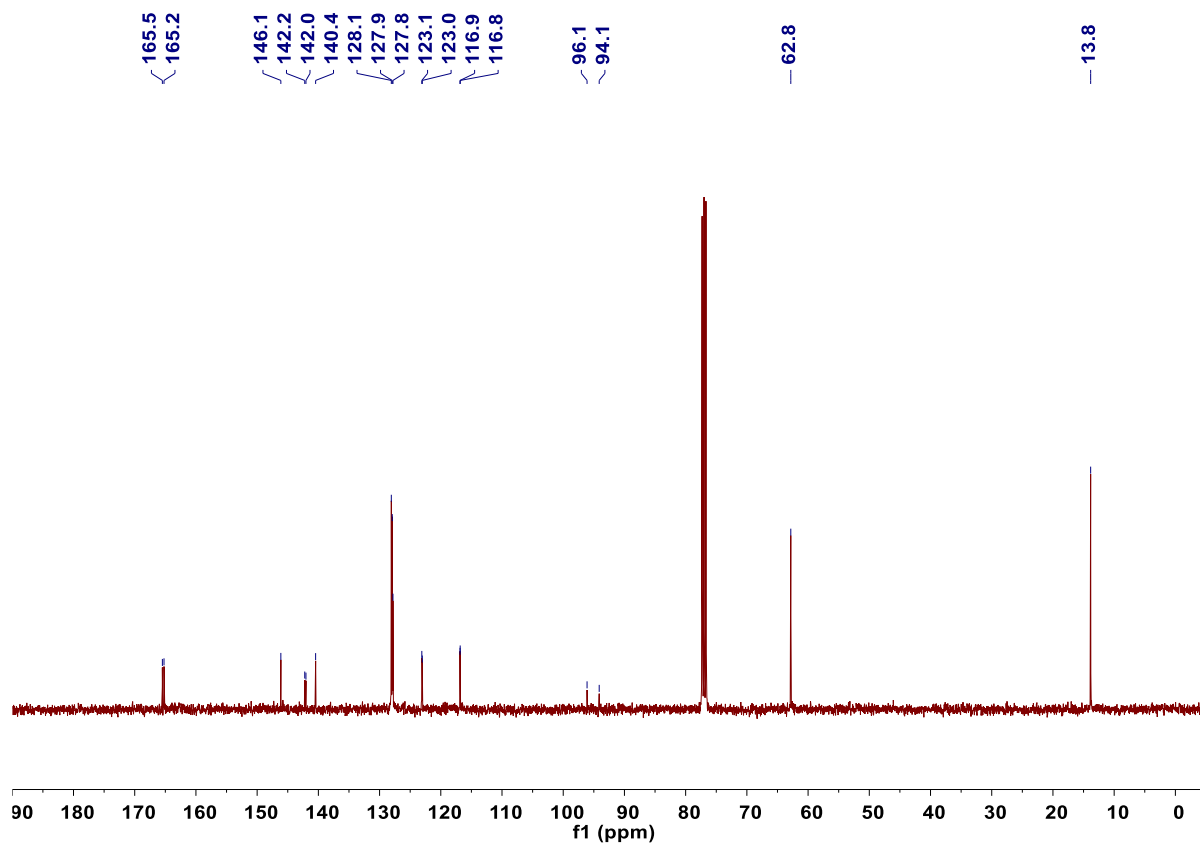
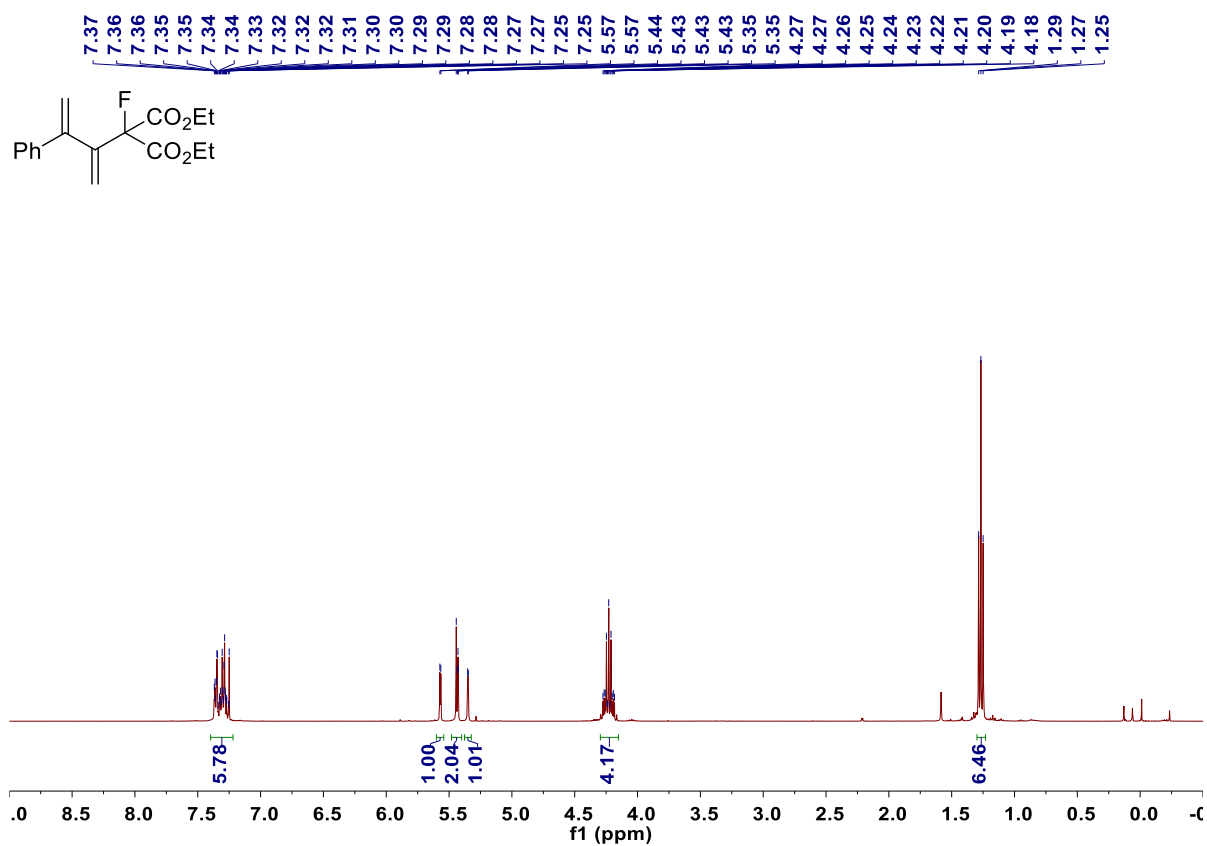
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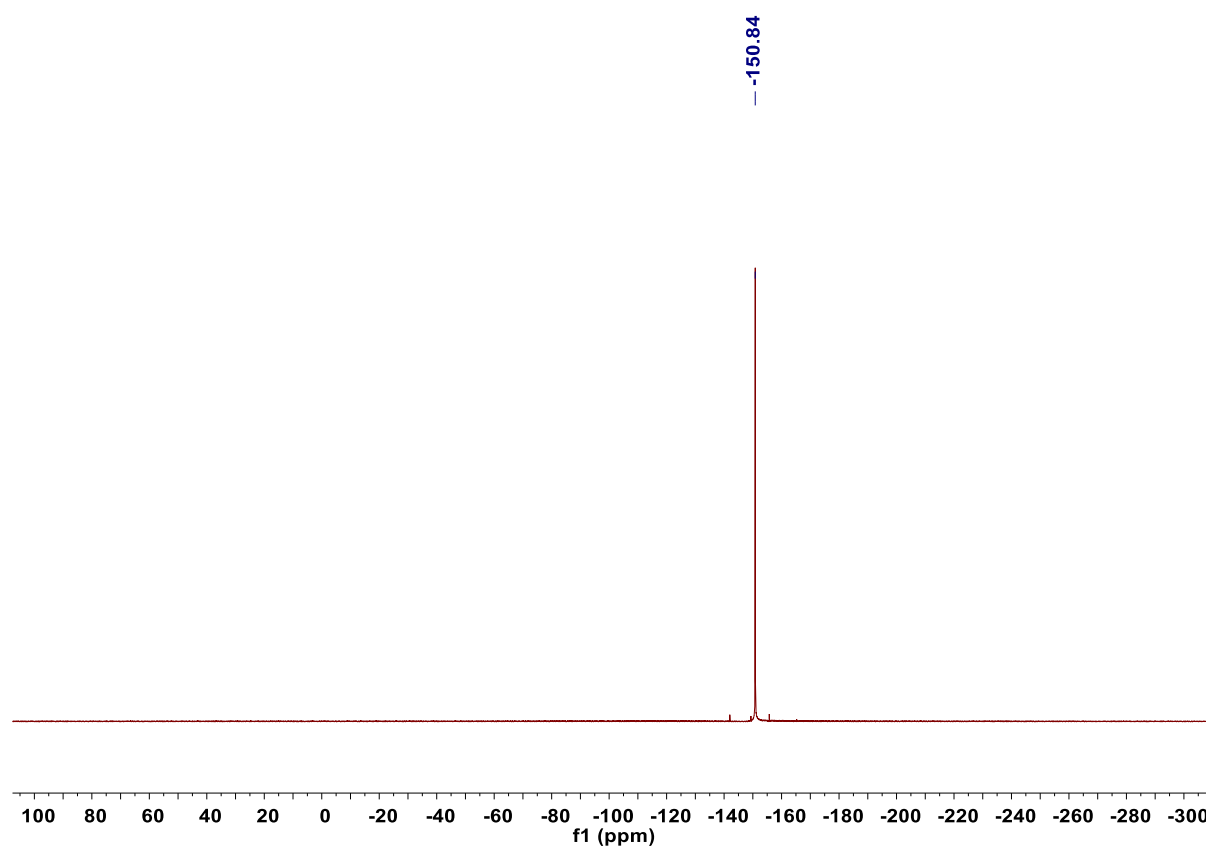


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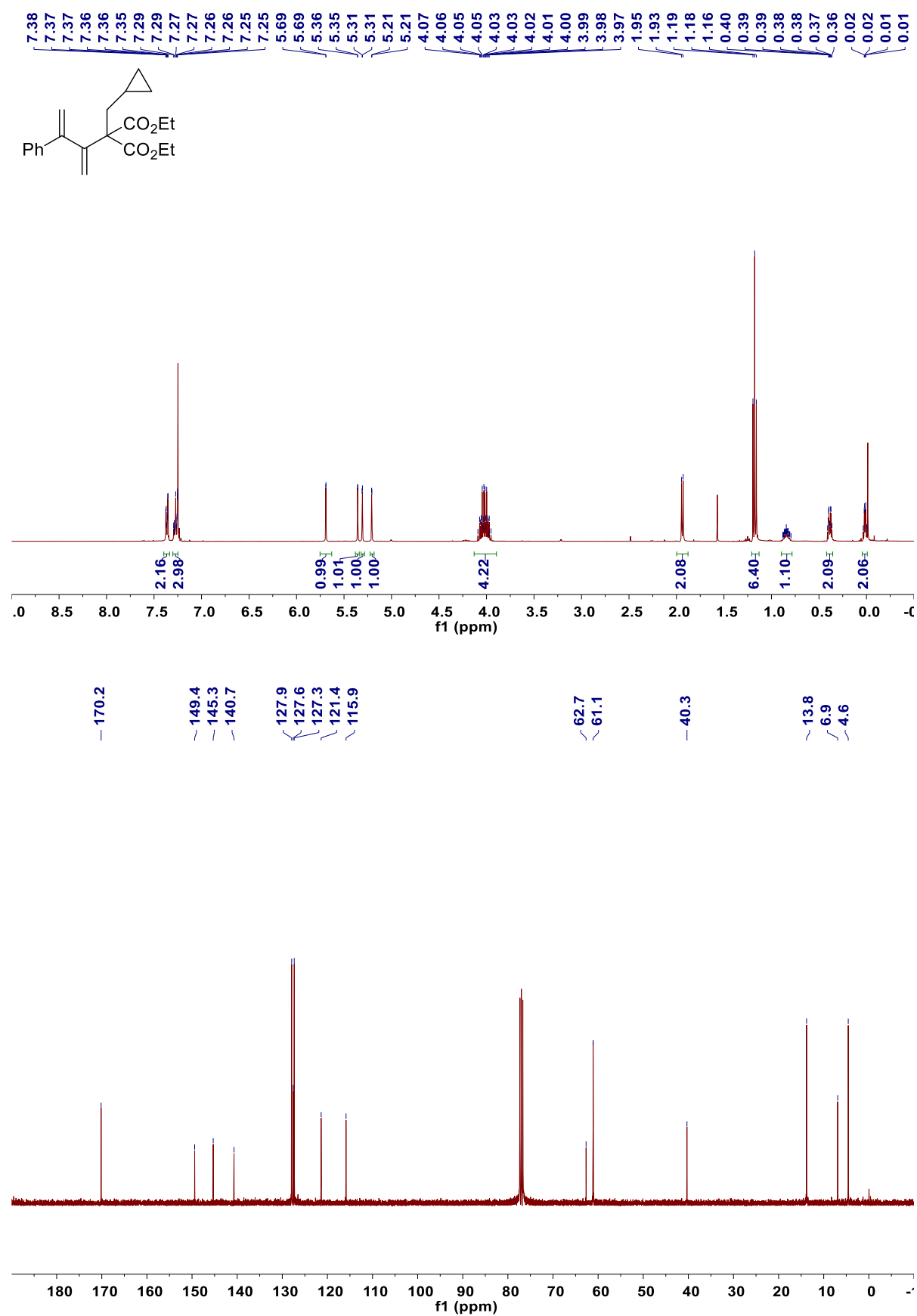
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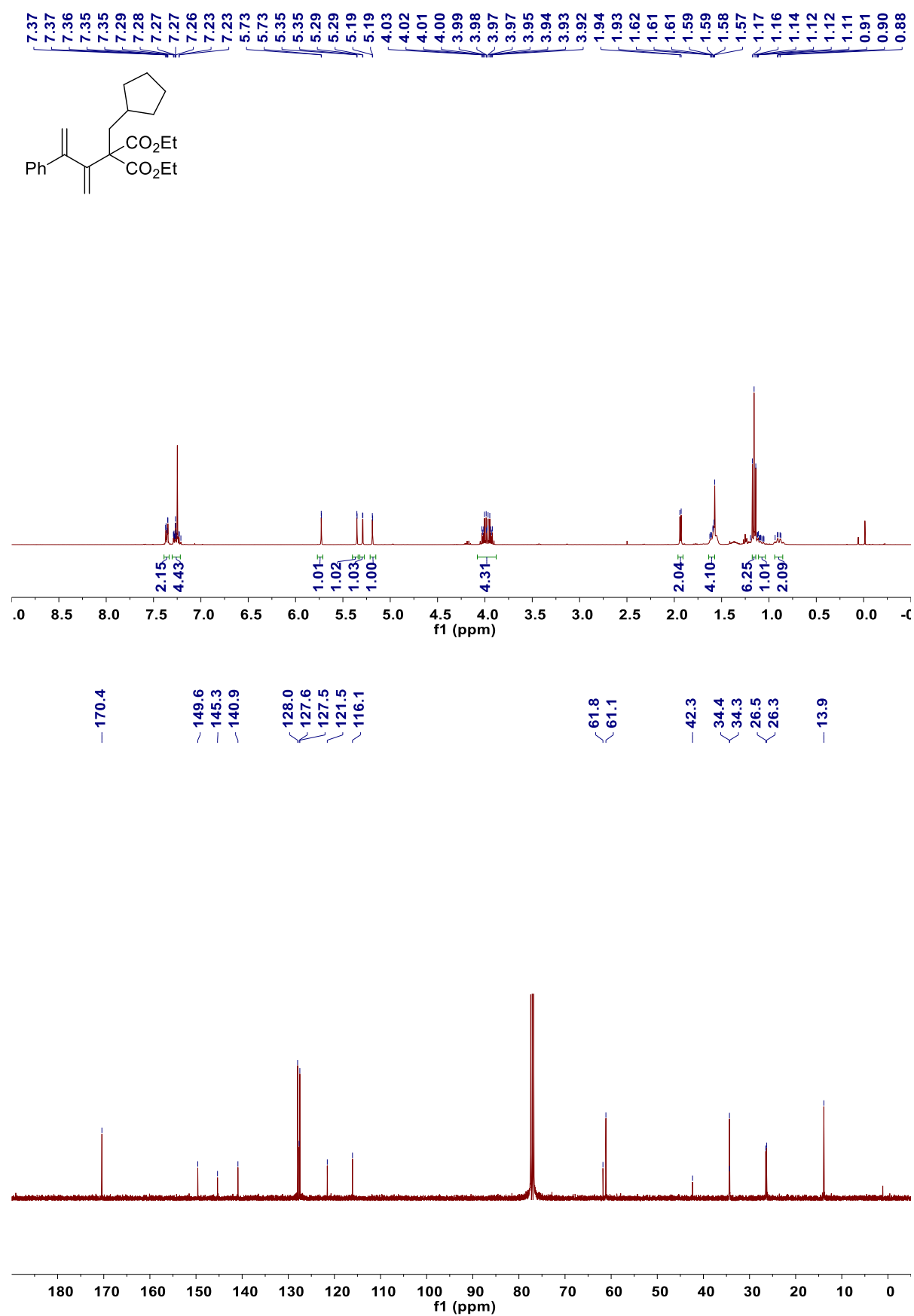


^1H , ^{13}C and ^{19}F NMR spectra for product 3af (400 MHz, CDCl_3)

SUPPORTING INFORMATION

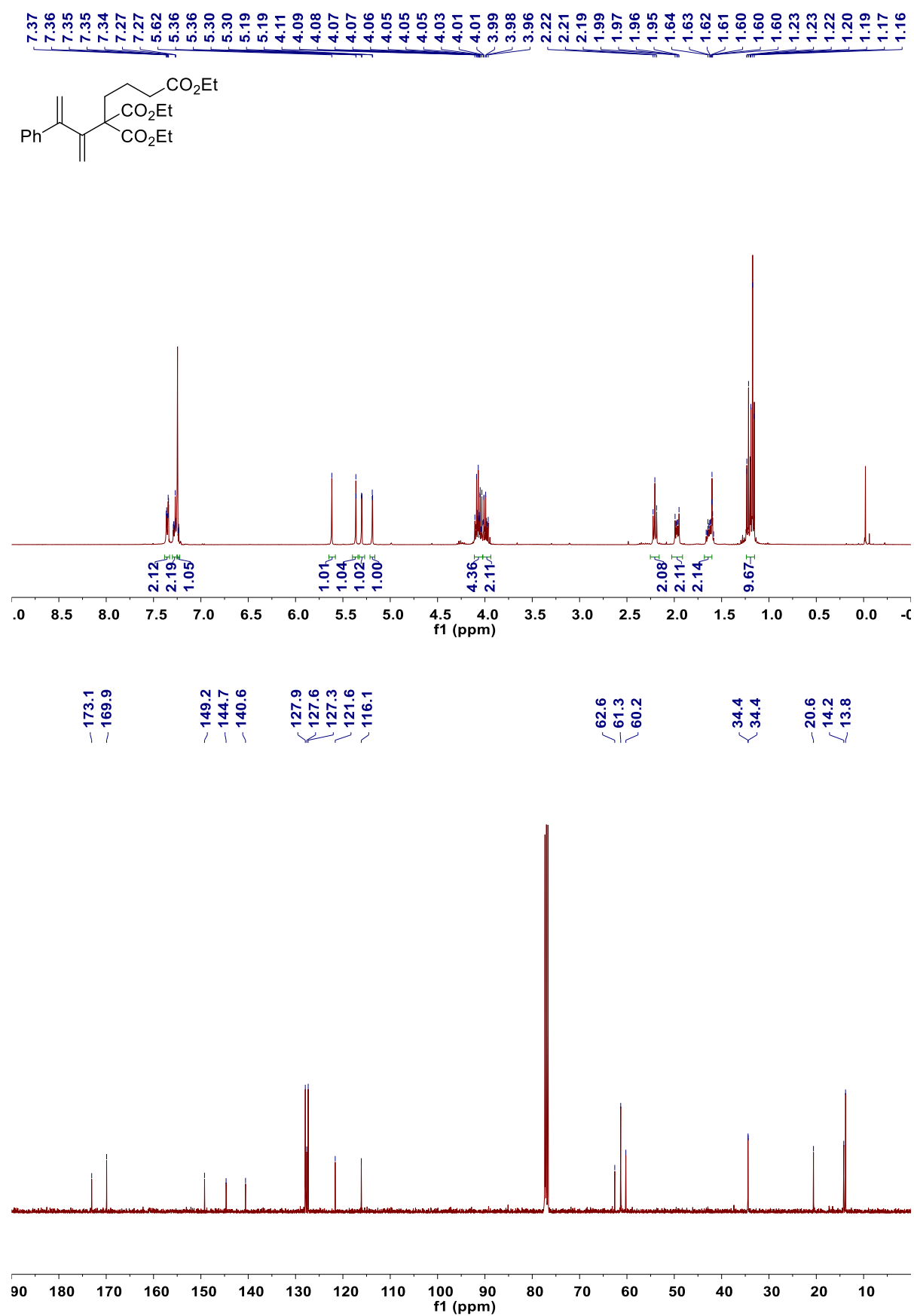


¹H and ¹³C NMR spectra for product 3ag (400 MHz, CDCl₃)



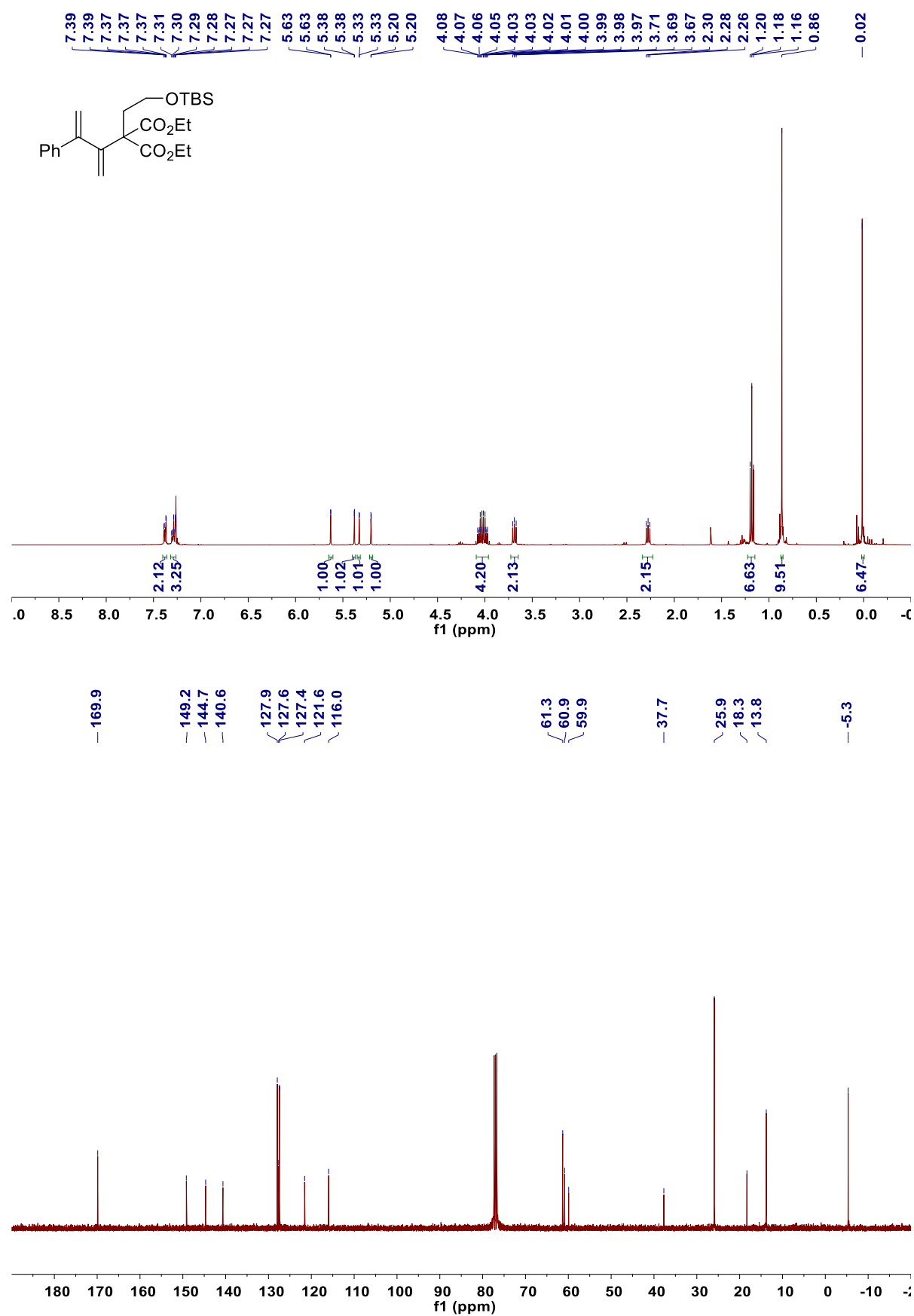
¹H and ¹³C NMR spectra for product 3ah (400 MHz, CDCl₃)

SUPPORTING INFORMATION

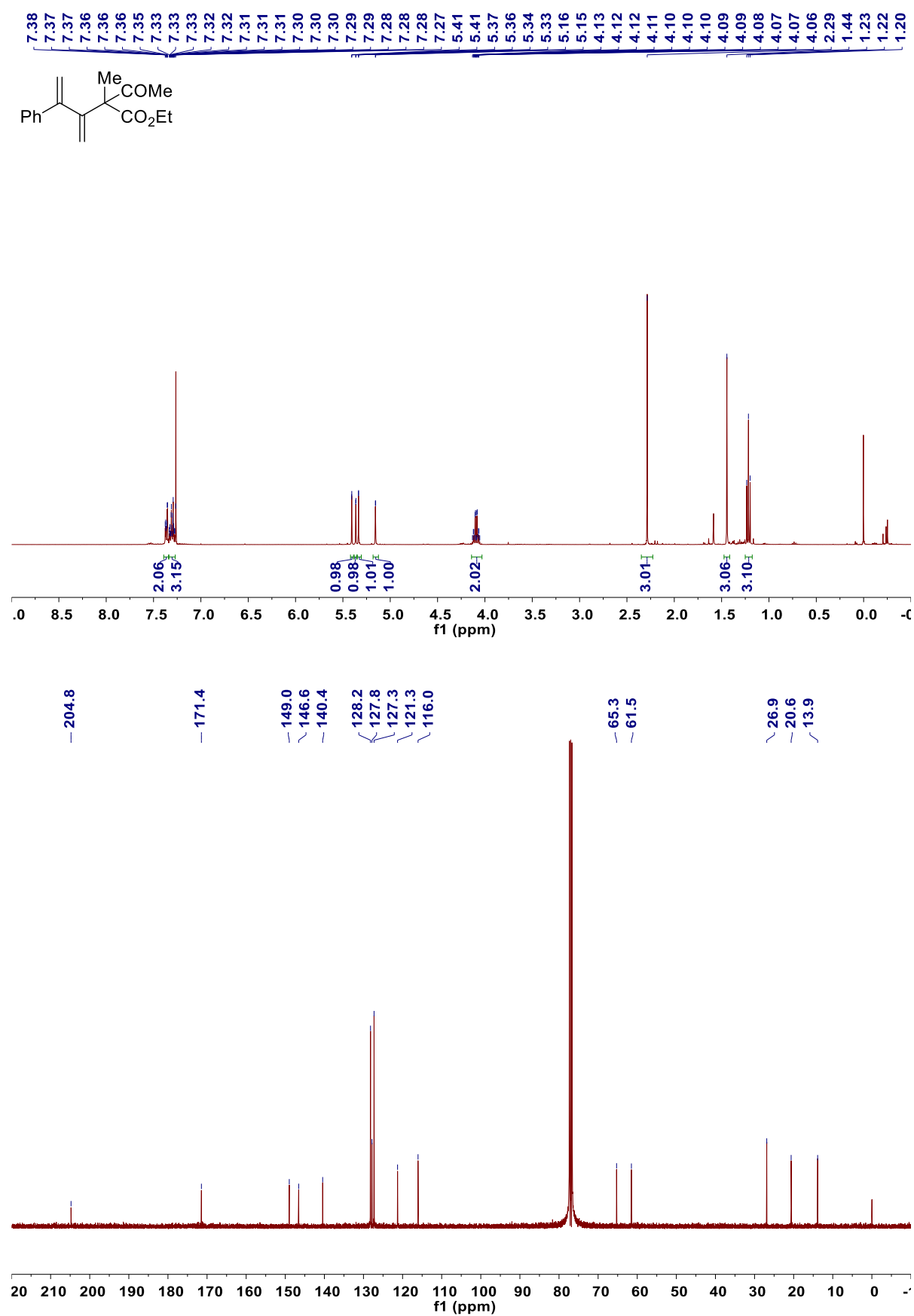


¹H and ¹³C NMR spectra for product 3ai (400 MHz, CDCl₃)

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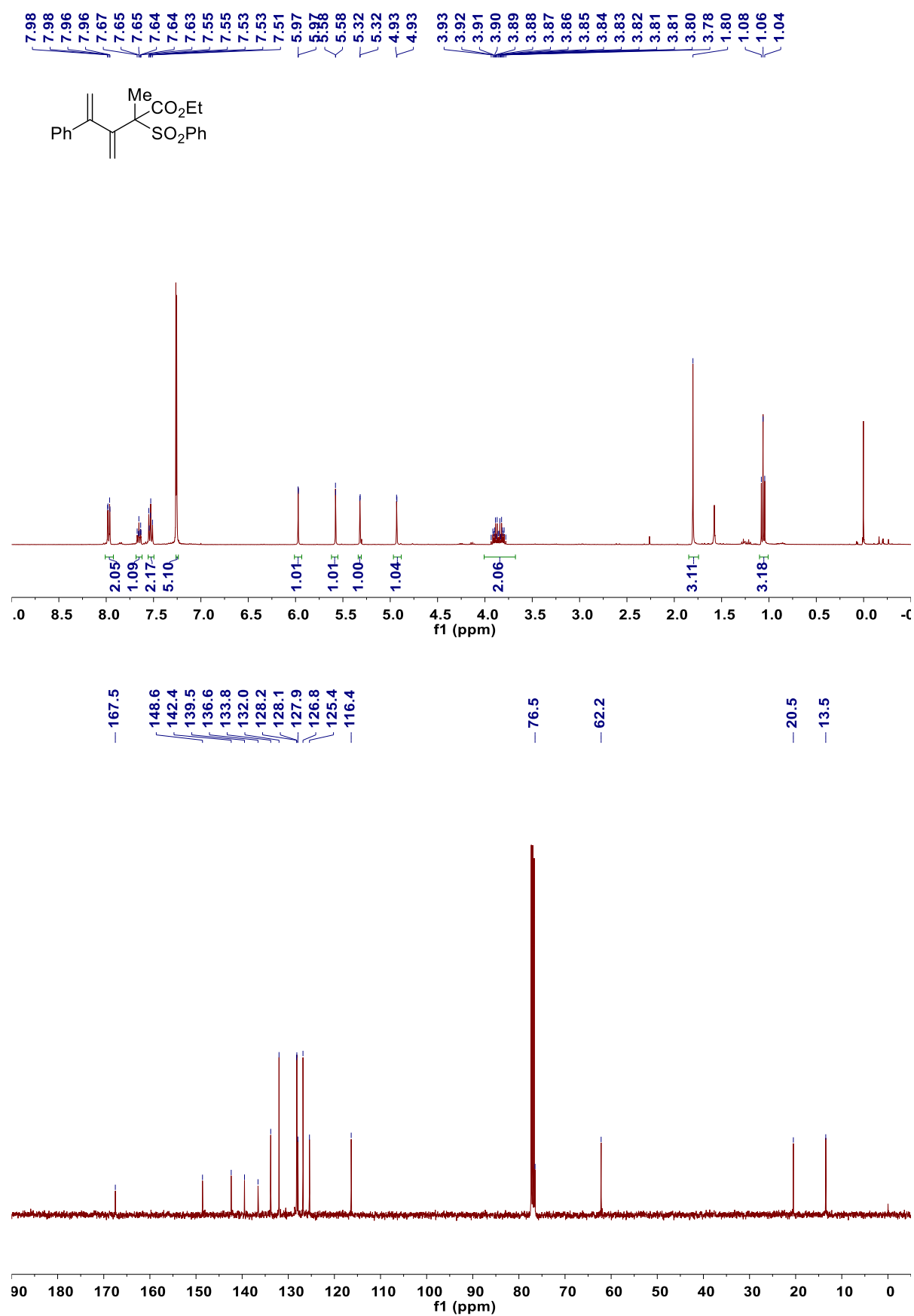


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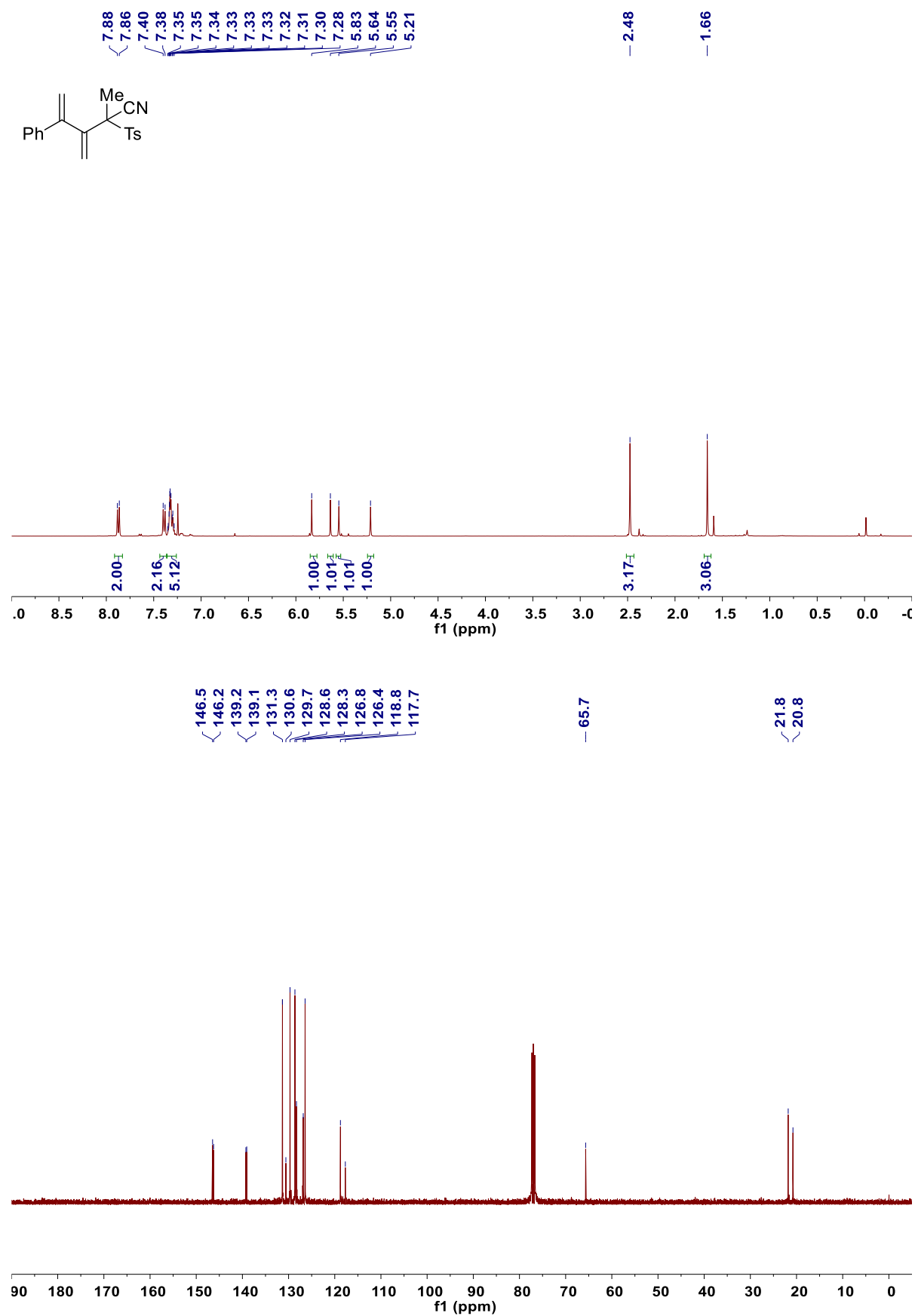
[illegible]

S82



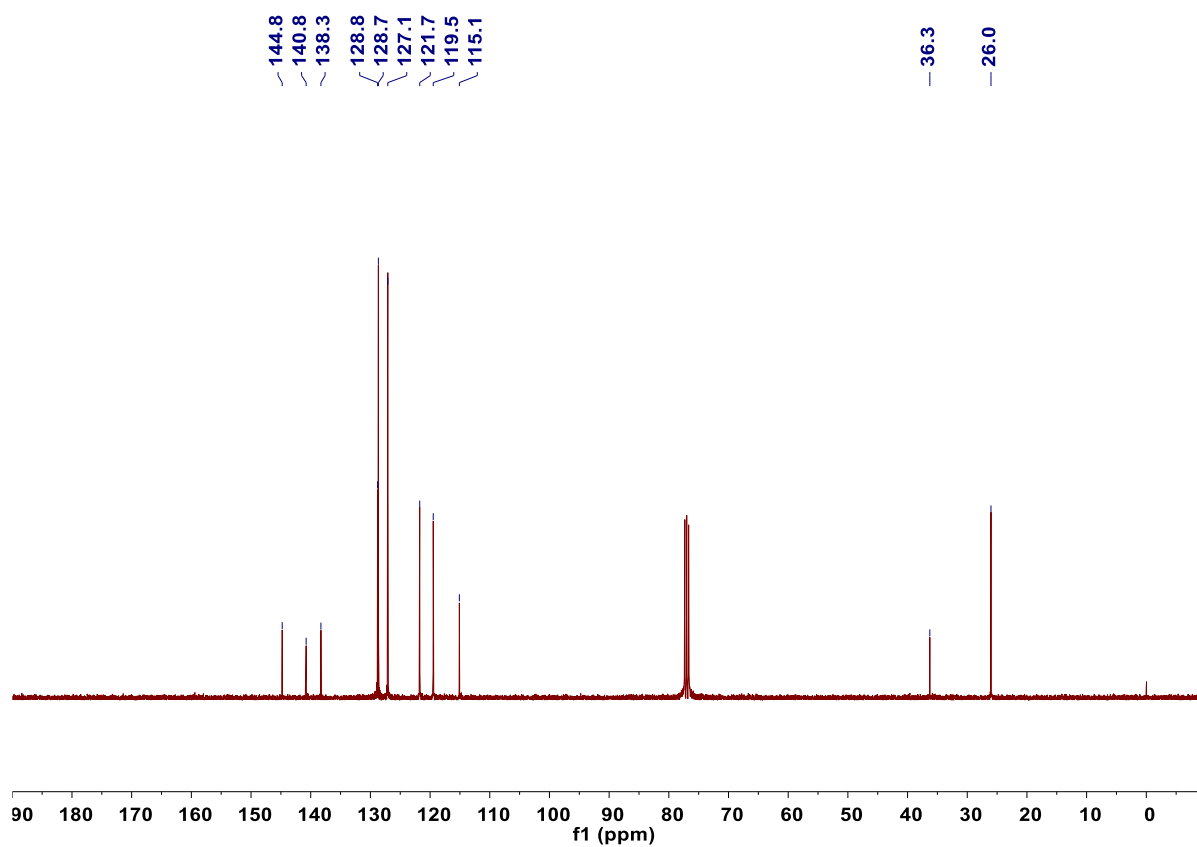
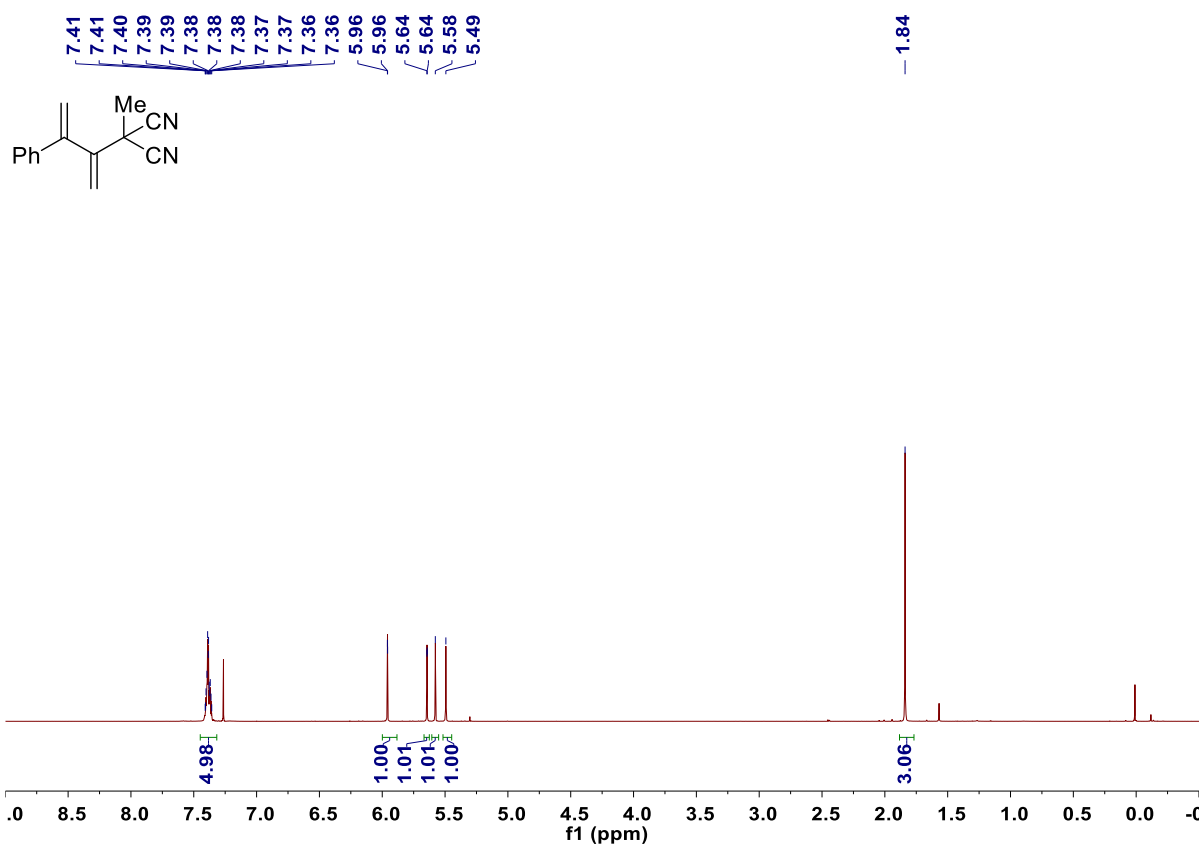
¹H and ¹³C NMR spectra for product 3am (400 MHz, CDCl₃)

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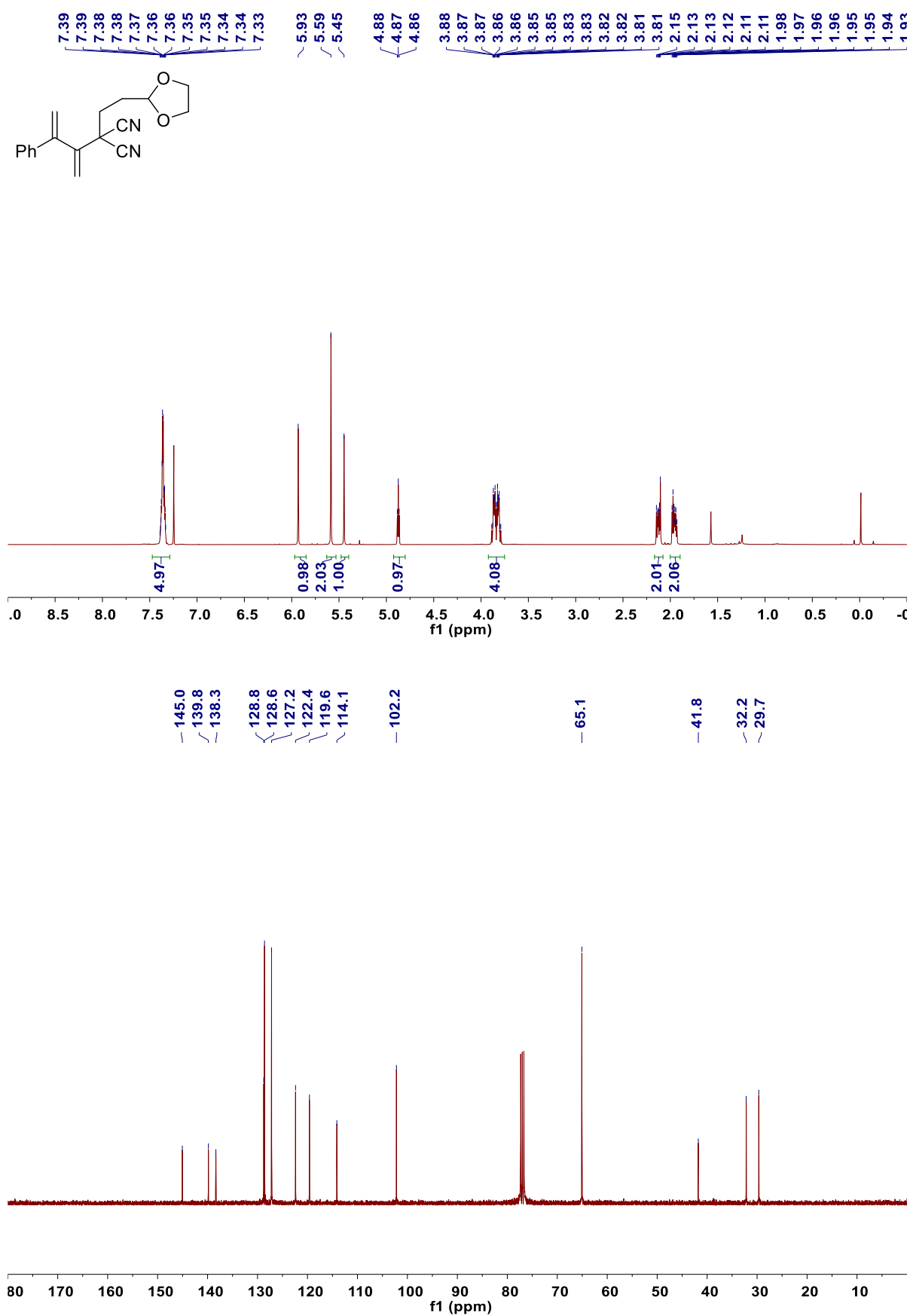
¹H and ¹³C NMR spectra for product 3an (400 MHz, CDCl₃)

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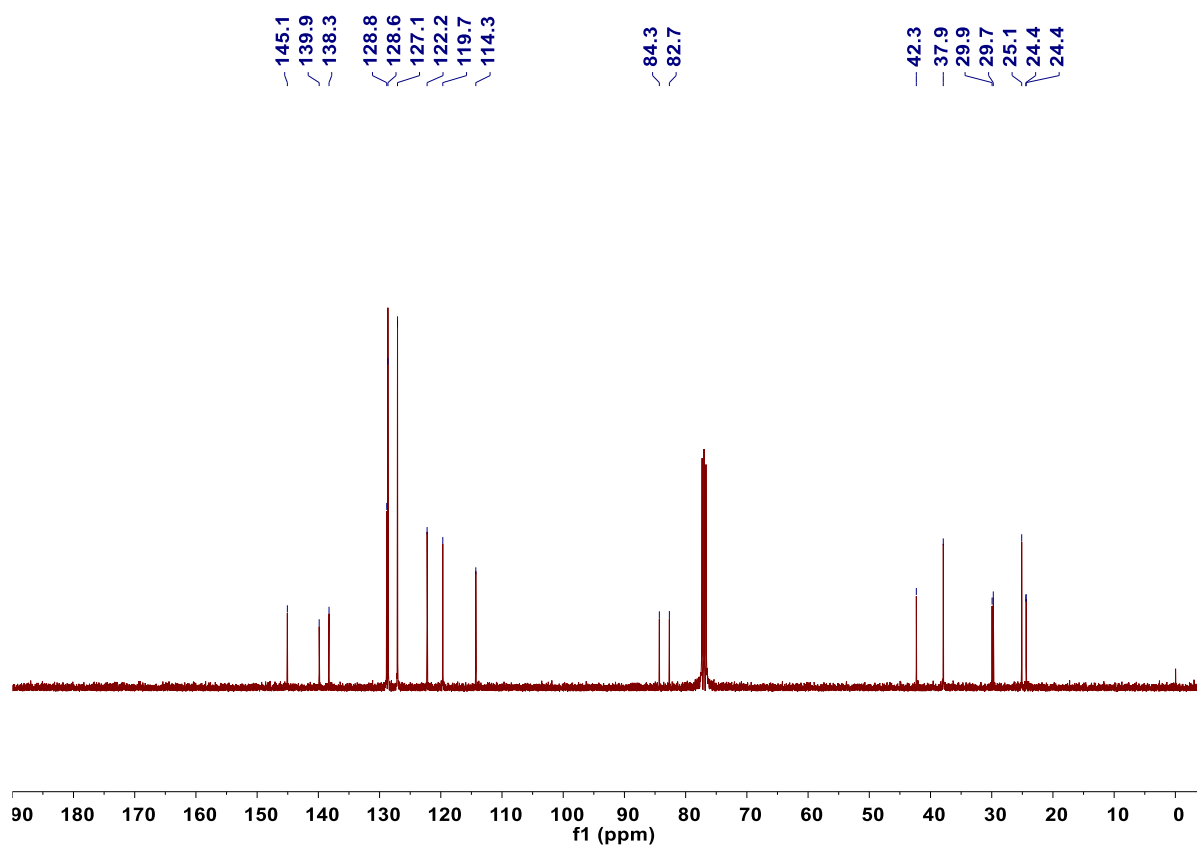
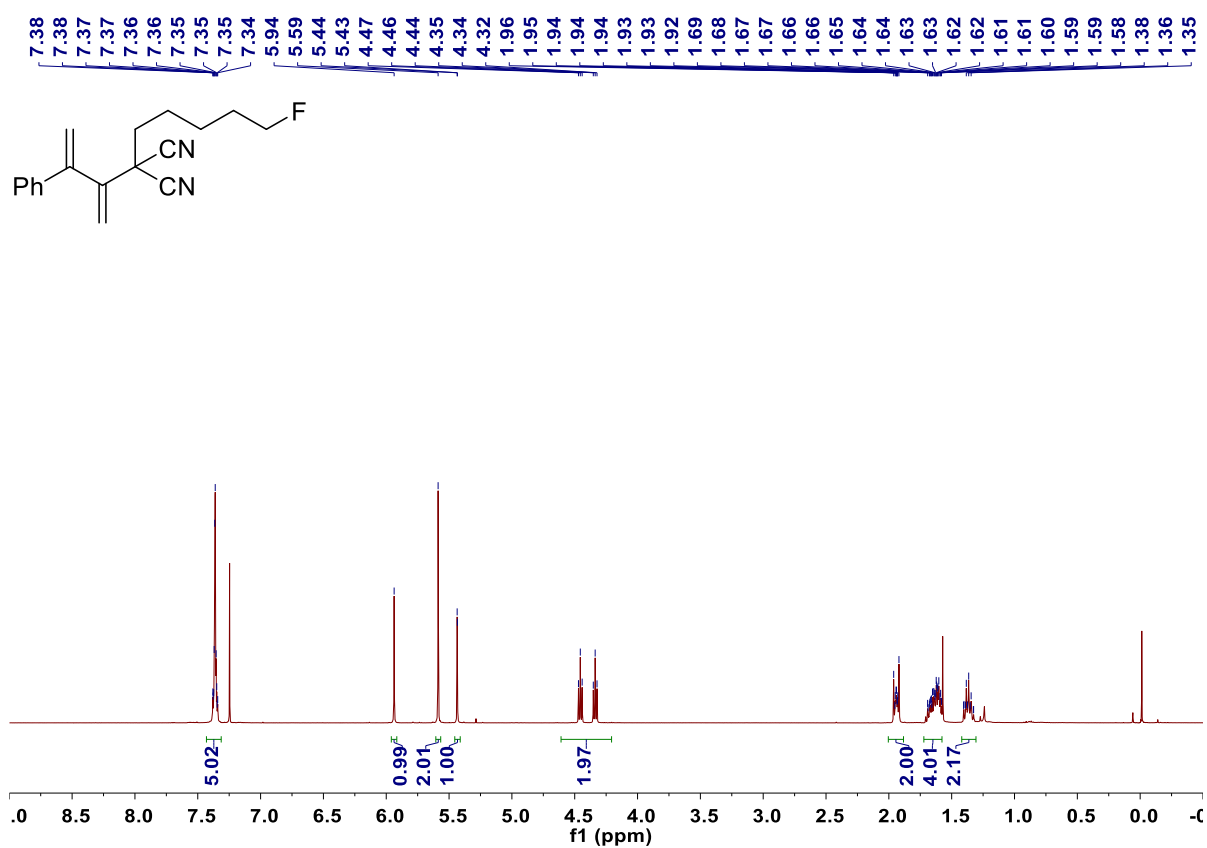
¹H and ¹³C NMR spectra for product 3ao (400 MHz, CDCl₃)

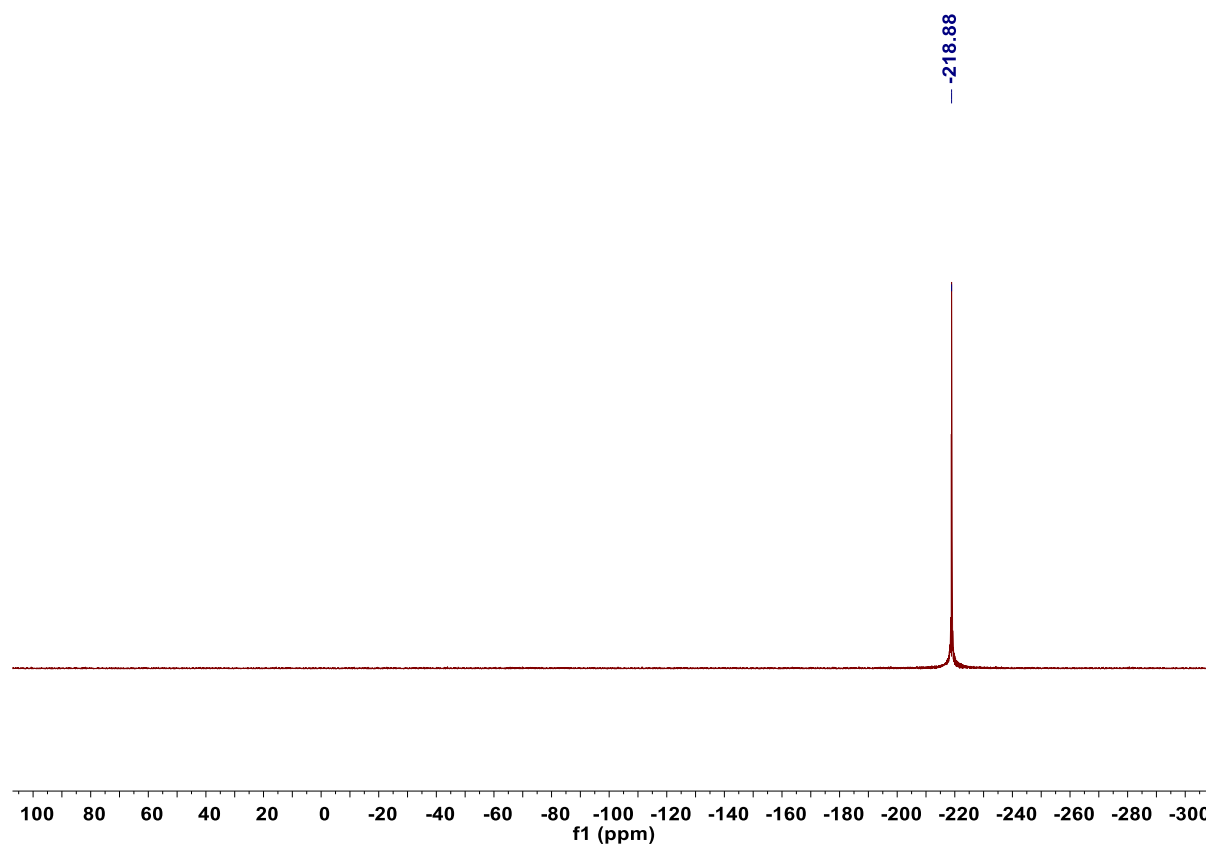
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¹H and ¹³C NMR spectra for product 3ap (400 MHz, CDCl₃)

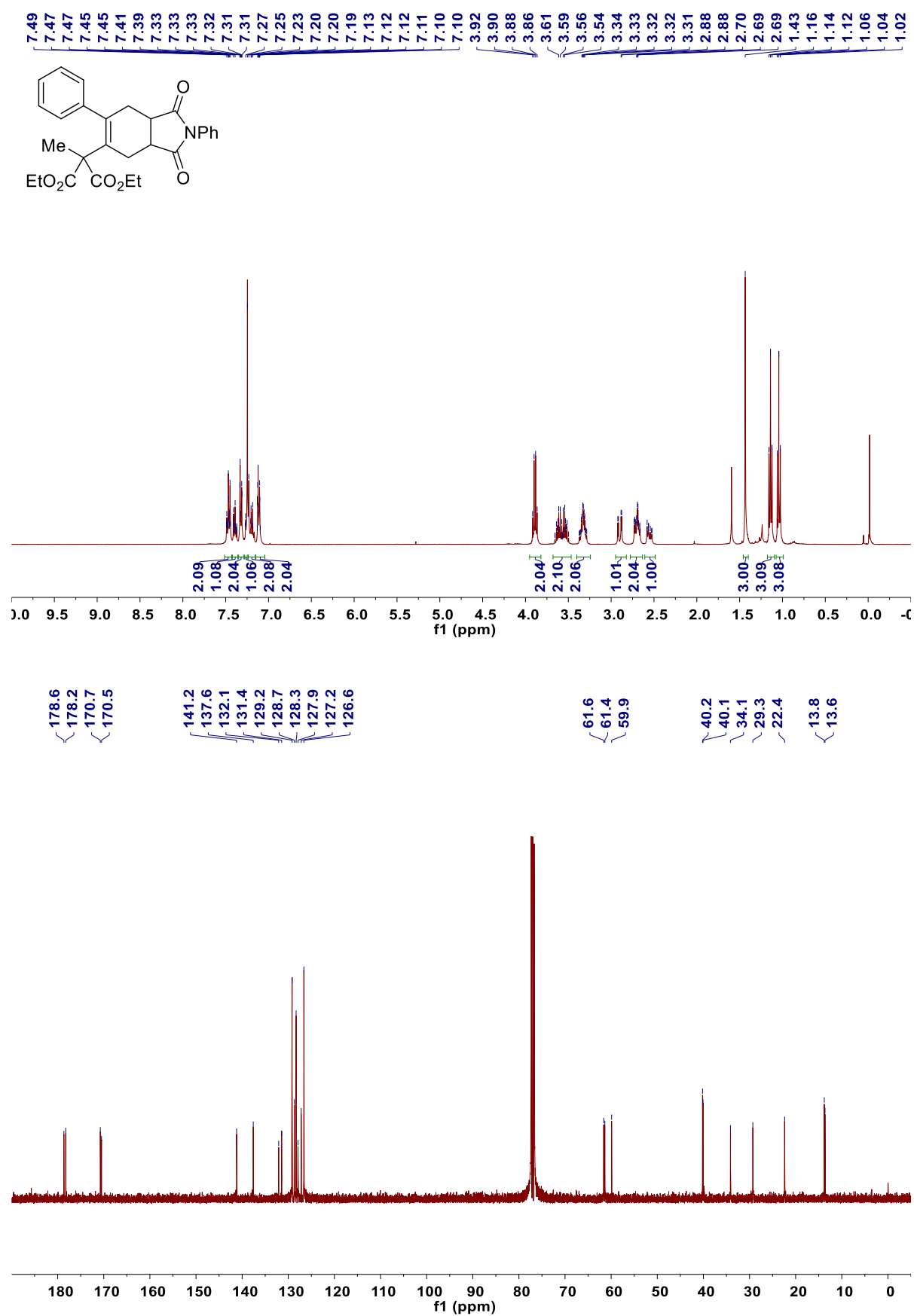
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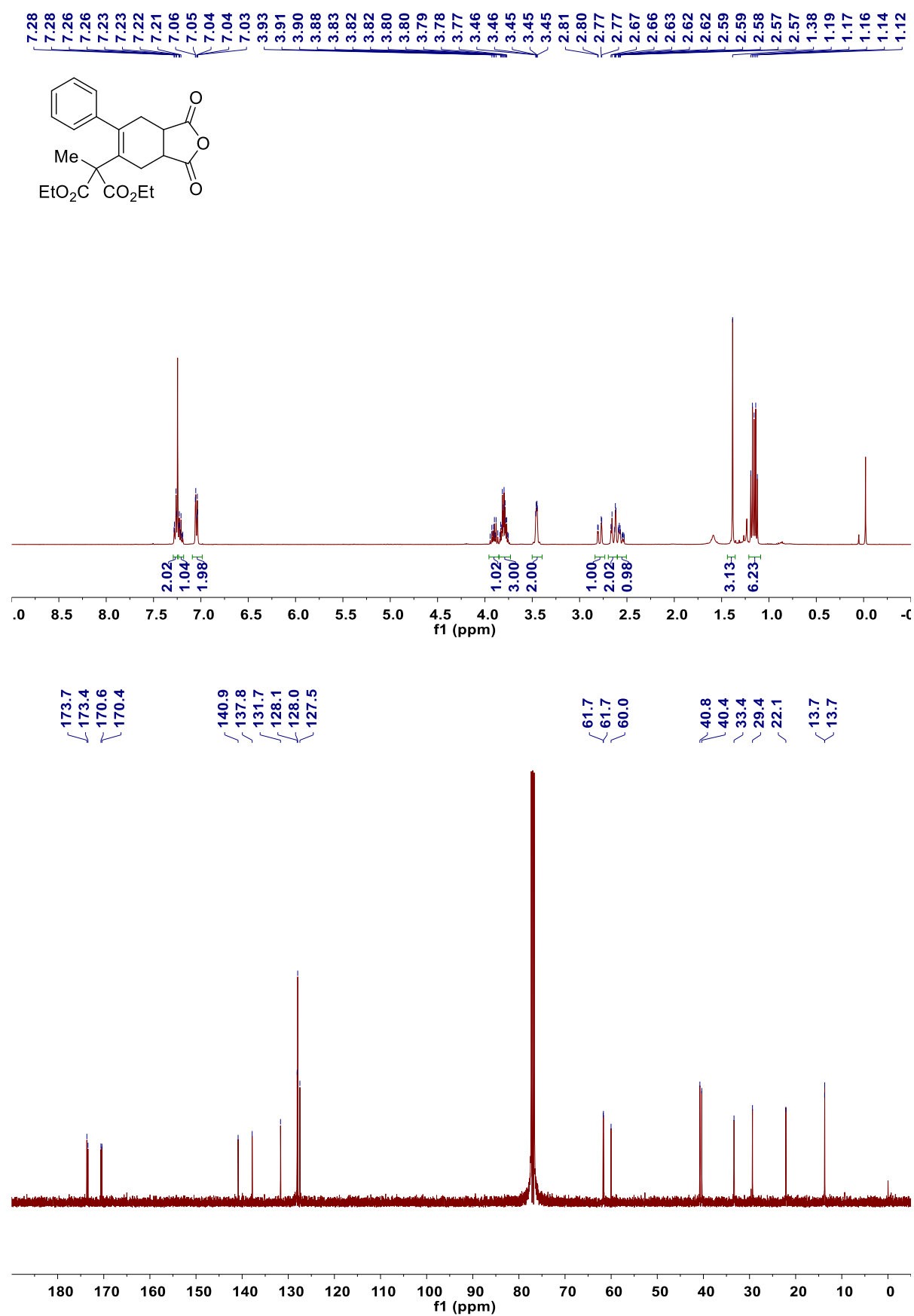


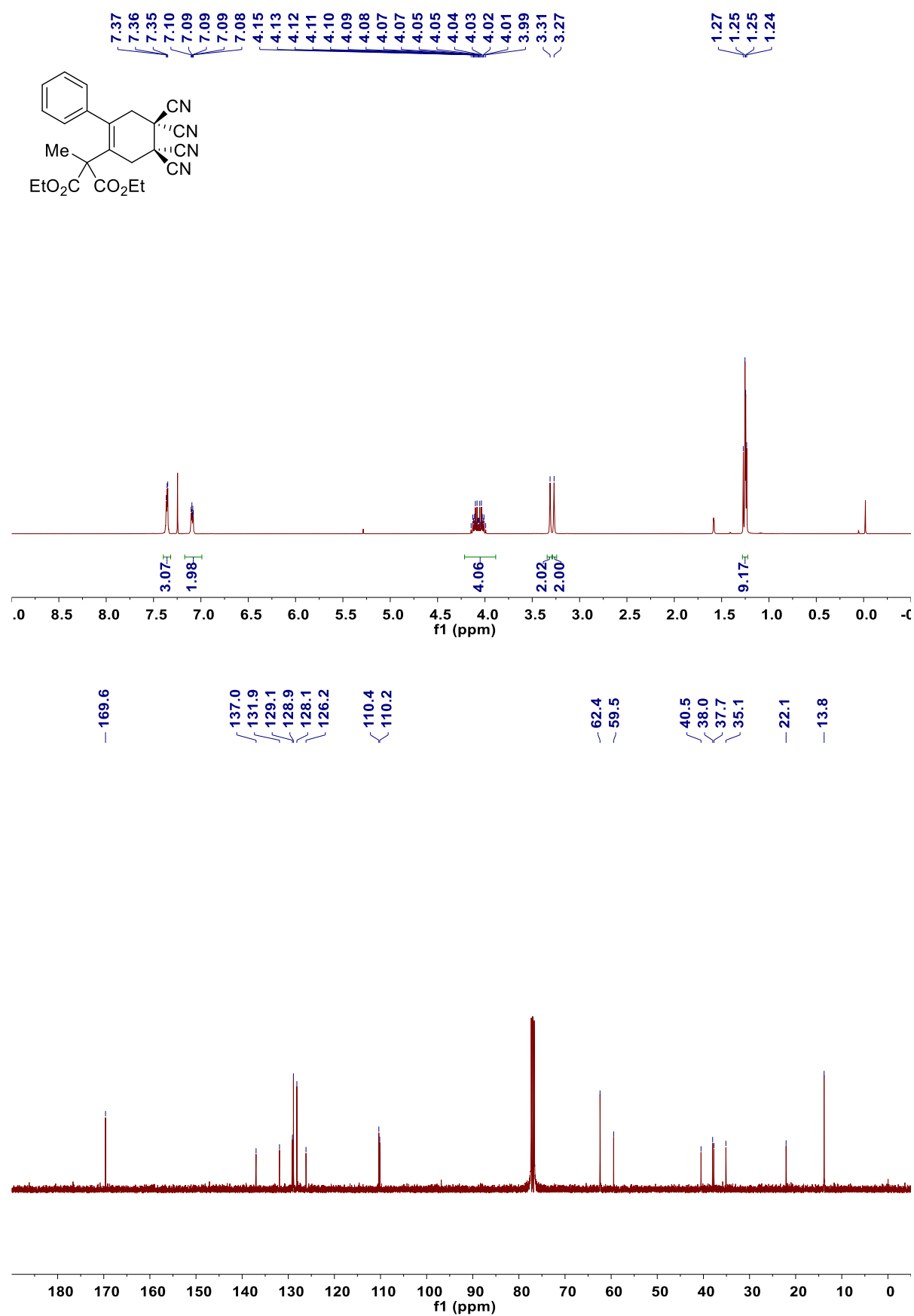
^1H , ^{13}C and ^{19}F NMR spectra for product 3aq (400 MHz, CDCl_3)

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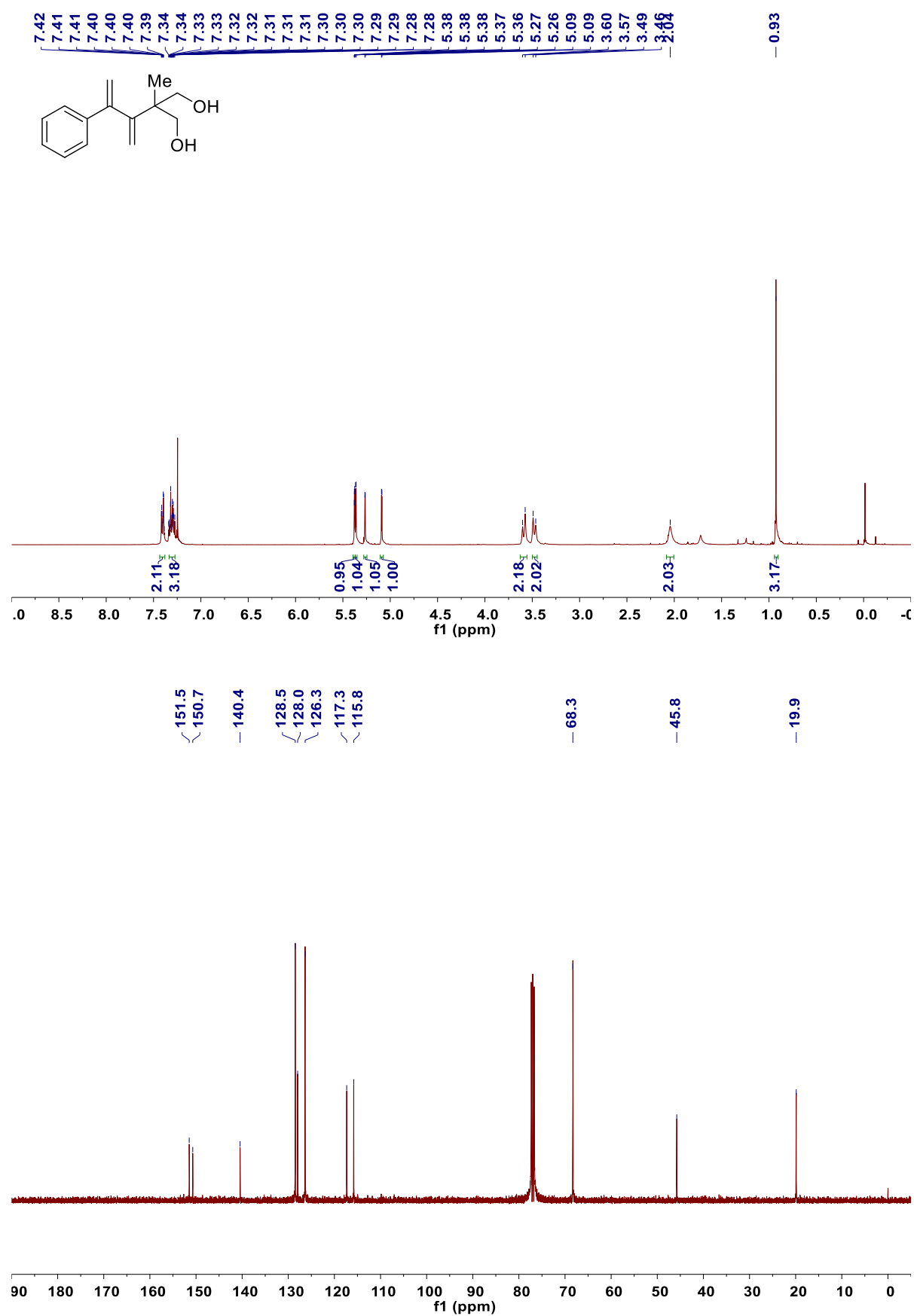


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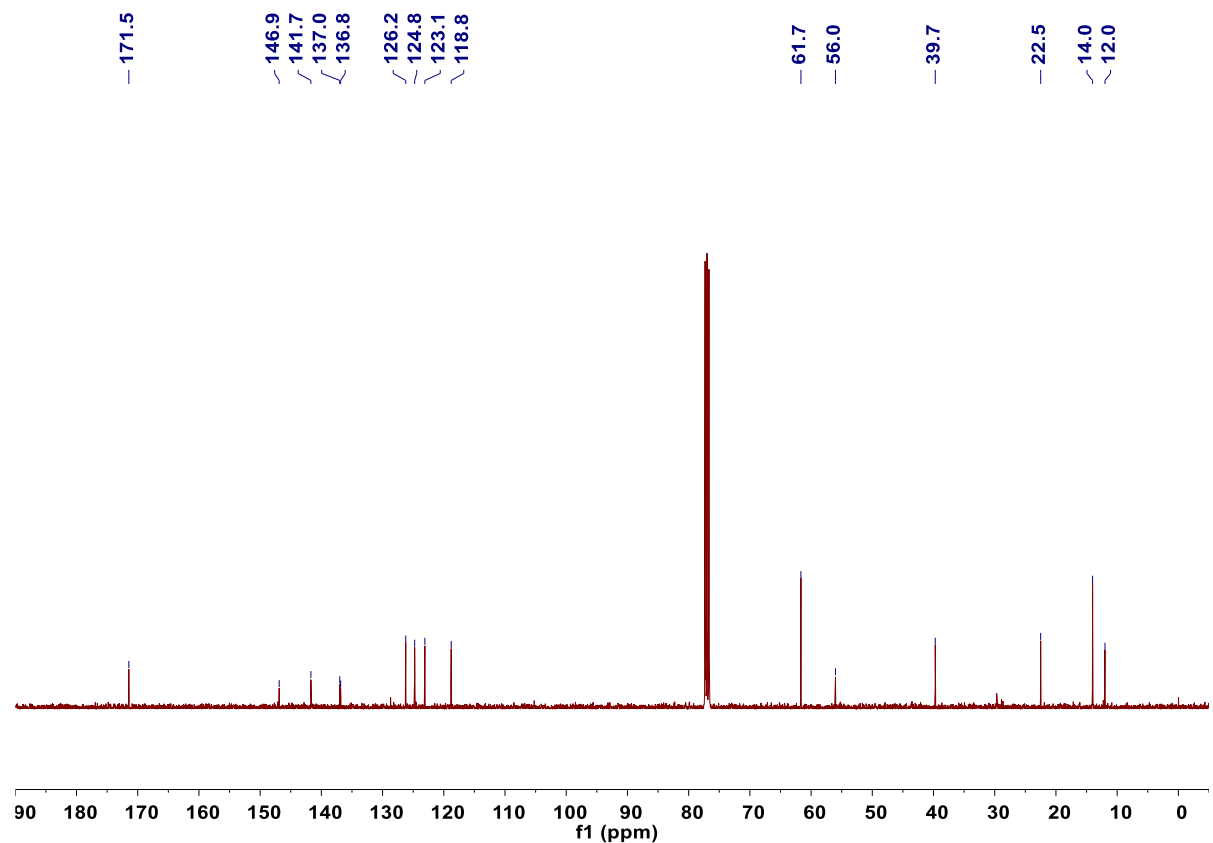
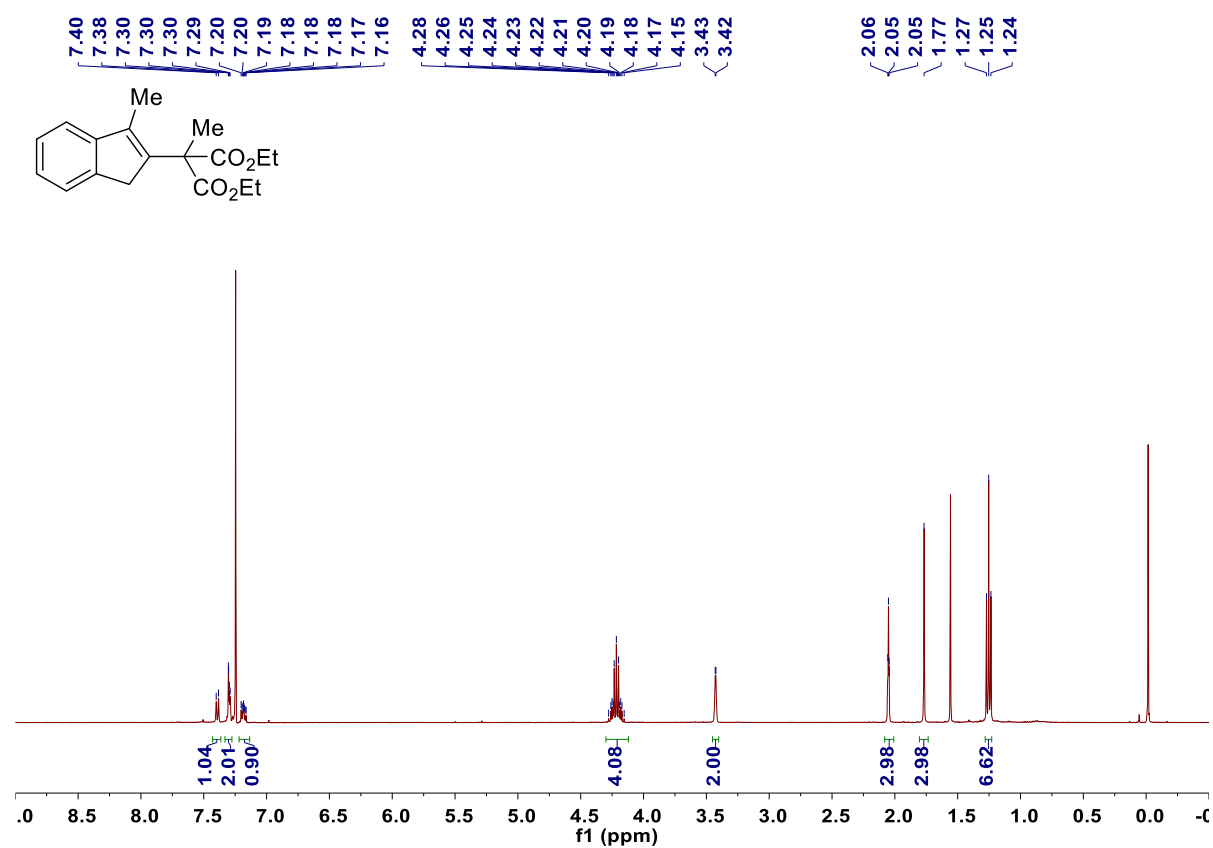


¹H and ¹³C NMR spectra for product 6 (400 MHz, CDCl₃)



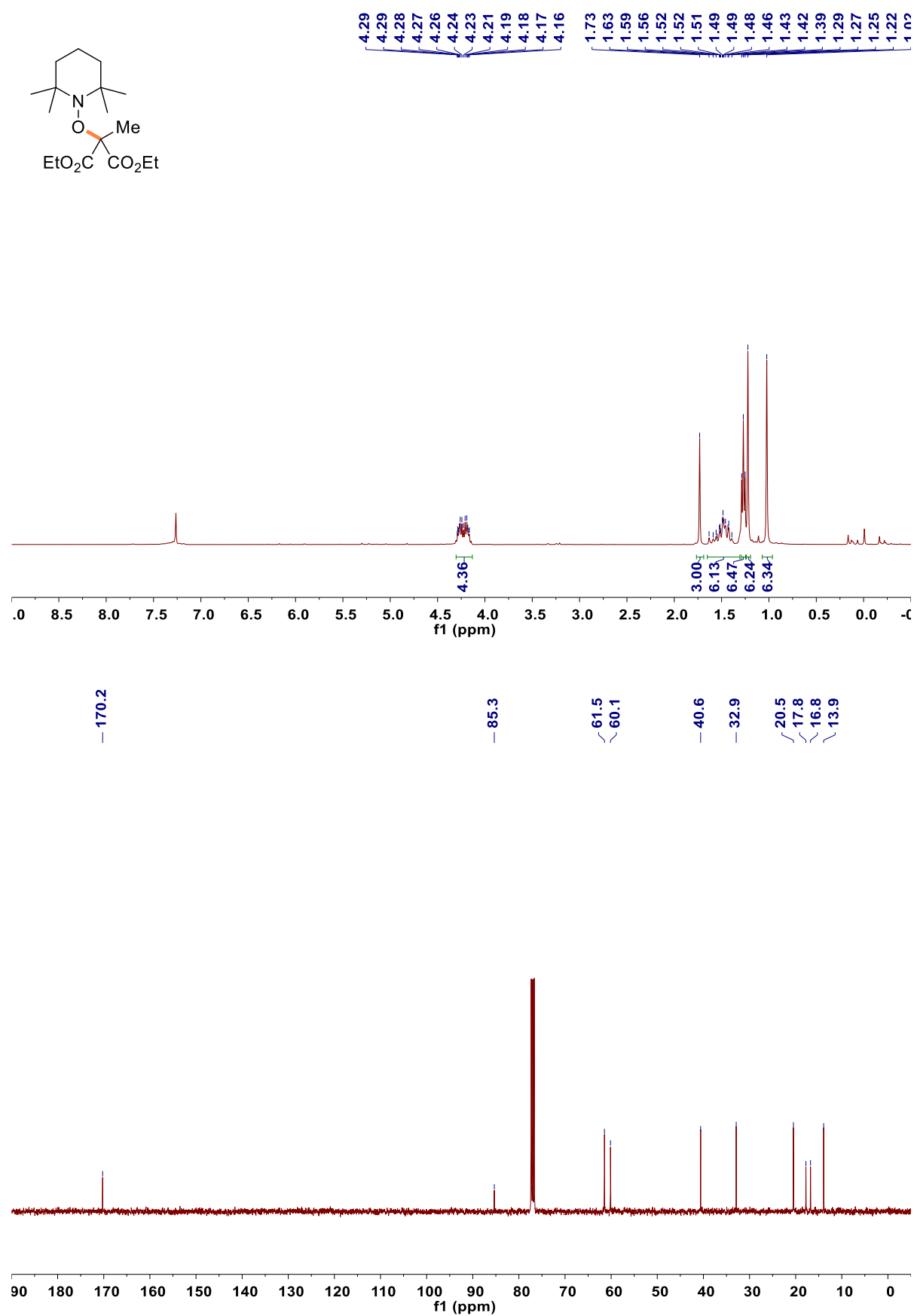
¹H and ¹³C NMR spectra for product 7 (400 MHz, CDCl₃)

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¹H and ¹³C NMR spectra for product 8 (400 MHz, CDCl₃)

SUPPORTING INFORMATION



¹H and ¹³C NMR spectra for product 9 (400 MHz, CDCl₃)