Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Visible-Light-Mediated Allylation of Alkyl Radicals with Allylic Sulfones via Deaminative Strategy

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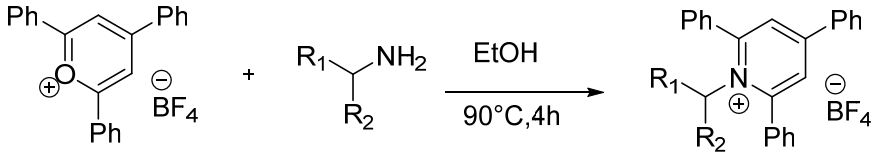
1. General remarks

^{1}H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR) agilent NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.16 ppm (for ^{13}C NMR). HRMS was recorded on a GCT Premier^{TM} (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1}. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates we are readily prepared according to known methods. (*J. Am. Chem. Soc.* **2017**, 139, 5313; *Org. Lett.* **2018**, 20, 3296; *Chem. Commun.* **2016**, 52, 9052.)

2. Synthesis of pyridinium salts and allyl sulfones

2.1 Synthesis of pyridinium salts



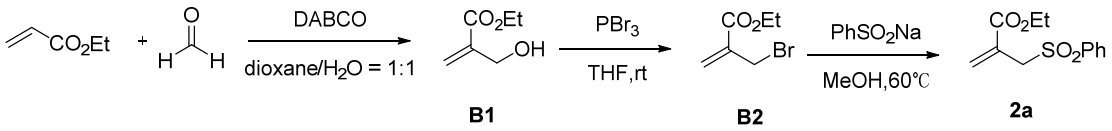
Synthetic procedures:

To a solution of triphenylpyrylium tetrafluoroborate (1.0 equiv) and the corresponding primary amine (1.2 equiv) in ethanol (1.0 M). The reaction mixture was heated to 90 °C and after 4 h cooled to rt. If precipitation occurred during this step, the solid was collected by filtration and washed with ethanol and MTBE. In case no precipitation occurred, MTBE was added to the reaction mixture and the resulting suspension was stirred at rt for at least 1 h to complete the precipitation process. The solid was collected by filtration and washed with MTBE. The solid was then dried under reduced pressure to give the analytically pure pyridinium salts. All pyridinium salts used in this study were prepared following this procedure. (*J. Am. Chem. Soc.* **2017**, 139, 5313.)

In case amine hydrochlorides were used as feedstock for the preparation of pyridinium salts, the amine hydrochloride (1.2 equiv.) and Et_3N (1.2 equiv.) were added in ethanol (1.0 M) stirred for 30 min at rt. Next, triphenylpyrylium tetrafluoroborate (1.0 equiv.) was added and the reaction mixture was heated to 90 °C for 4 h. To remove the water-soluble impurities, the collected solid was washed with water before washing with ethanol and/or MTBE.

2.2 Synthesis of allyl sulfones

Procedure for the synthesis of **2a-e**.



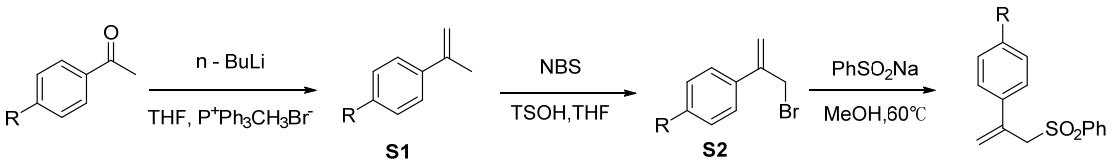
Typical synthetic procedures:

To a solution of paraformaldehyde (3.98 g, 133.2 mmol) and ethylacrylate (10.8 mL, 100 mmol) in 80 mL dioxane-water (1:1, v/v) was added DABCO (14.96 g, 133.2 mmol) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was partitioned with EtOAc (200 mL) and water (100 mL). The organic layer was separated and washed with brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give **B1** as a colorless oil (8.45 g, 65% yield).

To a solution of **B1** (8.45 g, 65 mmol) was added PBr_3 (2.15 ml, 22.6 mmol) in dry THF (65 mL) at -10 °C. The temperature was allowed to rise to rt and stirring was continued for 3 h. Water (20 mL) was then added and the mixture was extracted with petroleum ether (3 x 100 mL). The organic phase was washed with brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give **B2** as a colorless oil (10.36 g, 83% yield).

To a solution of **B2** (10.36 g, 54.0 mmol) in dry methanol (100 mL) was added sodium phenylsulfinate (10.63 g, 64.8 mmol). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by chromatography to give **2a** as a viscous oil (11.11 g, 81% yield). (*Org. Lett.* **2018**, 20, 3296.)

Procedure for the synthesis of **2f-k**.



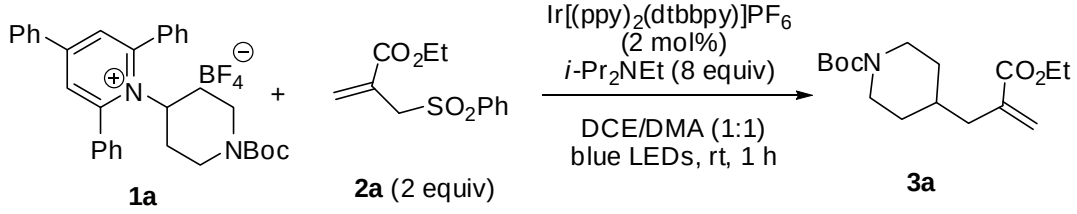
A mixture of methyltriphenylphosphonium bromide (1.2 equiv) in dry THF (0.5 M) under argon atmosphere was cooled to 0 °C. Then, *n*-BuLi (2.5 M solution in hexane, 1.2 equiv) was added slowly under stirring. After, the resulting orange mixture was maintained at 0 °C for 1 h, a solution of the corresponding ketone (1.0 equiv) in dry THF was added dropwisely at 0 °C. The reaction was allowed to warm up to rt, stirred overnight, and finally quenched with a saturated aqueous solution of NaCl. The resulting mixture was extracted with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to give the corresponding propene **S1**.

To a solution of NBS (1.05 equiv) and TSOH (0.1 equiv) in dry THF (0.5M) under

argon atmosphere. Then, **S1** (1.0 equiv) was added. The reaction solution was heated to 100 °C and stirred for 4 h, then cooled down to rt. Quenched with water, extracted with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to afford the product **S2**. (*Chem. Commun.* **2016**, 52, 9052.)

To a solution of **S2** (1.0 equiv) in dry methanol (0.5 M) was added sodium phenylsulfinate (1.2 equiv). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by chromatography to give **2f-k**.

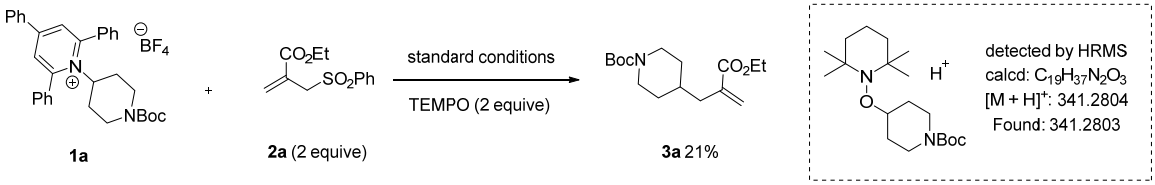
3. Typical experimental procedure



A 10 mL oven-dried Schlenk-tube was charged with **1a** (115.6 mg, 0.2 mmol), $Ir[(ppy)_2(dtbbpy)]PF_6$ (4 mg, 2 mol%), DIPEA (265 μL, 1.6 mmol), **2a** (101.6 mg, 0.4 mmol) and a magnetic stirring bar. The tube was evacuated and backfilled with argon (three times). 2 mL of DCE/DMA was injected into the tube by syringe. The resulting mixture was stirred at rt for 3 h upon irradiation with blue LEDs (22 W). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **3a** as a colorless oil (55 mg, 93 % yield).

4. Investigation on the reaction mechanism

4.1 Radical trapping experiment



When 2.0 equiv of TEMPO was added to the reaction of **1a** with **2a** under the standard conditions, the product **3a** was obtained in 21% yield. The crude product was also analyzed by HRMS (ESI) and the MS spectrum showed that an adduct of TEMPO with the cyclohexyl radical could be generated.

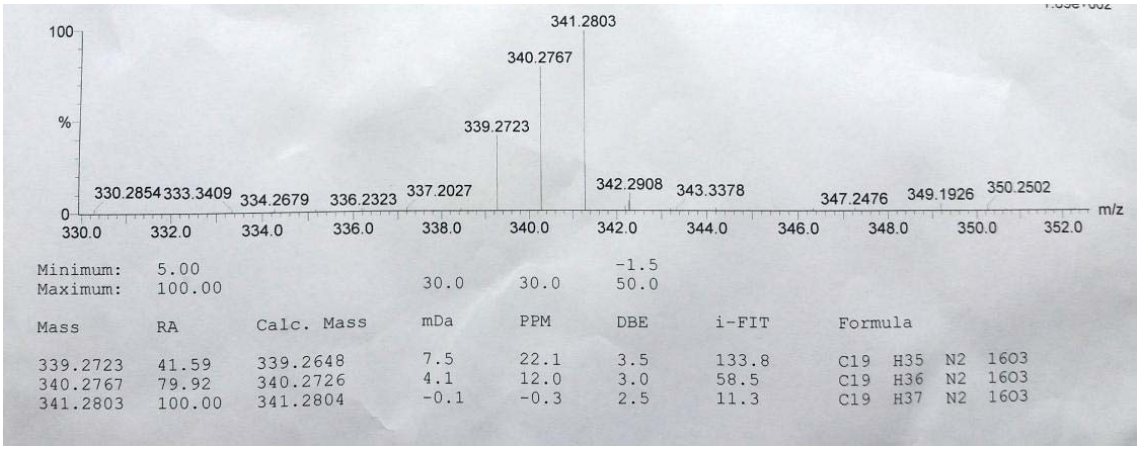


Figure S1. HRMS trace of the TEMPO trapping experiment.

4.2 Stern-Volmer luminescence quenching studies

Emission intensities were recorded using LS55 Luminescence Spectrometer for all experiments. All Ir[(ppy)$_2$(dtbbpy)]PF$_6$ solutions were excited at 420 nm and the emission intensity was collected at 560 nm. In a typical experiment, the DMF solution of Ir[(ppy)$_2$(dtbbpy)]PF$_6$ (30 μM) was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing with argon for 15 min, the emission spectra of the samples were collected. The results showed that DIPEA, Katritzky salts **1b** and **1e** quenched the photoexcited Ir[(ppy)$_2$(dtbbpy)]PF$_6$ effectively, while the allyl sulfone **2a** was not effective.

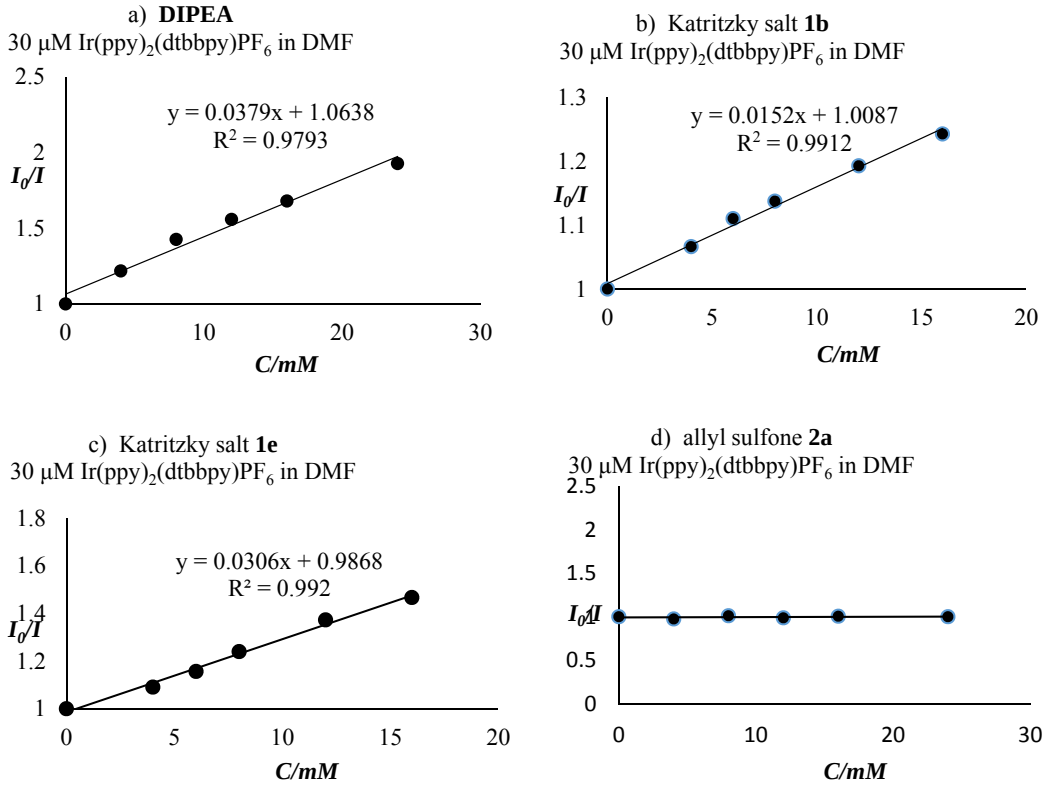
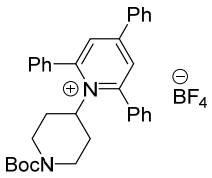
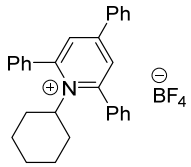


Figure S2. a) $Ir(ppy)_2(dtbbpy)PF_6$ emission quenching by DIPEA. b) $Ir(ppy)_2(dtbbpy)PF_6$ emission quenching by Katritzky salt **1b.** c) $Ir(ppy)_2(dtbbpy)PF_6$ emission quenching by Katritzky salt **1e**. d) $Ir(ppy)_2(dtbbpy)PF_6$ emission quenching by allyl sulfone **2a**.

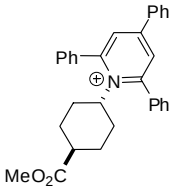
5. Characterization of the substrates and products



1-(1-(*tert*-Butoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1a): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.65 (m, 8H), 7.63 – 7.53 (m, 6H), 7.53 – 7.48 (m, 1H), 7.47 – 7.39 (m, 2H), 4.80 – 4.72 (m, 1H), 4.02 – 3.79 (m, 2H), 2.27 – 2.00 (m, 4H), 1.72 – 1.55 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 155.5, 154.3, 134.1, 133.9, 132.1, 131.2, 129.7, 129.4, 129.1, 128.4, 80.2, 70.0, 44.7, 43.8, 32.8, 28.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.96 (s), -153.01 (s).

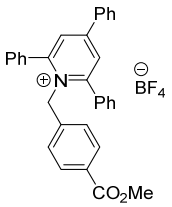


1-Cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1b): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.71 (t, J = 6.8 Hz, 6H), 7.63 – 7.52 (m, 6H), 7.49 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 4.64 – 4.55 (m, 1H), 2.15 – 2.05 (m, 2H), 1.61 – 1.52 (m, 2H), 1.52 – 1.40 (m, 2H), 1.37 – 1.30 (m, 1H), 0.78 – 0.67 (m, 2H), 0.65 – 0.54 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 155.1, 134.12, 134.09, 131.9, 130.9, 129.6, 129.4, 128.9, 128.4, 128.2, 72.0, 33.7, 26.6, 24.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -153.30 (s), -153.36 (s).

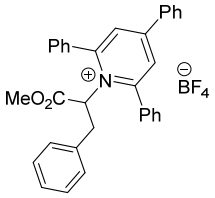


1-(4-(Methoxycarbonyl)cyclohexyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1c): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 6H), 7.65 (d, J = 7.5 Hz, 2H), 7.62 – 7.50 (m, 6), 7.47 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 4.59 (t, J = 12.2 Hz, 1H), 3.51 (s, 3H), 2.21 (d, J = 12.1 Hz, 2H), 1.91 – 1.75 (m, 3H), 1.68 (t, 1H), 1.59 – 1.49 (m, 2H), 0.96 – 0.87 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ

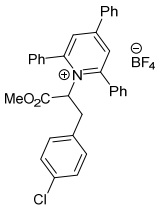
174.5, 157.0, 155.0, 133.9, 133.8, 131.9, 131.0, 129.5, 129.3, 128.8, 128.2, 128.1, 70.5, 51.7, 41.5, 32.0, 28.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -153.07 (s), -153.13 (s).



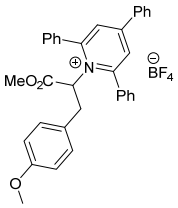
1-(4-(Methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.83 – 7.64 (m, 8H), 7.60 – 7.38 (m, 9H), 6.57 (d, *J* = 7.9 Hz, 2H), 5.87 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 157.48, 157.46, 156.5, 138.91, 138.87, 133.6, 132.54, 132.47, 131.1, 129.9, 129.8, 129.2, 129.1, 128.2, 126.5, 126.2, 58.0, 52.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.67 – -152.88 (m).



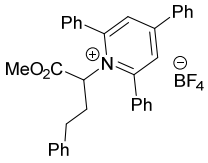
1-(1-Methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1e): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.89 – 7.68 (m, 4H), 7.65 – 7.39 (m, 11H), 7.15 – 7.04 (m, 3H), 6.77 (d, *J* = 7.3 Hz, 2H), 5.64 (dd, *J* = 7.5, 3.7 Hz, 1H), 3.69 (s, 3H), 3.50 – 3.41 (m, 1H), 2.93 (dd, *J* = 14.4, 8.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 157.1, 157.0, 136.4, 133.8, 132.5, 132.4, 131.7, 129.8, 129.6, 129.2, 129.1, 128.72, 128.66, 128.0, 127.3, 70.3, 53.9, 37.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.80 (d, *J* = 4.5 Hz), -152.86 (d, *J* = 3.5 Hz).



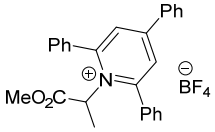
1-(3-(4-Chlorophenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1f): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.83 – 7.72 (m, 4H), 7.60 – 7.45 (m, 11H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 5.55 (d, *J* = 8.4 Hz, 1H), 3.67 (s, 3H), 3.49 (d, *J* = 14.3 Hz, 1H), 2.82 (dd, *J* = 14.3, 8.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 157.2, 156.8, 135.4, 133.9, 133.1, 132.5, 132.4, 131.7, 130.6, 129.8, 129.5, 129.3, 128.7, 128.6, 128.0, 70.0, 53.9, 37.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.57 (s), -152.62 (s).



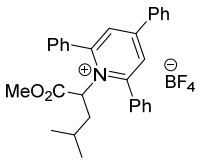
1-(1-Methoxy-3-(4-methoxyphenyl)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1g): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.86 – 7.69 (m, 4H), 7.63 – 7.37 (m, 11H), 6.67 (d, *J* = 8.2 Hz, 2H), 6.60 (d, *J* = 7.8 Hz, 2H), 5.58 (dd, *J* = 7.1, 4.9 Hz, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 3.31 (dd, *J* = 14.5, 4.3 Hz, 1H), 2.89 (dd, *J* = 14.6, 7.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.8, 158.7, 156.9, 133.6, 132.5, 132.2, 131.6, 130.1, 129.7, 129.5, 129.2, 128.6, 128.0, 127.8, 114.0, 70.4, 55.3, 53.8, 36.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.75 – -152.80 (m), -152.80 – -152.85 (m).



1-(1-Methoxy-1-oxo-4-phenylbutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1h): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.73 (br, 2H), 7.59 – 7.39 (m, 11H), 7.16 – 7.06 (m, 3H), 6.92 (d, *J* = 6.5 Hz, 2H), 5.37 (dd, *J* = 8.5, 2.1 Hz, 1H), 3.71 (s, 3H), 2.48 – 2.35 (m, 3H), 2.02 – 1.96 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 157.1, 156.9, 138.7, 134.0, 132.6, 132.4, 131.5, 129.8, 129.2, 128.71, 128.65, 128.56, 128.1, 126.6, 68.1, 53.8, 33.5, 33.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.86 (s), -152.92 (s).

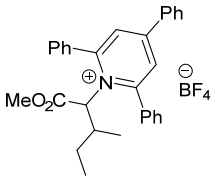


1-(1-Methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.79 – 7.69 (m, 4H), 7.66 – 7.44 (m, 11H), 5.52 (q, *J* = 7.0 Hz, 1H), 3.66 (s, 3H), 1.47 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 157.0, 156.8, 134.0, 132.7, 132.3, 131.5, 129.7, 129.2, 128.5, 127.9, 64.6, 53.8, 17.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -153.17 (s), -153.22 (s).

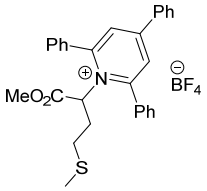


1-(1-Methoxy-4-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.81 (d, *J* = 7.3 Hz, 2H), 7.76 – 7.44 (m, 13H), 5.47 (dd, *J* = 7.8, 2.8 Hz, 1H), 3.75 (s, 3H), 1.81 –

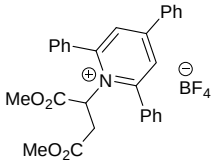
1.64 (m, 1H), 1.64 – 1.50 (m, 1H), 1.39 – 1.26 (m, 1H), 0.57 (d, *J* = 6.5 Hz, 3H), 0.42 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 156.8, 156.7, 133.7, 132.5, 132.3, 131.6, 129.6, 129.4, 129.1, 128.5, 127.9, 67.4, 53.9, 40.4, 26.1, 22.3, 20.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -153.01 (s), -153.07 (s).



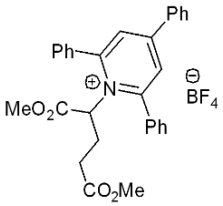
1-(1-Methoxy-3-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1k): *d.r.* (1.1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.75 – 7.43 (m, 13H), 5.31 (d, *J* = 10.2 Hz, 0.48H)/ 5.16 (d, *J* = 10.2 Hz, 0.52H), 3.75 – 3.68 (m, 3H), 2.04 – 1.64 (m, 2H), 1.42 – 0.90 (m, 2H), 0.87 – 0.66 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 166.8, 157.10, 157.06, 133.1, 133.0, 131.9, 129.9, 129.8, 129.7, 129.4, 129.2 128.9, 128.8, 128.6, 127.8, 73.5, 71.3, 53.93, 53.87, 36.0, 35.6, 27.8, 25.4, 18.5, 15.2, 11.1, 9.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -153.28 (s), -153.34 (s).



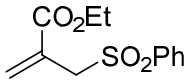
1-(1-Methoxy-4-(methylthio)-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.83 – 7.69 (m, 4H), 7.63 – 7.39 (m, 11H), 5.92 (d, *J* = 7.7 Hz, 1H), 3.73 (s, 3H), 2.37 – 2.16 (m, 3H), 1.94 – 1.85 (m, 1H), 1.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 156.9, 133.8, 132.5, 132.2, 131.5, 129.6, 129.1, 128.5, 66.7, 53.9, 31.4, 30.8, 14.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.74 (s), -152.79 (s).



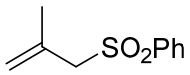
1-(1,4-Dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (br, 3H), 7.86 – 7.75 (m, 3H), 7.70 – 7.41 (m, 11H), 6.22 (d, *J* = 9.4 Hz, 1H), 3.63 (s, 3H), 3.53 (s, 3H), 3.38 (d, *J* = 17.4 Hz, 1H), 2.55 (dd, *J* = 17.4, 9.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 167.74, 167.70, 157.4, 133.9, 132.5, 131.7, 129.8, 129.4, 128.6, 64.1, 54.1, 52.6, 36.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.78 (d, *J* = 4.1 Hz), -152.83 (s).



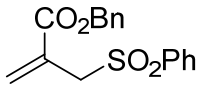
1-(1,5-Dimethoxy-1,5-dioxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1n): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.86 – 7.71 (m, 4H), 7.69 – 7.44 (m, 11H), 5.60 (t, *J* = 6.2 Hz, 1H), 3.71 (s, 3H), 3.46 (s, 3H), 2.26 (dt, *J* = 13.0, 6.3 Hz, 1H), 2.23 – 2.13 (m, 2H), 2.07 (td, *J* = 14.1, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 168.2, 157.2, 133.7, 132.5, 132.4, 131.7, 129.8, 129.4, 128.6, 128.1, 67.6, 54.0, 51.8, 30.8, 27.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -153.06 (s), -153.11 (s).



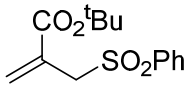
Ethyl 2-((phenylsulfonyl)methyl)acrylate (2a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 6.48 (s, 1H), 5.88 (s, 1H), 4.14 (s, 2H), 3.98 (q, *J* = 6.9 Hz, 2H), 1.14 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 138.4, 133.9, 133.4, 129.2, 129.1, 128.8, 61.5, 57.6, 14.0.



((2-Methylallyl)sulfonyl)benzene (2b): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 5.02 (s, 1H), 4.68 (s, 1H), 3.76 (s, 2H), 1.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 133.8, 133.5, 129.1, 128.6, 120.9, 64.6, 22.8.

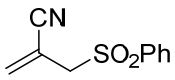


Benzyl 2-((phenylsulfonyl)methyl)acrylate (2c): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.26 (d, *J* = 7.3 Hz, 2H), 6.53 (s, 1H), 5.92 (s, 1H), 5.00 (s, 2H), 4.17 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.6, 138.2, 135.3, 133.9, 133.8, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 67.1, 57.4.

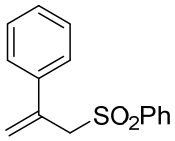


***tert*-Butyl 2-((phenylsulfonyl)methyl)acrylate (2d):** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 6.42 (s, 1H),

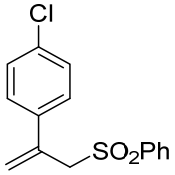
5.87 (s, 1H), 4.12 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 138.6, 133.9, 132.8, 130.4, 129.1, 128.9, 81.9, 57.5, 27.8.



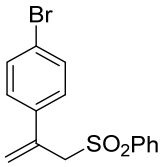
2-((Phenylsulfonyl)methyl)acrylonitrile (2e): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 6.22 (s, 1H), 6.01 (s, 1H), 3.93 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.6, 137.5, 134.9, 129.7, 128.9, 116.5, 111.6, 60.0.



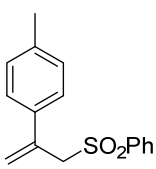
((2-Phenylallyl)sulfonyl)benzene (2f): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.18 (m, 5H), 5.58 (s, 1H), 5.20 (s, 1H), 4.27 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 138.3, 136.4, 133.7, 128.9, 128.6, 128.4, 128.0, 126.2, 121.9, 62.0.



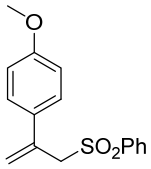
1-Chloro-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (2g): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.21 (s, 4H), 5.58 (s, 1H), 5.21 (s, 1H), 4.23 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 137.3, 135.6, 134.2, 133.9, 129.1, 128.7, 128.7, 127.7, 122.5, 62.1.



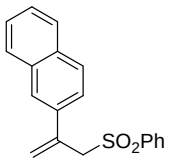
1-Bromo-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (2h): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 5.57 (s, 1H), 5.20 (s, 1H), 4.22 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 137.7, 135.6, 133.8, 131.5, 129.1, 128.6, 127.9, 122.5, 122.2, 62.0.



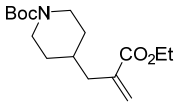
1-Methyl-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (2i): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.55 (t, 1H), 7.43 (t, *J* = 15.5, 7.9 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 5.55 (s, 1H), 5.13 (s, 1H), 4.26 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 138.0, 136.4, 135.9, 133.7, 129.2, 129.0, 128.7, 126.2, 121.1, 62.2, 21.2.



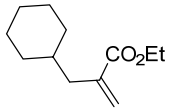
1-Methoxy-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (2j): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.50 (s, 1H), 5.07 (s, 1H), 4.24 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 138.4, 135.8, 133.7, 131.2, 128.9, 128.7, 127.5, 120.2, 113.8, 62.2, 55.4.



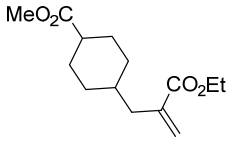
2-(3-(Phenylsulfonyl)prop-1-en-2-yl)naphthalene (2k) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.79 – 7.75 (m, 1H), 7.75 – 7.69 (m, 2H), 7.64 (s, 1H), 7.49 – 7.43 (m, 3H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 15.1, 7.3 Hz, 2H), 5.74 (s, 1H), 5.33 (s, 1H), 4.39 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 136.5, 136.0, 133.7, 133.2, 133.0, 129.0, 128.8, 128.4, 128.3, 127.6, 126.5, 125.6, 124.2, 122.3, 62.3.



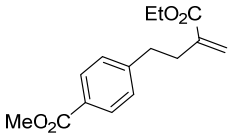
***tert*-Butyl 4-(2-(ethoxycarbonyl)allyl)piperidine-1-carboxylate (3a):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 93% yield (55 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 5.49 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.14 – 3.95 (m, 2H), 2.73 – 2.54 (m, 2H), 2.23 (d, *J* = 6.2 Hz, 2H), 1.68 – 1.55 (m, 3H), 1.44 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.12 – 1.00 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 155.0, 138.7, 126.3, 79.3, 60.8, 44.2, 39.3, 35.2, 32.1, 28.6, 14.4; FT-IR (thin film, KBr): ν (cm^{-1}): 2980, 2920, 2849, 1685, 1108; HRMS (CI) calcd $C_{16}H_{26}NO_4$ $[M - H]^+$: 296.1862, found: 296.1869.



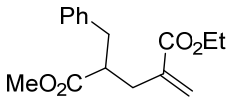
Ethyl 2-(cyclohexylmethyl)acrylate (3b): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 50:1) to give the colorless oil; 85% yield (33 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.13 (d, *J* = 1.7 Hz, 1H), 5.45 (d, *J* = 0.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.18 (d, *J* = 7.0 Hz, 2H), 1.72 – 1.66 (m, 4H), 1.63 – 1.59 (m, 1H), 1.48 – 1.38 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.26 – 1.08 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 139.6, 125.6, 60.7, 40.0, 36.8, 33.2, 26.7, 26.4, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2923, 2852, 1715, 1150, 1111; HRMS (CI) calcd $C_{12}H_{21}O_2$ $[M + H]^+$: 197.1542, found: 197.1537.



Methyl 4-(2-(ethoxycarbonyl)allyl)cyclohexane-1-carboxylate (3c): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 76% yield (39 mg); *d.r.* (1.5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.15 (s, 0.4H)/6.14 (s, 0.6H), 5.46 (s, 1H), 4.23 – 4.14 (m, 2H), 3.67 (s, 1.8H)/3.64(s, 1.2H), 2.56 – 2.48 (m, 0.6H), 2.27 – 2.16 (m, 2.4H), 2.03 – 1.90 (m, 2H), 1.79 (d, *J* = 12.4 Hz, 1H), 1.64 – 1.49 (m, 3H), 1.48 – 1.34 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.26 – 1.15 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.7/176.0, 167.5, 139.4/139.2, 125.9, 60.8/60.7, 51.63/51.61, 43.4/39.7, 40.5/38.1, 36.1/34.7, 32.1/29.2, 29.0/26.2, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2929, 1730, 1180, 1147, 1115; HRMS (CI) calcd $C_{14}H_{23}O_4$ $[M + H]^+$: 255.1596, found: 255.1603.

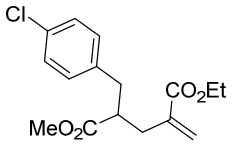


Methyl 4-(3-(ethoxycarbonyl)but-3-en-1-yl)benzoate (3d): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 68% yield (36 mg); ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.24 (d, 2H), 6.15 (s, 1H), 5.47 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 2.85 (t, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 167.1, 147.0, 139.8, 129.8, 128.7, 128.1, 125.6, 60.9, 52.1, 35.1, 33.7, 14.4; FT-IR (thin film, KBr): ν (cm^{-1}): 2956, 1709, 1275, 1177, 1102; HRMS (CI) calcd $C_{15}H_{19}O_4$ $[M + H]^+$: 263.1283, found: 263.1285.

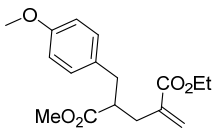


5-Ethyl 1-methyl 2-benzyl-4-methylenepentanedioate (3e): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 69% yield (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 6.9 Hz, 2H), 7.23 – 7.11 (m, 3H), 6.18 (s, 1H), 5.57 (s, 1H), 4.19 (q, *J* = 6.8 Hz, 2H), 3.54

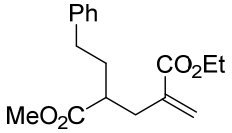
(s, 3H), 3.07 – 2.89 (m, 2H), 2.88 – 2.72 (m, 1H), 2.58 (d, J = 6.5 Hz, 2H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.3, 166.7, 138.9, 138.1, 129.0, 128.5, 126.9, 126.6, 60.9, 51.5, 46.7, 38.6, 34.8, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2962, 2920, 1719, 1185, 698; HRMS (CI) calcd $C_{16}H_{21}O_4$ $[M + H]^+$: 277.1440, found: 277.1441.



5-Ethyl 1-methyl 2-(4-chlorobenzyl)-4-methylenepentanedioate (3f): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 73% yield (45 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.18 (s, 1H), 5.57 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.54 (s, 3H), 2.97 (ddd, J = 14.6, 8.3, 6.5 Hz, 1H), 2.90 (dd, J = 13.6, 8.9 Hz, 1H), 2.75 (dd, J = 13.6, 6.1 Hz, 1H), 2.58 – 2.54 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 166.6, 137.9, 137.4, 132.4, 130.3, 128.6, 127.1, 60.9, 51.6, 46.6, 37.8, 35.0, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2985, 2950, 1712, 1165, 1132; HRMS (CI) calcd $C_{16}H_{20}O_4{}^{35}Cl$ $[M + H]^+$: 311.1050, found: 311.1056.

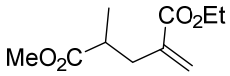


1-Ethyl 5-methyl 4-(4-methoxybenzyl)-2-methylenepentanedioate (3g): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 88% yield (54 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, J = 8.3 Hz, 2H), 6.80 (d, J = 8.3 Hz, 2H), 6.17 (s, 1H), 5.56 (s, 1H), 4.25 – 4.12 (m, 2H), 3.77 (s, 3H), 3.54 (s, 3H), 3.00 – 2.92 (m, 1H), 2.92 – 2.85 (m, 1H), 2.77 – 2.69 (m, 1H), 2.55 (d, J = 7.0 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.4, 166.7, 158.3, 138.1, 130.9, 129.9, 126.8, 113.9, 60.9, 55.3, 51.5, 47.0, 37.8, 34.8, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2950, 1715, 1510, 1174, 997; HRMS (CI) calcd $C_{17}H_{23}O_5$ $[M + H]^+$: 307.1545, found: 307.1548.

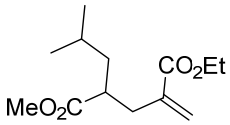


Ethyl 5-methyl 2-methylene-4-phenethylpentanedioate (3h): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 76% yield (44 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 6.17 (s, 1H), 5.54 (s, 1H), 4.19 (q, J = 6.9 Hz, 2H), 3.65 (s, 3H), 2.78 – 2.68 (m, 1H), 2.66 – 2.49 (m, 4H), 2.06 – 1.88 (m, 1H), 1.87 – 1.72 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8, 166.8, 141.5,

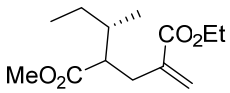
138.1, 128.5, 128.5, 126.8, 126.1, 60.9, 51.6, 44.4, 35.0, 34.1, 33.7, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2950, 1730, 1156, 1132, 695; HRMS (CI) calcd $C_{17}H_{23}O_4$ [M + H]$^+$: 291.1596, found: 291.1607.



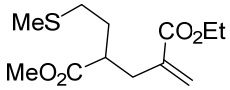
1-Ethyl 5-methyl 4-methyl-2-methylenepentanedioate (3i): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 74% yield (30 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.19 (s, 1H), 5.56 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 2.79 – 2.71 (m, 1H), 2.67 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.40 (dd, *J* = 13.9, 6.6 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.6, 166.9, 138.3, 126.9, 60.9, 51.7, 38.7, 36.3, 17.2, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2977, 2953, 1736, 1712, 1145; HRMS (CI) calcd $C_{10}H_{17}O_4$ [M + H]$^+$: 201.1127, found: 201.1127.



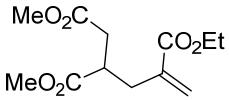
1-Ethyl 5-methyl 4-isobutyl-2-methylenepentanedioate (3j): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 75% yield (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 1H), 5.55 (s, 1H), 4.21 (q, *J* = 6.9 Hz, 2H), 3.62 (s, 3H), 2.82 – 2.69 (m, 1H), 2.50 (d, *J* = 7.3 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.35 – 1.22 (m, 4H), 0.89 (d, *J* = 5.6 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 166.8, 138.3, 126.7, 60.9, 51.5, 43.0, 41.8, 35.5, 26.2, 23.0, 22.2, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2959, 2869, 1733, 1712, 1147; HRMS (CI) calcd $C_{13}H_{23}O_4$ [M + H]$^+$: 243.1596, found: 243.1600.



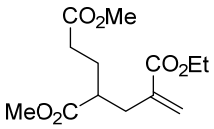
5-Ethyl 1-methyl 2-(sec-butyl)-4-methylenepentanedioate (3k): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 67% yield (33 mg); d.r. (1.2:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.14 (s, 1H), 5.56 (s, 0.54H)/5.55 (s, 0.46H), 4.25 – 4.15 (m, 2H), 3.61 (s, 3H), 2.63 – 2.56 (m, 2H), 2.54 – 2.44 (m, 1H), 1.74 – 1.64 (m, 1H), 1.54 – 1.39 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.26 – 1.15 (m, 1H), 0.96 – 0.87 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.6/175.3, 166.93/166.91, 138.8/138.7, 126.6, 60.9, 51.3/51.2, 50.1/49.6, 37.3/37.2, 32.6/31.2, 27.4/26.9, 16.5/16.2, 14.3, 11.7/11.2; FT-IR (thin film, KBr): ν (cm^{-1}): 2959, 1730, 1712, 1144, 1025; HRMS (CI) calcd $C_{13}H_{23}O_4$ [M + H]$^+$: 243.1596, found: 243.1602.



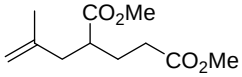
1-Ethyl 5-methyl 2-methylene-4-(2-(methylthio)ethyl)pentanedioate (3l): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 59% yield (31 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 1H), 5.56 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 2.87 – 2.76 (m, 1H), 2.64 – 2.42 (m, 4H), 2.07 (s, 3H), 2.01 – 1.86 (m, 1H), 1.82 – 1.68 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.4, 166.7, 137.9, 127.0, 61.0, 51.7, 43.8, 34.9, 31.9, 31.6, 15.5, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2950, 2914, 1717, 1439, 1153; HRMS (CI) calcd $C_{12}H_{21}O_4S$ $[M + H]^+$: 261.1161, found: 261.1156.



4-Ethyl 1,2-dimethyl pent-4-ene-1,2,4-tricarboxylate (3m): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 57% yield (30 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.22 (s, 1H), 5.57 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 3H), 3.66 (s, 3H), 3.17 – 3.08 (m, 1H), 2.74 – 2.65 (m, 2H), 2.54 – 2.44 (m, 2H), 1.30 (t, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.7, 172.2, 166.5, 137.5, 127.6, 61.1, 52.0, 51.9, 40.4, 35.5, 34.5, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2956, 1736, 1709, 1438, 1165; HRMS (CI) calcd $C_{12}H_{19}O_6$ $[M + H]^+$: 259.1182, found: 259.1190.

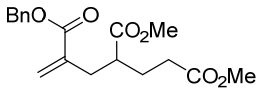


4-Ethyl 1,3-dimethyl hex-5-ene-1,3,5-tricarboxylate (3n): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 63% yield (34 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.18 (s, 1H), 5.57 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 3.63 (s, 3H), 2.75 – 2.66 (m, 1H), 2.59 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.49 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.38 – 2.26 (m, 2H), 1.95 – 1.81 (m, 2H), 1.28 (t, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 173.3, 166.7, 137.8, 127.1, 60.9, 51.8, 51.7, 43.9, 34.8, 31.8, 27.1, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}): 2956, 1712, 1435, 1159, 1138; HRMS (CI) calcd $C_{13}H_{21}O_6$ $[M + H]^+$: 273.1338, found: 273.1343.

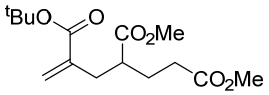


Dimethyl 2-(2-methylallyl)pentanedioate (4a): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 40:1 to 20:1) to give the colorless oil; 43% yield (19 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (s, 1H), 4.70 (s, 1H), 3.66 (s, 6H), 2.71 – 2.55 (m, 1H), 2.47 – 2.22 (m, 3H), 2.15 (dd, *J* = 14.1, 6.7 Hz, 1H), 1.86 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.71 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.7, 173.5, 142.6, 112.7, 51.8, 51.7, 43.1, 40.7, 31.8, 27.0, 22.2; FT-IR (thin film,

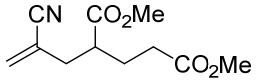
KBr): ν (cm^{-1}): 2950, 1720, 1435, 1159, 891; HRMS (CI) calcd $C_{11}H_{19}O_4$ $[M + H]^+$: 215.1283, found: 215.1286.



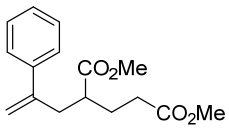
5-Benzyl 1,3-dimethyl hex-5-ene-1,3,5-tricarboxylate (4b): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 5:1) to give the colorless oil; 57% yield (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 5H), 6.25 (s, 1H), 5.62 (s, 1H), 5.20 (s, 2H), 3.65 (s, 3H), 3.62 (s, 3H), 2.79 – 2.68 (m, 1H), 2.67 – 2.58 (m, 1H), 2.57 – 2.47 (m, 1H), 2.40 – 2.24 (m, 2H), 1.97 – 1.79 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.2, 173.3, 166.5, 137.6, 136.0, 128.7, 128.3, 128.2, 127.6, 66.7, 51.8, 51.7, 43.9, 34.9, 31.8, 27.1; FT-IR (thin film, KBr): ν (cm^{-1}): 2953, 1714, 1432, 1156, 695; HRMS (CI) calcd $C_{18}H_{23}O_6$ $[M + H]^+$: 335.1495, found: 335.1500.



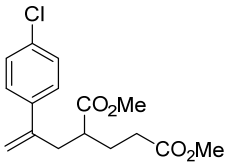
5-(*tert*-Butyl) 1,3-dimethyl hex-5-ene-1,3,5-tricarboxylate (4c): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 5:1) to give the colorless oil; 57% yield (34 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.09 (s, 1H), 5.49 (s, 1H), 3.65 (s, 3H), 3.64 (s, 3H), 2.75 – 2.66 (m, 1H), 2.55 (dd, J = 13.9, 8.6 Hz, 1H), 2.45 (dd, J = 13.9, 6.0 Hz, 1H), 2.39 – 2.26 (m, 2H), 1.95 – 1.80 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.3, 173.4, 165.9, 139.2, 126.2, 81.0, 51.8, 51.7, 44.0, 35.0, 31.8, 28.2, 27.1; FT-IR (thin film, KBr): ν (cm^{-1}): 2947, 1736, 1706, 1156, 846; HRMS (CI) calcd $C_{15}H_{25}O_6$ $[M + H]^+$: 301.1651, found: 301.1639.



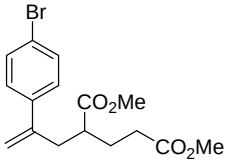
Dimethyl 2-(2-cyanoallyl)pentanedioate (4d): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 5:1) to give the colorless oil; 64% yield (29 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.92 (s, 1H), 5.79 (s, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 2.79 – 2.72 (m, 1H), 2.68 – 2.60 (m, 1H), 2.42 – 2.31 (m, 3H), 1.97 – 1.88 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 173.0, 132.9, 120.3, 118.1, 52.1, 51.9, 43.1, 37.0, 31.0, 26.7; FT-IR (thin film, KBr): ν (cm^{-1}): 2950, 1727, 1438, 1203, 1162; HRMS (CI) calcd $C_{11}H_{16}NO_4$ $[M + H]^+$: 226.1079, found: 226.1080.



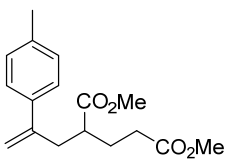
Dimethyl 2-(2-phenylallyl)pentanedioate (4e): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 67% yield (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 5H), 5.30 (s, 1H), 5.10 (s, 1H), 3.62 (s, 3H), 3.60 (s, 3H), 2.91 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.64 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.60 – 2.49 (m, 1H), 2.42 – 2.17 (m, 2H), 1.96 – 1.81 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 173.4, 145.7, 140.4, 128.5, 127.8, 126.4, 115.0, 51.7, 51.7, 43.5, 38.2, 31.8, 26.8; FT-IR (thin film, KBr): ν (cm^{-1}): 2953, 1726, 1203, 1162, 778; HRMS (CI) calcd $C_{16}H_{21}O_4$ $[M + H]^+$: 277.1440, found: 277.1440.



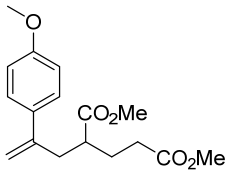
Dimethyl 2-(2-(4-chlorophenyl)allyl)pentanedioate (4f): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 62% yield (39 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 5.27 (s, 1H), 5.10 (s, 1H), 3.62 (s, 3H), 3.59 (s, 3H), 2.85 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.61 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.54 – 2.47 (m, 1H), 2.37 – 2.28 (m, 1H), 2.27 – 2.19 (m, 1H), 1.94 – 1.80 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.3, 173.3, 144.6, 138.9, 133.6, 128.7, 127.7, 115.5, 51.8, 51.7, 43.5, 38.2, 31.7, 26.8; FT-IR (thin film, KBr): ν (cm^{-1}): 2950, 1730, 1435, 1162, 831; HRMS (CI) calcd $C_{16}H_{20}O_4{}^{35}Cl$ $[M + H]^+$: 311.1050, found: 311.1054.



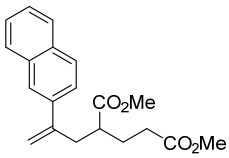
Dimethyl 2-(2-(4-bromophenyl)allyl)pentanedioate (4g): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 66% yield (47 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.28 (s, 1H), 5.11 (s, 1H), 3.62 (s, 3H), 3.59 (s, 3H), 2.85 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.60 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.36 – 2.28 (m, 1H), 2.28 – 2.18 (m, 1H), 1.93 – 1.82 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.1, 173.1, 144.5, 139.2, 131.5, 127.9, 121.6, 115.4, 51.6, 51.5, 43.3, 38.0, 31.6, 26.7; FT-IR (thin film, KBr): ν (cm^{-1}): 2947, 1726, 1432, 1162, 831; HRMS (CI) calcd $C_{16}H_{20}O_4{}^{79}Br$ $[M + H]^+$: 355.0545, found: 355.0554.



Dimethyl 2-(2-(p-tolyl)allyl)pentanedioate (4h): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 63% yield (37 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.26 (s, 1H), 5.05 (s, 1H), 3.62 (s, 3H), 3.60 (s, 3H), 2.88 (dd, *J* = 14.3, 7.7 Hz, 1H), 2.62 (dd, *J* = 14.3, 7.0 Hz, 1H), 2.57 – 2.50 (m, 1H), 2.35 (s, 3H), 2.32 – 2.28 (m, 1H), 2.28 – 2.19 (m, 1H), 1.92 – 1.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 173.4, 145.4, 137.5, 137.4, 129.2, 126.2, 114.1, 51.7, 51.6, 43.5, 38.2, 31.7, 26.8, 21.2; FT-IR (thin film, KBr): ν (cm^{-1}): 2953, 1726, 1432, 1159, 828; HRMS (CI) calcd $C_{17}H_{23}O_4$ $[M + H]^+$: 291.1596, found: 291.1599.



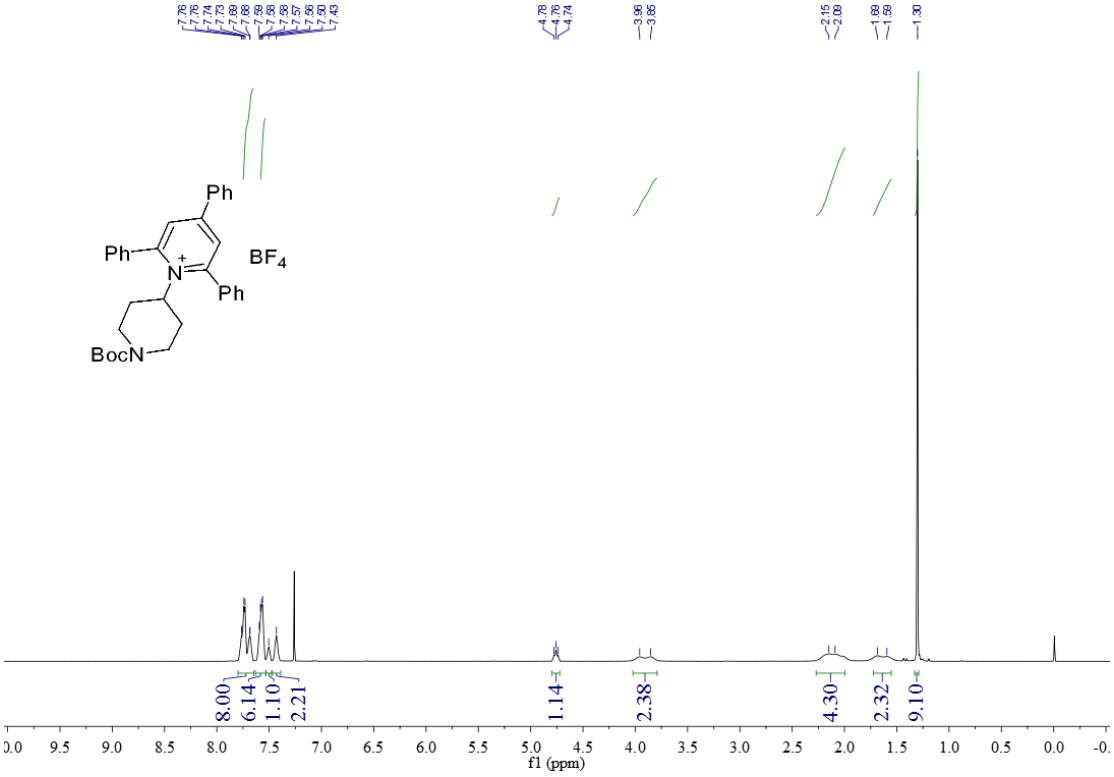
Dimethyl 2-(2-(4-methoxyphenyl)allyl)pentanedioate (4i): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 60% yield (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 5.22 (s, 1H), 4.99 (d, *J* = 15.6 Hz, 1H), 3.81 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 2.87 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.69 – 2.45 (m, 2H), 2.39 – 2.14 (m, 2H), 1.95 – 1.79 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 173.4, 159.3, 132.8, 130.1, 127.5, 113.9, 113.5, 55.4, 51.74, 51.68, 43.5, 38.3, 31.8, 26.8; FT-IR (thin film, KBr): ν (cm^{-1}): 2950, 1729, 1510, 1242, 831; HRMS (CI) calcd $C_{17}H_{23}O_5$ $[M + H]^+$: 307.1545, found: 307.1546.



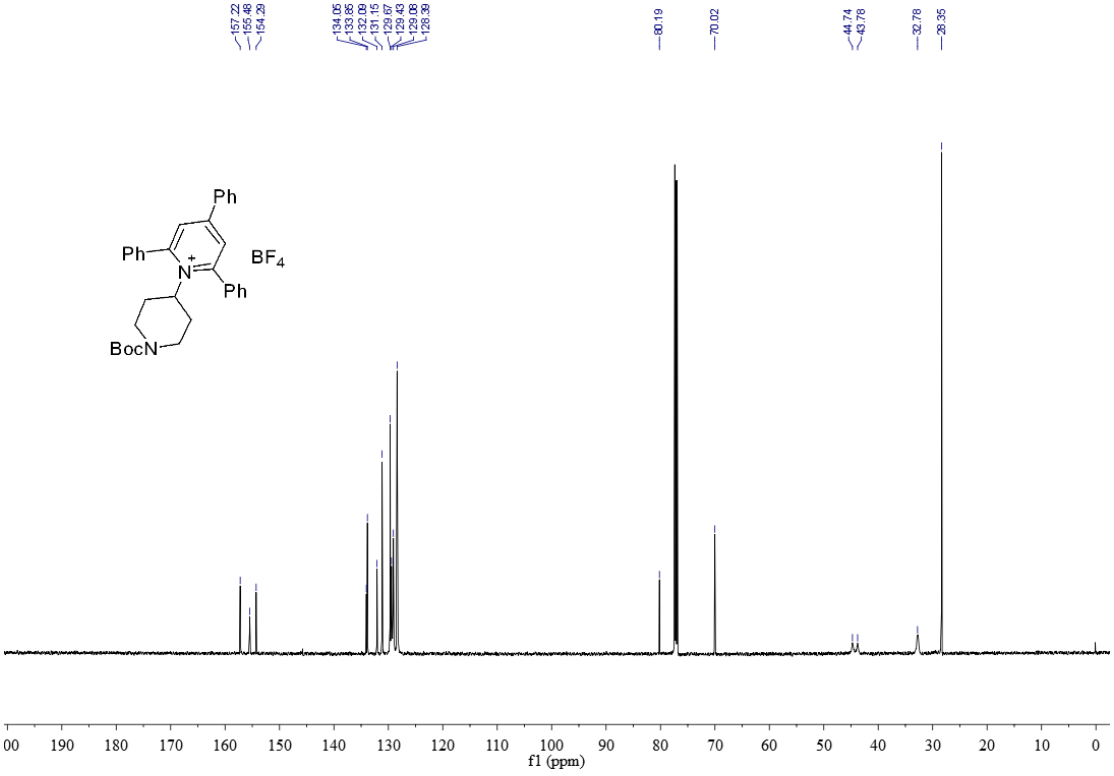
Dimethyl 2-(2-(naphthalen-2-yl)allyl)pentanedioate (4j): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 57% yield (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 4H), 7.57 – 7.42 (m, 3H), 5.45 (s, 1H), 5.21 (s, 1H), 3.60 (s, 6H), 3.03 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.76 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.65 – 2.54 (m, 1H), 2.40 – 2.19 (m, 2H), 2.00 – 1.88 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 173.4, 145.5, 137.7, 133.5, 133.0, 128.3, 128.1, 127.7, 126.3, 126.1, 125.0, 124.8, 115.5, 51.70, 51.67, 43.6, 38.2, 31.8, 26.9; FT-IR (thin film, KBr): ν (cm^{-1}): 2917, 1727, 1438, 1159, 748; HRMS (CI) calcd $C_{20}H_{23}O_4$ $[M + H]^+$: 327.1596, found: 327.1603.

6. NMR Spectra for the substrates and products

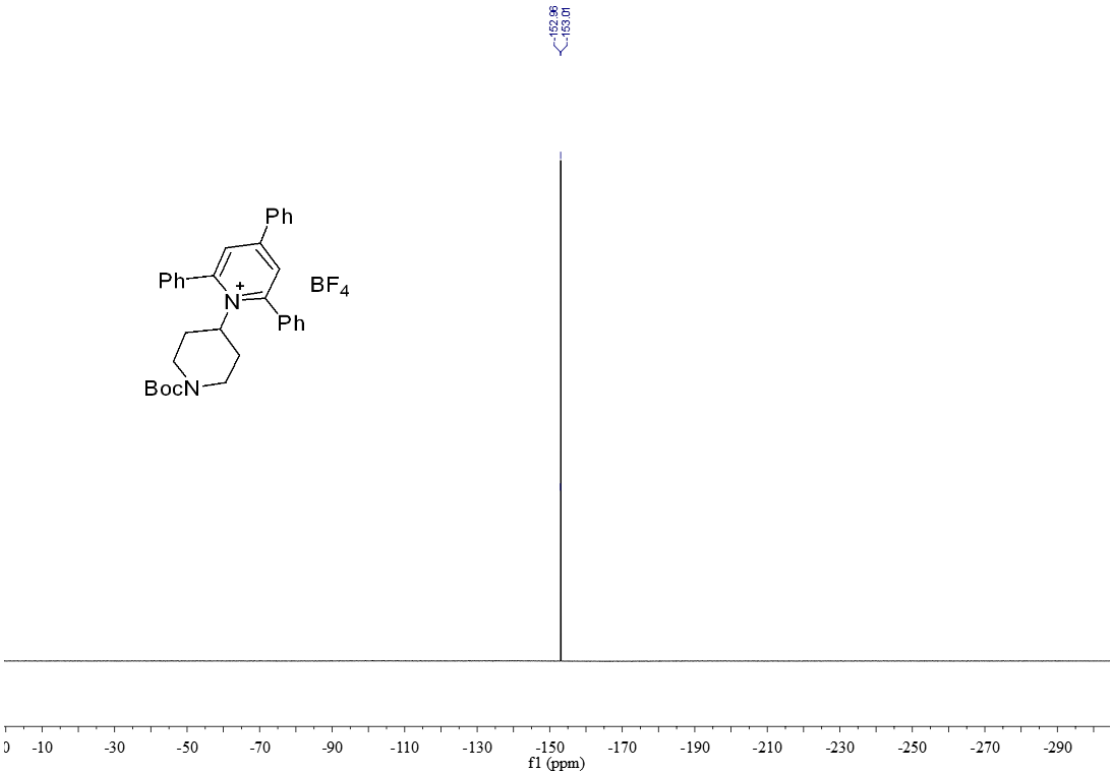
^{1}H NMR of **1a**



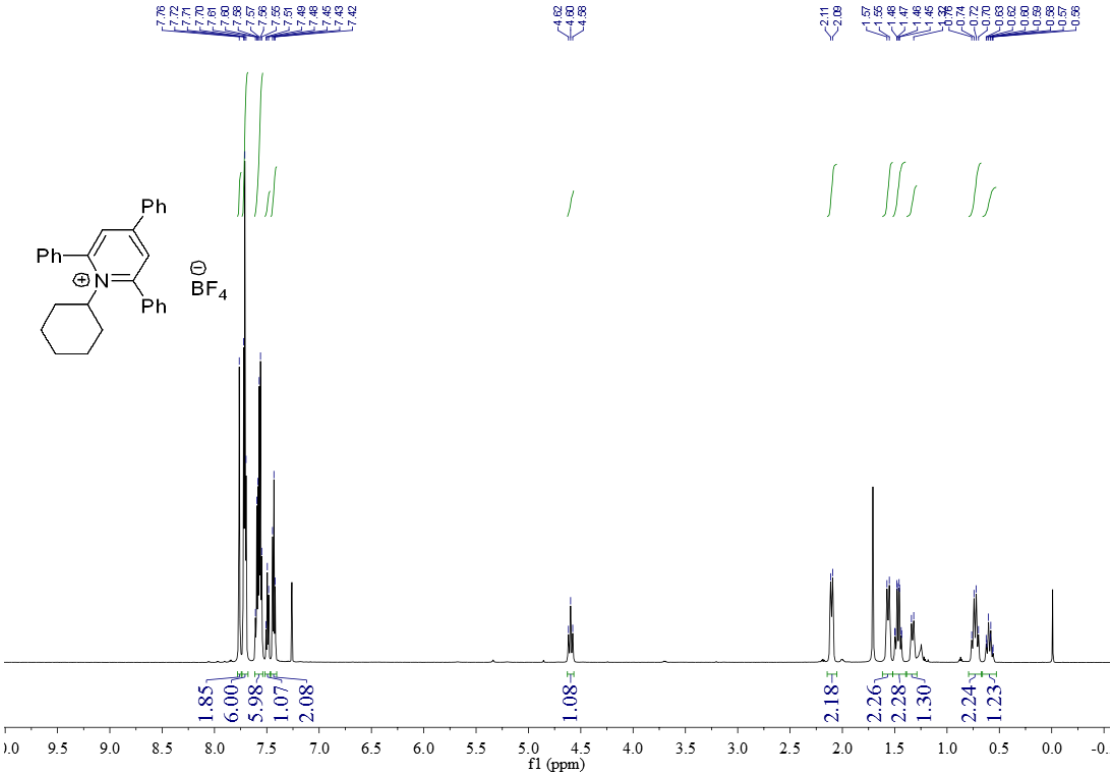
^{13}C NMR of **1a**



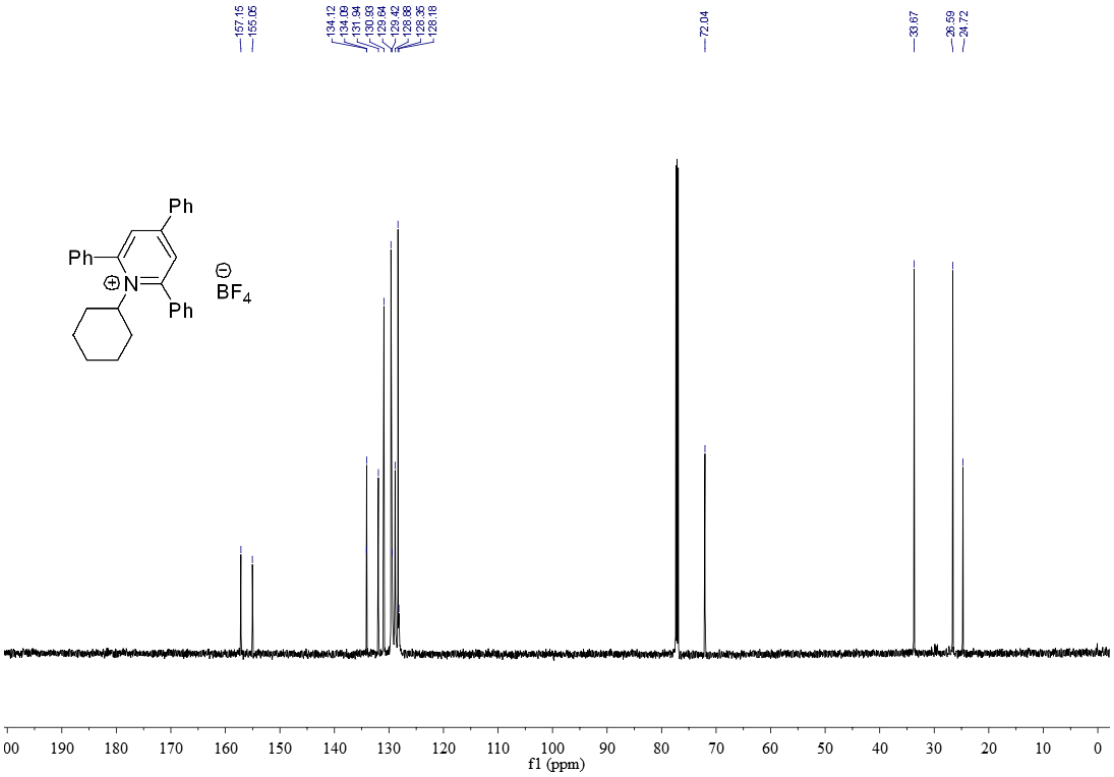
^{19}F NMR of **1a**



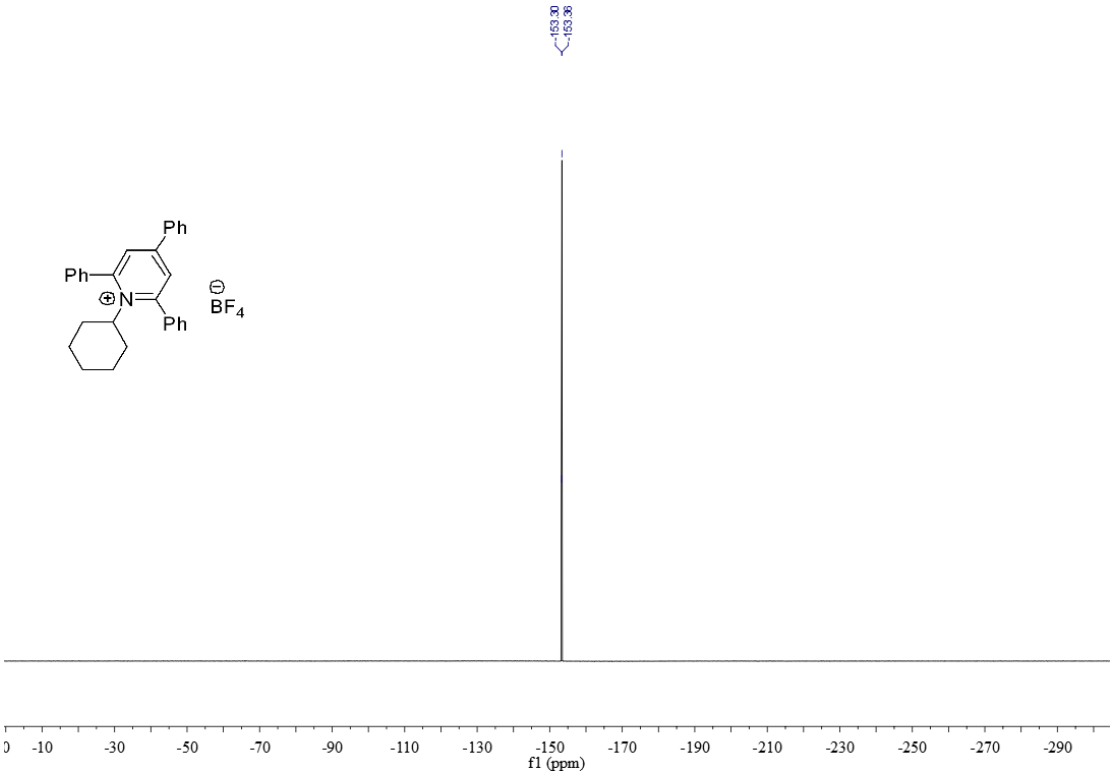
^{1}H NMR of **1b**



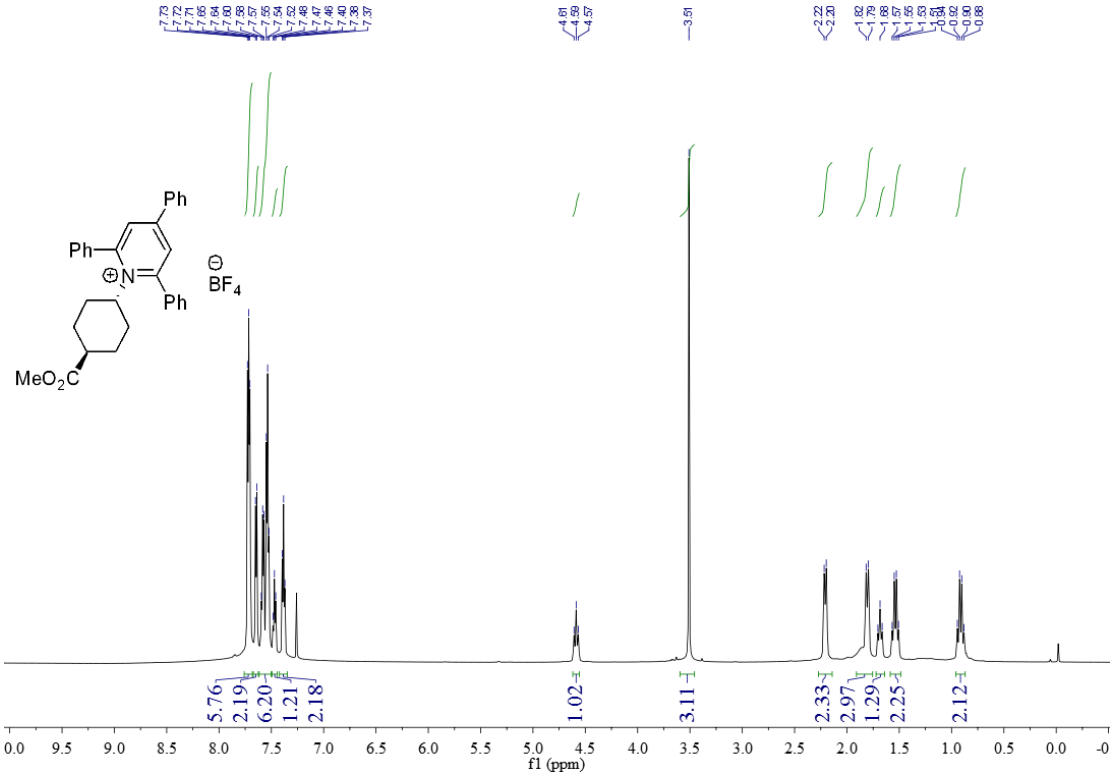
^{13}C NMR of **1b**



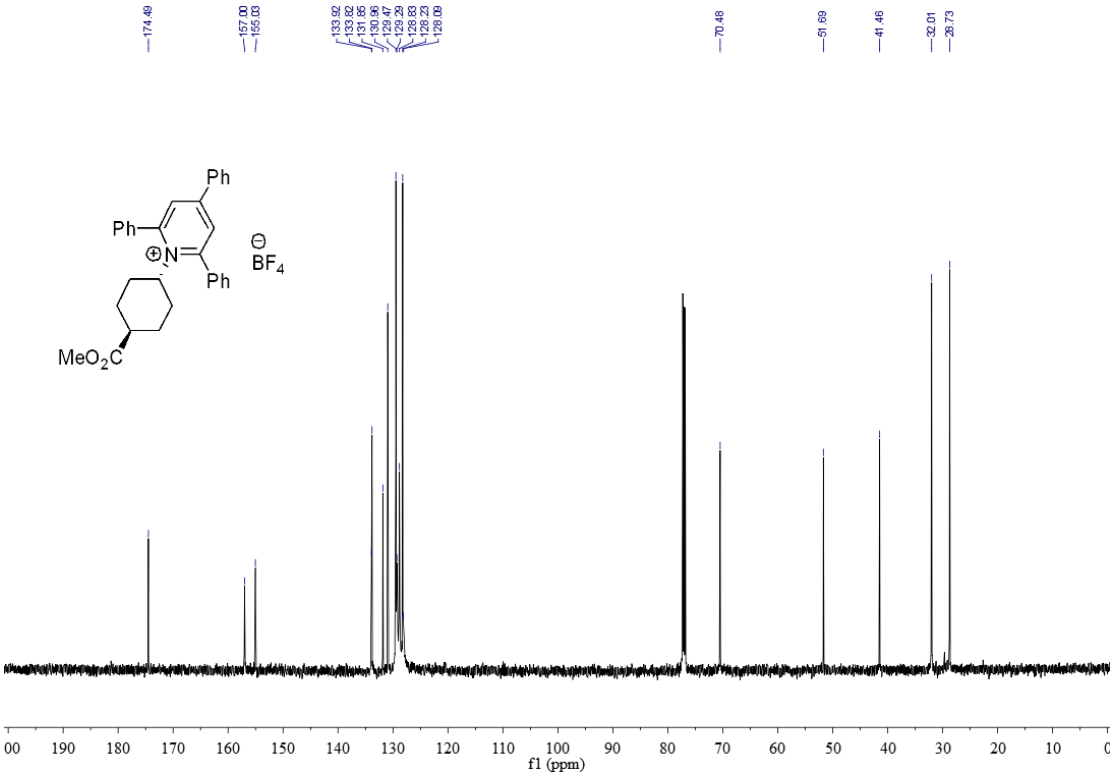
^{19}F NMR of **1b**



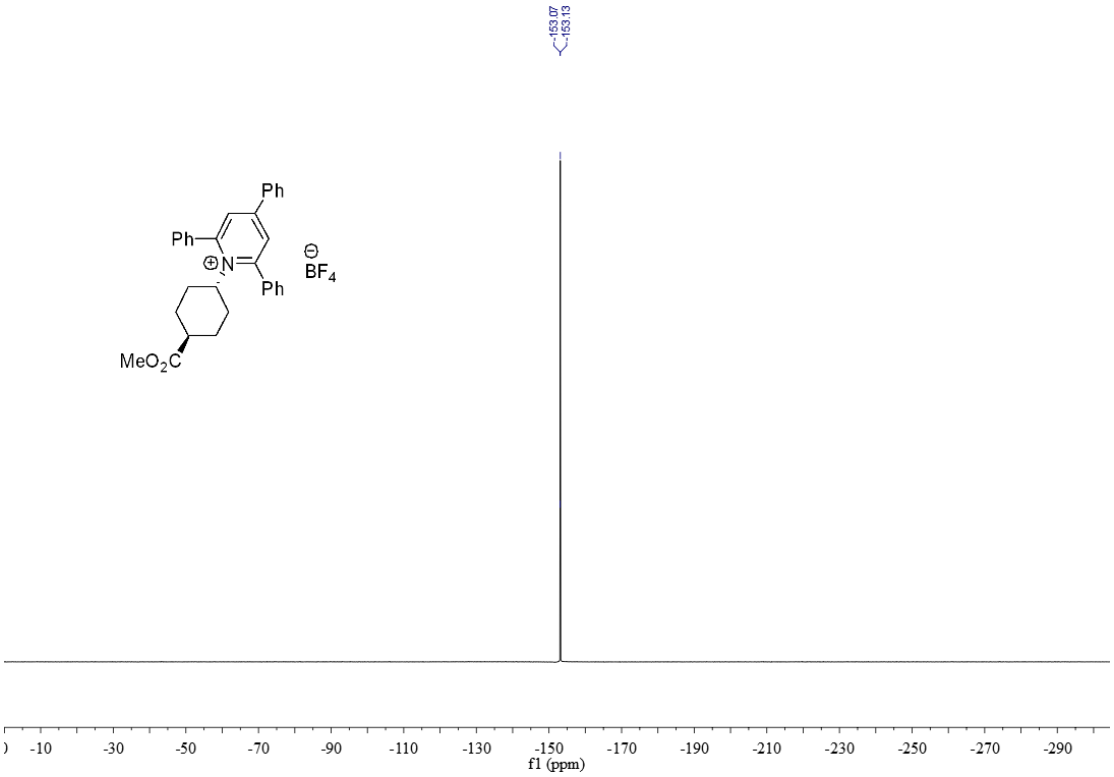
^{1}H NMR of **1c**



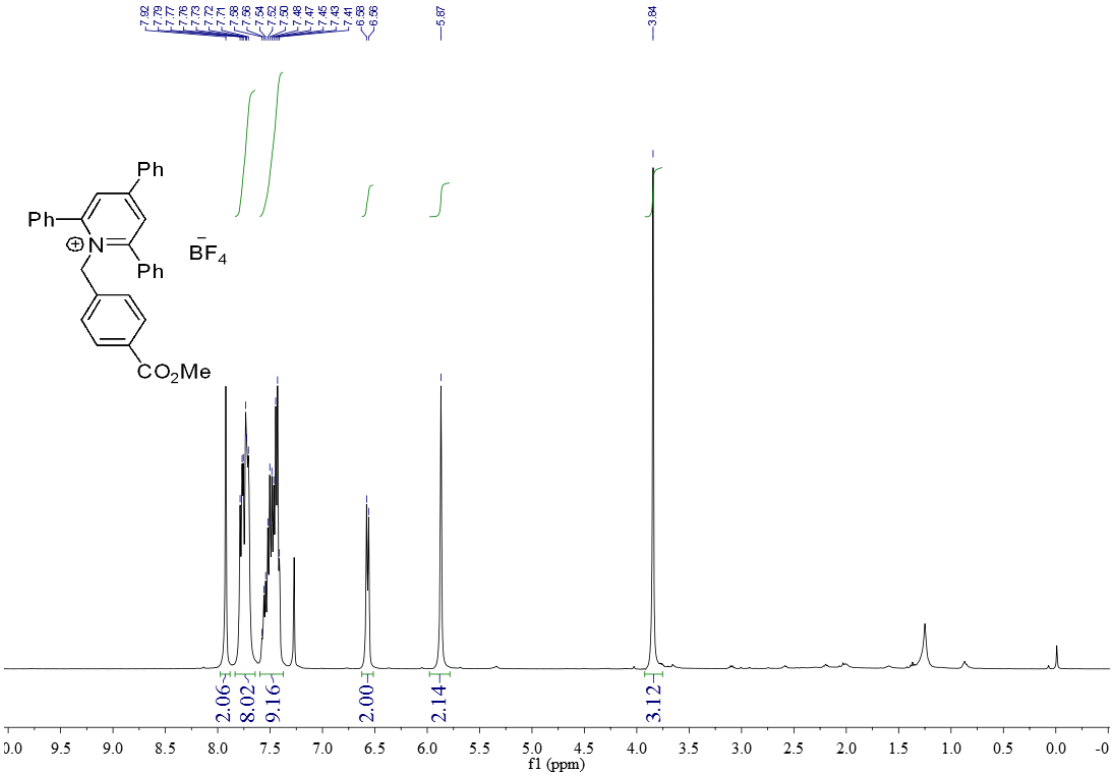
^{13}C NMR of **1c**



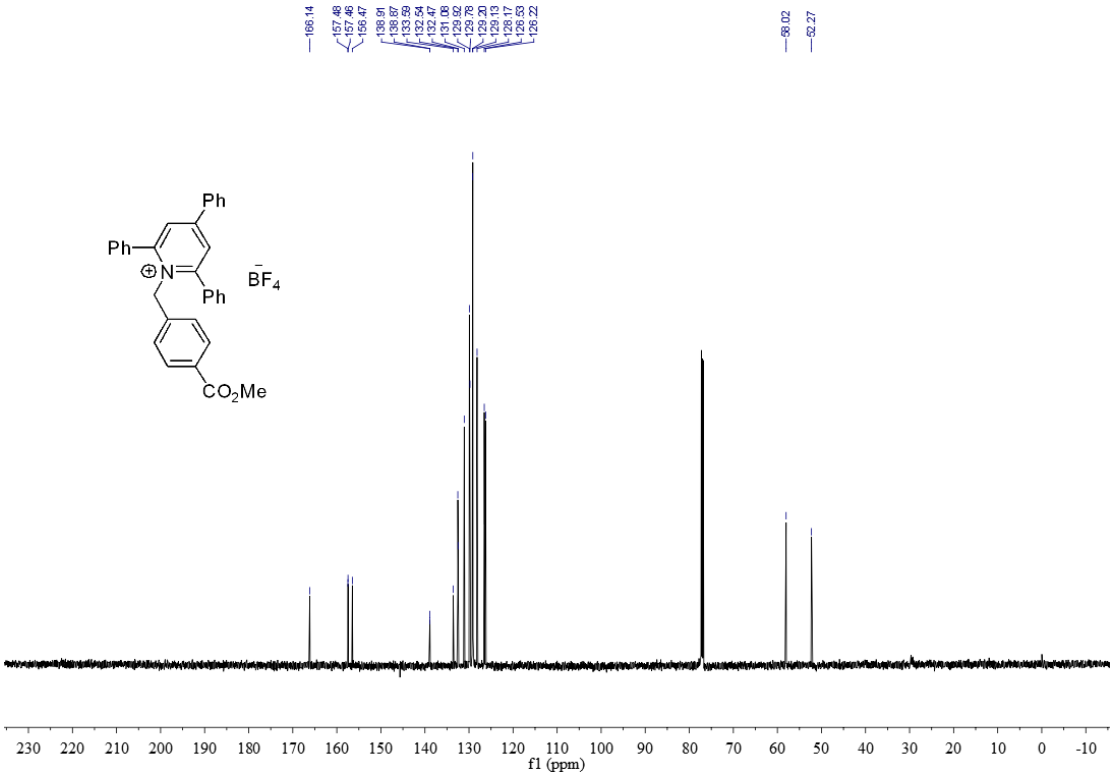
^{19}F NMR of **1c**



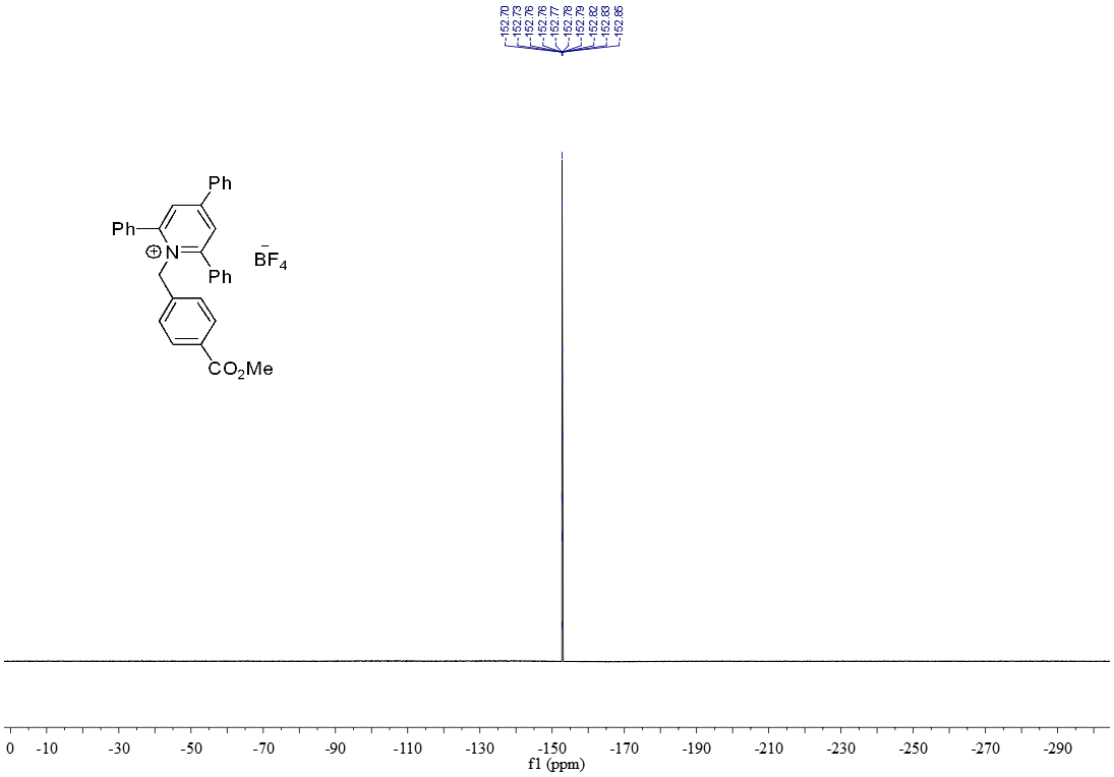
^{1}H NMR of **1d**



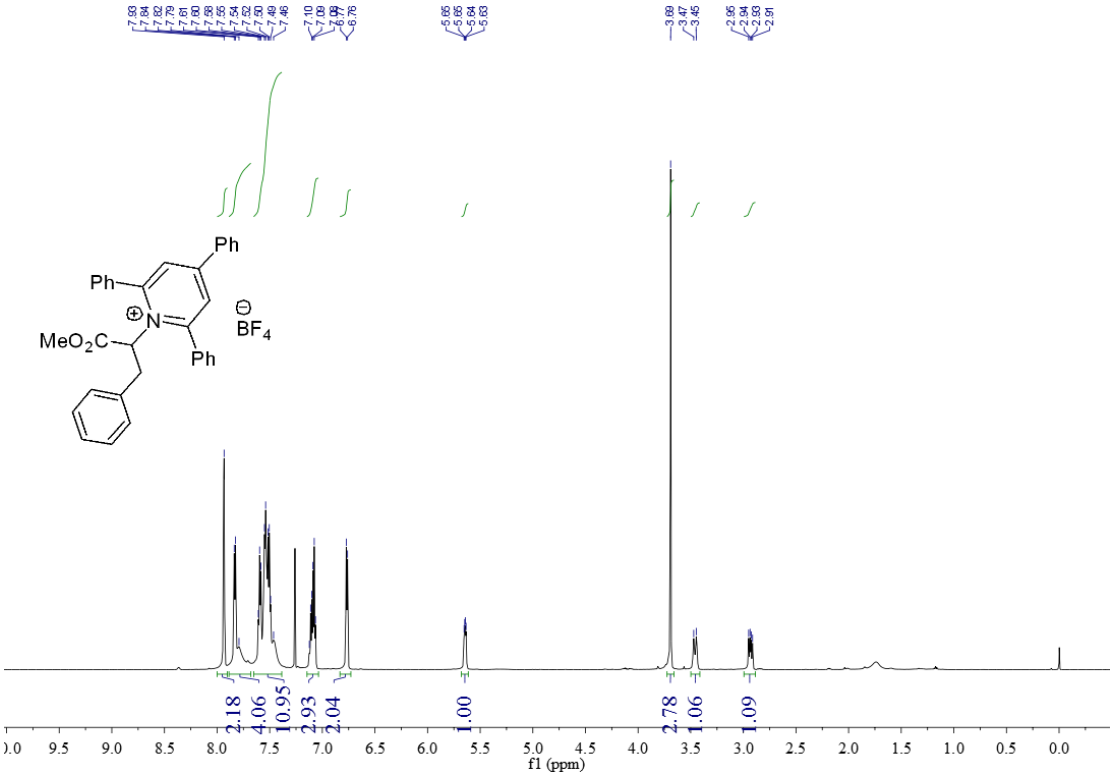
^{13}C NMR of **1d**



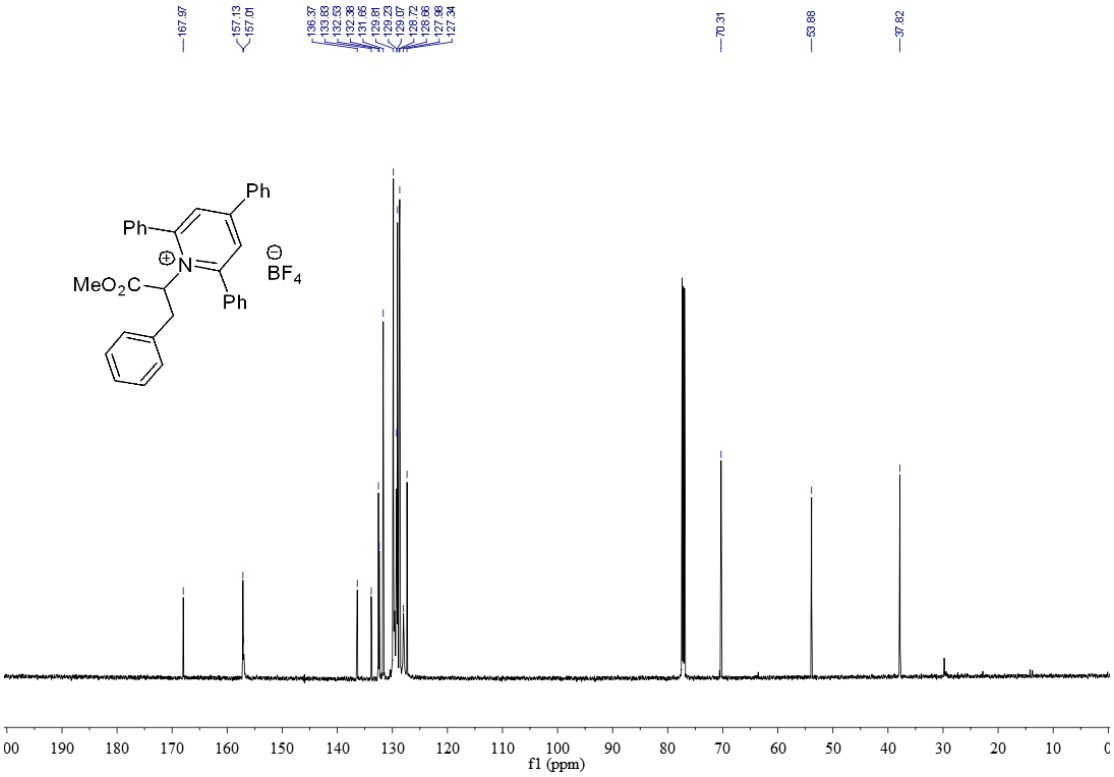
^{19}F NMR of **1d**



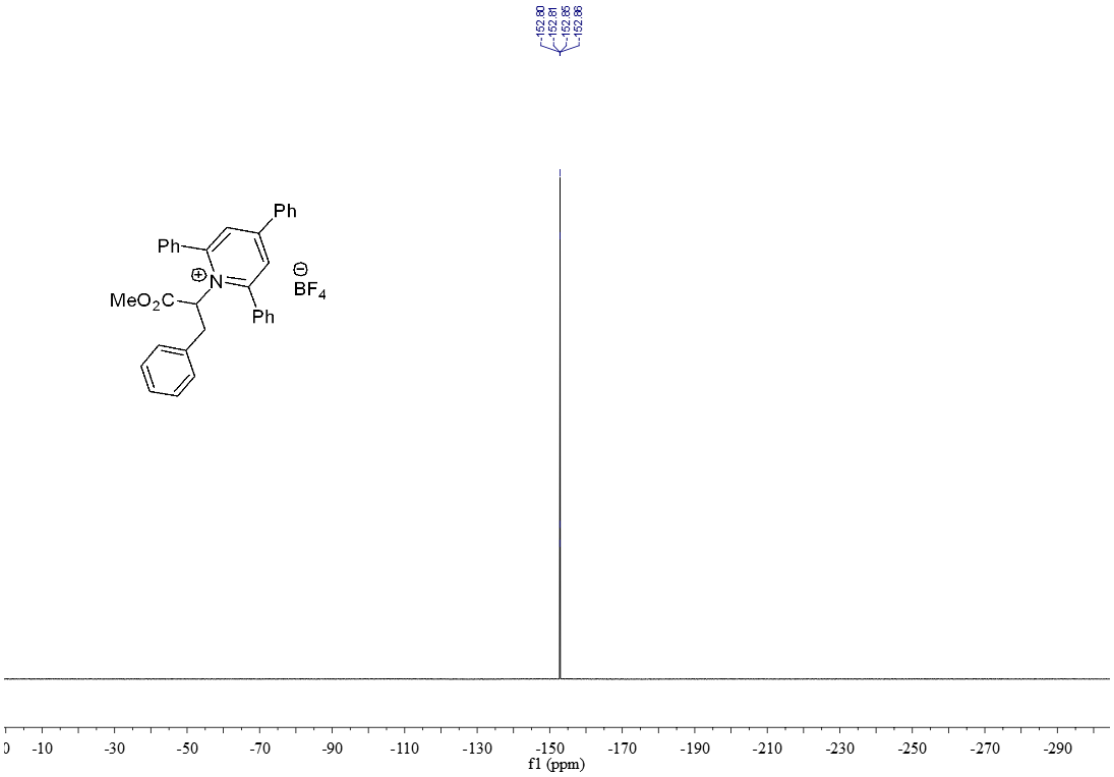
^{1}H NMR of **1e**



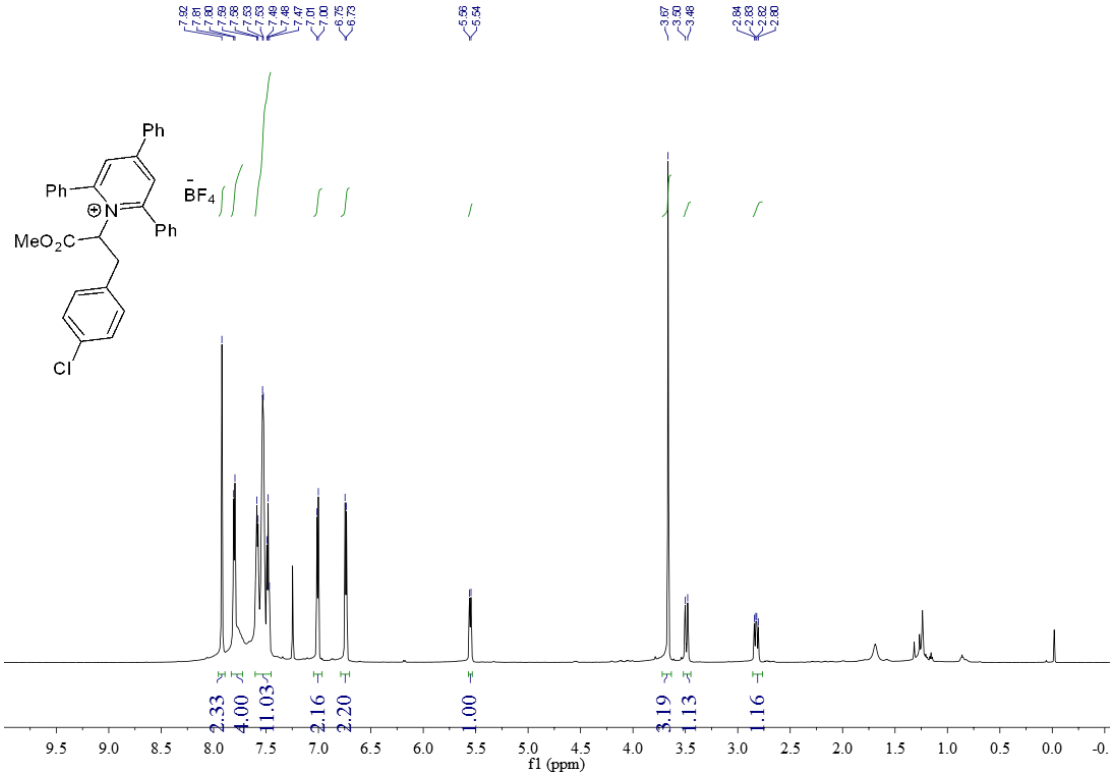
^{13}C NMR of **1e**



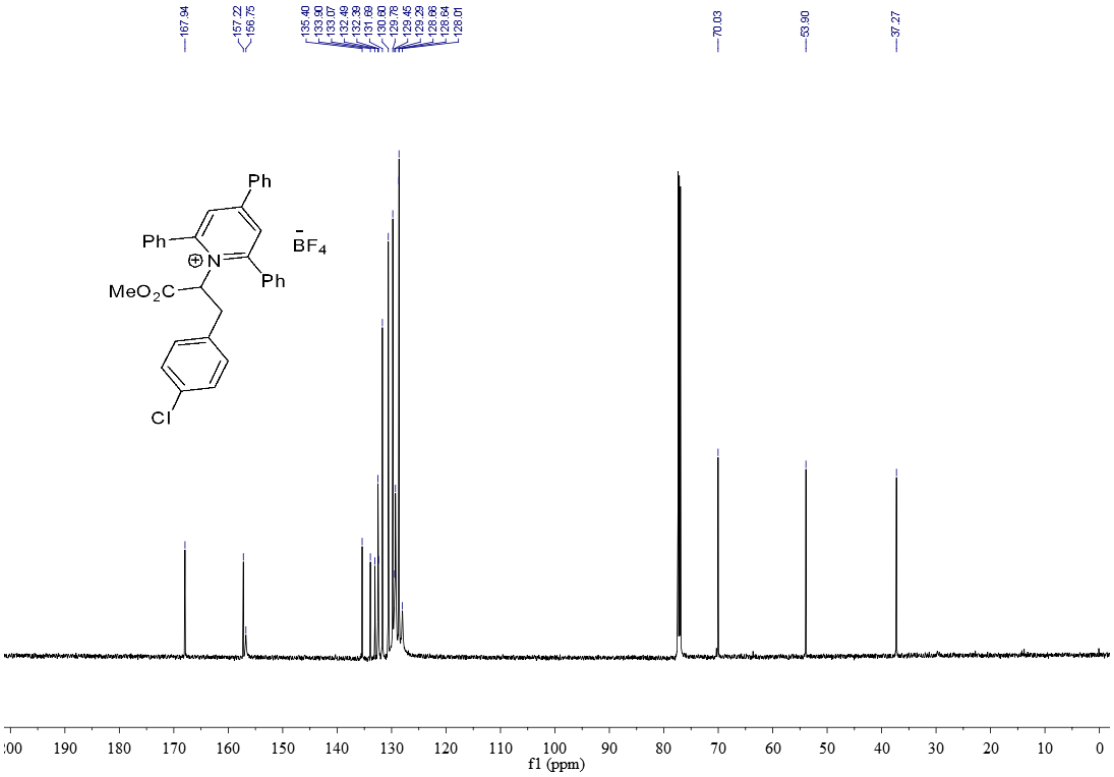
^{19}F NMR of **1e**



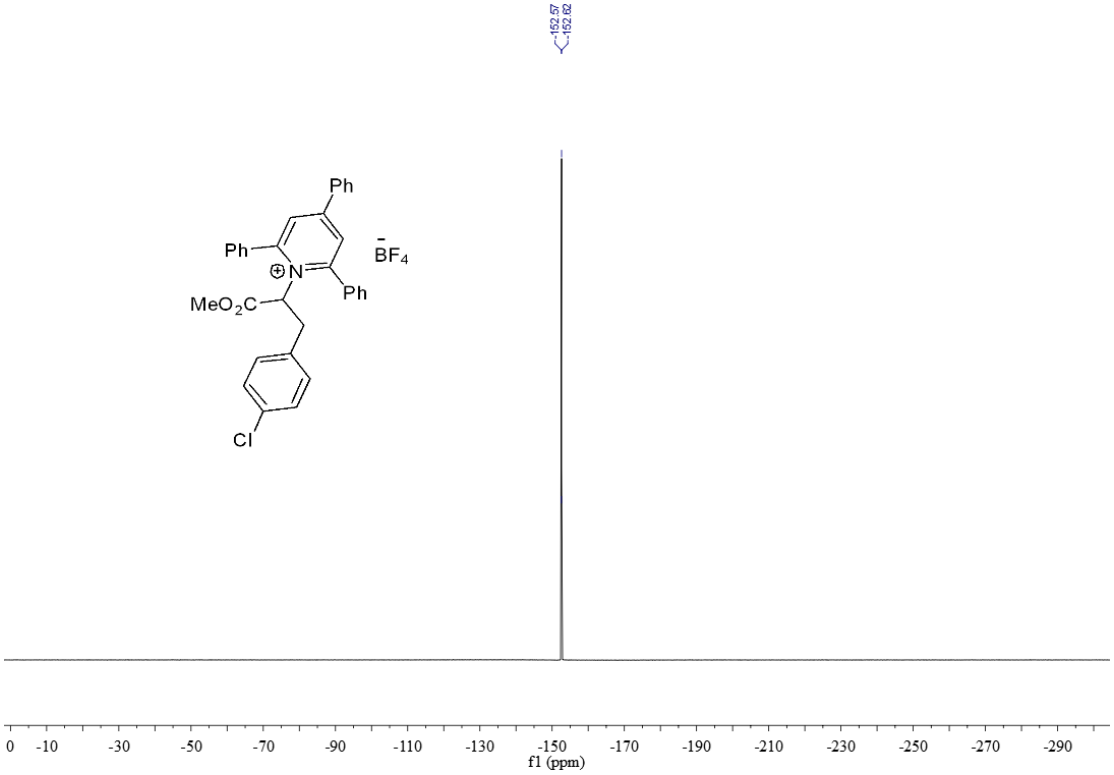
^{1}H NMR of **1f**



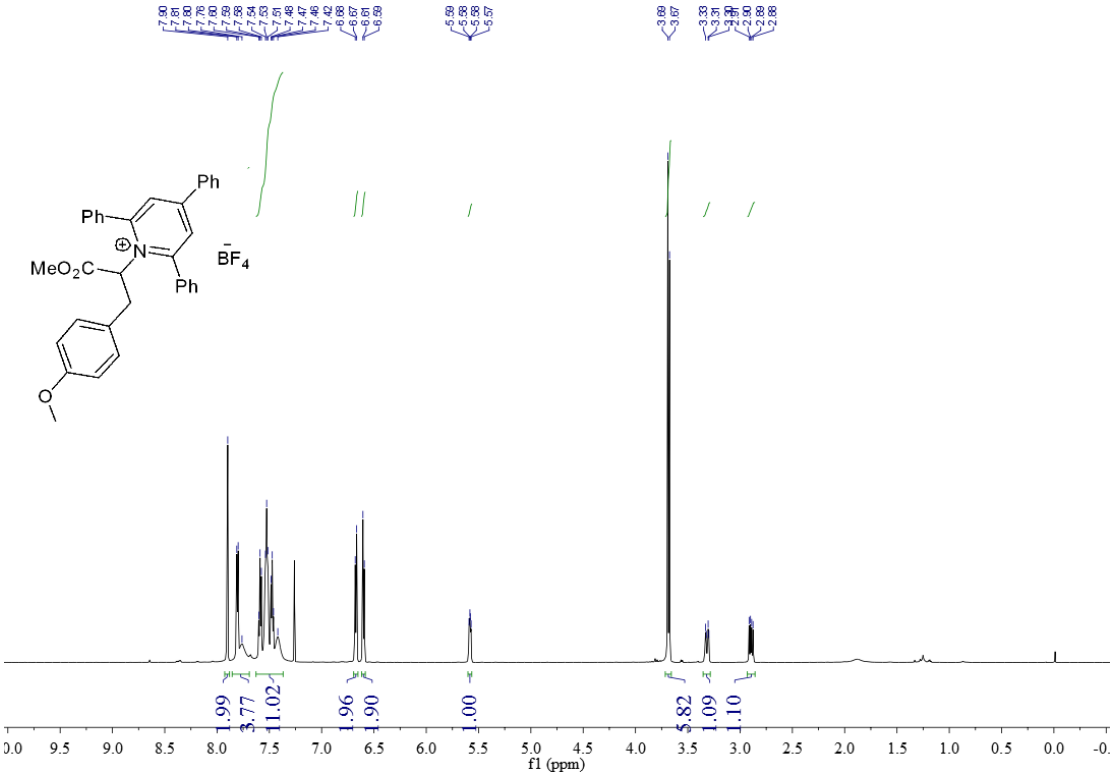
^{13}C NMR of **1f**



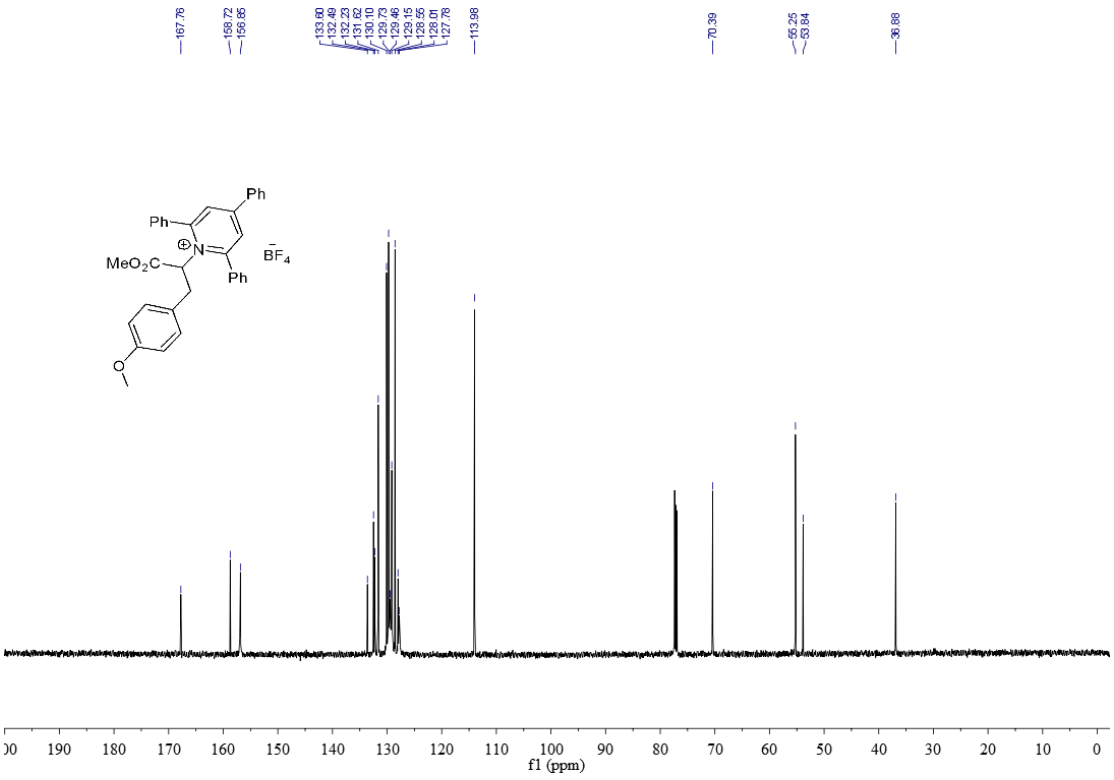
^{19}F NMR of **1f**



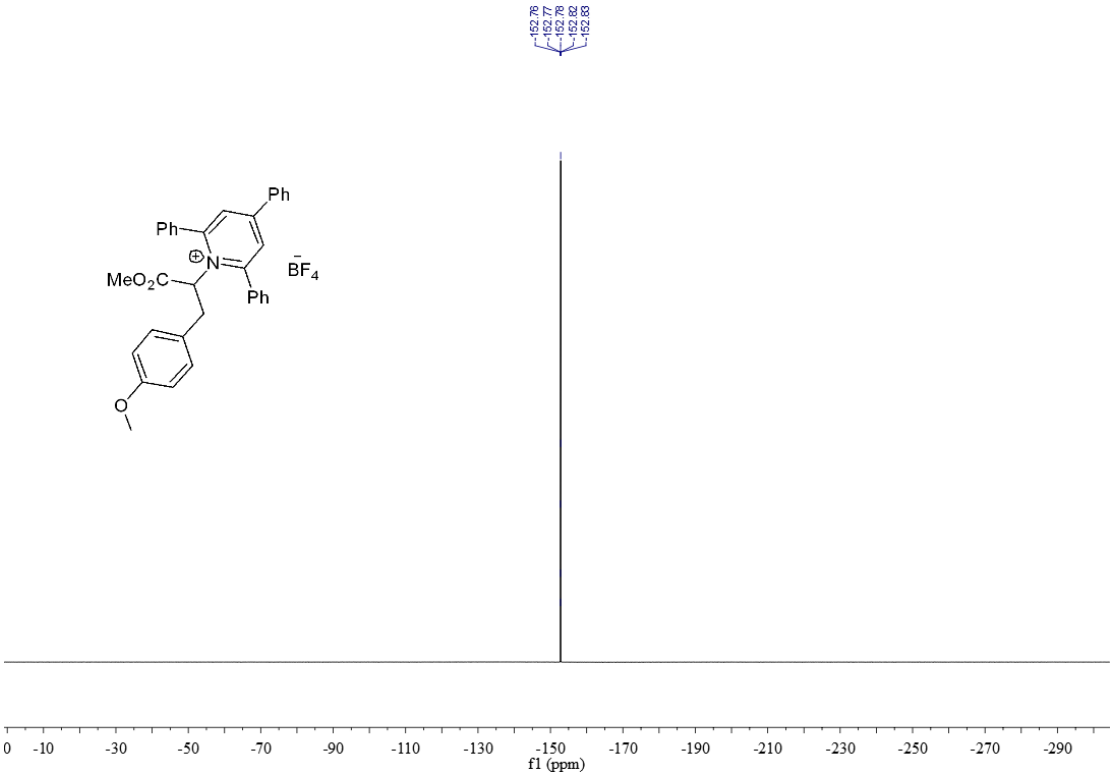
^{1}H NMR of **1g**



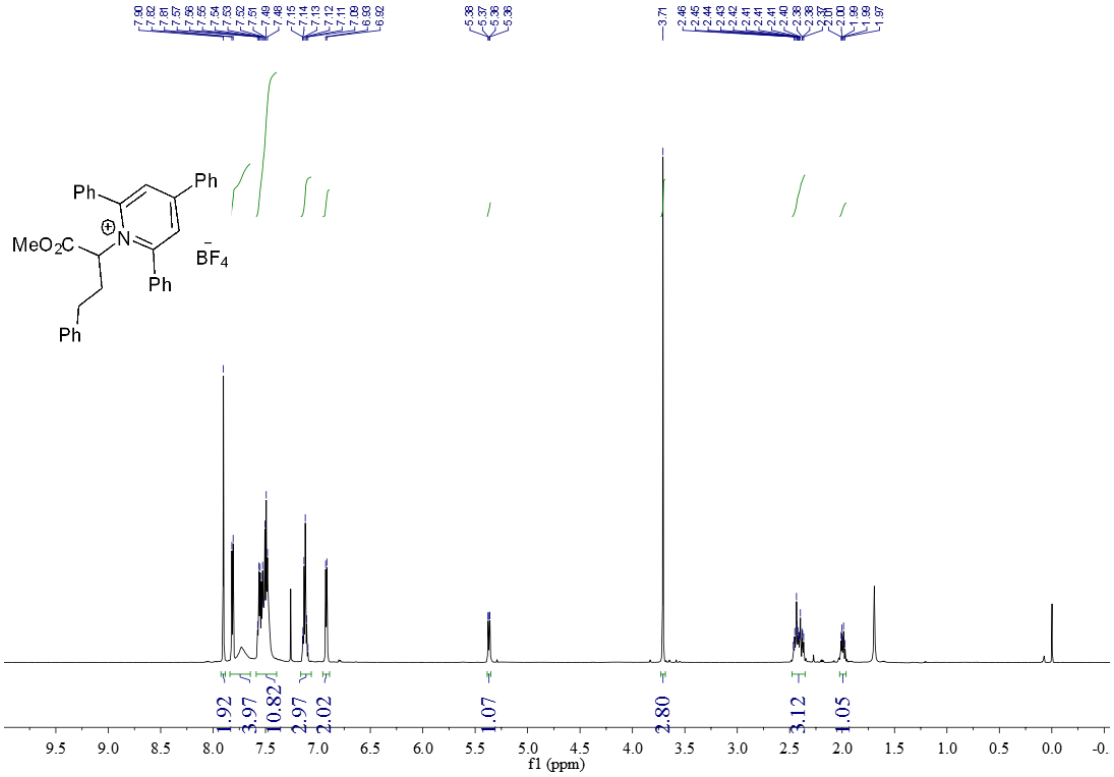
^{13}C NMR of **1g**



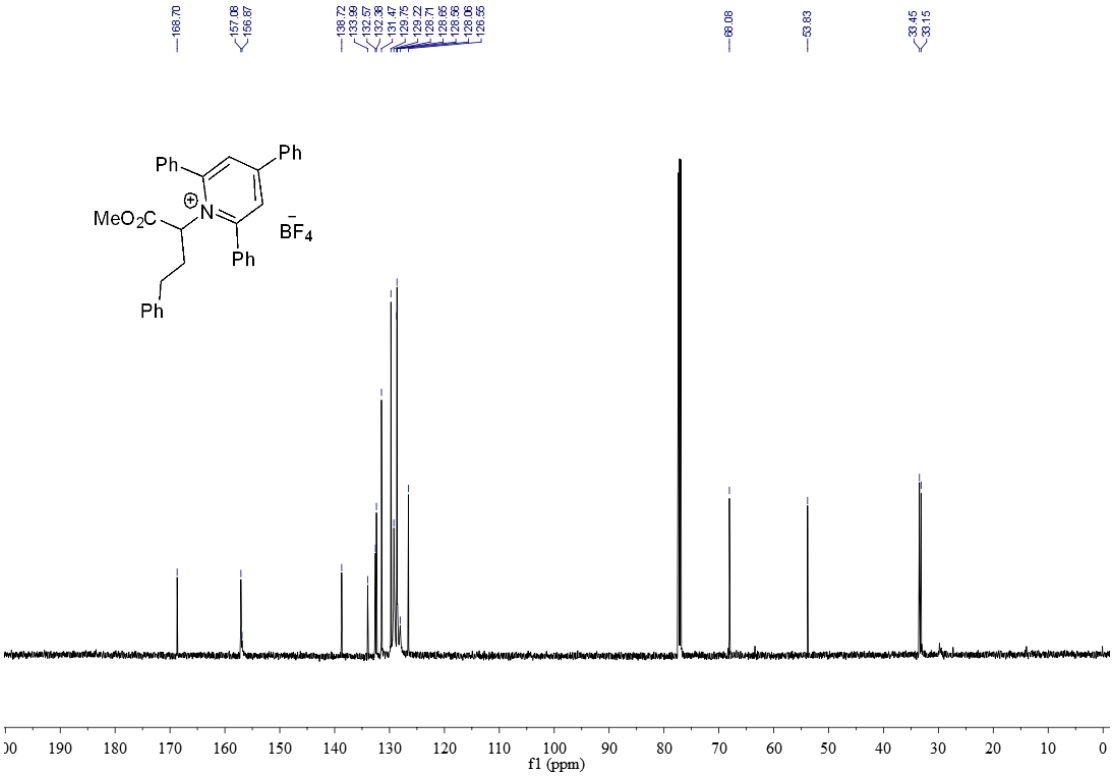
^{19}F NMR of **1g**



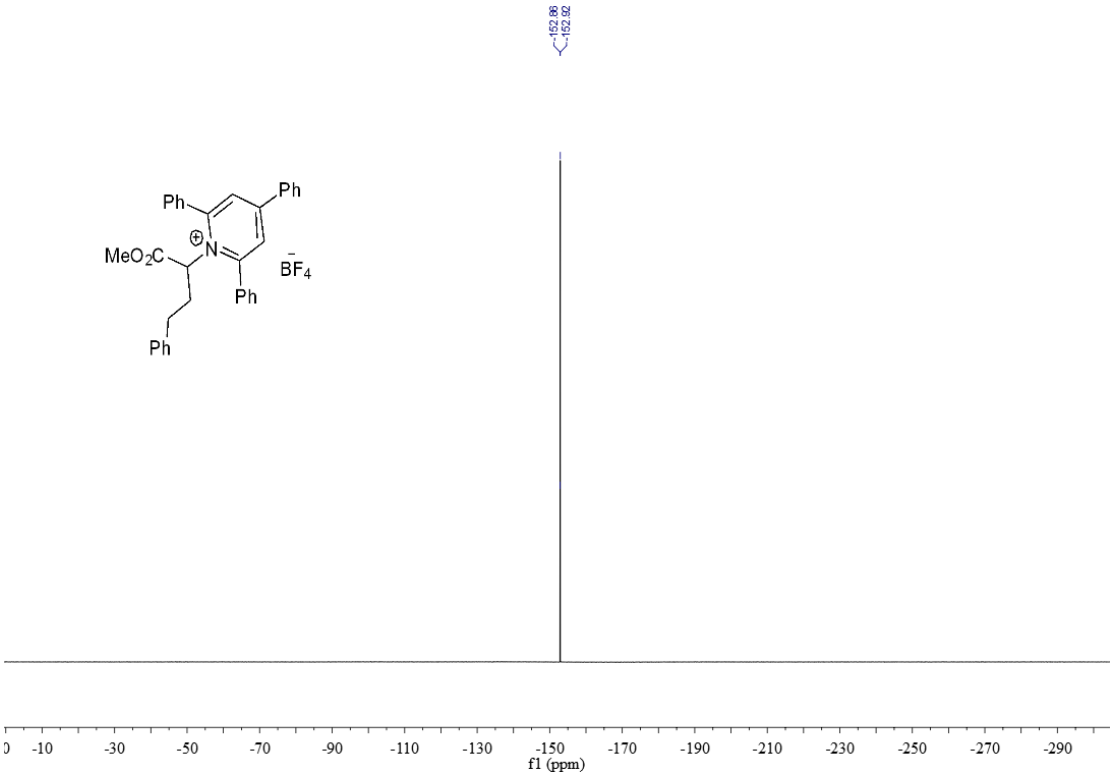
^{1}H NMR of **1h**



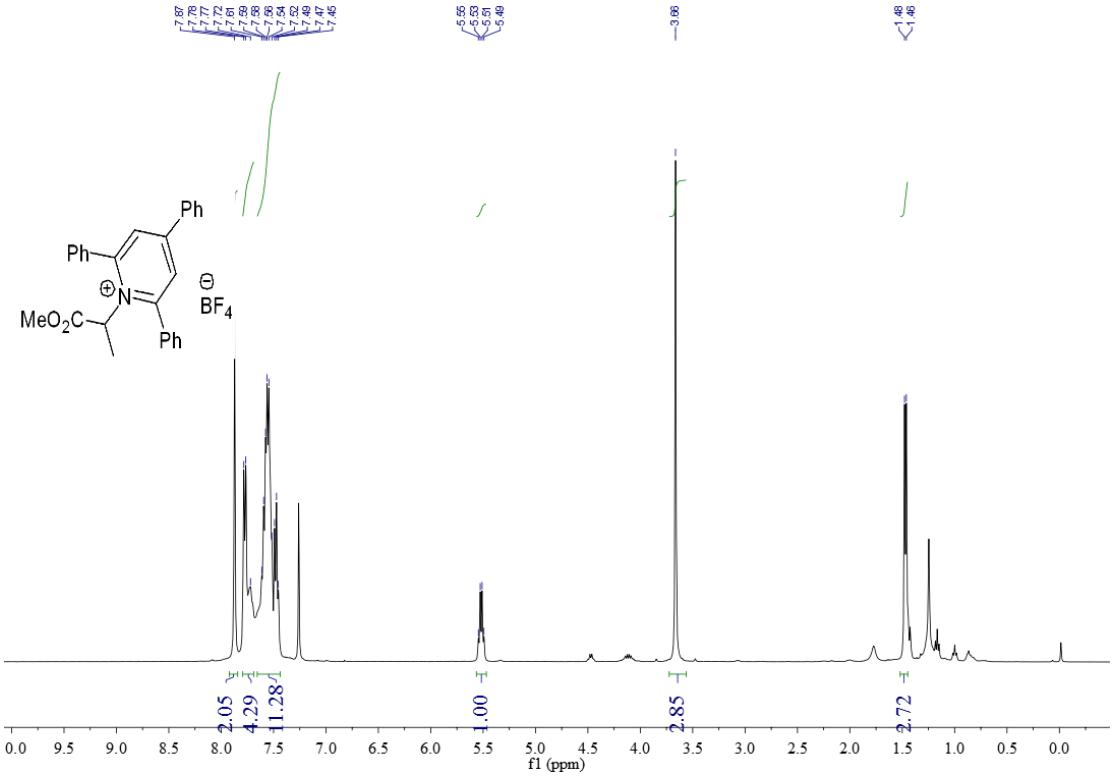
^{13}C NMR of **1h**



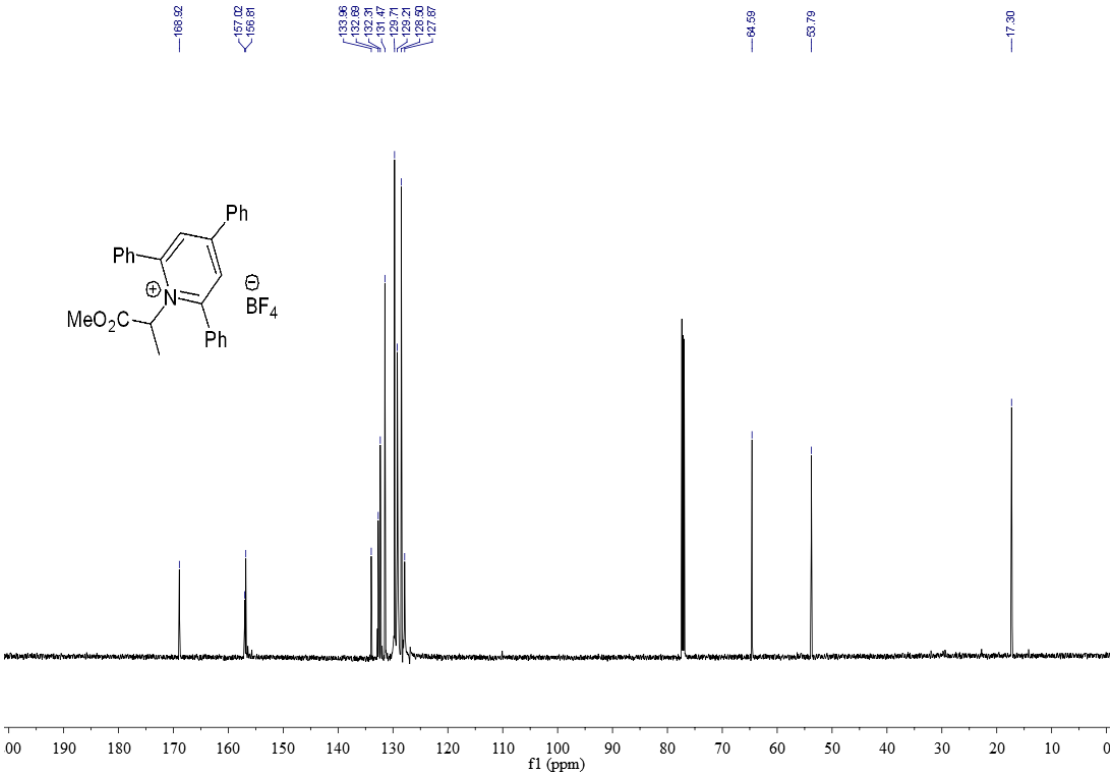
^{19}F NMR of **1h**



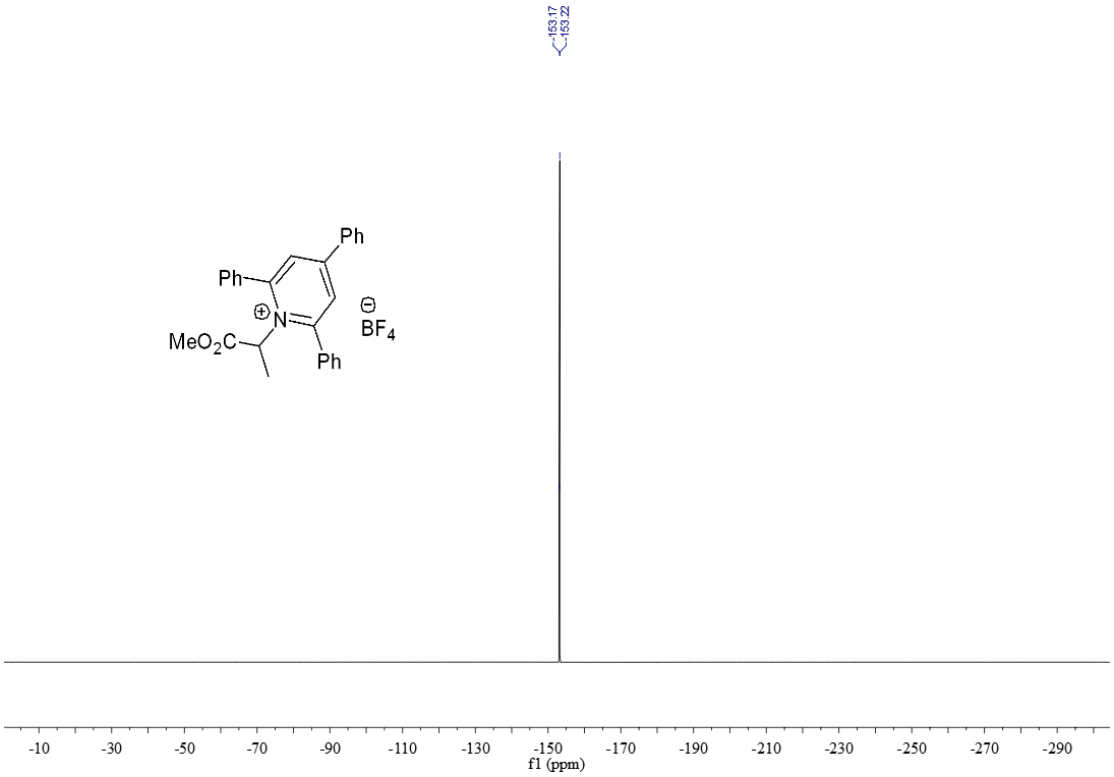
^{1}H NMR of **1i**



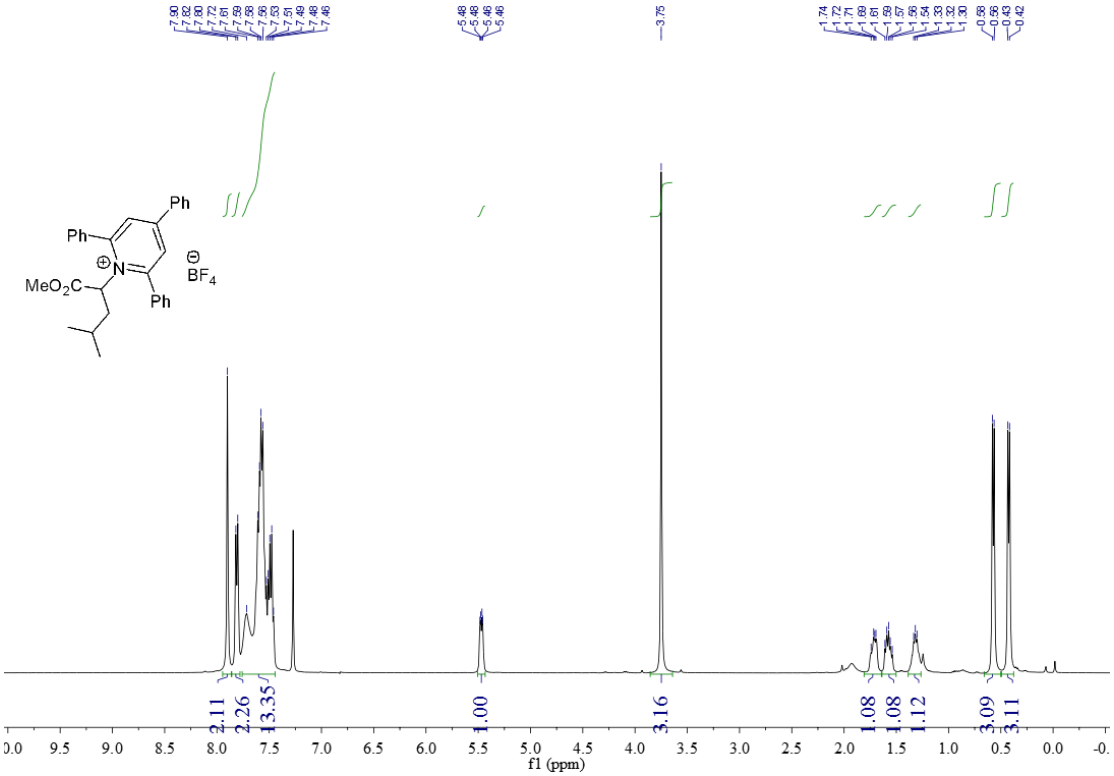
^{13}C NMR of **1i**



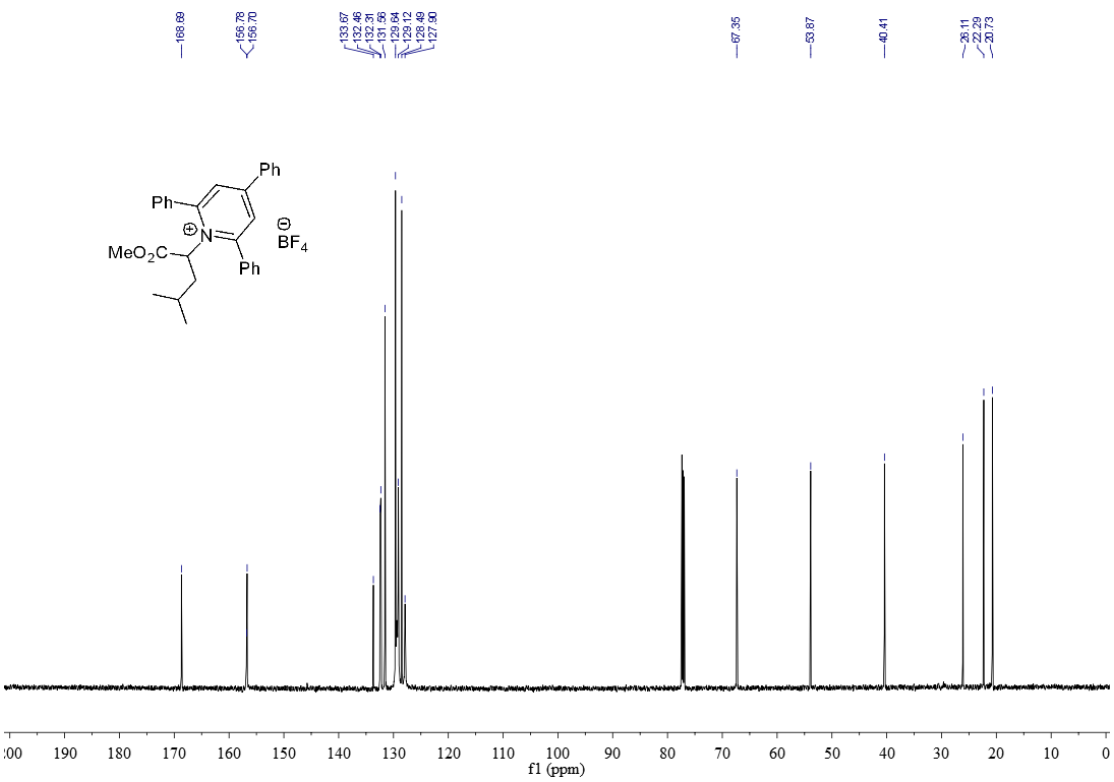
^{19}F NMR of **1i**



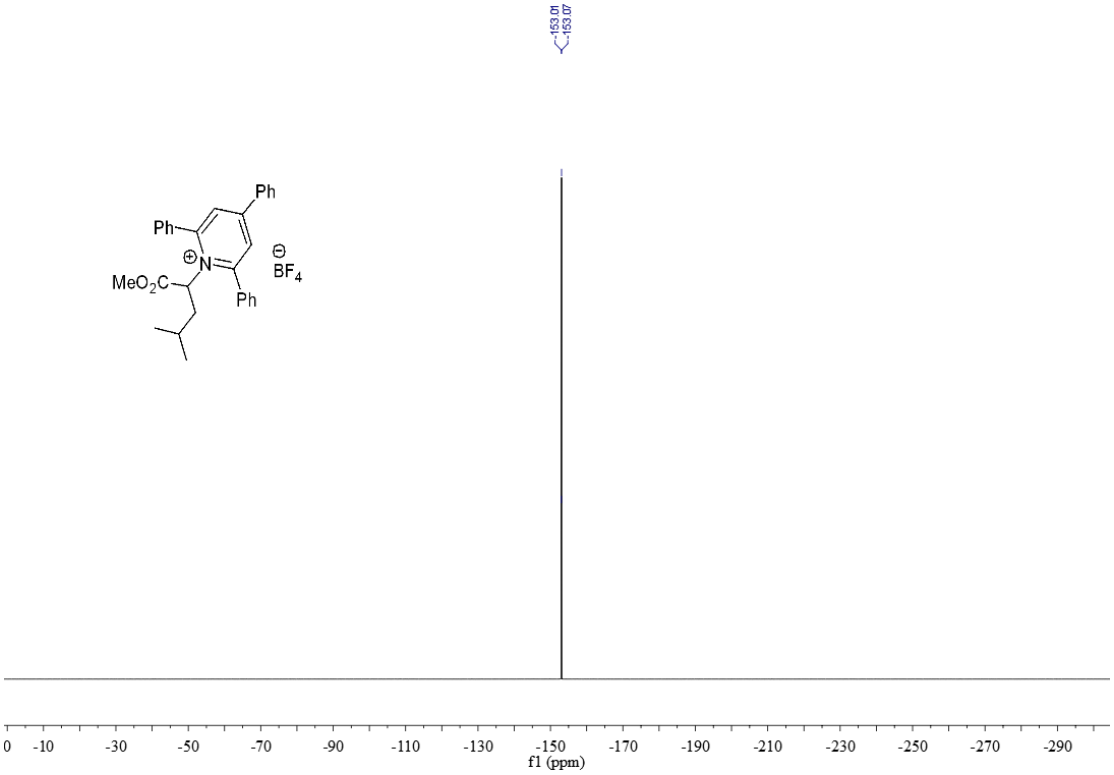
^{1}H NMR of **1j**



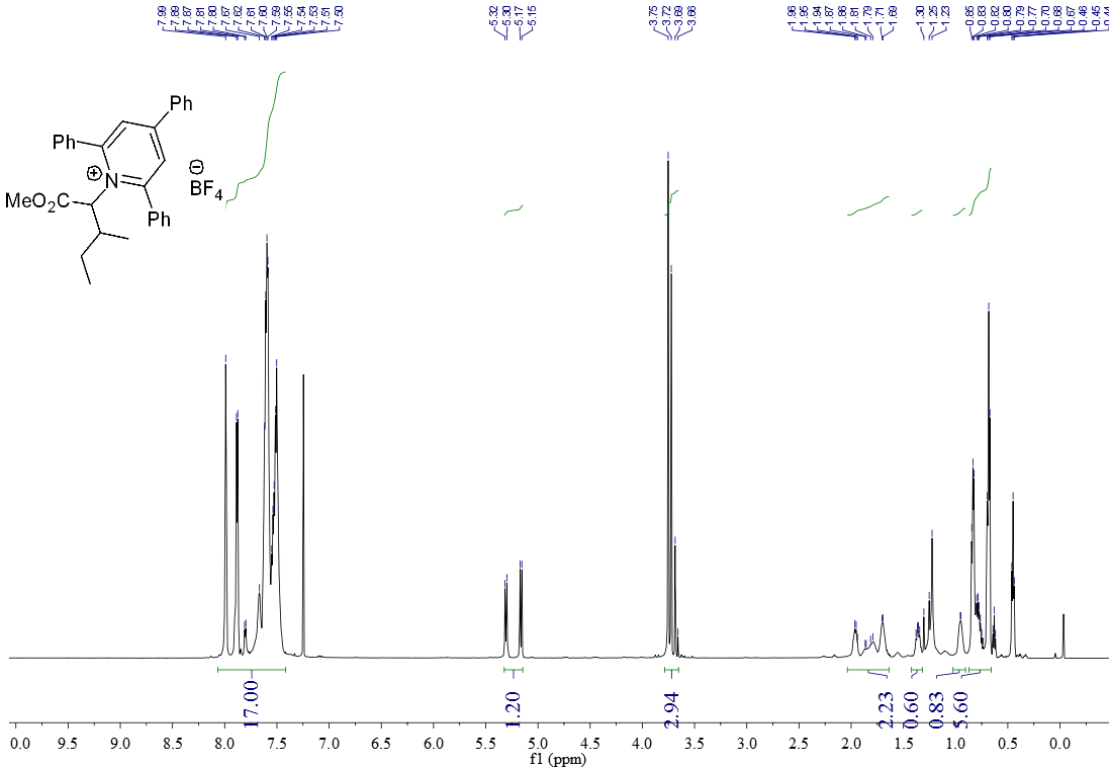
^{13}C NMR of **1j**



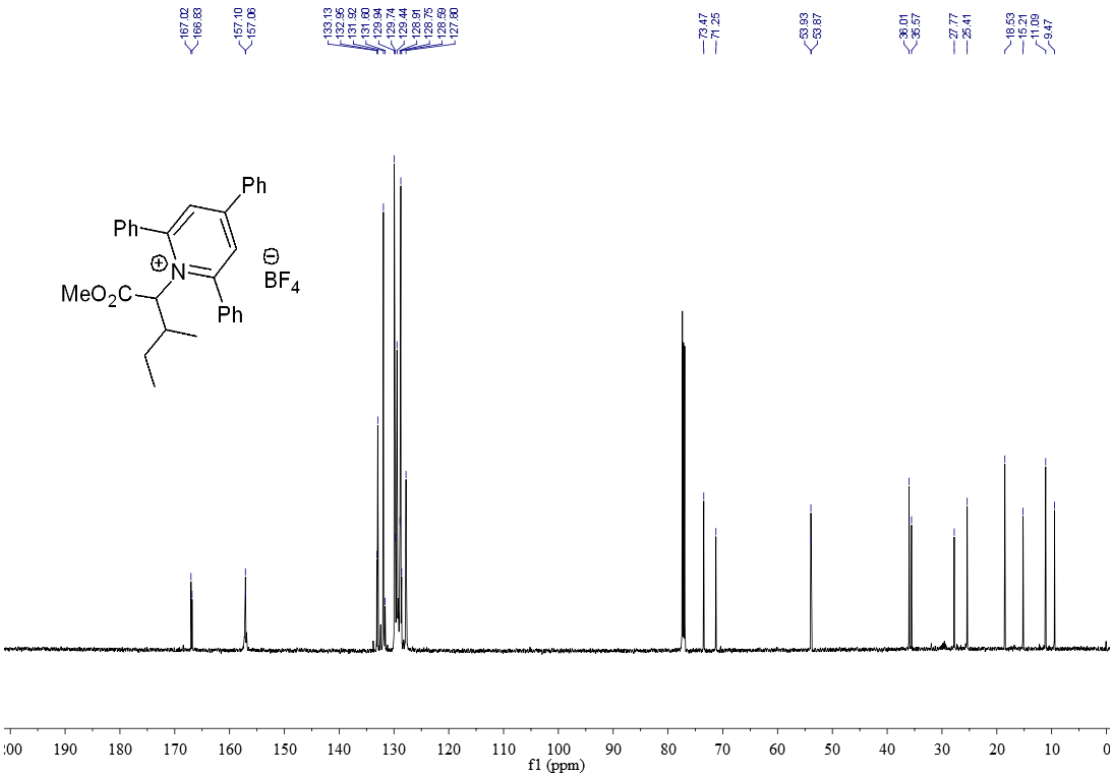
^{19}F NMR of **1j**



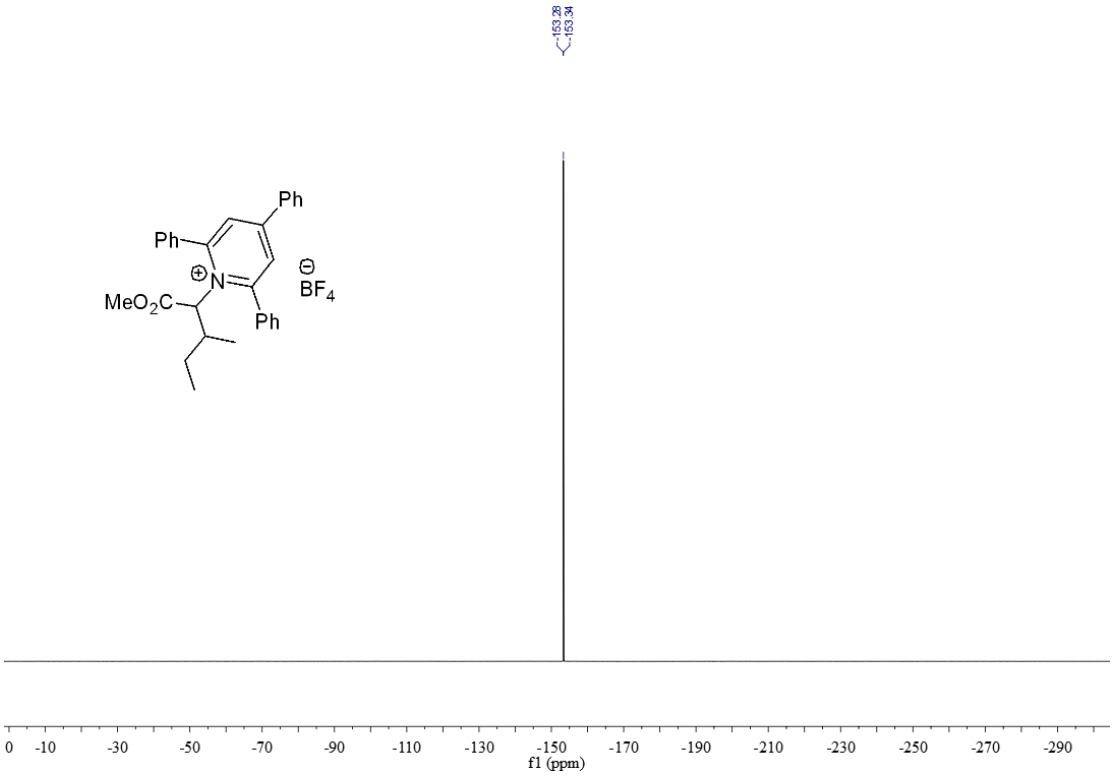
^{1}H NMR of **1k**



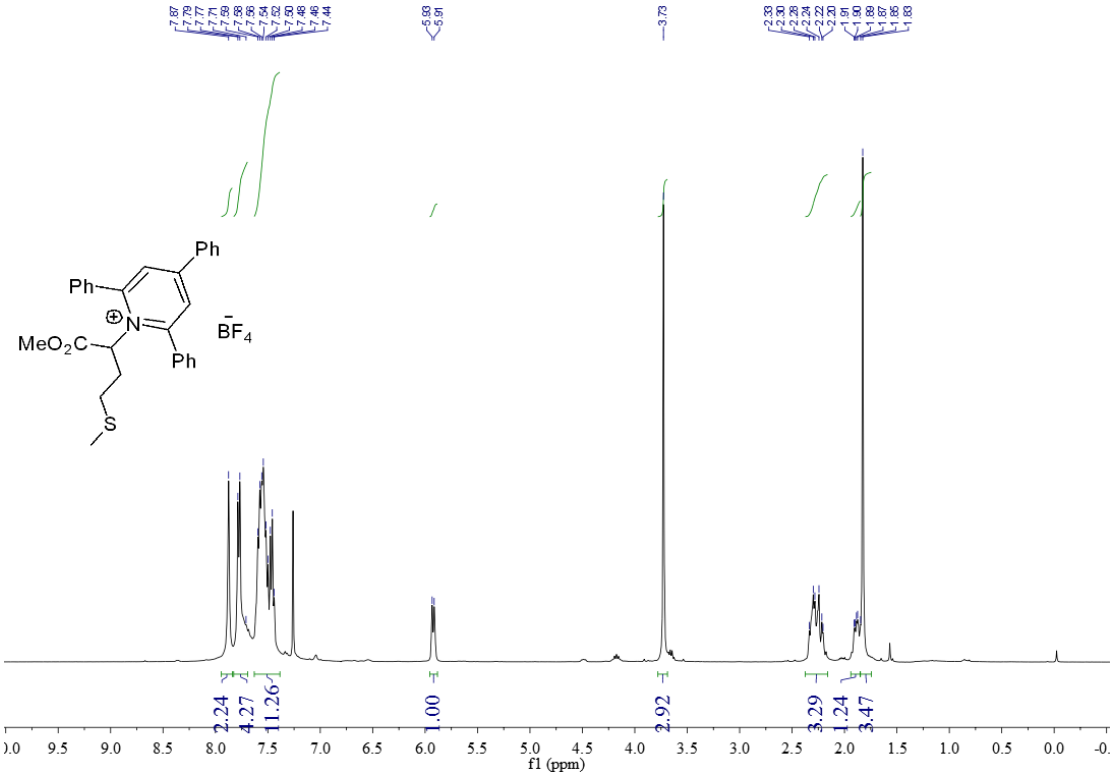
^{13}C NMR of **1k**



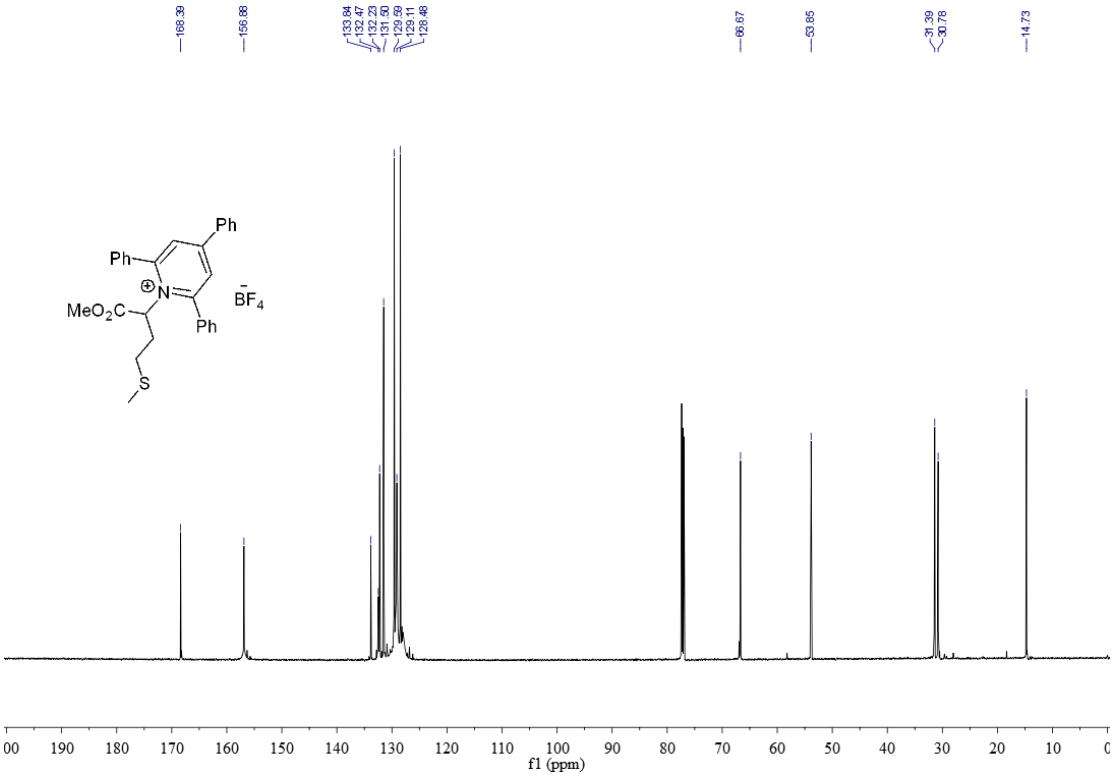
^{19}F NMR of **1k**



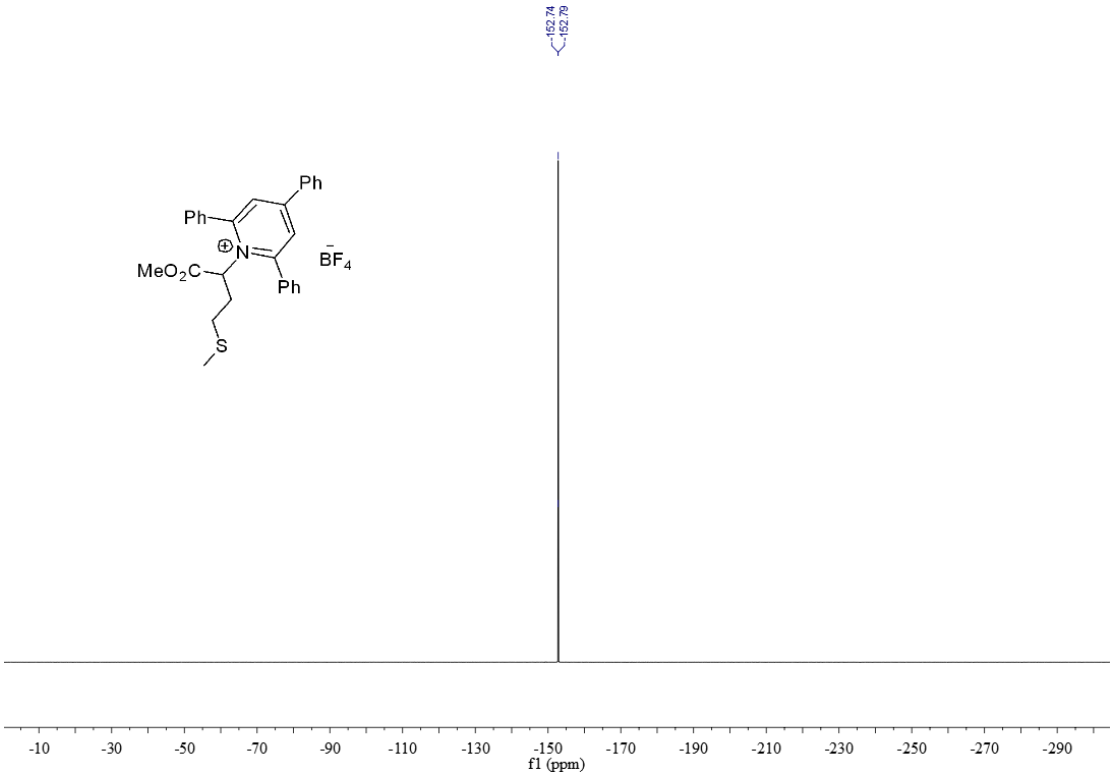
^{1}H NMR of **1l**



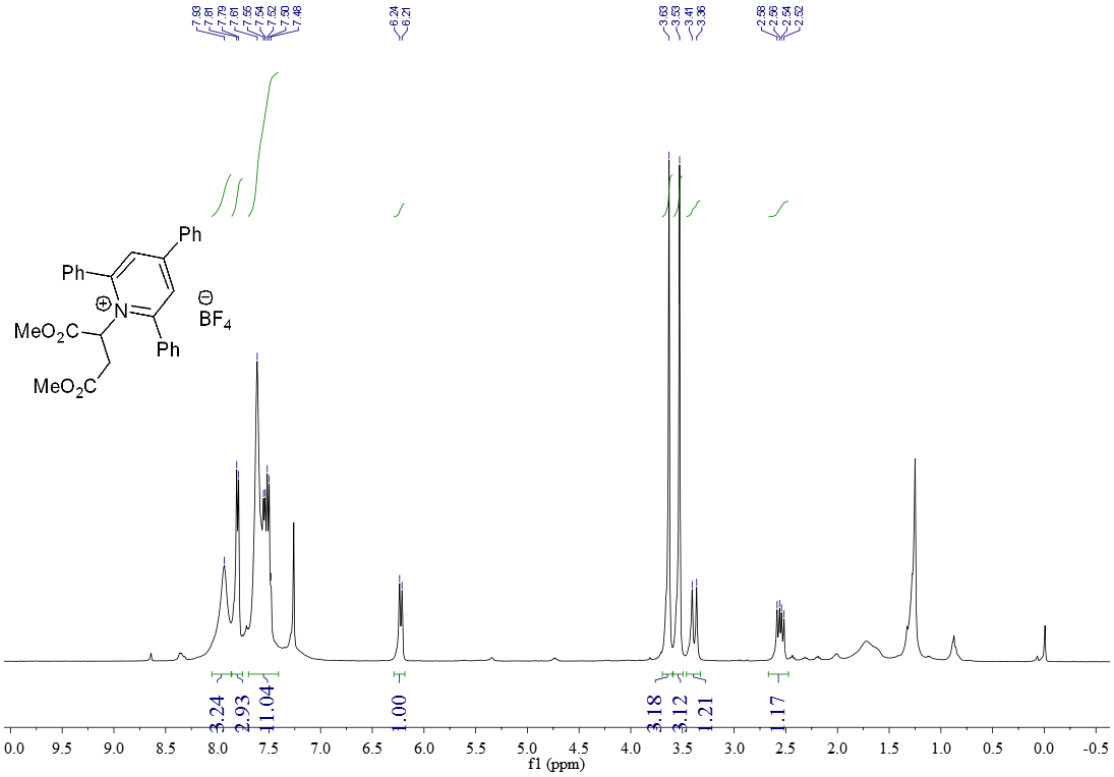
^{13}C NMR of **1l**



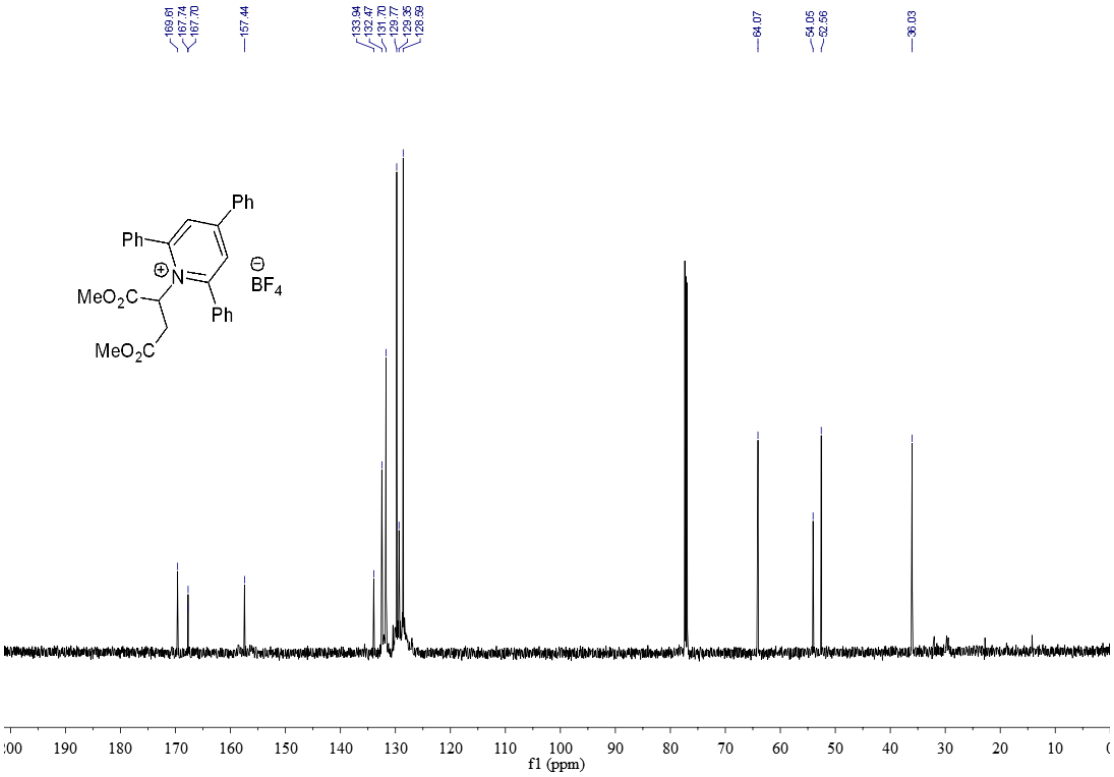
^{19}F NMR of **1l**



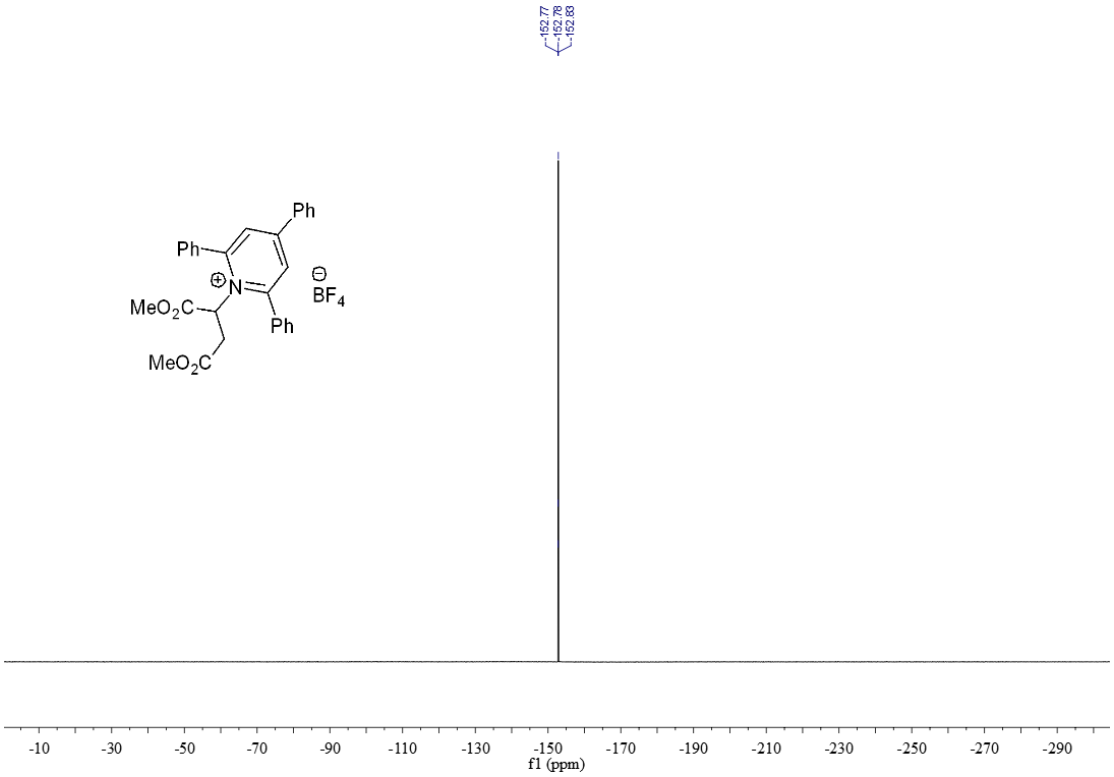
^{1}H NMR of **1m**



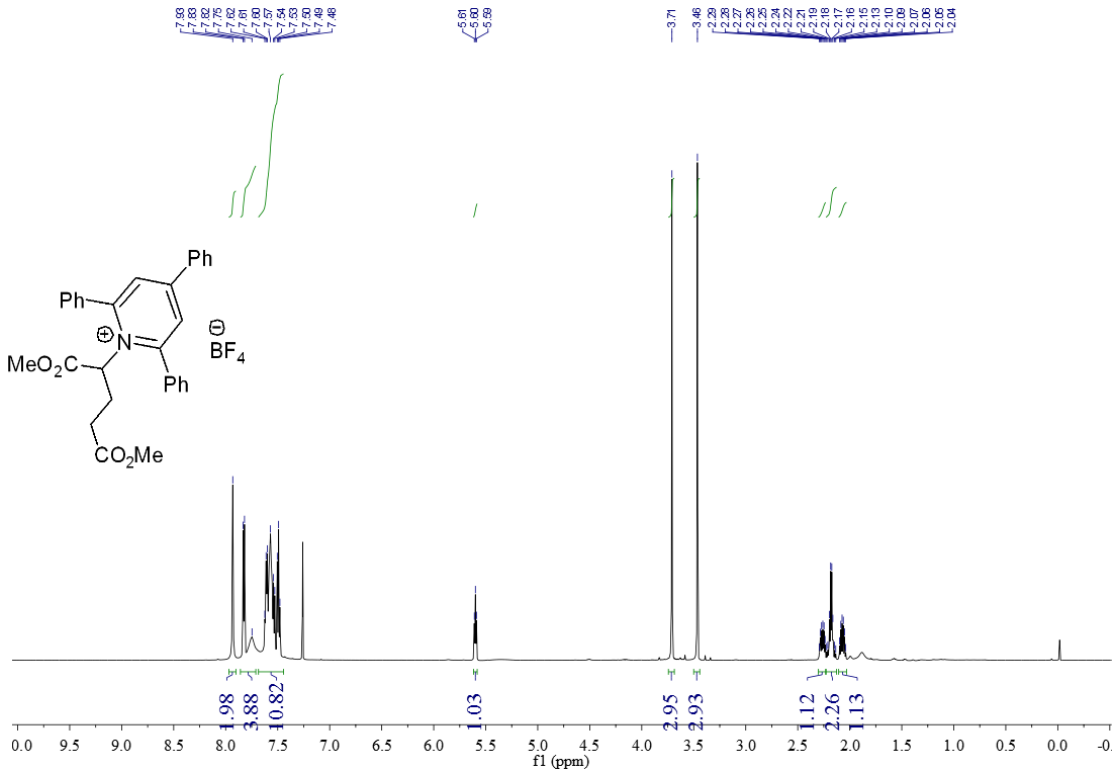
^{13}C NMR of **1m**



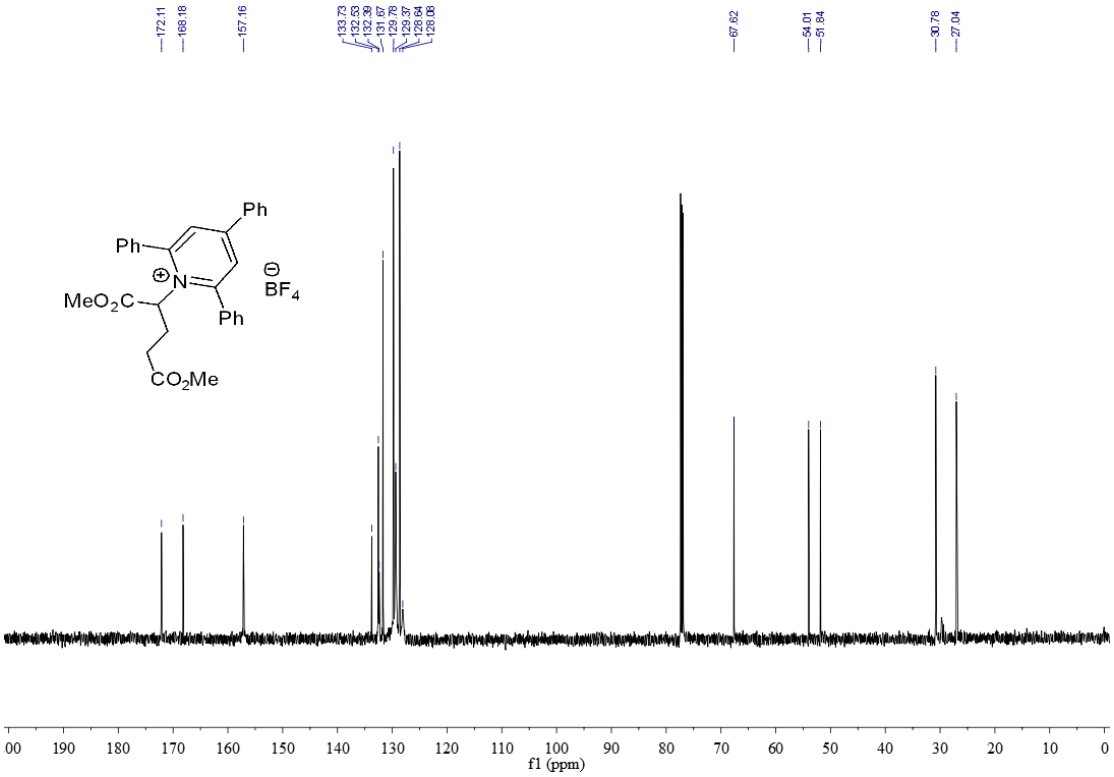
^{19}F NMR of **1m**



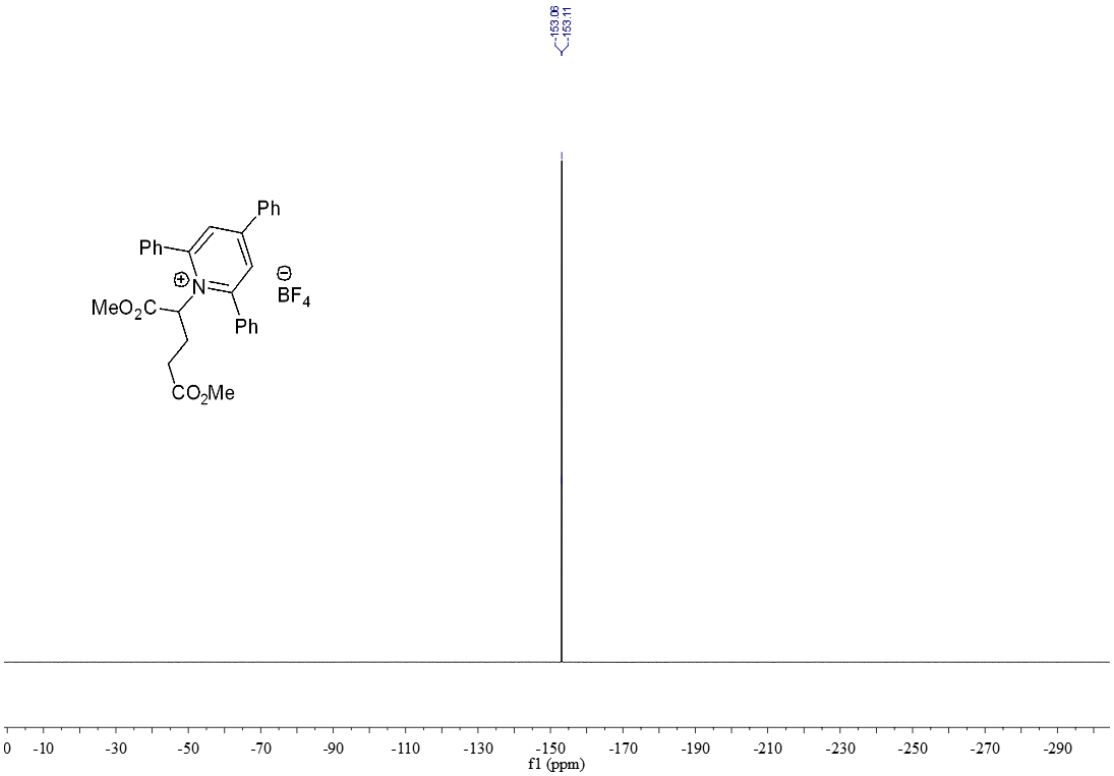
^{1}H NMR of **1n**



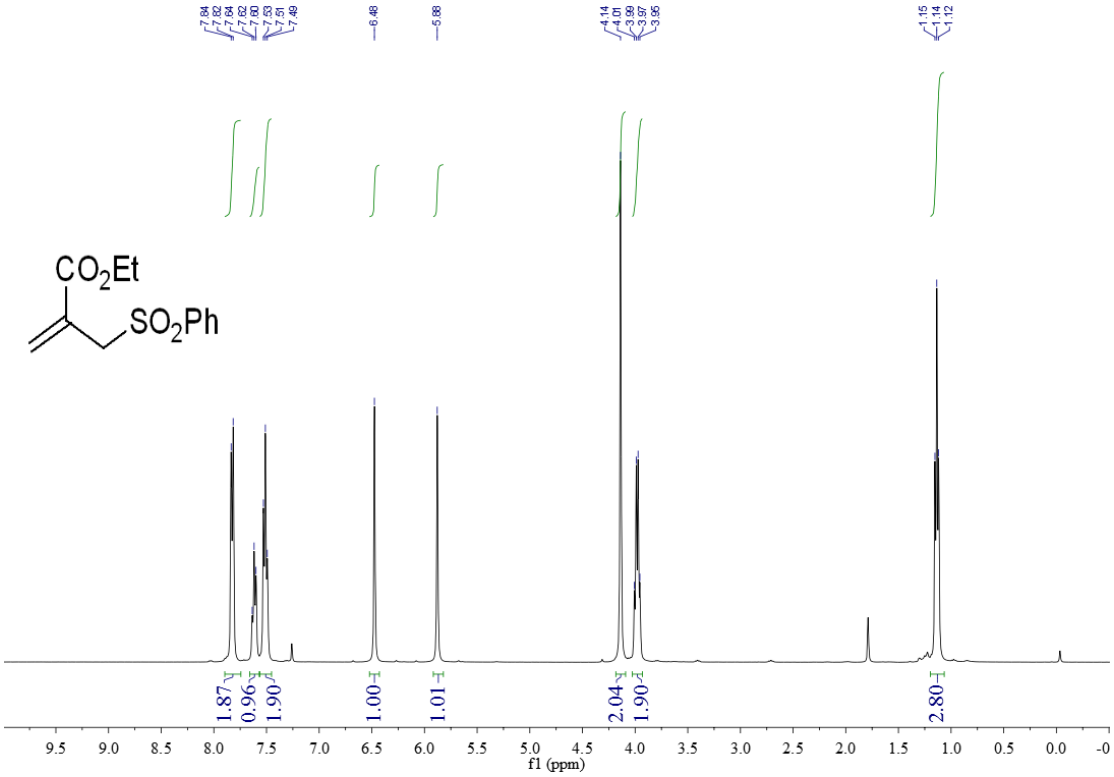
^{13}C NMR of **1n**



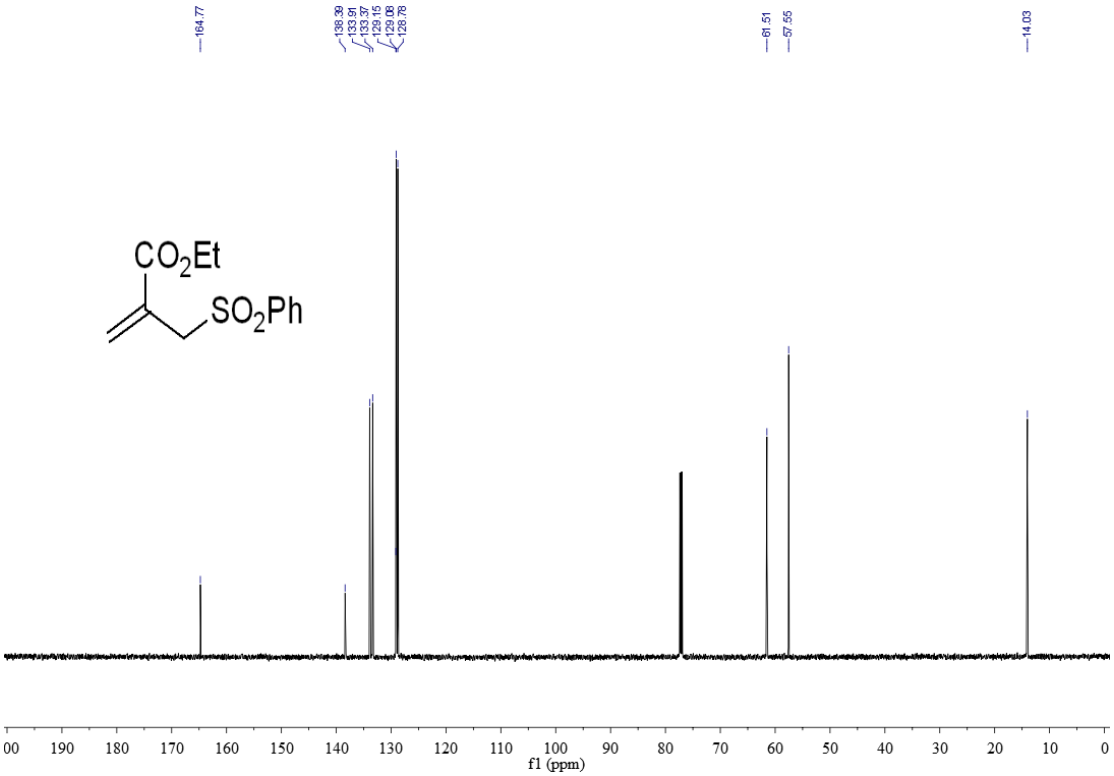
^{19}F NMR of **1n**



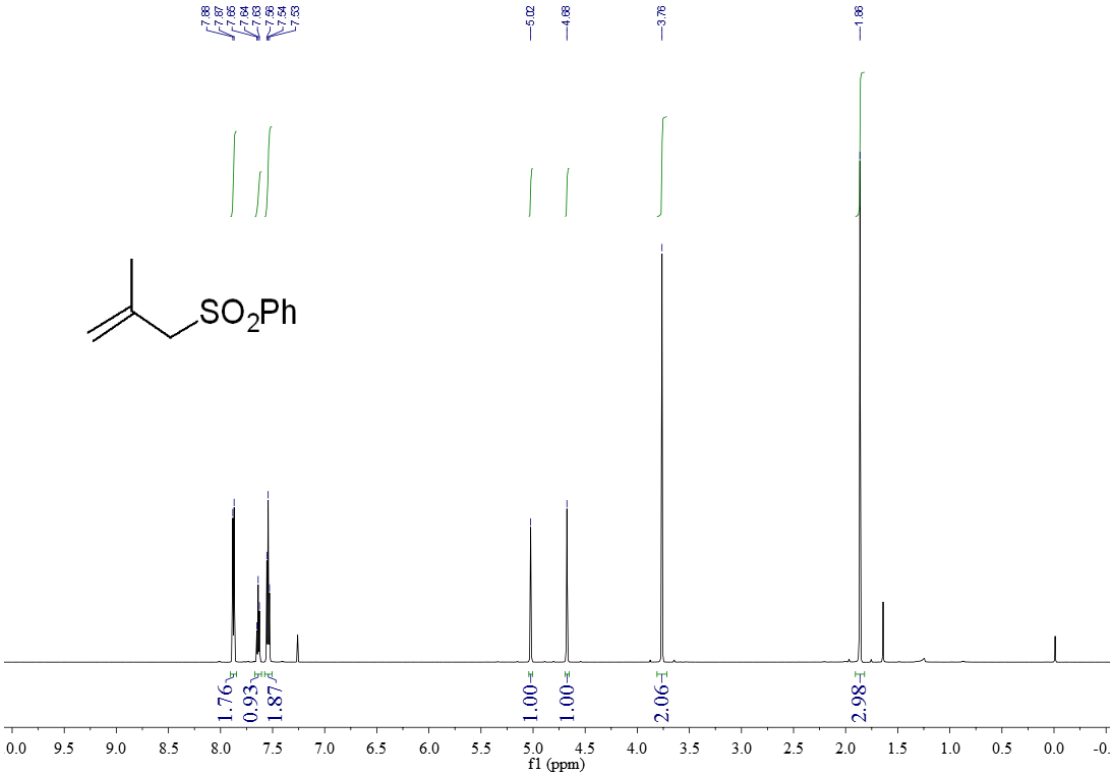
^{1}H NMR of **2a**



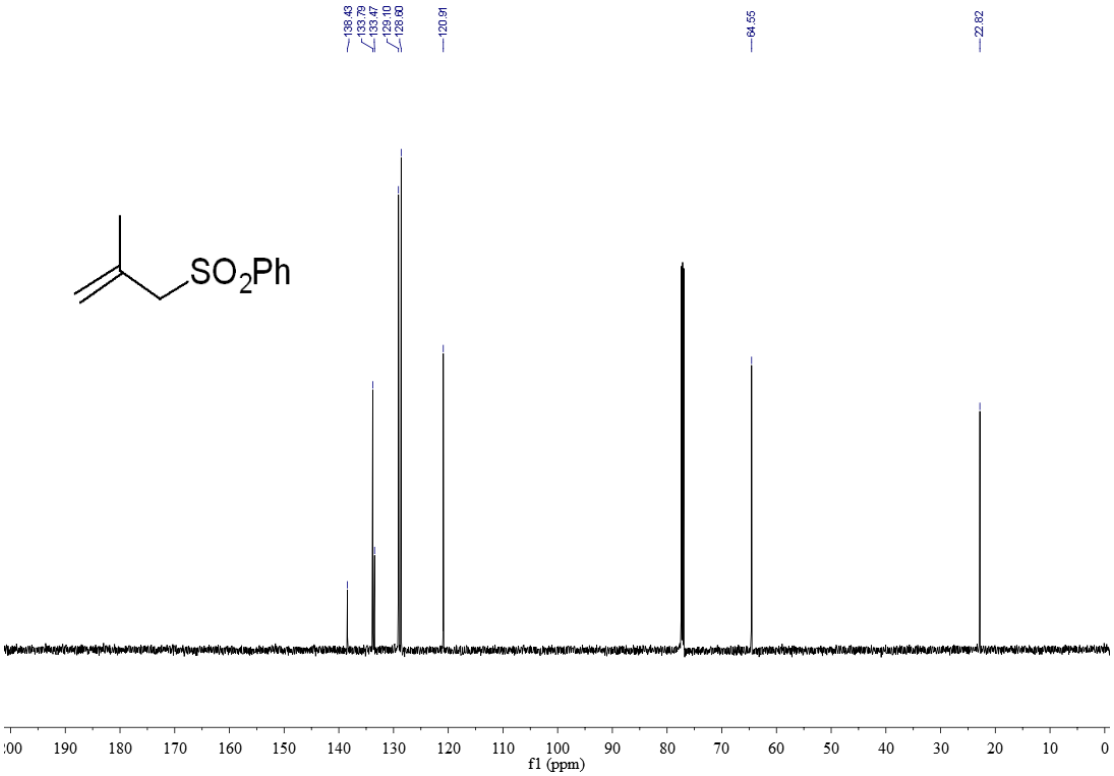
^{13}C NMR of **2a**



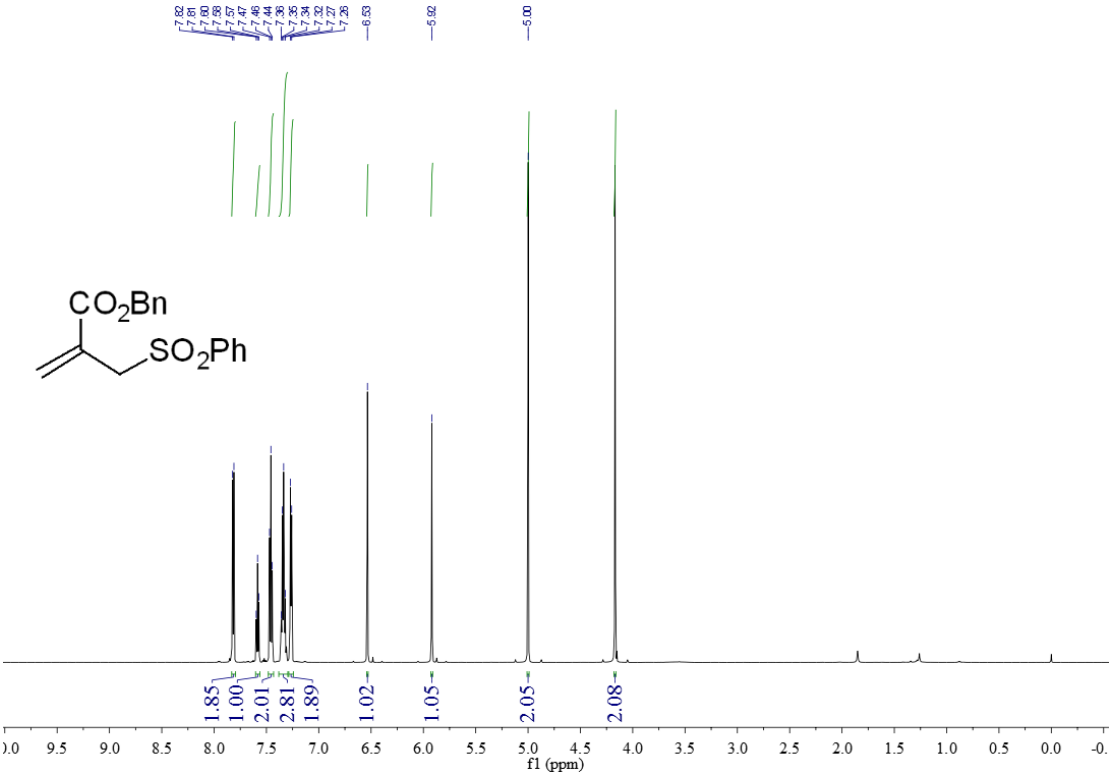
^{1}H NMR of **2b**



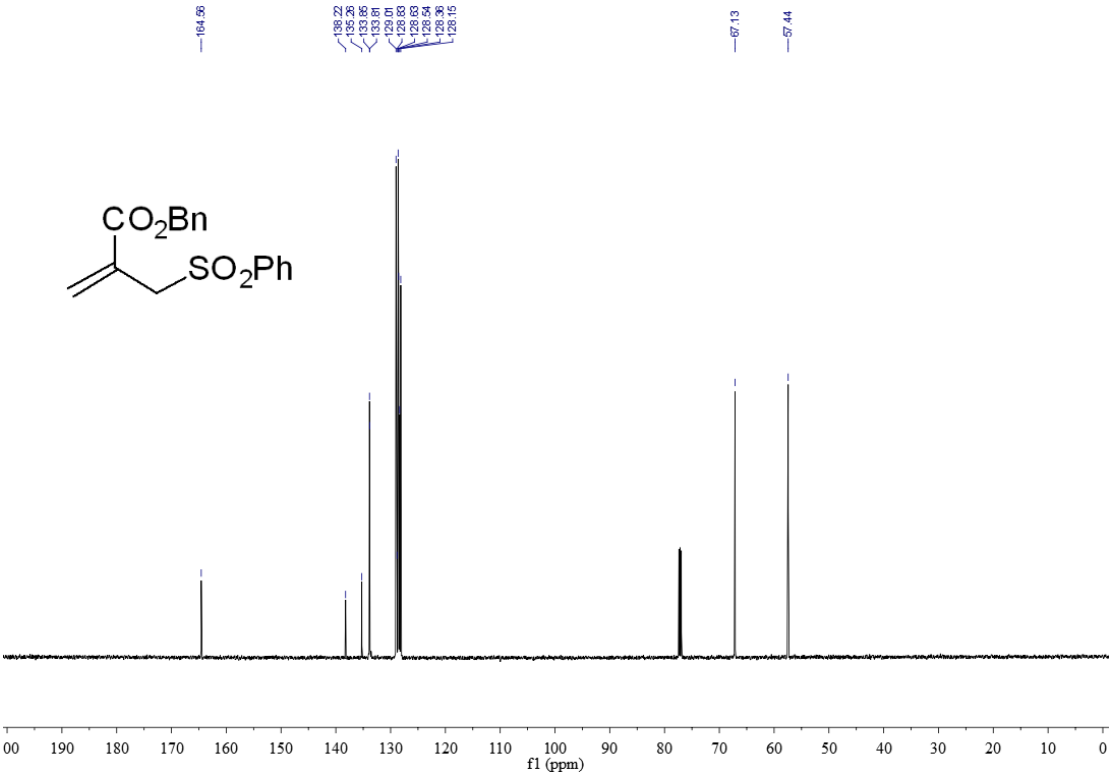
^{13}C NMR of **2b**



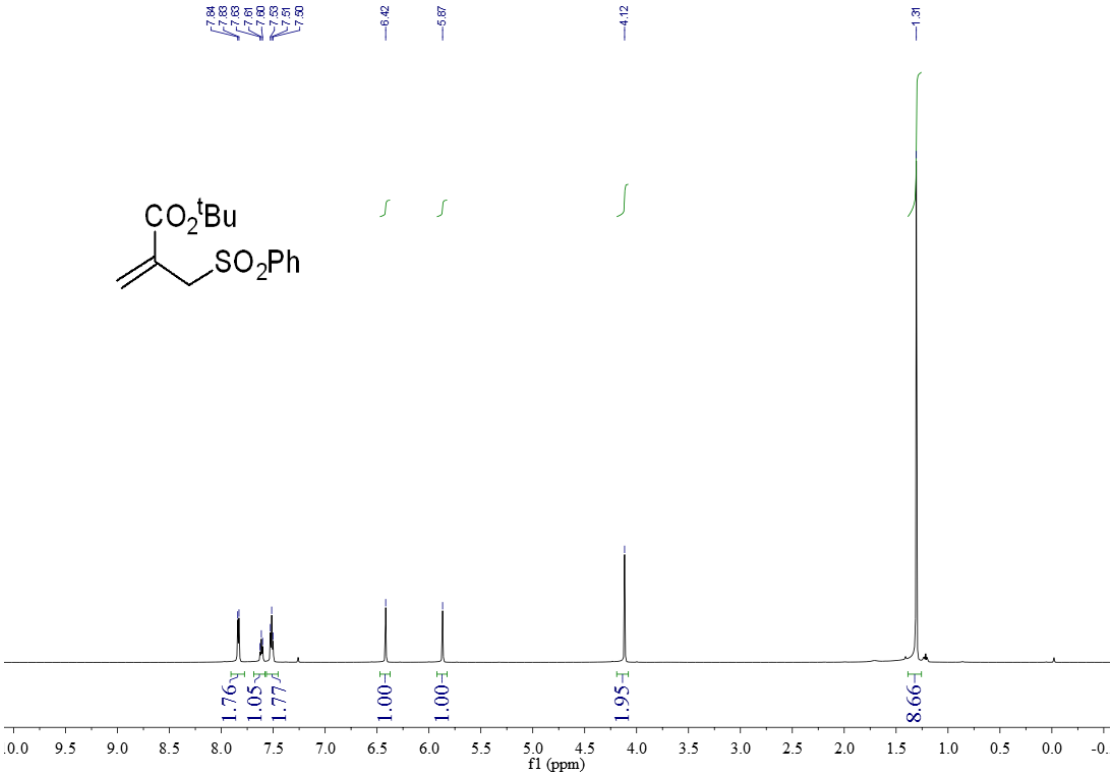
^{1}H NMR of **2c**



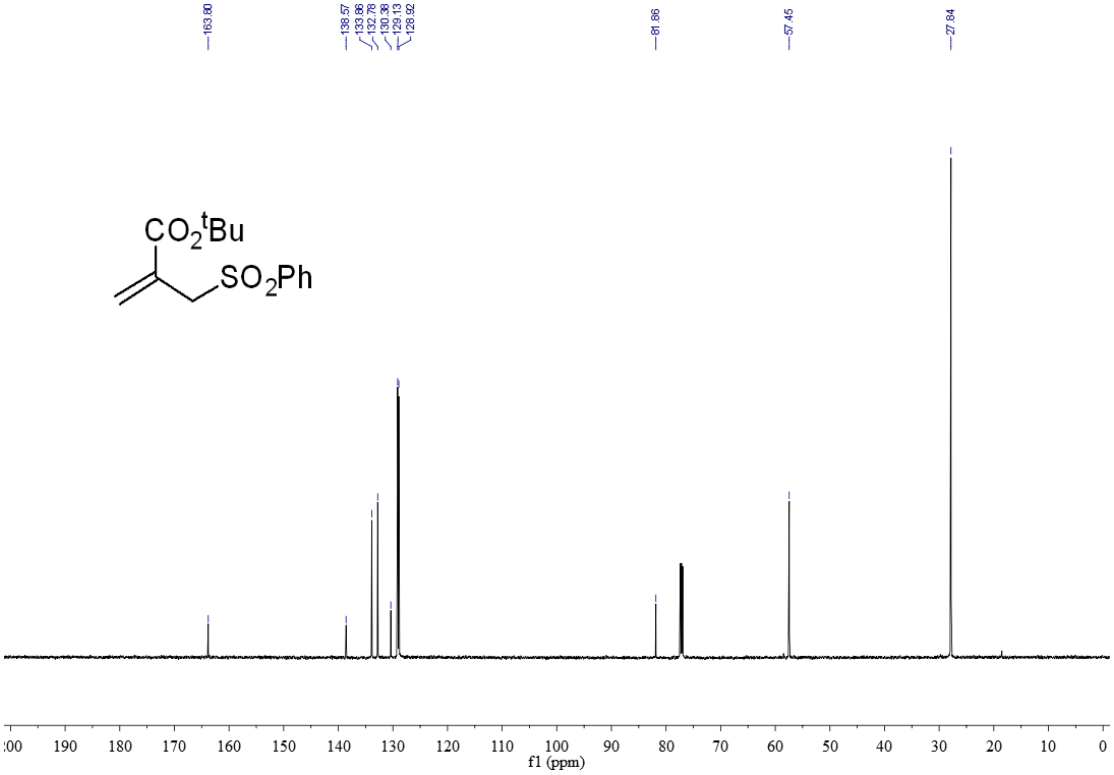
^{13}C NMR of **2c**



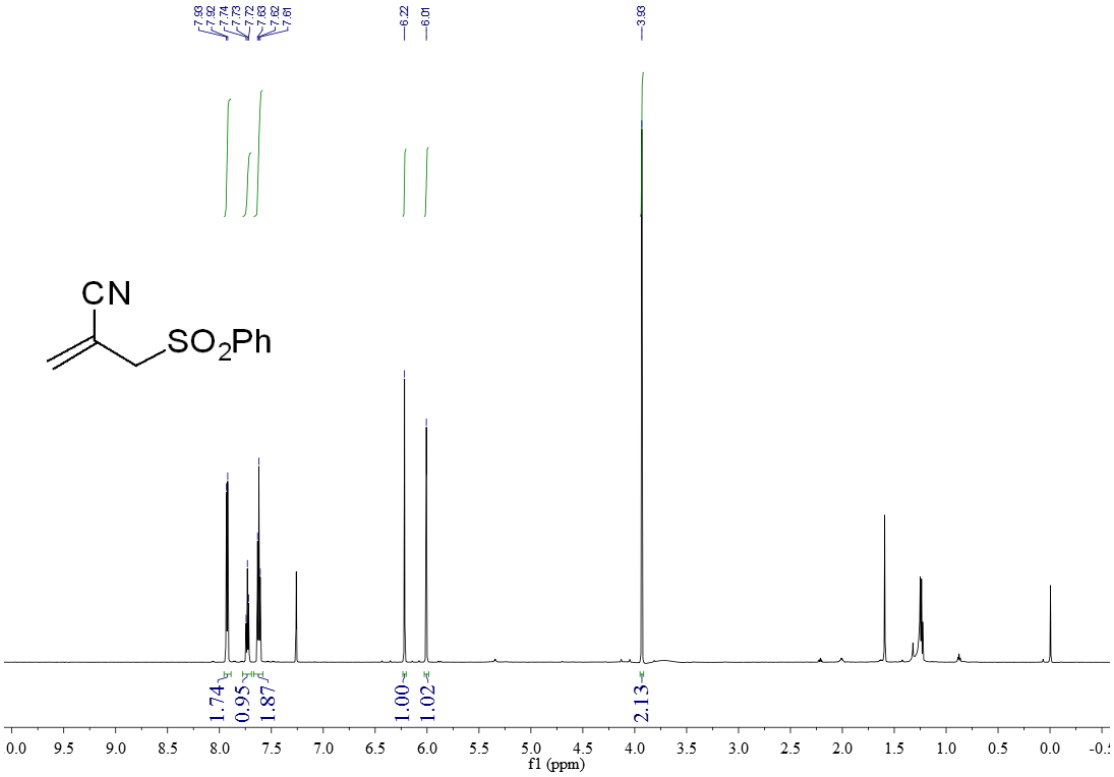
^{1}H NMR of **2d**



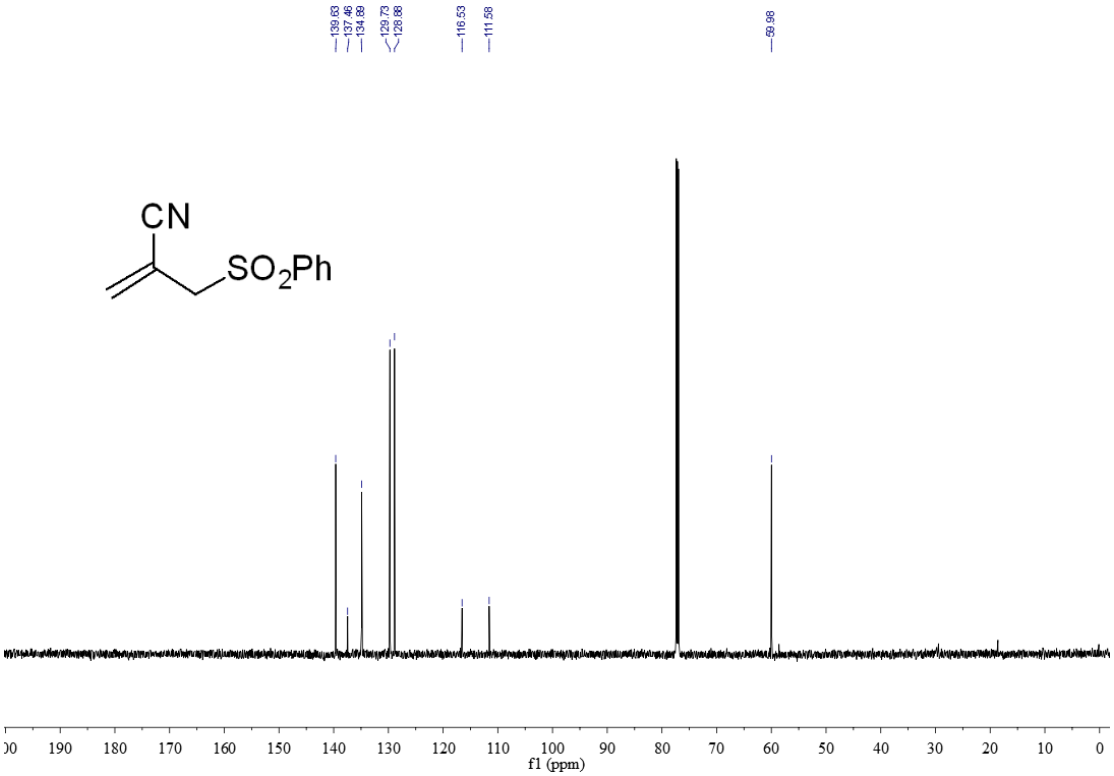
^{13}C NMR of **2d**



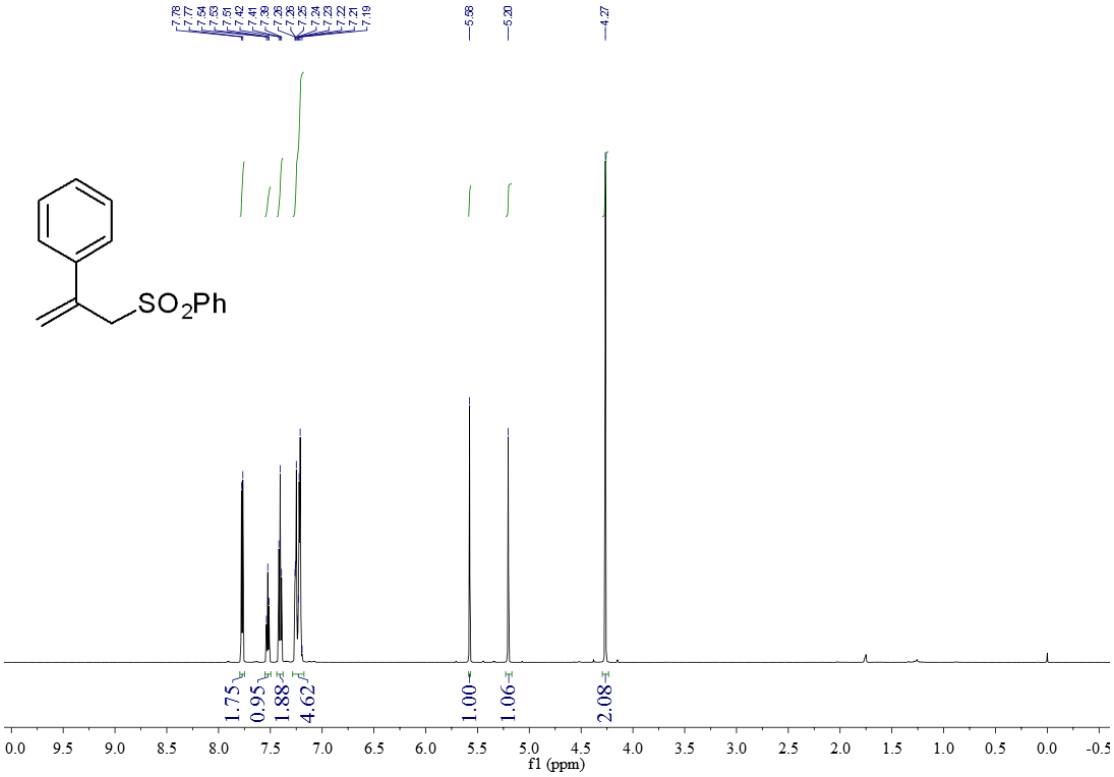
^{1}H NMR of **2e**



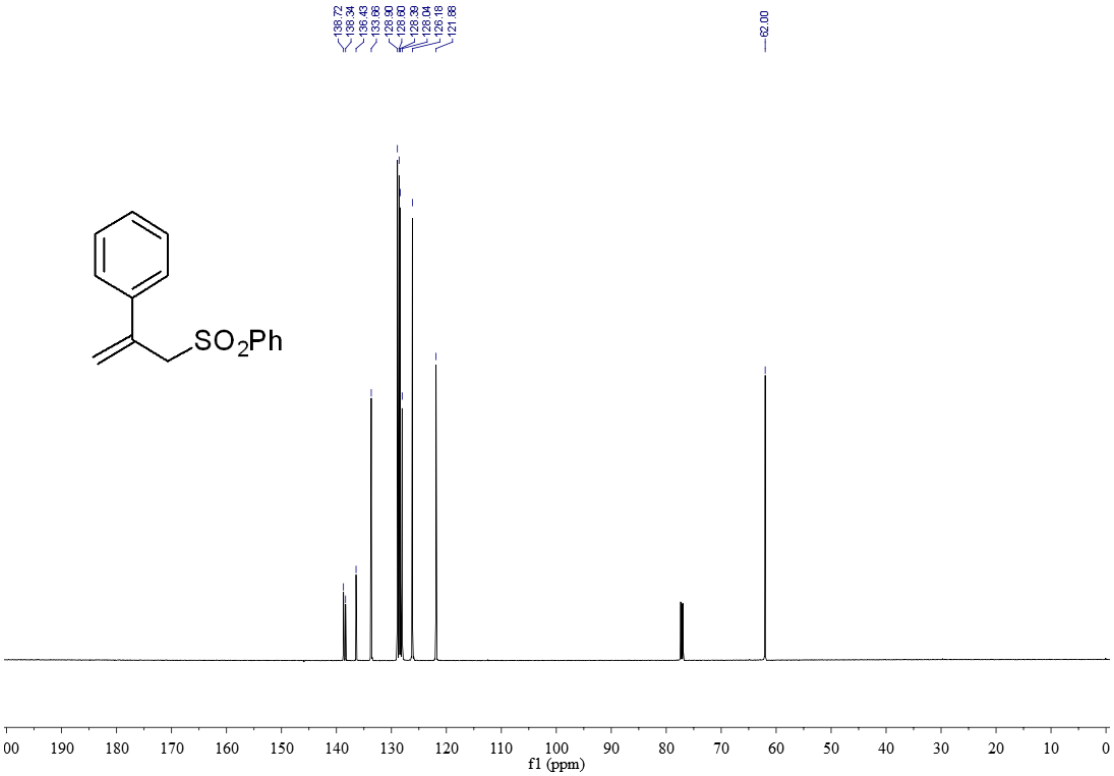
^{13}C NMR of **2e**



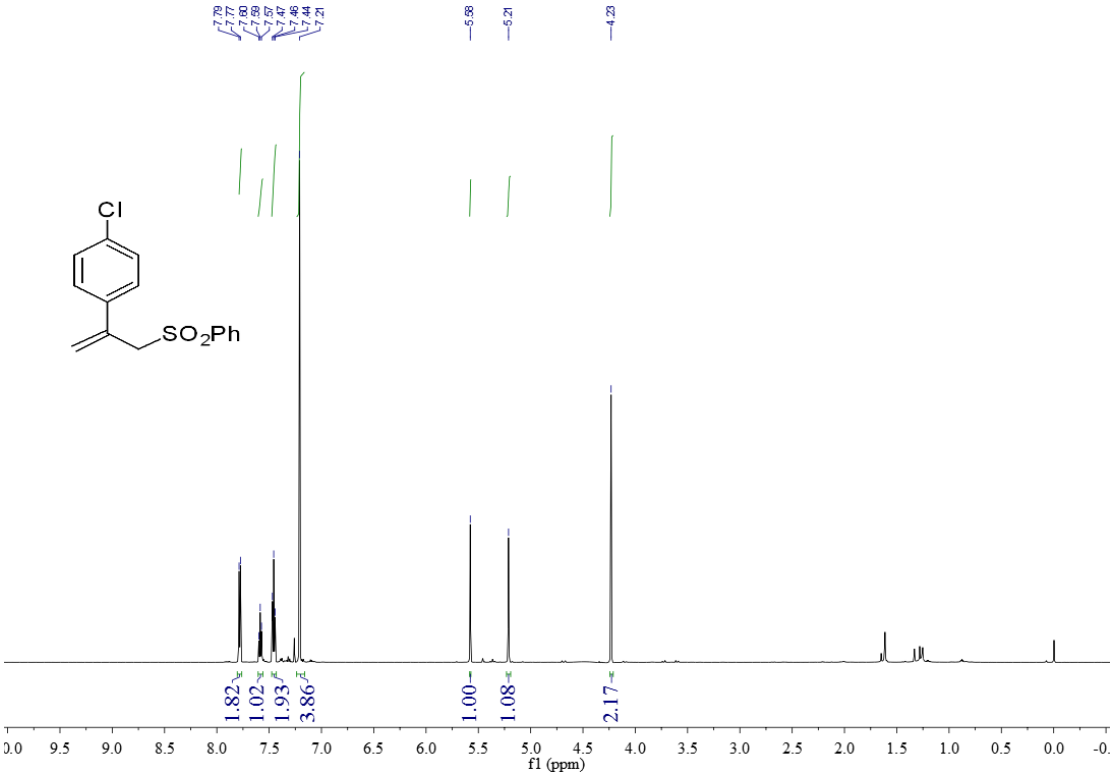
^{1}H NMR of **2f**



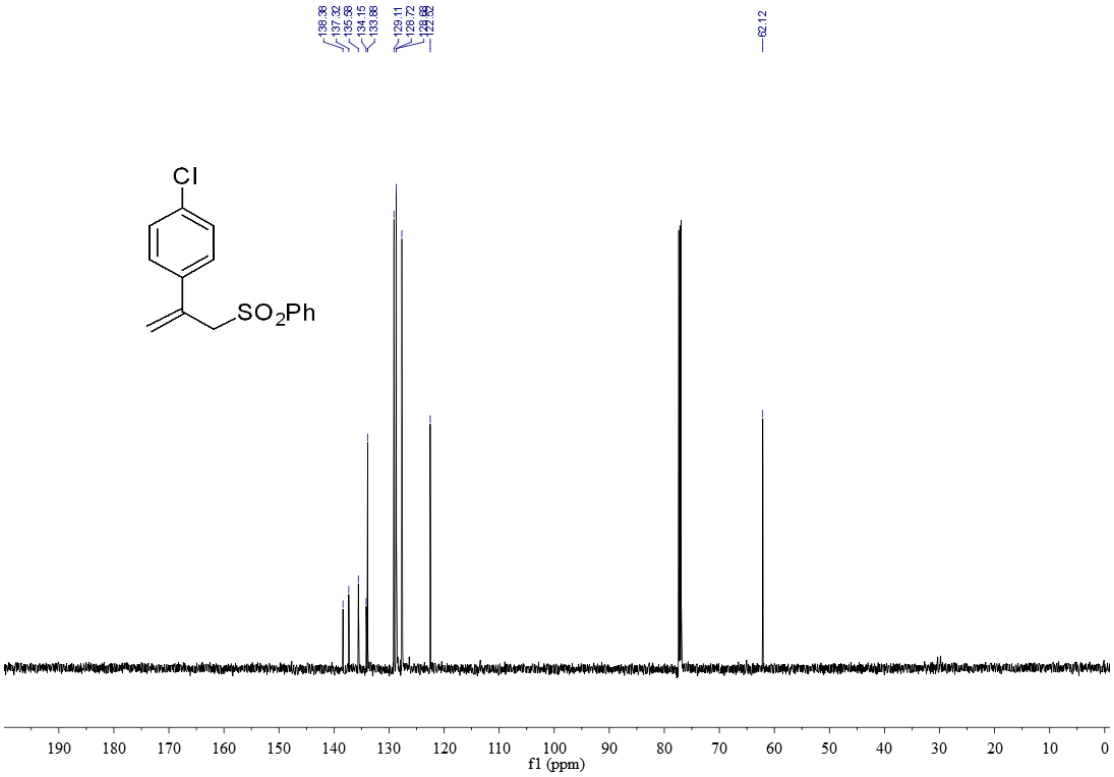
^{13}C NMR of **2f**



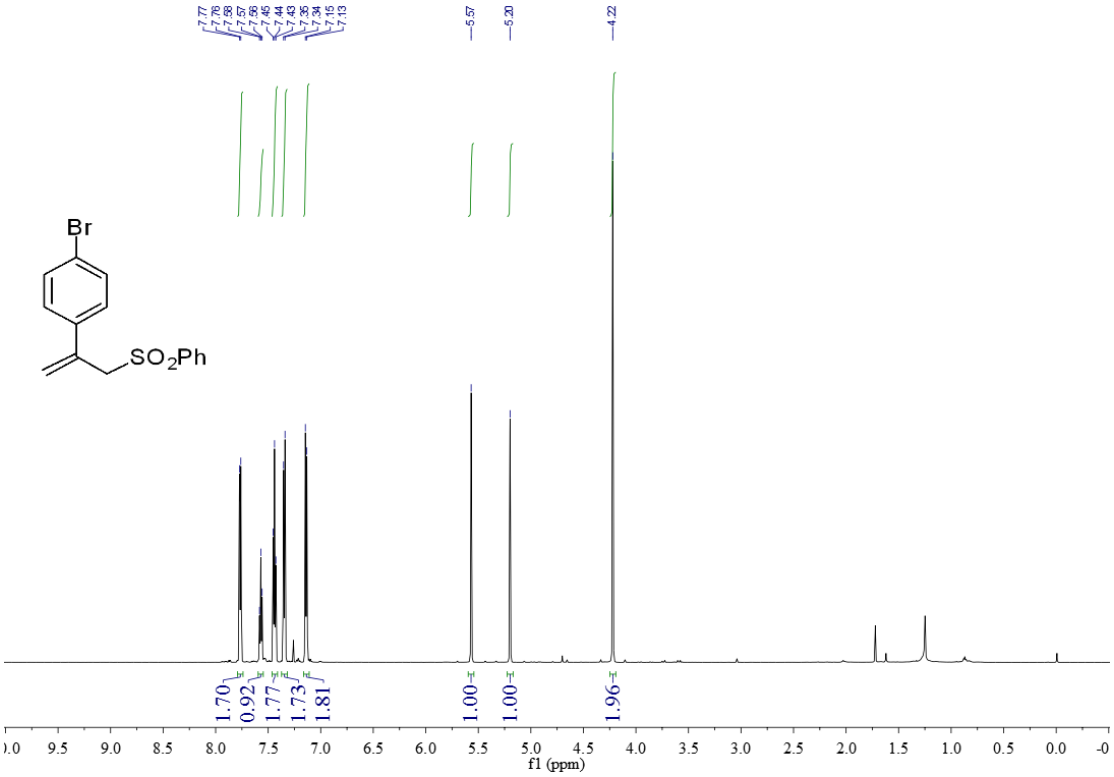
^{1}H NMR of **2g**



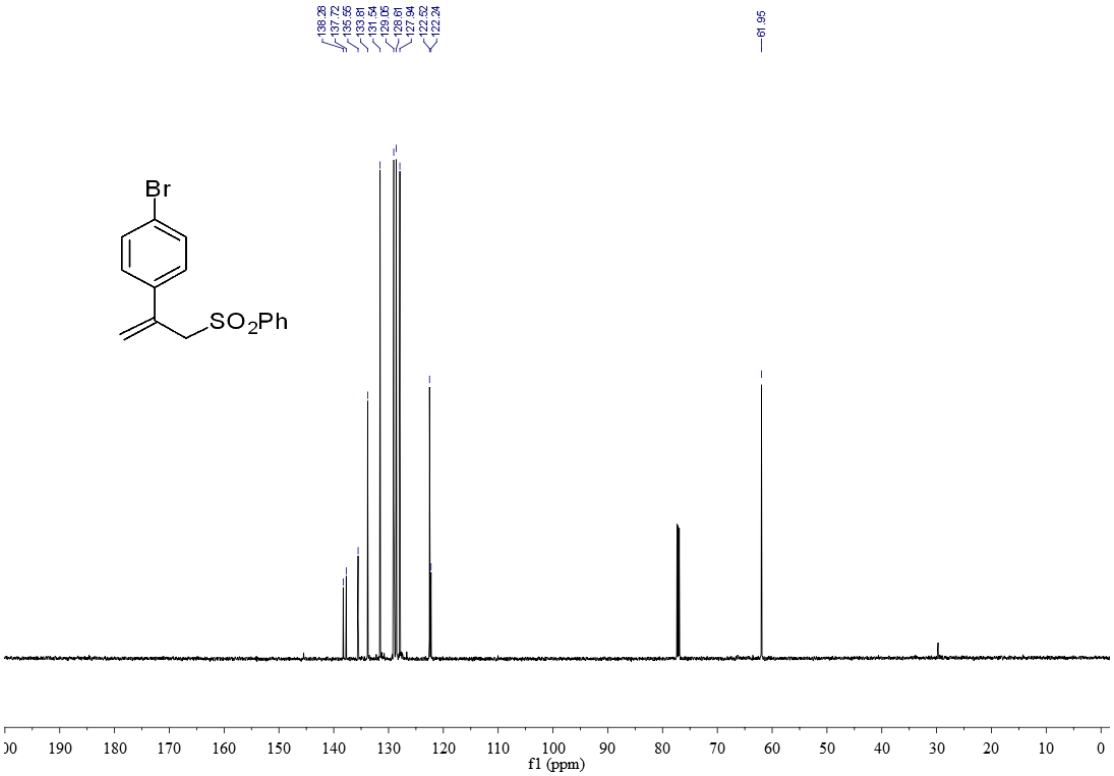
^{13}C NMR of **2g**



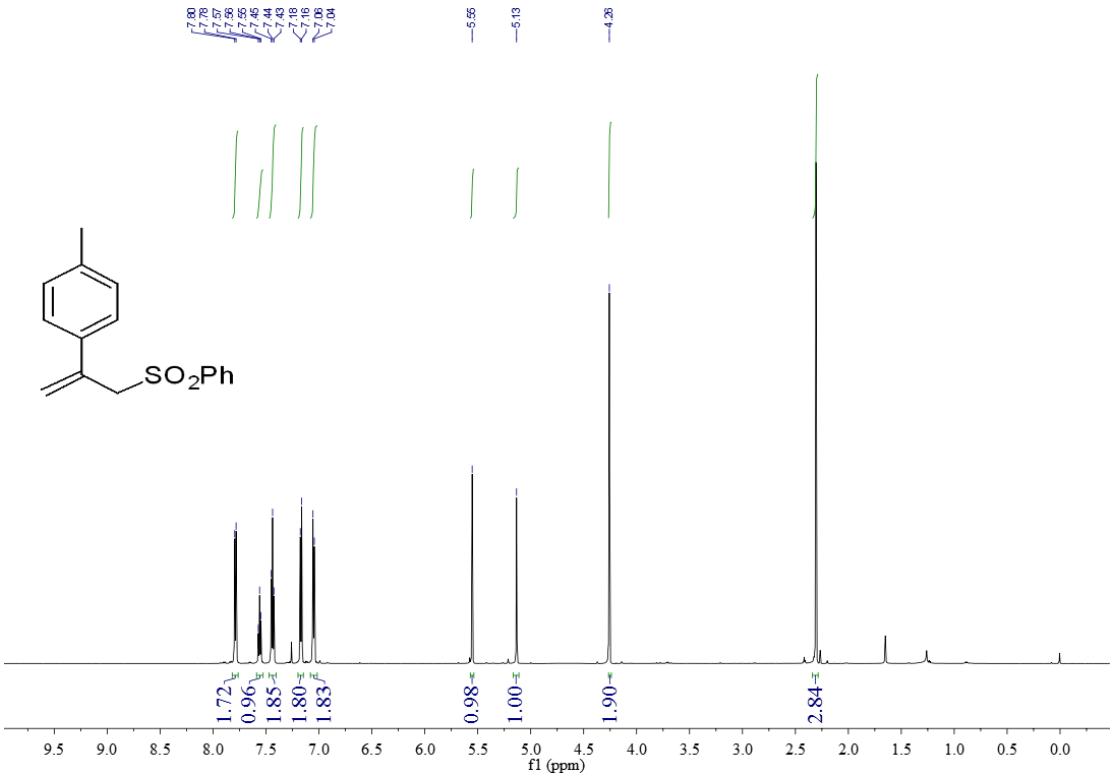
^{1}H NMR of **2h**



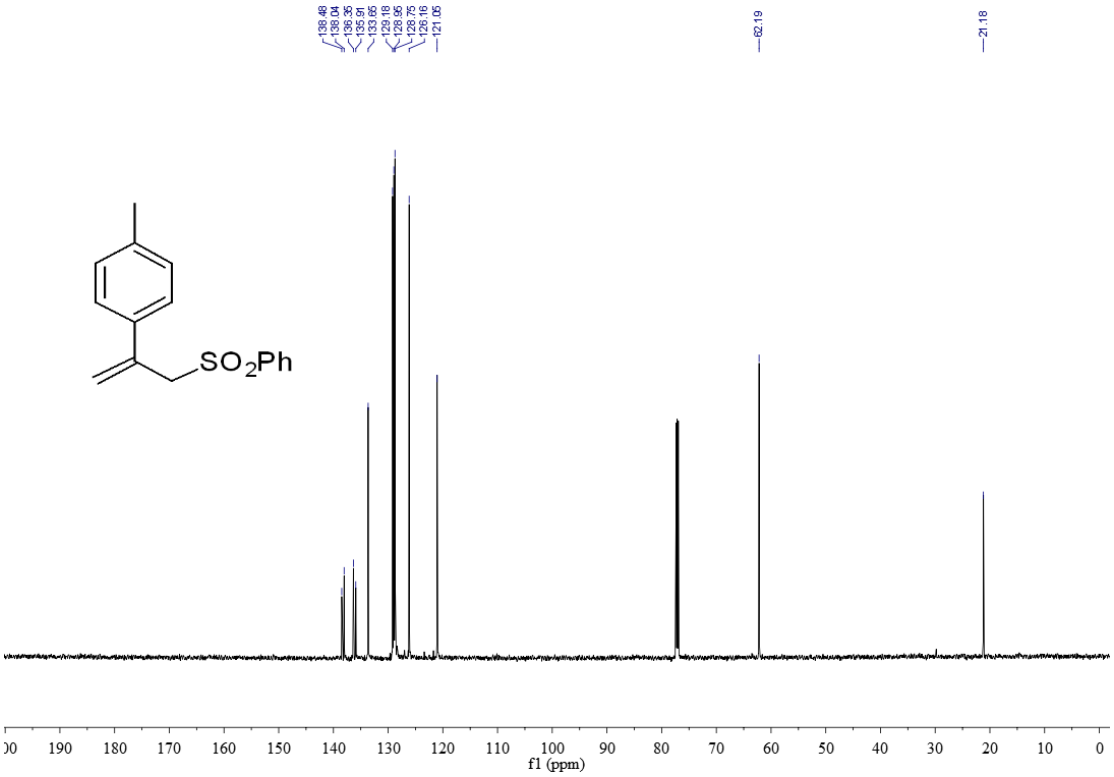
^{13}C NMR of **2h**



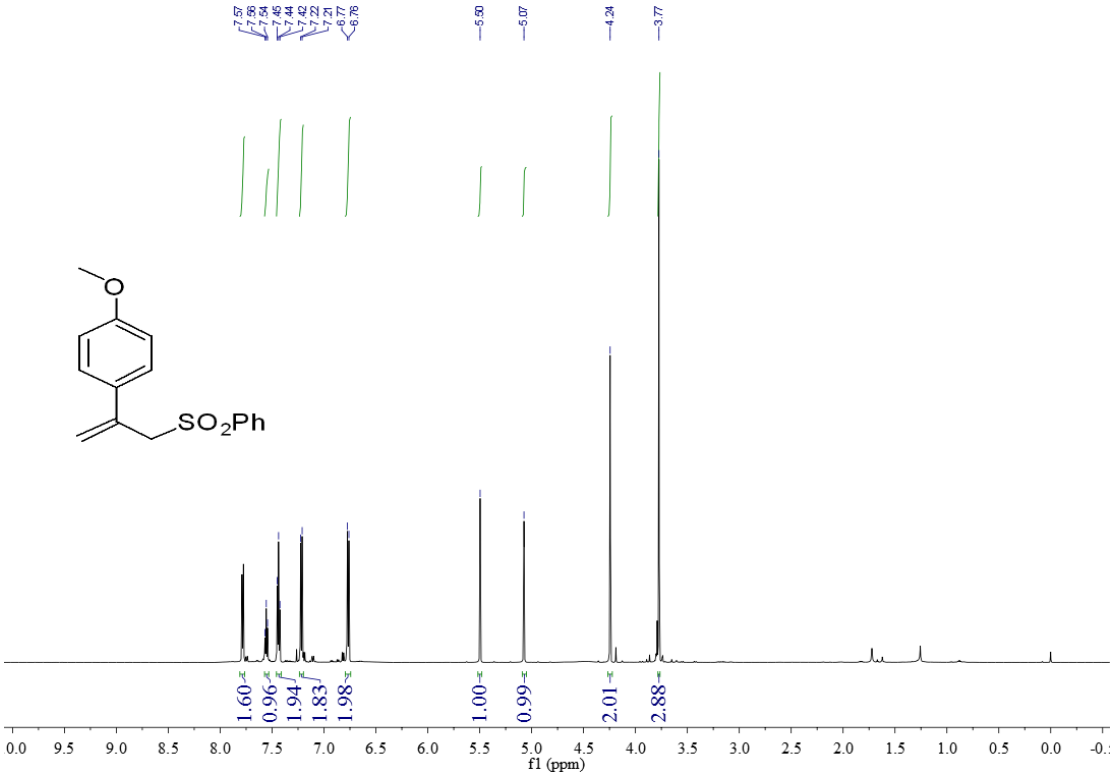
^{1}H NMR of **2i**



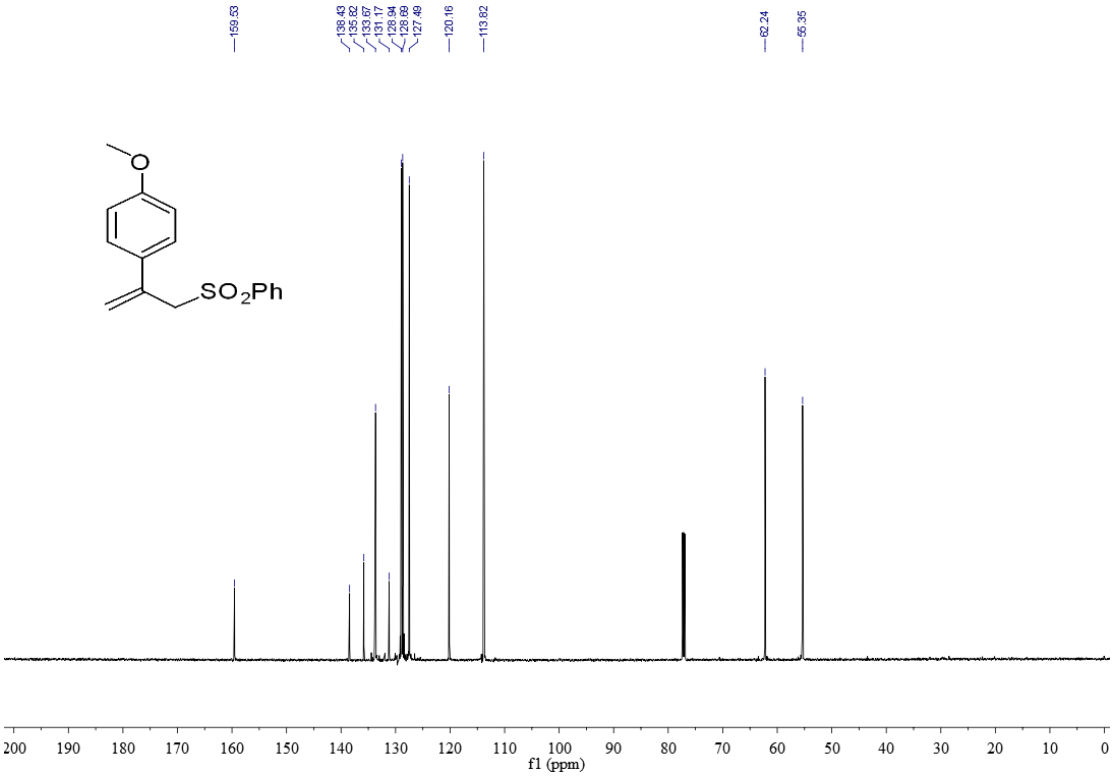
^{13}C NMR of **2i**



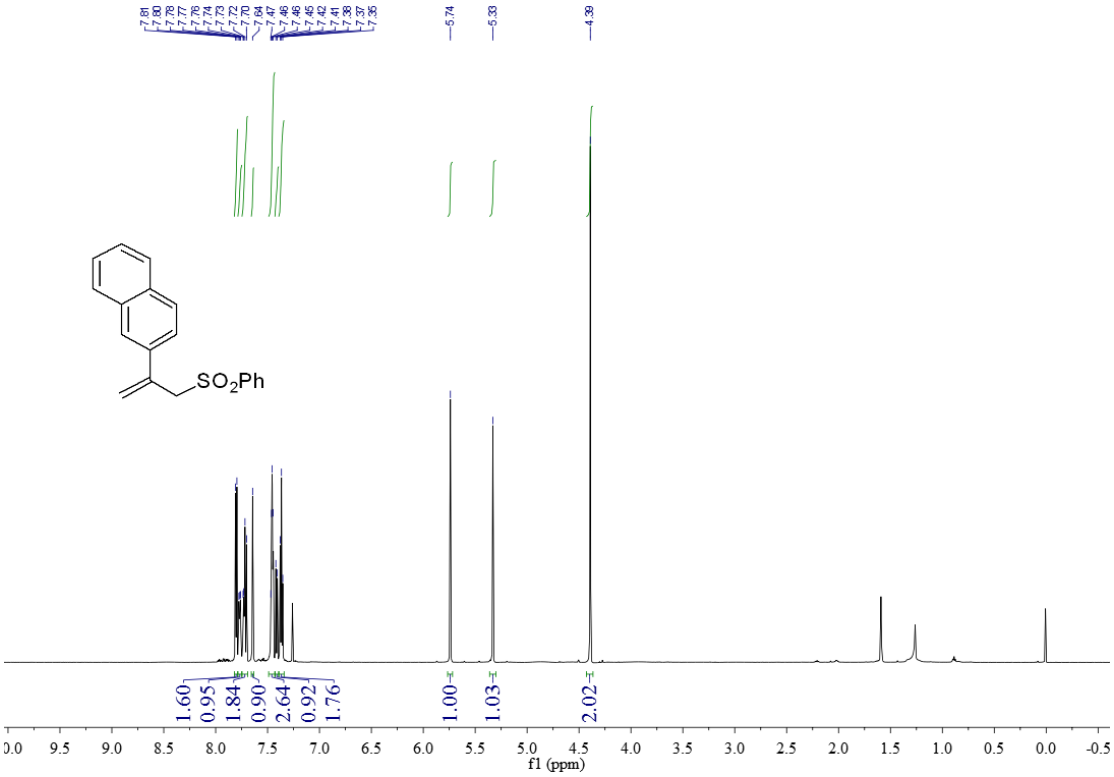
^{1}H NMR of **2j**



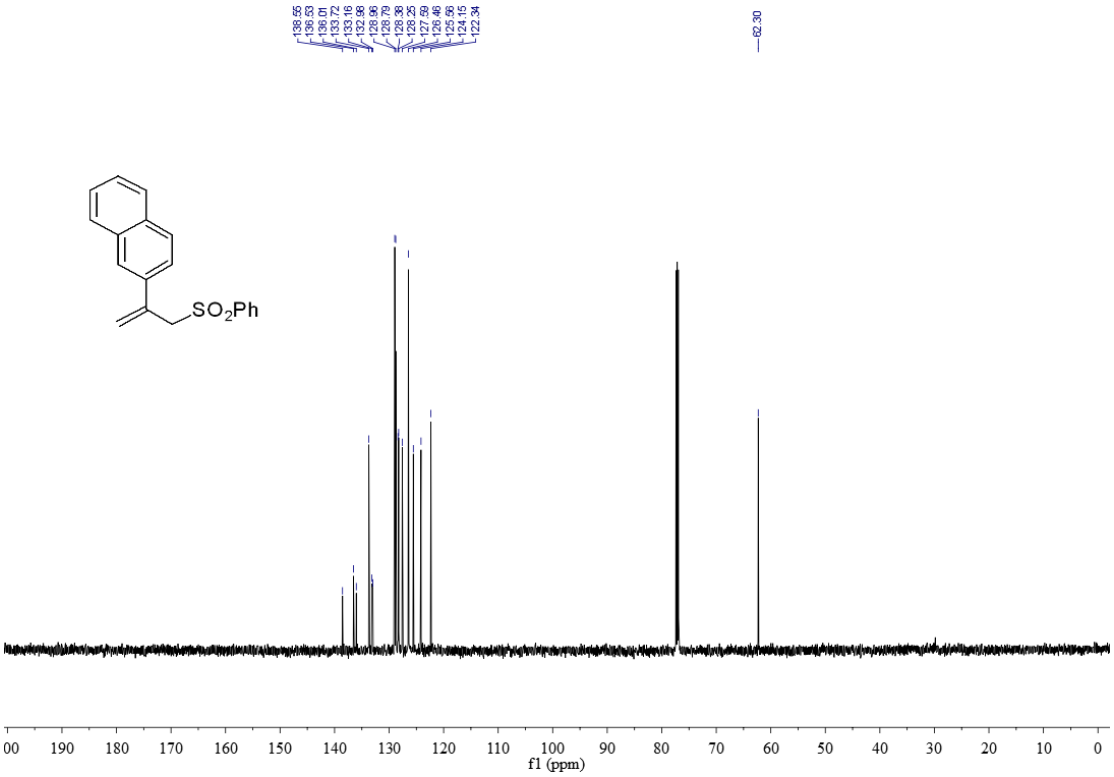
^{13}C NMR of **2j**



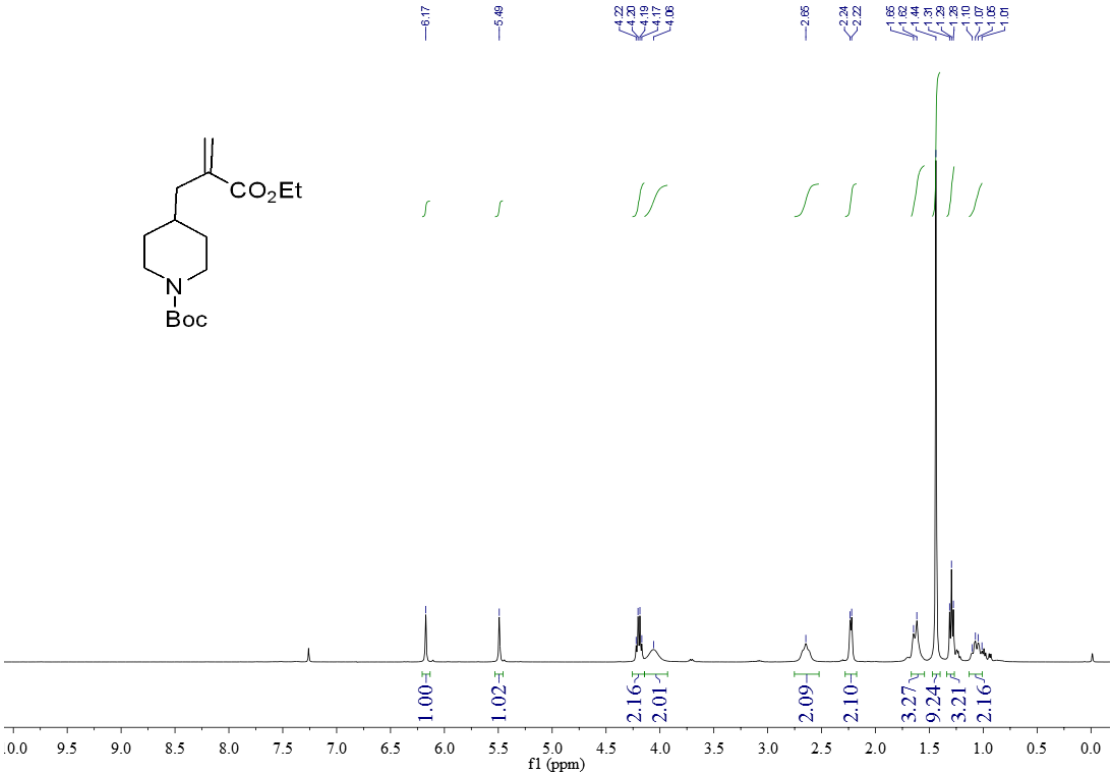
^{1}H NMR of **2k**



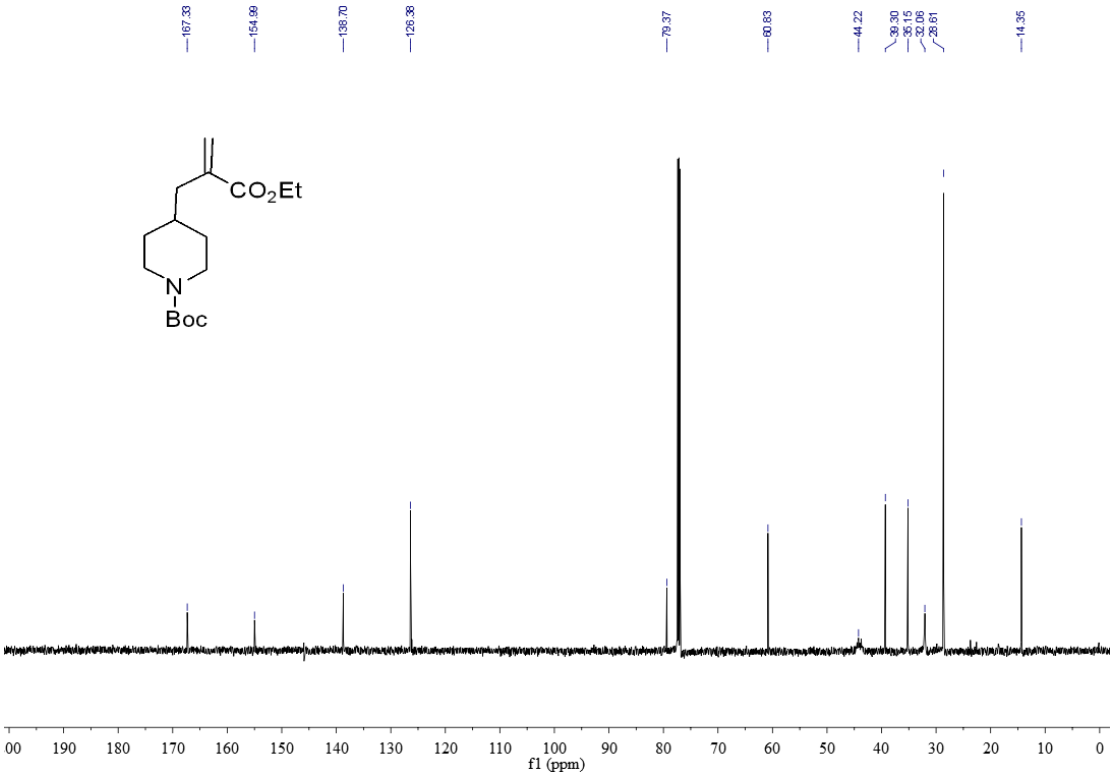
^{13}C NMR of **2k**



^{1}H NMR of **3a**



^{13}C NMR of **3a**



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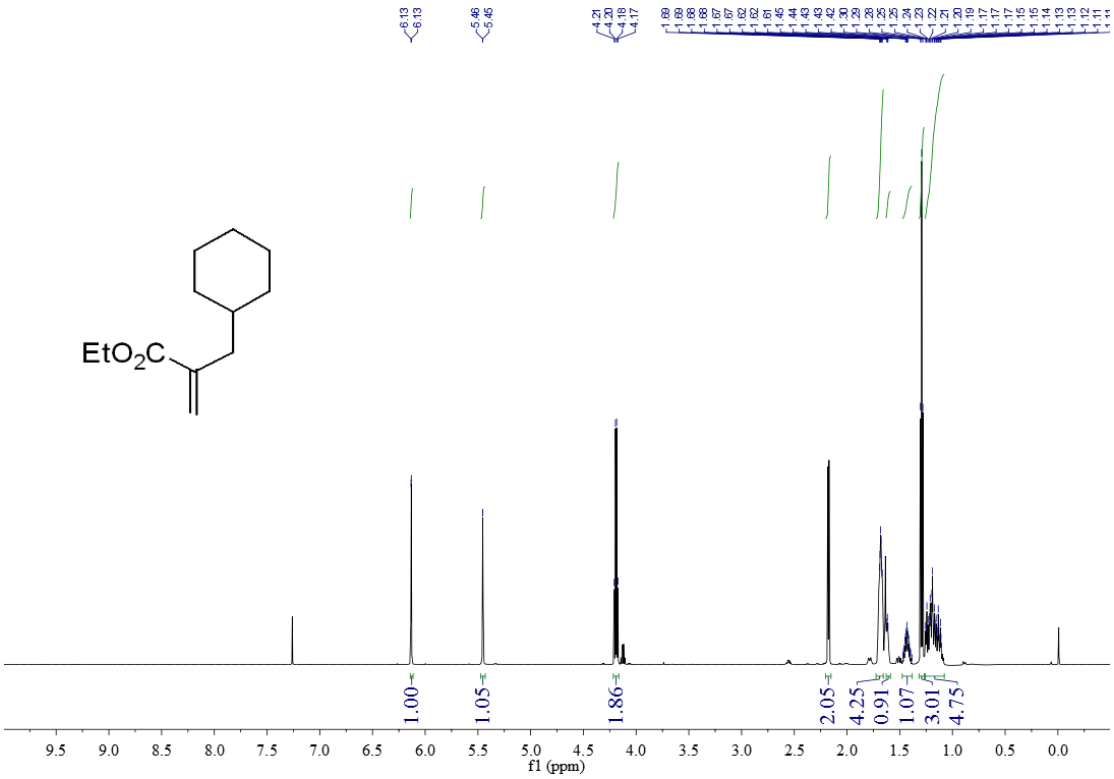

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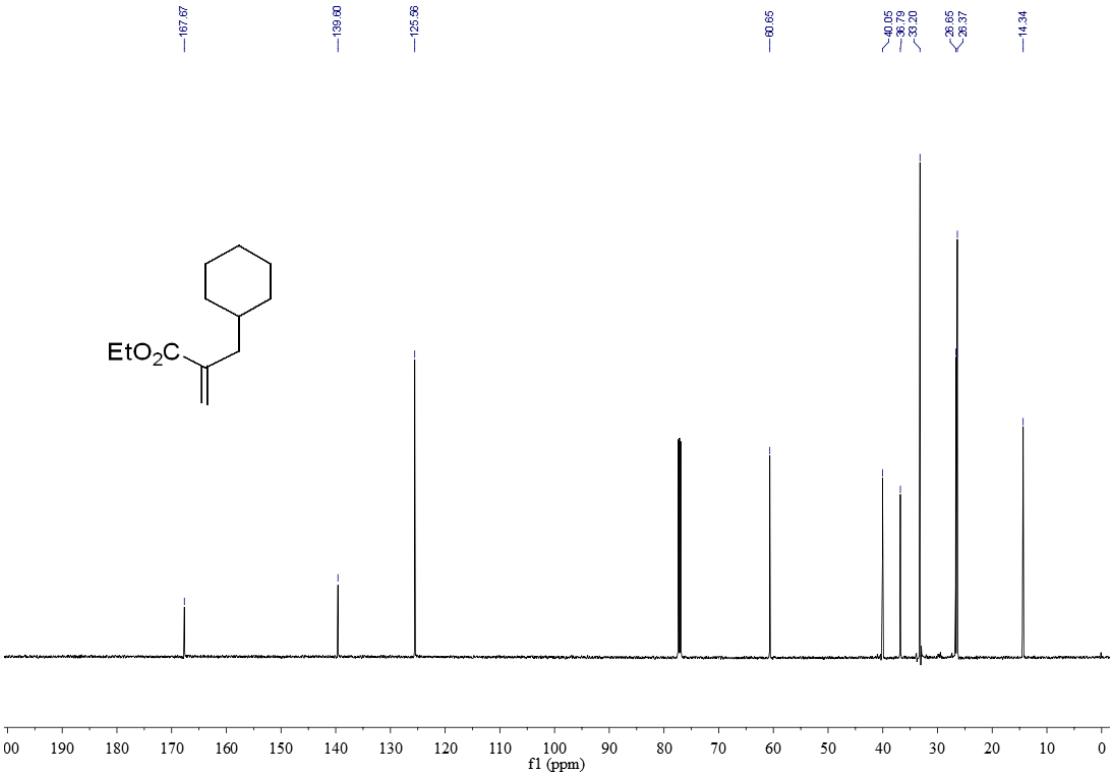
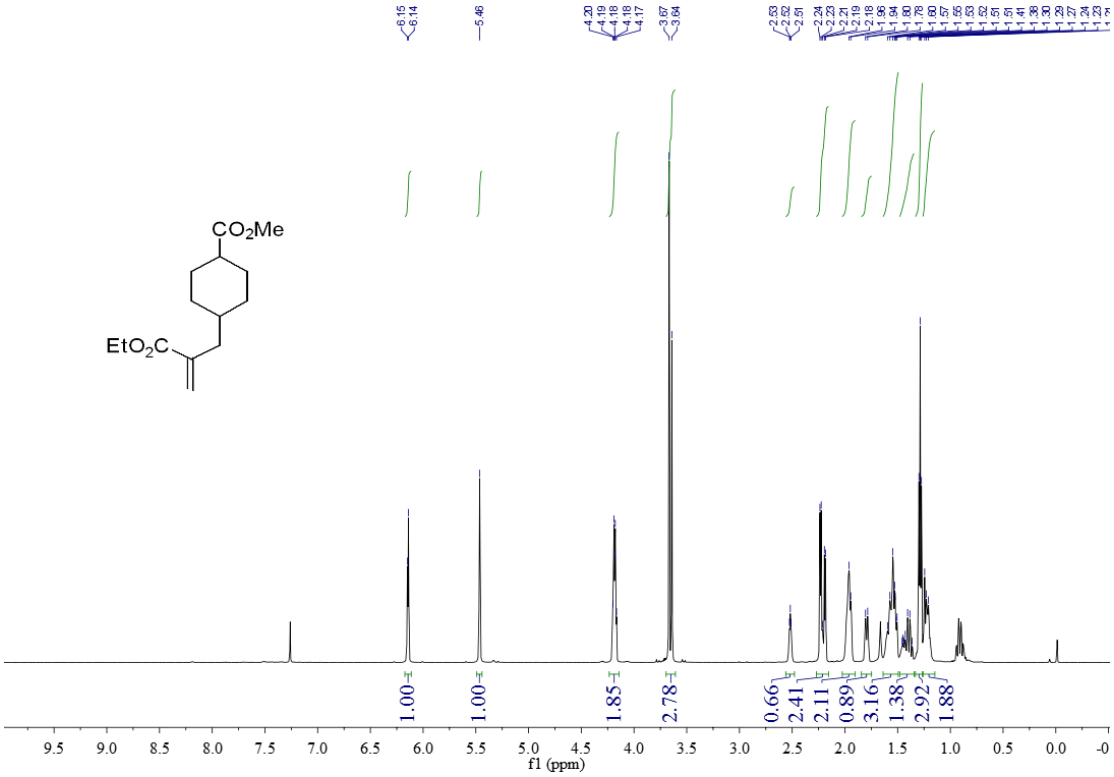


^{1}H NMR of **3c**



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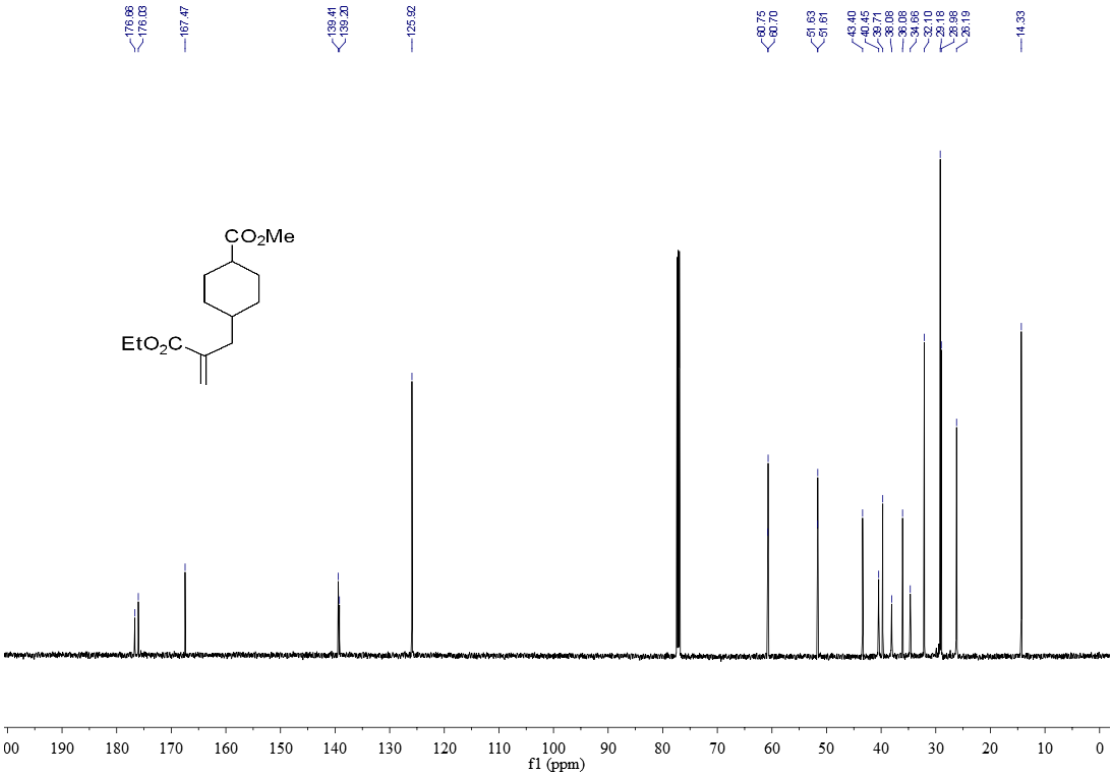
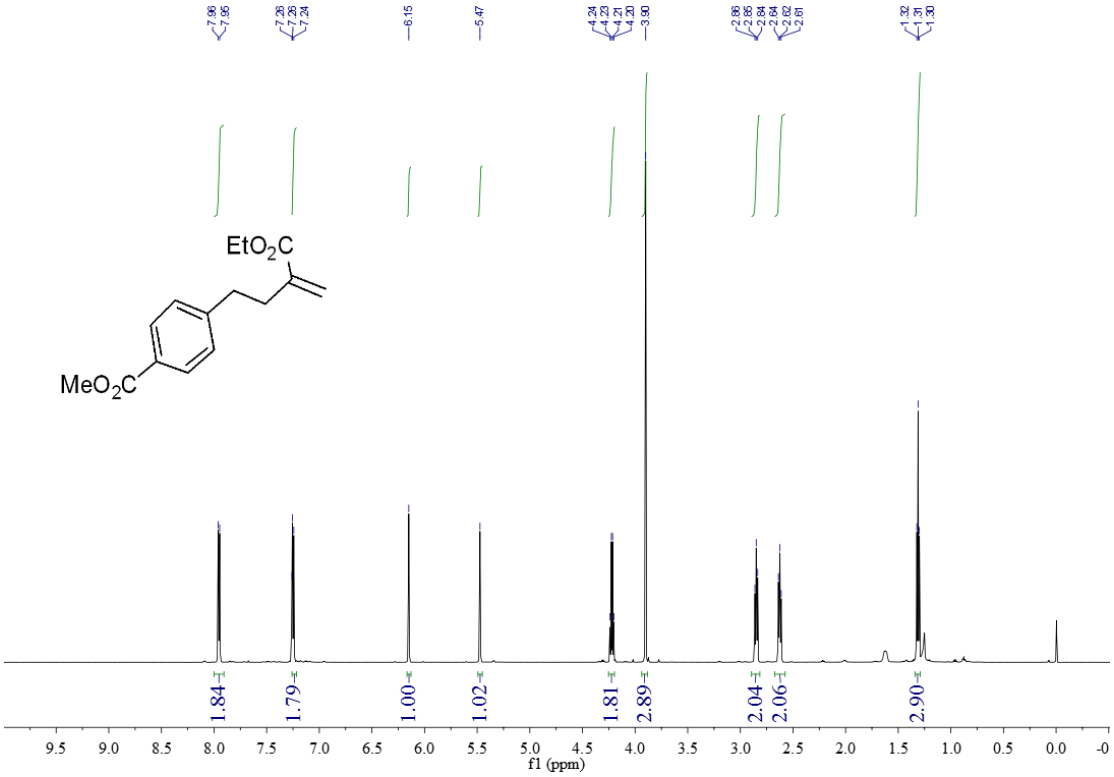
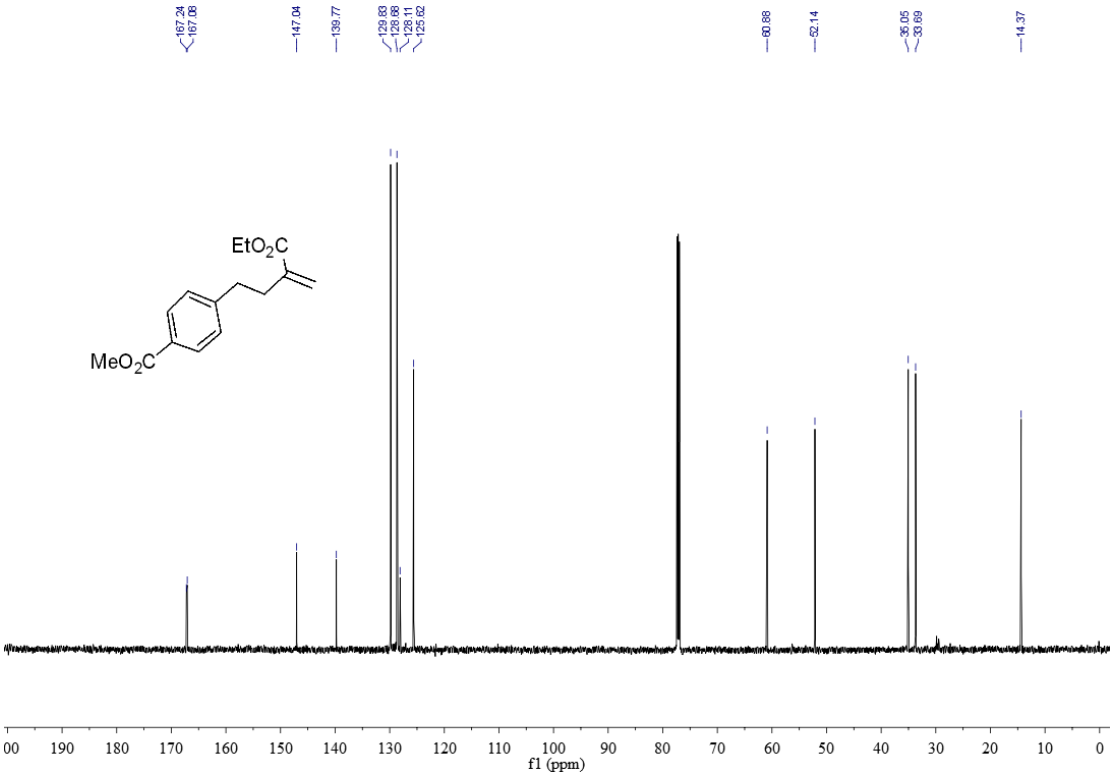


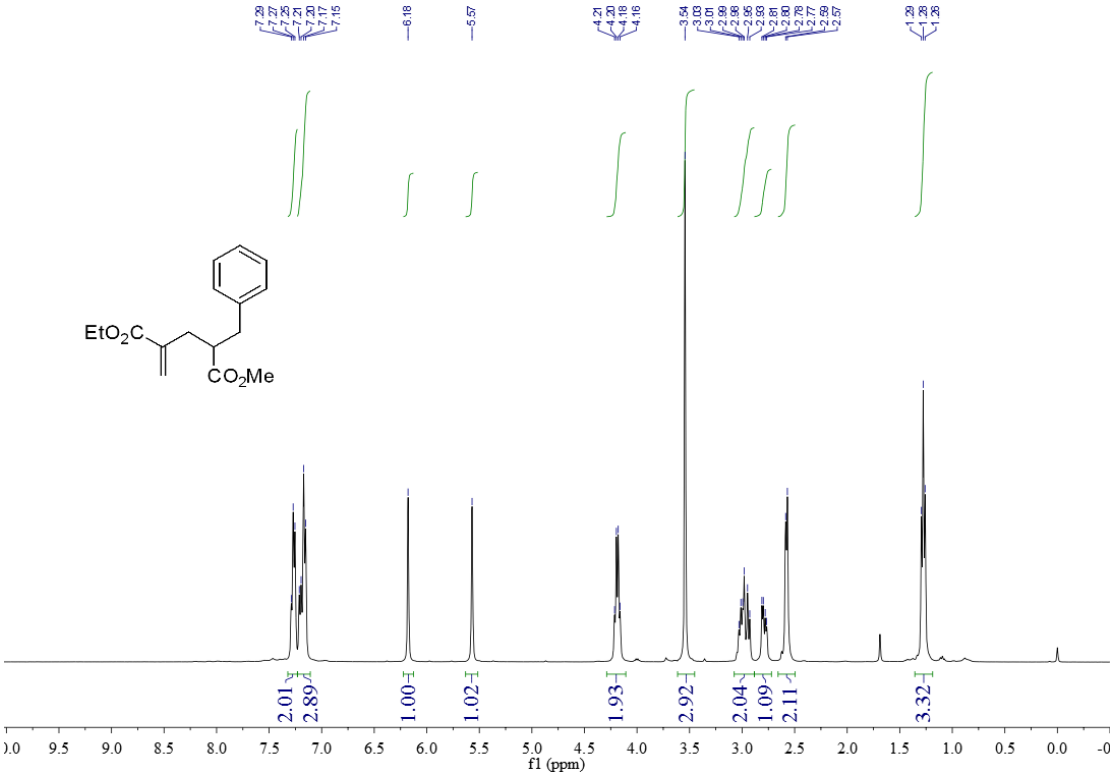
^{1}H NMR of **3d**



^{13}C NMR of **3d**



^{1}H NMR of **3e**



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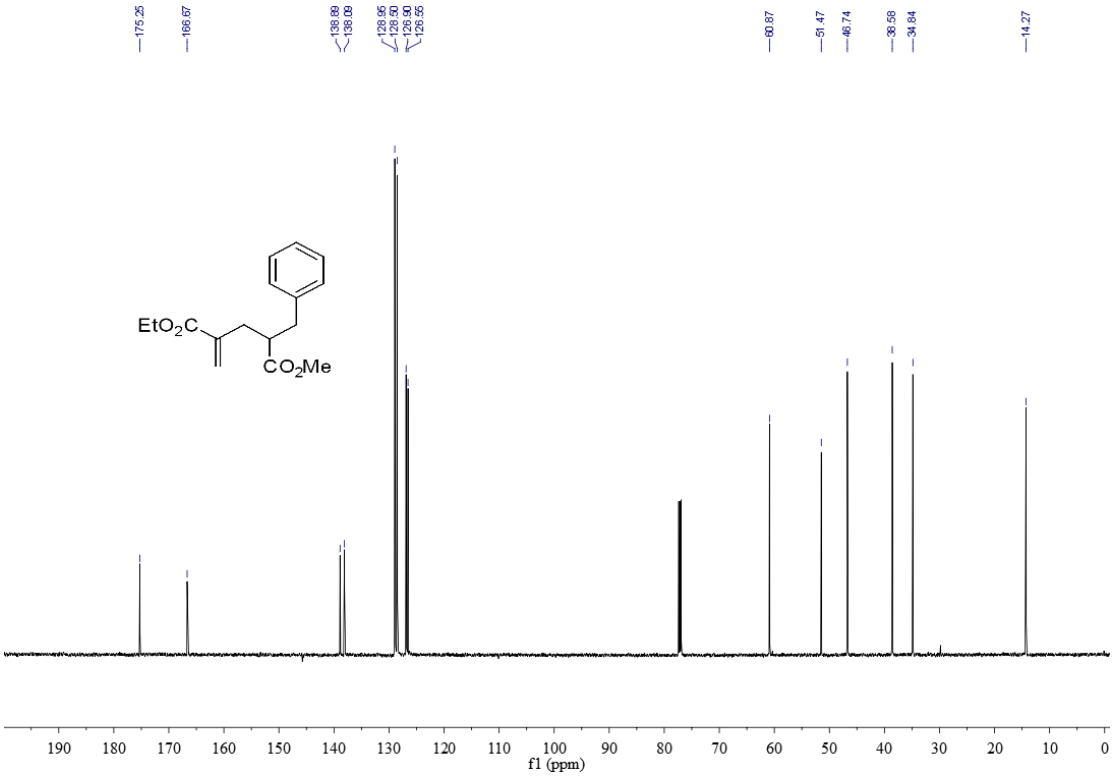
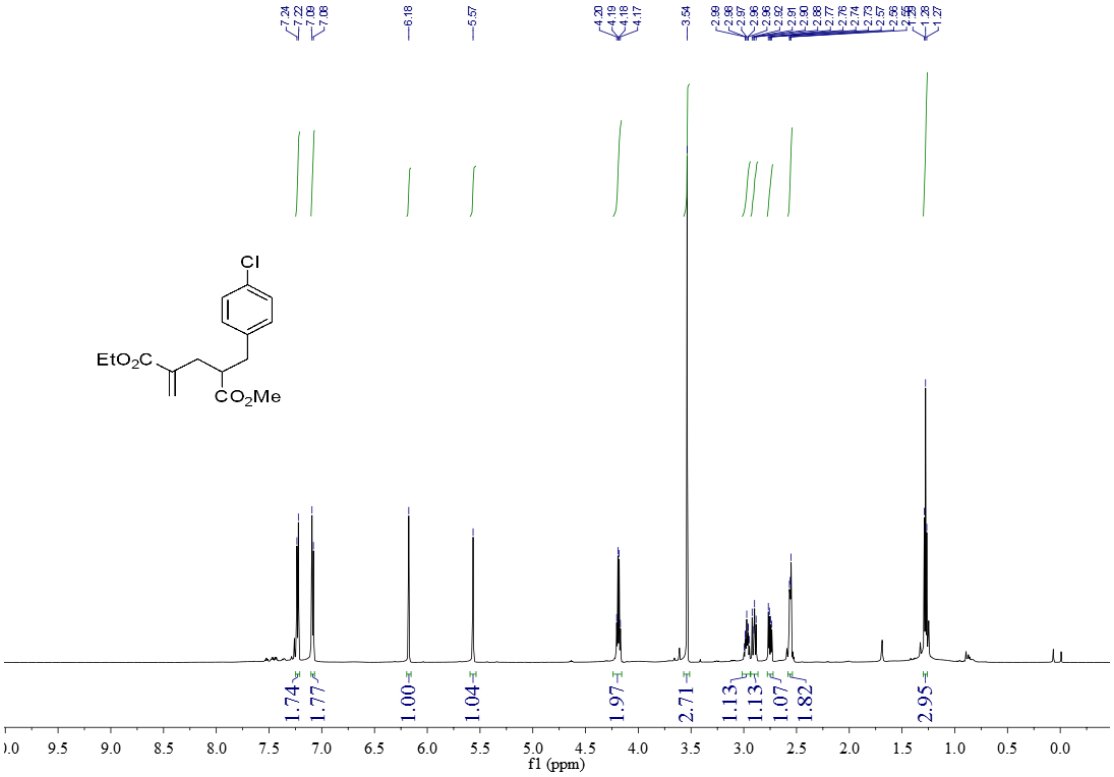


^{1}H NMR of **3f**



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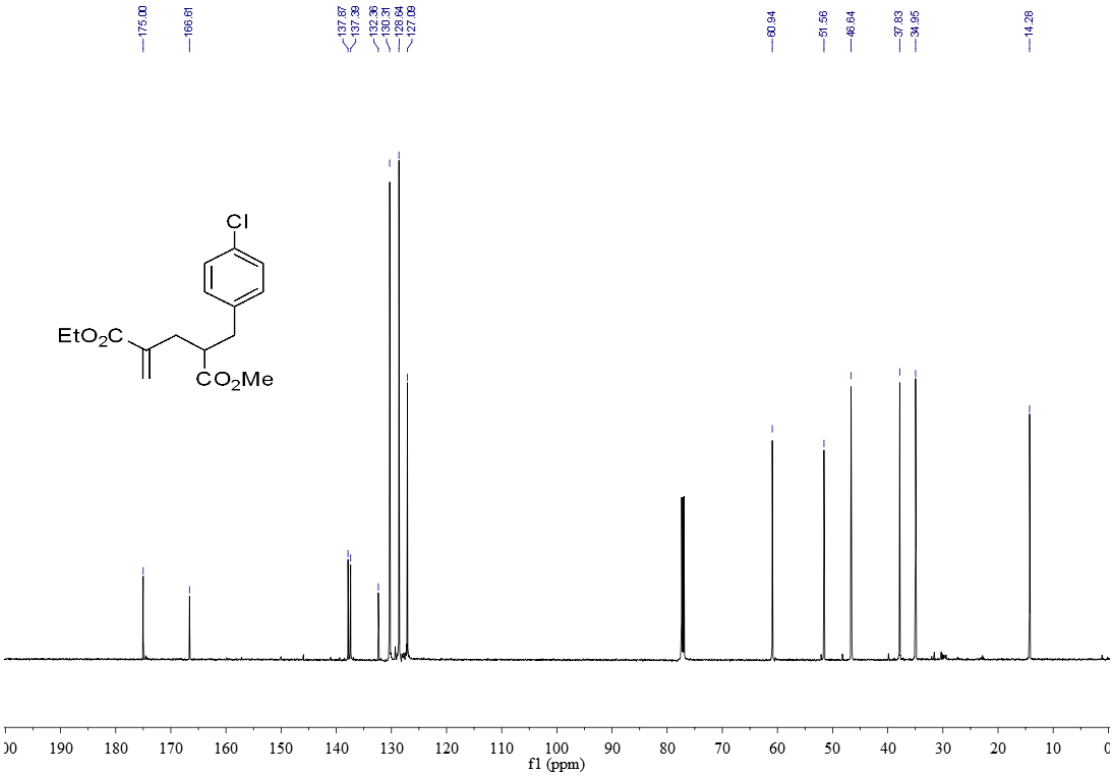
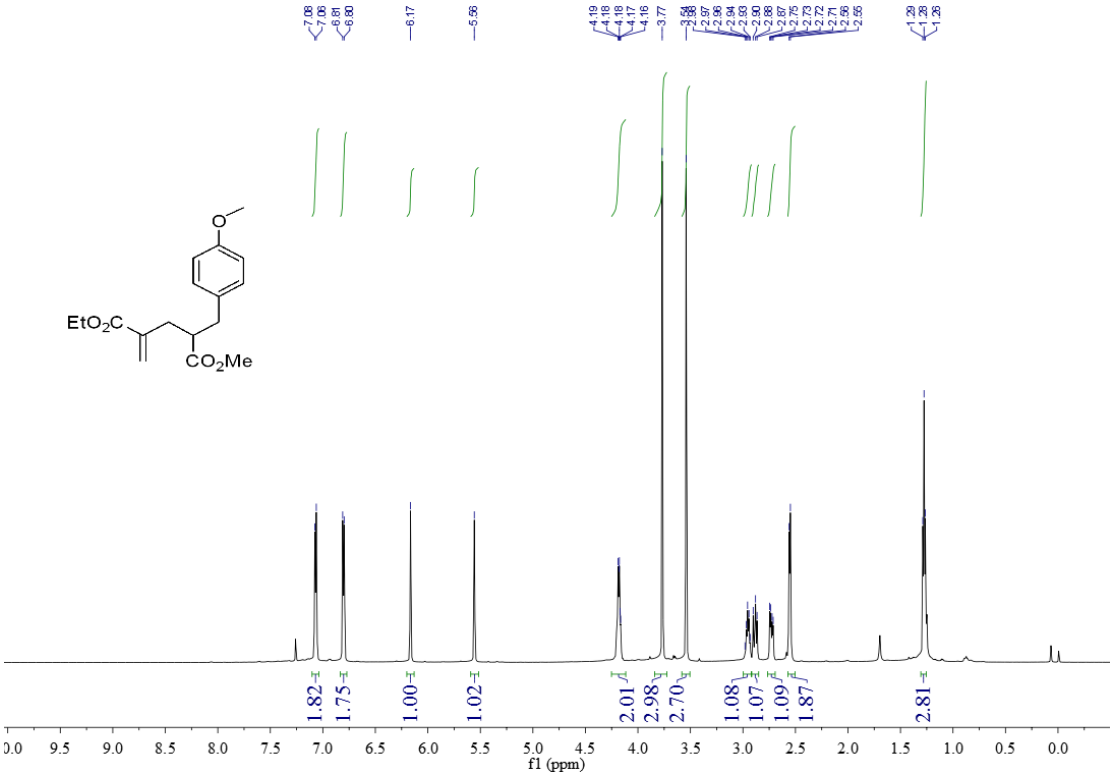
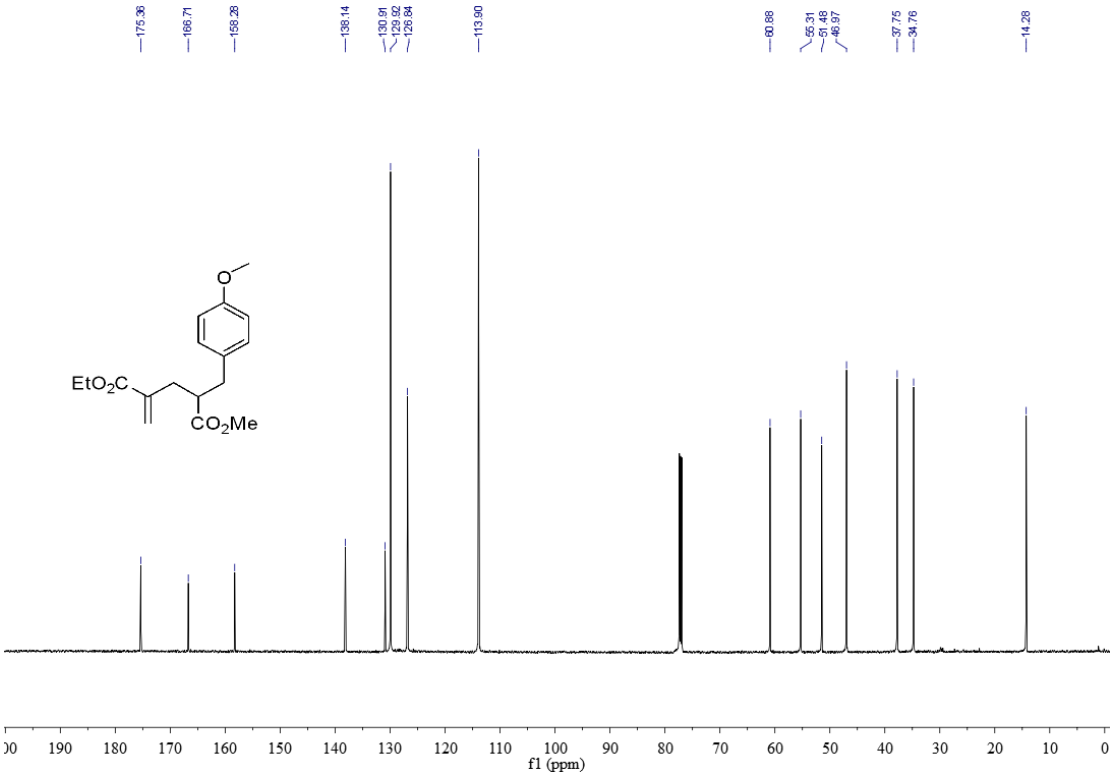


^{1}H NMR of **3g**



^{13}C NMR of **3g**



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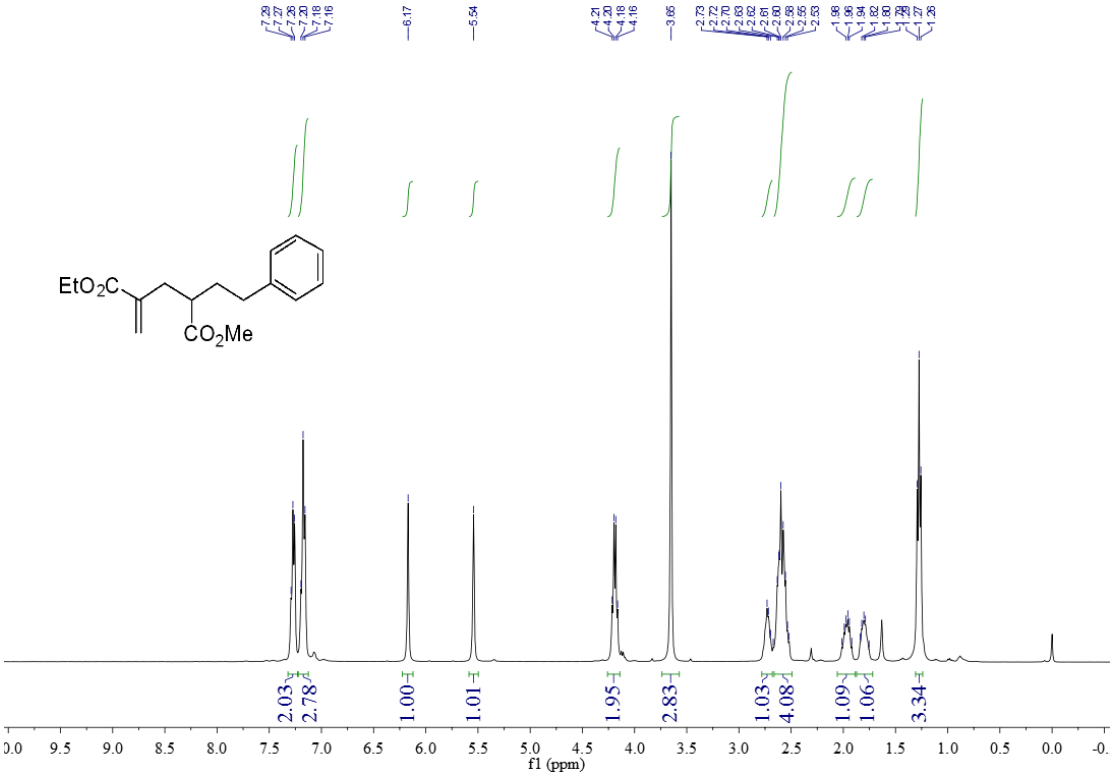
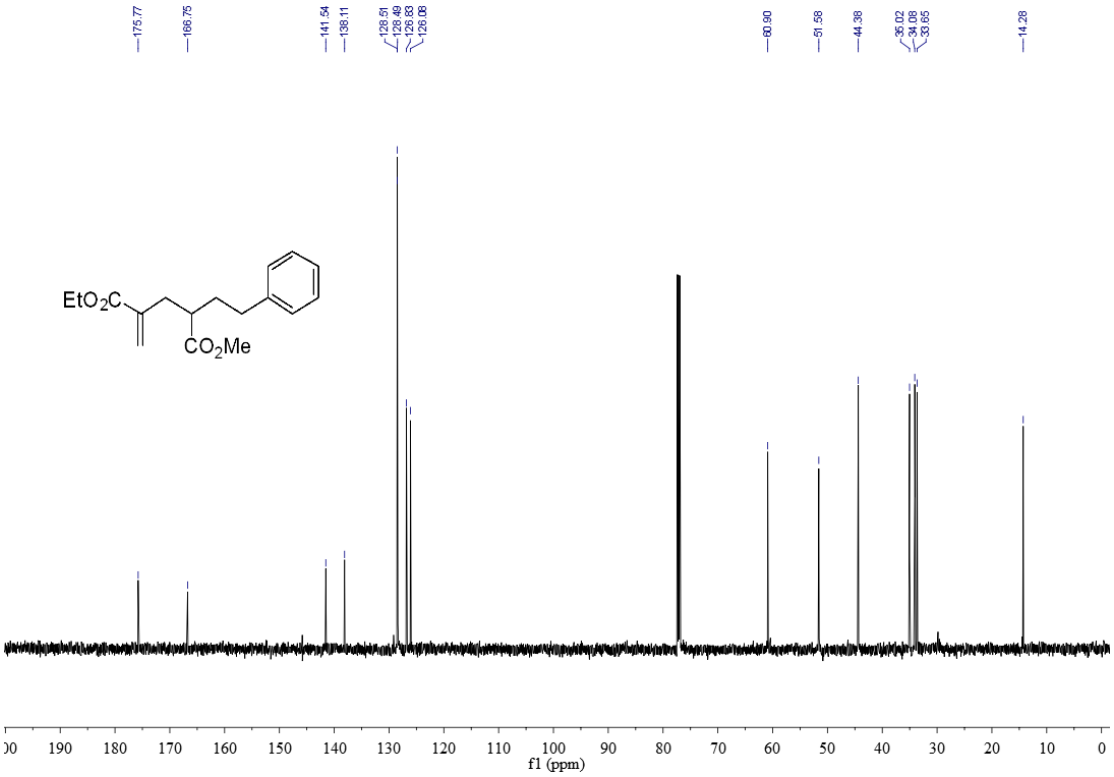


^{13}C NMR of **3h**



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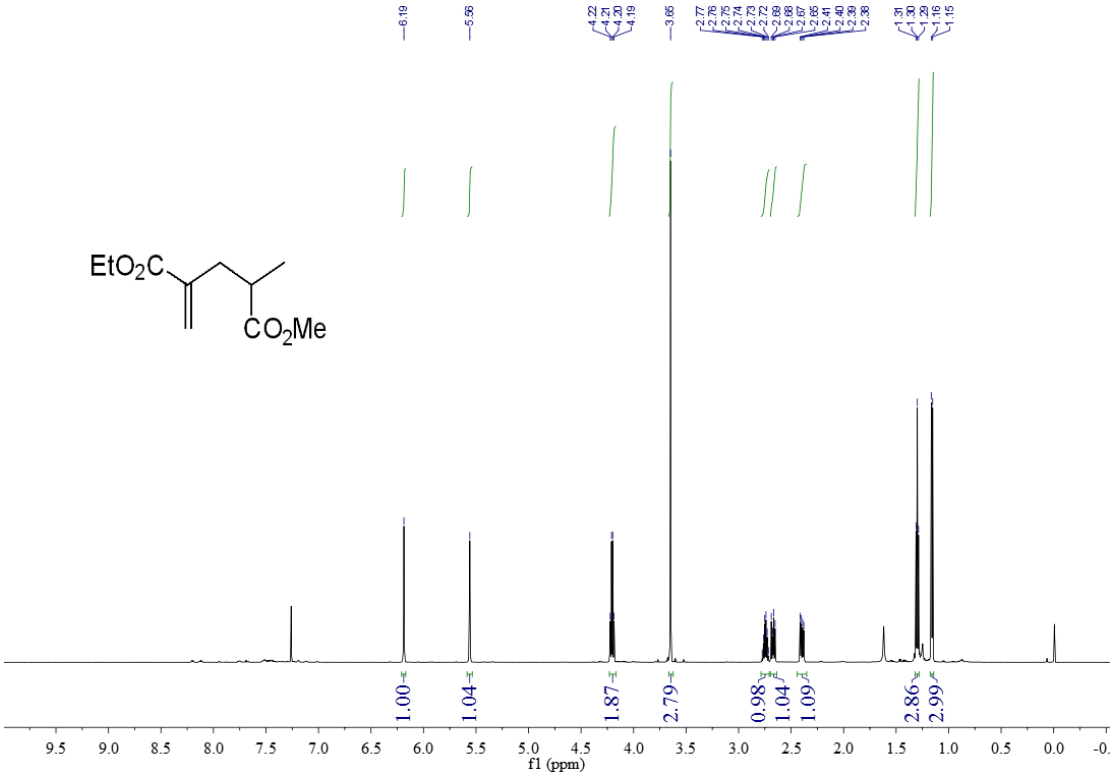
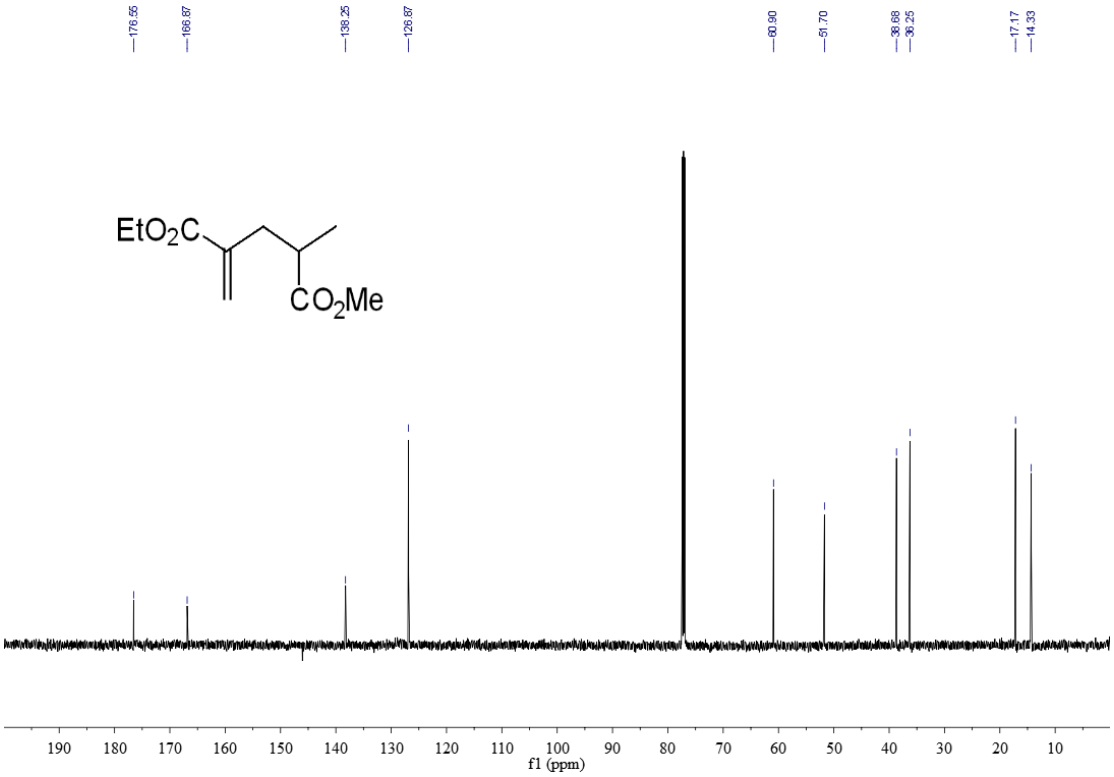
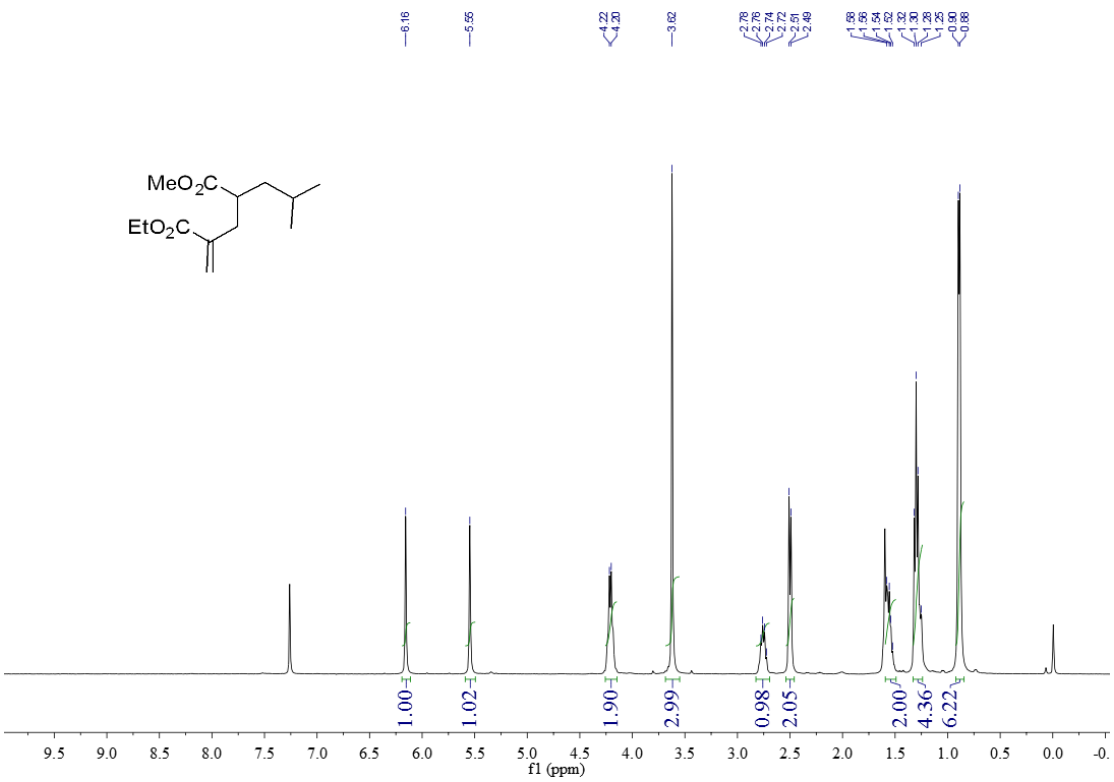


^{13}C NMR of **3i**



^{1}H NMR of **3j**



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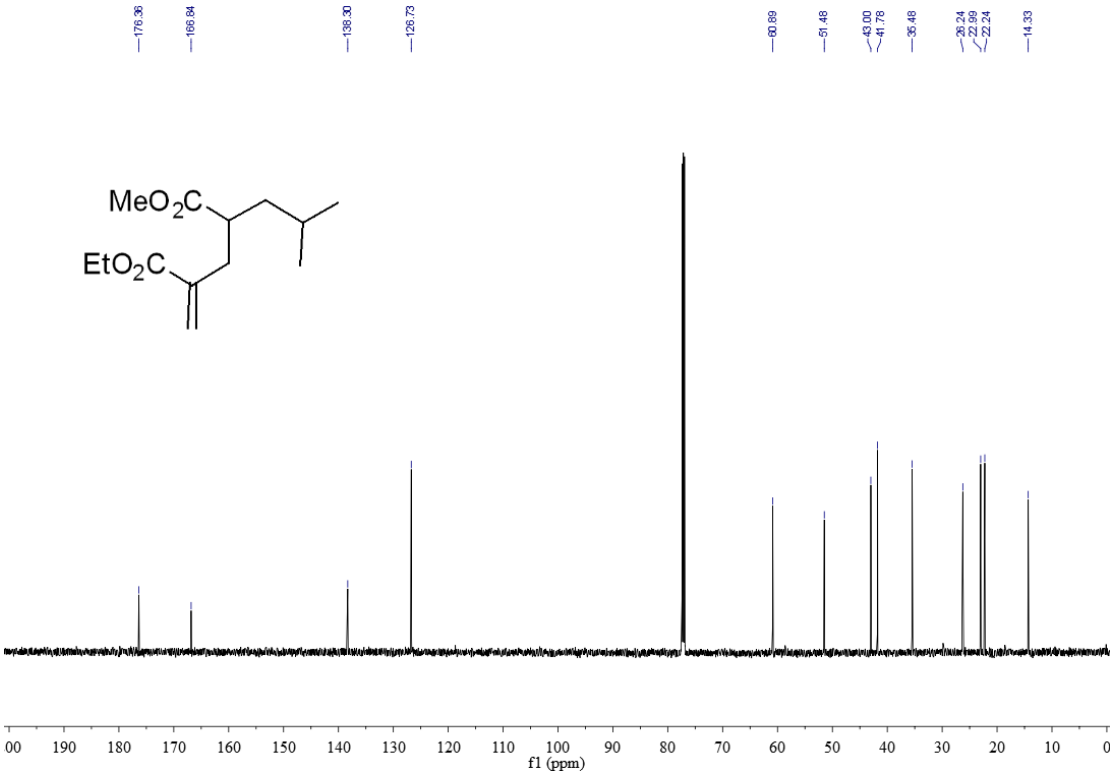
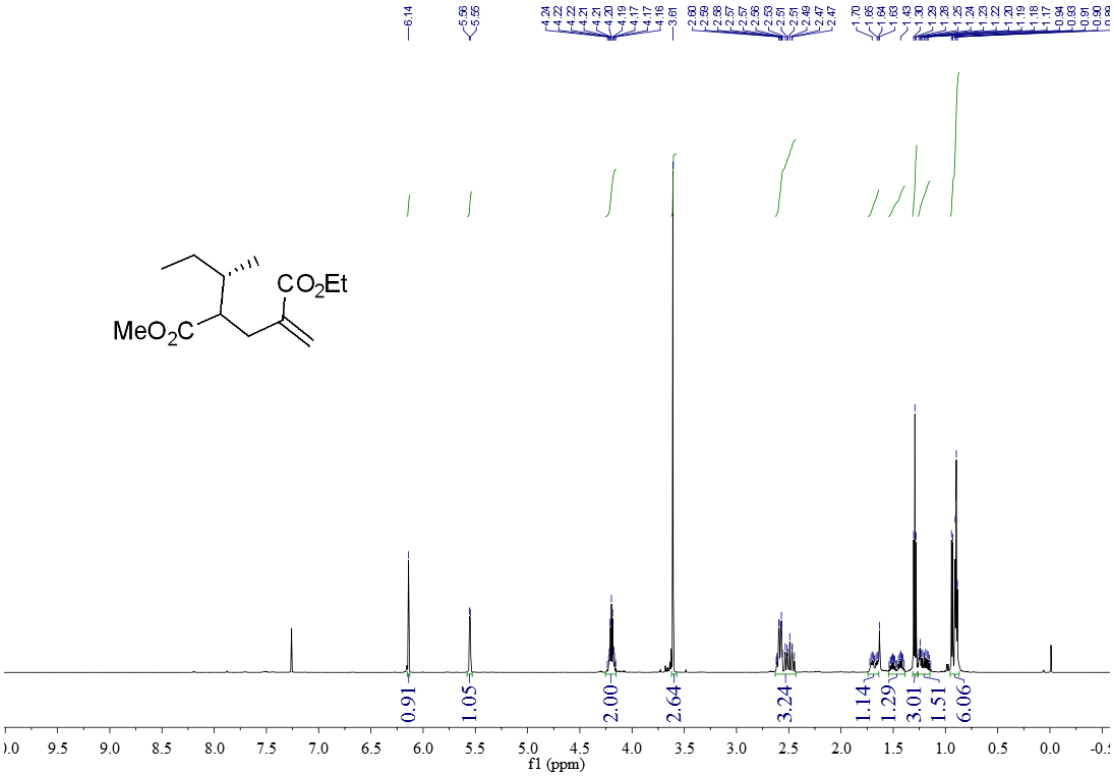
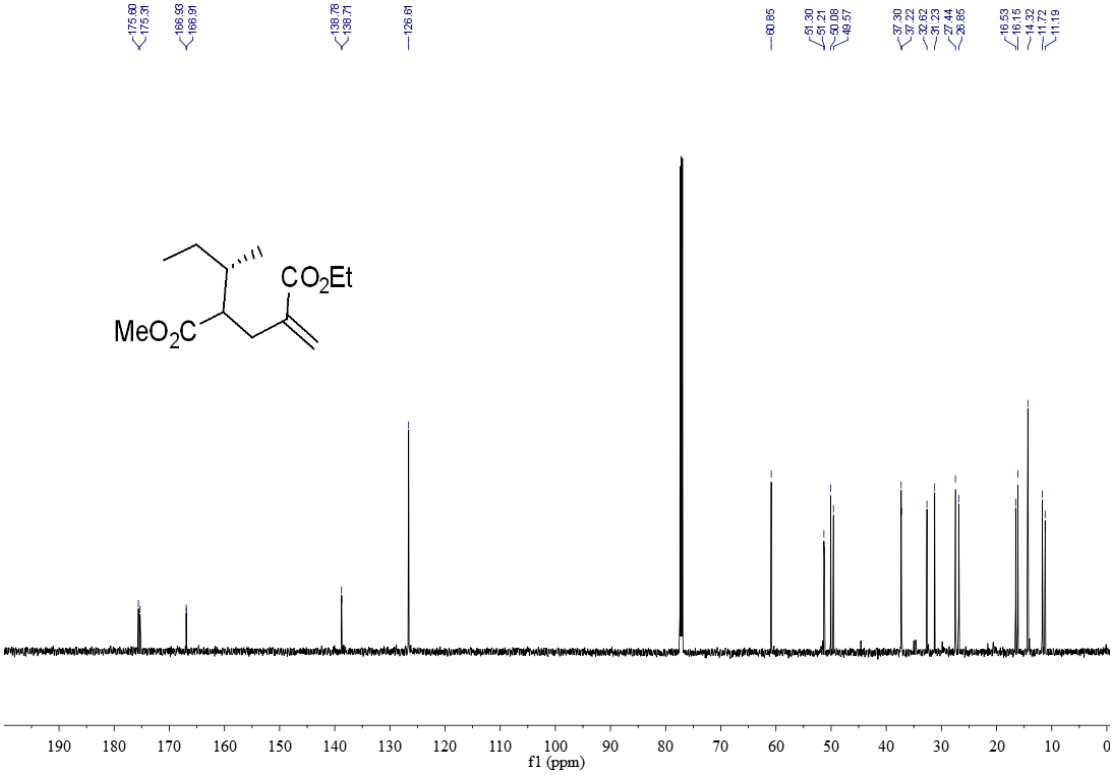


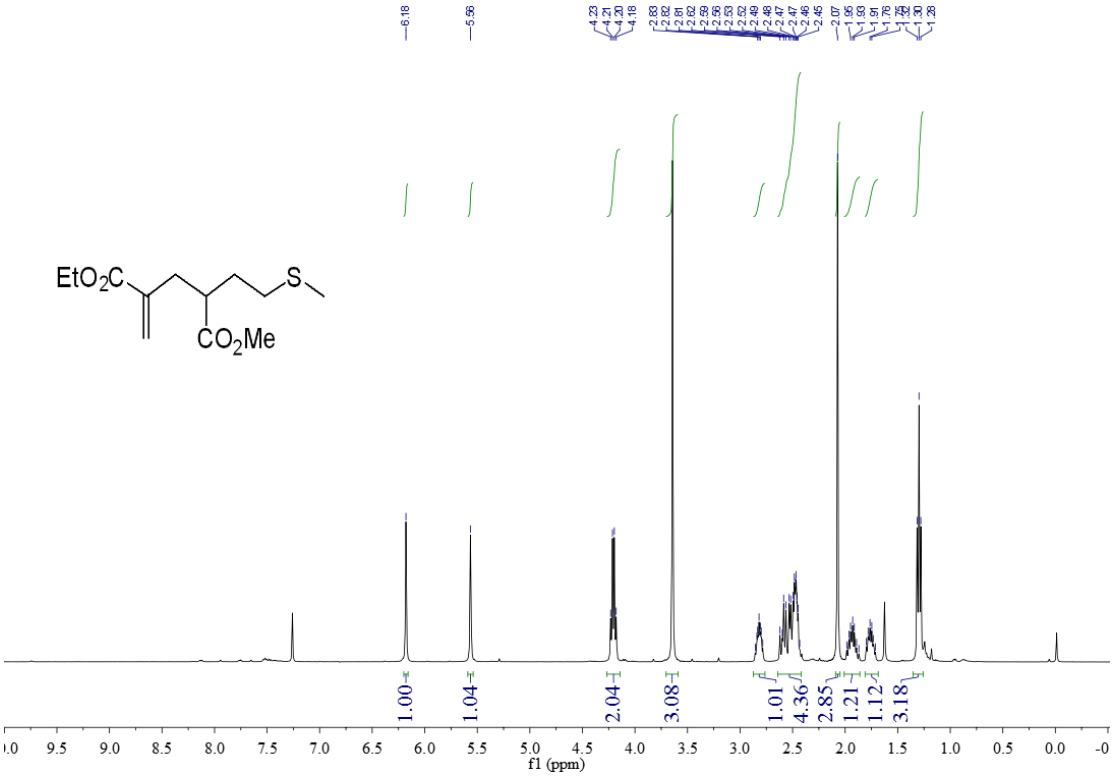
^{1}H NMR of **3k**



^{13}C NMR of **3k**



^{1}H NMR of **3l**



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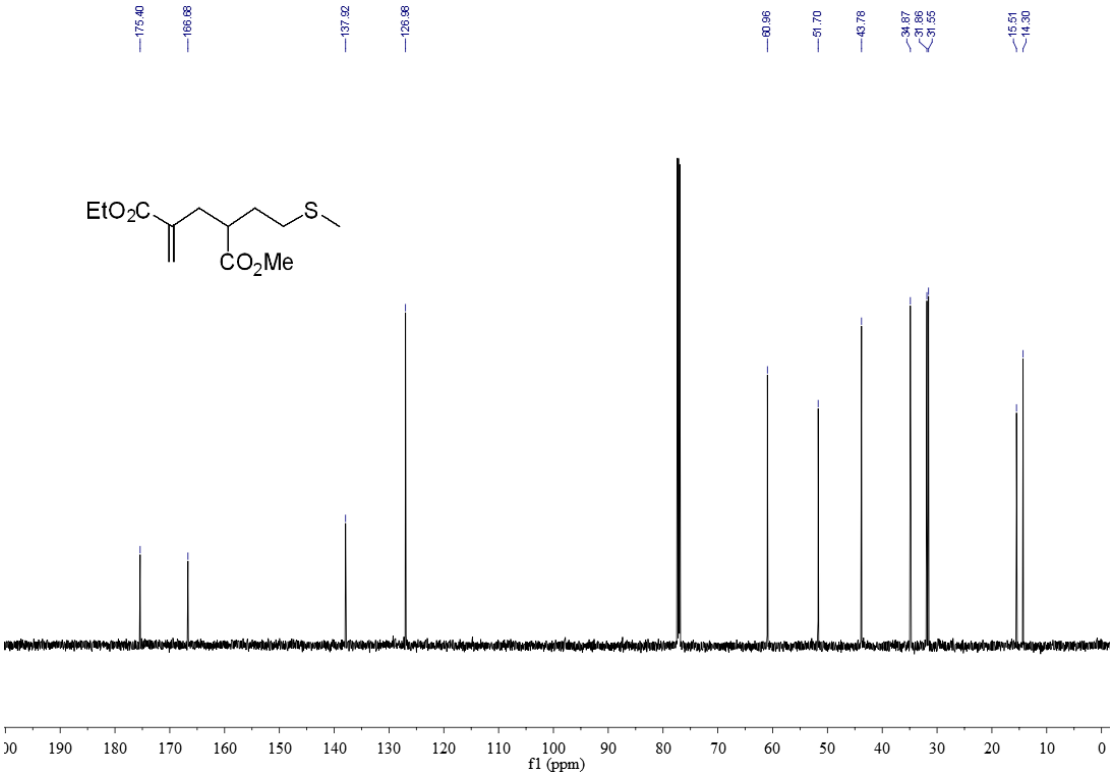
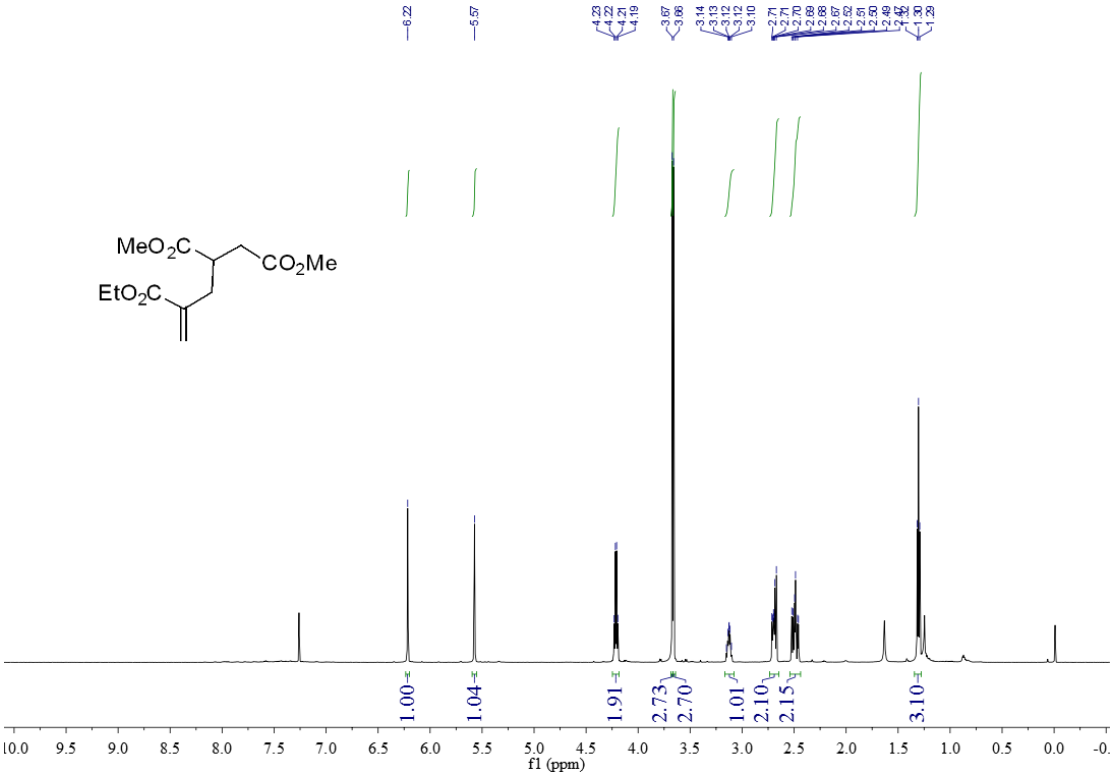
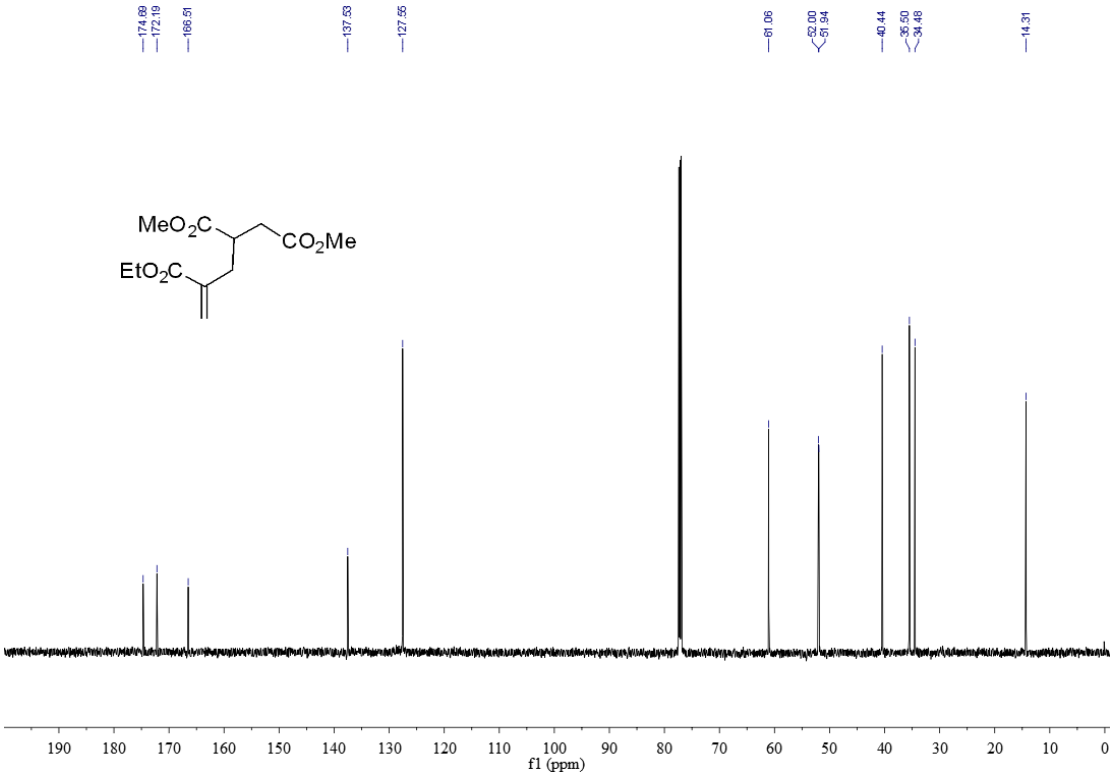


^{1}H NMR of **3m**



^{13}C NMR of **3m**



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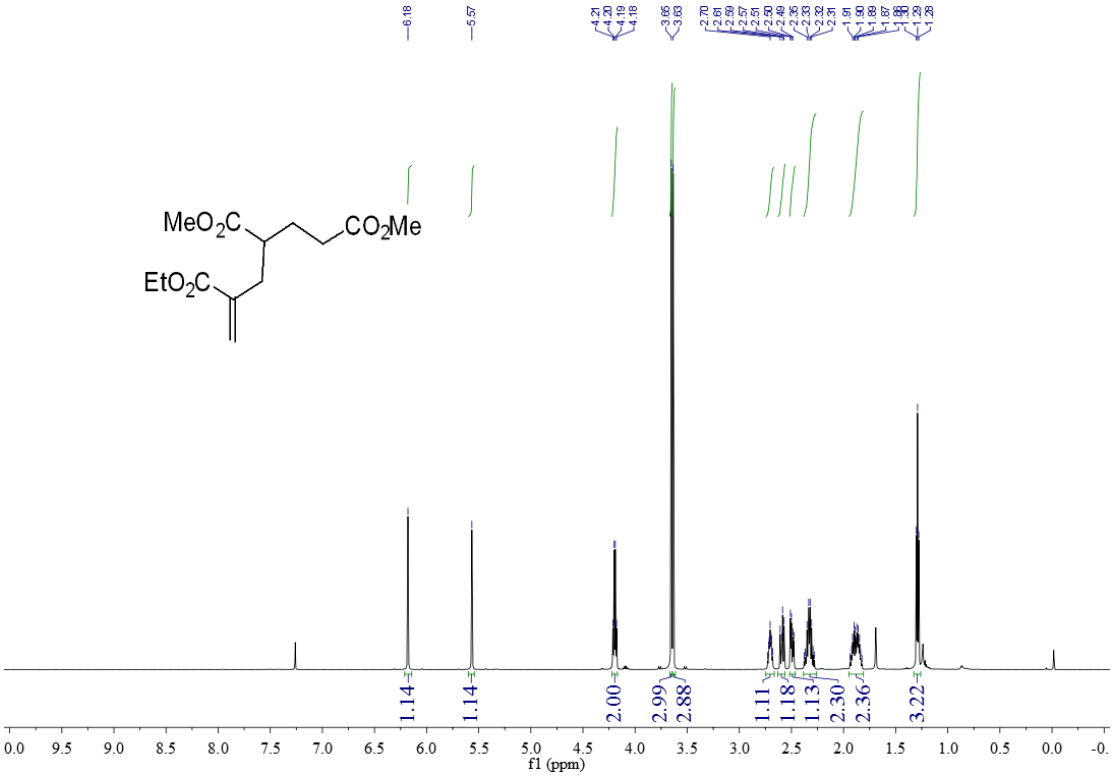
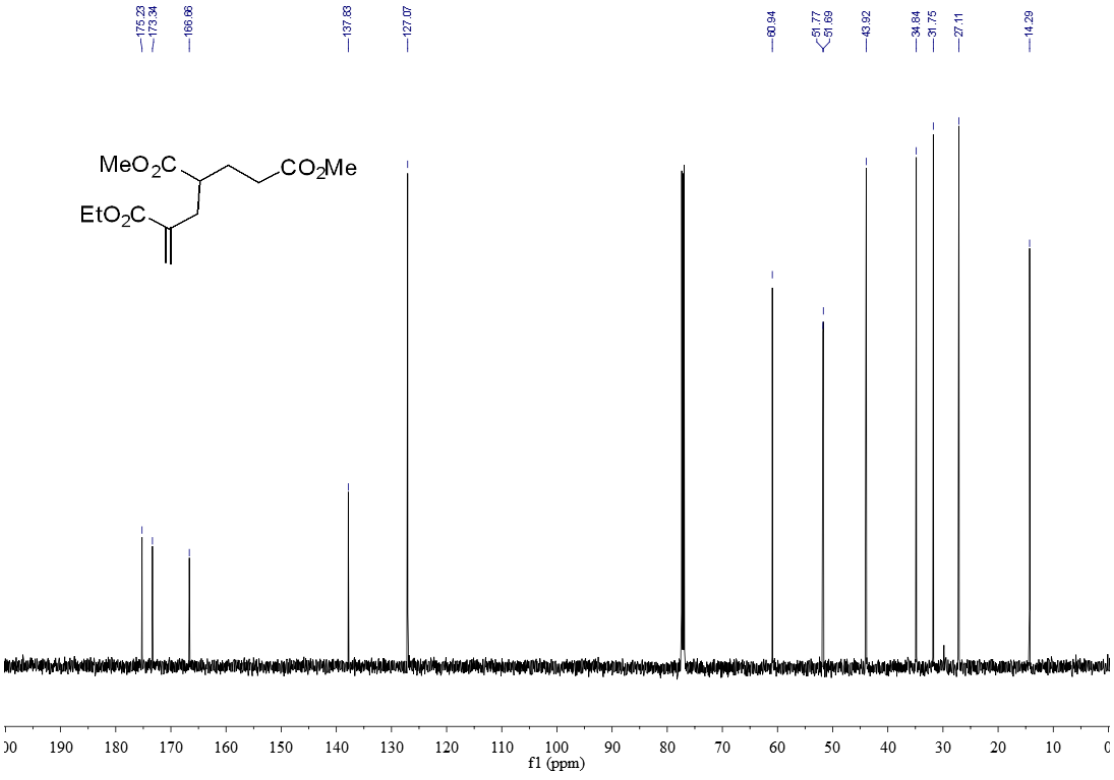
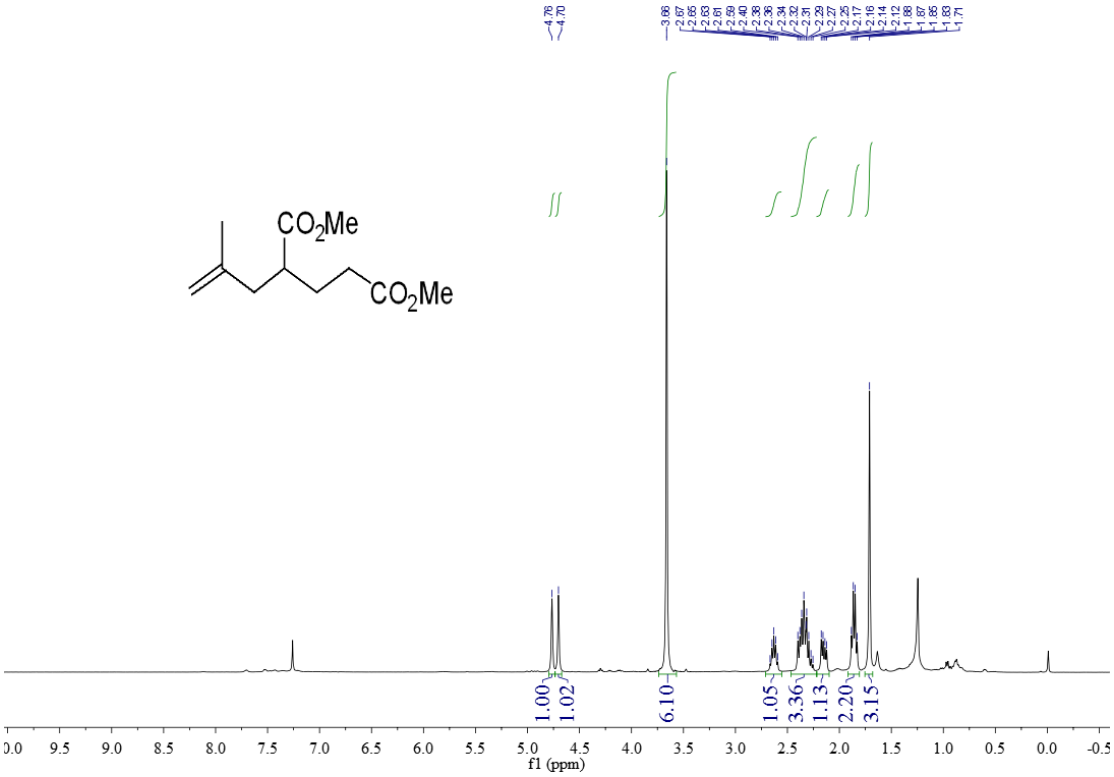


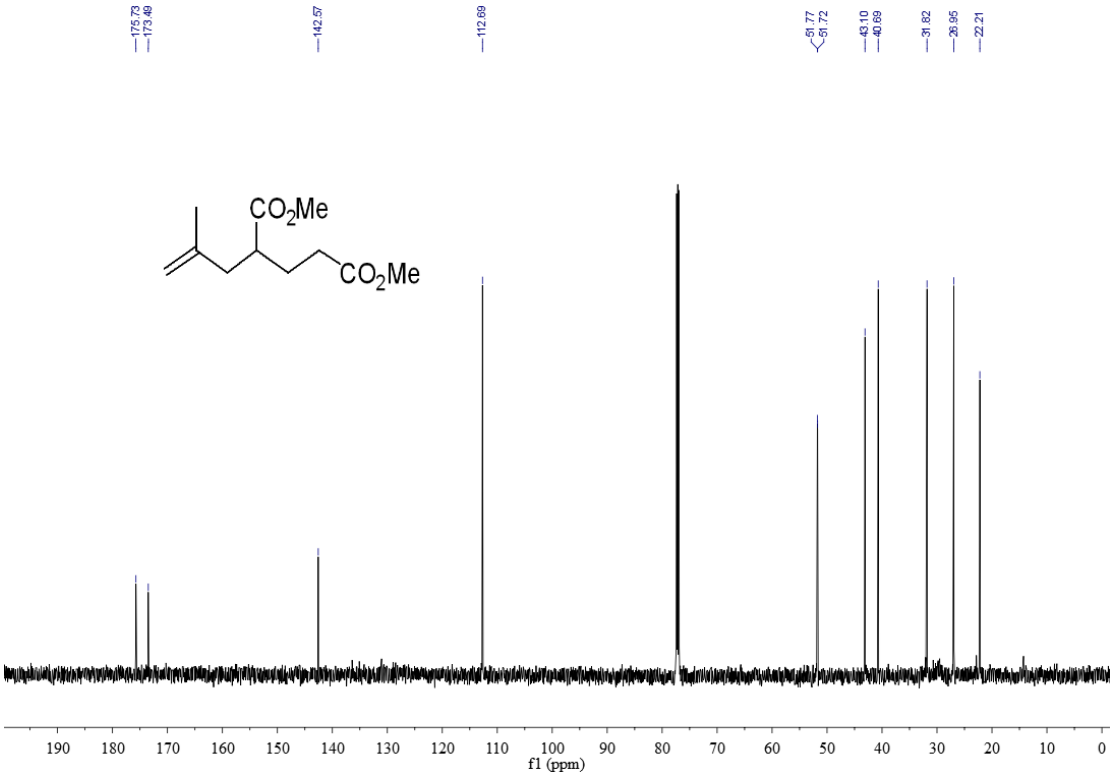
^{13}C NMR of **3n**



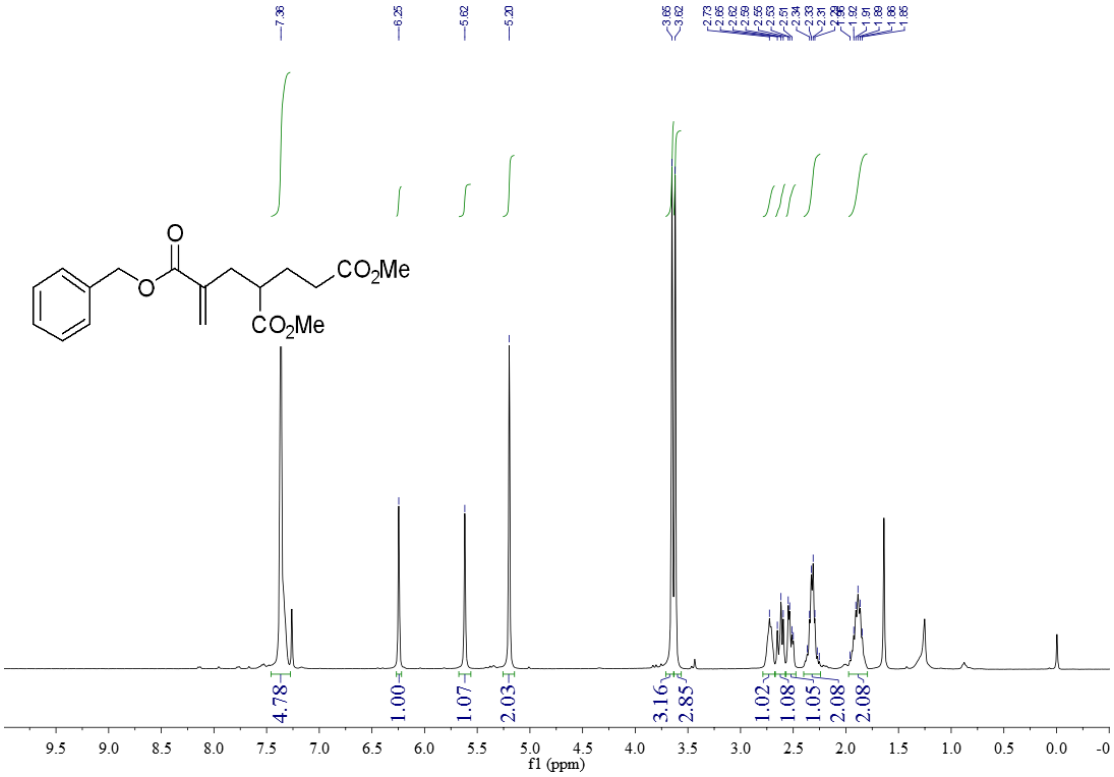
^{1}H NMR of **4a**



^{13}C NMR of **4a**



^{1}H NMR of **4b**



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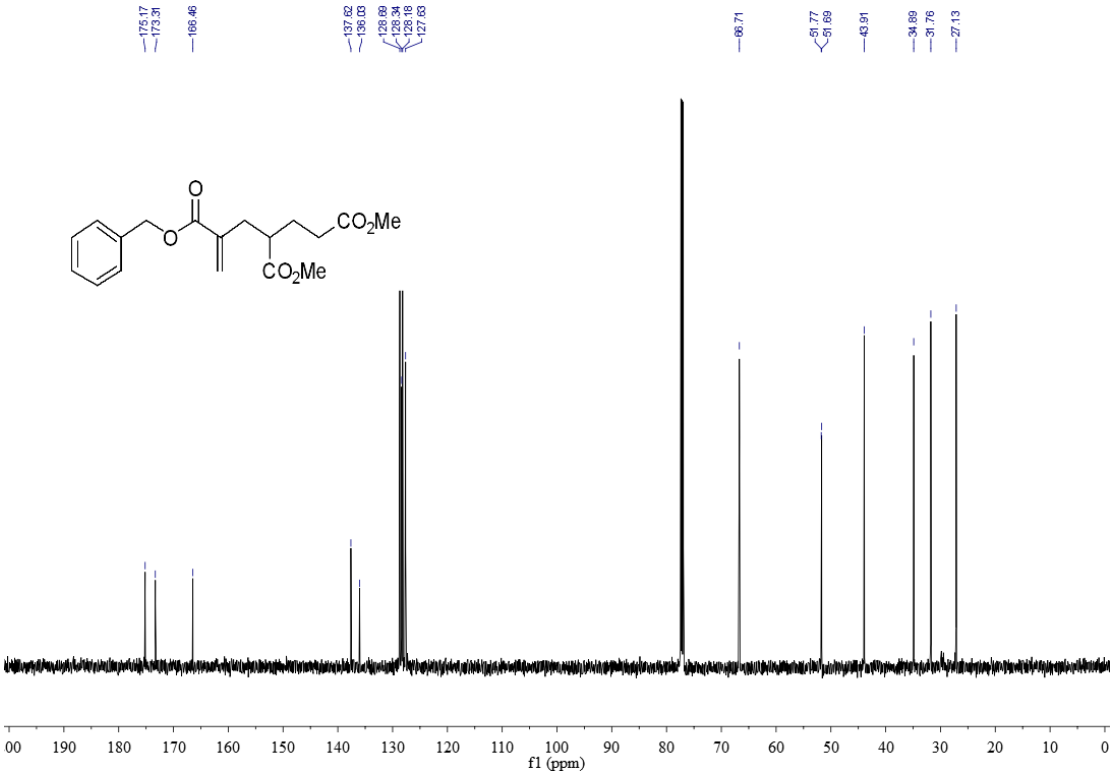

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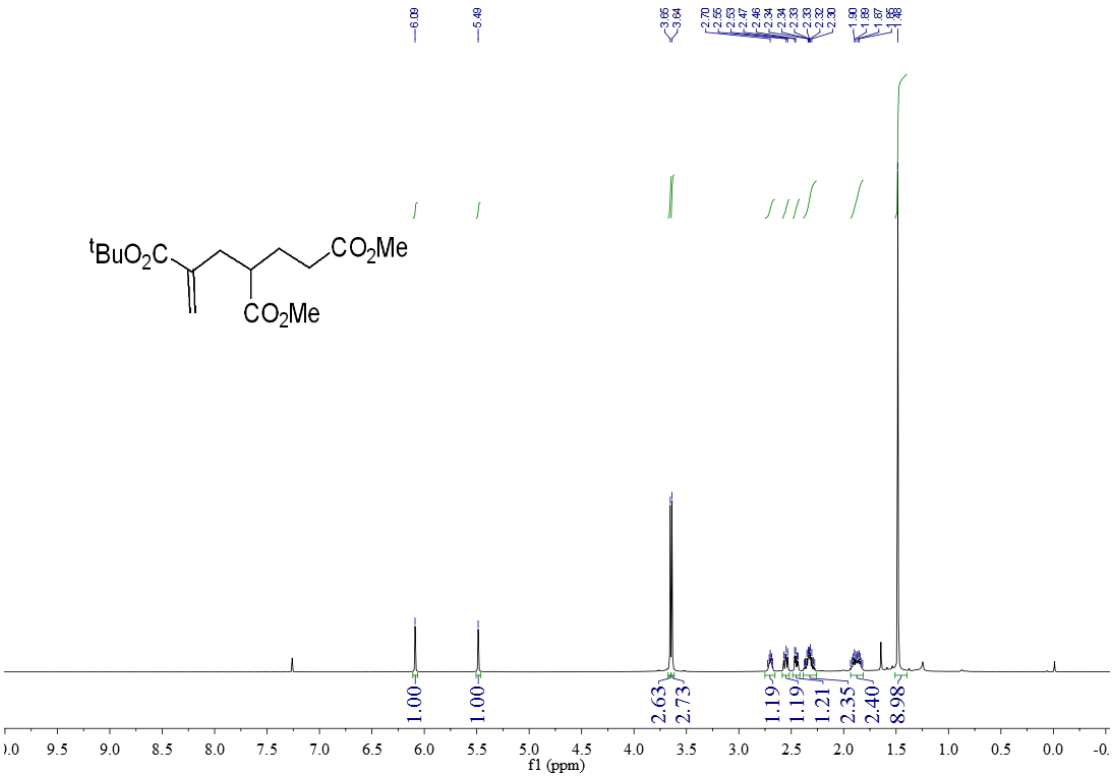
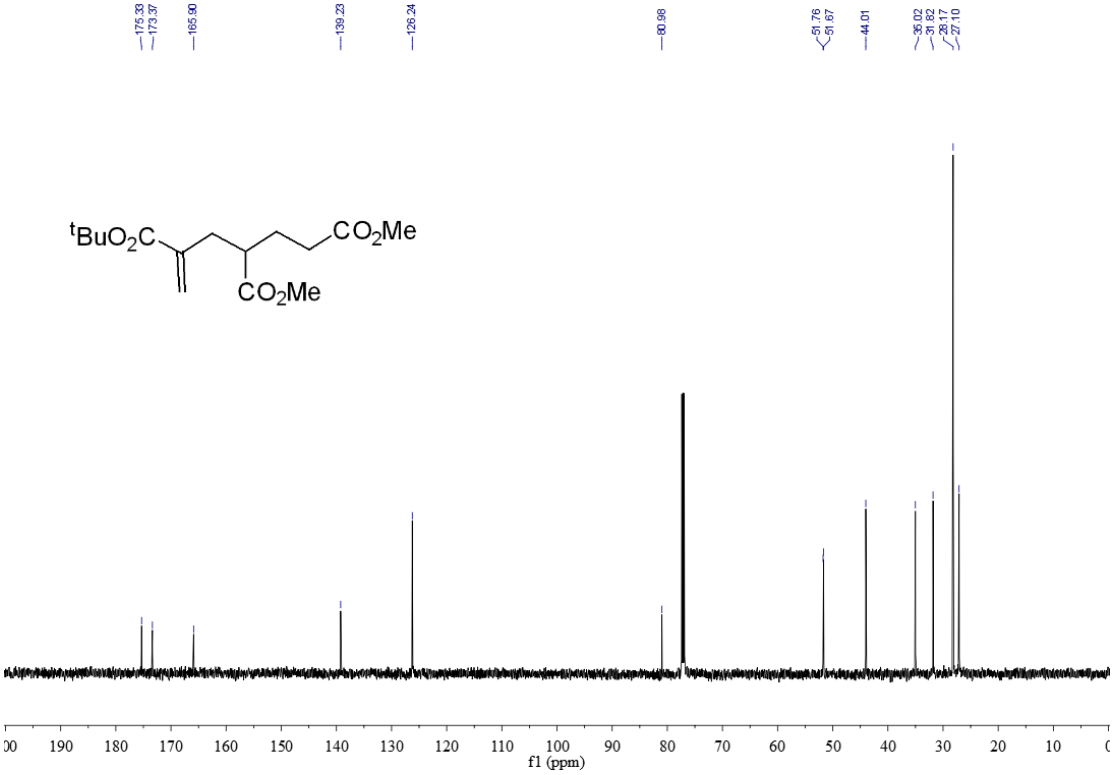


^{13}C NMR of **4c**



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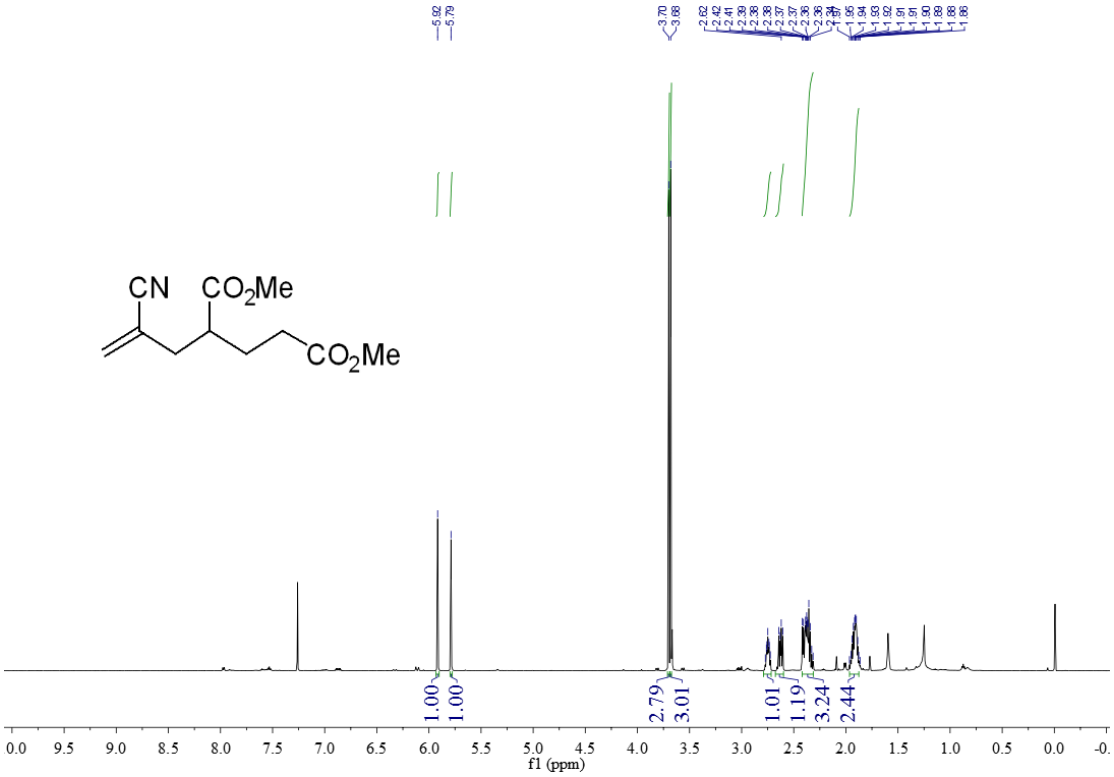
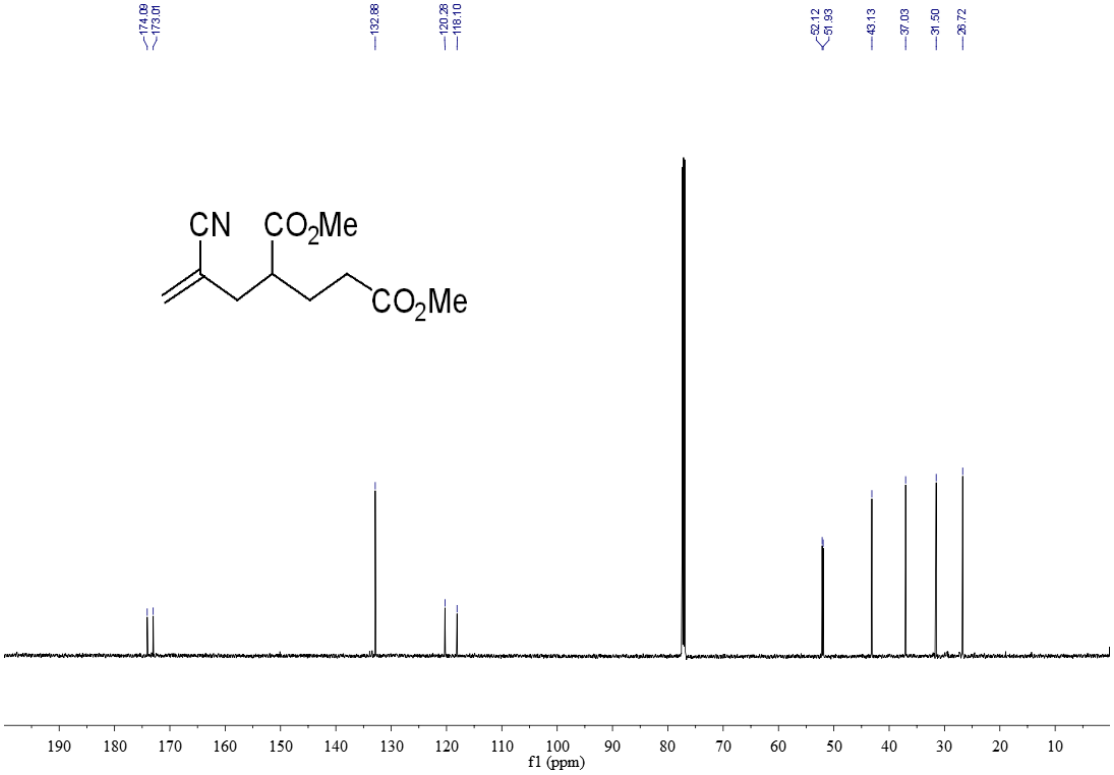


^{13}C NMR of **4d**



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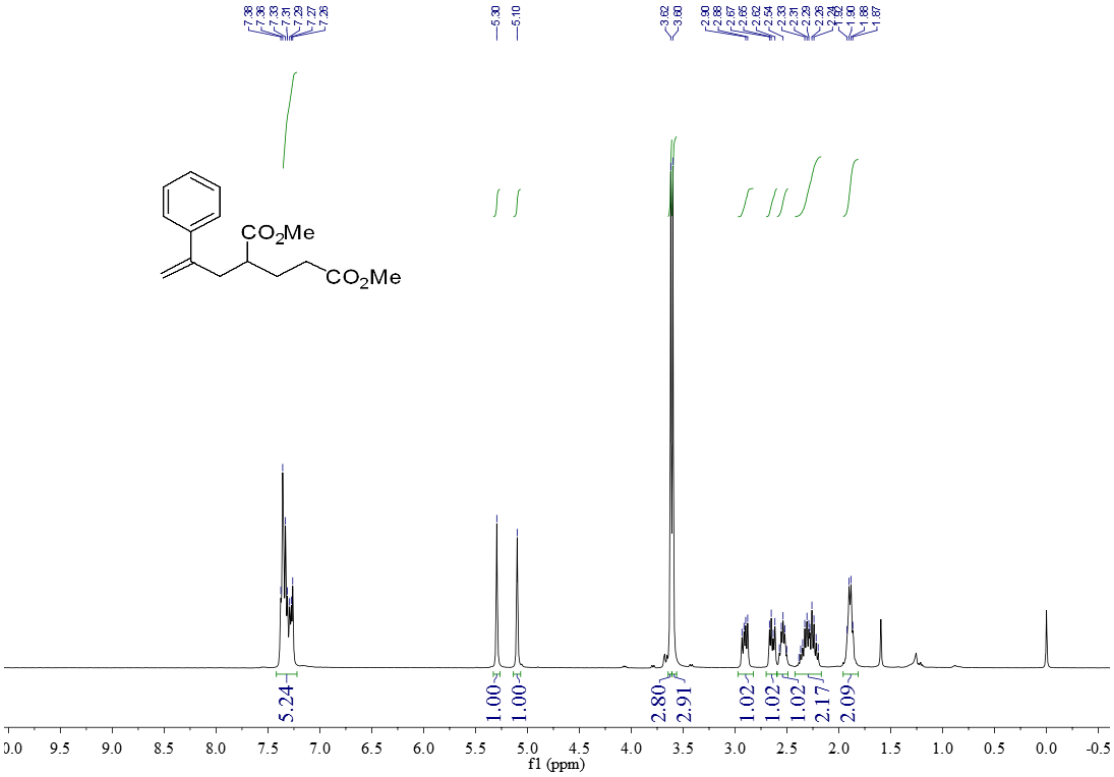
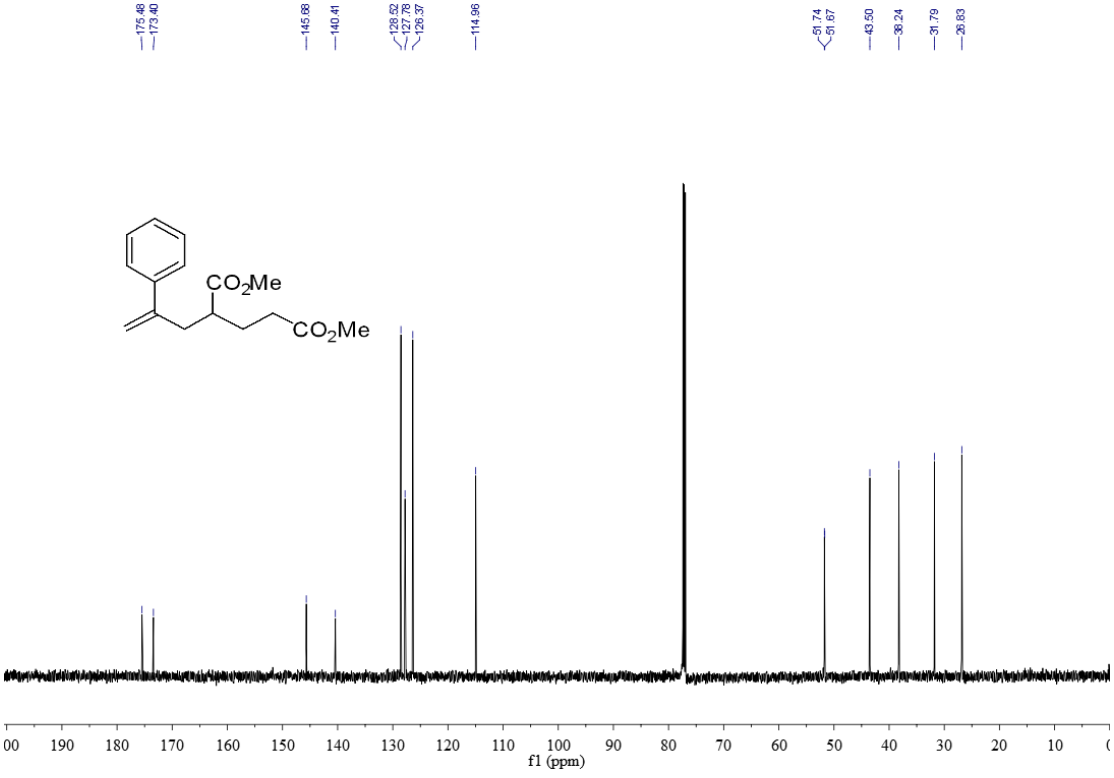
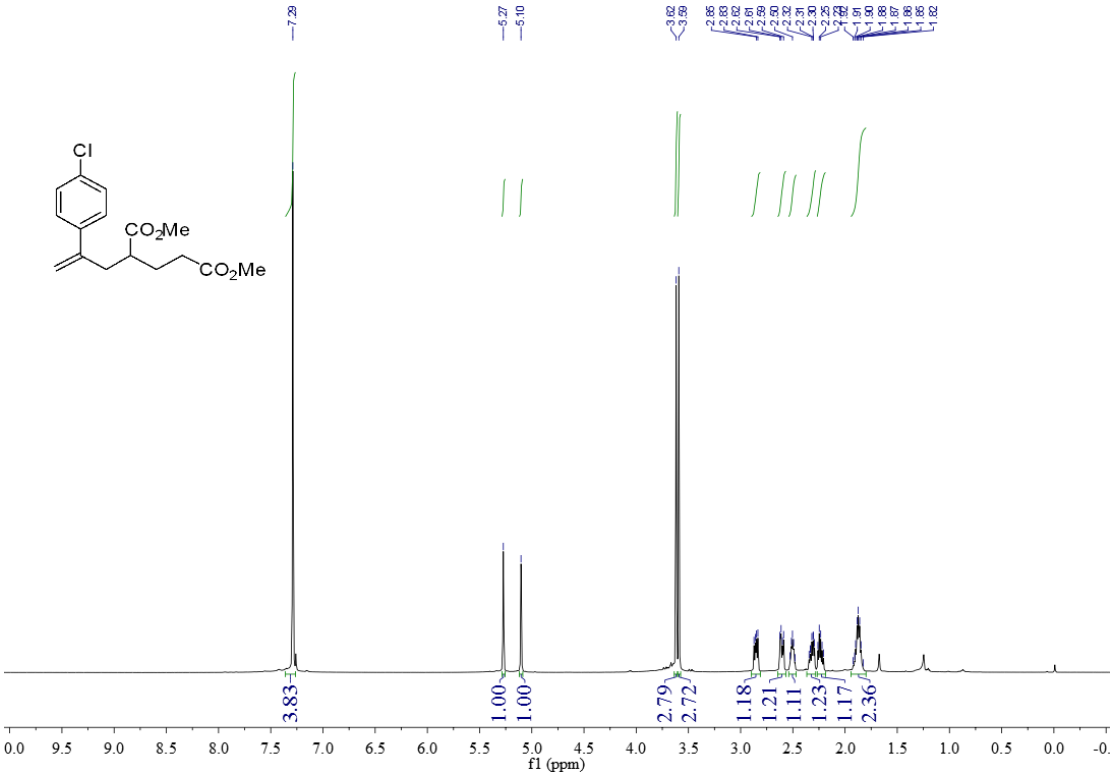


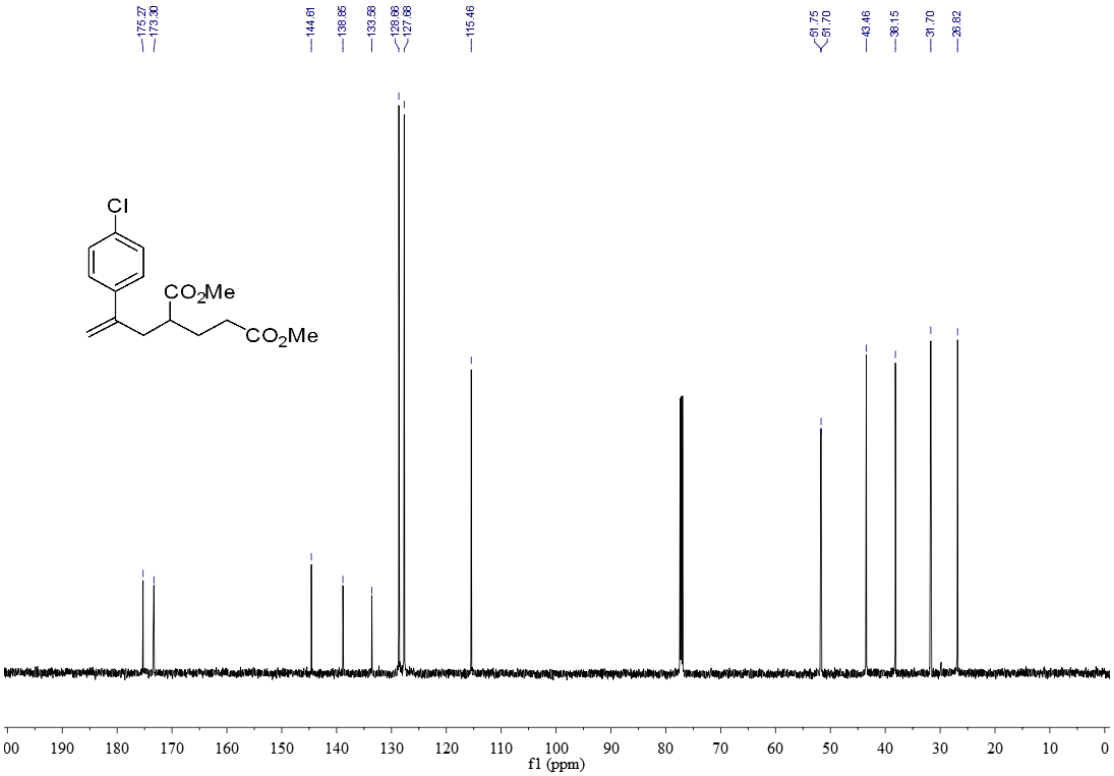
^{13}C NMR of **4e**



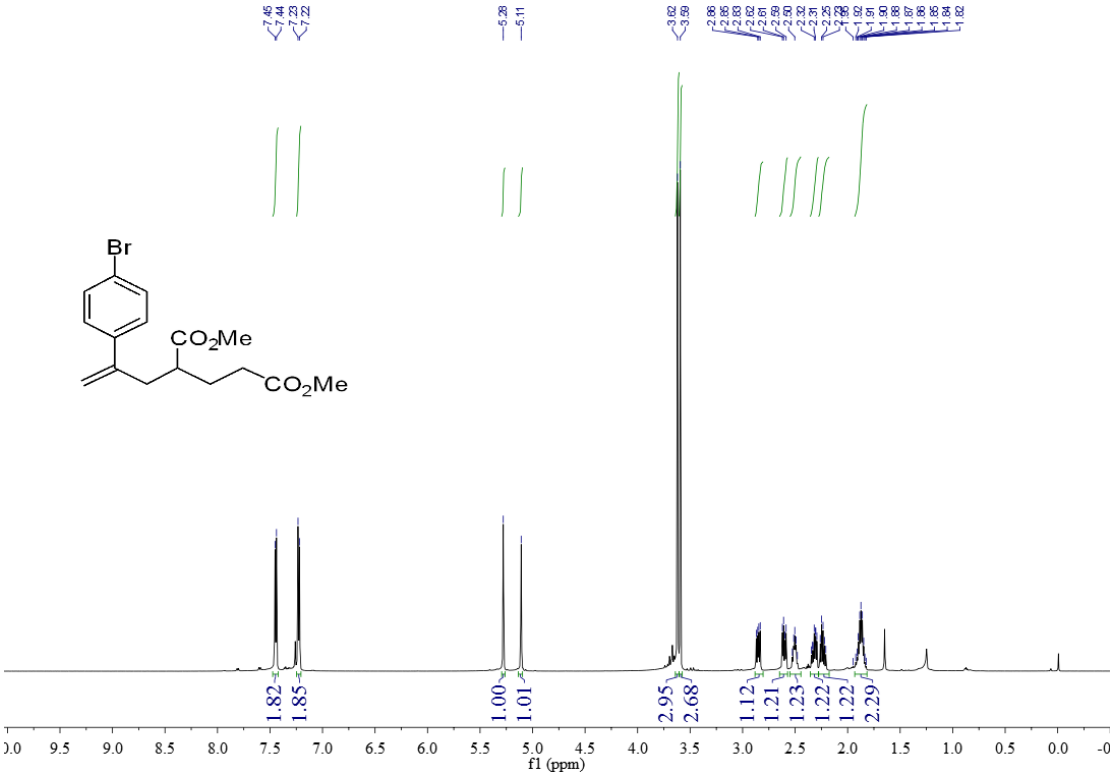
^{1}H NMR of **4f**



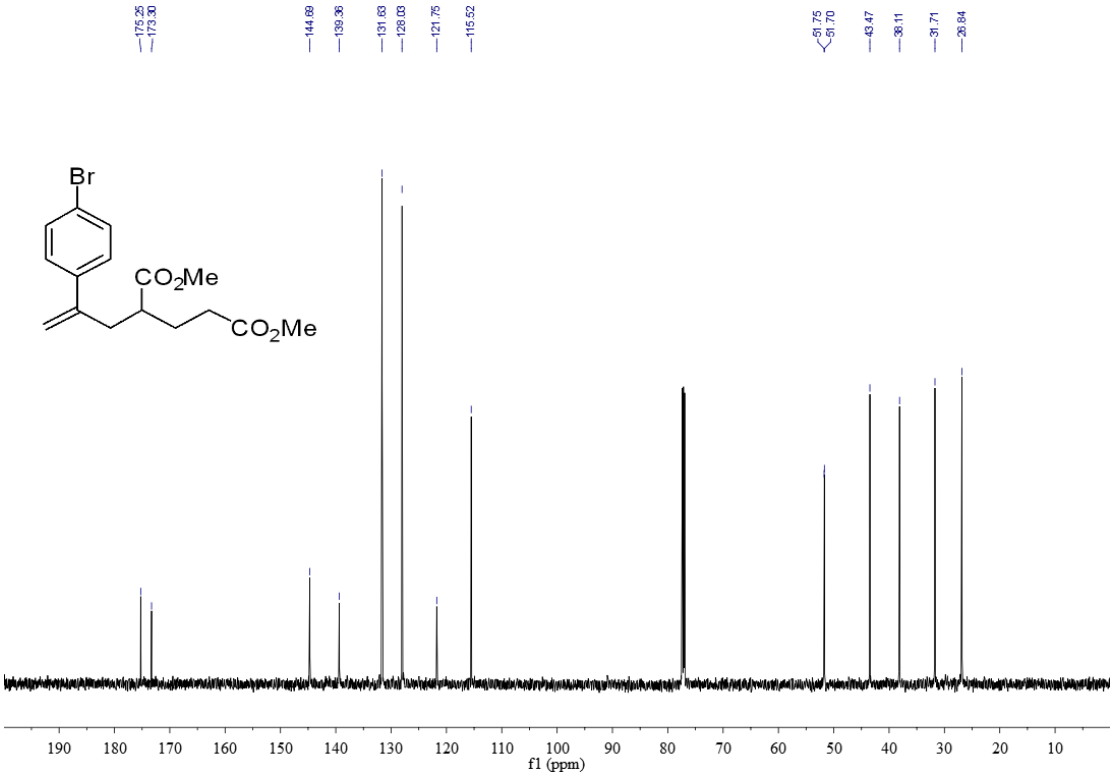
^{13}C NMR of **4f**



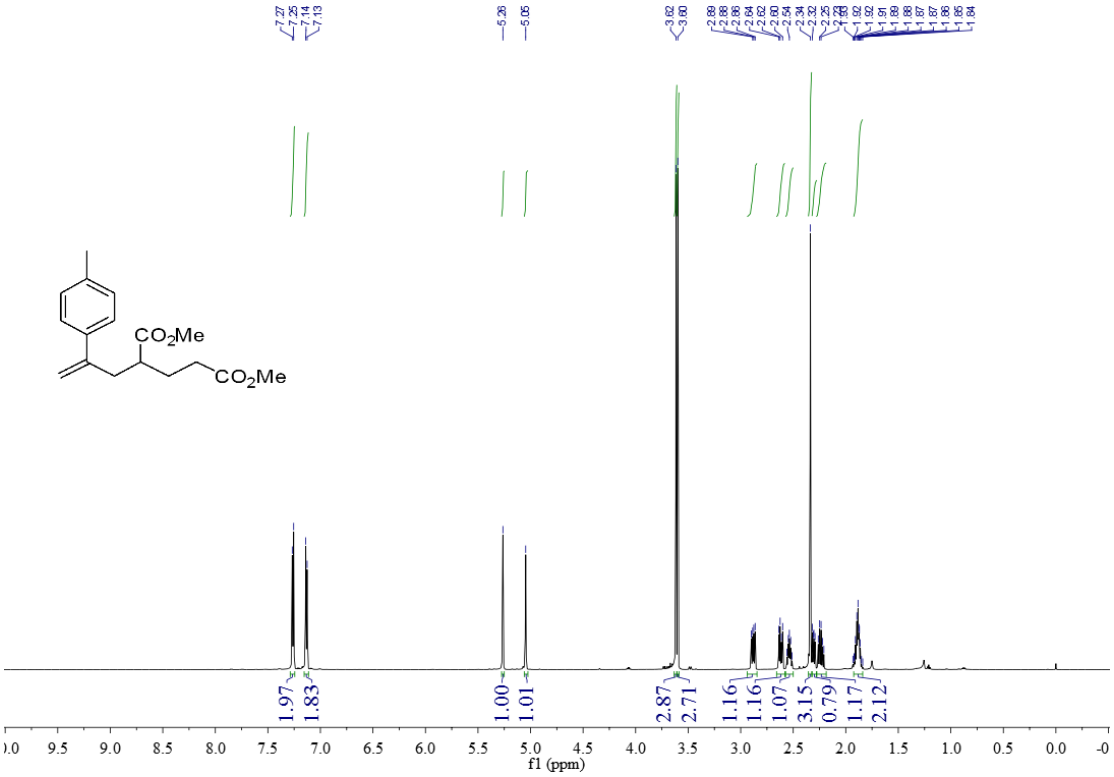
^{1}H NMR of **4g**



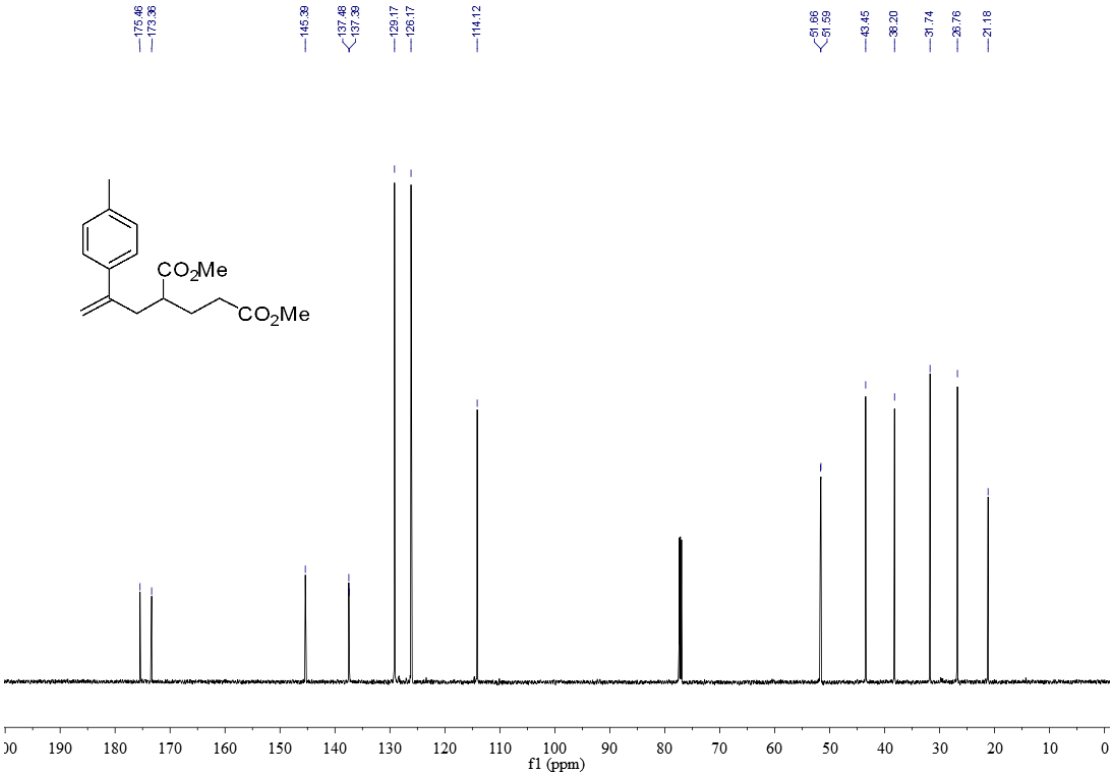
^{13}C NMR of **4g**



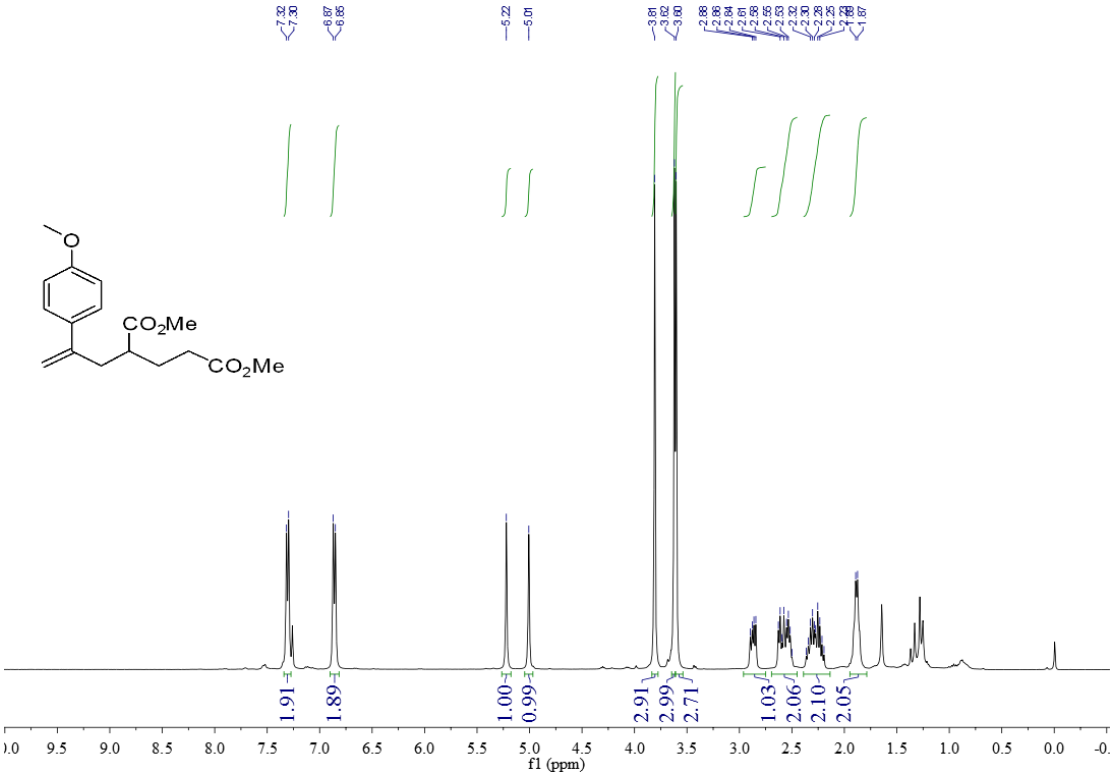
^{1}H NMR of **4h**



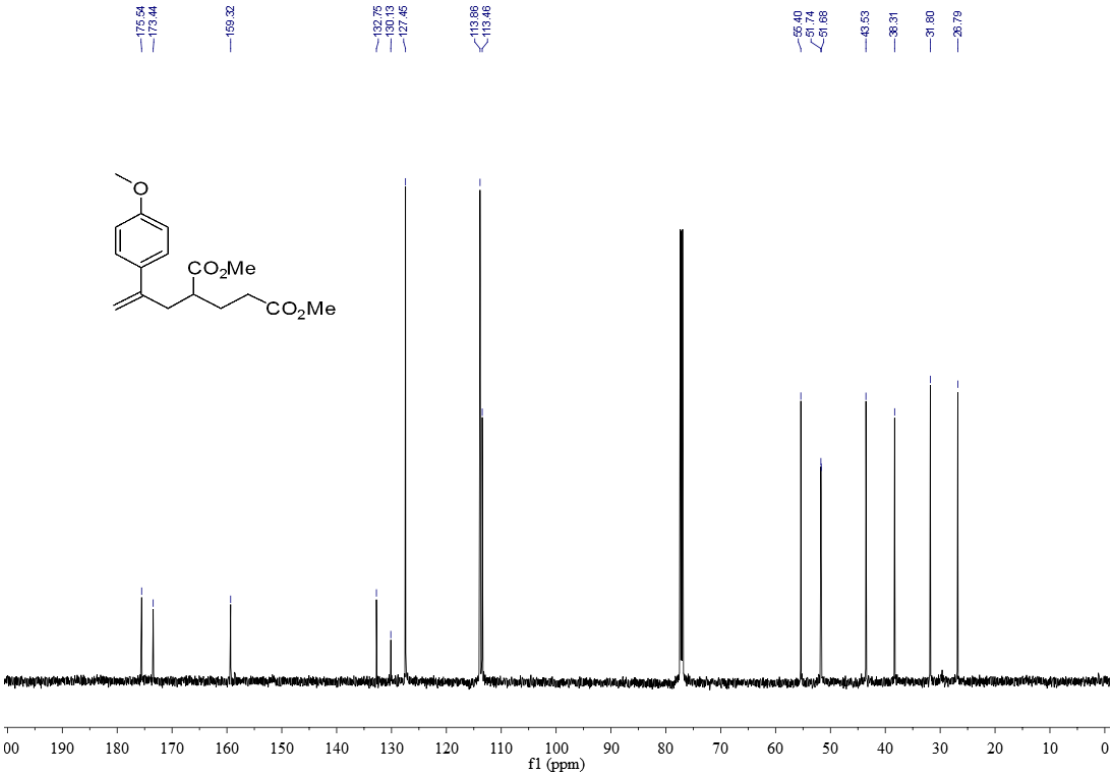
^{13}C NMR of **4h**



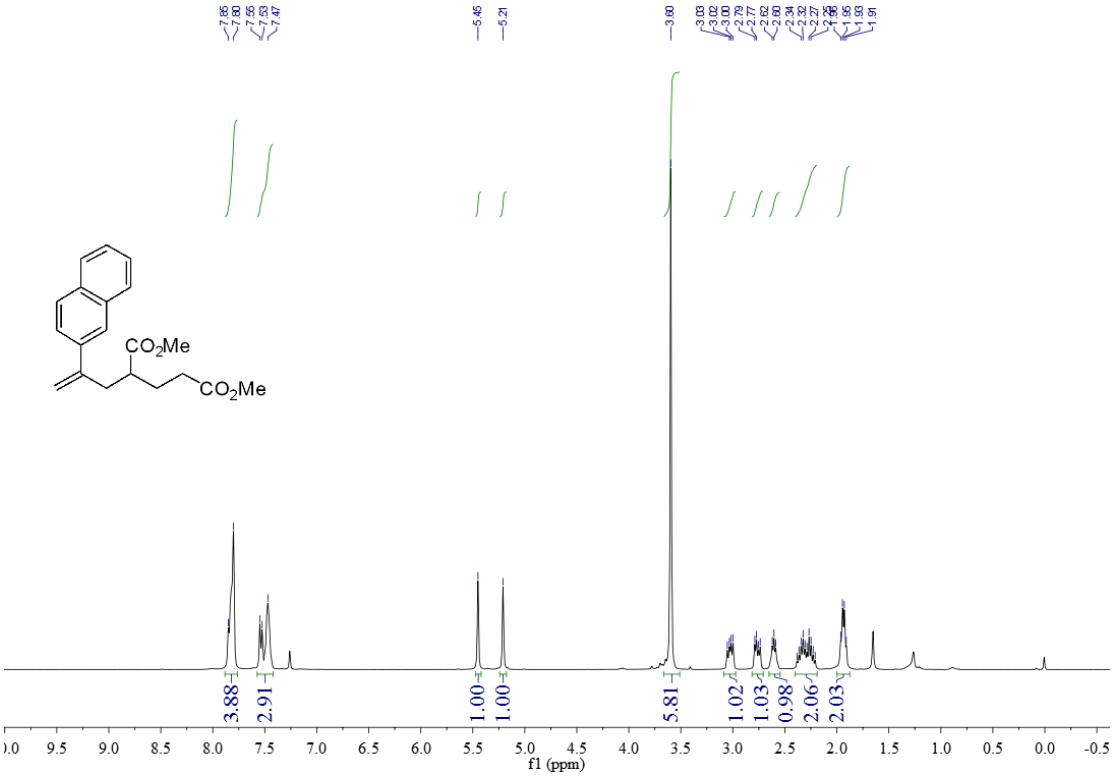
^{1}H NMR of **4i**



^{13}C NMR of **4i**



^{1}H NMR of **4j**



^{13}C NMR of **4j**