

*Electronic supplementary information (ESI) for*

**Transition-Metal-Free Three-component Reaction of  
Cyclopropene, Aldehyde and Amine**

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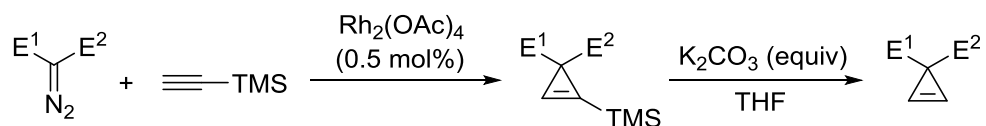
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## 1. General information

All the reactions were carried out in oven-dried glassware sealed with rubber septa under nitrogen condition. All solvents were distilled under nitrogen atmosphere prior to use. DCE was dried over calcium hydride. Purification of products was conducted by flash chromatography on silica gel (200-300 mesh, from Qingdao, China). NMR spectra were measured on a Bruker ARX400 ( $^1\text{H}$  at 400 MHz,  $^{13}\text{C}$  at 100 MHz) magnetic resonance spectrometer. Chemical shifts are reported in *ppm* using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, sept = septet, m = multiplet). Infrared spectra were recorded on a Nicolet Avatar 330 Fourier transform spectrometer (FT-IR) and are reported in wave numbers ( $\text{cm}^{-1}$ ). HRMS data were obtained on a VG ZAB-HS mass spectrometer, Bruker Apex IV FTMS spectrometer. The cyclopropenes used in this investigation were known and prepared with literature procedures.<sup>1</sup> All the aldehydes and amines were commercially available and they were used as received without purification.

## 2. Preparation of cyclopropenes

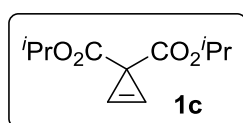
Cyclopropenes **1a**,<sup>1</sup> **1b**,<sup>2</sup> **1c**, **1d**,<sup>3</sup> **1e**, **1f**, and **1g** were synthesized following the previously reported procedures. The general procedure is shown below.



A solution of diazomalonate (1.58 g, 10 mmol) in trimethylsilylacetylene (2 mL) was added using syringe pump over 18 h to a refluxing stirred suspension of Rh<sub>2</sub>(OAc)<sub>4</sub> (11 mg, 0.025 mmol, 0.5 mol%) in trimethylsilylacetylene (20 mL). After the addition was complete, the reaction mixture was stirred at reflux for additional 4 h, then reflux condenser was changed for a distillation unit and most of the trimethylsilylacetylene was distilled from reaction mixture under ambient pressure. The crude residue was filtered through a short column of silica gel with EtOAc as eluent. The eluate was concentrated under reduced pressure and the crude product was dissolved in THF (50 mL). The solution was stirred at 0 °C and 10% aqueous K<sub>2</sub>CO<sub>3</sub> (20 mL) was added dropwise. The mixture was allowed to reach room temperature and was stirred until GC-MS analysis showed the reaction was complete. Aqueous layer was separated and the organic phase was concentrated in under reduced pressure. Ice-cold water (50 mL) was added to the crude residue, and the mixture was extracted with ether (3x20 mL). The combined ethereal phases were washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated under reduced pressure. The crude product was purified

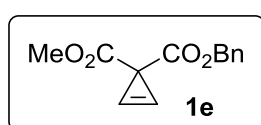
by flash column chromatography to afford the cyclopropene product.

### Diisopropyl cycloprop-2-ene-1,1-dicarboxylate (**1c**)



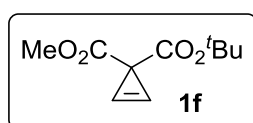
a colorless oil;  $R_f = 0.54$  (PE:EA = 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91(s, 2H), 5.04 (sept,  $J = 6.3$  Hz, 2H), 1.25 (d,  $J = 6.3$  Hz, 12H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 102.9, 68.7, 30.8, 21.7; IR (FT-IR): 3115 (w), 2979 (w), 2930 (w), 1725 (s), 1476 (w), 1371 (w), 1279 (s), 1254 (s), 1176 (w), 1142 (w), 1110 (m), 1056 (m), 653 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  235.0946, found 235.0940.

### 1-Benzyl 1-methyl cycloprop-2-ene-1,1-dicarboxylate (**1e**)



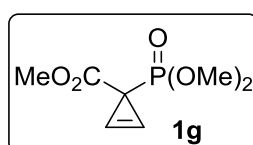
a colorless oil;  $R_f = 0.42$  (PE:EA = 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.37 (m, 5H), 6.91 (s, 2H), 5.17 (s, 2H), 3.72 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 170.6, 135.7, 128.5, 128.1, 127.9, 102.4, 66.9, 52.4, 30.0; IR (FT-IR): 3122 (w), 2948 (w), 1731 (s), 1665 (w), 1455 (w), 1430 (w), 1285(s), 1254 (s), 1149 (w), 1064 (s), 985 (w), 751 (m), 699 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{13}\text{H}_{13}\text{O}_4$   $[\text{M}+\text{H}]^+$  233.0814, found 233.0808.

### 1-(tert-Butyl) 1-methyl cycloprop-2-ene-1,1-dicarboxylate (**1f**)



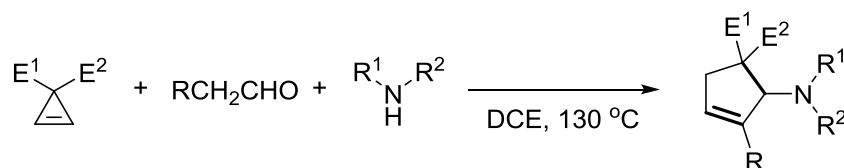
a white solid; (m.p. = 44-46 °C);  $R_f = 0.43$  (PE:EA = 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.90 (s, 2H), 3.72 (s, 3H), 1.46 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 170.1, 102.9, 81.5, 52.2, 31.0, 27.9; IR (FT-IR): 3121 (w), 2979 (w), 1726 (s), 1436 (w), 1369 (m), 1292 (s), 1254 (s), 1163 (s), 1064 (s), 1036 (w), 844 (w), 785 (w)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  221.0790, found 221.0784.

### Methyl 1-(dimethoxyphosphoryl)cycloprop-2-ene-1-carboxylate (**1g**)



a colorless oil;  $R_f = 0.32$  (EA);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (d,  $J = 4.3$  Hz, 2H), 3.80 (s, 3H), 3.76 (d,  $J = 8.3$  Hz, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.8 (d,  $J = 34.3$  Hz), 101.90, 53.2 (d,  $J = 6.6$  Hz), 52.7, 23.34 (d,  $J = 215$  Hz); IR (FT-IR): 3081 (w), 2958 (w), 2921 (w), 2853 (w), 1728 (m), 1439 (w), 1254 (s), 1179 (w), 1029 (s), 919 (w), 850 (m), 828 (w), 752 (m), 731 (m), 667(w), 652 (w)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_7\text{H}_{12}\text{O}_5\text{P}$   $[\text{M}+\text{H}]^+$  207.0422, found 207.0417.

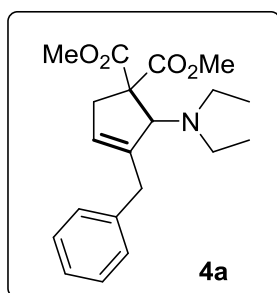
### 3. General procedure of the three-component reaction



In a 10 mL tube (A), dry DCE (0.5 mL) was added using a syringe. Amine (0.26 mmol, 1.3 equiv) and aldehyde (0.26 mmol, 1.3 equiv) were successively added to the tube (A). The mixture was stirred at rt for a few minutes. In another flame-dried 10 mL Schlenk tube (B), cyclopropene (0.20 mmol, 1 equiv) was added under an argon atmosphere. The reaction flask (B) was degassed three times with nitrogen and dry DCE (0.5 mL) was added using a syringe. Note that the cyclopropene in a liquid form was added to the reaction tube (B) by syringe after being added in the solvent. Then the amine-aldehyde mixture in tube (A) was added by syringe to the tube (B) at 130 °C for 2 h. The reaction was heated at 130 °C with stirring for another 2 h, then cooled to room temperature. Solvent was then removed *in vacuo* to leave a crude mixture, which was purified by silica gel (flushed with  $\text{NEt}_3$ ) column chromatography with PE/EtOAc/ $\text{NEt}_3$  (30:1:0.3, v/v/v) to afford pure product. Note that  $\text{NEt}_3$  is necessary because of the products' instability in silica gel.

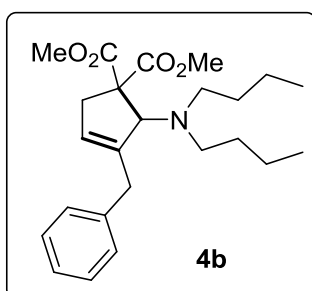
### 4. Characterization data for the products

#### Dimethyl 3-benzyl-2-(diethylamino)cyclopent-3-ene-1,1-dicarboxylate (4a)



Yield: 55.3 mg, 80%; a colorless oil;  $R_f = 0.22$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.31 (m, 2H), 7.18-7.22 (m, 3H), 5.19 (s, 1H), 4.57 (s, 1H), 3.68 (s, 6H), 3.47 (d,  $J = 16.2$  Hz, 1H), 3.30 (dd,  $J = 17.7$  Hz,  $J = 27.8$  Hz, 2H), 2.52-2.57 (m, 5H), 0.94 (t,  $J = 7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 170.1, 143.2, 139.0, 129.1, 128.2, 126.1, 125.6, 73.3, 65.0, 52.5, 52.0, 38.9, 36.9, 15.0; IR (FT-IR): 2970 (w), 1733 (s), 1433 (w), 1257 (m), 1231 (w), 1195 (w), 1155 (w), 1083 (w), 1052 (w), 703 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{20}\text{H}_{28}\text{NO}_4$   $[\text{M}+\text{H}]^+$  346.2013, found 346.2021.

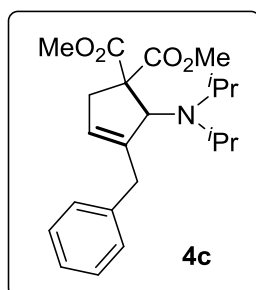
#### Dimethyl 3-benzyl-2-(dibutylamino)cyclopent-3-ene-1,1-dicarboxylate (4b)



Yield: 69.0 mg, 86%; a colorless oil;  $R_f = 0.28$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.31 (m, 2H), 7.17-7.22 (m, 3H), 5.20-5.21 (m, 1H), 4.54 (s, 1H), 3.68 (m, 6H), 3.50 (d,  $J = 15.9$  Hz, 1H), 3.26-3.36 (m, 2H), 2.53-2.54 (m, 5H), 1.19-1.38 (m, 8H), 0.86-0.89 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 170.0, 143.3, 139.0, 129.1, 128.2, 126.0, 125.5, 73.8, 64.6, 52.5, 52.0,

39.1, 36.9, 32.1, 20.4, 14.1; IR (FT-IR): 2955 (w), 1734 (s), 1454 (w), 1258 (m), 1155 (s), 1083 (w), 1052 (w), 703 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{24}\text{H}_{36}\text{NO}_4$   $[\text{M}+\text{H}]^+$  402.2639, found 402.2641.

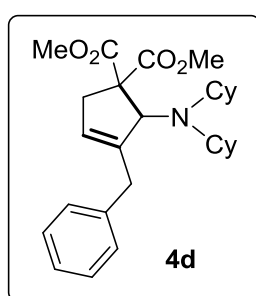
#### Dimethyl 3-benzyl-2-(diisopropylamino)cyclopent-3-ene-1,1-dicarboxylate (4c)



Yield: 45.5 mg, 61%; a colorless oil;  $R_f = 0.28$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.30 (m, 2H), 7.16-7.21 (m, 3H), 5.15 (m, 1H), 4.78 (s, 1H), 3.67-3.68 (m, 6H), 3.58 (d,  $J = 16.5$  Hz, 1H), 3.34-3.43 (m, 2H), 3.14-3.21 (m, 1H), 2.92-2.98 (m, 1H), 2.58-2.64 (m, 1H), 1.14 (d,  $J = 6.6$  Hz, 3H), 1.05 (d,  $J = 6.4$  Hz, 3H), 0.96-0.98 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 169.9, 144.5, 139.5, 129.1, 128.1, 126.4, 126.0, 68.4, 66.8, 52.4, 51.9, 48.0, 43.9, 38.8, 37.0, 24.4, 24.1, 23.8, 22.1; IR (FT-IR): 2962 (w), 1732 (s), 1434 (w), 1255 (m),

1229 (w), 1194 (w), 1155 (m), 1084 (w), 703 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{22}\text{H}_{32}\text{NO}_4$   $[\text{M}+\text{H}]^+$  374.2326, found 374.2331.

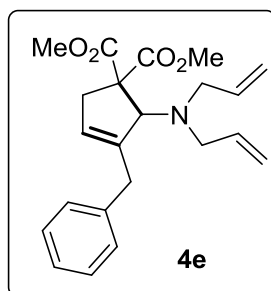
#### Dimethyl 3-benzyl-2-(dicyclohexylamino)cyclopent-3-ene-1,1-dicarboxylate (4d)



Yield: 60.8 mg, 67%; a colorless oil;  $R_f = 0.26$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.30 (m, 2H), 7.13-7.21 (m, 3H), 5.10-5.11 (m, 1H), 4.79 (s, 1H), 3.66-3.67 (m, 6H), 3.60 (d,  $J = 16.5$  Hz, 1H), 3.32-3.42 (m, 2H), 2.57-2.61 (m, 2H), 2.34-2.40 (m, 1H), 1.72-1.74 (m, 6H), 1.20-1.57 (m, 14H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 169.9, 145.1, 139.7, 129.1, 128.1, 125.9, 125.8, 69.7, 66.9, 57.4, 54.2, 52.4, 51.9, 38.8, 37.0, 35.8, 35.0, 34.2, 33.9, 27.0, 26.9, 26.8, 26.7, 26.0, 25.5; IR (FT-IR): 2928 (m), 2852 (m), 1732 (s), 1452 (w), 1252

(m), 1229 (w), 1162 (w), 1109 (w), 1082 (w), 910 (w), 702 (w)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{28}\text{H}_{40}\text{NO}_4$   $[\text{M}+\text{H}]^+$  454.2952, found 454.2949.

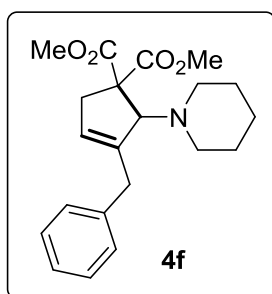
#### Dimethyl 3-benzyl-2-(diallylamino)cyclopent-3-ene-1,1-dicarboxylate (4e)



Yield: 40.6 mg, 55%; a colorless oil;  $R_f = 0.29$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.32 (m, 2H), 7.19-7.23 (m, 3H), 5.61-5.71 (m, 2H), 5.27 (s, 1H), 5.01-5.04 (m, 4H), 4.68 (m, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 3.53 (d,  $J = 16.3$  Hz, 1H), 3.22-3.39 (m, 4H), 3.02-3.06 (m, 2H), 2.55-2.60 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 170.0, 142.8, 138.8, 129.1, 128.3, 126.5, 126.2, 116.7, 71.1, 64.9, 52.5, 52.1, 38.9, 37.1; IR (FT-IR): 2809 (w), 1733 (s), 1434 (w),

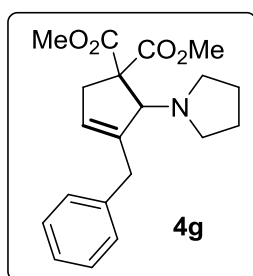
1262 (m), 1154 (m), 1085 (w), 920 (w), 703 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{22}\text{H}_{28}\text{NO}_4$   $[\text{M}+\text{H}]^+$  370.2013, found 370.2018.

#### Dimethyl 3-benzyl-2-(piperidin-1-yl)cyclopent-3-ene-1,1-dicarboxylate (4f)



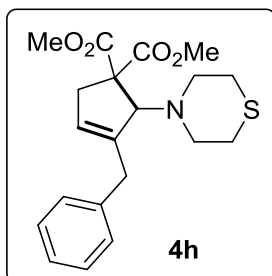
Yield: 50.7 mg, 71%; a white solid (m.p. = 102-103 °C);  $R_f$  = 0.25 (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.31 (m, 2H), 7.19-7.22 (m, 3H), 5.23 (s, 1H), 4.28 (s, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.52 (d,  $J$  = 15.7 Hz, 1H), 3.27-3.36 (m, 2H), 2.52-2.68 (m, 5H), 1.40 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 169.9, 142.7, 138.9, 129.1, 128.2, 126.1, 125.5, 76.5, 65.5, 52.5, 52.2, 39.0, 37.7, 27.4, 24.6; IR (FT-IR): 2935 (w), 1731 (s), 1438 (w), 1258 (m), 1228 (w), 1150 (w), 1083 (w), 1005 (w), 703 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{21}\text{H}_{28}\text{NO}_4$   $[\text{M}+\text{H}]^+$  358.2013, found 358.2020.

#### Dimethyl 3-benzyl-2-(pyrrolidin-1-yl)cyclopent-3-ene-1,1-dicarboxylate (4g)



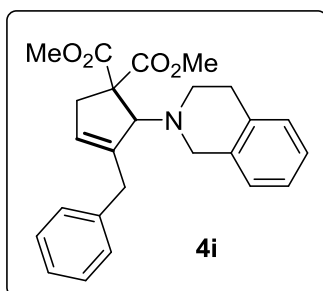
Yield: 45.3 mg, 66%; a white solid (m.p. = 97-98 °C);  $R_f$  = 0.22 (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.31 (m, 2H), 7.18-7.22 (m, 3H), 5.25 (s, 1H), 4.58 (s, 1H), 3.66-3.67 (m, 6H), 3.43 (d,  $J$  = 16.2 Hz, 1H), 3.35 (d,  $J$  = 17.6 Hz, 1H), 3.23 (d,  $J$  = 16.2 Hz, 1H), 2.74-2.76 (m, 4H), 2.57 (d,  $J$  = 17.3 Hz, 1H), 1.66 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 170.1, 142.2, 138.8, 129.1, 128.2, 126.1, 125.2, 70.5, 65.5, 52.4, 52.1, 49.1, 38.4, 37.3, 24.7; IR (FT-IR): 2950 (w), 1731 (s), 1435 (w), 1254 (m), 1233 (m), 1197 (w), 1152 (w), 1083 (w), 1052 (w), 702 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{20}\text{H}_{26}\text{NO}_4$   $[\text{M}+\text{H}]^+$  344.1856, found 344.1865.

#### Dimethyl 3-benzyl-2-thiomorpholinocyclopent-3-ene-1,1-dicarboxylate (4h)



Yield: 45.8 mg, 61%; a white solid (m.p. = 112-114 °C);  $R_f$  = 0.24 (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.32 (m, 2H), 7.18-7.23 (m, 3H), 5.30 (s, 1H), 4.28 (s, 1H), 3.74 (s, 3H), 3.68 (s, 3H), 3.55 (d,  $J$  = 16.7 Hz, 1H), 3.28-3.34 (m, 2H), 2.86-2.96 (m, 4H), 2.50-2.61 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.2, 169.9, 142.0, 138.5, 129.0, 128.3, 126.3, 126.2, 76.7, 65.1, 52.6, 52.4, 39.1, 37.2, 29.3; IR (FT-IR): 2945 (w), 1732 (s), 1433 (w), 1258 (m), 1233 (w), 1158 (w), 1080 (w), 966 (w), 703 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{20}\text{H}_{26}\text{NSO}_4$   $[\text{M}+\text{H}]^+$  376.1577, found 376.1580.

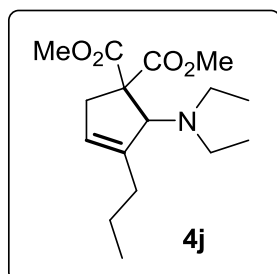
#### Dimethyl 3-benzyl-2-(3,4-dihydroisoquinolin-2(1H)-yl)cyclopent-3-ene-1,1-dicarboxylate (4i)



Yield: 55.0 mg, 68%; a yellow oil;  $R_f$  = 0.17 (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.32 (m, 2H), 7.17-7.24 (m, 3H), 7.07-7.10 (m, 3H), 6.95-6.98 (m, 1H), 5.35 (s, 1H), 4.58 (s, 1H), 3.88-4.01 (m, 2H), 3.69 (s, 3H), 3.41-3.56 (m, 5H), 3.31 (d,  $J$  = 16.3 Hz, 1H), 2.94-2.98 (m, 1H), 2.60-2.85 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 170.0, 142.2, 138.6, 135.6, 134.9,

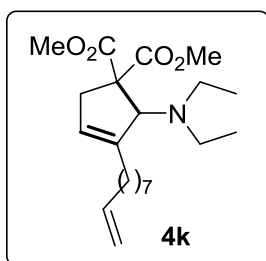
129.1, 128.7, 128.3, 126.4, 126.2, 126.2, 125.7, 125.3, 75.4, 65.3, 52.6, 52.3, 39.0, 37.4, 30.7; IR (FT-IR): 2950 (w), 1732 (s), 1433 (w), 1256 (m), 1152 (w), 1084 (w), 738 (m), 703 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{25}\text{H}_{28}\text{NO}_4$   $[\text{M}+\text{H}]^+$  406.2013, found 406.2013.

#### Dimethyl 2-(diethylamino)-3-propylcyclopent-3-ene-1,1-dicarboxylate (4j)



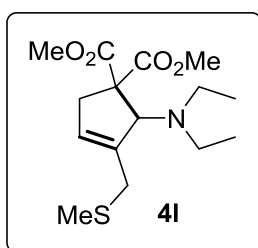
Yield: 48.1 mg; 81%; a yellow oil;  $R_f = 0.35$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.34-5.35 (m, 1H), 4.55 (m, 1H), 3.69-3.70 (m, 6H), 3.34 (tdd,  $J = 2.2$  Hz,  $J = 4.6$  Hz,  $J = 17.5$  Hz, 1H), 2.49-2.56 (m, 5H), 1.98-2.05 (m, 2H), 1.43-1.61 (m, 2H), 0.90-0.96 (m, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 170.2, 143.9, 122.9, 73.1, 64.9, 52.4, 52.0, 38.9, 32.5, 20.6, 14.8, 14.0; IR (FT-IR): 2956 (w), 1734 (s), 1433 (w), 1257 (m), 1234 (w), 1194 (w), 1155 (w), 1081 (w), 1052 (w)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{16}\text{H}_{28}\text{NO}_4$   $[\text{M}+\text{H}]^+$  298.2013, found 298.2019.

#### Dimethyl 3-allyl-2-(diethylamino)cyclopent-3-ene-1,1-dicarboxylate (4l)



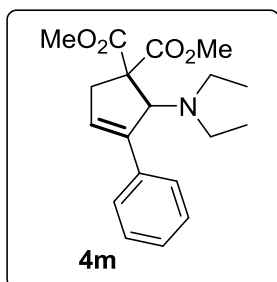
Yield: 62.2 mg; 82%; a yellow oil;  $R_f = 0.35$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.81 (tdd,  $J = 6.7$  Hz,  $J = 10.2$  Hz,  $J = 16.9$  Hz, 1H), 5.34 (m, 1H), 4.99 (ddd,  $J = 1.6$  Hz,  $J = 3.6$  Hz,  $J = 17.1$  Hz, 1H), 4.93 (tdd,  $J = 1.2$  Hz,  $J = 2.2$  Hz,  $J = 10.2$  Hz, 1H), 4.55 (m, 1H), 3.69-3.70 (m, 6H), 3.33 (tdd,  $J = 2.1$  Hz,  $J = 4.3$  Hz,  $J = 9.0$  Hz, 1H), 2.49-2.56 (m, 5H), 2.01-2.07 (m, 4H), 1.30-1.54 (m, 10H), 0.95 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 170.1, 144.1, 139.2, 122.7, 114.1, 73.2, 64.9, 52.4, 52.0, 38.8, 33.8, 30.3, 29.4, 29.3, 29.0, 28.9, 27.3, 14.8; IR (FT-IR): 2928 (w), 1734 (s), 1433 (w), 1258 (m), 1234 (w), 1194 (w), 1155 (w), 1084 (w), 1052 (w), 731 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{22}\text{H}_{38}\text{NO}_4$   $[\text{M}+\text{H}]^+$  380.2795, found 380.2791.

#### Dimethyl 2-(diethylamino)-3-((methylthio)methyl)cyclopent-3-ene-1,1-dicarboxylate (4k)



Yield: 30.9 mg; 49%; a yellow oil;  $R_f = 0.25$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.57 (m, 1H), 4.83-4.84 (m, 1H), 3.70-3.71 (m, 6H), 3.39 (dd,  $J = 1.9$  Hz,  $J = 17.9$  Hz, 1H), 3.28 (d,  $J = 14.3$  Hz, 1H), 2.99-3.04 (m, 1H), 2.45-2.64 (m, 5H), 2.00 (s, 3H), 0.97 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 170.0, 139.5, 127.1, 71.3, 64.7, 52.5, 52.1, 39.1, 33.5, 14.9, 14.6; IR (FT-IR): 2972 (w), 1732 (s), 1434 (w), 1260 (m), 1223 (w), 1195 (w), 1156 (w), 1083 (w), 1051 (w), 731 (w)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{15}\text{H}_{26}\text{NSO}_4$   $[\text{M}+\text{H}]^+$  316.1577, found 316.1585.

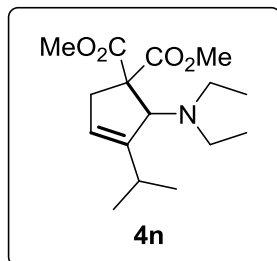
#### Dimethyl 2-(diethylamino)-3-phenylcyclopent-3-ene-1,1-dicarboxylate (4m)



Yield: 31.1 mg; 47%; a colorless oil;  $R_f = 0.35$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45-7.48 (m, 2H), 7.29-7.33 (m, 2H), 7.25-7.26 (m, 1H), 5.91 (t,  $J = 2.2$  Hz, 1H), 5.30 (d,  $J = 1.7$  Hz, 1H), 3.73-3.74 (m, 6H), 3.54 (td,  $J = 2.1$  Hz,  $J = 18.2$  Hz, 1H), 2.81 (dd,  $J = 3.2$  Hz,  $J = 18.2$  Hz, 1H), 2.47-2.55 (m, 2H), 2.37-2.40 (m, 2H), 0.88-0.91 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 169.9,

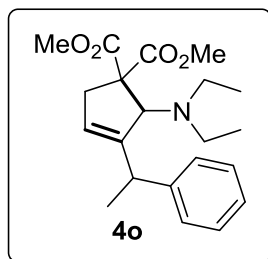
143.5, 136.8, 128.2, 127.5, 127.0, 126.0, 72.1, 65.3, 52.6, 52.2, 39.5, 14.7; IR (FT-IR): 2970 (w), 1733 (s), 1434 (w), 1265 (m), 1226 (w), 1194 (w), 1154 (w), 1082 (w), 1052 (w), 740 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{19}\text{H}_{26}\text{NO}_4$   $[\text{M}+\text{H}]^+$  332.18563, found 332.18649.

#### Dimethyl 2-(diethylamino)-3-isopropylcyclopent-3-ene-1,1-dicarboxylate (4n)



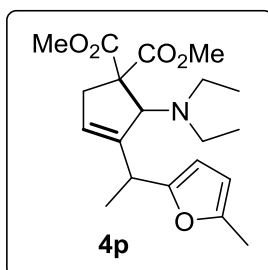
Yield: 36.8 mg; 62%; a yellow oil;  $R_f = 0.33$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.33 (m, 1H), 4.68 (m, 1H), 3.69 (m, 6H), 3.34 (ddd,  $J = 2.0$  Hz,  $J = 4.8$  Hz,  $J = 17.5$  Hz, 1H), 2.50-2.56 (m, 5H), 2.15-2.22 (m, 1H), 1.11 (d,  $J = 6.7$  Hz, 3H), 1.08 (d,  $J = 6.9$  Hz, 3H), 0.94-0.97 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 170.2, 150.5, 120.5, 72.0, 64.9, 52.4, 52.0, 38.8, 28.2, 21.8, 20.3, 14.9; IR (FT-IR): 2964 (w), 1733 (s), 1434 (w), 1259 (m), 1236 (w), 1195 (w), 1156 (m), 1081 (w), 1052 (w), 733 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{16}\text{H}_{28}\text{NO}_4$   $[\text{M}+\text{H}]^+$  298.2013, found 298.2014.

#### Dimethyl 2-(diethylamino)-3-(1-phenylethyl)cyclopent-3-ene-1,1-dicarboxylate (4o)



Yield: 50.1 mg; 70%, d.r. = 2.5:1; a yellow oil;  $R_f = 0.24$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.32 (m, 7.0H), 7.18-7.23 (m, 7.0H), 7.14-7.16 (m, 3.5H), 5.67 (m, 2.5H), 4.82 (d,  $J = 1.7$  Hz, 1H), 4.80 (d,  $J = 1.5$  Hz, 1H), 4.31 (d,  $J = 1.8$  Hz, 2.5H), 3.70 (m, 6.0H), 3.64-3.65 (m, 15.0H), 3.40-3.46 (m, 3.5H), 3.21-3.37 (m, 3.5H), 2.44-2.74 (m, 17.5H), 1.48 (d,  $J = 7.2$  Hz, 3.5H), 1.38 (d,  $J = 7.0$  Hz, 7.0H), 0.83-1.01 (m, 21.0H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 172.6, 170.2, 170.0, 149.4, 147.0, 144.7, 144.5, 128.2, 128.1, 127.8, 127.8, 126.5, 126.2, 124.4, 123.8, 72.5, 71.9, 65.0, 64.9, 52.5, 52.4, 52.0, 52.0, 40.5, 40.0, 39.2, 38.7, 22.2, 19.2, 15.2, 15.0; IR (FT-IR): 2970 (w), 1733 (s), 1434 (w), 1258 (m), 1232 (w), 1194 (w), 1155 (w), 1080 (w), 1051 (w), 702 (s)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{21}\text{H}_{30}\text{NO}_4$   $[\text{M}+\text{H}]^+$  360.2169, found 360.2179.

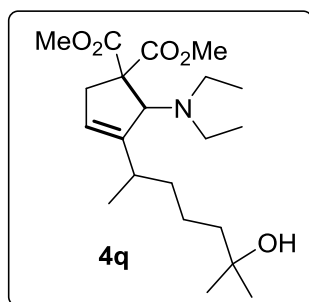
#### Dimethyl 2-(diethylamino)-3-(1-(5-methylfuran-2-yl)ethyl)cyclopent-3-ene-1,1-dicarboxylate (4p)



Yield: 50.8 mg; 70%, d.r. = 2.2:1; a yellow oil;  $R_f = 0.28$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.99 (d,  $J = 3.0$  Hz, 2.2H), 5.93 (d,  $J = 3.0$  Hz, 1H), 5.87 (m, 3.2H), 5.59 (m, 2.2H), 5.08 (m, 1H), 4.74-4.75 (m, 1H), 4.69 (m, 2.2H), 3.70 (m, 6H), 3.68 (m, 13.2H), 3.30-3.43 (m, 6.4H), 2.25-2.66 (m, 25.6H), 1.38-1.42 (m, 9.6H), 0.99 (m, 6H), 0.90 (t,  $J = 7.0$  Hz, 13.2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 172.6, 170.1, 170.1, 156.2, 155.8, 150.3, 147.1, 145.1, 124.0, 123.6, 105.9, 105.5, 105.3, 72.4, 72.1, 64.8, 64.7, 52.5, 52.4, 52.0, 52.0, 38.9, 38.7, 33.7, 18.4, 17.9, 15.1, 14.9, 13.5, 13.5; IR (FT-IR): 2972 (w), 1734 (s), 1434 (w), 1259 (m), 1234 (w), 1194 (w), 1156 (w), 1084 (w), 1052 (w), 734 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{20}\text{H}_{30}\text{NO}_5$   $[\text{M}+\text{H}]^+$  364.2119, found 364.2125.

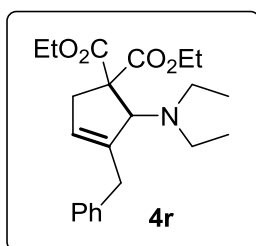


**Dimethyl 2-(diethylamino)-3-(6-hydroxy-6-methylheptan-2-yl)cyclopent-3-ene-1,1-dicarboxylate (4q)**



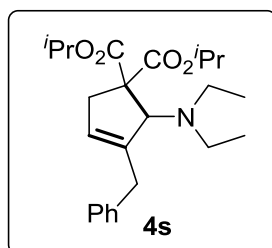
Yield: 52.0 mg; 68%, d.r. = 1.6:1; a yellow oil;  $R_f$  = 0.43 (PE:EA = 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.35-5.36 (m, 1.6H), 5.31 (m, 1H), 4.69 (m, 1H), 4.65-4.66 (m, 1.6H), 3.68-3.69 (m, 15.6H), 3.32-3.39 (m, 2.6H), 2.04-2.58 (m, 15.6H), 1.75 (s, 1.6H), 1.67 (s, 1H), 1.34-1.51 (m, 15.6H), 1.20-1.23 (m, 15.6H), 1.10 (d,  $J$  = 6.8 Hz, 4.8H), 1.06 (d,  $J$  = 6.9 Hz, 3H), 0.85-0.97 (m, 15.6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 172.8, 170.2, 170.1, 149.6, 149.1, 122.0, 120.7, 72.4, 72.2, 70.9, 70.8, 64.8, 64.7, 52.5, 52.4, 52.0, 46.2, 44.1, 44.1, 38.9, 38.8, 36.0, 35.2, 33.5, 32.8, 29.6, 29.3, 29.2, 28.8, 22.4, 20.2, 19.7, 17.6, 15.0, 11.5; IR (FT-IR): 2968 (w), 1732 (s), 1434 (w), 1260 (m), 1235 (w), 1196 (w), 1157 (w), 1084 (w), 1052 (w), 735 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{21}\text{H}_{38}\text{NO}_5$   $[\text{M}+\text{H}]^+$  384.2745, found 384.2740.

**Diethyl 3-benzyl-2-(diethylamino)cyclopent-3-ene-1,1-dicarboxylate (4r)**



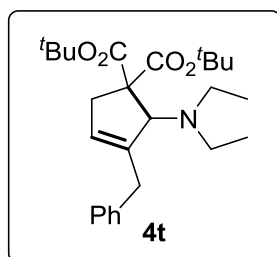
Yield: 62.7 mg; 84%; a yellow oil;  $R_f$  = 0.32 (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.31 (m, 2H), 7.18-7.22 (m, 3H), 5.19 (m, 1H), 4.58 (s, 1H), 4.18-4.26 (m, 2H), 4.02-4.13 (m, 2H), 3.48 (d,  $J$  = 16.2 Hz, 1H), 3.25-3.36 (m, 2H), 2.51-2.57 (m, 5H), 1.24 (t,  $J$  = 7.2 Hz, 3H), 1.21 (t,  $J$  = 7.1 Hz, 3H), 0.95 (t,  $J$  = 7.0 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.3, 169.8, 143.2, 139.1, 129.1, 128.2, 126.0, 125.7, 72.9, 64.9, 61.1, 60.8, 39.0, 36.9, 14.9, 14.0; IR (FT-IR): 2976 (w), 1729 (s), 1454 (w), 1254 (s), 1230 (w), 1177 (w), 1152 (w), 1078 (w), 1051 (w), 702 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{22}\text{H}_{32}\text{NO}_4$   $[\text{M}+\text{H}]^+$  374.2326, found 374.2322.

**Diisopropyl 3-benzyl-2-(diethylamino)cyclopent-3-ene-1,1-dicarboxylate (4s)**



Yield: 56.9 mg; 71%; a colorless oil;  $R_f$  = 0.34 (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.31 (m, 2H), 7.18-7.22 (m, 3H), 5.19 (m, 1H), 5.00 (qd,  $J$  = 6.3 Hz,  $J$  = 12.6 Hz, 2H), 4.60 (s, 1H), 3.46-3.50 (m, 1H), 3.25-3.35 (m, 2H), 2.49-2.59 (m, 5H), 1.19-1.26 (m, 12H), 0.96 (t,  $J$  = 7.1 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.8, 169.3, 143.1, 139.2, 129.1, 128.2, 126.0, 125.8, 72.3, 68.4, 68.3, 65.0, 39.3, 37.0, 21.8, 21.7, 21.5, 21.5, 14.6; IR (FT-IR): 2979 (w), 1725 (s), 1262 (m), 1231 (w), 1180 (w), 1155 (w), 1110 (w), 705 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{24}\text{H}_{36}\text{NO}_4$   $[\text{M}+\text{H}]^+$  402.2639, found 402.2634.

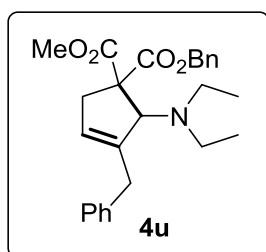
### ***di-tert*-Butyl 3-benzyl-2-(diethylamino)cyclopent-3-ene-1,1-dicarboxylate (4t)**



Yield: 36.9 mg; 43%; a colorless oil;  $R_f = 0.38$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.31 (m, 2H), 7.18-7.21 (m, 3H), 5.16 (m, 1H), 4.47 (s, 1H), 3.44-3.48 (m, 1H), 3.19-3.28 (m, 2H), 2.45-2.60 (m, 5H), 1.46 (s, 9H), 1.42 (s, 9H), 0.98 (t,  $J = 7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 168.8, 143.1, 139.2, 129.1, 128.2, 126.0, 125.8, 80.6, 80.4, 71.9, 66.3, 39.1, 37.1, 28.0, 27.8, 14.5;

IR (FT-IR): 2976 (w), 1724 (s), 1367 (m), 1280 (m), 1256 (w), 1173 (m), 1137 (s), 1077 (w), 852 (w), 702 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{26}\text{H}_{40}\text{NO}_4$   $[\text{M}+\text{H}]^+$  430.2952, found 430.2949.

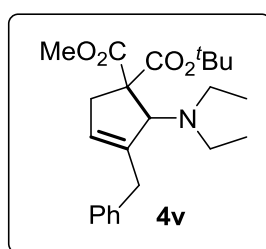
### **1-Benzyl 1-methyl 3-benzyl-2-(diethylamino)cyclopent-3-ene-1,1-dicarboxylate (4u)**



Yield: 74.1 mg; 88%, d.r. = 1.1:1; a yellow oil;  $R_f = 0.33$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.34 (m, 14.7H), 7.16-7.22 (m, 6.3H), 5.36 (d,  $J = 12.5$  Hz, 1H), 5.17-5.23 (m, 3.2H), 5.07 (d,  $J = 12.4$  Hz, 1.1H), 4.91 (d,  $J = 12.5$  Hz, 1H), 4.59 (m, 2.1H), 3.61 (m, 6.3H), 3.44-3.50 (m, 2.1H), 3.24-3.40 (m, 4.2H), 2.54-2.59 (m, 10.5H), 0.90-0.96 (m, 12.6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 172.0,

170.0, 169.4, 143.2, 138.9, 135.9, 135.8, 129.1, 129.1, 128.4, 128.4, 128.2, 128.2, 128.1, 127.9, 127.9, 127.8, 126.1, 125.7, 125.6, 73.4, 73.0, 66.8, 66.5, 65.1, 65.1, 52.4, 51.9, 39.0, 38.9, 36.9, 36.9, 15.0, 14.9; IR (FT-IR): 2967 (w), 1731 (s), 1454 (w), 1258 (m), 1230 (w), 1191 (w), 1152 (w), 1071 (w), 1050 (w), 734 (s), 700 (s)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{26}\text{H}_{32}\text{NO}_4$   $[\text{M}+\text{H}]^+$  422.2326, found 422.2324.

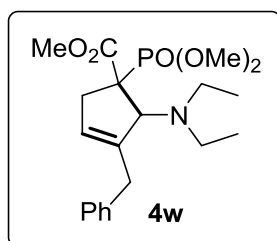
### **1-(*tert*-Butyl) 1-methyl 3-benzyl-2-(diethylamino)cyclopent-3-ene-1,1-dicarboxylate (4v)**



Yield: 52.6 mg; 68%, d.r. = 1.0:1; a colorless oil;  $R_f = 0.38$  (PE:EA = 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.32 (m, 4.0H), 7.18-7.22 (m, 6.0H), 5.20 (s, 1.0H), 5.17 (s, 1.0H), 4.52 (s, 2.0H), 3.68 (m, 6.0H), 3.42-3.51 (m, 2.0H), 3.25-3.29 (m, 4.0H), 2.48-2.59 (m, 10.0H), 1.43 (s, 9.0H), 1.40 (s, 9.0H), 0.93-0.99 (m, 12.0H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 171.1, 170.6, 168.4, 143.2, 143.2, 139.2, 139.0, 129.1,

129.1, 128.2, 128.2, 126.0, 126.0, 125.8, 125.6, 81.1, 80.8, 73.2, 71.9, 65.7, 52.1, 51.7, 39.0, 38.8, 37.1, 36.8, 28.0, 27.8, 15.1, 14.5; IR (FT-IR): 2976 (w), 1729 (s), 1368 (w), 1271 (m), 1232 (w), 1177 (w), 1146 (m), 1079 (w), 702 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{23}\text{H}_{34}\text{NO}_4$   $[\text{M}+\text{H}]^+$  388.2482, found 388.2485.

**Methyl 3-benzyl-2-(diethylamino)-1-(dimethoxyphosphoryl)cyclopent-3-ene-1-carboxylate (4w)**

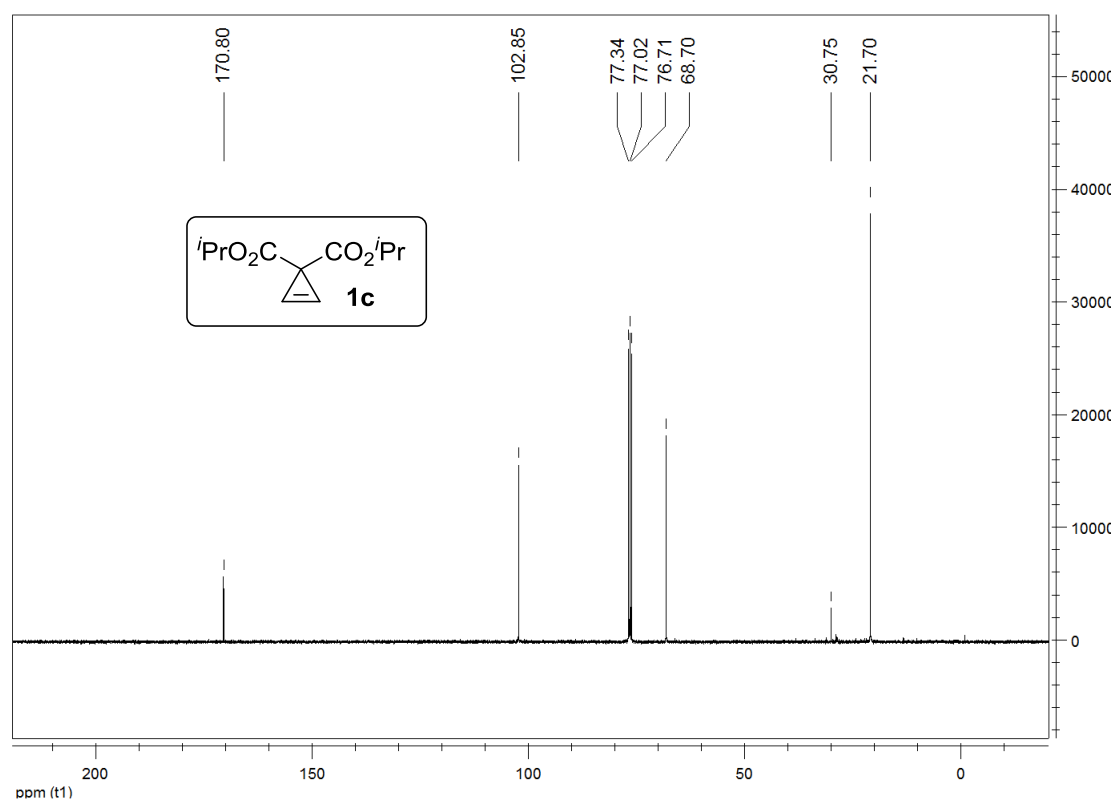
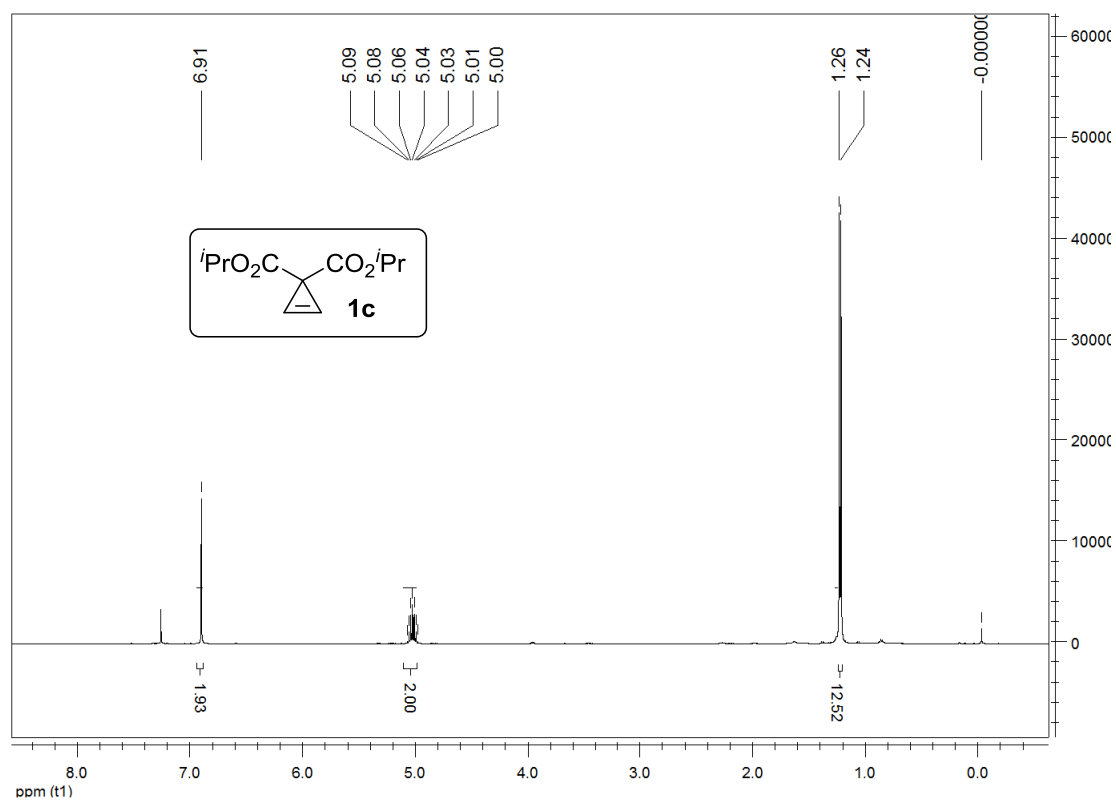


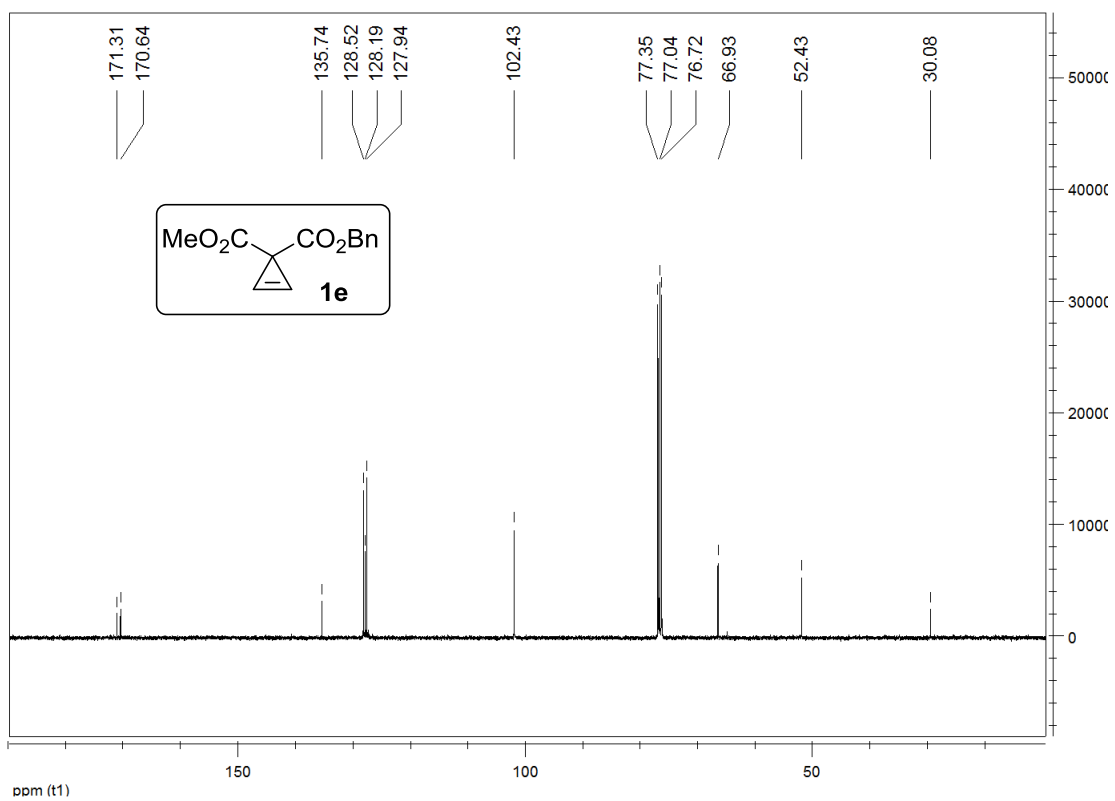
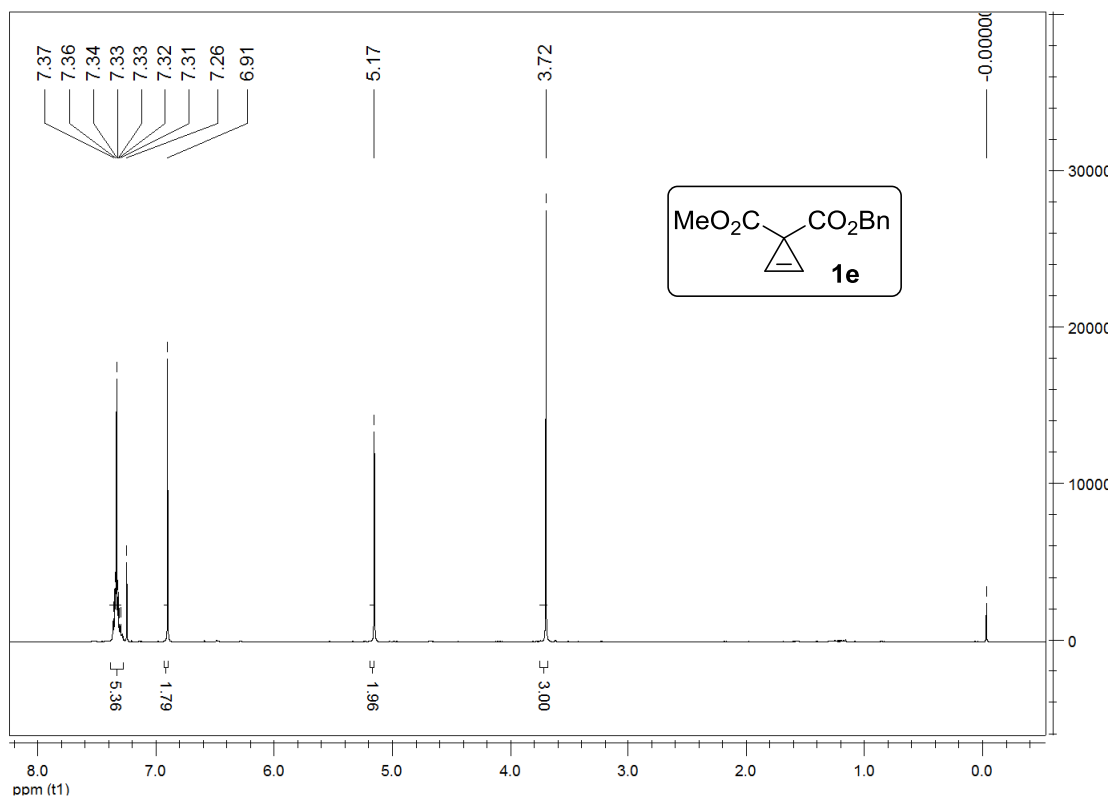
Yield: 49.9 mg; 63%, d.r.>20:1; a yellow oil;  $R_f = 0.33$  (EA);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.30 (m, 2H), 7.18-7.22 (m, 3H), 5.38 (s, 1H), 4.34 (dd,  $J = 1.9$  Hz,  $J = 19.4$  Hz, 1H), 3.76 (s, 3H), 3.73 (d,  $J = 10.5$  Hz, 3H), 3.63 (d,  $J = 10.8$  Hz, 3H), 3.50 (d,  $J = 15.8$  Hz, 1H), 3.32 (dd,  $J = 18.0$  Hz,  $J = 20.0$  Hz, 1H), 3.19 (d,  $J = 15.9$  Hz, 1H), 2.47-2.76 (m, 5H), 0.95 (t,  $J = 5.9$  Hz, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9 (d,  $J = 3.3$  Hz), 142.0 (d,  $J = 2.3$  Hz), 139.1, 129.0, 128.2, 127.0, 126.1, 73.6 (d,  $J = 0.9$  Hz), 58.8 (d,  $J = 134.9$  Hz), 54.2 (d,  $J = 6.5$  Hz), 52.7 (d,  $J = 7.4$  Hz), 52.3, 36.4 (d,  $J = 2.6$  Hz), 36.3, 15.1; IR (FT-IR): 2961 (w), 1735 (m), 1454 (w), 1257 (s), 1201 (w), 1057 (s), 1031 (s), 826 (w), 703 (m)  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/e$  calcd for  $\text{C}_{20}\text{H}_{31}\text{NO}_5\text{P}$   $[\text{M}+\text{H}]^+$  396.1934, found 396.1940.

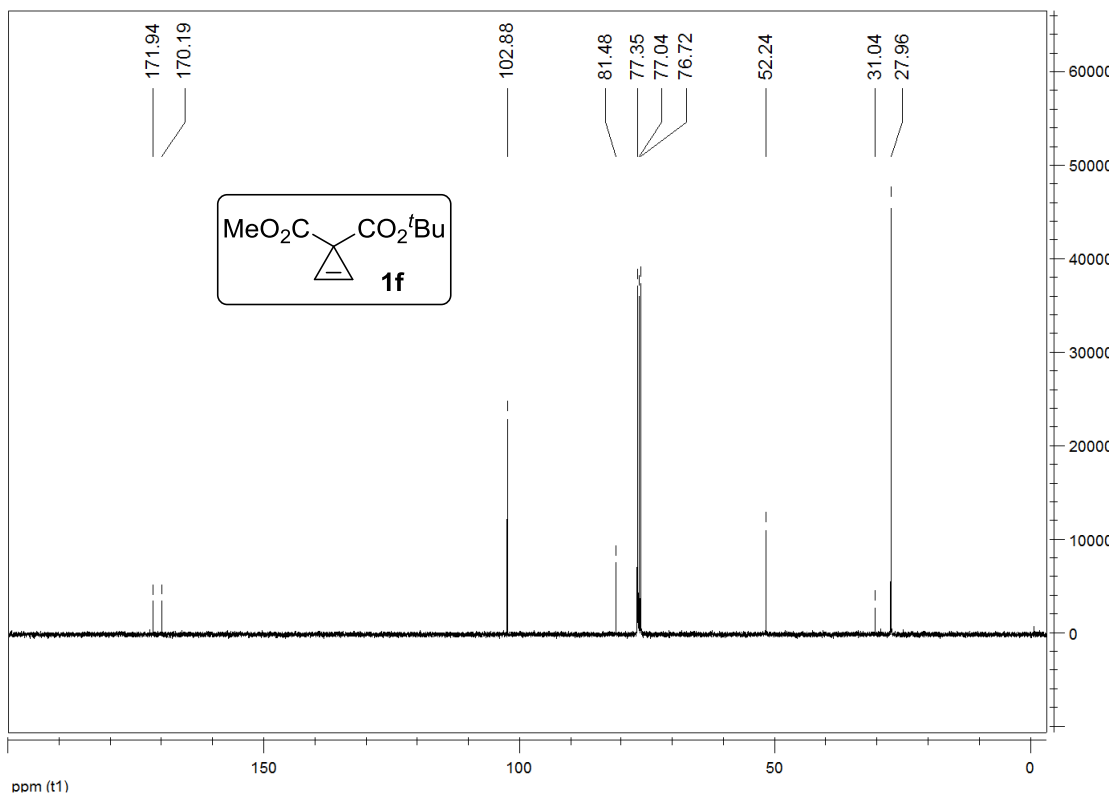
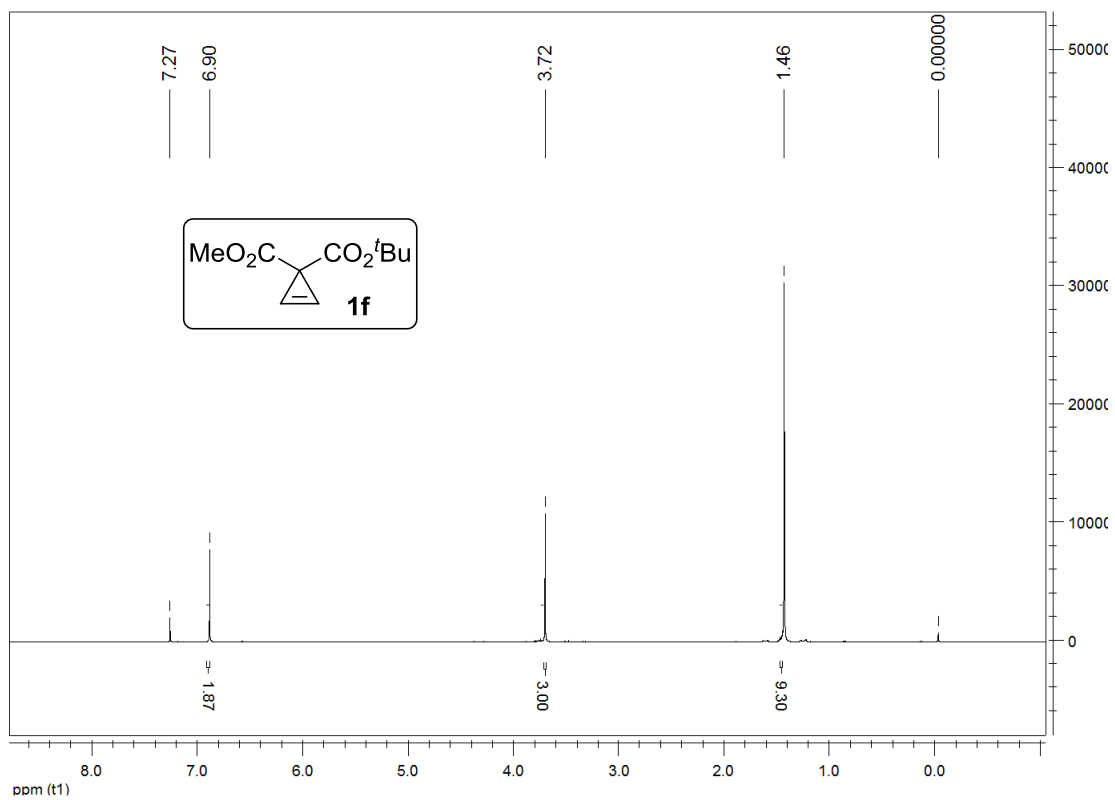
## 5. References

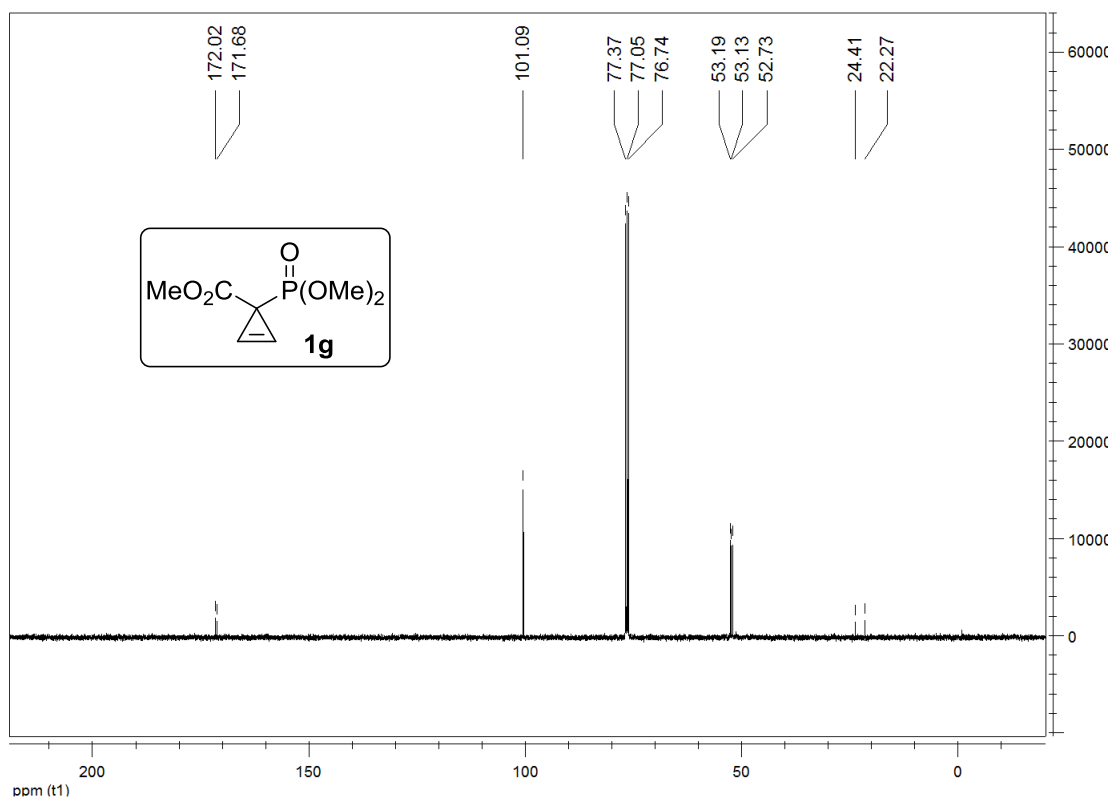
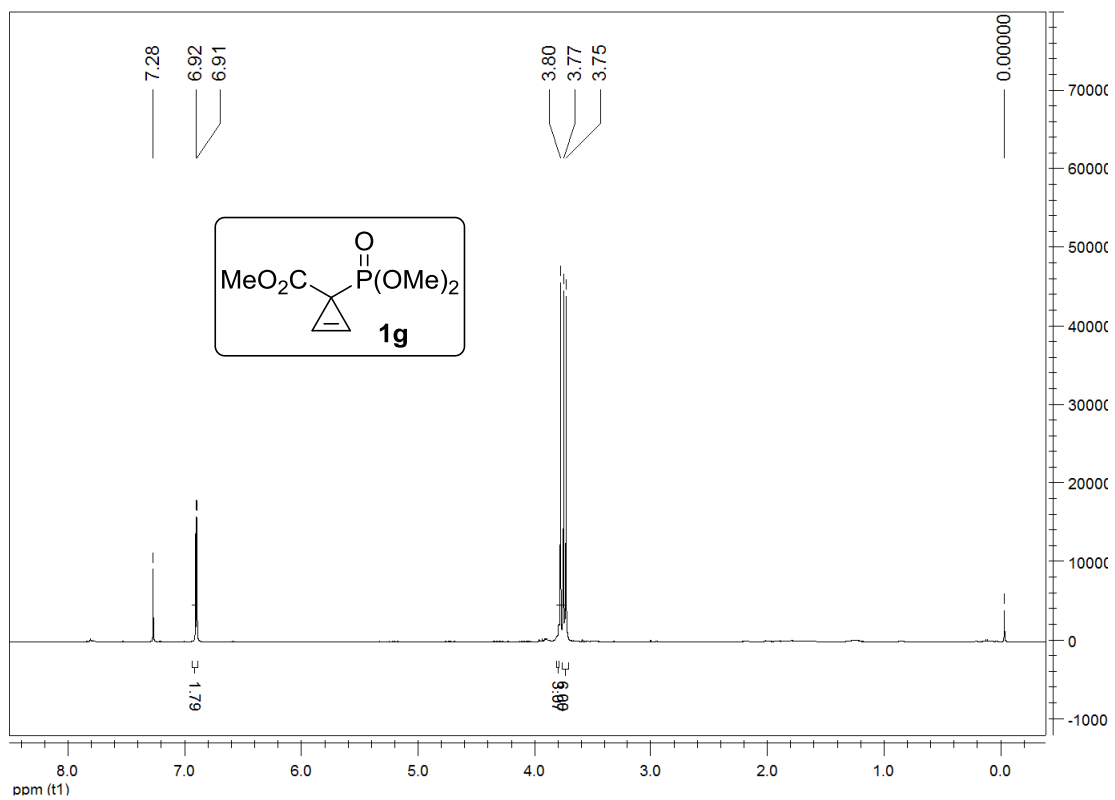
- 1 M. Rubina, M. Rubin, V. Gevorgyan, *J. Am. Chem. Soc.*, 2003, **125**, 7198.
- 2 D. T. Manning, J. J. Cappy, R. M. See, A. R. Cooke, C. D. Fritz, T. N. Wheeler, U.S. Patent 5, 292,937. March 8, 1994
- 3 G. Maier, B. Wolf, *Synthesis*, 1985, 871.

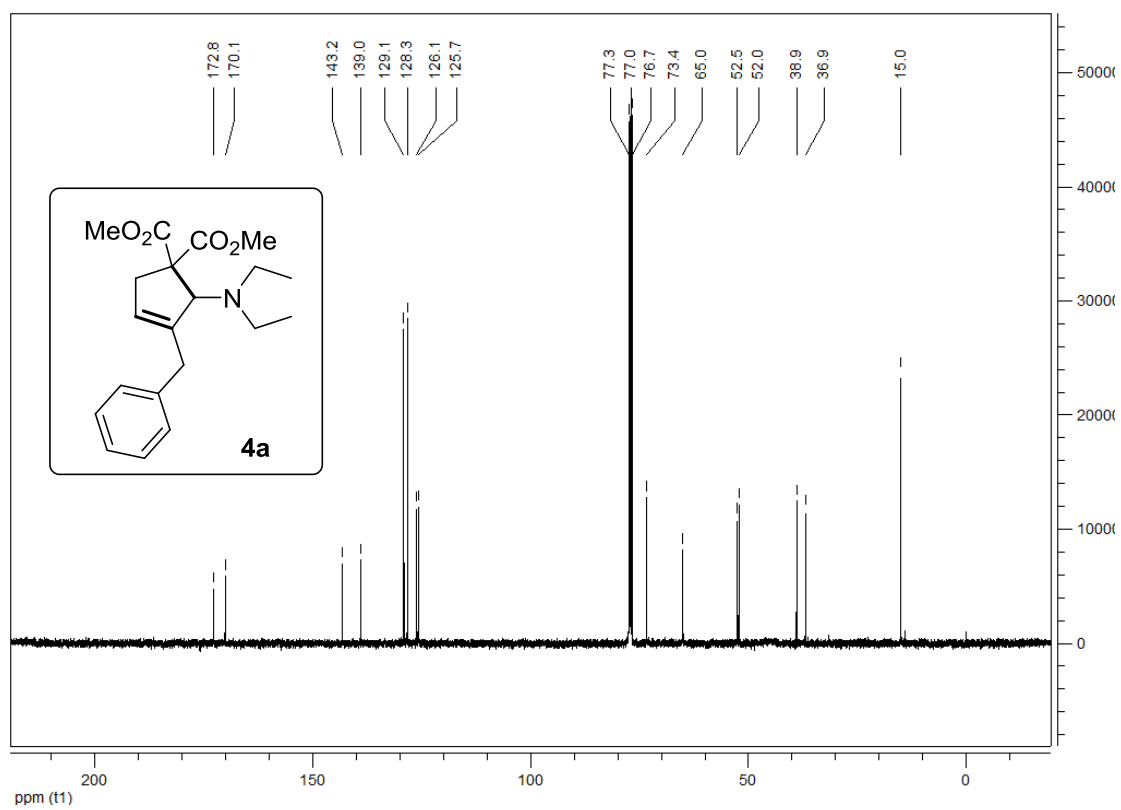
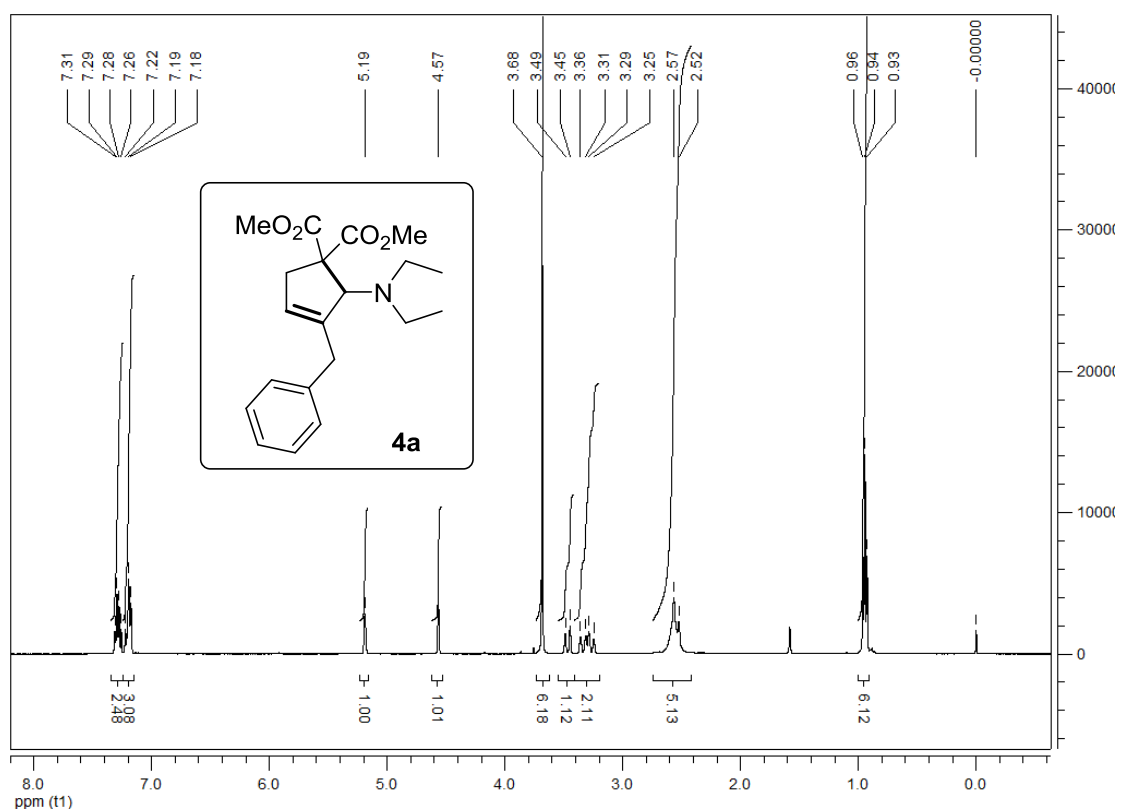
## 6. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra



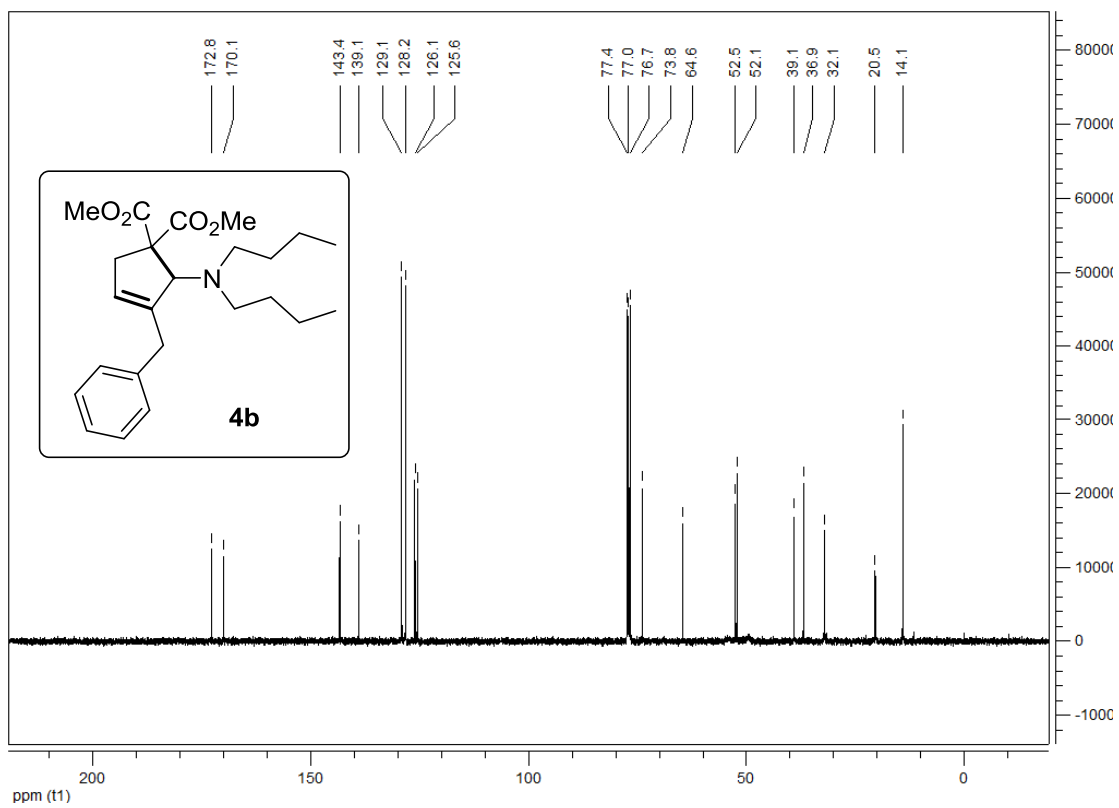
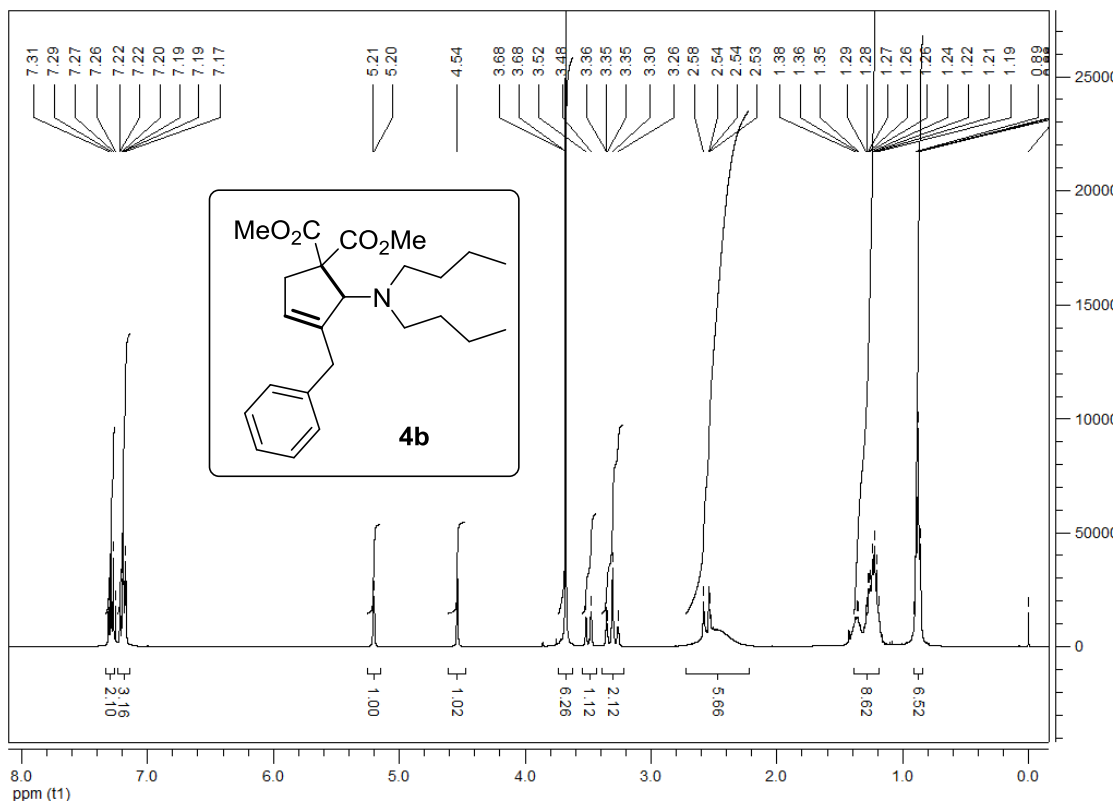


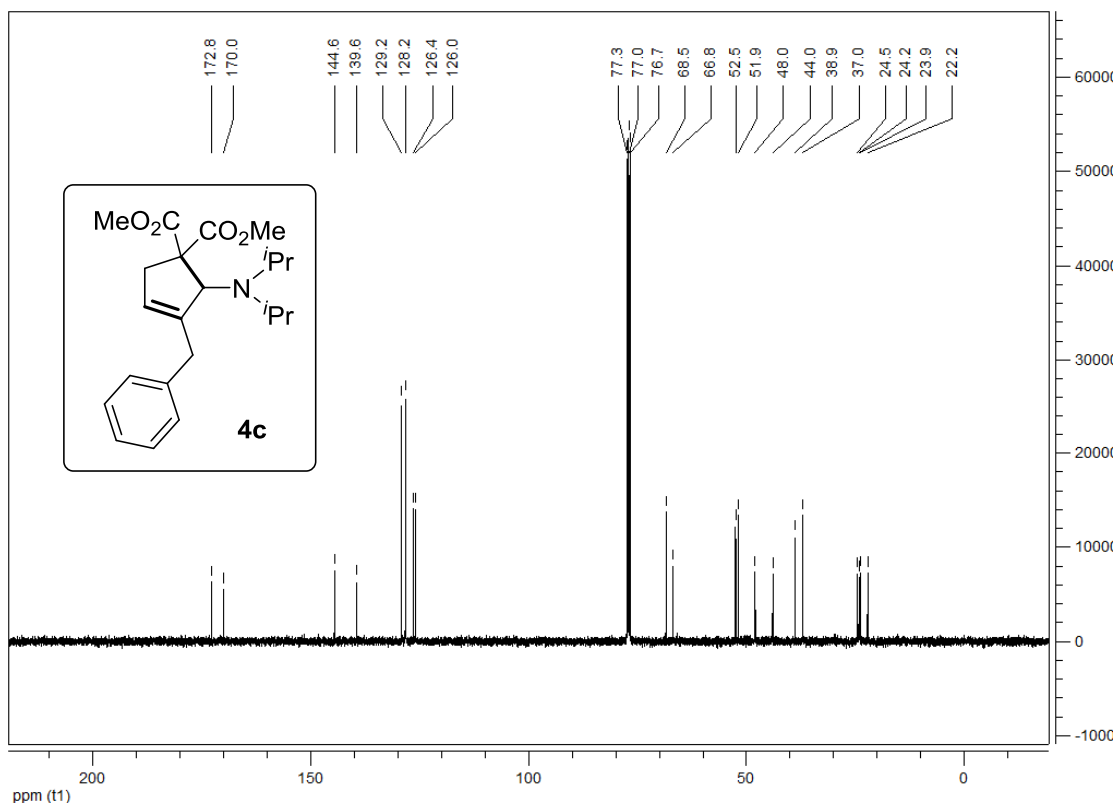
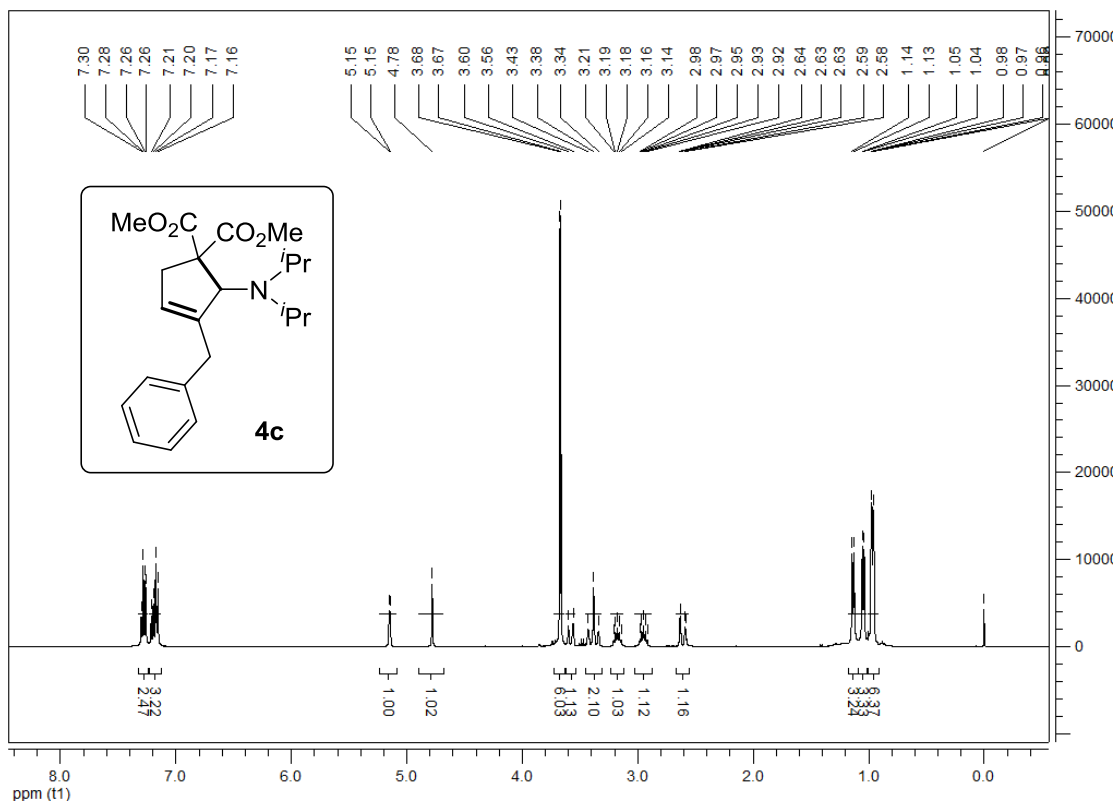


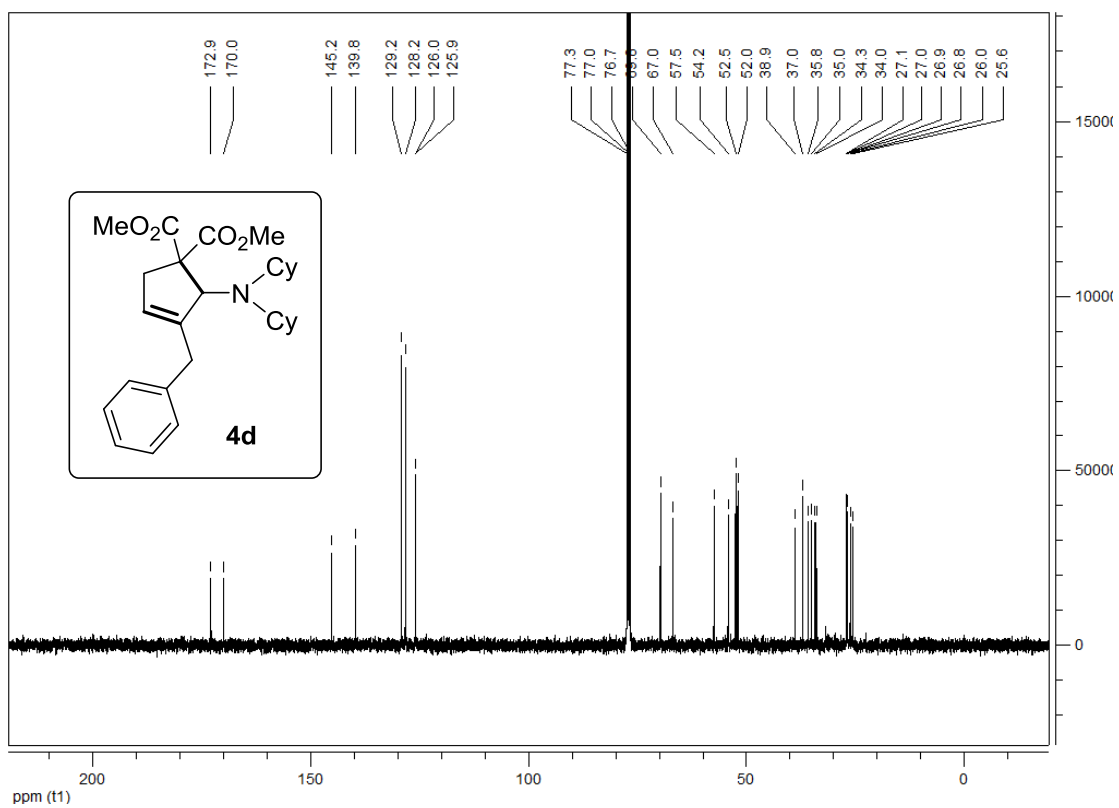
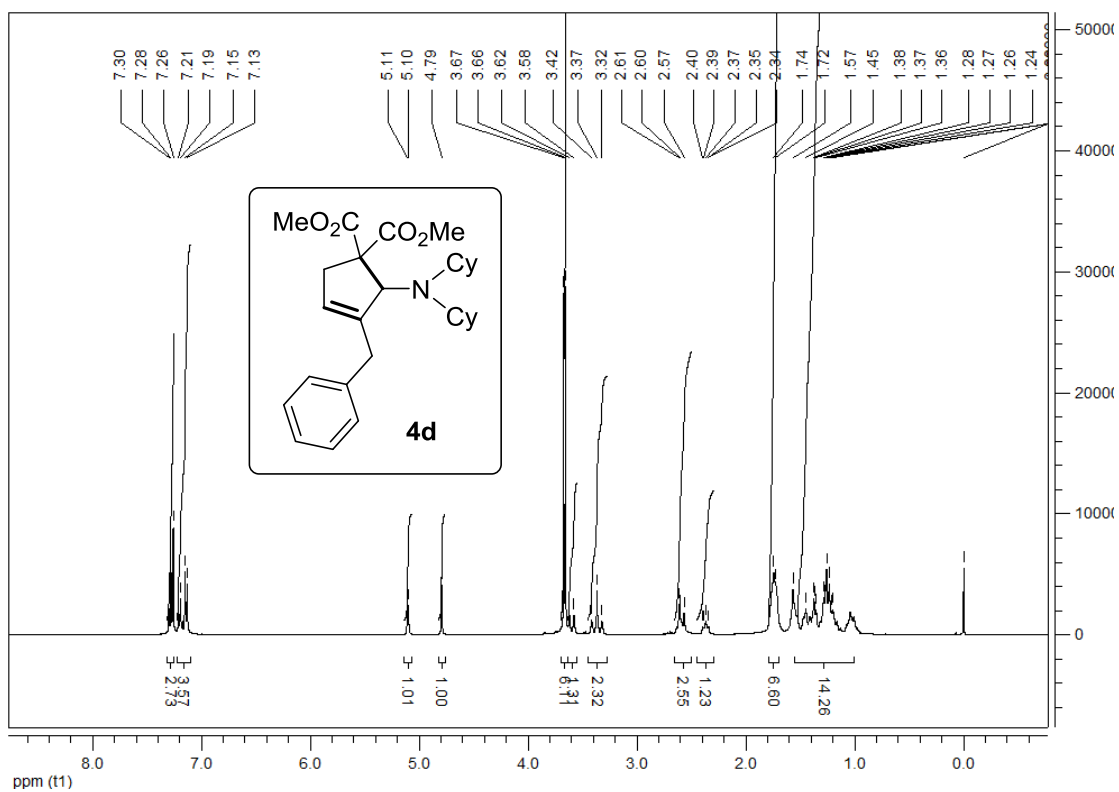


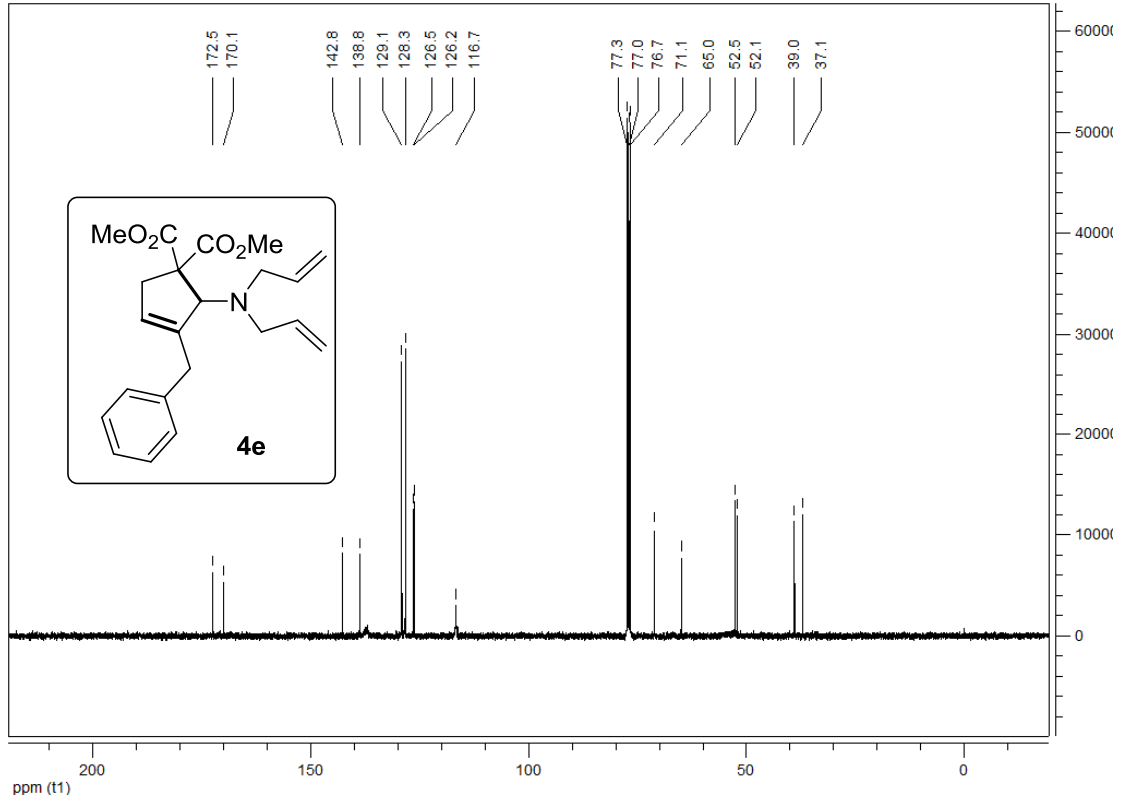
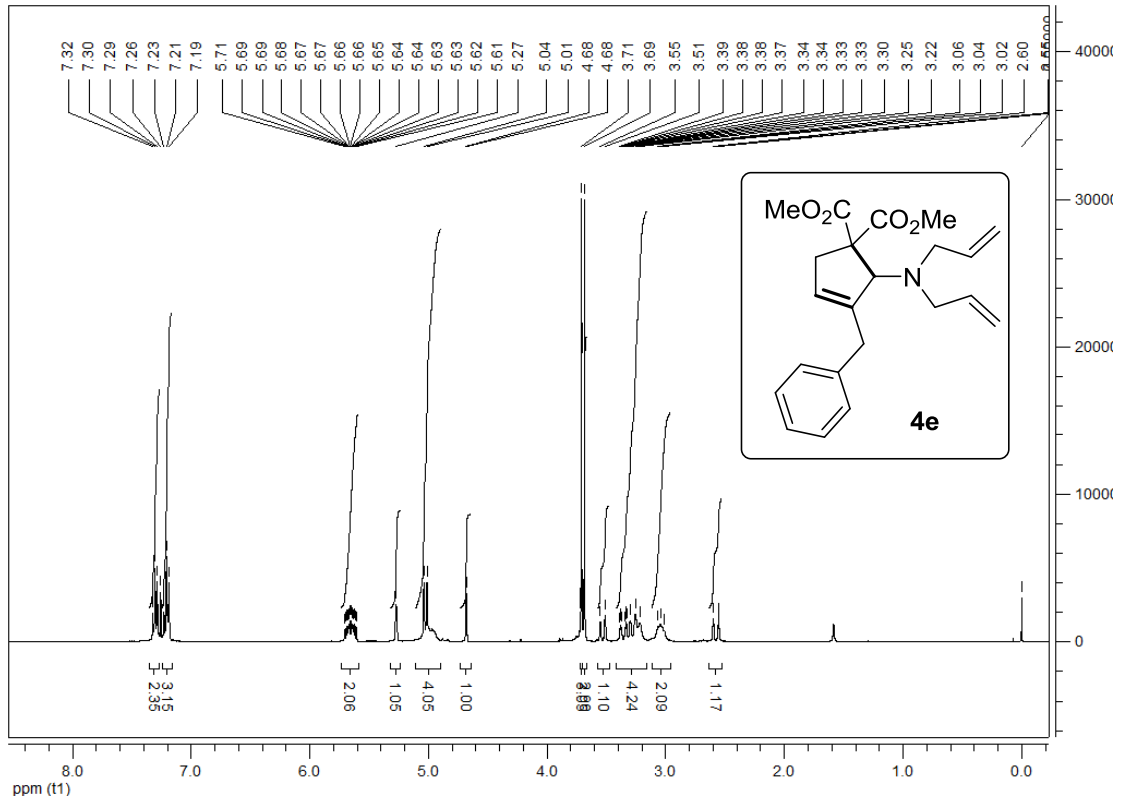


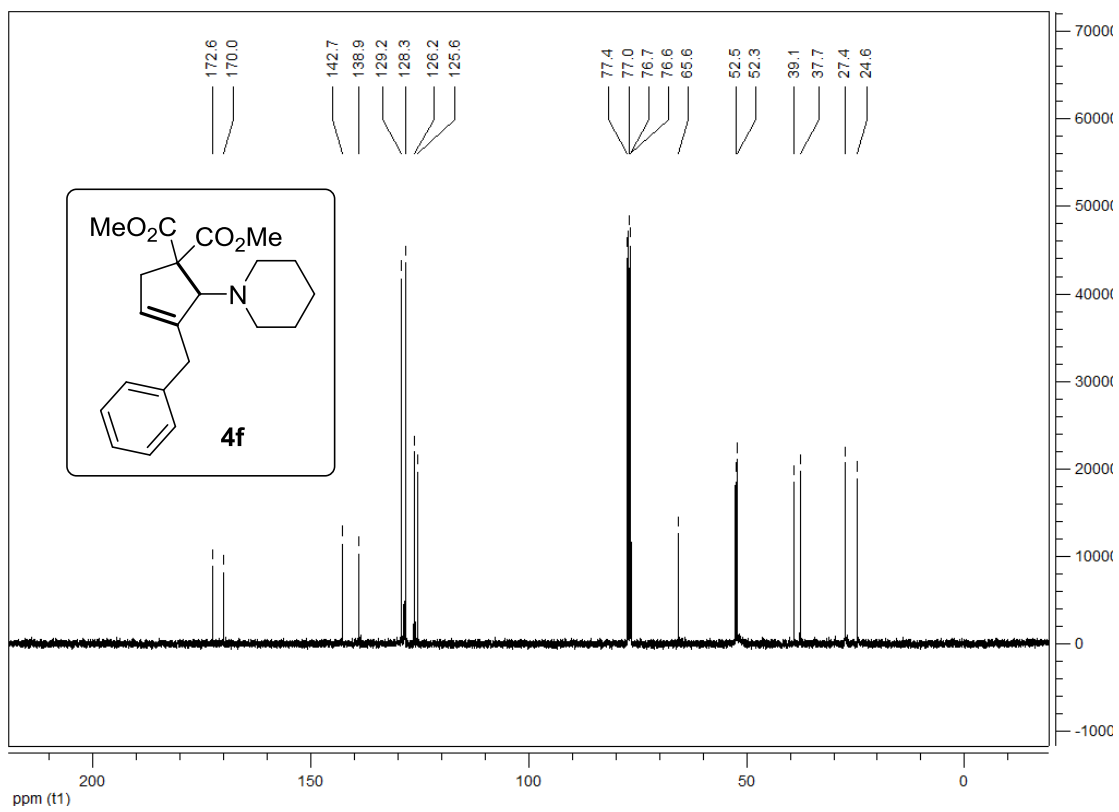
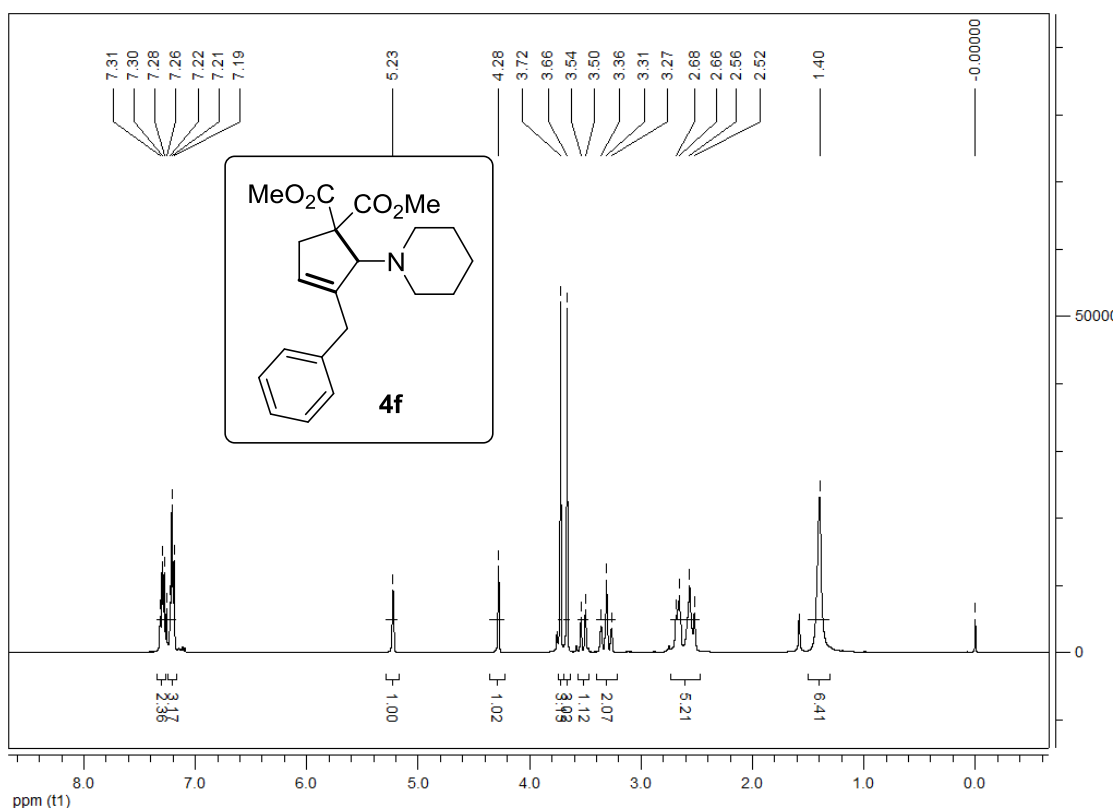


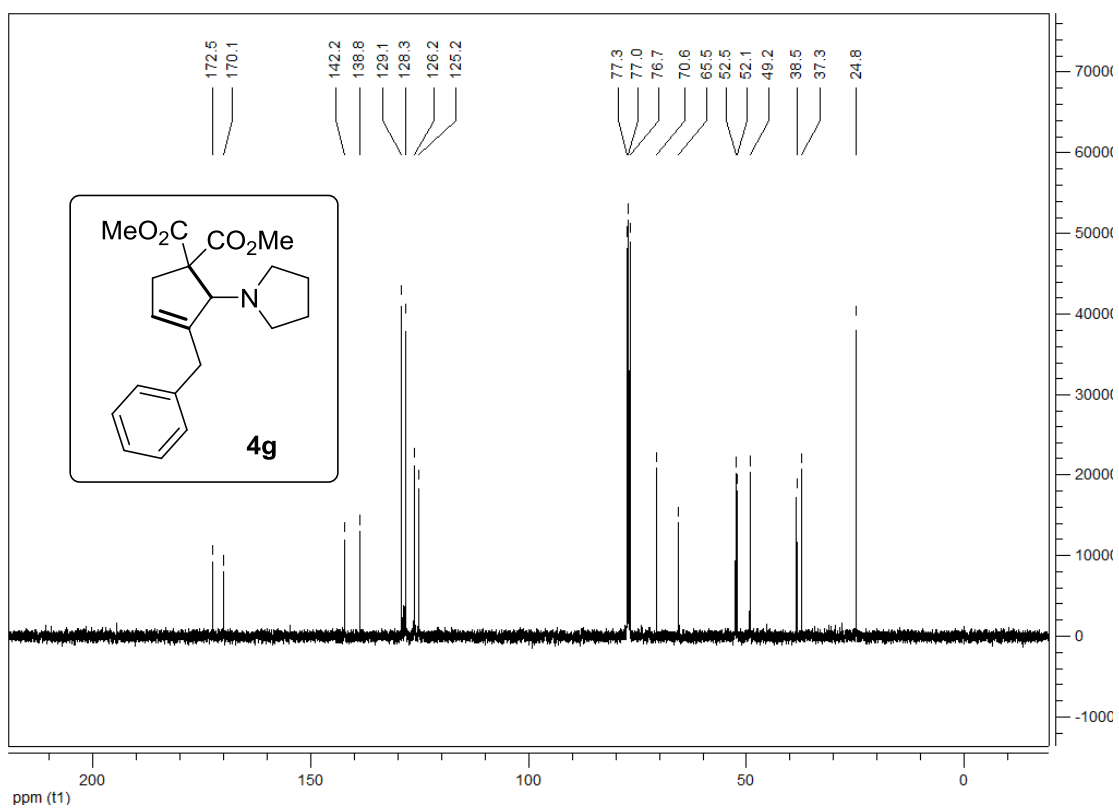
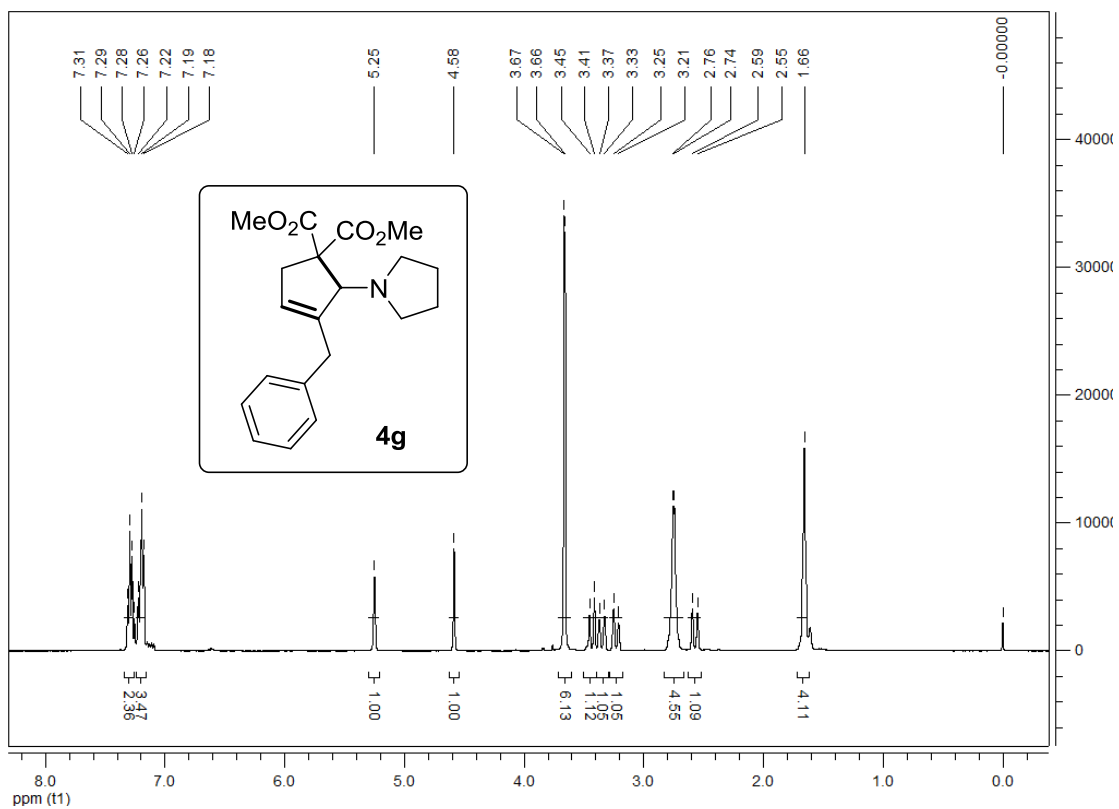


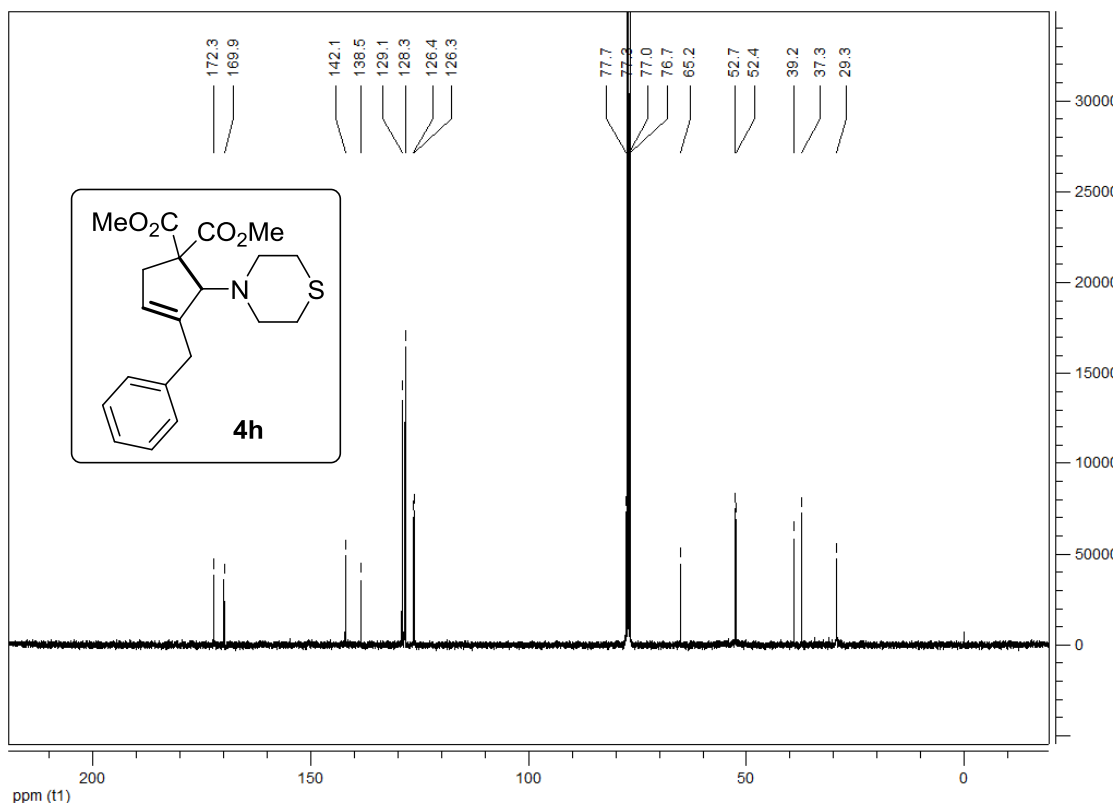
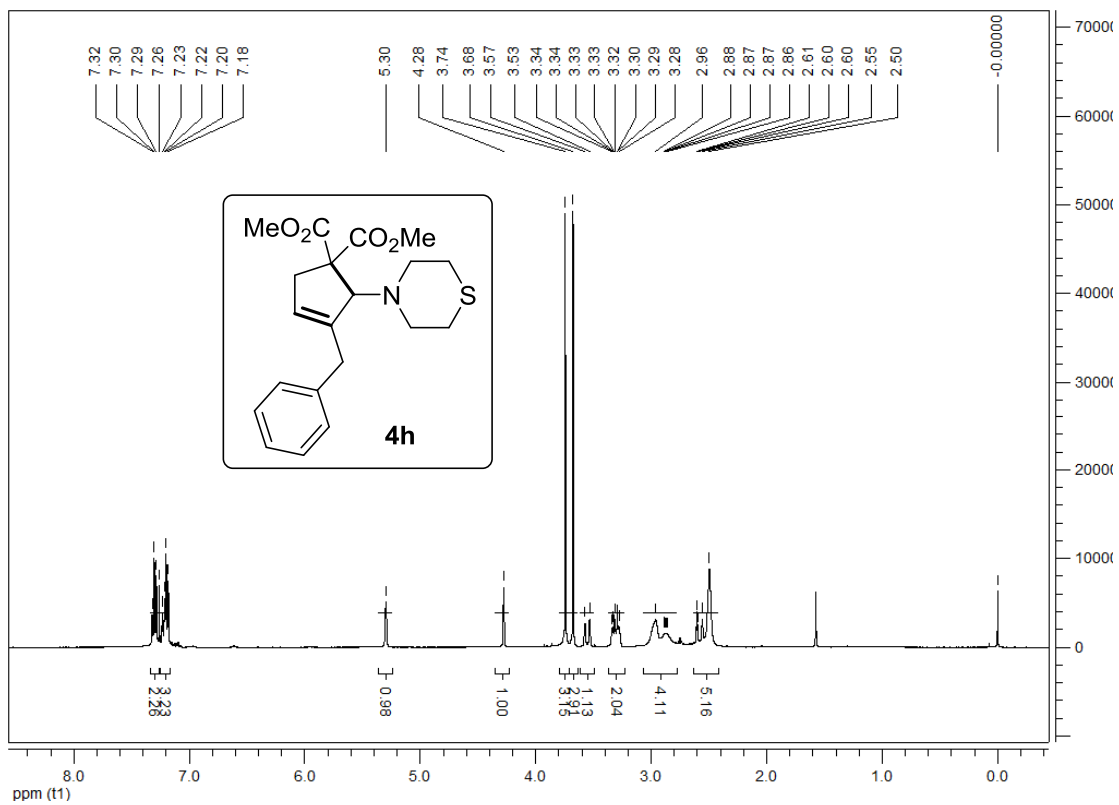


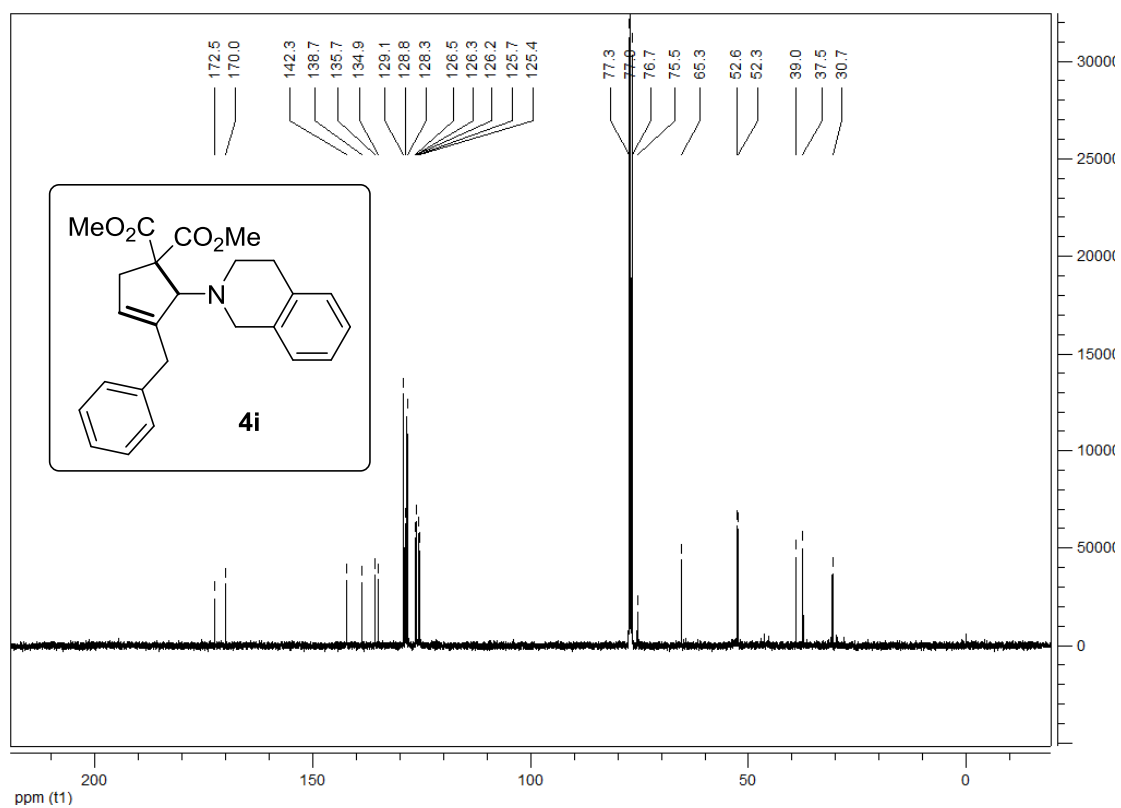
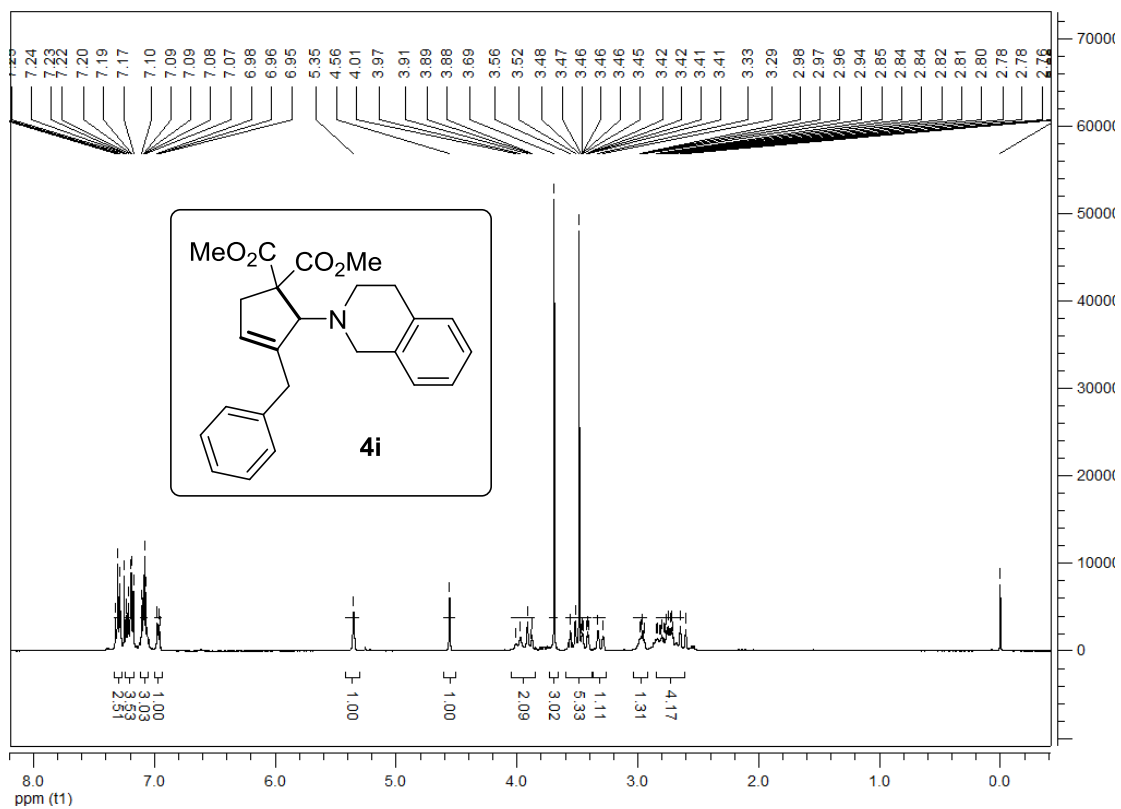




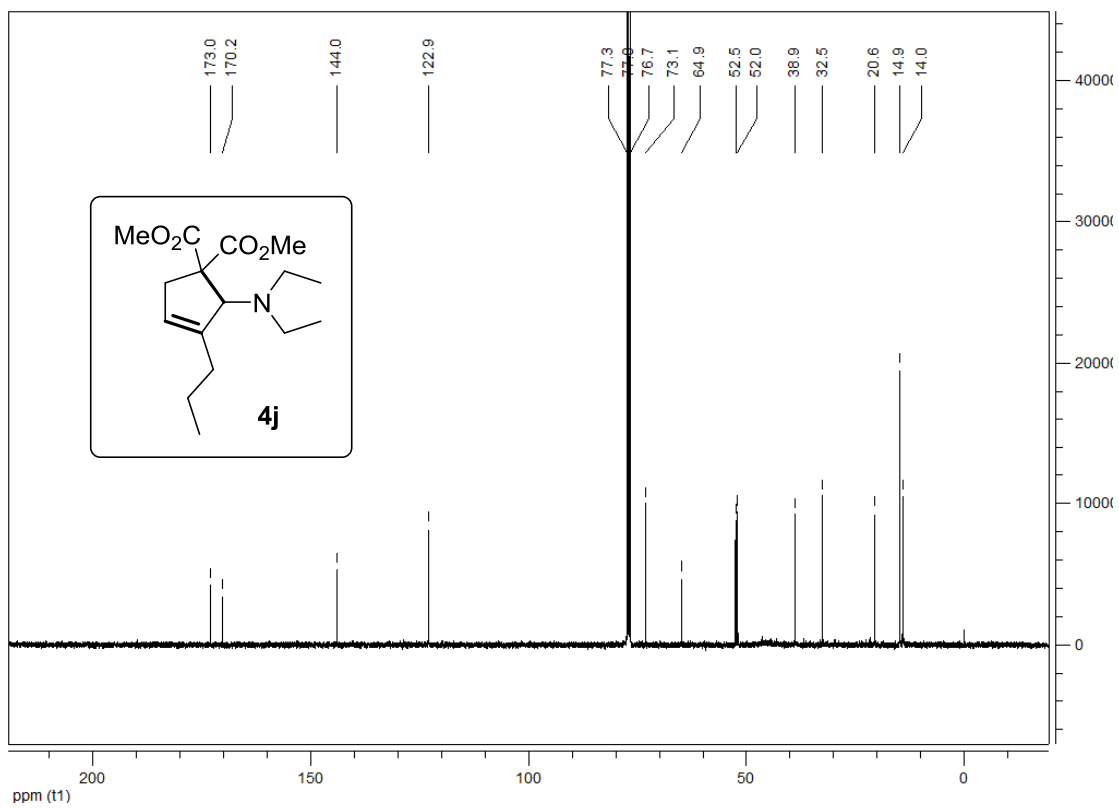
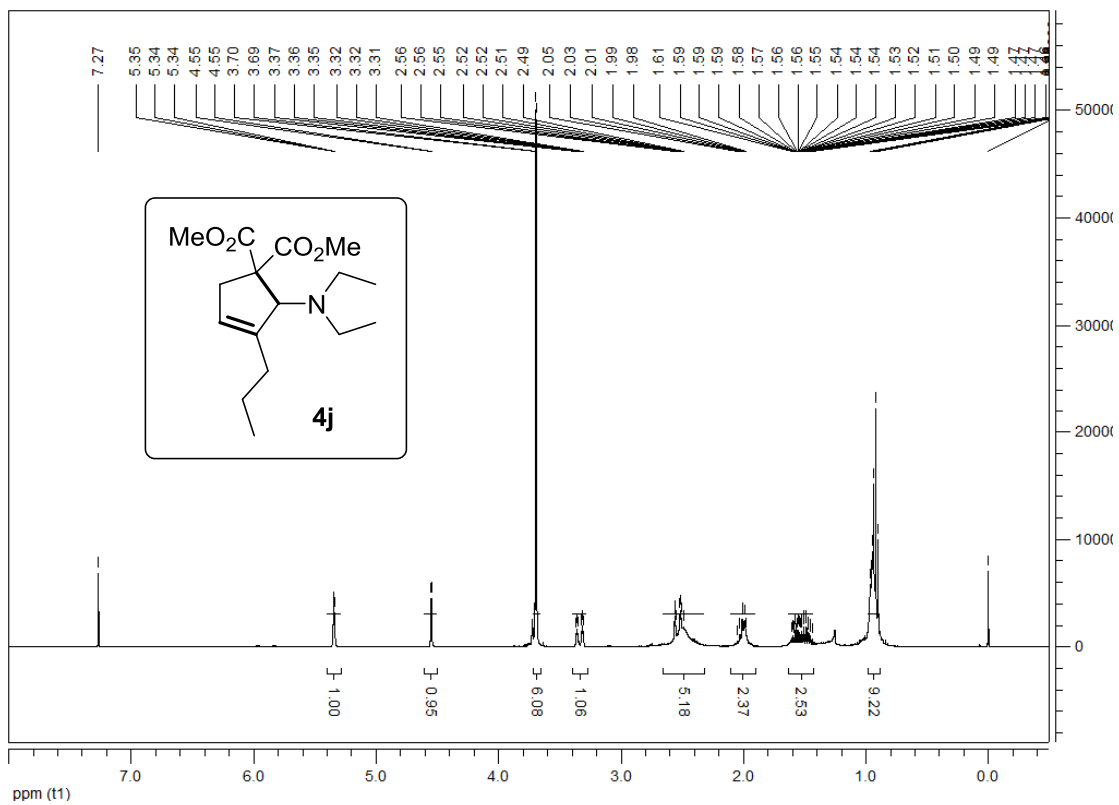


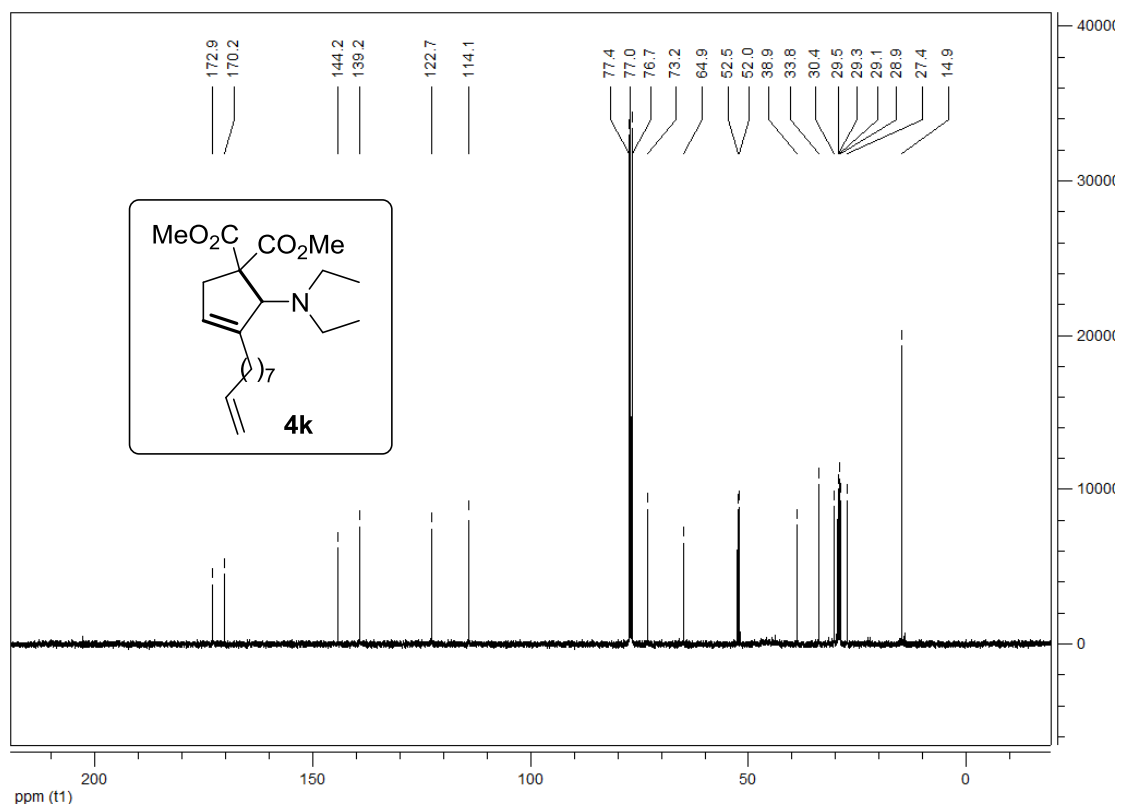
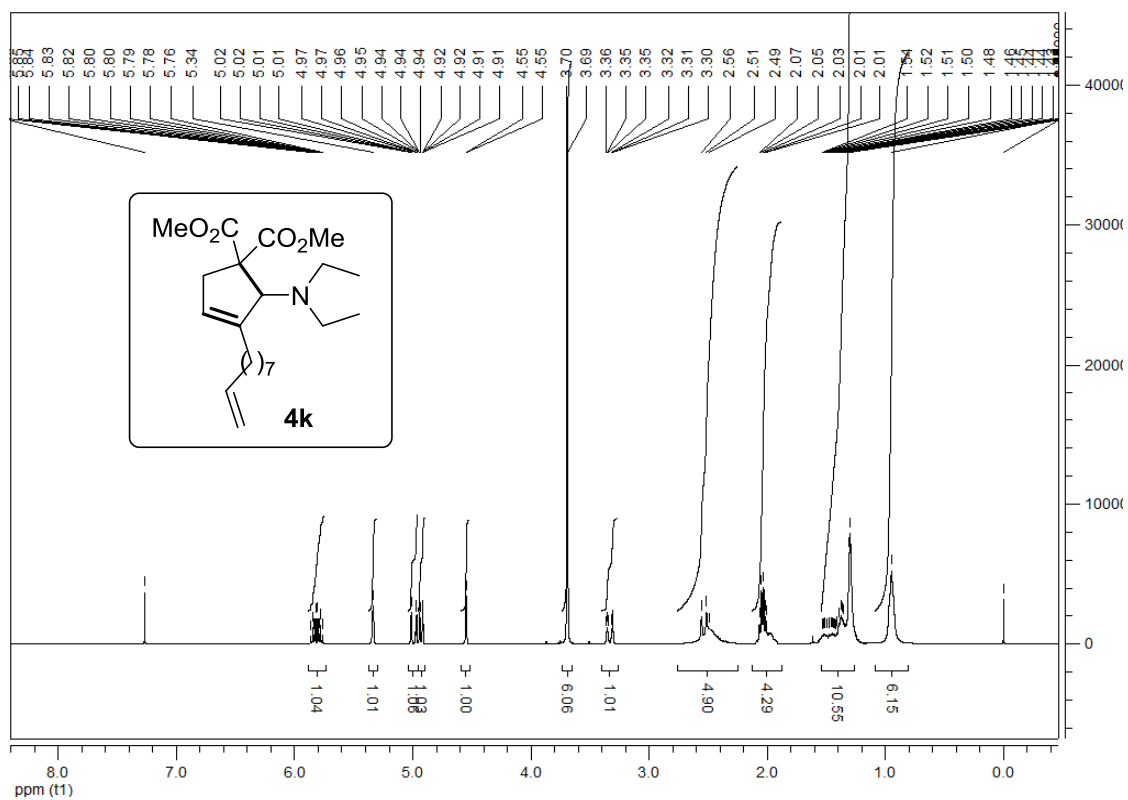


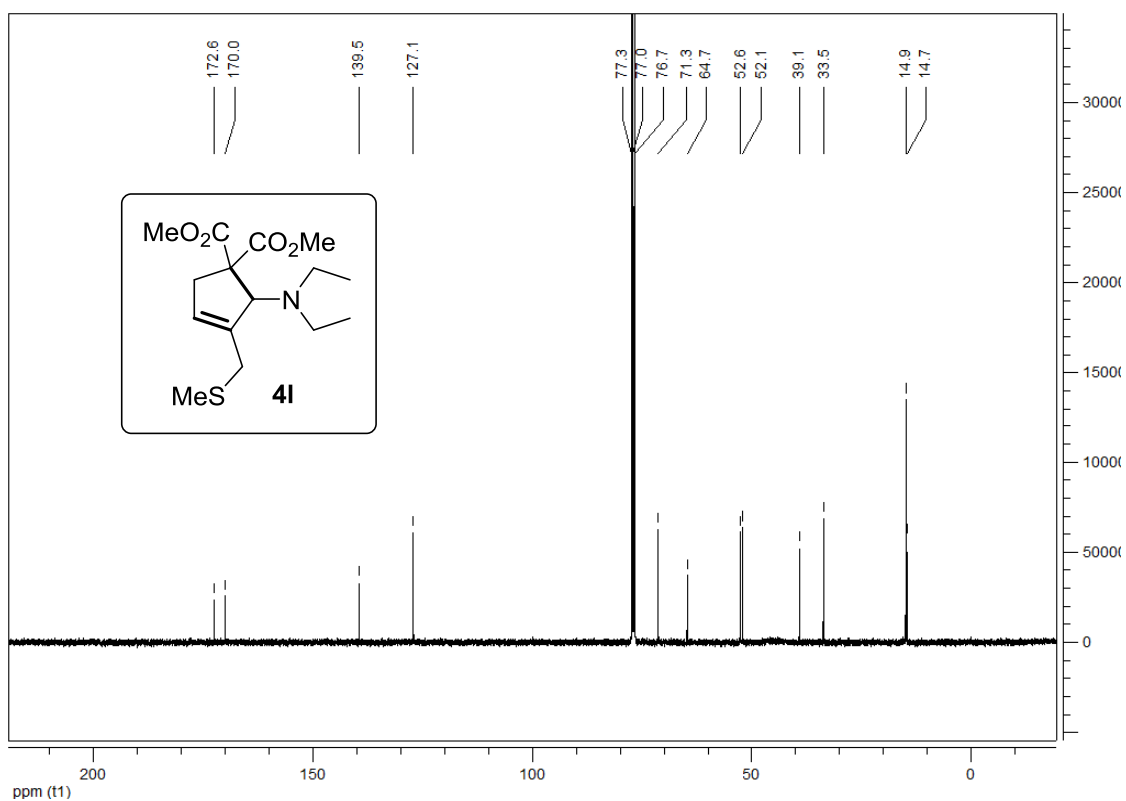
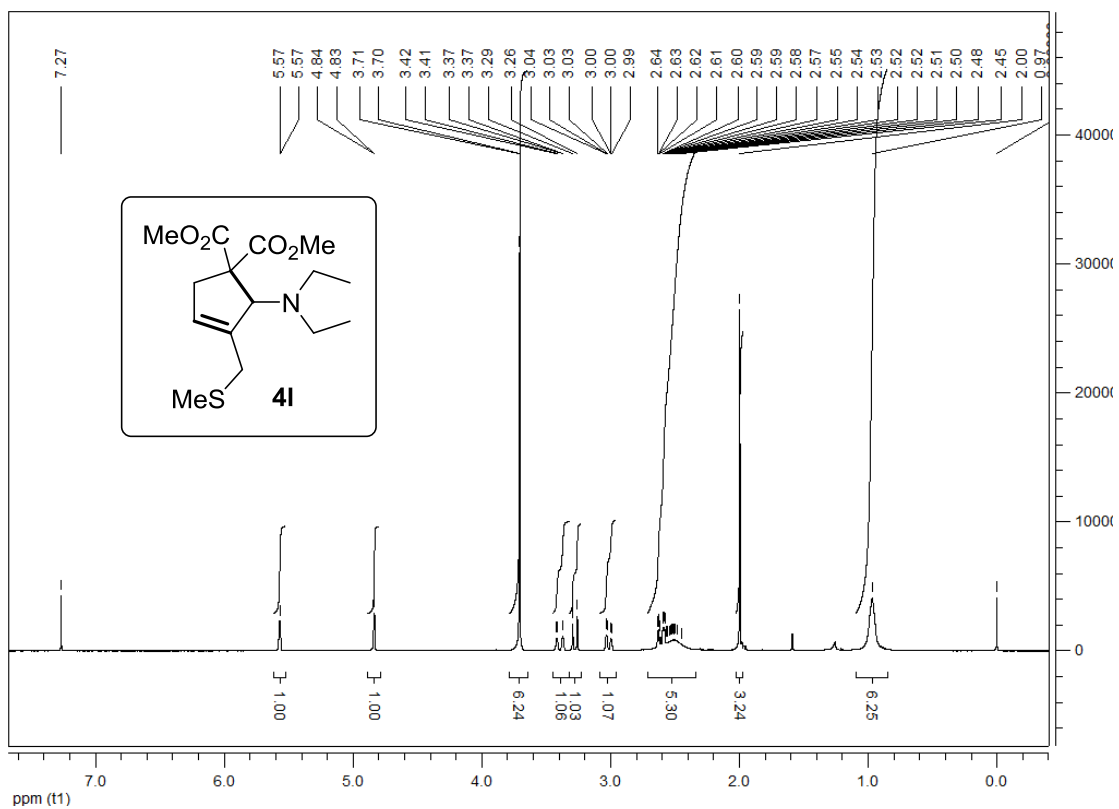


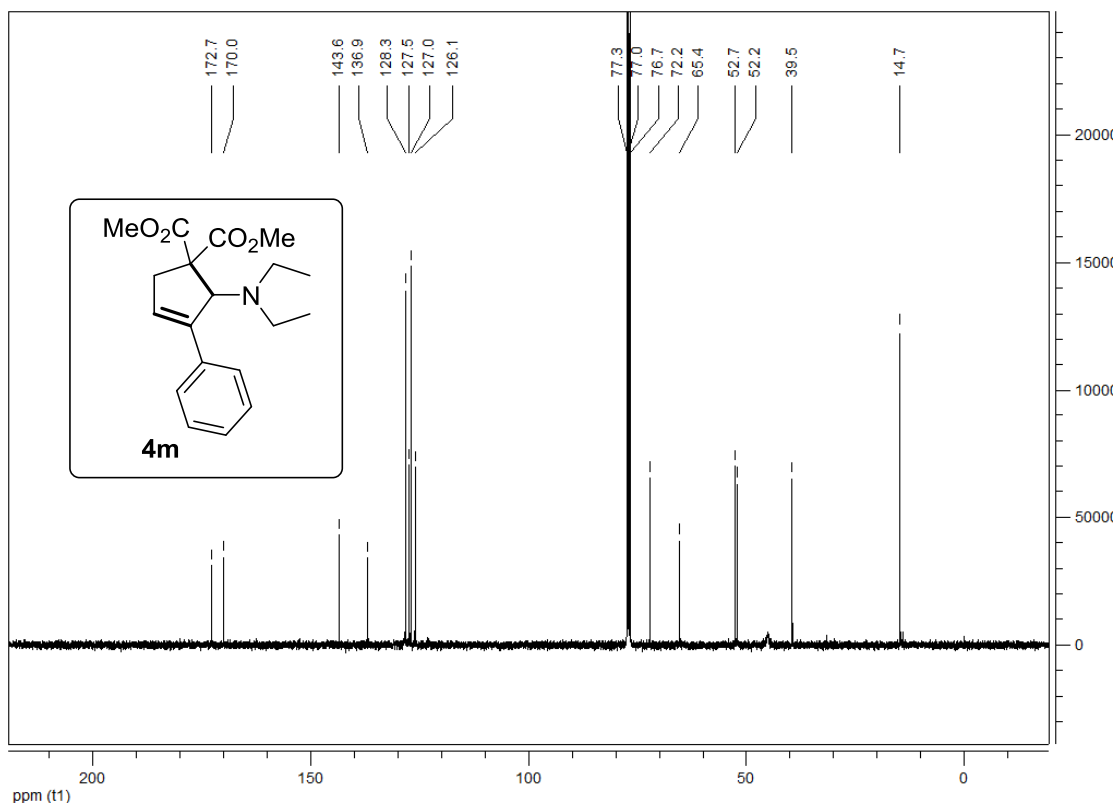
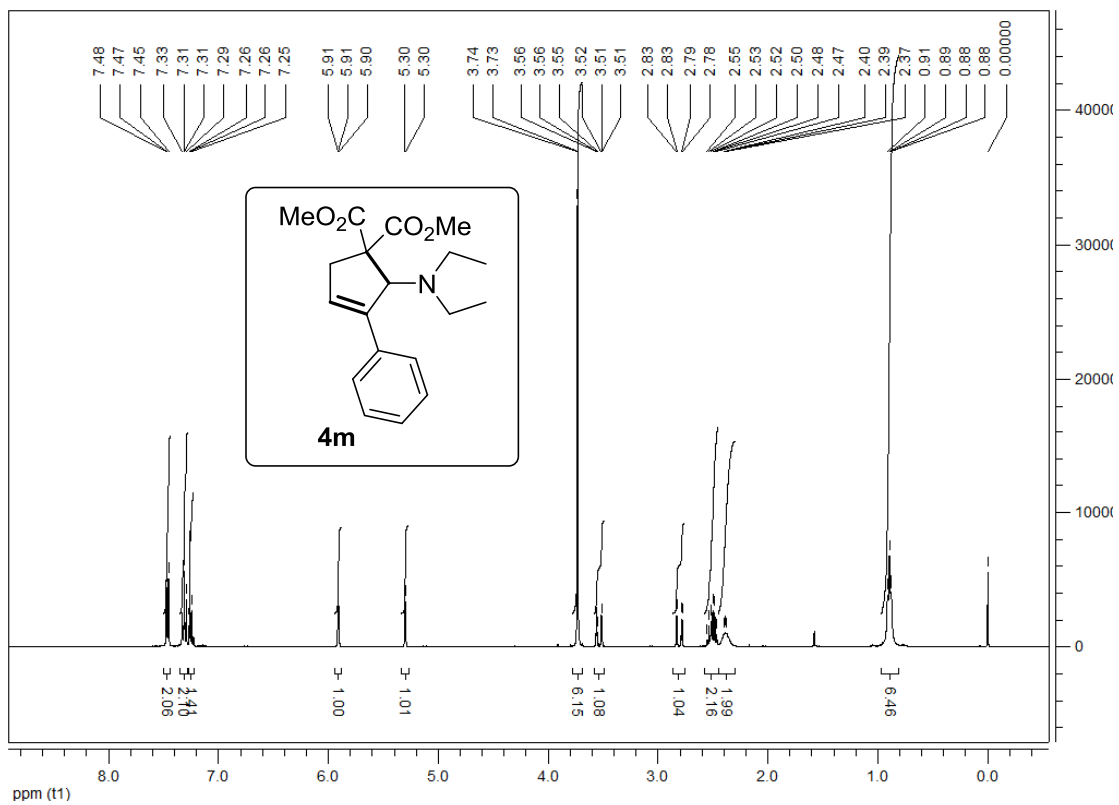


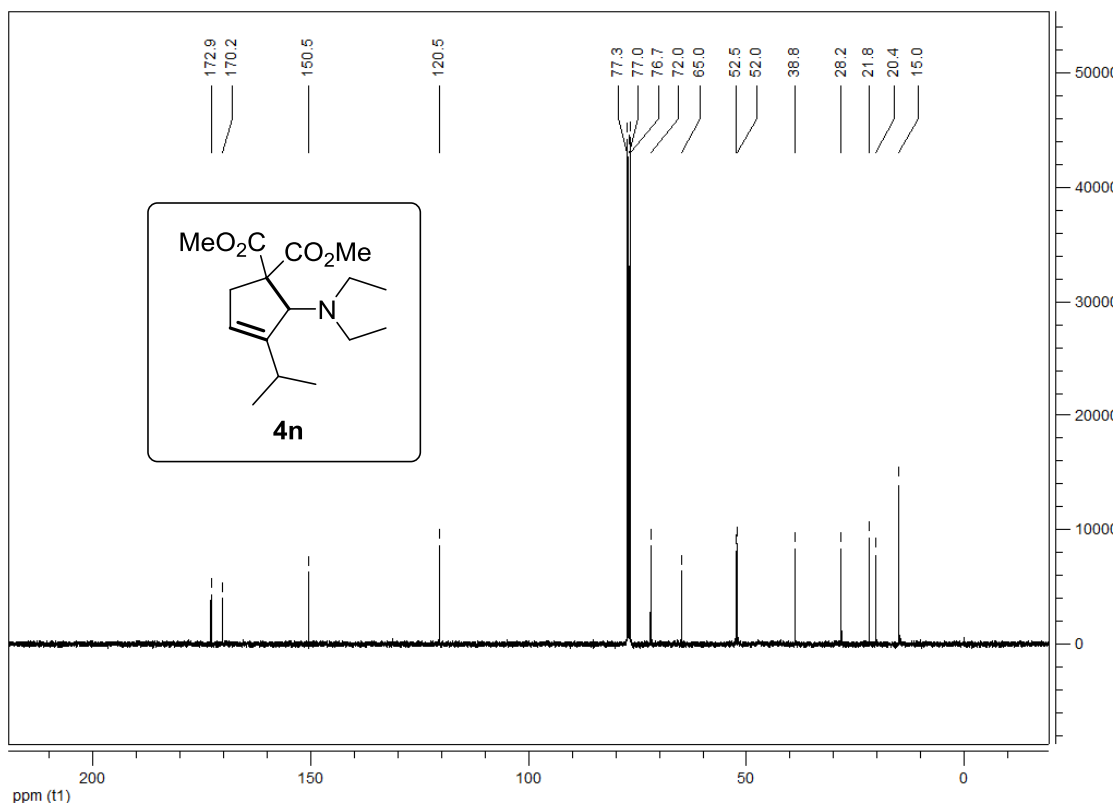
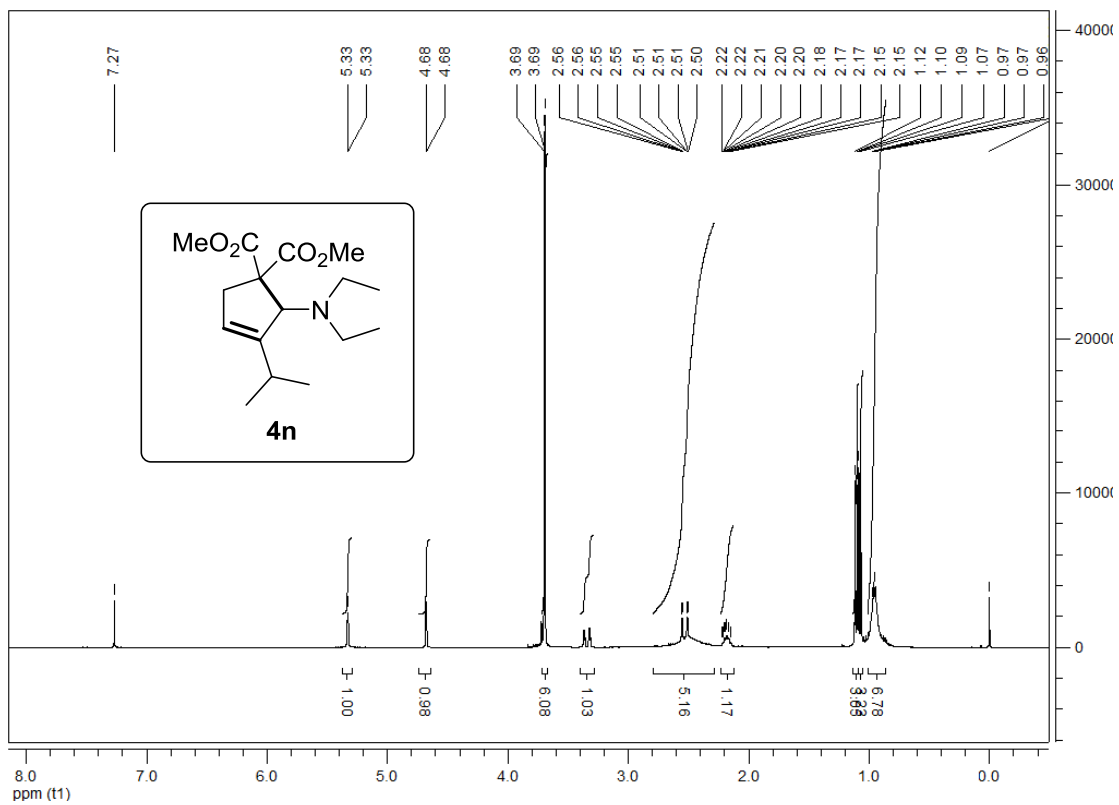


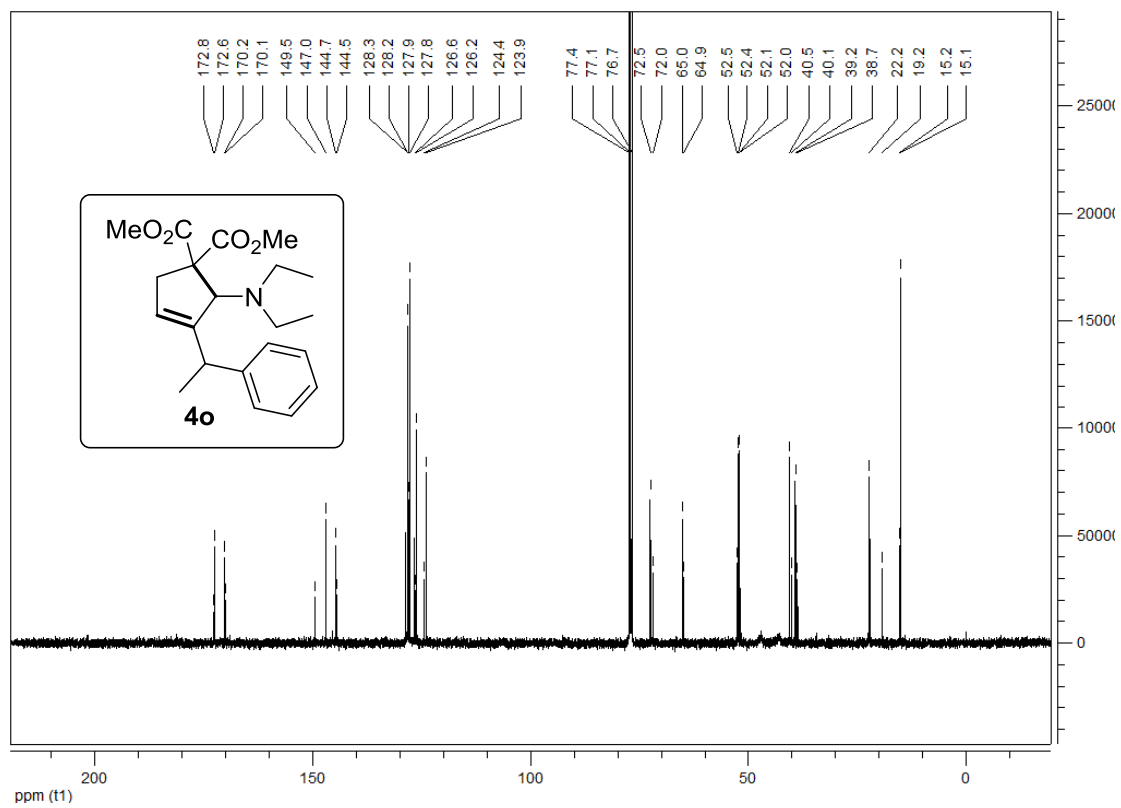
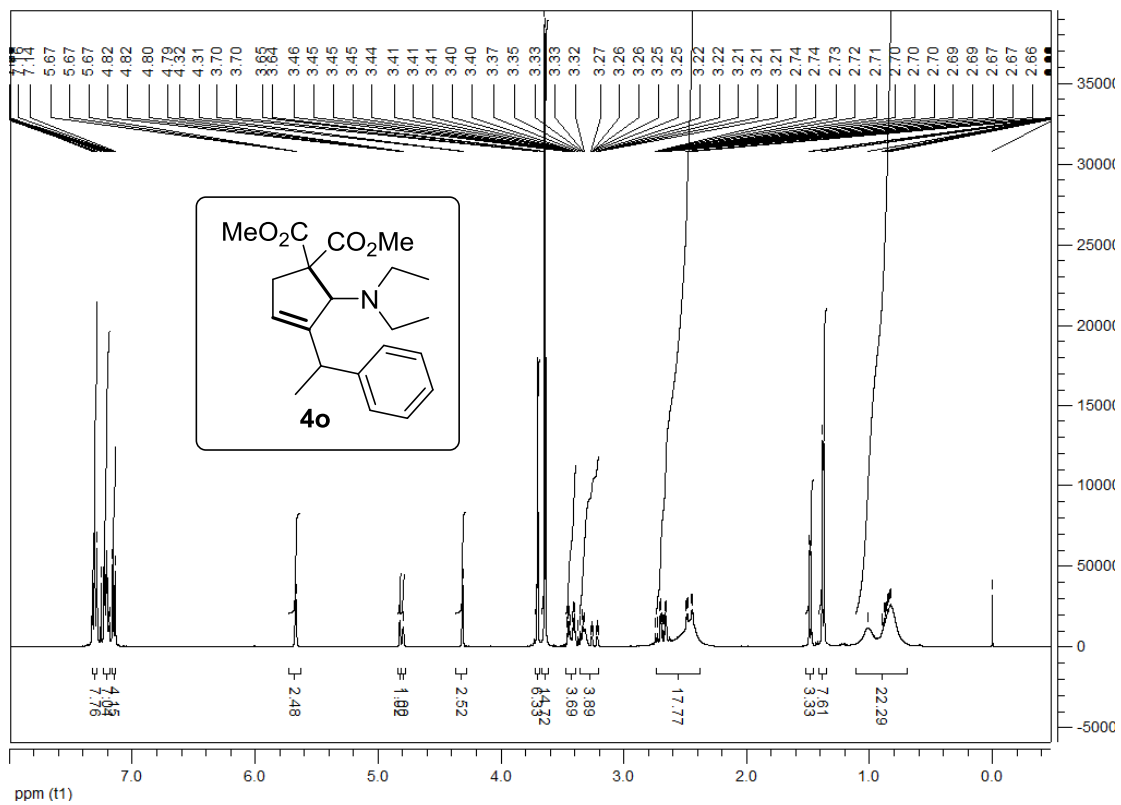


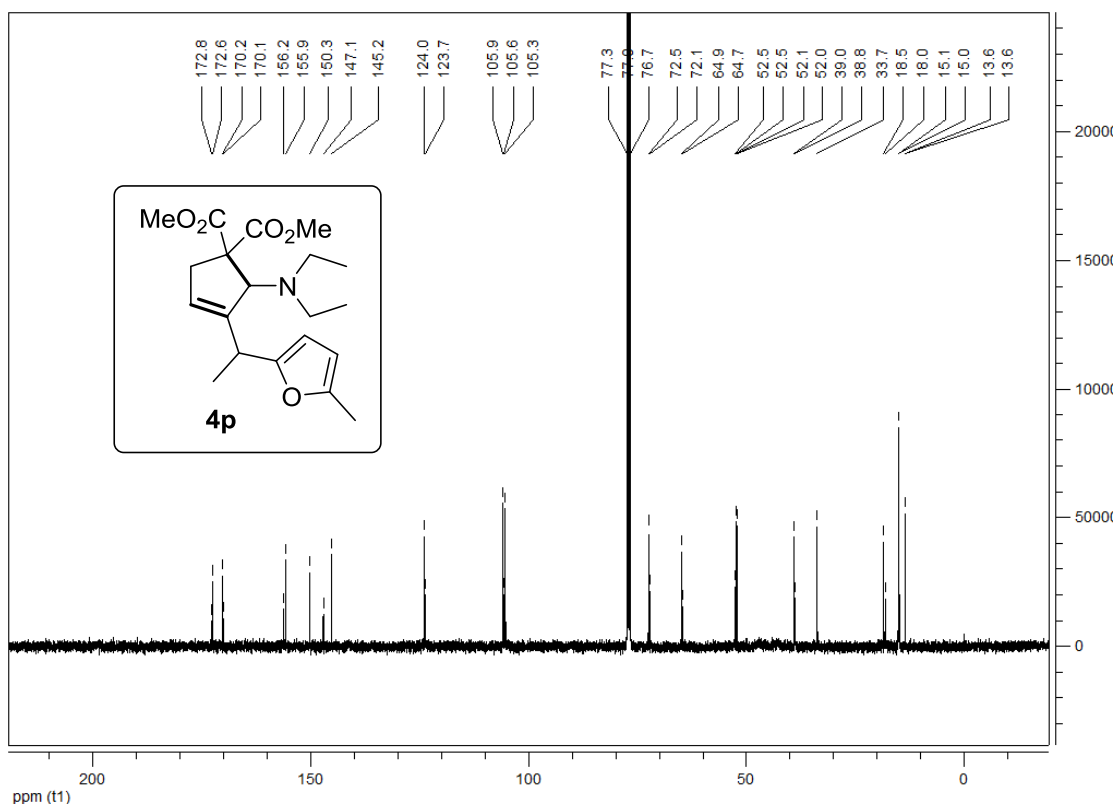
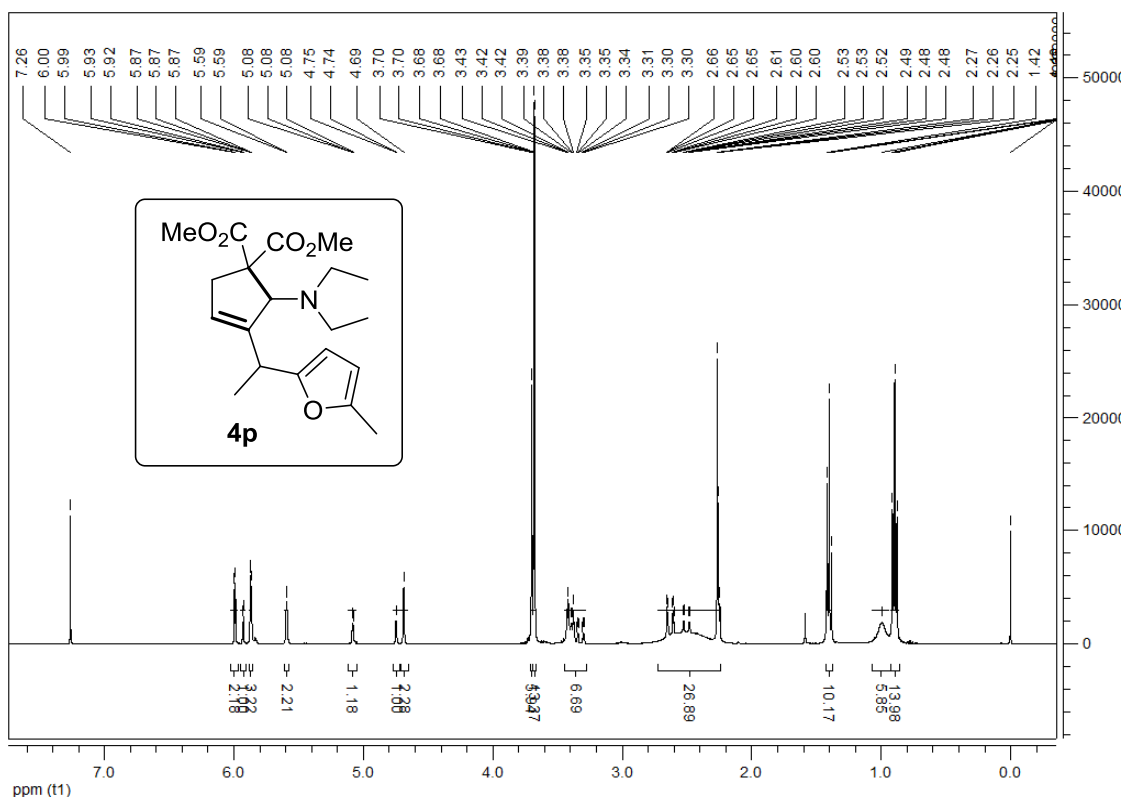


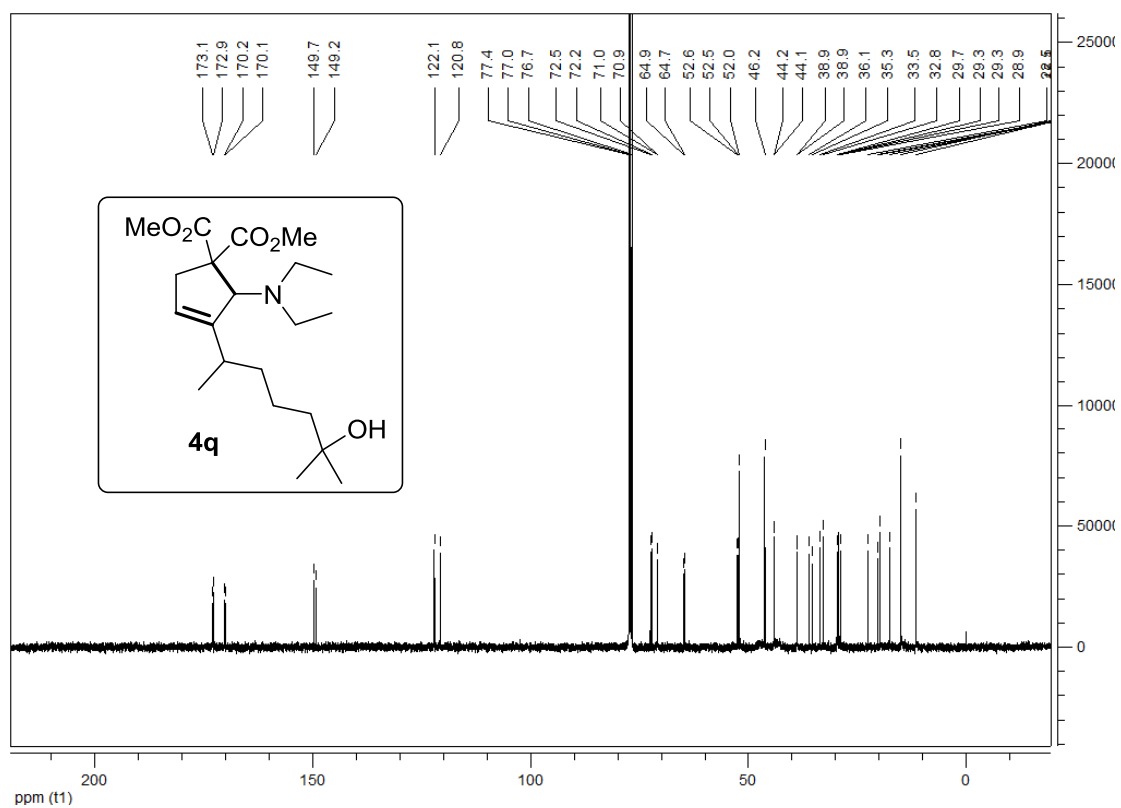
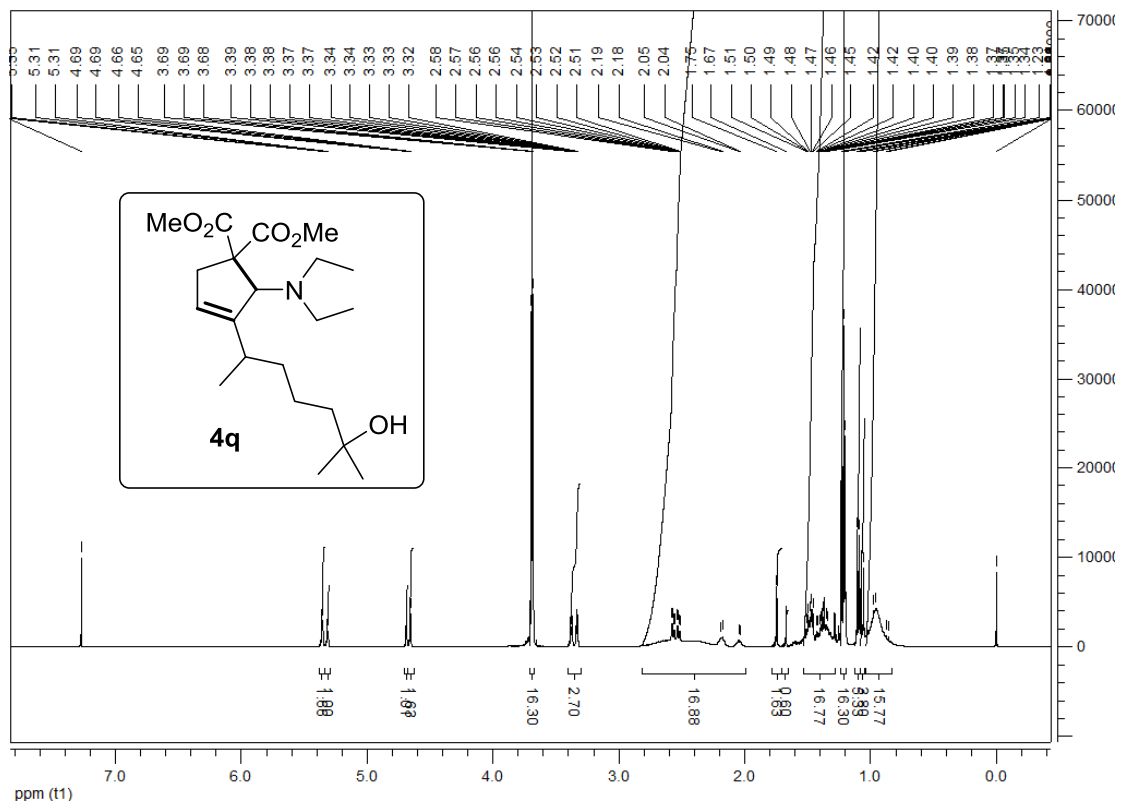




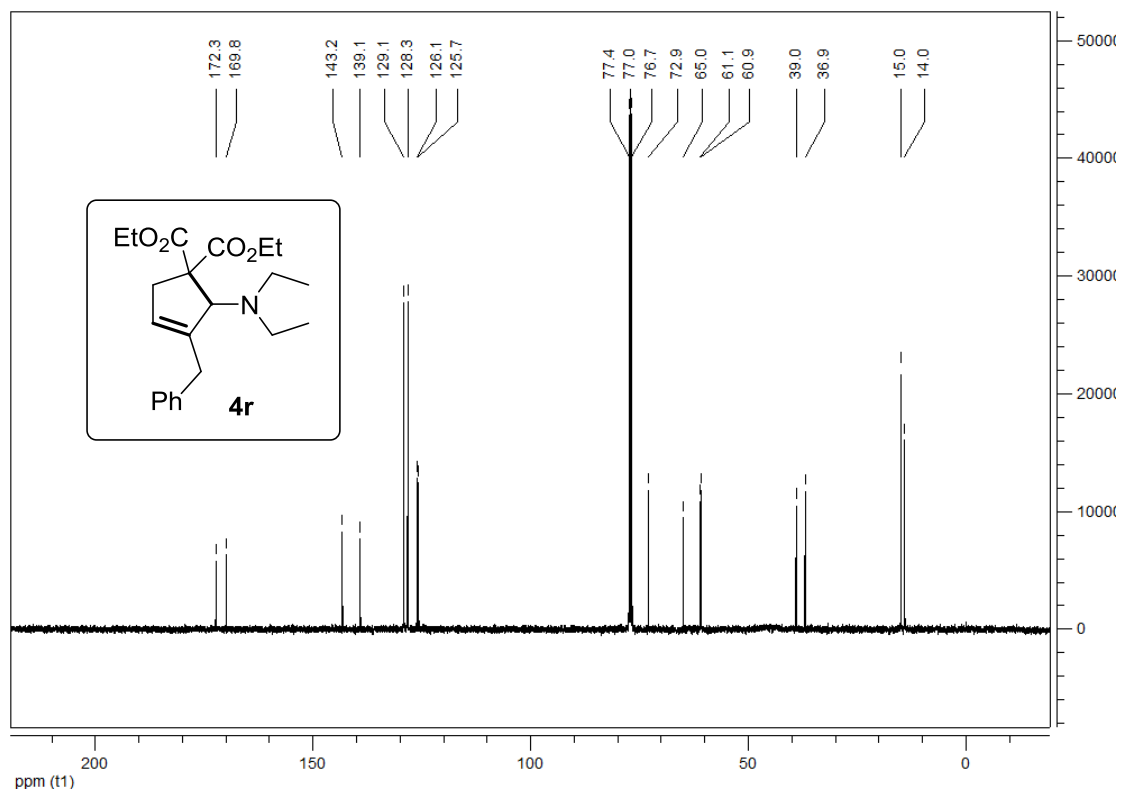
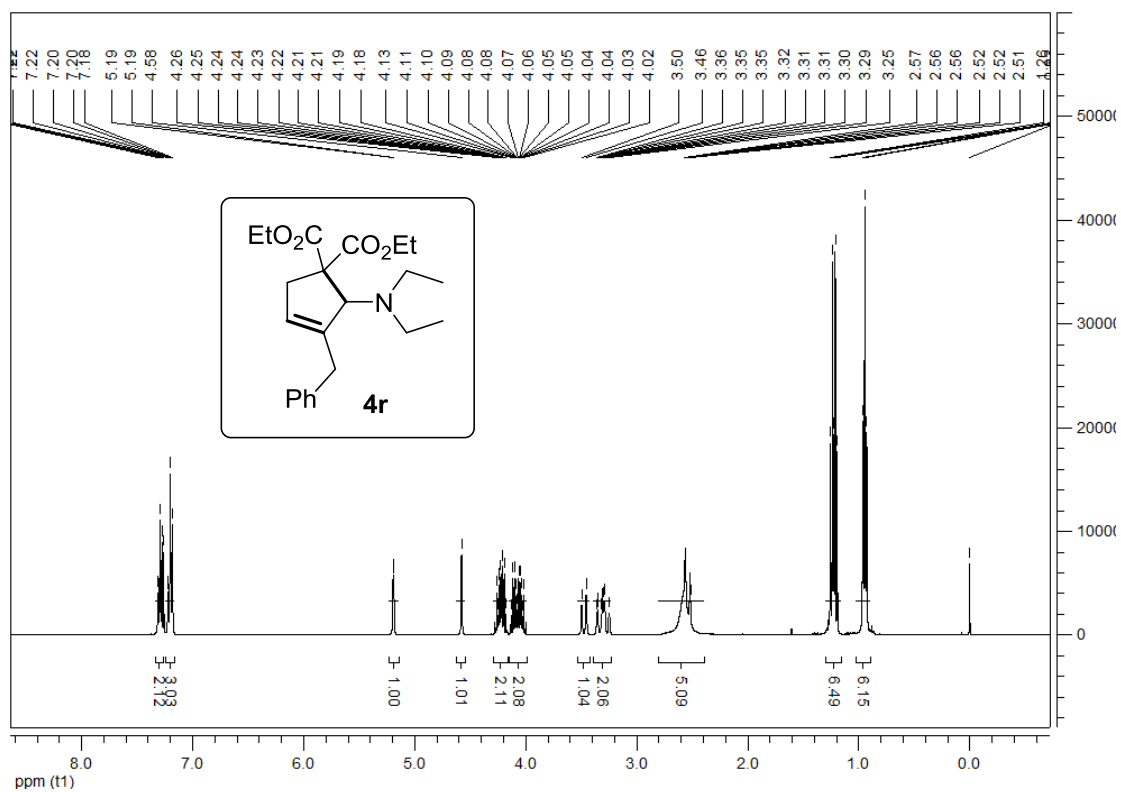




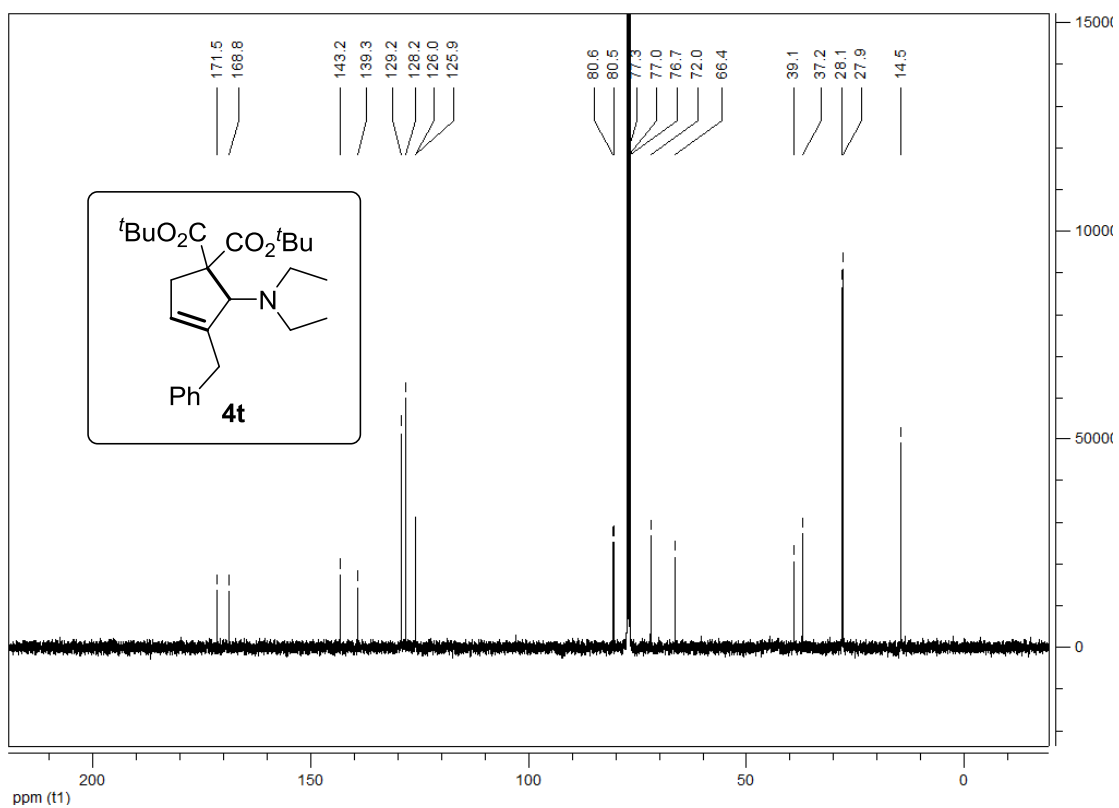
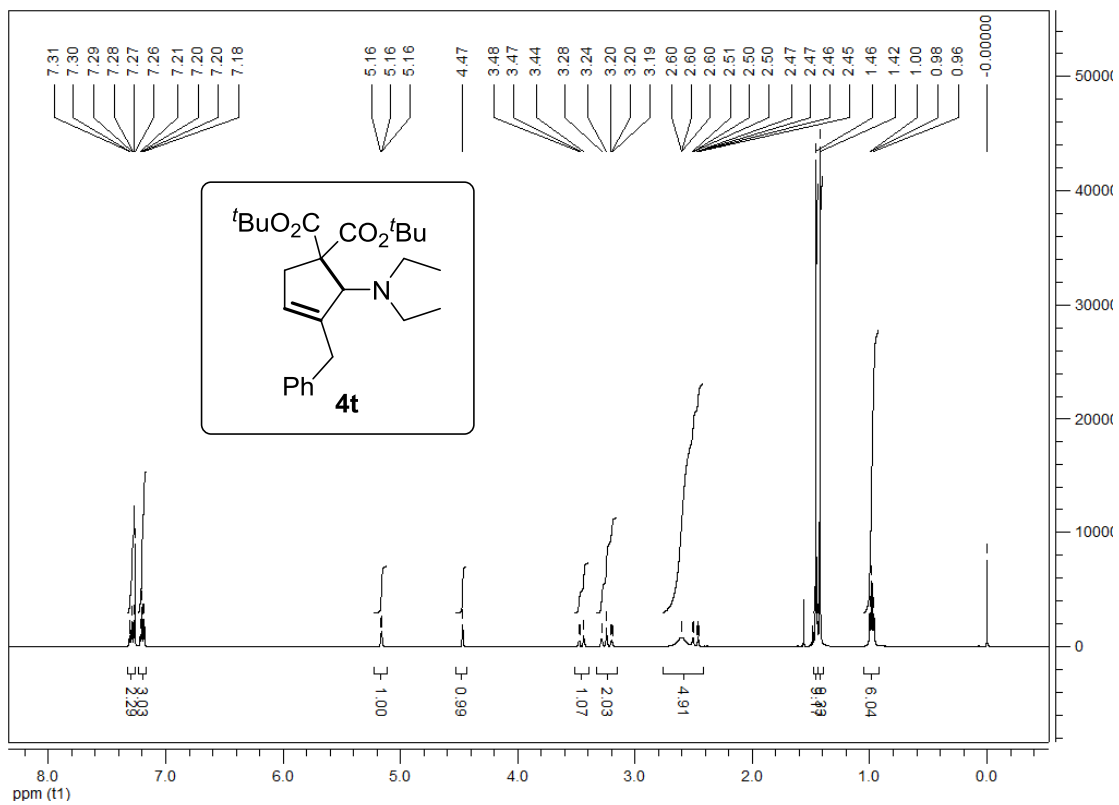


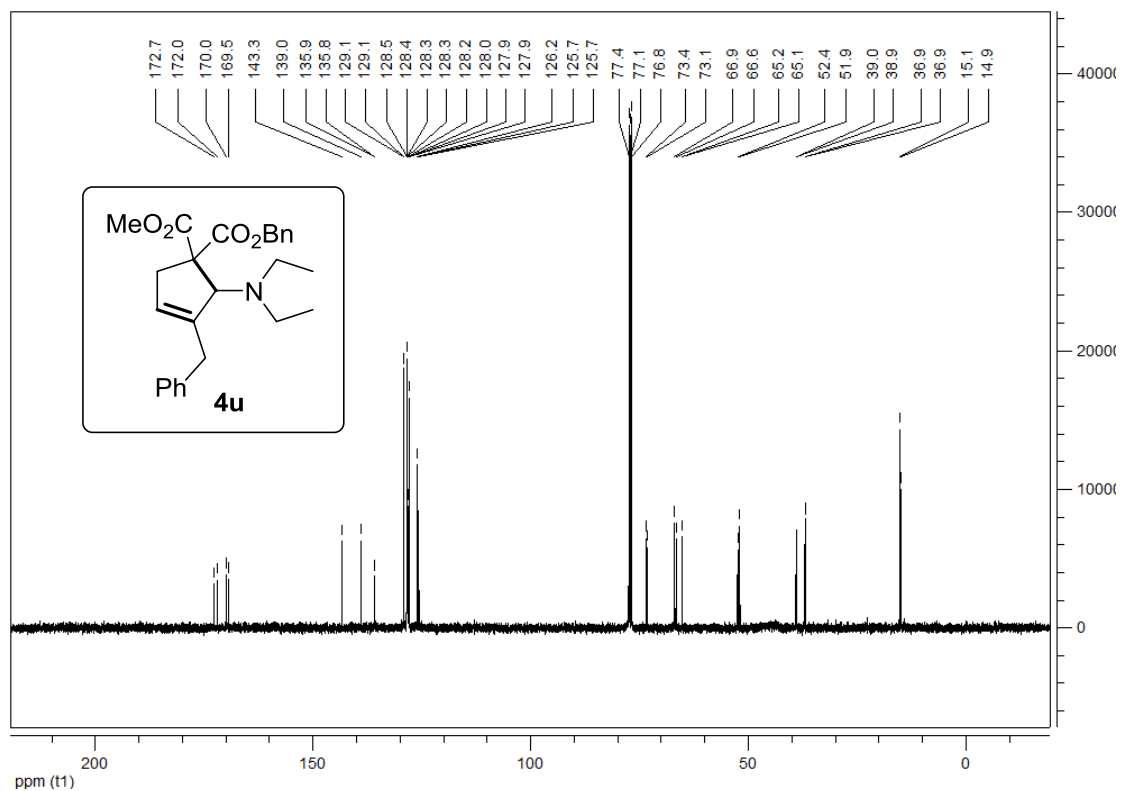
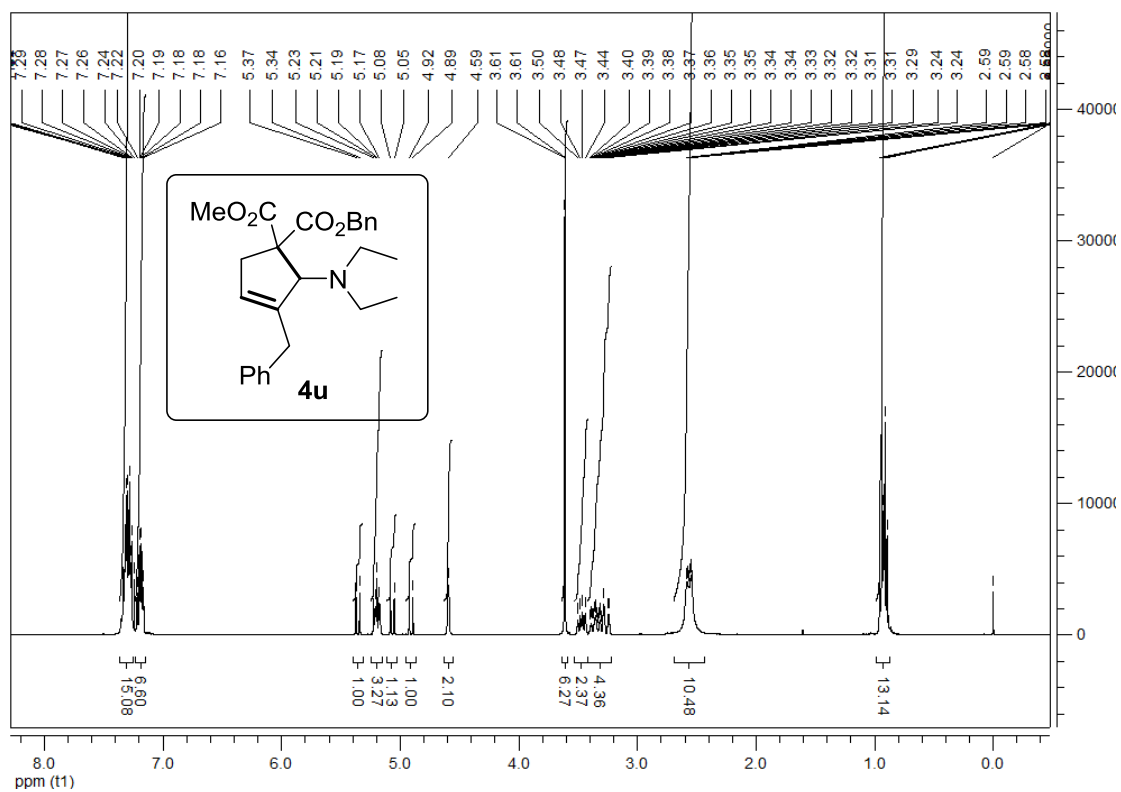


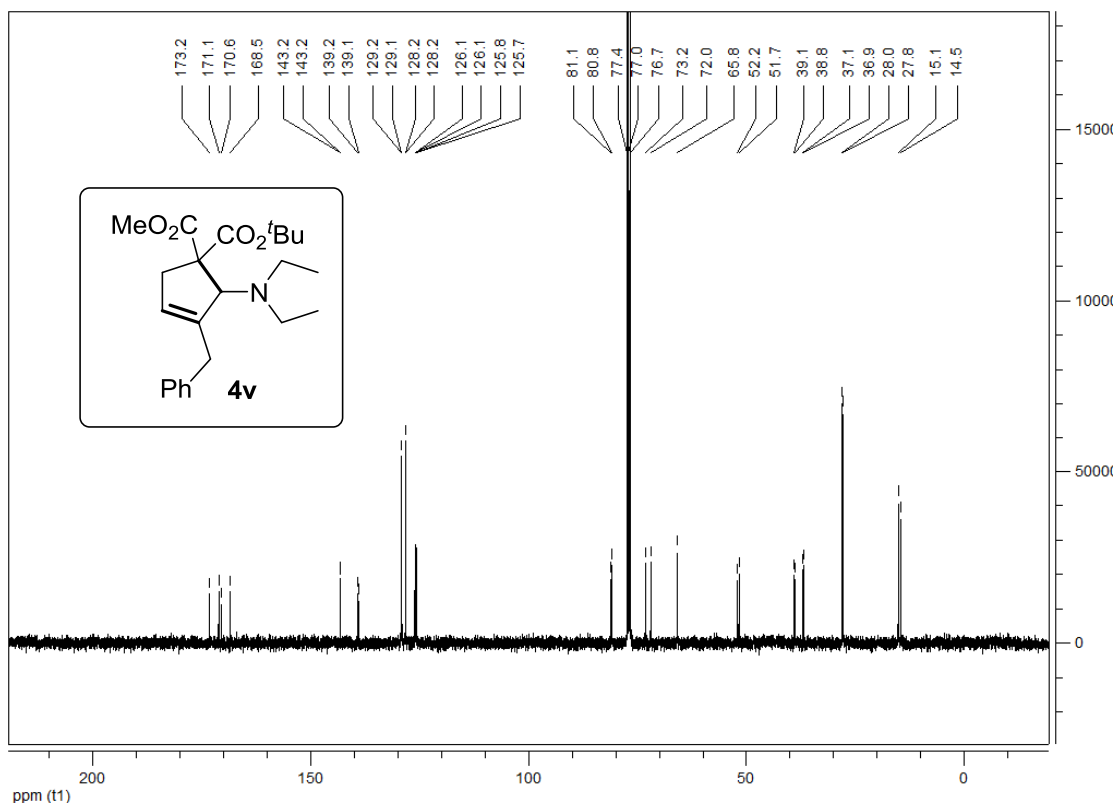
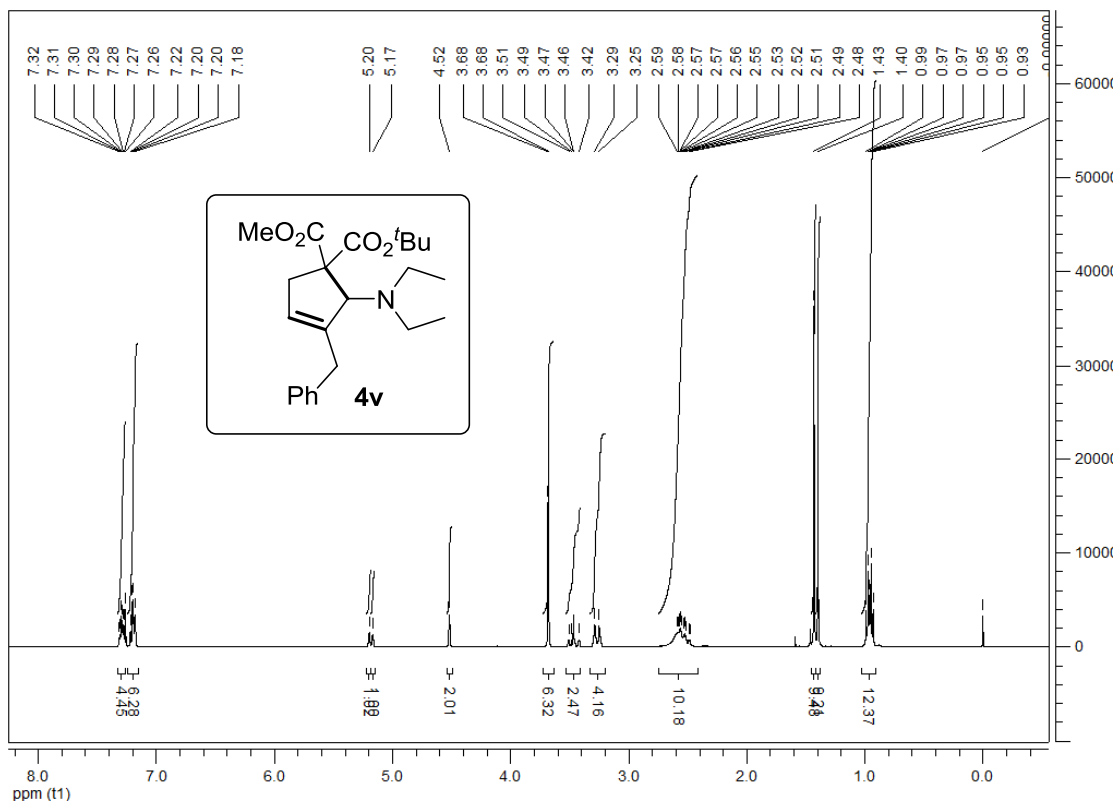


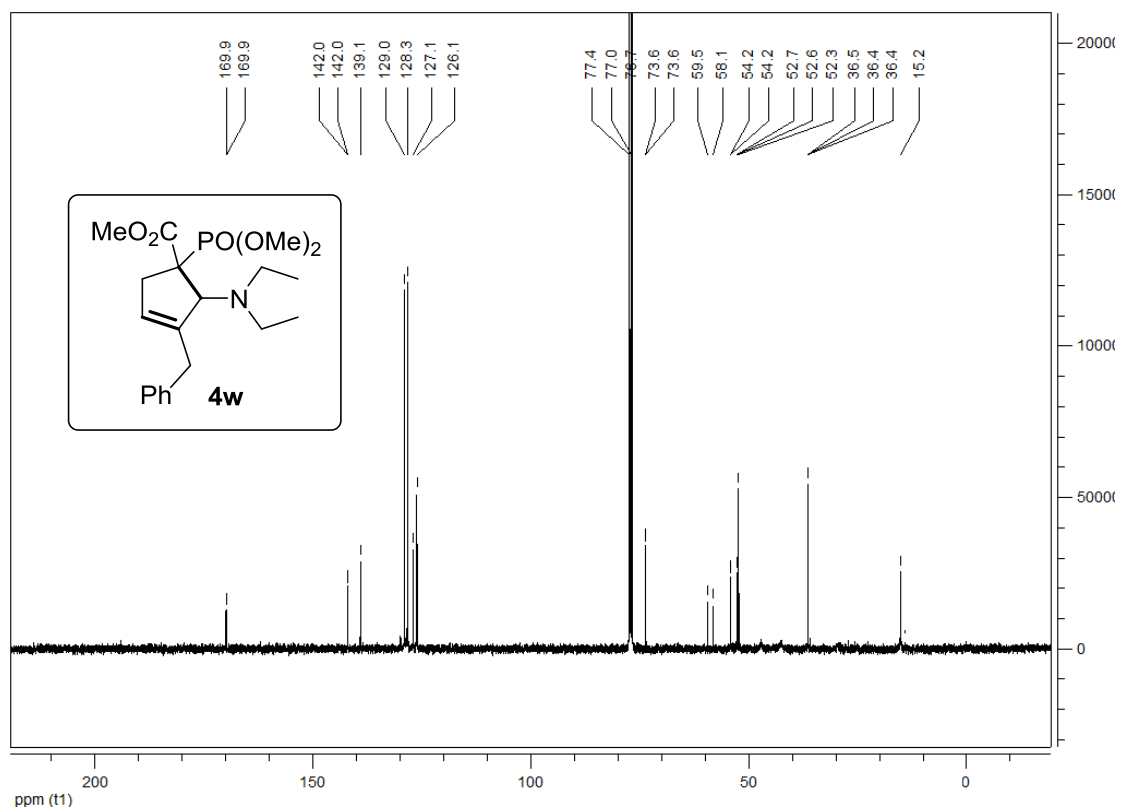
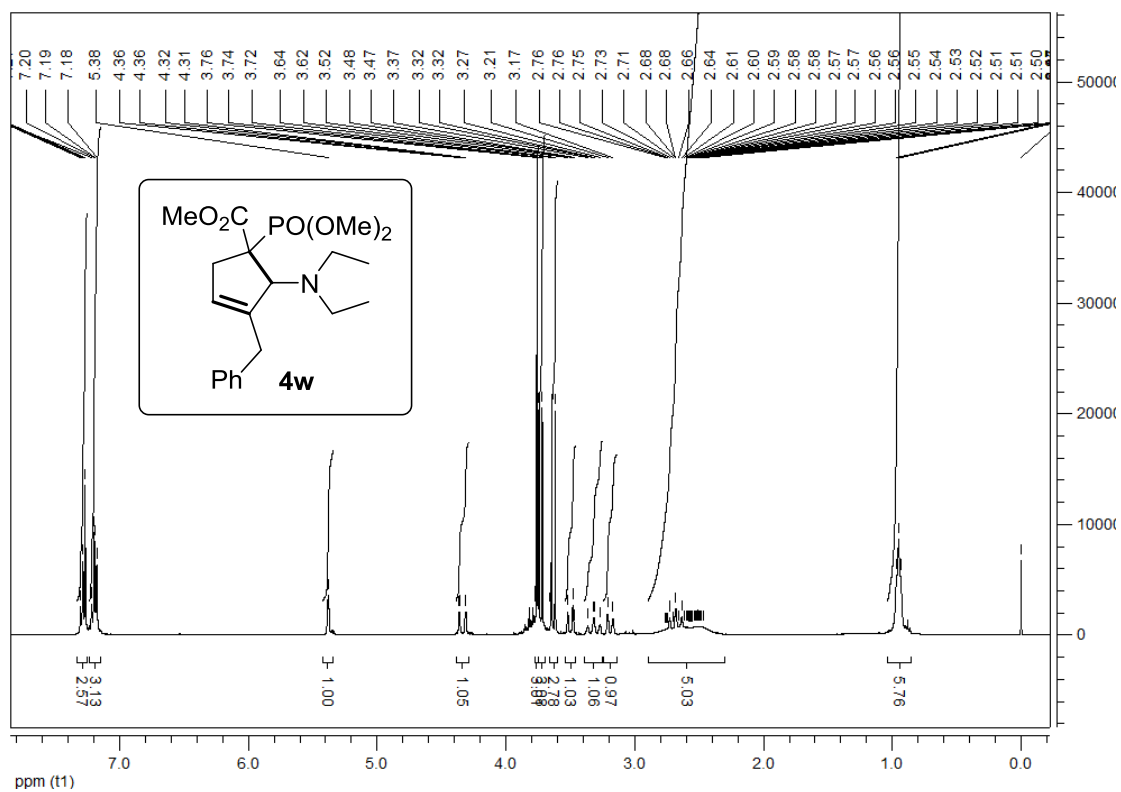












NOESY spectrum of **4w**

