

## Supporting Information

### Photo-induced decarboxylative hydroacylation of $\alpha$ -oxocarboxylic acids with terminal alkynes by radical addition-translocation-cyclization in water

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## 1. General Consideration

All reactions were carried out with magnetic stirring under a N<sub>2</sub> atmosphere. All <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (101 MHz) and <sup>19</sup>F NMR (376 MHz) spectra were recorded on a 400 MHz Quantum-I Plus 400 in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as a solvent and recorded in parts per million relative to the internal standard tetramethylsilane. The NMR spectra were referenced to tetramethylsilane (TMS, 0.0 ppm), CDCl<sub>3</sub> (7.26 ppm or 77.0 ppm for <sup>1</sup>H and <sup>13</sup>C respectively), (CD<sub>3</sub>)<sub>2</sub>SO (2.52 ppm or 44.73 ppm for <sup>1</sup>H and <sup>13</sup>C respectively). The <sup>1</sup>H NMR spectra are reported as follows:  $\delta$ , chemical shift; coupling constants (*J* are given in hertz, Hz); integration. Coupling constants are reported as follows: s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. High-resolution mass spectroscopy (HRMS) data of the products were collected on a Waters Xevo G2QTOF/UPLC mass spectrometer using electrospray ionization.

The chemicals and solvents were purchased from commercial suppliers without further purification unless otherwise specified. Analytical thin-layer chromatography (TLC) was performed on silicycle 250 mm silica gel F-254 plates. Products were purified by flash chromatography on 200-300 mesh silica gels, SiO<sub>2</sub>. All manipulations that require heating for starting materials were conducted with an oil bath. The photoreaction instrument (WPP-TEC-1020SL) was purchased from WATTCAS, China.

### SPECTROPHOTOCOLORMETER ANALYSIS REPORT

#### Color Parameters:

CIE (1931:) x =0.1776 y =0.0296

CIE (1960:) u =0.2367 v =0.0592

CIE (1976:) u' =0.2367 v' =0.0888

**Color Temperature:** Tc=25000K Dominant Wave: WL.D=435.20nm Purity: PUR=93.54

**Peak Wave:** WL.P=392.5nm Delta Wave: WL.H=18.0nm

**Color Tolerance:** SDCM=186.7 Ra:Ra=15.0

CRI1=56.1 CRI2=16.3 CRI3=0.0 CRI4=0.0 CRI5=47.6

CRI6=0.0 CRI7=0.0 CRI8=0.0 CRI9=0.0 CRI10=0.0

CRI11=0.0 CRI12=0.0 CRI13=42.0 CRI14=6.3 CRI15=66.7

**Photology Parameters:**

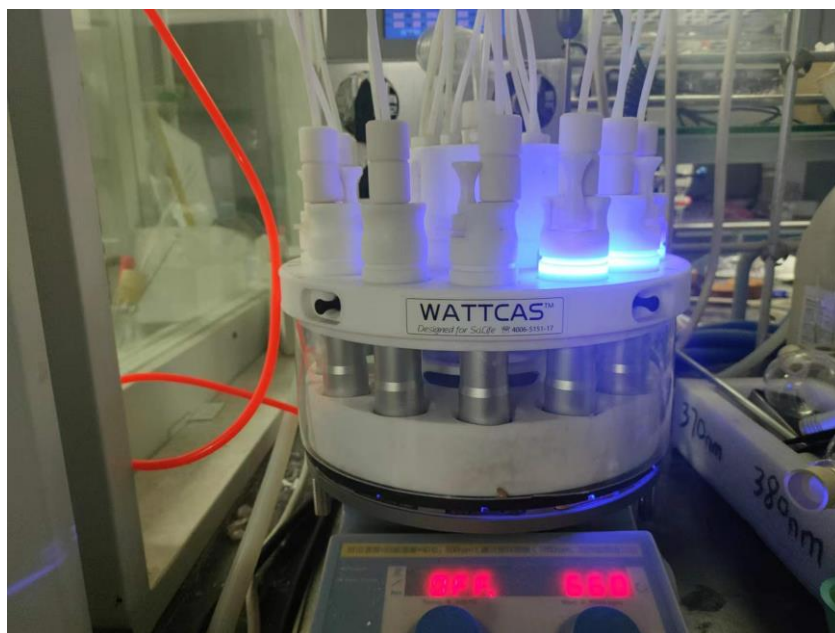
Lum Flux:  $\Phi(\text{lm})=4.75\text{lm}$  Optical Power:  $\Phi_e(\text{mW})=2769.6\text{mW}$   $\eta(\text{lm/W})=0.4\text{lm/W}$

**Electric Parameters:**

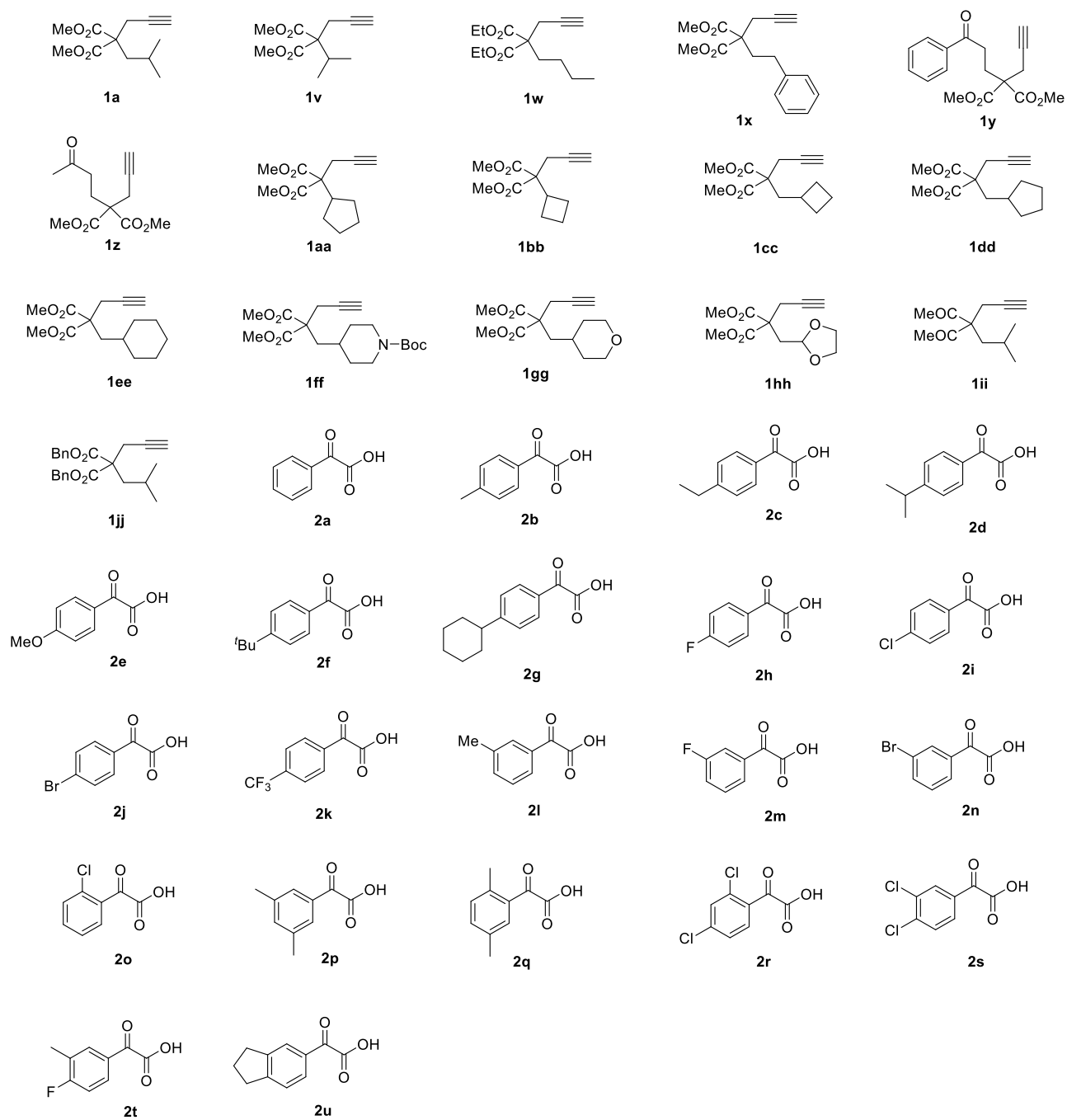
Forward Voltage:  $V_F = 22.68 \text{ V}$  Forward Current:  $I_F = 498.9 \text{ mA}$  Power = 11.32 W

**Status:**

Wavelength Range: 380nm--780nm Intergration Time : 1000 ms



**Figure S1.** Photoreactor for photoreaction



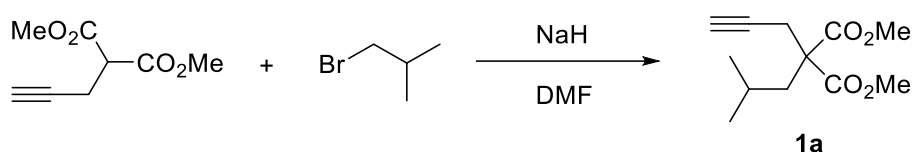
**Figure S2.** Structure of substrates **1** and **2**.

## 2. General Procedure and Characterization Data for Starting Materials

Phenylglyoxylic acid **2a** was purchased from commercial suppliers without further purification.

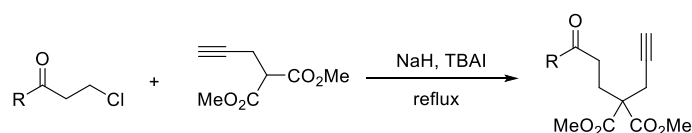
**2b-2u** <sup>[1-2]</sup> were known compounds and prepared according to literature procedures.

Alkynes **1a**, **1v-x**, and **1aa-jj** were prepared according to the literature methods. <sup>[3-5]</sup> A representative procedure for the preparation of **1a** is described as follows:



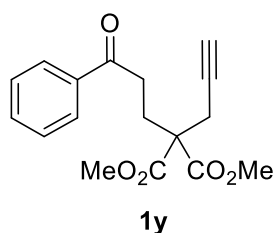
To a stirred suspension of NaH (~60 % in paraffin, 6.0 mmol, 1.2 equiv) in anhydrous DMF (20 mL) was added dropwise dimethyl propargylmalonate (5.0 mmol, 1 equiv) at 0 °C. The reaction mixture was warmed up to room temperature over 1 h. Isobutylbromide (7.0 mmol, 1.4 equiv) was added at room temperature. The reaction mixture was heated at 78 °C overnight. After cooling down to room temperature, the reaction mixture was treated with saturated NH<sub>4</sub>Cl (30 mL), extracted with EtOAc (3 x 30 mL) washed with brine and dried over MgSO<sub>4</sub>. Column chromatography on silica gel (petroleum ethers / EtOAc 100:0 to 15:1) gave **1a** (0.88 g, 3.9 mmol, 78 %) as a colorless oil; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 3.73 (s, 6H), 2.87 (d, *J* = 2.7 Hz, 2H), 2.05 (d, *J* = 6.3 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H), 1.70 – 1.60 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 6H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 171.1, 78.9, 71.4, 56.2, 52.7, 40.2, 24.0, 23.5, 23.0; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>19</sub>O<sub>4</sub>, 227.1278, Found: 227.1281.

### Procedure for the synthesis of substrates **1y** and **1z** <sup>[6]</sup>

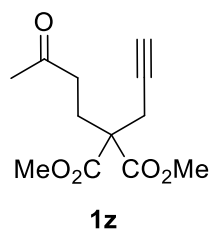


To a stirred suspension of NaH (~60 % in paraffin, 6.5 mmol, 1.3 equiv) in anhydrous THF (25 mL) was added dropwise dimethyl propargylmalonate (5.0 mmol, 1 equiv) at 0 °C. The reaction mixture was warmed up to room temperature over 30 min. The 3-chloropropiophenone or derivatives (10

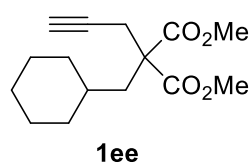
mmol, 2.0 eq) was added at room temperature. Tetrabutylammonium iodide (0.5 mmol, 0.1 eq.) was added in one portion. Then the reaction mixture was reflux overnight. After cooling down to room temperature, the reaction mixture was treated with saturated  $\text{NH}_4\text{Cl}$  (30 mL), extracted with EtOAc (3 x 30 mL) washed with brine and dried over  $\text{MgSO}_4$ . The crude mixture was purified by flash chromatography on silica gel affording the expected compound in a pure form.



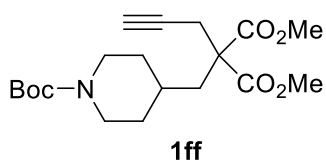
**Compound 1y:** 1.13 g, 75 % yield; white solid; Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 7.4$  Hz, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.75 (s, 6H), 3.08 – 3.04 (m, 2H), 2.91 (d,  $J = 2.5$  Hz, 2H), 2.54 – 2.50 (m, 2H), 2.06 (t,  $J = 2.5$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.5, 170.4, 136.5, 133.1, 128.5, 128.0, 78.4, 71.9, 56.1, 52.9, 33.6, 27.0, 23.9; **HRMS (ESI) m/z:**  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{19}\text{O}_5$ , 303.1227, Found: 303.1228.



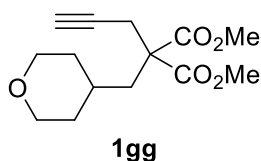
**Compound 1z:** 0.74 g, 62 % yield; brownish yellow oil; Flash column chromatography conditions: petroleum ethers / EtOAc = 9:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.74 (s, 6H), 2.82 (d,  $J = 2.6$  Hz, 2H), 2.53 – 2.47 (m, 2H), 2.36 – 2.29 (m, 2H), 2.15 (s, 3H), 2.04 (t,  $J = 2.9$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.1, 170.4, 78.4, 71.8, 56.0, 52.9, 38.5, 29.9, 26.4, 23.8. **HRMS (ESI) m/z:**  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{12}\text{H}_{17}\text{O}_5$ , 241.1071, Found: 241.1073.



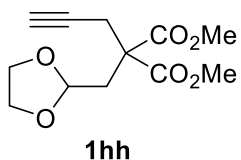
**Compound 1ee:** 1.01 g, 76 % yield; colorless oil; Flash column chromatography conditions: petroleum ethers / EtOAc = 15:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.73 (s, 6H), 2.86 (s, 2H), 2.05 – 2.01 (m, 3H), 1.67 – 1.58 (m, 5H), 1.26 – 1.10 (m, 4H), 1.01 – 0.92 (m, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 79.0, 71.3, 56.0, 52.6, 38.9, 34.0, 33.2, 26.2, 26.0, 23.1; **HRMS (ESI) m/z:**  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{23}\text{O}_4$ , 267.1591, Found: 267.1587.



**Compound 1ff:** 0.90 g, 49 % yield; white solid; Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.03 (s, 2H), 3.74 (s, 6H), 2.88 (s, 2H), 2.67 (s, 2H), 2.07 (d,  $J = 5.8$  Hz, 2H), 2.03 (s, 1H), 1.55 (d,  $J = 13.2$  Hz, 2H), 1.45 (s, 10H), 1.20 – 1.10 (m, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 154.7, 79.3, 78.6, 71.7, 55.8, 52.8, 38.1, 32.7, 31.7, 28.4, 23.2; **HRMS (ESI) m/z:**  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{30}\text{NO}_6$ , 368.2068, Found: 368.2069.



**Compound 1gg:** 0.91 g, 68 % yield; colorless oil; Flash column chromatography conditions: petroleum ethers / EtOAc = 9:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.90 (dd,  $J = 11.6, 2.3$  Hz, 2H), 3.74 (s, 6H), 3.35 (td,  $J = 11.7, 1.6$  Hz, 2H), 2.88 (d,  $J = 2.6$  Hz, 2H), 2.08 (d,  $J = 6.0$  Hz, 2H), 2.04 (t,  $J = 2.7$  Hz, 1H), 1.60 – 1.48 (m, 3H), 1.39 – 1.29 (m, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 78.6, 71.7, 67.7, 55.7, 52.8, 38.5, 33.5, 30.8, 23.2; **HRMS (ESI) m/z:**  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{21}\text{O}_5$ , 269.1384, Found: 269.1383.

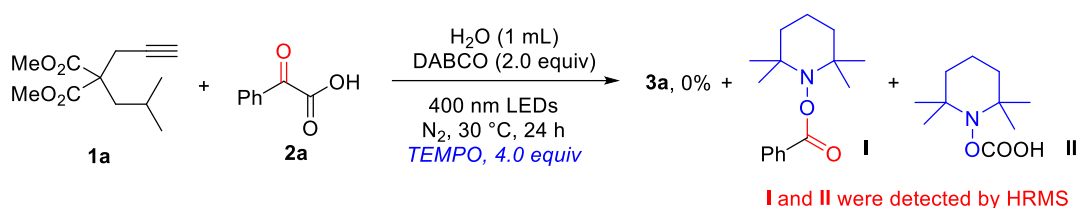


**Compound 1hh:** 0.67 g, 52 % yield; colorless oil; Flash column chromatography conditions: petroleum ethers / EtOAc = 5:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.00 (t,  $J = 4.7$  Hz, 1H), 3.94 – 3.91 (m, 2H), 3.84 – 3.80 (m, 2H), 3.74 (s, 6H), 2.98 (d,  $J = 2.6$  Hz, 2H), 2.50 (d,  $J = 4.7$  Hz, 2H), 2.05 –

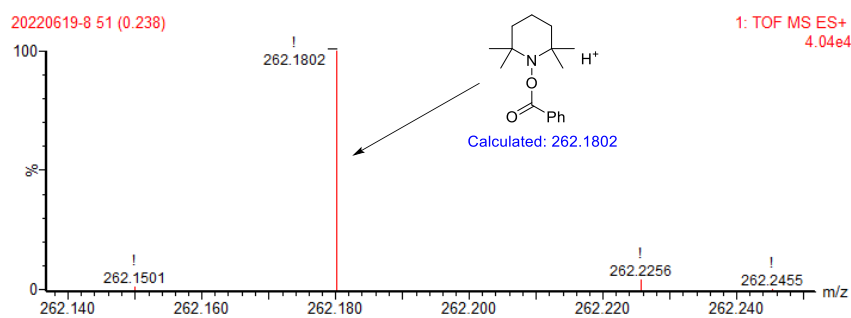
2.04 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 101.5, 78.9, 71.6, 64.8, 54.4, 52.9, 35.4, 23.5;  
 HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{12}\text{H}_{17}\text{O}_6$ , 257.1020, Found: 257.1025.

### 3. Mechanism Investigation

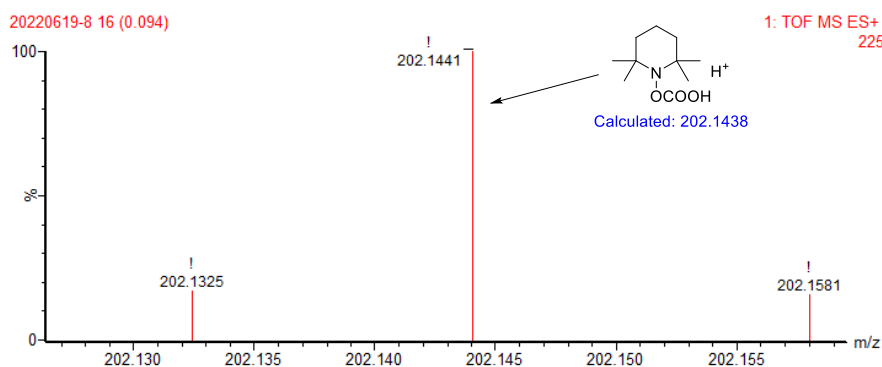
#### 3.1 Radical trapping experiments



A radical scavenger (2,2,6,6-tetramethylpiperidinoxy, TEMPO, 4.0 equiv) was added to the reaction solution of **1a** with **2a** under the standard reaction conditions. After 24 h, it is found the formation of product **3a** was completely suppressed, and the crude reaction mixture was detected by HRMS (ESI), TEMPO adducts **I** and **II** were detected by ESI-MS (Electrospray ionization mass spectrometry), as shown in Figure S3-4.



**Figure S3.** HRMS analysis of the TEMPO adduct **I** from benzoyl radical

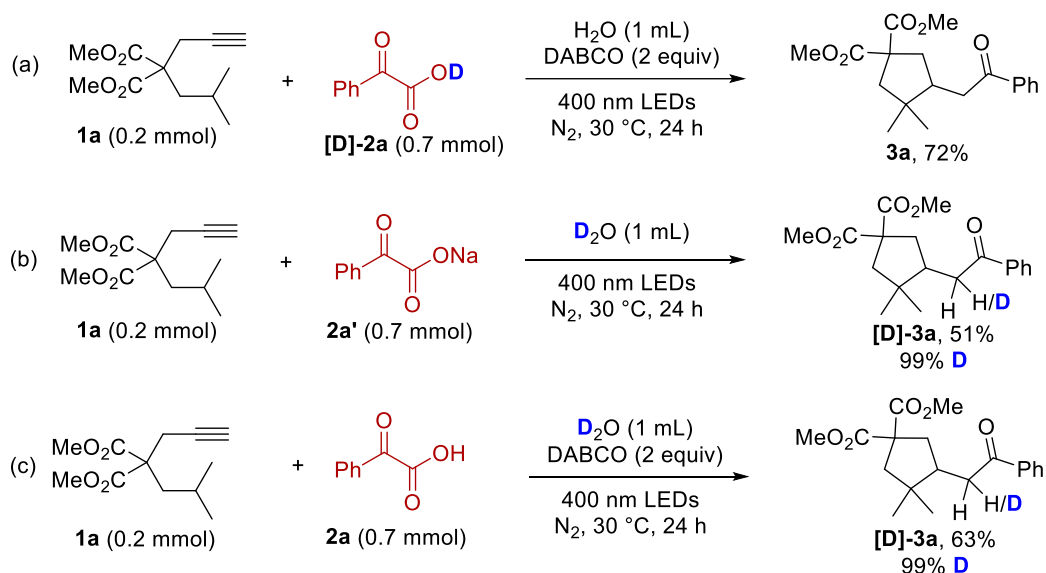


**Figure S4.** HRMS analysis of the TEMPO adduct **II** from carboxyl radical

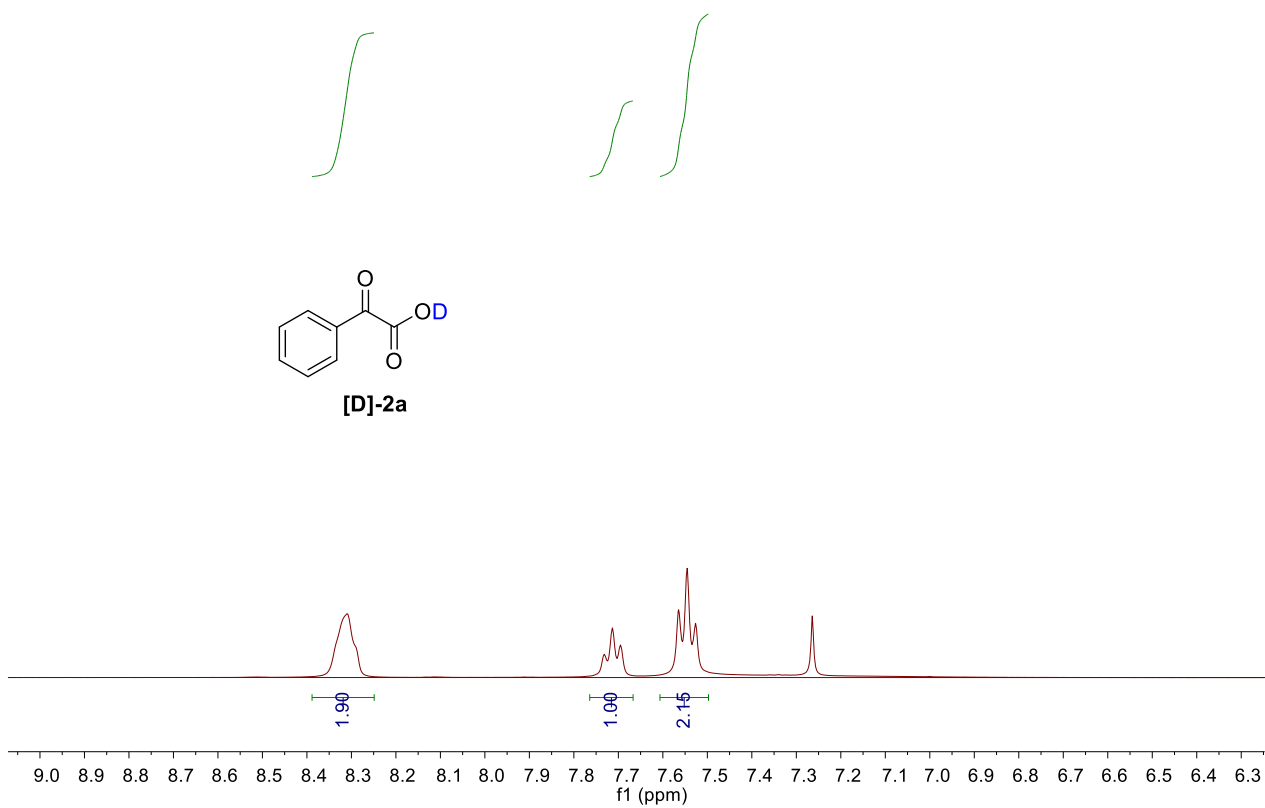
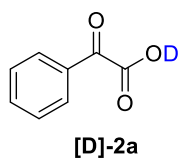
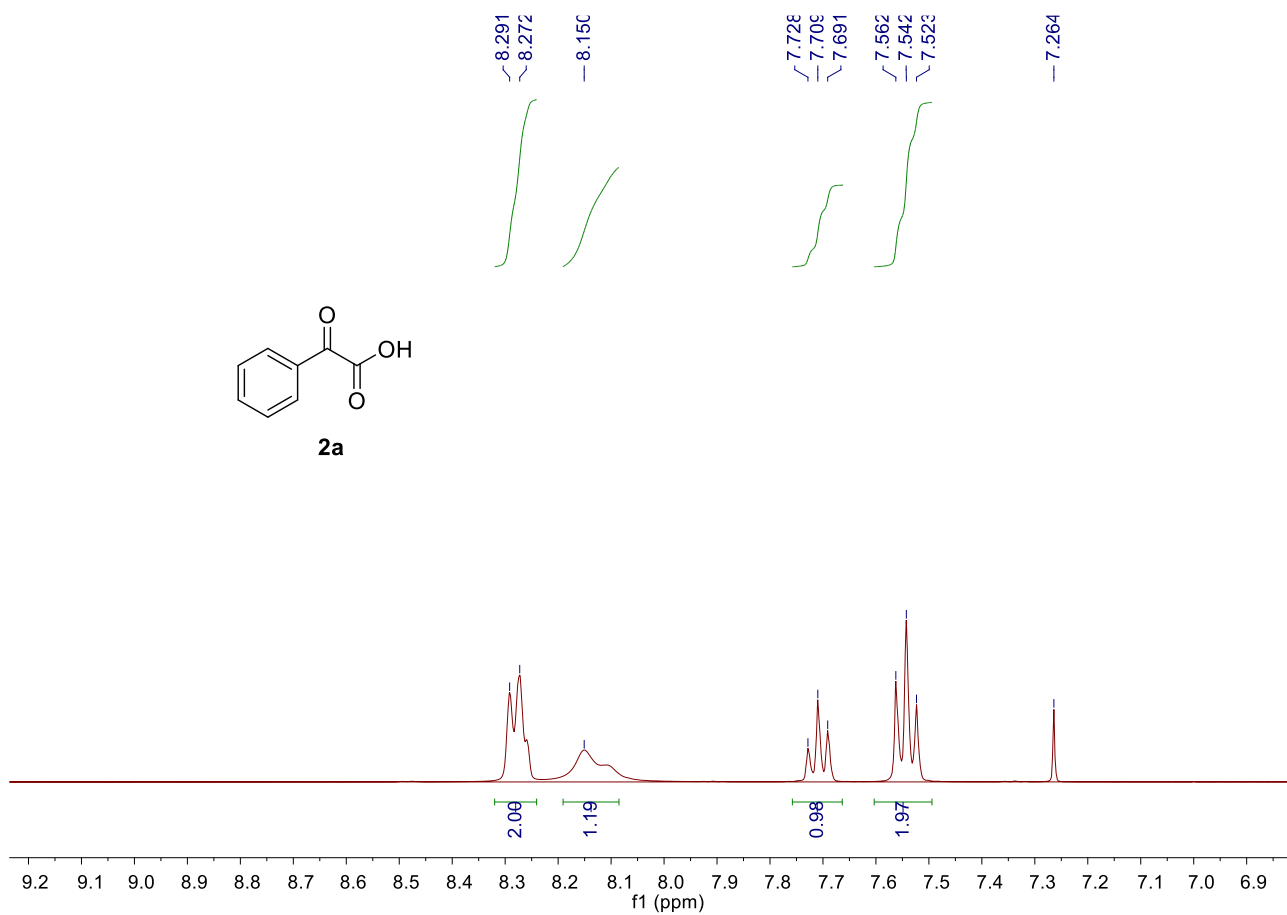
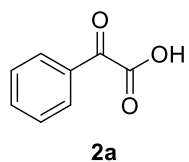


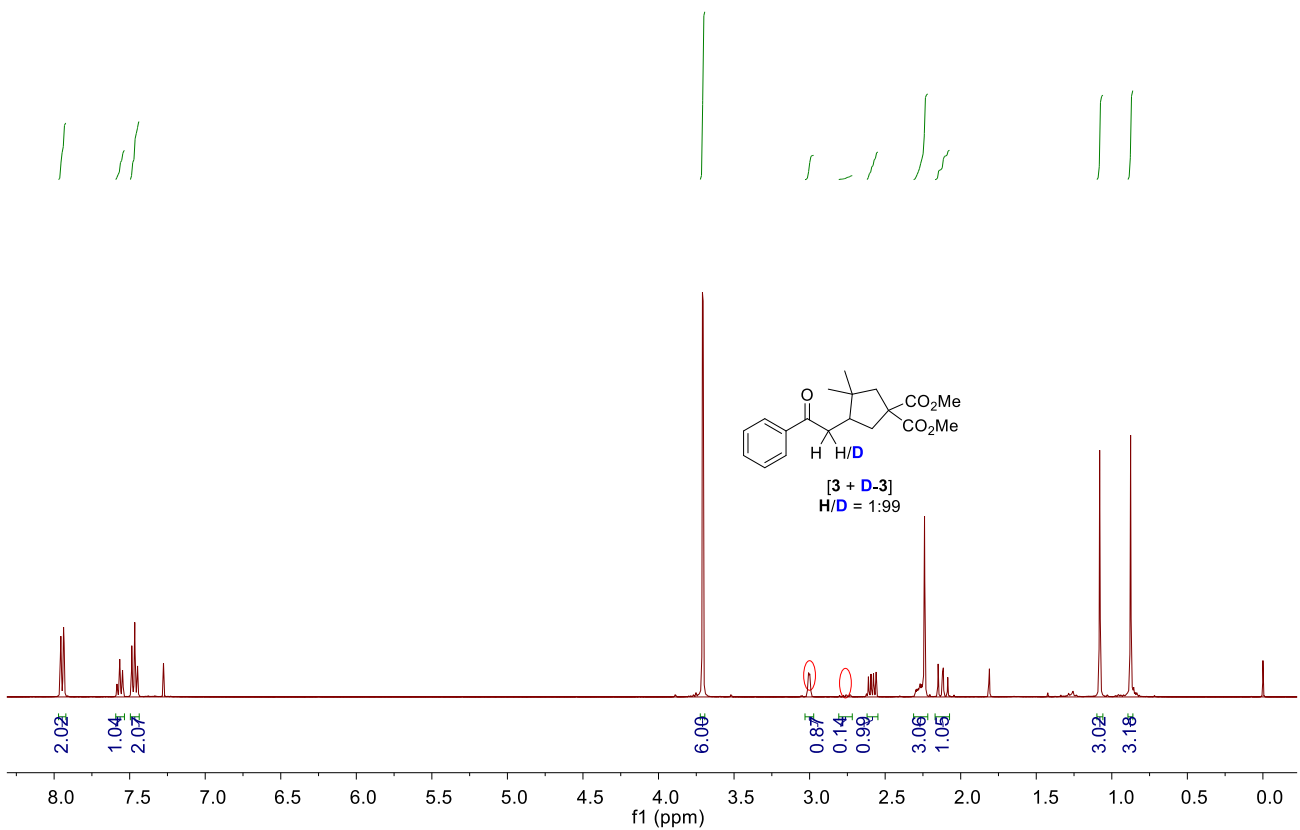
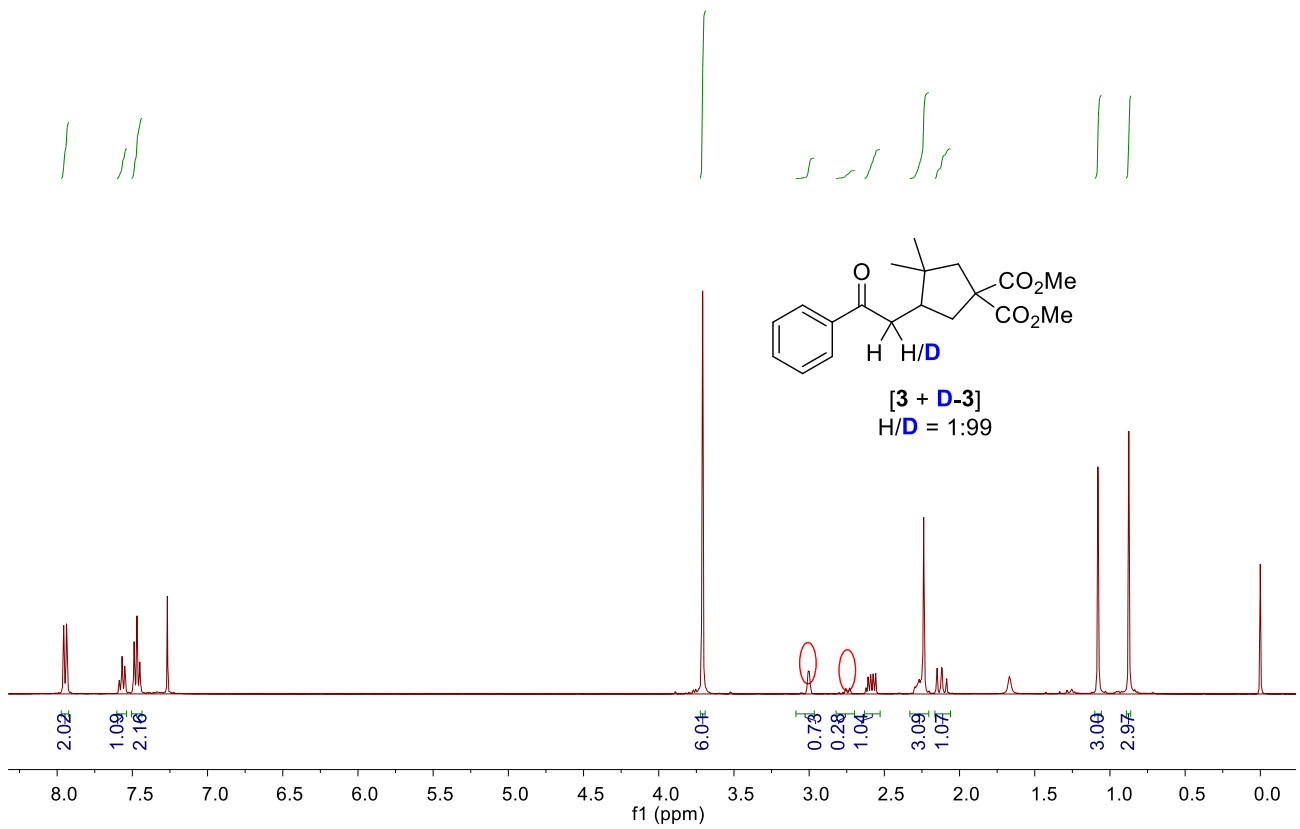
## 3.2 Isotope experiments

Several deuterium experiments were conducted to insight into the hydrogenation process of  $\alpha$ -position of the carbonyl group (Figure S5). First, the reaction of **1a** and [D]-**2a** were carried out in H<sub>2</sub>O under the optimized condition, **3a** was obtained with 72 % yield (Figure S5a). Then, when **2a'** reacted with **1a**, the product **3a** was obtained with 51 % yield, and the ratio of deuterium to hydrogen is 99 to 1 (Figure S5b). Finally, **1a** and **2a** were carried out in D<sub>2</sub>O under optimized condition, **3a** and [D]-**3a** was obtained with 63 % yield (Figure S5c). These results indicated H<sub>2</sub>O is the source of hydrogen for hydrogenation of  $\alpha$ -position of carbonyl group.



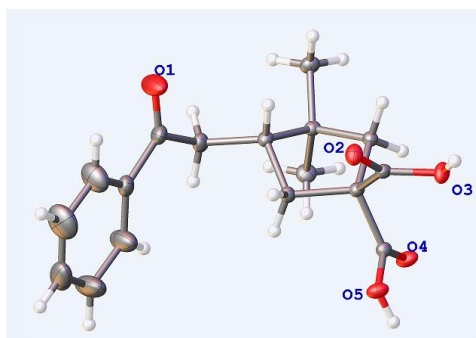
**Figure S5.** The deuterium experiments





### 3.3 X-Ray structure of 3a' and 3bb'

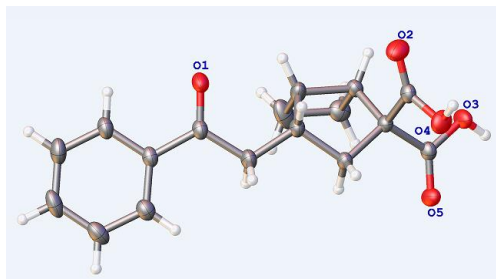
**Method for crystal growth:** Dicarboxylic acid (20 mg) was added into a clean tube, and dissolved by a mixed solvent (petroleum ether/ ethyl acetate /acetone = 15:4:1), then the mixture was evaporate slowly at room temperature under the air condition until the single crystal was obtained as a white crystal.



**Table 1 Crystal data and structure refinement for SW-5\_auto.**

Identification code	SW-5_auto
Empirical formula	C <sub>17</sub> H <sub>20</sub> O <sub>5</sub>
Formula weight	304.33
Temperature/K	299.98(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	16.6353(3)
b/Å	8.40370(10)
c/Å	11.3205(2)
α/°	90
β/°	100.263(2)
γ/°	90
Volume/Å <sup>3</sup>	1557.26(4)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.298
μ/mm <sup>-1</sup>	0.786
F(000)	648.0
Crystal size/mm <sup>3</sup>	0.14 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	11.838 to 152.644
Index ranges	-19 ≤ h ≤ 20, -10 ≤ k ≤ 10, -13 ≤ l ≤ 14
Reflections collected	9308
Independent reflections	2973 [R <sub>int</sub> = 0.0211, R <sub>sigma</sub> = 0.0191]

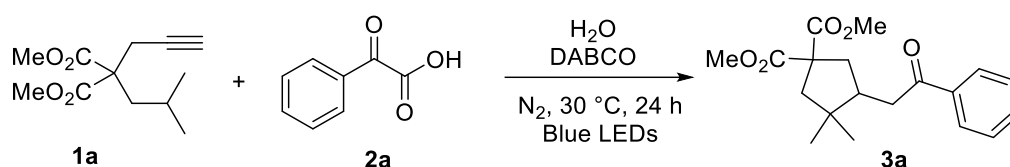
Data/restraints/parameters 2973/0/204  
 Goodness-of-fit on  $F^2$  1.039  
 Final R indexes [ $I \geq 2\sigma(I)$ ]  $R_1 = 0.0436$ ,  $wR_2 = 0.1151$   
 Final R indexes [all data]  $R_1 = 0.0482$ ,  $wR_2 = 0.1187$   
 Largest diff. peak/hole /  $e \text{ \AA}^{-3}$  0.25/-0.22



**Table 2 Crystal data and structure refinement for SW-6\_auto.**

Identification code	SW-6_auto
Empirical formula	$C_{17}H_{18}O_5$
Formula weight	302.31
Temperature/K	301.2(4)
Crystal system	monoclinic
Space group	$C2/c$
$a/\text{\AA}$	24.3135(11)
$b/\text{\AA}$	6.0438(3)
$c/\text{\AA}$	22.6595(12)
$\alpha/^\circ$	90
$\beta/^\circ$	114.521(6)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	3029.4(3)
Z	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.326
$\mu/\text{mm}^{-1}$	0.808
F(000)	1280.0
Crystal size/ $\text{mm}^3$	$0.14 \times 0.12 \times 0.11$
Radiation	$\text{Cu K}\alpha$ ( $\lambda = 1.54184$ )
$2\Theta$ range for data collection/ $^\circ$	7.994 to 153.332
Index ranges	$-29 \leq h \leq 30$ , $-7 \leq k \leq 2$ , $-27 \leq l \leq 27$
Reflections collected	9742
Independent reflections	2961 [ $R_{\text{int}} = 0.0663$ , $R_{\text{sigma}} = 0.0668$ ]
Data/restraints/parameters	2961/0/202
Goodness-of-fit on $F^2$	1.036
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0498$ , $wR_2 = 0.1208$
Final R indexes [all data]	$R_1 = 0.0804$ , $wR_2 = 0.1392$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.18/-0.17

## 4. General Procedure for the Photocatalytic Hydroacylation of Alkynes

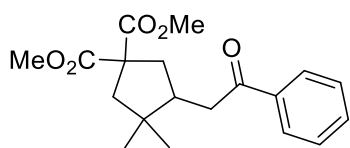


A typical experimental procedure for the synthesis of **3a** in 0.2 mmol scale: Alkyne (**1a**, 0.2 mmol), phenylglyoxylic acid (**2a**, 0.7 mmol) and DABCO (0.4 mmol) were added into an oven dried 20 mL reaction vial with 1.0 mL of  $\text{H}_2\text{O}$ . The tube containing the reactants and solvent was evacuated using a pump and back-filled with high-purified nitrogen (>99.99 %). The reaction mixture was stirred and irradiated using a 10 W 400 nm LED lamp (W A TTCAS: WP-TEC-1020SL) for 24 hours until the reaction was complete (monitored by TLC). After the reaction, the reaction mixture was extracted with EtOAc, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The crude product was purified by column chromatography on basic silica gel to afford the pure products (petroleum ethers / ethyl acetate). The analytical data of the products are summarized below.

### Large-scale:

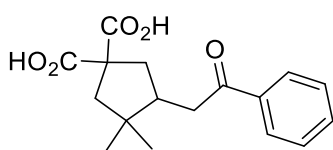
A typical experimental procedure for the synthesis of **3a** in 5.0 mmol scale: Alkyne (**1a**, 5.0 mmol), phenylglyoxylic acid (**2a**, 17.5 mmol) and DABCO (10.0 mmol) were added into an oven dried 50 mL quartz tube with 8 mL of  $\text{H}_2\text{O}$ . The tube containing the reactants and solvent was evacuated using a pump and back-filled with high-purified nitrogen (>99.99 %). The reaction mixture was stirred and irradiated using a 10 W 400 nm LED lamp (W A TTCAS: WP-TEC-1020SL) for 48 hours. After the reaction, the reaction mixture was extracted with EtOAc, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The crude product was purified by column chromatography on basic silica gel to afford the pure product **3a** in 63% yield (1.05g).

### dimethyl 3,3-dimethyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylate (**3a**)



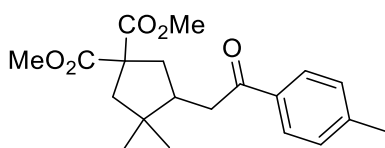
Colorless oil (54.5 mg, 82 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.71 (s, 6H), 3.03 (dd, *J* = 16.1, 3.5 Hz, 1H), 2.77 (dd, *J* = 16.1, 10.1 Hz, 1H), 2.60 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.30 – 2.24 (m, 3H), 2.15 – 2.09 (m, 1H), 1.08 (s, 3H), 0.88 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.5, 173.2, 136.9, 133.0, 128.6, 128.0, 57.5, 52.8, 52.7, 48.4, 44.6, 41.3, 39.1, 38.4, 27.5, 22.4; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>25</sub>O<sub>5</sub>, 333.1697, Found: 333.1071.

### 3,3-dimethyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylic acid (**3a'**)



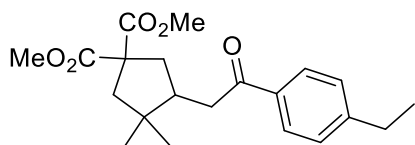
Lithium hydroxide (24.0 mg, 1.0 mmol) was added to a solution of dimethyl 3,3-dimethyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylate (**3a**, 66.5 mg, 0.2 mmol) in MeOH and H<sub>2</sub>O (3/1, 1.2 mL and 0.4 mL), and the mixture was stirred at 80 °C for 2 h. After the reaction completed, the reaction mixture was diluted with H<sub>2</sub>O and washed with diethyl ether. The resulting aqueous layer was acidified with 1.2 N HCl until the solution become pH 6, and then extracted with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification by column chromatography on silica gel (EtOAc / petroleum ethers 3:1) provided the desired product (57.8 mg, 95 %) as a white solid; **<sup>1</sup>H NMR** (400 MHz, DMSO) δ 12.62 (s, 2H), 7.98 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 3.08 (dd, *J* = 16.4, 3.2 Hz, 1H), 2.81 (dd, *J* = 16.5, 9.9 Hz, 1H), 2.34 (dd, *J* = 12.9, 6.5 Hz, 1H), 2.12 – 1.90 (m, 4H), 1.01 (s, 3H), 0.82 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, DMSO) δ 200.4, 174.7, 174.3, 137.3, 133.6, 129.2, 128.5, 57.5, 48.6, 45.0, 41.4, 39.2, 38.6, 28.0, 22.8; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>21</sub>O<sub>5</sub>, 305.1384, Found: 305.1388.

### dimethyl 3,3-dimethyl-4-(2-oxo-2-(p-tolyl)ethyl)cyclopentane-1,1-dicarboxylate (**3b**)



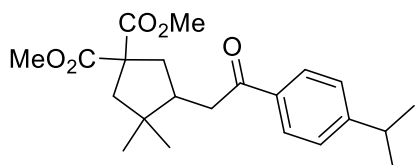
Colorless oil (54.7 mg, 79 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 3.70 (d, *J* = 2.3 Hz, 6H), 3.00 (dd, *J* = 15.9, 3.6 Hz, 1H), 2.73 (dd, *J* = 15.9, 10.1 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.41 (s, 3H), 2.30 – 2.23 (m, 3H), 2.15 – 2.08 (m, 1H), 1.07 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.3, 173.2, 143.8, 134.5, 129.2, 128.1, 57.5, 52.8, 52.7, 48.5, 44.8, 41.4, 39.1, 38.3, 27.6, 22.4, 21.6; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>27</sub>O<sub>5</sub>, 347.1853, Found: 347.1855.

**dimethyl 4-(2-(4-ethylphenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3c)**



Colorless oil (55.5 mg, 77 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.71 (d, *J* = 2.4 Hz, 6H), 3.00 (dd, *J* = 15.9, 3.5 Hz, 1H), 2.77 – 2.68 (m, 3H), 2.58 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.31 – 2.23 (m, 3H), 2.15 – 2.09 (m, 1H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.07 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.3, 173.3, 150.0, 134.7, 128.3, 128.1, 57.5, 52.8, 52.7, 48.5, 44.8, 41.4, 39.1, 38.3, 28.9, 27.6, 22.4, 15.2; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>29</sub>O<sub>5</sub>, 361.2010, Found: 361.2014.

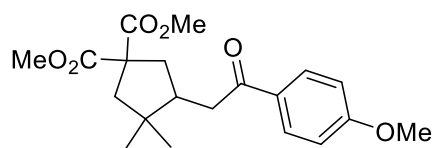
**dimethyl 4-(2-(4-isopropylphenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3d)**



Colorless oil (54.7 mg, 73 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.71 (d, *J* = 2.4 Hz, 6H), 3.03 – 2.93 (m, 2H), 2.73 (dd, *J* = 15.9, 10.1 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.31 – 2.23 (m, 3H), 2.15 – 2.09 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.08 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.3, 173.3, 154.5, 134.9, 128.3, 126.7, 57.5, 52.8, 52.7, 48.5, 44.8, 41.4, 39.1, 38.3, 34.2, 27.6, 23.6, 22.4; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>31</sub>O<sub>5</sub>, 375.2166, Found: 375.2168.

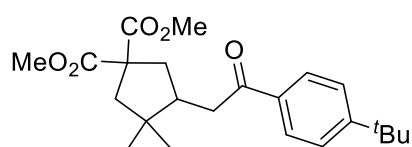


**dimethyl 4-(2-(4-methoxyphenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3e)**



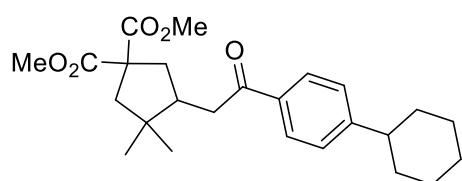
Colorless oil (39.1 mg, 54 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 6:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.9$  Hz, 2H), 6.94 (d,  $J = 8.9$  Hz, 2H), 3.87 (s, 3H), 3.71 (d,  $J = 3.0$  Hz, 6H), 2.97 (dd,  $J = 15.7, 3.5$  Hz, 1H), 2.71 (dd,  $J = 15.7, 10.1$  Hz, 1H), 2.57 (dd,  $J = 13.5, 6.8$  Hz, 1H), 2.30 – 2.23 (m, 3H), 2.15 – 2.09 (m, 1H), 1.07 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2, 173.3, 163.4, 130.3, 130.1, 113.7, 57.5, 55.4, 52.8, 52.7, 48.5, 44.9, 41.4, 39.1, 38.1, 27.6, 22.4; **HRMS (ESI) m/z**:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{27}\text{O}_6$ , 363.1803, Found: 363.1806.

**dimethyl 4-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3f)**



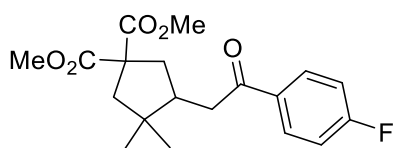
Colorless oil (48.9 mg, 63 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.5$  Hz, 2H), 7.48 (d,  $J = 8.5$  Hz, 2H), 3.71 (d,  $J = 2.9$  Hz, 6H), 3.02 (dd,  $J = 15.9, 3.5$  Hz, 1H), 2.74 (dd,  $J = 15.9, 10.1$  Hz, 1H), 2.58 (dd,  $J = 13.6, 6.9$  Hz, 1H), 2.31 – 2.24 (m, 3H), 2.16 – 2.10 (m, 1H), 1.34 (s, 9H), 1.08 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 173.2, 156.7, 134.4, 128.0, 125.5, 57.5, 52.8, 52.7, 48.5, 44.7, 41.4, 39.1, 38.3, 35.0, 31.0, 27.5, 22.4; **HRMS (ESI) m/z**:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{33}\text{O}_5$ , 389.2323, Found: 389.2327.

**dimethyl 4-(2-(4-cyclohexylphenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3g)**



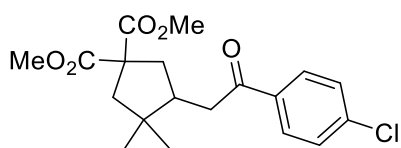
Colorless oil (59.7 mg, 72 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 9.1 Hz, 2H), 3.70 (s, 6H), 3.00 (dd, *J* = 15.9, 3.1 Hz, 1H), 2.73 (dd, *J* = 15.9, 10.2 Hz, 1H), 2.61 – 2.54 (m, 2H), 2.30 – 2.23 (m, 3H), 2.12 (t, *J* = 12.7 Hz, 1H), 1.87 (s, 5H), 1.45 – 1.38 (m, 5H), 1.07 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.2, 173.2, 153.6, 134.8, 128.2, 127.0, 57.5, 52.8, 52.7, 48.5, 44.7, 44.6, 41.3, 39.1, 38.3, 34.0, 27.5, 26.6, 25.9, 22.4; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>35</sub>O<sub>5</sub>, 415.2479, Found: 415.2481.

**dimethyl 4-(2-(4-fluorophenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3h)**



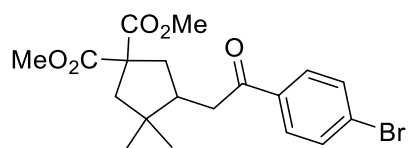
Colorless oil (53.3 mg, 76 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.98 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 3.71 (s, 6H), 3.00 (dd, *J* = 16.1, 3.4 Hz, 1H), 2.74 (dd, *J* = 16.1, 10.2 Hz, 1H), 2.59 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.30 – 2.22 (m, 3H), 2.14 – 2.08 (m, 1H), 1.08 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 197.9, 173.2, 165.6 (d, *J* = 255.5 Hz), 133.4 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 10.1 Hz), 115.7 (d, *J* = 22.2 Hz), 57.5, 52.8, 52.7, 48.4, 44.7, 41.4, 39.1, 38.3, 27.5, 22.4; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -105.3; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>24</sub>FO<sub>5</sub>, 351.1603, Found: 351.1602.

**dimethyl 4-(2-(4-chlorophenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3i)**



Colorless oil (60.9 mg, 83 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 3.71 (s, 6H), 2.99 (dd, *J* = 16.2, 3.5 Hz, 1H), 2.74 (dd, *J* = 16.2, 10.1 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.29 – 2.21 (m, 3H), 2.13 – 2.07 (m, 1H), 1.07 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 198.3, 173.2, 139.5, 135.3, 129.5, 128.9, 57.5, 52.8, 52.7, 48.4, 44.6, 41.4, 39.1, 38.4, 27.6, 22.4; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>24</sub>ClO<sub>5</sub>, 367.1307, Found: 367.1304.

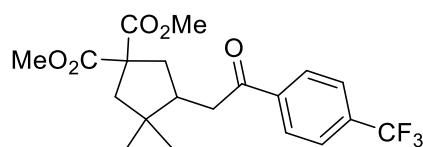
**dimethyl 4-(2-(4-bromophenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3j)**



Colorless oil (65.0 mg, 79 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 3.71 (s, 6H), 2.99 (dd, *J* = 16.2, 3.4 Hz, 1H), 2.73 (dd, *J* = 16.2, 10.1 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.28 – 2.21 (m, 3H), 2.13 – 2.06 (m, 1H), 1.07 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 198.5, 173.1, 135.6, 131.9, 129.5, 128.2, 57.5, 52.8, 52.7, 48.4, 44.6, 41.4, 39.0, 38.4, 27.5, 22.4; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>24</sub>BrO<sub>5</sub>, 411.0802, Found: 411.0807.

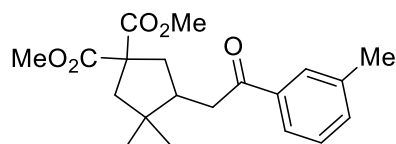
**dimethyl**

**3,3-dimethyl-4-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)cyclopentane-1,1-dicarboxylate (3k)**



Colorless oil (46.4 mg, 58 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 3.72 (s, 6H), 3.05 (dd, *J* = 16.4, 3.5 Hz, 1H), 2.80 (dd, *J* = 16.4, 10.1 Hz, 1H), 2.60 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.32 – 2.25 (m, 3H), 2.14 – 2.08 (m, 1H), 1.08 (s, 3H), 0.88 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 198.6, 173.2, 139.6, 134.3 (q, *J* = 32.3 Hz), 128.4, 125.7 (q, *J* = 4.0 Hz), 123.5 (q, *J* = 273.7 Hz), 57.5, 52.9, 52.8, 48.4, 44.5, 41.4, 39.0, 38.8, 27.6, 22.4; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -63.1; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>24</sub>F<sub>3</sub>O<sub>5</sub>, 401.1571, Found: 401.1576.

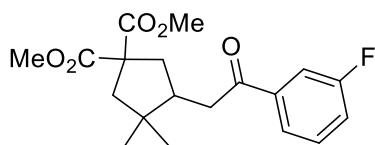
**dimethyl 3,3-dimethyl-4-(2-oxo-2-(m-tolyl)ethyl)cyclopentane-1,1-dicarboxylate (3l)**



Colorless oil (43.6 mg, 63 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 9.0 Hz, 2H), 7.39 – 7.33 (m, 2H), 3.71 (s, 6H), 3.01

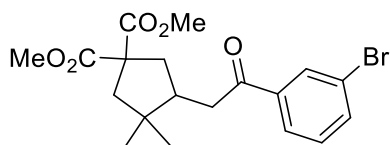
(dd,  $J = 16.1, 3.5$  Hz, 1H), 2.75 (dd,  $J = 16.1, 10.1$  Hz, 1H), 2.59 (dd,  $J = 13.6, 7.0$  Hz, 1H), 2.42 (s, 3H), 2.31 – 2.24 (m, 3H), 2.15 – 2.08 (m, 1H), 1.08 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 173.2, 138.4, 137.0, 133.8, 128.5, 128.4, 125.3, 57.5, 52.8, 52.7, 48.5, 44.7, 41.4, 39.1, 38.5, 27.6, 22.4, 21.3; **HRMS (ESI) m/z**:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{27}\text{O}_5$ , 347.1853, Found: 347.1853.

**dimethyl 4-(2-(3-fluorophenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3m)**



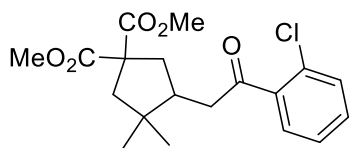
Colorless oil (42.7 mg, 61 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 7.7$  Hz, 1H), 7.62 (d,  $J = 9.5$  Hz, 1H), 7.45 (dd,  $J = 13.5, 8.0$  Hz, 1H), 7.27 (dd,  $J = 9.9, 8.2$  Hz, 1H), 3.72 (s, 6H), 3.01 (dd,  $J = 16.3, 3.5$  Hz, 1H), 2.75 (dd,  $J = 16.3, 10.2$  Hz, 1H), 2.60 (dd,  $J = 13.6, 7.0$  Hz, 1H), 2.31 – 2.23 (m, 3H), 2.14 – 2.07 (m, 1H), 1.08 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2, 173.2, 162.8 (d,  $J = 249.5$  Hz), 139.0 (d,  $J = 6.1$  Hz), 130.3 (d,  $J = 8.1$  Hz), 123.8 (d,  $J = 3.0$  Hz), 120.0 (d,  $J = 21.2$  Hz), 114.7 (d,  $J = 22.2$  Hz), 57.5, 52.8, 52.7, 48.4, 44.5, 41.4, 39.0, 38.6, 27.5, 22.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.7; **HRMS (ESI) m/z**:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{24}\text{FO}_5$ , 351.1603, Found: 351.1608.

**dimethyl 4-(2-(3-bromophenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3n)**



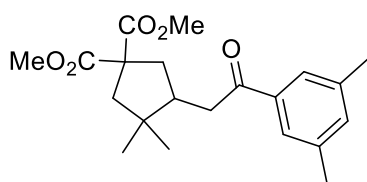
Colorless oil (58.4 mg, 71 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (t,  $J = 1.6$  Hz, 1H), 7.86 (d,  $J = 7.8$  Hz, 1H), 7.69 (d,  $J = 8.9$  Hz, 1H), 7.35 (t,  $J = 7.9$  Hz, 1H), 3.72 (s, 6H), 3.00 (dd,  $J = 16.4, 3.5$  Hz, 1H), 2.74 (dd,  $J = 16.4, 10.1$  Hz, 1H), 2.59 (dd,  $J = 13.6, 7.0$  Hz, 1H), 2.30 – 2.22 (m, 3H), 2.13 – 2.06 (m, 1H), 1.08 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.1, 173.2, 138.7, 135.9, 131.1, 130.2, 126.5, 123.0, 57.5, 52.8, 52.7, 48.4, 44.5, 41.4, 39.0, 38.5, 27.5, 22.4; **HRMS (ESI) m/z**:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{24}\text{BrO}_5$ , 411.0802, Found: 411.0807.

**dimethyl 4-(2-(2-chlorophenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3o)**



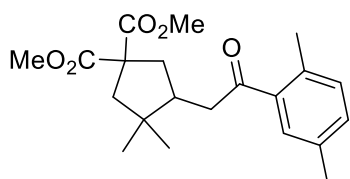
Colorless oil (49.9 mg, 68 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.38 (m, 3H), 7.36 – 7.31 (m, 1H), 3.71 (s, 6H), 3.03 (dd,  $J = 16.6, 3.3$  Hz, 1H), 2.73 (dd,  $J = 16.6, 10.2$  Hz, 1H), 2.61 (dd,  $J = 13.3, 6.6$  Hz, 1H), 2.26 – 2.18 (m, 3H), 2.14 – 2.07 (m, 1H), 1.05 (s, 3H), 0.81 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  202.9, 173.1, 173.09, 139.6, 131.6, 130.6, 130.4, 128.7, 126.9, 57.5, 52.8, 52.7, 48.3, 44.5, 43.0, 41.3, 38.8, 27.5, 22.4; **HRMS (ESI) m/z**:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{24}\text{ClO}_5$ , 367.1307, Found: 367.1305.

**dimethyl 4-(2-(3,5-dimethylphenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3p)**



Colorless oil (40.4 mg, 56 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (s, 2H), 7.20 (s, 1H), 3.71 (s, 6H), 3.00 (dd,  $J = 16.1, 3.5$  Hz, 1H), 2.73 (dd,  $J = 16.1, 10.1$  Hz, 1H), 2.59 (dd,  $J = 13.6, 7.0$  Hz, 1H), 2.37 (s, 6H), 2.28 – 2.23 (m, 3H), 2.14 – 2.08 (m, 1H), 1.08 (s, 3H), 0.88 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 173.2, 173.25, 138.2, 137.2, 134.6, 125.8, 57.6, 52.8, 52.7, 48.5, 44.7, 41.4, 39.1, 38.5, 27.6, 22.4, 21.2; **HRMS (ESI) m/z**:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{21}\text{H}_{29}\text{O}_5$ , 361.2010, Found: 361.2012.

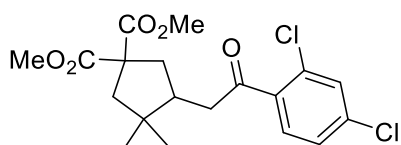
**dimethyl 4-(2-(2,5-dimethylphenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3q)**



Colorless oil (41.8 mg, 58 %); Flash column chromatography conditions: petroleum ethers / EtOAc =

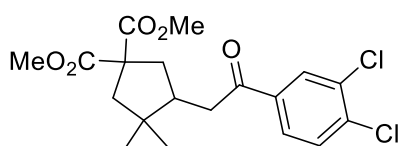
7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.37 (s, 1H), 7.20 – 7.11 (m, 2H), 3.71 (s, 6H), 2.94 (dd, *J* = 16.2, 3.3 Hz, 1H), 2.70 – 2.58 (m, 2H), 2.42 (s, 3H), 2.36 (s, 3H), 2.26 – 2.23 (m, 3H), 2.13 – 2.04 (m, 1H), 1.06 (s, 3H), 0.84 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 204.0, 173.2, 173.19, 138.3, 135.1, 134.4, 131.8, 131.75, 128.6, 57.6, 52.8, 52.7, 48.4, 44.7, 41.6, 41.3, 39.0, 27.5, 22.5, 20.9, 20.6; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>29</sub>O<sub>5</sub>, 361.2010, Found: 361.2018.

**dimethyl 4-(2-(2,4-dichlorophenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3r)**



Colorless oil (49.8 mg, 62 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.41 (m, 2H), 7.32 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.71 (s, 6H), 3.01 (dd, *J* = 16.6, 3.3 Hz, 1H), 2.71 (dd, *J* = 16.6, 10.2 Hz, 1H), 2.58 (dd, *J* = 13.3, 6.6 Hz, 1H), 2.25 – 2.18 (m, 3H), 2.14 – 2.05 (m, 1H), 1.05 (s, 3H), 0.81 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 201.6, 173.1, 173.08, 137.7, 137.2, 131.8, 130.4, 130.0, 127.4, 57.5, 52.9, 52.8, 48.3, 44.6, 43.0, 41.3, 38.8, 27.5, 22.4; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>23</sub>Cl<sub>2</sub>O<sub>5</sub>, 401.0918, Found: 401.0921.

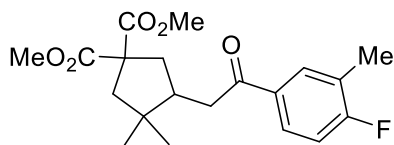
**dimethyl 4-(2-(3,4-dichlorophenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3s)**



Colorless oil (50.6 mg, 63 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 1.9 Hz, 1H), 7.76 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 3.72 (s, 6H), 2.98 (dd, *J* = 16.4, 3.4 Hz, 1H), 2.72 (dd, *J* = 16.4, 10.1 Hz, 1H), 2.58 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.28 – 2.21 (m, 3H), 2.16 – 2.05 (m, 1H), 1.07 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 197.2, 173.2, 137.6, 136.5, 133.3, 130.7, 130.1, 127.1, 57.5, 52.9, 52.8, 48.4, 44.5, 41.4, 39.0, 38.5, 27.6, 22.4; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>23</sub>Cl<sub>2</sub>O<sub>5</sub>, 401.0918, Found: 401.0920.

dimethyl

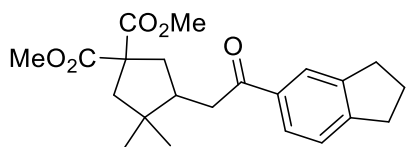
**4-(2-(4-fluoro-3-methylphenyl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3t)**



Colorless oil (53.2 mg, 73 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.82 – 7.76 (m, 2H), 7.07 (t, *J* = 8.8 Hz, 1H), 3.71 (s, 6H), 2.98 (dd, *J* = 16.0, 3.5 Hz, 1H), 2.72 (dd, *J* = 16.0, 10.1 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.33 (s, 3H), 2.27 – 2.22 (m, 3H), 2.14 – 2.07 (m, 1H), 1.07 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 198.2, 173.2, 164.3 (d, *J* = 254.5 Hz), 133.1 (d, *J* = 4.0 Hz), 131.8 (d, *J* = 6.1 Hz), 128.0 (d, *J* = 9.1 Hz), 125.3 (d, *J* = 17.8 Hz), 115.2 (d, *J* = 23.2 Hz), 57.5, 52.8, 52.7, 48.5, 44.7, 41.4, 39.1, 38.3, 27.5, 22.4, 14.6, 14.55; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -109.5; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>26</sub>FO<sub>5</sub>, 365.1759, Found: 365.1761.

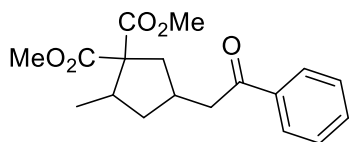
dimethyl

**4-(2-(2,3-dihydro-1H-inden-5-yl)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (3u)**



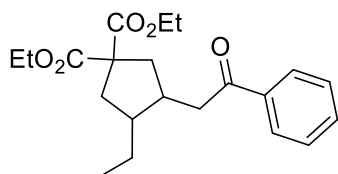
Colorless oil (49.9 mg, 67 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.80 (s, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 3.71 (d, *J* = 1.9 Hz, 6H), 2.98 – 2.93 (m, 5H), 2.74 (dd, *J* = 15.9, 10.1 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.30 – 2.23 (m, 3H), 2.15 – 2.08 (m, 3H), 1.07 (s, 3H), 0.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.6, 173.3, 173.26, 150.2, 144.8, 135.6, 126.6, 124.3, 124.0, 57.5, 52.8, 52.7, 48.5, 44.8, 41.4, 39.1, 38.4, 33.0, 32.5, 27.6, 25.3, 22.4; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>29</sub>O<sub>5</sub>, 373.2010, Found: 373.2019.

**dimethyl 3-methyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylate (3v)**



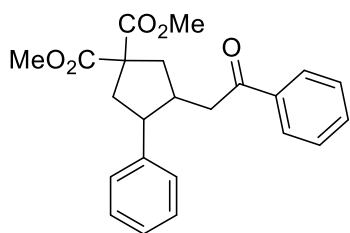
Both isomers (2.2:1 *dr*), colorless oil (47.1 mg, 74 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.95 (t, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.1 Hz, 2H), 3.73 (s, 6H), 3.19 – 3.00 (m, 2H), 2.90 – 2.40 (m, 3H), 2.21 – 2.10 (m, 1H), 1.83 – 1.64 (m, 1H), 1.27 – 1.17 (m, 1H), 1.00 (d, *J* = 6.9 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.6, 199.3, 172.9, 172.8, 172.2, 171.3, 136.9, 136.85, 133.0, 128.5, 128.0, 63.7, 63.1, 52.4, 52.0, 45.3, 44.3, 40.7, 40.5, 40.4, 40.2, 39.7, 39.5, 32.9, 32.1, 16.3, 16.26; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>23</sub>O<sub>5</sub>, 319.1540, Found: 319.1543.

**diethyl 3-ethyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylate (3w)**



Both isomers (2.1:1 *dr*), colorless oil (51.9 mg, 72 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.21 – 4.10 (m, 4H), 3.20 – 2.87 (m, 2H), 2.78 – 2.73 (m, 1H), 2.62 – 2.42 (m, 2H), 2.08 – 1.86 (m, 3H), 1.66 – 1.35 (m, 1H), 1.25 – 1.18 (m, 7H), 0.95 – 0.89 (m, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.7, 199.6, 173.0, 172.9, 172.7, 172.4, 137.2, 137.0, 133.0, 132.9, 128.5, 128.0, 127.95, 61.4, 61.3, 58.7, 58.6, 46.7, 43.6, 43.1, 40.4, 40.2, 39.5, 39.3, 38.3, 38.0, 37.3, 26.2, 22.6, 14.0, 13.9, 12.7, 12.5; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>29</sub>O<sub>5</sub>, 361.2010, Found: 361.2006.

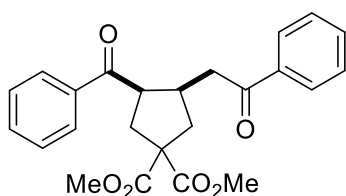
**dimethyl 3-(2-oxo-2-phenylethyl)-4-phenylcyclopentane-1,1-dicarboxylate (3x)**





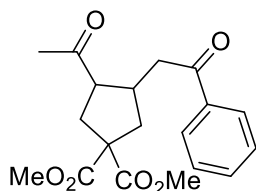
Both isomers (4.3:1 *dr*), colorless oil (61.6 mg, 81 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.81 – 7.67 (m, 2H), 7.57 – 7.44 (m, 1H), 7.39 – 7.33 (m, 2H), 7.30 – 7.23 (m, 3H), 7.18 – 7.16 (m, 2H), 3.78 – 3.74 (m, 6H), 3.58 (dd, *J* = 16.4, 8.2 Hz, 1H), 3.07 (dd, *J* = 14.2, 6.9 Hz, 1H), 2.86 (dd, *J* = 14.1, 7.9 Hz, 1H), 2.70 – 2.45 (m, 4H), 2.22 (dd, *J* = 14.6, 7.7 Hz, 1H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.5, 173.0, 172.9, 141.0, 137.1, 132.8, 129.1, 128.7, 128.5, 128.4, 128.35, 128.2, 128.0, 127.8, 127.7, 127.0, 126.5, 59.0, 58.4, 52.9, 52.86, 51.4, 46.5, 42.6, 42.3, 42.0, 40.0, 39.6, 39.2, 38.8, 38.3; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>25</sub>O<sub>5</sub>, 381.1697, Found: 381.1698.

**dimethyl (3R,4R)-3-benzoyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylate (3y)**



Light yellow oil (52.3 mg, 64 %, > 20:1 *dr*); Flash column chromatography conditions: petroleum ethers / EtOAc = 5:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 7.3 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.42 – 7.34 (m, 4H), 4.28 – 4.22 (m, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.21 – 3.16 (m, 1H), 3.05 – 2.98 (m, 1H), 2.92 – 2.86 (m, 1H), 2.77 – 2.72 (m, 1H), 2.67 – 2.62 (m, 2H), 2.39 – 2.34 (m, 1H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 201.4, 198.6, 172.9, 172.1, 136.9, 136.6, 133.3, 133.0, 128.6, 128.4, 128.3, 127.6, 58.7, 53.0, 52.8, 47.4, 39.9, 39.2, 37.8, 36.5; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>25</sub>O<sub>6</sub>, 409.1646, Found: 409.1651.

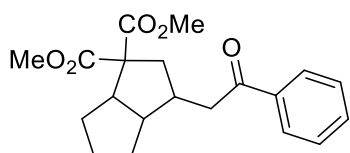
**dimethyl 3-acetyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylate (3z)**



Both isomers (1.3:1 *dr*), colorless oil (54.4 mg, 79 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 5:1; (major isomer): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 3.41 (q, *J* = 7.7 Hz, 1H), 3.08 – 2.98 (m, 3H), 2.56 – 2.51 (m, 3H), 2.29 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.14 (s, 3H); **<sup>13</sup>C**

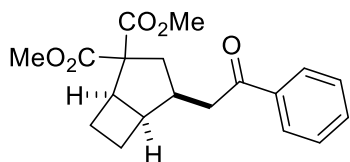
**NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  210.2, 199.0, 172.7, 172.1, 136.7, 133.1, 128.5, 127.9, 58.5, 52.9, 52.8, 52.78, 39.8, 38.9, 37.0, 36.0, 31.1; (minor isomer): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (d,  $J = 7.4$  Hz, 2H), 7.56 (t,  $J = 7.3$  Hz, 1H), 7.46 (t,  $J = 7.7$  Hz, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 3.20 (dd,  $J = 16.4, 5.2$  Hz, 1H), 2.98 (dd,  $J = 16.3, 7.9$  Hz, 1H), 2.92 – 2.87 (m, 1H), 2.82 – 2.76 (m, 1H), 2.76 – 2.70 (m, 1H), 2.66 (dd,  $J = 13.5, 8.1$  Hz, 1H), 2.38 (dd,  $J = 13.4, 9.6$  Hz, 1H), 2.22 (s, 3H), 1.99 (dd,  $J = 13.7, 8.8$  Hz, 1H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  208.7, 198.8, 172.5, 171.8, 136.6, 133.2, 128.6, 128.0, 59.0, 57.1, 52.9, 52.89, 43.0, 39.5, 37.1, 28.9; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>23</sub>O<sub>6</sub>, 347.1489, Found: 347.1492.

**dimethyl 3-(2-oxo-2-phenylethyl)hexahydropentalene-1,1(2H)-dicarboxylate (3aa)**



Both isomers (2.4:1 *dr*), colorless oil (54.4 mg, 79 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 – 7.92 (m, 2H), 7.56 (t,  $J = 7.3$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.74 – 3.70 (m, 6H), 3.31 – 3.21 (m, 1H), 3.12 – 2.74 (m, 3H), 2.51 – 2.29 (m, 1H), 2.21 – 2.02 (m, 1H), 1.83 – 1.49 (m, 4H), 1.34 – 1.08 (m, 2H), 0.97 – 0.85 (m, 1H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.5, 199.2, 173.6, 172.6, 171.4, 171.1, 137.0, 133.0, 128.6, 128.0, 127.9, 63.4, 63.0, 52.8, 52.7, 52.2, 50.8, 50.1, 47.6, 45.0, 43.9, 41.4, 40.7, 39.1, 36.8, 34.5, 31.8, 30.5, 29.3, 28.5, 27.1, 26.6; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>25</sub>O<sub>5</sub>, 345.1697, Found: 345.1702.

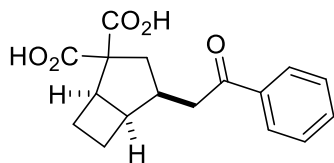
**dimethyl 4-(2-oxo-2-phenylethyl)bicyclo[3.2.0]heptane-2,2-dicarboxylate (3bb)**



Light yellow oil (56.8 mg, 86 %, > 20:1 *dr*); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d,  $J = 8.3$  Hz, 2H), 7.56 (t,  $J = 7.9$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 3.70 (d,  $J = 10.7$  Hz, 6H), 3.43 – 3.38 (m, 1H), 3.08 – 3.02 (m, 3H), 2.57 – 2.42 (m, 3H), 2.21 – 2.11 (m, 2H), 1.77 – 1.70 (m, 1H), 1.49 – 1.41 (m, 1H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.1, 172.1, 170.6, 136.9, 133.0, 128.6, 127.9, 63.7, 52.7, 52.4, 42.7, 40.2, 37.9,

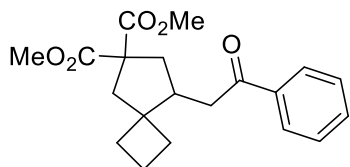
37.4, 35.9, 19.9, 17.4; **HRMS (ESI) m/z:**  $[M + H]^+$  Calcd for  $C_{19}H_{23}O_5$ , 331.1540, Found: 331.1544.

#### 4-(2-oxo-2-phenylethyl)bicyclo[3.2.0]heptane-2,2-dicarboxylic acid (**3bb'**)



Lithium hydroxide (24.0 mg, 1.0 mmol) was added to a solution of dimethyl 4-(2-oxo-2-phenylethyl)bicyclo[3.2.0]heptane-2,2-dicarboxylate (**3bb**, 66.1 mg, 0.2 mmol) in MeOH and  $H_2O$  (3/1, 1.2 mL and 0.4 mL), and the mixture was stirred at 80 °C for 2h. After the reaction completed, the reaction mixture was diluted with  $H_2O$  and washed with diethyl ether. The resulting aqueous layer was acidified with 1.2 N HCl until the solution become pH 6, and then extracted with EtOAc. The combined organic layer was dried over  $Na_2SO_4$  and concentrated. Purification by column chromatography on silica gel (EtOAc / petroleum ethers 3:1) provided the desired product (53.8 mg, 89 %) as a white solid;  **$^1H$  NMR** (400 MHz, DMSO)  $\delta$  12.59 (s, 2H), 7.96 (d,  $J = 7.6$  Hz, 2H), 7.63 (t,  $J = 7.3$  Hz, 1H), 7.52 (t,  $J = 7.6$  Hz, 2H), 3.22 – 3.06 (m, 3H), 2.87 – 2.81 (m, 1H), 2.33 – 2.27 (m, 2H), 2.22 – 2.17 (m, 1H), 2.16 – 2.02 (m, 1H), 1.84 – 1.73 (m, 2H), 1.46 – 1.38 (m, 1H);  **$^{13}C$  NMR** (101 MHz, DMSO)  $\delta$  204.8, 178.4, 176.5, 141.9, 138.4, 133.9, 133.2, 68.5, 47.0, 42.8, 42.0, 40.9, 24.8, 22.0; **HRMS (ESI) m/z:**  $[M + H]^+$  Calcd for  $C_{17}H_{19}O_5$ , 303.1227, Found: 303.1229.

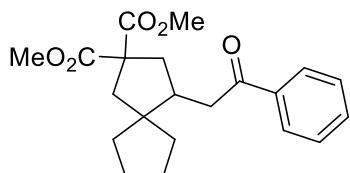
#### dimethyl 8-(2-oxo-2-phenylethyl)spiro[3.4]octane-6,6-dicarboxylate (**3cc**)



Colorless oil (57.2 mg, 83 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.97 (d,  $J = 7.2$  Hz, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 3.69 (d,  $J = 9.0$  Hz, 6H), 3.16 (dd,  $J = 16.6, 3.9$  Hz, 1H), 2.93 (dd,  $J = 16.6, 9.8$  Hz, 1H), 2.58 – 2.53 (m, 2H), 2.47 – 2.39 (m, 2H), 2.04 – 1.89 (m, 5H), 1.80 – 1.71 (m, 2H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  199.6, 173.3, 172.9, 137.1, 133.0, 128.6, 128.0, 57.7, 52.7, 52.70, 49.2, 46.2, 42.8,

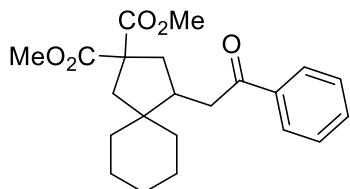
39.0, 38.4, 31.3, 27.9, 15.8; **HRMS (ESI) m/z:**  $[M + H]^+$  Calcd for  $C_{20}H_{25}O_5$ , 445.1697, Found: 445.1696.

**dimethyl 4-(2-oxo-2-phenylethyl)spiro[4.4]nonane-2,2-dicarboxylate (3dd)**



Colorless oil (60.9 mg, 85 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.95 (d,  $J = 7.3$  Hz, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 3.70 (d,  $J = 6.8$  Hz, 6H), 3.03 (dd,  $J = 16.3, 3.6$  Hz, 1H), 2.87 (dd,  $J = 16.3, 10.1$  Hz, 1H), 2.62 (dd,  $J = 13.6, 7.0$  Hz, 1H), 2.53 – 2.45 (m, 1H), 2.38 (d,  $J = 13.8$  Hz, 1H), 2.20 (d,  $J = 13.8$  Hz, 1H), 2.01 (dd,  $J = 13.6, 9.8$  Hz, 1H), 1.65 – 1.51 (m, 6H), 1.46 – 1.31 (m, 2H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  199.6, 173.4, 173.2, 137.1, 133.0, 128.6, 128.0, 57.9, 53.3, 52.8, 52.7, 46.7, 42.6, 39.7, 38.8, 37.3, 32.3, 24.6, 24.2; **HRMS (ESI) m/z:**  $[M + H]^+$  Calcd for  $C_{21}H_{27}O_5$ , 359.1853, Found: 359.1853.

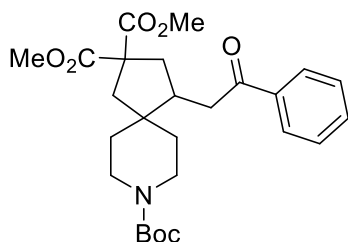
**dimethyl 4-(2-oxo-2-phenylethyl)spiro[4.5]decane-2,2-dicarboxylate (3ee)**



Colorless oil (60.3 mg, 81%); Flash column chromatography conditions: petroleum ethers/EtOAc = 7:1;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.95 (d,  $J = 7.2$  Hz, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.70 (d,  $J = 4.2$  Hz, 6H), 3.06 (dd,  $J = 16.1, 3.2$  Hz, 1H), 2.80 (dd,  $J = 16.1, 10.5$  Hz, 1H), 2.64 – 2.55 (m, 2H), 2.28 – 2.20 (m, 1H), 2.10 – 2.09 (m, 2H), 1.68 – 1.59 (m, 3H), 1.45 – 1.33 (m, 5H), 1.19 – 1.13 (m, 2H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  199.7, 173.3, 173.1, 137.0, 132.9, 128.5, 128.0, 57.9, 52.7, 52.65, 45.0, 44.99, 42.5, 38.3, 38.1, 37.2, 30.1, 26.2, 23.7, 22.2; **HRMS (ESI) m/z:**  $[M + H]^+$  Calcd for  $C_{22}H_{29}O_5$ , 373.2010, Found: 373.2013.

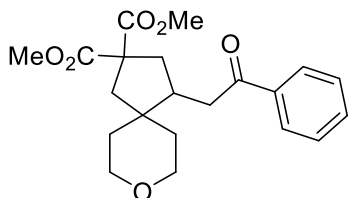
**8-(tert-butyl) 2,2-dimethyl 4-(2-oxo-2-phenylethyl)-8-azaspiro[4.5]decane-2,2,8-tricarboxylate**

**(3ff)**



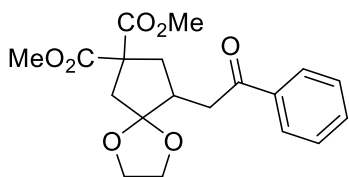
Colorless oil (78.6 mg, 83 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 5:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 7.2$  Hz, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 4.03 (br, 2H), 3.73 (s, 3H), 3.70 (s, 3H), 3.02 (d,  $J = 15.8$  Hz, 1H), 2.89 – 2.57 (m, 5H), 2.35 – 2.29 (m, 1H), 2.15 (d,  $J = 14.0$  Hz, 1H), 2.05 – 1.99 (m, 1H), 1.61 (t,  $J = 10.7$  Hz, 1H), 1.46 (s, 9H), 1.38 – 1.27 (m, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.0, 173.1, 172.8, 154.8, 136.8, 133.1, 128.6, 128.0, 79.5, 57.6, 52.9, 52.85, 43.5, 41.3, 38.2, 37.8, 29.7, 28.4; **HRMS (ESI) m/z:**  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{36}\text{NO}_7$ , 474.2487, Found: 474.2491.

**dimethyl 4-(2-oxo-2-phenylethyl)-8-oxaspiro[4.5]decane-2,2-dicarboxylate (3gg)**



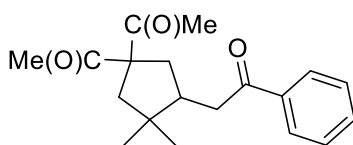
Colorless oil (66.6 mg, 89 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 5:1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.5$  Hz, 2H), 7.58 (t,  $J = 6.9$  Hz, 1H), 7.48 (t,  $J = 6.9$  Hz, 2H), 3.88 (d,  $J = 10.6$  Hz, 2H), 3.72 (d,  $J = 11.9$  Hz, 6H), 3.62 – 3.49 (m, 2H), 3.09 (d,  $J = 16.4$  Hz, 1H), 2.87 – 2.80 (m, 1H), 2.70 – 2.64 (m, 2H), 2.33 – 2.21 (m, 2H), 2.05 – 1.98 (m, 1H), 1.86 – 1.77 (m, 1H), 1.59 (t,  $J = 11.4$  Hz, 1H), 1.27 (d,  $J = 10.4$  Hz, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.0, 173.1, 172.8, 136.9, 133.1, 128.6, 127.9, 65.5, 64.3, 57.7, 52.9, 52.8, 44.6, 42.7, 41.9, 38.1, 37.8, 36.7, 30.7; **HRMS (ESI) m/z:**  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{21}\text{H}_{27}\text{O}_6$ , 375.1803, Found: 375.1805.

**dimethyl 9-(2-oxo-2-phenylethyl)-1,4-dioxaspiro[4.4]nonane-7,7-dicarboxylate (3hh)**



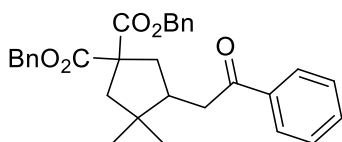
Colorless oil (53.6 mg, 74 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 3:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.90 (br, 4H), 3.74 (d, *J* = 5.6 Hz, 6H), 3.22 (dd, *J* = 16.3, 4.0 Hz, 1H), 2.95 – 2.82 (m, 2H), 2.74 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.58 (d, *J* = 14.1 Hz, 1H), 2.45 (d, *J* = 14.1 Hz, 1H), 2.13 – 2.05 (m, 1H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.0, 172.1, 137.0, 132.9, 128.5, 128.0, 115.9, 65.0, 64.4, 55.8, 53.0, 52.9, 42.1, 40.9, 37.7, 36.8; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>23</sub>O<sub>7</sub>, 363.1439, Found: 363.1436.

**1,1'-(3,3-dimethyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-diyl)bis(ethan-1-one) (3ii)**



Colorless oil (55.3 mg, 92%); Flash column chromatography conditions: petroleum ethers/EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.03 (dd, *J* = 16.3, 3.3 Hz, 1H), 2.72 (dd, *J* = 16.3, 10.4 Hz, 1H), 2.64 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.24 (d, *J* = 13.7 Hz, 1H), 2.14 – 2.07 (m, 7H), 2.01 (d, *J* = 13.7 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.06 (s, 3H), 0.78 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 205.0, 204.6, 199.5, 136.8, 133.1, 128.6, 128.0, 73.1, 44.9, 44.3, 41.2, 38.4, 35.4, 27., 26.6, 25.9, 22.3; **HRMS (ESI) m/z**: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>25</sub>O<sub>3</sub>, 301.1798, Found: 301.1801.

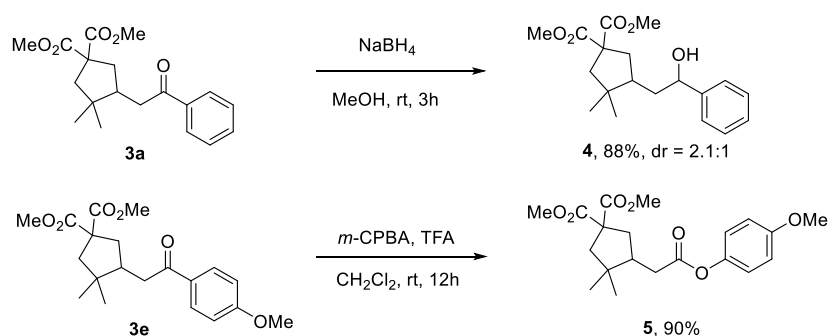
**dibenzyl 3,3-dimethyl-4-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylate (3jj)**



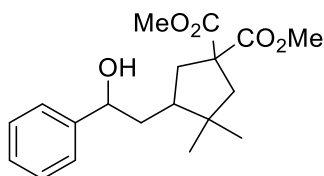
Colorless oil (85.3 mg, 88 %); Flash column chromatography conditions: petroleum ethers / EtOAc = 7:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* =

7.6 Hz, 2H), 7.31 – 7.20 (m, 10H), 5.15 – 5.02 (m, 4H), 3.01 (dd,  $J = 16.1, 3.5$  Hz, 1H), 2.75 (dd,  $J = 16.1, 10.1$  Hz, 1H), 2.64 (dd,  $J = 13.7, 6.9$  Hz, 1H), 2.32 – 2.25 (m, 3H), 2.17 – 2.10 (m, 1H), 1.05 (s, 3H), 0.85 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.5, 172.4, 137.0, 135.5, 135.4, 133.0, 128.6, 128.4, 128.1, 128.07, 128.0, 127.9, 127.8, 67.1, 57.8, 48.4, 44.7, 41.4, 39.1, 38.4, 27.6, 22.5; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{31}\text{H}_{33}\text{O}_5$ , 485.2323, Found: 485.2324.

## 5. Synthetic Transformations

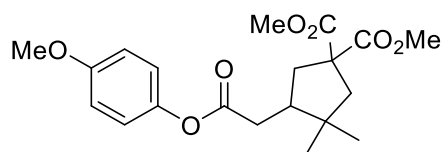


### dimethyl 4-(2-hydroxy-2-phenylethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (**4**)



To a stirred suspension of compound **3a** (66.5 mg, 0.2 mmol) in methanol (3 mL) was added  $\text{NaBH}_4$  (9.1 mg, 0.24 mmol) and the resulting mixture was allowed to react at room temperature for 3h. After that time, the reaction was quenched with water (5 ml) and extracted with  $\text{EtOAc}$  (3x10 ml); after drying ( $\text{Na}_2\text{SO}_4$ ) the solvent was evaporated under vacuum. Purification by column chromatography on silica gel (petroleum ethers /  $\text{EtOAc}$  3:1) provided **4** (58.9 mg, 88 %, 2.1:1 *dr*) as a colorless oil (both isomer);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.26 (m, 5H), 4.68 (d,  $J = 7.1$  Hz, 1H), 3.71 – 3.67 (m, 6H), 2.64 – 2.49 (m, 1H), 2.26 – 1.90 (m, 5H), 1.83 – 1.76 (m, 1H), 1.43 – 1.37 (m, 1H), 1.02 – 0.90 (m, 3H), 0.77 – 0.73 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 173.5, 173.3, 173.2, 145.3, 144.4, 128.5, 128.4, 127.7, 127.5, 125.9, 125.6, 74.5, 73.0, 57.6, 57.5, 52.8, 52.7, 48.8, 48.4, 46.3, 45.3, 41.5, 41.3, 39.5, 39.3, 38.7, 38.5, 27.4, 27.37, 22.1, 21.9; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{27}\text{O}_5$ , 335.1853, Found: 335.1854.

### dimethyl 4-(2-(4-methoxyphenoxy)-2-oxoethyl)-3,3-dimethylcyclopentane-1,1-dicarboxylate (**5**)



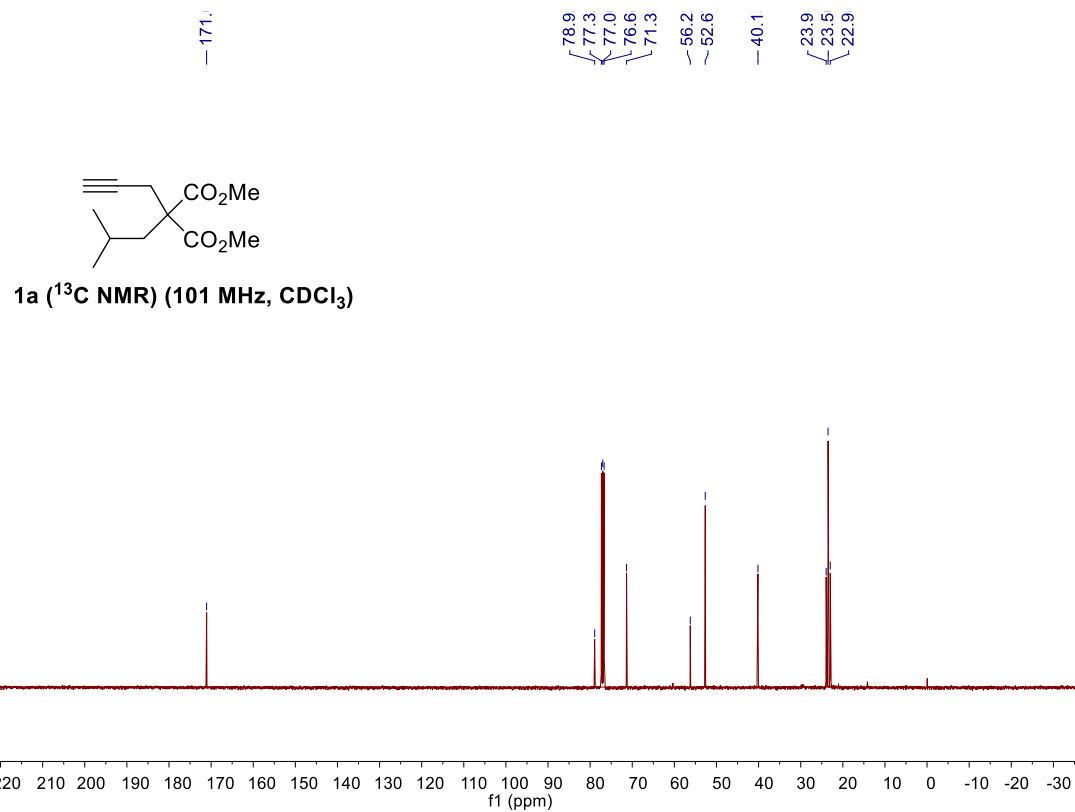
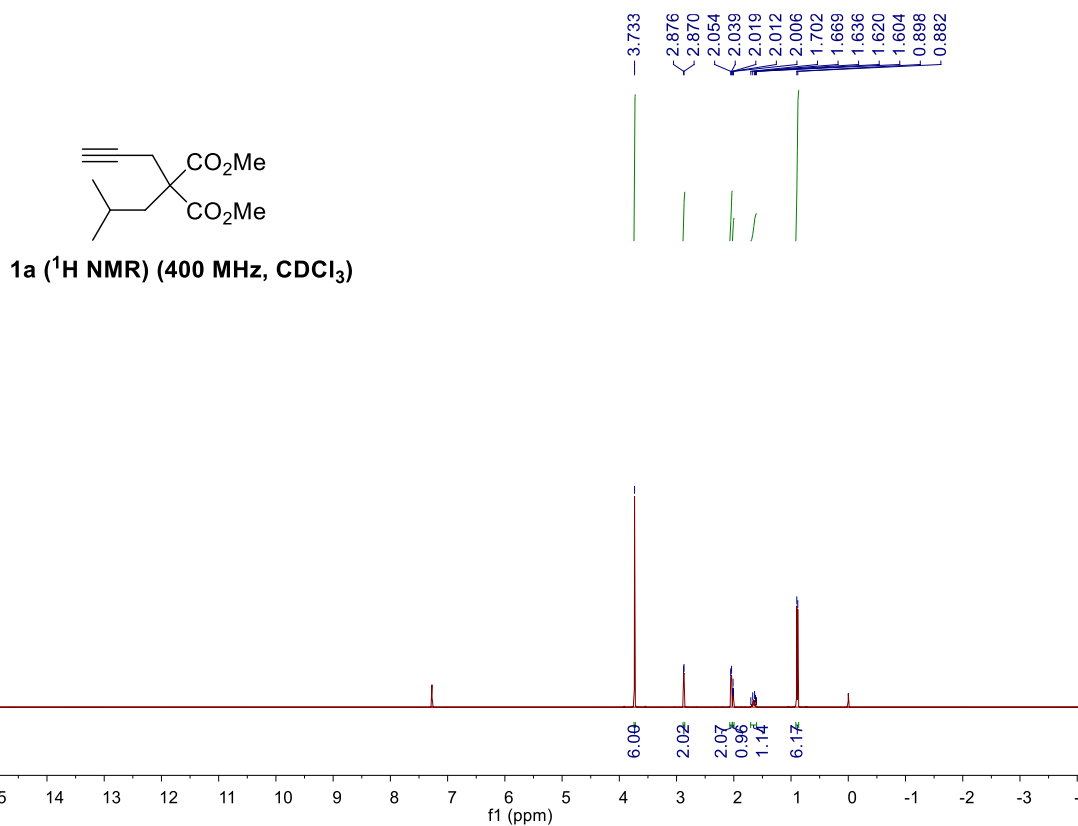
The compound (**3e**, 72.8 mg, 0.2 mmol) was dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and *m*-CPBA (technical grade: 85%, 105.6 mg, 0.52 mmol) was added. The suspension was cooled to 0 °C and TFA (22.8 mg, 0.2 mmol) was added dropwise. The reaction flask protected from light was stirred over night at room temperature. After the reaction, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) washed once each with 10 % aqueous Na<sub>2</sub>SO<sub>3</sub> solution, saturated aqueous K<sub>2</sub>CO<sub>3</sub> solution, and H<sub>2</sub>O. The organic phase was dried over MgSO<sub>4</sub> and evaporated. Column chromatography on silica gel (petroleum ethers/EtOAc = 5:1) gave **5** (68.1 mg, 90 %) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.00 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 3.72 (d, *J* = 4.8 Hz, 6H), 2.67 – 2.57 (m, 2H), 2.37 – 2.19 (m, 5H), 1.09 (s, 3H), 0.85 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.2, 173.0, 171.9, 157.2, 144.0, 122.2, 114.4, 57.3, 55.5, 52.8, 52.77, 48.5, 45.4, 41.3, 38.9, 34.5, 27.5, 22.2; HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>27</sub>O<sub>7</sub>, 379.1752, Found: 379.1755.

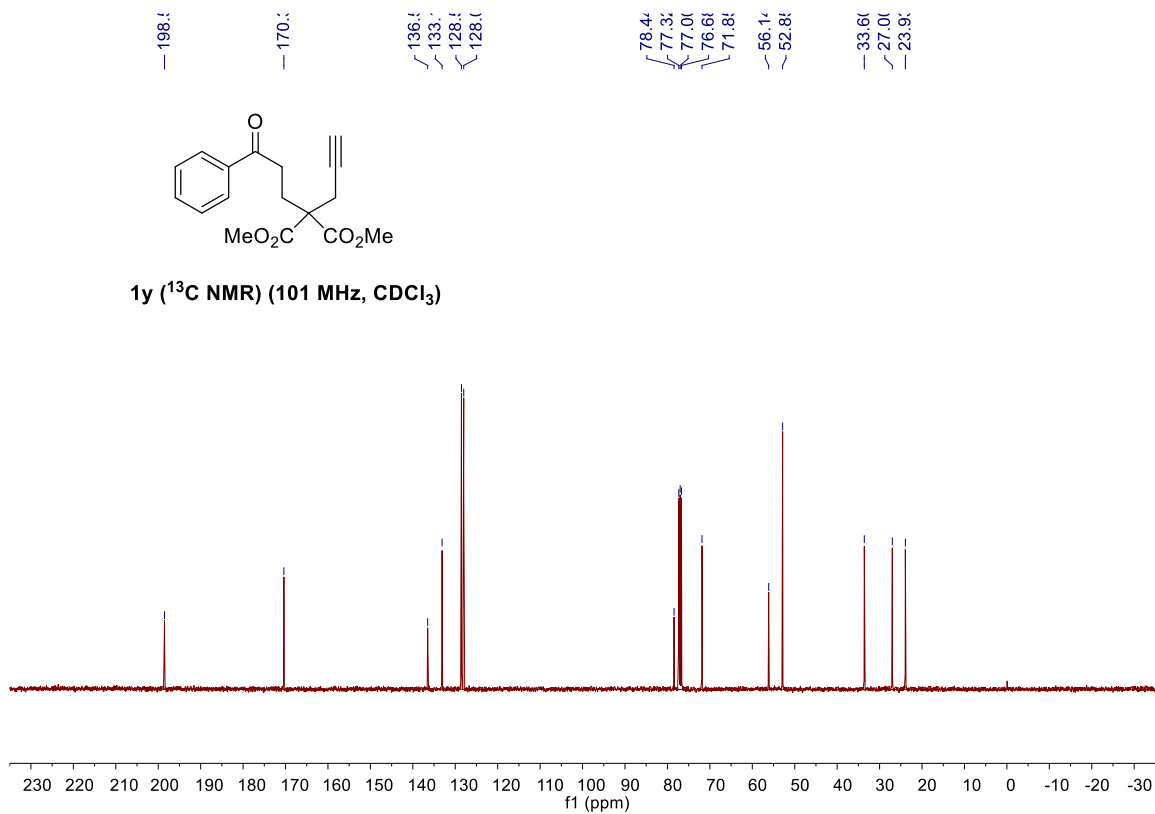
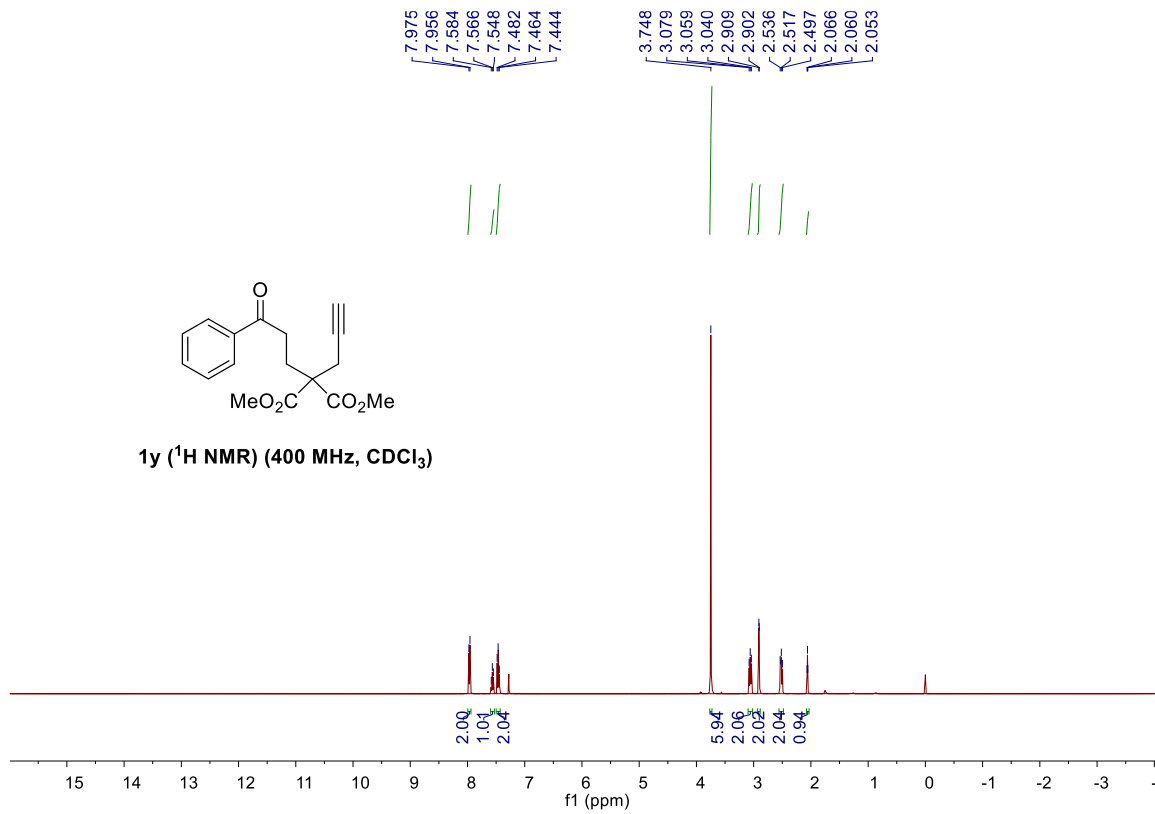
## 6. References

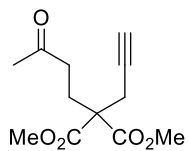
1. B. Yang, S - J. Li, Y. Wang, Y. Lan, S. Zhu, *Nat. Commun.*, 2021, **12**, 5257.
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6. B. Yu, S. Mohamed, J. Ardisson, M.-I. Lannou and G. Sorin, *Chem. Commun.*, 2022, **58**, 1374–1377.



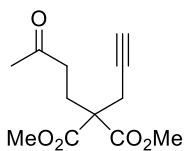
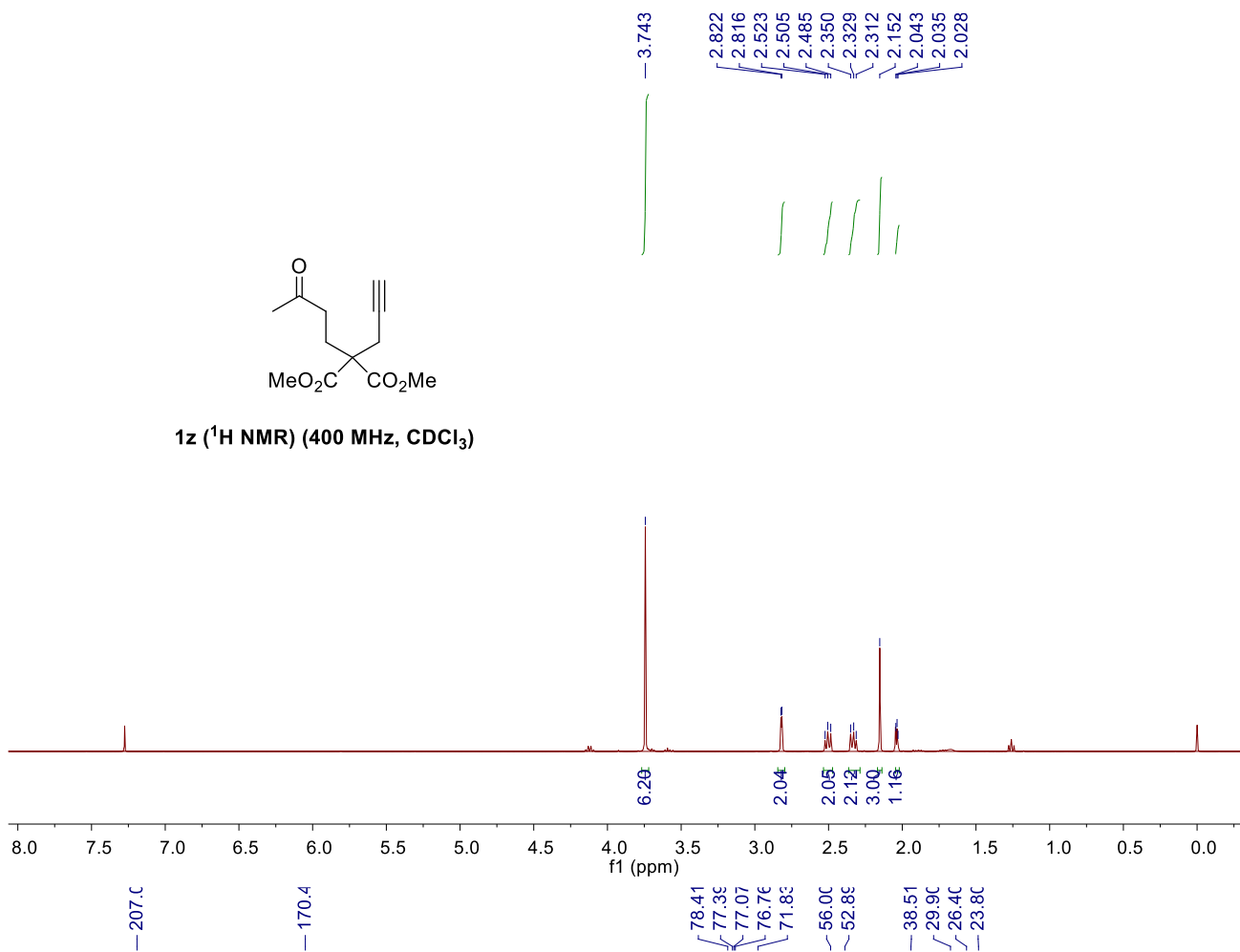
## 7. Copies of $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ NMR Spectra



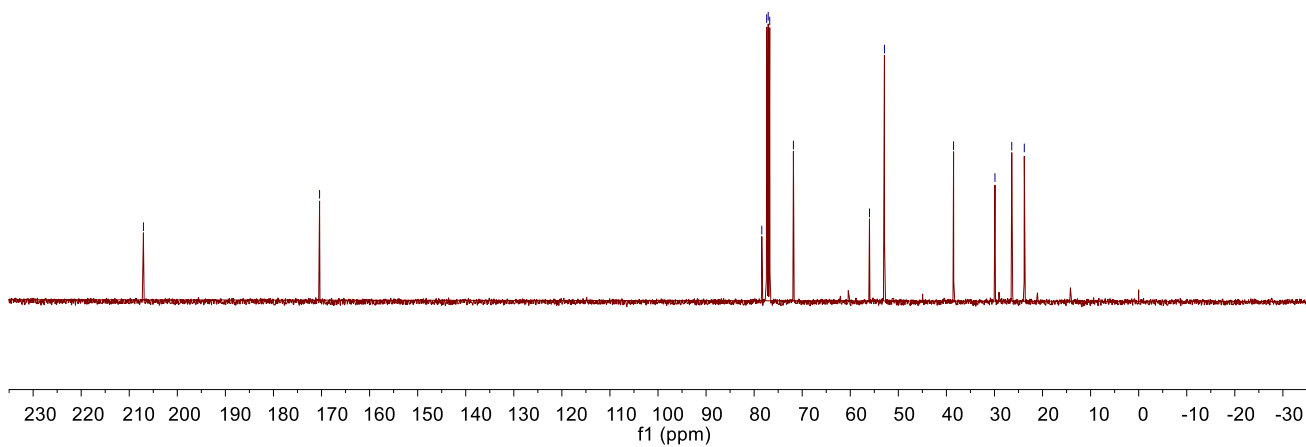


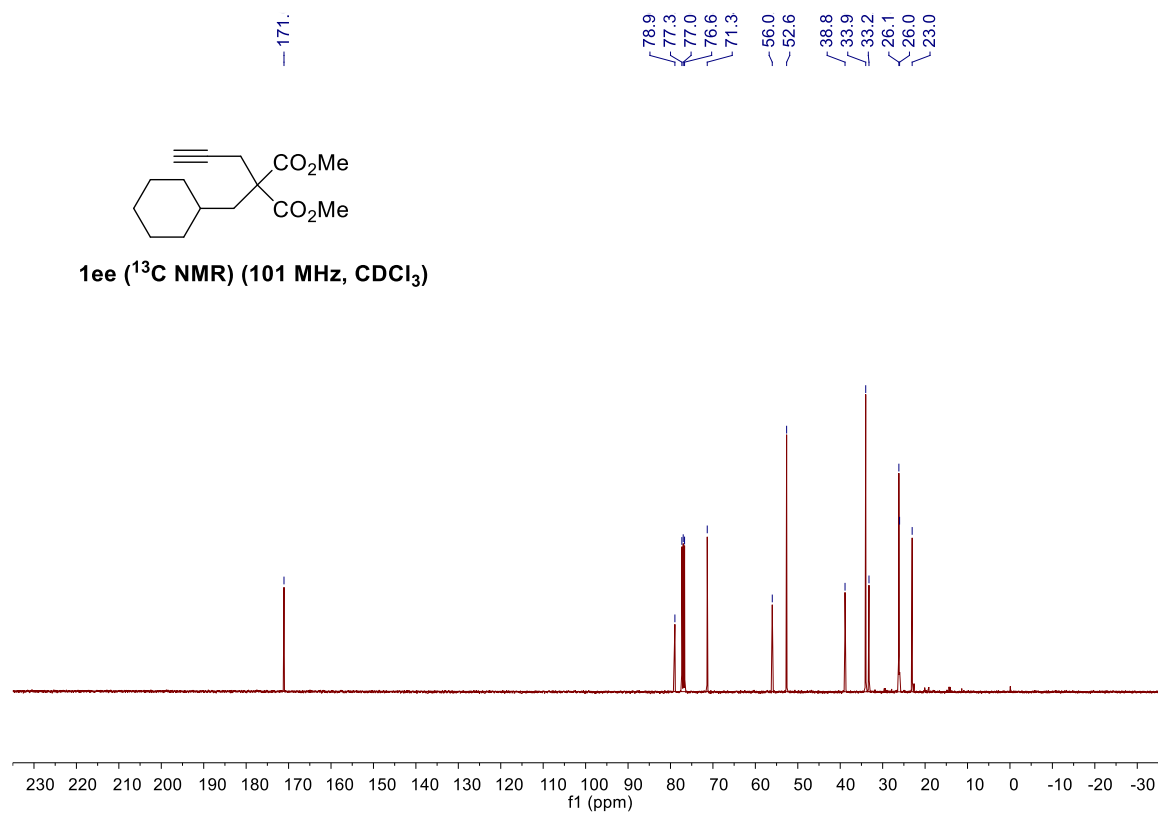
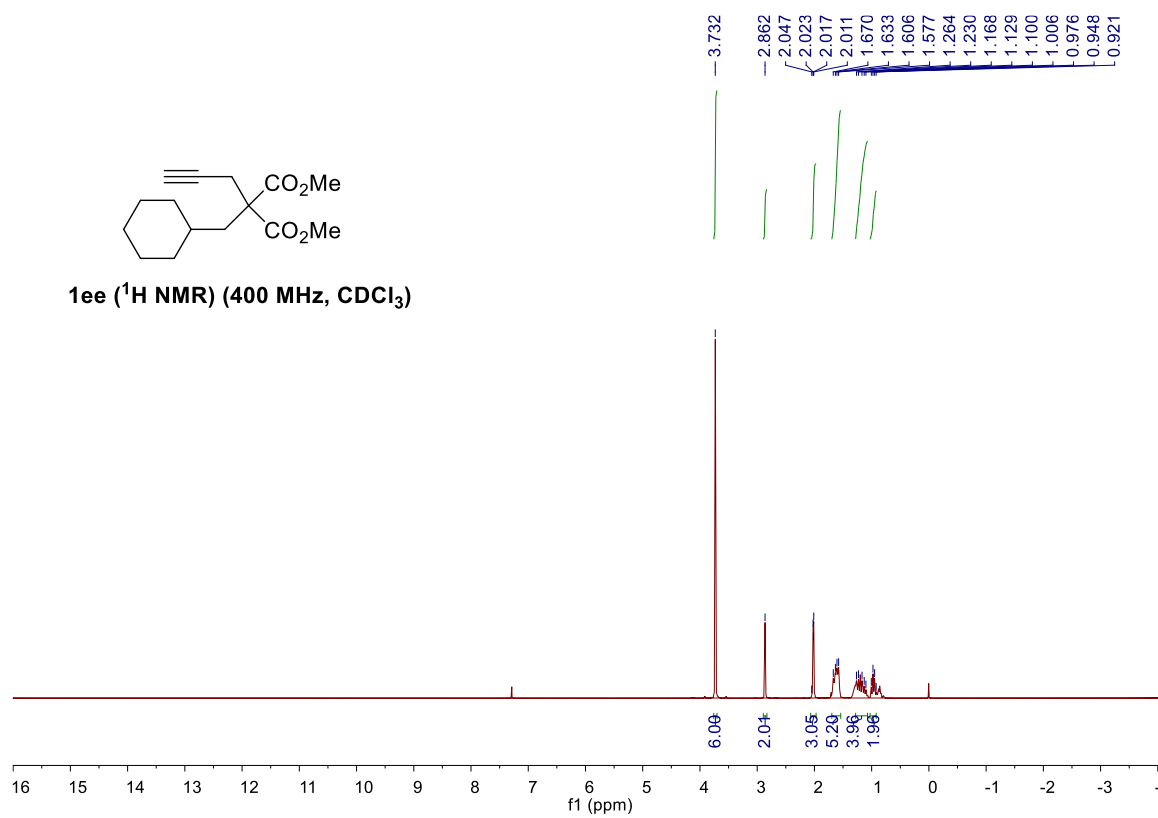


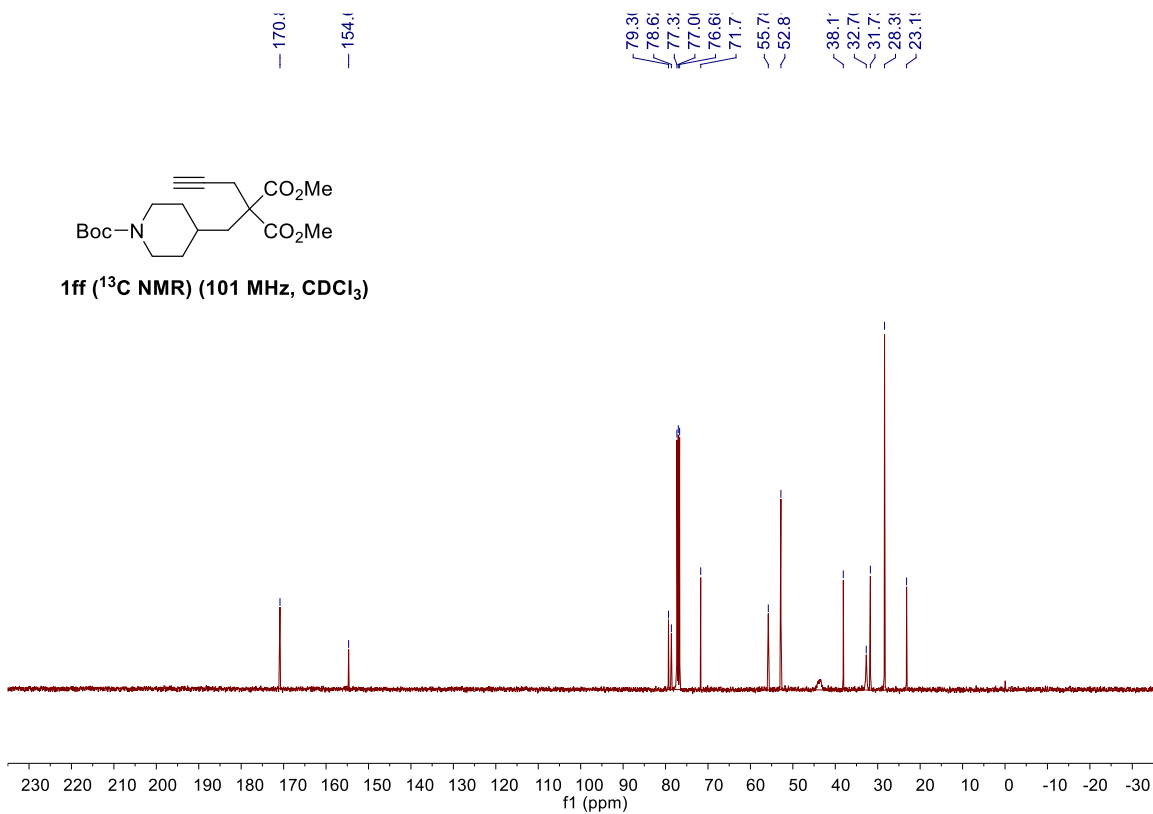
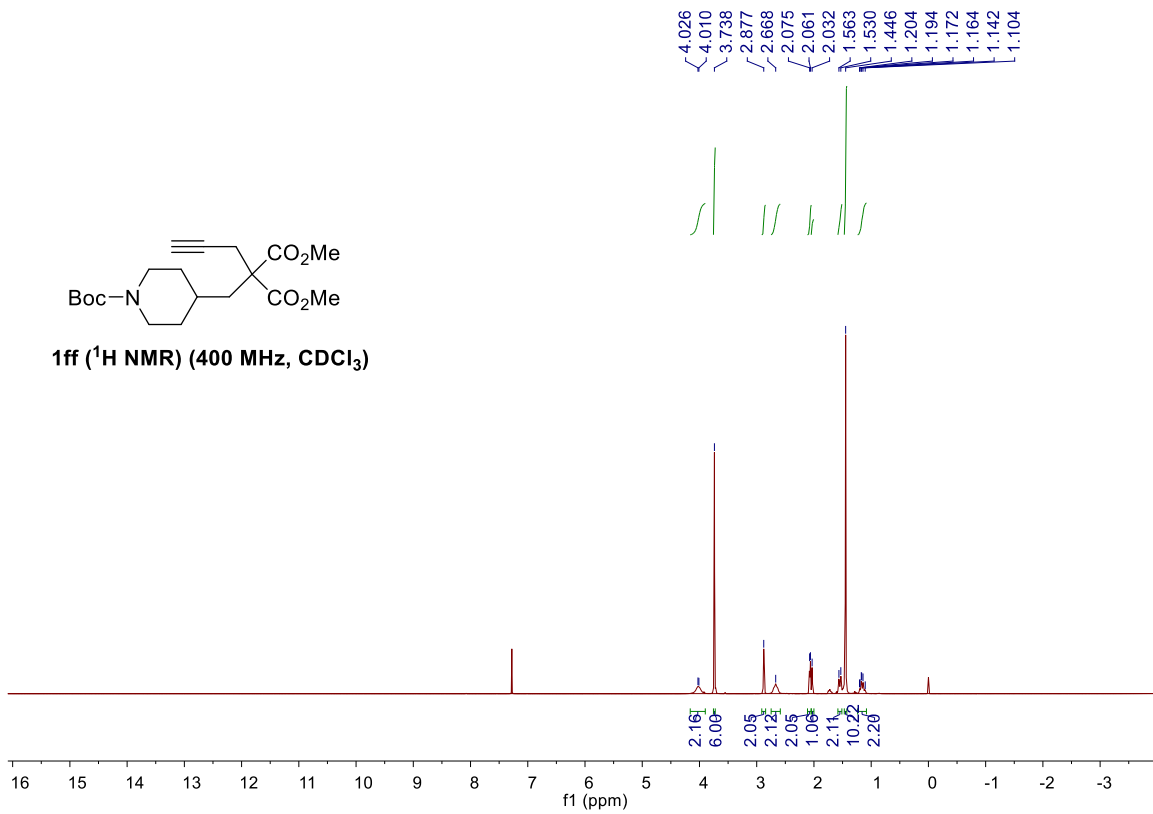
1z (<sup>1</sup>H NMR) (400 MHz, CDCl<sub>3</sub>)

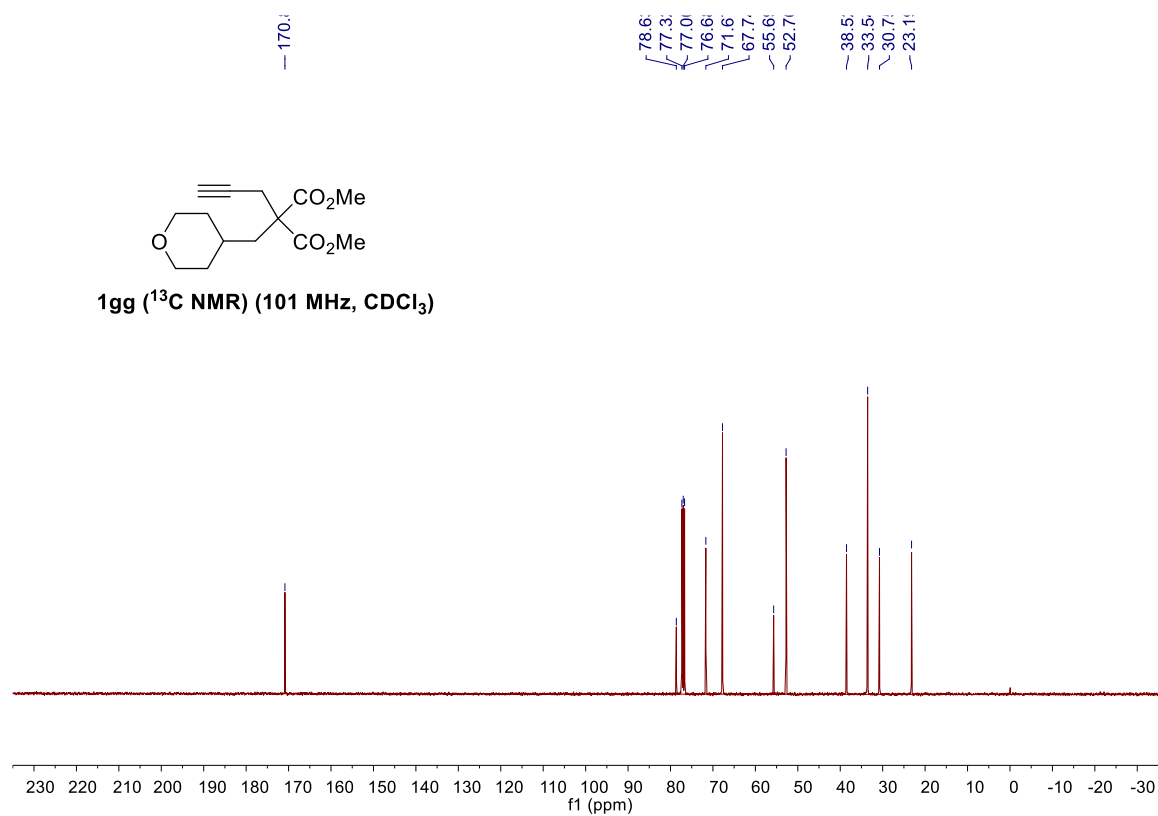
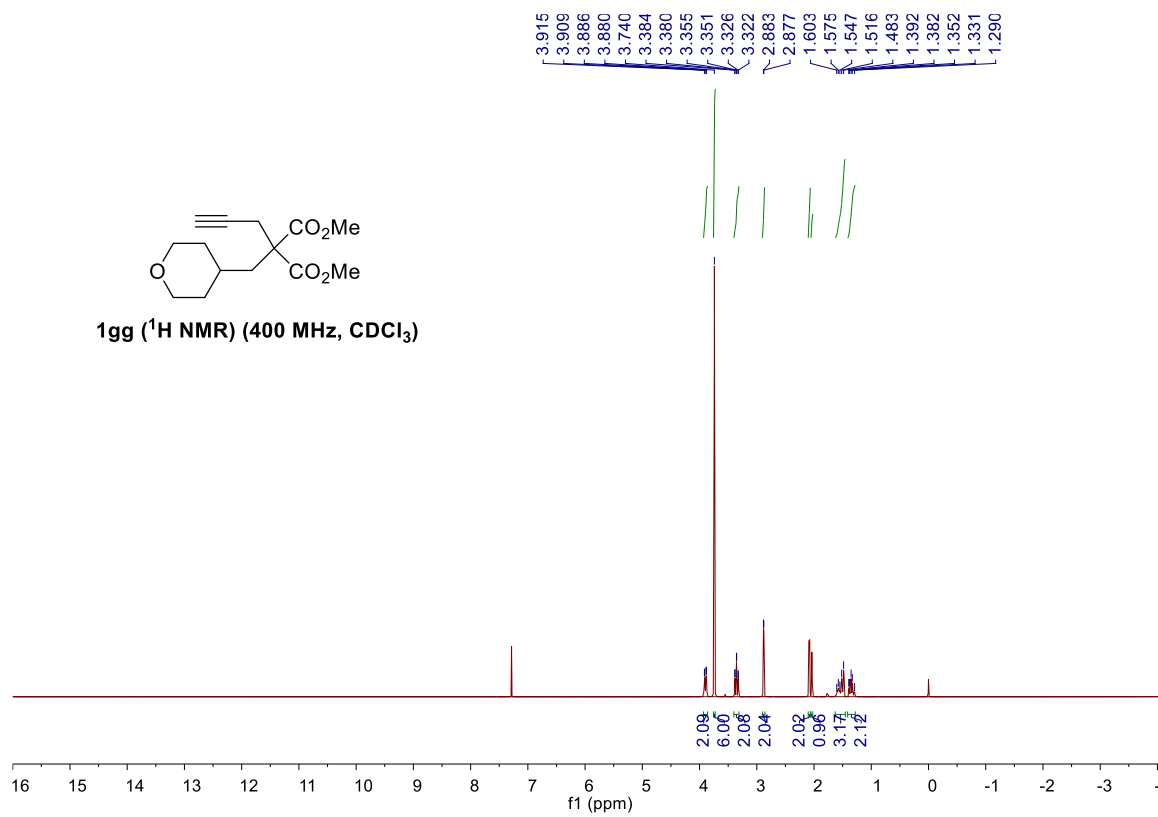


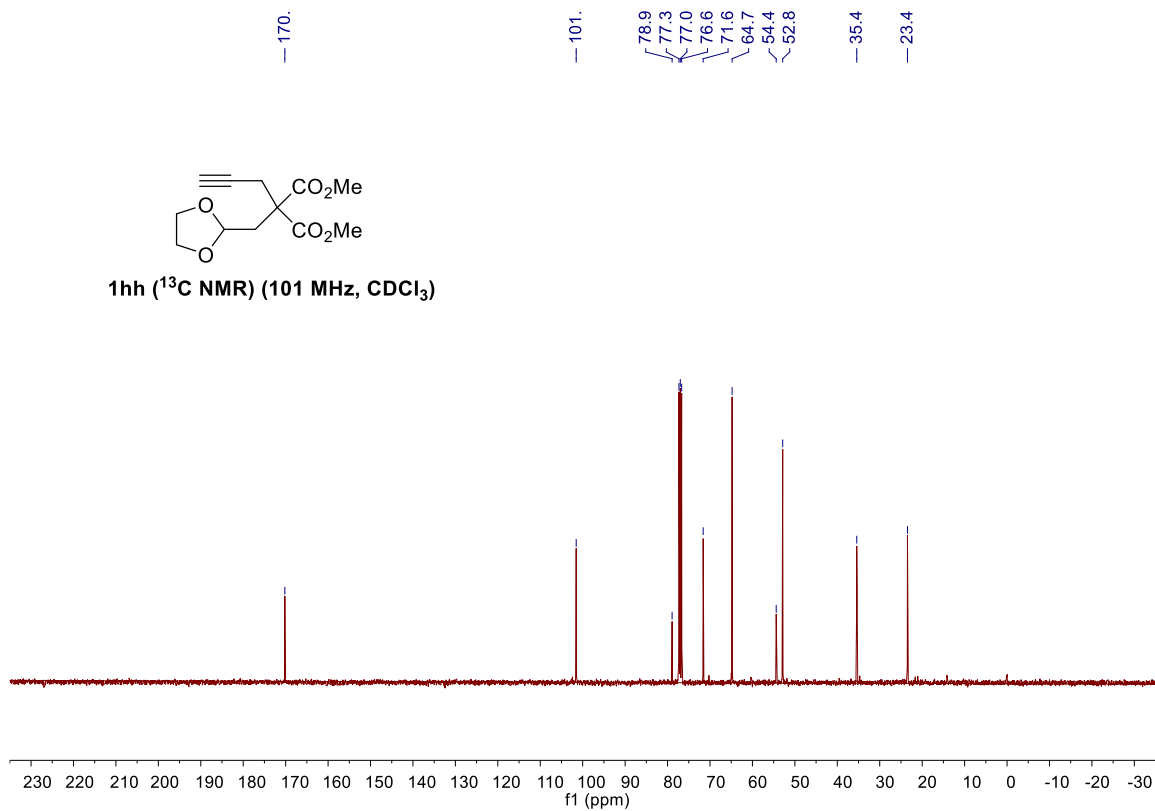
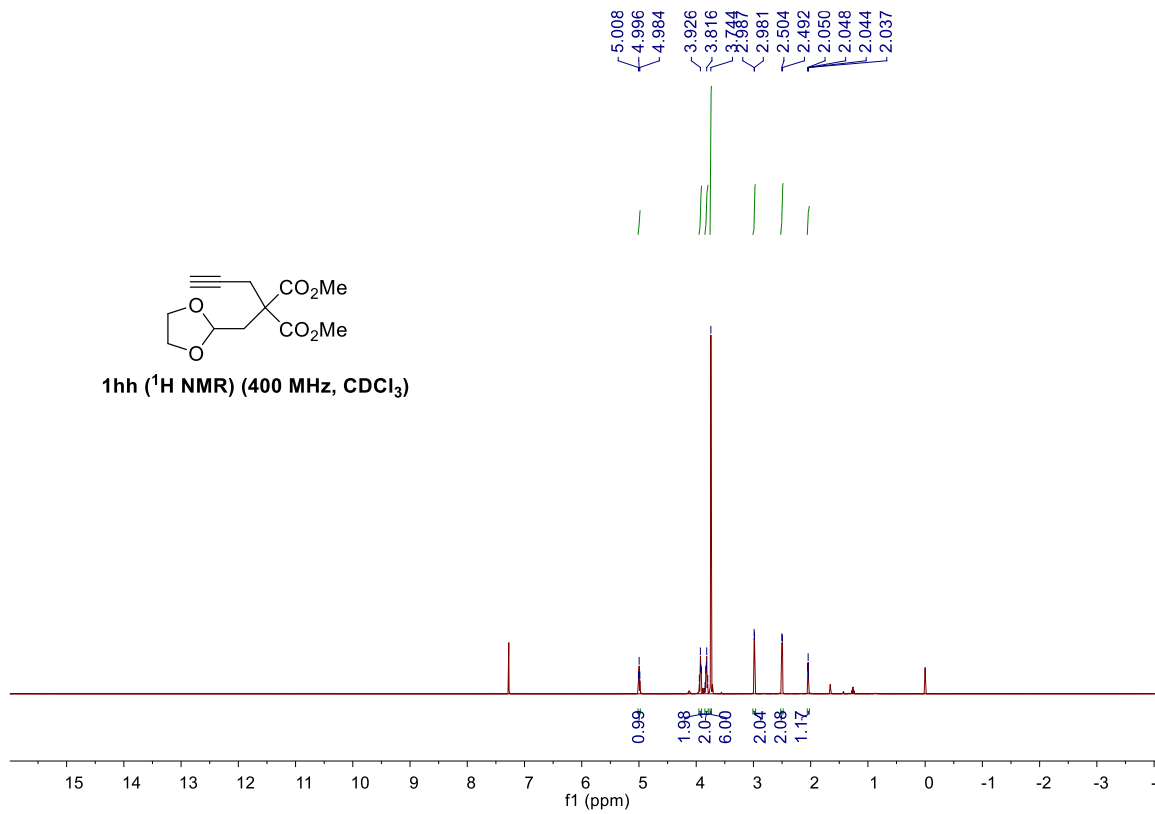
1z (<sup>13</sup>C NMR) (101 MHz, CDCl<sub>3</sub>)

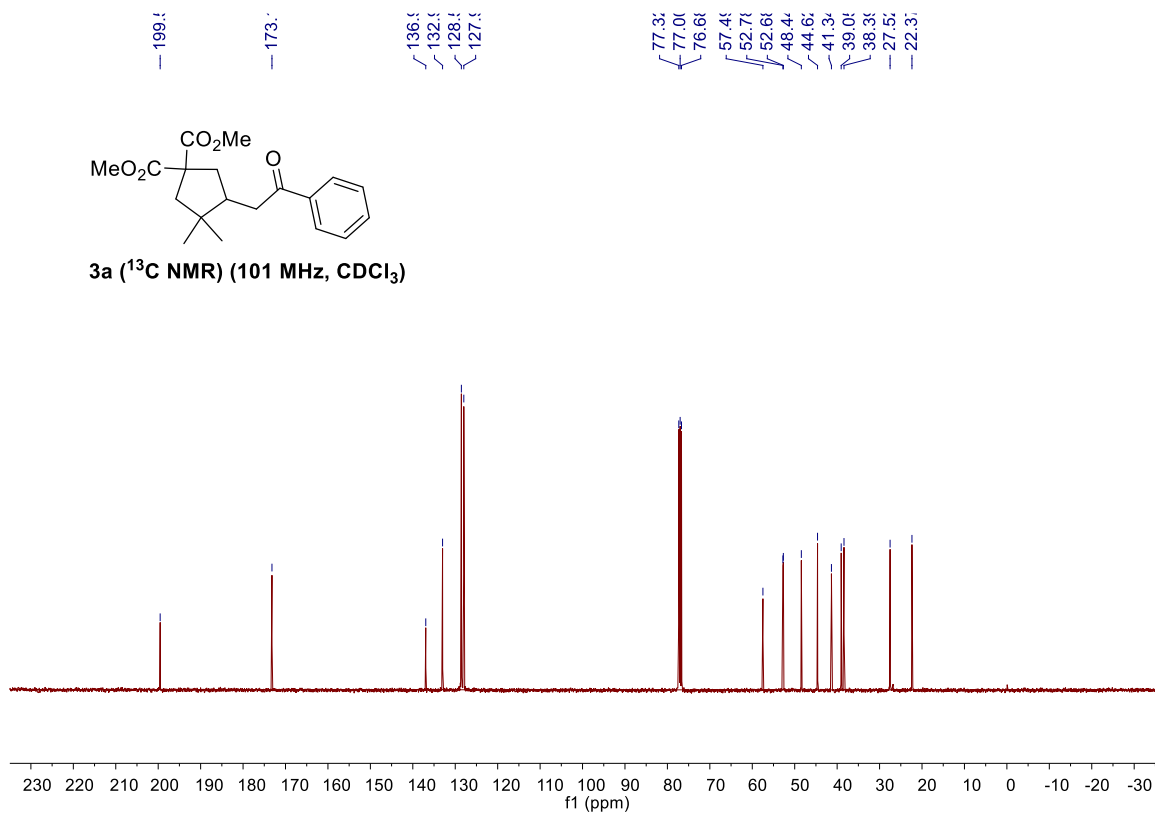
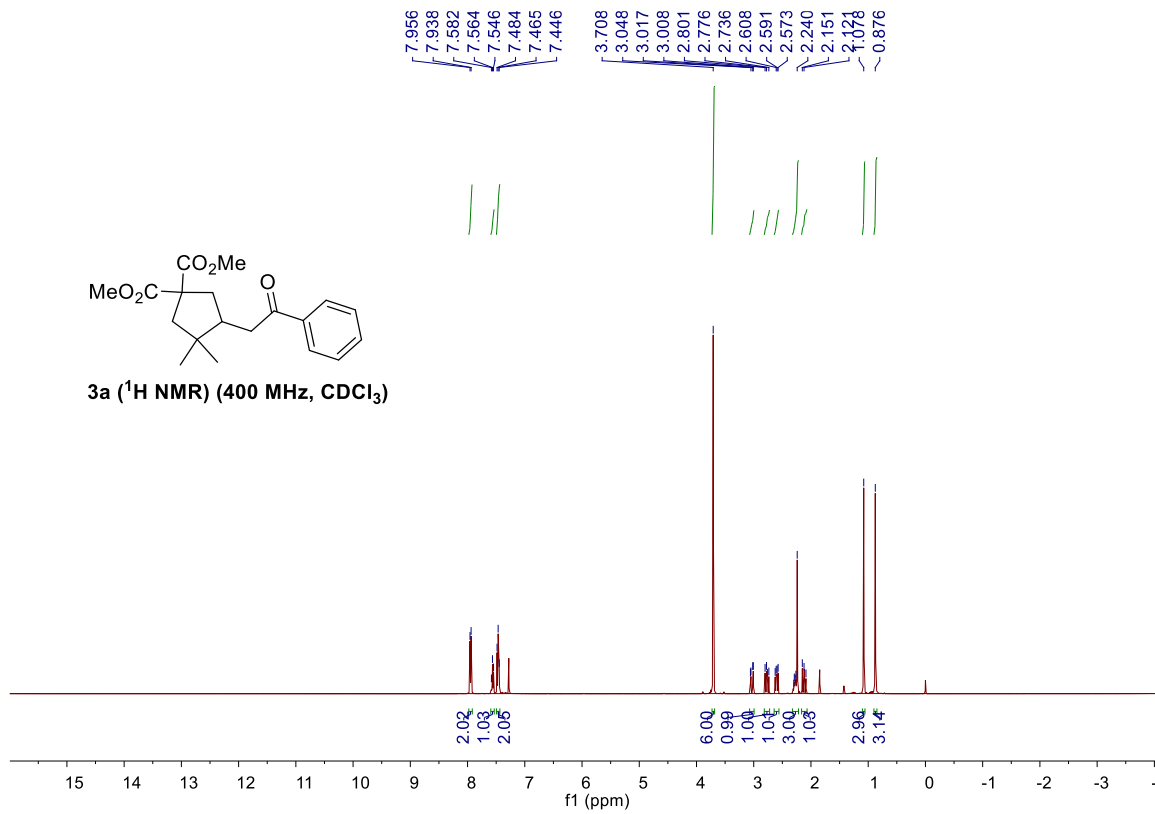




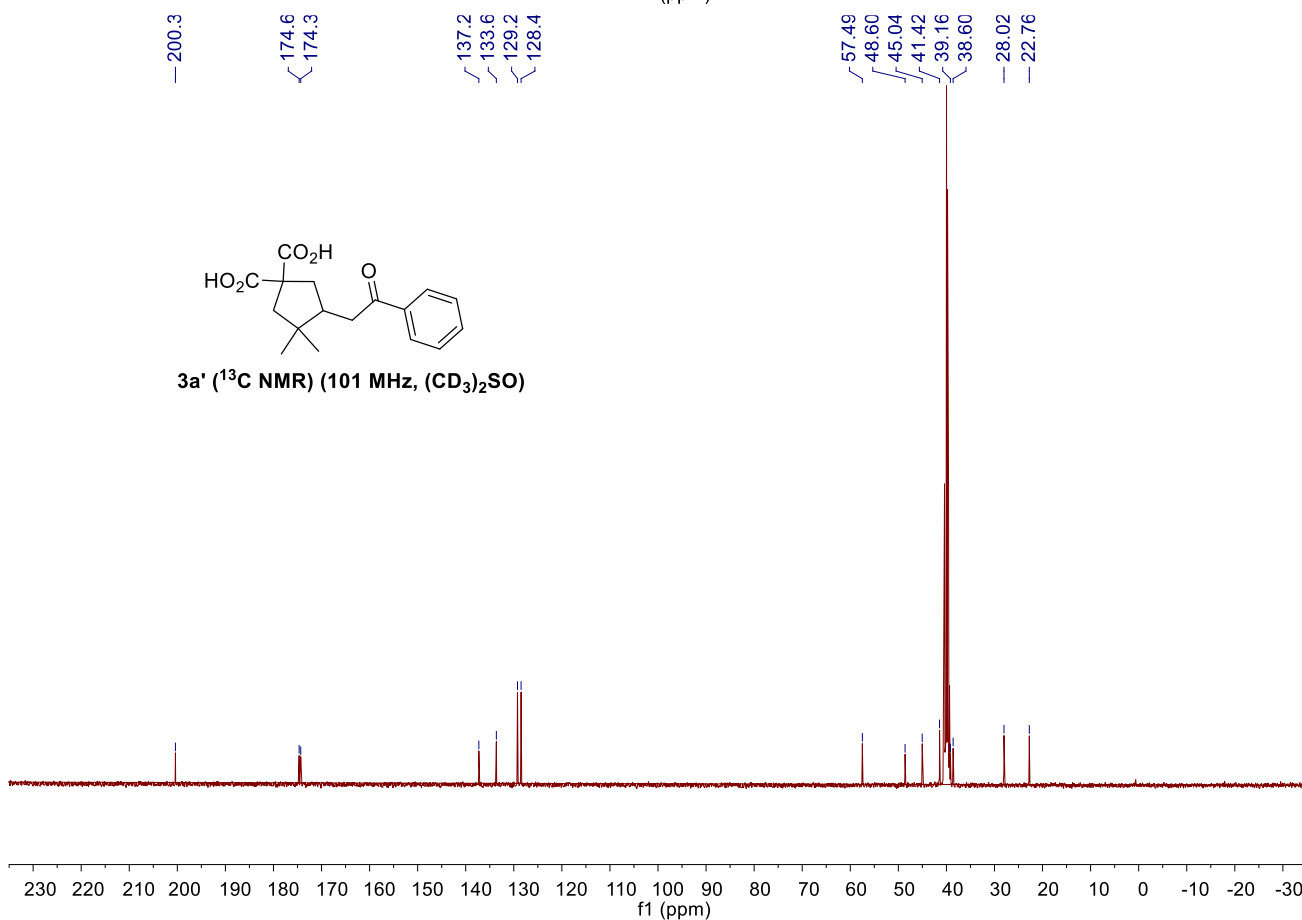
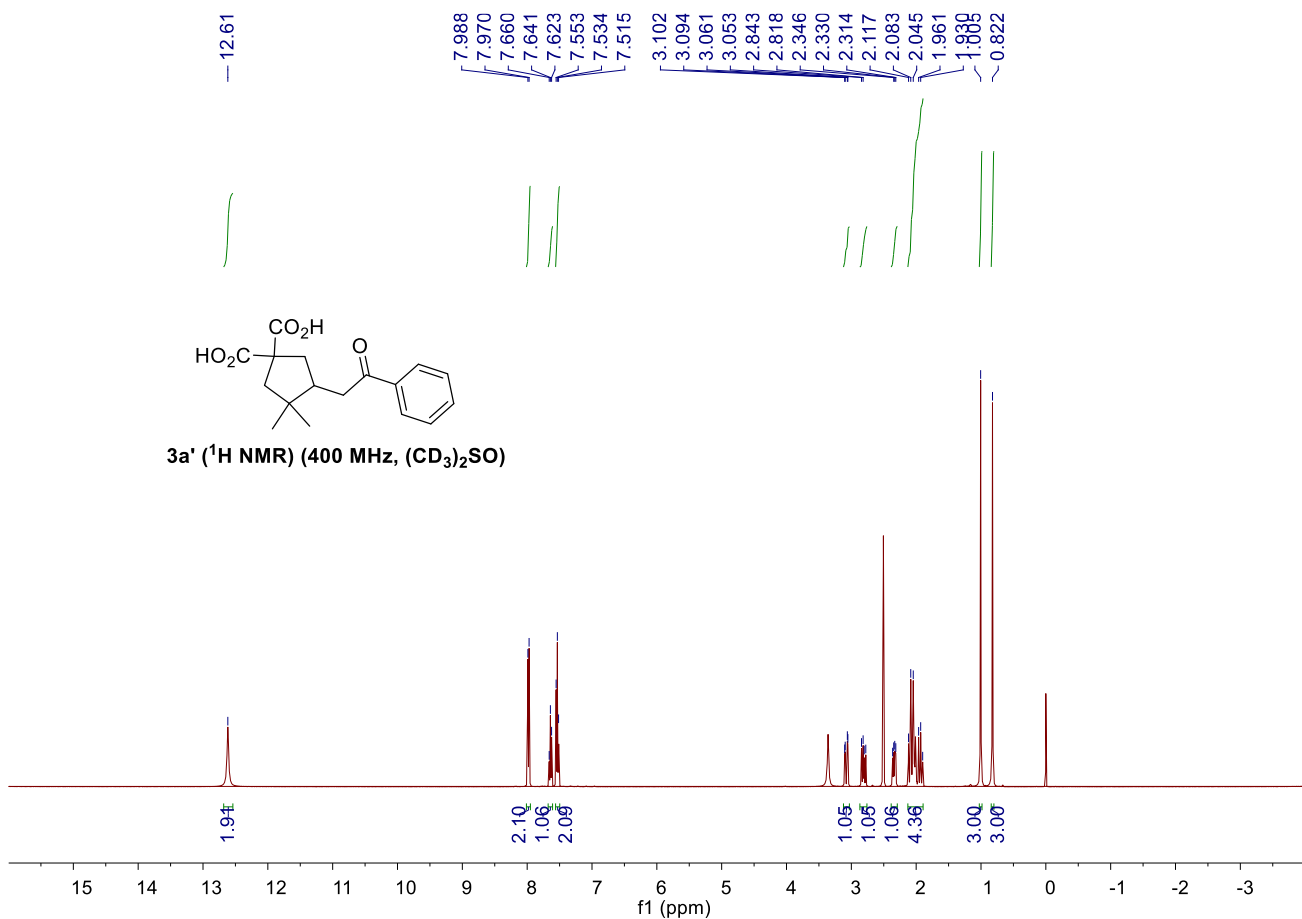


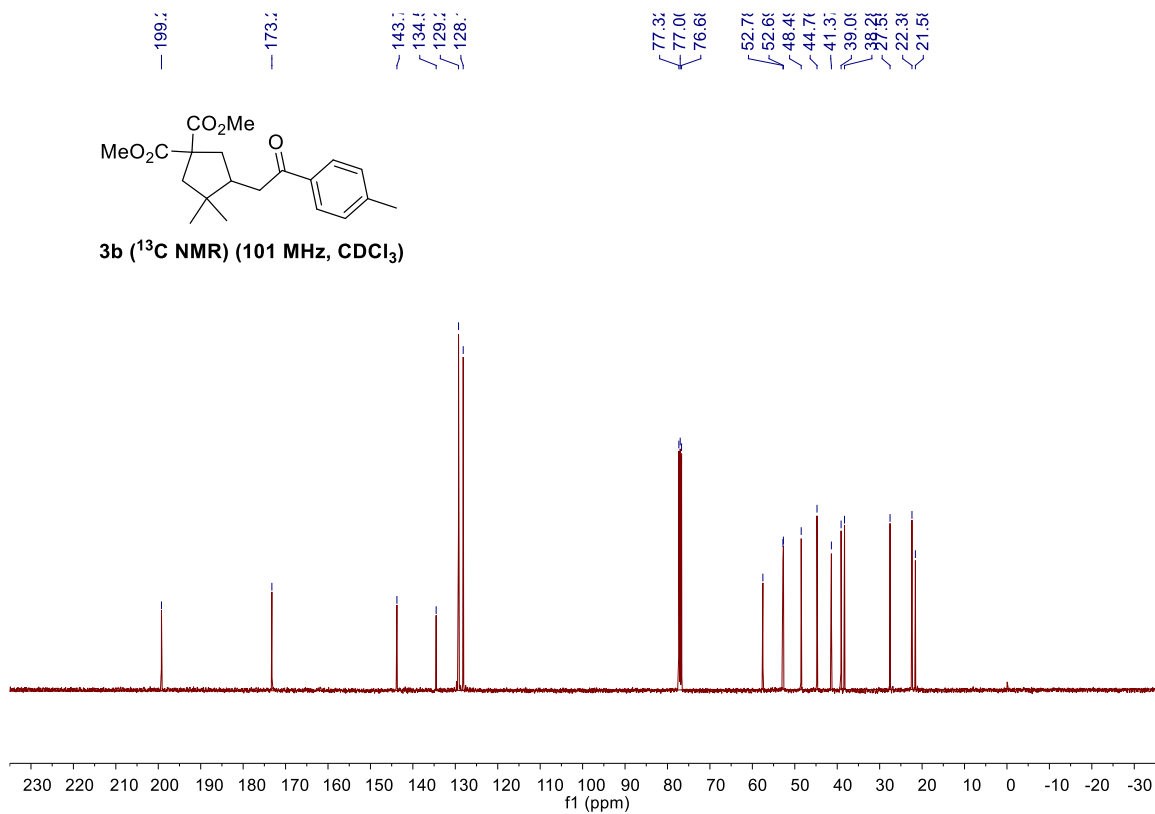
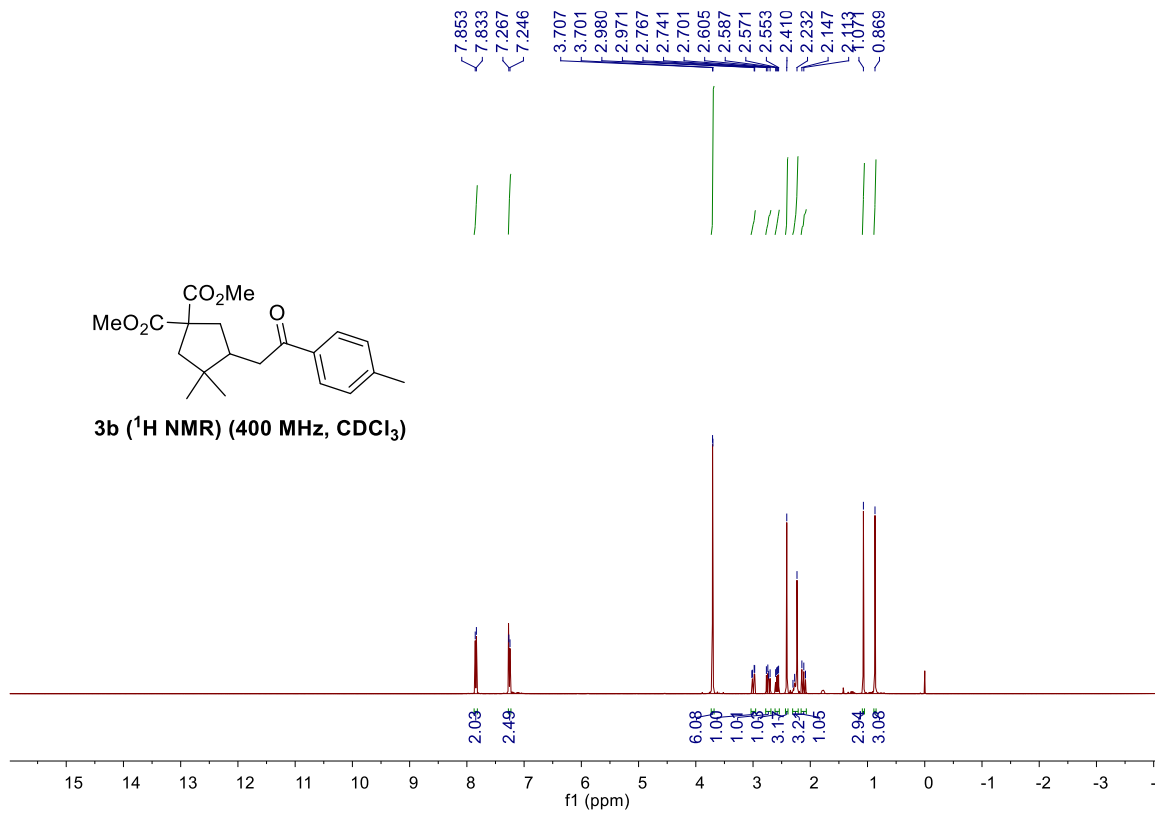


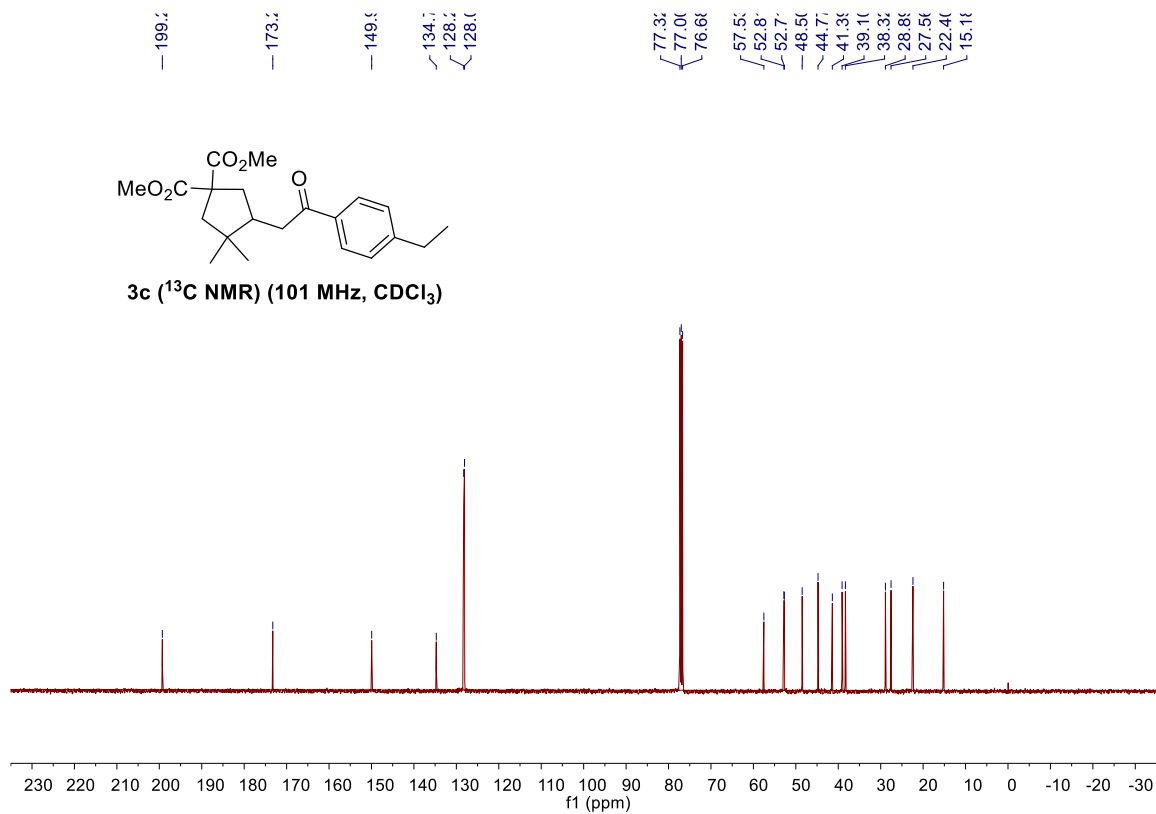
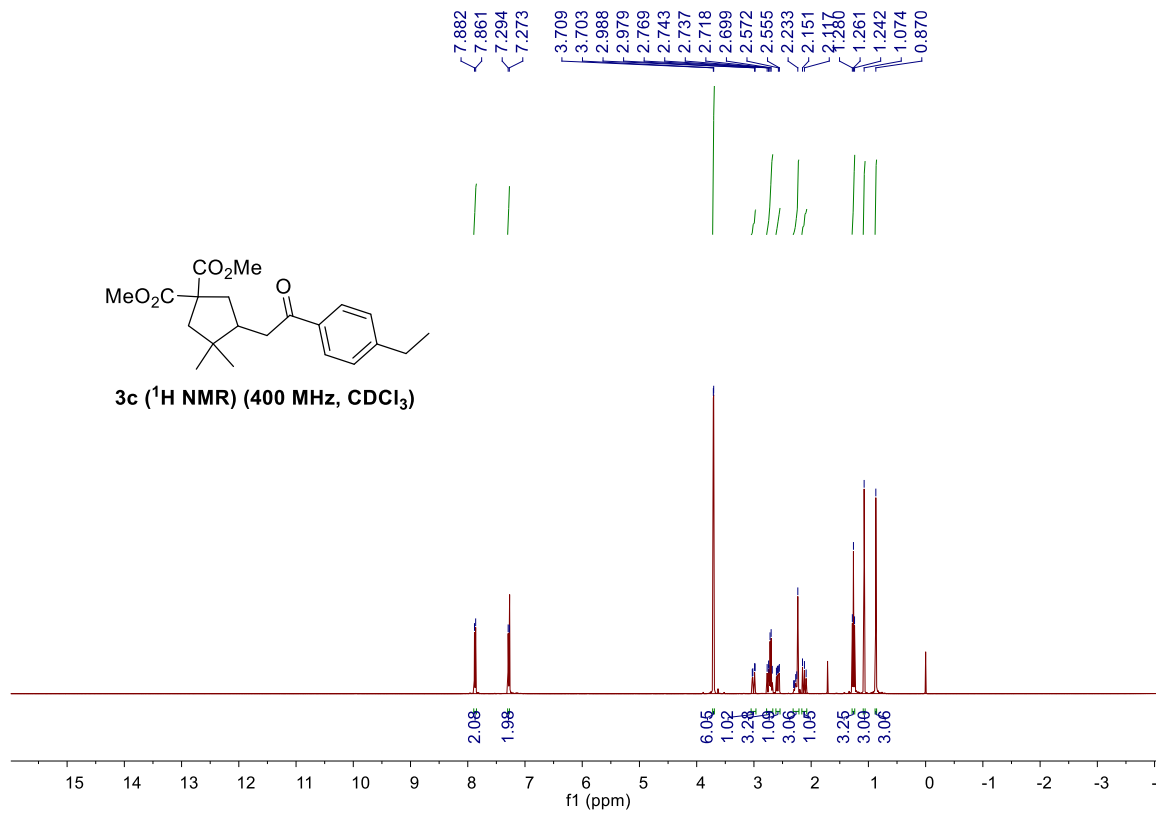


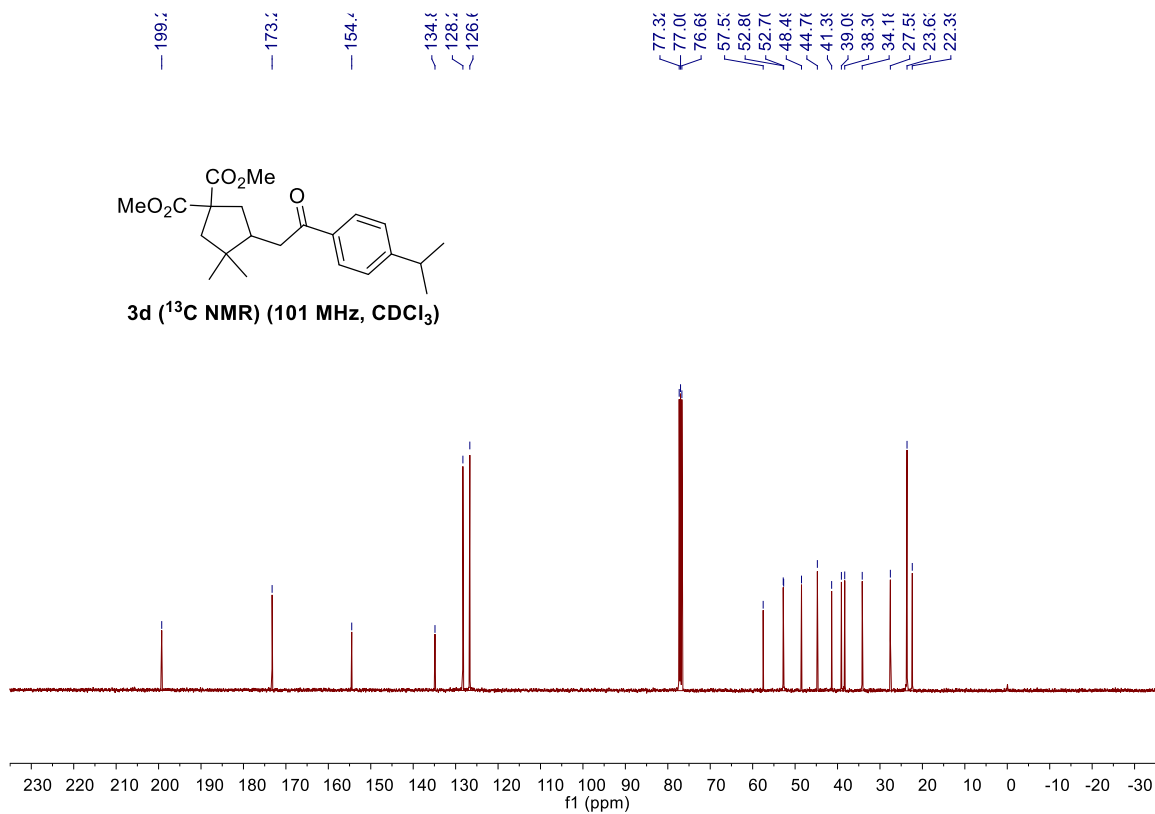
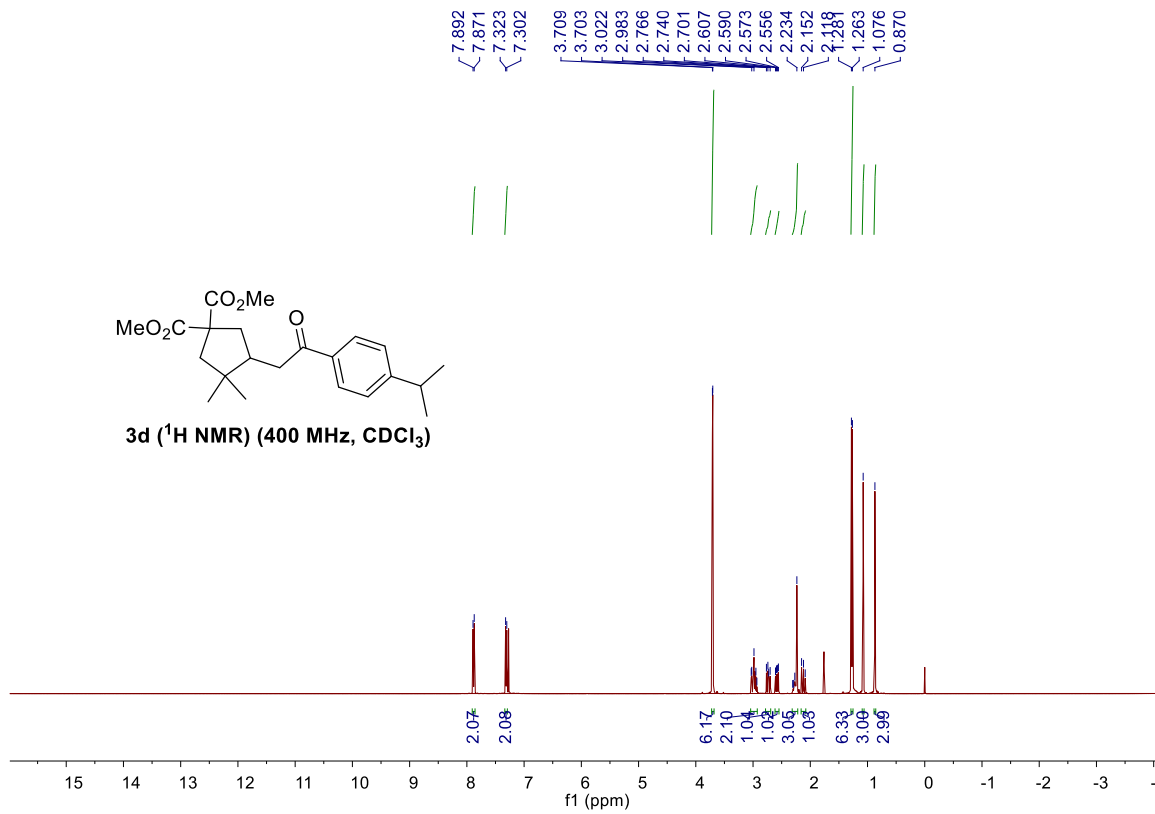


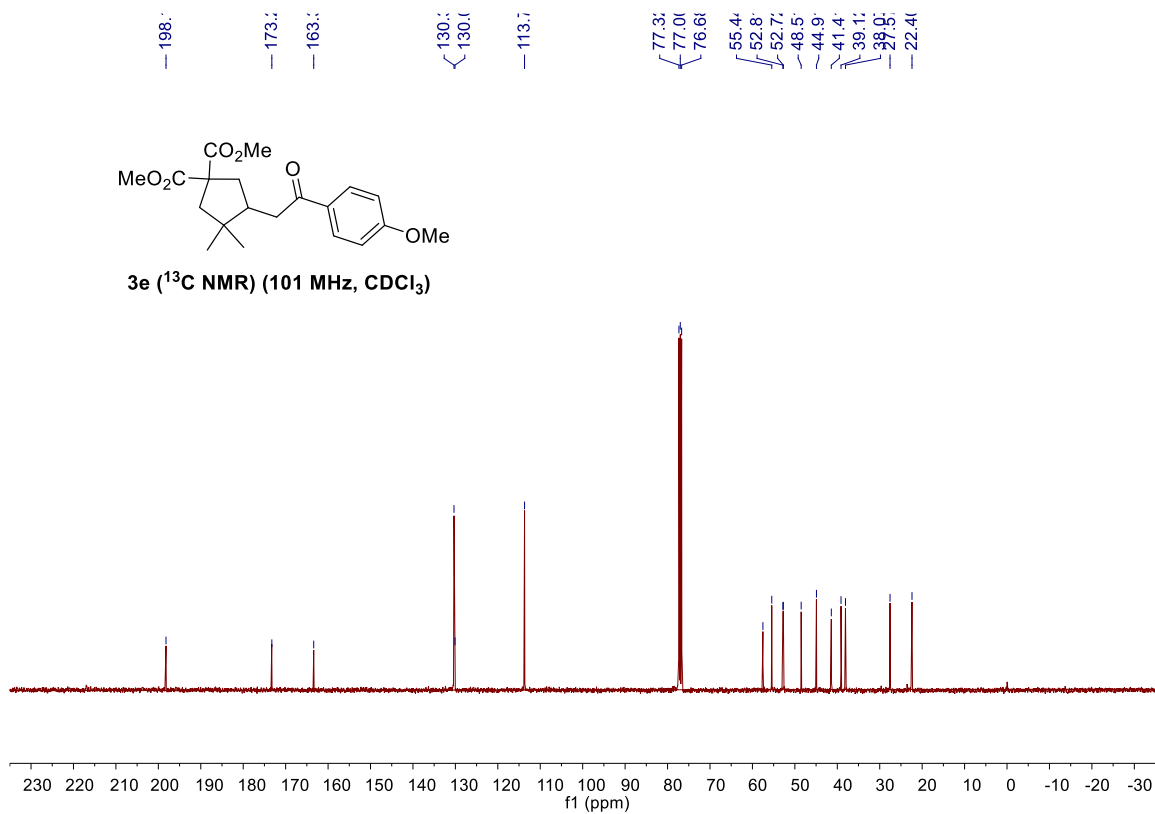
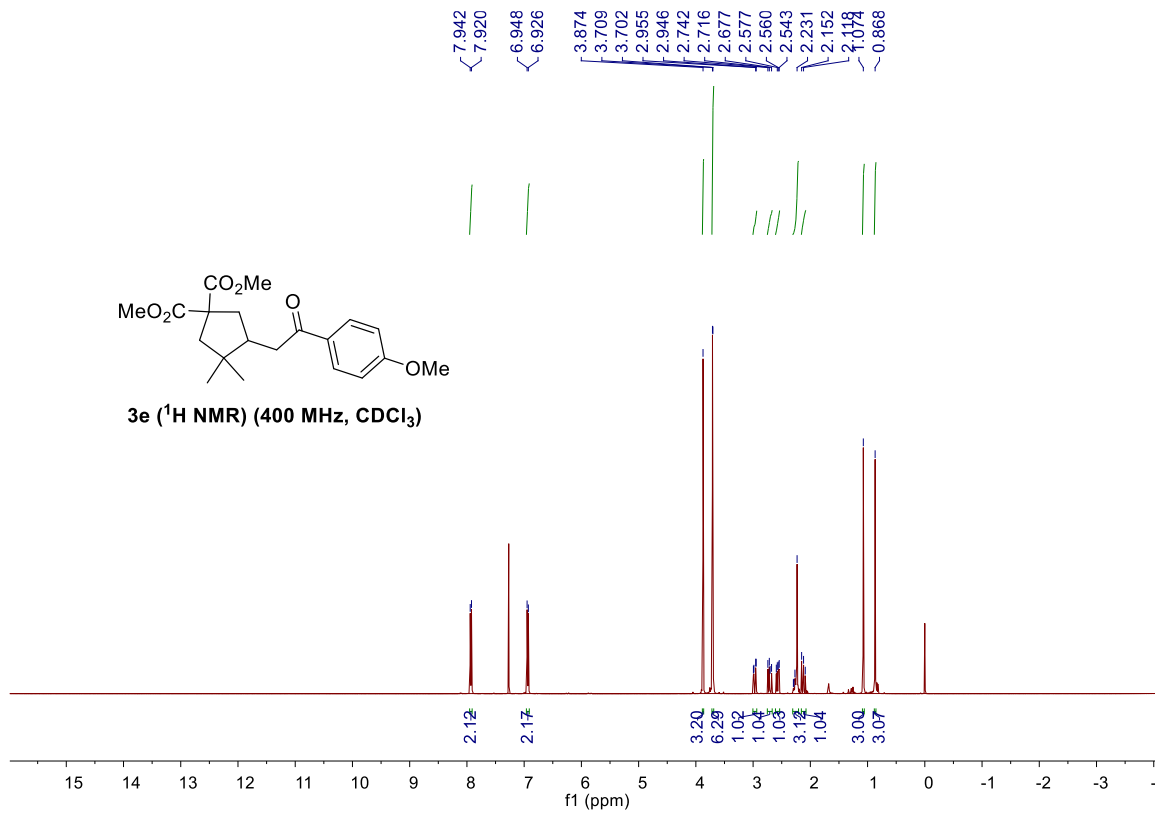


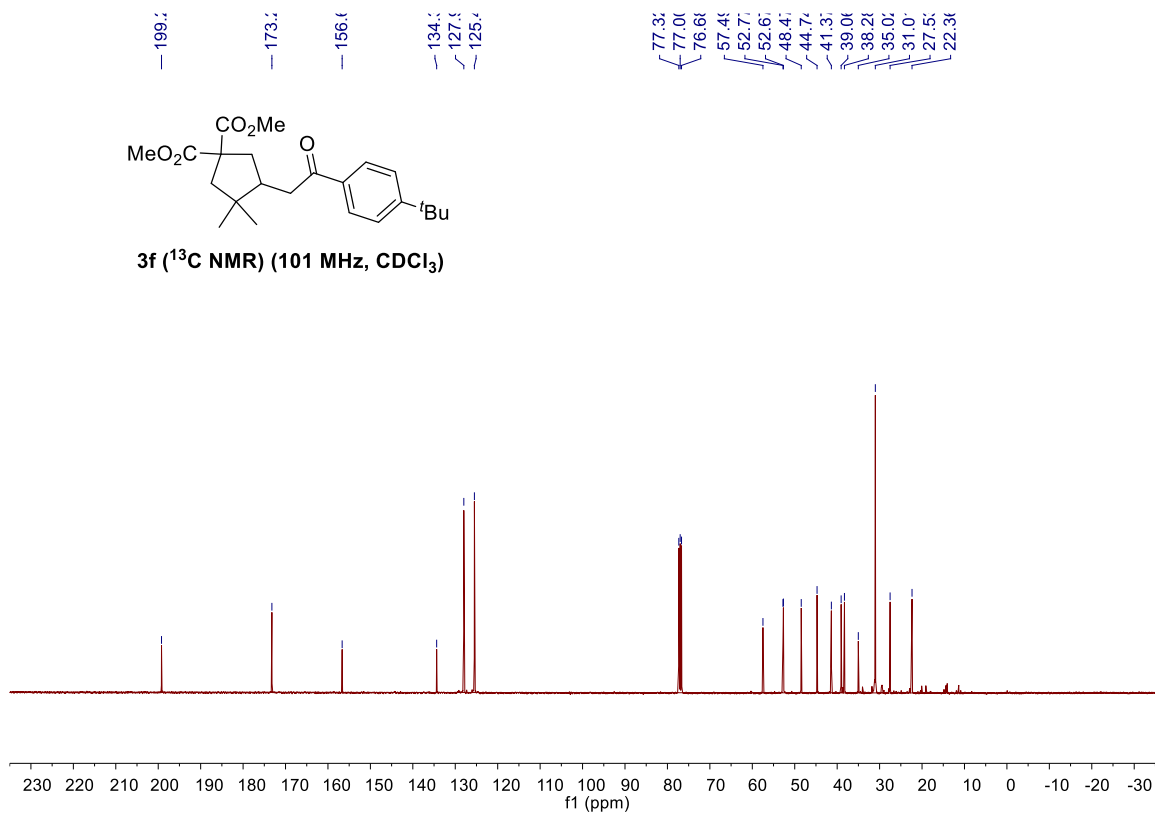
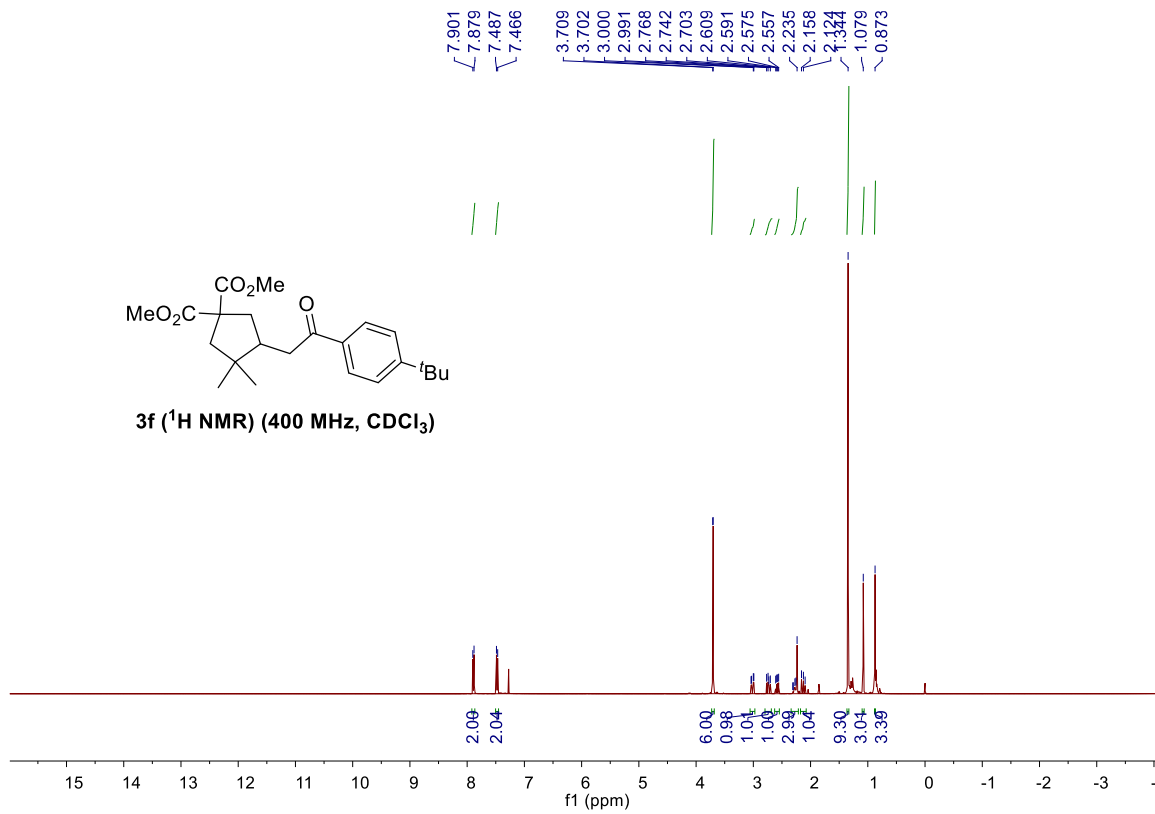


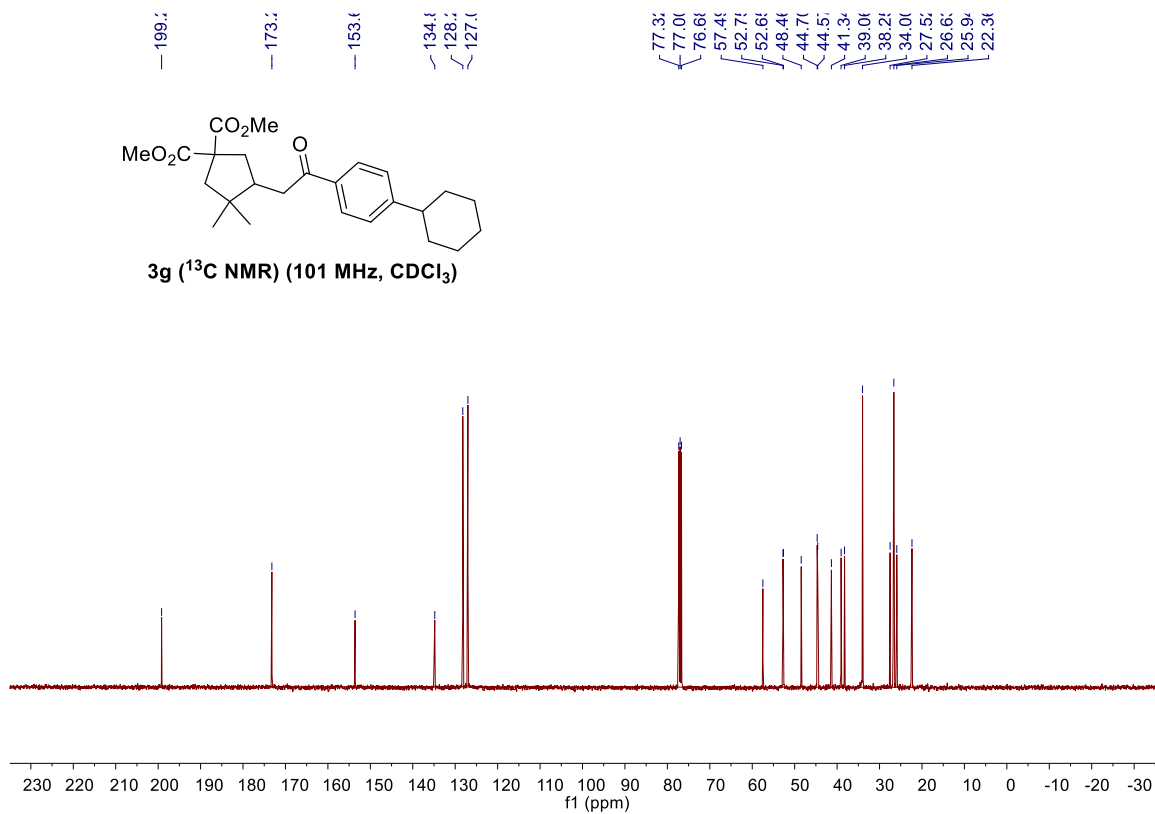
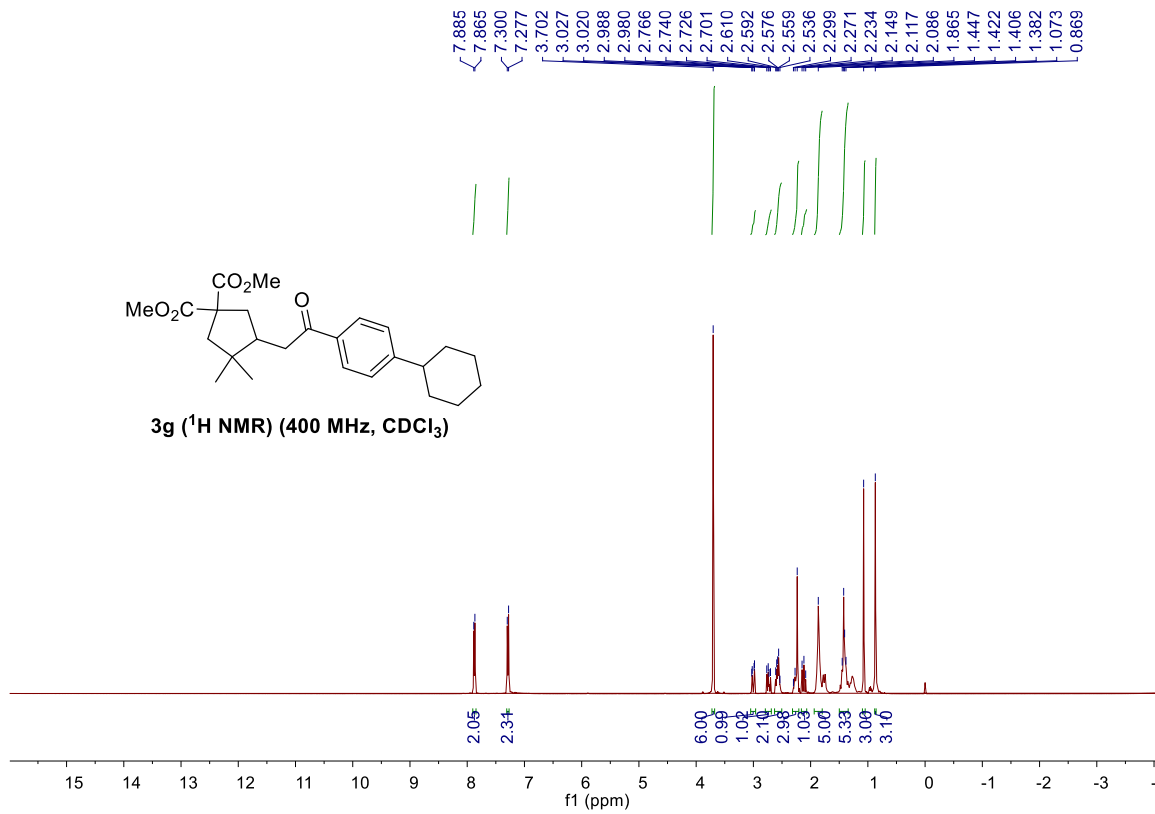


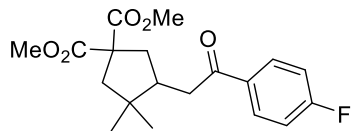
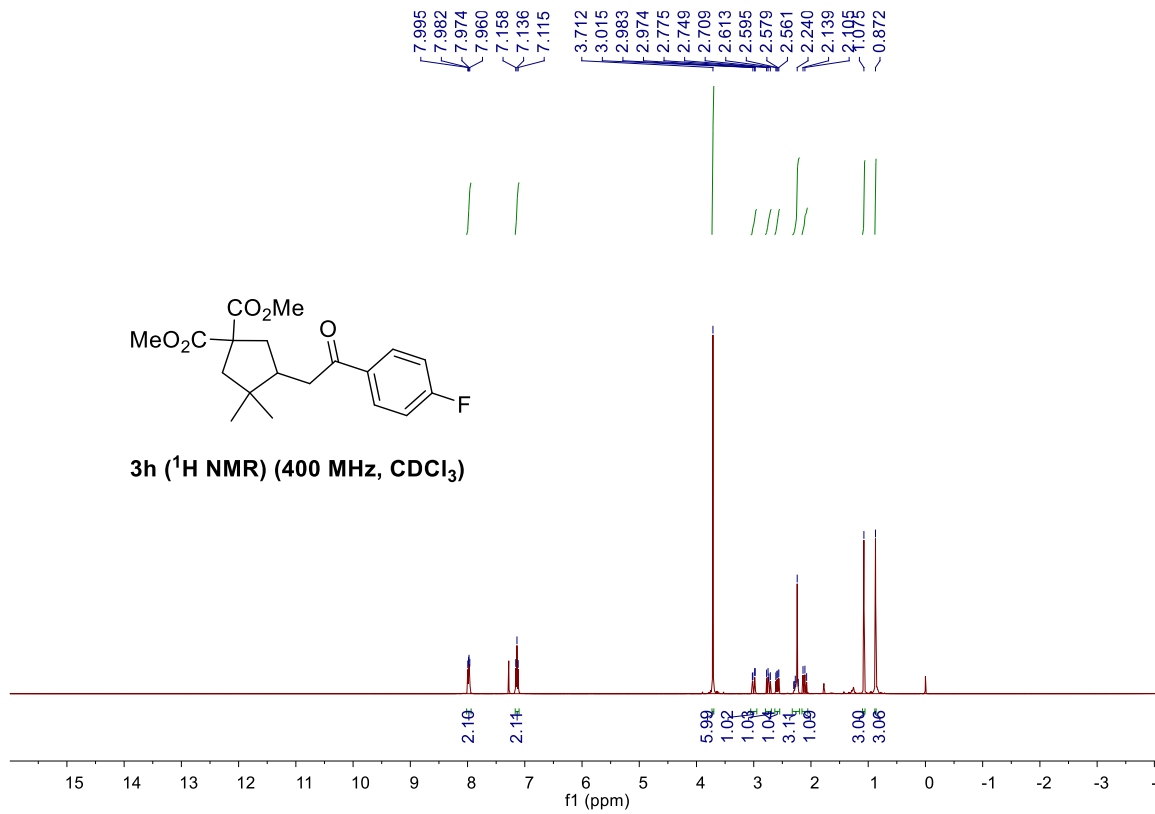




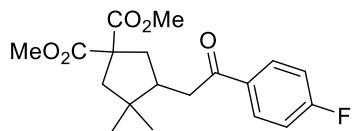
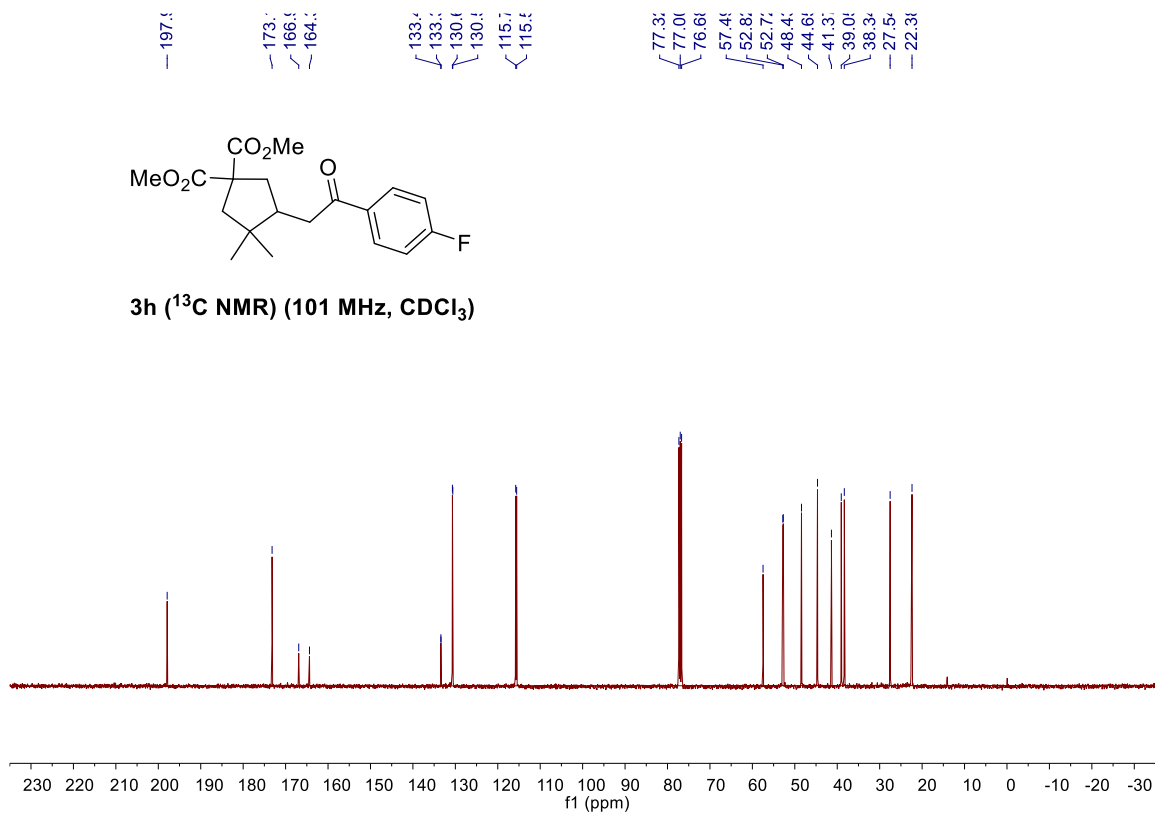








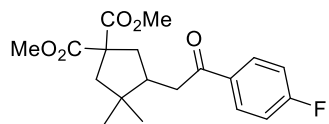
3h (<sup>1</sup>H NMR) (400 MHz, CDCl<sub>3</sub>)



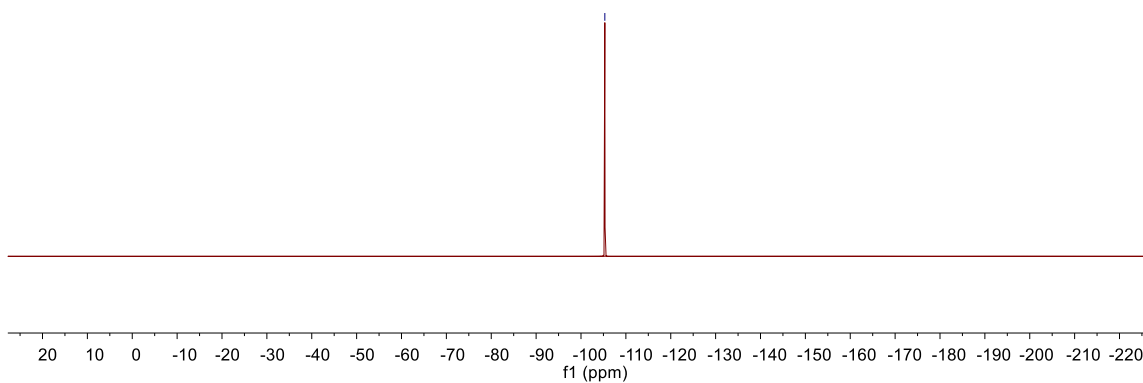
3h (<sup>13</sup>C NMR) (101 MHz, CDCl<sub>3</sub>)

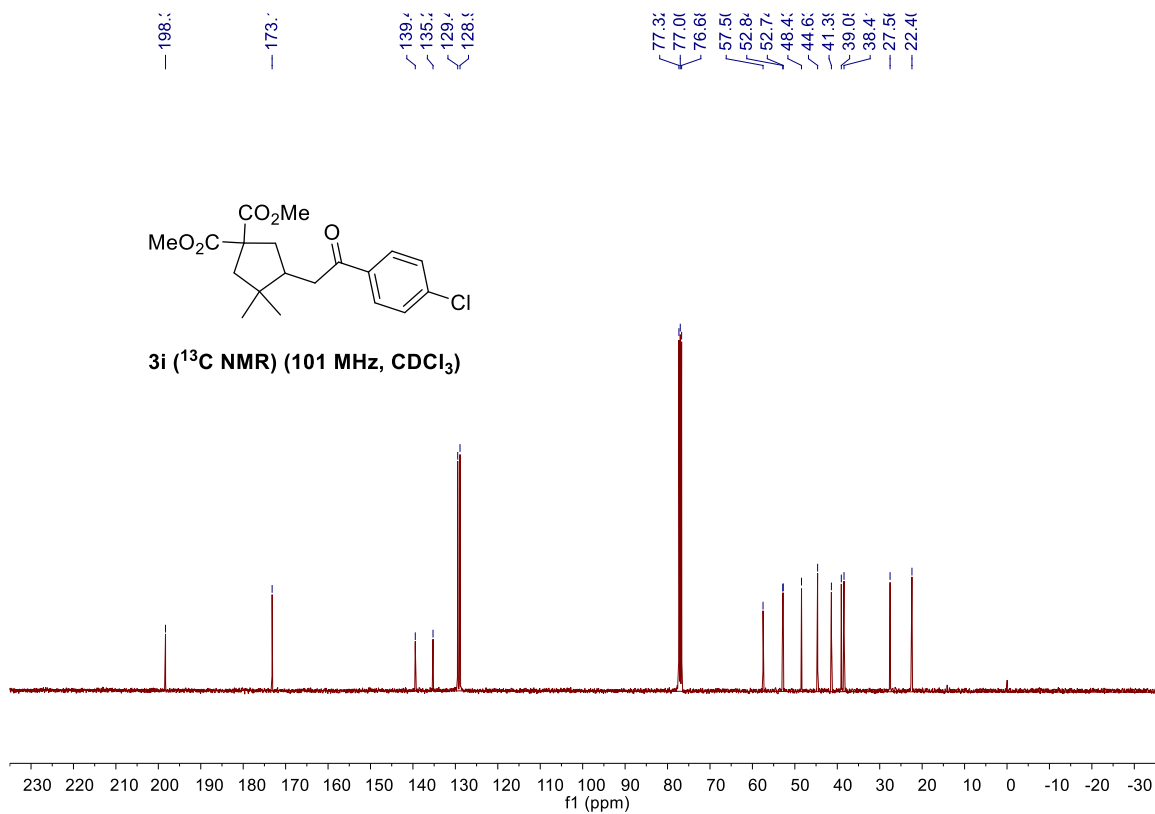
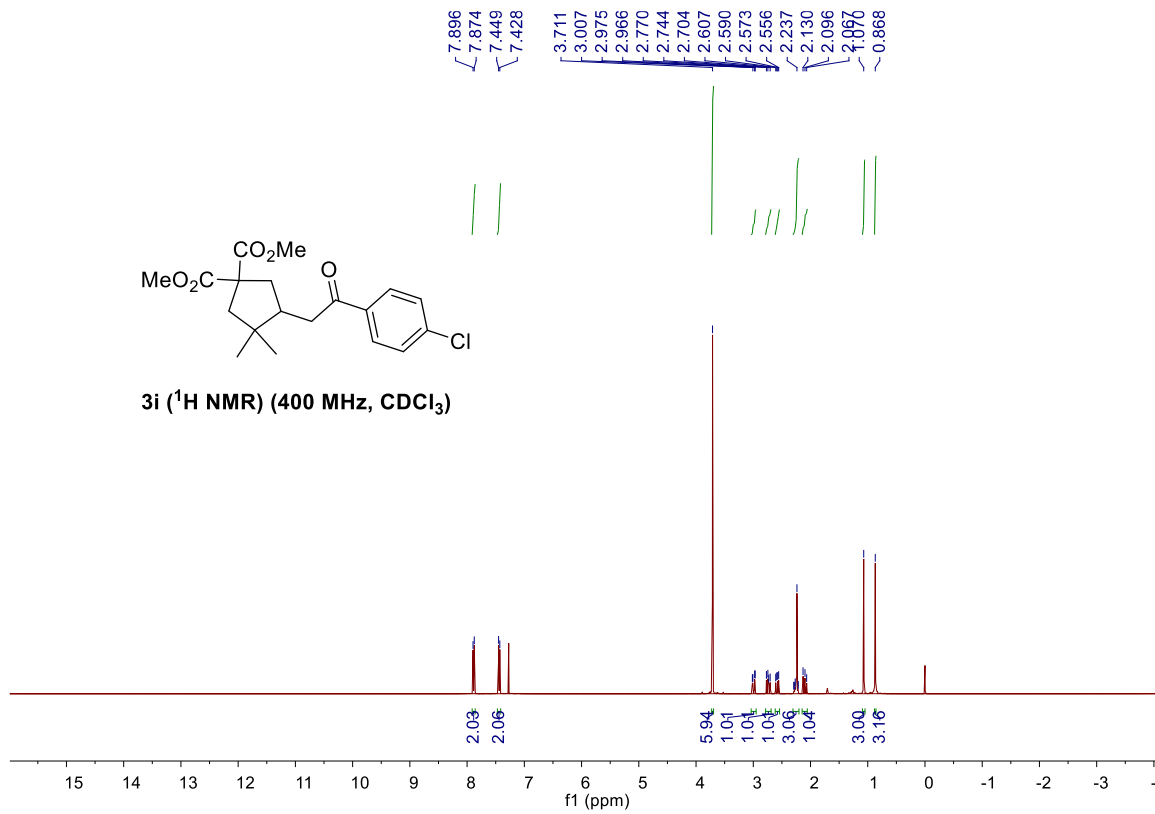


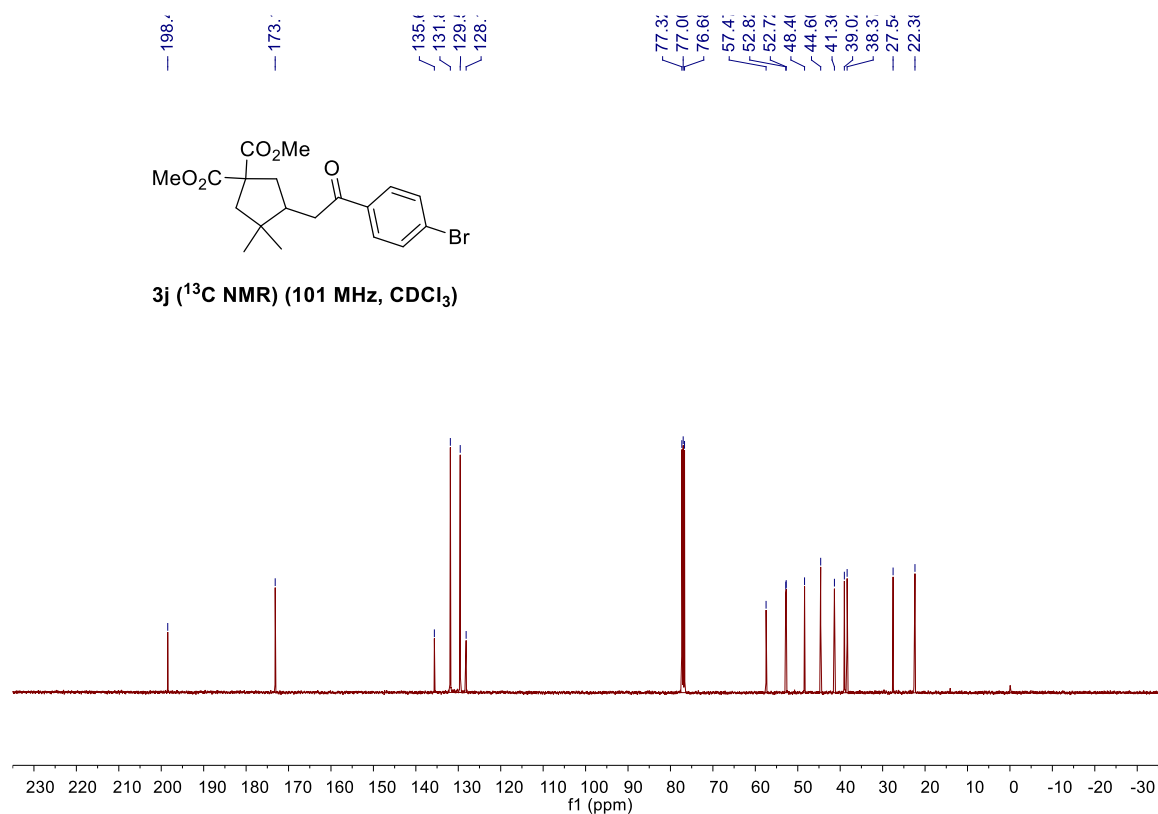
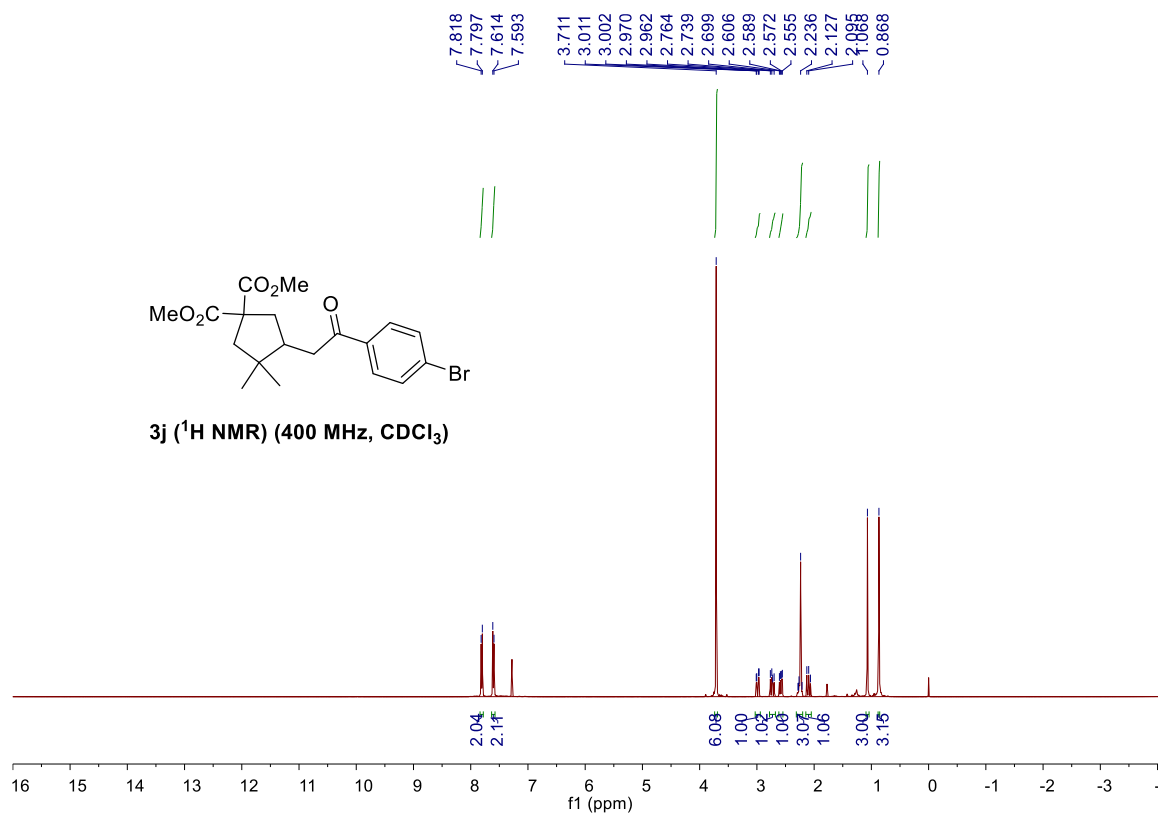
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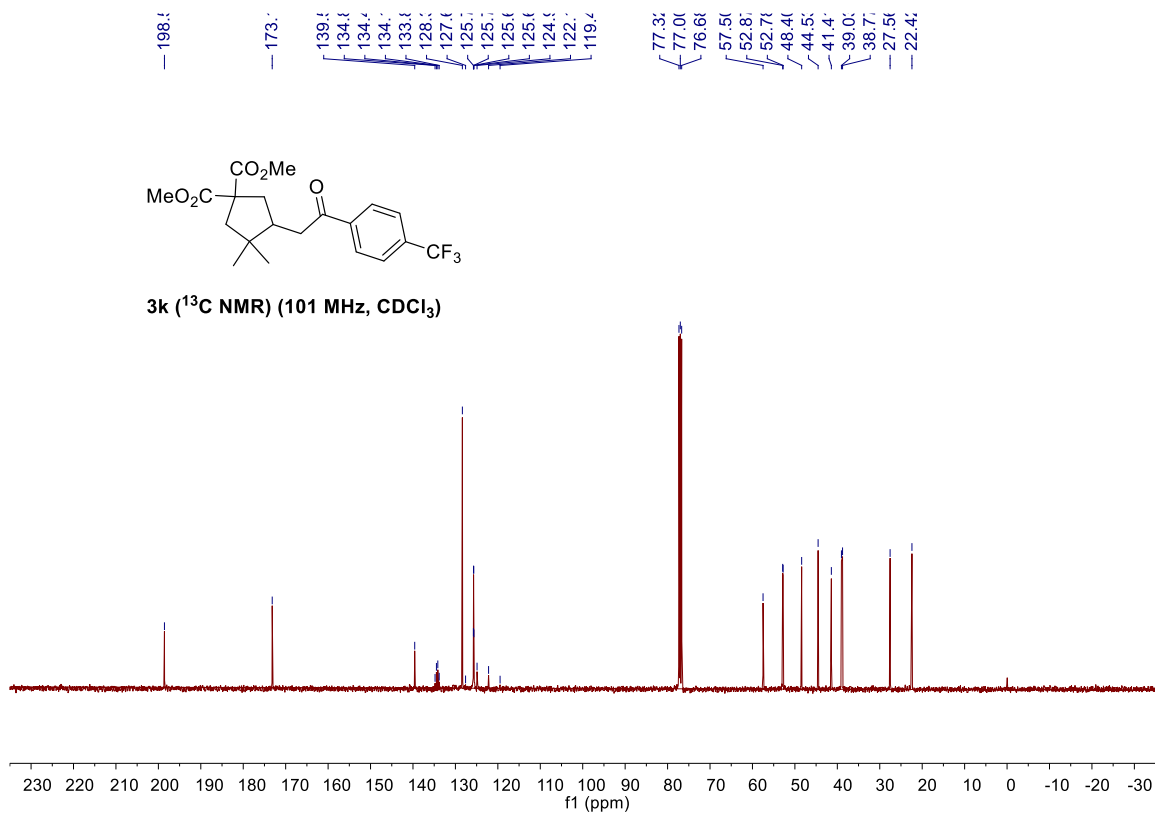
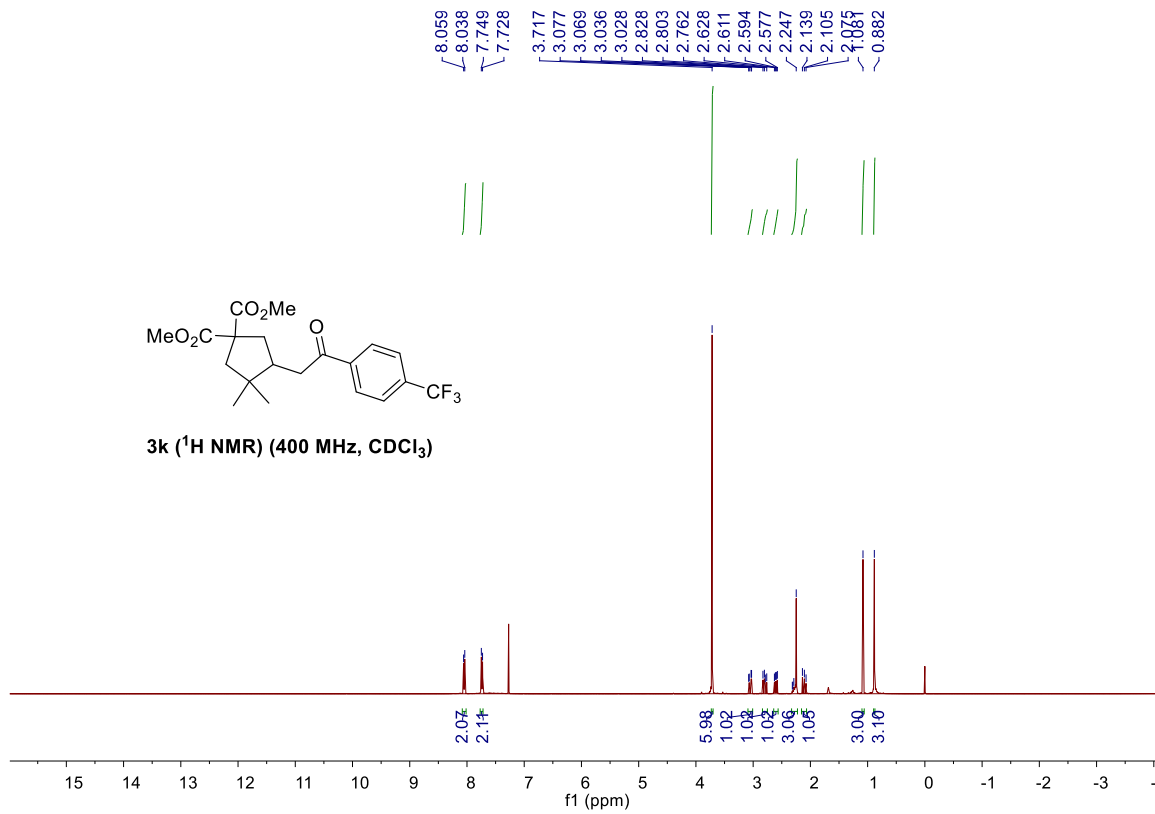


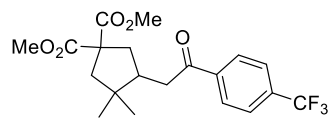
3h ( $^{19}\text{F}$  NMR) (376 MHz,  $\text{CDCl}_3$ )



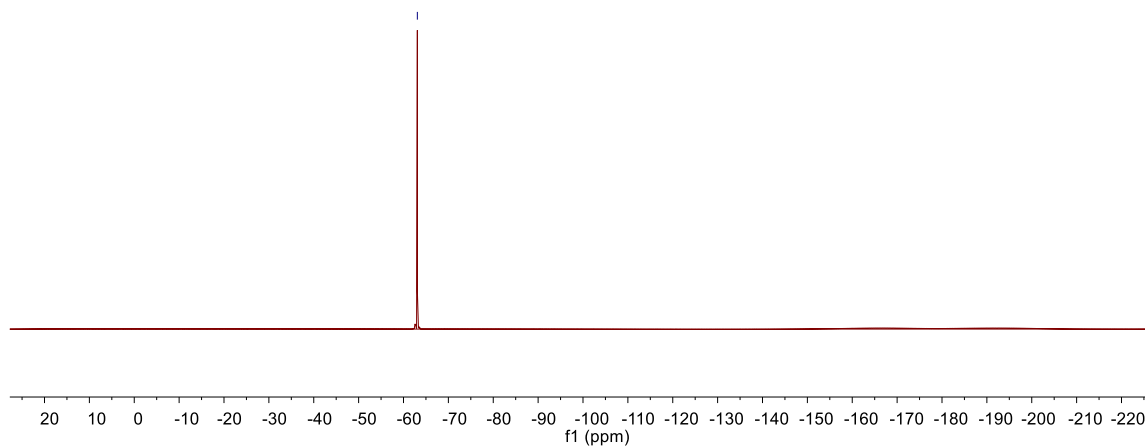


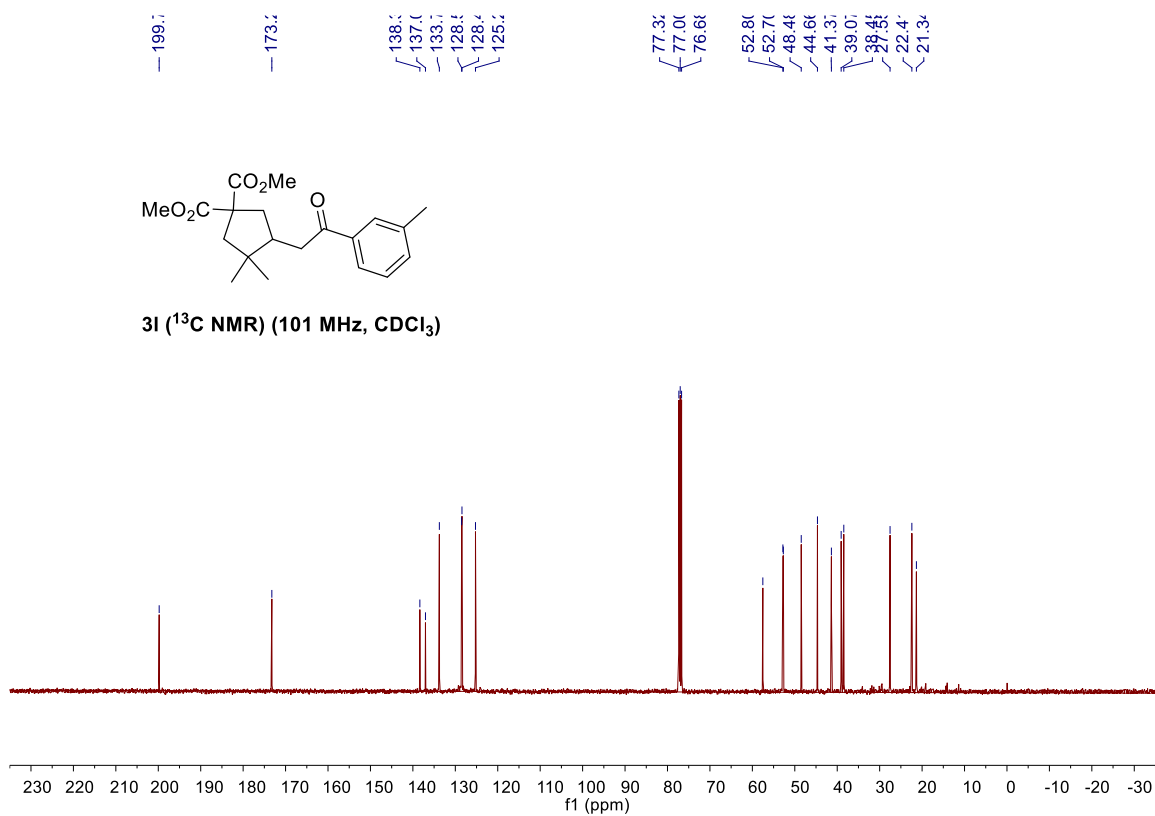
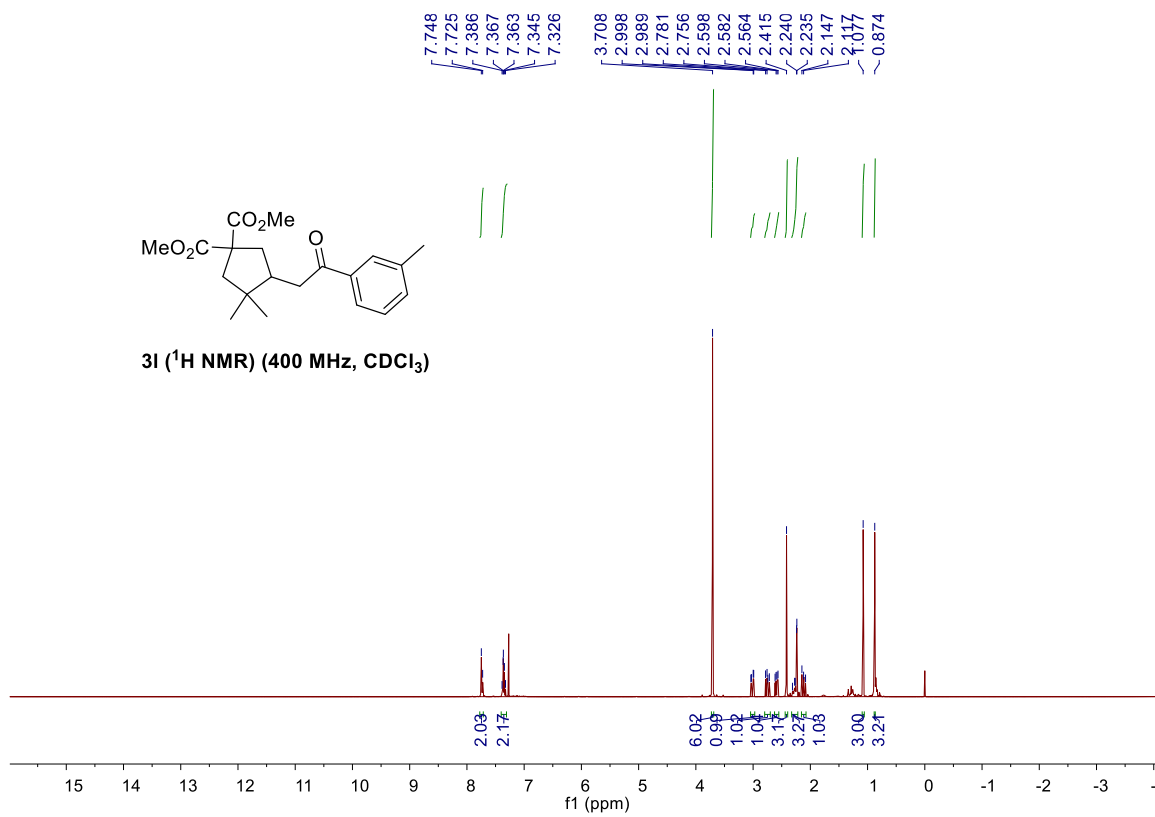


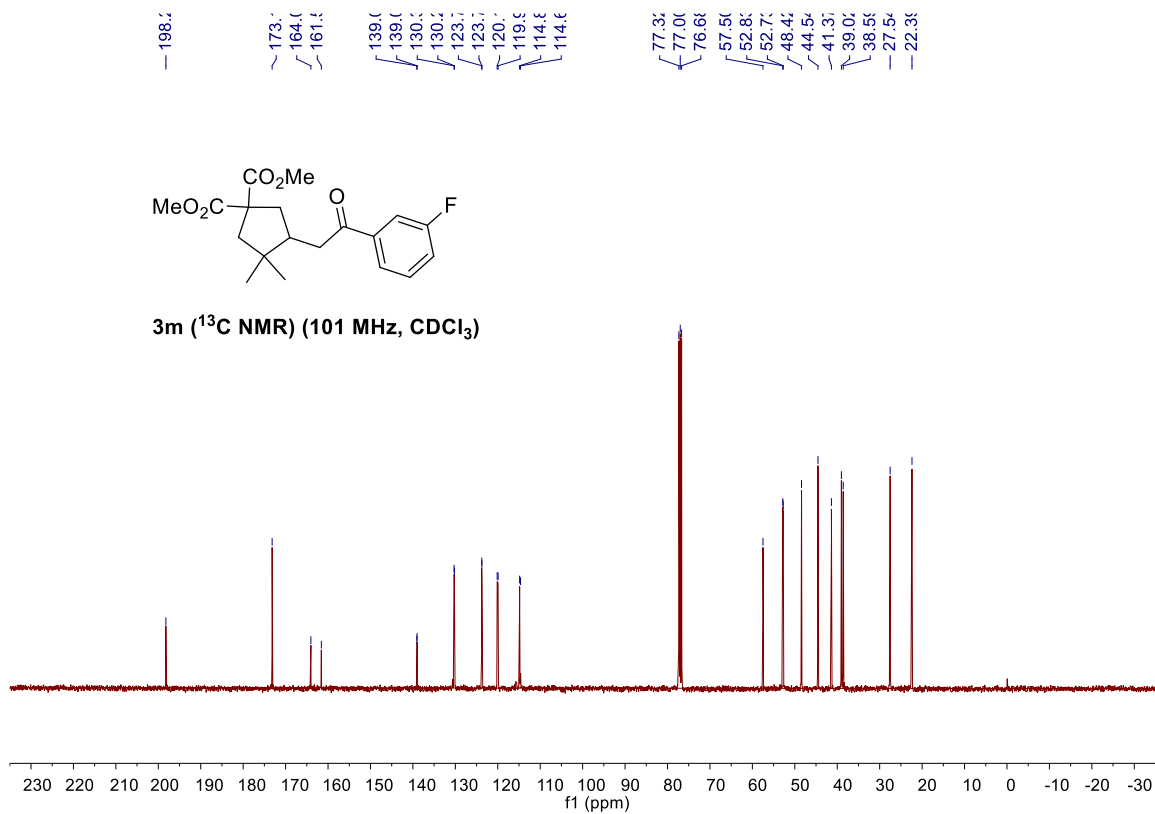
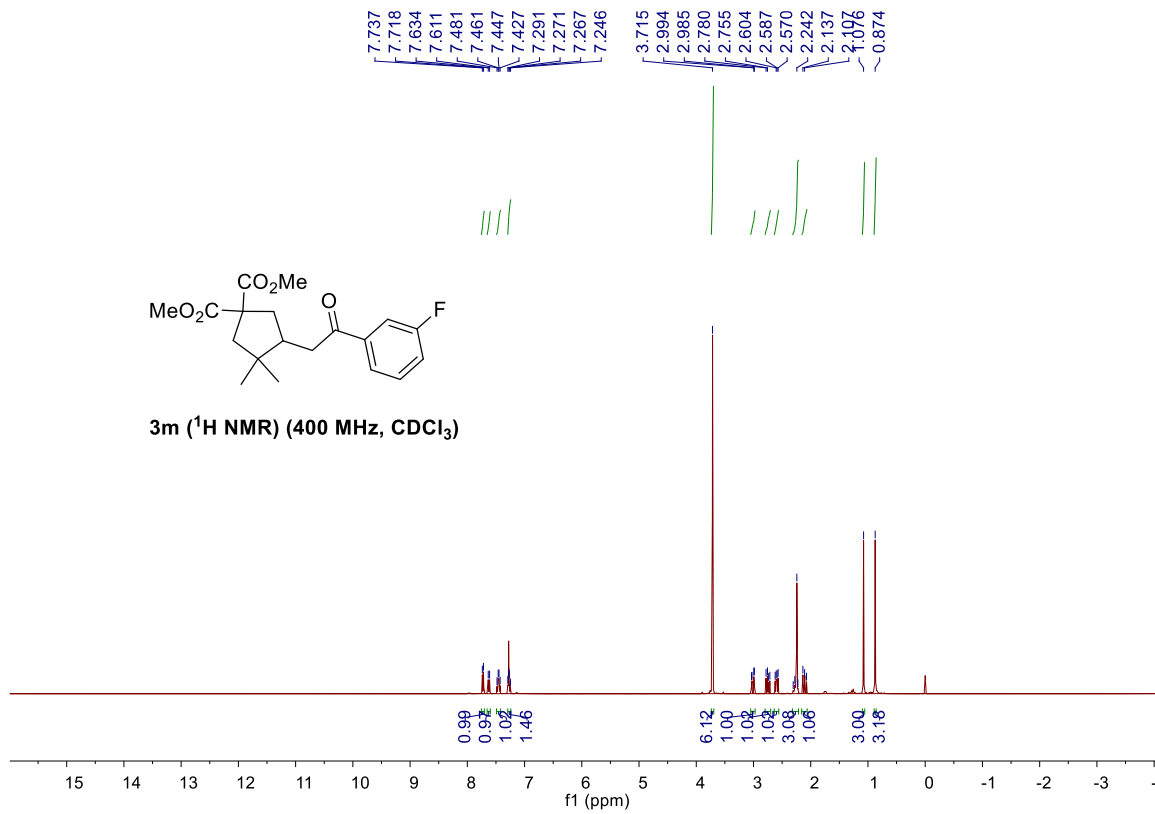


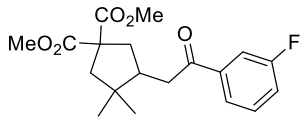


3k (<sup>19</sup>F NMR) (376 MHz, CDCl<sub>3</sub>)

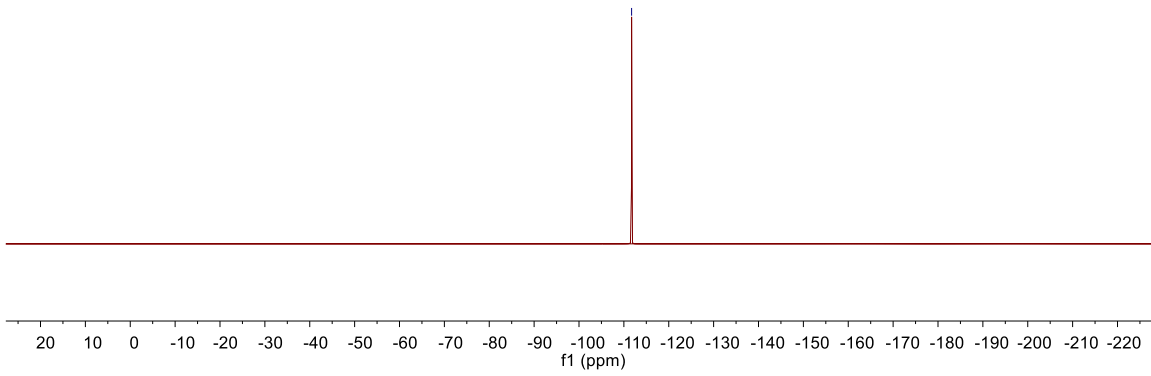




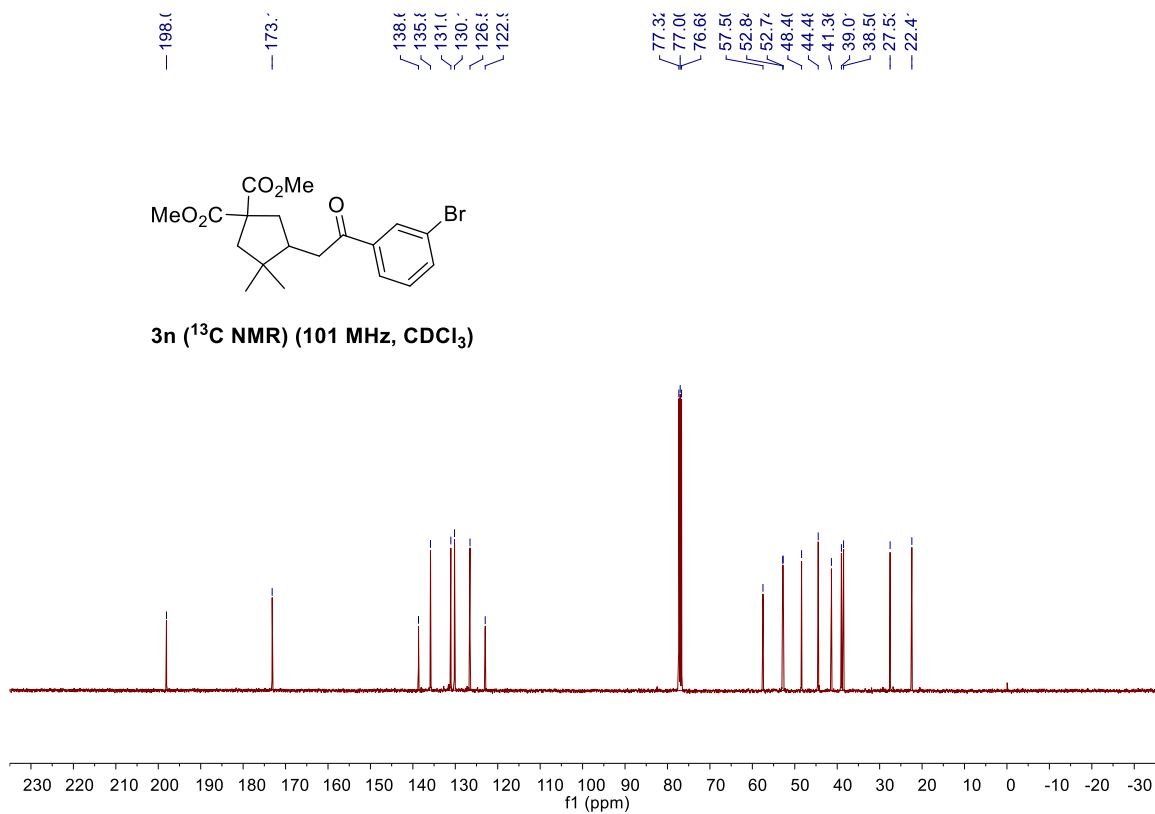
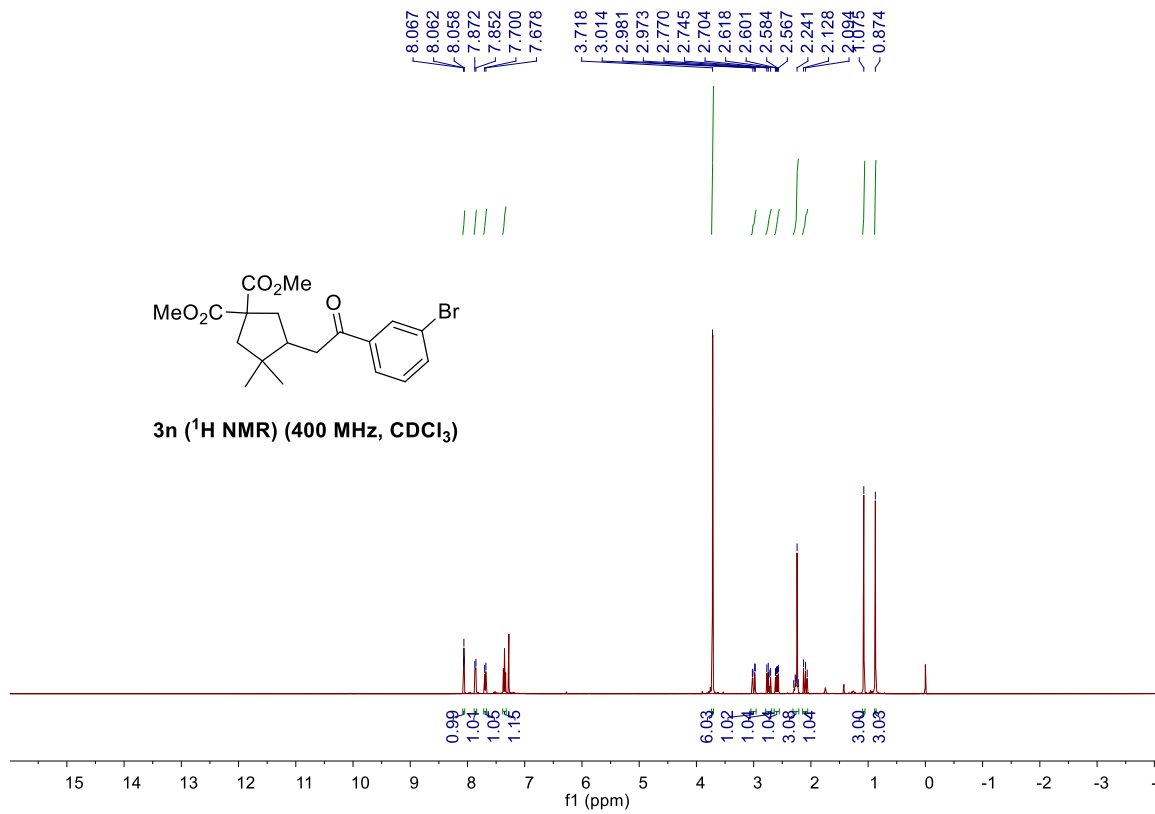


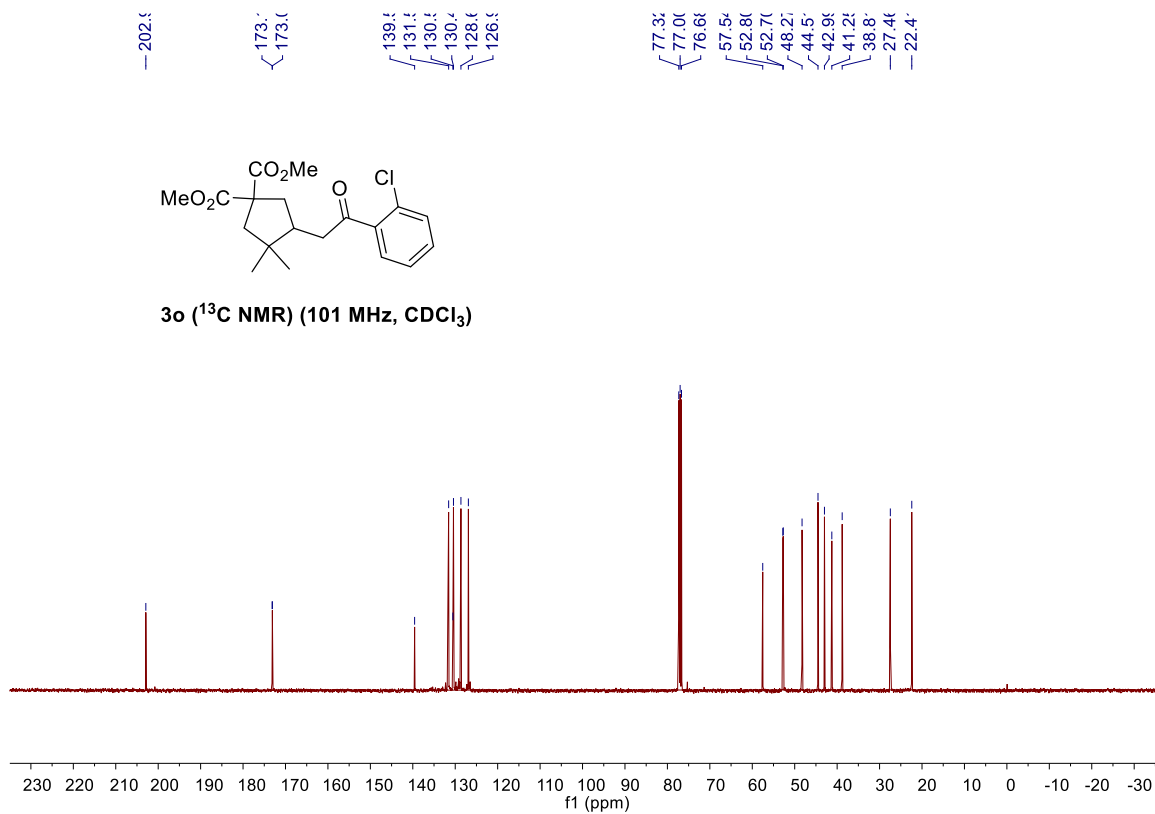
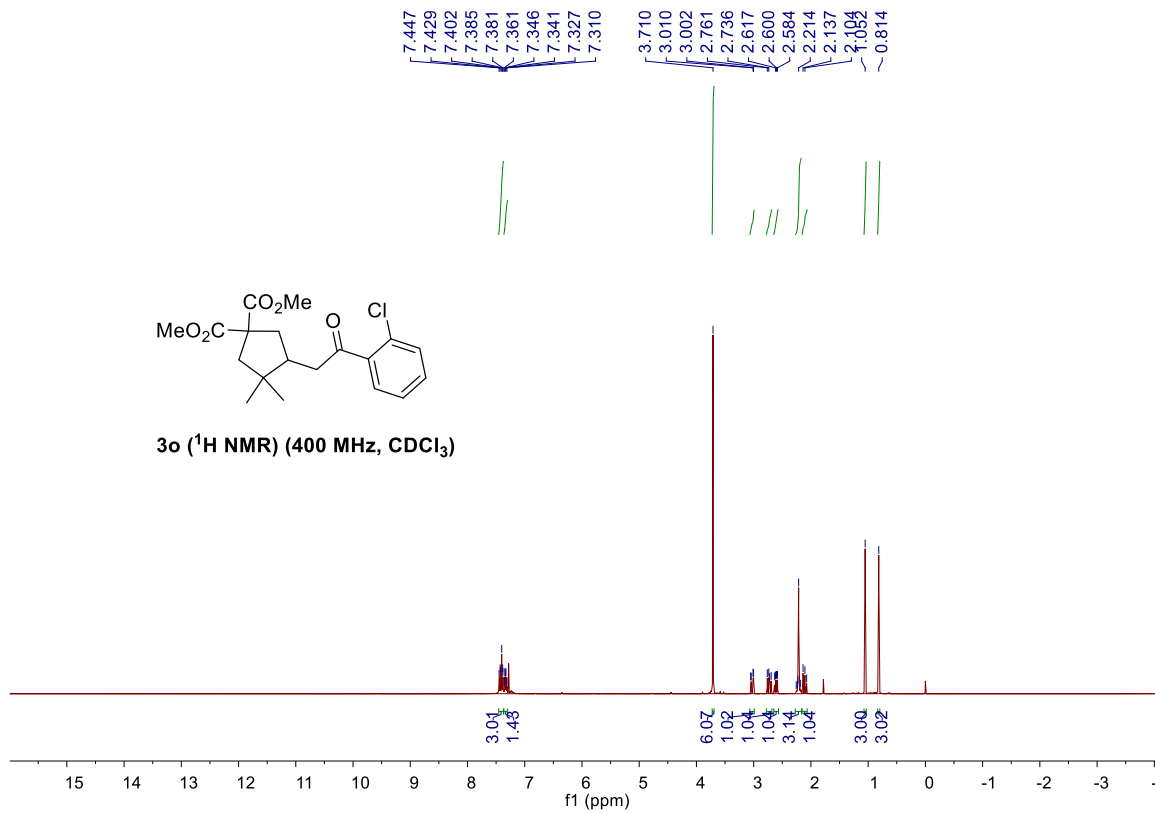


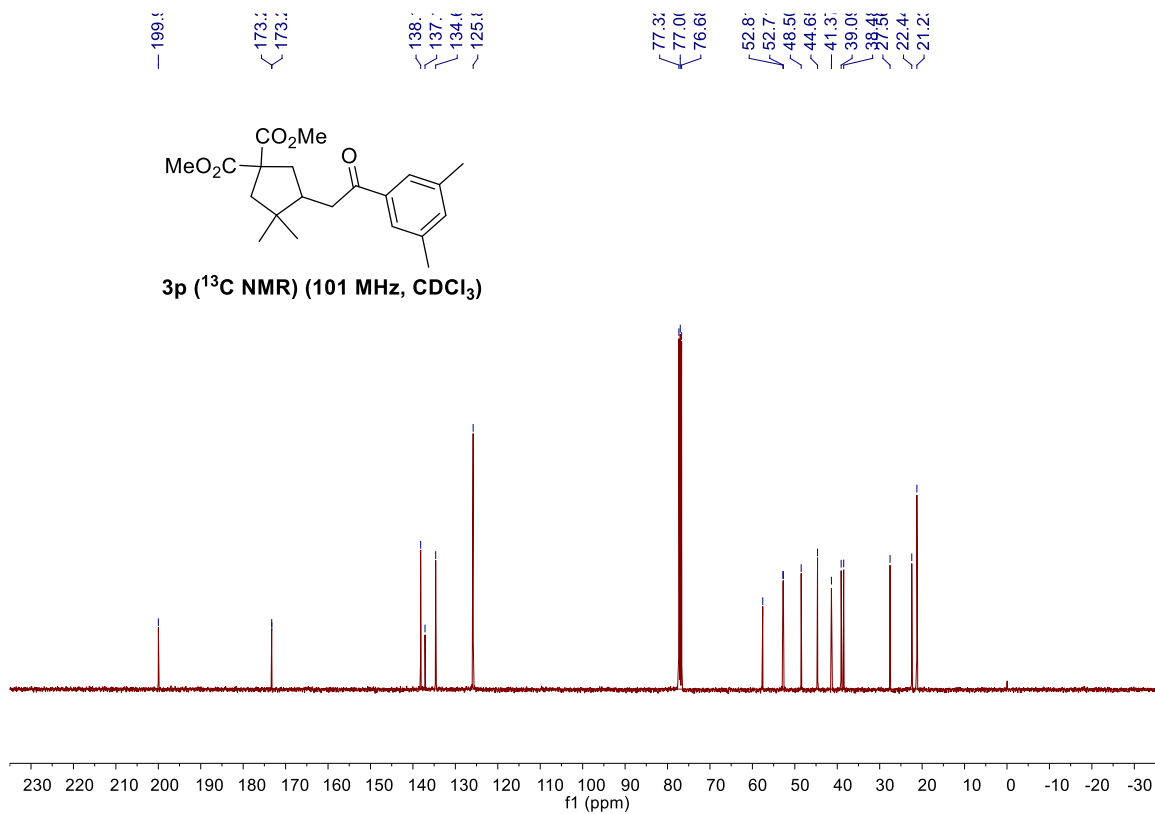
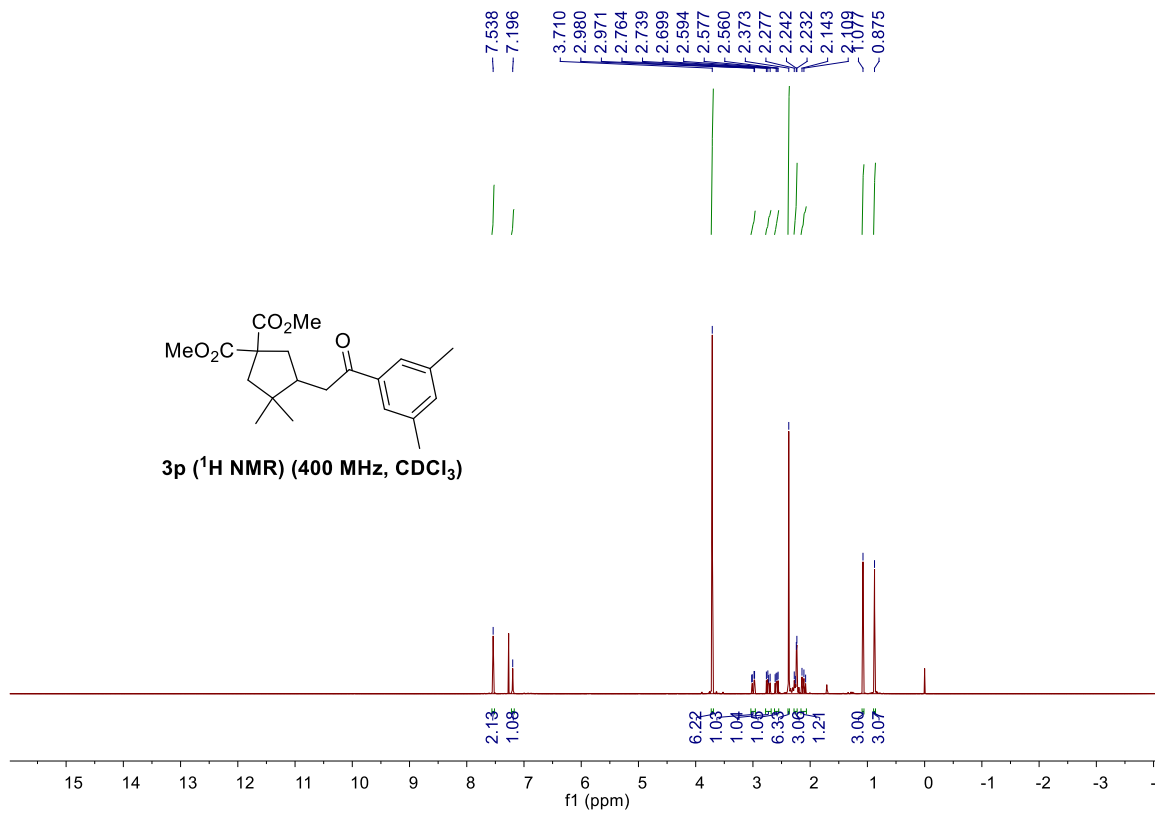
3m (<sup>19</sup>F NMR) (376 MHz, CDCl<sub>3</sub>)

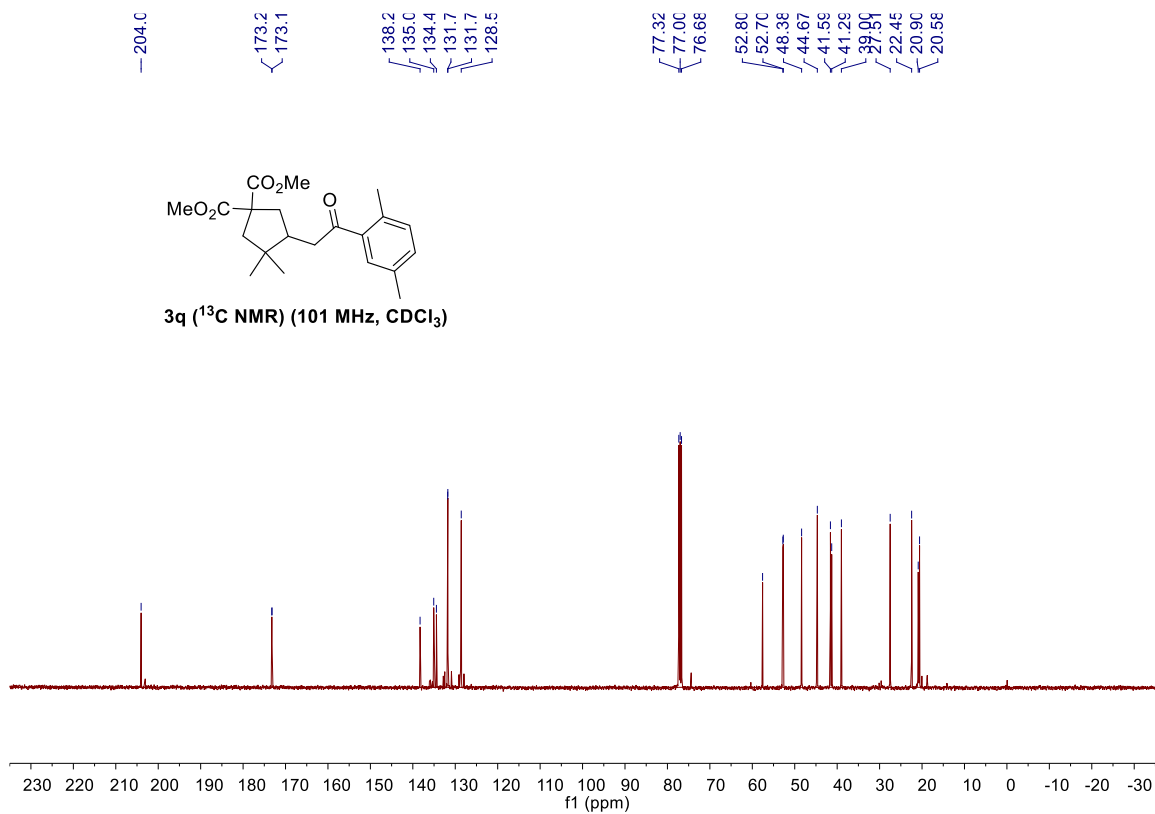
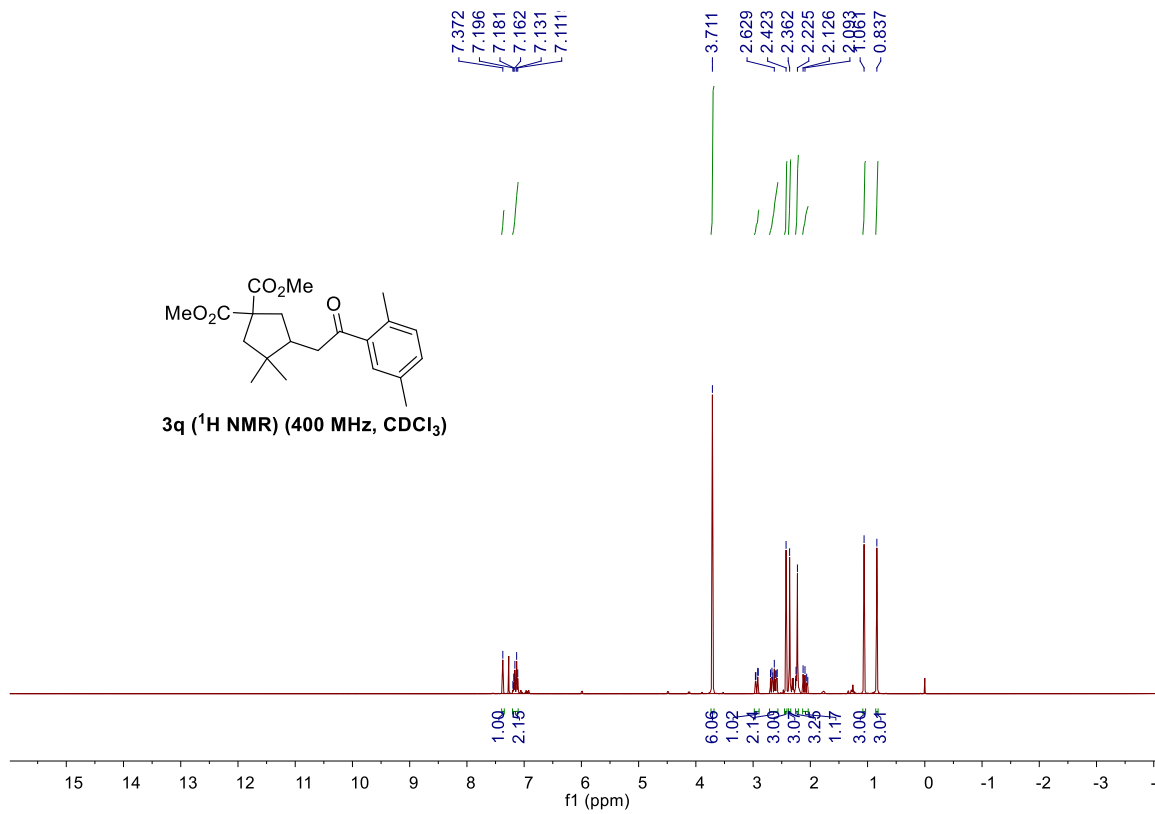


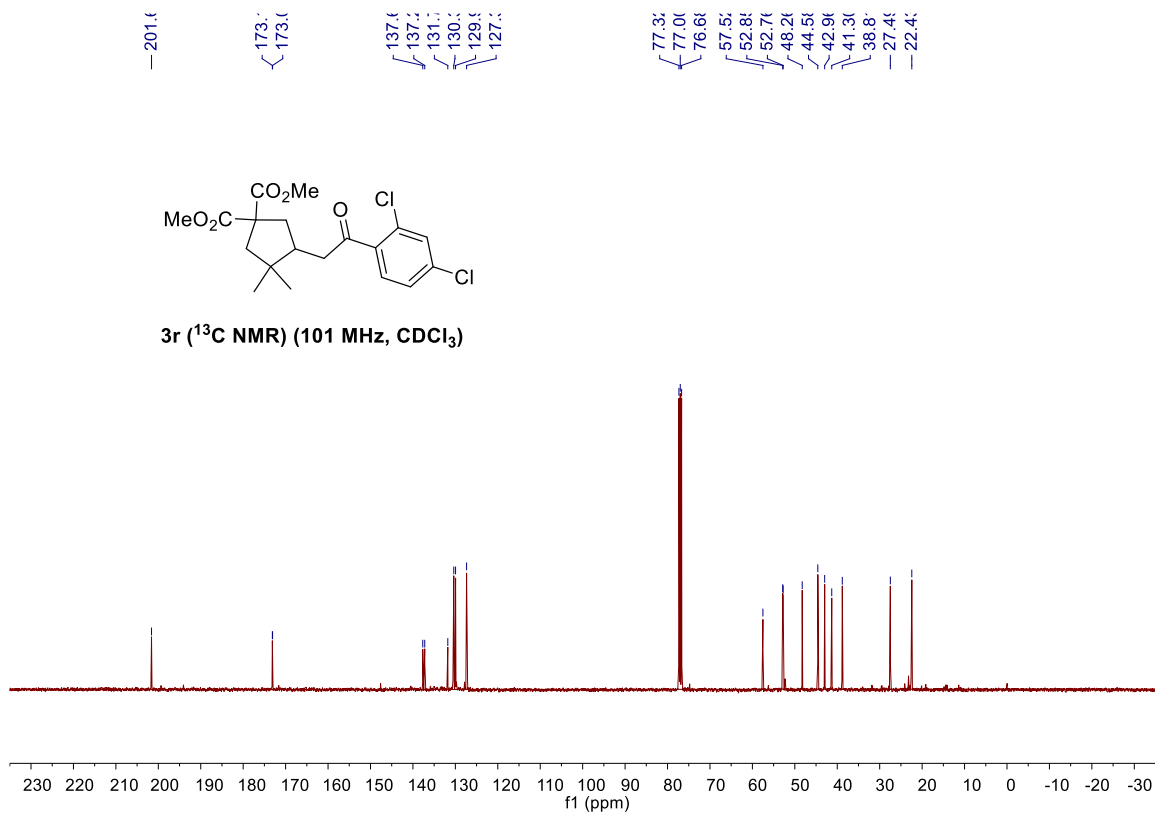
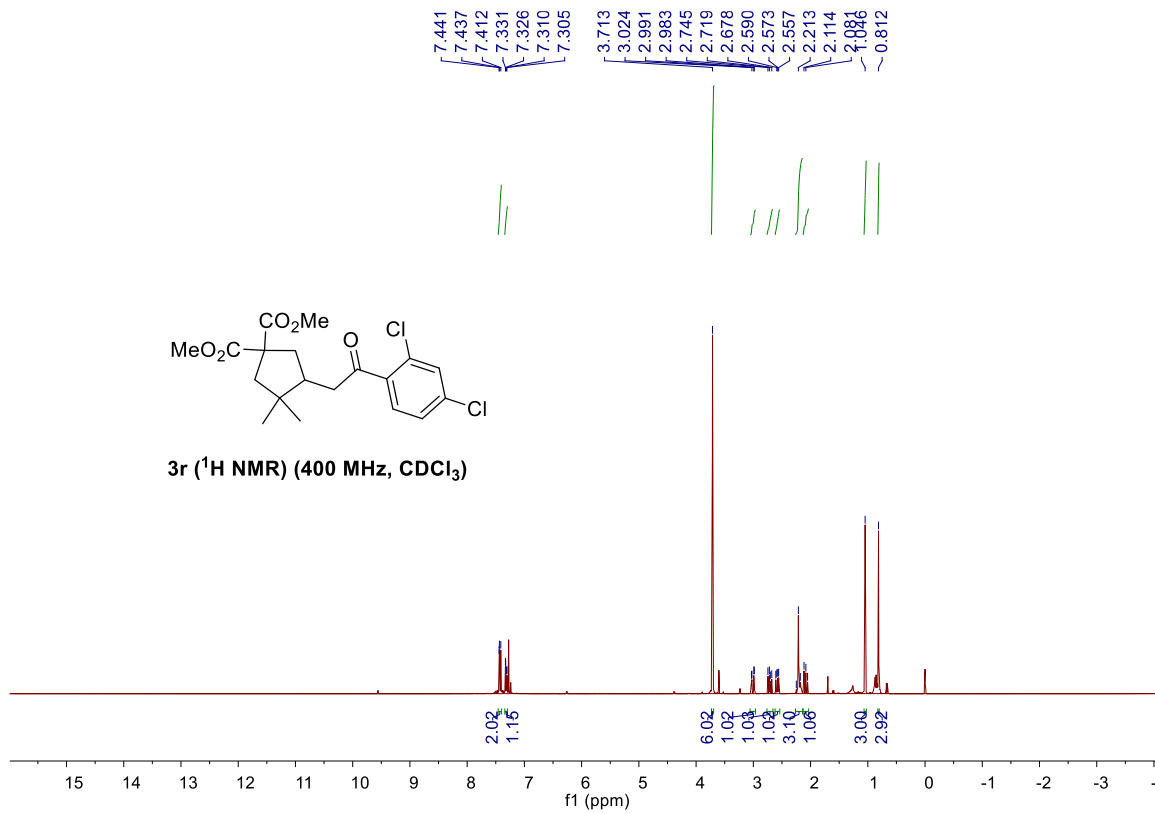


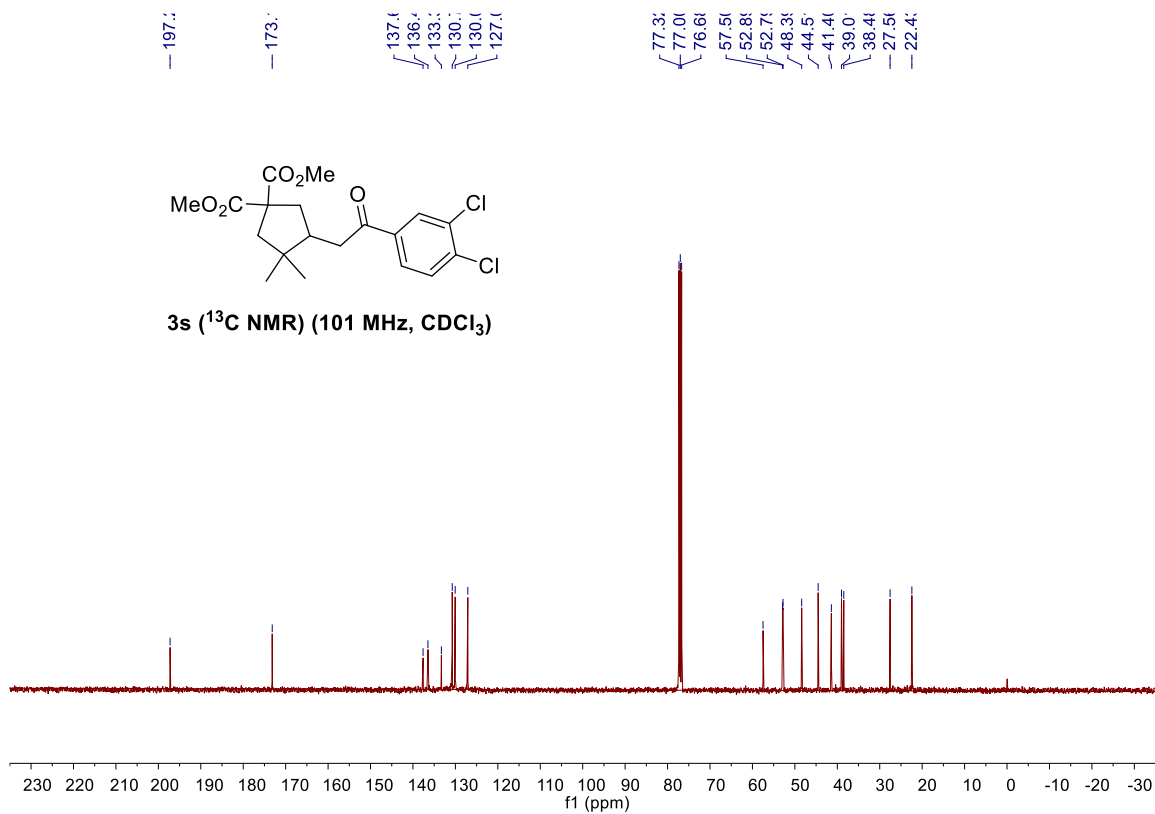
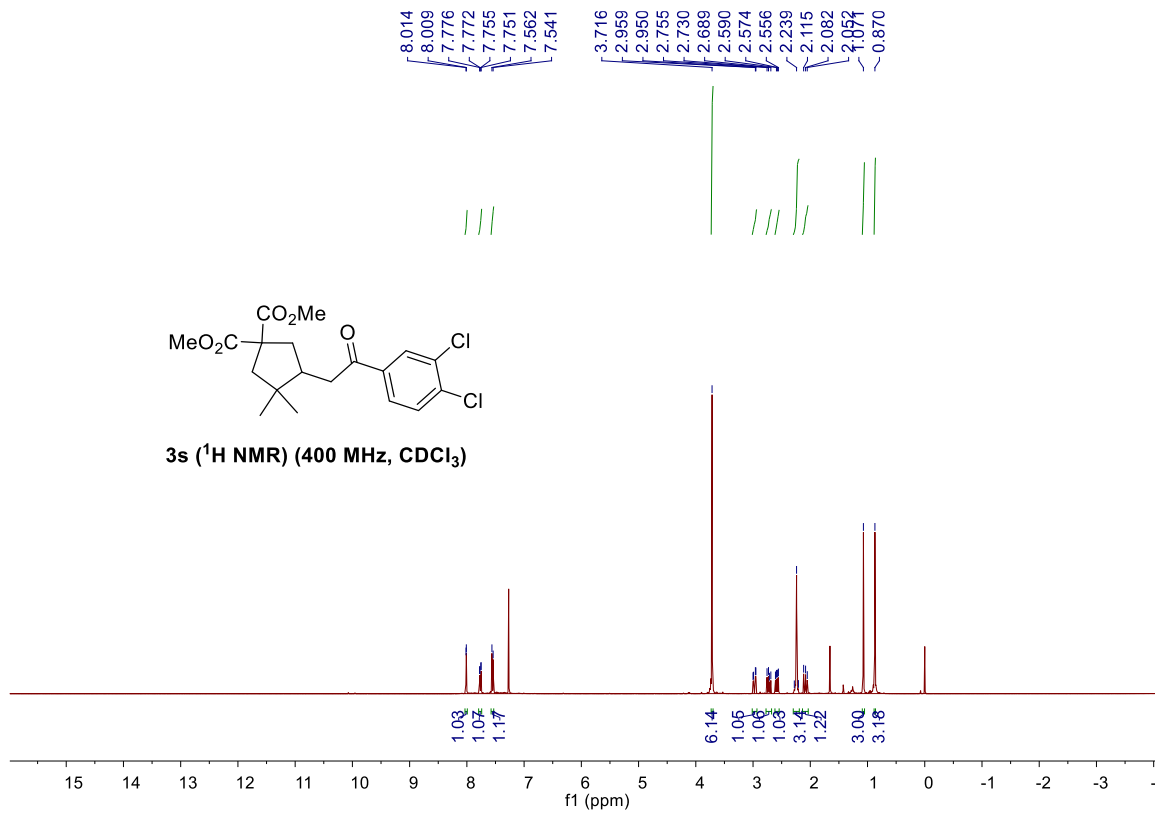


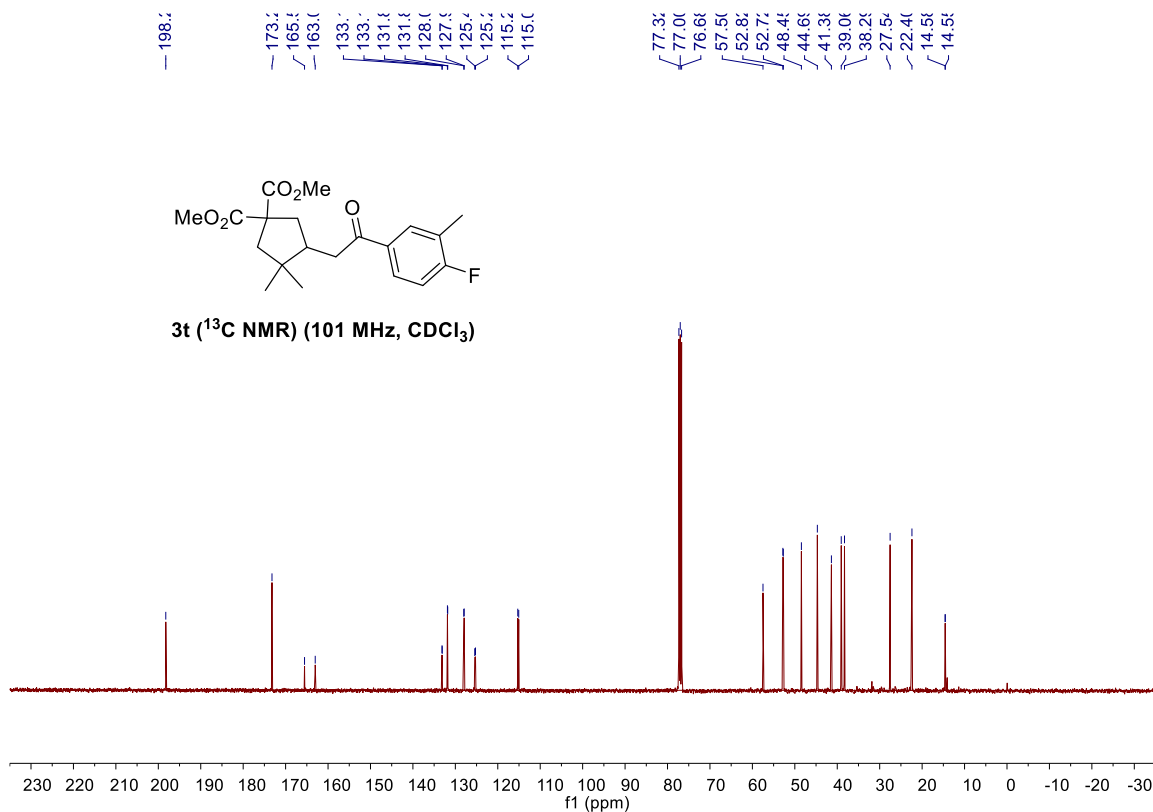
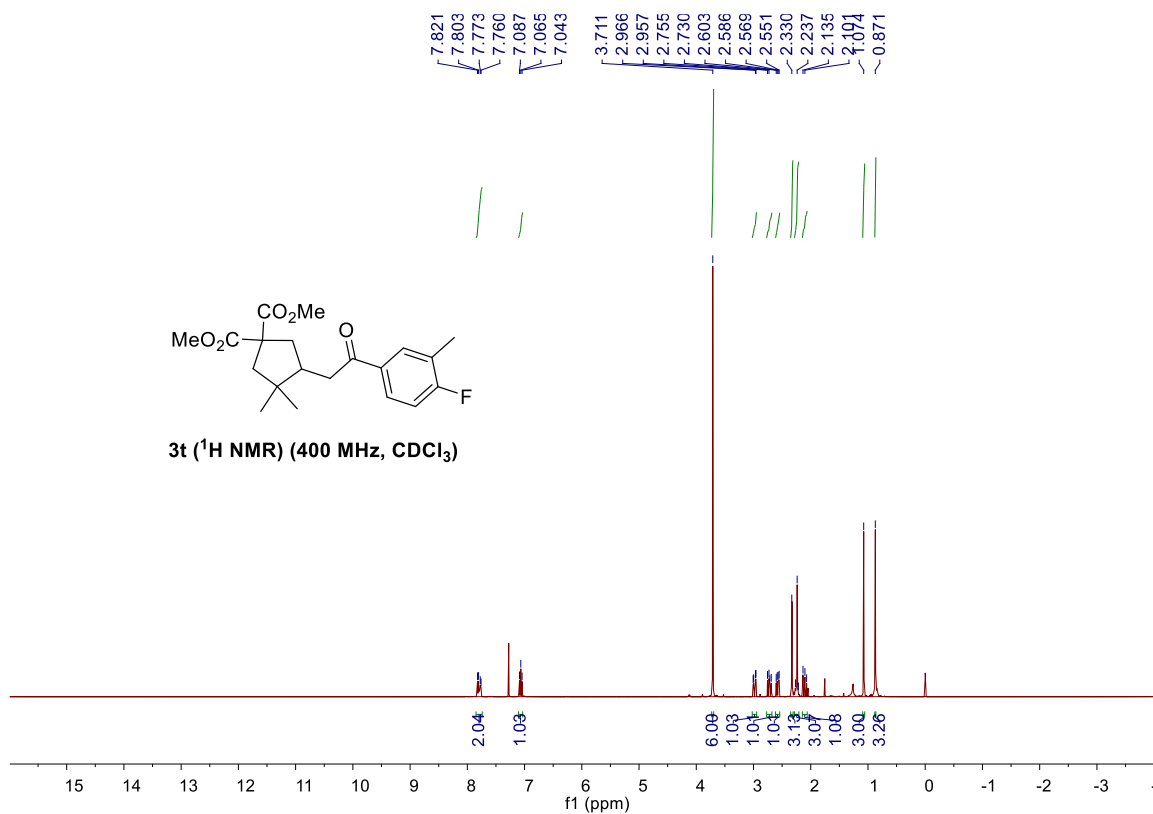


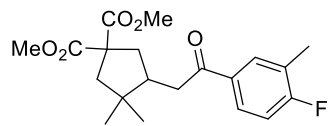




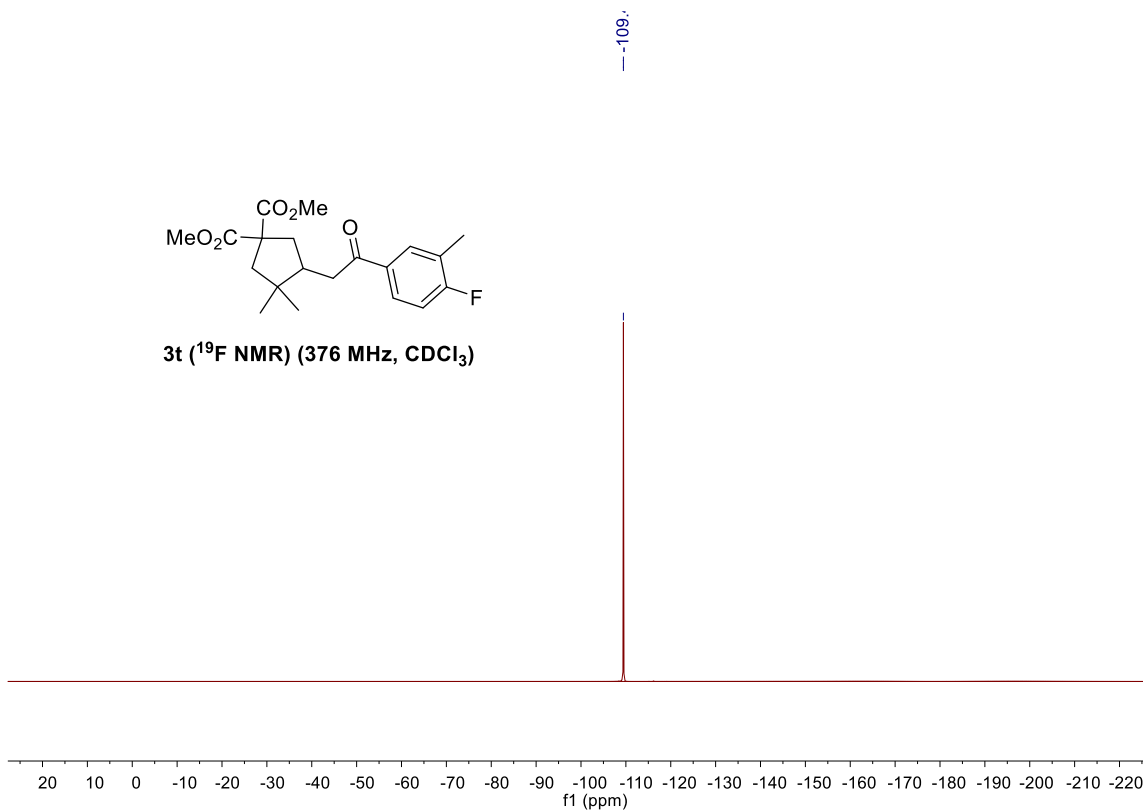




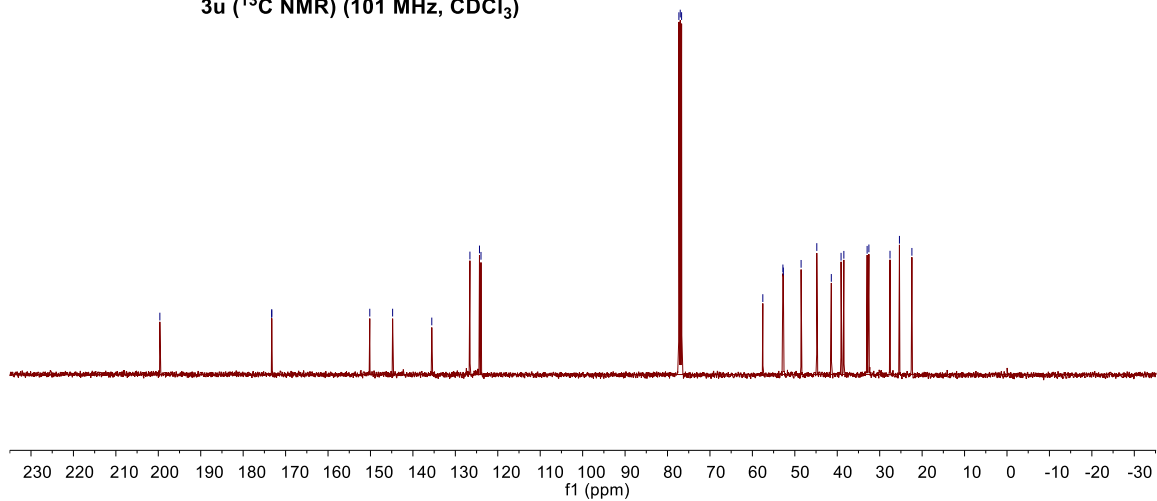
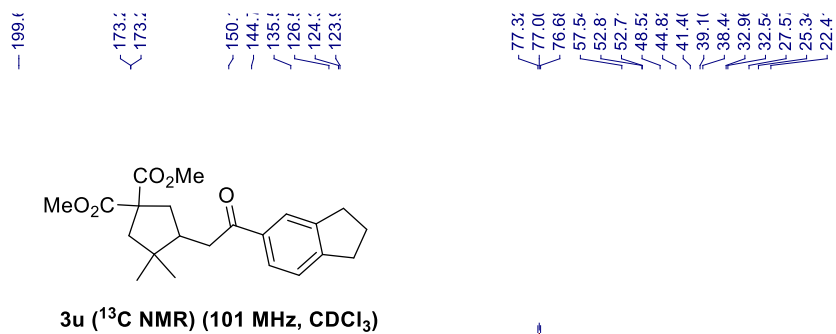
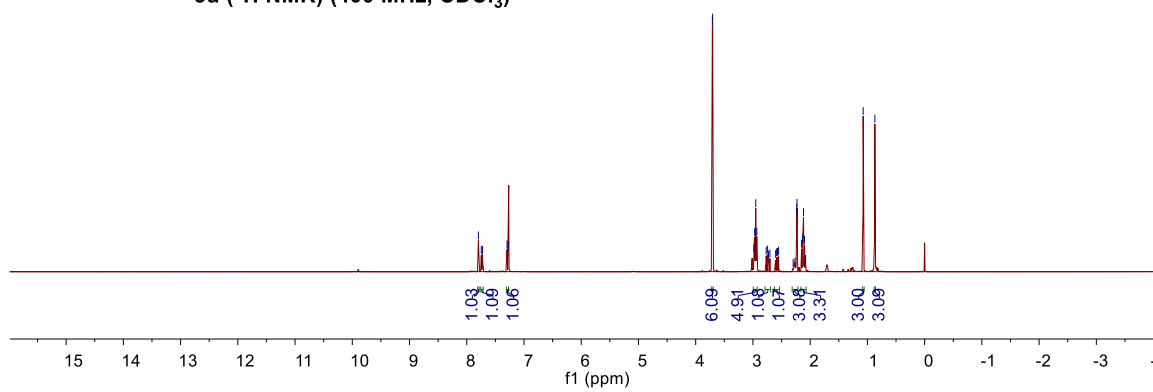
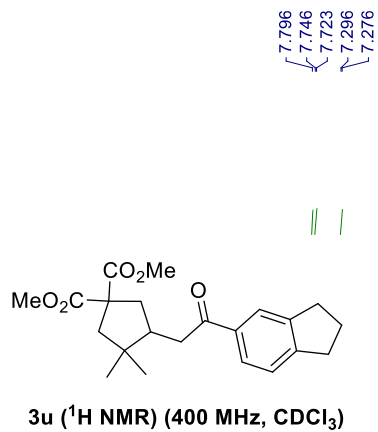


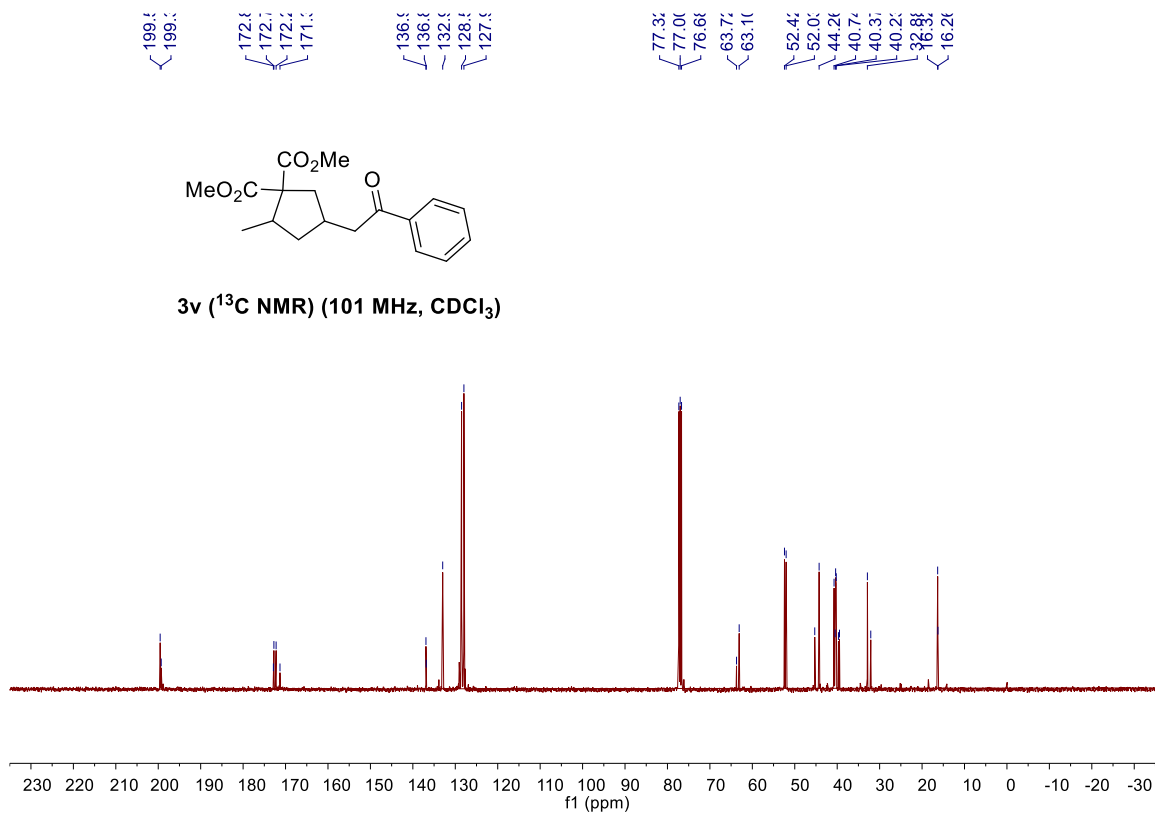
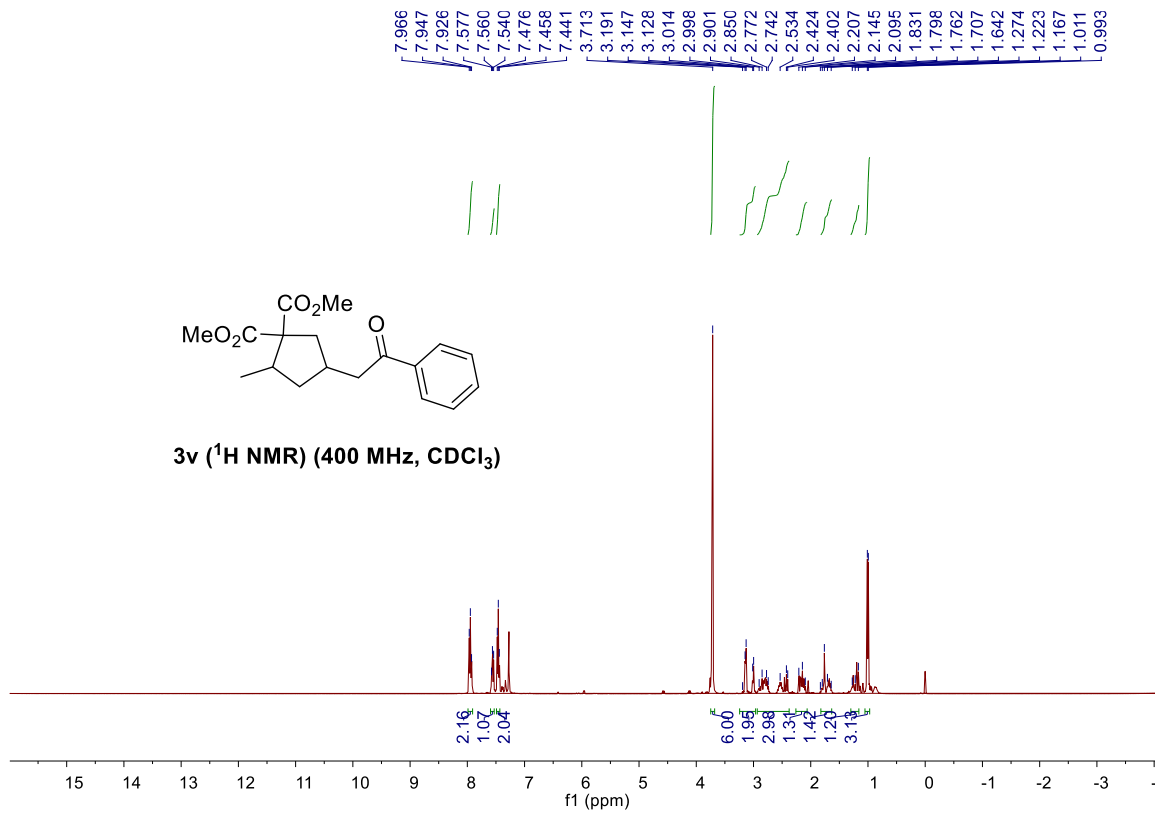


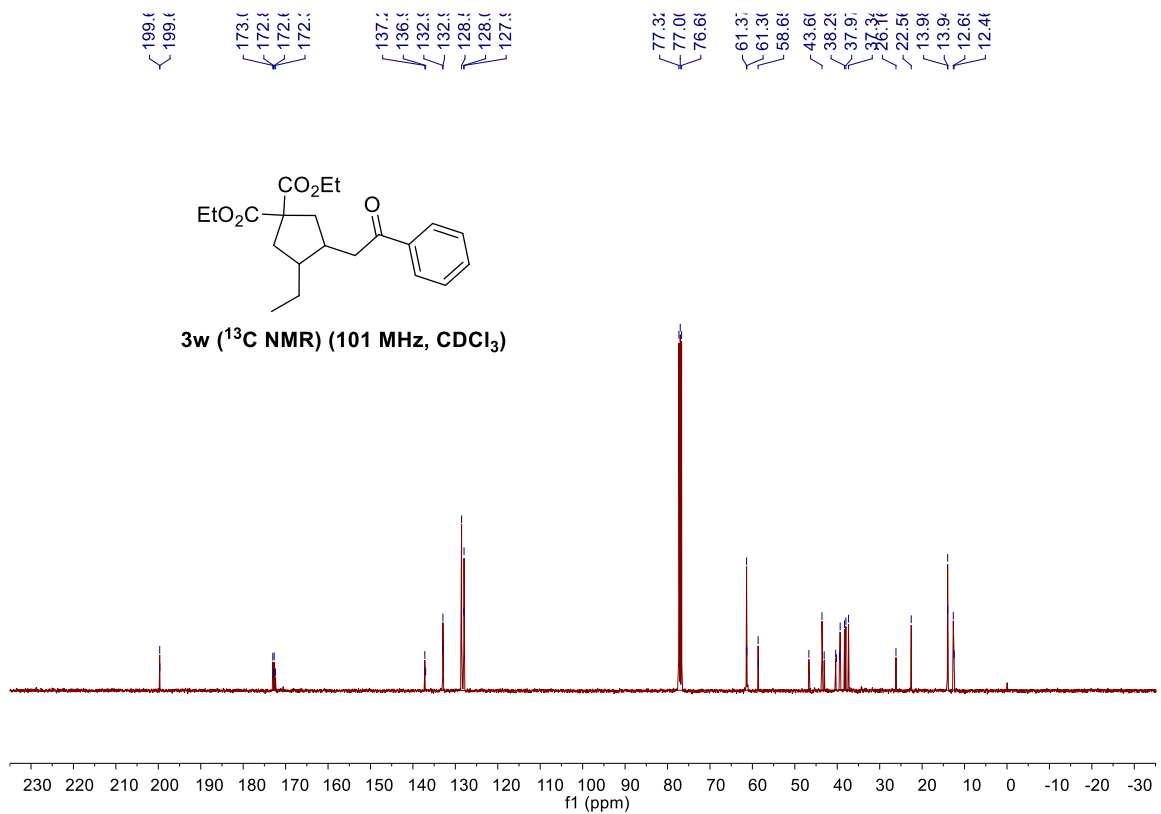
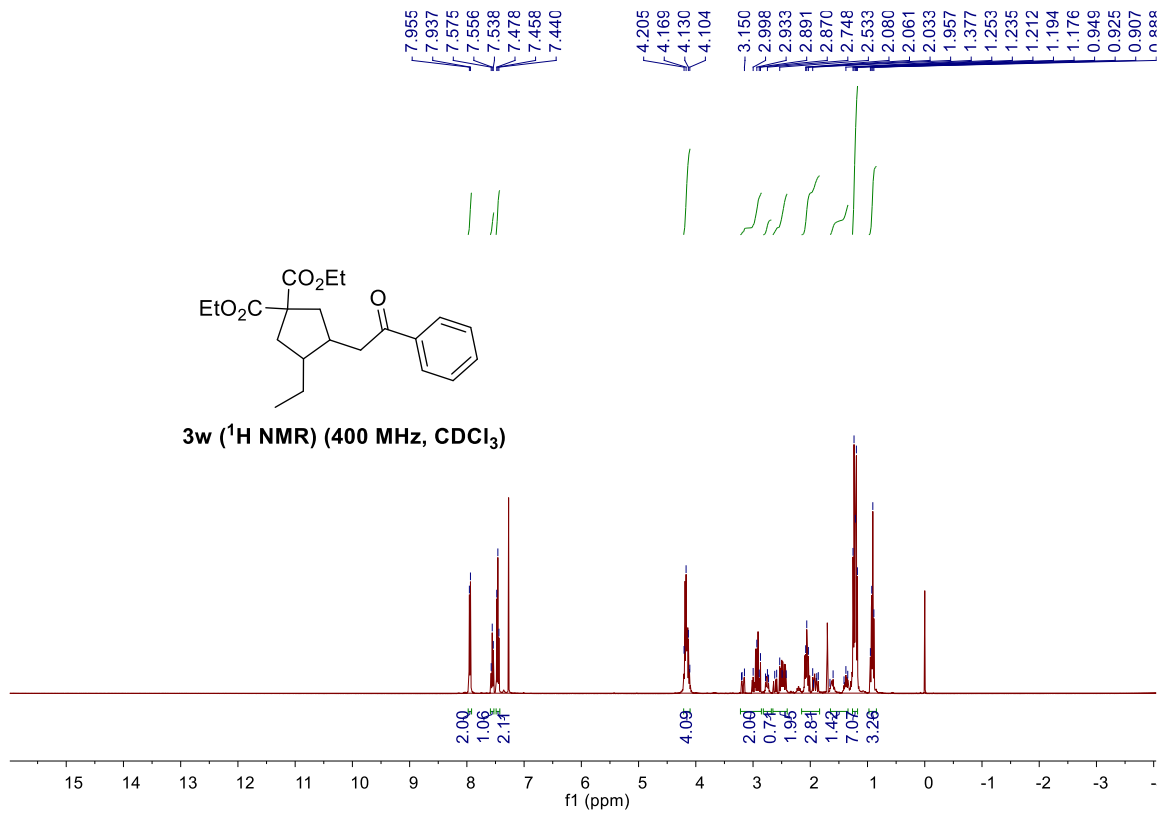
3t (<sup>19</sup>F NMR) (376 MHz, CDCl<sub>3</sub>)

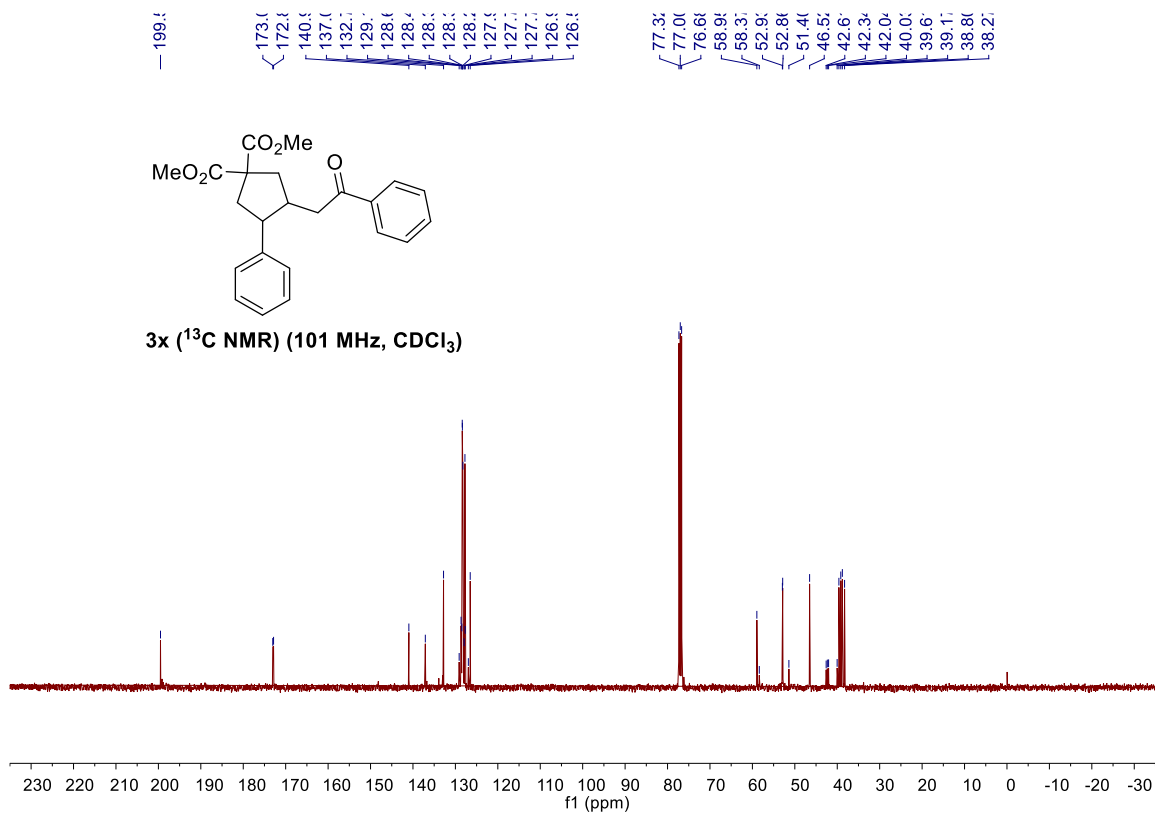
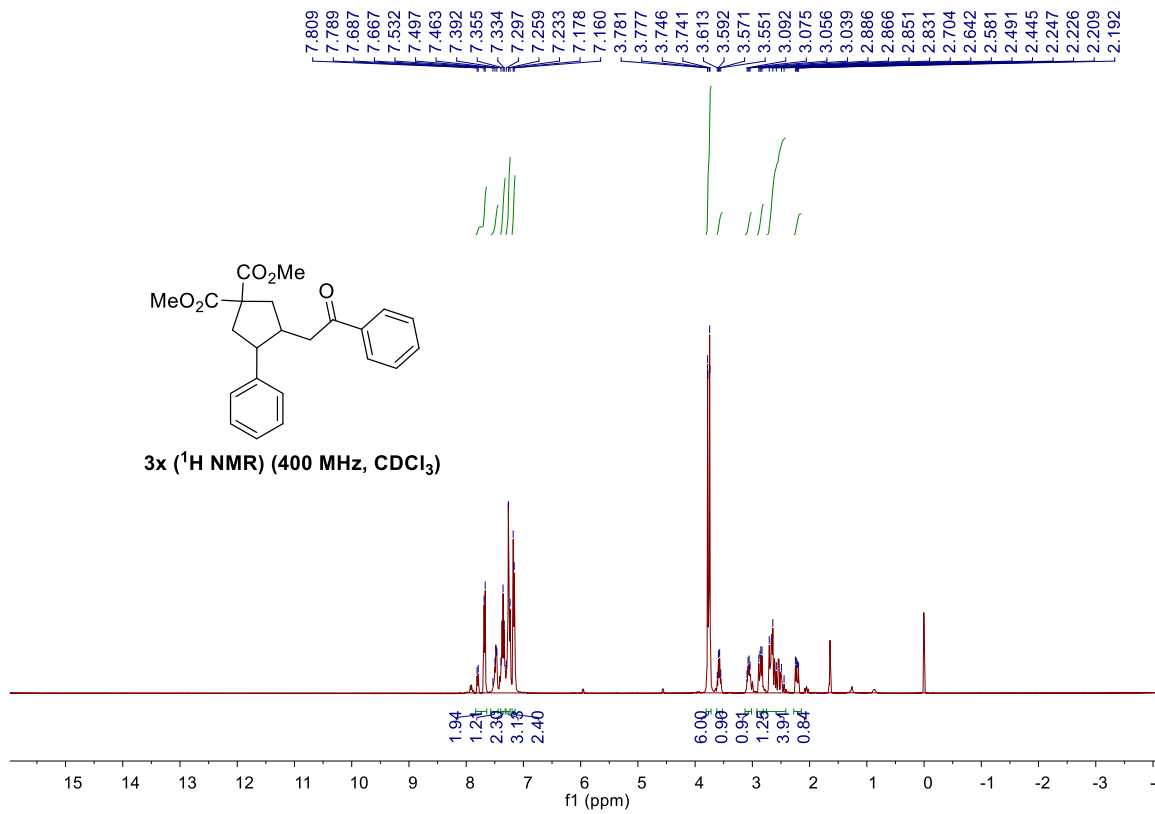


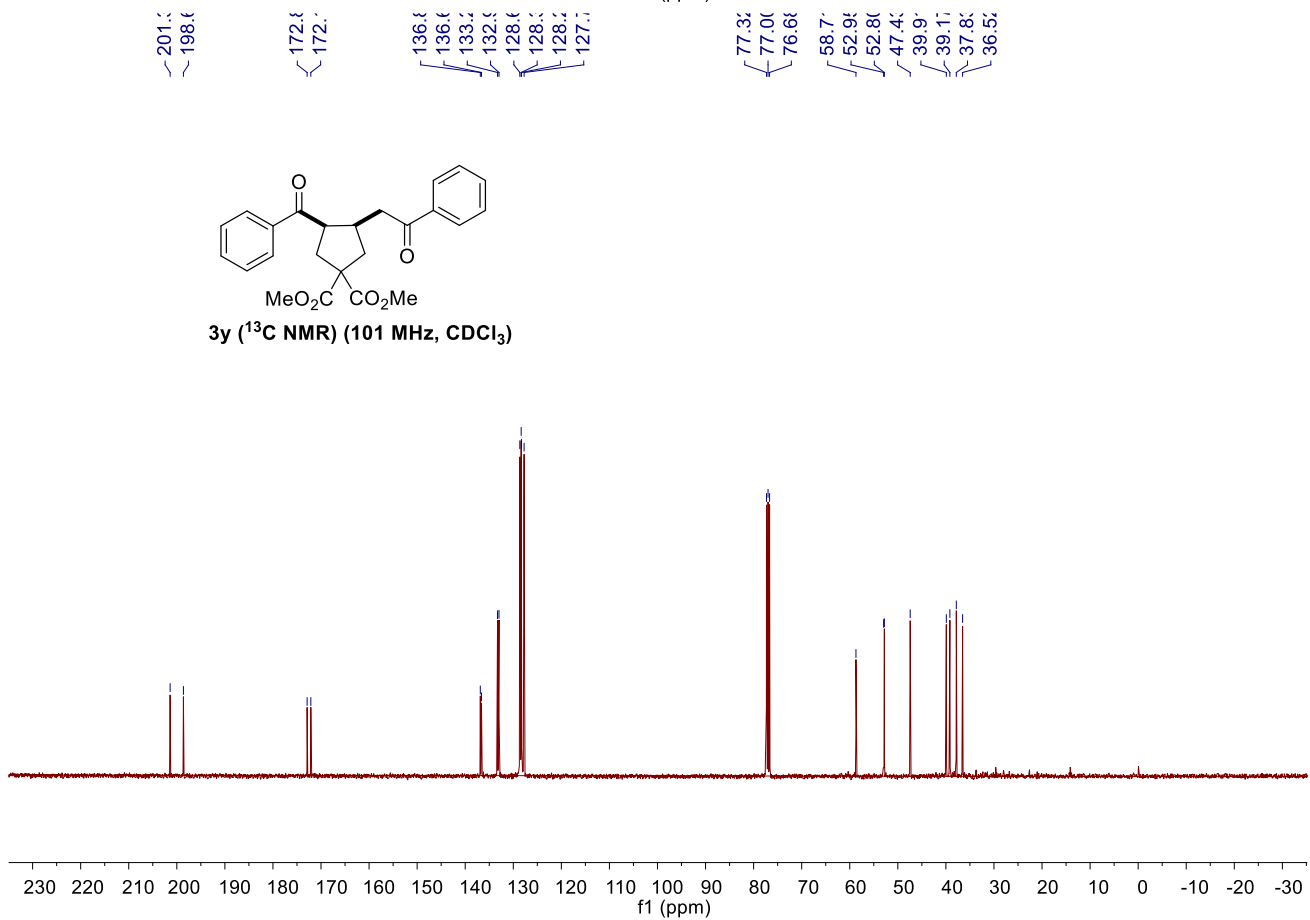
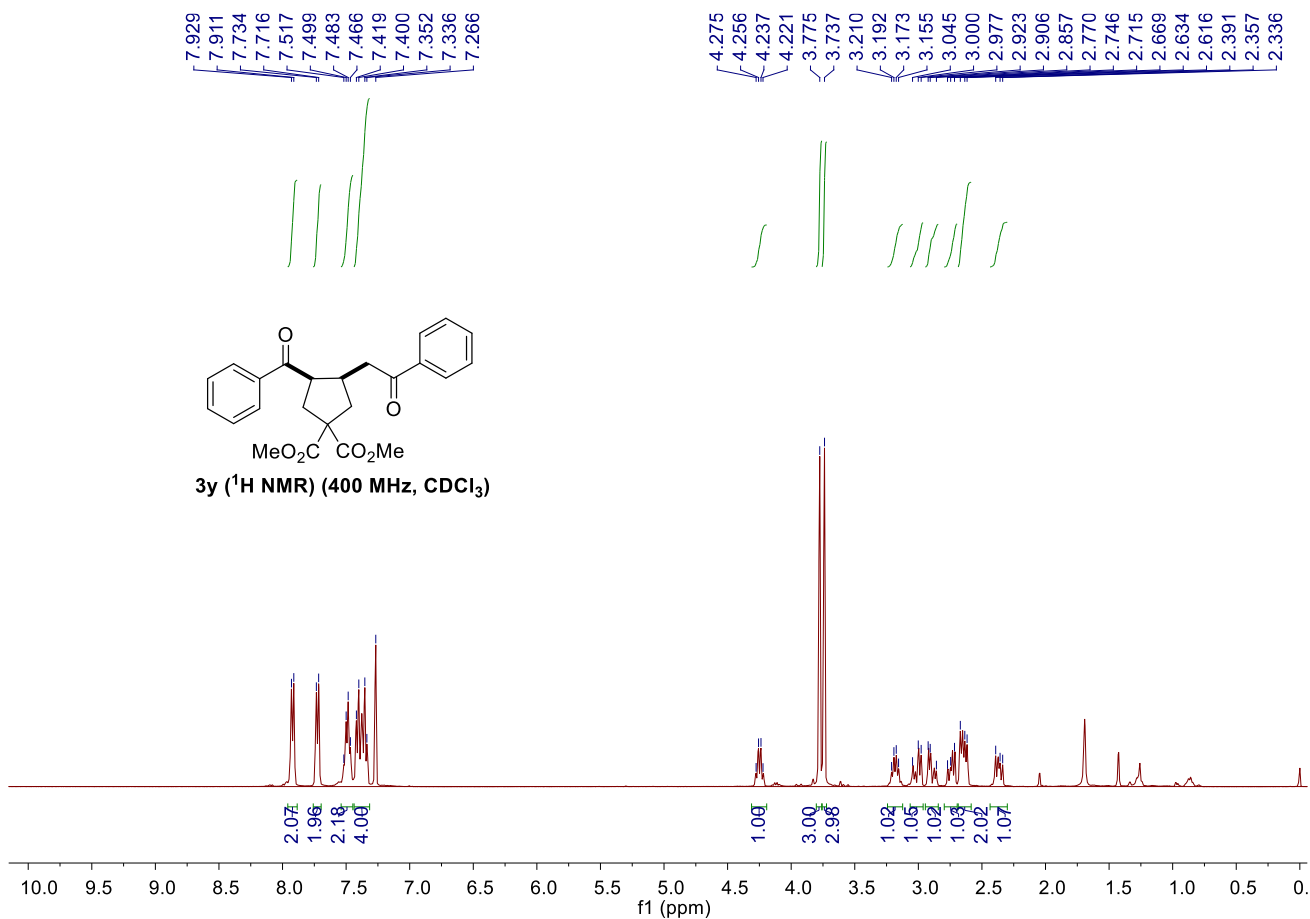




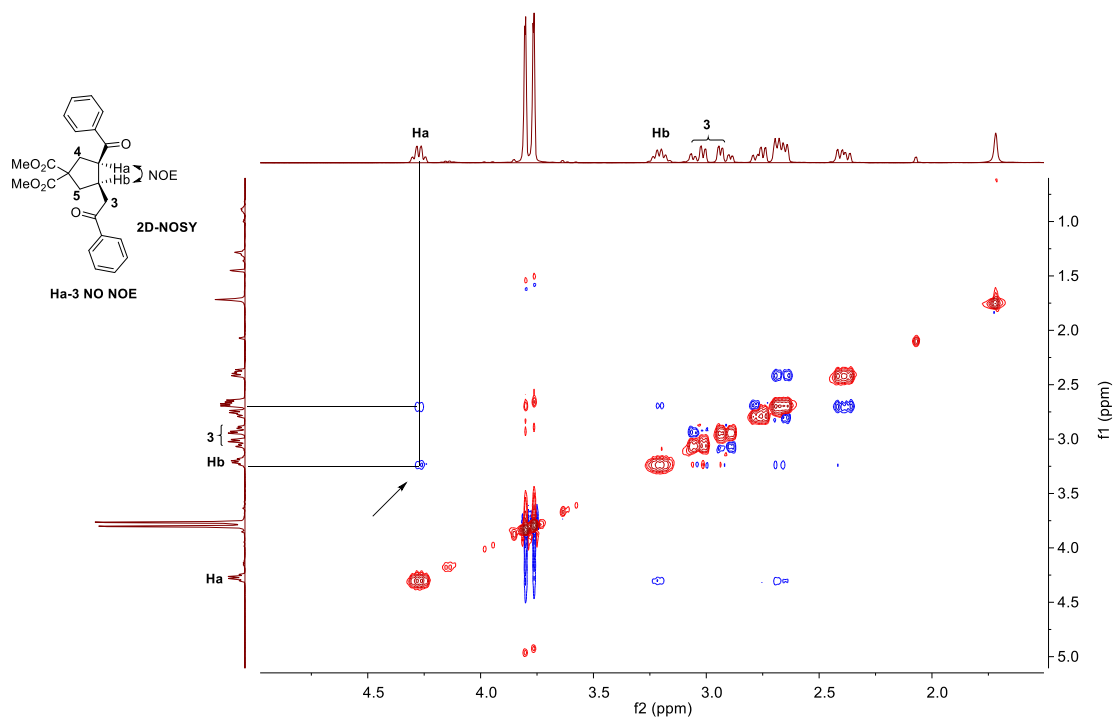
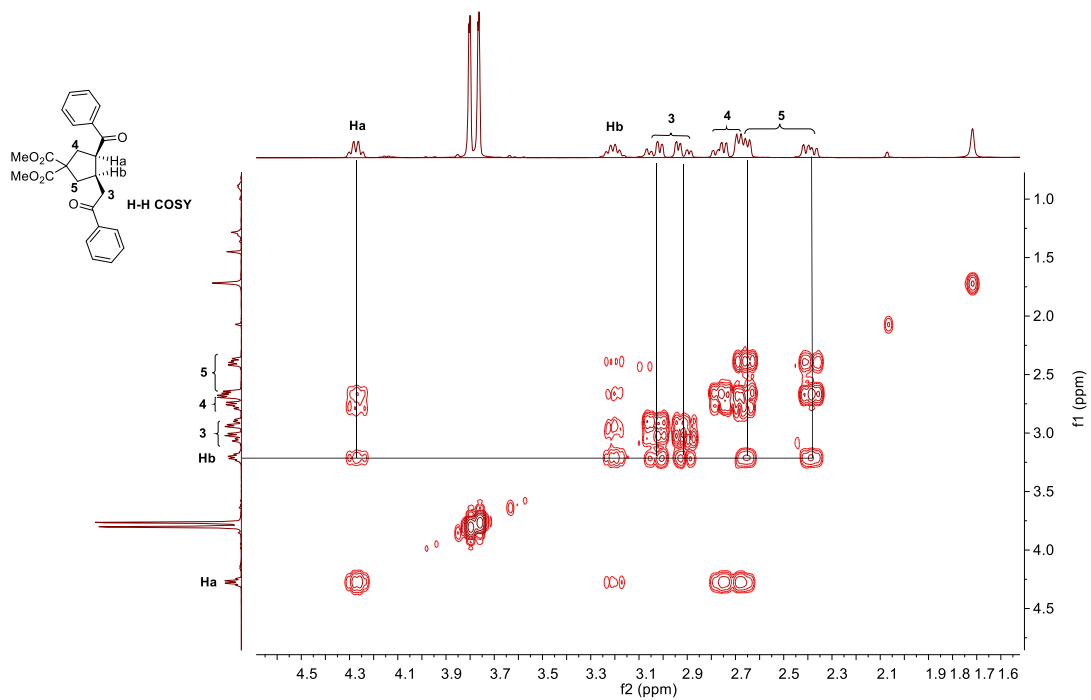


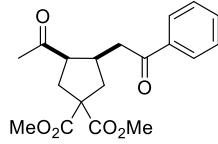
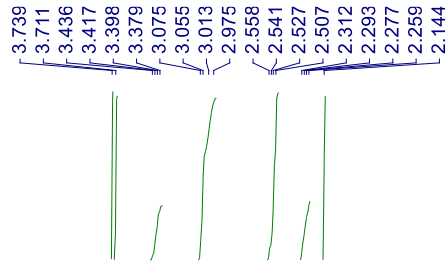
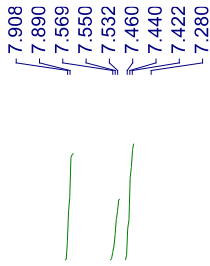




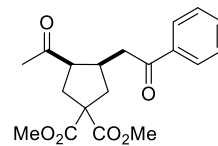
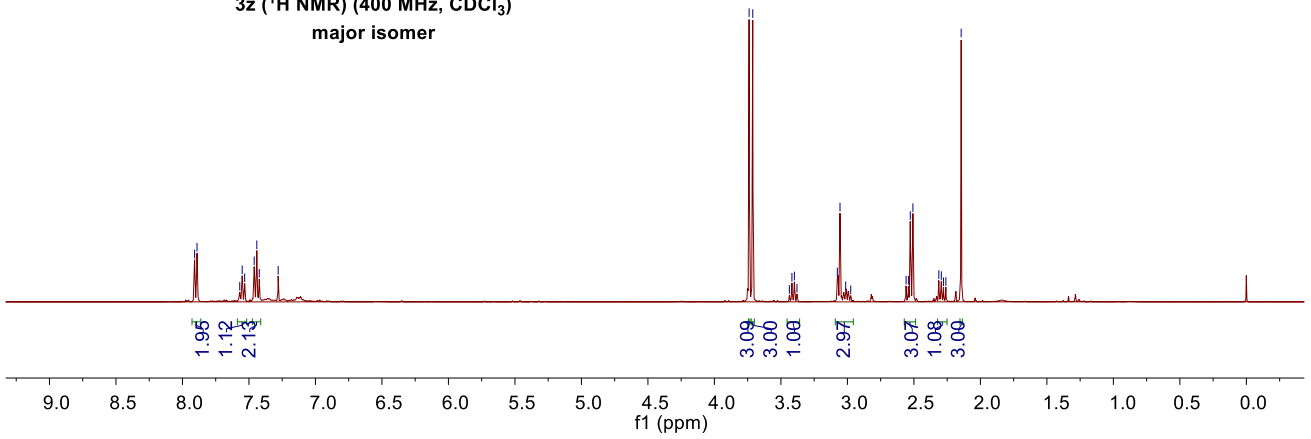


## 2D NMR spectra of 3y

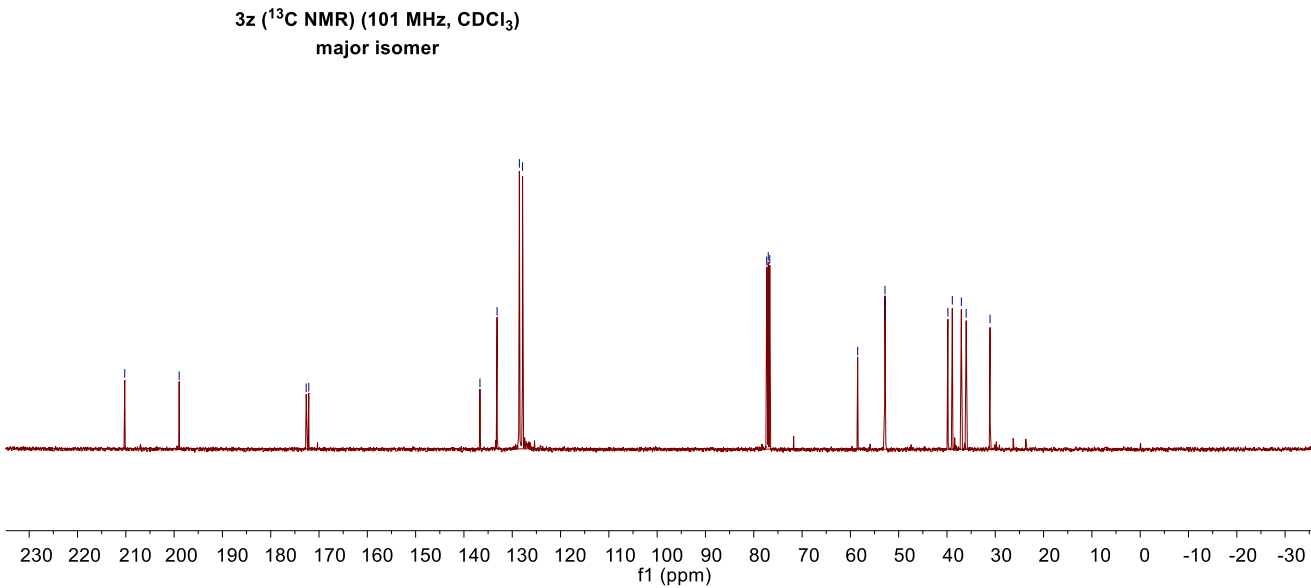


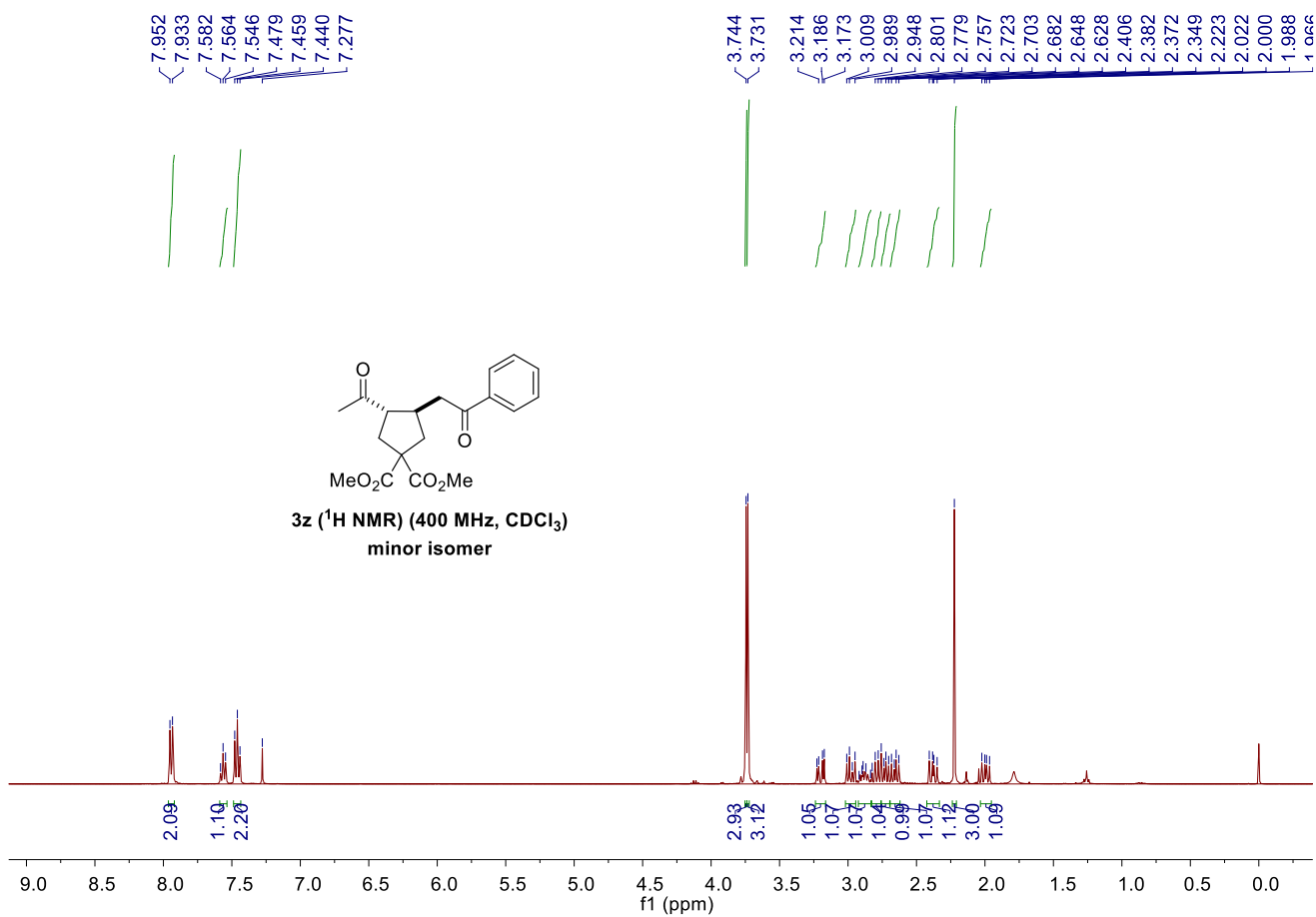


**3z** ( $^1\text{H}$  NMR) (400 MHz,  $\text{CDCl}_3$ )  
major isomer

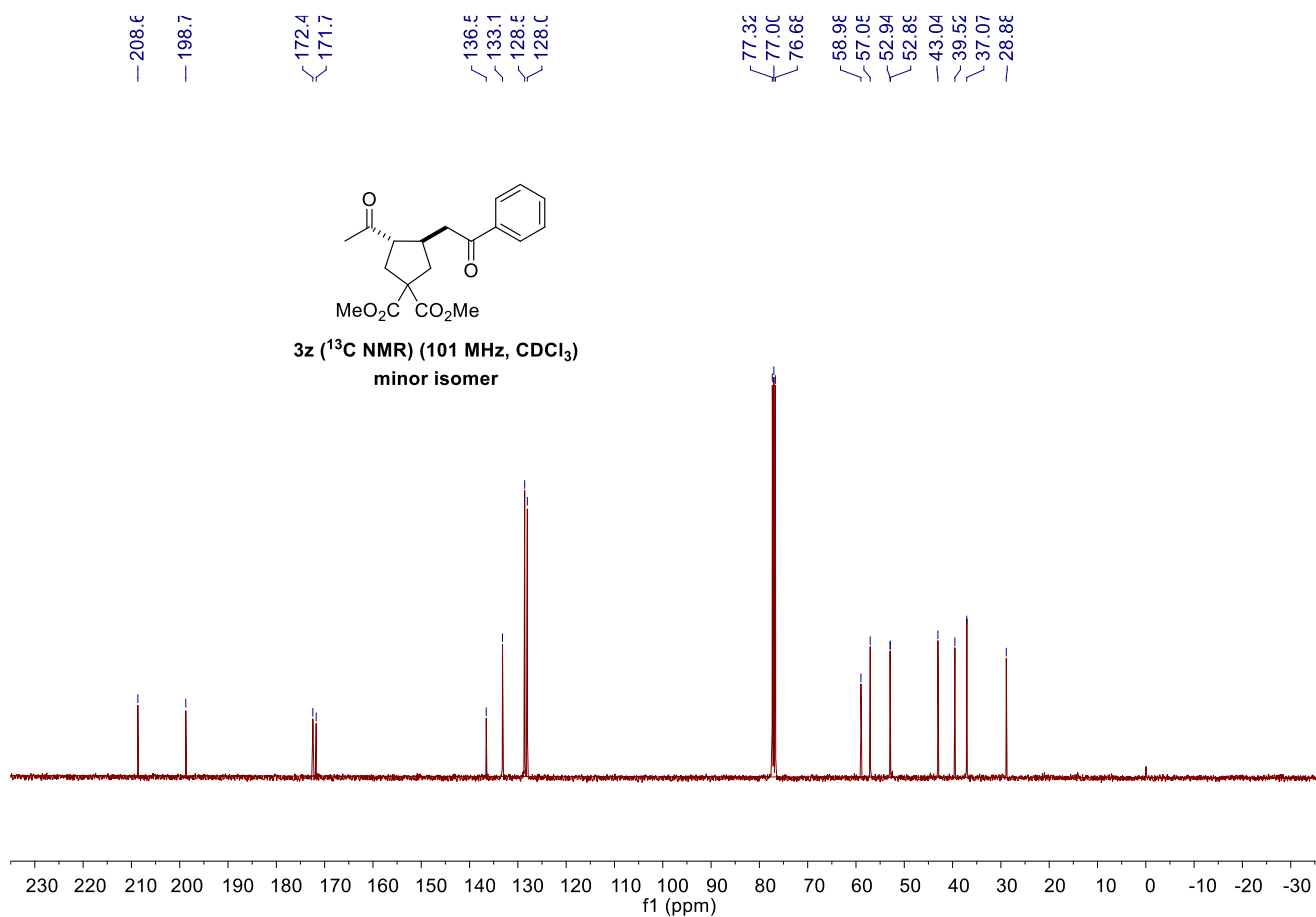


**3z** ( $^{13}\text{C}$  NMR) (101 MHz,  $\text{CDCl}_3$ )  
major isomer

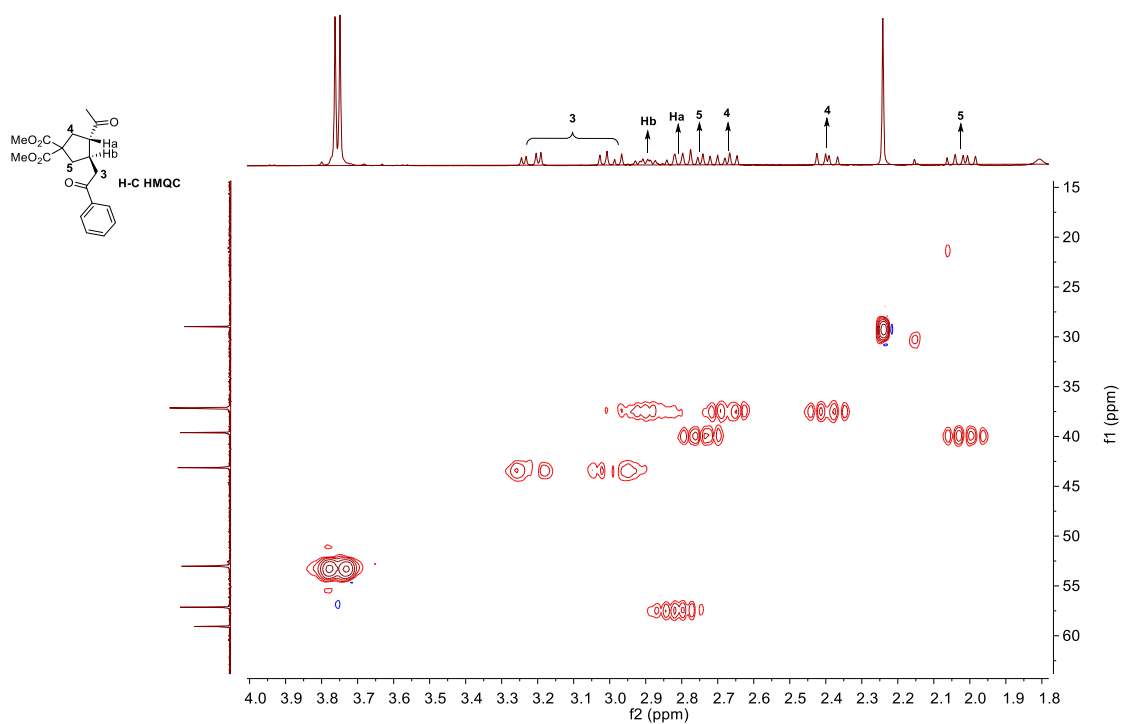


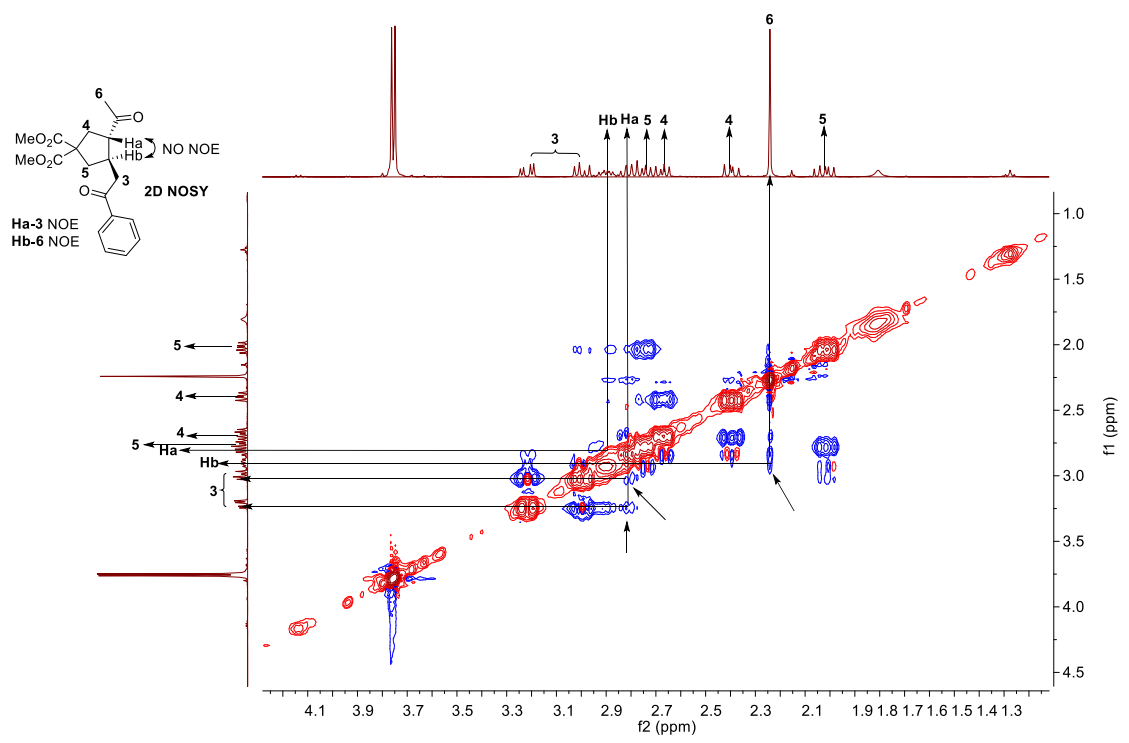
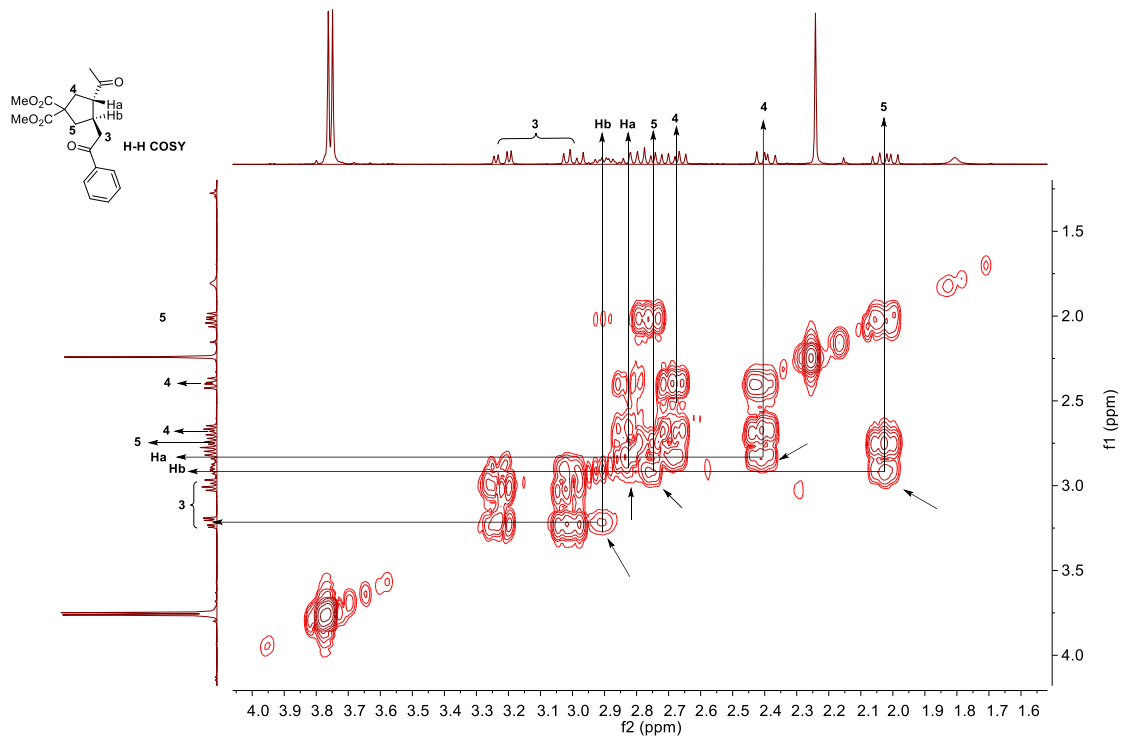


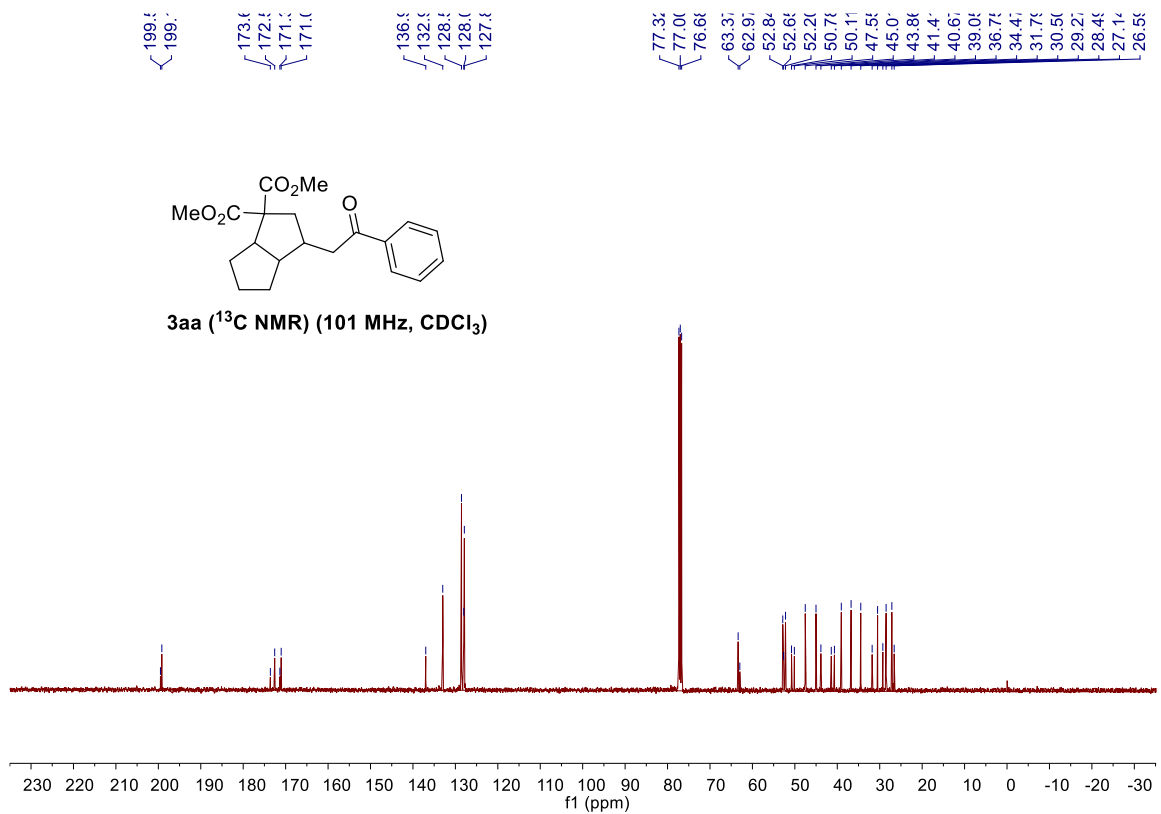
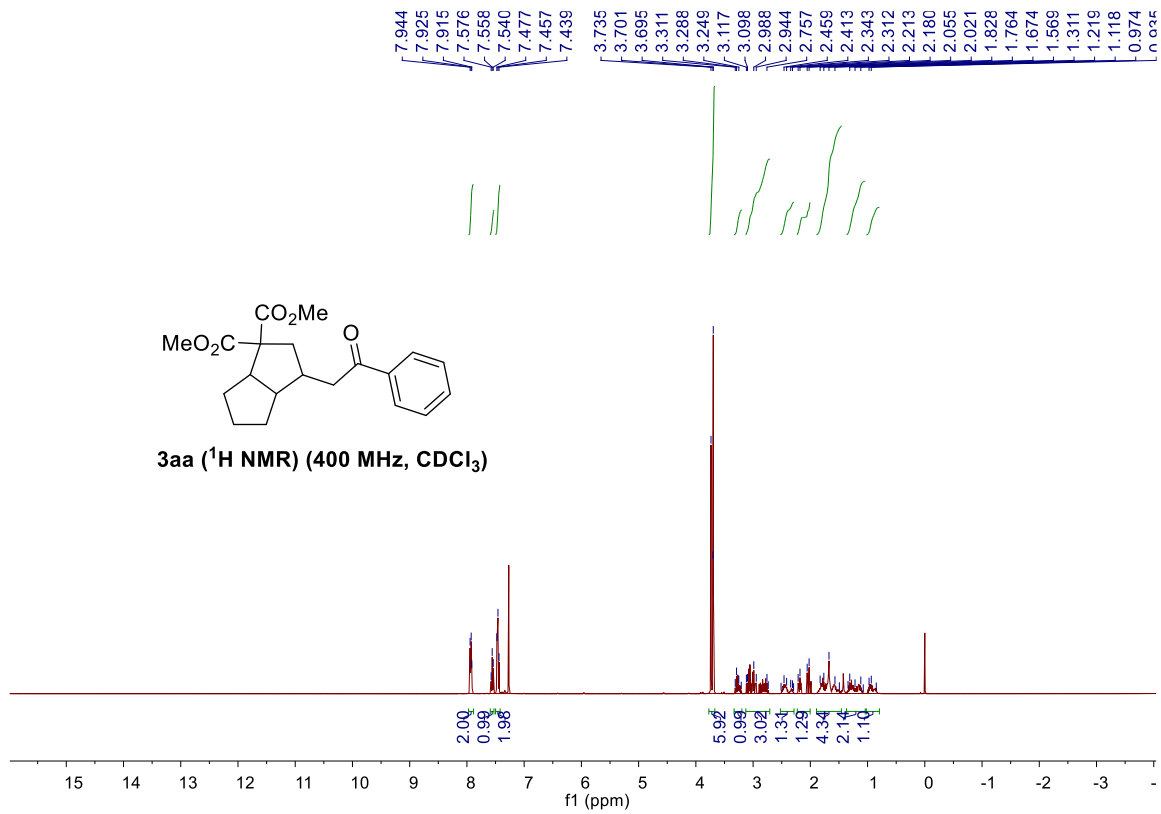


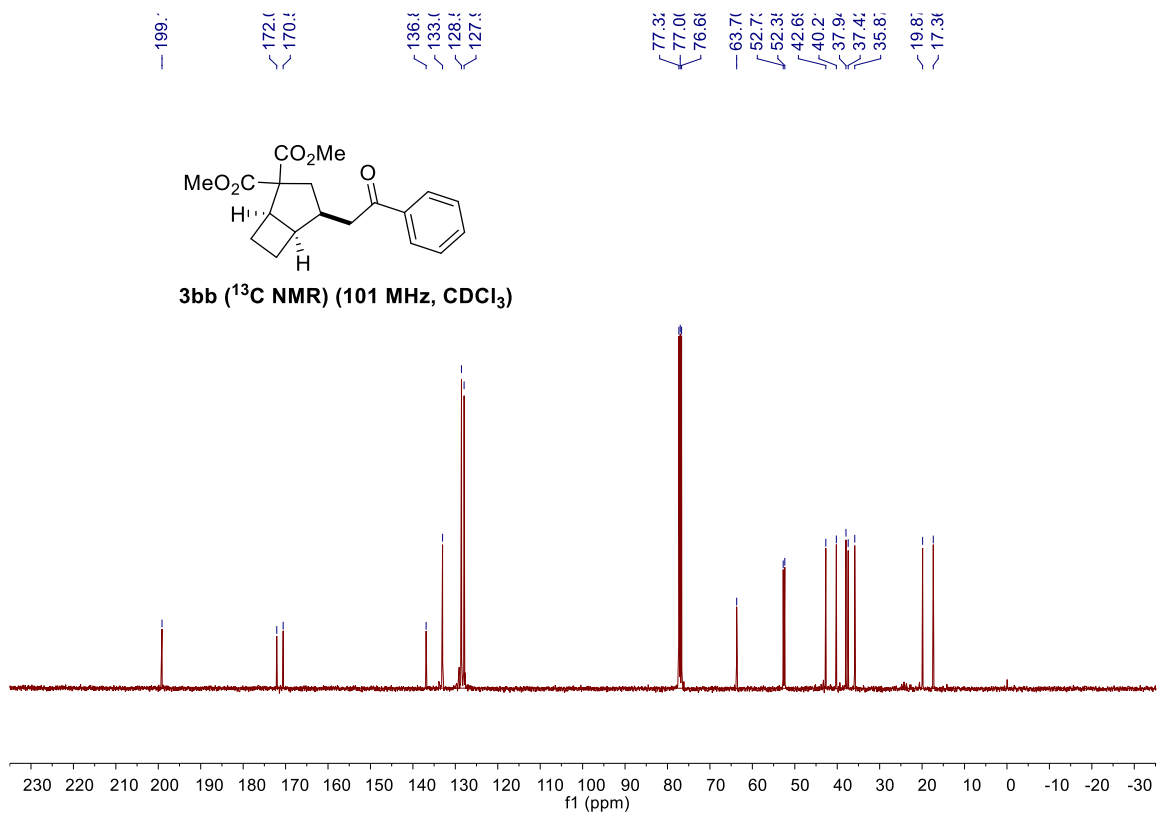
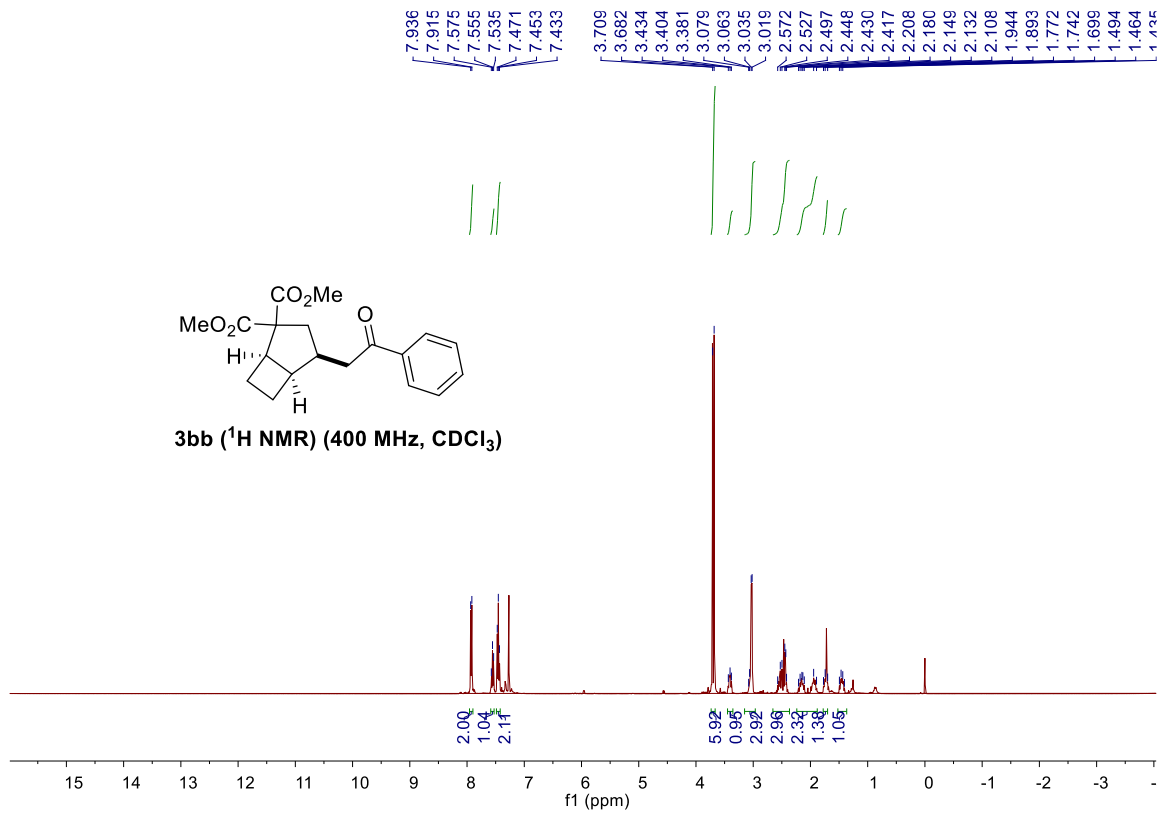


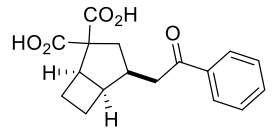
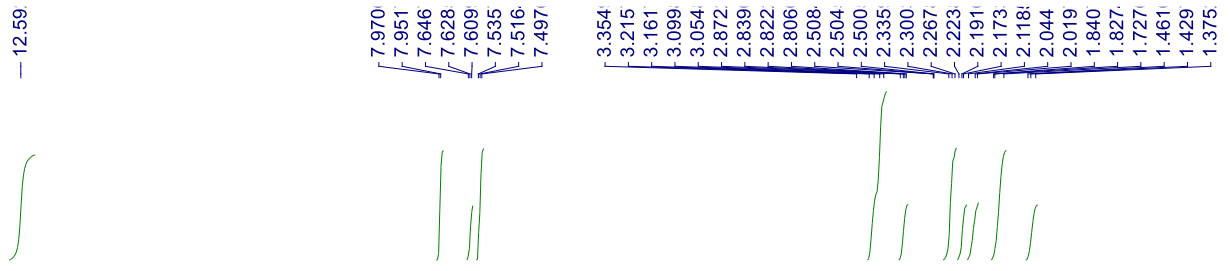
## 2D NMR spectra of 38 (minor isomer)



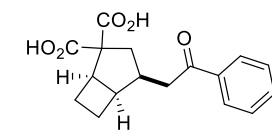
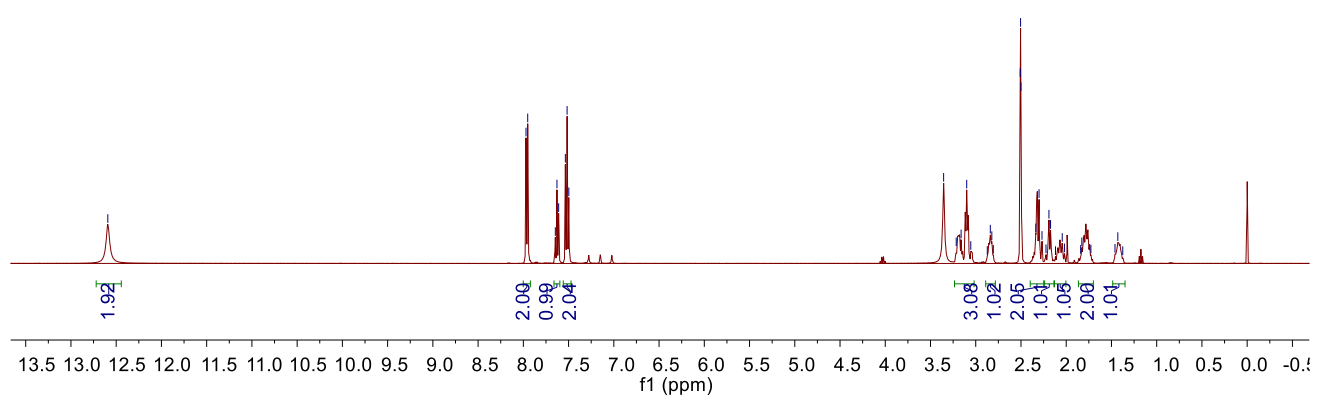




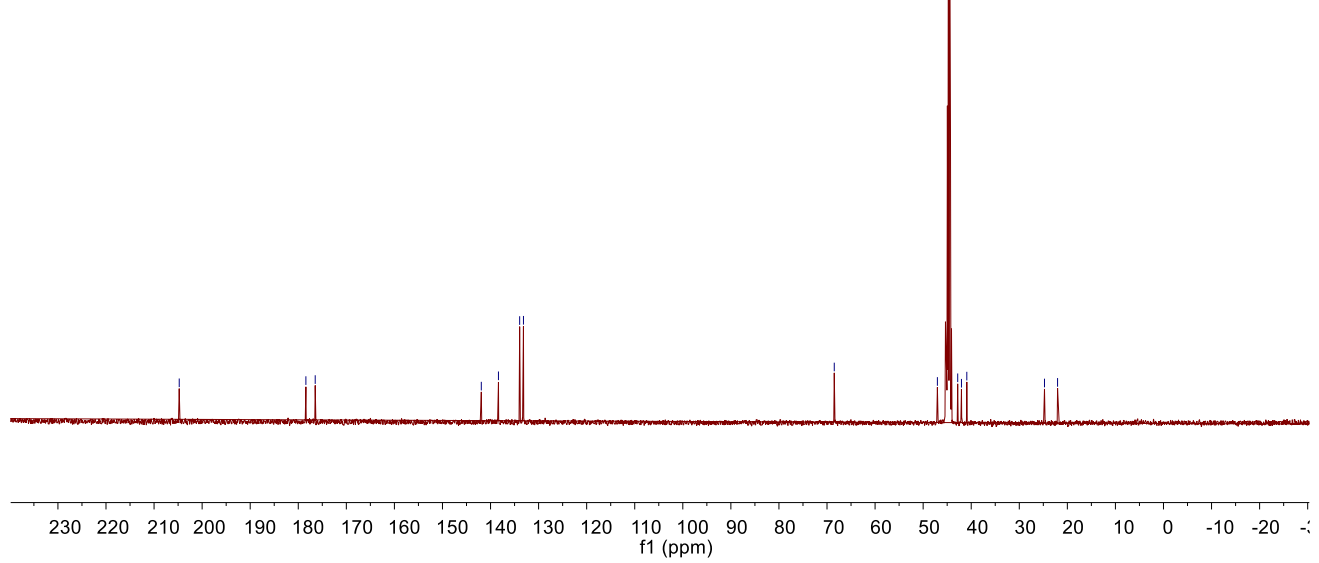


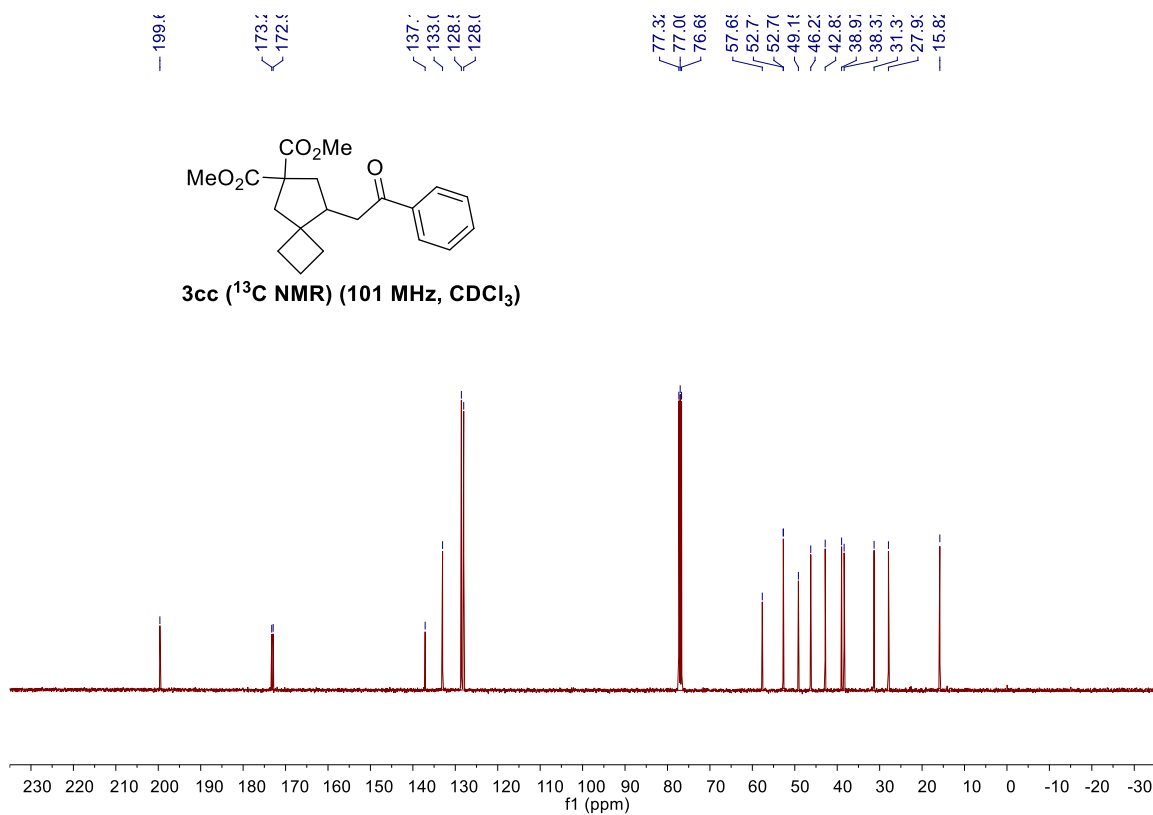
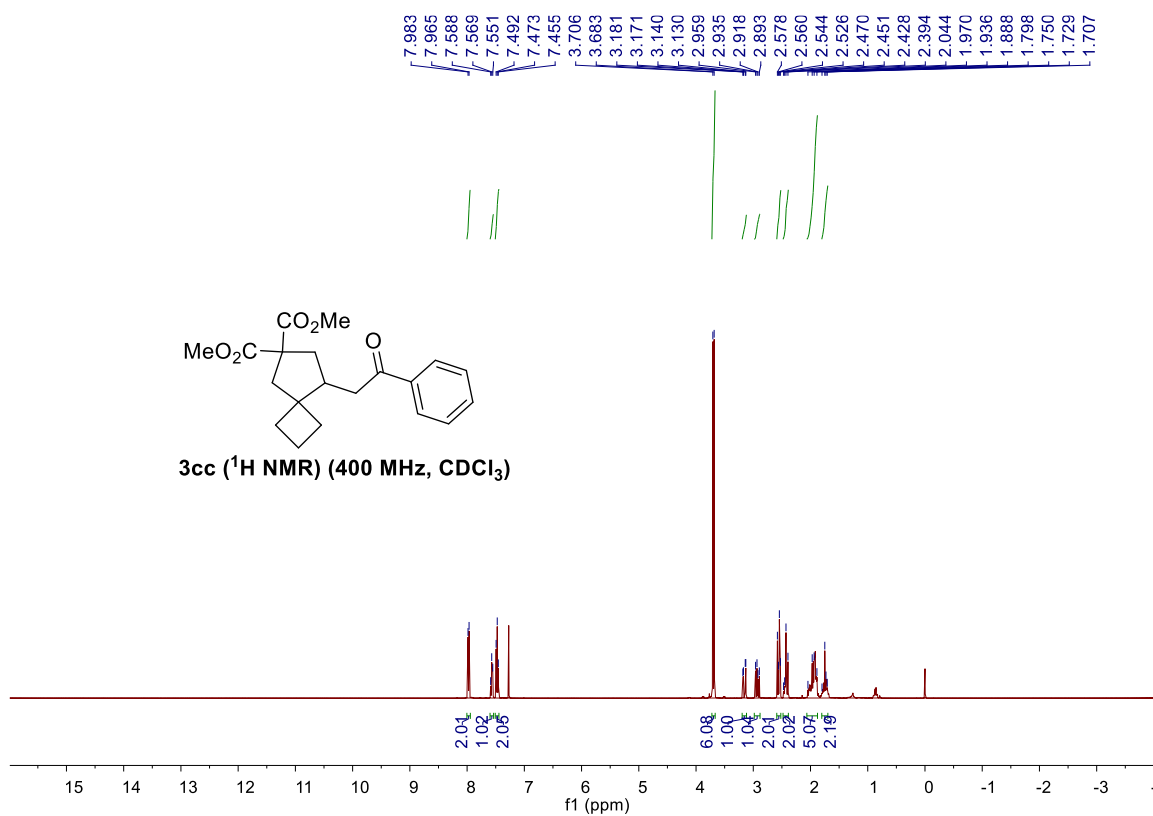


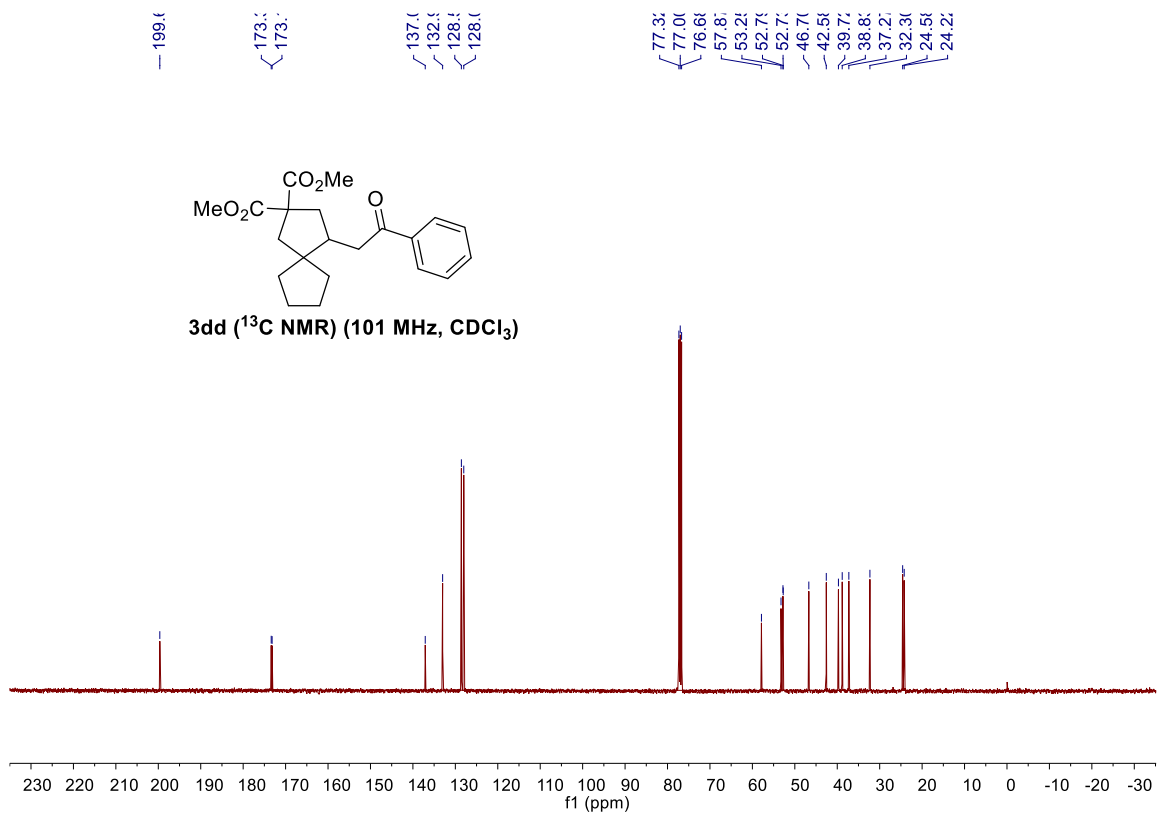
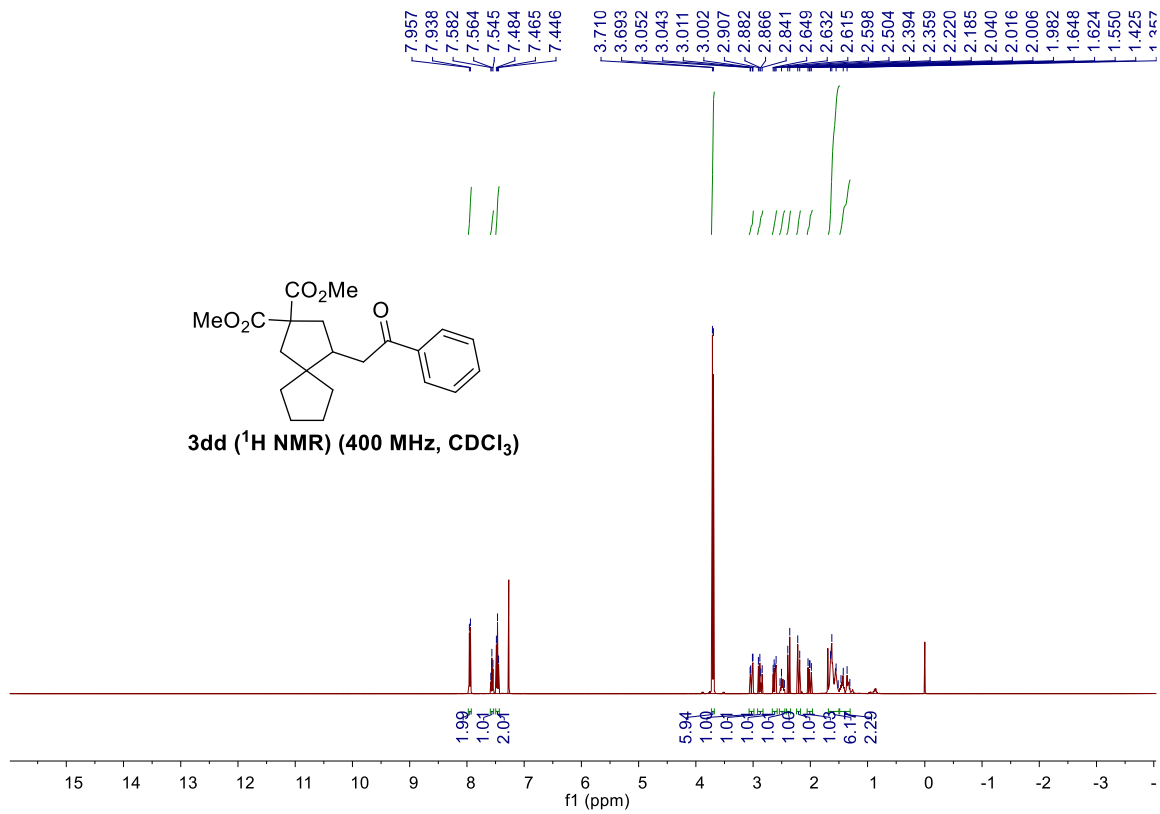
3bb' (<sup>1</sup>H NMR) (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO)

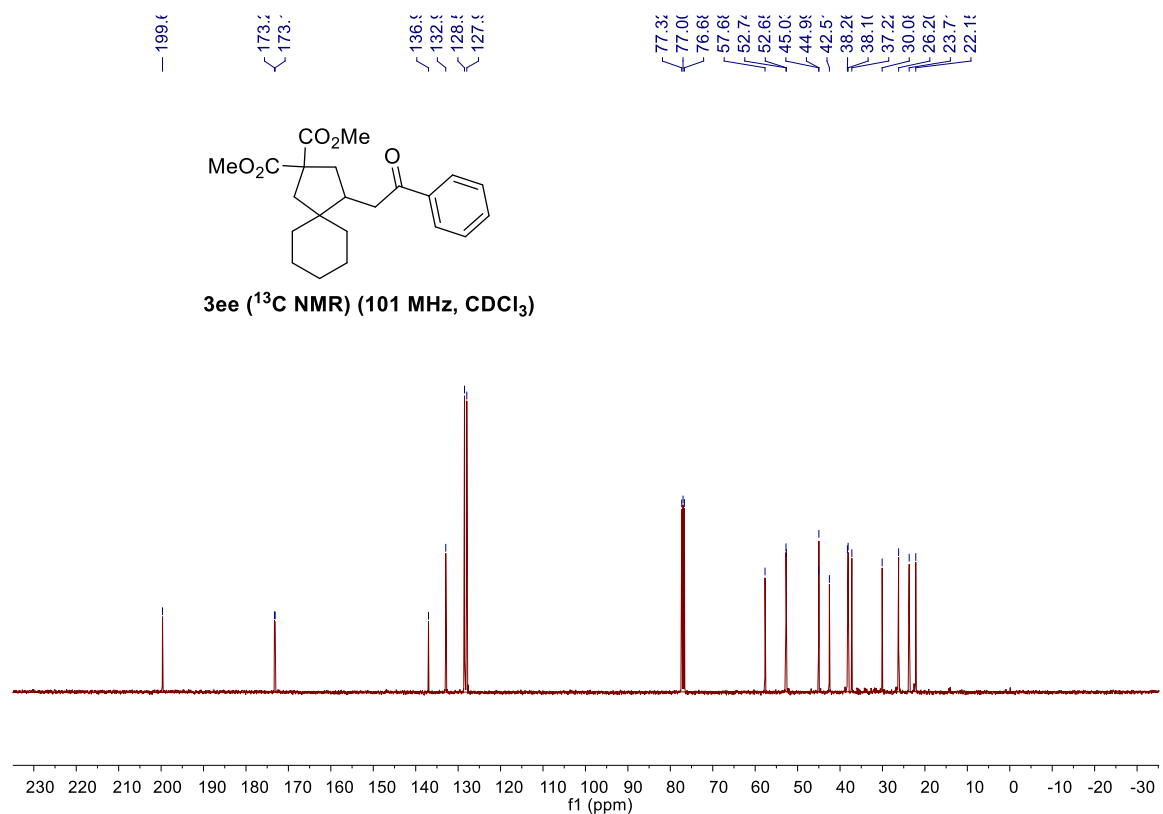
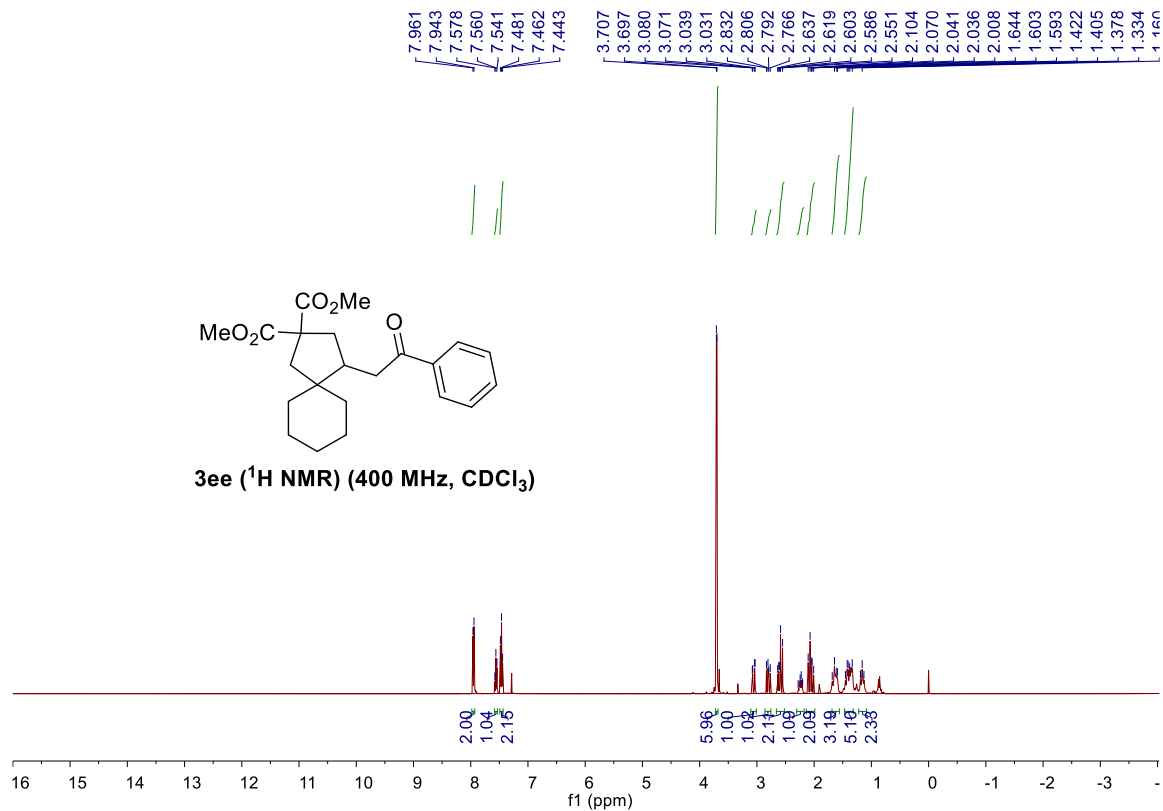


3bb' (<sup>13</sup>C NMR) (101 MHz, (CD<sub>3</sub>)<sub>2</sub>SO)

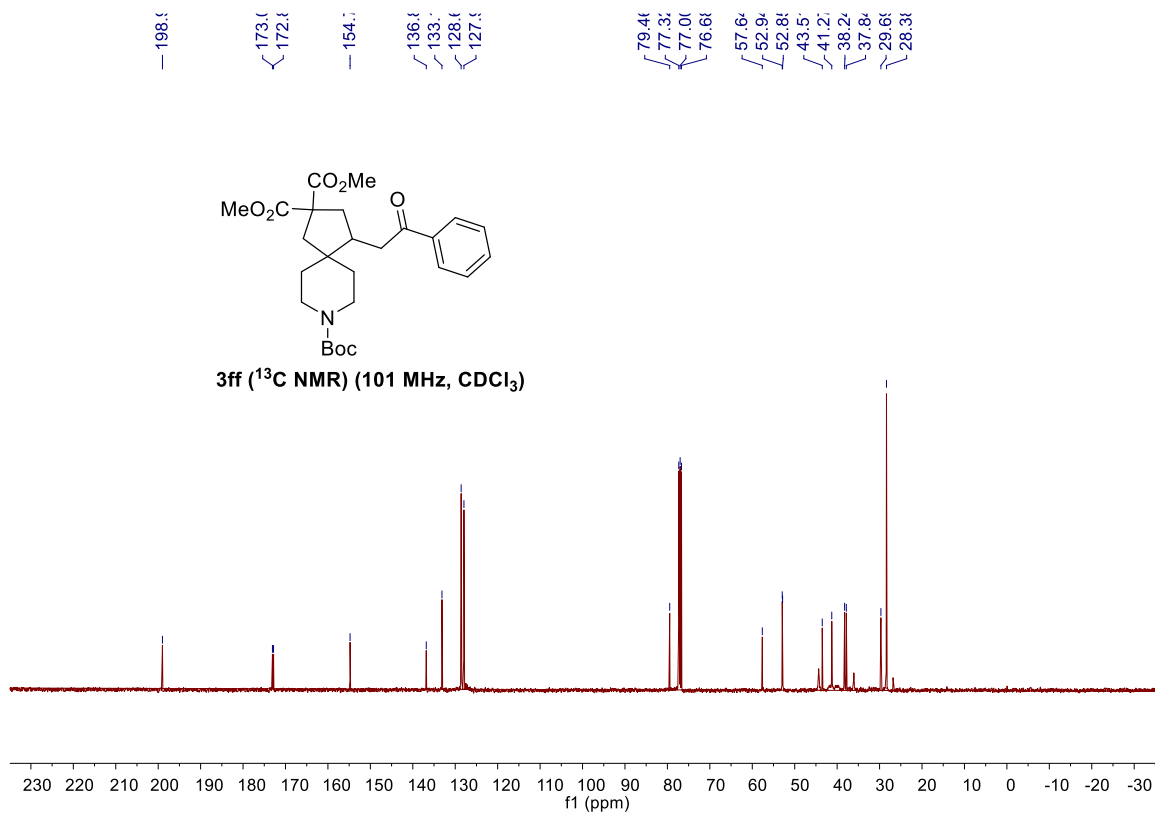
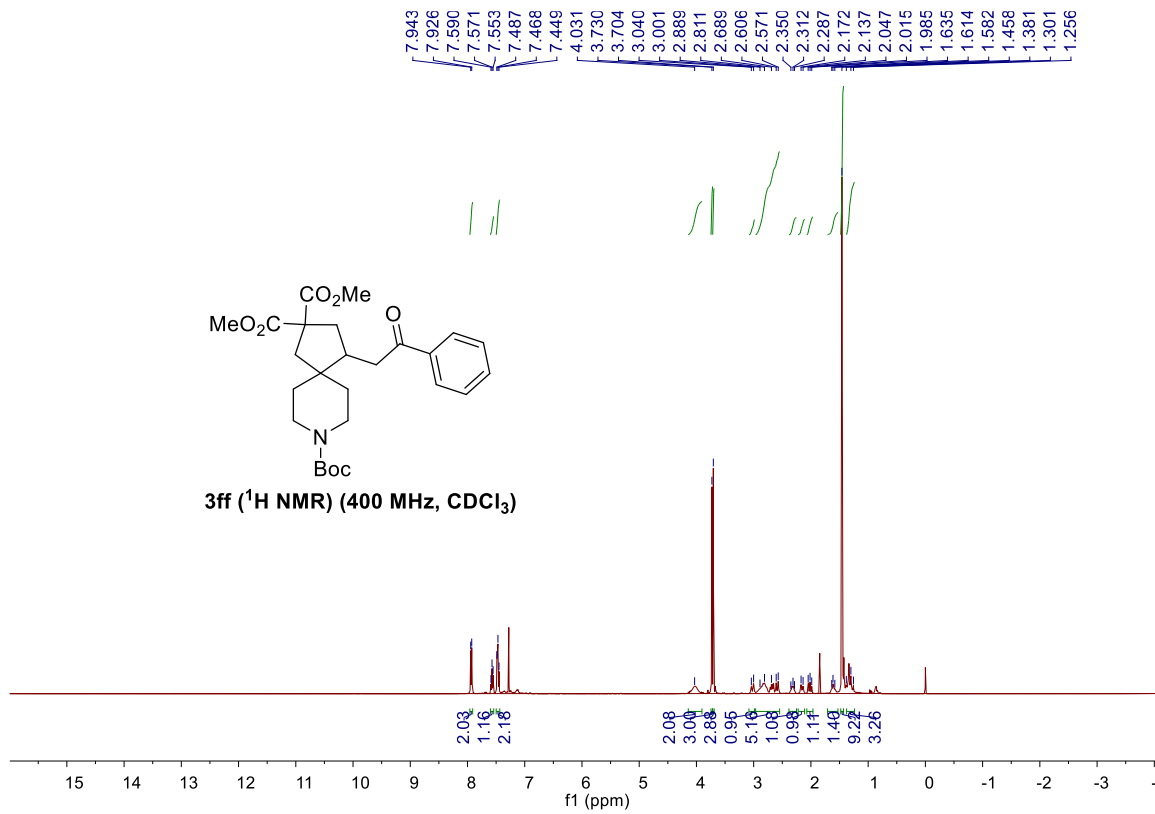


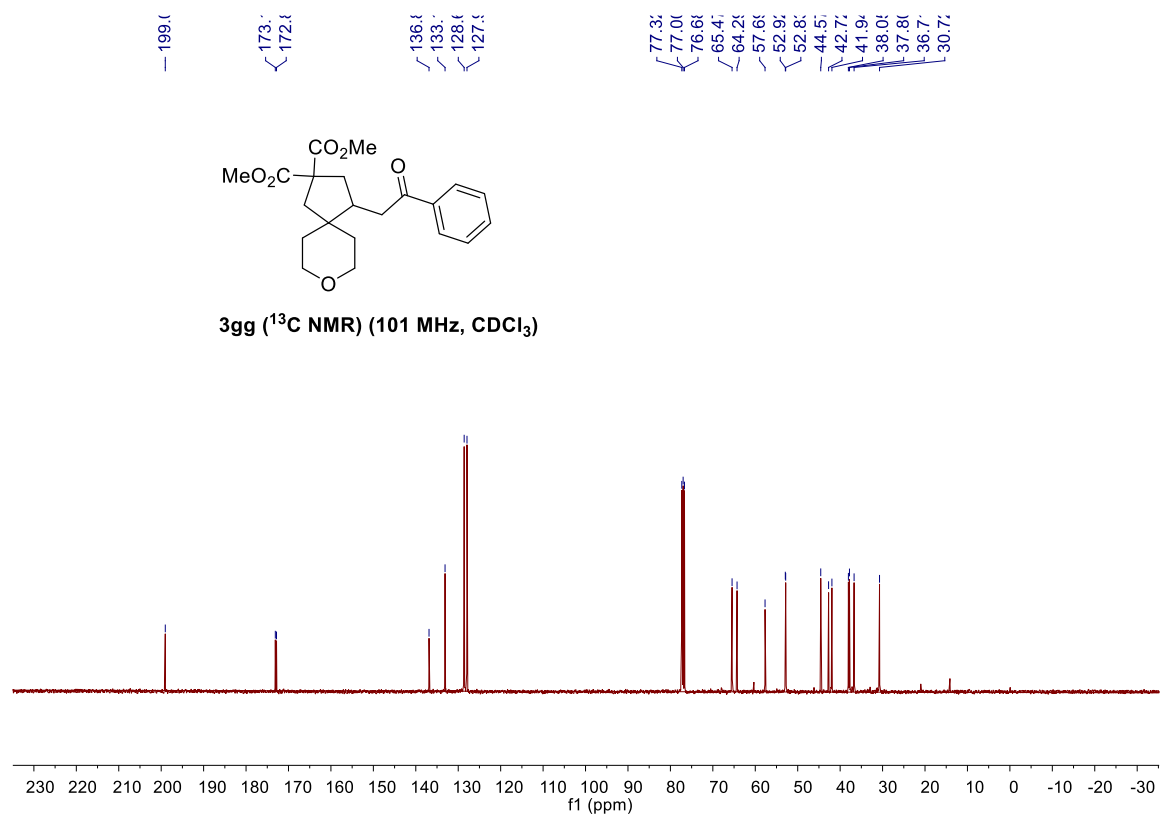
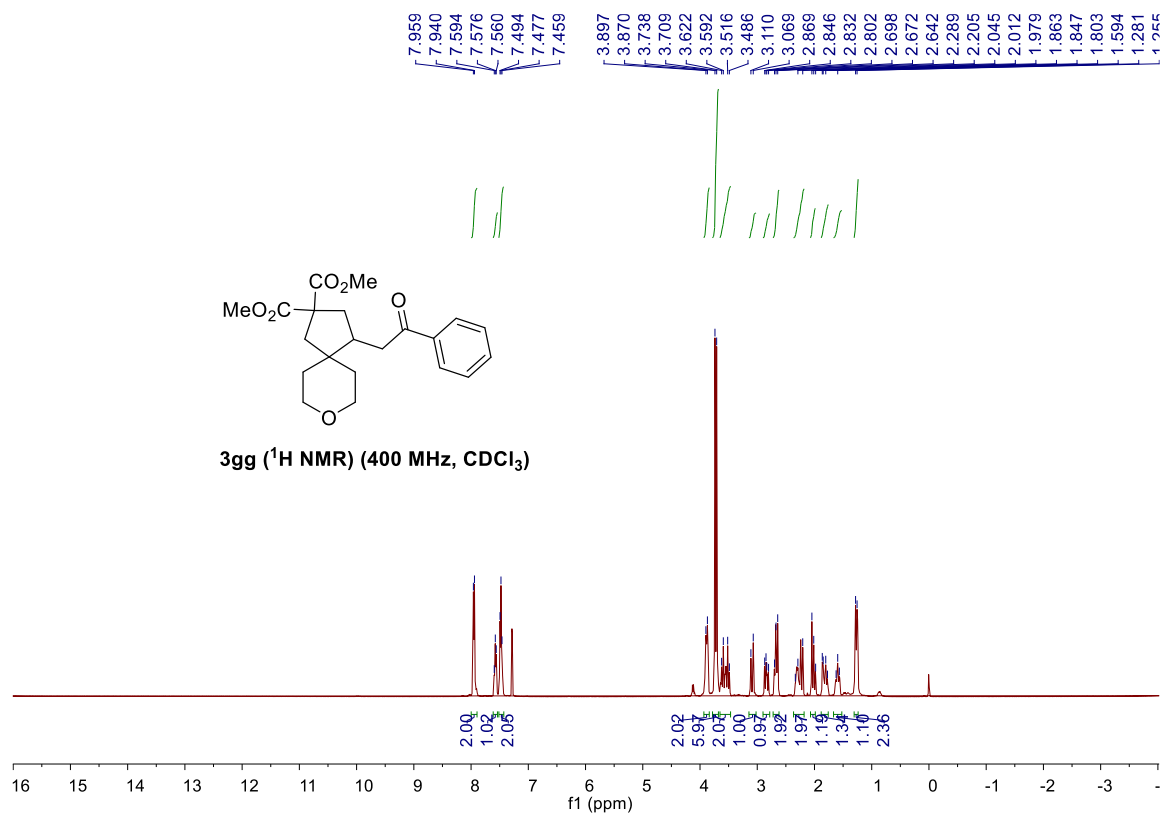


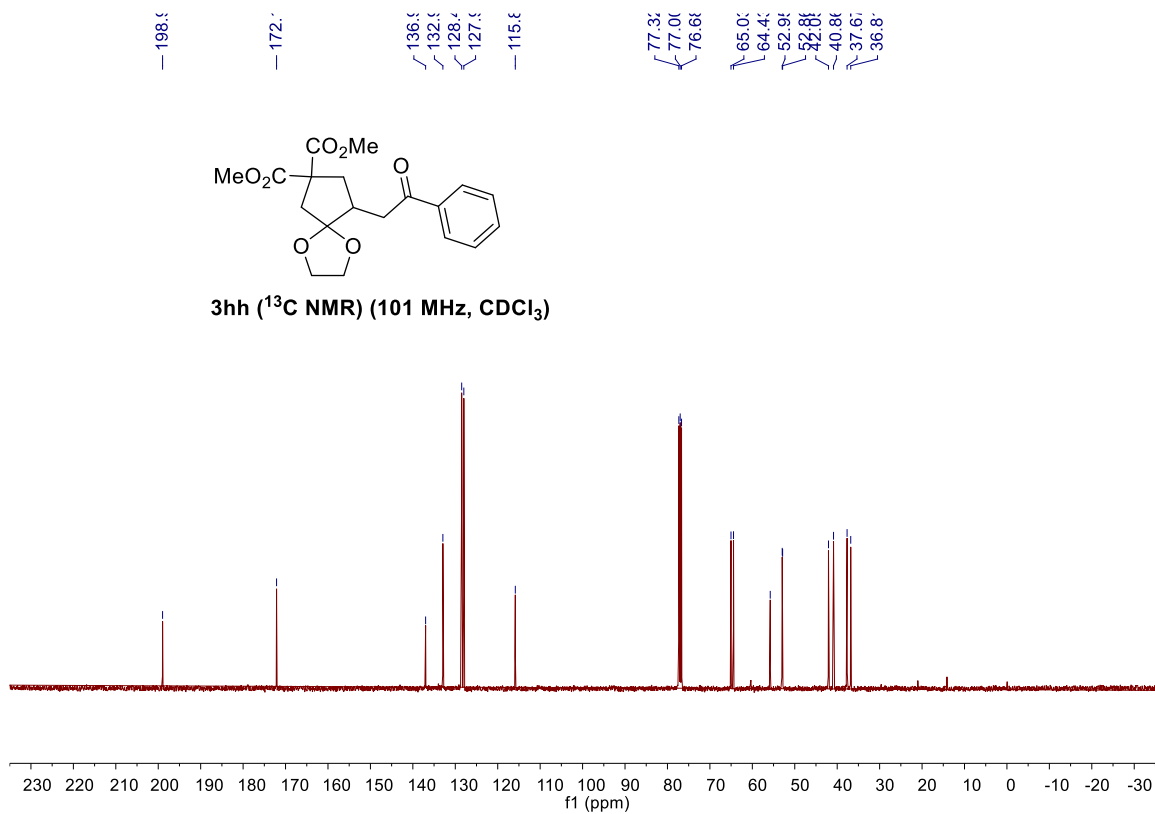
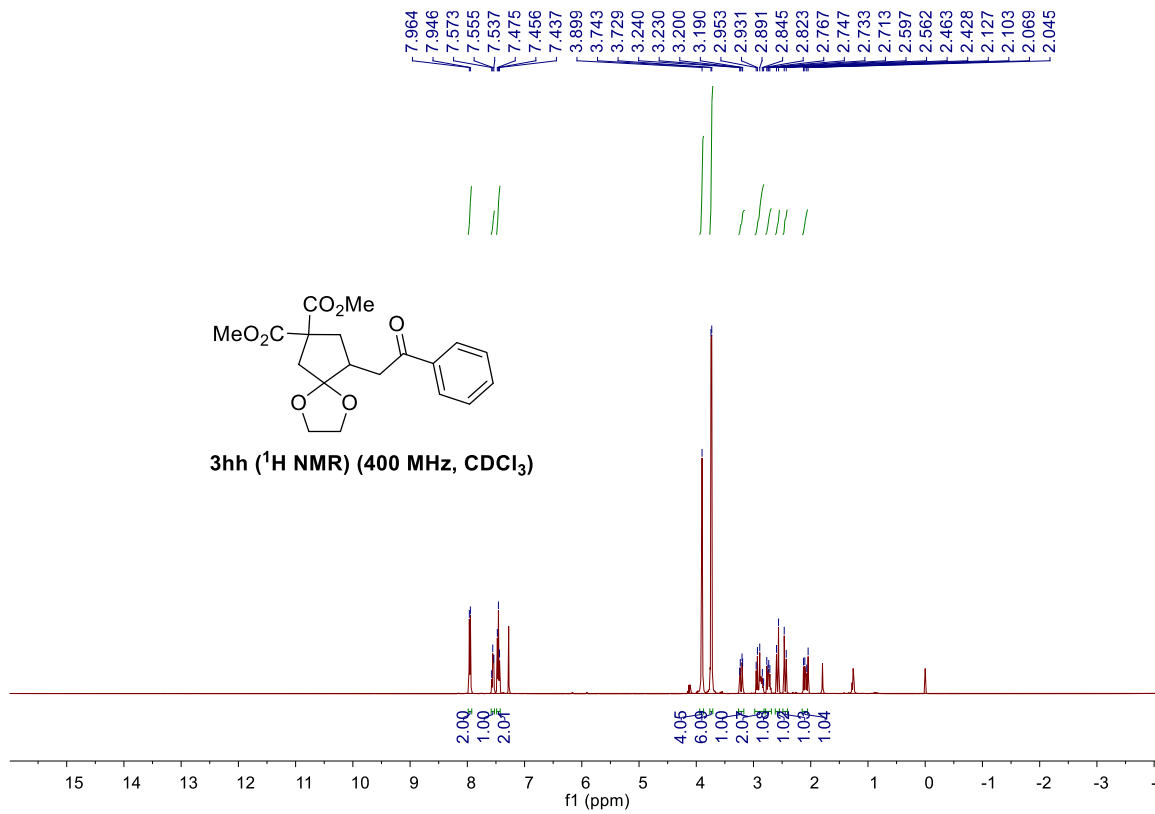


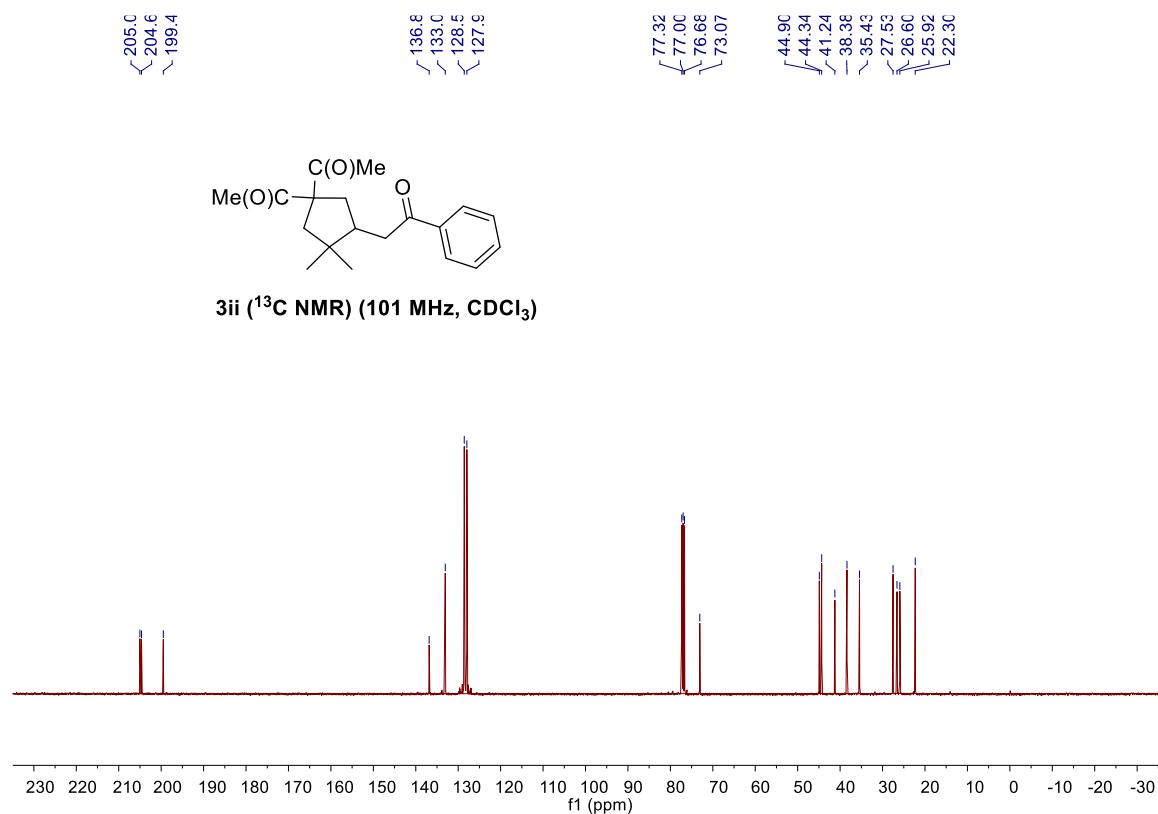
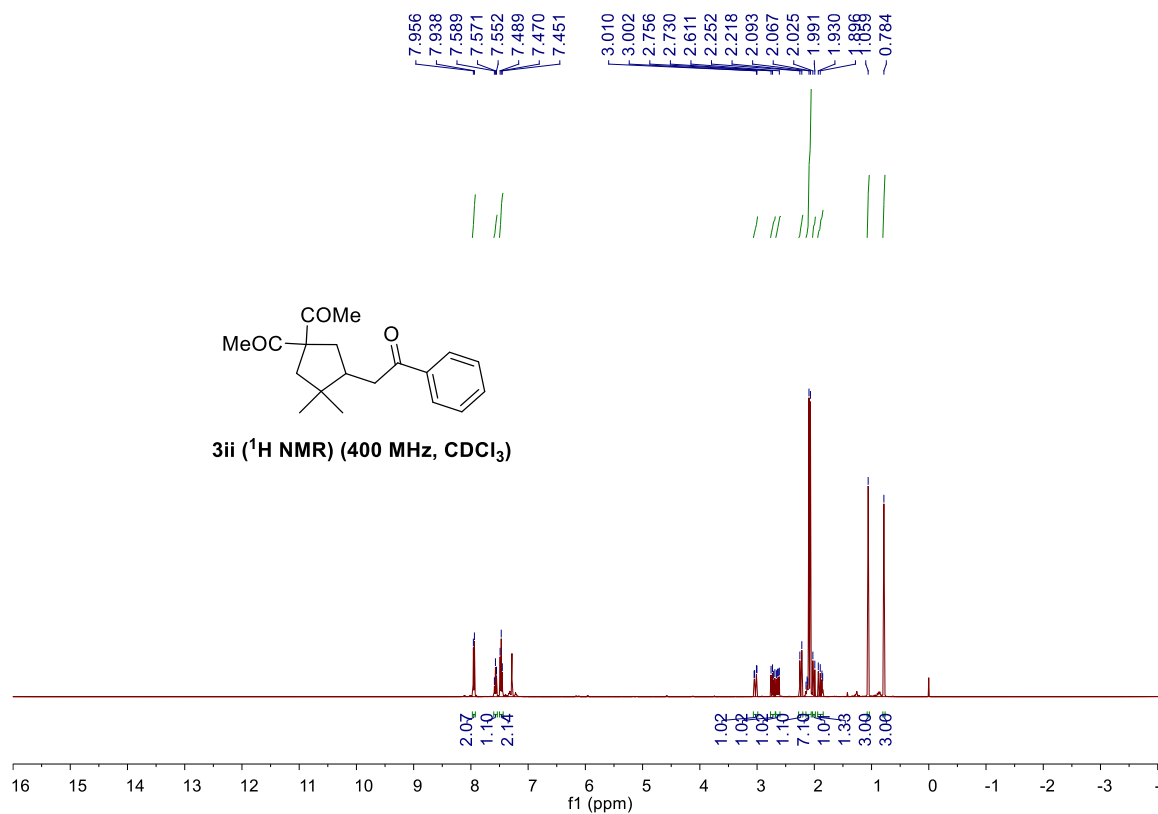


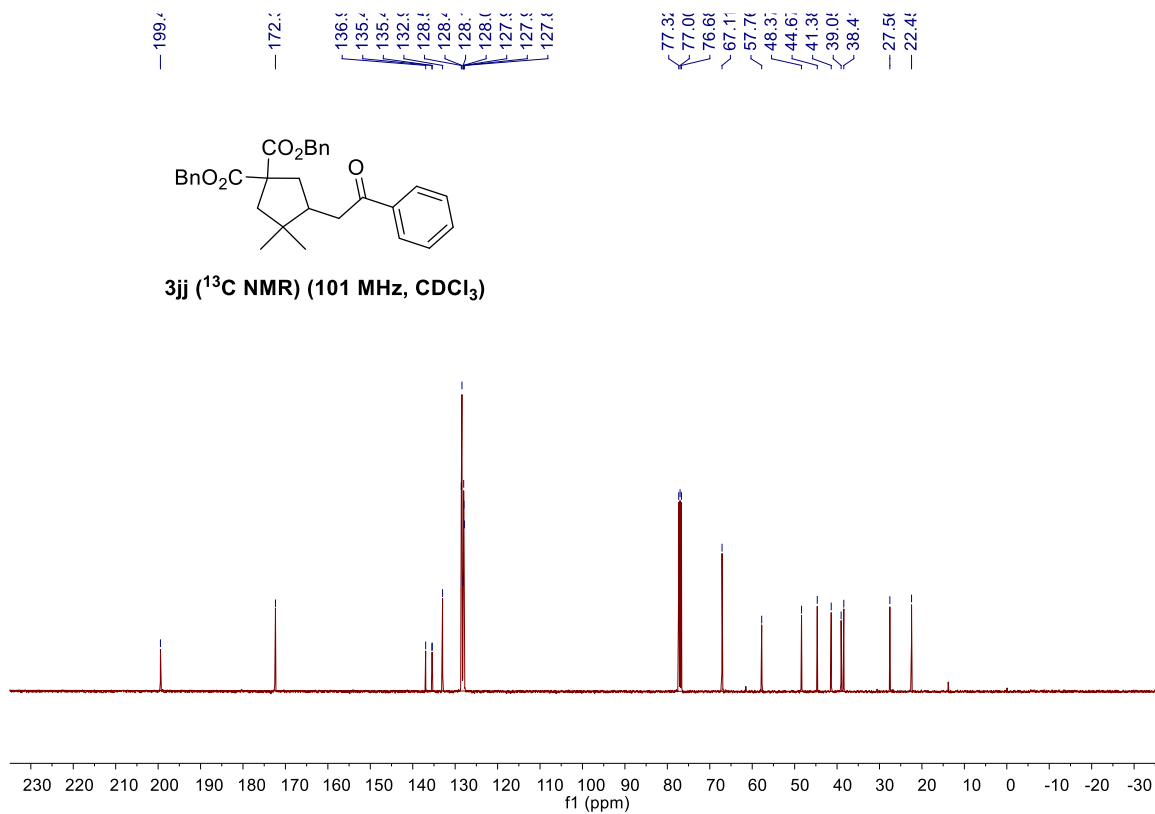
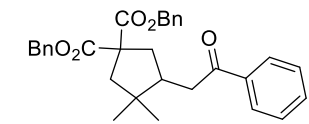
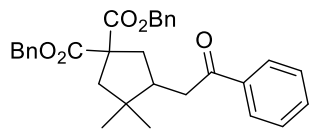
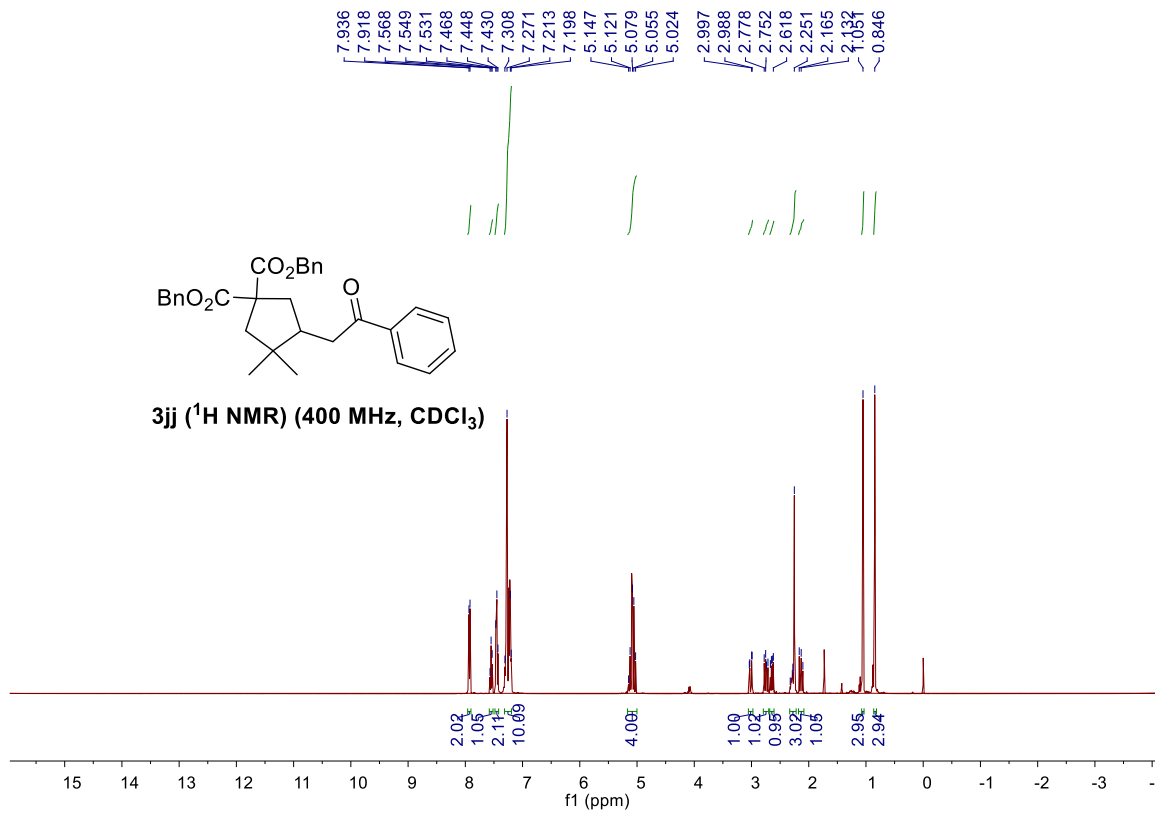


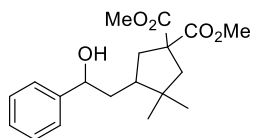
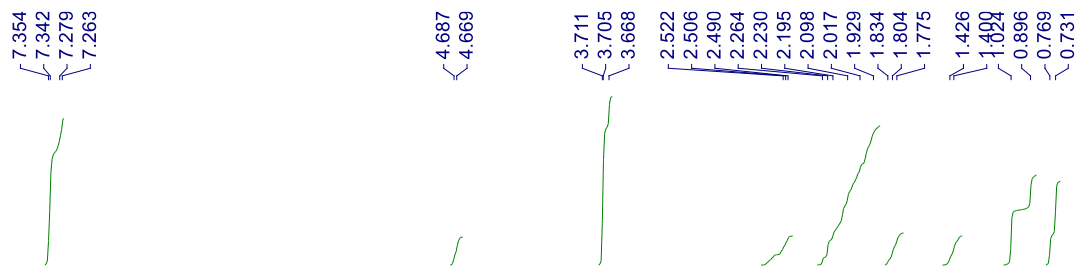




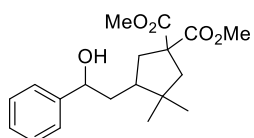
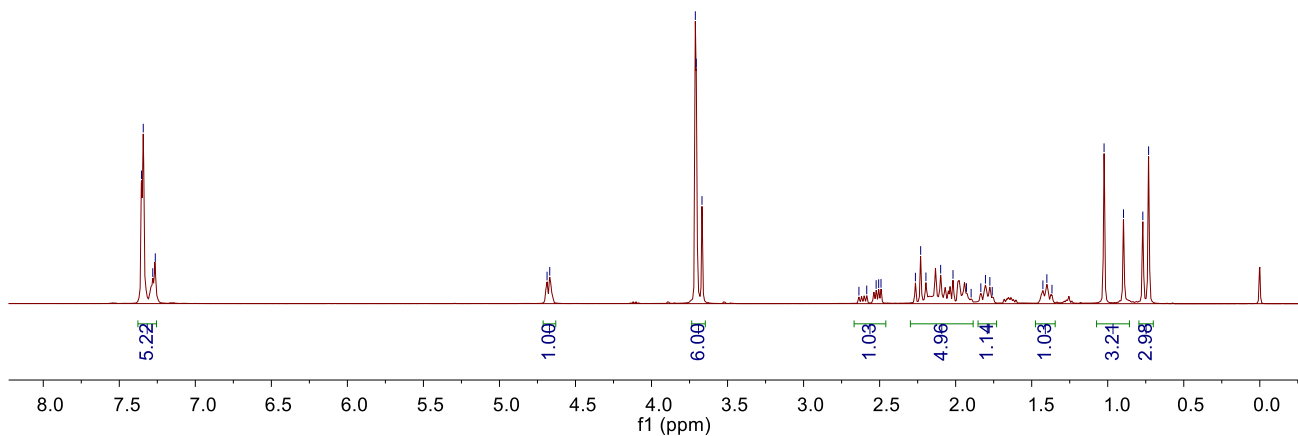








4 (<sup>1</sup>H NMR) (400 MHz, CDCl<sub>3</sub>)



4 (<sup>13</sup>C NMR) (101 MHz, CDCl<sub>3</sub>)

