

Supporting Information

**Copper-Catalyzed and Indium-Mediated  
Methoxycarbonylation of Unactivated Alkyl Iodides with  
Balloon CO**

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## **I. Experimental Section**

### **Part 1. General Information**

#### **1. Chemicals and Reagents**

Extra dry 1, 4-Dioxane (99.9%, with molecular sieves, water  $\leq$  30 ppm (by K.F.)) was purchased from Energy Chemical. Deuterated solvents were used as received ( $\text{CDCl}_3$  from J&K Co., China). The following reagents,  $\text{CuOTf}$  (Accela ChemBio Co., Ltd., China),  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  (Alfa Aesar),  $\text{CuCl}$  (Alfa Aesar),  $\text{CuBr}$  (Sigma Aldrich),  $\text{CuI}$  (Alfa Aesar),  $\text{CuOAc}$  (Acros),  $\text{Cu}$  (500 mesh, Alfa Aesar),  $\text{MgCO}_3$  (Macklin Biochemical Co., Ltd., China),  $\text{K}_2\text{CO}_3$  (J&K Co., Ltd., China),  $\text{Cs}_2\text{CO}_3$  (J&K Co., Ltd., China), Indium powders (200 mesh, Macklin Biochemical Co., Ltd. China),  $\text{InI}$  (ultra dry, 3A Chemicals Co., Ltd. China) were purchased, and used as received. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

#### **2. Physical Method**

Column chromatography was performed using silica gel 200-300 mesh (purchased from Accela ChemBio Co., Ltd. China) as the solid support. Nuclear magnetic resonance (NMR) spectra were recorded on a JNM-ECZ400s/L or a Bruker Avance 600 MHz.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts were reported in  $\delta$  units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. Reference peaks for dimethyl sulfoxide in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were set at 2.50 ppm and 39.51 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using an AB-SCIEX Triple TOF 4600. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

## Part 2. Details of Optimization

A typical procedure for optimization of the reaction conditions: To a flame-dried Schlenk tube equipped with a stir bar was added CuOTf (0.045 mmol, 9.6 mg, 15 mol%), 200 mesh indium powder (0.36 mmol, 41.4 mg, 120 mmol%) or indium iodide (0.30 mmol, 72.5 mg, 100 mol%), MgCO<sub>3</sub> (0.45 mmol, 37.8 mg, 150 mol%) or K<sub>2</sub>CO<sub>3</sub> (0.30 mmol, 41.4 mg, 100 mol%) and alkyl iodide (0.30 mmol, 100 mol%, if alkyl iodide is solid) in a glovebox under N<sub>2</sub> atmosphere. The tube was capped with a rubber septum and took out of glove-box. Subsequently, the tube was purged 3 times with CO and then a balloon filled with CO was inserted. Finally, alkyl iodide (0.30 mmol, 100 mol%, if alkyl iodide is liquid), 56  $\mu$ L of methanol (1.5 mmol, 500 mol%) and 2 mL of 1,4-dioxane were added via syringes. The resulting mixture was allowed to stir at room temperature for 24h. After which point, the reaction mixture was directly loaded onto a silica gel column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided a mixture containing the product. Yields were determined by <sup>1</sup>H NMR using 2, 5-dimethylfuran as internal standard.

**Table S1.** Optimization for methoxycarbonylation of secondary alkyl iodide.<sup>a</sup>

$  \begin{array}{c}  \text{Me} \\    \\  \text{RO}-(\text{CH}_2)_2-\text{I} + \text{CO} + \text{CH}_3\text{OH} \xrightarrow[\text{MgCO}_3 (150 \text{ mol } \%), \text{ 1,4-dioxane (2 mL), 25 }^\circ\text{C, 24 h}]{\text{method A} \\ \text{CuOTf (15 mol } \%), \text{ In (120 mol } \%) } \text{RO}-(\text{CH}_2)_2-\text{CO}_2\text{Me} \\  \text{1 (0.3 mmol)} \quad \quad \quad \text{1 atm} \quad \text{1.5 mmol} \quad \quad \quad \text{2, R = 4-MeOC}_6\text{H}_4\text{C(O)}  \end{array}  $					
entry <sup>a</sup>	variation from the standard conditions	yield (%) <sup>b</sup>			
		2	hydrogenation	hydrolysis	
1	None	78 (70) <sup>c</sup>	14	5	
2	CuCl instead of CuOTf	70	20	5	
3	CuCl <sub>2</sub> instead of CuOTf	N.D.	-	-	
4	CuBr instead of CuOTf	66	20	6	
5	CuI instead of CuOTf	74	16	6	
6	CuSO <sub>4</sub> instead of CuOTf	N.D.	-	-	
7	Cu(OTf) <sub>2</sub> instead of CuOTf	trace	-	-	
8	InI instead of In	61	9	22	
9	InCl <sub>3</sub> instead of In	N.D.	-	-	
10	Zn instead of In	trace	86	-	
11	Mn instead of In	N.D.	-	-	
12	K <sub>2</sub> CO <sub>3</sub> instead of MgCO <sub>3</sub>	76	14	3	
13	Et <sub>3</sub> N instead of MgCO <sub>3</sub>	<10	-	-	
14	Without In	N.D.	-	-	
15	without CuOTf	N.D.	-	-	
16	Without MgCO <sub>3</sub>	69	18	7	
17	2.0 atm. CO	68	16	14	
18	4.0 atm. CO	68	19	-	
19	None <sup>d</sup>	63 <sup>c</sup>	-	-	

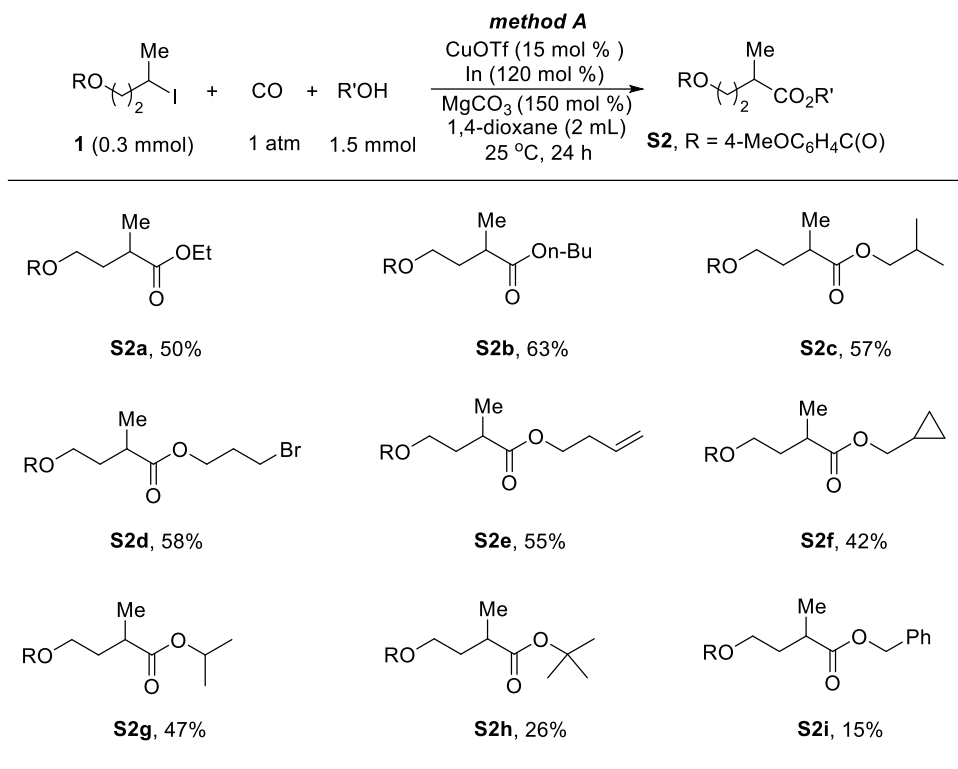
<sup>a</sup> Standard conditions: see Table 1, entry 1. <sup>b</sup> NMR yield using 2, 5-dimethylfuran as the internal reference. <sup>c</sup> Isolated yield. <sup>d</sup> The reaction was scaled up to 2 mmol.

**Table S2:** Optimization for the methoxycarbonylation of tertiary alkyl iodide

<p style="text-align: center;"><i>method B</i></p> <p style="text-align: center;"> </p> <p>0.3 mmol      1 atm      1.5 mmol      20 °C, 24 h      <b>22</b>, R = 4-Me-C<sub>6</sub>H<sub>4</sub>C(O)</p> <p>Byproducts:</p> <div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <p><b>22a</b> R' = OH <b>22b</b> R' = OMe <b>22c</b> R' = H</p> </div> <div style="text-align: center;"> <p><b>22d</b></p> </div> </div>							
entry	variation from <i>method B</i>	yield (%) <sup>a</sup>					
		<b>22</b>	<b>22a</b>	<b>22b</b>	<b>22c</b>	<b>22d</b>	<b>22e</b>
1	None	65 (60) <sup>b</sup>	16	4	7	-	-
2	Method A	5 <sup>b</sup>	-	-	-	-	-
3	Method A, but 4 atm CO	<10	-	-	-	-	-
4	Method A, but 50 nm indium	31	22	15	-	13	5
5	Without K <sub>2</sub> CO <sub>3</sub>	36	26	13	8	11	6
6	Without K <sub>2</sub> CO <sub>3</sub> , 4 atm of CO	46	10	-	22	8	4
7	MgCO <sub>3</sub> instead of K <sub>2</sub> CO <sub>3</sub>	55	22	6	9	4	2
8	Na <sub>2</sub> CO <sub>3</sub> instead of K <sub>2</sub> CO <sub>3</sub>	51	28	6	5	6	2
9	Cs <sub>2</sub> CO <sub>3</sub> instead of K <sub>2</sub> CO <sub>3</sub>	49	34	-	3	3	1
10	50 mg 4A MS instead of K <sub>2</sub> CO <sub>3</sub>	50	20	5	15	5	2
11	0.75 equiv InI	50	23	7	5	5	2
12	0.5 equiv InI	45	20	10	6	6	2
13	10 mol% CuOTf	54	26	3	4	4	1

<sup>a</sup> NMR yield using 2, 5-dimethylfuran as the internal reference. <sup>b</sup> Isolated yield.

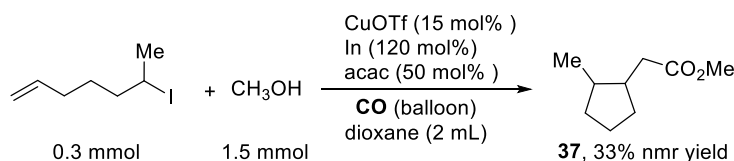
**Scheme 1.** Alkoxy carbonylation of **1** with selected alcohols.



a. Isolated yield.

### Part 3. Mechanistic consideration

1. Carbonylation of 6-iodo-hept-1-ene with methanol under 1 atm of CO



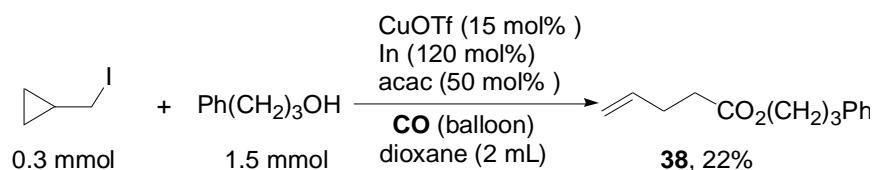
To a flame-dried Schlenk tube equipped with a stir bar was added CuOTf (0.045 mmol, 9.6 mg, 15 mol %), 200 mesh indium powder (0.36 mmol, 41.4 mg, 120 mmol %) in a glovebox under N<sub>2</sub> atmosphere. The tube was capped with a rubber septum and took out of glove-box. Subsequently, the tube was purged 3 times with CO and then a balloon filled with CO was inserted. Finally, 6-iodo-hept-1-ene (0.30 mmol, 67.2 mg, 100 mol %), 56  $\mu$ L of methanol (1.5 mmol, 500 mol %), acetylacetone (0.15 mmol, 15 mg, 50 mol %) and 2 mL of 1,4-dioxane were added via syringes. The resulting mixture was allowed to stir at room temperature for 24h. After which points, the reaction mixture was directly loaded onto a silica gel column without work-up. The residue in the reaction vessel was rinsed with small amount of ethyl acetate. Flash column chromatography provided the product containing a mixture of *cis*- and *trans*-isomers. Yields were determined by <sup>1</sup>H NMR using 2, 5-dimethylfuran as internal standard.

**Results:** 33% yield (a mix of *trans* and *cis* isomers) of (2-methyl-cyclopentyl)-acetic acid methyl ester was detected by <sup>1</sup>H NMR using 2, 5-dimethylfuran as internal standard. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  3.66 (s, 3H), 2.48 – 2.03 (m, 4H), 1.94 – 1.51 (m, 4H), 1.33 – 1.22 (m, 2H), 0.96 (d, *J* = 6.5 Hz, 0.6H (minor)), 0.81 (d, *J* = 7.1 Hz, 2.4H (major)). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$

174.3, 51.4, 51.3, 44.0, 40.4, 39.6, 39.0, 36.0, 35.3, 34.4, 33.1, 32.4, 30.1, 23.1, 22.5, 18.9, 15.1.

GC-MS calculated for  $[C_9H_{16}O_2]$ : 156.1, found 156.1 ( $M^+$ ), 141.1, 125.1.

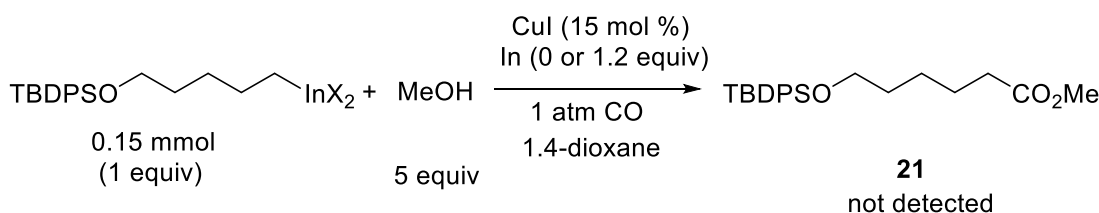
2. Carbonylation of (iodomethyl)cyclopropane with 3-phenyl-propan-1-ol under 1 atm of CO.



To a flame-dried Schlenk tube equipped with a stir bar was added CuOTf (0.045 mmol, 9.6 mg, 15 mol %), 200 mesh indium powder (0.36 mmol, 41.4 mg, 120 mmol %) in a glovebox under  $N_2$  atmosphere. The tube was capped with a rubber septum and took out of glove-box. Subsequently, the tube was purged 3 times with CO and then a balloon filled with CO was inserted. Finally, (iodomethyl)cyclopropane (0.30 mmol, 54.6 mg, 28  $\mu$ L, 100 mol %), 3-phenyl-propan-1-ol (1.5 mmol, 204.2 mg, 500 mol %), acetylacetone (0.15 mmol, 15 mg, 50 mol %) and 2 mL of 1,4-dioxane were added via syringes. After which point, the resulting mixture was allowed to stir at room temperature for 24h. Insoluble materials were separated by filtration with celite and washed with a small amount of EA. The filtrate was concentrated by reduced pressure. The residue was purified by flash column chromatography (5% of ethyl acetate in petroleum ether)

**Results:** 14.4 mg (22% yield) of pent-4-enoic acid 3-phenyl-propyl ester was obtained.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.32 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 5.91 – 5.79 (m, 1H), 5.11 – 5.00 (m, 2H), 4.11 (t,  $J$  = 6.5 Hz, 2H), 2.70 (t,  $J$  = 7.5 Hz, 2H), 2.45 – 2.35 (m, 4H), 2.01 – 1.92 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 173.1, 141.2, 136.7, 128.4, 128.4, 126.0, 115.5, 63.7, 33.5, 32.2, 30.2, 28.9. HRMS calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_2$  [ $M+H$ ]: 219.1396. Found 219.1395.

3. Carbonylation of alkyl-In $X_2$  reagent with methanol under 1 atm CO.



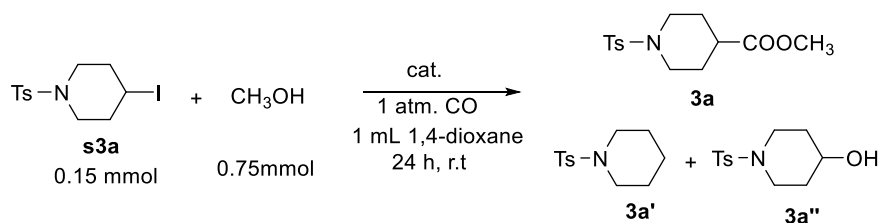
Preparation of alkyl-In $X_2$ : To an 10 mL sample vial, *tert*-butyl-(5-iodo-pentyloxy)-diphenylsilane (1.0 mmol, 452.4 mg, 1 equiv) was charged with indium (2 mmol, 229.6 mg, 2 equiv) and CuCl (2 mmol, 198.0 mg, 2 equiv) in 2 mL of THF- $d_8$  at room temperature. The reaction was stirred for 24 hours. After reaction, it was stood for around 30 minutes. Then the upper clear solution was carefully separated from the bottom black precipitate.<sup>1</sup>

To a flame-dried Schlenk tube equipped with a stir bar was added CuI (0.023 mmol, 4.3 mg, 15 mol%), 200 mesh indium powder (0.18 mmol, 20.7 mg, 120 mmol%) (or in the absence of indium powder) in a glovebox under  $N_2$  atmosphere. The tube was capped with a rubber septum and took out of glove-box. Subsequently, the tube was purged 3 times with CO and then a balloon filled with

CO was inserted. Finally, 28  $\mu$ L of methanol (0.75 mmol, 500 mol%), 2 mL of 1,4-dioxane and alkyl-InX<sub>2</sub> (0.3 mL, 0.15 mmol, obtained as above showed) were added via syringe. The resulting mixture was allowed to stir at room temperature for 24h. The reaction mixture was directly loaded onto a silica gel column without work-up. The residue in the reaction vessel was rinsed with small amount of ethyl acetate. Flash column chromatography provided a mixture containing the product. Yields were determined by <sup>1</sup>H NMR using 2, 5-dimethylfuran as internal standard.

**Results:** no ester product was detected either in the presence or in the absence of indium.

#### 4. Control experiments



To a flame-dried Schlenk tube equipped with a stir bar was added 4-iodo-1-(toluene-4-sulfonyl)-piperidine (0.15 mmol, 54.8 mg, 1 equiv) and catalysts in a glovebox under N<sub>2</sub> atmosphere. The tube was capped with a rubber septum and took out of the glovebox. Subsequently, the tube was purged 3 times with CO and then a balloon filled with CO was inserted. 28  $\mu$ L of methanol (0.75 mmol, 5.0 equiv) and 1 mL of 1, 4-dioxane were added via syringe. The resulting mixture was allowed to stir at room temperature for 24h. After which point, the reaction mixture was directly loaded onto a silica gel column without work-up. The residue in the reaction vessel was rinsed with small amount of ethyl acetate. Flash column chromatography provided a mixture containing the product. Yields were determined by <sup>1</sup>H NMR using 2, 5-dimethylfuran as internal standard. **Results:** showed as **table S3**

**Table S3:** Control experiments.

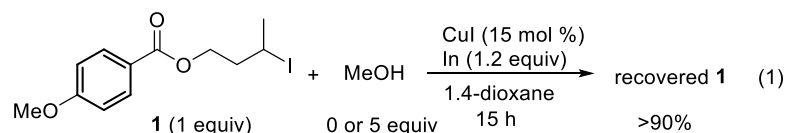
entry	catalysts	yield (%) <sup>a</sup>			
		<b>S3</b>	<b>3a</b>	<b>3a'</b>	<b>3a''</b>
1	1 equiv CuOTf	100	0	0	0
2	1.2 equiv Cu	100	0	0	0
3	1.2 equiv In	100	0	0	0
4	1.2 equiv In, 0.5 equiv Cu	100	0	0	0
5	0.5 equiv InCl <sub>3</sub> , 0.5 equiv Cu	100	0	0	0
6	1.2 equiv In, 0.5 equiv InCl <sub>3</sub> , 0.5	0	55	45	0

	equiv Cu				
4	0.15 equiv CuOTf, 1.2 equiv Zn	0	10	90	0
5	1.2 equiv Zn	100	0	0	0
6	1 equiv CuOTf, 1.2 equiv Zn	4	50	28	14
7	1 equiv Cu(OTf) <sub>2</sub> , 1.2 equiv Zn	4	28	50	2

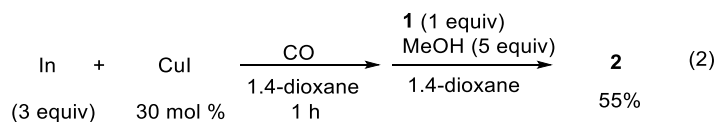
<sup>a</sup> NMR yield using 2, 5-dimethylfuran as the internal reference.

## 5. Control experiments and methoxycarbonylation in stepwise fashion.

- (1) To a suspension of CuI (4.3 mg, 0.023 mmol, 0.15 equiv) and indium powder (25.8 mg, 0.23 mmol, 1.5 equiv) in 1.0 mL of 1, 4-dioxane was added 4-methoxy-benzoic acid 3-iodo-butyl ester **1** (50.0 mg, 0.15 mmol, 1.0 equiv) and anhydrous methanol (28  $\mu$ L, 0.75 mmol, 5.0 equiv) (or in the absence of methanol). The mixture was stirred at room temperature for 15 hours. The resulting mixture was filtered through a plug of celite and washed with a small amount of EA. The filtrate was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by reduced pressure. The obtained residue was analyzed by <sup>1</sup>H NMR. Yields were determined by <sup>1</sup>H NMR using 2, 5-dimethylfuran as internal standard. **Results:** More than 90% of **1** was recovered either in the present or in the absence of methanol (eq 1).



- (2) To a suspension of CuI (8.3 mg, 0.044 mmol, 0.3 equiv) and indium powder (52.0 mg, 0.45 mmol, 3.0 equiv) in 0.5 mL of 1, 4-dioxane was bubbled CO until the solvent dried up (40 min ~ 60 min). To the resulting residue, **1** (50.0 mg, 0.15 mmol, 1.0 equiv) and anhydrous methanol (28  $\mu$ L, 0.75 mmol, 5.0 equiv) was added. Then, 1.0 mL of 1, 4-dioxane was added by syringe. The mixture was stirred at room temperature for 15 hours. The resulting mixture was filtered through a plug of celite and washed with a small amount of EA. The filtrate was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by reduced pressure. The residue was analyzed by <sup>1</sup>H NMR. Yields were determined by <sup>1</sup>H NMR using 2, 5-dimethylfuran as internal standard. **Results:** 55% of ester **2** and 32% of hydrolysis of **1** were detected (eq 2).



- (3) According to the procedure given for eq 2, exposure of CuI (8.3 mg, 0.044 mmol, 0.3 equiv) to CO prior to the addition of the rest of reaction components. **Results:** only 5% of ester **2** was detected and 70% of **1** was recovered. (eq 3).



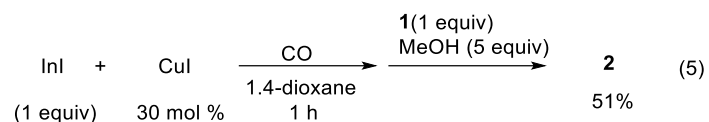
- (4) According to the procedure given for eq 2, exposure of indium (52.0 mg, 0.45 mmol, 3.0



equiv) to CO prior to the addition of the rest of reaction components. **Results:** no ester **2** was detected. 65% of **1** was recovered (eq 4).



- (5) According to the procedure given for equ.2, exposure of indium iodide (36.3 mg, 0.15 mmol, 1.0 equiv) and CuI (8.3 mg, 0.044 mmol, 0.3 equiv) to CO prior to the addition of **1** and methanol. **Results:** 51% of ester **2** and 28% of hydrolysis of **1** were detected (eq 5).



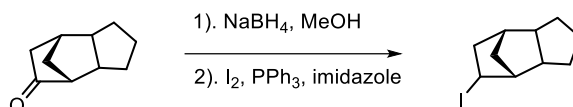
- (6) According to the procedure given for equ.2, exposure of indium iodide (36.3 mg, 0.15 mmol, 1.0 equiv) to CO prior to the addition of the rest of materials. **Results:** no ester **2** was detected. 27% of **1** was recovered (eq 6).



## Part 4. Preparation of Alkyl Halides.

Unless otherwise noted, procedures for the synthesis of primary and secondary alkyl iodides have been reported in our previous publications.<sup>2, 3</sup>

### Preparation of 5-iodo-octahydro-4, 7-methano-indene



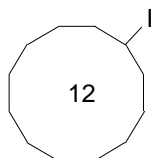
To a solution of corodane (3.0 g, 20 mmol, 1.0 equiv) in 40 mL of methanol was added  $\text{CaCl}_2$  (0.11 g, 1 mmol, 5 mol %) and  $\text{NaBH}_4$  (0.53 g, 14 mmol, 0.7 equiv) in portions while stirring at 0 °C. The reaction was slowly warmed to room temperature and stirred for another 1 hour. The resulting mixture was poured into 150 mL of water and extracted with ethyl acetate (3×100 mL). The combined organic phase was washed with brine, dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated in reduced pressure to afford 3.0 g of a colorless oil. The obtained octahydro-4, 7-methano-inden-5-ol was used without further purification.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.18 – 4.14 (m, 1H), 2.44 (q,  $J$  = 8.5 Hz, 1H), 2.02 – 1.82 (m, 6H), 1.66 – 1.60 (m, 1H), 1.36 – 1.32 (m, 1H), 1.22 – 1.15 (m, 1H), 1.03 – 0.85 (m, 3H), 0.75 – 0.70 (m, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  72.2, 48.1, 47.0, 41.4, 39.2, 37.4, 32.6, 31.8, 31.5, 27.0.

To the solution of octahydro-4, 7-methano-inden-5-ol (3.0 g, 20.0 mmol, 1.0 equiv) in DCM (60 mL) was added imidazole (1.3 g, 20.0 mmol, 1.0 equiv),  $\text{PPh}_3$  (5.2 g, 20.0 mmol, 1.0 equiv) and  $\text{I}_2$  (5.1 g, 20.0 mmol, 1.0 equiv) at 0 °C. The reaction mixture was stirred vigorously at room temperature until the reaction completed which was monitored by TLC. The brown suspension was washed with saturated  $\text{NaHCO}_3$  aqueous solution, saturated  $\text{Na}_2\text{S}_2\text{O}_4$  aqueous solution and water, successively. The organic phase was dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO<sub>2</sub>: 5% ethyl acetate in hexanes) afforded 4.2 g of a colorless oil (80% yield, a mix of two isomers: 5:1).

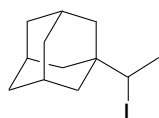
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.25 – 4.21 (m, 0.16H (minor)), 3.88 – 3.85 (m, 0.84H (major)), 2.41 – 2.36 (m, 1H), 2.31 – 2.25 (m, 0.2H), 2.18 – 2.14 (m, 1H), 2.00 – 1.78 (m, 5H), 1.75 – 1.56 (m, 2.8H), 1.51 – 1.42 (m, 1H), 1.31 – 1.08 (m, 1H), 1.02 – 0.88 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  52.5, 48.5, 47.8, 47.5, 47.1, 46.1, 44.3, 42.7, 42.0, 40.8, 32.3, 32.1, 31.9, 31.8, 30.8, 30.2, 29.4, 27.3, 27.0.

### Iodo-cyclododecane

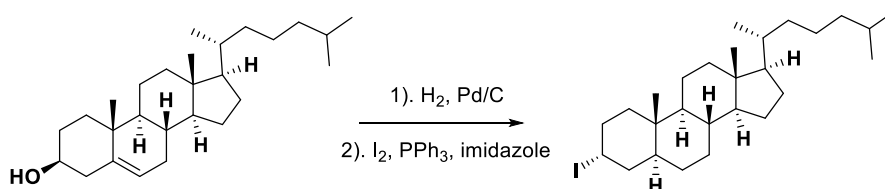


According to the procedure given for the synthesis of 5-iodo-octahydro-4, 7-methano-indene, iodo-cyclododecane was prepared from cyclododecanone and 1-(1-iodo-ethyl)-adamantane was prepared from 1-adamantyl methyl ketone.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.37 – 4.31 (m, 1H), 2.07 – 2.00 (m, 2H), 1.96 – 1.90 (m, 2H), 1.37 (m, 18H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  36.5, 33.7, 24.1, 23.7, 23.52, 23.50, 23.4.

**1-(1-Iodo-ethyl)-adamantane**

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.10 (q,  $J = 7.1$  Hz, 1H), 1.95 (s, 3H), 1.92 (d,  $J = 7.1$  Hz, 3H), 1.66 – 1.56 (m, 12H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  50.5, 40.5, 36.9, 36.8, 28.7, 22.8.

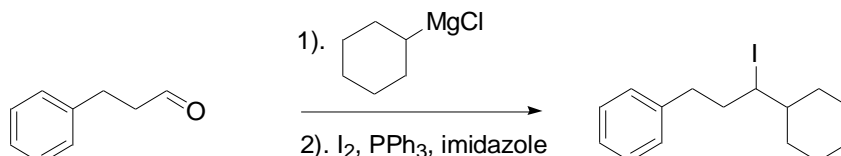
**Preparation of 3 $\alpha$ -iodo-5 $\alpha$ -cholestane**

A suspension of cholesterol (1.0 g, 2.6 mmol, 1 equiv) and Pd/C (10%, cat.) in  $\text{CH}_2\text{Cl}_2$ -iPrOH (1:1, 40 mL) in the presence of 2 drops AcOH (0.2 mL) was stirred under 1 atm  $\text{H}_2$  for 36 h. The resulting mixture was filtered and concentrated. The residue was purified by recrystallization from hexane to give 0.85 g of a white solid (84% yield). Physical and spectral data were in accordance with literature data.<sup>4</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.61 – 3.55 (m, 1H), 1.95 (dt,  $J = 12.6, 3.3$  Hz, 1H), 1.84 – 0.92 (m, 30 H), 0.89 (d,  $J = 6.5$  Hz, 3H), 0.85 (dd,  $J = 6.6, 2.8$  Hz, 6H), 0.79 (s, 3H), 0.64 (s, 3H), 0.63 – 0.53 (m, 1H).

To a solution of 17-(1,5-dimethyl-hexyl)-10,13-dimethyl-hexadecahydro-cyclopentaaphenanthren-3-ol (0.85 g, 2.2 mmol, 1.0 equiv) in DCM (30 mL) was added imidazole (0.15 g, 2.2 mmol, 1.0 equiv),  $\text{PPh}_3$  (0.58 g, 2.2 mmol, 1.0 equiv) and  $\text{I}_2$  (0.56 g, 2.2 mmol, 1.0 equiv) at 0 °C. The reaction mixture was stirred vigorously at room temperature until the reaction completed which was monitored by TLC. The brown suspension was washed with saturated  $\text{NaHCO}_3$  aqueous solution, saturated  $\text{Na}_2\text{S}_2\text{O}_4$  aqueous solution, and water. The organic phase was dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO<sub>2</sub>: 5% ethyl acetate in hexanes) afforded a white solid (1.0 g, 91% yield). Physical and spectral data were in accordance with literature data.<sup>5</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.94 (s, 1H), 1.97 (dt,  $J = 12.5, 3.3$  Hz, 1H), 1.94 – 1.88 (m, 1H), 1.86 – 1.78 (m, 1H), 1.73 – 1.61 (m, 4H), 1.60 – 1.49 (m, 4H), 1.48 – 1.41 (m, 2H), 1.39 – 1.20 (m, 8H), 1.18 – 0.94 (m, 9H), 0.90 (d,  $J = 6.6$  Hz, 3H), 0.86 (dd,  $J = 6.6, 2.9$  Hz, 6H), 0.85 – 0.81 (m, 1H), 0.79 (s, 3H), 0.65 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  56.4, 56.2, 53.8, 42.6, 42.0, 39.9, 39.5, 38.7, 38.3, 36.5, 36.1, 35.8, 35.4, 34.3, 32.7, 31.8, 28.2, 28.0, 27.8, 24.2, 23.9, 22.8, 22.6, 20.8, 18.7, 13.4, 12.1.

**Preparation of (3-cyclohexyl-3-iodo-propyl)-benzene**

To a solution of phenylacetaldehyde (2.7 g, 20 mmol, 1 equiv) in anhydrous THF (40 mL) was

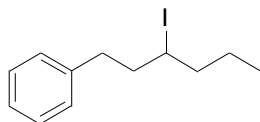
added newly prepared cyclohexylmagnesium bromide (24 mmol, 1 M in THF, 1.2 equiv) dropwise at -20 °C. The reaction mixture was slowly warmed to room temperature and stirred for another 4 hours. Then the reaction was quenched with saturated NH<sub>4</sub>Cl aqueous solution. The resulting mixture was extracted with ether. The combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The residue was purified by flash chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) to afford a colorless oil (2.6 g, 60 % yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 3.39 (ddd, *J* = 8.8, 5.4, 3.2 Hz, 1H), 2.92 – 2.78 (m, 1H), 2.70 – 2.57 (m, 1H), 1.88 – 1.60 (m, 7H), 1.38 – 1.31 (m, 1H), 1.28 – 0.95 (m, 5H).

To a solution of 1-cyclohexyl-3-phenyl-propan-1-ol (2.2 g, 10.0 mmol, 1.0 equiv) in DCM (60 mL) was added imidazole (0.68 g, 10.0 mmol, 1.0 equiv), PPh<sub>3</sub> (2.62 g, 10.0 mmol, 1.0 equiv) and I<sub>2</sub> (2.53 g, 10.0 mmol, 1.0 equiv) at 0 °C. The reaction mixture was stirred vigorously at room temperature until the reaction completed which was monitored by TLC. The brown suspension was washed with saturated NaHCO<sub>3</sub> aqueous solution, saturated Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> aqueous solution and water. The organic phase was dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO<sub>2</sub>: 5% ethyl acetate in hexanes) to afford a colorless oil (2.3 g).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.21 (m, 3H), 4.11 (dt, *J* = 9.9, 3.3 Hz, 1H), 2.98 (ddd, *J* = 13.8, 9.2, 4.7 Hz, 1H), 2.79 – 2.69 (m, 1H), 2.31 – 2.23 (m, 1H), 2.01 – 1.94 (m, 1H), 1.85 – 1.65 (m, 5H), 1.35 – 1.05 (m, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 141.0, 128.5, 128.4, 126.0, 49.2, 45.2, 39.5, 35.9, 32.6, 31.1, 26.3, 26.04, 25.96.

### (3-iodo-hexyl)-benzene



According to the procedure given for the synthesis of (3-cyclohexyl-3-iodo-propyl)-benzene, (3-iodo-hexyl)-benzene was prepared.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 4.08 – 4.03 (m, 1H), 2.91 – 2.85 (m, 1H), 2.75 – 2.67 (m, 1H), 2.20 – 2.12 (m, 1H), 2.01 – 1.83 (m, 2H), 1.70 – 1.64 (m, 1H), 1.60 – 1.51 (m, 1H), 1.46 – 1.34 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 140.8, 128.5, 128.4, 126.0, 42.7, 42.2, 39.0, 35.6, 22.7, 13.2.

### Preparation of tertiary alkyl iodide:

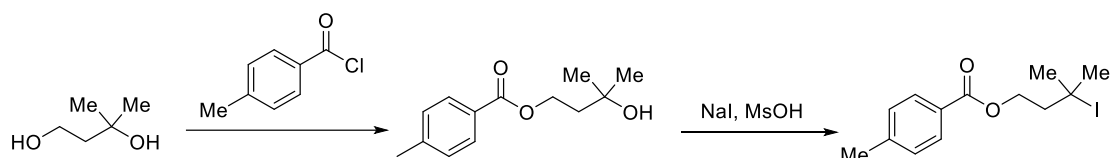
**General procedure I:** To a mixture of NaI (2.0 equiv) and tertiary alcohol (1.0 equiv) in MeCN (0.2 M) was added methanesulfonyl chloride (2.0 equiv) dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours, monitored by TLC. Next, the reaction mixture was diluted with diethyl ether, washed with water, saturated aqueous NaHCO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated on under reduced pressure.<sup>6</sup>

**General procedure II:** To a mixture of NaI (1.1 equiv) and tertiary alcohol (1.0 equiv) in dry MeCN (0.2 M) was added trichloromethylsilane (from 0.6 equiv to 1.0 equiv) at room temperature. The reaction mixture was stirred for 1 hour, monitored by TLC. Next, the reaction mixture was diluted with diethyl ether, washed with water, saturated aqueous NaHCO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and

concentrated on rotary evaporator. The obtained product was used without further purification.<sup>7</sup>

**General procedure III:** To a mixture of NaI (10 mmol, 1.0 equiv) and oven-dried Dowex 50W-X8 ion exchange resin (H<sup>+</sup>-form, 4.0 g) in dry MeOH (30 mL) was added olefin R<sup>1</sup>HC=CR<sup>2</sup> (R<sup>2</sup> ≠ H) (10 mmol, 1.0 equiv). The mixture was stirred for 15 ~ 45 min at room temperature. Dowex 50W-X8 was filtered off and MeOH was removed by evaporation in vacuo. The residue was dissolved in DCM (40 mL) and the insoluble solid was removed by filtration. The volatile was evaporated under reduced pressure to afford the product.<sup>8</sup>

**Preparation of 4-methyl-benzoic acid 3-iodo-3-methyl-butyl ester.**



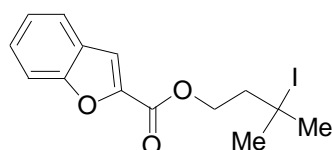
To a mixture of 3-methyl-butane-1,3-diol (3.1 g, 30.0 mmol, 1.5 equiv), DMAP (0.24 g, 2.0 mmol, 0.1 equiv), and Et<sub>3</sub>N (3.0 g, 30 mmol, 1.5 equiv) in DCM (100 mL) was added 4-methyl-benzoyl chloride (3.1g, 20 mmol, 1.0 equiv) in DCM (10.0 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for additional 4 hours. The mixture was washed with water, saturated aqueous NaHCO<sub>3</sub> and brine. The organic phase was dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO<sub>2</sub>: 30% ethyl acetate in hexanes) to afford the mono-protected alcohol (4-methyl-benzoic acid 3-hydroxy-3-methyl-butyl ester) as a colorless oil (3.6 g, 81% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.48 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.97 (t, *J* = 6.8 Hz, 2H), 1.82 (s, 1H), 1.32 (s, 6H).

4-methyl-benzoic acid 3-iodo-3-methyl-butyl ester was prepared from the alcohol precursor (4-methyl-benzoic acid 3-hydroxy-3-methyl-butyl ester, 3.6 g, 16.2 mmol) according to *General procedure I*. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), the target product was obtained as a colorless oil (5.1 g, 95% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 4.54 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 2.17 (t, *J* = 6.8 Hz, 2H), 2.03 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 166.5, 143.7, 129.6, 129.1, 127.3, 64.8, 48.2, 46.4, 38.5, 21.6. **HRMS** calcd for C<sub>13</sub>H<sub>18</sub>IO<sub>2</sub> [M+H]: 333.0352. Found 333.0345.

**Benzofuran-2-carboxylic acid 3-iodo-3-methyl-butyl ester**

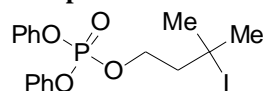


This compound was prepared according to the procedure for the synthesis of 4-methyl-benzoic acid 3-iodo-3-methyl-butyl ester.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 4.62 (t, *J* = 6.9 Hz, 2H), 2.20 (t, *J* = 6.9 Hz, 2H), 2.04 (s,

6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 155.8, 145.3, 127.7, 126.9, 123.8, 122.8, 114.0, 112.4, 65.5, 48.0, 45.6, 38.5. **HRMS** calcd for  $\text{C}_{14}\text{H}_{16}\text{IO}_3$   $[\text{M}+\text{H}]$ : 359.0144. Found 359.0133.

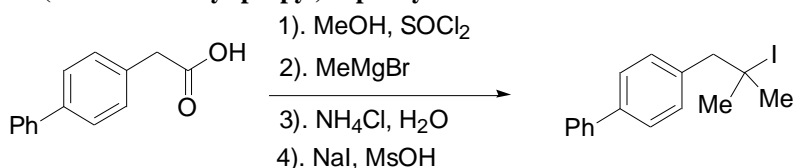
#### Phosphoric acid 3-iodo-3-methyl-butyl ester diphenyl ester



This compound was prepared according to the procedure for the synthesis of 4-methyl-benzoic acid 3-iodo-3-methyl-butyl ester.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (t,  $J$  = 7.9 Hz, 4H), 7.24 (d,  $J$  = 8.6 Hz, 4H), 7.20 (t,  $J$  = 7.4 Hz, 2H), 4.49 (dd,  $J$  = 14.7, 7.0 Hz, 2H), 2.09 (t,  $J$  = 6.9 Hz, 2H), 1.93 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  150.49, 150.44, 129.8, 125.4, 120.07, 120.04, 69.44, 69.40, 49.27, 49.22, 45.2, 38.4. **HRMS** calcd for  $\text{C}_{17}\text{H}_{21}\text{IO}_4\text{P}$   $[\text{M}+\text{H}]$ : 447.0222. Found 447.0226.

#### Preparation of 4-(2-iodo-2-methyl-propyl)-biphenyl



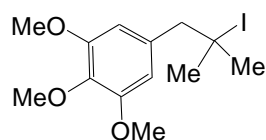
To a solution of biphenyl-4-yl-acetic acid (4.2 g, 20 mmol, 1.0 equiv) in 25 mL of methanol was added 2.0 mL of  $\text{SOCl}_2$  at 0  $^\circ\text{C}$ . The mixture was stirred at room temperature for 6 hours. After the volatiles were evaporated under reduced pressure, biphenyl-4-yl-acetic acid methyl ester was obtained (4.5 g, 100% yield) and used with further purification.

To a solution of biphenyl-4-yl-acetic acid methyl ester (4.5 g, 20 mmol, 1 equiv) in anhydrous THF (40 mL) was added methylmagnesium bromide dropwise (20 mL, 3.0 M in 2-Methyl-THF) at -78  $^\circ\text{C}$ . The reaction mixture was slowly warmed to room temperature and stirred for another 6 hours. The reaction was quenched with saturated  $\text{NH}_4\text{Cl}$  aqueous solution. The resulting mixture was extracted with ether. The combined organic phases were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated under vacuum. The residue was purified by flash chromatography to afford the tertiary alcohol as a white solid (3.4 g, 76% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J$  = 7.7 Hz, 2H), 7.56 (d,  $J$  = 7.6 Hz, 2H), 7.45 (t,  $J$  = 7.5 Hz, 2H), 7.35 (t,  $J$  = 7.3 Hz, 1H), 7.30 (d,  $J$  = 7.6 Hz, 2H), 2.82 (s, 2H), 1.49 (br s, 1H), 1.28 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 139.4, 136.8, 130.9, 128.7, 127.1, 127.0, 126.9, 70.8, 49.3, 29.2.

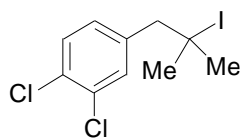
According to *General procedure 1*, 4-(2-Iodo-2-methyl-propyl)-biphenyl was prepared from biphenyl-4-yl-2-methyl-propan-2-ol (3.4 g, 15 mmol) obtained from above. The pure product was obtained by recrystallization of the crude product from hexanes (3.3 g, 65% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J$  = 7.7 Hz, 2H), 7.55 (d,  $J$  = 7.9 Hz, 2H), 7.45 (t,  $J$  = 7.6 Hz, 2H), 7.37 – 7.32 (m, 3H), 3.27 (s, 2H), 2.00 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 139.7, 136.7, 131.1, 128.8, 127.2, 127.0, 126.6, 55.8, 49.8, 37.5.

**5-(2-Iodo-2-methyl-propyl)-1, 2, 3-trimethoxy-benzene**

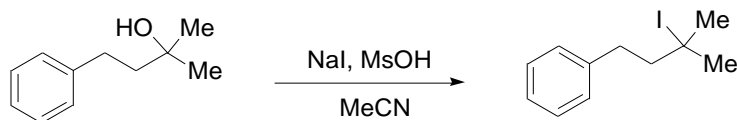
This compound was prepared according to the procedure for the synthesis of 4-(2-iodo-2-methyl-propyl)-biphenyl. After purification by column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in petroleum ether), the title compound was obtained as brown oil (59% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.48 (s, 2H), 3.86 (s, 6H), 3.84 (s, 3H), 3.14 (s, 2H), 1.97 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 152.6, 137.0, 133.2, 107.9, 60.8, 56.4, 56.1, 49.9, 37.6. HRMS calcd for C<sub>13</sub>H<sub>20</sub>IO<sub>3</sub> [M+H]: 351.0457. Found 351.0453.

**1, 2-Dichloro-4-(2-iodo-2-methyl-propyl)-benzene**

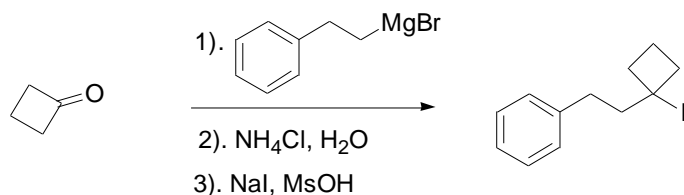
This compound was prepared according to the procedure for the synthesis of 4-(2-iodo-2-methyl-propyl)-biphenyl. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), the title compound was obtained as a colorless oil (55% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.09 (s, 2H), 1.95 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 137.8, 132.5, 131.9, 131.2, 130.1, 129.8, 54.8, 47.7, 37.5.

**Preparation of (3-iodo-3-methyl-butyl)-benzene**

This compound was prepared using 2-methyl-4-phenyl-butan-2-ol (4.9 g, 30 mmol) according to General procedure I. A crude brown oil was obtained and used without further purification. The physical and spectral data were in accordance with literature data.<sup>6</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 2.87 – 2.79 (m, 2H), 1.98 (s, 6H), 1.94 – 1.86 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 141.4, 128.44, 128.42, 126.0, 52.4, 51.3, 38.0, 35.1.

**Preparation of [2-(1-iodo-cyclobutyl)-ethyl]-benzene**

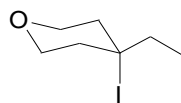
To a solution of cyclobutanone (1.4 g, 20 mmol, 1 equiv) in anhydrous THF (40 mL) was added newly prepared phenethylmagnesium bromide (25 mmol, 2.0 M in THF) dropwise at -20 °C with stirring. The reaction mixture was slowly warmed to room temperature and stirred for additional 4 hours. The

reaction was quenched with a saturated  $\text{NH}_4\text{Cl}$  aqueous solution. The resulting mixture was extracted with ether. The combined organic phases were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated under vacuum. The residue was purified by flash chromatography ( $\text{SiO}_2$ : 20% ethyl acetate in hexanes) to afford 2.6 g of 1-phenethyl-cyclobutanol as a colorless oil (75% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.17 (m, 5H), 2.76 – 2.69 (m, 2H), 2.18 – 2.00 (m, 4H), 1.97 – 1.91 (m, 3H), 1.84 – 1.74 (m, 1H), 1.63 – 1.51 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.5, 128.4, 128.3, 125.7, 75.2, 41.3, 36.0, 29.9, 12.1.

According to *General procedure I*, [2-(1-iodo-cyclobutyl)-ethyl]-benzene was prepared from 1-phenethyl-cyclobutanol (2.6 g, 15 mmol) obtained above. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), a brown oil (1.9 g, 44% yield) was obtained.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (t,  $J = 7.5$  Hz, 2H), 7.24 (d,  $J = 8.1$  Hz, 2H), 7.19 (t,  $J = 7.3$  Hz, 1H), 2.82 – 2.74 (m, 4H), 2.40 – 2.34 (m, 2H), 2.31 – 2.24 (m, 1H), 2.10 – 2.04 (m, 2H), 1.99 – 1.92 (m, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 128.5, 128.4, 126.0, 50.3, 49.1, 42.8, 35.2, 19.0.

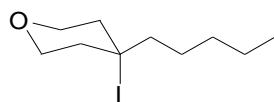
#### 4-Ethyl-4-iodo-tetrahydro-pyran



The title compound was prepared according to the procedure for the synthesis of [2-(1-iodo-cyclobutyl)-ethyl]-benzene. After purification by column chromatography ( $\text{SiO}_2$ : 20% ethyl acetate in petroleum ether), a colorless oil was obtained.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.91 (ddd,  $J = 11.6, 4.4, 1.7$  Hz, 2H), 3.81 (td,  $J = 11.8, 2.0$  Hz, 2H), 2.07 – 2.01 (m, 2H), 1.86 (q,  $J = 7.2$  Hz, 2H), 1.32 (ddd,  $J = 15.4, 11.0, 4.6$  Hz, 2H), 1.12 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  65.9, 63.1, 42.5, 42.3, 11.3. **HRMS** calcd for  $\text{C}_7\text{H}_{14}\text{IO}$  [ $\text{M}+\text{H}$ ]: 241.0089. Found: 241.0085.

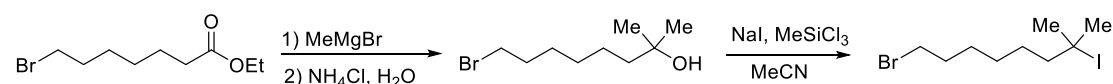
#### 4-Iodo-4-pentyl-tetrahydro-pyran



The title compound was prepared according to the procedure for the synthesis of [2-(1-iodo-cyclobutyl)-ethyl]-benzene. After purification by column chromatography ( $\text{SiO}_2$ : 20% ethyl acetate in petroleum ether), a colorless oil was obtained.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.91 – 3.87 (m, 2H), 3.83 – 3.78 (m, 2H), 2.02 (dd,  $J = 14.6, 1.7$  Hz, 2H), 1.85 – 1.78 (m, 2H), 1.61 – 1.56 (m, 2H), 1.38 – 1.30 (m, 6H), 0.91 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  65.9, 62.1, 49.5, 42.8, 31.5, 26.3, 22.5, 14.0. **HRMS** calcd for  $\text{C}_{10}\text{H}_{20}\text{IO}$  [ $\text{M}+\text{H}$ ]: 283.0559. Found 283.0554.

#### Preparation of 1-Bromo-7-iodo-7-methyl-octane



To a solution of ethyl 7-bromoheptanoate (4.8 g, 20 mmol, 1.0 equiv) in anhydrous THF (40 mL)



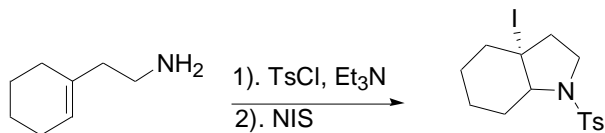
was added methylmagnesium bromide (20 mL, 3.0 M in 2-Methyl-THF, 6 equiv) dropwise at -78 °C. The reaction mixture was slowly warmed to room temperature and stirred for another 6 hours. Then reaction was quenched with saturated a NH<sub>4</sub>Cl aqueous solution. The resulting mixture was extracted with ether. The combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The residue was purified by flash chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) to afford 8-bromo-2-methyl-octan-2-ol as clear oil (4.0 g, 90% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 3.39 (t, *J* = 6.8 Hz, 2H), 1.87 – 1.82 (m, 2H), 1.47 – 1.41 (m, 4H), 1.38 – 1.28 (m, 5H), 1.19 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 70.9, 43.8, 33.9, 32.7, 29.2, 29.2, 28.1, 24.1.

According to *General procedure II*, 1-Bromo-7-iodo-7-methyl-octane was prepared from 8-bromo-2-methyl-octan-2-ol obtained above as a brown oil and used without further purification.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 3.41 (t, *J* = 6.8 Hz, 2H), 1.92 (s, 6H), 1.90 – 1.84 (m, 2H), 1.62 – 1.59 (m, 2H), 1.56 – 1.44 (m, 4H), 1.40 – 1.34 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 52.6, 50.3, 38.0, 33.9, 32.7, 28.5, 28.3, 28.0.

#### Preparation of 3*α*-iodo-1-[(4-methylphenyl)sulfonyl]octahydro-1H-indole



To a solution of 2-cyclohex-1-enyl-ethylamine (3.8 g, 30 mmol, 1.0 equiv), Et<sub>3</sub>N (3.3 g, 33 mmol, 1.1 equiv) in 60 mL of DCM was added 4-methyl-benzenesulfonyl chloride (6.3 g, 33 mmol, 1.0 M in DCM, 1.1 equiv) at 0 °C. The reaction mixture was warmed to room temperature and stirred for another 8 hours. The reaction was poured into saturated aqueous Na<sub>2</sub>CO<sub>3</sub>. The aqueous phase was extracted with DCM. The combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The residue was purified by flash chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) to afford N-(2-cyclohex-1-enyl-ethyl)-4-methyl-benzenesulfonamide as a white solid (7.6 g, 91% yield).

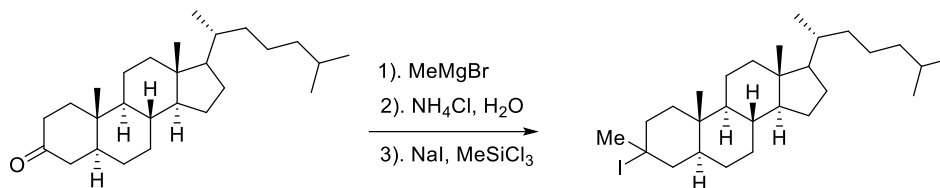
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.29 (m, 2H), 5.43 – 5.31 (m, 1H), 4.41 (t, *J* = 5.6 Hz, 1H), 3.02 – 2.96 (m, 2H), 2.42 (s, 3H), 2.04 (t, *J* = 6.3 Hz, 2H), 1.98 – 1.92 (m, 2H), 1.74 – 1.67 (m, 2H), 1.57 – 1.44 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.3, 136.7, 133.4, 129.6, 127.1, 124.8, 40.4, 37.3, 27.4, 25.1, 22.6, 22.1, 21.5.

To a solution of N-(2-cyclohex-1-enyl-ethyl)-4-methyl-benzenesulfonamide (2.5 g, 8.9 mmol, 1.0 equiv) obtained above in 40 mL of DCM was added NIS (2.2 g, 9.8 mmol, 1.1 equiv) in portions while stirring at 0 °C. The reaction was further stirred at room temperature for about 2 hours until the consumption of the alcohol (monitored by TLC). The mixture was washed with a saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution, a saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution and brine, and dried over MgSO<sub>4</sub>, filtered and concentrated in reduced pressure. The residue was purified by flash chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) to afford the tertiary alkyl iodide as a white solid (2.6 g, 72% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.88 (dd, *J* = 8.5, 5.8 Hz, 1H), 3.63 (ddd, *J* = 9.5, 8.1, 3.2 Hz, 1H), 3.50 – 3.44 (m, 1H), 2.50 – 2.41 (m, 1H), 2.41 – 2.34 (m, 4H), 2.25 – 2.19 (m, 1H), 2.11 – 2.01 (m, 2H), 1.74 – 1.65 (m, 2H), 1.44 – 1.35 (m, 3H). <sup>13</sup>C NMR

(151 MHz, CDCl<sub>3</sub>)  $\delta$  143.3, 134.8, 129.5, 127.6, 69.9, 52.5, 47.1, 42.4, 40.5, 31.8, 23.9, 22.2, 21.5. HRMS calcd for C<sub>15</sub>H<sub>21</sub>INO<sub>2</sub>S [M+H]: 406.0338. Found 406.0332. M.P.: 77.2 ~ 78.9 °C.

### Preparation of 3-iodo-3-methyl-5 $\alpha$ -cholestane



To a solution of 5 $\alpha$ -cholestan-3-one (3.0 g, 7.8 mmol, 1.0 equiv) in anhydrous THF (10 mL) was added methylmagnesium bromide (4 mL, 3.0 M in 2-Methyl-THF, 1.5 equiv) dropwise at -78 °C. The reaction mixture was slowly warmed to room temperature and stirred for another 6 hours. The resulting mixture was quenched with saturated NH<sub>4</sub>Cl aqueous solution and extracted with ether. The combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The residue was purified by flash chromatography to afford a major isomer as a white solid (1.0 g, 32% yield) and a minor isomer also as a white solid (0.6 g, 19% yield).

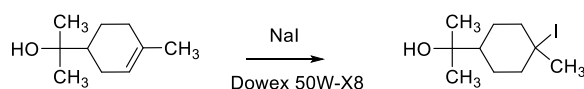
The major isomer: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  1.96 (dt,  $J$  = 12.5, 3.2 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.68 – 1.62 (m, 1H), 1.58 – 1.42 (m, 7H), 1.39 – 1.30 (m, 5H), 1.28 – 1.20 (m, 6H), 1.19 (s, 3H), 1.17 – 0.95 (m, 9H), 0.90 (d,  $J$  = 6.5 Hz, 3H), 0.86 (dd,  $J$  = 6.6, 2.8 Hz, 6H), 0.74 (s, 3H), 0.64 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  69.8, 56.5, 56.2, 54.2, 42.6, 41.9, 41.1, 40.1, 39.5, 36.2, 35.8, 35.5, 34.9, 34.0, 32.0, 31.6, 28.5, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.0, 18.7, 12.1, 11.2.

The minor isomer: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  1.96 (dt,  $J$  = 12.6, 3.3 Hz, 1H), 1.84 – 1.77 (m, 1H), 1.67 – 1.43 (m, 9H), 1.38 – 1.25 (m, 7H), 1.24 (s, 3H), 1.23 – 1.19 (m, 3H), 1.16 – 0.95 (m, 10H), 0.90 (d,  $J$  = 6.6 Hz, 3H), 0.86 (dd,  $J$  = 6.6, 2.7 Hz, 6H), 0.80 (s, 3H), 0.64 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  71.5, 56.5, 56.3, 54.5, 44.3, 43.4, 42.6, 40.1, 39.5, 36.6, 36.5, 36.2, 36.0, 35.8, 35.5, 32.1, 28.7, 28.2, 28.0, 26.7, 24.2, 23.8, 22.8, 22.6, 21.2, 18.7, 12.1, 11.9.

According to *General procedure II*, 3-iodo-3-methyl-5 $\alpha$ -cholestane was prepared from the above major isomer as a white solid and used without further purification.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  2.13 (s, 3H), 2.00 – 1.95 (m, 2H), 1.86 – 1.78 (m, 1H), 1.71 (dt,  $J$  = 15.1, 2.7 Hz, 1H), 1.69 – 1.61 (m, 3H), 1.58 – 1.49 (m, 4H), 1.43 (td,  $J$  = 13.3, 3.5 Hz, 1H), 1.38 – 1.20 (m, 10H), 1.18 – 0.94 (m, 12H), 0.91 (d,  $J$  = 6.5 Hz, 3H), 0.87 (dd,  $J$  = 6.6, 2.8 Hz, 6H), 0.74 (s, 3H), 0.65 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  61.3, 56.4, 56.3, 53.8, 48.2, 44.8, 42.6, 42.2, 40.0, 39.6, 39.5, 37.1, 36.2, 36.0, 35.8, 35.5, 31.8, 28.3, 28.0, 27.7, 24.2, 23.9, 22.8, 22.6, 21.0, 18.7, 13.6, 12.1. M.P.: 113.2 ~ 114.6 °C.

### Preparation of 2-(4-Iodo-4-methyl-cyclohexyl)-propan-2-ol

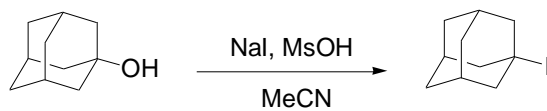


The title compound was prepared from terpineol according to *General procedure III* as a white solid.<sup>7</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.22 – 2.15 (m, 2H), 2.12 (s, 3H), 1.84 – 1.74 (m, 2H), 1.65 – 1.50 (m, 2H), 1.39 (s, 1H), 1.30 (tt,  $J$  = 12.3, 3.5 Hz, 1H), 1.22 (s, 6H), 0.95 – 0.84 (m, 2H). <sup>13</sup>C NMR (101

MHz, CDCl<sub>3</sub>)  $\delta$  72.7, 59.4, 48.1, 45.6, 39.2, 27.0, 26.0. M.P.: 61.3 ~ 63.0 °C.

**Preparation of 1-iodo-adamantane**



The title compound was prepared from adamantan-1-ol (3.0 g, 20 mmol) according to *General procedure I*. The physical and spectral data were in accordance with literature data.<sup>9</sup>

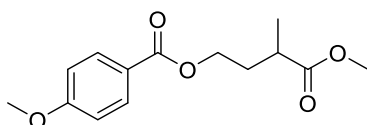
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  2.63 (d,  $J$  = 2.0 Hz, 6H), 1.95 (br s, 3H), 1.84 – 1.77 (m, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  52.4, 51.1, 35.6, 33.1.

## Part 5. Carbonylation of Alkyl Halides under Balloon CO

General procedures for methoxycarbonylation of primary and secondary alkyl iodide under balloon CO (method A): To a flame-dried Schlenk tube equipped with a stir bar was added CuOTf (0.045 mmol, 9.6 mg, 15 mol %), 200 mesh indium powder (0.36 mmol, 41.4 mg, 120 mmol %), MgCO<sub>3</sub> (0.45 mmol, 37.8 mg, 150 mol %) and alkyl iodide (0.30 mmol, 100 mol %, if alkyl iodide is solid) in glovebox under N<sub>2</sub> atmosphere. The tube was capped with a rubber septum and took out of glove-box. Subsequently, the tube was purged 3 times with CO and then a balloon filled with CO was inserted. Finally, alkyl iodide (0.30 mmol, 100 mol %, if alkyl iodide is liquid), 56  $\mu$ L of methanol (1.5 mmol, 500 mol %) and 2 mL of 1,4-dioxane were added via syringe. The resulting mixture was allowed to stir at room temperature for 24h. The reaction was diluted with 20 mL of ethyl acetate, filtered through a plug of celite. The obtained filtrate was washed with saturated NH<sub>4</sub>Cl aqueous solution and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated in vacuum. The residue was purified by flash chromatography.

General procedures for methoxycarbonylation of tertiary alkyl iodide under balloon CO (method B): To a flame-dried Schlenk tube equipped with a stir bar was added CuOTf (0.045 mmol, 9.6 mg, 15 mol %), InI (0.30 mmol, 72.5 mg, 100 mmol %), K<sub>2</sub>CO<sub>3</sub> (0.30 mmol, 41.4 mg, 100 mol %) and alkyl iodide (0.30 mmol, 100 mol %, if alkyl iodide is solid) in glovebox under N<sub>2</sub> atmosphere. The tube was capped with a rubber septum and took out of glove-box. Subsequently, the tube was purged 3 times with CO and then a balloon filled with CO was inserted. Finally, alkyl iodide (0.30 mmol, 100 mol %, if alkyl iodide is liquid), 56  $\mu$ L of methanol (1.5 mmol, 500 mol %) and 2 mL of 1,4-dioxane were added via syringe. The resulting mixture was allowed to stir at room temperature for 24h. The reaction was diluted with 20 mL of ethyl acetate, filtered through a plug of celite. The obtained filtrate was washed with saturated NH<sub>4</sub>Cl aqueous solution and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated in vacuum. The residue was purified by flash chromatography.

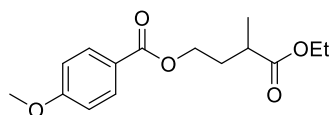
### 4-Methoxy-benzoic acid 3-methoxycarbonyl-butyl ester (2)



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (56 mg, 70% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ . 7.95 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.34 – 4.25 (m, 2H), 3.82 (s, 3H), 3.62 (s, 3H), 2.67 – 2.61 (m, 1H), 2.18 – 2.12 (m, 1H), 1.87 – 1.82 (m, 1H), 1.22 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  176.4, 166.1, 163.3, 131.5, 122.5, 113.5, 62.4, 55.3, 51.6, 36.5, 32.4, 17.1. HRMS calcd for C<sub>14</sub>H<sub>19</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 267.1232. Found 267.1230.

### 4-Ethoxy-3-methyl-4-oxobutyl 4-methoxybenzoate (S2a)

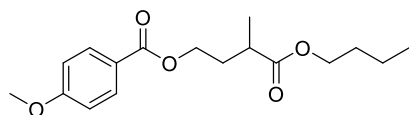


The title compound was prepared according to method A. After purification by column

chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (42 mg, 50% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.95 (m, 2H), 6.95 – 6.86 (m, 2H), 4.37 – 4.27 (m, 2H), 4.15 – 4.06 (m, 2H), 3.85 (s, 3H), 2.70 – 2.58 (m, 1H), 2.22 – 2.12 (m, 1H), 1.91 – 1.82 (m, 1H), 1.25 – 1.21 (m, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.0, 166.2, 163.3, 131.6, 122.6, 113.6, 62.5, 60.4, 55.4, 36.7, 32.5, 17.2, 14.2.

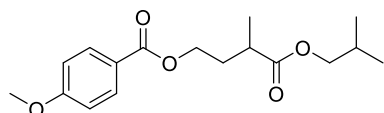
#### 4-Butoxy-3-methyl-4-oxobutyl 4-methoxybenzoate (S2b)



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (58.2 mg, 63% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.93 (m, 2H), 6.98 – 6.86 (m, 2H), 4.36 – 4.28 (m, 2H), 4.08 – 4.00 (m, 2H), 3.85 (s, 3H), 2.69 – 2.59 (m, 1H), 2.19 – 1.14 (m, 1H), 1.89 – 1.82 (m, 1H), 1.60 – 1.52 (m, 2H), 1.38 – 1.30 (m, 2H), 1.23 (d, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.1, 166.2, 163.3, 131.6, 122.6, 113.5, 64.4, 62.5, 55.4, 36.7, 32.5, 30.6, 19.1, 17.2, 13.6. HRMS calcd for C<sub>17</sub>H<sub>25</sub>O<sub>5</sub> [M+H]: 309.1702. Found 309.1700.

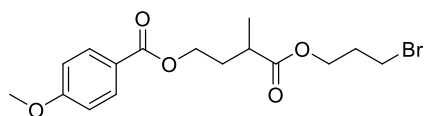
#### 4-Isobutoxy-3-methyl-4-oxobutyl 4-methoxybenzoate (S2c)



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (52.7 mg, 57% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.92 (m, 2H), 6.93 – 6.86 (m, 2H), 4.41 – 4.27 (m, 2H), 3.88 – 3.78 (m, 5H), 2.70 – 2.61 (m, 1H), 2.23 – 2.11 (m, 1H), 1.95 – 1.82 (m, 2H), 1.24 (d, *J* = 7.1 Hz, 3H), 0.89 (dd, *J* = 6.7, 2.9 Hz, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.0, 166.2, 163.3, 131.6, 122.6, 113.5, 70.6, 62.5, 55.4, 36.8, 32.5, 27.7, 19.02, 19.00, 17.3. HRMS calcd for C<sub>17</sub>H<sub>25</sub>O<sub>5</sub> [M+H]: 309.1702. Found 309.1699.

#### 4-(3-Bromopropoxy)-3-methyl-4-oxobutyl 4-methoxybenzoate (S2d)

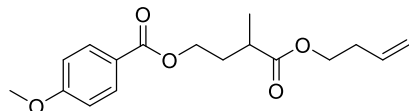


The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (64.7 mg, 58% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.94 (m, 2H), 6.94 – 6.87 (m, 2H), 4.36 – 4.28 (m, 2H), 4.21 – 4.14 (m, 2H), 3.85 (s, 3H), 3.41 (t, *J* = 6.5 Hz, 2H), 2.69 – 2.62 (m, 1H), 2.20 – 2.11 (m, 3H), 1.90 – 1.83 (m, 1H), 1.23 (t, 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 175.8, 166.1, 163.4, 131.5, 122.5, 113.6, 62.4, 62.2, 55.4, 36.6, 32.4, 31.5, 29.3, 17.2. HRMS calcd for C<sub>16</sub>H<sub>22</sub>BrO<sub>5</sub> [M+H]: 373.0651.

Found 373.0647.

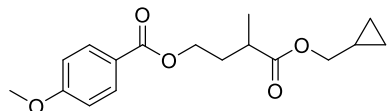
**4-(But-3-en-1-yloxy)-3-methyl-4-oxobutyl 4-methoxybenzoate (S2e)**



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (50.5 mg, 55% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.98 – 7.95 (m, 2H), 6.94 – 6.85 (m, 2H), 5.74 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.09 – 5.02 (m, 2H), 4.36 – 4.27 (m, 2H), 4.16 – 4.06 (m, 2H), 3.84 (s, 3H), 2.68 – 2.61 (m, 1H), 2.37 – 2.32 (m, 2H), 2.18 – 2.12 (m, 1H), 1.88 – 1.82 (m, 1H), 1.23 (d, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 175.9, 166.1, 163.3, 133.9, 131.6, 122.6, 117.2, 113.5, 63.4, 62.5, 55.4, 36.7, 33.0, 32.4, 17.2. HRMS calcd for C<sub>17</sub>H<sub>23</sub>O<sub>5</sub> [M+H]: 307.1546. Found 307.1539.

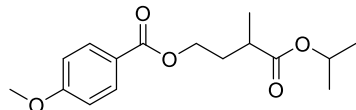
**4-(Cyclopropylmethoxy)-3-methyl-4-oxobutyl 4-methoxybenzoate (S2f)**



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (38.6 mg, 42% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.38 – 4.25 (m, 2H), 3.95 – 3.79 (m, 5H), 2.73 – 2.59 (m, 1H), 2.20 – 2.14 (m, 1H), 1.90 – 1.84 (m, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.12 – 1.04 (m, 1H), 0.57 – 0.48 (m, 2H), 0.26 – 0.20 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.1, 166.2, 163.3, 131.6, 122.6, 113.5, 69.2, 62.5, 55.4, 36.7, 32.5, 17.3, 9.7, 3.1. HRMS calcd for C<sub>17</sub>H<sub>23</sub>O<sub>5</sub> [M+H]: 307.1546. Found 307.1543.

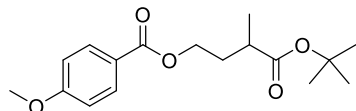
**4-Isopropoxy-3-methyl-4-oxobutyl 4-methoxybenzoate (S2g)**



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (41.5 mg, 47% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.94 (m, 2H), 6.96 – 6.87 (m, 2H), 5.02 – 4.94 (m, 1H), 4.36 – 4.27 (m, 2H), 3.84 (s, 3H), 2.65 – 2.53 (m, 1H), 2.17 – 2.11 (m, 1H), 1.87 – 1.81 (m, 1H), 1.20 (dd, *J* = 12.8, 6.7 Hz, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 175.5, 166.2, 163.3, 131.6, 122.6, 113.5, 67.6, 62.5, 55.4, 36.8, 32.4, 21.71, 21.69, 17.2. HRMS calcd for C<sub>16</sub>H<sub>23</sub>O<sub>5</sub> [M+H]: 295.1546. Found 295.1542.

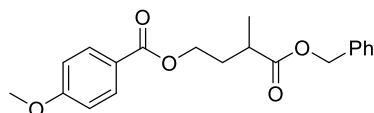
**4-(Tert-butoxy)-3-methyl-4-oxobutyl 4-methoxybenzoate (S2h)**



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (24.0 mg, 26% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.96 (m, 2H), 6.92 – 6.87 (m, 2H), 4.34 – 4.27 (m, 2H), 3.84 (s, 3H), 2.57 – 2.48 (m, 1H), 2.14 – 2.07 (m, 1H), 1.85 – 1.78 (m, 1H), 1.43 (s, 9H), 1.19 (d, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 175.3, 166.2, 163.3, 131.6, 122.7, 113.5, 80.3, 62.5, 55.4, 37.4, 32.5, 28.0, 17.2. HRMS calcd for C<sub>17</sub>H<sub>25</sub>O<sub>5</sub> [M+H]: 309.1702. Found 309.1702.

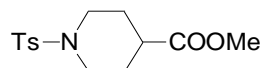
#### 4-(Benzyloxy)-3-methyl-4-oxobutyl 4-methoxybenzoate (S2i)



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (15.4 mg, 15% yield).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.95 (m, 2H), 7.38 – 7.29 (m, 5H), 6.93 – 6.88 (m, 2H), 5.09 (q, *J* = 12.4 Hz, 2H), 4.8 – 4.29 (m, 1H), 3.86 (s, 3H), 2.76 – 2.69 (m, 1H), 2.24 – 2.16 (m, 1H), 1.93 – 1.86 (m, 1H), 1.27 (d, *J* = 7.1 Hz, 3H).

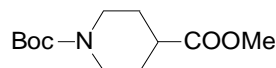
#### 1-(Toluene-4-sulfonyl)-piperidine-4-carboxylic acid methyl ester (3a)



The title compound was prepared according to method A in the absence of MgCO<sub>3</sub>. After purification by column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in petroleum ether), it was obtained as a white solid (61.6 mg, 69% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 3.63 (s, 3H), 3.62 – 3.57 (m, 2H), 2.46 – 2.39 (m, 5H), 2.27 – 2.21 (m, 1H), 1.97 – 1.91 (m, 2H), 1.82 – 1.74 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 174.2, 143.5, 133.0, 129.6, 127.6, 51.8, 45.3, 39.8, 27.4, 21.5. HRMS calcd for C<sub>14</sub>H<sub>20</sub>NO<sub>4</sub>S [M+H]: 298.1113. Found 298.1103. M.P.: 128 °C ~ 129 °C.

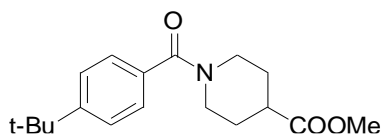
#### Piperidine-1, 4-dicarboxylic acid 1-*tert*-butyl ester 4-methyl ester (3b)



The title compound was prepared according to method A in the absence of MgCO<sub>3</sub>. After purification by column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in petroleum ether), it was obtained as a colorless oil (36.5 mg, 50% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 3.97 (br s, 2H), 3.65 (s, 3H), 2.79 (t, *J* = 11.8 Hz, 2H), 2.44 – 2.38 (m, 1H), 1.83 (d, *J* = 10.9 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.41 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 174.9, 154.6, 79.5, 51.7, 42.9 (br), 40.9, 28.3, 27.9. HRMS calcd for C<sub>12</sub>H<sub>22</sub>NO<sub>4</sub> [M+H]: 244.1549. Found 244.1538.

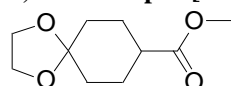
#### 1-(4-*tert*-Butyl-benzoyl)-piperidine-4-carboxylic acid methyl ester (3c)



The title compound was prepared according to method A in the absence of  $\text{MgCO}_3$ . After purification by column chromatography ( $\text{SiO}_2$ : 20% ethyl acetate in petroleum ether), it was obtained as white solid (49.2 mg, 54% yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 8.1$  Hz, 2H), 7.32 (d,  $J = 8.1$  Hz, 2H), 4.52 (br s, 1H), 3.80 (br s, 1H), 3.70 (s, 3H), 3.04 (br s, 1H), 2.61 – 2.55 (m, 1H), 2.07 – 1.65 (m, 4H), 1.31 (s, 9H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  174.6, 170.6, 152.9, 133.0, 126.7, 125.3, 51.8, 47.0 (br), 41.5 (br), 41.0, 34.8, 31.2, 28.3 (br). **HRMS** calcd for  $\text{C}_{18}\text{H}_{26}\text{NO}_3$  [ $\text{M}+\text{H}$ ]: 304.1913. Found 304.1912. M.P.: 154.2 °C ~ 155.2 °C.

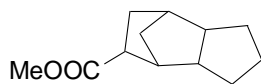
#### 1, 4-Dioxa-spiro[4.5]decane-8-carboxylic acid methyl ester (4)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 10% ethyl acetate in petroleum ether), it was obtained as an oil (31.2 mg, 52% yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.92 (s, 4H), 3.65 (s, 3H), 2.36 – 2.30 (m, 1H), 1.95 – 1.87 (m, 2H), 1.83 – 1.73 (m, 4H), 1.53 (td,  $J = 12.8$ , 4.0 Hz, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  175.0, 108.0, 64.27, 64.25, 51.6, 41.5, 33.7, 26.3. **HRMS** calcd for  $\text{C}_{10}\text{H}_{17}\text{O}_4$  [ $\text{M}+\text{H}$ ]: 201.1127. Found 201.1126

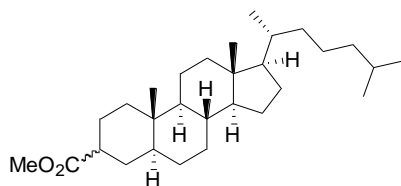
#### Octahydro-4, 7-methano-indene-5-carboxylic acid methyl ester (5)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as oil (46.6 mg, 80 % yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.64 (s, 3H), 2.27 – 2.19 (m, 2H), 2.02 (d,  $J = 3.6$  Hz, 1H), 1.92 – 1.75 (m, 5H), 1.67 – 1.59 (m, 1H), 1.40 – 1.35 (m, 1H), 1.30 (d,  $J = 10.5$  Hz, 1H), 1.20 – 1.12 (m, 2H), 0.97 – 0.85 (m, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 51.6, 48.1, 47.5, 45.9, 45.0, 40.3, 33.3, 32.2, 31.8, 30.2, 27.2. **HRMS** calcd for  $\text{C}_{12}\text{H}_{19}\text{O}_2$  [ $\text{M}+\text{H}$ ]: 195.1385. Found 195.1386.

#### 17-(1, 5-Dimethyl-hexyl)-10, 13-dimethyl-hexadecahydro-cyclopentaaphenanthrene-3-carboxylic acid methyl ester (6)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as a white solid comprising two isomers (major/minor = 2/1, 87.9 mg, 68% yield). The two isomers were separated by preparative thin layer chromatography.

Major isomer:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.68 (s, 3H), 2.64 (t,  $J = 5.4$  Hz, 1H), 2.02 – 1.91 (m,

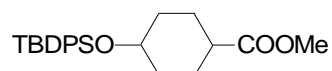


2H), 1.85 – 0.92 (m, 28H), 0.89 (d,  $J = 6.6$  Hz, 3H), 0.86 (dd,  $J = 6.6, 1.9$  Hz, 6H), 0.78 (s, 3H), 0.70 – 0.65 (m, 1H), 0.63 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 56.5, 56.2, 54.2, 51.5, 42.6, 42.5, 40.0, 39.5, 39.4, 36.2, 35.8, 35.4, 35.1, 31.8, 29.7, 28.7, 28.2, 28.0, 24.2, 23.8, 22.82, 22.79, 22.6, 20.7, 18.6, 12.0, 11.7

Minor isomer:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.65 (s, 3H), 2.31 (tt,  $J = 12.3, 4.1$  Hz, 1H), 1.96 (dt,  $J = 12.4, 3.1$  Hz, 1H), 1.83 – 0.92 (m, 29H), 0.88 (d,  $J = 6.5$  Hz, 3H), 0.85 (dd,  $J = 6.6, 1.7$  Hz, 6H), 0.79 (s, 3H), 0.69 – 0.59 (m, 4H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 56.5, 56.3, 54.3, 51.5, 46.0, 43.7, 42.6, 40.0, 39.5, 37.7, 36.2, 35.8, 35.7, 35.4, 32.0, 31.2, 29.7, 28.7, 28.2, 28.0, 24.6, 24.2, 23.8, 22.8, 22.6, 20.9, 18.7, 12.2.

**HRMS** calcd for  $\text{C}_{29}\text{H}_{50}\text{O}_2$  [ $\text{M}^+$ ]: 430.3811 Found 430.3805.

#### 4-(*tert*-Butyl-diphenyl-silanyloxy)-cyclohexanecarboxylic acid methyl ester (7a)

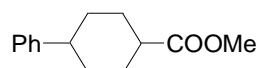


The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 10% ethyl acetate in petroleum ether), it was obtained as oil (trans/cis = 1/1, 73.8 mg, 62% yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 6.7$  Hz, 4H), 7.45 – 7.40 (m, 2H), 7.38 (t,  $J = 7.3$  Hz, 4H), 3.95 (br s, 0.5 H), 3.71 (s, 1.5H), 3.62 (s, 1.5H), 3.61 – 3.58 (m, 0.5H), 2.27 (dt,  $J = 44.9, 11.3, 3.6$  Hz, 1H), 2.10 – 2.01 (m, 1H), 1.91 – 1.85 (m, 2H), 1.73 – 1.64 (m, 2H), 1.43 – 1.26 (m, 4H), 1.08 (d,  $J = 13.7$  Hz, 9H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.14, 176.12, 135.74, 135.71, 134.51, 134.48, 129.51, 129.48, 127.5, 71.2, 67.4, 51.50, 51.47, 42.07, 42.04, 34.5, 32.4, 27.01, 26.98, 26.94, 23.5, 19.2, 19.1.

**HRMS** calcd  $\text{C}_{24}\text{H}_{33}\text{O}_3\text{Si}$  for [ $\text{M}+\text{H}$ ]: 397.2199. Found 397.2190.

#### 4-Phenyl-cyclohexanecarboxylic acid methyl ester (7b)



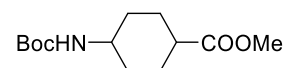
The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as an oil (trans/cis = 2/3, 42.2 mg, 50% yield). The trans and cis isomers were separated by preparative thin layer chromatography.

Cis isomer:  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 3.73 (s, 3H), 2.74 – 2.71 (m, 1H), 2.58 – 2.52 (m, 1H), 2.28 – 2.23 (m, 2H), 1.81 – 1.75 (m, 2H), 1.71 – 1.62 (m, 4H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  175.6, 147.1, 128.3, 126.8, 125.9, 51.5, 43.5, 38.9, 30.4, 27.5.

Trans isomer:  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.28 (m, 2H), 7.23 – 7.17 (m, 3H), 3.69 (s, 3H), 2.52 (tt,  $J = 12.0, 3.4$  Hz, 1H), 2.37 (tt,  $J = 12.2, 3.6$  Hz, 1H), 2.14 – 2.08 (m, 2H), 2.01 – 1.96 (m, 2H), 1.60 (ddd,  $J = 25.4, 13.0, 3.1$  Hz, 2H), 1.49 (ddd,  $J = 25.6, 13.0, 3.1$  Hz, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 146.8, 128.4, 126.7, 126.1, 51.6, 43.6, 42.9, 33.3, 29.3.

**HRMS** calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_2$  [ $\text{M}+\text{H}$ ]: 219.1385. Found 219.1380.

#### 4-*tert*-Butoxycarbonylamino-cyclohexanecarboxylic acid methyl ester (8a)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as oil (cis/trans = 1.8/1,

54.0 mg, 70% yield). The trans and cis isomers were separated by preparative thin layer chromatography.

*Cis isomer:*  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.57 (s, 1H), 3.67 (s, 3H), 3.62 (s, 1H), 2.48 – 2.42 (m, 1H), 1.88 – 1.81 (m, 2H), 1.72 – 1.64 (m, 4H), 1.57 – 1.52 (m, 2H), 1.42 (s, 9H).

$^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  175.6, 155.2, 79.1, 51.6, 46.8, 40.3, 29.6, 28.4, 24.8.

*Trans isomer:*  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.40 (s, 1H), 3.64 (s, 3H), 3.39 (s, 1H), 2.20 (tt,  $J$  = 12.1, 3.5 Hz, 1H), 2.07 – 1.95 (m, 4H), 1.50 (ddd,  $J$  = 26.1, 13.3, 3.1 Hz, 2H), 1.41 (s, 9H), 1.09 (qd,  $J$  = 12.8, 3.3 Hz, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  175.8, 155.1, 79.1, 51.8, 48.9, 42.3, 32.5, 28.4, 27.8.

**HRMS** calcd for  $\text{C}_{13}\text{H}_{24}\text{NO}_4$  [M+H]: 258.1705. Found 258.1703.

#### 4-Benzoyloxycarbonylamino-cyclohexanecarboxylic acid methyl ester (8b)



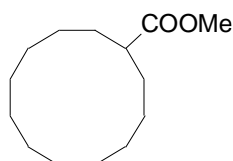
The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as an oil (cis/trans = 2/1, 66.4 mg, 76% yield). The trans and cis isomers were separated by preparative thin layer chromatography.

*Cis isomer:*  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.29 (m, 5H), 5.08 (s, 2H), 4.82 (br s, 1H), 3.71 (br s, 1H), 3.67 (s, 3H), 2.50 – 2.44 (m, 1H), 1.90 – 1.82 (m, 2H), 1.75 – 1.66 (m, 4H), 1.61 – 1.54 (m, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 155.5, 136.5, 128.5, 128.10, 128.07, 66.5, 51.6, 47.4, 40.2, 29.6, 24.8.

*Trans isomer:*  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.29 (m, 5H), 5.08 (s, 2H), 4.64 (br s, 1H), 3.66 (s, 3H), 3.48 (br s, 1H), 2.23 (tt,  $J$  = 12.1, 3.6 Hz, 1H), 2.09 (d,  $J$  = 11.0 Hz, 2H), 2.01 (d,  $J$  = 12.6 Hz, 2H), 1.54 (q,  $J$  = 12.6 Hz, 2H), 1.14 (ddd,  $J$  = 24.7, 12.9, 3.4 Hz, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 155.5, 136.5, 128.5, 128.1, 66.6, 51.6, 49.5, 42.3, 32.4, 29.7, 27.7.

**HRMS** calcd for  $\text{C}_{16}\text{H}_{22}\text{NO}_4$  [M+H]: 292.1549. Found 292.1538.

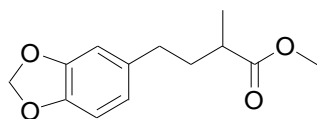
#### Cyclododecanecarboxylic acid methyl ester (9)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as an oil (34.6 mg, 51 % yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.65 (s, 3H), 2.49 (p,  $J$  = 6.4 Hz, 1H), 1.62 – 1.57 (m, 4H), 1.40 – 1.28 (m, 18H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  177.2, 51.4, 40.2, 26.7, 23.6, 23.5, 23.5, 23.4, 22.4. **HRMS** calcd for  $\text{C}_{14}\text{H}_{27}\text{O}_2$  [M+H]: 227.2011. Found 227.2011.

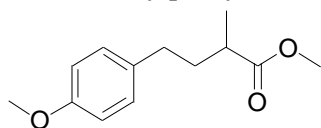
#### 4-Benzo [1, 3] dioxol-5-yl-2-methyl-butyrac acid methyl ester (10)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 10% ethyl acetate in petroleum ether), it was obtained as an oil (39.0 mg, 55% yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.72 (d,  $J = 7.9$  Hz, 1H), 6.66 (s, 1H), 6.61 (d,  $J = 7.9$  Hz, 1H), 5.91 (s, 2H), 3.68 (s, 3H), 2.53 (t,  $J = 7.9$  Hz, 2H), 2.50 – 2.42 (m, 1H), 1.99 – 1.92 (m, 1H), 1.70 – 1.64 (m, 1H), 1.18 (d,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9, 147.5, 145.6, 135.4, 121.1, 108.8, 108.1, 100.7, 51.5, 38.7, 35.6, 33.2, 17.1. **HRMS** calcd for  $\text{C}_{13}\text{H}_{17}\text{O}_4$   $[\text{M}+\text{H}]$ : 237.1127. Found 237.1123.

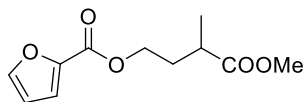
#### 4-(4-Methoxy-phenyl)-2-methyl-butyrac acid methyl ester (11)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as a colorless oil (33.3 mg, 50% yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.09 (d,  $J = 8.4$  Hz, 2H), 6.83 (d,  $J = 8.4$  Hz, 2H), 3.78 (s, 3H), 3.68 (s, 3H), 2.56 (t,  $J = 7.9$  Hz, 2H), 2.51 – 2.44 (m, 1H), 2.01 – 1.96 (m, 1H), 1.69 – 1.65 (m, 1H), 1.19 (d,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 157.8, 133.6, 129.2, 113.7, 55.2, 51.5, 38.8, 35.6, 32.5, 17.1. **HRMS** calcd for  $\text{C}_{13}\text{H}_{19}\text{O}_3$   $[\text{M}+\text{H}]$ : 223.1334. Found 223.1338.

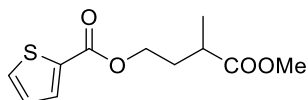
#### Furan-2-carboxylic acid 3-methoxycarbonyl-butyl ester (12)



To a vial (10 mL) equipped with a stir bar was added CuOTf (0.045 mmol, 9.6 mg, 15 mol %), 200 mesh indium powder (0.36 mmol, 41.4 mg, 120 mol %),  $\text{MgCO}_3$  (0.45 mmol, 37.8 mg, 150 mol %), furan-2-carboxylic acid 3-iodo-butyl ester (0.30 mmol, 88.2 mg, 100 mol %), 5 mL of 1,4-dioxane and 56  $\mu\text{L}$  of methanol (1.5 mmol, 500 mol %) in sequence. Subsequently, the vial was placed into an autoclave. The reactor was purged with CO for 5 min and then pressurized to 4 atm CO. The reaction mixture was allowed to stir at 25  $^\circ\text{C}$  for 24h. The autoclave was depressurized. The reaction was diluted with 20 mL of ethyl acetate and filtered through a plug of celite. The filtrate was washed with saturated  $\text{NH}_4\text{Cl}$  aqueous solution and brine, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated in vacuum. The residue was purified by flash chromatography ( $\text{SiO}_2$ : 20% ethyl acetate in petroleum ether) to offer 40.7 mg of oil (60% yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (dd,  $J = 1.6, 0.7$  Hz, 1H), 7.15 (dd,  $J = 3.5, 0.6$  Hz, 1H), 6.48 (dd,  $J = 3.5, 1.7$  Hz, 1H), 4.32 (t,  $J = 6.4$  Hz, 2H), 3.64 (s, 3H), 2.67 – 2.59 (m, 1H), 2.17 – 2.10 (m, 1H), 1.87 – 1.81 (m, 1H), 1.21 (d,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 158.5, 146.3, 144.5, 117.9, 111.8, 62.7, 51.7, 36.4, 32.3, 17.1. **HRMS** calcd for  $\text{C}_{11}\text{H}_{15}\text{O}_5$   $[\text{M}+\text{H}]$ : 227.0920. Found 227.0916.

#### Thiophene-2-carboxylic acid 3-methoxycarbonyl-butyl ester (13)

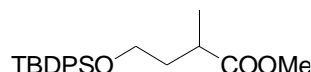


To a vial (10 mL) equipped with a stir bar was added CuOTf (0.045 mmol, 9.6 mg, 15 mol %), 200 mesh indium powder (0.36 mmol, 41.4 mg, 120 mol %),  $\text{MgCO}_3$  (0.45 mmol, 37.8 mg, 150 mol %), thiophene-2-carboxylic acid 3-iodo-butyl ester (0.30 mmol, 93.1 mg, 100 mol %), 5 mL of 1,4-dioxane and 56  $\mu\text{L}$  of methanol (1.5 mmol, 500 mol %) in sequence. Subsequently, the vial was placed into an

autoclave. The reactor was purged with CO for 5 min and then pressurized to 4 atm CO. The reaction mixture was allowed to stir at 25 °C for 24h. The autoclave was depressurized. The reaction was diluted with 20 mL of ethyl acetate and filtered through a plug of celite. The filtrate was washed with saturated NH<sub>4</sub>Cl aqueous solution and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated in vacuum. The residue was purified by flash chromatography (SiO<sub>2</sub>: 20% ethyl acetate in petroleum ether) to offer 40.0 mg of oil (55% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.78 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.09 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.36 – 4.29 (m, 2H), 3.66 (s, 3H), 2.69 – 2.62 (m, 1H), 2.19 – 2.13 (m, 1H), 1.89 – 1.83 (m, 1H), 1.24 (d, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.3, 162.1, 133.7, 133.4, 132.4, 127.7, 62.9, 51.7, 36.4, 32.3, 17.2. HRMS calcd for C<sub>11</sub>H<sub>15</sub>O<sub>4</sub>S [M+H]: 243.0691. Found 243.0687

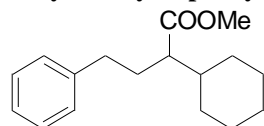
#### 4-(*tert*-Butyl-diphenyl-silanyloxy)-2-methyl-butyric acid methyl ester (14)



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 5% ethyl acetate in petroleum ether), it was obtained as an oil (77.8 mg, 70% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.72 – 7.66 (m, 4H), 7.47 – 7.39 (m, 6H), 3.71 (t, *J* = 6.2 Hz, 2H), 3.65 (s, 3H), 2.76 (h, *J* = 7.0 Hz, 1H), 2.06 – 1.98 (m, 1H), 1.70 – 1.62 (m, 1H), 1.18 (d, *J* = 7.1 Hz, 3H), 1.08 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 177.1, 135.53, 135.51, 133.76, 133.71, 129.6, 127.6, 127.53, 61.5, 51.5, 36.2, 36.0, 26.8, 19.2, 17.1. HRMS calcd for C<sub>22</sub>H<sub>31</sub>O<sub>3</sub>Si [M+H]: 371.2042. Found 371.2039.

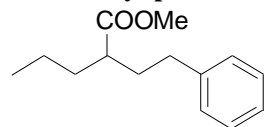
#### 2-Cyclohexyl-4-phenyl-butyric acid methyl ester (15)



The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 5% ethyl acetate in petroleum ether), it was obtained as an oil (41.4 mg, 53% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.27 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.15 (m, 2H), 3.68 (s, 3H), 2.63 – 2.56 (m, 1H), 2.50 – 2.44 (m, 1H), 2.23 – 2.19 (m, 1H), 1.96 – 1.89 (m, 1H), 1.85 – 1.49 (m, 8H), 1.24 – 1.17 (m, 1H), 1.14 – 1.09 (m, 1H), 1.05 – 0.98 (m, 1H), 0.96 – 0.88 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.1, 141.8, 128.4, 128.3, 125.8, 51.6, 51.2, 40.3, 34.1, 31.2, 30.9, 30.6, 26.30, 26.27, 26.25. HRMS calcd for C<sub>17</sub>H<sub>25</sub>O<sub>2</sub> [M+H]: 261.1855. Found 261.1852.

#### 2-Phenethyl-pentanoic acid methyl ester (16)

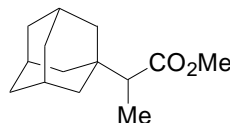


The title compound was prepared according to method A. After purification by column chromatography (SiO<sub>2</sub>: 5% ethyl acetate in petroleum ether), it was obtained as an oil (33.0 mg, 50% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.27 (m, 2H), 7.20 – 7.17 (m, 3H), 3.69 (s, 3H), 2.64 – 2.55 (m, 2H), 2.45 – 2.40 (m, 1H), 2.00 – 1.93 (m, 1H), 1.79 – 1.73 (m, 1H), 1.67 – 1.59 (m, 1H), 1.50 – 1.42

(m, 1H), 1.33 – 1.26 (m, 2H), 0.89(t, 7.3 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 141.7, 128.4, 128.3, 125.9, 51.4, 45.0, 34.6, 34.1, 33.7, 20.5, 13.9. **HRMS** calcd for  $\text{C}_{14}\text{H}_{21}\text{O}_2$  [M+H]: 221.1542. Found 221.1537.

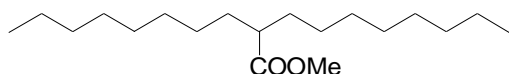
#### 2-Adamantan-1-yl-propionic acid methyl ester (17)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as an oil (28.7 mg, 43 % yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.64 (s, 3H), 2.13 (q,  $J$  = 7.1 Hz, 1H), 1.97 (s, 3H), 1.72 – 1.59 (m, 9H), 1.48 – 1.44 (m, 3H), 1.06 (d,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.0, 50.9, 50.4, 39.7, 37.0, 34.4, 28.6, 10.8. **HRMS** calcd for  $\text{C}_{14}\text{H}_{23}\text{O}_2$  [M+H]: 223.1698. Found 223.1695.

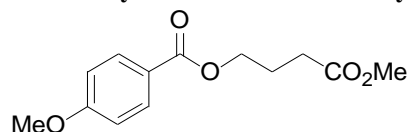
#### 2-Octyl-decanoic acid methyl ester (18)



The title compound was prepared according to method A. After purification by column chromatography ( $\text{SiO}_2$ : 10% ethyl acetate in petroleum ether), it was obtained as a colorless oil (49.3 mg, 55% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.65 (s, 3H), 2.33 – 2.28 (m, 1H), 1.61 – 1.55 (m, 2H), 1.4 – 1.38 (m, 2H), 1.30 – 1.1 (m, 24H), 0.86 (t,  $J$  = 7.0 Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  177.1, 51.2, 45.7, 32.5, 31.8, 29.5, 29.4, 29.2, 27.5, 22.6, 14.1. GC-MS (EI) calculated for  $[\text{C}_{19}\text{H}_{38}\text{O}_2]$ : 298.2, found 298.2 ( $\text{M}^+$ ), 267.2, 255.2, 199.1.

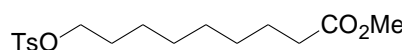
#### 4-Methoxy-benzoic acid 3-methoxycarbonyl-propyl ester (19)



The title compound was prepared according to method A but in the absence of  $\text{MgCO}_3$ . After purification by column chromatography ( $\text{SiO}_2$ : 10% ethyl acetate in petroleum ether), it was obtained as an oil (34.1 mg, 45% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J$  = 8.8 Hz, 2H), 6.91 (d,  $J$  = 8.8 Hz, 2H), 4.32 (t,  $J$  = 6.3 Hz, 2H), 3.85 (s, 3H), 3.66 (s, 3H), 2.48 (t,  $J$  = 7.4 Hz, 2H), 2.12 – 2.07 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 166.2, 163.4, 131.6, 122.5, 113.6, 63.6, 55.4, 51.6, 30.8, 24.2. **HRMS** calcd for  $\text{C}_{13}\text{H}_{17}\text{O}_5$  [M+H]: 253.1076. Found 253.1073.

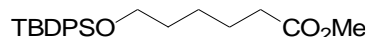
#### 9-(Toluene-4-sulfonyloxy)-nonanoic acid methyl ester (20)



The title compound was prepared according to method A in the absence of  $\text{MgCO}_3$ . After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as an oil (42.1 mg, 41% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 8.3 Hz, 2H), 7.34 (d,  $J$  = 8.0 Hz, 2H), 4.01 (t,  $J$  = 6.5 Hz, 2H), 3.66 (s, 3H), 2.45 (s, 3H), 2.29 (dd,  $J$  = 17.2, 9.7 Hz, 2H), 1.65 – 1.56 (m, 4H), 1.32 – 1.21 (m, 8H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 144.6, 133.3, 129.8, 127.9, 70.6, 51.5, 34.0, 29.0, 28.9, 28.8, 28.7, 25.3, 24.8, 21.6. HRMS calcd for  $\text{C}_{17}\text{H}_{27}\text{O}_5\text{S}$  [ $\text{M}+\text{H}$ ]: 343.1579. Found 343.1574.

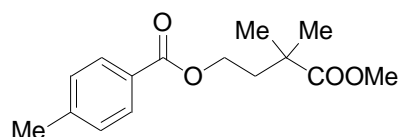
#### 6-(tert-Butyl-diphenyl-silanyloxy)-hexanoic acid methyl ester (21)



The title compound was prepared according to method A in the absence of  $\text{MgCO}_3$ . After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as an oil (57.7 mg, 50% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.66 (m, 4H), 7.45 – 7.36 (m, 6H), 3.69 – 3.66 (m, 5H), 2.31 (t,  $J$  = 7.6 Hz, 2H), 1.66 – 1.56 (m, 4H), 1.44 – 1.38 (m, 2H), 1.06 (s, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 135.5, 134.0, 129.5, 127.6, 63.6, 51.4, 34.1, 32.2, 26.8, 25.4, 24.7, 19.2. HRMS calcd for  $\text{C}_{23}\text{H}_{33}\text{O}_3\text{Si}$  [ $\text{M}+\text{H}$ ]: 385.2199. Found 385.2191.

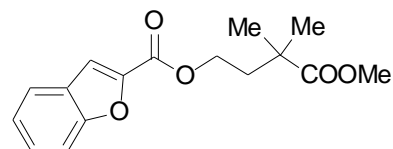
#### 4-Methyl-benzoic acid 3-methoxycarbonyl-3-methyl-butyl ester (22)



The title compound was prepared according to method B. After purification by column chromatography ( $\text{SiO}_2$ : 10% ethyl acetate in petroleum ether), it was obtained as an oil (47.6 mg, 60 % yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J$  = 8.1 Hz, 2H), 7.21 (d,  $J$  = 8.0 Hz, 2H), 4.34 (t,  $J$  = 6.8 Hz, 2H), 3.59 (s, 3H), 2.39 (s, 3H), 2.04 (t,  $J$  = 6.8 Hz, 2H), 1.27 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  177.7, 166.5, 143.5, 129.6, 129.0, 127.4, 61.7, 51.8, 40.8, 38.7, 25.4, 21.6. HRMS calcd for  $\text{C}_{15}\text{H}_{21}\text{O}_4$  [ $\text{M}+\text{H}$ ]: 265.1440. Found 265.1442.

#### Benzofuran-2-carboxylic acid 3-methoxycarbonyl-3-methyl-butyl ester (23)

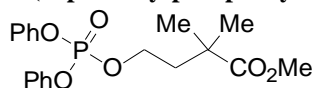


To a vial (10 mL) equipped with a stir bar was added  $\text{CuOTf}$  (0.045 mmol, 9.6 mg, 15 mol %),  $\text{InI}$  (0.30 mmol, 72.5 mg, 100 mol %),  $\text{K}_2\text{CO}_3$  (0.30 mmol, 41.4 mg, 100 mol %), benzofuran-2-carboxylic acid 3-iodo-3-methyl-butyl ester (0.30 mmol, 107.5 mg, 100 mol %), 5 mL of 1,4-dioxane and 56  $\mu\text{L}$  of methanol (1.5 mmol, 500 mol %) in sequence. Subsequently, the vial was placed into an autoclave. The reactor was purged with CO for 5 min and then pressurized to 4 atm CO. The reaction mixture was allowed to stir at 25  $^\circ\text{C}$  for 24h. The autoclave was depressurized. The reaction was diluted with 30 mL of ethyl acetate and filtered through a plug of celite. The filtrate was washed with saturated  $\text{NH}_4\text{Cl}$  aqueous solution and brine, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated in vacuum. The residue was purified by flash chromatography ( $\text{SiO}_2$ : 30% ethyl acetate in petroleum ether) to offer 44.4 mg of oil (51% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J$  = 7.8 Hz, 1H), 7.58 (d,  $J$  = 8.4 Hz, 1H), 7.50 (s, 1H), 7.44 (t,  $J$  = 7.7 Hz, 1H), 7.30 (t,  $J$  = 7.5 Hz, 1H), 4.42 (t,  $J$  = 6.9 Hz, 2H), 3.65 (s, 3H), 2.08 (t,  $J$  = 6.9 Hz, 2H), 1.28 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  177.6, 159.4, 155.7, 145.4, 127.6, 126.9, 123.8, 122.8, 113.9,

112.3, 62.3, 51.9, 40.7, 38.6, 25.4. HRMS calcd for  $C_{16}H_{19}O_5$  [M+H]: 291.1232. Found 291.1228.

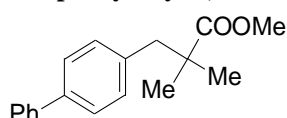
**4-(Diphenoxy-phosphoryloxy)-2, 2-dimethyl-butyrac acid methyl ester (24)**



The title compound was prepared according to method B. After purification by column chromatography (SiO<sub>2</sub>: 2% methanol in dichloromethane), it was obtained as an oil (51.1 mg, 45% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.31 (m, 4H), 7.24 – 7.16 (m, 6H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 1.99 (t, *J* = 7.0 Hz, 2H), 1.20 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 177.4, 150.5, 150.4, 129.8, 125.32, 125.31, 120.05, 120.01, 66.3, 66.2, 52.0, 40.6, 40.0, 39.9, 25.3. HRMS calcd for  $C_{19}H_{24}O_6P$  [M+H]: 379.1311. Found 379.1329.

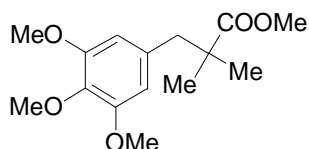
**3-Biphenyl-4-yl-2, 2-dimethyl-propionic acid methyl ester (25)**



The title compound was prepared according to method B. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as an oil (44.3 mg, 55% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 3.69 (s, 3H), 2.90 (s, 2H), 1.22 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 177.9, 140.9, 139.3, 137.0, 130.5, 128.7, 127.1, 127.0, 126.7, 51.7, 46.0, 43.7, 25.0. HRMS calcd for  $C_{18}H_{21}O_2$  [M+H]: 269.1542. Found 269.1549.

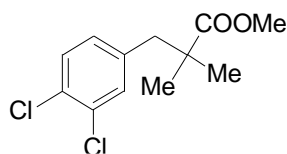
**2, 2-Dimethyl-3-(3, 4, 5-trimethoxy-phenyl)-propionic acid methyl ester (26)**



The title compound was prepared according to method B. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as an oil (25.4 mg, 30% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.31 (s, 2H), 3.81 (s, 9H), 3.66 (s, 3H), 2.79 (s, 2H), 1.19 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 177.8, 152.7, 136.7, 133.6, 107.0, 60.8, 56.0, 51.7, 46.8, 43.8, 25.1. HRMS calcd for  $C_{15}H_{23}O_5$  [M+H]: 283.1546. Found 238.1546.

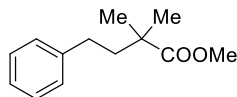
**3-(3, 4-Dichloro-phenyl)-2, 2-dimethyl-propionic acid methyl ester (27)**



The title compound was prepared according to method B. After purification by column chromatography (SiO<sub>2</sub>: 10% ethyl acetate in petroleum ether), it was obtained as an oil (36.8 mg, 47% yield).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 8.3$  Hz, 1H), 7.20 (d,  $J = 1.9$  Hz, 1H), 6.94 (dd,  $J = 8.2$ , 1.9 Hz, 1H), 3.66 (s, 3H), 2.80 (s, 2H), 1.18 (s, 6H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  177.3, 138.2, 131.90, 131.85, 130.6, 129.9, 129.4, 51.8, 45.3, 43.6, 24.9. **HRMS** calcd for  $\text{C}_{12}\text{H}_{15}\text{Cl}_2\text{O}_2$  [ $\text{M}+\text{H}$ ]: 261.0449. Found 261.0447.

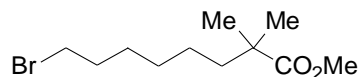
## 2, 2-Dimethyl-4-phenyl-butyric acid methyl ester (28)



The title compound was prepared according to method B. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as an oil (27.9 mg, 45% yield). Physical and spectral data were in accordance with literature data.<sup>10</sup>

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 3.66 (s, 3H), 2.53 (dt,  $J = 8.5$ , 3.5 Hz, 2H), 1.83 (dt,  $J = 8.9$ , 4.0 Hz, 2H), 1.24 (s, 6H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  178.1, 142.1, 128.30, 128.26, 125.7, 51.7, 42.7, 42.3, 31.5, 25.2. **HRMS** calcd for  $\text{C}_{13}\text{H}_{19}\text{O}_2$  [ $\text{M}+\text{H}$ ]: 207.1385. Found 207.1382.

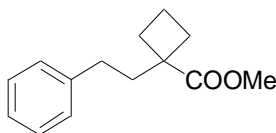
## 8-Bromo-2, 2-dimethyl-octanoic acid methyl ester (29)



The title compound was prepared according to method B. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as an oil (58.5 mg), which is composed of an inseparable mixture of **29** and 1-bromo-7-methoxy-7-methyl-octane in a ratio of 5:3, as determined by  $^1\text{H NMR}$  spectroscopy. The yield for **29** was estimated to be 48%. **HRMS** calcd for  $\text{C}_{11}\text{H}_{22}\text{BrO}_2$  [ $\text{M}+\text{H}$ ] (**29**): 265.0803 and 267.0783. Found 265.0802 and 267.0781.

According to a literature procedure,<sup>11</sup> the above mixture was treated with  $\text{LiBH}_4$  (0.2 mL, 2.0 M in THF) and MeOH (15  $\mu\text{L}$ ) in  $\text{CH}_2\text{Cl}_2$  (2 mL) for 8 hours. After purification by column chromatography ( $\text{SiO}_2$ : 20% ethyl acetate in petroleum ether), 8-bromo-2, 2-dimethyl-octan-1-ol was obtained (30.7 mg) of as a colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.41 (t,  $J = 6.8$  Hz, 2H), 3.31 (s, 2H), 1.90 – 1.80 (m, 2H), 1.49 – 1.40 (m, 2H), 1.34 – 1.19 (m, 6H), 0.86 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  72.0, 38.5, 35.0, 34.0, 32.8, 29.7, 28.2, 23.8, 23.7.

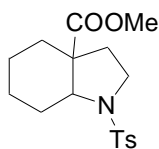
## 1-Phenethyl-cyclobutanecarboxylic acid methyl ester (30)



The title compound was prepared according to method B. After purification by column chromatography ( $\text{SiO}_2$ : 10% ethyl acetate in petroleum ether), it was obtained as an oil (45.8 mg, 70 % yield).

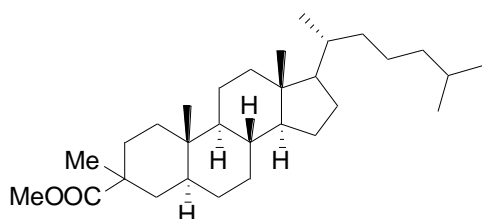
$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.22 (m, 2H), 7.16 – 7.13 (m, 3H), 3.65 (s, 3H), 2.48 – 2.41 (m, 4H), 2.08 – 2.05 (m, 2H), 1.94 – 1.85 (m, 4H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  177.3, 141.8, 128.3, 125.8, 51.6, 47.6, 39.8, 31.3, 30.0, 15.6. **HRMS** calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_2$  [ $\text{M}+\text{H}$ ]: 219.1385. Found 219.1388.



**1-[(4-Methylphenyl)sulfonyl]octahydro-1H-indole -3 $\alpha$ -carboxylic acid methyl ester (31)**


The title compound was prepared according to method B. After purification by column chromatography (SiO<sub>2</sub>: 65% n-hexane in DCM), it was obtained as an oil (29.9 mg, 30% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d,  $J$  = 8.2 Hz, 2H), 7.29 (d,  $J$  = 8.0 Hz, 2H), 3.90 (dd,  $J$  = 8.1, 5.4 Hz, 1H), 3.56 – 3.49 (m, 1H), 3.38 (s, 3H), 3.28 – 3.22 (m, 1H), 2.41 (s, 3H), 2.05 – 2.00 (m, 2H), 1.97 – 1.91 (m, 1H), 1.83 – 1.61 (m, 4H), 1.47 – 1.29 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  175.3, 143.0, 135.3, 129.5, 127.4, 60.8, 52.6, 52.1, 45.8, 30.5, 30.2, 29.6, 21.8, 21.5, 21.4. HRMS calcd for C<sub>17</sub>H<sub>24</sub>NO<sub>4</sub>S [M+H]: 338.1426. Found: 338.1421.

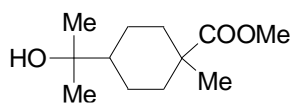
**17-(1, 5-Dimethyl-hexyl)-3, 10, 13-trimethyl-hexadecahydro-cyclopenta[ $\alpha$ ]phenanthrene-3-carboxylic acid methyl ester (32)**


The title compound was prepared according to method B. After purification by column chromatography (SiO<sub>2</sub>: 5% ethyl acetate in petroleum ether), it was obtained as a white solid (64.0 mg, 48% yield). The isolated solid comprised a mixture of two isomers in a 3:2 ratio as determined by <sup>1</sup>H NMR spectroscopy. The two isomers were separated by preparative thin layer chromatography.

Major isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.67 (s, 3H), 2.08 – 2.00 (m, 1H), 1.94 (dt,  $J$  = 12.5, 3.4 Hz, 1H), 1.83 – 1.74 (m, 2H), 1.64 – 1.42 (m, 5H), 1.35 – 0.93 (m, 24H), 0.89 (d,  $J$  = 6.5 Hz, 3H), 0.86 (dd,  $J$  = 6.6, 1.9 Hz, 6H), 0.76 (s, 3H), 0.63 (s, 3H), 0.62 – 0.56 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  178.3, 56.5, 56.2, 54.3, 51.7, 44.2, 43.8, 42.6, 40.0, 39.5, 38.3, 36.3, 36.2, 35.8, 35.42, 35.39, 31.9, 31.4, 28.6, 28.5, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 20.9, 18.6, 12.1, 12.0.

Minor isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.66 (s, 3H), 1.96 (dt,  $J$  = 12.4, 3.2 Hz, 1H), 1.90 – 1.75 (m, 2H), 1.71– 0.95 (m, 30H), 0.90 (d,  $J$  = 6.5 Hz, 3H), 0.86 (dd,  $J$  = 6.6, 1.8 Hz, 6H), 0.78 (s, 3H), 0.72 – 0.65 (m, 1H), 0.64 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  179.6, 56.5, 56.3, 54.4, 51.7, 42.6, 42.1, 40.9, 40.0, 39.5, 36.5, 36.2, 36.0, 35.8, 35.5, 33.7, 32.0, 29.5, 28.6, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.1, 20.9, 18.7, 12.1, 11.7.

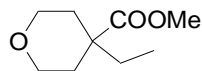
HRMS calcd for C<sub>30</sub>H<sub>52</sub>O<sub>2</sub> [M<sup>+</sup>]: 444.3967. Found 444.3962.

**4-(1-Hydroxy-1-methyl-ethyl)-1-methyl-cyclohexanecarboxylic acid methyl ester (33)**


The title compound was prepared according to method B. After purification by column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in petroleum ether), it was obtained as oil (30.9 mg, a mixture of trans and cis isomers, dr = 1.6:1, 48% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.67 (s, 2H (major)), 3.66 (s, 1H (minor)), 2.31 – 2.20 (m, 1H), 1.79 – 1.57 (m, 4H), 1.28 – 1.20 (m, 3H), 1.19 (s, 1H (minor)), 1.18 (s, 2H (major)), 1.14 (s, 2H (minor)), 1.13 (s, 4H (major)), 1.09 – 1.00 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.4, 177.7, 72.7, 72.6, 51.7, 51.6, 48.5, 48.4, 43.4, 41.4, 36.0, 33.8, 28.2, 27.03, 26.96, 24.8, 22.1, 19.7. **HRMS** calcd for  $\text{C}_{12}\text{H}_{23}\text{O}_3$   $[\text{M}+\text{H}]$ : 215.1647. Found 215.1655.

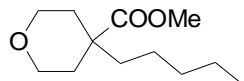
#### 4-Ethyl-tetrahydro-pyran-4-carboxylic acid methyl ester (34)



The title compound was prepared according to method B. After purification by column chromatography ( $\text{SiO}_2$ : 20% ethyl acetate in petroleum ether), it was obtained as an oil (26.9 mg, 52% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82 (dt,  $J$  = 11.9, 3.7 Hz, 2H), 3.71 (s, 3H), 3.42 (td,  $J$  = 11.7, 2.1 Hz, 2H), 2.07 (dd,  $J$  = 13.7, 2.1 Hz, 2H), 1.57 (q,  $J$  = 7.5 Hz, 2H), 1.52 – 1.43 (m, 2H), 0.80 (t,  $J$  = 7.5 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 65.5, 51.7, 45.4, 33.9, 33.5, 8.2. **HRMS** calcd for  $\text{C}_9\text{H}_{17}\text{O}_3$   $[\text{M}+\text{H}]$ : 173.1178. Found 173.1177.

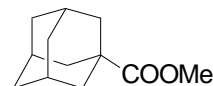
#### 4-Pentyl-tetrahydro-pyran-4-carboxylic acid methyl ester (35)



The title compound was prepared according to method B. After purification by column chromatography ( $\text{SiO}_2$ : 20% ethyl acetate in petroleum ether), it was obtained as an oil (25.7 mg, 40% yield).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.81 (dt,  $J$  = 11.9, 3.6 Hz, 2H), 3.71 (s, 3H), 3.42 (td,  $J$  = 11.7, 2.1 Hz, 2H), 2.07 (dd,  $J$  = 13.6, 1.9 Hz, 2H), 1.52 – 1.46 (m, 4H), 1.30 – 1.15 (m, 6H), 0.86 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.4, 65.5, 51.7, 45.0, 40.8, 34.3, 32.0, 23.3, 22.4, 13.9. **HRMS** calcd for  $\text{C}_{12}\text{H}_{23}\text{O}_3$   $[\text{M}+\text{H}]$ : 215.1647. Found 215.1647.

#### Adamantane-1-carboxylic acid methyl ester (36)

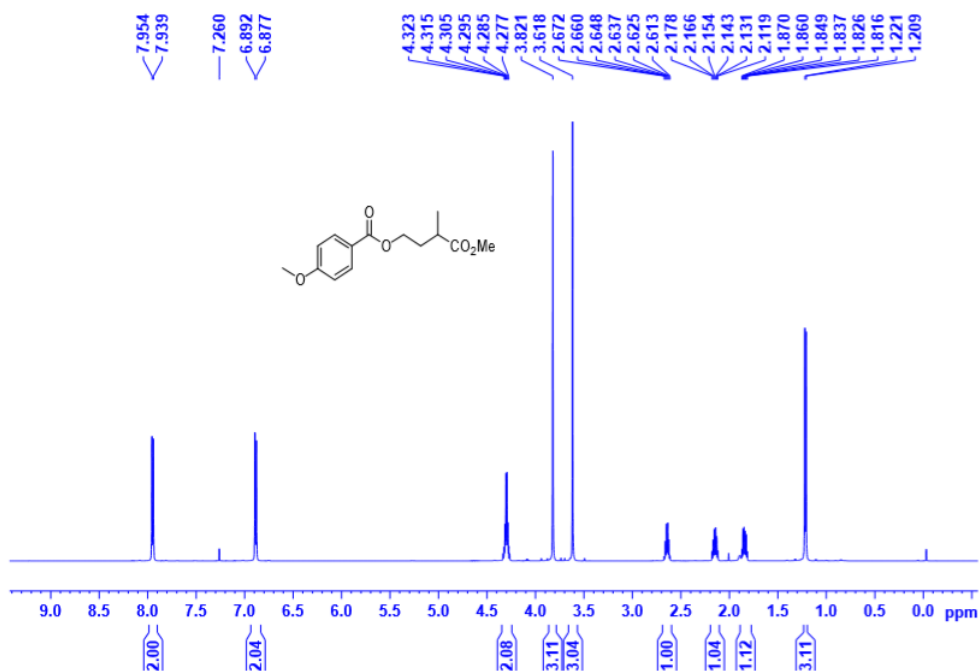


The title compound was prepared according to method B. After purification by column chromatography ( $\text{SiO}_2$ : 5% ethyl acetate in petroleum ether), it was obtained as a white solid (29.1 mg of 50 % yield). The physical and spectral data were in accordance with literature data.<sup>12</sup>

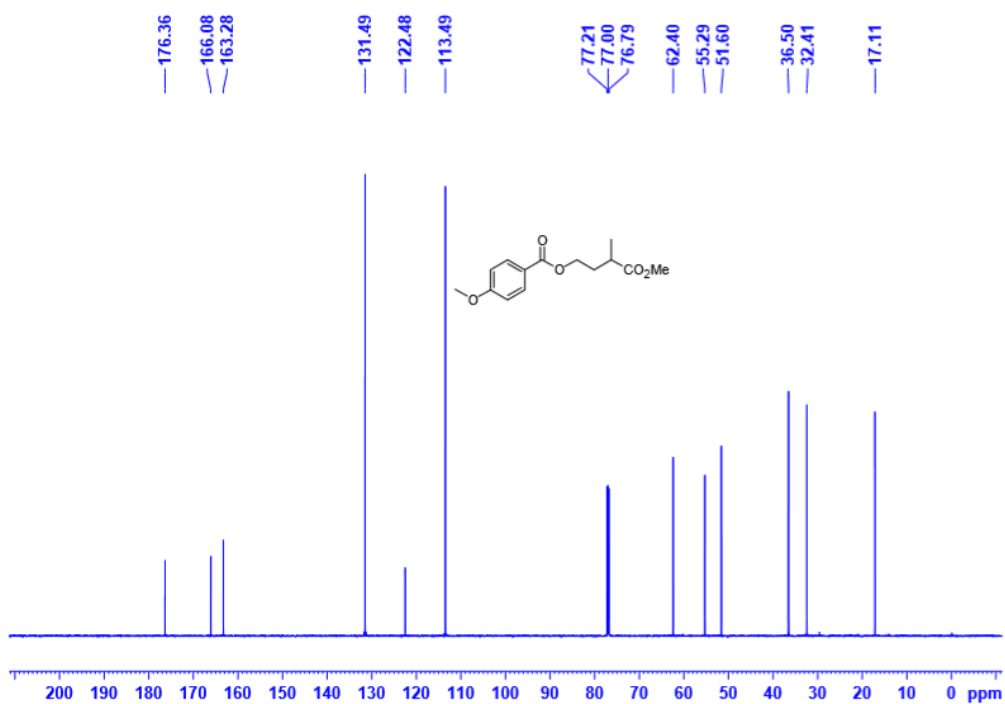
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.64 (s, 3H), 2.00 (s, 3H), 1.88 (m, 6H), 1.70 (m, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  178.2, 51.5, 40.7, 38.8, 36.5, 27.9. **HRMS** calcd for  $\text{C}_{12}\text{H}_{19}\text{O}_2$   $[\text{M}+\text{H}]$ : 195.1385. Found 195.1385.

## II. Spectral Data for New Compounds

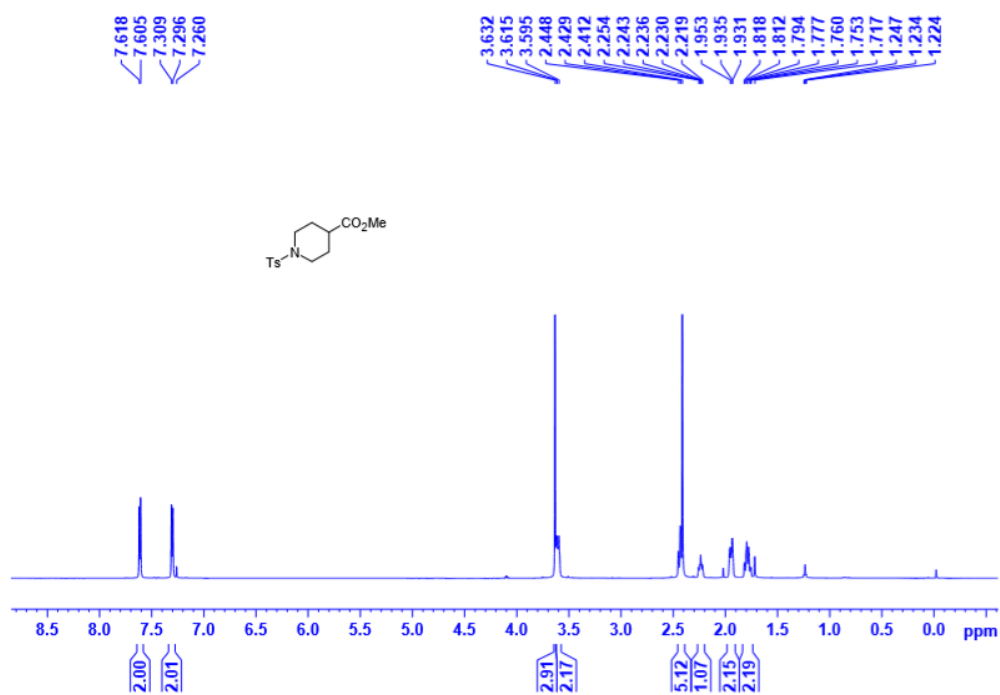
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **2**



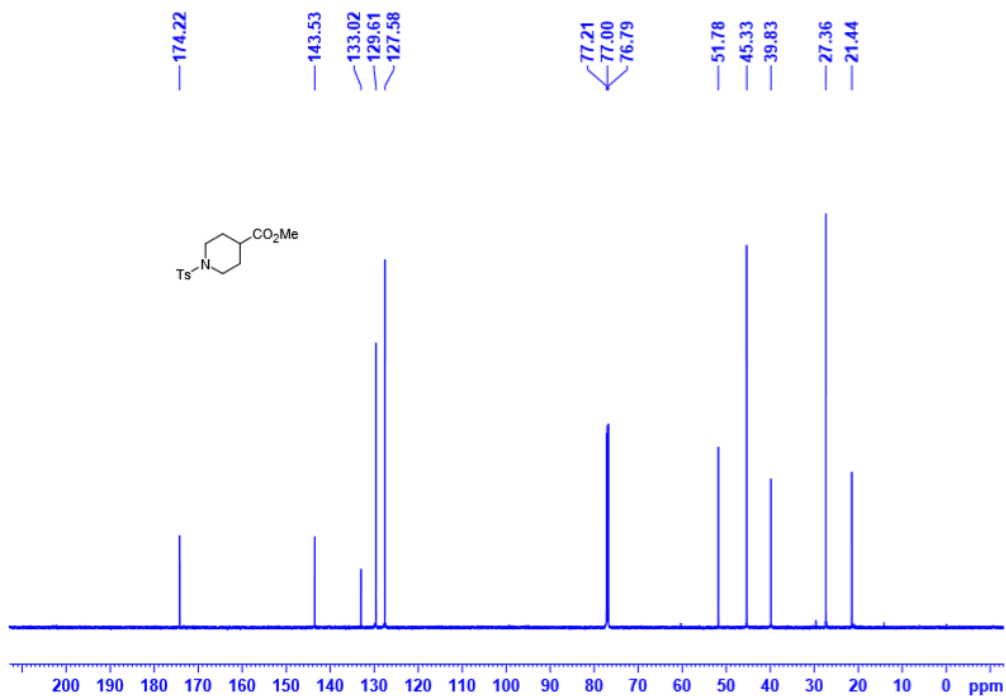
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **2**



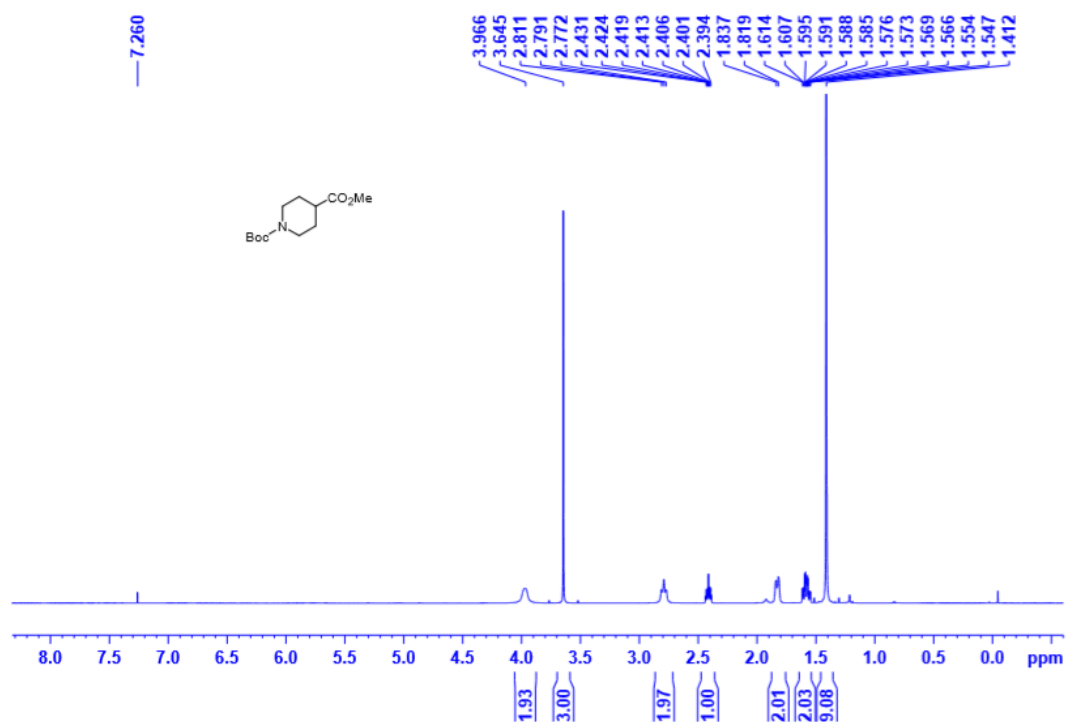
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **3a**



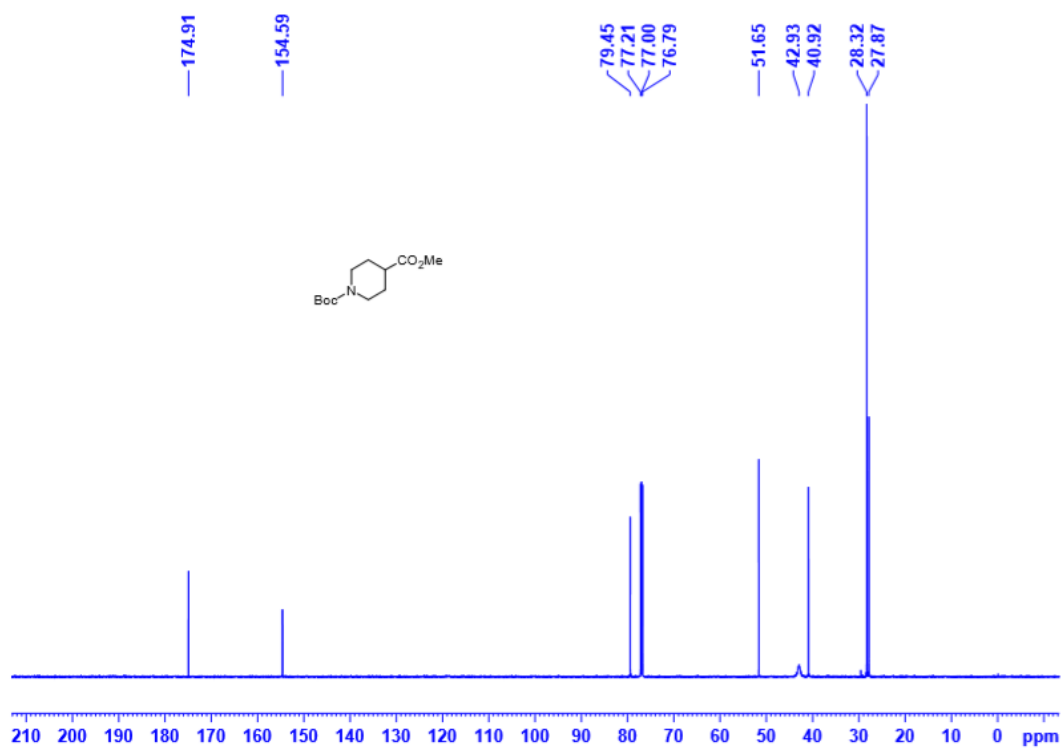
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **3a**



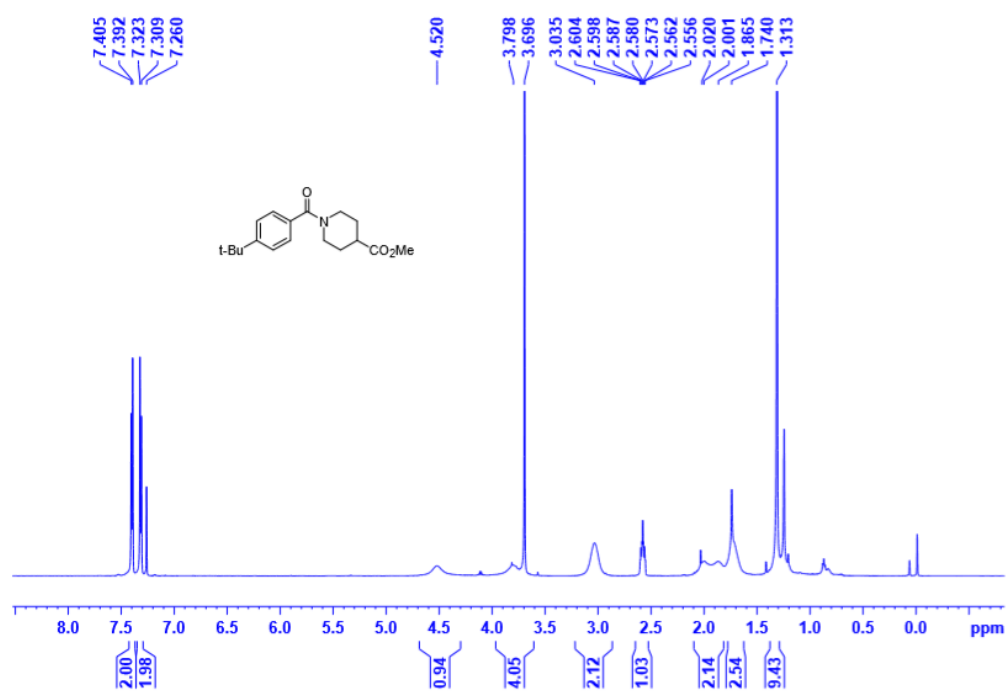
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **3b**



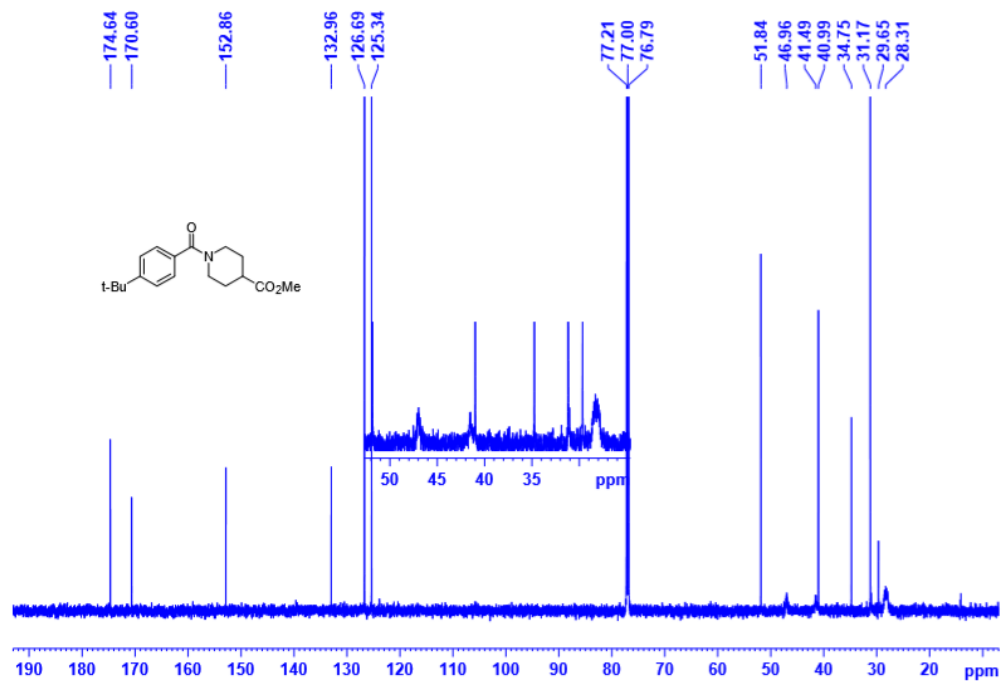
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **3b**

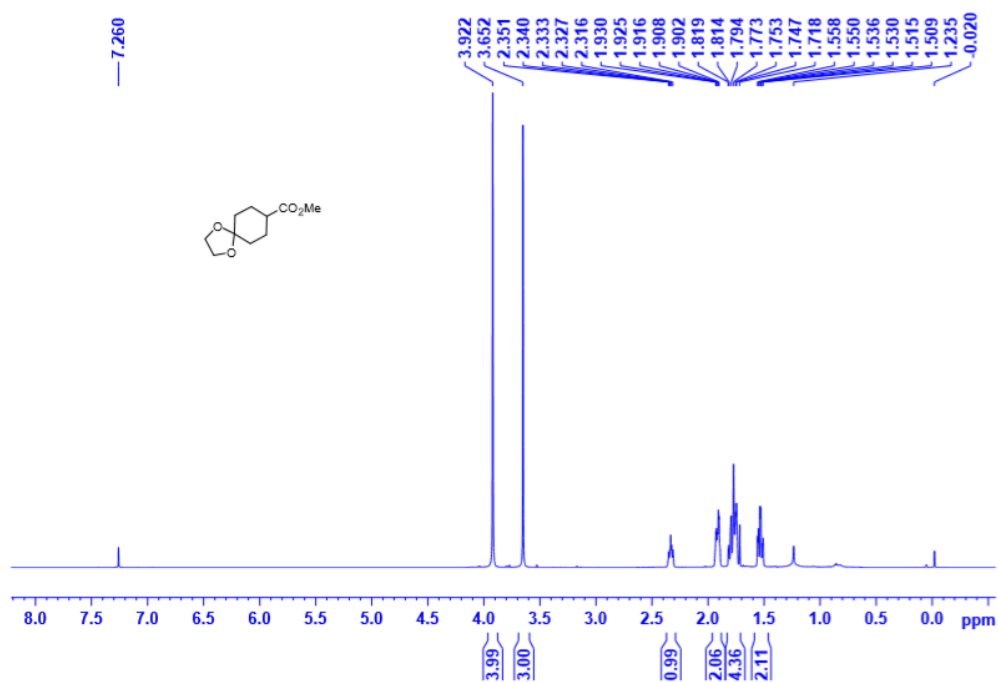
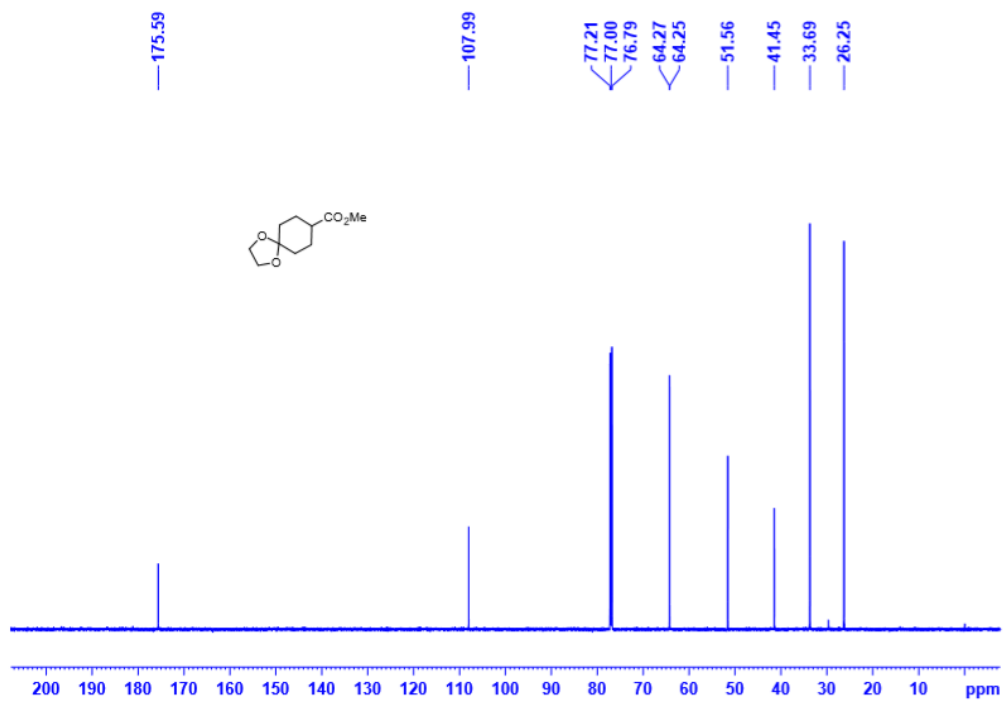


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **3c**

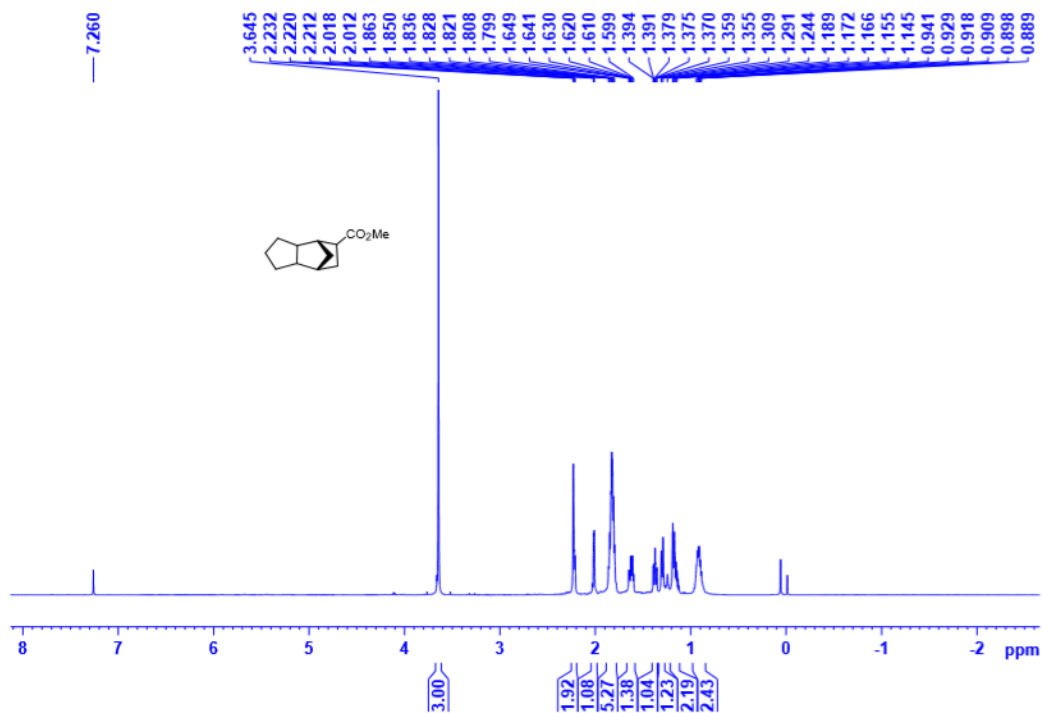


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **3c**

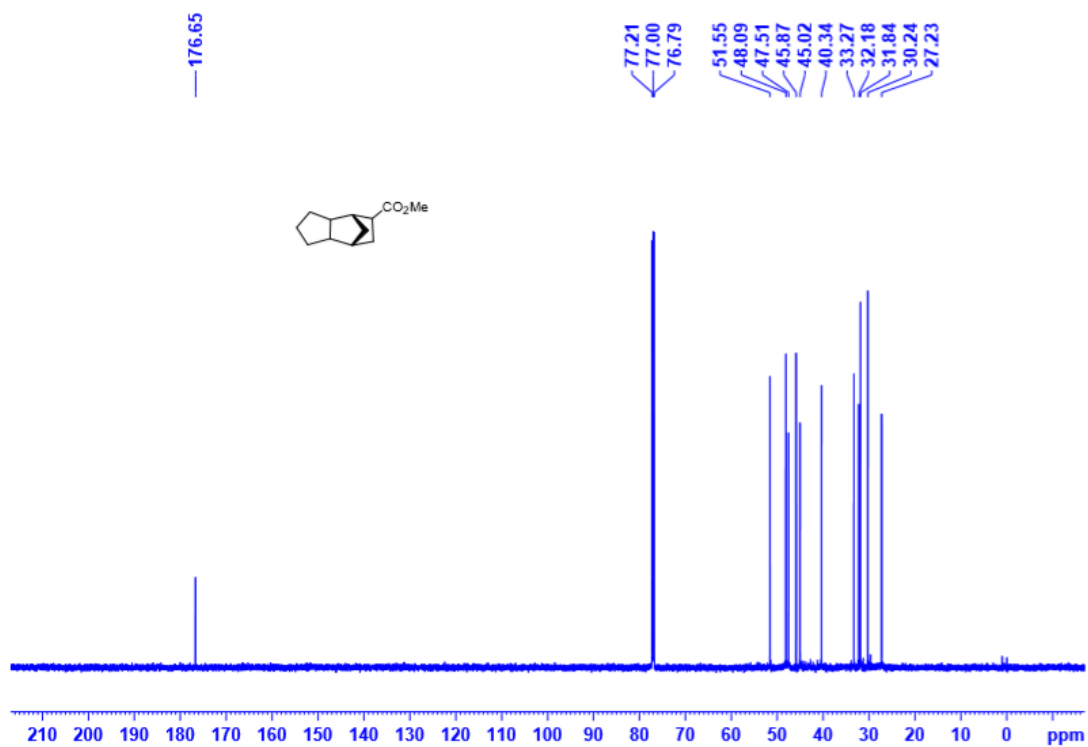


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **4** $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **4**

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **5**

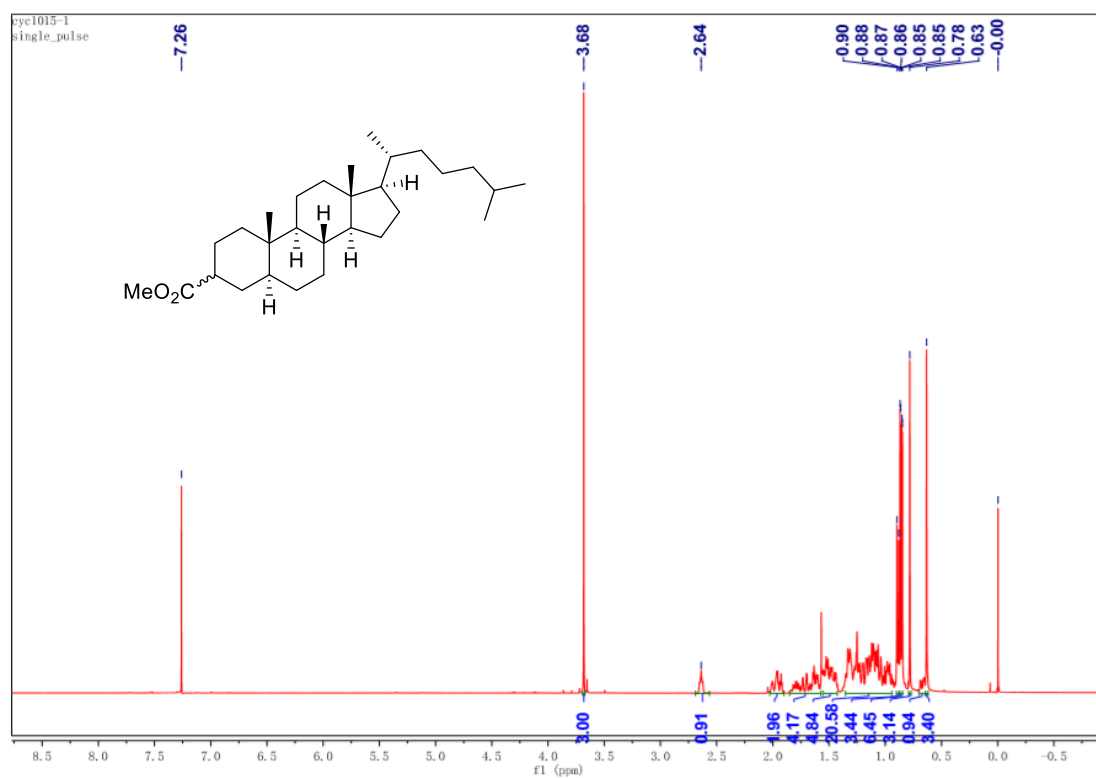


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **5**

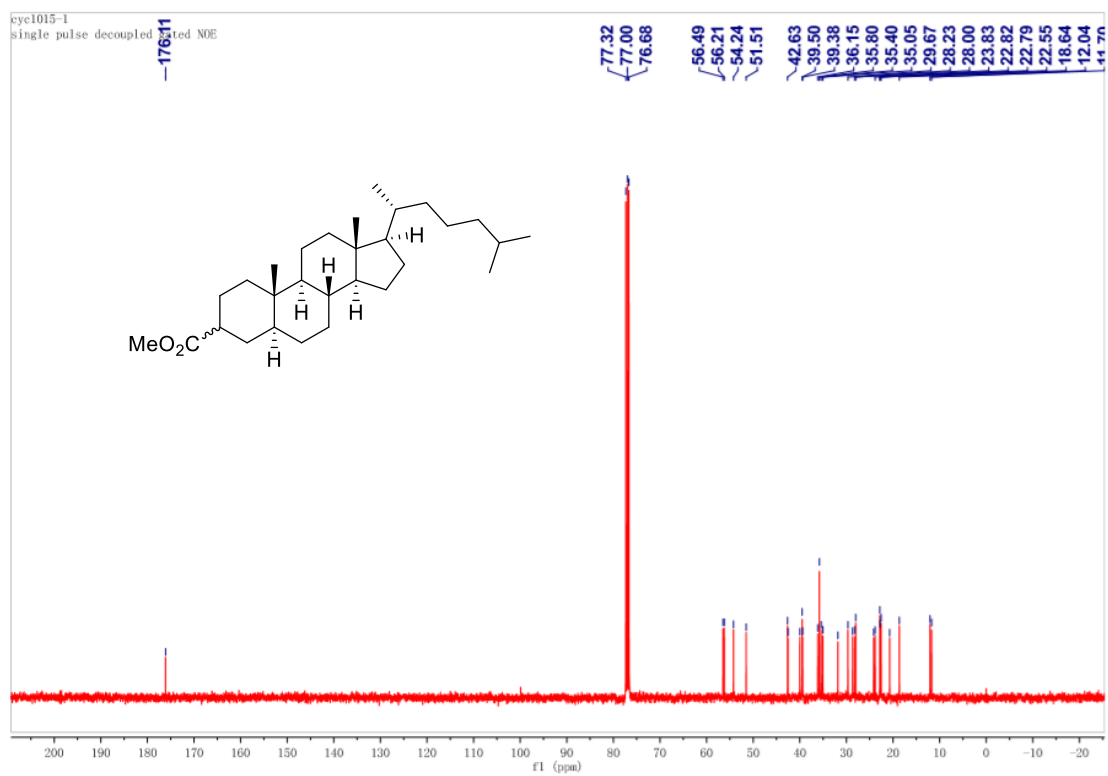




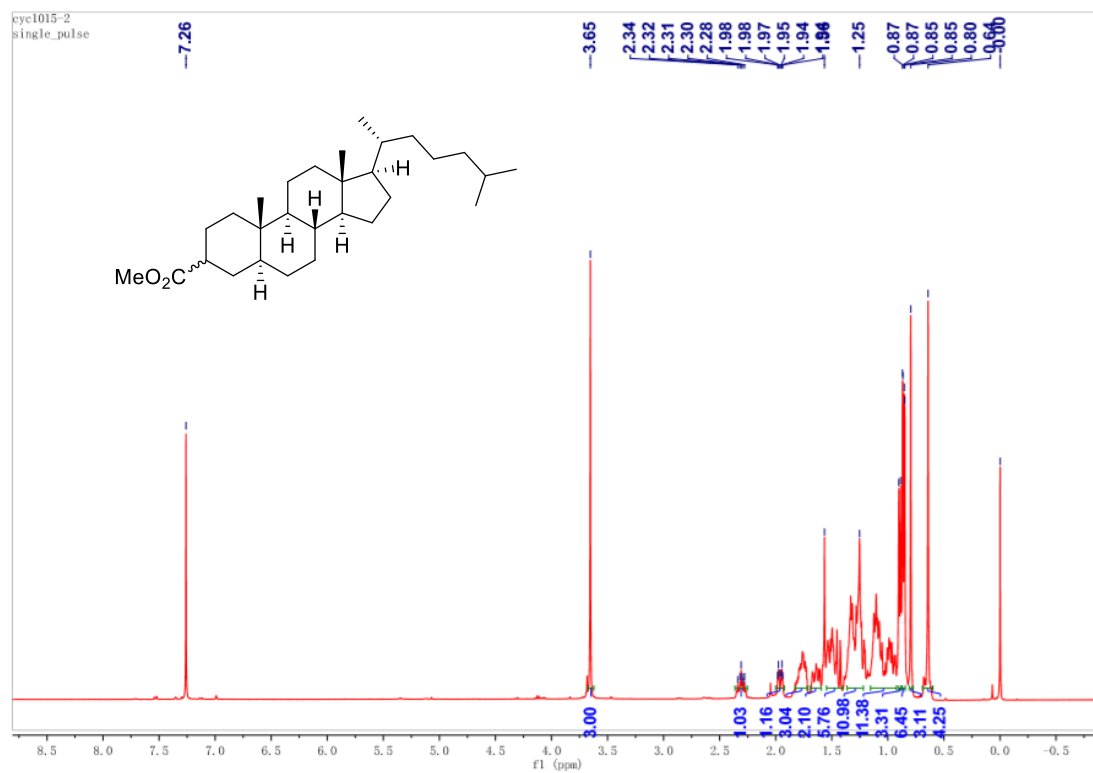
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **6** (major isomer)



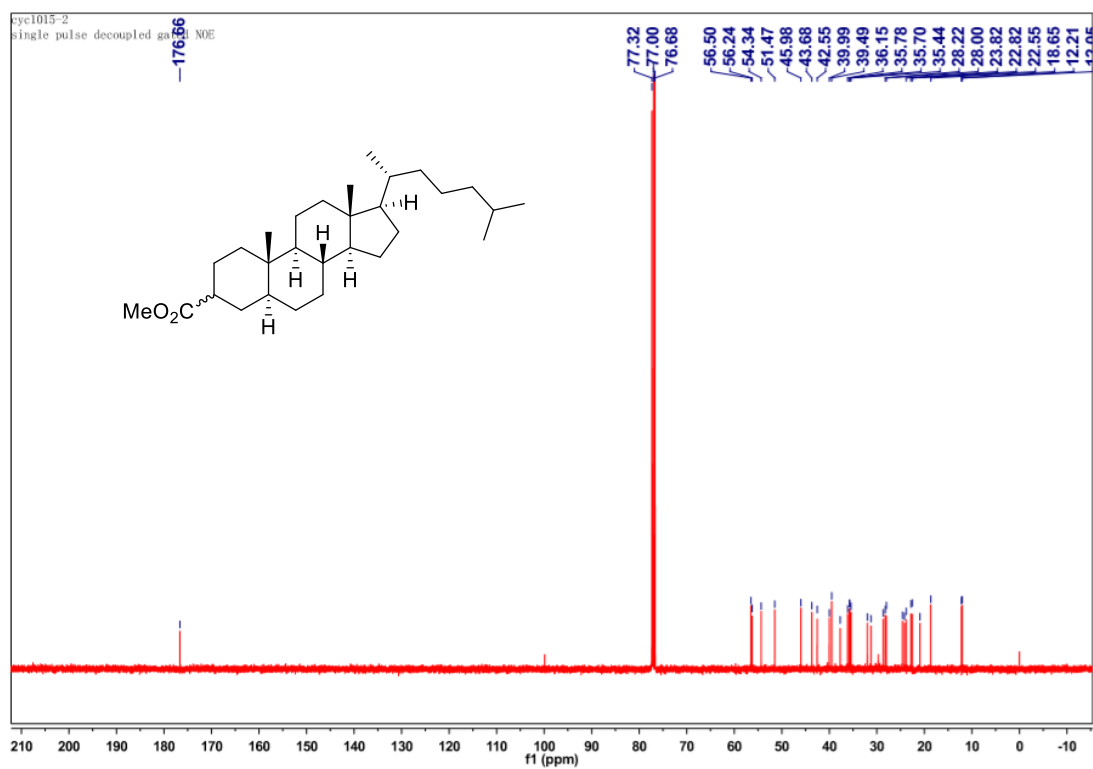
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **6** (major isomer)

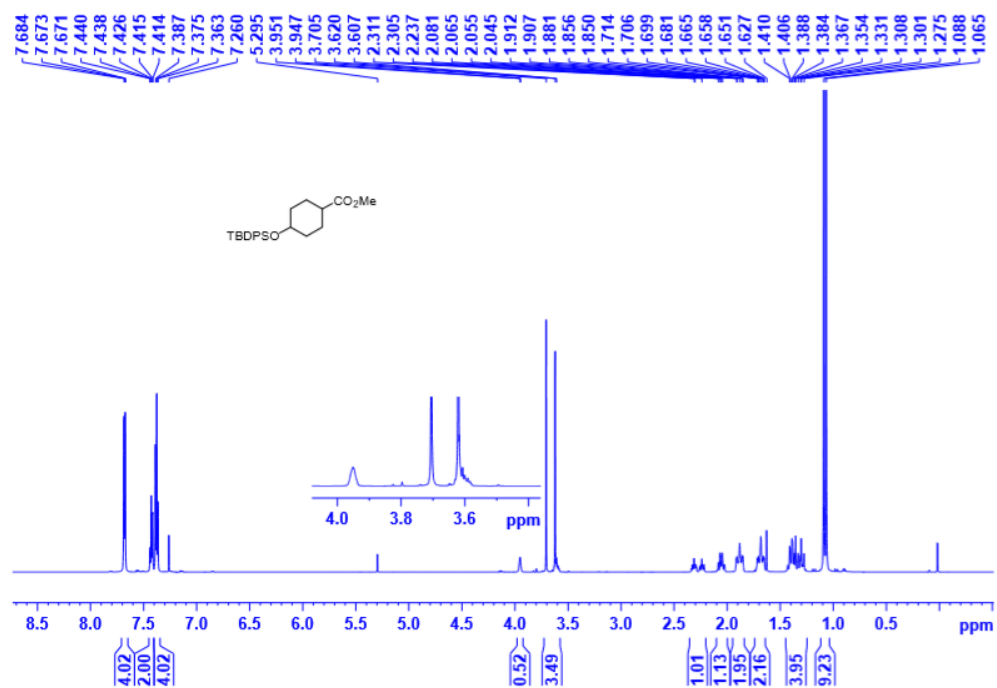
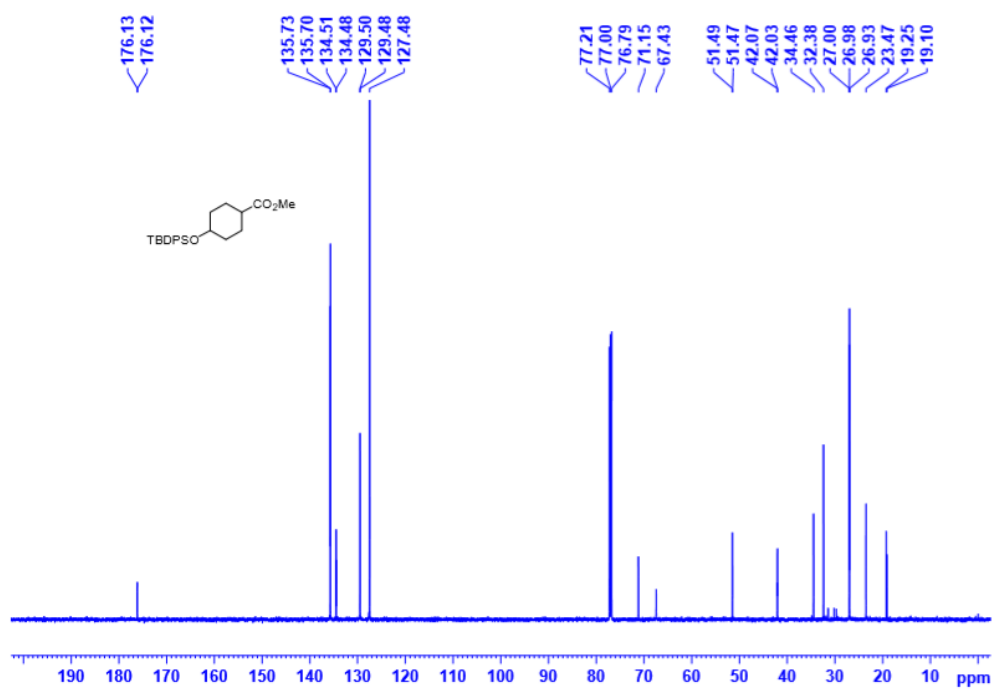


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **6** (minor isomer)

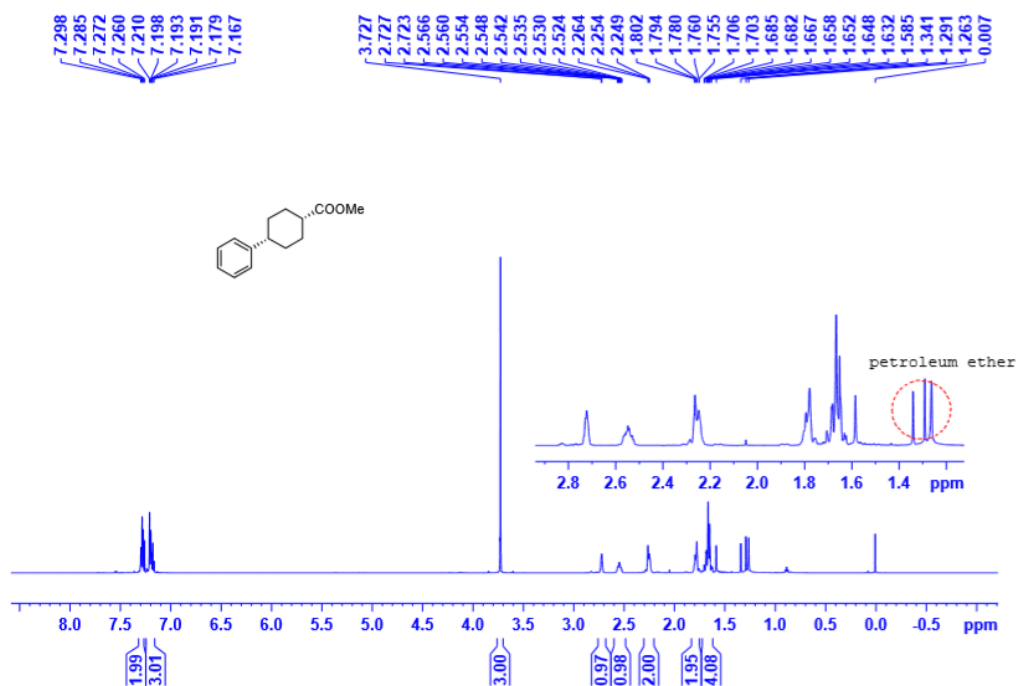


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **6** (minor isomer)

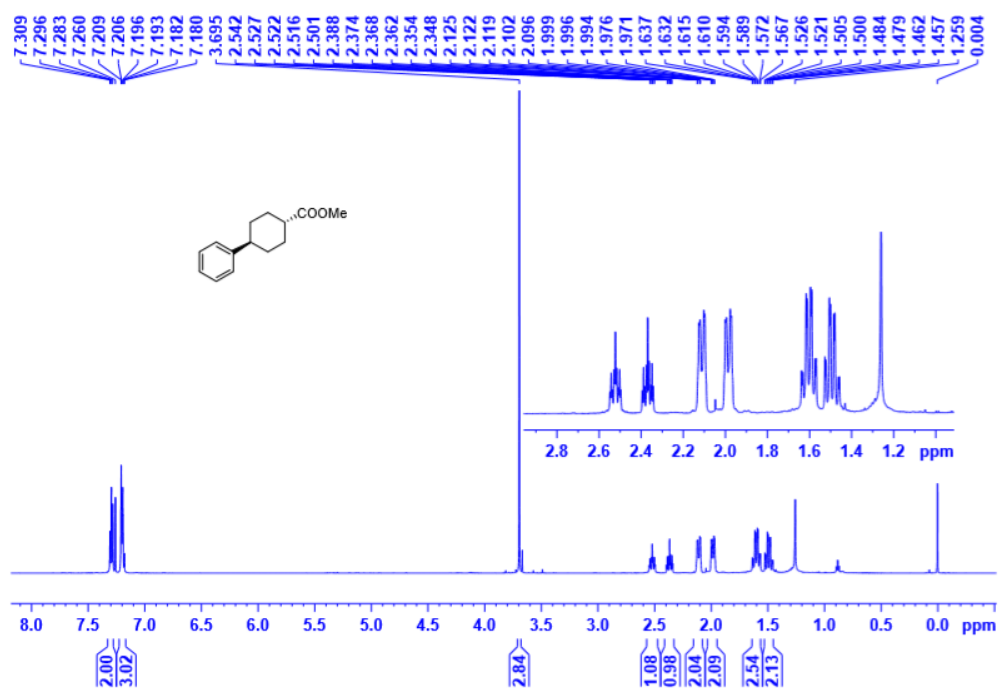


<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of **7a**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) of **7a**

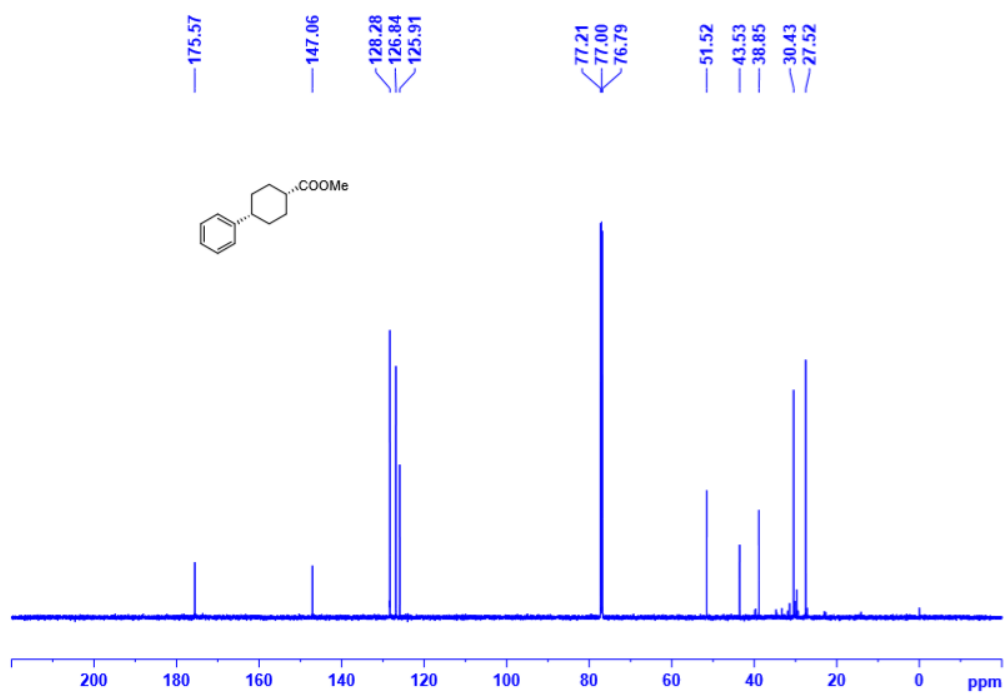
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **7b** (cis isomer)



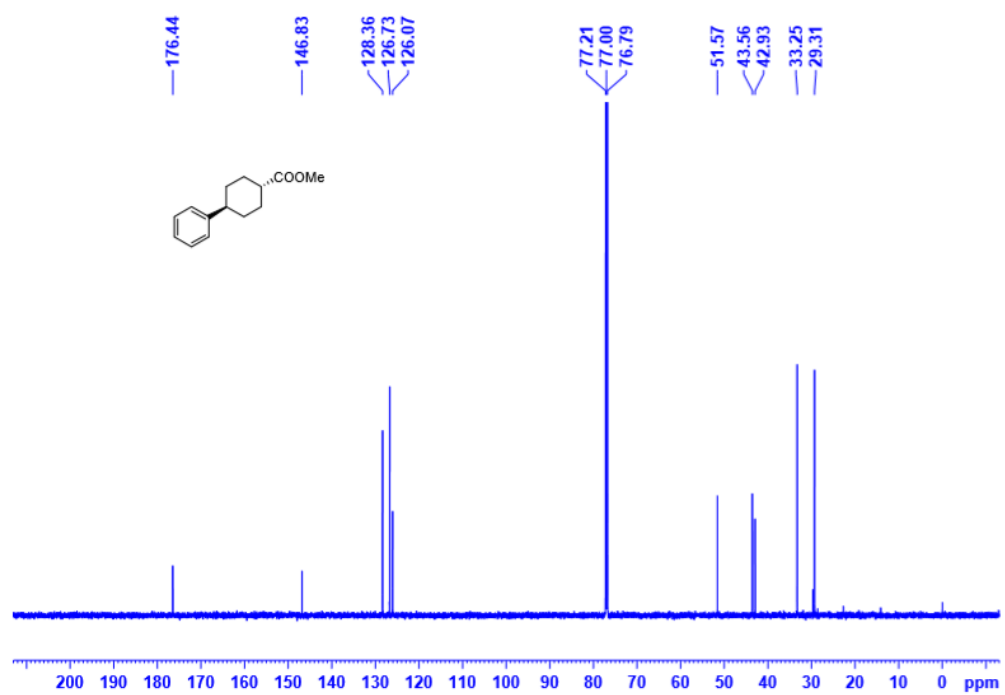
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **7b** (trans isomer)



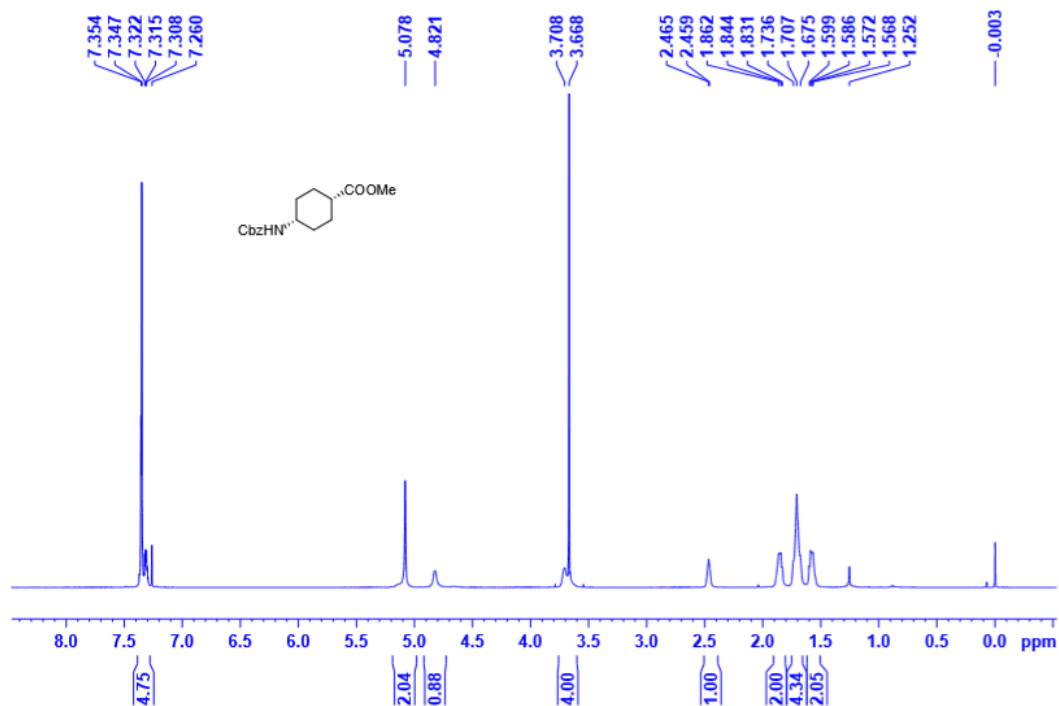
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **7b** (cis isomer)



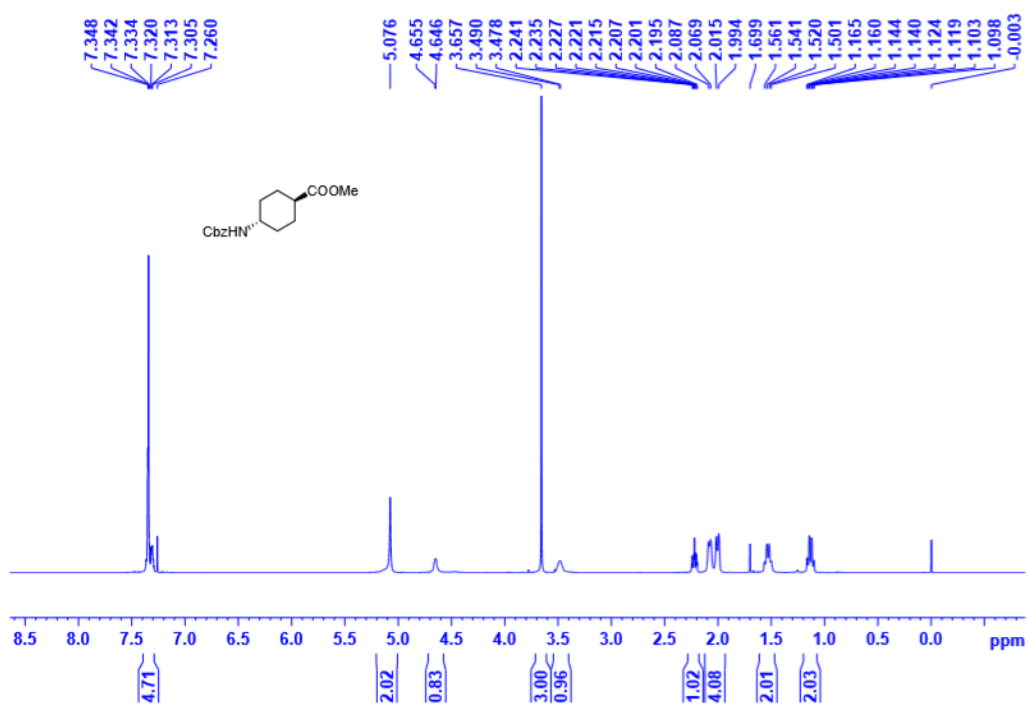
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **7b** (trans isomer)



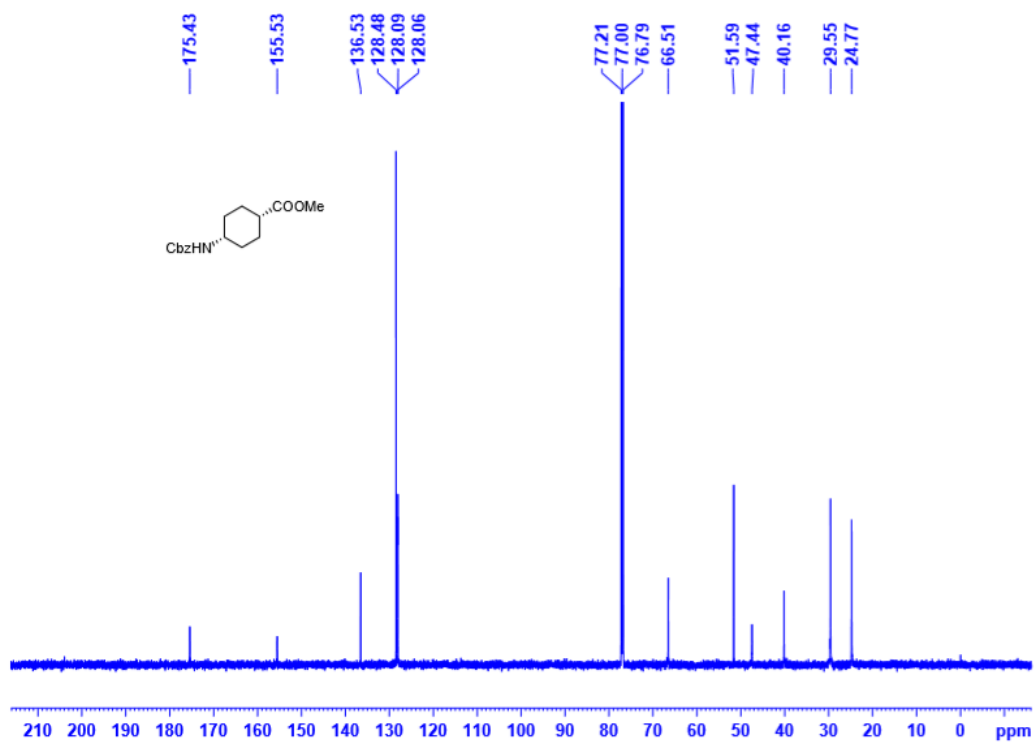
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **8a** (cis isomer)



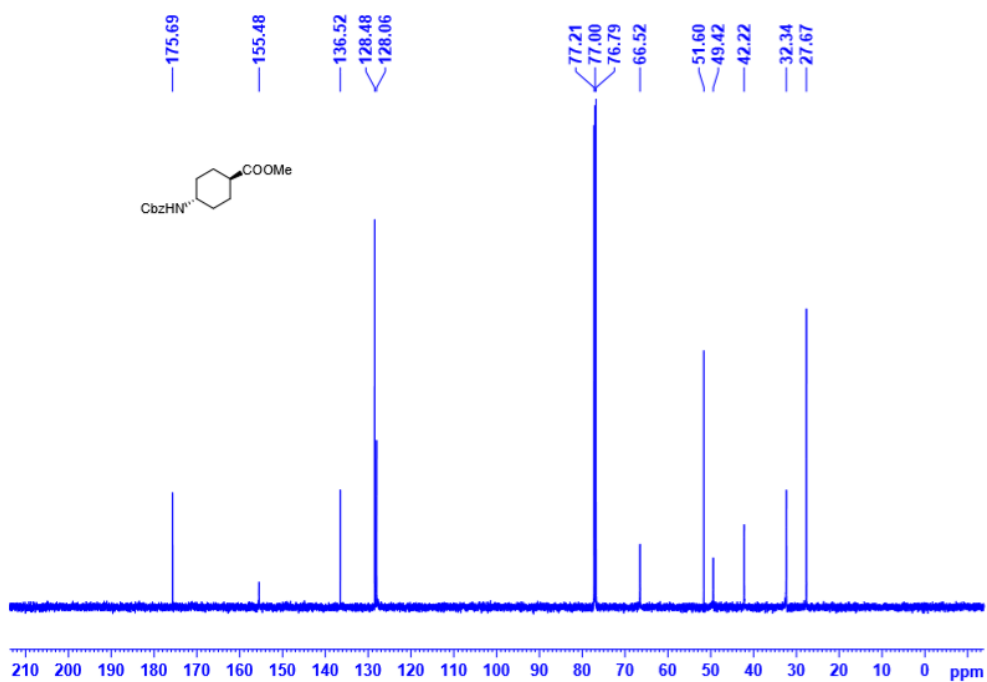
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **8a** (trans isomer)



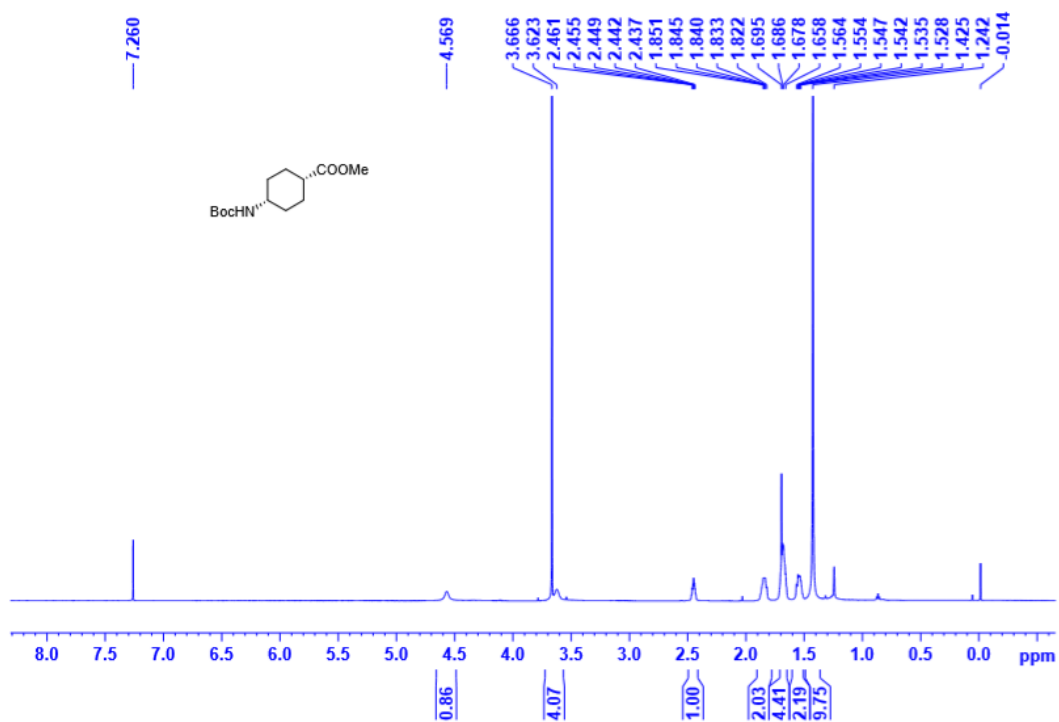
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **8a** (cis isomer)



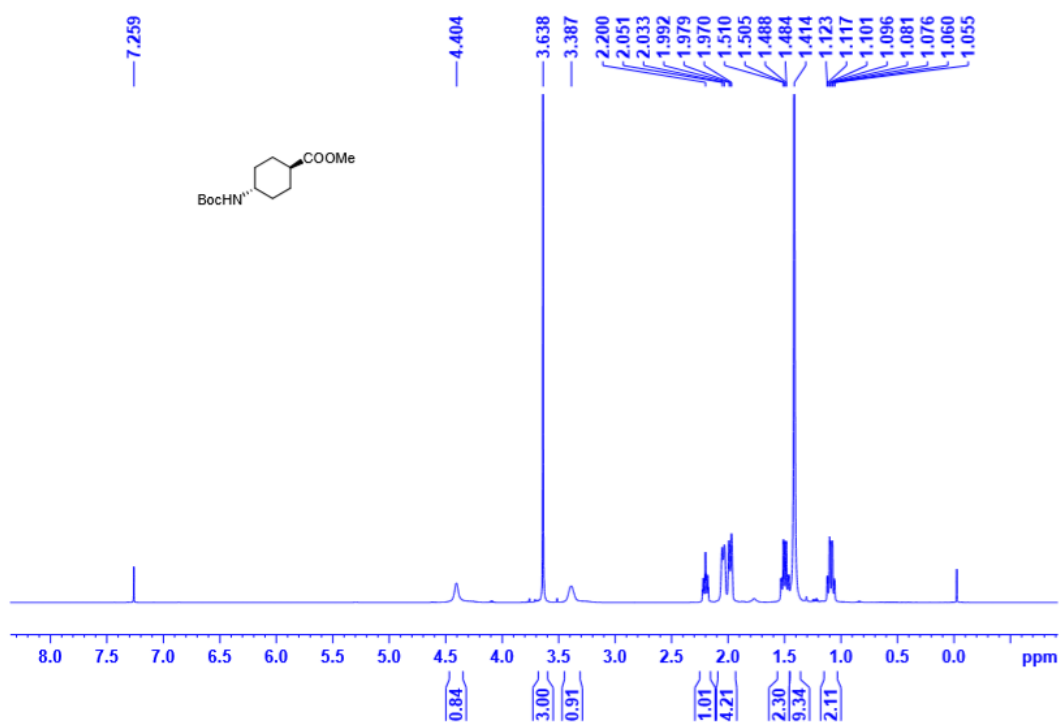
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **8a** (trans isomer)



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **8b** (cis isomer)

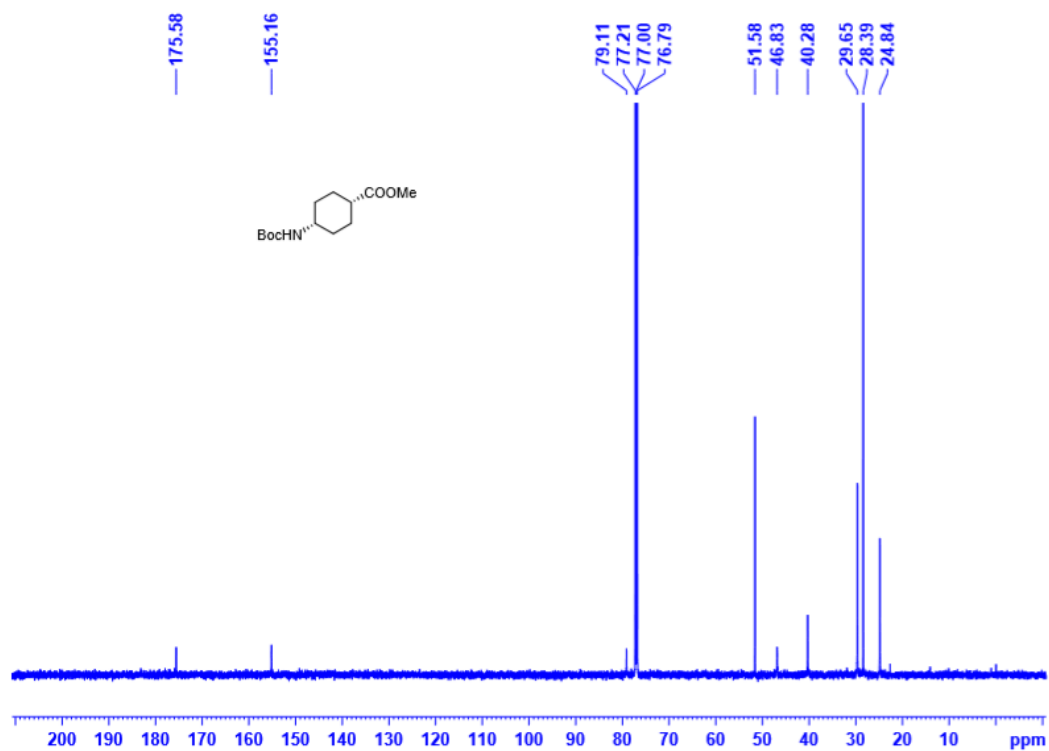


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **8b** (trans isomer)

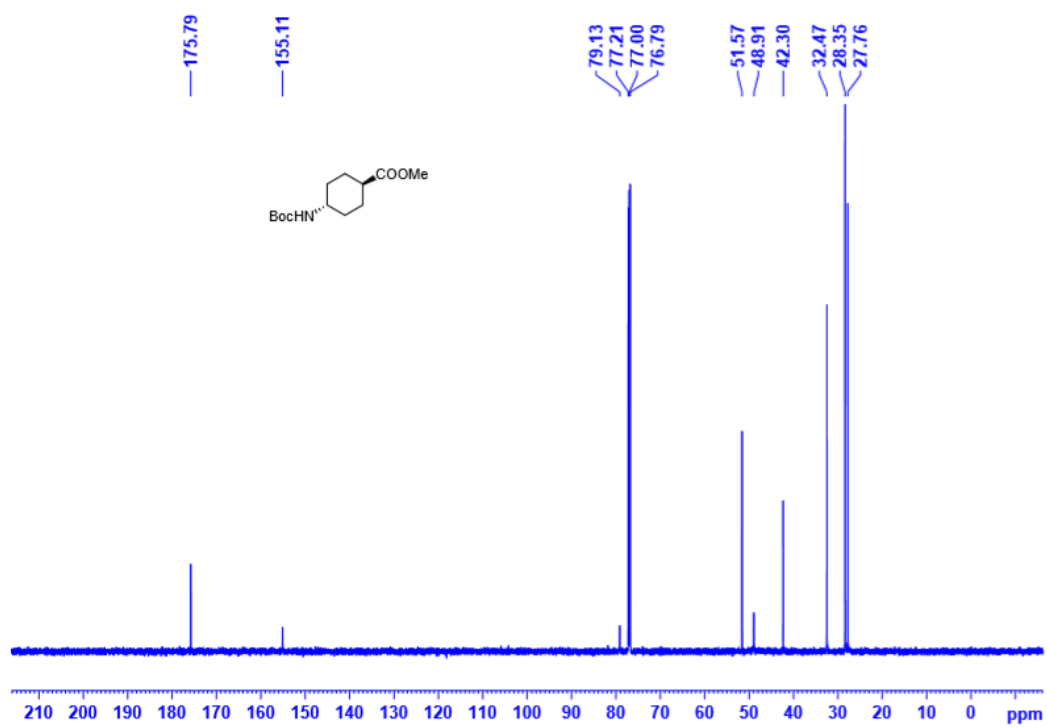




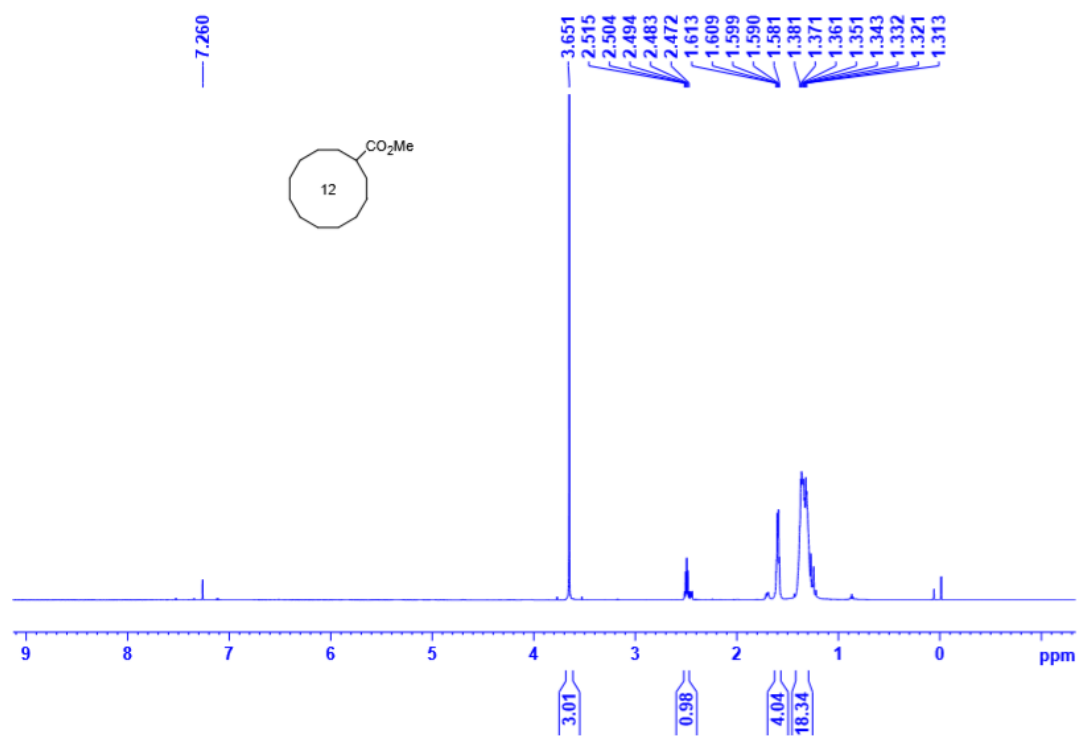
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **8b** (cis isomer)



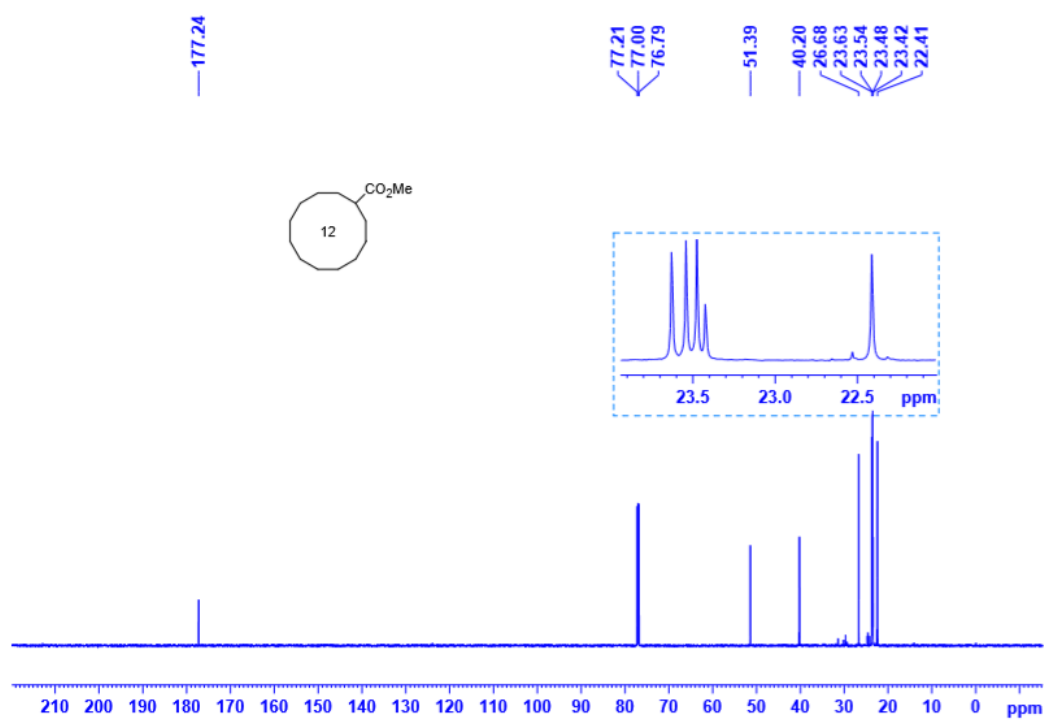
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **8b** (trans isomer)



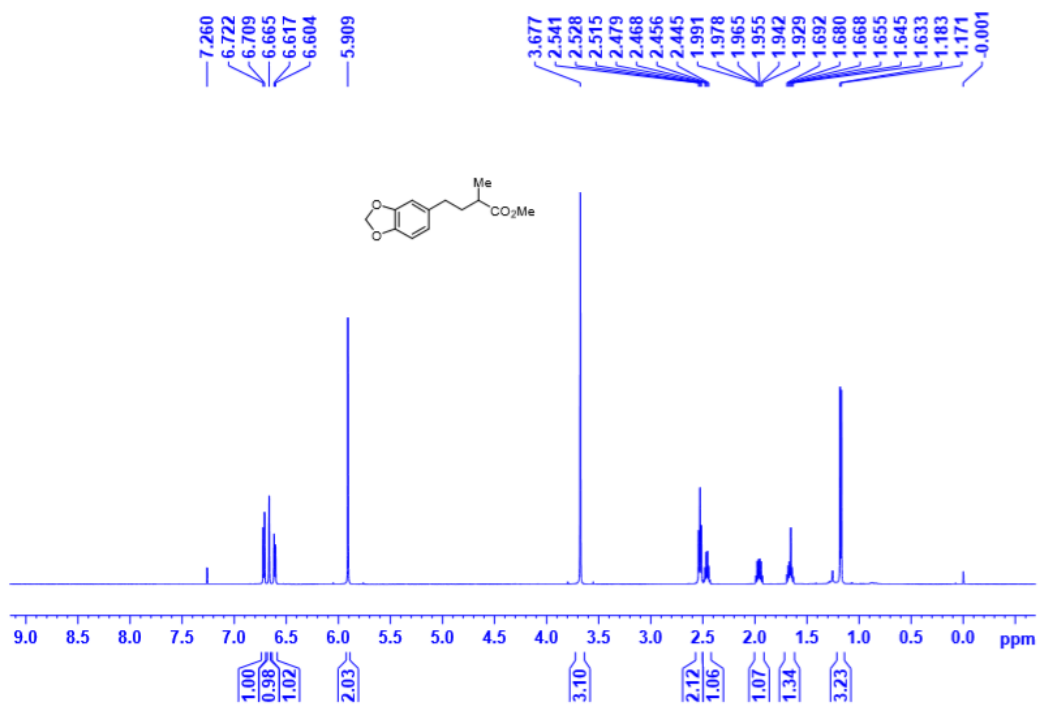
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **9**



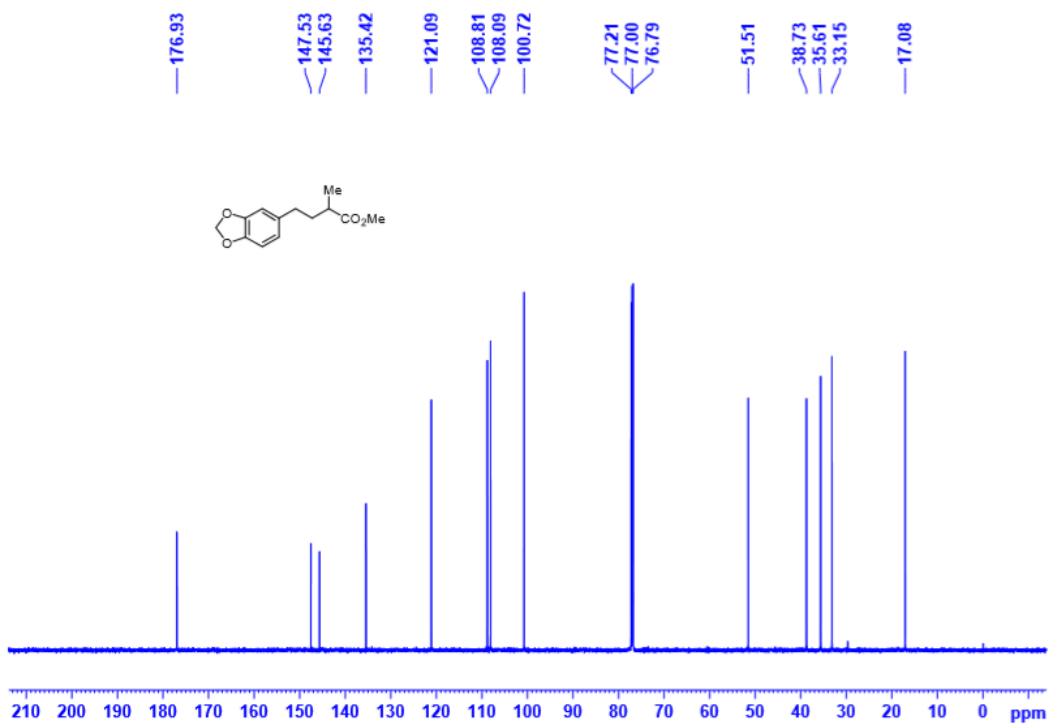
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **9**



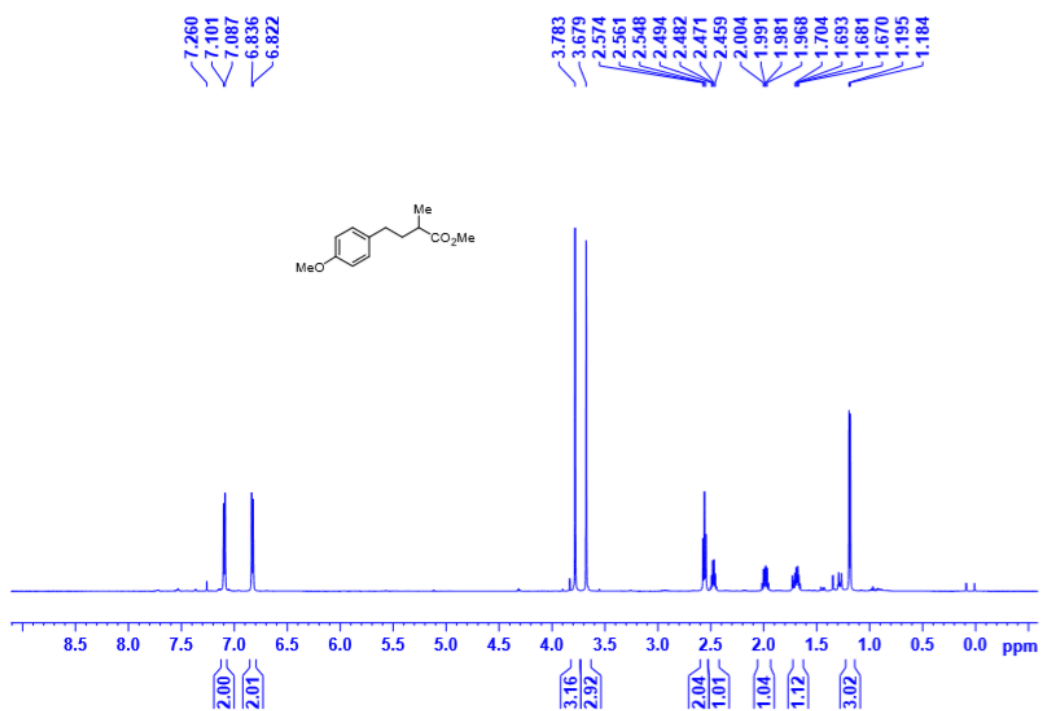
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **10**



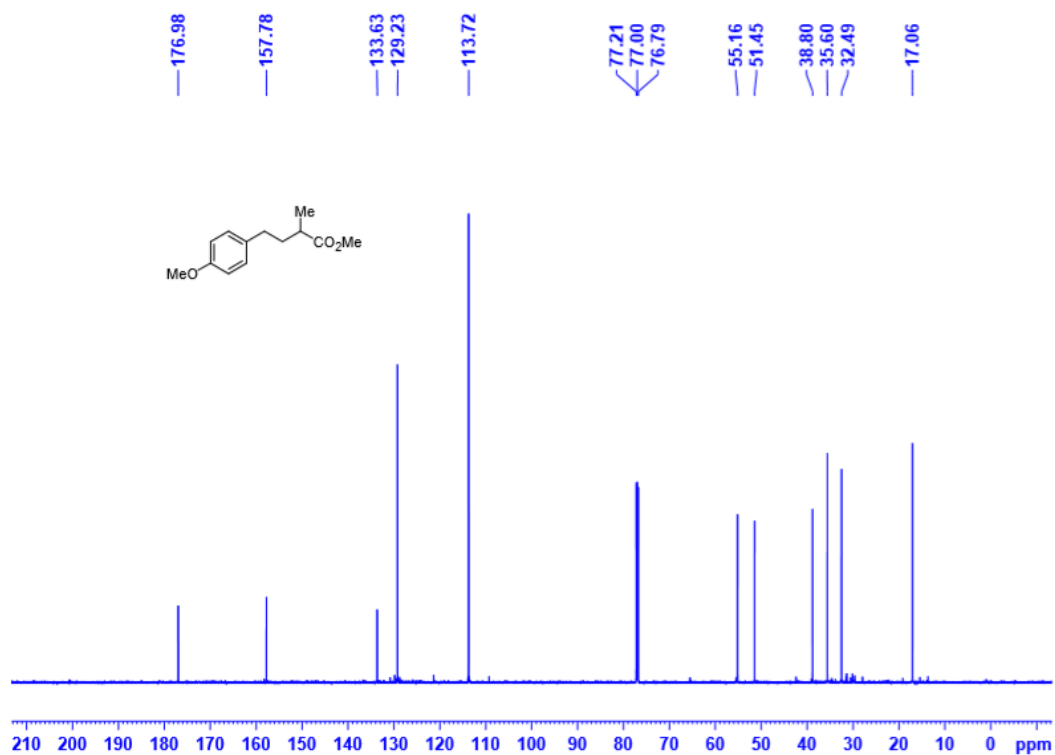
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **10**

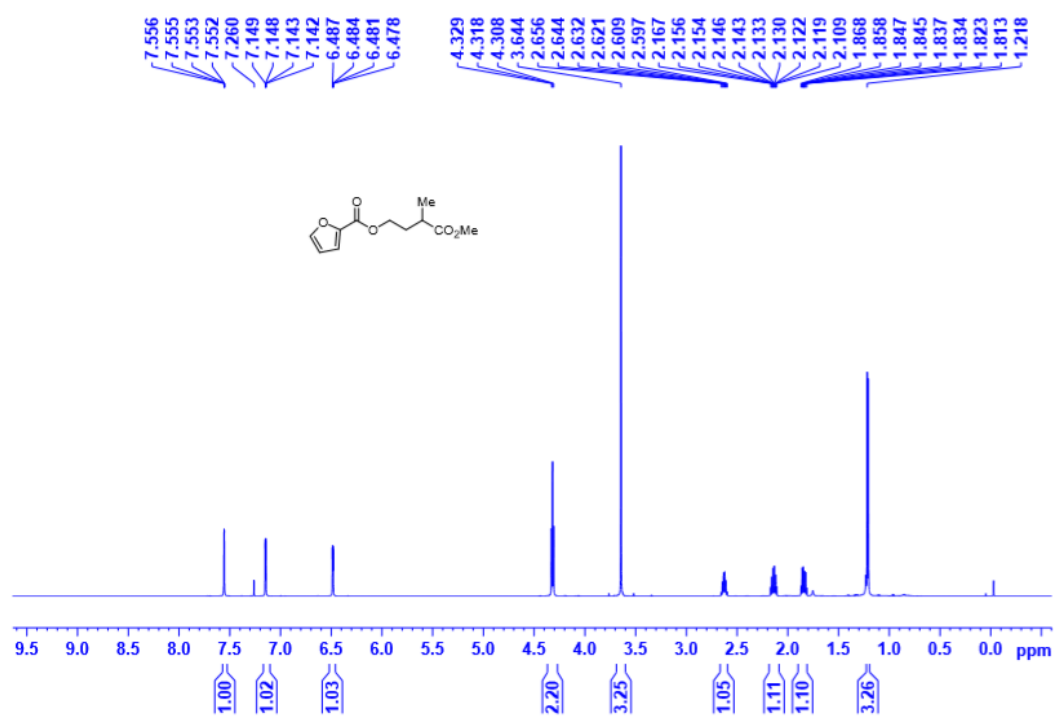
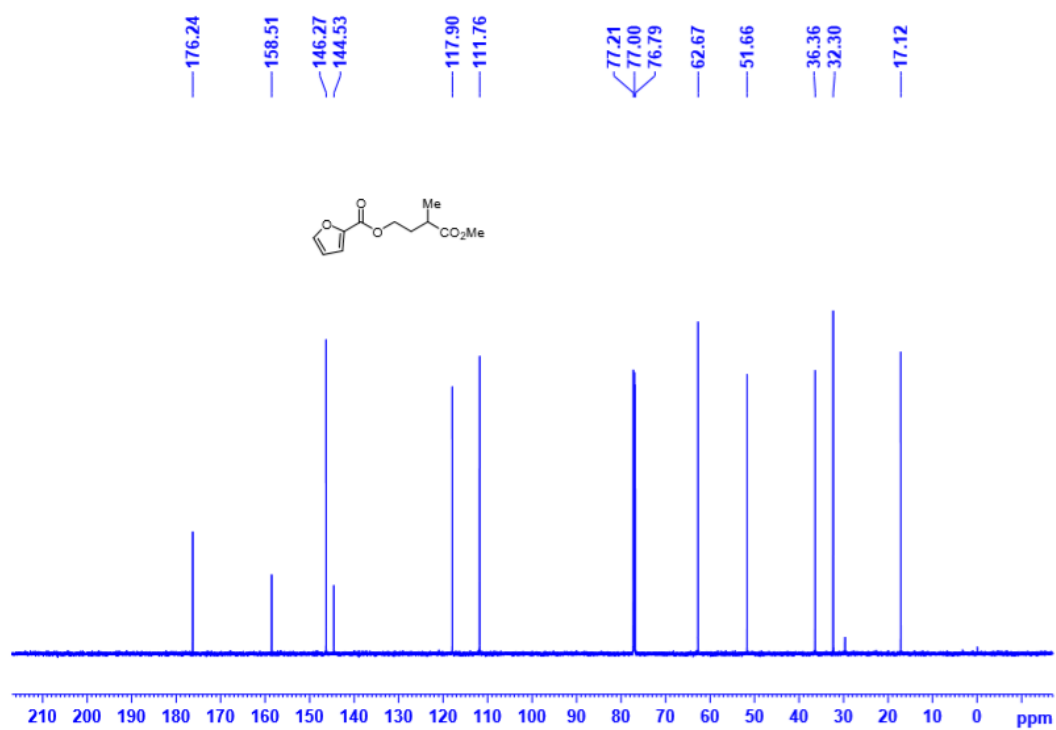


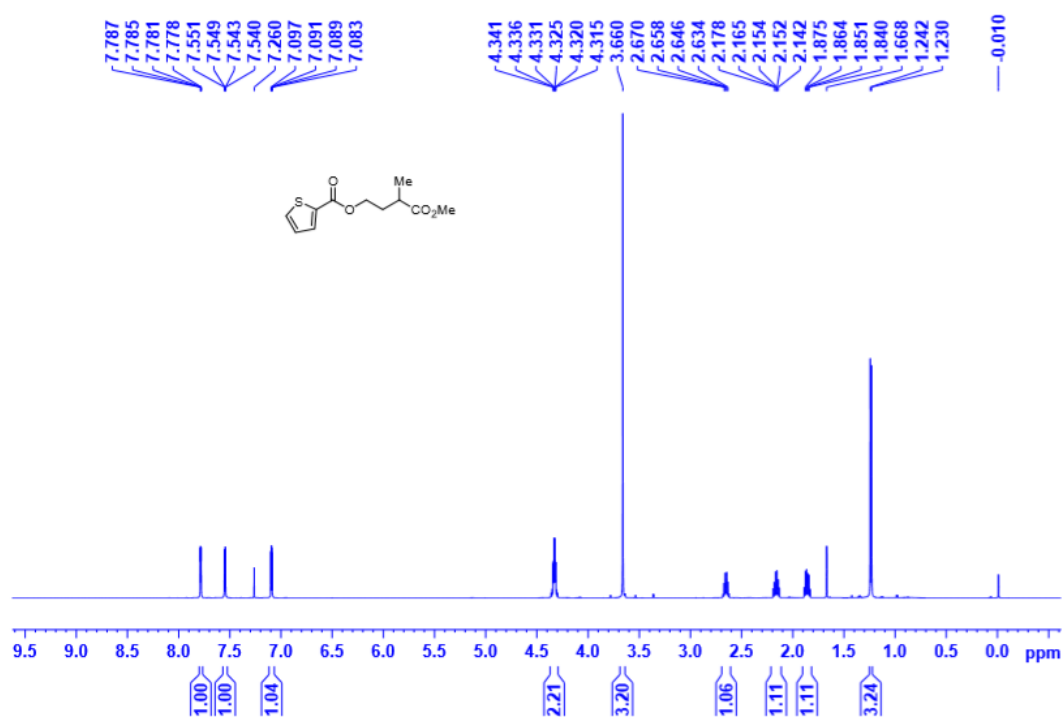
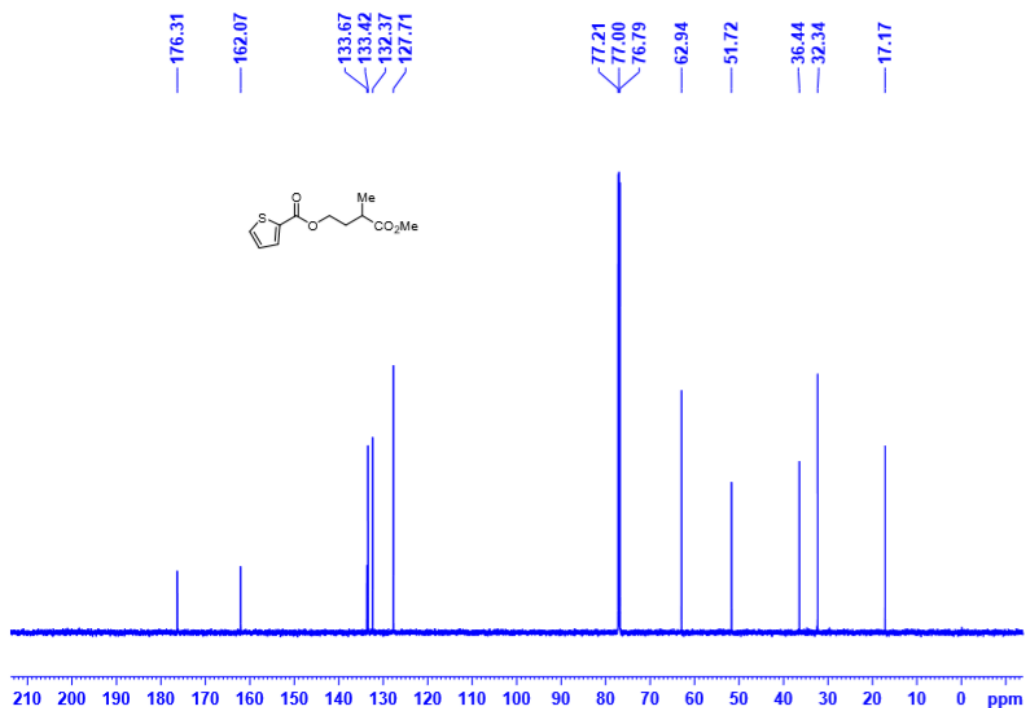
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **11**

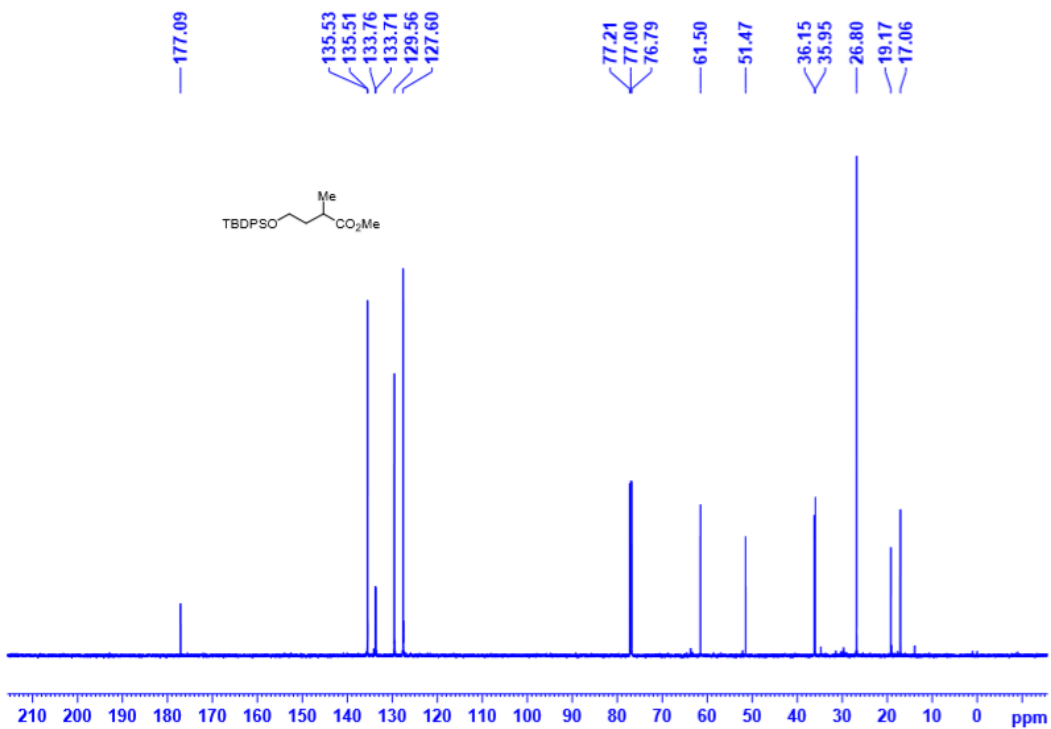


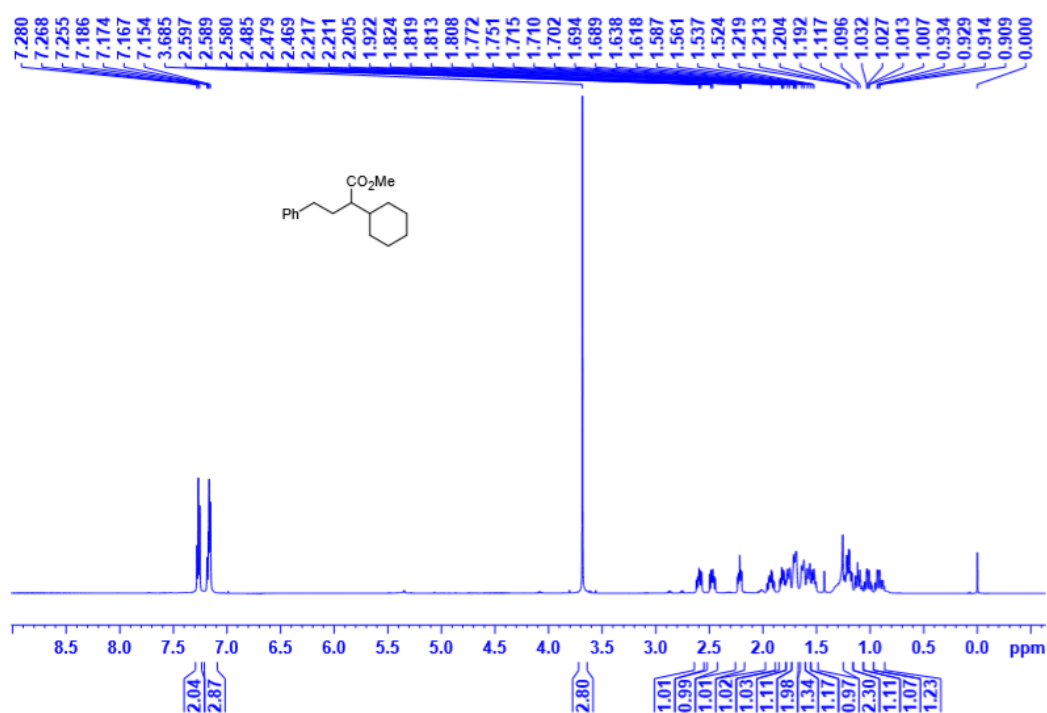
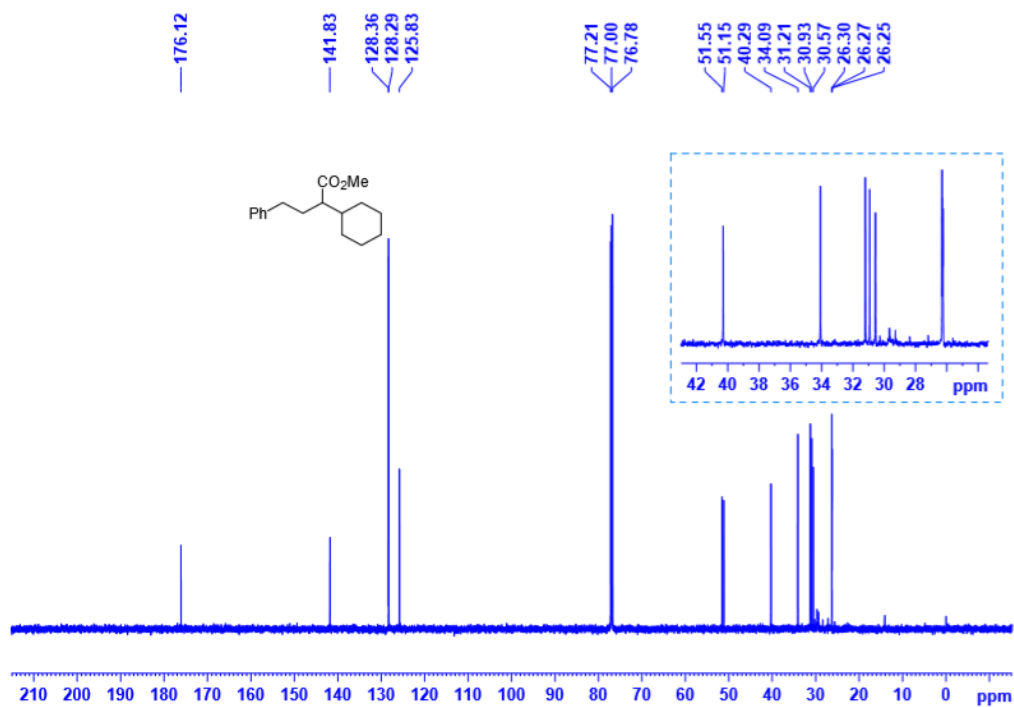
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **11**



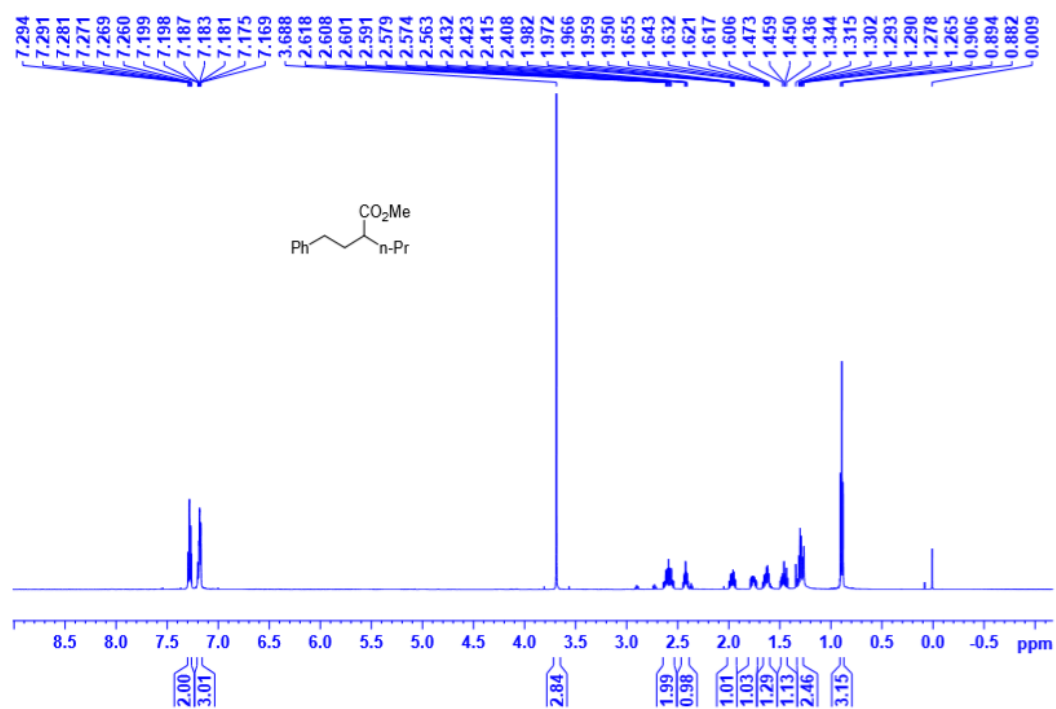
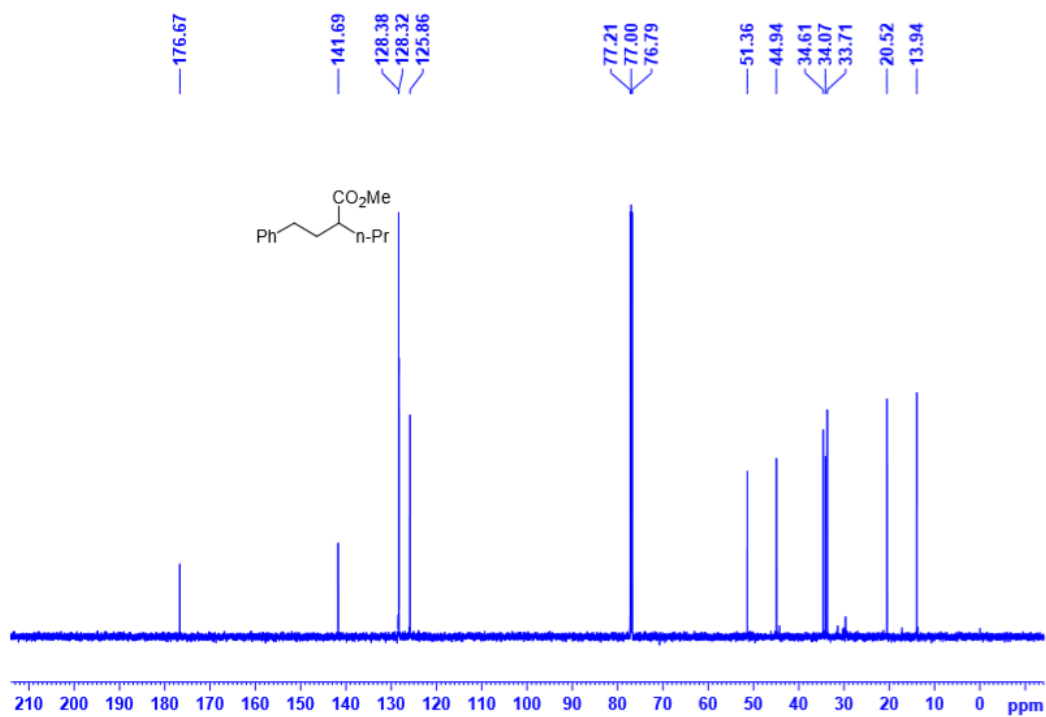
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **12** $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **12**

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **13** $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **13**

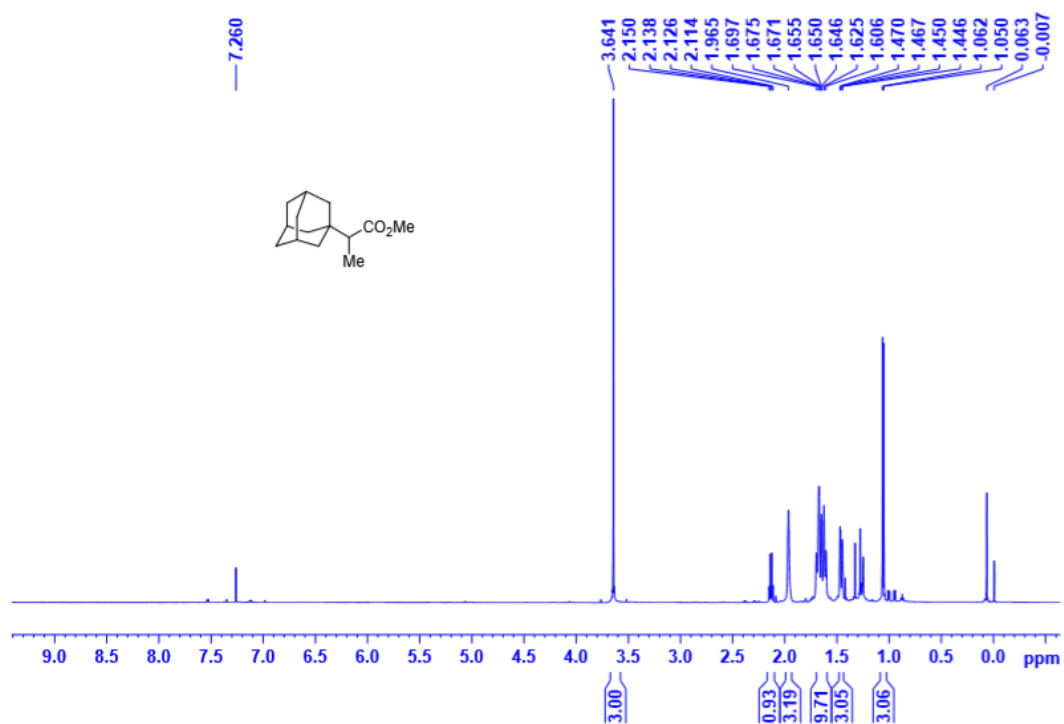


<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of **15**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) of **15**

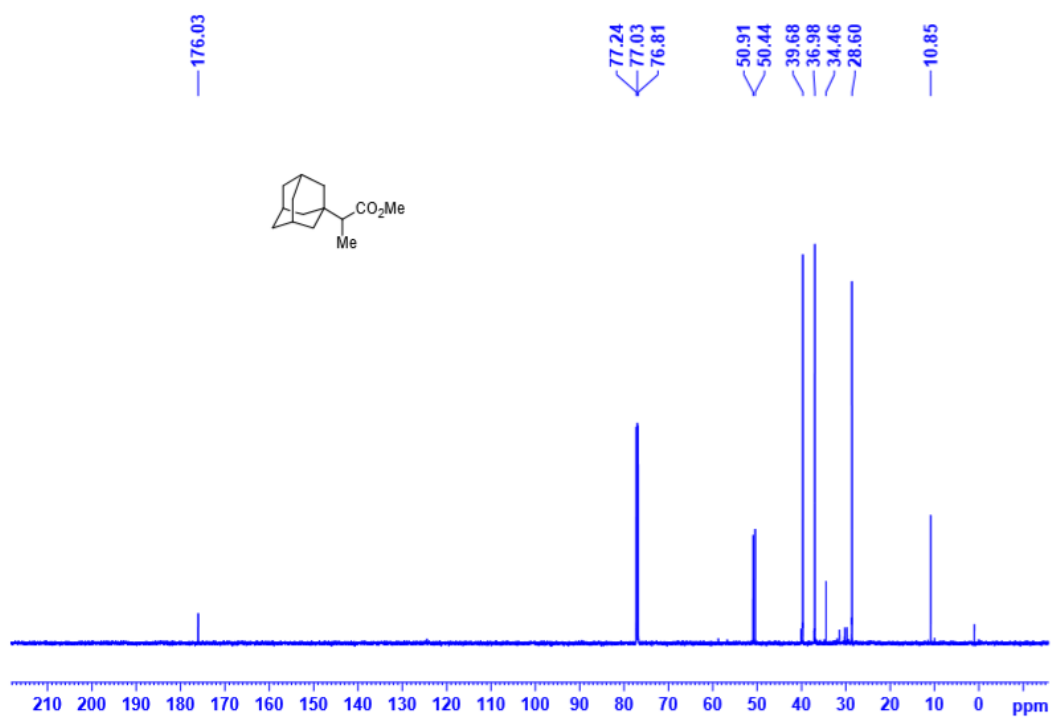


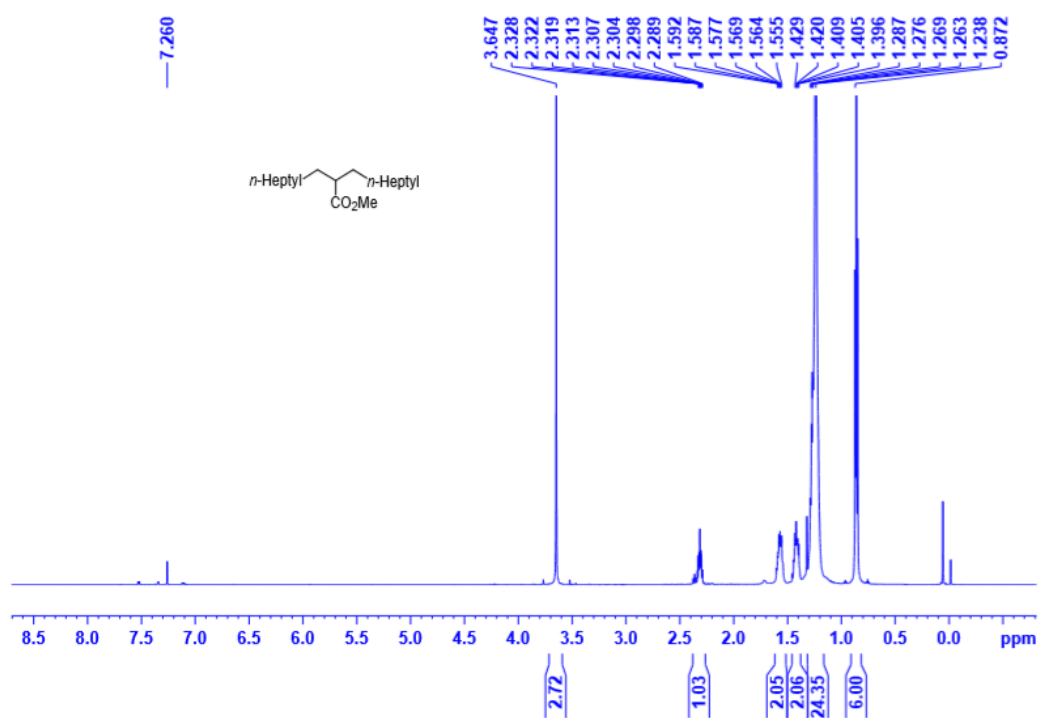
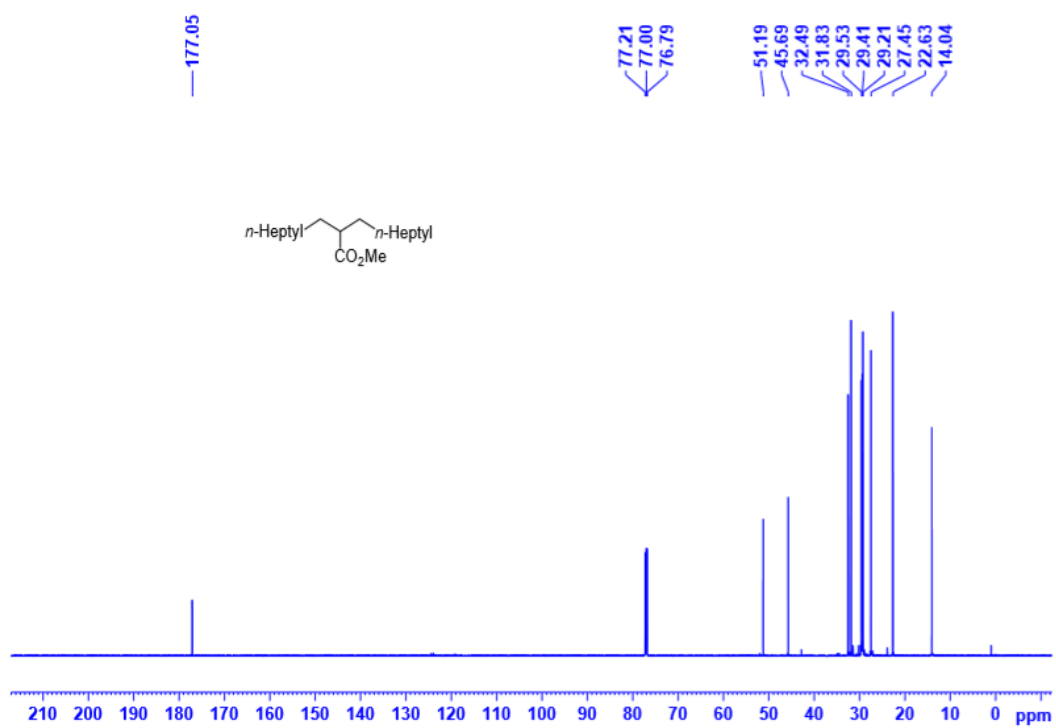
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **16** $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **16**

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **17**

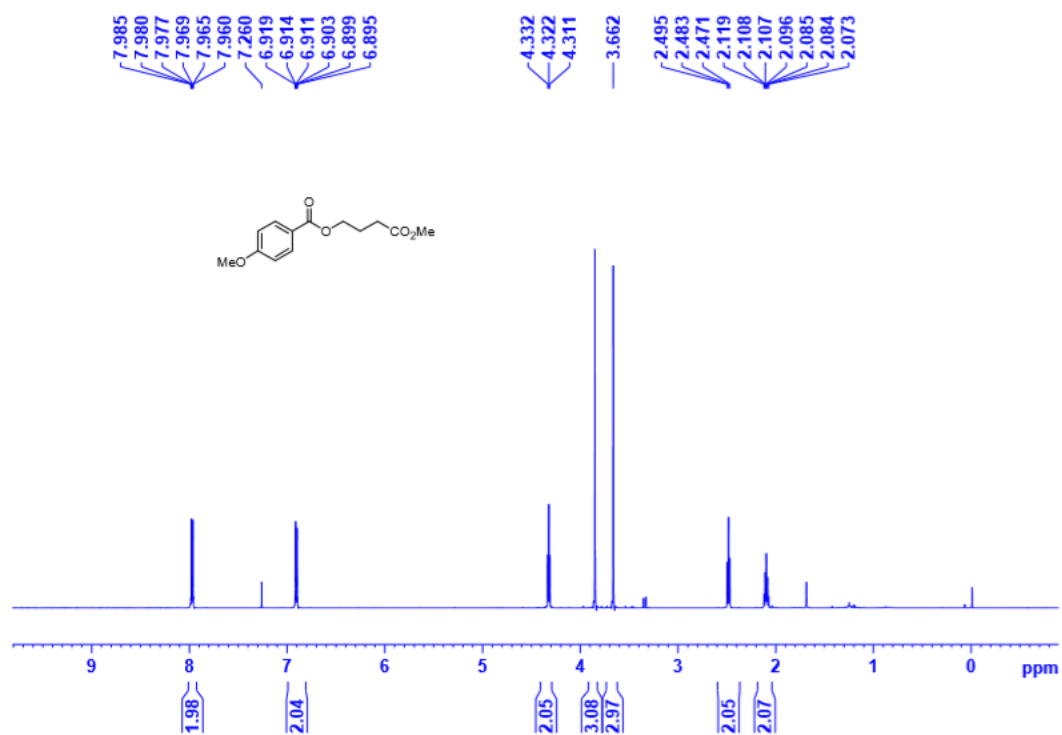


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **17**

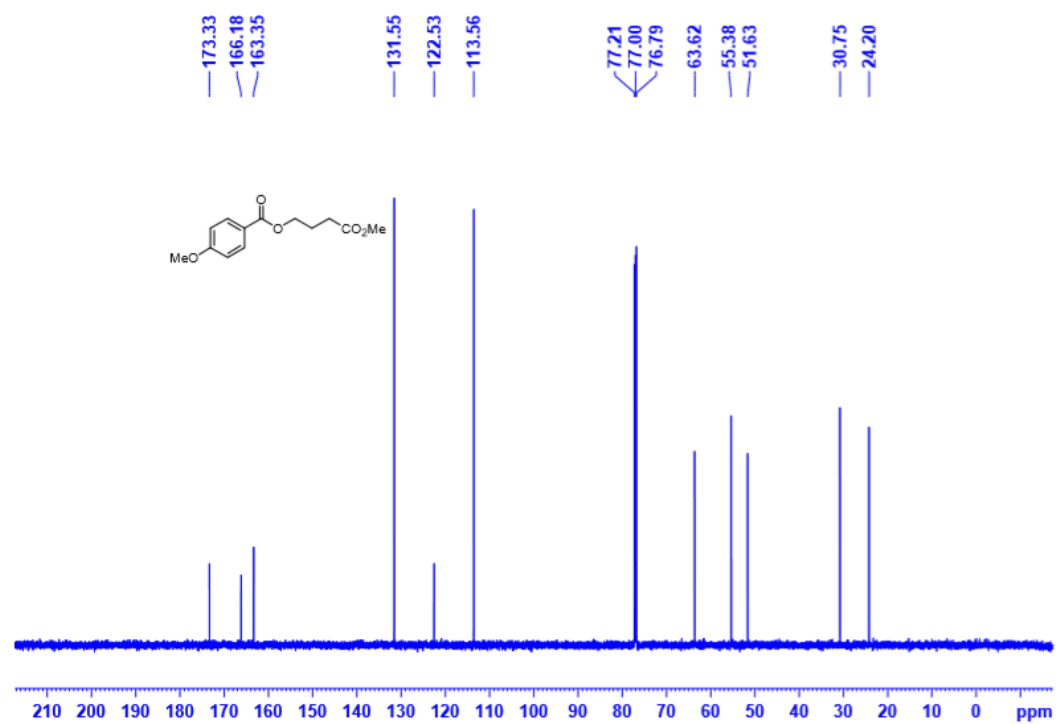


<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of **18**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) of **18**

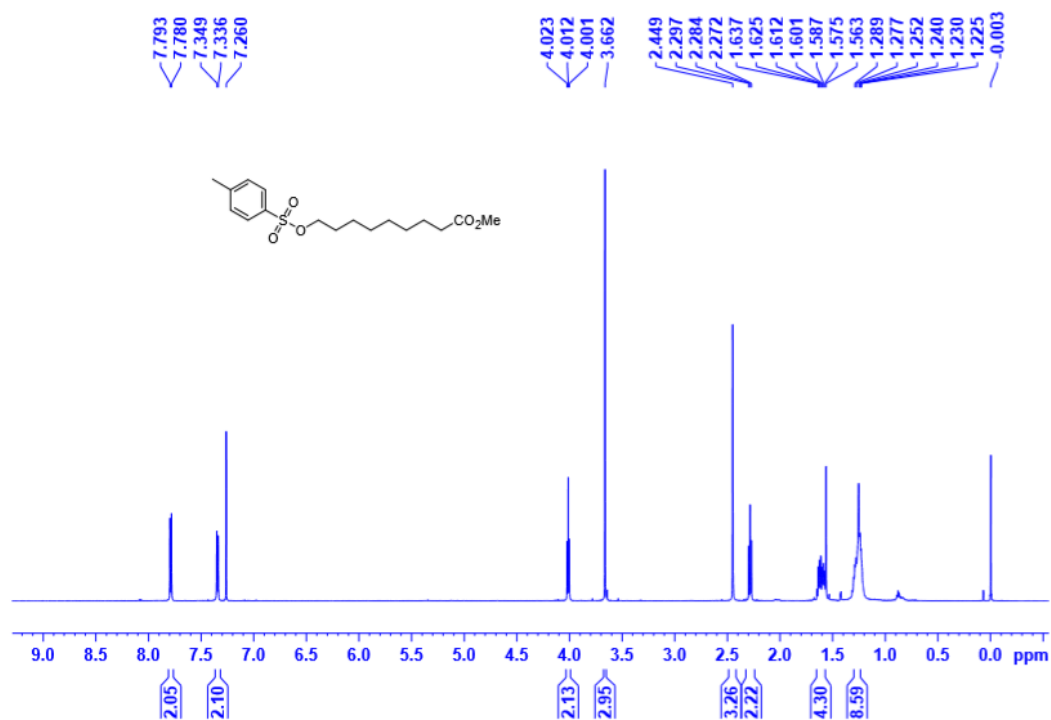
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **19**



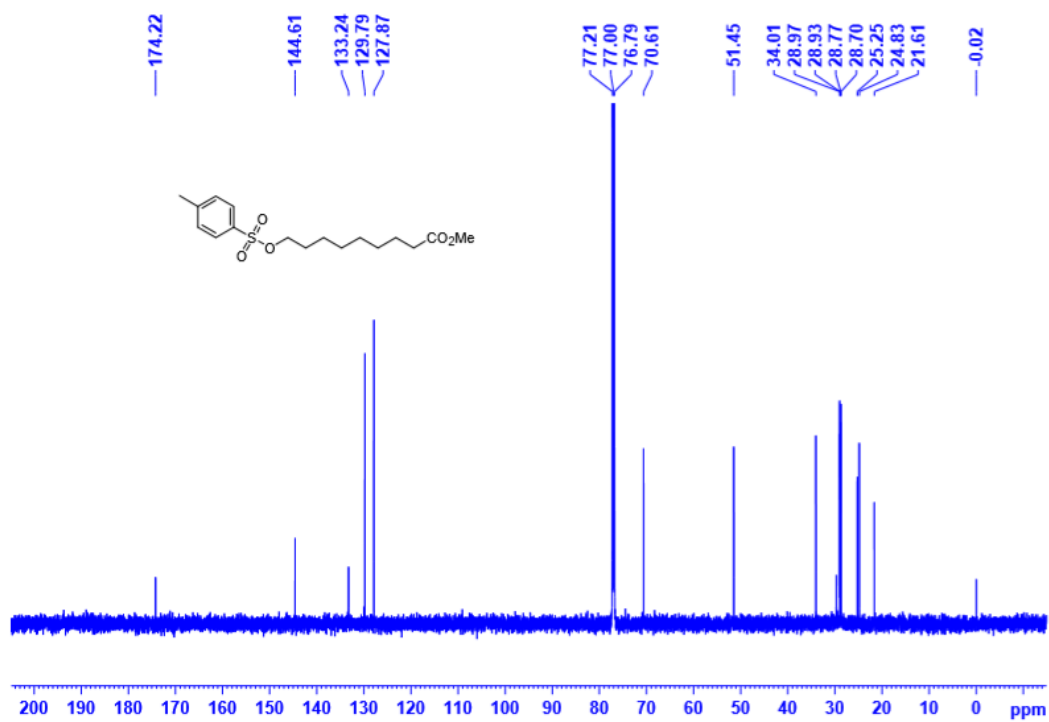
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **19**

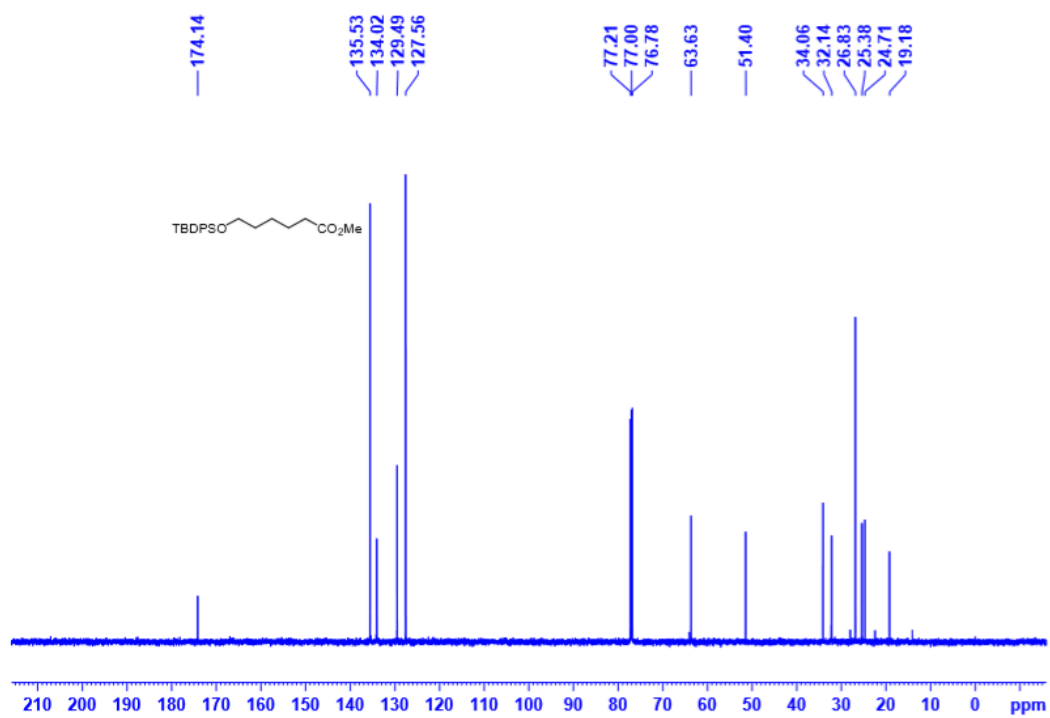


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **20**

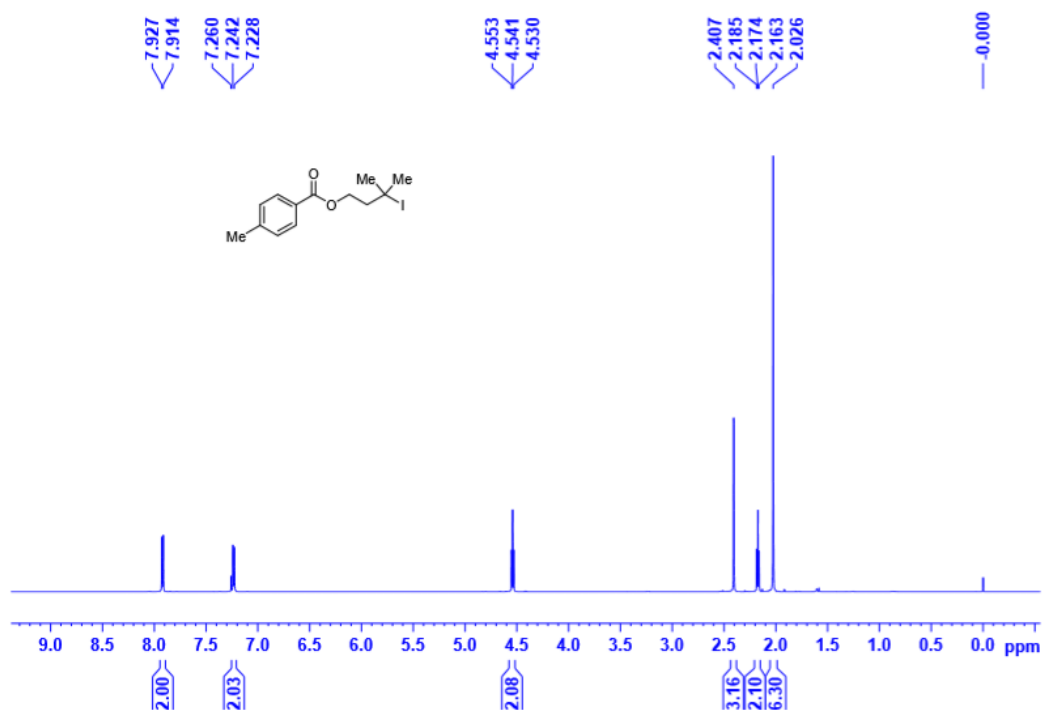


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **20**

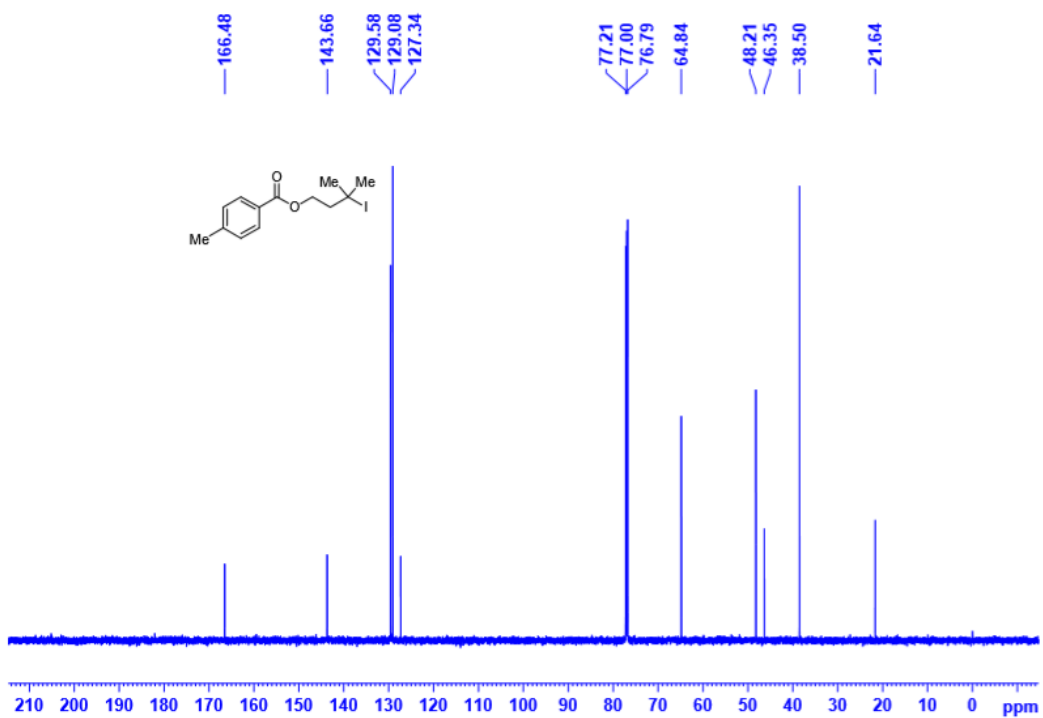




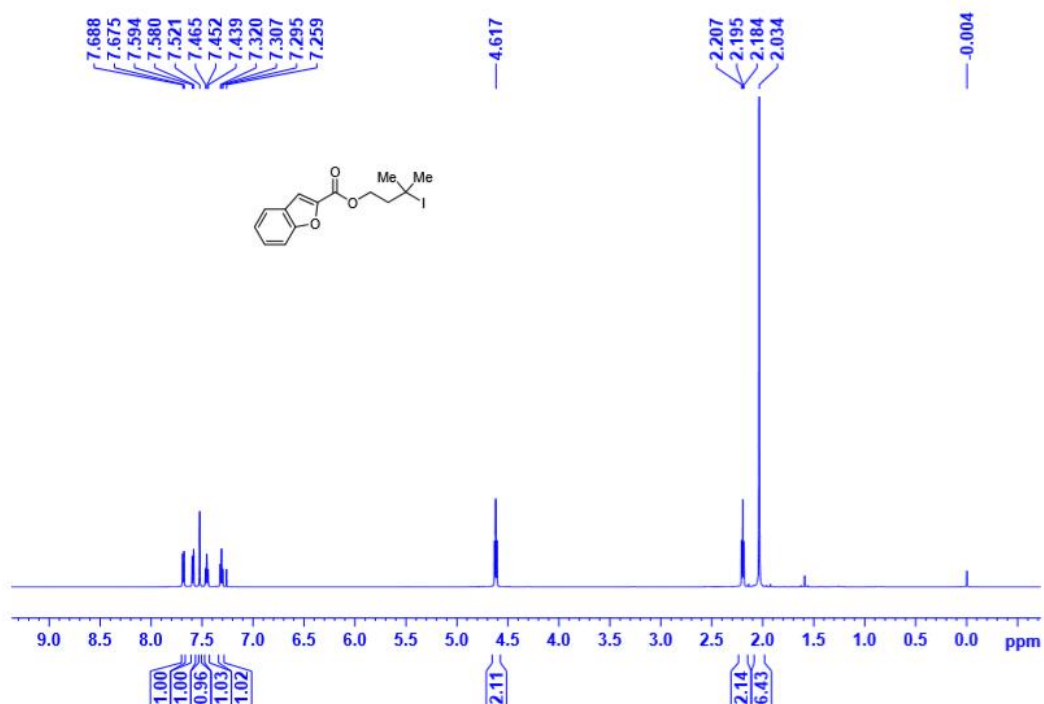
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 4-methyl-benzoic acid 3-iodo-3-methyl-butyl ester



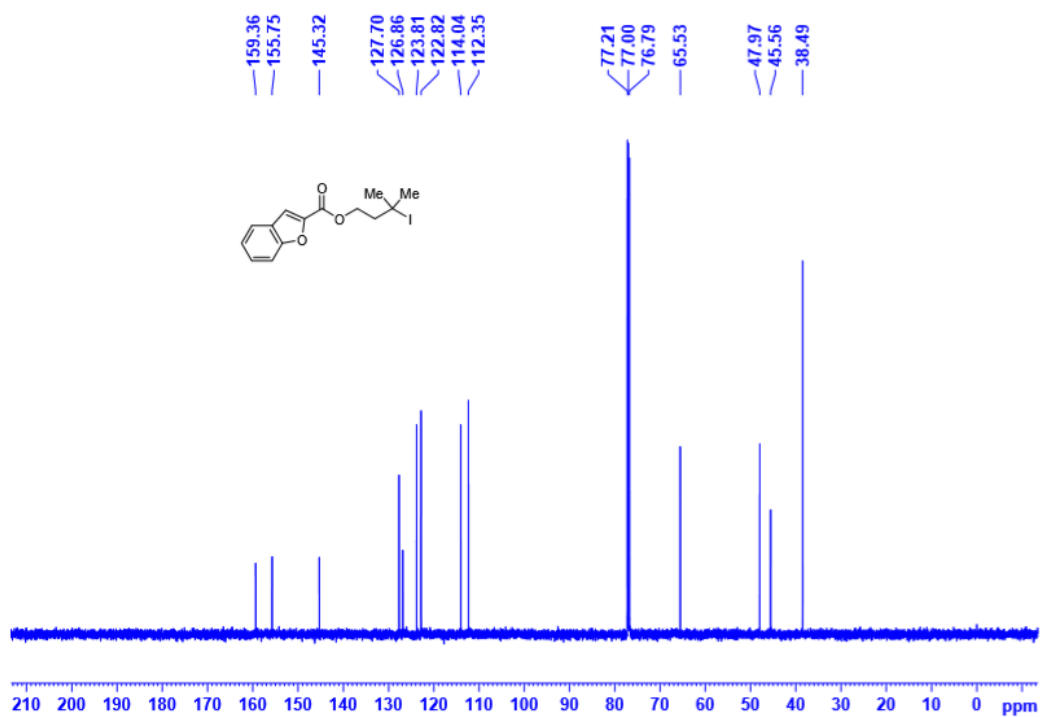
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 4-methyl-benzoic acid 3-iodo-3-methyl-butyl ester



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of benzofuran-2-carboxylic acid 3-iodo-3-methyl-butyl ester

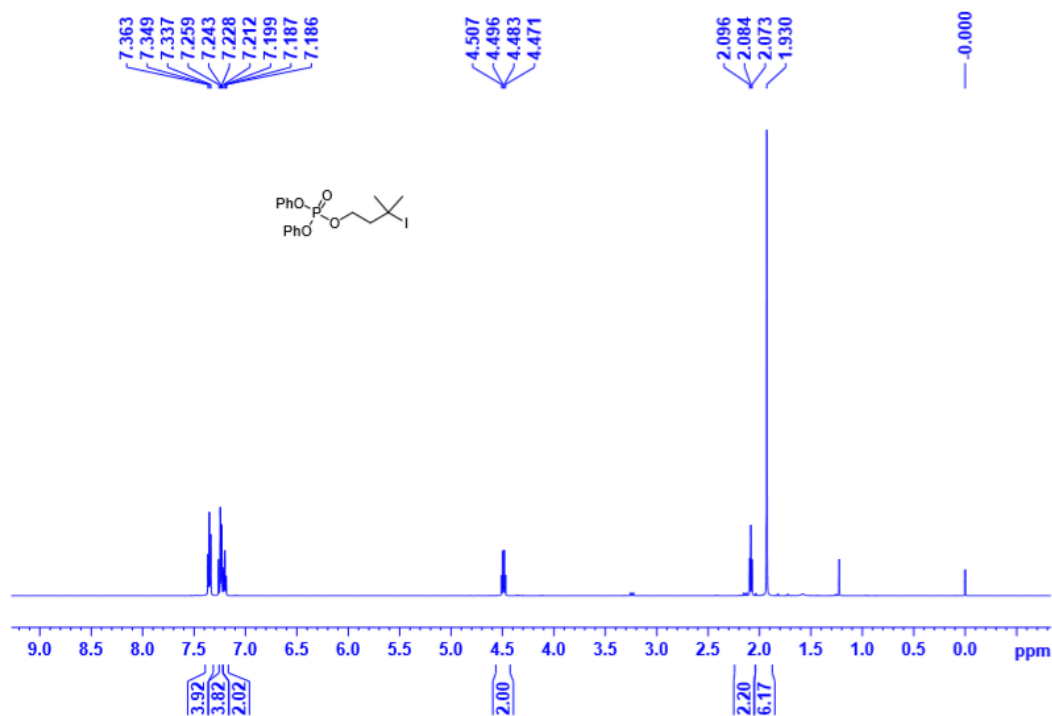


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of benzofuran-2-carboxylic acid 3-iodo-3-methyl-butyl ester

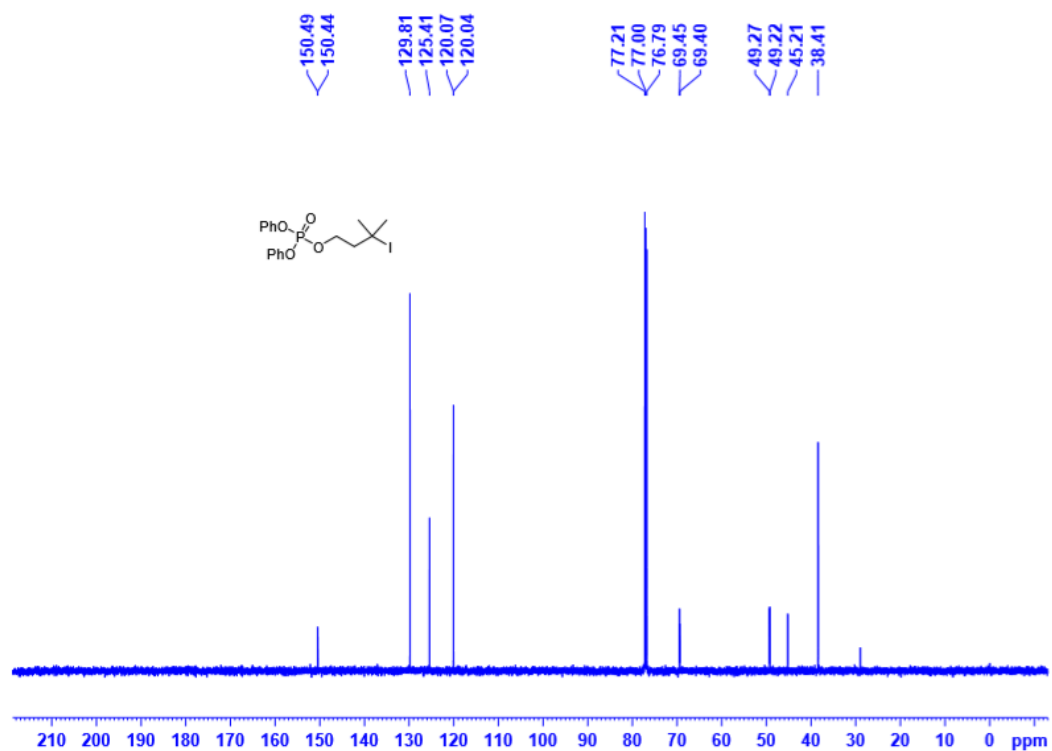




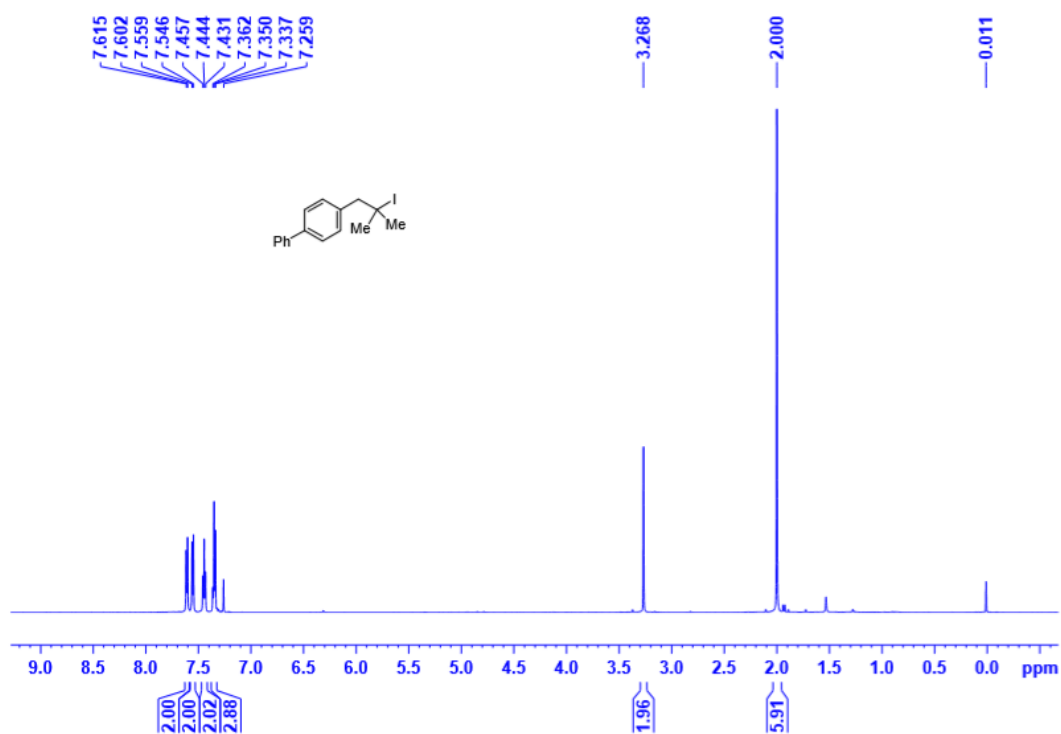
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of phosphoric acid 3-iodo-3-methyl-butyl ester diphenyl ester



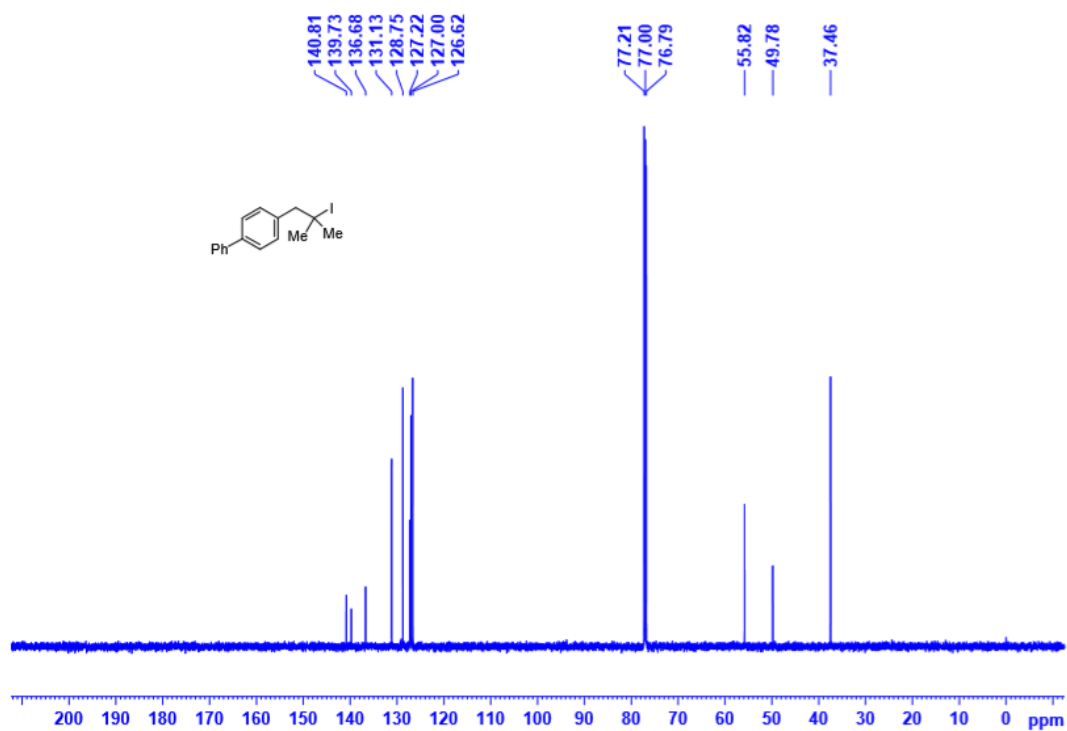
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of phosphoric acid 3-iodo-3-methyl-butyl ester diphenyl ester



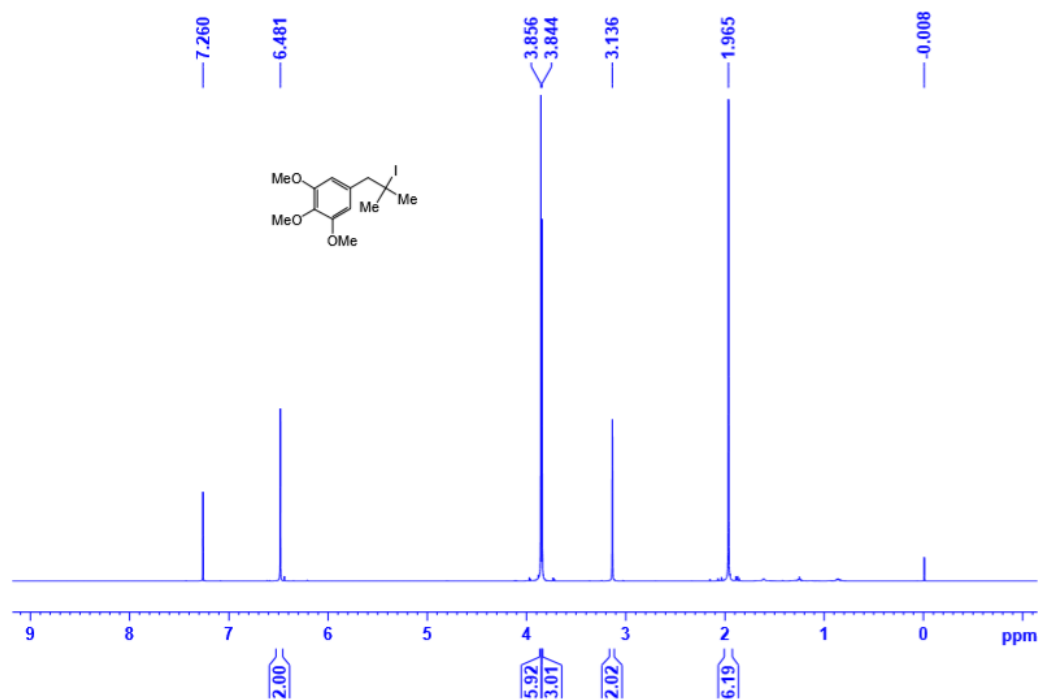
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 4-(2-iodo-2-methyl-propyl)-biphenyl



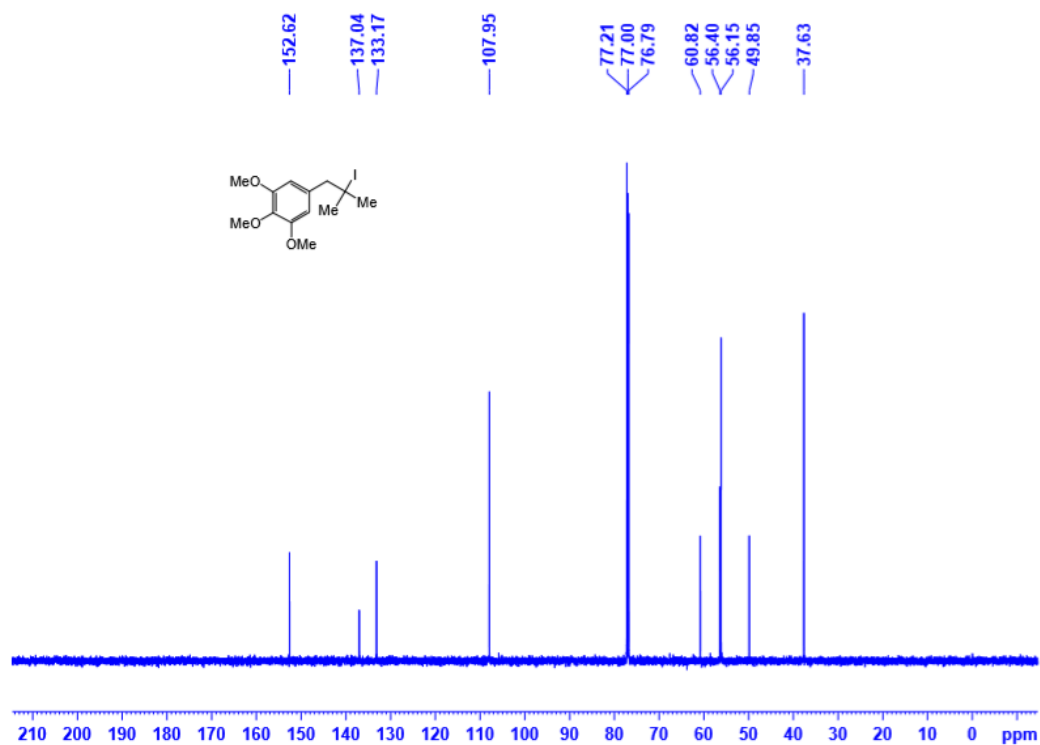
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 4-(2-iodo-2-methyl-propyl)-biphenyl



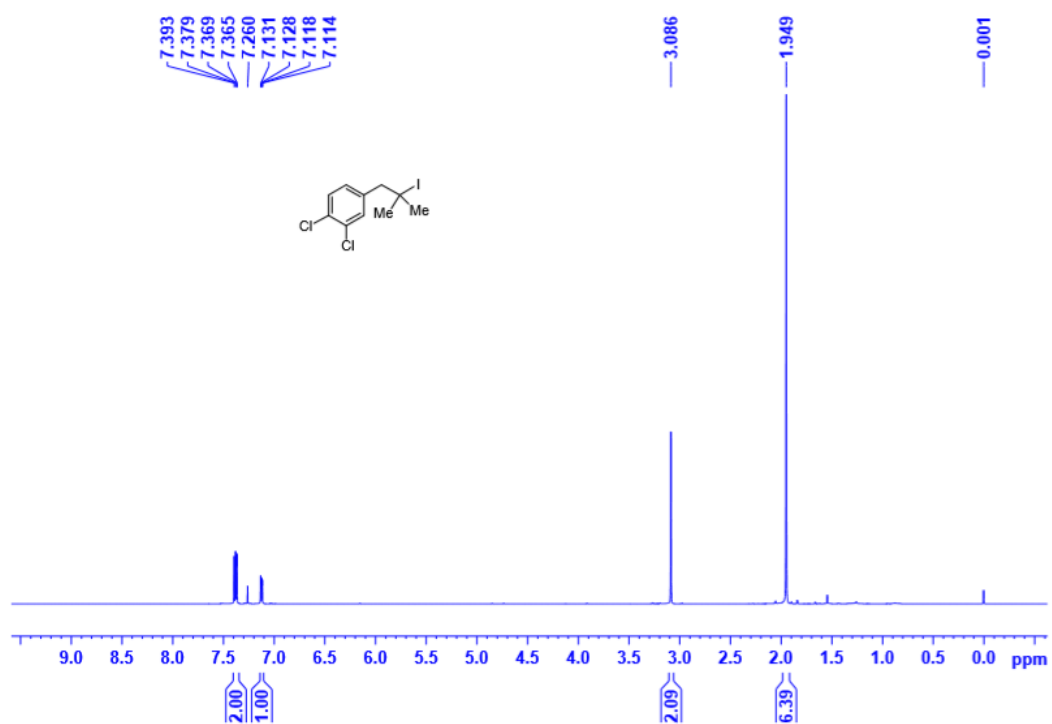
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 5-(2-iodo-2-methyl-propyl)-1, 2, 3-trimethoxy-benzene



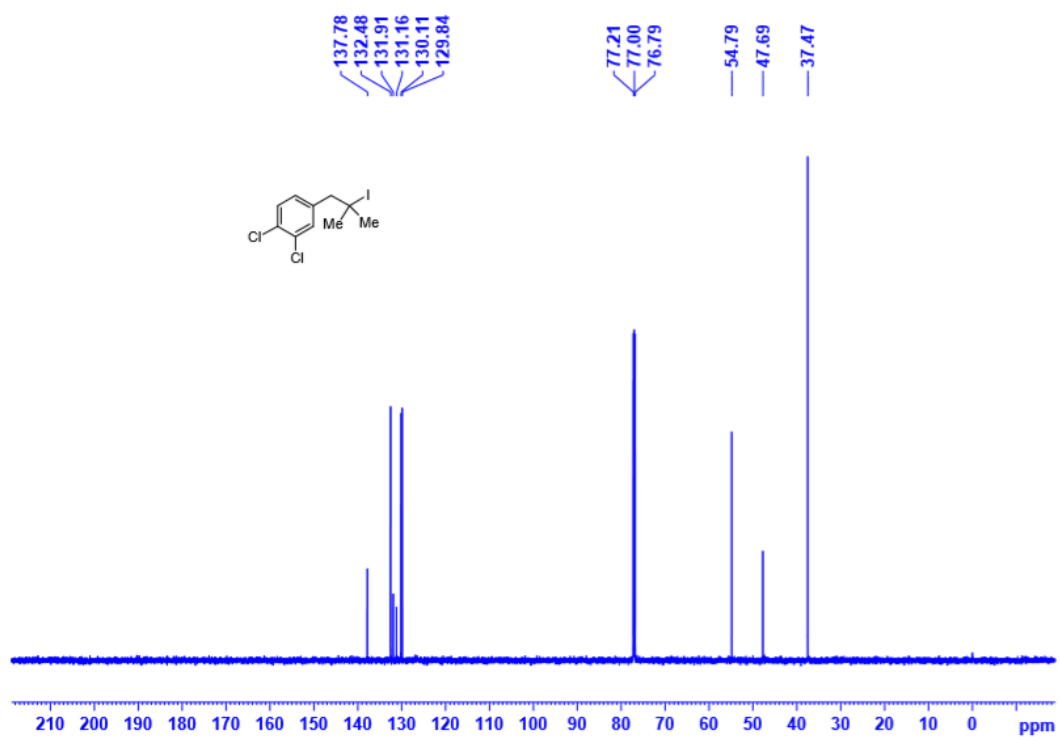
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 5-(2-iodo-2-methyl-propyl)-1, 2, 3-trimethoxy-benzene



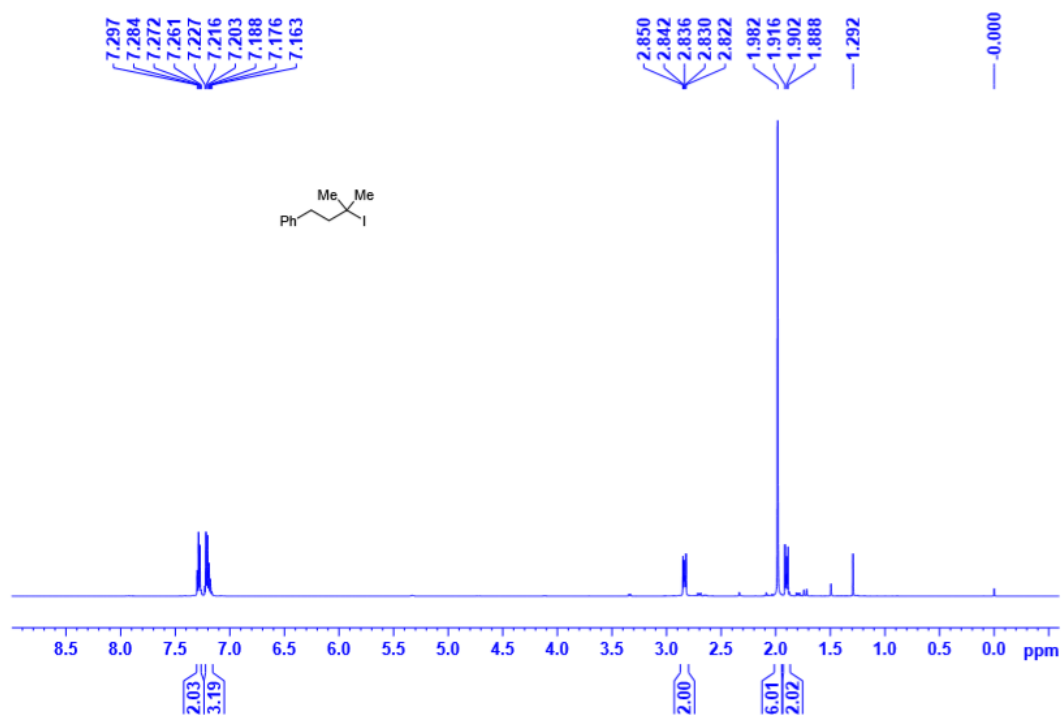
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 1, 2-dichloro-4-(2-iodo-2-methyl-propyl)-benzene



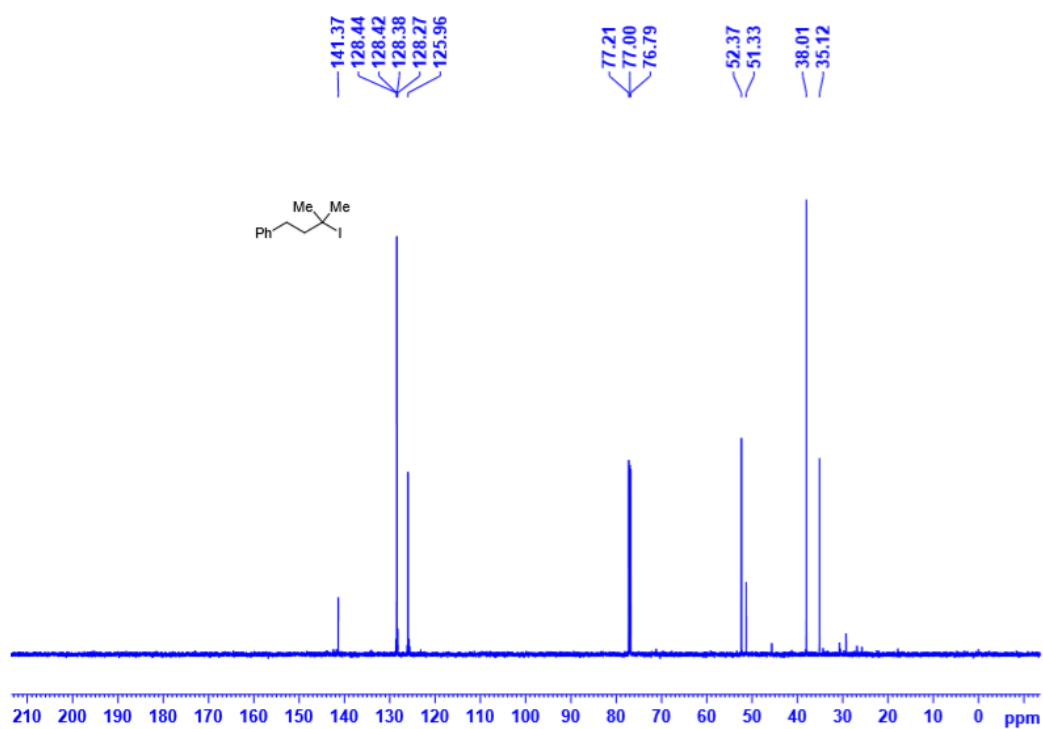
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 1, 2-dichloro-4-(2-iodo-2-methyl-propyl)-benzene



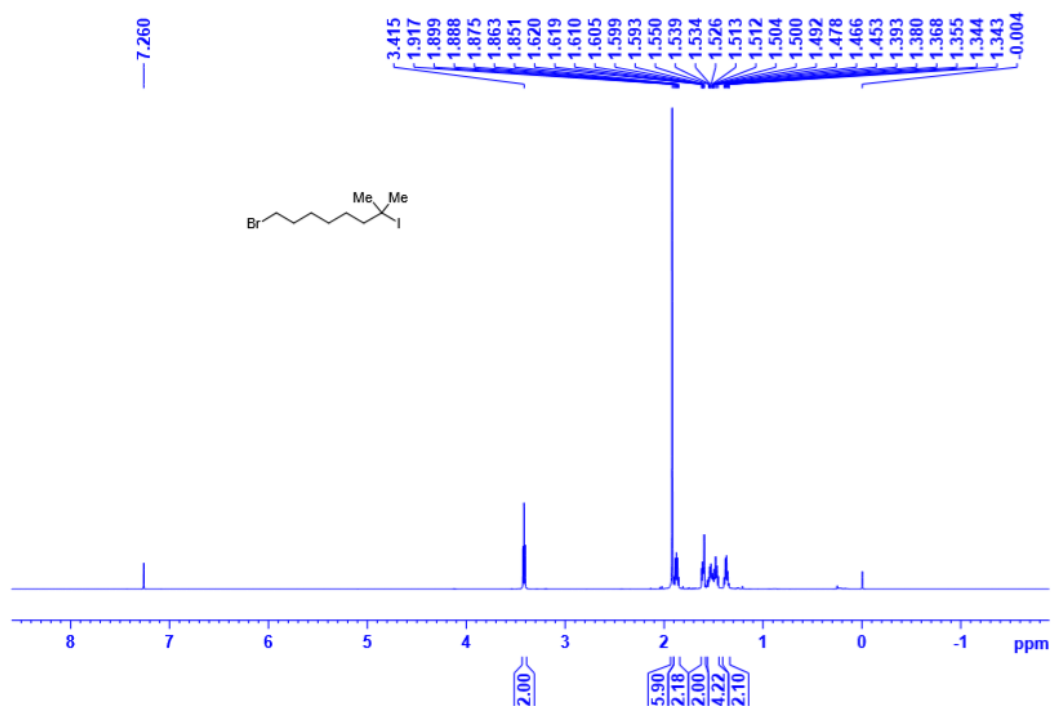
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of (3-iodo-3-methyl-butyl)-benzene



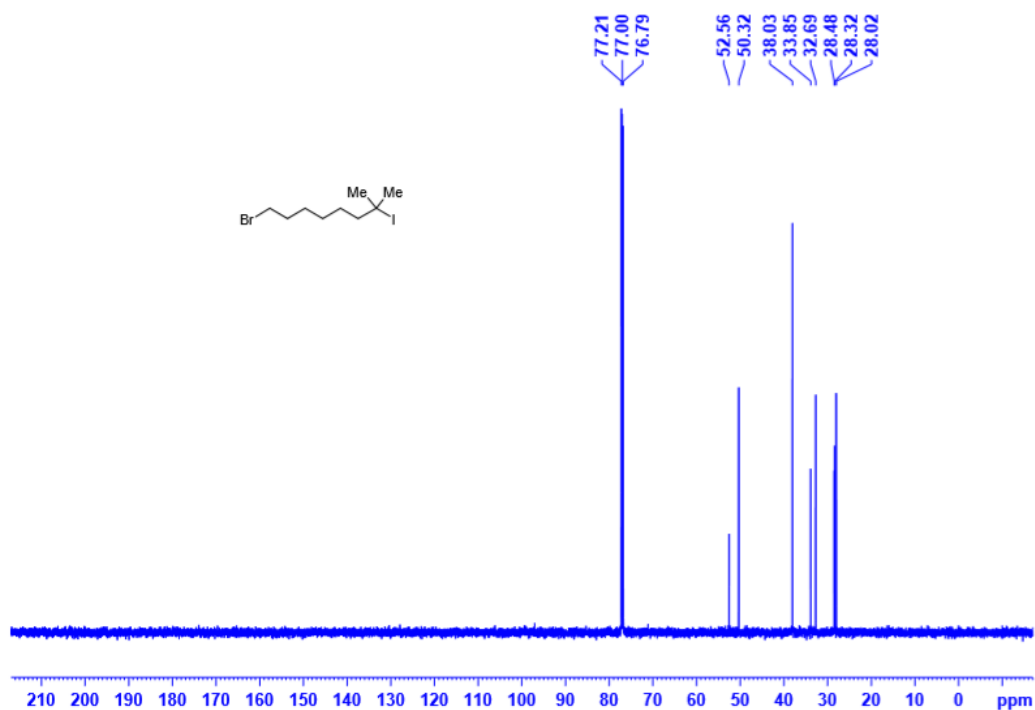
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of (3-iodo-3-methyl-butyl)-benzene



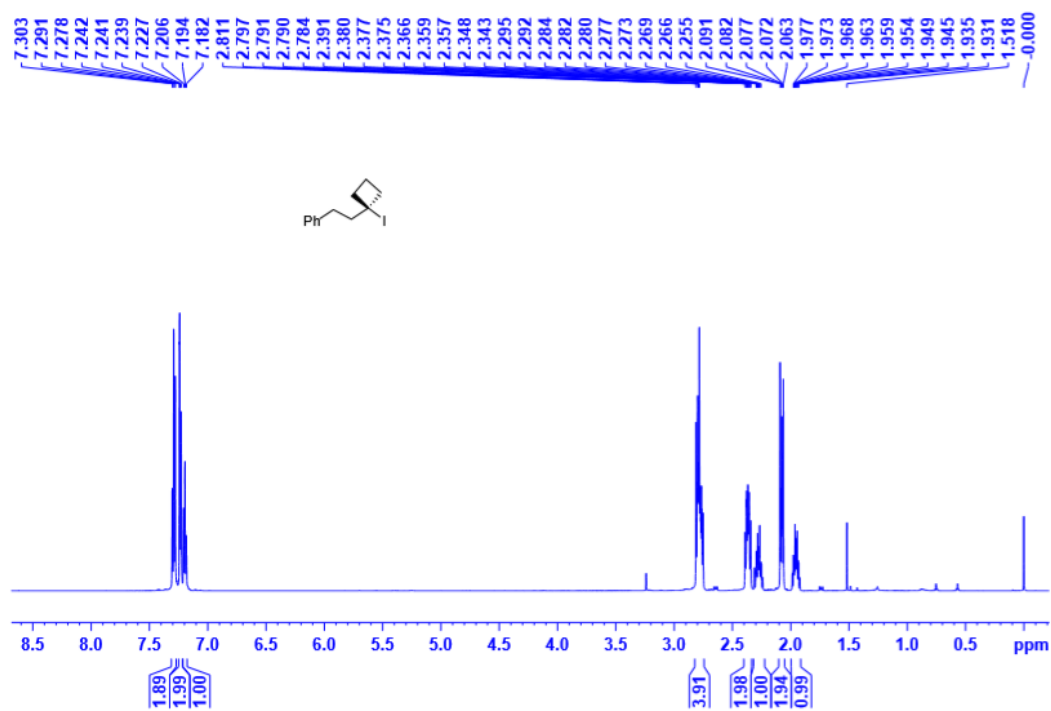
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 1-bromo-7-iodo-7-methyl-octane



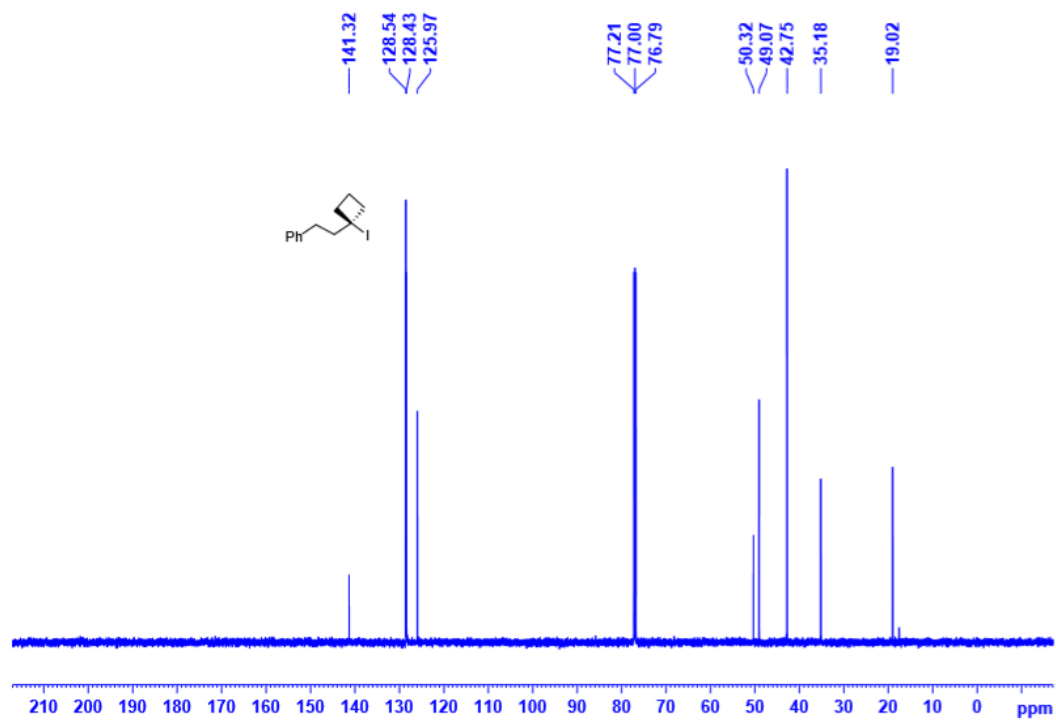
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 1-bromo-7-iodo-7-methyl-octane



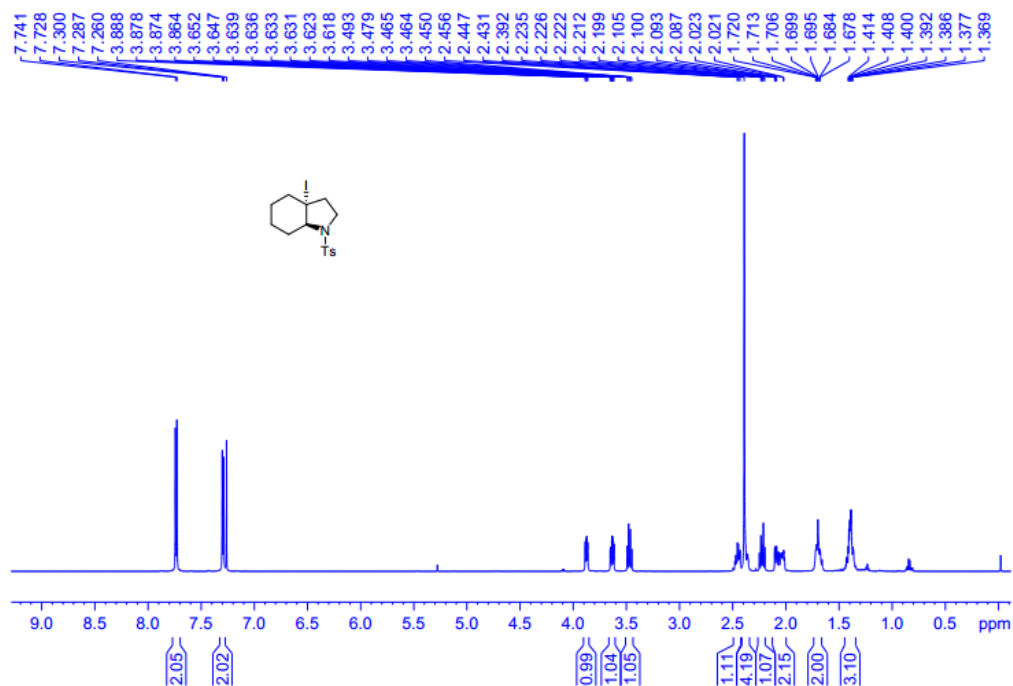
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of [2-(1-iodo-cyclobutyl)-ethyl]-benzene



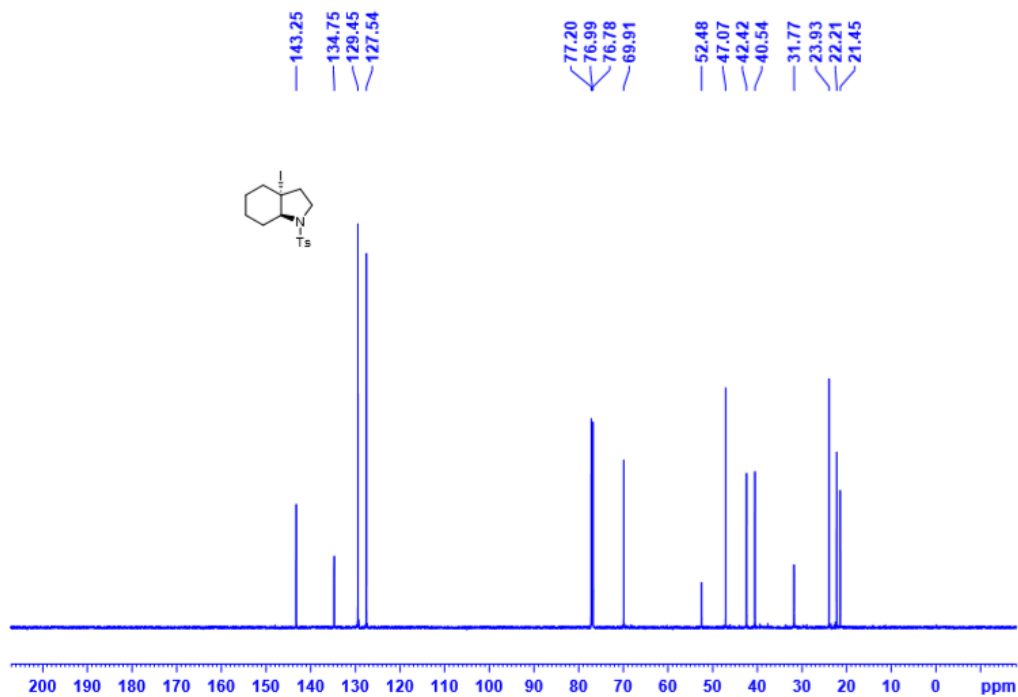
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of [2-(1-iodo-cyclobutyl)-ethyl]-benzene



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 3 $\alpha$ -iodo-1-[(4-methylphenyl)sulfonyl]octahydro-1H-indole

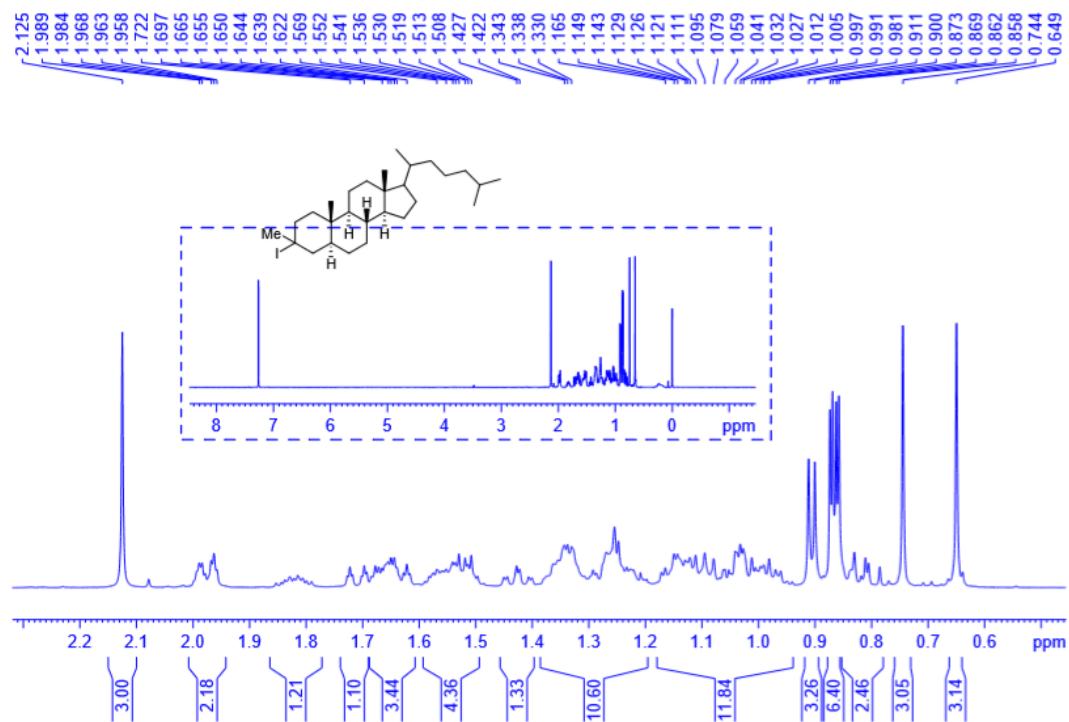


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 3 $\alpha$ -iodo-1-[(4-methylphenyl)sulfonyl]octahydro-1H-indole

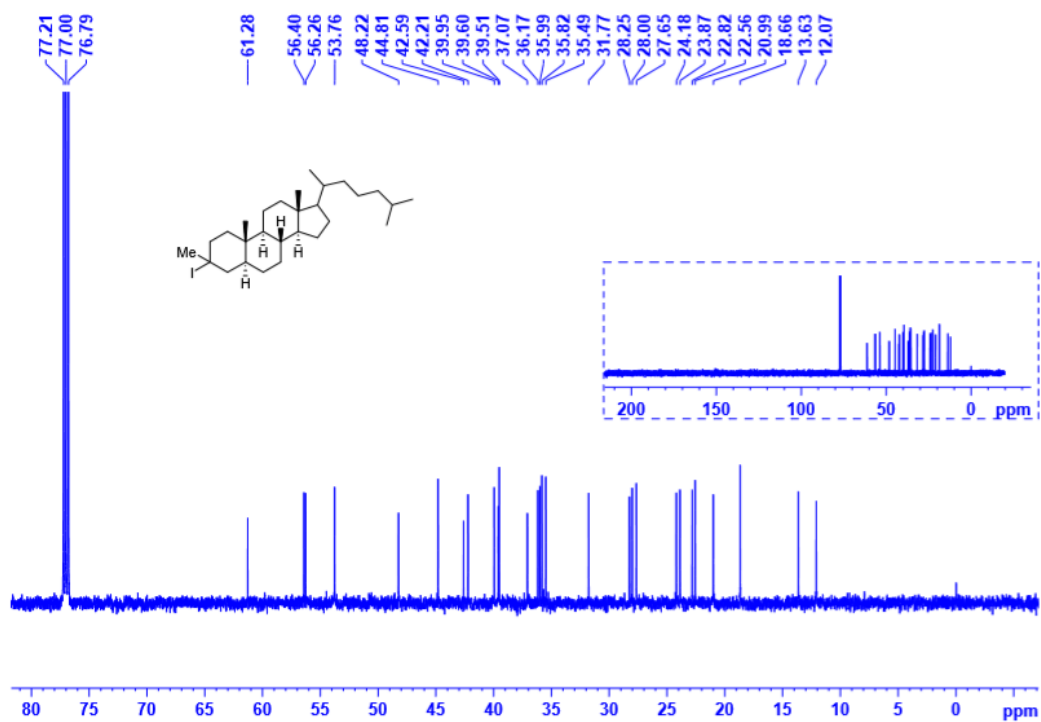




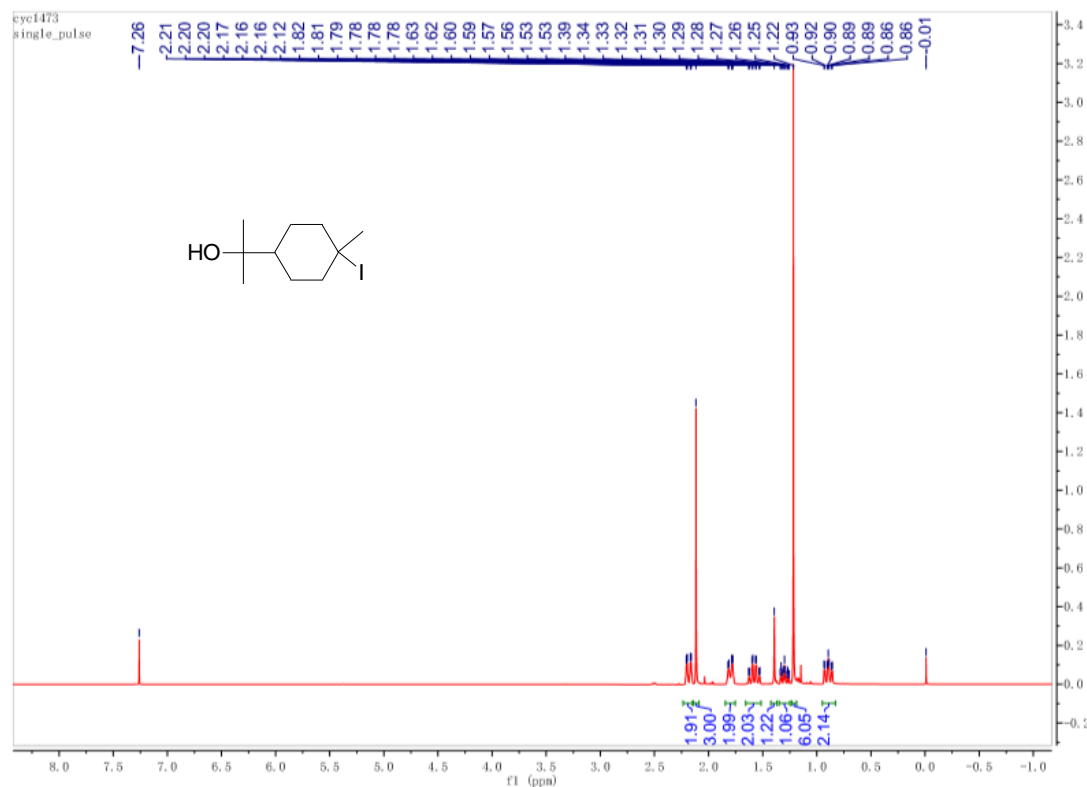
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 3-iodo-3-methyl-5 $\alpha$ -cholestane



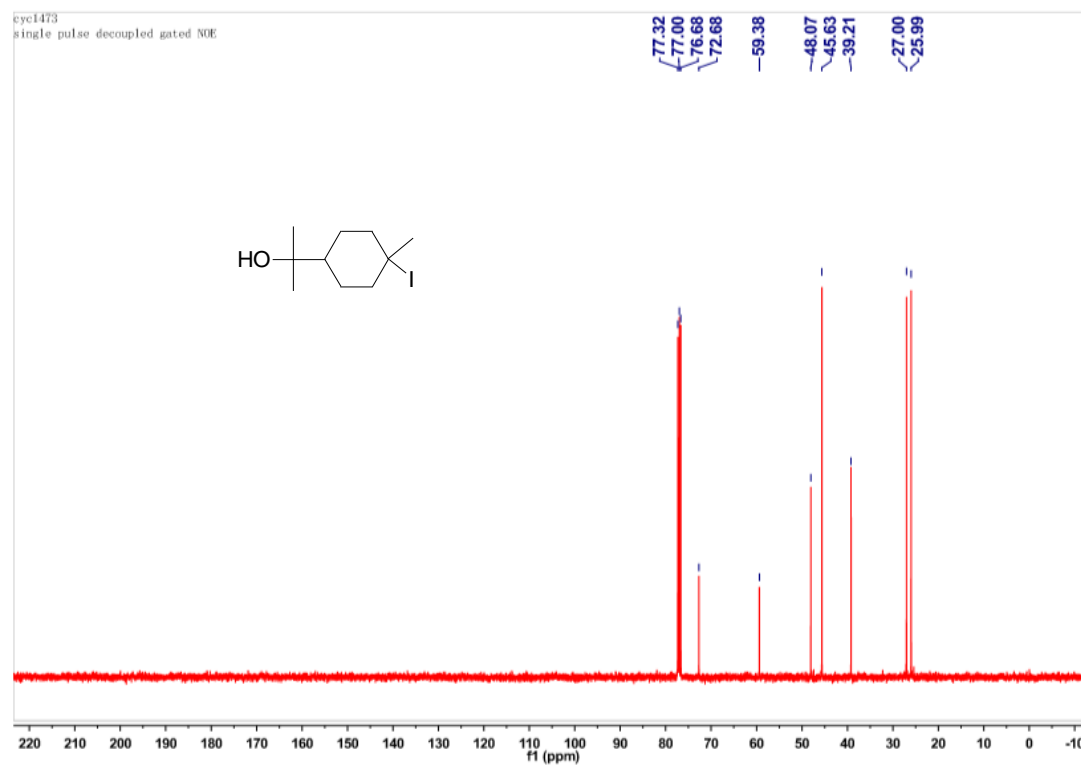
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 3-iodo-3-methyl-5 $\alpha$ -cholestane



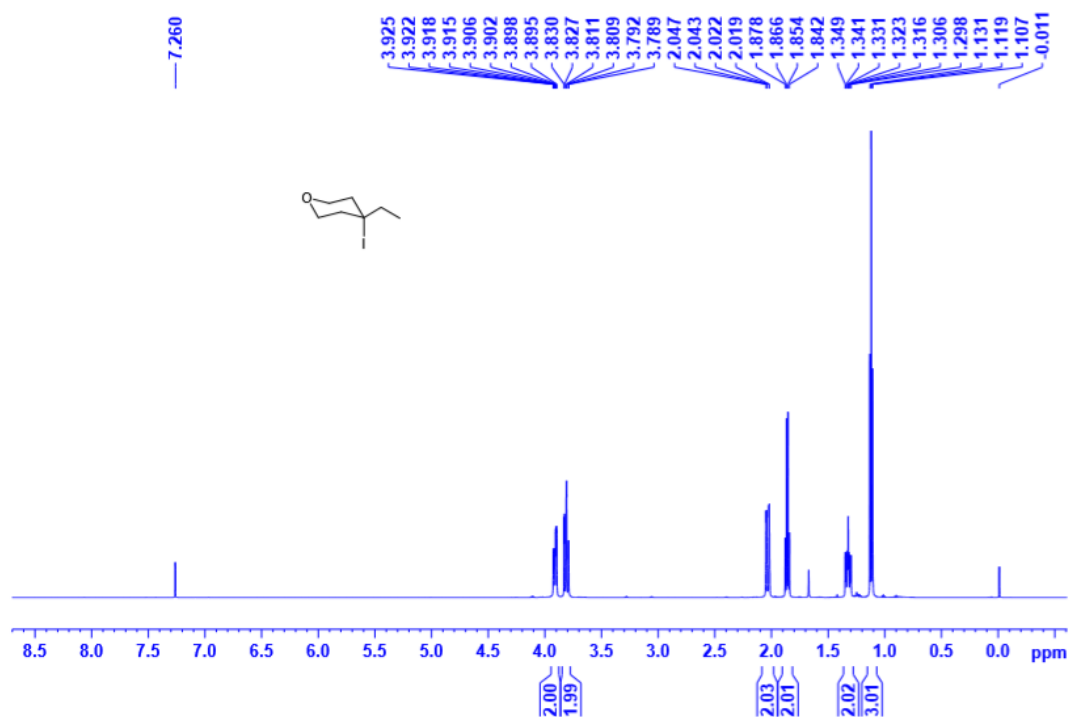
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of 2-(4-iodo-4-methyl-cyclohexyl)-propan-2-ol



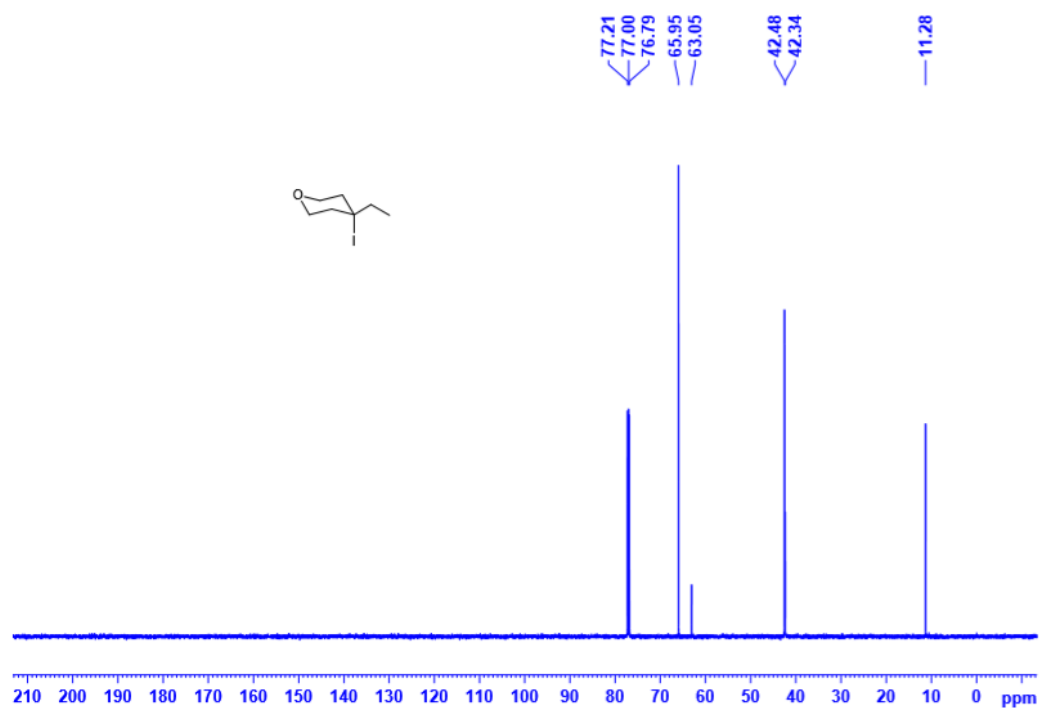
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 2-(4-iodo-4-methyl-cyclohexyl)-propan-2-ol



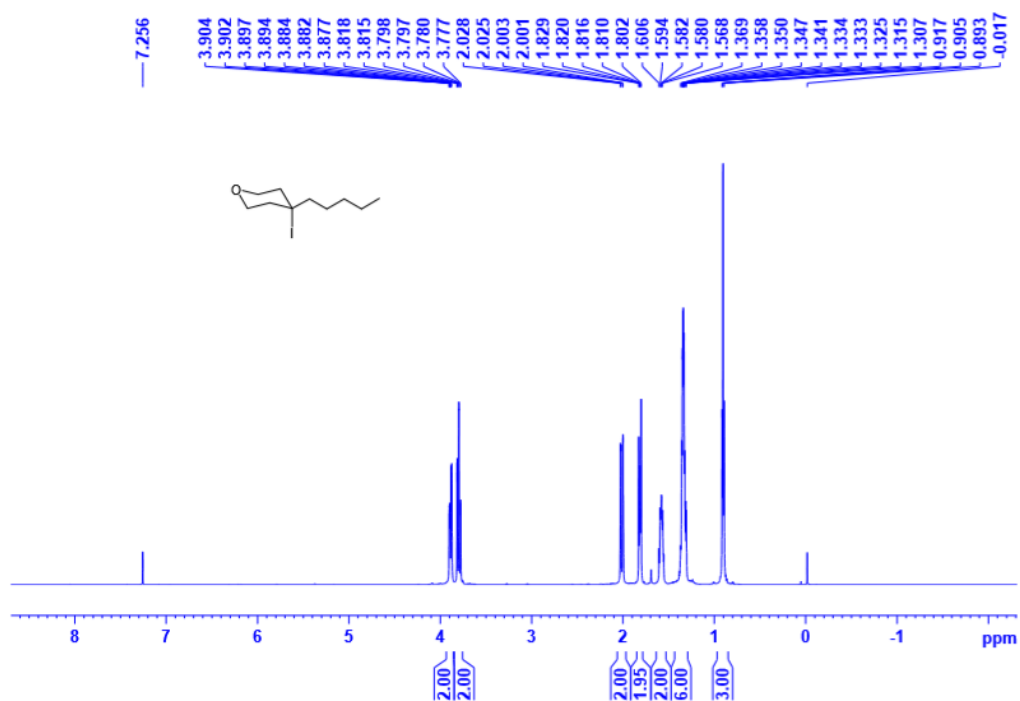
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 4-iodo-4-ethyl-tetrahydro-pyran



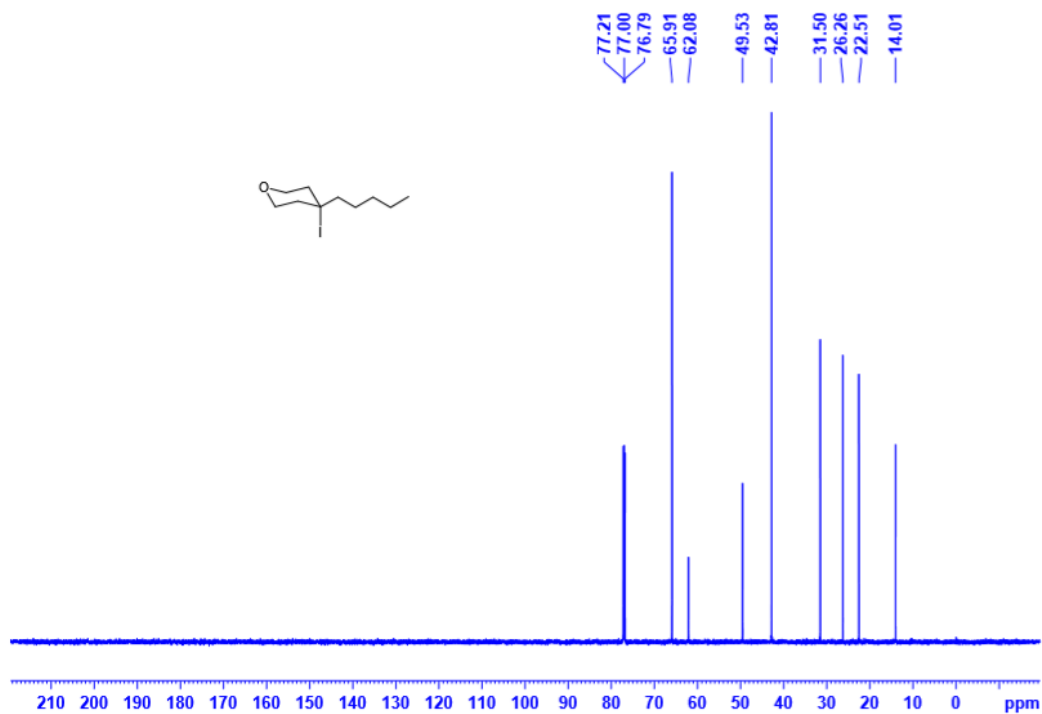
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 4-iodo-4-ethyl-tetrahydro-pyran



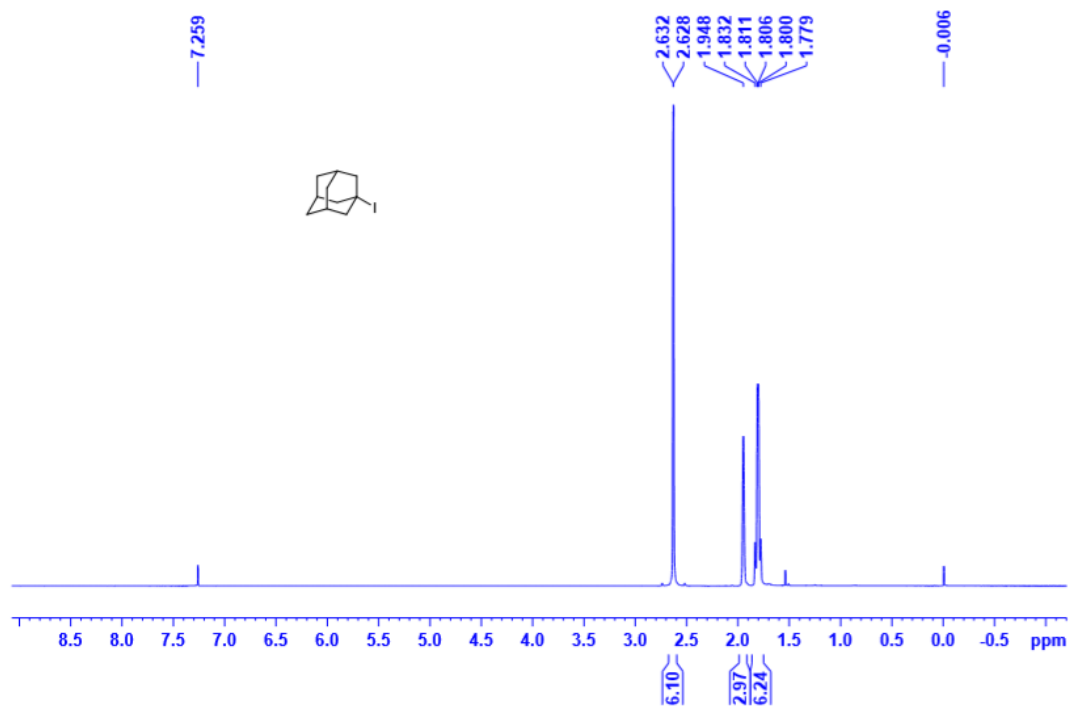
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 4-iodo-4-pentyl-tetrahydro-pyran



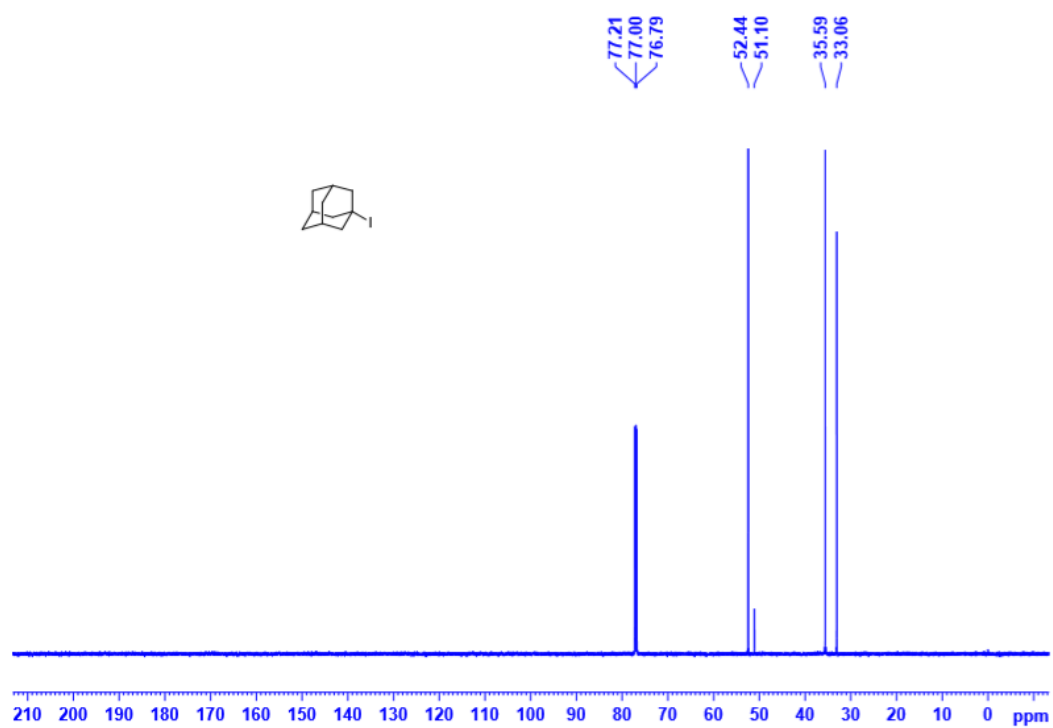
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 4-iodo-4-pentyl-tetrahydro-pyran



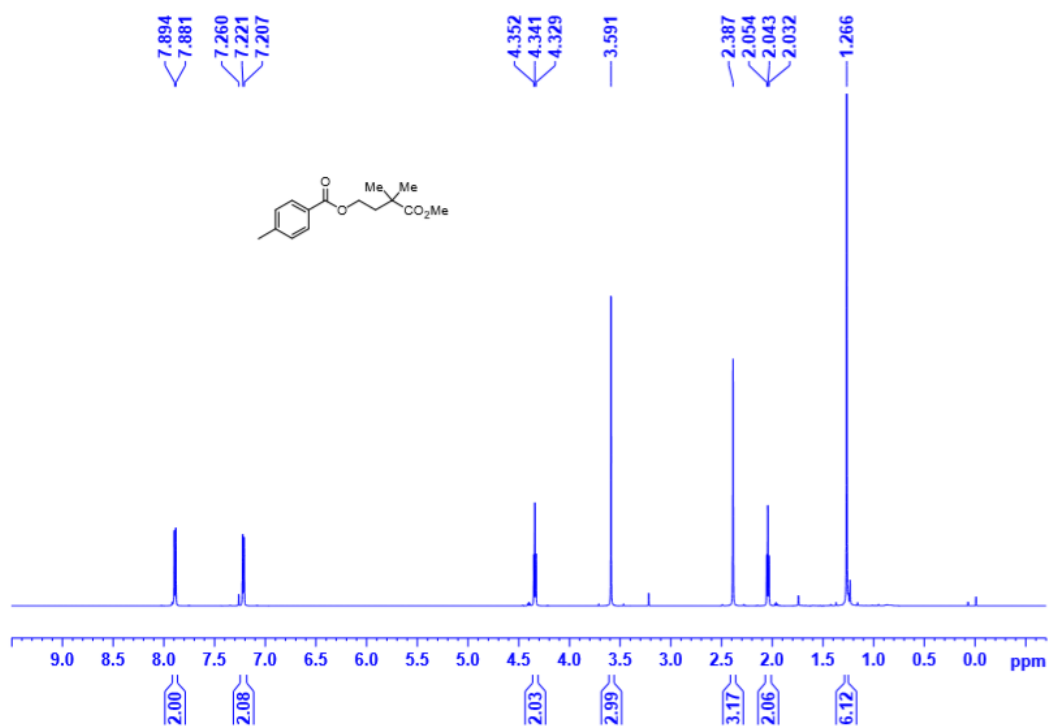
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of 1-iodo-adamantane



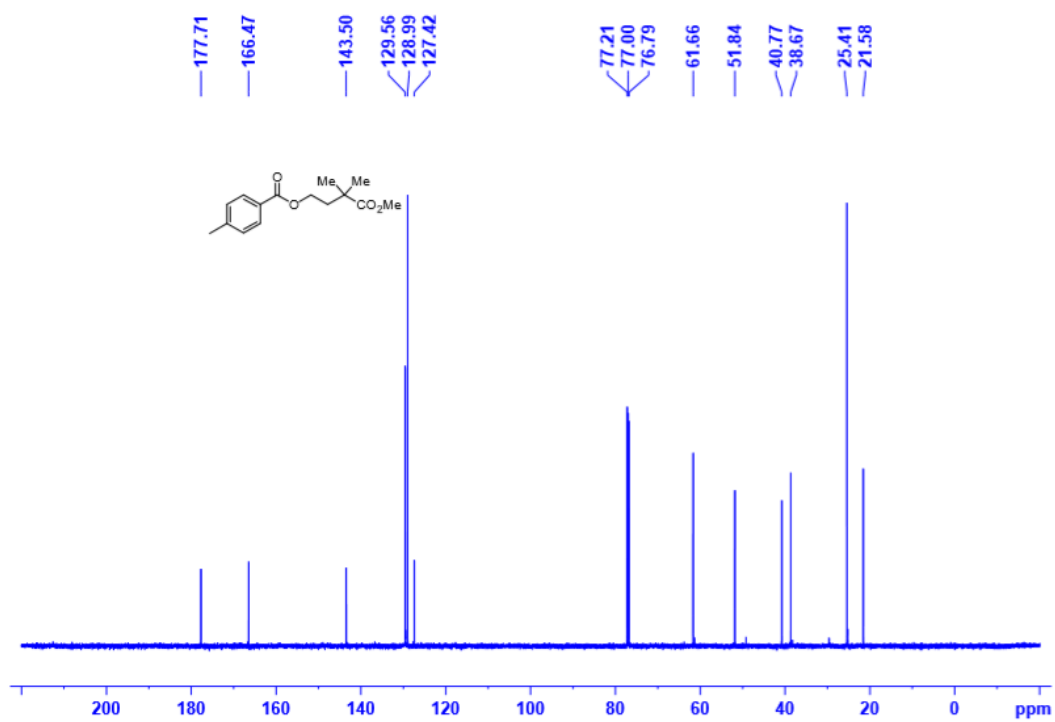
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of 1-iodo-adamantane

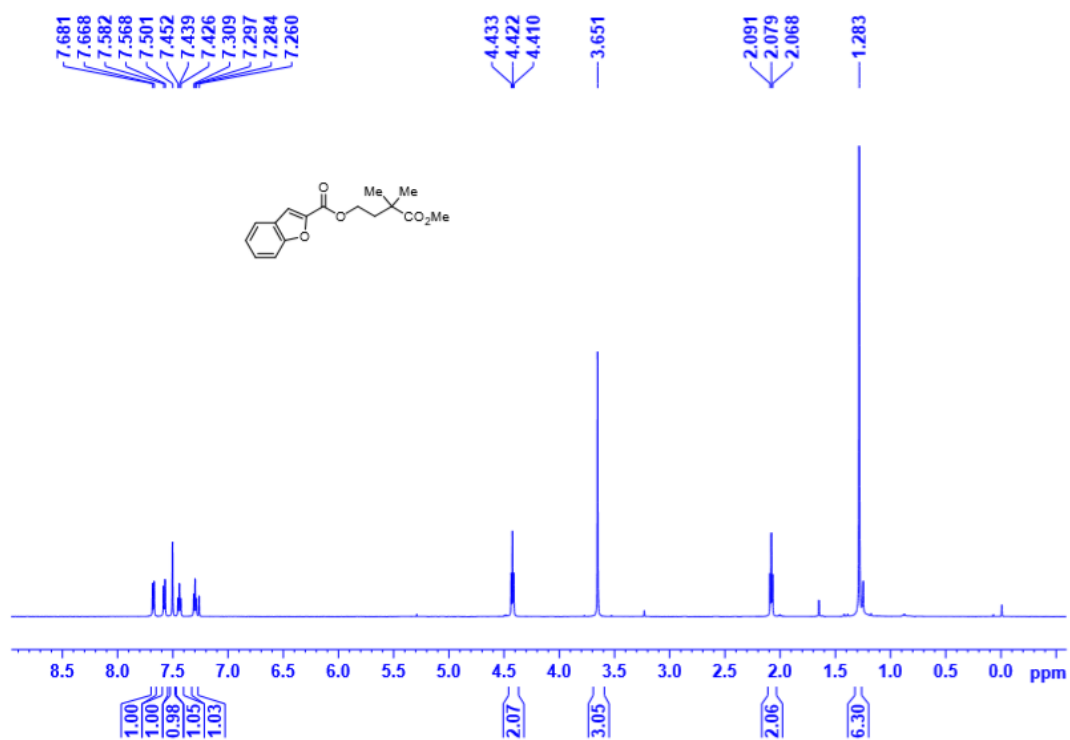
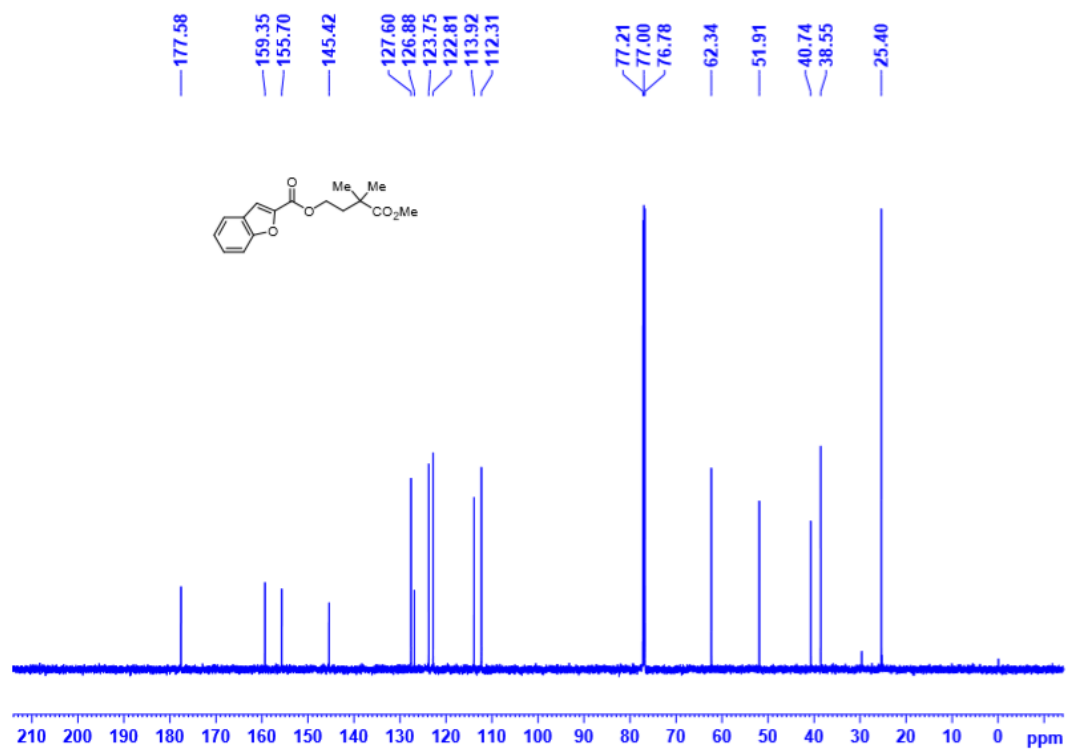


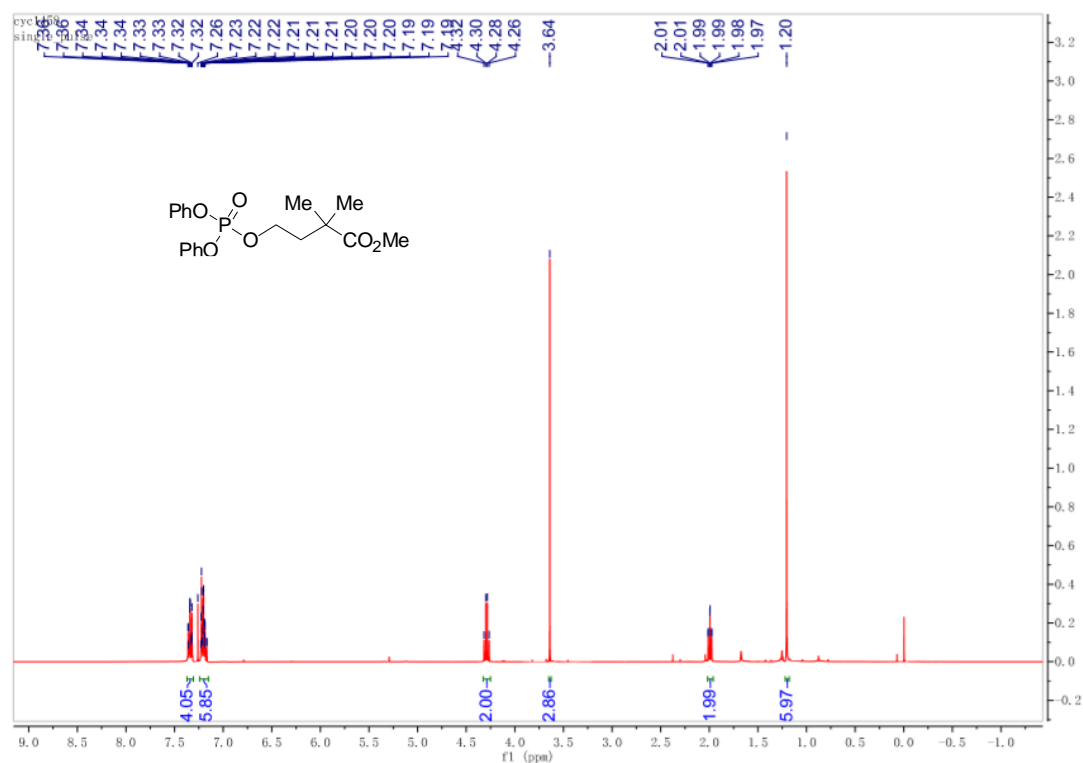
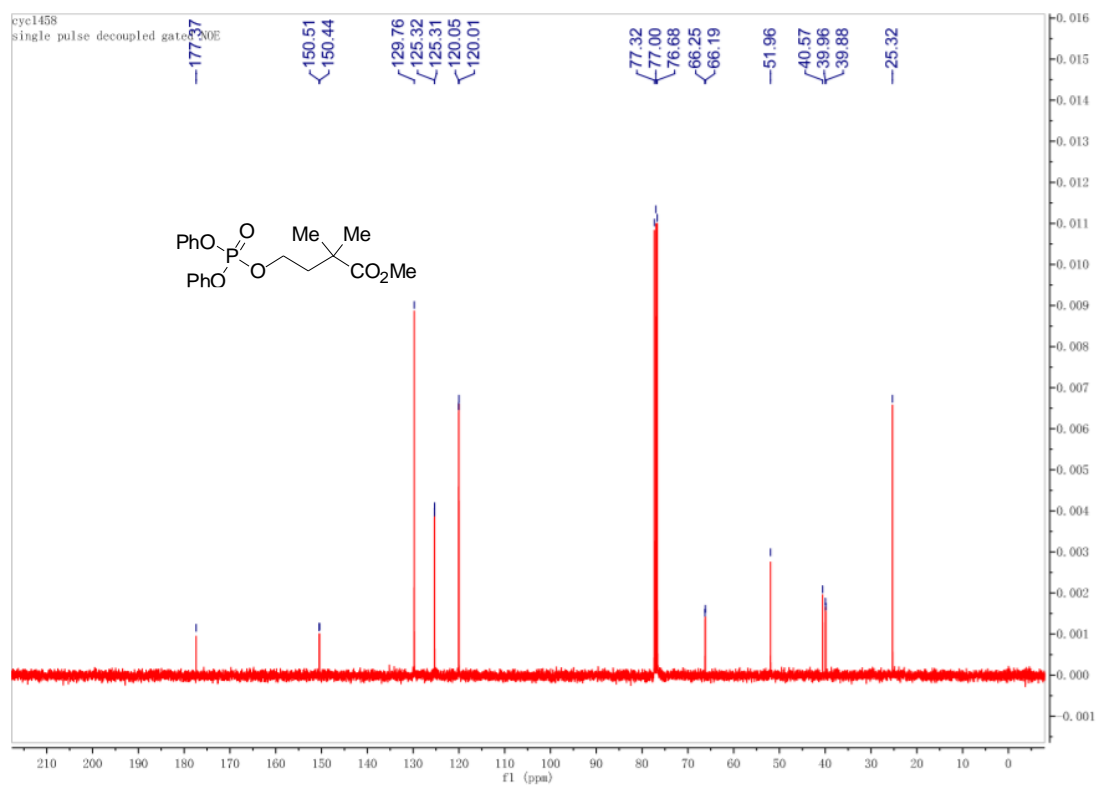
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **22**



$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **22**

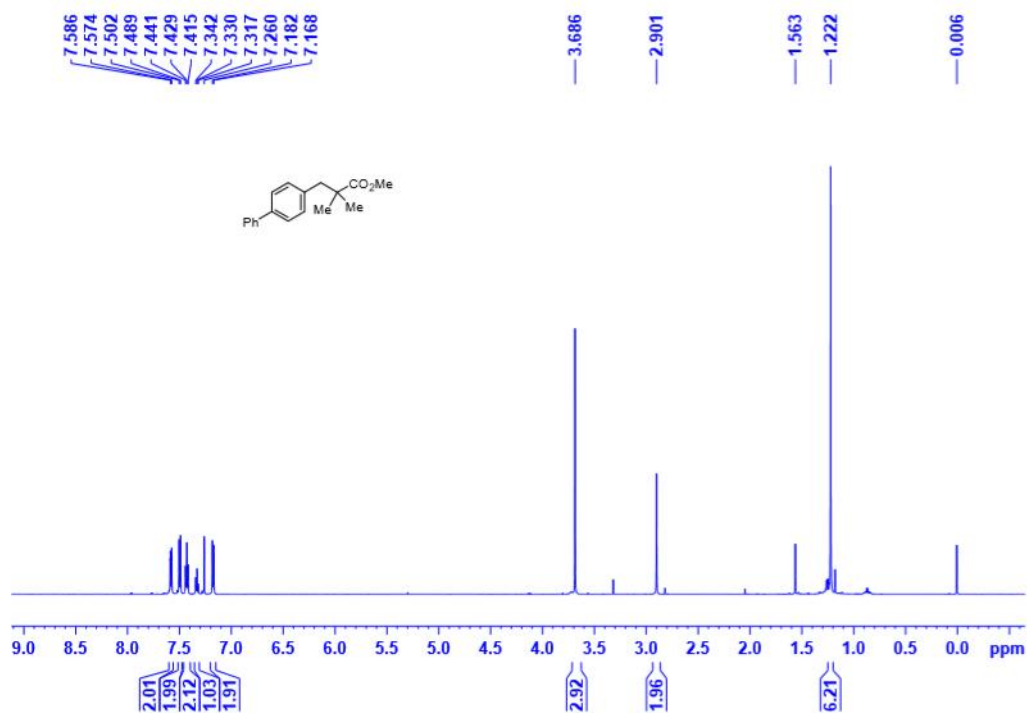


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **23** $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **23**

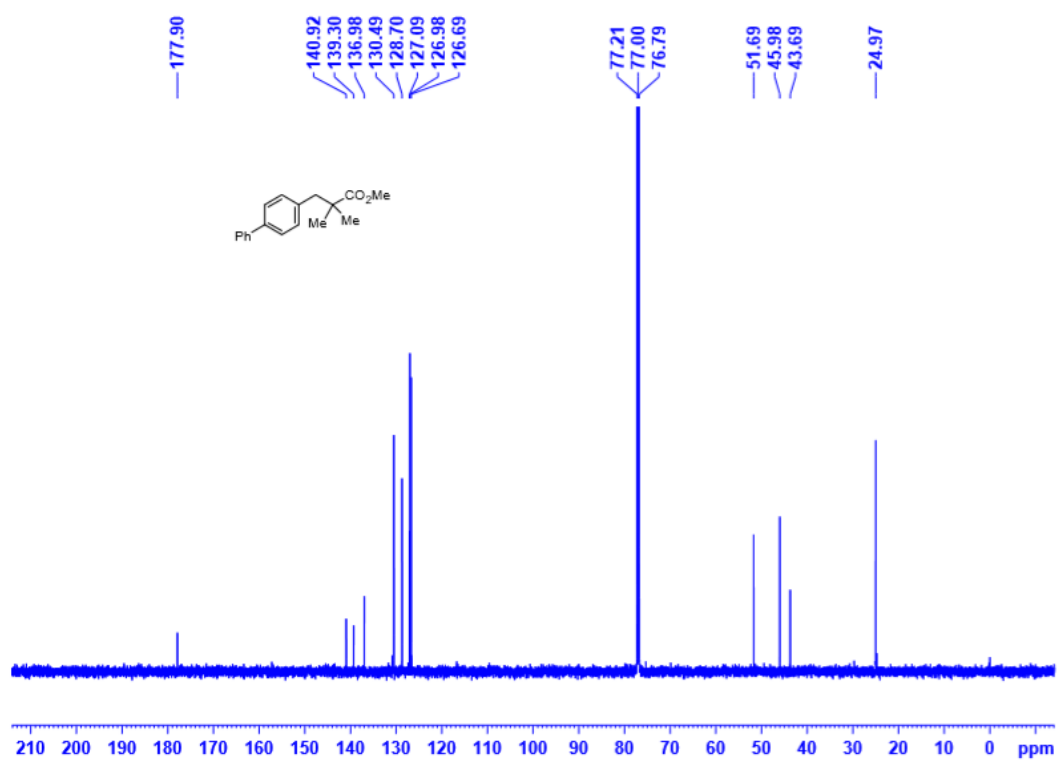
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **24** $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **24**



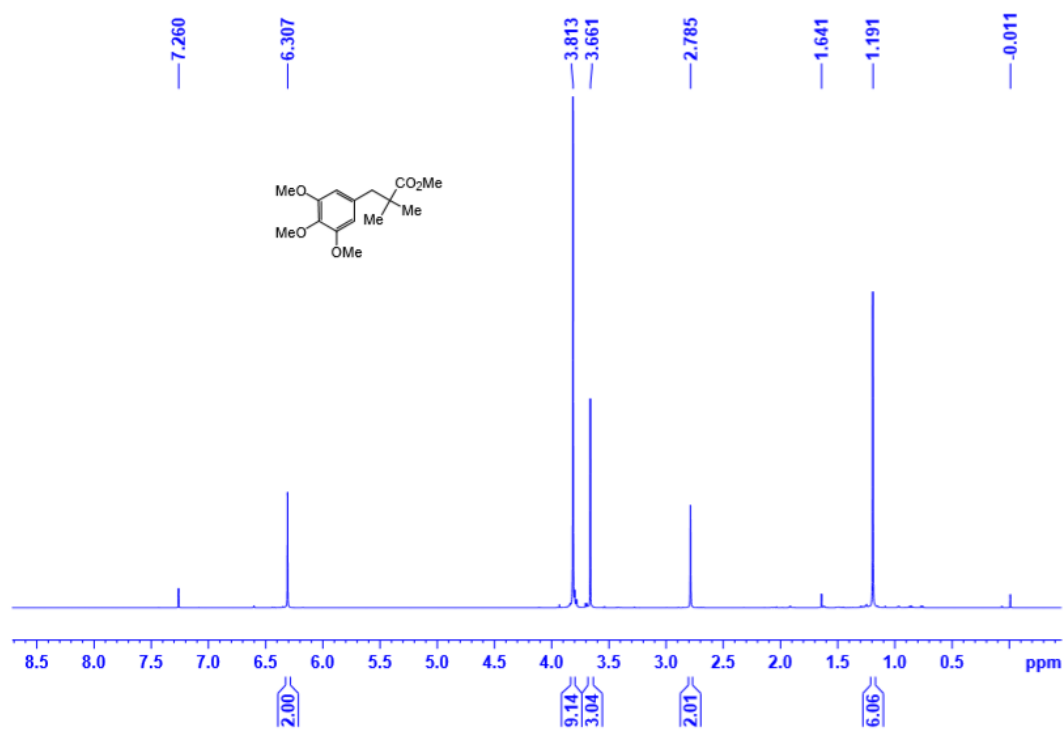
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **25**



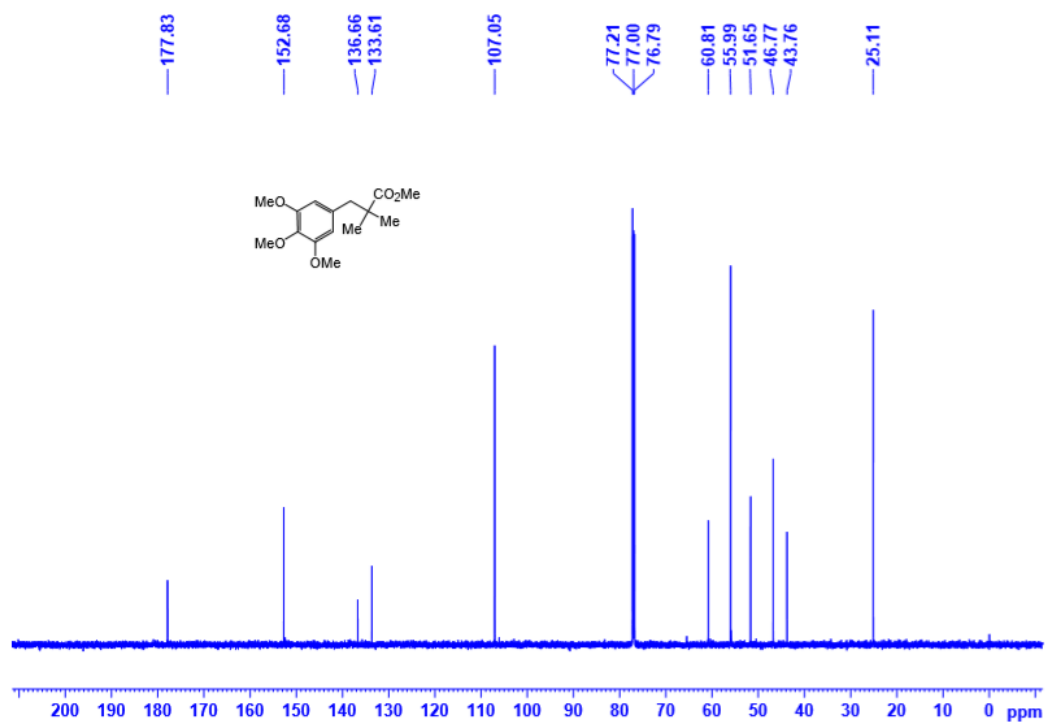
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **25**



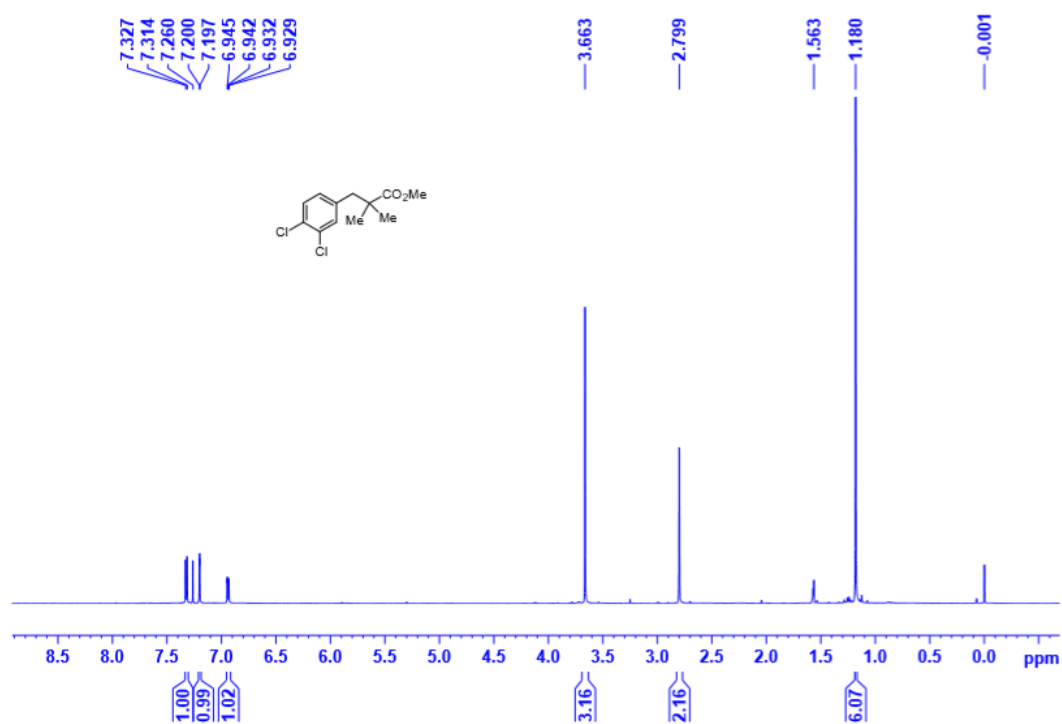
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **26**



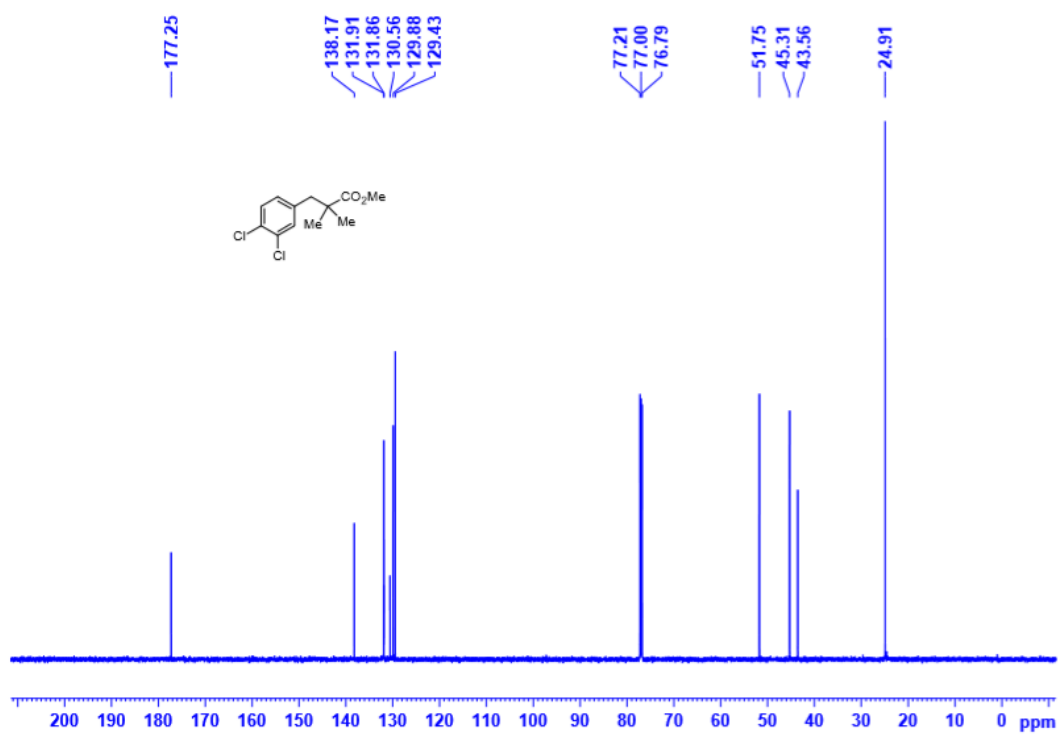
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **26**



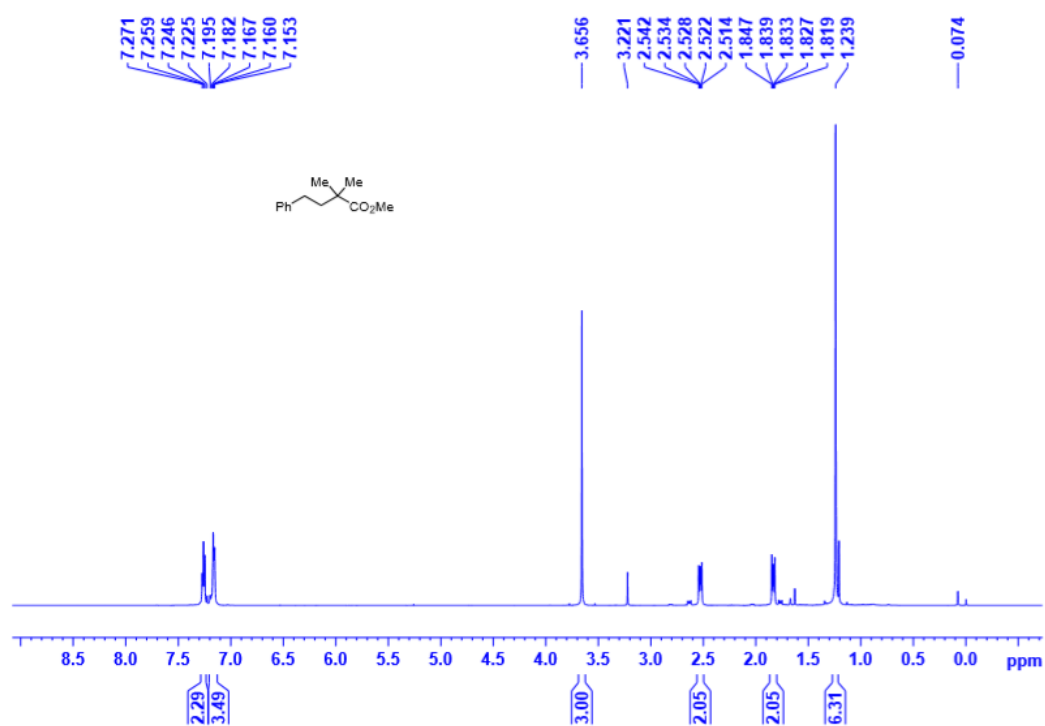
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **27**



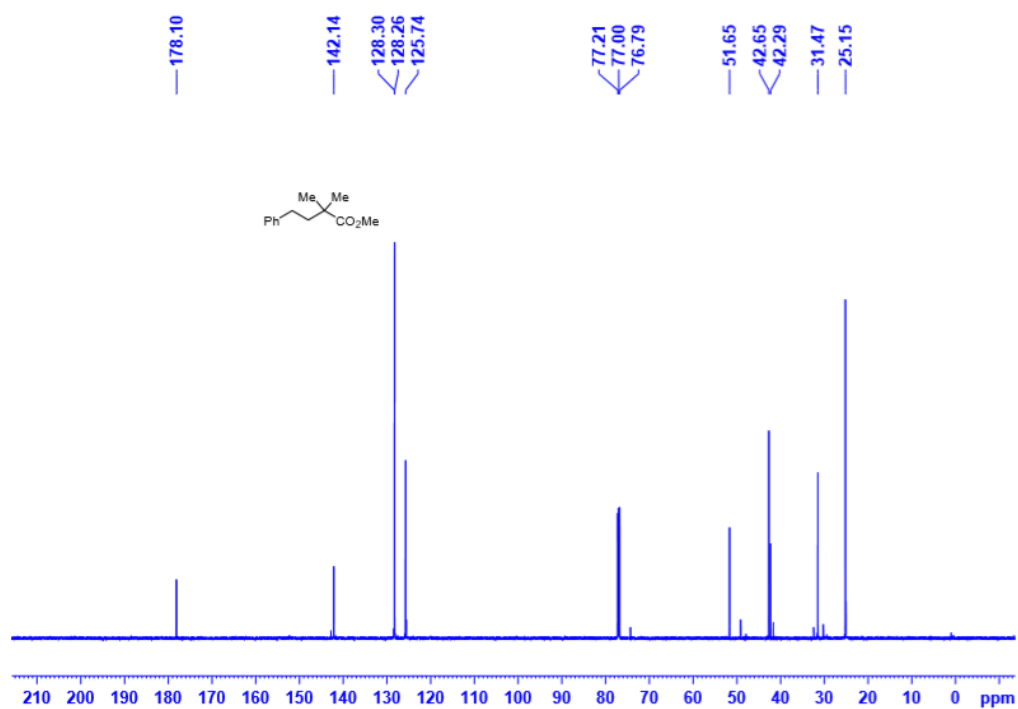
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **27**

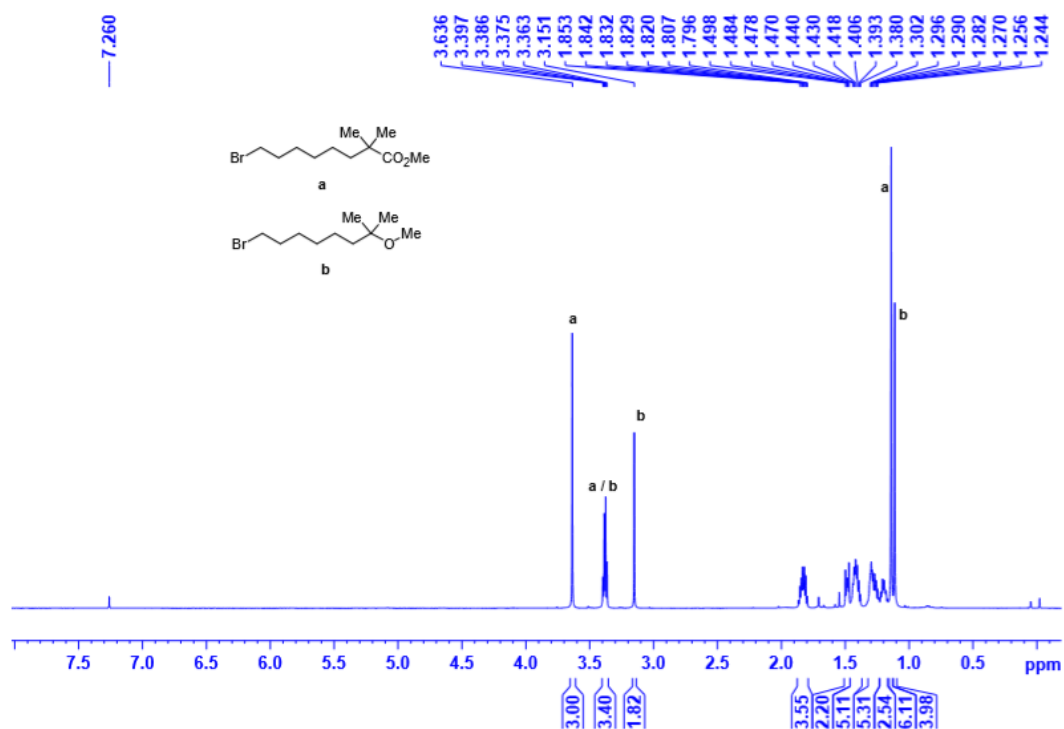
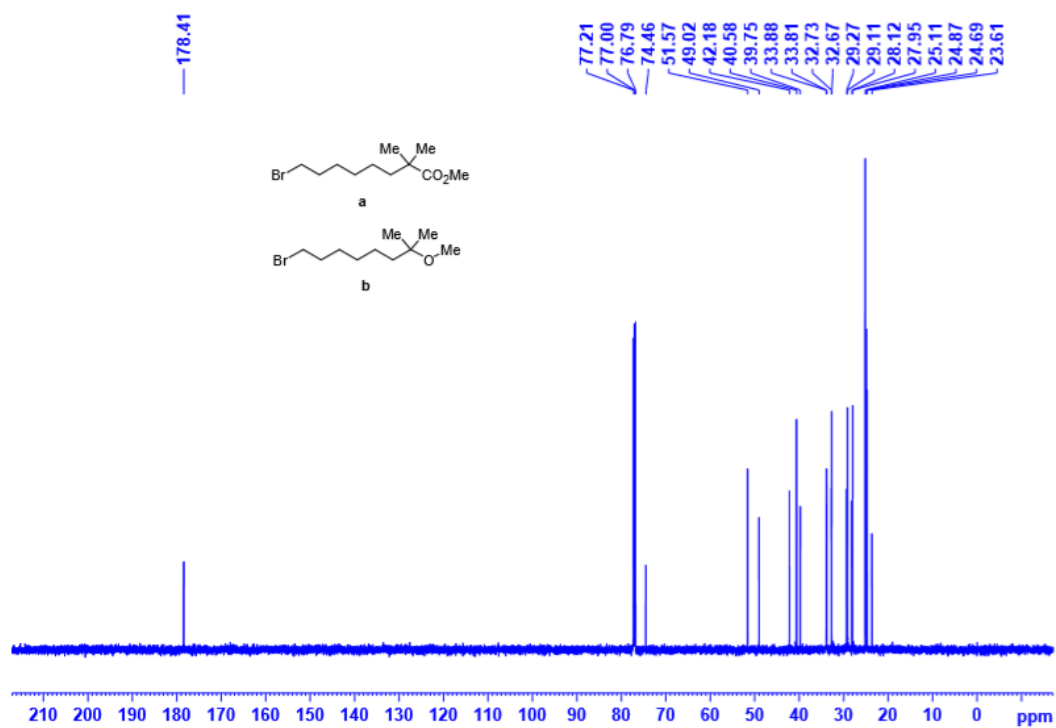


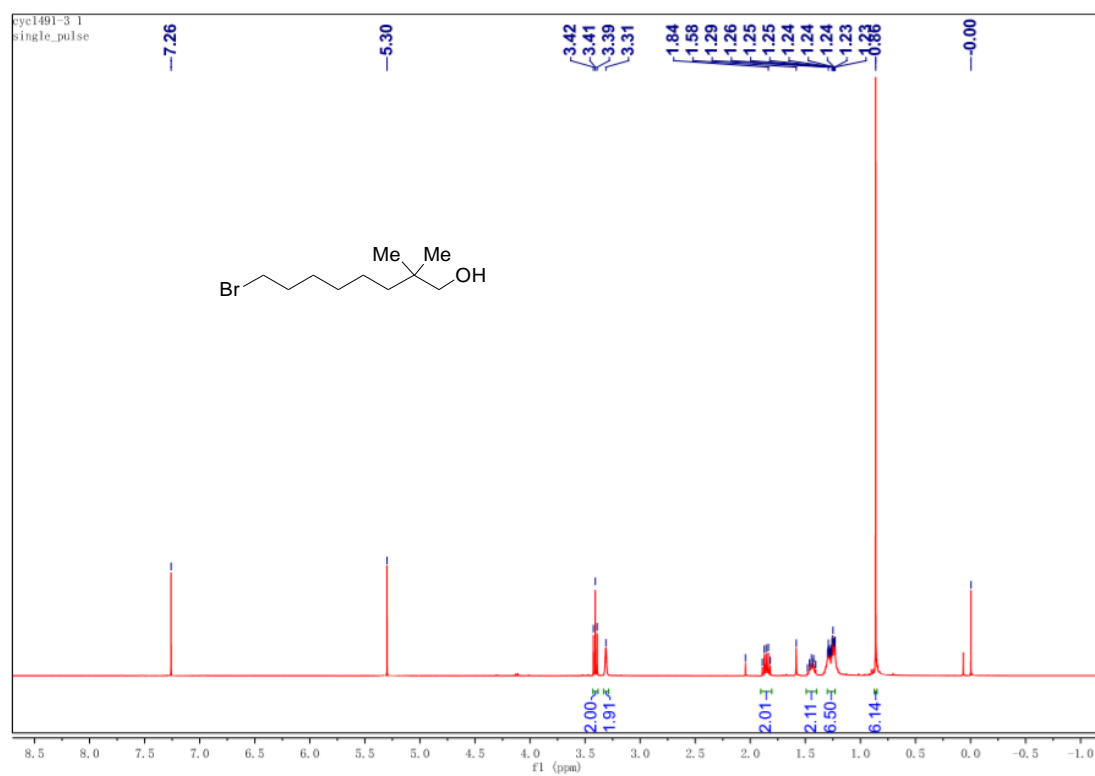
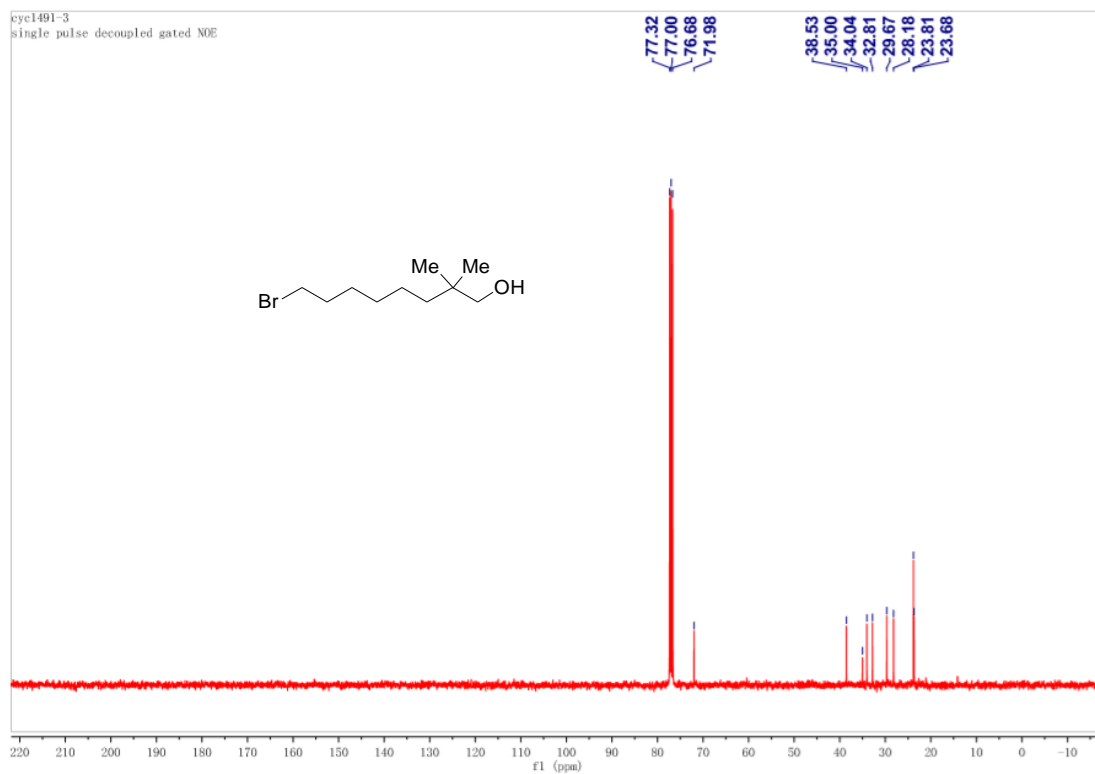
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **28**

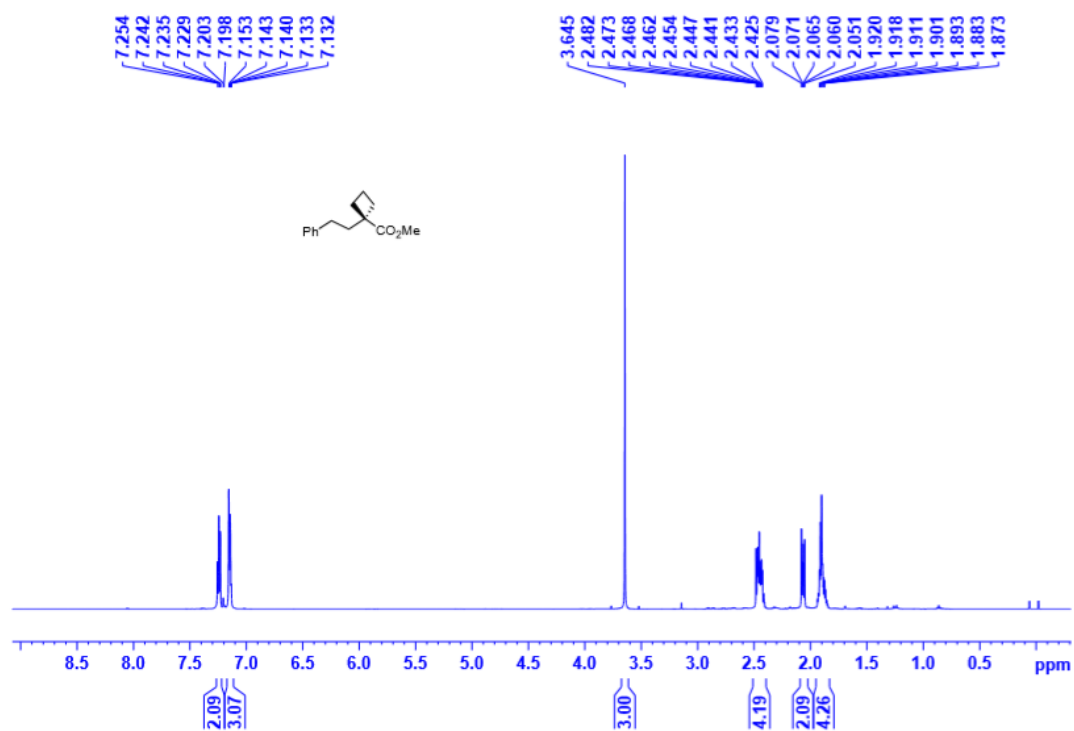
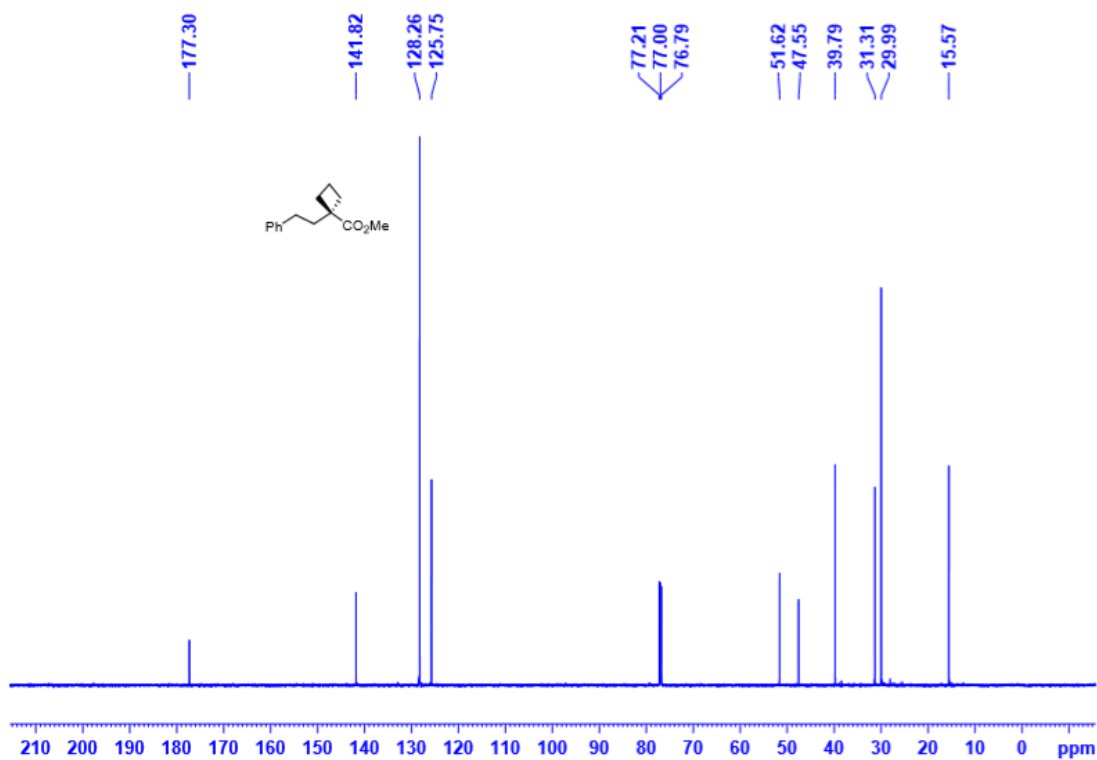


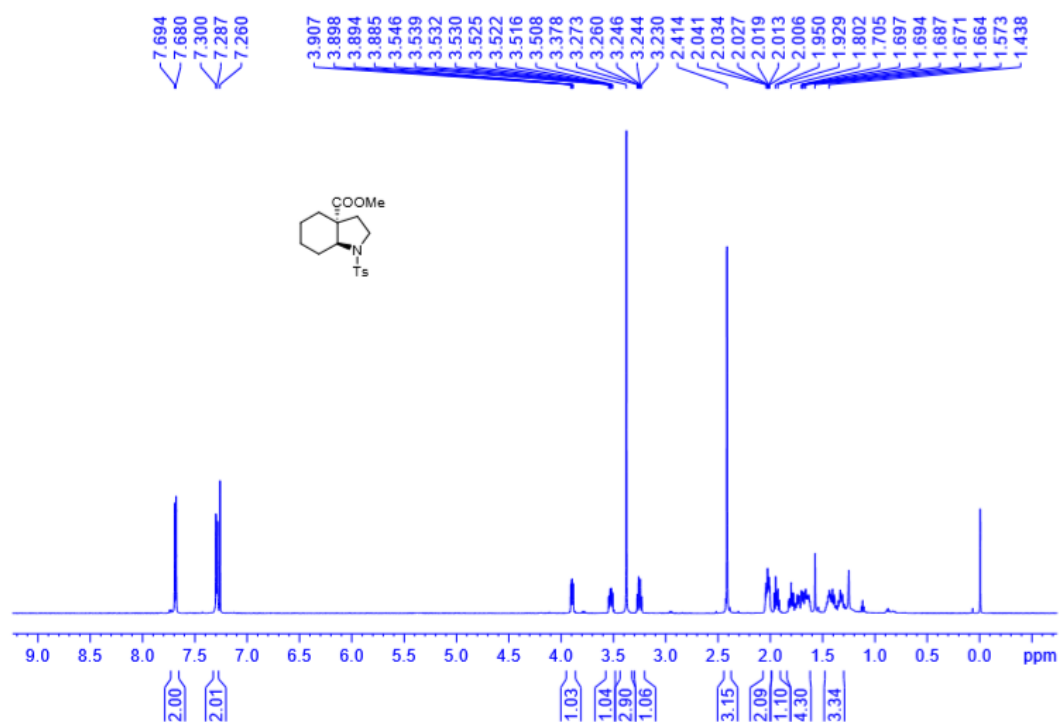
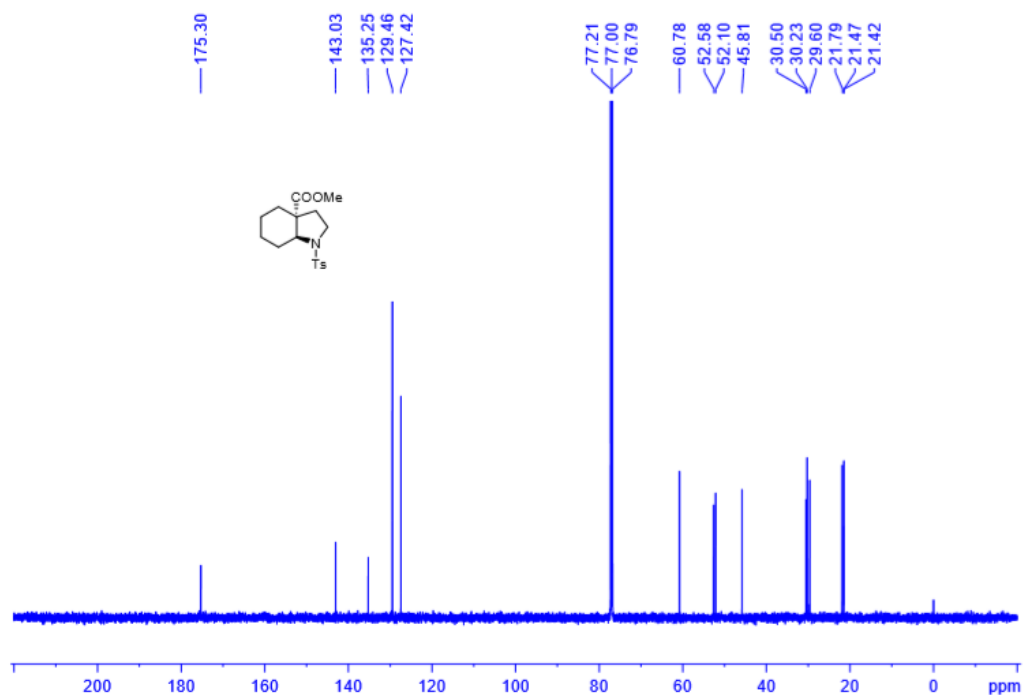
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **28**



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **29** $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **29**

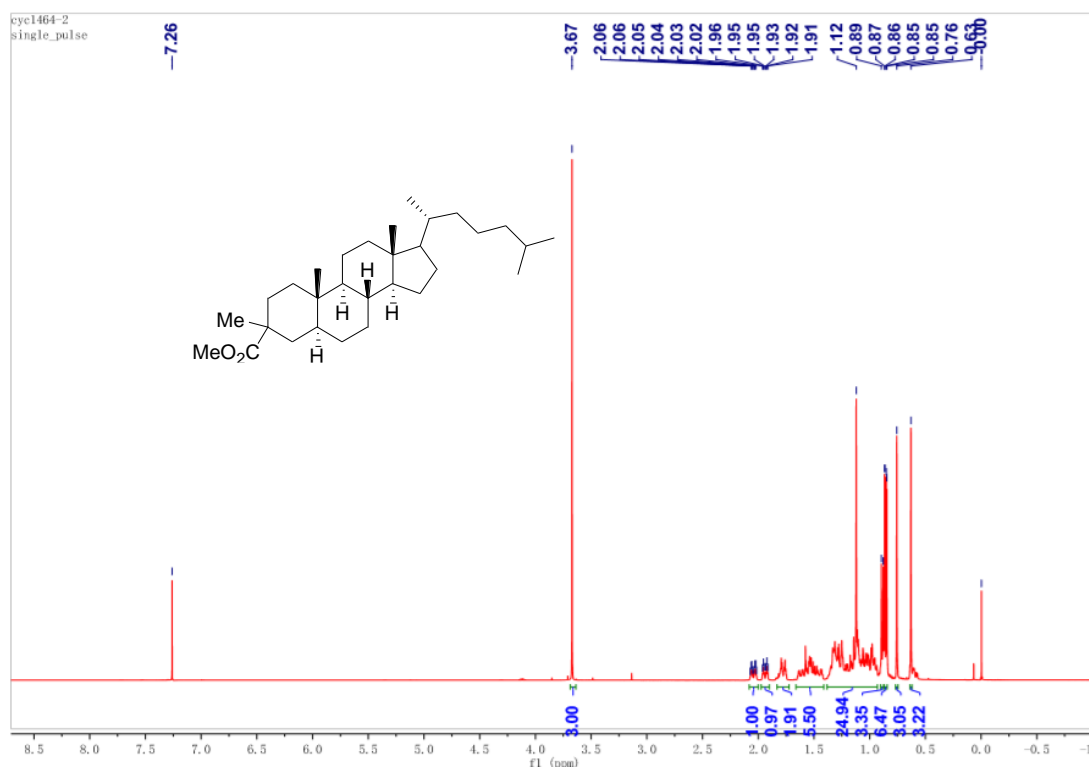
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of 8-bromo-2, 2-dimethyl-octan-1-ol $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 8-bromo-2, 2-dimethyl-octan-1-ol

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **30** $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **30**

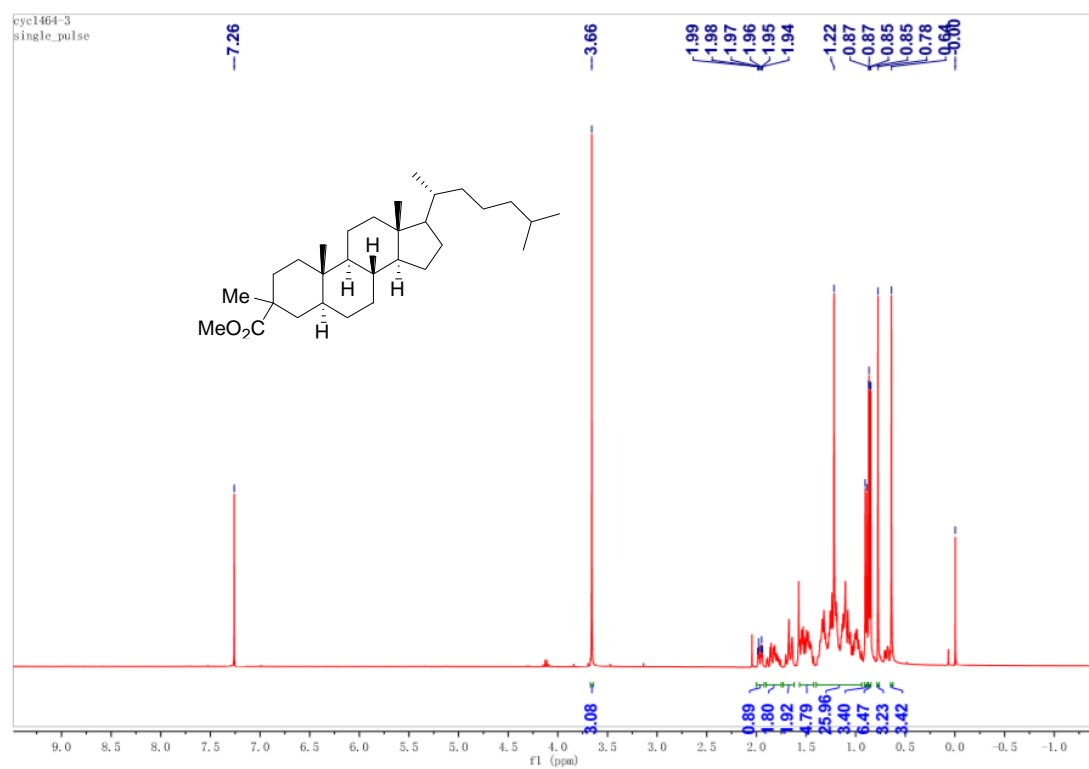
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of **31**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) of **31**



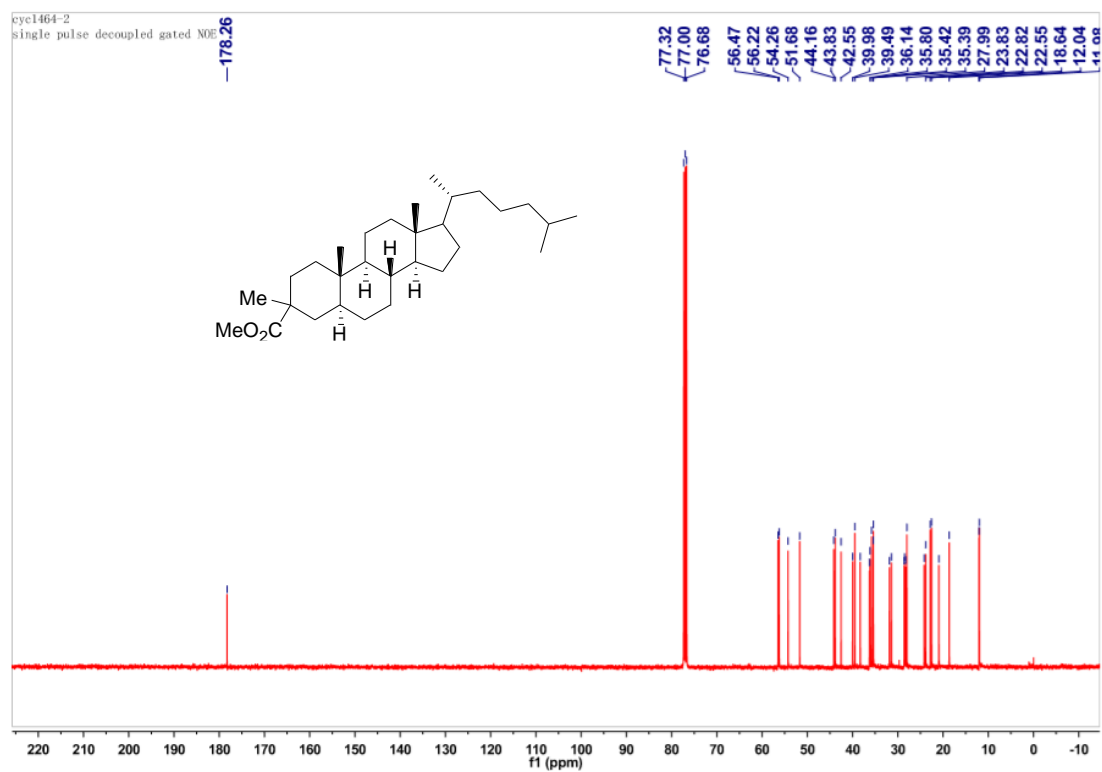
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **32** (major isomer)



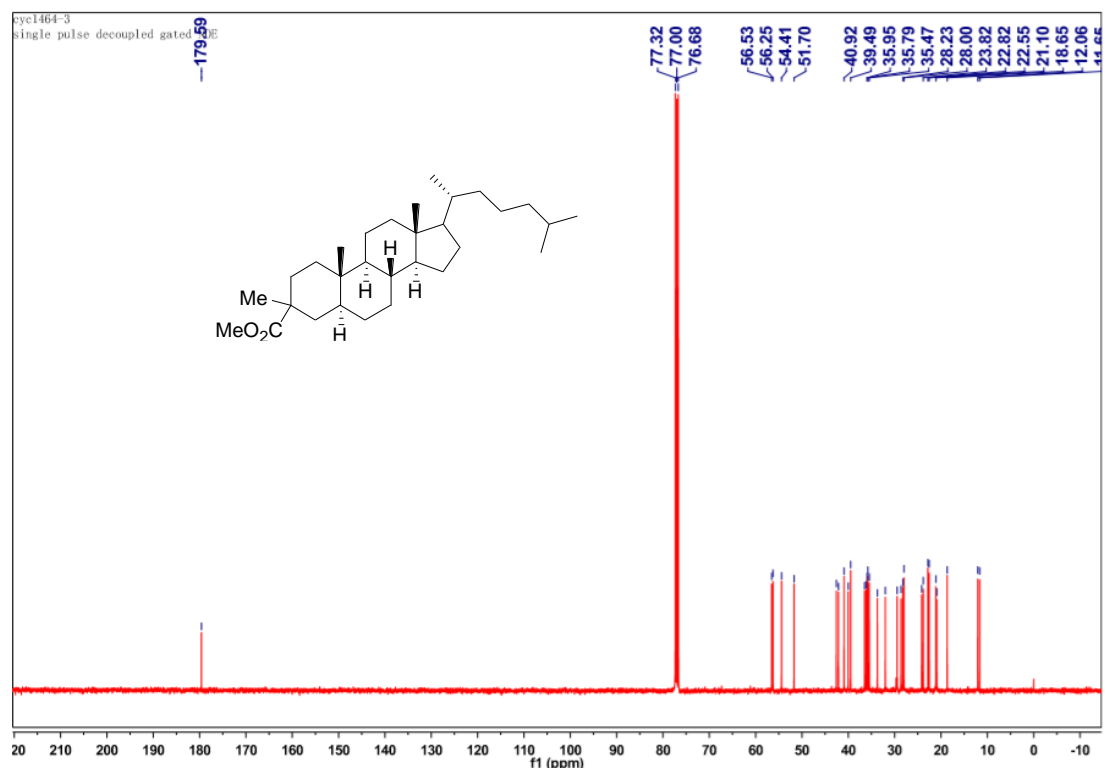
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **32** (minor isomer)

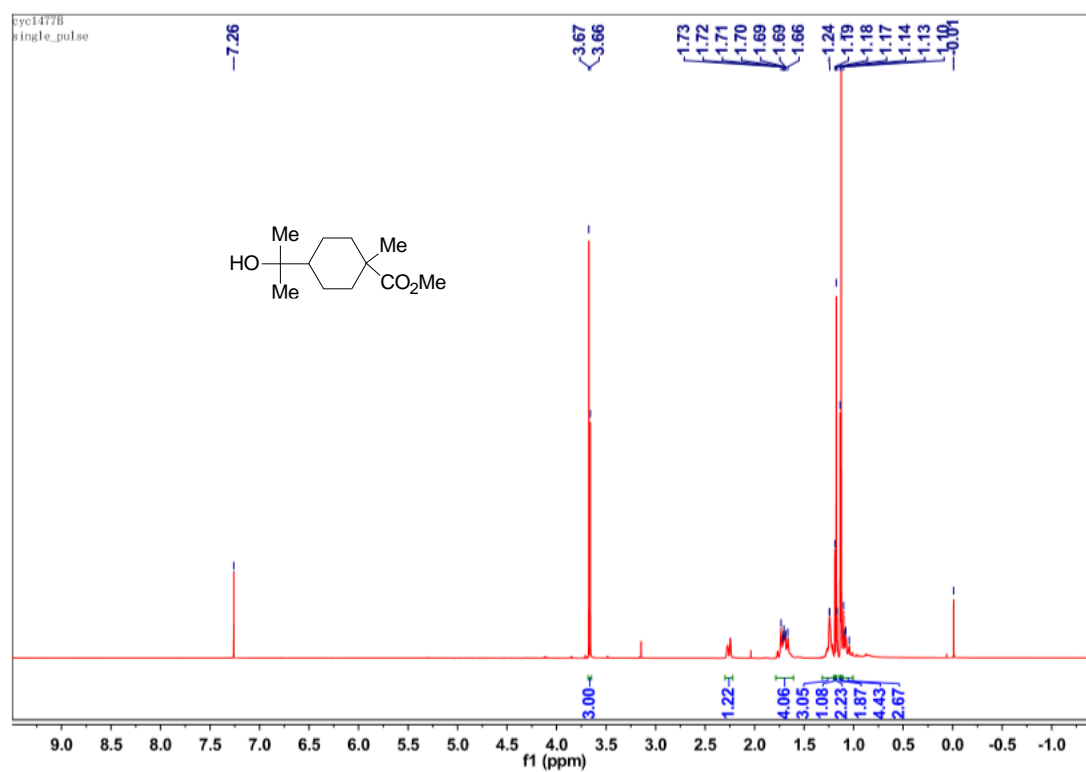
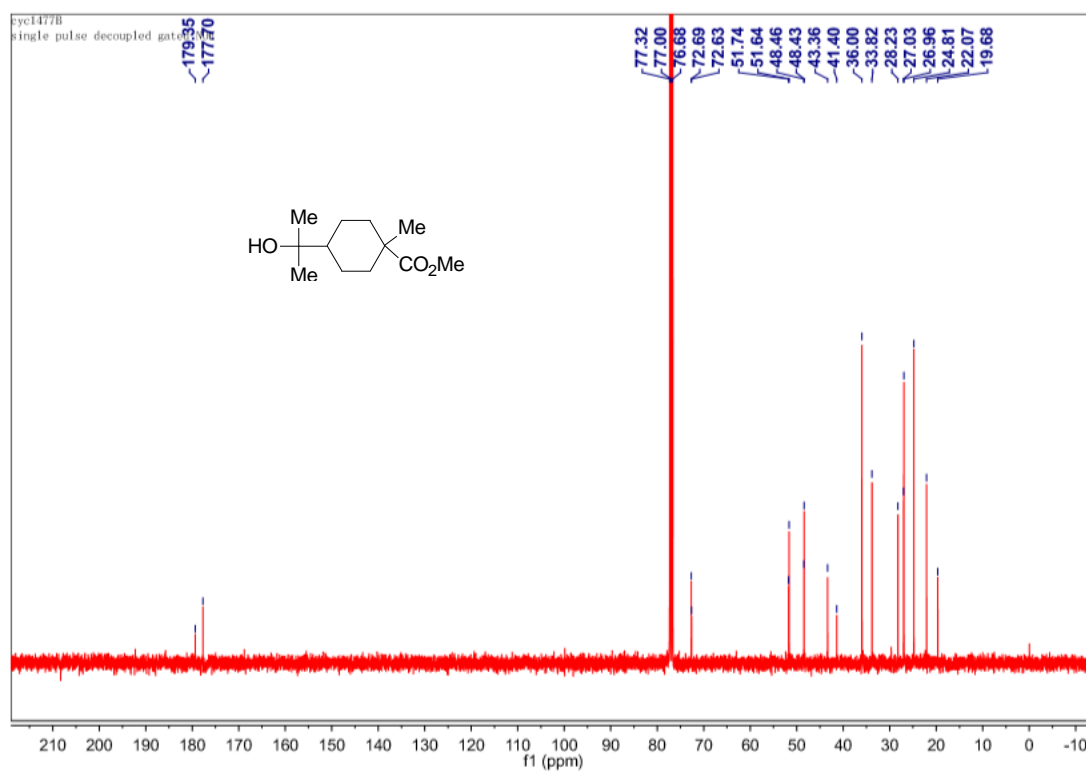


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **32** (major isomer)

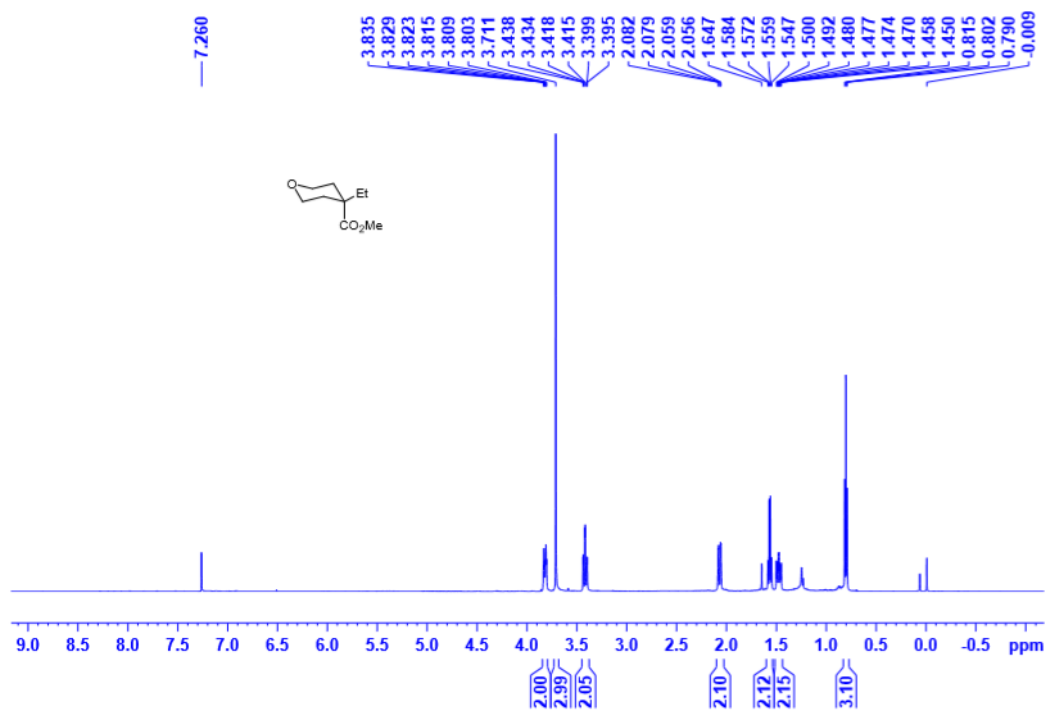


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **32** (minor isomer)

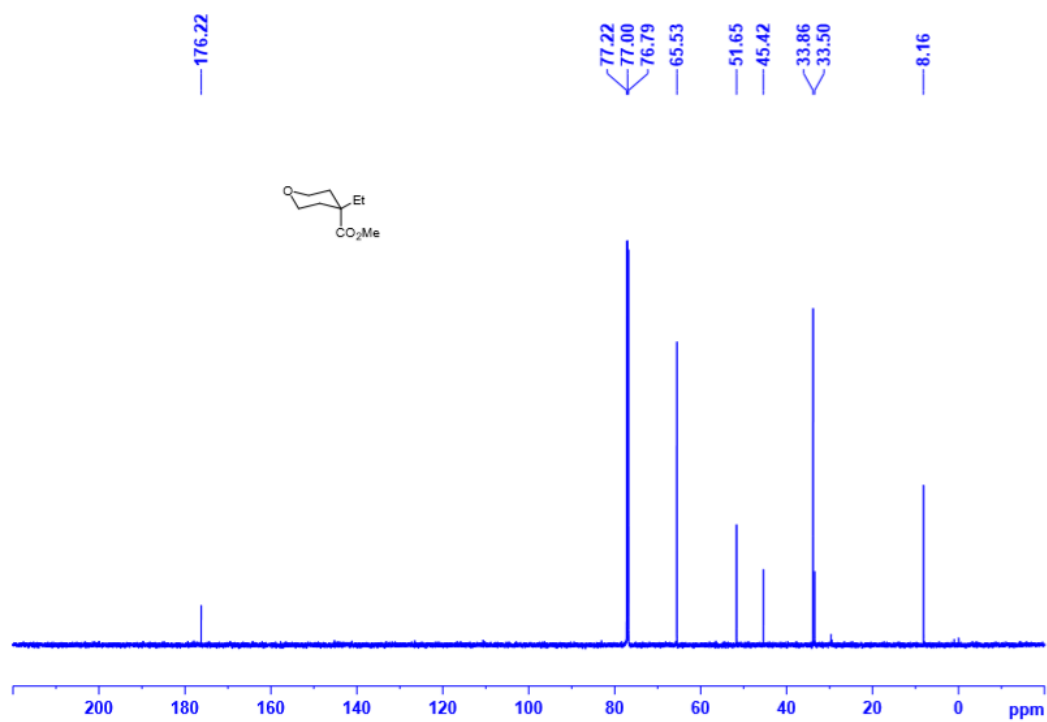


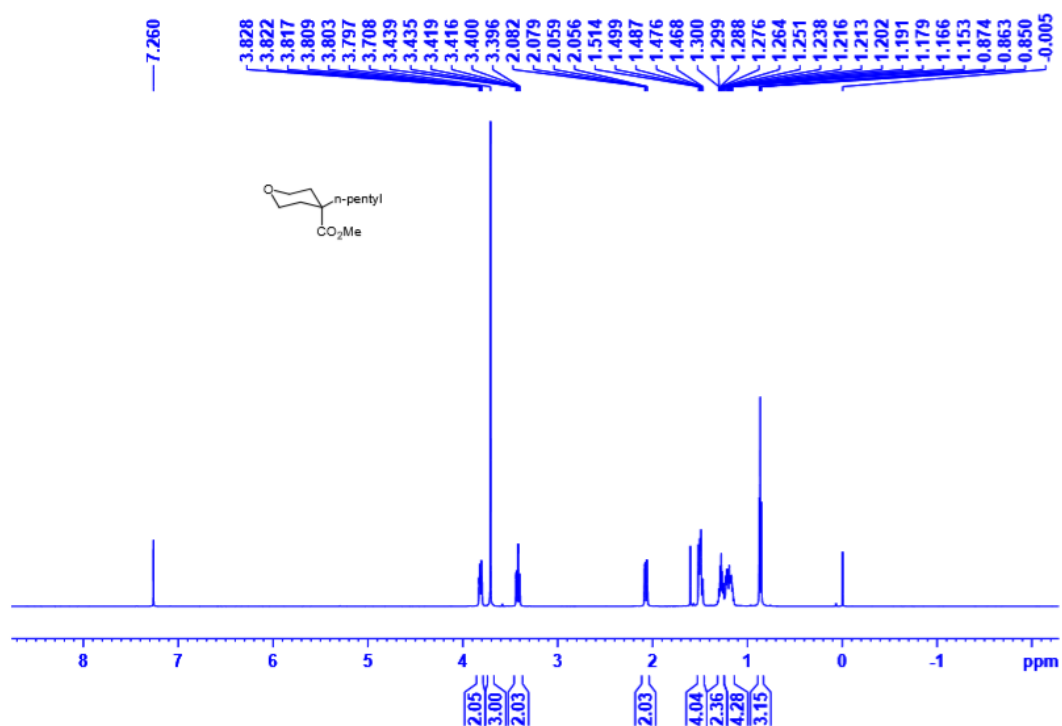
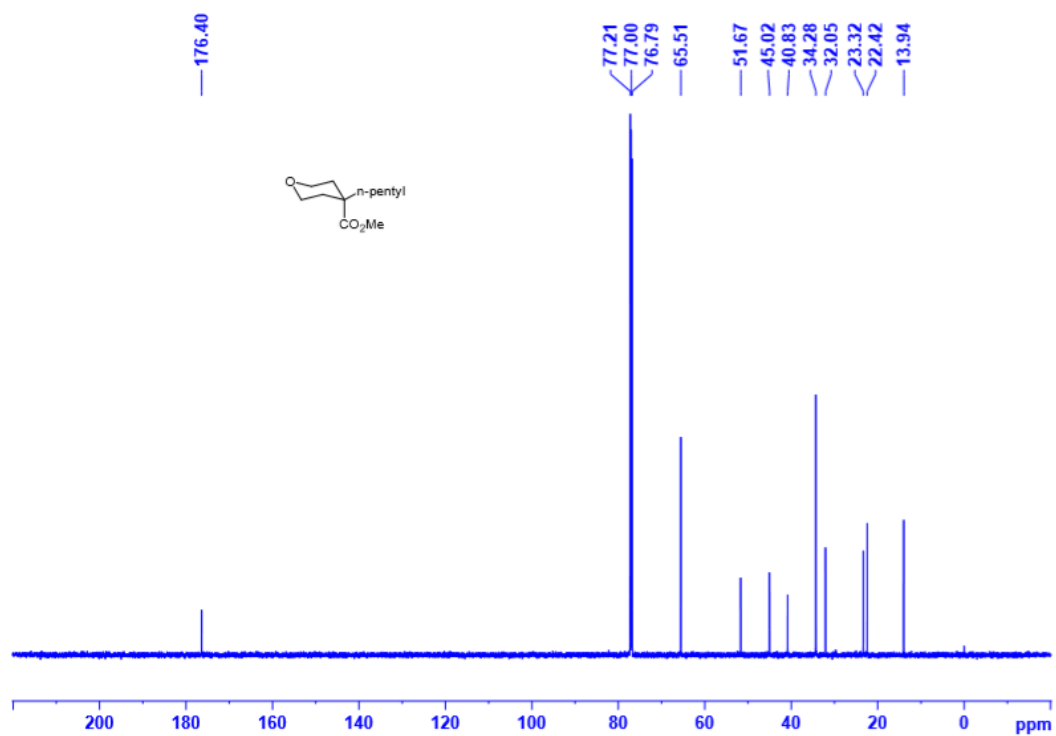
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **33** $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **33**

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **34**

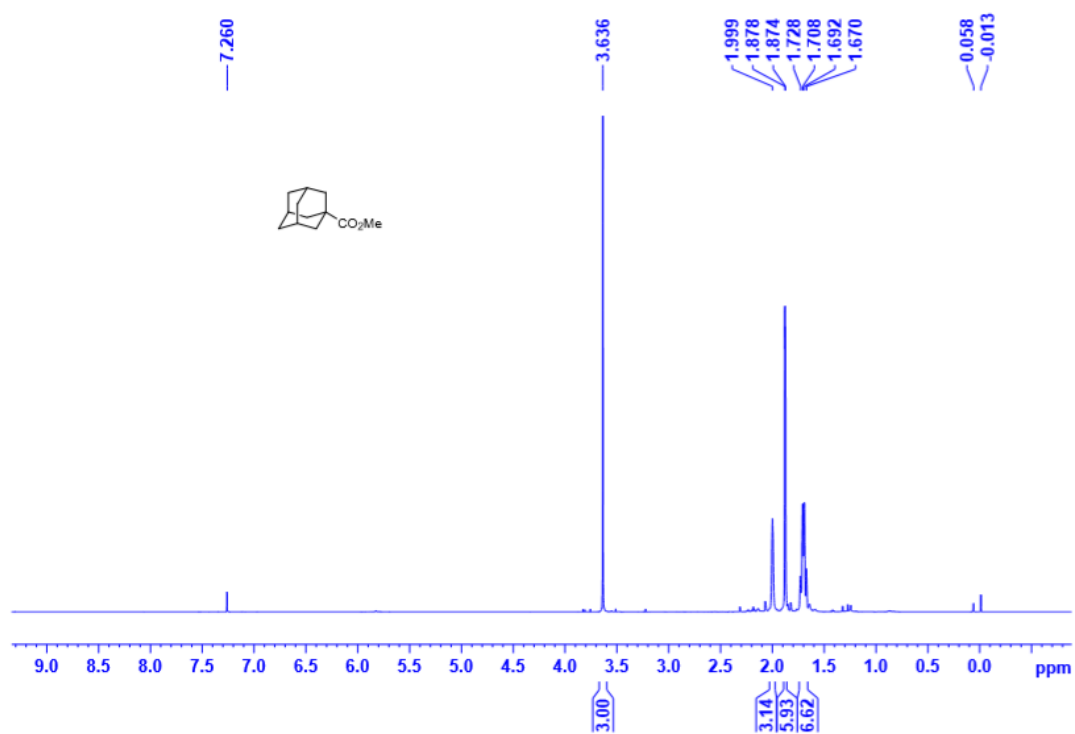


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **34**

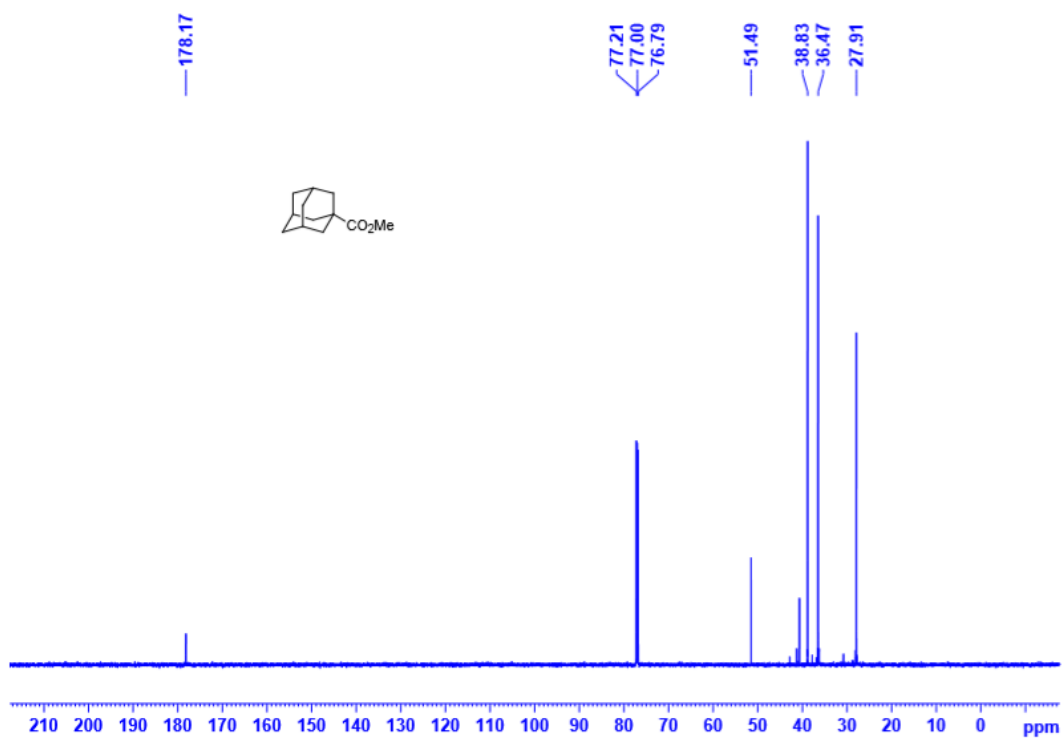


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **35** $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **35**

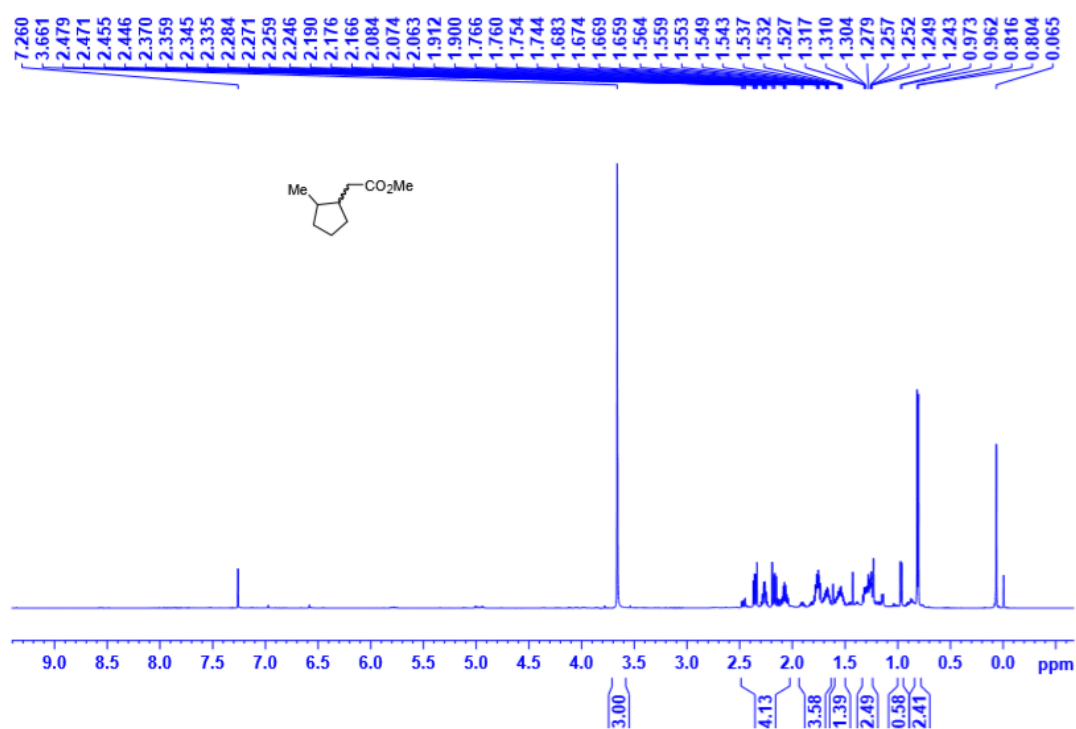
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **36**



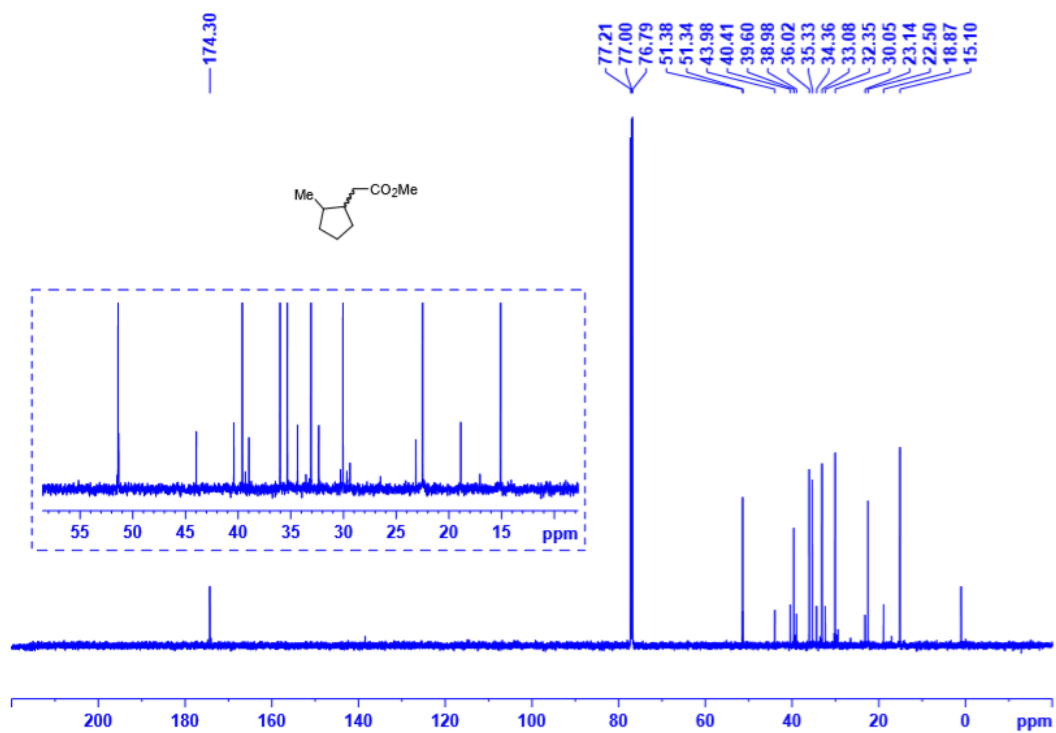
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **36**



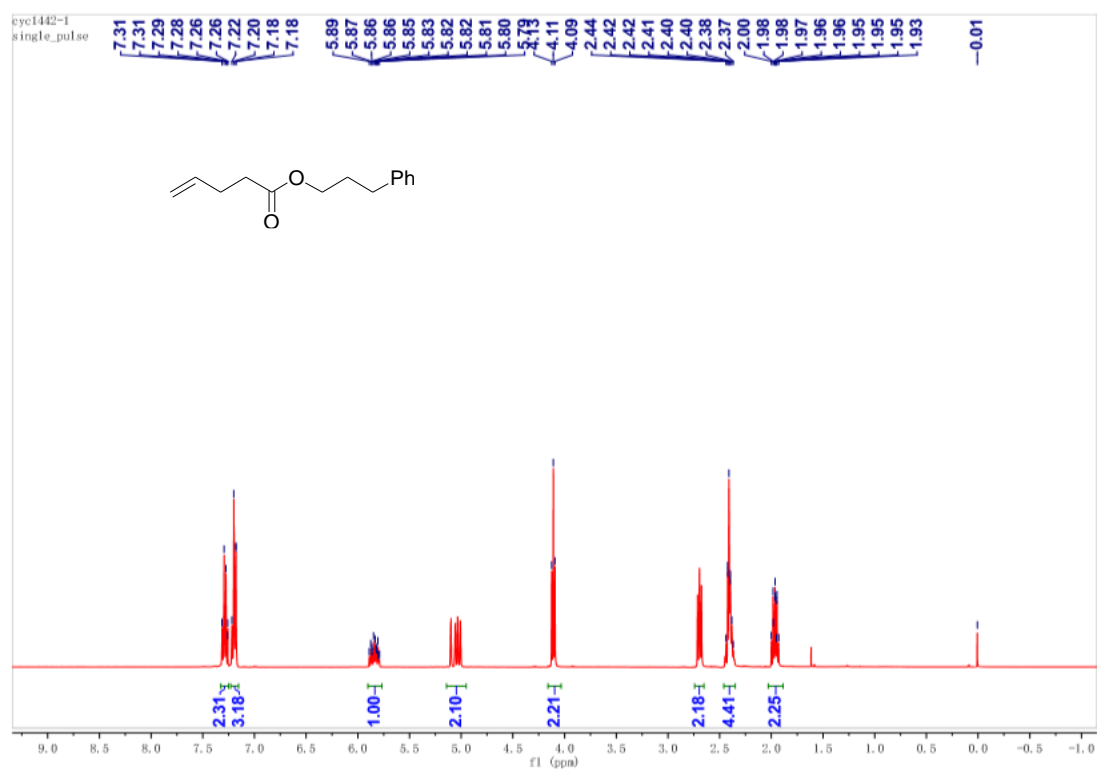
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of (2-Methyl-cyclopentyl)-acetic acid methyl ester



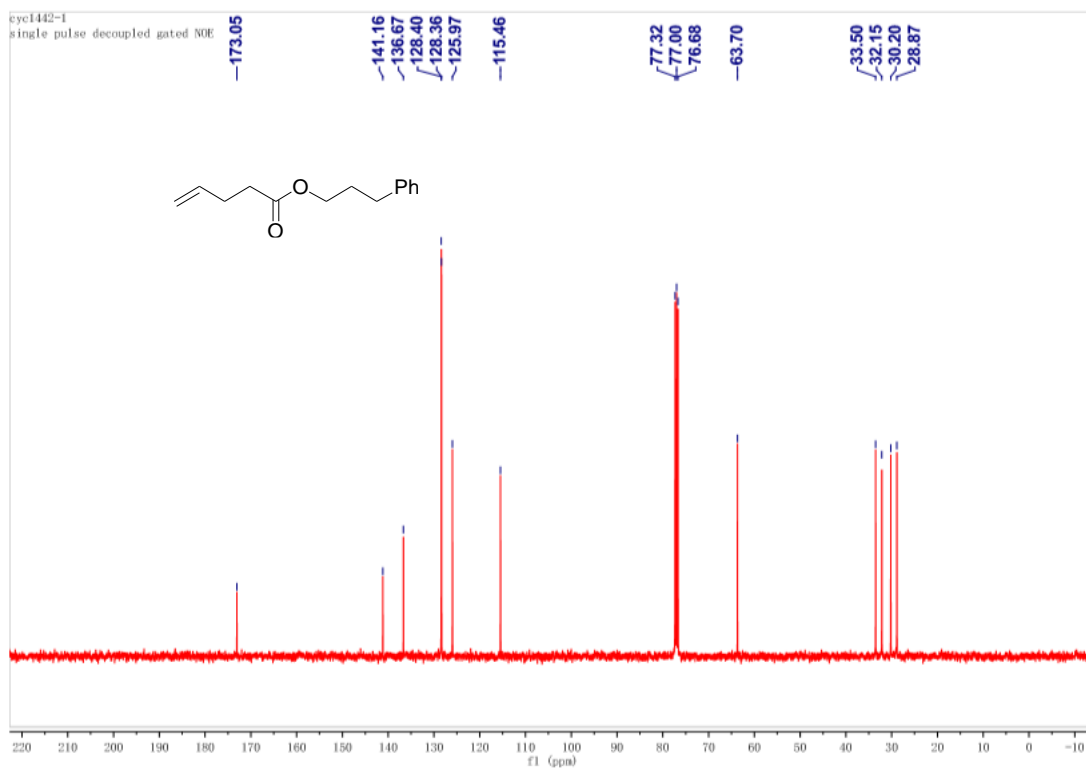
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of (2-Methyl-cyclopentyl)-acetic acid methyl ester



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of pent-4-enoic acid 3-phenyl-propyl ester



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of pent-4-enoic acid 3-phenyl-propyl ester





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