

# Electronic Supplementary Information

## Superacid $\text{BF}_3\text{-H}_2\text{O}$ promoted benzylation of arenes with benzyl alcohols and acetates initiated by the trace of water

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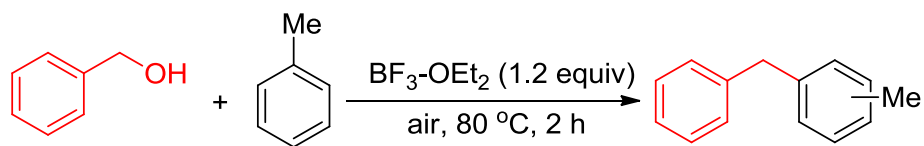
## 1. General Methods

All reactions were carried out without any precautions against air and moisture, unless otherwise specified.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a 500 MHz NMR spectrometer at 20-25 °C.  $^{11}\text{B}$  NMR spectra were recorded on a 600 MHz NMR spectrometer at 20-25 °C.  $^1\text{H}$  NMR spectra were reported in parts per million using TMS ( $\delta = 0.00$  ppm) as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constants (Hz), and integration.  $^{13}\text{C}$  NMR spectra were reported in parts per million using solvent  $\text{CDCl}_3$  ( $\delta = 77.2$  ppm) as an internal standard.  $^{11}\text{B}$  NMR spectra were reported using saturated aqueous  $\text{H}_3\text{BO}_3$  solution ( $\delta = 19.49$  ppm) as an external standard. Reactions were monitored by TLC. All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified.

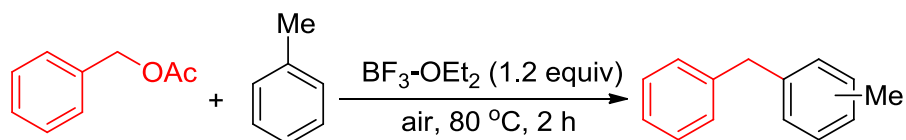
*Toluene distillation:* Toluene purchased from chemical supplier was firstly dried over 4 Å molecular sieve for one week, and then transferred to distillation apparatus under nitrogen protection. Na slice was added, and after reflux for half a day, dry toluene was collected for use.

## 2. Experimental Procedures

### 2.1 Typical procedure for benzylation reaction



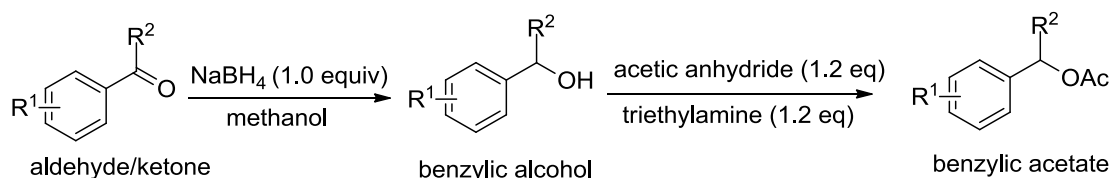
**Method A:** In a round-bottom flask, phenylmethanol (108.1 mg, 1.0 mmol) and  $\text{BF}_3\text{-OEt}_2$  (151  $\mu\text{L}$ , 1.2 mmol) were dissolved in toluene (2.0 mL). After stirring for 2 h at  $80^\circ\text{C}$  in atmosphere, the rest toluene was removed under vacuum by a rotary evaporator. The residue was isolated by column chromatography on silica gel using petroleum ether as eluent to give colorless oil.



**Method B:** In a round-bottom flask, benzyl acetate (150.2 mg, 1.0 mmol) and  $\text{BF}_3\text{-OEt}_2$  (151  $\mu\text{L}$ , 1.2 mmol) were dissolved in toluene (2.0 mL). After stirring for 2 h at  $80^\circ\text{C}$  in atmosphere, the rest toluene was removed under vacuum by a rotary evaporator. The residue was isolated by column chromatography on silica gel using petroleum ether as eluent to give colorless oil.

The same procedure was utilized for all the benzylation reactions unless otherwise noted. A small sample in  $\text{CDCl}_3$  solution was taken for NMR analysis.

### 2.2 Typical procedure for preparation of 1-phenylethanol and 1-phenylethyl acetate



Step 1: To a solution of acetophenone (3.60 g, 30.0 mmol) and methanol (20 mL) was added sodium borohydride (1.14g, 30.0 mmol) in portions under ice bath. The mixture was stirred at room temperature for 2.0 h, and quenched with diluted hydrochloric acid. The extra methanol was removed in vacuo and the residue was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL×3). The combined organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure to provide the crude product. The crude product was purified by column chromatography using 1:15 (v/v) EtOAc-petroleum ether as eluent to give the corresponding 1-phenylethanol (colorless oil, 2.93 g, 80% yield).

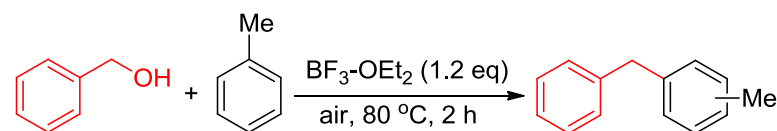
Step 2: To a round-bottom flask was added a solution of 1-phenylethanol (1.22g, 10.0 mmol), acetic anhydride (1.13 mL, 12.0 mmol) and triethylamine (1.68 mL, 12.0 mmol). The mixture was then stirred at room temperature for 2.0 h. The crude product was then purified by column chromatography using 1:40 (v/v) EtOAc-petroleum ether as eluent to give 1-phenylethyl acetate (light yellow oil, 1.48g, 90% yield).

The same procedure was utilized for all the synthesis of benzylic alcohols and acetates.

### 3. Optimization of reaction conditions

#### 3.1 Investigation on solvent effects

**Table S1.** Solvent effects on benzylation reaction of phenylmethanol and toluene.<sup>[a]</sup>



Entry	Solvent	Amount (mL)	Yield (%) <sup>[b]</sup>
1	CH <sub>3</sub> CN	1.5	18

2	Et <sub>2</sub> O	1.5	32
3	DCE	1.5	40
4	DCM	1.5	44
5	CHCl <sub>3</sub>	1.5	58
6 <sup>[c]</sup>	DMF/CH <sub>3</sub> OH/DMSO	1.5/1.5/1.5	N. R <sup>[d]</sup>
7 <sup>[e]</sup>	toluene	2.0	89

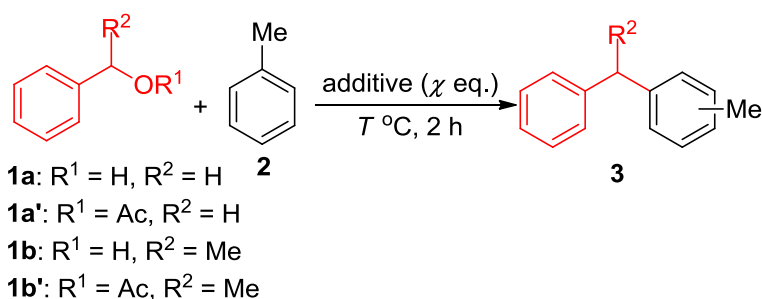
[a] Conditions: phenylmethanol (1.0 mmol), BF<sub>3</sub>-OEt<sub>2</sub> (1.2 mmol) and Toluene (0.5 mL, 4.6 mmol) in the solvent (specified amount) at 80 °C for 2 h in air. [b] Yields of isolated products. [c] DMF, CH<sub>3</sub>OH and DMSO are utilized as solvent respectively. [d] N. R = no reaction. [e] Toluene is employed as solvent as well as reactant.

### 3.2 Investigation on the influences of boron fluorides, amount and temperature

We chose the reaction of simple benzyl alcohol (**1a**) with toluene (**2**) as a starting point for our investigation. The treatment of benzyl alcohol (**1a**) with 20 mol% BF<sub>3</sub>-THF only yielded trace amounts of desired product **3** (Table 2S, entry 2). Increasing the amount of BF<sub>3</sub>-THF to 1.0 equivalent resulted in a significant increase in yield giving 71% of **3** as a mixture isomers (Table 2S, entry 3). 1.2 Equivalents resulted in an increased yield of 82% and a similar ratio of isomers (Table 2S, entry 4). Increasing the amount of BF<sub>3</sub>-THF beyond 1.2 equivalents had no beneficial effects on neither the yield nor the ratio of observed products **3** (Table 2S, entry 5). Simply changing to BF<sub>3</sub>-Et<sub>2</sub>O resulted in an improvement of the yield giving 89% of the desired product (Table 2S, entry 6). Again, this had no influence on the product distribution, indicating a cationic intermediate. Yields could be improved when increasing the amount of BF<sub>3</sub>-Et<sub>2</sub>O reaching near quantitative yields (Table 2S, entries 7, 8 and 10). By using 2.0 equivalents we could also use benzyl acetate (**1a'**), 1-phenyl ethanol (**1b**) and 1-phenyl ethylacetate (**1b'**) (Table 2S, entries 9, 15 and 16). The yields were excellent for all three benzyl donors. As expected the

regioselectivities were significantly better favoring the *para*-product **3** when using sterically more encumbered **1b** and **1b'**. Increased reaction temperatures of 100 and 120 °C proved to be less favorable as the yields were slightly lower compared to reactions run at 80 °C (Table 2S, entries 12 and 13). In agreement with the report by Schäfer and Bode, we observed only 6% NMR-yield of the desired product when running the reaction at 25 °C (Table 2S, entry 14). In an attempt to reduce the amount of arene we tested CHCl<sub>3</sub> as a solvent which resulted in a diminished, yet promising yield of 58% (Table 2S, entry 11).

**Table S2.** Optimization of reaction conditions.<sup>[a]</sup>



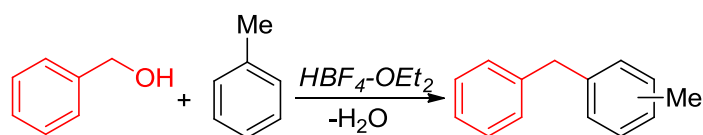
Entry	<b>1</b>	Additive	<i>X</i>	<i>T</i> [°C]	Yield [%] <sup>[b]</sup> ratio ( <i>o</i> - : <i>p</i> - : <i>m</i> -) <sup>[c]</sup>
1	<b>1a</b>	-	-	80	0
2 <sup>[d]</sup>	<b>1a</b>	BF <sub>3</sub> -THF	0.2	80	2 (-)
3	<b>1a</b>	BF <sub>3</sub> -THF	1.0	80	71 (42:52:6)
4	<b>1a</b>	BF <sub>3</sub> -THF	1.2	80	82 (40:54:6)
5	<b>1a</b>	BF <sub>3</sub> -THF	1.5	80	78 (40:52:8)
6	<b>1a</b>	BF <sub>3</sub> -OEt <sub>2</sub>	1.2	80	89 (42:53:5)
7	<b>1a</b>	BF <sub>3</sub> -OEt <sub>2</sub>	1.5	80	91 (44:50:6)
8	<b>1a</b>	BF <sub>3</sub> -OEt <sub>2</sub>	2.0	80	96 (41:53:6)
9	<b>1a'</b>	BF <sub>3</sub> -OEt <sub>2</sub>	2.0	80	86 (42:51:7)

10	<b>1a</b>	BF <sub>3</sub> -OEt <sub>2</sub>	2.5	80	93 (41:53:6)
11 <sup>[e]</sup>	<b>1a</b>	BF <sub>3</sub> -OEt <sub>2</sub>	1.2	80	58 (44:49:7)
12	<b>1a</b>	BF <sub>3</sub> -OEt <sub>2</sub>	1.2	120	80 (41:52:7)
13	<b>1a</b>	BF <sub>3</sub> -OEt <sub>2</sub>	1.2	100	81 (41:52:7)
14 <sup>[d]</sup>	<b>1a</b>	BF <sub>3</sub> -OEt <sub>2</sub>	1.2	25	6 (-)
15	<b>1b</b>	BF <sub>3</sub> -OEt <sub>2</sub>	2.0	80	91 (5:90:5)
16 <sup>[f]</sup>	<b>1b'</b>	BF <sub>3</sub> -OEt <sub>2</sub>	2.0	80	89 (12:88)

[a] Conditions: benzylic alcohols or acetates (**1**; 1.0 mmol), toluene (**2**; 2.0 mL), additive (specified), temperature (specified), 2 h in air. [b] Yields of isolated products. [c] Isomer ratios determined by <sup>13</sup>C NMR. [d] Yield determined by <sup>1</sup>H NMR using 1,3,5-trimethylbenzene as an internal standard. [e] Toluene (**2**, 0.5 mL, 4.6 mmol), CHCl<sub>3</sub> (1.5 mL). [f] No *m*-isomer was detected.

### 3.3 Investigation on the influences of HBF<sub>4</sub>-OEt<sub>2</sub>

**Table 3S.** Investigation on the amount of HBF<sub>4</sub>-OEt<sub>2</sub>.<sup>[a]</sup>

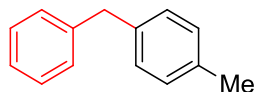


Entry	Amount (eq.)	Yield (%)
1	0.2	35
2	1.0	76
3	1.2	87 (87) <sup>[b]</sup>
4	1.5	87

[a] Conditions: benzylic alcohols or acetates (**1**; 1.0 mmol), toluene (**2**; 2.0 mL), HBF<sub>4</sub>-OEt<sub>2</sub> (specified), 80 °C, 2 h in air. [b] Under N<sub>2</sub>.

#### 4. $^1\text{H}$ - and $^{13}\text{C}$ -NMR analytical data

Only the structures of the major products are shown. The ratios of regioisomers were determined by  $^{13}\text{C}$  NMR.



**1-benzyl-4-methylbenzene (3a)**<sup>4c</sup>: Method A: Prepared from phenylmethanol (108.1 mg, 1.0 mmol) and toluene (2.0 mL);

isolated as colorless oil (162.2 mg, 89%, *o*- : *p*- : *m*- = 42:53:5 mixture of isomers).

Method B: Prepared from benzyl acetate (150.2 mg, 1.0 mmol) and toluene (2.0 mL);

isolated as colorless oil (145.8 mg, 80%, *o*- : *p*- = 42:58 mixture of isomers).  $^1\text{H}$  NMR

(500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.25-7.24 (m, 3.3H, ArH), 7.17-7.16 (m, 3.3H, ArH),

7.14-7.13 (m, 1.9H, ArH), 7.13-7.09 (m, 2.4H, ArH), 7.07 (s, 3.5H, ArH), 6.97-7.00

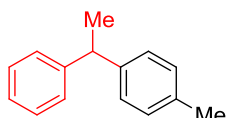
(m, 0.4H, ArH), 3.97 (s, 1.4H,  $\text{CH}_2$ ), 3.94 (s, 2H,  $\text{CH}_2$ ), 2.30 (s, 3H,  $\text{CH}_3$ ), 2.23 (s,

2.1H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 141.6 (major), 140.6 (minor),

139.1 (minor), 138.3 (major), 136.8 (minor), 135.7 (major), 130.5, 130.1 (minor),

129.3 (major), 129.1, 129.0 (major), 128.9 (major), 128.6(1), 128.5(7), 126.6, 126.2

(major), 126.1, 41.7 (major), 39.6 (minor), 21.1 (major), 19.8 (minor).



**1-methyl-4-(1-phenylethyl)benzene (3b)**<sup>17</sup>: Method A: Prepared

from 1-phenylethanol (122.2 mg, 1.0 mmol) and toluene (2.0 mL);

isolated as colorless oil (178.6 mg, 91%, *o*- : *p*- : *m*- = 5:90:5 mixture of isomers).

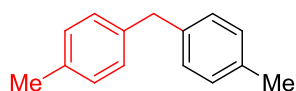
Method B: Prepared from 1-phenylethyl acetate (164.2 mg, 1.0 mmol) and toluene

(2.0 mL); isolated as colorless oil (174.7 mg, 89%, *o*- : *p*- = 12:88 mixture of isomers).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.27-7.24 (m, 2.4H, ArH), 7.21-7.19 (m, 2.1H,



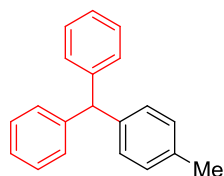
ArH), 7.17-7.14 (m, 1.6H, ArH), 7.11-7.07 (m, 4.1H, ArH), 4.30 (q,  $J = 7.0$  Hz, 0.1H, CH), 4.10 (q,  $J = 7.0$  Hz, 1H, CH), 2.29 (s, 3.1H, CH<sub>3</sub>), 2.22 (s, 0.3H, CH<sub>3</sub>), 1.61 (d,  $J = 7.0$  Hz, 3.5H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 146.8 (major), 143.6 (major), 135.6 (major), 129.2 (major), 128.5 (major), 127.7 (major), 127.6 (major), 126.1 (major), 44.5 (major), 22.1 (major), 21.1 (major).



**di-*p*-tolylmethane (3c)<sup>17</sup>:** Method A: Prepared from *p*-tolylmethanol (122.2 mg, 1.0 mmol) and toluene (2.0 mL);

isolated as colorless oil (182.5 mg, 93%, *o*- : *p*- : *m*- = 4:69:27 mixture of isomers).

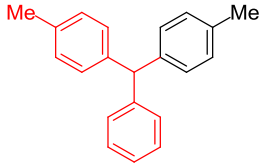
Method B: Prepared from 4-methylbenzyl acetate (164.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (190.1 mg, 97%, *o*- : *p*- : *m*- = 4:66:30 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.06 (s, 8H, ArH), 3.88 (s, 2H, CH<sub>2</sub>), 2.29 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 139.3 (minor), 138.5 (major), 137.4 (minor), 136.7 (minor), 135.6 (major), 135.5 (minor), 130.4 (minor), 130.0 (minor), 129.3 (major), 128.9 (major), 128.8 (minor), 126.5 (minor), 126.1 (minor), 41.2 (major), 39.2 (minor), 21.2 (major), 19.8 (minor).



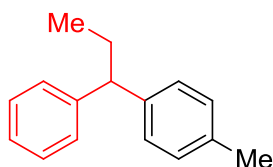
**(*p*-tolylmethylene)dibenzene (3d)<sup>4e</sup>:** Method A: Prepared from diphenylmethanol (184.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as white solid (237.7 mg, 92%, *o*- : *p*- =

9:91 mixture of isomers). Method B: Prepared from benzhydryl acetate (226.3 mg, 1.0 mmol) and toluene (2.0 mL); isolated as white solid (229.9 mg, 89%, *o*- : *p*- = 13:87 mixture isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm)

7.28-7.25 (m, 4.7H, ArH), 7.21-7.18 (m, 2.6H, ArH), 7.17-7.15 (m, 0.3H, ArH)  
 7.12-7.08 (m, 6.3H, ArH) 7.06-7.05 (m, 0.6H, ArH), 7.01-6.99 (m, 2H, ArH),  
 5.67 (s, 0.1H, CH), 5.51 (s, 1H, CH), 2.31 (s, 3H, CH<sub>3</sub>), 2.21 (s, 0.4H, CH<sub>3</sub>);  
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 144.3 (major), 141.1 (major), 136.0  
 (major), 129.6 (major), 129.5 (major), 129.2 (major), 128.4 (major), 126.4  
 (major), 56.6 (major), 21.2 (major).

**4,4'-(phenylmethylene)bis(methylbenzene) (3e):** Method  

 A: Prepared from phenyl(*p*-tolyl)methanol (198.3 mg, 1.0  
 mmol) and toluene (2.0 mL); isolated as colorless oil

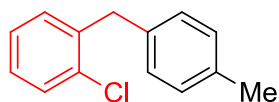
(247.9 mg, 91%, *o*- : *p*- = 12:88 mixture of isomers). Method B: Prepared from  
 phenyl(*p*-tolyl)methyl acetate (240.3 mg, 1.0 mmol) and toluene (2.0 mL);  
 isolated as colorless oil (248.0 mg, 96%, *o*- : *p*- = 11:89 mixture of isomers). <sup>1</sup>H  
 NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.25-7.13 (m, 3H, ArH), 7.25-7.13 (m, 5H,  
 ArH), 7.11-7.06 (m, 6H, ArH), 7.11-6.81 (m, 8H, ArH), 7.00-6.98 (m, 4H,  
 ArH), 5.62 (s, 1H, CH), 5.46 (s, 1H, CH), 2.29 (s, 6H, CH<sub>3</sub>), 2.29 (s, 6H, CH<sub>3</sub>);  
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 144.5 (major), 143.8 (minor), 142.7  
 (minor), 141.6 (minor), 141.3 (major), 140.5 (minor), 138.2 (minor), 136.7  
 (minor), 135.9 (major), 129.7 (minor), 129.6 (minor), 129.5 (major), 129.4  
 (major), 129.1 (major), 129.0 (minor), 128.9 (minor), 128.6 (minor), 128.4  
 (major), 126.5 (minor), 126.3 (major), 126.1 (minor), 125.9 (minor), 56.3  
 (major), 53.3 (minor), 21.2 (minor), 21.2 (major), 20.1 (minor).



**methyl-4-(1-phenylpropyl)benzene (3f):** Method A:

Prepared from 1-phenylpropan-1-ol (136.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (191.4 mg,

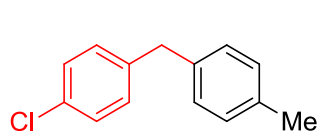
91%, *o*- : *p*- = 7:93 mixture of isomers). Method B: Prepared from 1-phenylpropyl acetate (178.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (187.0 mg, 89%, *o*- : *p*- = 11:89 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.27-7.21 (m, 4H, ArH), 7.16-7.07 (m, 5H, ArH), 3.75 (t, *J* = 7.5 Hz, 1H, CH), 2.29 (s, 3H, CH<sub>3</sub>), 2.05 (quin, *J* = 7.0 Hz, 2H, CH<sub>2</sub>), 0.89 (t, *J* = 7.5 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 145.6 (major), 142.4 (major), 135.6 (major), 129.2 (major), 128.5 (major), 128.0 (major), 127.9 (major), 126.1 (major), 53.0 (major), 28.8 (major), 21.1 (major), 13.0 (major).



**chloro-2-(4-methylbenzyl)benzene (3g)**<sup>30</sup>: Method A:

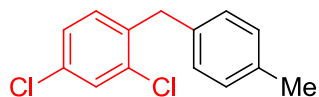
Prepared from (2-chlorophenyl)methanol (142.6 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (204.1 mg, 94%, *o*- : *p*- : *m*- = 42:49:9 mixture of isomers). Method B: Prepared from 2-chlorobenzyl acetate (184.6 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (199.8 mg, 92%, *o*- : *p*- : *m*- = 38:48:14 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.23-7.21 (m, 3.5H, ArH), 7.16 (s, 2.2H, ArH), 7.10-7.08 (m, 4.1H, ArH), 7.05-7.03 (m, 3.3H, ArH), 6.96-6.94 (m, 0.3H, ArH), 3.93 (s, 1.5H, CH<sub>2</sub>), 3.89 (s, 2H, CH<sub>2</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 2.21 (s, 2.1H, CH<sub>3</sub>);

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 140.1, 139.1, 138.5, 138.4 (minor) 137.7, 136.7 (minor), 136.0 (major), 132.0, 131.9 (minor), 130.6, 130.4 (minor), 130.2, 130.1, 129.8, 129.4, 128.9, 128.6(9), 128.6(7), 127.2, 126.9, 126.3, 126.1, 41.4, 41.0 (major), 39.0 (minor), 21.6, 21.2 (major), 19.8 (minor).



**chloro-4-(4-methylbenzyl)benzene (3h)**<sup>30</sup>: Method A:

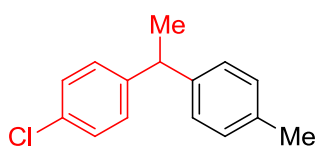
Prepared from (4-chlorophenyl)methanol (142.6 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (221.1 mg, 95%, *o*- : *p*- : *m*- = 41:51:8 mixture of isomers). Method B: Prepared from 4-chlorobenzyl acetate (184.6 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (221.1 mg, 95%, *o*- : *p*- : *m*- = 42:44:14 mixture of isomers).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.23-7.21 (m, 3.5H, ArH), 7.18-7.12 (m, 2.2H, ArH), 7.10-7.06 (m, 4.2H, ArH), 7.04-7.02 (m, 3.3H, ArH), 3.93 (s, 1.5H,  $\text{CH}_2$ ), 3.89 (s, 2H,  $\text{CH}_2$ ), 2.31 (s, 3H,  $\text{CH}_3$ ), 2.21 (s, 2.1H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 140.1 (major), 139.1 (minor), 138.5 (minor), 137.7 (major), 136.7 (minor), 136.0 (major), 132.0 (major), 131.9 (minor), 130.6, 130.4, 130.2, 130.1, 129.4, 128.9, 128.6(9), 128.6(6), 126.9, 126.3, 41.0 (major), 39.0 (minor), 21.2 (minor), 19.8 (major).



**2,4-dichloro-1-(4-methylbenzyl)benzene (3i):**

Method A: Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (243.6 mg, 97%, *o*- : *p*- : *m*- = 40:45:15 mixture of

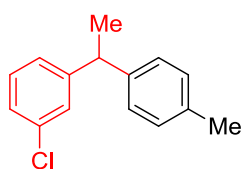
isomers). Method B: Prepared from 2,4-dichlorobenzyl acetate (218.0 mg, 1.0 mmol) and toluene (2.0 mL), isolated as colorless oil (236.0 mg, 94%, *o*- : *p*- : *m*- = 40:45:15 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.41-7.38 (d, *J* = 16.5 Hz, 1H, ArH), 7.41-7.38 (d, *J* = 16.5 Hz, 1H, ArH), 7.24-7.18 (m, 1H, ArH), 7.24-7.18 (m, 1H, ArH), 7.16-7.13 (m, 1H, ArH), 7.16-7.13 (m, 1H, ArH), 7.11-7.09 (m, 2H, ArH), 7.06-6.95 (m, 2H, ArH), 7.06-6.95 (m, 3H, ArH), 6.80-6.78 (m, 1H, ArH), 4.01 (s, 2H, CH<sub>2</sub>), 4.01 (s, 2H, CH<sub>2</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 2.21 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 137.8 (minor), 136.9 (minor), 136.0 (minor), 135.0 (minor), 132.7 (minor), 132.0 (minor), 131.8 (major), 131.1 (major), 130.6 (major), 129.9 (major), 129.5 (major), 129.4 (major), 129.3 (major), 129.0 (major), 128.6 (minor), 128.4 (minor), 127.4 (minor), 127.2 (major), 127.0 (minor), 126.4 (major), 126.1 (minor), 125.5 (minor), 38.4 (major), 36.4 (minor), 21.2 (minor), 19.6 (major).



**chloro-4-(1-p-tolylethyl)benzene (3j):** Method A:

Prepared from 1-(4-chlorophenyl)ethanol (156.6 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (196.1 mg, 85 %, *o*- : *p*- : *m*- = 9:85:6 mixture of isomers). Method B: Prepared from 1-(4-chlorophenyl)ethyl acetate (198.6 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (209.9 mg, 91%, *o*- : *p*- : *m*- = 6:78:16 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.33-7.31 (m, 1H, ArH),

7.22-7.21 (m, 2H, ArH), 7.22-7.21 (m, 1H, ArH), 7.19-7.15 (m, 4H, ArH), 7.13-7.11 (m, 2H, ArH), 7.13-7.11 (m, 2H, ArH), 7.08-7.07 (d,  $J = 3.0$  Hz, 4H, ArH), 4.26 (q,  $J = 7.0$  Hz, 1H, ArH), 4.06 (q,  $J = 7.5$  Hz, 1H, CH), 2.29 (s, 3H, CH<sub>3</sub>), 2.19 (s, 3H, CH<sub>3</sub>), 1.58 (d,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>), 1.51 (d,  $J = 28.0$  Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 145.3 (major), 143.0 (major), 135.9 (major), 131.8 (major), 129.3 (major), 129.1 (major), 128.6 (major), 127.5 (major), 43.9 (major), 22.0 (major), 21.1 (major).

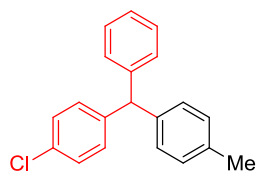


**chloro-3-(1-*p*-tolylethyl)benzene (3k)**<sup>30</sup>: Method A:

Prepared from 1-(3-chlorophenyl)ethanol (156.6 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (219.0

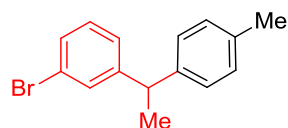
mg, 95%, *o*- : *p*- : *m*- = 12:84:4 mixture of isomers). Method B: Prepared from 1-(3-chlorophenyl)ethyl acetate (198.6 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (203.0 mg, 88%, *o*- : *p*- : *m*- = 16:80:4 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.24-7.23 (m, 1H, ArH), 7.21-7.13 (m, 4H, ArH), 7.21-7.13 (m, 1H, ArH), 7.09 (s, 4H, ArH), 7.07 (s, 4H, ArH), 7.00-6.99 (m, 2H, ArH), 4.27 (q,  $J = 7.0$  Hz, 1H, CH), 4.07 (q,  $J = 7.5$  Hz, 1H, CH), 2.30 (s, 3H, CH<sub>3</sub>), 2.21 (s, 3H, CH<sub>3</sub>), 1.59 (d,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>), 1.58 (d,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 148.9 (major), 148.9, 148.6, 143.2 (minor), 142.7 (major), 136.2 (minor), 136.0 (major), 134.3 (major), 130.7, 129.8 (major), 129.4 (major), 128.5, 128.0, 127.9

(major), 127.6 (major), 127.3, 126.8, 126.6, 126.3 (major), 126.2, 126.1, 126.0 (major), 44.7, 44.3 (major), 41.0, 22.1, 21.9, 21.7, 21.2 (major), 19.9.



**chloro-4-(phenyl(*p*-tolyl)methyl)benzene (3l):** Method A:

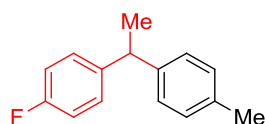
Prepared from (4-chlorophenyl)(phenyl)methanol (218.7 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (287.0 mg, 98%, *o*- : *p*- = 9:91 mixture of isomers). Method B: Prepared from (4-chlorophenyl)(phenyl)methyl acetate (260.7 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (281.1 mg, 96%, *o*- : *p*- = 11:89 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.29-7.26 (m, 2H, ArH), 7.29-7.26 (m, 2H, ArH), 7.24-7.23 (m, 3H, ArH), 7.24-7.23 (m, 3H, ArH), 7.21-7.09 (m, 4H, ArH), 7.21-7.09 (m, 4H, ArH), 7.04-7.02 (m, 2H, ArH), 7.04-7.02 (m, 2H, ArH), 6.98-6.96 (m, 2H, ArH), 6.98-6.96 (m, 2H, ArH), 5.63 (m, 1H, CH), 5.47 (s, 1H, CH), 2.32 (s, 3H, CH<sub>3</sub>), 2.19 (m, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 143.8 (major), 142.9 (major), 140.6 (major), 136.3 (major), 132.2 (major), 131.1 (major), 130.9 (major), 129.5 (major), 129.4 (major), 129.3 (major), 128.6 (major), 126.6 (major), 56.0 (major), 21.2 (major).



**bromo-3-(1-*p*-tolylethyl)benzene (3m):** Method A:

Prepared from 1-(3-bromophenyl)ethanol (201.1 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (231.1 mg, 84%, *o*- : *p*- : *m*- = 13:83:4 mixture of isomers). Method B:

Prepared from 1-(3-bromophenyl)ethyl acetate (243.1 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (250.4 mg, 91%, *o*- : *p*- : *m*- = 15:80:5 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.36 (s, 1H, ArH), 7.30 (s, 1H, ArH), 7.30 (s, 1H, ArH), 7.24-7.18 (m, 1H, ArH), 7.13 (s, 2H, ArH), 7.13 (s, 3H, ArH), 7.09 (s, 3H, ArH), 7.09 (s, 3H, ArH), 7.02-7.00 (m, 1H, ArH), 4.27 (q, *J* = 7.0 Hz, 1H, CH), 4.07 (q, *J* = 7.0 Hz, 1H, CH), 2.31 (s, 3H, CH<sub>3</sub>), 2.22 (s, 3H, CH<sub>3</sub>), 1.59 (d, *J* = 7.0 Hz, 3H, CH<sub>3</sub>), 1.58 (d, *J* = 5.5 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 149.2 (major), 143.2 (minor), 142.7 (major), 136.2 (minor), 136.0 (major), 130.9 (minor), 130.8 (major), 130.7 (minor), 130.0 (major), 129.4 (major), 129.2 (minor), 129.2 (minor), 127.6 (major), 126.8 (minor), 126.7 (minor), 126.5 (major), 126.4 (minor), 122.7 (minor), 44.3 (major), 41.0 (minor), 31.1 (minor), 21.9 (major), 21.2 (major), 19.9 (minor).

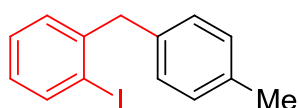


**1-fluoro-4-(1-*p*-tolylethyl)benzene (3n):** Method A:

Prepared from 1-(4-fluorophenyl)ethanol (140.1 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (180.0 mg, 84%, *o*- : *p*- : *m*- = 9:86:5 mixture of isomers). Method B: Prepared from 1-(4-fluorophenyl)ethyl acetate (182.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (173.0 mg, 81%, *o*- : *p*- : *m*- = 10:87:3 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.20-7.13 (m, 2H, ArH), 7.20-7.13 (m, 3H, ArH), 7.09 (s, 4H, ArH), 7.08-7.07 (m, 1H, ArH), 7.00-6.89

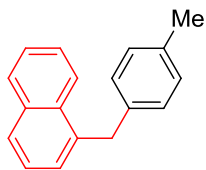


(m, 2H, ArH), 7.00-6.89 (m, 4H, ArH), 4.29 (q,  $J = 7.0$  Hz, 1H, CH), 4.09 (q,  $J = 7.5$  Hz, 1H, CH), 2.30 (s, 3H, CH<sub>3</sub>), 2.21 (s, 3H, CH<sub>3</sub>), 1.59 (d,  $J = 7.5$  Hz, 3H, CH<sub>3</sub>), 1.59 (d,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.4 (major), 143.4 (major), 135.8 (major), 129.3 (major), 129.1 (major), 127.6 (major), 115.3 (major), 115.1 (major), 43.8 (major), 22.3 (major), 21.1 (major).

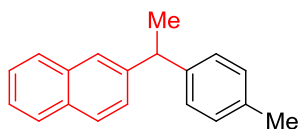


**1-iodo-2-(4-methylbenzyl)benzene (3o):** Method A:

Prepared from (2-iodophenyl)methanol (234.0 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (279.0 mg, 91%, *o*- : *p*- : *m*- = 35:53:12 mixture of isomers). Method B: Prepared from 2-iodobenzyl acetate (276.1 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (276.1 mg, 91%, *o*- : *p*- : *m*- = 34:53:13 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.87-7.85 (m, 1H, ArH), 7.87-7.82 (m, 1H, ArH), 7.24-7.17 (m, 2H, ArH), 7.24-7.17 (m, 2H, ArH), 7.16-7.13 (m, 1H, ArH), 7.10-7.02 (m, 4H, ArH), 7.00-6.93 (m, 2H, ArH), 6.90-6.86 (m, 1H, ArH), 6.90-6.86 (m, 1H, ArH), 6.85-6.83 (m, 1H, ArH), 4.05 (s, 2H, CH<sub>2</sub>), 4.00 (s, 2H, CH<sub>2</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 2.22 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 139.7 (major), 130.5 (major), 129.8 (major), 129.4 (major), 129.1 (major), 128.5 (major), 128.1 (major), 126.8 (major), 126.3 (major), 101.5 (major), 46.3 (major), 21.2 (major).

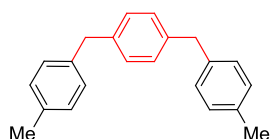


**1-(4-methylbenzyl)naphthalene (3p):** Method A: Prepared from naphthalen-1-ylmethanol (158.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (164.8 mg, 71%, *o*- : *p*- = 16:84 mixture of isomers). Method B: Prepared from naphthalen-1-ylmethyl acetate (200.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (144.0 mg, 62%, *o*- : *p*- : *m*- = 17:78:5 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 8.00-7.98 (m, 1H, ArH), 8.00-7.98 (m, 1H, ArH), 7.85-7.83 (m, 1H, ArH), 7.85-7.83 (m, 1H, ArH), 7.75-7.73 (m, 1H, ArH), 7.74 (d, *J* = 8.5 Hz, 1H, ArH), 7.48-7.43 (m, 2H, ArH), 7.48-7.43 (m, 2H, ArH), 7.41-7.34 (m, 1H, ArH), 7.41-7.34 (m, 1H, ArH), 7.28-7.26 (m, 1H, ArH), 7.28-7.26 (m, 1H, ArH), 7.23-7.02 (m, 4H, ArH), 7.23-7.02 (m, 4H, ArH), 4.40 (s, 2H, CH<sub>2</sub>), 4.40 (s, 2H, CH<sub>2</sub>), 2.32 (s, 3H, CH<sub>3</sub>), 2.29 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 138.6 (major), 137.7 (major), 136.3 (major), 134.1 (major), 132.3 (major), 130.3 (major), 129.8 (major), 129.3 (major), 128.8 (major), 127.4 (major), 127.2 (major), 126.1 (major), 125.7 (major), 124.5 (major), 38.8 (major), 36.4 (minor), 21.2 (major), 19.8 (minor).



**2-(1-*p*-tolylethyl)naphthalene (3q):** Method A: Prepared from 1-(naphthalen-2-yl)ethanol (172.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (145.4 mg, 59%, *o*- : *p*- = 9:91 mixture of isomers). Method B: Prepared from

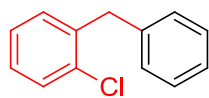
1-(naphthalen-2-yl)ethyl acetate (214.3 mg, 1.0 mmol) and toluene (2.0 mL); isolated as colorless oil (165.0 mg, 67%, *o*- : *p*- = 8:92 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.88-7.76 (m, 2H, ArH), 7.88-7.76 (m, 2H, ArH), 7.74-7.71 (m, 2H, ArH), 7.74-7.71 (m, 2H, ArH), 7.50-7.35 (m, 2H, ArH), 7.50-7.35 (m, 2H, ArH), 7.30-7.17 (m, 1H, ArH), 7.30-7.17 (m, 1H, ArH), 7.15-7.13 (m, 2H, ArH), 7.15-7.13 (m, 2H, ArH), 7.09-7.05 (m, 2H, ArH), 7.09-7.05 (m, 2H, ArH), 4.47 (q, *J* = 7.0 Hz, 1H, CH), 4.26 (q, *J* = 7.0 Hz, 1H, CH), 2.30 (s, 3H, CH<sub>3</sub>), 2.26 (s, 3H, CH<sub>3</sub>), 1.70 (d, *J* = 7.5 Hz, 3H, CH<sub>3</sub>), 1.69 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 144.2 (major), 143.4 (major), 135.8 (major), 133.7 (major), 132.2 (major), 129.3 (major), 128.1 (major), 127.9 (major), 127.8 (major), 127.7 (major), 127.0 (major), 126.1 (major), 125.5 (major), 125.4 (major), 44.6 (major), 22.0 (major), 21.2 (major).



**1,4-bis(4-methylbenzyl)benzene (3r):** Method A:

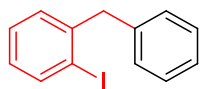
Prepared from 1,4-phenylenedimethanol (138.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as white solid (92.0 mg, 32 %, *o*- : *p*- : *m*- = 33:62:5 mixture of isomers). Method B: Prepared from 1,4-phenylenebis(methylene) diacetate (222.2 mg, 1.0 mmol) and toluene (2.0 mL); isolated as white solid (243.2 mg, 85%, *o*- : *p*- : *m*- = 35:60:5 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.15-7.14 (m, 6H, ArH), 7.10-7.08 (m, 12H, ArH), 7.04-7.03 (m, 6H, ArH), 3.95 (s, 4H, CH<sub>2</sub>), 3.91 (s,

4H, CH<sub>2</sub>), 2.32 (s, 6H, CH<sub>3</sub>), 2.24 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 130.4 (major), 129.3 (major), 129.1 (major), 129.0 (major), 129.0 (major), 126.1 (major), 41.3 (major), 21.2 (major).



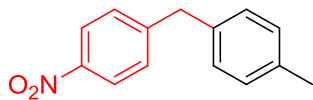
**1-benzyl-2-chlorobenzene (3s):** Prepared from (2-chlorophenyl)methanol (142.6 mg, 1.0 mmol) and benzene

(2.0 mL); isolated as colorless oil (176.3 mg, 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.37-7.36 (m, 1H, ArH), 7.30-7.27 (m, 2H, ArH), 7.23-7.14 (m, 6H, ArH), 4.10 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 139.7, 138.9, 134.4, 131.2, 129.7, 129.1, 128.6, 127.8, 127.0, 126.4, 39.4.



**1-benzyl-2-iodobenzene (3t):** Prepared from (2-iodophenyl)methanol (234.0 mg, 1.0 mmol) and

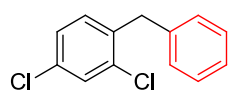
benzene (2.0 mL); isolated as colorless oil (255.9 mg, 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.84 (d, *J* = 8.0 Hz, 1H, ArH), 7.28 (q, *J* = 7.5 Hz, 2H, ArH), 7.23 (t, *J* = 7.0 Hz, 2H, ArH), 7.17 (d, *J* = 7.5 Hz, 2H, ArH), 7.09 (d, *J* = 7.5 Hz, 1H, ArH), 6.89 (t, *J* = 7.5 Hz, 1H, ArH), 4.10 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 143.8, 139.7, 130.5, 129.2, 128.6, 128.5, 128.2, 126.4, 101.5, 46.6.



**1-methyl-4-(4-nitrobenzyl)benzene (3u)** Prepared from (4-nitrophenyl)methanol (153.1 mg, 1.0 mmol)

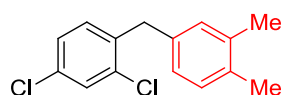
and toluene (4 ml); isolated as colorless oil (47.9 mg, 21%, *o*- : *p*- : *m*- = 18:41:41 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 8.1-8.11 (m,

3.2H, ArH), 7.33-7.32 (m, 2.01H, ArH), 7.27-7.25 (m, 1.47H, ArH), 7.20-6.98 (m, 6.51H, ArH), 4.08 (s, 1.33H, CH<sub>2</sub>), 4.03 (s, 2H, CH<sub>2</sub>), 2.33 (s, 3H, CH<sub>3</sub>), 2.20 (s, 1.96H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 149.4, 149.3(8), 149.2, 149.1(9), 148.6, 148.5, 146.6, 146.5(9), 139.3, 138.7, 137.3, 136.7, 136.5, 136.3, 130.8, 130.2, 129.9, 129.8, 129.7(5), 129.6(6), 129.5(6), 129.0, 128.9, 127.7, 127.4, 126.5, 126.2, 123.9, 123.8, 41.8, 41.5, 39.6, 21.6, 21.2, 19.8.



**1-benzyl-2,4-dichlorobenzene (4a):** Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and

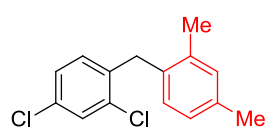
benzene (2.0 mL); isolated as colorless oil (220.5 mg, 93%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.38 (d, *J* = 2.0 Hz, 1H, ArH), 7.30-7.27 (m, 2H, ArH), 7.23-7.20 (m, 1H, ArH), 7.16-7.14 (m, 3H, ArH), 7.06-7.04 (m, 1H, ArH), 4.05 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 139.1, 137.5, 135.0, 132.8, 131.9, 129.4, 129.1, 128.8, 127.3, 126.6, 38.8.



**2,4-dichloro-1-(3,4-dimethylbenzyl)benzene (4b) :**

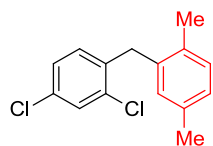
Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and *o*-xylene (2.0 mL); isolated as colorless oil (241.0 mg, 91%, 3- : 4- = 34:66 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.40 (d, *J* = 2.0 Hz, 1H, ArH), 7.37 (d, *J* = 2.0 Hz, 1H, ArH), 7.14-7.01 (m, 3H, ArH), 7.14-7.01 (m, 3H, ArH), 6.93 (s, 1H, ArH), 6.89-6.86 (m, 1H, ArH), 6.89-6.85 (m, 1H, ArH), 6.76-6.74 (m, 1H, ArH), 4.02 (s, 2H, ArH), 3.98 (s, 2H, CH<sub>2</sub>),

2.30 (s, 3H, CH<sub>3</sub>), 2.22 (s, 6H, CH<sub>3</sub>), 2.08 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 137.9, 136.9, 136.5, 134.8, 132.6, 131.9, 130.4, 130.0, 129.4, 128.8, 127.2, 126.4, 38.3 (major), 37.0 (minor), 20.8 (minor), 20.0 (major), 19.5 (major), 15.4 (minor).



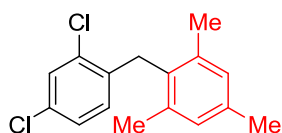
**2,4-dichloro-1-(2,4-dimethylbenzyl)benzene (4c):**

Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and *m*-xylene (2.0 mL); isolated as colorless oil (238.7 mg, 90%, 2- : 4- : 5- = 16:79:5 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.40-7.39 (d, *J* = 2.0 Hz, 1H, ArH), 7.17-6.95 (m, 3H, ArH), 6.86 (d, *J* = 7.5 Hz, 1H, ArH), 3.96 (s, 2H, CH<sub>2</sub>), 2.30 (s, 3H, CH<sub>3</sub>), 2.17 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 137.1, 136.7, 136.6, 133.9, 132.5, 131.4, 131.1, 129.8, 129.2, 128.5, 127.2, 127.0, 36.0, 21.1, 19.6.



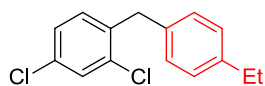
**2,4-dichloro-1-(2,5-dimethylbenzyl)benzene (4d):**

Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and *p*-xylene (2.0 mL); isolated as colorless oil (243.9 mg, 92%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.44-7.43 (d, *J* = 2.0 Hz, 1H, ArH), 7.14-7.09 (m, 2H, ArH), 7.03-7.02 (m, 1H, ArH), 6.84-6.81 (m, 2H, ArH), 3.99 (s, 2H, CH<sub>2</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 2.19 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 137.0, 136.8, 135.8, 135.0, 133.7, 132.5, 131.1, 130.7, 130.5, 129.2, 127.7, 127.2, 36.4, 21.1, 19.2.



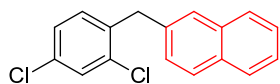
**2-(2,4-dichlorobenzyl)-1,3,5-trimethylbenzene (4e):**

Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and mesitylene (2.0 mL); isolated as white solid (262.0 mg, 94%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.39 (d, *J* = 2.0 Hz, 1H, ArH), 7.00-6.98 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H, ArH), 6.90 (s, 2H, ArH), 6.49-6.48 (d, *J* = 8.0 Hz, 1H, ArH), 3.96 (s, 2H, CH<sub>2</sub>), 2.29 (s, 3H, CH<sub>3</sub>), 2.12 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 137.3, 136.4, 136.3, 135.0, 132.3, 132.2, 129.2, 129.2, 129.0, 127.2, 32.0, 21.1, 20.0.



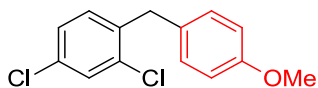
**2,4-dichloro-1-(4-ethylbenzyl)benzene (4f):**

Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and ethylbenzene (2.0 mL); isolated as colorless oil (233.0 mg, 88%, *o*- : *p*- : *m*- = 38:46:16 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.40-7.37 (m, 1H, ArH), 7.40-7.37 (m, 1H, ArH), 7.23-7.19 (m, 1H, ArH), 7.23-7.19 (m, 1H, ArH), 7.13-7.11 (m, 2H, ArH), 7.13-7.11 (m, 2H, ArH), 7.08-7.03 (m, 2H, ArH), 7.08-7.03 (m, 2H, ArH), 7.00-6.95 (m, 1H, ArH), 6.79-6.78 (m, 1H, ArH), 4.04 (s, 2H, CH<sub>2</sub>), 4.01 (d, *J* = 5.5 Hz, 2H, CH<sub>2</sub>), 2.61 (q, *J* = 7.0 Hz, 2H, CH<sub>2</sub>), 2.55 (q, *J* = 7.0 Hz, 2H, CH<sub>2</sub>), 1.21 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>), 1.16 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 142.6 (major), 137.8 (major), 136.2 (major), 132.7 (major), 131.9 (major), 129.4 (major), 129.0 (major), 128.2 (major), 127.2 (major), 126.3 (major), 38.4 (major), 28.6 (major), 15.7 (major).



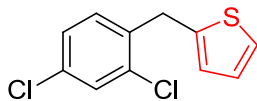
**2-(2,4-dichlorobenzyl)naphthalene (4g):** Prepared from

(2,4-dichlorophenyl) methanol (177.0 mg, 1.0 mmol) and naphthalene (512.8 mg, 4.0 mmol) in  $\text{CHCl}_3$  (2.0 mL); isolated as colorless oil (206.8 mg, 72%, *1*- : *2*- = 47:53 mixture of isomers).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.87-7.86 (m, 1H, ArH), 7.82-7.74 (m, 2H, ArH), 7.82-7.74 (m, 3H, ArH), 7.56 (s, 1H, ArH), 7.44-7.40 (m, 3H, ArH), 7.44-7.40 (m, 4H, ArH), 7.28 (d,  $J = 9.0$  Hz, 1H, ArH), 7.21-7.13 (m, 2H, ArH), 7.05 (d,  $J = 8.0$  Hz, 1H, ArH), 7.02-7.00 (m, 1H, ArH), 6.76-6.74 (m, 1H, ArH), 4.45 (s, 2H,  $\text{CH}_2$ ), 4.19 (s, 2H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 136.6, 134.8, 133.7, 132.9, 132.4, 132.0, 129.5, 128.4, 127.8, 127.5, 127.3, 126.3, 125.8, 124.1, 38.9 (major), 36.0 (minor).



**2,4-dichloro-1-(4-methoxybenzyl)benzene (4h):**

Prepared from (2,4-dichlorophenyl) methanol (177.0 mg, 1.0 mmol) and anisole (2.0 mL); isolated as colorless oil (163.0 mg, 61%, *p*- > 99).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.37 (s, 1H, ArH), 7.13 (d,  $J = 8.0$  Hz, 1H, ArH), 7.07 (d,  $J = 7.5$  Hz, 2H, ArH), 7.03 (d,  $J = 8.0$  Hz, 1H, ArH), 6.83 (d,  $J = 7.5$  Hz, 2H, ArH), 3.98 (s, 2H,  $\text{CH}_2$ ), 3.77 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 158.4, 138.0, 134.9, 132.6, 131.8, 131.1, 130.0, 129.4, 127.2, 114.2, 55.4, 37.9.

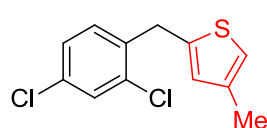


**2-(2,4-dichlorobenzyl)thiophene (4i):** Prepared from

(2,4-dichlorophenyl) methanol (177.0 mg, 1.0 mmol) and

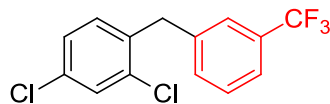


thiophene (2.0 mL); isolated as colorless oil (214.0 mg, 88%, 3- : 2- = 36:64 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.38 (s, 1H, ArH), 7.38 (s, 1H, ArH), 7.16-7.14 (m, 2H, ArH), 7.16-7.07 (m, 5H, ArH), 6.92 (s, 2H, ArH), 6.80 (s, 1H, ArH), 4.22 (s, 2H, CH<sub>2</sub>), 4.04 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 141.5, 136.9, 134.6, 133.2, 131.5, 129.5, 127.4, 125.9, 124.5, 122.0, 33.6 (minor), 33.1 (major).



**2-(2,4-dichlorobenzyl)-3-methylthiophene (4j):** Prepared

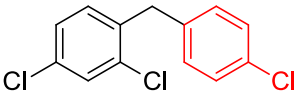
from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and 3-methylthiophene (2.0 mL); isolated as yellow oil (154.0 mg, 60%, 4- : 5- : 2- = 16:45:39 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 7.43-7.41 (m, 1H, ArH), 7.43-7.41 (m, 1H, ArH), 7.22-7.16 (m, 1H, ArH), 7.22-7.16 (m, 2H, ArH), 7.12-7.10 (dd, *J*<sub>1</sub> = 5.0 Hz, *J*<sub>2</sub> = 2.5 Hz, 1H, ArH), 7.02 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H, ArH), 6.89 (s, 1H, ArH), 6.87-6.86 (m, 1H, ArH), 6.63 (s, 1H, ArH), 4.19 (s, 2H, CH<sub>2</sub>), 4.14 (s, 2H, CH<sub>2</sub>), 2.22 (d, *J* = 2.5 Hz, 3H, CH<sub>3</sub>), 2.18 (d, *J* = 2.0 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 137.7, 136.7, 134.5, 132.9, 131.0, 19.3, 128.3, 127.3, 122.7, 119.5, 33.2 (minor), 32.4 (minor), 30.9 (major), 15.9 (major), 14.6 (minor), 13.9 (minor).

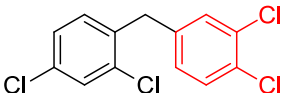


**2,4-dichloro-1-(3-(trifluoromethyl)benzyl)benzene**

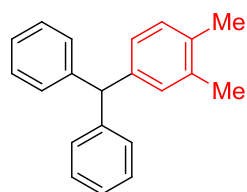
**(4k):** Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and (trifluoromethyl)benzene (4.0 mL); isolated as colorless oil (128.0 mg, 42%, *m*- > 99). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm)

7.49-7.48 (m, 1H, ArH), 7.43-7.41 (m, 3H, ArH), 7.33 (d,  $J = 7.0$  Hz, 1H, ArH), 7.19 (d,  $J = 8.0$  Hz, 1H, ArH), 7.07 (d,  $J = 8.0$  Hz, 1H, ArH), 4.11 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 140.1, 136.4, 135.1, 133.4, 132.4, 131.9, 131.2, 129.7, 129.2, 127.5, 125.7, 123.6, 38.6.

 **2,4-dichloro-1-(4-chlorobenzyl)benzene (4l):** Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and chlorobenzene (4.0 mL); isolated as colorless oil (268.0 mg, 99%, *o*- : *p*- : *m*- = 24:72:4 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.40-7.37 (m, 1H, ArH), 7.40-7.37 (m, 2H, ArH), 7.25-7.23 (m, 2H, ArH), 7.19-7.12 (m, 2H, ArH), 7.08-7.02 (m, 2H, ArH), 7.08-7.02 (m, 4H, ArH), 6.92-6.91 (d,  $J = 7.5$  Hz, 1H, ArH), 4.14 (s, 2H, CH<sub>2</sub>), 4.00 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 137.5, 136.9, 135.0, 133.1, 132.5, 131.8, 130.3, 129.6, 128.9, 127.4, 38.2 (major), 36.4 (minor).

 **1,2-dichloro-4-(2,4-dichlorobenzyl)benzene (4m):** Prepared from (2,4-dichlorophenyl)methanol (177.0 mg, 1.0 mmol) and 1,2-dichlorobenzene (2.0 mL); isolated as colorless oil (226.0 mg, 74%, 3- : 4- = 13:87 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.42-7.39 (m, 1H, ArH), 7.35-7.33 (d,  $J = 8.0$  Hz, 1H, ArH), 7.25-7.23 (m, 1H, ArH), 7.19 (dd,  $J_1 = 6.5$  Hz,  $J_2 = 1.5$  Hz, 1H, ArH), 7.08-7.06 (m, 1H, ArH), 6.99-6.98 (m, 1H, ArH), 4.00 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

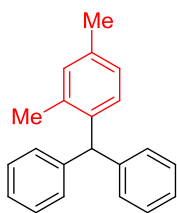
$\delta$  (ppm) 139.3, 136.1, 135.0, 133.4, 132.7, 131.8, 130.8, 130.6, 129.7, 128.8, 128.4, 127.5, 38.0 (major), 37.3(minor).



**((2,3-dimethylphenyl)methylene)dibenzene (5a)<sup>30</sup>:**

Prepared from diphenylmethanol (184.2 mg, 1.0 mmol) and *o*-xylene (2.0 mL); isolated as white solid (253.3 mg, 93%,

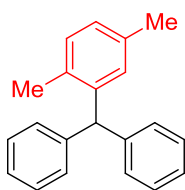
3- : 4- =4:96 mixture of isomers). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.29-7.27 (m, 3H, ArH), 7.26 (s, 1H, ArH), 7.21-7.18 (m, 2H, ArH), 7.12 (s, 2H, ArH), 7.11 (s, 2H, ArH), 7.04 (d, *J* = 7.5 Hz, 1H, ArH), 6.91 (s, 1H, ArH), 6.82 (d, *J* = 8.0 Hz, 1H, ArH), 5.48 (s, 1H, CH), 2.22 (s, 3H, CH<sub>3</sub>), 2.19 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 144.4, 141.5, 136.6, 134.7, 130.9, 129.7, 129.6, 128.4, 127.0, 126.3, 56.7, 20.0, 19.5.



**((2,4-dimethylphenyl)methylene)dibenzene (5b)<sup>30</sup>:**

Prepared from diphenylmethanol (184.2 mg, 1.0 mmol) and *m*-xylene (2.0 mL); isolated as white solid (250.6 mg, 92%). <sup>1</sup>H NMR

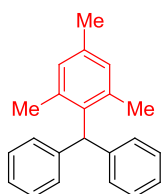
(500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.28-7.24 (m, 4H, ArH), 7.21-7.18 (m, 2H, ArH), 7.05 (d, *J* = 7.5 Hz, 4H, ArH), 6.98 (s, 1H, ArH), 6.90 (d, *J* = 8.0 Hz, 1H, ArH), 6.69 (d, *J* = 7.5 Hz, 1H, ArH), 5.63 (s, 1H, CH), 2.29 (s, 3H, CH<sub>3</sub>), 2.17 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 143.8, 139.6, 136.6, 136.0, 131.4, 129.8, 129.6, 128.4, 126.6, 126.3, 53.4, 21.1, 20.0.



**((2,5-dimethylphenyl)methylene)dibenzene (5c)<sup>30</sup>:**

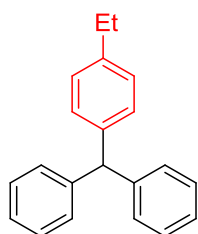
Prepared from diphenylmethanol (184.2 mg, 1.0 mmol) and *p*-xylene (2.0

mL); isolated as white solid (234.3 mg, 86%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.28-7.25 (m, 4H, ArH), 7.23-7.18 (m, 2H, ArH), 7.06-7.04 (m, 5H, ArH), 6.95-6.94 (m, 1H, ArH), 6.62 (s, 1H, ArH), 5.64 (s, 1H, CH), 2.20 (s, 3H,  $\text{CH}_3$ ), 2.16 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 143.7, 142.2, 135.2, 133.6, 130.5, 130.3, 129.8, 128.4, 127.2, 126.4, 53.7, 21.4, 19.6.




**(mesitylmethylene)dibenzene (5d)**<sup>30</sup>: Prepared from diphenylmethanol (184.2 mg, 1.0 mmol) and mesitylene (2.0 mL); isolated as white solid (277.0 mg, 97%).  $^1\text{H}$  NMR (500

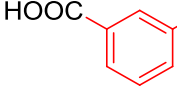
MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.26-7.23 (m, 4H, ArH), 7.19-7.17 (m, 2H, ArH), 7.10-7.07 (m, 4H, ArH), 6.85 (s, 2H, ArH), 6.00 (s, 1H, CH), 2.27 (s, 3H,  $\text{CH}_3$ ), 2.00 (s, 6H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 137.7, 137.2, 136.2, 130.3, 129.5, 128.3, 127.1, 126.1, 51.2, 22.1, 21.0.

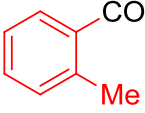


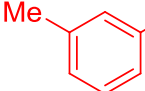
**((4-ethylphenyl)methylene)dibenzene (5e)**<sup>30</sup>: Prepared from diphenylmethanol (184.2 mg, 1.0 mmol) and ethylbenzene (2.0 mL); isolated as colorless oil (272.0 mg, 99%, *o*- : *p*- = 18:82 mixture of isomers).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.25 (s,

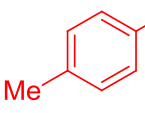
2H, major, ArH), 7.25 (s, 2H, ArH), 7.23 (s, 1H, ArH), 7.23 (s, 3H, ArH), 7.21-7.19 (m, 2H, ArH), 7.19-7.17 (m, 2H, ArH), 7.19-7.17 (m, 2H, ArH), 7.10 (t,  $J = 7.0$  Hz, 5H, ArH), 7.10 (t,  $J = 7.0$  Hz, 5H, ArH), 7.03-7.01 (m, 2H, ArH), 6.90-6.89 (m, 1H, ArH), 6.67 (s, 1H, ArH), 5.66 (s, 1H, CH), 5.51 (s, 1H, CH), 2.60 (q,  $J = 7.0$  Hz, 2H,  $\text{CH}_2$ ), 2.60 (q,  $J = 7.0$  Hz, 2H,  $\text{CH}_2$ ), 2.21 (t,  $J = 7.0$  Hz, 3H,  $\text{CH}_3$ ), 1.12 (t,  $J = 7.0$  Hz, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 144.3, 142.3, 141.3, 129.6, 129.0, 128.4, 128.0, 126.4, 56.7, 28.6, 15.7.

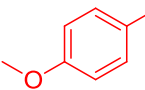
 **benzoic acid (3a')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 12.40 (b, 1H, COOH), 8.14 (s, 1H, ArH), 8.13 (s, 1H, ArH), 7.62 (t,  $J = 7.5$  Hz, 1H, ArH), 7.48 (t,  $J = 7.5$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 172.7, 134.0, 130.4, 129.5, 128.7.

 **isophthalic acid (3b')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm) 13.2 (b, 1H, COOH), 8.48 (s, 1H, ArH), 8.17 (d,  $J = 2.0$  Hz, 1H, ArH), 8.15 (d,  $J = 1.5$  Hz, 1H, ArH), 7.64 (t,  $J = 7.5$  Hz, 1H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm) 166.8, 133.6, 131.4, 130.2, 129.3.

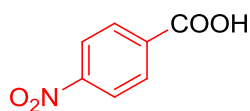
 **2-methylbenzoic acid (3c')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 12.51 (b, 1H, COOH), 8.08 (d,  $J = 8.0$  Hz, 1H, ArH), 7.46 (t,  $J = 7.5$  Hz, 1H, ArH), 7.29 (t,  $J = 8.0$  Hz, 2H, ArH), 2.67 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 173.7, 141.6, 133.2, 132.1, 131.8, 128.5, 126.0, 22.3.

 **3-methylbenzoic acid (3d')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 12.73 (b, 1H, COOH), 7.93-7.92 (m, 2H, ArH), 7.41 (d,  $J = 7.5$  Hz, 1H, ArH), 7.35 (t,  $J = 7.5$  Hz, 1H, ArH), 2.41 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 173.0, 138.5, 134.8, 130.9, 129.4, 128.5, 127.6, 21.4.

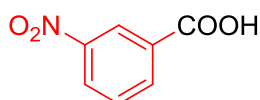
 **4-methylbenzoic acid (3e')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.82 (b, 1H, COOH), 8.01 (d,  $J = 8.0$  Hz, 2H, ArH), 7.27 (d,  $J = 8.0$  Hz, 2H, ArH), 2.43 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 172.7, 144.8, 130.4, 129.4, 126.8, 21.9.

 **4-methoxybenzoic acid (3f')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.08 (d,  $J = 8.0$  Hz, 2H, ArH), 6.95 (d,  $J = 8.0$  Hz,

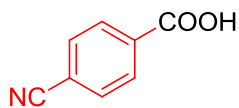
2H, ArH), 3.88 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 171.8, 164.2, 132.6, 121.8, 113.9, 55.7.



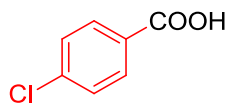
**4-nitrobenzoic acid (3g')**: white solid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 8.32 (d, *J* = 8.5 Hz, 2H, ArH), 8.16 (d, *J* = 9.0 Hz, 2H, ArH); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 166.0, 150.1, 136.5, 130.8, 123.8.



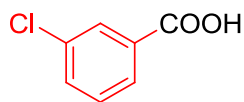
**3-nitrobenzoic acid (3h')**: white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 11.86 (b, 1H, COOH), 8.96 (s, 1H, ArH), 8.50 (d, *J* = 8.0 Hz, 1H, ArH), 8.47 (d, *J* = 7.5 Hz, 1H, ArH), 7.74 (t, *J* = 7.5 Hz, 1H, ArH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 148.6, 136.0, 131.1, 130.1, 128.5, 125.4.



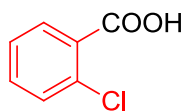
**4-cyanobenzoic acid (3i')**: white solid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 13.6 (b, 1H, COOH), 8.06 (d, *J* = 8.0 Hz, 2H, ArH), 7.96 (d, *J* = 8.0 Hz, 2H, ArH); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 166.1, 134.9, 132.7, 129.9, 118.2, 115.1.



**4-chlorobenzoic acid (3j')**: white solid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 7.93 (d, *J* = 8.5 Hz, 2H, ArH), 7.55 (d, *J* = 8.5 Hz, 2H, ArH); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 166.6, 137.9, 131.2, 129.7, 128.8.

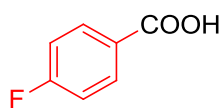


**3-chlorobenzoic acid (3k')**: white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 12.06 (b, 1H, , COOH), 8.09 (s, 1H, ArH), 8.01 (d, *J* = 7.5 Hz, 1H, ArH), 7.59 (d, *J* = 7.5 Hz, 1H, ArH), 7.43 (t, *J* = 8.0 Hz, 1H, ArH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 171.4, 135.0, 134.1, 131.2, 130.5, 130.0, 128.5.

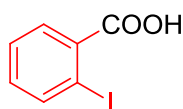


**2-chlorobenzoic acid (3l')**: white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 11.55 (b, 1H, COOH), 8.04 (d, *J* = 7.0 Hz, 1H, ArH),

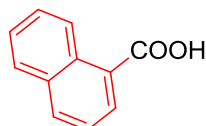
7.51-7.47 (m, 2H, ArH), 7.38-7.35 (m, 1H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 171.3, 135.0, 133.8, 132.7, 131.7, 128.6, 126.9.



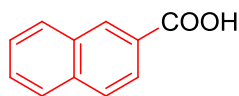
**4-fluorobenzoic acid (3m')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 12.12 (b, 1H, COOH), 8.16-8.13 (m, 2H, ArH), 7.16 (t,  $J = 8.5$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 171.4, 167.6, 165.6, 133.1, 125.7, 116.0, 115.9.



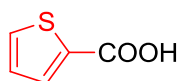
**2-iodobenzoic acid (3n')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 11.61 (b, 1H, COOH), 8.07 (d,  $J = 8.0$  Hz, 1H, ArH), 8.04 (d,  $J = 8.0$  Hz, 1H, ArH), 7.46 (t,  $J = 8.0$  Hz, 1H, ArH), 7.21 (t,  $J = 7.5$  Hz, 1H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 171.4, 142.2, 133.8, 133.3, 132.3, 128.2, 94.9.



**1-naphthoic acid (3o')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 12.48 (b, 1H, COOH), 9.10 (d,  $J = 9.0$  Hz, 1H, ArH), 8.43 (d,  $J = 7.0$  Hz, 1H, ArH), 8.11 (d,  $J = 8.0$  Hz, 1H, ArH), 7.93 (d,  $J = 8.5$  Hz, 1H, ArH), 7.69-7.66 (m, 1H, ArH), 7.57 (q,  $J_1 = 14.5$  Hz,  $J_2 = 7.5$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 173.3, 134.9, 134.1, 132.1, 131.8, 128.9, 128.3, 126.5, 126.1, 125.7, 124.7.

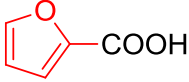


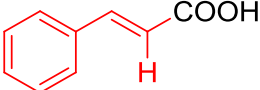
**2-naphthoic acid (3p')**: white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 12.27 (b, 1H, COOH), 8.73 (s, 1H, ArH), 8.13 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.5$  Hz, 1H, ArH), 7.99 (d,  $J = 8.0$  Hz, 1H, ArH), 7.91 (t,  $J = 8.5$  Hz, 2H, ArH), 7.62 (t,  $J = 7.5$  Hz, 1H, ArH), 7.57 (t,  $J = 8.0$  Hz, 1H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 172.6, 136.2, 132.6, 132.4, 129.8, 128.9, 128.5, 128.0, 127.0, 126.7, 125.6.

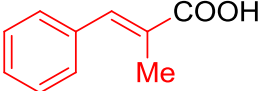


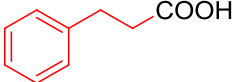
**thiophene-2-carboxylic acid (3q')**: white solid.  $^1\text{H}$  NMR (500 MHz,

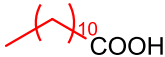
CDCl<sub>3</sub>)  $\delta$  (ppm) 10.97 (b, 1H, COOH), 7.91 (d,  $J$  = 3.5 Hz, 1H, ArH), 7.66 (d,  $J$  = 4.5 Hz, 1H, ArH), 7.15 (t,  $J$  = 4.5 Hz, 1H, ArH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 168.0, 135.2, 134.2, 133.0, 128.3.

 **furan-2-carboxylic acid (3r')**: white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 11.34 (b, 1H, COOH), 7.66 (s, 1H, ArH), 7.35 (d,  $J$  = 3.5 Hz, 1H, ArH), 6.58-6.57 (m, 1H, ArH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.9, 147.6, 144.0, 120.4, 112.5.

 **cinnamic acid (3s')**: white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 12.04 (b, 1H, COOH), 7.80 (d,  $J$  = 16.0 Hz, 1H, CH), 7.56-7.55 (m, 2H, ArH), 7.41-7.40 (m, 3H, ArH), 6.46 (d,  $J$  = 16.5 Hz, 1H, CH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 172.9, 147.3, 134.2, 130.9, 129.1, 128.6, 117.5.

 **(E)-2-methyl-3-phenylacrylic acid (3t')**: white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 12.40 (b, 1H, COOH), 7.85 (s, 1H, CH), 7.44-7.39 (m, 4H, ArH), 7.36-7.33 (m, 1H, ArH), 2.15 (d,  $J$  = 1.0 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 174.8, 141.3, 135.7, 130.0, 128.9, 128.6, 127.8, 13.9.

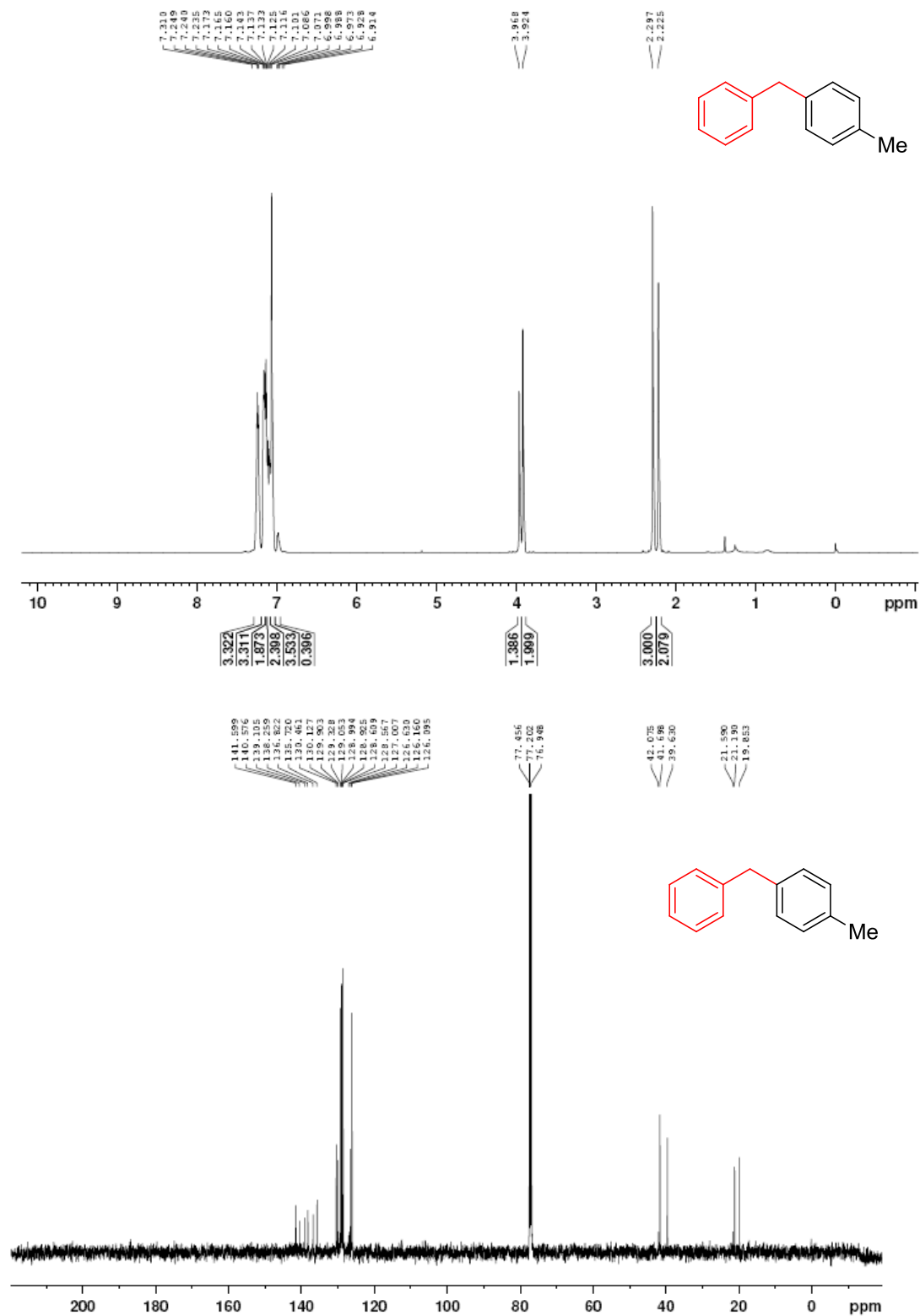
 **3-phenylpropanoic acid (3u')**: white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.31-7.28 (m, 2H, ArH), 7.23-7.20 (m, 3H, ArH), 2.96 (t,  $J$  = 8.0 Hz, 2H, CH<sub>2</sub>), 2.69 (t,  $J$  = 8.0 Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 179.6, 140.3, 128.7, 128.4, 126.5, 35.8, 30.7.

 **dodecanoic acid (3v')**: white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 10.93 (b, 1H, COOH), 2.35 (t,  $J$  = 7.5 Hz, 2H, CH<sub>2</sub>), 1.63 (quin,  $J$  = 7.5 Hz, 2H, CH<sub>2</sub>), 1.30-1.26 (m, 16H, CH<sub>2</sub>), 0.88 (t,  $J$  = 7.0 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 180.6, 34.3, 32.1, 29.8, 29.6, 29.5, 29.4, 29.2, 24.9, 22.9, 14.3.

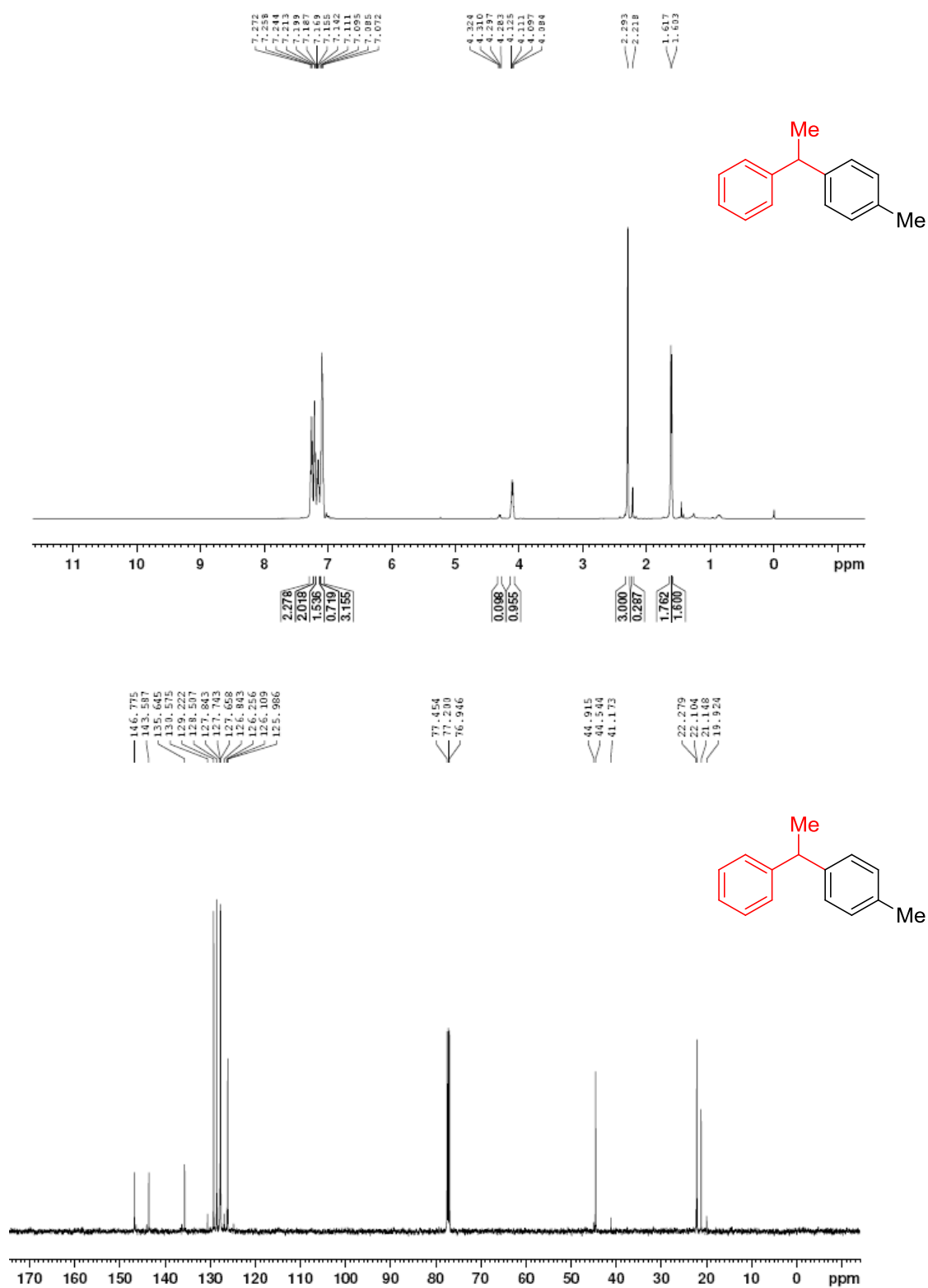


## 5. $^1\text{H}$ - and $^{13}\text{C}$ -NMR spectra

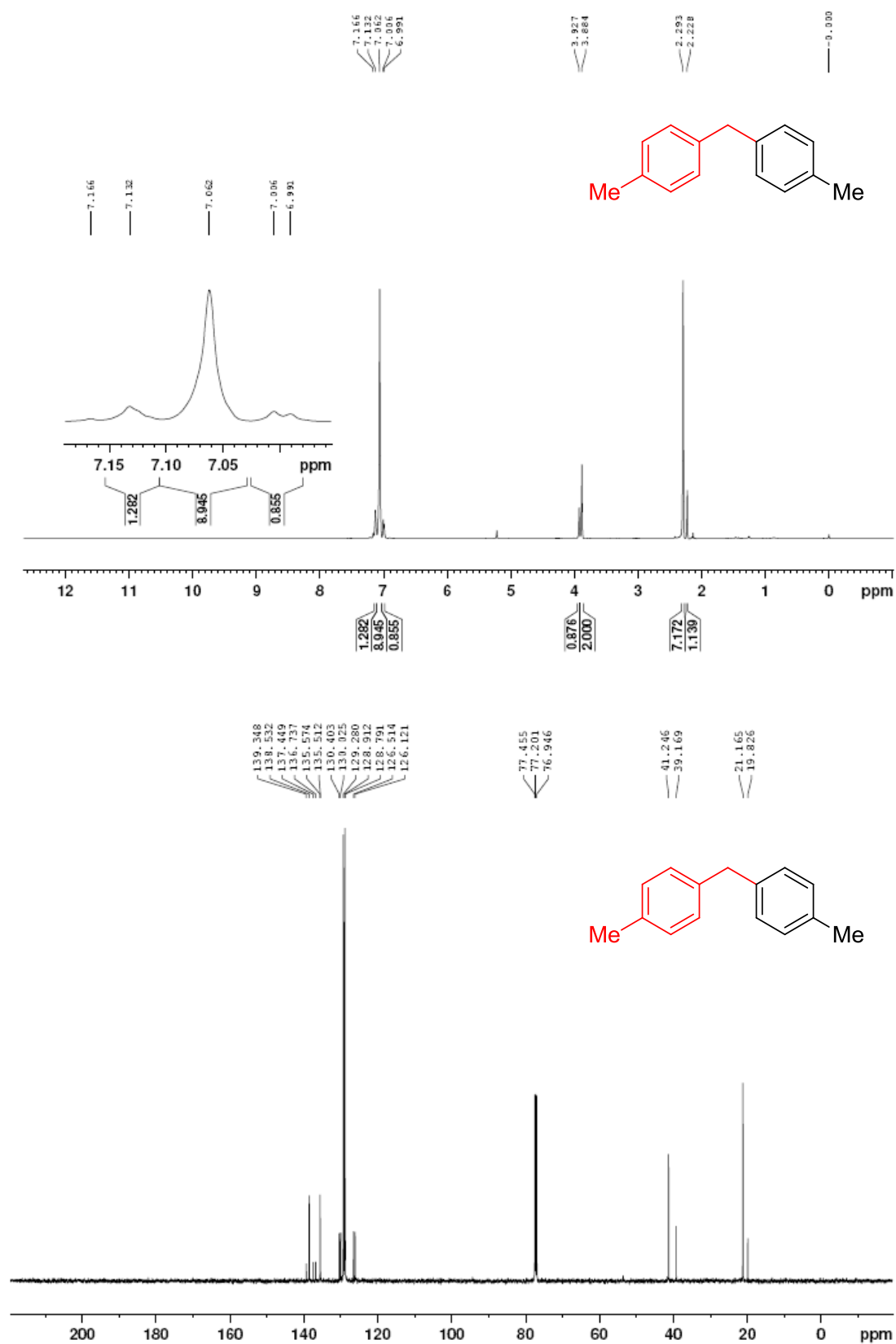
### 1-benzyl-4-methylbenzene (3a)



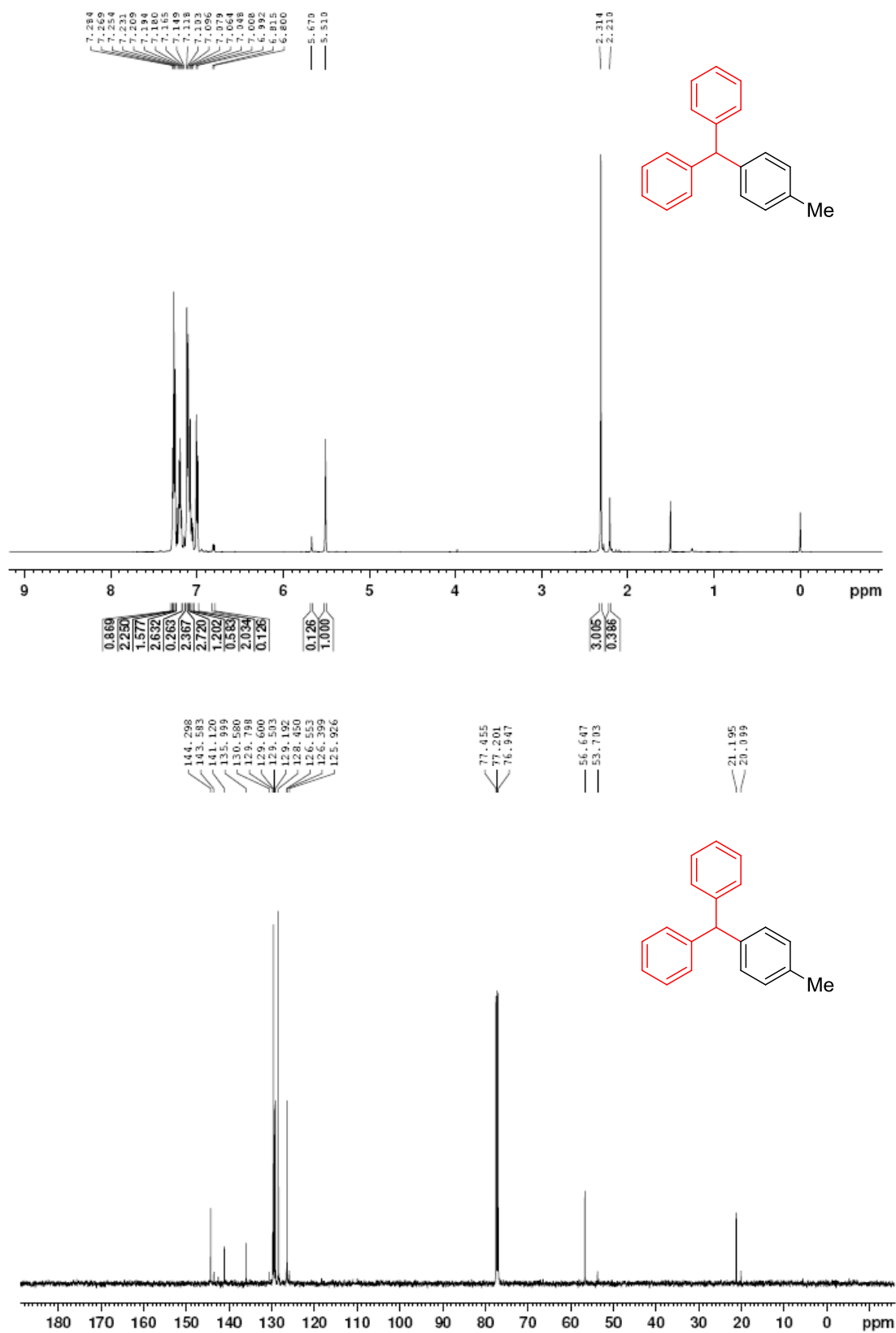
**1-methyl-4-(1-phenylethyl)benzene (3b)**



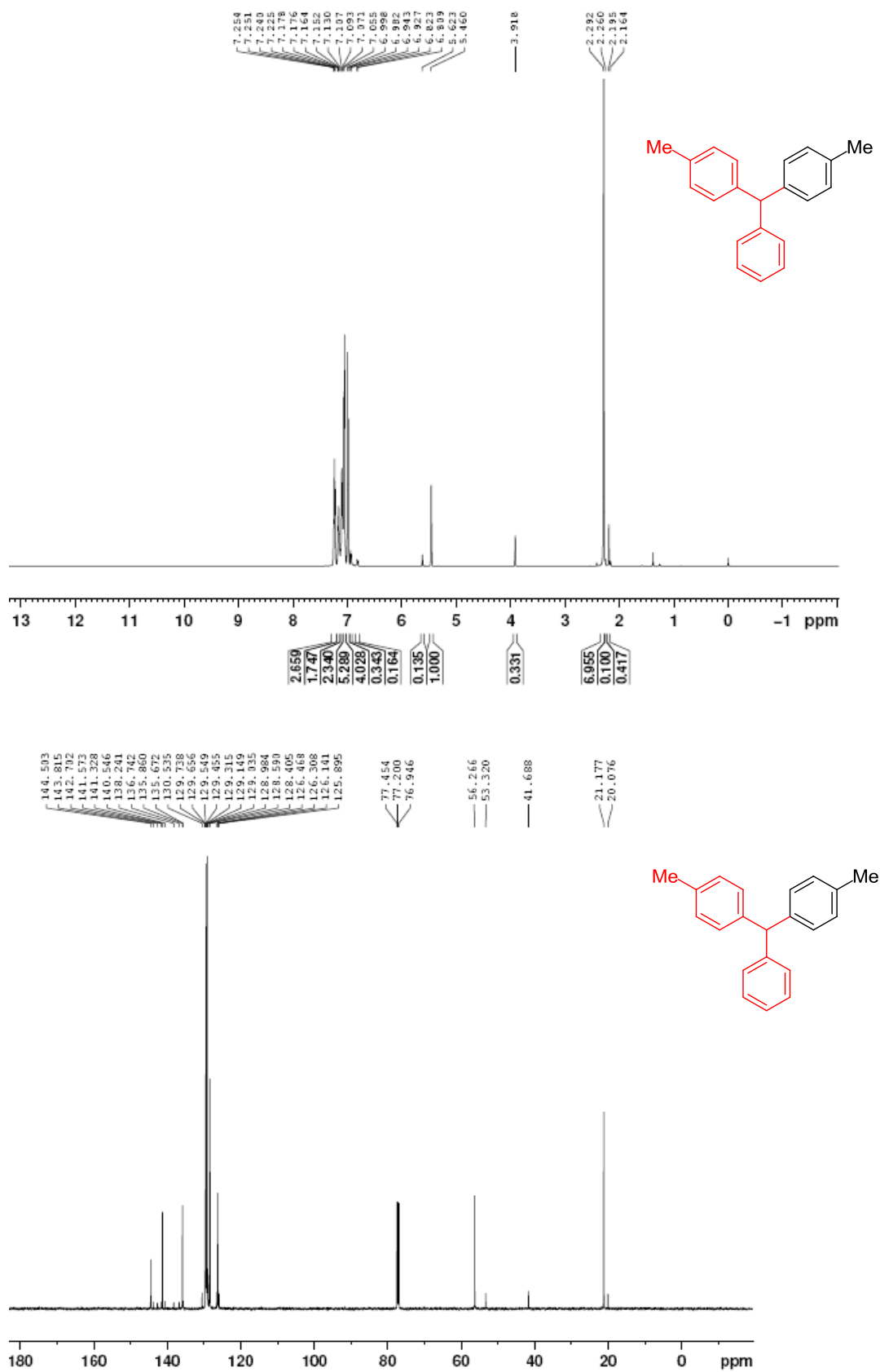
di-*p*-tolylmethane (3c)



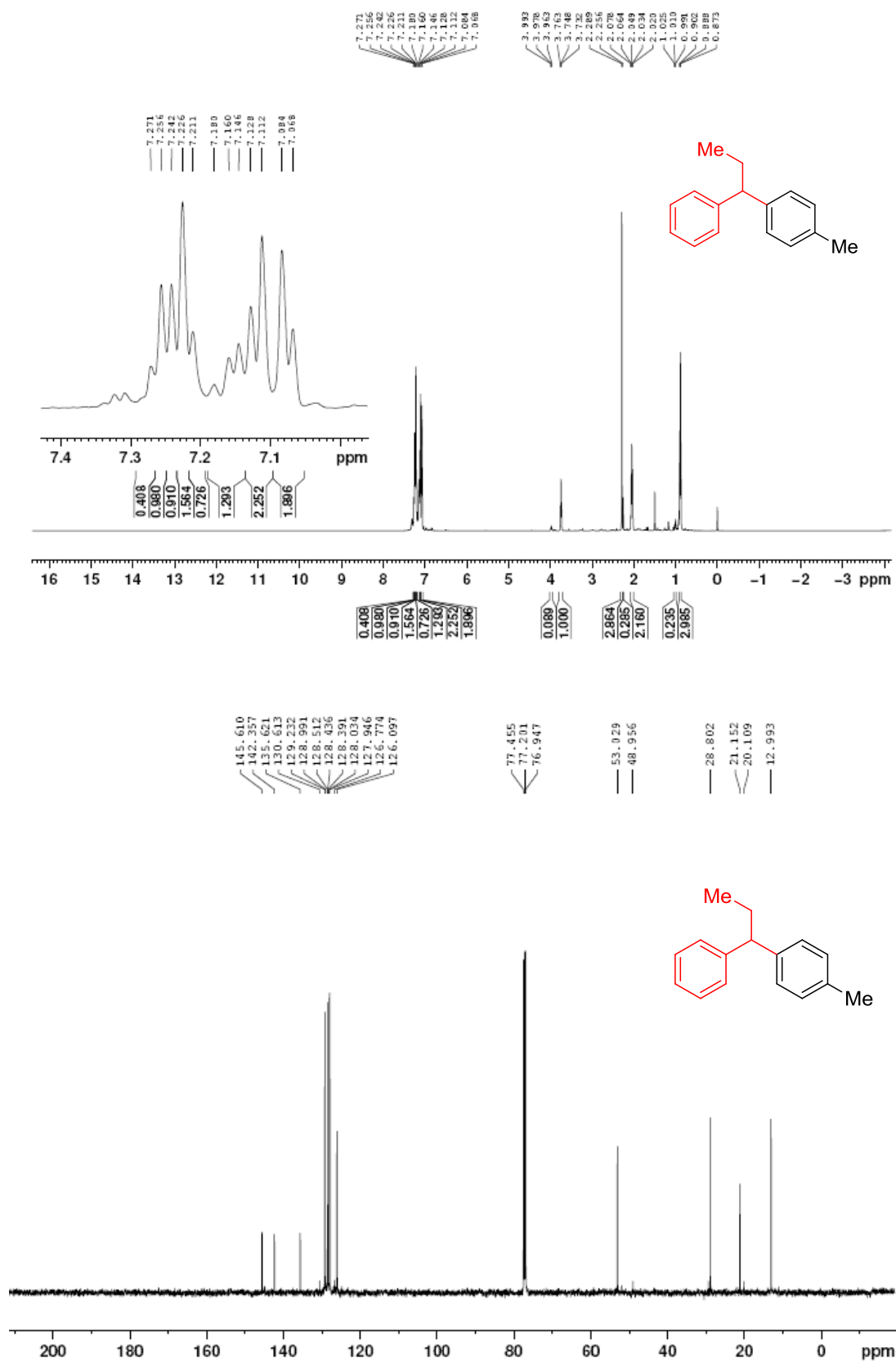
(*p*-tolylmethylene)dibenzene (3d)



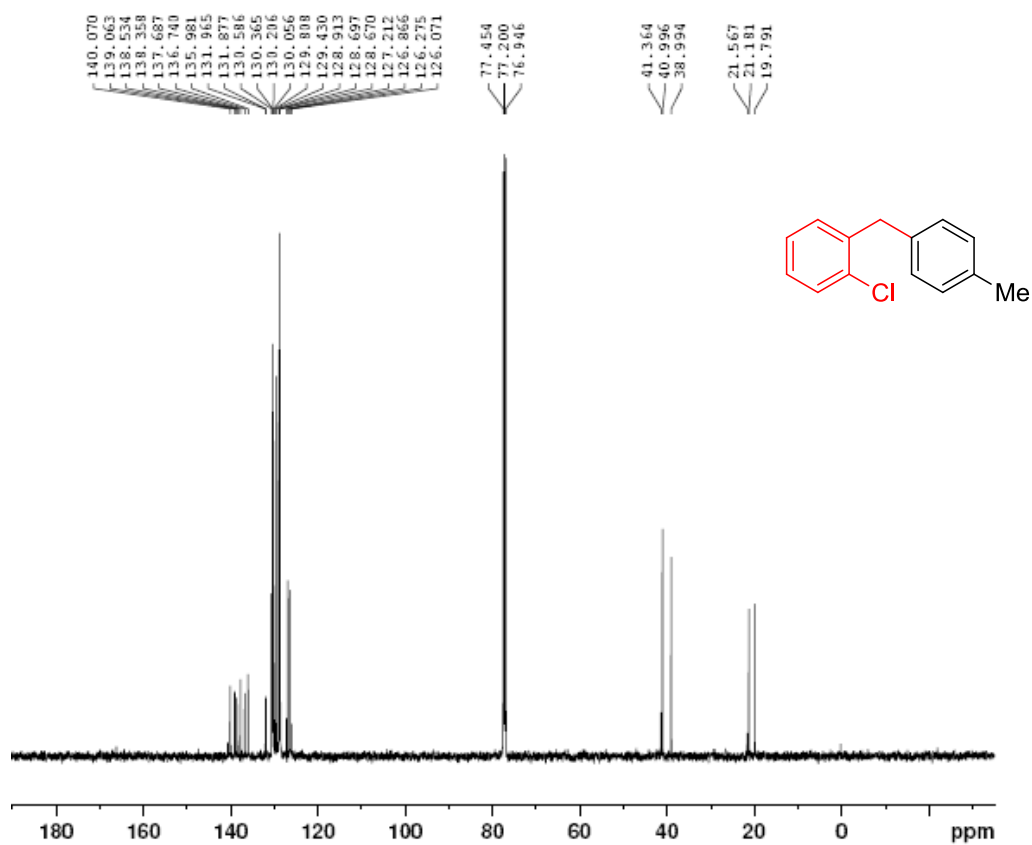
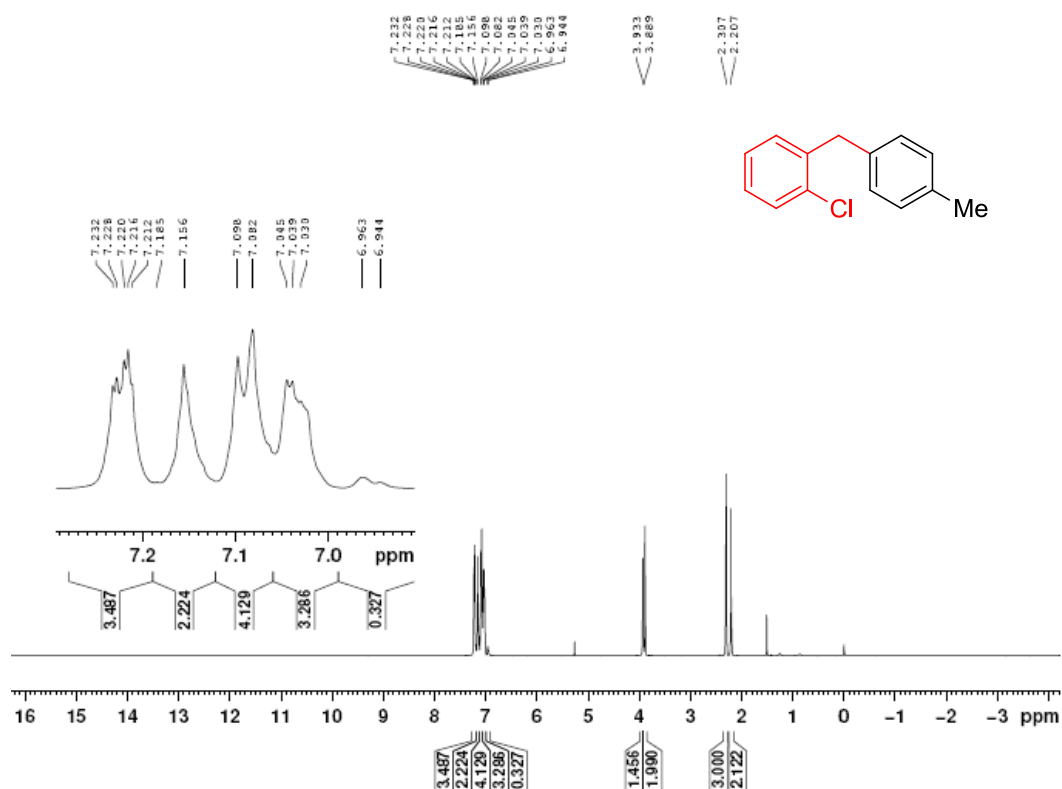
4,4'-(phenylmethylene)bis(methylbenzene) (3e)



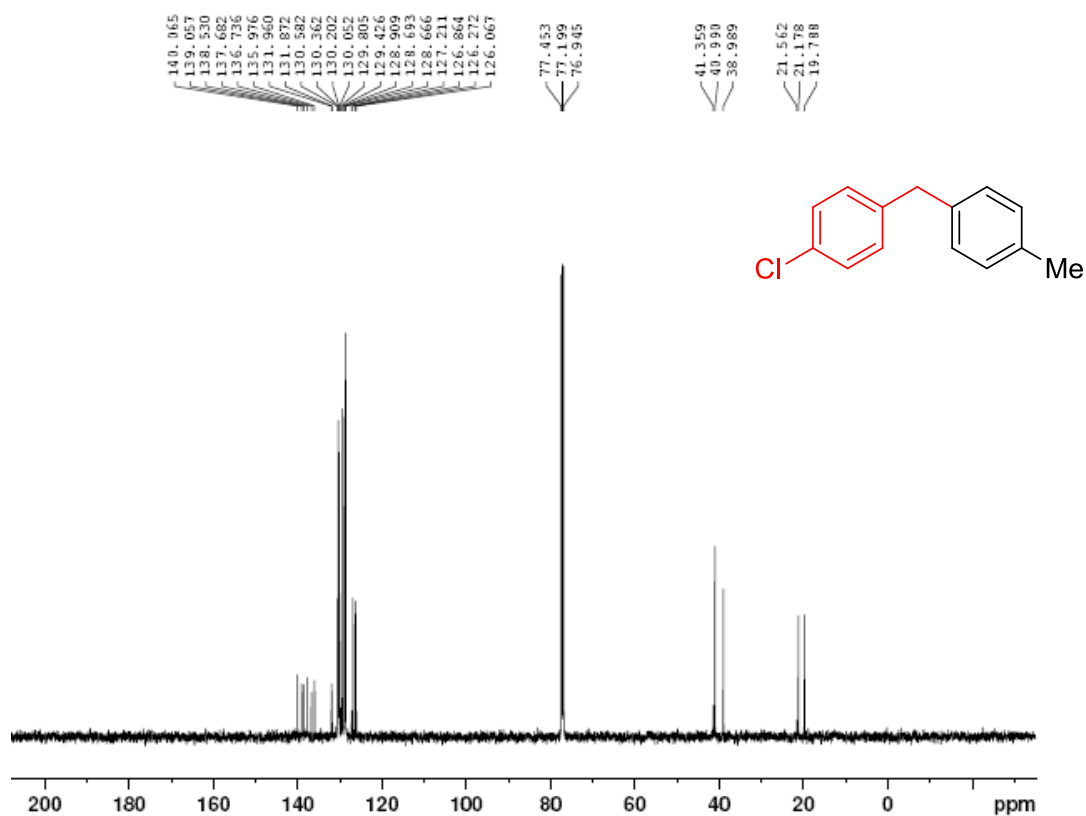
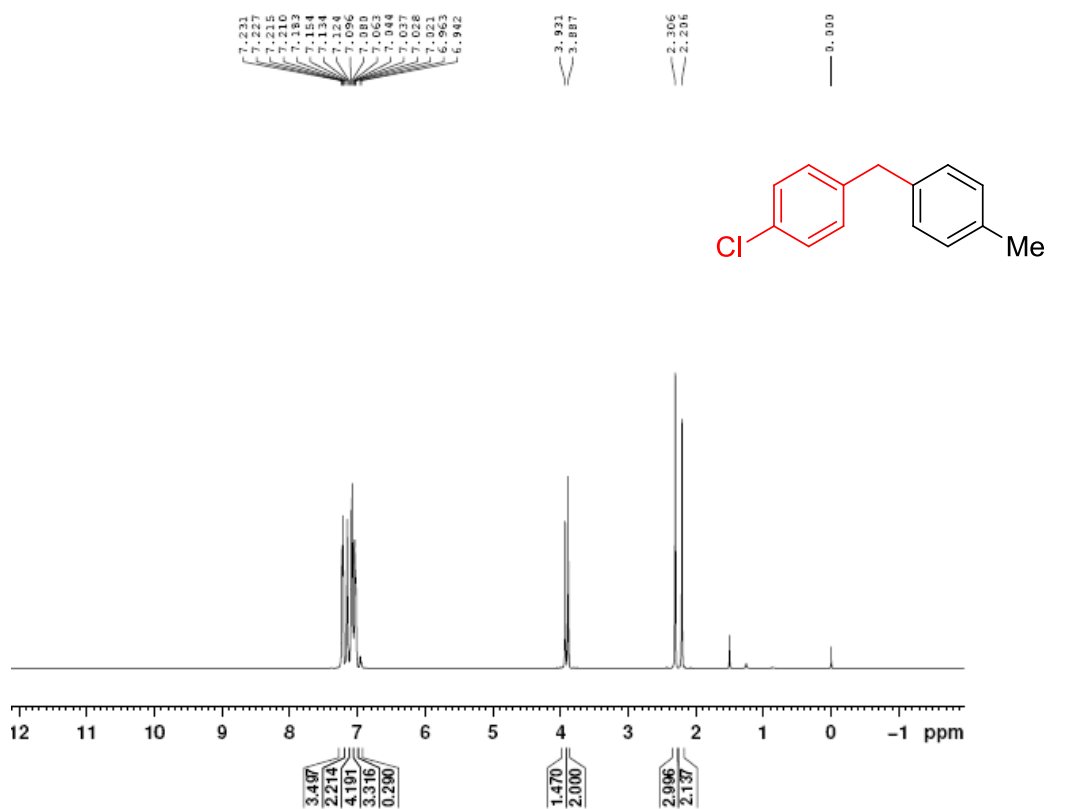
1-methyl-4-(1-phenylpropyl)benzene (3f)



# 1-chloro-2-(4-methylbenzyl)benzene (3g)

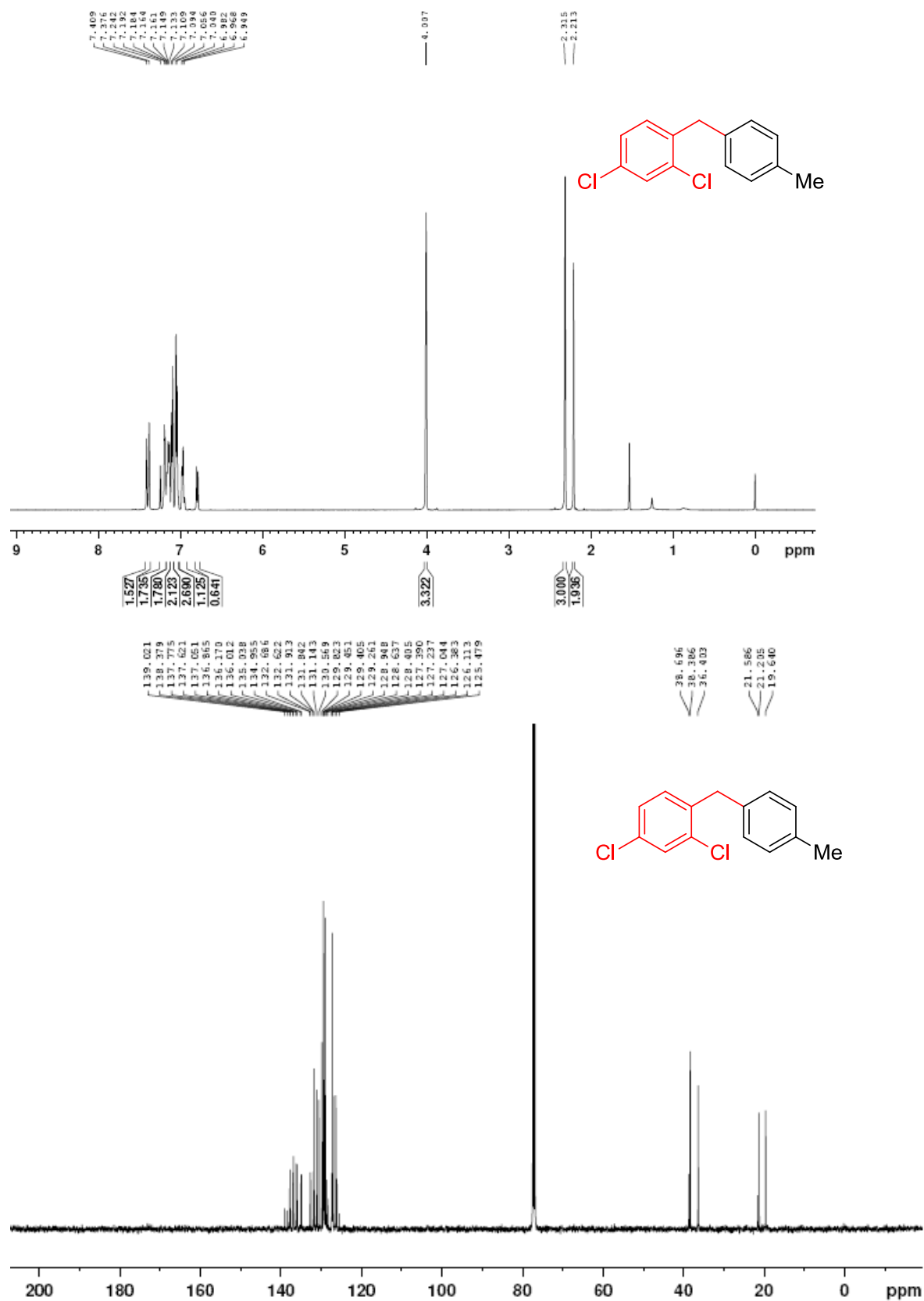


1-chloro-4-(4-methylbenzyl)benzene (3h)

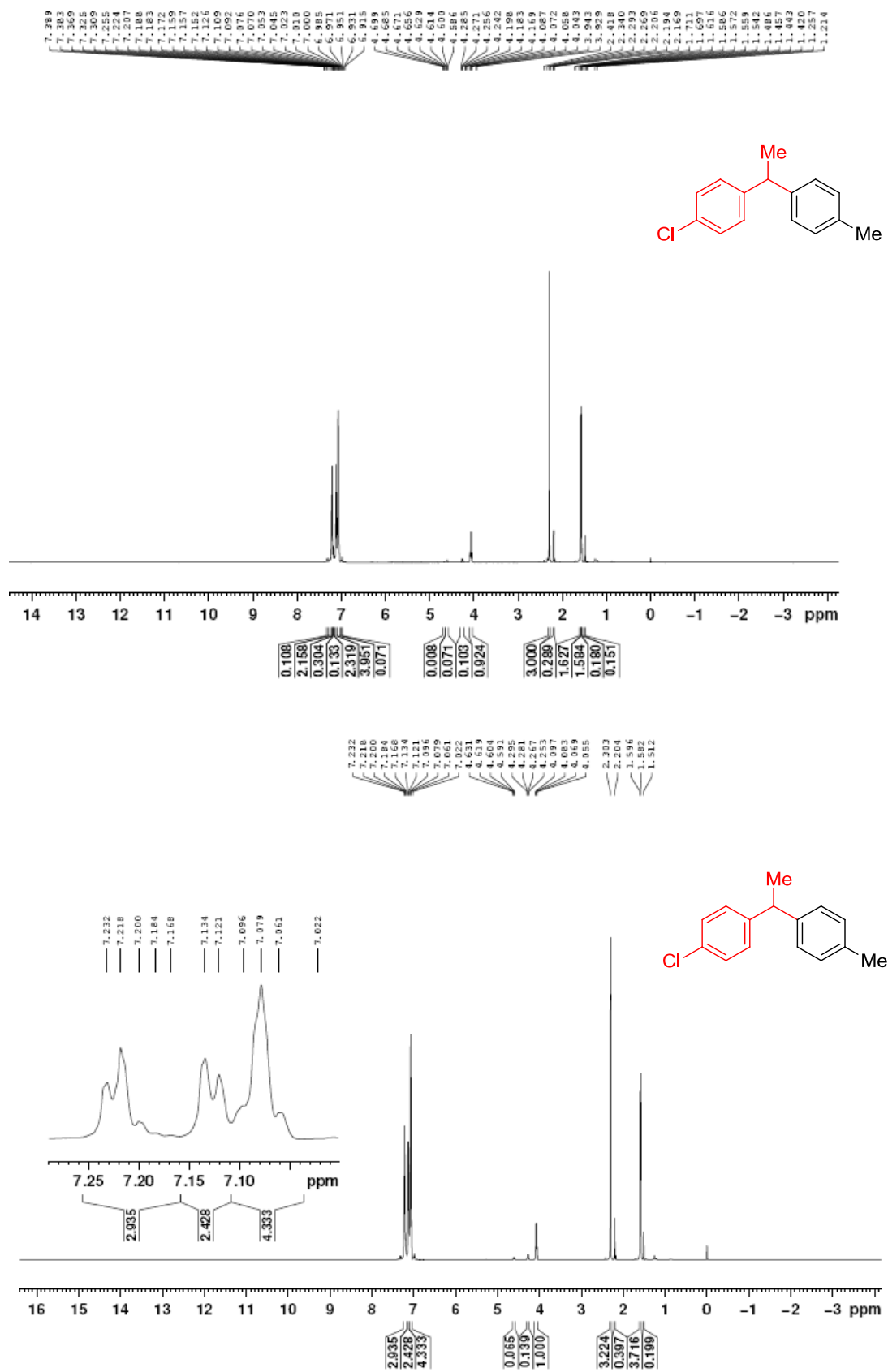




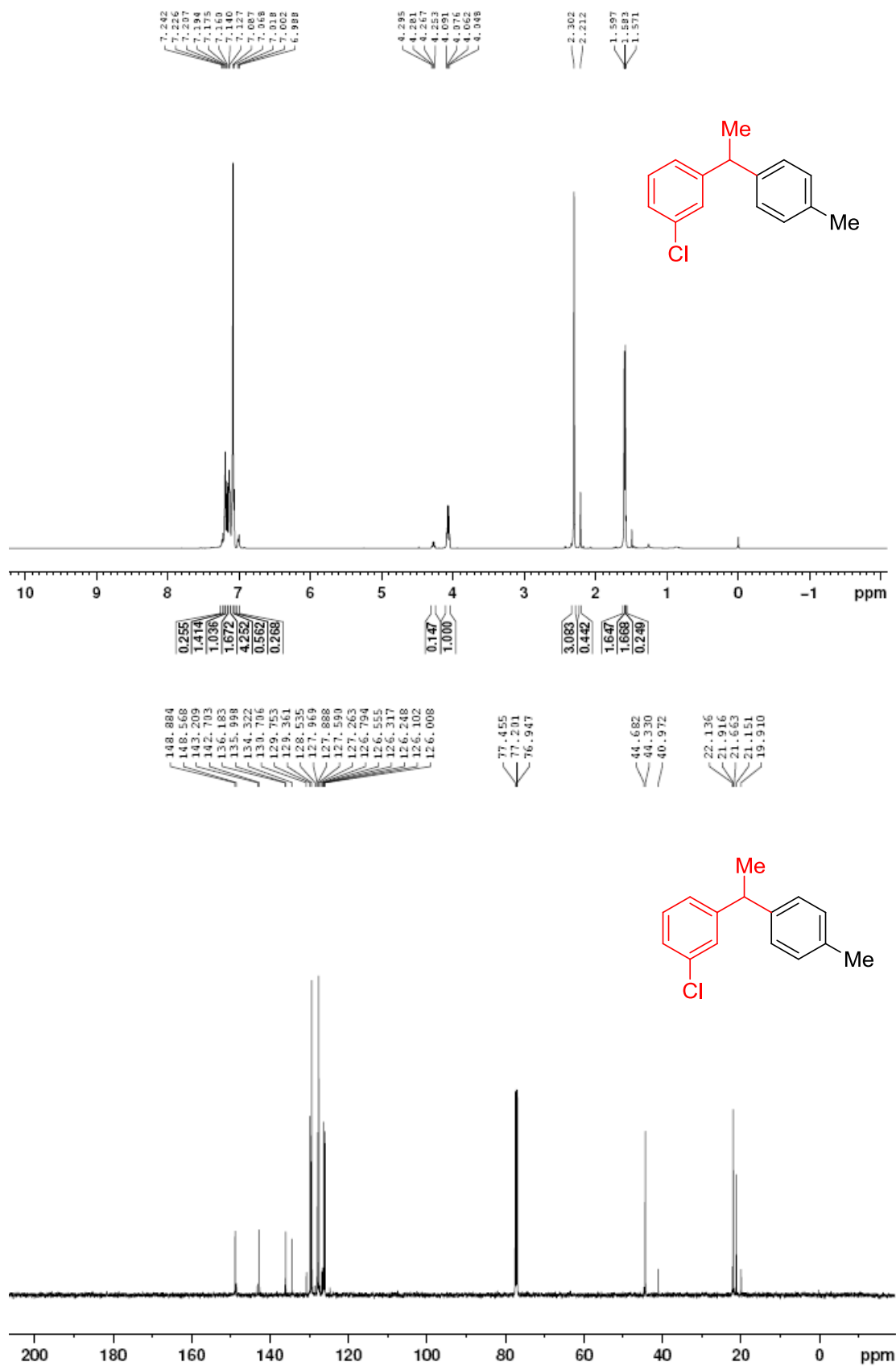
2,4-dichloro-1-(4-methylbenzyl)benzene (3i)



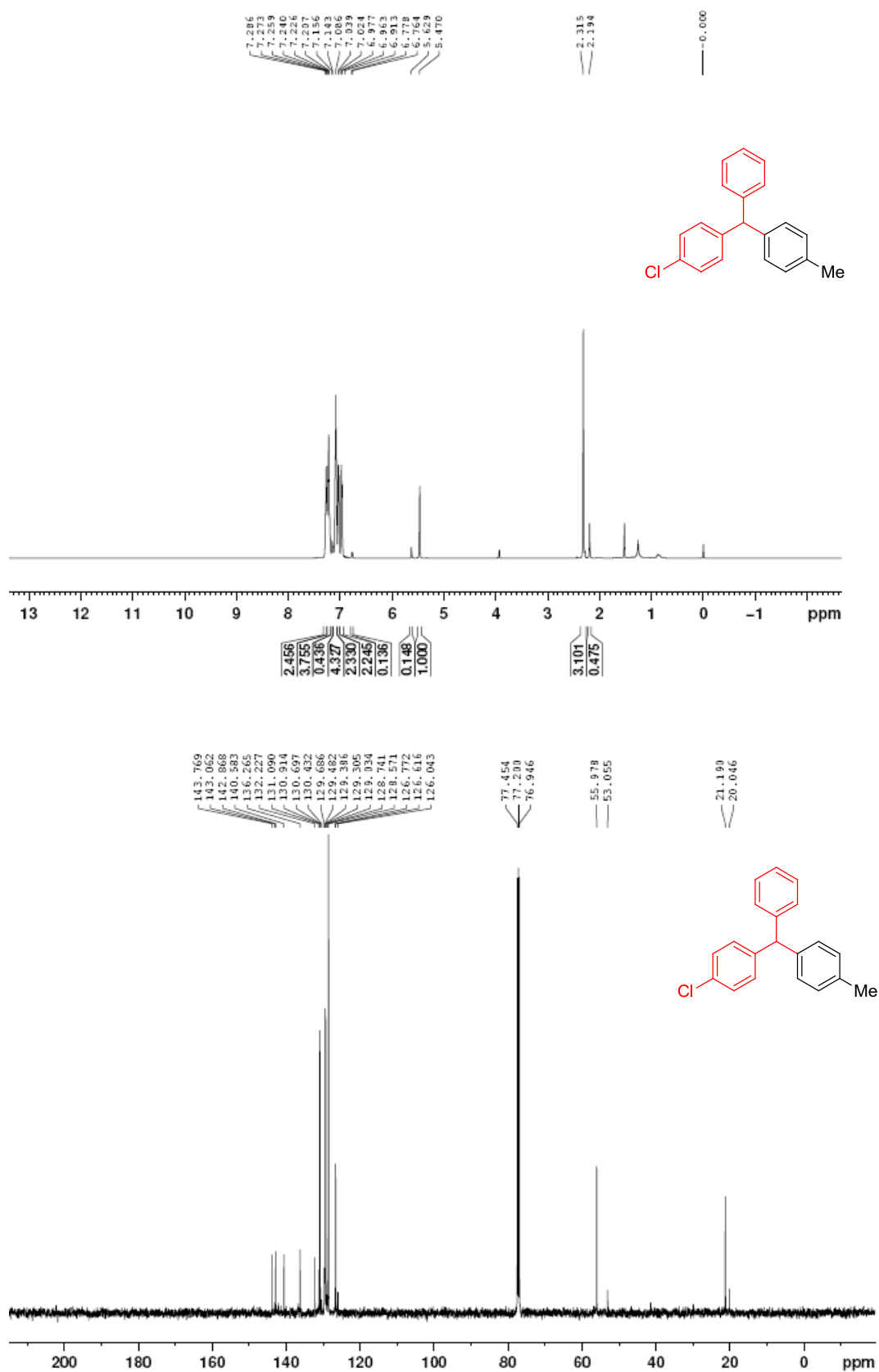
1-chloro-4-(1-*p*-tolylethyl)benzene (3j)



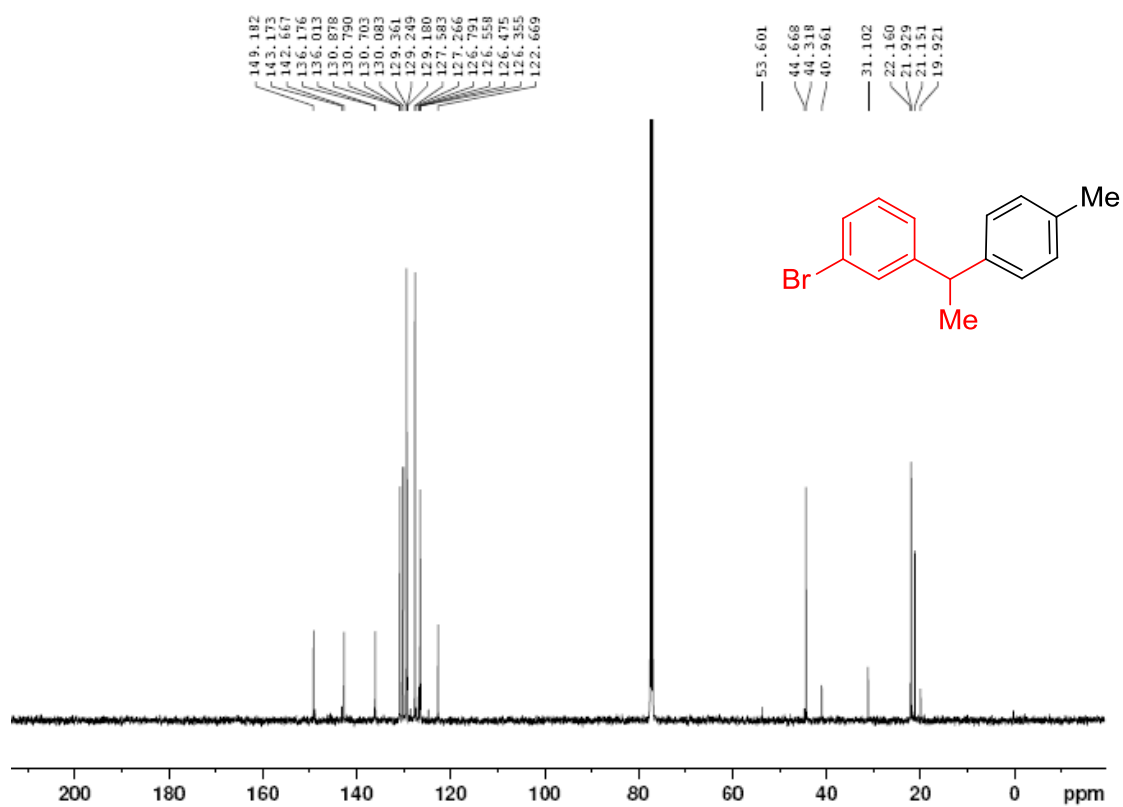
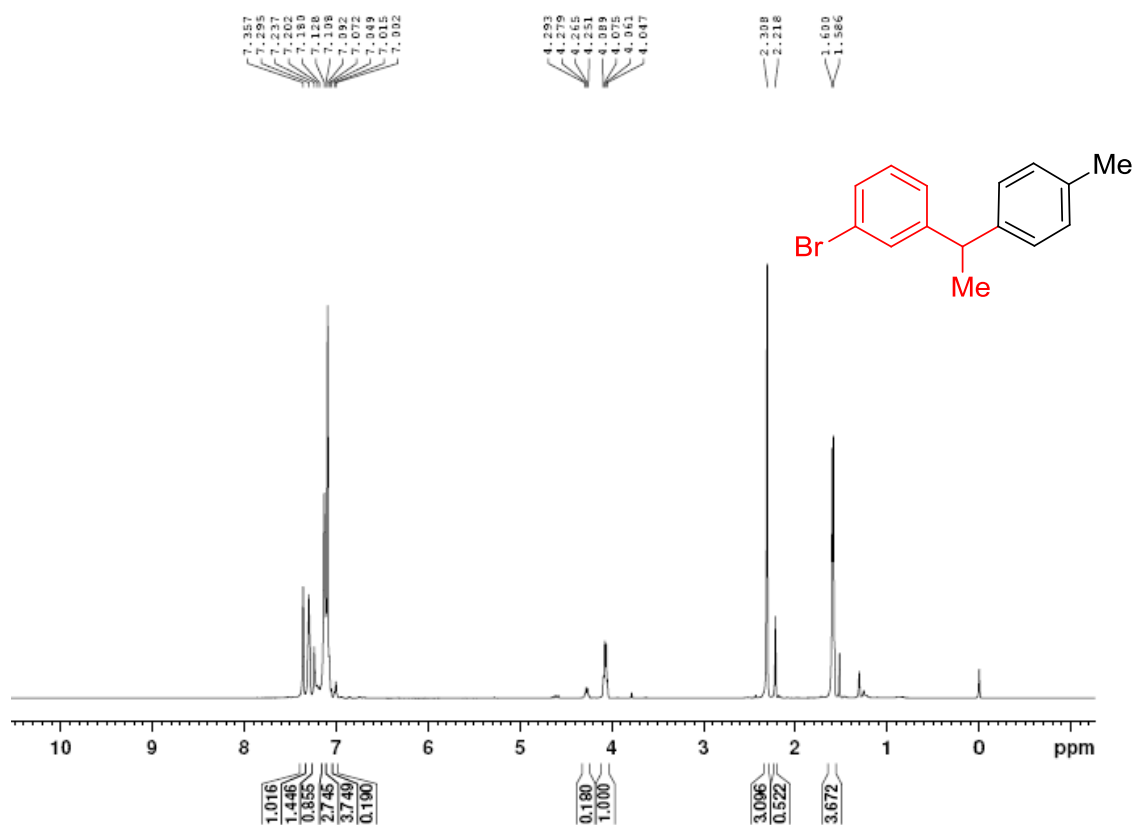
1-chloro-3-(1-*p*-tolylethyl)benzene (3k)



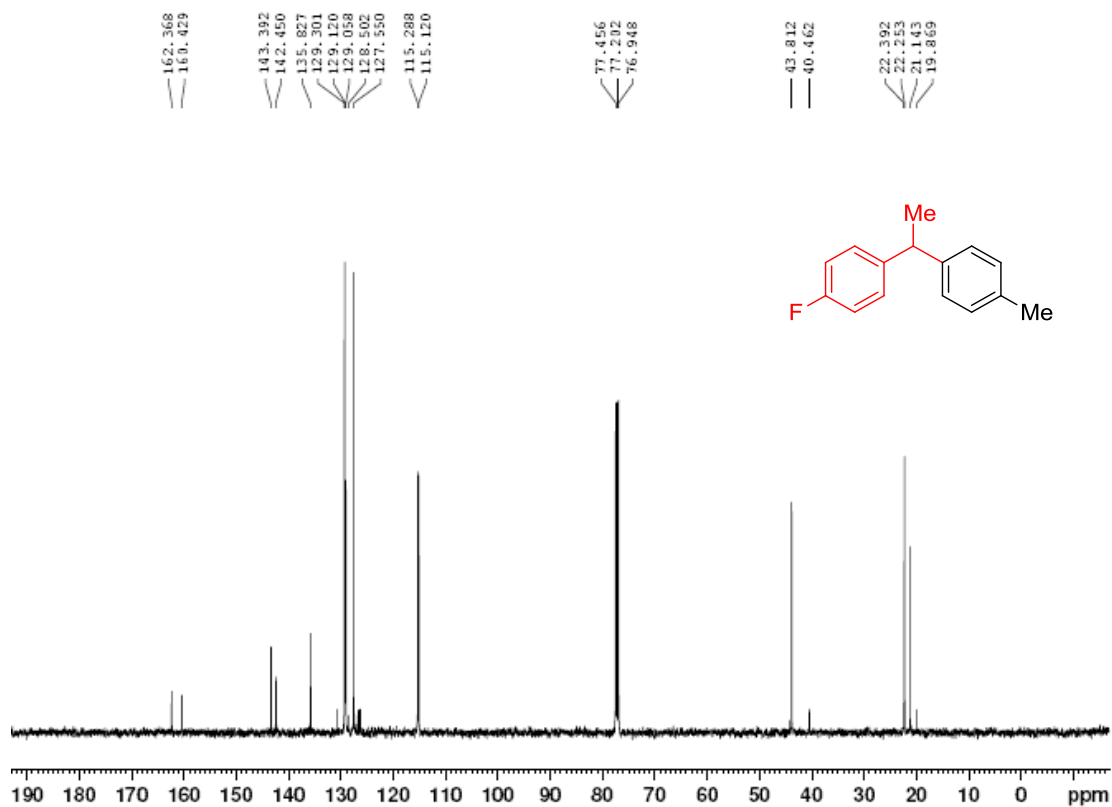
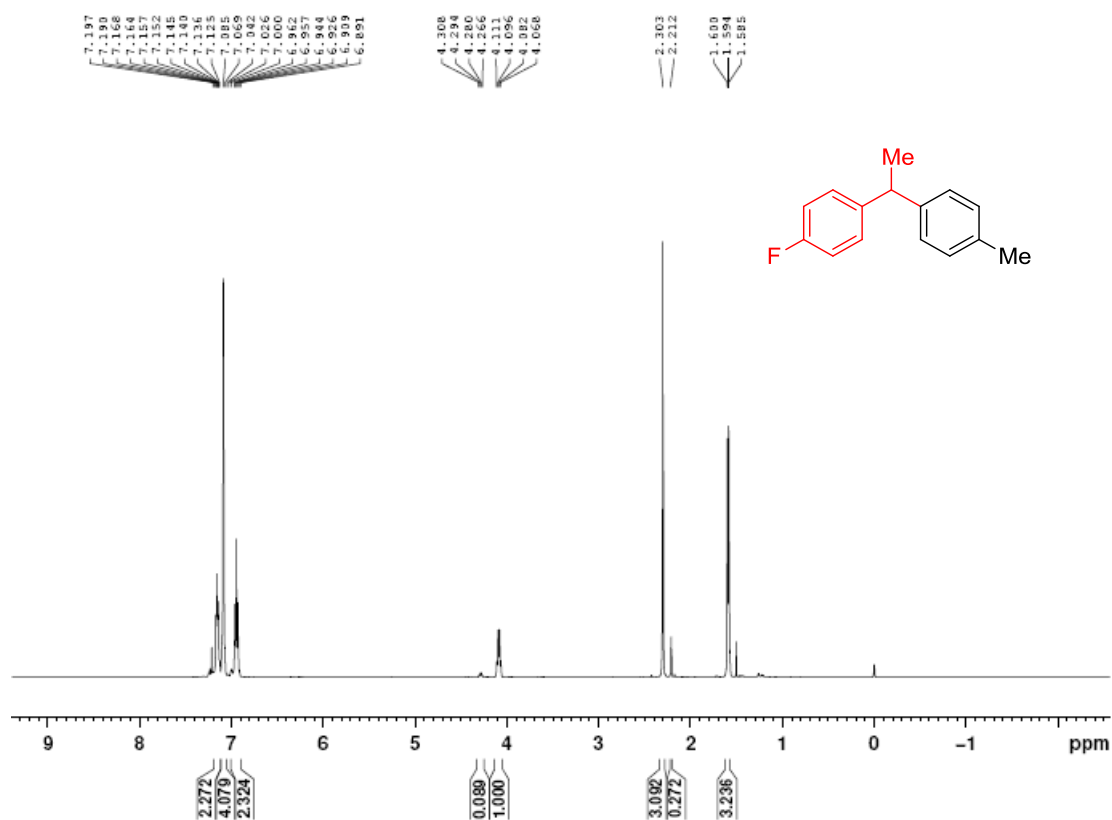
**1-chloro-4-(phenyl(*p*-tolyl)methyl)benzene (3l)**



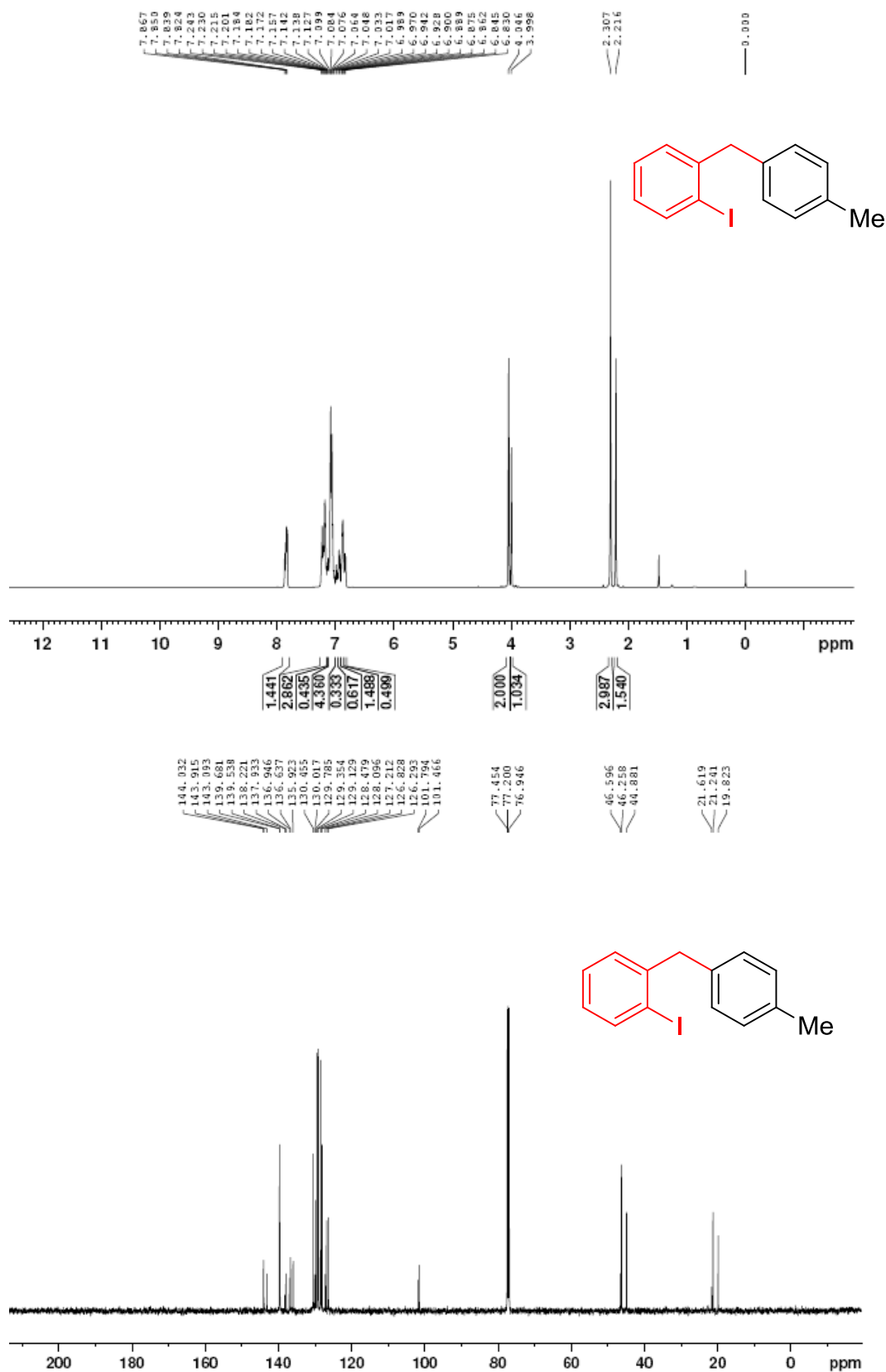
**1-bromo-3-(1-*p*-tolylethyl)benzene (3m)**



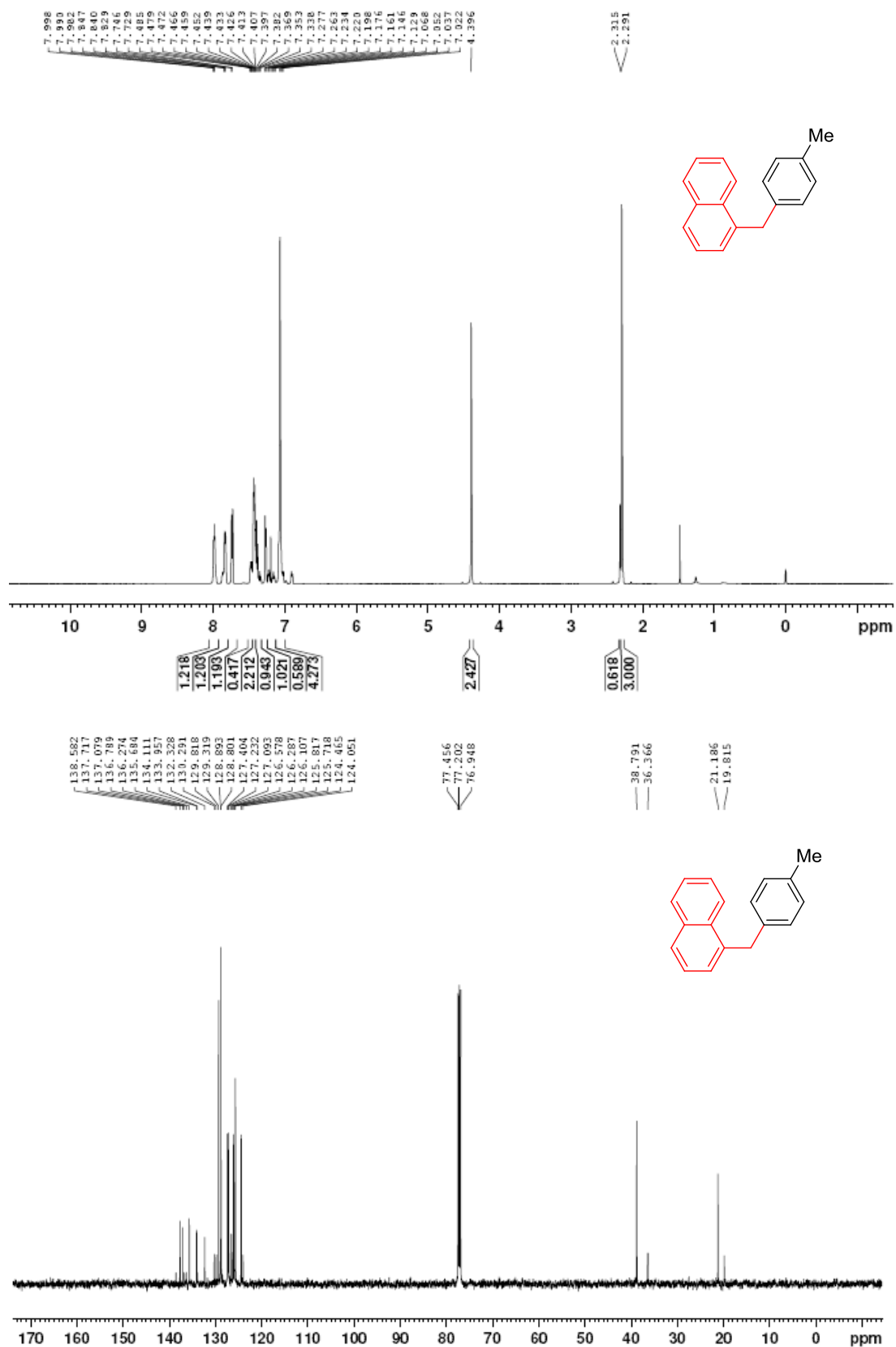
**1-fluoro-4-(1-*p*-tolylethyl)benzene (3n)**



**1-iodo-2-(4-methylbenzyl)benzene (3o)**

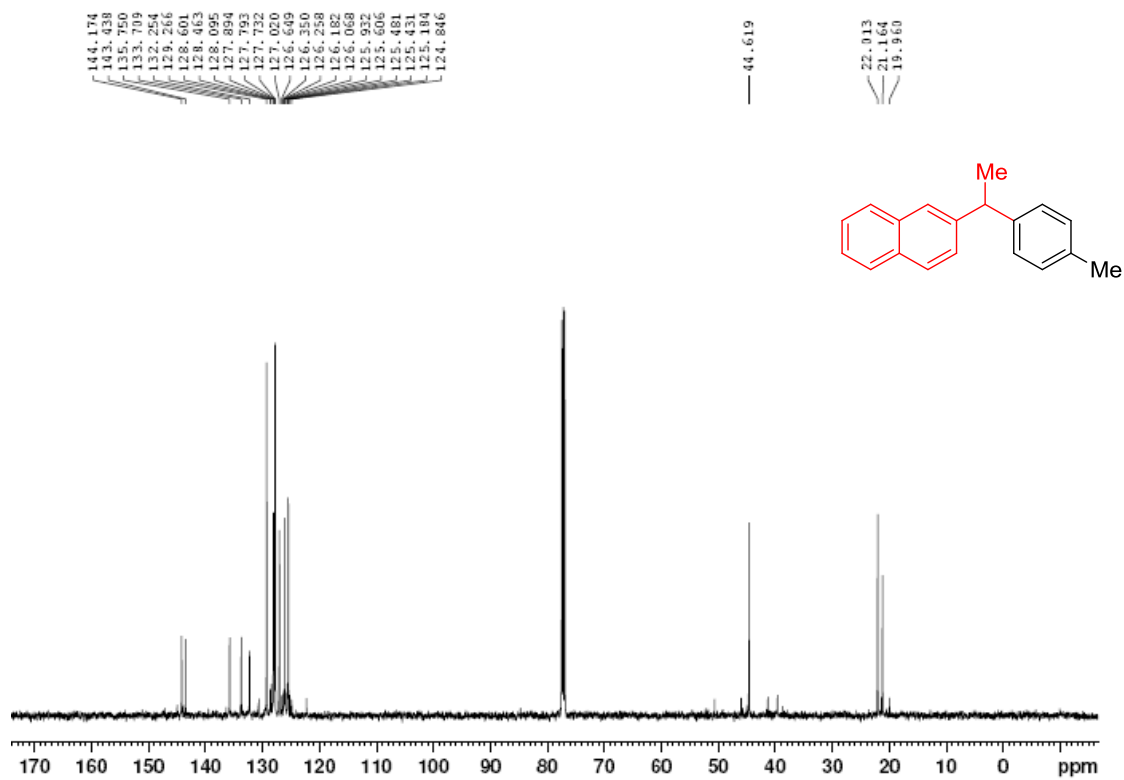
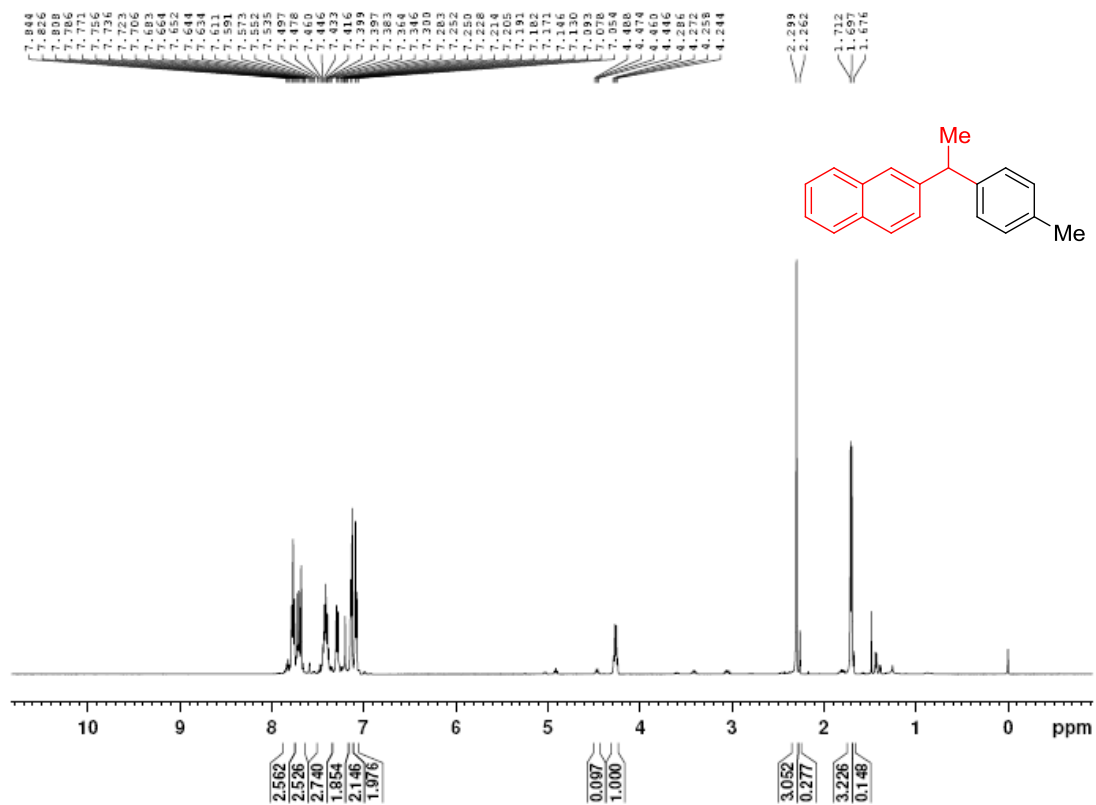


# 1-(4-methylbenzyl)naphthalene (3p)

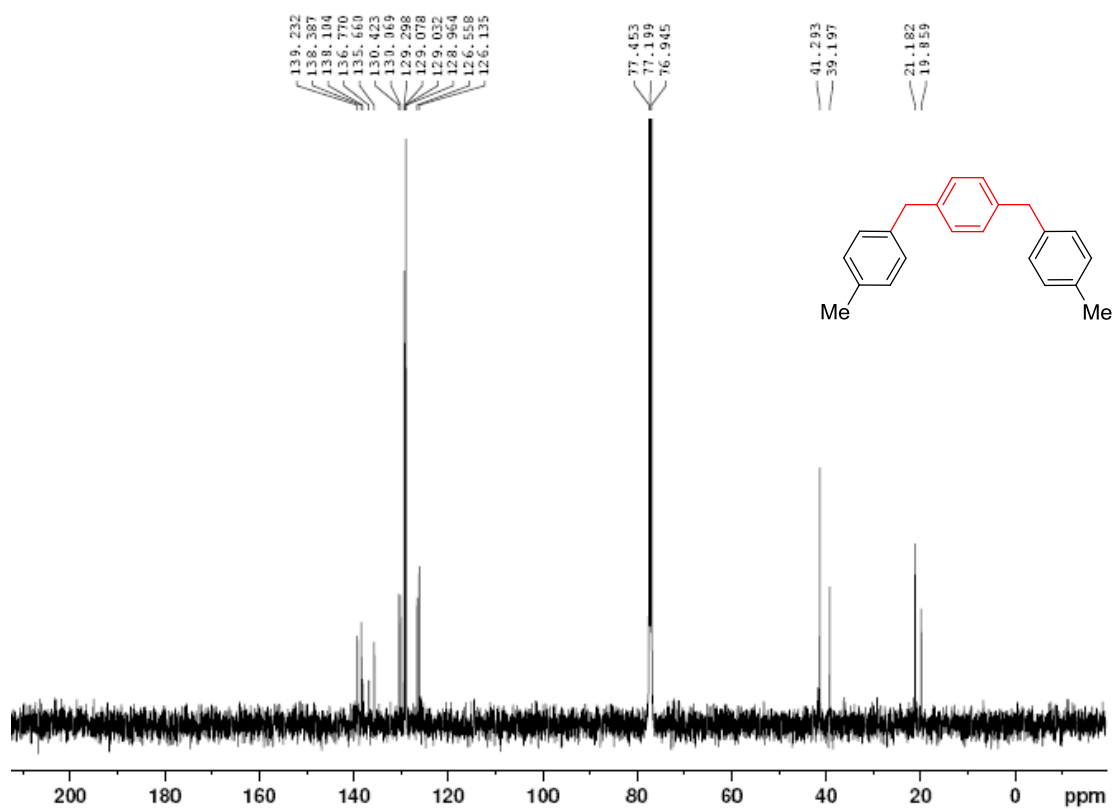
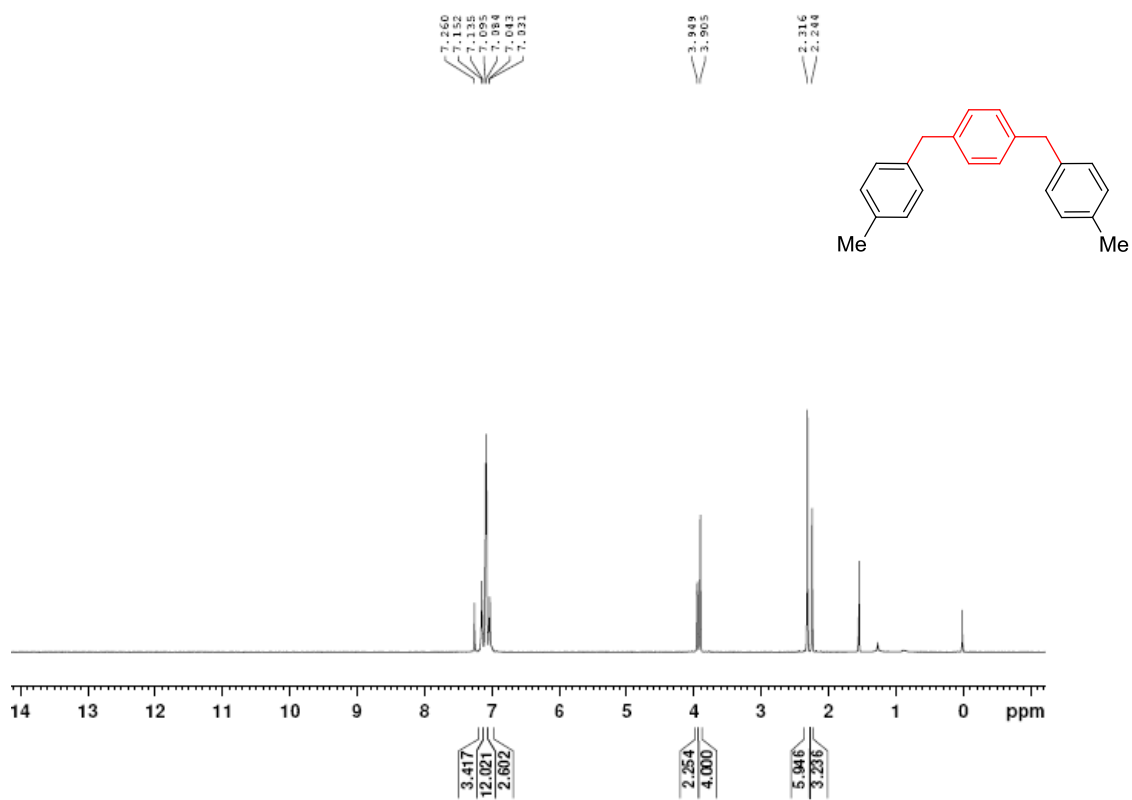




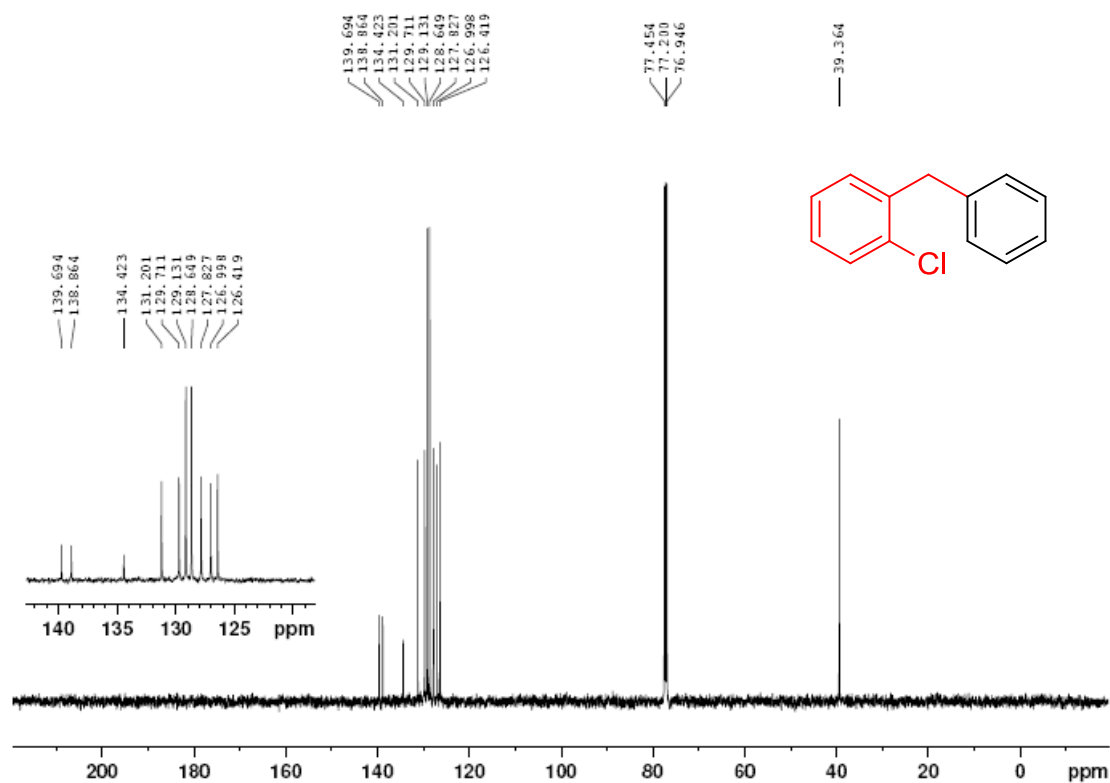
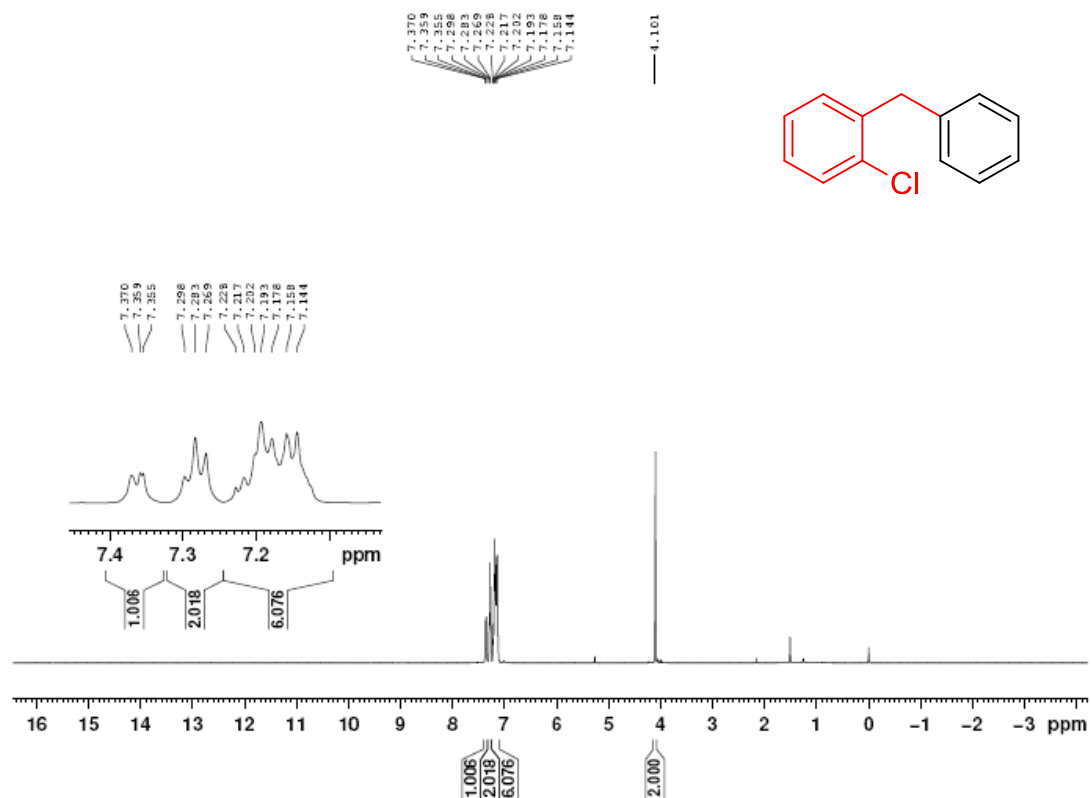
# 2-(1-*p*-tolylethyl)naphthalene (3q)



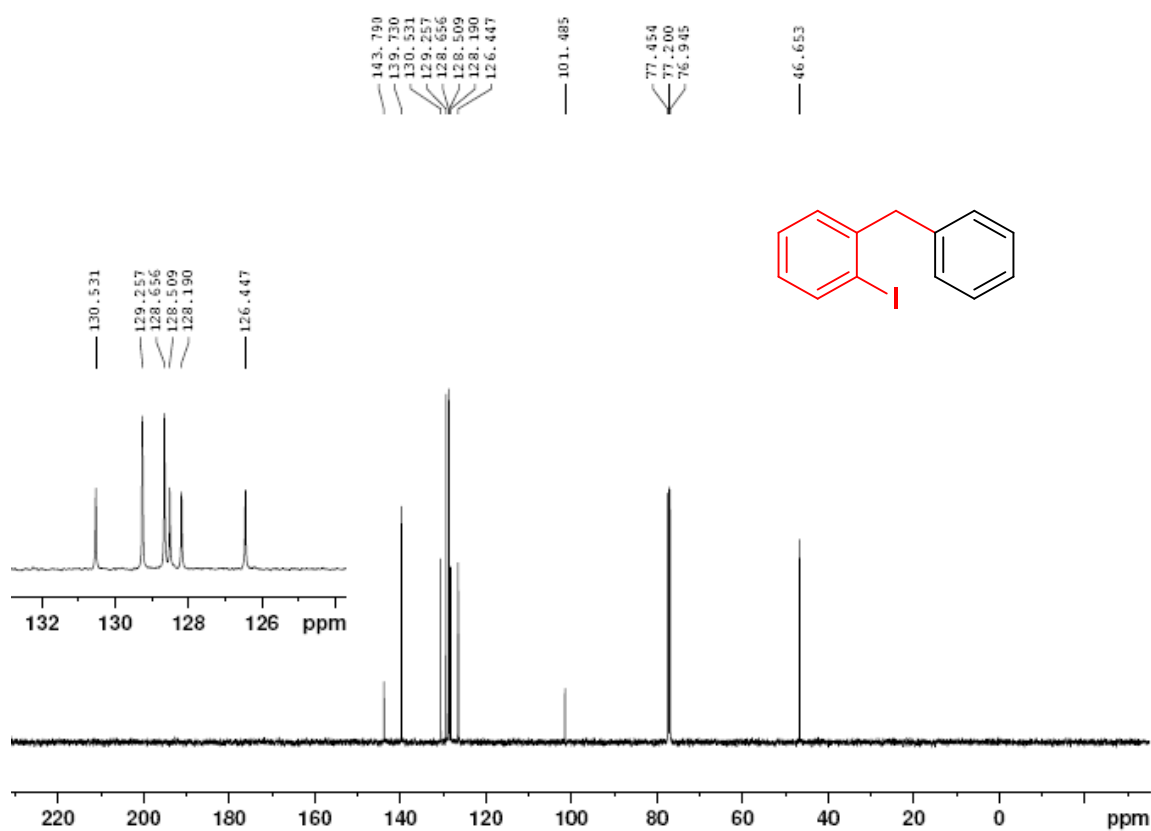
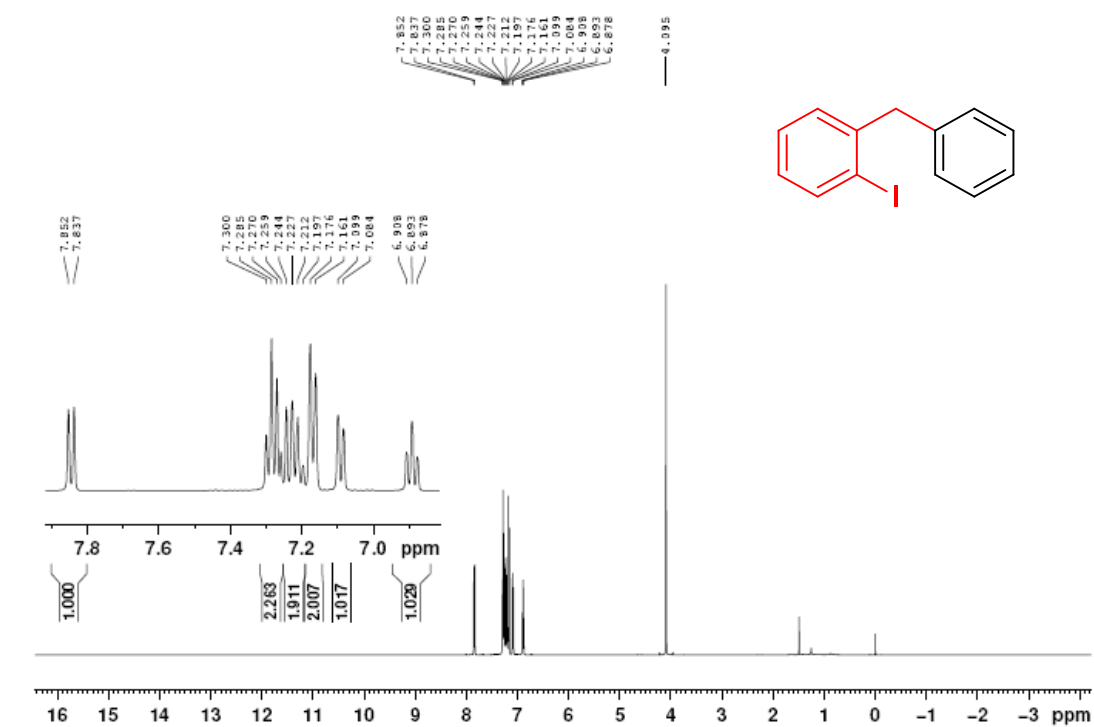
**1,4-bis(4-methylbenzyl)benzene (3r)**



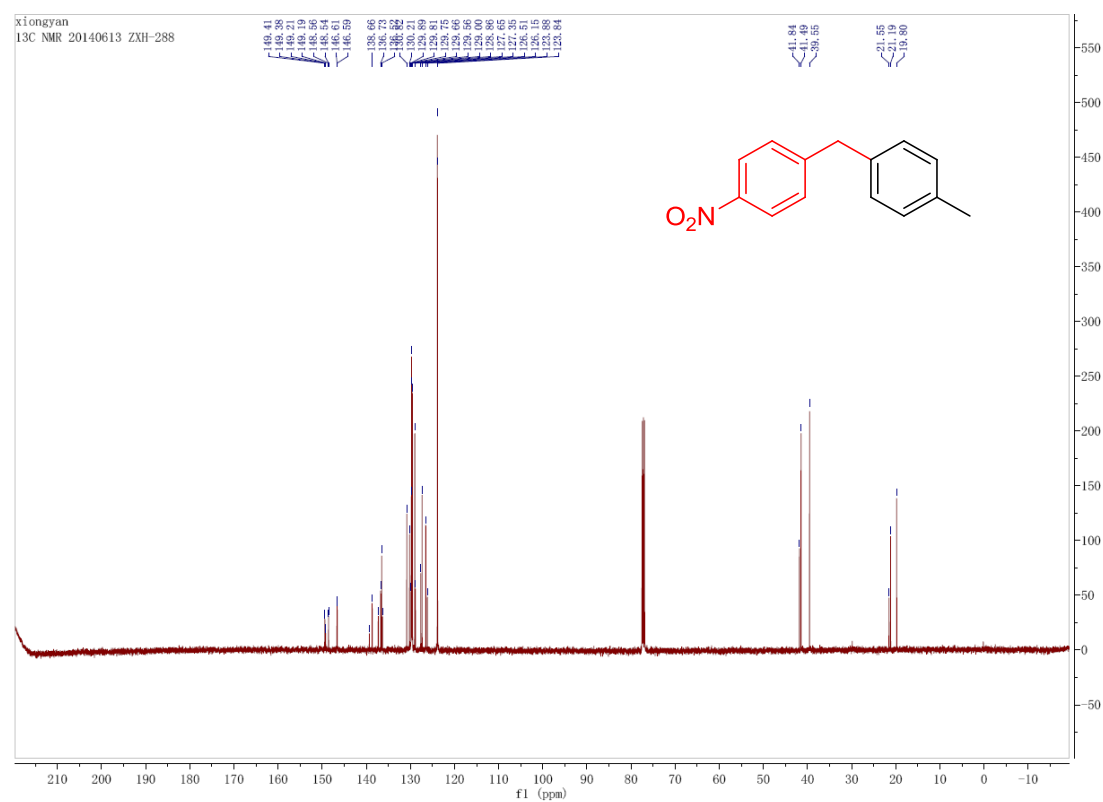
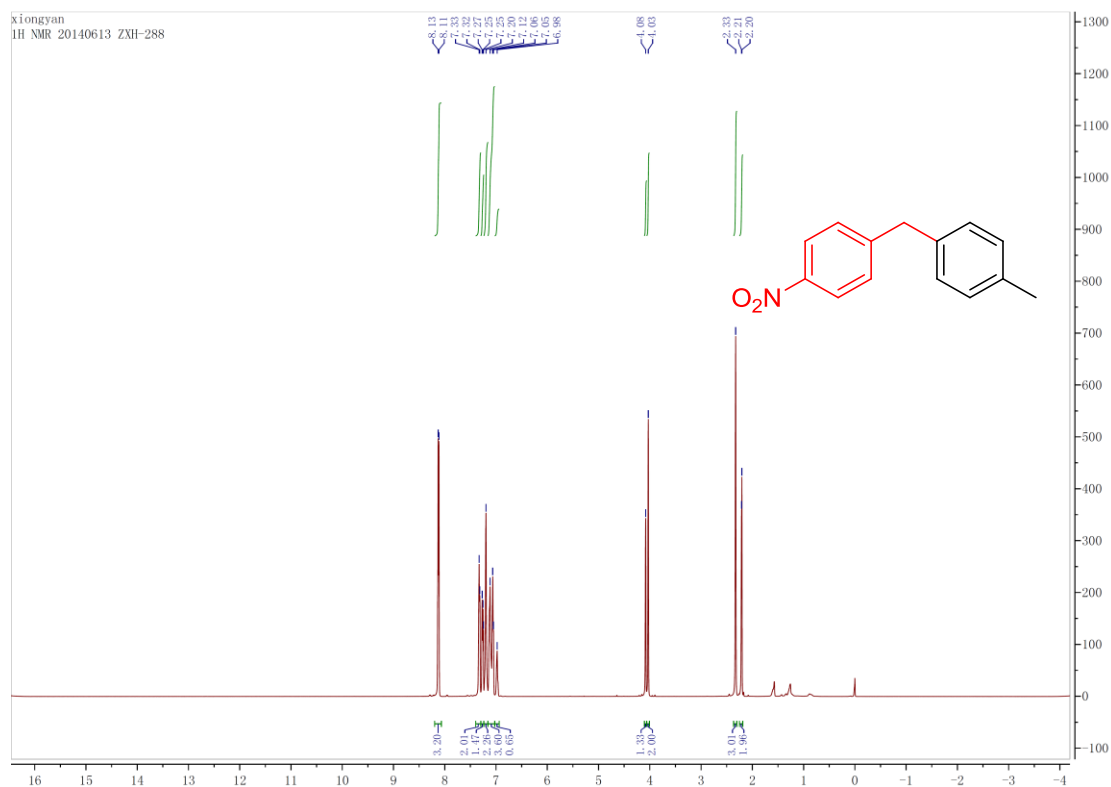
# 1-benzyl-2-chlorobenzene (3s)



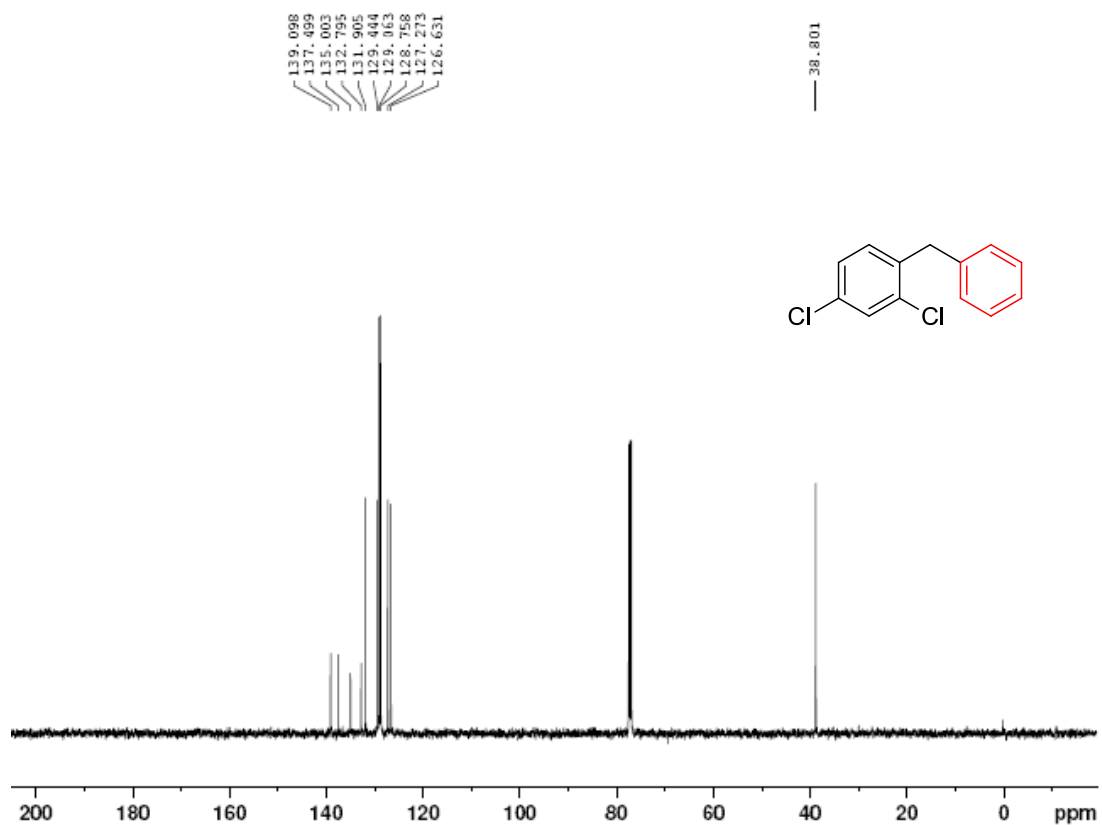
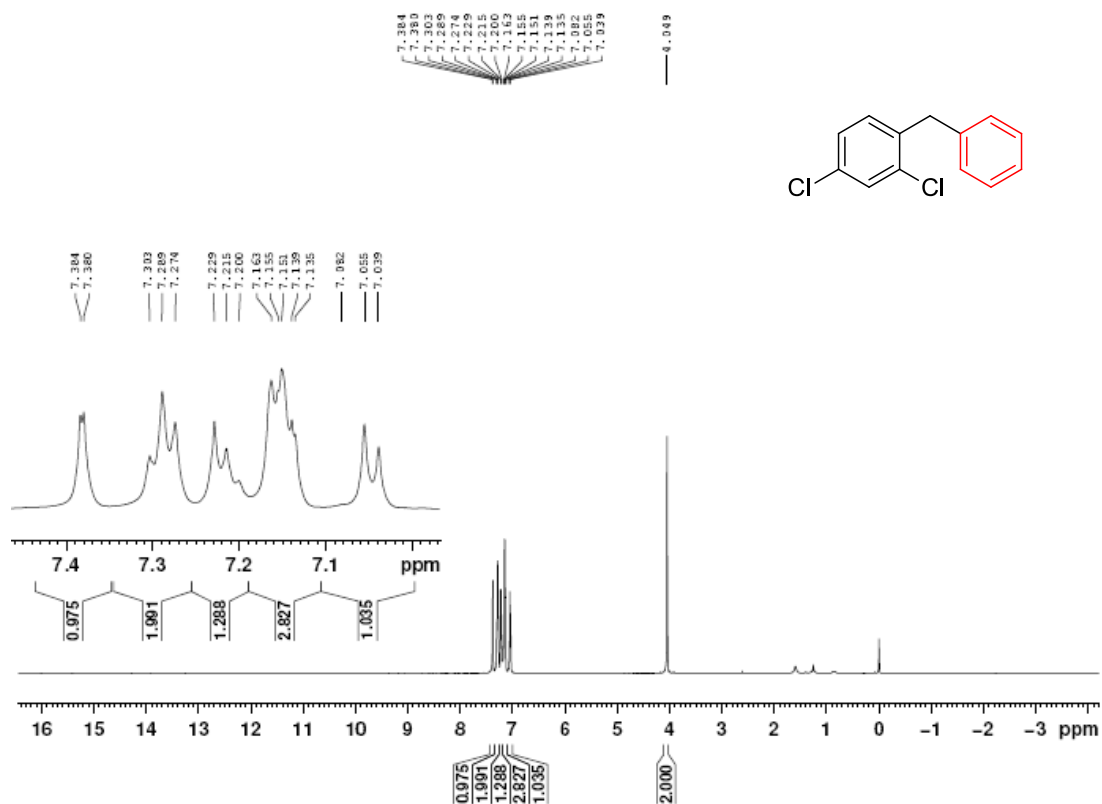
# 1-benzyl-2-iodobenzene (3t)



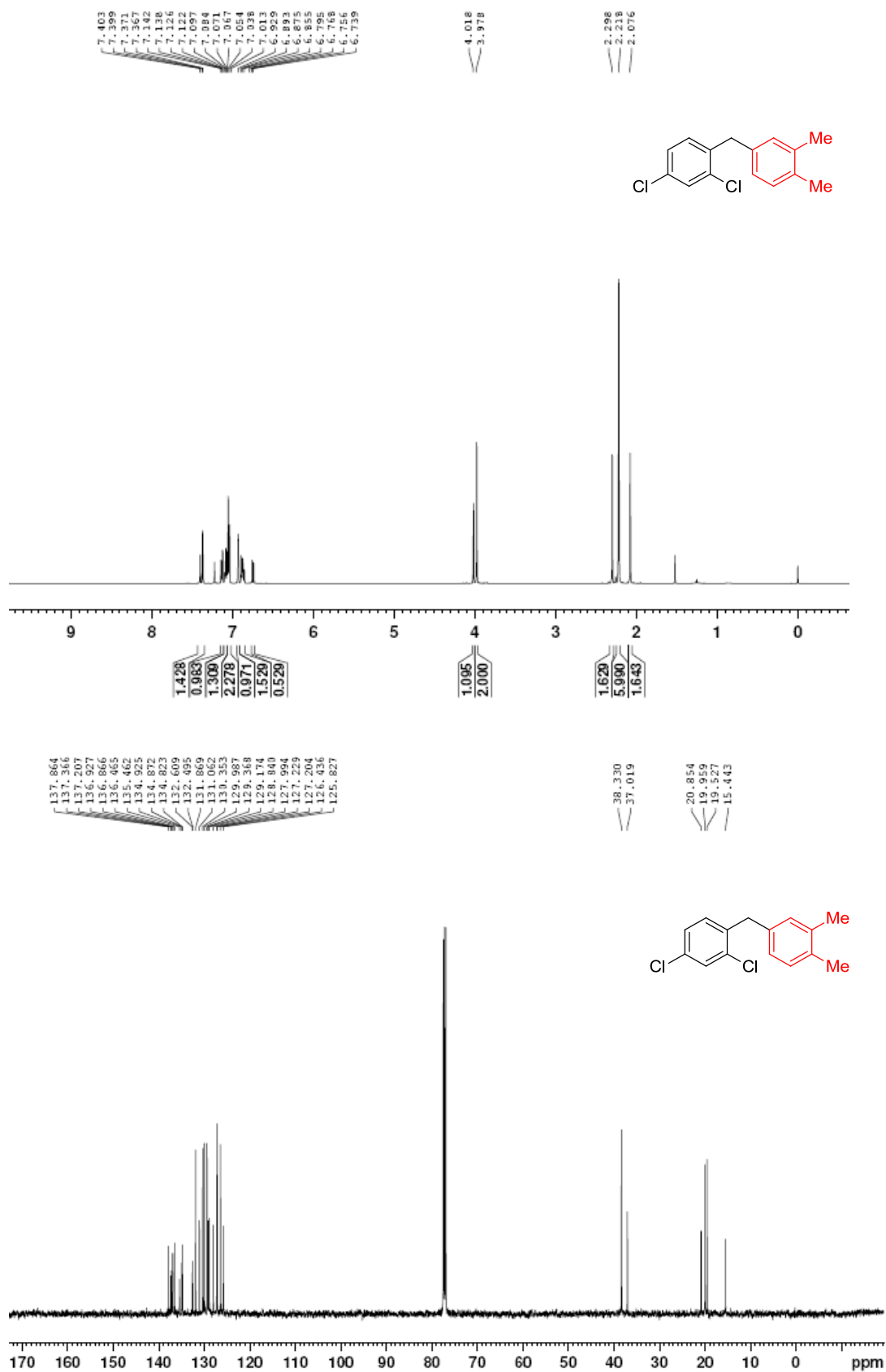
# **methyl-4-(4-nitrobenzyl)benzene (3u)**



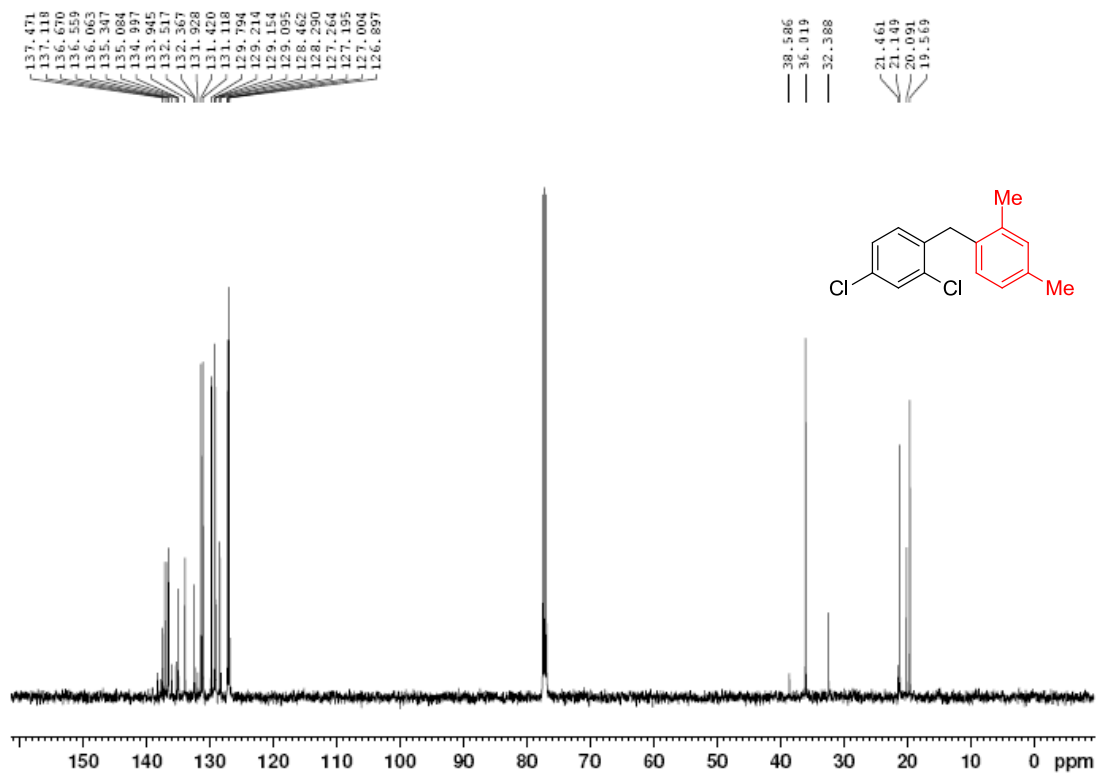
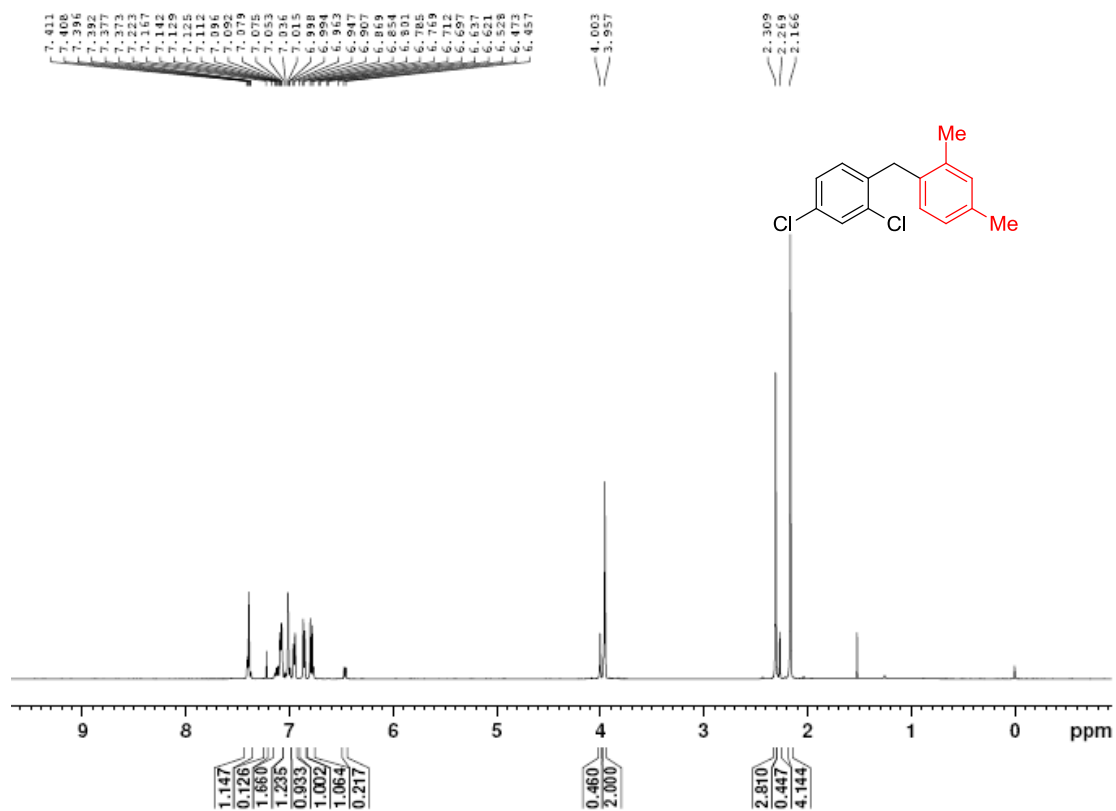
# 1-benzyl-2,4-dichlorobenzene (4a)



2,4-dichloro-1-(3,4-dimethylbenzyl)benzene (4b)

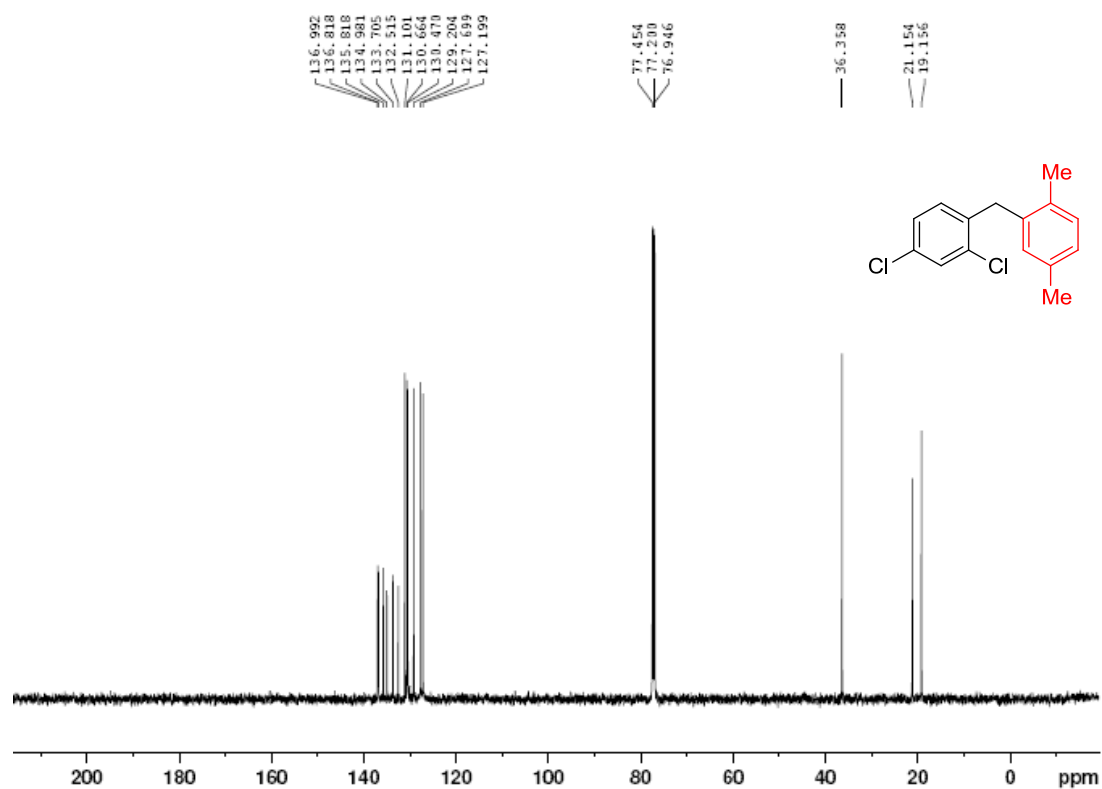
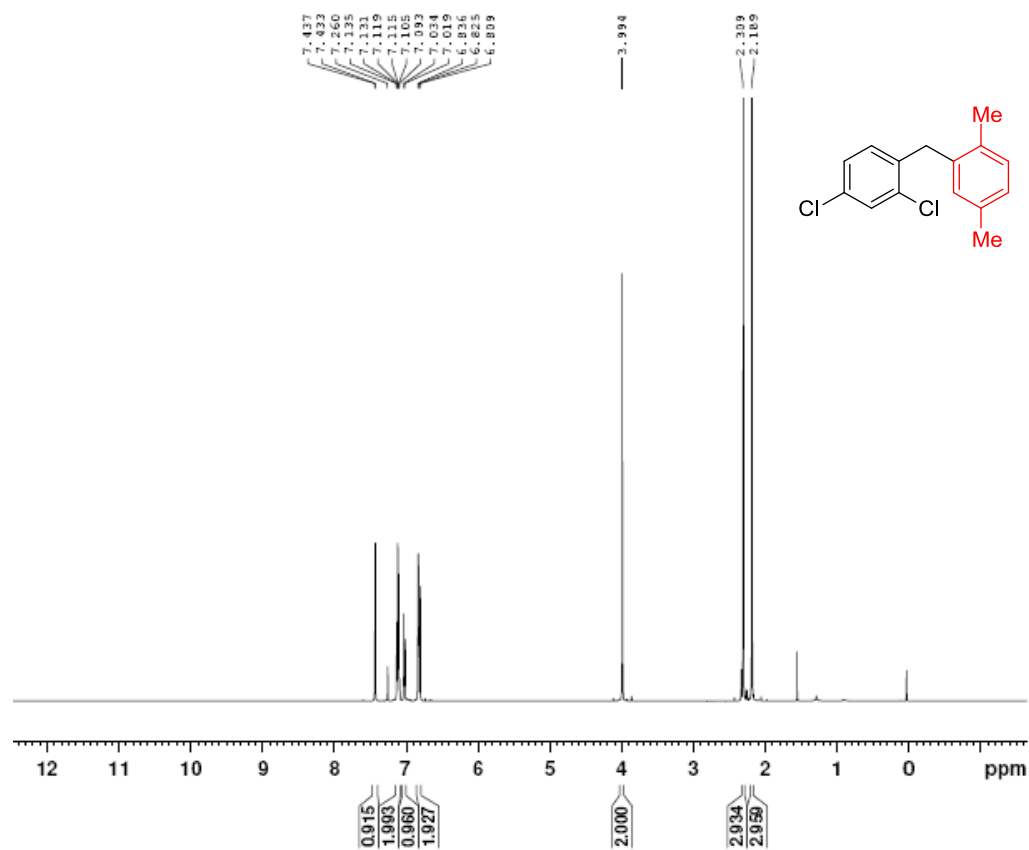


2,4-dichloro-1-(2,4-dimethylbenzyl)benzene (4c)





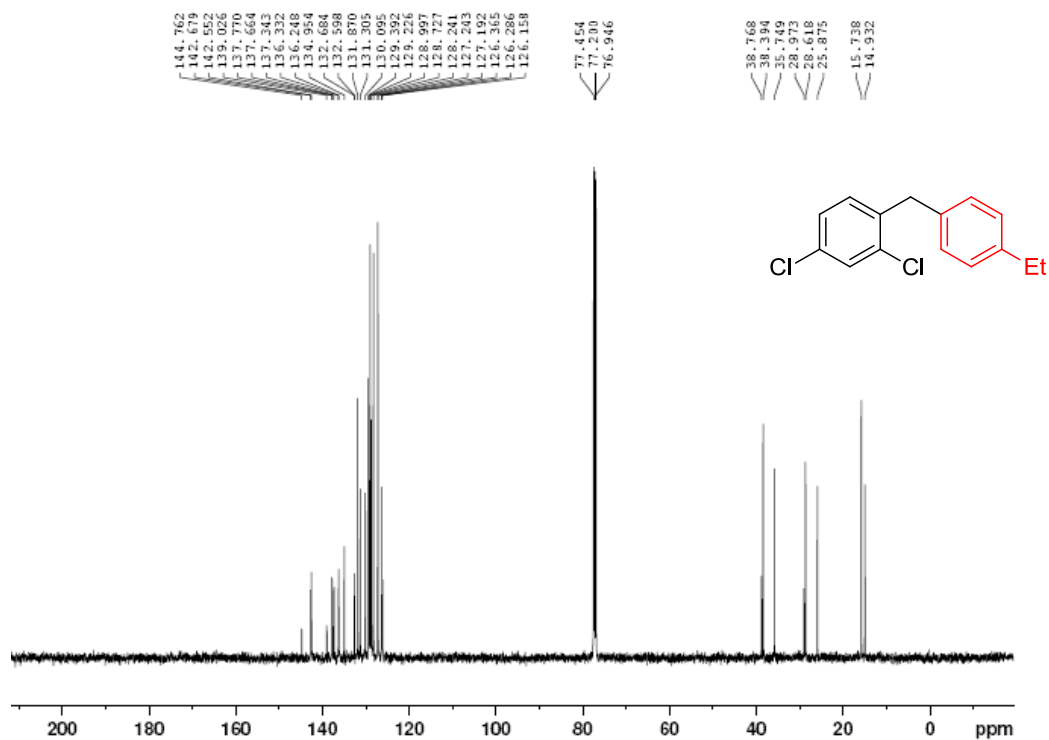
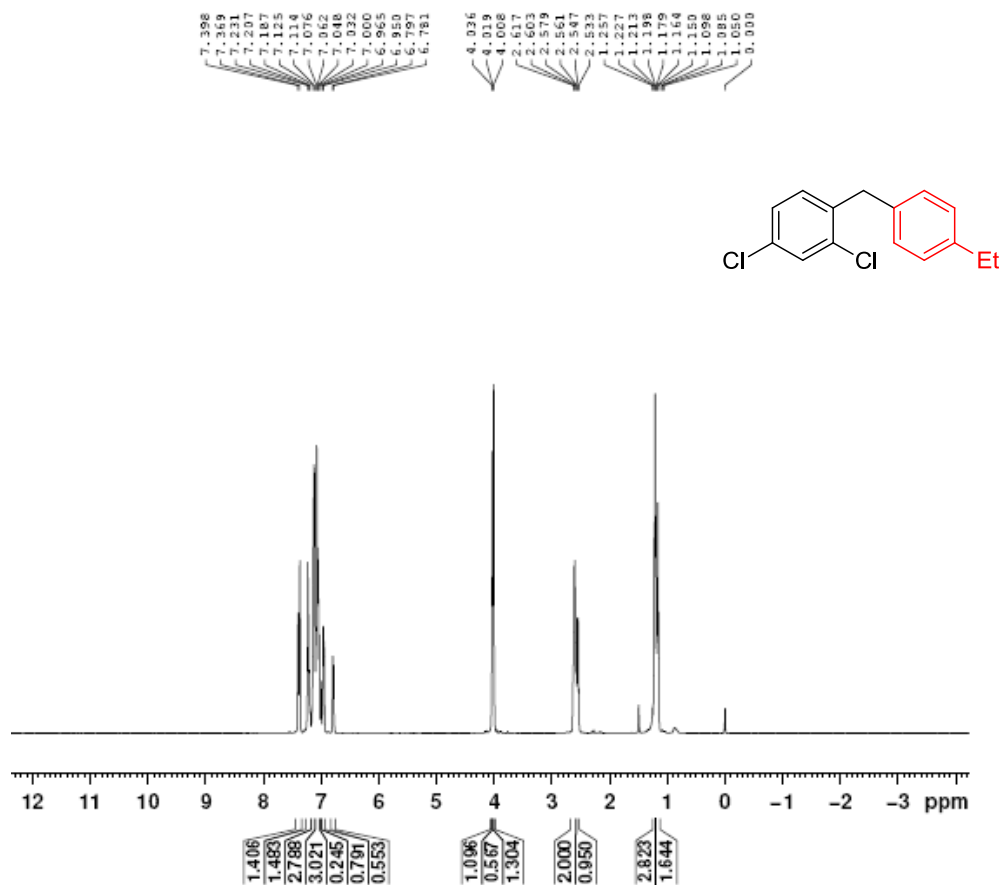
2,4-dichloro-1-(2,5-dimethylbenzyl)benzene (4d)



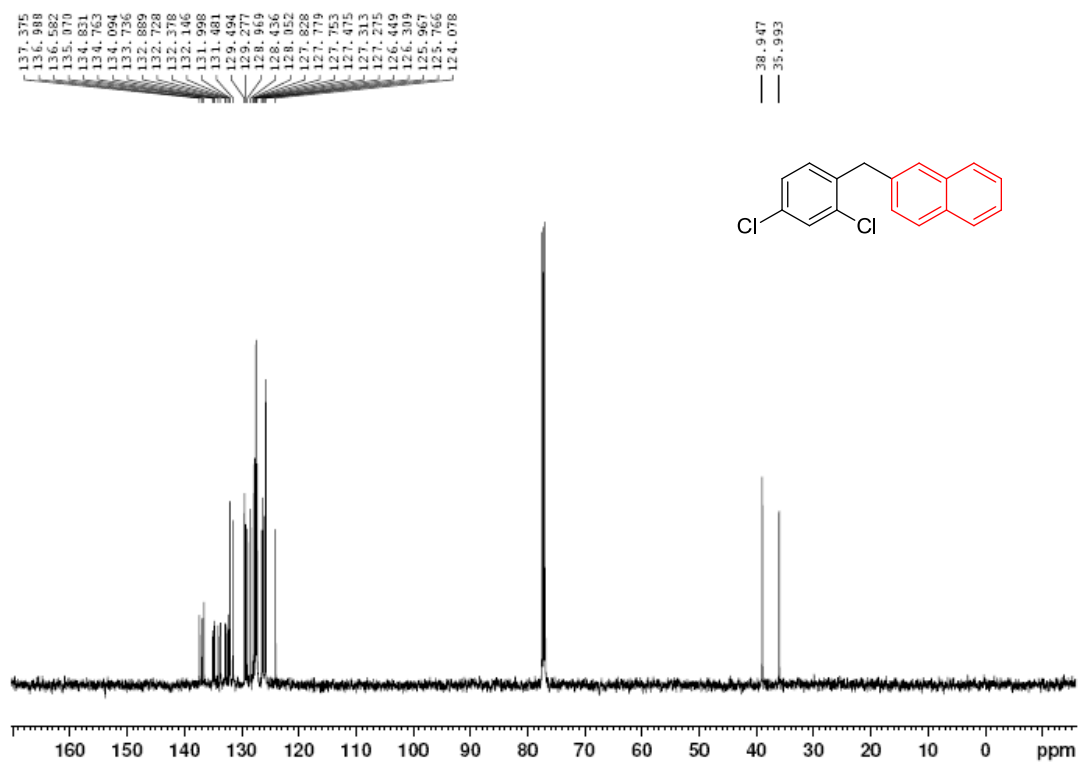
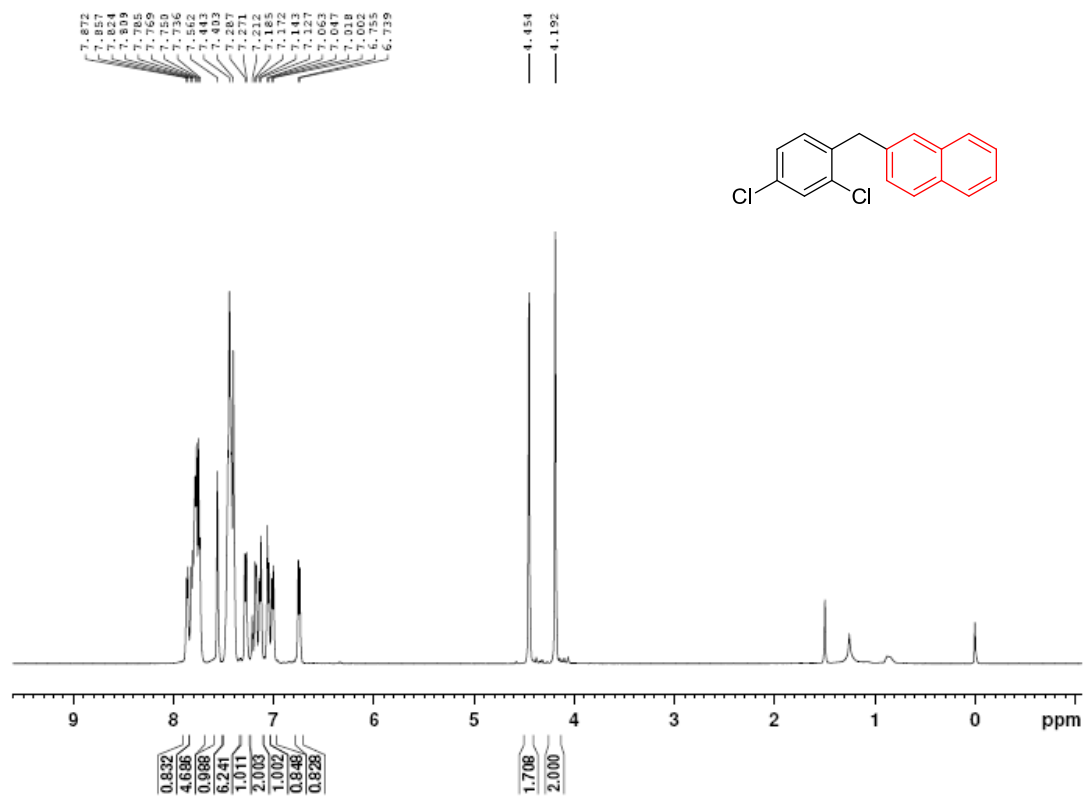
2-(2,4-dichlorobenzyl)-1,3,5-trimethylbenzene (4e)



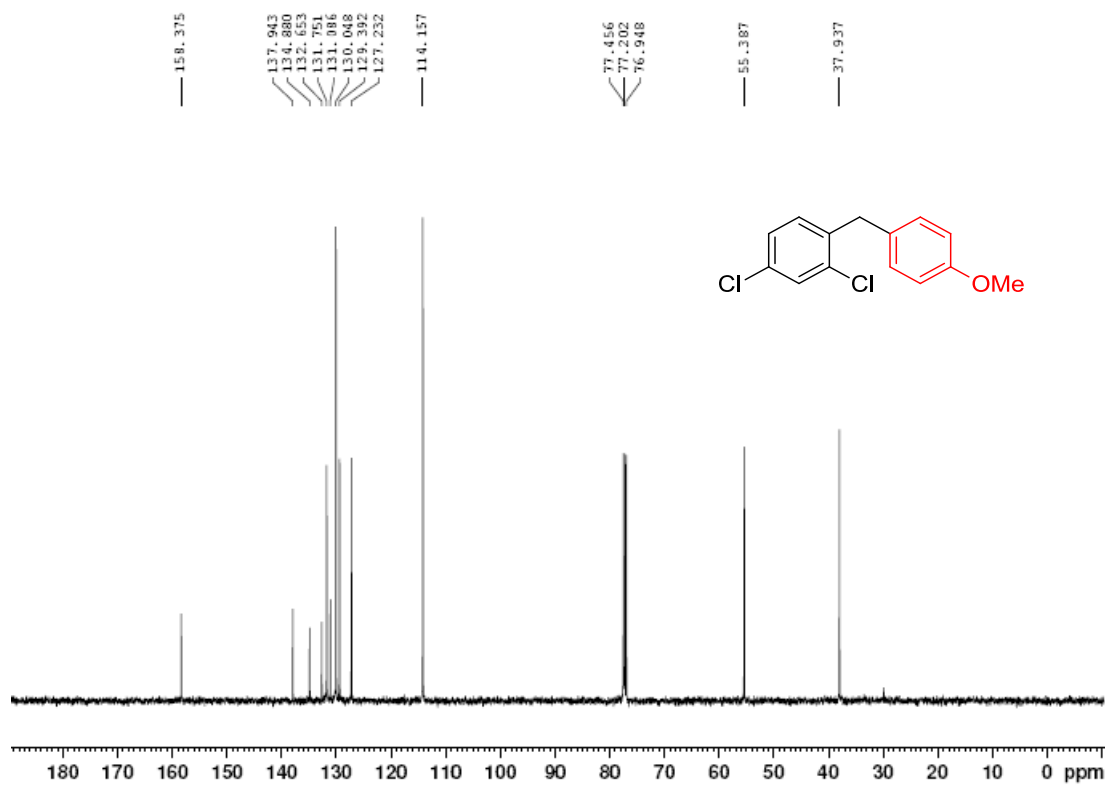
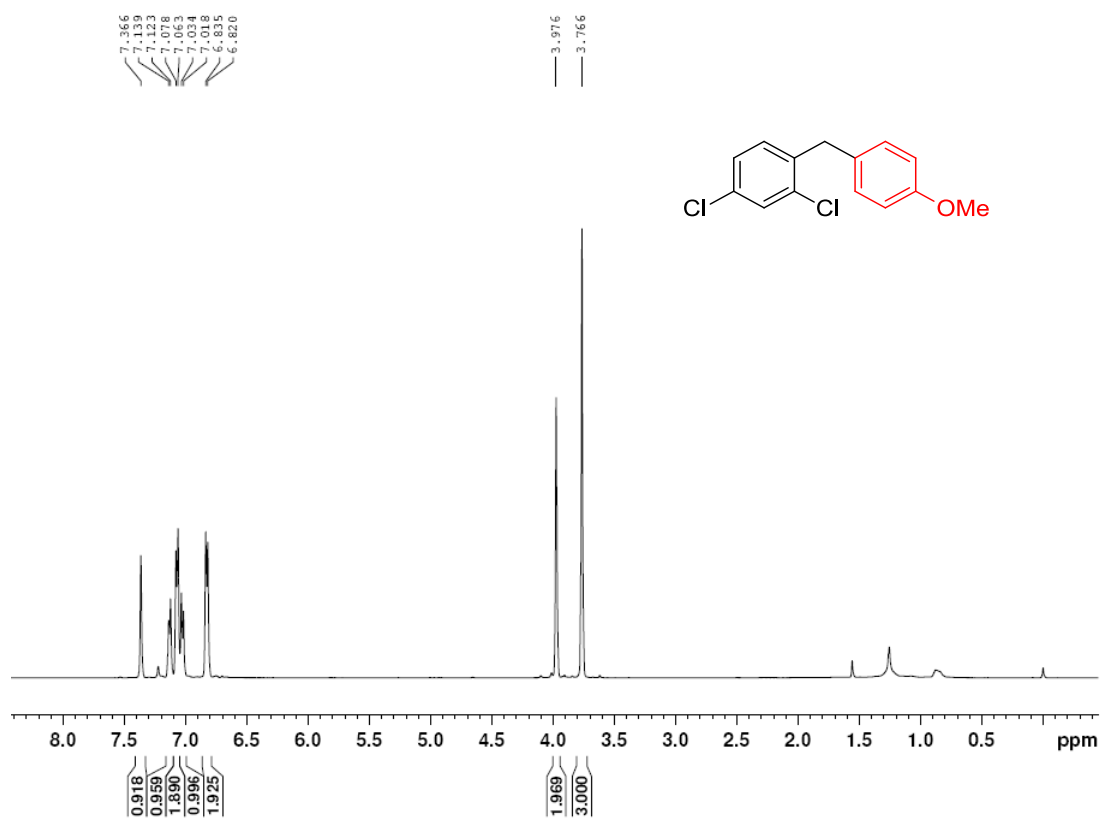
2,4-dichloro-1-(4-ethylbenzyl)benzene (4f)



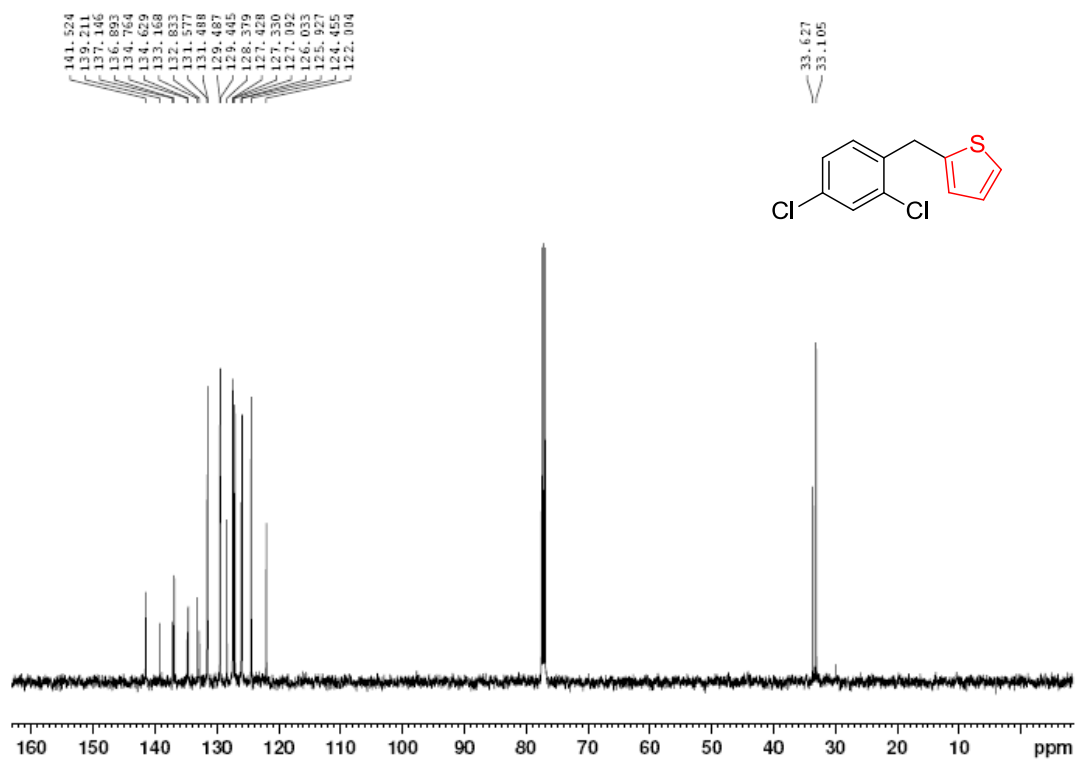
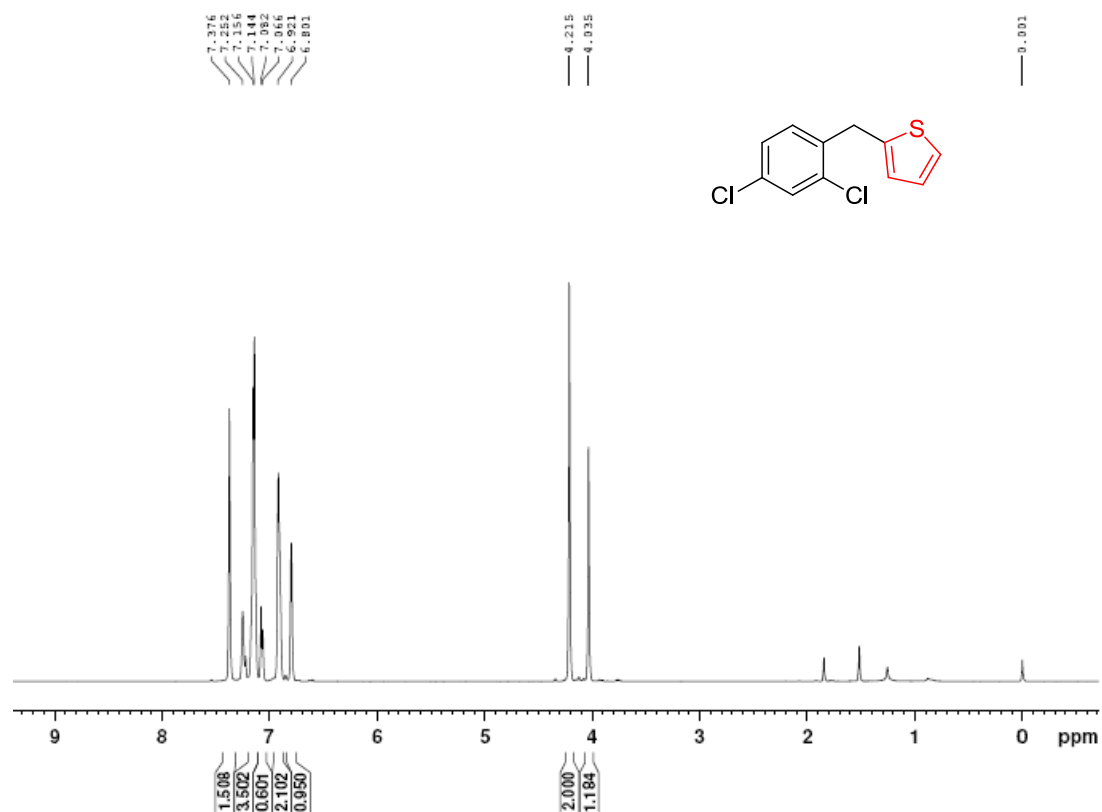
2-(2,4-dichlorobenzyl)naphthalene (4g)



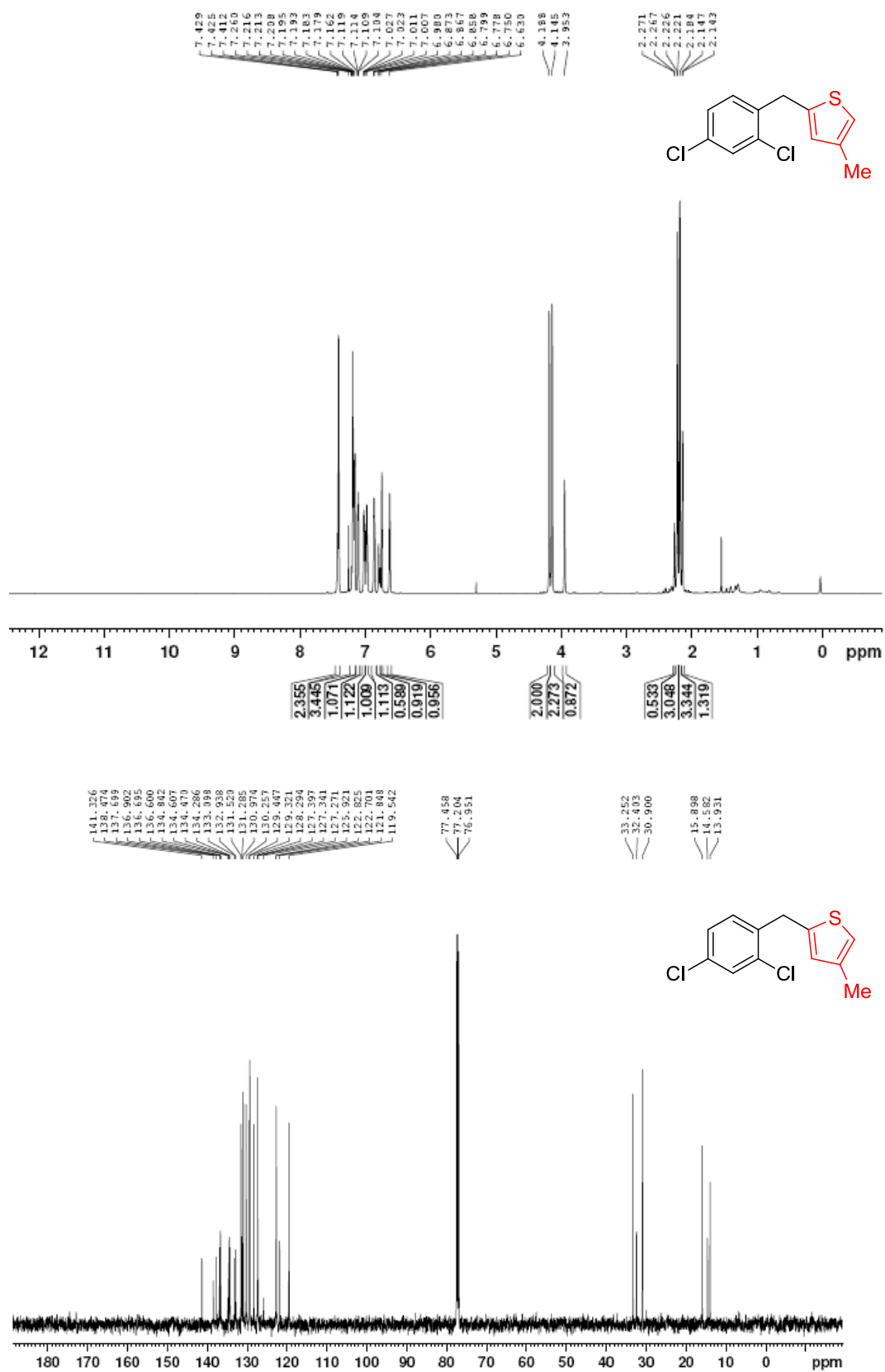
**2,4-dichloro-1-(4-methoxybenzyl)benzene (4h)**



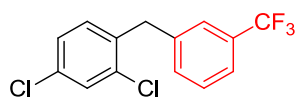
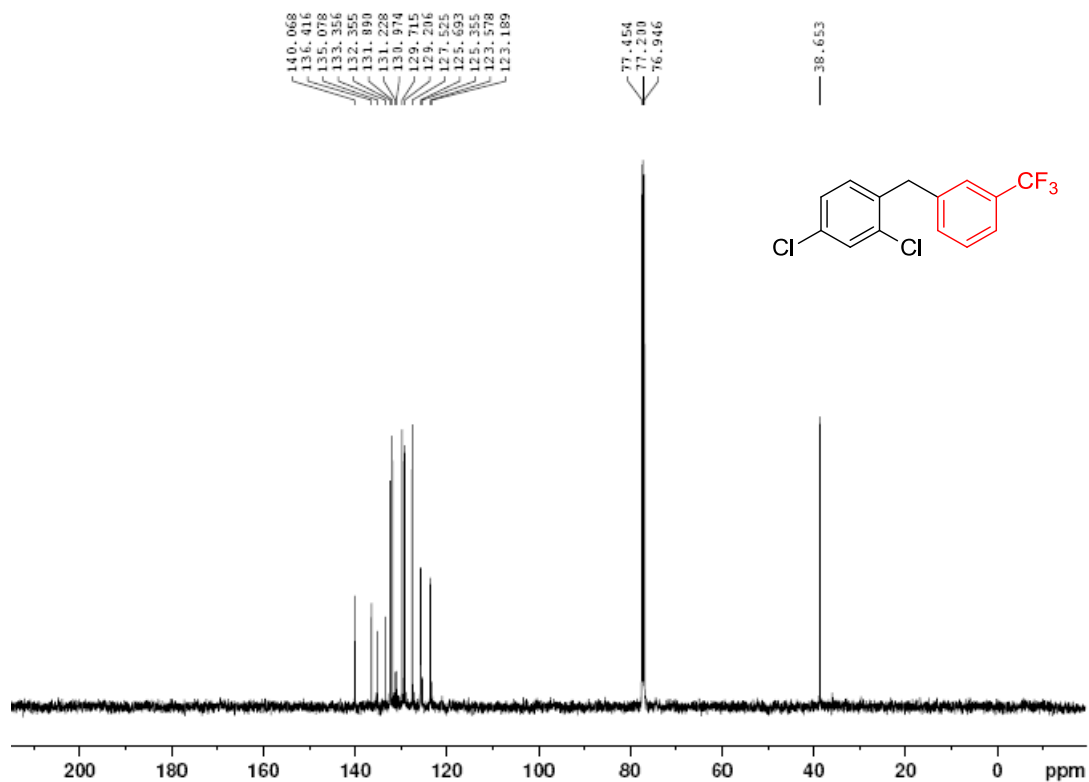
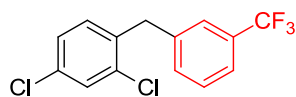
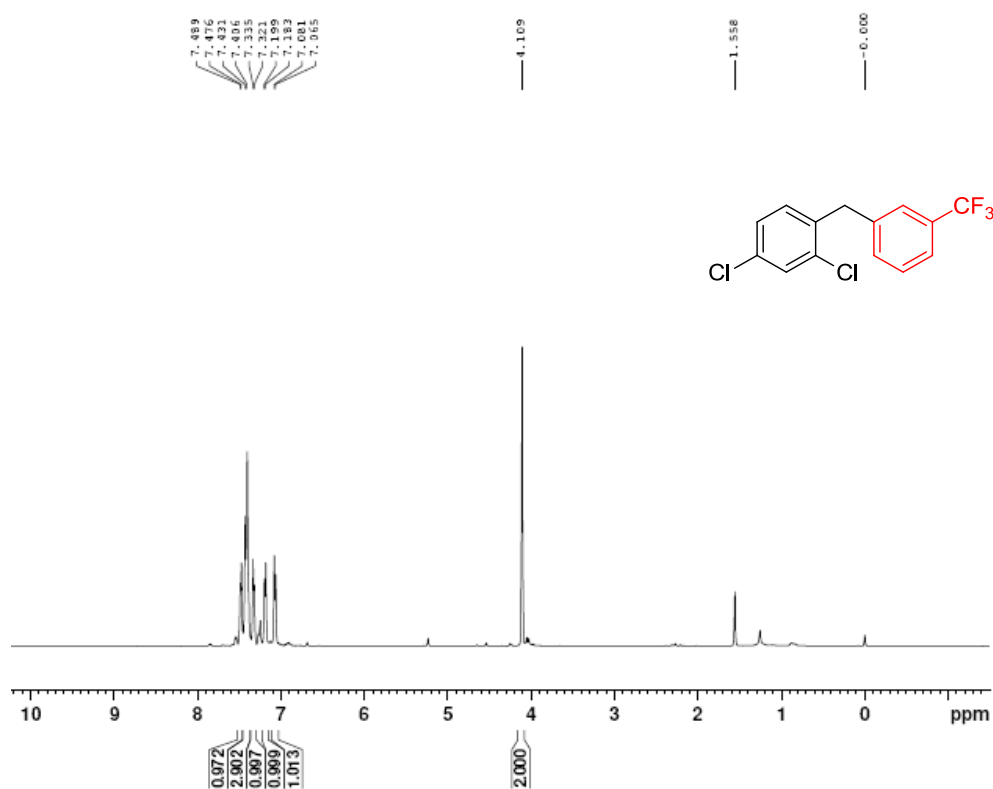
2-(2,4-dichlorobenzyl)thiophene (4i)



2-(2,4-dichlorobenzyl)-3-methylthiophene (4j)

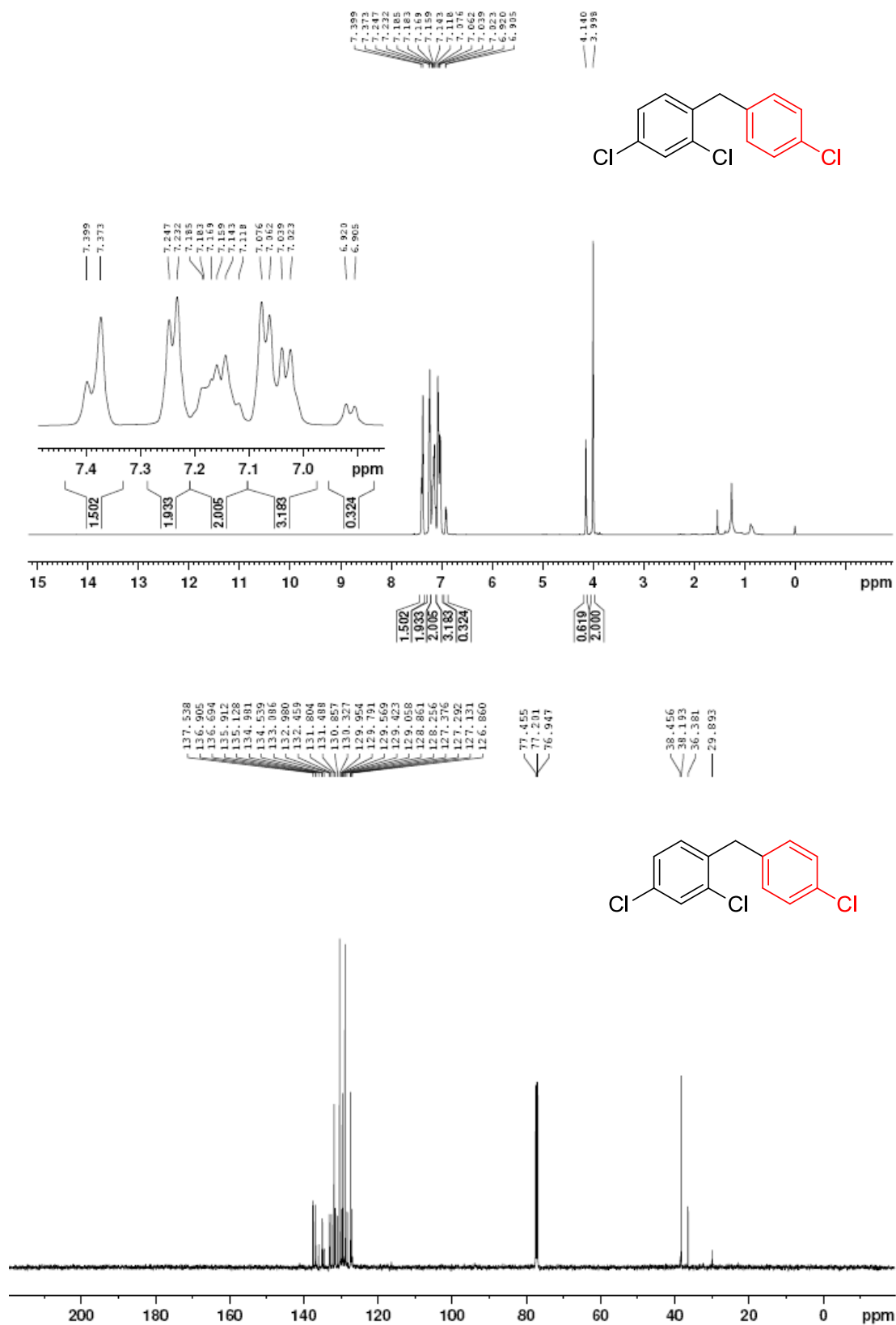


2,4-dichloro-1-(3-(trifluoromethyl)benzyl)benzene (4k)





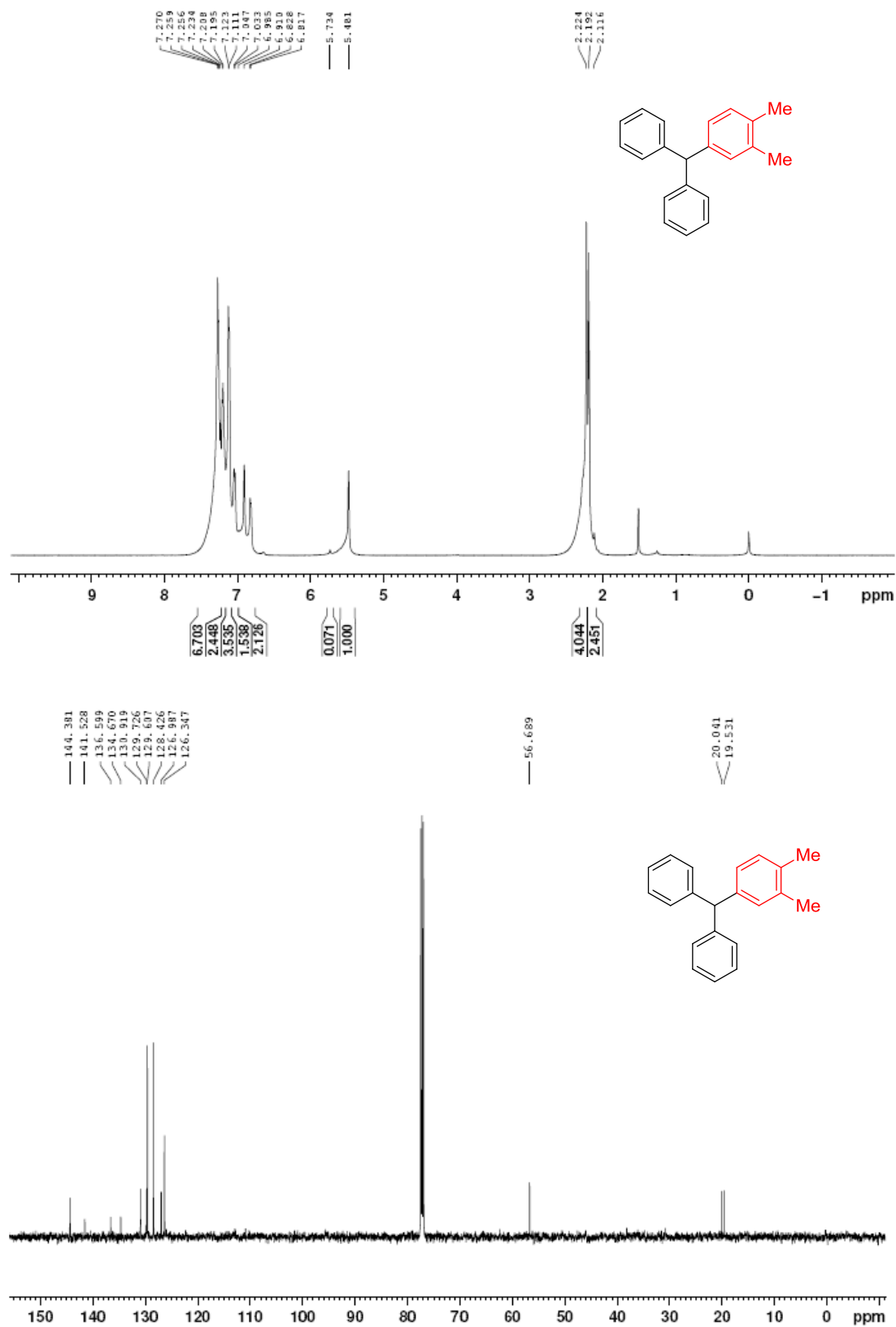
2,4-dichloro-1-(4-chlorobenzyl)benzene (4l)



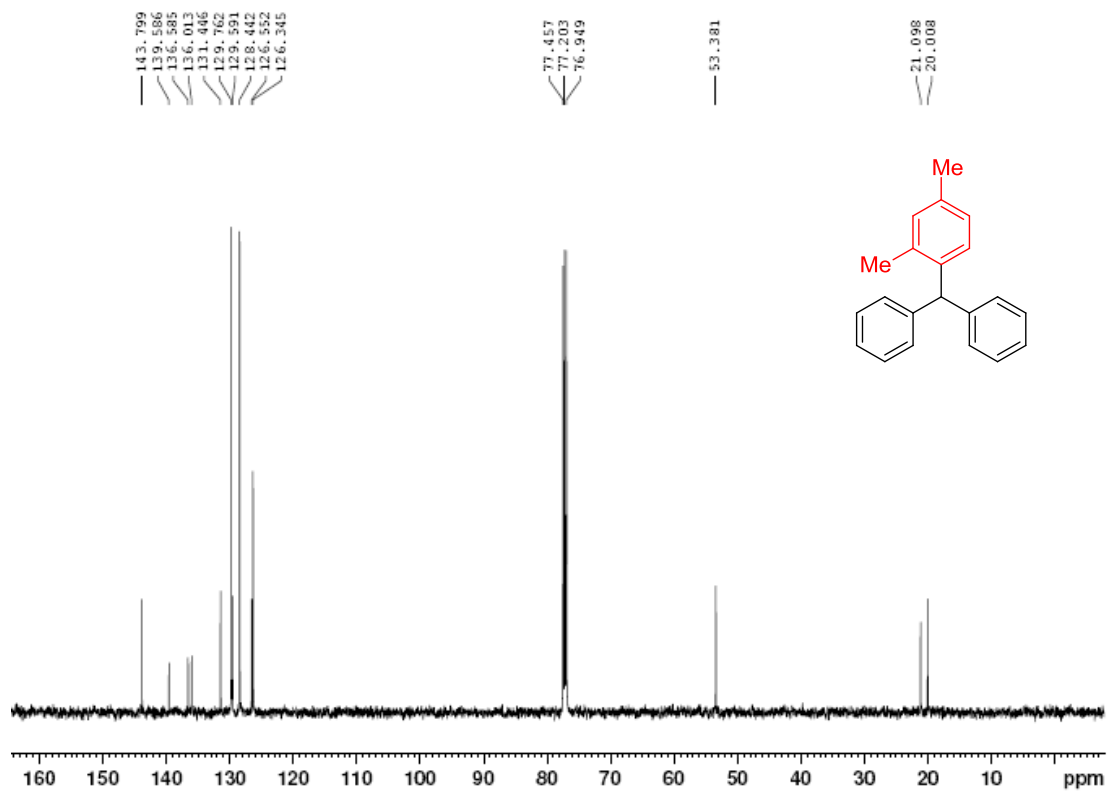
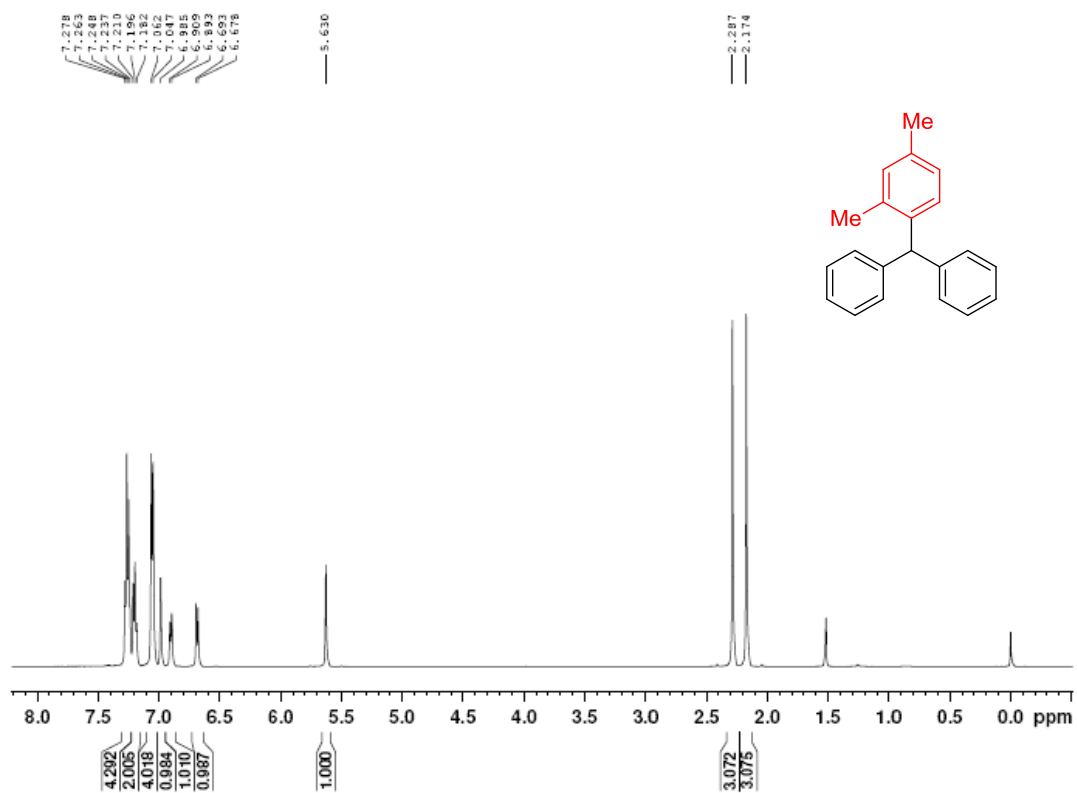
1,2-dichloro-4-(2,4-dichlorobenzyl)benzene (4m)



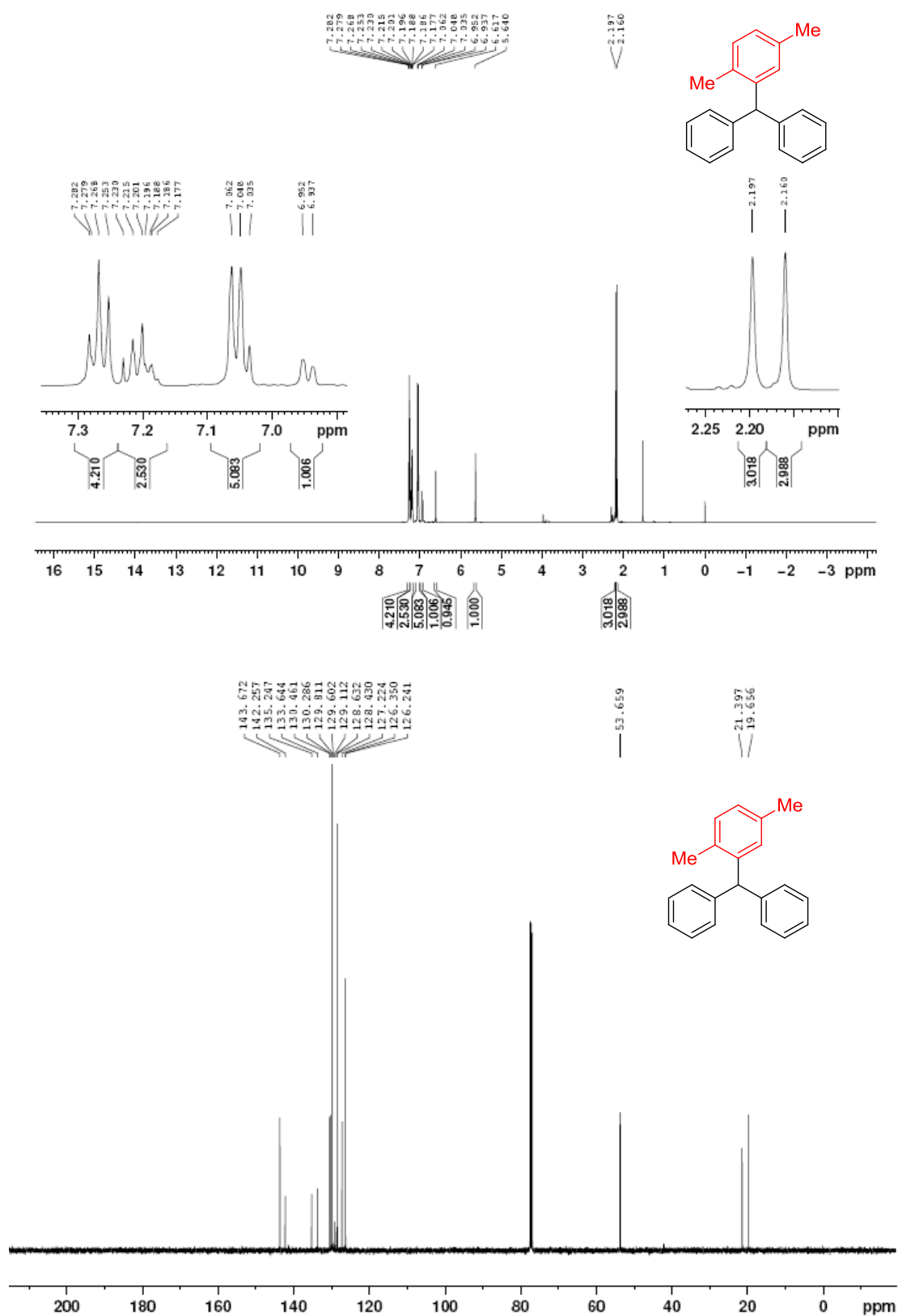
**((2,3-dimethylphenyl)methylene)dibenzene (5a)**



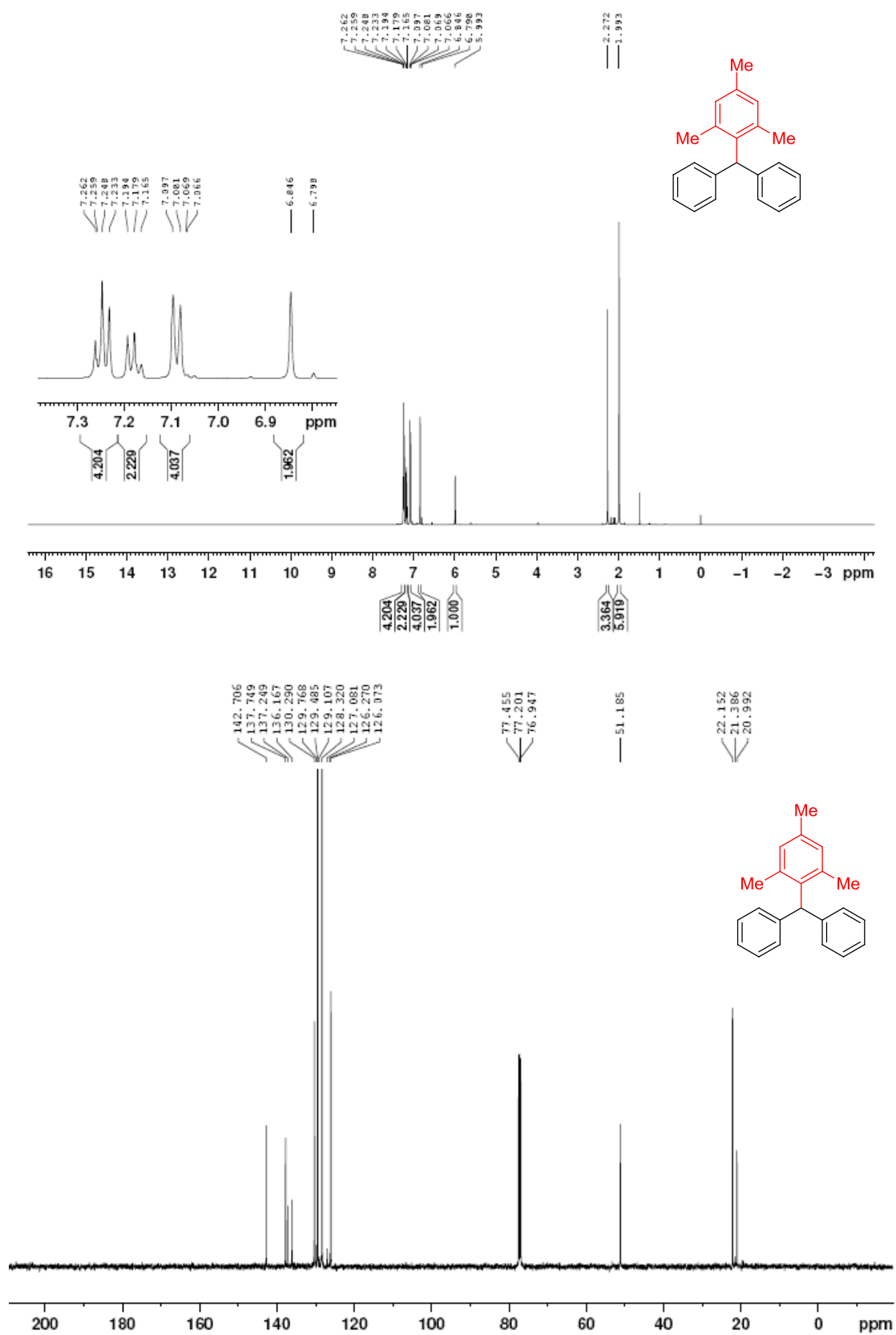
**((2,4-dimethylphenyl)methylene)dibenzene (5b)**



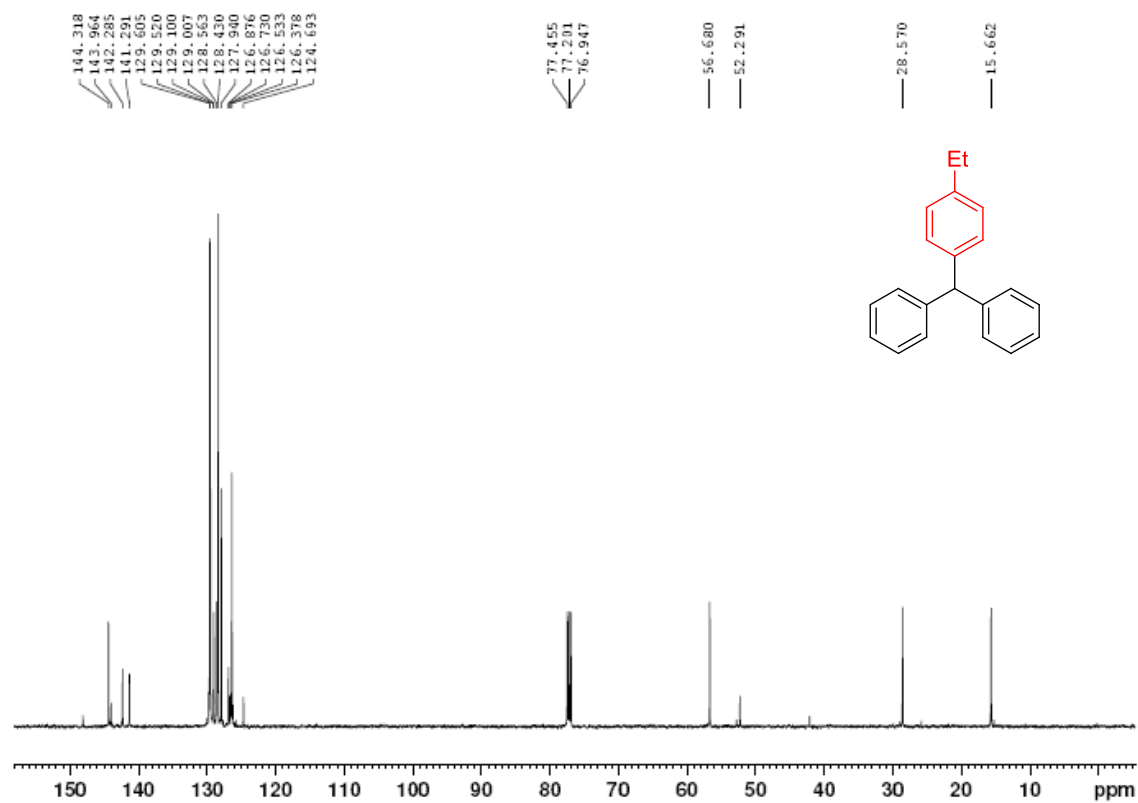
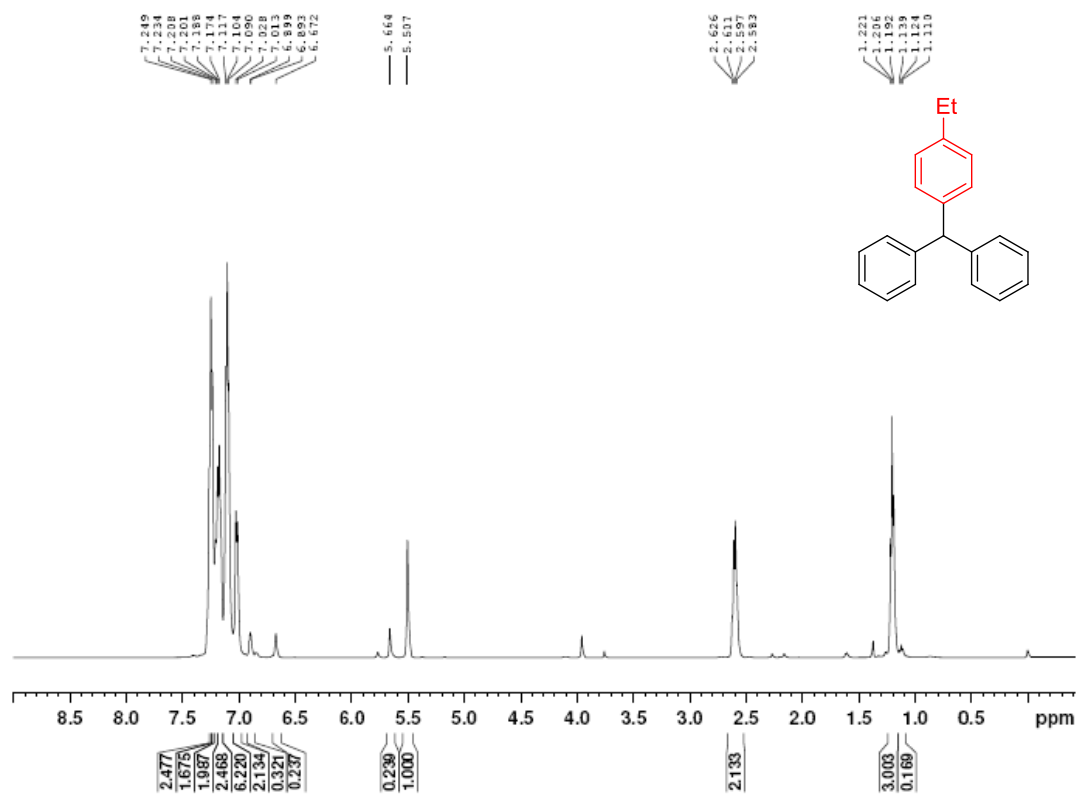
((2,5-dimethylphenyl)methylene)dibenzene (5c)



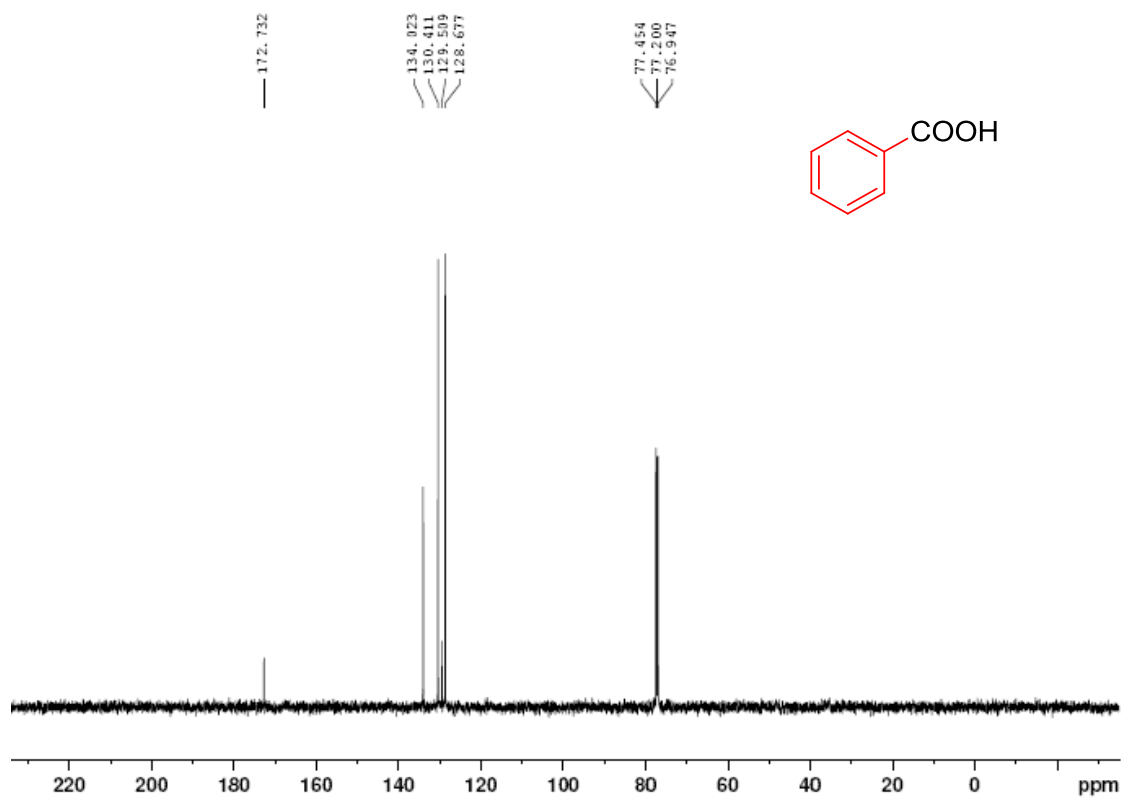
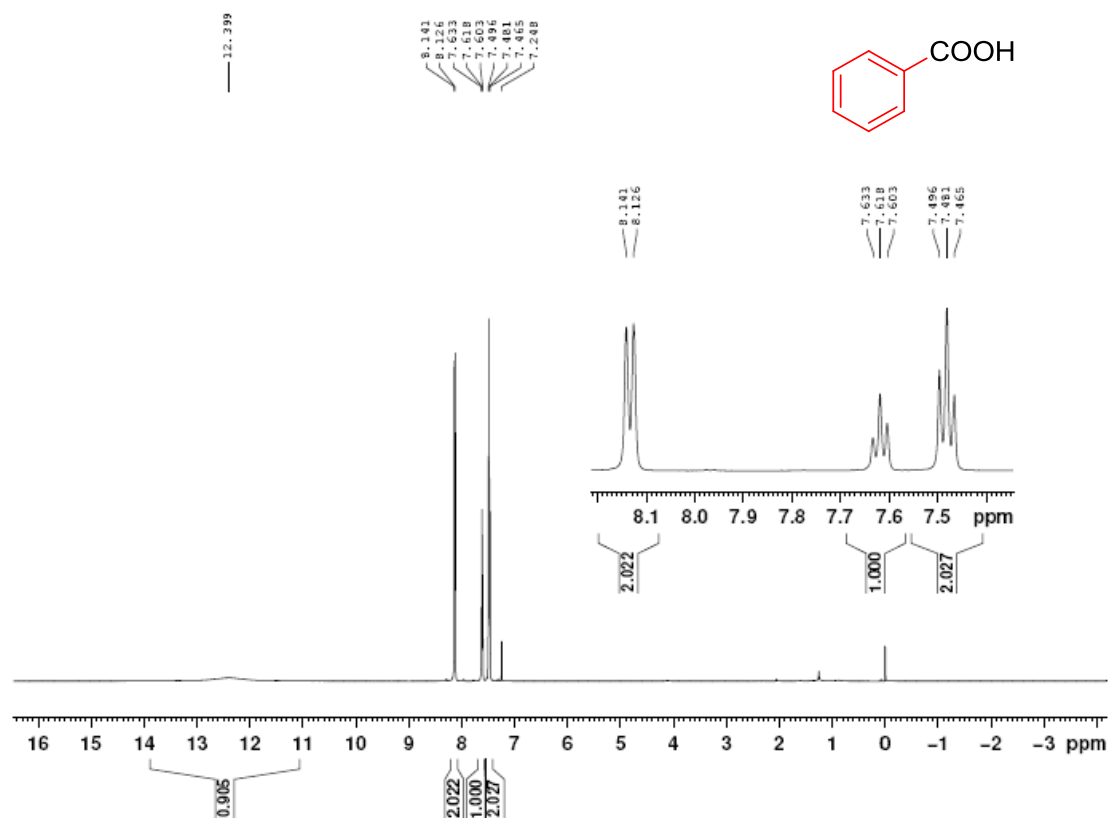
(mesitylmethylene)dibenzene (5d)



((4-ethylphenyl)methylene)dibenzene (**5e**)

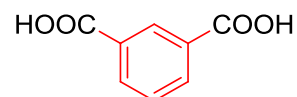
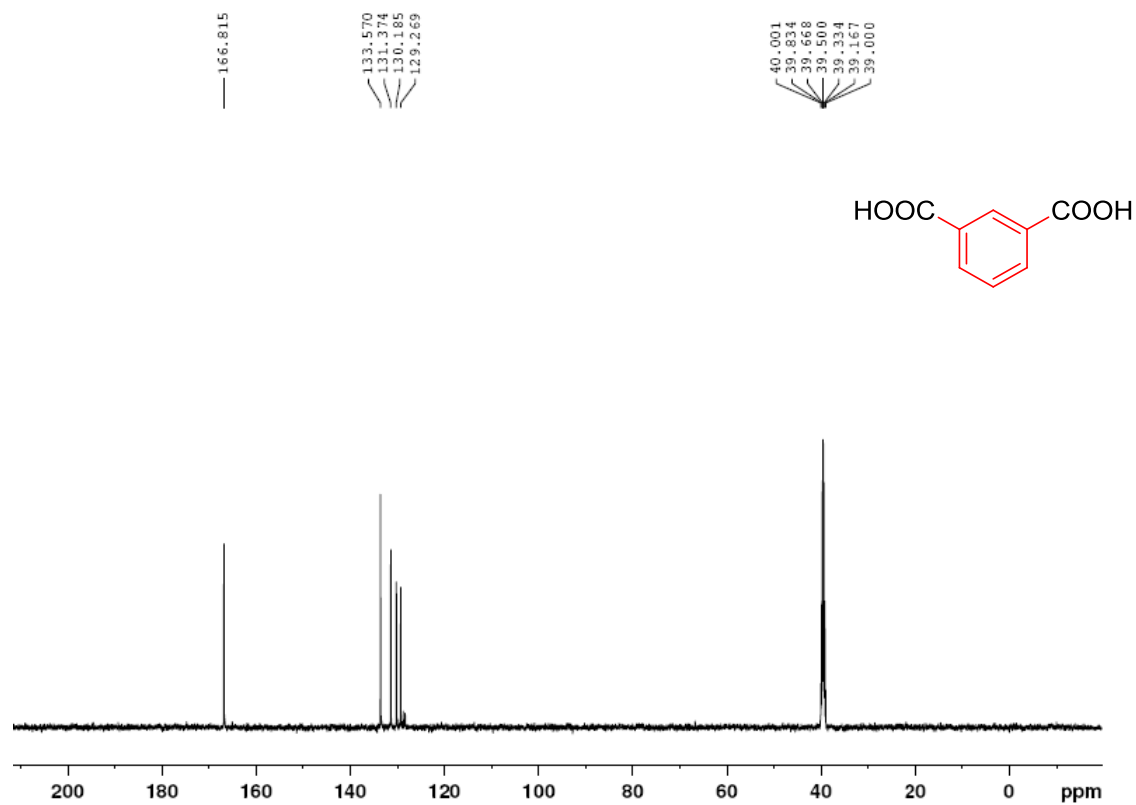
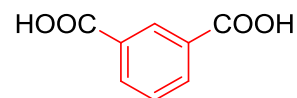
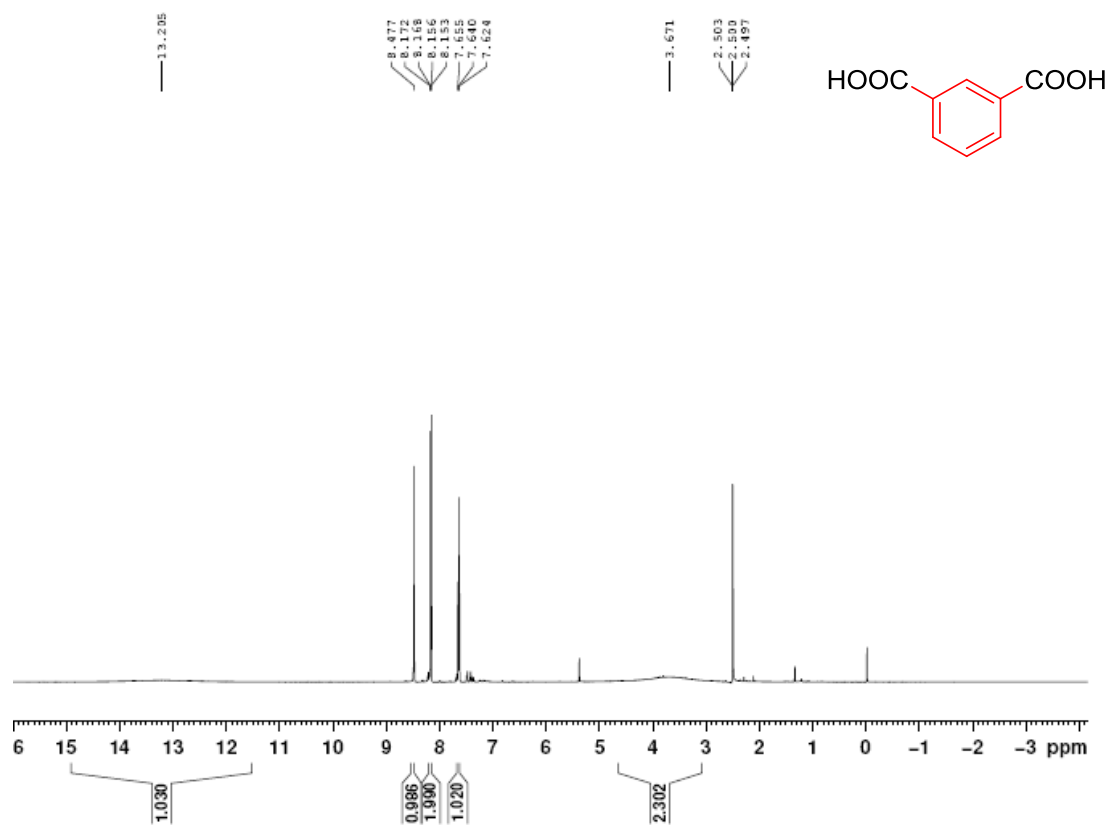


benzoic acid (3a')

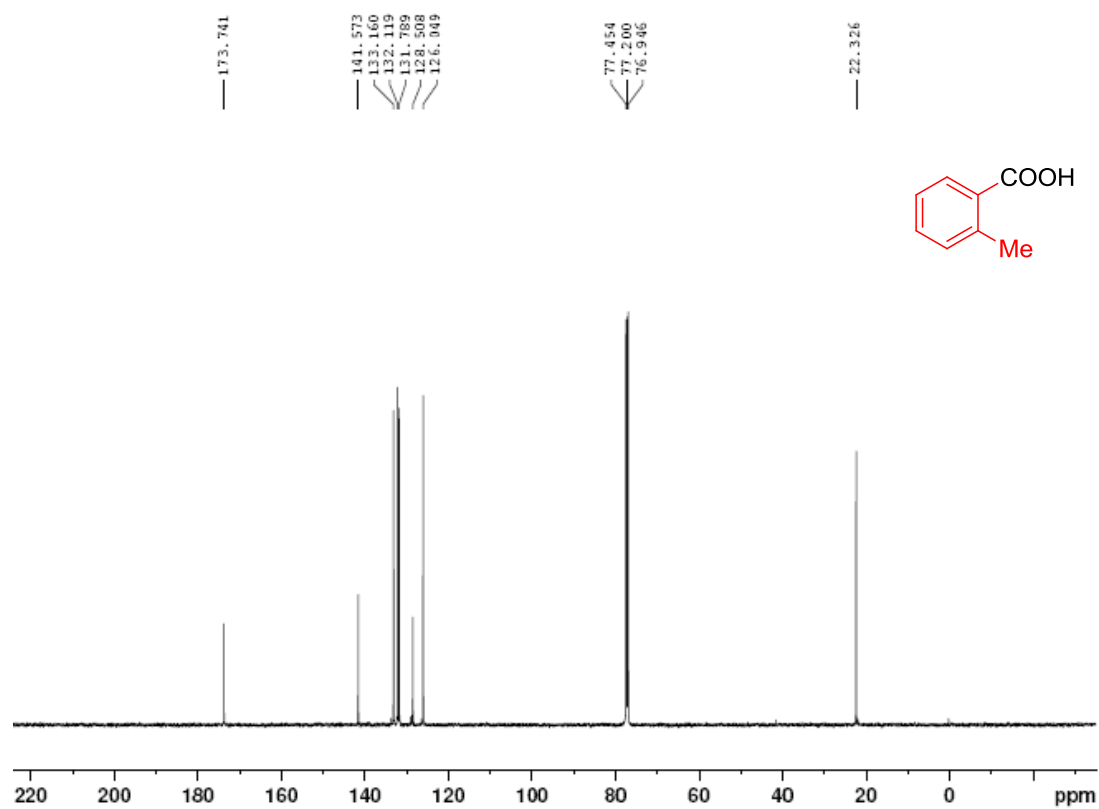
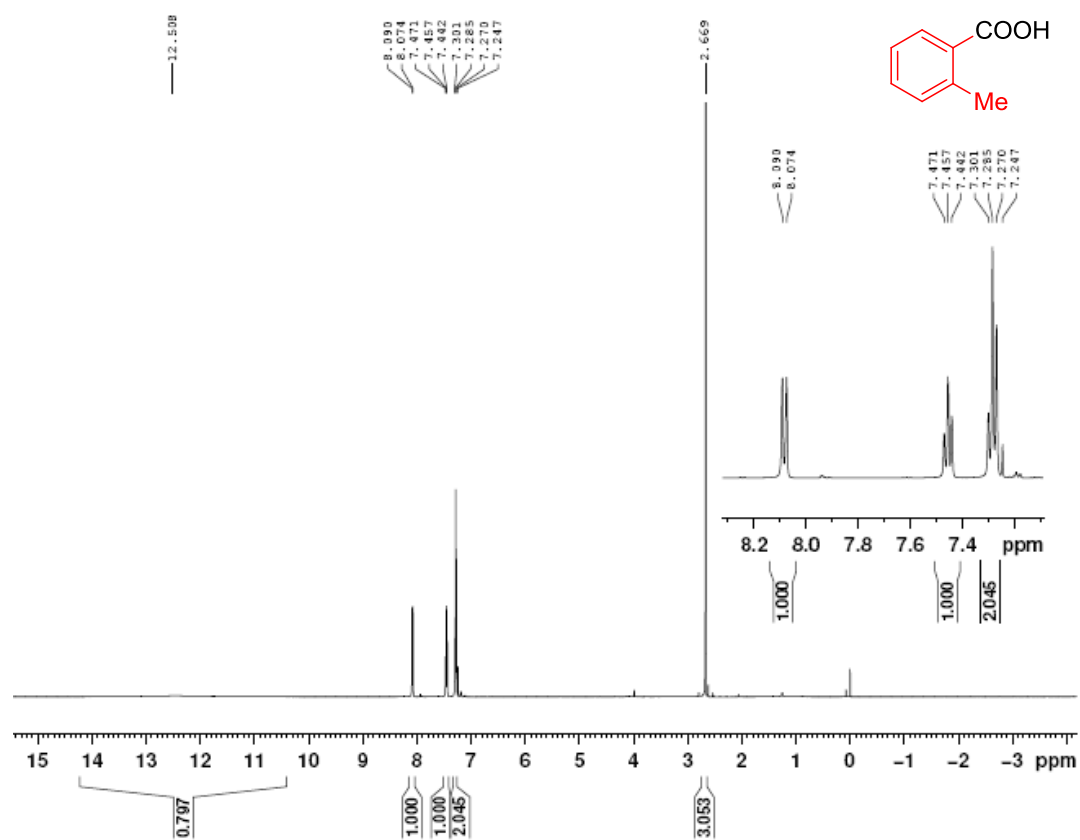




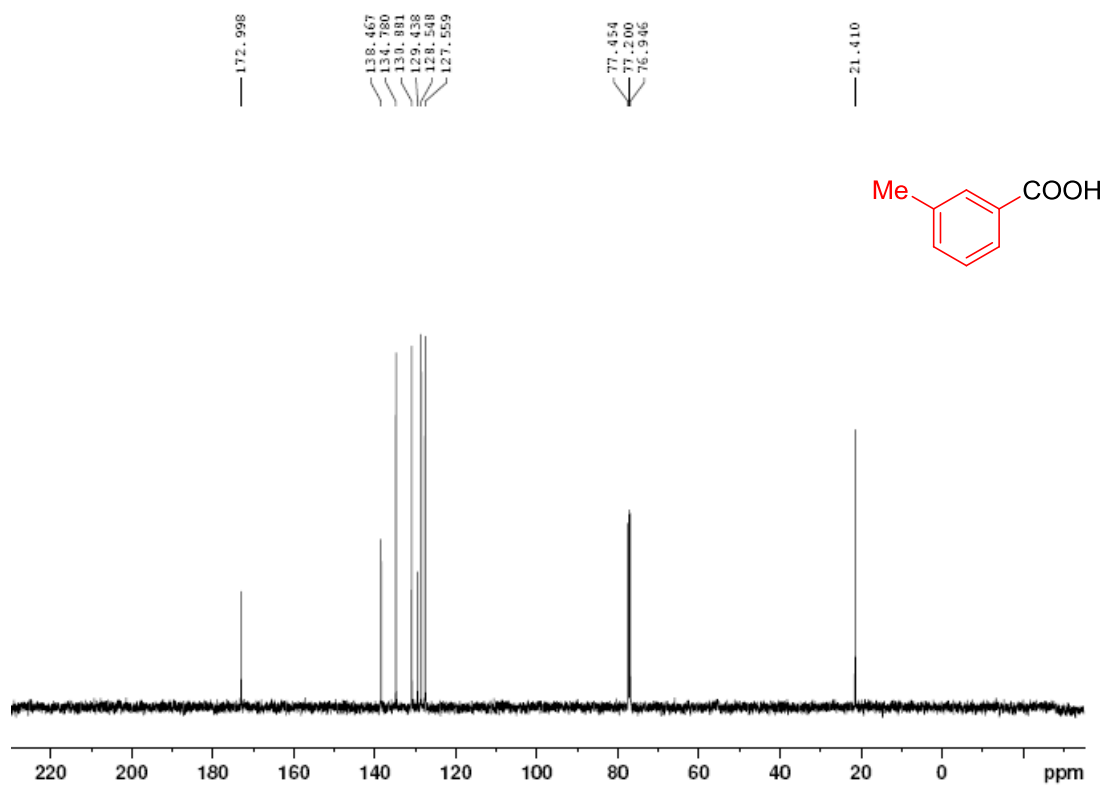
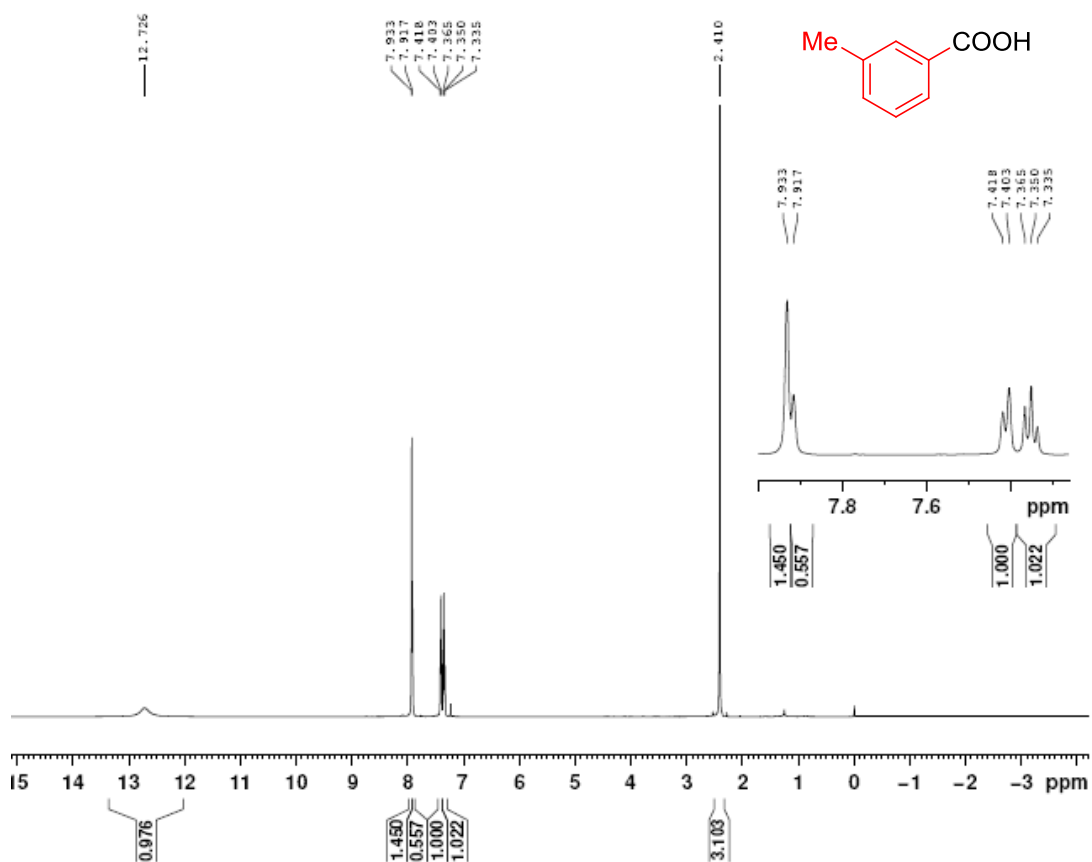
isophthalic acid (3b')



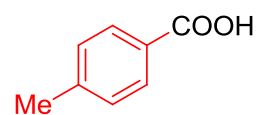
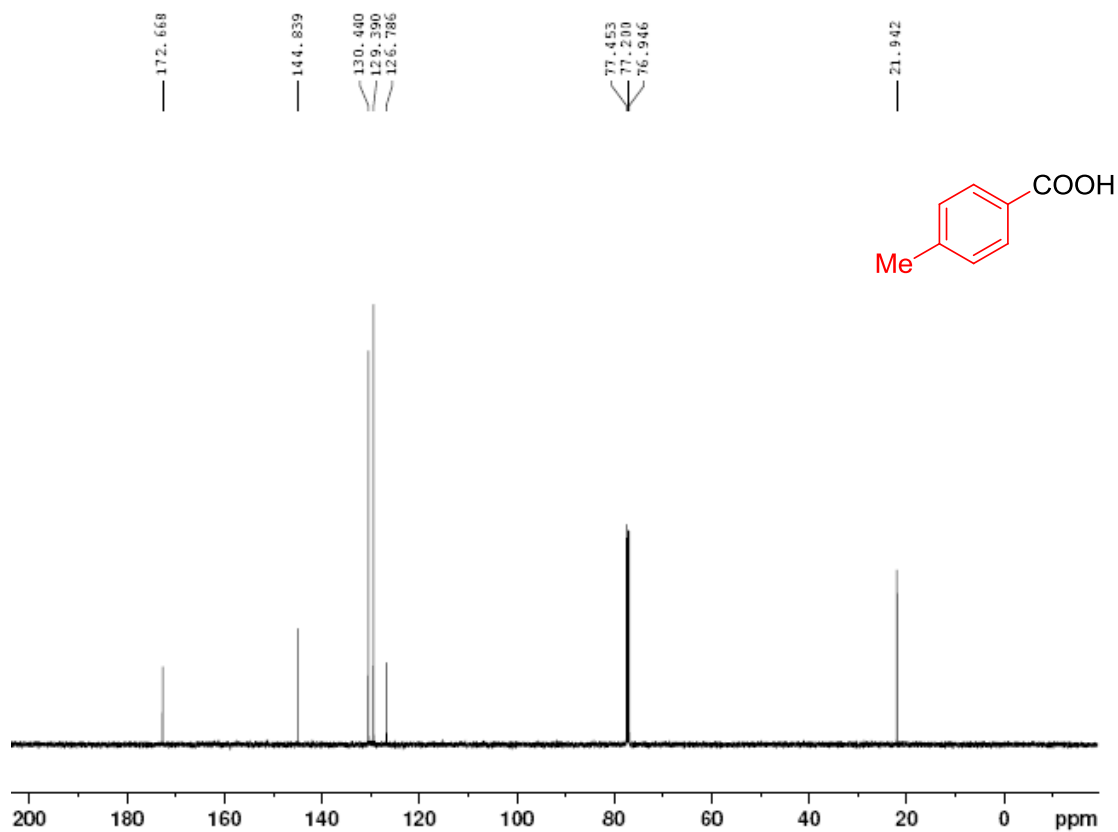
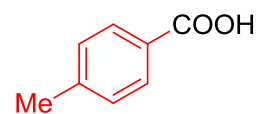
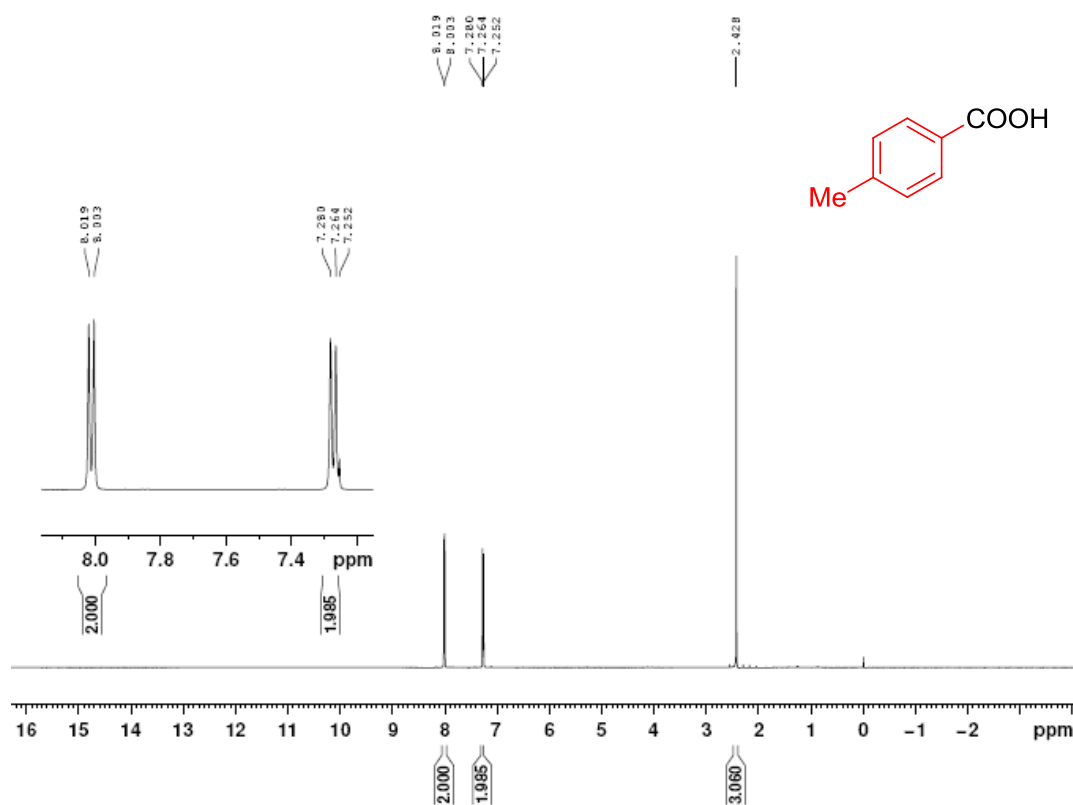
# 2-methylbenzoic acid (3c')



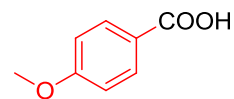
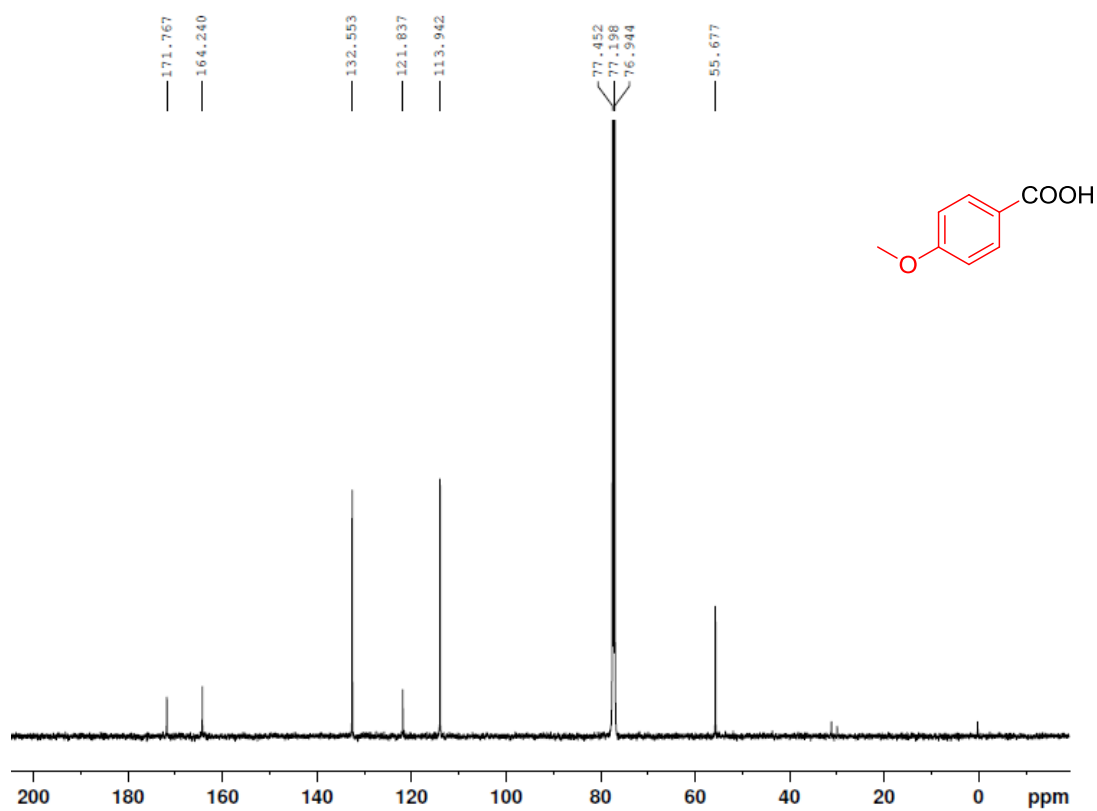
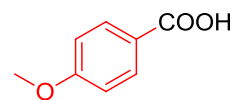
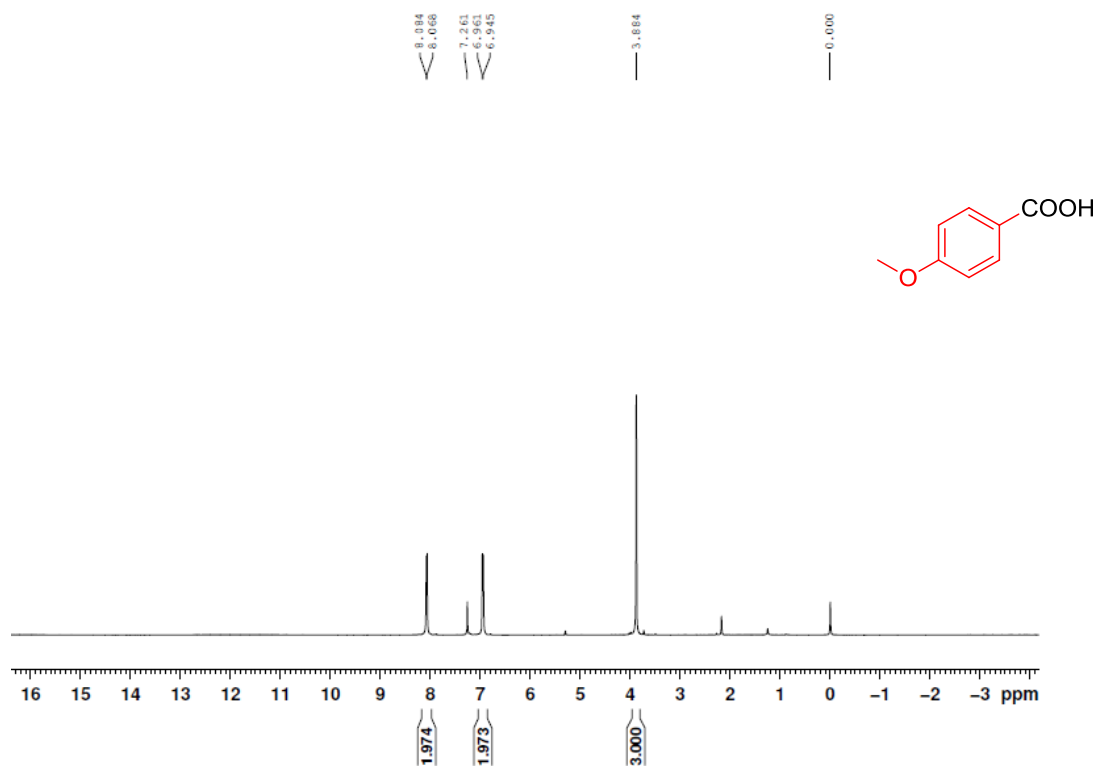
### 3-methylbenzoic acid (3d')



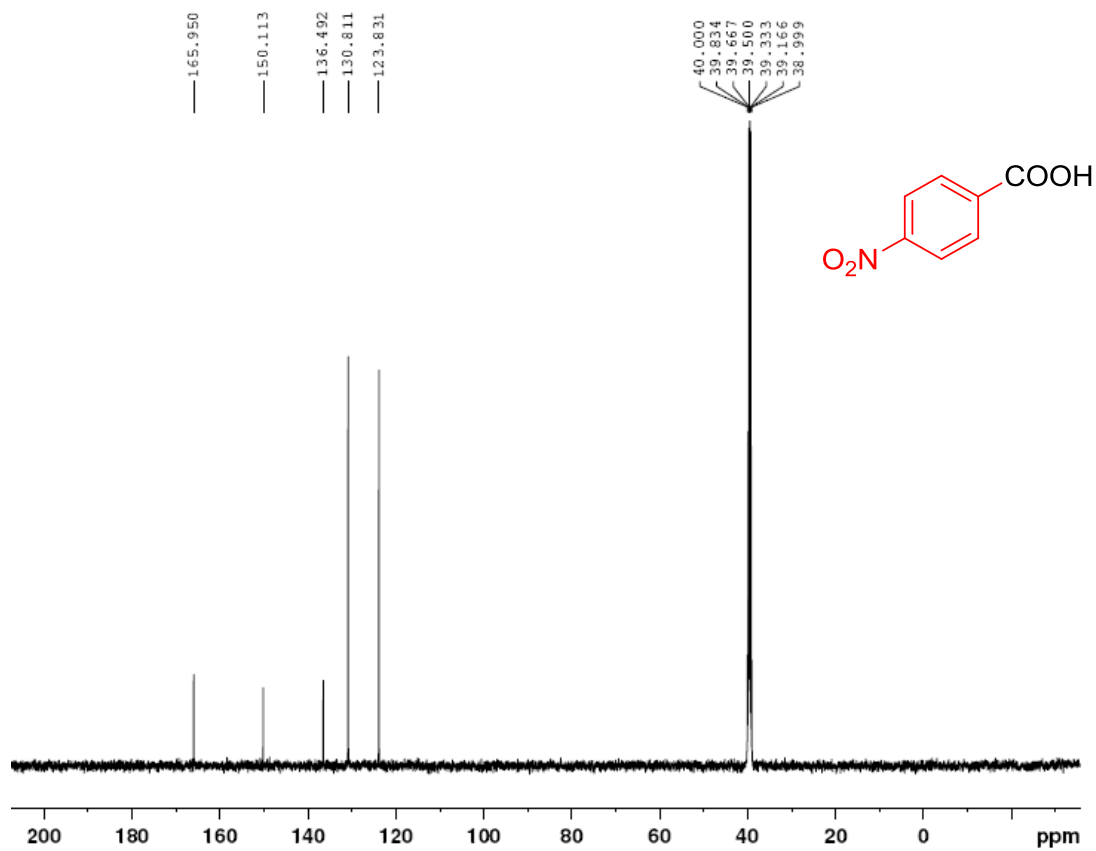
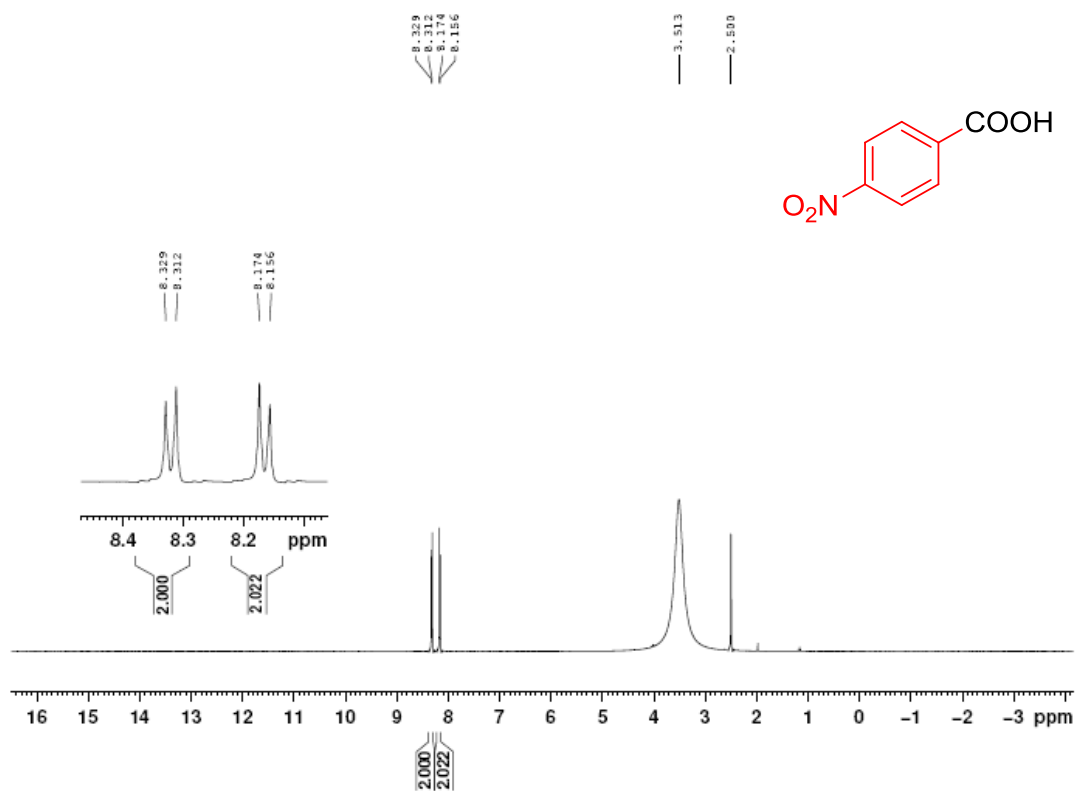
# 4-methylbenzoic acid (3e')



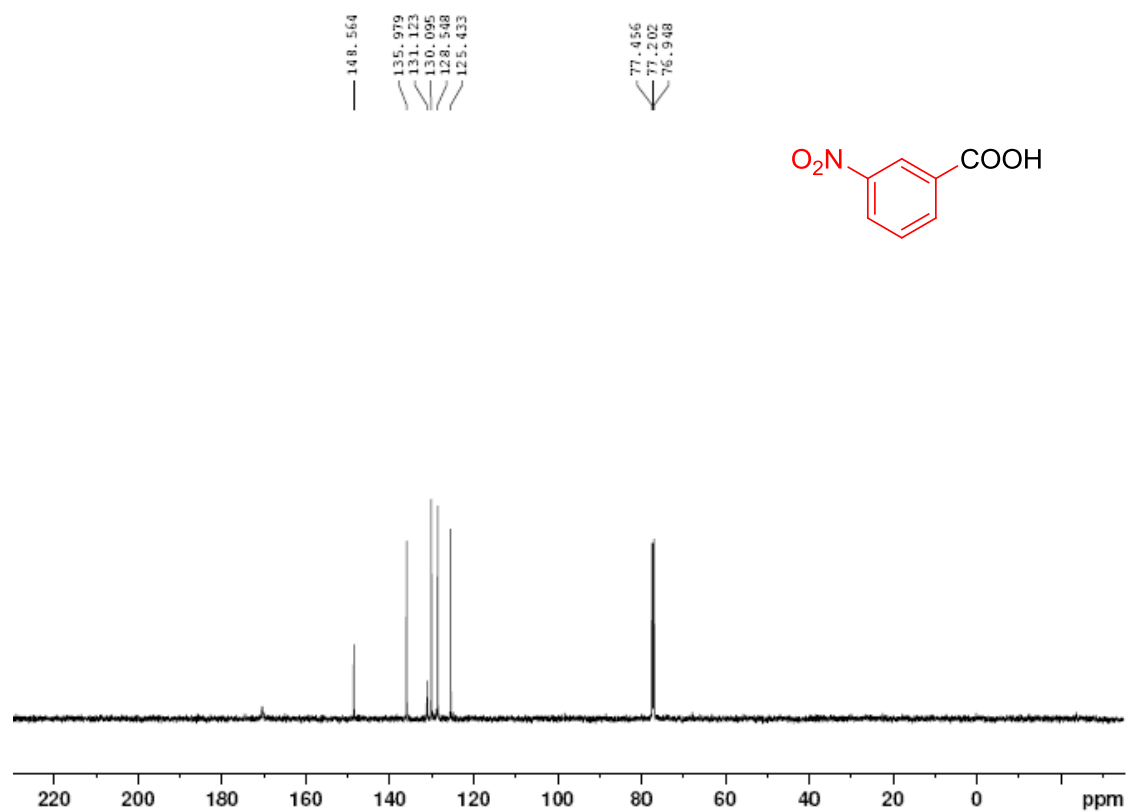
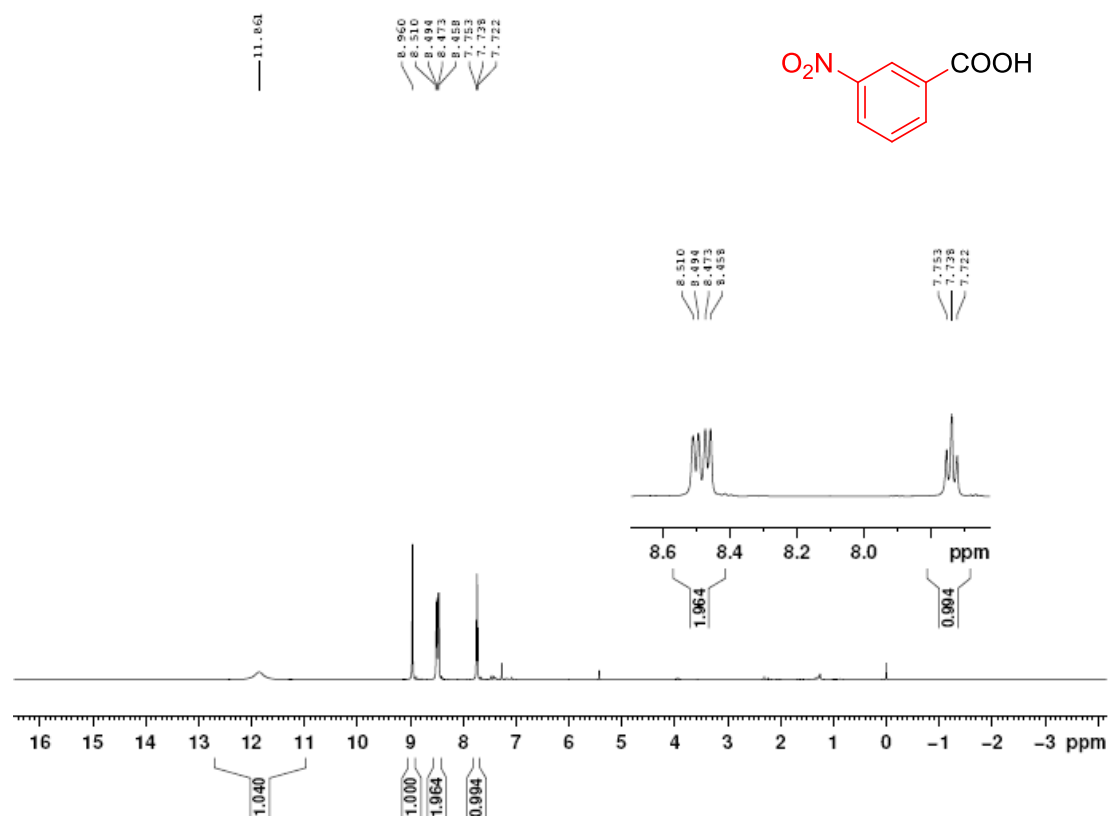
4-methoxybenzoic acid (3f')



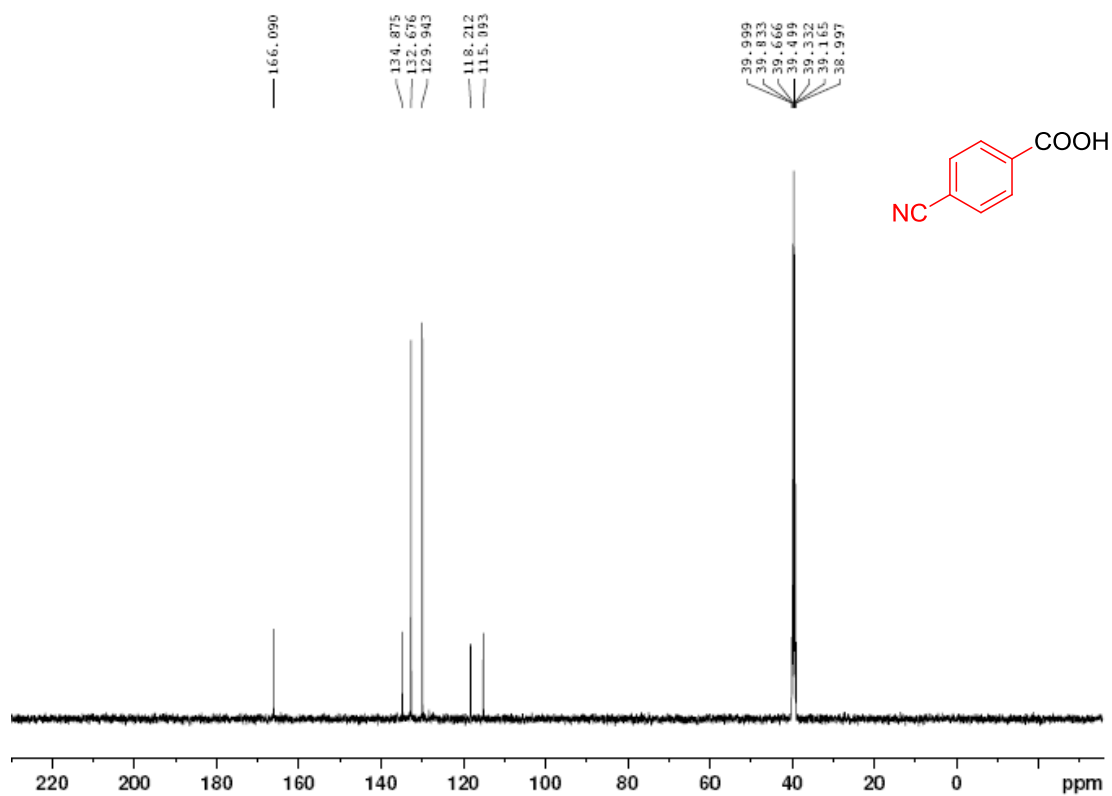
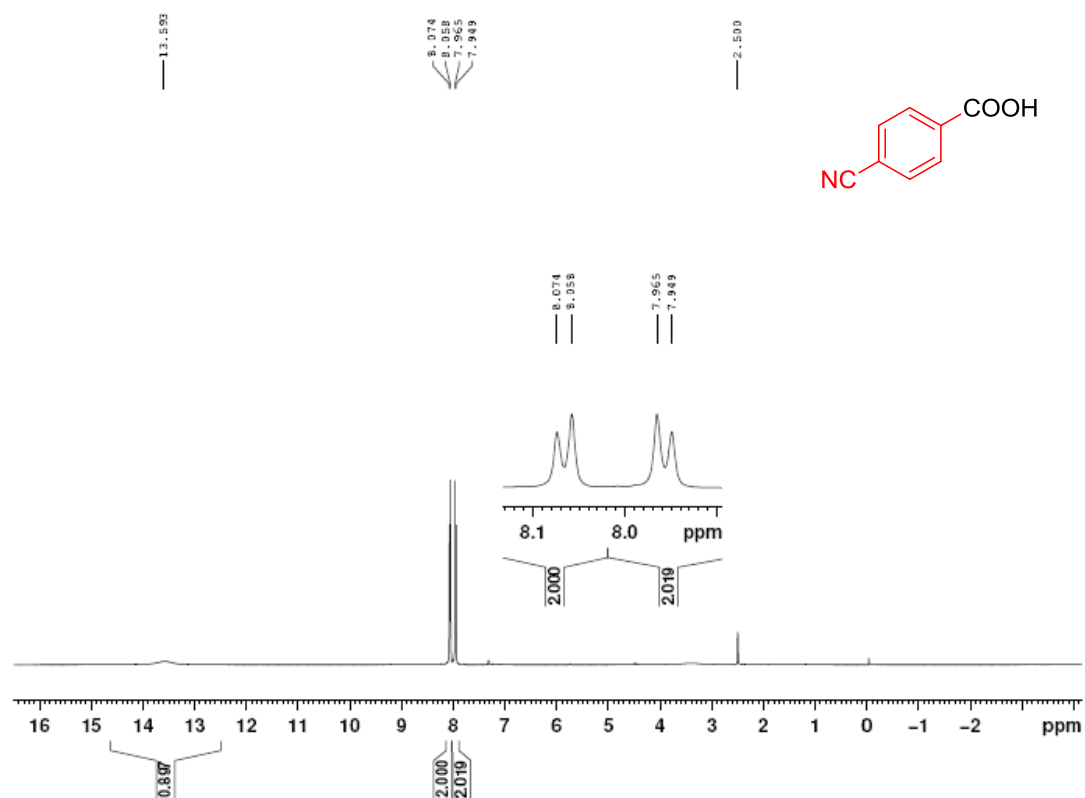
# 4-nitrobenzoic acid (3g')



### 3-nitrobenzoic acid (3h')

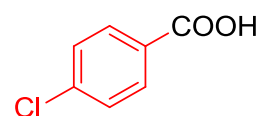
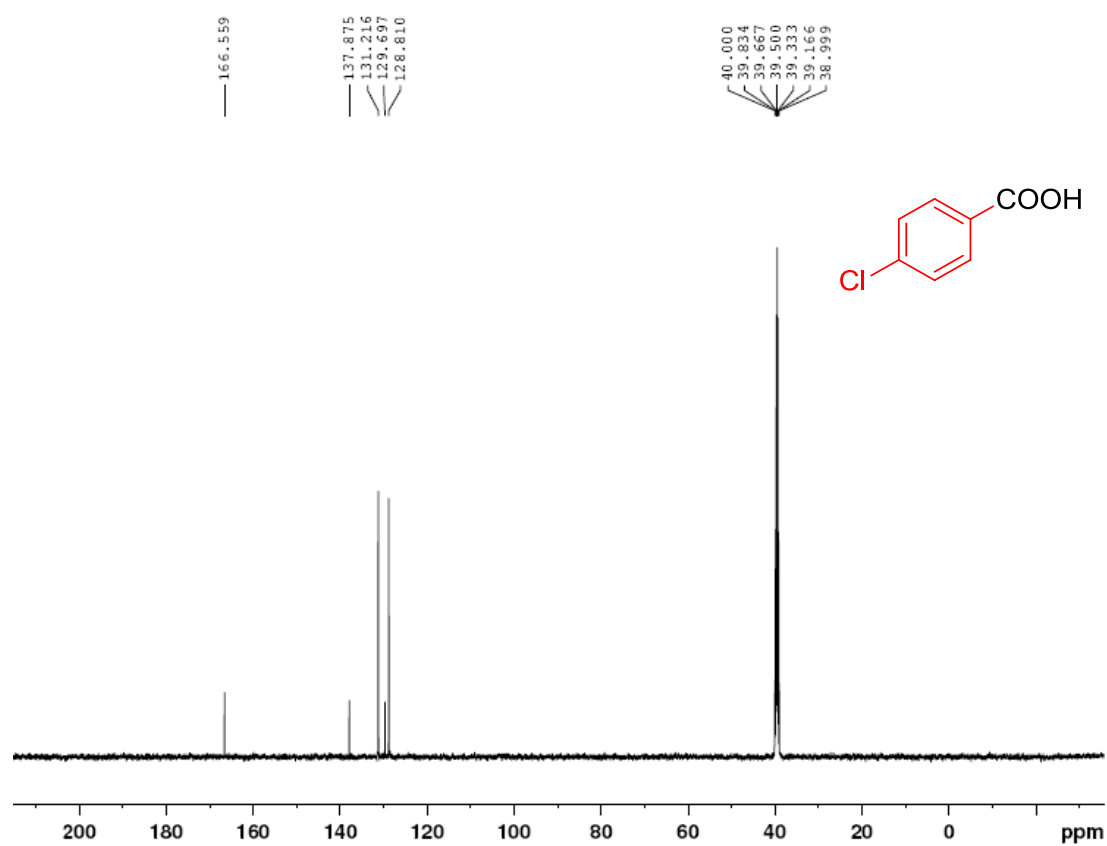
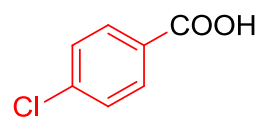
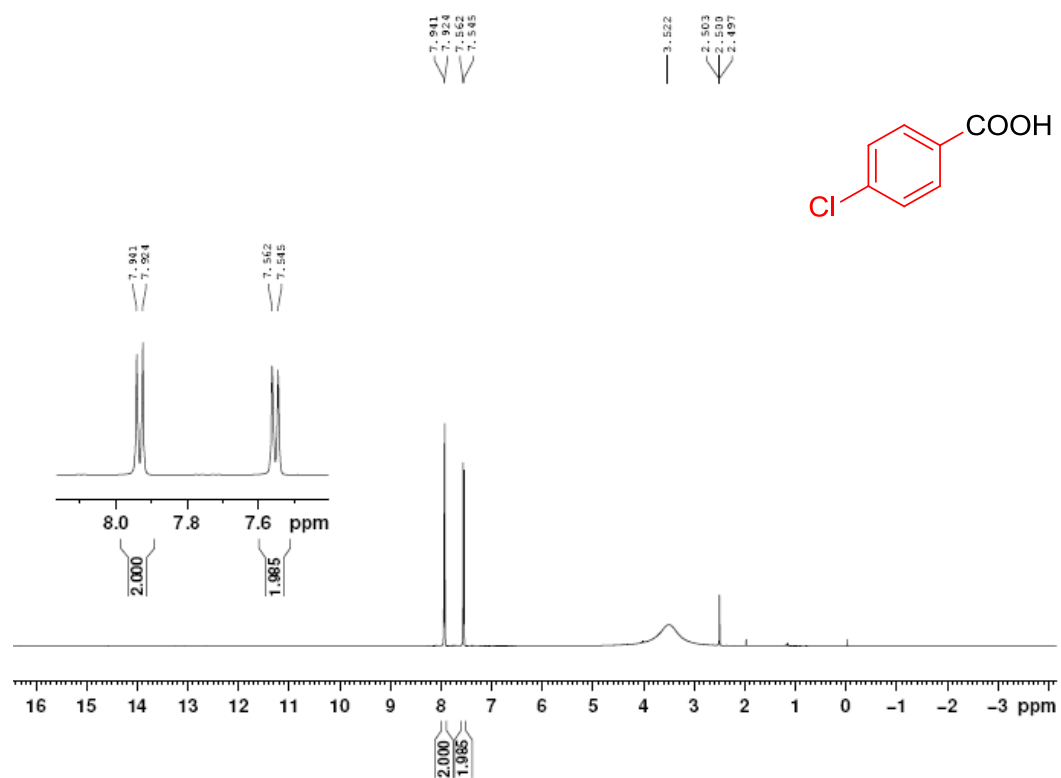


# 4-cyanobenzoic acid (3i')

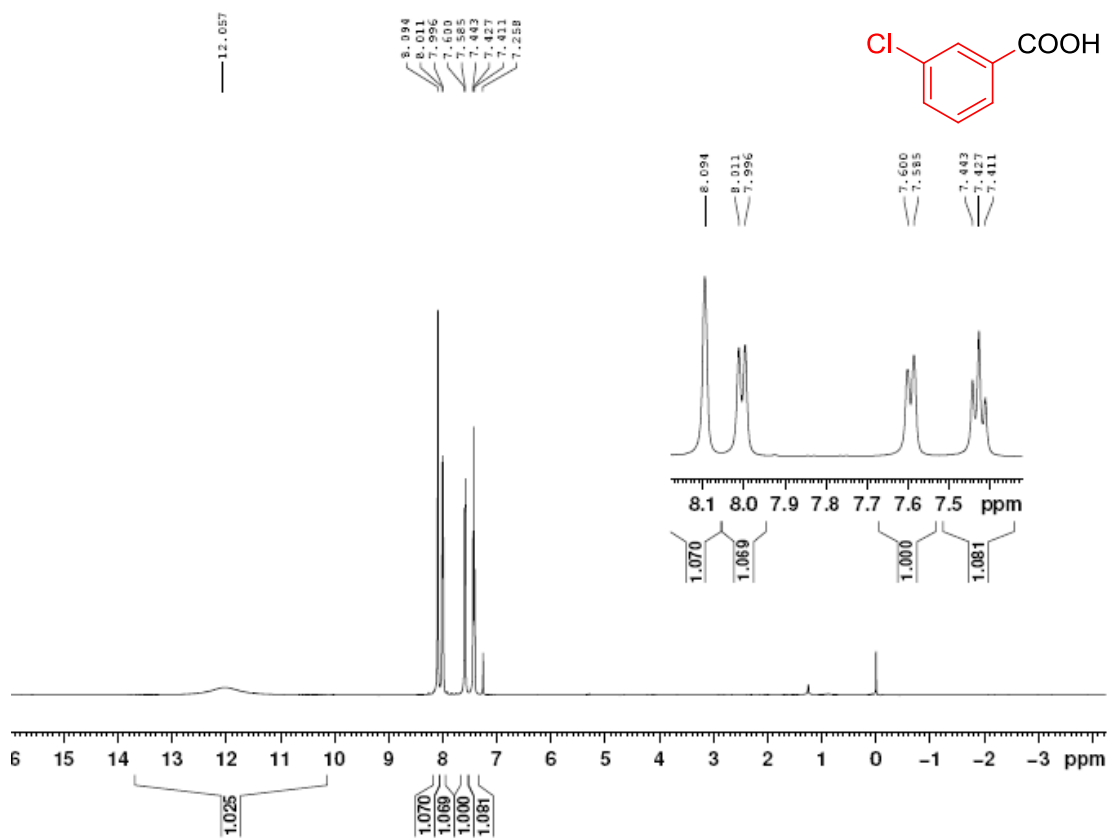
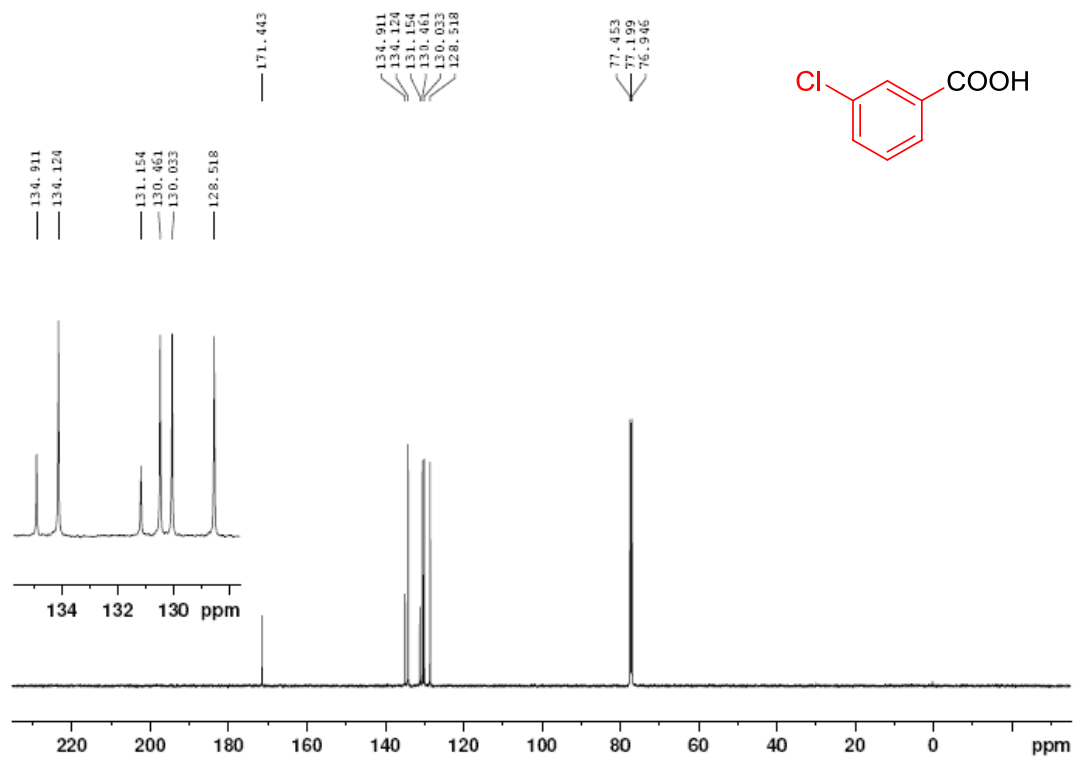




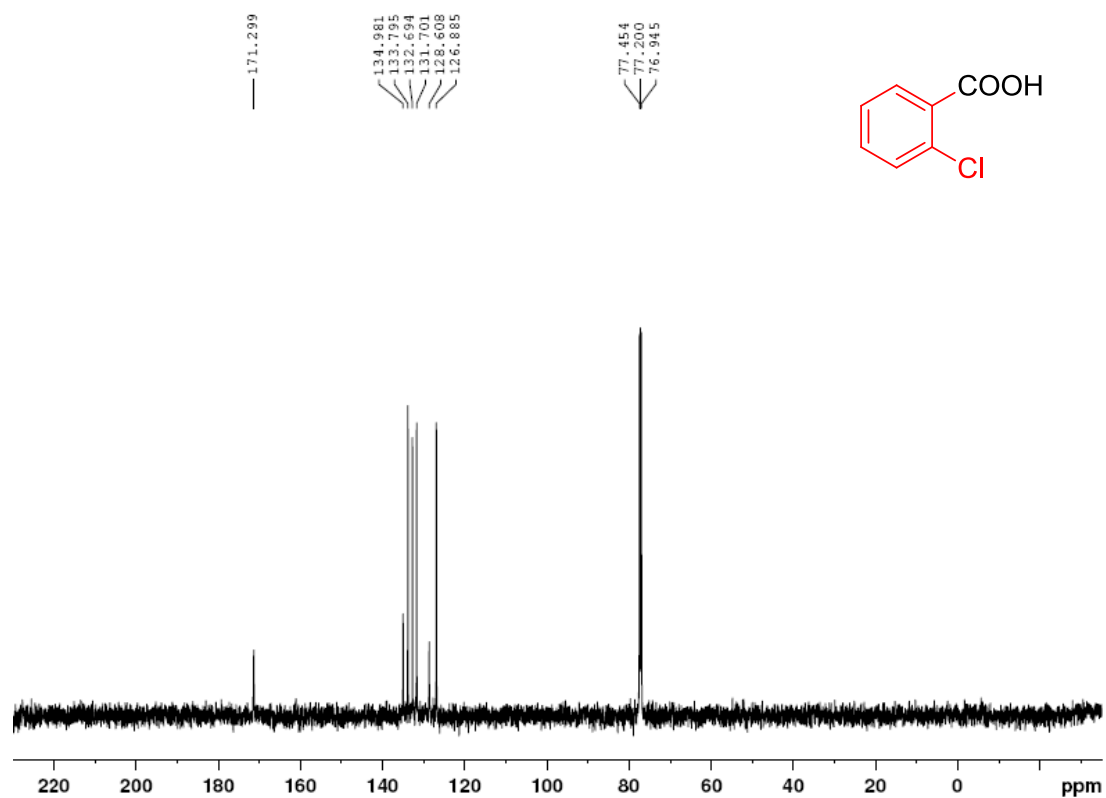
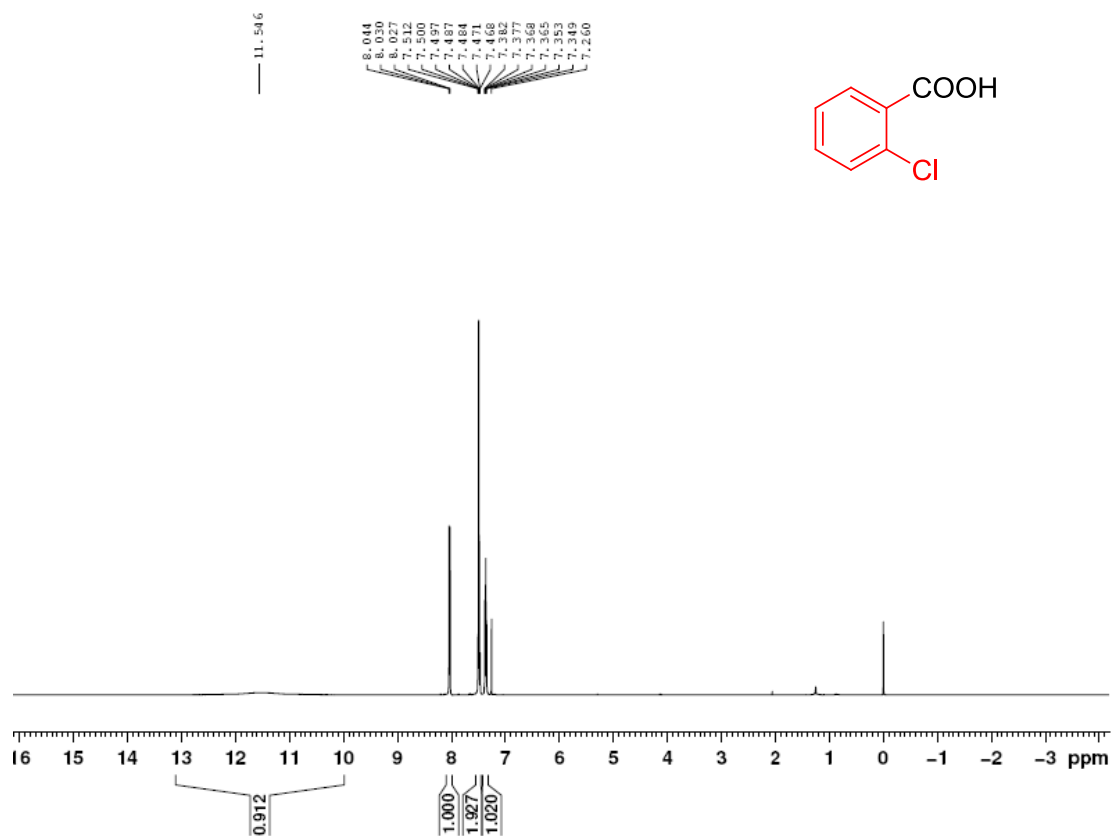
# 4-chlorobenzoic acid (3j')



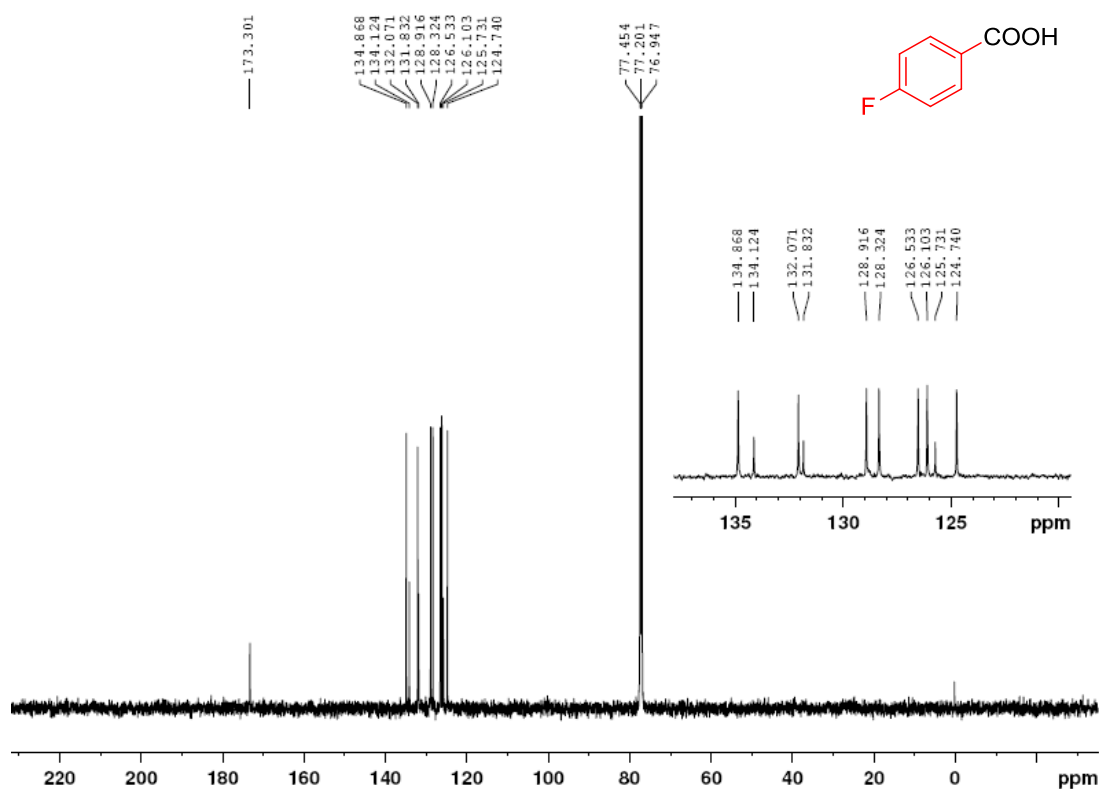
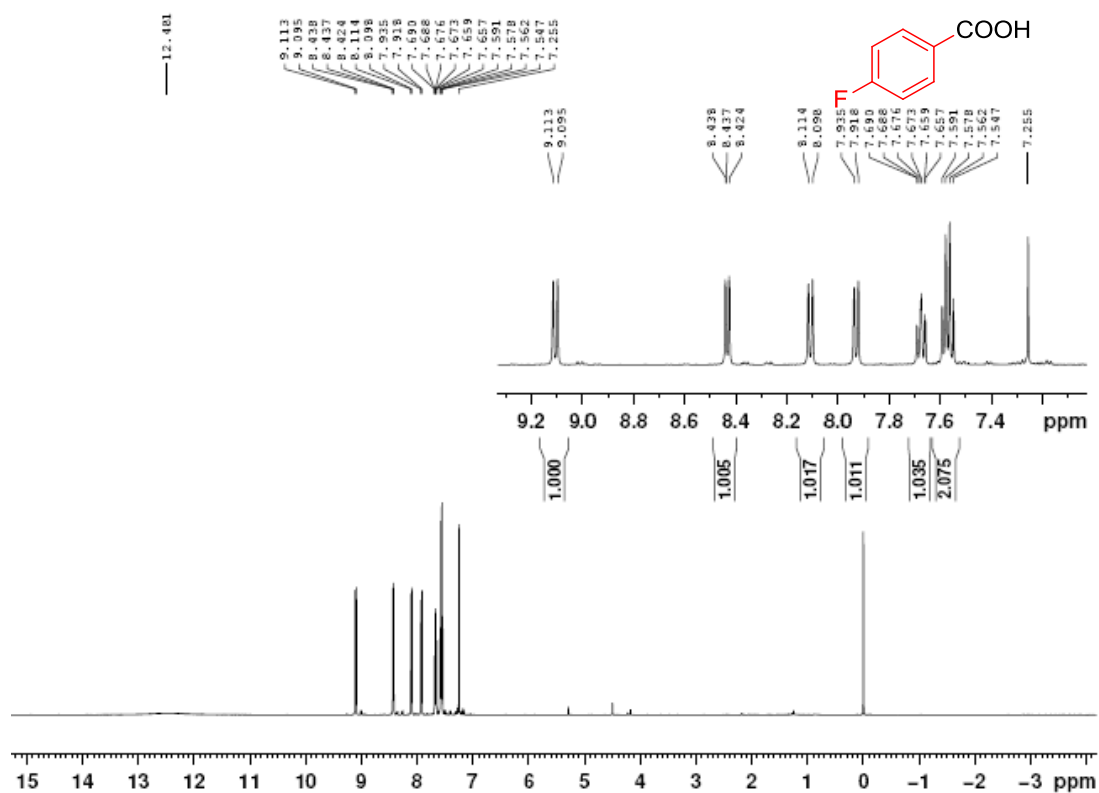
### 3-chlorobenzoic acid (3k')



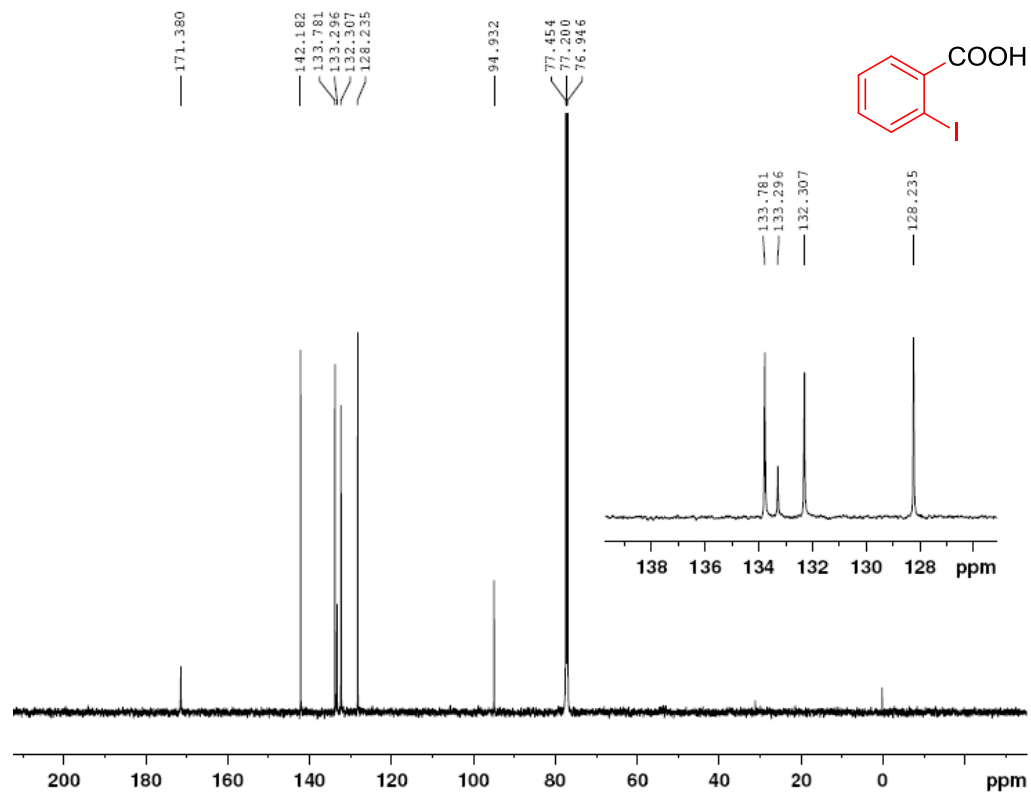
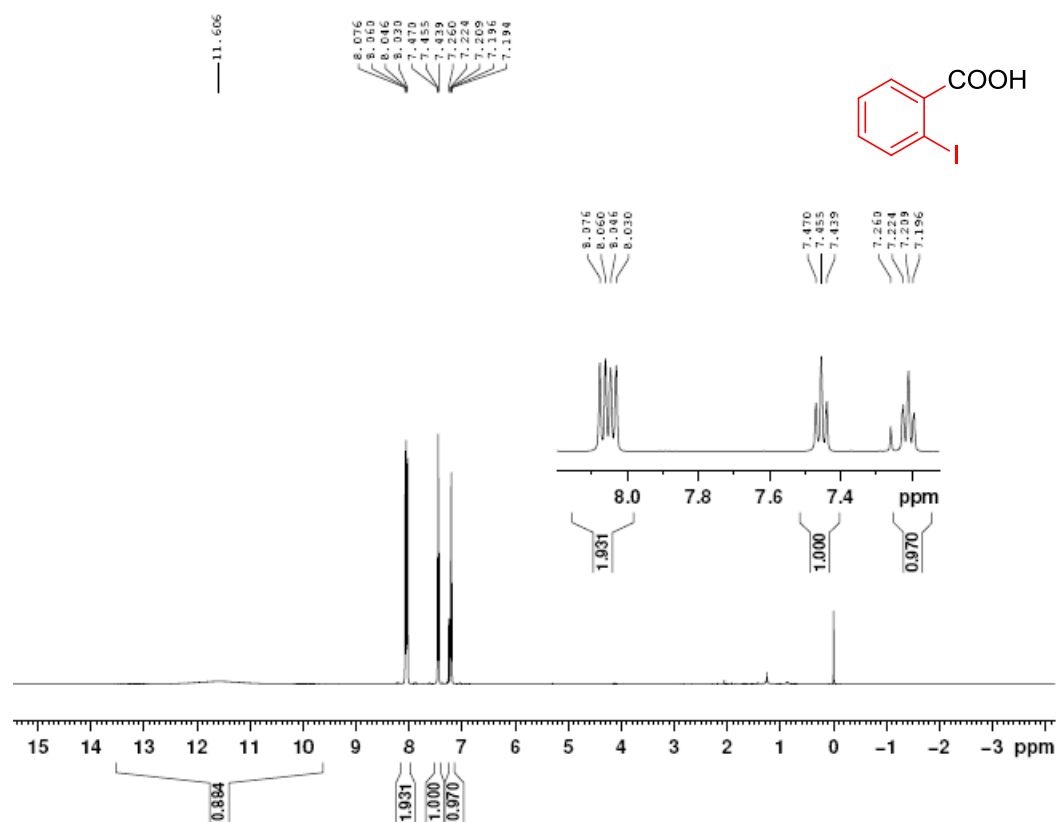
# 2-chlorobenzoic acid (3I')



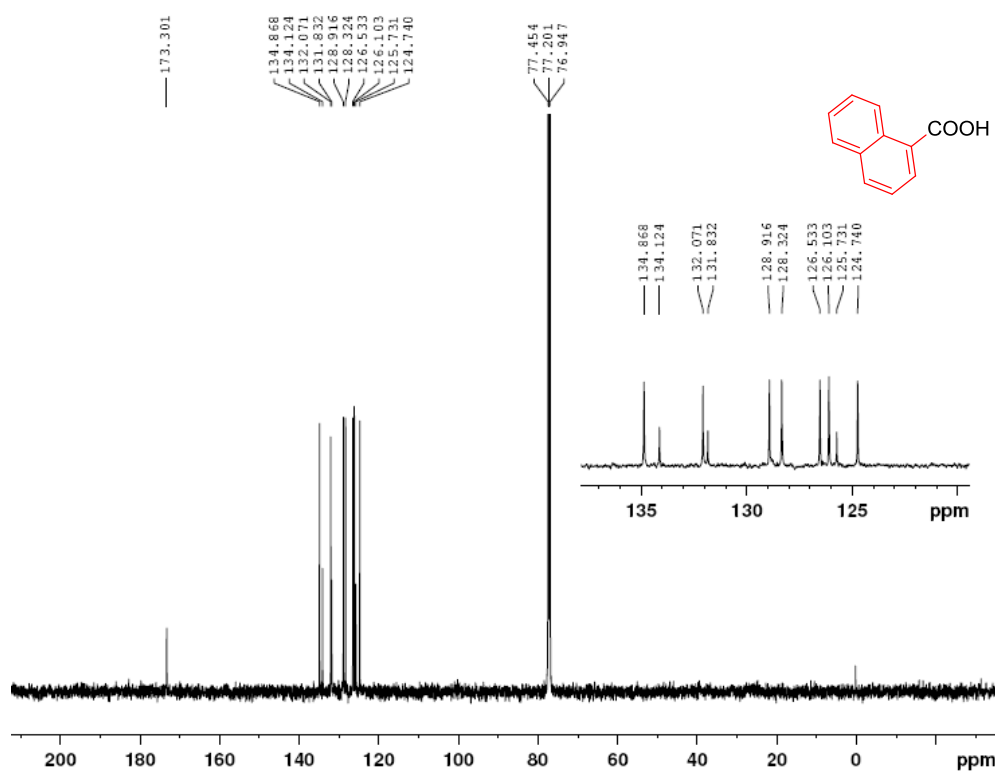
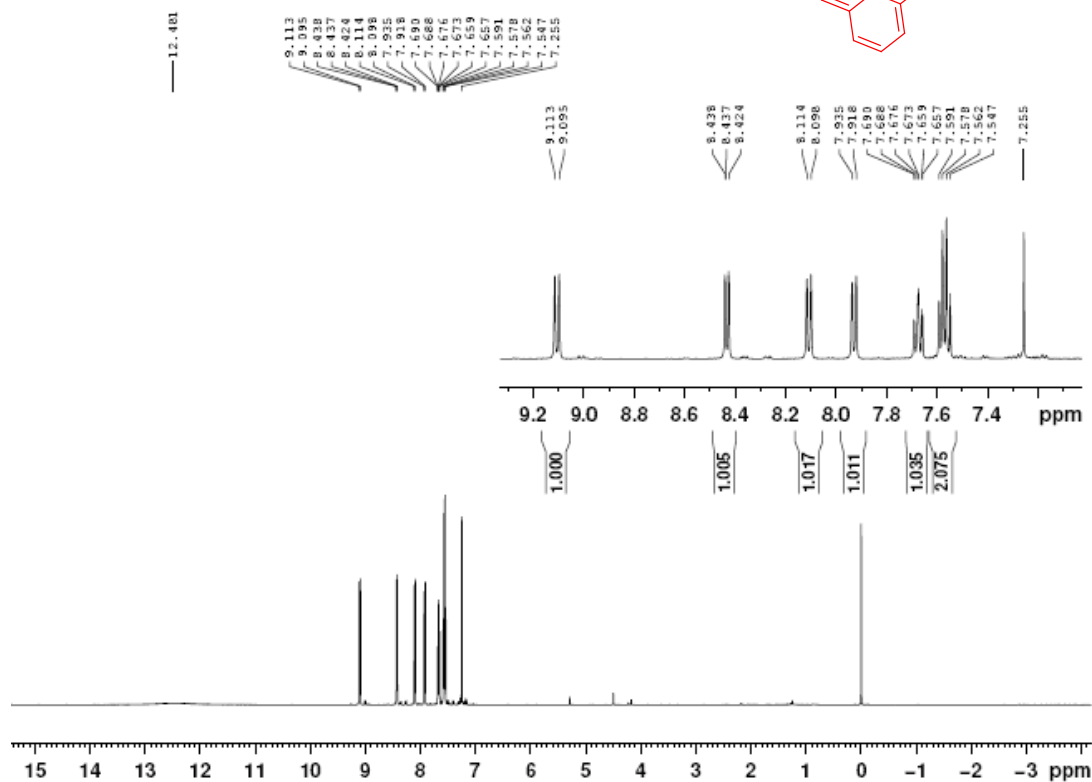
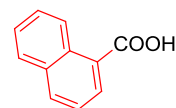
# 4-fluorobenzoic acid (3m')



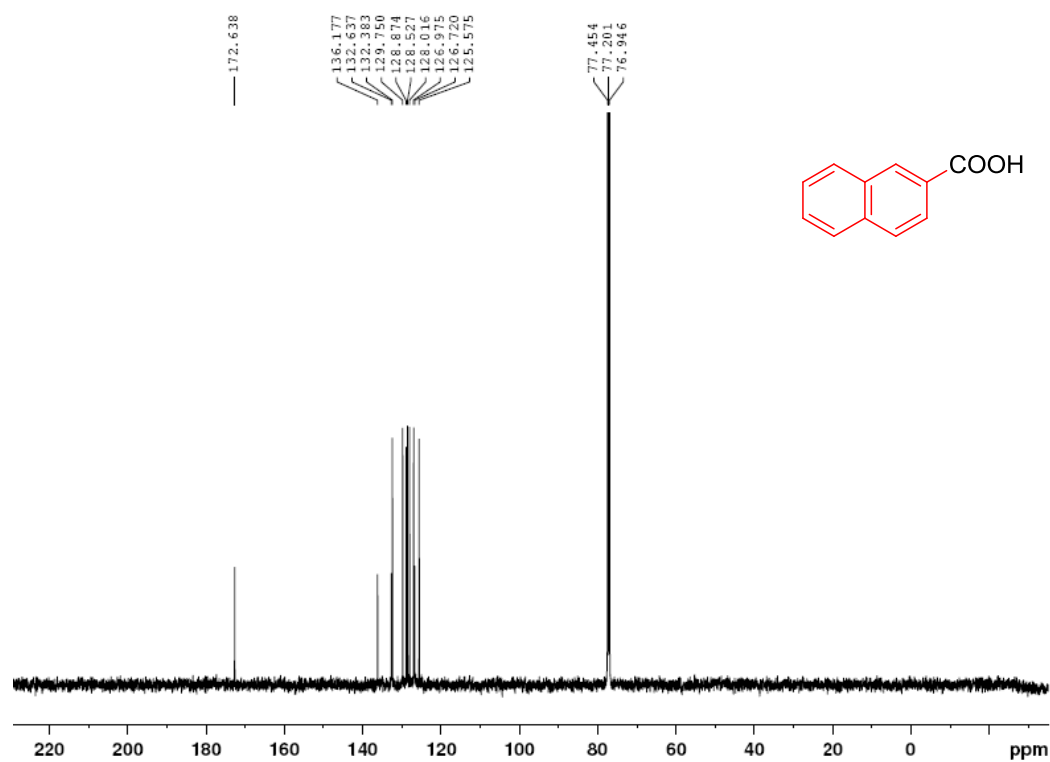
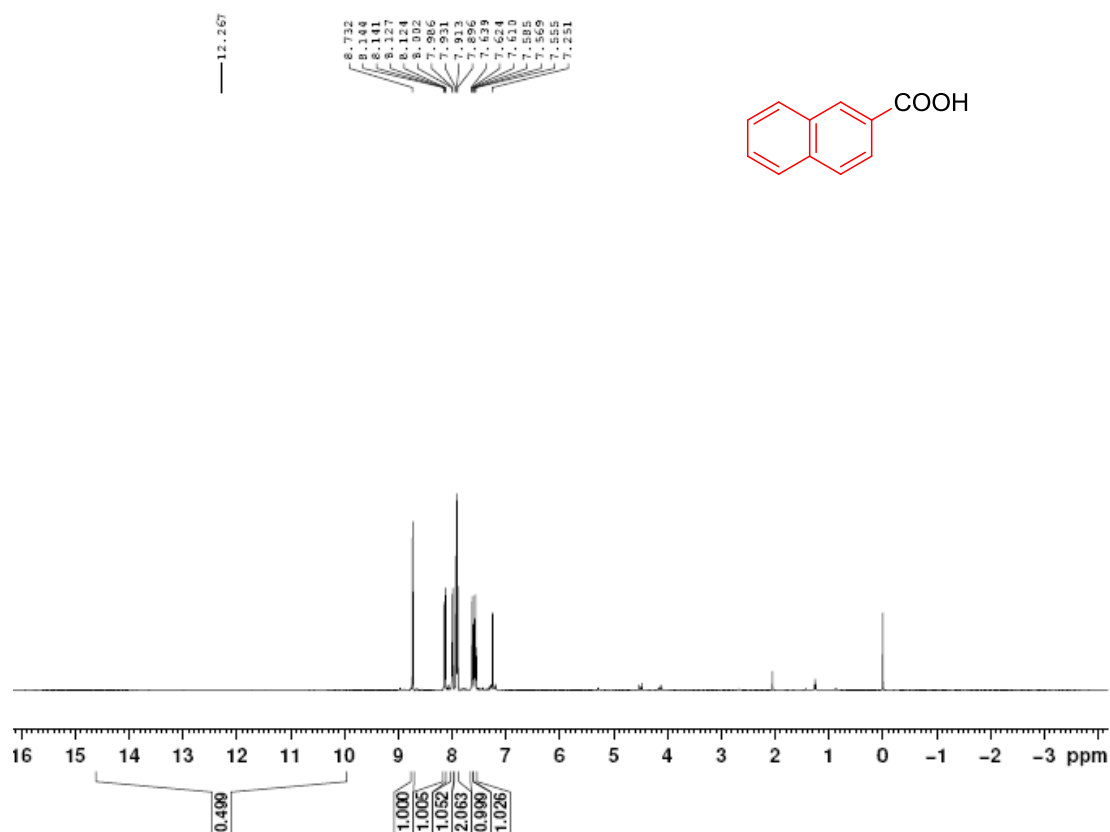
# 2-iodobenzoic acid (3n')



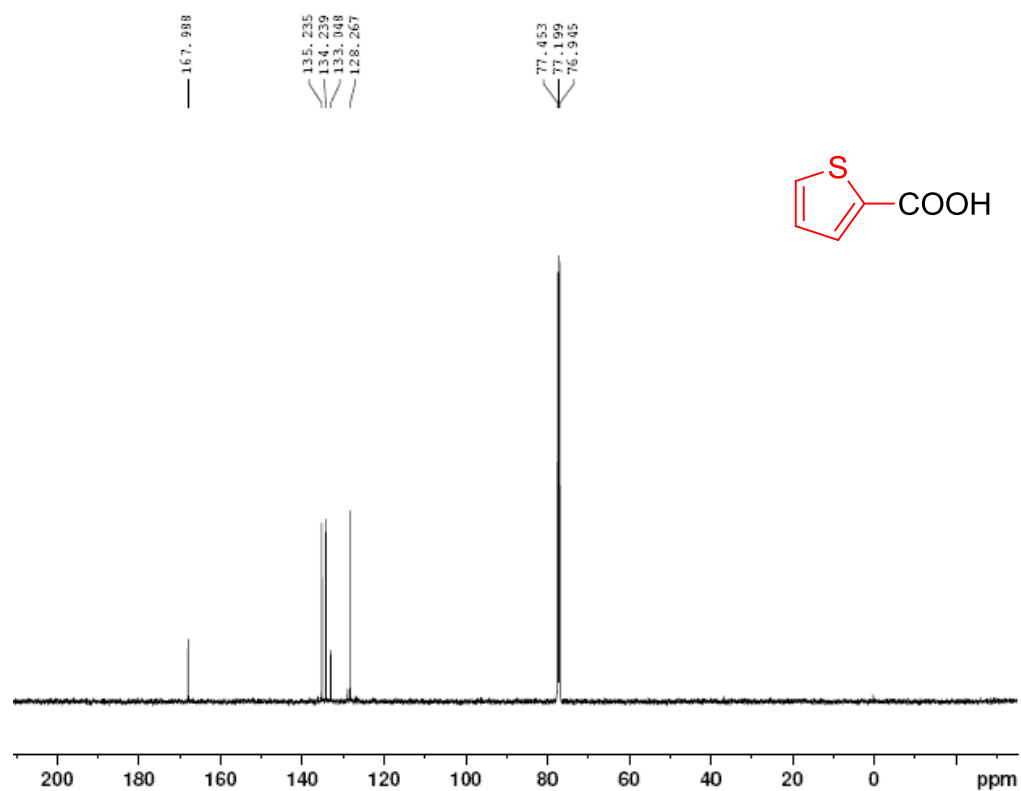
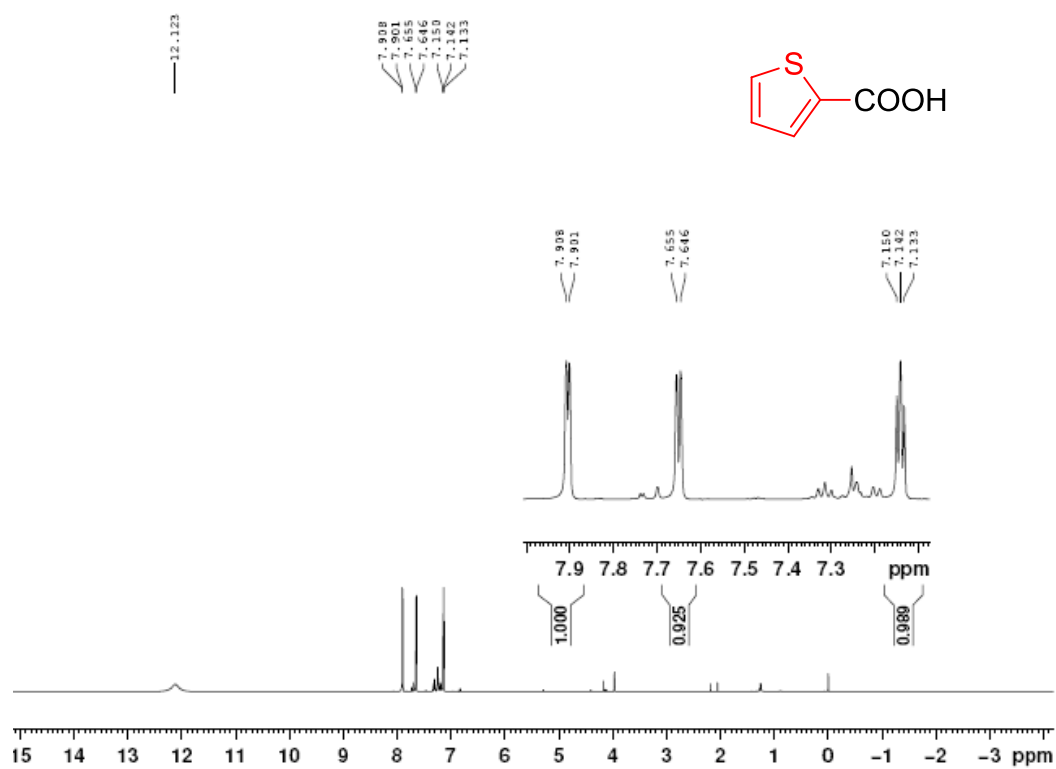
# 1-naphthoic acid (3o')



# 2-naphthoic acid (3p')

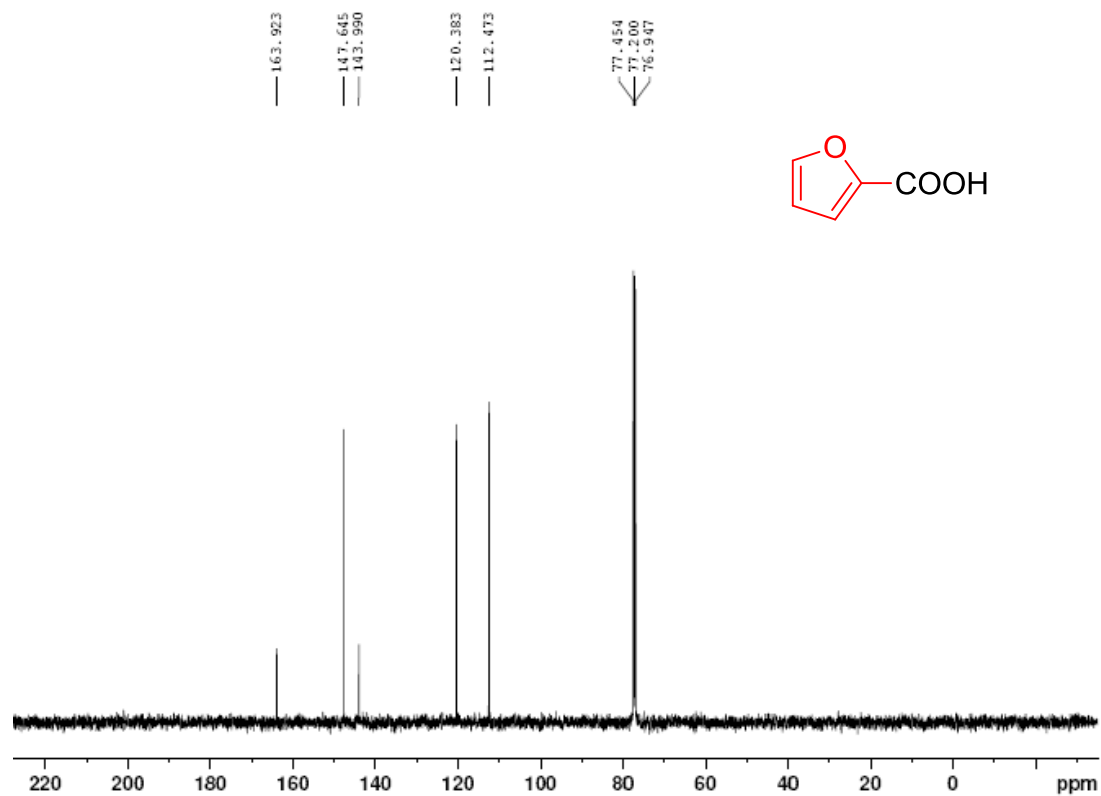
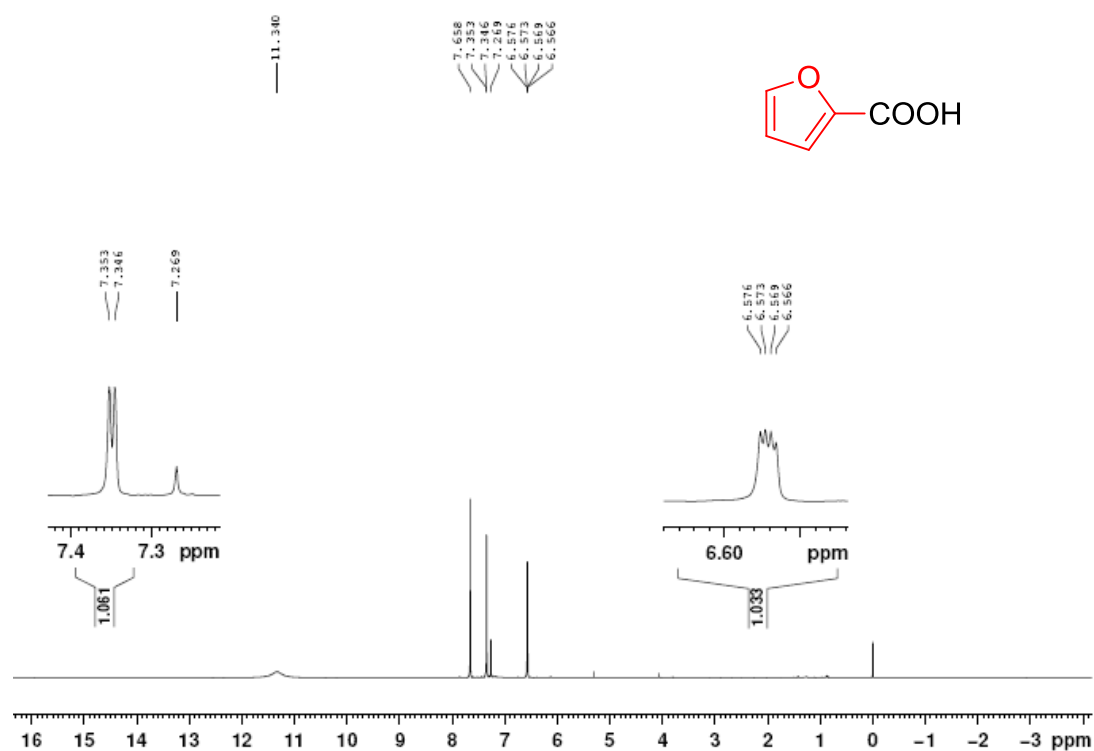


thiophene-2-carboxylic acid (3q')

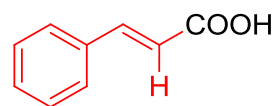
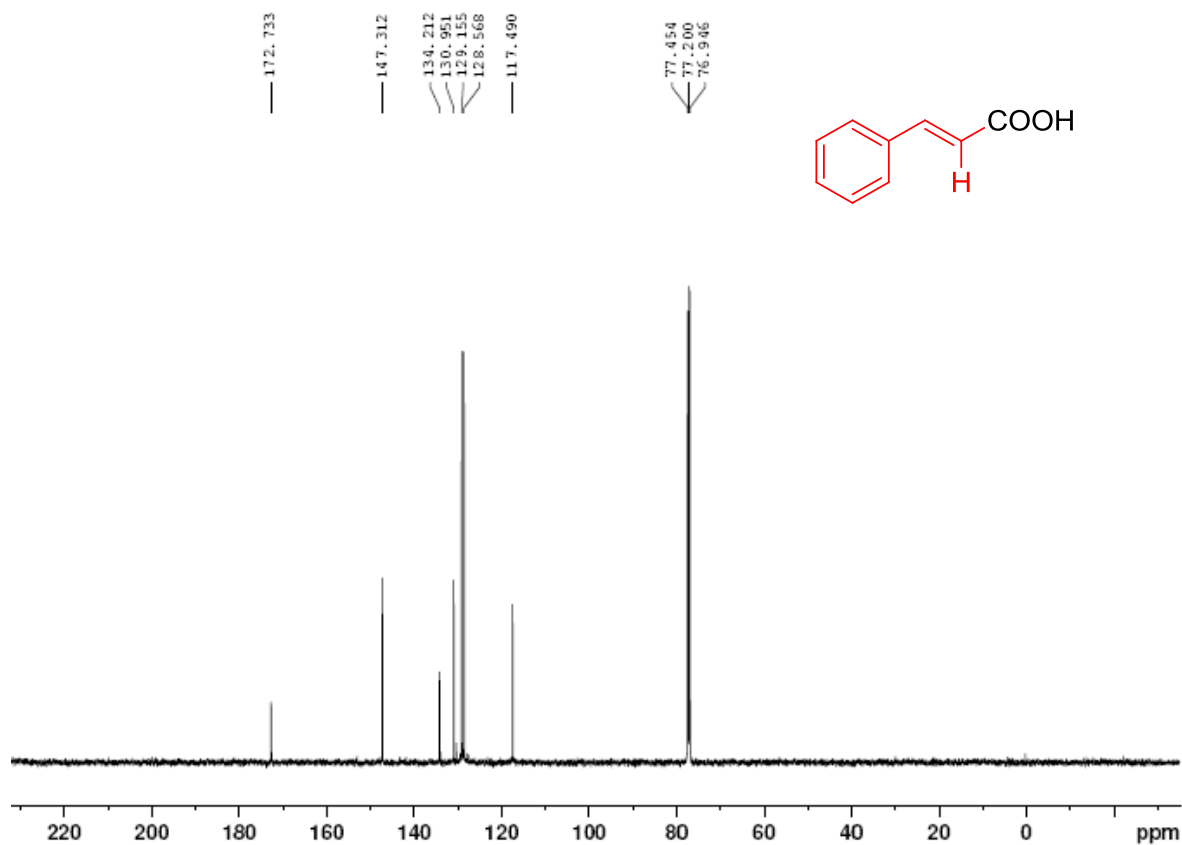
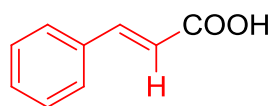
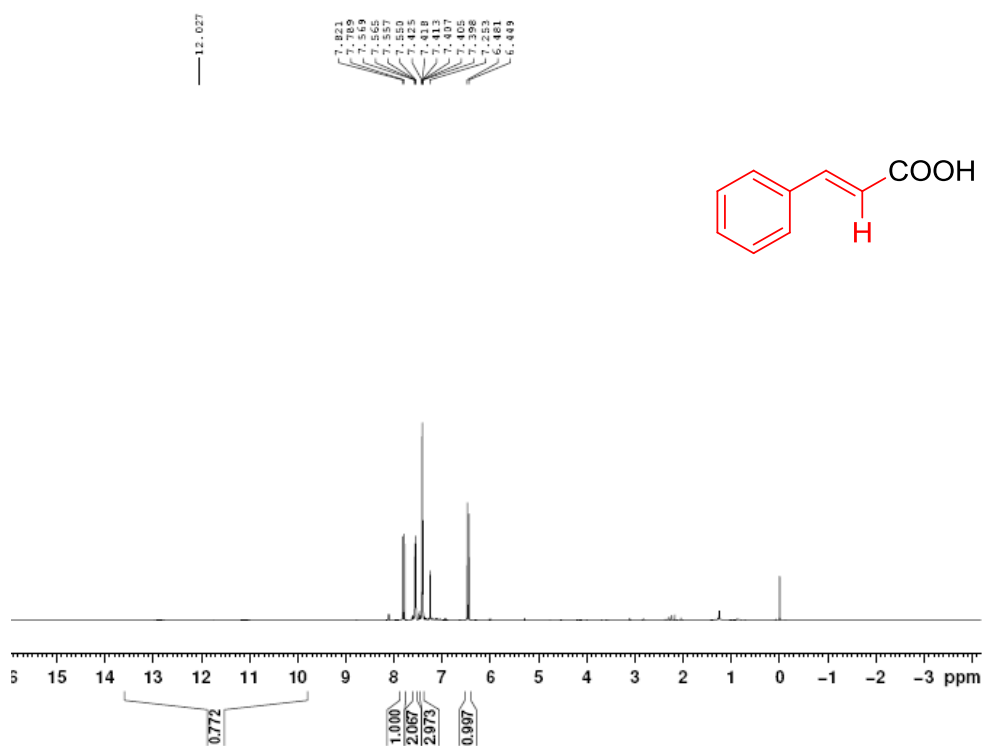




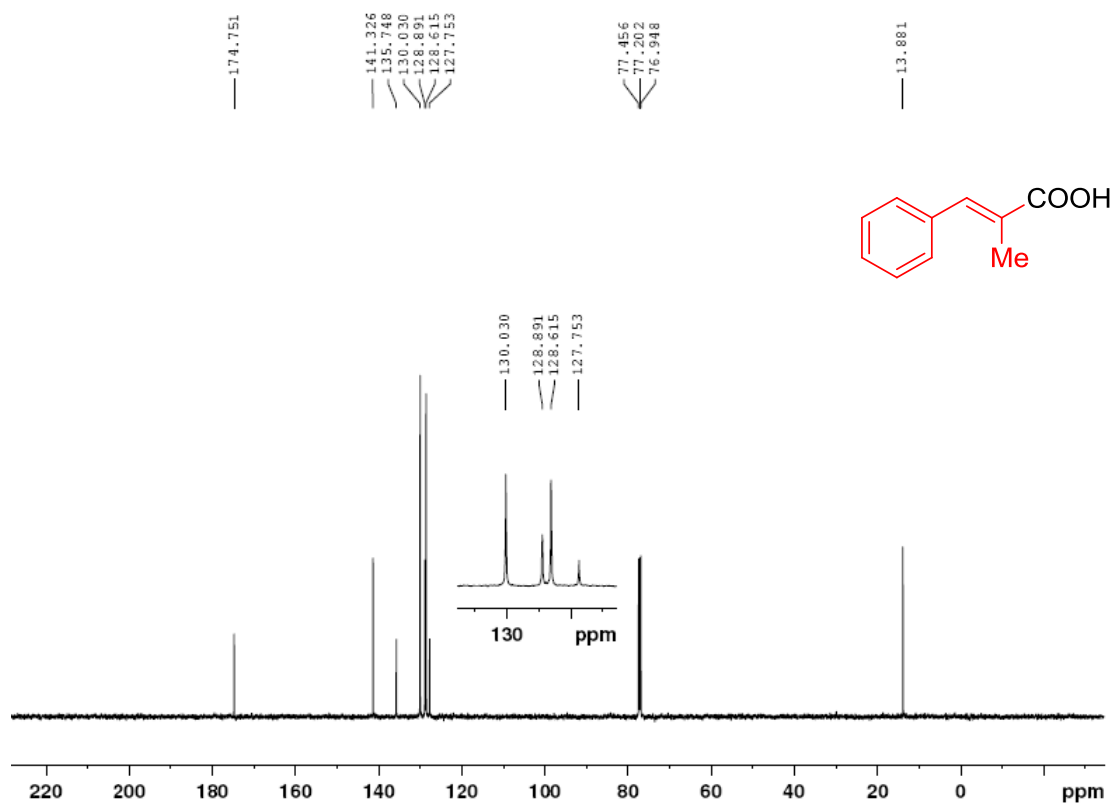
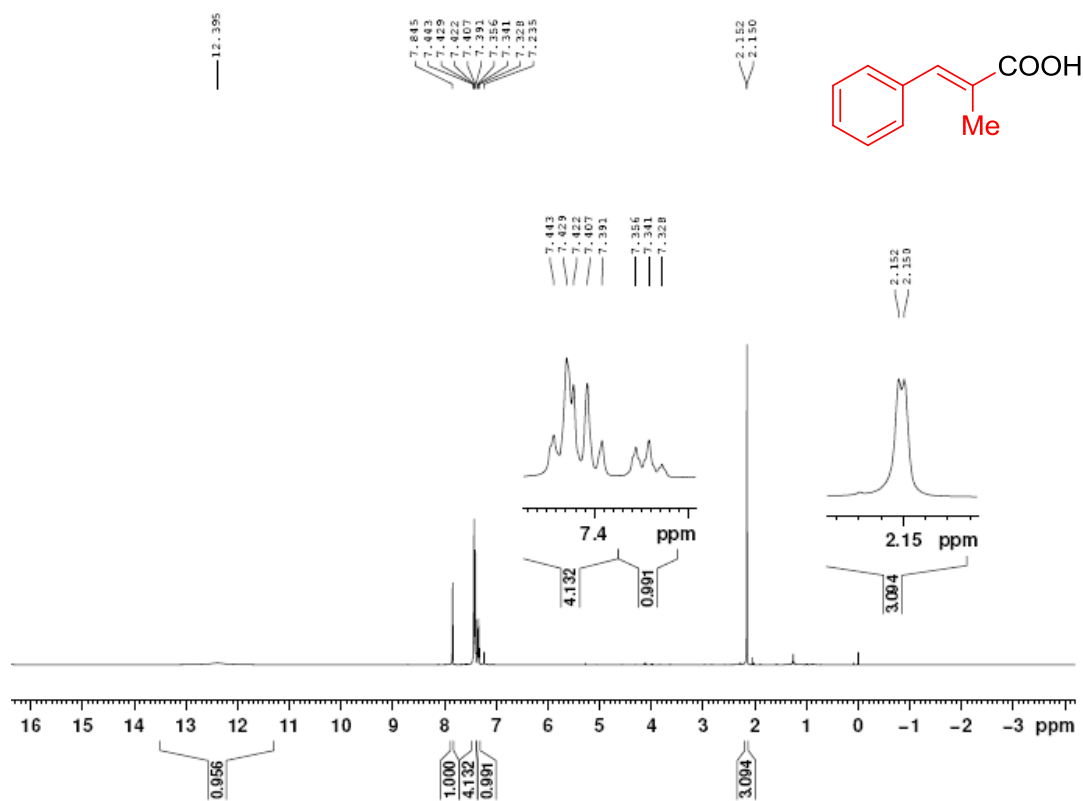
furan-2-carboxylic acid (3r')



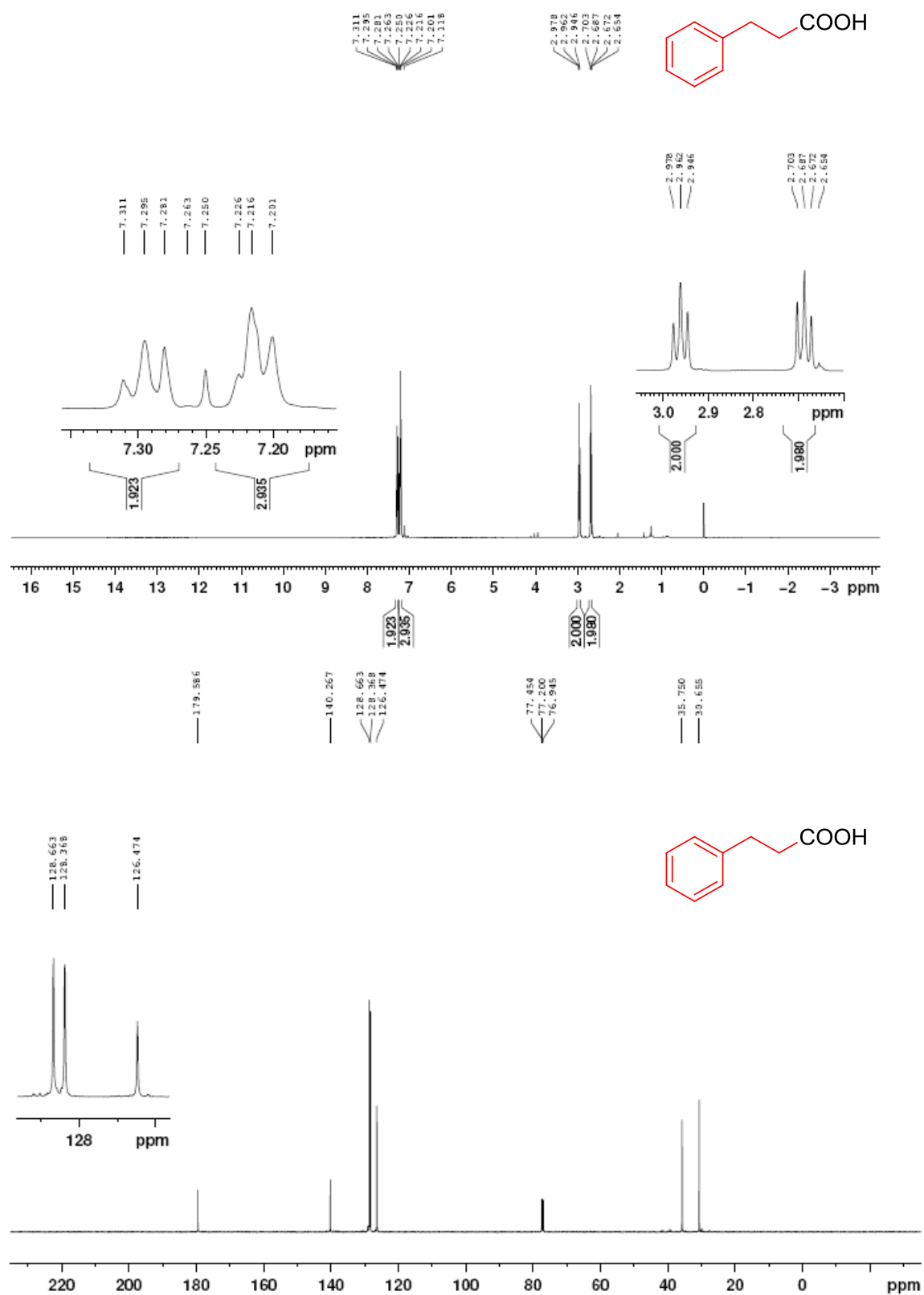
# Cinnamic acid (3s')



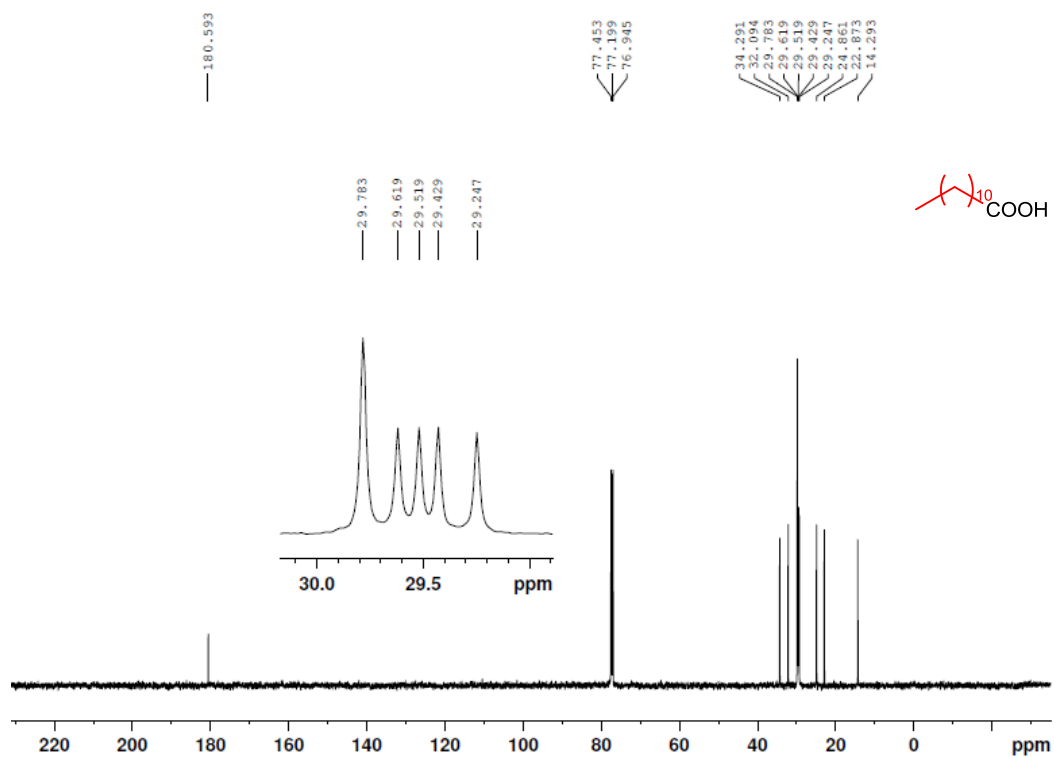
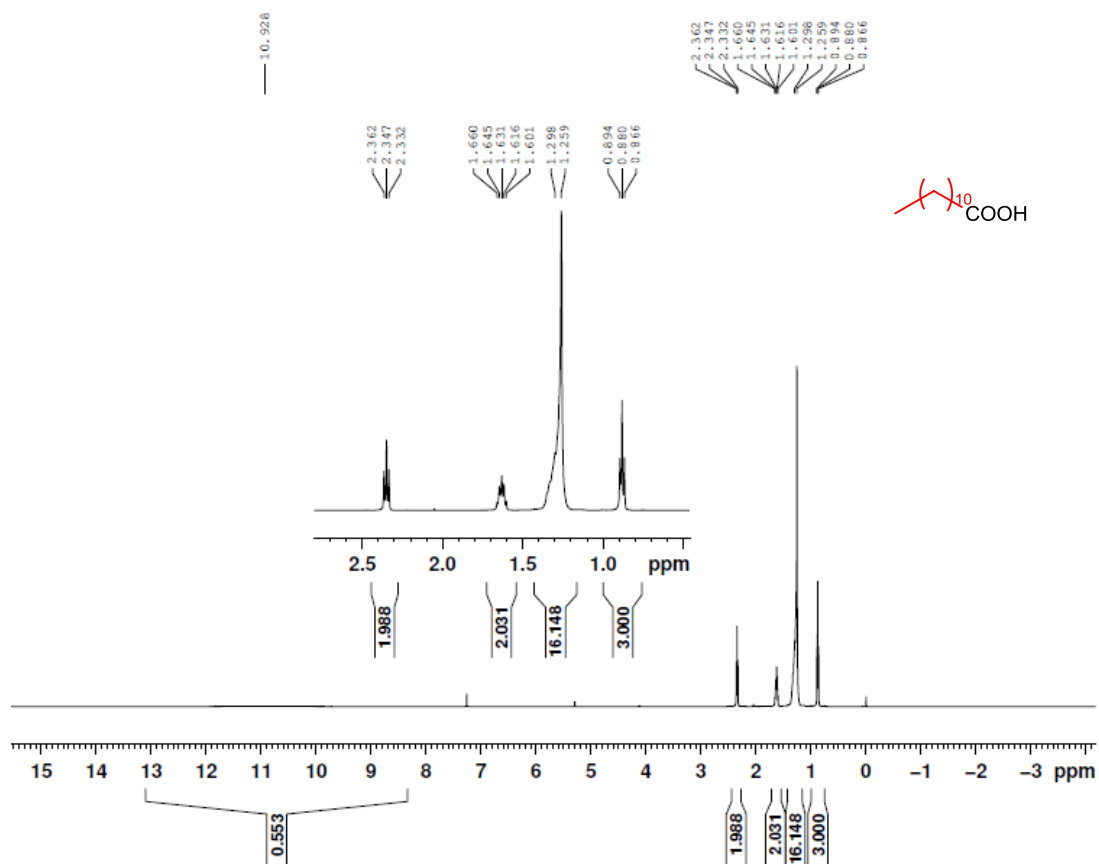
**(E)-2-methyl-3-phenylacrylic acid (3t')**



### 3-phenylpropanoic acid (3u')

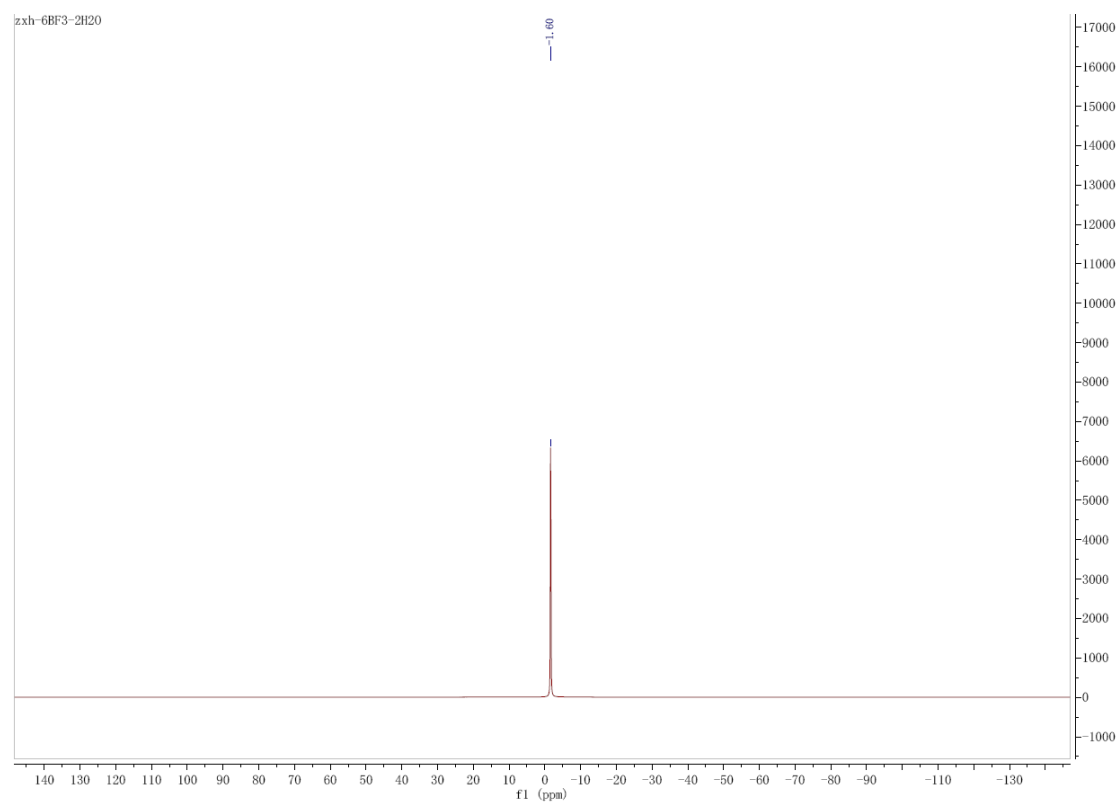


dodecanoic acid (3v')

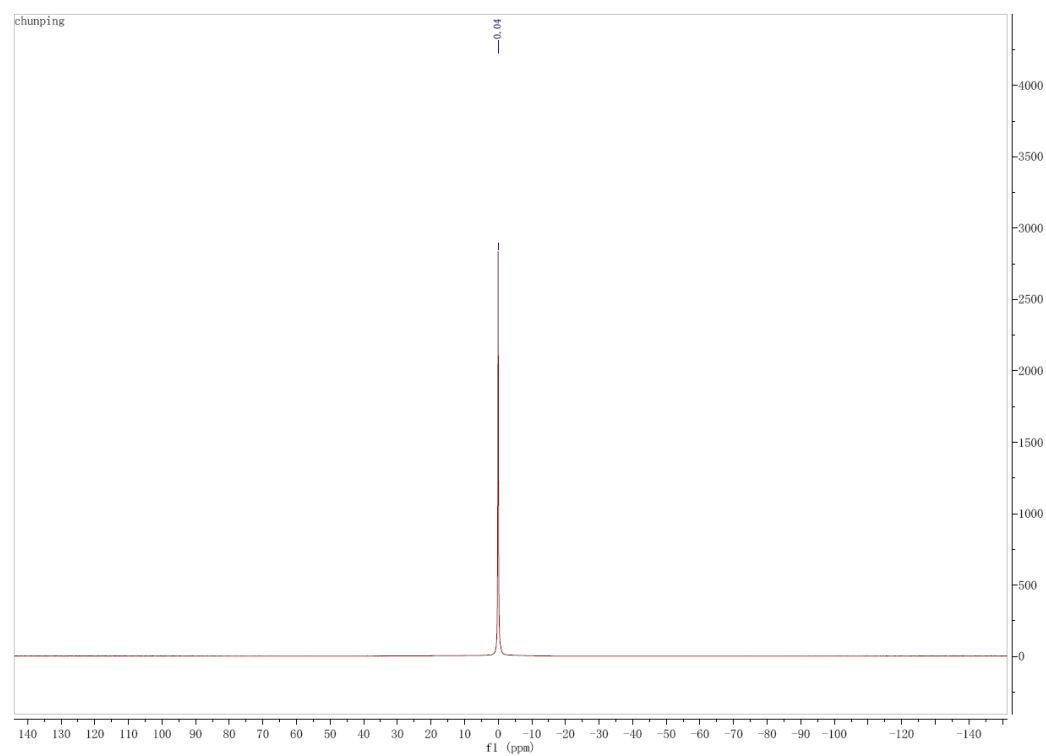


## 6. $^{11}\text{B}$ NMR spectra

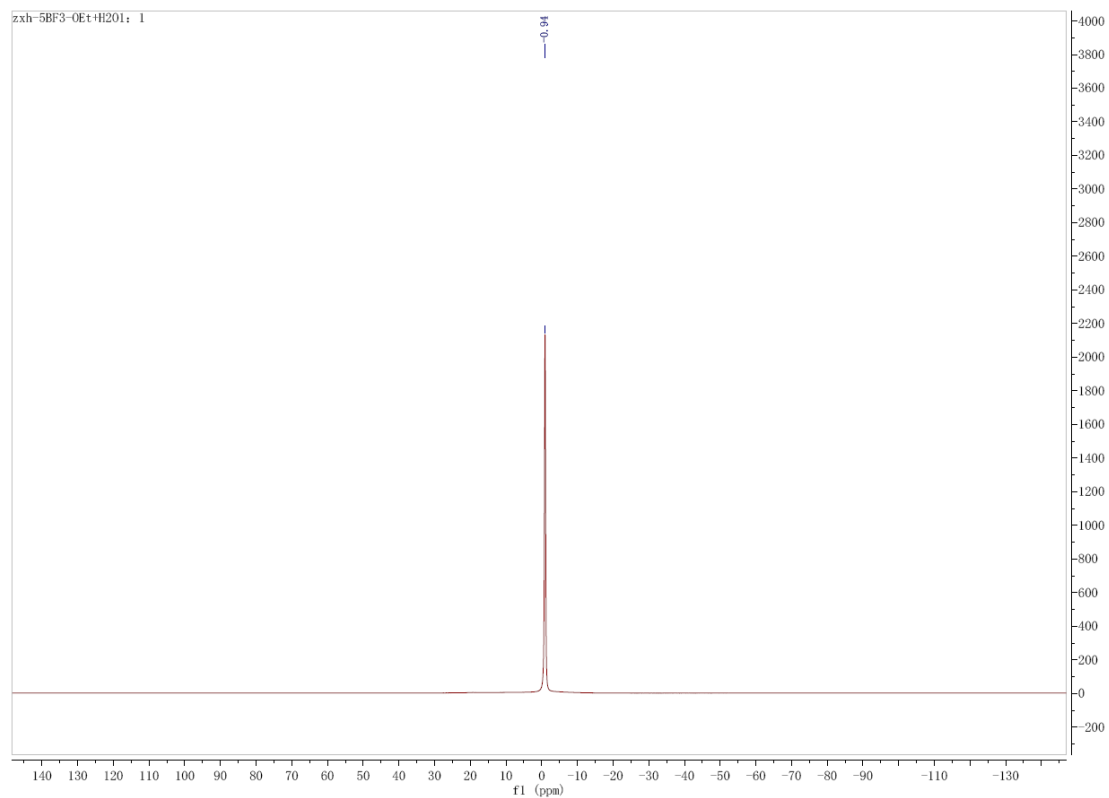
### $\text{BF}_3\cdot 2\text{H}_2\text{O}$



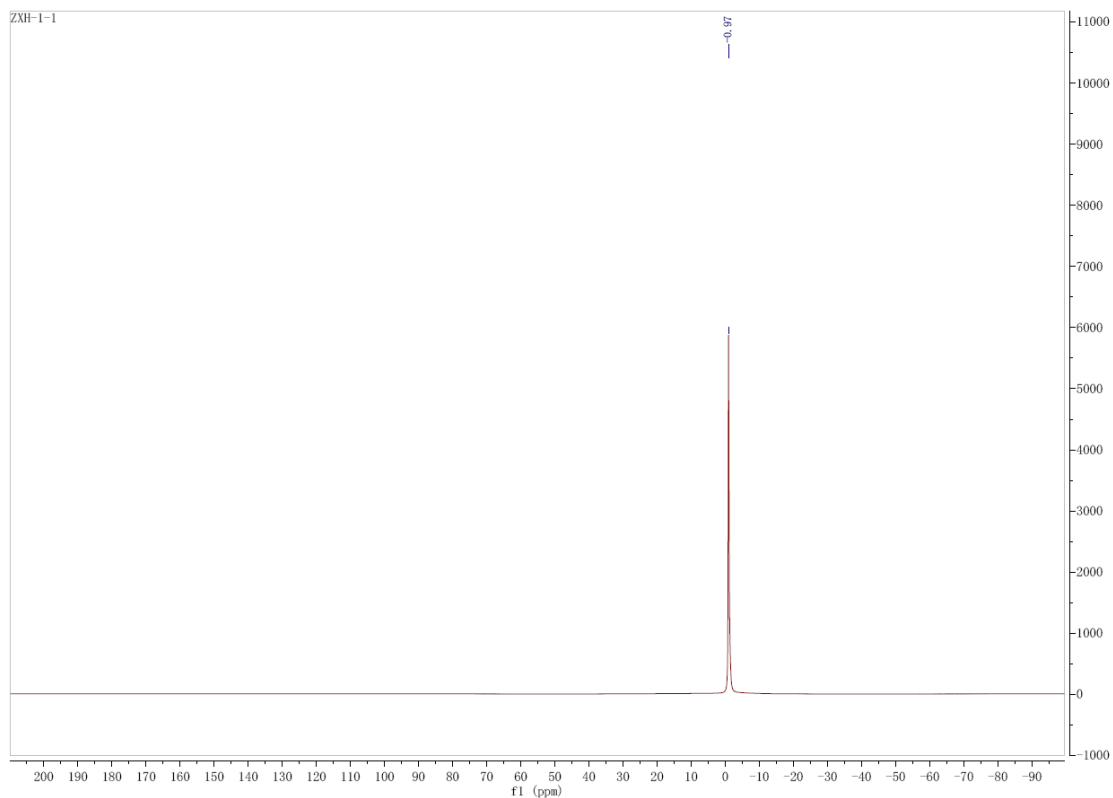
### $\text{BF}_3\cdot \text{OEt}_2$



**$\text{BF}_3\text{-OEt}_2 : \text{H}_2\text{O} = 1:1$**



**The low layer after reaction:**



S95

