

## Chemoselective Dehydrogenative Esterification of Aldehydes and Alcohols with a Dimeric Rhodium(II) Catalyst

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## Supporting Information

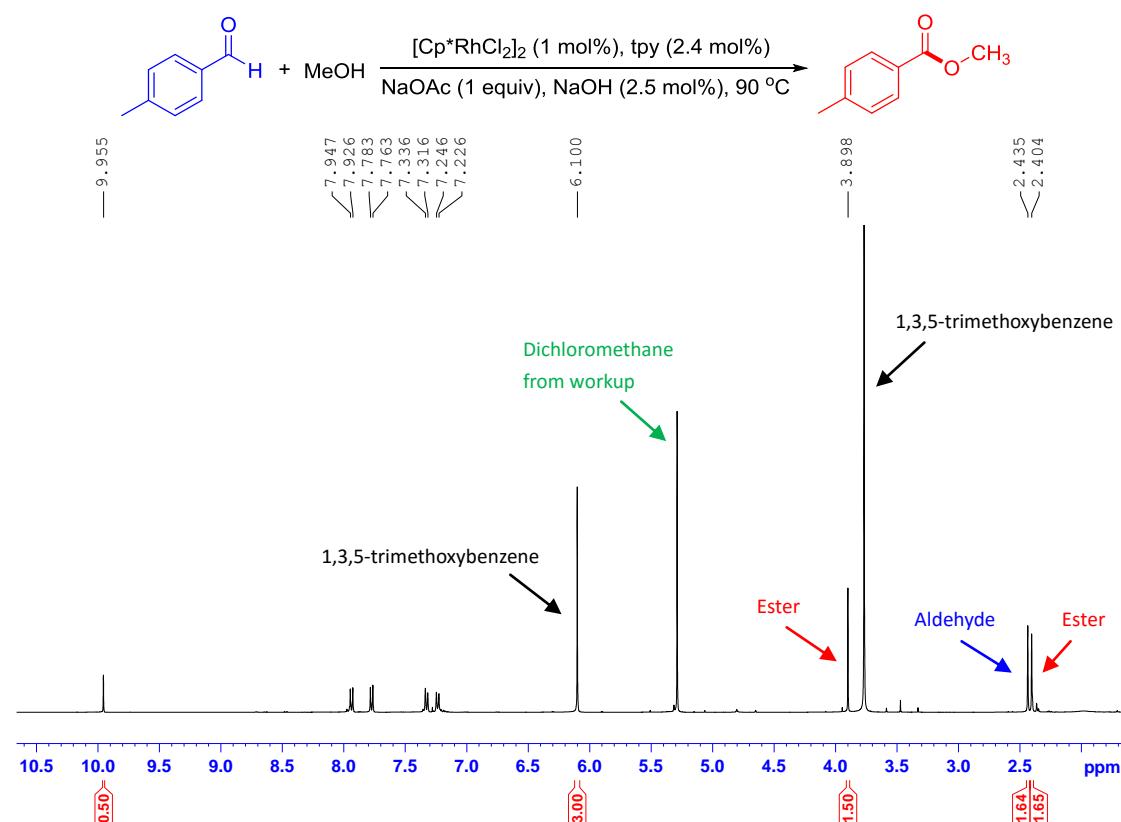
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## **1. General information**

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with TMS as the internal standard. GC and GC-MS analysis was carried out on an Agilent 7890A GC with a HP-5 MS column (quartz capillary column, 30 m x 0.25 mm x 0.25  $\mu\text{m}$ ) and an Agilent 5975C mass-selective detector (58 psi helium gas, 58 psi hydrogen gas, injector temperature 250 °C, FID detector, temperature 300 °C). The GC trace of hydrogen gas was recorded on a HT SP-6890 instrument with a 5 Å molecular sieves column (3 m x 4 mm) and a TCD detector. HRMS (ESI) data were recorded on a Bruker Apex IV FTMS spectrometer.

## 2. Evidence for high chemoselectivity in cross-coupling of aldehyde with alcohol



**Figure S1.** The crude  $^1\text{H}$  NMR of a mixture resulting from reacting 0.5 mmol of 4-methylbenzaldehyde with 1.5 mmol MeOH (1,3,5-trimethoxybenzene as internal standard in  $\text{CDCl}_3$ ). *The crude  $^1\text{H}$  NMR showed that no 4-methylbenzylalcohol was observed in the reaction mixture.* Reaction conditions: 4-methylbenzaldehyde (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol), NaOAc (0.5 mmol), MeOH (1.5 mL), 90 °C, 12 h.

### 3. Optimisation of conditions for cross-coupling of alcohols

**Table S1** The effect of base on **11** catalysed cross-coupling of alcohols

The reaction scheme shows the conversion of 4-methylbenzyl alcohol to 4-methylbenzaldehyde methyl ester. The starting material is 4-methylbenzyl alcohol (a benzene ring with a -CH<sub>2</sub>OH group at position 4). It reacts with MeOH (methanol) in the presence of 1 mol% of catalyst **11** (a Rh complex with a tridentate NHC ligand) and a base at 90 °C. The product is 4-methylbenzaldehyde methyl ester (a benzene ring with a -CH<sub>2</sub>COOCH<sub>3</sub> group at position 4).

Entry	Base	Equivalent	Yield (%)
1	Pyridine	1	0
2	DBU	1	0
3	Triethylamine	1	40
4	Diisopropylamine	1	44
5	NaOAc	1	22
6	NaOH	1	20
7	<i>t</i> -BuOK	1	44
8	NaHCO <sub>3</sub>	1	58
9	NaHCO <sub>3</sub>	0.5	<b>70</b>

Reaction conditions: 4-methylbenzaldehyde (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), base, 90 °C. Yields were determined by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard.

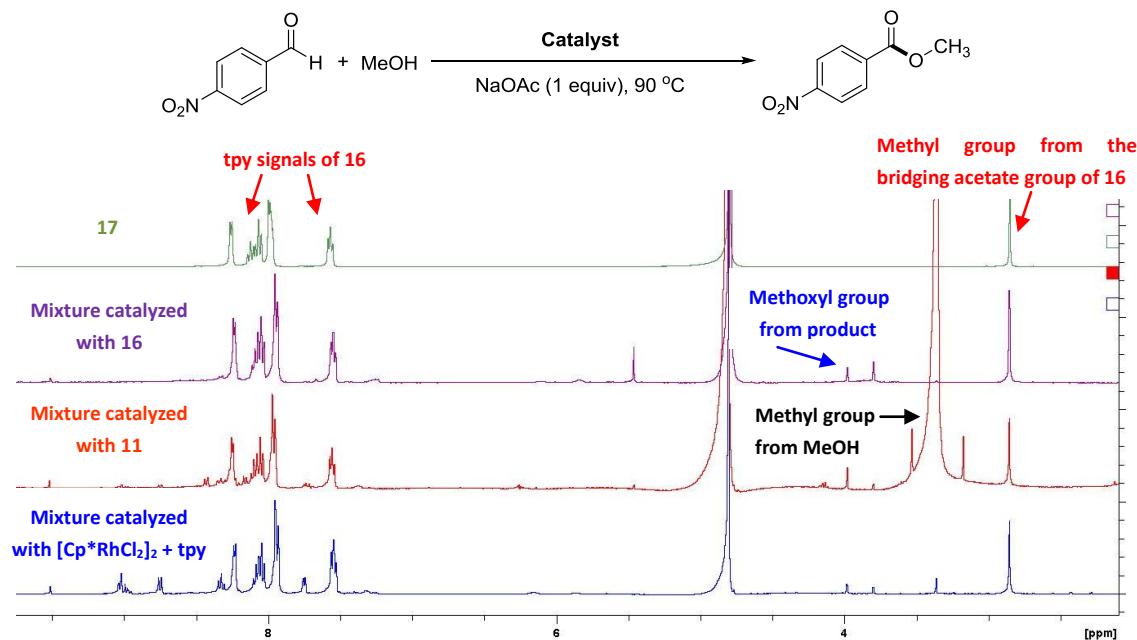
#### 4. Comparison of activity of in situ catalyst and isolated complexes

**Table S2** Results obtained in a model reaction

Catalyst			
Entry	Catalyst	Time (h)	Yield (%)
1	$[\text{Cp}^*\text{RhCl}_2]_2 + \text{tpy}$ in situ	3	23
2	<b>11</b>	3	33
3	<b>13</b>	3	37
4	<b>14</b>	3	9
5	<b>16</b>	3	<b>39</b>

Reaction conditions: aldehyde (0.5 mmol), NaOAc (0.5 mmol) (no NaOH added), MeOH (2 mL), under Ar atmosphere, 90 °C, substrate/Rh molar ratio = 50:1. Yields were determined by  $^1\text{H}$  NMR with 1,3,5-trimethoxybenzene as internal standard.

#### 5. Evidence supporting **16** as the real catalyst

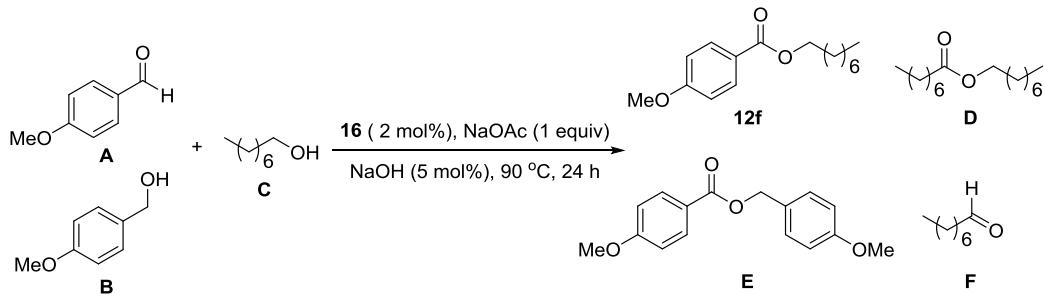


**Figure S2.** The  $^1\text{H}$  NMR traces of **16** and those of reaction mixtures using 50% of **16**, **11**, and  $[\text{Cp}^*\text{RhCl}_2]_2 + \text{tpy}$ , respectively (D<sub>2</sub>O as solvent). Reaction conditions: catalyst (0.025 mmol), *p*-nitrobenzaldehyde (0.05 mmol), NaOAc (0.05 mmol),

MeOH (1.5 mL), 90 °C, 6 h. After each reaction, MeOH was removed under reduced pressure and the mixture dissolved in D<sub>2</sub>O for <sup>1</sup>H NMR measurement. The low intensity of the product peaks is due to its low solubility in D<sub>2</sub>O.

## 6. Chemoselectivity studies for 16

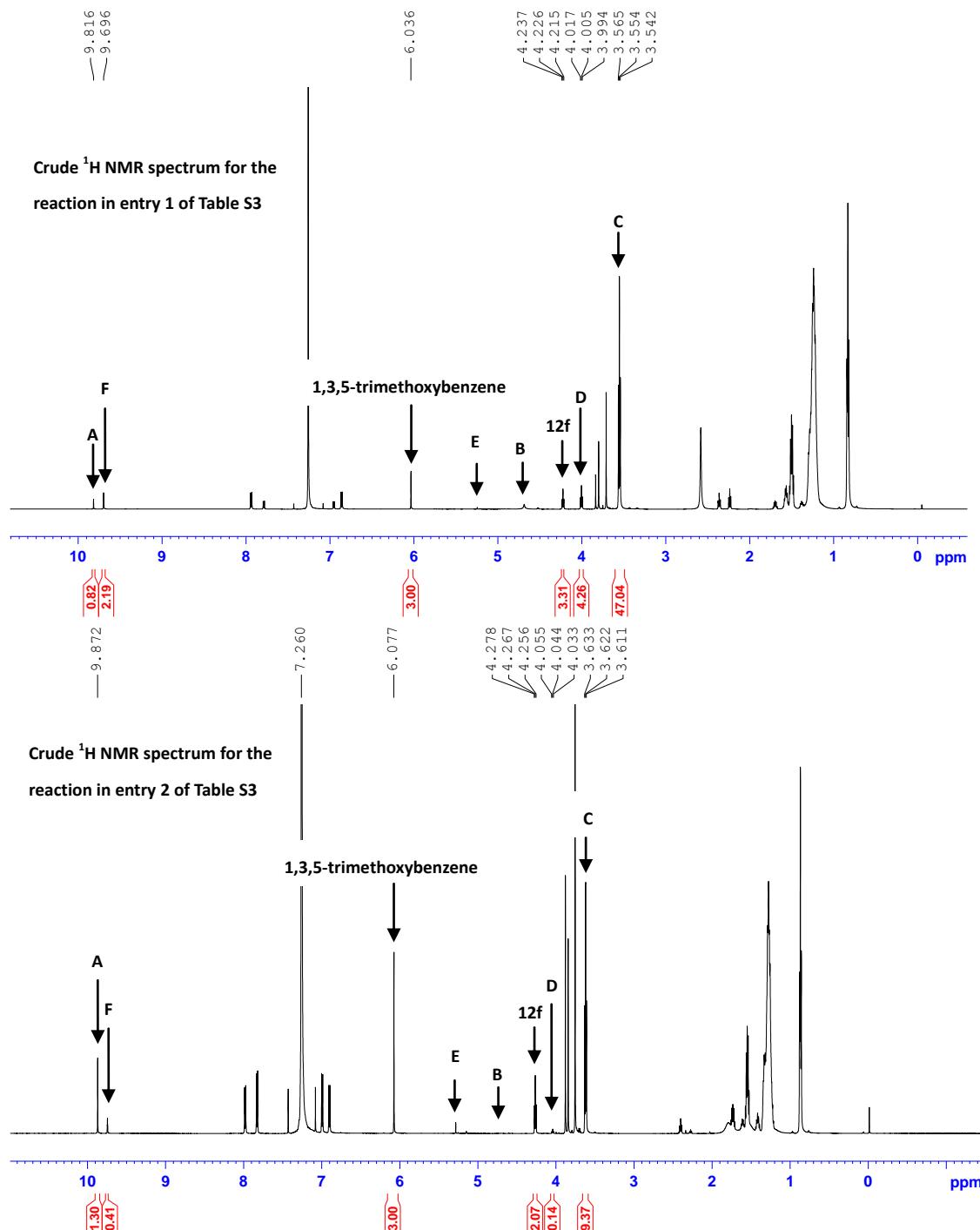
**Table S3** Chemoselectivity for **16** catalysed couplings

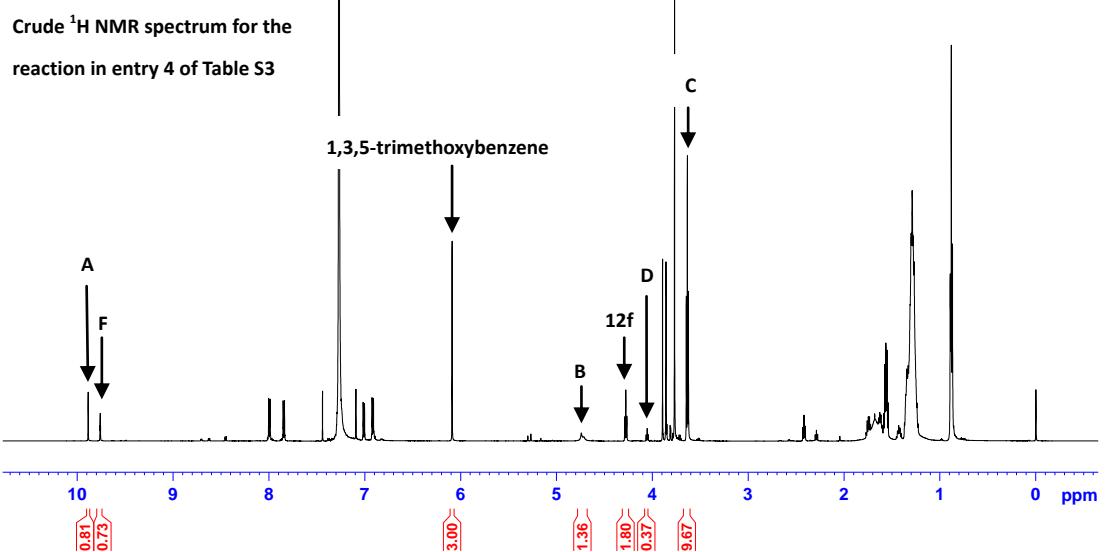
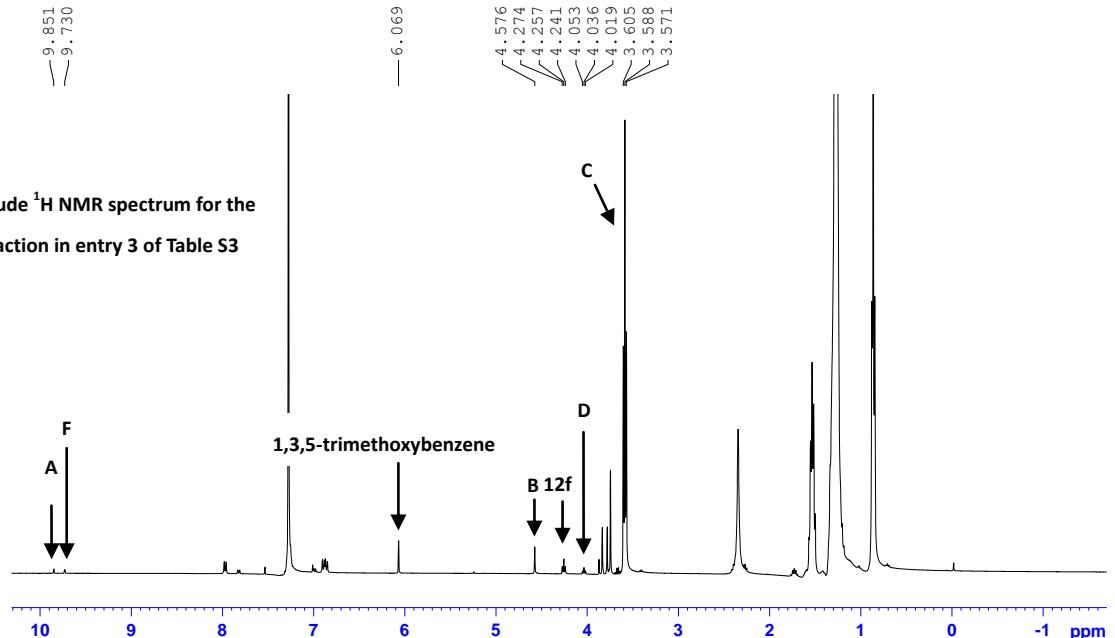


Substrates	Amount of <b>C</b>	<b>12f (%)</b>	<b>A (%)</b>	<b>B (%)</b>	<b>C (%)</b>	<b>D (%)<sup>a</sup></b>	<b>E (%)</b>	<b>F (%)<sup>a</sup></b>
<b>A+C</b>	6.4 mmol	66	33	trace	73	13	trace	7
<b>A+C</b>	1.5 mmol	41	52	0	62 <sup>b</sup>	2	ca. 5	6
<b>B+C</b>	8 mmol	50	2	46	93	1	trace	<1
<b>B+C</b>	1.5 mmol	36	32	27	64 <sup>b</sup>	5	ca. 5	10

Reaction conditions: **A** or **B** (0.5 mmol), octan-1-ol (1.5 mmol, 6.4 mmol or 8 mmol), **16** (2 mol%), NaOAc (0.5 mmol), NaOH (5 mol%), under Ar atmosphere with an empty balloon, 90 °C, 24 h. Yields were determined by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard (0.2 mmol). <sup>a</sup> Yields based on octan-1-ol.

<sup>b</sup> The mass balance for octan-1-ol was less than 100% when a relatively small amount of starting material was used, probably due to its evaporation.





## **7. Procedure for isolation of metal complexes**

### **7.1 Formation of complex 13**

[Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.062 g, 0.1 mmol) was placed in a flask. MeOH (8 mL) and 2,2':6',2"-tripyridine (0.046 g, 0.2 mmol) were added, and the mixture was stirred for 60 min at room temperature. The solvent was evaporated, and the product purified by flash chromatography using methylene chloride and methanol as eluent. Yield: 0.071 g, 70%. Single crystals of **11** were formed in a methanol solution of **13** at room temperature.

### **7.2 Isolation of complexes **11** and **14****

[Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.062 mg, 0.1 mmol) was placed in a flask. MeOH (8 mL) and 2,2':6',2"-tripyridine (0.046 g, 0.2 mmol) were added, and the mixture was refluxed for 6 h. After evaporation of solvent, the residue was washed with 30 mL of methylene chloride. The resulting solid was then dissolved in methanol. The insoluble deep orange solid was identified to be **11** (ca. 10% yield), whilst evaporation of the solvent from the methanol solution gave an orange solid of **8**. Yield: 0.047 g, 50%.

### **7.3 Preparation of **11** with a known method<sup>[1]</sup>**

A solution of RhCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> (0.253 g, 0.96 mmol) in EtOH (4 mL) was poured into a solution of 2,2':6',2"-tripyridine (0.224 g, 0.96 mmol) in 4 mL of EtOH. The dark orange mixture was heated under reflux for 2 h. After cooling to room temperature, the resulting yellow microcrystalline solid was filtered off, washed with EtOH and Et<sub>2</sub>O sequentially, and then dried in vacuo. Yield: 0.425 g, 76%.

### **7.4 Isolation of complex **16**<sup>[2]</sup>**

CH<sub>3</sub>COOAg (0.05 g, 0.3 mmol) and **11** (0.066 g, 0.15 mmol) were refluxed in methanol (6 mL) for 12 h. After cooling to rt, the reaction mixture was filtered. The solvent of the filtrate was removed under reduced pressure, and the residue washed with 30 mL of methylene chloride. The resulting solid was dissolved in 50 mL of methanol and the insoluble solid removed by filtration. The methanol solution was

concentrated to 15 mL, to which were added 5 mL of methylene chloride and 20 mL of petroleum ether sequentially. The resulting red precipitate was collected by filtration and dried in vacuo. Yield: 0.030 g, 48%.

### 7.5 Preparation of $[\text{Rh}(\text{tpy})_2]\text{[PF}_6\text{]}_3$ <sup>[3]</sup>

$[\text{RhCl}_3(\text{tpy})]$  (0.022 g, 0.05 mmol) and 2,2':6',2"-tripyridine (0.012 g, 0.05 mmol) and were refluxed in ethanol-water (1:1, 7 mL) for 5 h. The reaction mixture was filtered, and  $\text{NH}_4\text{PF}_6$  (0.025 g, 0.15 mmol) was added to the filtrate. The pink precipitate thus produced was isolated by filtration and washed sequentially with 1.5 mL of water, ethanol and diethyl ether. The resulting solid was dissolved in a minimum volume of acetonitrile and then precipitated by addition of diethyl ether, yielding  $[\text{Rh}(\text{tpy})_2]\text{[PF}_6\text{]}_3$  in 70% yield (0.035 g). This complex has the same cation as **14**.

## 8. General procedure for the esterification reaction

### 8.1 General procedure for coupling of aldehydes with alcohols

Aldehyde (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol), 2,2':6',2"-tripyridine (0.012 mmol),  $\text{CH}_3\text{COONa}$  (0.5 mmol),  $\text{NaOH}$  (0.0125 mmol),  $\text{MeOH}$  (2 mL) and a magnetic stir bar were placed in a Radleys Carousel tube. The mixture was bubbled with argon for 15 min and the tube was sealed and connected to an empty balloon. The mixture was then heated at 90 °C for 6-48 h. After cooling to room temperature, the mixture was extracted with methylene chloride (3 x 10 mL). The organic layers were washed with brine and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure and the product purified by flash chromatography using petroleum ether and ethyl acetate as eluent. The reactions of aldehydes with other alcohols were carried out with  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.010 mmol), 2,2':6',2"-tripyridine (0.024 mmol) and 1 mL of alcohol.

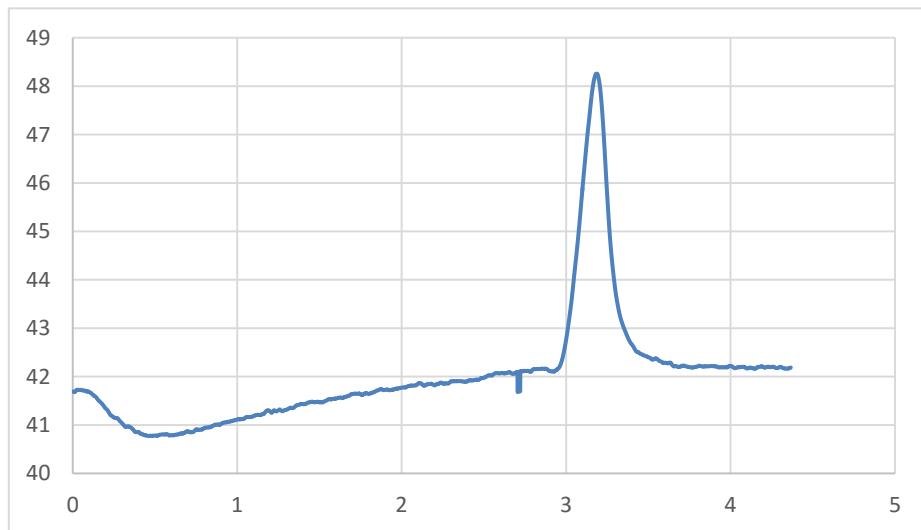
### 8.2 General procedure for cross-coupling of alcohols

A benzyl alcohol (0.5 mmol), **11** (0.005 mmol),  $\text{NaHCO}_3$  (0.25 mmol), an aliphatic

alcohol (2 mL, but 1 mL for alcohols other than MeOH) and a magnetic stir bar were placed in a Radleys Carousel tube. The mixture was bubbled with argon for 15 min and the tube was sealed and connected to an empty balloon. The mixture was then heated at 90 °C for 12-48 h. After cooling to room temperature, the mixture was extracted with methylene chloride (3 x 10 mL). The organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure and the product purified by flash chromatography using petroleum ether and ethyl acetate as eluent.

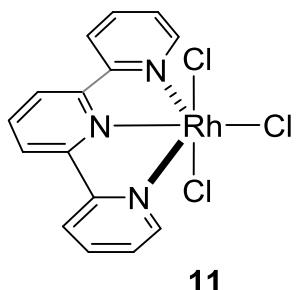
## 9. Detection of hydrogen gas

In a Radleys Carousel tube, *p*-nitrobenzaldehyde (2 mmol), methanol (4 mL), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (2 mol%), tpy (4.8 mol%), and NaOAc (2 mmol) were stirred under a nitrogen atmosphere for 3 h at 90 °C. The head gas was collected by a gas-tight syringe and analyzed by GC. H<sub>2</sub> was detected (Figure S3).

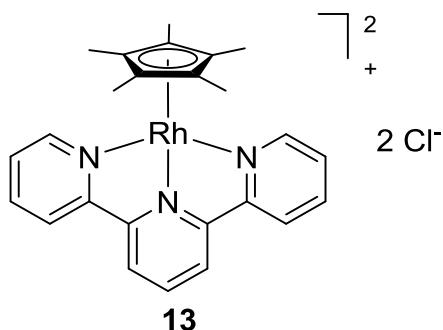


**Figure S3.** Detection of hydrogen gas with GC. GC parameters: injection temperature = 120 °C, column temperature = 70 °C, detector temperature = 120 °C. 5 Å molecular sieves column was used, and the carrier gas was N<sub>2</sub>.

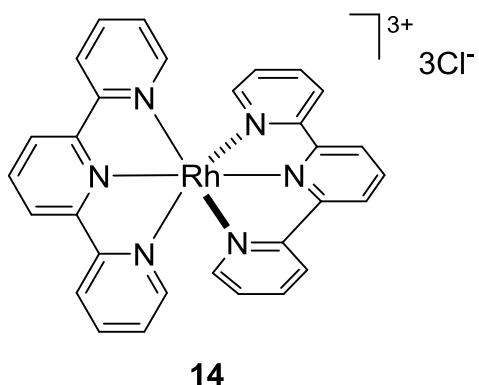
## 10. Analytic data of metal complexes



**5:**<sup>[1]</sup> deep orange solid;  $^1\text{H}$  NMR (DMSO-d<sub>6</sub>, 400 MHz)  $\delta$  (ppm): 9.28 (d,  $J$  = 5.6 Hz, 2H), 8.82 (d,  $J$  = 8.0 Hz, 2H), 8.78 (d,  $J$  = 8.0 Hz, 2H), 8.55 (t,  $J$  = 8.0 Hz, 1H), 8.39 (t,  $J$  = 8.0 Hz, 2H), 7.94-7.98 (m, 2H).  $^{13}\text{C}$  NMR (DMSO-d<sub>6</sub>, 100 MHz)  $\delta$  (ppm): 157.2, 155.2, 153.2, 140.5, 140.3, 128.4, 125.1, 124.4.

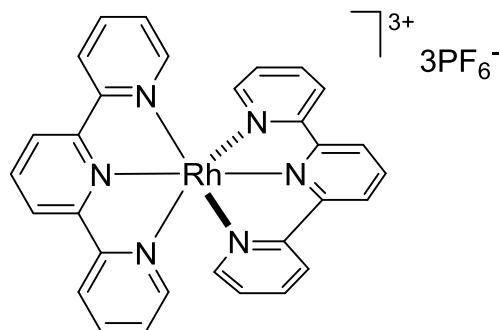


**13:** red solid;  $^1\text{H}$  NMR (CD<sub>3</sub>OD, 400 MHz)  $\delta$  (ppm): 8.93 (d,  $J$  = 4.8 Hz, 2H), 8.87 (d,  $J$  = 8.0 Hz, 2H), 8.58 (d,  $J$  = 8.0 Hz, 2H), 8.44 (t,  $J$  = 8.0 Hz, 1H), 8.21 (td,  $J$  = 1.6, 8.0 Hz, 2H), 7.78-7.82 (m, 2H), 1.19 (s, 15H).  $^{13}\text{C}$  NMR (CD<sub>3</sub>OD, 100 MHz)  $\delta$  (ppm): 161.0, 156.8, 152.7, 142.2, 140.5, 128.3, 128.1, 127.1, 99.0, 8.62; HRMS (ESI) for C<sub>25</sub>H<sub>26</sub>ClN<sub>3</sub>Rh[M+Cl]<sup>+</sup>: calc.: 506.0870; found: 506.0868.

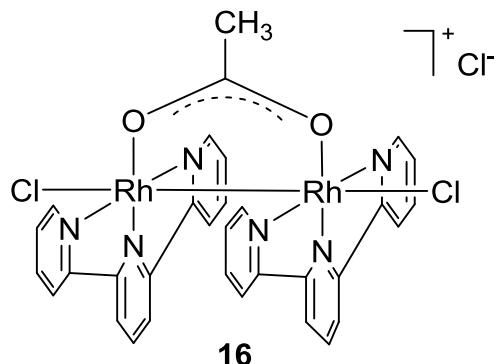


**14:** orange solid;  $^1\text{H}$  NMR (CD<sub>3</sub>OD, 400 MHz)  $\delta$  (ppm): 9.17 (d,  $J$  = 8.0 Hz, 2H),

9.01 (t,  $J = 8.0$  Hz, 1H), 8.92 (d,  $J = 8.0$  Hz, 2H), 8.39 (td,  $J = 8.0, 1.2$  Hz, 2H), 7.91 (d,  $J = 5.6$  Hz, 2H), 7.60-7.64 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz)  $\delta$  (ppm): 158.5, 155.4, 153.8, 145.5, 144.2, 131.5, 129.0, 128.7; HRMS (ESI) for  $\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{N}_6\text{Rh} [\text{M}+2\text{Cl}]^+$ : calc.: 639.0338; found: 639.0348.

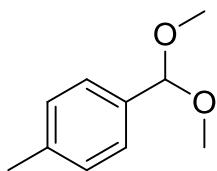


$[[\text{Rh}(\text{tpy})_2]\text{[PF}_6\text{]}_3]$ :<sup>[3]</sup> pink solid;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$  (ppm): 9.09 (d,  $J = 8.4$  Hz, 2H), 8.94-8.98 (m, 1H), 8.83 (d,  $J = 8.4$  Hz, 2H), 8.32-8.35 (m, 2H), 7.81 (d,  $J = 5.2$  Hz, 2H), 7.55-7.56 (m, 2H).

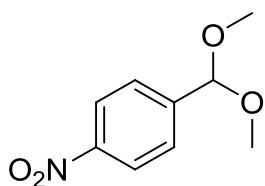


**16:**<sup>[2]</sup> red solid;  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 400 MHz)  $\delta$  (ppm): 8.14 (d,  $J = 5.6$  Hz, 4H), 7.85-8.02 (m, 14H), 7.44 (t,  $J = 6.6$  Hz, 4H), 2.72 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ , 100 MHz)  $\delta$  (ppm): 192.3, 155.2, 154.7, 151.5, 140.2, 139.2, 129.1, 124.6, 123.8, 24.5; HRMS (ESI) for  $\text{C}_{32}\text{H}_{25}\text{Cl}_2\text{N}_6\text{O}_2\text{Rh}_2$   $[\text{M}]^+$ : calc.: 800.9526; found: 800.9530; IR (in KBr,  $\text{cm}^{-1}$ ): 1447 ( $V^\delta$  COO), 1546 ( $V^\text{as}$ , COO); UV-Vis ( $\text{H}_2\text{O}$ , nm): 230, 270, 315, 345.

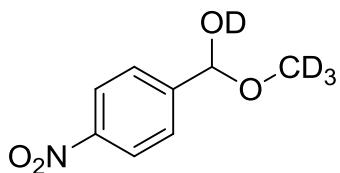
## 11. Analytic data of intermediates and products



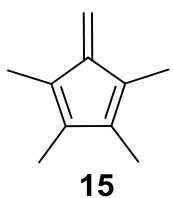
**1-(Dimethoxymethyl)-4-methylbenzene:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.34 (d,  $J = 8.0$  Hz, 2H), 7.18 (d,  $J = 8.0$  Hz, 2H), 5.37 (s, 1H), 3.33 (s, 6H), 2.36 (s, 3H).



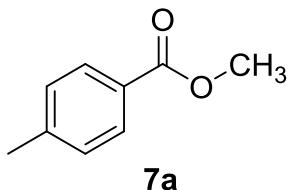
**1-(Dimethoxymethyl)-4-nitrobenzene:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.21 (d,  $J = 8.4$  Hz, 2H), 7.63 (d,  $J = 8.8$  Hz, 2H), 5.46 (s, 1H), 3.33 (s, 6H).



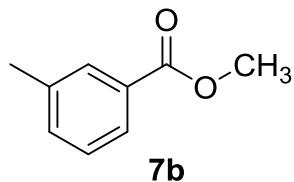
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.19 (d,  $J = 8.8$  Hz, 2H), 7.69 (d,  $J = 8.8$  Hz, 2H), 5.60 (s, 1H).



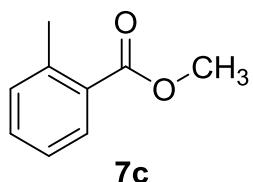
**1,2,3,4-Tetramethyl-5-methylenecyclopenta-1,3-diene:**  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$  (ppm): 5.41 (s, 2H), 1.86 (s, 6H), 1.81 (s, 6H). MS (EI) for  $\text{C}_{10}\text{H}_{14} [\text{M}]^+$ : 134.



**Methyl 4-methylbenzoate:**<sup>[4]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 94% yield in 12 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 96% yield in 12 h; both yields were determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.92 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 167.2, 143.5, 129.6, 129.1, 127.5, 51.9, 21.6; MS (EI) for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> [M]<sup>+</sup>: 150.

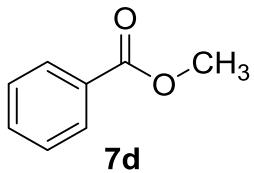


**Methyl 3-methylbenzoate:**<sup>[5]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 92% yield in 12 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 89% yield in 18 h; both yields determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.83-7.86 (m, 2H), 7.26-7.36 (m, 2H), 3.90 (s, 3H), 2.39 (s, 3H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.2, 137.1, 132.6, 129.1, 127.2, 125.6, 50.9, 20.2; MS (EI) for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> [M]<sup>+</sup>: 150.

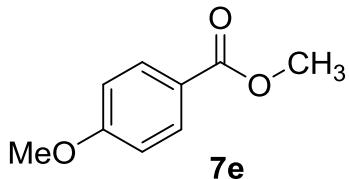


**Methyl 4-methylbenzoate:**<sup>[5]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 75% yield in 24 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 59% yield in 24 h; both yields determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.91-7.93 (m, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.23-7.27 (m, 2H), 3.89 (s, 3H), 2.60 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100

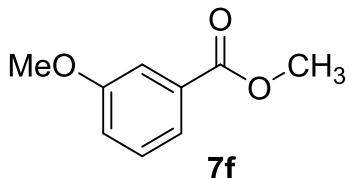
MHz)  $\delta$  (ppm): 168.0, 140.1, 131.9, 131.6, 130.5, 129.5, 125.6, 51.7, 21.7; MS (EI) for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> [M]<sup>+</sup>: 150.



**Methyl benzoate:**<sup>[4]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 90% yield in 12 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 85% yield in 12 h; both yields determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as internal standard; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.04 (d, *J* = 6.8 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.92 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 167.1, 132.9, 130.2, 129.6, 128.3, 52.1; MS (EI) for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> [M]<sup>+</sup>: 136.

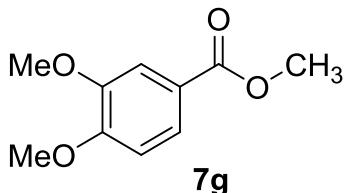


**Methyl 4-methoxybenzoate:**<sup>[4]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 78 mg; 94% yield in 12 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 94% yield in 18 h; white solid; m.p. = 49-50 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 166.9, 163.3, 131.6, 122.6, 113.6, 55.4, 51.8; MS (EI) for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> [M]<sup>+</sup>: 166.

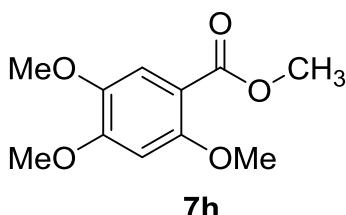


**Methyl 3-methoxybenzoate:**<sup>[8]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 76 mg; 92% yield in 12 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol),

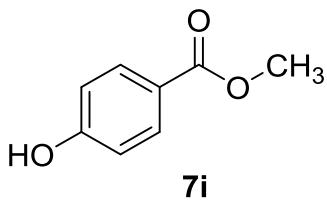
MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 73% yield in 18 h; white solid; m.p. = 45-46 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.63 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.56 (q, *J* = 1.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.08-7.11(m, 1H), 3.91 (s, 3H), 3.84 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 167.0, 159.6, 131.5, 129.4, 122.0, 119.5, 114.0, 55.4, 52.2; MS (EI) for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> [M]<sup>+</sup>: 166.



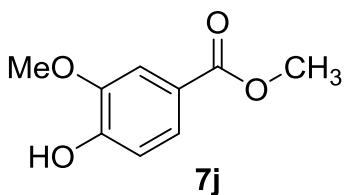
**Methyl 3,4-dimethoxybenzoate:**<sup>[4]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 93 mg; 95% yield in 6 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 96% yield in 18 h; white solid; m.p. = 55-56 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 3.93 (s, 3H), 3.927 (s, 3H), 3.89 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.9, 153.0, 148.6, 123.6, 122.7, 112.0, 110.3, 56.0, 52.0; MS (EI) for C<sub>10</sub>H<sub>12</sub>O<sub>4</sub> [M]<sup>+</sup>: 196.



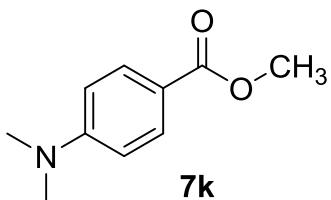
**Methyl 2,4,5-trimethoxybenzoate:**<sup>[10]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 105 mg; 93% yield in 6 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 88% yield in 18 h; white solid; m.p. = 89-90 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.40 (s, 1H), 6.52 (s, 1H), 3.93 (s, 3H) 3.90 (s, 3H), 3.86 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.1, 155.7, 153.6, 142.6, 114.5, 110.7, 97.8, 57.1, 56.4, 56.0, 51.8; MS (EI) for C<sub>11</sub>H<sub>14</sub>O<sub>5</sub> [M]<sup>+</sup>: 226.



**Methyl 4-hydroxybenzoate:**<sup>[4]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOH (0.024 mmol) and NaOAc (0.5 mmol); 65 mg; 86% yield in 24 h; white solid; m.p = 115-116 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.95 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 167.4, 160.2, 132.0, 122.4, 115.3, 52.1; MS (EI) for C<sub>8</sub>H<sub>8</sub>O<sub>3</sub> [M]<sup>+</sup>: 152.

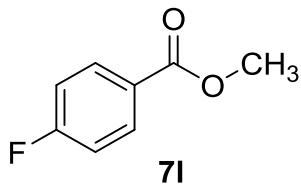


**Methyl 4-hydroxy-3-methoxybenzoate:**<sup>[4]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 76 mg; 83% yield in 24 h; white solid; m.p. = 64-65 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 (d, *J* = 1.6 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.02, (s, 1H), 3.95 (s, 3H) 3.89 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.9, 150.0, 146.2, 124.2, 122.3, 114.1, 111.7, 56.1, 52.0; MS (EI) for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub><sub>4</sub> [M]<sup>+</sup>: 182.

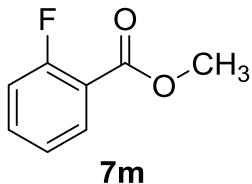


**Methyl 4-(dimethylamino)benzoate:**<sup>[9]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 85 mg; 95% yield in 6 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **5** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 94% yield in 24 h; white solid; m.p. = 101-102 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.91 (d, *J* = 8.8 Hz, 2H), 6.65 (d,

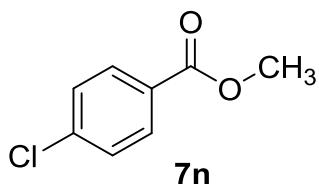
*J* = 8.8 Hz, 2H), 3.85, (s, 3H), 3.04 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 167.5, 153.3, 131.3, 117.0, 110.7, 51.5, 40.0; MS (EI) for  $\text{C}_{10}\text{H}_{13}\text{NO}_2$  [M] $^+$ : 179.



**Methyl 4-fluorobenzoate:**<sup>[5]</sup> Aldehyde substrate (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 90% yield in 24 h; Yield was determined by  $^1\text{H}$  NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.03-8.08 (m, 2H), 7.11 (t, *J* = 8.8 Hz, 2H), 3.91 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 166.1, 165.8 (d,  $^1J_{\text{C}-\text{F}} = 252.2$  Hz), 132.1 (d,  $^3J_{\text{C}-\text{F}} = 9.4$  Hz), 126.4 (d,  $^4J_{\text{C}-\text{F}} = 3.0$  Hz), 115.5 (d,  $^2J_{\text{C}-\text{F}} = 21.9$  Hz), 52.2; MS (EI) for  $\text{C}_8\text{H}_7\text{FO}_2$  [M] $^+$ : 154.

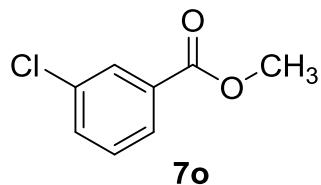


**Methyl 2-fluorobenzoate:**<sup>[9]</sup> Aldehyde substrate (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 90% yield in 24 h; determined by  $^1\text{H}$  NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.94 (td, *J* = 2.0, 7.6 Hz, 1H), 7.49-7.54 (m, 1H), 7.18-7.22 (m, 1H), 7.10-7.16 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 164.9 (d,  $^4J_{\text{C}-\text{F}} = 3.6$  Hz), 161.9 (d,  $^1J_{\text{C}-\text{F}} = 258.1$  Hz), 134.4 (d,  $^3J_{\text{C}-\text{F}} = 9.0$  Hz), 132.1, 123.9 (d,  $^4J_{\text{C}-\text{F}} = 4.0$  Hz), 118.6 (d,  $^3J_{\text{C}-\text{F}} = 9.9$  Hz), 116.9 (d,  $^2J_{\text{C}-\text{F}} = 22.2$  Hz), 52.3; MS (EI) for  $\text{C}_8\text{H}_7\text{FO}_2$  [M] $^+$ : 154.

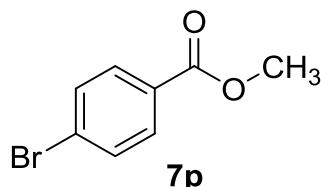


**Methyl 4-chlorobenzoate:**<sup>[4]</sup> Starting from aldehyde: substrate (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 94% yield in 24 h; Starting from alcohol:  $\text{RCH}_2\text{OH}$  (0.5 mmol), MeOH (2

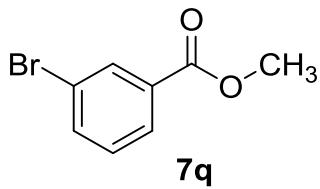
mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 97% yield in 18 h; both yields were determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.96 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 165.2, 138.3, 129.9, 127.7, 127.6, 51.2; MS (EI) for C<sub>8</sub>H<sub>7</sub>ClO<sub>2</sub> [M]<sup>+</sup>: 170.



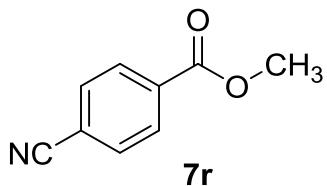
**Methyl 3-chlorobenzoate:**<sup>[8]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 92% yield in 24 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 85% yield in 24 h; both yields were determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.99-8.00 (m, 1H), 7.89-7.92 (m, 1H), 7.50-7.52 (m, 1H), 7.34-7.38 (m, 1H), 3.91 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 165.8, 134.5, 132.9, 131.9, 129.7, 127.7, 52.4; MS (EI) for C<sub>8</sub>H<sub>7</sub>ClO<sub>2</sub> [M]<sup>+</sup>: 170.



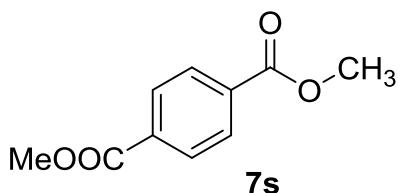
**Methyl 4-bromobenzoate:**<sup>[5]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOH (0.024 mmol) and NaOAc (0.5 mmol); 95 mg; 89% yield in 24 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.01 mmol), NaHCO<sub>3</sub> (0.5 mmol); 85% yield in 24 h; white solid; m.p. = 77-78 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.90 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.4, 131.7, 131.1, 129.1, 128.0, 52.3; MS (EI) for C<sub>8</sub>H<sub>7</sub>BrO<sub>2</sub> [M]<sup>+</sup>: 213.



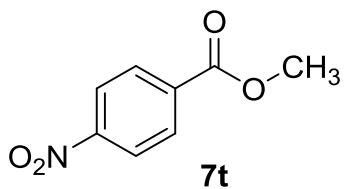
**Methyl 3-bromobenzoate:**<sup>[4]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOH (0.024 mmol) and NaOAc (0.5 mmol); 93 mg; 87% yield in 24 h; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.17 (t, *J* = 1.6 Hz, 1H), 7.95-7.97 (m, 1H), 7.66-7.69 (m, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 3.92 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 165.7, 135.8, 132.6, 132.0, 129.9, 128.1, 122.4, 52.4; MS (EI) for C<sub>8</sub>H<sub>7</sub>BrO<sub>2</sub> [M]<sup>+</sup>: 213.



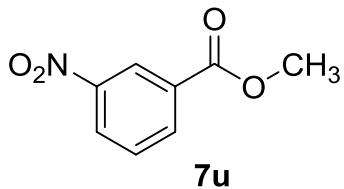
**Methyl 4-cyanobenzoate:**<sup>[6]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 72 mg; 90% yield in 24 h; white solid; m.p. = 61-62 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.14 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 165.4, 134.0, 132.2, 130.1, 117.9, 116.4, 52.7; MS (EI) for C<sub>9</sub>H<sub>7</sub>N<sub>1</sub>O<sub>2</sub> [M]<sup>+</sup>: 161.



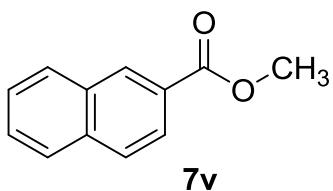
**Dimethyl terephthalate:**<sup>[7]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 89 mg; 92% yield in 12 h; 85% yield in 24 h starting from terephthalaldehyde; white solid; m.p. = 134-135 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.1 (s, 4H), 3.95 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.3, 133.9, 129.6, 52.4; MS (EI) for C<sub>10</sub>H<sub>10</sub>O<sub>4</sub> [M]<sup>+</sup>: 194.



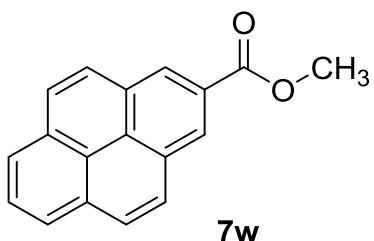
**Methyl 4-nitrobenzoate:**<sup>[4]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOAc (0.5 mmol); 83 mg; 92% yield in 6 h; white solid; m.p. = 87-88 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.29 (d, *J* = 9.2 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 3.98 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 165.2, 150.6, 135.5, 130.7, 123.5, 52.8; HRMS (ESI) for C<sub>8</sub>H<sub>7</sub>NO<sub>4</sub> [M+Na]<sup>+</sup>: calc.: 204.0273; found: 204.0269.



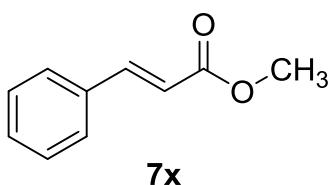
**Methyl 3-nitrobenzoate:**<sup>[7]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOAc (0.5 mmol); 83 mg; 91% yield in 6 h; white solid; m.p. = 72-73 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.86-8.87 (m, 1H), 8.40-8.43 (m, 1H), 8.35-8.38 (m, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 3.99 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 165.0, 148.3, 135.3, 131.9, 129.6, 127.4, 124.6, 52.8; MS (EI) for C<sub>8</sub>H<sub>7</sub>NO<sub>4</sub> [M]<sup>+</sup>: 181.



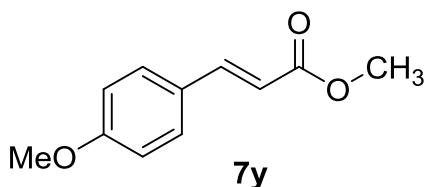
**Methyl 2-naphthoate:**<sup>[6]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 74 mg; 80% yield in 12 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 89% yield in 48 h; white solid; m.p. = 72-73 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.62 (s, 1H), 8.07 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.53-7.62 (m, 2H), 3.99 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 167.3, 135.5, 132.5, 131.1, 129.4, 128.23, 128.15, 127.8, 127.4, 126.6, 125.2, 52.2; MS (EI) for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub> [M]<sup>+</sup>: 186.



**Methyl 3a<sup>1</sup>, 5a<sup>1</sup>-dihydropyrene-1-carboxylate:** Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 126 mg; 96% yield in 12 h; white solid; m.p. = 79-80 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 9.27 (d, *J* = 9.6 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.23-8.28 (m, 3H), 8.16-8.19 (m, 2H), 8.04-8.09 (m, 2H), 4.11 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 168.5, 134.3, 131.1, 131.0, 130.4, 129.6, 129.5, 128.4, 127.2, 126.32, 126.30, 126.2, 124.92, 124.86, 124.2, 124.1, 123.5, 52.3; HRMS (ESI) for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub> [M+Na]<sup>+</sup>: calc.: 283.0735; found: 283.0755.

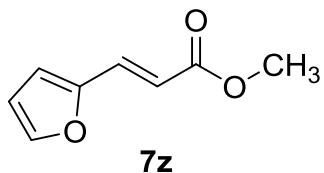


**Methyl cinnamate:**<sup>[4]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 71 mg; 88% yield in 24 h; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.70 (d, *J* = 16 Hz, 1H), 7.51-7.54 (m, 2H), 7.37-7.39 (m, 3H), 6.45 (d, *J* = 16 Hz, 1H), 3.81 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7; MS (EI) for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub> [M]<sup>+</sup>: 162.

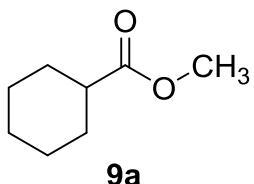


**(E)-methyl 3-(4-methoxyphenyl)acrylate:**<sup>[19]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOH (0.024 mmol) and NaOAc (0.5 mmol); 77 mg; 80% yield in 24 h; white solid; m.p. = 81-82 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.65 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* =

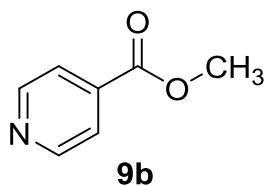
8.8 Hz, 2H), 6.31 (d,  $J$  = 16.0 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 167.8, 161.4, 144.5, 129.7, 127.1, 115.3, 114.3, 55.4, 51.6; MS (EI) for  $\text{C}_{11}\text{H}_{12}\text{O}_3$  [M] $^+$ : 192.



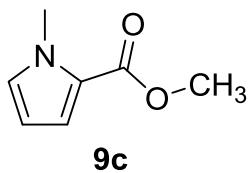
**(E)-methyl 3-(funan-2-yl)acrylate:**<sup>[18]</sup> Aldehyde substrate (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.01 mmol), tpy (0.024 mmol), NaOH (0.024 mmol) and NaOAc (0.5 mmol); 85% yield in 24 h; yield was determined by NMR analysis; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.46 (d,  $J$  = 1.2 Hz, 1H), 7.42 (d,  $J$  = 15.6 Hz, 1H), 6.59 (d,  $J$  = 3.6 Hz, 1H), 6.45 (dd,  $J$  = 3.6, 1.6 Hz, 1H), 6.31 (d,  $J$  = 15.6 Hz, 1H), 3.77 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 167.4, 150.8, 144.7, 131.1, 115.4, 114.8, 112.2, 51.6; MS (EI) for  $\text{C}_8\text{H}_8\text{O}_3$  [M] $^+$ : 152.



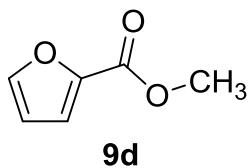
**Methyl cyclohexanecarboxylate:**<sup>[22]</sup> 75% yield in 24 h determined by GC analysis; colorless oil; MS (EI) for  $\text{C}_8\text{H}_{14}\text{O}_2$  [M] $^+$ : Found: 142.



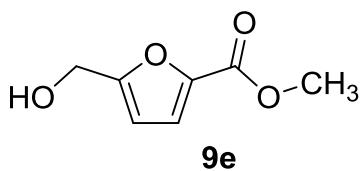
**Methyl isonicotinate:**<sup>[13]</sup> Aldehyde substrate (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 87% yield in 24 h; determined by  $^1\text{H}$  NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.69 (d,  $J$  = 4.4 Hz, 2H), 7.75 (d,  $J$  = 4.4 Hz, 2H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 165.3, 150.4, 137.1, 122.6, 52.5; MS (EI) for  $\text{C}_7\text{H}_7\text{NO}_2$  [M] $^+$ : 137.



**Methyl 1-methyl-1 N-pyrrole-2-carboxylate:**<sup>[14]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOH (0.024 mmol) and NaOAc (0.5 mmol); 75% yield in 48 h; yield was determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 6.94 (dd, *J* = 4.0, 2.4 Hz, 1H), 6.78 (t, *J* = 2.0 Hz, 1H), 6.11 (dd, *J* = 4.0, 2.4 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 161.7, 129.4, 122.3, 117.7, 107.8, 50.9, 36.7; MS (EI) for C<sub>7</sub>H<sub>9</sub>NO<sub>2</sub> [M]<sup>+</sup>: 139.

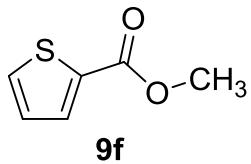


**Methyl funan-2-carboxylate:**<sup>[4]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 80% yield in 24 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 62% yield in 24 h; both yields were determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.57 (s, 1H), 7.18 (d, *J* = 3.2 Hz, 1H), 6.51 (dd, *J* = 3.2, 1.6 Hz, 1H), 3.90 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 159.1, 146.3, 144.6, 117.9, 111.8, 51.9; MS (EI) for C<sub>6</sub>H<sub>6</sub>O<sub>3</sub> [M]<sup>+</sup>: 126.

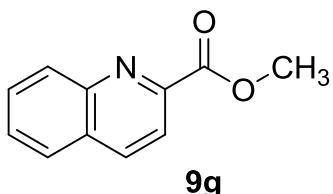


**Methyl 5-(hydroxymethyl)furan-2-carboxylate:**<sup>[17]</sup> Starting from aldehyde: substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 64 mg; 82% yield in 24 h; Starting from alcohol: RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.01 mmol), NaHCO<sub>3</sub> (0.25 mmol); 63% yield in 48 h; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.08 (d, *J* = 3.6 Hz,

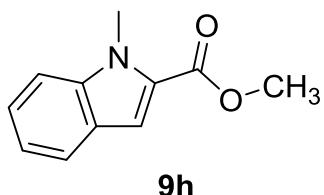
1H), 6.37 (d,  $J = 3.2$  Hz, 1H), 4.62 (s, 2H), 3.84 (s, 3H), 3.32 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 159.2, 158.6, 143.7, 118.9, 109.3, 57.3, 51.8; MS (EI) for  $\text{C}_7\text{H}_8\text{O}_4$  [M] $^+$ : 156.



**Methyl thiophene-2-carboxylate:**<sup>[5]</sup> Starting from aldehyde: substrate (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 82% yield in 24 h; Starting from alcohol:  $\text{RCH}_2\text{OH}$  (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol),  $\text{NaHCO}_3$  (0.25 mmol); 76% yield in 24 h; both yields were determined by  $^1\text{H}$  NMR analysis with 1,3,5-trimethoxybenzene as internal standard; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.79 (dd,  $J = 4.0, 0.8$  Hz, 1H), 7.54 (dd,  $J = 4.8, 0.8$  Hz, 1H), 7.08-7.10 (m, 1H), 3.88 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 162.5, 133.5, 133.4, 132.3, 127.7, 52.0; MS (EI) for  $\text{C}_6\text{H}_6\text{O}_2\text{S}$  [M] $^+$ : 142.

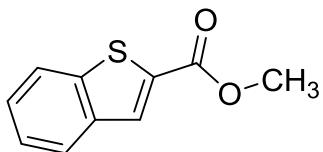


**Methyl quinoline-2-carboxylate:**<sup>[14]</sup> Aldehyde substrate (0.5 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 75 mg; 80% yield in 24 h; white solid; m.p. = 77-78 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.32 (dd,  $J = 8.4, 1.6$  Hz, 2H), 8.21 (d,  $J = 8.4$  Hz, 1H), 7.90 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.78-7.82 (m, 1H), 7.64-7.68 (m, 1H), 4.09 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 166.0, 147.9, 147.6, 137.3, 130.7, 130.3, 129.4, 128.7, 127.6, 121.0, 53.2; MS (EI) for  $\text{C}_{11}\text{H}_9\text{NO}_2$  [M] $^+$ : 187.



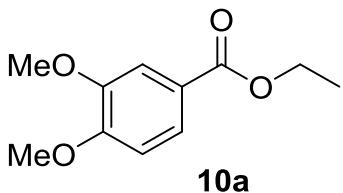
**Methyl 1-methyl-1N-indole-2-carboxylate:**<sup>[15]</sup> Aldehyde substrate (0.5 mmol),

[Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 91 mg; 96% yield in 24 h; white solid; m.p. = 90-91 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.68 (d, *J* = 8.0 Hz, 1H), 7.34-7.41 (m, 2H), 7.30 (s, 1H), 7.14-7.18 (m, 1H), 4.09 (s, 3H), 3.92 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 162.7, 139.7, 127.7, 125.9, 125.0, 122.6, 120.6, 110.2, 51.6, 31.6; MS (EI) for C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub> [M]<sup>+</sup>: 189.



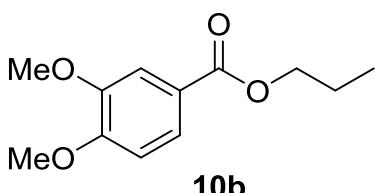
**9i**

**Methyl benzo[*b*]thiophene-2-carboxylate:**<sup>[16]</sup> Aldehyde substrate (0.5 mmol), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.005 mmol), tpy (0.012 mmol), NaOH (0.012 mmol) and NaOAc (0.5 mmol); 91 mg; 95% yield in 24 h; white solid; m.p. = 65-66 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.07 (s, 1H), 7.86-7.89 (m, 2H), 7.44-7.48 (m, 1H), 7.39-7.43 (m, 1H), 3.95 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 163.3, 142.2, 138.7, 133.3, 130.6, 127.0, 125.6, 124.9, 122.8, 52.5; MS (EI) for C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>S [M]<sup>+</sup>: 192.



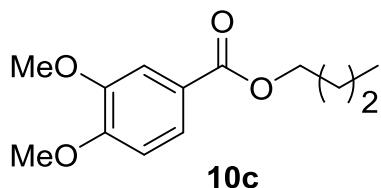
**10a**

**Ethyl 3,4-dimethoxybenzoate:**<sup>[20]</sup> : Aldehyde (0.5 mmol), alcohol (1 mL), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 79 mg; 75% yield in 48 h; white solid; m.p. = 35-36 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.69 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.55 (d, *J* = 1.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 6H), 1.39 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.4, 152.9, 148.6, 123.5, 123.1, 112.0, 110.2, 60.8, 56.0, 14.4; MS (EI) for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub> [M]<sup>+</sup>: 210.

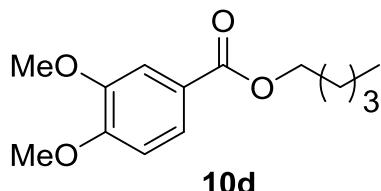


**10b**

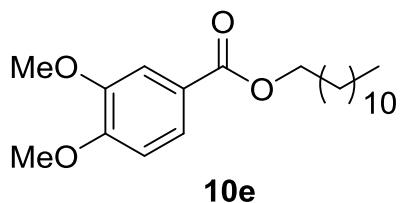
**Prpoyl 3,4-dimethoxybenzoate:**<sup>[20]</sup> Aldehyde (0.5 mmol), alcohol (1 mL), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 87 mg; 78% yield in 48 h; white solid; m.p. = 56-57 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 6H), 1.73-1.82 (m, 2H), 1.01 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.3, 152.8, 148.5, 123.4, 123.0, 111.9, 110.1, 66.3, 55.9, 22.1, 10.4; MS (EI) for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub> [M]<sup>+</sup>: 224.



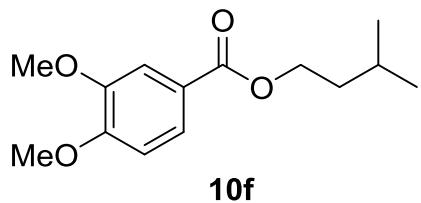
**Butyl 3,4-dimethoxybenzoate:**<sup>[20]</sup> Aldehyde (0.5 mmol), alcohol (1 mL), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 83 mg; 70% yield in 48 h; white solid; m.p. = 153-154 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.30 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 1.71-1.78 (m, 2H), 1.43-1.52 (m, 2H), 0.98 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.5, 152.9, 148.6, 123.5, 123.1, 112.0, 110.2, 64.7, 56.0, 30.9, 19.3, 13.8; MS (EI) for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub> [M]<sup>+</sup>: 238.



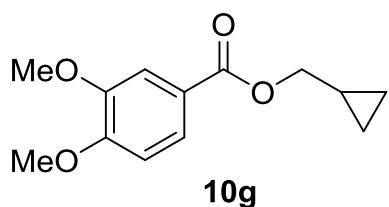
**Penyl 3,4-dimethoxybenzoate:**<sup>[20]</sup> Aldehyde (0.5 mmol), alcohol (1 mL), [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 102 mg; 82% yield in 24 h; white solid; m.p. = 39-40 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 4.29 (t, *J* = 6.4 Hz, 2H), 3.93 (s, 6 H), 1.73-1.80 (m, 2H), 1.36-1.44 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.4, 152.9, 148.6, 123.4, 123.1, 112.0, 110.2, 64.9, 55.9, 28.4, 28.2, 22.3, 13.9; MS (EI) for C<sub>14</sub>H<sub>20</sub>O<sub>4</sub> [M]<sup>+</sup>: 252.



**Dodecyl 3,4-dimethoxybenzoate:**<sup>[21]</sup> Aldehyde (0.5 mmol), alcohol (1 mL), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 150 mg; 86% yield in 24 h; white solid; m.p. = 45-46 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.29 (t, *J* = 6.4 Hz, 2H), 3.93 (s, 6H), 1.72-1.79 (m, 2H), 1.39-1.45 (m, 2H), 1.20-1.39 (m, 16H), 0.88 (t, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.5, 152.9, 148.6, 123.5, 123.1, 112.0, 110.2, 65.0, 56.0, 31.9, 29.65, 29.63, 29.58, 29.54, 29.34, 29.30, 28.8, 26.1, 22.7, 14.1; HRMS (ESI) for C<sub>21</sub>H<sub>34</sub>O<sub>4</sub> [M+Na]<sup>+</sup>: calc.: 373.2355; found: 373.2334.

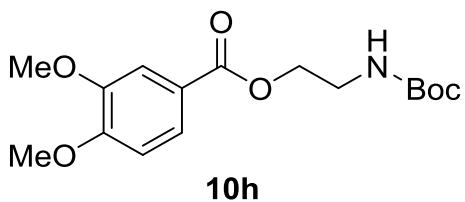


**Isopentyl 3,4-dimethoxybenzoate:**<sup>[20]</sup> Aldehyde (0.5 mmol), alcohol (1 mL), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 98 mg; 78% yield in 24 h; white solid; m.p. = 105-106 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.67 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.33 (t, *J* = 6.8 Hz, 2H), 3.933 (s, 3H), 3.930 (s, 3H), 1.74-1.84 (m, 1H), 1.66 (q, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.4 Hz, 6H), 0.97 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.4, 152.9, 148.6, 123.1, 112.0, 110.2, 63.5, 56.0, 37.5, 25.3, 22.5; MS (EI) for C<sub>14</sub>H<sub>20</sub>O<sub>4</sub> [M]<sup>+</sup>: 252.

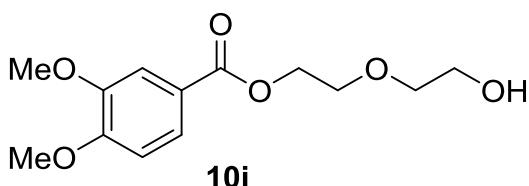


**Cyclopropylmethyl 3,4-dimethoxybenzoate:** Aldehyde (0.5 mmol), alcohol (1 mL),

$[\text{Cp}^*\text{RhCl}_2]_2$  (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 39 mg; 33% yield in 48 h; white solid; m.p. = 44-45 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) δ (ppm): 7.71 (dd,  $J$  = 8.4, 2.0 Hz, 1H), 7.56 (d,  $J$  = 1.6 Hz, 1H), 6.89 (d,  $J$  = 8.4 Hz, 1H), 4.13 (d,  $J$  = 7.2 Hz, 2H), 3.94 (s, 6H), 1.23-1.28 (m, 1H), 0.58-0.63 (m, 2H), 0.34-0.38 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) δ (ppm): 166.5, 152.9, 148.6, 123.5, 123.1, 112.0, 110.2, 69.5, 56.0, 10.0, 3.3; HRMS (ESI) for  $\text{C}_{13}\text{H}_{16}\text{O}_4$  [ $\text{M}+\text{Na}]^+$ : calc.: 259.0946; found: 259.0937.

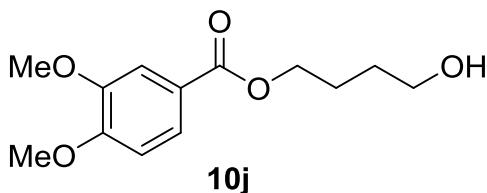


**2-(Tert-butoxycarbonyl)aminoethyl 3,4-dimethoxybenzoate:** Aldehyde (0.5 mmol), alcohol (1 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 81 mg; 50% yield in 48 h; white solid; m.p. = 90-91 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) δ (ppm): 7.68 (dd,  $J$  = 8.4, 2.0 Hz, 1H), 7.54 (d,  $J$  = 2.0 Hz, 1H), 6.88 (d,  $J$  = 8.4 Hz, 1H), 4.84 (brs, 1H), 4.36 (t,  $J$  = 5.2 Hz, 2H), 3.939 (s, 3H), 3.935 (s, 3H), 3.52-3.53 (m, 2H), 1.44 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) δ (ppm): 166.3, 155.8, 153.2, 148.7, 123.7, 122.4, 112.1, 110.2, 79.6, 64.1, 56.0, 39.9, 28.3; HRMS (ESI) for  $\text{C}_{16}\text{H}_{22}\text{NO}_6$  [ $\text{M}+\text{Na}]^+$ : calc.: 348.1423; found: 348.1415.

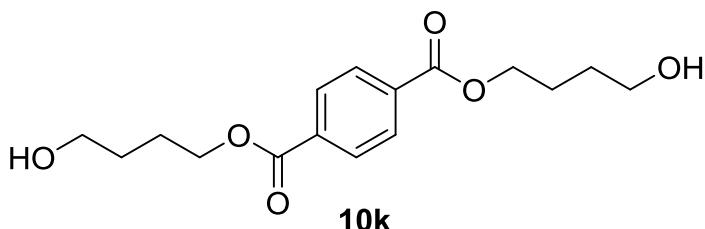


**4-Hydroxybutyl 3,4-dimethoxybenzoate:** Aldehyde (0.5 mmol), alcohol (1 mL),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 94 mg; 74% yield in 48 h; white solid; m.p. = 41-42 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) δ (ppm): 7.69 (dd,  $J$  = 8.4, 1.6 Hz, 1H), 7.54 (d,  $J$  = 1.6 Hz, 1H), 6.88 (d,  $J$  = 8.4 Hz, 1H), 4.47 (t,  $J$  = 4.4 Hz, 2H), 3.93 (s, 3H), 3.927 (s, 3H), 3.83 (t,  $J$  = 4.4 Hz, 2H), 3.74 (s, 2H), 3.65 (t,  $J$  = 4.4 Hz, 2H), 2.19 (brs, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) δ (ppm): 166.4, 153.1, 148.6, 123.7, 122.5, 112.0, 110.2, 72.4, 69.3, 63.9, 61.8,

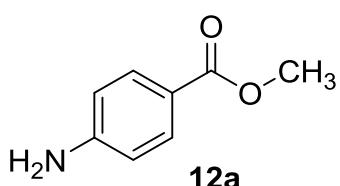
56.0; MS (EI) for  $C_{13}H_{18}O_5 [M]^+$ : 254.



**2-(2-Hydroxyethoxy)ethyl 3,4-dimethoxybenzoate:** Aldehyde (0.5 mmol), alcohol (1 mL),  $[Cp^*RhCl_2]_2$  (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 101 mg; 75% yield in 48 h; white solid; m.p. = 43-44 °C;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  (ppm): 7.68 (dd,  $J$  = 8.4, 2.0 Hz, 1H), 7.54 (d,  $J$  = 2.0 Hz, 1H), 6.88 (d,  $J$  = 8.4 Hz, 1H), 4.34 (t,  $J$  = 6.4 Hz, 2H), 3.935 (s, 3H), 3.931 (s, 3H), 3.73 (t,  $J$  = 6.4 Hz, 2H), 1.83-1.90 (m, 2H), 1.69-1.76 (m, 2H), 1.44 (brs, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  (ppm): 166.4, 152.9, 148.6, 123.5, 122.8, 111.9, 110.2, 64.6, 62.4, 56.0, 29.2, 25.3; MS (EI) for  $C_{13}H_{18}O_6 [M]^+$ : 270.

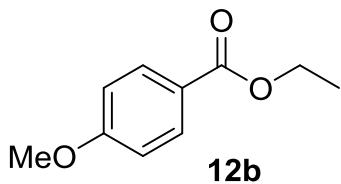


**4-Hydroxybutyl 4-(5-hydroxypentanoyl)benzoate:** Aldehyde (0.5 mmol), alcohol (1 mL),  $[Cp^*RhCl_2]_2$  (0.01 mmol), tpy (0.024 mmol), NaOAc (0.5 mmol), NaOH (0.025 mmol); 106 mg; 72% yield in 48 h; white solid; m.p. = 67-68 °C;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  (ppm): 8.066 (s, 2H), 8.064 (s, 2H), 4.37 (t,  $J$  = 6.4 Hz, 4H), 3.71 (t,  $J$  = 6.4 Hz, 4H), 1.97 (brs, 2H), 1.83-1.90 (m, 4H), 1.67-1.75 (m, 4H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  (ppm): 165.9, 134.1, 129.5, 65.3, 62.3, 29.1, 25.2; HRMS (ESI) for  $C_{16}H_{22}O_5 [M+Na]^+$ : calc.: 333.1314; found: 333.1316.

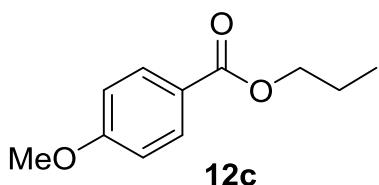


**Methyl 4-aminobenzoate:**<sup>[12]</sup> RCH<sub>2</sub>OH (0.5 mmol), MeOH (2 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol); 56 mg; 74% yield in 24 h; white solid; m.p. = 103-104 °C;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  (ppm): 7.84 (d,  $J$  = 8.4 Hz, 2H), 6.63 (d,  $J$  = 8.8 Hz, 2H),

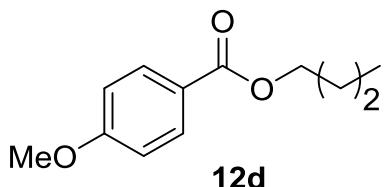
4.06 (brs, 2H), 3.85 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 167.1, 150.7, 131.6, 119.7, 113.8, 51.6; MS (EI) for  $\text{C}_8\text{H}_9\text{NO}_2$   $[\text{M}]^+$ : 151.



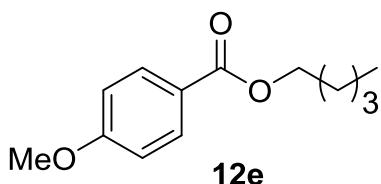
**Ethyl 4-methoxybenzoate:**<sup>[23]</sup>  $\text{RCH}_2\text{OH}$  (0.5 mmol),  $\text{R}'\text{OH}$  (1 mL), **11** (0.005 mmol),  $\text{NaHCO}_3$  (0.25 mmol),  $\text{NaOH}$  (0.05 mmol); 65 mg; 72% yield in 48 h; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.98 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 4.34 (q,  $J = 7.2$  Hz, 2H), 3.83 (s, 3H), 1.36 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 166.4, 163.2, 131.5, 122.9, 113.5, 60.6, 55.4, 14.4; MS (EI) for  $\text{C}_{10}\text{H}_{12}\text{O}_3$   $[\text{M}]^+$ : 180.



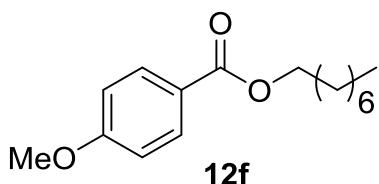
**Propyl 4-methoxybenzoate:**<sup>[24]</sup>  $\text{RCH}_2\text{OH}$  (0.5 mmol),  $\text{R}'\text{OH}$  (1 mL), **11** (0.005 mmol),  $\text{NaHCO}_3$  (0.25 mmol),  $\text{NaOH}$  (0.05 mmol); 80 mg; 83% yield in 48 h; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.01 (d,  $J = 8.8$  Hz, 2H), 6.92 (d,  $J = 8.8$  Hz, 2H), 4.25 (t,  $J = 6.8$  Hz, 2H), 3.85 (s, 3H), 1.73-1.82 (m, 2H), 1.02 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 166.5, 163.3, 131.5, 123.0, 113.6, 66.2, 55.4, 22.2, 10.5; MS (EI) for  $\text{C}_{11}\text{H}_{14}\text{O}_3$   $[\text{M}]^+$ : 194.



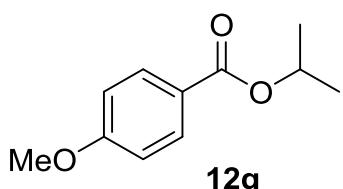
**Butyl 4-methoxybenzoate:**<sup>[26]</sup>  $\text{RCH}_2\text{OH}$  (0.5 mmol),  $\text{R}'\text{OH}$  (1 mL), **11** (0.005 mmol),  $\text{NaHCO}_3$  (0.25 mmol),  $\text{NaOH}$  (0.05 mmol); 81 mg; 78% yield in 48 h; colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.00 (d,  $J = 9.2$  Hz, 2H), 6.92 (d,  $J = 9.2$  Hz, 2H), 4.29 (t,  $J = 6.4$  Hz, 2H), 3.86 (s, 3H), 1.70-1.77 (m, 2H), 1.43-1.52 (m, 2H), 0.97 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 166.5, 163.2, 131.5, 123.0, 113.6, 64.5, 55.4, 30.9, 19.3, 13.8; MS (EI) for  $\text{C}_{12}\text{H}_{16}\text{O}_3$   $[\text{M}]^+$ : 208.



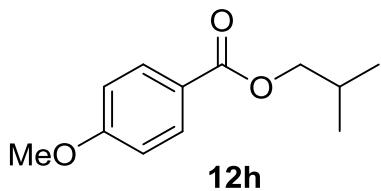
**Pentyl 4-methoxybenzoate:**<sup>[25]</sup> RCH<sub>2</sub>OH (0.5 mmol), R'OH (1 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol), NaOH (0.05 mmol); 82 mg; 74% yield in 48 h; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.01 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 9.2 Hz, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 1.72-1.79 (m, 2H), 1.37-1.43 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.5, 163.2, 131.5, 123.0, 113.6, 64.8, 55.4, 28.5, 28.2, 22.4, 14.0, MS (EI) for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub> [M]<sup>+</sup>: 222.



**Octyl 4-methoxybenzoate:**<sup>[28]</sup> RCH<sub>2</sub>OH (0.5 mmol), R'OH (1 mL), **11** (0.01 mmol), NaHCO<sub>3</sub> (0.25 mmol), NaOH (0.05 mmol); 88 mg; 67% yield in 48 h; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.99 (d, *J* = 9.2 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 1.71-1.78 (m, 2H), 1.28-1.43 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.5, 163.2, 131.5, 123.0, 113.6, 64.9, 55.4, 31.8, 29.3, 29.2, 28.8, 26.1, 22.7, 14.1; HRMS (ESI) for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub> [M+Na]<sup>+</sup>: calc.: 287.1623; found: 287.1615.



**Isopropyl 4-methoxybenzoate:**<sup>[25]</sup> RCH<sub>2</sub>OH (0.5 mmol), R'OH (1 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol), NaOH (0.05 mmol); 52 mg; 54% yield in 48 h; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.00 (d, *J* = 9.2 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.18-5.27 (m, 1H), 3.86 (s, 3H), 1.36 (d, *J* = 6.4 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.5, 163.8, 132.1, 124.0, 114.1, 68.5, 56.0, 22.6; MS (EI) for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> [M]<sup>+</sup>: 194.



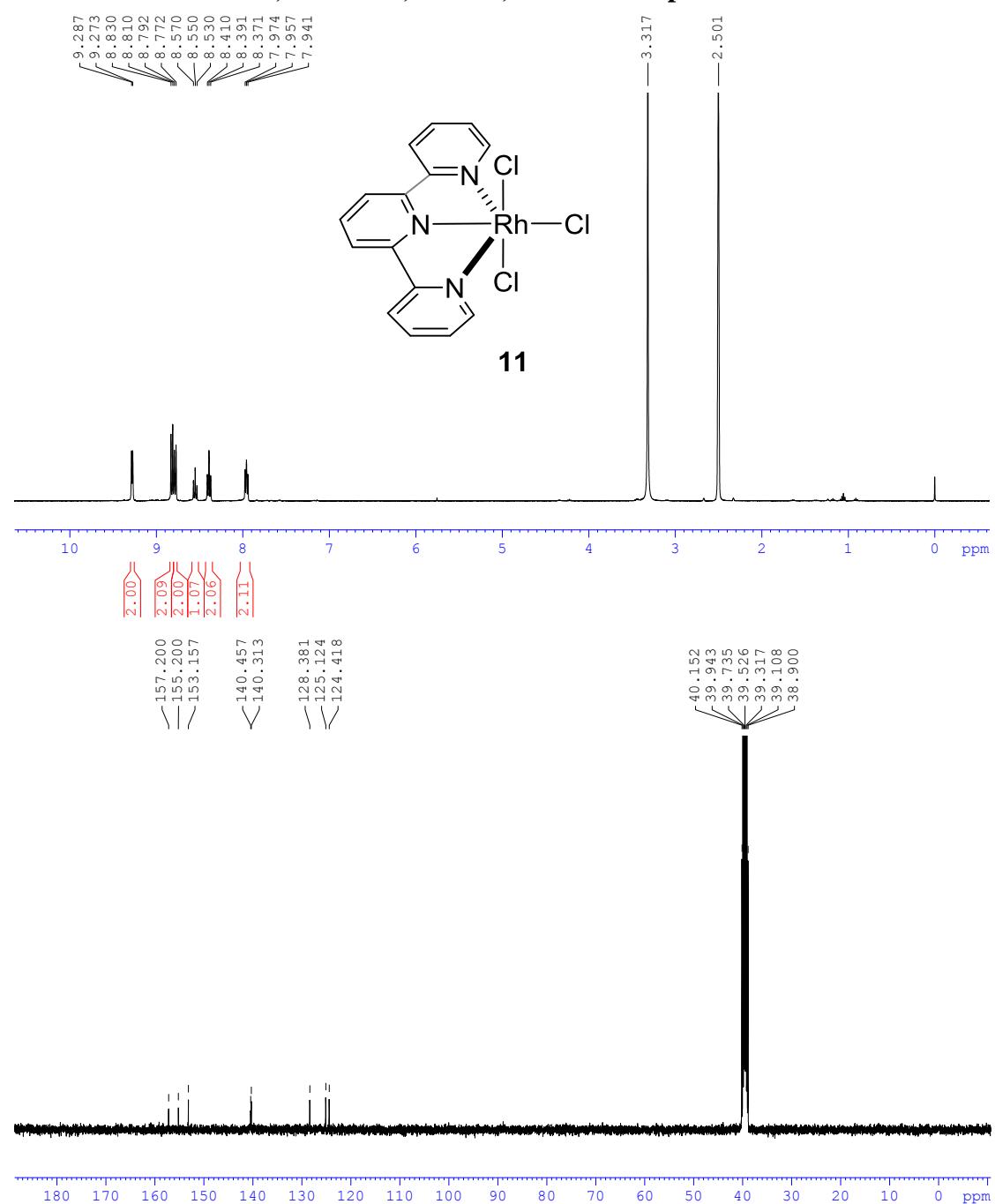
**Isobutyl 4-methoxybenzoate:**<sup>[27]</sup> RCH<sub>2</sub>OH (0.5 mmol), R'OH (1 mL), **11** (0.005 mmol), NaHCO<sub>3</sub> (0.25 mmol), NaOH (0.05 mmol); 72 mg; 69% yield in 48 h; colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.00 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 2H), 4.06 (d, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 2.01-2.11 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 166.4, 163.3, 131.5, 123.0, 113.6, 70.7, 55.4, 27.9, 19.2, MS (EI) for C<sub>12</sub>H<sub>16</sub>O<sub>3</sub> [M]<sup>+</sup>: 208.

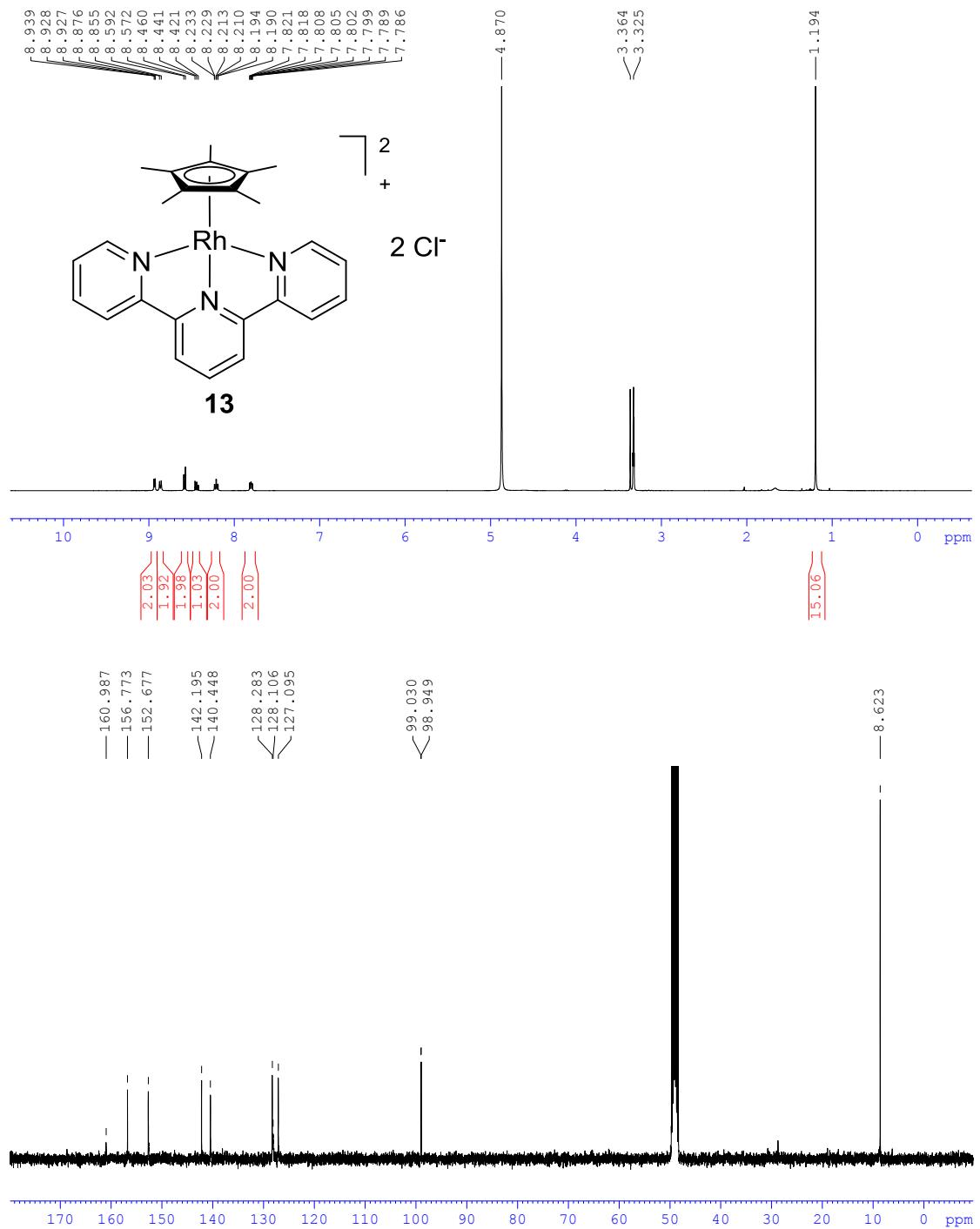
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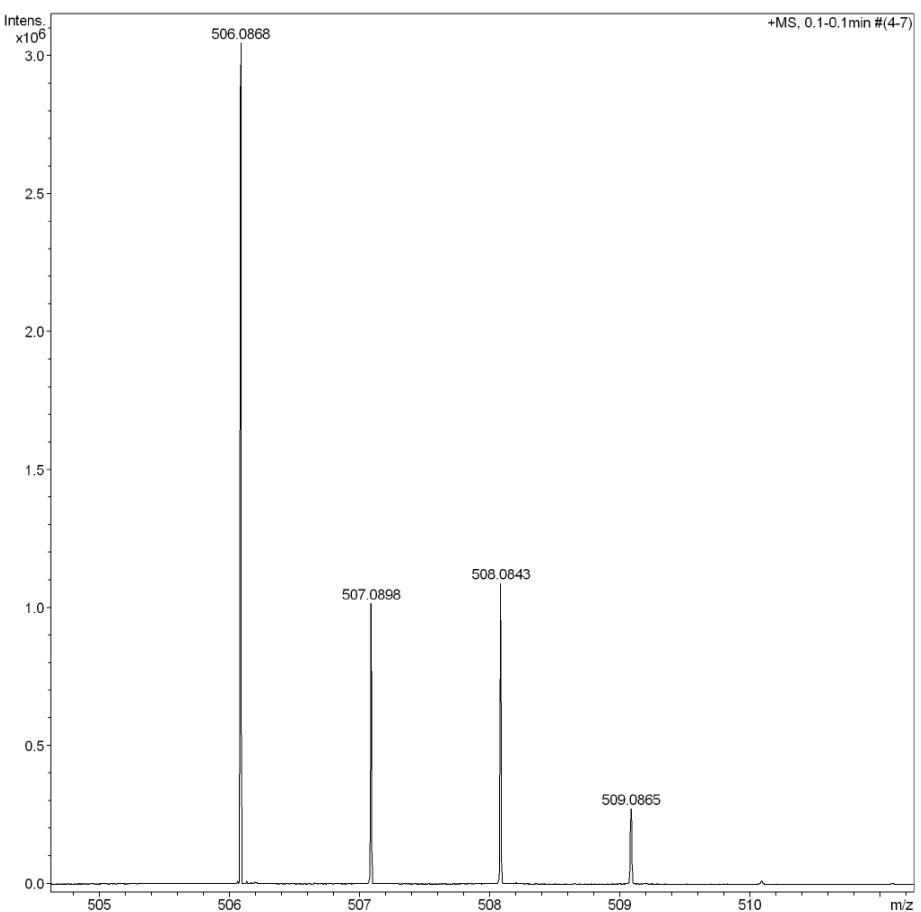
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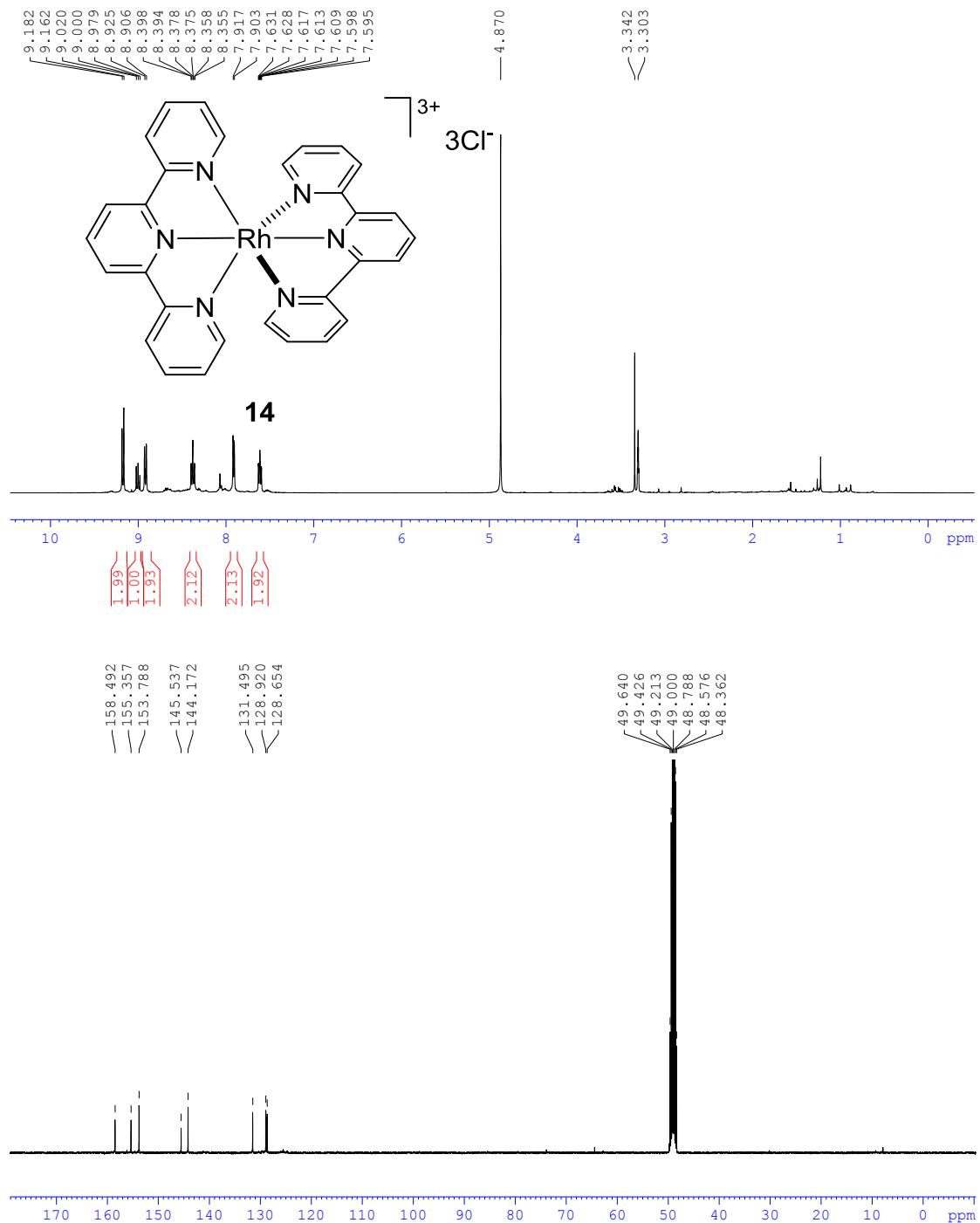
**13. Traces of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, HRMS, IR and GC spectra**

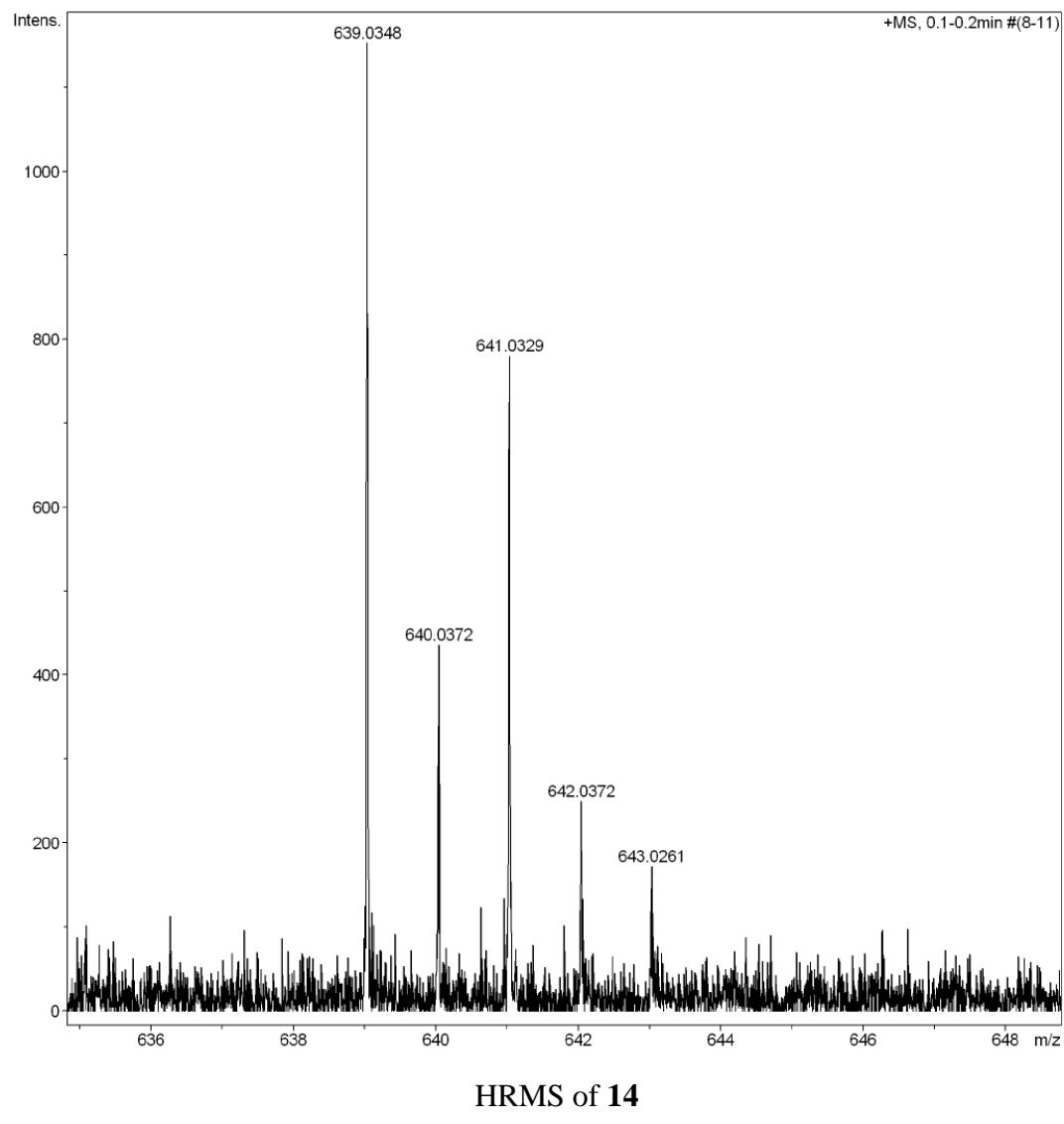


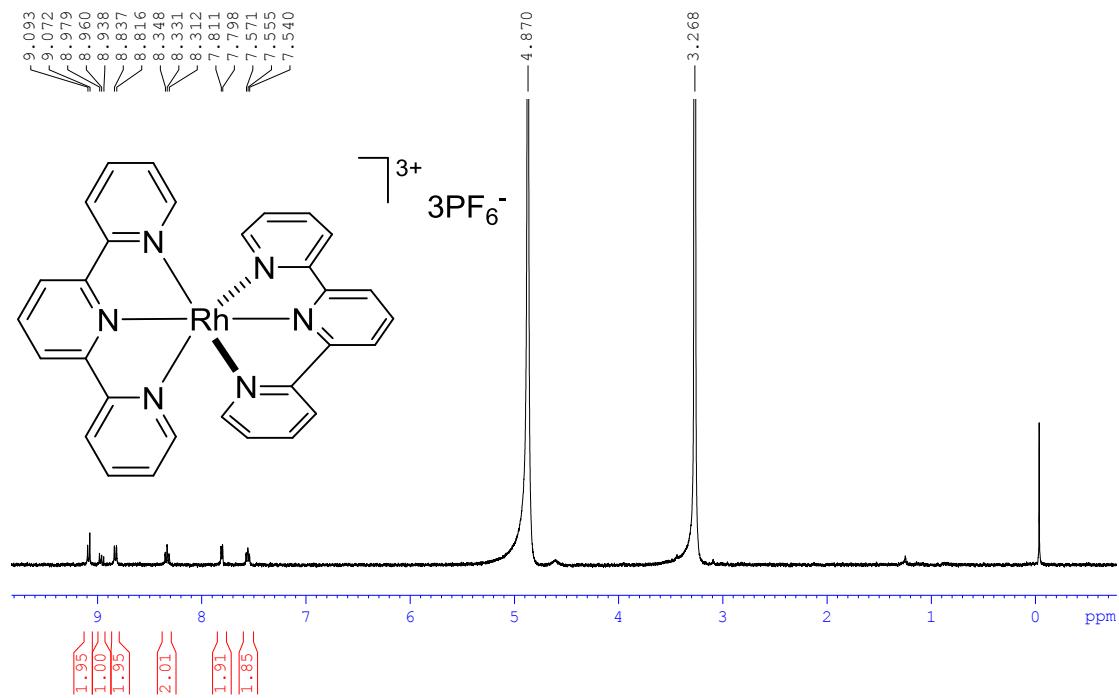


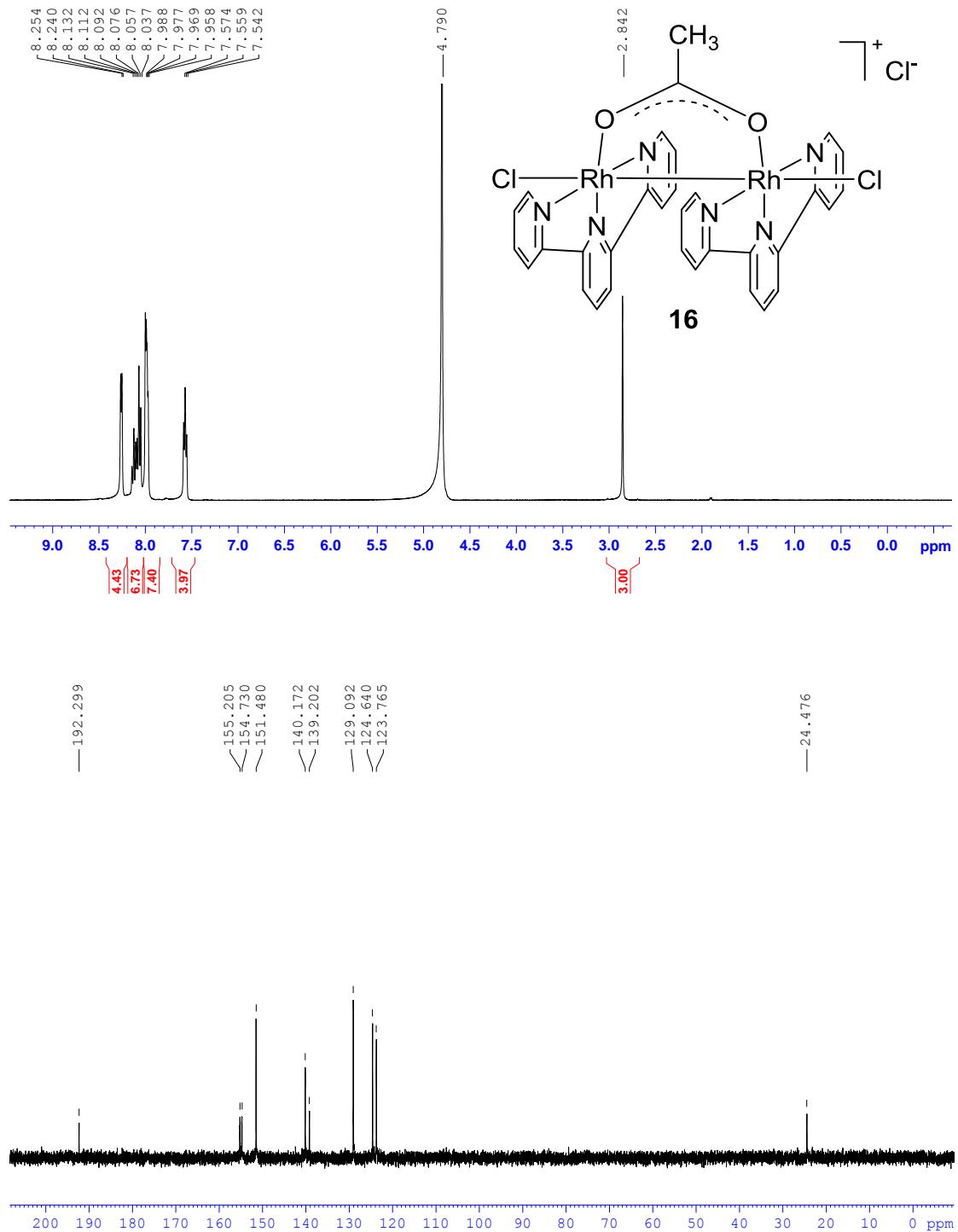


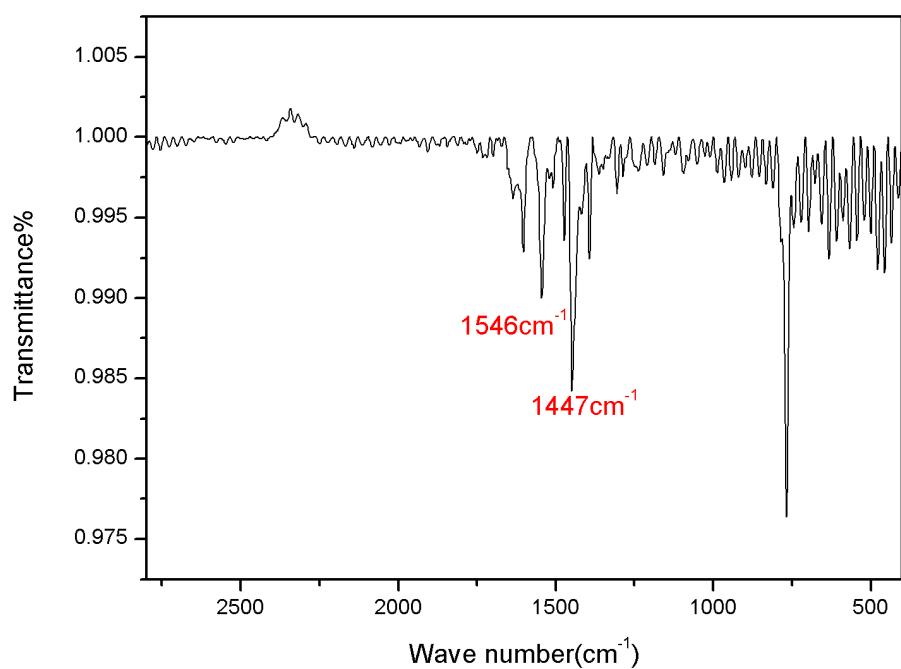
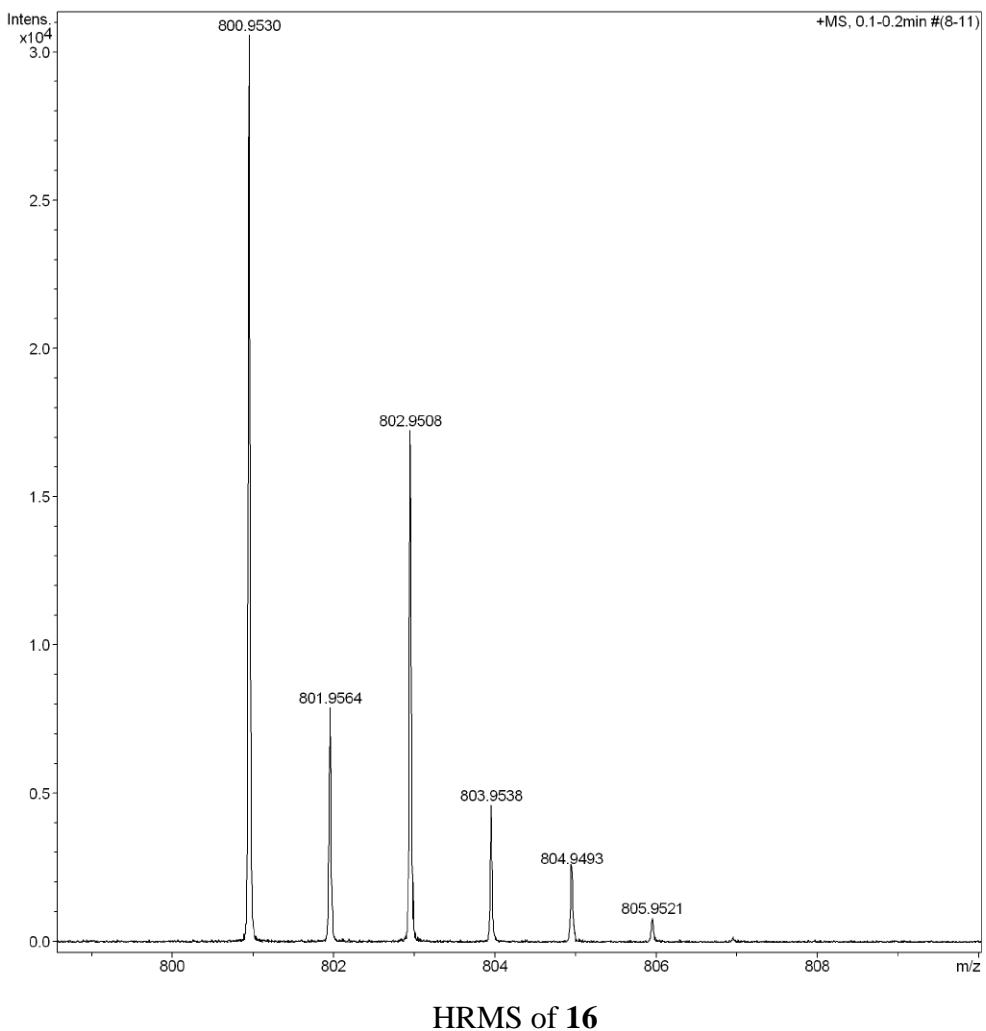
HRMS of **13**



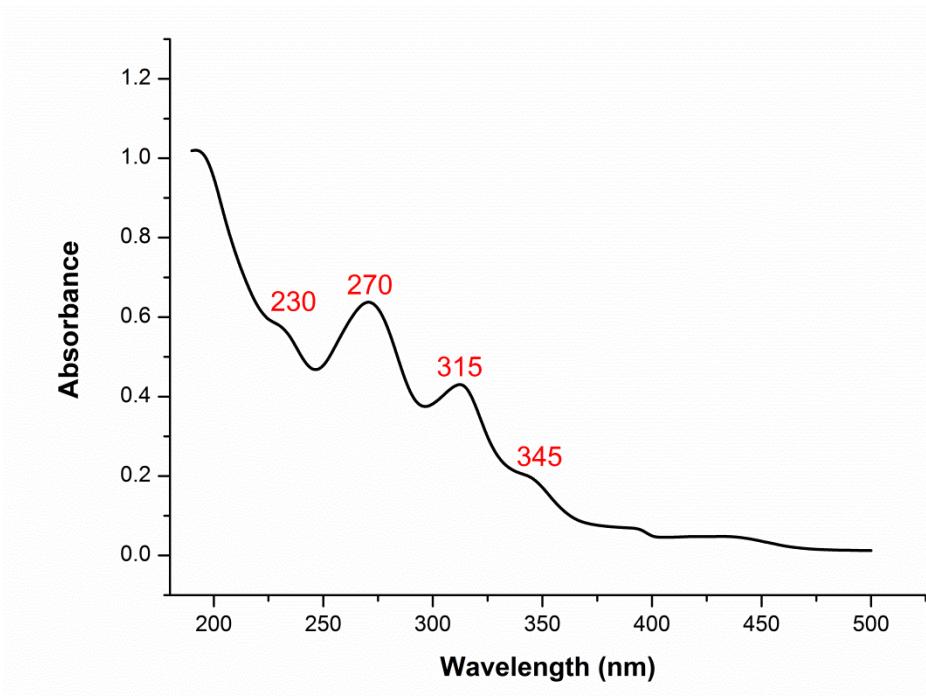




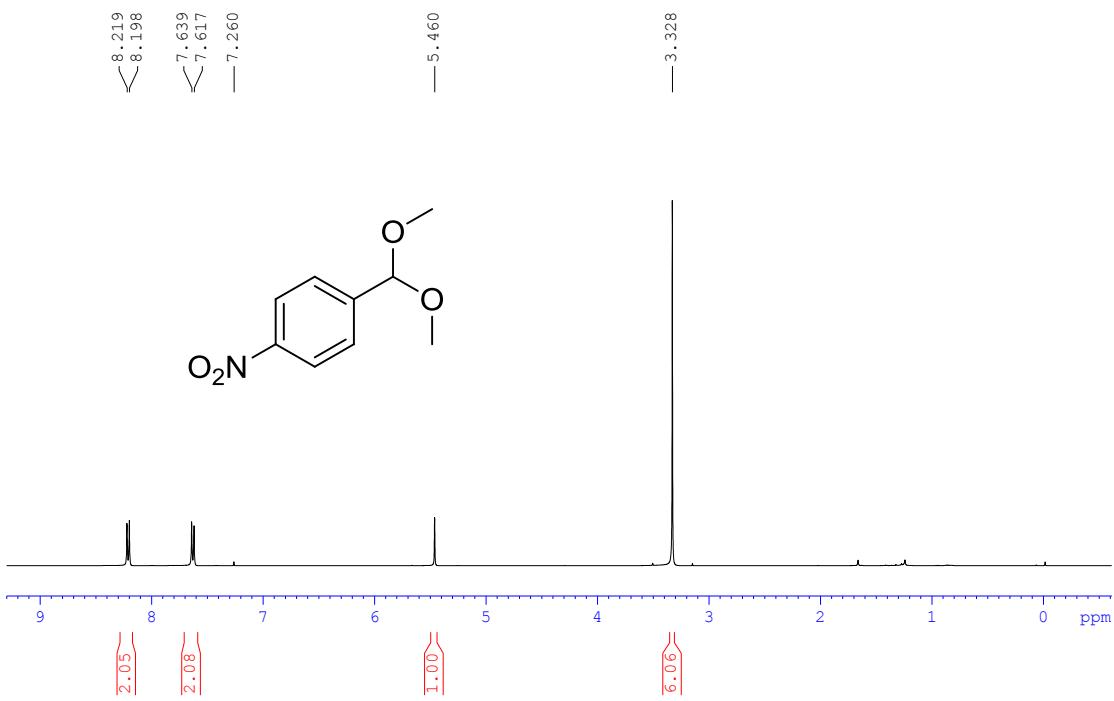
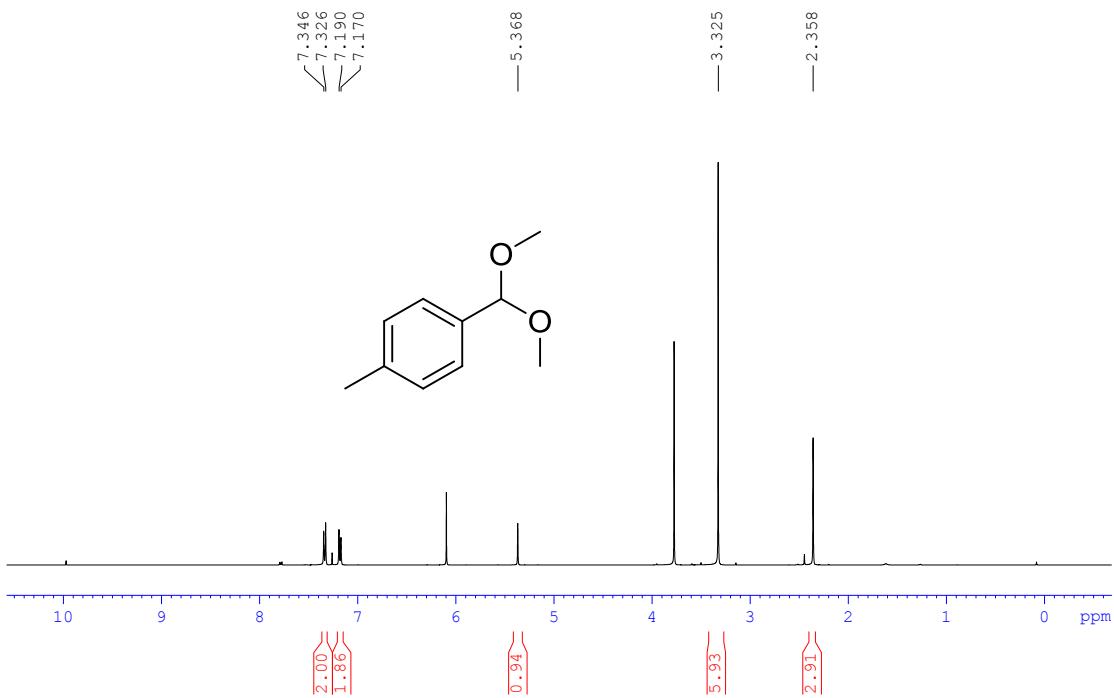


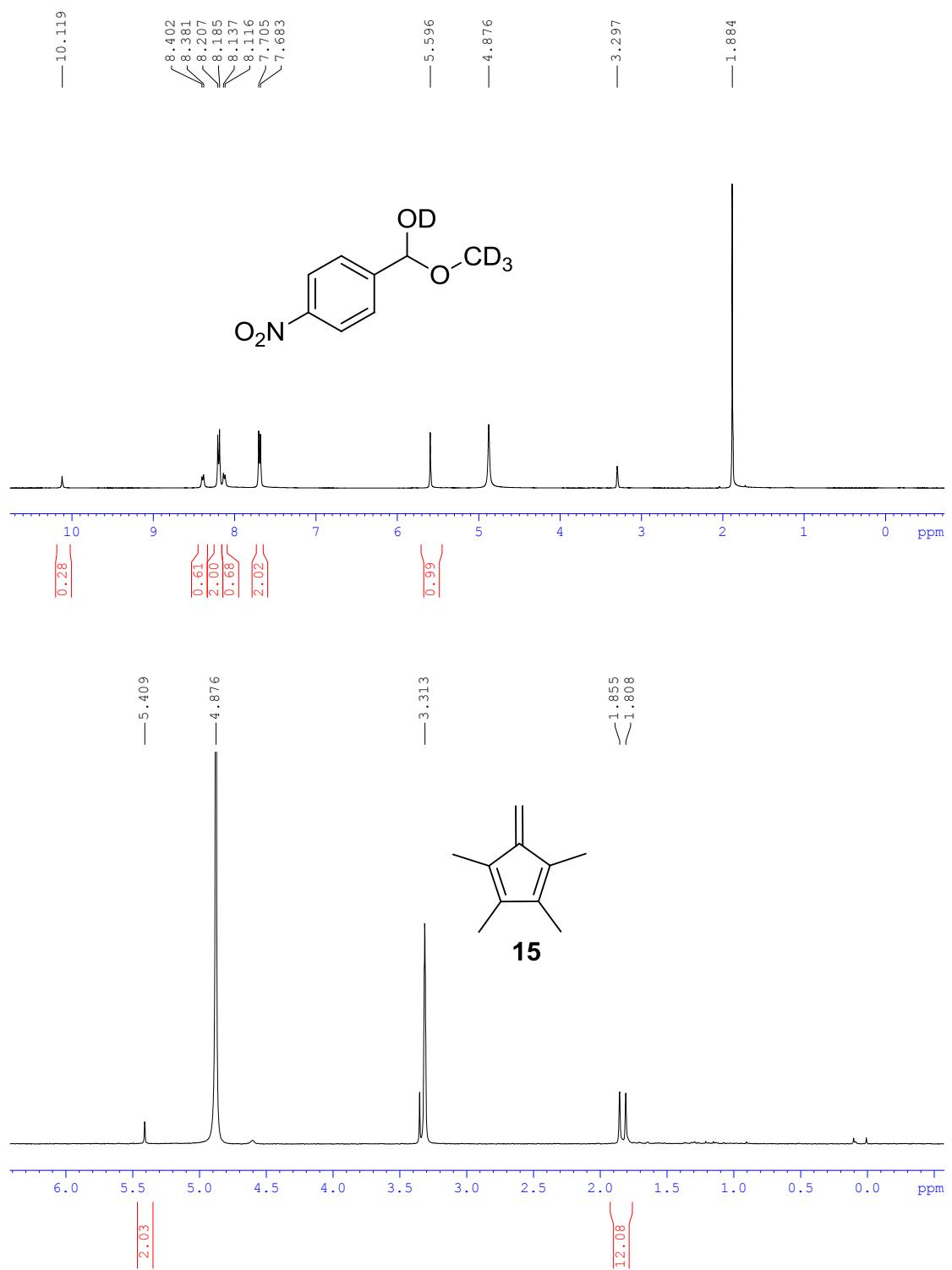


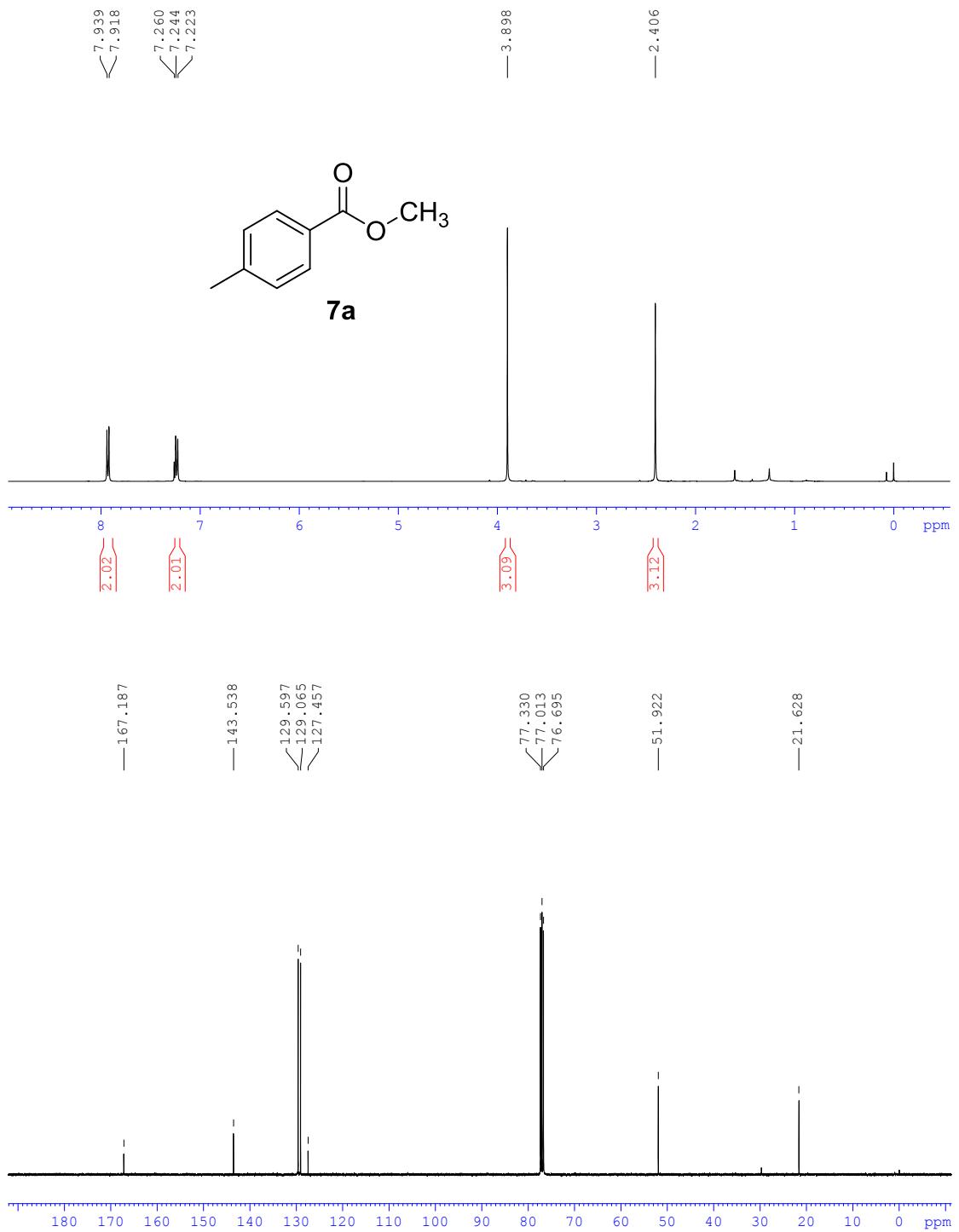
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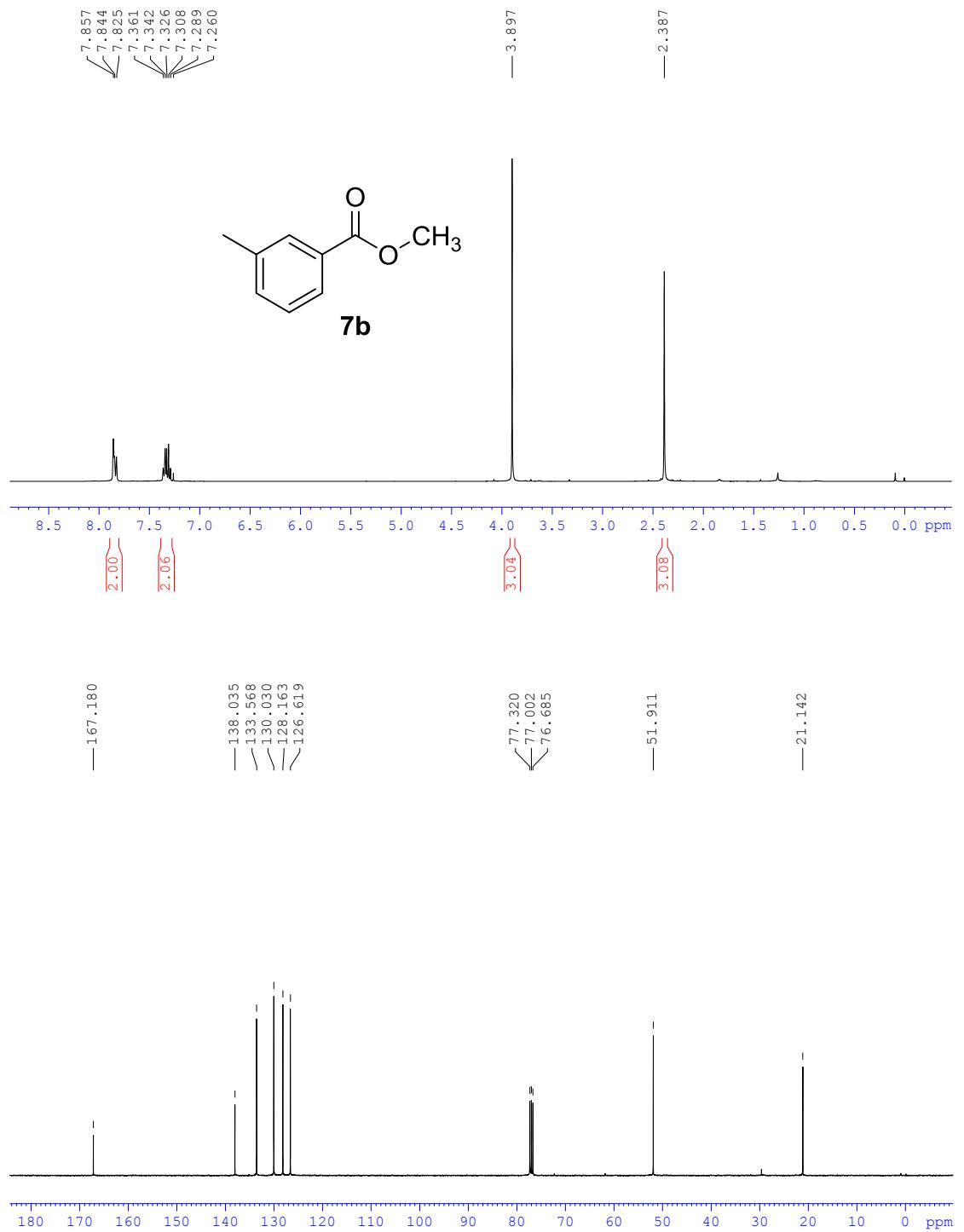


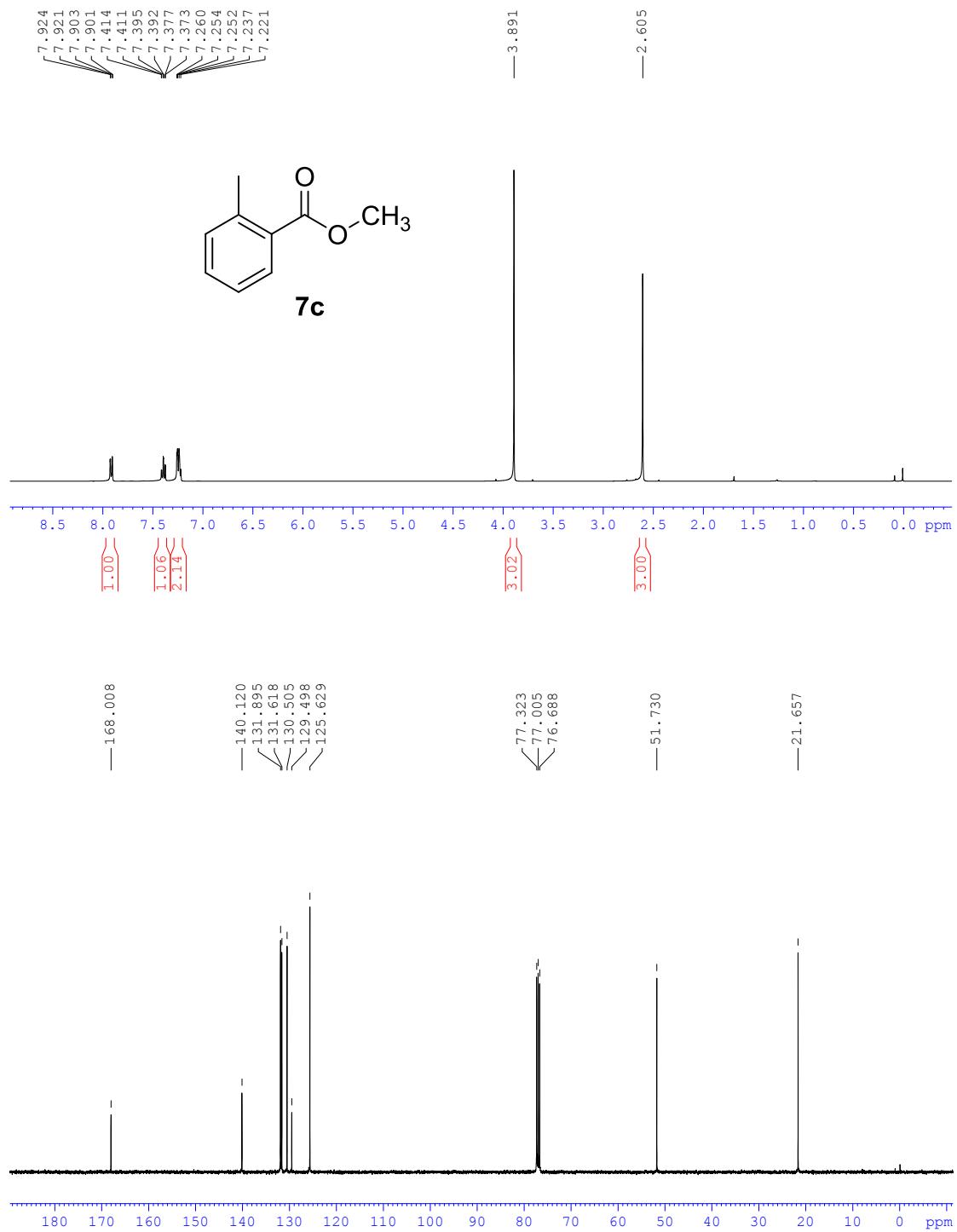
UV of **16**



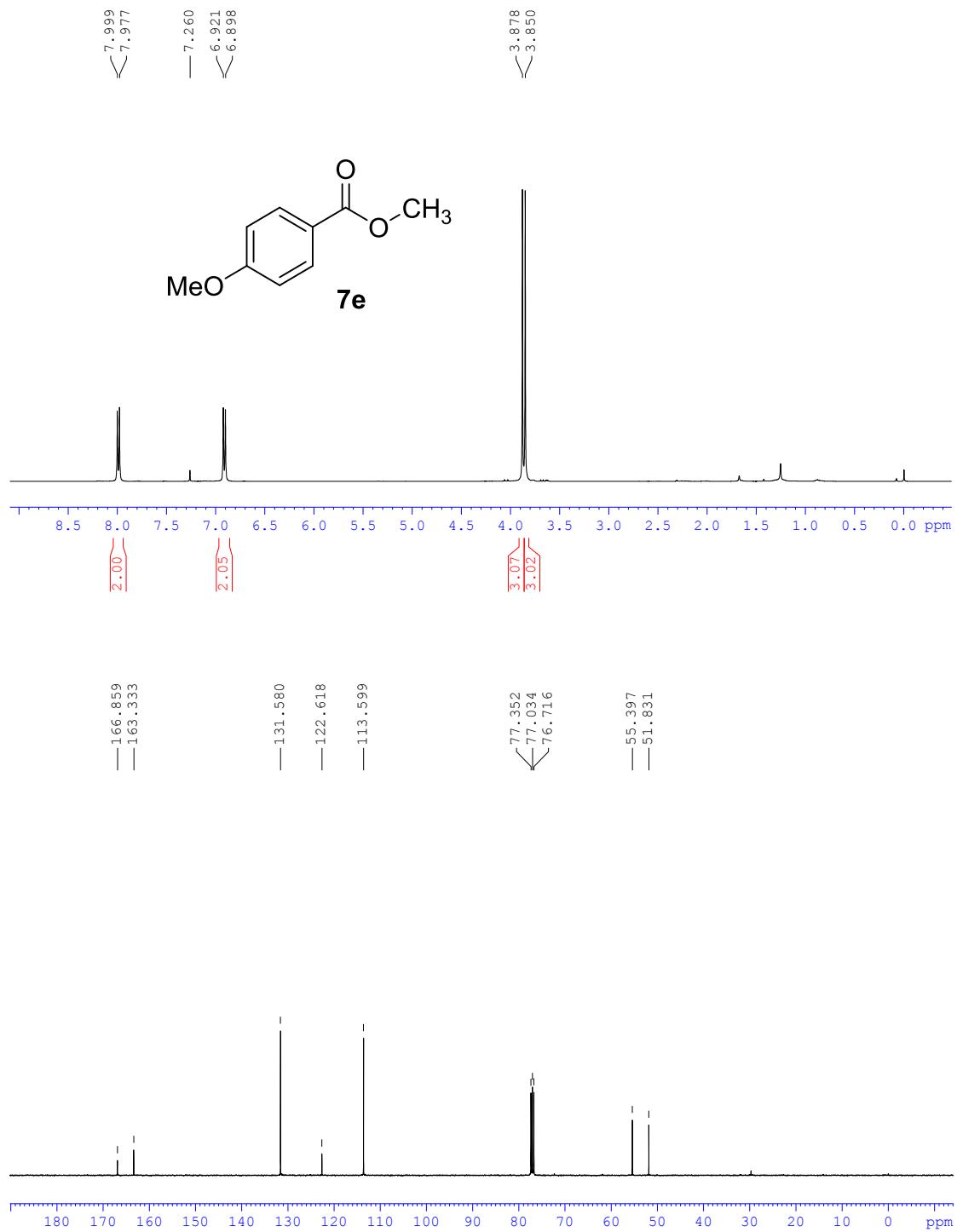


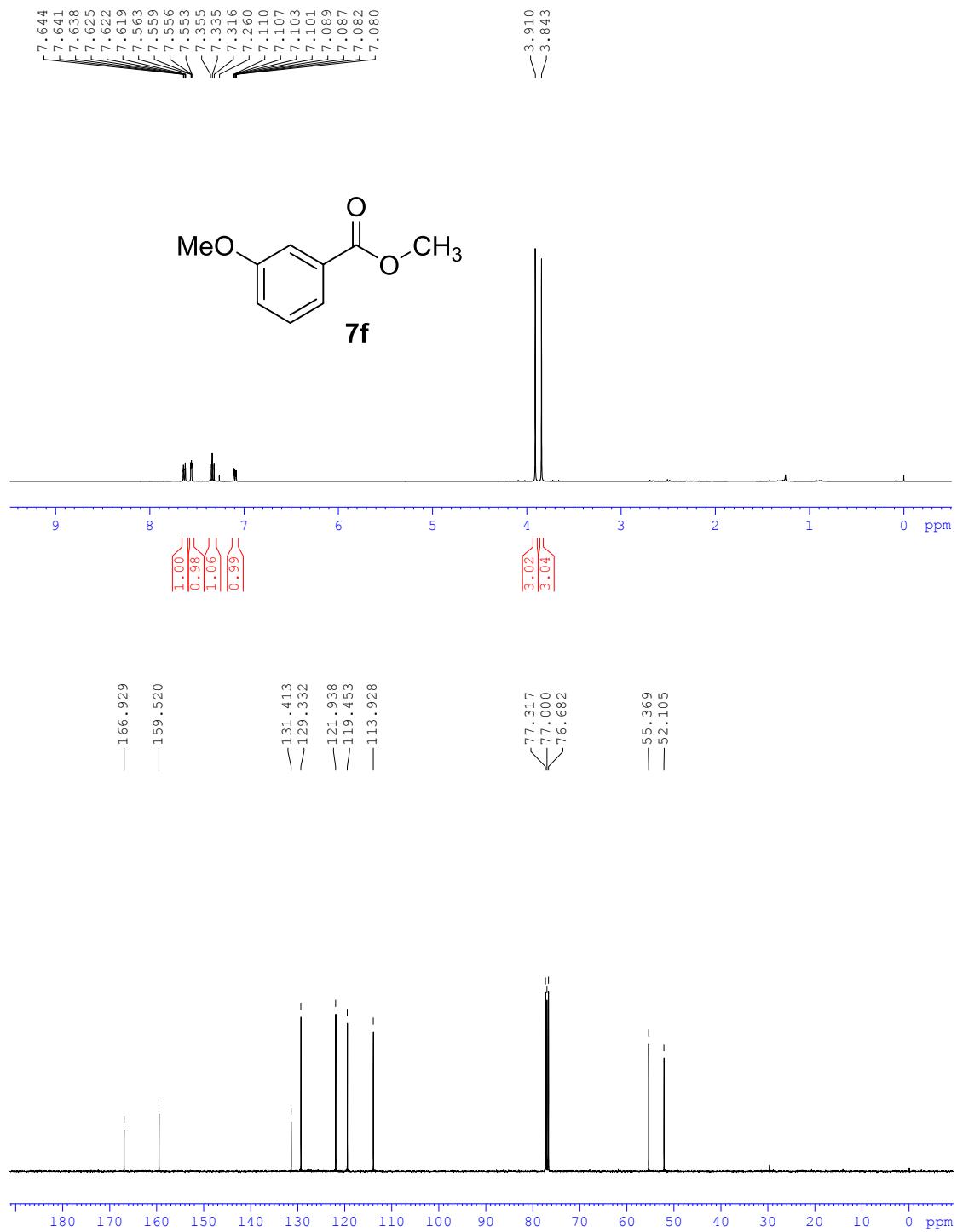


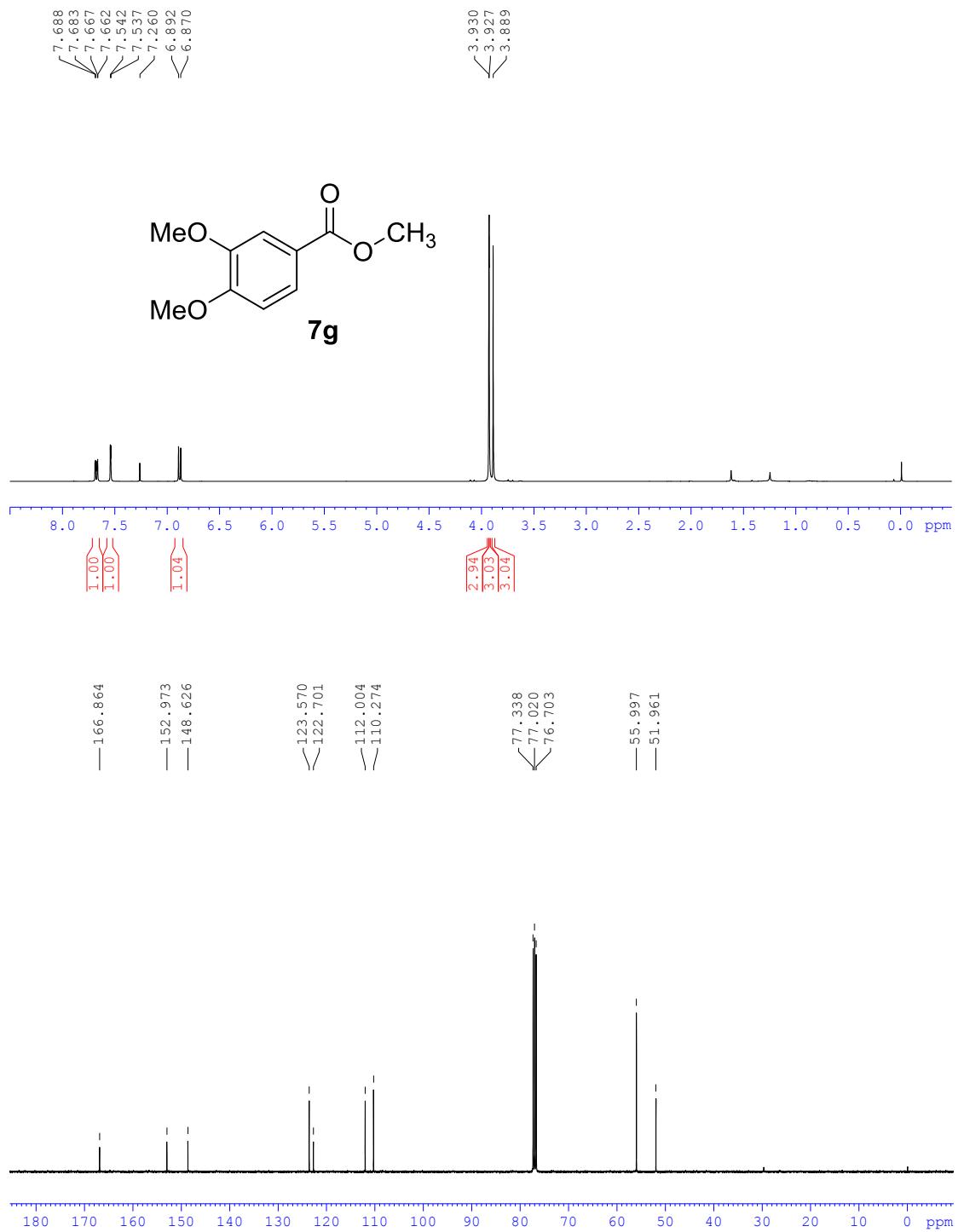


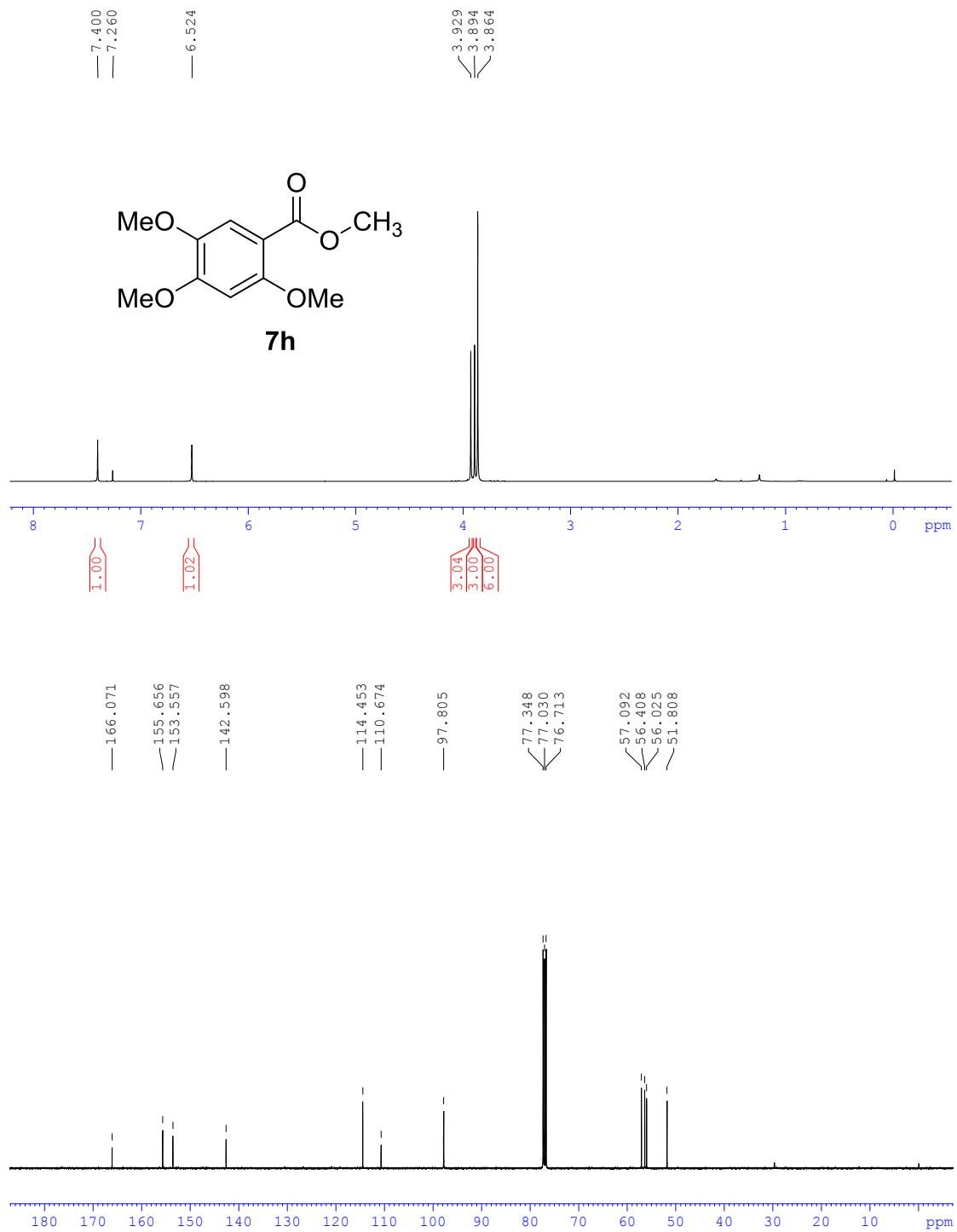




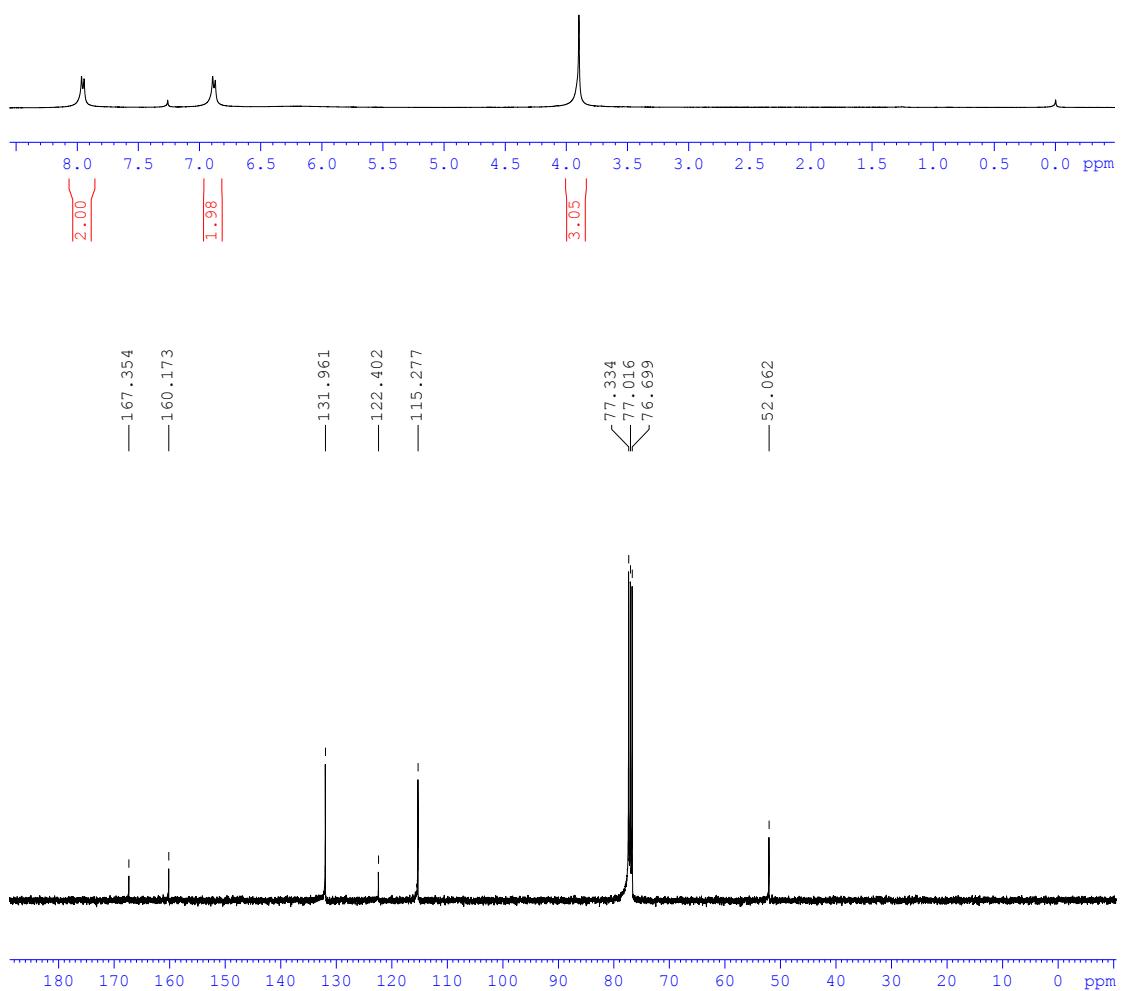
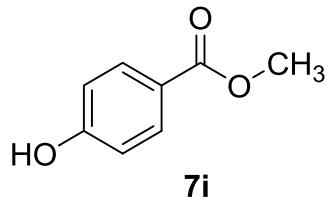


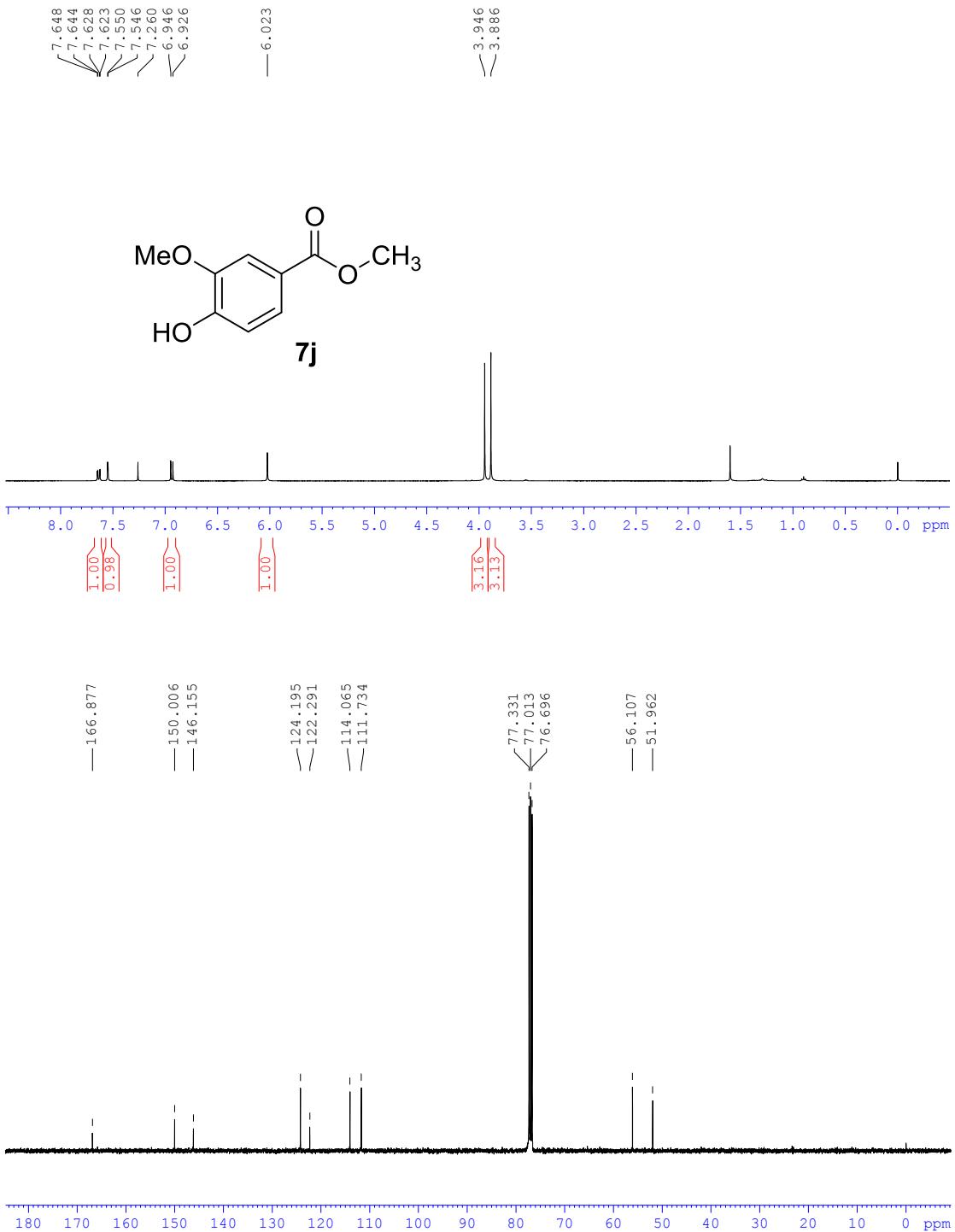
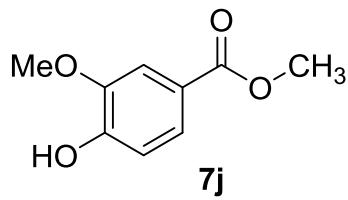


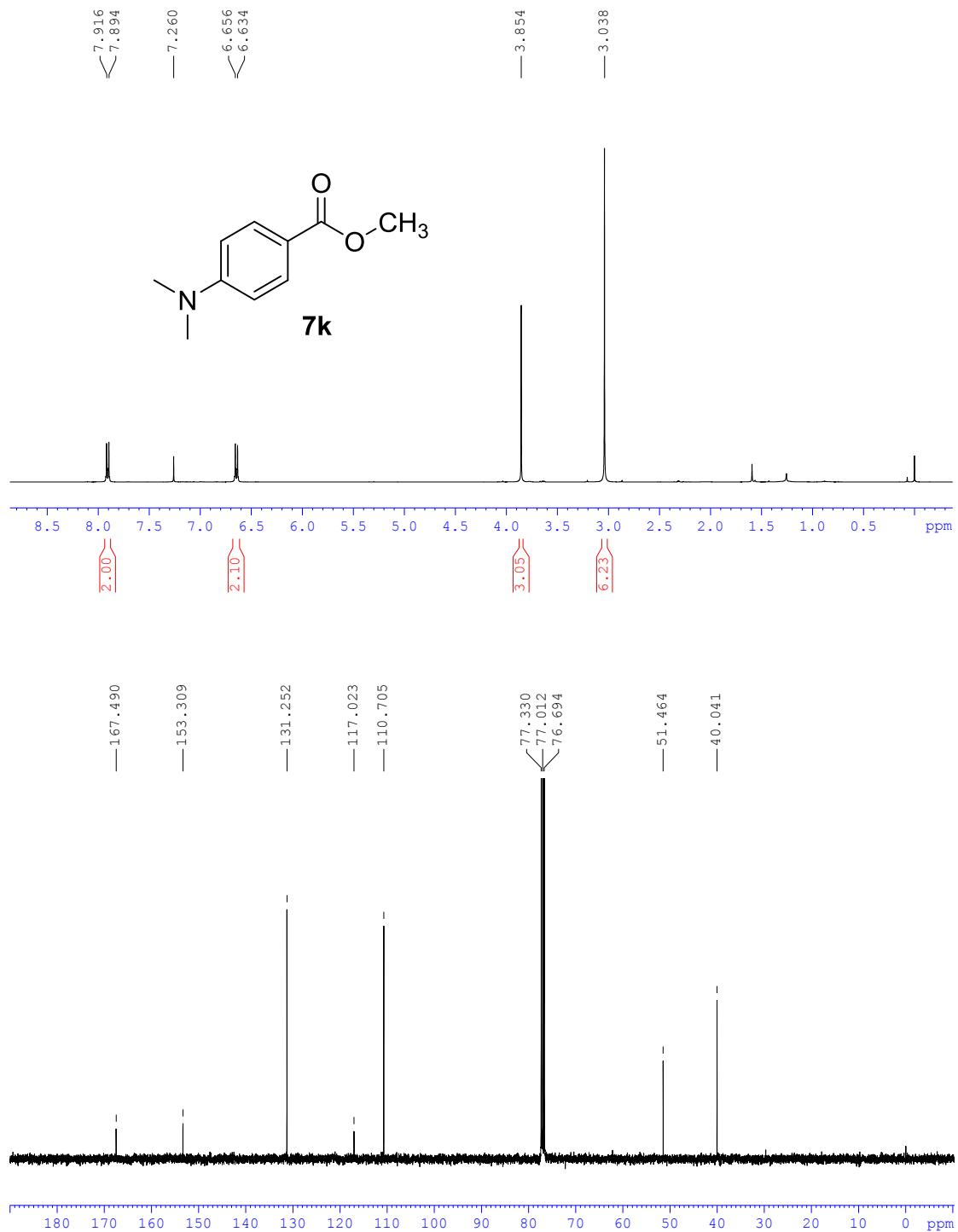


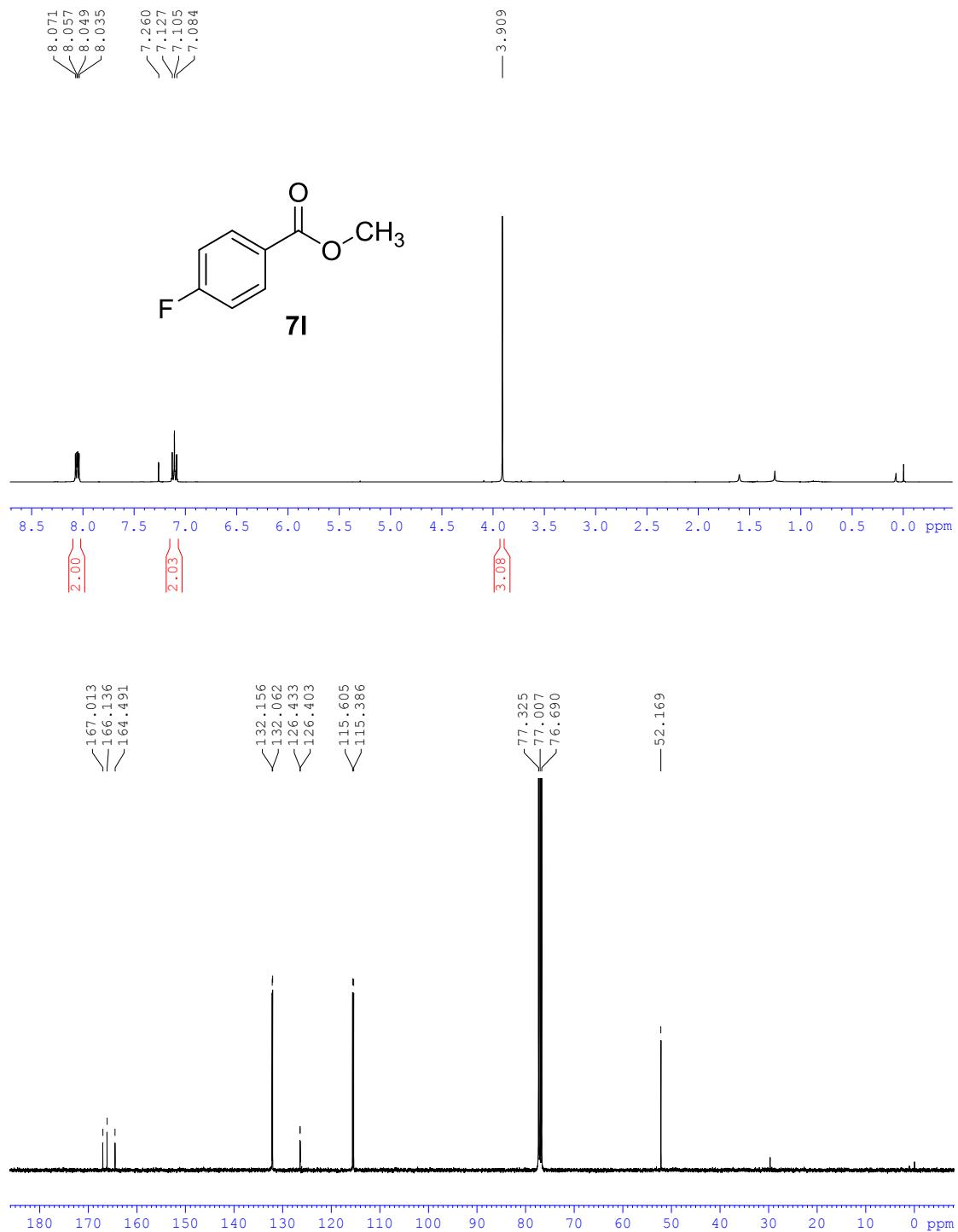


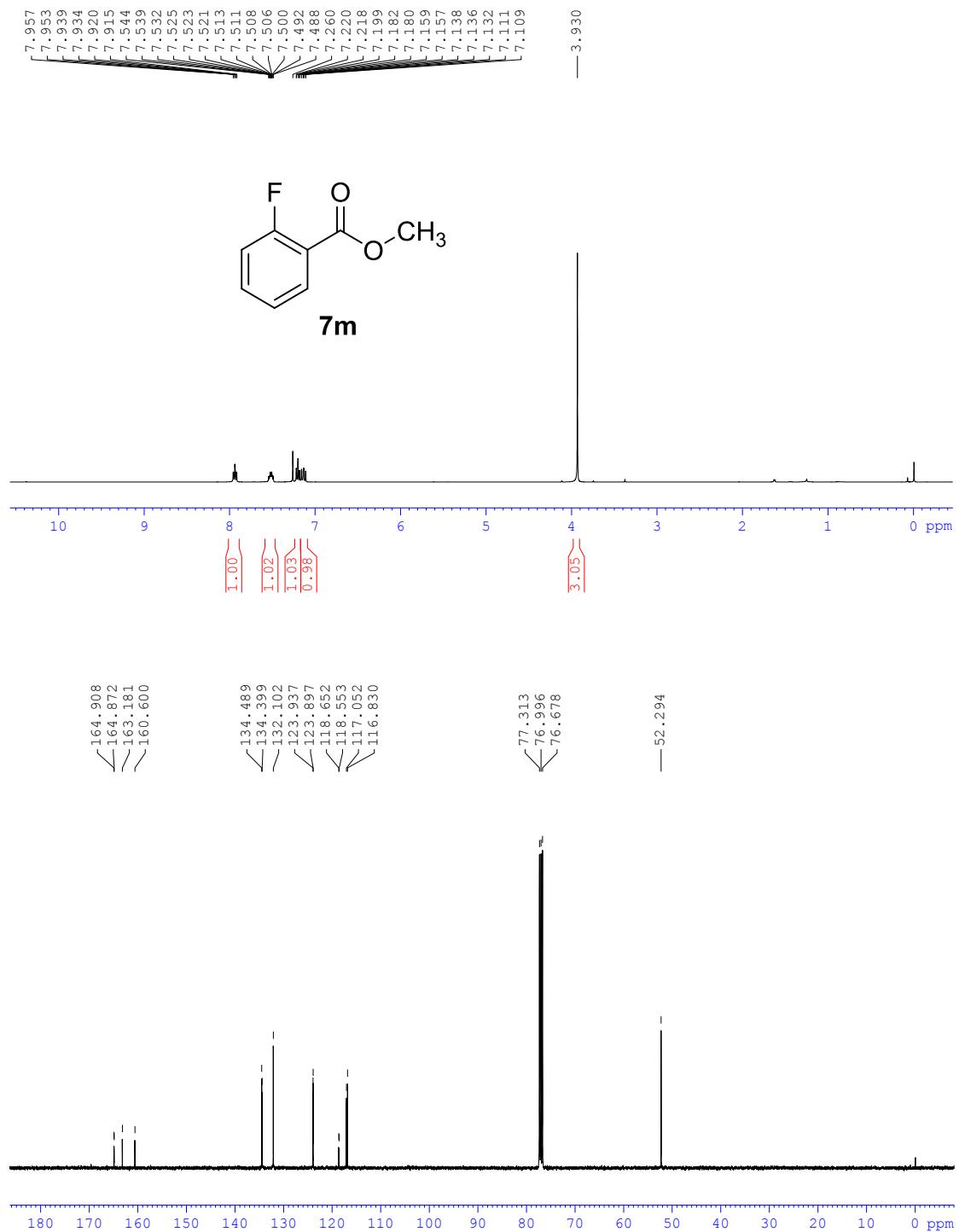
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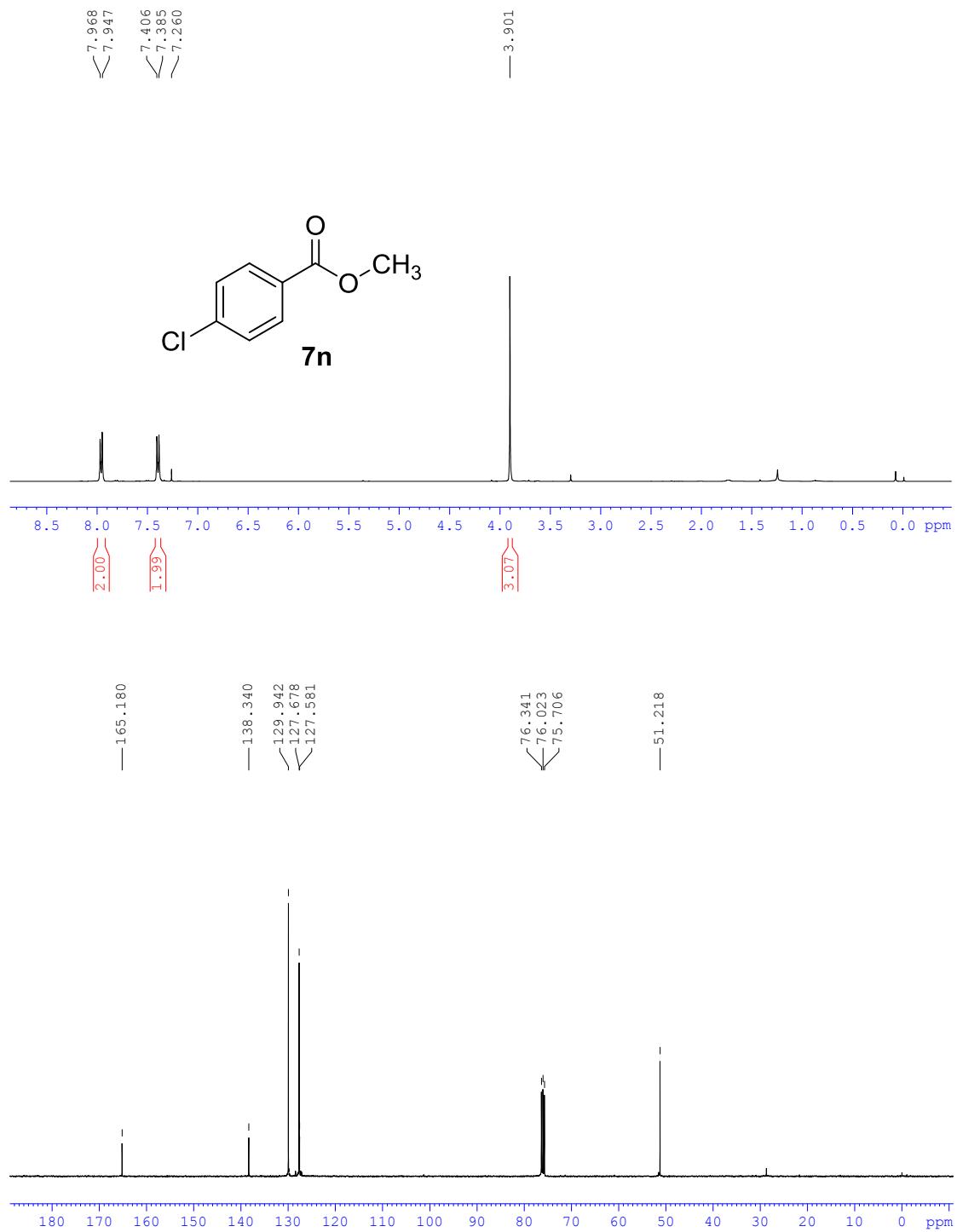


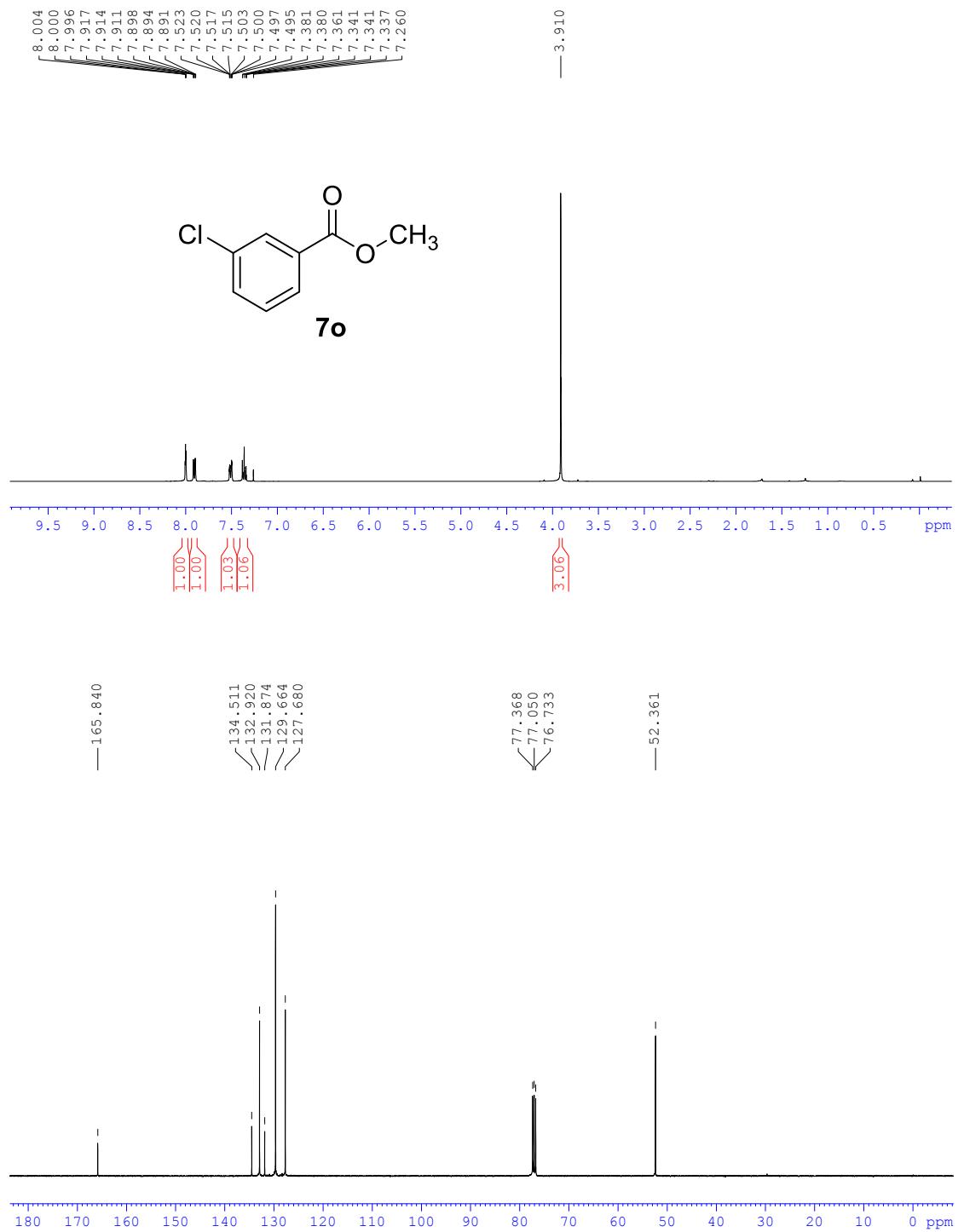


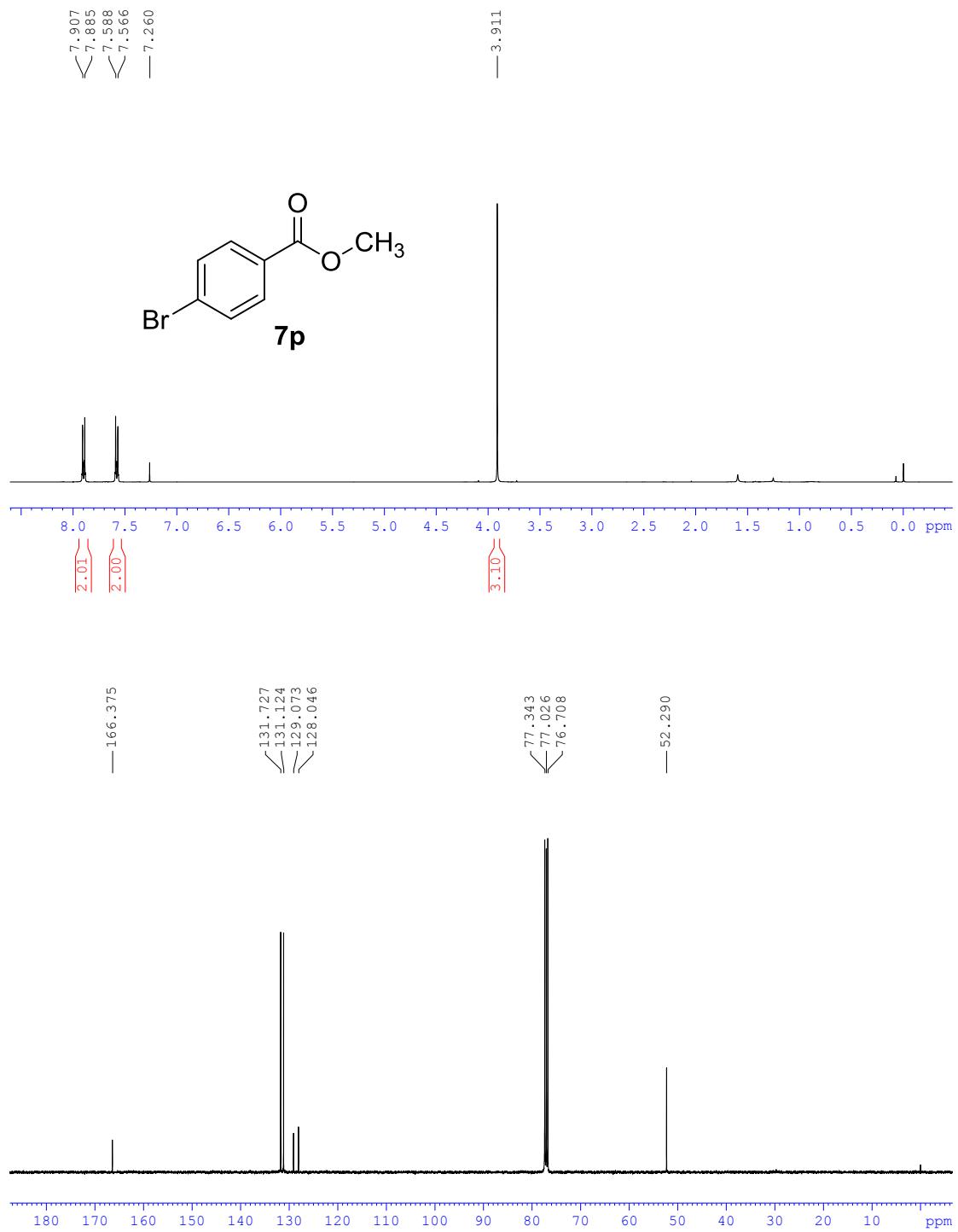


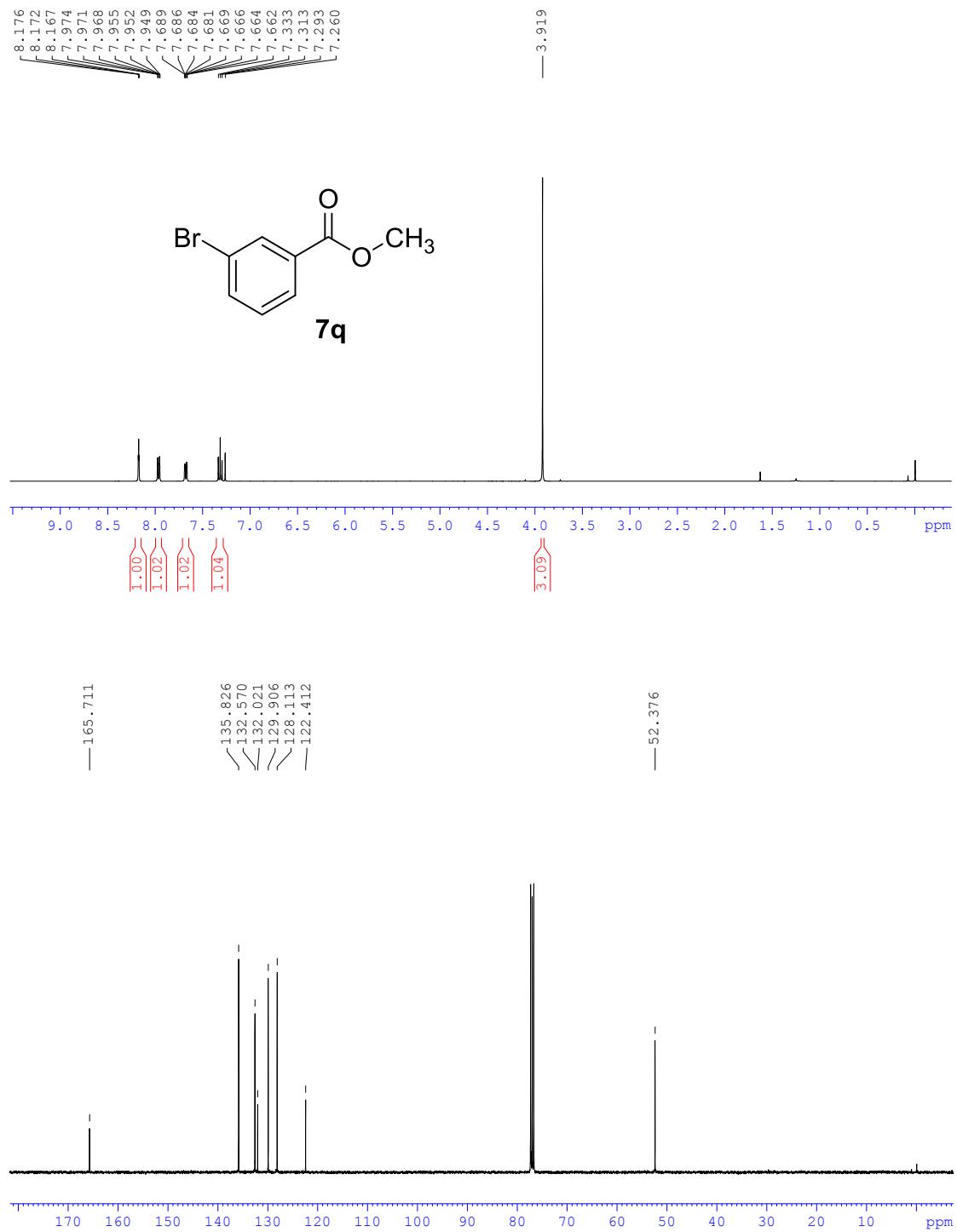


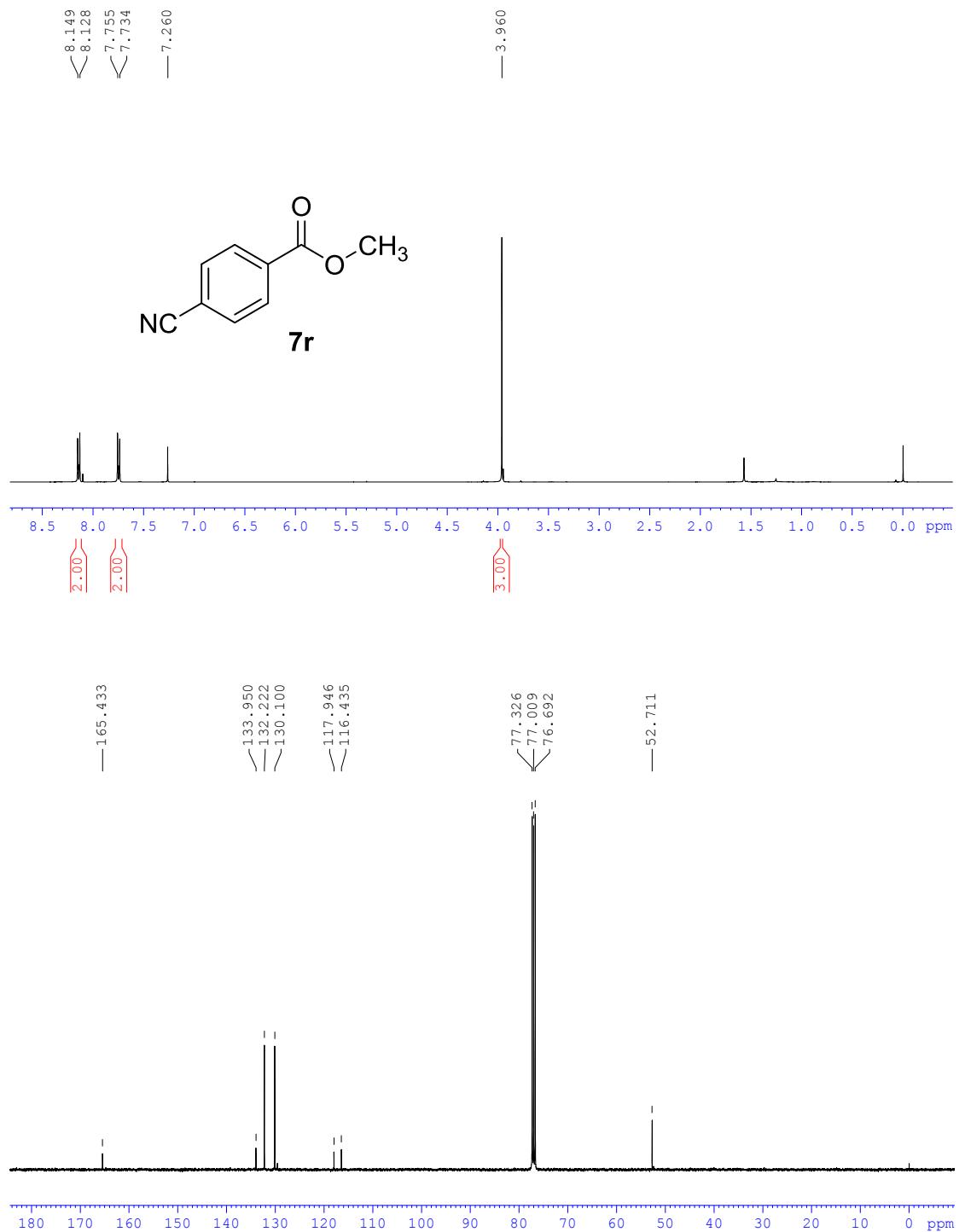


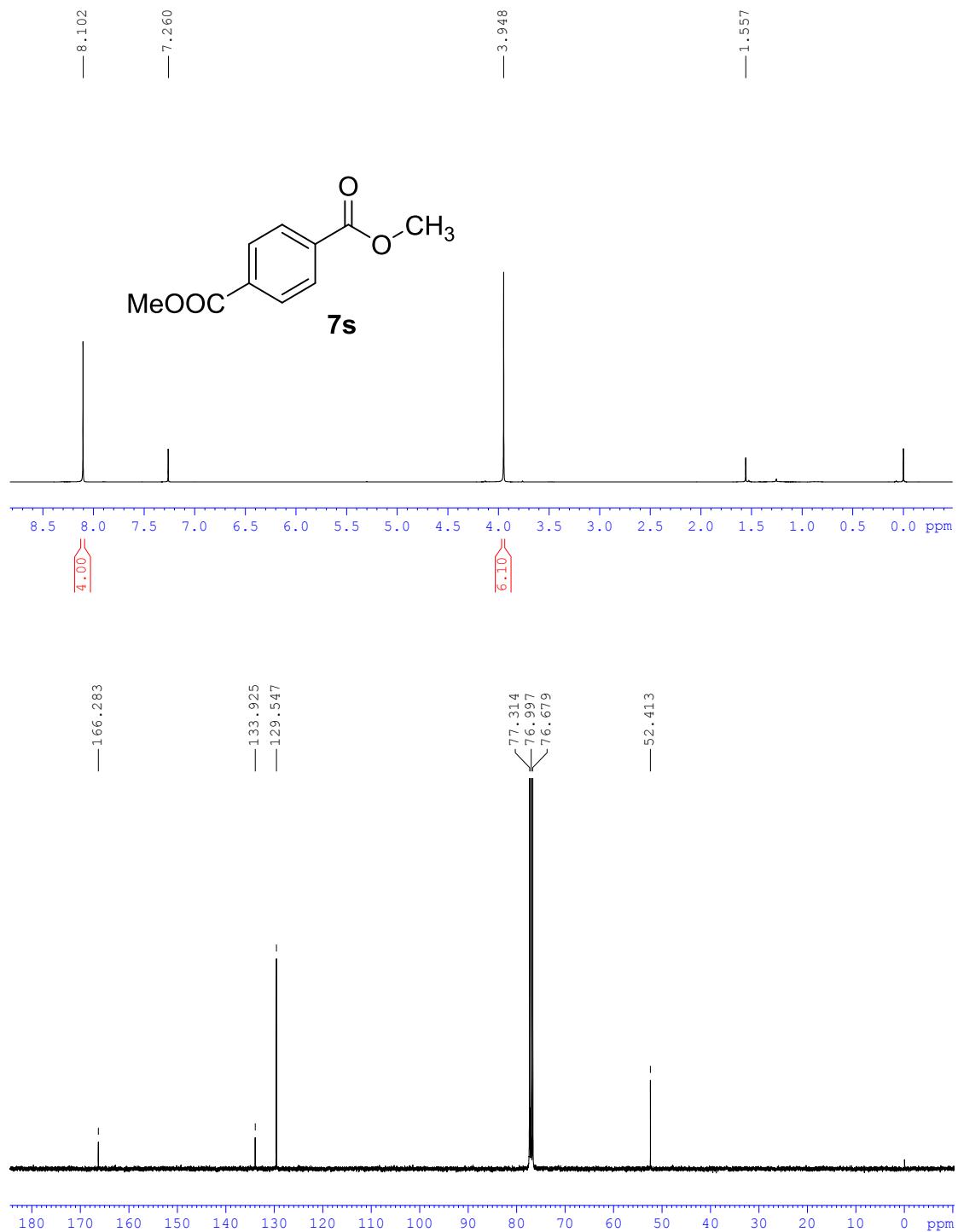


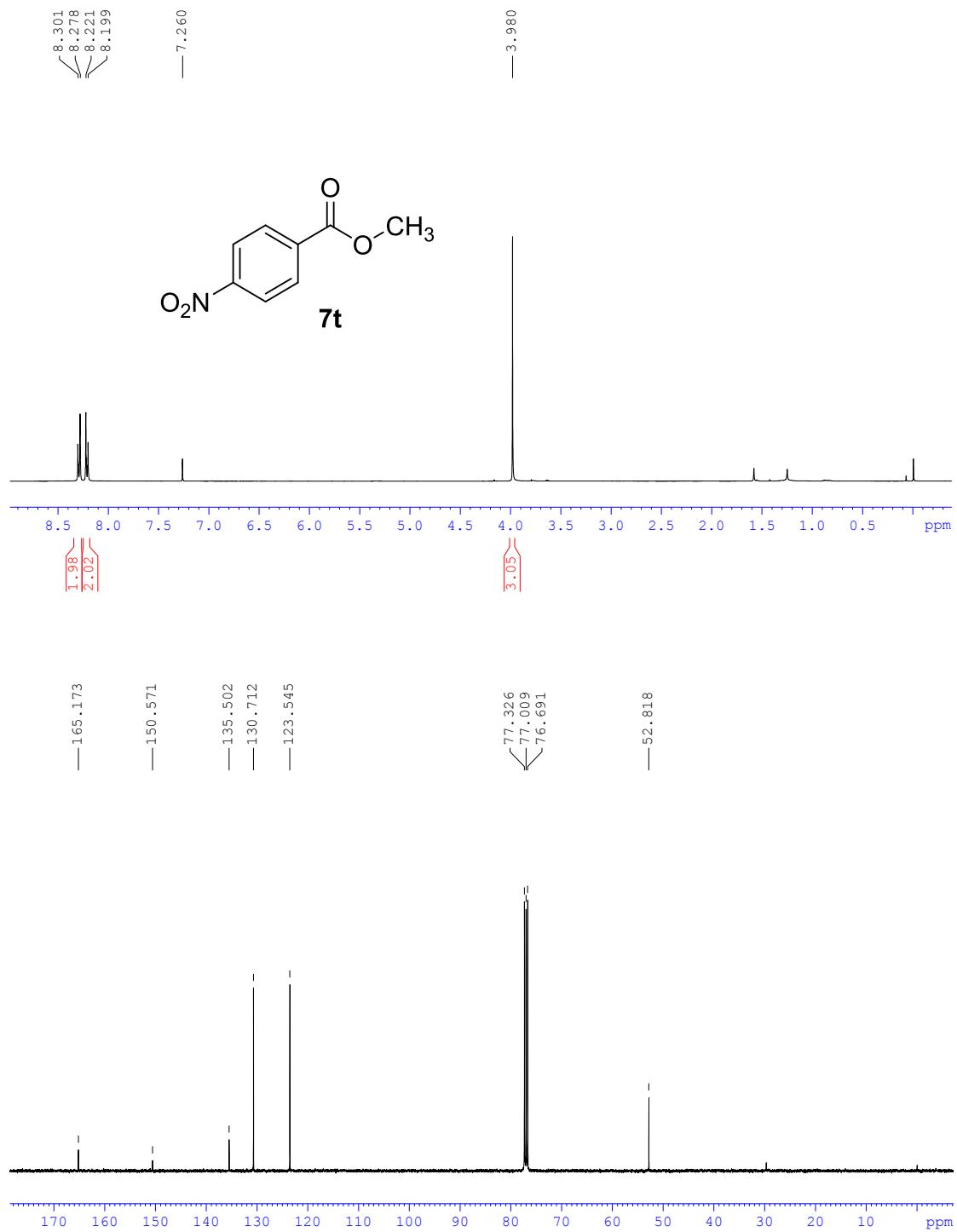


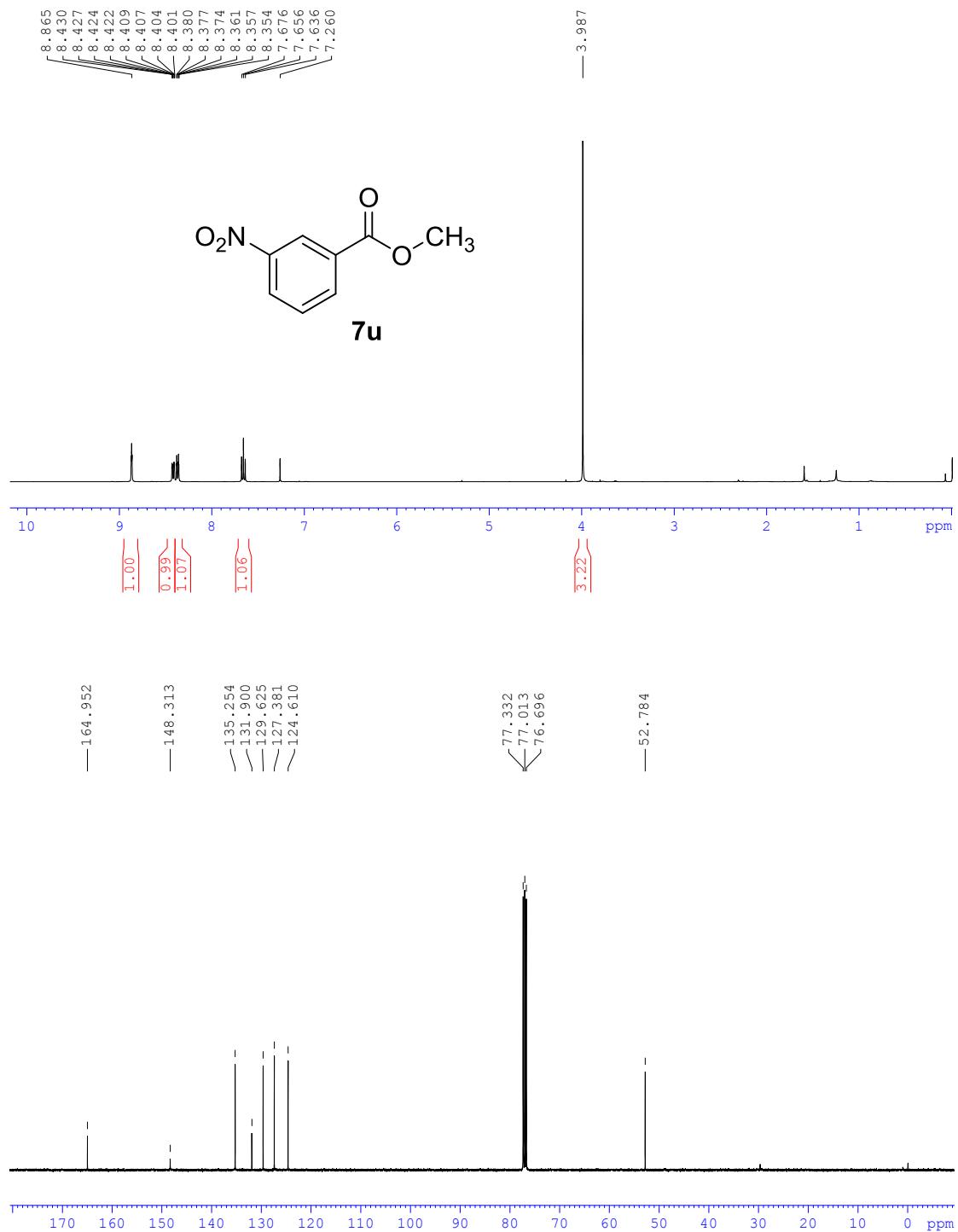


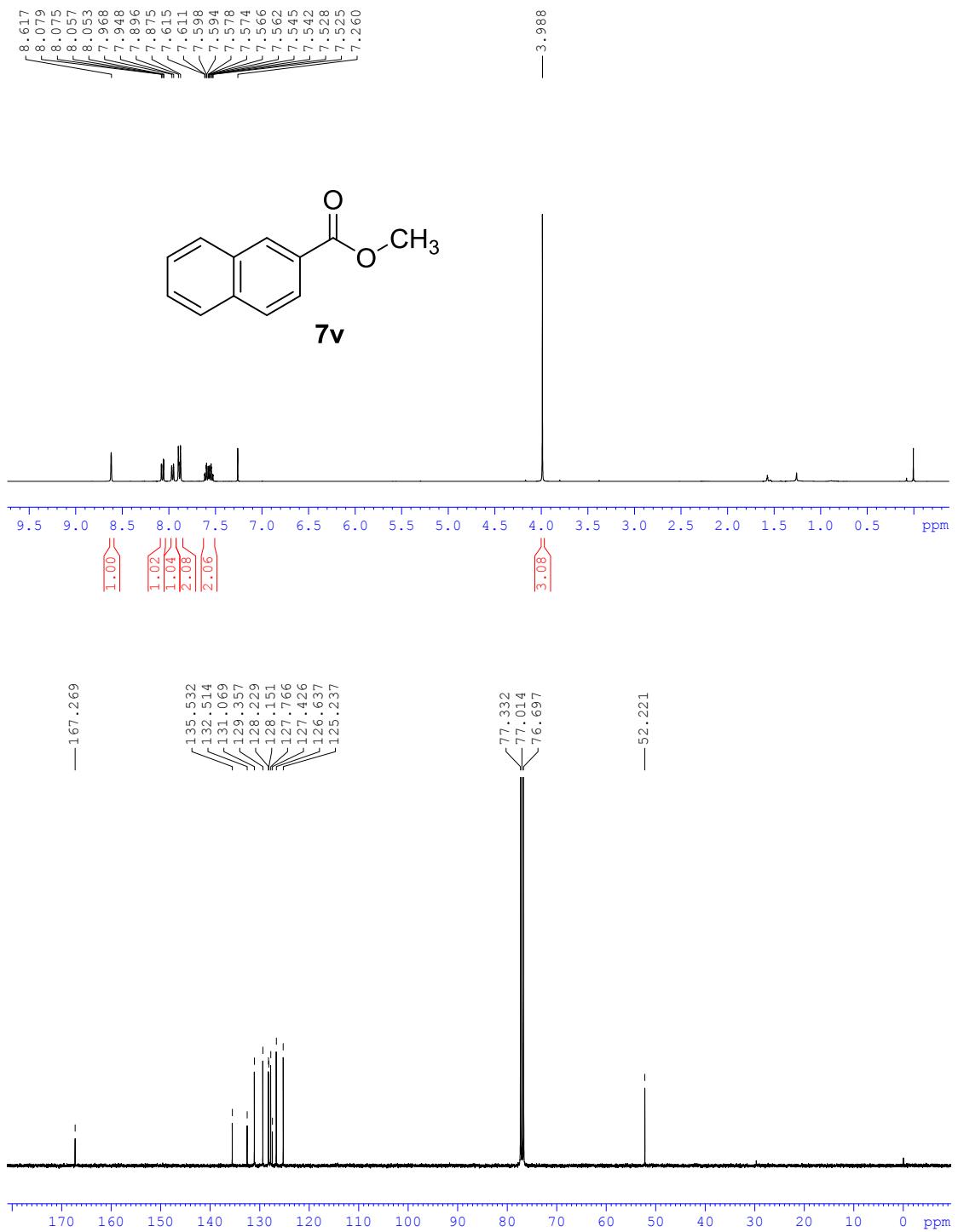


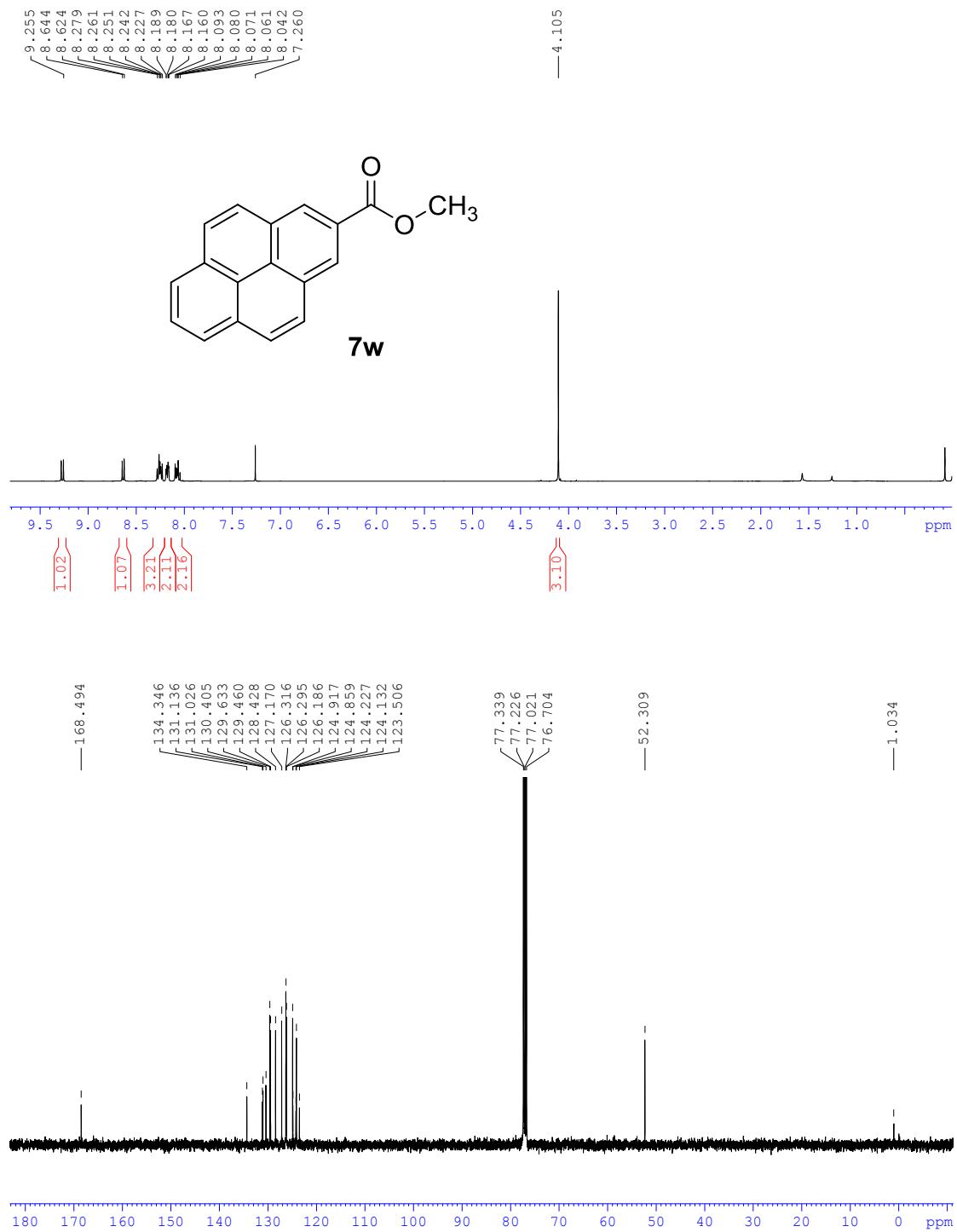


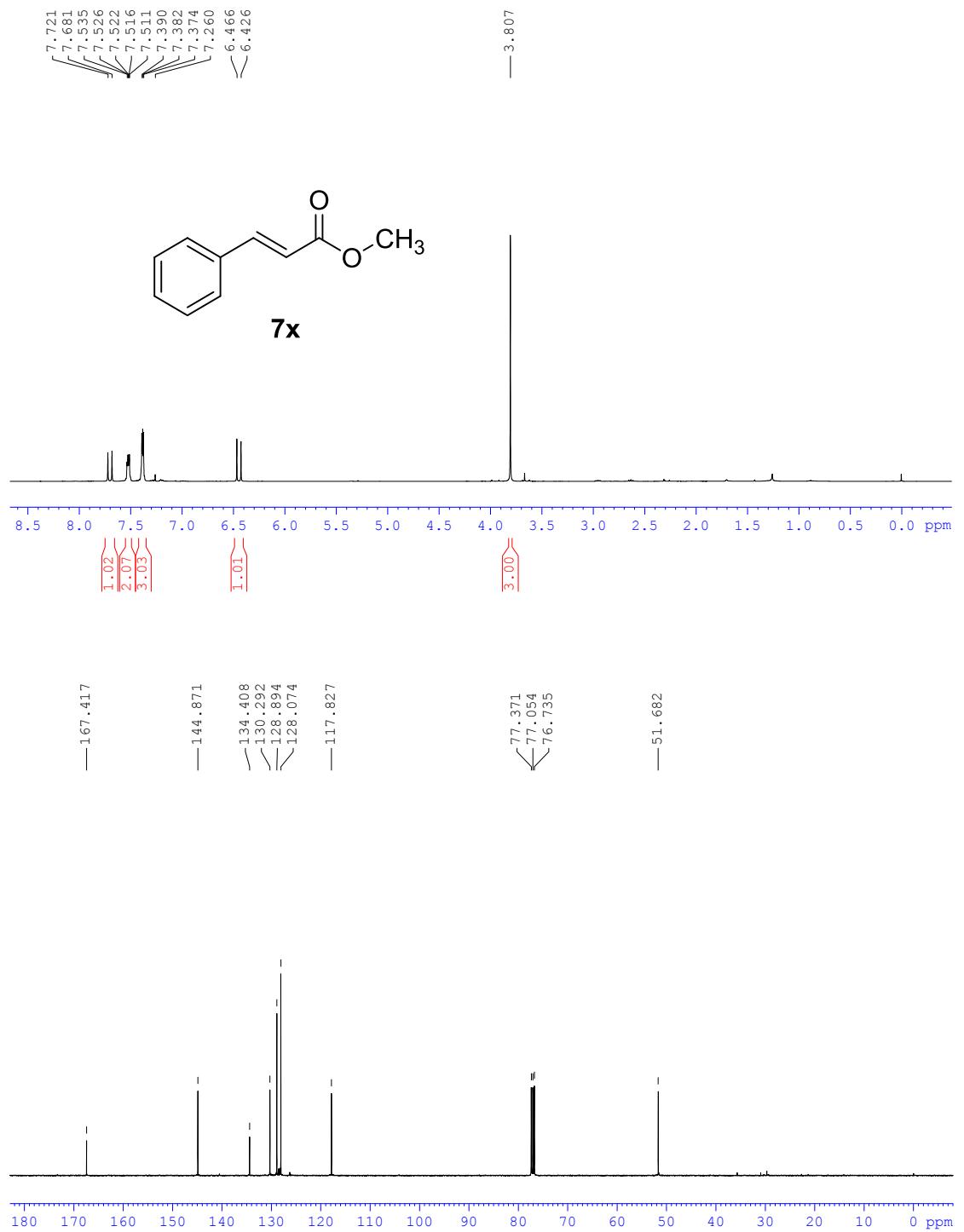


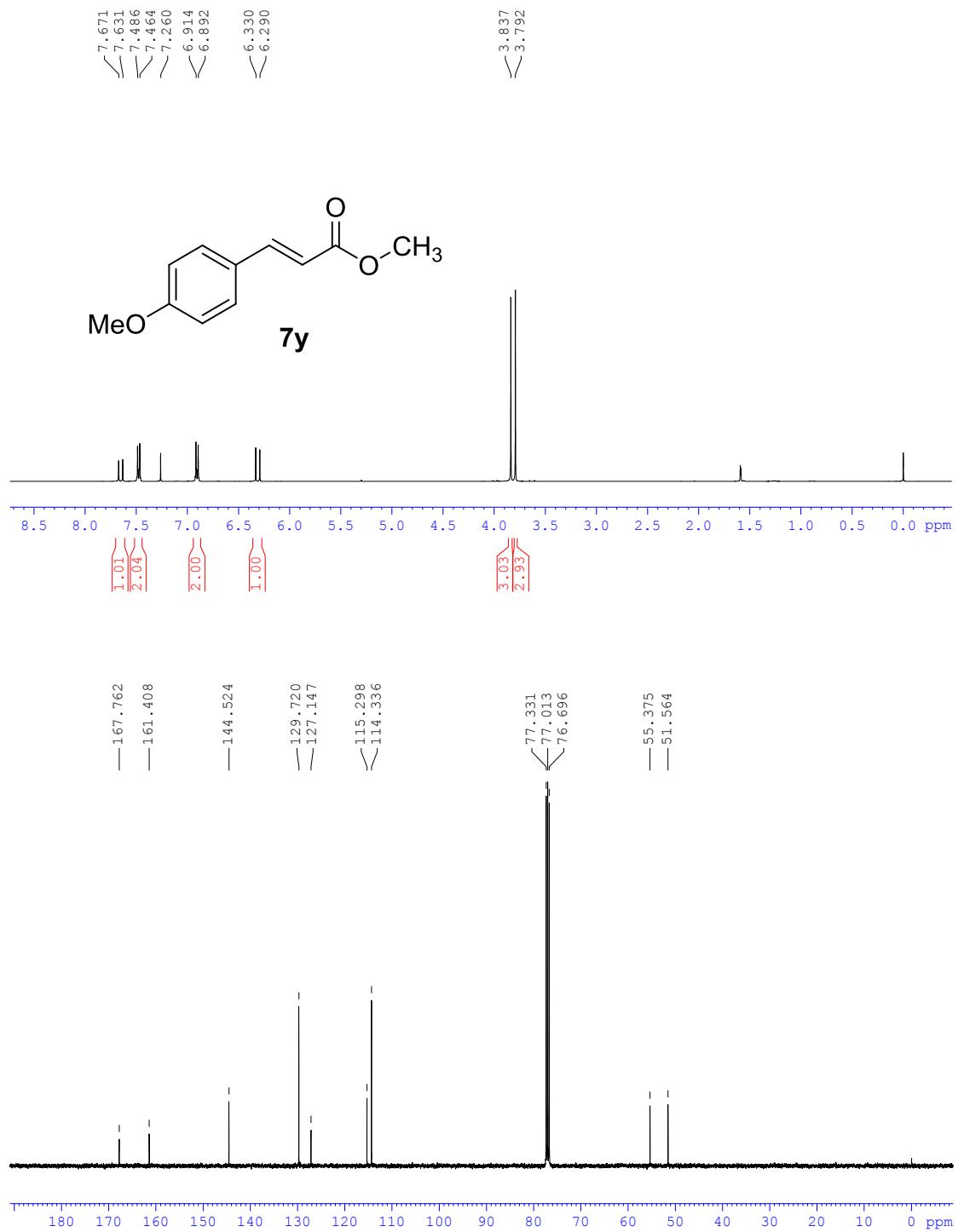


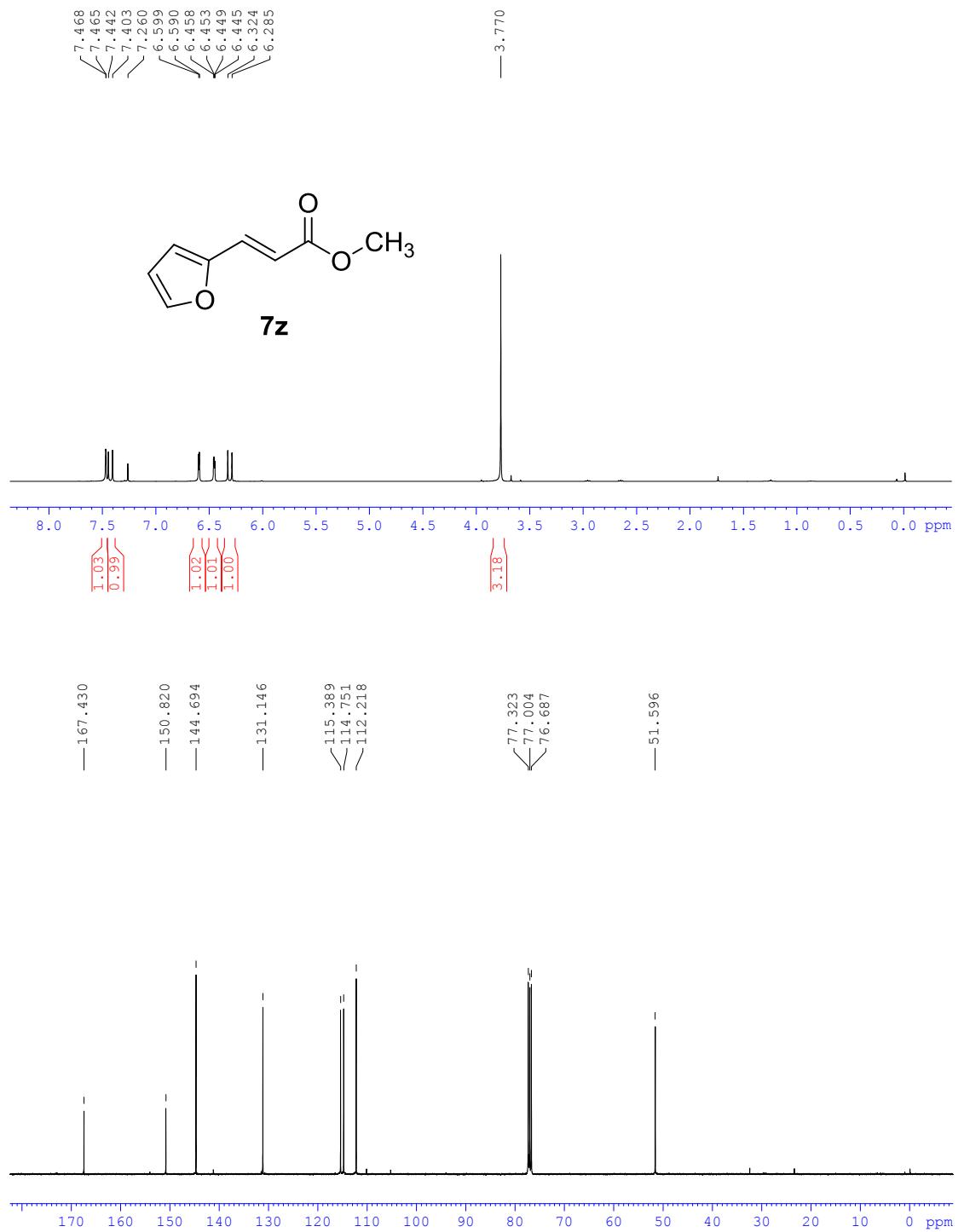


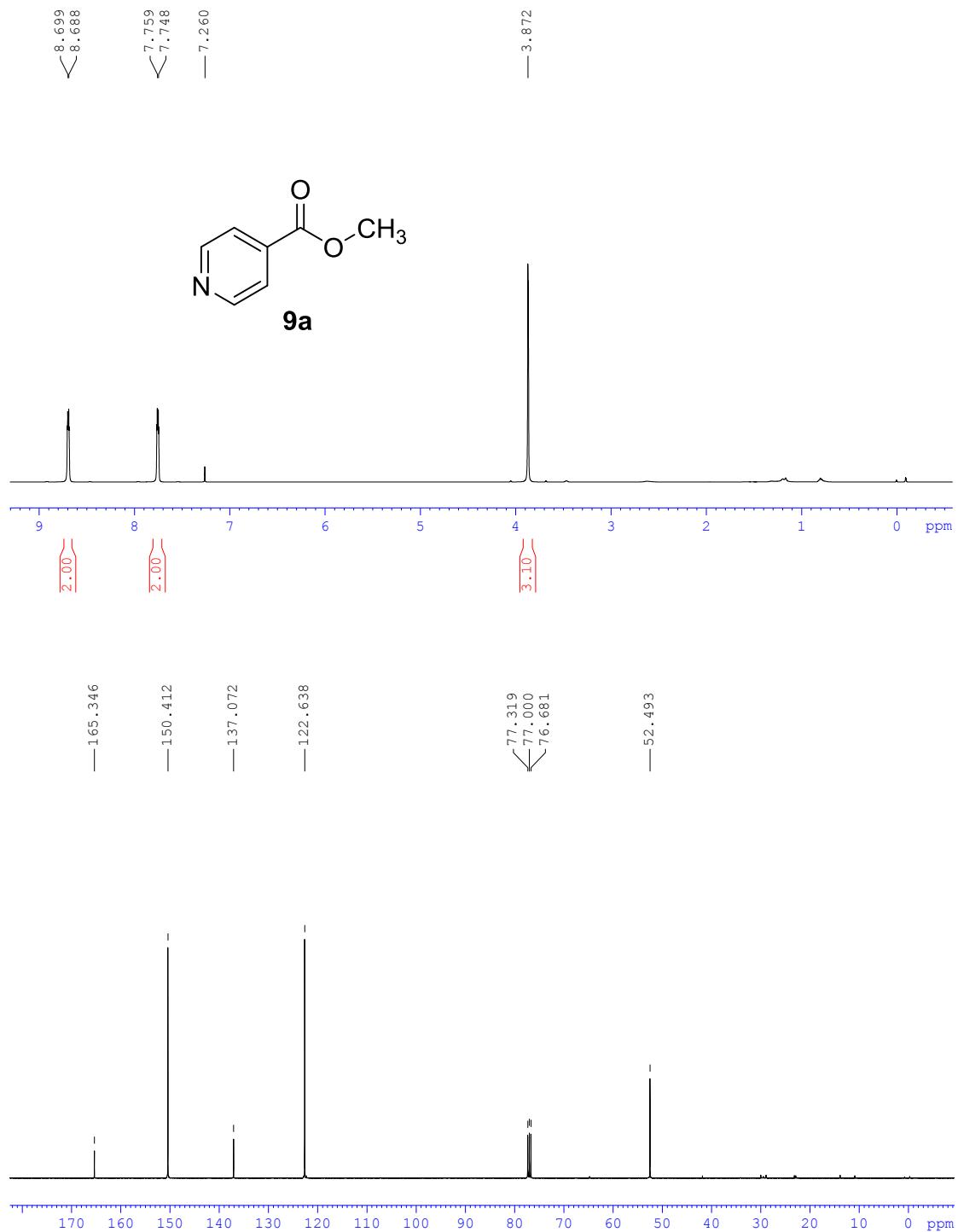


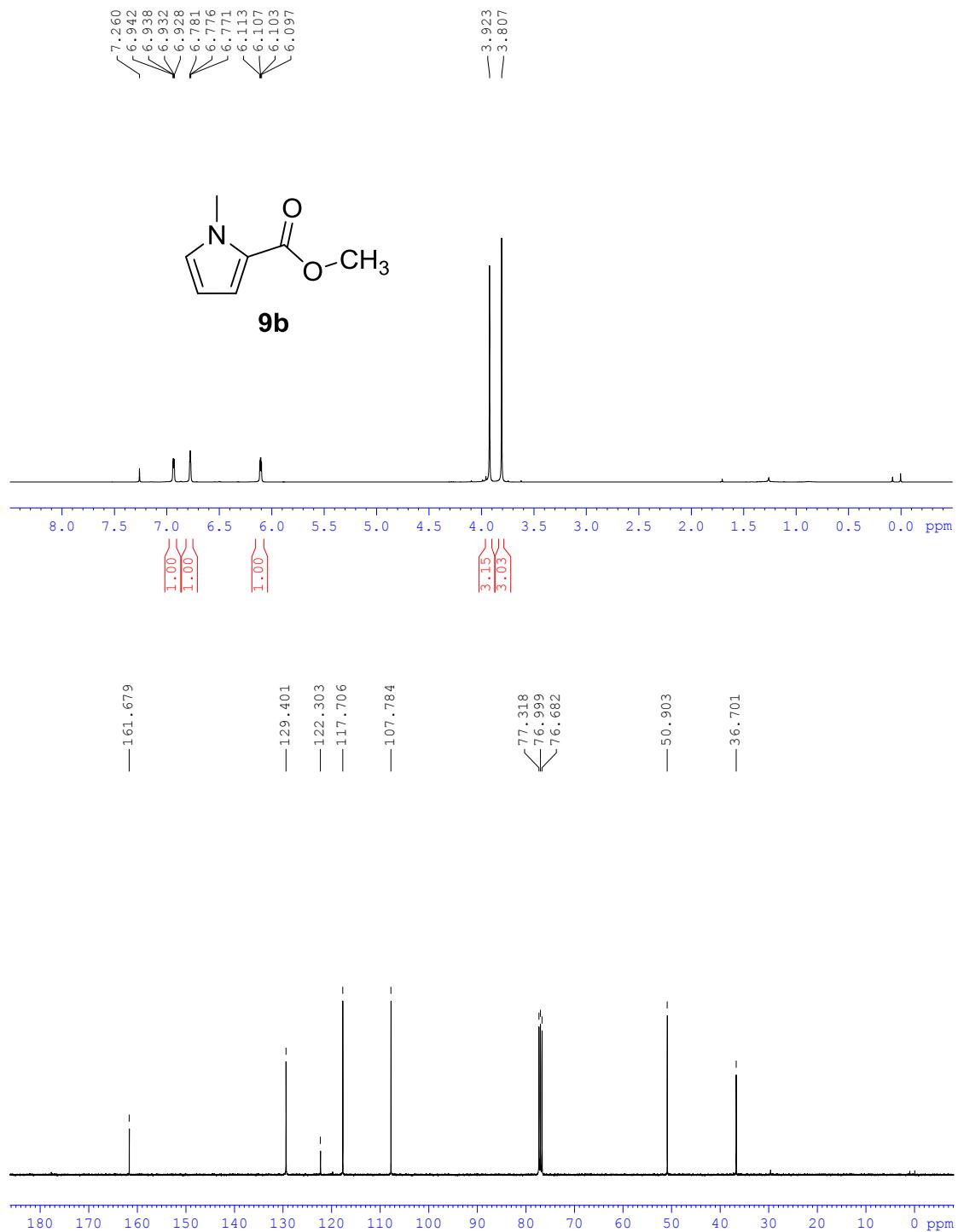


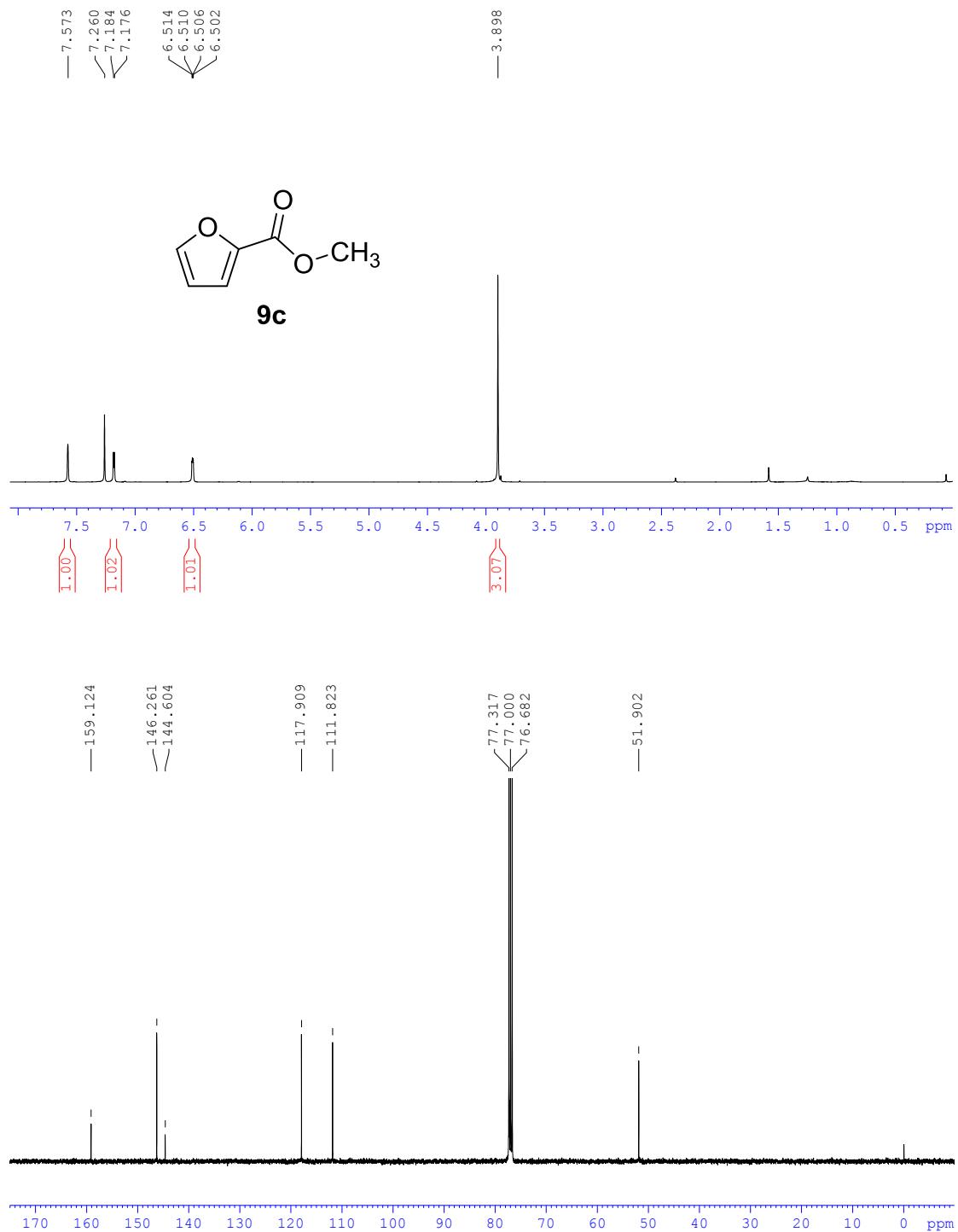


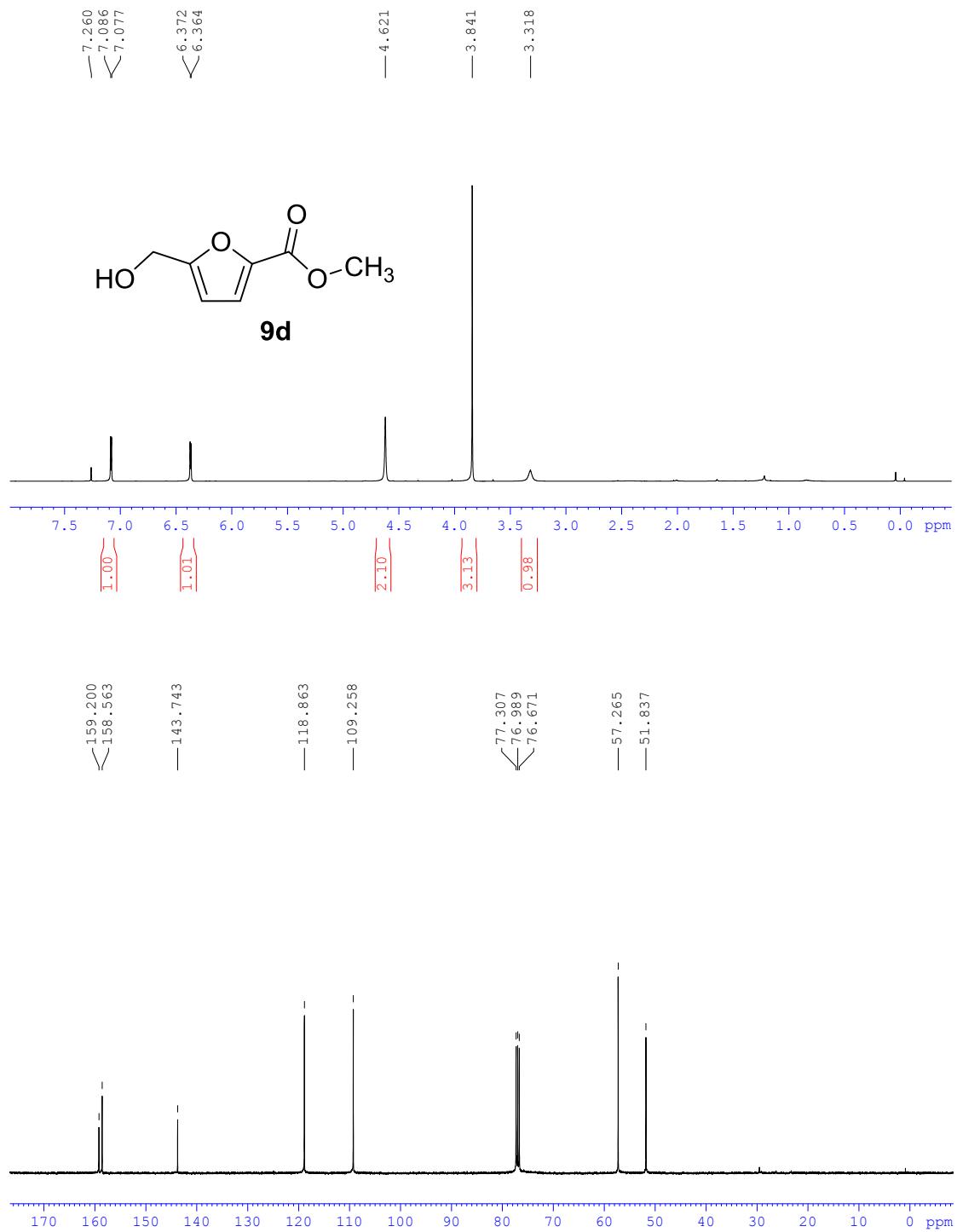


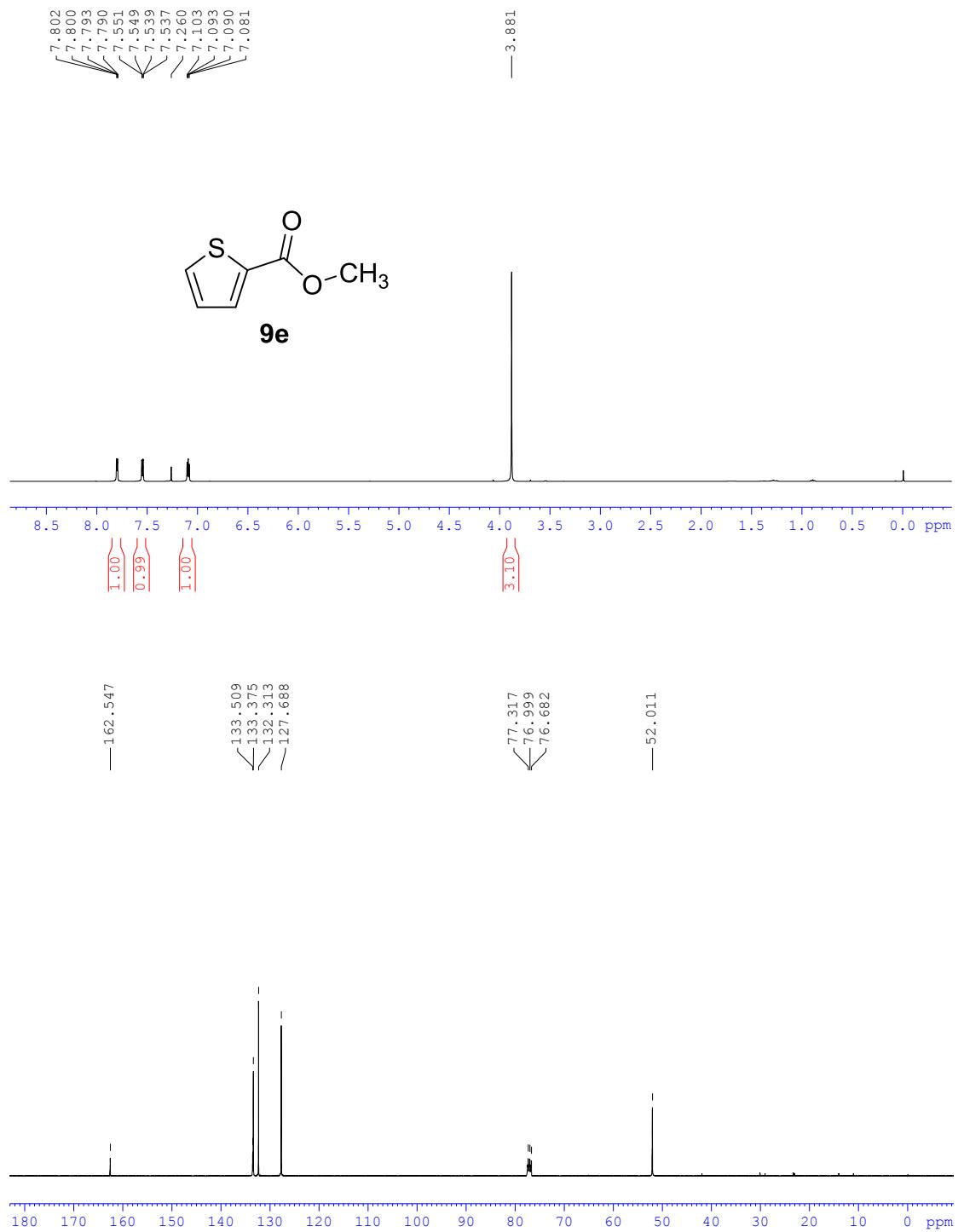




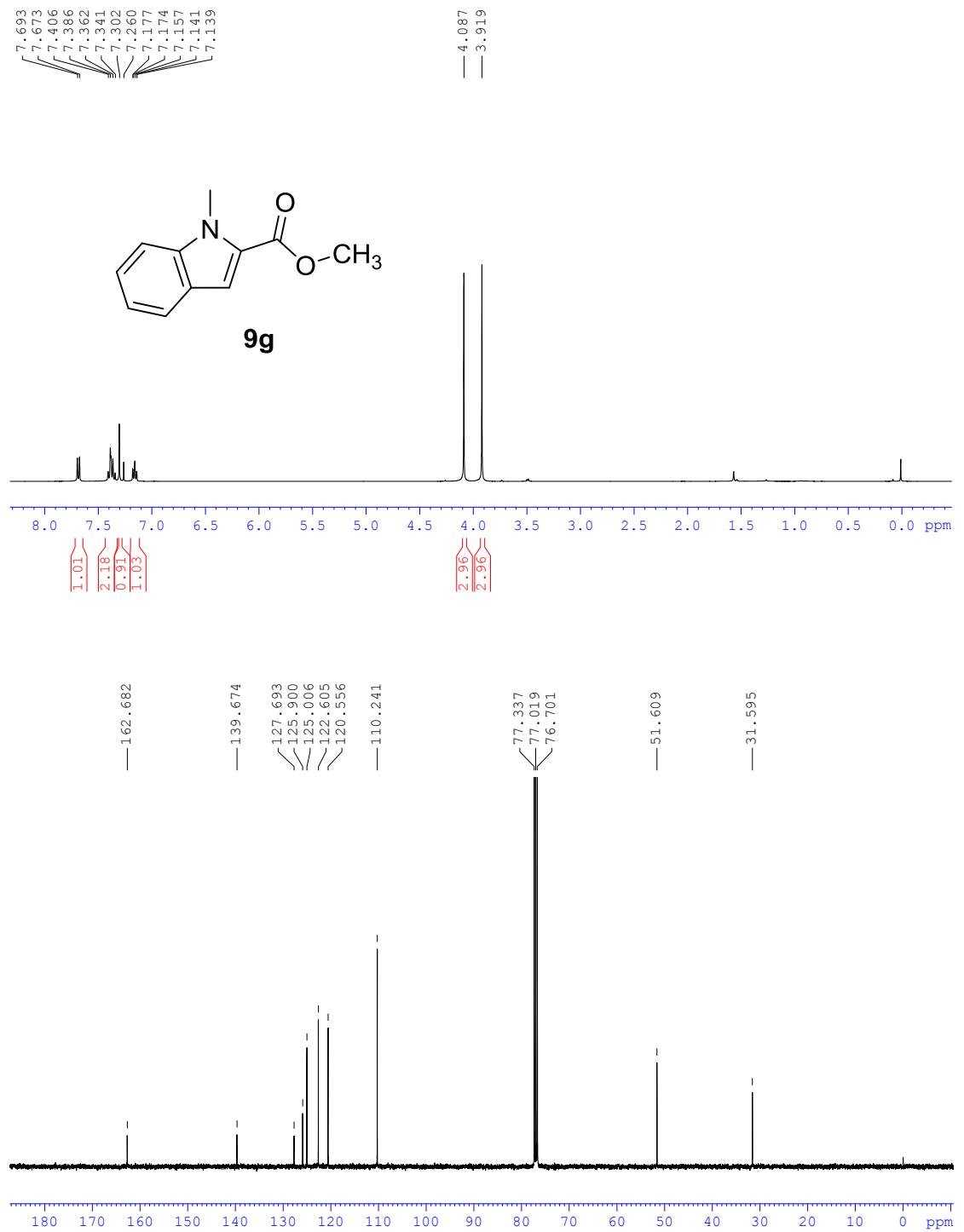


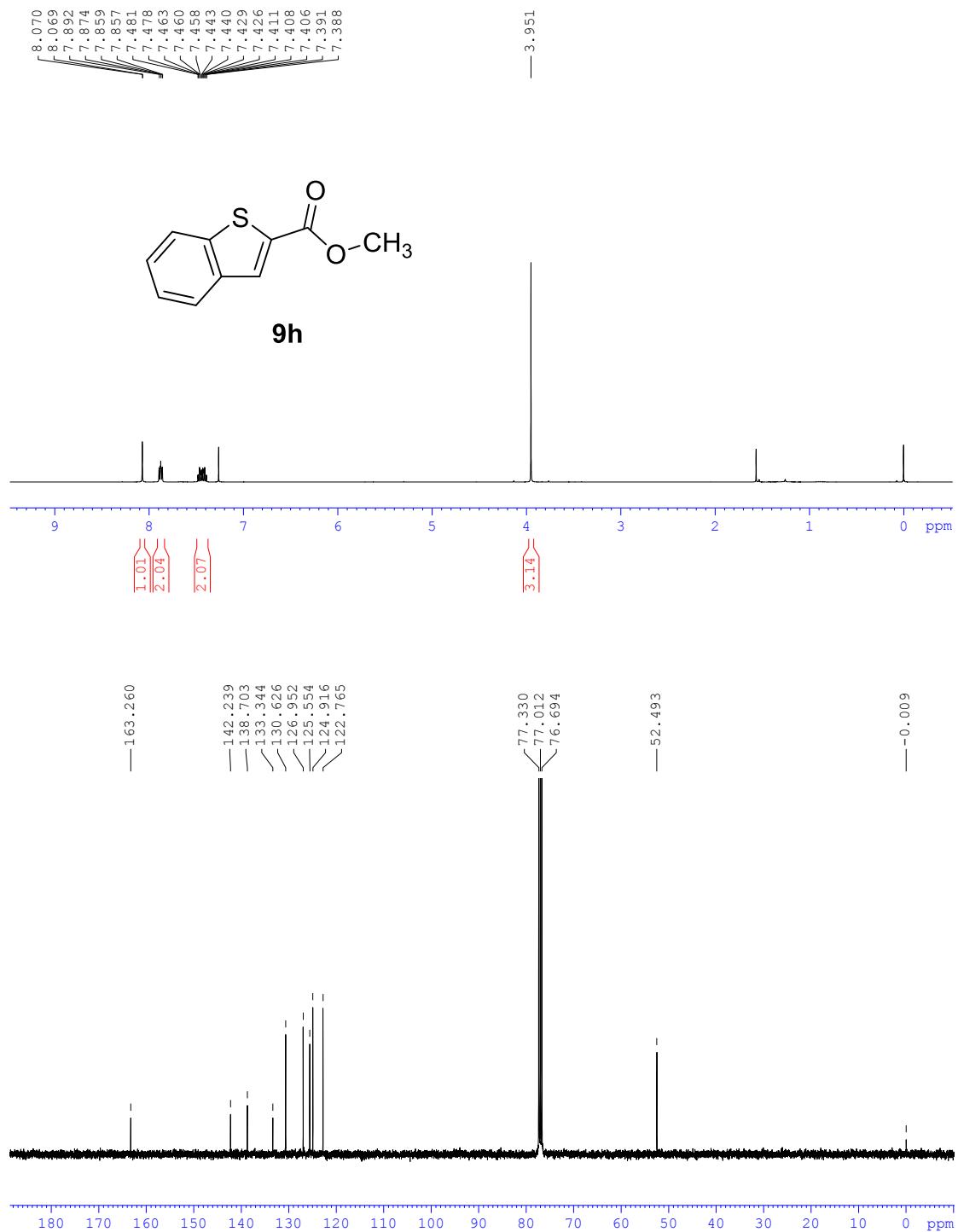


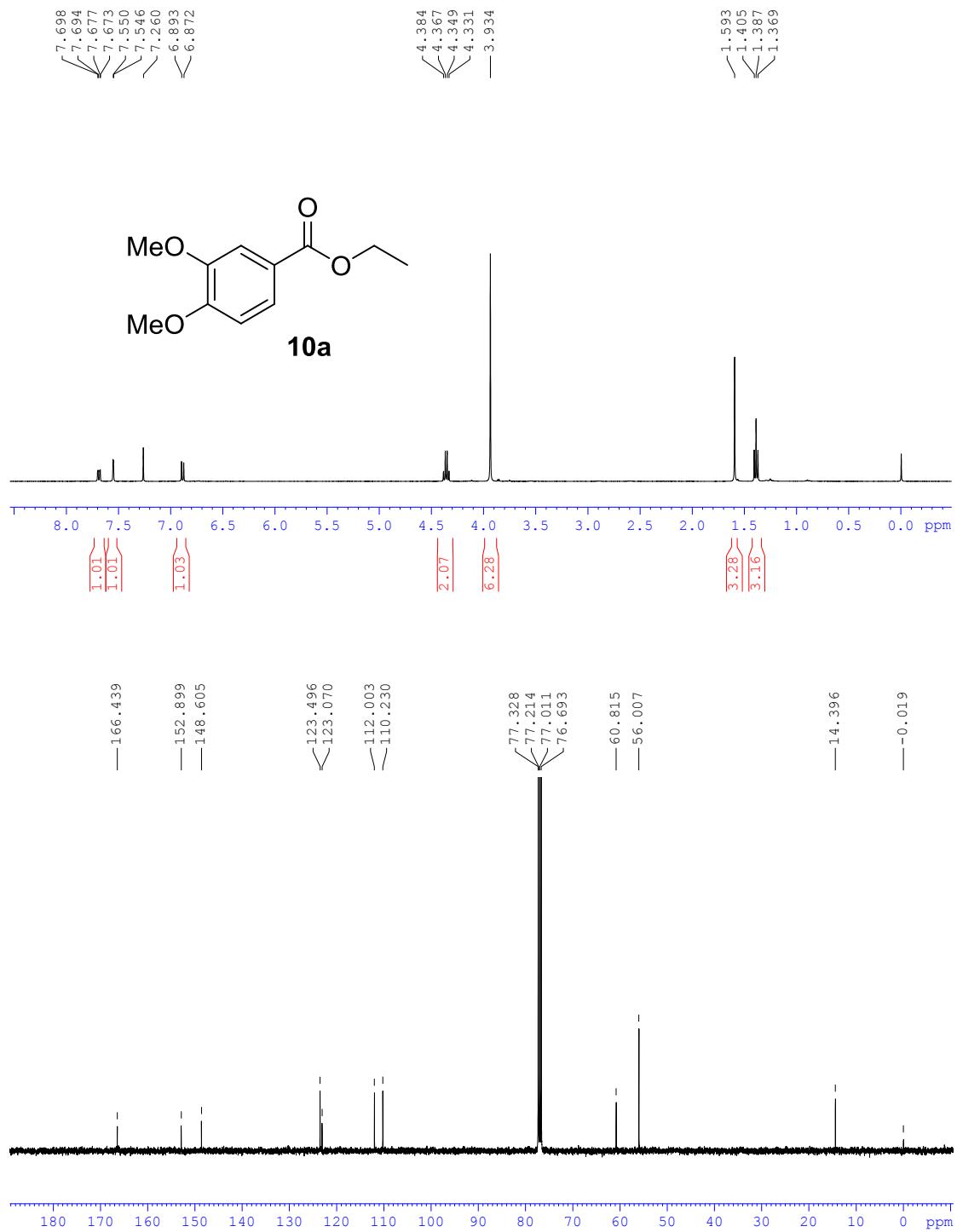




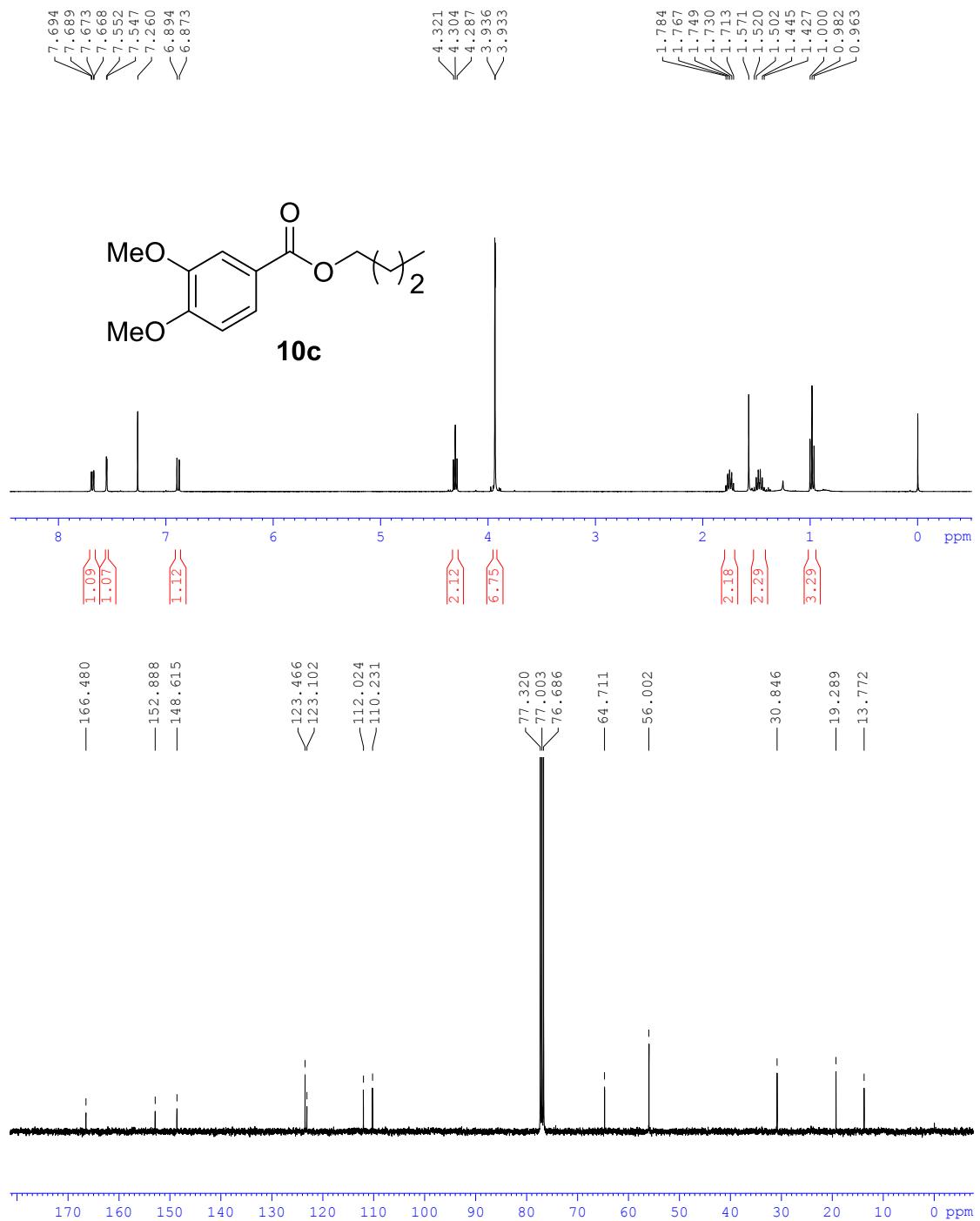


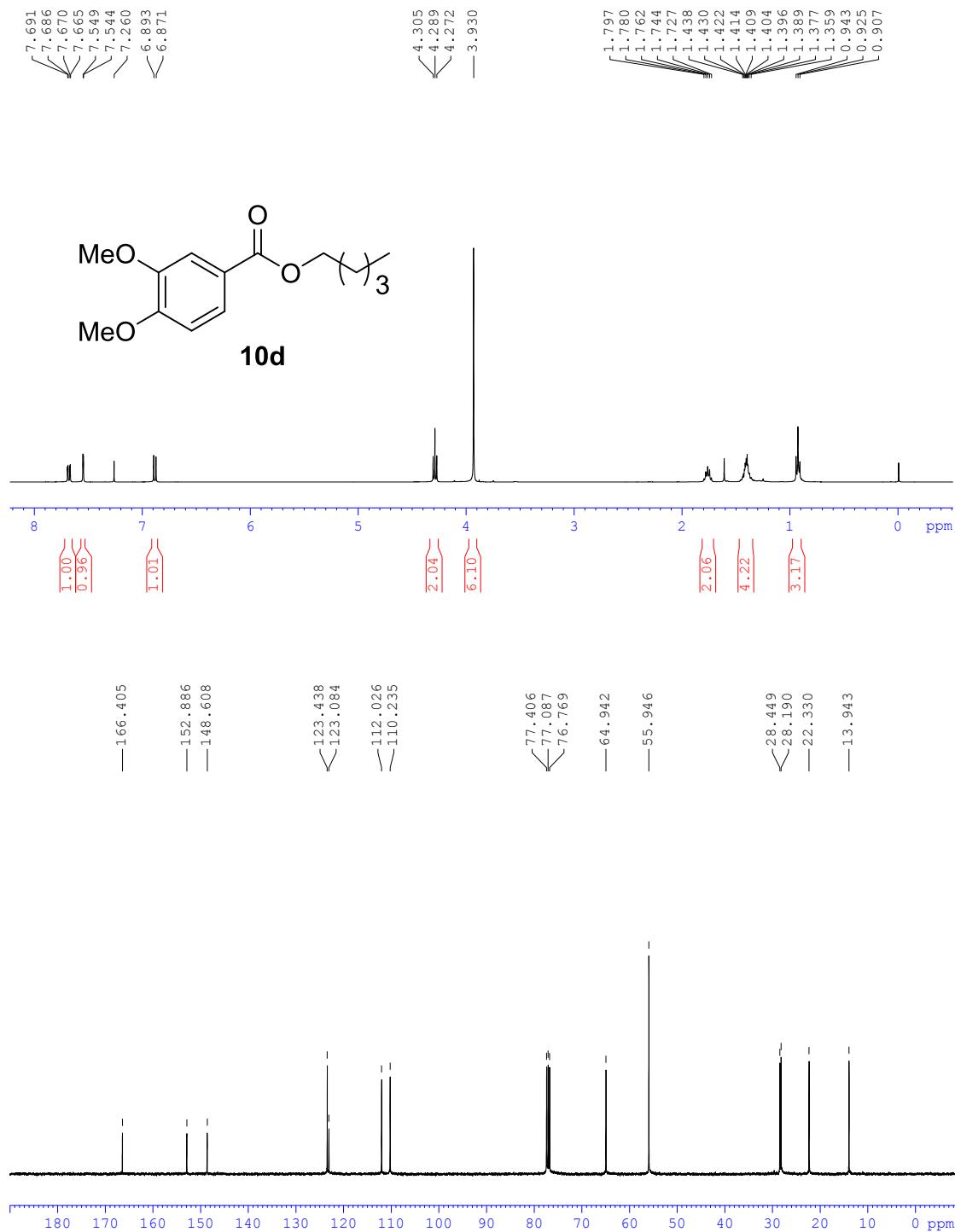


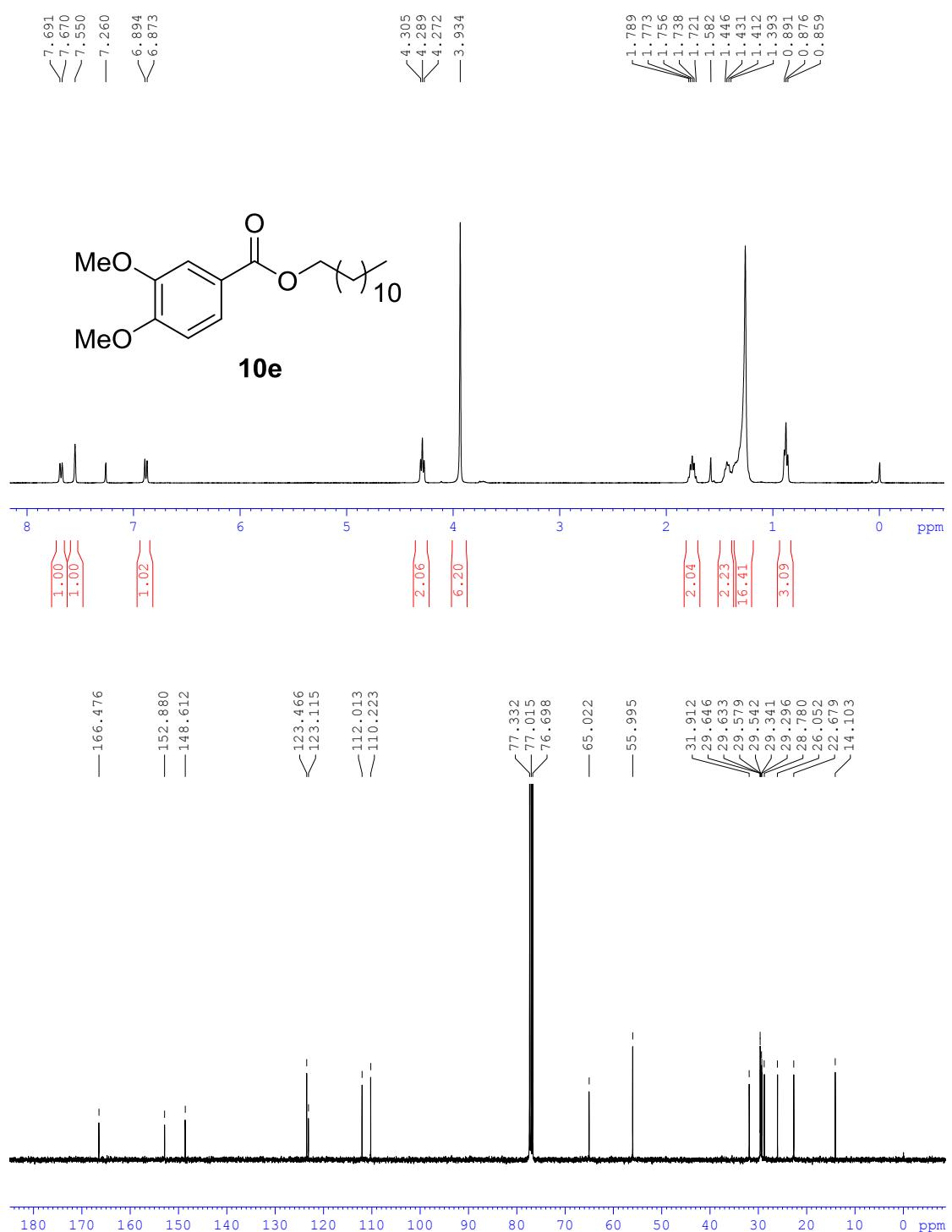


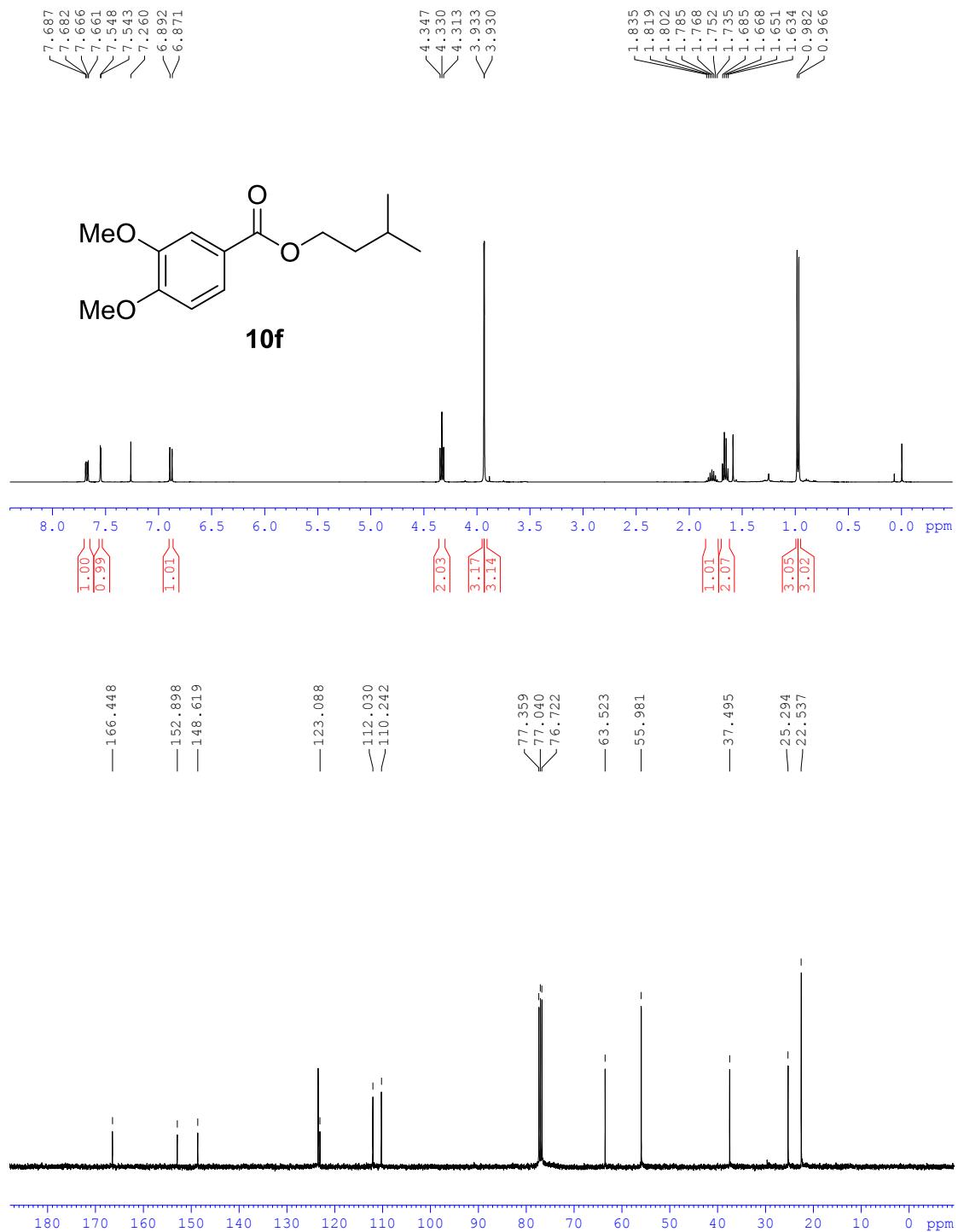


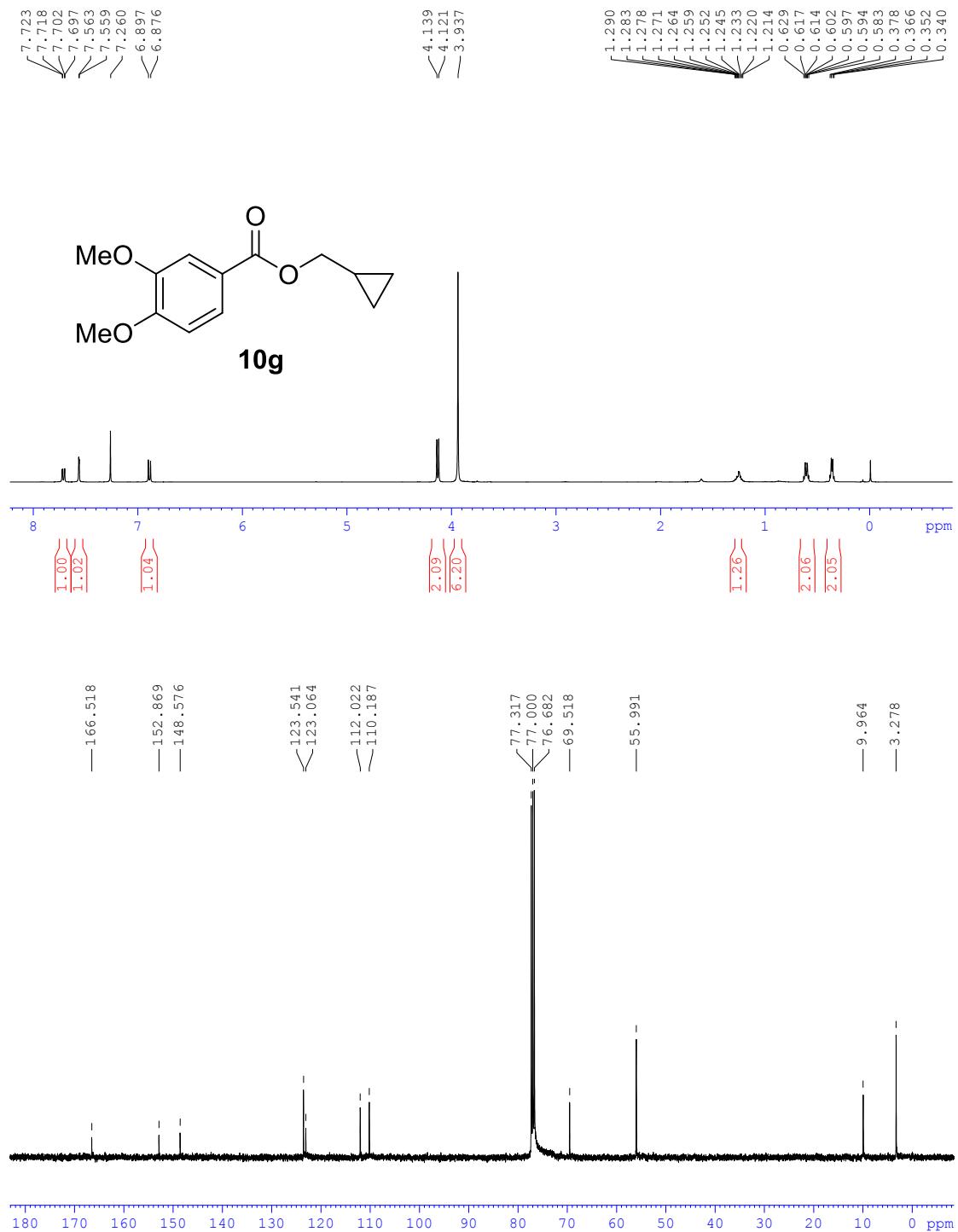


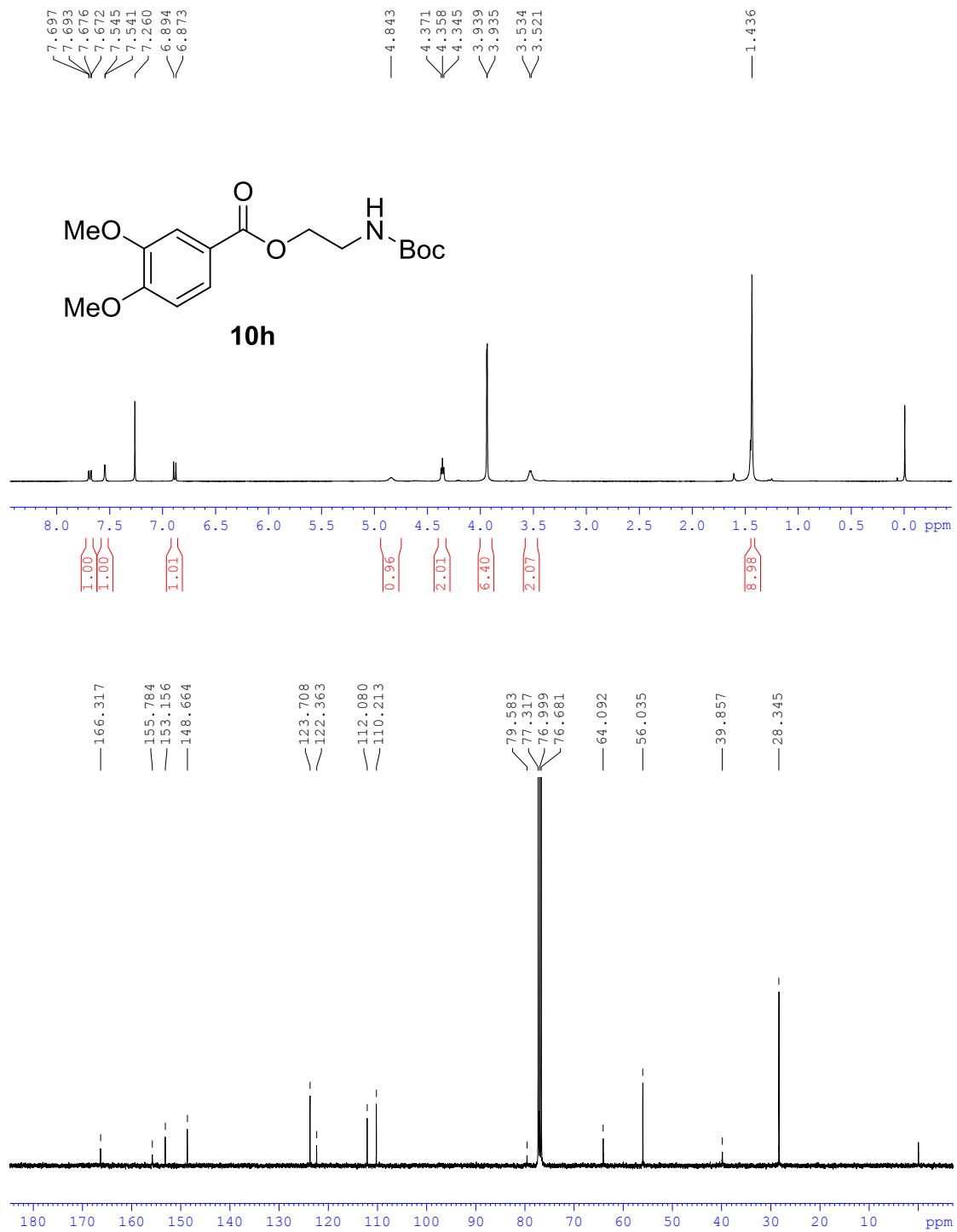


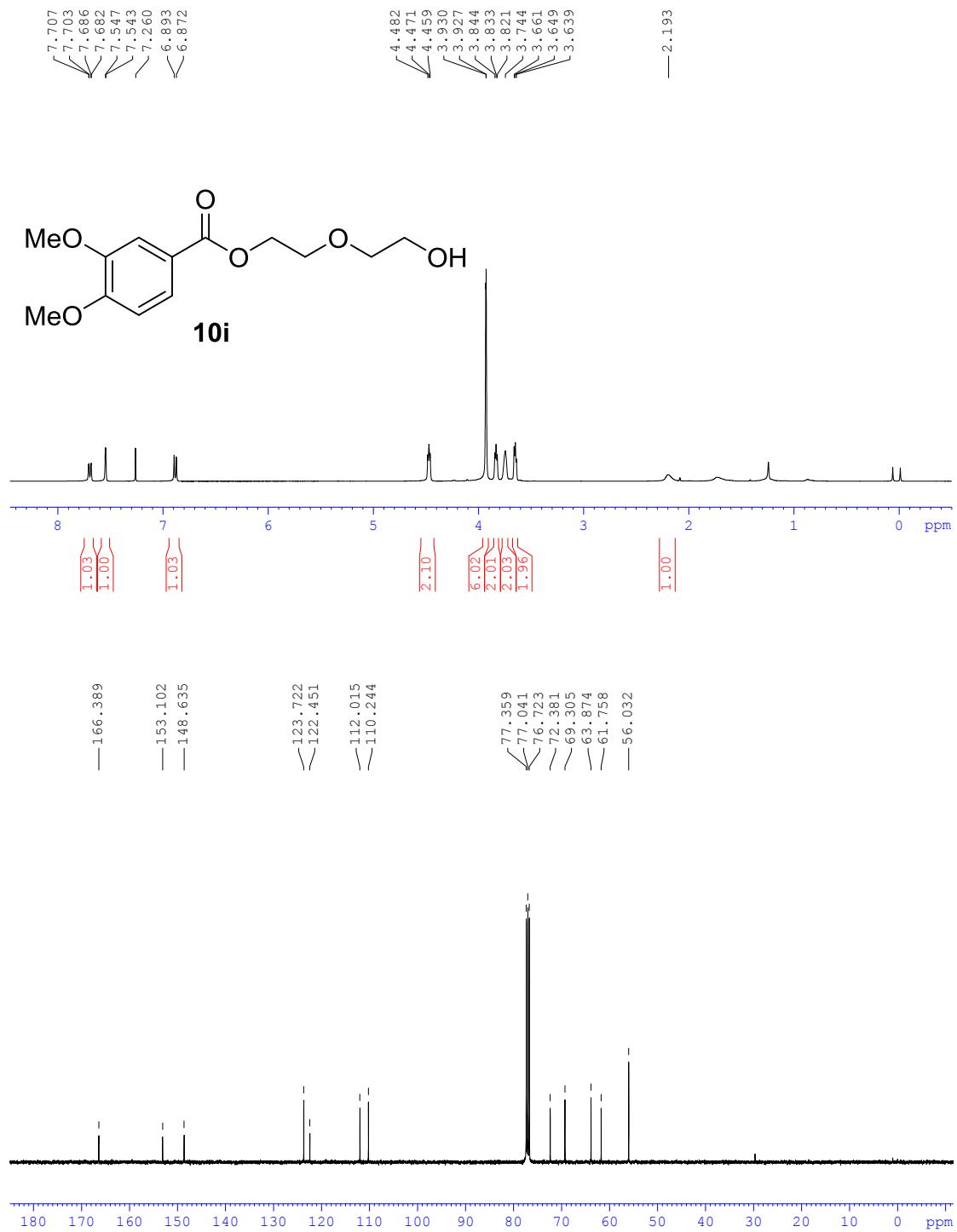


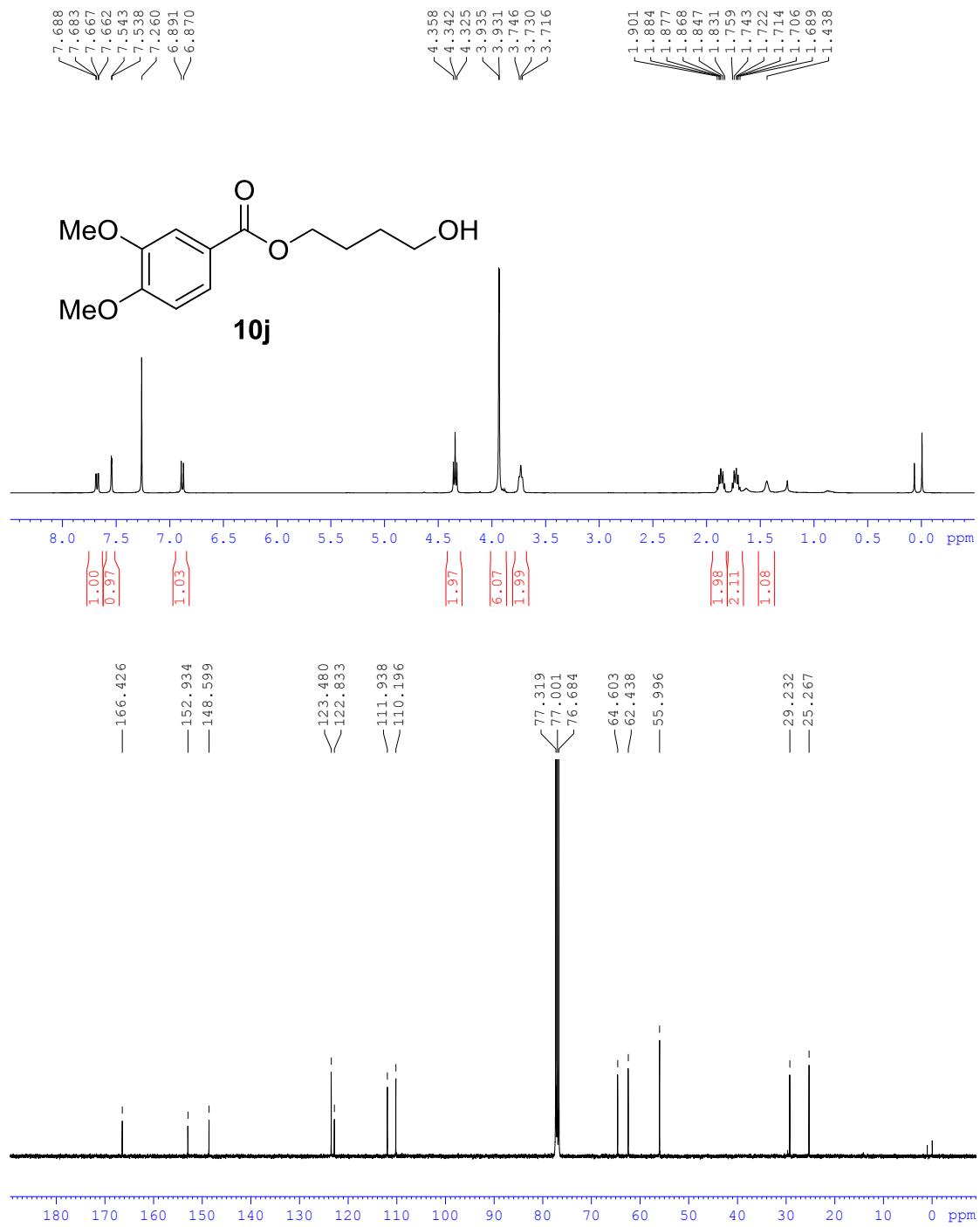


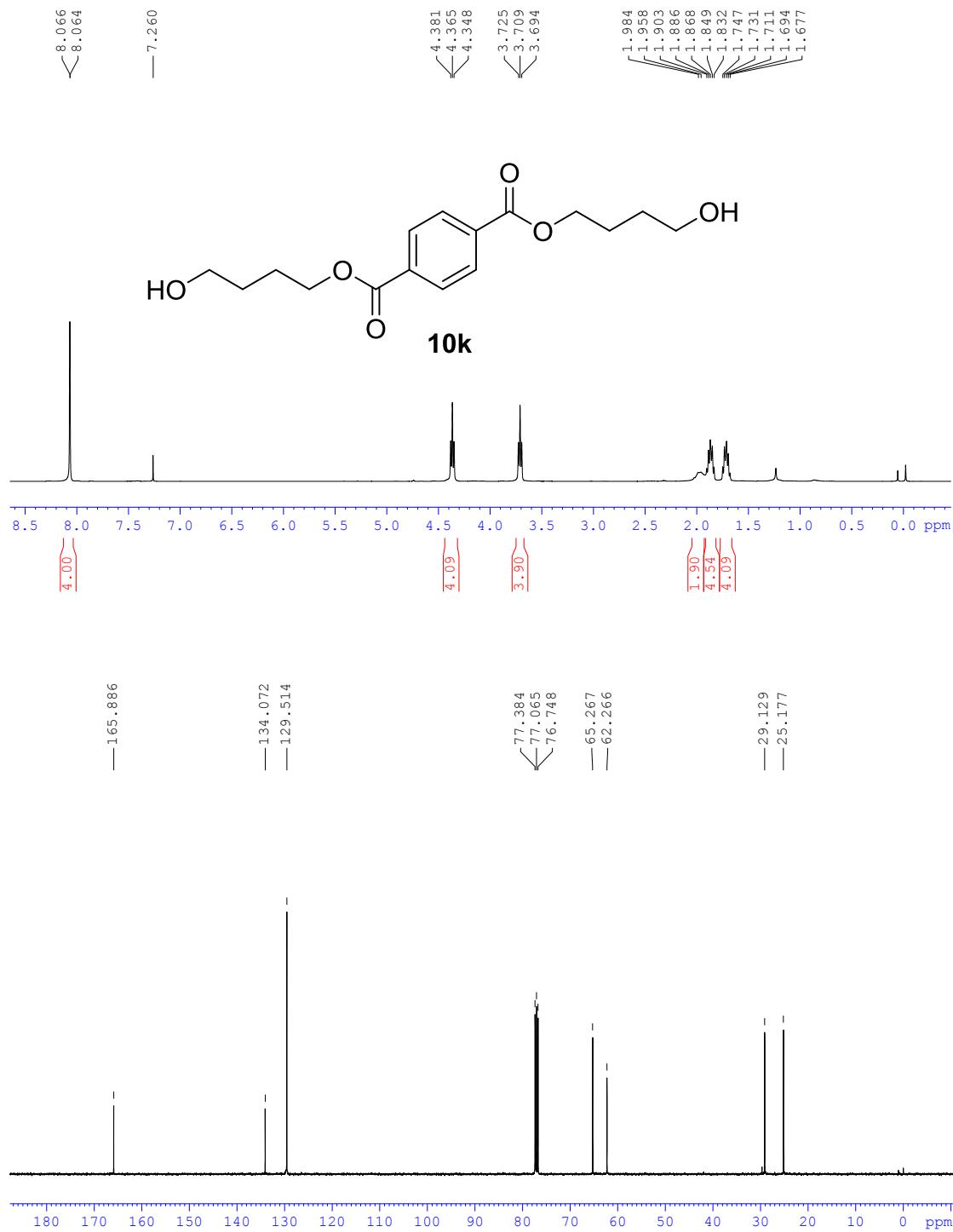




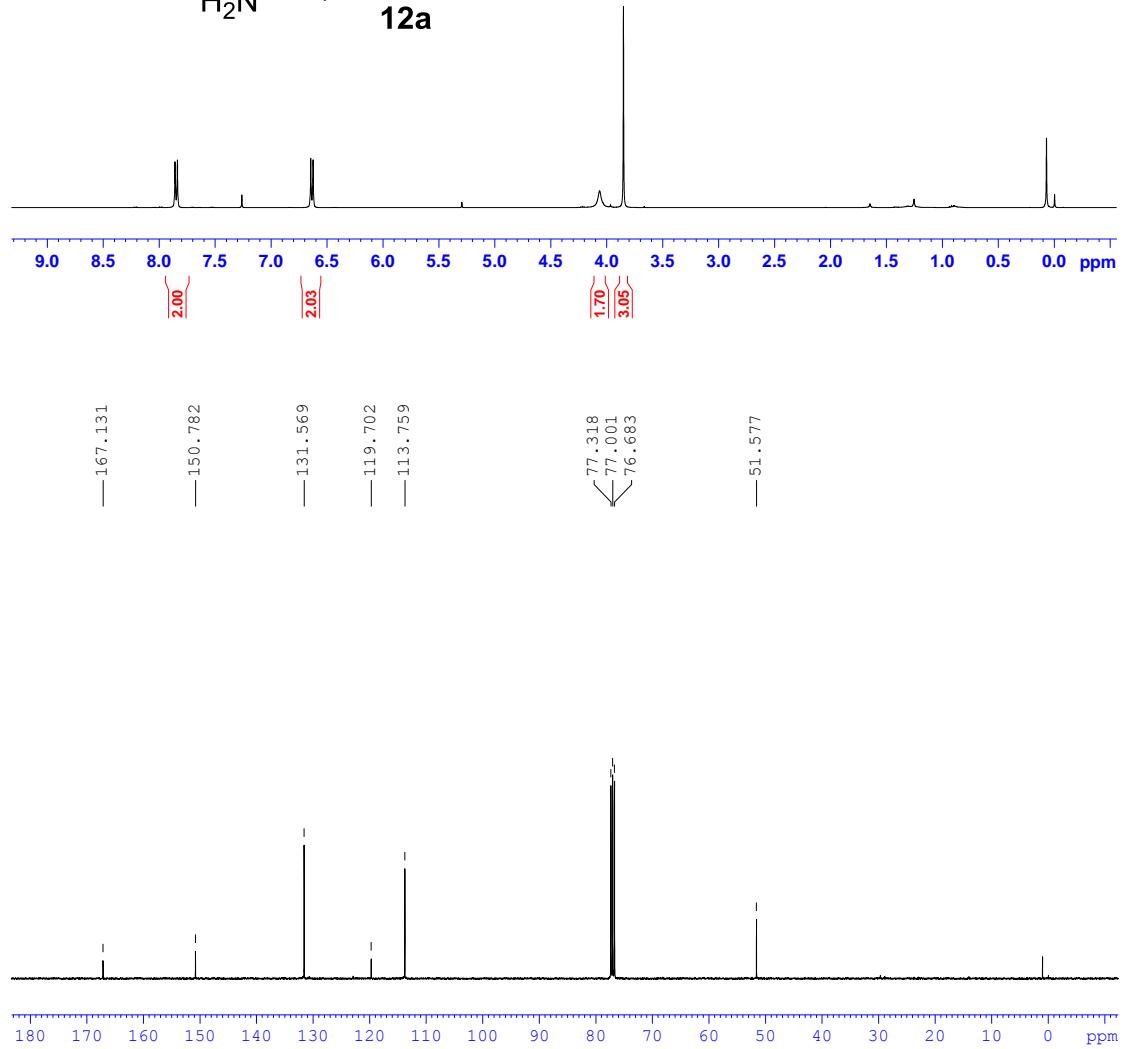
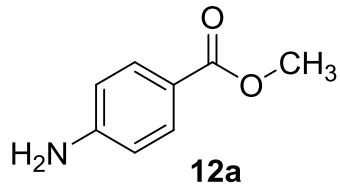


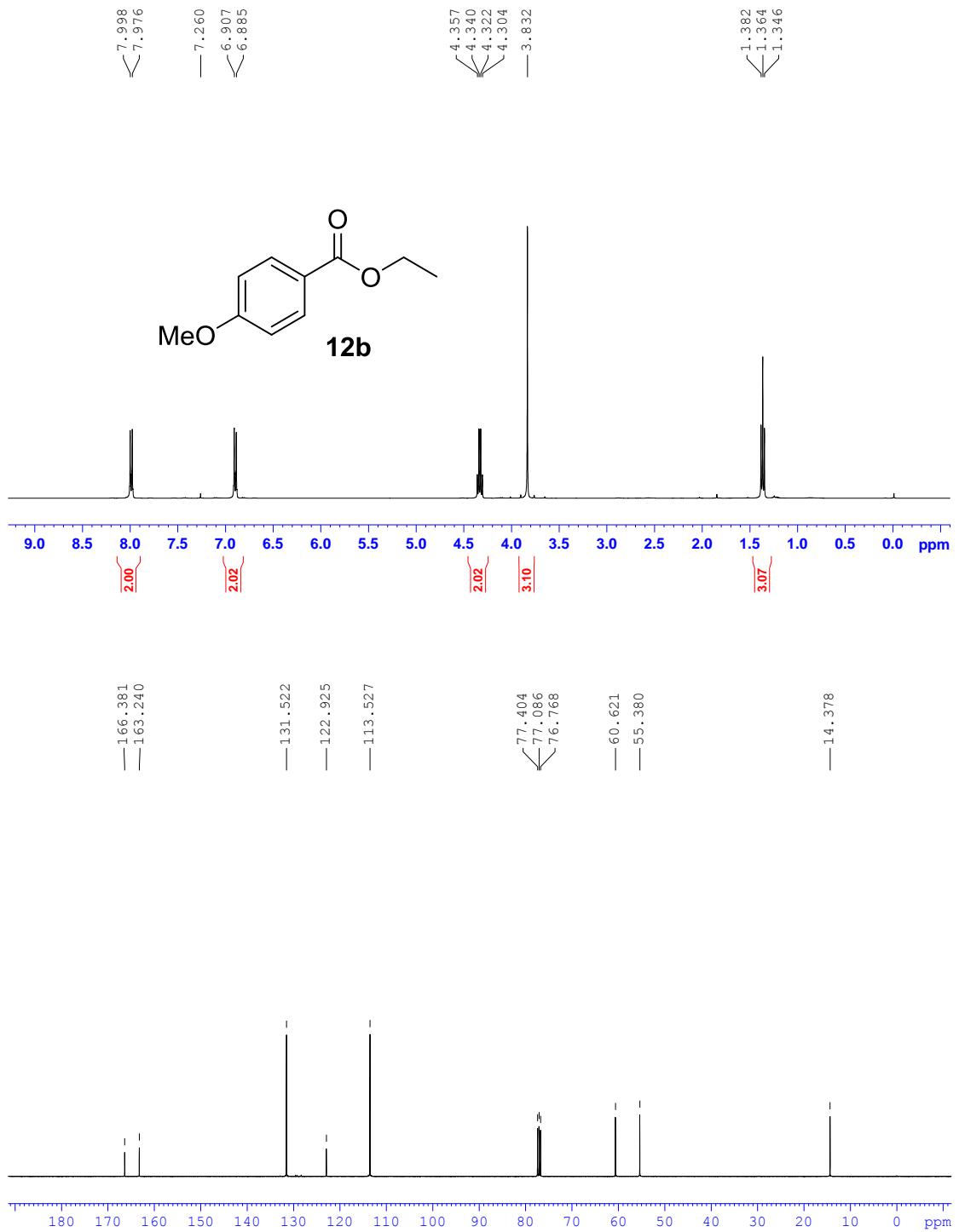


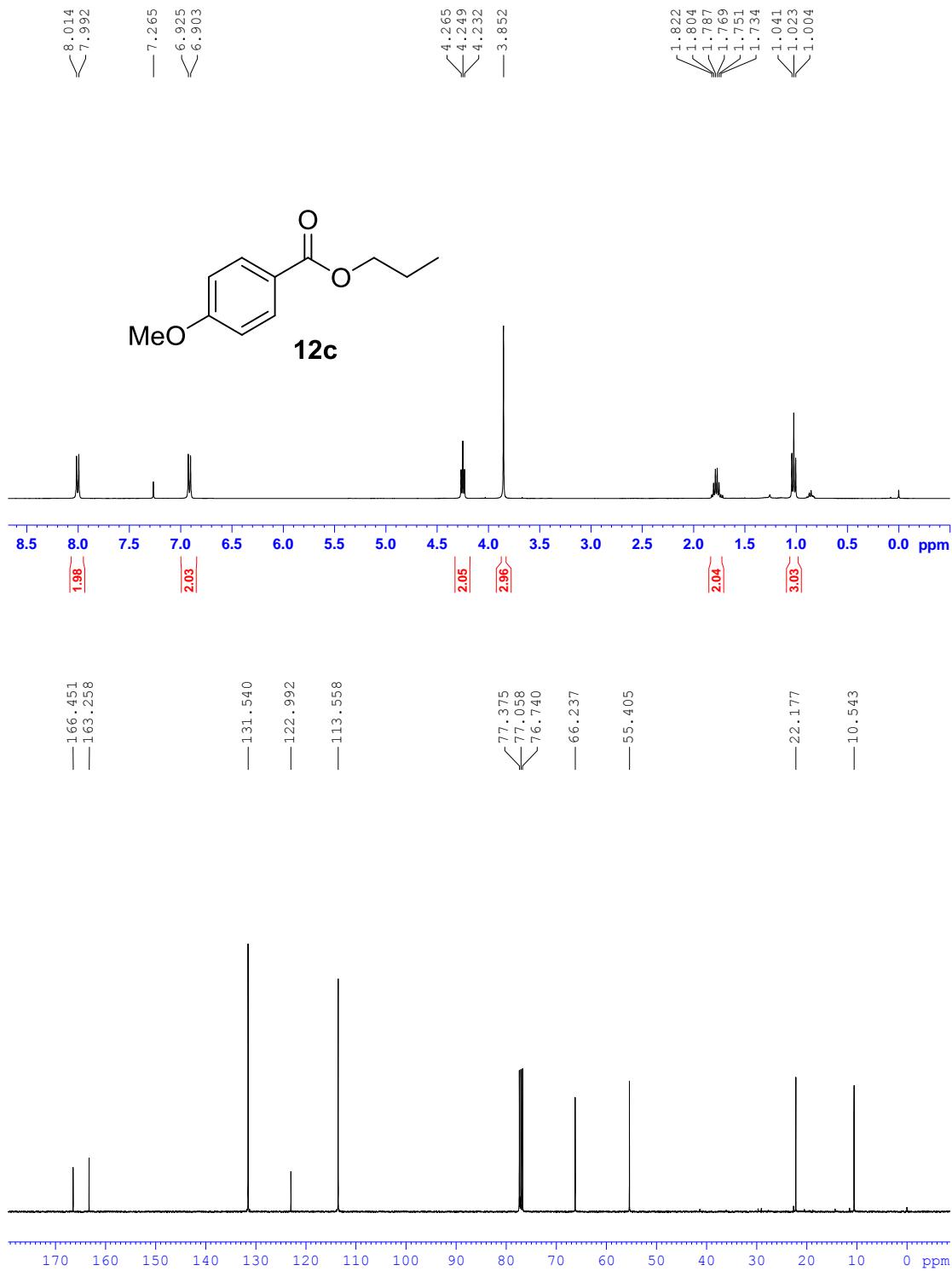
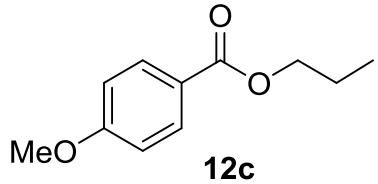


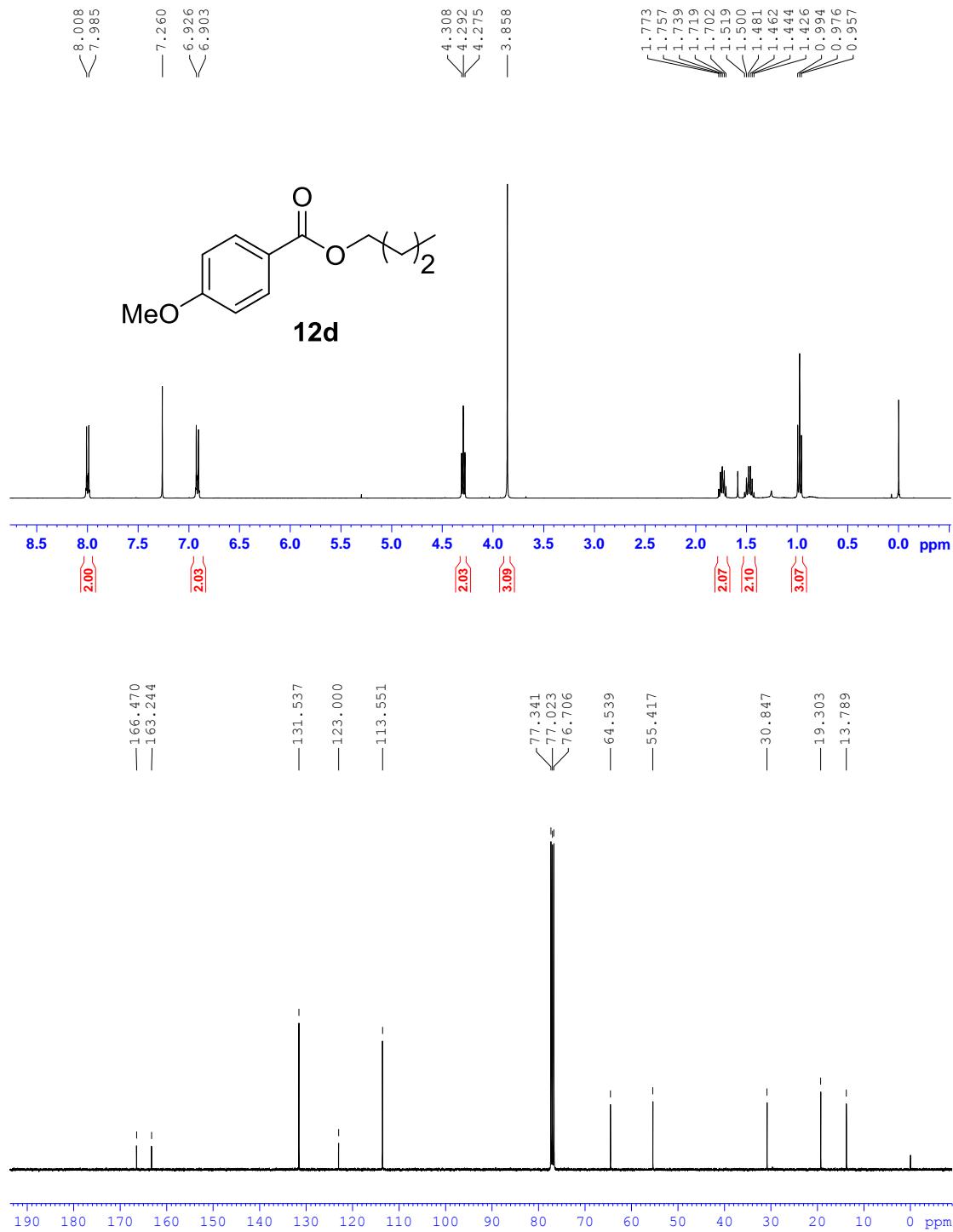


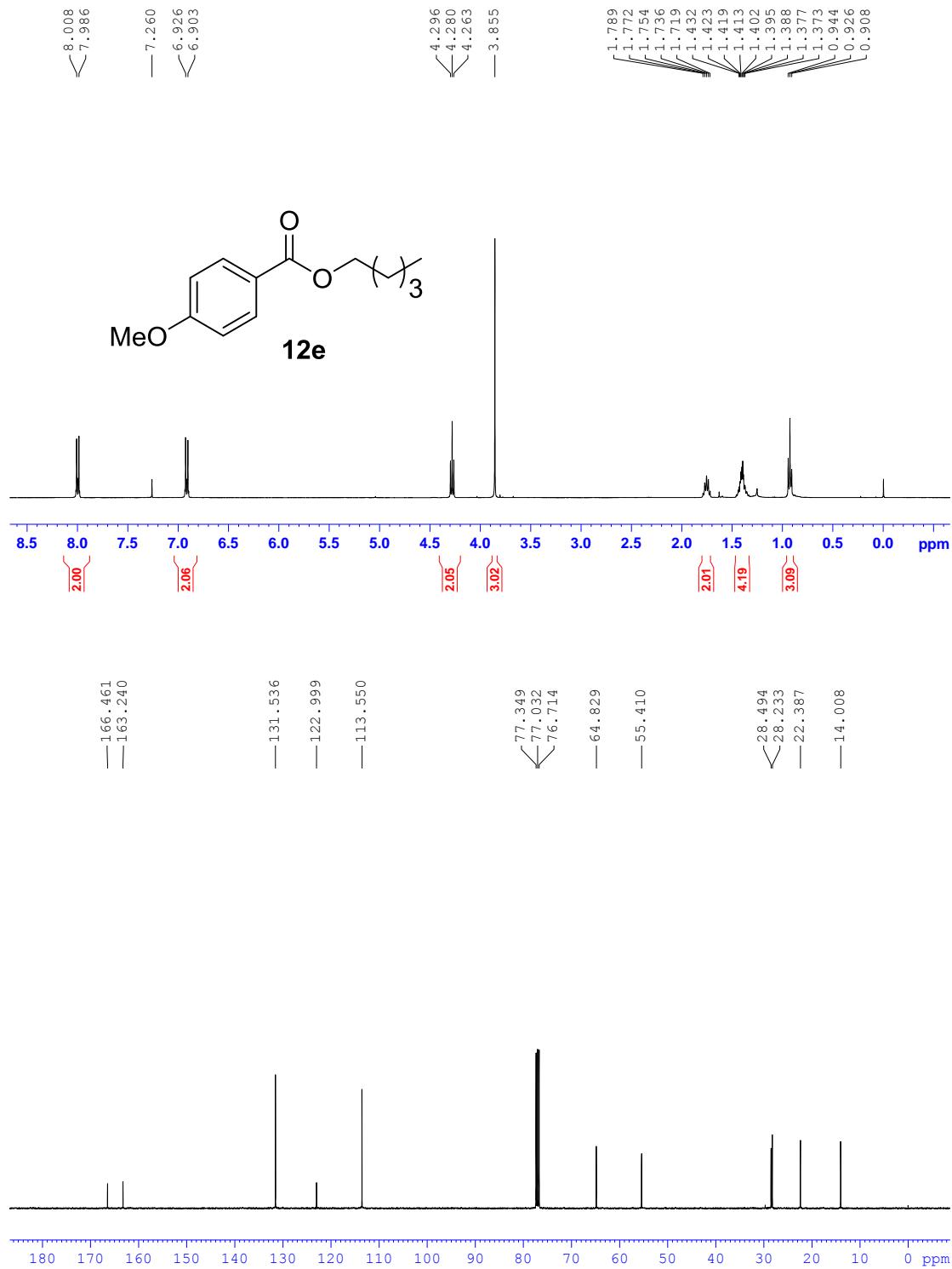
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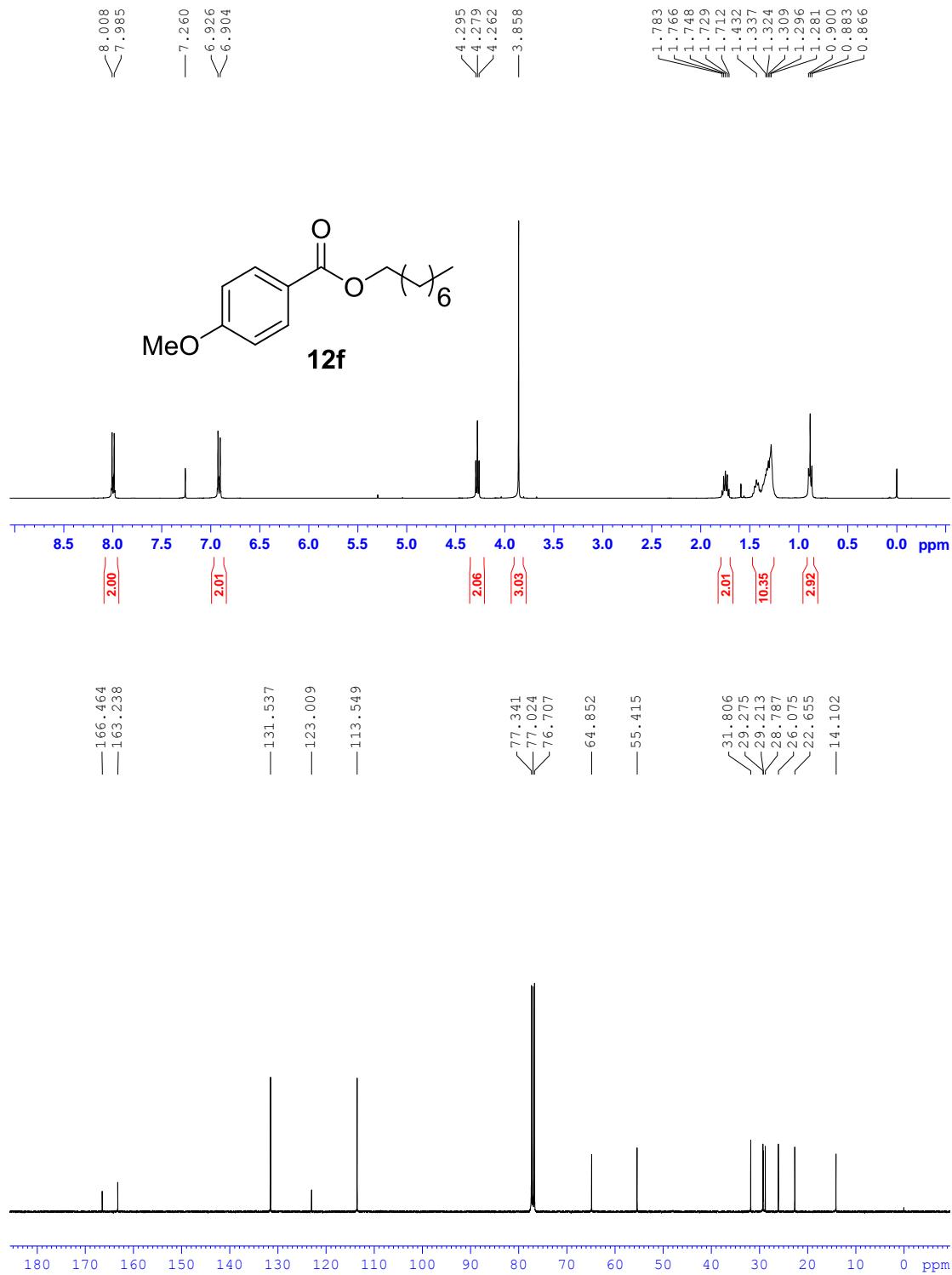


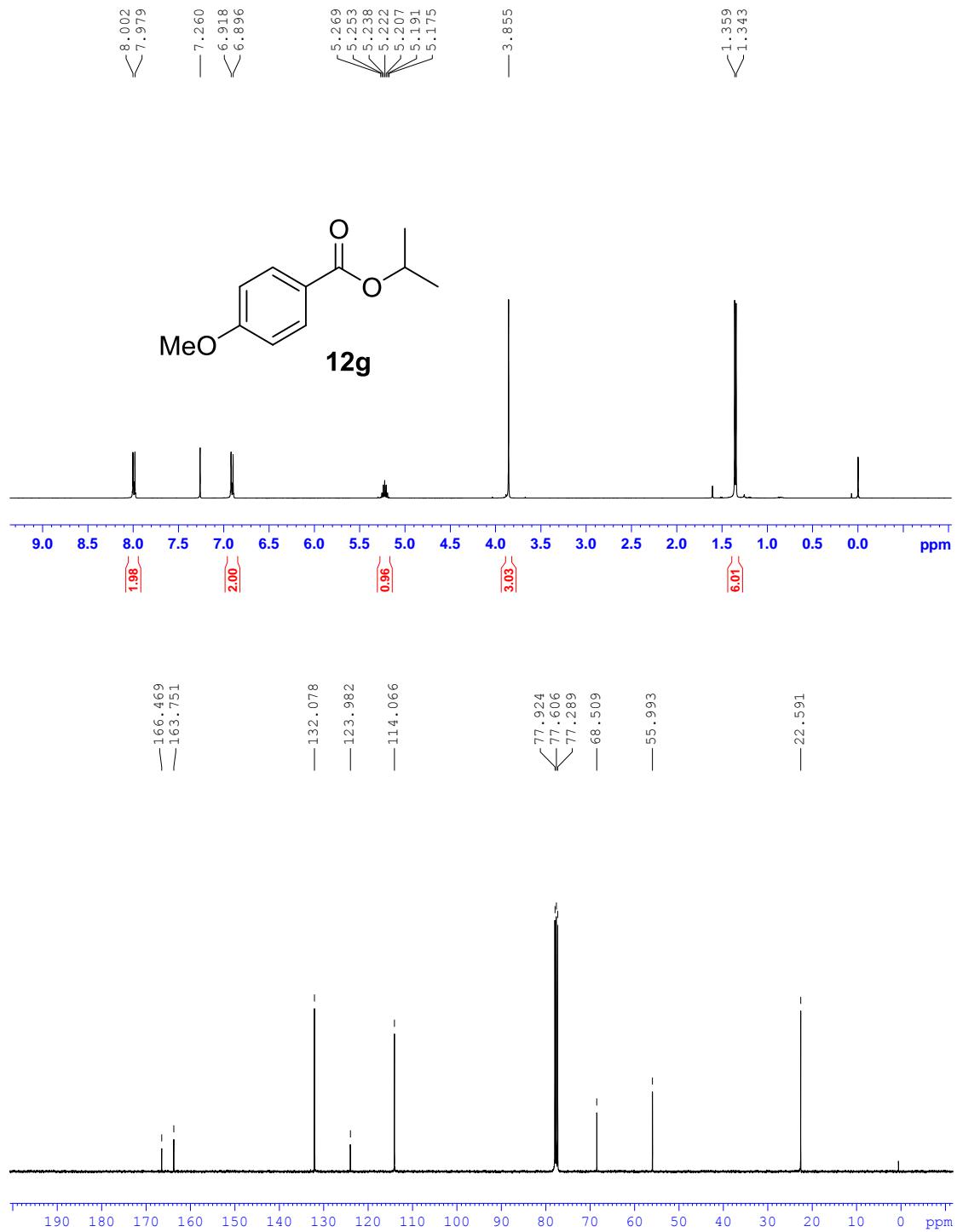


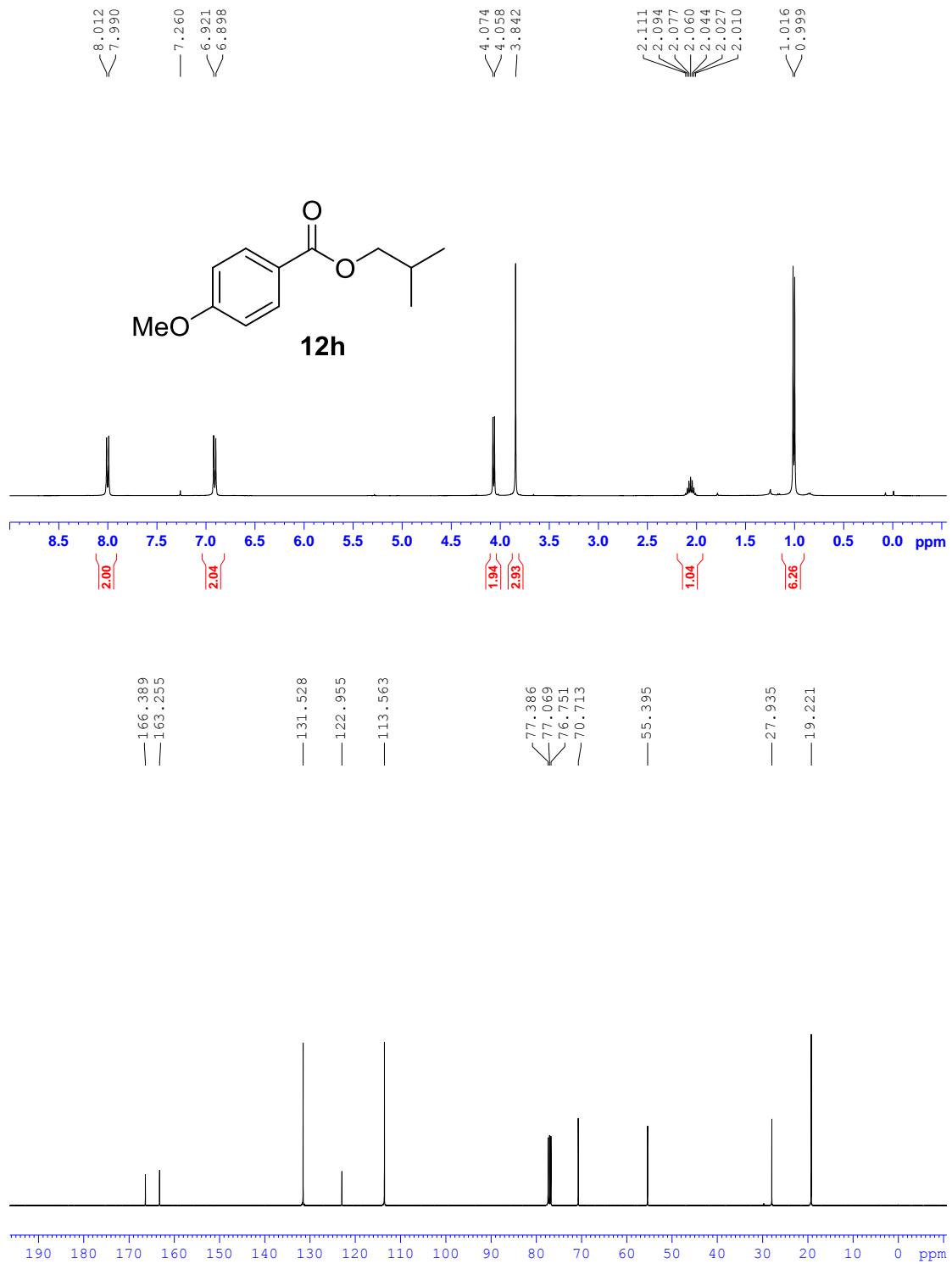


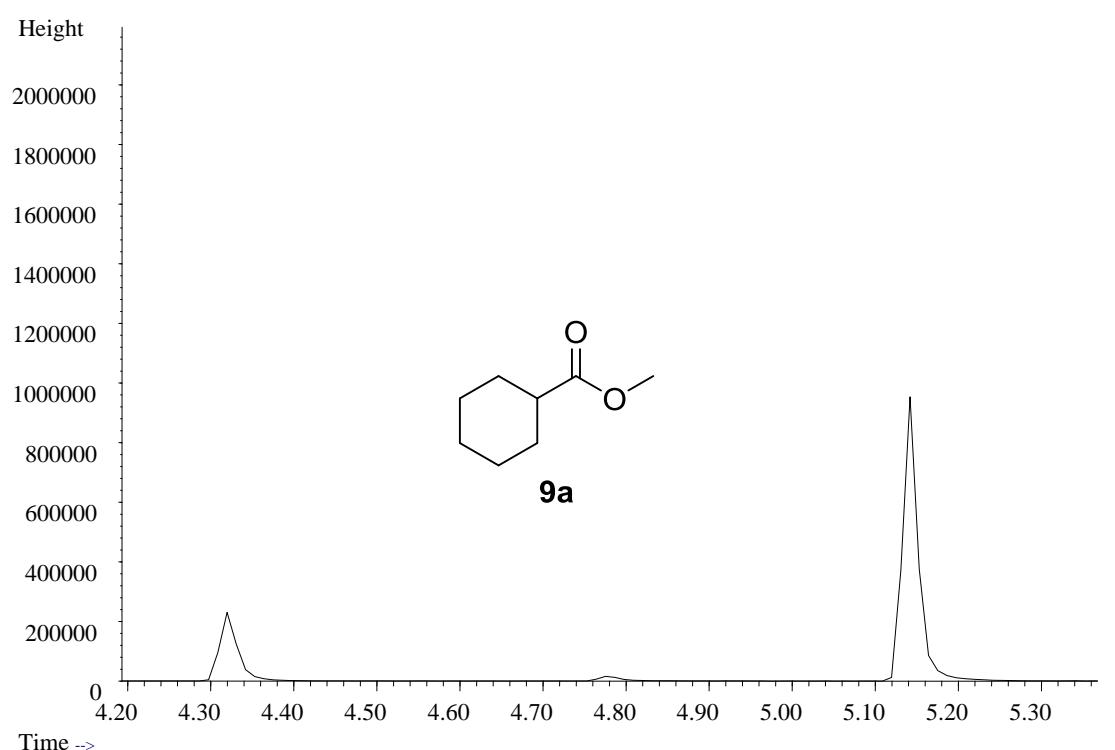








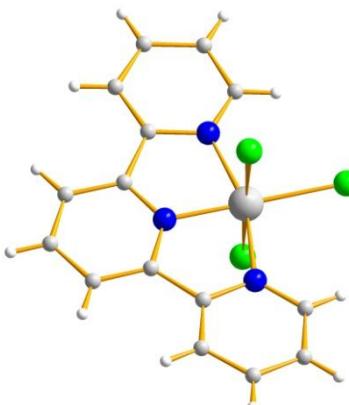
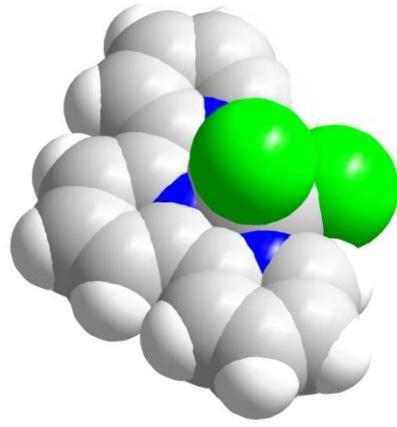




	Time	Area	Area%
1	4.320	348437	21.2
2	4.775	32484	2.0
3	5.142	1260619	76.8

1: cyclohexanecarbaldehyde, 2: cyclohexylmethanol, 3: methyl cyclohexanecarboxylate.

#### 14. Crystallographic data for complex **11**\*

<p><math>C_{15}H_{11}Cl_3N_3Rh</math>  <math>M = 442.53</math>  <math>0.30 \times 0.30 \times 0.20 \text{ mm}^3</math>          Monoclinic, space group <math>P21/n</math>  <math>a = 8.5110(10) \text{ \AA}</math>  <math>b = 13.8850(10) \text{ \AA}</math>  <math>c = 13.7120(10) \text{ \AA}</math>  <math>\alpha = 90^\circ</math>  <math>\beta = 105.412(9)^\circ</math>  <math>\gamma = 90^\circ</math>  <math>V = 1562.1(2) \text{ \AA}^3</math>  <math>Z = 4</math>  <math>D_c = 1.882 \text{ g/cm}^3</math>  <math>T = 298(2) \text{ K}</math>  <math>2\theta_{\max} = 51.2^\circ</math>          16682 reflections collected,          2935 unique          Multiscan absorption correction  <math>R_{\text{int}} = 0.0829</math>          Final <math>GooF = 1.067</math>  <math>RI = 0.0645</math>  <math>wR2 = 0.1591</math>          199 parameters, 0 restraints  <math>\mu = 1.603 \text{ mm}^{-1}</math></p>	 
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\*The structure of **11** has been determined, see: F. P. Pruchnik, P. Jakimowicz, Z. Ciunik, J. Zakrzewska-Czerwinska, A. Opolski, J. Wietrzyk, E. Wojdat, *Inorg. Chim. Acta.* **2002**, *334*, 59.

Table 1. Crystal data and structure refinement for **11**.

Identification code	11
Empirical formula	$C_{15}H_{11}Cl_3N_3Rh$
Formula weight	442.53
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	$a = 8.5110(10) \text{ \AA}$ $\beta = 90^\circ$

	$b = 13.8850(10) \text{ \AA}$	$= 105.412(9)^\circ$
	$c = 13.7120(10) \text{ \AA}$	$= 90^\circ$
Volume	$1562.1(2) \text{ \AA}^3$	
Z	4	
Density (calculated)	$1.882 \text{ Mg/m}^3$	
Absorption coefficient	$1.603 \text{ mm}^{-1}$	
F(000)	872	
Crystal size	$0.30 \times 0.30 \times 0.20 \text{ mm}^3$	
Theta range for data collection	3.31 to $25.60^\circ$	
Index ranges	$-10 \leq h \leq 10, -16 \leq k \leq 16, -16 \leq l \leq 16$	
Reflections collected	16682	
Independent reflections	2935 [ $R(\text{int}) = 0.0829$ ]	
Completeness to theta = $25.60^\circ$	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7398 and 0.6448	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	2935 / 0 / 199	
Goodness-of-fit on $F^2$	1.067	
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0645, wR_2 = 0.1591$	
R indices (all data)	$R_1 = 0.1123, wR_2 = 0.1852$	
Largest diff. peak and hole	1.259 and $-1.112 \text{ e. \AA}^{-3}$	

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for w. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
Rh(1)	4743(1)	1336(1)	7694(1)	43(1)
Cl(1)	2270(3)	1113(2)	6460(2)	60(1)
Cl(3)	3292(4)	1618(2)	8907(2)	75(1)
Cl(2)	7198(4)	1539(2)	8917(2)	75(1)
C(1)	4454(11)	3515(7)	7541(8)	56(2)
C(15)	4479(12)	-672(7)	8515(7)	57(2)
C(8)	7431(14)	706(10)	5255(9)	77(3)
N(2)	5866(8)	1097(5)	6686(5)	41(2)
C(13)	5150(14)	-2080(8)	7728(9)	73(3)
C(6)	6178(11)	1802(7)	6133(7)	53(2)
C(11)	5619(11)	-519(7)	7152(7)	51(2)

C(2)	4644(13)	4407(7)	7120(10)	70(3)
C(12)	5701(12)	-1517(7)	7068(9)	64(3)
C(10)	6202(11)	148(6)	6508(7)	48(2)
N(1)	4926(9)	2708(5)	7188(5)	48(2)
C(9)	7010(14)	-55(8)	5789(8)	69(3)
C(4)	5862(13)	3617(8)	5968(9)	67(3)
N(3)	4972(8)	-124(5)	7853(5)	48(2)
C(7)	7011(12)	1624(9)	5417(7)	64(3)
C(5)	5643(12)	2750(7)	6407(7)	55(2)
C(14)	4576(14)	-1669(8)	8449(10)	74(3)
C(3)	5361(14)	4445(8)	6336(10)	76(3)

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Table 3. Bond lengths [Å] and angles [°] for **11**.

Rh(1)-N(2)	1.907(7)
Rh(1)-N(3)	2.043(7)
Rh(1)-N(1)	2.048(8)
Rh(1)-Cl(2)	2.323(3)
Rh(1)-Cl(1)	2.345(3)
Rh(1)-Cl(3)	2.353(3)
C(1)-N(1)	1.326(12)
C(1)-C(2)	1.393(14)
C(1)-H(1)	0.9300
C(15)-N(3)	1.335(11)
C(15)-C(14)	1.392(15)
C(15)-H(15)	0.9300
C(8)-C(7)	1.358(16)
C(8)-C(9)	1.385(16)
C(8)-H(8)	0.9300
N(2)-C(6)	1.308(12)
N(2)-C(10)	1.384(10)
C(13)-C(14)	1.341(16)
C(13)-C(12)	1.370(16)
C(13)-H(13)	0.9300
C(6)-C(7)	1.378(13)
C(6)-C(5)	1.474(14)
C(11)-N(3)	1.345(11)
C(11)-C(12)	1.394(13)

C(11)-C(10)	1.455(13)
C(2)-C(3)	1.371(16)
C(2)-H(2)	0.9300
C(12)-H(12)	0.9300
C(10)-C(9)	1.373(13)
N(1)-C(5)	1.367(11)
C(9)-H(9)	0.9300
C(4)-C(3)	1.369(16)
C(4)-C(5)	1.381(13)
C(4)-H(4)	0.9300
C(7)-H(7)	0.9300
C(14)-H(14)	0.9300
C(3)-H(3)	0.9300
N(2)-Rh(1)-N(3)	81.5(3)
N(2)-Rh(1)-N(1)	79.5(3)
N(3)-Rh(1)-N(1)	161.0(3)
N(2)-Rh(1)-Cl(2)	91.0(2)
N(3)-Rh(1)-Cl(2)	90.1(2)
N(1)-Rh(1)-Cl(2)	89.8(2)
N(2)-Rh(1)-Cl(1)	88.9(2)
N(3)-Rh(1)-Cl(1)	89.3(2)
N(1)-Rh(1)-Cl(1)	90.7(2)
Cl(2)-Rh(1)-Cl(1)	179.39(10)
N(2)-Rh(1)-Cl(3)	178.5(2)
N(3)-Rh(1)-Cl(3)	98.2(2)
N(1)-Rh(1)-Cl(3)	100.7(2)
Cl(2)-Rh(1)-Cl(3)	90.56(11)
Cl(1)-Rh(1)-Cl(3)	89.60(10)
N(1)-C(1)-C(2)	121.4(10)
N(1)-C(1)-H(1)	119.3
C(2)-C(1)-H(1)	119.3
N(3)-C(15)-C(14)	119.2(10)
N(3)-C(15)-H(15)	120.4
C(14)-C(15)-H(15)	120.4
C(7)-C(8)-C(9)	120.9(10)
C(7)-C(8)-H(8)	119.5
C(9)-C(8)-H(8)	119.5

C(6)-N(2)-C(10)	121.8(8)
C(6)-N(2)-Rh(1)	120.6(6)
C(10)-N(2)-Rh(1)	117.4(6)
C(14)-C(13)-C(12)	120.0(11)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
N(2)-C(6)-C(7)	120.1(9)
N(2)-C(6)-C(5)	113.3(8)
C(7)-C(6)-C(5)	126.4(10)
N(3)-C(11)-C(12)	120.3(10)
N(3)-C(11)-C(10)	116.4(8)
C(12)-C(11)-C(10)	123.3(9)
C(3)-C(2)-C(1)	118.9(10)
C(3)-C(2)-H(2)	120.5
C(1)-C(2)-H(2)	120.5
C(13)-C(12)-C(11)	118.6(11)
C(13)-C(12)-H(12)	120.7
C(11)-C(12)-H(12)	120.7
C(9)-C(10)-N(2)	119.3(9)
C(9)-C(10)-C(11)	128.5(9)
N(2)-C(10)-C(11)	112.3(8)
C(1)-N(1)-C(5)	119.4(8)
C(1)-N(1)-Rh(1)	127.3(7)
C(5)-N(1)-Rh(1)	113.3(6)
C(10)-C(9)-C(8)	118.1(10)
C(10)-C(9)-H(9)	120.9
C(8)-C(9)-H(9)	120.9
C(3)-C(4)-C(5)	118.7(11)
C(3)-C(4)-H(4)	120.7
C(5)-C(4)-H(4)	120.7
C(15)-N(3)-C(11)	121.1(8)
C(15)-N(3)-Rh(1)	126.9(7)
C(11)-N(3)-Rh(1)	112.0(6)
C(8)-C(7)-C(6)	119.5(10)
C(8)-C(7)-H(7)	120.3
C(6)-C(7)-H(7)	120.3
N(1)-C(5)-C(4)	121.3(10)
N(1)-C(5)-C(6)	113.2(8)

C(4)-C(5)-C(6)	125.5(10)
C(13)-C(14)-C(15)	120.7(11)
C(13)-C(14)-H(14)	119.6
C(15)-C(14)-H(14)	119.6
C(4)-C(3)-C(2)	120.3(10)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9

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