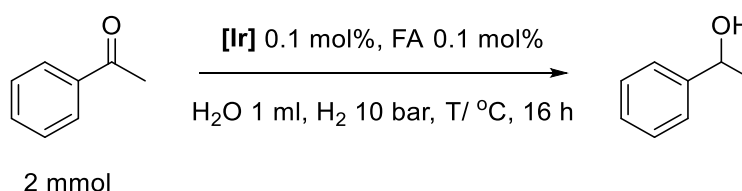


# Base-free reduction of ketones using a bpy-iridium catalyst. Focus on the synthesis of $\gamma$ -valerolactone General Information

Liwei Guo, Zilong Li, Remi Marchal, Boris Le Guennic and C. Fischmeister \*

All reactions were carried out with dried glassware using pressure resistant ACE tubes<sup>®</sup> flushed with argon for transfer hydrogenation reactions using formic acid as dihydrogen donor. A polycarbonate protection shield was systematically used due to pressure generation in the tubes. Hydrogenation reactions were carried in 22 mL Parr<sup>®</sup> reactors. NMR spectra were recorded on Bruker spectrometers Avance I 300 MHz or Avance III 400 MHz. Coupling constants ( $j$ ) and chemical shifts ( $\delta$ ) are given in Hz and ppm respectively. Chemical shifts are given vs TMS using the residual signal of deuterated solvents. The peak patterns are indicated as follows (s- singlet, d- doublet, t- triplet, q- quadrat, quin-quintet, m- multiplet, and br- broad peak). All reagent were obtained from commercial sources and used as received. Catalysts **Ir1**, **Ir2** and **Ir3** were prepared as reported in *Organometallics*, 2017, 36, 3152; *ChemSusChem*, 2019, 12, 179; *ACS Catal*, 2023, 13, 13626 and **Ir4** as reported in *Adv. Synth. Catal.*, 2003, 345, 497.

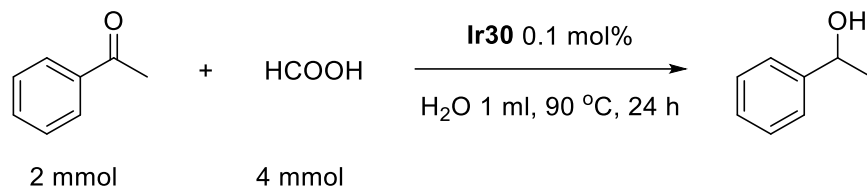
## 1 General procedure A for hydrogenation of ketones



A GC vial was loaded with the catalyst **Ir4** (1.3 mg, 0.1 mol%, 2 mmol) and a magnetic stirring bar. The catalyst was dissolved in water (1.0 mL) and the substrate (0.24 g, 2 mmol) was added. Finally, the GC vial was installed into a high-pressure reactor which was charged with 10 bar of H<sub>2</sub>. The reaction was stirred (600 rpm) and 90 °C (oil bath temperature) for 16 h.



## 2 General procedure B for transfer hydrogenation of ketones

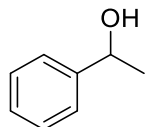


A dried Ace<sup>®</sup> Pressure Tube was loaded with the catalyst **Ir4** (0.1 mol%) and flushed with argon for 2 minutes. Degassed water (1.0 mL) and the substrate (0.24 g, 2 mmol) were added under a flow of argon. Then, formic acid (0.15 mL, 4 mmol, 2 equivalents) was added. Finally, the tube was closed and placed in an oil bath at 90 °C for 24 h, behind a polycarbonate safety shield.



### 3 Product characterization

All the products are known compounds. They were characterized by their  $^1\text{H}$  and  $^{13}\text{C}$  vs reported data or vs commercial references. For reactions with very high conversion (>95%), the product was isolated by simple filtration of the reaction media over Celite. Otherwise, the products were isolated by standard column chromatography on silica gel.

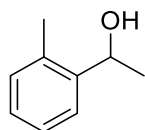


#### 1-phenylethanol 1

The title compound was prepared according to the general procedure A and purification by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a light-yellow oil, 94% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.35 (m, 4H), 7.34 – 7.27 (m, 1H), 4.83 (q,  $J = 6.0$  Hz, 1H), 3.26 (s, 1H), 1.48 (d,  $J = 6.0$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 128.3, 127.2, 125.4, 70.0, 25.1.

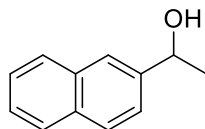


#### 1-(*o*-tolyl)-ethanol 2

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a light-yellow oil, 92% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (dd,  $J = 7.6, 1.5$  Hz, 1H), 7.25 (td,  $J = 7.4, 1.7$  Hz, 1H), 7.19 (td,  $J = 7.3, 1.5$  Hz, 1H), 7.17 – 7.12 (m, 1H), 5.10 (q,  $J = 6.4$  Hz, 1H), 2.35 (s, 3H), 1.46 (d,  $J = 6.4$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 134.2, 130.4, 127.1, 126.4, 124.6, 66.8, 23.9, 18.9.

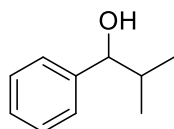


#### 1-(naphthalen-2-yl)ethan-1-ol 4

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a light-yellow solid, 70% yield.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (dd,  $J = 8.9, 3.1$  Hz, 4H), 7.55 – 7.45 (m, 3H), 5.08 (qd,  $J = 6.4, 3.4$  Hz, 1H), 1.91 (d,  $J = 3.4$  Hz, 1H), 1.59 (d,  $J = 6.4$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.3, 133.5, 128.5, 128.1, 127.8, 126.3, 126.0, 124.0, 70.7, 25.3.

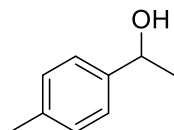


#### 2-methyl-1-phenylpropan-1-ol 5

The title compound was prepared according to the general procedure A with 0.2 mol% **Ir4** and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a light-yellow oil, 53% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.23 (m, 5H), 4.32 (dd,  $J = 7.0, 2.4$  Hz, 1H), 2.04 – 1.87 (m, 1H), 1.01 (d,  $J = 6.7$  Hz, 3H), 0.81 (d,  $J = 6.8$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.7, 128.2, 127.4, 126.7, 80.0, 35.3, 19.0, 18.4.

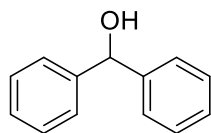


#### 1-(p-tolyl)ethan-1-ol 6

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a light-yellow oil, 80% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (d,  $J = 7.4$  Hz, 2H), 7.03 (d,  $J = 7.4$  Hz, 2H), 4.68 (q,  $J = 6.5$  Hz, 1H), 2.23 (s, 3H), 1.33 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 137.0, 129.1, 125.4, 70.1, 25.1, 21.1.

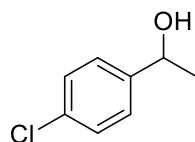


### Diphenylmethanol 7

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a white solid, 10% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.70 (m, 8H), 7.22 – 7.35 (m, 2H), 5.85 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 128.6, 127.7, 126.7, 76.4.

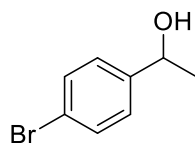


### 1-(4-chlorophenyl)-ethanol 8

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a light-yellow oil, 77% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 7.12 (m, 4H), 4.71 (q,  $J$  = 6.5 Hz, 1H), 1.33 (dd,  $J$  = 6.5, 1.1 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 133.1, 128.7, 126.9, 69.8, 25.3.

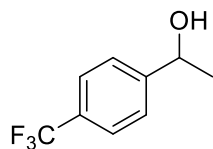


### 1-(4-bromophenyl)-ethanol 9

The title compound was prepared according to the general procedure A with 0.2 mol% **Ir4** and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a light-yellow oil, 47% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d, 6.5 Hz, 2H), 7.39 (d, 6.5 Hz, 2H), 7.23 – 7.15 (m, 2H), 4.78 (q,  $J$  = 7.5 Hz, 1H), 1.41 (dd,  $J$  = 7.5, 1.2 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.8, 131.6, 127.2, 121.1, 69.7, 25.2.

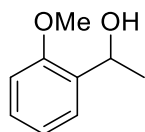


### 1-(4-(Trifluorophenyl)-ethanol **10**

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a colorless liquid, 79% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J$  = 8.0 Hz, 2H), 7.45 (d,  $J$  = 8.0 Hz, 2H), 4.91 (q,  $J$  = 6.6 Hz, 1H), 1.47 (dd,  $J$  = 6.5, 1.1 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8, 129.6 (q,  $^2J_{\text{C-F}}$  = 32.4 Hz), 125.7, 125.4 (q,  $^3J_{\text{C-F}}$  = 3.8 Hz), 124.2 (q,  $^1J_{\text{C-F}}$  = 273.0 Hz), 69.9, 25.4.

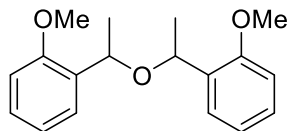


### 1-(2-methoxyphenyl)ethanol

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give the colorless oil, 91% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (dd,  $J$  = 7.6, 1.8 Hz, 1H), 7.25 (ddd,  $J$  = 8.1, 7.4, 1.8 Hz, 1H), 6.97 (td,  $J$  = 7.5, 1.1 Hz, 1H), 6.88 (dd,  $J$  = 8.2, 1.1 Hz, 1H), 5.16 – 5.06 (m, 1H), 3.84 (s, 3H), 1.50 (d,  $J$  = 6.5 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 133.7, 128.2, 126.0, 120.8, 110.4, 66.2, 55.2, 23.0.

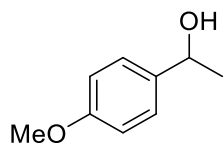


### 2,2'-(oxybis(ethane-1,1-diyl))bis(methoxybenzene) **11'**

The title compound was obtained as a side-product of the synthesis of **11**. It was by column chromatography (Heptane: EtOAc v/v 20:1- 10:1) to give the colorless oil obtained in 3% yield as a pair of diastereoisomers.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (dd,  $J = 7.6, 1.8$  Hz, 1H), 7.54 – 7.47 (m, 1H), 7.28 (ddd,  $J = 8.4, 7.5, 1.9$  Hz, 1H), 7.21 (ddd,  $J = 8.2, 7.4, 1.8$  Hz, 1H), 7.07 (td,  $J = 7.4, 1.1$  Hz, 1H), 6.94 (td,  $J = 7.5, 1.1$  Hz, 1H), 6.85 (ddd,  $J = 18.6, 8.2, 1.1$  Hz, 2H), 4.98 (q,  $J = 6.3$  Hz, 1H), 4.77 (q,  $J = 6.4$  Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 1.47 (d,  $J = 6.3$  Hz, 3H), 1.43 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 156.1, 133.3, 133.3, 127.9, 127.6, 126.7, 126.1, 120.9, 120.7, 110.4, 110.1, 69.5, 68.9, 55.3, 55.2, 23.2, 22.4.

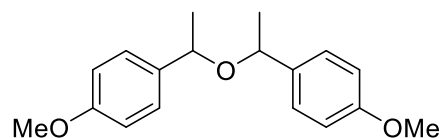


### 1-(4-methoxyphenyl)ethanol **12**

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a colorless oil, 59% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.20 (m, 2H), 6.88 – 6.80 (m, 2H), 4.76 (q,  $J = 6.5$  Hz, 1H), 3.76 (s, 3H), 1.42 (dd,  $J = 6.5, 0.9$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 138.2, 126.7, 113.7, 69.7, 69.7, 55.2, 25.0.

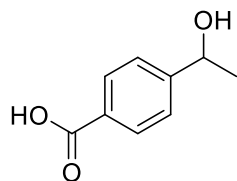


#### 4,4'-(oxybis(ethane-1,1-diyl))bis(methoxybenzene) 12'

The title compound was obtained as a side product of the synthesis of 12 and purified by column chromatography (Heptane: EtOAc v/v 20:1- 10:1) to give a colorless oil, 16% yield. 12' was obtained as a mixture of diastereoisomers.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (dt,  $J = 8.7, 2.1$  Hz, 4H), 6.93 (dd,  $J = 8.6, 1.5$  Hz, 2H), 6.90 – 6.83 (m, 2H), 4.51 (qd,  $J = 6.4, 1.7$  Hz, 1H), 4.23 (qd,  $J = 6.5, 1.9$  Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 1.48 (dd,  $J = 6.4, 1.7$  Hz, 3H), 1.40 (dd,  $J = 6.5, 1.8$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 158.8, 136.5, 136.3, 127.6, 127.5, 113.9, 113.7, 73.9, 73.8, 55.3, 55.3, 24.8, 22.9.

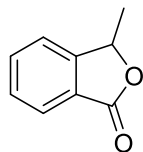


#### 4-(1-hydroxyethyl)benzoic acid 13

The title compound was prepared according to the general procedure B and without purification, light yellow liquid, 96% yield.

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  7.89 (d,  $J = 8.3$  Hz, 2H), 7.45 (d,  $J = 8.2$  Hz, 2H), 5.30 (s, 1H), 4.78 (q,  $J = 6.5$  Hz, 1H), 1.32 (d,  $J = 6.4$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  167.4, 152.5, 129.2, 129.1, 125.4, 67.8, 25.8.

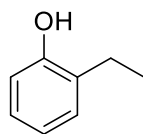


### 3-methylisobenzofuran-1(3H)-one 14

The title compound was prepared according to the general procedure B and obtained without purification as light-yellow oil, 99% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 7.7$ , 1H), 7.67 (td,  $J = 7.5$ , 1.1 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.43 (dt,  $J = 7.6$ , 0.9 Hz, 1H), 5.55 (q,  $J = 6.7$  Hz, 1H), 1.63 (d,  $J = 6.7$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 151.3, 134.2, 129.2, 125.9, 125.8, 121.7, 77.8, 20.5.

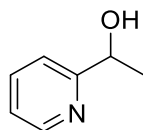


### 2-ethylphenol 15'

The title compound was prepared according to the general procedure A and without purification, light yellow liquid, 97% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (dd,  $J = 7.3$ , 1.7 Hz, 1H), 7.14 (td,  $J = 7.7$ , 1.7 Hz, 1H), 6.95 (td,  $J = 7.5$ , 1.2 Hz, 1H), 6.80 (dd,  $J = 8.0$ , 1.2 Hz, 1H), 5.03 (s, 1H), 2.70 (q,  $J = 7.5$  Hz, 2H), 1.30 (t,  $J = 7.6$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 130.1, 129.4, 127.1, 121.1, 115.3, 23.0, 14.1.

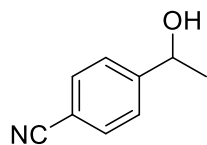


### 1-(pyridin-2-yl)ethan-1-ol 16

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 10:1- 2:1) to give a light-yellow oil, 90% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (bs, 1H), 7.65 (td,  $J = 7.7$ , 1.7 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.16 (dd,  $J = 7.5$ , 4.9 Hz, 1H), 4.87 (q,  $J = 6.6$  Hz, 1H), 1.48 (d,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 148.2, 136.9, 122.3, 119.9, 69.0, 24.3.

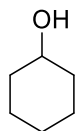


#### 4-(1-hydroxyethyl)benzonitrile 17

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a light-yellow oil, 72% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.50 (m, 2H), 7.45 – 7.38 (m, 2H), 4.87 (bq, 1H), 1.41 (dd,  $J$  = 6.4, 1.9 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.5, 132.2, 126.1, 118.9, 110.5, 69.3, 25.2.

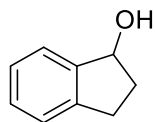


#### Cyclohexanol 18

The title compound was prepared according to the general procedure A and purification by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a colorless liquid, 90% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.57 (dq,  $J$  = 9.1, 4.5 Hz, 1H), 2.14 – 1.94 (m, 1H), 1.86 (dt,  $J$  = 9.9, 4.6 Hz, 2H), 1.71 (dt,  $J$  = 8.5, 4.3 Hz, 2H), 1.51 (dt,  $J$  = 12.6, 4.0 Hz, 1H), 1.37 – 0.99 (m, 5H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  70.4, 35.6, 35.6, 25.6, 24.2.

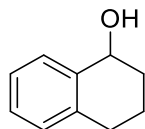


#### 2,3-dihydro-1H-inden-1-ol 19

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a colorless liquid, 88% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (dd,  $J$  = 6.4, 2.1 Hz, 1H), 7.33 – 7.21 (m, 3H), 5.20 (q,  $J$  = 5.7 Hz, 1H), 3.05 (ddd,  $J$  = 16.1, 8.6, 4.7 Hz, 1H), 2.88 – 2.70 (m, 2H), 2.52 – 2.39 (m, 1H), 1.92 (dddd,  $J$  = 13.6, 8.6, 6.7, 5.3 Hz, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.1, 143.3, 128.2, 126.6, 124.8, 124.3, 76.2, 76.2, 35.8, 29.8.



### 1,2,3,4-tetrahydronaphthalen-1-ol 20

The title compound was prepared according to the general procedure A and purified by column chromatography (Heptane: EtOAc v/v 20:1- 5:1) to give a colorless liquid, 82% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (dt,  $J = 6.1, 3.6$  Hz, 1H), 7.28 – 7.17 (m, 2H), 7.13 (dt,  $J = 5.2, 3.5$  Hz, 1H), 4.75 (dd,  $J = 5.5, 3.9$  Hz, 1H), 2.90 – 2.69 (m, 2H), 2.05 – 1.71 (m, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.9, 137.1, 129.0, 128.7, 127.5, 126.1, 68.1, 32.3, 29.3, 18.9.

## 4 Determination of formate amounts

1 Based on dissociation coefficient  $\alpha$

For a weak acid  $K_a = \frac{\alpha^2 C_0}{1-\alpha}$  or  $C_0 \alpha^2 + K_a \alpha - K_a = 0$

$C_0$ neat (4 mmol in 0.35 mL)	11.43 mol.L $^{-1}$
$\alpha$	0.0039
$[\text{HCOO}^-] = \alpha C_0$	0.045 mol.L $^{-1}$
nHCOO $^-$ in 0.35 mL	$\approx$ <b>0.016</b> mmol

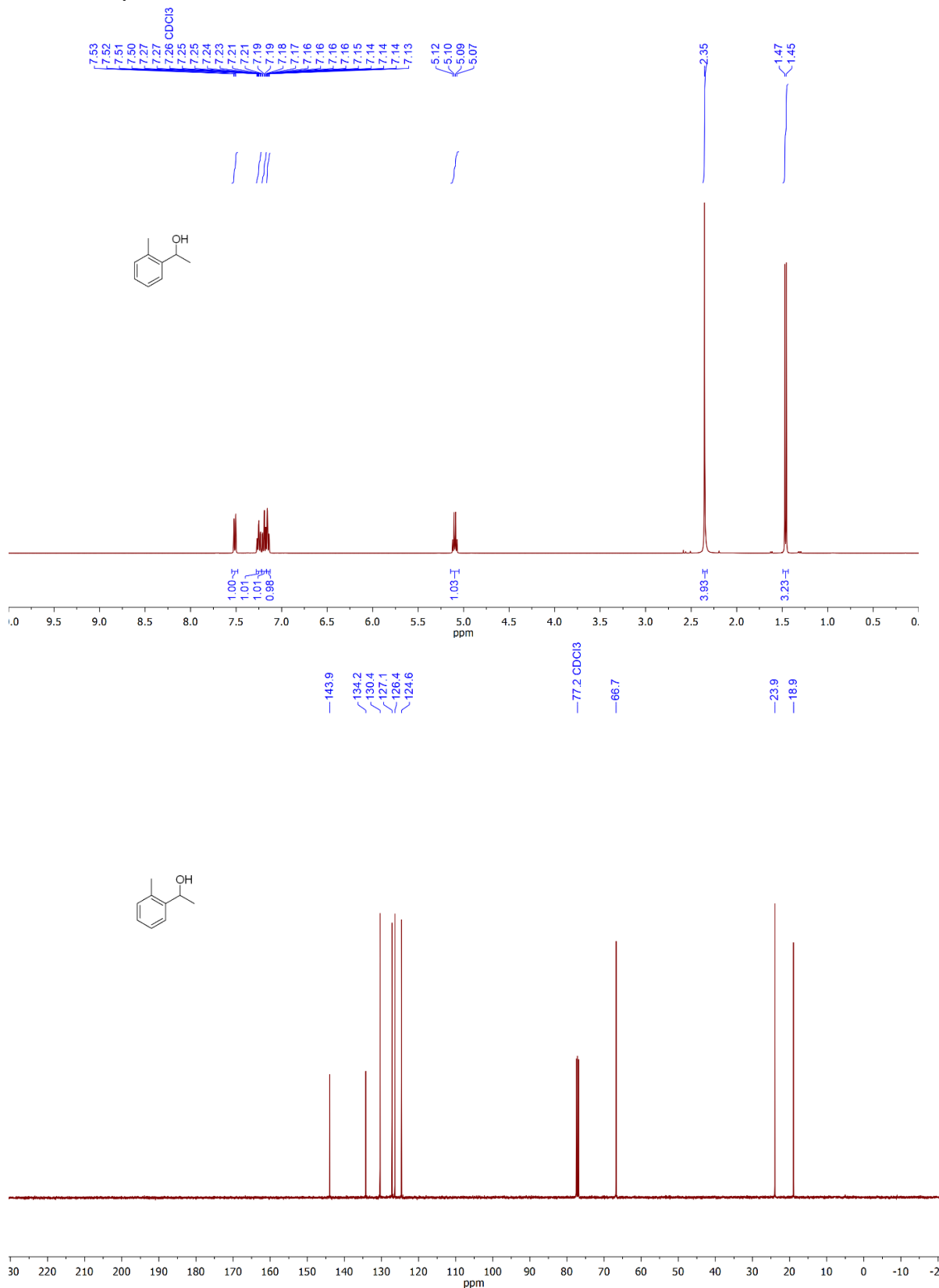
- Based on pH

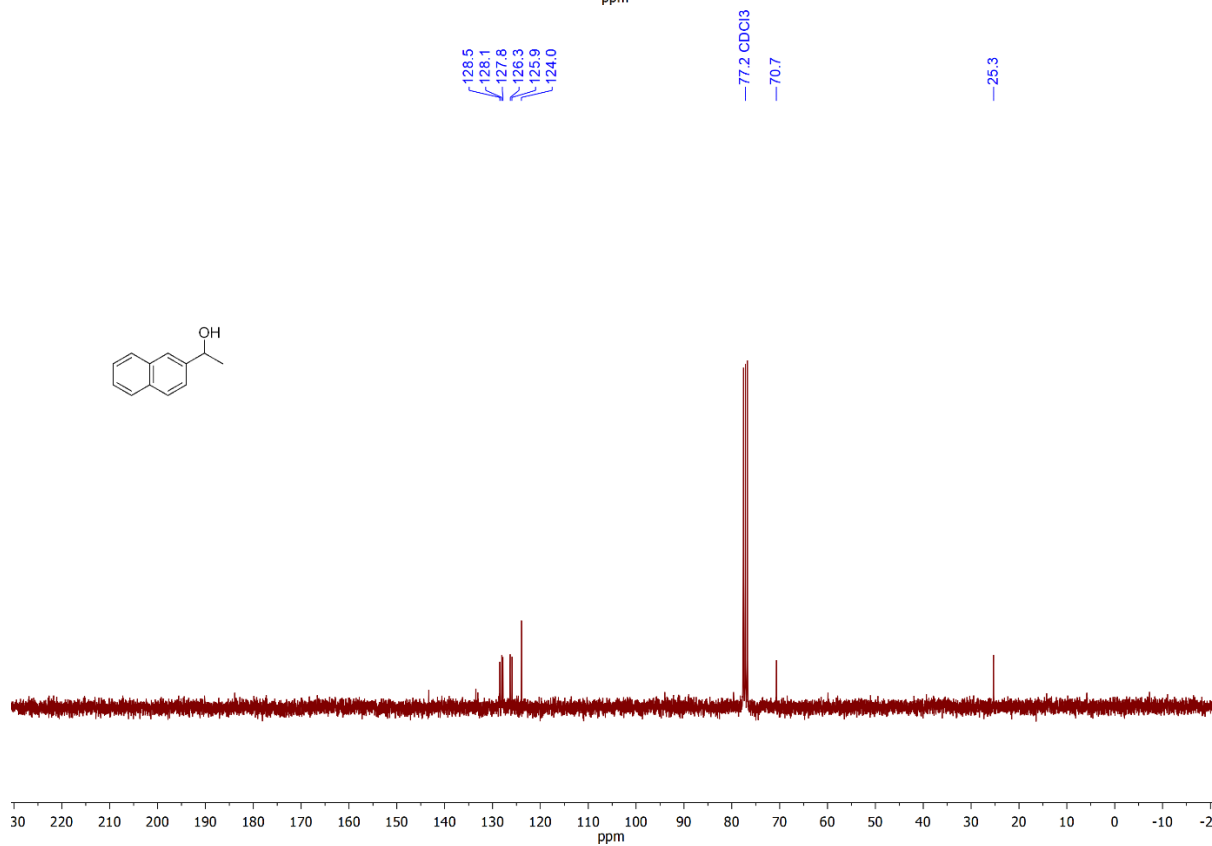
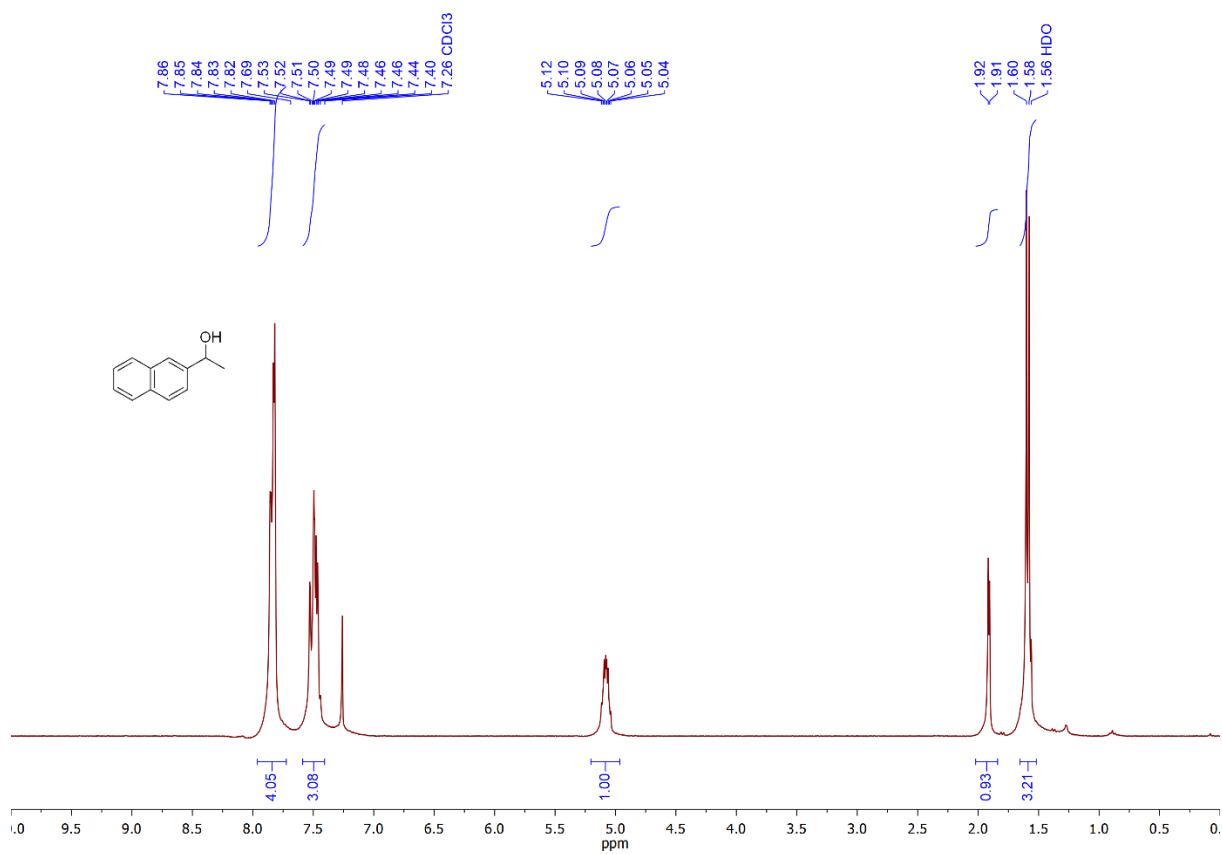
pH exp = 1.2

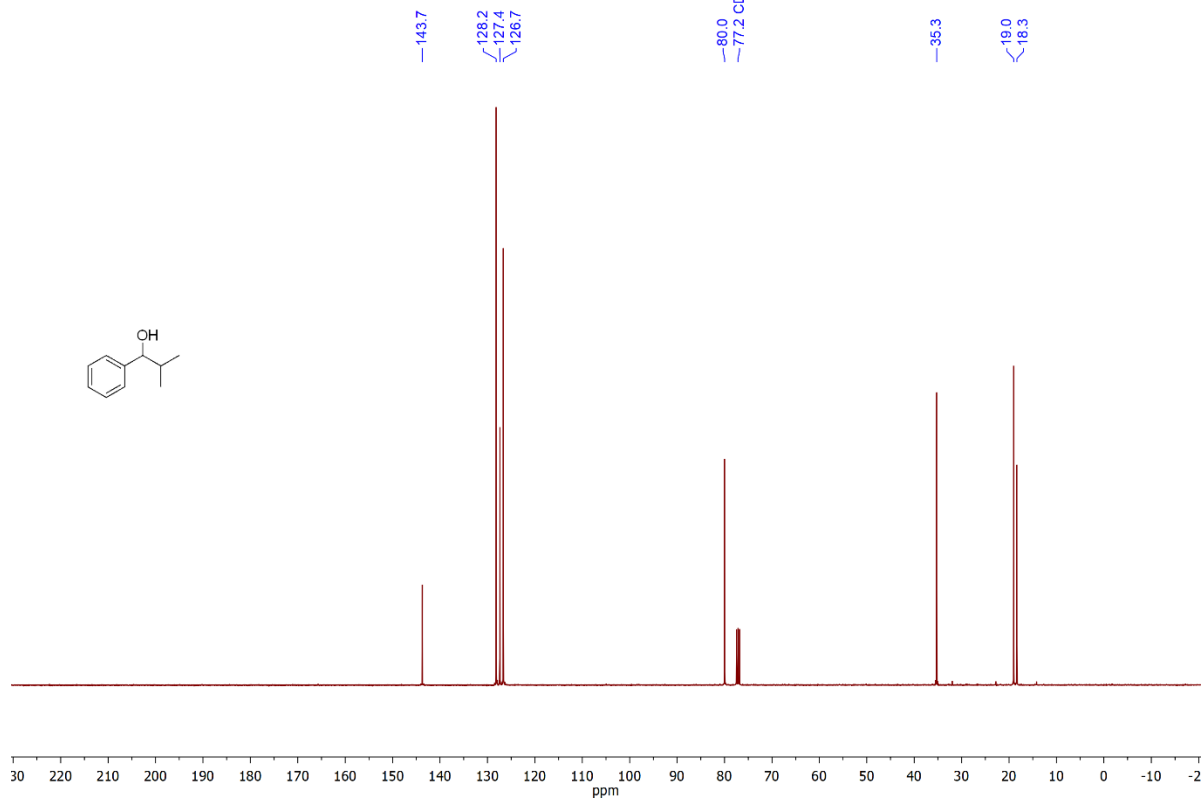
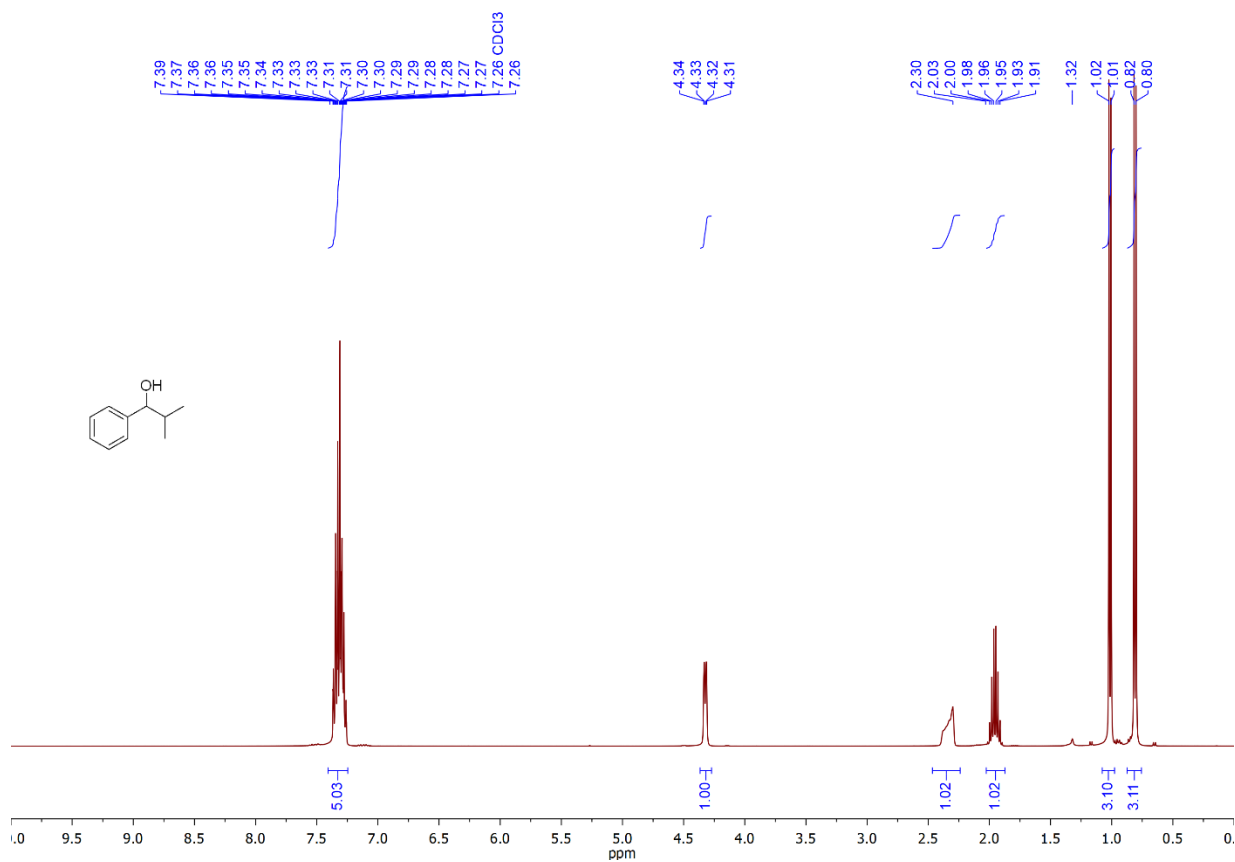
$[\text{H}_3\text{O}^+] = [\text{HCOO}^-] = 0.063$  M

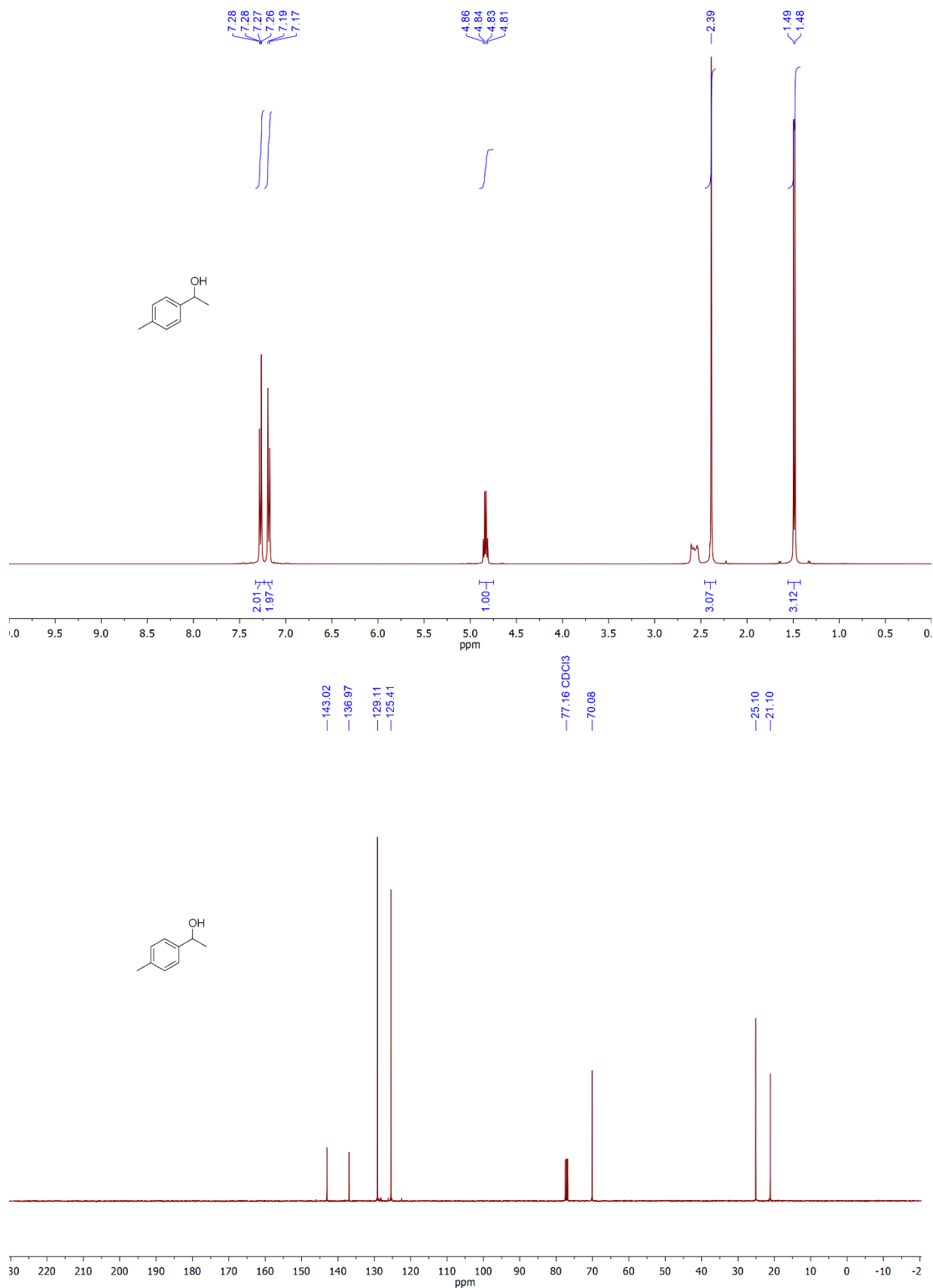
nHCOO $^-$  in 0.35 mL  $\approx$  0.022 mmol

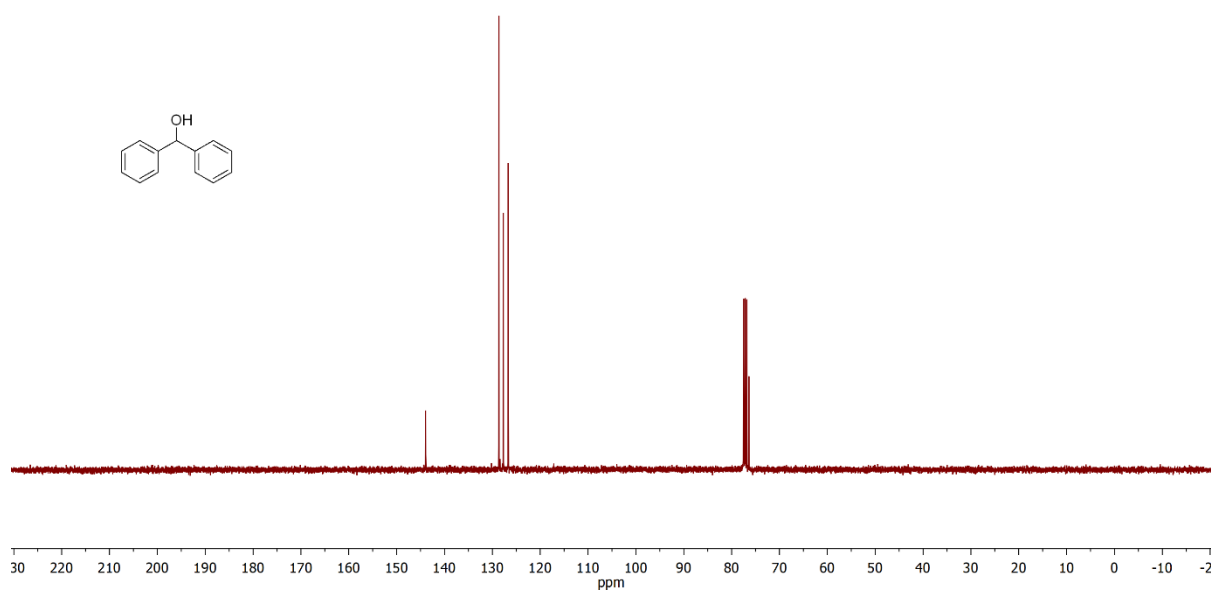
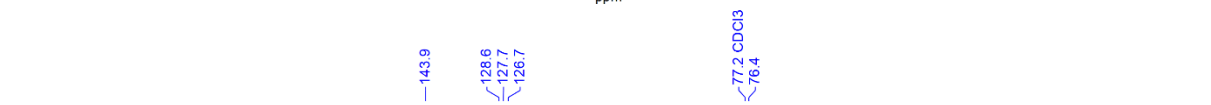
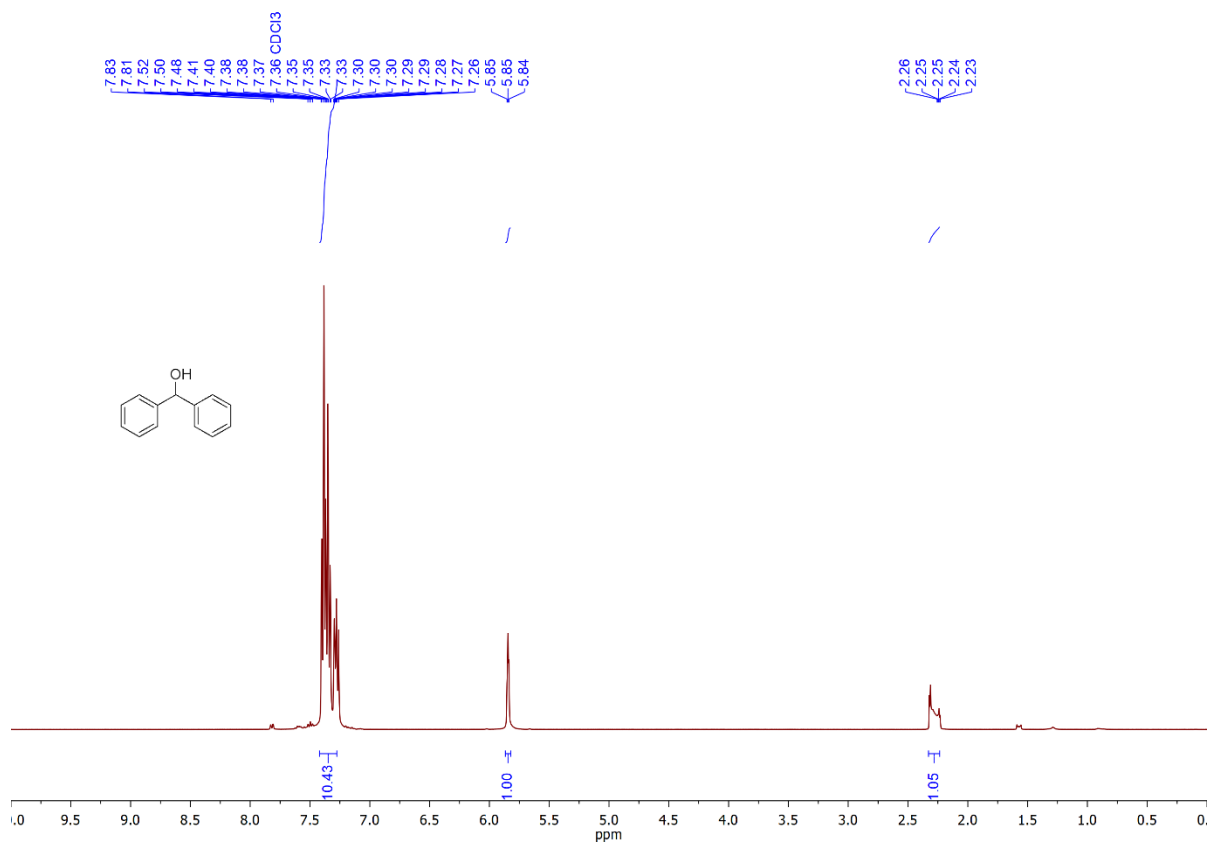
## 5 NMR spectra

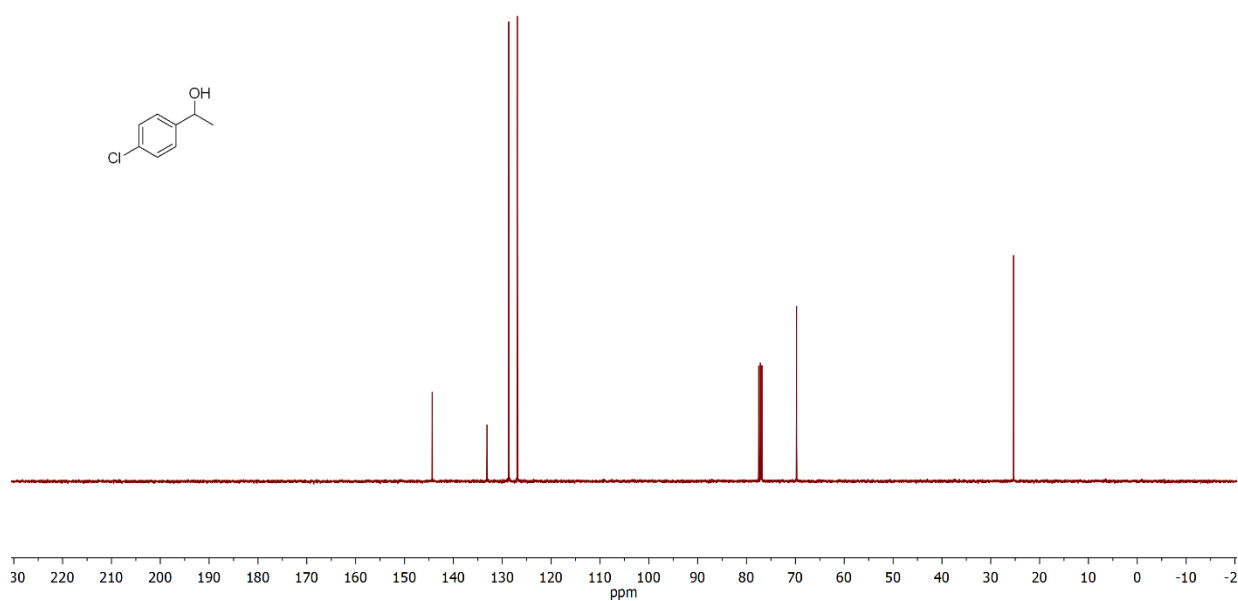
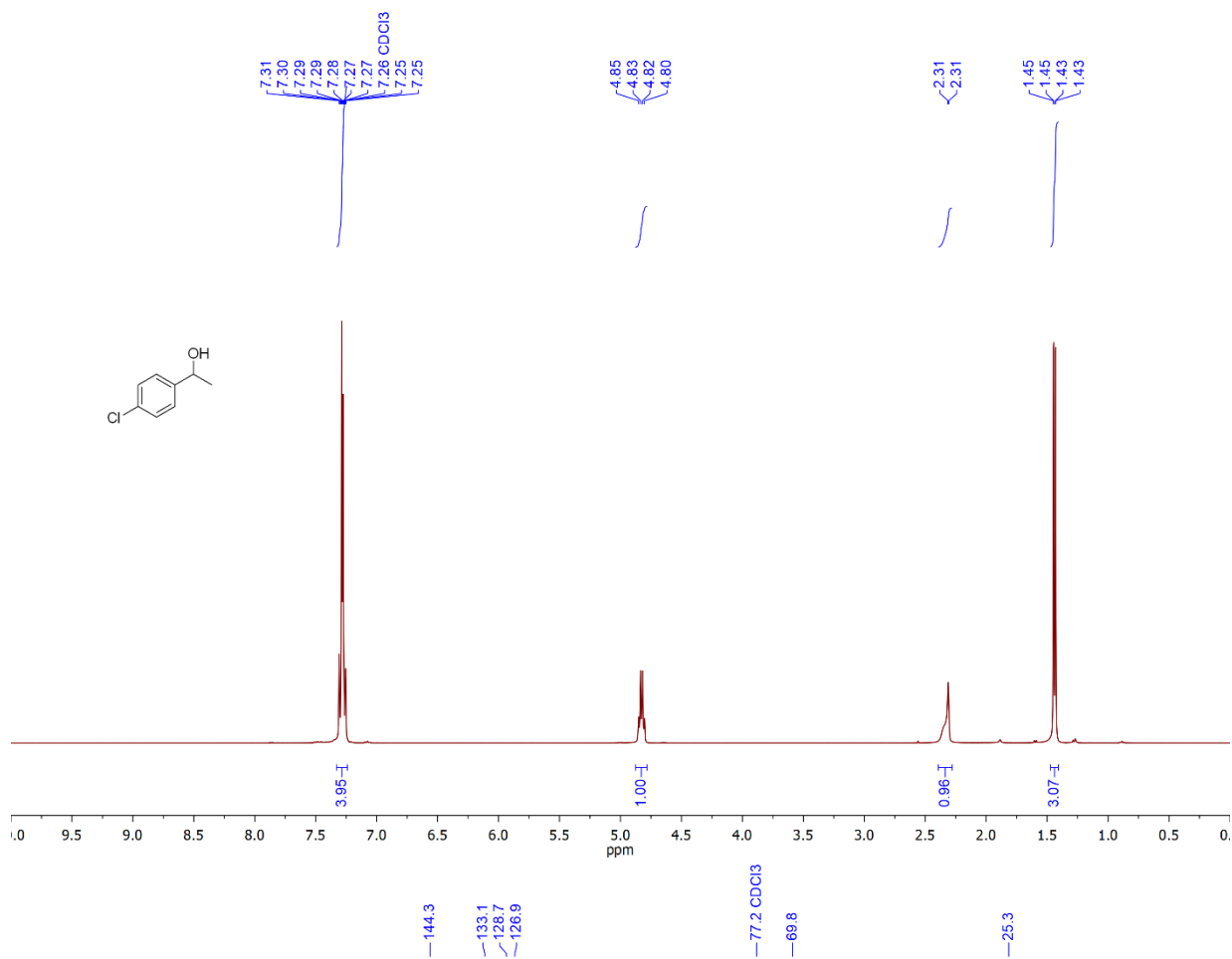


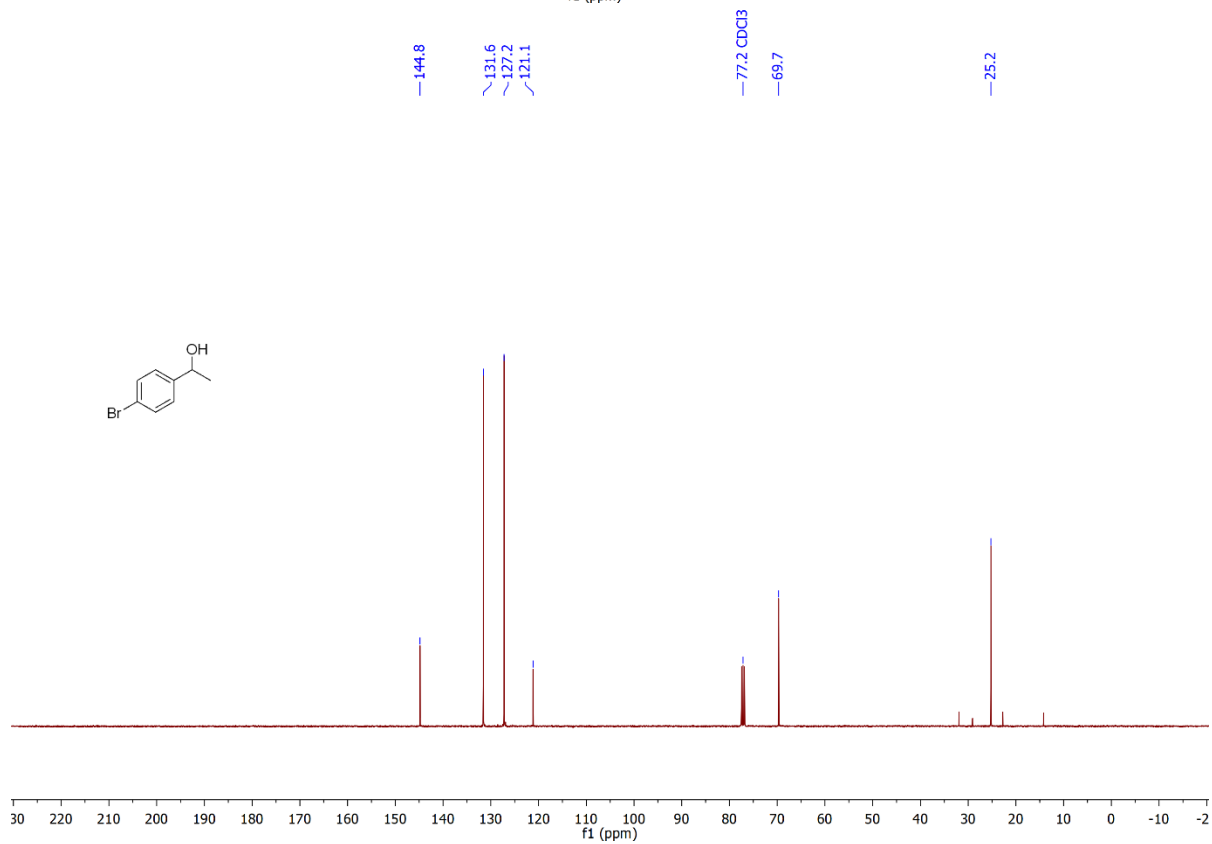
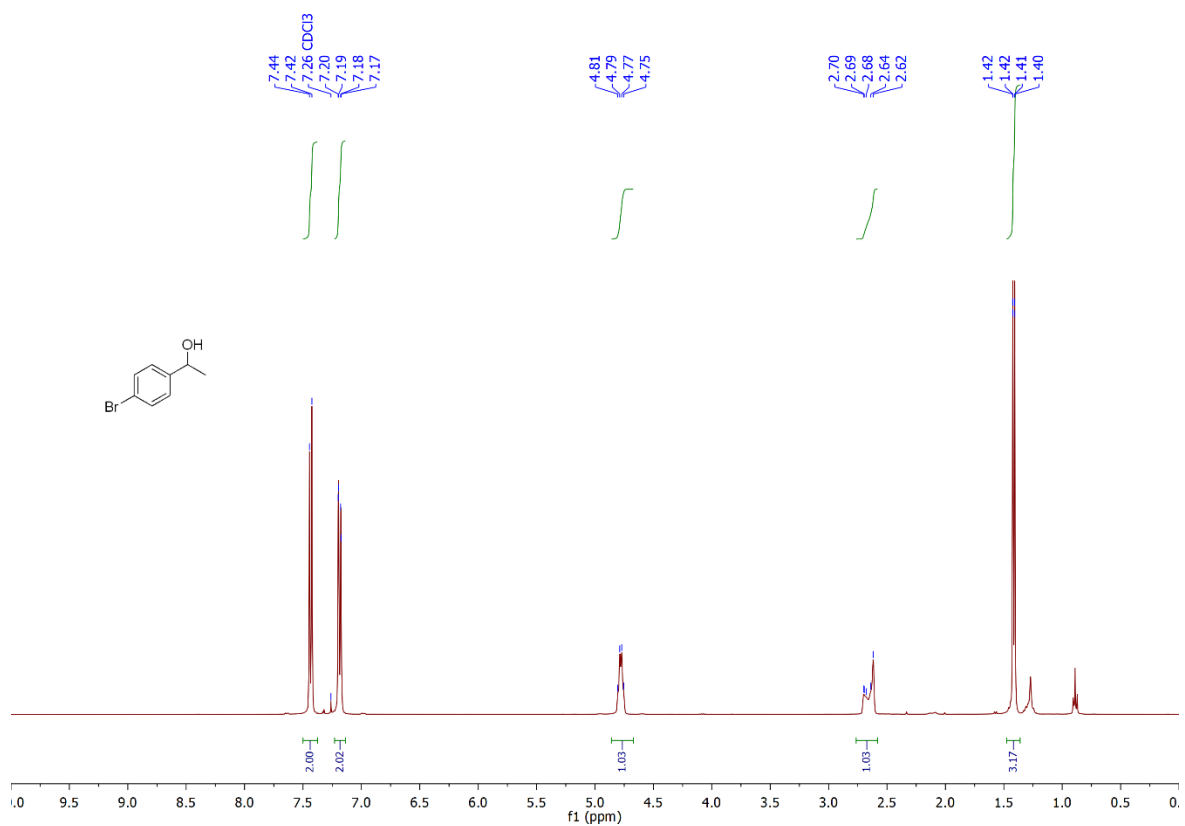


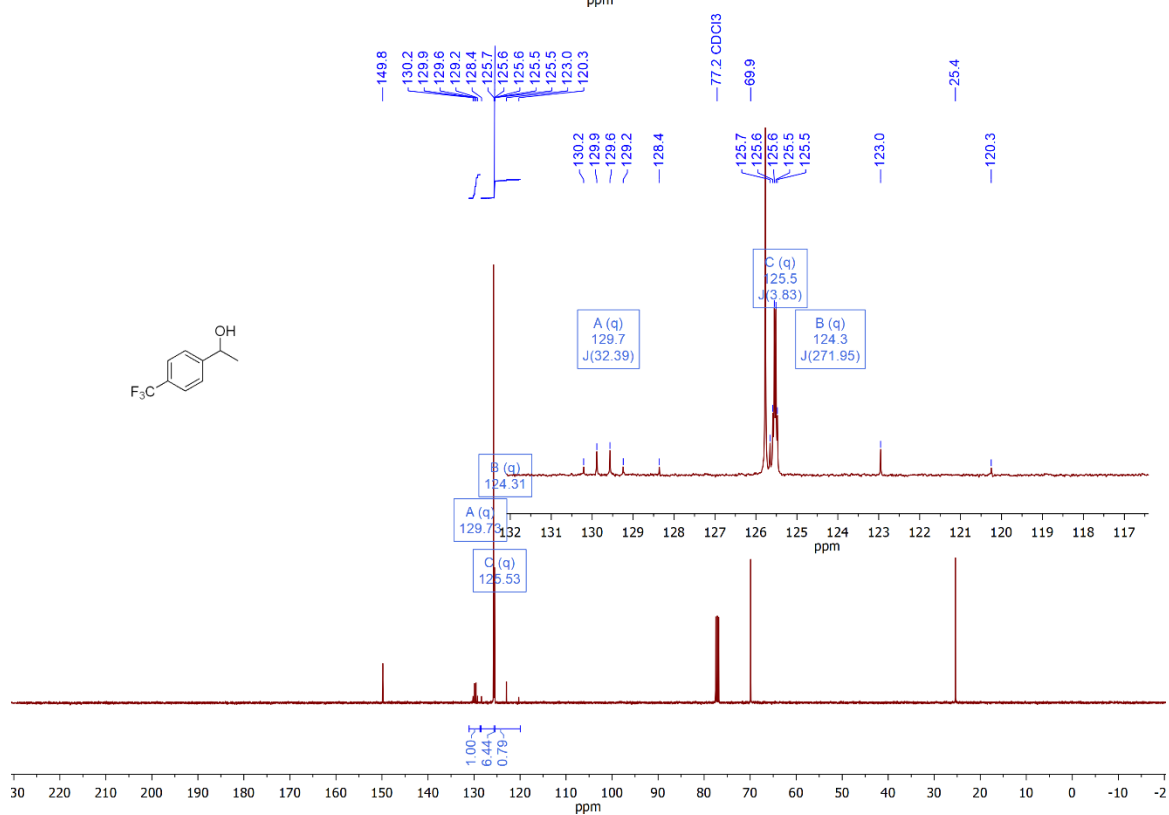
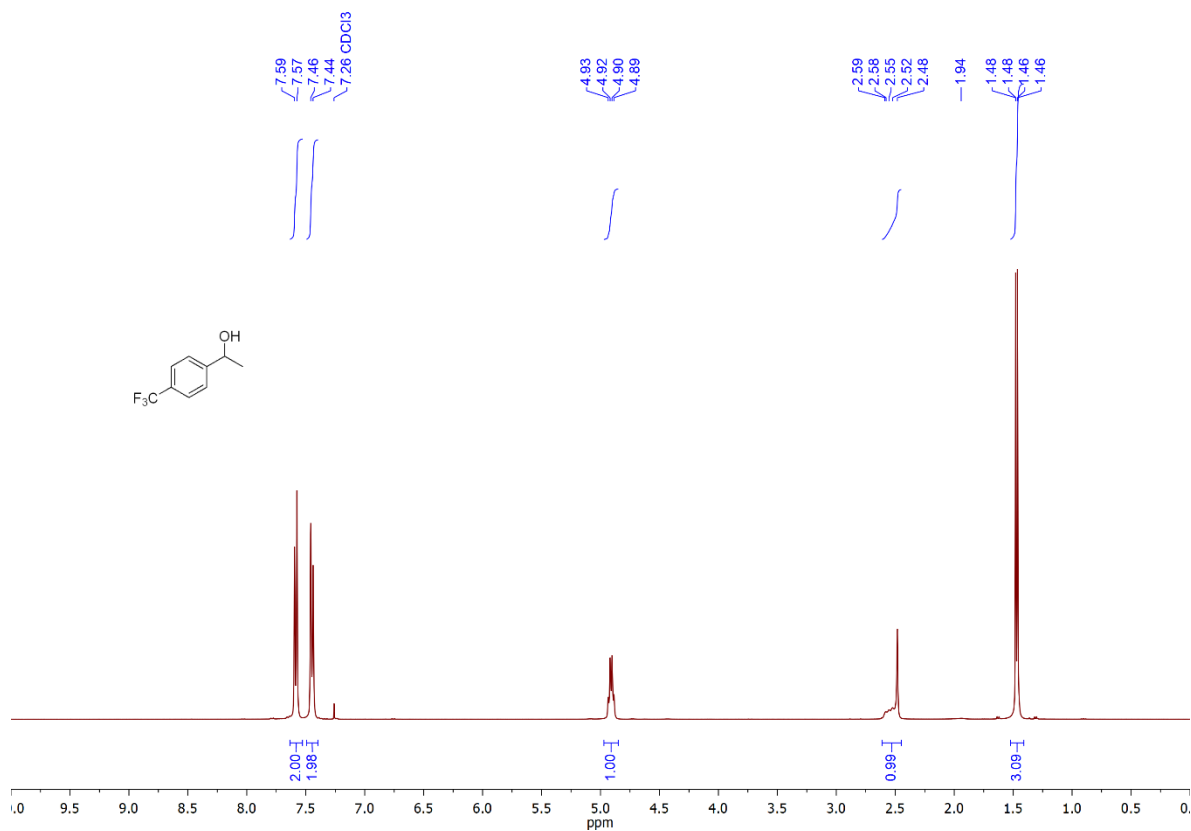


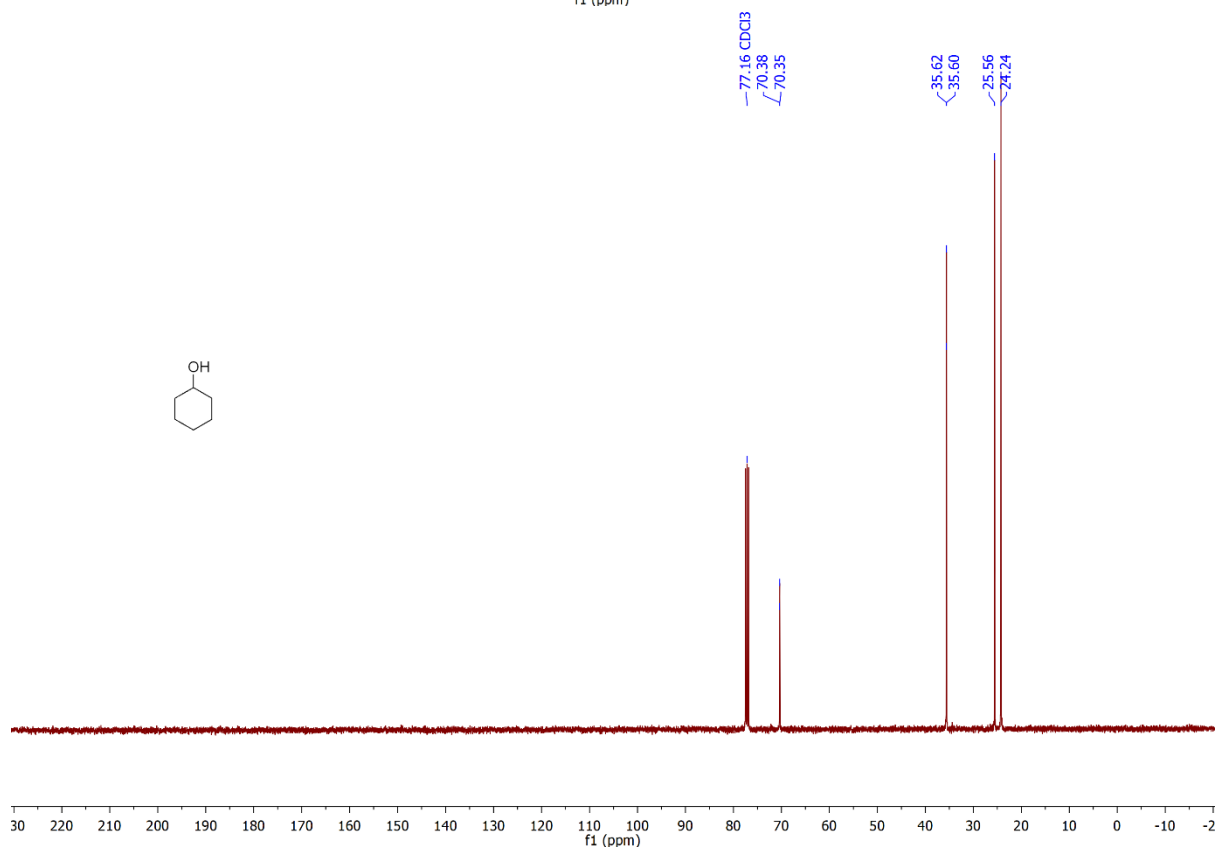
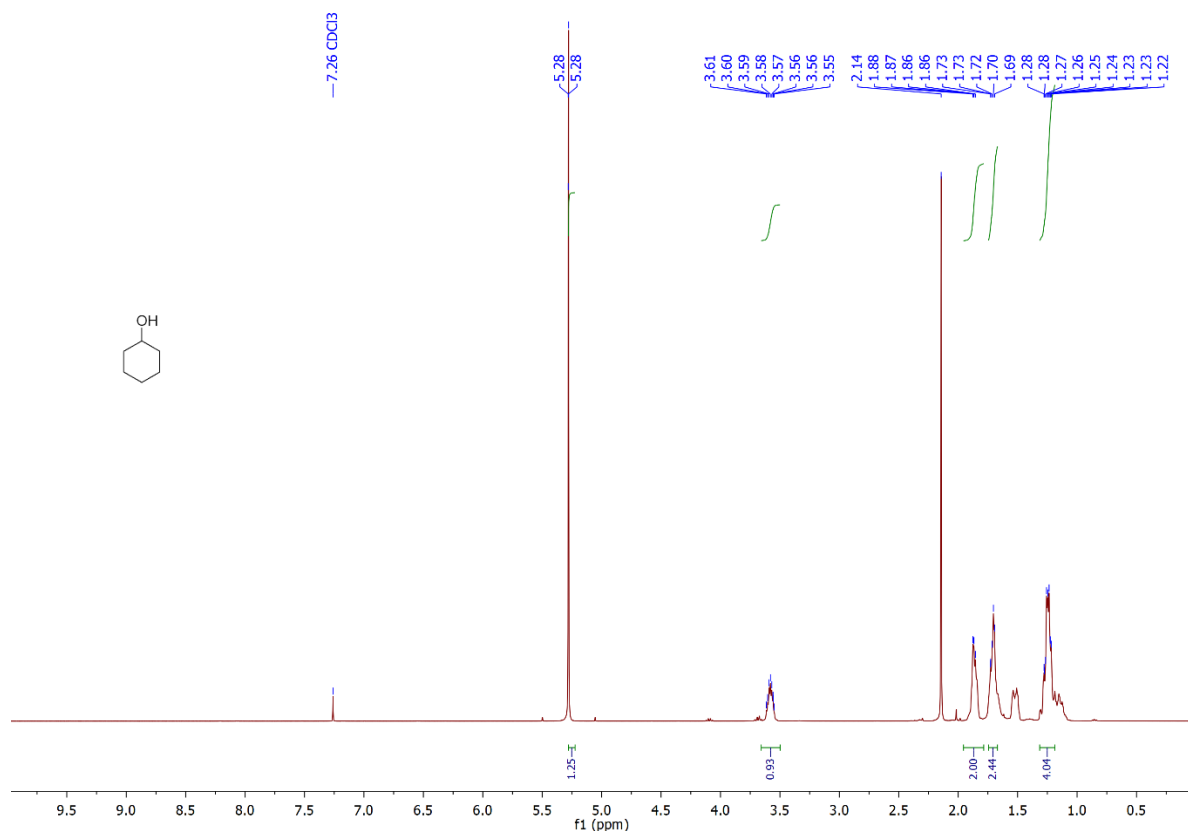


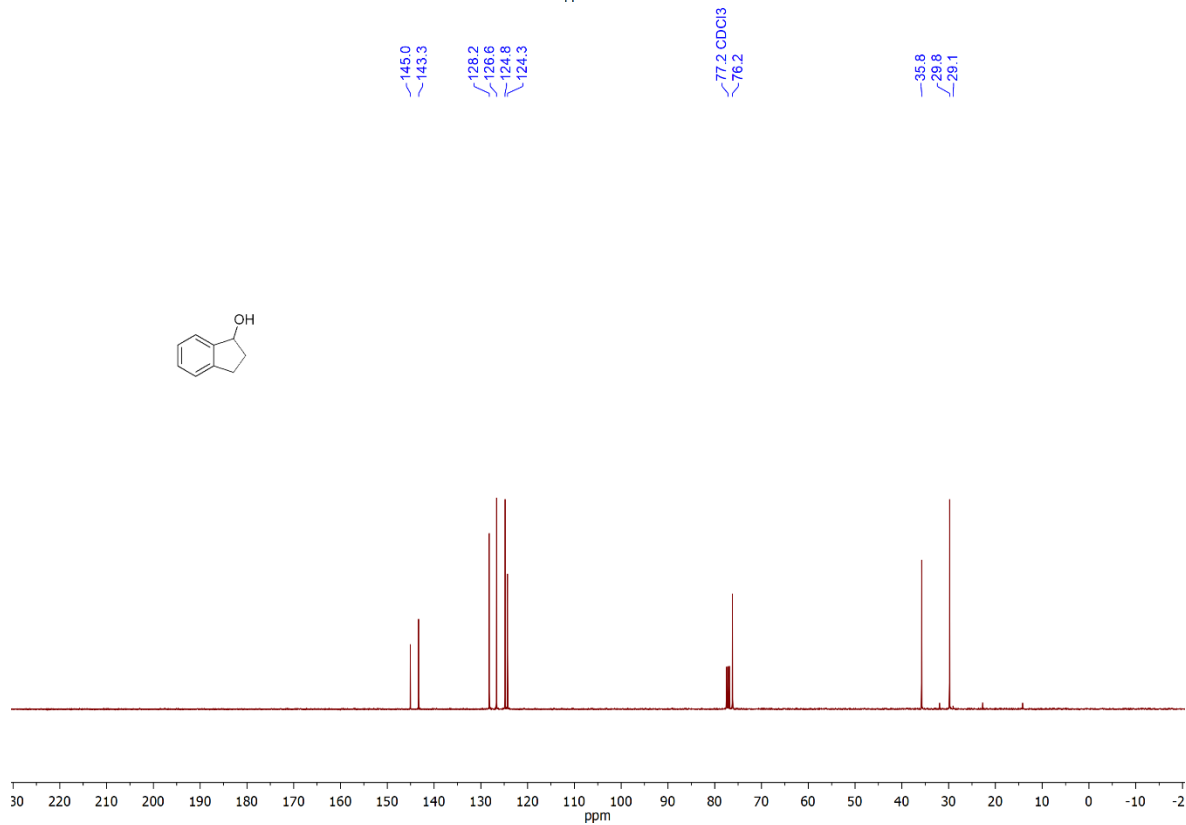
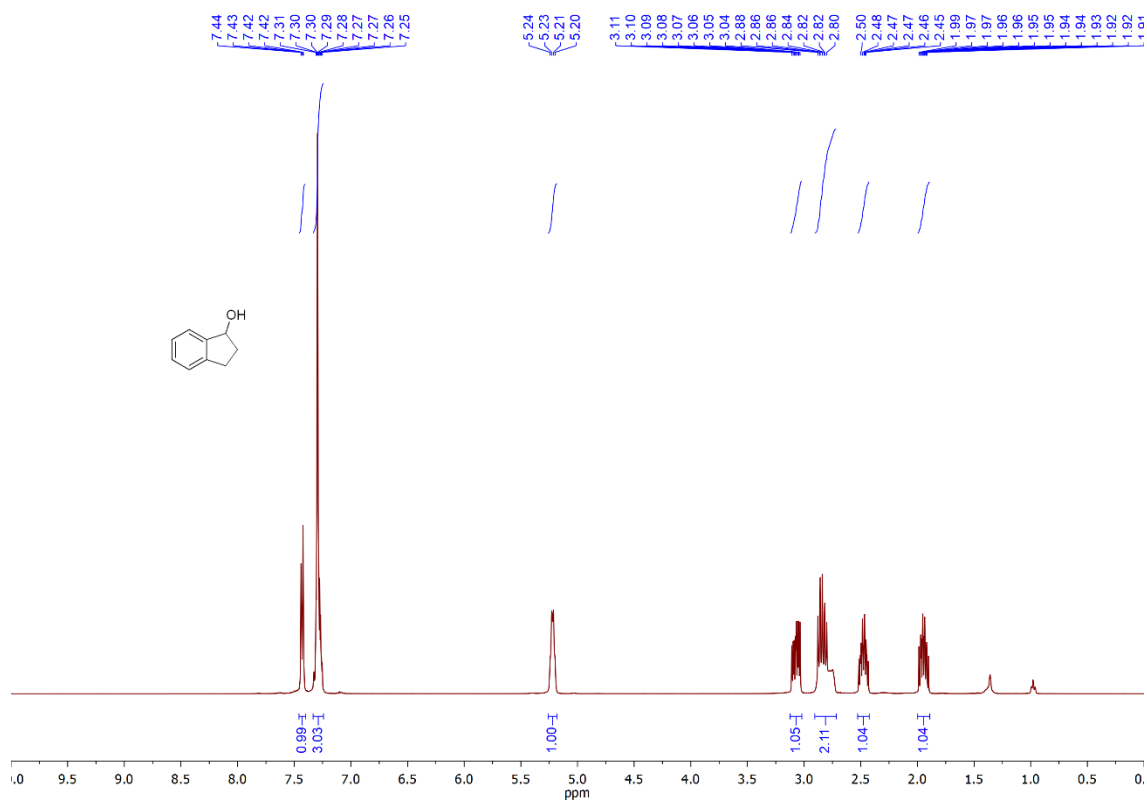


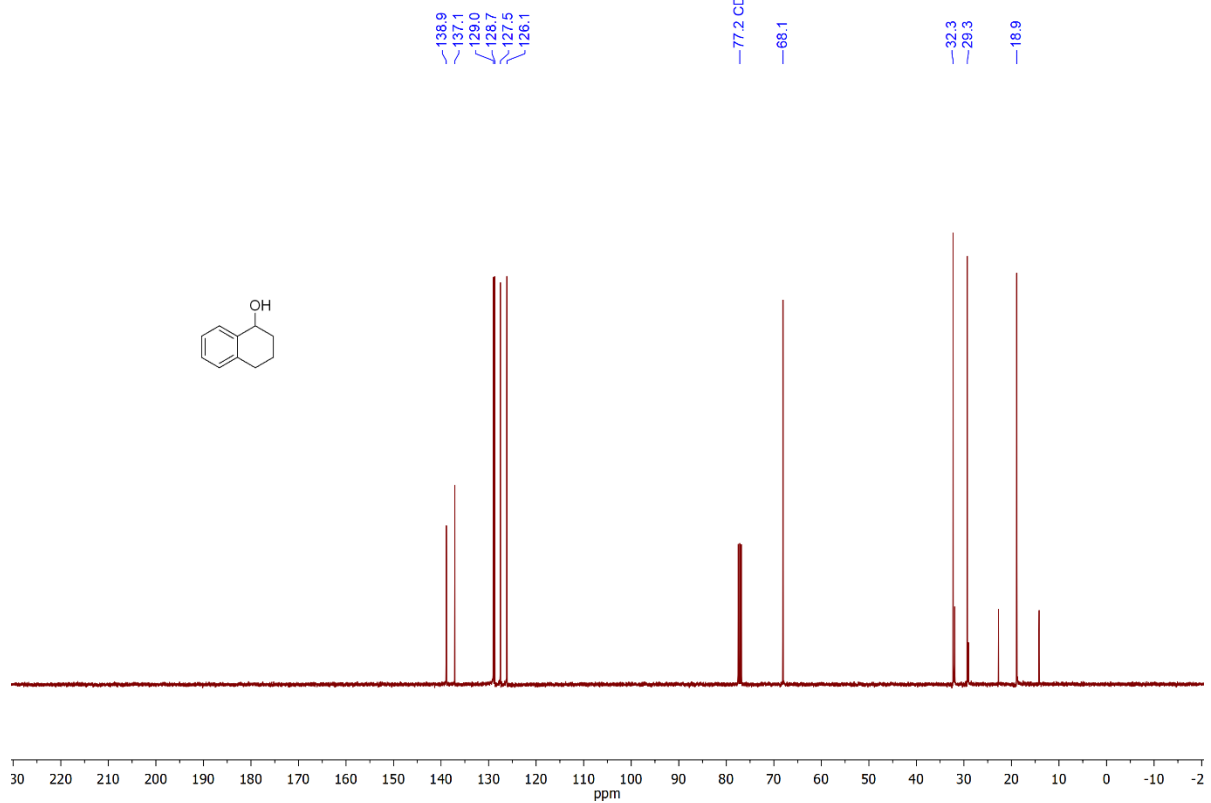
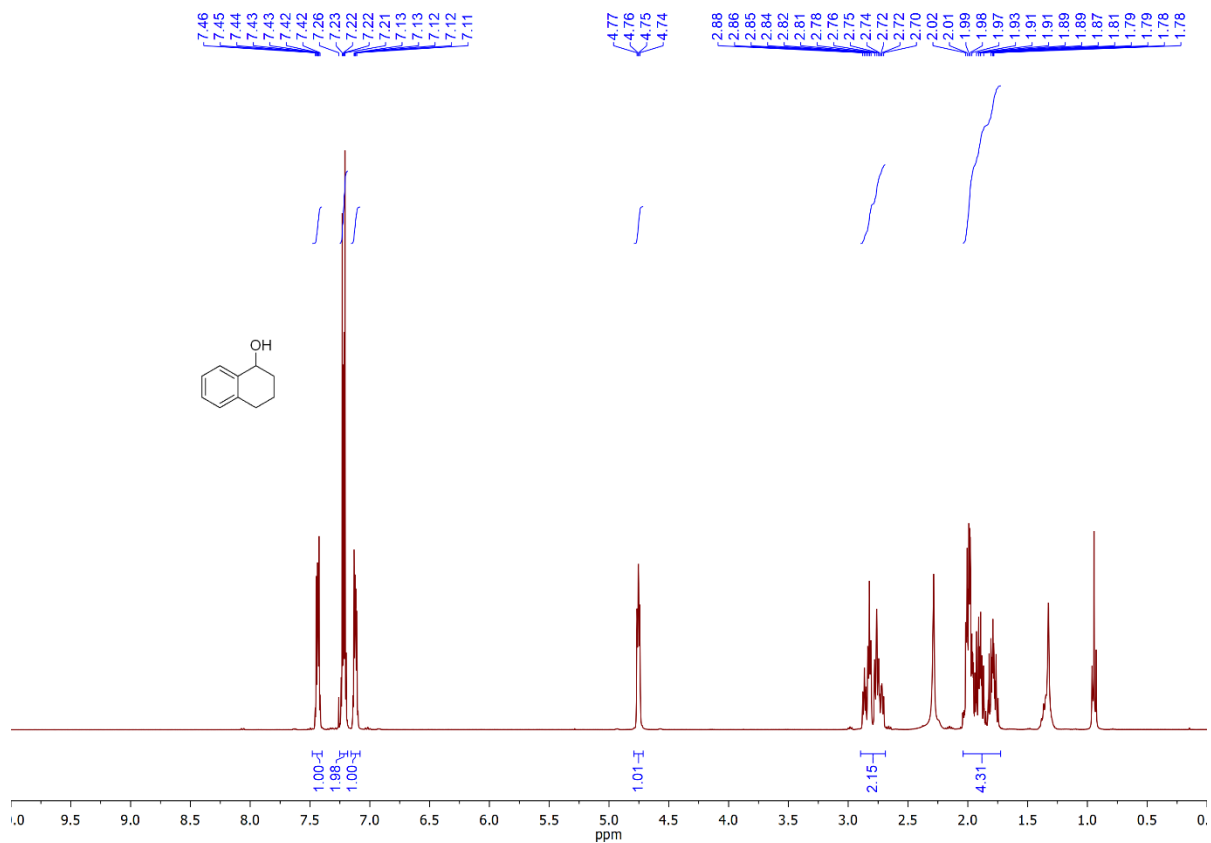


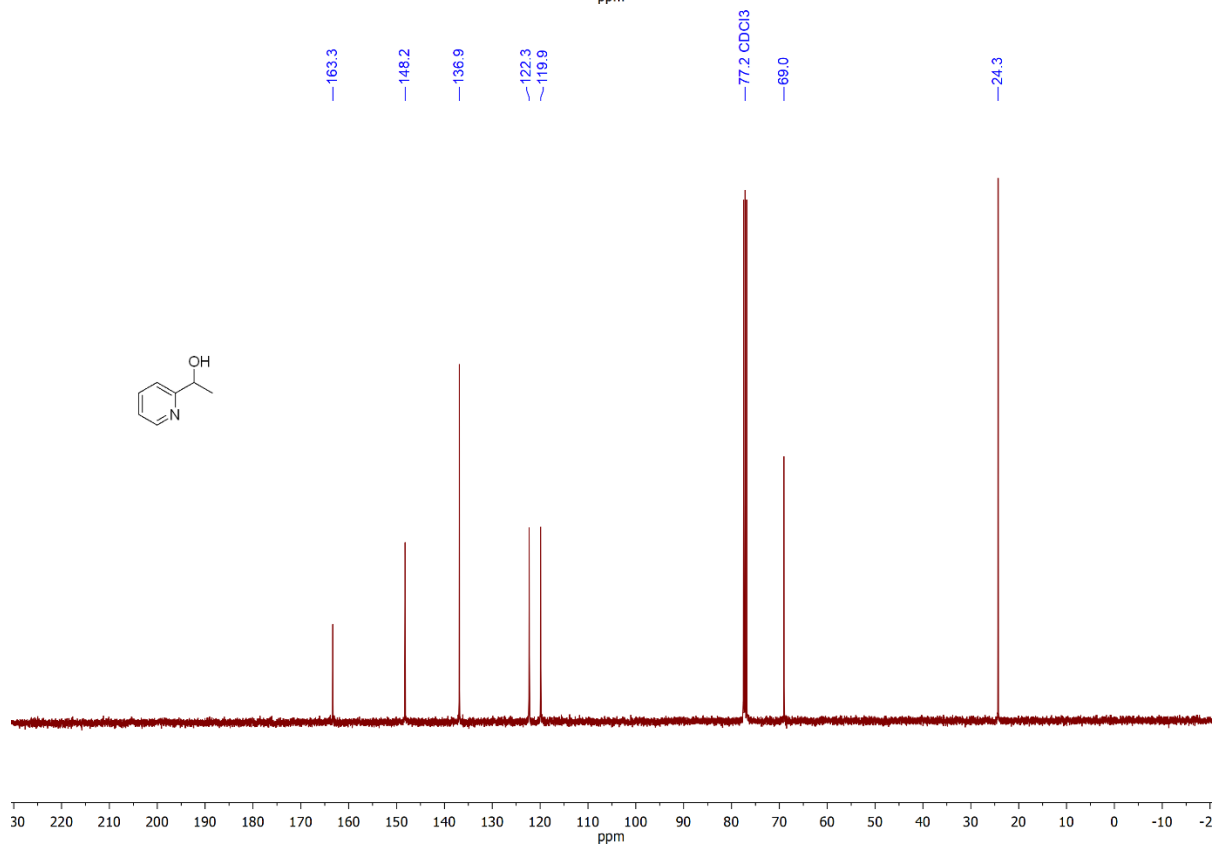
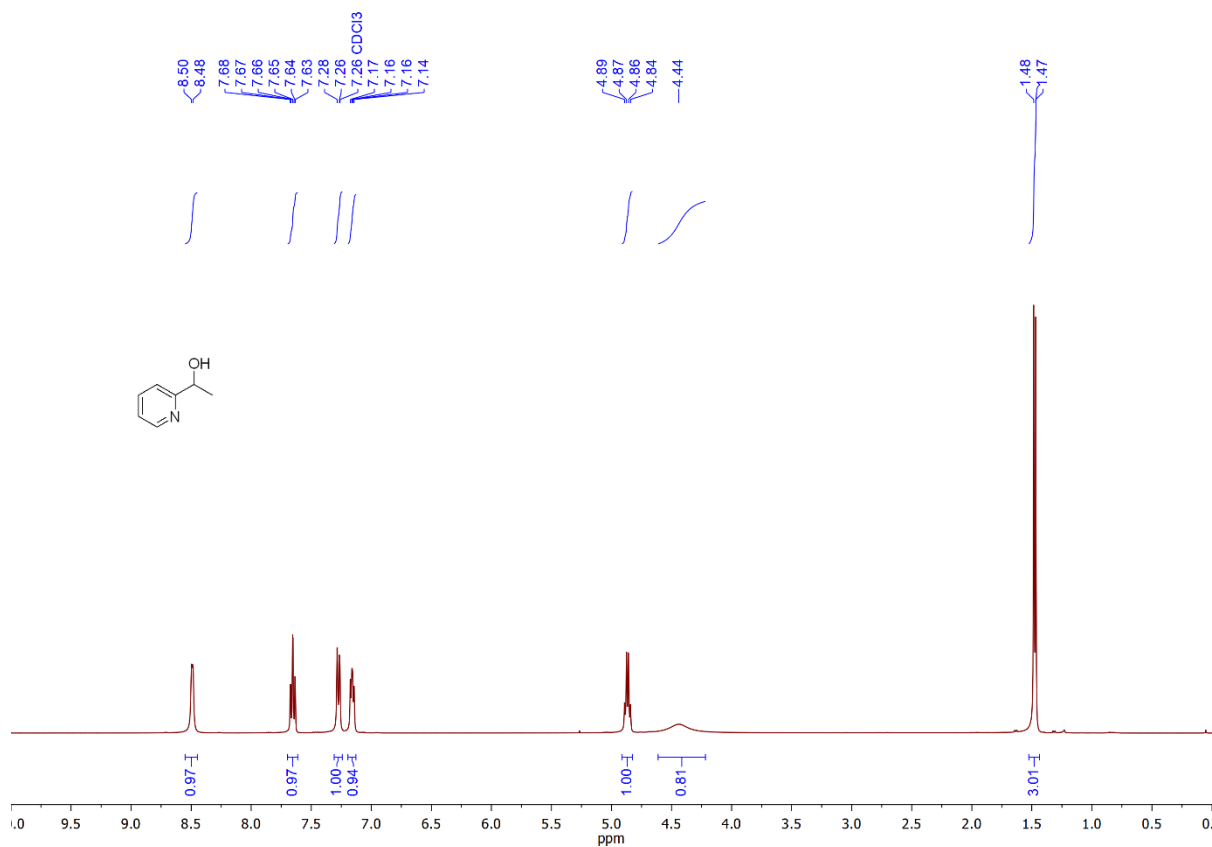


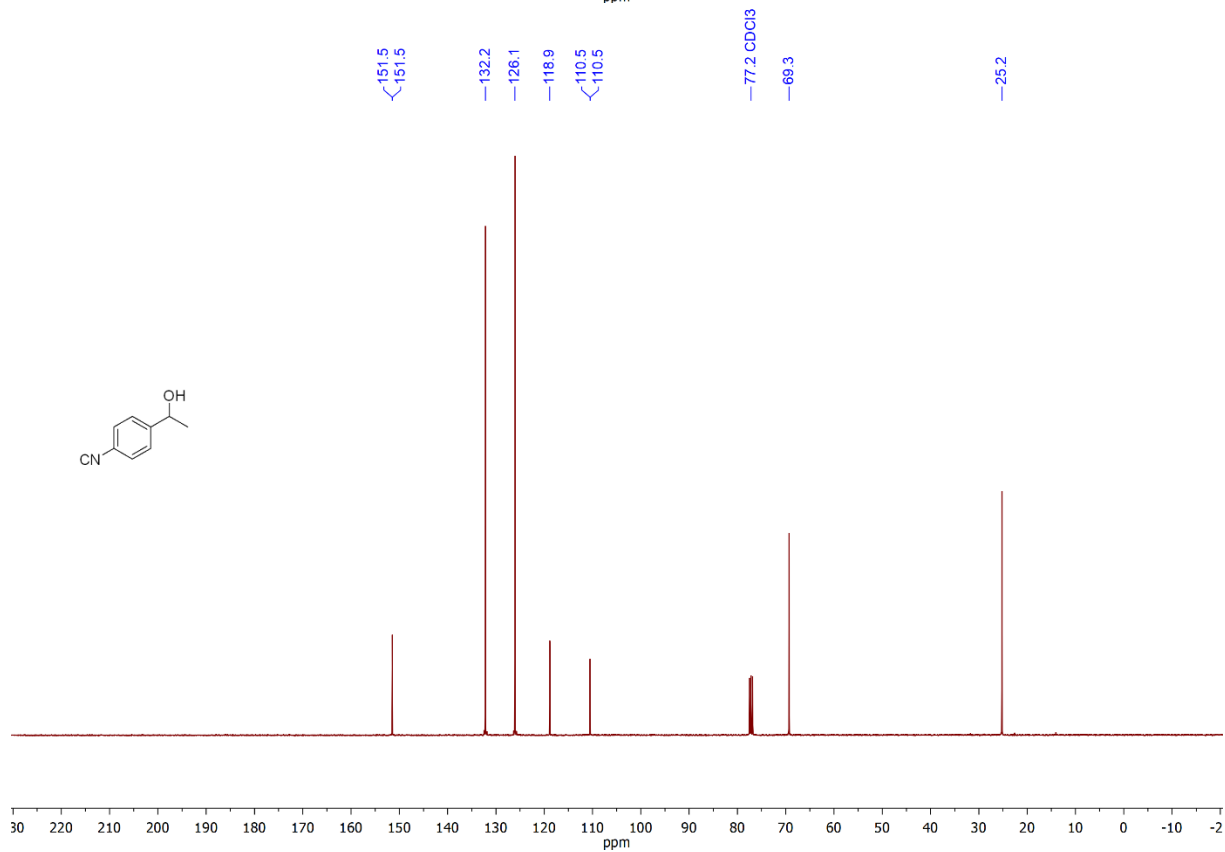
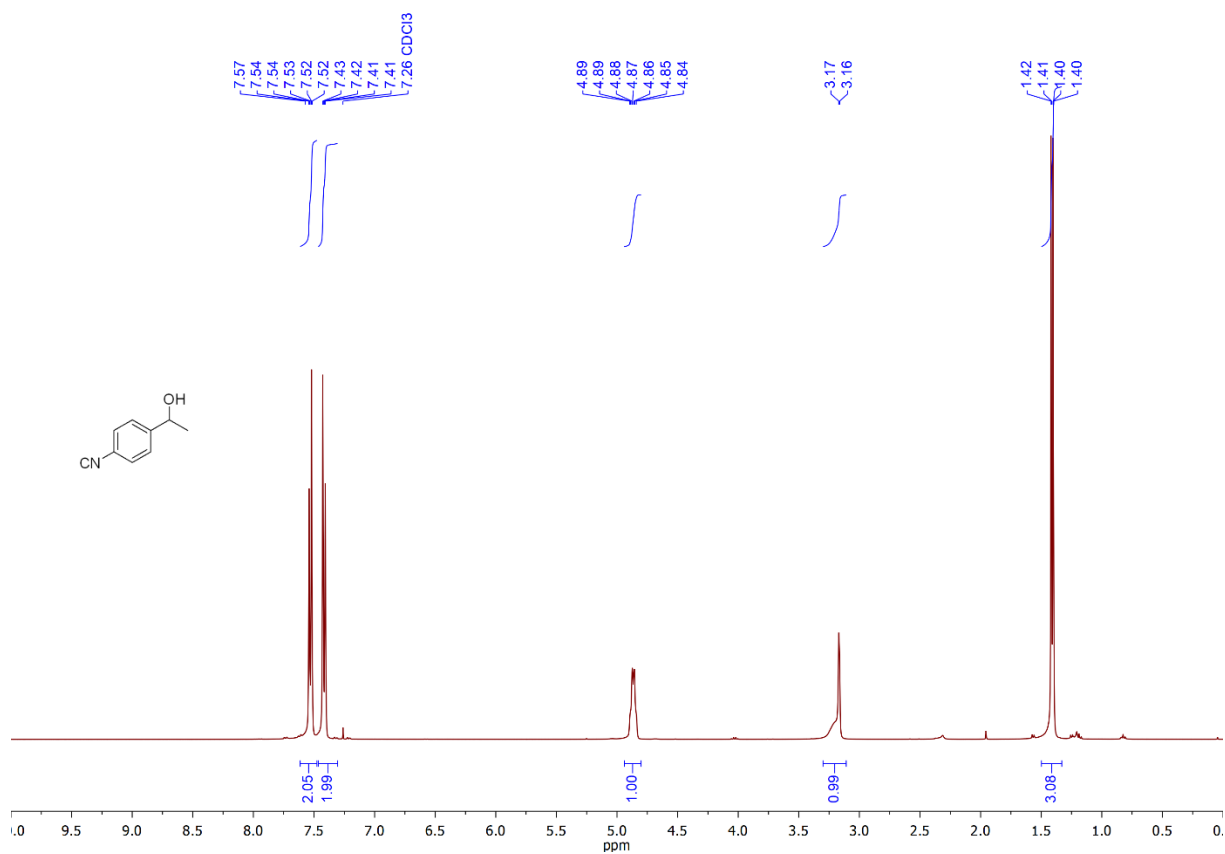


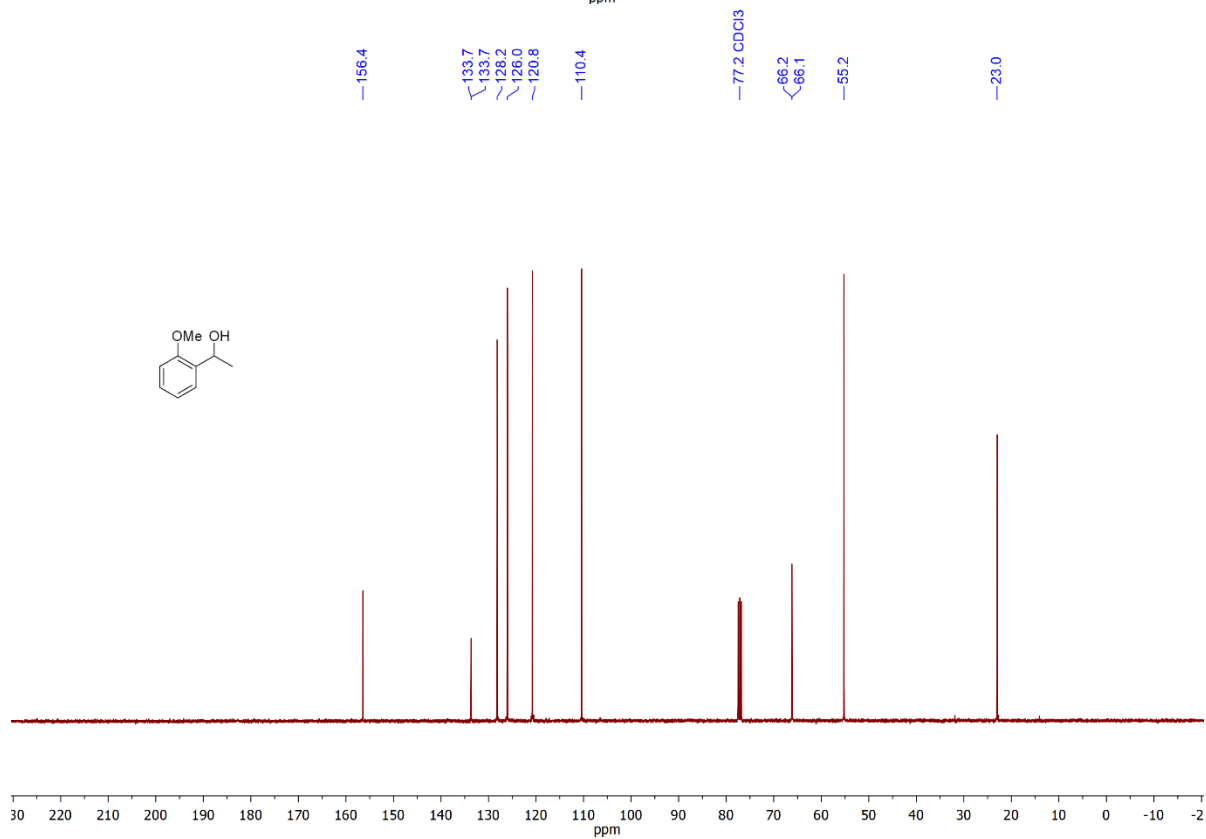
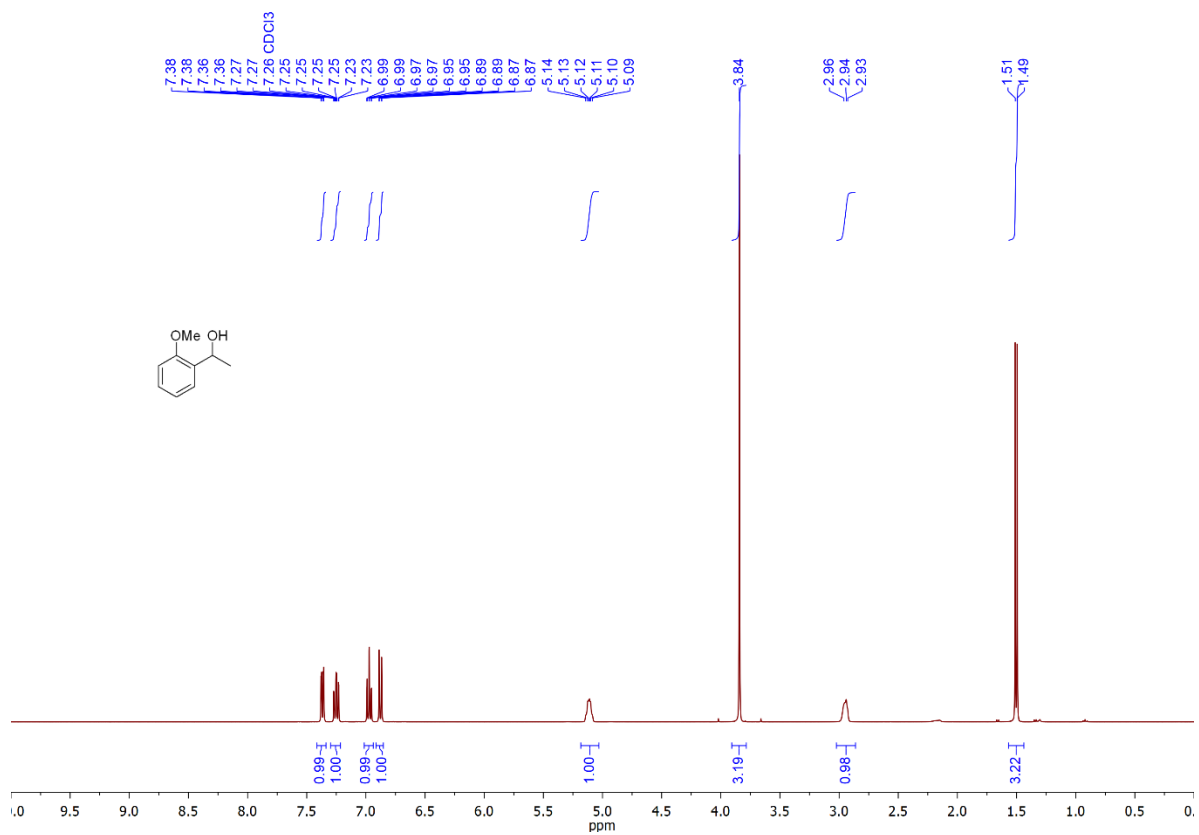


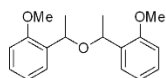
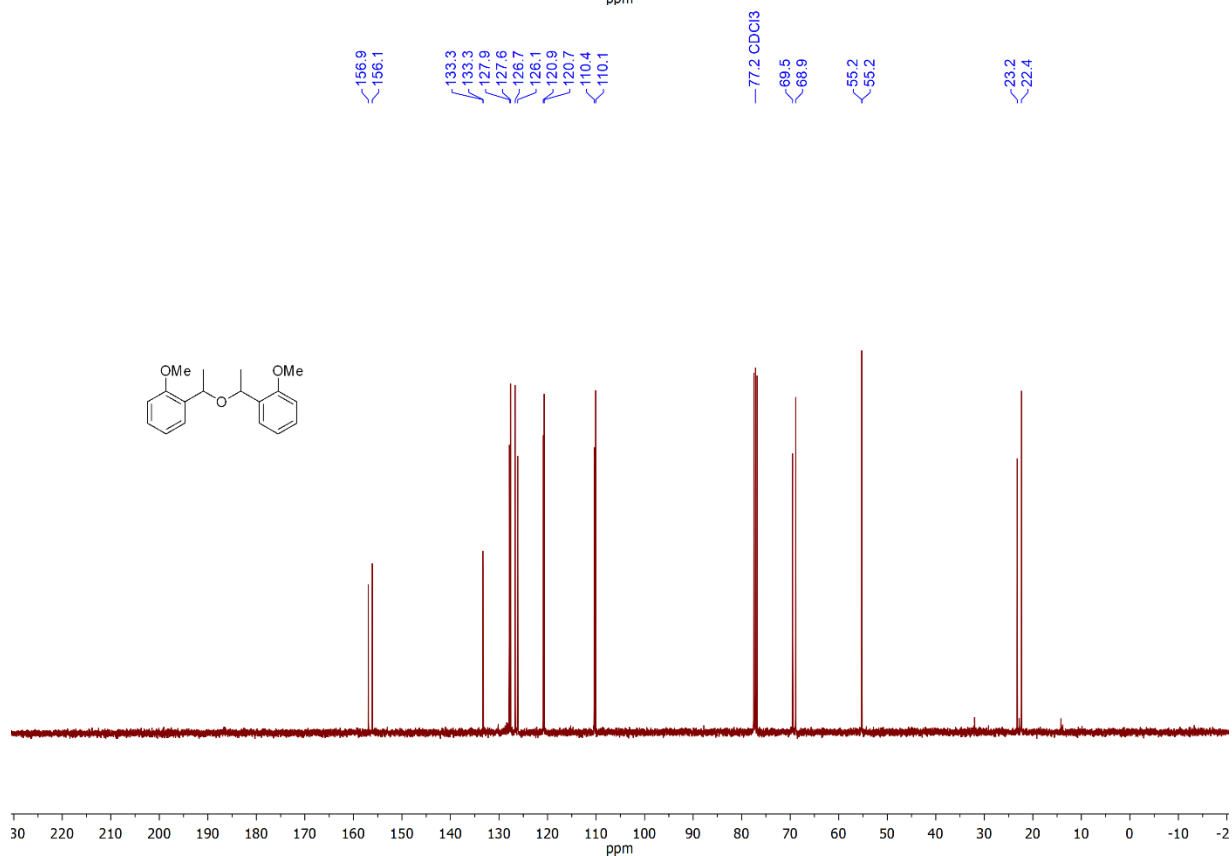
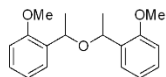
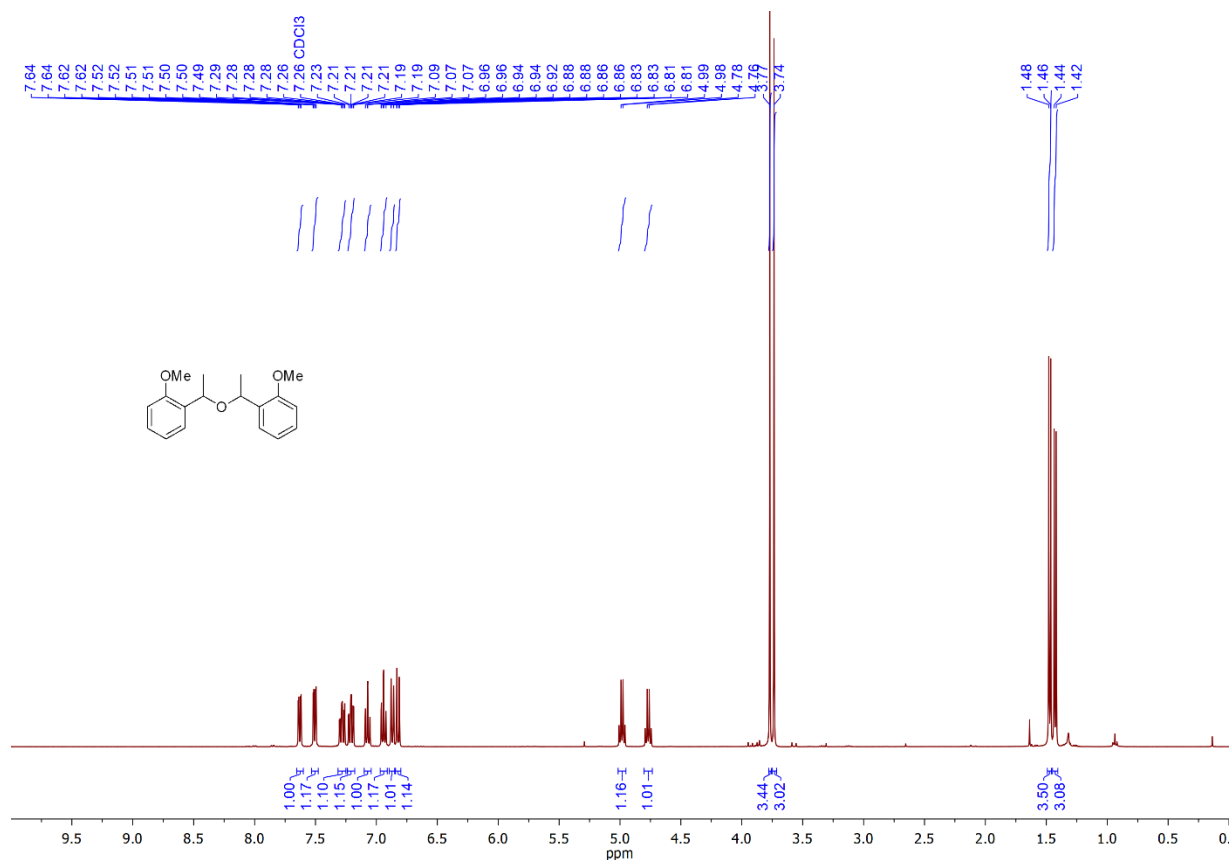


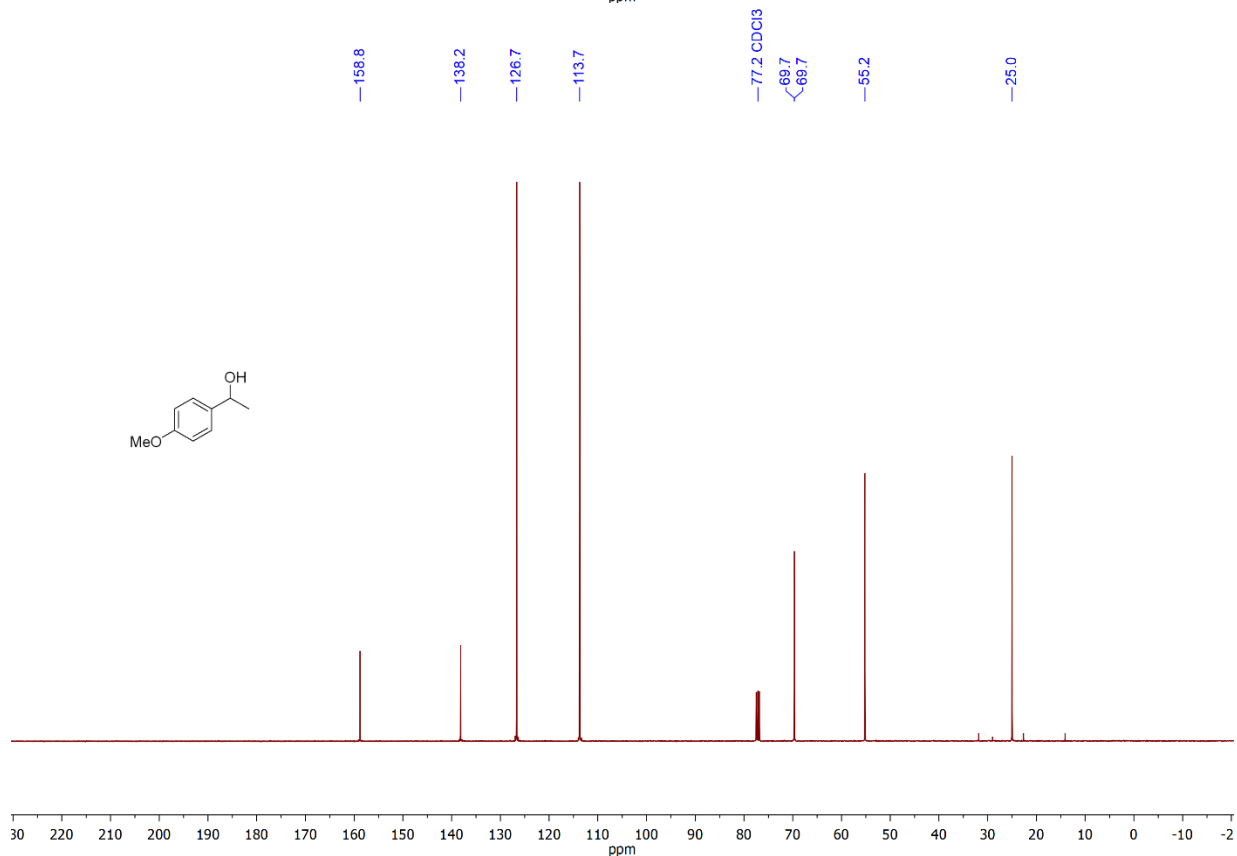
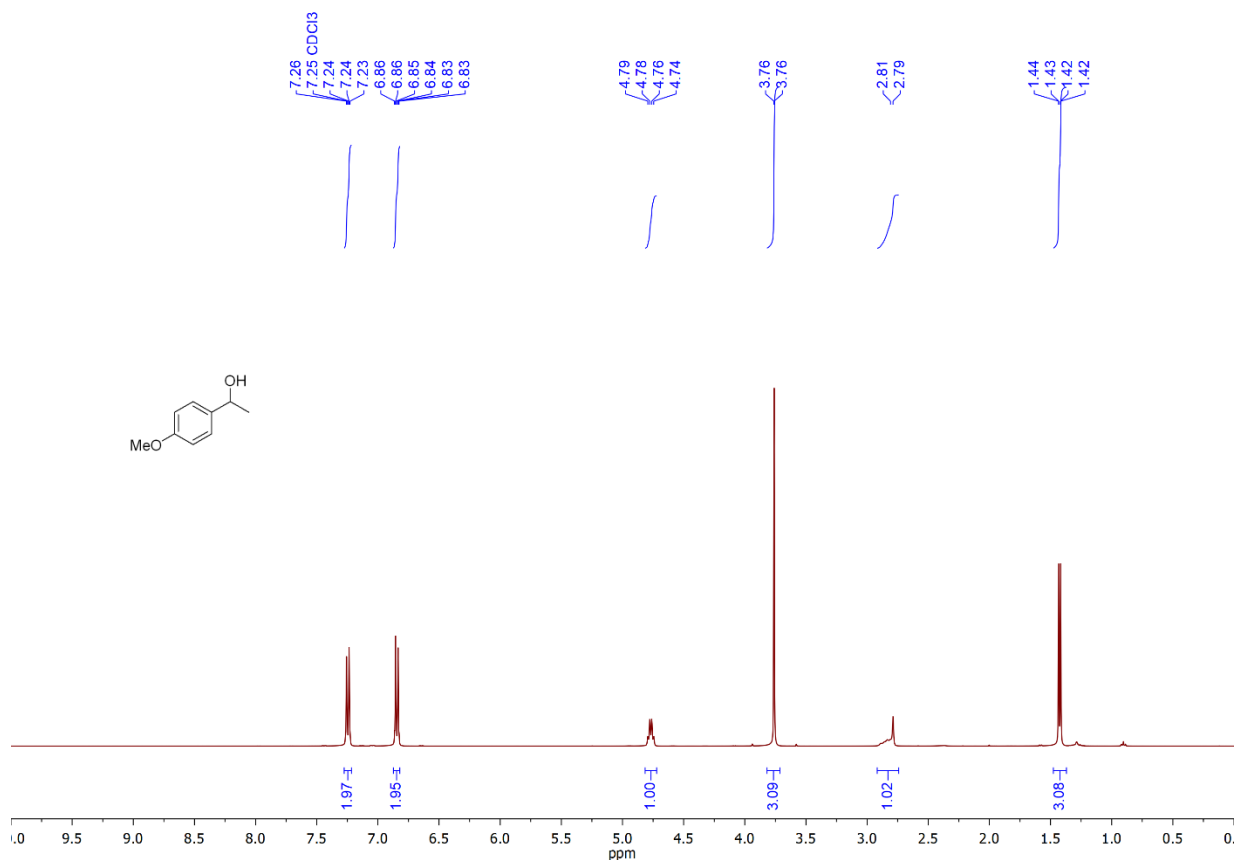


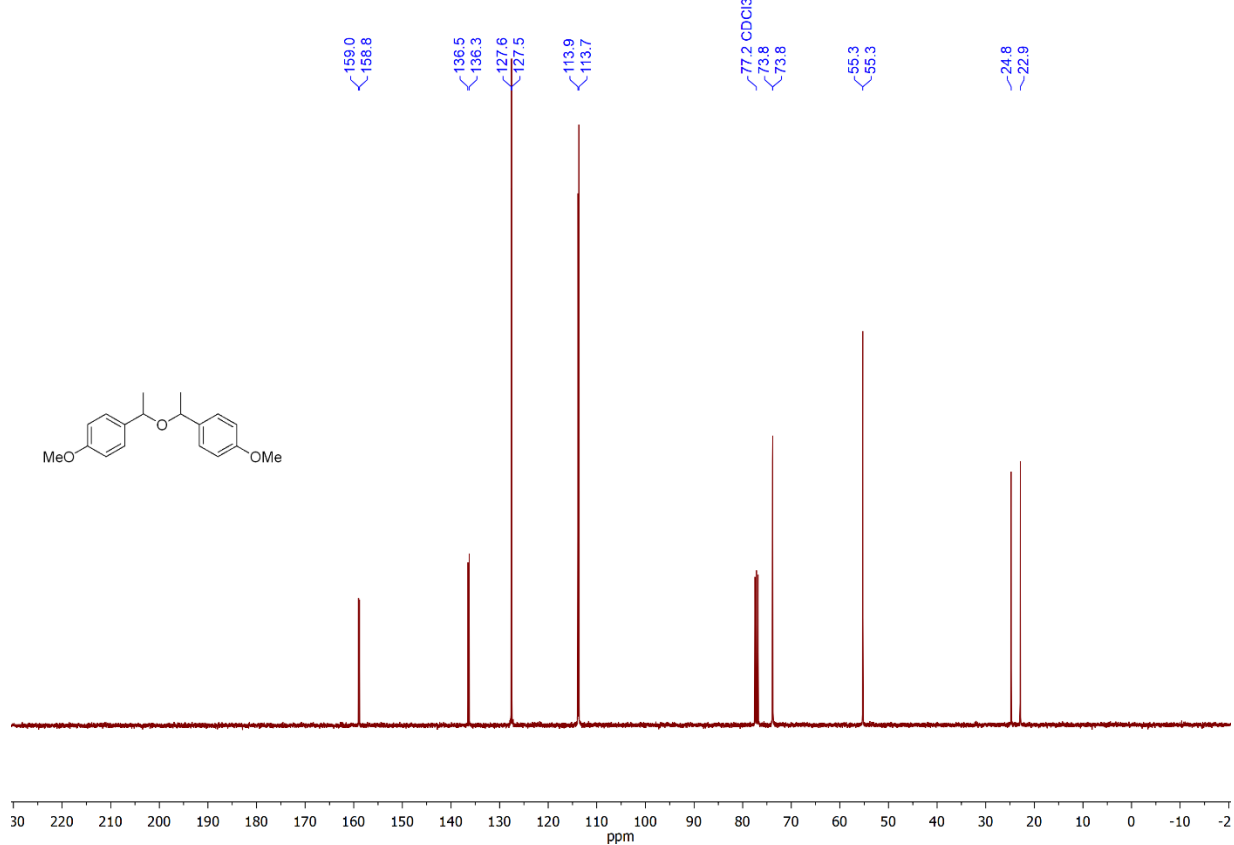
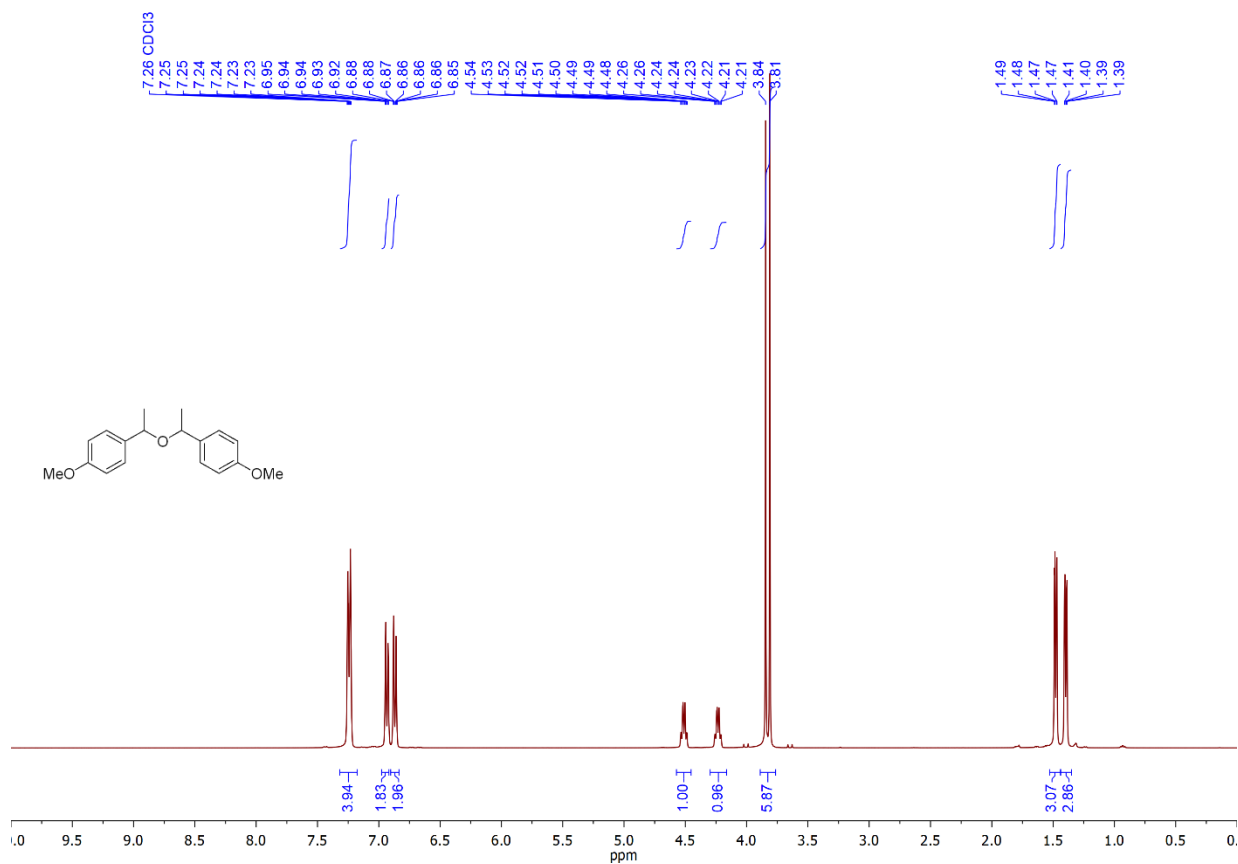


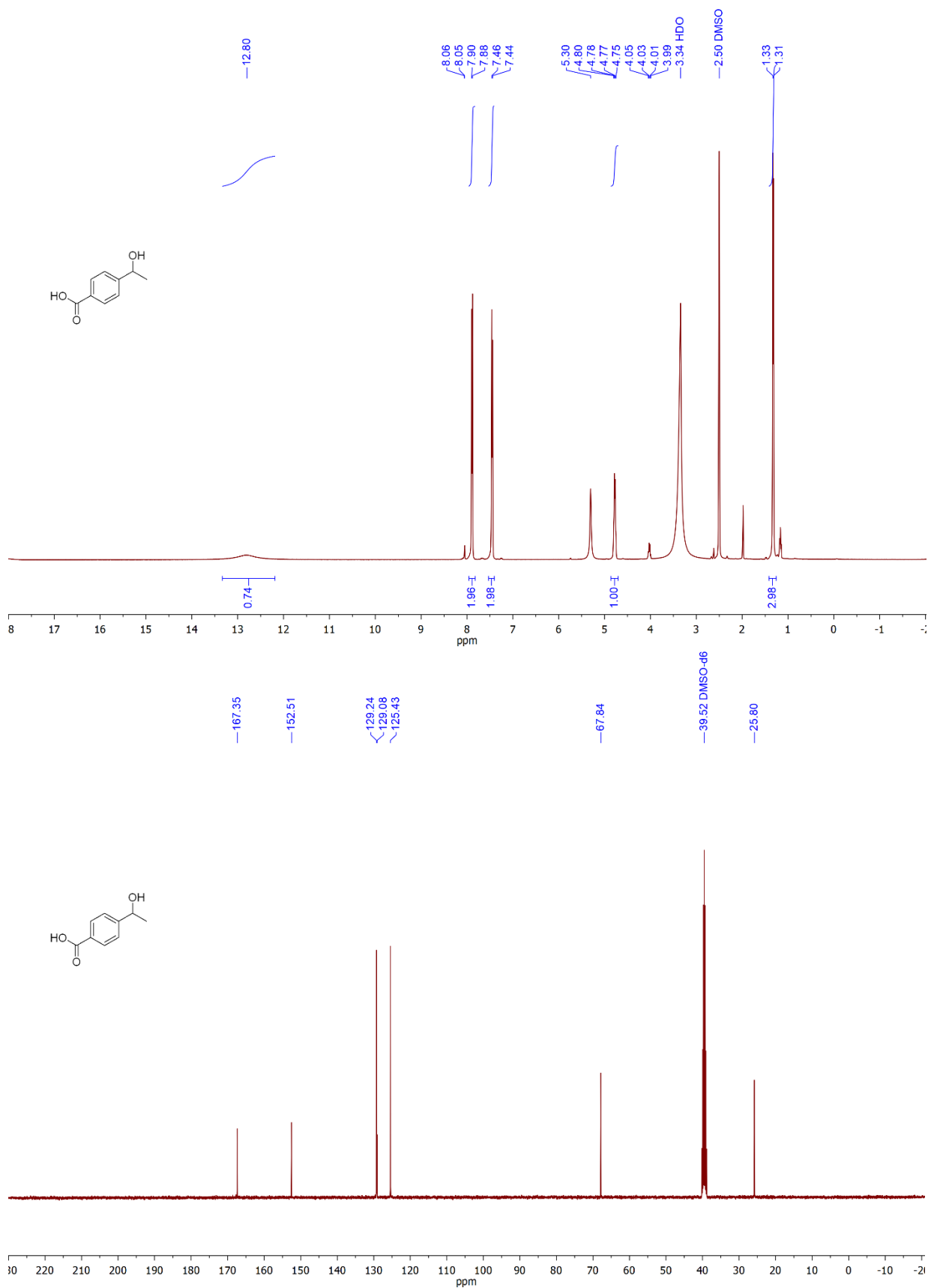


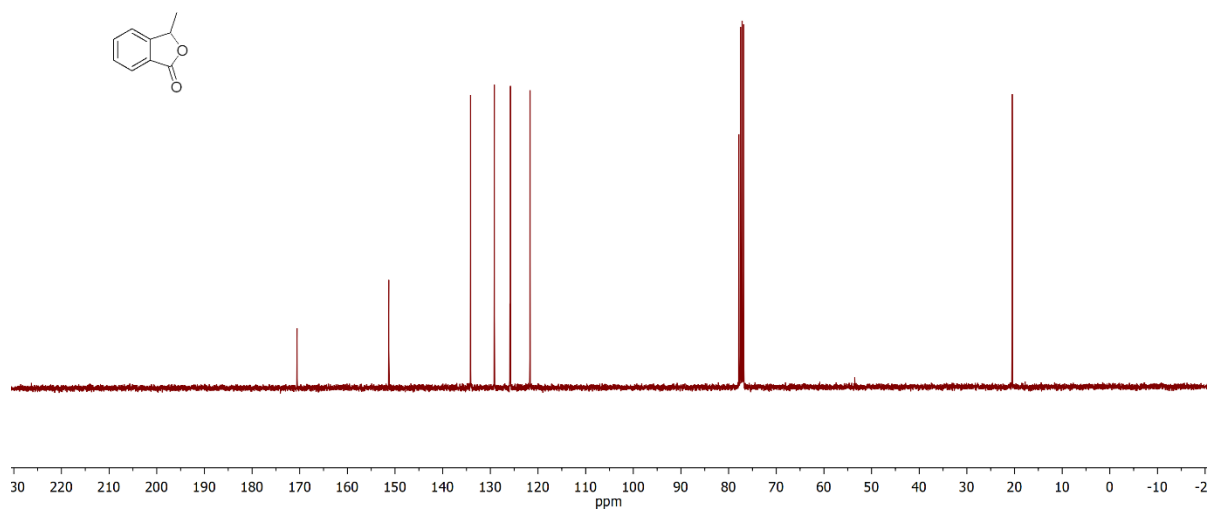
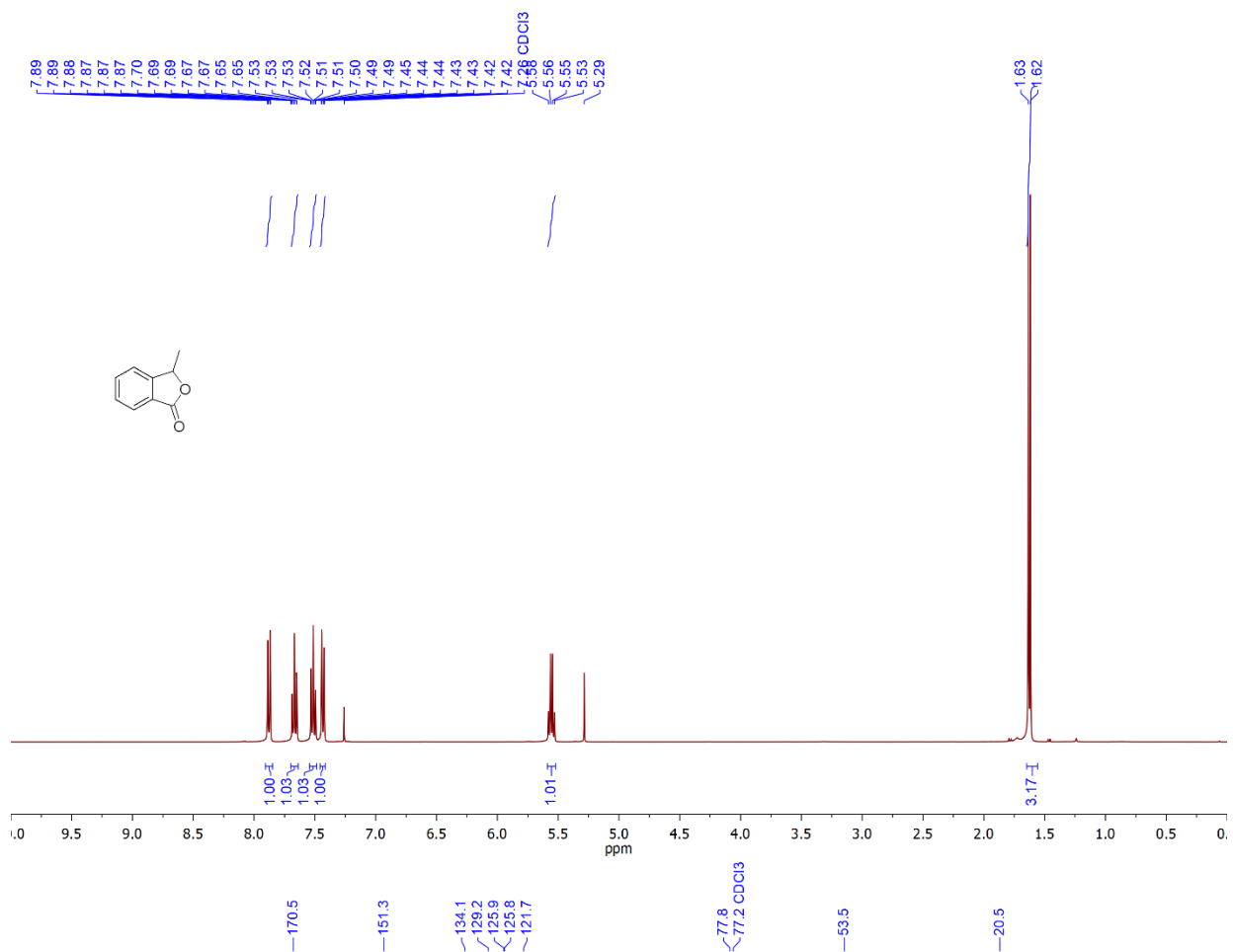


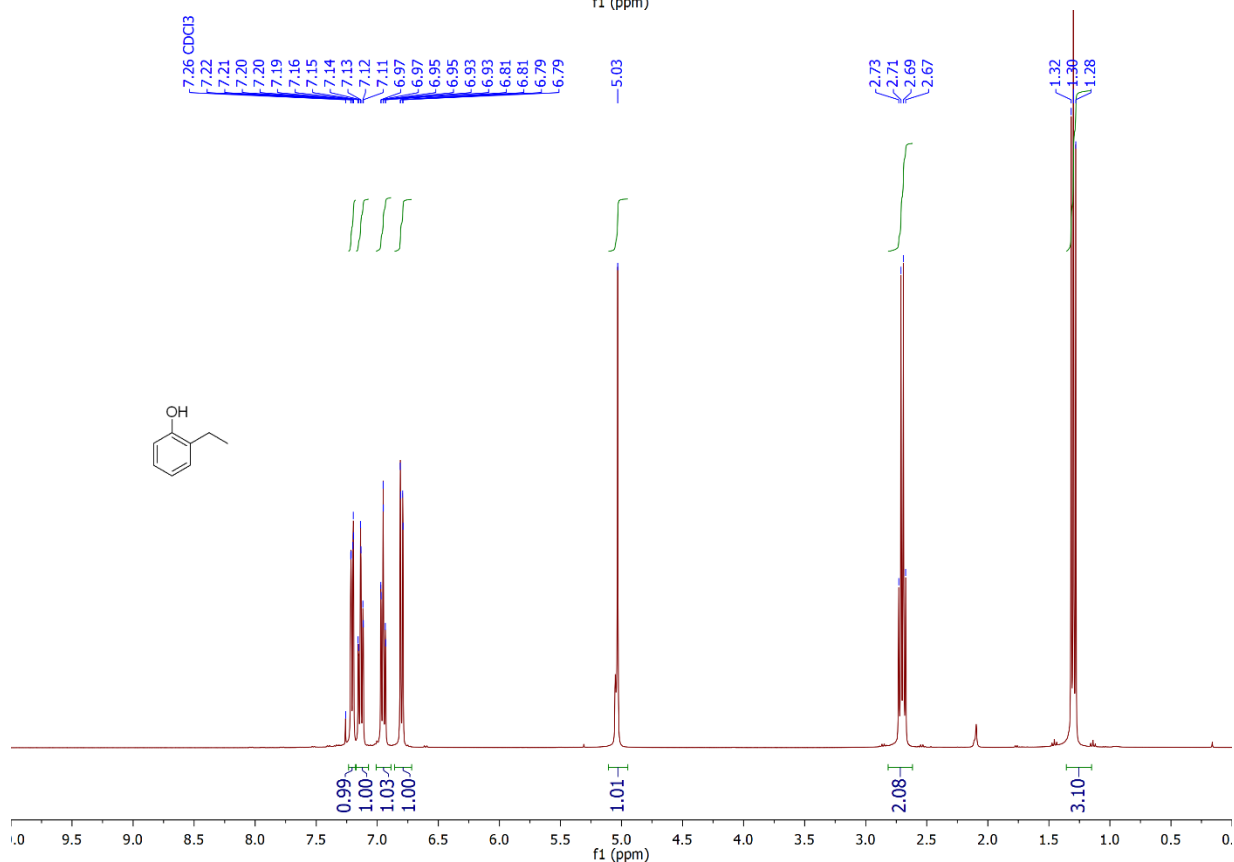
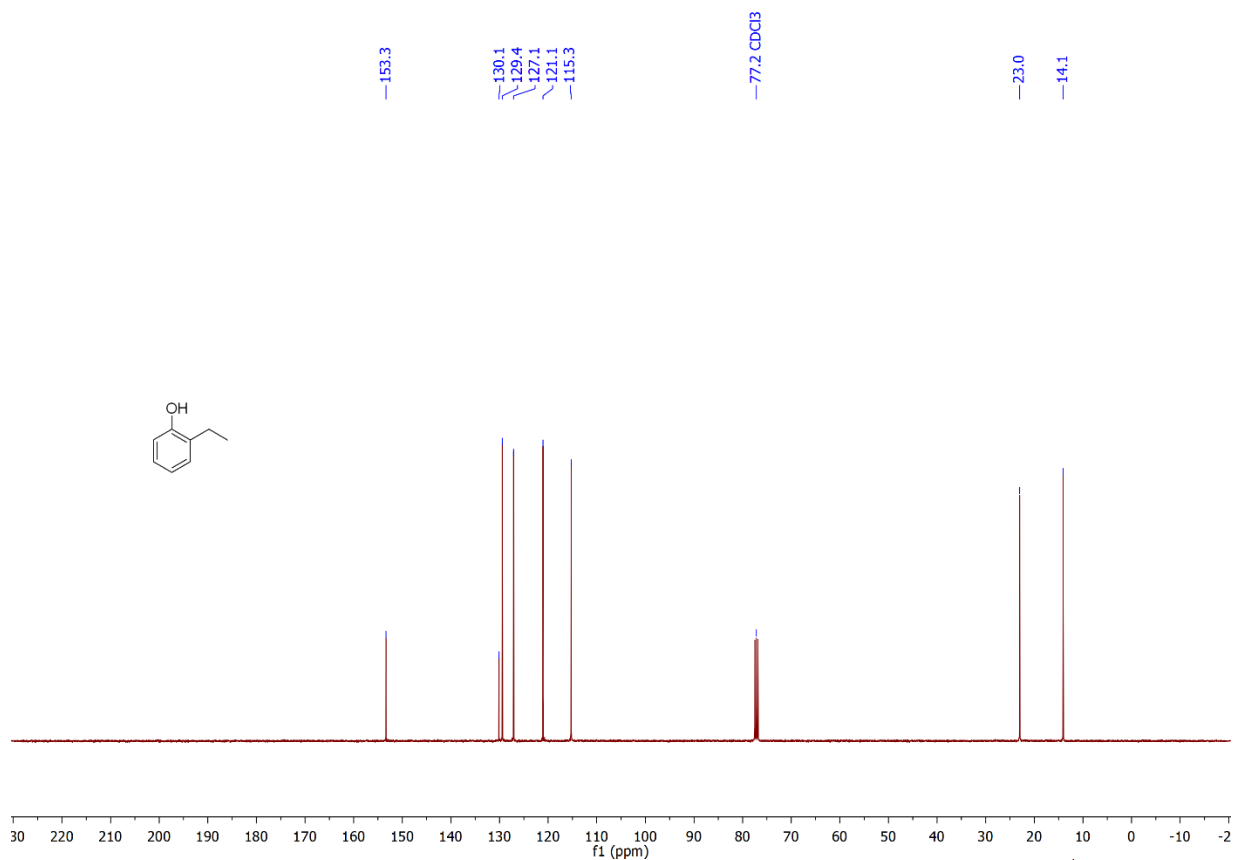










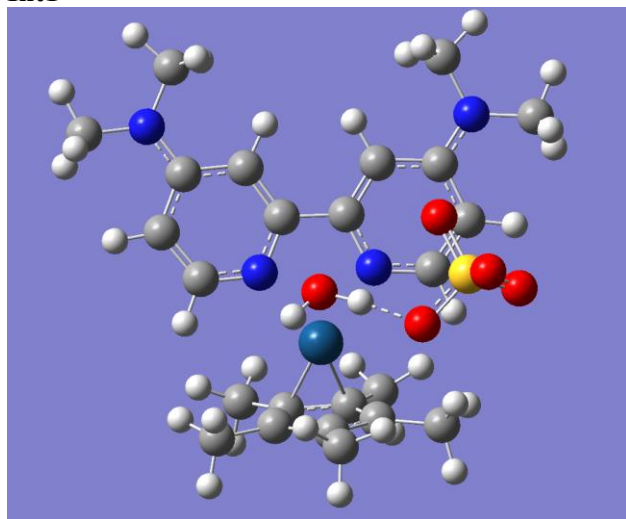


## 6 DFT computations

### 6.1 General information

All calculations were performed with the Gaussian 16 program package.<sup>1</sup> We carried out geometry optimizations and vibrational frequency calculations for all species. Solvent effects were taken into consideration using the SMD<sup>2</sup> solvation model. We carried out DFT calculations using the M06L<sup>3</sup> functional, Stevens/Basch/Krauss relativistic effective core potential triple-split basis (CEP-121G)<sup>4</sup> for Ir, and the 6-31G(d,p)<sup>5</sup> basis set for other atoms. Single point energy was performed with larger def2TZVP<sup>6</sup> basis set. Frequency calculations were performed to determine free energy corrections, and to verify the nature of all stationary points of encountered structures as intermediates (no imaginary frequency) or transition states (one and only one imaginary frequency).<sup>7</sup> The intrinsic reaction coordinate (IRC) method was performed to ensure that transition states led to expected intermediates.<sup>8</sup>

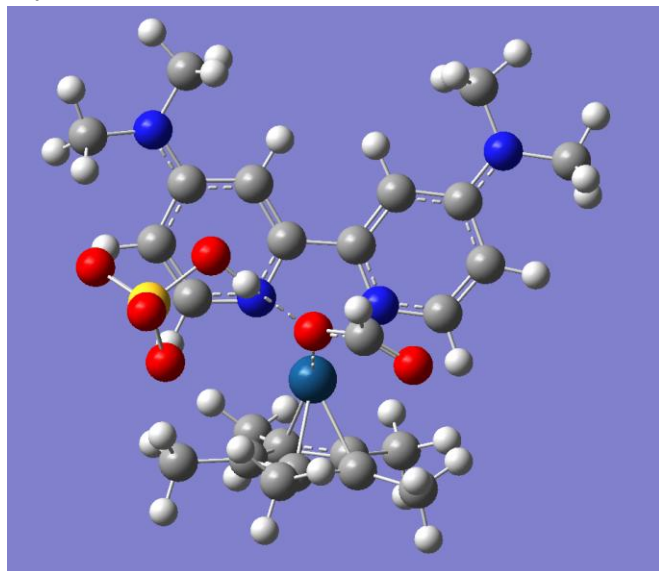
#### Int1



Ir	-0.37966400	-1.31731700	0.19433500
C	-1.27257700	-2.18452600	1.90759500
C	-0.26741900	-3.07577000	1.37755000
C	-0.65738000	-3.44574100	0.03241100
C	-2.30197700	-2.01677900	0.89637900
C	-1.91121600	-2.79014600	-0.24395000
C	0.03578500	-4.40005700	-0.87067700
H	-0.45671900	-5.37889300	-0.84640100
H	0.02343000	-4.05186500	-1.90767600
H	1.07676100	-4.55295200	-0.57496900
C	0.93535100	-3.55730000	2.09963000
H	0.68526900	-4.45513800	2.67552800
H	1.74165600	-3.82330700	1.41160900
H	1.31299900	-2.80797300	2.79951300

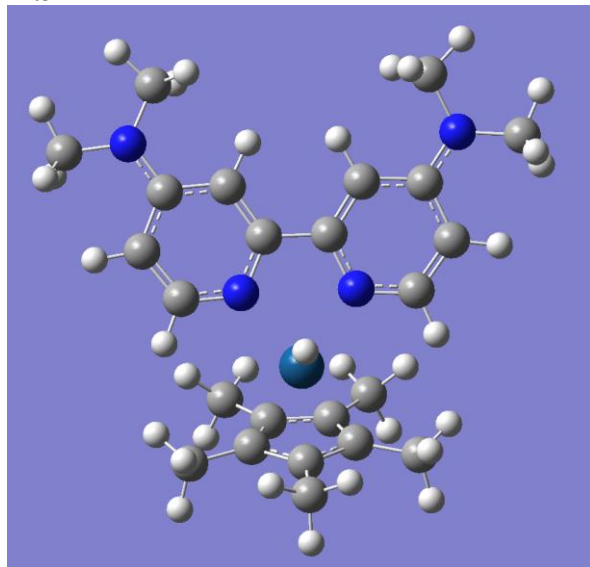
C	-2.65626300	-2.88023700	-1.52252700
H	-1.97951700	-2.96478200	-2.37706700
H	-3.28742100	-3.77635200	-1.51571100
H	-3.30329500	-2.01406400	-1.67381500
C	-3.57835700	-1.27167700	1.05087800
H	-3.80805300	-0.66782600	0.16830100
H	-4.40686400	-1.97359500	1.19845200
H	-3.55447600	-0.61196200	1.92179600
C	-1.29118300	-1.58986600	3.26680300
H	-1.87669700	-2.21836200	3.94693700
H	-0.28279200	-1.50140400	3.67789100
H	-1.74669000	-0.59549000	3.26173700
C	0.96939600	1.35906400	0.57823500
C	-1.26657400	1.47043800	1.18757100
C	-1.17551600	2.80718500	1.49133800
C	0.05410600	3.48227600	1.31351800
C	1.13686300	2.70562200	0.84158400
C	2.04894900	0.47918200	0.11574200
C	2.62212000	-1.69956400	-0.44045300
C	3.91479300	-1.34391600	-0.74265500
C	4.31674300	0.00721700	-0.60922200
C	3.32755900	0.91796800	-0.17299800
H	-2.21300900	0.94885000	1.27944200
H	-2.06688700	3.32641200	1.81959800
H	2.10568500	3.16119400	0.68218200
H	2.29169500	-2.72739400	-0.55437600
H	4.59766200	-2.10748000	-1.09266700
H	3.56231500	1.96950800	-0.06997300
N	-0.22791900	0.73497400	0.74873100
N	1.69149900	-0.82710700	-0.00855000
S	-2.93625300	1.99889400	-1.98440300
O	-1.58935300	2.66054100	-1.92599800
O	-3.65642900	2.37230900	-3.24687600
O	-3.76477700	2.35471800	-0.78317500
O	-2.72287900	0.47539700	-1.98415900
O	-0.26813500	-0.30142500	-1.86167200
H	-1.21759200	0.06205100	-1.94054400
H	-0.26190000	-1.07247900	-2.44519700
N	0.18993600	4.80512500	1.58312100
N	5.58186400	0.40916900	-0.88431200
C	-0.99452900	5.59694600	1.87019600
H	-1.50890900	5.22835100	2.76224500
H	-0.69451700	6.62663500	2.05689800
H	-1.70664600	5.58701500	1.03559000
C	1.41935100	5.49204000	1.22592100
H	2.28045300	5.04838400	1.73403000
H	1.60838500	5.46751400	0.14555700
H	1.34653900	6.53183800	1.53993600
C	6.52368400	-0.52912800	-1.47073600
H	7.49422500	-0.04454000	-1.56119800
H	6.64596500	-1.41130800	-0.83634100
H	6.20789700	-0.86384900	-2.46656300
C	5.89943200	1.82704600	-0.91141800
H	5.31482700	2.36489900	-1.66757300
H	5.71235600	2.29291600	0.06049000
H	6.95615600	1.94742400	-1.14320800

## Int2



Ir	0.92284400	-1.33256300	-0.15004100
C	1.35320500	-2.75956600	-1.62750800
C	0.01787200	-3.03383400	-1.12263000
C	0.12888000	-3.30377900	0.27262300
C	2.29152000	-2.95526100	-0.53392100
C	1.53984700	-3.23855500	0.64468900
C	-0.98589800	-3.60614200	1.19960700
H	-1.12018800	-4.69184200	1.27188700
H	-0.78493300	-3.23194500	2.20597800
H	-1.92792600	-3.17291000	0.85495900
C	-1.21557900	-3.06131900	-1.94526000
H	-1.28099500	-4.02093100	-2.47008200
H	-2.11777700	-2.95660300	-1.33749100
H	-1.21422300	-2.27515000	-2.70524200
C	2.07380900	-3.47159400	2.00833300
H	1.38611400	-3.09832400	2.77138500
H	2.21140200	-4.54438600	2.18521900
H	3.04012100	-2.98221400	2.15121500
C	3.76589500	-2.87166500	-0.66622300
H	4.26329200	-2.81653900	0.30398200
H	4.13175800	-3.77005100	-1.17575500
H	4.07235500	-2.01087300	-1.26732200
C	1.71247800	-2.49796900	-3.04046900
H	1.85821700	-3.44866600	-3.56701400
H	0.92295700	-1.94902800	-3.55907300
H	2.64175800	-1.92908100	-3.11820600
C	1.67607700	1.59201100	-0.18910500
C	3.43499200	0.29049800	0.60315400
C	4.23745000	1.38626600	0.79143600
C	3.75073800	2.67436800	0.45528200
C	2.42584200	2.74070800	-0.03921800
C	0.28077600	1.58122200	-0.64580600
C	-1.57766100	0.24674200	-1.05334200

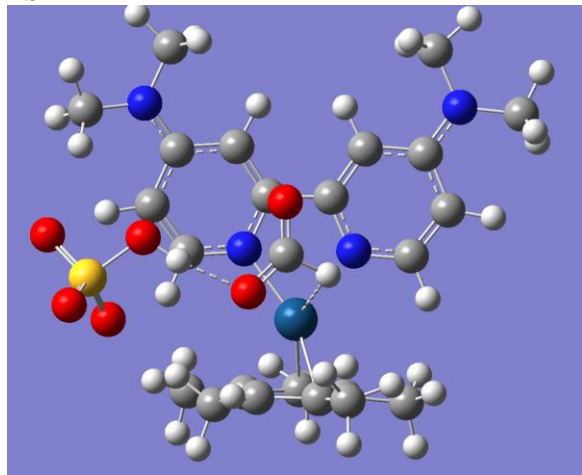
C	-2.38694400	1.33528100	-1.25492700
C	-1.83623500	2.63803000	-1.18034500
C	-0.45951800	2.72466700	-0.86385600
H	3.78609300	-0.70285500	0.86122500
H	5.23007100	1.24293500	1.19851200
H	1.98924300	3.69706700	-0.29651900
H	-1.98783800	-0.75589300	-1.08625800
H	-3.44397700	1.16928300	-1.42368500
H	0.01040800	3.69107900	-0.73718800
N	2.17734100	0.36012100	0.11462300
N	-0.26252700	0.33774500	-0.76600400
O	-1.94866100	-0.55566700	2.12716900
H	-3.26339600	0.31083700	1.77443900
N	4.50892600	3.78233800	0.60296300
N	-2.58822500	3.74631500	-1.38444200
C	5.83294400	3.67988000	1.19407000
H	6.47399400	3.00868800	0.61463100
H	6.29355800	4.66562000	1.20312300
H	5.78967600	3.30798800	2.22403300
C	3.94738300	5.09539000	0.33227200
H	3.59807400	5.17109900	-0.70189200
H	3.10579500	5.32168500	0.99665000
H	4.71846400	5.84791300	0.48443100
C	-4.03587900	3.62530800	-1.46210200
H	-4.45694500	4.59900700	-1.70742200
H	-4.32977300	2.92478200	-2.24767400
H	-4.46838900	3.28204200	-0.51488100
C	-2.02764500	5.05992600	-1.11251200
H	-1.77535300	5.18916200	-0.05296100
H	-1.12551900	5.23155600	-1.70493800
H	-2.75821900	5.81808500	-1.38856500
C	-0.90699300	0.16408500	2.18020600
H	0.06222100	-0.41925900	2.11739500
O	-0.81986300	1.40180000	2.29450200
S	-5.12287000	-0.08449700	0.72398700
O	-6.04453800	-0.58546600	1.76819300
O	-4.05127000	0.87653300	1.48526000
O	-4.32414600	-1.15974500	0.08722500
O	-5.77350700	0.83044200	-0.24037600

**Int3**

Ir	1.33468800	-0.02626600	-0.34388000
C	2.53003700	-0.65861500	1.44250500
C	2.54247000	0.75615700	1.37534500
C	3.09792600	1.14667300	0.08290100
C	3.07173600	-1.18015300	0.19080200
C	3.47992800	-0.05497000	-0.60751600
C	3.43453800	2.53635400	-0.32711900
H	4.45878500	2.78843000	-0.02651500
H	3.36815200	2.66892200	-1.41042100
H	2.77446000	3.26916400	0.14559900
C	2.04896100	1.71367000	2.39788000
H	2.88441400	2.15892800	2.95047800
H	1.49625600	2.53954100	1.93643300
H	1.38941600	1.22919900	3.12188200
C	4.19790400	-0.12273800	-1.90753100
H	3.96842500	0.73766000	-2.54086200
H	5.28073900	-0.12823400	-1.73644200
H	3.94655600	-1.03101100	-2.46059300
C	3.38423500	-2.60763400	-0.08690500
H	3.30475700	-2.84105900	-1.15220500
H	4.40774700	-2.84552500	0.22729100
H	2.71805200	-3.28136000	0.45939400
C	2.02058800	-1.50686200	2.55040200
H	2.85028100	-1.93724000	3.12306500
H	1.39633900	-0.93759900	3.24347600
H	1.42700600	-2.34557100	2.16958000
C	-1.59808000	-0.72462200	-0.14842000
C	-0.28962000	-2.63785000	-0.13676400
C	-1.38920100	-3.45818800	-0.04608900
C	-2.68529500	-2.89187600	-0.00371100
C	-2.75408300	-1.48395600	-0.07504200
C	-1.58657200	0.73971600	-0.19393800
C	-0.25209300	2.62915500	-0.33501600
C	-1.33578800	3.47053500	-0.24419200
C	-2.63765500	2.92778100	-0.13142400

C	-2.72682000	1.51967900	-0.10051000
H	0.70926300	-3.05918000	-0.19003200
H	-1.23574500	-4.52952000	-0.02105400
H	-3.71423500	-0.98469500	-0.07459100
H	0.75107400	3.03154600	-0.43433600
H	-1.16640700	4.53968100	-0.25925400
H	-3.68878200	1.03715200	0.01279100
N	-0.36201000	-1.29284000	-0.18493000
N	-0.34503000	1.28480300	-0.31208900
N	-3.80160900	-3.66080700	0.10646300
N	-3.74142600	3.71773100	-0.06129300
C	-3.68780700	-5.10273500	-0.03405300
H	-3.01783400	-5.51990600	0.72290600
H	-4.67023800	-5.54958800	0.10900500
H	-3.31332500	-5.39676300	-1.02290300
C	-5.11008500	-3.05407900	-0.06825800
H	-5.26835800	-2.24768500	0.65303300
H	-5.24782600	-2.64388200	-1.07701700
H	-5.87549300	-3.80894200	0.10492700
C	-3.58177400	5.15082500	0.11497500
H	-4.56568200	5.61653600	0.12941200
H	-3.06621100	5.39867000	1.05131800
H	-3.01612600	5.58908600	-0.71195200
C	-5.03314700	3.12176200	0.23068000
H	-5.30067600	2.37462400	-0.52198100
H	-5.05518300	2.63836000	1.21561300
H	-5.79400400	3.90036000	0.21188900
H	1.00209100	-0.11800700	-1.94027200

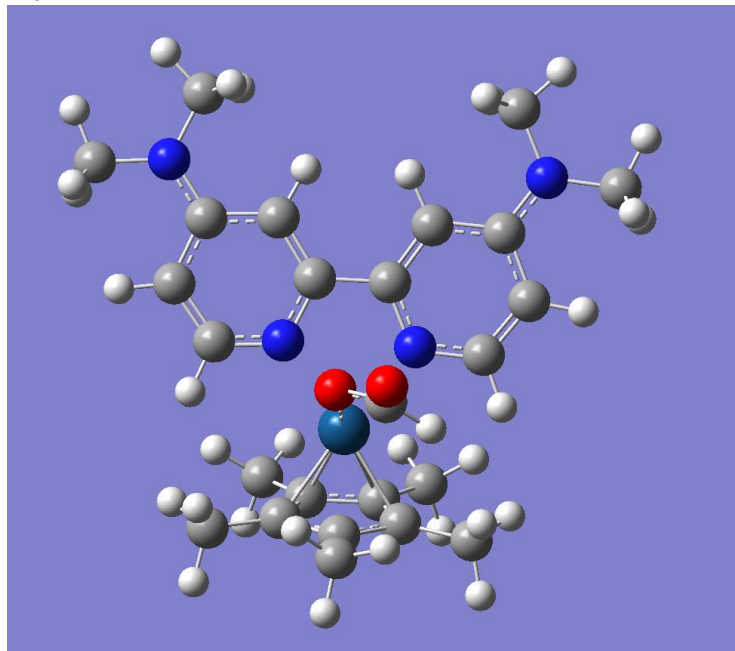
## TS1



Ir	0.58305760	-1.26290325	-0.22786444
C	0.78808060	-2.96401825	-1.44537044
C	-0.62537940	-2.80642625	-1.13614844
C	-0.78398440	-2.89256925	0.27552156
C	1.48906560	-3.22471125	-0.19803644
C	0.53739260	-3.11402525	0.85929156
C	-2.06829640	-2.86279725	1.01011756
H	-2.56052040	-3.83559325	0.88109856
H	-1.91441440	-2.68538825	2.07312256
H	-2.75029940	-2.08416925	0.64732256
C	-1.71956840	-2.62356425	-2.12293544
H	-1.95868440	-3.58495025	-2.59133544
H	-2.63147540	-2.25112225	-1.64685744
H	-1.44064540	-1.93444225	-2.92534044
C	0.78829960	-3.19224125	2.31936856
H	0.15581660	-2.46617725	2.84046356
H	0.55056060	-4.19130925	2.70160556
H	1.83140360	-2.97831325	2.56595556
C	2.92590760	-3.57998325	-0.08427744
H	3.31515060	-3.40855025	0.92234456
H	3.06340760	-4.64527425	-0.29918744
H	3.54843560	-3.03009725	-0.79583844
C	1.37815660	-3.02632625	-2.80359244
H	1.37352160	-4.05960025	-3.17019244
H	0.81221760	-2.42219525	-3.51588144
H	2.41378360	-2.67881525	-2.81406744
C	1.86500360	1.42598875	-0.28291244
C	3.40497860	-0.18192025	0.37946756
C	4.39129760	0.75172675	0.55963756
C	4.12016860	2.11498975	0.28554856
C	2.81077960	2.42167675	-0.13737144
C	0.47929960	1.66204975	-0.68060944
C	-1.56136940	0.63860675	-1.13885344
C	-2.20326840	1.83946575	-1.24368444
C	-1.48220040	3.03434375	-1.02598744
C	-0.09197640	2.90971175	-0.79871044
H	3.59315160	-1.22694325	0.59864156
H	5.35946860	0.42521575	0.91567256

H	2.52587260	3.44558975	-0.34042444
H	-2.13587440	-0.27409225	-1.20855044
H	-3.27973640	1.82911875	-1.37876844
H	0.51179760	3.78556175	-0.59825844
N	2.16110260	0.11273275	-0.05371044
N	-0.24613740	0.51953375	-0.84650844
O	-1.20185240	-0.32255625	2.16913256
H	-2.65867540	0.62524875	1.75390356
N	5.06918860	3.07206875	0.42721056
N	-2.10579940	4.23461975	-1.01363744
C	6.38594360	2.72063475	0.92495856
H	6.87260160	1.98054575	0.28178056
H	7.01323460	3.60982375	0.93662156
H	6.34751060	2.32111475	1.94501056
C	4.73327560	4.46618575	0.20980556
H	4.37881060	4.63848575	-0.81177244
H	3.96364660	4.81618575	0.90747756
H	5.62197560	5.07661875	0.35754356
C	-3.56178340	4.29408875	-1.02255044
H	-3.87318940	5.27410375	-0.66116644
H	-3.96611240	4.16131775	-2.03347844
H	-3.99931940	3.52378075	-0.37764244
C	-1.35038140	5.45218375	-0.81082544
H	-0.94679140	5.52857175	0.20711956
H	-0.51757840	5.52708475	-1.51720344
H	-2.00012740	6.30910175	-0.98318544
C	-0.15864440	0.38942375	2.15204756
H	0.80748860	-0.22929725	2.10292056
O	-0.00023240	1.61641875	2.15390456
S	-4.60329940	0.50719375	0.72631756
O	-5.47121640	0.00047875	1.79869256
O	-3.34498040	1.27430775	1.45166056
O	-3.99979240	-0.57419125	-0.10445444
O	-5.18642040	1.59859575	-0.08481844

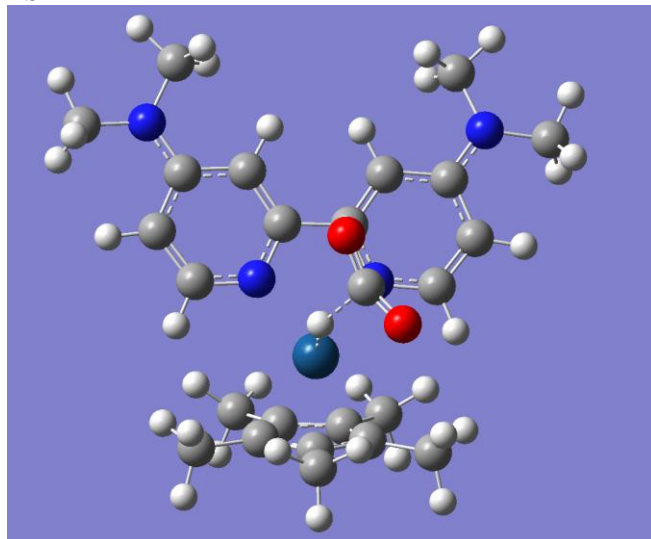
## Int 4



Ir	-1.26781900	0.07358800	-0.01180300
C	-2.55322600	-0.48136800	-1.64231400
C	-2.54316500	0.94610000	-1.50868600
C	-3.02875200	1.28275100	-0.17865400
C	-3.06307200	-1.04580700	-0.39989500
C	-3.36691100	0.04824600	0.47988600
C	-3.27870300	2.64508200	0.36243600
H	-4.34707200	2.88442500	0.33039700
H	-2.95371200	2.73631900	1.40266500
H	-2.76914900	3.41689500	-0.22026300
C	-2.11905300	1.92455800	-2.54131400
H	-2.98455700	2.28030800	-3.10994600
H	-1.64002600	2.80359400	-2.10073600
H	-1.41286400	1.48789600	-3.25049500
C	-3.87995300	-0.06435400	1.86782600
H	-3.40779200	0.66514600	2.53037400
H	-4.95978700	0.11820600	1.88468700
H	-3.70745100	-1.05770500	2.28870800
C	-3.36072200	-2.47934700	-0.14223500
H	-3.09393500	-2.78149000	0.87528600
H	-4.43019300	-2.67798400	-0.27026300
H	-2.83617400	-3.13773500	-0.83936200
C	-2.15491600	-1.26413400	-2.83959800
H	-3.03115300	-1.51651300	-3.44599500
H	-1.46068700	-0.70942100	-3.47398000
H	-1.66753300	-2.20479500	-2.56679500
C	1.62479000	-0.71216800	-0.17444000
C	0.26269500	-2.58492000	-0.27183900
C	1.33691100	-3.43992800	-0.29414000
C	2.64925700	-2.91220700	-0.25780100
C	2.75684200	-1.50557800	-0.19126000
C	1.65373200	0.75208600	-0.10704800
C	0.36754700	2.67662400	-0.01375800

C	1.47469300	3.48713500	0.03761900
C	2.76495400	2.90760000	0.00877900
C	2.81672800	1.49783500	-0.05638100
H	-0.75080500	-2.97505900	-0.27989300
H	1.15415300	-4.50580000	-0.33082000
H	3.73151500	-1.03735700	-0.14999400
H	-0.62940500	3.10394900	0.03180900
H	1.33441500	4.55765000	0.10947700
H	3.77214500	0.98979700	-0.06328700
N	0.37507300	-1.24427500	-0.22748900
N	0.42688900	1.33605400	-0.10433200
N	3.74190400	-3.71216400	-0.28321300
N	3.88852600	3.66336700	0.04579700
C	3.58313300	-5.15407000	-0.32487500
H	3.03109200	-5.47279400	-1.21523900
H	4.56513600	-5.62137100	-0.36022700
H	3.06171800	-5.53368000	0.56099000
C	5.07043300	-3.13555200	-0.20286300
H	5.27029600	-2.46261700	-1.04366700
H	5.21892700	-2.58061200	0.73031300
H	5.80992700	-3.93301500	-0.23607400
C	3.78687500	5.10710600	0.15069300
H	4.78617600	5.53765400	0.14489900
H	3.23612900	5.53385100	-0.69406400
H	3.29265100	5.41641700	1.07859600
C	5.19315400	3.03013600	0.06050700
H	5.33149400	2.39723200	0.94455500
H	5.35424800	2.41882100	-0.83385300
H	5.96406000	3.79784700	0.07723500
C	-0.85248900	-1.03209900	2.70311100
O	-0.60881300	-1.17071500	3.88759200
O	-0.61093900	0.04550500	2.00409600
H	-1.32317000	-1.86586800	2.11237400

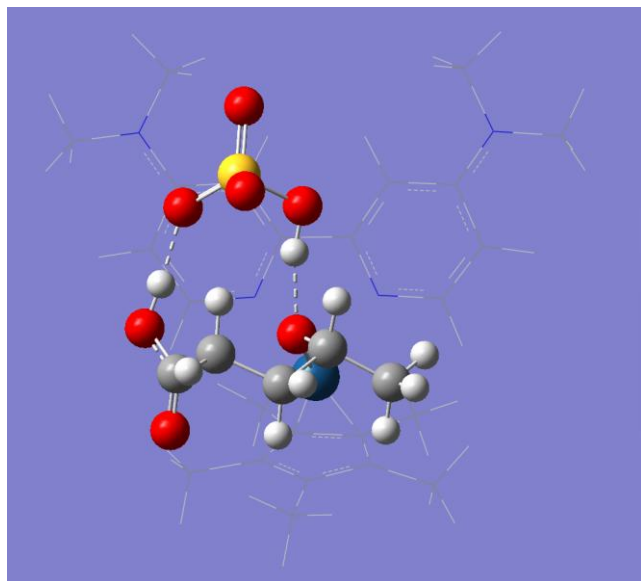
## TS2



Ir	1.31418600	-0.11902700	0.05589600
C	2.56848600	0.57527700	-1.60472000
C	2.50208200	-0.85207700	-1.63136300
C	3.03927800	-1.35217400	-0.37443800
C	3.13590200	0.98055900	-0.32726200
C	3.46006800	-0.21751200	0.39981500
C	3.28282200	-2.77868300	-0.03481100
H	4.31007100	-3.06179100	-0.29258500
H	3.14697700	-2.97133100	1.03287000
H	2.61736900	-3.44574600	-0.58902000
C	1.98883600	-1.70299500	-2.73429200
H	2.81561300	-2.07057300	-3.35289300
H	1.45902000	-2.57937400	-2.34788800
H	1.30455600	-1.15219300	-3.38417600
C	4.10116300	-0.26402200	1.73840600
H	3.82251000	-1.16593700	2.28844600
H	5.19168000	-0.26496400	1.62837500
H	3.83216900	0.60532800	2.34328300
C	3.48934300	2.36664200	0.07768200
H	3.31606700	2.53472500	1.14445600
H	4.54968600	2.56488300	-0.11811500
H	2.91474200	3.10951200	-0.48166500
C	2.12828300	1.50589300	-2.67284600
H	2.98550200	1.82614100	-3.27591500
H	1.40446400	1.03737700	-3.34367800
H	1.67224000	2.40888700	-2.25505100
C	-1.58737900	0.71128300	-0.11785000
C	-0.19909200	2.57052200	-0.08112900
C	-1.26252800	3.43666300	-0.16850400
C	-2.58013700	2.92266700	-0.24201500
C	-2.70827500	1.51644600	-0.21108700
C	-1.63664700	-0.75311900	-0.06773900
C	-0.37945700	-2.69963400	0.04835100
C	-1.50174000	-3.49249100	0.03532600
C	-2.78271800	-2.89313500	-0.03577800
C	-2.81278500	-1.48170400	-0.07552300

H	0.81745800	2.94716200	-0.01697300
H	-1.06688300	4.50128600	-0.18451000
H	-3.68676500	1.05755900	-0.26772900
H	0.60884200	-3.14292500	0.11709800
H	-1.37941700	-4.56679200	0.08902600
H	-3.75913800	-0.95733400	-0.10578900
N	-0.33045600	1.22897900	-0.06813200
N	-0.41594700	-1.35303700	-0.00527000
O	1.21615600	1.58144800	3.10372500
N	-3.66222100	3.73537100	-0.33175400
N	-3.91910000	-3.63350300	-0.06762500
C	-3.47390400	5.16421700	-0.51397300
H	-2.93897700	5.39354900	-1.44331200
H	-4.44826600	5.64758800	-0.54934900
H	-2.91299700	5.59872300	0.31830200
C	-4.97891200	3.16311600	-0.55239100
H	-5.03181000	2.60464900	-1.49518200
H	-5.25862800	2.48651800	0.26113200
H	-5.71277900	3.96671000	-0.58664300
C	-3.84699900	-5.06795300	0.15228900
H	-4.85021100	-5.48557800	0.08416300
H	-3.22790900	-5.55407300	-0.60783200
H	-3.43458700	-5.31395100	1.13876000
C	-5.21204800	-2.97640100	0.01252700
H	-5.35401700	-2.45471700	0.96750700
H	-5.33316200	-2.24872600	-0.79525800
H	-5.99585700	-3.72473400	-0.09241600
C	0.32901600	0.83031100	2.81037700
H	0.92991700	-0.11672200	1.71818300
O	-0.78886300	0.42318700	2.95696400

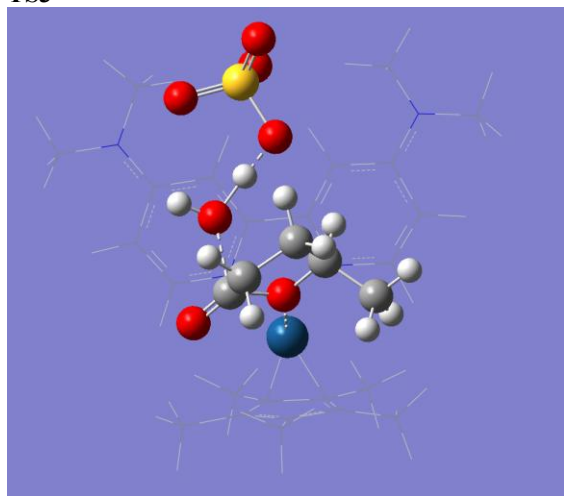
## Int5



Ir	1.59719300	0.22294400	-0.32648900
C	2.87885900	0.19191900	-2.03640600
C	3.15657000	1.35271600	-1.24567800
C	3.60956000	0.91393200	0.06605100
C	3.14907000	-0.98220800	-1.22021400
C	3.62558800	-0.52605200	0.05315800
C	4.19516200	1.80988600	1.10003500
H	5.12279500	2.25960200	0.72766300
H	4.44114300	1.27266300	2.01776700
H	3.53157700	2.63601000	1.37696500
C	3.06693200	2.76731400	-1.69119300
H	4.01126600	3.08417400	-2.14761600
H	2.87144500	3.44588800	-0.85637800
H	2.27677800	2.91620300	-2.43137200
C	4.11539000	-1.42918200	1.12253100
H	4.15693000	-0.94114700	2.09877400
H	5.13516000	-1.74942700	0.87567100
H	3.49199500	-2.32472500	1.20258000
C	3.12479400	-2.39687600	-1.67641300
H	2.66037800	-3.05801400	-0.93576800
H	4.14889400	-2.74995200	-1.84743500
H	2.59626400	-2.50291700	-2.62788800
C	2.40540400	0.17223600	-3.44420900
H	3.24788100	0.06199700	-4.13578400
H	1.87900700	1.09309500	-3.70700900
H	1.71994200	-0.66021300	-3.62869800
C	-1.28733800	0.39031400	-1.19099700
C	-0.33658800	-1.61027700	-1.85907900
C	-1.54182800	-2.09546500	-2.30219600
C	-2.71166200	-1.32461000	-2.13288800
C	-2.53595700	-0.03306800	-1.59931300
C	-1.04310700	1.67849600	-0.53640600
C	0.50358800	2.98039000	0.58919800

C	-0.38908200	4.01287500	0.75161300
C	-1.69763000	3.88458800	0.23091900
C	-1.99681400	2.67375300	-0.42299200
H	0.55143600	-2.23143400	-1.89180000
H	-1.57740000	-3.10914300	-2.67809500
H	-3.39442300	0.58598200	-1.37694400
H	1.51087800	3.05599200	0.99052000
H	-0.07186500	4.90009000	1.28419500
H	-2.98348700	2.50081200	-0.83158500
N	-0.18672600	-0.39305900	-1.30948500
N	0.21180300	1.83096500	-0.04207700
H	-0.30984500	-0.33743800	3.09596700
S	-3.16532600	-1.39734000	1.67009700
O	-3.00069800	-1.87677400	3.05080300
O	-2.64009700	-2.36547900	0.65361600
O	-4.49414900	-0.87480600	1.32867800
O	-2.20318600	-0.07507500	1.51912000
H	-1.27159800	-0.37275200	1.33104800
C	-4.08696900	-3.25155000	-2.56184200
H	-3.49256500	-3.64395200	-3.39080900
H	-5.12865100	-3.49032800	-2.77508200
H	-3.78950300	-3.76084400	-1.63580100
C	-2.30225800	6.06106800	1.12794900
H	-3.14023600	6.75457800	1.08153300
H	-1.42546200	6.58014700	0.72782500
H	-2.11230900	5.82854100	2.18341100
C	0.67126500	-0.55364100	2.63005100
C	1.10697300	-1.91304300	3.17498700
H	1.04434900	-1.89123500	4.27043500
C	0.23360500	-3.03029800	2.62320300
C	0.63687000	-3.41965400	1.22185000
O	0.42657100	-0.62520900	1.23983200
C	1.61675700	0.54943300	3.05281000
H	2.62219200	0.37245000	2.66240200
H	-0.82779700	-2.76310800	2.68835300
H	1.69127400	0.60572900	4.14443600
O	1.79820000	-3.68677700	0.93846900
H	1.27704400	1.52567000	2.69150900
O	-0.32127200	-3.57401000	0.31173700
H	2.15487400	-2.11884300	2.92209500
H	-1.17887600	-3.14564800	0.59277700
H	0.36951600	-3.93622800	3.22708500
N	-3.94712200	-1.80913900	-2.45019300
N	-2.61700500	4.88003000	0.34952500
C	-3.98413800	4.64971300	-0.07355700
H	-4.04006200	4.43752800	-1.14644000
H	-4.45072500	3.81672100	0.46653700
H	-4.57292800	5.54615800	0.11329500
C	-5.11048300	-1.10226400	-1.92698000
H	-5.09655700	-1.04479400	-0.82955800
H	-5.16245600	-0.09194000	-2.34252900
H	-6.00971200	-1.62441000	-2.25455900

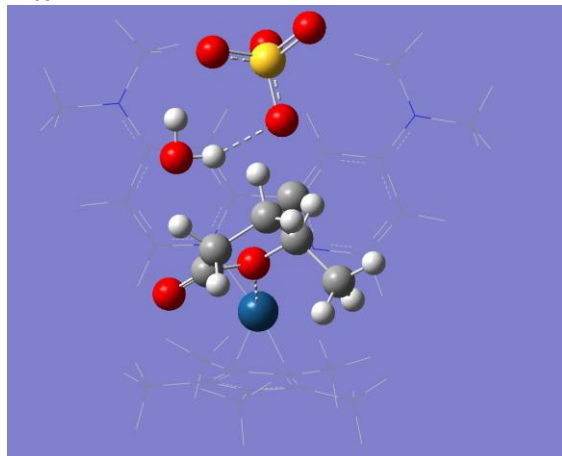
## TS3



Ir	1.95636100	-0.06787200	-0.26891200
C	3.54863500	-1.02669700	-1.26496300
C	3.69519200	0.41007200	-1.38114100
C	3.84587700	0.96014600	-0.05263300
C	3.63178700	-1.37091800	0.14273500
C	3.78638100	-0.14577900	0.87312800
C	4.16212800	2.37284600	0.28300500
H	5.23562200	2.56066700	0.16836700
H	3.89875400	2.61540800	1.31479500
H	3.64718400	3.08584400	-0.36827700
C	3.72982500	1.18142000	-2.64859900
H	3.39710800	2.21302900	-2.50863200
H	3.10072800	0.73029600	-3.41905800
H	4.75316500	1.22236800	-3.03694700
C	3.82936000	-0.04287300	2.35220300
H	3.41663400	0.90808600	2.69895600
H	4.86479300	-0.10545900	2.70495400
H	3.25349300	-0.84865500	2.81350600
C	3.64289600	-2.73241400	0.73874600
H	2.91889800	-2.81186200	1.55460900
H	4.63680200	-2.96117800	1.13828300
H	3.41758600	-3.50081000	-0.00494600
C	3.41329300	-1.99073500	-2.38552000
H	4.39407200	-2.38274700	-2.67529400
H	2.96690100	-1.52622500	-3.26720300
H	2.78564000	-2.84268200	-2.10984200
C	-0.82884700	-0.76403100	-1.08394400
C	0.34391200	-2.65537200	-0.44048400
C	-0.75441900	-3.45794900	-0.62374400
C	-1.96918400	-2.89286900	-1.07735000
C	-1.97725100	-1.49680300	-1.29018100
C	-0.76308900	0.68895400	-1.21567500
C	0.63669100	2.53889100	-1.23256600
C	-0.42165600	3.40184200	-1.39507200
C	-1.74312400	2.89208000	-1.39880900
C	-1.87540400	1.48734500	-1.36637000
H	1.26891400	-3.06714700	-0.05464400

H	-0.66834700	-4.51025400	-0.38546400
H	-2.90736500	-0.97713300	-1.50378900
H	1.65163200	2.92140800	-1.16045600
H	-0.21506000	4.46257900	-1.45410700
H	-2.85531200	1.01521900	-1.35041000
N	0.34494300	-1.33589600	-0.69482000
N	0.49757500	1.20846500	-1.09854300
H	-0.75249300	1.78867100	1.22068500
S	-4.41598400	-0.01526100	0.78328000
O	-5.47239800	0.73044900	1.49301800
O	-4.27179600	-1.43820300	1.20393800
O	-4.57780400	0.09153500	-0.71451900
O	-3.03441700	0.68606800	1.13011900
H	-2.22136900	-0.14154100	1.41981300
C	-3.08534900	-5.02713500	-0.85986100
H	-2.27353400	-5.60559400	-1.31185700
H	-4.02313300	-5.49105700	-1.16376200
H	-3.00161000	-5.11159300	0.23207800
C	-2.61890200	5.14416400	-1.36981200
H	-3.57624600	5.64722400	-1.50763500
H	-1.94998500	5.48846700	-2.16238700
H	-2.20506600	5.46269600	-0.40208400
C	-0.00782300	1.59200500	2.00250000
C	-0.70690000	1.23849700	3.32755700
H	-1.77443800	1.10561600	3.14606700
C	-0.06784200	-0.06602600	3.76727300
C	0.38744900	-0.72730400	2.49165200
O	0.72031100	0.38572000	1.62339200
C	0.98356800	2.72258900	2.11829200
H	1.66988300	2.55990500	2.95781500
H	-0.73215700	-0.71978000	4.33186800
H	0.46116800	3.66805300	2.29212200
O	1.02440600	-1.75569400	2.34536900
H	1.57597700	2.83446800	1.20523700
O	-1.36224900	-0.96398100	1.70010300
H	-0.57376200	2.04142600	4.05896900
H	-1.84703100	-1.69913800	2.08890200
H	0.83348000	0.10077900	4.37455600
N	-2.83096700	3.71271100	-1.44361200
N	-3.06935100	-3.65271300	-1.31260400
C	-4.11910400	3.26695100	-0.91766600
H	-4.30444100	2.20454700	-1.08692600
H	-4.17965400	3.43335400	0.16470300
H	-4.91063500	3.84147700	-1.40505600
C	-4.35187500	-3.00481100	-1.56589400
H	-4.68718100	-2.42406900	-0.69881300
H	-4.27417600	-2.32961300	-2.42196400
H	-5.08067100	-3.77635000	-1.81815000

## Int6



Ir	2.03838500	0.04370700	-0.29295300
C	3.78270600	-0.59496700	-1.28102900
C	3.79992700	0.85505600	-1.13464400
C	3.80897500	1.16144300	0.27216800
C	3.80308300	-1.17910300	0.04043600
C	3.78547300	-0.09498000	0.98172900
C	3.95344600	2.50447300	0.89111600
H	5.01336200	2.75791300	1.00425300
H	3.50397000	2.54758700	1.88614200
H	3.50499900	3.29751100	0.28648400
C	3.85365100	1.83506800	-2.24695400
H	3.44537100	2.80617600	-1.95701600
H	3.30030000	1.48926600	-3.12288200
H	4.89217000	1.99849900	-2.55440600
C	3.76295300	-0.23743200	2.45754100
H	3.13215700	0.52444000	2.92511900
H	4.77550000	-0.10657800	2.85577700
H	3.39971600	-1.21932200	2.76348900
C	3.90075000	-2.62131700	0.38617700
H	3.15635900	-2.90574400	1.13425700
H	4.89318300	-2.84591400	0.79127100
H	3.76953800	-3.25738200	-0.49258600
C	3.81258300	-1.33886000	-2.56418300
H	4.84668300	-1.55090900	-2.85645400
H	3.34939500	-0.76992000	-3.37287100
H	3.28825400	-2.29500800	-2.49044900
C	-0.70185900	-0.65843300	-1.17512900
C	0.61348500	-2.56545800	-0.92833700
C	-0.45859700	-3.39030000	-1.13690300
C	-1.74293400	-2.83047100	-1.34132700
C	-1.83148100	-1.41771700	-1.37974100
C	-0.70317700	0.80011100	-1.12497300
C	0.60721100	2.69434100	-0.78792800
C	-0.47639800	3.52630500	-0.92301500
C	-1.76470400	2.97330200	-1.13450700
C	-1.83789000	1.56607400	-1.26740000
H	1.59285900	-2.97610600	-0.70816300
H	-0.30413000	-4.45957400	-1.08056100
H	-2.80394900	-0.91986200	-1.43801200

H	1.59320100	3.10083700	-0.58106900
H	-0.32154200	4.59224200	-0.81901200
H	-2.79402000	1.06159400	-1.39622500
N	0.52612300	-1.22037800	-0.93915200
N	0.52427400	1.35184400	-0.85545500
H	-1.08059800	1.37335500	1.49388900
S	-4.50285000	0.12683300	0.54554800
O	-5.47405900	1.14565500	1.02482600
O	-4.79315700	-1.22934700	1.14650600
O	-4.54335100	0.02522800	-0.97459300
O	-3.07884100	0.53341000	0.93230400
H	-2.16092900	-1.12521900	1.22003700
C	-2.74900500	-5.00964000	-1.12619500
H	-2.02092500	-5.54226500	-1.74504500
H	-3.71791600	-5.48097500	-1.28617300
H	-2.47110400	-5.13853100	-0.07149300
C	-2.74251300	5.17393300	-0.94863200
H	-3.70343800	5.65348300	-1.13334500
H	-2.00909500	5.63804600	-1.61351200
H	-2.45194600	5.38641800	0.08963200
C	-0.38600500	1.03449300	2.26930000
C	-1.14200600	0.32112000	3.39087200
H	-2.13341000	0.05297800	3.01766300
C	-0.32207100	-0.92686300	3.67615700
C	0.48364900	-1.15654000	2.43407700
O	0.41624400	-0.03942600	1.64321200
C	0.55983900	2.12062800	2.71233800
H	1.20514300	1.78757200	3.53433400
H	-0.92721800	-1.81242200	3.86687700
H	-0.00577600	2.98663800	3.06693200
O	1.17329800	-2.09441000	2.11208800
H	1.19301600	2.45661800	1.88429000
O	-2.17504700	-2.03470800	1.57939600
H	-1.25132800	0.97260200	4.26156700
H	-3.15004000	-2.07716800	1.64283300
H	0.38807000	-0.80857400	4.50499900
N	-2.87115200	3.75518600	-1.21280200
N	-2.83907000	-3.60993500	-1.49270200
C	-4.20283800	3.19262700	-0.99638300
H	-4.32145700	2.21240000	-1.45983400
H	-4.42173100	3.04255200	0.06670600
H	-4.93664500	3.87577900	-1.42973600
C	-4.16678900	-3.00054100	-1.46036900
H	-4.40330700	-2.55634900	-0.48189000
H	-4.24322800	-2.19902600	-2.19563500
H	-4.89826300	-3.76880200	-1.71628400

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<sup>1</sup>Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**

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