

# **Pt/CB-Catalyzed Chemoselective Hydrogenation Using *in situ*-Generated Hydrogen by Microwave Mediated Dehydrogenation of Methylcyclohexane under Continuous-Flow Conditions**

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## **Supporting Information**

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## 1. General

All reagents and solvents were obtained from commercial sources and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on JEOL JNM ECA-500 (500 MHz for  $^1\text{H}$  NMR and 125 MHz for  $^{13}\text{C}$  NMR) and ECZ-400 (400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR) spectrometers.  $\text{CDCl}_3$  was used as the solvent for NMR measurements. The chemical shifts ( $\delta$ ) are expressed in parts per million and internally referenced (0.00 ppm for tetramethylsilane and 77.0 ppm for  $\text{CDCl}_3$  in  $^{13}\text{C}$  NMR). The continuous-flow microwave reactor (EYELA, MR-2G-100) was developed by Tokyo Rikakikai Co., Ltd. (Tokyo, Japan); see product URL: <https://eyela.actibookone.com/content/detail?param=eyJjb250ZW50TnVtIjoyMTY4MX0=&detailFlg=1&pNo=44>. The quartz tube used as the catalyst cartridge was purchased from Tokyo Rikakikai Co., Ltd. An FMR-100 (Saida FDS Inc., Shizuoka, Japan) was used to flow the reaction solution. Thermo FLEX F50 was used as a thermal imaging camera for monitoring the temperature of a quartz cartridge. Catalysts such as 5% Pt/CB, 5% Pd/CB, 5% Rh/CB, and CB were obtained from N.E. CHEMCAT Co. (Tokyo, Japan). The  $^1\text{H}$  NMR spectra of known products are identical to those reported in the literature.

## 2. MW flow device (EYELA), catalyst cartridge, and peripheral devices

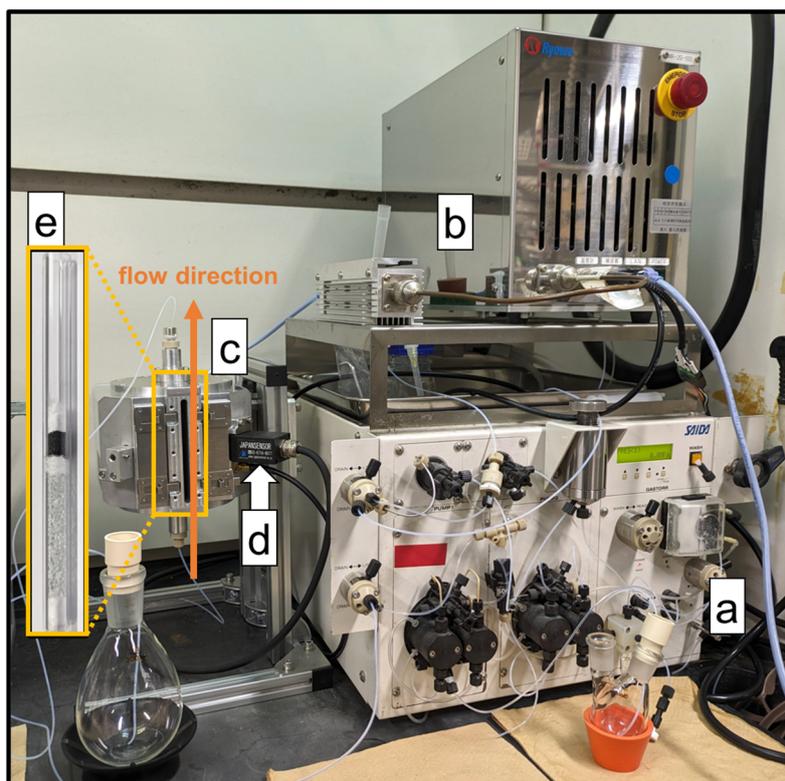


Figure. S1 The microwave flow reactor (EYELA, MR-2G-100) (a) pump, (b) Microwave controller unit, (c) Microwave generator unit, (d) Thermography unit, (e) 5% Pt/CB-packed Quartz tube (catalyst cartridge)

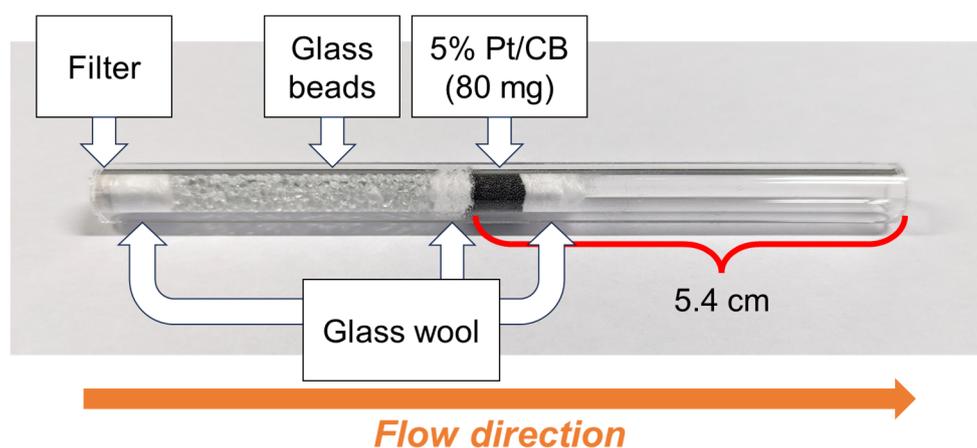


Figure. S2 The quartz tube for the continuous flow microwave reactor (EYELA, MR-2G-100)

### Preparation of 5% Pt/CB-packed cartridge

Glass beads and glass wool were put on the glass filter inside an EYELA quartz reaction tube to a depth of 5.4 cm from the top to the quartz tube. 5% Pt/CB (80.0 mg) was tightly filled on the glass wool by tapping the tube, and another glass wool was then placed on the catalyst to prevent movement of the 5% Pt/CB from the cartridge.

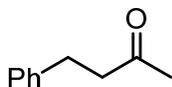
### **3. Thermographic measurements of the temperature of a 5% Pt/CB-packed cartridge (Figure 2)**

Thermographic measurements were conducted to monitor the temperature of a quartz cartridge packed with 5% Pt/CB (80 mg) in an MW cavity (heater) mechanically set at 140 °C with the slit open. An MCH solution of **1** (0.05 M) was pumped for 30 minutes, after which the temperature of the catalyst layer was measured using thermography. The same procedure was followed for the MCH / 2-PrOH = 19 / 1 solution of **1** (0.05 M). This observation is illustrated in Figure 2.

#### 4. Spectral data of products

##### 4-Phenyl-2-butanone (2) [CAS Reg. No. 2550-26-7]<sup>1</sup>

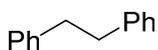
Obtained in 91% yield (33.7 mg, 228  $\mu\text{mol}$ ; colorless solid) from 4-phenyl-3-buten-2-one (34.5 mg, 250  $\mu\text{mol}$ ).



<sup>1</sup>H NMR [400 MHz (ECZ-400, CDCl<sub>3</sub>)]  $\delta$  7.31–7.26 (m, 2H), 7.22–7.18 (m, 3H), 2.90 (t,  $J$  = 7.6 Hz, 2H), 2.77 (t,  $J$  = 7.6 Hz, 2H), 2.15 (s, 3H); <sup>13</sup>C NMR [100 MHz (ECZ-400, CDCl<sub>3</sub>)]  $\delta$  208.0, 140.9, 128.5, 128.3, 126.1, 45.2, 30.1, 29.7.

##### 1,2-Diphenylethane (6) [CAS Reg. No. 103-29-7]<sup>2</sup>

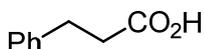
Obtained in 95% yield (43.0 mg, 236  $\mu\text{mol}$ ; colorless solid) from diphenylacetylene (44.6 mg, 250  $\mu\text{mol}$ ).



<sup>1</sup>H NMR [400 MHz (ECZ-400, CDCl<sub>3</sub>)]  $\delta$  7.31–7.27 (m, 4H), 7.22–7.18 (m, 6H), 2.92 (s, 4H); <sup>13</sup>C NMR [100 MHz (ECZ-400, CDCl<sub>3</sub>)]  $\delta$  141.7, 128.4, 128.3, 125.9, 37.9.

##### 3-Phenylpropionic acid (9) [CAS Reg. No. 501-52-0]<sup>2</sup>

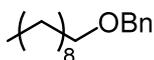
Obtained in 76% yield (30.1 mg, 201  $\mu\text{mol}$ ; colorless solid) from benzyl 3-phenylpropionate (60.1 mg, 250  $\mu\text{mol}$ ).



<sup>1</sup>H NMR [400 MHz (ECZ-400, CDCl<sub>3</sub>)]  $\delta$  7.32–7.29 (m, 2H), 7.23–7.21 (m, 3H), 2.97 (t,  $J$  = 7.8 Hz, 2H), 2.69 (t,  $J$  = 7.8 Hz, 2H); <sup>13</sup>C NMR [100 MHz (ECZ-400, CDCl<sub>3</sub>)]  $\delta$  179.2, 140.1, 128.5, 128.2, 126.4, 35.6, 30.5.

##### Benzyl decyl ether (10) [CAS Reg. No. 87220-50-6]<sup>3</sup>

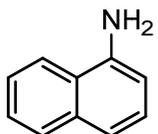
Recovered in 88% yield (54.7 mg, 220  $\mu\text{mol}$ ; colorless liquid).



<sup>1</sup>H NMR [400 MHz (ECZ-400, CDCl<sub>3</sub>)]  $\delta$  7.37–7.28 (m, 5H), 4.50 (s, 2H), 3.46 (t,  $J$  = 6.6 Hz, 2H), 1.65–1.58 (m, 2H), 1.37–1.26 (m, 14H), 0.88 (t,  $J$  = 6.9 Hz, 3H); <sup>13</sup>C NMR [100 MHz (ECZ-400, CDCl<sub>3</sub>)]  $\delta$  138.7, 128.3, 127.6, 127.4, 72.8, 70.5, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 26.2, 22.7, 14.1.

##### 1-Amino naphthalene (13) [CAS Reg. No. 134-32-7]<sup>4</sup>

Obtained in 68% yield (24.3 mg, 170  $\mu\text{mol}$ ; red solid) from 4-nitronaphthalene (43.3 mg, 250  $\mu\text{mol}$ ).

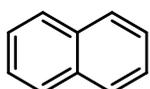


$^1\text{H}$  NMR [400 MHz (ECZ-400,  $\text{CDCl}_3$ )]  $\delta$  7.81–7.72 (m, 2H), 7.45–7.37 (m, 2H), 7.31–7.24 (m, 2H), 6.72 (dd,  $J$  = 7.1, 1.6 Hz, 1H), 3.95 (brs, 2H);  $^{13}\text{C}$  NMR [100 MHz (ECZ-400,  $\text{CDCl}_3$ )]  $\delta$  142.0, 134.3, 128.5, 126.3, 125.8, 124.8, 123.5, 120.7, 118.8, 109.6.

#### Naphthalene (14) [CAS Reg. No. 91-20-3]<sup>5</sup>

Obtained in 80% yield (25.6 mg, 200  $\mu\text{mol}$ ; colorless solid) from 4-nitronaphthalene (43.3 mg, 250  $\mu\text{mol}$ ).

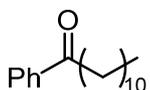
Obtained in 89% yield (28.5 mg, 223  $\mu\text{mol}$ ; colorless solid) from 4-chloronaphthalene (40.7 mg, 250  $\mu\text{mol}$ ).



$^1\text{H}$  NMR [400 MHz (ECZ-400,  $\text{CDCl}_3$ )]  $\delta$  7.87–7.83 (m, 4H), 7.50–7.46 (m, 4H);  $^{13}\text{C}$  NMR [100 MHz (ECZ-400,  $\text{CDCl}_3$ )]  $\delta$  133.4, 127.9, 125.8.

#### 1-Dodecaphenone (15) [CAS Reg. No. 1674-38-0]<sup>6</sup>

Recovered in 91% yield (59.3 mg, 228  $\mu\text{mol}$ ; colorless solid).

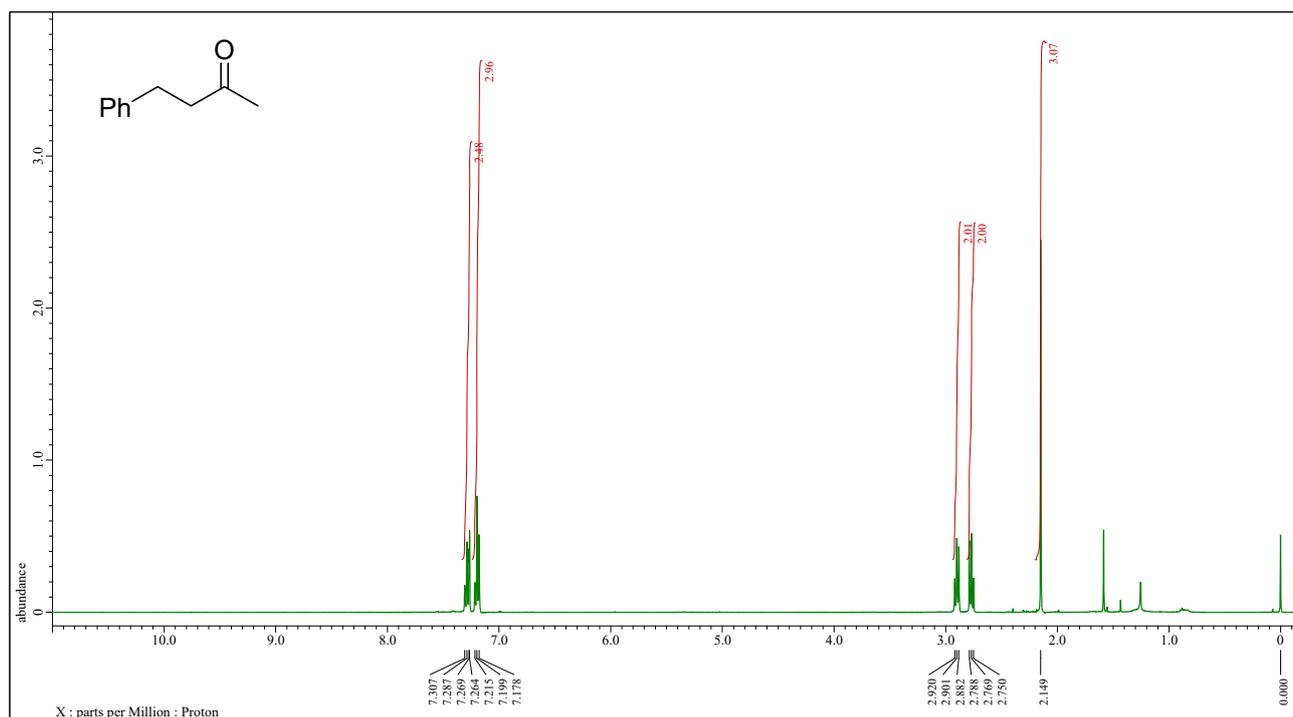


$^1\text{H}$  NMR [400 MHz (ECZ-400,  $\text{CDCl}_3$ )]  $\delta$  7.98–7.95 (m, 2H), 7.56 (t,  $J$  = 7.2 Hz, 1H), 7.46 (t,  $J$  = 7.4 Hz, 2H), 2.96 (t,  $J$  = 7.5 Hz, 2H), 1.77–1.70 (m, 2H), 1.39–1.26 (m, 16H), 0.88 (t,  $J$  = 6.9 Hz, 3H);  $^{13}\text{C}$  NMR [100 MHz (ECZ-400,  $\text{CDCl}_3$ )]  $\delta$  200.6, 137.0, 132.8, 128.5, 128.0, 38.6, 31.9, 29.6, 29.5, 29.5, 29.4, 29.3, 24.3, 22.7, 14.1.

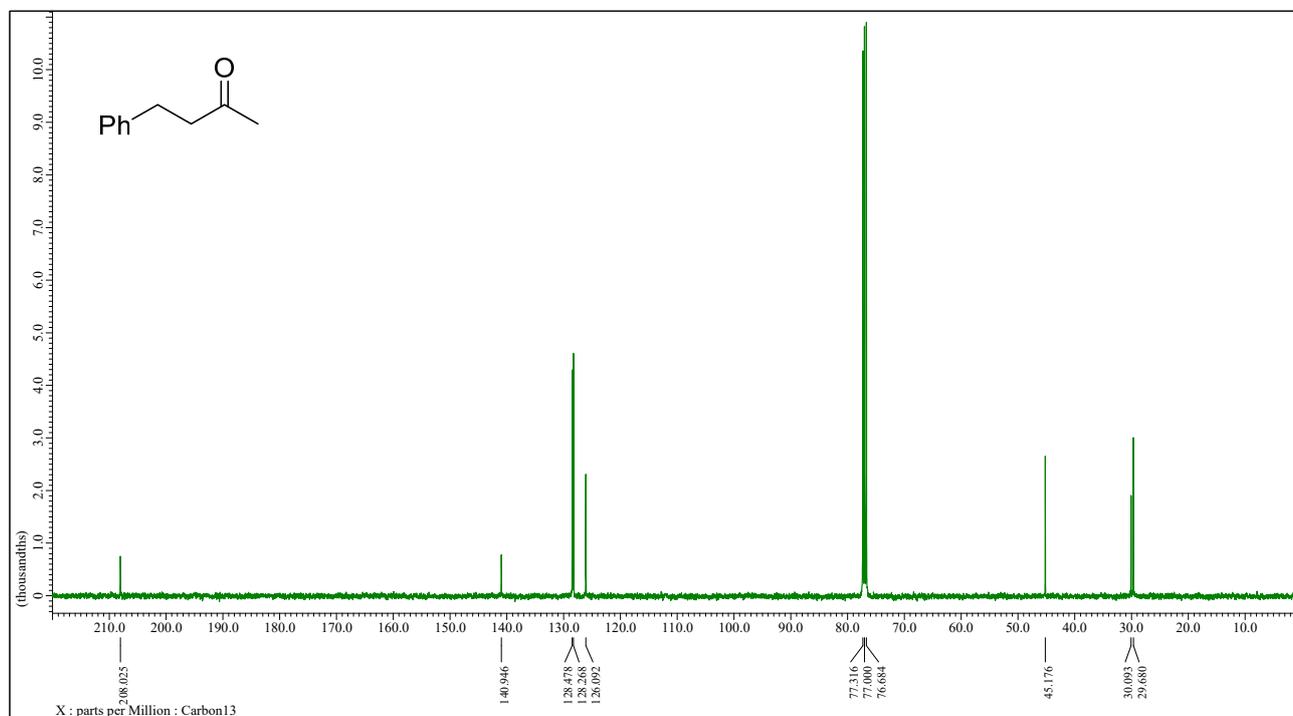
## 5. References

- 1) P. Colbon, J. Ruan, M. Purdie, K. Mulholland, J. Xiao, *Org. Lett.* **2011**, *13*, 5456–5459.
- 2) Y. Monguchi, T. Ida, T. Maejima, T. Yanase, Y. Sawama, Y. Sasai, S. Kondo, H. Sajiki, *Adv. Synth. Catal.* **2014**, *356*, 313–318.
- 3) Y. Gao, C. Yang, S. Bai, X. Liu, Q. Wu, J. Wang, C. Jiang, X. Qi, *Chem* **2020**, *6*, 675–688.
- 4) H. Yue, L. Guo, X. Liu, M. Rueping, *Org. Lett.* **2017**, *19*, 1788–1791.
- 5) T. Yamada, A. Ogawa, H. Masuda, W. Teranishi, A. Fujii, K. Park, Y. Ashikari, N. Tomiyasu, T. Ichikawa, R. Miyamoto, H. Bai, K. Matsuyama, A. Nagaki, H. Sajiki, *Catal. Sci. Technol.* **2020**, *10*, 6359–6367.
- 6) P. Hu, M. Tan, L. Cheng, H. Zhao, R. Feng, W. Gu, W. Han, *Nat. Commun.* **2019**, *10*, 2425.

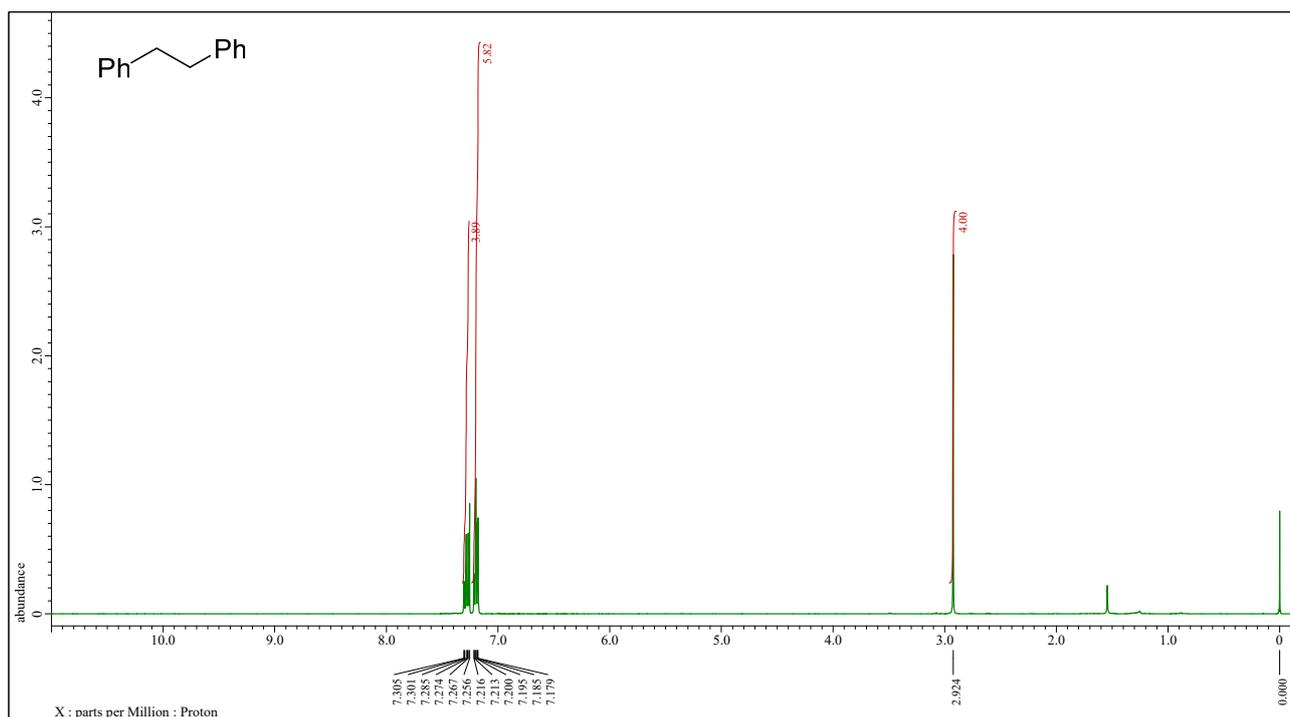
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 4-phenyl-2-butanone (2)



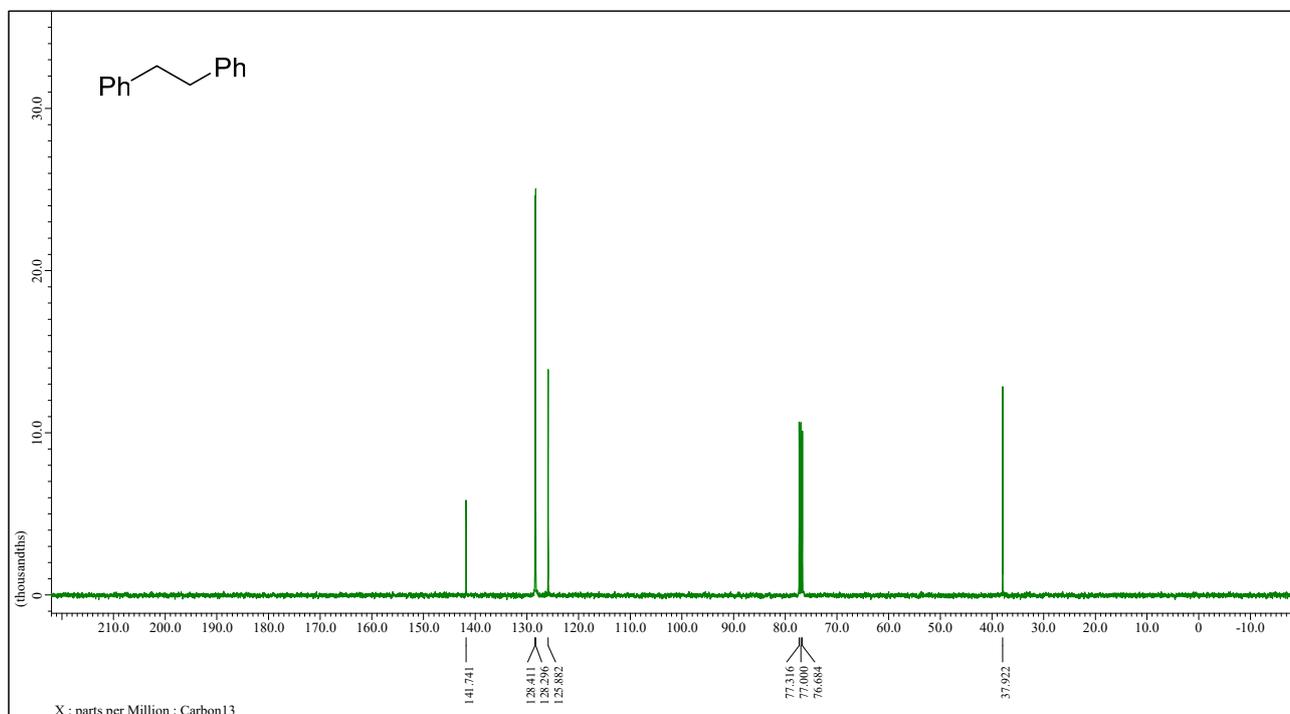
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 4-phenyl-2-butanone (2)



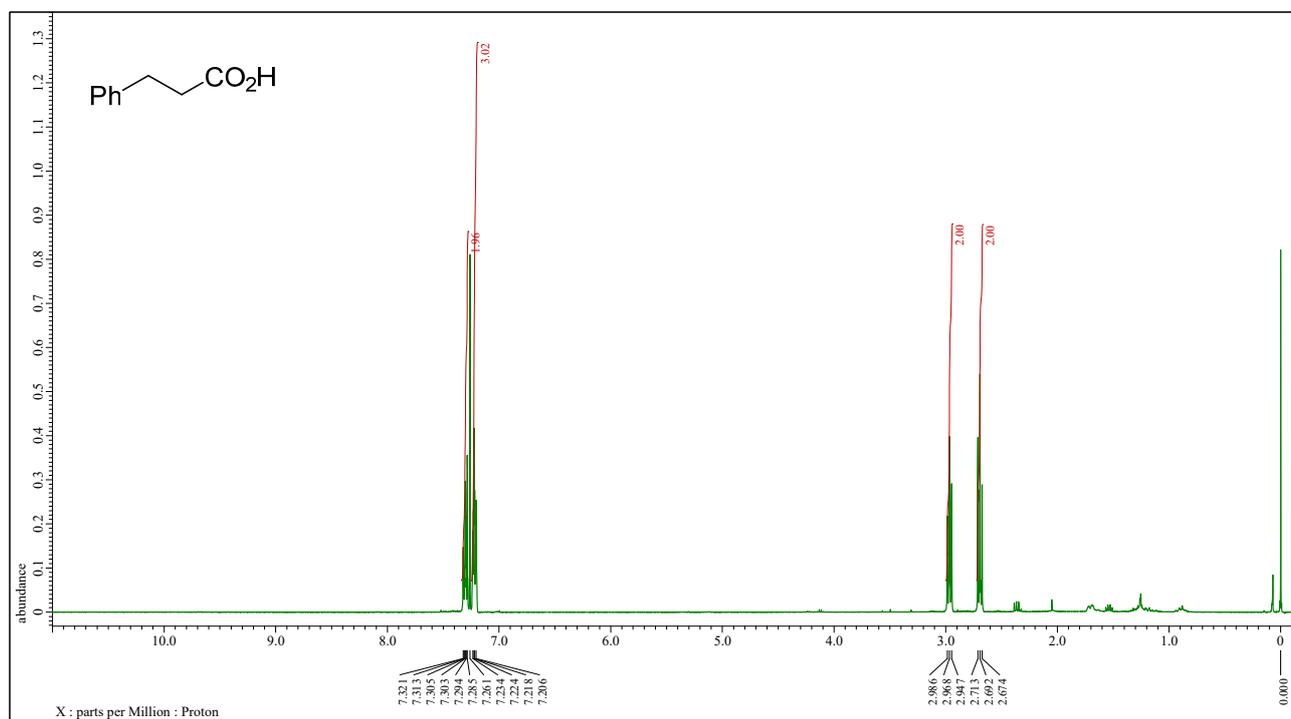
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1,2-diphenylethane (6)**



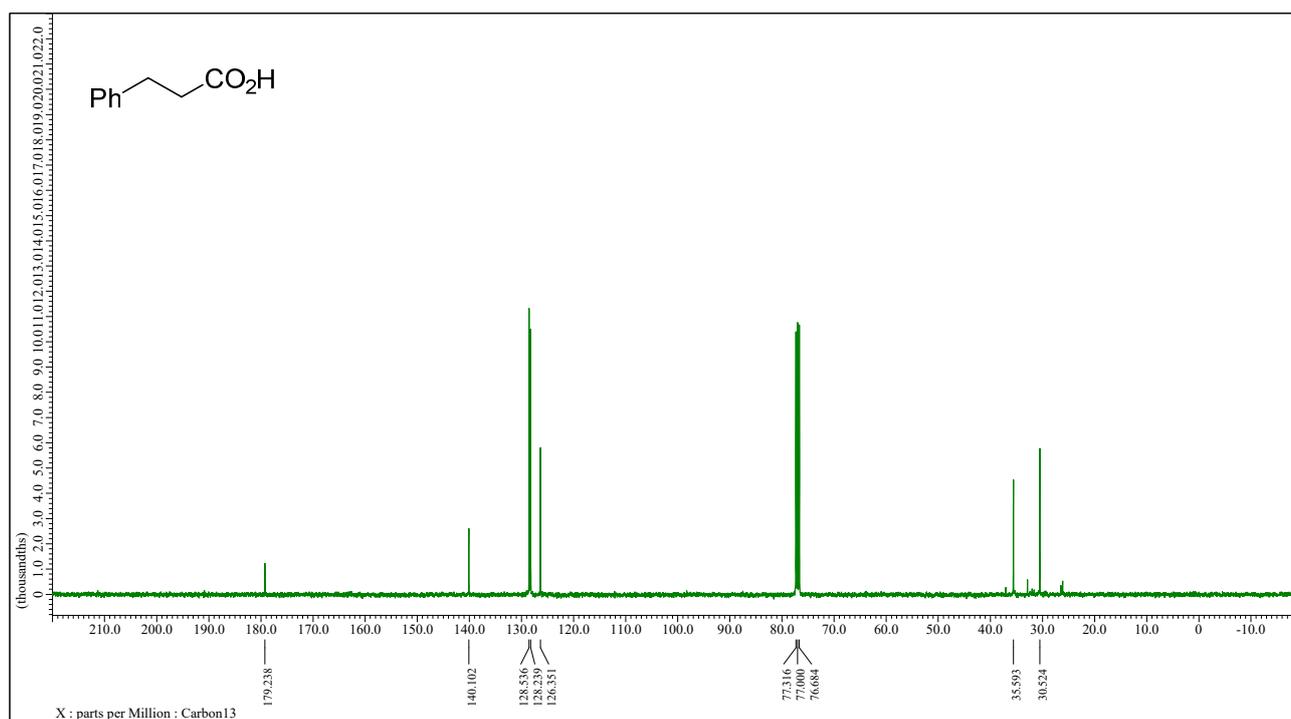
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1,2-diphenylethane (6)**



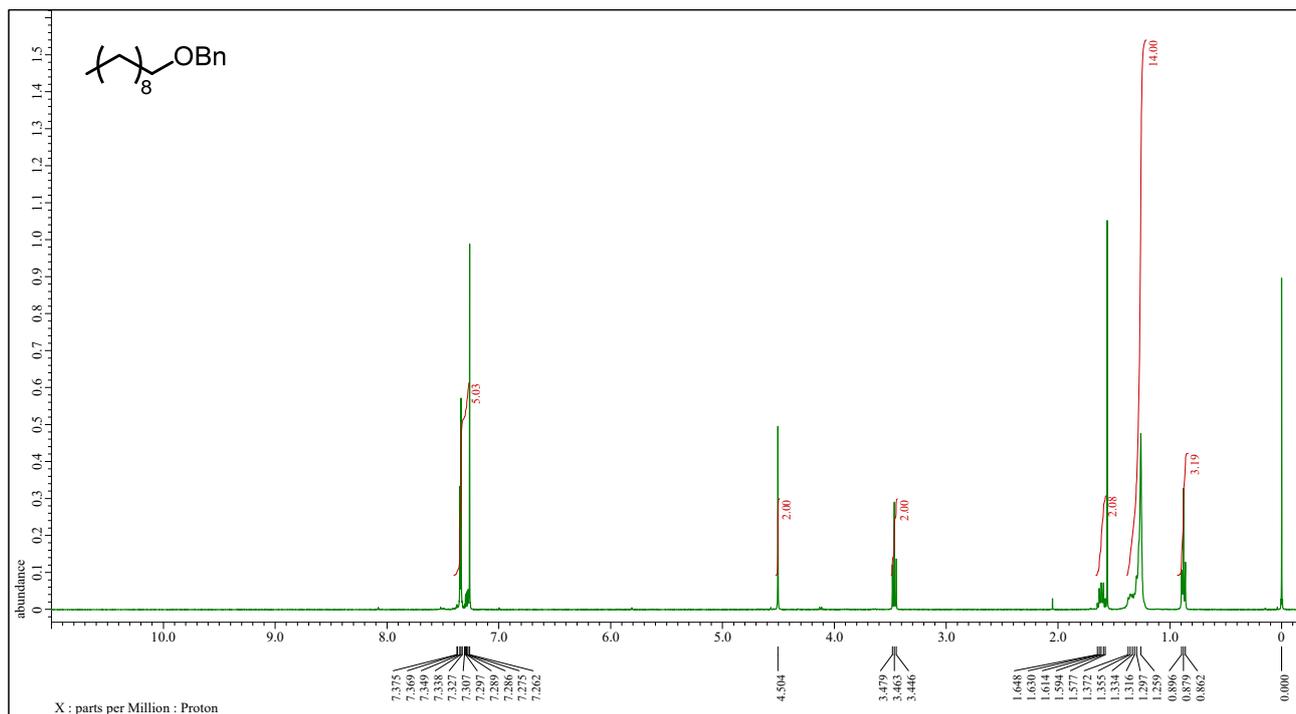
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3-phenylpropionic acid (9)**



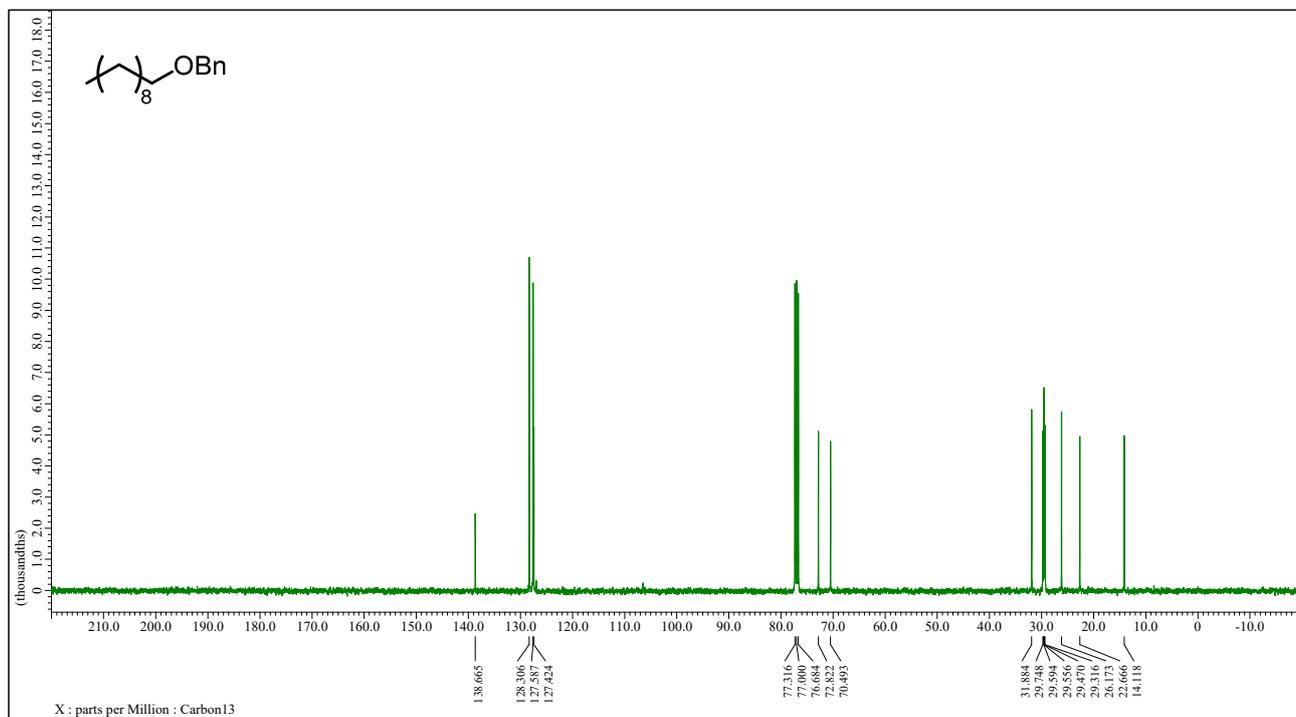
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3-phenylpropionic acid (9)**



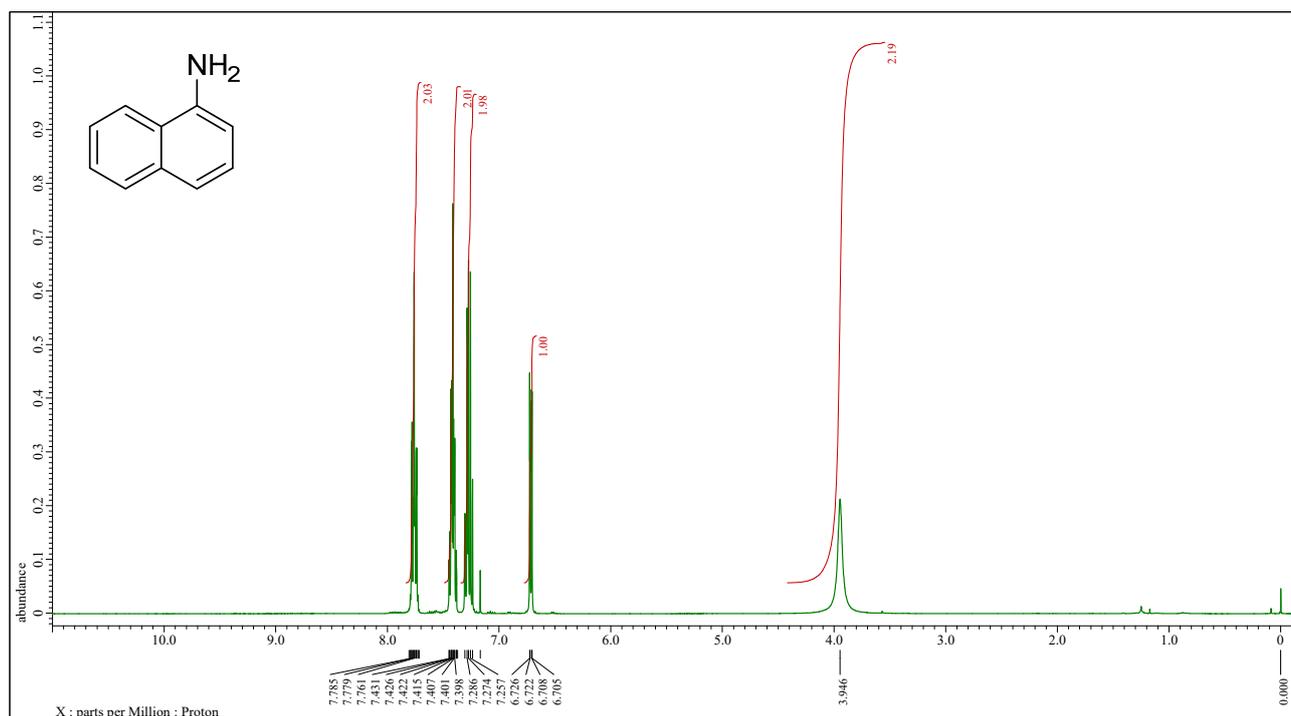
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of benzyl decyl ether (14)



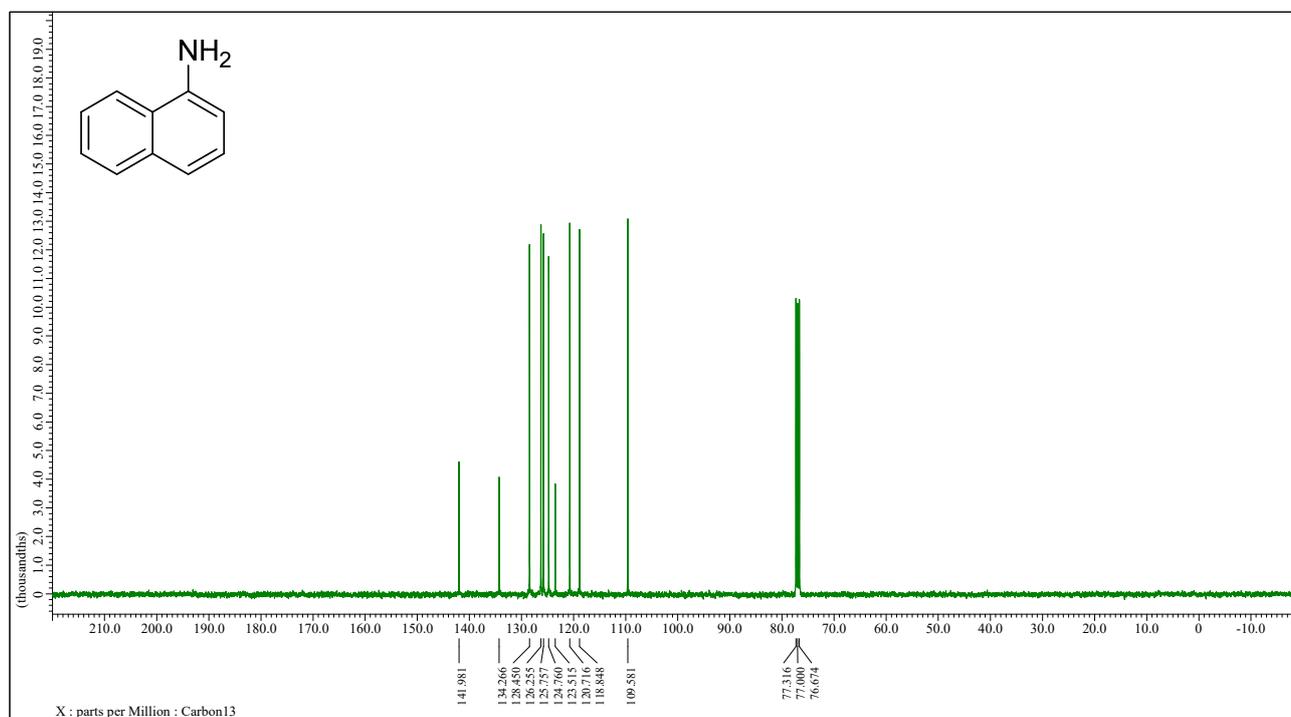
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of benzyl decyl ether (14)



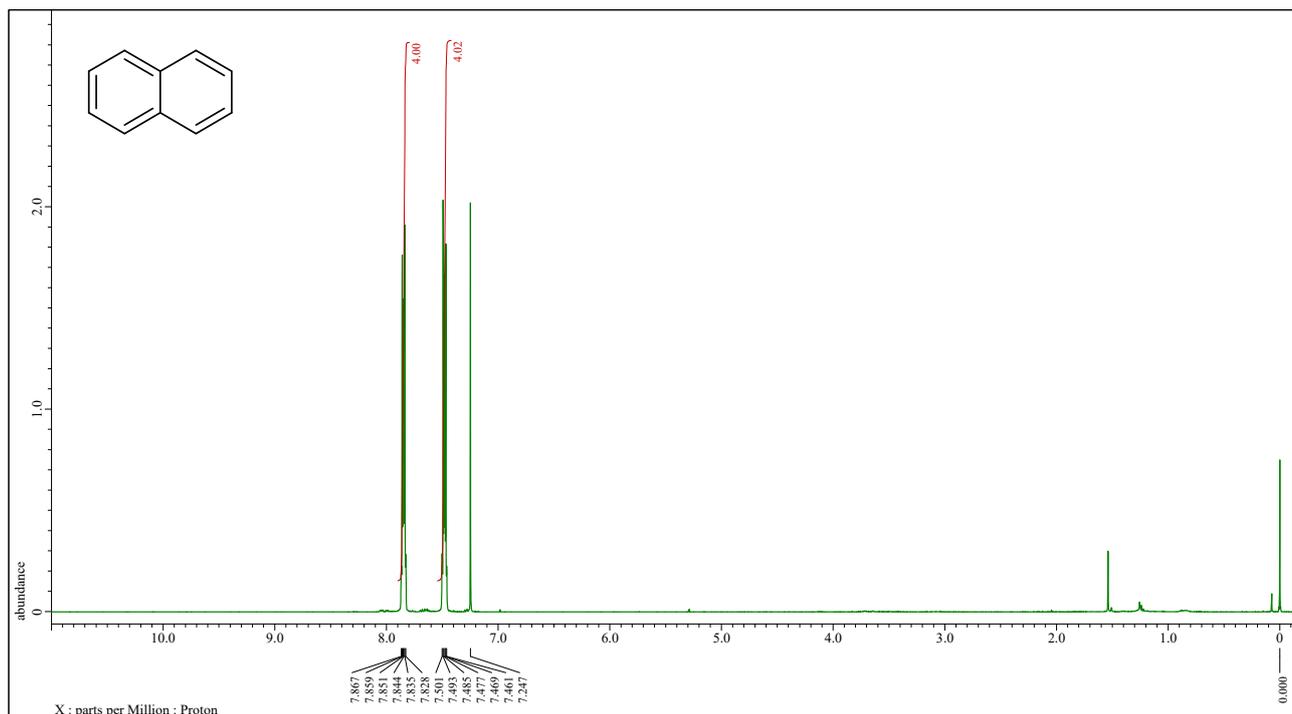
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **1-amino naphthalene (13)**



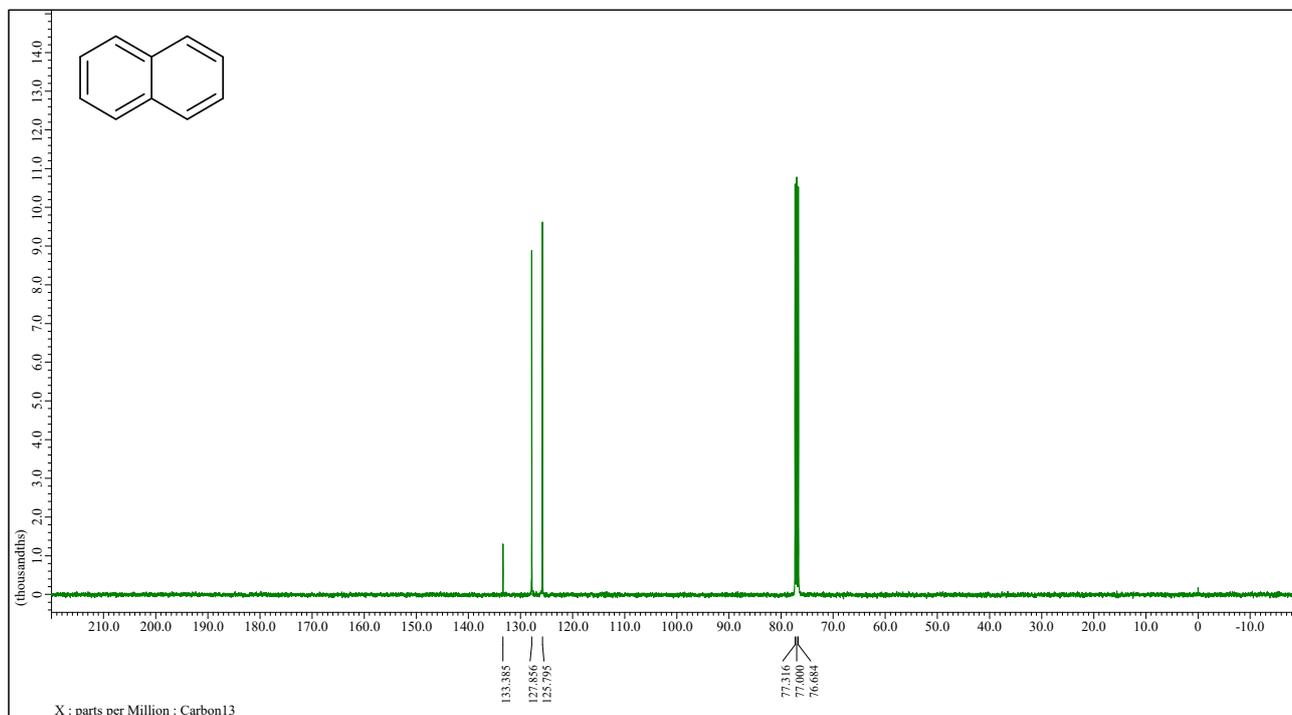
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **1-amino naphthalene (13)**



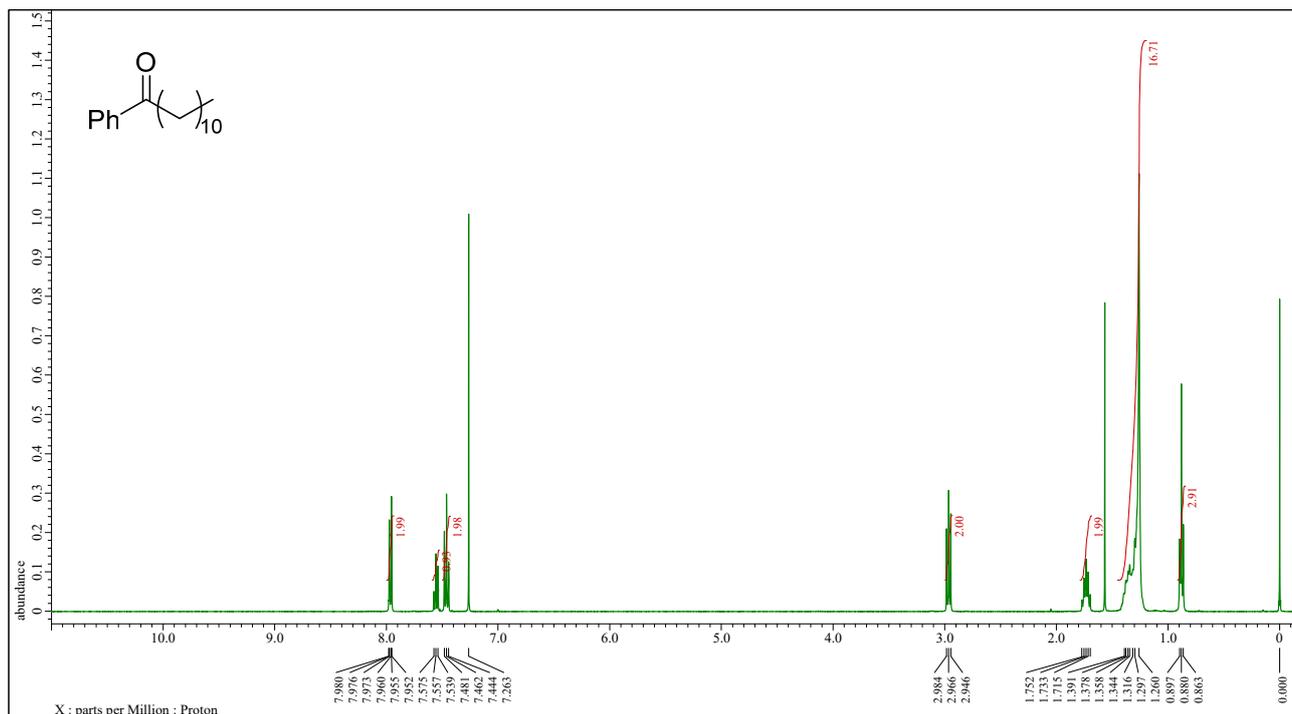
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of naphthalene (14)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of naphthalene (14)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **1-dodecaphenone (15)**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **1-dodecaphenone (15)**

