

Pt/CB-Catalyzed Chemoselective Hydrogenation Using In Situ-Generated Hydrogen by Microwave Mediated Dehydrogenation of Methylcyclohexane under Continuous-Flow Conditions

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

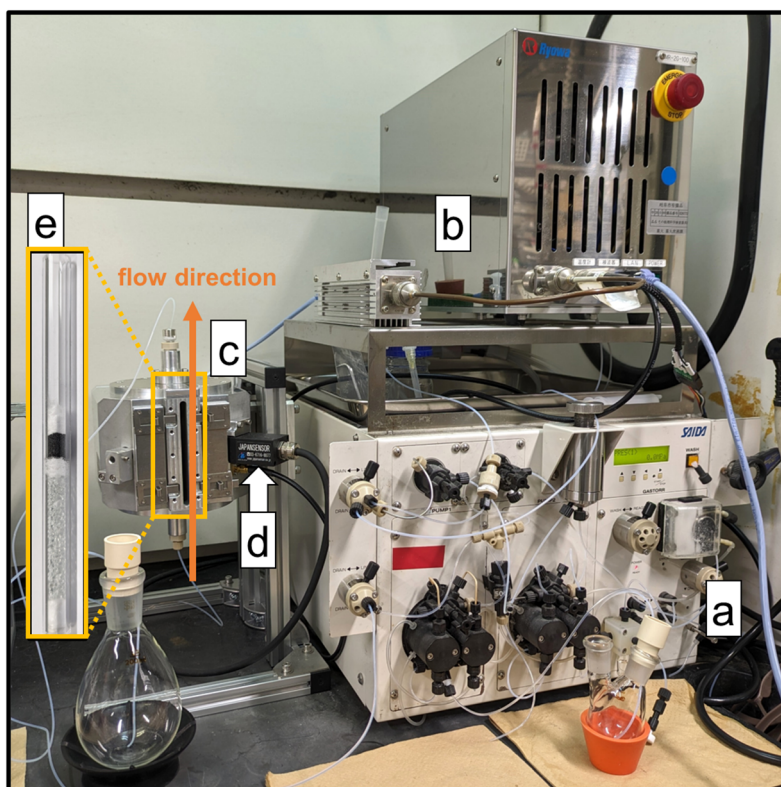


Figure. S1 The microwave flow reactor (EYELA, MR-2G-100) (a) pump, (b) Microwave controller unit, (c) Microwave generator unit, (d) Thermography unit, (e) 5% Pt/CB-packed Quartz tube (catalyst cartridge)

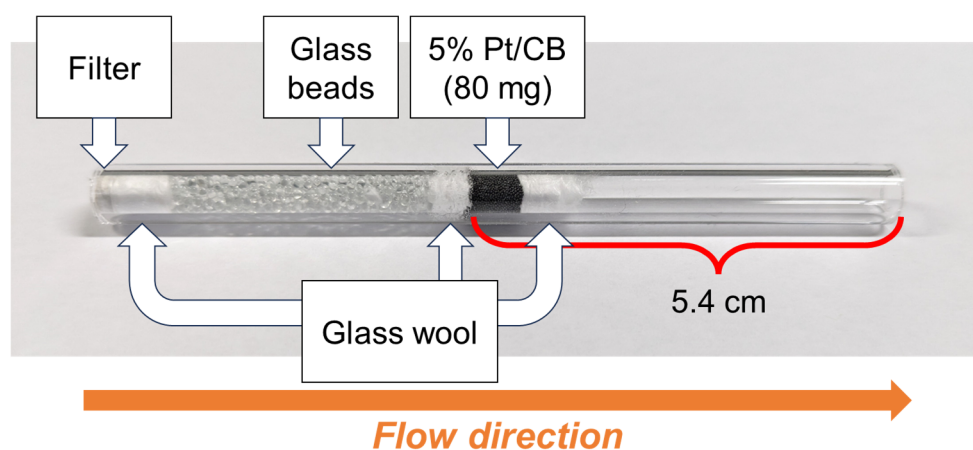


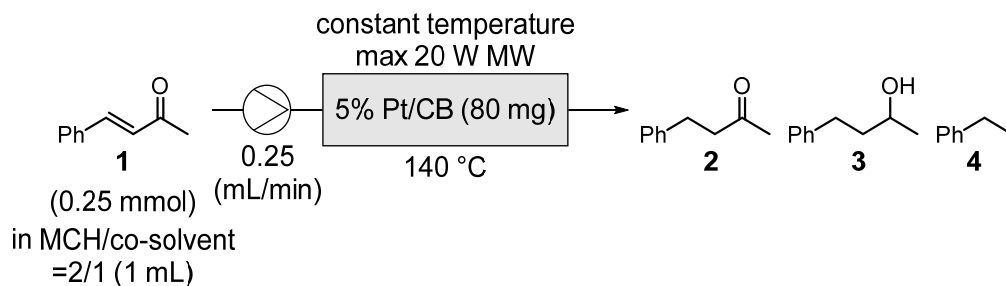
Figure. S2 The quartz tube for the continuous flow microwave reactor (EYELA, MR-2G-100)

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.

2. Optimization of the MW-mediated continuous-flow hydrogenation reaction conditions

Table S1. The effect of co-solvent on MW-mediated continuous-flow hydrogenation reaction



Entry	Co-solvent	Product ratio ^a (1 : 2 : 3 : 4)
1	Toluene	2 : 78 : 0 : 20
2	<i>o</i> -Xyrene	94 : 3 : 0 : 3
3	<i>n</i> -Heptane	86 : 8 : 0 : 6
4	2-PrOH	39 : 54 : 0 : 7
5	1-Butanol	60 : 30 : 0 : 10

^a The product ratio was determined by GC-FID using decane as the internal standard.

The ratio of the formation of **4** relative to **2** was efficiently suppressed in the case using 2-PrOH as a co-solvent.

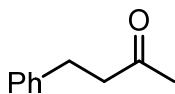
3. Thermographic measurements of the temperature of a 5% Pt/CB-packed cartridge (Figure 2)

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]¹

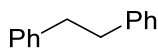
Obtained in 91% yield (33.7 mg, 228 μ mol; colorless solid) from 4-phenyl-3-buten-2-one (34.5 mg, 250 μ mol).



¹H NMR [400 MHz (ECZ-400, CDCl₃)] δ 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); ¹³C NMR [100 MHz (ECZ-400, CDCl₃)] δ 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]²

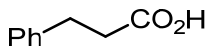
Obtained in 95% yield (43.0 mg, 236 μ mol; colorless solid) from diphenylacetylene (44.6 mg, 250 μ mol).



¹H NMR [400 MHz (ECZ-400, CDCl₃)] δ 7.31–7.27 (m, 4H), 7.22–7.18 (m, 6H), 2.92 (s, 4H); ¹³C NMR [100 MHz (ECZ-400, CDCl₃)] δ 141.7, 128.4, 128.3, 125.9, 37.9.

3-Phenylpropionic acid (9) [CAS Reg. No. 501-52-0]²

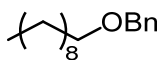
Obtained in 76% yield (30.1 mg, 201 μ mol; colorless solid) from benzyl 3-phenylpropionate (60.1 mg, 250 μ mol).



¹H NMR [400 MHz (ECZ-400, CDCl₃)] δ 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); ¹³C NMR [100 MHz (ECZ-400, CDCl₃)] δ 179.2, 140.1, 128.5, 128.2, 126.4, 35.6, 30.5.

Benzyl decyl ether (10) [CAS Reg. No. 87220-50-6]³

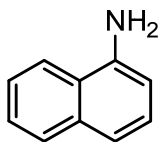
Recovered in 88% yield (54.7 mg, 220 μ mol; colorless liquid).



¹H NMR [400 MHz (ECZ-400, CDCl₃)] δ 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); ¹³C NMR [100 MHz (ECZ-400, CDCl₃)] δ 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]⁴

Obtained in 68% yield (24.3 mg, 170 μ mol; red solid) from 4-nitronaphthalene (43.3 mg, 250 μ mol).

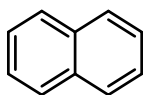


^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 7.81–7.72 (m, 2H), 7.45–7.37 (m, 2H), 7.31–7.24 (m, 2H), 6.72 (dd, J = 7.1, 1.6 Hz, 1H), 3.95 (brs, 2H); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 142.0, 134.3, 128.5, 126.3, 125.8, 124.8, 123.5, 120.7, 118.8, 109.6.

Naphthalene (14) [CAS Reg. No. 91-20-3]⁵

Obtained in 80% yield (25.6 mg, 200 μmol ; colorless solid) from 4-nitronaphthalene (43.3 mg, 250 μmol).

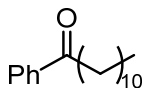
Obtained in 89% yield (28.5 mg, 223 μmol ; colorless solid) from 4-chloronaphthalene (40.7 mg, 250 μmol).



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 7.87–7.83 (m, 4H), 7.50–7.46 (m, 4H); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 133.4, 127.9, 125.8.

1-Dodecaphenone (15) [CAS Reg. No. 1674-38-0]⁶

Recovered in 91% yield (59.3 mg, 228 μmol ; colorless solid).



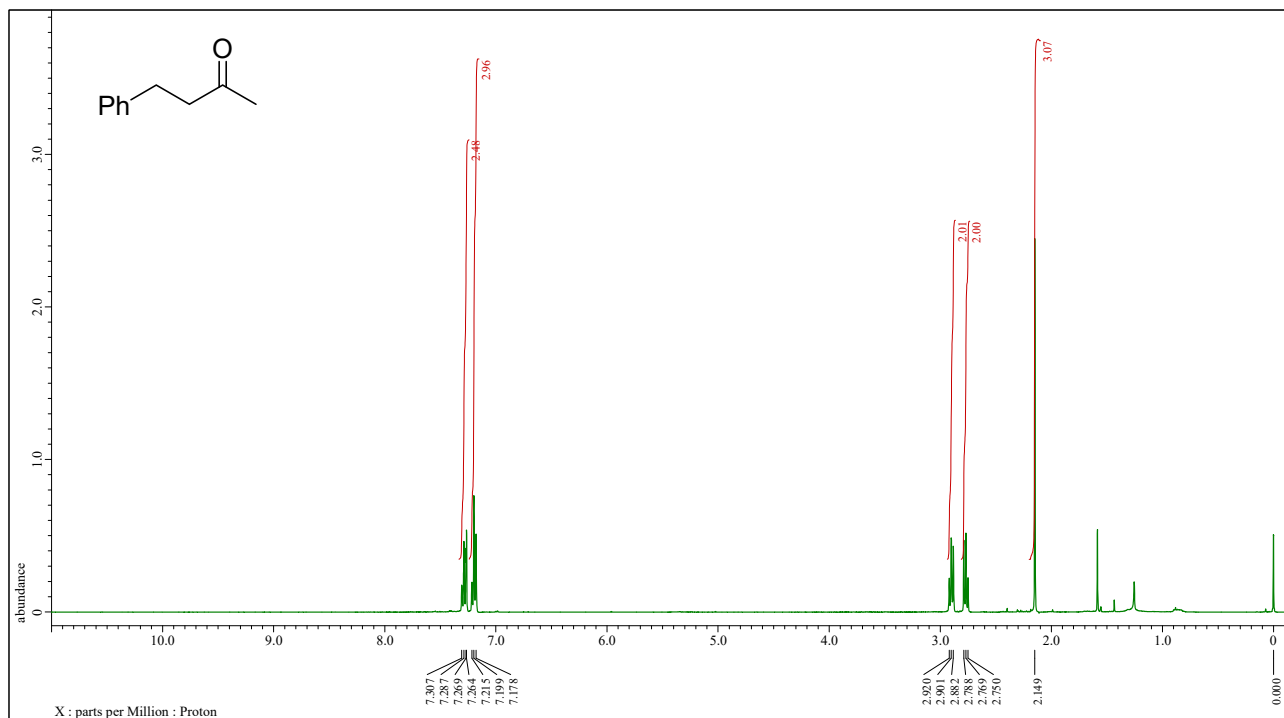
^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 7.98–7.95 (m, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 2.96 (t, J = 7.5 Hz, 2H), 1.77–1.70 (m, 2H), 1.39–1.26 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 200.6, 137.0, 132.8, 128.5, 128.0, 38.6, 31.9, 29.6, 29.5, 29.5, 29.4, 29.3, 24.3, 22.7, 14.1.

5. References

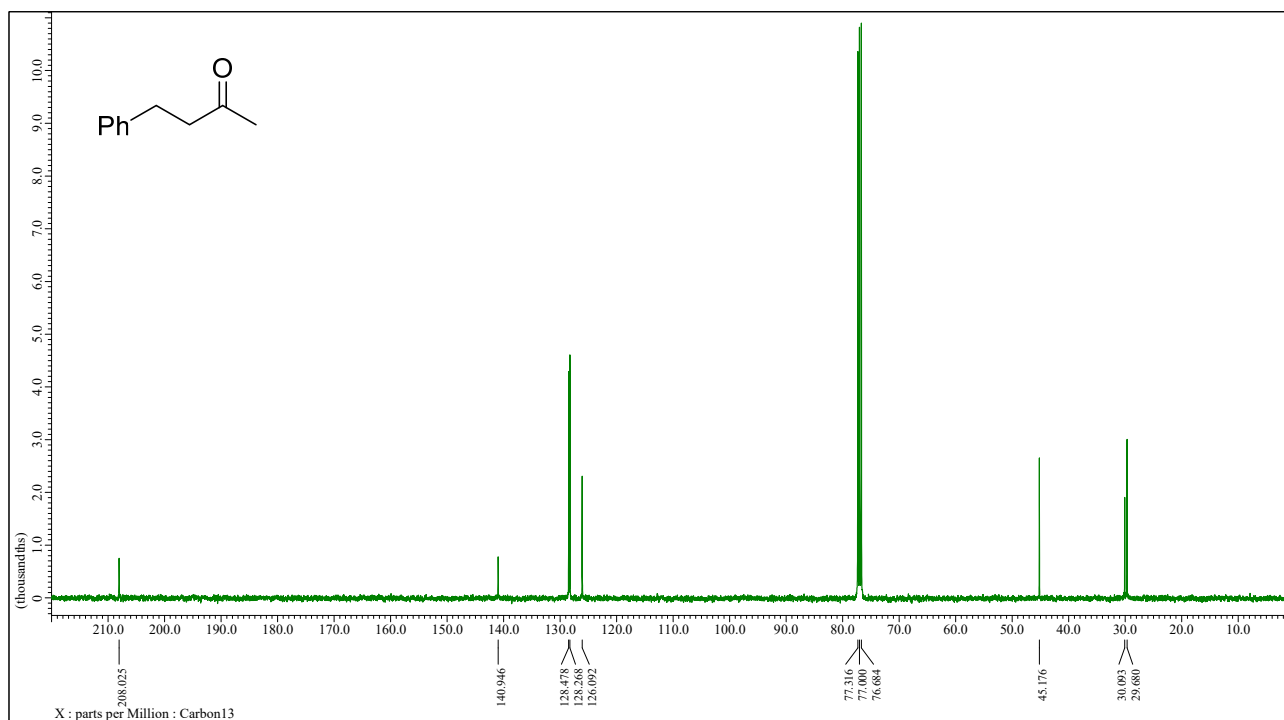
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6. ^1H and ^{13}C spectra of products

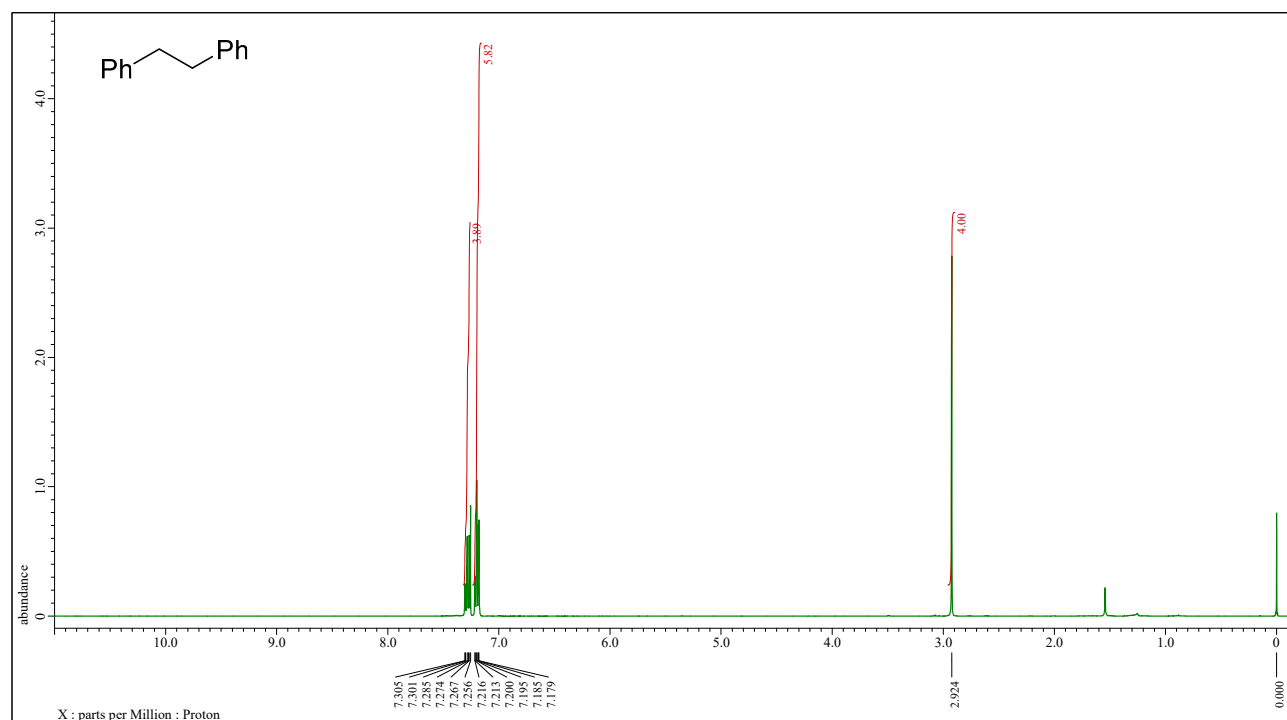
^1H NMR (400 MHz, CDCl_3) of 4-phenyl-2-butanone (2)



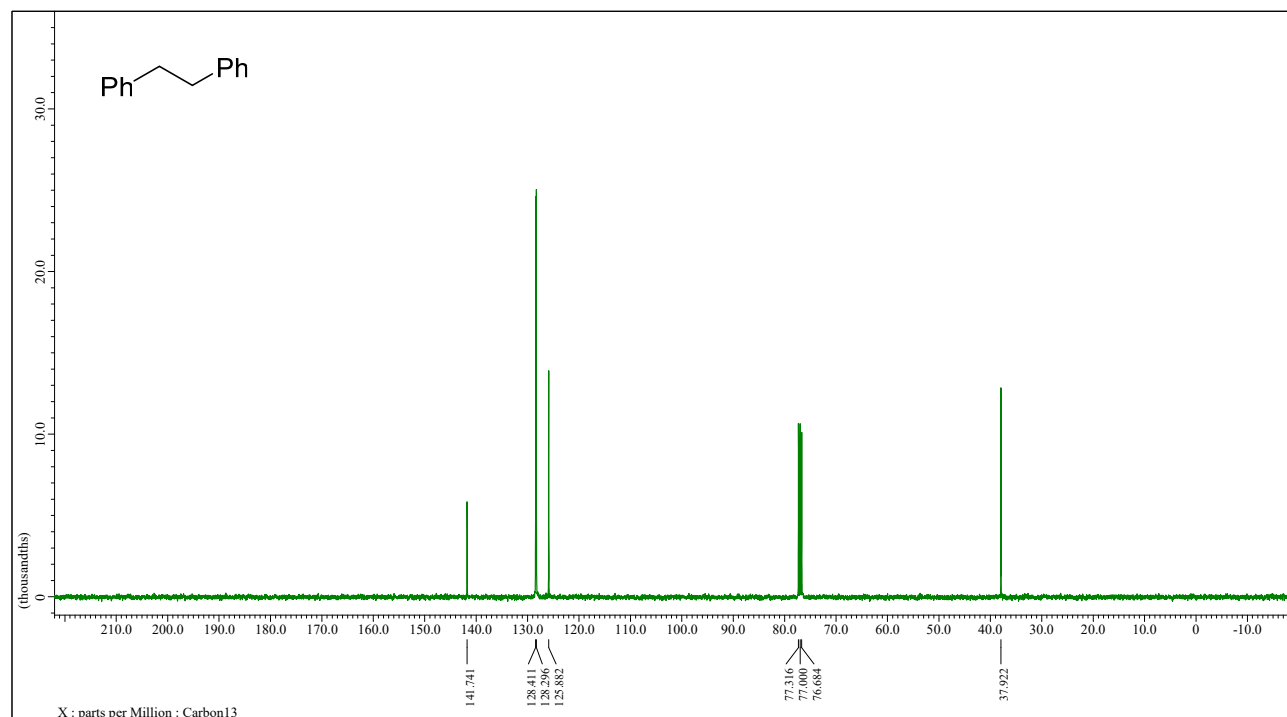
^{13}C NMR (100 MHz, CDCl_3) of 4-phenyl-2-butanone (2)



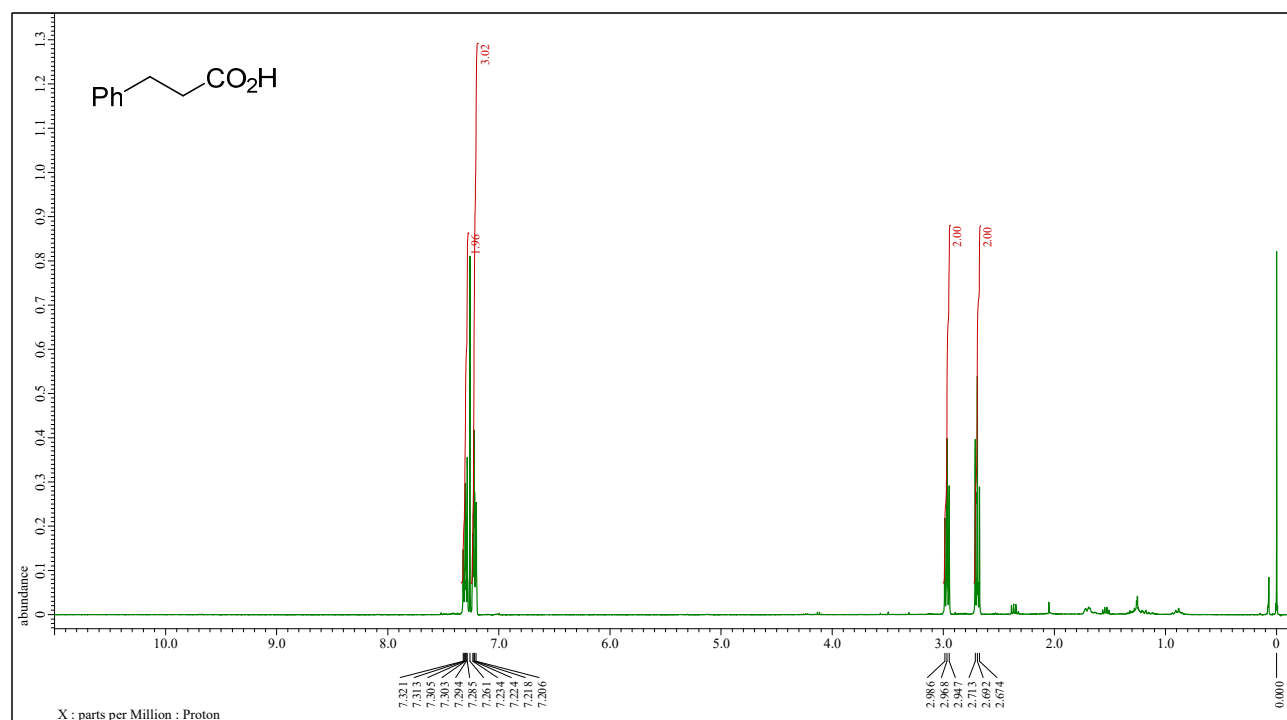
^1H NMR (400 MHz, CDCl_3) of **1,2-diphenylethane (6)**



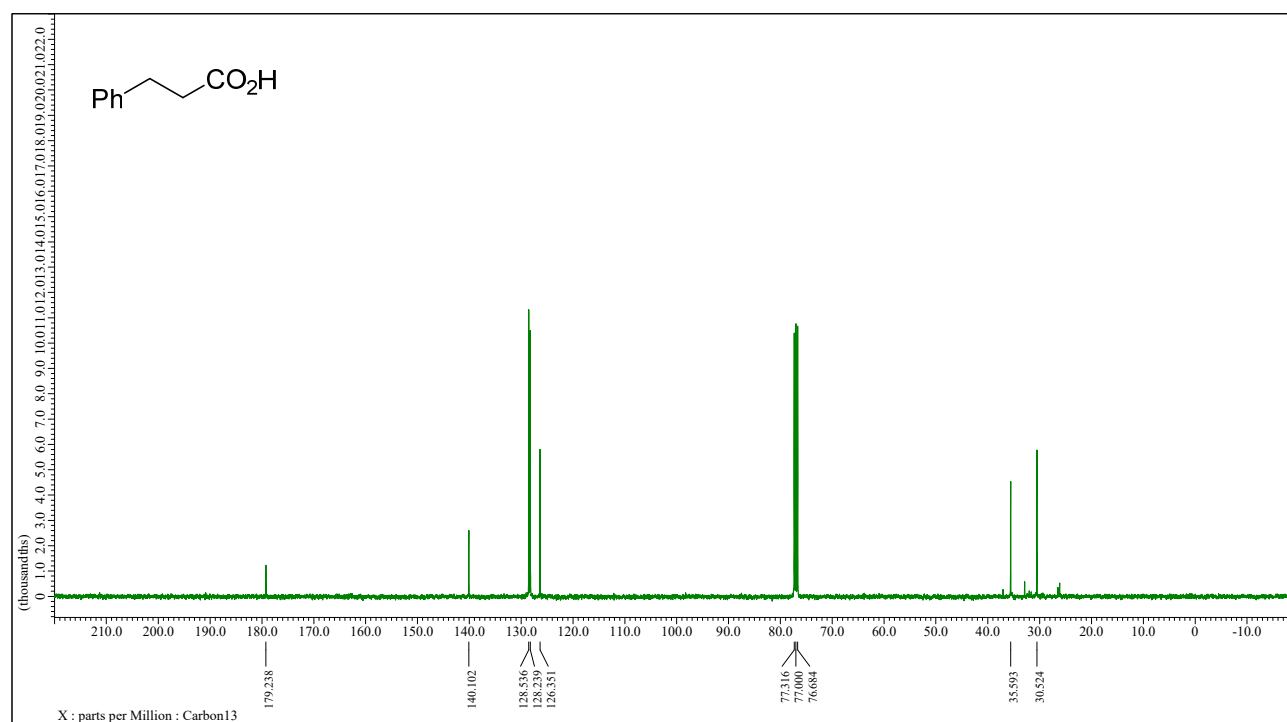
^{13}C NMR (100 MHz, CDCl_3) of **1,2-diphenylethane (6)**



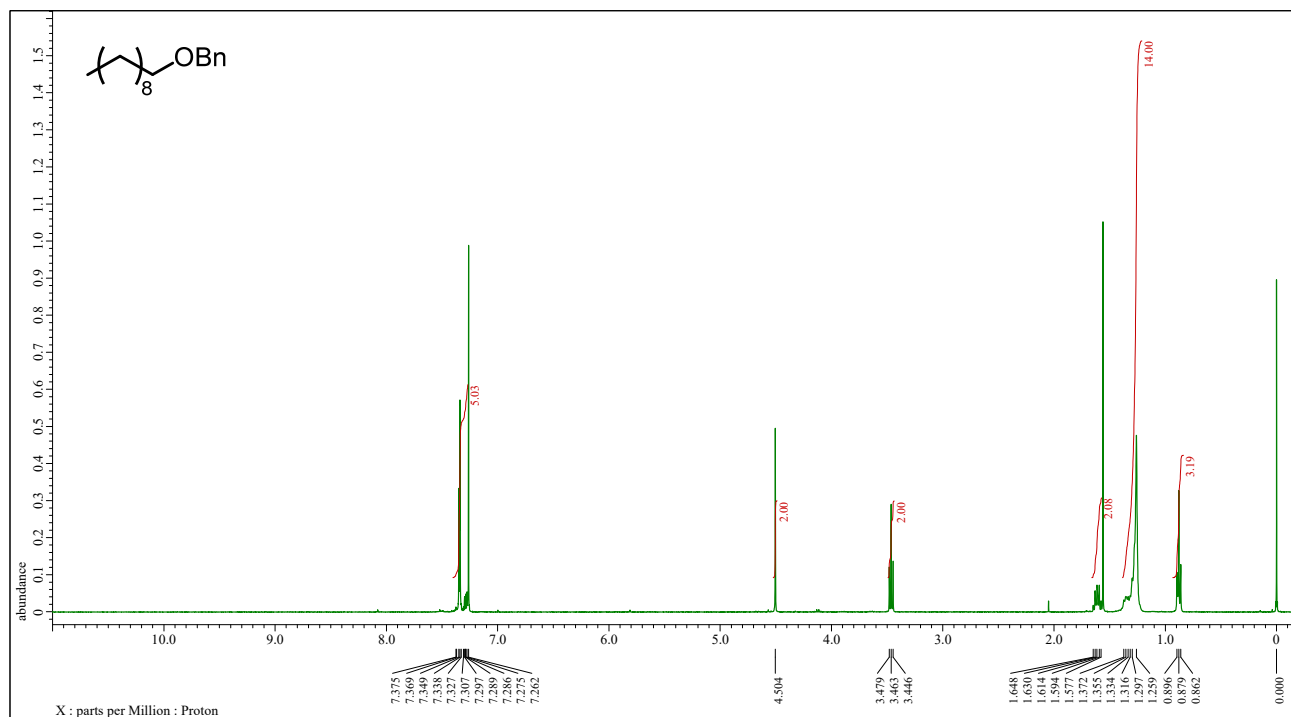
^1H NMR (400 MHz, CDCl_3) of **3-phenylpropionic acid (9)**



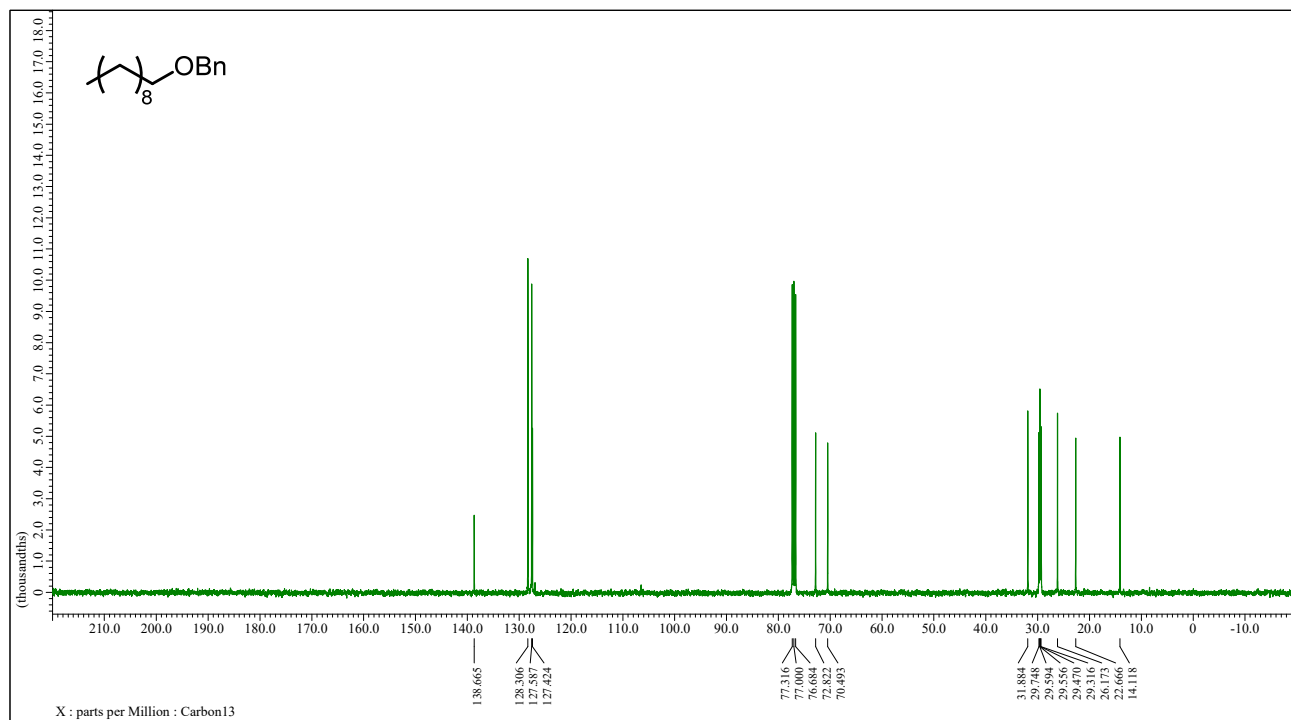
^{13}C NMR (100 MHz, CDCl_3) of **3-phenylpropionic acid (9)**



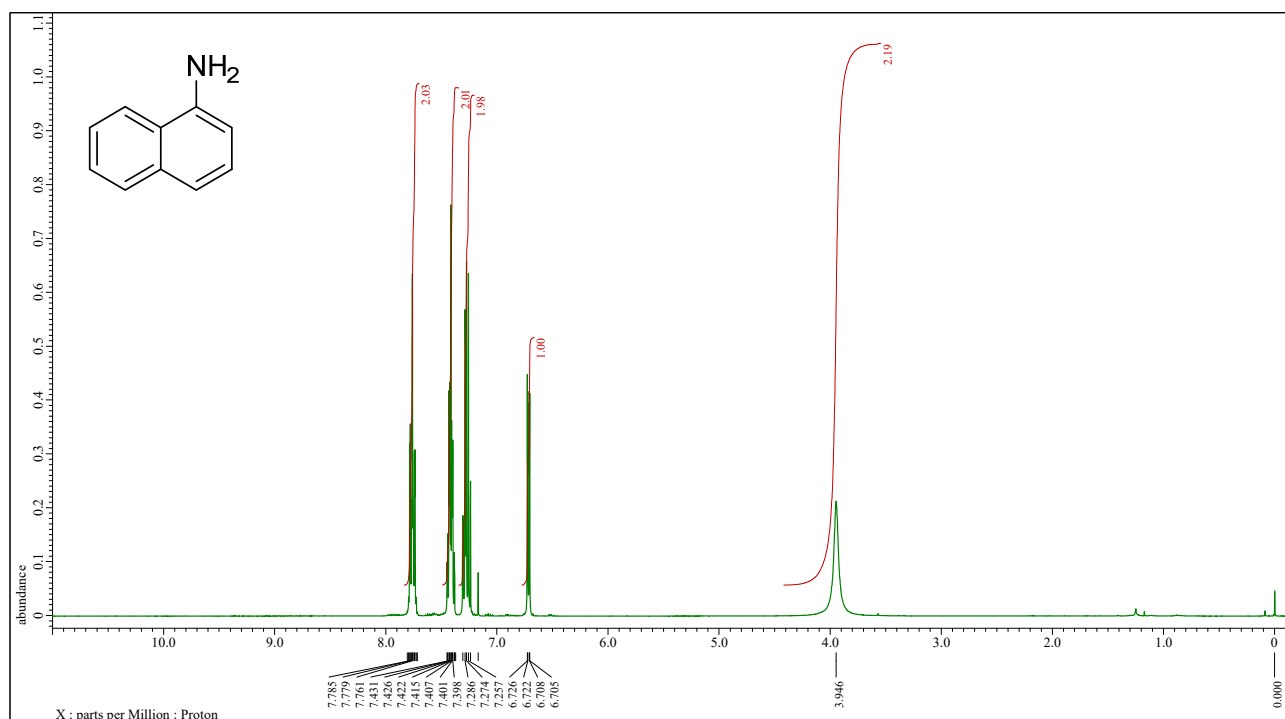
¹H NMR (400 MHz, CDCl₃) of **benzyl decyl ether (14)**



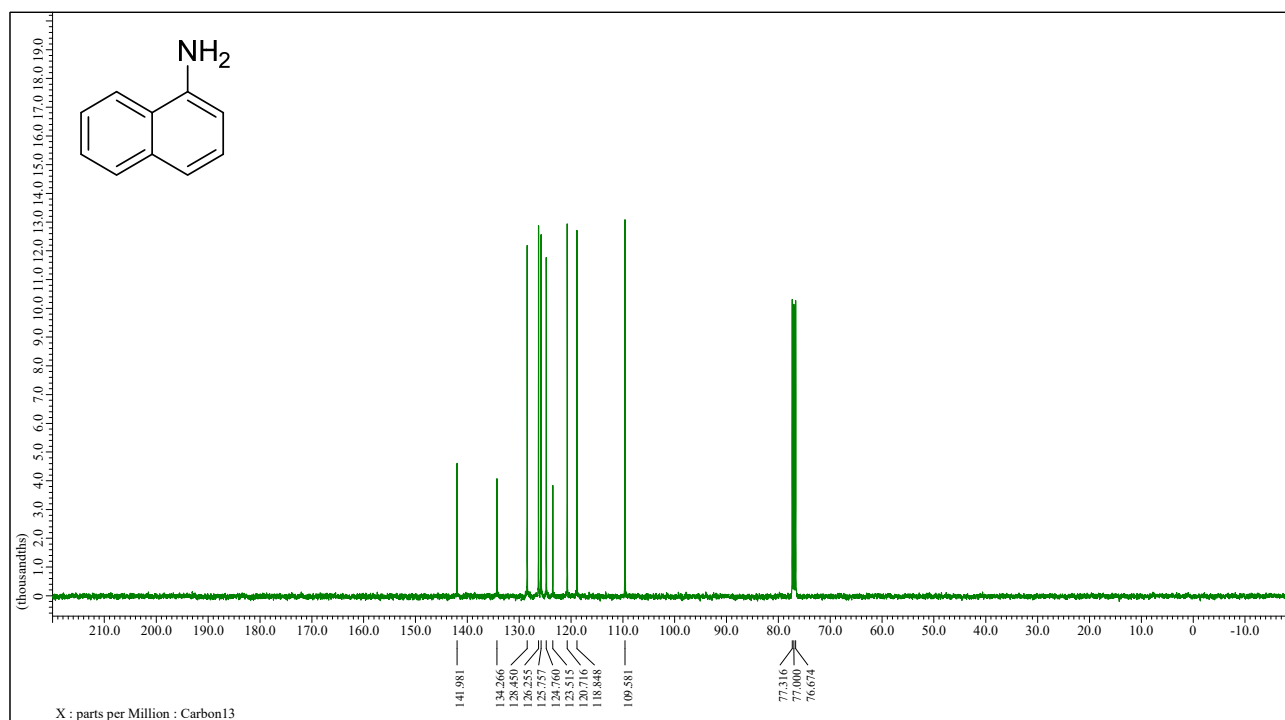
¹³C NMR (100 MHz, CDCl₃) of **benzyl decyl ether (14)**



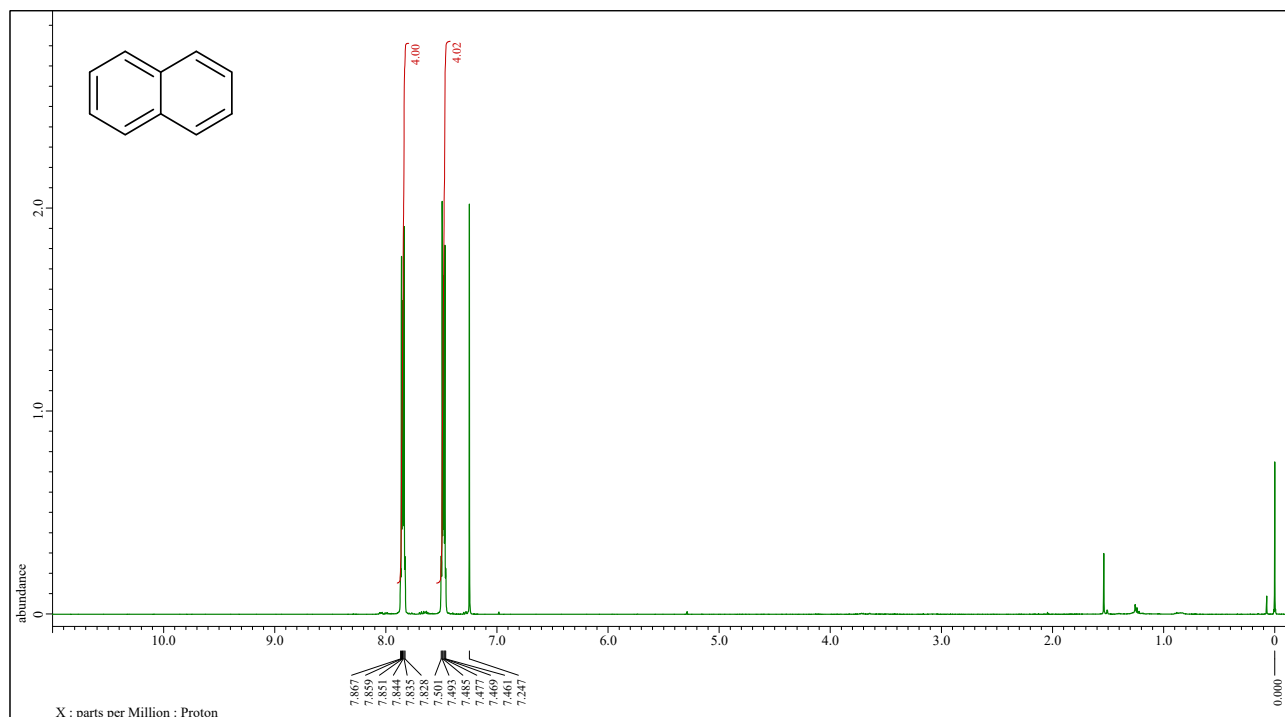
^1H NMR (400 MHz, CDCl_3) of **1-amino naphthalene (13)**



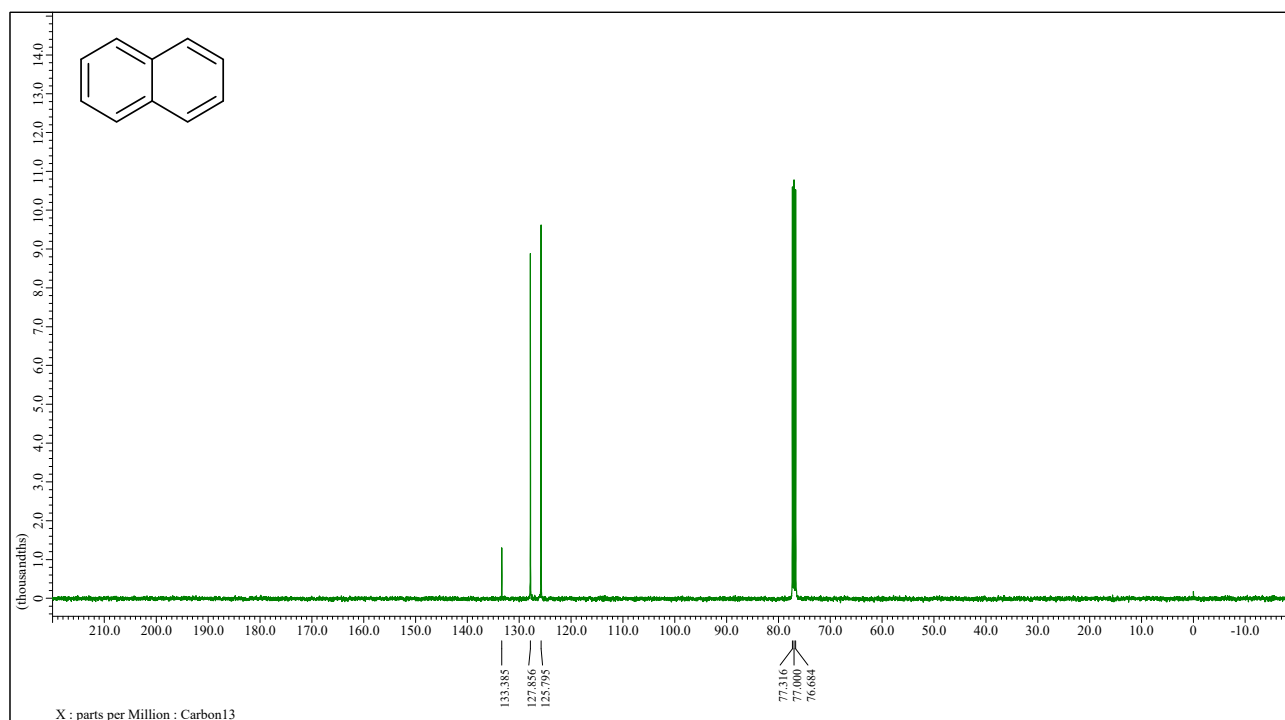
^{13}C NMR (100 MHz, CDCl_3) of **1-amino naphthalene (13)**



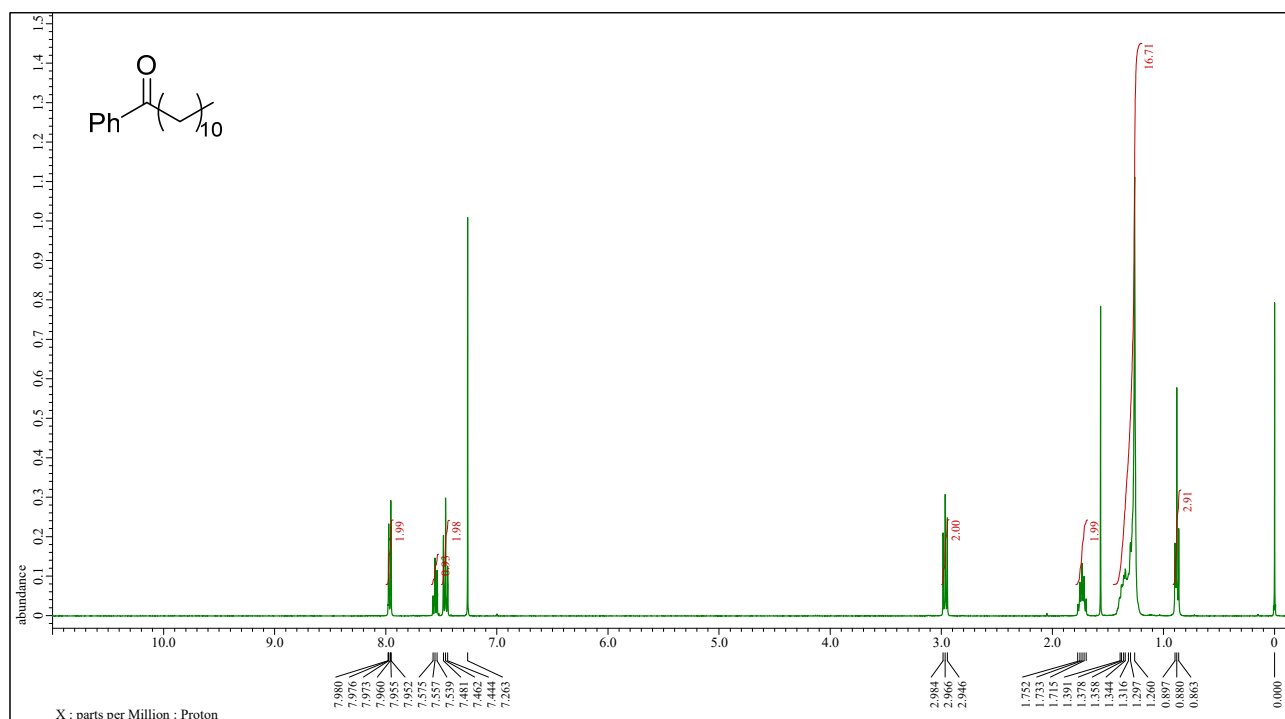
¹H NMR (400 MHz, CDCl₃) of **naphthalene (14)**



¹³C NMR (100 MHz, CDCl₃) of **naphthalene (14)**



¹H NMR (400 MHz, CDCl₃) of **1-dodecaphenone (15)**



¹³C NMR (100 MHz, CDCl₃) of **1-dodecaphenone (15)**

