

Supplementary Information

**Pd Catalysts Supported on Dual-Pore Monolithic Silica Beads
for Chemoselective Hydrogenation Under Batch and Flow**

Reaction Conditions

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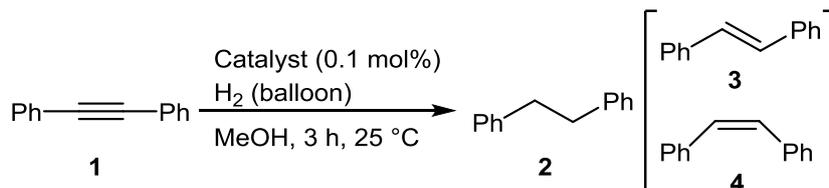
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1. General

Pd(OAc)₂ were obtained from N.E. Chemcat Corporation, Japan. Dual-pore monolithic silica beads was obtained from SnG Inc., Japan. Other reagents were obtained from commercial sources and used without further purification unless otherwise noted. ¹H and ¹³C NMR spectra were recorded by a JEOL ECZ-400 (¹H: 400 MHz, ¹³C: 100 MHz), or ECA-500 spectrometer (¹H: 500 MHz, ¹³C: 125 MHz). Chemical shifts (δ) are indicated in ppm and are internally referenced (0.00 ppm for tetramethylsilane for ¹H NMR, 7.26 ppm for CDCl₃ for ¹H NMR, and 77.0 ppm for CDCl₃ for ¹³C NMR). Transmission electron microscopy (TEM) were measured by JEOL JEM-2010. The solid structures of the samples were measured by X-ray diffraction (XRD) using Cu-Kα radiation (PANalytical, Empyrean). X-ray photoelectron spectroscopy (XPS) of 5% Pd/SM was measured by ULVAC Quantera-SXM-GC. The Pd content of the filtrates of the 5% Pd/SM was measured by Atomic Absorption Spectrometry (SHIMADZU AA-7000).

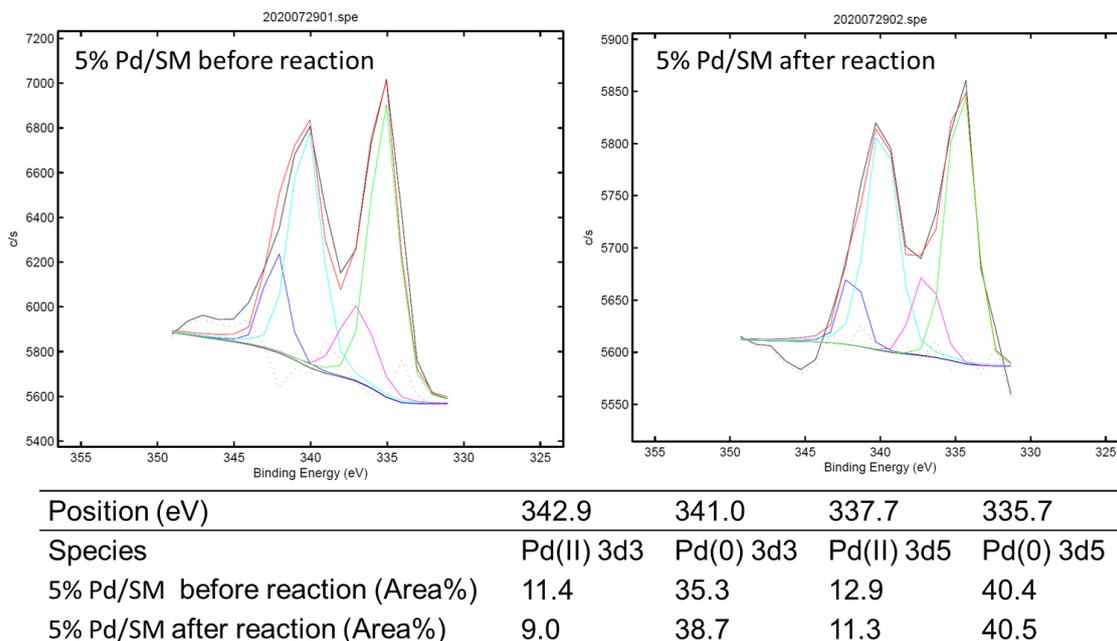
2. Original data before calculating the average shown in Table 1



Catalyst	Run	¹ H NMR ratio ^a (1 : 2 : 3 : 4)
Cat. C [5% Pd/SM (MeOH)]	1 st	0 : 72 : 4 : 24
	2 nd	0 : 74 : 3 : 23
Cat. B [5% Pd/SM (EtOAc)]	1 st	79 : 1 : 3 : 17
	2 nd	73 : 2 : 3 : 22
Cat. A [5% Pd/SM (CH ₃ CN)]	1 st	0 : 100 : 0 : 0
	2 nd	0 : 100 : 0 : 0

^aSuspension of diphenylacetylene (**1**, 0.25 mmol, 44.6 mg) and 0.1 mol% of 5% Pd/SM (0.53 mg, 2.5 μmol) in MeOH (1.0 mL) were stirred at 25 °C under hydrogen atmosphere.

3. XPS spectra of 5% Pd/SM before and after the reaction



4. General procedures for hydrogenation

General procedure for chemoselective hydrogenation catalysed by 5% Pd/SM- and 0.25% Pd/SM(sc) under batch reaction conditions

A mixture of a substrate (0.25 mmol) and 0.1 mol% of 5% Pd/SM (0.53 mg, 0.25 μ mol) or 0.05 mol% of 0.25% Pd/SM(sc) (5.3 mg, 125 nmol) in MeOH (1 mL) was stirred at 25 °C in a test tube equipped with a H₂ balloon. The reaction was monitored continuously using thin-layer chromatography. After a specific time, the mixture was filtered through a membrane filter (pore size: 0.45 μ m). The catalyst on the filter was washed with EtOAc or diethyl ether (5 mL \times 3). The combined filtrates were concentrated in vacuo to afford the corresponding analytically pure product. If necessary, the product was further purified using silica gel column chromatography (hexane/EtOAc).

General procedure for chemoselective hydrogenation catalysed by 5% Pd/SM under flow conditions

A solution of substrate in MeOH (0.1 or 0.05 M) was pumped at 0.1 mL/min into a catalyst-packed cartridge [5% Pd/SM (100 mg); ϕ 4.6 \times 50 mm, SUS-316] along with 14 bar hydrogen gas at either 25 °C or 50 °C, after MeOH and hydrogen gas had been flowed through the cartridge under the same conditions for approximately 10 min. The entire reaction mixture was collected and concentrated in vacuo to afford the corresponding analytically pure product.

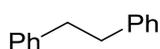
General procedure for Pd/SM(sc)-catalysed hydrogenation of prenil under flow conditions

Prenol (3-methyl-2-buten-1-ol) or its ethanol solution (3.06 or 4.71 mol/L) was pumped at 1.0 mL/min into a cartridge [$\phi 4.6 \times 100$ mm, stainless steel] filled with 0.2% Pd/SM(sc) along with hydrogen gas at a flow rate of 140, 210, or 280 mL/min at 120 °C with or without a back pressure of 3.45 MPa. The reaction solution was analysed by gas chromatography to determine the conversion of prenol using commercial chemicals as authentic samples.

5. Spectroscopic data of products

The spectral data of the product were identical to those in the literature.

1,2-Diphenylethane (CAS Registry Number: 103-29-7)¹ (Table 2, Entries 1 and 2; Table 4, Entry 2)



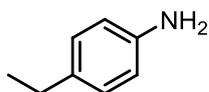
1,2-Diphenylethane was obtained in 99% yield (44.6 mg, 247 μ mol; colorless solid) from diphenylacetylene (45 mg, 250 μ mol) by using catalyst **A** (0.53 mg, 0.25 μ mol) in Table 2, Entry 1.

1,2-Diphenylethane was obtained in 98% yield (44.7 mg, 245 μ mol) from diphenylacetylene (45 mg, 250 μ mol) by using catalyst **B** (5.3 mg, 125 nmol) in Table 2, Entry 2.

1,2-Diphenylethane was obtained in 96% yield (2.52 g, 13.8 mmol) from diphenylacetylene (2.57 g, 14.4 mmol) by using catalyst **A** (100 mg, 47.0 μ mol) in Table 4, Entry 2.

¹H NMR (400 MHz, CDCl₃) δ 7.29–7.25 (m, 4H), 7.20–7.17 (m, 6H), 2.91 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 128.4, 128.3, 125.9, 37.9.

4-Aminoethylbenzene (CAS Registry Number: 589-16-2)² (Table 2, Entries 3, 4, 5 and 6)



4-Aminoethylbenzene was obtained in 88% yield (26.7mg, 220 μ mol; yellow oil) from 1-azido-4-ethylbenzene (36.8 mg, 250 μ mol) by using catalyst **A** (0.53 mg, 0.25 μ mol) in Table 2, Entry 3.

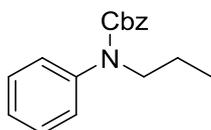
4-Aminoethylbenzene was obtained in quantitative yield from 1-azido-4-ethylbenzene (36.8 mg, 250 μ mol) by using catalyst **B** (5.3 mg, 125 nmol) in Table 2, Entry 4.

4-Aminoethylbenzene was obtained in quantitative yield (31.0 mg, 250 μ mol) from 4-ethylnitrobenzene (37.8 mg, 250 μ mol) by using catalyst **A** (0.53 mg, 0.25 μ mol) in Table 2, Entry 5.

4-Aminoethylbenzene was obtained in quantitative yield (31.0 mg, 250 μmol) from 4-ethylnitrobenzene (37.8 mg, 250 μmol) by using catalyst **B** (15.9 mg, 0.38 μmol) in Table 2, entry 6.

^1H NMR (400 MHz, CDCl_3) δ 6.99 (d, $J = 8.2$ Hz, 2H), 6.63 (d, $J = 8.2$ Hz, 2H), 3.52 (brs, 2H), 2.54 (q, $J = 7.7$ Hz, 2H), 1.18 (t, $J = 7.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0, 134.4, 128.5, 115.2, 27.9, 15.9.

***N*-phenyl-*N*-propylcarbamate (CAS Registry Number: 634917-15-0)³ (Table 2, Entry 7; Table 4, Entry 3)**

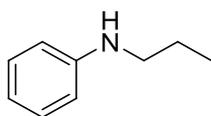


N-phenyl-*N*-propylcarbamate was obtained in 92% yield (61.9 mg, 230 μmol ; yellow oil) from *N*-allyl-*N*-benzyloxycarbonylaniline (66.8 mg, 250 μmol) and THF (1 mL) by using catalyst **A** (0.53 mg, 0.25 μmol) in Table 2, Entry 7.

N-phenyl-*N*-propylcarbamate was obtained in quantitative yield (970 mg, 3.6 mmol) from *N*-allyl-*N*-benzyloxycarbonylaniline (962 mg, 3.6 mmol) by using catalyst **A** (100 mg, 47.0 μmol) in Table 4, Entry 3.

^1H NMR (400 MHz, CDCl_3) δ 7.36–7.19 (m, 10H), 5.14 (s, 2H), 3.64 (t, $J = 7.5$ Hz, 2H), 1.55 (sext, $J = 7.5$ Hz, 2H), 0.87 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 141.8, 136.7, 128.8, 128.3, 127.7, 127.3, 126.5, 66.9, 52.0, 21.4, 11.0.

***N*-Propylaniline (CAS Registry Number: 622-80-0)⁴ (Table 2, Entries 8 and 9)**

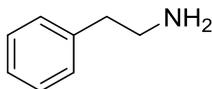


N-Propylaniline was obtained in quantitative yield (33.8 mg, 250 μmol ; blown oil) from *N*-allyl-*N*-benzyloxycarbonylaniline (66.8 mg, 250 μmol) by using catalyst **A** (5.3 mg, 2.5 μmol) in Table 2, Entry 8.

N-Propylaniline was obtained in 85% yield (28.7 mg, 213 μmol) from *N*-allyl-*N*-benzyloxycarbonylaniline (66.8 mg, 250 μmol) by using catalyst **B** (15.9 mg, 0.38 μmol) in Table 2, Entry 9.

^1H NMR (500 MHz, CDCl_3) δ 7.17 (t, $J = 7.6$ Hz, 2H), 6.68 (t, $J = 7.6$, 1.2 Hz, 1H), 6.60 (d, $J = 7.6$ Hz, 2H), 3.63 (brs, 1H), 3.08 (t, $J = 7.3$ Hz, 2H), 1.68–1.60 (m, 2H), 1.00 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 148.5, 129.2, 117.0, 112.6, 45.7, 22.7, 11.6.

Phenethylamine (CAS Registry Number: 64-04-0)⁵ (Table 2, Entries 10 and 11; Table 4, Entry 4)

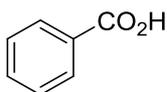


Phenethylamine was obtained in 75% yield (25.4 mg, 188 μmol ; colorless oil) from benzyl phenethylcarbamate (63.8 mg, 250 μmol) by using catalyst **B** (5.3 mg, 0.125 μmol) in Table 2, Entry 11.

Phenethylamine was obtained in 85% yield (185 mg, 1.53 mmol) from phenethyl azide (265 mg, 1.8 mmol) by using catalyst **A** (100 mg, 47.0 μmol) in Table 4, Entry 4.

^1H NMR (400 MHz, CDCl_3) δ 7.31–7.18 (m, 5H), 2.95 (t, $J = 6.8$ Hz, 2H), 2.73 (t, $J = 6.8$ Hz, 2H), 1.24 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.7, 128.7, 128.3, 126.0, 43.5, 40.0.

Benzoic acid (CAS Registry Number: 65-85-0)⁶ (Table 2, Entries 12 and 13)

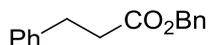


Benzoic acid was obtained in 91% yield (27.8 mg, 228 μmol ; colorless solid) from benzyl benzoate (53.1mg, 250 μmol) by using catalyst **A** (0.53 mg, 0.25 μmol) in Table 2, Entry 13.

Benzoic acid was obtained in quantitative yield (30.1 mg, 246 μmol) from benzyl benzoate (53.1mg, 250 μmol) by using catalyst **B** (20.1 mg, 0.5 μmol) in Table 2, Entry 13.

^1H NMR (400 MHz, CDCl_3) δ 10.6 (brs, 1H), 8.13 (dd, $J = 1.0, 7.9$ Hz, 2H), 7.62 (t, $J = 7.9$ Hz, 1H), 7.49 (t, $J = 7.9$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.1, 133.8, 130.2, 129.3, 128.5.

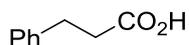
Benzyl benzenepropanoate (CAS Registry Number: 22767-96-0)⁷ (Table 2, Entry 14)



Benzyl benzenepropanoate was obtained in quantitative yield (60.1 mg, 250 μmol ; colorless oil) from cinnamic acid benzyl ester (59.6 mg, 250 μmol) by using catalyst **A** (0.53 mg, 0.25 μmol) in Table 2, Entry 14.

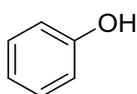
^1H NMR (400 MHz, CDCl_3) δ 7.35–7.16 (m, 10H), 5.10 (s, 2H), 2.96 (t, $J = 7.8$ Hz, 2H), 2.67 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 140.4, 135.9, 128.5, 128.5, 128.3, 128.2, 126.2, 66.3, 35.9, 30.9.

Benzenepropanoic acid (CAS Registry Number: 501-52-0)⁸ (Table 2, Entry 15)



Benzenepropanoic acid was obtained in 96% yield (36.0 mg, 240 μmol ; colorless oil) from cinnamic acid benzyl ester (59.6 mg, 250 μmol) by using catalyst **B** (20.1 mg, 0.5 μmol) in Table 2, Entry 15. ^1H NMR (400 MHz, CDCl_3) δ 9.84 (brs, 1H) 7.31–7.19 (m, 5H), 2.95 (t, $J = 7.8$ Hz, 2H), 2.68 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 128.5, 128.2, 126.4, 65.9, 35.5, 30.5.

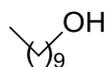
Phenol (CAS Registry Number: 108-95-2)⁹ (Table 2, Entries 16 and 17)



Phenol was obtained in 94% yield (22.1 mg, 235 μmol ; colorless solid) from benzyl phenyl ether (46.1 mg, 250 μmol) by using catalyst **B** (5.3 mg, 0.125 μmol) and EtOAc as a solvent in Table 2, Entry 17.

^1H NMR (400 MHz, CDCl_3) δ 7.25 (t, $J = 8.0$ Hz, 2H), 6.94 (t, $J = 8.0$ Hz, 1H), 6.84–6.83 (dd, $J = 8.0, 1.0$ Hz, 2H), 5.01 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.2, 129.7, 120.8, 115.3.

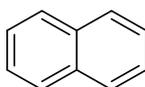
1-Decanol (CAS Registry Number: 112-30-1)¹⁰ (Table 2, Entries 18 and 19)



1-Decanol was obtained in 75% yield (29.7 mg, 188 μmol ; colorless oil) from ((decyloxy)methyl)benzene (62.1mg, 250 μmol) by using catalyst **B** (5.3 mg, 0.125 μmol) in Table 2, Entry 19.

^1H NMR (400 MHz, CDCl_3) δ 3.64–3.60 (m, 2H), 2.02 (brs, 1H), 1.59–1.53 (m, 2H), 1.31–1.27 (m, 14H), 0.88 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 62.9, 32.7, 31.8, 29.6, 29.5, 29.4, 29.3, 25.7, 22.6, 14.0.

Naphthalene (CAS Registry Number: 91-20-3)¹¹ (Table 2, Entries 20, 21, 22 and 23)

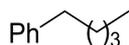


Naphthalene was obtained in quantitative yield (32.0 mg, 250 μmol ; colorless solid) from bromonaphthalene (51.8 mg, 250 μmol) by using catalyst **B** (5.3 mg, 0.125 μmol) in Table 2, Entry 21.

Naphthalene was obtained in 72% yield (23.1 mg, 180 μmol) from chloronaphthalene (40.7 mg, 250 μmol) by using catalyst **B** (21.2 mg, 0.5 μmol) and Et_3N (27.8 mg, 275 μmol) in Table 2, Entry 23.

^1H NMR (400 MHz, CDCl_3) δ 7.86–7.82 (m, 4H), 7.50–7.46 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.4, 127.9, 125.8.

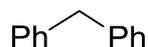
Pentylbenzene (CAS Registry Number: 495-40-9)¹² (Table 2, Entries 24 and 25)



Pentylbenzene was obtained in 78% yield (28.9 mg, 195 μmol ; colorless oil) from valerophenone (40.6 mg, 250 μmol) by using catalyst **B** (5.3 mg, 0.125 μmol) in Table 2, Entry 25.

^1H NMR (400 MHz, CDCl_3) δ 7.29–7.25 (m, 2H), 7.18–7.15 (m, 3H), 2.60 (t, $J = 8.0$ Hz, 2H), 1.65–1.57 (m, 2H), 1.36–1.29 (m, 4H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.9, 128.4, 128.2, 125.5, 35.9, 31.5, 31.2, 22.6, 14.0.

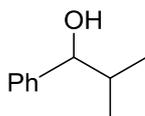
1,1-Diphenylmethane (CAS Registry Number: 101-81-5)¹³ (Table 2, Entries 26 and 27)



1,1-Diphenylmethane was obtained in quantitative yield (42.1 mg, 250 μmol ; colorless oil) from benzophenone (45.5 mg, 250 μmol) by using catalyst **B** (21.2 mg, 0.5 μmol) in Table 2, Entry 27.

^1H NMR (400 MHz, CDCl_3) δ 7.37–7.17 (m, 10H), 3.98 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 128.9, 128.4, 126.0, 41.9.

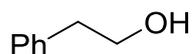
1-Phenyl-2-methylpropan-1-ol (CAS Registry Number: 611-69-8)¹⁴ (Table 2, Entries 28 and 29)



1-Phenyl-2-methylpropan-1-ol was obtained in 97% yield (36.4 mg, 243 μmol ; colorless oil) from allyl glycidyl ether (28 mg, 250 μmol) by using catalyst **B** (5.32 mg, 125 nmol) in Table 2, Entry 29.

^1H NMR (400 MHz, CDCl_3) δ 7.35–7.25 (m, 5H), 4.3 (d, $J = 6.8$ Hz, 1H), 2.01–1.89 (m, 2H), 1.00 (d, $J = 6.8$ Hz, 3H), 0.79 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 128.1, 127.4, 126.5, 80.0, 35.2, 19.0, 18.2.

Phenethyl alcohol (CAS Registry Number: 60-12-8)¹⁵ (Table 2, Entries 30 and 31)

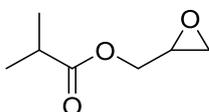


Phenethyl alcohol was obtained in 96% yield (29.4 mg, 240 μmol ; colorless oil) from styrene oxide (30.0 mg, 250 μmol) by using catalyst **A** (0.53 mg, 0.25 μmol) in Table 2, Entry 30.

Phenethyl alcohol was obtained in 74% yield (22.5 mg, 185 μmol) from styrene oxide (30.0 mg, 250 μmol) by using catalyst **B** (5.32 mg, 125 nmol) in Table 2, Entry 31.

^1H NMR (400 MHz, CDCl_3) δ 7.34–7.23 (m, 5H), 3.87 (t, $J = 6.6$ Hz, 2H), 2.88 (t, $J = 6.6$ Hz, 2H), 1.43 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 129.0, 128.6, 126.5, 63.7, 39.2.

Glycidyl isobutyrate (CAS Registry Number: 3669-66-7)¹⁴ (Table 2, Entries 32 and 33)

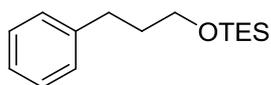


Glycidyl isobutyrate was obtained in 79% yield (28.5 mg, 198 μmol ; brown oil) from glycidyl methacrylate (35.5 mg, 250 μmol) by using catalyst **A** (0.53 mg, 0.25 μmol) in Table 2, Entry 32.

Glycidyl isobutyrate was obtained in 74% yield (26.7 mg, 185 μmol) from glycidyl methacrylate (35.5 mg, 250 μmol) by using catalyst **B** (5.32 mg, 125 nmol) in Table 2, Entry 33.

^1H NMR (400 MHz, CDCl_3) δ 4.42 (dd, $J = 2.8, 12.4$ Hz, 1H), 3.92 (dd, $J = 6.0, 12.4$ Hz, 1H), 3.26–3.19 (m, 1H), 2.85 (t, $J = 4.6$ Hz, 1H), 2.67–2.59 (m, 2H), 1.20 (d, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.8, 64.7, 49.4, 44.5, 33.8, 18.9.

Phenylpropyl triethylsilyl ether (CAS Registry Number: 2290-40-6)¹⁶ (Table 2, Entries 34 and 35)

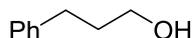


Phenylpropyl triethylsilyl ether was obtained in 83% yield (61.4 mg, 208 μmol ; colorless oil) from 1-(triethylsilyloxy)-3-phenyl-2-propene (62.1 mg, 250 μmol) by using catalyst **A** (0.53 mg, 0.25 μmol) and THF (1 mL) as a solvent in Table 2, Entry 34.

Phenylpropyl triethylsilyl ether was obtained in 90% yield (67.9 mg, 225 μmol) from 1-(triethylsilyloxy)-3-phenyl-2-propene (62.1 mg, 250 μmol) by using catalyst **B** (5.32 mg, 125 nmol) in Table 2, Entry 35.

^1H NMR (400 MHz, CDCl_3) δ 7.29–7.15 (m, 5H), 3.64 (t, $J = 6.4$ Hz, 2H), 2.68 (t, $J = 7.8$ Hz, 2H), 1.89–1.83 (m, 2H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.60 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.2, 128.4, 128.2, 125.6, 62.1, 34.5, 32.1, 6.79, 4.41.

3-Phenyl-1-propanol (CAS Registry Number: 122-97-4)¹⁷ (Table 4, Entry 1)



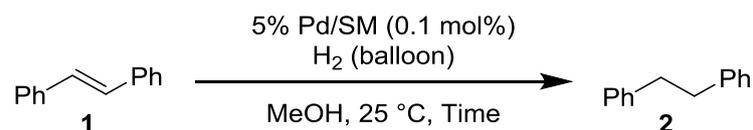
3-Phenyl-1-propanol was obtained in 94% yield (5.5 g, 40.6 mmol; colorless oil) from cinnamyl alcohol (5.8 g, 43.2 mmol) by using catalyst A (100 mg, 47.0 μmol) in Table 4, Entry 1.

^1H NMR (400 MHz, CDCl_3) δ 7.30–7.17 (m, 5H), 3.66 (t, $J = 6.4$ Hz, 2H), 2.70 (t, $J = 7.8$ Hz, 2H), 1.92–1.65 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.8, 128.4, 128.3, 125.8, 62.1, 34.1, 32.0.

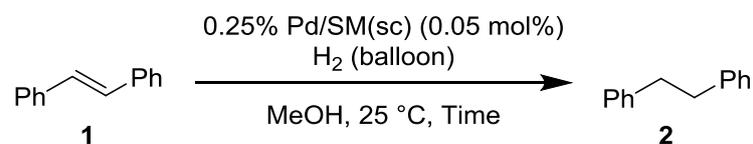
6. Reuse test of 5% Pd/SM and 0.25% Pd/SM (sc) for the hydrogenation of *trans*-stilbene

A mixture of *trans*-stilbene (4.3 g, 24.0 mmol) and 5% Pd/SM (50.0 mg, 23.5 μmol) in MeOH (100 mL) was stirred at 25 °C under H_2 atmosphere (balloon). After 6 h, the mixture was filtered through a funnel (1 mm filter paper). The catalyst on the filter was washed with EtOAc (3 mL \times 5), and the filtrate was concentrated in vacuo to afford 1,2-diphenylethane in 74% yield (3.2 g, 17.8 mmol). The catalyst on the filter was dried in vacuo at room temperature overnight, and then weighed (49.5 mg, 99% recovery). The reaction for the second run was carried out in a procedure similar to the first run except for the amount of *trans*-stilbene (3.9 g, 21.5 mmol) and 5% Pd/SM (45.0 mg, 21.1 μmol) for 12 h. 1,2-diphenylethane was obtained 82% yield (3.2 g, 17.6 mmol). The reaction for the third run was also carried out likewise the first run except for the usage of substrate and catalyst. The results were summarized in the following table (Table S1).

A mixture of *trans*-stilbene (415 mg, 2.3 mmol) and 0.25% Pd/SM(sc) (50.0 mg, 1.2 μmol) in MeOH (10 mL) was stirred at 25 °C under H_2 atmosphere (balloon). After 6 h, the mixture was filtered through a funnel (1 mm filter paper). The catalyst on the filter was washed with EtOAc (3 mL \times 5), and the filtrate was concentrated in vacuo to afford 1,2-diphenylethane in quantitative yield (420 mg, 2.3 mmol). The catalyst on the filter was dried in vacuo at room temperature overnight, and then weighed (49.1 mg, 98% recovery). The reaction for the second run was carried out in a procedure similar to the first run except for the amount of *trans*-stilbene (373 mg, 2.1 mmol) and 0.25% Pd/SM(sc) (45.0 mg, 1.1 μmol) for 6 h. 1,2-diphenylethane was in obtained quantitative yield (383 mg, 2.1 mmol). The reaction for the third run was also carried out likewise the first run except for the usage of substrate and catalyst. The results were summarized in the following table (Table S2).

Table S1 Reuse study of 5% Pd/SM

Run (Time)	Substrate usage	Catalyst usage	Yield of 2 (%)	Recoverd catalyst
1st (6 h)	4.3 g, 24.0 mmol	50.0 mg	3.2 g, 17.8 mmol, 74%	49.5 mg (99%)
2nd (12 h)	3.9 g, 21.5 mmol	45.0 mg	3.2 g, 17.6 mmol, 82%	45.0 mg (quant.)
3rd (23 h)	3.4 g, 19.1 mmol	40.0 mg	3.1 g, 17.0 mmol, 89%	40.0 mg (quant.)

Table S2 Reuse study of 0.25% Pd/SM(sc)

Run (Time)	Substrate usage	Catalyst usage	Yield of 2 (%)	Recoverd catalyst
1st (6 h)	415 mg, 2.3 mmol	50.0 mg	420 mg, 2.3 mmol, quant.	49.0 mg (98%)
2nd (6 h)	373 mg, 2.1 mmol	45.0 mg	383 mg, 2.1 mmol, quant.	45.0 mg (quant.)
3rd (6 h)	332 mg, 1.8 mmol	40.0 mg	312 mg, 1.7 mmol, 95%	33.2 mg (83%)

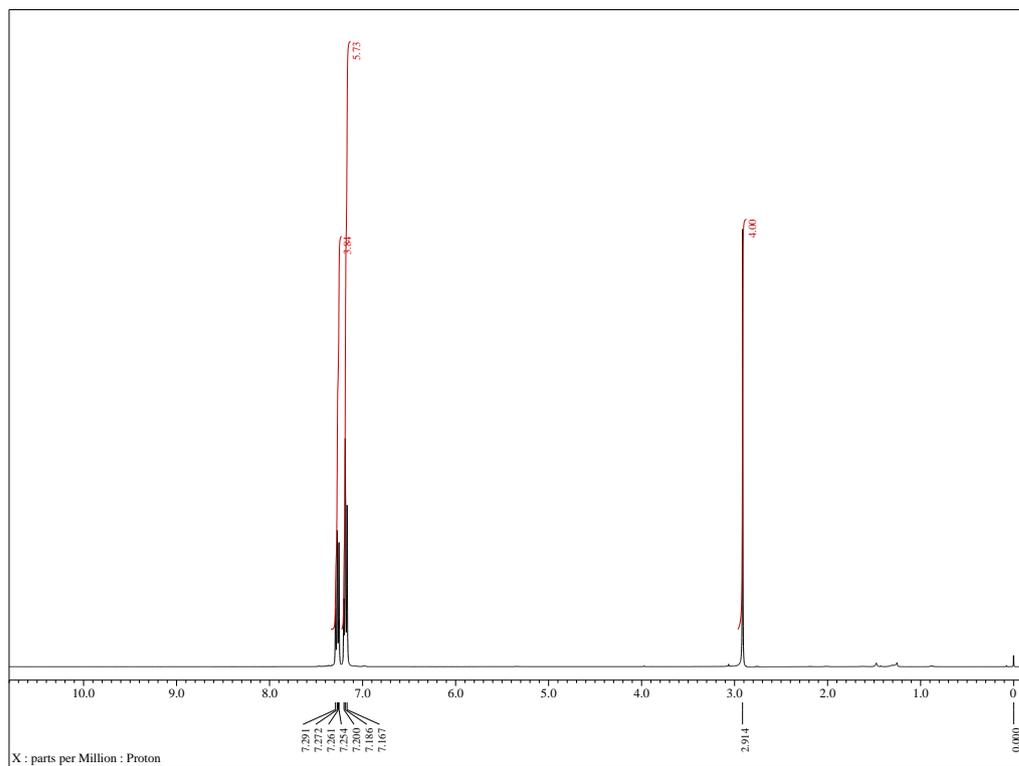
7. References

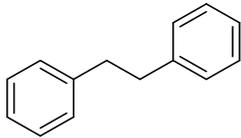
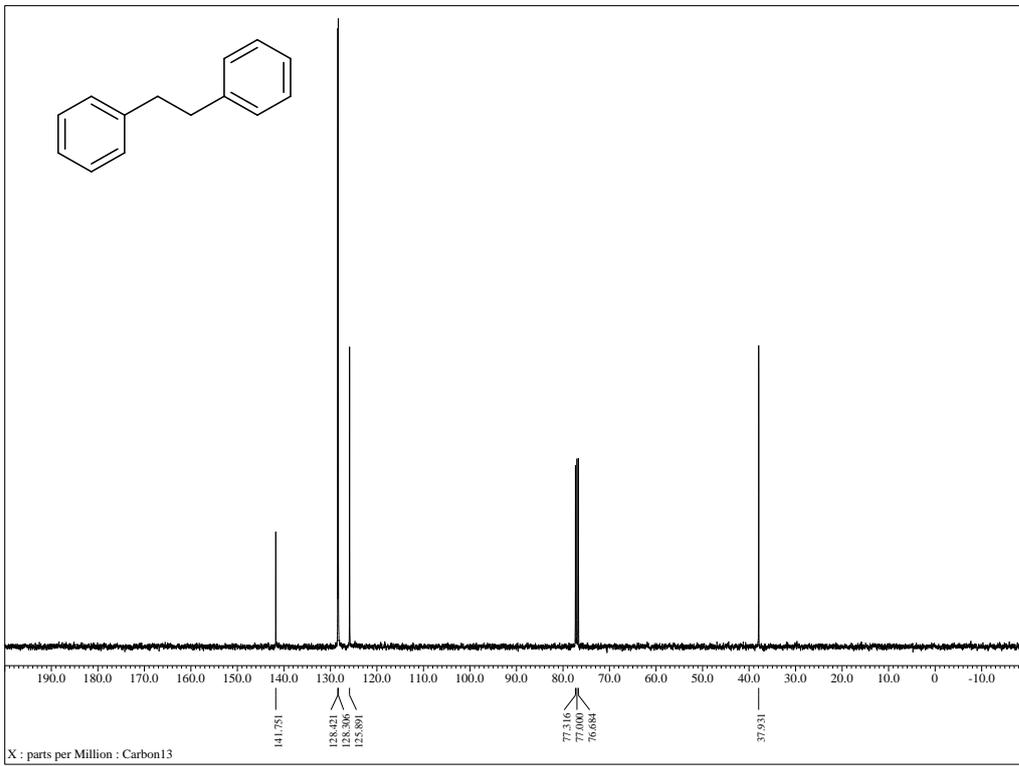
- 1 Bryden A. F. Le Bailly, Mark D. Greenhalgh, Stephen P. Thomas, *Chem. Commun.* **2012**, 48, 1580–1582.
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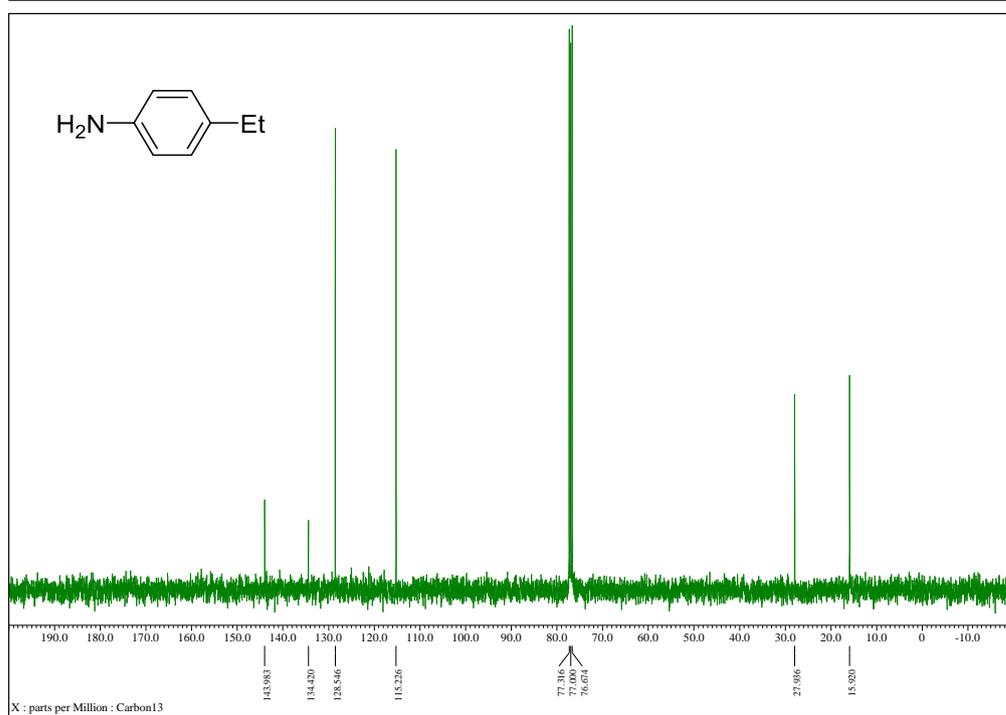
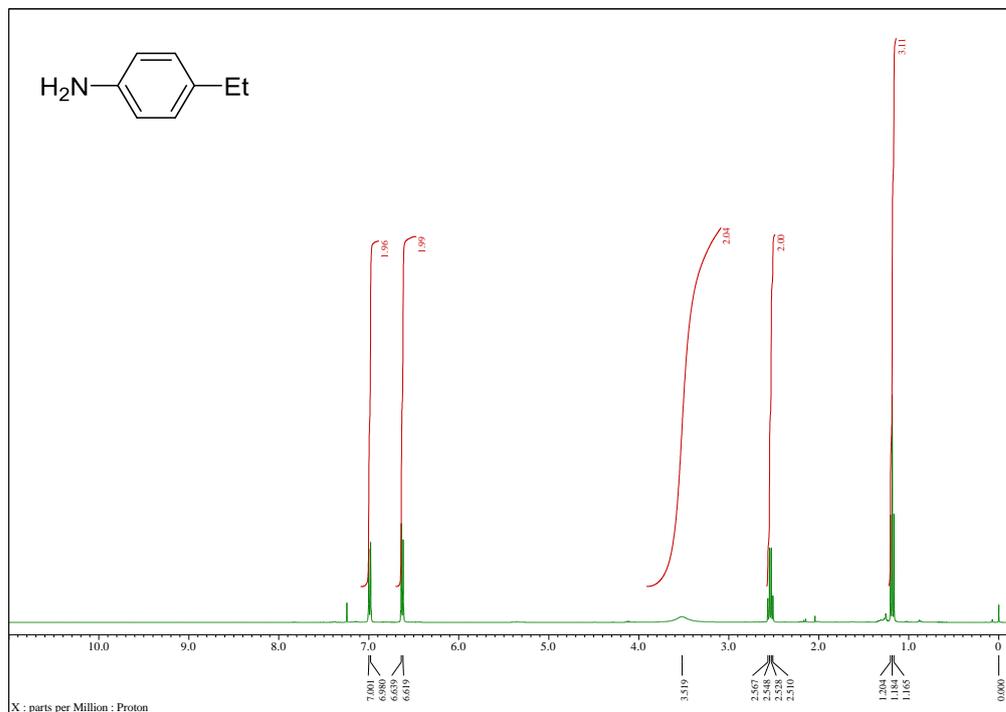
8. ^1H and ^{13}C spectra of products

Bibenzyl (CAS Registry Number: 103-29-7) (Table 2, Entries 1 and 2; Table 4, Entry 2)

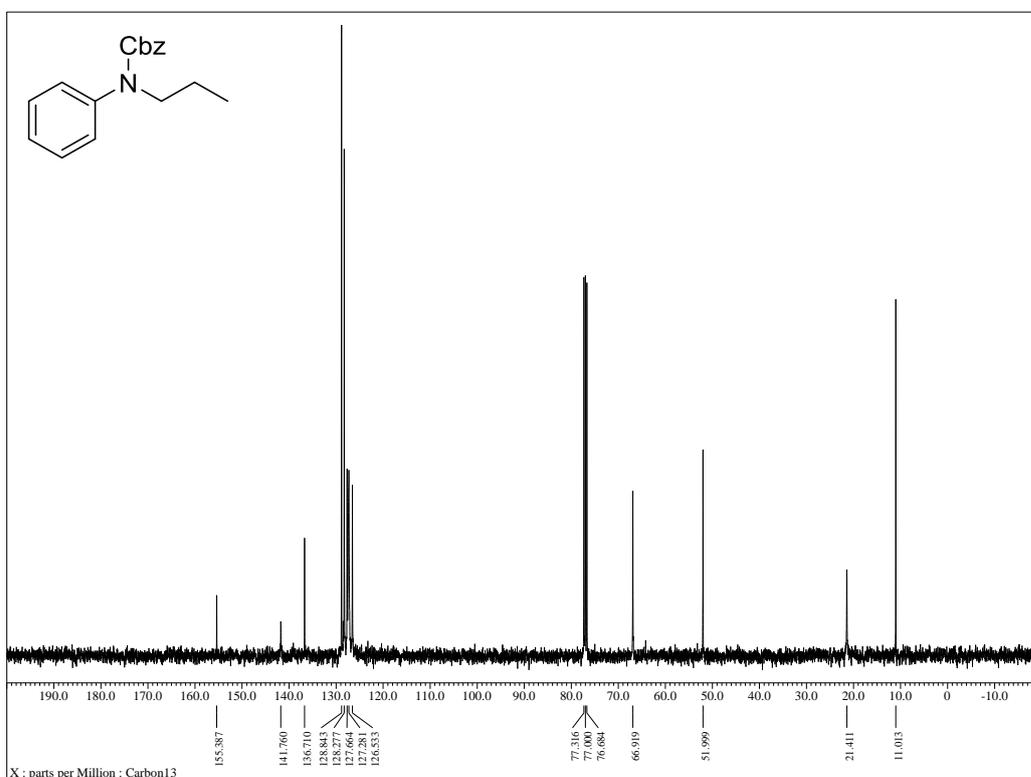
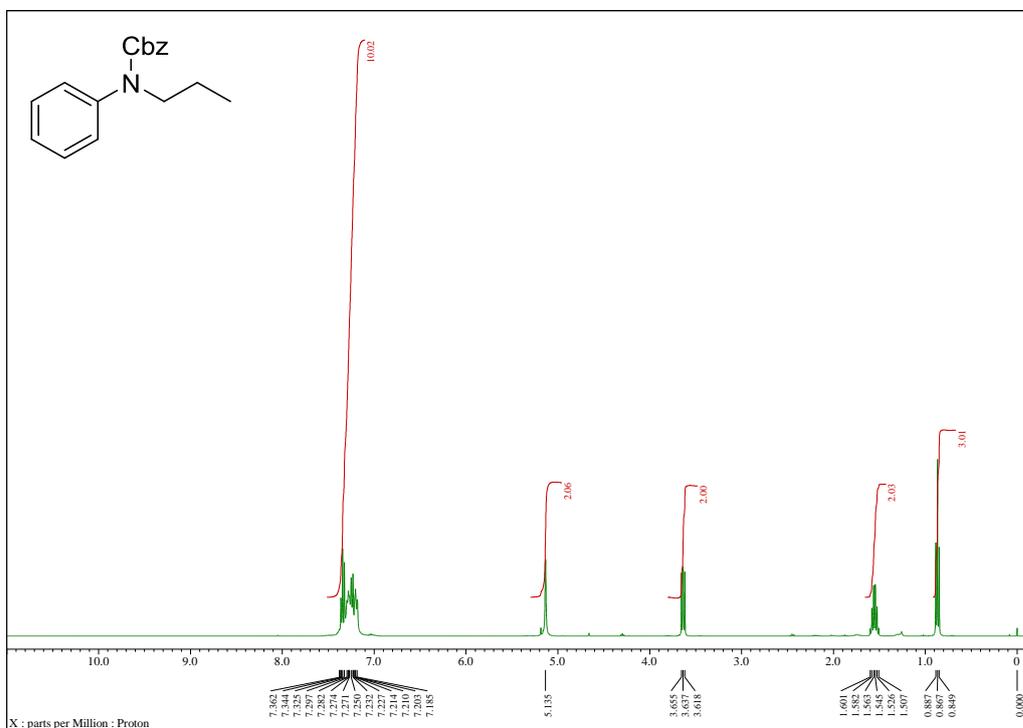




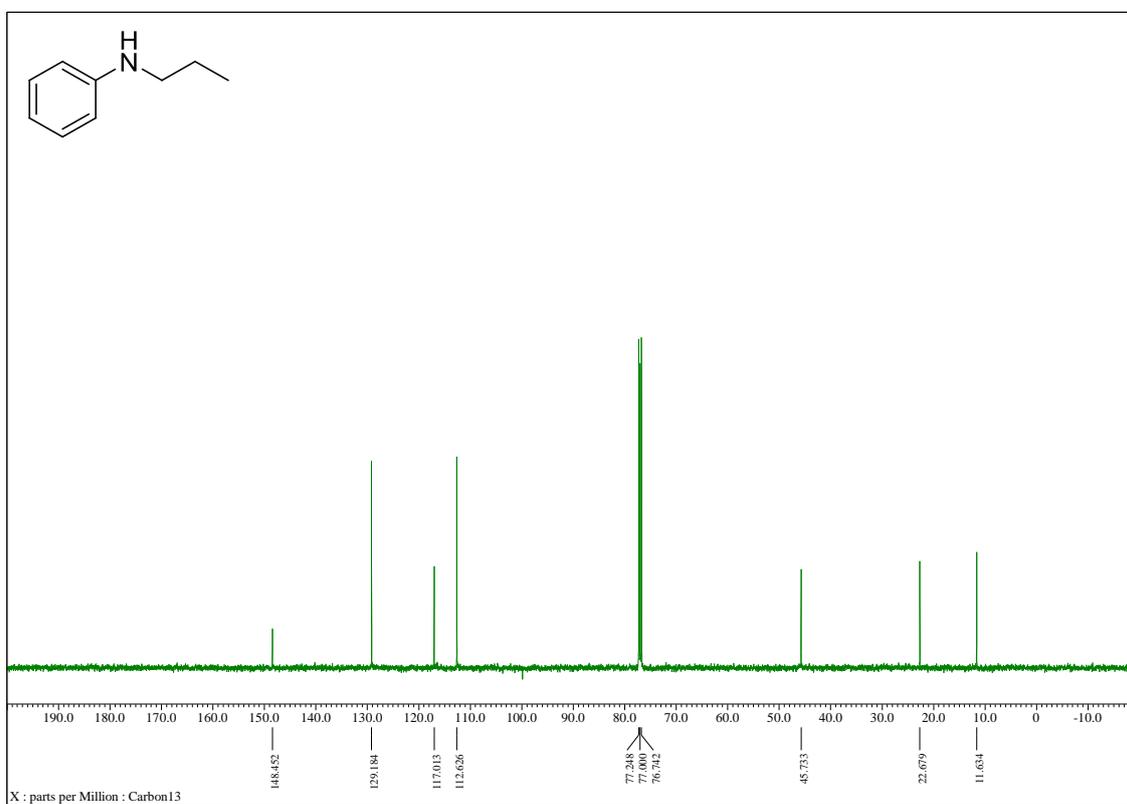
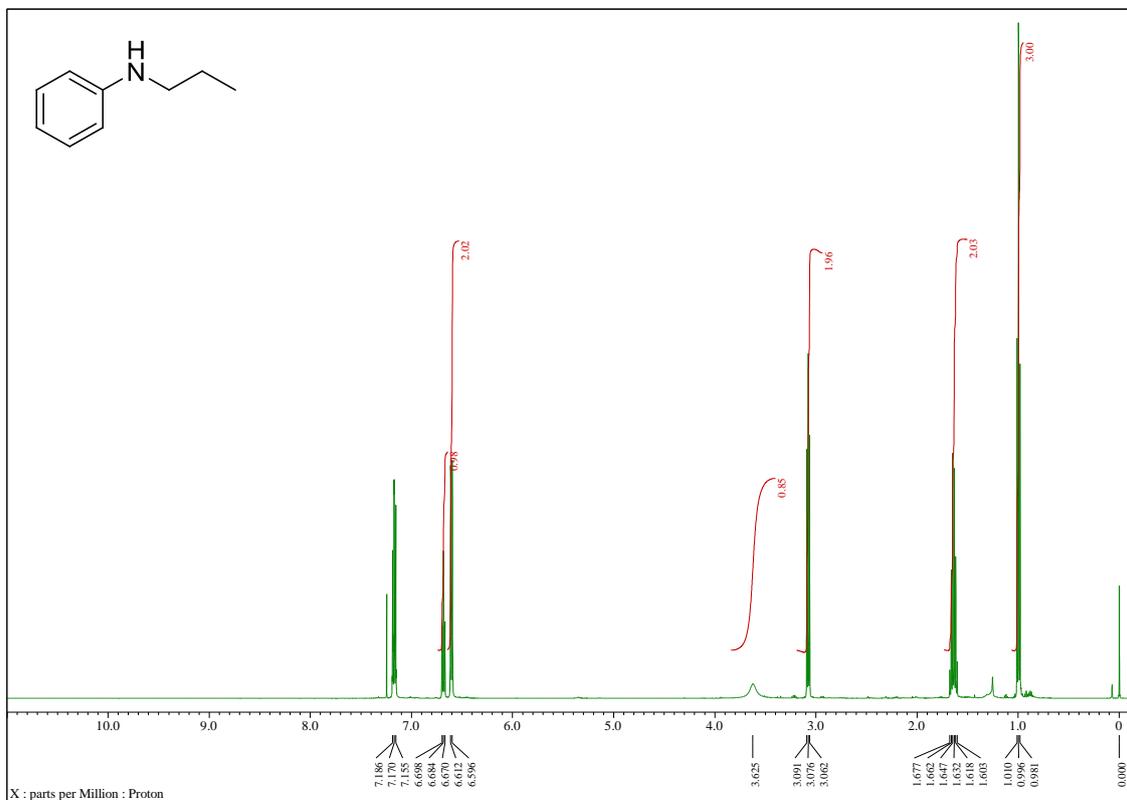
4-Ethylnitrobenzene (CAS Registry Number: 589-16-2) (Table 2, Entries 3, 4, 5, and 6)



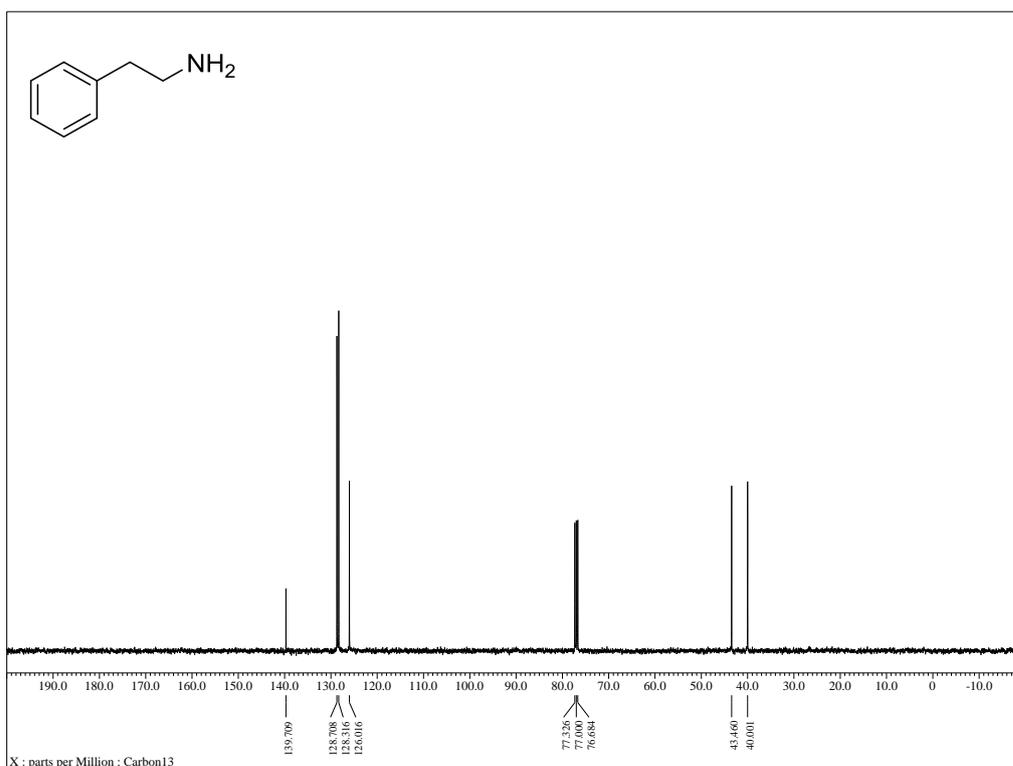
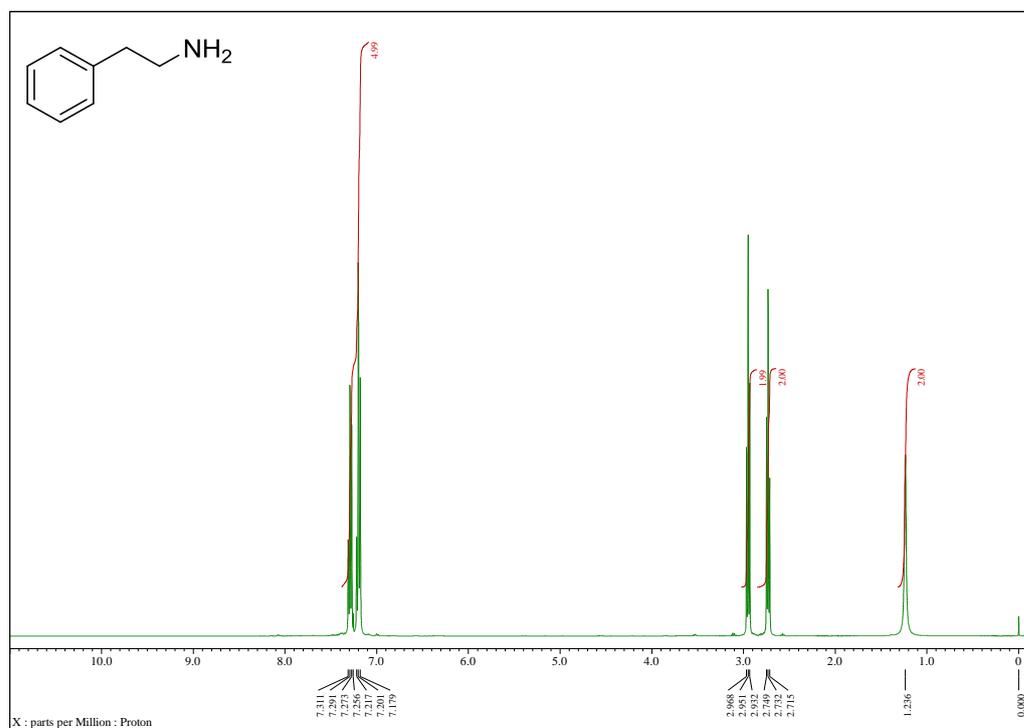
***N*-phenyl-*N*-propylcarbamate (CAS Registry Number: 634917-15-0) (Table 2, Entry 7; Table 4, Entry 3)**



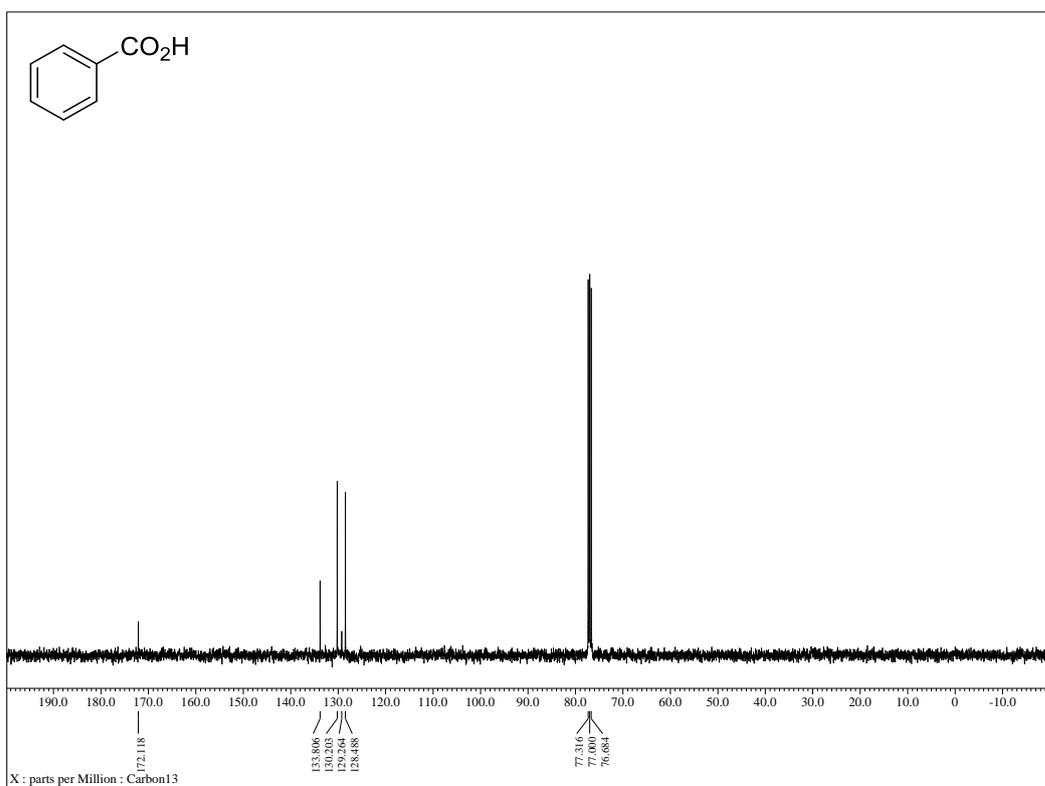
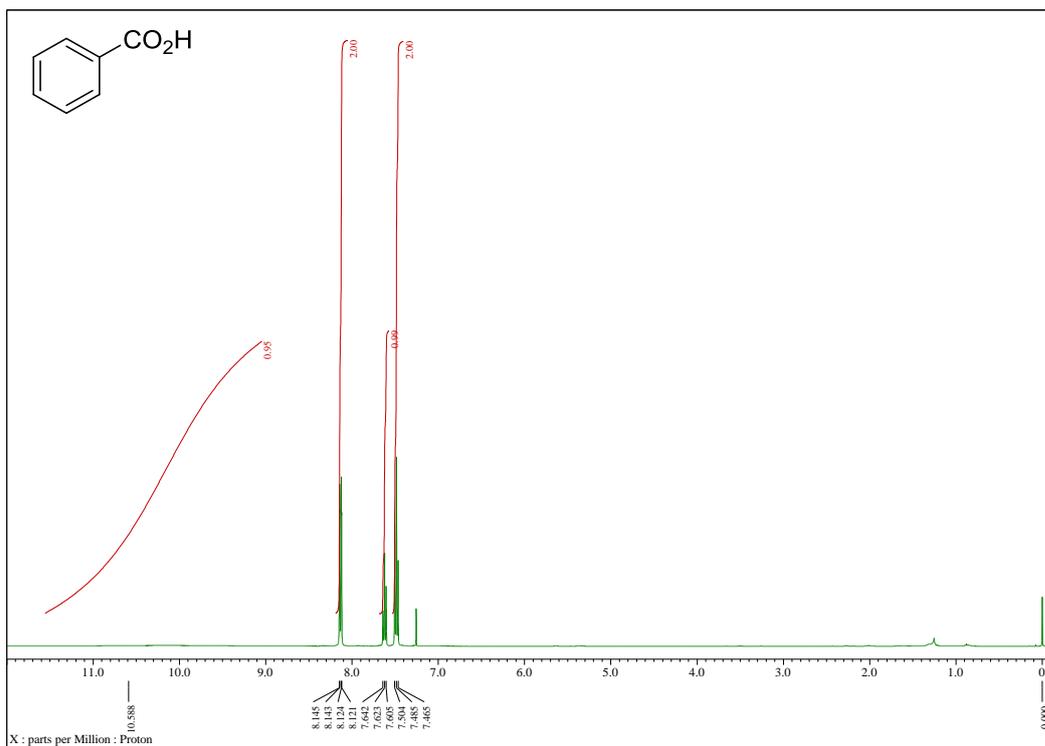
N-Propylaniline (CAS Registry Number: 622-80-0) (Table 2, Entries 8 and 9)



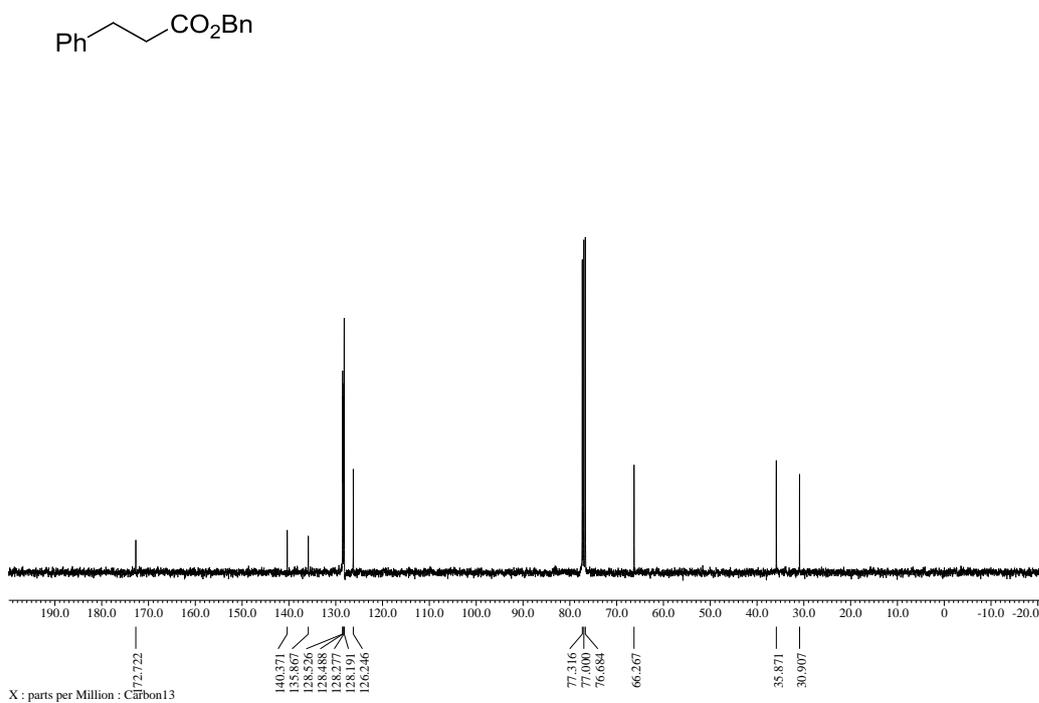
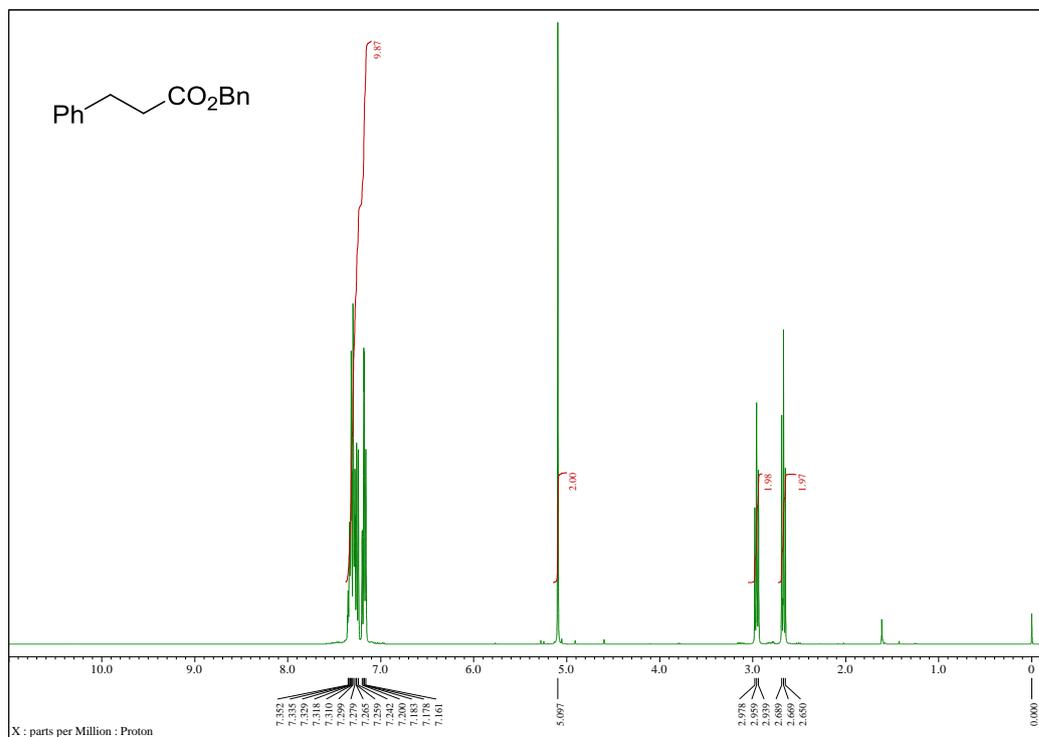
Phenethylamine (CAS Registry Number: 64-04-0) (Table 2, Entries 10 and 11;
Table 4, Entry 4)



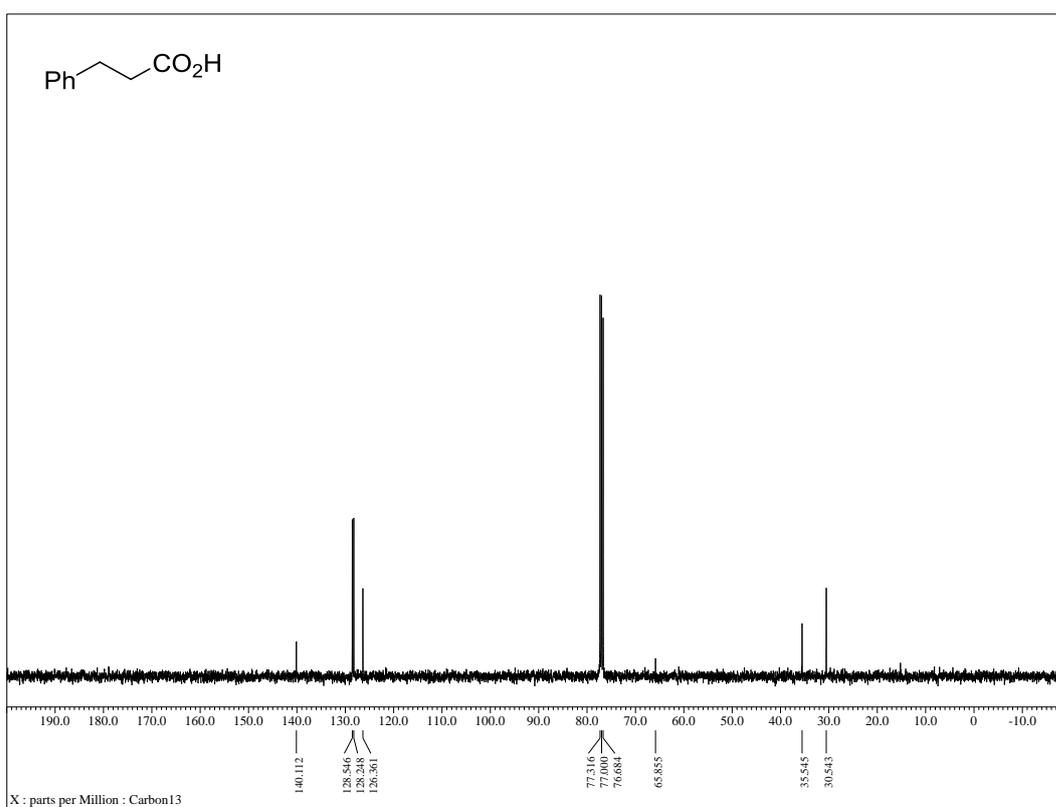
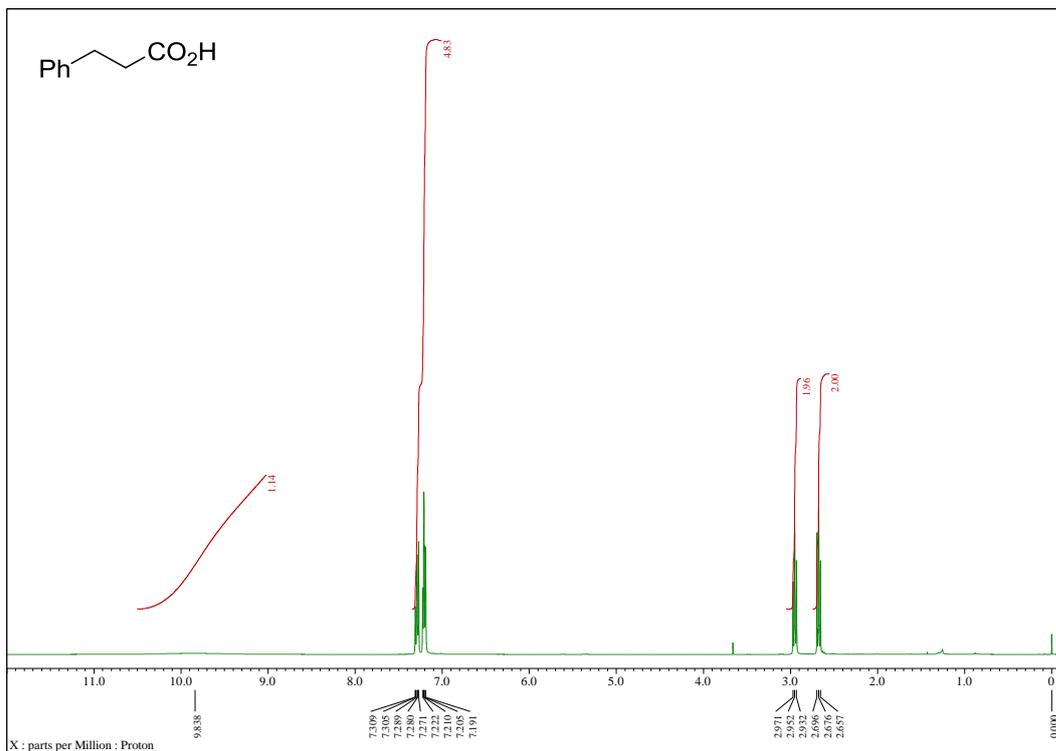
Benzoic acid (CAS Registry Number: 65-85-0) (Table 2, Entries 12 and 13)



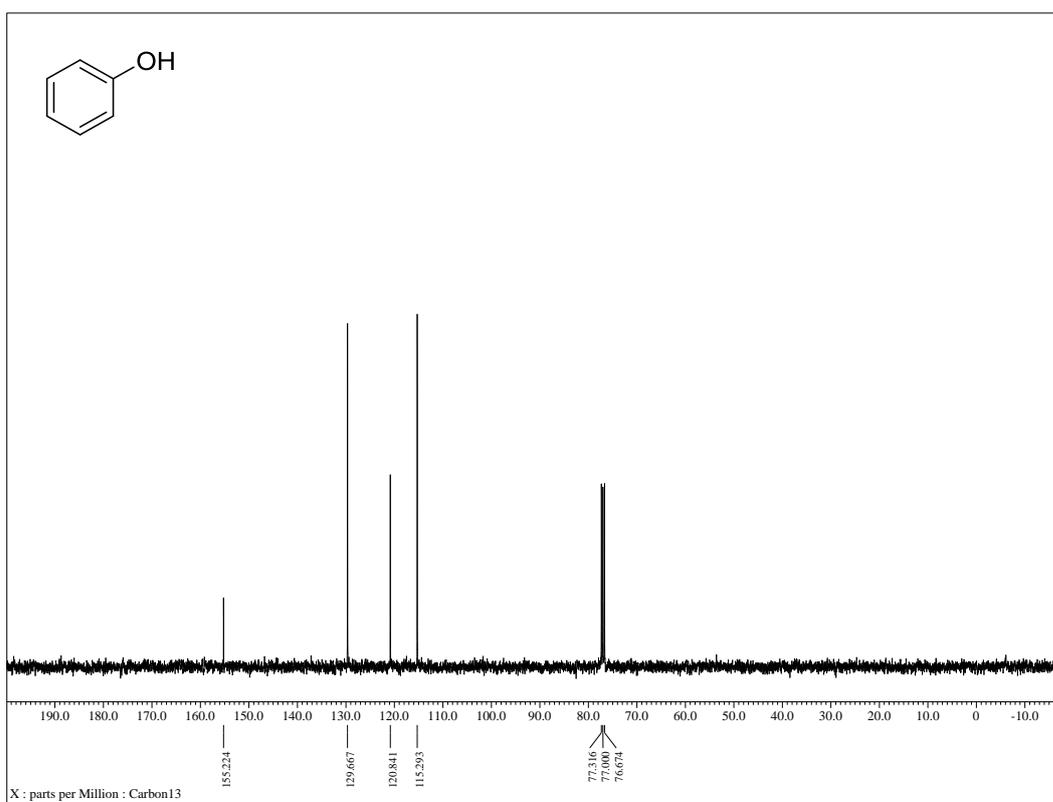
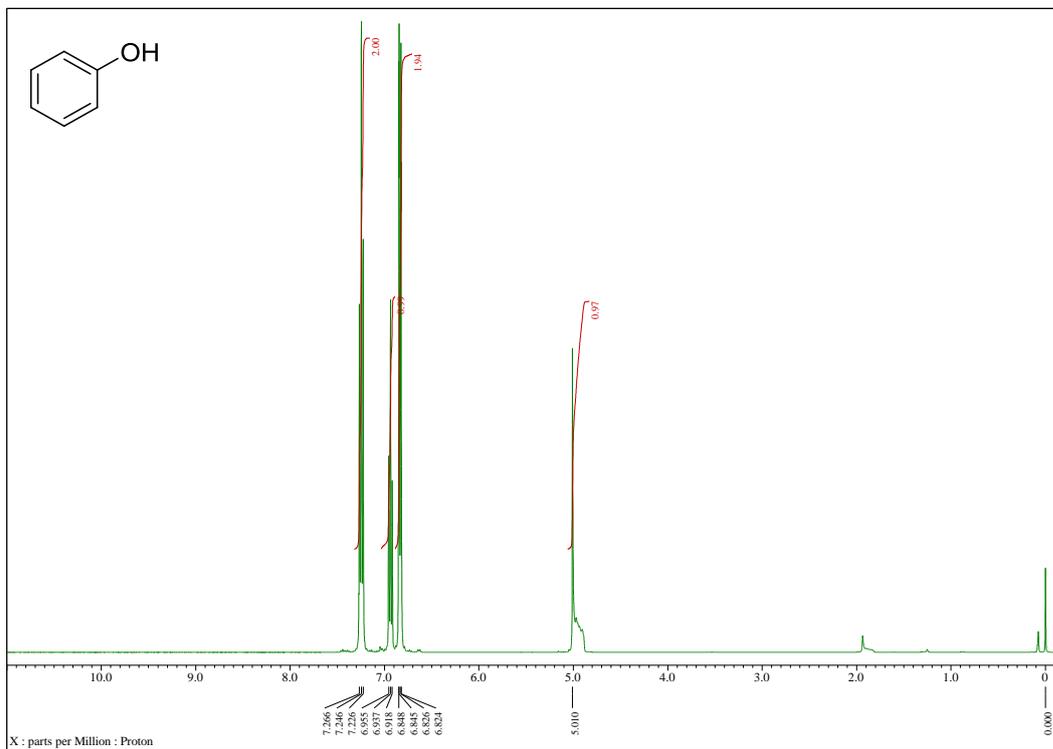
Benzyl benzenepropanoate (CAS Registry Number: 22767-96-0) (Table 2, Entry 14)



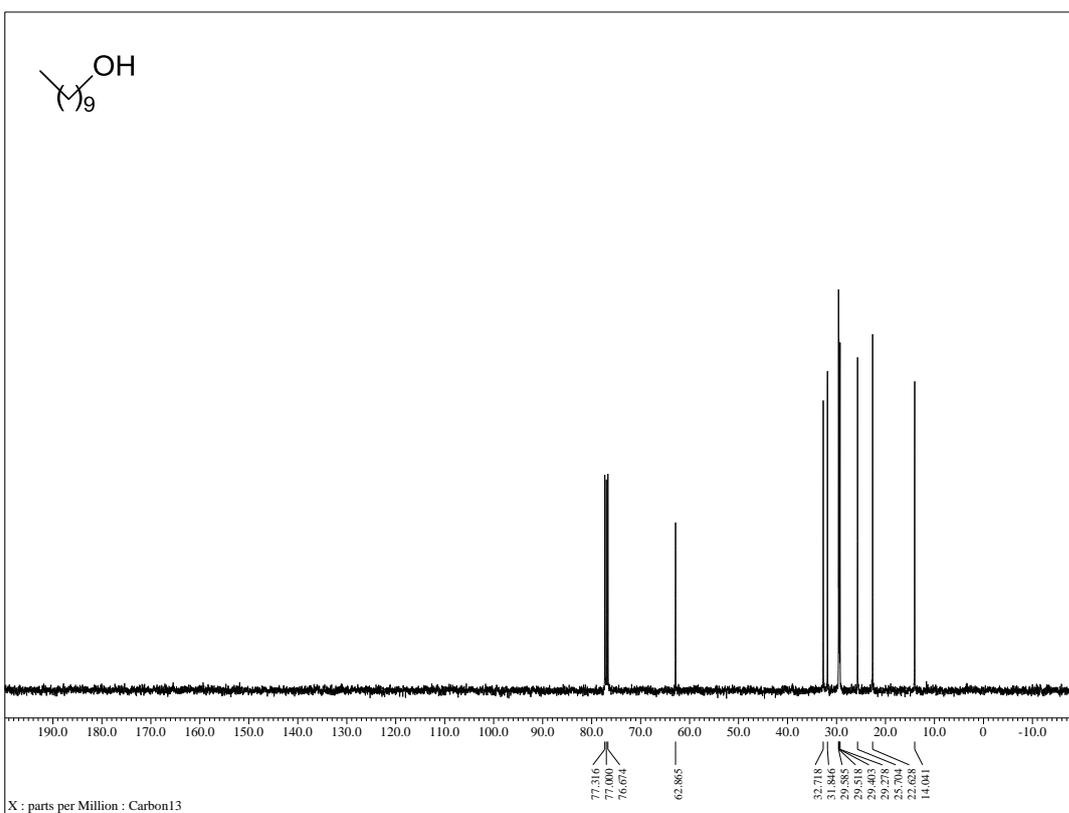
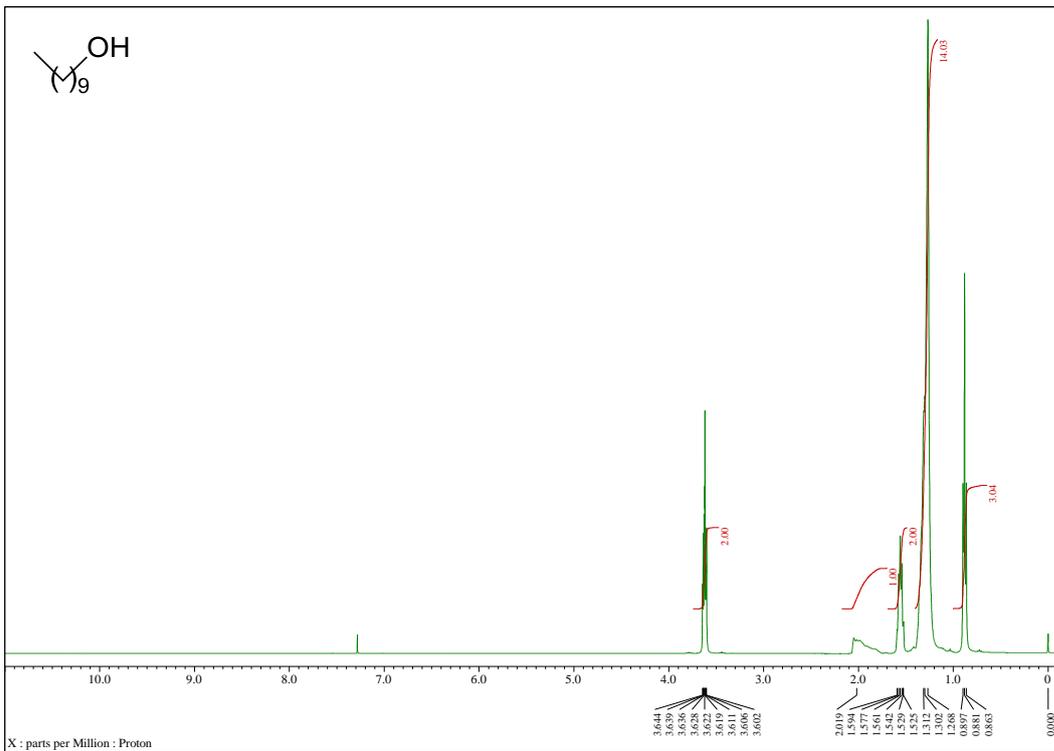
Benzenepropanoic acid (CAS Registry Number: 22767-96-0) (Table 2, Entry 15)



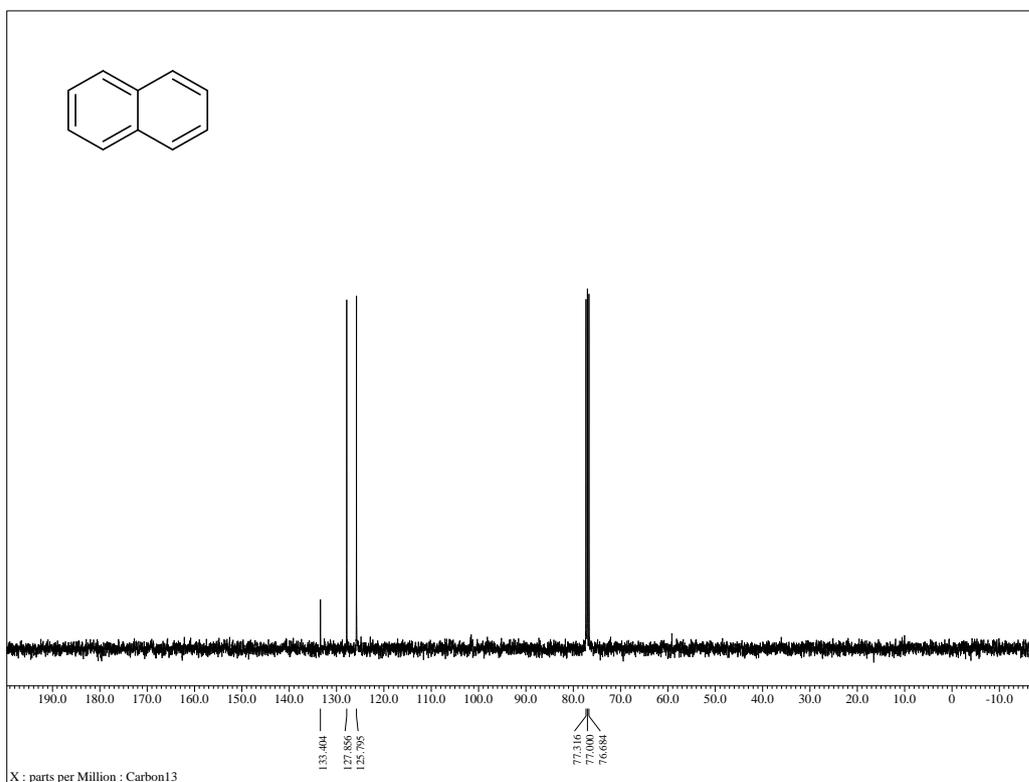
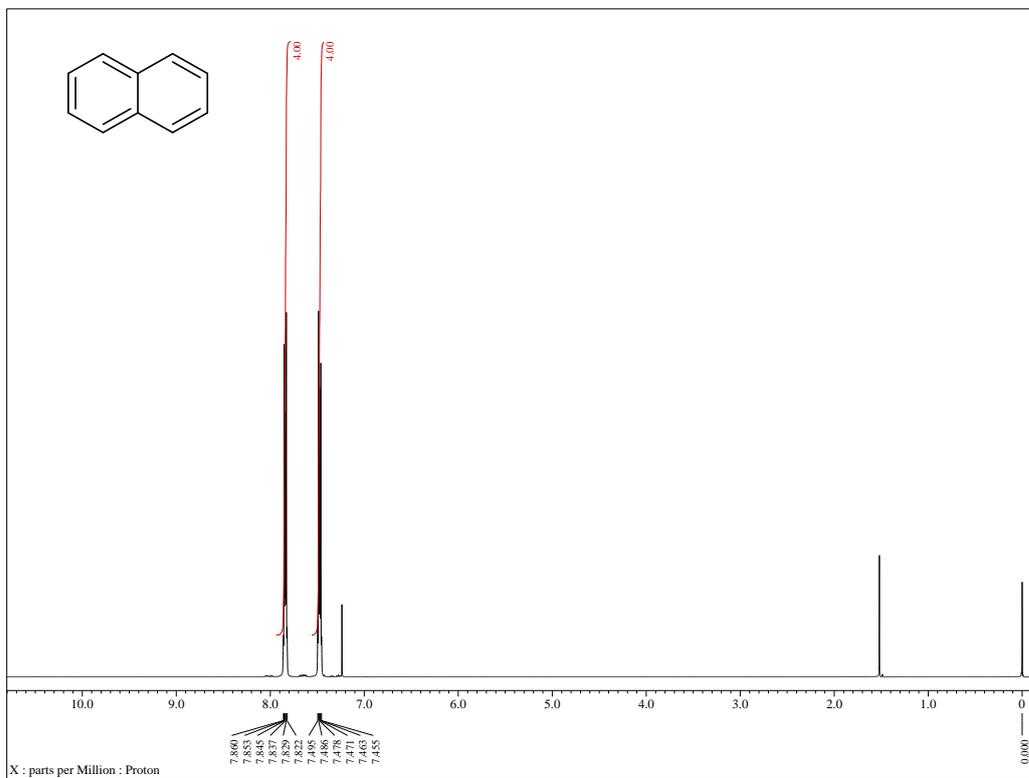
Phenol (CAS Registry Number: 108-95-2) (Table 2, Entries 16 and 17)



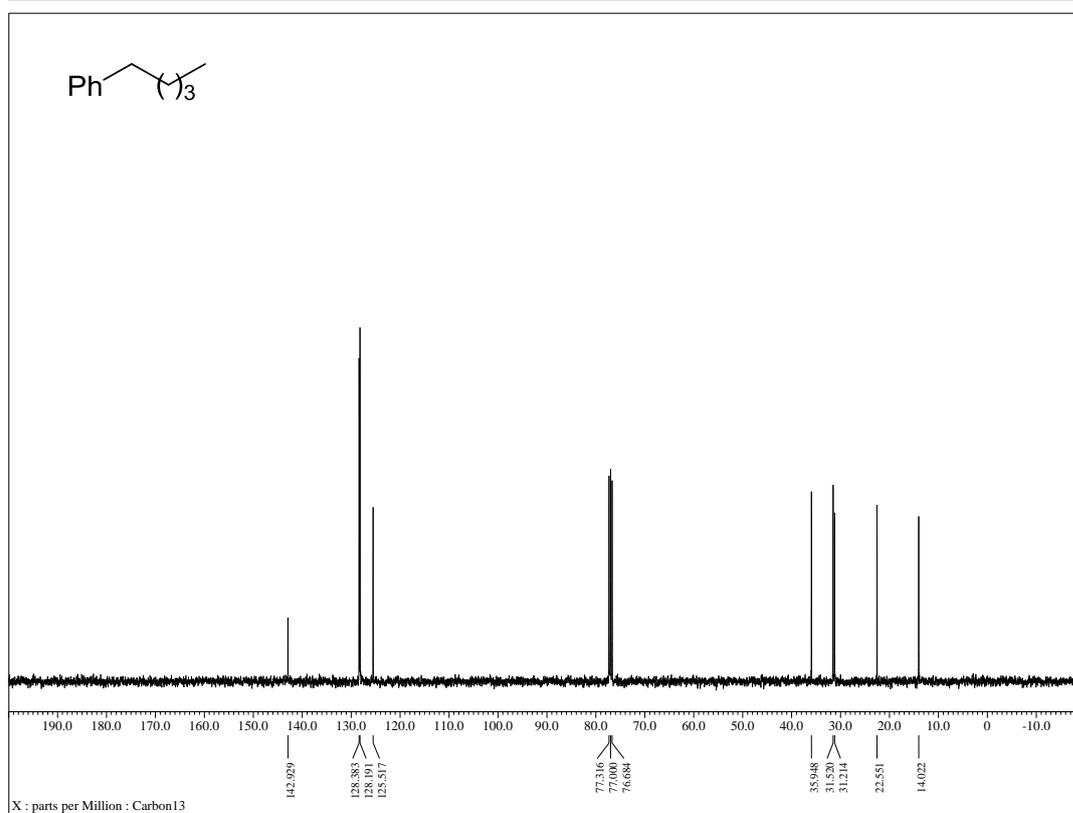
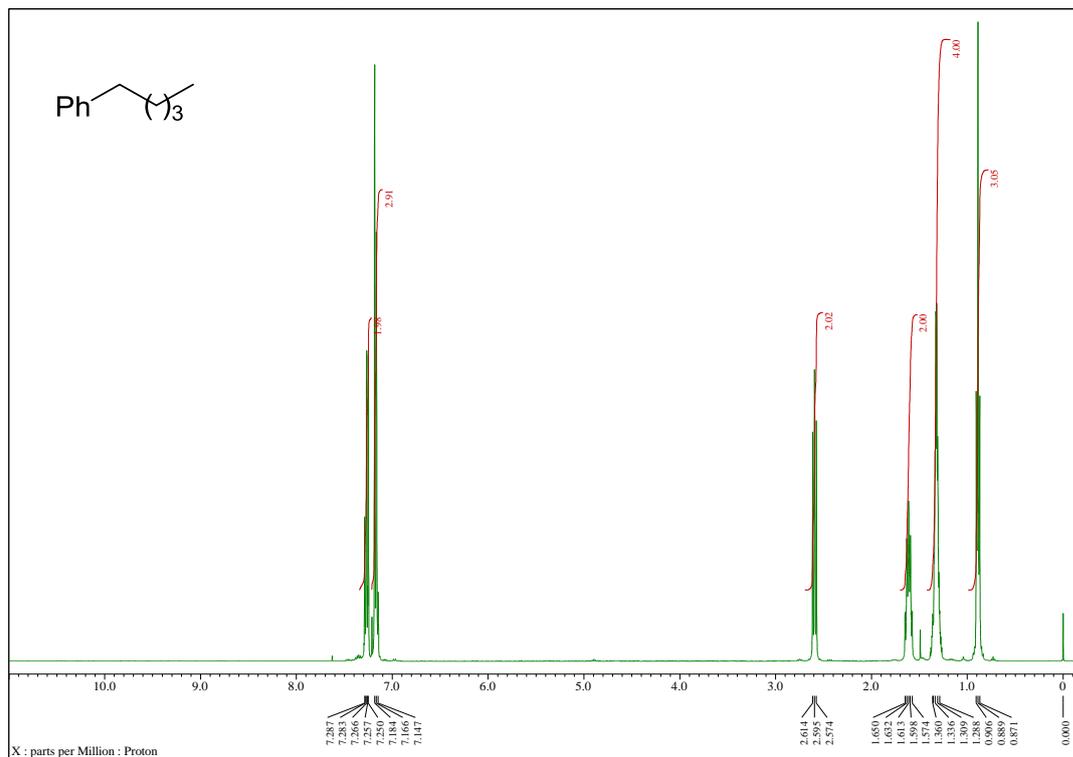
1-Decanol (CAS Registry Number: 112-30-1) (Table 2, Entries 18 and 19)



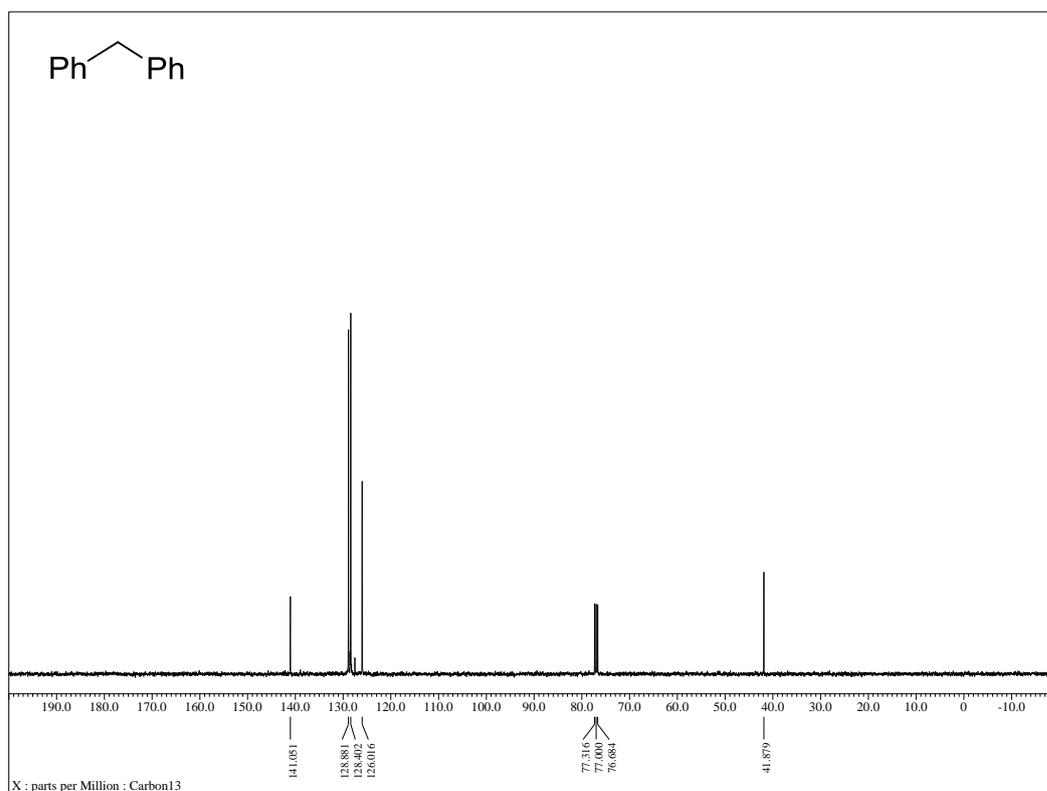
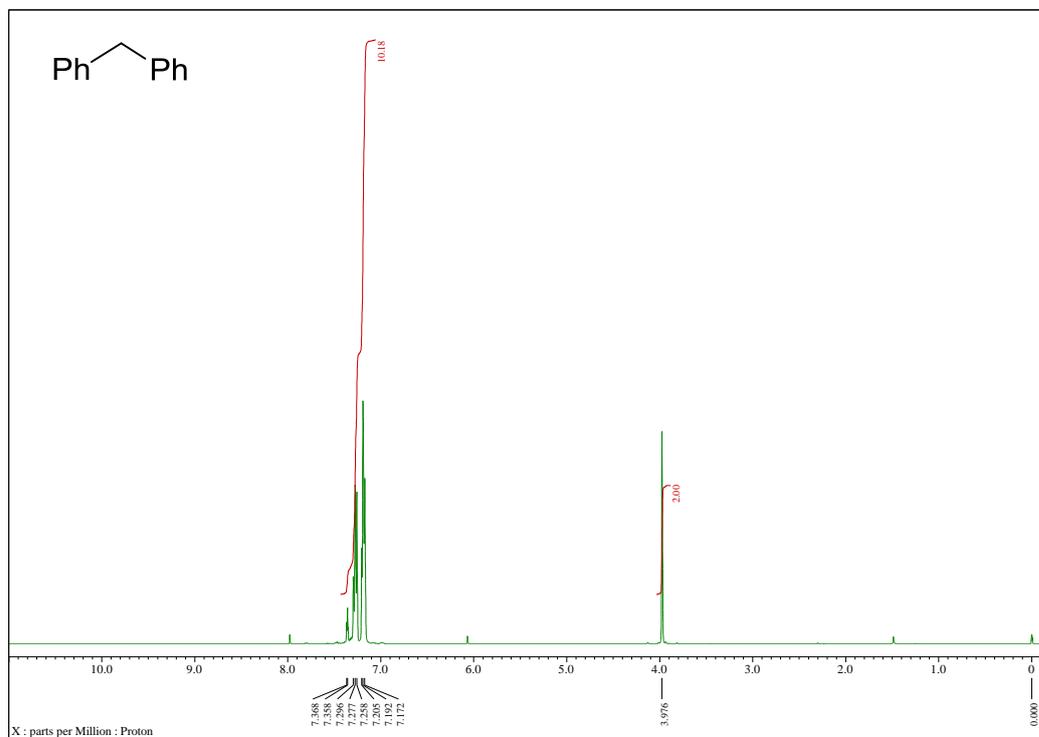
Naphthalene (CAS Registry Number: 91-20-3) (Table 2, Entries 20, 21, 22, and 23)



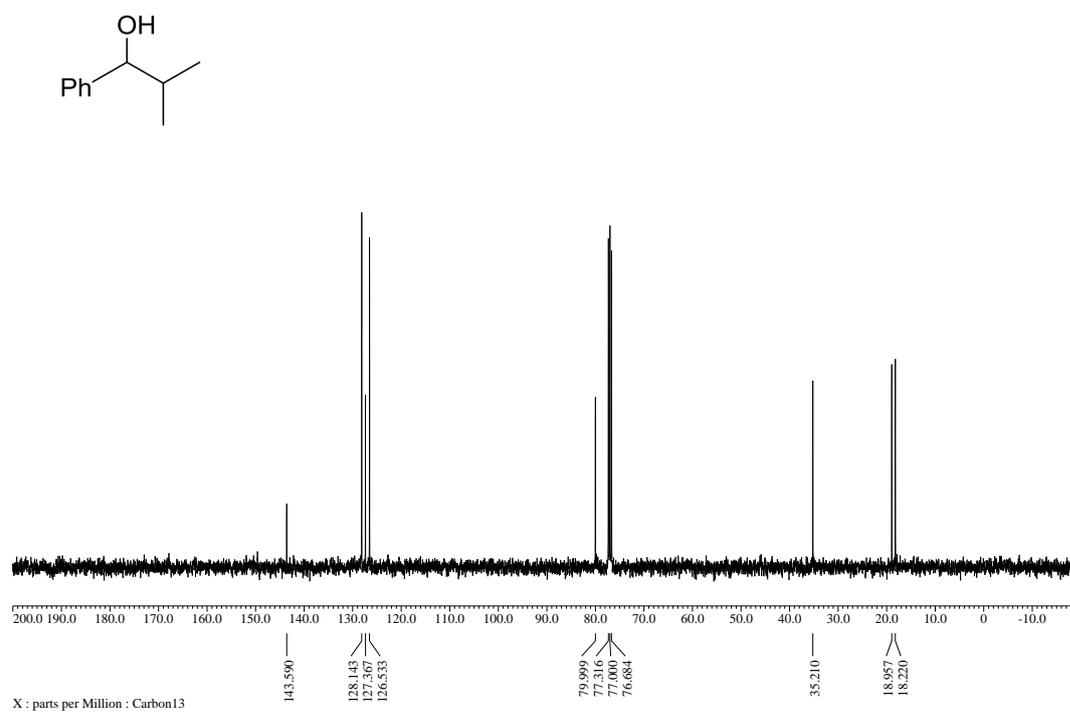
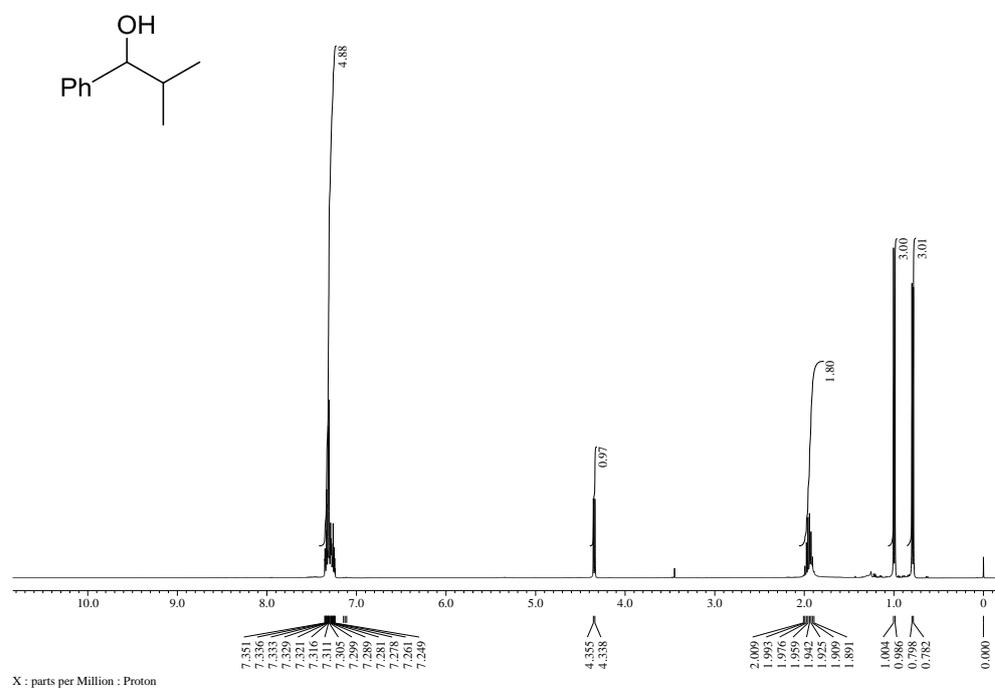
Pentylbenzene (CAS Registry Number: 495-40-9) (Table 2, Entries 24 and 25)



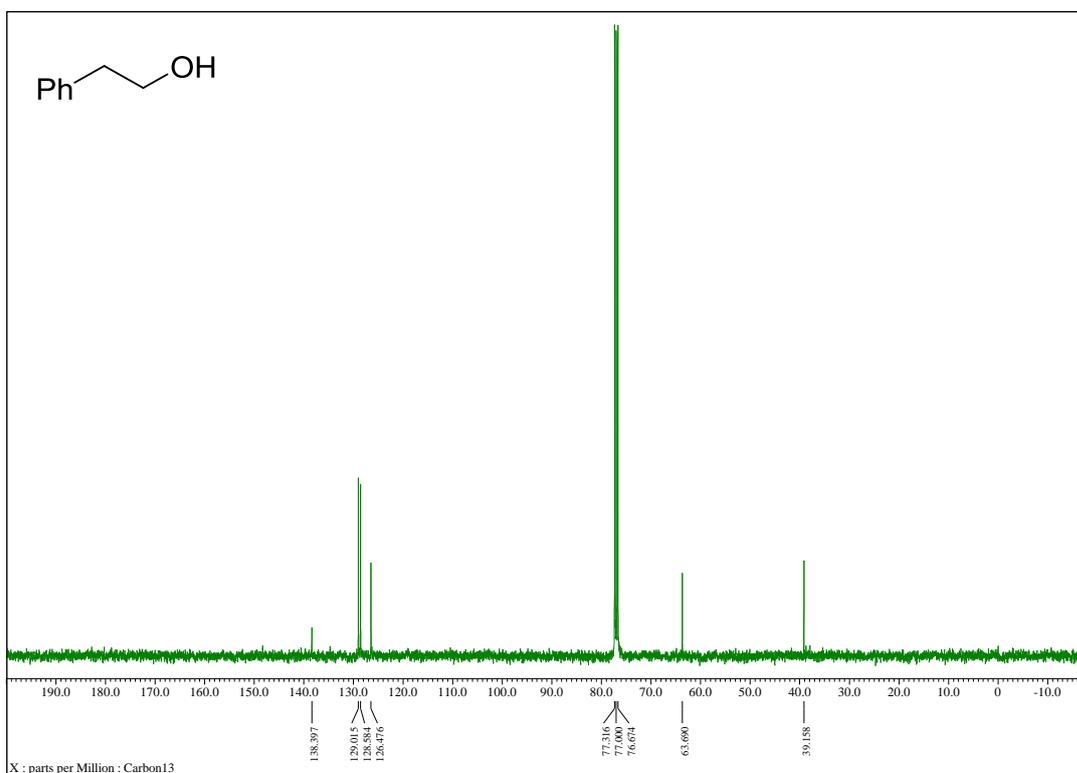
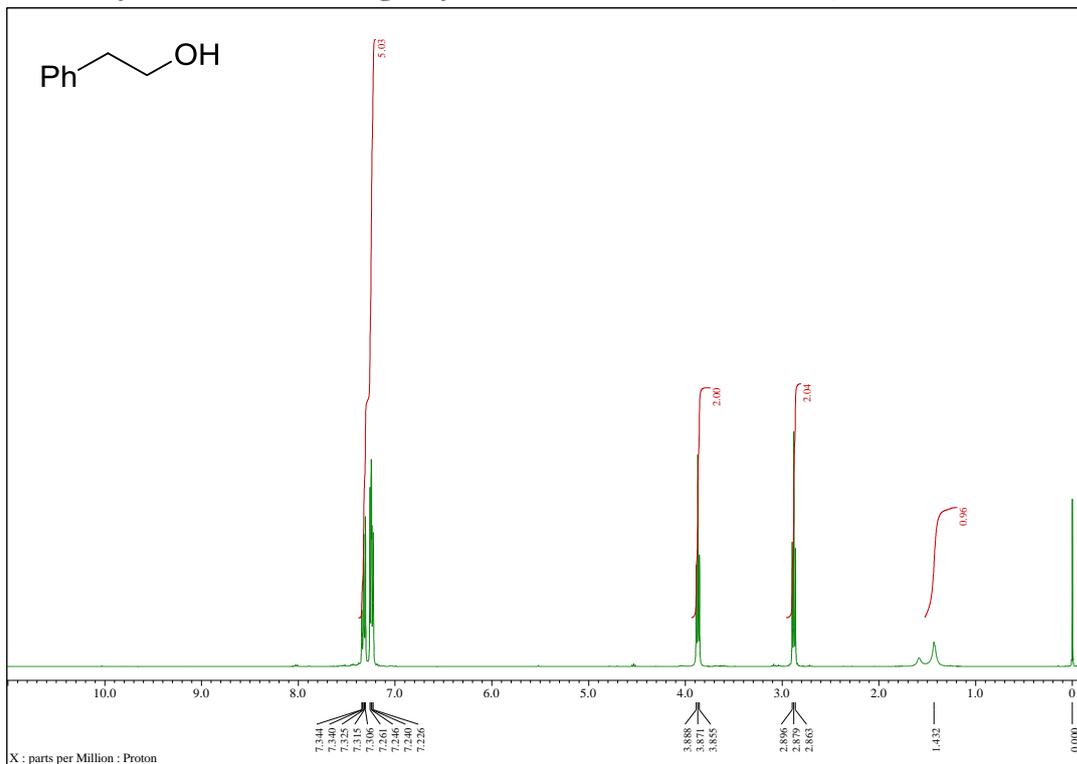
1,1-Diphenylmethane (CAS Registry Number: 101-81-5) (Table 2, Entries 26 and 27)



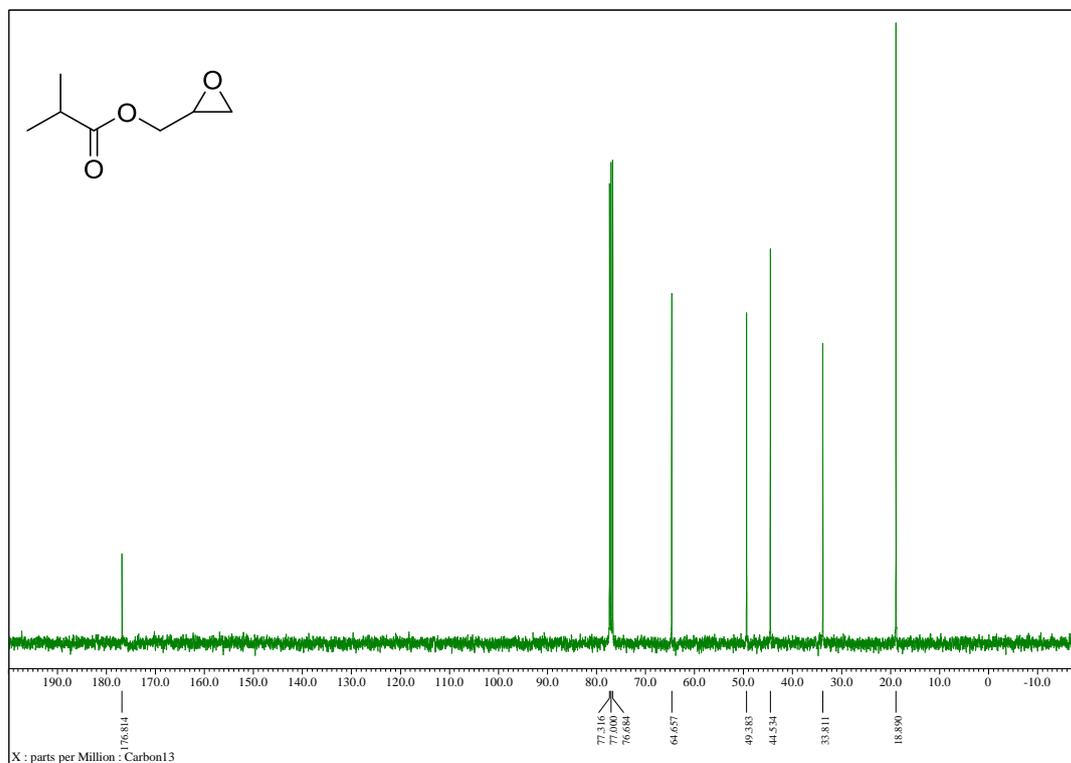
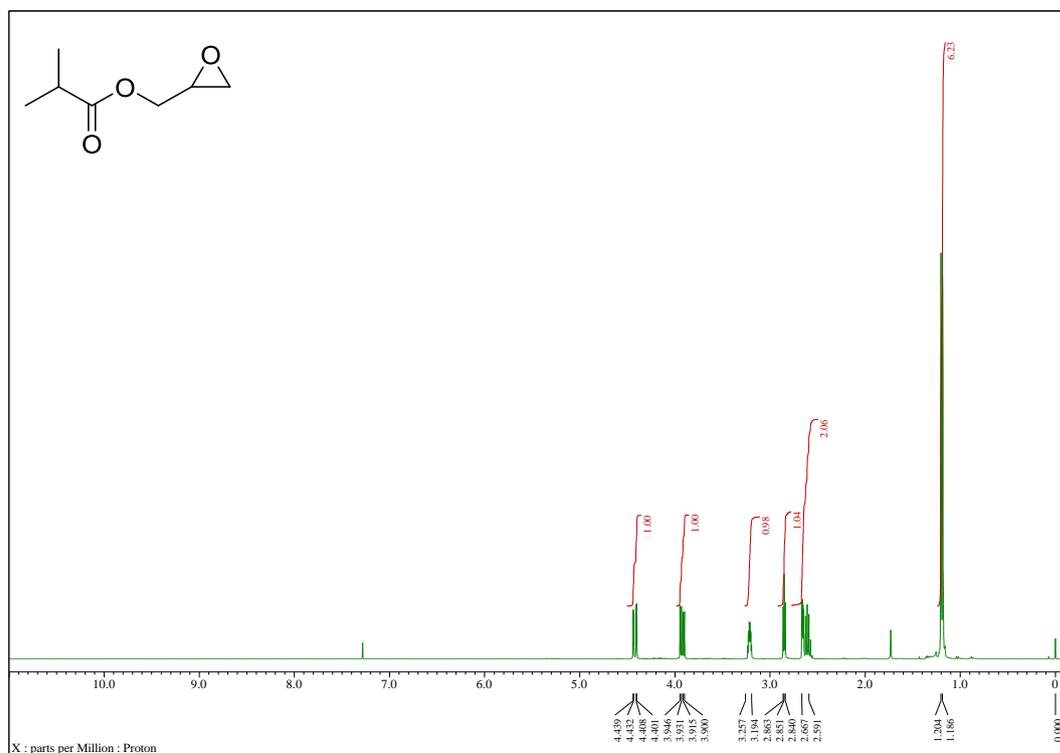
1-Phenyl-2-methylpropan-1-ol (CAS Registry Number: 611-69-8) (Table 2, Entries 28 and 29)



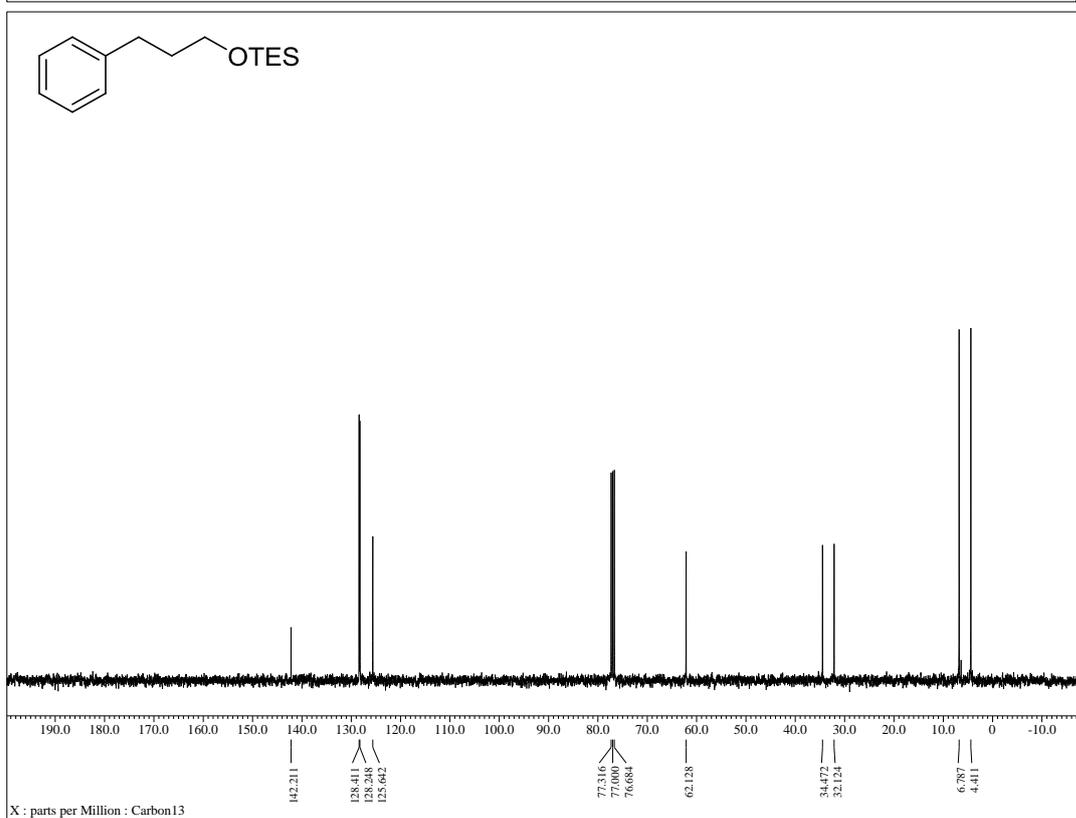
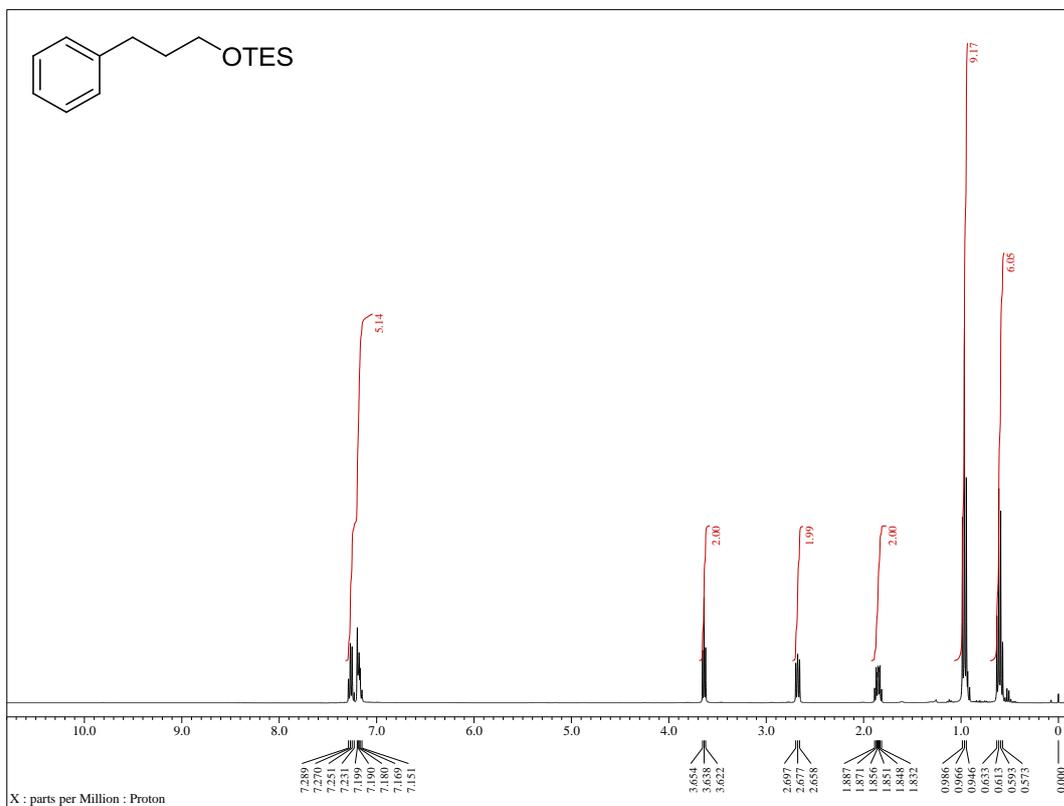
Phenethyl alcohol (CAS Registry Number: 60-12-8) (Table 2, Entries 30 and 31)



Glycidyl isobutyrate (CAS Registry Number: 3669-66-7) (Table 2, Entries 32 and 33)



Phenylpropyl triethylsilyl ether (CAS Registry Number: 2290-40-6) (Table2, Entries 34 and 35)



3-Phenyl-1-propanol (CAS Registry Number: 122-97-4)¹⁷ (Table 4, Entry 1)

