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Supporting Information

Osmium on Chelate Resin: Non-volatile Catalyst for Synthesis of Diols from Alkenes

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General Experimental.

DIAION CR11 was obtained from Mitsubishi Chemical Co. (Tokyo, Japan). OsO_4 and MeOH (HPLC grade) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). NMO was obtained from Tokyo Chemical Industry Co., Ltd. (TCI, Tokyo, Japan). Both TBHP (70% in H_2O) and potassium ferricyanide (III) were purchased from Sigma-Aldrich Co. LLC (St. Louis, MO, USA). Anhydrous acetone and *t*BuOH were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan) and Nacalai tesque, Inc. (Kyoto, Japan), respectively. *t*BuOH was distilled from sodium. All other reagents were purchased from commercially sources and used without further purification. Flash column chromatography was performed using Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 µm spherical, neutral). ^1H and ^{13}C NMR spectra were recorded on a JEOL ECS 400 (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR). Chemical shifts (δ) are expressed in ppm based on internal standard [TMS (0 ppm)] for ^1H NMR and residual solvent [$CDCl_3$ (77.0 ppm)] for ^{13}C NMR.

For Table 1

A mixture of styrene (26.0 mg, 250 µmol), 5% Os/CR11 (47.6 mg, 12.5 µmol, 5 mol%), the oxidizing reagent (1.5 equiv), and solvent (0.5 mL) in a 15-mL test tube was stirred under an Ar atmosphere at room temperature. After 5 h, the mixture was filtered through a Celite pad, and the pad was washed with acetone (30 mL) and concentrated *in vacuo*. The yield was determined by ^1H NMR using 1,3-benzodioxole (28.7 µL, 250 µmol) as the internal standard.

Entries 8: H_2O (9.0 µL, 500 µmol) was added.

For Table 2

According to the procedure for Table 1, the reactions were carried out using specific amount of 5% Os/CR11 and *N*-methyl morphorine *N*-oxide (NMO) in acetone (0.35 mL)–H_2O (0.15 mL).

Entries 7–10: The reaction was carried out in *t*BuOH (0.5 mL) in the presence or absence of H_2O (9.0 µL, 500 µmol, for Entries 9 and 10).

For Table 3, Entries 1–10

A mixture of alkene (250 µmol), 5% Os/CR11 (9.5 mg, 2.50 µmol, 1 mol%), NMO (32.2 mg, 275 µmol), and acetone–H_2O (7 : 3, 0.5 mL) in a 15 mL-test tube was stirred under an Ar atmosphere at room temperature. After the specific time [the consumption of the starting material was confirmed by TLC analysis (hexane–EtOAc)], the mixture was filtered through a Celite pad, and the pad was washed with acetone (30 mL) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane–EtOAc) to give the corresponding diol.

For Table 3, Entries 11–14

A mixture of alkene (250 µmol), 5% Os/CR11 (47.6 mg, 12.5 µmol, 5 mol%), NMO (43.9 mg, 375 μmol), H_2O (9.0 μL, 500 μmol), and *t*BuOH (0.5 mL) in a 15 mL-test tube was stirred under an Ar atmosphere at room temperature. After 24 h, the mixture was filtered through a Celite pad, and the pad was washed with MeOH (HPLC grade, 30 mL) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane–EtOAc) to give the corresponding diol.

1-Phenyl-1,2-ethanediol [CAS Reg. No. 93-56-1] (Table 3, Entries 1 and 11)[1]

^{1}H NMR δ = 7.25–7.35 (m, 5H), 4.76 (dd, J = 8.2, 3.2 Hz 1H), 6.91 (d, J = 8.0, 2H), 3.70 (dd, J = 11.4, 3.2 Hz, 1H), 3.61 (dd, J = 11.4, 8.2 Hz, 1H), 3.43 (br s, 1H), 3.07 (brs, 1H); ^{13}C NMR ($CDCl_3$): δ = 140.4, 128.5, 127.9, 126.3, 74.7, 68.0.

4-Phenyl-1,2-butanediol [CAS Reg. No. 1199-97-9] (Table 3, Entry 2)[1]

^{1}H NMR δ = 7.27 (m, 2H), 7.16–7.20 (m, 3H), 3.71 (m, 1H), 3.63 (dd, J = 11.0, 3.0 Hz, 1H), 3.45 (dd, J = 11.0, 7.8 Hz, 1H), 2.63–2.83 (m, 2H), 2.45–2.83 (br s, 2H), 1.71–1.78 (m, 2H); ^{13}C NMR: δ = 141.7, 128.4, 125.9, 71.5, 66.7, 34.6, 31.8.

1,2-Hexanediol [CAS Reg. No. 6920-22-5] (Table 3, Entry 3)[2]

^{1}H NMR: δ = 3.93 (br s, 2H), 3.70 (m, 1H), 3.64 (dd, J = 3.0, 11.0 Hz, 1H), 3.42 (dd, J = 7.8, 11.0 Hz, 1H), 1.32–1.43 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ = 72.3, 66.8, 32.8, 27.7, 22.7, 14.0.

1-Cyclohexyl-1,2-ethanediol [CAS Reg. No. 59411-58-4] (Table 3, Entries 4 and 12)[3]

^{1}H NMR: δ = 3.70 (dd, J = 10.8, 2.8 Hz, 1H), 3.52 (dd, J = 11.0, 8.2 Hz, 1H), 3.44 (m, 1H), 2.56 (br s, 2H), 1.87 (dd, J = 12.4, 1.2 Hz, 1H), 1.63–1.78 (m, 4H), 1.41 (m, 1H), 0.99–1.30 (m, 5H); ^{13}C NMR: δ = 76.5, 64.8, 40.7, 28.9, 28.6, 26.4, 26.0, 26.0.

3-Phenoxy-1,2-propanediol [CAS Reg. No. 538-43-2] (Table 3, Entries 5 and 13)[4]

^{1}H NMR: δ = 7.29 (m, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 4.11 (m, 1H), 4.02–4.04 (m, 2H), 3.83 (dd, J = 11.6, 3.6 Hz, 1H), 3.74 (dd, J = 5.4, 11.4 Hz, 1H), 2.77 (br s, 1H), 2.23 (br s, 1H); ^{13}C NMR: δ = 158.4, 129.6, 121.3, 114.5, 70.4, 69.1, 63.7.

***erythro*-1-Phenyl-1,2-propanediol [CAS Reg. No.1075-04-3] (Table 3, Entry 6)**[5]

^{1}H NMR: δ = 7.27–7.36 (m, 5H), 4.67 (d, J = 3.6 Hz, 1H), 4.01 (m, 1H), 2.53 (br s, 1H), 2.01 (br s, 1H), 1.07–1.10 (m, 3H); ^{13}C NMR: δ = 140.3, 128.4, 127.8, 126.6, 77.5, 71.3, 17.3.

(*R,*S**)-α,β-Dihydroxybenzenepropanoic acid ethyl ester [CAS Reg. No. 56503-12-9] (Table 3, Entry 7)**[6]

^{1}H NMR: δ = 7.28–7.41 (m, 5H), 4.98 (d, J = 3.2 Hz, 1H), 4.33 (d, J = 3.2 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 172.7, 139.9, 128.3, 128.0, 126.2, 74.8, 74.5, 62.1, 14.0.

cis-1,2-Cyclohexanediol [CAS Reg. No. 1792-81-0] (Entry 8)[2]

^{1}H NMR: δ = 3.77 (m, 2H), 2.14 (br s, 2H), 1.72–1.79 (m, 2H), 1.75 (m, 4H), 1.27–1.34 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 70.6, 29.9, 21.4.

1-Phenyl-_cis_-1,2-cyclohexanediol [CAS Reg. No. 4912-59-8] (Table 3, Entries 9 and 14)[1]

^{1}H NMR: δ = 7.48 (m, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.24 (m, 1H), 3.94 (m, 1H), 2.62 (s, 1H), 1.81–1.88 (m, 3H), 1.51 (m, 1H), 1.38 (m, 1H); ^{13}C NMR: δ = 146.4, 128.4, 126.9, 125.1, 75.7, 74.5, 38.5, 29.2, 24.3, 21.0.

2-Methyl-2,3-heptanediol [CAS Reg. No. 1068-81-1] (Table 3, Entry 10)[2]

^{1}H NMR: δ = 3.37 (dd, J = 10.0, 2.0 Hz, 1H), 2.52–3.35 (br s, 2H), 1.26–1.59 (m, 6H), 1.20 (s, 3H), 1.15 (s, 3H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR: δ = 78.6, 73.2, 31.3, 28.9, 26.5, 23.0, 22.7, 14.0.

Test of volatility of catalyst (Scheme 1)

Two NMR tube were cut to the length of approximately 11 cm. 5% Os/CR11 (9.5 mg, 2.50 μmol) was added to one of the tubes, and 4% aqueous OsO_4 (15.2 μL, 2.50 μmol) to the other tube. A piece of cotton (ca. 14 mg) was placed ca. 6 cm above the bottom of each tube. Both tubes were closed with the cap, sealed with teflon tape, and left for two weeks. The cotton in the tube for 4% OsO_4 turned black, but no change in color of the cotton in the other tube for 5% Os/CR11 was observed even at least 6 months later.

Reuse of 5% Os/CR11 (Table 4)

Conditions A

For 1st run: Six test tubes were prepared, and allyl phenyl ether (33.5 mg, 0.250 mmol), 5% Os/CR11 (9.5 mg, 2.50 μmol, 1 mol%), NMO (33.2 mg, 0.275 mmol), acetone (0.35 mL), and H_2O (0.15 mL) were placed in each test tube. The mixture in each test tube was stirred under Ar atmosphere at room temperature for 4 h, and all mixtures were then filtered using a Kiriyama funnel (1 μm filter paper). The catalyst on the filter paper was washed with acetone (20 mL for each test tube), and the filtrate was concentrated *in vacuo*. The yield was determined by ^{1}H NMR of the residue using 4-nitrotoluene (34.3 mg, 250 μmol) as the internal standard. The recovered catalyst was dried at room temperature under reduced pressure for 12 h, and then weighed [48.2 mg, 85%, 48.2 ÷ (9.5 × 6) × 100].

For 2nd run: The reaction was carried out in the same way as the 1st run, but using five test tubes (total catalyst amounts, 47.5 mg). 42.1 mg of the catalyst was recovered (89%, 42.1 ÷ 47.5 × 100).

For 3rd run: The reaction was carried out in the same way as the 1st run, but using four test tubes (total catalyst amounts, 38.0 mg). 37.9 mg of the catalyst was recovered (100%, 37.9 ÷ 38.0 × 100).

Run	Quantity			Yield of diol[a]
	Alkene	Used catalyst	Recovered catalyst	
1st	33.5 mg (250 μmol) × 6 = 201 mg (1.50 mmol)	9.5 mg (2.50 μmol) × 6 = 57.0 mg (15.0 μmol)	48.2 mg (85%)	100%
2nd	33.5 mg (250 μmol) × 5 = 168 mg (1.25 mmol)	9.5 mg (2.50 μmol) × 5 = 47.5 mg (12.5 μmol)	42.1 mg (89%)	87%
3rd	33.5 mg (250 μmol) × 4 = 134 mg (1.00 mmol)	9.5 mg (2.50 μmol) × 4 = 38.0 mg (10.0 μmol)	37.9 mg (100%)	36%

[a] Determined by ^{1}H NMR using 4-nitrotoluene as an internal standard.

Conditions B

For 1st run: Six test tubes were prepared, and allyl phenyl ether (33.5 mg, 0.250 mmol), 5% Os/CR11 (47.6 mg, 12.5 μmol, 5 mol%), NMO (43.9 mg, 0.375 mmol), H_2O (9.0 μL, 500 μmol), and *t*BuOH (0.5 mL) were placed in each test tube. The mixture in each test tube was stirred under Ar atmosphere at room temperature for 24 h, and all mixtures were then filtered using a Kiriyama funnel (1 μm filter paper). The catalyst on the filter paper was washed with MeOH (HPLC grade, 20 mL for each test tube), and the filtrate was concentrated *in vacuo*. The yield was determined by ^{1}H NMR of the residue using 4-nitrotoluene (34.3 mg, 250 μmol) as the internal standard. The catalyst was dried at room temperature under reduced pressure for 12 h, and then weighed [277 mg, 97%, 277 ÷ (47.6 × 6) × 100].

For 2nd run: The reaction was carried out in the same way as the 1st run, but using five test tubes (total catalyst amounts, 238 mg). 205 mg of the catalyst was recovered (86%, 205 ÷ 238 × 100).

For 3rd run: The reaction was carried out in the same way as the 1st run, but using four test tubes. (total catalyst amounts, 190 mg) 183 mg of the catalyst was recovered (96%, 183 ÷ 190 × 100).

Run	Quantity			Yield of diol[a]
	Alkene	Used catalyst	Recovered catalyst	
1st	33.5 mg (250 μmol) × 6 = 201 mg (1.50 mmol)	47.6 mg (12.5 μmol) × 6 = 286 mg (75.0 μmol)	277 mg (97%)	86%
2nd	33.5 mg (250 μmol) × 5 = 168 mg (1.25 mmol)	47.6 mg (12.5 μmol) × 5 = 238 mg (62.5 μmol)	205 mg (86%)	79%

3rd	33.5 mg (250 μmol) × 4 = 134 mg (1.00 mmol)	47.6 mg (12.5 μmol) × 4 = 190 mg (50.0 μmol)	183 mg (96%)	41%

[a] Determined by ^{1}H NMR using 4-nitrotoluene as an internal standard.

Assay of residual osmium in the reaction media

1) 70% aqueous acetone

A mixture of allyl phenyl ether (1.00 mL, 7.30 mmol), 5% Os/CR11 (277 mg, 73.0 μmol), NMO (941 mg, 8.03 mmol), acetone (10.5 mL) and H_2O (4.5 mL) in a 30-mL round bottom flask was stirred under an Ar atmosphere at room temperature. After 4 h, the mixture was filtered through a Celite pad, and the pad was washed with acetone (20 mL). The filtrate was passed through a membrane filter (0.20 μm, Milipore Corporation) and transferred to a 100-mL volumetric flask, and acetone was added up to 100 mL of total volume, and the residual palladium was assayed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using SPS-3100 machine (Hitachi High-Tech Science Corporation). The osmium concentration was determined 99 mg/L (71% of the used catalyst).

2) *t*BuOH–H_2O (2 equiv)

A mixture of allyl phenyl ether (1.00 mL, 7.30 mmol), 5% Os/CR11 (139 mg, 365 μmol), NMO (1.82 g, 11.0 mmol), H_2O (263 μL, 14.6 mmol), and *t*BuOH (15 mL) in a 100-mL round bottom flask was stirred under an Ar atmosphere at room temperature. After 24 h, the mixture was filtered through a Celite pad, and the pad was washed with MeOH (HPLC grade, 20 mL). The filtrate was passed through a membrane filter (0.20 μm, Milipore Corporation) and transferred to a volumetric flask, and MeOH (HPLC grade) was added up to 100 mL of total volume, and the residual palladium was assayed by ICP-AES using SPS-3100 machine (Hitachi High-Tech Science Corporation). The osmium concentration was determined 6.3 mg/L (0.91% of the used catalyst).

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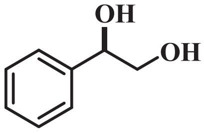
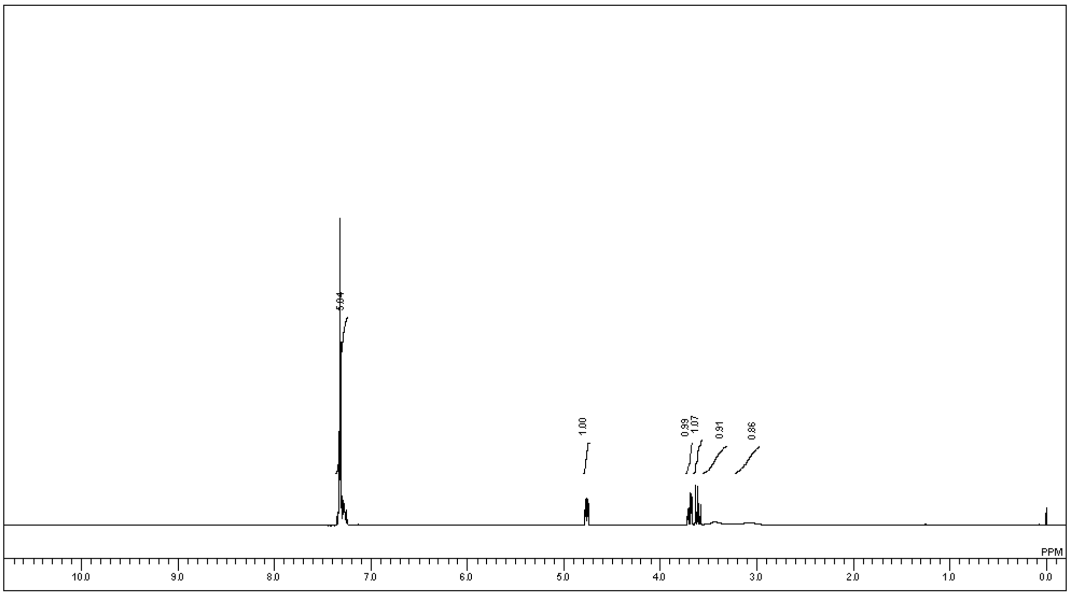
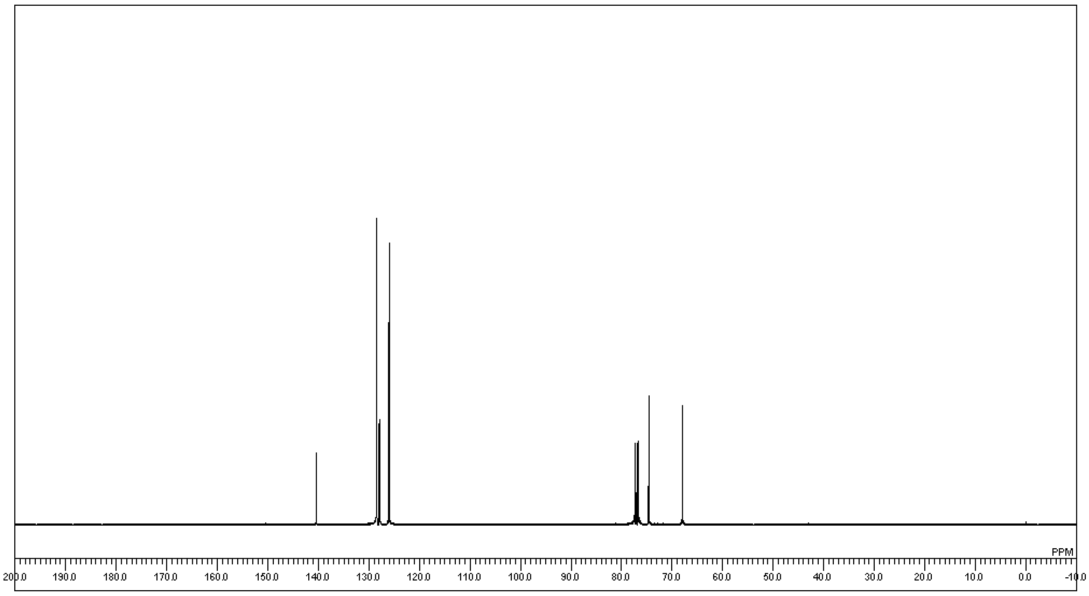
1-Phenyl-1,2-ethanediol (Table 3, Entries 1 and 11)







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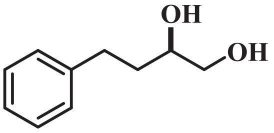
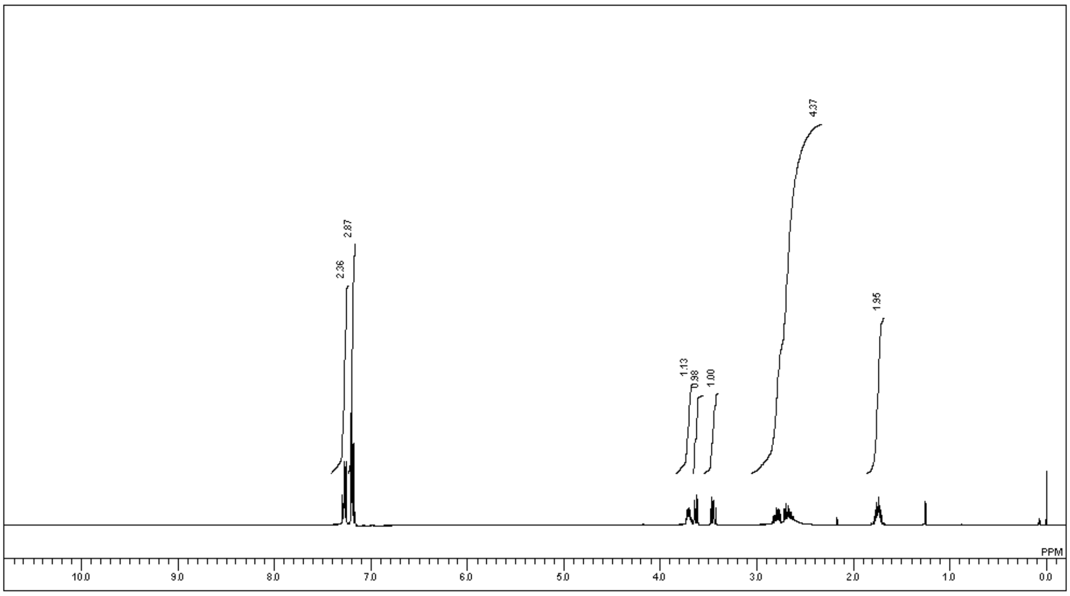
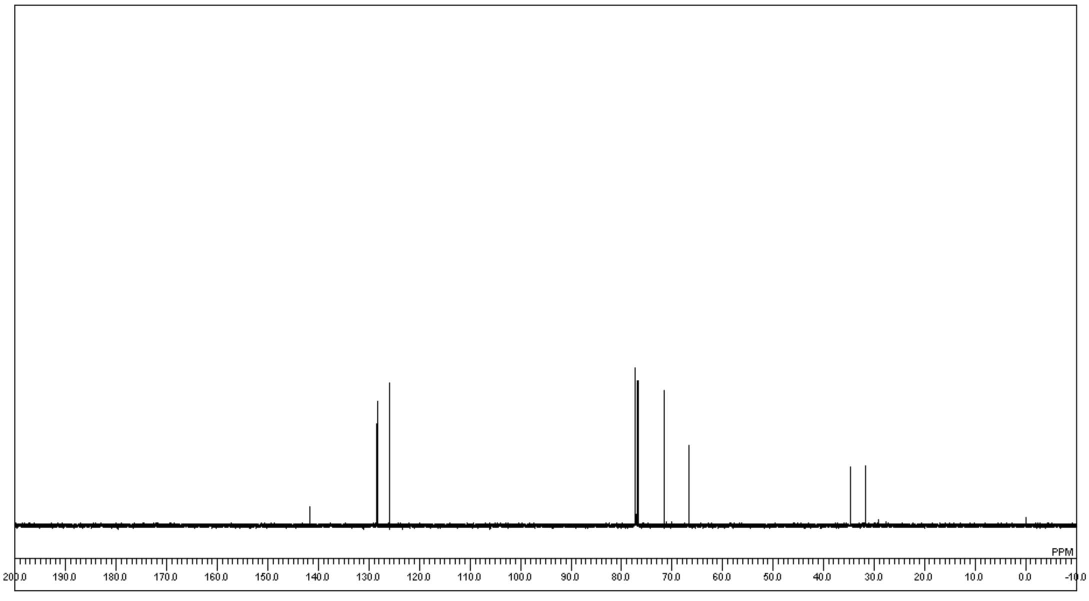
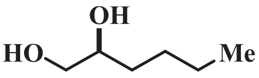
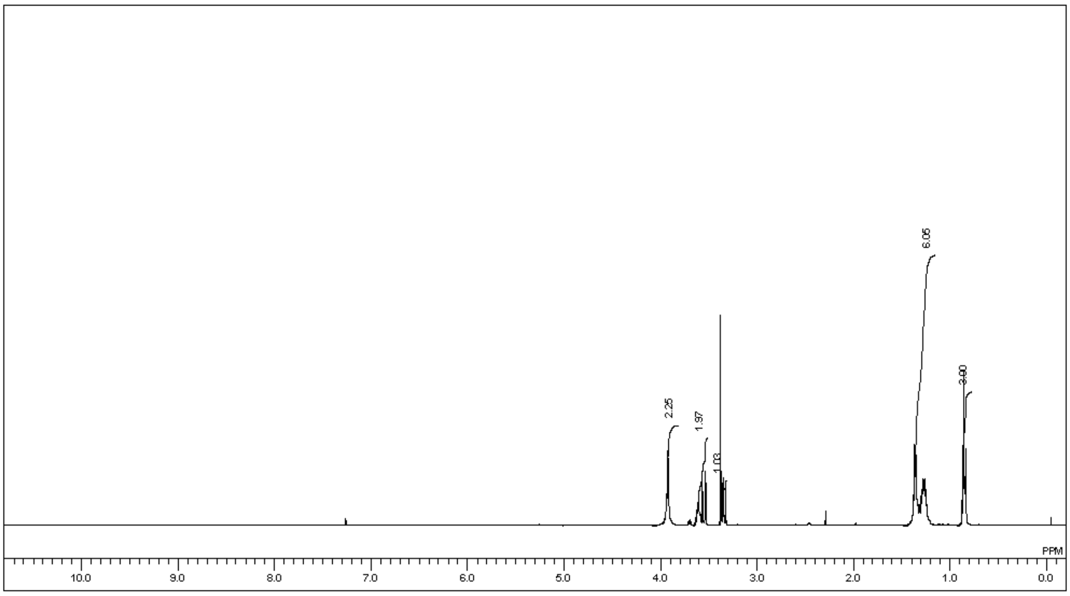


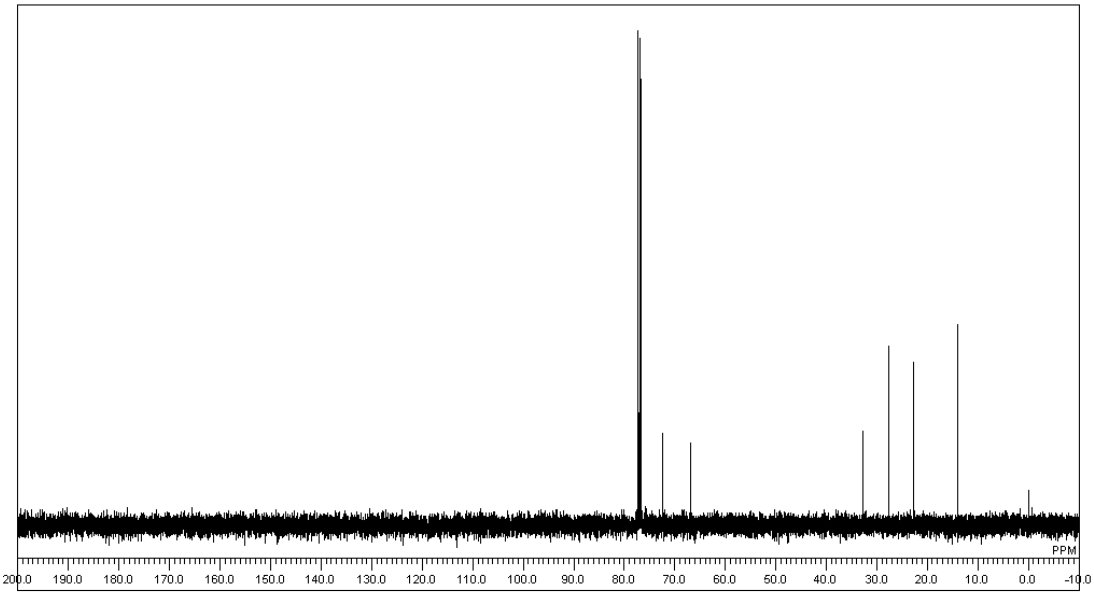




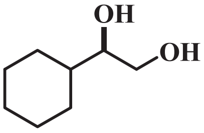
1,2-Hexanediol (Table 3, Entry 3)

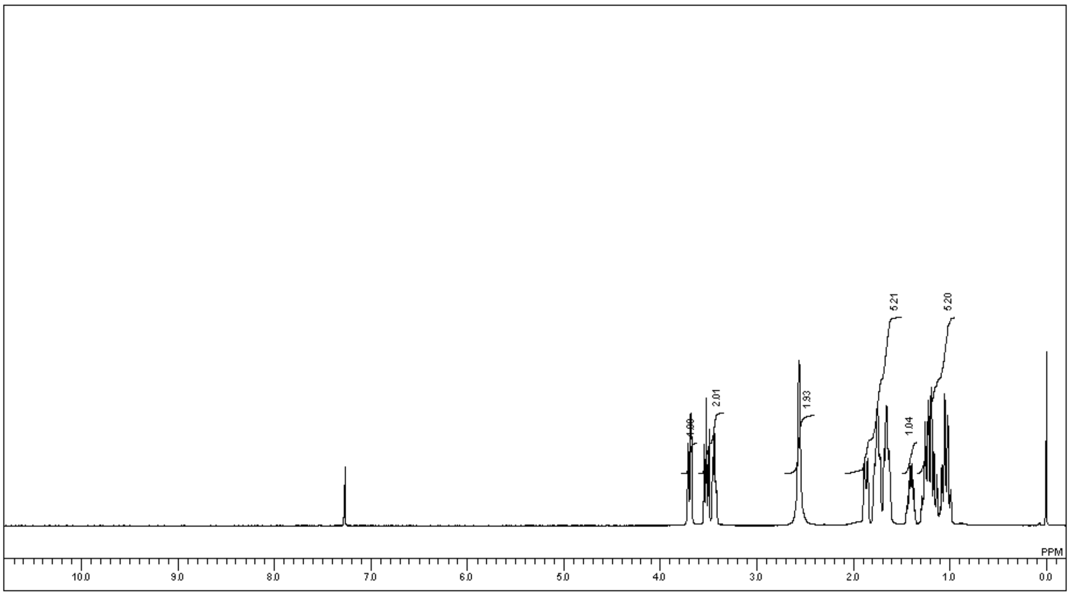


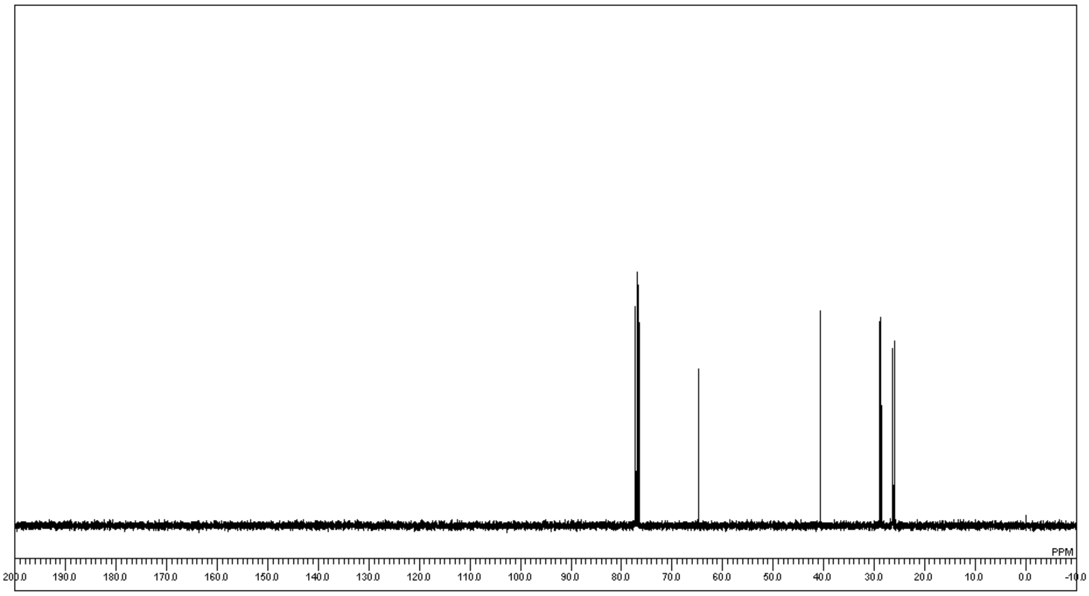




1-Cyclohexyl-1,2-ethanediol (Table 3, Entries 4 and 12)







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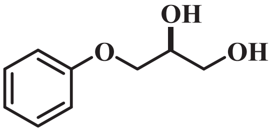
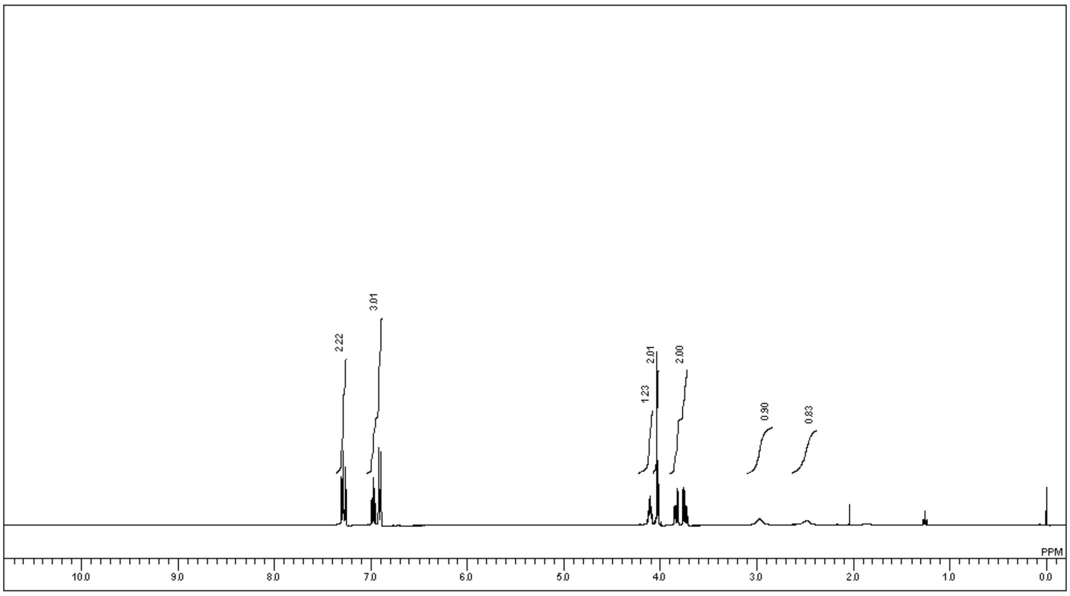
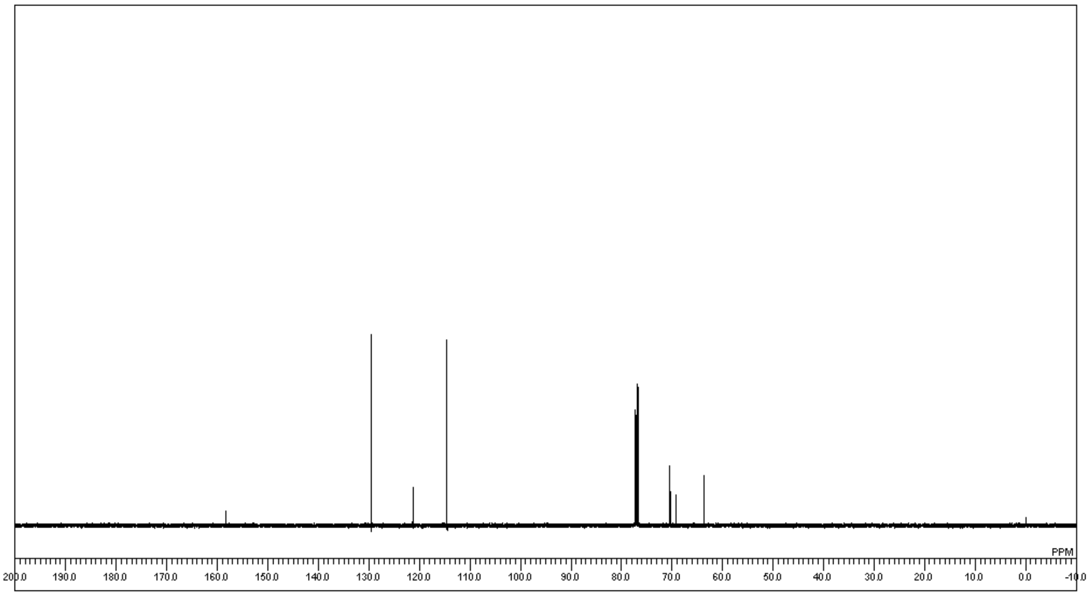
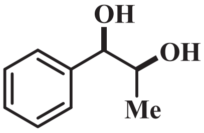
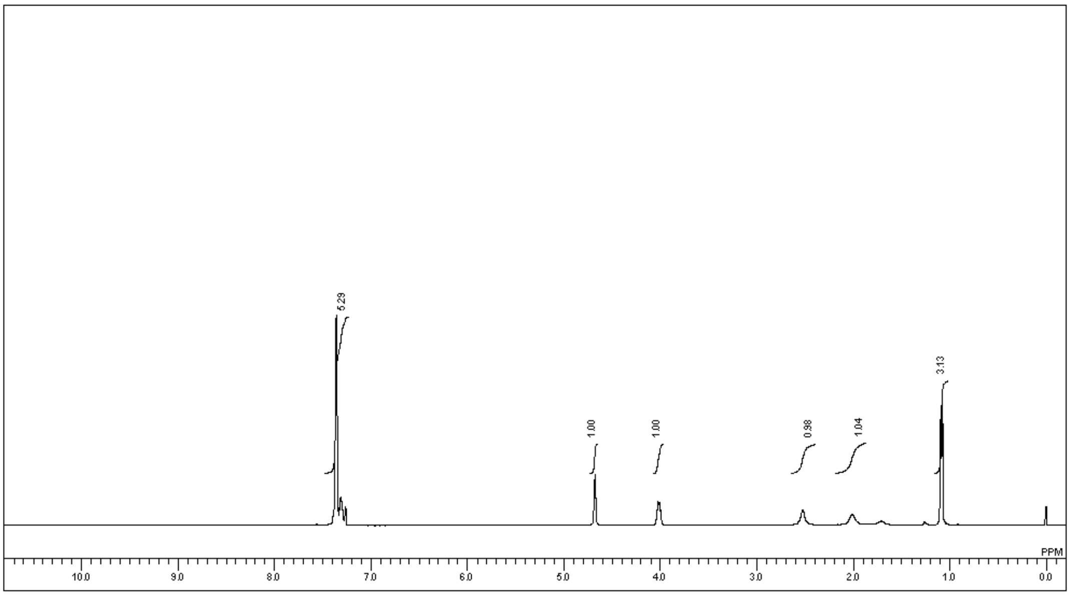


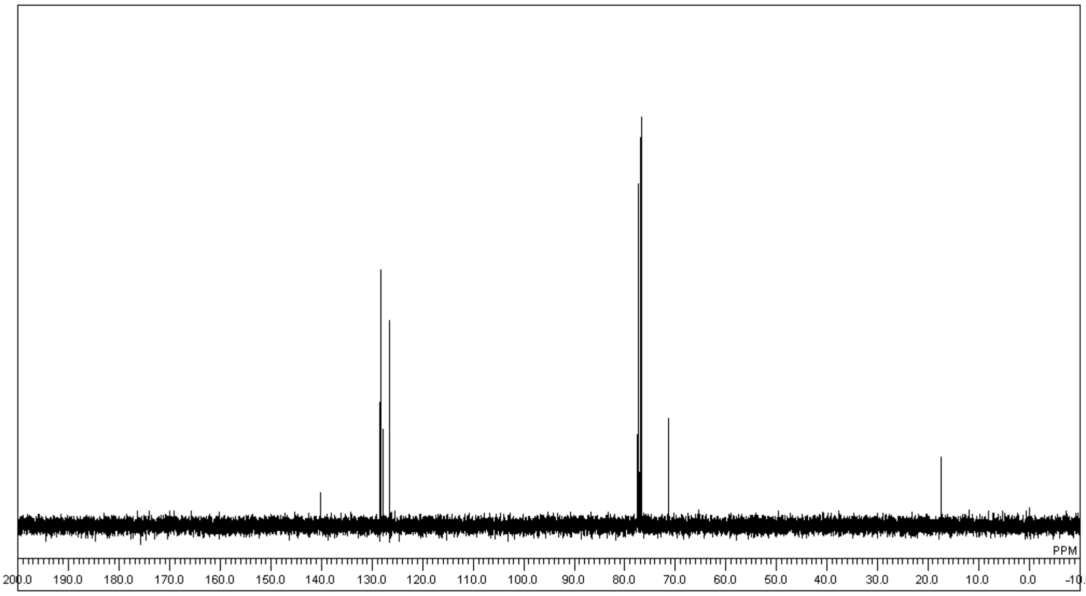




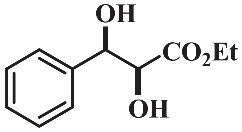
erythro-1-Phenyl-1,2-propanediol (Table 3, Entry 6)

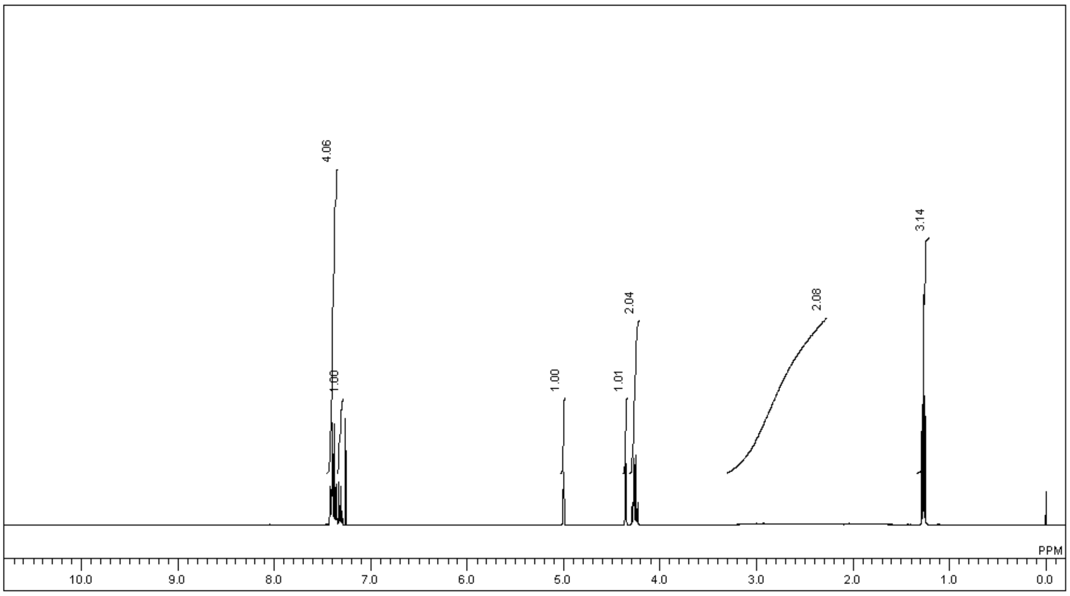


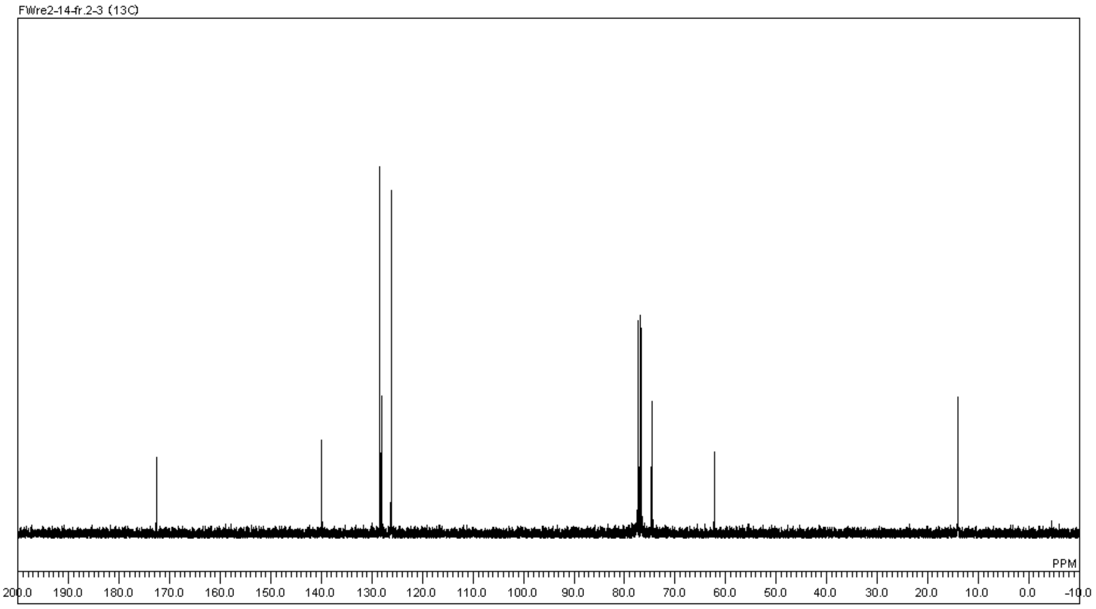




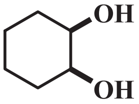
(*R,*S**)-α,β-Dihydroxybenzenepropanoic acid ethyl ester (Table 3, Entry 7)**

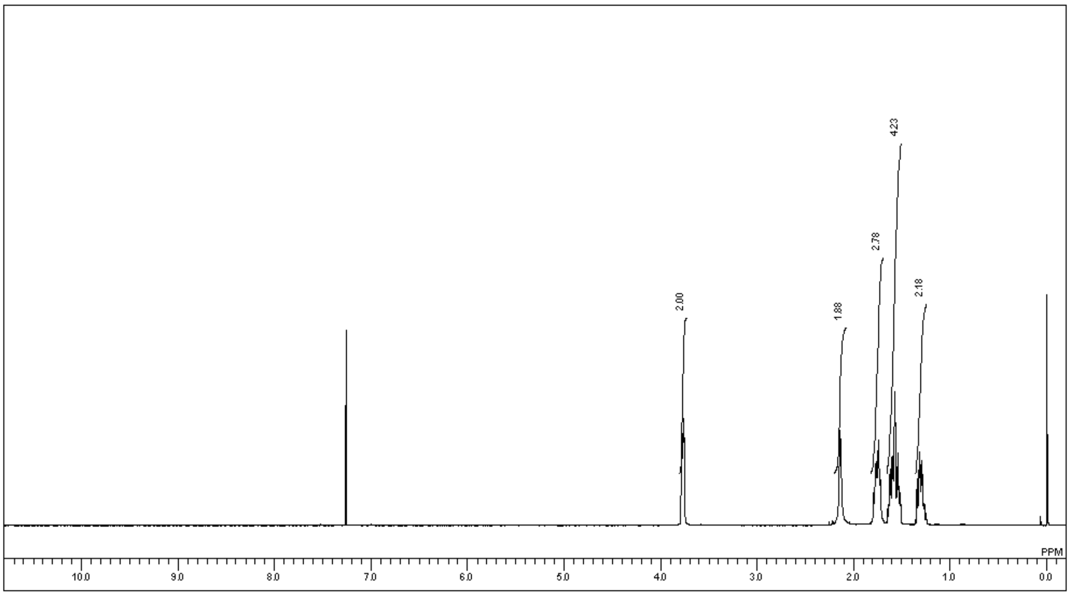


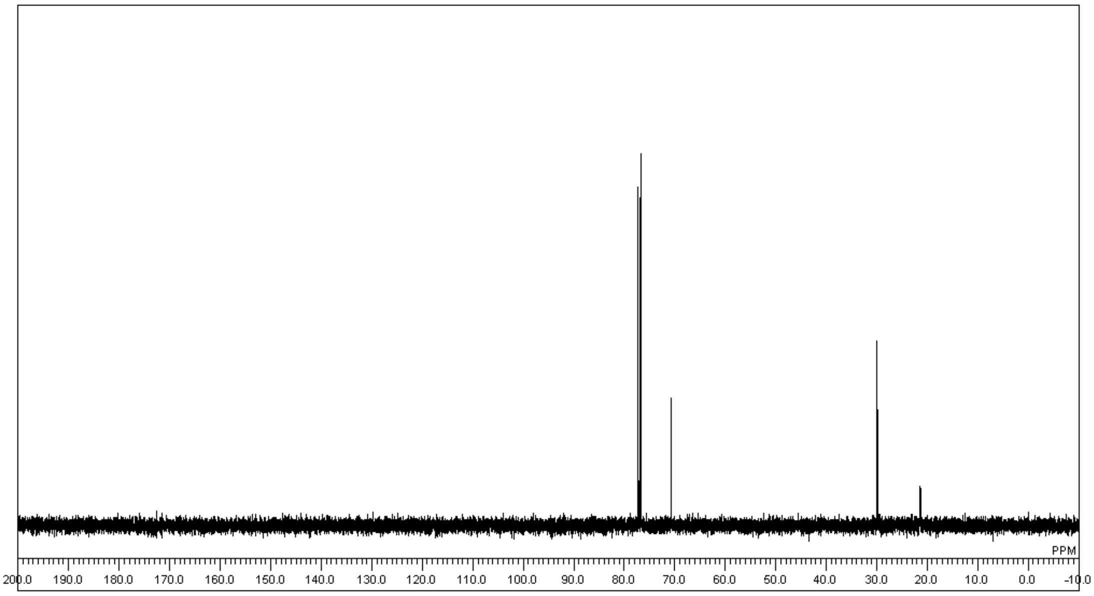




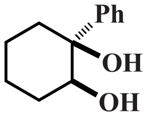
cis-1,2-Cyclohexanediol (Table 3, Entry 8)

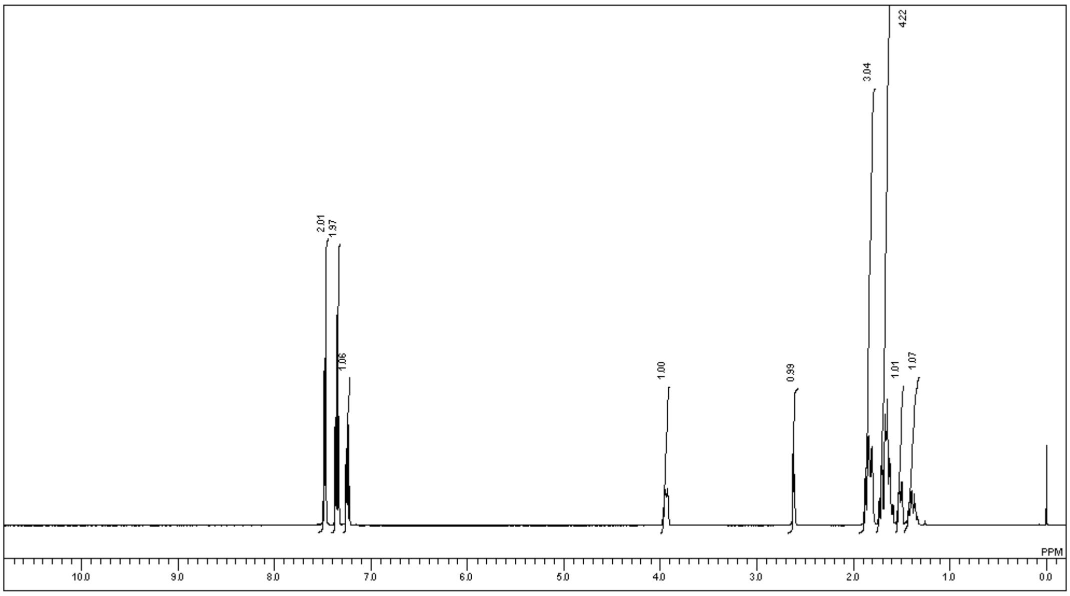


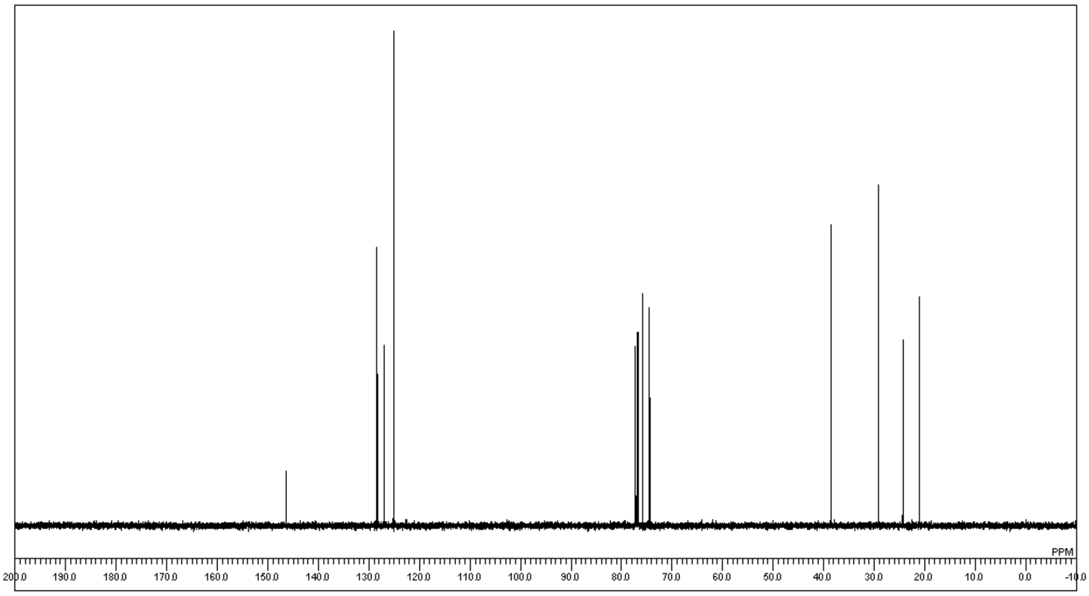




1-Phenyl-*cis*-1,2-cyclohexanediol (Table 3, Entries 9 and 14)







2-Methyl-2,3-heptanediol (Table 3, Entry 10)