Supplementary Information

Carbocation-Guided Regioselective Deoxygenation of Unsymmetrical Diols via $B(C_6F_5)_3$ Catalysis with Silane Economy

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1. General Experimental Details

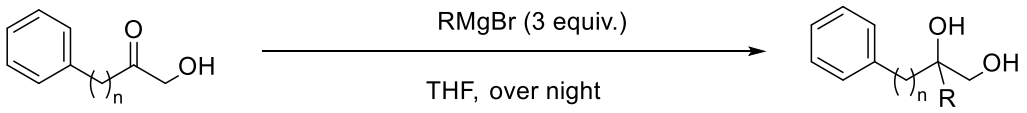
General Experimental Procedures: Inside an argon-filled glovebox, diols (0.1 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (2.56 mg, 5 mol %) were dissolved in CH_2Cl_2 (0.5 ml) in a 4-ml screw-cap vial equipped with a magnetic stir bar. The silane was added dropwise to the solution, the vial was then closed and the reaction mixture was stirred for 8 hours before it was quenched with TBAF solution (150 µl, 0.15 mmol, 1.5 equiv.). The yield of the corresponding products and remaining starting materials was determined by ^{1}H-NMR analysis of the crude-reaction mixture using CH_2Br_2 as the analytical standard. Flash column chromatography was performed using a Teledyne ISCO CombiFlash NextGen 300+ automated flash chromatography system equipped with RediSep Bronze normal-phase silica cartridges (4 g, 40–60 µm, 230–400 mesh, 55–60 Å pore size), using hexane/ethyl acetate (95:5 v/v) as the eluent.

Materials: Unless otherwise noted, all reagents and starting materials were purchased from commercial suppliers (e.g., Sigma-Aldrich , TCI, Alfa Aesar) and used as received without further purification. $B(C_6F_5)_3$ and silane reagents (Ph_2SiH_2, $PhSiH_3$, Ph_2SiD_2) were obtained from commercial sources and used as received. Most diol substrates were prepared according to reported procedures (see the section 2 of the Supplementary Infromation), while some were purchased from commercial suppliers. All solvents, including anhydrous dichloromethane (CH_2Cl_2), were used as received from Sigma-Aldrich without further purification. Solvents for extraction and chromatography were ACS reagent grade. Reaction yields were determined by crude ^{1}H NMR analysis using dibromomethane (CH_2Br_2) as an internal standard, unless otherwise noted.

Instrumentation: NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer. ^{1}H chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks ($CDCl_3$: δ 7.26; CD_2Cl_2: δ 5.32; CD_3OD: δ 3.31). ^{13}C spectra were proton-decoupled and referenced to the solvent resonances ($CDCl_3$: δ 77.16; CD_2Cl_2: δ 53.84; CD_3OD: δ 49). All spectra were processed using MestReNova 15.0.1 (Mestrelab Research). High-resolution mass spectra (HRMS) were acquired on a Supercritical Fluid Chromatograph combined with a Xevo G2-XS QTOF Mass Spectrometer (Waters, Milford, MA, USA, NFEC-2022-12-283850) at the Chiral Material Core Facility Center of Sungkyunkwan University using an electrospray ionization (ESI) source. For selected compounds (2a, 2b, 2h, 3c, 3d, and 3i), gas chromatography–high-resolution mass spectrometry (GC–HRMS) analyses were performed at the National Center for Inter-University Research Facilities (NCIRF), Seoul National University, using a double-focusing mass spectrometer in electron ionization (EI) mode. Infrared Spectroscopy (IR) were recorded on a Bruker LUMOS FT-IR spectrometer equipped with a microscope and mercury cadmium telluride (MCT) detector.

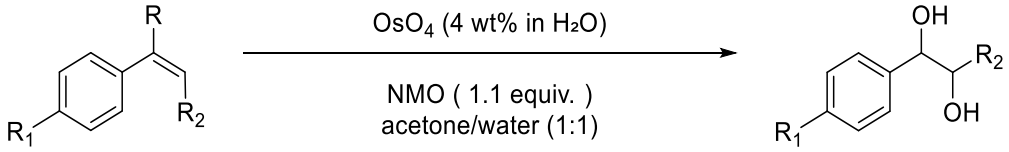
2. Procedures for the Preparation of Starting Materials

General Experimental Procedures A:



diols were prepared according to the literature procedure.[1] An α-hydroxy ketone (5.0 mmol) was dissolved in THF (5.0 mL) under a nitrogen atmosphere and cooled to 0 °C. A Grignard reagent (15 mmol, 1.0 M solution in THF; R = aryl or alkyl) was added dropwise, and the reaction mixture was allowed to warm to room temperature and stirred until complete consumption of the starting material as monitored by TLC. The reaction was quenched with saturated aqueous NH_4Cl, and the resulting mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (n-hexane/EtOAc = 3:1) to afford the corresponding 1,2-diol.

General Experimental Procedures B:

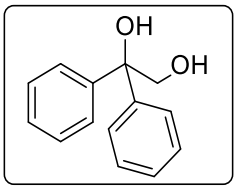


R = R_3 or H

The corresponding diols were obtained according to the published method.[2] An alkene (5.0 mmol) was dissolved in acetone/H_2O (1:1, 50 mL), and N-methylmorpholine N-oxide (1.1 equiv.) was added. The solution was cooled to 0 °C, and OsO_4 (5 mol%, 4% aqueous solution) was added. The reaction mixture was then allowed to warm to room temperature and stirred overnight until complete consumption of the starting material as monitored by TLC. The reaction was quenched by the addition of saturated aqueous $NaHSO_3$ (3 mL) and stirred for an additional 20 min. The mixture was extracted with EtOAc (3 × 30 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (EtOAc/hexane = 40:60) to afford the corresponding diol

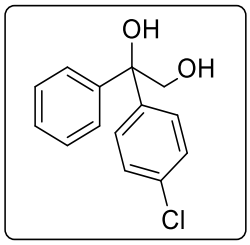
2.1. Starting materials

1,1-diphenylethane-1,2-diol (1a)



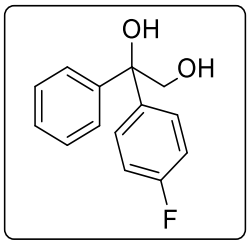
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 4H), 7.35 (tt, *J* = 6.8, 0.8 Hz, 4H), 7.30 – 7.26 (m, 2H), 4.18 (d, *J* = 6.5 Hz, 2H), 3.15 (s, 1H), 1.82 (t, *J* = 6.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.93, 128.59, 127.63, 126.53, 78.70, 69.58. **IR** (CH_2Cl_2, cm^{-1}) 3370, 3057, 3021, 2982, 1442, 1359, 1264, 1103, 1043, 880, 731, 700, 654. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{13}O_2^-$, 213.0921; Found, 213.0915.

1-(4-chlorophenyl)-1-phenylethane-1,2-diol (1b)



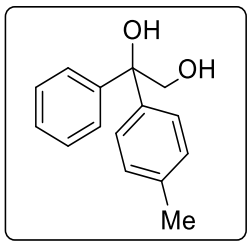
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46 – 7.26 (m, 9H), 4.22 – 4.07 (m, 2H), 3.16 (s, 1H), 1.83 (t, J=6.3, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.52, 142.54, 133.51, 128.71, 128.65, 128.06, 127.84, 126.44, 78.34, 69.35. **IR** (CH_2Cl_2, cm^{-1}) 3402, 3061, 3029, 2943, 2883, 1490, 1450, 1400, 1265, 1180, 1092, 942, 825, 759, 701 **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{12}ClO_2^-$, 247.0531; Found, 247.0523.

1-(4-fluorophenyl)-1-phenylethane-1,2-diol (1c)



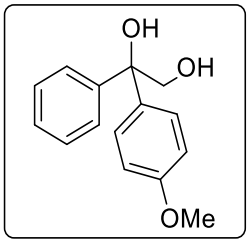
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 – 7.33 (m, 6H), 7.31 – 7.27 (m, 1H), 7.06 – 6.98 (m, 2H), 4.15 (qdd, J=11.4, 6.3, 1.0, 2H), 3.16 (q, J=1.4, 1H), 1.83 (q, J=6.3, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.18 (d, *JCF* = 247.5 Hz), 143.75, 139.80 (d, *JCF* = 3.0 Hz), 128.66, 128.40 (d, *JCF* = 8.1 Hz), 127.76, 126.47, 115.32 (d, *JCF* = 21.2 Hz), 78.35, 69.49. **IR** (CH_2Cl_2, cm^{-1}) 3402, 3064, 3025, 2943, 2883, 1603, 1507, 1227, 1162, 1066, 946, 833, 758, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{12}FO_2^-$, 231.0827; Found, 231.0820.

1-phenyl-1-(p-tolyl)ethane-1,2-diol (1d)



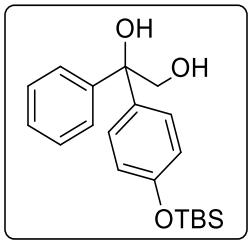
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.48 – 7.40 (m, 2H), 7.38 – 7.30 (m, 4H), 7.28 (t, J=1.4, 1H), 7.25 (s, 1H), 7.20 – 7.11 (m, 2H), 4.16 (dd, J=6.4, 1.4, 2H), 3.10 (s, 1H), 2.33 (s, 3H), 1.81 (t, J=6.5, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.10, 141.00, 137.30, 129.26, 128.52, 127.51, 126.50, 126.46, 78.60, 69.58, 21.15. **IR** (CH_2Cl_2, cm^{-1}) 3397, 3061, 3028, 2929, 2879, 1448, 1266, 1173, 1064, 936, 815, 757, 700, 652. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{15}O_2^-$, 227.1077; Found, 227.1071.

1-(4-methoxyphenyl)-1-phenylethane-1,2-diol (1e)



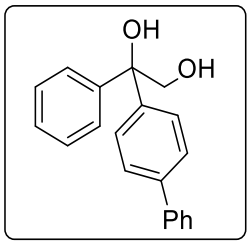
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47 – 7.40 (m, 2H), 7.39 – 7.31 (m, 4H), 7.29 (t, J=1.4, 1H), 6.87 (d, J=8.9, 2H), 4.14 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.97, 144.16, 136.12, 128.51, 127.87, 127.51, 126.52, 113.87, 78.46, 69.62, 55.39. **IR** (CH_2Cl_2, cm^{-1}) 3418, 3007, 2958, 2836, 1609, 1510, 1450, 1257, 1177, 1034, 830, 755, 702 **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{15}O_3^-$, 243.1026; Found, 243.1021.

1-(4-((tert-butyldimethylsilyl)oxy)phenyl)-1-phenylethane-1,2-diol (1f)



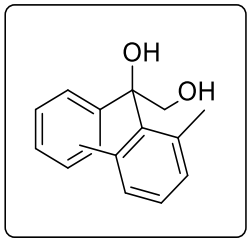
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 – 7.40 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.26 (m, 3H), 6.82 – 6.77 (m, 2H), 4.13 (d, J=1.1, 2H), 0.97 (s, 9H), 0.18 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.17, 144.14, 136.57, 128.52, 127.84, 127.53, 126.58, 120.00, 78.55, 69.74, 25.80, 18.32, -4.26. **IR** (CH_2Cl_2, cm^{-1}) 3403, 3004, 2950, 2854, 1509, 1265, 915, 837, 754. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{20}H_{27}O_3Si^-$, 343.1735; Found, 343.1729.

1-([1,1'-biphenyl]-4-yl)-1-phenylethane-1,2-diol (1g)



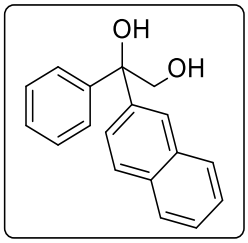
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60 – 7.54 (m, 4H), 7.53 – 7.47 (m, 4H), 7.46 – 7.40 (m, 2H), 7.39 – 7.27 (m, 4H), 4.22 (d, J=6.4, 2H), 3.21 (s, 1H), 1.91 (t, J=6.5, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.89, 142.98, 140.71, 140.42, 128.90, 128.60, 127.64, 127.49, 127.26, 127.20, 127.00, 126.51, 78.61, 69.50. **IR** (CH_2Cl_2, cm^{-1}) 3463, 3057, 3032, 2893, 1689, 1449, 1268, 1068, 834, 754, 697 **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{20}H_{17}O_2^-$, 289.1234; Found, 241.1228.

1-(2,6-dimethylphenyl)-1-phenylethane-1,2-diol (1h)



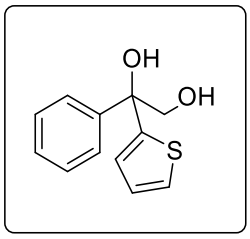
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37 (d, J=1.4, 1H), 7.33 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 7.10 – 6.93 (m, 2H), 4.27 (dd, J=11.4, 4.3, 1H), 3.95 (dd, J=11.4, 5.3, 1H), 3.09 (s, 1H), 2.39 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.95, 140.91, 135.14, 134.86, 132.98, 128.67, 128.28, 127.32, 127.27, 126.31, 79.09, 70.08, 21.43, 20.97. **IR** (CH_2Cl_2, cm^{-1}) 3389, 3246, 3007, 1449, 1264, 1048, 897, 814, 753. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{16}H_{17}O_2^-$, 241.1234; Found, 241.1234.

1-(naphthalen-2-yl)-1-phenylethane-1,2-diol (1i)



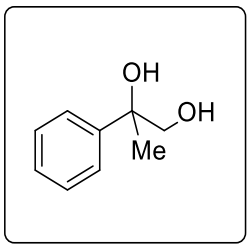
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, J=1.9, 1H), 7.89 – 7.76 (m, 3H), 7.54 – 7.42 (m, 5H), 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 4.29 (qd, J=11.5, 6.4, 2H), 3.26 (s, 1H), 1.88 (t, J=6.5, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.82, 141.26, 133.18, 132.75, 128.62, 128.44, 128.41, 127.71, 127.68, 126.63, 126.41, 126.35, 125.13, 124.91, 78.84, 69.47. **IR** (CH_2Cl_2, cm^{-1}) 3403, 3061, 3011, 1270, 1065, 818, 754, 702 **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{15}O_2^-$, 263.1077; Found, 263.1074.

1-phenyl-1-(thiophen-2-yl)ethane-1,2-diol (1j)



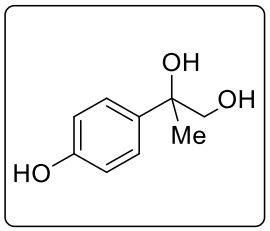
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.56 – 7.48 (m, 2H), 7.41 – 7.27 (m, 4H), 7.06 – 6.87 (m, 2H), 4.22 – 4.04 (m, 2H), 3.39 (d, J=2.2, 1H), 1.92 (t, J=5.9, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 148.82, 142.93, 128.57, 127.99, 126.92, 126.08, 125.77, 124.99, 77.66, 70.74. **IR** (CH_2Cl_2, cm^{-1}) 3417, 3007, 1270, 754, 709. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_{11}O_2S^-$, 219.0485; Found, 219.0475.

2-phenylpropane-1,2-diol (1k)



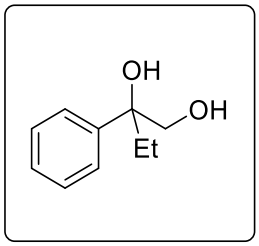
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.43 (m, 2H), 7.38 (dd, J=8.6, 6.8, 2H), 7.29 (d, J=7.2, 1H), 3.81 (dd, J=11.1, 4.6, 1H), 3.65 (dd, J=11.1, 8.2, 1H), 2.53 (s, 1H), 1.72 (dd, J=8.2, 4.7, 1H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.09, 128.56, 127.32, 125.21, 74.98, 71.21, 26.15. **IR** (CH_2Cl_2, cm^{-1}) 3365, 3061, 2986, 2940, 2879, 1447, 1375, 1269, 1038, 954, 864, 759, 698, 638. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{11}O_2^-$, 151.0764; Found, 151.0767.

2-(4-hydroxyphenyl)propane-1,2-diol (1l)



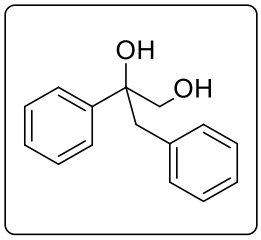
Prepared according to **General Procedure B.** **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.24 – 7.14 (m, 2H), 6.87 – 6.70 (m, 2H), 3.57 (dd, J=11.1, 3.9, 1H), 3.41 (dd, J=11.1, 7.8, 1H), 3.07 (d, J=1.6, 3H), 1.76 (s, 1H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 156.81, 133.25, 128.20, 115.48, 79.63, 71.62, 50.37, 19.53. **IR** (CH_2Cl_2, cm^{-1}) 3253, 2983, 2943, 2829, 1513, 1450, 1268, 1233, 1173, 1025, 1002, 831, 755. **HRMS** (ESI) m/z: $[M-H]^-$Calcd for $C_9H_{11}O_3^-$, 167.0713; Found, 167.0706.

2-phenylbutane-1,2-diol (1m)



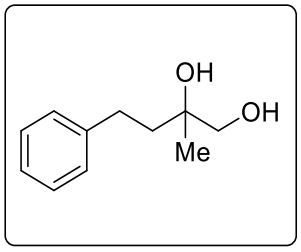
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.34 (m, 4H), 7.30 – 7.26 (m, 1H), 3.86 (d, J=11.1, 1H), 3.70 (d, J=11.1, 1H), 2.56 (s, 1H), 1.85 (p, J=7.4, 2H), 1.60 (s, 1H), 0.78 (t, J=7.5, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.31, 128.51, 127.15, 125.75, 77.62, 70.54, 31.26, 7.53. **IR** (CH_2Cl_2, cm^{-1}) 3386, 2972, 2943, 2883, 1451, 1269, 1052, 756, 701. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{13}O_2^-$, 165.0921; Found, 165.0913.

2,3-diphenylpropane-1,2-diol (1n)



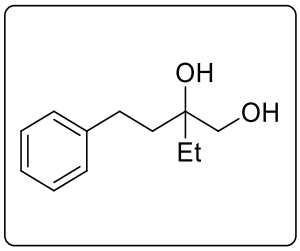
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 7.24 – 7.12 (m, 3H), 7.00 – 6.89 (m, 2H), 3.90 – 3.74 (m, 2H), 3.23 – 3.09 (m, 2H), 2.46 (s, 1H), 1.78 (s, 1H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 143.96, 136.58, 130.96, 128.53, 128.33, 127.41, 126.92, 126.08, 77.42, 69.91, 45.21. **IR** (CH_2Cl_2, cm^{-1}) 3403, 3029, 2943, 2883, 1450, 1269, 1066, 755, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{15}O_2^-$, 227.1077; Found, 227.1070.

2-methyl-4-phenylbutane-1,2-diol (1o)



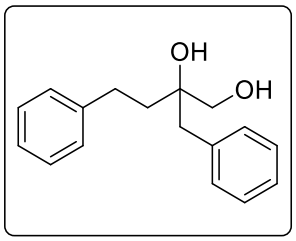
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 (dd, J=8.1, 6.9, 2H), 7.25 – 7.11 (m, 3H), 3.65 – 3.33 (m, 2H), 2.71 (ddd, J=9.6, 6.7, 2.2, 2H), 1.90 – 1.76 (m, 2H), 1.67 (s, 2H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.36, 128.61, 128.44, 126.03, 72.93, 70.00, 40.62, 30.23, 23.48. **IR** (CH_2Cl_2, cm^{-1}) 3371, 3028, 2979, 2940, 2872, 1456, 1271, 1051, 919, 753, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{11}H_{15}O_2^-$, 179.1077; Found, 179.1069.

2-ethyl-4-phenylbutane-1,2-diol (1p)



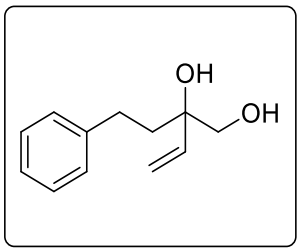
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.31 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 3.53 (s, 2H), 2.72 – 2.58 (m, 2H), 1.79 (ddt, J=11.7, 6.2, 3.0, 2H), 1.62 (dddd, J=11.8, 9.1, 6.0, 2.8, 2H), 0.94 (td, J=7.6, 2.4, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.42, 128.54, 128.38, 125.95, 75.07, 67.63, 37.21, 29.84, 28.32, 8.02. **IR** (CH_2Cl_2, cm^{-1}) 3372, 3025, 2940, 2879, 1455, 1400, 1270, 1053, 897, 753, 698. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_{17}O_2^-$, 193.1234; Found, 193.1225.

2-benzyl-4-phenylbutane-1,2-diol (1q)



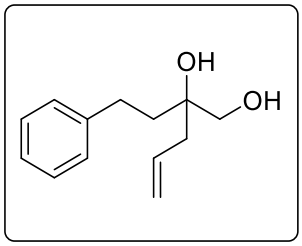
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 5H), 7.19 (d, J=7.2, 3H), 3.54 (d, J=1.4, 2H), 2.91 (s, 2H), 2.77 (dd, J=10.8, 6.5, 2H), 1.79 (dddd, J=8.4, 7.0, 4.5, 1.4, 2H), 1.63 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.27, 136.84, 130.50, 128.67, 128.61, 128.45, 126.92, 126.05, 74.61, 67.35, 42.72, 38.41, 29.99. **IR** (CH_2Cl_2, cm^{-1}) 3344, 3027, 2941, 2868, 1495, 1453, 1272, 1035, 913, 751, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{19}O_2^-$, 255.1390; Found, 255.1383.

2-phenethylbut-3-ene-1,2-diol (1r)



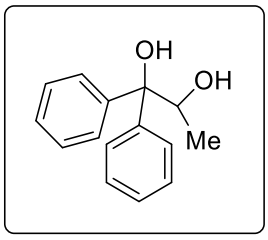
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.31 – 7.26 (m, 2H), 7.20 – 7.16 (m, 3H), 5.94 – 5.80 (m, 1H), 5.46 – 5.31 (m, 2H), 3.60 – 3.50 (m, 2H), 2.76 – 2.62 (m, 2H), 1.95 – 1.89 (m, 1H), 1.83 – 1.77 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.32, 140.61, 128.59, 128.47, 126.02, 115.93, 76.09, 69.07, 38.88, 29.67. **IR** (CH_2Cl_2, cm^{-1}) 3393, 3025, 2940, 2868, 1454, 1267, 1035, 923, 748, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_{15}O_2^-$, 191.1077; Found, 191.1069.

2-phenethylpent-4-ene-1,2-diol (1s)



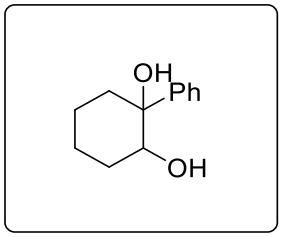
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 5.95 – 5.80 (m, 1H), 5.23 – 5.19 (m, 1H), 5.18 (t, J=1.1, 1H), 3.54 (s, 2H), 2.75 – 2.65 (m, 2H), 2.37 (dt, J=7.5, 1.1, 2H), 1.83 – 1.79 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.32, 133.35, 128.62, 128.44, 126.06, 119.32, 74.14, 67.97, 41.03, 38.47, 29.86. **IR** (CH_2Cl_2, cm^{-1}) 3373, 3075, 3029, 2937, 2872, 1641, 1495, 1451, 1272, 1034, 914, 750, 697. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{13}H_{17}O_2^-$, 205.1234; Found, 205.1228.

1,1-diphenylpropane-1,2-diol (1t)



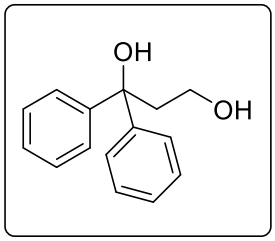
Prepared according to **General Procedure B.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 – 7.59 (m, 2H), 7.47 – 7.41 (m, 2H), 7.36 (dd, J=8.5, 7.0, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.15 (m, 2H), 4.91 – 4.76 (m, 1H), 2.96 (s, 1H), 1.83 (d, J=3.8, 1H), 1.12 (d, J=6.3, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.72, 144.02, 128.79, 128.29, 127.40, 126.92, 126.36, 125.69, 80.03, 71.76, 16.78. **IR** (CH_2Cl_2, cm^{-1}) 3448, 3057, 3029, 2983, 2940, 1449, 1267, 1070, 997, 889, 754, 700, 656. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{15}O_2^-$, 227.1077; Found, 227.1068.

1-phenylcyclohexane-1,2-diol (1u)



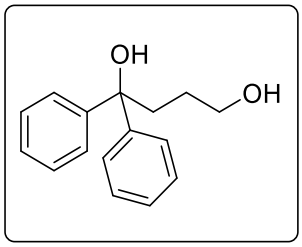
Prepared according to **General Procedure B.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 – 7.46 (m, 2H), 7.36 (dd, J=8.4, 7.0, 2H), 7.25 (tt, J=6.8, 1.3, 1H), 4.06 – 3.84 (m, 1H), 2.62 (s, 1H), 1.91 – 1.79 (m, 3H), 1.75 – 1.60 (m, 4H), 1.53 (dtdd, J=10.3, 4.2, 3.4, 1.5, 1H), 1.46 – 1.33 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 146.48, 128.57, 127.12, 125.24, 75.89, 74.64, 38.63, 29.34, 24.48, 21.19. **IR** (CH_2Cl_2, cm^{-1}) 3418, 3025, 2938, 2865, 1454, 1270, 1060, 997, 755, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_{15}O_2^-$, 191.1077; Found, 191.1067.

1,1-diphenylpropane-1,3-diol (1v)



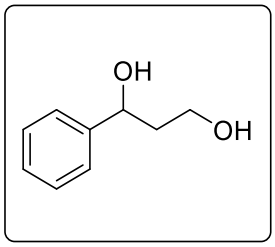
Prepared according to **General Procedure A.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 – 7.22 (m, 8H), 7.21 – 7.14 (m, 2H), 4.13 (s, 1H), 3.60 (t, J=6.4, 2H), 2.31 (dt, J=7.9, 6.4, 2H), 1.37 – 1.18 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.61, 128.67, 127.99, 126.42, 61.24, 47.49, 38.35. **IR** (CH_2Cl_2, cm^{-1}) 3356, 3059, 3032, 2958, 2893, 1491, 1447, 1264, 1183, 1057, 852, 756, 699, 643. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{15}O_2^-$, 227.1077; Found, 227.1068.

1,1-diphenylbutane-1,4-diol (1w)



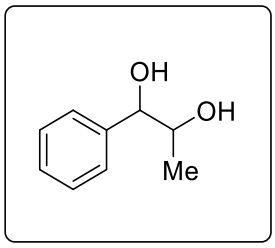
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 – 7.39 (m, 4H), 7.34 – 7.27 (m, 4H), 7.25 – 7.17 (m, 2H), 3.68 (t, J=6.0, 2H), 2.48 – 2.38 (m, 2H), 1.64 – 1.56 (m, 2H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 145.05, 128.60, 127.97, 126.31, 63.04, 51.28, 31.98, 31.46. **IR** (CH_2Cl_2, cm^{-1}) 3365, 3057, 3036, 2950, 2876, 1447, 1269, 1053, 1012, 972, 754, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{16}H_{17}O_2^-$, 241.1234; Found, 241.1227.

1-phenylpropane-1,3-diol (1x)



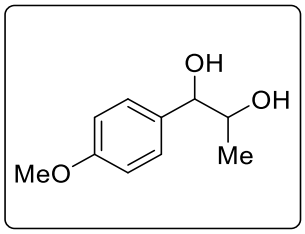
The ^{1}H and ^{13}C NMR spectra are identical to those previously reported.[3] **IR** (CH_2Cl_2, cm^{-1}) 3320, 2945, 2886, 1451, 1336, 1273, 1211, 1048, 918, 754, 698. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{11}O_2^-$, 151.0764; Found, 151.0755.

1-phenylpropane-1,2-diol (1y)



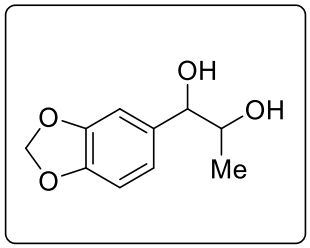
Prepared according to **General Procedure B.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 4.4 Hz, 4H), 7.34 – 7.28 (m, 1H), 4.69 (dd, *J* = 4.5, 2.7 Hz, 1H), 4.03 (d, *J* = 5.2 Hz, 1H), 2.29 (s, 1H), 1.81 (s, 1H), 1.10 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, MeOD) δ = 143.41, 128.97, 128.25, 128.05, 79.04, 72.40, 18.15. **IR** (CH_2Cl_2, cm^{-1}) 3366, 3064, 3032, 2983, 2890, 1451, 1382, 1266, 1127, 1074, 992, 933, 858, 749, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{11}O_2^-$, 151.0764; Found, 151.0755.

1-(4-methoxyphenyl)propane-1,2-diol (1z)



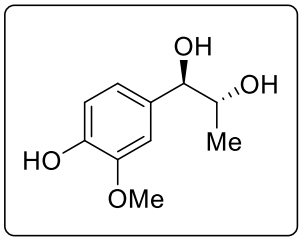
Prepared according to **General Procedure B.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.28 (s, 1H), 7.26 (s, 1H), 6.89 (d, J=8.7, 2H), 4.33 (d, J=7.6, 1H), 3.90 – 3.82 (m, 1H), 3.81 (s, 3H), 2.44 (s, 2H), 1.05 (d, J=6.3, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.63, 133.31, 128.17, 114.07, 79.31, 72.44, 55.43, 18.88. **IR** (CH_2Cl_2, cm^{-1}) 3377, 2975, 2933, 2897, 2836, 1612, 1513, 1458, 1247, 1177, 1128, 1030, 829, 751. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{13}O_3^-$, 181.0870; Found, 181.0869

1-(benzo[d][1,3]dioxol-5-yl)propane-1,2-diol (1aa')



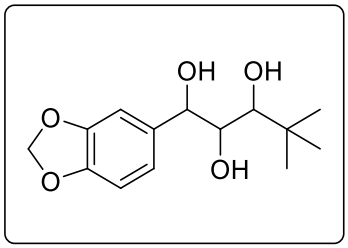
Prepared according to **General Procedure B.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.85 (d, J=1.4, 1H), 6.82 – 6.75 (m, 2H), 5.96 (s, 2H), 4.29 (d, J=7.5, 1H), 3.81 (dq, J=7.6, 6.3, 1H), 2.51 (s, 2H), 1.05 (d, J=6.3, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 147.98, 147.57, 135.13, 120.57, 108.33, 107.22, 101.24, 79.51, 72.41, 18.93. **IR** (CH_2Cl_2, cm^{-1}) 3375, 2983, 2893, 1488, 1441, 1242, 1123, 1093, 1032, 929, 809, 749, 632. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{11}O_4^-$, 195.0663; Found, 195.0655

1-(4-hydroxy-3-methoxyphenyl)propane-1,2-diol (1ab')



Prepared according to **General Procedure B.** **^{1}H NMR** (400 MHz, MeOD) δ = 6.96 (d, J=1.6, 1H), 6.78 (s, 2H), 4.26 (d, J=7.3, 1H), 3.87 (s, 3H), 3.82 – 3.77 (m, 1H), 0.97 (d, J=6.4, 3H). **^{13}C NMR** (100 MHz, MeOD) δ = 148.81, 147.12, 134.76, 120.97, 115.81, 111.55, 80.26, 72.97, 56.33, 19.29. **IR** (CH_2Cl_2, cm^{-1}) 3382, 2968, 2936, 2883, 2844, 1710, 1607, 1516, 1456, 1368, 1269, 1123, 1031, 855, 819, 747. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{13}O_4^-$, 197.0819; Found, 197.0811.

1-(benzo[d][1,3]dioxol-5-yl)-4,4-dimethylpentane-1,2,3-triol (1ac)



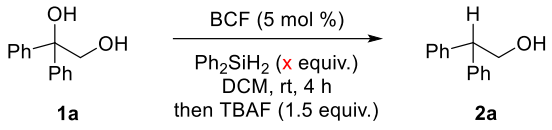
Prepared according to **General Procedure B.** **^{1}H NMR** (400 MHz, MeOD) δ = 6.99 (d, J=1.6, 1H), 6.91 – 6.84 (m, 1H), 6.78 (d, J=8.0, 1H), 5.92 (d, J=0.9, 2H), 5.02 (d, J=1.5, 1H), 3.56 (dd, J=7.9, 1.5, 1H), 3.42 (d, J=8.0, 1H), 1.02 (s, 9H). **^{13}C NMR** (100 MHz, MeOD) δ = 148.84, 147.82, 138.90, 120.52, 108.58, 108.30, 102.06, 79.93, 77.11, 74.14, 35.77, 27.21. **IR** (CH_2Cl_2, cm^{-1}) 3395, 2959, 2879, 1490, 1442, 1260, 1037, 932, 754. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{19}O_5^-$, 267.1238; Found, 267.1230.

3. Procedures for the Optimization Study

3.1. General Experimental Procedures

Inside an argon-filled glovebox, substrate **1a** (0.1 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (2.56 mg, 5 mol %) were dissolved in CH_2Cl_2 (0.5 ml) in a 4-ml screw-cap vial equipped with a magnetic stir bar. The silane was added dropwise to the solution, the vial was then closed and the reaction mixture was stirred for another 8 hours before it was quenched with TBAF solution (150 µl, 0.15 mmol, 1.5 equiv.). The yield of the corresponding products and remaining starting materials was determined by ^{1}H-NMR analysis of the crude-reaction mixture using CH_2Br_2 as the analytical standard. Flash column chromatography was performed using a Teledyne ISCO CombiFlash NextGen 300+ automated flash chromatography system equipped with RediSep Bronze normal-phase silica cartridges (4 g, 40–60 µm, 230–400 mesh, 55–60 Å pore size), using hexane/ethyl acetate (95:5 v/v) as the eluent.

Table S1. Optimization of the silane loading

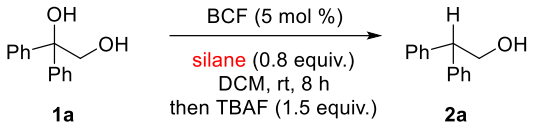


Entry	amount of silane (x equiv.)	yield (%)[a]
1	1.3	88
2	1.0	84
3	0.8	87
4	0.5	60

[a]Yield was determined by ^{1}H NMR using CH_2Br_2 as the internal standard.

The effect of the silane loading on the BCF-catalyzed deoxygenation was examined using substrate **1a**. Varying the amount of Ph_2SiH_2 revealed that the reaction efficiency remained high even with substoichiometric silane quantities (Table S1). When 1.3 equiv. of silane was employed, product **2a** was obtained in 88% yield, while 1.0 equiv. gave a comparable yield of 84%. Remarkably, decreasing the silane loading to 0.8 equiv. still afforded 2a in 87% yield, indicating that the BCF–silane system effectively promotes hydride transfer under silane-limited conditions. However, a further decrease to 0.5 equiv. led to a notable drop in yield (60%), suggesting insufficient hydride availability for complete reduction. Thus, 0.8 equiv. of Ph_2SiH_2 was chosen as the optimal condition, as it provides excellent yield while minimizing reagent consumption, demonstrating the high silane economy and turnover efficiency of this catalytic system.

Table S2. Screening of silane reducing agents

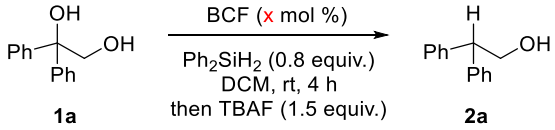


entry	silane	yield(%)[a]
1	$PhSiH_3$	85
2	Ph_2SiH_2	88
3	Ph_3SiH	N.R
4	Et_2SiH_2	34
5	Et_3SiH	23[b]

[a]Yield was determined by ^1H NMR using CH_2Br_2 as the internal standard. [b]The reaction using this silane was conducted for 24 h.

To identify the most effective hydride source for the BCF-catalyzed deoxygenation, various silanes were evaluated (Table S2). Among them, Ph_2SiH_2 provided the highest yield of **2a** (88%), demonstrating superior hydride transfer efficiency and compatibility with the catalytic system. Although $PhSiH_3$ also gave a high yield (85%), its performance was slightly lower than that of Ph_2SiH_2, leading to the selection of Ph_2SiH_2 as the optimal reducing agent. In contrast, bulkier or less reactive silanes such as Ph_3SiH, Et_2SiH_2, and Et_3SiH showed poor conversion or no reaction, indicating that both steric and electronic factors critically affect reactivity. Nevertheless, $PhSiH_3$ was employed in certain substrate scopes where its reactivity offered practical advantages.

Table S3. Optimization of the $B(C_6F_5)_3$ loading

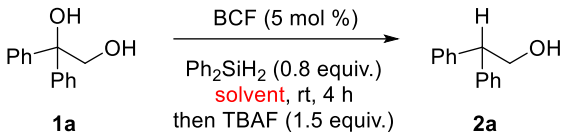


entry	amount of BCF	yield(%)[a]
1	1 mol %	67
2	3 mol %	81.5
3	5 mol %	87
4	10 mol %	90

[a]Yield was determined by ^1H NMR using CH_2Br_2 as the internal standard.

The effect of catalyst loading on the BCF-catalyzed deoxygenation was investigated by varying the molar percentage of BCF (Table S3). The yield of **2a** increased steadily with higher catalyst loading, from 67% at 1 mol % to 87% at 5 mol %. A further increase to 10 mol % afforded **2a** in 90% yield, showing only a marginal improvement. Considering both reactivity and efficiency, 5 mol % of BCF was selected as the optimal catalyst loading, providing reliable performance across substrates.

Table S4 Optimization of the solvent

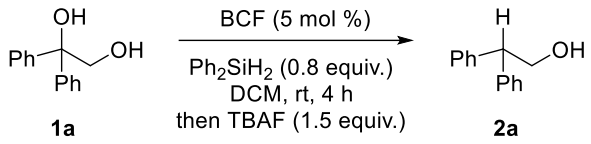


entry	solvent	yield(%)[a]
1	DCM	87
2	Toluene	68
3	THF	N.R.
4	Hexane	61
5	Pentane	74

[a]Yield was determined by ^{1}H NMR using CH_2Br_2 as the internal standard.

The influence of solvent on the BCF-catalyzed deoxygenation of **1a** was examined under otherwise identical conditions (Table S4). Among the solvents tested, DCM afforded the highest yield of 2a (87%), indicating that a moderately polar, non-coordinating environment is favorable for efficient hydride transfer. In contrast, reactions conducted in toluene, hexane, or pentane gave lower yields, while THF resulted in no reaction, likely due to coordination of the ether oxygen to BCF, which inhibits catalyst activity. Therefore, DCM was selected as the optimal solvent, providing the best balance between catalyst stability and reactivity.

Table S5. Optimization of the atmosphere

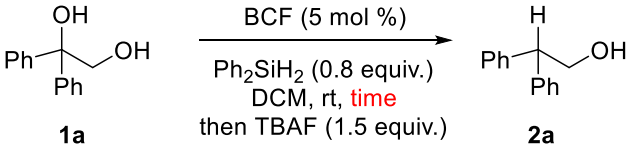


entry	reaction atmosphere	yield(%)[a]
1	air	64
2	air + H_2O(1 equiv.)	N.R.
3	Ar	87

[a]Yield was determined by ^1H NMR using CH_2Br_2 as the internal standard.

The effect of reaction atmosphere on the BCF-catalyzed deoxygenation was investigated (Table S5). The reaction performed under air afforded **2a** in a moderate yield (64%), whereas the presence of moisture (air + H_2O) completely suppressed product formation, indicating that both oxygen and water strongly deactivate the Lewis acidic catalyst. In contrast, conducting the reaction under an argon atmosphere provided a significantly improved yield of 87%, demonstrating that strict exclusion of moisture and oxygen is essential for efficient catalysis. Therefore, the reaction was carried out under argon in subsequent studies as the optimal atmosphere.

Table S6. Optimization of the reaction time

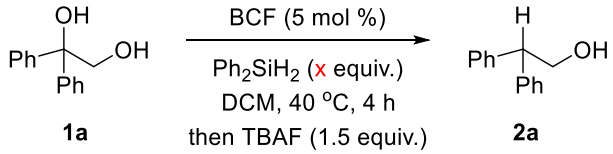


entry	reaction time	yield(%)[a]
1	4 h	87
2	8 h	99
3	16 h	> 99
4	24 h	> 99

[a]Yield was determined by ^1H NMR using CH_2Br_2 as the internal standard.

To determine the optimal reaction duration, the BCF-catalyzed deoxygenation of 1a was monitored over time (Table S6). The reaction progressed smoothly, affording **2a** in 87% yield after 4 h, and the yield increased to 99% after 8 h, indicating nearly complete conversion. Extending the reaction period to 16 or 24 h gave no further improvement (>99%), suggesting that the transformation reaches completion within 8 h. Thus, 8 h was established as the optimal reaction time, balancing high yield and operational efficiency.

Table S7. Optimization of the silane loading screeing under 40 ˚C

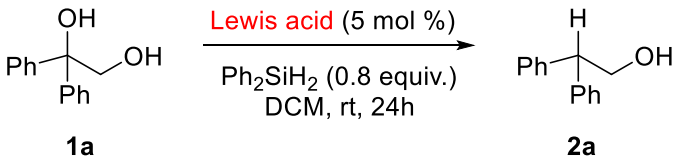


entry	Equivalents of silane	yield(%)[a]
1	1.3 equiv.	85
2	1.0 equiv.	89
3	0.8 equiv.	83
4	0.5 equiv.	63

[a]Yield was determined by ^{1}H NMR using CH_2Br_2 as the internal standard.

The effect of silane equivalents on the BCF-catalyzed deoxygenation was also examined at elevated temperature (40 °C) to assess whether heating could further enhance conversion (Table S7). Similar trends were observed to those obtained under ambient conditions, with Ph_2SiH_2 (1.0 equiv.) providing the highest yield of **2a** (89%). Increasing or decreasing the silane amount resulted in slightly lower yields, suggesting that the reaction remains efficient without excess hydride donor even at higher temperature. Overall, temperature was found to have no significant effect on the conversion for this substrate, and heating was applied only for specific substrates that exhibited lower reactivity under standard conditions.

Table S8. Comparison of Lewis acid catalysts under the standard conditions



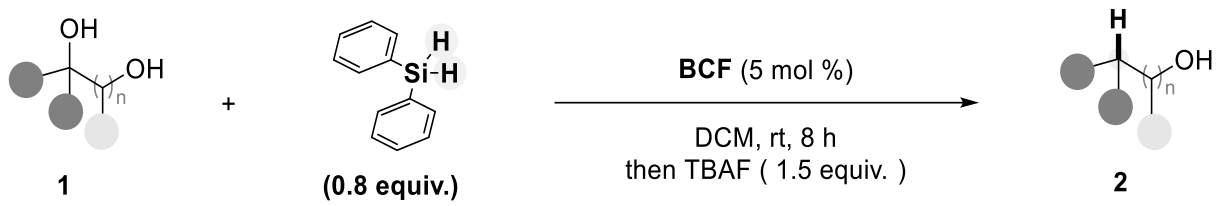
1a **2a**

entry	Lewis acid (cat.)	conversion(%)[a]	yield(%)[a]
1	$BF_3{\cdot}Et_2O$	*full conversion*	6
2	$InCl_3$	56	N.D.
3	Pd/C	N.R.	N.R.
4	$Cp_2{*}TiCl_2$	N.R.	N.R.
5	$Sc(OTf)_3$	*full conversion*	N.D.

[a]Conversion and yield were determined by ^1H NMR using CH_2Br_2 as the internal standard.

The performance of conventional Lewis acid catalysts was evaluated under the standard reaction conditions to assess whether similar reactivity could be achieved compared to $B(C_6F_5)_3$ catalytic system (Table S8). When $BF_3{\cdot}Et_2O$ was employed as the Lewis acid catalyst, full consumption of the starting material was observed; however, the desired deoxygenated product 2a was obtained in only 6% yield (entry 1). $InCl_3$ resulted in partial conversion of the substrate, but no detectable amount of the target product was formed (entry 2). Other Lewis acids, including Pd/C and Cp_2TiCl_2, showed no reactivity under these conditions, and the starting material was largely recovered (entries 3 and 4). Although $Sc(OTf)_3$ led to full conversion of the substrate, formation of 2a was not observed (entry 5). Notably, in the cases of $BF_3{\cdot}Et_2O$, $InCl_3$, and $Sc(OTf)_3$, additional aldehyde signals were detected in the crude NMR spectra, indicating the Sinvolvement of competing, non-productive reaction pathways rather than selective deoxygenation.

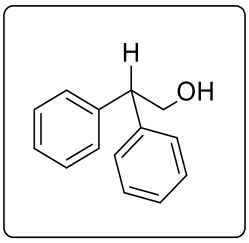
4. Procedures for the BCF-catalyzed regioselective deoxygenation of diol



Inside an argon-filled glovebox, diols (0.1 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (2.56 mg, 5 mol %) were dissolved in CH_2Cl_2 (0.5 ml) in a 4-ml screw-cap vial equipped with a magnetic stir bar. The silane was added dropwise to the solution, the vial was then closed and the reaction mixture was stirred for 8 hours before it was quenched with TBAF solution (150 µl, 0.15 mmol, 1.5 equiv.). The yield of the corresponding products and remaining starting materials was determined by ^{1}H-NMR analysis of the crude-reaction mixture using CH_2Br_2 as the analytical standard. Flash column chromatography was performed using a Teledyne ISCO CombiFlash NextGen 300+ automated flash chromatography system equipped with RediSep Bronze normal-phase silica cartridges (4 g, 40–60 µm, 230–400 mesh, 55–60 Å pore size), using hexane/ethyl acetate (95:5 v/v) as the eluent.

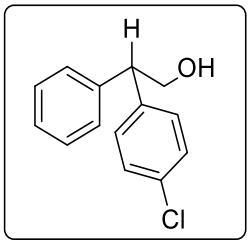
4.1. Characterization Data for deoxygenated products

2,2-diphenylethan-1-ol (2a)



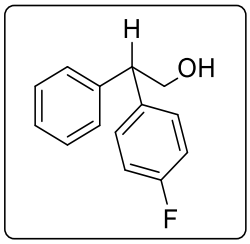
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.30 (m, 4H), 7.29 – 7.22 (m, 6H), 4.26 – 4.13 (m, 3H), 1.50 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.50, 128.87, 128.45, 126.97, 66.29, 53.79. **IR** (CH_2Cl_2, cm^{-1}) 3358, 3061, 3027, 2933, 2882, 1603, 1493, 1451, 1124,1055, 741, 698, 632. **HRMS** (EI) m/z: [M] Calcd for $C_{14}H_{14}O$, 198.1045; Found, 198.1042.

2-(4-chlorophenyl)-2-phenylethan-1-ol (2b)



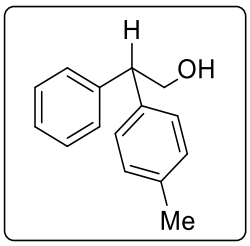
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.27 (m, 5H), 7.27 – 7.18 (m, 4H), 4.27 – 4.06 (m, 3H), 1.64 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.04, 140.14, 132.73, 129.80, 128.96, 128.93, 128.37, 127.16, 66.08, 53.05. **IR** (CH_2Cl_2, cm^{-1}) 3360, 3061, 3029, 2929, 2886, 1490, 1452, 1407, 1089, 1055, 1015, 821, 751, 699, 624. **HRMS** (EI) m/z: [M] Calcd for $C_{14}H_{13}ClO$, 232.0655; Found, 232.0649.

2-(4-fluorophenyl)-2-phenylethan-1-ol (2c)



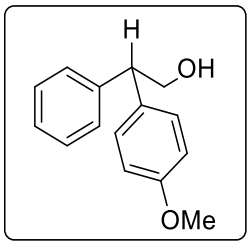
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (ddd, J=8.8, 6.5, 0.8, 2H), 7.33 – 7.20 (m, 5H), 7.04 (t, J=8.7, 2H), 4.27 – 4.11 (m, 3H), 1.54 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.84 (d, *JCF* = 246.4 Hz), 141.32, 137.31 (d, *JCF* = 3.0 Hz), 129.91 (d, *JCF* = 8.1 Hz), 128.95, 128.37, 127.10, 115.65 (d, *JCF* = 21.2 Hz), 66.27, 52.95. **IR** (CH_2Cl_2, cm^{-1}) 3350, 3061, 3029, 2933, 2886, 1603, 1506, 1224, 1160, 1057, 1021, 830, 753, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{12}FO^-$, 215.0877; Found, 215.0873.

2-phenyl-2-(p-tolyl)ethan-1-ol (2d)



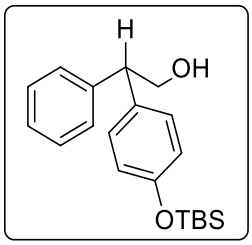
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (t, J=7.4, 2H), 7.28 (ddd, J=5.3, 4.0, 2.0, 3H), 7.17 (t, J=6.0, 4H), 4.18 (q, J=4.9, 3H), 2.34 (s, 3H), 1.28 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.73, 138.43, 136.57, 129.57, 128.83, 128.38, 128.31, 126.88, 66.32, 53.39, 21.14. **IR** (CH_2Cl_2, cm^{-1}) 3360, 3025, 2923, 2879, 1512, 1452, 1269, 1120, 1058, 1024,813, 753, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{15}O^-$, 211.1128; Found, 211.1130.

2-(4-methoxyphenyl)-2-phenylethan-1-ol (2e)



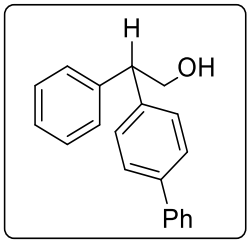
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.26 (m, 2H), 7.25 – 7.16 (m, 4H), 6.90 – 6.83 (m, 2H), 4.20 – 4.10 (m, 3H), 3.79 (s, 3H), 1.26 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.58, 141.84, 133.52, 129.43, 128.85, 128.36, 126.89, 114.28, 66.41, 55.40, 52.95. **IR** (CH_2Cl_2, cm^{-1}) 3392, 3007, 2926, 2861, 1610, 1512, 1459, 1253, 1179, 1033, 754, 701. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{15}O_2^-$, 227.1077; Found, 227.1077.

2-(4-((tert-butyldimethylsilyl)oxy)phenyl)-2-phenylethan-1-ol (2f)



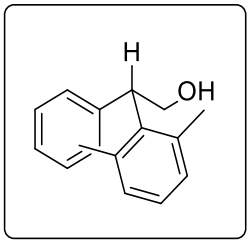
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 7.11 (d, J=8.5, 2H), 6.79 (d, J=8.6, 2H), 4.20 – 4.08 (m, 3H), 0.97 (s, 9H), 0.18 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.61, 141.86, 133.95, 129.37, 128.82, 128.42, 126.87, 120.33, 66.46, 53.03, 25.80, 18.31, -4.27. **IR** (CH_2Cl_2, cm^{-1}) 3350, 2950, 2932, 2886, 2858, 1508, 1468, 1258, 1057, 914, 835, 778, 751, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{20}H_{27}O_2Si^-$, 327.1786; Found, 327.1776.

2-([1,1'-biphenyl]-4-yl)-2-phenylethan-1-ol (2g)



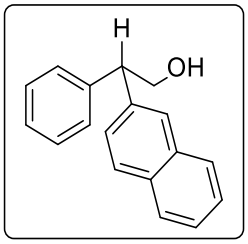
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 – 7.53 (m, 4H), 7.46 – 7.40 (m, 2H), 7.38 – 7.29 (m, 7H), 7.29 – 7.26 (m, 1H), 4.31 – 4.18 (m, 3H), 1.53 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.44, 140.90, 140.59, 139.92, 128.94, 128.90, 128.86, 128.47, 127.60, 127.38, 127.18, 127.06, 66.30, 53.49. **IR** (CH_2Cl_2, cm^{-1}) 3332, 3027, 2926, 2883, 1488, 1270, 1060, 756, 698. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{20}H_{17}O^-$, 273.1285; Found, 273.1285.

2-(2,6-dimethylphenyl)-2-phenylethan-1-ol (2h)



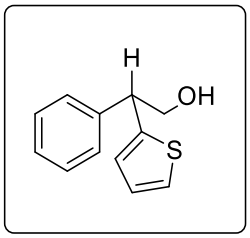
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 7.13 (d, J=1.8, 1H), 7.06 (d, J=7.7, 1H), 6.98 (dd, J=7.8, 1.8, 1H), 4.37 (t, J=7.2, 1H), 4.22 – 4.06 (m, 2H), 2.34 (s, 3H), 2.21 (s, 3H), 1.57 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.25, 139.06, 135.71, 134.17, 130.97, 128.75, 128.65, 127.55, 127.32, 126.77, 66.21, 49.65, 21.42, 19.47. **IR** (CH_2Cl_2, cm^{-1}) 3371, 3022, 2929, 2876, 1733, 1496, 1451, 1376, 1263, 1050, 809, 741, 699, 638. **HRMS** (EI) m/z: [M] Calcd for $C_{16}H_{18}O$, 226.1358; Found, 226.1359.

2-(naphthalen-2-yl)-2-phenylethan-1-ol (2i)



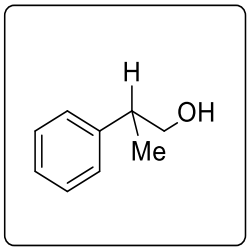
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.74 (m, 4H), 7.52 – 7.42 (m, 2H), 7.39 – 7.29 (m, 5H), 7.28 – 7.20 (m, 1H), 4.38 (d, J=7.1, 1H), 4.29 (dd, J=7.2, 3.2, 2H), 1.27 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.43, 138.96, 133.64, 132.56, 128.90, 128.60, 128.57, 127.92, 127.76, 127.05, 126.99, 126.76, 126.33, 125.91, 66.19, 53.81. **IR** (CH_2Cl_2, cm^{-1}) 3367, 3050, 3029, 2929, 2883, 1450, 1452, 1266, 1056, 1023, 857, 745, 700, 661. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{15}O^-$, 247.1128; Found, 247.1128.

2-phenyl-2-(thiophen-2-yl)ethan-1-ol (2j)



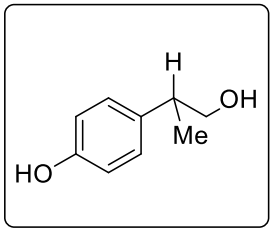
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.31 (m, 5H), 7.24 (dd, J=5.1, 1.2, 1H), 7.00 (dd, J=5.1, 3.5, 1H), 6.94 (dt, J=3.5, 1.1, 1H), 4.44 (d, J=7.1, 1H), 4.16 (d, J=6.8, 2H), 1.64 (t, J=6.6, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.89, 141.08, 128.96, 128.27, 127.44, 126.99, 125.10, 124.47, 67.27, 49.57. **IR** (CH_2Cl_2, cm^{-1}) 3386, 3018, 2926, 2865, 1267, 1061, 753, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_{11}OS^-$, 203.0536; Found, 203.0540.

2-phenylpropan-1-ol (2k)



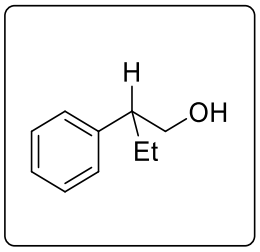
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.31 (m, 2H), 7.27 – 7.22 (m, 3H), 3.71 (d, J=6.8, 2H), 2.96 (h, J=7.0, 1H), 1.34 (s, 1H), 1.29 (d, J=7.0, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.78, 128.79, 127.62, 126.83, 68.86, 42.58, 17.72. **IR** (CH_2Cl_2, cm^{-1}) 3352, 2961, 2925, 2876, 1493, 1453, 1378, 1267, 1033, 907, 755, 698. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{11}O^-$, 135.0815; Found, 135.0806.

4-(1-hydroxypropan-2-yl)phenol (2l)



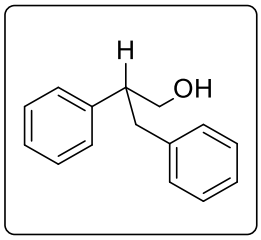
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 (d, J=8.5, 2H), 6.83 – 6.77 (m, 2H), 3.66 (dd, J=6.9, 5.5, 2H), 2.90 (q, J=6.9, 1H), 1.55 (s, 2H), 1.24 (d, J=7.1, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 154.94, 128.94, 115.67, 69.04, 41.97, 17.97. **IR** (CH_2Cl_2, cm^{-1}) 3314, 2965, 2922, 2876, 1514, 1452, 1261, 1231, 1177, 1122, 1013, 830, 746, 701. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{11}O_2^-$, 151.0764; Found, 151.0756.

2-phenylbutan-1-ol (2m)



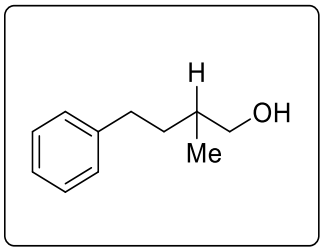
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.30 (m, 2H), 7.27 – 7.18 (m, 3H), 3.76 (qd, J=10.8, 6.9, 2H), 2.70 (ddd, J=14.1, 8.6, 5.8, 1H), 1.84 – 1.70 (m, 1H), 1.64 – 1.54 (m, 1H), 1.26 (s, 1H), 0.84 (td, J=7.4, 1.3, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.38, 128.78, 128.25, 126.86, 67.49, 50.65, 25.13, 12.12. **IR** (CH_2Cl_2, cm^{-1}) 3342, 2961, 2928, 2874, 1455, 1379, 1269, 1038, 755, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{13}O^-$, 149.0972; Found, 149.0968.

2,3-diphenylpropan-1-ol (2n)



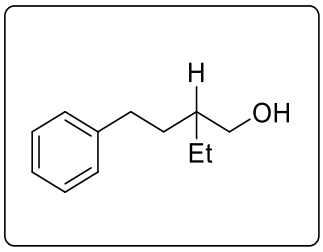
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.28 (m, 2H), 7.26 – 7.25 (m, 1H), 7.25 – 7.18 (m, 4H), 7.19 – 7.13 (m, 1H), 7.12 – 7.02 (m, 2H), 3.80 (dd, J=6.3, 1.6, 2H), 3.15 – 2.99 (m, 2H), 2.92 (dd, J=13.3, 7.4, 1H), 1.47 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.03, 140.05, 129.20, 128.80, 128.40, 128.23, 127.02, 126.18, 66.53, 50.33, 38.85. **IR** (CH_2Cl_2, cm^{-1}) 3364, 3026, 2922, 2858, 1453, 1267, 1026, 754, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{15}O^-$, 211.1128; Found, 211.1121.

2-methyl-4-phenylbutan-1-ol (2o)



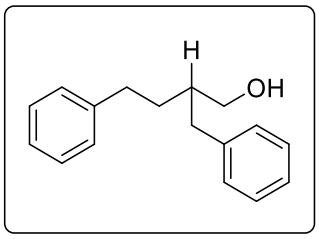
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.29 – 7.23 (m, 2H), 7.22 – 7.11 (m, 3H), 3.53 – 3.38 (m, 2H), 2.70 (ddd, J=13.6, 10.2, 5.6, 1H), 2.59 (ddd, J=13.8, 10.2, 6.3, 1H), 1.75 – 1.69 (m, 1H), 1.66 – 1.60 (m, 1H), 1.45 – 1.39 (m, 1H), 0.97 (d, J=6.6, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 143.30, 128.71, 128.64, 125.99, 68.33, 35.86, 35.48, 33.64, 16.64. **IR** (CH_2Cl_2, cm^{-1}) 3367, 3018, 2928, 2868, 1269, 1036, 754. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{11}H_{15}O^-$, 163.1128; Found, 163.1124.

2-ethyl-4-phenylbutan-1-ol (2p)



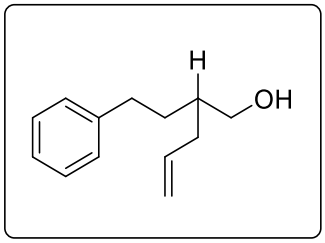
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 3.61 (dd, J=5.3, 1.0, 2H), 2.65 (t, J=8.1, 2H), 1.76 – 1.58 (m, 2H), 1.51 – 1.39 (m, 3H), 0.93 (t, J=7.4, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.86, 128.48, 125.85, 65.23, 41.74, 33.39, 32.53, 23.41, 11.18. **IR** (CH_2Cl_2, cm^{-1}) 3339, 2965, 2927, 2870, 1456, 1268, 1043, 752, 698. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_{17}O^-$, 177.1285; Found, 177.1277.

2-benzyl-4-phenylbutan-1-ol (2q)



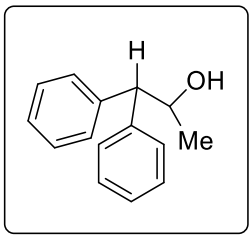
The ^{1}H and ^{13}C NMR spectra are identical to those previously reported.[4] **IR** 3392, 3026, 2934, 2868, 1494, 1454, 1270, 1035, 914, 753, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{19}O^-$, 239.1441; Found, 239.1439.

2-phenethylpent-4-en-1-ol (2s)



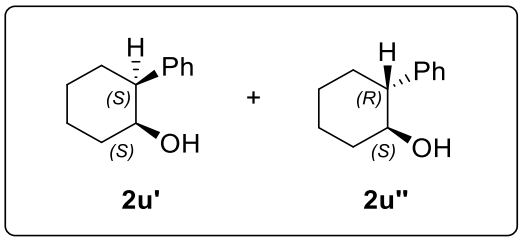
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.26 (m, 2H), 7.19 (d, J=7.1, 3H), 5.82 (ddt, J=17.2, 10.2, 7.2, 1H), 5.16 – 5.00 (m, 2H), 3.61 (d, J=4.9, 2H), 2.66 (dd, J=8.6, 6.9, 2H), 2.23 – 2.15 (m, 2H), 1.74 – 1.60 (m, 3H), 1.44 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.60, 136.93, 128.50, 128.47, 125.91, 116.59, 65.48, 40.05, 35.80, 33.37, 32.60. **IR** (CH_2Cl_2, cm^{-1}) 3337, 3025, 2923, 2861, 1452, 1269, 1031, 912, 753, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{13}H_{17}O^-$, 189.1285; Found, 189.1275.

1,1-diphenylpropan-2-ol (2t)



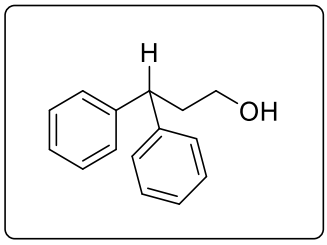
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.11 (m, 11H), 4.52 (ddt, J=9.4, 6.2, 3.1, 1H), 3.78 (d, J=8.7, 1H), 1.64 (s, 1H), 1.17 (d, J=6.1, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.62, 141.64, 129.02, 128.78, 128.76, 128.32, 127.06, 126.70, 70.20, 60.75, 21.54. **IR** (CH_2Cl_2, cm^{-1}) 3414, 3054, 3022, 2972, 2897, 1493, 1450, 1265, 1119, 1082, 949, 752, 698, 641. **HRMS** (ESI) m/z: [M-H]$^-$ Calcd for $C_{15}H_{15}O^-$, 211.1128; Found, 211.1121.

2-phenylcyclohexan-1-ol (2u)



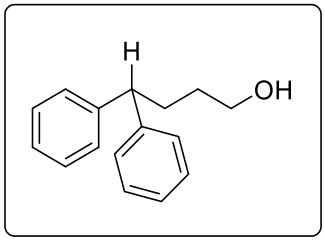
The ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[5, 6] **IR** (CH_2Cl_2, cm^{-1}) 3403, 3022, 2935, 2865, 1445, 1268, 1122, 1059, 997, 754, 700, 642, 609. **HRMS** (ESI) m/z: [M-H]$^-$ Calcd for $C_{12}H_{15}O^-$, 175.1128; Found, 175.1131.

3,3-diphenylpropan-1-ol (2v)



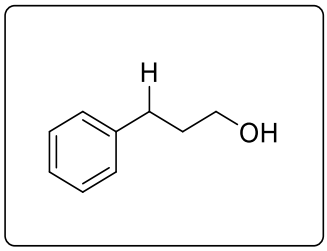
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.04 (m, 10H), 4.15 (t, J=7.9, 1H), 3.62 (t, J=6.4, 2H), 2.33 (dt, J=7.9, 6.4, 2H), 1.29 (s, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.61, 128.67, 127.99, 126.42, 61.24, 47.49, 38.35. **IR** (CH_2Cl_2, cm^{-1}) 3322, 3057, 3026, 2937, 2876, 1493, 1450, 1268, 1029, 752, 698, 626. **HRMS** (ESI) m/z: [M-H]$^-$ Calcd for $C_{15}H_{15}O^-$, 211.1128; Found, 211.1124.

4,4-diphenylbutan-1-ol (2w)



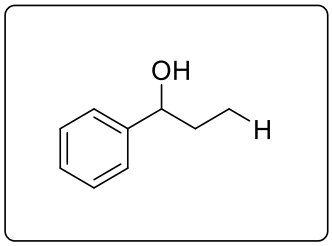
The ^{1}H and ^{13}C NMR spectra are identical to those previously reported.[7]
IR (CH_2Cl_2, cm^{-1}) 3325, 3054, 3022, 2934, 2867, 1493, 1450, 1268, 1053, 924, 752, 699, 628. **HRMS** (ESI) m/z: [M-H]$^-$ Calcd for $C_{16}H_{17}O^-$, 225.1285; Found, 225.1277.

3-phenylpropan-1-ol (2x)



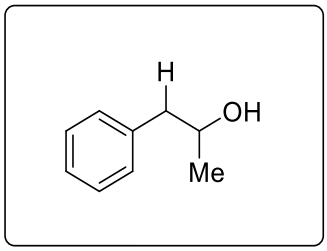
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, J=11.7, 3H), 7.20 (d, J=7.0, 2H), 3.69 (t, J=6.3, 2H), 2.72 (t, J=7.6, 2H), 1.90 (p, J=6.5, 2H), 1.50 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.95, 128.58, 128.55, 126.02, 62.47, 34.38, 32.22. **IR** (CH_2Cl_2, cm^{-1}) 3346, 3007, 2930, 2865, 1455, 1269, 1131, 754, 698. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{11}O^-$, 135.0815; Found, 135.0805.

1-phenylpropan-1-ol (2x')



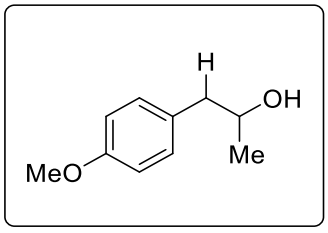
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (s, 4H), 7.32 – 7.26 (m, 1H), 4.60 (dd, J=7.1, 6.0, 1H), 1.85 – 1.74 (m, 2H), 0.92 (t, J=7.4, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.73, 128.55, 127.64, 126.11, 76.18, 32.03, 10.28. **IR** (CH_2Cl_2, cm^{-1}) 3350, 3036, 2967, 2933, 2868, 1454, 1269, 1093, 1011, 973, 899, 754, 698. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{11}O^-$, 135.0815; Found, 135.0811.

1-phenylpropan-2-ol (2y)



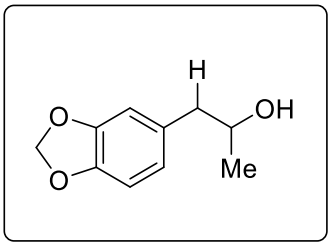
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.31 (m, 2H), 7.29 – 7.21 (m, 3H), 4.05 (dqd, J=8.0, 6.2, 4.8, 1H), 2.89 – 2.64 (m, 2H), 1.59 (s, 1H), 1.27 (d, J=6.2, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 138.64, 129.53, 128.71, 126.64, 69.03, 45.94, 22.95. **IR** (CH_2Cl_2, cm^{-1}) 3355, 3022, 2972, 2929, 1454, 1269, 1116, 1080, 940, 839, 752, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{11}O^-$, 135.0815; Found, 135.0818.

1-(4-methoxyphenyl)propan-2-ol (2z)



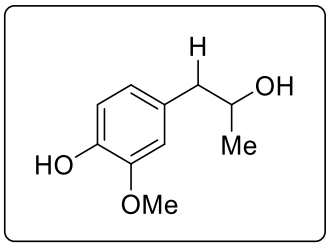
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, J=8.6, 2H), 6.86 (d, J=8.7, 2H), 3.97 (dqd, J=8.0, 6.2, 4.8, 1H), 3.79 (s, 3H), 2.79 – 2.56 (m, 2H), 1.57 (s, 1H), 1.23 (d, J=6.2, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.44, 130.60, 130.47, 114.12, 69.08, 55.39, 44.98, 22.82. **IR** (CH_2Cl_2, cm^{-1}) 3360, 2972, 2933, 2840, 1511, 1244, 1178, 1111, 1077, 1034, 939, 843, 807, 754. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{13}O_2^-$, 165.0921; Found, 165.0915.

1-(benzo[d][1,3]dioxol-5-yl)propan-1-ol (2aa)



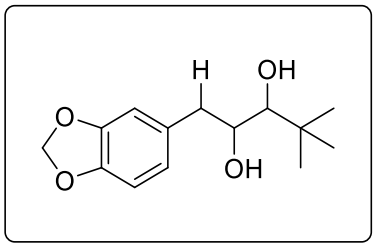
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.80 – 6.62 (m, 3H), 5.94 (s, 2H), 3.96 (dqd, J=8.0, 6.1, 4.6, 1H), 2.77 – 2.54 (m, 2H), 1.55 (s, 1H), 1.23 (d, J=6.1, 3H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 148.11, 146.54, 133.01, 122.63, 109.99, 108.45, 101.42, 69.20, 45.77, 23.01. **IR** (CH_2Cl_2, cm^{-1}) 3381, 2968, 2921, 1489, 1442, 1246, 1190, 1098, 1038, 931, 805, 754. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{11}O_3^-$, 179.0713; Found, 179.0705.

4-(2-hydroxypropyl)-2-methoxyphenol (2ab)



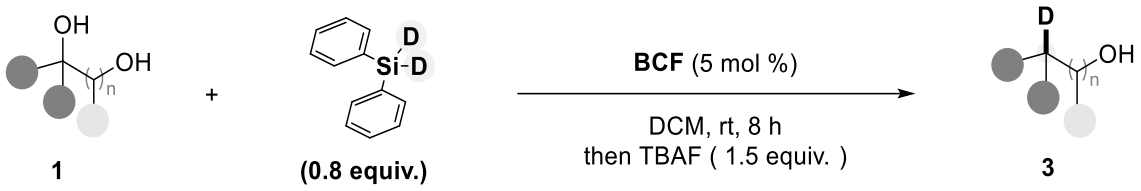
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.90 – 6.82 (m, 1H), 6.71 (d, J=7.4, 2H), 5.53 (s, 1H), 4.02 – 3.93 (m, 1H), 3.88 (s, 3H), 2.74 (dd, J=13.6, 4.5, 1H), 2.59 (dd, J=13.6, 8.2, 1H), 1.24 (d, J=6.2, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 146.66, 144.44, 130.43, 122.14, 114.58, 111.97, 69.10, 56.03, 45.58, 22.84. **IR** (CH_2Cl_2, cm^{-1}) 3382, 2972, 2936, 2844, 1516, 1458, 1172, 1269, 1122, 1036, 942, 754 **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{13}O_3^-$, 181.0870; Found, 181.0862.

1-(benzo[d][1,3]dioxol-5-yl)-4,4-dimethylpentane-2,3-diol (2ac)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.79 – 6.73 (m, 2H), 6.69 (dd, J=7.9, 1.7, 1H), 5.94 (s, 2H), 3.86 (ddd, J=10.3, 4.5, 2.8, 1H), 3.43 (d, J=4.6, 1H), 3.00 (dd, J=13.9, 2.7, 1H), 2.65 (dd, J=13.9, 10.2, 1H), 1.04 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 148.14, 146.52, 132.21, 122.55, 109.88, 108.61, 101.10, 81.50, 73.36, 38.95, 34.50, 26.94. **IR** (CH_2Cl_2, cm^{-1}) 3427, 2960, 2876, 1490, 1265, 1039, 931, 754. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{19}O_4^-$, 251.1289; Found, 251.1291.

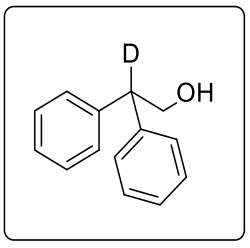
5. Procedures for the deoxygenative deuteration



Inside an argon-filled glovebox, diols (0.1 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (2.56 mg, 5 mol %) were dissolved in CH_2Cl_2 (0.5 ml) in a 4-ml screw-cap vial equipped with a magnetic stir bar. The deuterated silane was added dropwise to the solution, the vial was then closed and the reaction mixture was stirred for 8 hours before it was quenched with TBAF solution (150 µl, 0.15 mmol, 1.5 equiv.). The yield of the corresponding products and remaining starting materials was determined by ^{1}H-NMR analysis of the crude-reaction mixture using CH_2Br_2 as the analytical standard. Flash column chromatography was performed using a Teledyne ISCO CombiFlash NextGen 300+ automated flash chromatography system equipped with RediSep Bronze normal-phase silica cartridges (4 g, 40–60 µm, 230–400 mesh, 55–60 Å pore size), using hexane/ethyl acetate (95:5 v/v) as the eluent.

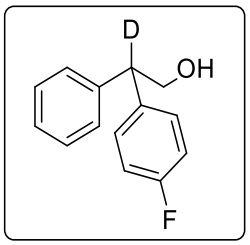
5.1. Characterization Data for deuterated products

2,2-diphenylethan-2-d-1-ol (3a)



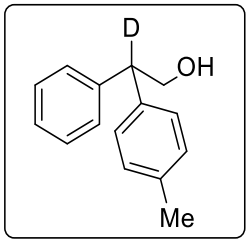
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.30 (m, 4H), 7.29 – 7.20 (m, 6H), 4.18 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.45, 128.87, 128.43, 126.97, 66.23, 53.70. **IR** (CH_2Cl_2, cm^{-1}) 3371, 3061, 3026, 2883, 1607, 1493, 1449, 1266, 1057, 977, 748, 699, 628. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{12}DO^-$, 198.1034; Found, 198.1033.

2-(4-fluorophenyl)-2-phenylethan-2-d-1-ol (3c)



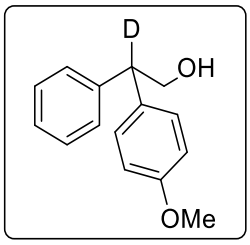
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.30 (m, 2H), 7.28 – 7.19 (m, 5H), 7.01 (t, J=8.7, 2H), 4.15 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.84 (d, *JCF* = 245.4 Hz), 141.27, 137.25 (d, *JCF* = 3.0 Hz), 129.89 (d, *JCF* = 8.1 Hz), 128.95, 128.35, 127.11, 115.65 (d, *JCF* = 21.2 Hz), 66.22, 52.87. **IR** (CH_2Cl_2, cm^{-1}) 3364, 3061, 3025, 2926, 2886, 1603, 1506, 1265, 1224, 1160, 1057, 979, 831, 748, 699. **HRMS** (EI) m/z: [M] Calcd for $C_{14}H_{12}DFO$, 217.1013; Found, 217.1012.

2-phenyl-2-(p-tolyl)ethan-2-d-1-ol (3d)



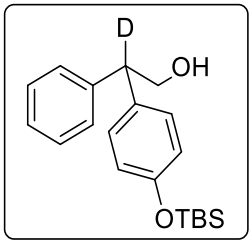
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.27 (m, 3H), 7.27 – 7.21 (m, 2H), 7.21 – 7.11 (m, 4H), 4.15 (s, 2H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.67, 138.38, 136.58, 129.58, 128.84, 128.37, 128.29, 126.89, 66.28, 53.32, 21.15. **IR** (CH_2Cl_2, cm^{-1}) 3358, 3023, 2922, 2876, 1512, 1448, 1268, 1061, 978, 812, 754, 700. **HRMS** (EI) m/z: [M] Calcd for $C_{15}H_{15}DO$, 213.1264; Found, 213.1268.

2-(4-methoxyphenyl)-2-phenylethan-2-d-1-ol (3e)



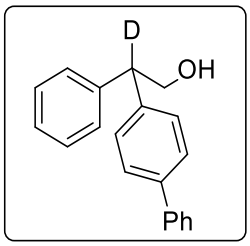
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.28 (m, 2H), 7.27 – 7.16 (m, 5H), 6.93 – 6.79 (m, 2H), 4.13 (s, 2H), 3.79 (s, 3H), 1.47 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.57, 141.83, 133.51, 129.43, 129.41, 128.84, 128.35, 126.89, 114.28, 66.34, 55.40, 52.86 **IR** (CH_2Cl_2, cm^{-1}) 3375, 3025, 2922, 2840, 1614, 1509, 1454, 1246, 1178, 1064, 1031, 825, 752, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{14}DO_2^-$, 228.1140; Found, 228.1130.

2-(4-((tert-butyldimethylsilyl)oxy)phenyl)-2-phenylethan-2-d-1-ol (3f)



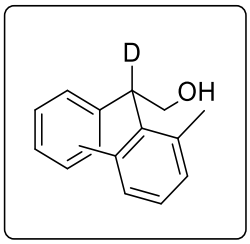
^{1}H NMR 400 MHz, $CDCl_3$) δ = 7.36 – 7.29 (m, 2H), 7.26 – 7.20 (m, 2H), 7.11 (dd, J=8.5, 1.6, 2H), 6.79 (d, J=8.5, 2H), 4.14 (s, 2H), 1.44 (s, 1H), 0.97 (s, 9H), 0.18 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.61, 141.86, 133.95, 129.37, 128.82, 128.41, 126.87, 120.33, 66.39, 52.94, 25.80, 18.31, -4.27. **IR** (CH_2Cl_2, cm^{-1}) 3378, 2954, 2932, 2858, 1610, 1507, 1468, 1258, 1173, 1065, 912, 834, 752, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{20}H_{26}DO_2Si^-$, 328.1848; Found, 328.1840.

2-([1,1'-biphenyl]-4-yl)-2-phenylethan-2-d-1-ol (3g)



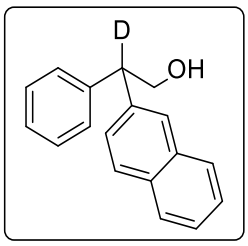
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.52 (m, 4H), 7.46 – 7.39 (m, 2H), 7.39 – 7.28 (m, 7H), 7.28 – 7.22 (m, 2H), 4.22 (s, 2H), 1.26 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.40, 140.90, 140.54, 139.92, 128.94, 128.90, 128.83, 128.45, 127.60, 127.38, 127.17, 127.06, 66.24, 53.40. **IR** (CH_2Cl_2, cm^{-1}) 3343, 3022, 2923, 2861, 1486, 1450, 1265, 1066, 976, 836, 755, 696. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{20}H_{16}DO^-$, 274.1347; Found, 274.1348.

2-(2,6-dimethylphenyl)-2-phenylethan-2-d-1-ol (3h)



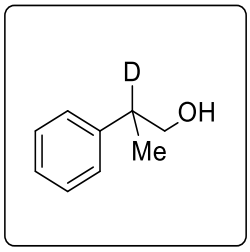
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 7.13 (d, J=2.0, 1H), 7.06 (d, J=7.6, 1H), 6.98 (dd, J=7.8, 2.0, 1H), 4.36 (d, J=7.2, 1H), 4.14 (d, J=6.1, 2H), 2.34 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.25, 141.20, 139.07, 139.01, 135.71, 134.16, 130.97, 128.75, 128.65, 128.64, 127.55, 127.32, 126.78, 66.15, 49.58, 21.42, 19.46. **IR** (CH_2Cl_2, cm^{-1}) 3371, 015, 2921, 2868, 1496, 1450, 1378, 1265, 1064, 810, 749, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{16}H_{16}DO^-$, 226.1347; Found, 226.1347.

2-(naphthalen-2-yl)-2-phenylethan-2-d-1-ol (3i)



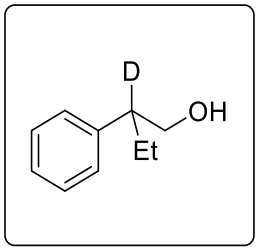
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.75 (m, 4H), 7.51 – 7.42 (m, 2H), 7.38 – 7.29 (m, 5H), 7.28 – 7.21 (m, 1H), 4.28 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.38, 138.91, 133.63, 132.55, 128.89, 128.59, 128.54, 127.91, 127.75, 127.04, 126.99, 126.96, 126.74, 126.32, 125.90, 66.11, 53.71. **IR** (CH_2Cl_2, cm^{-1}) 3357, 3053, 3022, 2926, 2879, 1497, 1268, 1063, 896, 855, 818, 752, 701. **HRMS** (EI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{15}DO$, 249.1264; Found, 249.1260.

2-phenylpropan-2-d-1-ol (3k)



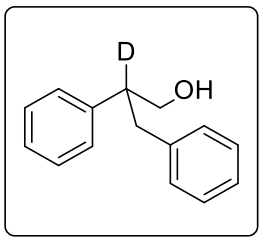
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.31 (m, 2H), 7.26 – 7.21 (m, 3H), 3.71 (s, 2H), 1.42 (d, J=6.4, 1H), 1.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.74, 128.80, 127.62, 126.84, 68.80, 42.14, 17.62. **IR** (CH_2Cl_2, cm^{-1}) 3354, 3029, 2965, 2927, 2872, 1603, 1494, 1451, 1270, 1033, 754, 699. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{10}DO^-$, 136.0878; Found, 136.0876

2-phenylbutan-2-d-1-ol (3m)



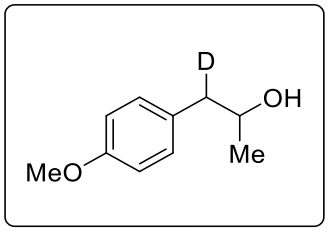
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (dd, J=8.1, 6.7, 2H), 7.27 – 7.15 (m, 3H), 3.75 (q, J=10.8, 2H), 1.75 (dq, J=14.5, 7.6, 1H), 1.58 (dddd, J=13.1, 8.7, 7.4, 5.8, 1H), 1.39 (s, 1H), 0.84 (t, J=7.4, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.30, 128.55, 127.19, 125.75, 70.61, 31.28, 29.86, 7.54. **IR** (CH_2Cl_2, cm^{-1}) 3350, 3022, 2962, 2927, 2872, 1454, 1268, 1046, 754, 700. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{12}DO^-$, 150.1034; Found, 150.1034

2,3-diphenylpropan-2-d-1-ol (3n)



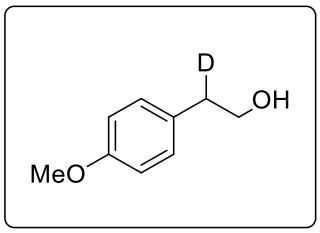
The ^{1}H and ^{13}C NMR spectra are identical to those previously reported.[8] **IR** (CH_2Cl_2, cm^{-1}) 3358, 3061, 3026, 2923, 2868, 1494, 1450, 1266, 1061, 1029, 752, 697. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{14}DO^-$, 212.1191; Found, 212.1199.

1-(4-methoxyphenyl)propan-1-d-2-ol (3z)



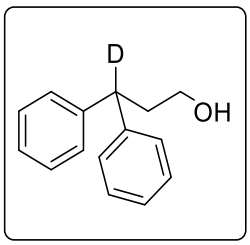
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, J=8.6, 2H), 6.86 (d, J=8.6, 2H), 4.03 – 3.89 (m, 1H), 3.80 (s, 3H), 2.82 – 2.45 (m, 1H), 1.50 (s, 1H), 1.23 (d, J=6.2, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.46, 130.48, 114.15, 69.06, 55.41, 44.62, 44.43, 22.82. **IR** (CH_2Cl_2, cm^{-1}) 3382, 2967, 2908, 2833, 1612, 1512, 1459, 1244, 1178, 1110, 1035, 808, 754. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{10}H_{12}DO_2^-$, 166.0984; Found, 166.0986.

2-(4-methoxyphenyl)ethan-2-d-1-ol (3ad)



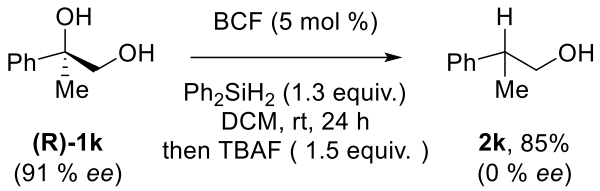
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 – 7.14 (m, 2H), 6.86 (d, J=8.6, 2H), 3.83 – 3.81 (m, 2H), 3.80 (s, 3H), 2.81 (d, J=6.1, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.45, 130.49, 130.11, 114.19, 63.94, 55.42, 38.05. **IR** (CH_2Cl_2, cm^{-1}) 3346, 3004, 2929, 2836, 1612, 1511, 1462, 1244, 1178, 1031, 810, 754. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_9H_{10}DO_2^-$, 152.0827; Found, 152.0818.

3,3-diphenylpropan-3-d-1-ol (3v)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.23 (m, 8H), 7.19 (td, J=6.4, 2.6, 2H), 3.62 (t, J=6.4, 2H), 2.32 (t, J=6.4, 2H), 1.26 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.57, 128.68, 127.97, 126.43, 61.23, 47.07, 38.27. **IR** (CH_2Cl_2, cm^{-1}) 3327, 3057, 3025, 2934, 2876, 1492, 1446, 1265, 1036, 887, 749, 697. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{14}DO^-$, 212.1191; Found, 212.1187.

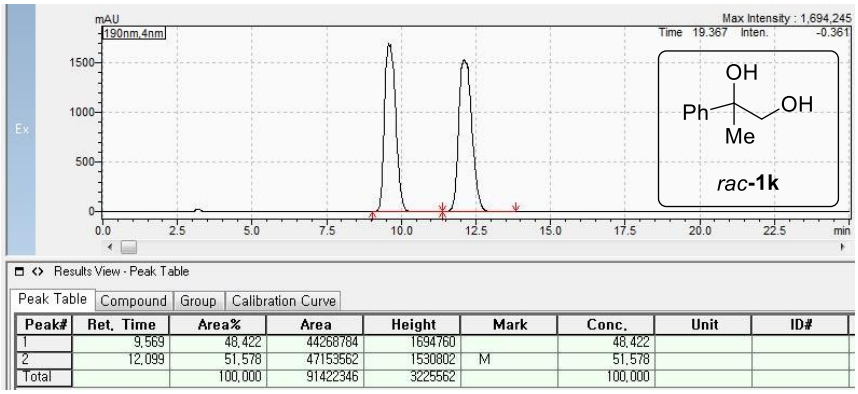
6. Racemization Study



Inside an argon-filled glovebox, chiral substrate **(R)-1k** (0.1 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (2.56 mg, 5 mol %) were dissolved in CH_2Cl_2 (0.5 ml) in a 4-ml screw-cap vial equipped with a magnetic stir bar. The silane was added dropwise to the solution, the vial was then closed and the reaction mixture was stirred for 24 hours before it was quenched with TBAF solution (150 µl, 0.15 mmol, 1.5 equiv.). The yield of the corresponding products **2k** and remaining starting materials was determined by ^{1}H-NMR analysis of the crude-reaction mixture using CH_2Br_2 as the analytical standard.

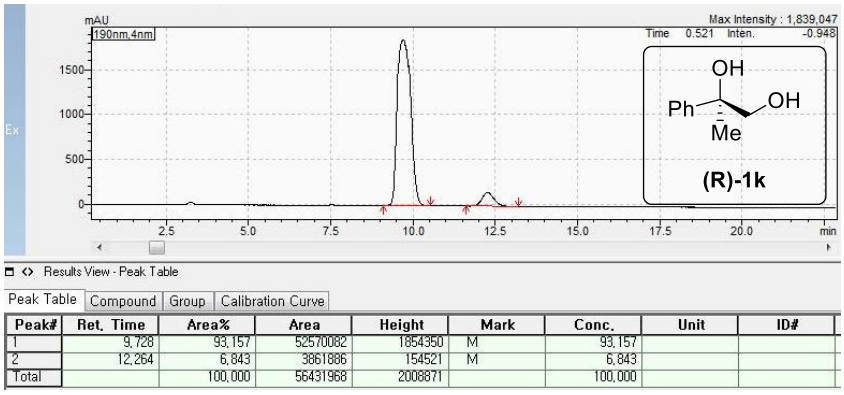
6.1. Chiral HPLC analysis of starting material(1k)

Chiral assay was conducted on Chiralpak ® IG column using IPA:n-Hex (10:90) as an eluent (1 mL/min).



Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.	Unit	ID#
1	9.569	48.422	44268784	1694760		48.422		
2	12.099	51.578	47153562	1530802	M	51.578		
Total		100.000	91422346	3225562		100.000		

Figure S1. Chiral HPLC chromatographic data of Racemic **1k**

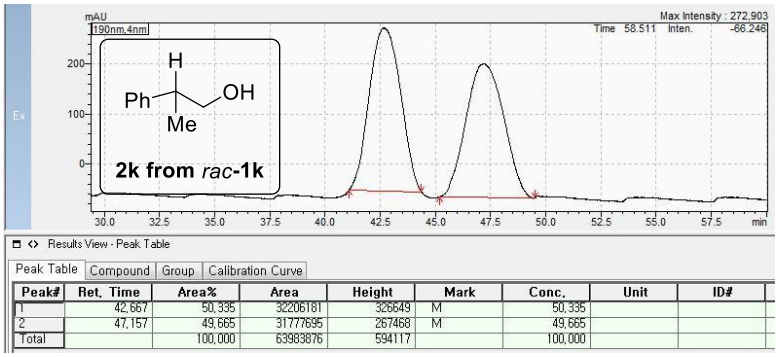


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.	Unit	ID#
1	9.728	93.157	52570082	1854350	M	93.157		
2	12.264	6.843	3861886	154521	M	6.843		
Total		100.000	56431968	2008871		100.000		

Figure S2. Chiral HPLC chromatographic data of Enantio-riched **(R)-1k** (R/S = 93:7)

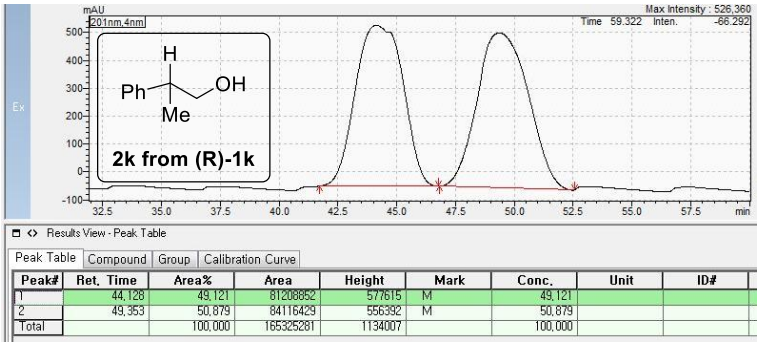
6.2. Chiral HPLC analysis of product(2k)

Chiral assay was conducted on Chiralpak ® IA column using IPA:n-Hex (1:99) as an eluent (1 mL/min).



Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.	Unit	ID#
1	42.667	50.335	32206181	326649	M	50.335		
2	47.157	49.665	31777695	267468	M	49.665		
Total		100.000	63983876	594117		100.000		

Figure S3. Chiral HPLC chromatographic data of **2k** obtained from *rac*-**1k**



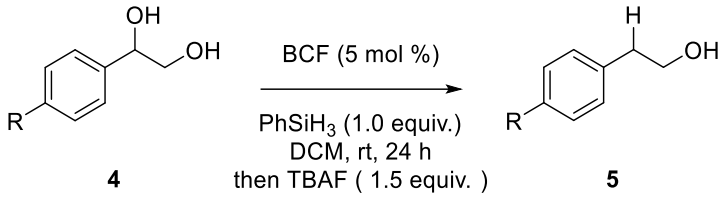
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.	Unit	ID#
1	44.128	49.121	81208852	577615	M	49.121		
2	49.353	50.879	84116429	556392	M	50.879		
Total		100.000	165325281	1134007		100.000		

Figure S4. Chiral HPLC chromatographic data of **2k** obtained from **(R)-1k**

The stereochemical stability of the benzylic center during the BCF-catalyzed deoxygenation was examined using both racemic(*rac*-**1k)** and enantiopure substrates(**(R)-1k)** (Fig. S1 and Fig. S2). When enantiopure **(R)-1k** (91% ee) was subjected to the standard conditions, the product **2k** was obtained in 85 % yield as a racemic mixture, indicating complete loss of enantiomeric excess. The chiral HPLC chromatogram of **2k** obtained from **(R)-1k** was identical to that of **2k** obtained from *rac*-**1k** (Fig. S3 and Fig. S4), confirming that full racemization occurred during the transformation. These results suggest that the BCF-catalyzed deoxygenation proceeds via a carbocationic intermediate that allows for enantiomeric equilibration before hydride delivery. Such behavior contrasts with the stereoretentive pathway observed in less stabilized systems and supports the involvement of a partially dissociative, S_N1-type mechanism for this benzylic substrate.

7. Hammett analysis

7.1. General Experimental Procedures



Inside an argon-filled glovebox, substrate **4** (0.1 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (2.56 mg, 0.005mmol, 0.05equiv.) were dissolved in CH_2Cl_2 (0.5 ml) in a 4-ml screw-cap vial equipped with a magnetic stir bar. The silane was added dropwise to the solution, the vial was then closed and the reaction mixture was stirred for another 24h before it was quenched with TBAF solution (150 µl, 0.15 mmol, 1.5 equiv.). The yield of the corresponding products **5** and remaining starting materials was determined by ^{1}H-NMR analysis of the crude-reaction mixture using CH_2Br_2 as the analytical standard.

The conversions of the corresponding para-substituted aryl diols were determined by ^{1}H NMR analysis of the crude mixtures using CH_2Br_2 as an internal standard. The relative rate ratios (k_X/k_H) were calculated from the conversion ratios of the corresponding deoxygenated products ($5_X/5_H$) obtained under identical reaction conditions. Plotting $\log(k_X/k_H)$ against the σ^+ constants of the substituents afforded a linear correlation ($\rho = -0.31$, $R^2 = 0.946$),[9] indicating a modest negative ρ value consistent with a slight accumulation of positive charge at the benzylic position in the rate-determining step (Table S9).

Entry	R	4x	5x, yield[a]	σ^+	k_x/k_H	$\log(k_x/k_H)$
1	OMe	4a	**5a**, 66%	-0.778	1.98	+0.2968
2	Me	4b	**5b**, 46%	-0.311	1.13	+0.0535
3	H	4c	**5c**, 42%	0.00	1.00	0.0000
4	Cl	4d	**5d**, 40%	+0.114	0.94	-0.0279
5	CF_3	4e	**5e**, 32%	+0.612	0.708	-0.1500

Table S9. Hammett σ^+ parameters for *para*-substituted aryl diols and the relative rate ratios (k_x/k_H) in the $B(C_6F_5)_3$-catalyzed deoxygenation reaction. [a]Yield was determined by ^{1}H NMR using CH_2Br_2 as the internal standard. Hammett σ^+ values were taken from the literature.[9]

7.2. Hammett plot

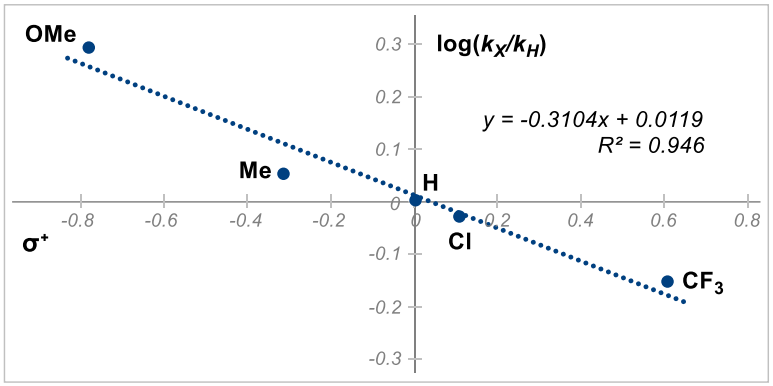


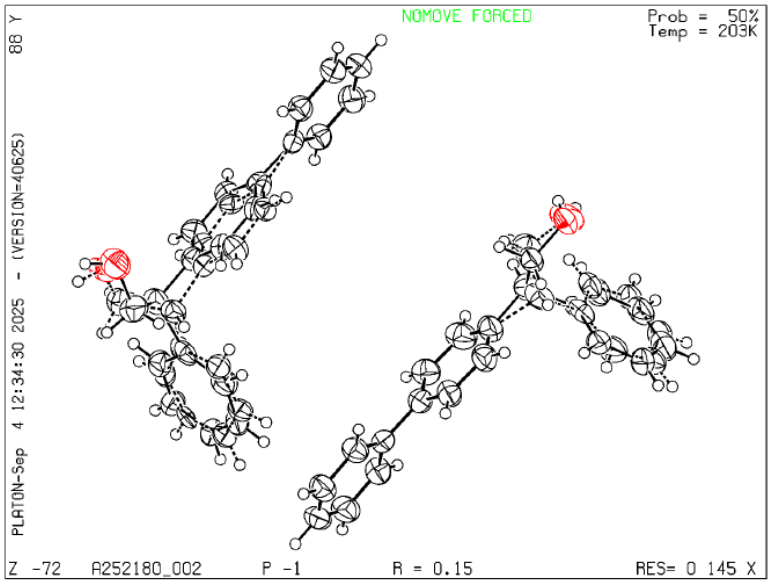
Figure S5. Hammett plot of log (k_x/k_H) versus σ^+ constants for para-substituted aryl diols.

7.3. Substrates Used in the Hammett Study Characterization

Spectral data for the substrates and products used in the Hammett study are available in the previously reported work: **4a**, [10] **4b**, [11] **4c**, [12] **4d**, [11] **4e**, [13] **5a**, [14] **5b**, [15] **5c**, [16] **5d**, [17] **5e**. [17]

8. Crystallography Information

Crystallographic data of **2g** (CCDC 2501997)



Empirical formula	C_{20} H_{18} O	
Formula weight	274.34	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 6.0056(4) Å	α = 92.939(4)°
	b = 15.2590(10) Å	β = 94.439(4)°
	c = 16.5611(10) Å	γ = 98.901(4)°
Volume	1491.79(17) $Å^3$	
Z	4	
Density (calculated)	1.222 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	584	
Crystal size	0.141 x 0.056 x 0.018 mm^3	
Theta range for data collection	2.472 to 25.189°.	
Index ranges	–7<=h<=7, –18<=k<=18, –19<=l<=19	
Reflections collected	19887	
Independent reflections	5264 [R(int) = 0.1192]	
Completeness to theta = 25.189°	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6521	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5264 / 918 / 493	
Goodness-of-fit on F^2	1.177	
Final R indices [I>2sigma(I)]	R1 = 0.1494, wR2 = 0.1711	
R indices (all data)	R1 = 0.2874, wR2 = 0.2058	
Extinction coefficient	0.0021(4)	
Largest diff. peak and hole	0.198 and –0.200 $e \cdot Å^{-3}$	

9. Computational Data

9.1. General details

All calculations were conducted using density functional theory (DFT)[18] implemented in Gaussian 09 suite of program.[19] All molecular structures were optimized by B3LYP-D3 functional[20] with 6-31G** basis set[21]. Vibrational frequency calculations were carried out at the same level of theory as the geometry optimizations, wherein thermochemistry correction energy (G – E) was acquired. The single-point calculations of the optimized geometries were performed with B3LYP-D3 functional and the 6-311+G** basis set. The solvent effect was reflected by using the SMD[22] solvation model and carried out at the same level as single-point calculations (solvent = dichloromethane). Finally, to increase the accuracy of the integration grid, we used the int = ultrafine option for all types of calculations. Final solution phase Gibbs free energies (G_{Sol}) were calculated as follows:

$$G_{Sol} = E_{Sol} + (G - E) \quad (1)$$

$$\Delta G_{Sol} = \Sigma G_{Sol} \text{ for products} - \Sigma G_{Sol} \text{ for reactants} \quad (2)$$

9.2. Potential energy surface for BCF-catalyzed silylative deoxgenation pathway

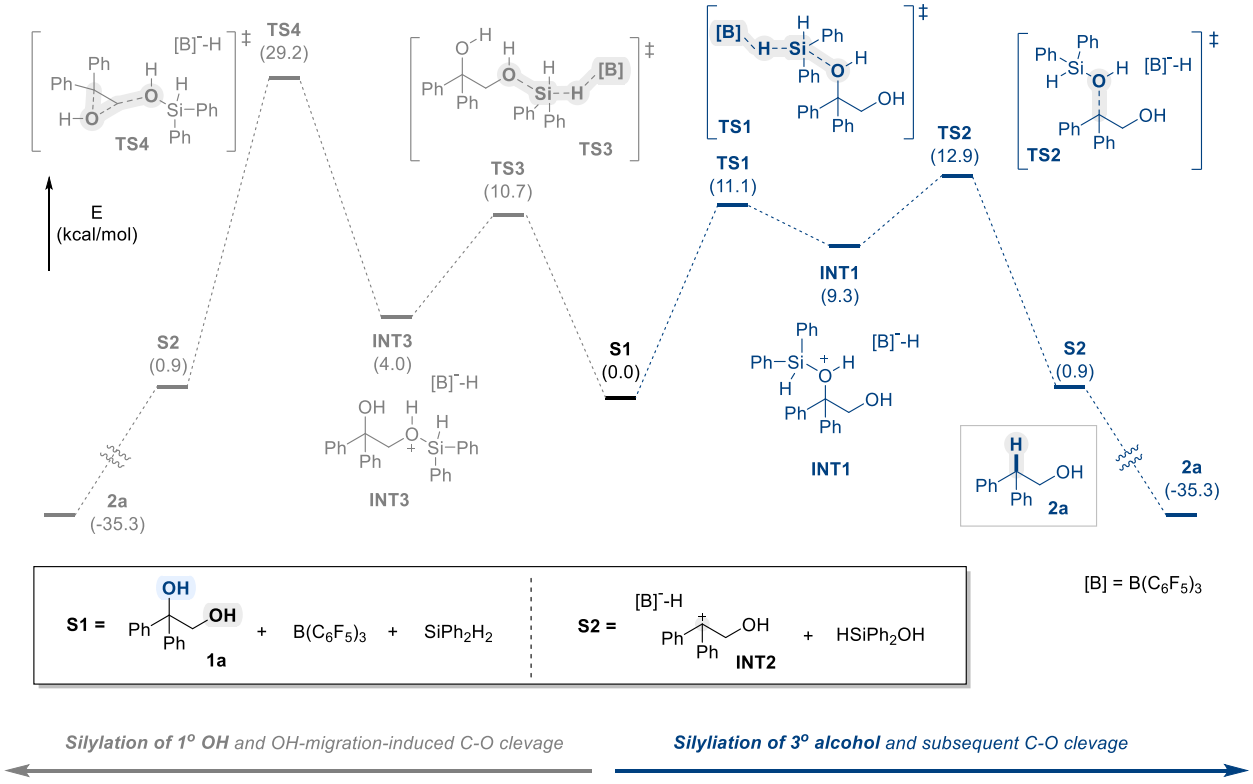


Figure S6. Reaction Energy Profiles for Competing Silylation Pathways of 1º vs 3º Alcohol.

DFT calculation was carried out to examine the mechanistic feasibility of the two competing pathways involving the silylation of either the 1º or the 3º alcohol followed by C–O bond cleavage (Fig. S6). For the 3º alcohol silylation pathway, the initial activation barrier corresponding to transition state **TS1** was calculated to be 11.1 kcal/mol, leading to the formation of the silyloxonium intermediate **INT1** (ΔG = 9.3 kcal/mol). Subsequent cleavage of the C–O bond through **TS2** requires 12.9 kcal/mol, which ultimately delivers the stabilized carbocationic intermediate **S2** (0.9 kcal/mol). This intermediate smoothly collapses to furnish the deoxygenated product **2a**, which is highly exergonic (−35.3 kcal/mol). These results indicate that the silylation of the tertiary hydroxyl group, followed by C–O bond cleavage, is energetically viable and exergonic overall.

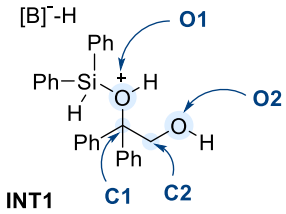
In contrast, the pathway initiated by silylation of the 1º alcohol followed by OH-migration and subsequent C–O cleavage features slightly different energetics. The migration-induced transition state **TS3** requires 10.7 kcal/mol to deliver intermediate **INT3** (4.0 kcal/mol), which is stabilized by a hydrogen-bonded network with the silane species. Progression through **TS4**, however, was found to involve a

substantially higher barrier of 29.2 kcal/mol, rendering this pathway less favorable compared to the tertiary OH silylation route.

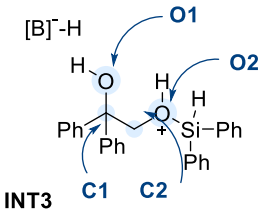
The comparison clearly demonstrates that although both silylation modes can in principle lead to the same product **2a**, the tertiary OH silylation pathway is strongly preferred. The much lower barrier associated with **TS2** (12.9 kcal/mol) relative to **TS4** (29.2 kcal/mol) explains the predominance of the former route. Thus, the calculations support the mechanistic proposal that regioselectivity in this system is controlled at the initial silylation step, favoring the tertiary OH over the primary OH, which in turn directs the subsequent C–O bond cleavage toward the observed deoxygenated product

9.3. Key intermediate Analysis

A) NBO charge analysis

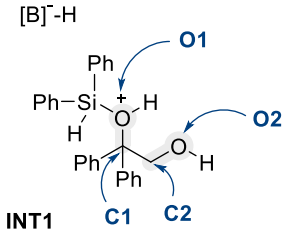


atom	*NBO Charge*
C1	0.30156
C2	-0.05835
O1	-0.90569
O2	-0.74275

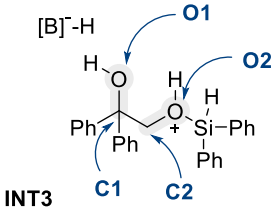


atom	*NBO Charge*
C1	0.22932
C2	-0.04358
O1	-0.76716
O2	-0.80715

B) Bond length analysis



bond	*length*
C1-O1	**1.544 Å**
C2-O2	1.416 Å



bond	*length*
C1-O1	1.445 Å
C2-O2	1.460 Å

Figure S7. Electronic (NBO charge) and Geometric (Bond Length) analysis of **INT1** and **INT3**.

To complement these energetic comparisons, we next examined the electronic and structural features of the silyloxonium intermediates, focusing on the natural bond orbital (NBO) charge distribution and bond metrics at the ionizing C–O bond. The tertiary silyloxonium **INT1** ($\Delta q = 1.208$, defined as $|qC - qO|$) exhibits markedly greater polarization across the C–O bond than the primary-silylated **INT3** ($\Delta q = 0.996$), indicating stronger predisposition toward heterolysis. Notably, the oxygen atom O1 in **INT1** carries a more negative charge (–0.906) compared to O1 in **INT3** (–0.767), while the corresponding C1 is more positively charged (+0.302 vs +0.229). This enhanced charge separation underscores the heightened electrophilicity of C1 in **INT1**, consistent with its ability to undergo facile ionization.

Bond-length analysis further reinforces this interpretation. The cleaving C1–O1 bond in **INT1** is significantly elongated (1.544 Å) relative to the analogous bond in **INT3** (1.445 Å), reflecting its weakened character and advanced progression toward bond rupture. By contrast, **INT3** shows nearly equivalent C–O distances (1.445 and 1.460 Å), indicating more balanced bonding and the absence of a strongly activated cleavage pathway. The elongation in **INT1** is thus diagnostic of selective destabilization of one specific C–O bond, in line with carbocation-directed reactivity.

Taken together, these electronic and structural features reveal that **INT1** is electronically primed and structurally predisposed to undergo direct heterolysis through **TS2**, leading to tertiary carbocation formation. In contrast, **INT3**, with its lower charge polarization, shorter C–O bond, and symmetric bond distribution, lacks such intrinsic activation, necessitating a higher-energy rearrangement pathway via **TS4** to achieve bond cleavage. These observations provide a mechanistic rationale for the divergent selectivity profiles of the two silyloxonium intermediates.

9.4. Energy components of all optimized geometries

Table S10. Summarized energy components of DFT-optimized structures

Optimized Structures	**E_{Sol}** [eV] B3LYP-D3/6-311+G** SMD (dichloromethane)	**G-E** [eV] B3LYP-D3/6-31G** SMD (dichloromethane)	**G_{Sol}** [eV]
1a	-18846.57	5.616	-18840.953
$B(C_6F_5)_3$	-60109.419	2.557	-60106.861
$SiPh_2H_2$	-20522.301	4.343	-20517.958
$HSiPh_2OH$	-22571.496	4.484	-22567.011
INT1	-99479.335	13.968	-99465.368
INT2	-76907.409	8.687	-76898.722
INT3	-99479.452	13.855	-99465.597
2a	-16798.947	5.518	-16793.429
TS1	-99479.119	13.827	-99465.292
TS2	-99479.092	13.881	-99465.211
TS3	-99479.118	13.81	-99465.308
TS4	-99478.437	13.933	-99464.504

9.5. Cartesian coordinates and Vibrational frequencies of all optimized geometries

Table S11. Cartesian Coordinates of the Optimized Geometries

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1a

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C	0.677396	0.562009	1.732806
C	2.150740	0.123297	1.808380
O	2.429624	-0.215985	3.167026
O	0.518904	1.674348	2.616223
C	-0.313548	-0.543328	2.123680
C	0.038166	-1.889273	2.264670
C	-0.928577	-2.844882	2.593341
C	-2.255567	-2.465250	2.787882
C	-2.613133	-1.119558	2.658238
C	-1.649491	-0.169641	2.330427
C	0.413144	1.050363	0.307830
C	0.437510	2.416285	0.005495
C	0.250280	2.850386	-1.308588
C	0.047852	1.926426	-2.334820
C	0.027388	0.561464	-2.038844
C	0.204816	0.127144	-0.725559
H	2.341790	-0.718642	1.128475
H	2.755334	0.976066	1.474244
H	3.382916	-0.171604	3.304929
H	0.892287	1.377448	3.459896
H	1.069812	-2.200784	2.147786
H	-0.637580	-3.885954	2.703091
H	-3.005588	-3.208558	3.043093
H	-3.643886	-0.812414	2.812351
H	-1.917063	0.877722	2.234249
H	0.594859	3.129080	0.806221
H	0.262308	3.914332	-1.529105
H	-0.097664	2.266129	-3.356400
H	-0.135669	-0.165955	-2.829172
H	0.163539	-0.933570	-0.495645

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$B(C_6F_5)_3$

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B	0.134878	0.763411	0.061996
C	0.209754	-0.730311	0.526992
C	-1.233644	1.524510	0.091806
C	1.427879	1.495869	-0.432553
C	-0.835860	-1.639053	0.300088
C	-0.783787	-2.970193	0.697465
C	0.345023	-3.436089	1.369829
C	1.407327	-2.570946	1.627527
C	1.326828	-1.250920	1.199069
C	2.437273	0.833294	-1.148696
C	3.587150	1.468676	-1.603216
C	3.770456	2.822929	-1.327978
C	2.801417	3.524362	-0.612233
C	1.656069	2.859528	-0.189479
C	-2.196201	1.296644	1.087856
C	-3.412363	1.968369	1.135573
C	-3.713290	2.902324	0.145366
C	-2.794341	3.158578	-0.871115
C	-1.580855	2.480357	-0.875829
F	0.408502	-4.706002	1.765387
F	-1.944212	-1.247650	-0.349461
F	-1.799152	-3.802109	0.444953
F	2.486611	-3.016881	2.277991
F	2.376177	-0.461518	1.480552
F	-3.086429	4.049567	-1.823819
F	-4.877106	3.548925	0.170454
F	-4.291294	1.728050	2.113608
F	2.981021	4.821307	-0.342988
F	4.869846	3.445725	-1.748207
F	4.513816	0.798363	-2.295168
F	-0.737545	2.762189	-1.882275
F	-1.957175	0.413733	2.071156
F	0.760470	3.583401	0.501427
F	2.310957	-0.469537	-1.448880

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$SiPh_2H_2$

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Si	1.129534	0.354552	-1.398613
H	2.572066	0.080621	-1.654837
H	0.537511	0.839178	-2.677774
C	0.343880	-1.253026	-0.821887
C	0.944307	-2.492926	-1.104345
C	0.353790	-3.690627	-0.696693
C	-0.851152	-3.669633	0.008444
C	-1.460766	-2.448553	0.305660
C	-0.867389	-1.254110	-0.105336
C	0.885263	1.706872	-0.115666
C	0.663695	3.040141	-0.504222
C	0.503377	4.051589	0.444788
C	0.557051	3.745653	1.806072
C	0.769033	2.426601	2.213670
C	0.930334	1.419323	1.261227
H	1.887999	-2.525668	-1.644223
H	0.835212	-4.637825	-0.924059
H	-1.310700	-4.600361	0.329531
H	-2.395412	-2.427264	0.859434
H	-1.345440	-0.310564	0.146781
H	0.609377	3.293080	-1.560718
H	0.331701	5.075151	0.123083
H	0.429172	4.530689	2.546275
H	0.805531	2.183041	3.271985
H	1.079128	0.394667	1.593320

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$HSiPh_2OH$

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O	2.019253	1.984915	2.601366
Si	0.525529	1.788186	1.872739
H	2.678932	1.313446	2.395378
H	-0.305497	2.837895	2.511697
C	-0.254166	0.119083	2.223832
C	-0.032913	-0.995139	1.392492
C	-0.588939	-2.240153	1.690810
C	-1.383016	-2.393947	2.829506
C	-1.619725	-1.300802	3.666303
C	-1.059827	-0.058750	3.363863
C	0.715244	2.024371	0.020838

C	1.839688	2.699281	-0.488180
C	1.996984	2.906010	-1.859808
C	1.026918	2.441431	-2.750628
C	-0.097149	1.768162	-2.266188
C	-0.248282	1.561056	-0.894185
H	0.568211	-0.884512	0.493016
H	-0.407887	-3.087507	1.035109
H	-1.819433	-3.361495	3.061927
H	-2.241330	-1.416560	4.549925
H	-1.255082	0.785341	4.021743
H	2.599180	3.061437	0.200367
H	2.873689	3.427951	-2.233710
H	1.147176	2.601151	-3.818657
H	-0.851757	1.401905	-2.956952
H	-1.120400	1.021344	-0.532702

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INT1

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C	-0.763779	-1.155540	0.079298
C	0.392916	-2.166905	0.178347
O	-0.238350	0.170256	0.672224
O	1.584326	-1.597250	-0.334056
H	-0.765254	0.974671	0.311045
Si	0.577037	0.594884	2.214164
H	-0.503533	1.131367	3.051460
C	-1.984015	-1.533772	0.906752
C	-2.052009	-2.709817	1.665165
C	-3.178436	-2.984598	2.444818
C	-4.243990	-2.085646	2.482426
C	-4.191265	-0.917174	1.718329
C	-3.074757	-0.648475	0.930478
C	-1.063186	-0.854186	-1.382988
C	-0.241810	0.006797	-2.120327
C	-0.533630	0.278321	-3.455451
C	-1.621117	-0.335516	-4.077579
C	-2.409243	-1.236119	-3.360391
C	-2.135474	-1.493379	-2.018228
C	1.248659	-0.963311	2.970156
C	2.580303	-1.363931	2.745670
C	3.060553	-2.563623	3.271492
C	2.220892	-3.371508	4.044833
C	0.908545	-2.970435	4.306428
C	0.427325	-1.772072	3.776874
C	1.874818	1.799693	1.694460
C	2.677865	1.536910	0.566269
C	3.711613	2.405080	0.219921
C	3.955527	3.544276	0.991110
C	3.163166	3.818286	2.107275
C	2.125987	2.953769	2.458006
H	0.535355	-2.489220	1.209509
H	0.076075	-3.036434	-0.414290
H	2.320662	-1.978521	0.159289
H	-1.238817	-3.425848	1.663302
H	-3.215930	-3.902245	3.024409
H	-5.113832	-2.295234	3.097735
H	-5.012727	-0.209931	1.734057
H	-3.065156	0.243762	0.317466
H	0.598842	0.492307	-1.646618
H	0.087549	0.981100	-4.001934
H	-1.857733	-0.109807	-5.112844
H	-3.256911	-1.719365	-3.836303
H	-2.774948	-2.167987	-1.459427
H	3.241970	-0.726563	2.164503
H	4.088742	-2.863808	3.091036
H	2.594558	-4.305352	4.454708
H	0.261687	-3.589537	4.920943
H	-0.600332	-1.479130	3.973384
H	2.479401	0.660665	-0.044399
H	4.309333	2.209966	-0.664739
H	4.742821	4.234541	0.703887
H	3.337687	4.717008	2.690812
H	1.496552	3.194362	3.308039
C	-2.665047	3.021667	1.749704
B	-1.901608	3.191717	0.311814
C	-0.621707	4.198838	0.250949
C	-2.880500	3.546269	-0.950022
C	-2.072408	3.243646	2.995700
C	-3.959437	2.500289	1.835234
C	-2.697456	3.012683	4.218988
C	-4.627204	2.250112	3.031680
C	-3.995040	2.512407	4.241126
F	-0.781073	3.646396	3.081948
F	-4.628342	2.126247	0.718445
F	-2.046762	3.237080	5.371657
F	-5.856980	1.703753	3.020747
F	-4.611254	2.261287	5.403393
C	0.432683	3.927168	-0.620972
C	-0.513268	5.411972	0.934281
C	1.527400	4.765412	-0.803648
C	0.576542	6.270381	0.804683
C	1.607726	5.942388	-0.070182
F	0.432577	2.783563	-1.352132
F	-1.483959	5.807642	1.778842
F	2.521136	4.432552	-1.646813
F	0.644549	7.408220	1.514464
F	2.680545	6.739389	-0.189384
C	-3.286293	2.584195	-1.872259
C	-3.313276	4.841792	-1.238041
C	-4.014126	2.862751	-3.024753
C	-4.056172	5.172036	-2.371415
C	-4.403597	4.174497	-3.277990
F	-2.986758	1.282149	-1.668111
F	-3.014628	5.857900	-0.403097
F	-4.346373	1.881399	-3.881564
F	-4.436953	6.439095	-2.597392
F	-5.111068	4.472453	-4.376781
H	-1.467230	2.054790	0.054844

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INT2

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C	-0.270626	-0.468845	-0.404345
C	-0.157051	-0.122972	-1.881138
O	-0.841843	1.123947	-2.018292
C	-1.482741	-1.064900	0.051826
C	-2.671370	-1.007589	-0.736531
C	-3.792762	-1.717299	-0.354916
C	-3.758392	-2.530478	0.793659
C	-2.607879	-2.605104	1.580320
C	-1.479832	-1.880155	1.221371
C	0.813544	-0.148393	0.479269
C	2.165276	-0.265169	0.056274
C	3.200701	-0.008107	0.937943

C	2.920188	0.405010	2.246005
C	1.598245	0.566390	2.673230
C	0.553216	0.280254	1.808933
H	0.896576	-0.034035	-2.163512
H	-0.607859	-0.917627	-2.482995
H	-0.690950	1.446035	-2.916756
H	-2.695999	-0.370845	-1.612361
H	-4.696700	-1.664788	-0.952493
H	-4.632441	-3.118239	1.058588
H	-2.555630	-3.259112	2.443175
H	-0.563690	-2.028462	1.776479
H	2.390822	-0.664628	-0.924849
H	4.228107	-0.181175	0.638379
H	3.737884	0.594079	2.934280
H	1.387706	0.907762	3.681313
H	-0.472389	0.431310	2.125203
B	1.383754	-4.059857	1.169798
C	2.816490	-3.986351	0.396925
C	1.449140	-4.873501	2.574791
C	0.129081	-4.506022	0.211575
C	3.820728	-3.180030	0.932371
C	3.134183	-4.574756	-0.825655
C	5.018014	-2.899071	0.281038
C	4.330145	-4.342519	-1.505827
C	5.279500	-3.487992	-0.952354
F	3.634922	-2.581162	2.132043
F	2.255852	-5.400526	-1.435353
F	5.902970	-2.029323	0.813771
F	4.571276	-4.923254	-2.692539
F	6.425652	-3.229821	-1.600427
C	0.616963	-4.530528	3.637859
C	2.301031	-5.948266	2.824782
C	0.623996	-5.170587	4.872464
C	2.352587	-6.619995	4.046026
C	1.507513	-6.226723	5.079462
F	-0.293751	-3.523860	3.496339
F	3.126886	-6.399994	1.856958
F	-0.207579	-4.787867	5.857580
F	3.199255	-7.644739	4.233641
F	1.538224	-6.861092	6.260722
C	-0.152560	-3.760789	-0.934713
C	-0.823560	-5.488101	0.489313
C	-1.284696	-3.910170	-1.724807
C	-1.982588	-5.676193	-0.269521
C	-2.223345	-4.876062	-1.382627
F	0.693310	-2.755508	-1.301294
F	-0.693977	-6.305390	1.552527
F	-1.508928	-3.097165	-2.780240
F	-2.878781	-6.612565	0.073673
F	-3.344608	-5.020914	-2.103121
H	1.149967	-2.900502	1.454820

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INT3

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C	-2.015027	0.073808	2.341340
C	-0.587728	-0.477796	2.577848
O	-2.582397	-0.767488	1.312680
O	-0.131192	-0.908558	1.259250
Si	1.544743	-1.064068	0.617017
H	-0.939654	-1.282691	0.815912
H	2.332474	-1.734613	1.649964
C	-1.935296	1.494649	1.772653
C	-1.377138	2.513737	2.555818
C	-1.251663	3.806055	2.052305
C	-1.690585	4.099322	0.758029
C	-2.257672	3.091597	-0.021464
C	-2.380388	1.792784	0.481890
C	-2.839234	0.009338	3.622465
C	-2.248935	-0.148659	4.882177
C	-3.046615	-0.244438	6.024974
C	-4.435302	-0.184075	5.918855
C	-5.027954	-0.009605	4.665620
C	-4.235219	0.095040	3.525714
C	1.152067	-2.022211	-0.915161
C	1.516164	-1.543991	-2.186407
C	1.237677	-2.293308	-3.330304
C	0.591427	-3.525978	-3.215450
C	0.216800	-4.009726	-1.958734
C	0.494203	-3.265665	-0.813678
C	2.059296	0.703134	0.425859
C	3.295908	1.130821	0.943848
C	3.690589	2.464868	0.834359
C	2.846452	3.391168	0.218255
C	1.609394	2.985786	-0.290675
C	1.220989	1.651292	-0.192386
H	0.115472	0.270926	2.933728
H	-0.567239	-1.355770	3.215756
H	-3.111934	-1.478399	1.706787
H	-1.052304	2.298290	3.570451
H	-0.815308	4.584567	2.670713
H	-1.597215	5.107807	0.365874
H	-2.609636	3.311536	-1.025331
H	-2.823024	1.011143	-0.123300
H	-1.171588	-0.225010	4.992033
H	-2.578530	-0.391012	6.993287
H	-5.053818	-0.283229	6.805158
H	-6.108820	0.034799	4.575553
H	-4.693980	0.228601	2.550807
H	2.017221	-0.584033	-2.282333
H	1.525374	-1.917722	-4.307851
H	0.379683	-4.111152	-4.105735
H	-0.283805	-4.969058	-1.869045
H	0.198250	-3.654008	0.155884
H	3.949529	0.421345	1.445939
H	4.647423	2.782390	1.237858
H	3.148709	4.431838	0.142162
H	0.941577	3.707661	-0.749422
H	0.247459	1.357329	-0.573757
C	0.872503	-5.309664	2.617263
B	0.580365	-3.924133	3.425755
C	1.692588	-3.612036	4.576428
C	-0.963766	-3.829805	3.963268
C	1.805008	-5.334257	1.580605
C	0.227092	-6.524319	2.851545
C	2.058489	-6.450869	0.787564
C	0.451305	-7.671666	2.092304
C	1.373358	-7.633758	1.049357
F	2.513032	-4.215728	1.279499
F	-0.671722	-6.634019	3.851727
F	2.950200	-6.399154	-0.216325
F	-0.207159	-8.811989	2.354859
F	1.598822	-8.725984	0.304189
C	2.174283	-2.326247	4.807559

C	2.251628	-4.594611	5.396516
C	3.154206	-2.013070	5.746587
C	3.234621	-4.336391	6.349215
C	3.692530	-3.032359	6.524648
F	1.682905	-1.262729	4.101460
F	1.830336	-5.870661	5.299791
F	3.576169	-0.746048	5.909114
F	3.738535	-5.322804	7.106238
F	4.635998	-2.761419	7.437779
C	-1.977035	-3.562230	3.047112
C	-1.401776	-3.915619	5.287028
C	-3.305165	-3.342922	3.389526
C	-2.726425	-3.707502	5.677204
C	-3.693154	-3.414465	4.720586
F	-1.681192	-3.426015	1.719452
F	-0.534907	-4.190843	6.278427
F	-4.197020	-2.962356	2.436041
F	-3.076359	-3.757969	6.970882
F	-4.961053	-3.173862	5.077715
H	0.677067	-3.042710	2.602369

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2a

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C	0.782263	0.450777	1.727600
C	2.238734	-0.032821	1.708626
O	2.641363	-0.345616	3.037346
H	0.746790	1.265399	2.463369
C	-0.241340	-0.600621	2.154817
C	0.104853	-1.899392	2.545005
C	-0.881456	-2.822019	2.907109
C	-2.227678	-2.460795	2.892102
C	-2.584465	-1.163356	2.514055
C	-1.600425	-0.248083	2.148212
C	0.460001	1.037083	0.356928
C	0.504848	2.419499	0.141836
C	0.263877	2.955032	-1.125341
C	-0.021089	2.109946	-2.198820
C	-0.067077	0.728249	-1.995731
C	0.169335	0.197659	-0.727924
H	2.323887	-0.903433	1.037459
H	2.859778	0.769264	1.282395
H	3.565417	-0.623245	3.013670
H	1.148019	-2.185297	2.603608
H	-0.590587	-3.825057	3.207456
H	-2.992025	-3.178938	3.175314
H	-3.629625	-0.866538	2.500127
H	-1.885014	0.754021	1.837753
H	0.727809	3.081633	0.975242
H	0.295777	4.031152	-1.271713
H	-0.211203	2.523997	-3.184917
H	-0.293128	0.063551	-2.824924
H	0.111261	-0.875251	-0.567159

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TS1

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C	-2.034526	0.520446	2.062057
C	-0.770239	-0.050313	2.738213
O	-2.666833	-0.663744	1.524480
O	-0.010164	-0.831243	1.834159
Si	2.650927	-1.550625	1.159929
H	-0.650758	-1.363289	1.336169
H	2.340275	-2.221529	2.441175
C	-1.757885	1.504803	0.922790
C	-0.472202	1.896385	0.535907
C	-0.293569	2.775264	-0.536024
C	-1.392738	3.272747	-1.235483
C	-2.682024	2.899660	-0.846882
C	-2.859906	2.030707	0.228089
C	-2.903509	1.167234	3.142493
C	-3.993675	0.484398	3.689922
C	-4.746589	1.063412	4.714187
C	-4.409901	2.324227	5.208405
C	-3.316040	3.007508	4.670491
C	-2.569561	2.433726	3.642228
C	1.687854	-2.127124	-0.341273
C	0.850589	-1.254864	-1.061084
C	0.216397	-1.672837	-2.231609
C	0.403416	-2.973794	-2.704004
C	1.219453	-3.857831	-1.995473
C	1.859433	-3.436038	-0.828435
C	2.786707	0.304591	1.367876
C	2.717057	0.866903	2.655298
C	2.878191	2.239004	2.854049
C	3.121381	3.078361	1.764813
C	3.193800	2.538840	0.478496
C	3.024397	1.166943	0.281944
H	-0.130167	0.755187	3.107246
H	-1.100004	-0.648152	3.599298
H	-3.155389	-0.410815	0.731280
H	0.398039	1.514361	1.051882
H	0.714625	3.062543	-0.817070
H	-1.249019	3.953102	-2.069851
H	-3.547476	3.295217	-1.370750
H	-3.867552	1.779577	0.553110
H	-4.243871	-0.497781	3.304805
H	-5.596017	0.526081	5.126733
H	-4.995475	2.773423	6.005392
H	-3.048527	3.990784	5.046993
H	-1.731272	2.975229	3.212453
H	0.690994	-0.243226	-0.704477
H	-0.418355	-0.979608	-2.776656
H	-0.082421	-3.296912	-3.620313
H	1.369493	-4.870892	-2.358513
H	2.513829	-4.128209	-0.307852
H	2.540252	0.223923	3.513321
H	2.828947	2.650561	3.857848
H	3.260390	4.144464	1.917844
H	3.389799	3.185959	-0.372192
H	3.079753	0.769408	-0.724322
B	5.858294	-2.225558	0.342300
H	4.066542	-2.019180	0.857975
C	5.476981	-2.828610	-1.070058
C	6.194465	-0.692357	0.519296
C	6.204514	-3.214300	1.530627
C	5.838244	-4.121656	-1.475171
C	4.666769	-2.133442	-1.977551
C	6.673990	0.124463	-0.511601
C	5.982008	-0.043192	1.744139
C	5.408173	-4.322146	1.838752
C	7.327176	-3.039372	2.347026
C	5.675947	-5.190639	2.889560
F	4.300984	-4.579555	1.111101

C	6.808113	-4.976036	3.673805
F	4.869261	-6.226401	3.148880
C	7.641914	-3.895276	3.399367
F	7.091276	-5.803729	4.681610
F	8.733390	-3.688781	4.145655
F	8.174399	-2.017383	2.129237
C	5.410147	-4.690998	-2.671671
F	6.640754	-4.882944	-0.711211
C	4.580446	-3.962749	-3.520498
F	5.784835	-5.930716	-3.009876
C	4.204600	-2.668711	-3.171832
F	4.141526	-4.505288	-4.657844
F	3.386830	-1.971056	-3.966112
F	4.244854	-0.889637	-1.681241
C	6.897915	1.489569	-0.356173
F	6.948746	-0.394399	-1.721110
C	6.648493	2.088680	0.875855
F	7.346730	2.230036	-1.377968
C	6.194799	1.314641	1.940040
F	6.839463	3.399960	1.035403
F	5.947691	1.885777	3.124300
F	5.496285	-0.731327	2.795714

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TS2

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C	-0.321122	-1.211230	-0.610621
C	1.106153	-1.691496	-0.846735
O	0.436522	0.307625	0.600134
O	1.959687	-0.702437	-1.386207
H	1.188724	0.574737	0.045408
Si	0.707727	0.709543	2.254029
H	-0.256481	1.700796	2.745834
C	-1.191306	-1.954554	0.268545
C	-0.738745	-3.086148	0.992170
C	-1.608636	-3.780284	1.815976
C	-2.936298	-3.351454	1.954150
C	-3.394569	-2.229321	1.261950
C	-2.531618	-1.527882	0.429352
C	-0.913633	-0.446486	-1.738228
C	-0.540174	0.858717	-2.112051
C	-1.034330	1.418063	-3.288113
C	-1.882162	0.686665	-4.122404
C	-2.273442	-0.600347	-3.753220
C	-1.807799	-1.159820	-2.566180
C	0.570609	-0.880706	3.231705
C	1.606422	-1.835869	3.207910
C	1.503221	-3.030777	3.920757
C	0.361342	-3.288194	4.685017
C	-0.670940	-2.349697	4.728656
C	-0.568892	-1.157511	4.008854
C	2.416694	1.460092	2.213579
C	3.499935	0.842558	1.557334
C	4.760474	1.439085	1.535194
C	4.958678	2.670808	2.164360
C	3.892803	3.307828	2.802640
C	2.632378	2.709248	2.822771
H	1.565182	-2.006195	0.090345
H	1.026951	-2.571480	-1.506156
H	1.606441	-0.413040	-2.241542
H	0.287493	-3.422292	0.917330
H	-1.252107	-4.639058	2.373119
H	-3.609227	-3.889604	2.615147
H	-4.415546	-1.885569	1.381077
H	-2.878345	-0.638678	-0.080130
H	0.033983	1.477348	-1.438542
H	-0.779128	2.443290	-3.534666
H	-2.272174	1.132743	-5.031352
H	-2.975121	-1.154748	-4.366837
H	-2.122494	-2.158365	-2.284223
H	2.516639	-1.636071	2.646997
H	2.315896	-3.751668	3.894590
H	0.282176	-4.213568	5.249177
H	-1.562821	-2.543121	5.317806
H	-1.394430	-0.456619	4.039132
H	3.362416	-0.102654	1.035714
H	5.584143	0.949402	1.023451
H	5.938976	3.138483	2.145201
H	4.038556	4.275680	3.273157
H	1.805532	3.233843	3.291890
H	-2.272328	1.504529	0.027159
B	-3.164985	2.312921	0.157250
C	-3.784491	2.510867	-1.337804
C	-4.229459	1.654503	1.217678
C	-2.511583	3.647864	0.832719
C	-3.664856	3.651809	-2.131916
C	-4.387805	1.429093	-1.978986
C	-5.620165	1.767097	1.179448
C	-3.747503	0.892553	2.276550
C	-1.138739	3.852719	0.931147
C	-3.288531	4.642640	1.429657
C	-0.557311	4.911655	1.624851
F	-0.261814	2.986906	0.350691
C	-1.375368	5.862685	2.224032
F	0.783561	5.014474	1.730637
C	-2.758523	5.731800	2.117225
F	-0.839370	6.893548	2.895068
F	-3.557692	6.651505	2.680916
F	-4.634055	4.569383	1.358422
C	-4.090482	3.715602	-3.461191
F	-3.094107	4.776462	-1.649270
C	-4.673256	2.599986	-4.050701
F	-3.925918	4.838098	-4.181120
C	-4.829077	1.441844	-3.295020
F	-5.043808	2.621950	-5.342096
F	-5.330314	0.330184	-3.867944
F	-4.522772	0.244027	-1.323353
C	-6.466493	1.147547	2.099951
F	-6.217505	2.487481	0.212262
C	-5.925806	0.379535	3.129968
F	-7.799000	1.281375	2.008435
C	-4.543728	0.248991	3.217915
F	-6.725759	-0.229598	4.018813
F	-3.988747	-0.512163	4.186248
F	-2.407406	0.707766	2.412520

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TS3

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C	-1.871341	0.853638	2.405684
C	-0.450683	0.610828	2.957517
O	-2.484839	-0.450122	2.528399
O	0.183445	-0.464811	2.290000
Si	2.684606	-1.411524	1.338299

H	-0.492306	-1.154550	2.194186
H	2.719994	-1.529289	2.812391
C	-1.918075	1.296733	0.941172
C	-0.776129	1.520315	0.165461
C	-0.894971	1.894275	-1.176007
C	-2.151907	2.048376	-1.760147
C	-3.298992	1.842807	-0.989163
C	-3.179800	1.479372	0.350943
C	-2.566926	1.876461	3.306094
C	-3.460269	1.466469	4.300237
C	-4.047937	2.405394	5.151295
C	-3.739477	3.760376	5.024197
C	-2.840704	4.174604	4.037610
C	-2.260440	3.238803	3.182416
C	1.466802	-2.519939	0.442757
C	0.427766	-1.990899	-0.344855
C	-0.411436	-2.827955	-1.081110
C	-0.231020	-4.212316	-1.041261
C	0.786039	-4.756389	-0.254402
C	1.629779	-3.917232	0.475915
C	2.706847	0.377456	0.788911
C	2.867919	1.395682	1.745890
C	2.955060	2.736135	1.366871
C	2.889958	3.085424	0.016317
C	2.729210	2.088678	-0.948822
C	2.635013	0.749237	-0.566011
H	0.172752	1.499790	2.831605
H	-0.546785	0.409317	4.033542
H	-3.133523	-0.546197	1.820090
H	0.210724	1.392506	0.589114
H	0.006758	2.059699	-1.756883
H	-2.239442	2.335829	-2.803889
H	-4.283937	1.978661	-1.426570
H	-4.076366	1.364659	0.956840
H	-3.689158	0.411028	4.396275
H	-4.746291	2.075456	5.915422
H	-4.196531	4.489748	5.686753
H	-2.597098	5.227737	3.929383
H	-1.576777	3.565628	2.403672
H	0.271176	-0.918602	-0.382554
H	-1.201428	-2.396981	-1.689991
H	-0.877902	-4.864043	-1.621661
H	0.931946	-5.832553	-0.220182
H	2.433723	-4.356926	1.057851
H	2.931344	1.137201	2.799474
H	3.087981	3.505229	2.122039
H	2.970706	4.126312	-0.282613
H	2.684916	2.353623	-2.001773
H	2.506380	-0.007855	-1.330108
H	4.033382	-1.972405	0.913271
B	5.674118	-2.385673	0.106100
C	5.914401	-0.908475	-0.399292
C	6.356916	-2.836258	1.462824
C	5.037576	-3.486813	-0.835399
C	6.086290	-0.563653	-1.745101
C	5.925014	0.169030	0.498306
C	7.614754	-2.368894	1.858990
C	5.743317	-3.726185	2.350463
C	3.992657	-3.190285	-1.720678
C	5.400486	-4.840621	-0.787151
C	3.319025	-4.143159	-2.472060
F	3.550164	-1.923706	-1.834208
C	3.708672	-5.475889	-2.376213
F	2.291505	-3.799495	-3.254669
C	4.762308	-5.826196	-1.535756
F	3.070913	-6.413516	-3.079498
F	5.148968	-7.104878	-1.451013
F	6.411060	-5.254539	-0.003203
C	6.226370	0.751516	-2.179316
F	6.129031	-1.516232	-2.692943
C	6.206153	1.786238	-1.247650
F	6.376781	1.030192	-3.480669
C	6.063024	1.493470	0.105596
F	6.318980	3.053823	-1.650080
F	6.036167	2.483882	1.004511
F	5.741802	-0.049642	1.815100
C	8.225107	-2.748487	3.051668
F	8.305241	-1.523331	1.072913
C	7.565244	-3.626055	3.907811
F	9.434384	-2.278997	3.380509
C	6.308705	-4.117424	3.557705
F	8.132699	-3.996648	5.057407
F	5.668112	-4.959964	4.376594
F	4.527251	-4.235252	2.061263

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TS4

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C	-0.970884	0.469605	2.128958
C	0.332301	0.264644	2.769686
O	-0.789077	1.640967	3.065552
O	1.193837	-1.612668	1.986518
Si	2.509414	-1.496947	0.893863
H	1.440314	-2.018252	2.838170
H	3.511010	-2.489784	1.339037
C	-2.124604	-0.404270	2.527452
C	-1.932745	-1.685825	3.055432
C	-3.034872	-2.442625	3.460001
C	-4.323307	-1.922576	3.336878
C	-4.517530	-0.646958	2.796337
C	-3.422750	0.109128	2.386422
C	-0.939644	0.959824	0.703847
C	-0.641865	2.289794	0.387504
C	-0.523013	2.672514	-0.949407
C	-0.672980	1.729356	-1.968285
C	-0.965712	0.401414	-1.650103
C	-1.113378	0.019975	-0.317712
C	1.781516	-1.892929	-0.779087
C	2.307518	-1.357323	-1.967591
C	1.754371	-1.681038	-3.208061
C	0.666409	-2.553725	-3.281004
C	0.134262	-3.102829	-2.110748
C	0.688756	-2.774501	-0.873198
C	3.182425	0.238894	1.022873
C	4.053960	0.556912	2.084850
C	4.412870	1.880633	2.343236
C	3.907063	2.909653	1.544772
C	3.046162	2.613751	0.484950
C	2.684956	1.289836	0.227162
H	1.199355	0.780740	2.386972
H	0.390627	-0.221675	3.730330
H	-1.151627	1.421400	3.948541
H	-0.939136	-2.105959	3.137171
H	-2.873206	-3.427997	3.882855

H	-5.177709	-2.509665	3.660000
H	-5.520447	-0.243747	2.695307
H	-3.564360	1.098048	1.959736
H	-0.497457	3.016688	1.177928
H	-0.301601	3.707623	-1.191713
H	-0.560961	2.027360	-3.006466
H	-1.061808	-0.344986	-2.431051
H	-1.337103	-1.011195	-0.070098
H	3.149816	-0.671455	-1.926639
H	2.171043	-1.253403	-4.115553
H	0.236631	-2.808290	-4.245844
H	-0.709723	-3.784910	-2.164092
H	0.259617	-3.192320	0.033833
H	4.425938	-0.228174	2.736241
H	5.057573	2.109209	3.184390
H	4.174889	3.940319	1.759755
H	2.642568	3.411680	-0.131895
H	1.988416	1.080554	-0.579869
H	2.105833	-1.089479	4.305844
C	2.123242	0.746941	5.609339
C	0.827033	-1.645685	6.137463
C	3.488717	-1.606969	6.037073
C	3.293876	1.499741	5.461534
C	0.970548	1.531018	5.627964
C	0.174744	-1.282742	7.319531
C	0.290757	-2.766673	5.508535
C	4.364921	-2.262715	5.175127
C	3.856292	-1.634267	7.381669
C	3.321084	2.887986	5.346306
F	4.492771	0.887258	5.343190
C	0.938058	2.915666	5.503921
F	-0.274293	0.941858	5.661524
C	-0.929033	-1.963987	7.829752
F	0.572480	-0.196534	8.005256
C	-0.812839	-3.476357	5.971803
F	0.818252	-3.218170	4.328304
C	5.527608	-2.904416	5.594945
F	4.128102	-2.287157	3.834915
C	5.006468	-2.263574	7.852818
F	3.077791	-1.021966	8.297697
C	5.849107	-2.906337	6.949266
F	6.336429	-3.515468	4.714116
F	6.960812	-3.519010	7.379021
F	5.311231	-2.257809	9.159572
C	2.132731	3.611561	5.365187
F	4.485655	3.530504	5.155778
F	2.138803	4.942826	5.221169
F	-0.239830	3.563677	5.461956
C	-1.432080	-3.069775	7.147603
F	-1.525558	-1.557401	8.959462
F	-2.504759	-3.725533	7.609976
F	-1.306471	-4.518923	5.274036
B	2.130185	-0.890063	5.500359

Table S12. Vibrational Frequencies of All Optimized Geometries

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1a

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33.74 35.91 65.18 112.59 137.68 207.25
234.25 244.00 245.19 296.25 331.31 352.92
366.85 412.37 417.05 439.75 473.20 534.78
558.32 606.01 633.54 633.80 665.29 711.16
717.72 728.75 771.92 784.05 854.64 866.98
893.27 925.61 934.39 969.39 971.12 981.76
995.65 1000.60 1016.76 1018.12 1045.53 1059.34
1067.38 1085.62 1097.05 1116.19 1156.58 1194.38
1195.14 1198.63 1201.54 1218.57 1222.56 1263.27
1301.96 1342.51 1347.79 1363.28 1367.67 1390.46
1442.67 1488.72 1491.48 1525.38 1538.08 1539.74
1639.23 1639.97 1659.27 1662.93 3017.06 3065.14
3175.30 3175.53 3184.35 3185.60 3194.70 3199.24
3204.45 3210.44 3217.97 3229.93 3774.13 3842.43

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$B(C_6F_5)_3$

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22.25 22.39 36.07 36.78 36.83 45.39
111.12 116.92 117.06 134.52 134.59 134.66
150.96 151.05 165.18 167.38 172.21 172.27
232.46 234.04 234.15 268.69 268.76 268.77
277.80 277.86 278.85 315.66 316.01 316.10
349.26 349.33 356.34 356.94 390.42 390.54
403.98 404.04 405.07 443.58 445.30 445.30
473.65 473.68 497.96 546.81 578.57 578.59
582.76 620.05 620.07 632.06 651.65 651.67
655.68 655.72 659.23 686.03 686.14 708.39
786.31 786.35 786.81 869.13 1000.32 1001.32
1001.33 1040.68 1040.73 1140.13 1173.28 1178.15
1178.17 1201.84 1201.93 1327.97 1333.28 1333.32
1340.24 1355.30 1355.33 1411.87 1411.98 1431.83
1507.03 1520.32 1520.42 1558.71 1558.72 1559.97
1653.52 1656.28 1656.29 1678.94 1678.96 1680.57

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$SiPh_2H_2$

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20.37 36.30 57.19 152.39 160.56 200.78
242.76 393.76 404.01 408.06 423.58 430.93
480.68 610.25 632.83 632.87 697.07 709.00
711.92 716.59 726.57 759.17 779.55 866.64
873.75 874.62 937.25 939.20 975.06 982.65
984.18 1006.12 1006.44 1013.14 1013.65 1052.92
1054.00 1105.81 1107.23 1131.35 1136.34 1196.95
1196.98 1222.07 1223.54 1317.76 1322.17 1362.47
1363.58 1468.50 1471.44 1527.84 1528.69 1623.63
1624.83 1646.95 1647.03 2215.54 2221.25 3167.09
3167.17 3170.92 3171.85 3181.85 3182.22 3192.05
3192.24 3203.37 3203.70

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$HSiPh_2OH$

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27.45 43.82 65.44 105.90 130.84 170.41
191.54 244.56 273.09 316.04 396.09 405.12
411.35 444.60 487.63 498.51 632.05 633.04
694.27 712.70 716.59 720.26 752.68 757.19
815.51 832.94 875.29 878.23 884.17 917.44
940.88 945.24 986.23 990.15 1008.12 1009.09

1012.57 1013.42 1053.37 1054.13 1104.50 1107.18
1133.81 1140.07 1196.52 1197.11 1219.77 1222.69
1317.44 1321.99 1361.19 1363.27 1467.73 1470.58
1526.63 1528.00 1622.73 1623.85 1647.06 1647.65
2260.62 3166.64 3168.94 3170.49 3173.81 3181.54
3183.14 3191.93 3192.31 3203.01 3203.46 3880.71

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INT1

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12.37 15.01 23.20 25.70 29.79 34.92
37.49 39.98 44.82 48.73 50.63 52.05
56.59 60.04 62.40 78.37 82.59 85.90
89.26 97.98 105.18 110.57 112.66 118.16
121.81 127.78 131.41 134.58 142.26 145.95
148.00 158.58 162.60 171.40 175.53 179.57
180.50 187.56 192.84 202.80 207.81 231.88
233.39 241.13 242.21 250.58 254.97 266.17
266.69 266.92 277.46 280.28 285.90 302.26
306.38 312.19 318.43 323.31 332.41 338.40
348.63 349.38 358.39 368.47 372.30 378.00
402.58 404.50 406.13 408.88 411.05 412.47
414.57 417.28 421.11 425.87 450.21 452.36
452.67 453.19 470.92 473.35 481.58 482.95
489.63 515.04 532.11 563.18 577.57 580.57
584.55 603.23 606.49 611.19 625.07 629.65
630.11 631.29 631.99 633.69 634.04 641.82
648.36 652.82 653.91 669.42 669.88 674.88
705.95 708.08 712.33 713.97 716.69 718.25
719.78 726.62 751.27 752.25 754.02 759.25
769.96 772.34 779.51 792.38 805.49 823.95
855.33 861.68 861.87 879.91 882.59 885.14
919.71 926.47 935.60 940.54 950.53 952.79
955.04 976.09 981.78 989.51 994.86 995.65
996.70 998.25 999.40 1009.40 1012.69 1014.75
1017.46 1018.57 1019.40 1041.20 1043.88 1043.92
1051.57 1053.09 1055.83 1069.56 1072.41 1089.16
1109.72 1111.15 1112.50 1114.20 1127.26 1128.26
1134.79 1136.00 1137.64 1148.05 1148.96 1156.78
1161.58 1199.95 1200.03 1202.03 1204.06 1212.10
1224.57 1227.56 1230.99 1235.93 1245.30 1299.38
1311.68 1313.23 1315.35 1317.96 1322.53 1325.60
1328.03 1333.72 1335.76 1346.73 1352.45 1366.79
1371.79 1373.44 1377.33 1407.32 1414.45 1422.85
1442.98 1465.78 1469.71 1471.87 1489.61 1492.14
1496.48 1505.14 1515.72 1526.58 1530.28 1533.60
1540.22 1547.42 1551.46 1553.35 1555.63 1621.21
1623.11 1637.37 1641.03 1644.66 1647.14 1656.01
1659.24 1660.50 1660.98 1662.98 1678.03 1678.96
1681.14 2158.67 2356.73 2767.12 3028.62 3140.51
3178.13 3183.81 3187.31 3187.36 3187.94 3191.80
3193.69 3198.26 3200.76 3202.78 3203.89 3208.42
3210.74 3212.48 3215.92 3218.65 3221.01 3232.02
3252.60 3268.10 3837.95

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INT2

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14.07 22.99 26.59 29.52 30.91 37.02
41.55 47.65 53.87 59.67 61.96 78.58
91.66 103.55 104.40 109.78 117.46 120.78
129.33 132.28 135.67 147.23 149.78 154.55
156.14 159.18 173.59 179.64 185.41 194.23
225.86 232.40 234.65 237.80 244.18 265.71
266.48 268.20 276.77 277.51 284.31 297.51
311.70 313.75 319.31 320.50 345.91 346.83
349.57 353.80 360.32 383.89 384.94 405.96
406.77 409.61 414.92 427.79 441.65 447.62
448.26 448.88 465.07 469.95 472.13 488.49
540.94 560.94 575.16 575.63 580.44 600.45
602.20 603.30 621.07 622.21 623.95 630.35
632.41 649.54 650.12 651.78 673.67 680.82
689.42 693.30 703.64 714.01 741.16 765.62
770.30 787.98 789.73 816.74 849.54 852.19
871.55 885.58 926.15 937.50 959.00 982.85
987.02 991.09 992.94 996.52 1005.27 1008.43
1014.36 1025.65 1035.15 1041.72 1048.73 1053.65
1064.36 1086.04 1087.94 1101.77 1107.12 1131.66
1133.07 1142.45 1147.19 1147.34 1152.45 1156.01
1206.30 1209.01 1226.61 1236.15 1244.62 1269.70
1307.37 1310.51 1314.30 1320.89 1332.91 1336.68
1338.62 1339.23 1375.85 1383.85 1389.20 1395.39
1412.42 1417.76 1438.53 1463.07 1484.73 1490.75
1495.56 1506.95 1508.94 1530.00 1534.30 1544.98
1546.72 1551.17 1556.13 1601.07 1606.71 1641.27
1650.48 1654.68 1657.53 1660.13 1668.45 1674.26
1678.56 2420.36 3064.17 3116.43 3198.90 3202.22
3214.24 3214.62 3223.82 3227.25 3231.06 3237.26
3238.04 3253.43 3818.56

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INT3

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6.90 9.93 16.54 17.64 22.82 23.75
25.77 29.70 32.00 37.44 39.07 42.69
46.14 48.69 54.64 58.16 59.65 63.92
76.59 80.62 84.30 93.40 97.40 108.01
117.07 126.22 131.78 136.61 138.84 145.22
148.98 151.75 152.87 170.87 174.30 175.76
179.36 185.84 191.64 212.79 226.95 231.74
234.53 237.23 245.43 264.94 266.37 266.64
266.74 276.51 278.79 280.33 289.41 311.34
312.04 315.71 316.80 344.38 344.89 345.49
354.51 356.24 362.00 375.75 389.04 390.06
402.34 405.06 405.54 407.11 408.53 410.67
411.49 415.04 447.61 448.46 449.23 451.56
464.80 467.12 470.68 471.59 487.36 497.60
509.54 518.14 554.40 562.04 574.34 575.28
581.12 599.93 602.75 619.41 622.27 628.86
629.77 630.77 631.71 633.09 633.63 637.68
648.70 648.91 649.82 678.59 687.56 693.69
704.02 706.74 709.13 710.14 715.57 717.44
721.79 730.48 742.21 747.26 758.92 760.12
764.63 767.51 773.04 793.02 794.40 840.13
857.49 860.63 865.43 870.96 872.50 881.38
928.60 931.74 935.52 937.04 943.69 955.81
976.42 978.71 980.76 982.38 985.07 985.87
994.62 999.12 1001.43 1003.73 1010.83 1011.51
1013.00 1014.68 1016.42 1018.45 1018.88 1052.26
1053.34 1053.97 1062.61 1074.23 1089.21 1104.29
1105.53 1110.09 1110.72 1111.54 1120.27 1136.77
1138.18 1145.42 1147.55 1149.27 1150.49 1157.40
1157.81 1193.98 1197.32 1199.97 1200.66 1201.22
1215.83 1223.37 1225.27 1227.24 1230.84 1243.70
1303.83 1313.26 1315.27 1318.65 1323.99 1325.99
1332.89 1335.01 1340.03 1345.92 1350.96 1365.04

1366.36 1370.57 1373.82 1387.63 1403.12 1407.32
1417.12 1444.21 1469.85 1471.59 1488.75 1492.41
1499.71 1504.47 1509.21 1522.28 1528.17 1529.78
1538.40 1543.09 1548.15 1549.28 1551.86 1622.73
1624.01 1639.42 1640.78 1647.15 1647.75 1655.83
1658.87 1658.99 1659.31 1662.78 1674.69 1676.60
1678.79 2393.17 2485.96 3153.53 3174.37 3177.24
3177.62 3184.38 3186.23 3187.80 3188.25 3192.50
3192.70 3196.77 3198.55 3201.01 3204.76 3207.24
3208.49 3208.98 3214.64 3214.84 3217.96 3231.39
3232.09 3346.26 3762.48
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2a
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25.89 37.42 69.09 109.29 151.59 207.29
237.89 251.23 272.99 305.82 331.04 414.93
417.68 445.85 487.67 546.47 608.59 634.35
636.44 648.73 714.68 717.82 751.23 774.45
803.64 860.55 862.53 867.60 926.20 932.15
974.21 974.67 996.06 997.29 1007.05 1016.61
1018.07 1053.03 1059.86 1064.40 1091.40 1112.91
1129.47 1194.60 1195.45 1202.50 1214.29 1217.65
1227.83 1247.00 1259.01 1293.22 1346.89 1356.00
1364.17 1372.24 1377.05 1458.58 1491.90 1495.15
1536.06 1538.83 1542.88 1637.11 1640.81 1659.54
1663.97 2980.42 3018.52 3037.77 3169.73 3172.01
3177.63 3179.45 3187.13 3189.85 3195.42 3202.34
3205.55 3228.83 3825.97
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TS1
==========
-25.17 6.96 11.73 16.14 20.21 25.79
29.49 31.33 34.84 36.63 39.94 43.86
50.62 52.20 55.69 60.18 63.03 67.47
72.05 82.46 88.38 89.02 94.98 111.31
115.94 123.82 127.88 130.41 137.32 141.58
150.24 155.14 160.93 166.77 167.75 170.32
176.50 179.14 186.15 198.48 208.42 236.23
237.51 239.19 240.64 243.55 247.92 258.74
267.55 268.14 268.34 272.35 278.17 278.91
280.59 301.87 314.20 315.95 318.29 333.61
339.31 348.42 348.86 350.60 358.31 376.18
393.62 394.85 404.94 405.47 409.04 409.39
410.40 413.48 416.80 419.06 437.37 440.71
445.31 447.80 449.57 455.39 474.34 475.42
484.82 488.37 498.70 514.76 534.80 568.62
579.07 580.16 584.43 605.77 616.68 617.91
622.73 632.09 633.00 633.42 634.46 637.42
649.76 651.15 653.73 656.19 659.01 671.56
687.98 693.58 698.95 700.77 710.08 714.42
718.31 719.64 720.30 731.18 744.19 759.01
773.97 774.98 782.40 784.13 785.21 790.72
860.55 866.45 869.04 873.98 879.01 891.03
902.35 932.66 937.25 940.93 946.12 975.02
982.24 983.67 986.64 990.01 992.94 994.93
996.20 998.24 1002.94 1003.41 1004.03 1007.18
1015.15 1016.45 1016.91 1018.16 1031.28 1032.27
1038.23 1053.46 1055.34 1058.51 1061.98 1077.84
1097.84 1107.85 1111.26 1118.18 1130.09 1132.30
1133.01 1142.42 1167.53 1170.32 1171.76 1183.58
1188.49 1195.32 1196.67 1197.12 1197.66 1203.12
1214.23 1224.50 1225.83 1227.99 1228.76 1238.32
1318.23 1322.81 1328.12 1332.93 1333.11 1334.36
1338.92 1342.03 1344.10 1345.24 1355.07 1362.67
1366.05 1368.51 1371.54 1378.99 1414.57 1418.70
1425.42 1431.76 1467.88 1471.16 1488.38 1489.60
1505.80 1517.59 1519.33 1521.13 1529.72 1530.47
1536.15 1540.34 1558.81 1559.63 1560.85 1621.91
1623.74 1637.27 1639.31 1645.98 1646.29 1656.54
1658.52 1659.44 1660.07 1661.44 1681.48 1681.85
1683.01 1963.60 2278.24 3026.23 3118.92 3165.50
3176.02 3176.69 3176.91 3181.05 3184.12 3185.30
3186.61 3193.66 3193.90 3199.61 3201.02 3205.26
3207.22 3211.21 3213.44 3220.18 3220.97 3232.95
3258.12 3759.90 3830.00
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TS2
==========
-92.61 11.24 14.18 18.38 25.16 27.28
30.97 33.41 36.20 37.62 39.31 40.93
46.02 50.97 52.79 63.21 72.74 73.93
76.69 82.02 92.17 98.17 102.69 110.16
117.52 122.48 124.85 130.87 134.73 139.68
141.15 146.34 151.58 157.92 166.09 171.38
172.11 176.18 180.21 190.77 193.18 228.03
230.84 232.84 240.48 245.69 266.25 266.38
266.59 268.89 278.14 279.38 280.22 284.72
302.77 309.56 313.28 315.70 316.51 328.32
343.52 346.30 349.93 362.39 369.35 377.15
393.29 396.19 403.84 405.08 405.42 406.30
415.04 416.31 424.80 426.00 431.13 448.47
450.07 450.34 459.82 469.49 471.96 473.26
486.54 488.50 493.26 545.32 551.81 567.76
575.08 576.88 582.27 585.80 599.18 600.60
619.29 625.68 626.87 628.79 629.81 631.21
632.85 646.67 647.90 649.69 650.38 677.35
687.32 692.12 698.45 706.23 711.68 713.71
717.90 722.62 724.06 755.25 755.64 756.33
760.67 770.02 770.69 788.90 795.12 821.90
848.73 855.38 856.28 868.13 874.30 879.65
914.58 927.36 934.36 935.78 941.11 945.60
957.88 972.18 976.69 980.62 989.50 991.42
992.70 998.70 999.67 1000.25 1007.20 1012.76
1013.55 1014.74 1015.28 1015.74 1027.29 1031.36
1052.89 1053.63 1057.95 1069.08 1094.93 1097.49
1099.62 1105.85 1109.32 1113.60 1123.88 1131.88
1134.46 1135.35 1142.29 1144.28 1145.20 1148.06
1151.02 1153.94 1197.01 1199.23 1206.06 1206.65
1211.99 1225.20 1230.35 1235.31 1239.17 1268.28
1307.93 1308.04 1310.76 1319.40 1320.09 1323.21
1334.23 1336.03 1336.53 1339.37 1362.31 1366.26
1370.72 1373.01 1386.37 1389.76 1406.55 1410.33
1417.07 1436.27 1467.85 1470.47 1480.89 1489.20
1499.24 1501.66 1503.79 1507.88 1528.13 1528.86
1530.56 1540.53 1545.37 1547.20 1549.71 1618.17
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TS3

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TS4

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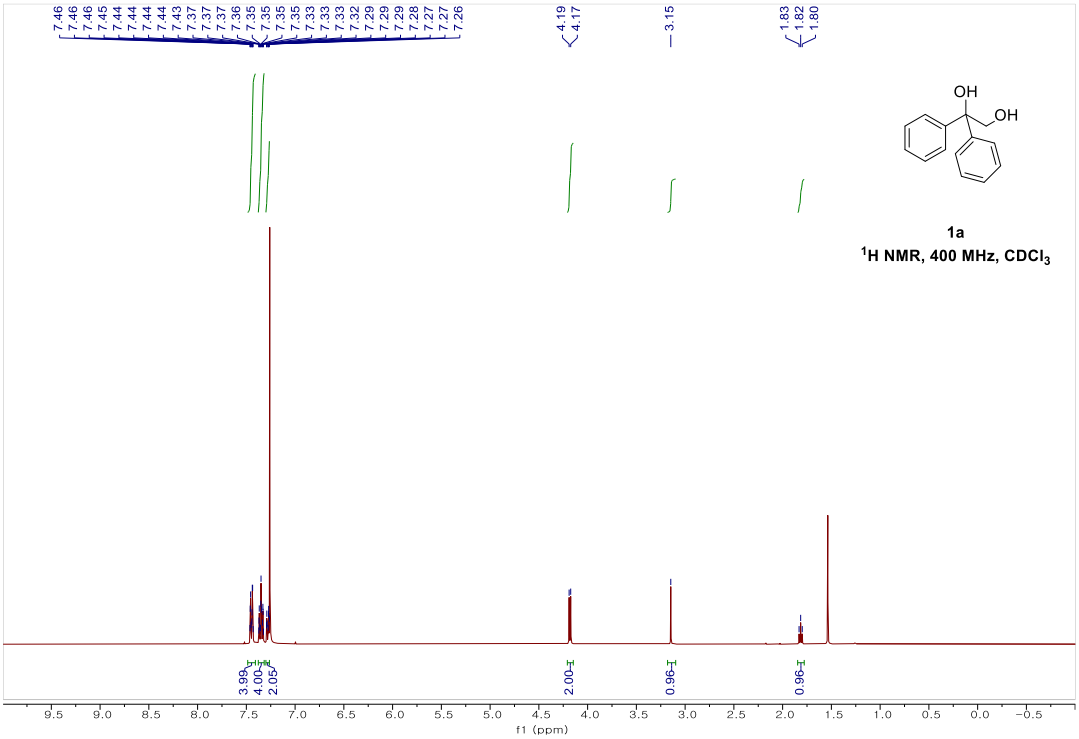
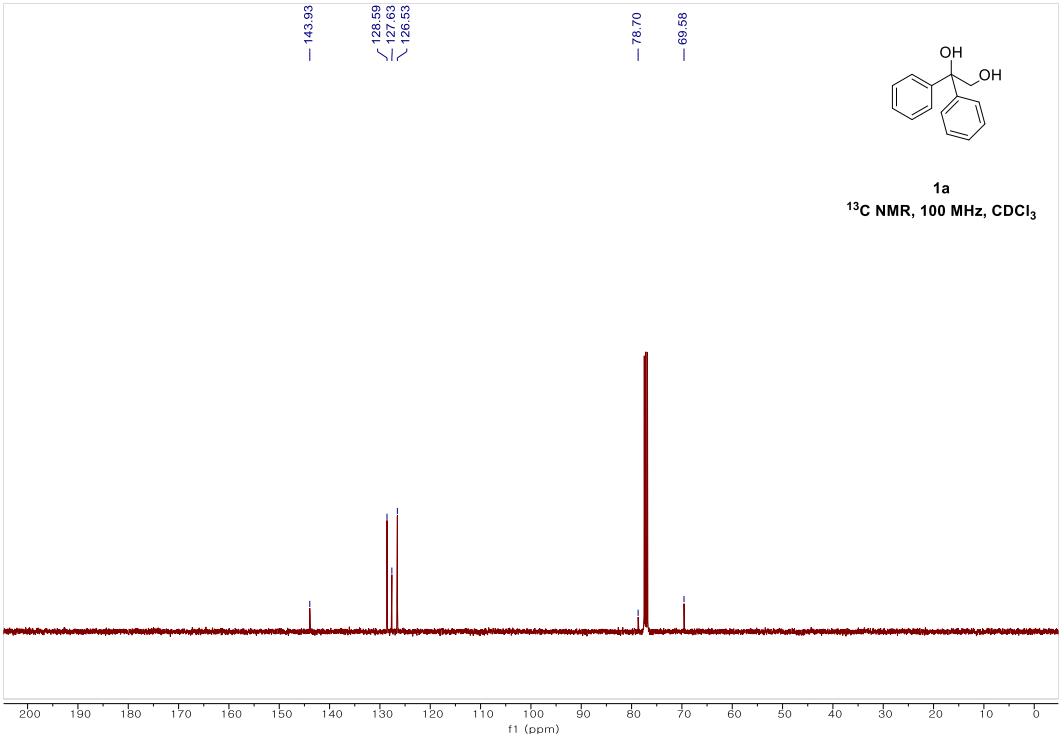
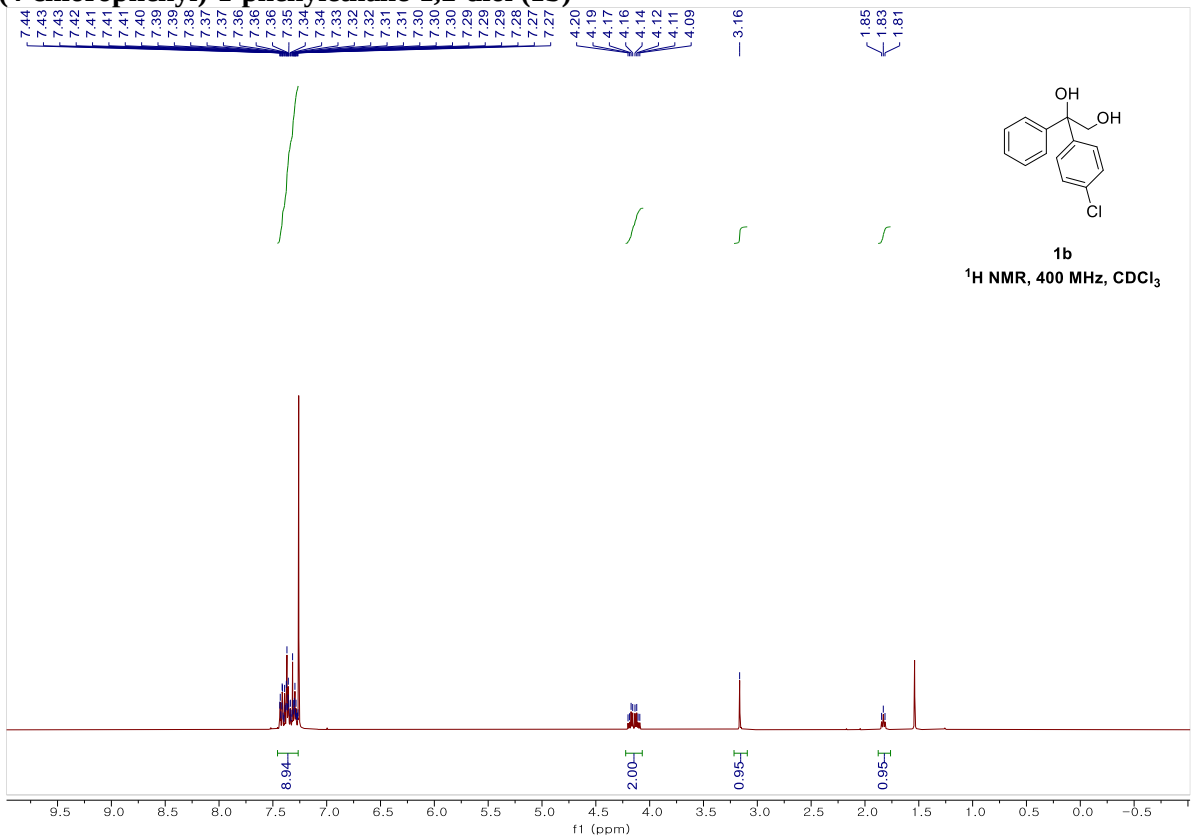
10. Spectral copies of ^{1}H and ^{13}C NMR

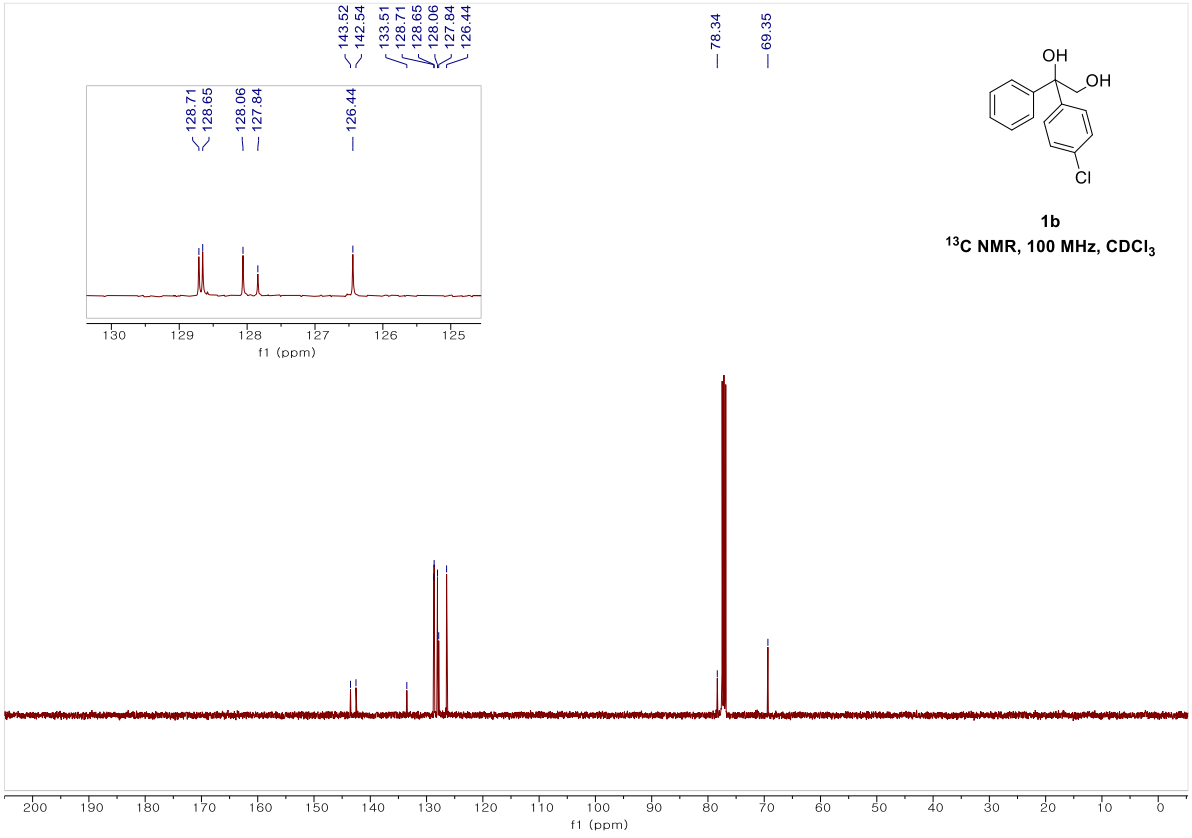
1,1-diphenylethane-1,2-diol (1a)





1-(4-chlorophenyl)-1-phenylethane-1,2-diol (1b)





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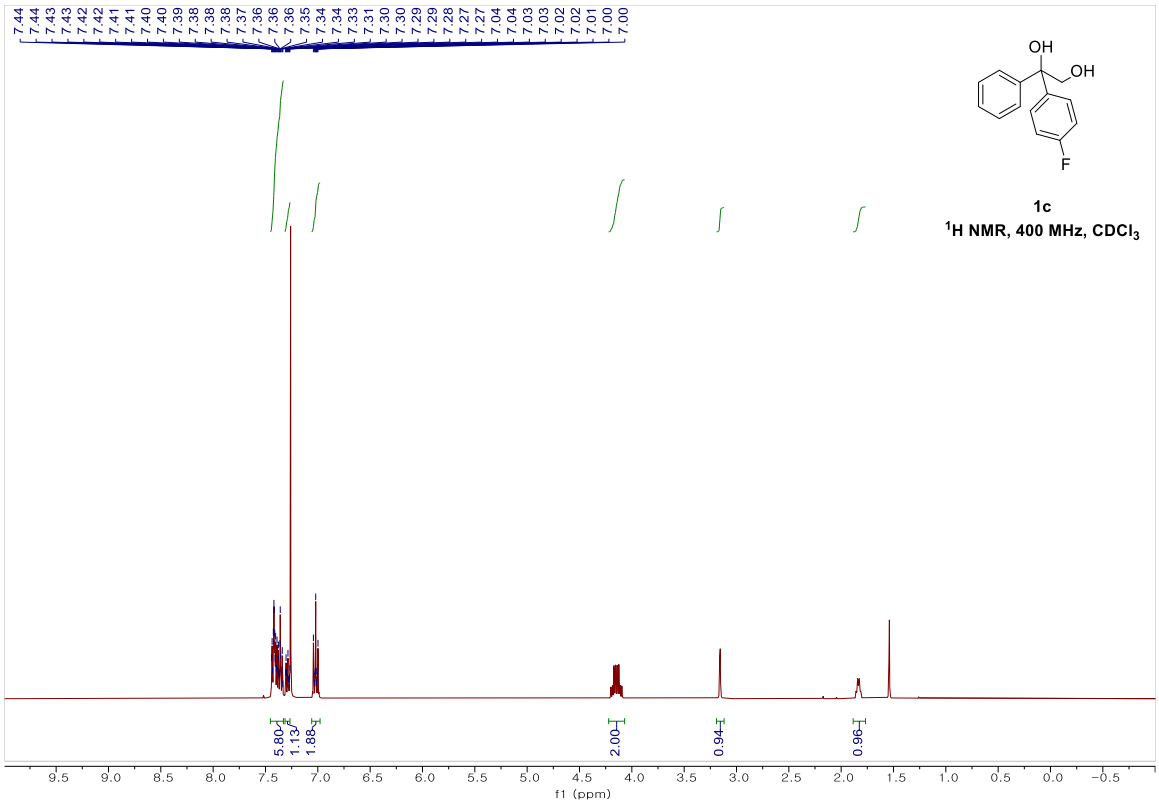
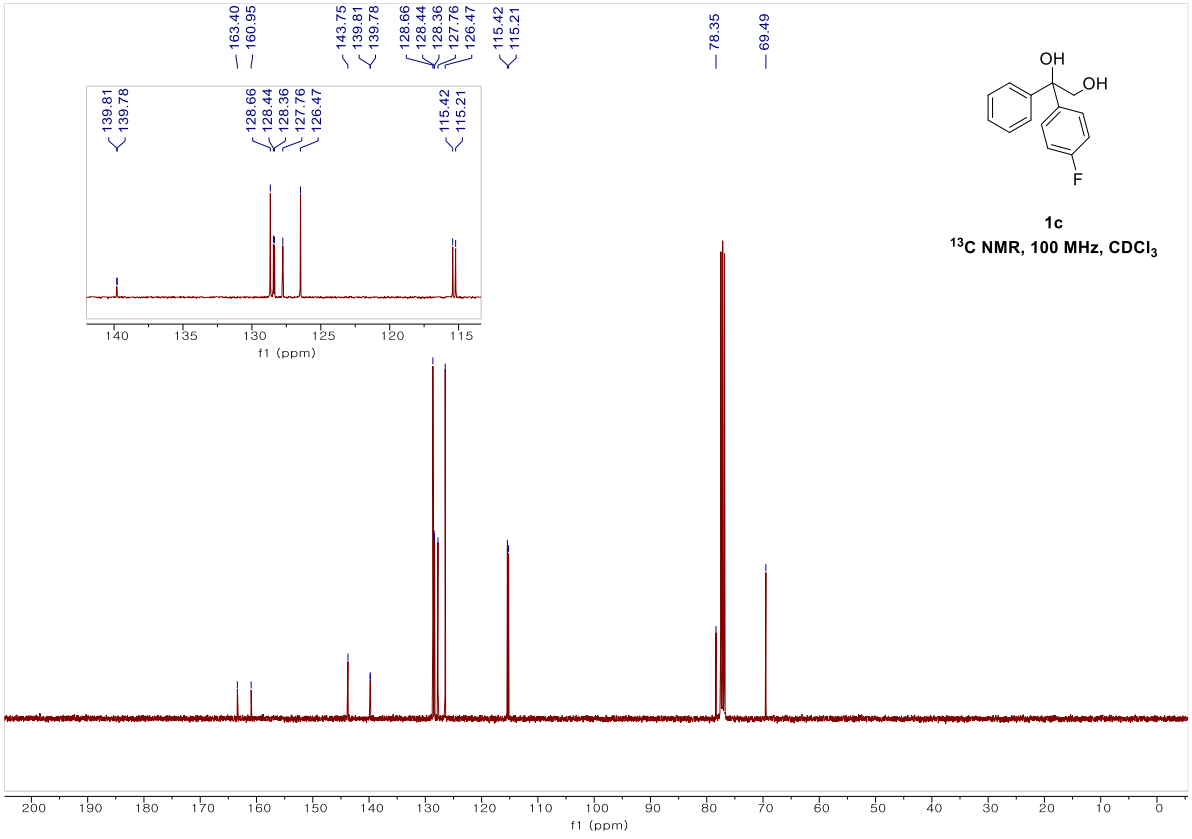
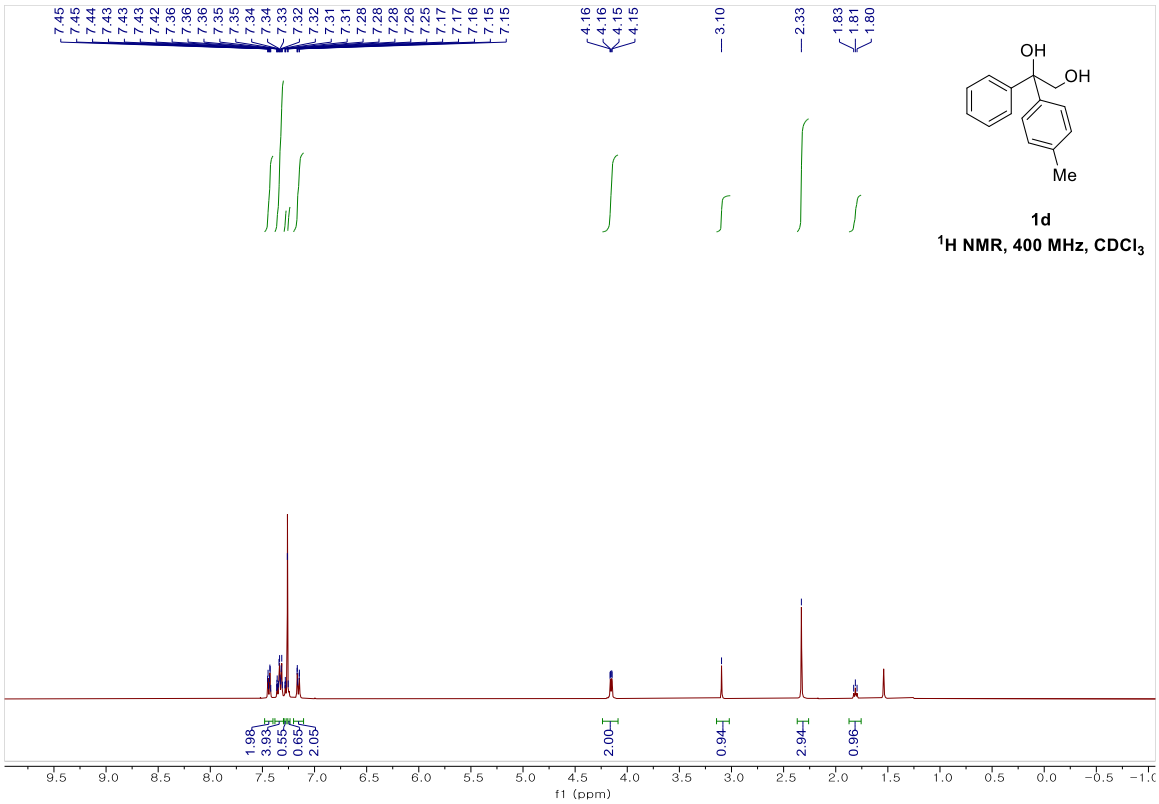
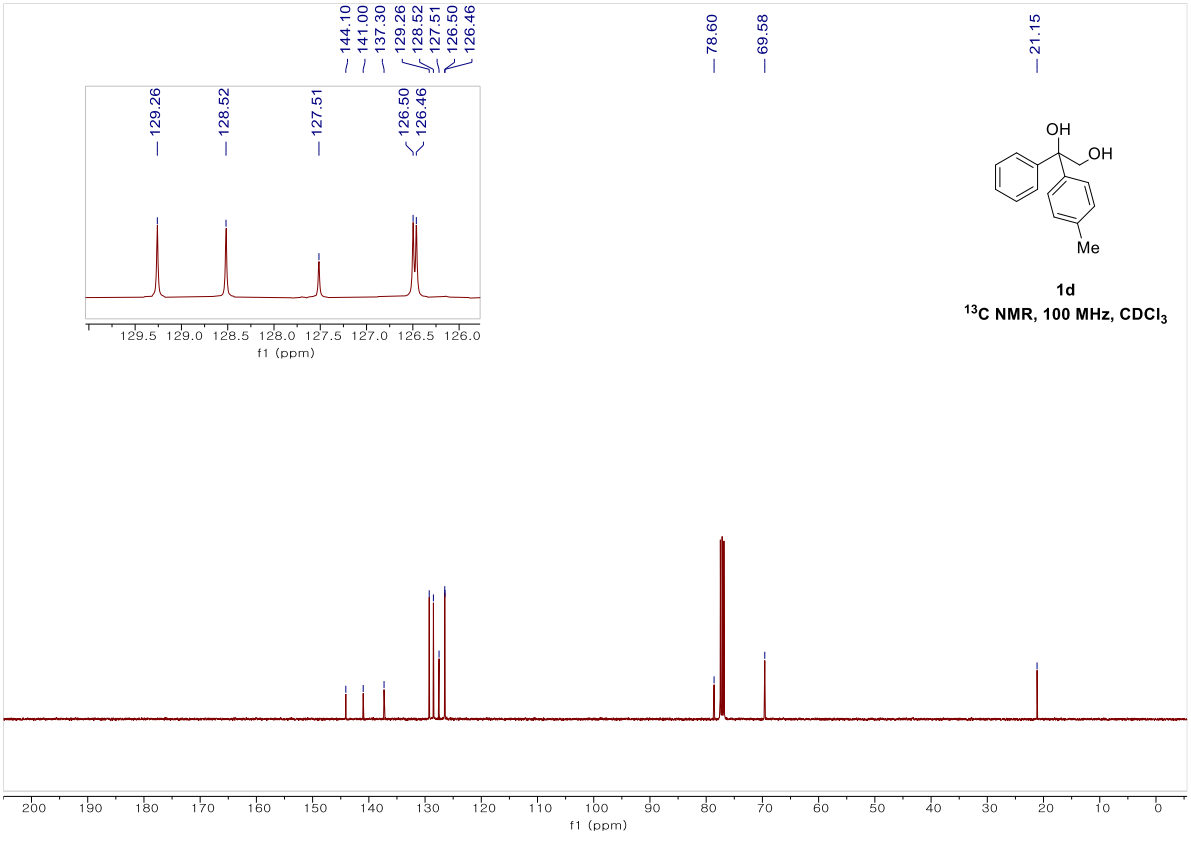


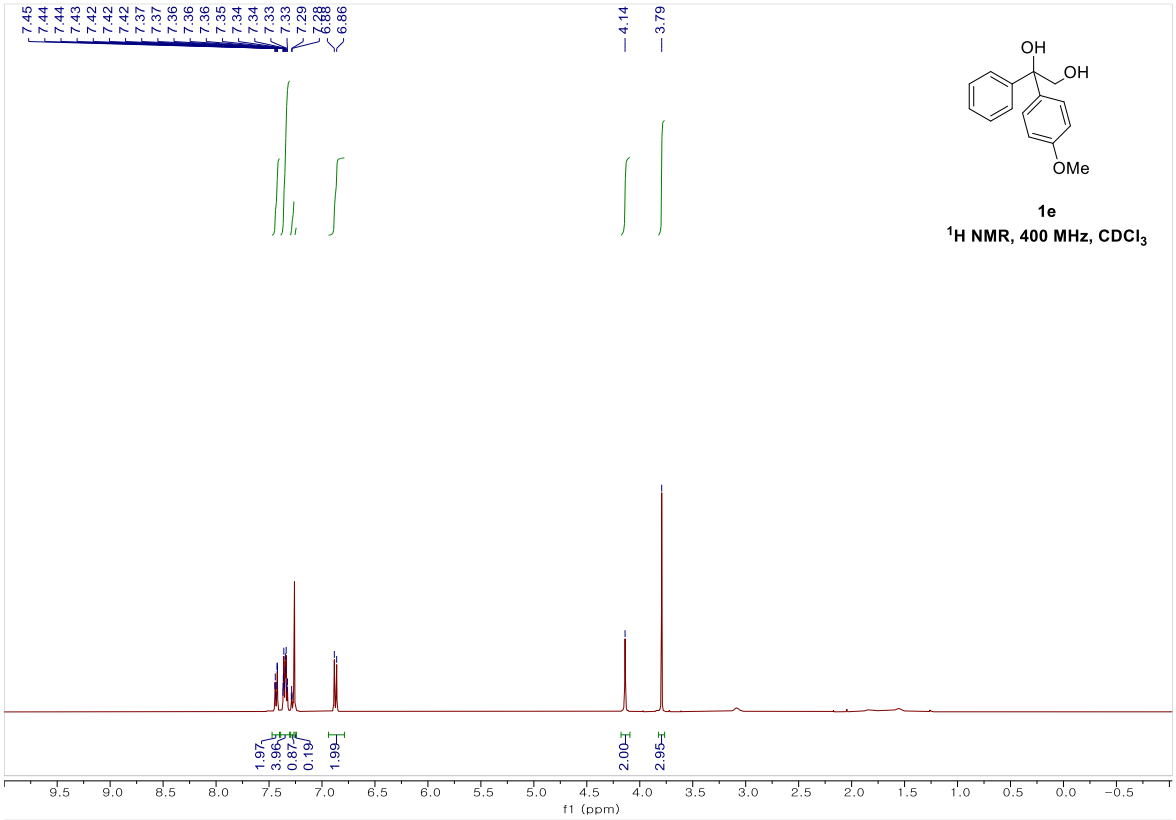


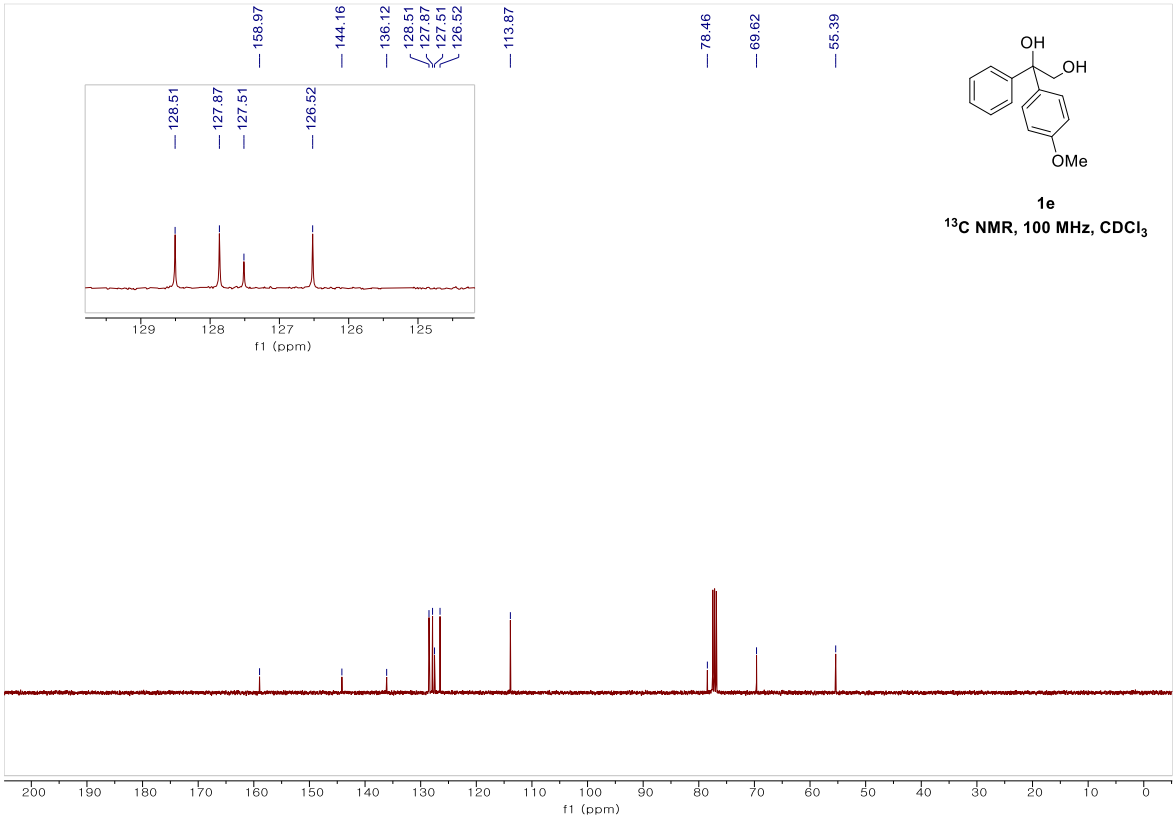
1-phenyl-1-(p-tolyl)ethane-1,2-diol (1d)



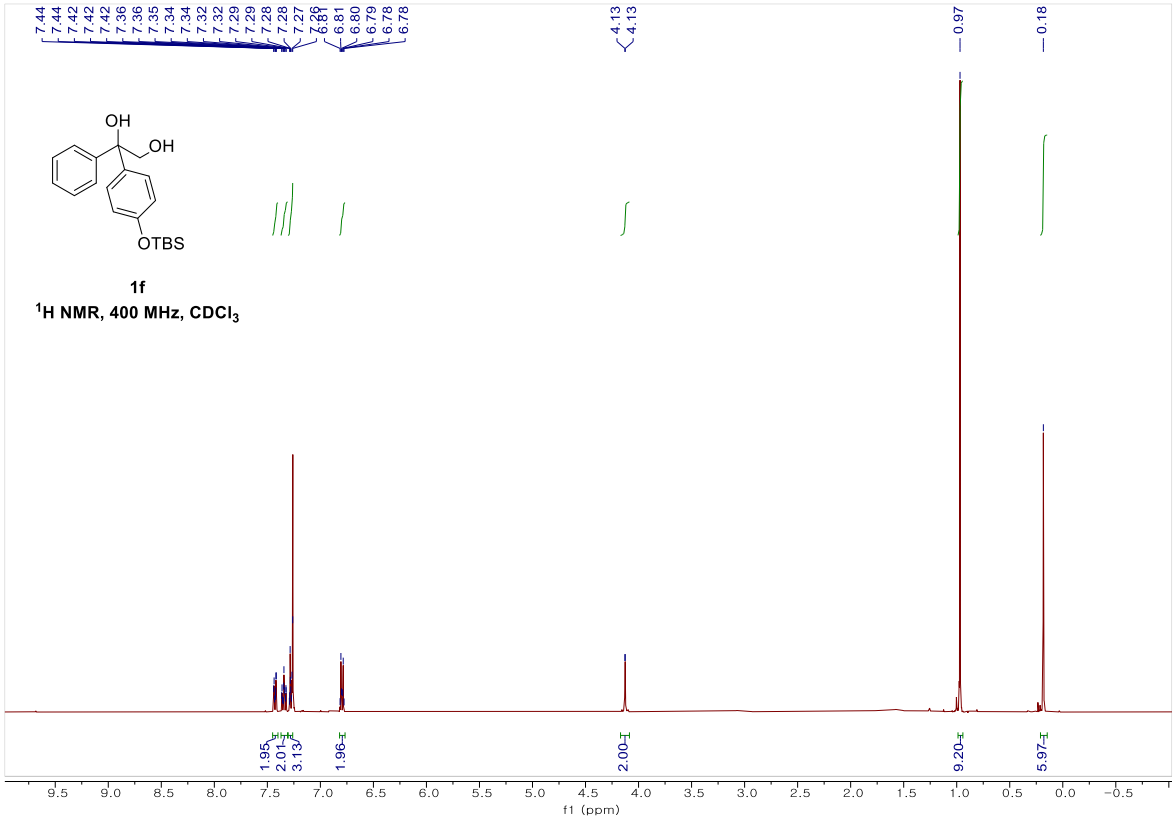


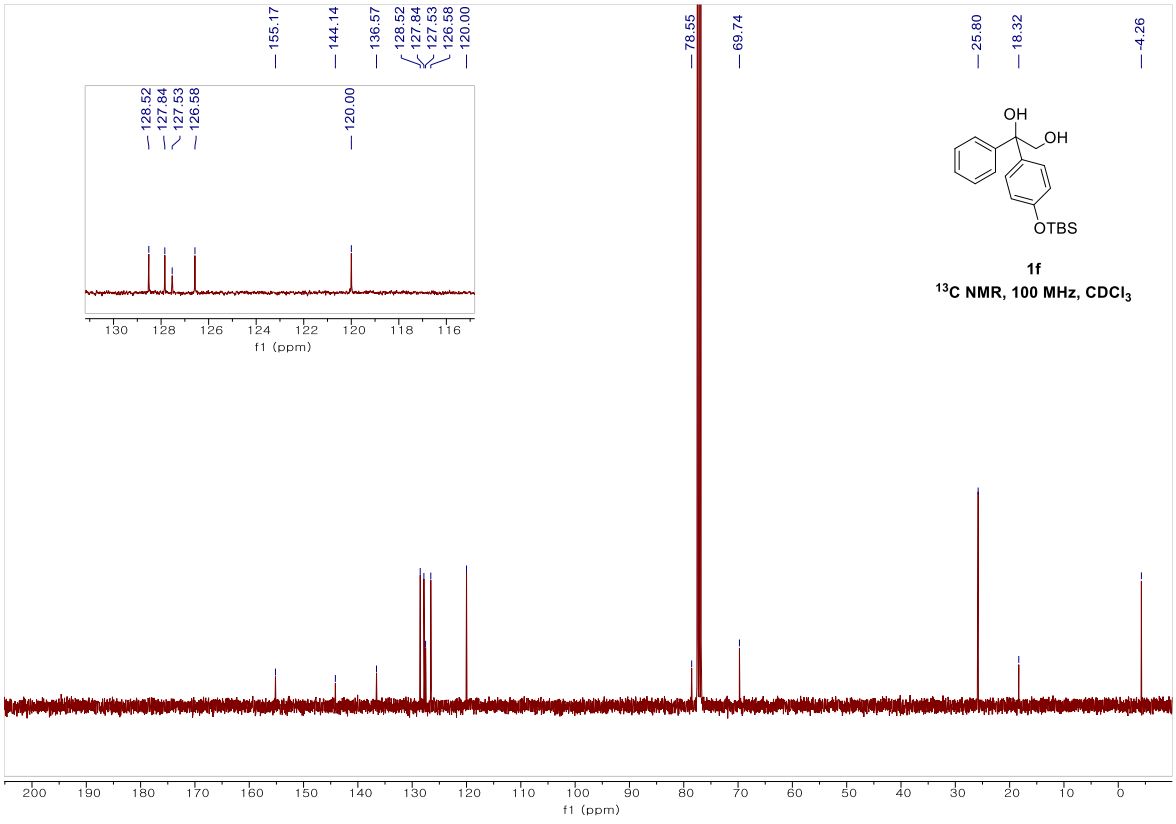
1-(4-methoxyphenyl)-1-phenylethane-1,2-diol (1e)



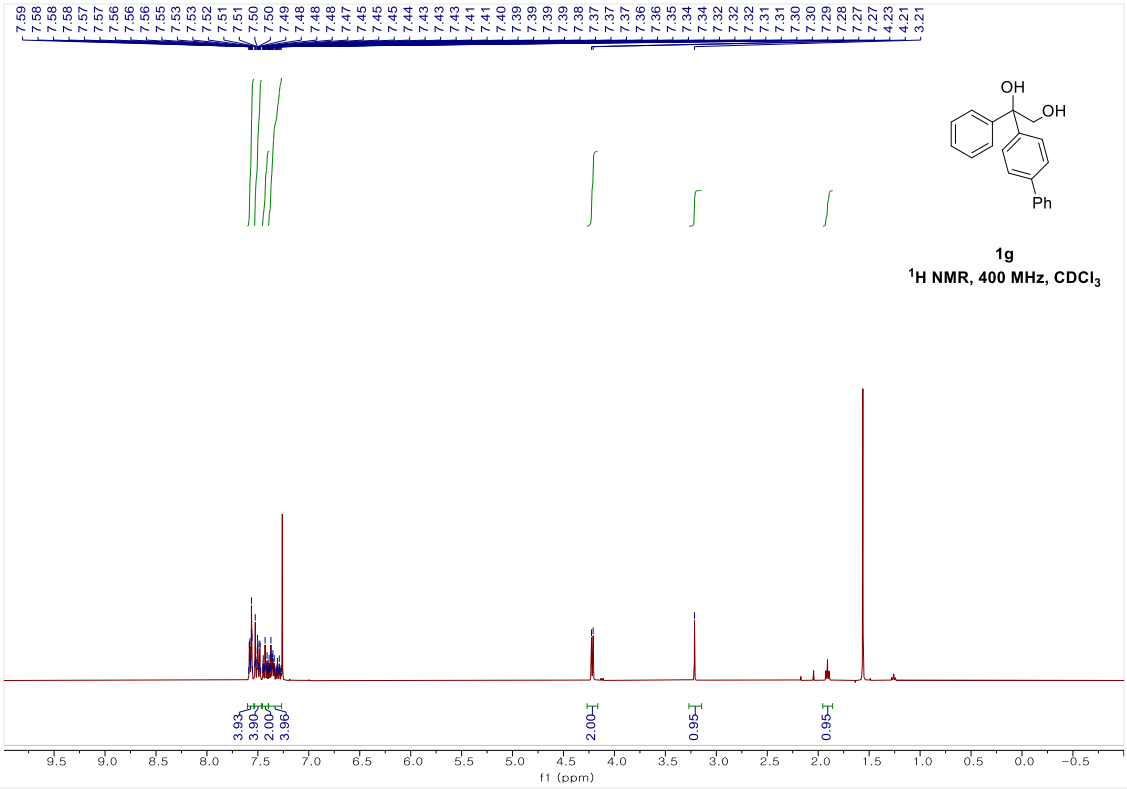


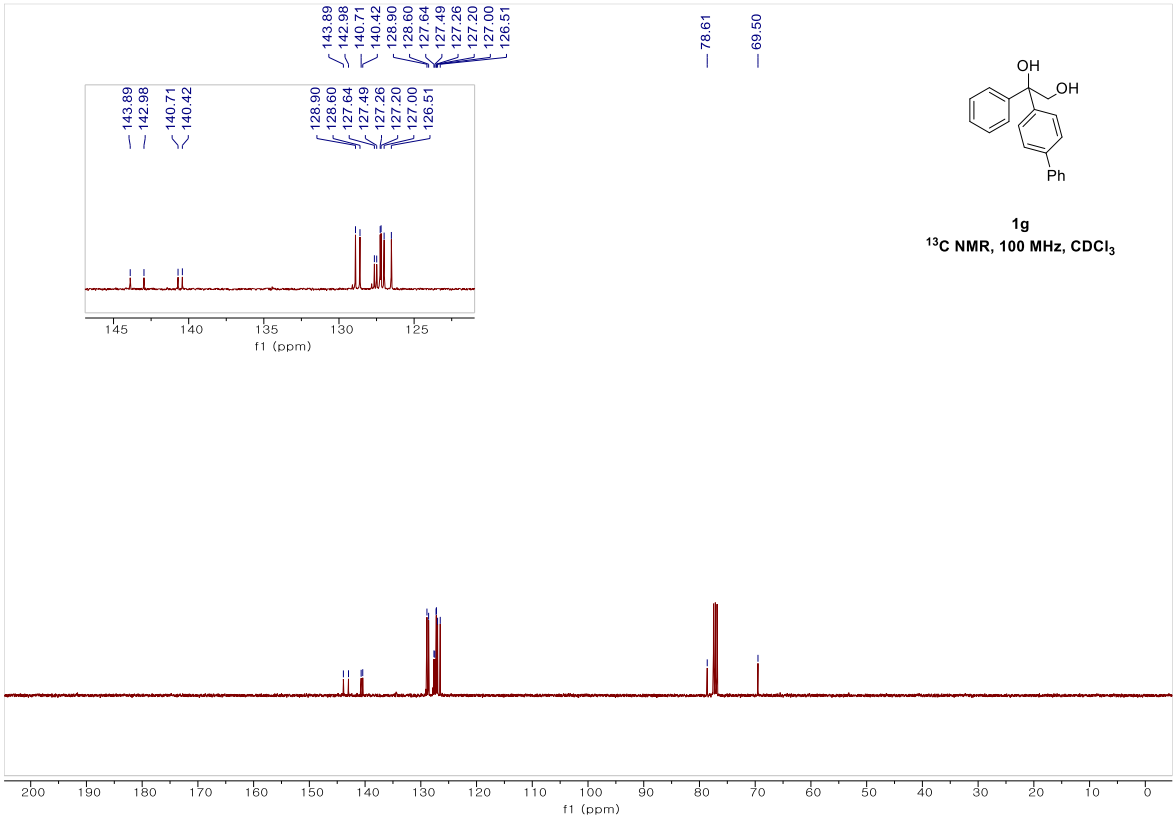
1-(4-((tert-butyldimethylsilyl)oxy)phenyl)-1-phenylethane-1,2-diol (1f)



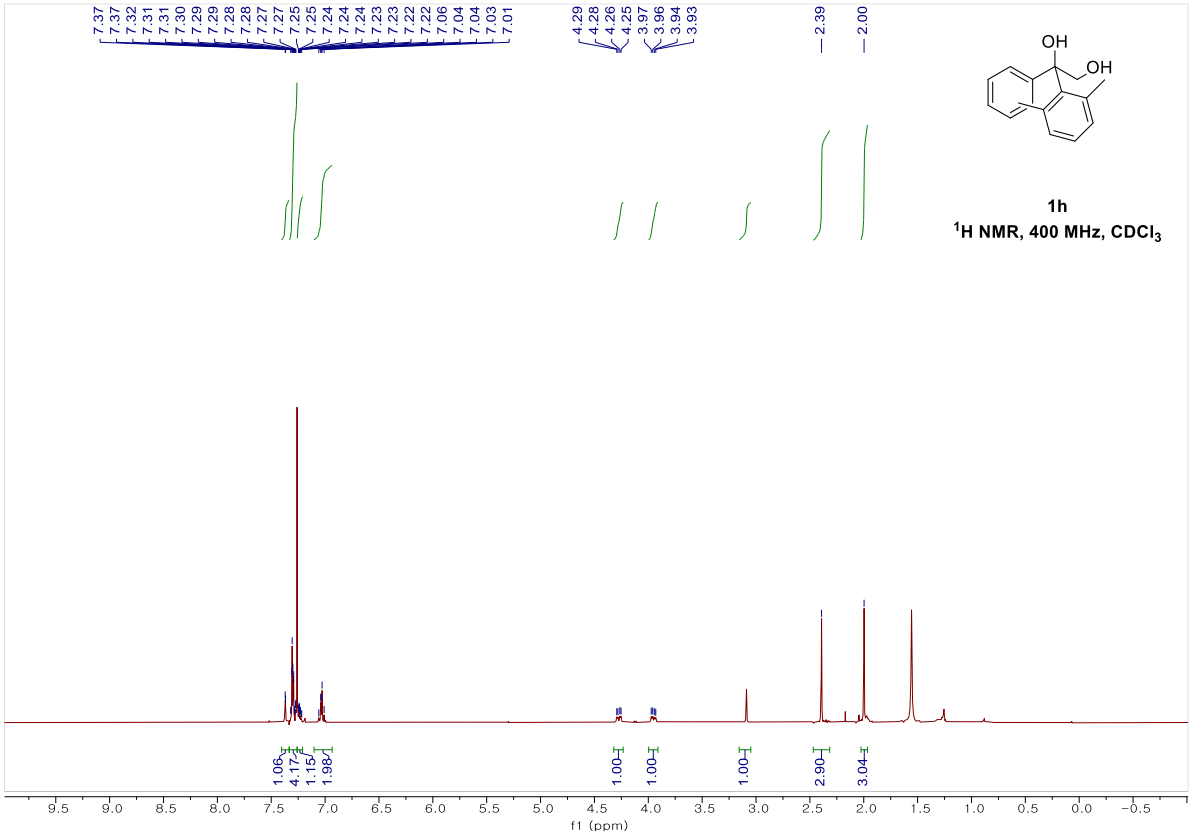


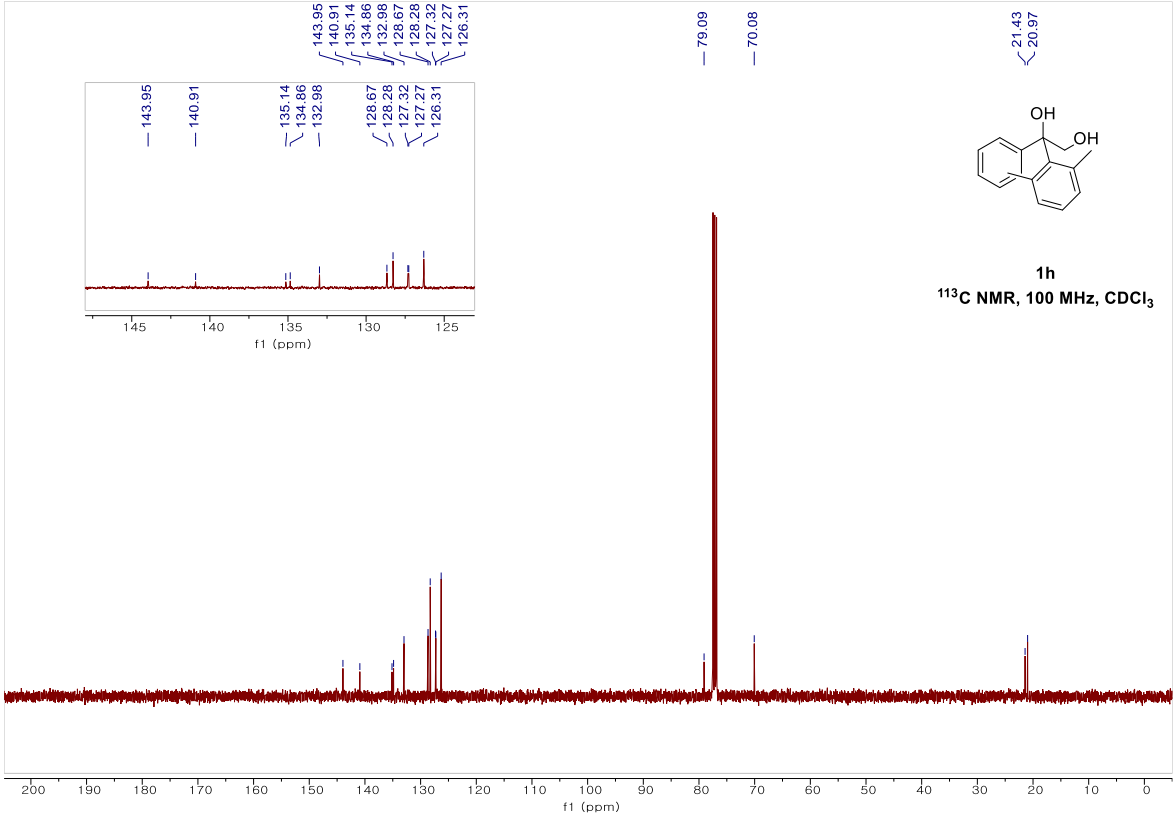
1-([1,1'-biphenyl]-4-yl)-1-phenylethane-1,2-diol (1g)



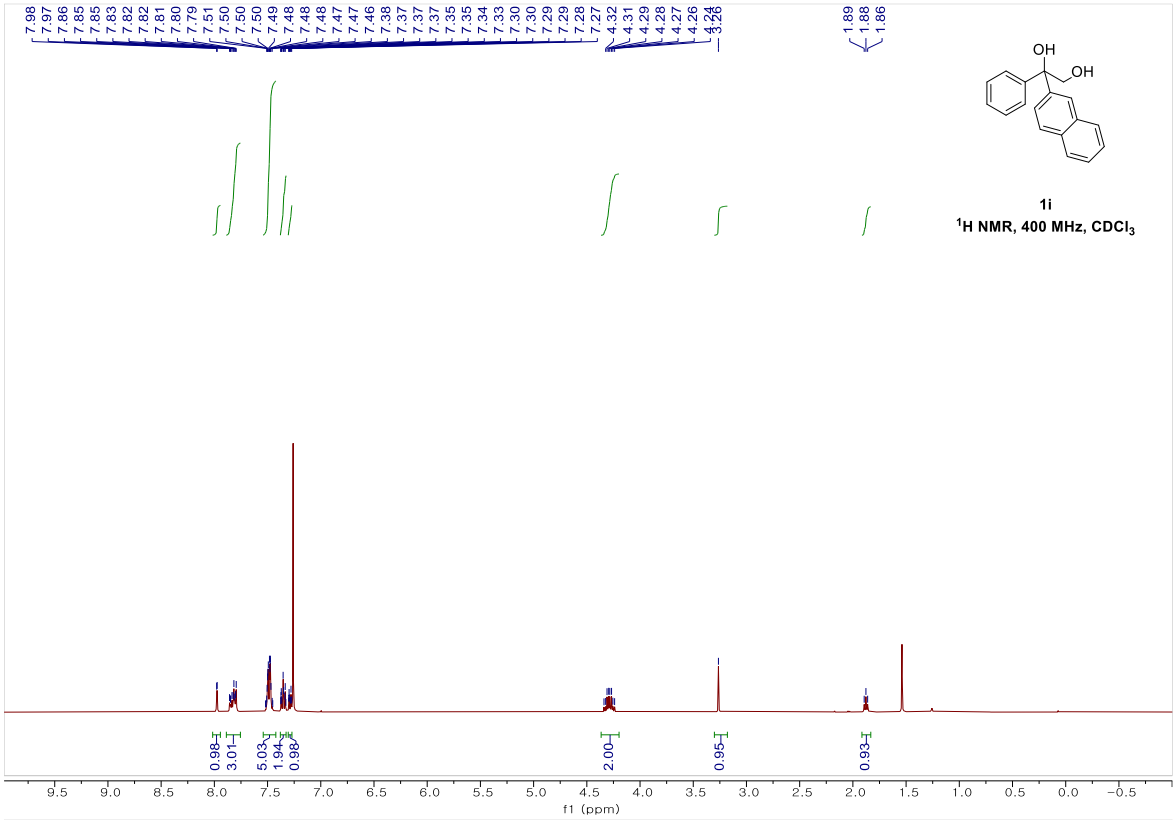


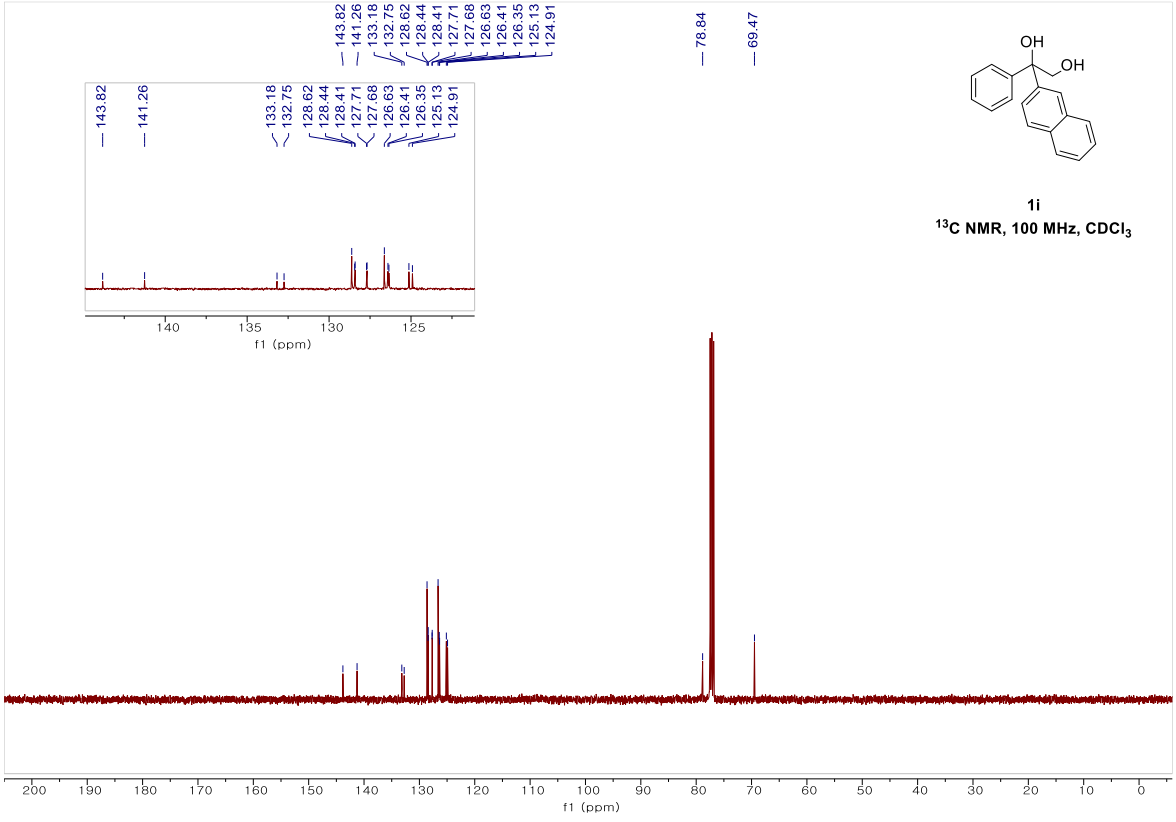
1-(2,6-dimethylphenyl)-1-phenylethane-1,2-diol (1h)



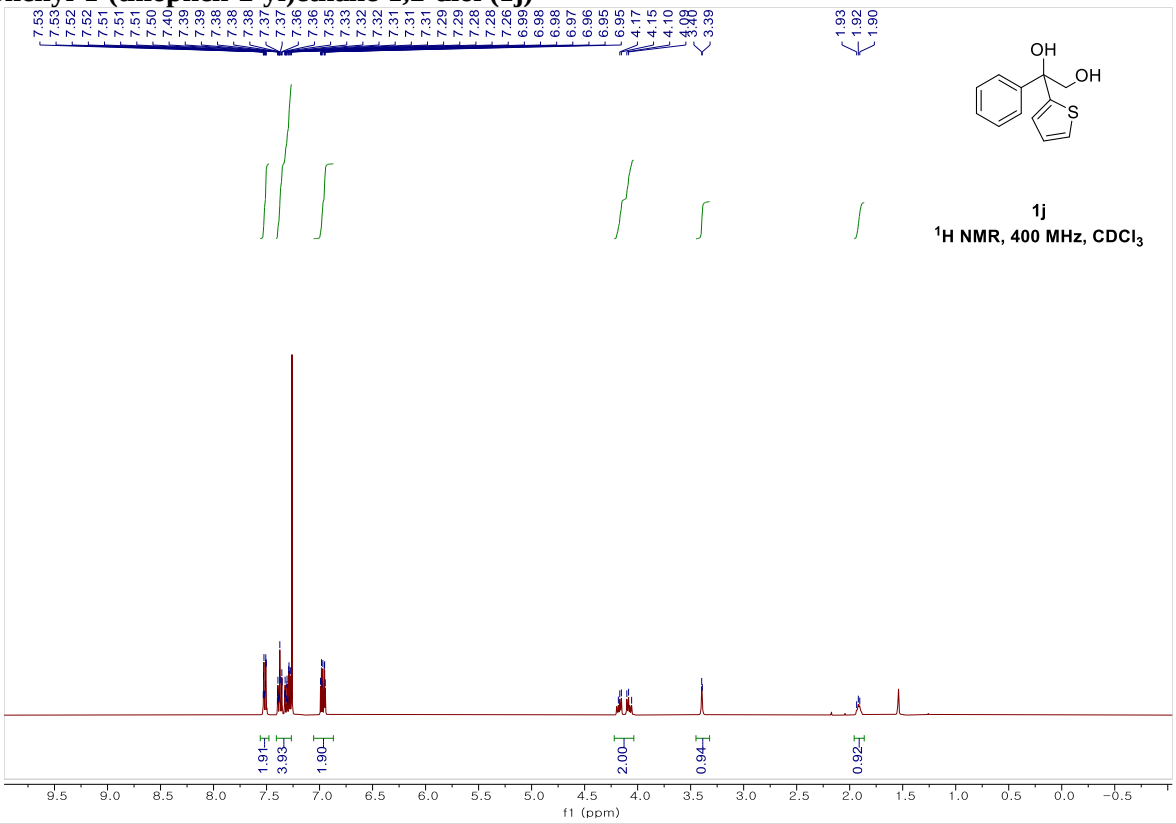


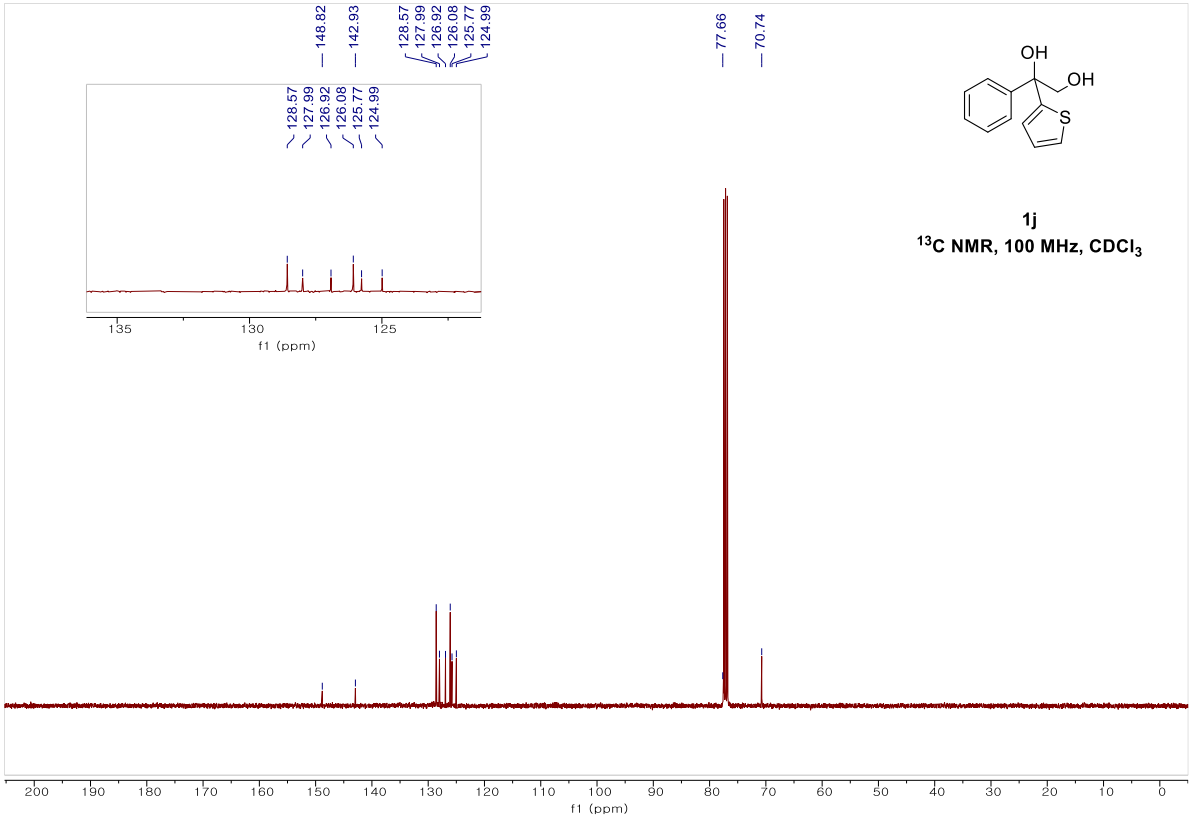
1-(naphthalen-2-yl)-1-phenylethane-1,2-diol (1i)



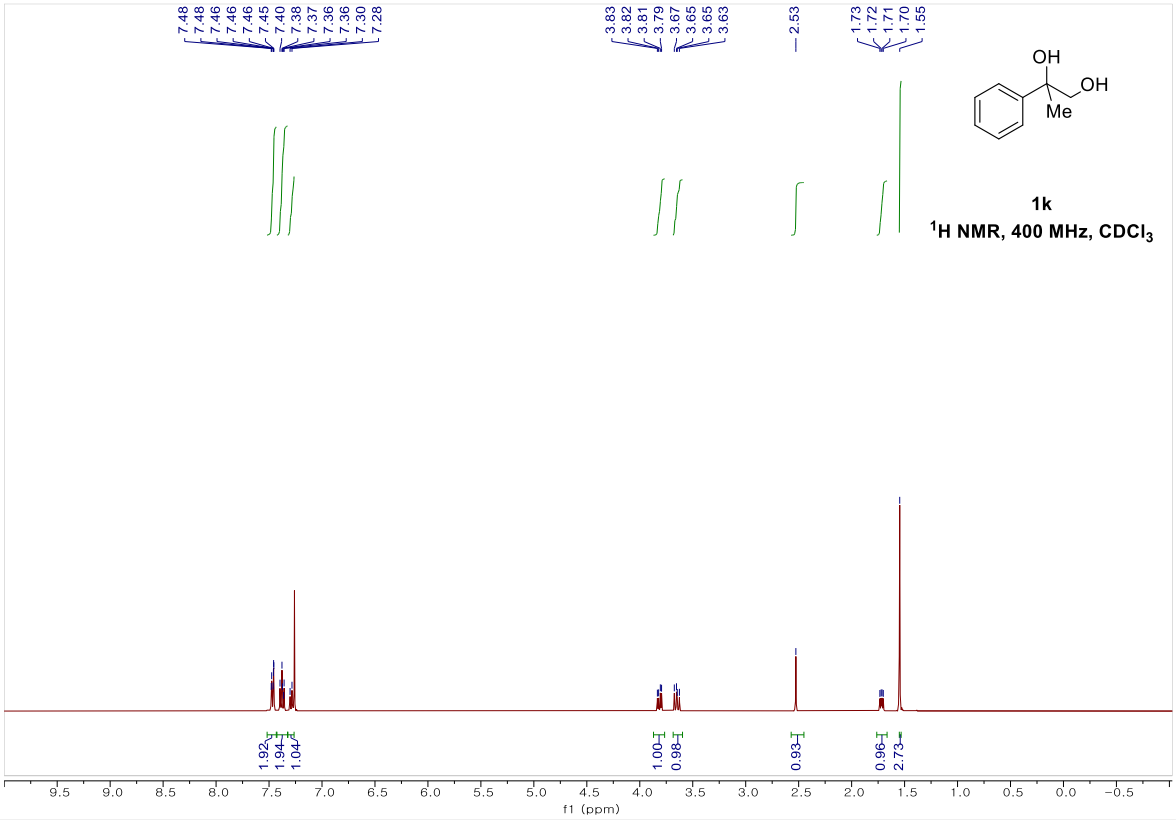


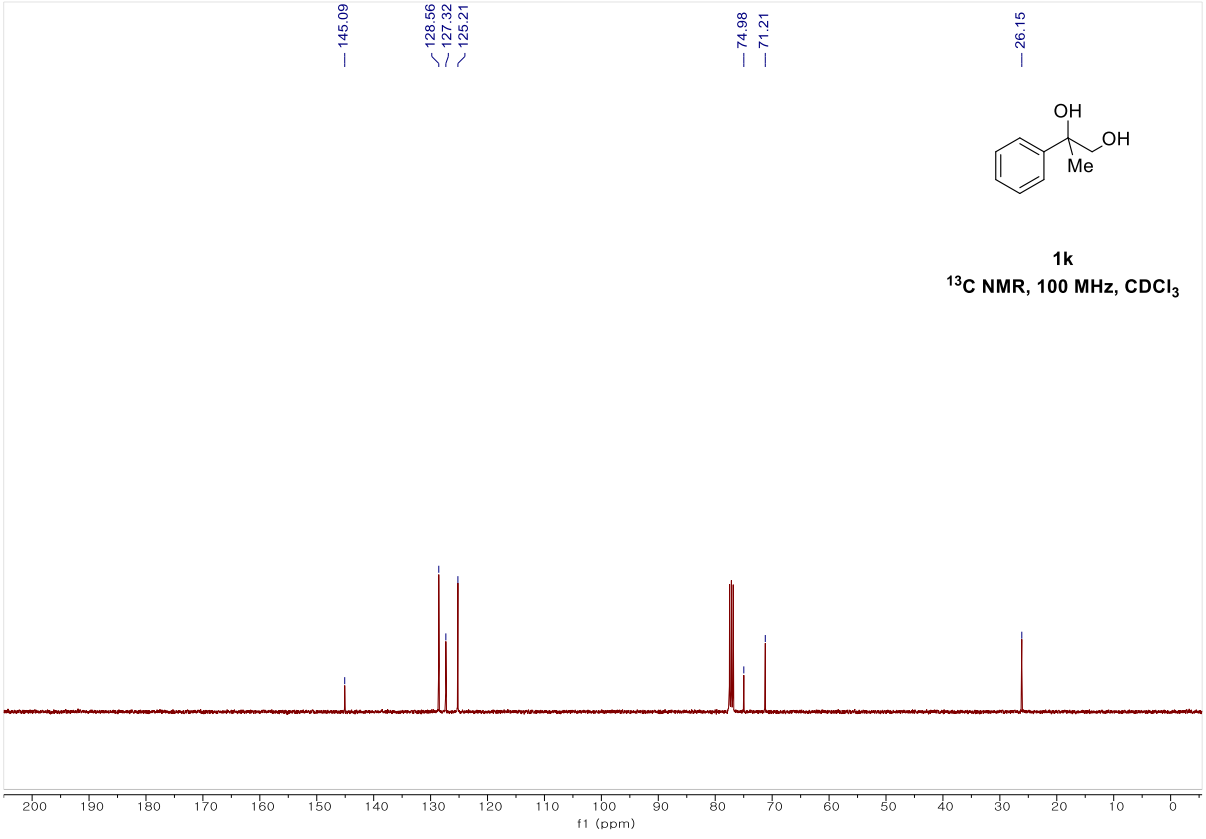
1-phenyl-1-(thiophen-2-yl)ethane-1,2-diol (1j)



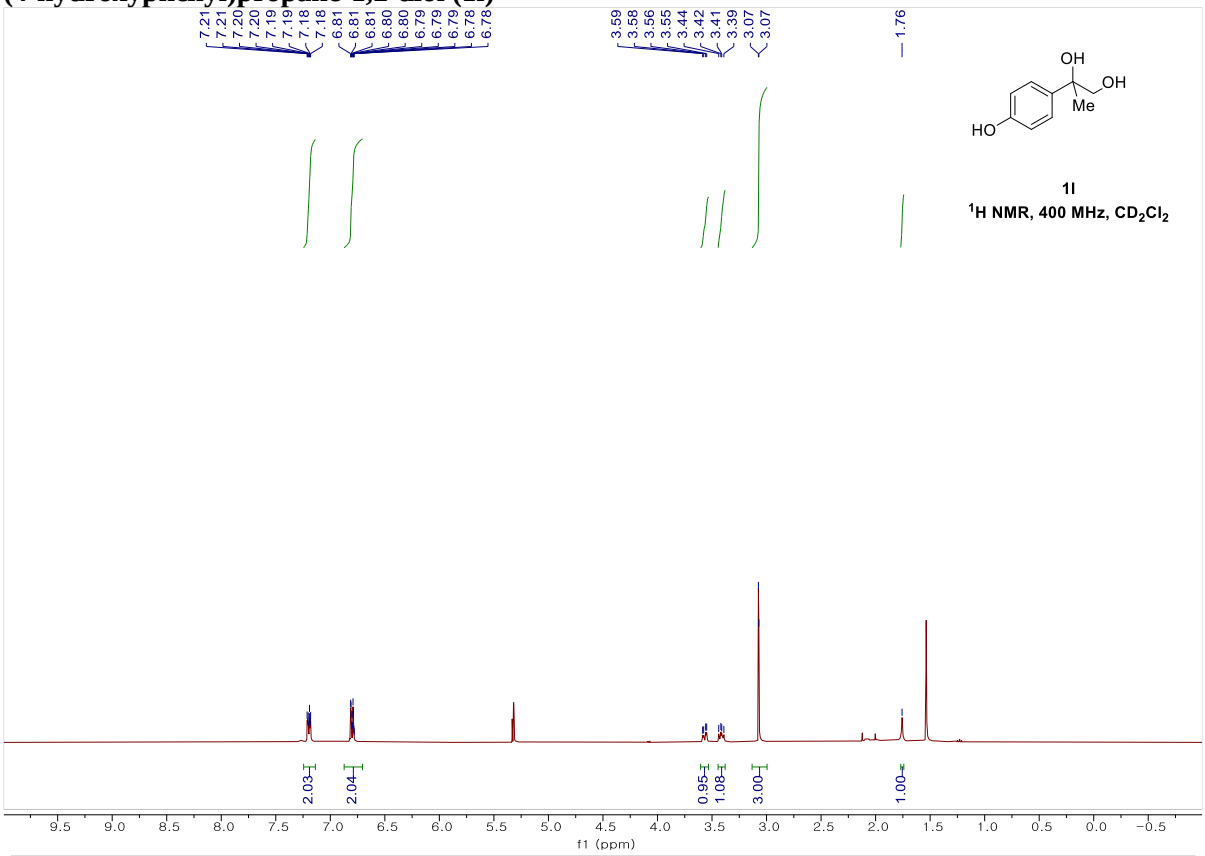


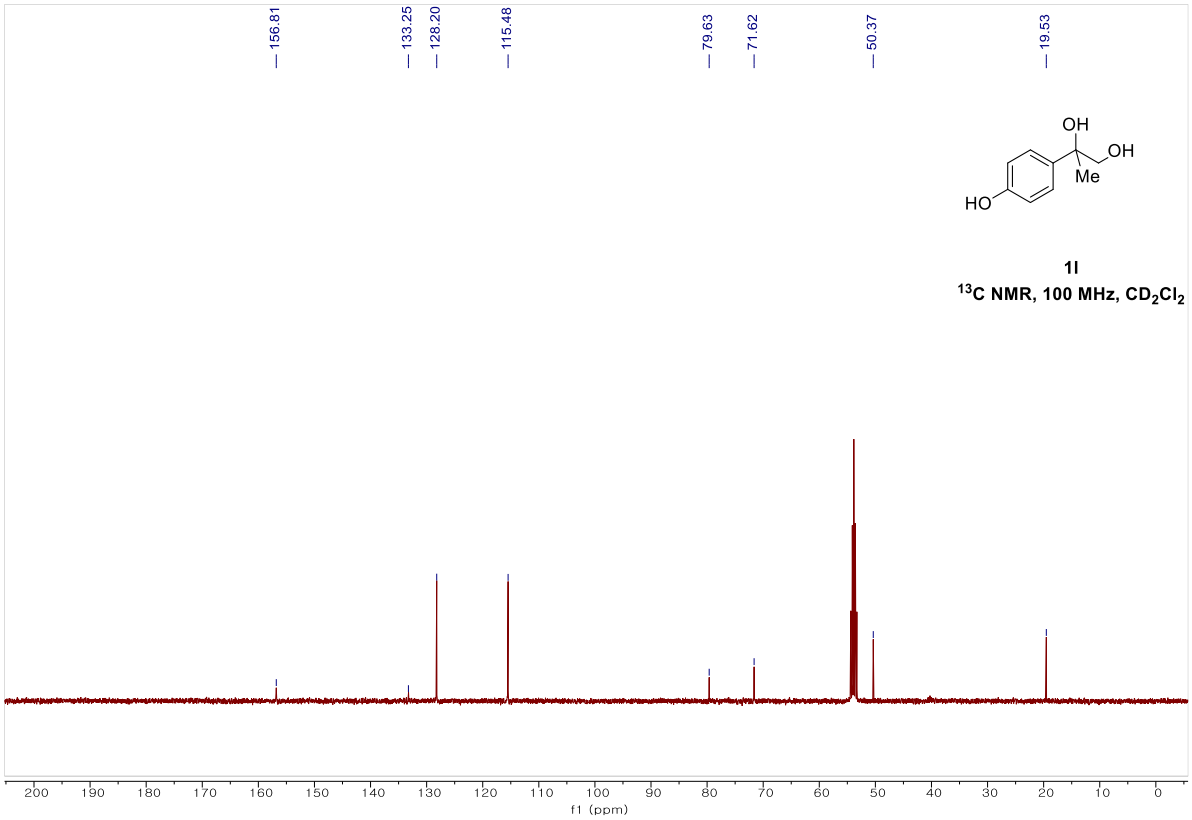
2-phenylpropane-1,2-diol (1k)



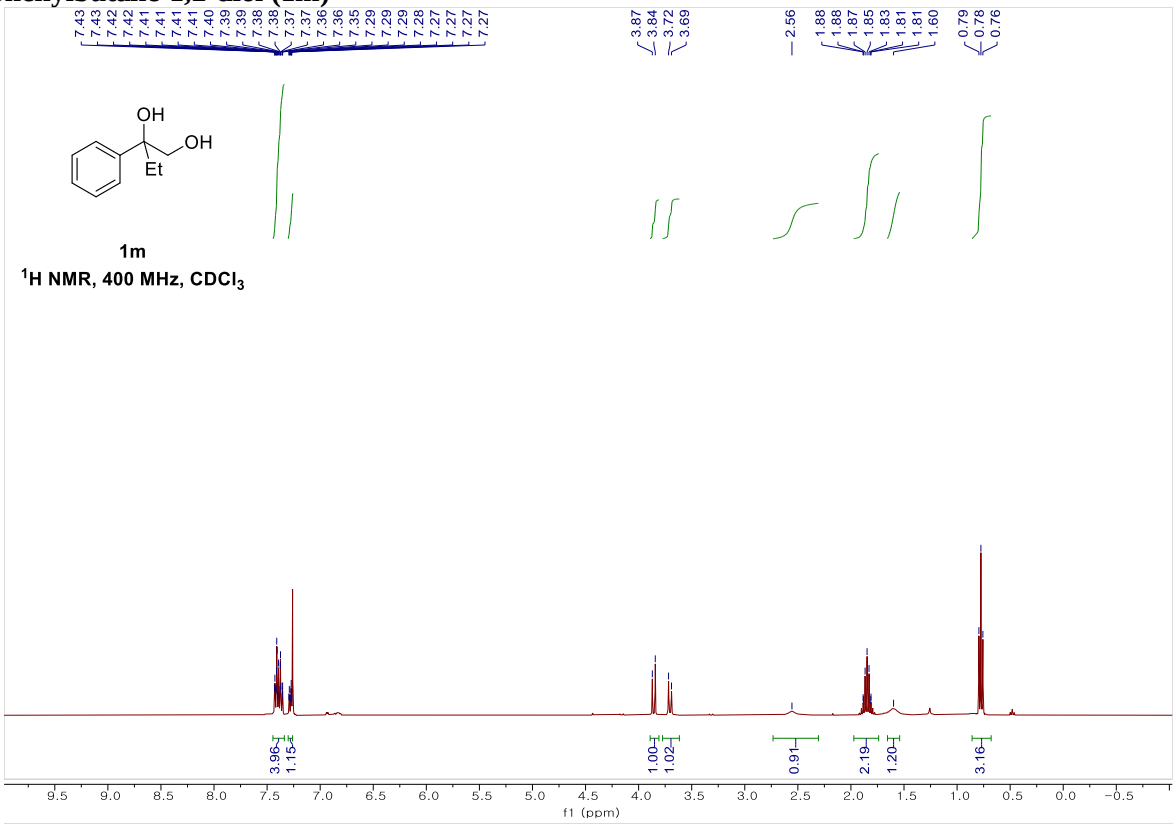


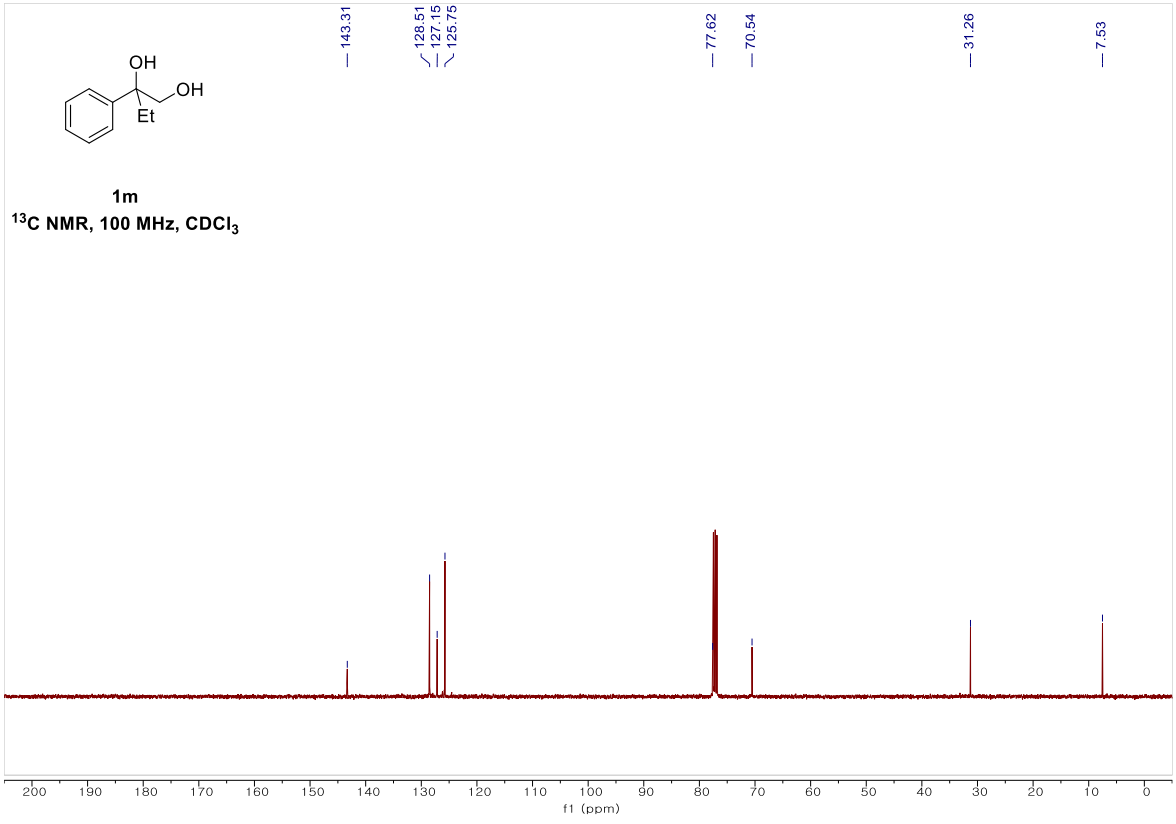
2-(4-hydroxyphenyl)propane-1,2-diol (1l)



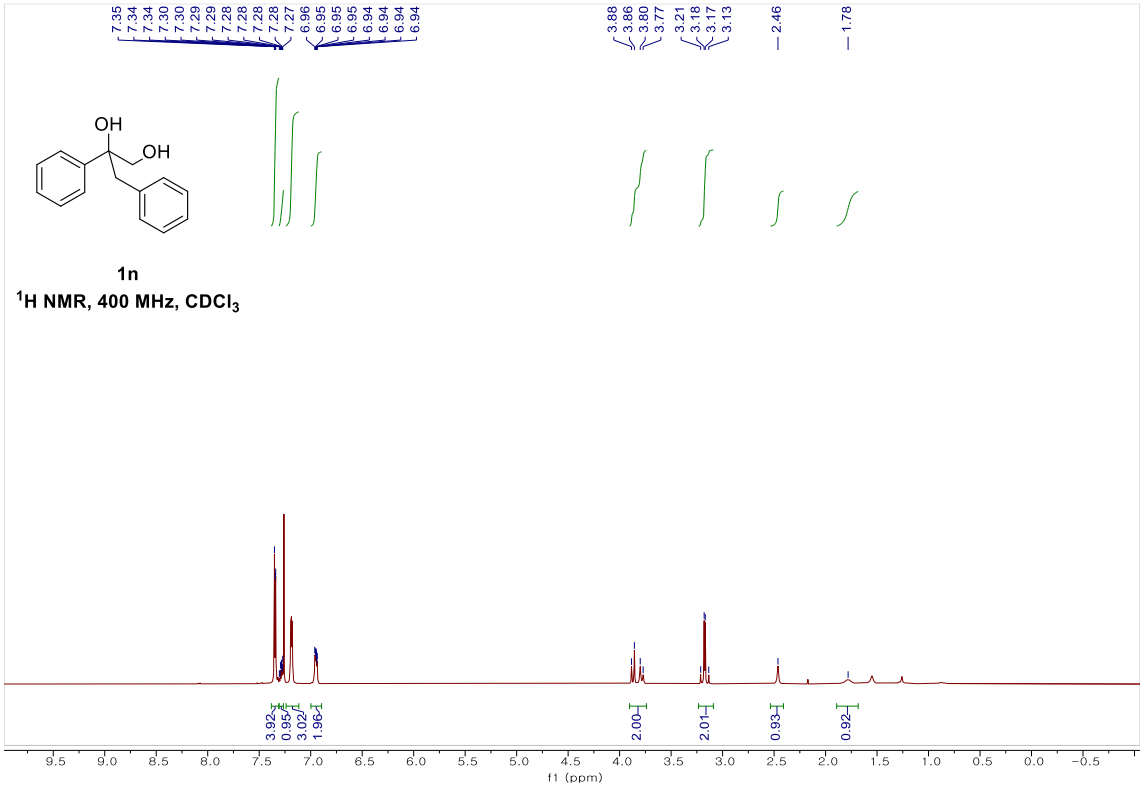


2-phenylbutane-1,2-diol (1m)



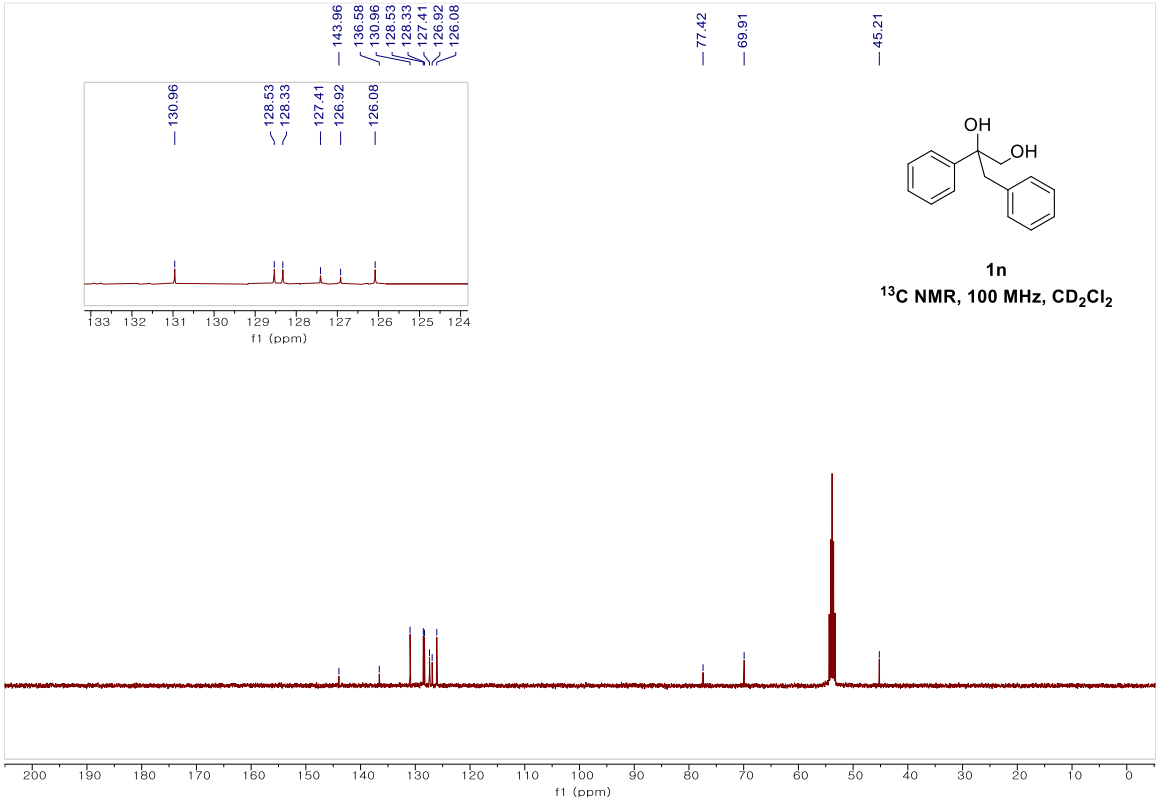


2,3-diphenylpropane-1,2-diol (1n)



1n

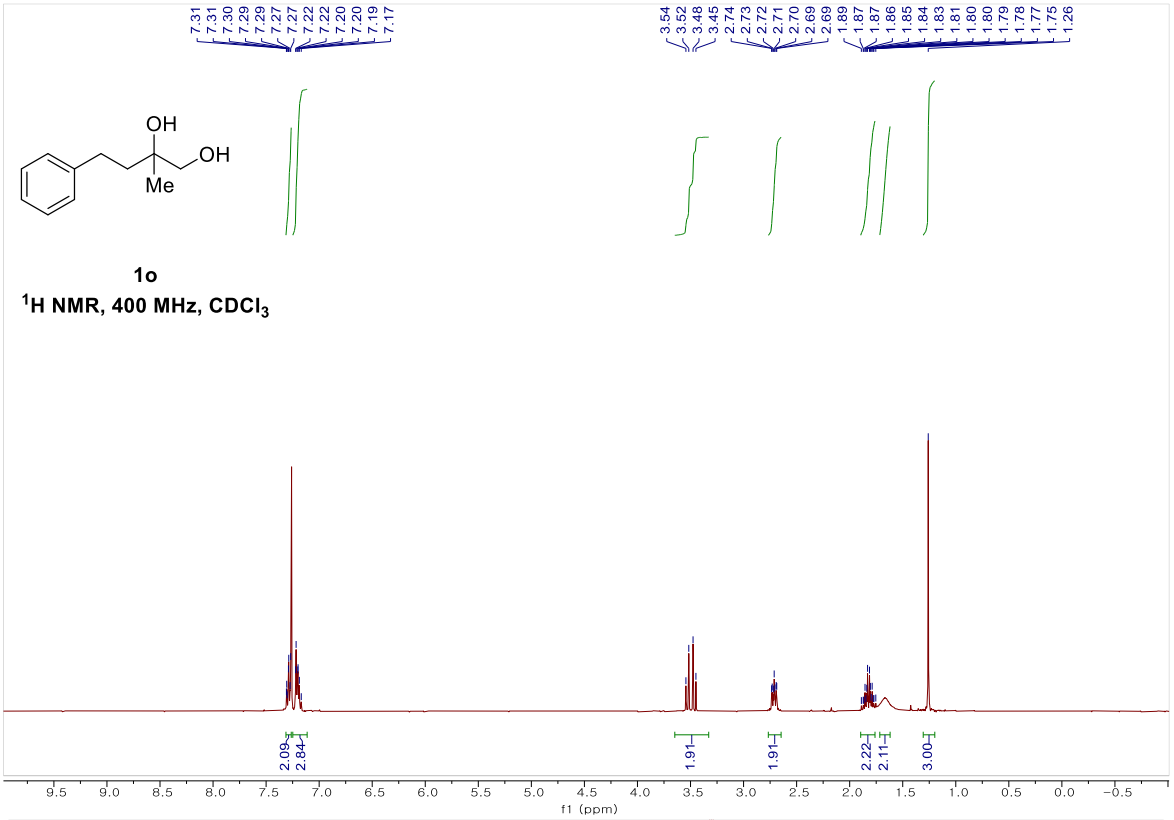
^{1}H NMR, 400 MHz, $CDCl_3$

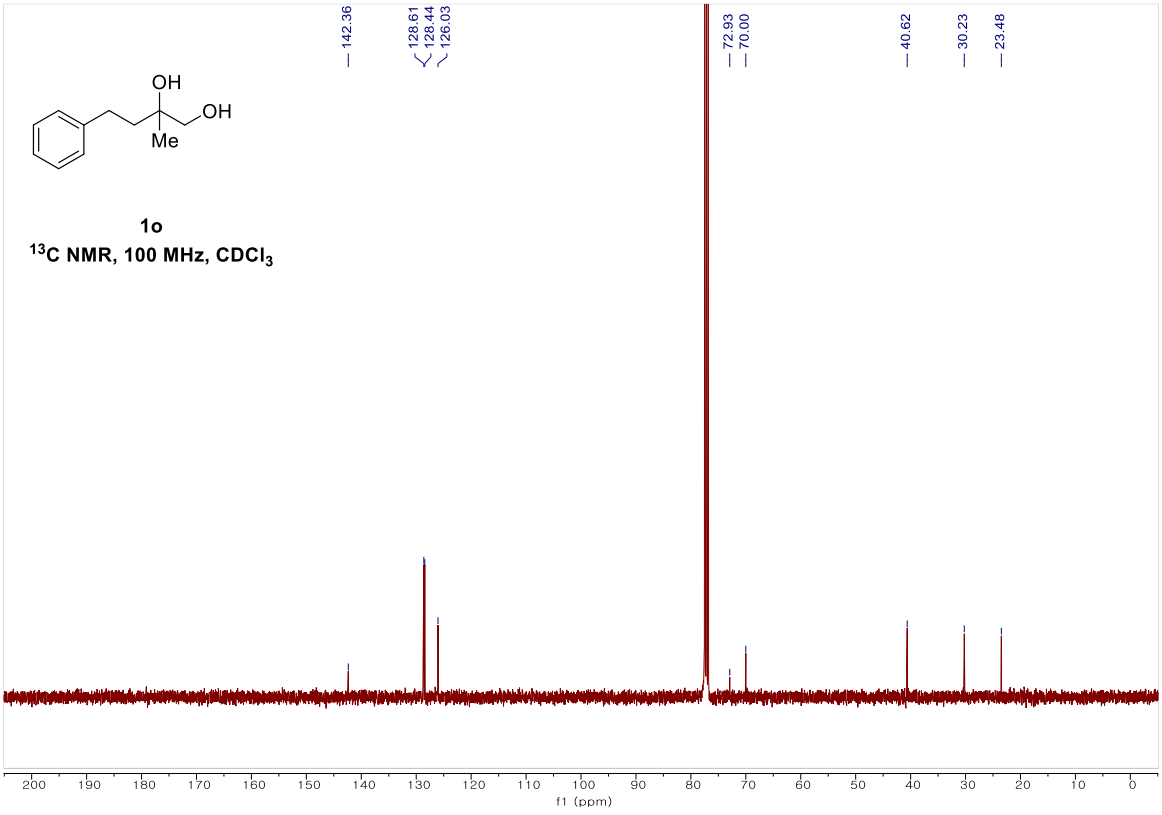


1n

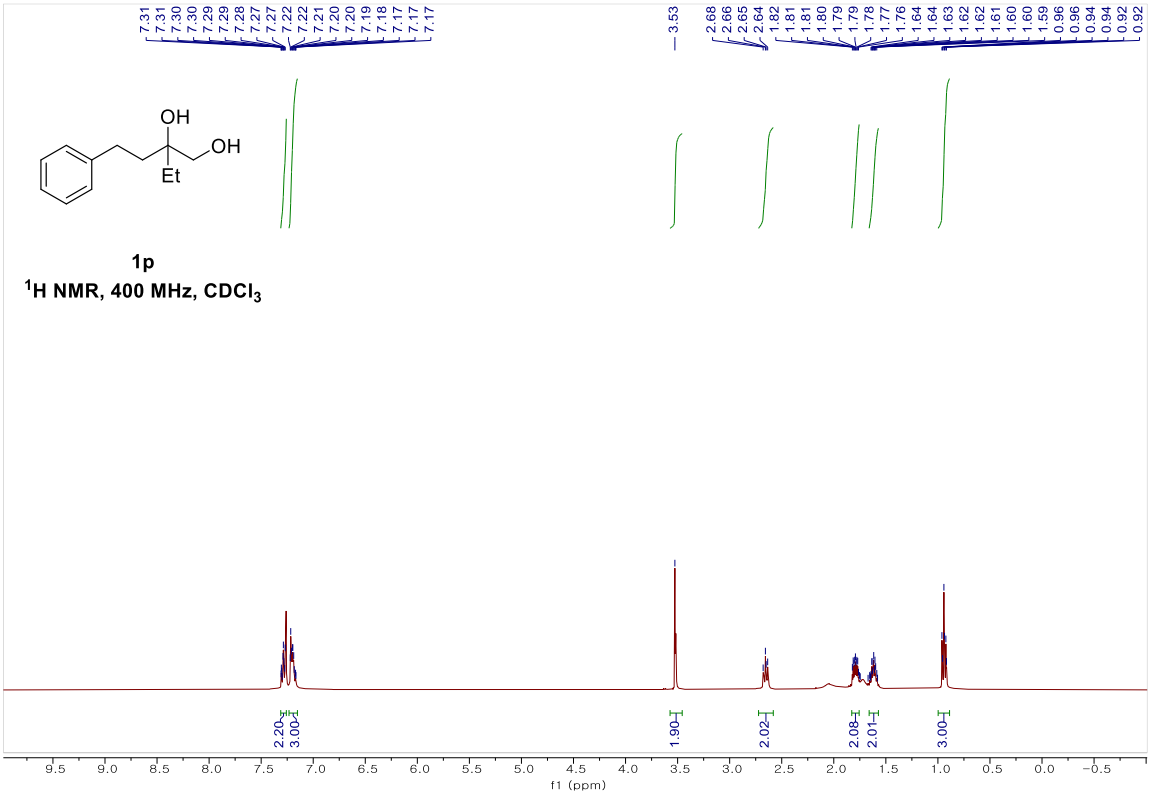
^{13}C NMR, 100 MHz, CD_2Cl_2

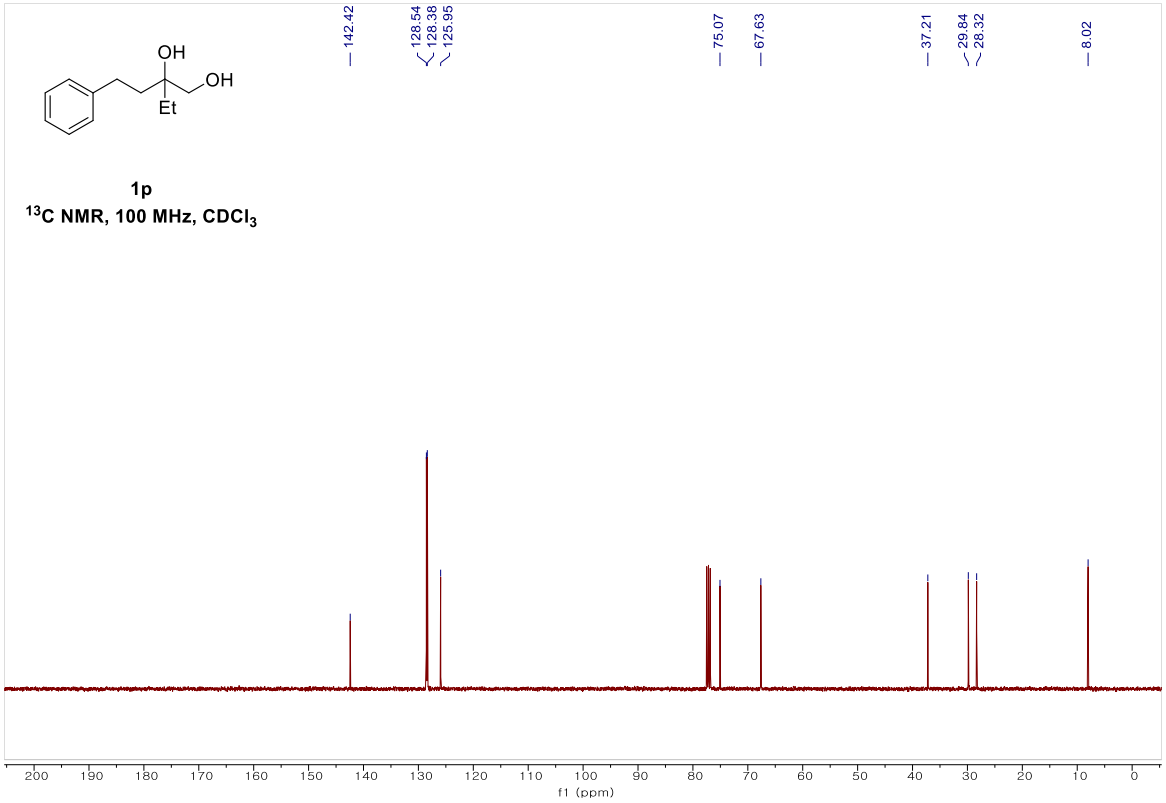
2-methyl-4-phenylbutane-1,2-diol (1o)



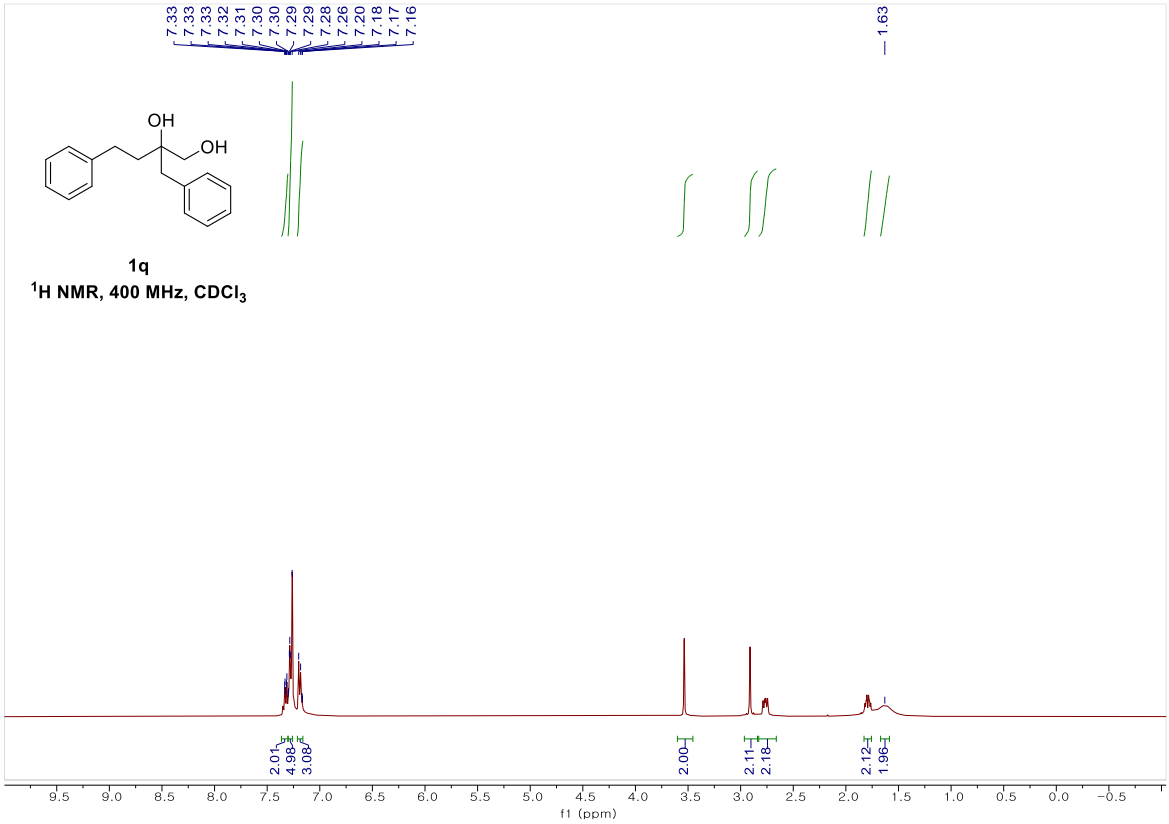


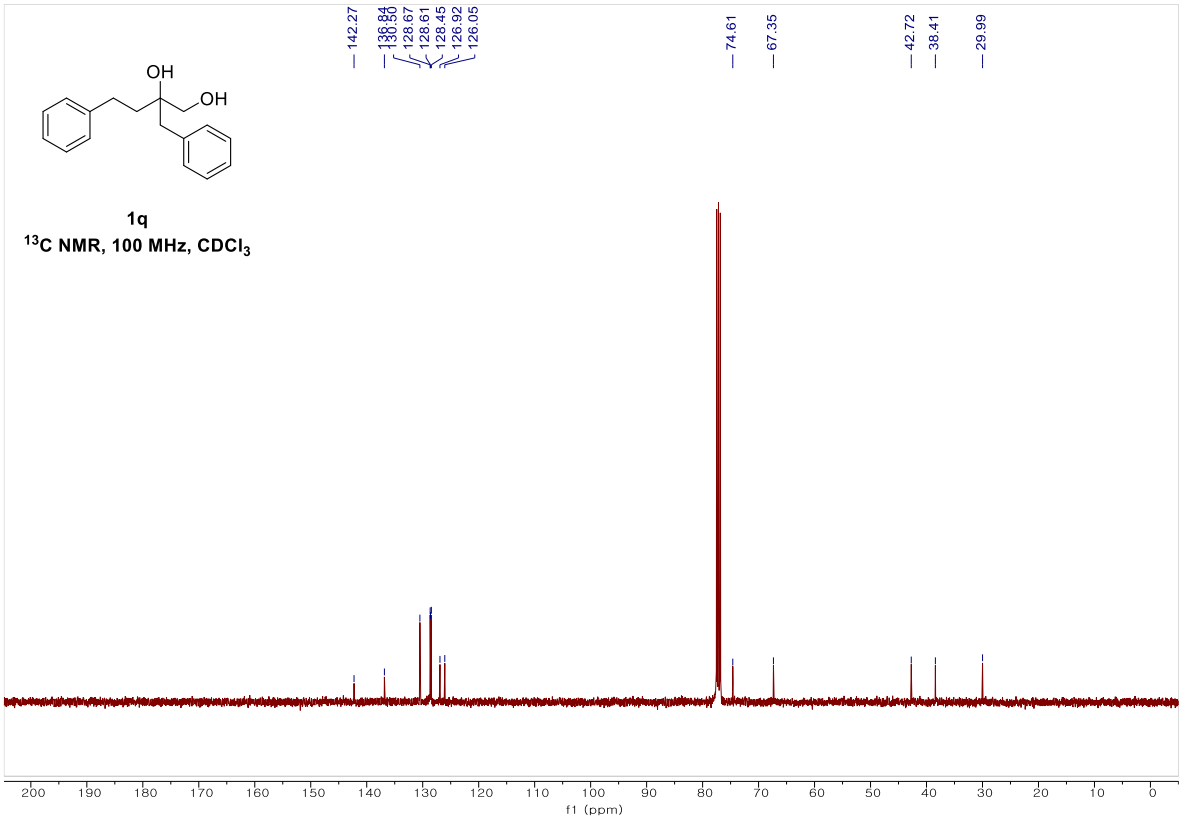
2-ethyl-4-phenylbutane-1,2-diol (1p)



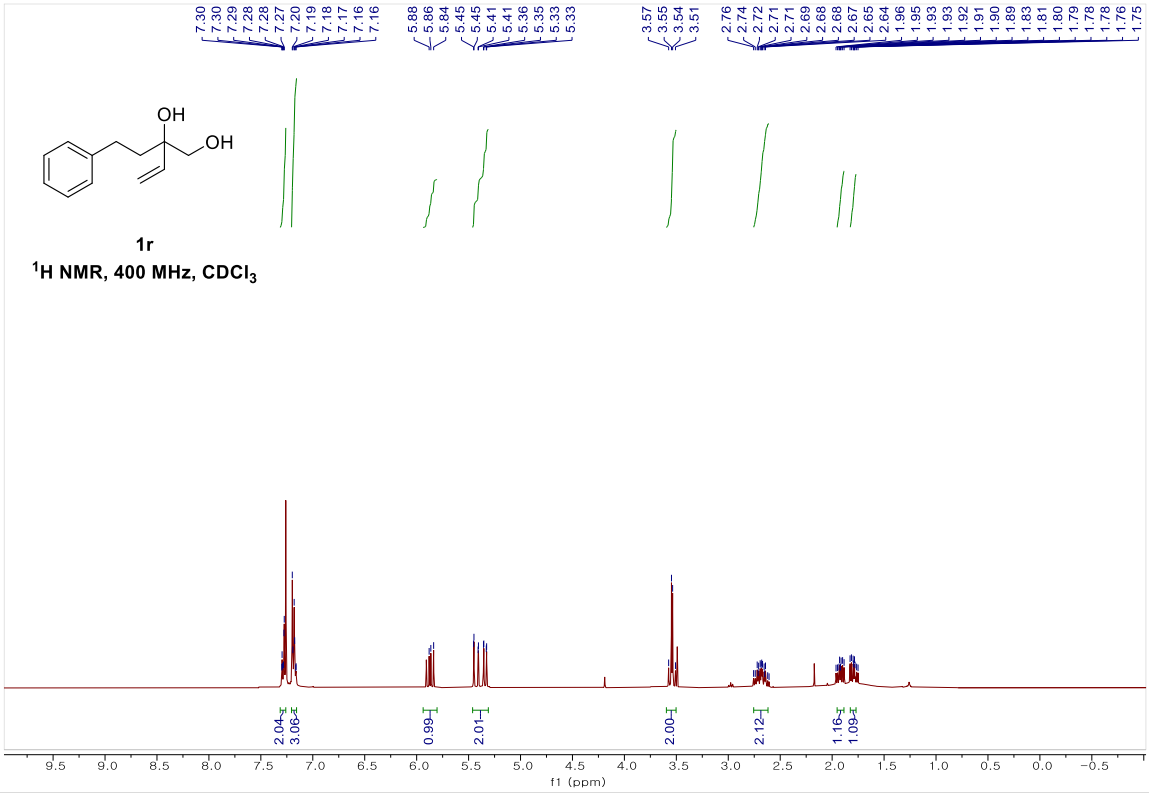


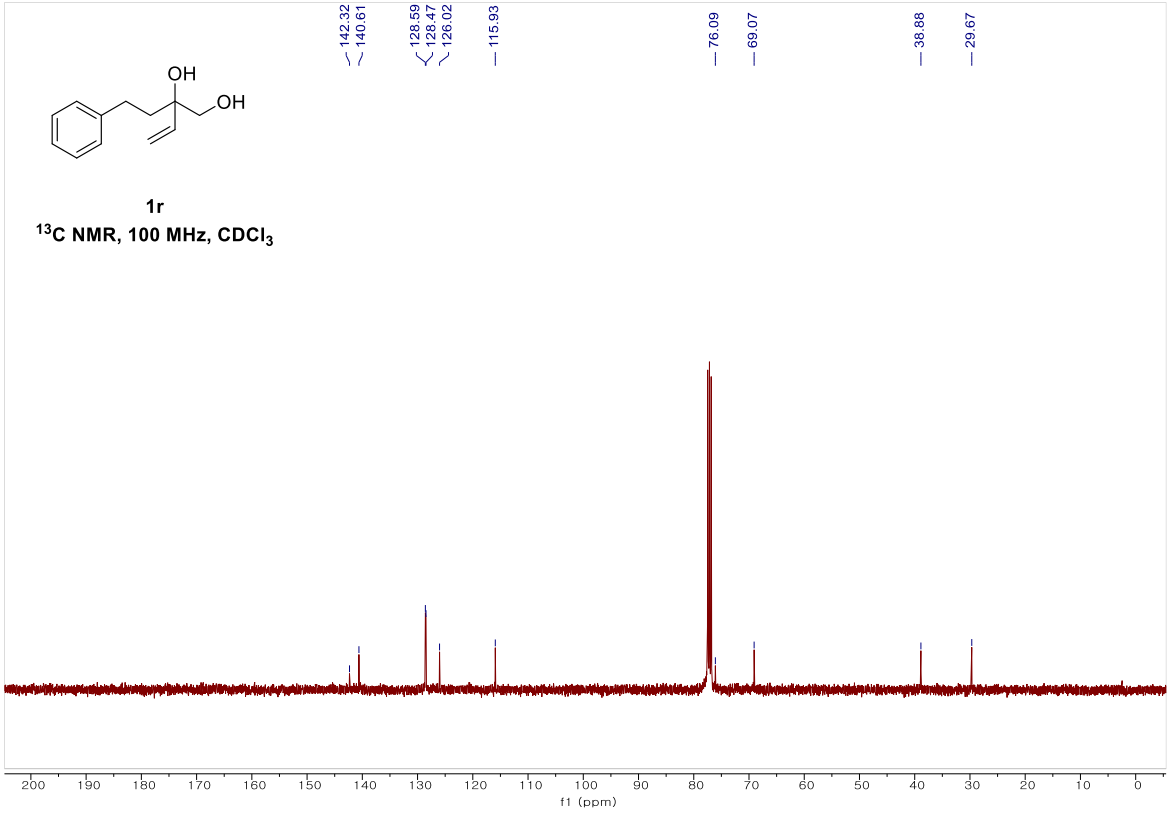
2-benzyl-4-phenylbutane-1,2-diol (1q)



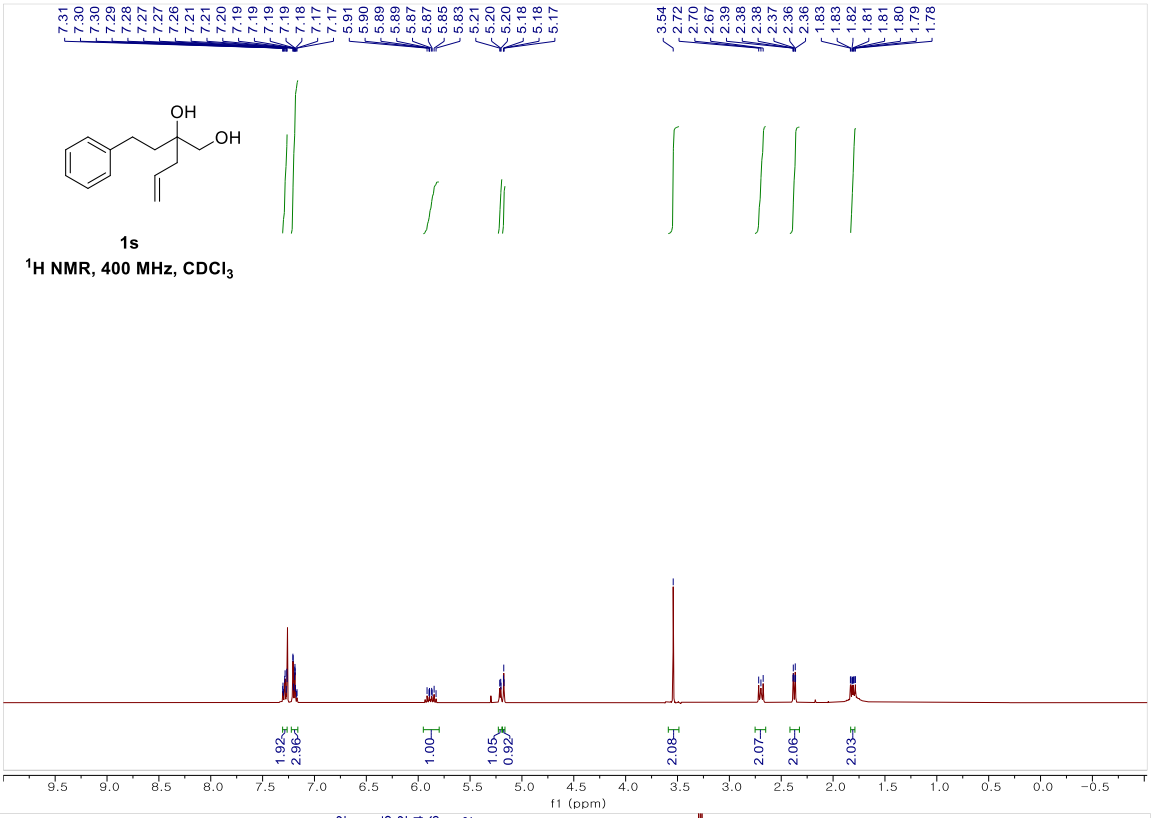


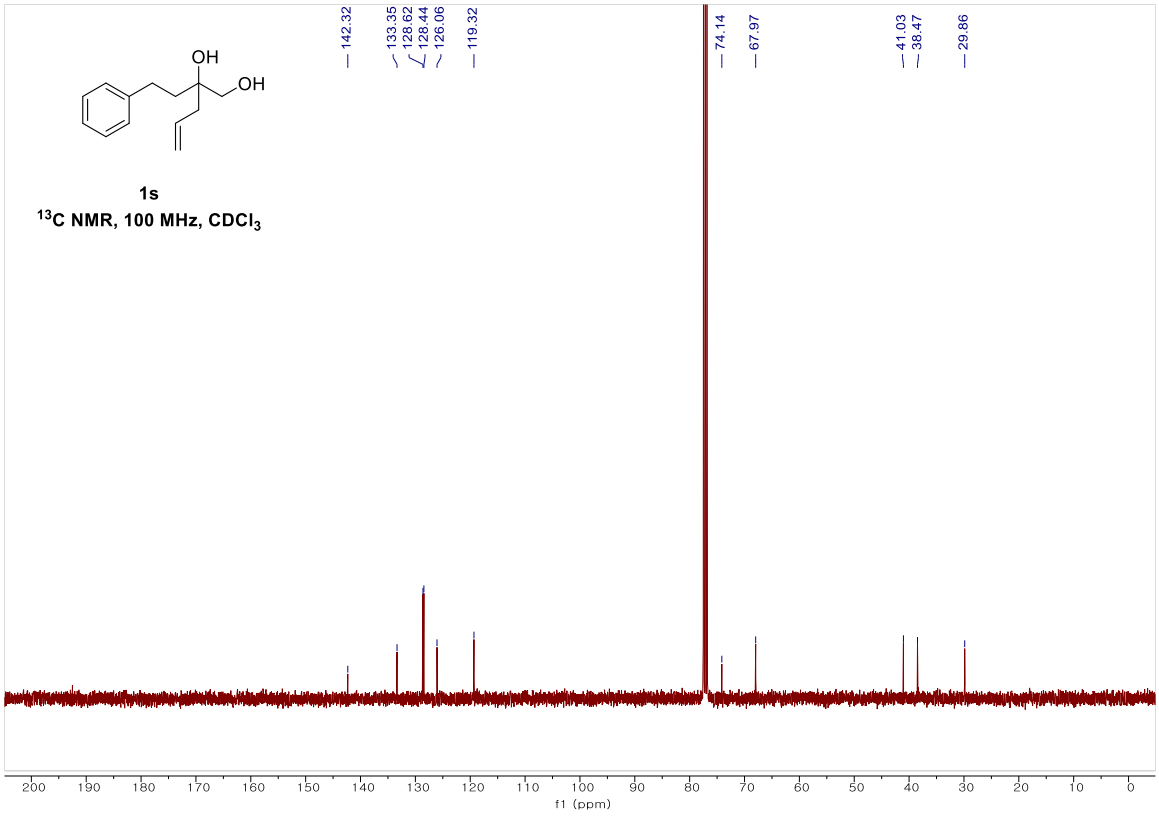
2-phenethylbut-3-ene-1,2-diol (1r)



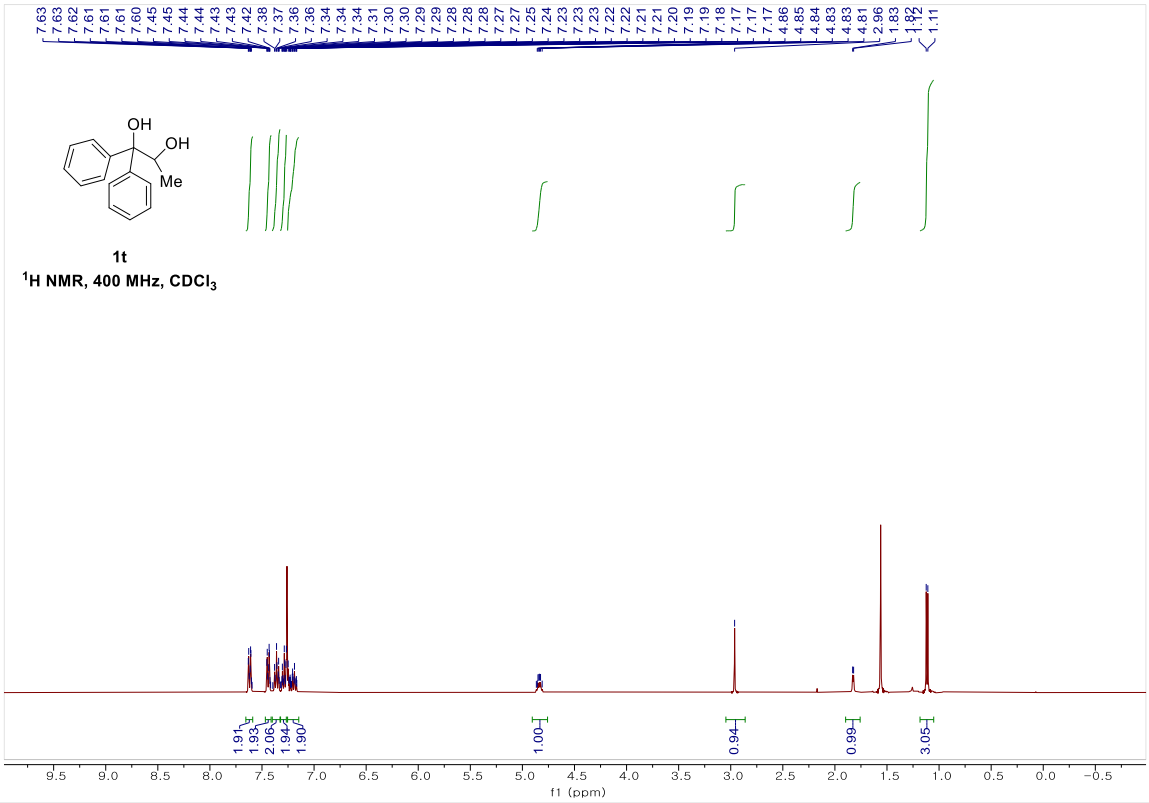


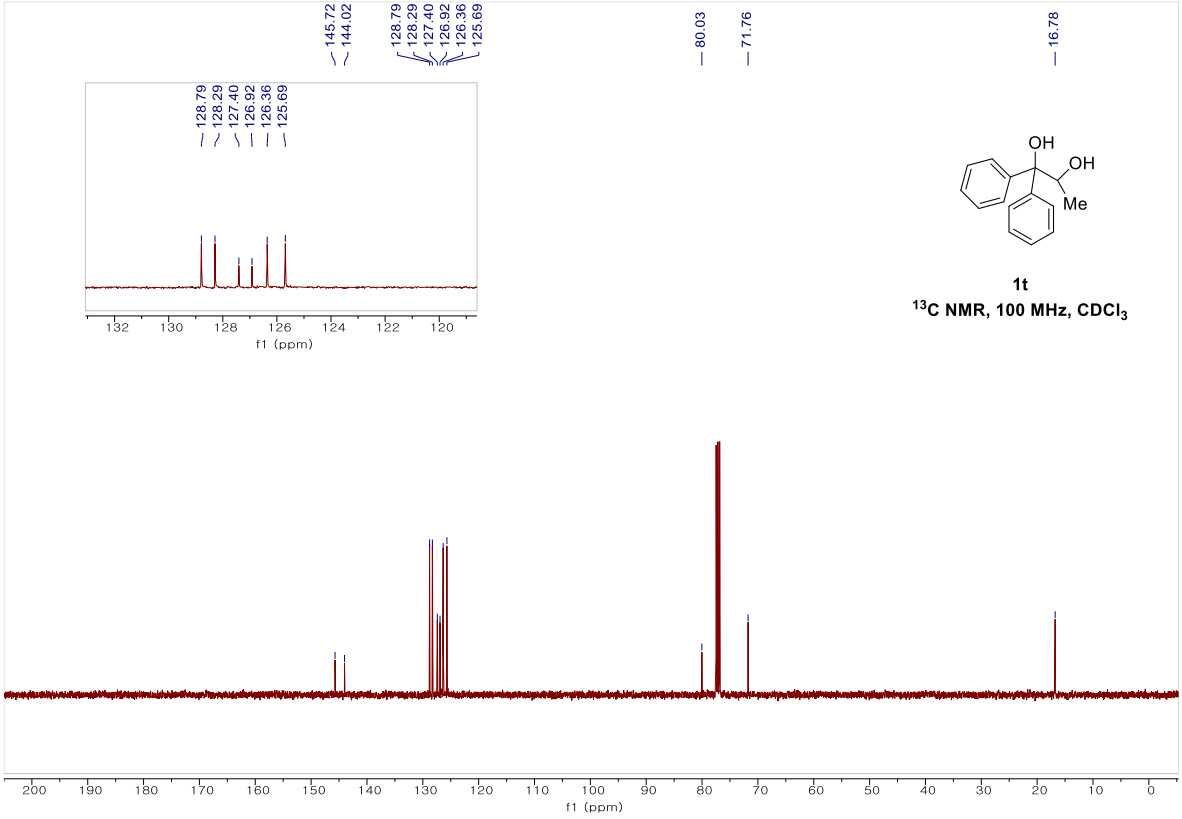
2-phenethylpent-4-ene-1,2-diol (1s)



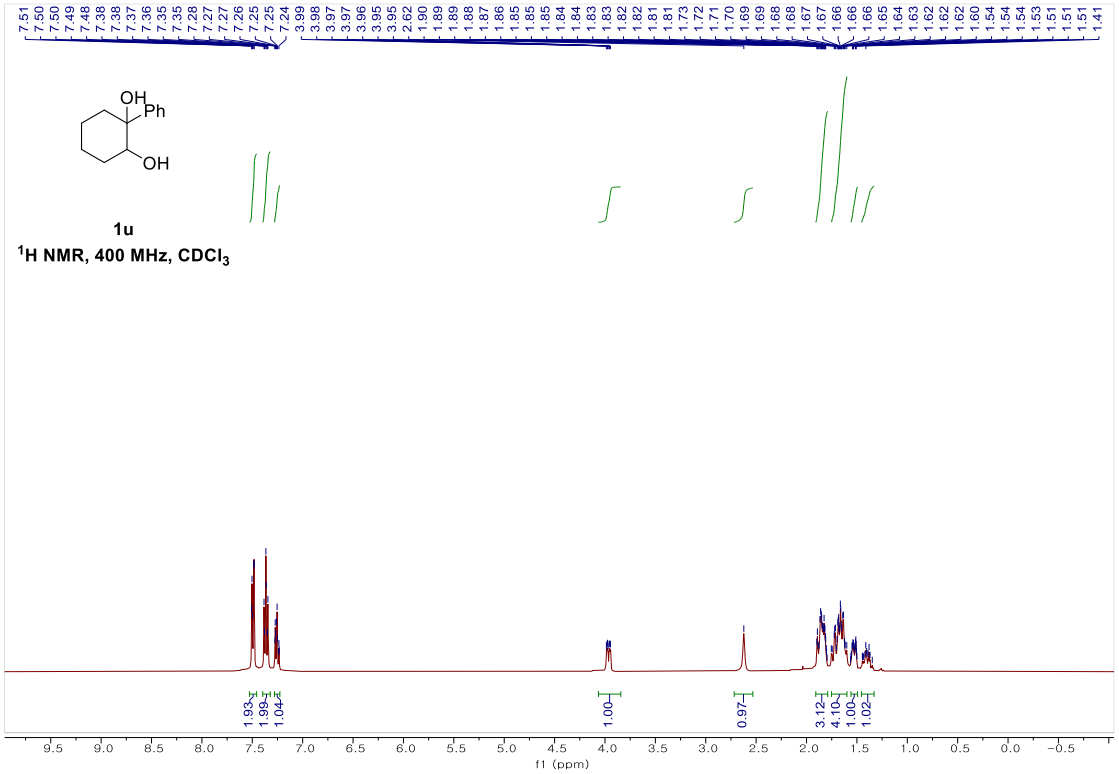


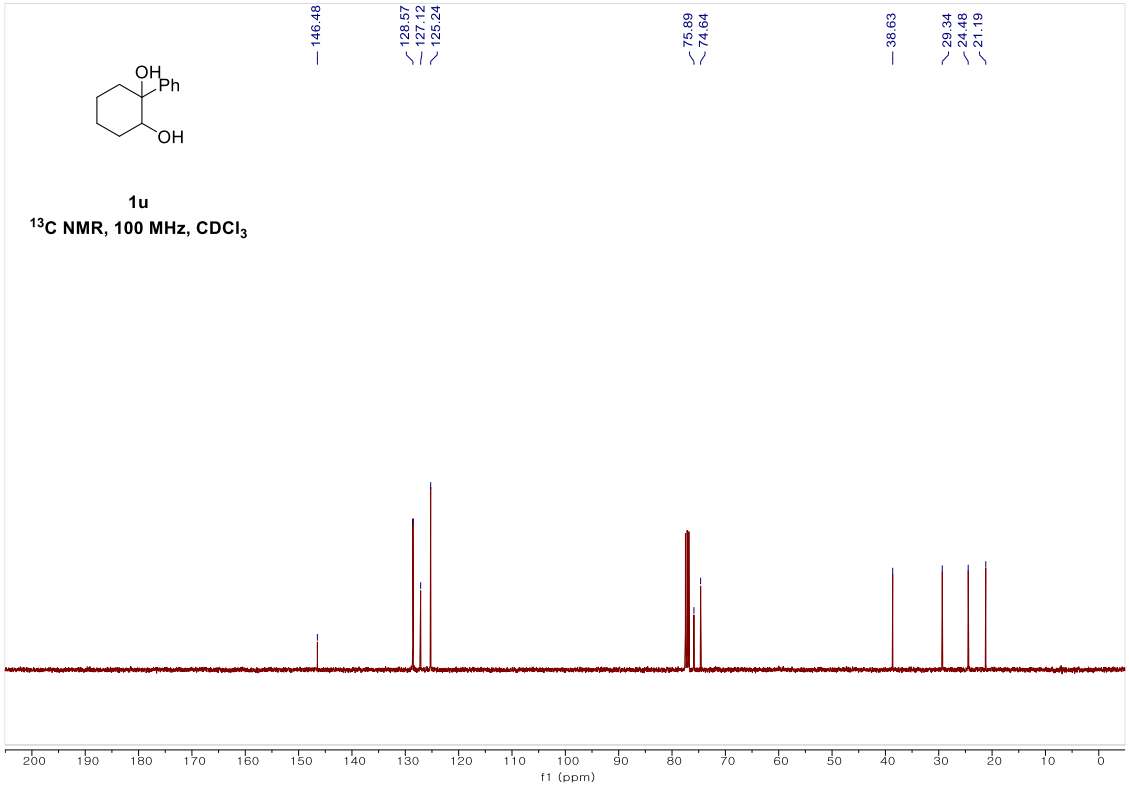
1,1-diphenylpropane-1,2-diol (1t)



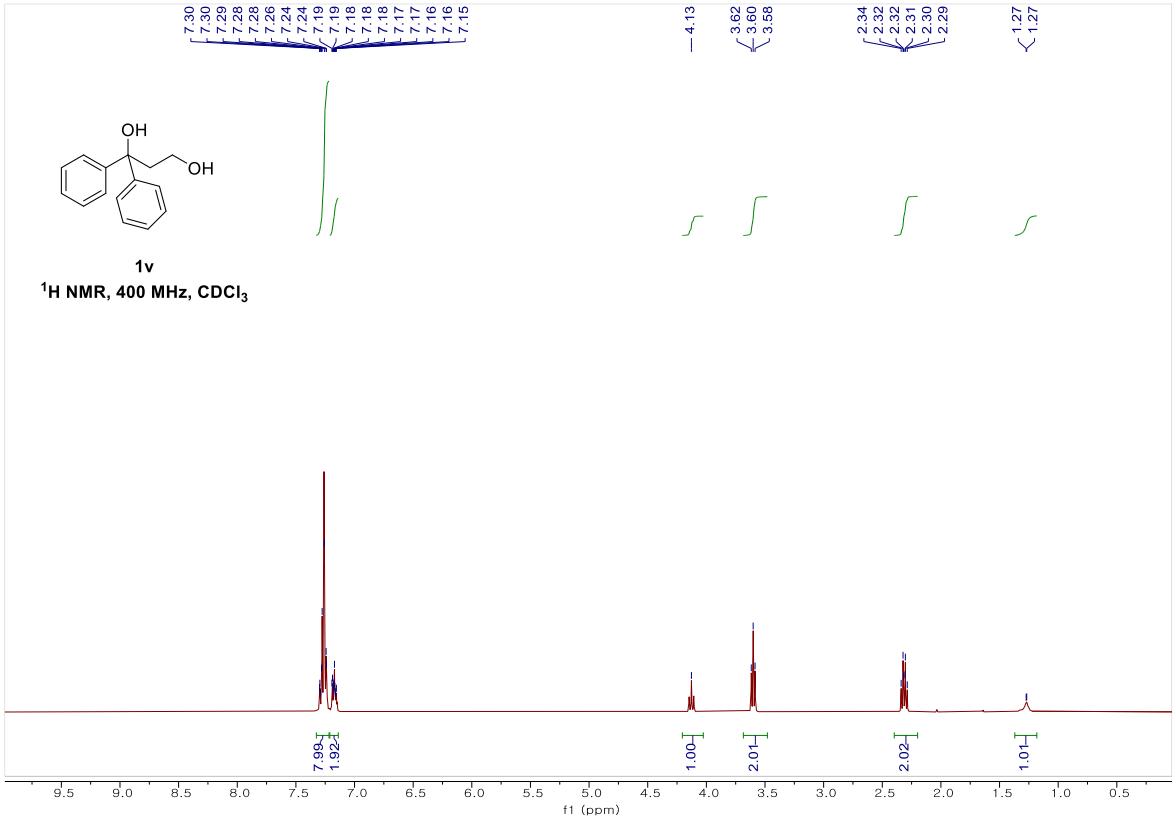


phenylcyclohexane-1,2-diol (1u)



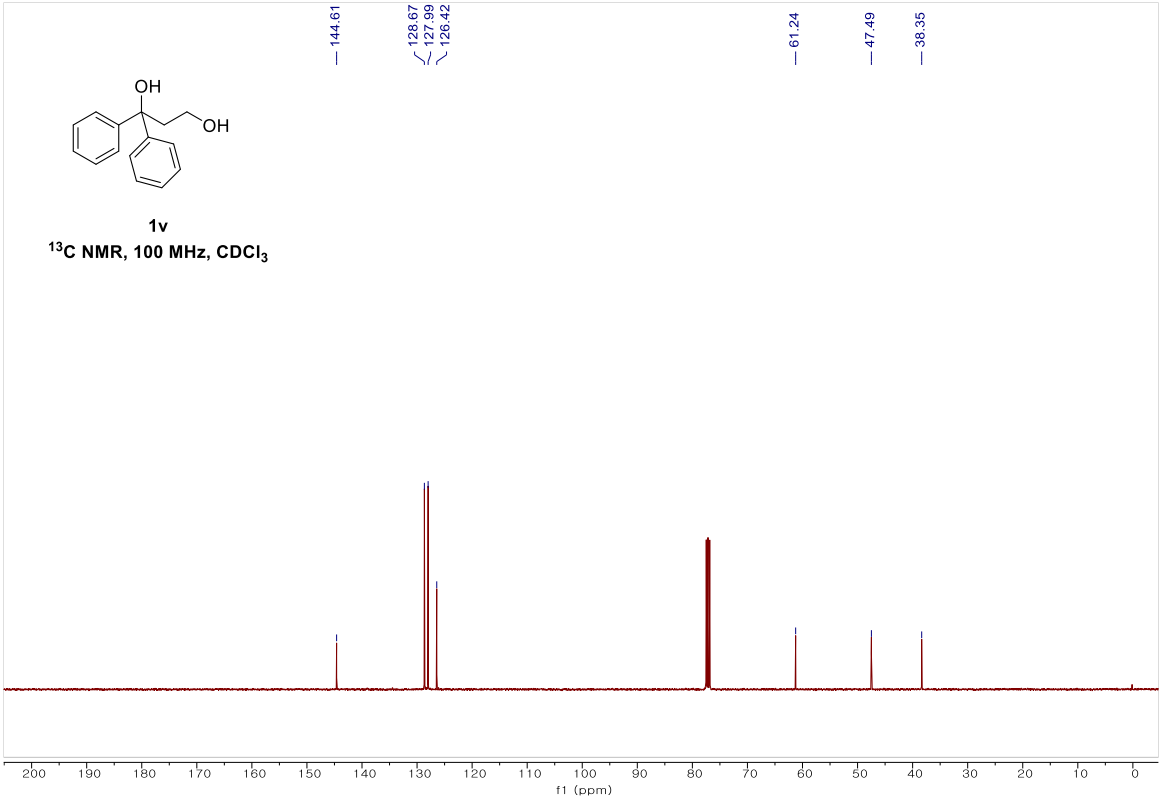


1,1-diphenylpropane-1,3-diol (1v)



1v

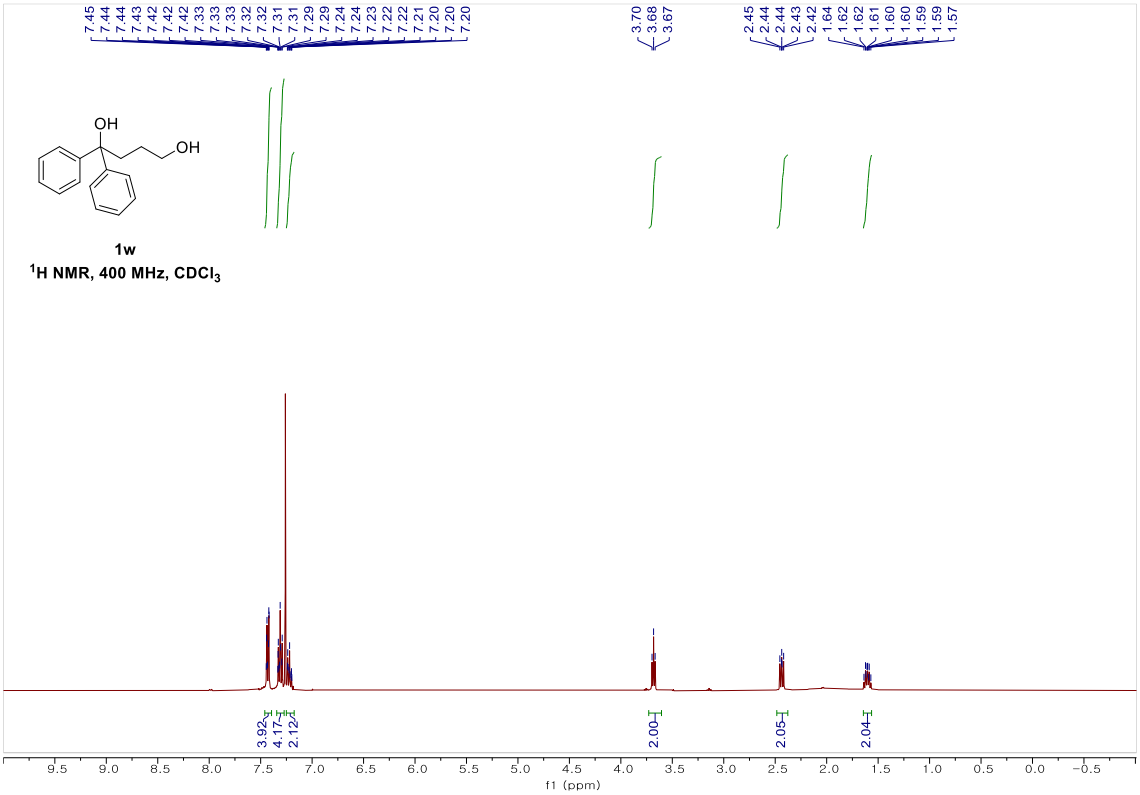
^{1}H NMR, 400 MHz, $CDCl_3$

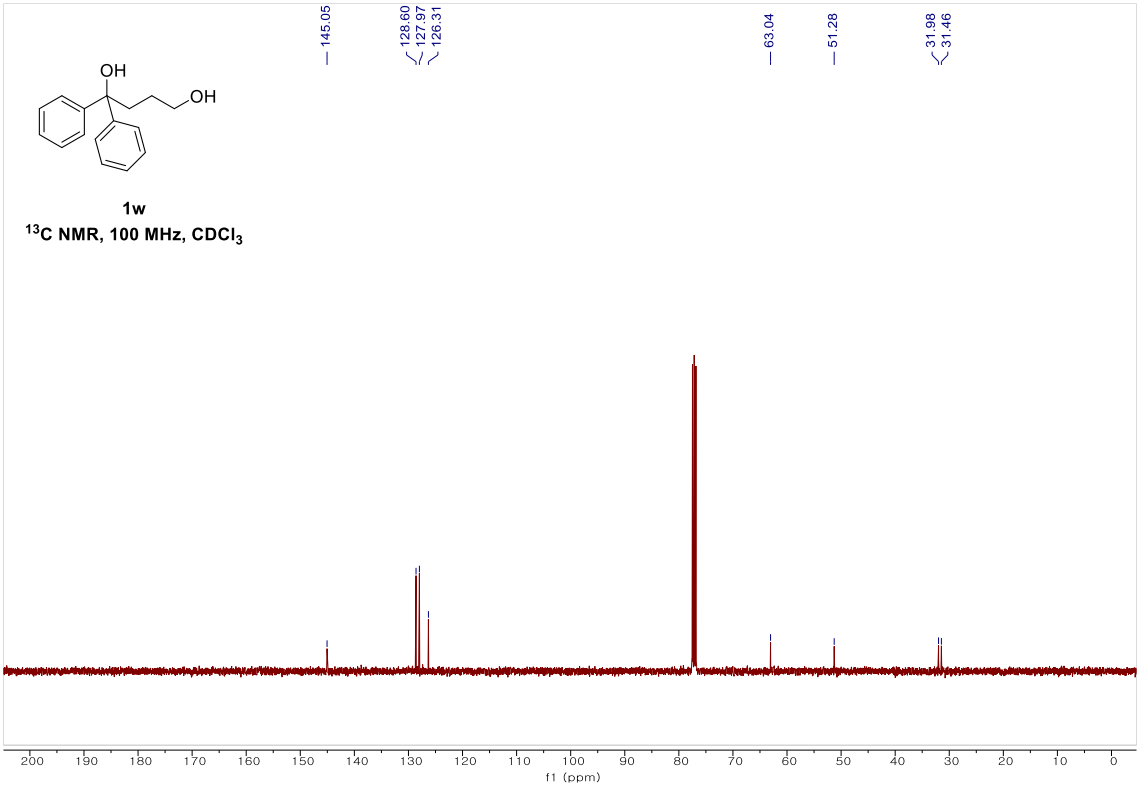


1v

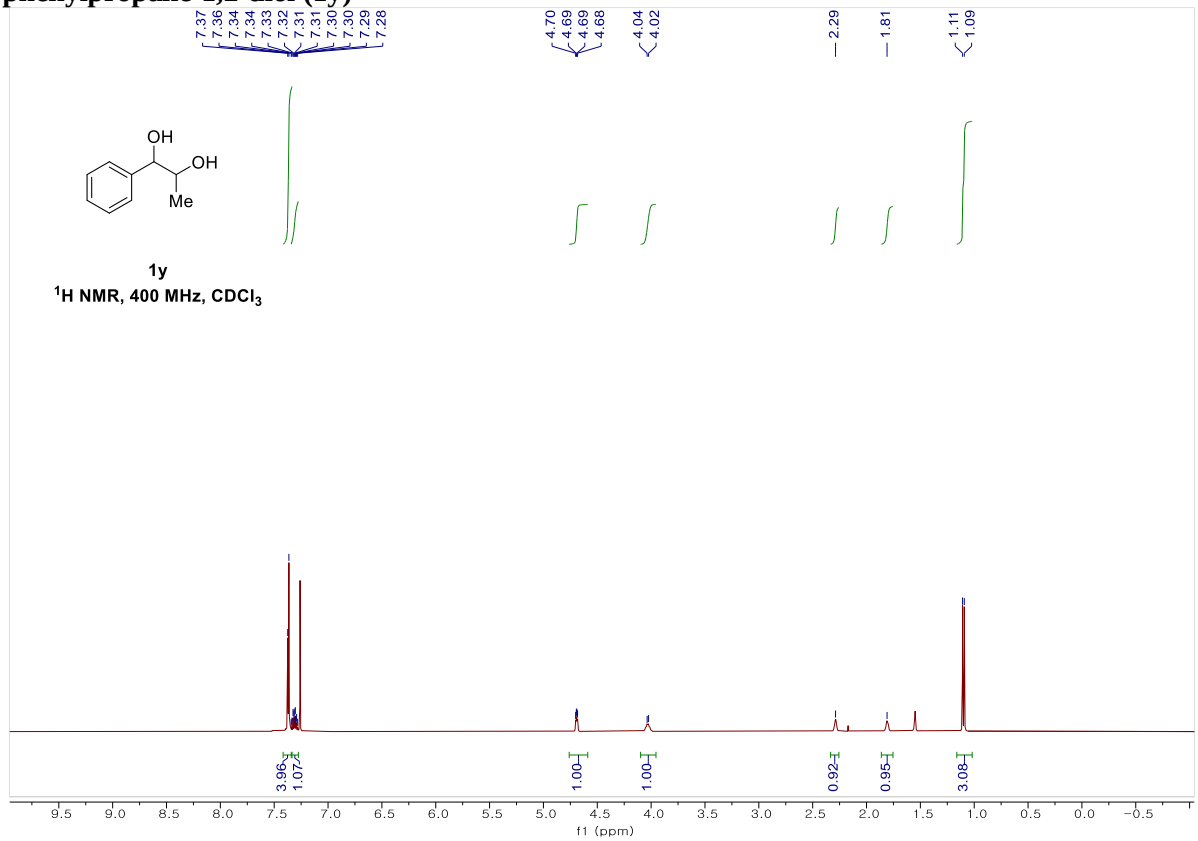
^{13}C NMR, 100 MHz, $CDCl_3$

1,1-diphenylbutane-1,4-diol (1w)



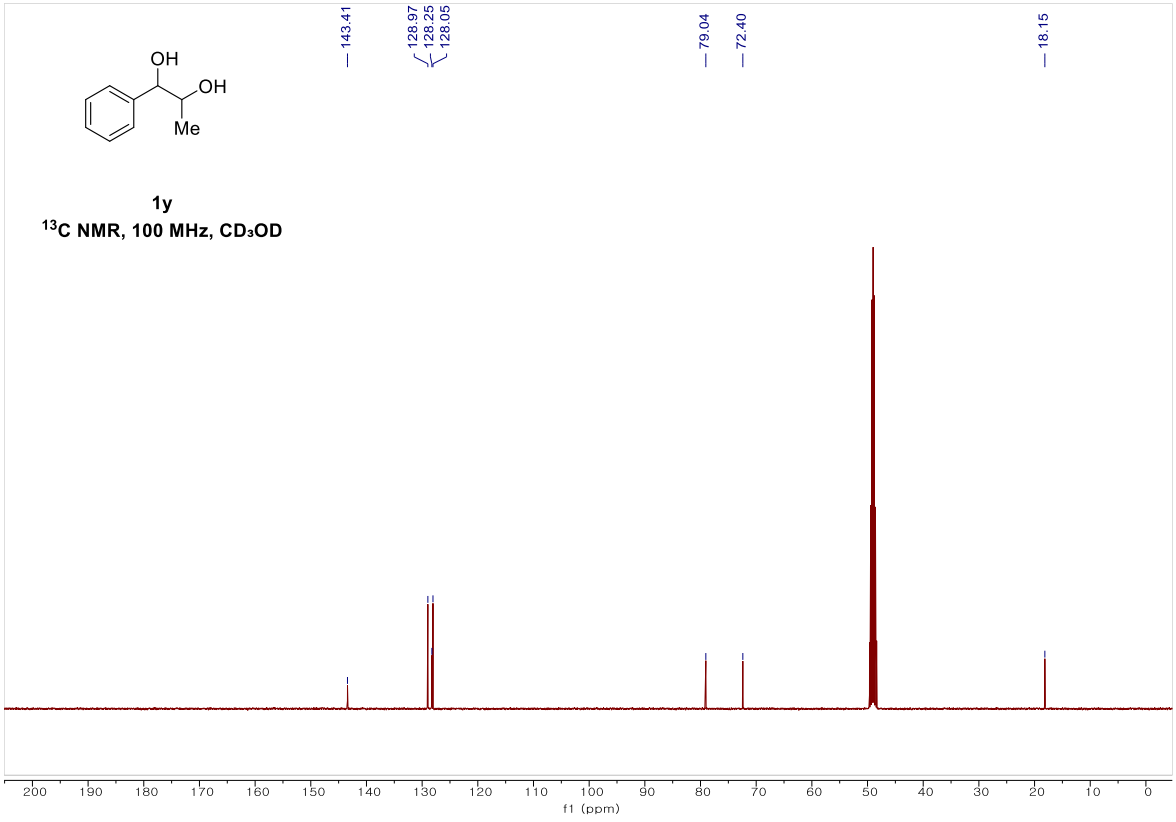


1-phenylpropane-1,2-diol (1y)



1y

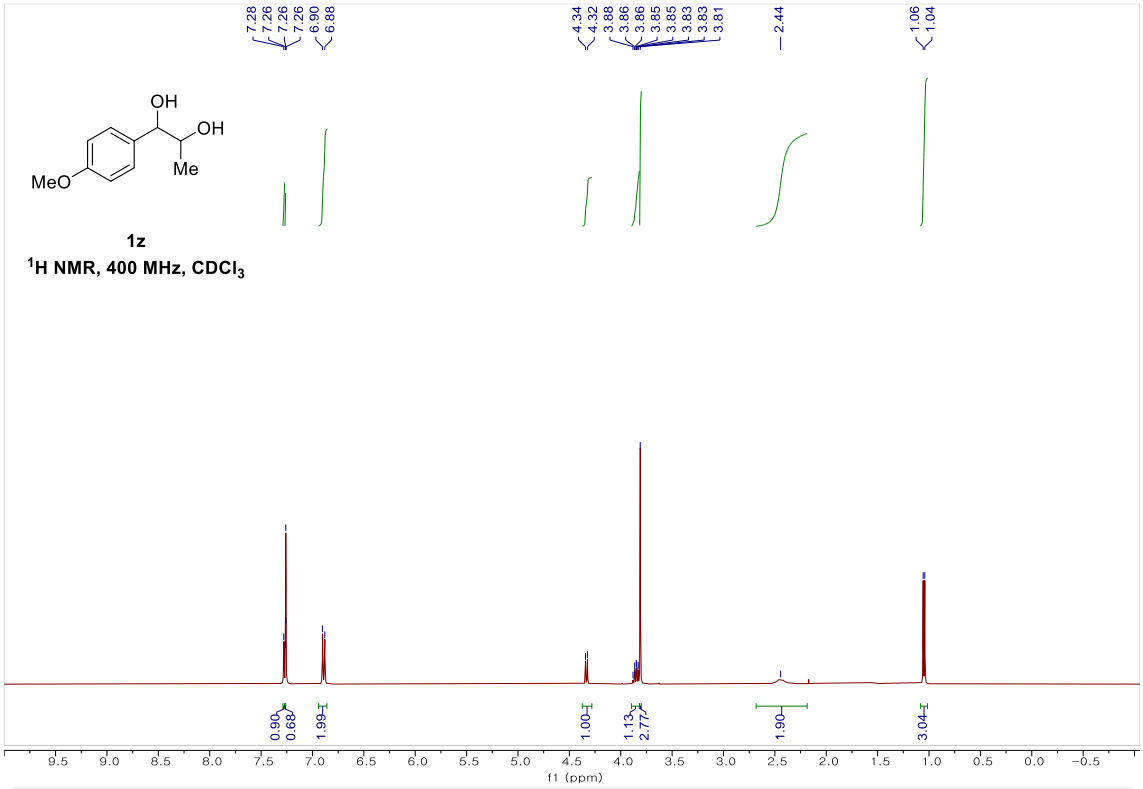
^{1}H NMR, 400 MHz, $CDCl_3$

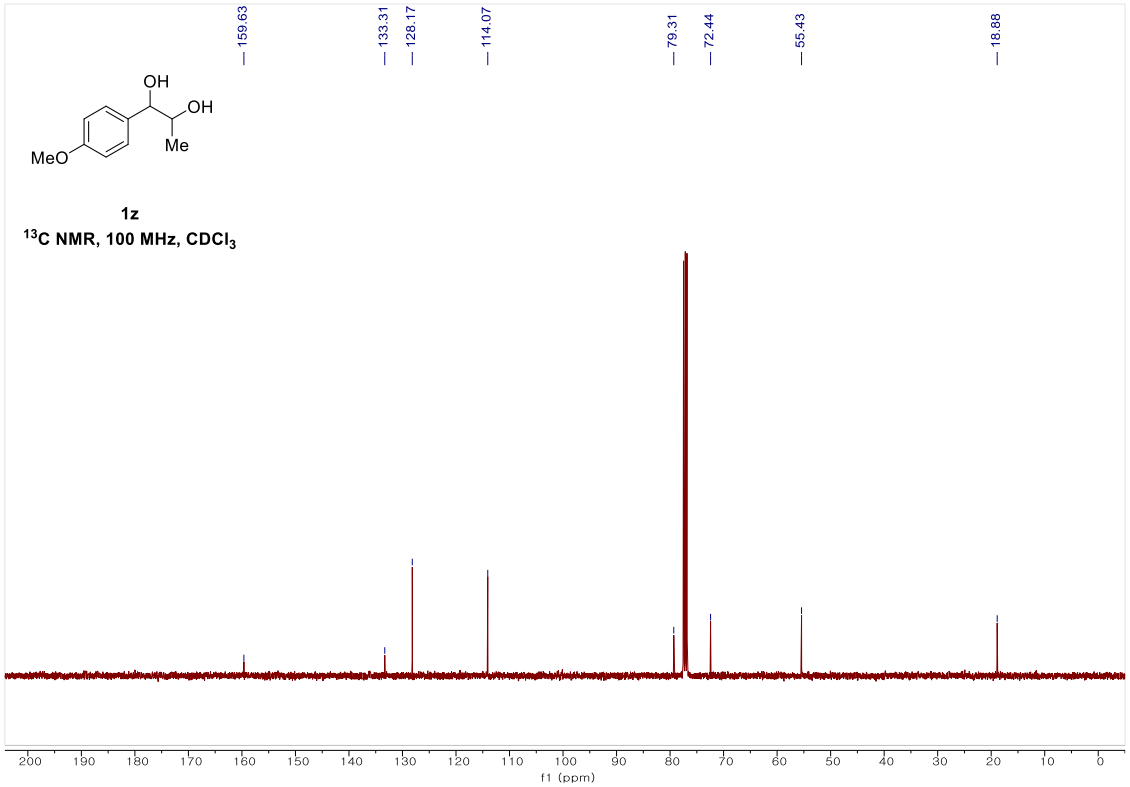


1y

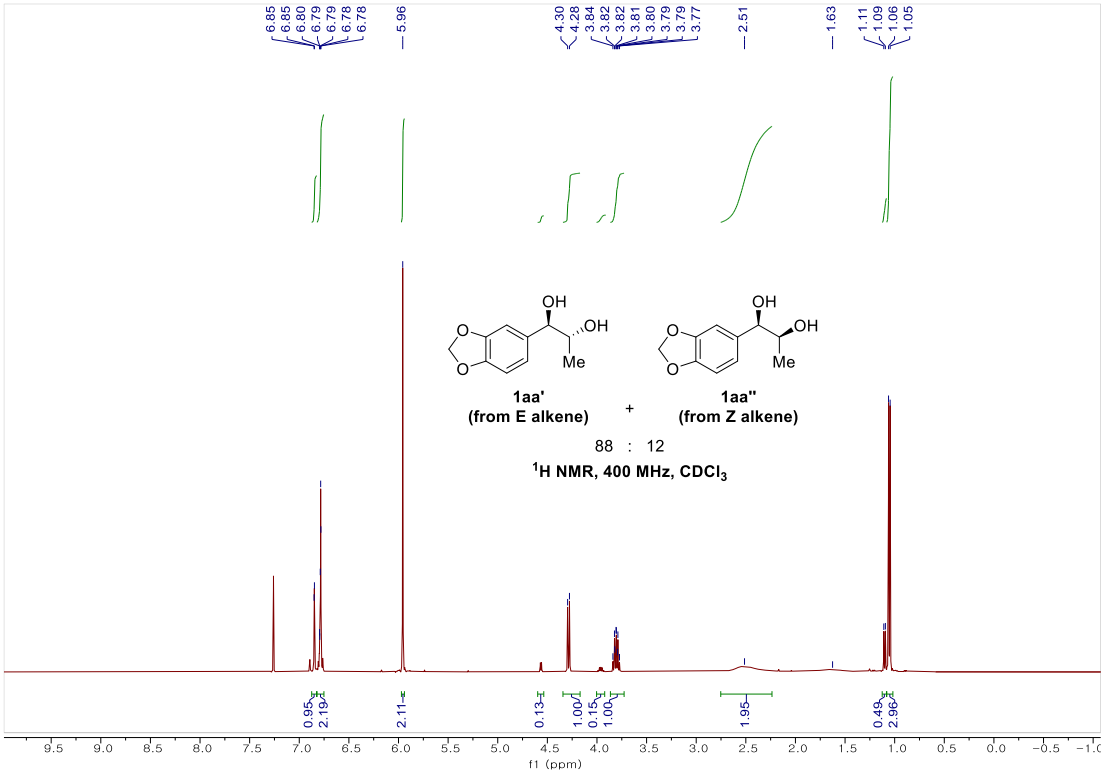
^{13}C NMR, 100 MHz, CD_3OD

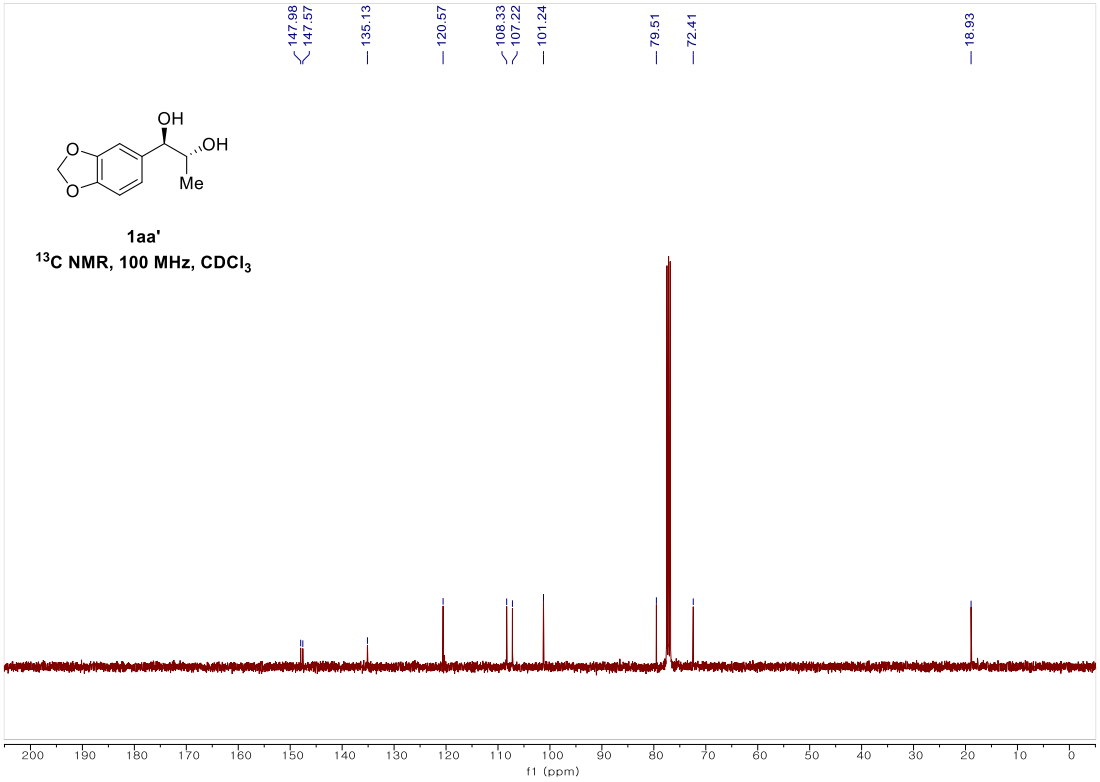
1-(4-methoxyphenyl)propane-1,2-diol (1z)





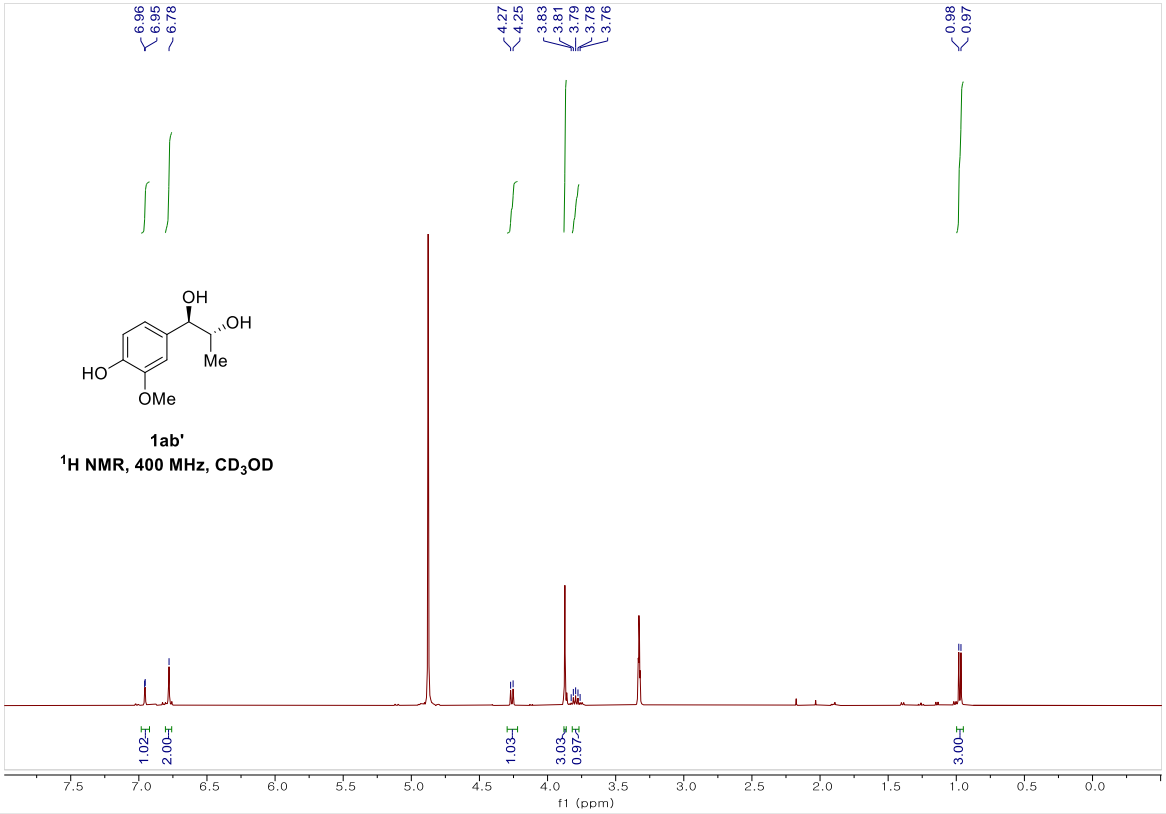
1-(benzo[d][1,3]dioxol-5-yl)propane-1,2-diol (1aa)

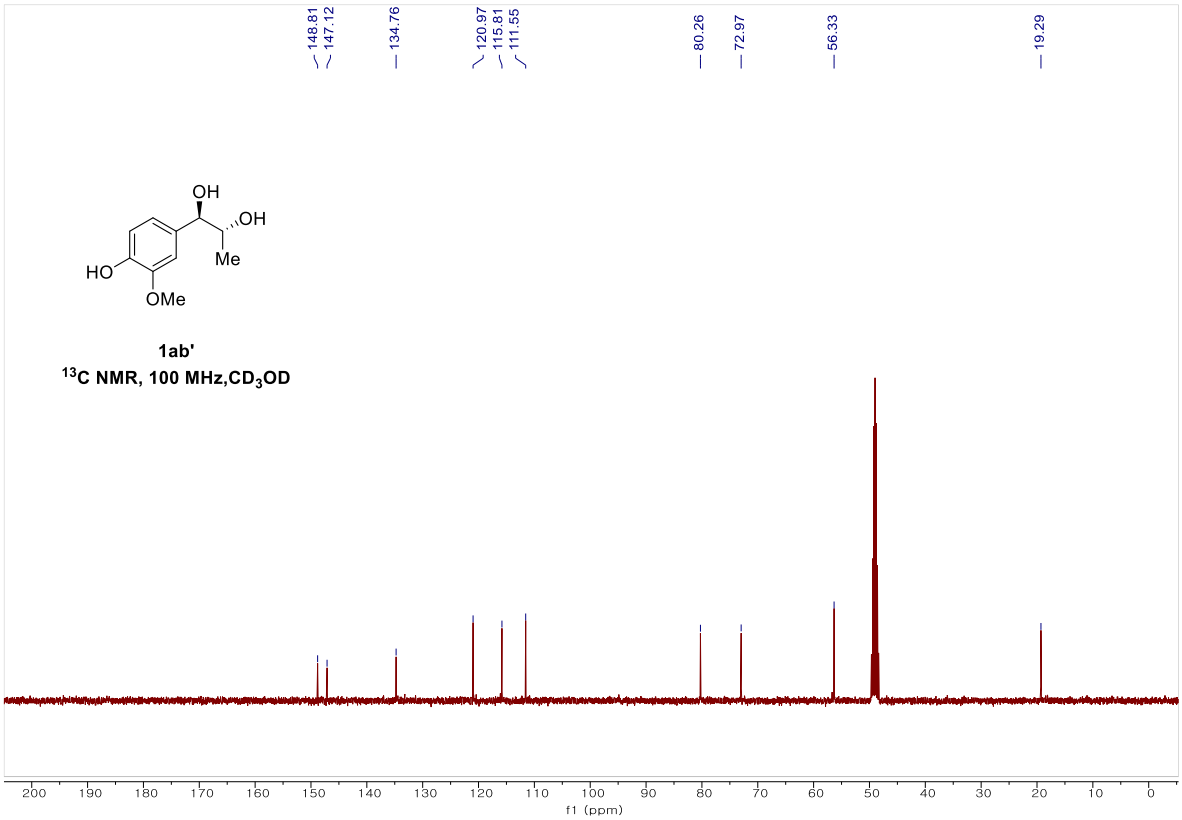




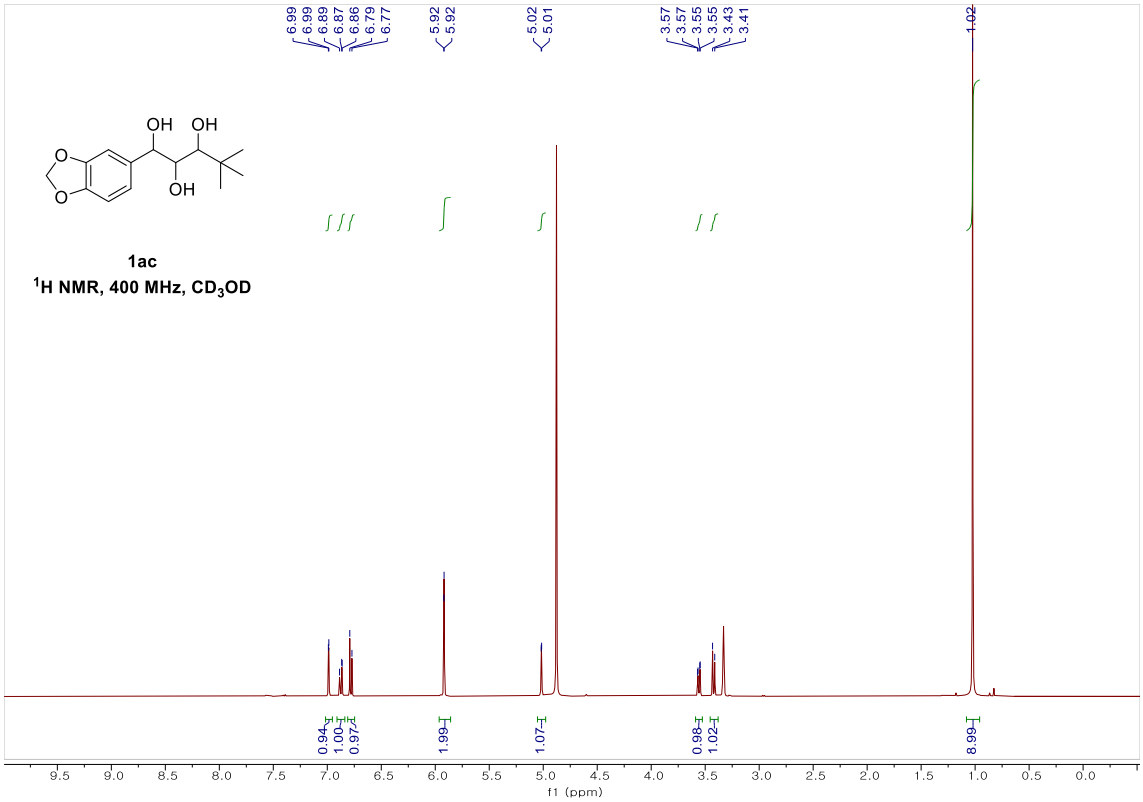
*For compound **1aa**, ^{1}H NMR spectra were obtained from a diastereomeric mixture, while ^{13}C NMR data were recorded and integrated for the major diastereomer only.

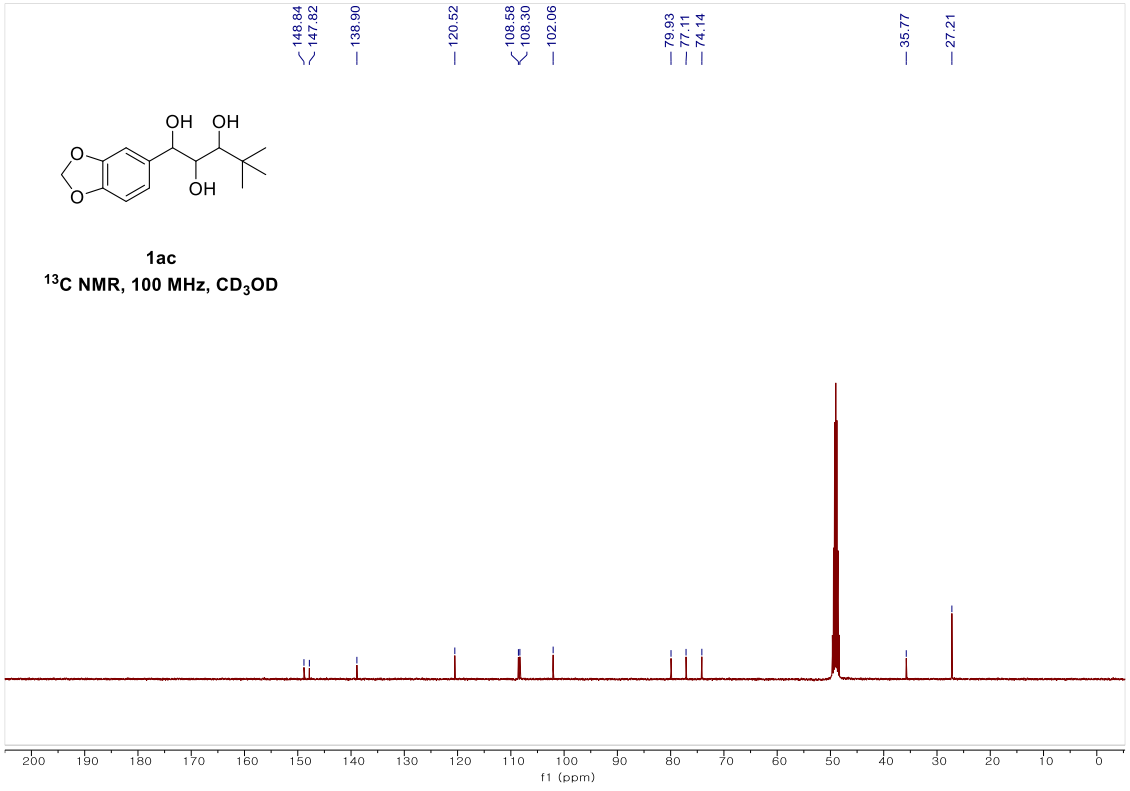
1-(4-hydroxy-3-methoxyphenyl)propane-1,2-diol (1ab)



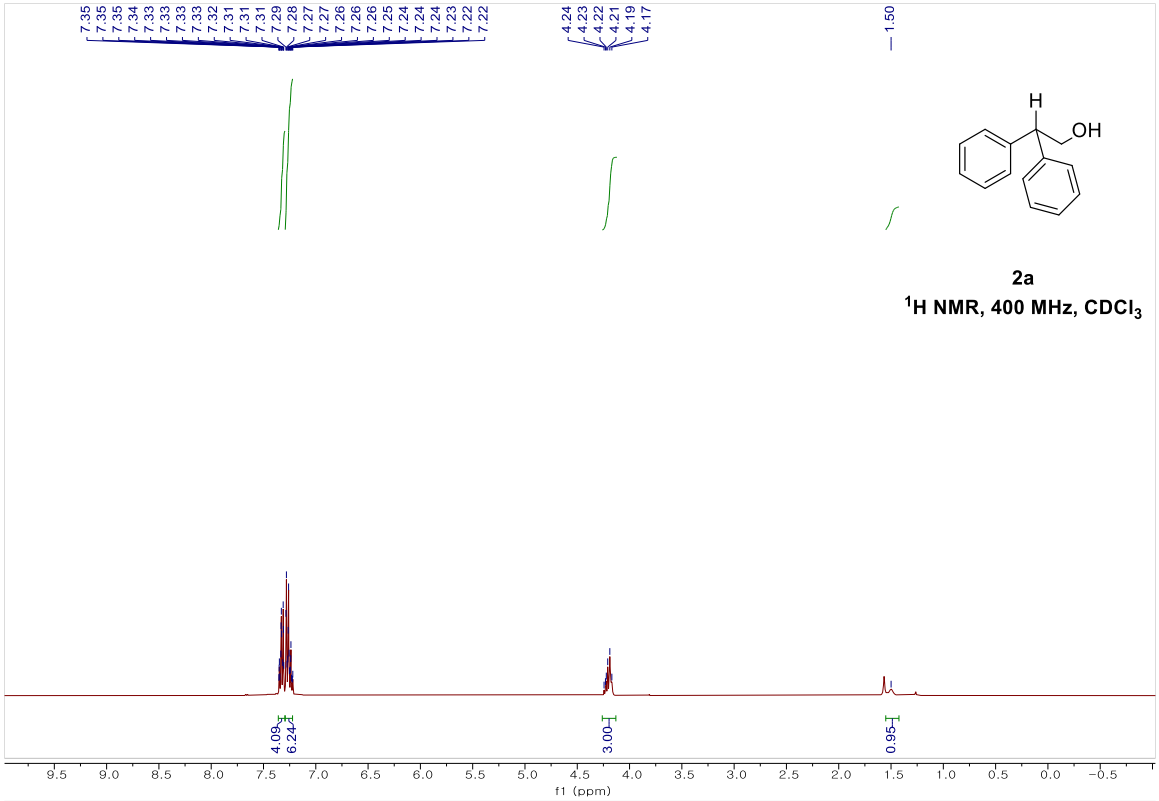


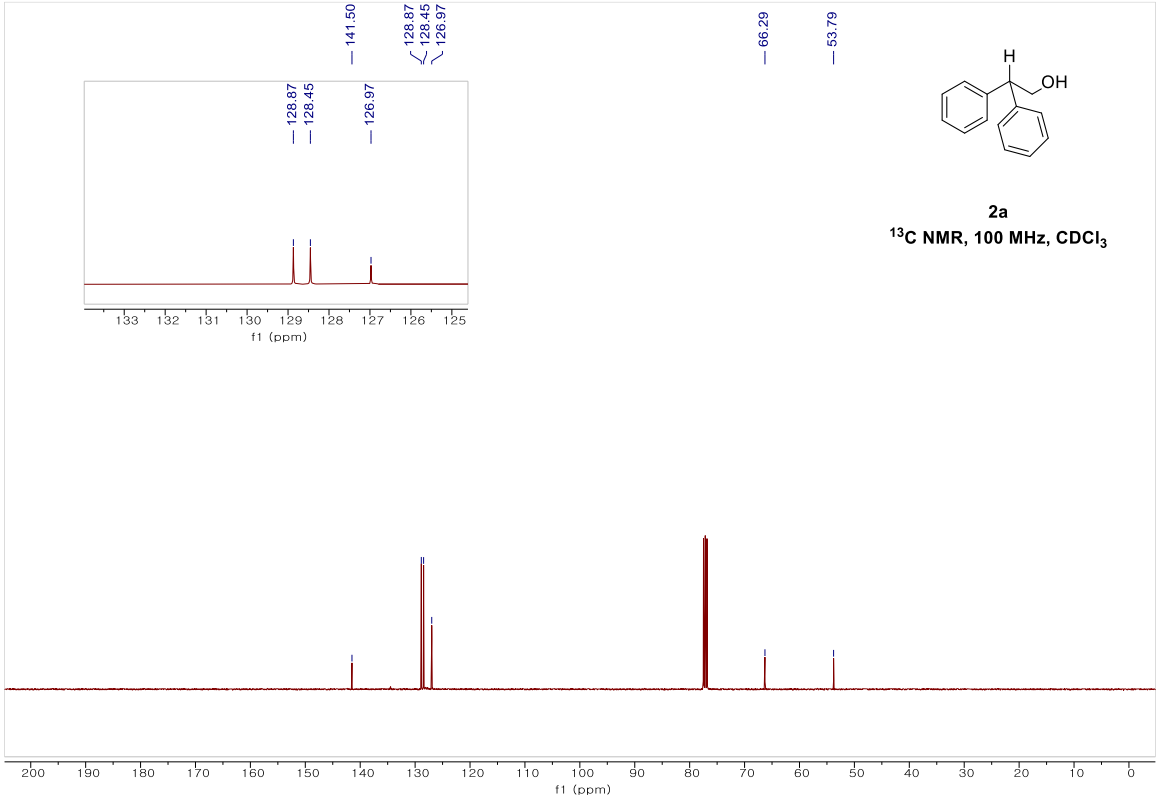
1-(benzo[d][1,3]dioxol-5-yl)-4,4-dimethylpentane-1,2,3-triol (1ac)



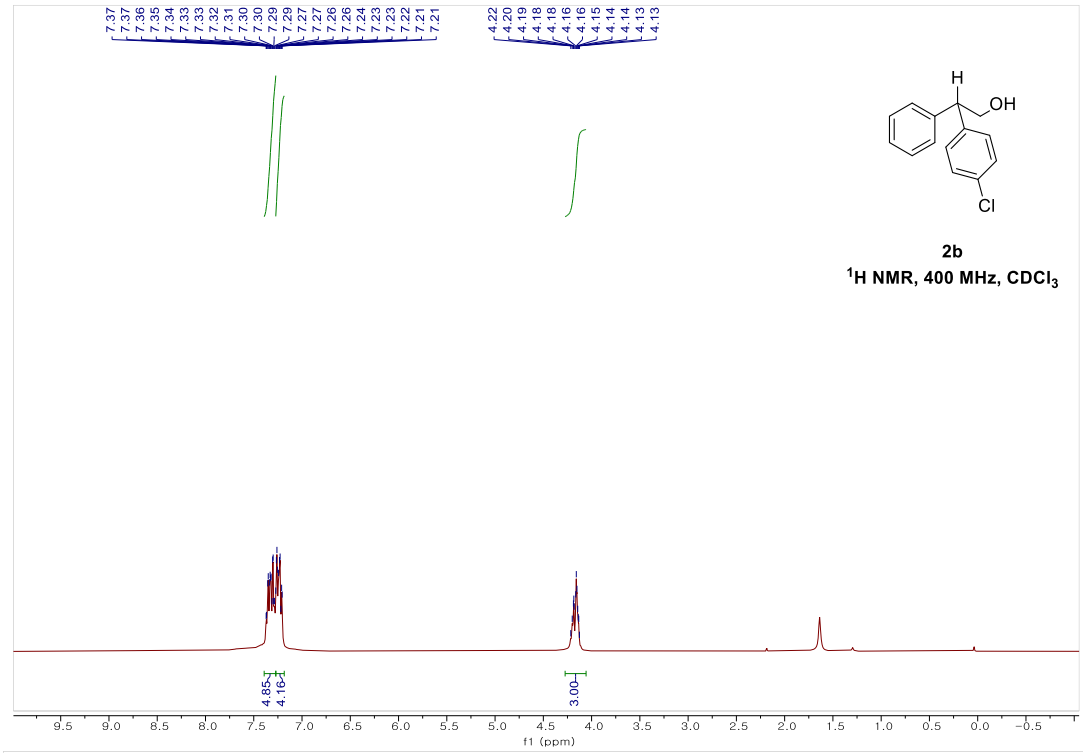


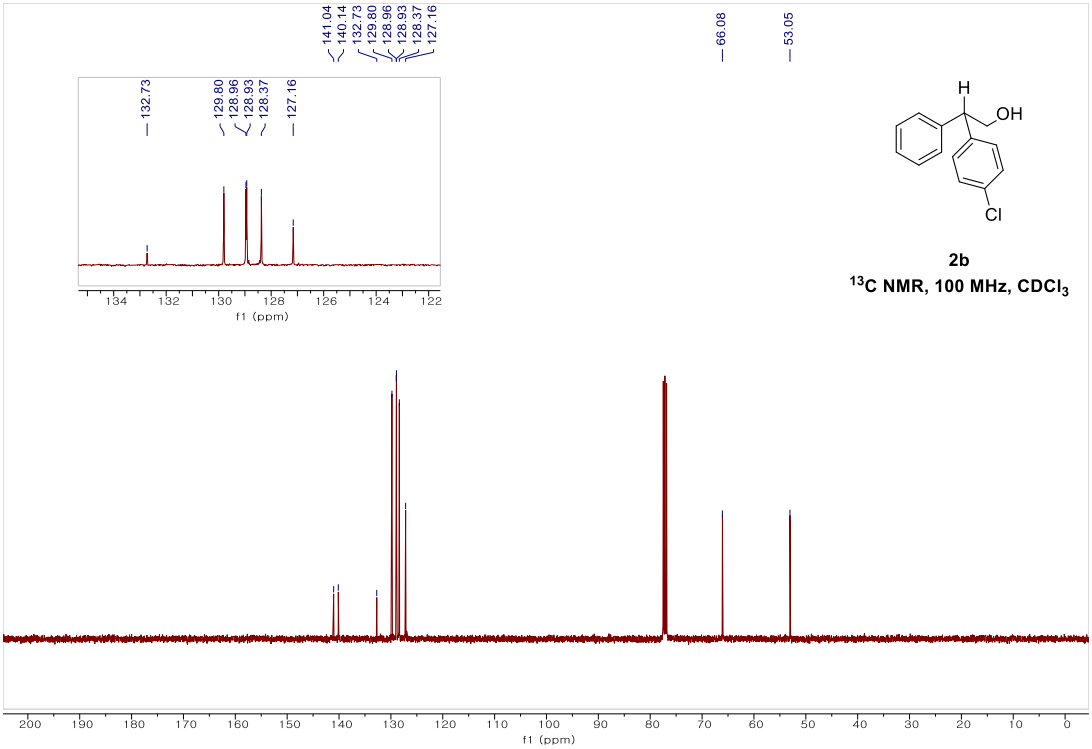
2,2-diphenylethan-1-ol (2a)



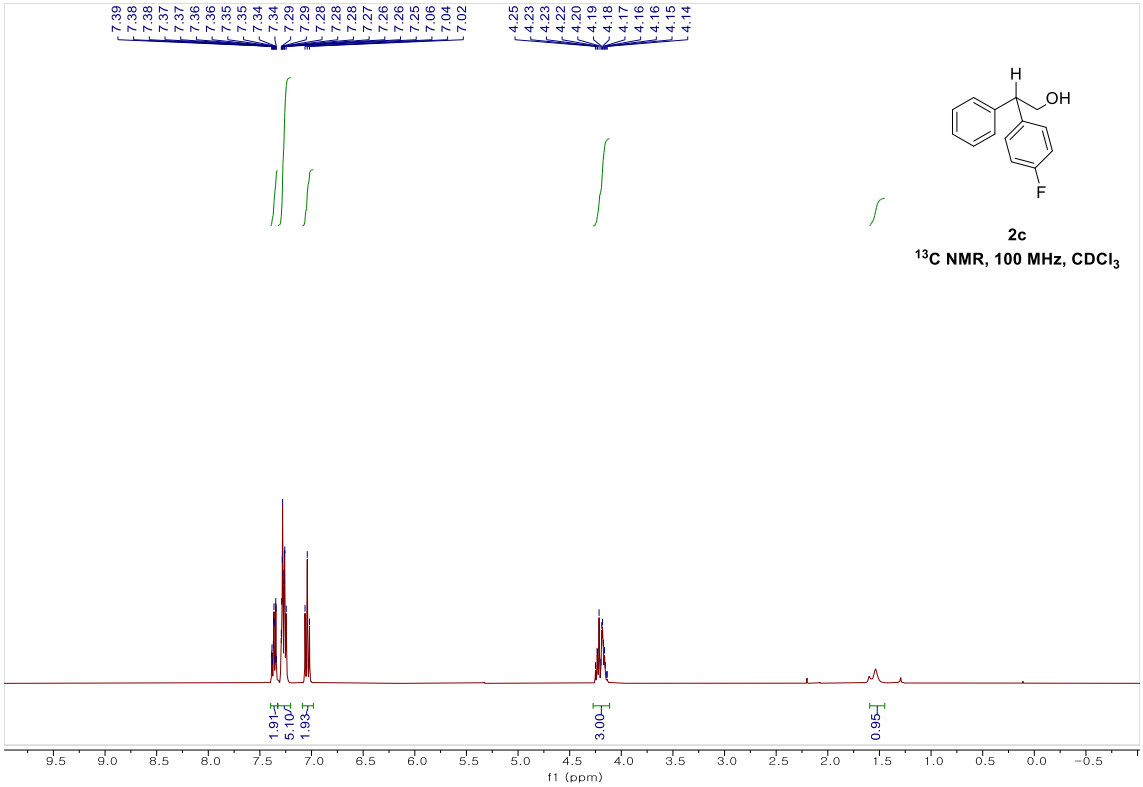


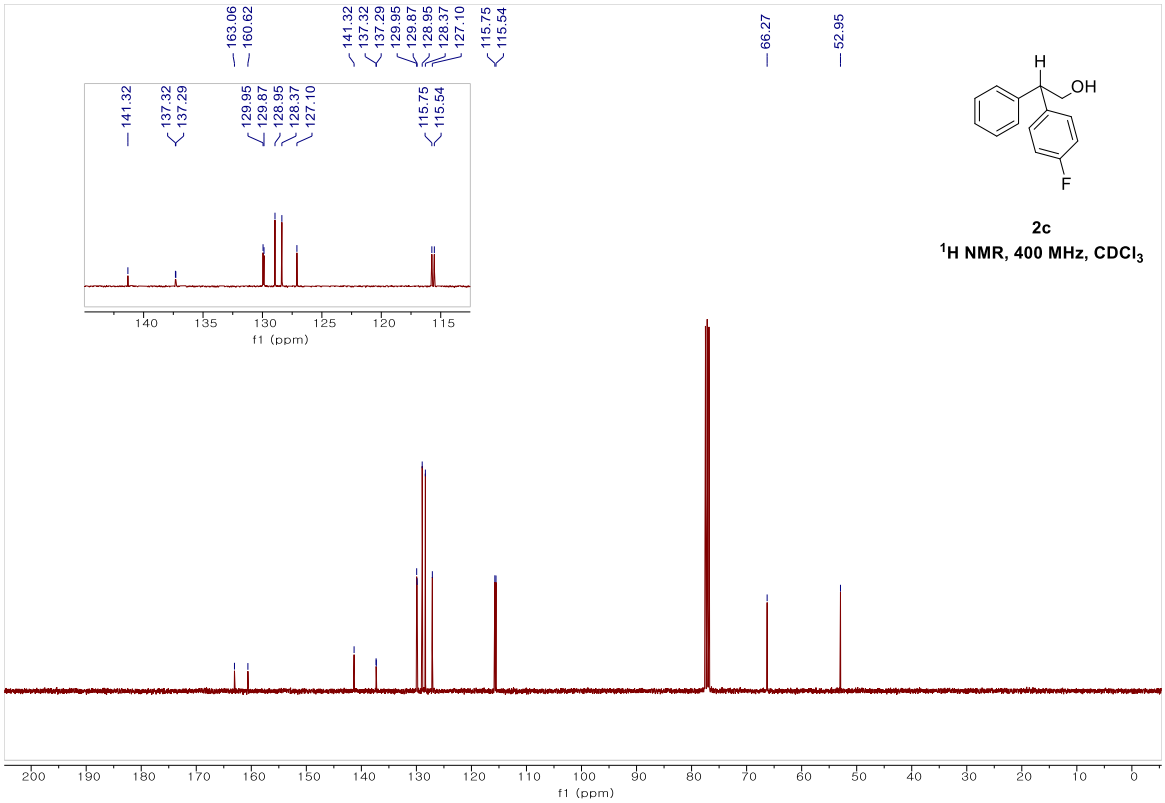
2-(4-chlorophenyl)-2-phenylethan-1-ol (2b)



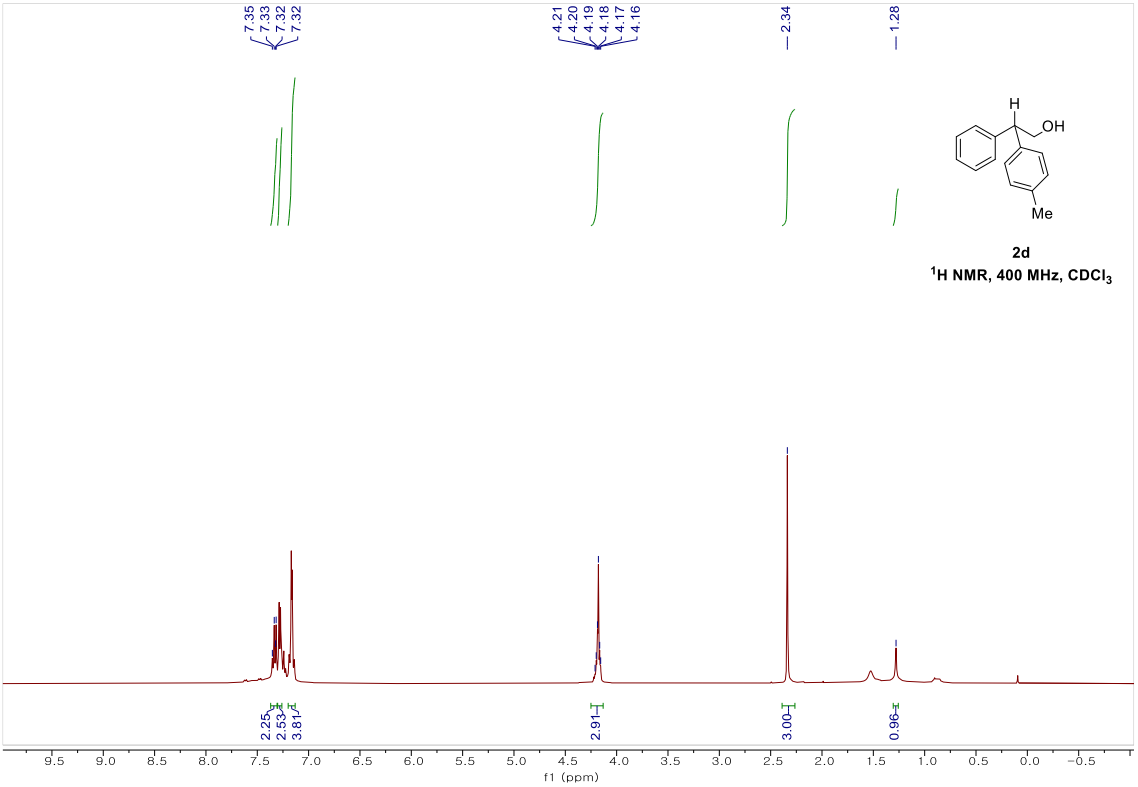


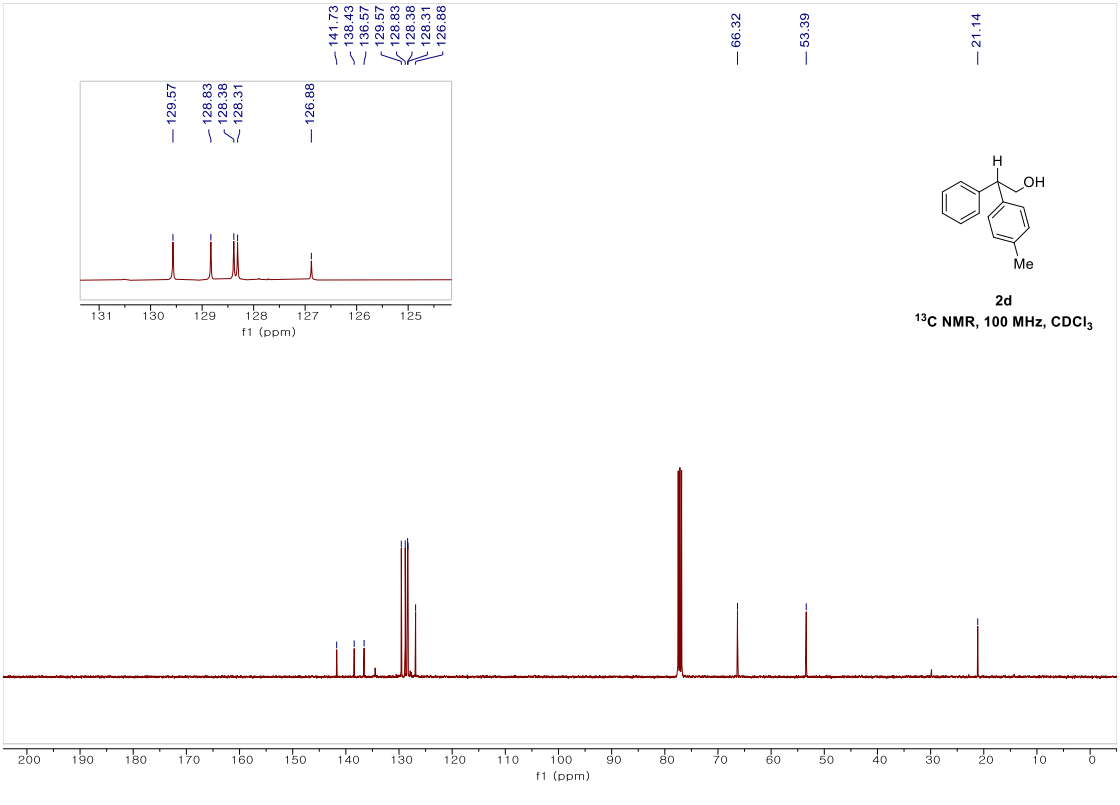
2-(4-fluorophenyl)-2-phenylethan-1-ol (2c)



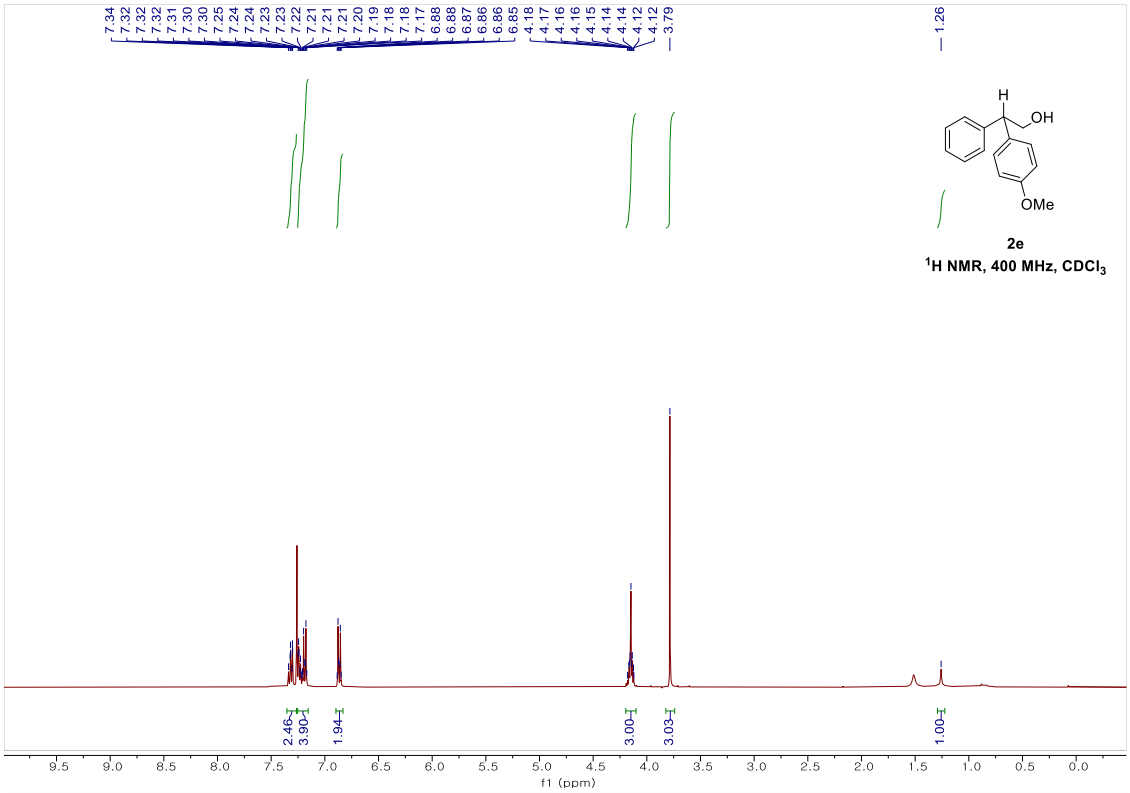


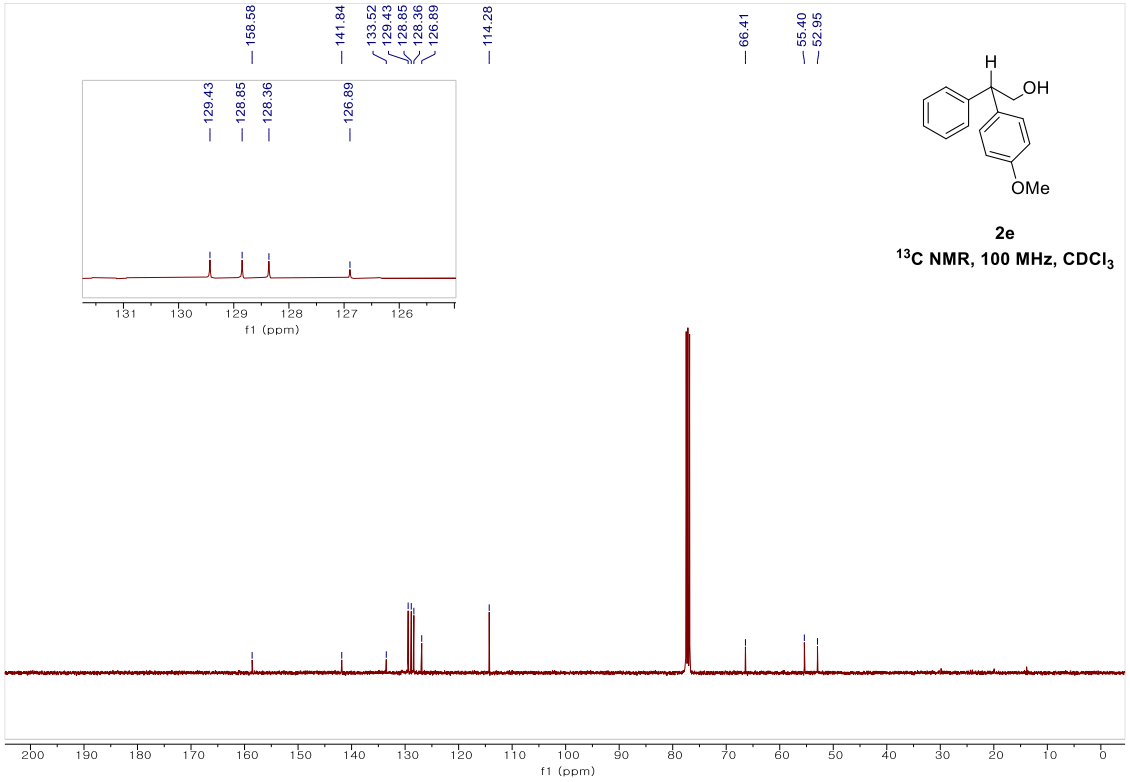
2-phenyl-2-(p-tolyl)ethan-1-ol (2d)



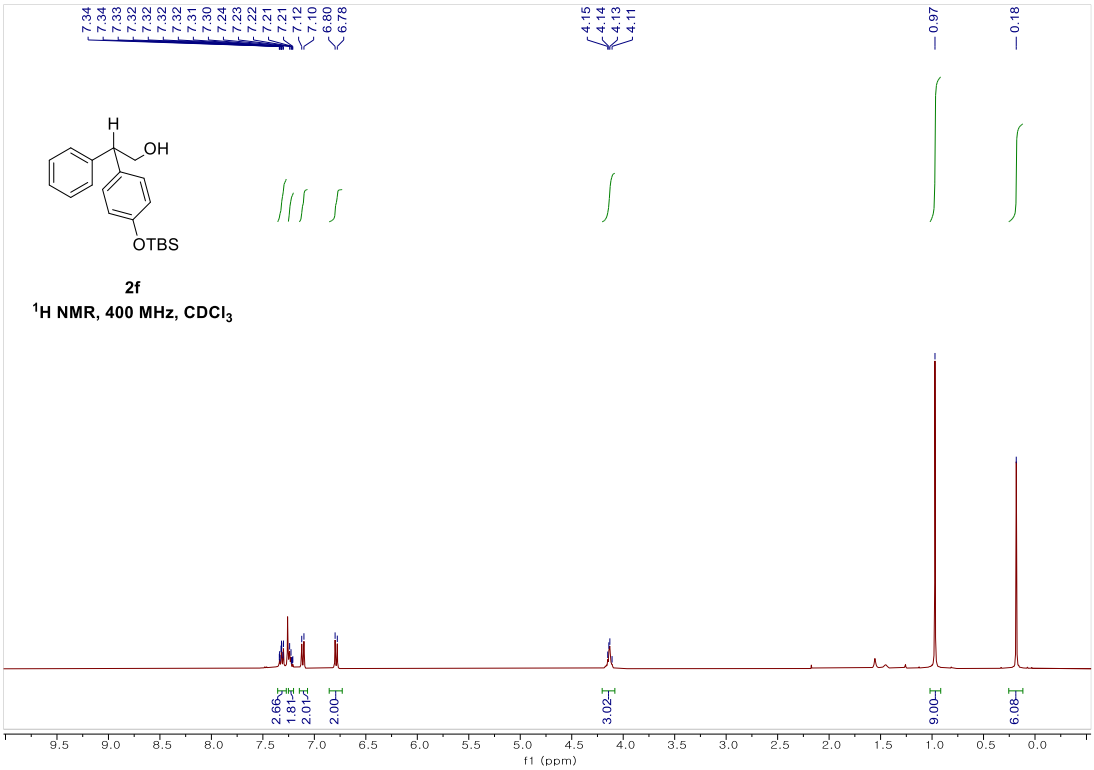


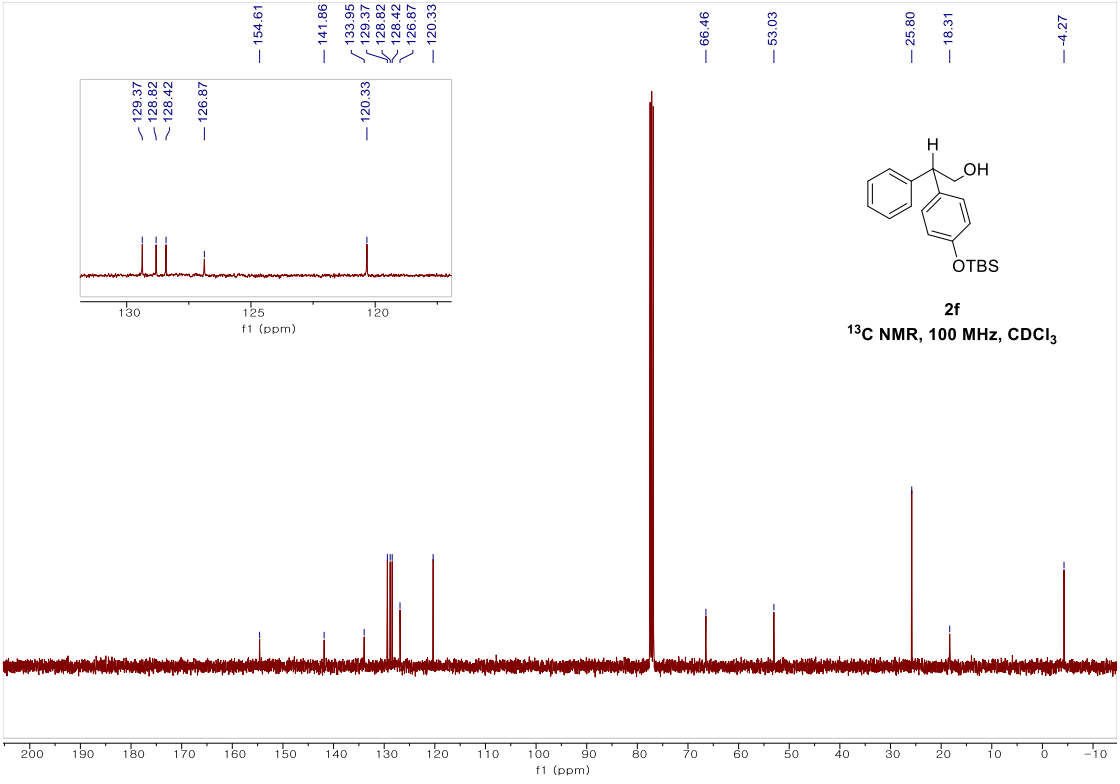
2-(4-methoxyphenyl)-2-phenylethan-1-ol (2e)



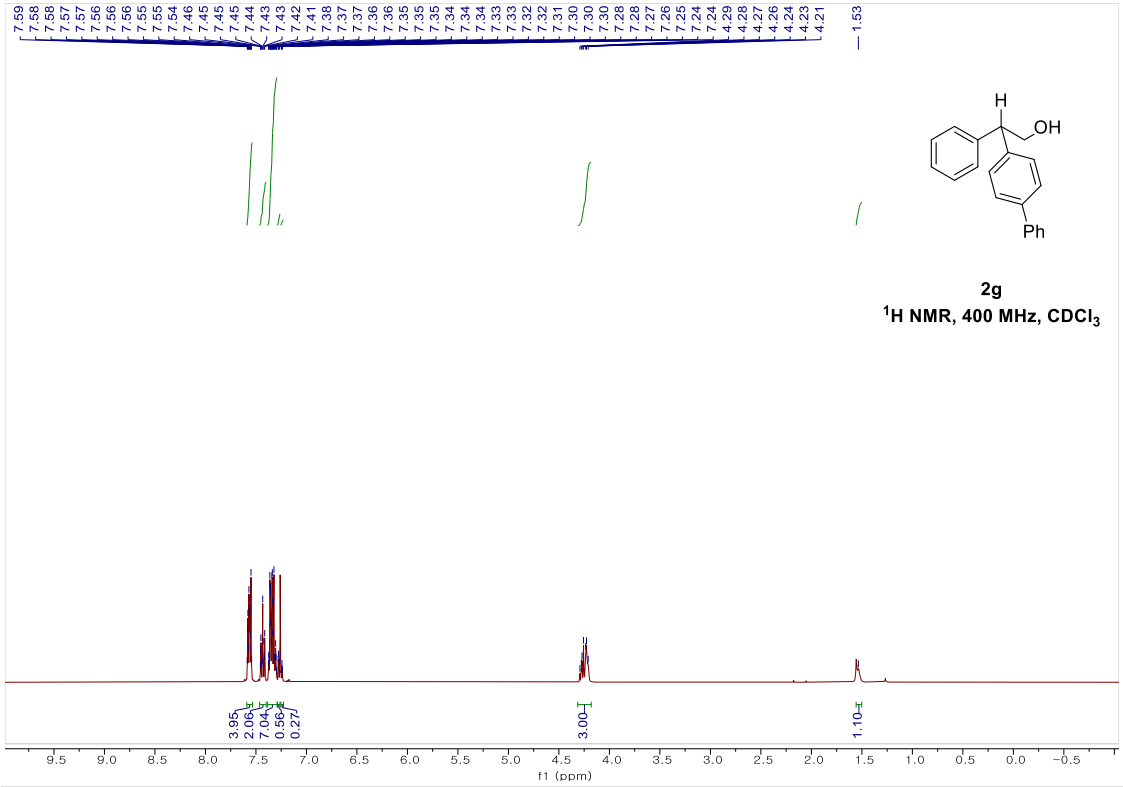


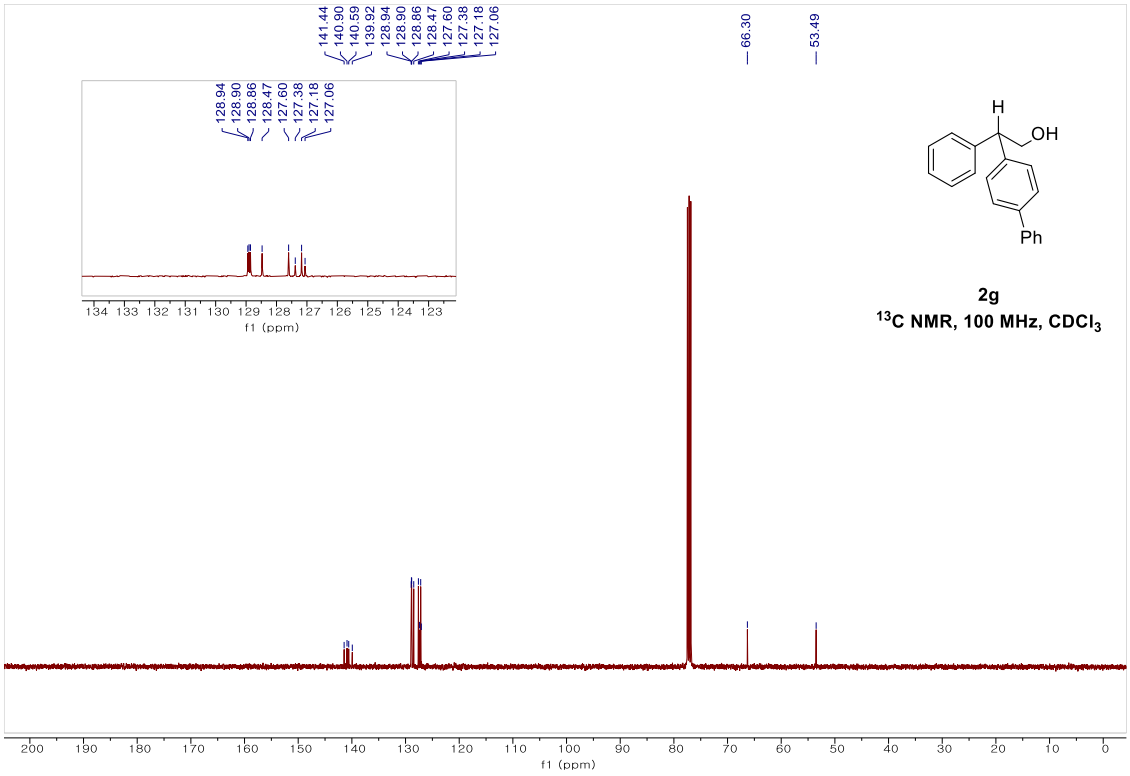
2-(4-((tert-butyldimethylsilyl)oxy)phenyl)-2-phenylethan-1-ol (2f)



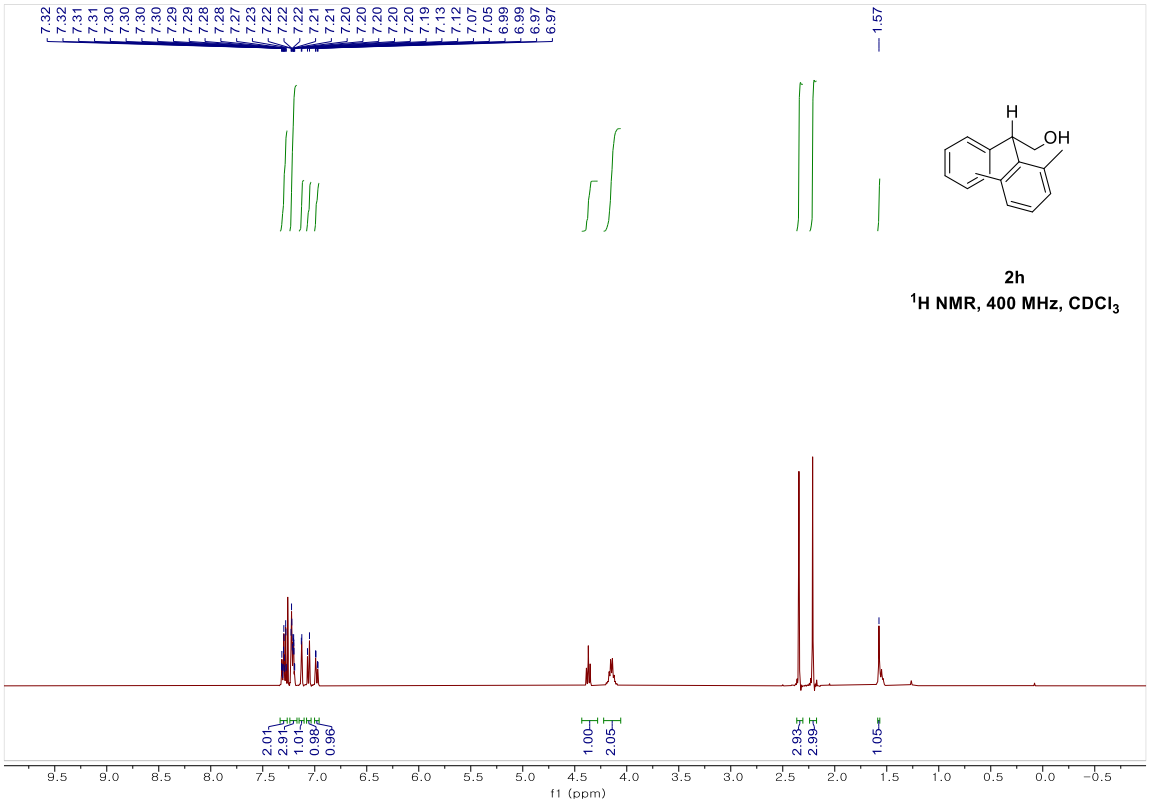


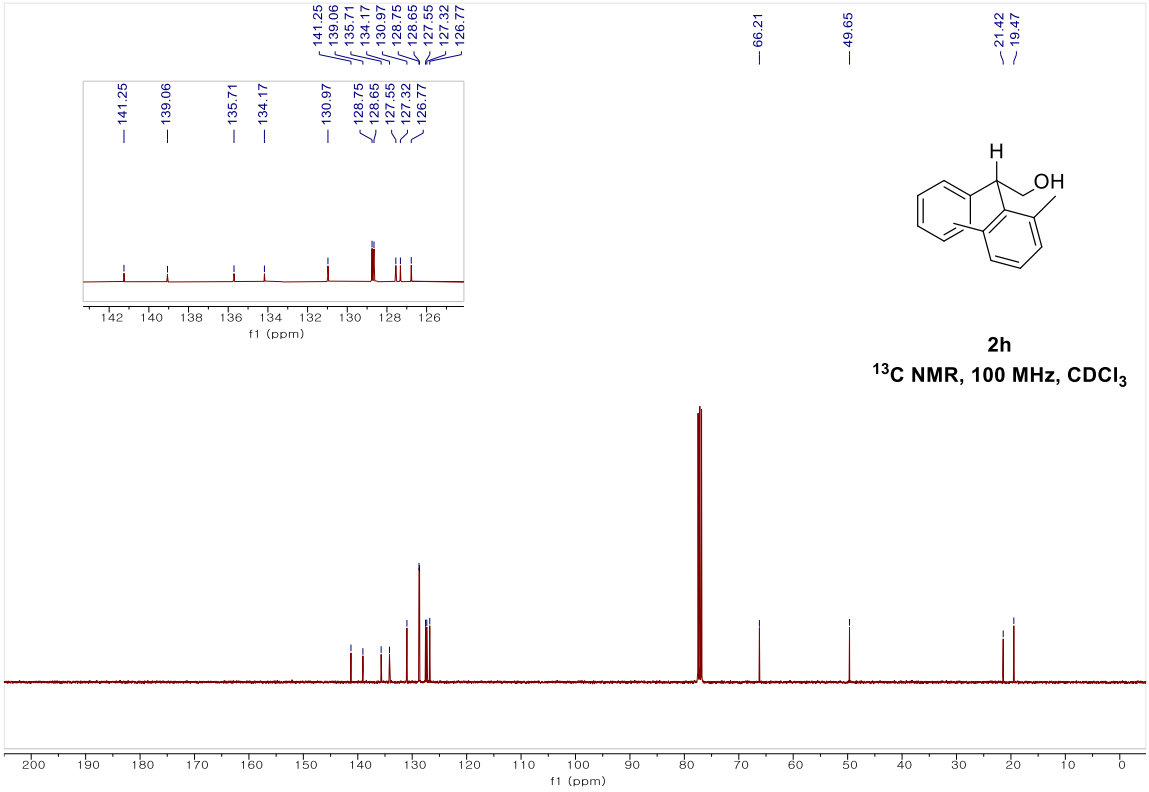
2-([1,1'-biphenyl]-4-yl)-2-phenylethan-1-ol (2g)



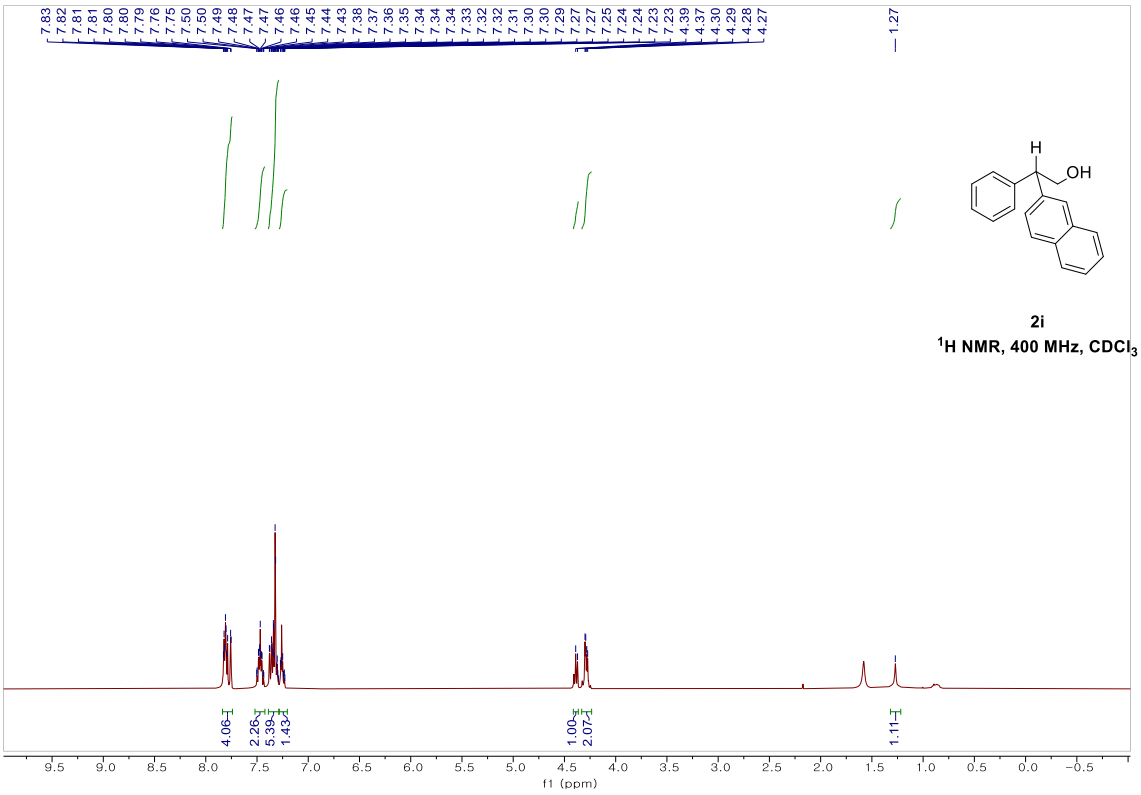


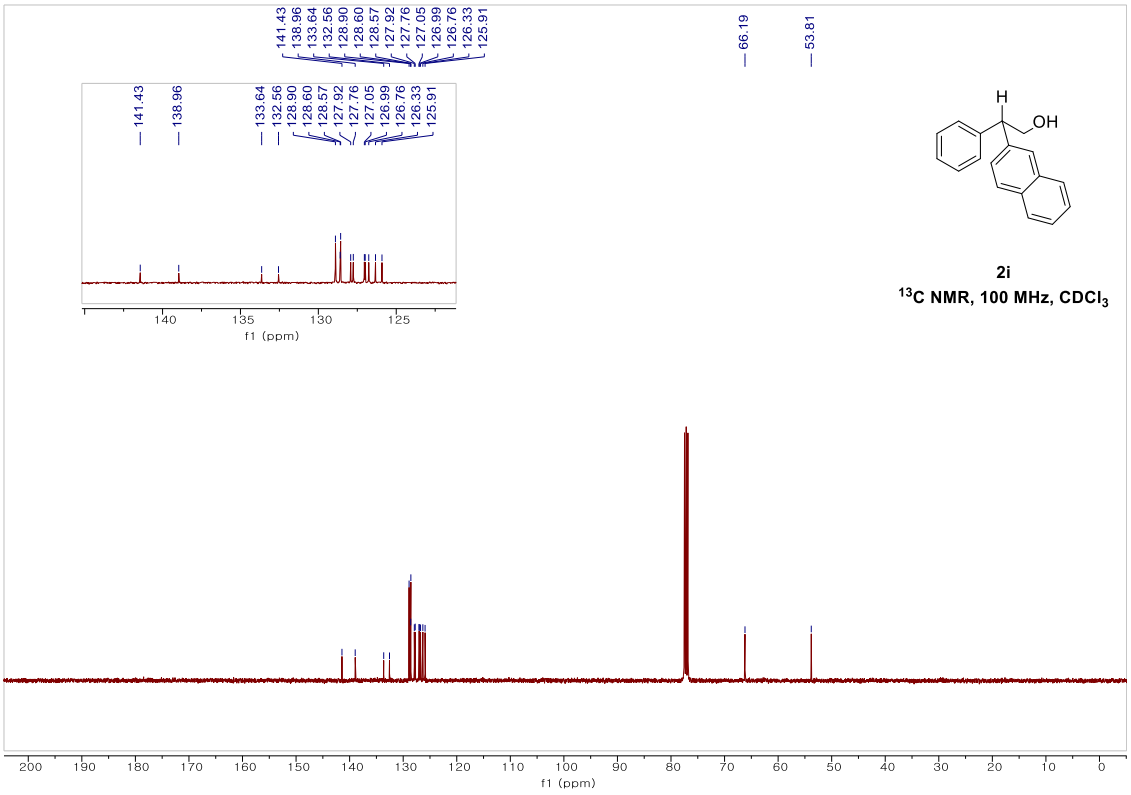
2-(2,6-dimethylphenyl)-2-phenylethan-1-ol (2h)



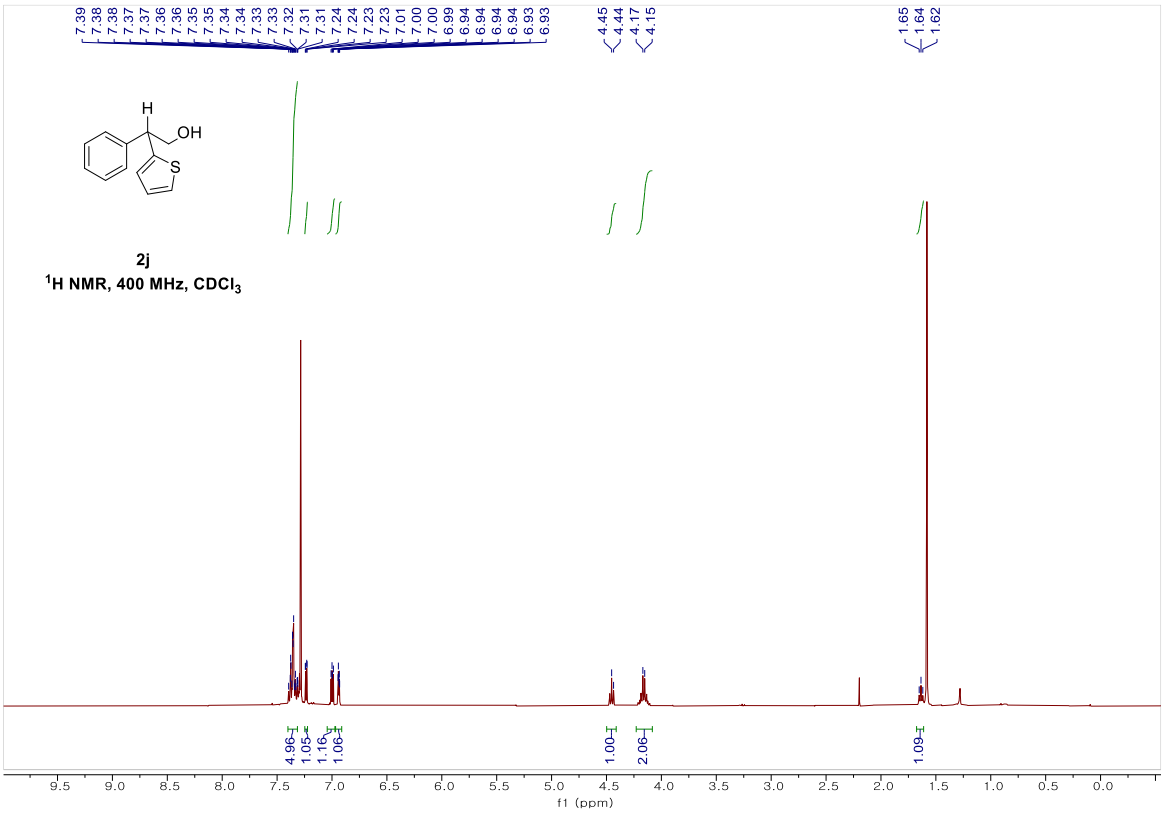


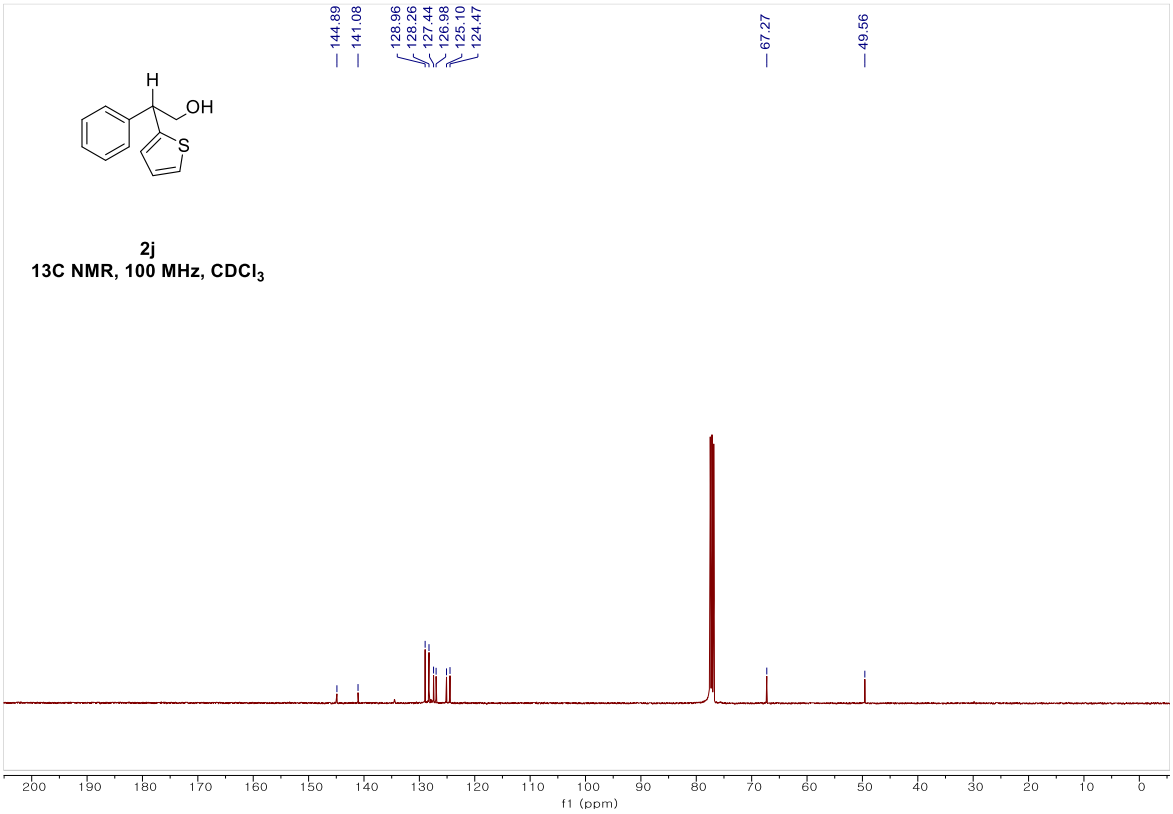
2-(naphthalen-2-yl)-2-phenylethan-1-ol (2i)



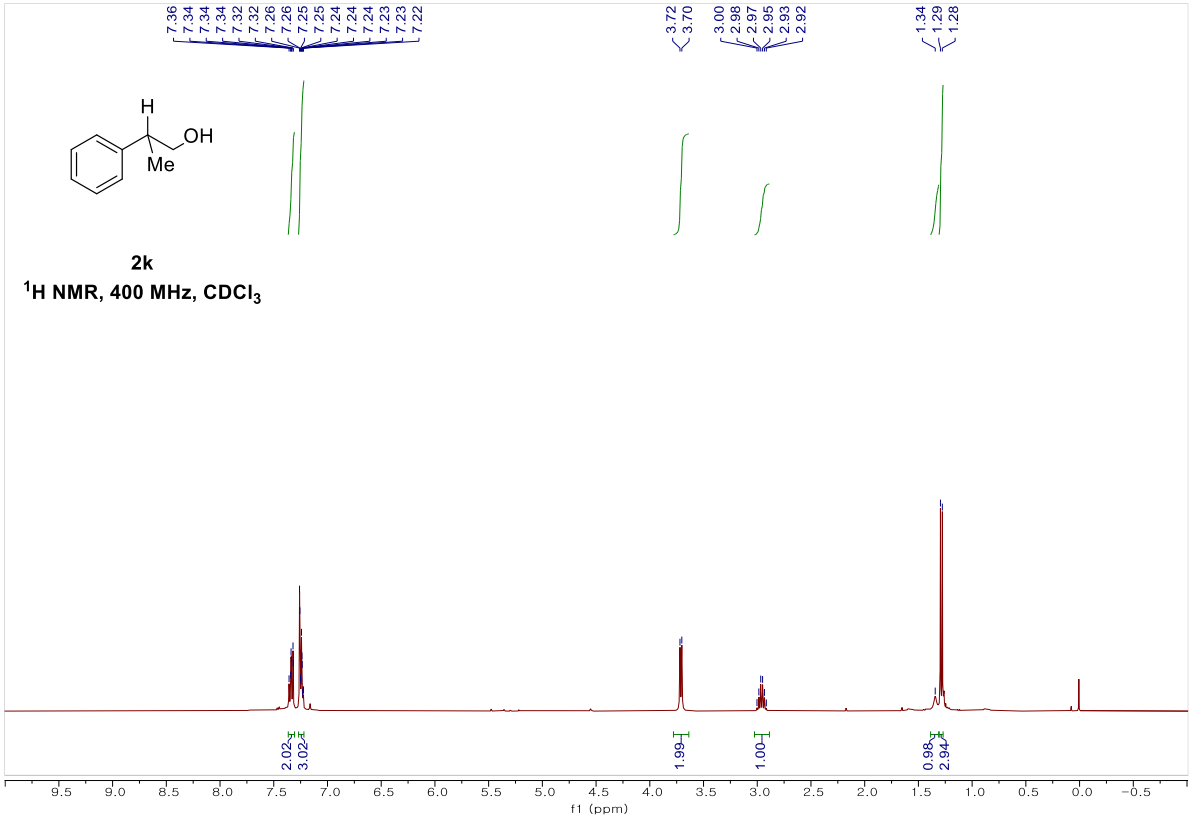


2-phenyl-2-(thiophen-2-yl)ethan-1-ol (2j)



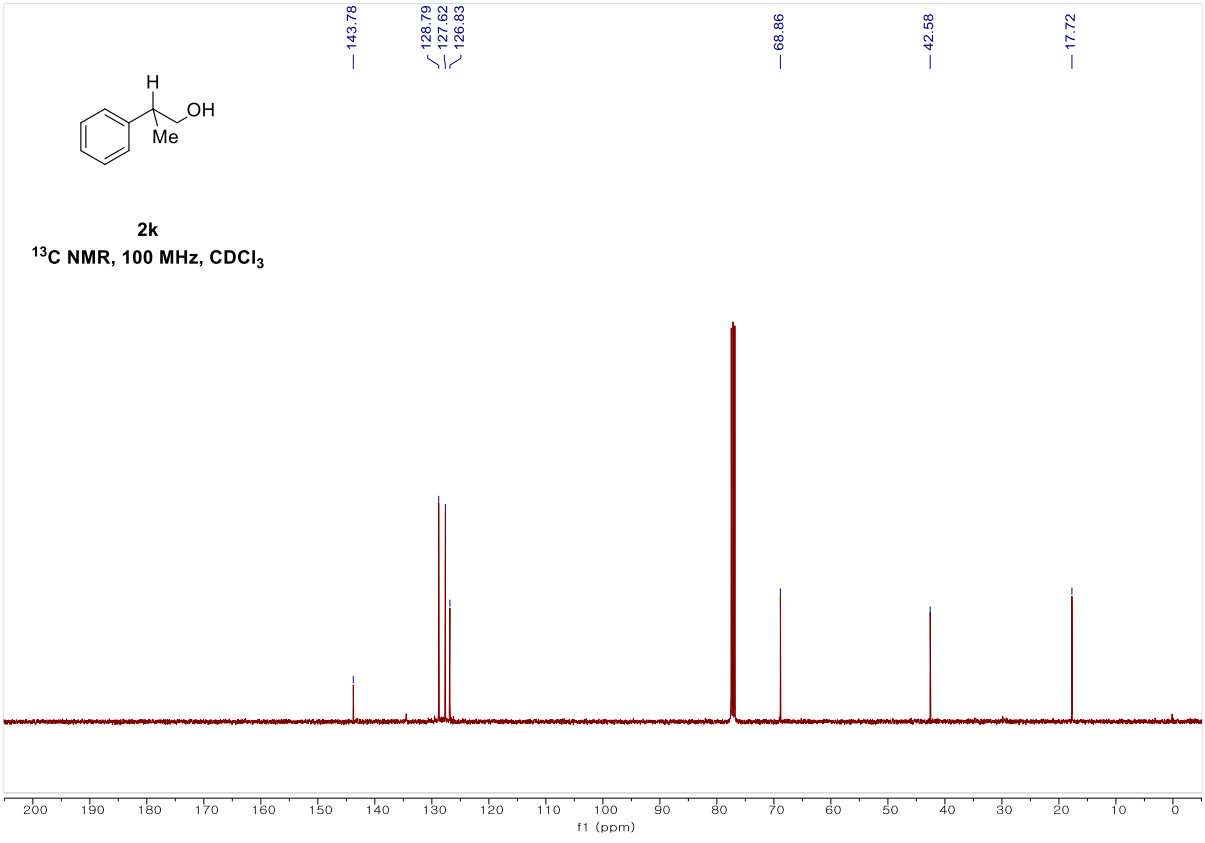


2-phenylpropan-1-ol (2k)



2k

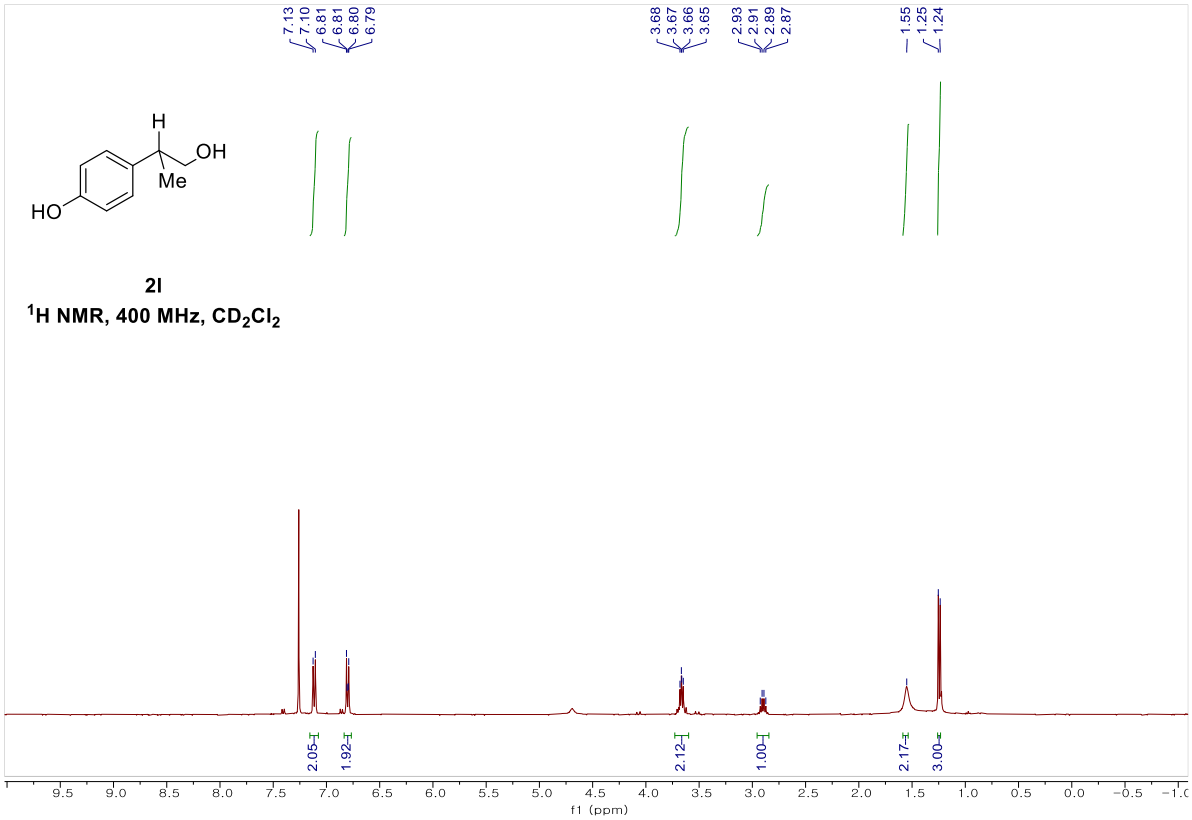
^{1}H NMR, 400 MHz, $CDCl_3$



2k

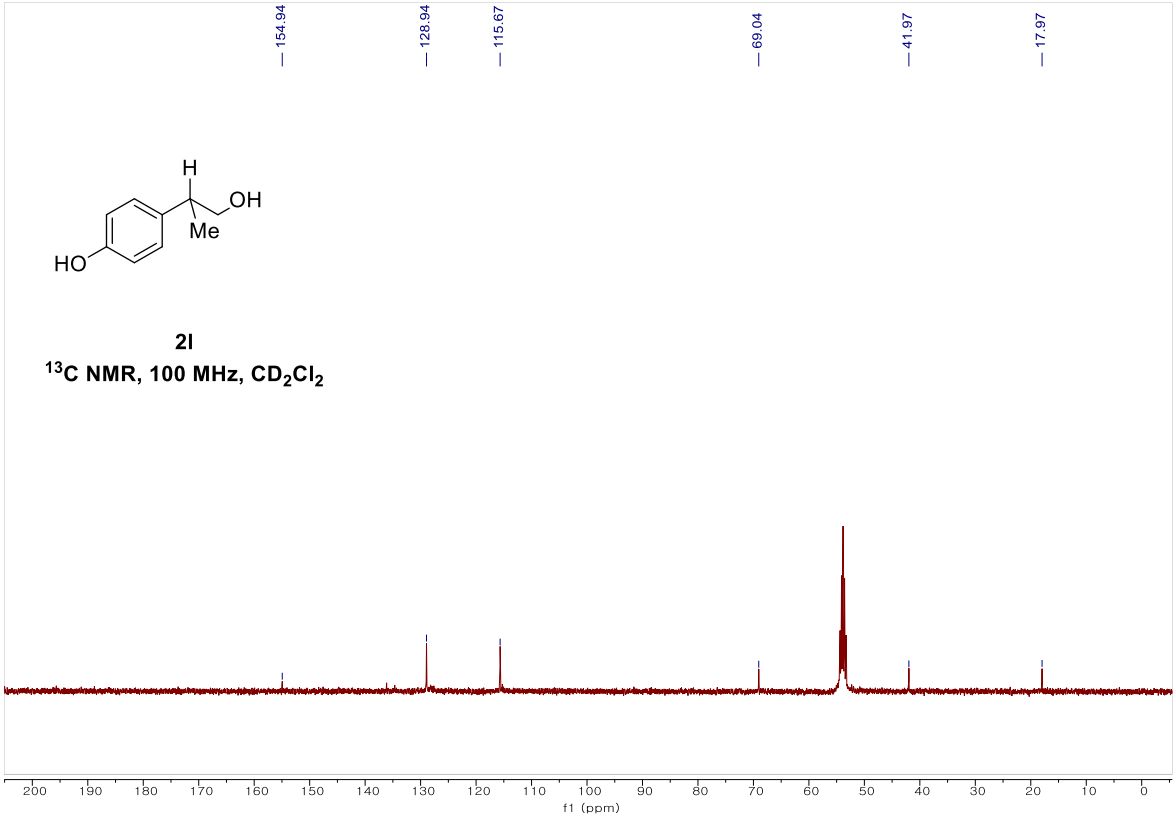
^{13}C NMR, 100 MHz, $CDCl_3$

4-(1-hydroxypropan-2-yl)phenol (2l)



2l

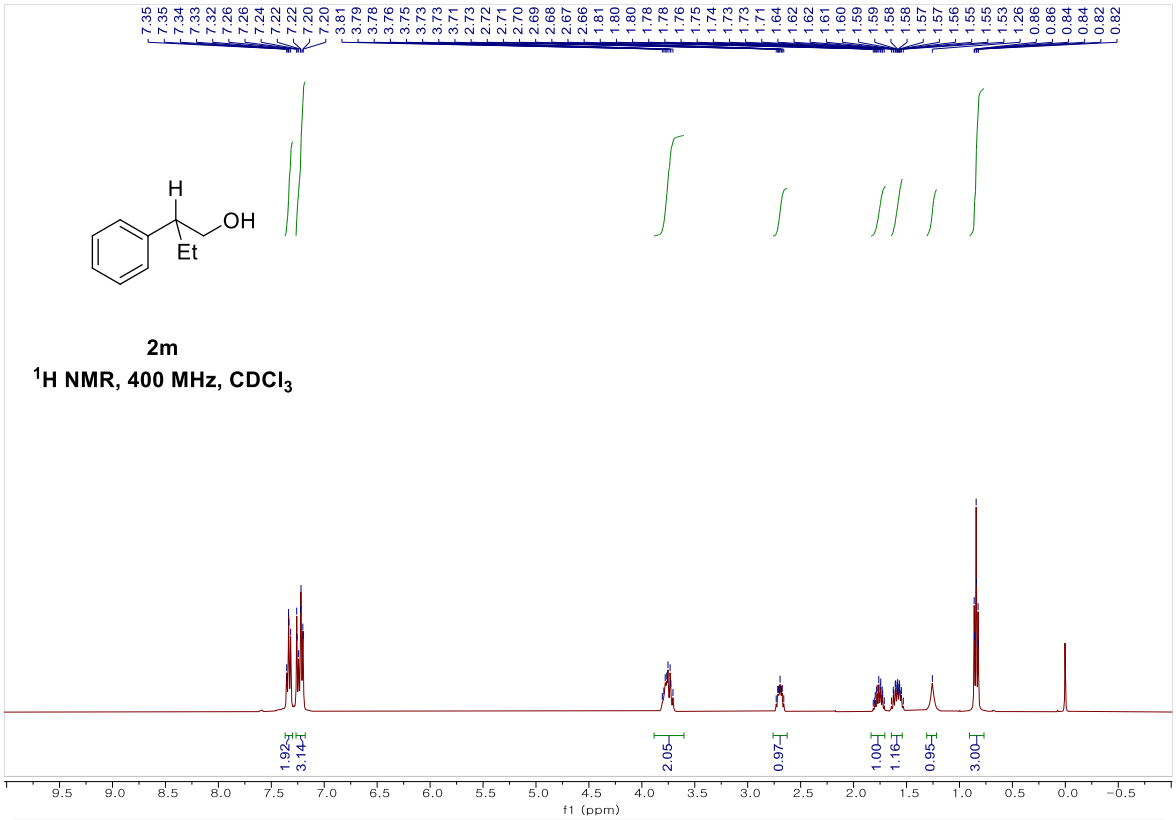
^{1}H NMR, 400 MHz, CD_2Cl_2



2l

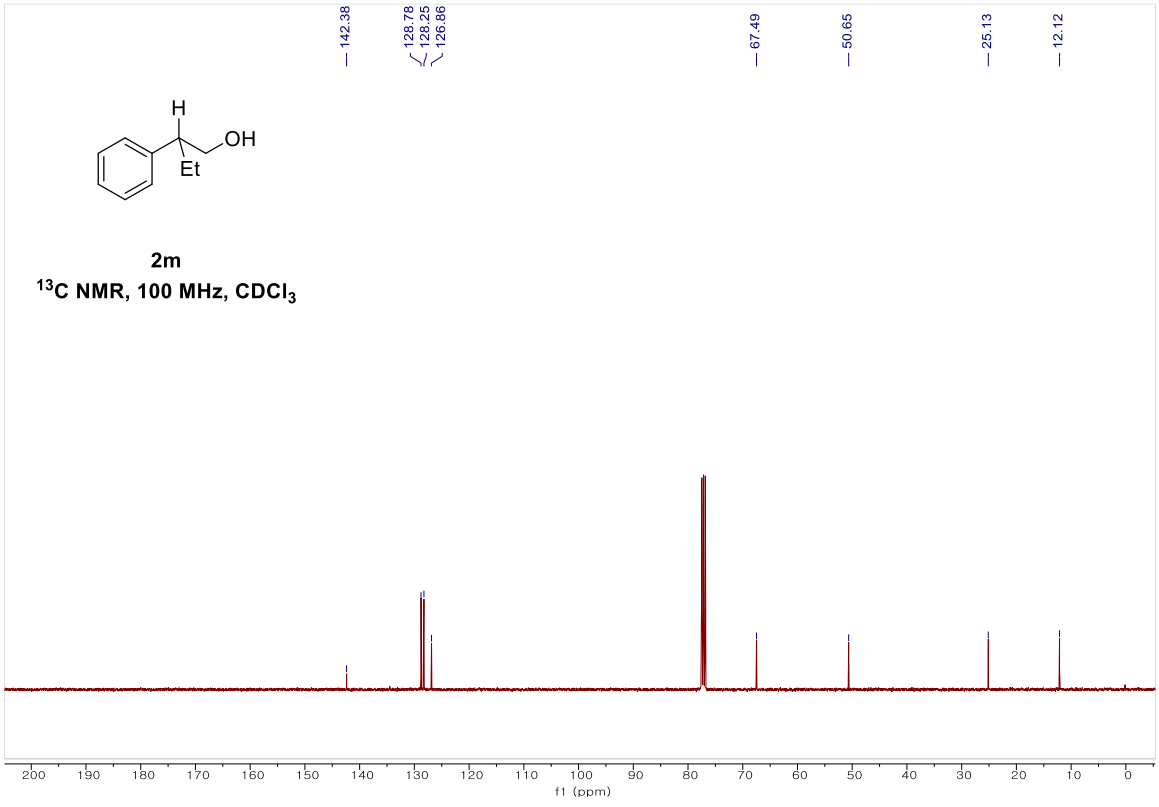
^{13}C NMR, 100 MHz, CD_2Cl_2

2-phenylbutan-1-ol (2m)



2m

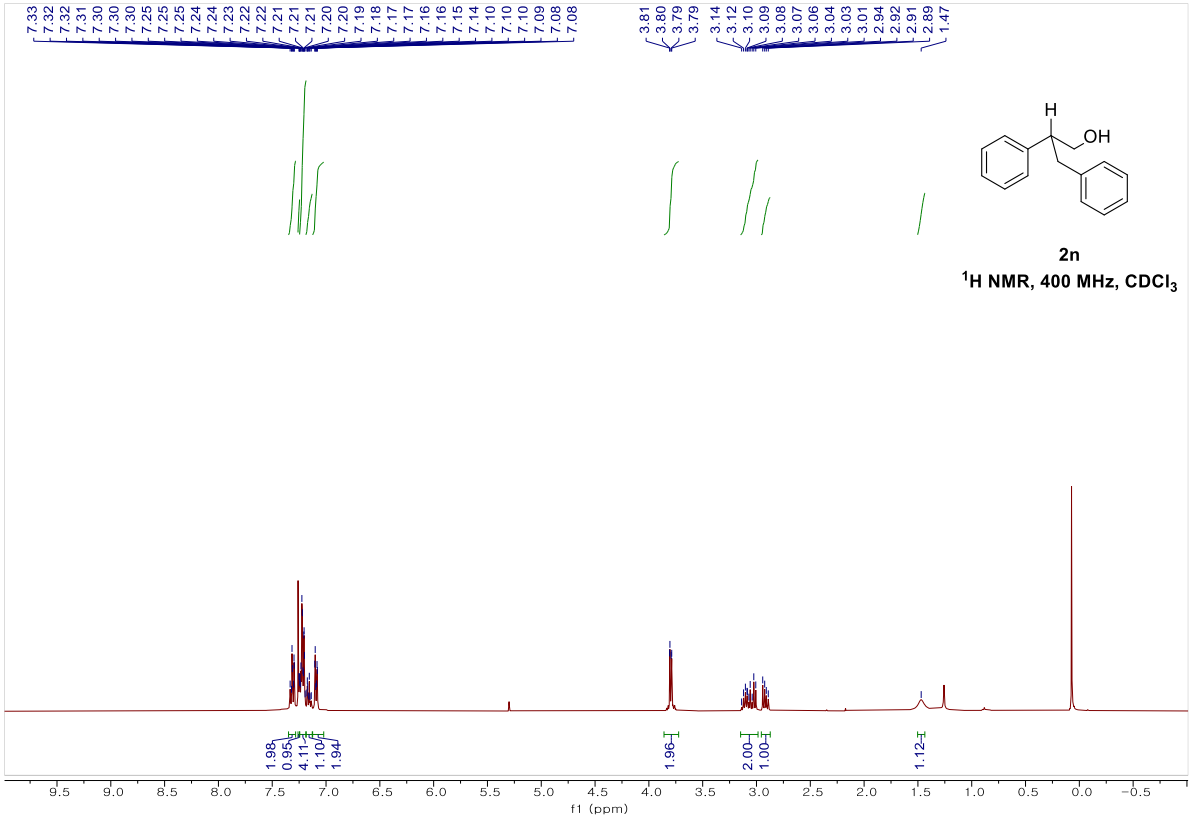
^{1}H NMR, 400 MHz, $CDCl_3$

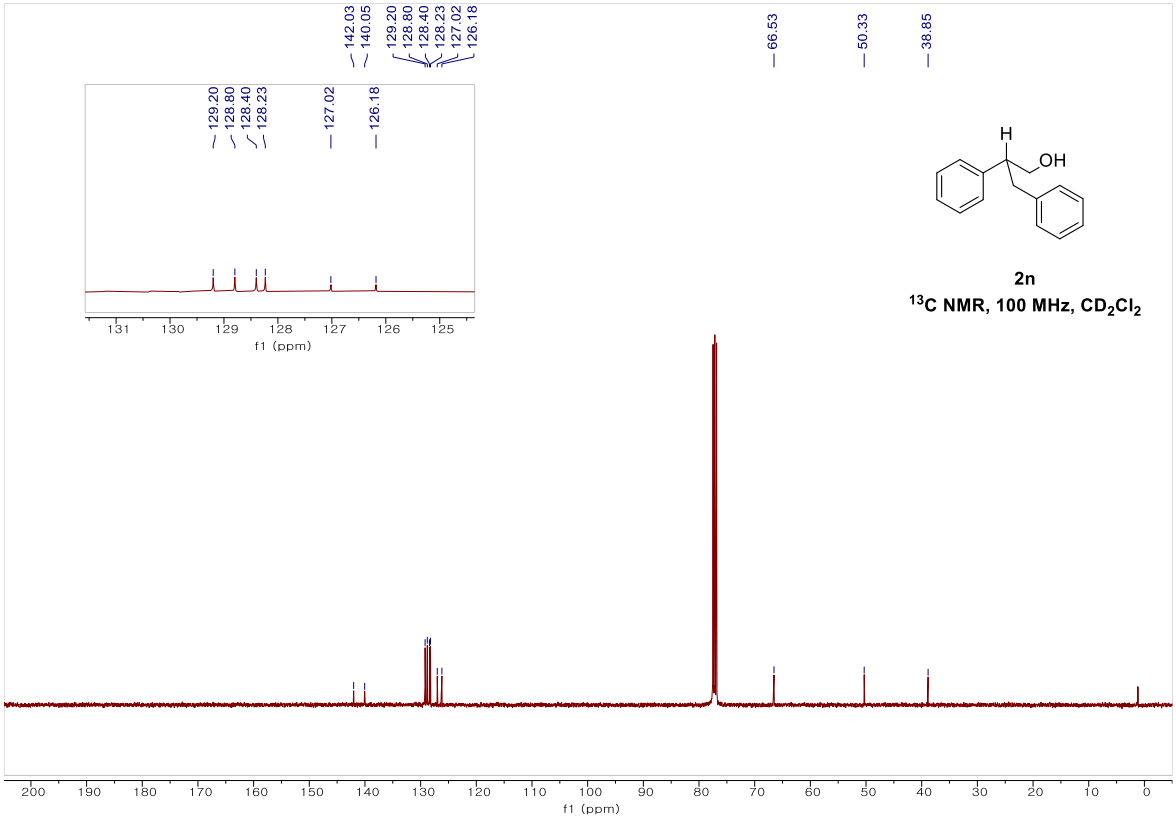


2m

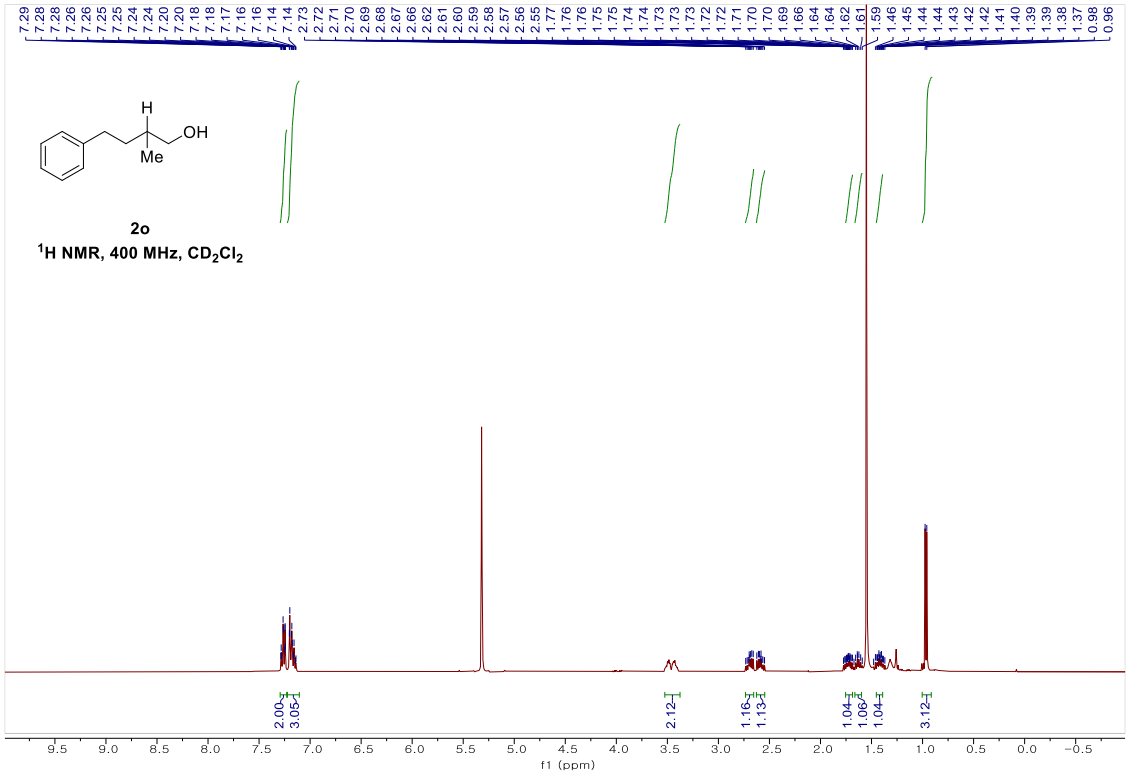
^{13}C NMR, 100 MHz, $CDCl_3$

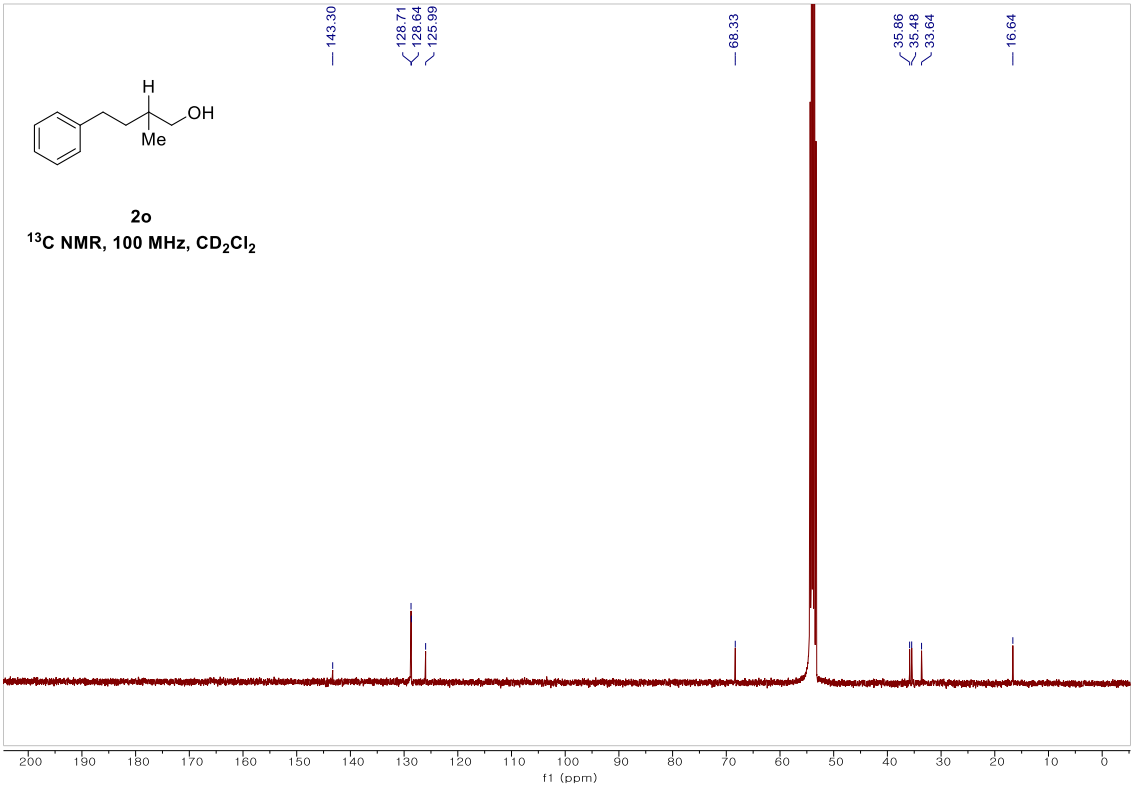
2,3-diphenylpropan-1-ol (2n)



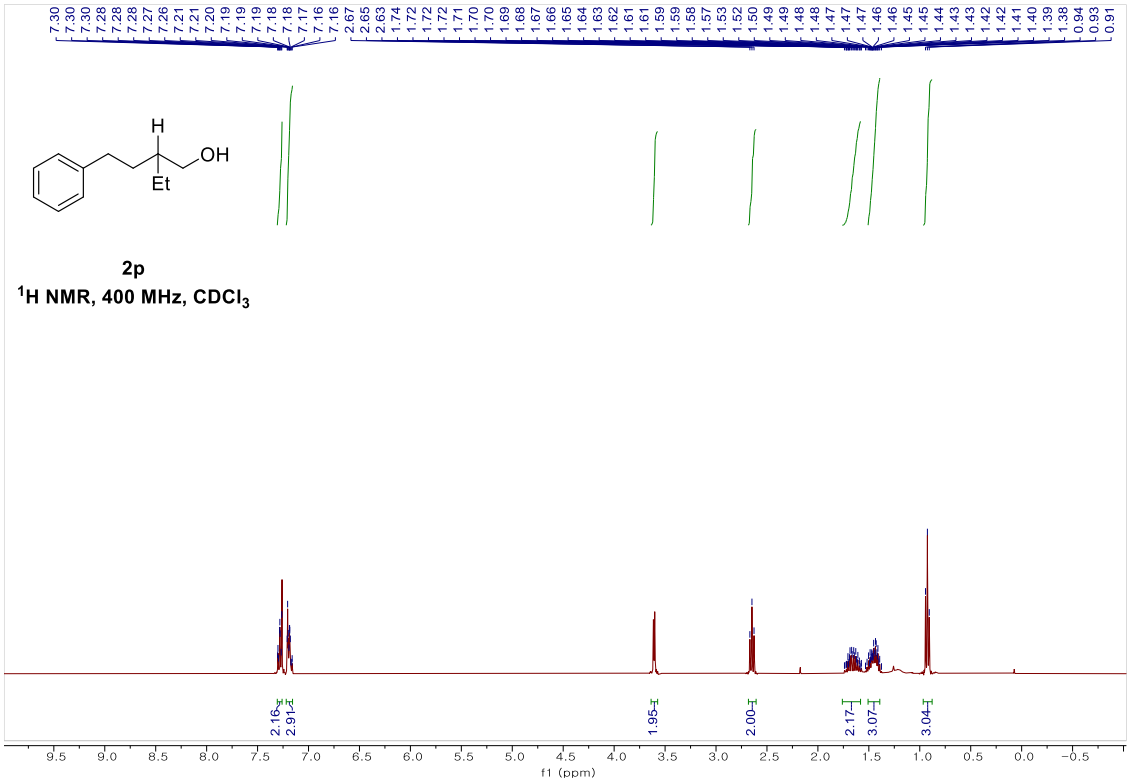


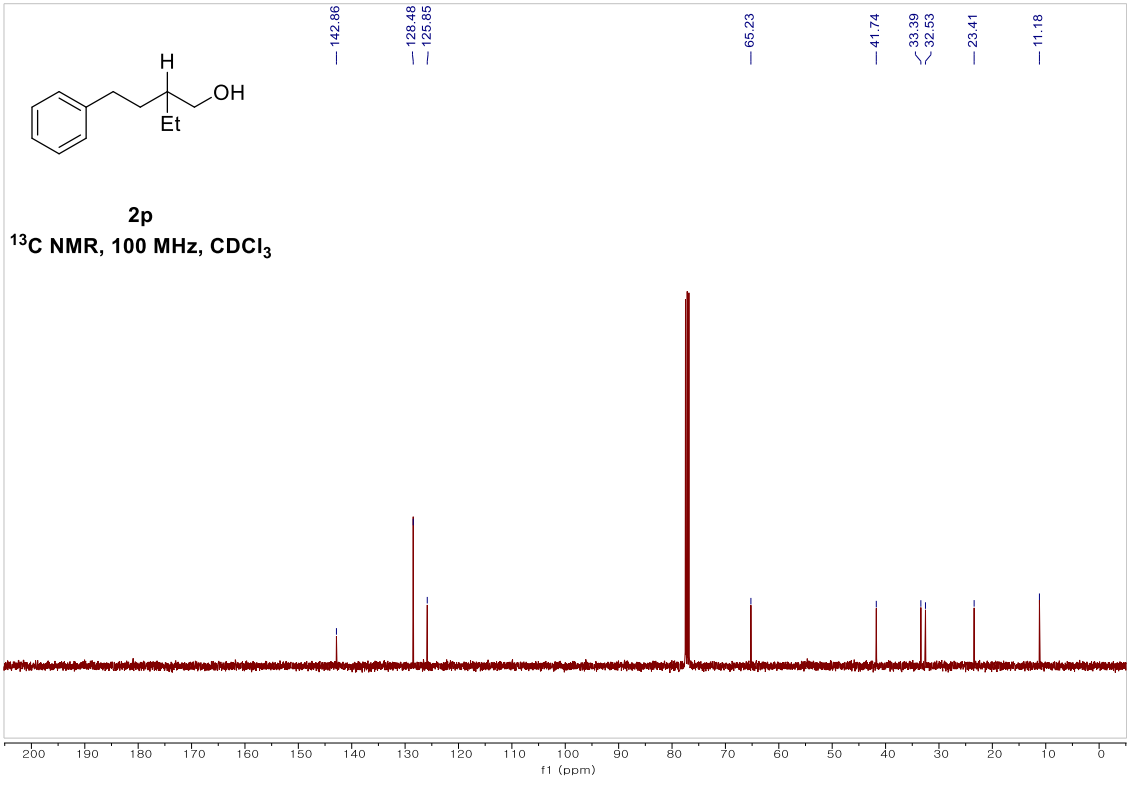
2-methyl-4-phenylbutan-1-ol (2o)



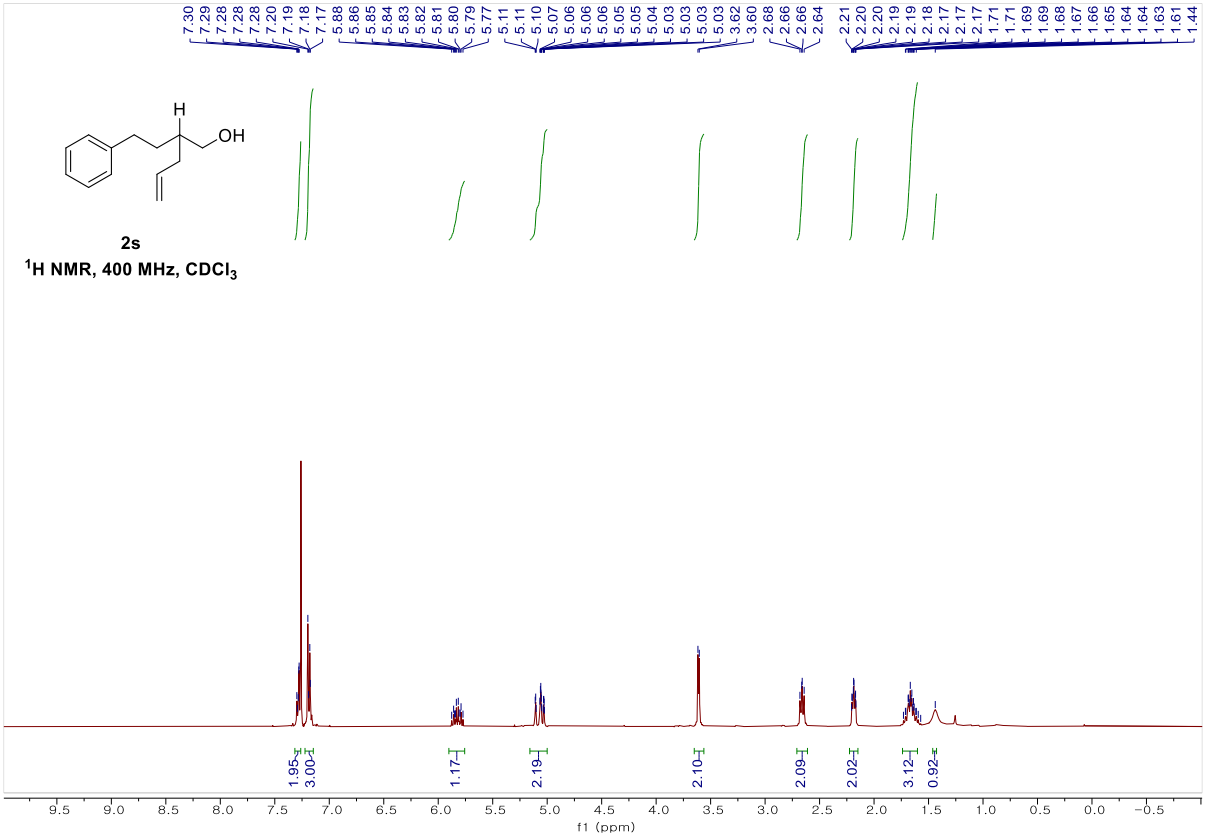


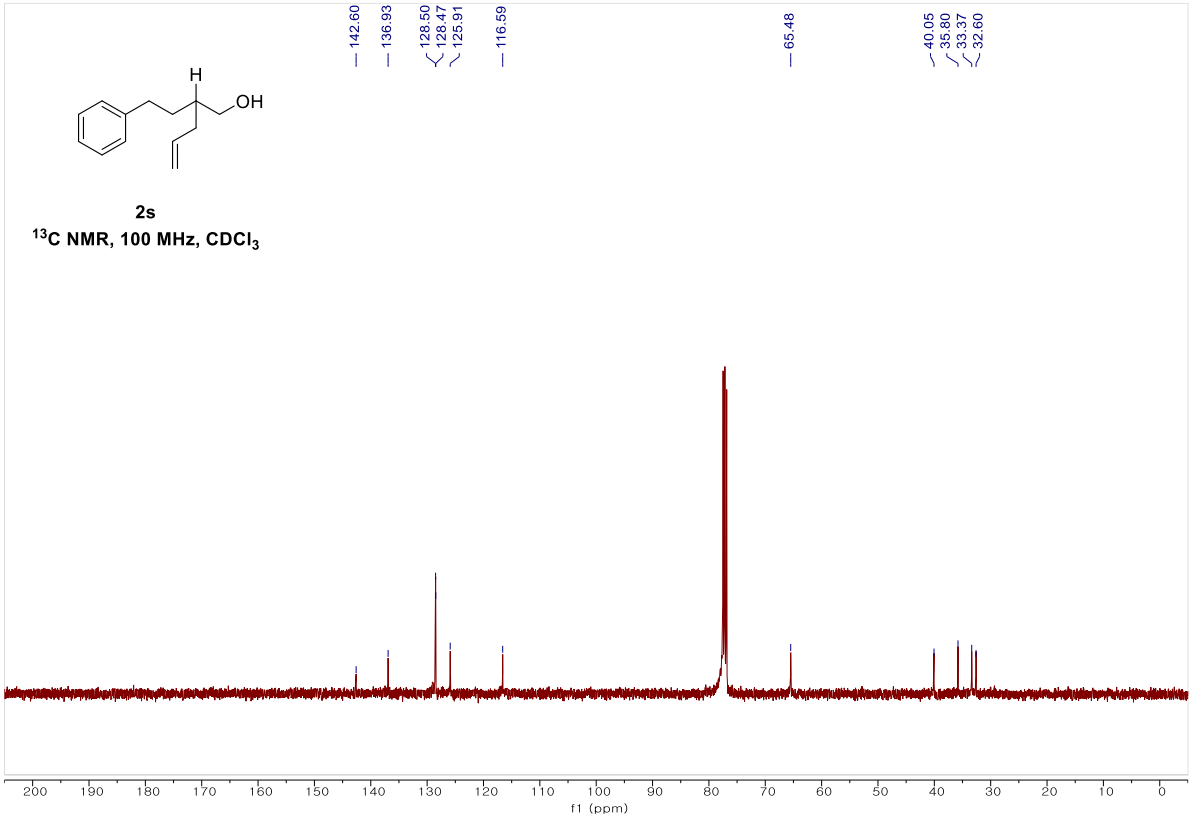
2-ethyl-4-phenylbutan-1-ol (2p)



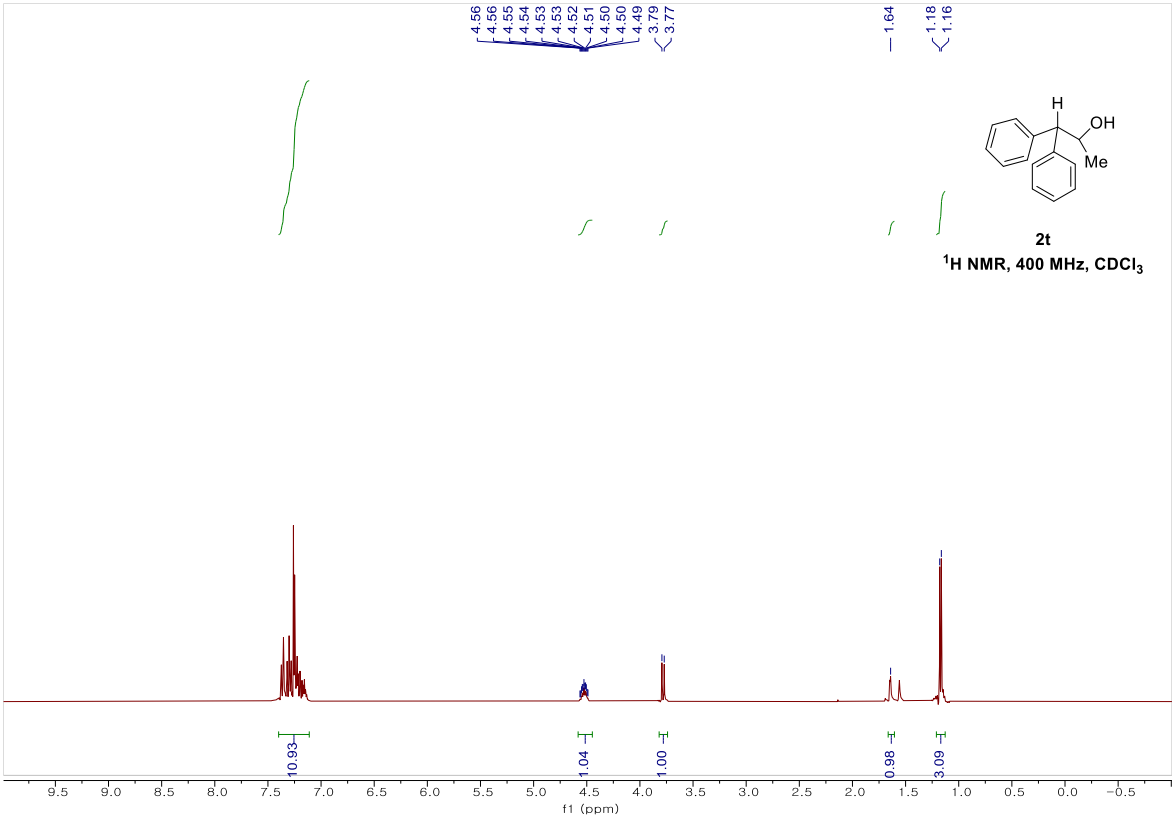


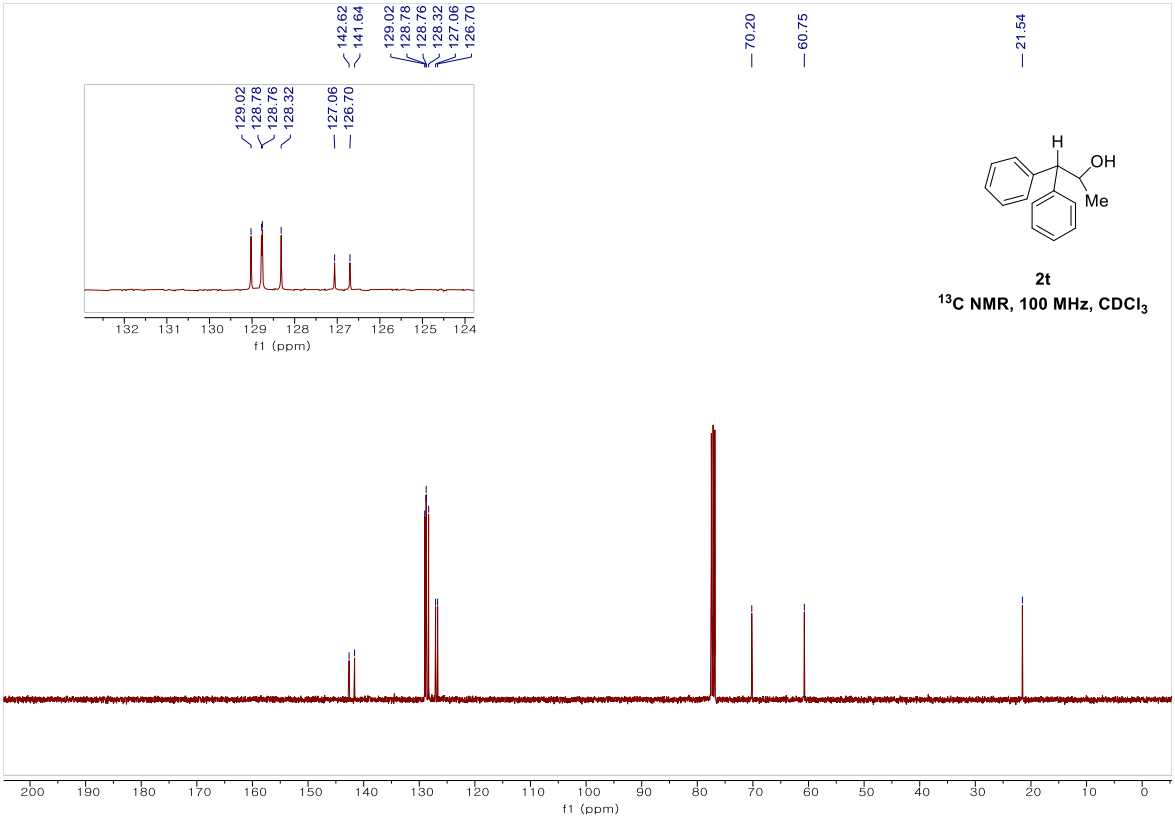
2-phenethylpent-4-en-1-ol (2s)



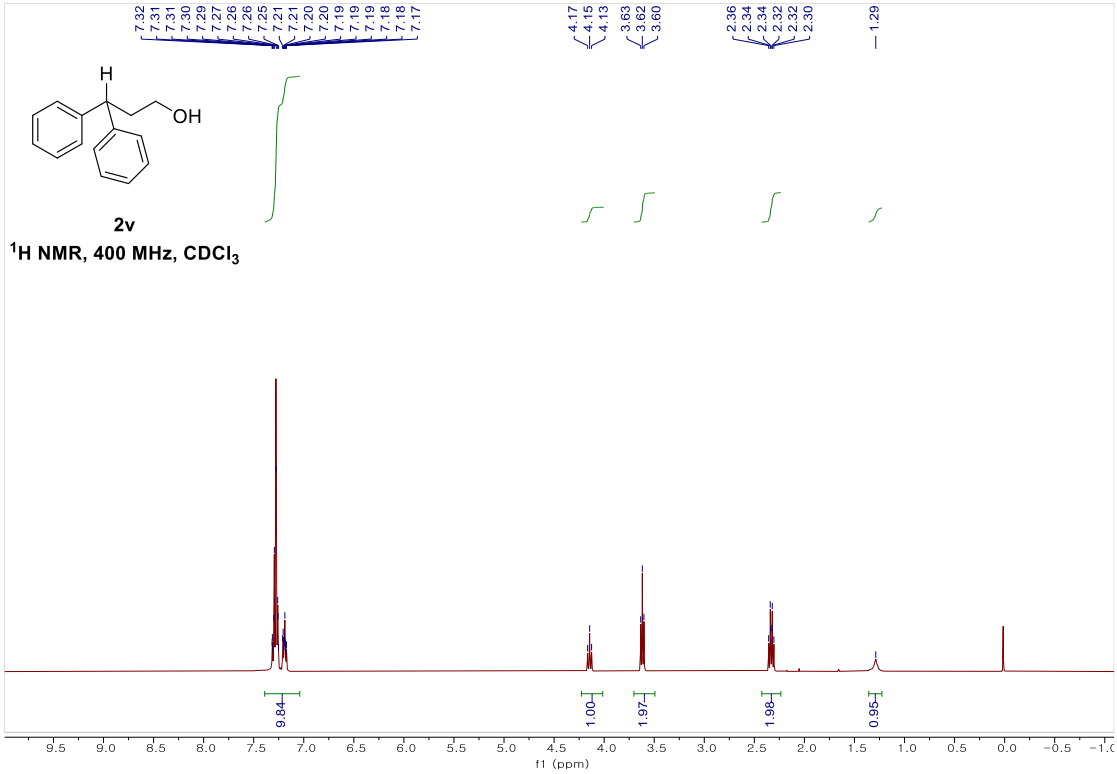


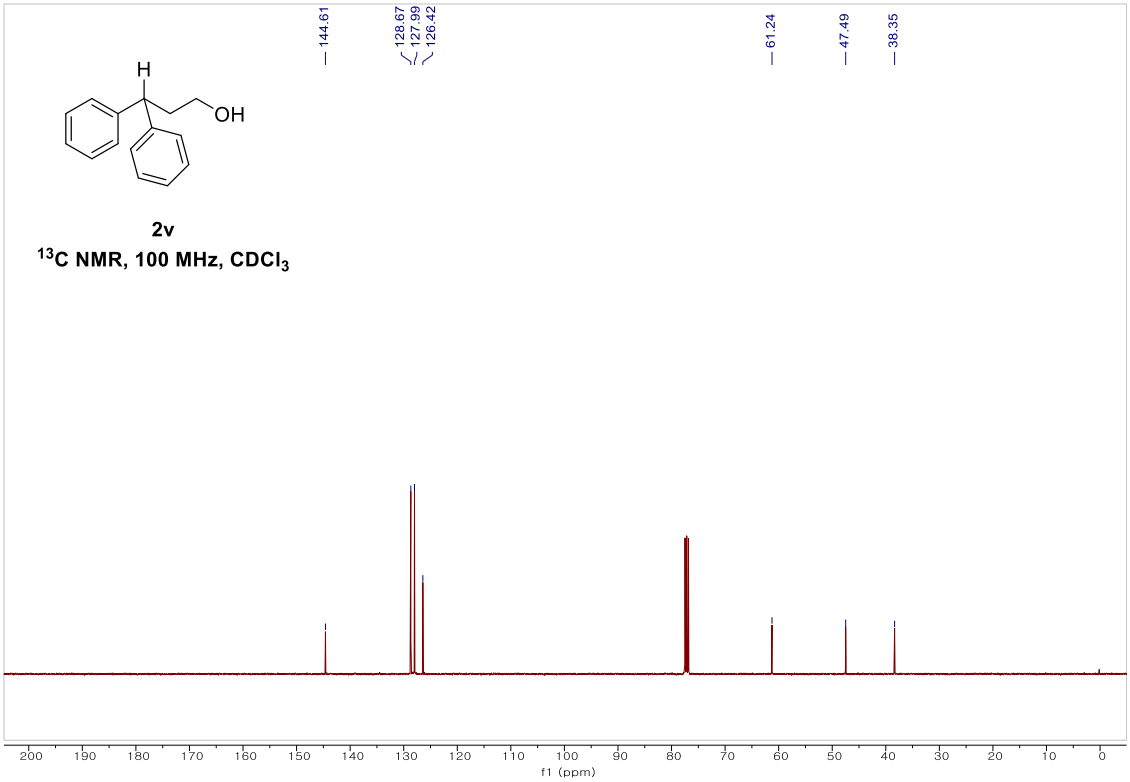
1,1-diphenylpropan-2-ol (2t)



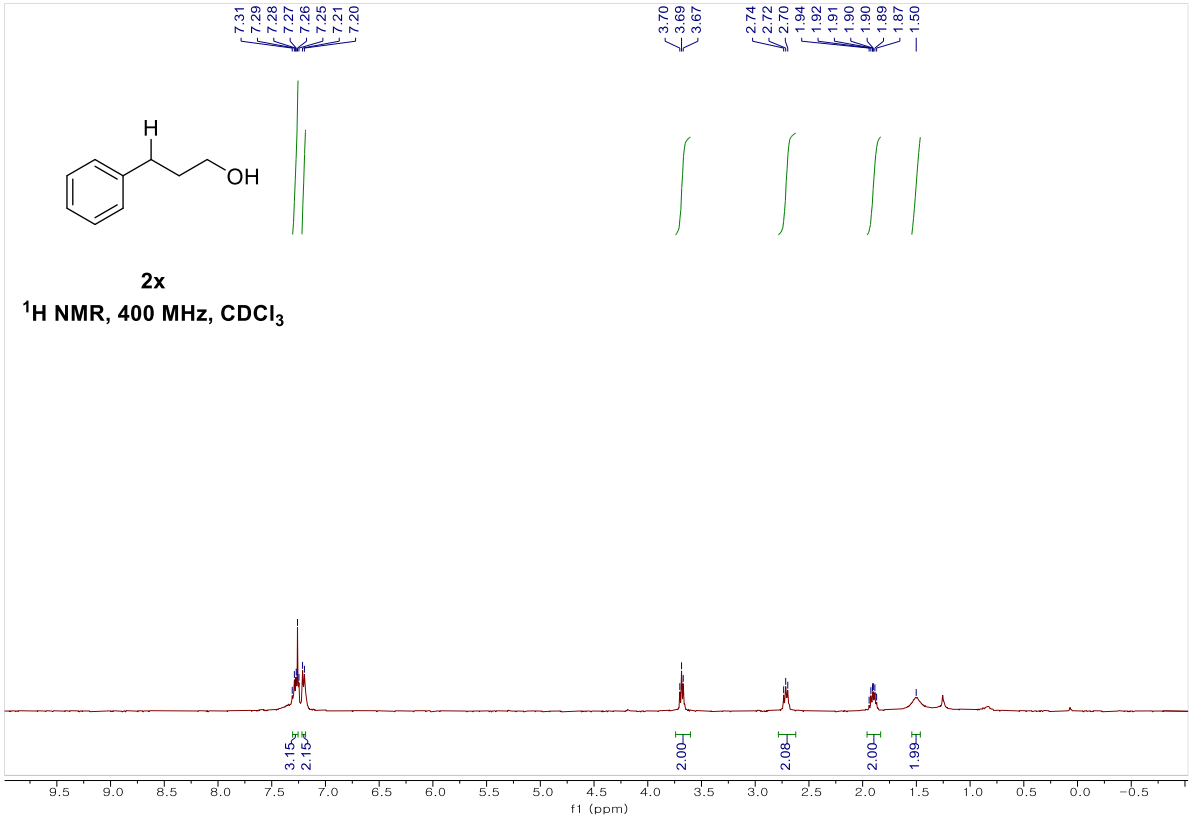


3,3-diphenylpropan-1-ol (2v)



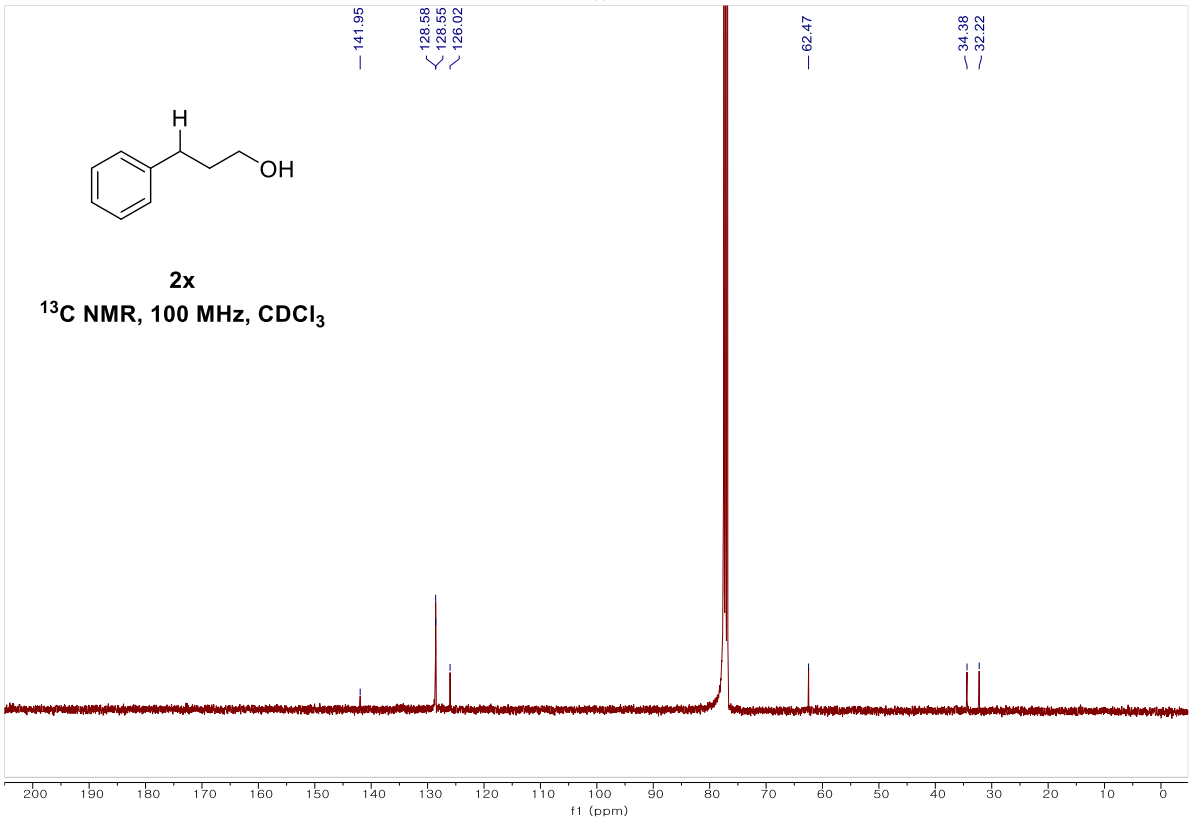


3-phenylpropan-1-ol (2x)



2x

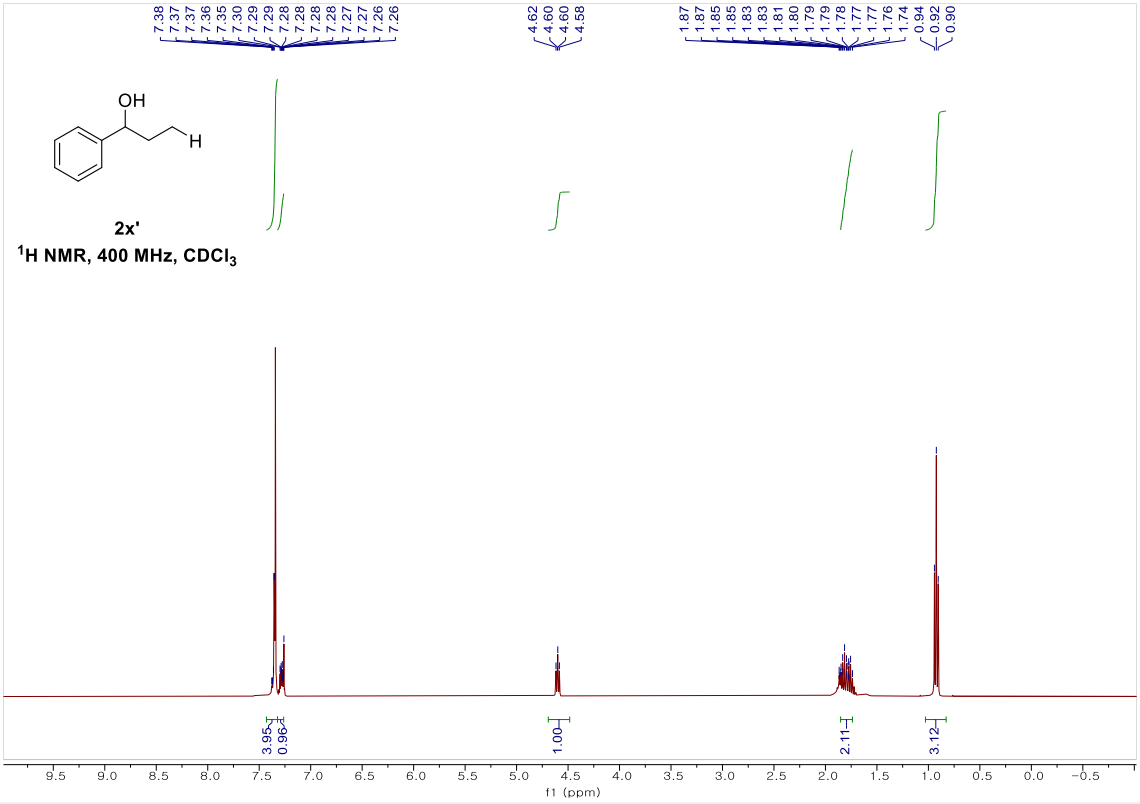
^{1}H NMR, 400 MHz, $CDCl_3$

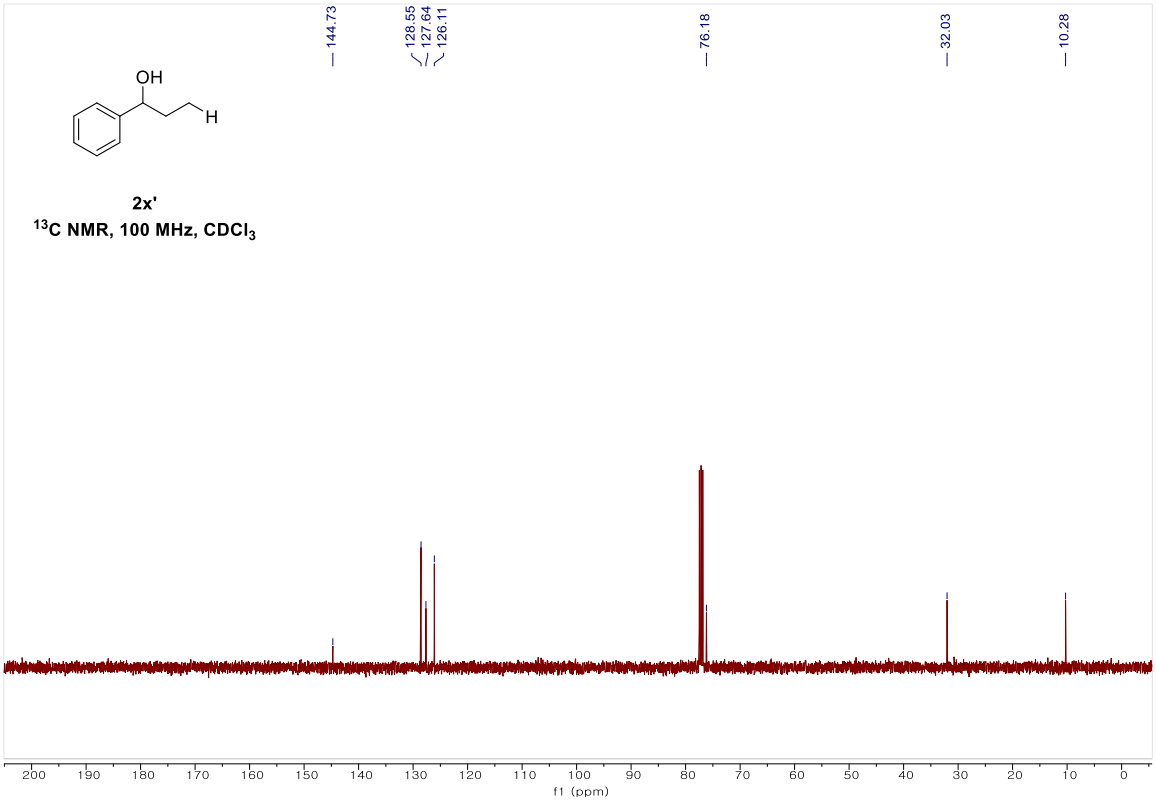


2x

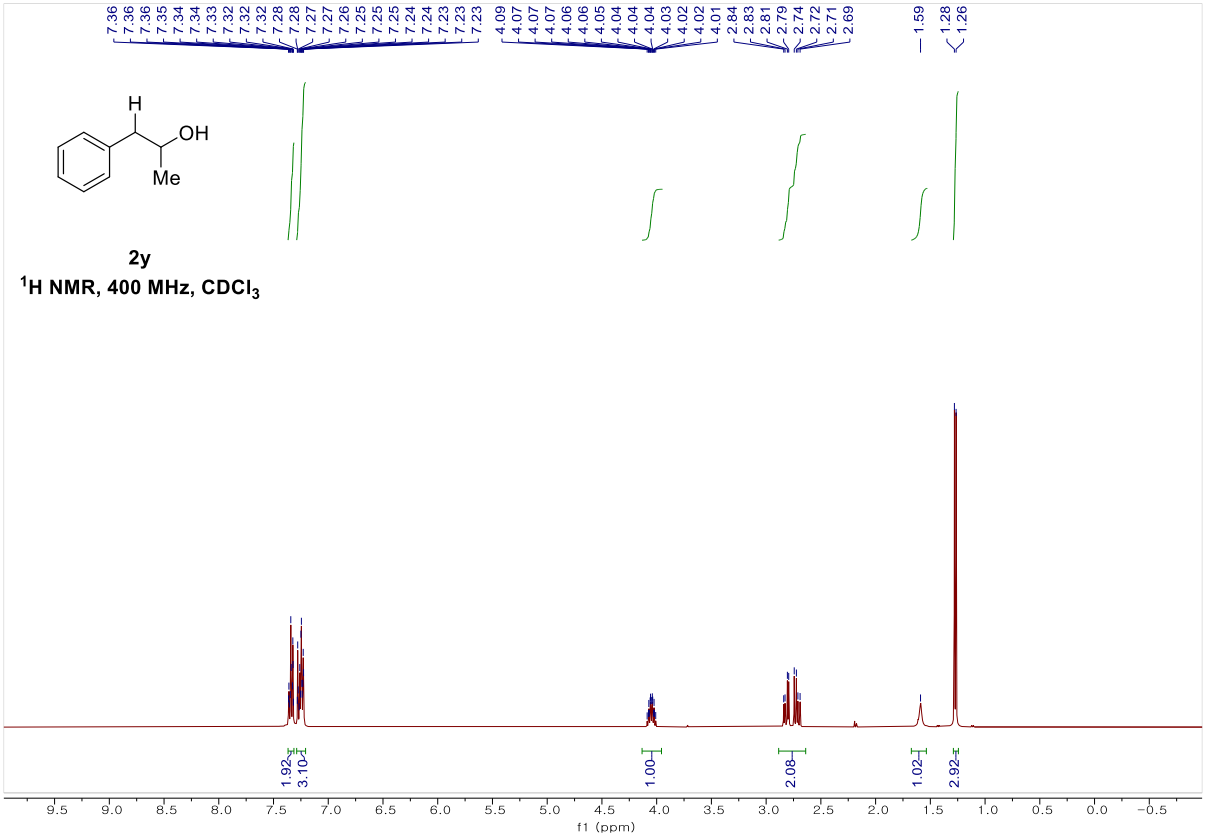
^{13}C NMR, 100 MHz, $CDCl_3$

1-phenylpropan-1-ol (2x')



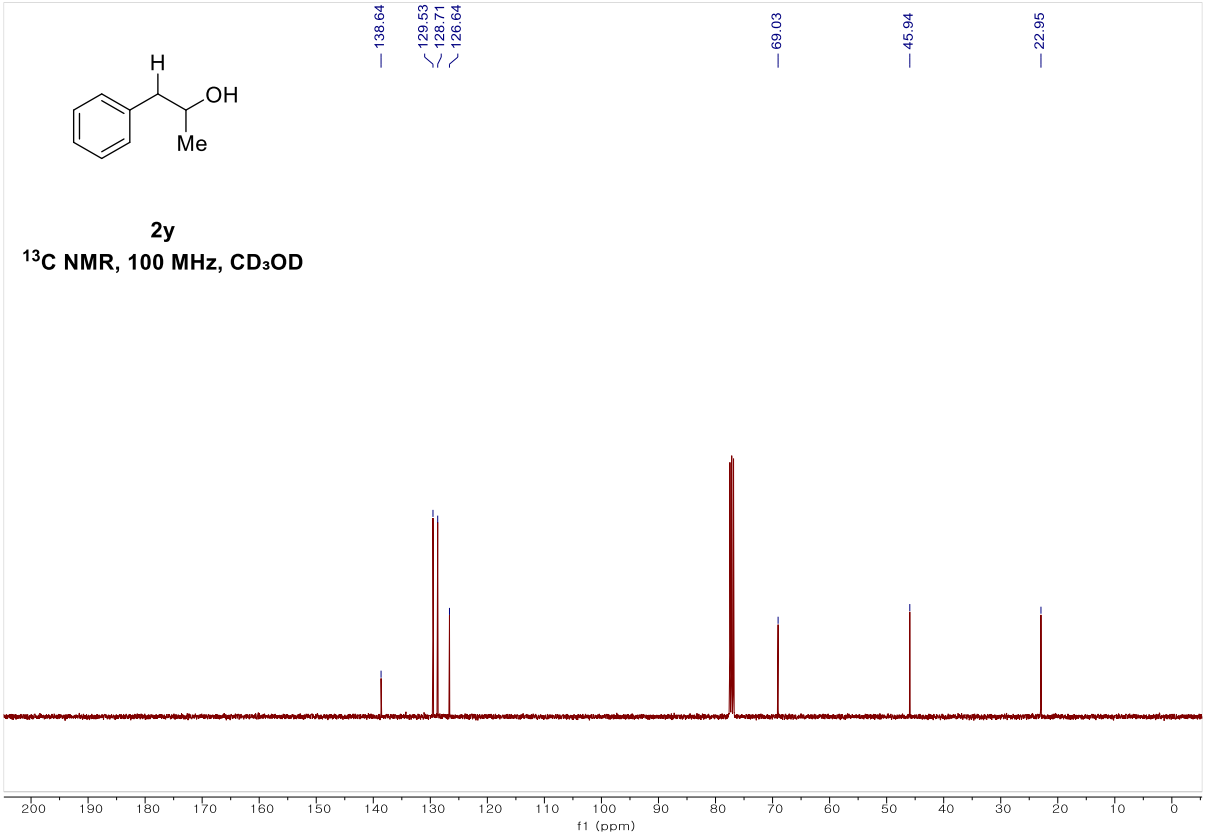


1-phenylpropan-2-ol (2y)



2y

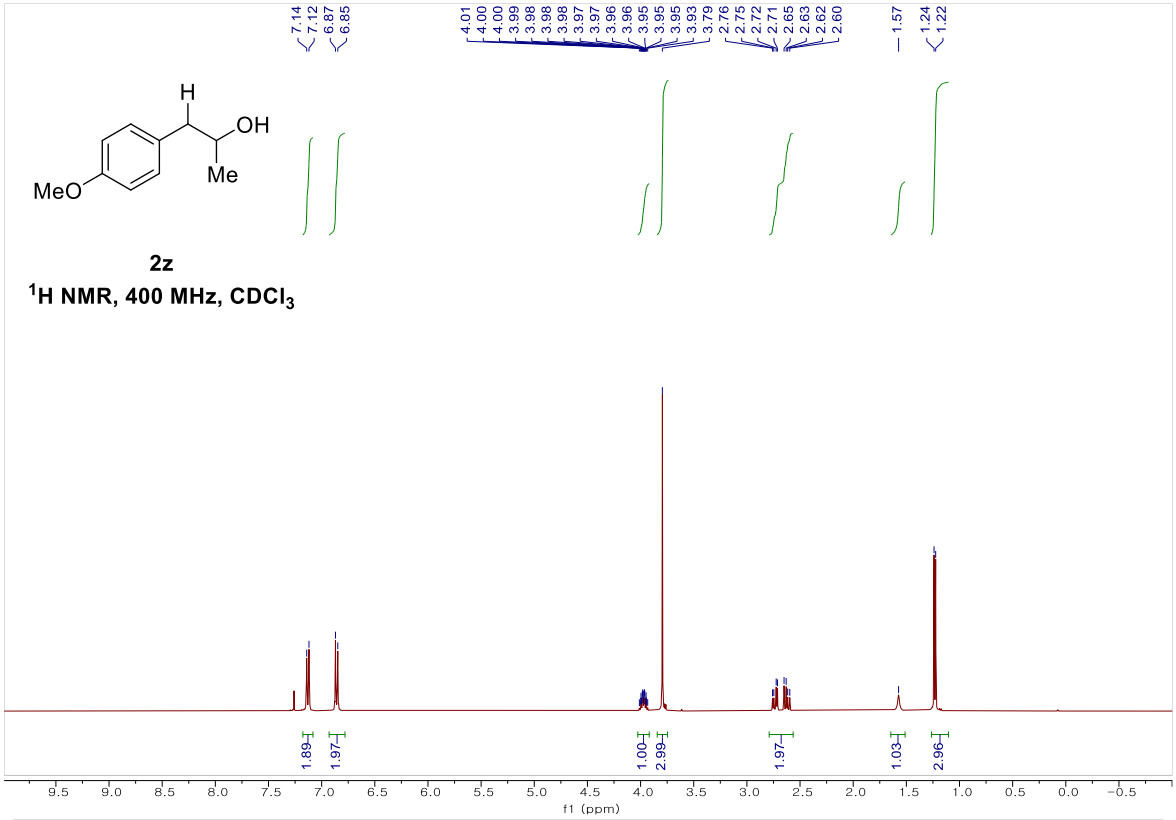
^{1}H NMR, 400 MHz, $CDCl_3$

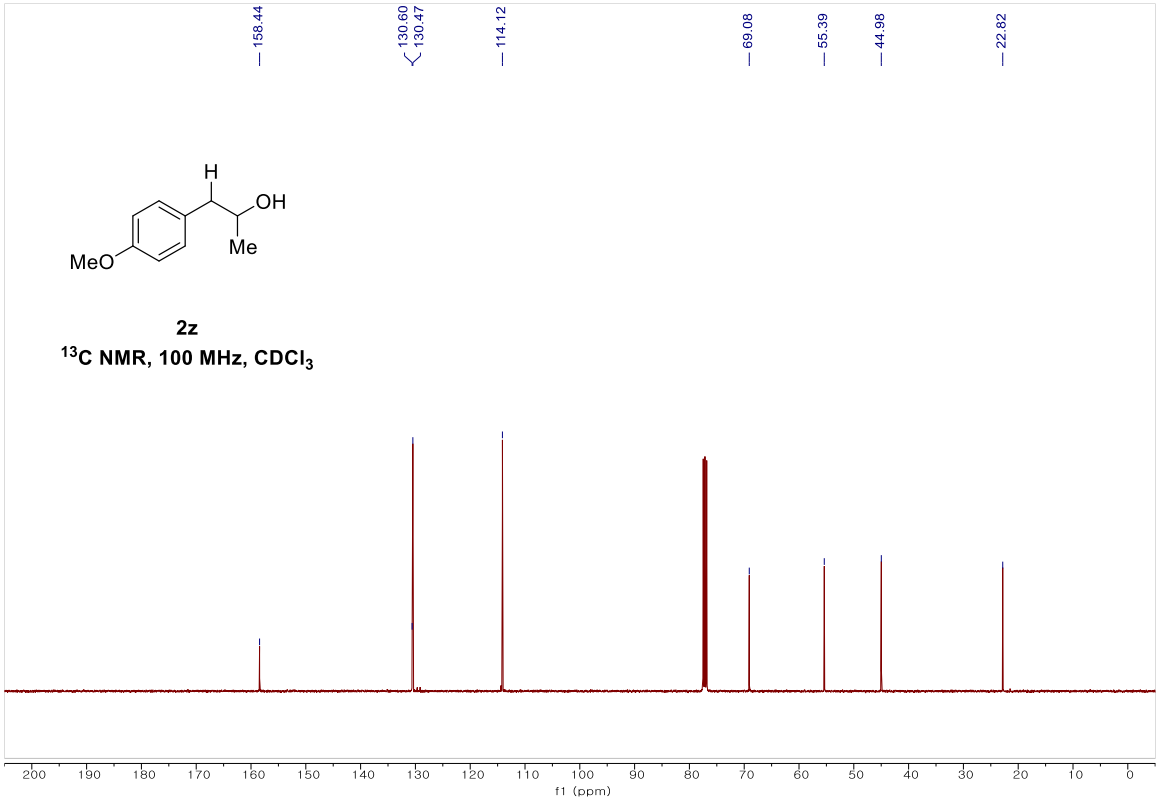


2y

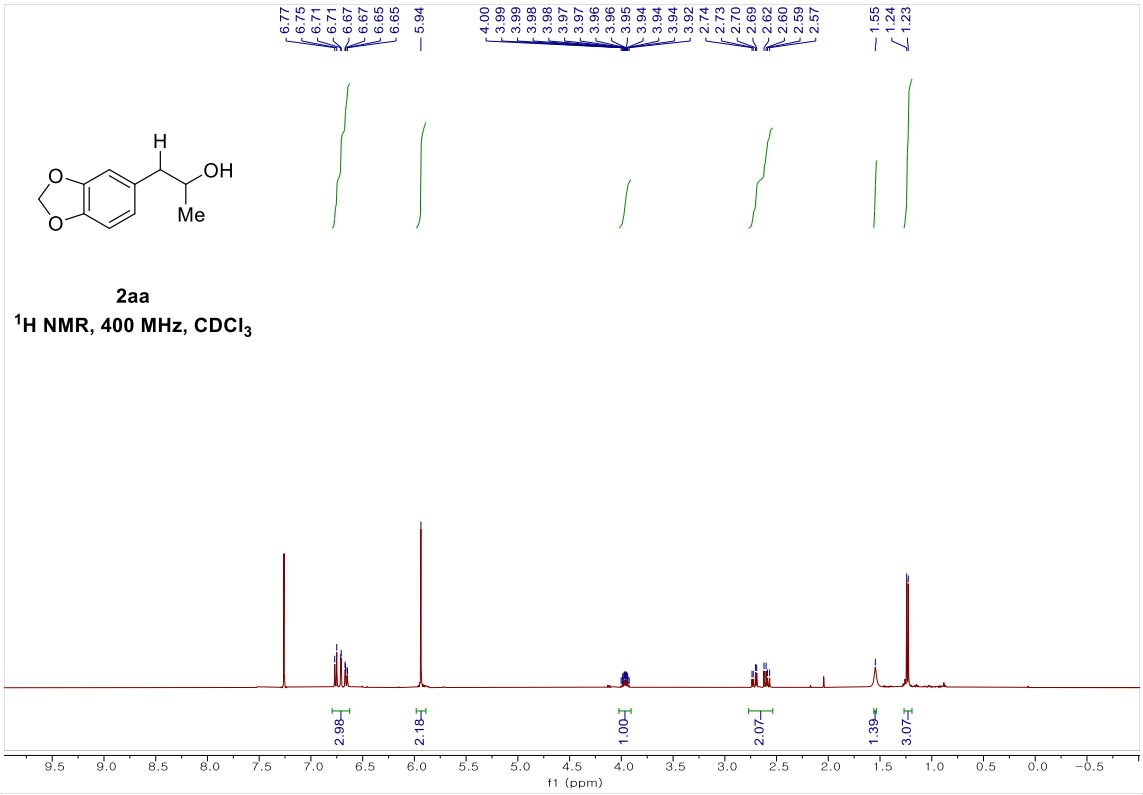
^{13}C NMR, 100 MHz, CD_3OD

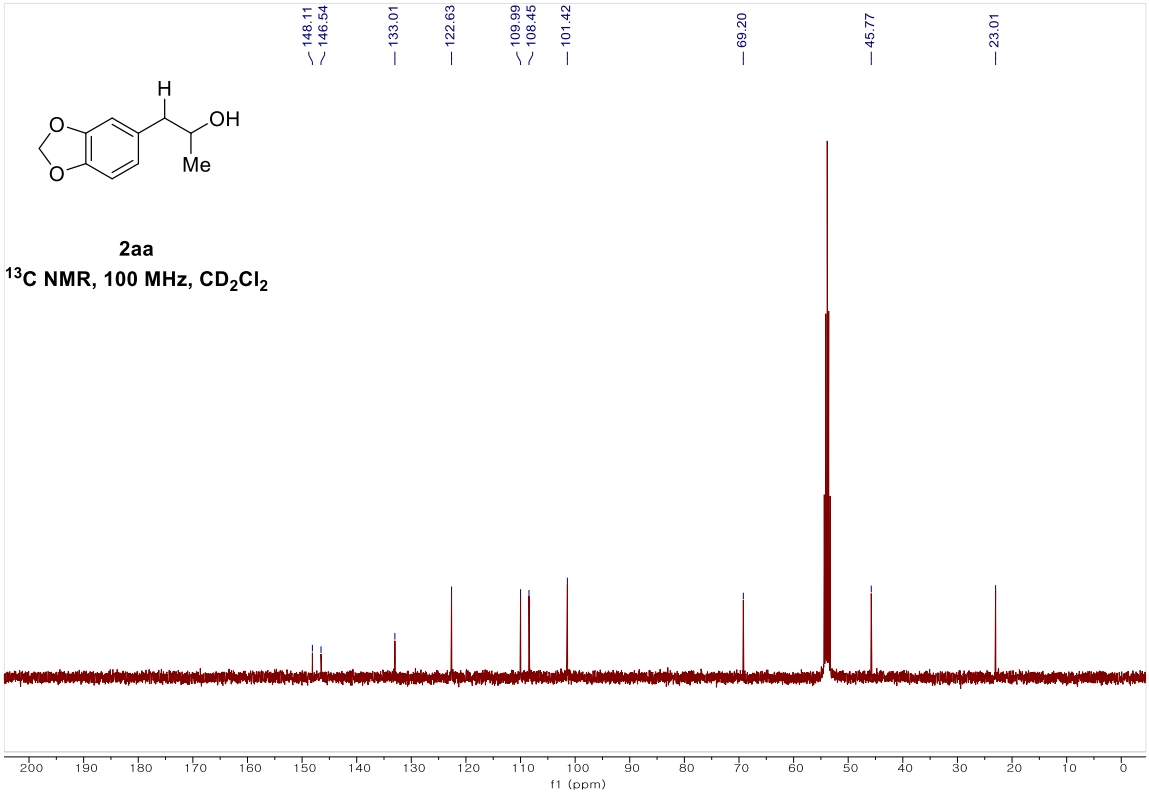
1-(4-methoxyphenyl)propan-2-ol (2z)



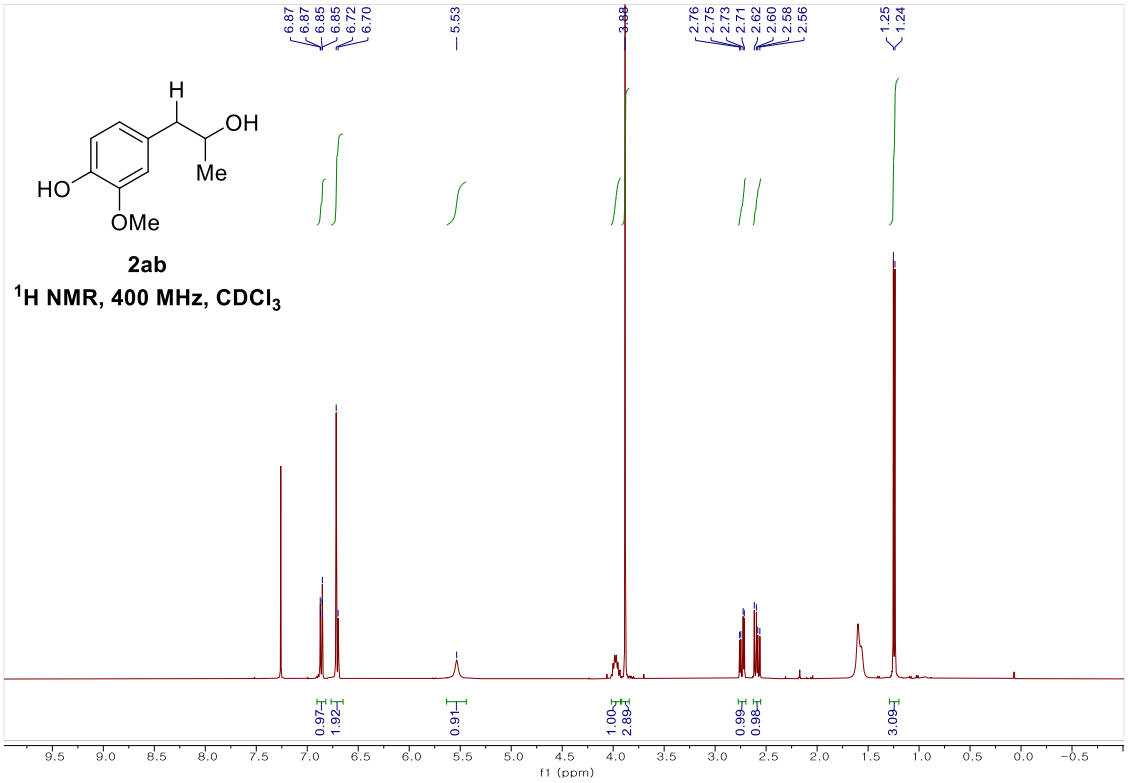


1-(benzo[d][1,3]dioxol-5-yl)propan-1-ol (2aa)



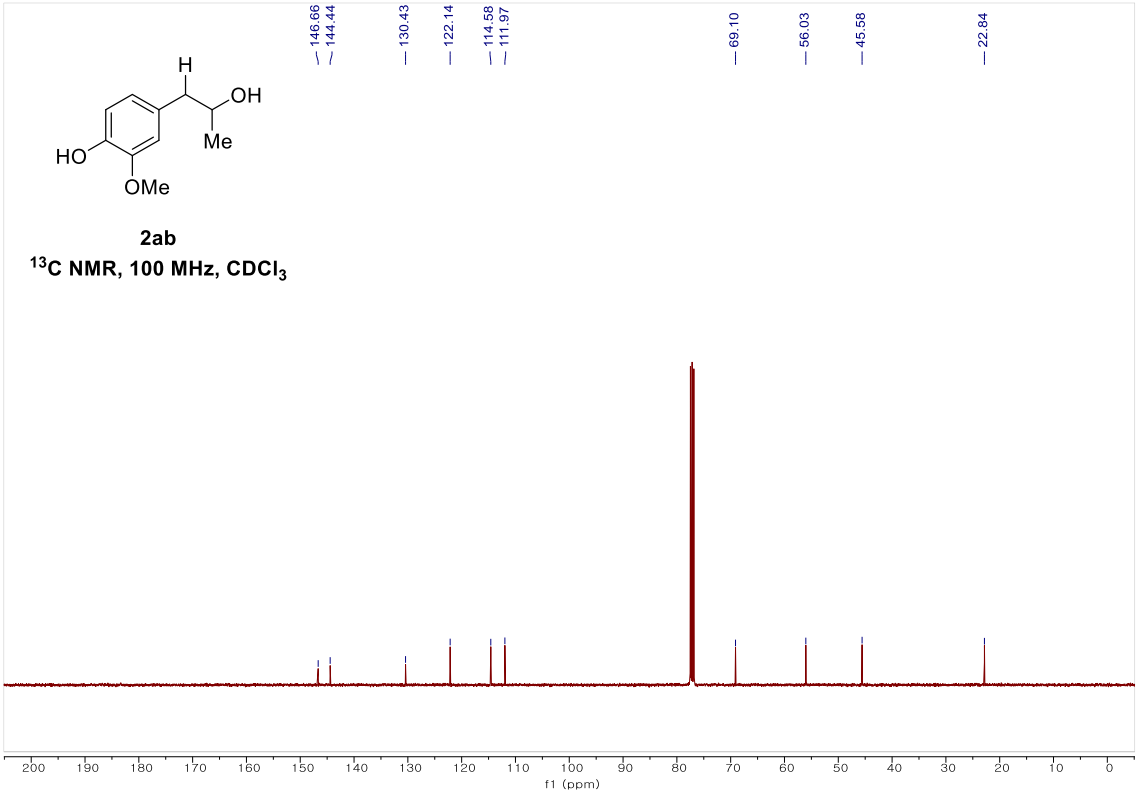


4-(2-hydroxypropyl)-2-methoxyphenol (2ab)



2ab

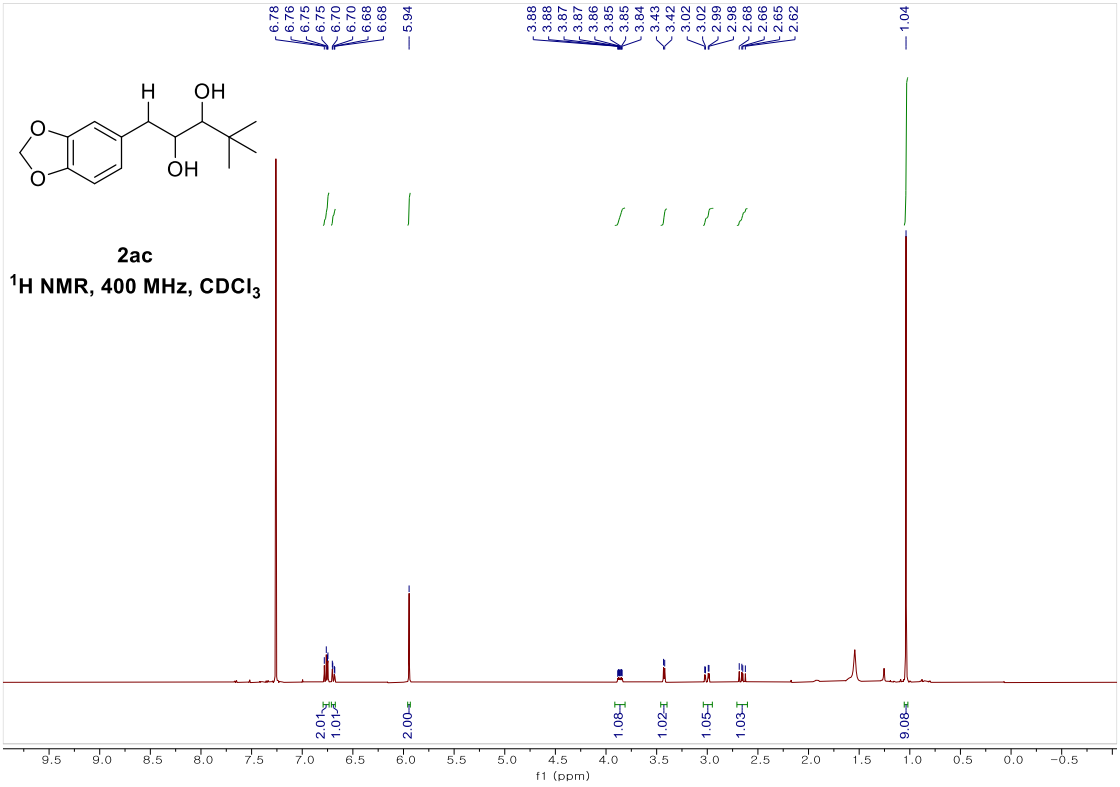
^{1}H NMR, 400 MHz, $CDCl_3$

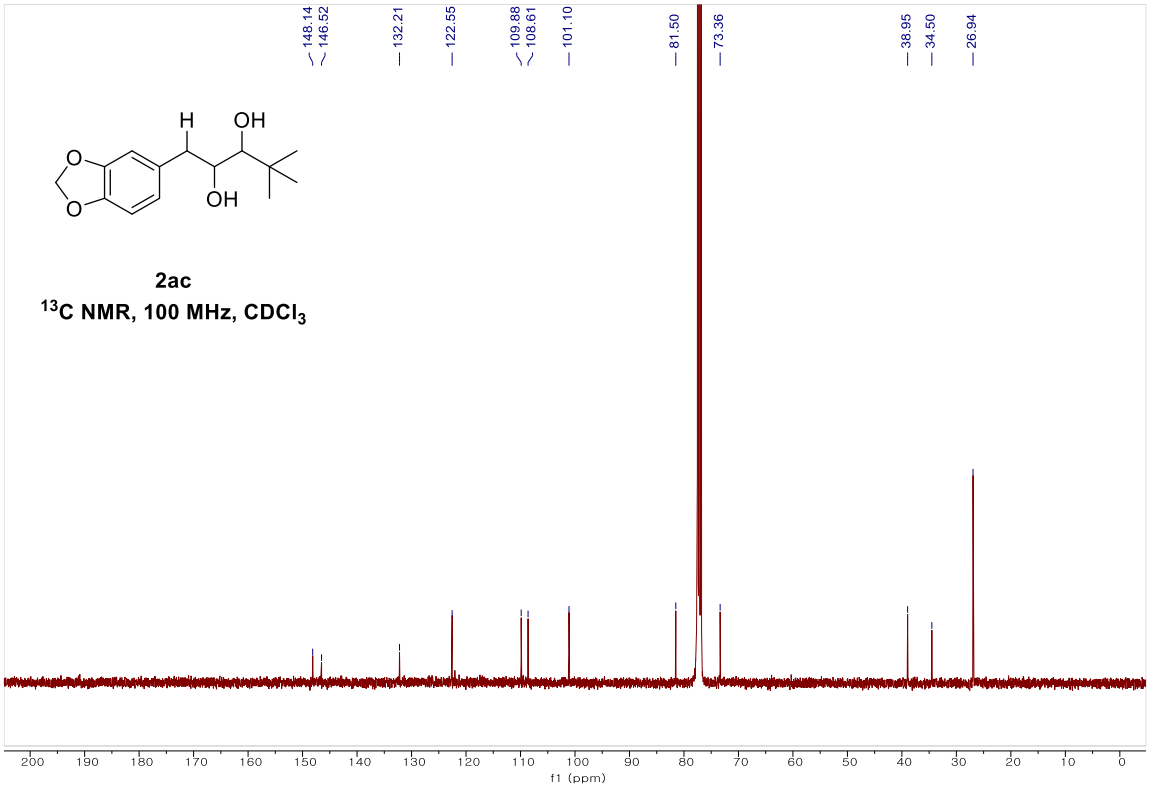


2ab

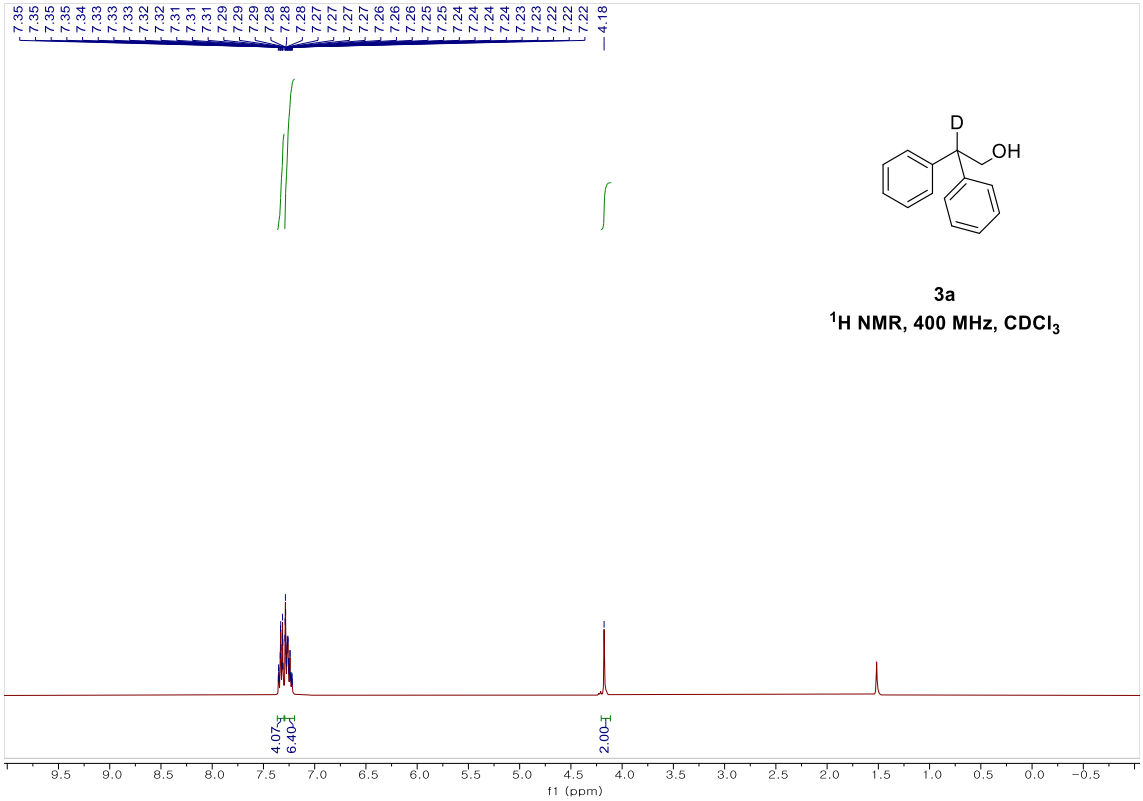
^{13}C NMR, 100 MHz, $CDCl_3$

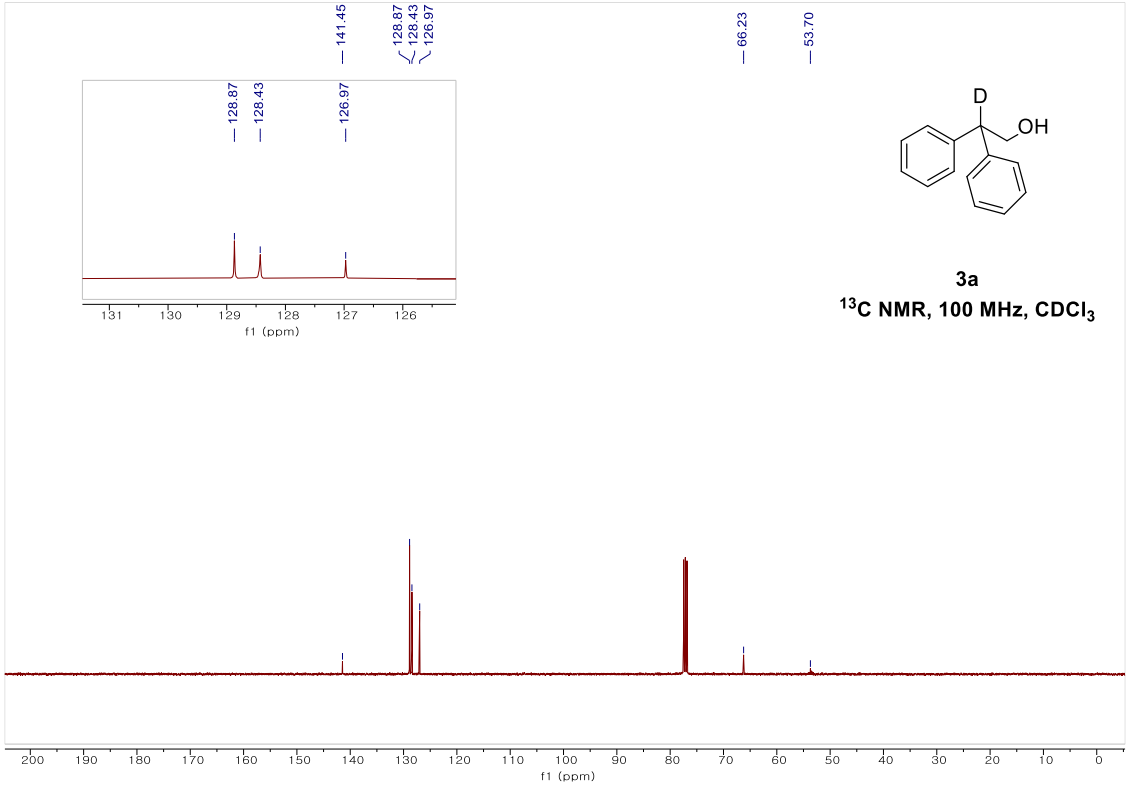
1-(benzo[d][1,3]dioxol-5-yl)-4,4-dimethylpentane-2,3-diol (2ac)



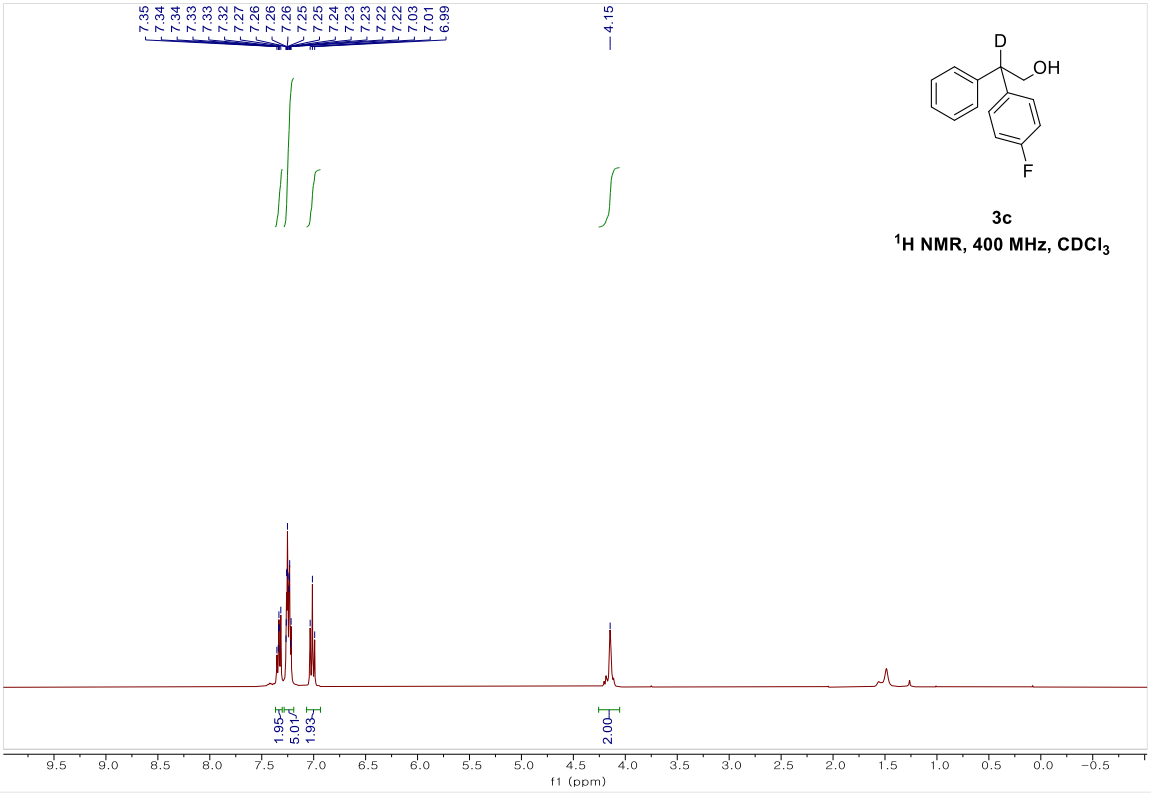


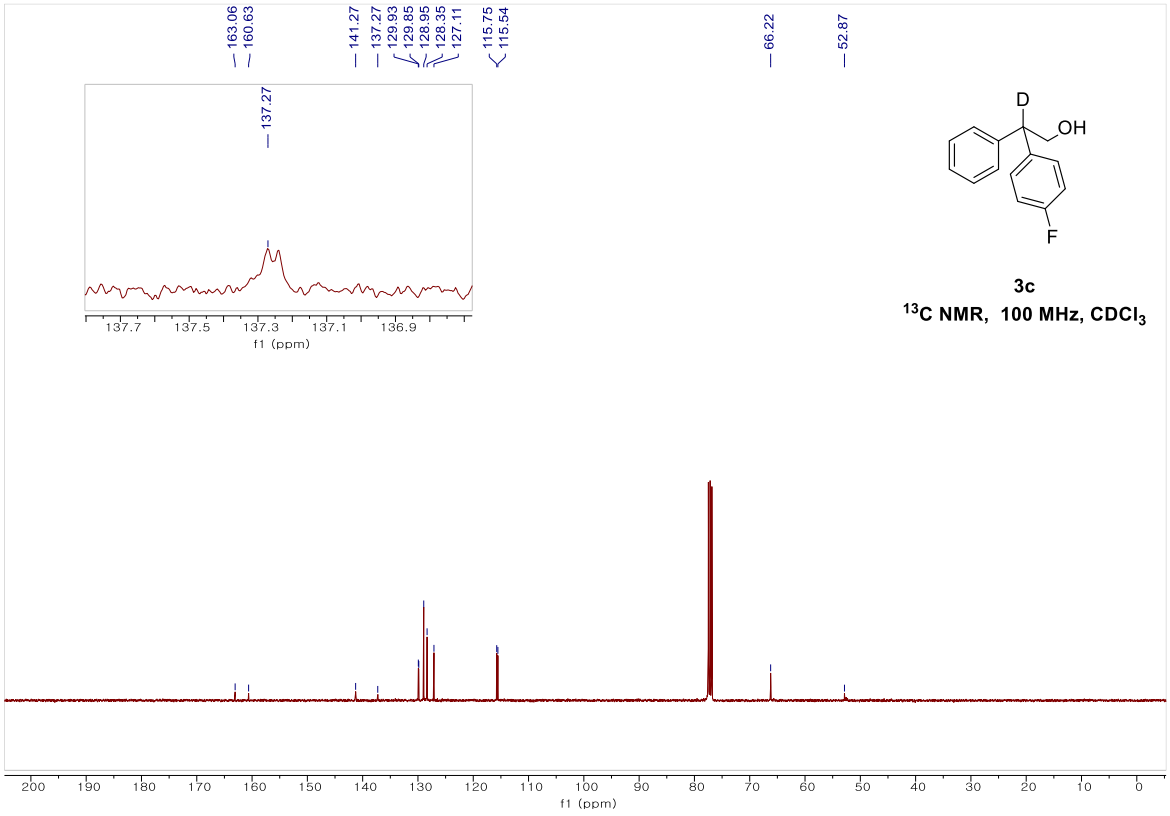
2,2-diphenylethan-2-d-1-ol (3a)



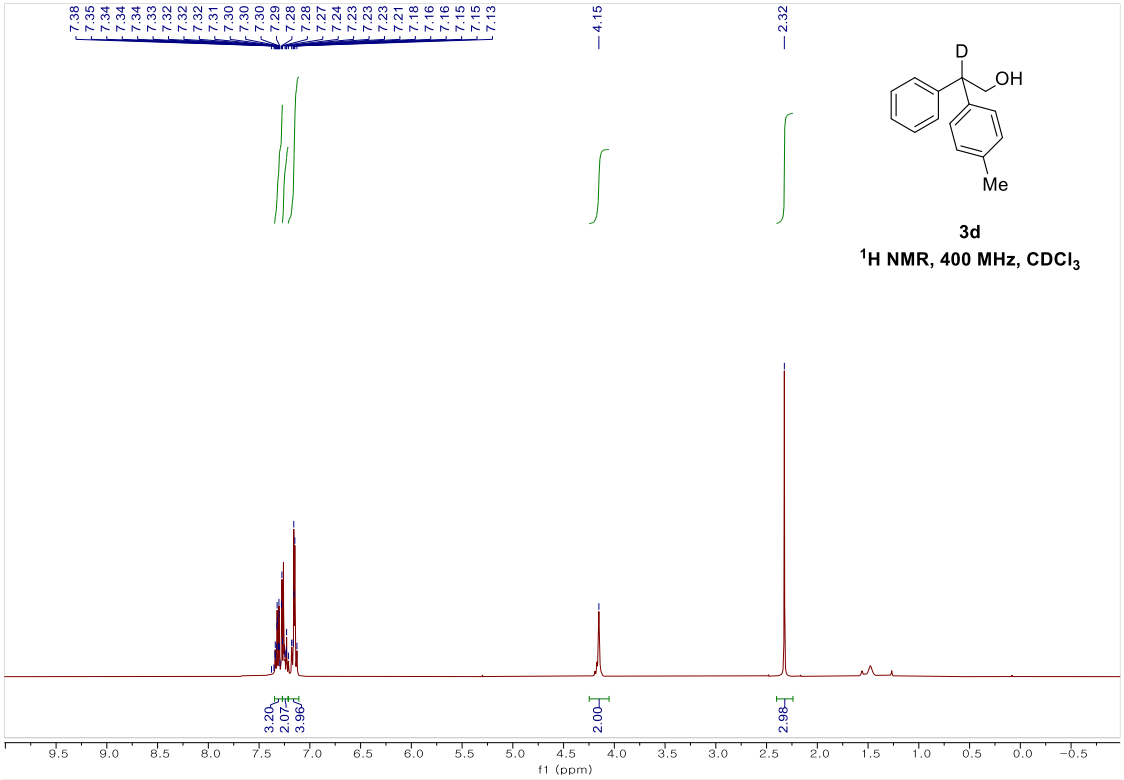


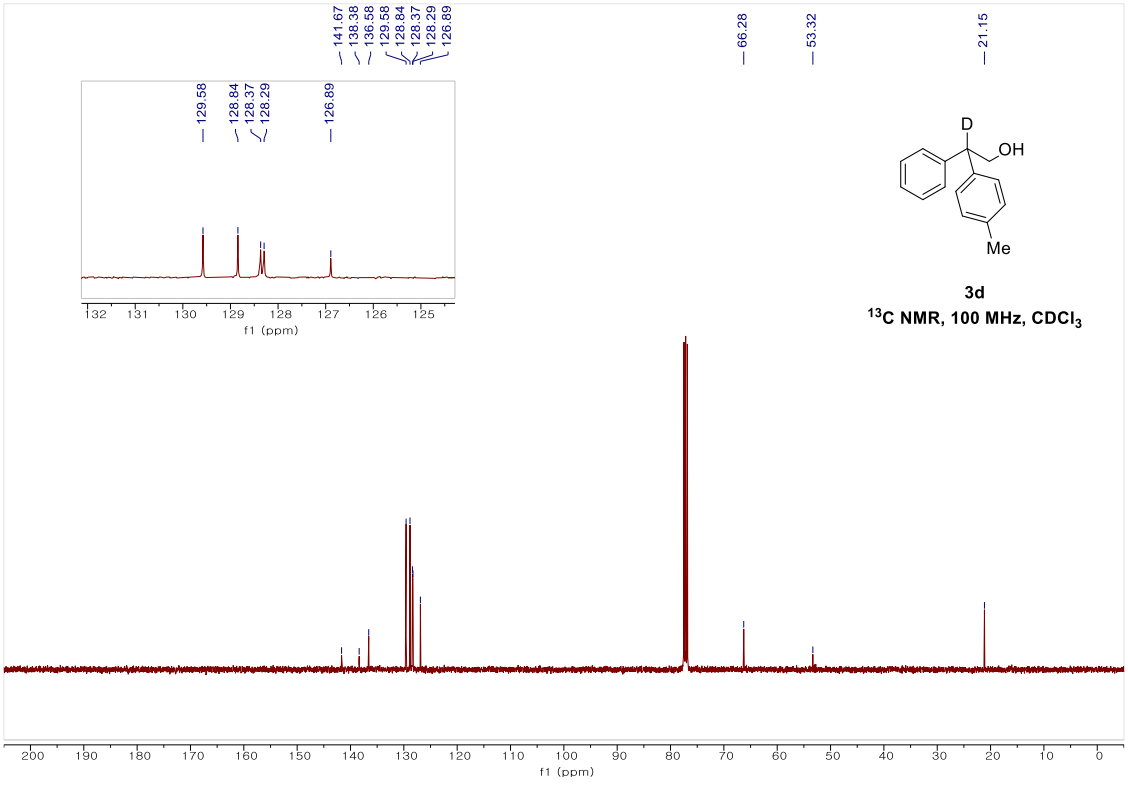
2-(4-fluorophenyl)-2-phenylethan-2-d-1-ol (3c)



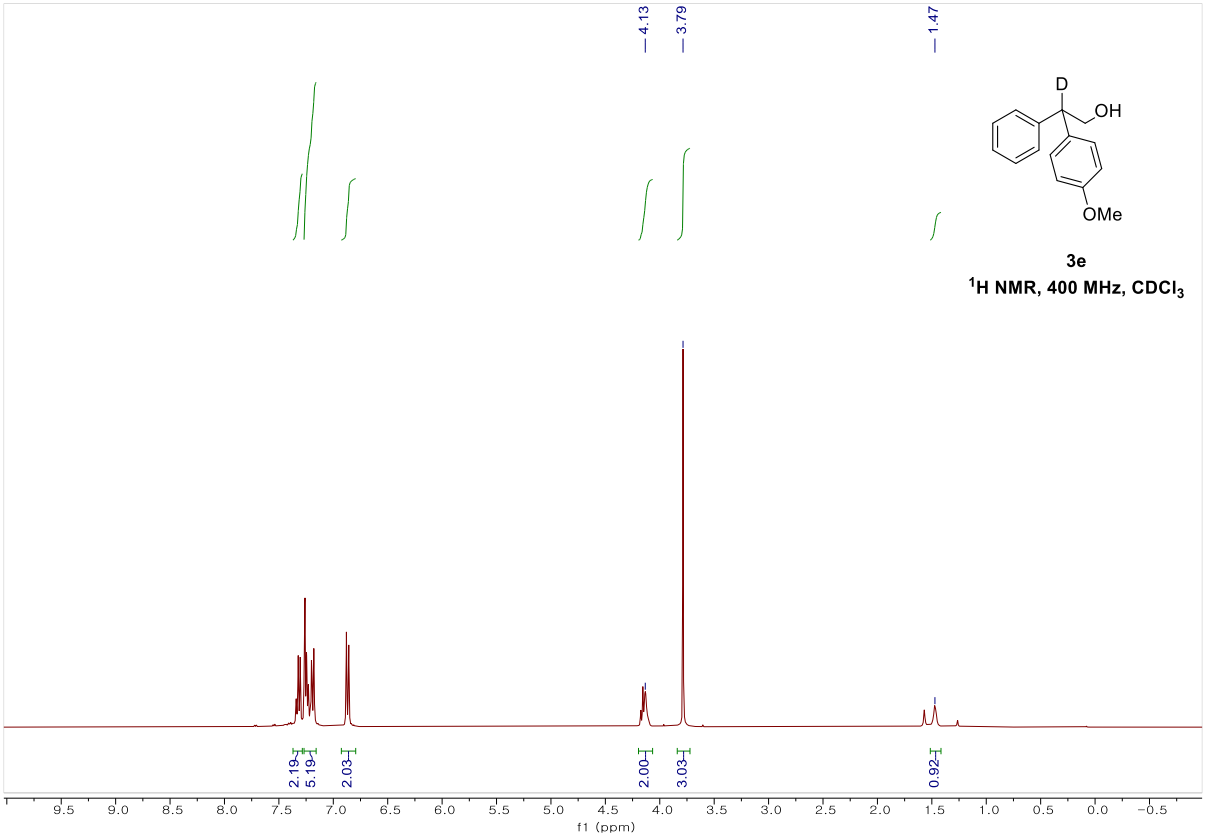


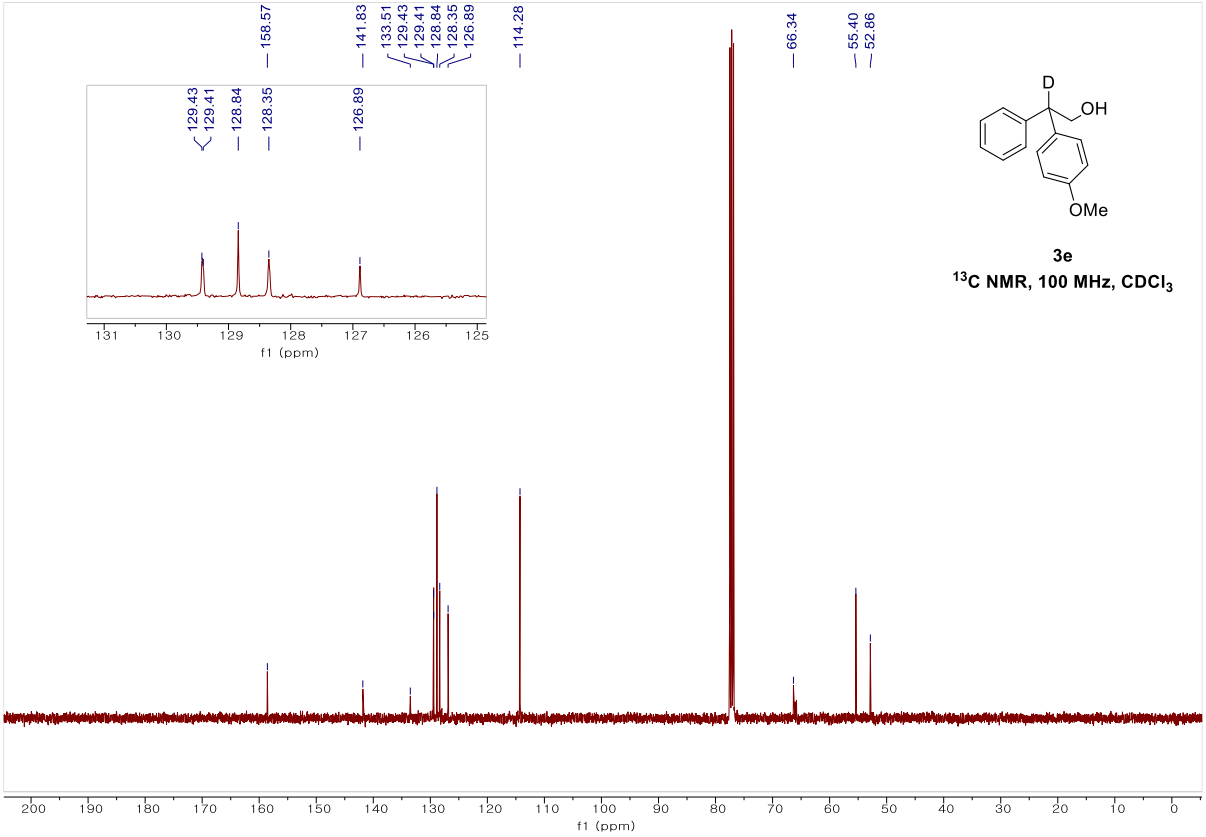
2-phenyl-2-(p-tolyl)ethan-2-d-1-ol (3d)



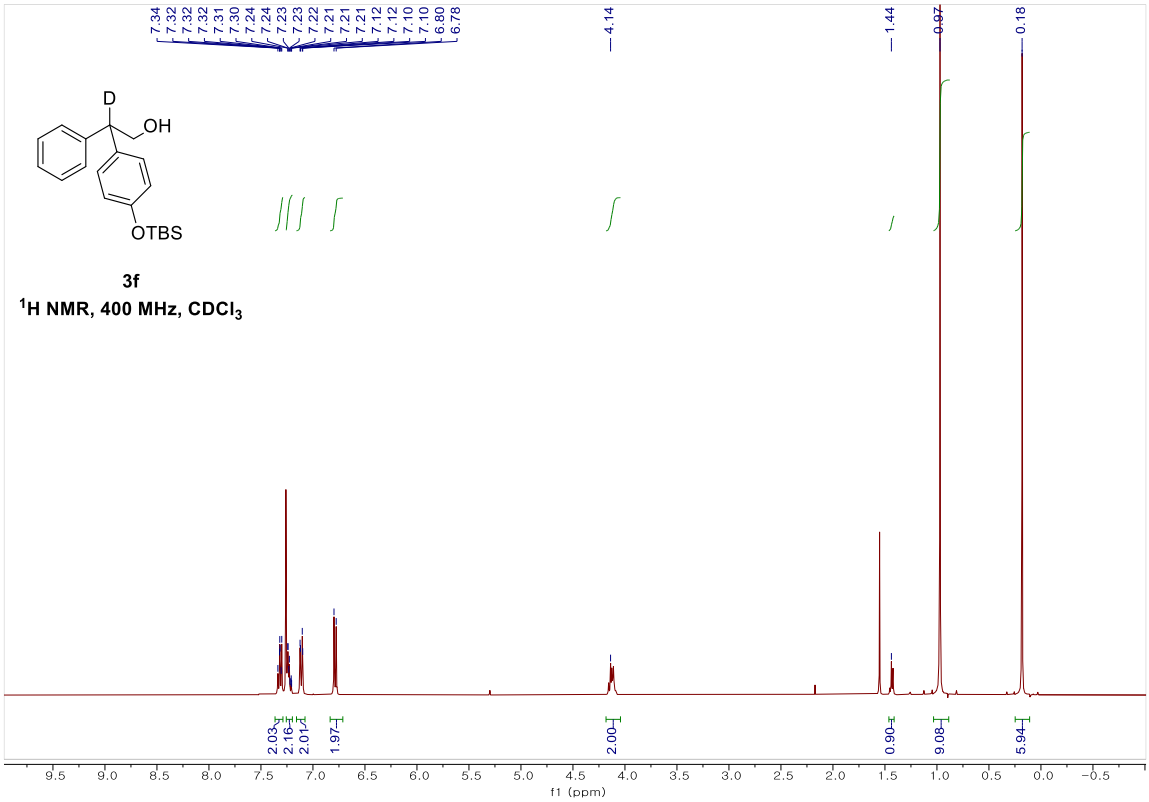


2-(4-methoxyphenyl)-2-phenylethan-2-d-1-ol (3e)



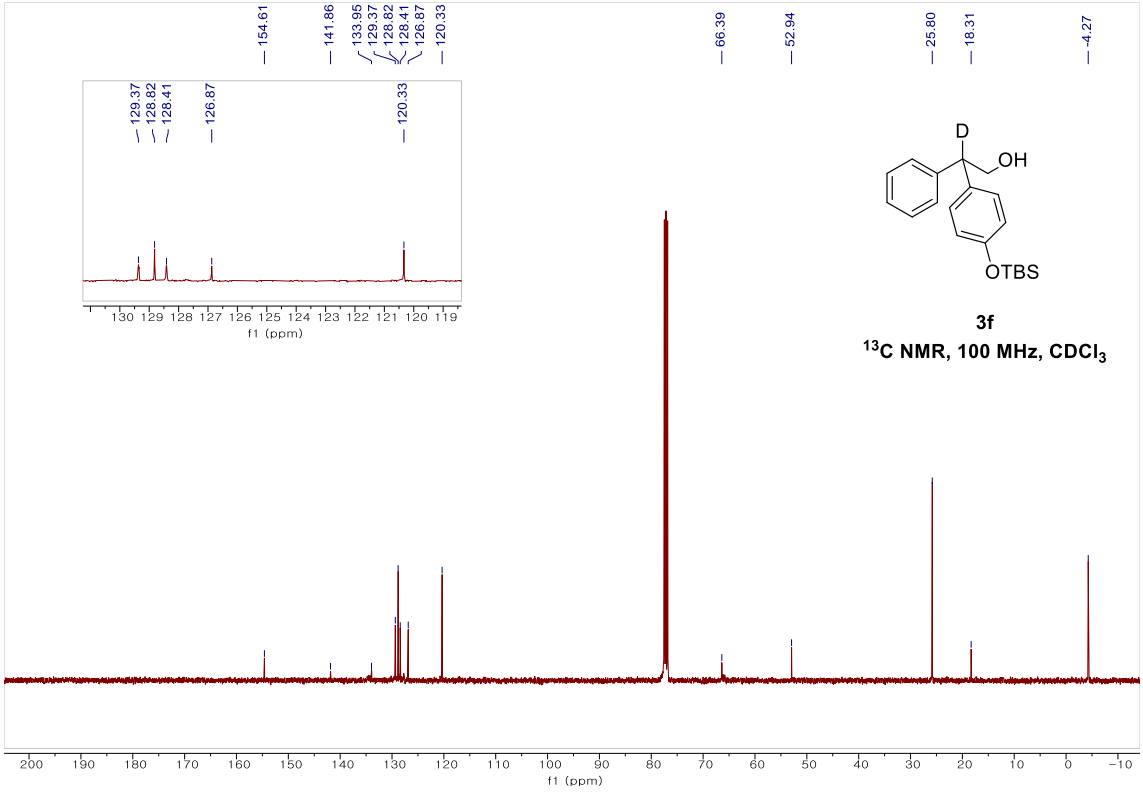


2-(4-((tert-butyldimethylsilyl)oxy)phenyl)-2-phenylethan-2-d-1-ol (3f)



3f

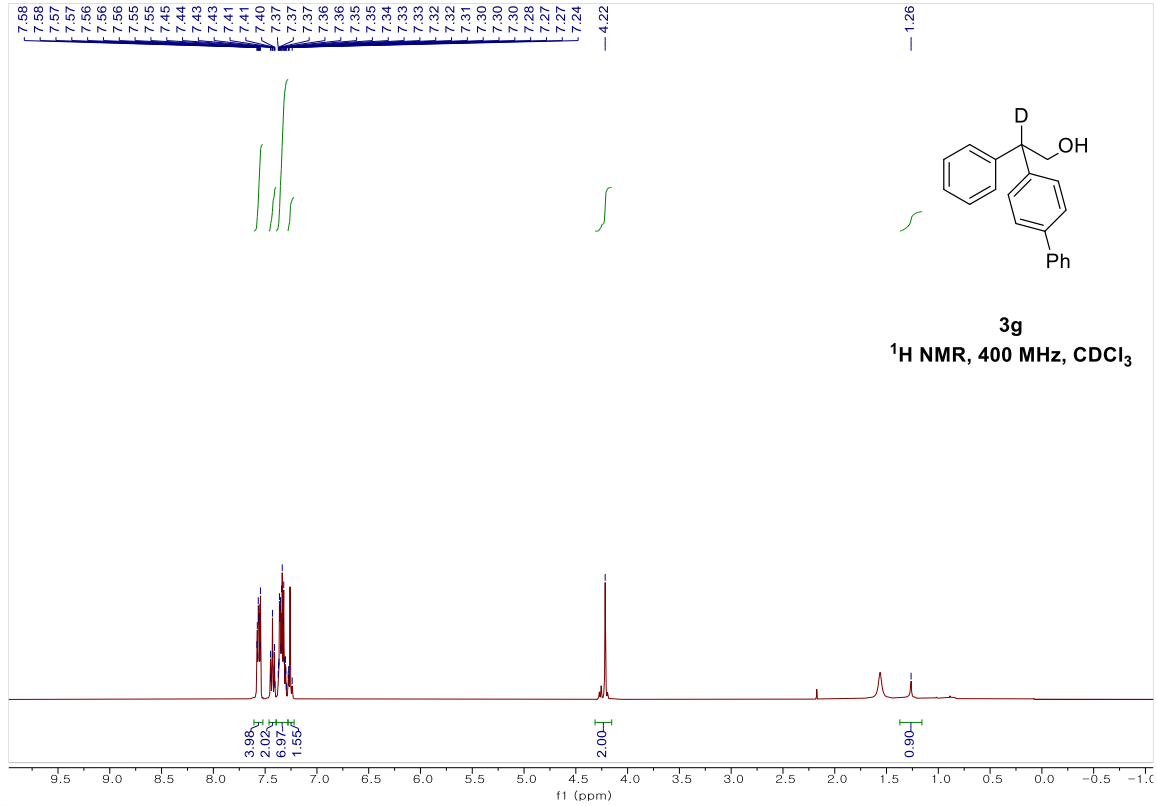
^{1}H NMR, 400 MHz, $CDCl_3$

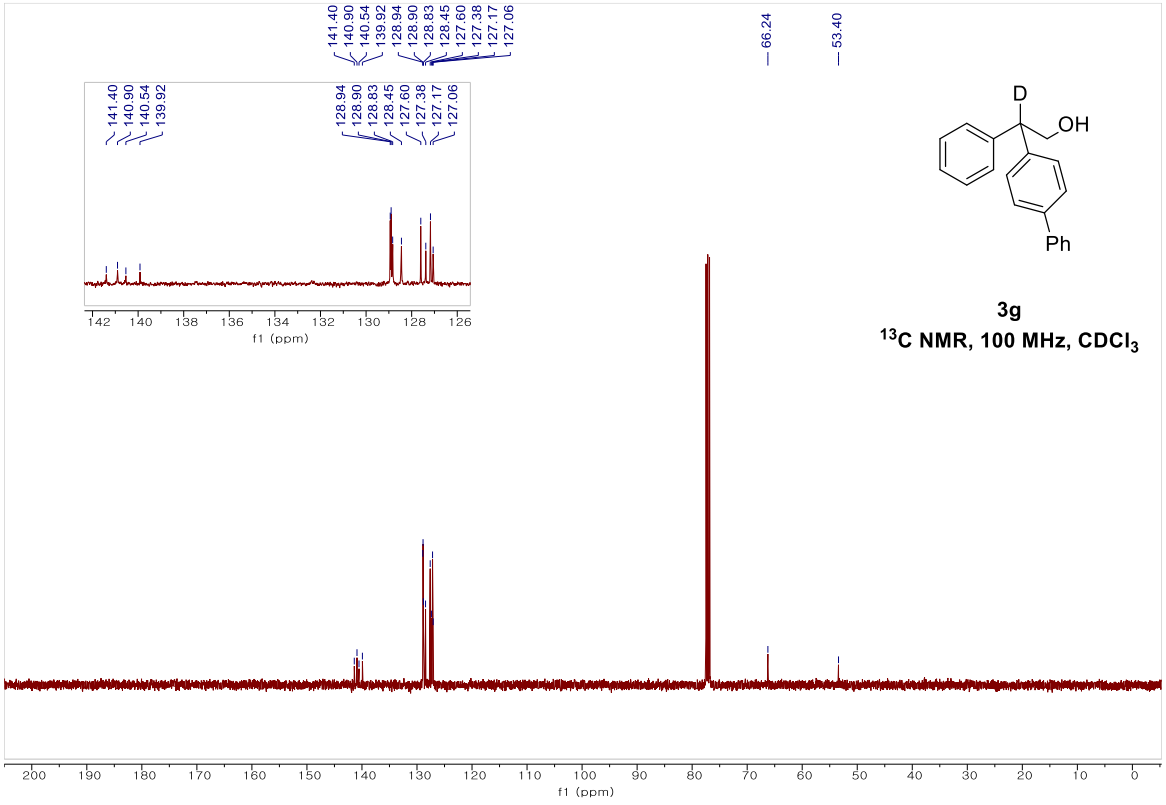


3f

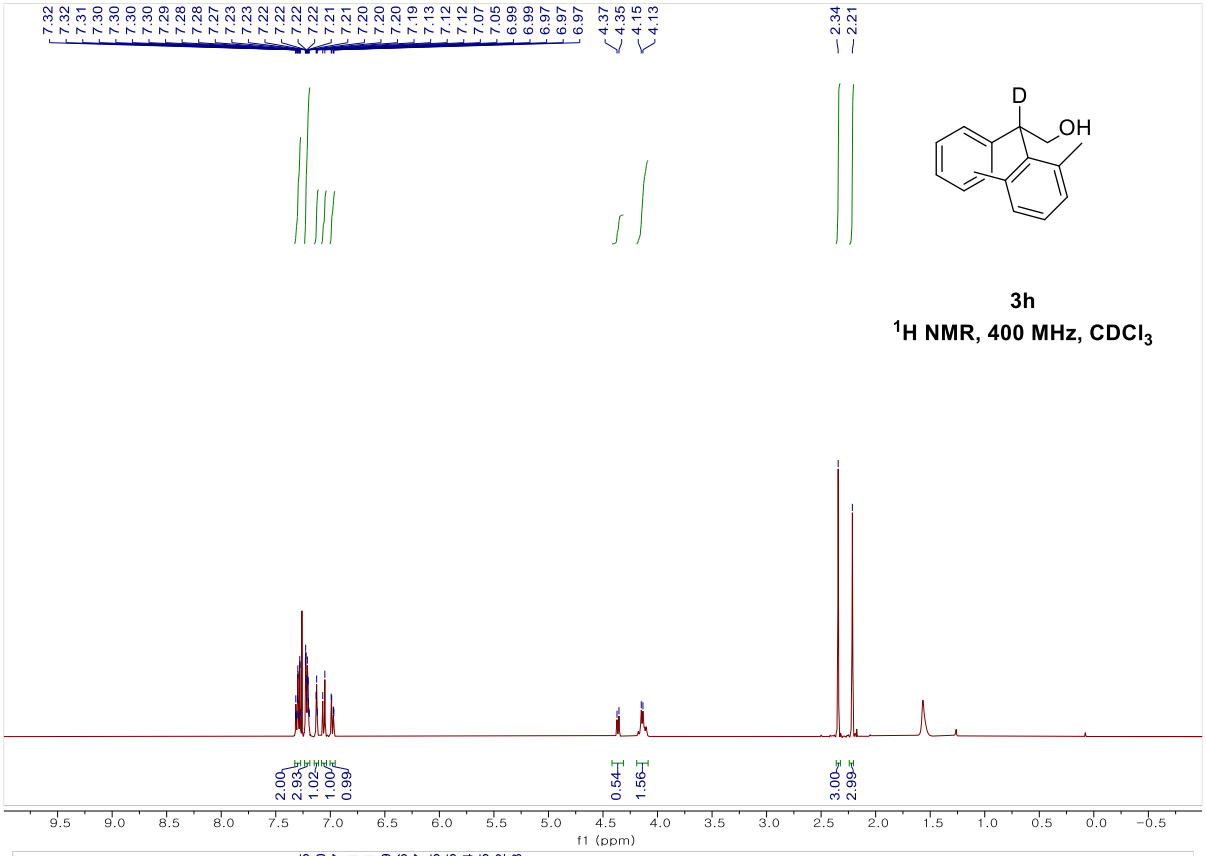
^{13}C NMR, 100 MHz, $CDCl_3$

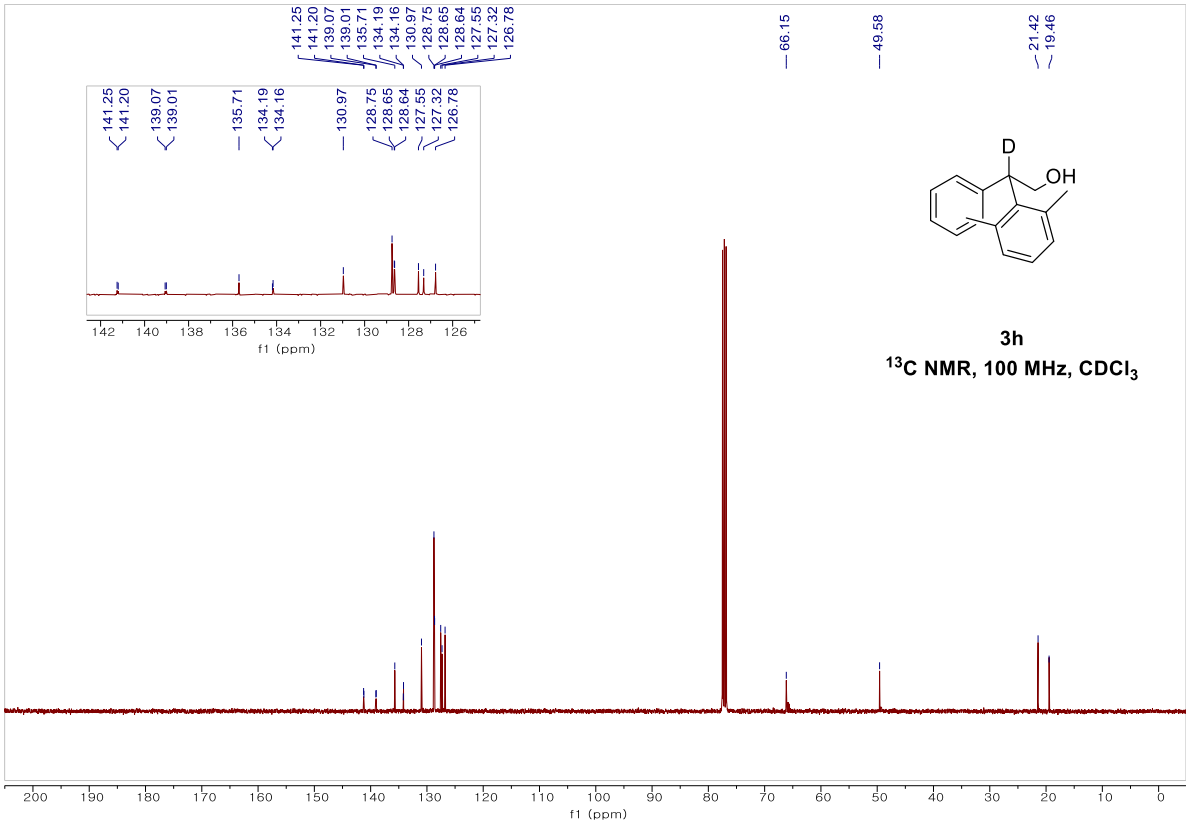
2-([1,1'-biphenyl]-4-yl)-2-phenylethan-2-d-1-ol (3g)



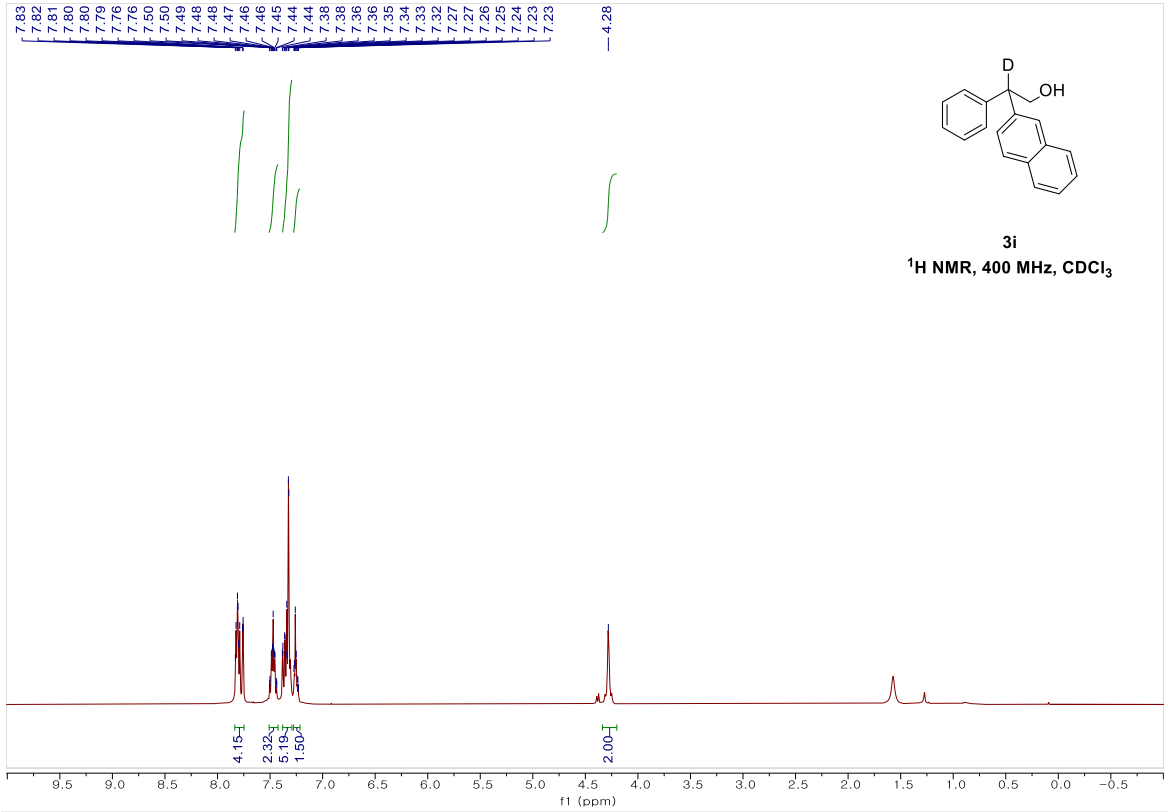


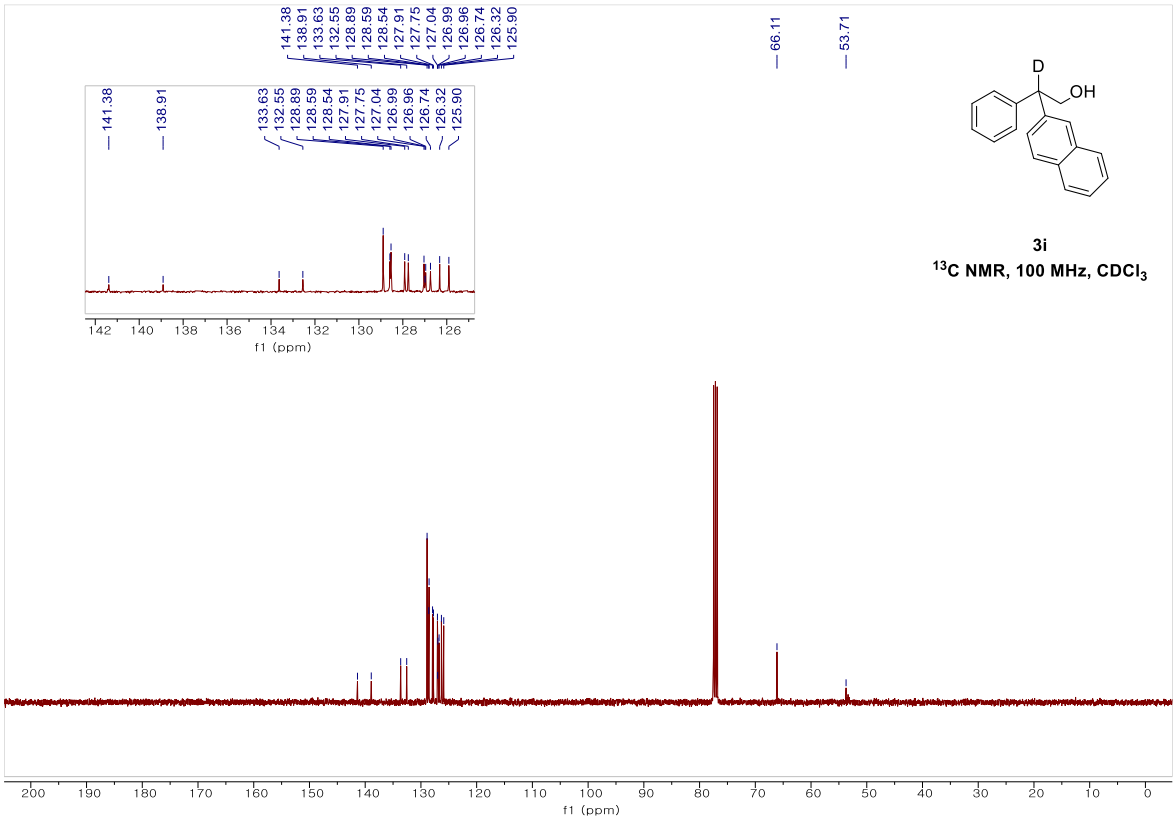
2-(2,6-dimethylphenyl)-2-phenylethan-2-d-1-ol (3h)



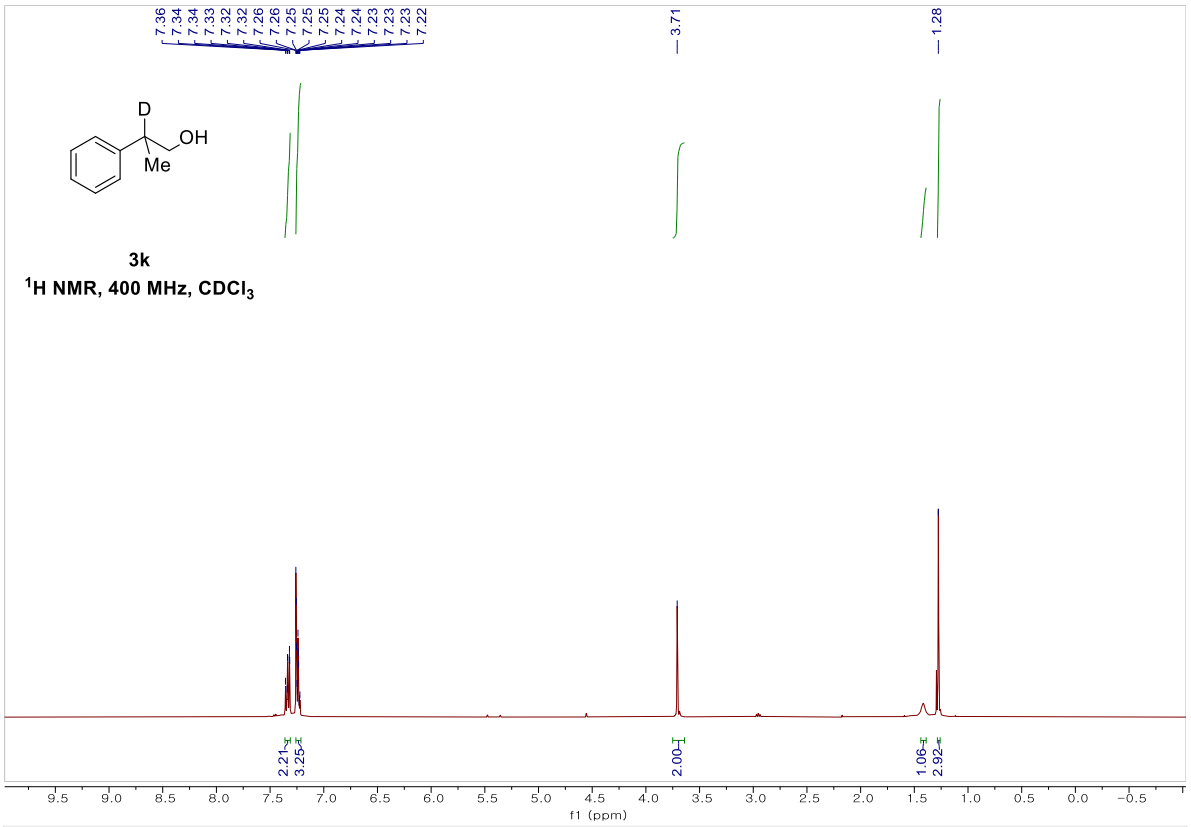


2-(naphthalen-2-yl)-2-phenylethan-2-d-1-ol (3i)



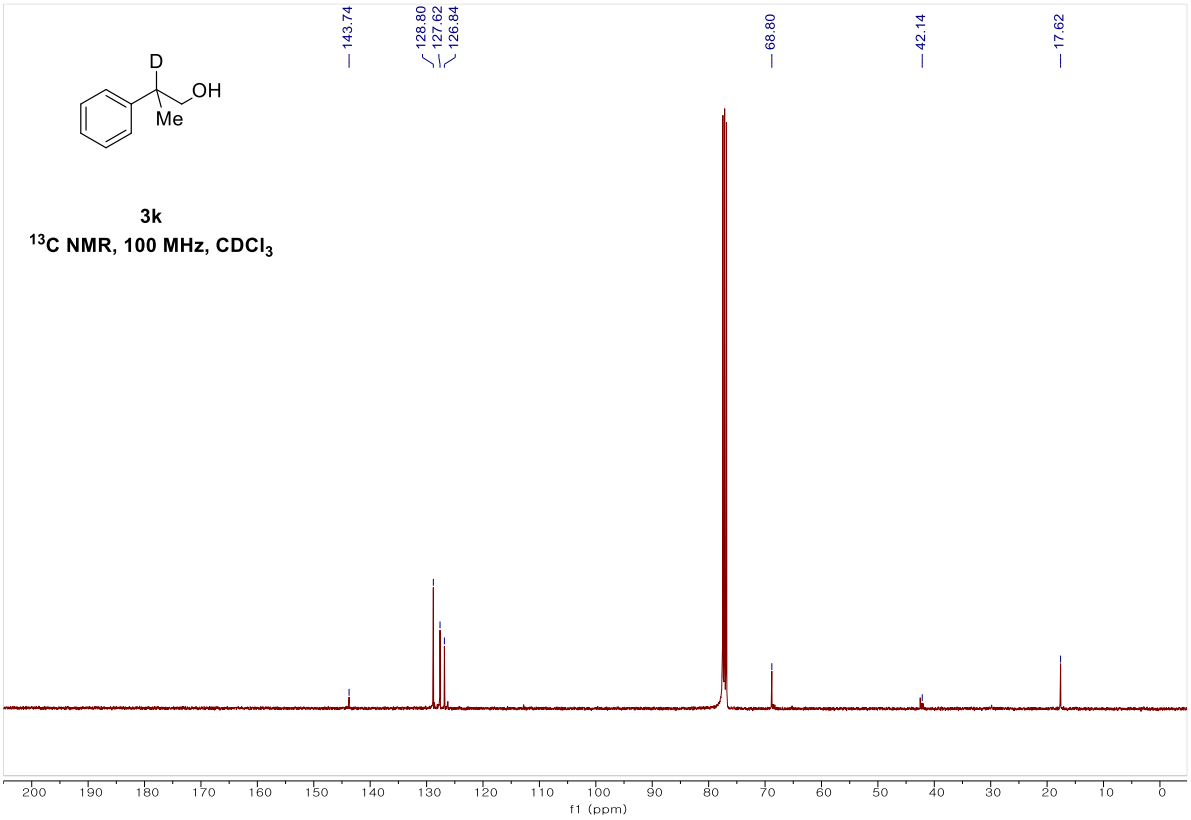


2-phenylpropan-2-d-1-ol (3k)



3k

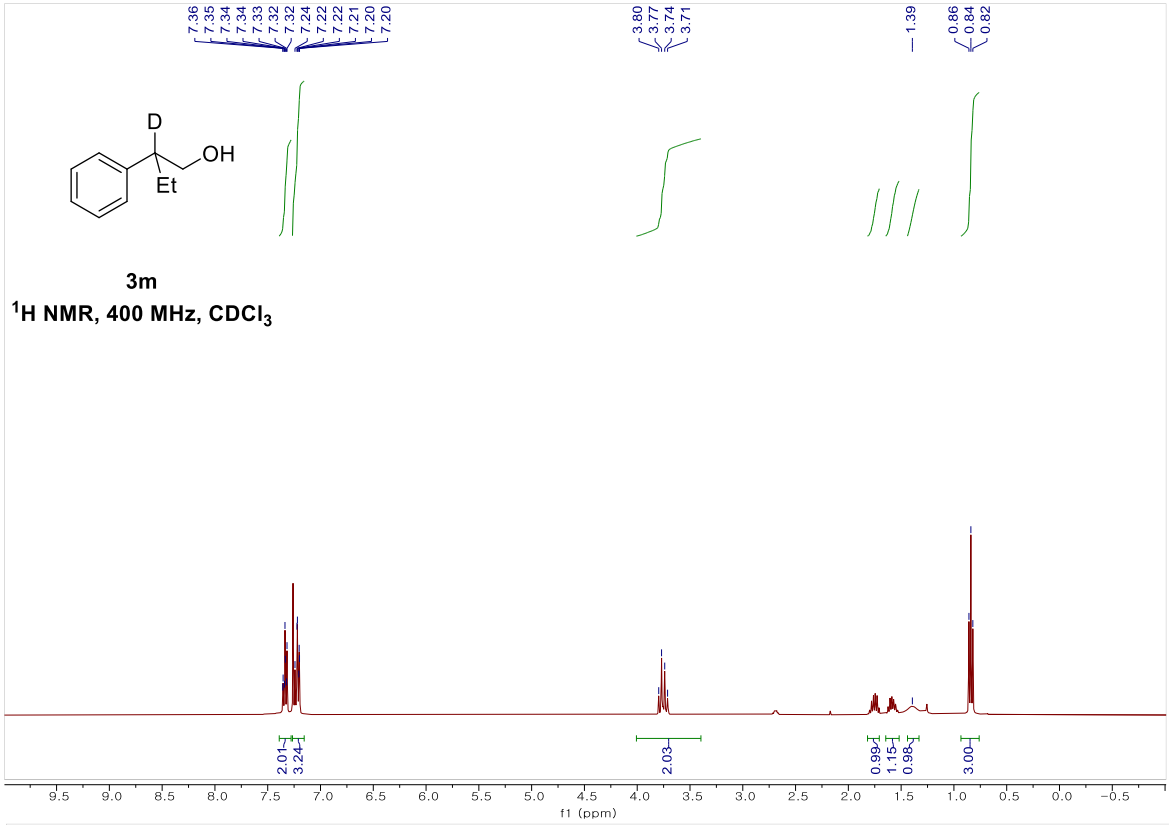
^{1}H NMR, 400 MHz, $CDCl_3$



3k

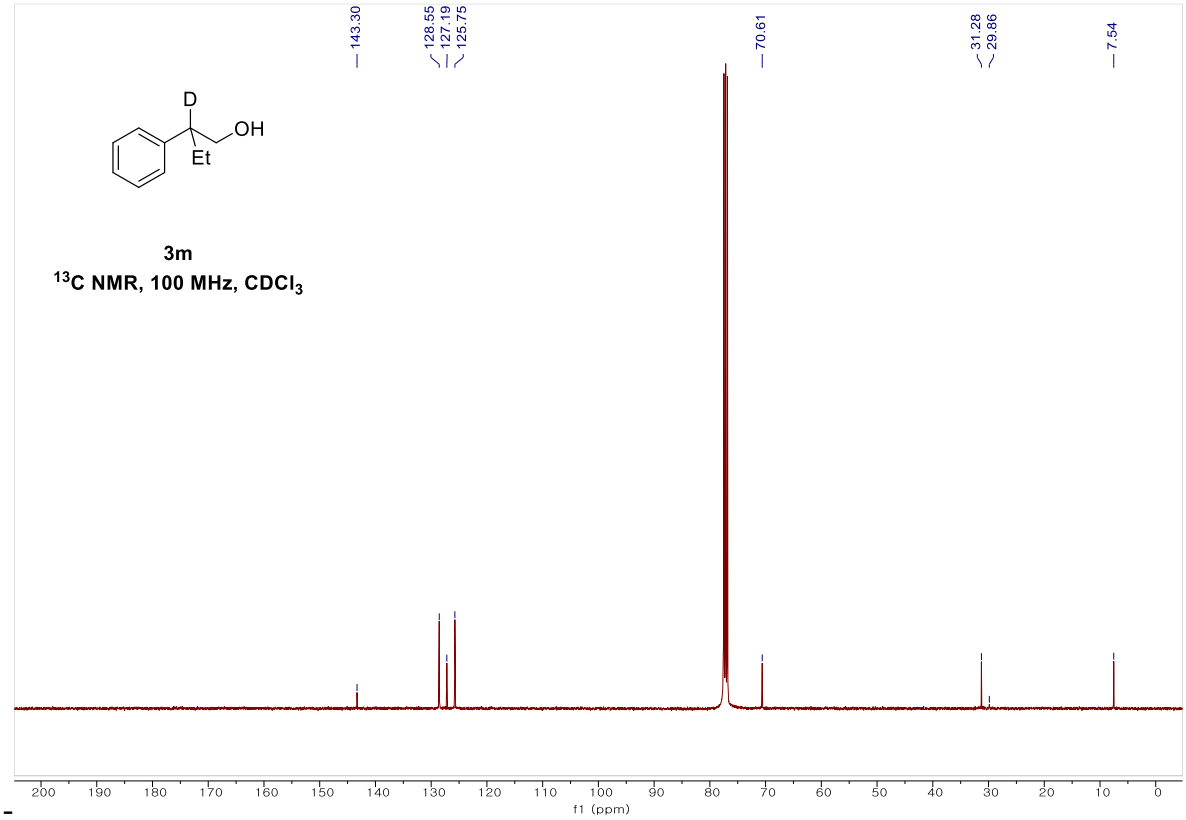
^{13}C NMR, 100 MHz, $CDCl_3$

2-phenylbutan-2-d-1-ol (3m)



3m

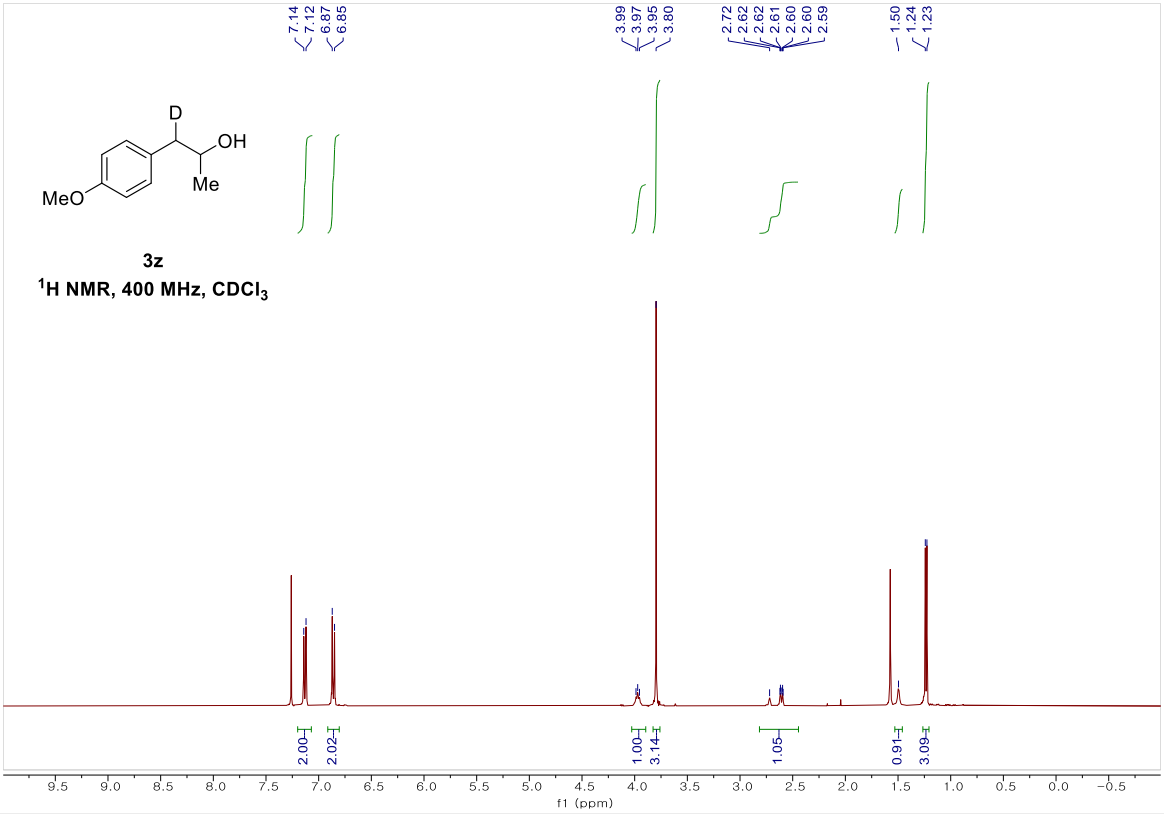
^{1}H NMR, 400 MHz, $CDCl_3$

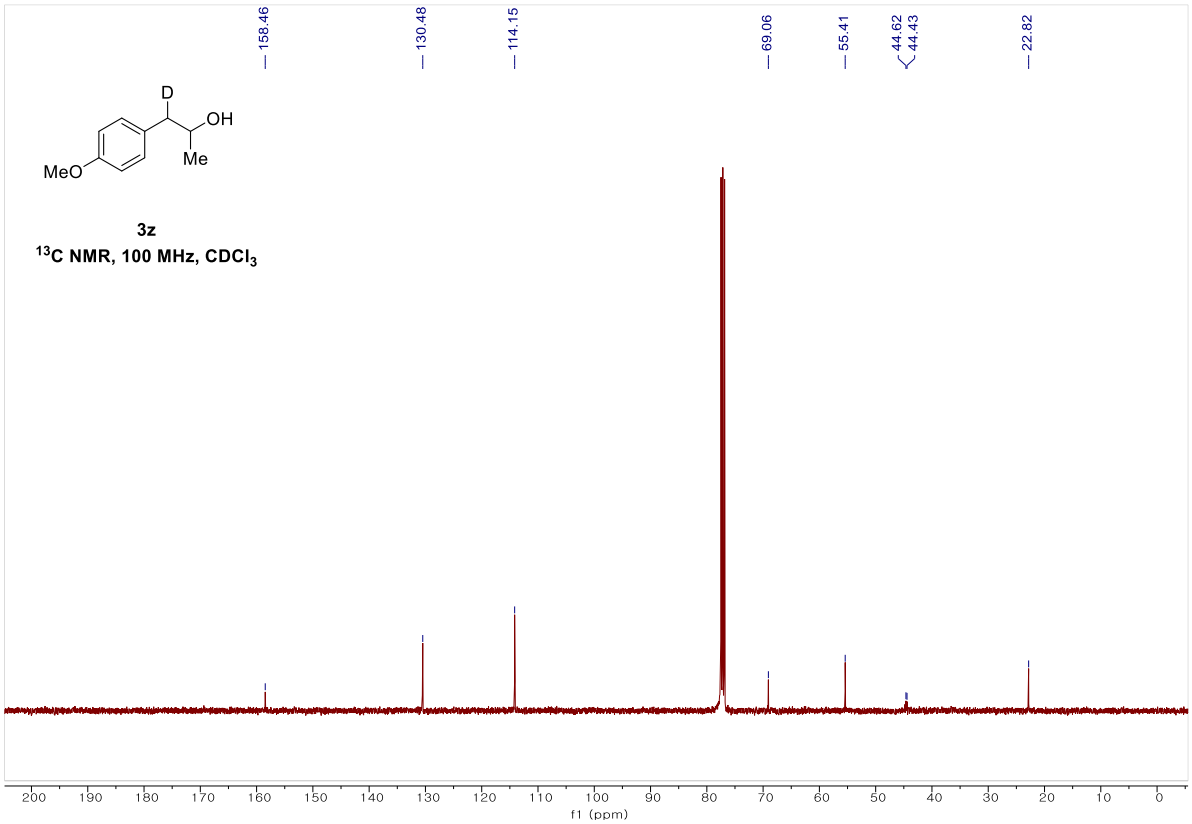


3m

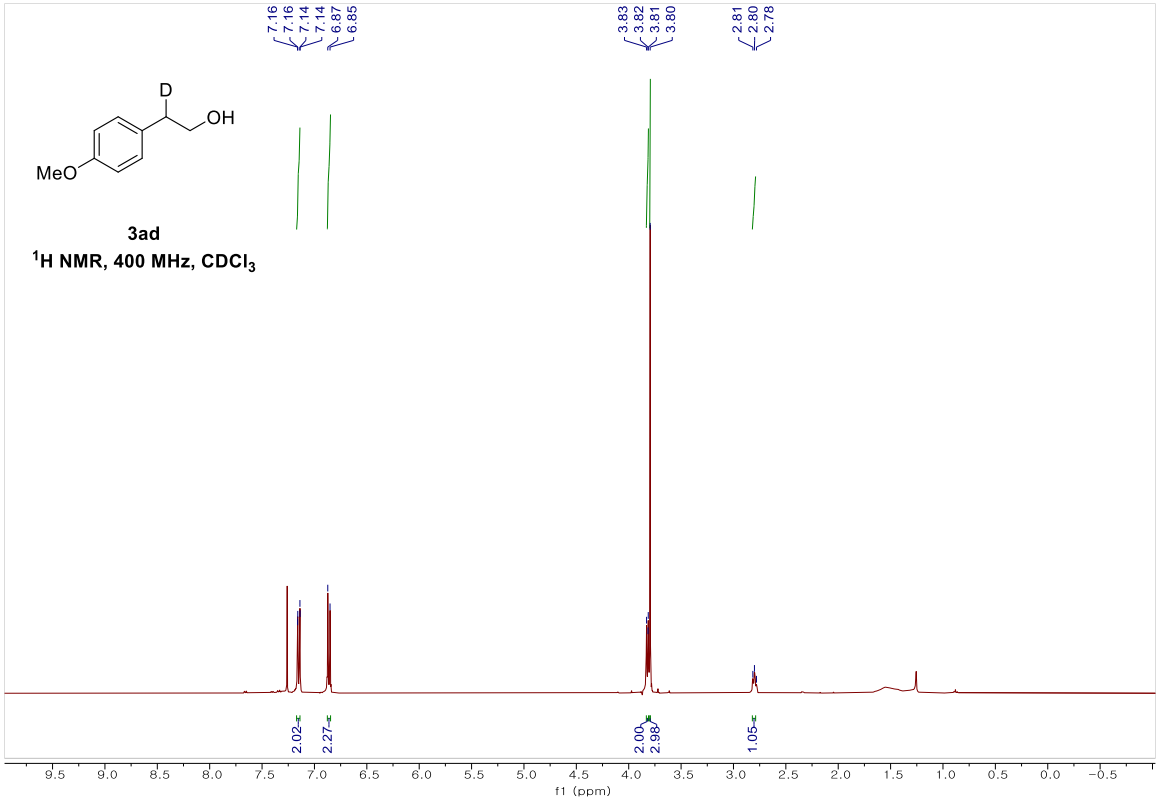
^{13}C NMR, 100 MHz, $CDCl_3$

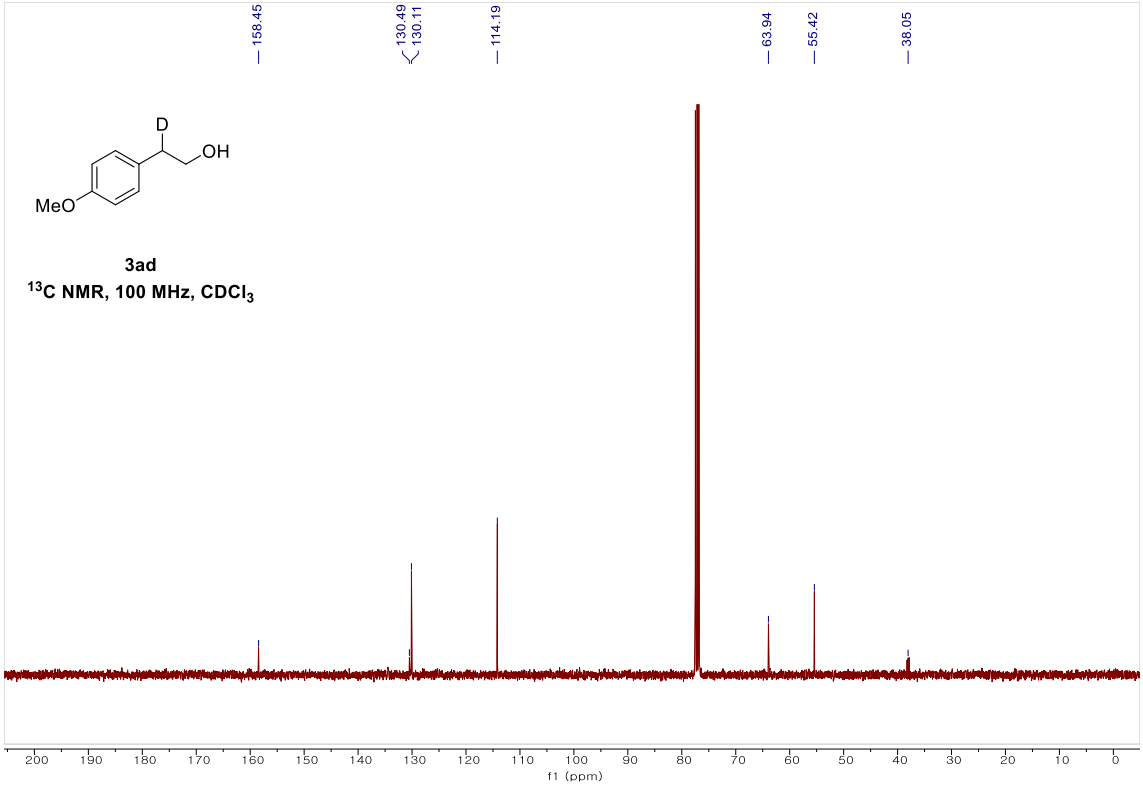
1-(4-methoxyphenyl)propan-1-d-2-ol (3z)



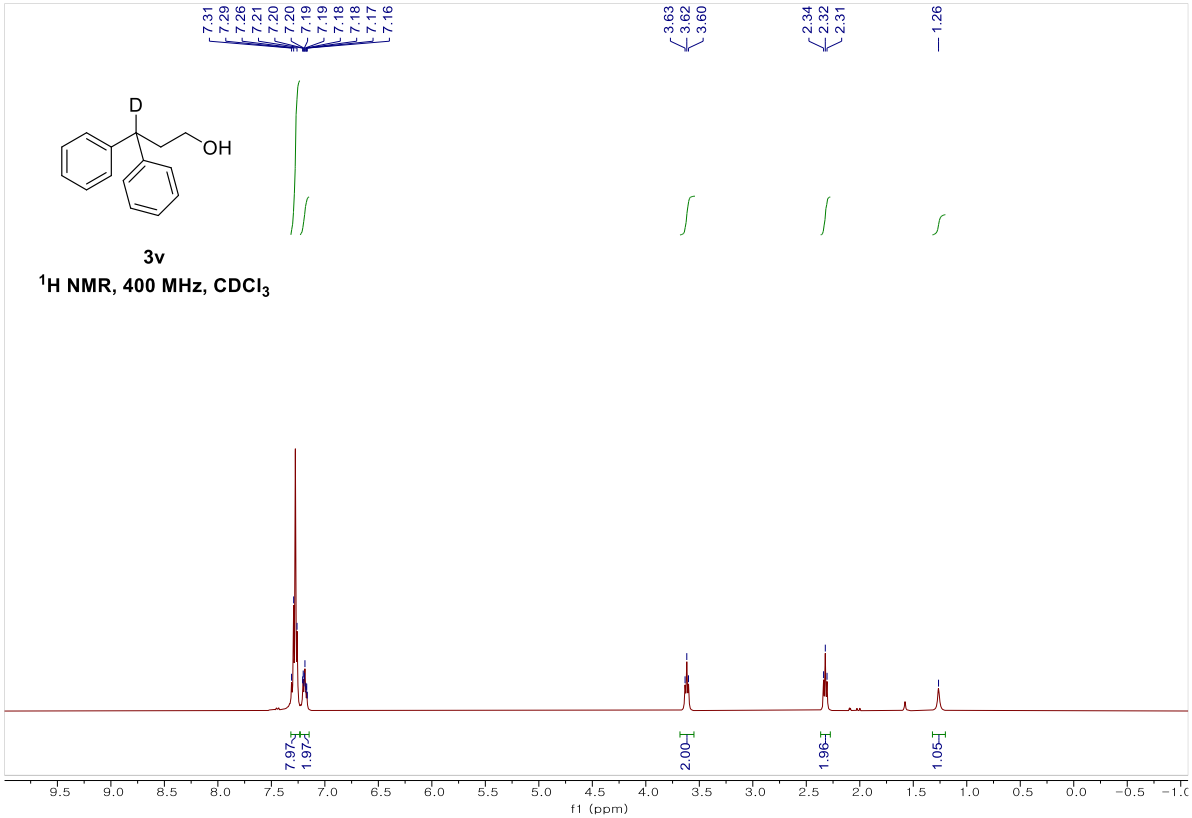


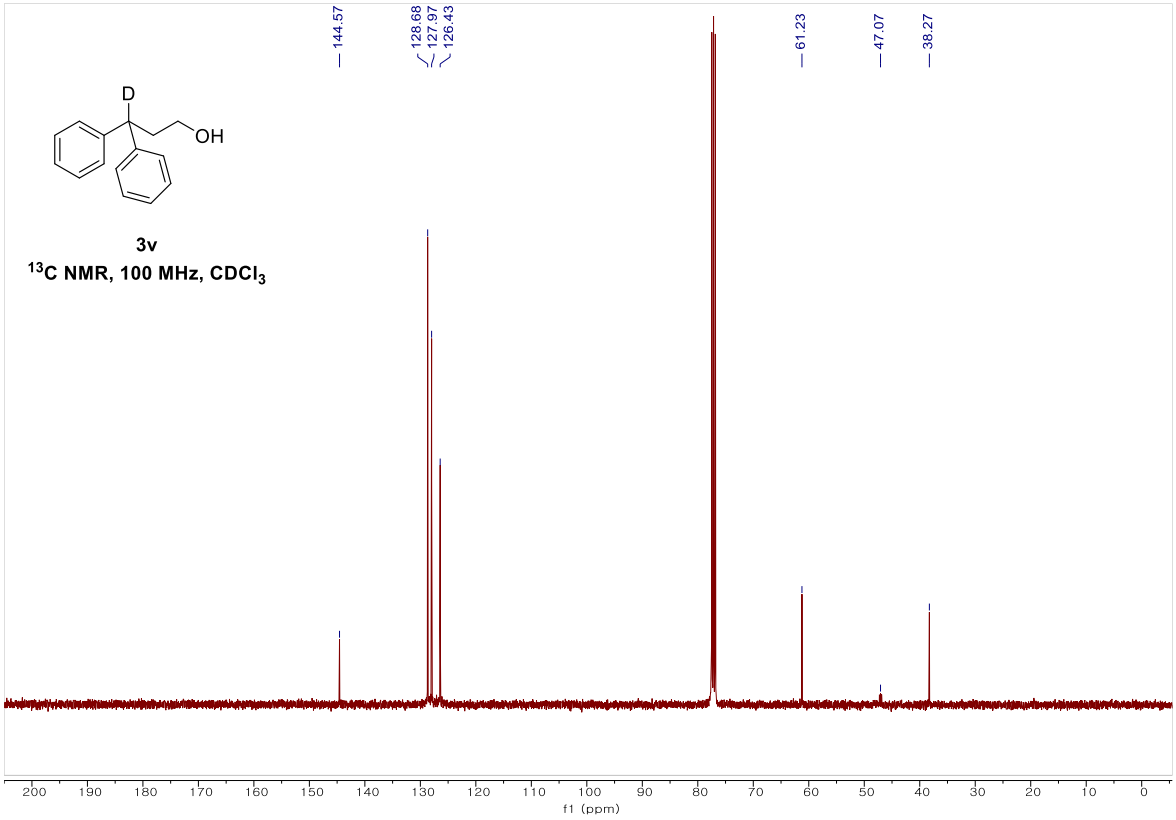
2-(4-methoxyphenyl)ethan-2-d-1-ol (3ad)





3,3-diphenylpropan-3-d-1-ol (3v)





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