Supplementary Information

Cooperative π–π Interactions Enable Site-Selective Electrophile Transfer Catalysis

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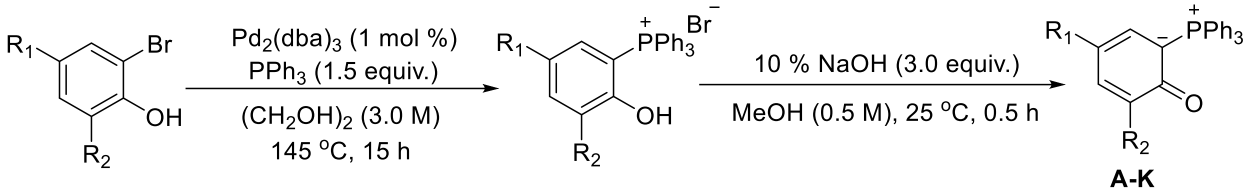
I. General Methods

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All solvents were dried and distilled according to standard methods before use. All reactions were carried out under an atmosphere of nitrogen in flame- or oven-driedd glassware with magnetic stirring. Deionized water was used in the preparation of all aqueous solutions and for all aqueous extractions. Solvents used for extraction and chromatography were ACS or HPLC grade. TLC (thin-layer chromatography) analyses were carried out on Merck silica gel 60 F254 TLC plates and was visualized with UV lamp and $KMnO_4$ solution. Purification of reactions mixtures was performed by flash column chromatography on SiO_2 using a CombiFlash® Rf + system with RediSep® Rf Silica columns (230 - 400 mesh) using a proper eluent. ^1H and ^{13}C NMR spectra were recorded on a Bruker (400 MHz) spectrometer with TMS as an internal standard. ^1H 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 4.87 & 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 49.1; DMSO-d_6: δ 39.52). 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. Infrared Spectroscopy (IR) were recorded on a Bruker LUMOS FT-IR spectrometer equipped with a microscope and mercury cadmium telluride (MCT) detector. The data collection for X-ray single crystal structure analysis was performed at room temperature on a Bruker D8 QUEST diffractometer equipped with Mo x-ray tube ($\lambda = 0.71073$ Å) and Photon II detector. The oil coated crystals were mounting on goniometer for diffraction experiment. The diffraction data were processed by using the Bruker APEX5 software. Single crystal X-ray diffraction experiments with synchrotron radiation and Dectris EIGER 9M detector were performed at the 7A beamline in the Pohang Accelerator Laboratory. The diffraction data of synchrotron radiation were processed by using the HKL2000 software.

II. Procedures for the Preparation of Phosphonium Ylide Catalysts



Procedure for the preparation of phosphonium salt

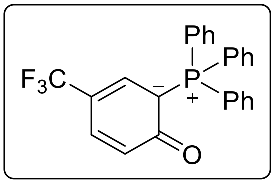
The phosphonium salt was prepared according to a reported literature procedure.[1] A test tube equipped with a magnetic stir bar was charged with 2-bromo-substituted phenol (2.0 mmol, 1.0 equiv.), triphenylphosphine (3.0 mmol, 1.5 equiv.), $Pd_2(dba)_3$ (1 mol %) and ethylene glycol (0.67 mL). The reaction vessel was evacuated and backfilled with argon three times to ensure an inert atmosphere. The resulting mixture was stirred for 15 h at 145 °C. Upon completion, the reaction was allowed to cool to room temperature. Water was added, and the aqueous layer was extracted with dichloromethane (3 times). The combined organic layers were washed with brine (2 times), dried over anhydrous sodium sulfate (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography using a mixture of methanol and dichloromethane (1:10, v/v) as the eluent to afford the desired phosphonium salt.

Procedure for the preparation of phosphonium ylide

A test tube equipped with a magnetic stir bar was charged with the phosphonium salt (0.60 mmol, 1.0 equiv.) and methanol (1.2 mL). Aqueous sodium hydroxide (10 %, 0.72 mL, 1.8 mmol) was added, and the reaction mixture was stirred at room temperature for 30 minutes. After completion, the mixture was diluted with water, and the aqueous phase was extracted with dichloromethane (3 times). The combined organic extracts were washed with water (2 times), dried over anhydrous sodium sulfate (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent: methanol/dichloromethane = 1:10, v/v) to afford the product as a yellowish solid (**A-K**).

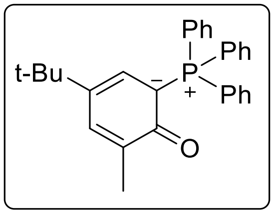
Chemical information regarding phosphonium ylide **A**, **B**, **D**, **E** and **I** have been already reported in literature.[1-5]

Phosphonium ylide-C



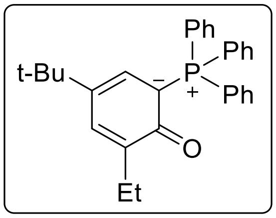
White solid (64%, 4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 7H), 7.66 (t, J = 1.7 Hz, 2H), 7.61 – 7.55 (m, 6H), 7.51 (dd, J = 9.1, 2.5 Hz, 1H), 6.87 (dd, J = 15.0, 1.6 Hz, 1H), 6.74 (dd, J = 9.0, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.69, 134.00 , 133.40 , 133.30 – 132.54, 132.12, 129.44, 123.50 , 122.39 , 121.48 , 99.99, 99.00; **IR** (CH_2Cl_2, cm^{-1}) 3663, 3062, 1694, 1604, 1506, 1435, 1375, 1314, 1278, 1131, 1099, 1063, 837, 747, 716, 688; **High Resolution MS** (EI): Calculated for $C_{25}H_{18}F_3OP$ $[M+H]^+$: 423.1120, Found: 423.1128. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Phosphonium ylide-F



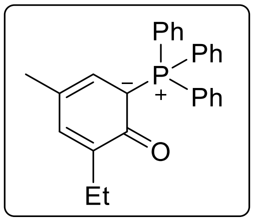
Yellow solid (72%, 4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (ddd, *J* = 12.7, 5.2, 3.3 Hz, 6H), 7.64 – 7.59 (m, 3H), 7.55 – 7.48 (m, 6H), 7.34 (d, *J* = 2.5 Hz, 1H), 6.37 (dd, *J* = 14.6, 2.5 Hz, 1H), 2.15 (s, 3H), 1.10 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.00, 134.18, 132.61, 130.29, 128.98, 126.86, 124.29 , 123.38, 33.65 , 31.34, 17; **IR** (CH_2Cl_2, cm^{-1}) 2959, 1603, 1479, 1439, 1262, 1165, 1106, 864, 751, 693; **High Resolution MS** (EI): Calculated for $C_{29}H_{29}OP$ $[M+H]^+$: 425.2029, Found: 425.2031. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Phosphonium ylide-G



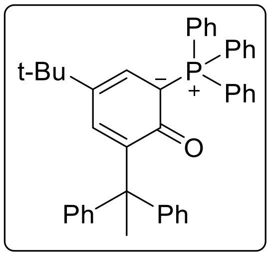
Yellow solid (74%, 4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 6H), 7.63 (dd, J = 7.7, 5.9 Hz, 2H), 7.52 (td, J = 7.6, 3.1 Hz, 6H), 7.33 (d, J = 2.1 Hz, 1H), 6.40 – 6.32 (m, 1H), 2.68 – 2.58 (m, 2H), 1.21 (t, J = 7.5 Hz, 3H), 1.12 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.96, 136.09, 134.14, 132.61 , 132.39 , 128.92 , 126.60 , 124.45, 123.57 , 33.78 , 31.37, 30.95, 23.48, 13.79; **IR** (CH_2Cl_2, cm^{-1}) 3660, 3054, 2958, 1477, 1436, 1264, 1164, 1105, 905, 831, 721, 690; **High Resolution MS** (EI): Calculated for $C_{30}H_{31}OP$ $[M+H]^+$: 439.2186, Found: 439.2187. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.* **X-ray crystal structure** is available in the *Appendix II.*

Phosphonium ylide-H



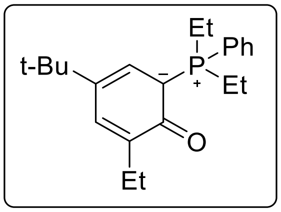
Yellow solid (71%, 4 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 9H), 7.53 – 7.48 (m, 6H), 7.11 (d, *J* = 2.1 Hz, 1H), 6.22 (dd, *J* = 13.4, 1.7 Hz, 1H), 2.59 (q, *J* = 7.4 Hz, 2H), 2.08 (s, 3H), 1.20 (t, *J* = 7.5 Hz, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 174.03, 136.92, 135.72, 134.03, 132.47, 130.0, 128.97, 124.51, 123.60 , 118.14, 96.71, 95.20, 23.02 , 20.70, 13.77; **IR** (CH_2Cl_2, cm^{-1}) 3667, 3054, 2962, 1471, 1435, 1266, 1210,1104, 918, 849, 748, 717, 689; **High Resolution MS** (EI): Calculated for $C_{27}H_{25}OP$ [M+H]$^{+}$: 397.1716, Found: 397.1717. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

Phosphonium ylide-J



Yellow solid (69%, 4 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.54 (m, 9H), 7.49 – 7.42 (m, 6H), 7.27 – 7.21 (m, 8H), 7.19 – 7.12 (m, 2H), 6.82 (d, J = 2.5 Hz, 1H), 6.27 (dd, J = 14.2, 2.6 Hz, 1H), 2.36 (s, 3H), 0.92 (s, 9H); ^{13}**C NMR (**100 MHz, $CDCl_3$) δ 138.73, 134.12, 132.34, 131.37, 128.76, 126.79, 124.76, 63.49, 30.96, 20.97; **IR** (CH_2Cl_2, cm^{-1}) 3421, 3061, 2924, 1594, 1438, 1261, 1190, 1106, 1029, 750, 723, 694; **High Resolution MS** (EI): Calculated for $C_{42}H_{39}OP$ [M+H]$^{+}$: 591.2812, Found: 591.2809. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

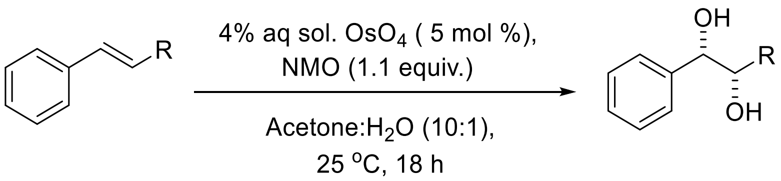
Phosphonium ylide-K



Yellow solid (74%, 4 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.63 (dt, *J* = 4.9, 2.1 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.29 (d, *J* = 3.3 Hz, 1H), 6.56 (dd, *J* = 13.4, 2.6 Hz, 1H), 2.97 – 2.82 (m, 2H), 2.75 – 2.60 (m, 4H), 1.22 (d, *J* = 7.5 Hz, 3H), 1.20 (s, 9H), 1.17 (d, *J* = 3.6 Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 173.63, 135.29, 132.5, 132.32 – 131.44, 129.32, 124.72, 123.09, 122.28, 94.01, 93.07, 33.76 , 31.52, 22.91 (, 14.55, 13.92, 6.70; **IR** (CH_2Cl_2, cm^{-1}) 3663, 2957, 1602, 1456, 1264, 1170, 1115, 1043, 831, 732, 694, 654; **High Resolution MS** (EI): Calculated for $C_{52}H_{75}OP$ [M+H]$^{+}$: 747.5629, Found: 747.5638 ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

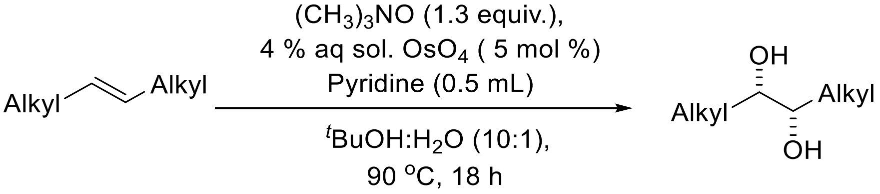
III. Procedures for the Preparation of Unsymmtrical Diols

Method A[6]



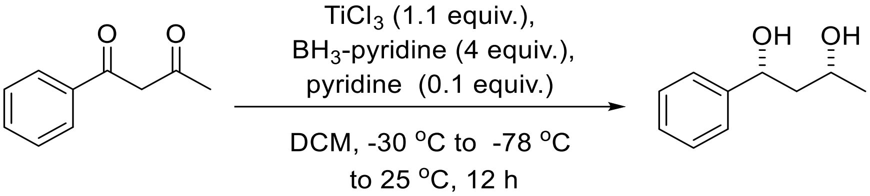
To a stirred solution of N-methylmorpholine N-oxide (4.4 mmol, 1.1 equiv.) in H_2O (3 mL) and acetone (30 mL) was added the olefin (4.0 mmol, 1.0 equiv.) under a nitrogen atmosphere. A solution of osmium tetroxide (4 wt% in H_2O, 5 mol %, 0.2 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of saturated aqueous sodium hydrosulfite solution, and acetone was removed under reduced pressure. The resulting mixture was extracted with ethyl acetate (3 times). The combined organic layers were dried, concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (n-hexane/EtOAc = 4:1) to afford the corresponding diol.

Method B[7]



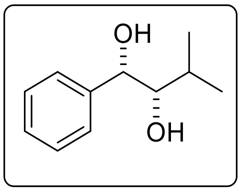
To a solution of trimethylamine N-oxide (6.8 mmol, 1.3 equiv.), pyridine (0.5 mL), water (1 mL) and tertiary butanol (10 mL), olefin (5.0 mmol, 1.0 equiv.) was added under a nitrogen atmosphere. Then, osmium tetroxide solution (4 wt. % in H_2O) (5 mol %, 0.2 mmol) was added. The resulting solution was refluxed at 90 °C and stirred for 18 h. The reaction was quenched by adding saturated aqueous sodium hydrosulfite solution, and tertiary butanol was removed under vacuum. The mixture was extracted with ethyl acetate (3 times). The combined ethyl acetate layers were dried, evaporated and the residue was purified by flash column chromatography on silica gel (eluent: n-hexane/EtOAc = 4:1) to afford resulting diol.

Method C[8]



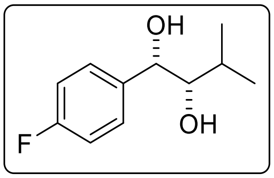
To a solution of 1,3-diketone 1 (6 mmol, 0.9 g, 1.0 equiv.) in DCM was added $TiCl_4$ (1 M in DCM, 1.1 equiv.) and pyridine (1.0 equiv.) at −30 °C. After stirring for 30 min, the reaction mixture was cooled to −78 °C, and BH_3·pyridine (8 M in pyridine, 4.0 equiv.) was added dropwise. The mixture was stirred for 2 h at −78 °C. The reaction was then quenched with aqueous HCl (1 M), and the resulting mixture was allowed to stir for 12 h while warming to room temperature. The organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (n-hexane/EtOAc = 4:1) to afford *syn*-**1y** as the corresponding diol.

Methyl-1-phenylbutane-1,2-diol (1a)



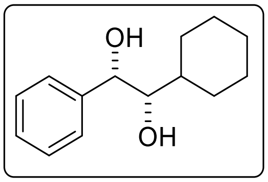
Prepared according to **Method A.** White solid (75%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.33 – 7.30 (m, 1H), 4.68-4.67 (d, J = 6.2 Hz, 1H), 3.54-3.53 (t, J = 5.2 Hz, 1H), 2.61 (s, 1H), 2.21 (s, 1H), 1.67 – 1.60 (m, 1H), 1.00-0.98 (dd, J = 6.8, 3.5 Hz, 6H); **^{13}C NMR** (100 MHz, CD_3OD) δ 142.61, 127.88, 127.13, 126.66, 80.02, 74.97, 29.30, 19.36, 15.46; **IR** (CH_2Cl_2, cm^{-1}) 3290, 2960, 2876, 1453, 1199, 1066, 1001, 846, 760, 697, 649; **High Resolution MS** (EI): Calculated for $C_{11}H_{16}O_2$ $[M-H]^-$: 179.1077, Found: 179.1072. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-Fluorophenyl)-3-methylbutane-1,2-diol (1b)



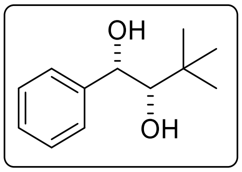
Prepared according to **Method A**. White solid (89%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.11 – 7.02 (m, 2H), 4.66 (dd, J = 6.3, 3.3 Hz, 1H), 3.52 – 3.45 (m, 1H), 2.62 (d, J = 3.8 Hz, 1H), 2.15 (d, J = 4.1 Hz, 1H), 1.67 – 1.61 (m, 1H), 0.98 (dd, J = 6.8, 5.7 Hz, 6H); **^{13}C NMR** (100 MHz, CD_3OD) δ 163.52, 161.10, 144.23, 137.08, 134.94, 129.18, 128.15, 127.23, 114.64, 114.43, 91.83, 72.03, 29.21, 20.11, 18.81, 16.59; **IR** (CH_2Cl_2, cm^{-1}) 3288, 2962, 1606,1511, 1367, 1229, 1137, 1007, 858, 838, 739; **High Resolution MS** (EI): Calculated for $C_{11}H_{15}FO_2$ $[M-H]^-$: 197.093, Found: 197.095. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Cyclohexyl-2-phenylethane-1,2-diol (1c)



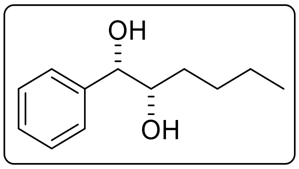
Prepared according to **Method A**. White solid (77%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 4.74 (d, J = 5.7 Hz, 1H), 3.50 (t, J = 5.2 Hz, 1H), 1.91 – 1.62 (m, 5H), 1.40 – 1.15 (m, 6H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.82, 128.54, 127.84, 126.56, 80.04, 74.27, 39.17, 30.18, 27.22, 26.32, 26.02; **IR** (CH_2Cl_2, cm^{-1}) 3304,2924, 2852, 1495, 1450, 1260, 1106, 1052, 1009, 760, 698, 631; **High Resolution MS** (EI): Calculated for $C_{14}H_{20}O_2$ [M-H]$^-$: 219.1390, Found: 219.1389. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

3,3-Dimethyl-1-phenylbutane-1,2-diol (1d)



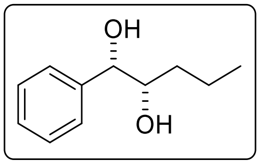
Prepared according to **Method A.** light orange solid (69%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 4.81 (s, 1H), 3.36 (s, 1H), 1.00 (d, J = 0.8 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD) δ 145.04, 127.72, 126.63, 126.10, 81.85, 71.67, 34.74 , 25.77; **IR** (CH_2Cl_2, cm^{-1}) 3439, 3304, 2958, 1275, 1203,1011,750, 697; **High Resolution MS** (EI): Calculated for $C_{12}H_{18}O_2$ [M-H]$^-$: 193.1234, Found: 193.1227. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Phenylhexane-1,2-diol (1e)



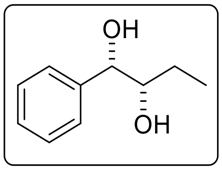
Prepared according to **Method A**. White solid (66%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 4.43-4.42 (d, J = 6.8 Hz, 1H), 3.70-3.66 (td, J = 7.9, 3.7 Hz, 1H), 3.00 (s, 1H), 2.65 (s, 1H), 1.36 – 1.31 (m, 1H), 1.30 – 1.25 (m, 5H), 0.88-0.86 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.31, 128.51, 128.03, 126.88, 77.91, 75.97, 32.37, 27.81, 22.59, 13.98; **IR** (CH_2Cl_2, cm^{-1}) 3364, 2955, 2932, 2866, 1453, 1264, 1049, 843, 760, 735, 699; **High Resolution MS** (EI): Calculated for $C_{12}H_{18}O_2$ [M-H]$^-$: 193.1234, Found: 193.1226. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Phenylpentane-1,2-diol (1f)



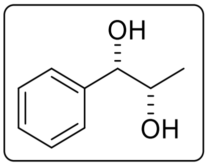
Prepared according to **Method A**. White solid (59%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 4.47-4.45 (d, J = 6.8 Hz, 1H), 3.75 – 3.70 (m, 1H), 2.40 (s, 2H), 1.52 – 1.36 (m, 1H), 1.35 – 1.29 (m, 3H), 0.90-0.86 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 142.11, 127.84, 127.23, 126.87, 77.69, 75.18, 34.70, 18.61, 13.05; **IR** (CH_2Cl_2, cm^{-1}) 3365, 2958, 2873, 1453, 1264, 1128, 1057, 1026, 851, 760, 699, 636; **High Resolution MS** (EI): Calculated for $C_{11}H_{16}O_2$ [M-H]$^-$: 179.1077, Found: 179.1069. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Phenylbutane-1,2-diol (1g)



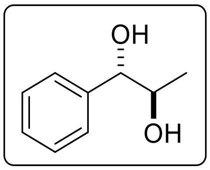
Prepared according to **Method A**. White solid solid (71%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 4.47-4.45 (d, *J* = 6.7 Hz, 1H), 3.65-3.60 (dd, *J* = 11.8, 6.7 Hz, 1H), 2.85 (s, 1H), 2.54 (s, 1H), 1.44 – 1.36 (m, 2H), 0.97-0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 142.13, 127.83, 127.21, 126.83, 77.37, 76.95, 25.36, 9.24; **IR** (CH_2Cl_2, cm^{-1}) 3365, 2965, 1454, 1124, 1081, 1046, 970, 843, 759, 698, 636; **High Resolution MS** (EI): Calculated for $C_{10}H_{14}O_2$ [M-H]$^-$: 165.0921 Found: 165.0917. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Phenylpropane-1,2-diol (1h)



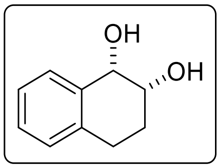
Prepared according to **Method A**. White solid (82%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 5H), 4.42 (d, J = 7.3 Hz, 1H), 3.90 (dq, J = 12.7, 6.3 Hz, 1H), 2.55 (s, 1H), 2.44 (s, 1H), 1.10 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 141.92, 127.79, 127.25, 126.81, 8.88, 71.48, 17.81; **IR** (CH_2Cl_2, cm^{-1}) 3357, 2972, 2887, 1456, 1264, 1127, 1079, 1036, 1022, 870, 757, 699, 637; **High Resolution MS** (EI): Calculated for $C_9H_{12}O_2$ [M-H]$^-$: 151.0764 Found: 151.0762. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Phenylpropane-1,2-diol (1h^{erythro})



Prepared according to **Method A.** **^{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, CD_3OD) δ 143.41, 128.97, 128.25, 128.05, 79.05, 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; **High Resolution MS** (EI): Calculated for $C_9H_{12}O_2$ [M-H]$^-$: 151.0764; Found, 151.0755. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

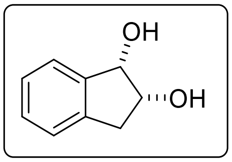
1,2,3,4-Tetrahydronaphthalene-1,2-diol (1i^{erythro})



Prepared according to **Method A.** **^{1}H NMR** (400 MHz, CD_3OD) δ 7.41 – 7.36 (m, 1H), 7.23 – 7.16 (m, 2H), 7.14 – 7.10 (m, 1H), 4.63 (d, *J* = 3.4 Hz, 1H), 3.93 (dt, *J* = 10.4, 3.4 Hz, 1H), 2.98 (dt, *J* = 17.1, 5.2 Hz, 1H), 2.85 – 2.75 (m, 1H), 2.09 (dtd, *J* = 12.8, 10.2, 5.9 Hz, 1H), 1.87 (dddd, *J* = 8.2, 6.6, 5.0, 3.5 Hz, 1H); **^{13}C NMR** (100 MHz, CD_3OD) δ 136.96, 136.11, 129.75, 128.03, 127.39 , 125.61 , 69.87 , 69.57, 26.93, 25.34; **IR** (CH_2Cl_2, cm^{-1}) 3348, 2930, 1455, 1274, 1211, 1110, 1065, 959, 771, 740, 641; **High Resolution MS** (EI):

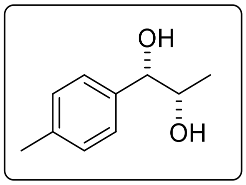
Calculated for $C_9H_{12}O_2$ $[M-H]^-$: 163.0759; Found, 163.0761. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

2,3-Dihydro-1H-indene-1,2-diol (1j^{erythro})



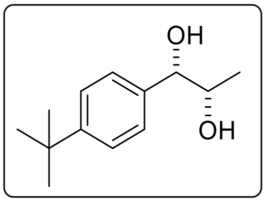
Prepared according to **Method A. ^{1}H NMR** (400 MHz, CD_3OD) δ 7.40 (dd, *J* = 5.4, 2.1 Hz, 1H), 7.27 – 7.18 (m, 3H), 4.91 (d, *J* = 4.9 Hz, 1H), 4.40 (dt, *J* = 5.8, 4.8 Hz, 1H), 3.05 (dd, *J* = 15.9, 5.9 Hz, 1H), 2.93 (dd, *J* = 15.8, 4.4 Hz, 1H); **^{13}C NMR** (100 MHz, CD_3OD) δ 142.58, 140.45, 128.01, 126.41, 124.67, 75.42 , 73.34, 37.70; **IR** (CH_2Cl_2, cm^{-1}) 3520, 3438, 3295, 3154, 1322, 1155, 1102, 1060, 985, 736, 633; **High Resolution MS** (EI): Calculated for $C_9H_{11}O_2$ $[M-H]^-$: 149.0603; Found, 149.0607. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(*p*-Tolyl)propane-1,2-diol (1k)



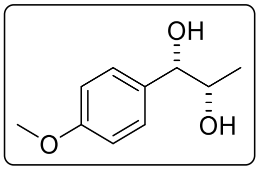
Prepared according to **Method A**. White solid (69%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.17 (d, J = 8.1 Hz, 2H), 7.19-7.17 (d, J = 8.0 Hz, 2H), 4.36-4.34 (d, J = 7.4 Hz, 1H), 3.90-3.83 (dq, J = 12.7, 6.3 Hz, 1H), 2.59 (s, 2H), 2.37 (s, 3H), 1.07-1.06 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 138.85, 137.00, 128.42 , 126.74, 78.82, 71.53, 19.79, 17.84; **IR** (CH_2Cl_2, cm^{-1}) 3368, 2974, 2924, 1516, 1452, 1368, 1275, 1128, 1034, 874, 812, 750; **High Resolution MS** (EI): Calculated for $C_{10}H_{14}O_2$ $[M-H]^-$: 166.0994; Found, 166.0916. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-(*tert*-Butyl)phenyl)propane-1,2-diol (1l)



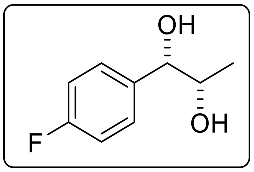
Prepared according to **Method A**. Light brown solid (73%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.39 (d, J = 8.4 Hz, 2H), 7.31-7.28 (d, J = 8.6 Hz, 2H), 4.40-4.37 (dd, J = 7.2, 1.8 Hz, 1H), 3.93-3.87 (p, J = 6.1 Hz, 1H), 2.52-2.51 (d, J = 5.4 Hz, 2H), 1.34 (s, 9H), 1.10-1.09 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 150.28, 138.86, 126.58, 124.69, 78.71, 71.49, 33.97, 30.50, 17.93; **IR** (CH_2Cl_2, cm^{-1}) 3378, 2964, 2495, 1363, 1267, 1107, 1043, 975, 931, 827, 737, 702; **High Resolution MS** (EI): Calculated for $C_{13}H_{20}O_2$ $[M-H]^-$: 207.1390; Found, 207.1390. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-Methoxyphenyl)propane-1,2-diol (1m)



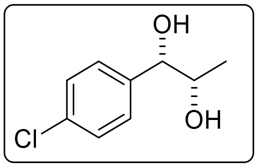
Prepared according to **Method A**. White solid (76%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, J = 1.9 Hz, 2H), 6.93 – 6.90 (m, 2H), 4.37-4.35 (d, J = 7.6 Hz, 1H), 3.91 – 3.85 (m, 1H), 3.83 (s, 3H), 2.47 (s, 2H), 1.08-1.07 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 158.71, 135.41, 128.55, 113.52 , 77.74, 71.24, 19.23; **IR** (CH_2Cl_2, cm^{-1}) 3357, 2969, 1611, 1512, 1245, 1176, 1128, 1111, 1027, 873, 827, 750; **High Resolution MS** (EI): Calculated for $C_{10}H_{14}O_3$ $[M-H]^-$: 181.0870; Found, 181.0865. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-Fluorophenyl)propane-1,2-diol (1n)



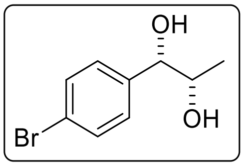
Prepared according to **Method A**. White solid (76%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.30 (dq, J = 5.1, 2.8 Hz, 2H), 7.08 – 7.03 (m, 2H), 4.38-4.35 (dd, J = 7.3, 4.4 Hz, 1H), 3.85 – 3.78 (m, 1H), 1.06-1.05 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 163.52, 161.10, 137.99, 128.60, 114.52, 114.30, 77.96, 71.40,17.77; **IR** (CH_2Cl_2, cm^{-1}) 3365, 2976, 2894, 1605, 1509, 1222, 1128, 1097, 1033, 874, 853, 830, 750; **High Resolution MS** (EI): Calculated for $C_9H_{11}FO_2$ $[M-H]^-$: 169.0670; Found, 169.0667.**^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-Chlorophenyl)propane-1,2-diol (1o)



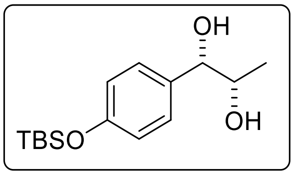
Prepared according to **Method A**. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.41 – 7.32 (m, 4H), 4.39 (d, J = 6.5 Hz, 1H), 3.86 – 3.77 (m, 1H), 3.37 – 3.31 (m, 1H), 1.01-0.99 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 140.86, 132.82, 128.38, 127.69 (d, J = 17.4 Hz), 77.77, 71.21, 17.67; **IR** (CH_2Cl_2, cm^{-1}) 3361, 2976, 2891, 2488, 1491, 1264, 1088, 1038, 1012, 820, 792, 737, 701, 660; **High Resolution MS** (EI): Calculated for $C_9H_{11}ClO_2$ $[M-H]^-$: 185.0375; Found, 185.0379. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-Bromophenyl)propane-1,2-diol (1p)



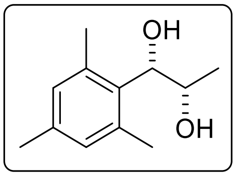
Prepared according to **Method A**. Pale yellow liquid (69%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 2H), 7.24 – 7.22 (m, 2H), 4.35-4.33 (d, J = 7.3 Hz, 1H), 3.84-3.77 (dq, J = 12.8, 6.4 Hz, 1H), 1.08-1.06 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 141.34, 130.80, 128.73, 120.82, 77.80, 71.16, 17.70; **IR** (CH_2Cl_2, cm^{-1}) 3361, 2980, 2887, 1491, 1402, 1263, 1127, 1068, 1036, 1008, 839, 817, 736, 702, 656; **High Resolution MS** (EI): Calculated for $C_9H_{11}BrO_2$ $[M-H]^-$: 228.9869; Found, 228.9865. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)propane-1,2-diol (1q)



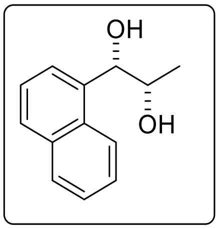
Prepared according to **Method A**. White solid (74%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.20 (d, J = 8.5 Hz, 2H), 6.85-6.83 (d, J = 8.5 Hz, 2H), 4.33-4.31 (d, J = 7.6 Hz, 1H), 3.87 – 3.81 (m, 1H), 1.05-1.03 (d, J = 6.3 Hz, 3H), 1.00 (s, 9H), 0.21 (s, 6H); **^{13}C NMR** (100 MHz, CD_3OD) δ 155.19, 144.59, 133.98, 133.06, 129.40, 127.66, 127.45, 119.37, 82.53, 74.61, 24.78, 20.26, 17.67, 16.04, 5.69,5.68; **IR** (CH_2Cl_2, cm^{-1}) 3400, 2859, 1274, 1261, 918, 750; **High Resolution MS** (EI): Calculated for $C_{15}H_{26}O_3Si$ $[M-H]^-$: 281.1578; Found, 281.1578. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Mesitylpropane-1,2-diol (1r)



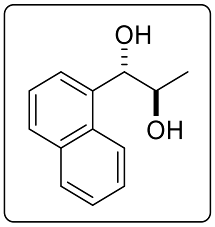
Prepared according to **Method A**. White solid (79%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 4.92-4.90 (d, J = 9.1 Hz, 1H), 4.37-4.30 (dq, J = 9.1, 6.3 Hz, 1H), 2.44 (s, 6H), 2.27 (s, 3H), 1.05-1.04 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$)) δ 136.54 , 136.22, 135.70, 130.02, 75.66, 69.21, 21.35, 20.82, 19.80; **IR** (CH_2Cl_2, cm^{-1}) 3402, 2972, 1453, 1275, 1122, 1039, 1014, 850, 750; **High Resolution MS** (EI): Calculated for $C_{12}H_{18}O_2$ $[M-H]^-$: 193.1234; Found, 193.1231. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(Naphthalen-1-yl)propane-1,2-diol (1s)



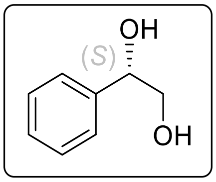
Prepared according to **Method A**. White solid (77%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16-8.14 (d, J = 8.7 Hz, 1H), 7.91 – 7.82 (dd, 2H), 7.62-7.60 (d, J = 7.1 Hz, 1H), 7.56 – 7.47 (m, 3H), 5.20-5.19 (d, J = 6.6 Hz, 1H), 4.21-4.15 (p, J = 6.4 Hz, 1H), 2.95 (s, 1H), 2.69 (s, 1H), 1.12-1.11 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.98, 133.91, 130.97, 128.99, 128.59, 126.18, 125.68, 125.35, 124.59, 123.39, 75.75, 71.75, 19.22; **IR** (CH_2Cl_2, cm^{-1}) 3365, 3051, 2972, 1509, 1363, 1263, 1126, 1042, 995, 798, 776, 734, 635; **High Resolution MS** (EI): Calculated for $C_{13}H_{14}O_2$ $[M-H]^-$: 201.0921; Found, 201.0916. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(Naphthalen-1-yl)propane-1,2-diol (1s*erythro*)



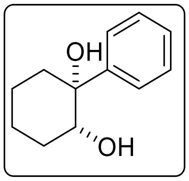
Prepared according to **Method A**. White solid (77%, 5 mmol scale); **^{1}H NMR** ^{1}H NMR (400 MHz, CD_3OD) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.77 (dd, *J* = 21.2, 7.7 Hz, 2H), 7.57 – 7.45 (m, 3H), 5.47 (d, *J* = 4.4 Hz, 1H), 4.15 (qt, *J* = 6.6, 3.3 Hz, 1H), 1.14 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 137.82 , 133.81, 130.95, 128.43 , 127.33 , 125.46, 124.95, 123.78, 122.93, 73.82, 70.28, 15.85; **IR** (CH_2Cl_2, cm^{-1}) 3365, 3051, 2972, 1509, 1363, 1263, 1126, 1042, 995, 798, 776, 734, 635; **High Resolution MS** (EI): Calculated for $C_{13}H_{14}O_2$ $[M-H]^-$: 201.0921; Found, 201.0916. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

(*S*)-Phenylethane-1,2-diol (1t)



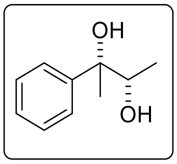
Prepared according to **Method A**. White solid (89%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 7H), 7.36 – 7.30 (m, 2H), 4.88-4.85 (dd, J = 8.0, 2.9 Hz, 2H), 3.82-3.79 (d, J = 11.3 Hz, 2H), 3.73 – 3.68 (m, 2H), 2.49 (s, 2H), 2.03 (s, 2H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.48, 128.54 , 127.98, 126.10, 74.73, 68.06; **IR** (CH_2Cl_2, cm^{-1}) ; 3240, 2937, 1448, 1345, 1271, 1087, 1053, 1024, 887, 833, 748, 697, 633; **High Resolution MS** (EI): Calculated for $C_8H_{10}O_2$ $[M-H]^-$: 137.0611; Found, 137.0615. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

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



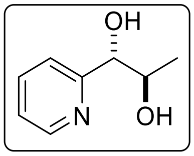
Prepared according to **Method A**. White solid (89%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.40 (m, 2H), 7.39 – 7.30 (m, 2H), 7.29 – 7.27 (m, 1H), 4.05-4.01 (dd, J = 11.0, 4.7 Hz, 1H), 2.60 (s, 1H), 1.92 – 1.88 (m, 3H), 1.86 – 1.67 (m, 3H), 1.58 – 1.45 (m, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 147.41, 127.61, 126.00, 125.06, 75.67, 73.97, 39.01, 30.01, 24.34, 20.92; **IR** (CH_2Cl_2, cm^{-1}) 3403, 2933, 2862, 1444, 1266, 1057, 993, 971, 754, 693, 641, 607; **High Resolution MS** (EI): Calculated for $C_{12}H_{16}O_2$ $[M-H]^-$: 191.1077; Found, 191.1069. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

2-Phenylbutane-2,3-diol (1v)



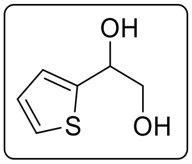
Prepared according to **Method A**. White solid (78%, 5 mmol scale); **^{1}H NMR** (400 MHz, CD_3OD) δ 7.55 – 7.47 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.20 (m, 1H), 3.85 (q, J = 6.4 Hz, 1H), 1.54 (s, 3H), 1.00 (d, J = 6.4 Hz, 3H);**^{13}C NMR** (100 MHz, CD_3OD) δ 145.70, 127.34, 126.25, 125.80, 76.14, 74.02, 22.84, 16.30; **IR** (CH_2Cl_2, cm^{-1}) 3420, 3030, 2962, 2925, 1601, 1495, 1452, 1125, 1070, 755, 702; **High Resolution MS** (EI): $C_{10}H_{14}O_2$ [M-H]$^-$: 165.0921; Found, 165.0921. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(Pyridin-2-yl)propane-1,2-diol (1w*^{erythro}*)



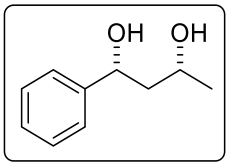
Prepared according to **Method A**. White solid (35%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56-8.55 (d, J = 4.7 Hz, 1H), 7.75-7.70 (tt, J = 5.5, 2.8 Hz, 1H), 7.36-7.34 (d, J = 7.8 Hz, 1H), 7.28 – 7.24 (m, 1H), 4.51-4.50 (d, J = 4.3 Hz, 1H), 4.04-3.98 (qd, J = 6.4, 4.5 Hz, 1H), 1.27-1.25 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$)) δ 156.32, 149.16, 144.98, 136.84, 133.66, 130.14 , 128.12 , 123.63, 122.86, 88.26 , 68.02 , 21.49 , 19.74; **IR** (CH_2Cl_2, cm^{-1}) 3291, 3183, 2972, 1598, 1435, 1260, 1138, 1089, 1064, 1001, 750, 701, 657; **High Resolution MS** (EI): Calculated for $C_8H_{11}NO_2$ [M-H]$^-$: 154.0863; Found, 154.0865. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(Thiophen-2-yl)ethane-1,2-diol (1x)



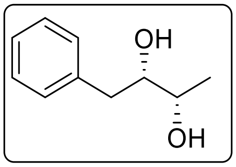
Prepared according to **Method A**. Transparent liquid (67%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 1H), 7.06 – 7.01 (m, 2H), 5.10-5.07 (dd, J = 7.3, 3.8 Hz, 1H), 3.89-3.78 (m, 2H), 2.84 (s, 1H), 2.31 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.89 , 126.89, 125.20 , 124.50, 70.71, 67.75; **IR** (CH_2Cl_2, cm^{-1}) 3338, 2923, 2866, 1264, 1228, 1075, 1026, 879, 851, 833, 735, 696; **High Resolution MS** (EI): Calculated for $C_6H_8SO_2$ [M-H]$^-$: 143.0172; Found, 143.0167. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Phenylbutane-1,3-diol (*syn*-1y)



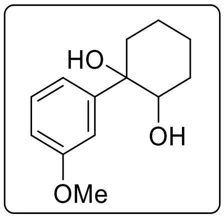
Prepared according to **Method C**. White solid (66%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 4H), 7.34 – 7.29 (m, 1H), 4.99-4.96 (dd, J = 10.0, 3.0 Hz, 1H), 4.22 – 4.14 (m, 1H), 3.17 (s, 1H), 2.96 (s, 1H), 1.93-1.81 (dt, J = 14.6, 8.1 Hz, 1H), 1.78-1.76 (dt, J = 14.6, 2.7 Hz, 1H), 1.27-1.25 (d, J = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.45, 128.56, 127.68, 125.65, 75.44, 68.91, 47.14, 24.19; **IR** (CH_2Cl_2, cm^{-1}) 3305, 2972, 1453, 1277, 1128, 1062, 1028, 844, 754, 698, 627; **High Resolution MS** (EI): Calculated for $C_{10}H_{14}O_2$ [M-H]$^-$: 165.0921; Found, 165.0915. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Phenylbutane-2,3-diol (1z)



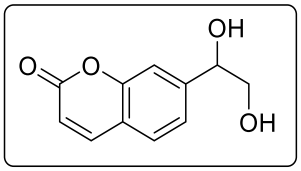
Prepared according to **Method A**. White solid (89%, 5 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.33 (dd, J = 5.1, 2.2 Hz, 2H), 7.28 – 7.25 (m, 2H), 3.91-3.82 (ddt, J = 9.5, 6.6, 3.3 Hz, 2H), 2.88-2.84 (dd, J = 13.8, 3.8 Hz, 1H), 2.75 – 2.68 (m, 1H), 2.04 (s, J = 3.2 Hz, 1H), 1.94-1.93 (s, J = 2.8 Hz, 1H), 1.29 – 1.27 (m, 3H); ^{13}**C NMR** (100 MHz, CD_3OD) δ 139.45, 129.10, 127.84 , 125.62, 76.62 , 69.97, 39.08, 17.26; **IR** (CH_2Cl_2, cm^{-1}) 3366, 2937, 2503, 1453, 1271, 1127, 1059, 986, 739, 697, 654; **High Resolution MS** (EI): Calculated for $C_{10}H_{14}O_2$ [M-H]$^-$: 165.0921; Found, 165.0924. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

1-(3-Methoxyphenyl)cyclohexane-1,2-diol (1aa)



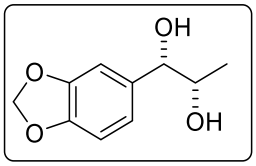
Prepared according to **Method A**. White solid (77%, 2 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.30 (t, J = 6.1 Hz, 1H), 7.13 – 7.10 (m, 1H), 7.07 – 7.03 (m, 1H), 6.83 – 6.79 (m, 1H), 3.97 (dd, J = 11.1, 4.6 Hz, 1H), 3.83 (s, 3H), 2.67 (s, 1H), 1.92 – 1.81 (m, 3H), 1.74 – 1.68 (m, 2H), 1.65 (dd, J = 12.7, 2.8 Hz, 1H), 1.58 – 1.51 (m, 1H), 1.47 – 1.35 (m, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 159.82, 148.33, 129.48, 117.29, 112.13, 111.44, 75.82, 74.51, 55.23, 38.46, 29.18, 24.35, 21.06; **IR** (CH_2Cl_2, cm^{-1}) 3403, 2933, 2862, 1601, 1583, 1508, 1262, 1125, 1032, 756, 698; **High Resolution MS** (EI): Calculated for $C_{13}H_{18}O_3$ [M-H]$^-$: 221.1178; Found, 221.1166. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

7-(1,2-Dihydroxyethyl)-2H-chromen-2-one (6b) (from Coumarin)



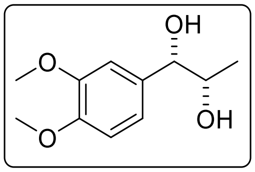
Prepared according to **Method A**. Light yellow color solid (69%, mmol scale); ^{1}**H NMR** (400 MHz, CD_3OD) δ 7.95 (d, *J* = 9.5 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.37 (m, 2H), 6.42 (d, *J* = 9.5 Hz, 1H), 4.80 (dd, *J* = 6.6, 4.9 Hz, 1H), 3.68 (qd, *J* = 11.3, 5.8 Hz, 2H), 3.33 (dt, *J* = 3.2, 1.6 Hz, 1H); ^{13}**C NM** (100 MHz, CD_3OD) δ 161.59, 153.90, 147.58, 144.10, 127.77, 122.57, 118.07, 115.27, 113.97, 73.73, 66.99; **IR** (CH_2Cl_2, cm^{-1}) 3368, 2923, 1709, 1619, 1261, 1087, 851, 750; **High Resolution MS** (EI): Calculated for $C_{11}H_{10}O_4$ [M-H]$^-$: 205.0506; Found, 205.0499. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

1-(Benzo[d][1,3]dioxol-5-yl)propane-1,2-diol (6c) (from Isosafrole)



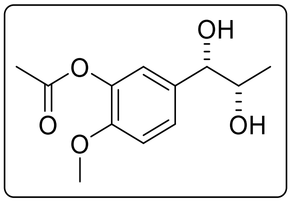
Prepared according to **Method A**. White solid (76%, 5 mmol scale); ^{1}**H NMR** (400 MHz, CD_3OD) δ 6.87 (d, J = 1.3 Hz, 1H), 6.81 (dt, J = 15.5, 4.7 Hz, 2H), 5.94 (d, J = 1.0 Hz, 2H), 4.27 (d, J = 7.1 Hz, 1H), 3.77 (dd, J = 13.2, 6.6 Hz, 1H), 3.37 – 3.27 (m, 1H), 0.98-0.97 (d, J = 6.4 Hz, 3H); ^{13}**C NMR** (100 MHz, CD_3OD) δ 147.63, 147.09, 135.93, 120.25, 107.36, 106.89, 100.86, 78.65, 71.50, 17.81; **IR** (CH_2Cl_2, cm^{-1}) 3389, 2980, 2887, 1503, 1442, 1486, 1243, 1094, 1034, 932, 809, 734, 702; **High Resolution MS** (EI): Calculated for $C_{10}H_{12}O_4$ $[M\text{-}H]^-$: 195.0663; Found, 195.0654. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

1-(3,4-Dimethoxyphenyl)propane-1,2-diol (6d) (from Isoeugenol)



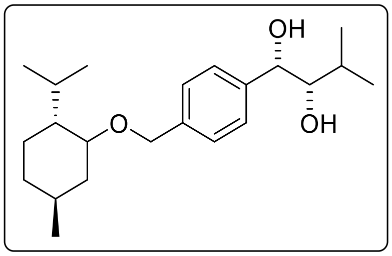
Prepared according to **Method A**. White solid (76%, 5 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 6.89 (dd, J = 15.1, 8.9 Hz, 3H), 4.35 (d, J = 7.4 Hz, 1H), 3.92 (s, J = 0.4 Hz, 3H), 3.91 (s, 3H), 3.89 – 3.85 (m, 1H), 1.09 (d, J = 5.9 Hz, 3H); ^{13}**C NMR** (100 MHz, CD_3OD) δ 148.91, 148.63, 134.81, 119.46, 111.22, 110.47, 78.65, 71.51, 55.06 , 17.90; **IR** (CH_2Cl_2, cm^{-1}) 3397, 2972, 2933, 1595, 1514, 1461, 1418, 1260, 1233, 1137, 1025, 809, 749; **High Resolution MS** (EI): Calculated for $C_{11}H_{16}O_4$ $[M\text{-}H]^-$: 211.0976; Found, 211.0967. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

5-(1,2-Dihydroxypropyl)-2-methoxyphenyl acetate (6e) (from Isovanillin)



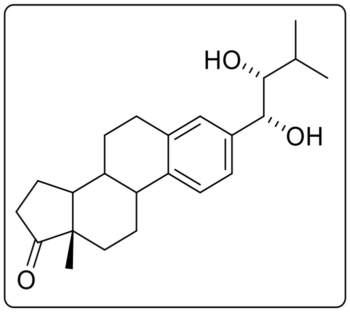
Prepared according to **Method A**. White solid (73%, 5 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.02 (dd, *J* = 6.3, 5.0 Hz, 2H), 6.92 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.38 (d, *J* = 7.1 Hz, 1H), 3.89-3.84 (m, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 2.58 (s, 1H), 2.33 (s, 3H), 1.12 (d, *J* = 6.3 Hz, 3H); ^{13}**C NMR** (100 MHz, CD_3OD) δ 169.53, 150.95, 141.26, 139.06, 121.88, 118.96, 110.91, 78.21, 71.37, 54.96, 19.14, 17.86; **IR** (CH_2Cl_2, cm^{-1}) 3400, 2976, 1761, 1369, 1267, 1215, 1194, 1118, 1031, 733, 701; **High Resolution MS** (EI): Calculated for $C_{12}H_{16}O_5$ $[M\text{-}H]^-$: 239.0925; Found, 239.0916. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

1-(4-((((2R,5S)-2-*iso*-Propyl-5-methylcyclohexyl)oxy)methyl)phenyl)-3-methylbutane-1,2-diol (6f) (from (-)-Menthol)



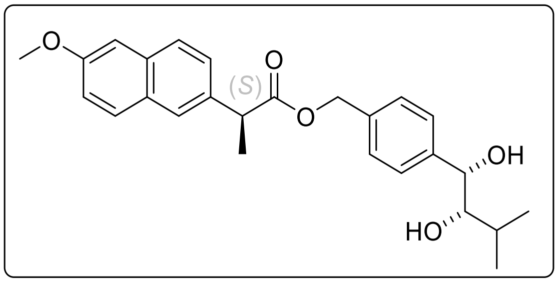
Prepared according to **Method A**. White solid (69%, 2mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.41 – 7.31 (m, 4H), 4.65 (dd, *J* = 14.1, 6.9 Hz, 2H), 4.41 (d, *J* = 11.4 Hz, 1H), 3.54 – 3.45 (m, 1H), 3.19 (td, *J* = 10.6, 4.1 Hz, 1H), 2.31 (dtd, *J* = 9.4, 6.9, 2.6 Hz, 2H), 2.25 – 2.16 (m, 1H), 1.75 – 1.58 (m, 3H), 1.45 – 1.27 (m, 2H), 0.96 (ddd, *J* = 6.5, 3.0, 1.9 Hz, 9H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.73 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 140.78, 138.88, 128.12, 126.6, 80.45, 78.89, 75.01, 70.18, 48.29, 40.32, 34.56, 31.59, 29.03, 25.53, 23.24, 22.38, 21.03, 20.17, 16.37 – 15.96; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3393, 2954, 2920, 2868, 1454, 1367, 1262, 1066, 1000, 818, 745; **High Resolution MS** (EI): Calculated for C$_{22}$H$_{36}$O$_3$ [M-H]$^-$: 347.2591; Found, 347.2599. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

(13S)-3-(1,2-Dihydroxy-3-methylbutyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (6g) (from Estrone)



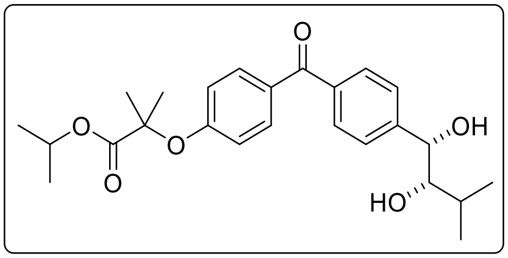
Prepared according to **Method A**. White solid (65%, 5 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.31 – 7.26 (m, 1H), 7.16 – 7.06 (m, 2H), 4.57 (d, J = 6.3 Hz, 1H), 3.54 – 3.45 (m, 1H), 2.93 (dd, J = 8.8, 4.0 Hz, 2H), 2.55 – 2.48 (m, 1H), 2.46 – 2.40 (m, 1H), 2.36 – 2.27 (m, 1H), 2.20 – 2.02 (m, 3H), 1.97 (dd, J = 9.4, 2.4 Hz, 1H), 1.68 – 1.58 (m, 3H), 1.57 – 1.43 (m, 4H), 0.96 (t, J = 6.8 Hz, 6H), 0.92 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 221.06, 139.38, 139.17, 136.64, 127.24, 125.44, 124.13, 80.23, 74.81, 50.51, 48.00, 44.39, 38.12, 35.87, 31.59, 29.46, 29.19, 26.51, 25.72, 21.60, 20.24, 16.33, 13.85; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3428, 2931, 1734, 1263, 1083, 1053, 1003, 820, 732, 702, 643; **High Resolution MS** (EI): Calculated for C$_{23}$H$_{32}$O$_3$ [M-H]$^-$: 355.2278; Found, 355.2271. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

4-(1,2-Dihydroxy-3-methylbutyl)benzyl 2-(6-methoxynaphthalen-2-yl)propanoate (6h) (from Naproxen)



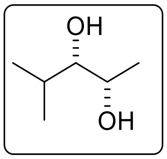
Prepared according to **Method A**. White solid (71%, 2 mmol scale); **^{1}H NMR** (400 MHz, CD_3OD) δ 7.71 – 7.60 (m, 3H), 7.35 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.10 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.09 (d, *J* = 2.4 Hz, 2H), 4.56 (d, *J* = 6.2 Hz, 1H), 3.93 – 3.88 (m, 1H), 3.87 (s, 3H), 3.38 – 3.35 (m, 1H), 3.35 – 3.32 (m, 1H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.52 – 1.46 (m, 1H), 0.91 (dd, *J* = 10.5, 4.1 Hz, 6H); **^{13}C NMR** ((100 MHz, CD_3OD) δ 174.65, 157.76 , 142.66, 135.58 , 135.33, 133.86, 128.91, 127.52, 126.77 , 125.70, 118.61, 105.21, 79.96, 74.51, 65.86, 54.35, 45.21, 29.35, 19.28, 17.48, 15.61; **IR** (CH_2Cl_2, cm^{-1}) 3428, 2965, 1728, 1602, 1381, 1261, 1147, 1174, 1100, 1002, 928, 851, 66, 736; **High Resolution MS** (EI): Calculated for $C_{26}H_{30}O_5$ [M-H]$^-$: 421.2020; Found, 421.2014. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

iso**-Propyl-2-(4-(4-(1,2-dihydroxy-3-methylbutyl)benzoyl)phenoxy)-2-methylpropanoate (6i)** (from Fenofibrate)



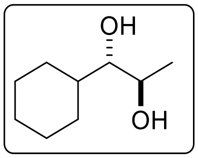
Prepared according to **Method A**. White solid (69%, 1 mmol scale); **^{1}H NMR** (400 MHz, CD_3OD) δ 7.79 – 7.69 (m, 4H), 7.55 (d, *J* = 8.1 Hz, 2H), 6.95 – 6.90 (m, 2H), 5.08 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.76 (d, *J* = 5.2 Hz, 1H), 3.41 (t, *J* = 5.4 Hz, 1H), 3.33 (dt, *J* = 3.2, 1.6 Hz, 1H), 1.71 (dd, *J* = 13.0, 6.3 Hz, 1H), 1.67 (s, 6H), 1.22 (d, *J* = 6.3 Hz, 6H), 1.00 (dd, *J* = 6.8, 4.9 Hz, 6H); **^{13}C NMR** (100 MHz, CD_3OD) δ 195.87, 173.08, 159.80, 148.03, 136.77, 131.72, 130.47, 129.34, 126.54, 117.02, 80.0, 79.25, 74.02, 69.32, 29.76, 24.40, 20.40, 19.12, 16.33; **IR** (CH_2Cl_2, cm^{-1}) 3467, 2965, 1731, 1604, 1459, 1378, 1261, 1232, 1173, 1150, 1053,, 1033, 852, 748; **High Resolution MS** (EI): Calculated for $C_{25}H_{32}O_6$ [M-H]$^-$: 427.2126; Found, 427.2128. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

4-Methylpentane-2,3-diol (3a)



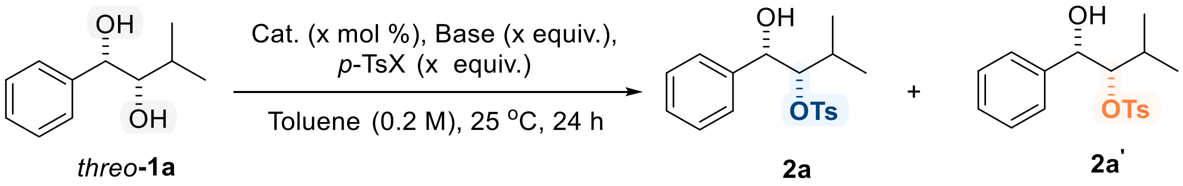
Prepared according to **Method B**.Transparent liquid (50%, 5 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.83 – 3.76 (m, 1H), 3.15-3.11 (dd, J = 10.5, 5.3 Hz, 1H), 2.26 (s, 1H), 2.18 (s, J = 5.5 Hz, 1H), 1.83 – 1.79 (m, 1H), 1.22-1.21 (d, J = 6.3 Hz, 3H), 1.01-1.00 (d, J = 6.9 Hz, 3H), 0.96-0.92 (d, J = 6.8 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 80.60, 68.47, 29.88, 19.98, 19.72, 16.17; **IR** (CH_2Cl_2, cm^{-1}) 3393, 3322, 2966, 1369, 1262, 1138, 1075, 1000, 914, 749; **High Resolution MS** (EI): Calculated for $C_6H_{14}O_2$ [M-H]$^-$: 117.0921; Found, 117.0929. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

1-Cyclohexylpropane-1,2-diol (3b^{erythro})



Prepared according to **Method B**. Transparent liquid (60%, 3 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.90 (s, 1H), 3.35 (d, J = 8.2 Hz, 1H), 2.39 (s, 2H), 2.09 – 1.99 (m, 1H), 1.82 – 1.71 (m, 2H), 1.71 – 1.62 (m, 1H), 1.60 – 1.51 (m, 1H), 1.41 – 1.30 (m, 1H), 1.27 – 1.20 (m, 2H), 1.15 (d, J = 6.4 Hz, 3H), 1.07 – 0.95 (m, 2H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 78.87, 68.03, 40.03, 29.46, 28.78, 26.37, 25.87, 15.91; **IR** (CH_2Cl_2, cm^{-1}) 3320, 2930, 2855, 1465, 1370, 1125, 1070; **High Resolution MS** (EI): Calculated for $C_6H_{14}O_2$ [M-H]$^-$; 157.1230; Found, 157.1236. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

IV. Reaction Optimization for the Regioselective Tosylation of Unsymmetrical Diol



To an oven-dried screw-cap vial equipped with a triangular teflon-coated stir bar were added diol **1a** (0.10 mmol), catalyst (x mol%), *p*-TsX (x equiv.), solvent, and base (x equiv.). The reaction mixture was stirred at 25 °C for 24 h. After completion, the reaction mixture was concentrated under reduced pressure. The yield and site-selectivity of the tosylated products (**2a**:**2a′**) were determined by ^{1}H NMR analysis of the crude reaction mixture using dibromomethane as an internal standard.

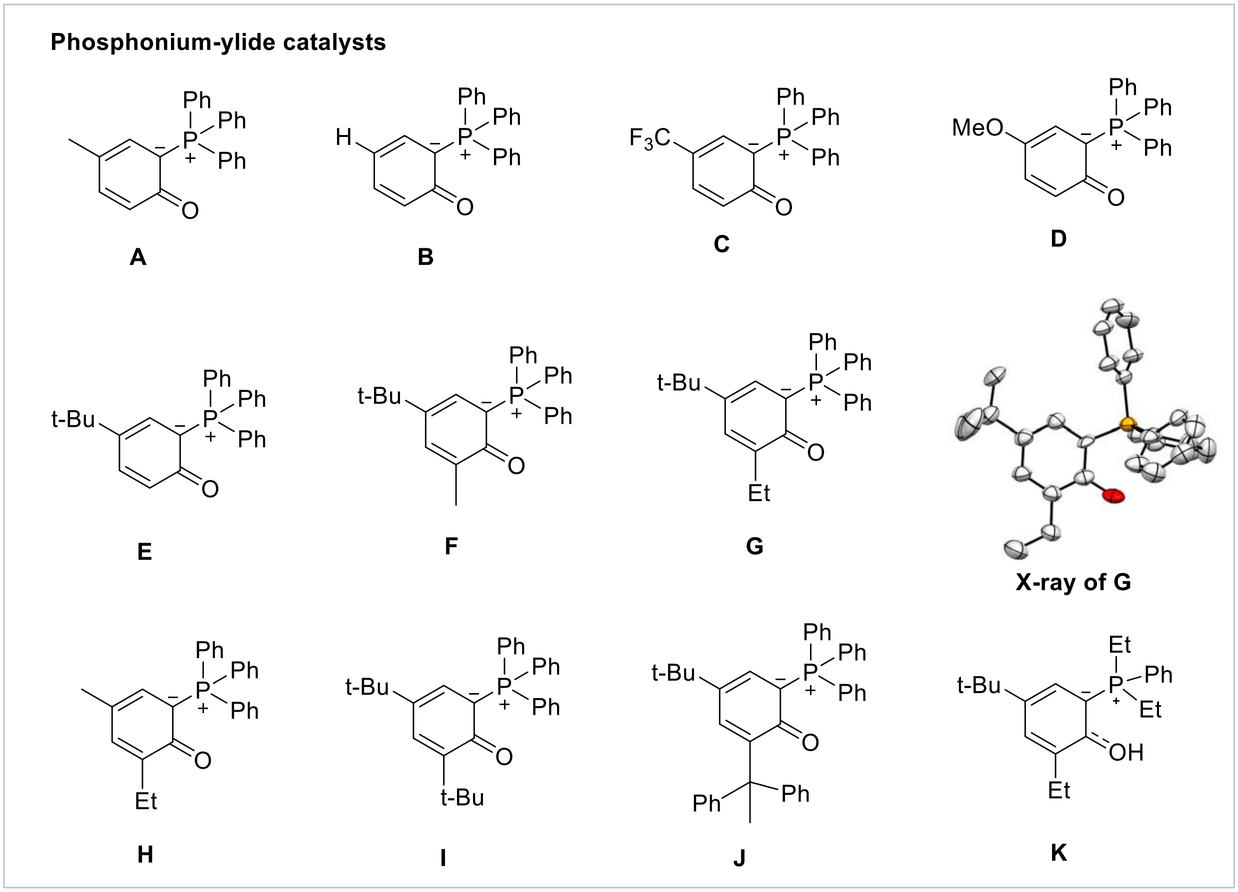
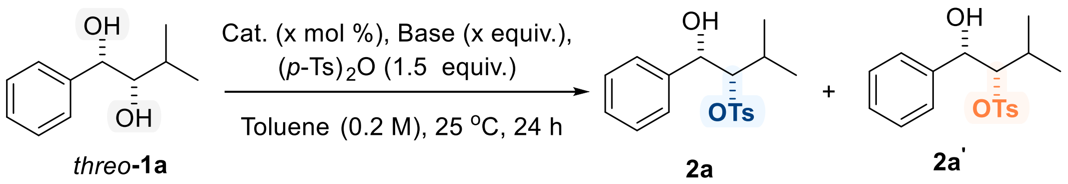


Figure S1. Phosphonium-ylide catalysts (**A**–**K**) synthesized and examined in this work.

Systematic structural modification was carried out on the aryl substituents and the phosphine unit. An X-ray crystal structure of catalyst G is shown.

Table S1: Optimization for the regioselective tosylation of diol (**1a**).



Entry	Cat. (x mol %)	Base (x equiv.)	Yield [%]^a 2a+2a'	Selectivity 2a:2a'
1	Bu_2SnO (2)^b	Et_3N (1)	31	0:31
2	KI (20)^b	Ag_2O (1.5)	5	0:5
3	DMAP (10)^c	DIPEA (1)	59	2.8:1
4	no cat^b	Pyridine (1.5)	94	1.93:1
5	no cat	DIPEA (1)	37	1.4:1
6	P-Ylide A (10)	DIPEA (1)	63	5.3:1
7	P-Ylide B (10)	DIPEA (1)	67	2.4:1
8	P-Ylide C (10)	DIPEA (1)	56	5.2:1
9	P-Ylide D (10)	DIPEA (1)	59	4..9:1
10	P-Ylide E (10)	DIPEA (1)	58	6.3:1
11	P-Ylide F (10)	DIPEA (1)	65	12:1
12	P-Ylide G (10)	DIPEA (1)	89	88:1
13	P-Ylide H (10)	DIPEA (1)	60	11:1
14	P-Ylide I (10)	DIPEA (1)	56	10.2:1
15	P-Ylide J (10)	DIPEA (1)	55	10:1
16	P-Ylide K (10)	DIPEA (1)	50	7.3:1

previous conditions (entries 1–4)

a) NMR yield was determined by using CH_2Br_2 as an internal standard,
b) *p*-TsCl (1.05 equiv) instead of (*p*-Ts)$_2$O (1.5 equiv) c) DCM as a solvent

Abbreviation for diisopropylethyl amine (DIPEA), dimethylamino pyridine (DMAP) and *p*-toluene sulfonic anhydride ((*p*-Ts)$_2$O). P-ylide G (10 mol%), DIPEA (1 equiv.), (*p*-Ts)$_2$O (1.5 equiv.) and toluene (0.2 M) was chosen as an optimal conditions since it offered highest yield and selectivity of product **2a**.

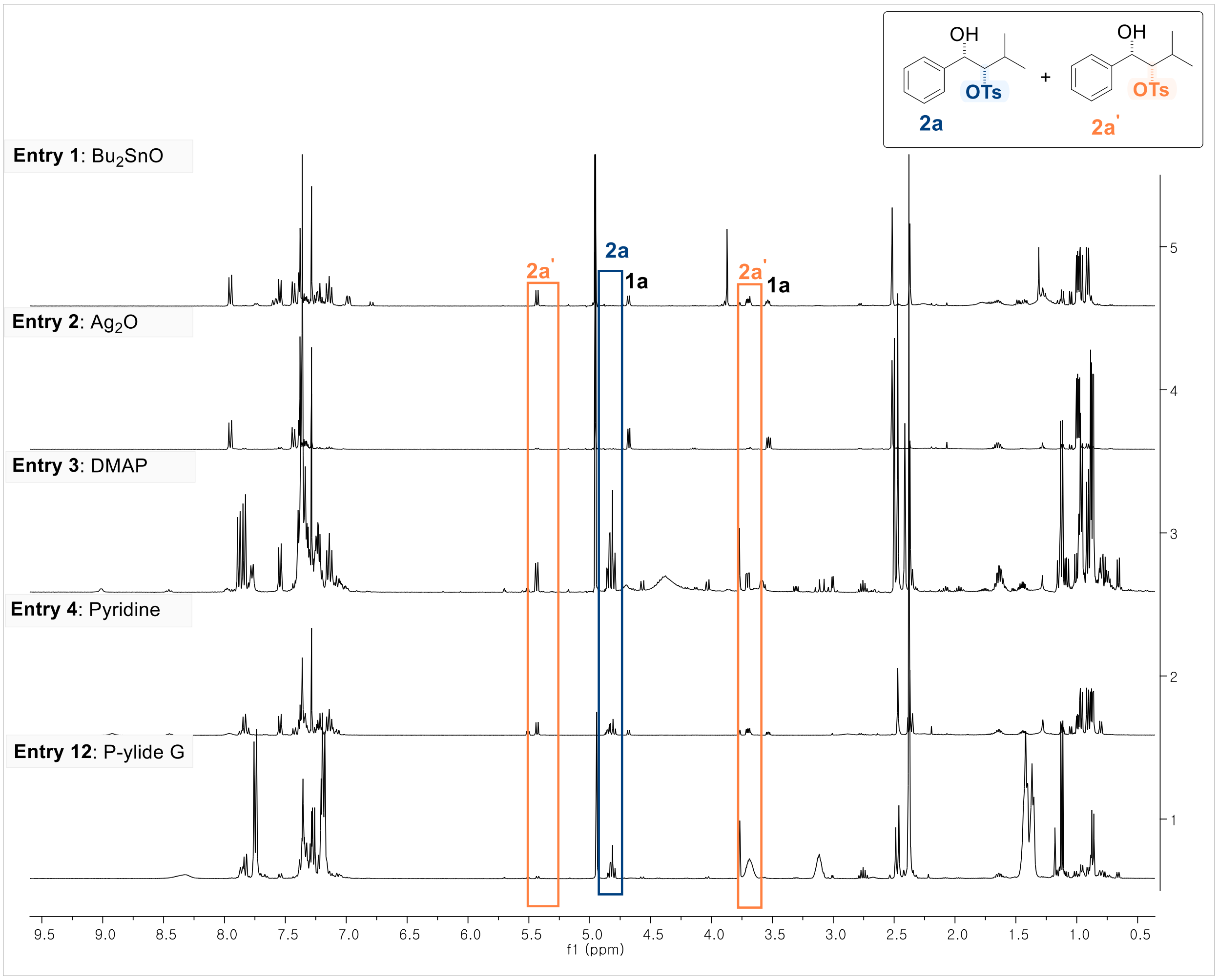
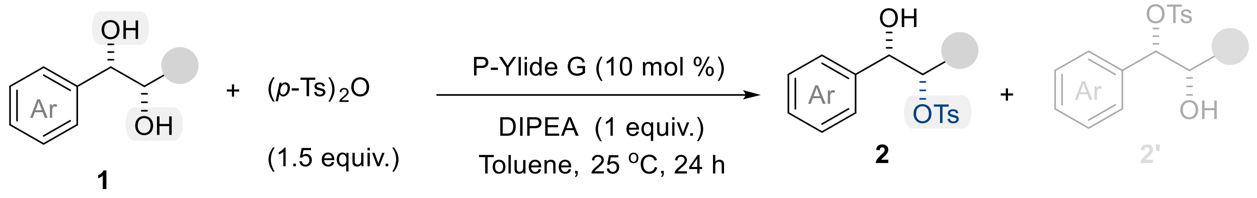


Figure S2. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of crude reaction mixture of entry 1-4 and 12.

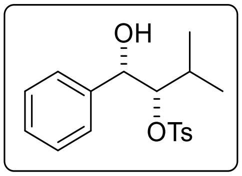
We screened some previously reported site-selective tosylation conditions including tin-[9] and silver[10] mediated protocols tosylation proceeded predominantly at the benzylic secondary alcohol to afford regioisomer **2a**', while the corresponding aliphatic tosylation product **2a** was not detected (entries 1-2). In contrast, DMAP-based[11] electrophile-transfer systems and pyridine-mediated[12] tosylation exhibited poor regioselectivity, furnishing mixtures of **2a** and **2a′** with only marginal bias (entries 3-4).

IV-1) General Procedure for the P-ylide-Catalyized Site-Selective Tosylation of Diols.



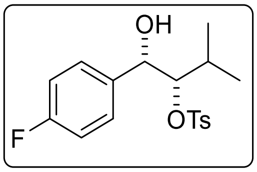
To an oven-dried screwed vial equipped with a triangular-shaped Teflon stirrer bar was added diol **1**(0.40 mmol, 1.0 equiv.) **phosphonium ylide G** (17.53 mg, 10 mol %), *p*-toluene sulfonic anhydride (0.6 mmol, 1.5 equiv.), toluene (0.1 M), diisopropylethylamine (1 equiv.) and the reaction mixture was stirred at 25 °C for 24 h. After finishing the reaction, Upon completion, the reaction concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (eluent: n-hexane/EtOAc = 6:1) to afford the corresponding mono-tosylated product **2**.

1-Hydroxy-3-methyl-1-phenylbutan-2-yl 4-methylbenzenesulfonate (2a)



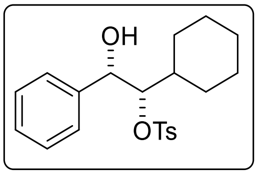
Prepared according to general procedure **IV-1**.White solid (87%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.41 – 7.31 (m, 7H), 4.85 (dd, J = 8.1, 2.6 Hz, 1H), 4.80 (d, J = 8.1 Hz, 1H), 2.47 (s, 3H), 1.65 (ddd, J = 13.7, 6.9, 2.5 Hz, 1H), 0.88 (dd, J = 6.9, 3.4 Hz, 6H); **^{13}C NMR** (100 MHz, CD_3OD) δ 144.45, 141.96, 134.97, 130.08, 128.49, 127.79, 127.16, 91.85, 72.50, 28.94, 21.53, 20.32, 17.56; **IR** (CH_2Cl_2, cm^{-1}) 3521, 3033, 2965,1336, 1170, 1094, 903, 867, 811, 760, 736, 700, 671. **High Resolution MS** (EI): Calculated for $C_{18}H_{22}O_4S$ [M-H]$^{-}$: 333.1166; Found, 333.1159. **X-ray crystal structure** is available in the *Appendix II*. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I*.

1-(4-Fluorophenyl)-3-methylbutane-1,2-diol (2b)



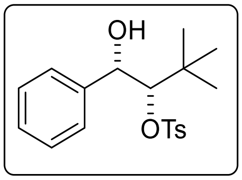
Prepared according to general procedure **IV-1**.White solid (62 %, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.11 – 7.02 (m, 2H), 4.66 (dd, J = 6.3, 3.3 Hz, 1H), 3.52 – 3.45 (m, 1H), 2.62 (d, J = 3.8 Hz, 1H), 2.15 (d, J = 4.1 Hz, 1H), 1.67 – 1.61 (m, 1H), 0.98 (dd, J = 6.8, 5.7 Hz, 6H); **^{13}C NMR** (100 MHz, CD_3OD) δ 163.52, 161.10, 144.23, 137.08, 134.94, 129.18, 128.15, 127.23, 114.64, 114.43, 91.83, 72.03, 29.21, 20.11, 18.81, 16.59; **IR** (CH_2Cl_2, cm^{-1}) 3524, 2972, 1605, 1510, 1347, 1222, 1172, 1095, 901, 834, 813, 767, 683; **High Resolution MS** (EI): Calculated for $C_{18}H_{21}FO_4S$ [M+Na]$^{+\cdot}$: 375.1037; Found, 375.1042. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I*.

Cyclohexyl-2-hydroxy-2-phenylethyl-4-methylbenzenesulfonate (2c)



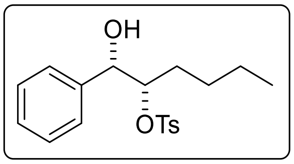
Prepared according to general procedure **IV-1**.Pale yellow solid (47%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.39 – 7.30 (m, 7H), 4.86 (d, J = 7.6 Hz, 1H), 4.79 (dd, J = 7.6, 3.0 Hz, 1H), 2.47 (s, 3H), 1.76 – 1.65 (m, 3H), 1.54 (d, J = 16.0 Hz, 2H), 1.39 – 1.31 (m, 1H), 1.26 – 1.03 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.58, 139.73, 134.27, 129.68, 128.73, 128.38, 127.74, 126.90, 91.88, 73.63, 38.92, 30.34, 26.55, 26.13, 25.75, 21.67; **IR** (CH_2Cl_2, cm^{-1}) 3524, 3037, 2927, 2851, 1451, 1344, 1171, 1095, 1051, 895, 811, 759, 700; **High Resolution MS** (EI): Calculated for $C_{21}H_{26}O_4S$ [M-H]$^-$: 373.1479; Found, 373.1476. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-3,3-dimethyl-1-phenylbutan-2-yl-4-methylbenzenesulfonate (2d)



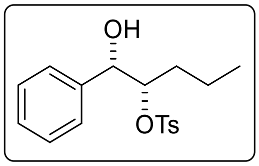
Prepared according to general procedure **IV-1**.Light brown solid (72%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.31 – 7.29 (m, 4H), 7.24 (dd, J = 8.5, 0.6 Hz, 2H), 4.92 (d, J = 4.5 Hz, 1H), 4.86 (d, J = 4.6 Hz, 1H), 2.44 (s, 3H), 0.97 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.23, 141.43, 134.49, 129.57, 128.52, 127.85, 127.49, 126.49, 94.16, 72.24, 35.33, 27.11, 21.62; **IR** (CH_2Cl_2, cm^{-1}) 3563, 2958, 1341, 1170, 948, 906, 888, 851, 906, 746, 697, 683; **High Resolution MS** (EI): Calculated for $C_{19}H_{24}O_4S$ [M+Na]$^+$: 371.1287; Found, 371.1297. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I*. **X-ray crystal structure** is available in the *Appendix II*.

1-Hydroxy-1-phenylhexan-2-yl-4-methylbenzenesulfonate (2e)



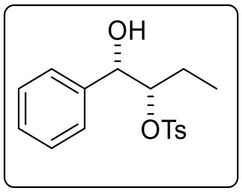
Prepared according to general procedure **IV-1**.Transparent liquid (59%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (t, J = 5.1 Hz, 2H), 7.37 – 7.31 (m, 7H), 4.85 – 4.72 (m, 2H), 2.47 (s, 3H), 1.51 – 1.40 (m, 2H), 1.24 – 1.09 (m, 4H), 0.76 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.76, 139.23, 133.95, 129.75, 128.57, 128.36, 127.82, 126.99, 87.22, 75.26, 30.41, 26.85, 22.22, 21.66, 13.73; **IR** (CH_2Cl_2, cm^{-1}) 3531, 3029, 2958, 2866, 1353, 1172, 1094, 953, 900, 814, 761, 728, 702, 665; **High Resolution MS** (EI): Calculated for $C_{19}H_{24}O_4S$ [M-H]$^-$; 347.1322; Found, 347.1322. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-1-phenylpentan-2-yl-4-methylbenzenesulfonate (2f)



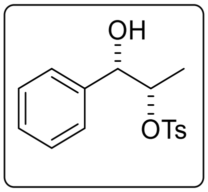
Prepared according to general procedure **IV-1**.Transparent liquid (61%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 2H), 7.37 – 7.30 (m, 7H), 4.85 – 4.80 (m, 1H), 4.76 (d, J = 6.9 Hz, 1H), 2.47 (s, 3H), 1.48 – 1.39 (m, 2H), 1.36 – 1.26 (m, 1H), 1.20 (dd, J = 9.9, 9.1, 4.7 Hz, 1H), 0.77 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.77, 139.21, 133.93, 129.76, 128.58, 128.37, 127.80, 127.00, 87.00, 75.31, 32.82, 21.67, 18.12, 13.67; **IR** (CH_2Cl_2, cm^{-1}) 3531, 2961, 1355, 1261, 1173, 1096, 1049, 891, 814, 761, 702; **High Resolution MS** (EI): Calculated for $C_{18}H_{22}O_4S$ [M-H]$^-$: 333.1166; Found, 333.1164. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-1-phenylbutan-2-yl 4-methylbenzenesulfonate (2g)



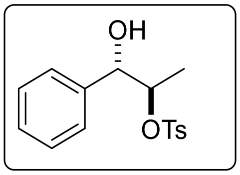
Prepared according to general procedure **IV-1**.White solid (81%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.34 (dt, J = 4.3, 1.9 Hz, 7H), 4.82 – 4.71 (m, 2H), 2.47 (s, 3H), 1.60 – 1.53 (m, 1H), 1.47 – 1.39 (m, 1H), 0.82 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.78, 139.19, 133.92, 129.78, 128.51, 127.81, 127.01, 88.42, 75.08, 23.96, 21.68, 9.32; **IR** (CH_2Cl_2, cm^{-1}) 3531, 2972, 2923, 1348, 1172, 1050, 929, 887, 858, 763, 747, 701, 686, 666; **High Resolution MS** (EI): Calculated for $C_{17}H_{20}O_4S$ [M-H]$^-$: 319.1009; Found, 319.1009. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Hydroxy-1-phenylpropan-2-yl-4-methylbenzenesulfonate (2h)



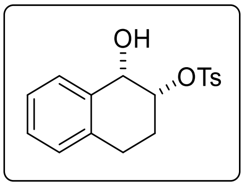
Prepared according to general procedure **IV-1**.White solid (88%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.78 (d, J = 8.2 Hz, 2H), 7.35 – 7.29 (m, 7H), 4.81-4.75 (p, J = 6.5 Hz, 1H), 4.65-4.63 (d, J = 7.1 Hz, 1H), 2.47 (s, 3H), 1.15-1.14 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_3CO$) δ 144.46, 140.52, 134.41, 129.72, 127.89, 127.54, 126.92, 82.18, 74.69, 20.61, 16.13; **IR** (CH_2Cl_2, cm^{-1}) 3528, 2930, 1348, 1172, 1020, 914, 888, 813, 759, 701, 686 665.; **High Resolution MS** (EI): Calculated for $C_{16}H_{18}O_4S$ [M-H]$^-$; 305.0853; Found, 305.0857. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Hydroxy-1-phenylpropan-2-yl-4-methylbenzenesulfonate (2h ^{erythro})



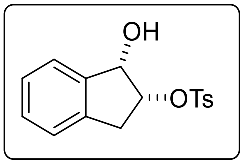
Prepared according to general procedure **IV-1**.Transparent liquid (89%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.78 (d, J = 8.2 Hz, 2H), 7.35 – 7.29 (m, 7H), 4.81-4.75 (p, J = 6.5 Hz, 1H), 4.65-4.63 (d, J = 7.1 Hz, 1H), 2.47 (s, 3H), 1.15-1.14 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_3CO$) δ 144.46, 140.52, 134.41, 129.72, 127.89, 127.54, 126.92, 82.18, 74.69, 20.61, 16.13; **IR** (CH_2Cl_2, cm^{-1}) 3524, 2990, 2937, 1354, 1174, 1096, 1032, 913, 892, 815, 751, 702, 664; **High Resolution MS** (EI): Calculated for $C_{16}H_{18}O_4S$ $[M-H]^-$: 305.0853; Found, 305.0846. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I*.**X-ray crystal structure** is available in the *Appendix II*.

1-Hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (2i ^{erythro})



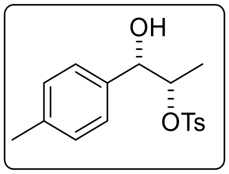
Prepared according to general procedure **IV-1**.Yellow liquid (63%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.26 – 7.20 (m, 2H), 7.15 – 7.10 (m, 1H), 4.93 (dt, *J* = 9.6, 3.1 Hz, 1H), 4.82 (d, *J* = 3.3 Hz, 1H), 3.00 (dt, *J* = 17.2, 6.0 Hz, 1H), 2.86 – 2.74 (m, 1H), 2.49 (s, 3H), 2.42 – 2.32 (m, 1H), 1.92 (dtd, *J* = 9.1, 6.2, 2.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.07, 135.18, 133.87, 130.00, 129.39, 128.45 , 127.82, 126.60, 81.02 , 68.76, 26.38, 23.95 , 21.71.; **IR** (CH_2Cl_2, cm^{-1}) 3524, 2930, 1351, 1171, 964, 883, 843, 814, 770, 746, 689, 671; **High Resolution MS** (EI): Calculated for $C_{17}H_{18}O_4S$ $[M+Na]^+$: 341.0818; Found, 341.0822. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-2,3-dihydro-1H-inden-2-yl 4-methylbenzenesulfonate (2j ^{erythro})



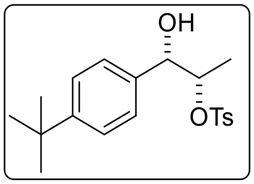
Prepared according to general procedure **IV-1**.Yellow liquid (65%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.43 (dd, *J* = 9.0, 6.2 Hz, 2H), 7.30 (dd, *J* = 6.1, 2.7 Hz, 2H), 7.23 – 7.19 (m, 1H), 5.19 – 5.08 (m, 2H), 3.21 (dd, *J* = 16.7, 3.8 Hz, 1H), 3.08 (dd, *J* = 16.5, 5.3 Hz, 1H), 2.49 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.21, 140.62, 138.22, 133.41, 130.01, 129.27 , 127.98, 127.66, 124.96, 82.53, 74.95, 35.98, 21.72; **IR** (CH_2Cl_2, cm^{-1}) 3514, 2926, 1356, 1173, 1096, 1015, 901, 876, 848, 814, 745, 700, 664; **High Resolution MS** (EI): Calculated for $C_{16}H_{16}O_4S$ $[M+Na]^+$: 327.0661; Found, 327.0667. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-1-(p-tolyl)propan-2-yl-4-methylbenzenesulfonate (2k)



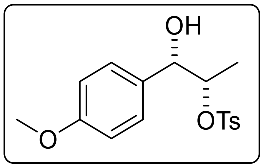
Prepared according to general procedure **IV-1**.White solid (90%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 2H), 7.34-7.32 (d, J = 8.0 Hz, 2H), 7.19 – 7.13 (m, 4H), 4.78-4.73 (p, J = 13.2, 6.7 Hz, 1H), 4.61-4.59 (d, J = 7.1 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H), 1.15-1.13 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_3SO$) δ 144.76, 138.05, 136.77, 133.91, 130.26, 128.77, 127.79, 127.07, 82.77, 73.75, 21.55, 21.20 16.95; **IR** (CH_2Cl_2, cm^{-1}) 3531, 2983, 2919, 1349, 1172, 1020, 921, 893, 811, 790, 752, 684, 664; **High Resolution MS** (EI): Calculated for $C_{17}H_{20}O_4S$ [M-H]$^-$: 319.1009; Found, 319.1014. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-(*tert*-Butyl)phenyl)-1-hydroxypropan-2-yl-4-methylbenzene sulfonate (2l)



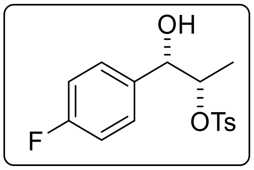
Prepared according to general procedure **IV-1**.Brown solid (89%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (d, 2H), 7.38-7.34 (dt, J = 8.5, 4.5 Hz, 4H), 7.24-7.22 (d, J = 8.3 Hz, 2H), 4.82 – 4.75 (p, 1H), 4.62-4.60 (t, J = 8.2 Hz, 1H), 2.47 (s, 3H), 1.33 (s, 9H), 1.15-1.13 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_3SO$) δ 150.10, 144.83, 137.93, 133.98, 130.32, 127.86, 127.10 , 124.97, 82.49, 73.71, 34.64, 31.64, 21.56, 16.69; **IR** (CH_2Cl_2, cm^{-1}) 3524, 2965, 1357, 1173, 1097, 1018, 895, 814, 766, 749, 687, 663; **High Resolution MS** (EI): Calculated for $C_{20}H_{26}O_4S$ [M-H]$^-$: 361.1479; Found, 361.1474. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-1-(4-methoxyphenyl)propan-2-yl-4-methylbenzene sulfonate (2m)



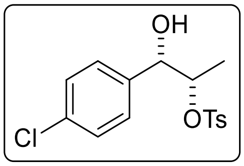
Prepared according to general procedure **IV-1**.White solid (89%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.86 (dd, J = 8.3 Hz, 2H), 7.36 – 7.33 (d, 2H), 7.23-7.21 (d, J = 8.8 Hz, 2H), 6.88-6.85 (d, J = 8.7 Hz, 2H), 4.75 – 4.71 (p, 1H), 4.60-4.58 (d, J = 7.2 Hz, 1H), 3.82 (s, 3H), 2.47 (s, 3H), 2.01 (s, 1H), 1.14-1.12 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_3SO$) δ 158.98, 144.77, 133.97, 132.97, 130.29, 128.29, 127.80, 113.61, 82.88, 73.52, 55.42, 21.54, 16.91; **IR** (CH_2Cl_2, cm^{-1}) 3400, 3050, 2960, 2925, 1600, 1510, 1360, 1250, 1180, 1090, 1030, 820; **High Resolution MS** (EI): Calculated for $C_{17}H_{20}O_5S$ [M+Na]$^+$: 359.0923; Found, 359.0930. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-Fluorophenyl)-1-hydroxypropan-2-yl-4-methylbenzene sulfonate (2n)



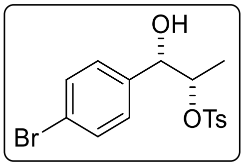
Prepared according to general procedure **IV-1**.White solid (94%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.76 (d, J = 8.3 Hz, 2H), 7.35 – 7.28 (d, 2H), 7.27 – 7.26 (d, 2H), 7.04 – 6.99 (m, 2H), 4.77-4.70 (p, J = 6.4 Hz, 1H), 4.66-4.64 (d, J = 6.8 Hz, 1H), 2.47 (s, 3H), 2.36 (s, 1H), 1.16-1.15 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_3SO$) δ 163.10, 160.69, 144.84, 137.36, 133.74, 130.28, 128.91 (d, J = 8.2 Hz), 127.75, 115.02 , 114.81, 82.70, 73.17, 21.51, 17.11; **IR** (CH_2Cl_2, cm^{-1}) 3531, 2990, 1510, 1350, 1174, 1222, 1096, 924, 894, 815, 752,, 684; **High Resolution MS** (EI): Calculated for $C_{16}H_{17}FO_4S$ $[M-H]^-$: 323.0759; Found, 323.0758. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-Chlorophenyl)-1-hydroxypropan-2-yl-4-methylbenzenesulfonate (2o)



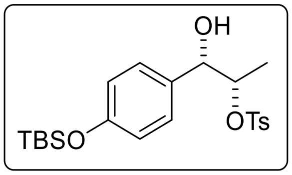
Prepared according to general procedure **IV-1**.White solid (86%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.21 (d, J = 8.4 Hz, 2H), 4.71 (dd, J = 12.7, 6.3 Hz, 1H), 4.64 (d, J = 4.5 Hz, 1H), 2.61 (d, J = 2.9 Hz, 1H), 2.48 (s, 3H), 1.20 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.96, 137.41, 134.23, 133.59, 129.85, 128.67, 128.16, 127.70, 82.79, 75.89, 21.69, 17.37; **IR** (CH_2Cl_2, cm^{-1}); 3307, 2990, 2937, 1361, 1173, 1093, 1033, 926, 896, 811, 750, 726, 686; **High Resolution MS** (EI): Calculated for $C_{16}H_{17}ClO_4S$ $[M+Na]^+$: 363.0428; Found, 363.0435. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-Bromophenyl)-1-hydroxypropan-2-yl-4-methylbenzene sulfonate (2p)



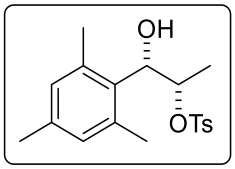
Prepared according to general procedure **IV-1**.White solid (89%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.44-7.42 (d, J = 8.5 Hz, 2H), 7.33-7.28 (d, J = 8.0 Hz, 2H), 7.16-7.15 (d, J = 8.3 Hz, 2H), 4.75-4.68 (p, J = 6.4 Hz, 1H), 4.64-4.62 (d, J = 6.2 Hz, 1H), 2.48 (s, 3H), 1.21-1.20 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_3SO$)δ 144.80, 140.79, 133.50 , 130.97, 130.22, 129.06 , 127.67, 120.81, 82.62, 73.16, 21.64, 17.41; **IR** (CH_2Cl_2, cm^{-1}) 3521, 3325, 2923, 1357, 1171, 1010, 923, 891, 809, 767, 745, 682, 643; **High Resolution MS** (EI): Calculated for $C_{16}H_{17}BrO_4S$ $[M+Na]^+$: 406.9923; Found, 406.9930. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-1-hydroxypropan-2-yl 4-methyl benzene sulfonate (2q)



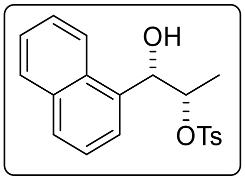
Prepared according to general procedure **IV-1**.White solid (64%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.74 (dq, *J* = 12.8, 6.4 Hz, 1H), 4.57 (d, *J* = 7.4 Hz, 1H), 2.47 (s, 3H), 1.11 (d, *J* = 6.4 Hz, 3H), 1.00 (s, 9H), 0.20 (d, *J* = 1.4 Hz, 6H); **^{13}C NMR** (100 MHz, CD_3OD) δ 155.19, 144.59, 133.98, 133.06, 129.40, 127.66, 127.44, 119.37, 82.53, 74.61, 24.78, 20.26, 17.67, 16.04, 5.69,5.68; **IR** (CH_2Cl_2, cm^{-1}) 3464, 2955, 2937, 2855, 1510, 1357, 1256, 1172, 897, 836, 809, 778, 685, 665; **High Resolution MS** (EI): Calculated for $C_{22}H_{32}O_5Si$ $[M\text{-}H]^-$; 435.1667; Found, 435.1657. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-1-mesitylpropan-2-yl-4-methylbenzenesulfonate (2r)



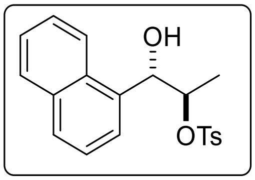
Prepared according to general procedure **IV-1**.White solid (73%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 2H), 5.22 (dq, *J* = 8.9, 6.4 Hz, 1H), 5.11 (d, *J* = 8.9 Hz, 1H), 2.48 (s, 3H), 2.36 (s, 6H), 2.28 (s, 1H), 2.25 (s, 3H), 1.09 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_3SO$) δ 144.72, 136.50, 134.15, 130.13, 128.07, 82.58, 71.96, 21.55, 20.87, 17.76; **IR** (CH_2Cl_2, cm^{-1}); 3542, 2926, 1349, 1173, 1036, 1010, 890, 852, 813, 759, 685, 663; **High Resolution MS** (EI): Calculated for $C_{19}H_{24}O_4S[M\text{-}H]^-$: 347.1322; Found, 347.1321. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-1-(naphthalen-1-yl)propan-2-yl-4-methylbenzene sulfonate (2s)



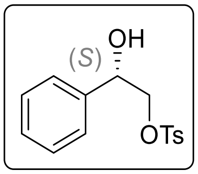
Prepared according to general procedure **IV-1**.White solid (73%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 1H), 7.87 – 7.83 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.55 (d, *J* = 6.6 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.36 (dd, *J* = 6.3, 3.6 Hz, 1H), 5.04 (p, *J* = 6.4 Hz, 1H), 2.74 (d, *J* = 4.1 Hz, 1H), 2.40 (s, 3H), 1.26 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.55, 134.63, 133.89, 133.25, 130.53, 129.61, 128.98, 127.63, 126.32, 125.64, 125.29 , 123.06 , 82.73, 74.10, 21.65, 18.12; **IR** (CH_2Cl_2, cm^{-1}); 3524, 3058, 2983, 2926, 1351, 1261, 1174, 1096, 917, 891, 802, 750, 686, 657; **High Resolution MS** (EI): Calculated for $C_{20}H_{20}O_4S[M+Na]^+$: 379.0974; Found, 379.0975. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-1-(naphthalen-1-yl)propan-2-yl-4-methylbenzene sulfonate (2s *erythro*)

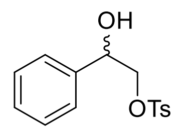


Prepared according to general procedure **IV-1**.Transparent liquid (81%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.90 – 7.86 (m, 1H), 7.83 – 7.78 (m, 4H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.84 (d, *J* = 2.9 Hz, 1H), 4.93 (qd, *J* = 6.5, 3.1 Hz, 1H), 2.47 (s, 3H), 2.23 (s, 1H), 1.15 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 144.83 , 134.19, 133.59, 129.93, 128.98, 128.54, 127.85, 126.51, 125.64, 125.44, 124.15, 122.42, 81.75, 71.99, 21.68 , 13.38. δ; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3531, 3503, 3054, 2990, 2930, 1353, 1187, 1172, 1907, 800, 776, 751, 703, 679, 663; **High Resolution MS** (EI): Calculated for $C_{20}H_{20}O_4S[M+Na]^+$: 379.0974; Found, 379.0975. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.* **X-ray crystal structure** is available in the *Appendix II.*

(*S*)-2-Hydroxy-2-phenylethyl 4-methylbenzenesulfonate (2t)

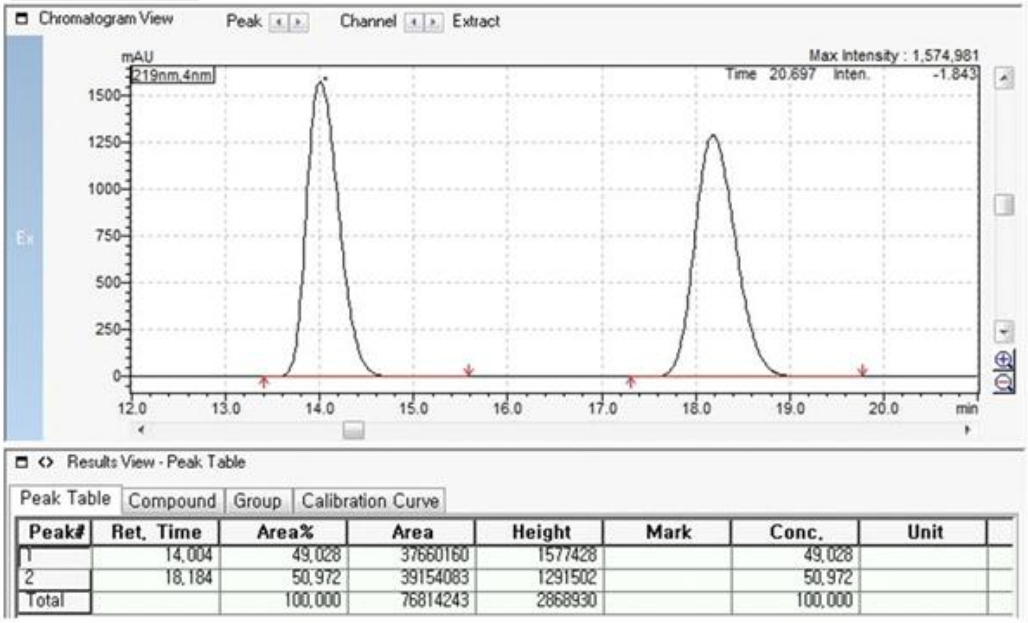


Prepared according to general procedure **IV-1**.Transparent liquid (99%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.32 (m, 7H), 5.01 (dd, *J* = 8.6, 3.1 Hz, 1H), 4.16 (s, 1H), 4.07 (dd, *J* = 10.4, 8.6 Hz, 1H), 2.54 (s, 1H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 145.11, 138.25, 132.65, 129.97, 128.62 , 127.98, 126.21, 74.35, 71.95, 21.68; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3528, 3029, 1353, 1172, 1095, 965, 917, 866, 813, 762, 699, 664; **High Resolution MS** (EI): Calculated for $C_{15}H_{16}O_4S[M-H]^-$: 291.0696; Found, 291.0697. Optical purity assay was obtained on Shimadzu HPLC (LC-20A Prominence Series) using Chiralpak ® IK column (5 µm particle size, 4.6 mm x 250 mm) with IPA and n-hexane as mobile phase**^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

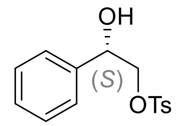


2t

Racemic (IK column 80 % hexanes / 20 % iso-propanol)

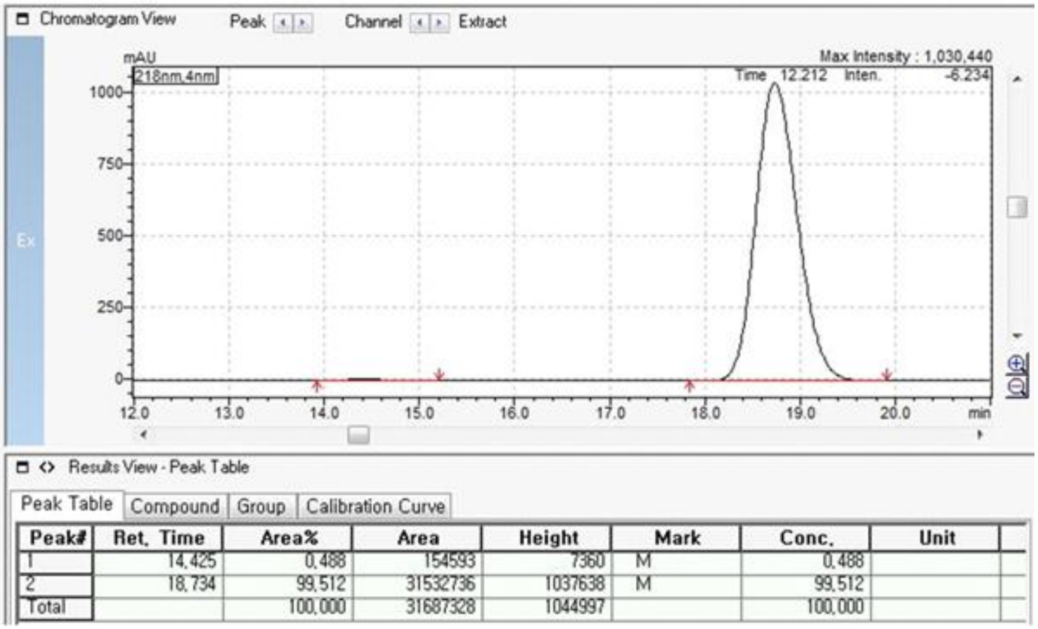


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.	Unit
1	14.004	49.028	37660160	1577428		49.028	
2	18.184	50.972	39154083	1291502		50.972	
Total		100.000	76814243	2868930		100.000	



2t

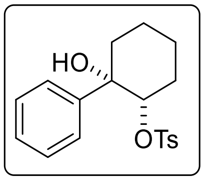
Chiral (IK column 80 % hexanes / 20 % iso-propanol)



Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.	Unit
1	14.425	0.488	154593	7360	M	0.488	
2	18.734	99.512	31532736	1037638	M	99.512	
Total		100.000	31687328	1044997		100.000	

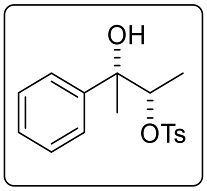
Figure S3. HPLC traces for the racemic and chiral **2t**.

2-Hydroxy-2-phenylcyclohexyl-4-methylbenzenesulfonate (2u)



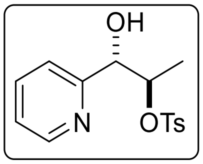
Prepared according to general procedure **IV-1**.Transparent liquid (95%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.29 – 7.24 (m, 4H), 7.22 – 7.18 (m, 3H), 7.07 (d, J = 8.2 Hz, 2H), 4.93 (dd, J = 11.3, 5.0 Hz, 1H), 2.40 (s, 3H), 2.27 – 2.22 (m, 1H), 2.17 – 2.10 (m, 1H), 1.88 (dd, J = 8.9, 3.2 Hz, 2H), 1.72 (ddd, J = 19.5, 11.0, 3.3 Hz, 2H), 1.57 – 1.42 (m, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 144.92, 144.07, 133.64 , 129.49, 128.20, 127.36, 126.77, 124.53, 85.81, 75.36, 39.76, 28.92, 24.25, 21.57, 20.65; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3596, 3467, 2937, 2859, 1350, 1275, 1172, 956, 925, 882, 840, 754, 700, 666; **High Resolution MS** (EI): Calculated for $C_{19}H_{22}O_4S$ [M-H]$^-$: 345.1166; Found, 345.1156. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

3-Hydroxy-3-phenylbutan-2-yl 4-methylbenzenesulfonate (2v)



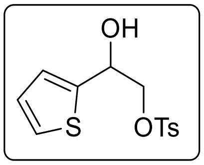
Prepared according to general procedure **IV-1**.White solid (69%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.86 – 7.76 (m, 2H), 7.43 – 7.32 (m, 6H), 7.27 (t, *J* = 2.4 Hz, 1H), 4.82 (q, *J* = 6.4 Hz, 1H), 2.47 (s, 3H), 2.04 (s, 1H), 1.57 (s, 3H), 1.03 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 144.78, 143.18, 134.18, 129.85, 128.33, 127.78, 127.27, 125.09, 85.34, 75.66, 27.71, 21.67, 15.12; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3425, 3031, 2962, 2931, 2872, 1601, 1495, 1453, 1124, 1072, 756, 702; **High Resolution MS** (EI): Calculated for $C_{17}H_{20}O_4S$ [M-H]$^-$: 319.1009; Found, 319.1003. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-1-(pyridin-2-yl)propan-2-yl 4-methylbenzenesulfonate (2w^{erythro})



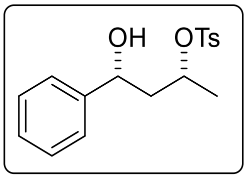
Prepared according to general procedure **IV-1**.Transparent liquid (77%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.53 – 8.48 (m, 1H), 7.77 – 7.71 (m, 2H), 7.71 – 7.63 (m, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.20 (m, 3H), 5.40 (d, *J* = 4.5 Hz, 1H), 4.22 – 4.09 (m, 1H), 3.71 (d, *J* = 5.0 Hz, 1H), 2.42 (s, 3H), 1.09 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 156.32, 149.16, 144.98, 136.84, 133.66, 130.14, 128.12, 123.63, 122.86, 88.26, 68.02, 21.49, 19.74; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3261, 2980, 1363, 1275, 1176, 1095, 968, 931, 843, 812, 750, 684; **High Resolution MS** (EI): Calculated for $C_{15}H_{17}NO_4S$[M-H]$^-$: 306.0805; Found, 306.0797. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

2-Hydroxy-2-(thiophen-2-yl)ethyl-4-methylbenzenesulfonate (2x)



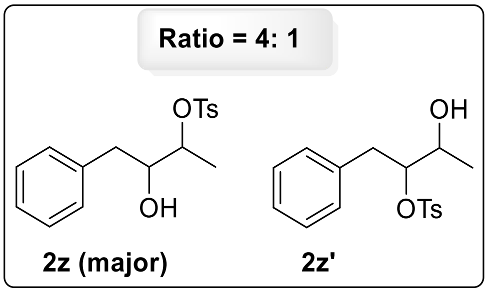
Prepared according to general procedure **IV-1**.Transparent liquid (52%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.02 – 6.98 (m, 2H), 5.31 – 5.19 (m, 1H), 4.24 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.17 (dd, *J* = 10.3, 8.0 Hz, 1H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.22, 141.45, 132.55, 130.00, 128.02, 126.97, 125.66, 125.00, 73.69, 68.29, 21.69; **IR** (CH_2Cl_2, cm^{-1}) 3517, 2926, 1354, 1172, 1094, 967, 861, 833, 812, 751, 701, 662; **High Resolution MS** (EI): Calculated for $C_{13}H_{14}O_4S_2$ [M+Na]$^+$: 297.0261; 321.0226 Found, 321.0234. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Hydroxy-4-phenylbutan-2-yl-4-methylbenzenesulfonate (*syn*-2y)



Prepared according to general procedure **IV-1**.Transparent liquid (77%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 2H), 7.42 – 7.29 (m, 6H), 5.06 – 4.95 (m, 1H), 4.79 (dd, J = 10.5, 2.7 Hz, 1H), 2.49 (s, 3H), 1.97 (ddd, J = 14.8, 10.1, 2.8 Hz, 1H), 1.85 (ddd, J = 14.8, 10.5, 2.8 Hz, 1H), 1.26 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.88, 145.04, 134.37, 130.54, 128.60, 127.82, 127.42, 126.03, 78.88, 69.10, 46.45, 21.60; **IR** (CH_2Cl_2, cm^{-1}) 3535, 2983, 2930, 1344, 1172, 1118, 1097, 1038, 894, 815, 752, 700, 662; **High Resolution MS** (EI): Calculated for $C_{17}H_{20}O_4S$[M-H]$^-$: 319.1009; Found, 319.1001. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Mixture of 3-hydroxy-4-phenylbutan-2-yl 4-methylbenzenesulfonate (2z) and **3-hydroxy-1-phenylbutan-2-yl 4-methylbenzenesulfonate (2z')**



Product (95%, 0.1 mmol scale), **IR** (CH_2Cl_2, cm^{-1}) 3539, 2990, 2926, 1352, 1173, 1097, 1031, 898, 813, 748, 699, 665; **High Resolution MS** of isomeric mixture: Calculated for $C_{17}H_{20}O_4S[M-H]^-$: 319.1009, Found: 319.1006.

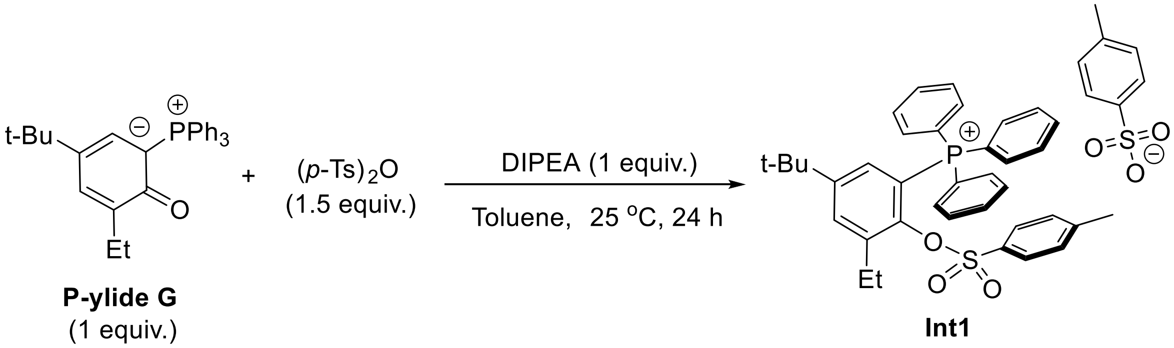
3-Hydroxy-4-phenylbutan-2-yl 4-methylbenzenesulfonate (2z, major) **^{1}H NMR** (400 MHz, CD Cl_3) δ 7.81 – 7.73 (dd, 2H), 7.36 – 7.27 (m, 4H), 7.20 – 7.14 (m, 3H), 4.63 – 4.56 (m, 1H), 3.94 (m, 1H), 2.78 – 2.67 (m, 2H), 2.65 (dd, J = 14.0, 9.0 Hz, 2H), 2.47 (s, 3H), 1.33 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.82, 137.26, 133.96, 129.89, 129.17, 128.68, 127.80, 126.75, 81.79, 74.13, 38.74, 21.67, 14.96. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

3-Hydroxy-1-phenylbutan-2-yl 4-methylbenzenesulfonate (2z') **^{1}H NMR** (400 MHz, CD Cl_3) δ 7.66 – 7.51 (m, 2H), 7.53 – 7.48 (m, 2H), 7.24 – 7.20 (m, 2H), 7.08 – 6.91 (m, 3H), 4.75 (ddd, *J* = 8.1, 5.3, 2.8 Hz, 1H), 4.04 (qd, *J* = 6.5, 2.8 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.42 (s, 3H), 1.27 (d, *J* = 6.5 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.52, 136.17, 133.19, 129.65, 129.38, 128.50 , 127.69, 126.62, 87.71, 68.45, 36.13, 30.95, 17.67. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

V. Mechanistic Investigations

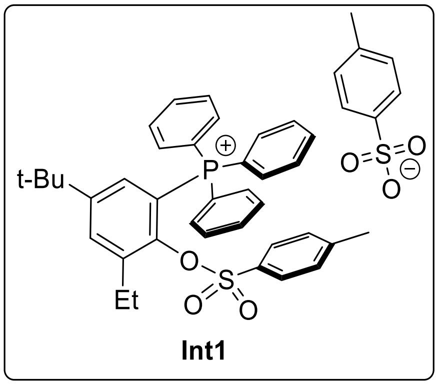
V-I) Investigation of Key Intermediate in Site-Selective Tosylation Reaction

V-I-1) Procedure for the preparation of Int1:



A flame-dried round-bottom flask was charged with phosphonium ylide **G** (219.12 mg, 0.50 mmol, 1.0 equiv.), *p*-toluenesulfonic anhydride (244.79 mg, 0.75 mmol, 1.5 equiv.), and diisopropylethylamine (0.132 mL, 0.75 mmol, 1.5 equiv.) in toluene (0.1 M). The reaction mixture was stirred at 25 °C for 24 h. Upon completion of the reaction, the mixture was quenched with water (10 mL) and extracted with dichloromethane. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (methanol/dichloromethane = 1:10, v/v) to afford **Int1**.

(5-(*tert*-Butyl)-3-ethyl-2-(tosyloxy)phenyl)triphenylphosphonium-4-methylbenzenesulfonate (Int1)



Prepared according to general procedure **V-I-1**.Yellow solid (96%, 0.5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 5H), 7.74 (ddd, J = 11.4, 7.4, 2.8 Hz, 7H), 7.64 (dd, J = 13.1, 7.7 Hz, 6H), 7.14 (d, J = 8.2 Hz, 2H), 7.07 – 6.95 (m, 5H), 2.63 (q, J = 7.5 Hz, 2H), 2.40 (s, 3H), 2.24 (s, 3H), 1.16 (d, J = 7.6 Hz, 3H), 1.14 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.77, 147.98, 146.36, 144.96, 141.22, 137.95, 135.88, 135.42, 134.38, 132.60 – 132.03, 130.41, 129.99, 128.08, 126.98, 126.35, 118.74, 117.84, 112.46, 111.57, 34.99, 30.84, 24.59, 21.76, 21.27, 13.85; **IR** (CH_2Cl_2, cm^{-1}); 3050, 2960, 2925, 1600, 1500, 1350, 1175, 1030, 815, 760; **High Resolution MS** (EI): Calculated for $C_{37}H_{38}O_3PS^+$ [M+H]$^+$: 594.2352, Found: 594.2313 (without negative anion i.e. $^-$OTs). **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I*. **X-ray crystal structure** is available in the *Appendix II.*

Key features in X-ray crystallography of Int1:

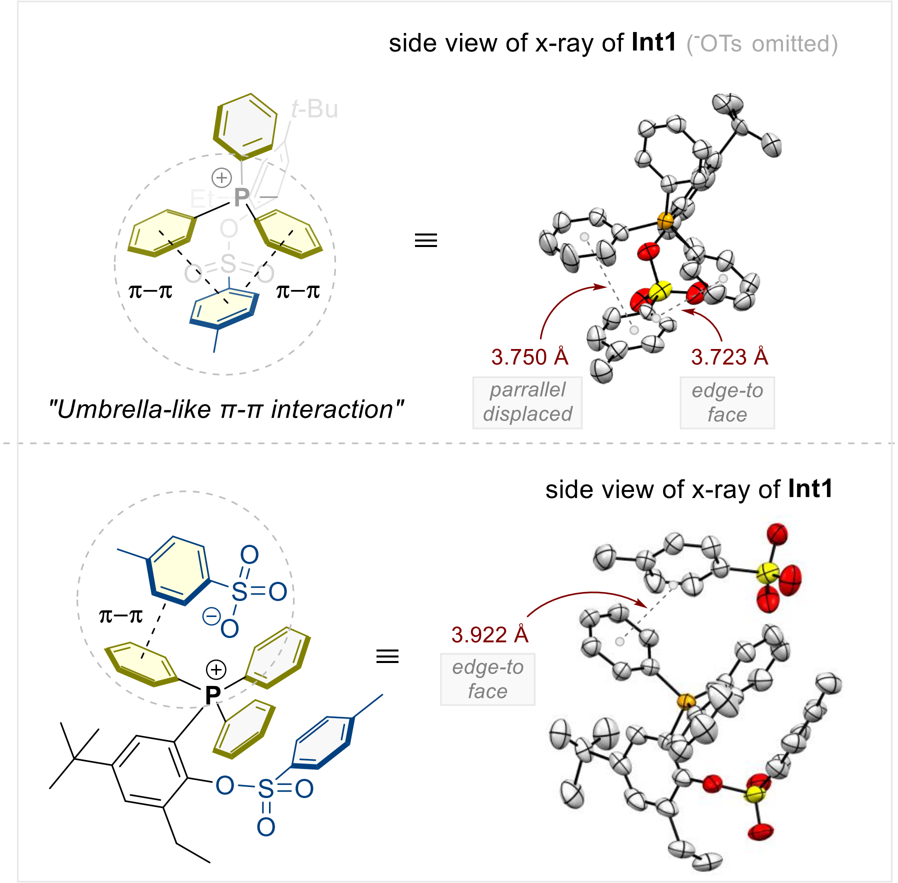
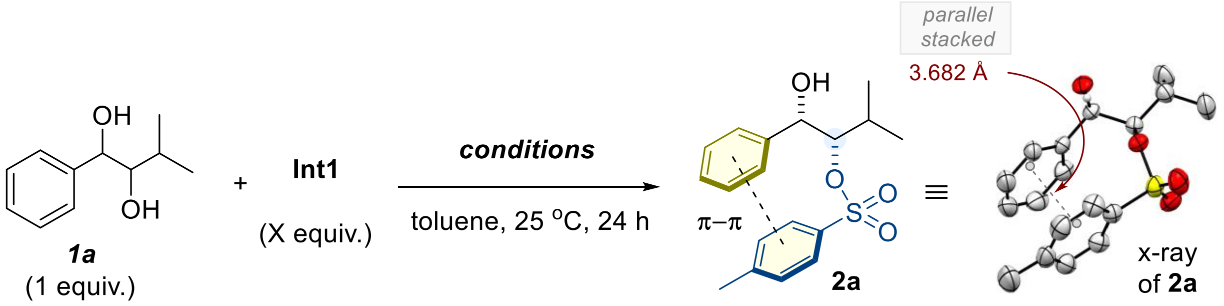


Figure S4. X-ray evidence for cooperative π–Interactions in **Int1**.

Detailed analysis of the crystal structure of **Int1** revealed an unexpected and highly organized network of π–π interactions between the tosyl group and the triphenylphosphine moiety. Two phenyl rings of the triphenylphosphine unit engage the toluyl fragment of the tosyl group through a combination of parallel-displaced (3.750 Å) and edge-to-face (3.723 Å) π–π interactions, effectively encapsulating the aryl sulfonyl moiety. To the best of our knowledge, direct structural evidence for cooperative π–π interactions involving a triphenylphosphine framework has not been reported. On the basis of its geometric features, we term this interaction motif an "umbrella-like" π–π interaction. In addition, an edge-to-face aryl–π contact (3.922 Å) is observed between the tosylate counteranion and the remaining phenyl ring of the triphenylphosphine unit. Together with the primary π–π interactions, this secondary interaction may contribute to a compact stacked architecture compatible with the isolability of **Int1**.

V-I-2) Valdiation of **Int1** as the Key Intermediate



entry	***Int 1*** *(**X** equiv.)*	*conditions*	*yield, **2a** (%)*
1	1.0	none	N.D.
2	1.0	DIPEA (1 equiv.)	**87**
3	0.1	DIPEA (1 equiv.) (p-Ts)$_2$O (1.5 equiv.)	**83**

Figure S5. Evaluation of **Int1** reactivity in catalyst-controlled site-selective tosylation.

After confirming the structure of **Int1**, its reactivity toward the model diol substrate *threo*-**1a** was investigated (**Figure S5**). Under base-free conditions, **Int1** showed no reactivity toward the diol. However, upon addition of one equivalent of DIPEA, selective tosylation proceeded efficiently to give **2a** in 87% yield. When a catalytic amount of **Int1** was used in the presence of external tosyl anhydride, exclusive formation of **2a** was again observed, suggesting that Int1 acts as the active tosylating species in the catalytic cycle. Single-crystal X-ray diffraction analysis of product **2a** revealed a parallel *π–π* stacking interaction (3.682 Å) between the tosyl group and the aromatic substituent of the diol. This structural feature likely contributes to stabilization of the tosylated product, despite the inherently reactive nature of the tosyl functional group.

V-II. Chemical Shift Perturbation Experiments

V-II-1) General description

Chemical shift perturbation spectra were recorded on a Bruker AVANCE 400 / 376 / 100 MHz (^{1}H/^{19}F/^{13}C) spectrometer at 298 K. To evaluate the extent to which the observed chemical-shift changes may reflect π–π stacking interactions, as opposed to acid–base or deprotonation effects, control experiments with different counterions were performed (**Figure S6**). The intermediate tosylate salt (***Int1***) induced partial deprotonation of 1-(4-fluorophenyl)-3-methylbutane-1,2-diol (**1b**), indicating that this form was unsuitable for probing noncovalent interactions. In contrast, no detectable deprotonation was observed for the hexafluorophosphate salt (PF_6^-) under the conditions examined. Accordingly, the corresponding hexafluorophosphate salt (***Int2***) was employed as the guest species in subsequent experiments designed to minimize contributions from acid–base processes when examining π–π stacking interactions.

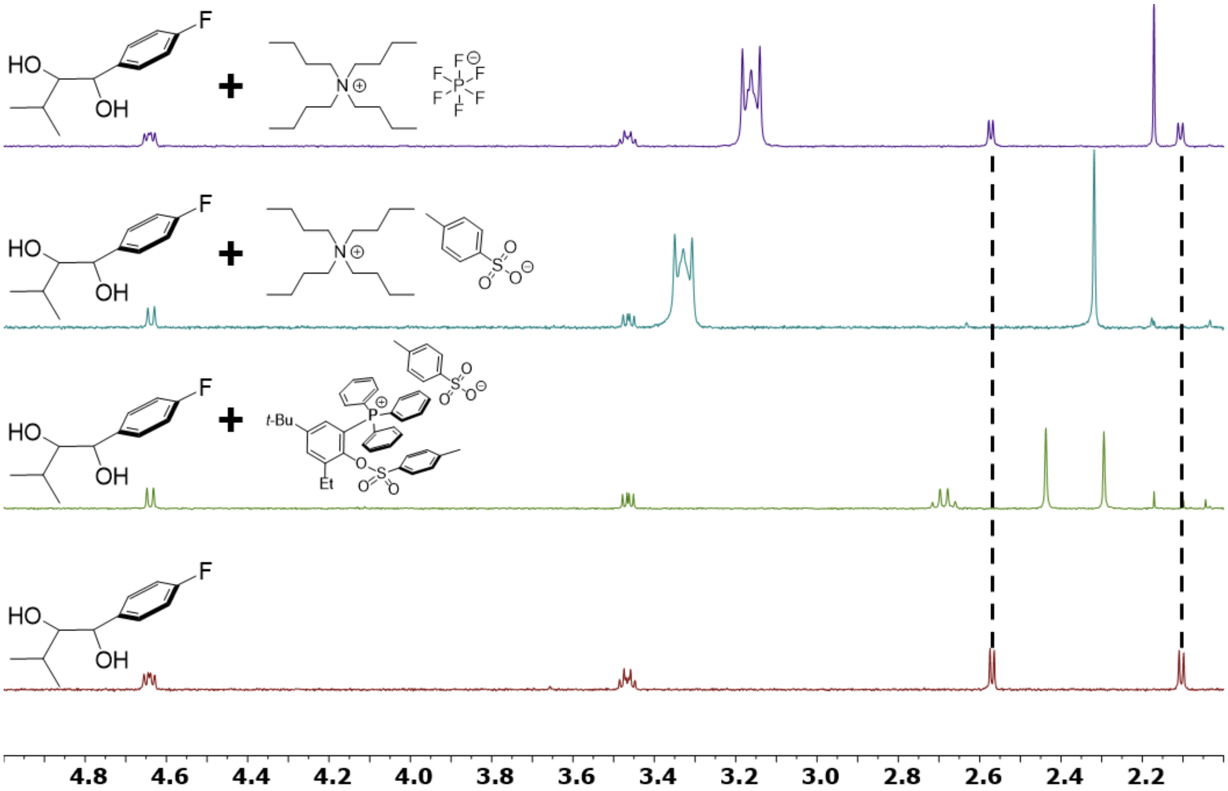
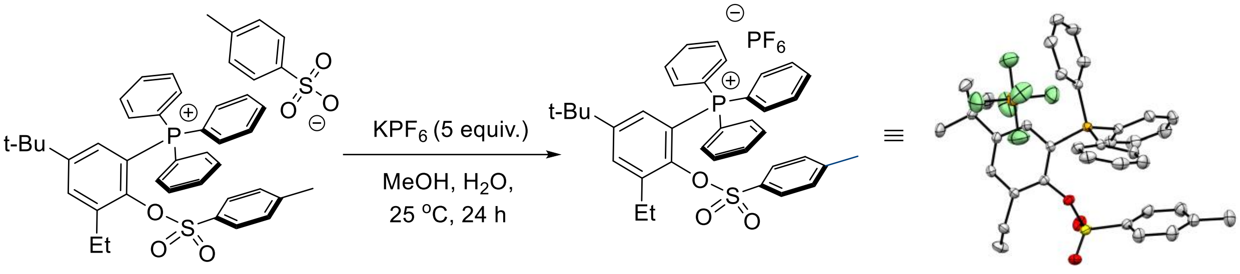


Figure S6. ^{1}H NMR spectra showing the interaction between **1b** (0.5 mM) and various salts in $CDCl_3$ at 298 K (2 equiv of each salt added).

The bottom spectrum corresponds to the free host (**1b**). Upon addition of the intermediate tosylate salt (**Int1**), clear deprotonation features were observed. To confirm that the deprotonation was induced by the tosylate anion rather than the intermediate itself, tetrabutylammonium tosylate (TBAOTs) was added to the host solution, which resulted in similar deprotonation behavior. To examine whether this effect could be suppressed by changing the counterion, the tosylate was replaced with hexafluorophosphate (PF_6^-), and the corresponding tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was tested. No significant deprotonation or host–anion interaction was observed in this case.Than the tosylate anion was therefore exchanged with PF_6^- to afford **Int2** which did not induce detectable deprotonation and proved suitable for subsequent binding studies.

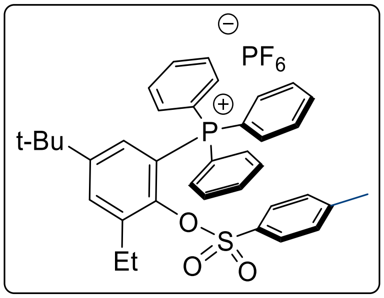
Procedure for the preparation of Int 2



Int1 **Int2** **X-ray of Int2**

A flame-dried vial was charged with phosphonium ylide **Int 1** (113.6 mg, 0.30 mmol, 1.0 equiv.) and MeOH (4 mL) and stirred until complete dissolution. In a separate vial, potassium hexafluorophosphate (276.1 mg, 1.50 mmol, 5.0 equiv.) was dissolved in distilled H_2O (1 mL). The aqueous KPF_6 solution was added to the MeOH solution of **Int 1** at room temperature, and the mixture was stirred at 25 ºC for 24 h. The resulting precipitate was collected by vacuum filtration, washed with cold H_2O to remove inorganic residues, followed by a small volume of cold acetone (or Et_2O), and dried under reduced pressure to afford **Int 2** as a solid (99 % yield).

(5-(*tert*-Butyl)-3-ethyl-2-(tosyloxy)phenyl)triphenylphosphonium hexafluorophosphane (Int2)



Prepared according to general procedure **V-I-1**.Yellow solid (96%, 0.5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 4H), 7.77 – 7.64 (m, 12H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.02 (td, *J* = 5.2, 2.6 Hz, 3H), 2.70 (q, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 1.22 (d, *J* = 7.5 Hz, 3H), 1.18 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.80, 148.07, 146.40, 141.20, 136.04 , 135.25, 134.38 , 132.47 , 132.19 , 130.33, 129.98, 126.97, 118.87, 117.97, 112.21, 111.31, 35.00, 30.81, 24.66 , 21.66 , 13.85; **IR** (CH_2Cl_2, cm^{-1}) 3050, 2960, 2925, 1600, 1500, 1350, 1175, 1030, 840, 560, 760; **High Resolution MS** (EI): Calculated for $C_{37}H_{38}O_3PS^+$ [M+H]$^+$: 594.2352, Found: 594.2313 (without negative anion i.e. $^-PF_6$). **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I*. **X-ray crystal structure** is available in the *Appendix II*.

V-II-2) ^{19}F NMR titration

A solution of 1-(4-fluorophenyl)-3-methylbutane-1,2-diol (**1b**) in 0.5 mL of $CDCl_3$ (0.5 mM) was used as the host for the titration experiments. A ^{19}F NMR spectrum was acquired after each stepwise addition of a 50 mM solution of the intermediate hexafluorophosphate salt (**Int2**) using a micropipette. ^{1}H NMR spectra were simultaneously recorded to verify the exact guest equivalents.To examine the possible influence of aggregation, ^{19}F NMR spectra were recorded at various **1b** concentrations (40, 20, 10, 5, 2.5, 1, and 0.25 mM). No significant chemical-shift changes were observed, indicating that aggregation effects were negligible under these conditions. NMR chemical shift titration data were analyzed under a fast-exchange assumption, with observed shifts modeled as host-weighted population averages (host resonances only). Candidate models included 1:1 binding (**H** + **G** ⇌ **HG**), 1:2 binding (**H** + **G** ⇌ **HG**; **HG** + **G** ⇌ **HG$_2$**), 2:1 binding (**H** + **G** ⇌ **HG**; **H** + **HG** ⇌ **H$_2$G**), and a non-binding linear drift. Parameters were estimated by nonlinear least squares (scipy.optimize.least_squares). The 1:1 model was solved analytically, while 1:2 and 2:1 were solved pointwise via Newton-Raphson on free guest with bisection fallback. Parameter uncertainties were obtained from bootstrap resampling, in which repeated refits with slightly varied initial guesses were used to assess fitting variability. Model comparison used Gaussian log-likelihood BIC as the primary criterion with AICc as a supplementary metric [Supramol. Chem. 2024, 36, 18]. Replicate datasets were fit simultaneously with shared binding constants and replicate-specific chemical shifts. Bootstrap confidence intervals were estimated with 1000 iterations using residual resampling.

Based on simultaneous fitting of replicate titration datasets, 1:1 binding model is best supported among the evaluated candidates. Among the evaluated models, this model has the lowest Bayesian Information Criterion (BIC = -389.73).

Code is available at https://github.com/dhsohn/nmr_bind_fit. The analysis runs with Python ≥ 3.9 and the following dependencies: numpy, pandas, scipy, matplotlib, openpyxl

Table S2. ^{19}F NMR titration data showing the chemical shift (δ, ppm) of **1b** (0.5 mM) upon incremental addition of **Int2**. Listed are the **Int2** concentrations used and the corresponding observed ^{19}F chemical shifts for three independent repeats (**Entry 1–3**).

Entry1		Entry2		Entry3	
Int2 Conc.	ppm	Int2 Conc.	ppm	Int2 Conc.	ppm
0	-117.4990	0	-117.5009	0	-117.5000
3.38E-05	-117.5026	2.18333E-05	-117.5037	2.95E-05	-117.5028
7.42E-05	-117.5063	4.96667E-05	-117.5047	5.18E-05	-117.5053
0.000107	-117.5084	0.000101	-117.5081	0.000124	-117.5092
0.000143	-117.5098	0.000192	-117.5142	0.000268	-117.5175

0.00018	-117.5135	0.000277	-117.5187	0.000511	-117.5250
0.000256	-117.5171	0.000497	-117.5259	0.000756	-117.5357
0.000398	-117.5227	0.000627167	-117.5334	0.001008	-117.5410
0.000605	-117.5296	0.001007	-117.5406	0.001225	-117.5451
0.000748	-117.5352	0.0011905	-117.5442	0.001363	-117.5473
0.000997	-117.5388	0.001499	-117.5502	0.001515	-117.5484
0.00137	-117.5460	0.0017515	-117.5515	0.001774	-117.5524
0.001594	-117.5496				

Table S3. Summary of model comparison metrics for binding analysis. The table reports the fitted binding constant with its confidence interval and standard error, together with residual sum of squares (RSS), root mean square error (RMSE), Bayesian Information Criterion (BIC), and corrected Akaike Information Criterion (AICc) for each candidate model. These metrics provide a basis for comparing relative fit quality and model complexity among the tested models.

Model	Binding Constant	Confidence Interval	Standard Error	Residual Sum of Squares	Root Mean Square Error	Bayesian Information Criterion	Corrected Akaike Information Criterion
H : G = 1 : 1	1006.38	[906.241, 1109.23]	51.1515	2.23189e-05	0.000776669	-389.73	-397.378
H : G = 1 : 2	15789.9;803.538	[1255.07, 1.22011e+11];[13.2475, 1020.3]	5.13254e+15; 301.616	2.03852e-05	0.000742261	-379.97	-383.432
H : G = 2 : 1	1221.12;4862.3	[27.3293, 2805.93];[196.48, 243879]	868.714;66978.6	2.08684e-05	0.000751006	-378.941	-382.403
Non-Binding	N/A	N/A	N/A	0.000650927	0.00419436	-267.807	-275.639

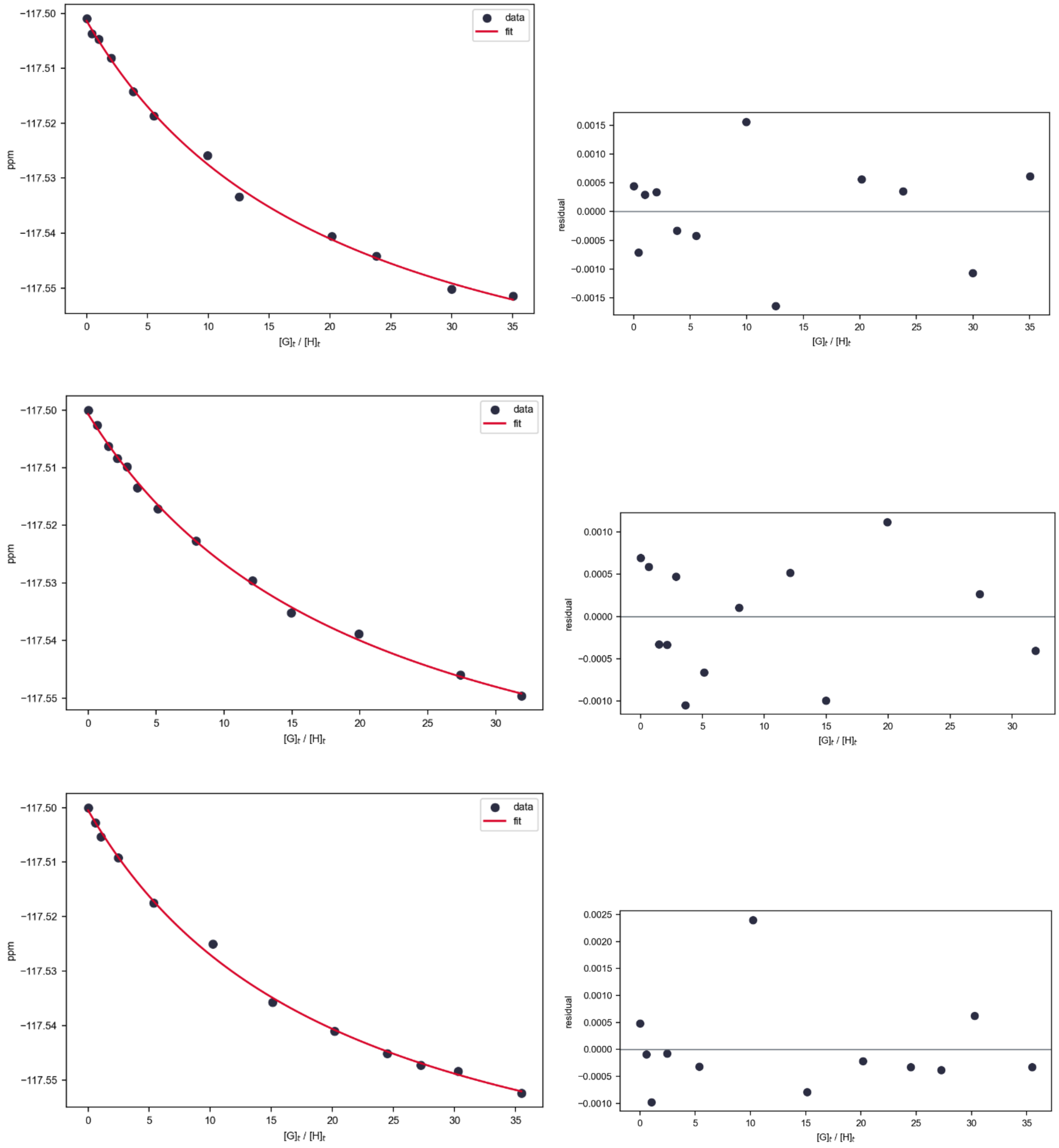


Figure S7. Binding isotherms for entries 1–3 fitted using an H:G = 1:1 model (left), together with the corresponding residual plots (right).

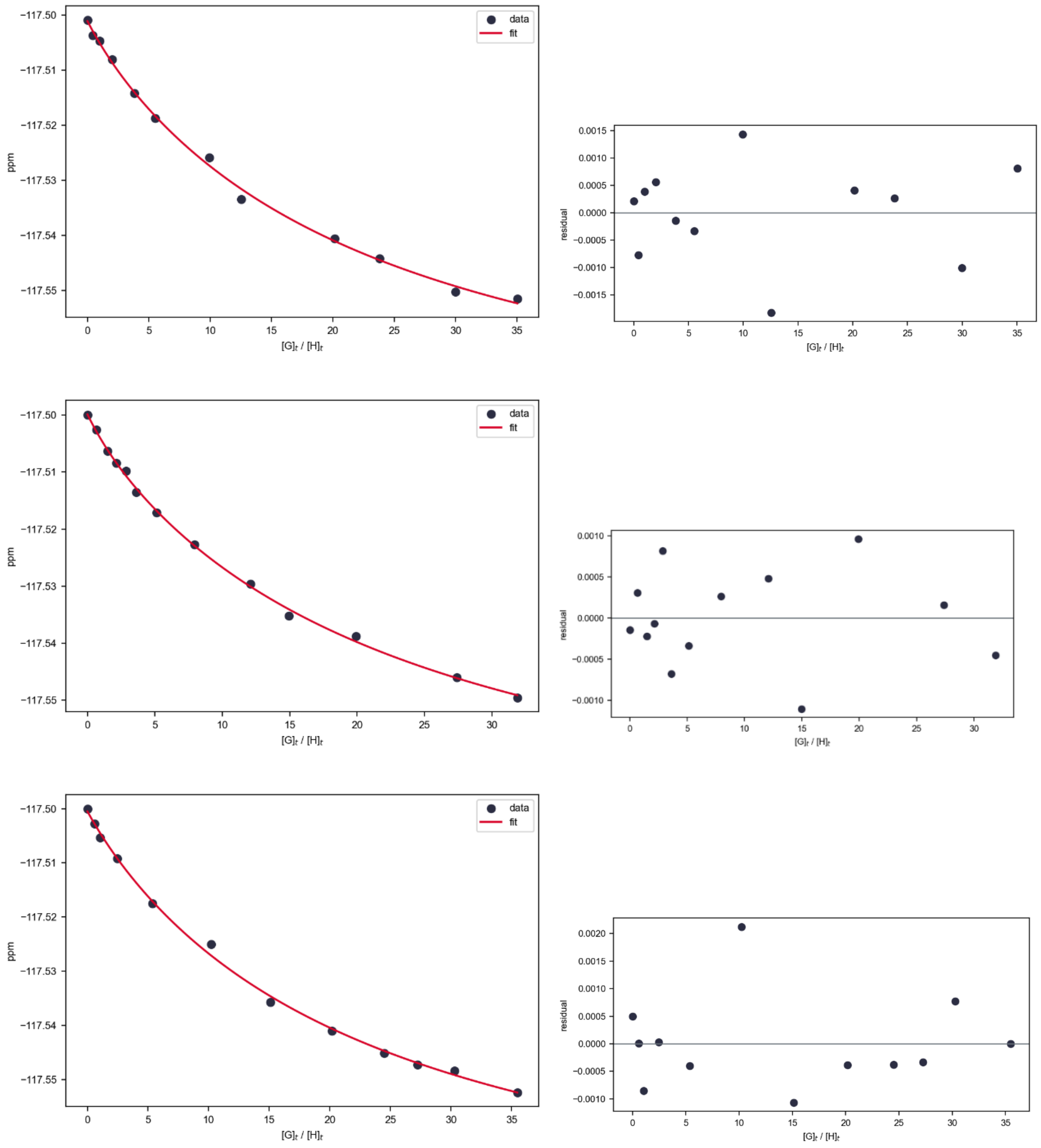


Figure S8. Binding isotherms for entries 1–3 fitted using an H:G = 1:2 model (left), together with the corresponding residual plots (right).

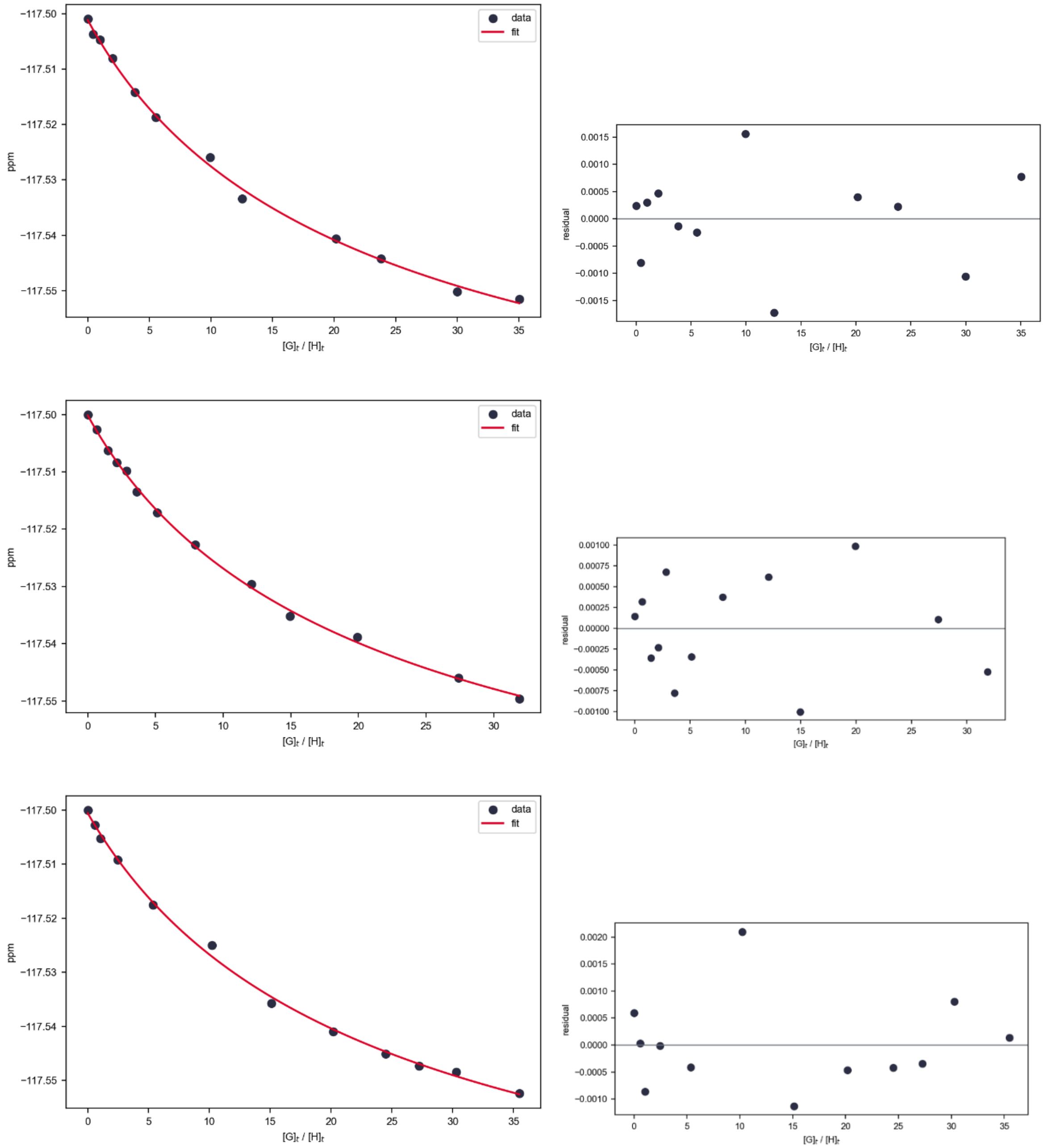


Figure S9. Binding isotherms for entries 1–3 fitted using an H:G = 2:1 model (left), together with the corresponding residual plots (right).

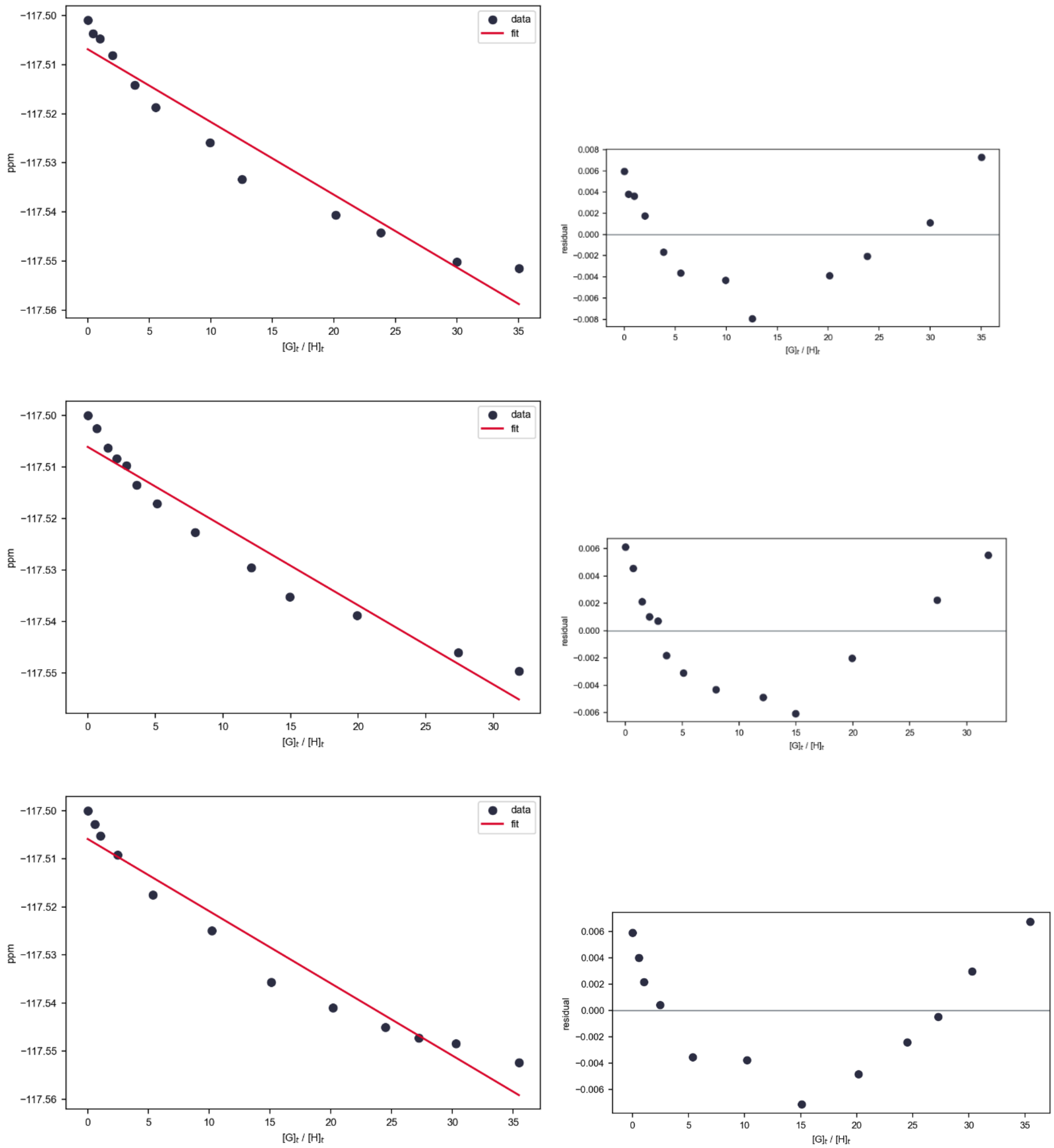


Figure S10. Binding isotherms for entries 1–3 fitted using a non-binding model (left), together with the corresponding residual plots (right).

V-II-3) ^{1}H DOSY NMR

All ^{1}H DOSY experiments were performed using the ledbpgp2s pulse sequence. Diffusion parameters were kept constant across measurements (p30 = 1000 µs; d20 = 60 ms). Spectra were acquired with 16 gradient increments (5–95% gradient strength), using NS = 16, DS = 4, and a relaxation delay of D1 = 10 s. All measurements were conducted at 20 mM in $CDCl_3$ at 298 K.

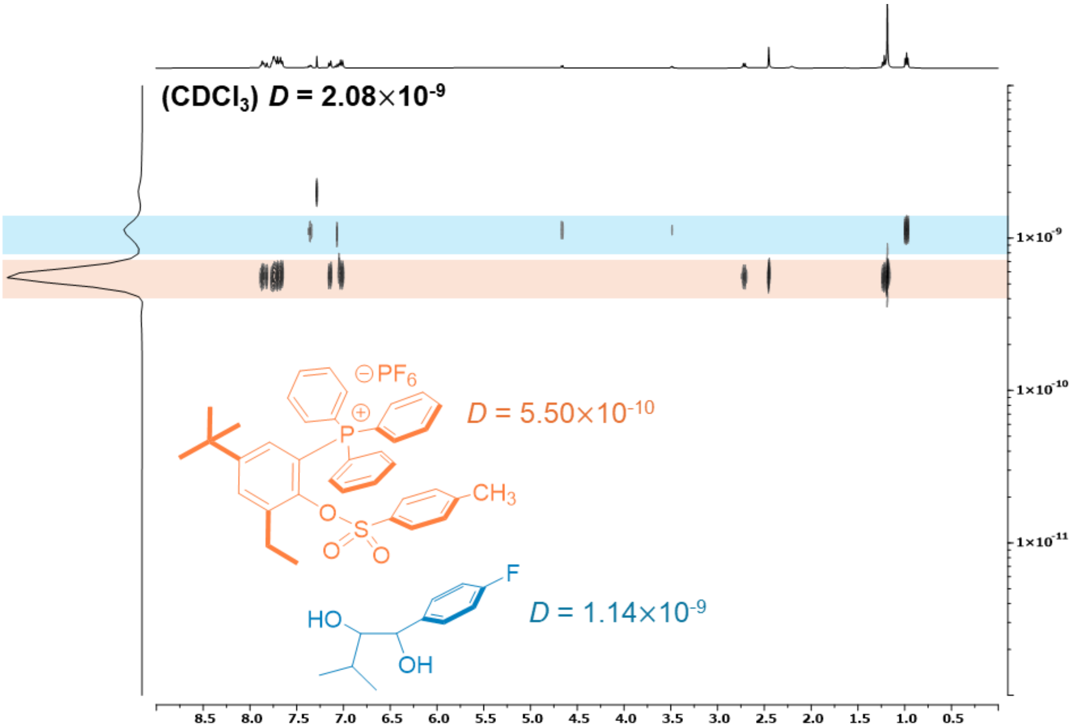


Figure S11. DOSY NMR spectrum in $CDCl_3$ of a mixture containing an orange PF_6^- salt (**Int2**) and a fluorinated aryl diol (**1b**). The components display distinct diffusion coefficients (D = 5.50×10^{-10} m^2 s^{-1} for **Int2**; D = 1.14×10^{-9} m^2 s^{-1} for **1b**). The diffusion coefficient of $CDCl_3$ is indicated for reference.

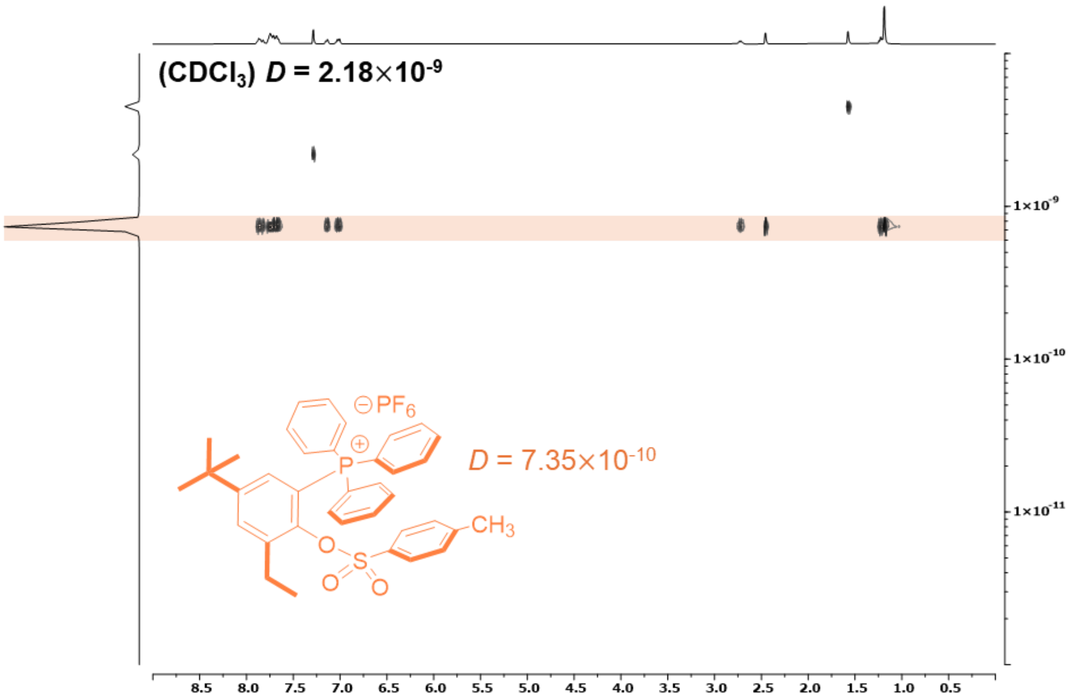


Figure S12. DOSY NMR spectrum in CDCl$_3$ of **Int2** (orange; PF$_6^-$ salt). The apparent diffusion coefficient is D = 7.35 × 10^{-10} m^2 s^{-1}; the diffusion coefficient of CDCl$_3$ is shown for reference.

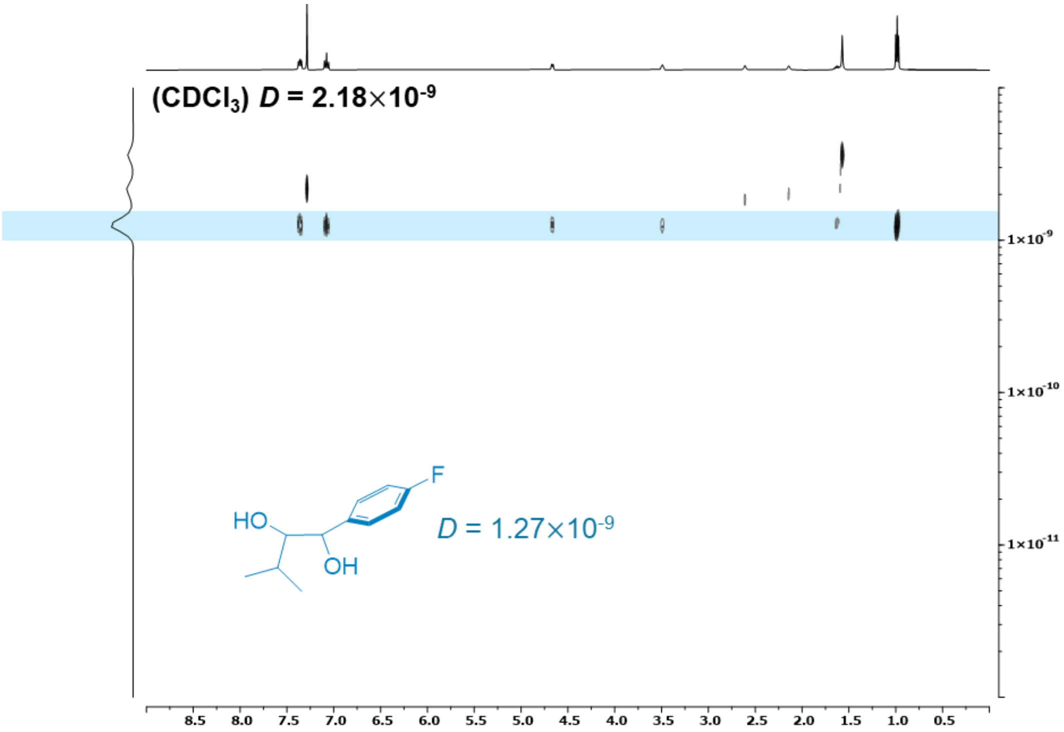


Figure S13. DOSY NMR spectrum in CDCl$_3$ of **1b** (blue; fluorinated aryl diol). The apparent diffusion coefficient is D = 1.27 × 10^{-9} m^2 s^{-1}; the diffusion coefficient of CDCl$_3$ is shown for reference.

V-II-4) ^{1}H–^{13}C HSQC NMR

All ^{1}H–^{13}C HSQC experiments were acquired using the hsqcetgpsisp2.2 pulse sequence. The one-bond heteronuclear coupling constant was defined as CNST2 (^{1}JCH) = 145 Hz. The 90° pulse lengths were calibrated as p1 (^{1}H 90°) = 9.8 µs and p3 (^{13}C 90°) = 10 µs. HSQC spectra were recorded with TD(F2) = 1024 and TD(F1) = 256, using NS = 8, DS = 32, and a relaxation delay of D1 = 2 s. All measurements were performed in $CDCl_3$ at 298 K.

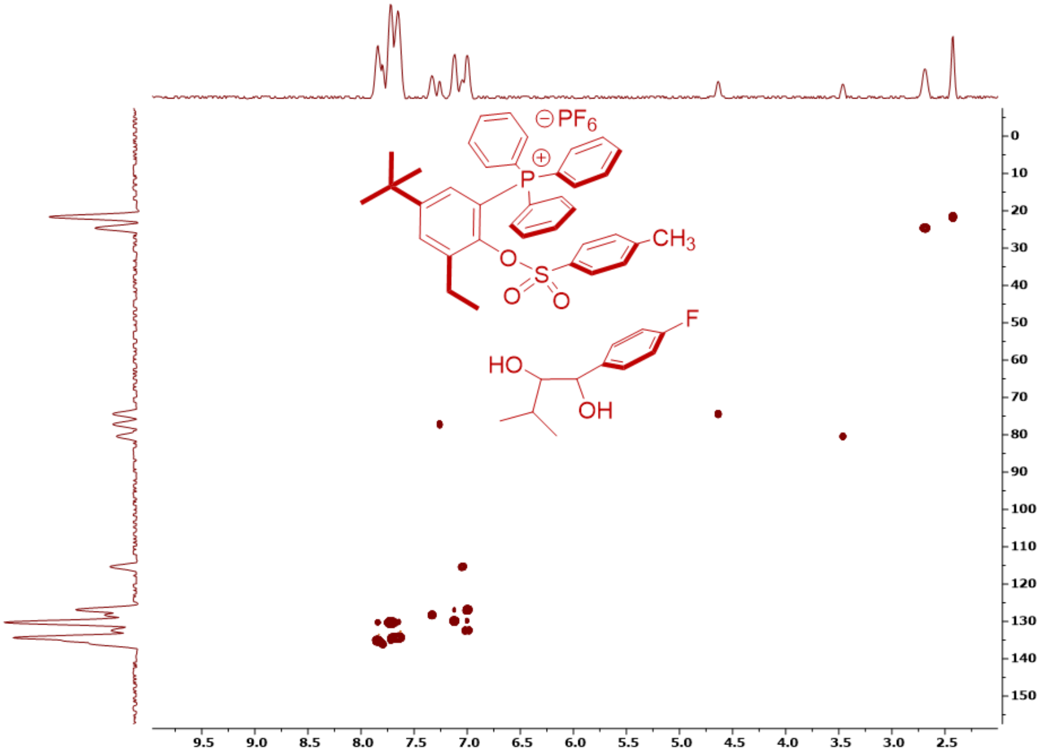


Figure S14. ^{1}H–^{13}C HSQC spectrum of 20 mM **1b** in the presence of 1 equiv. **Int2** recorded in $CDCl_3$ at 298 K.

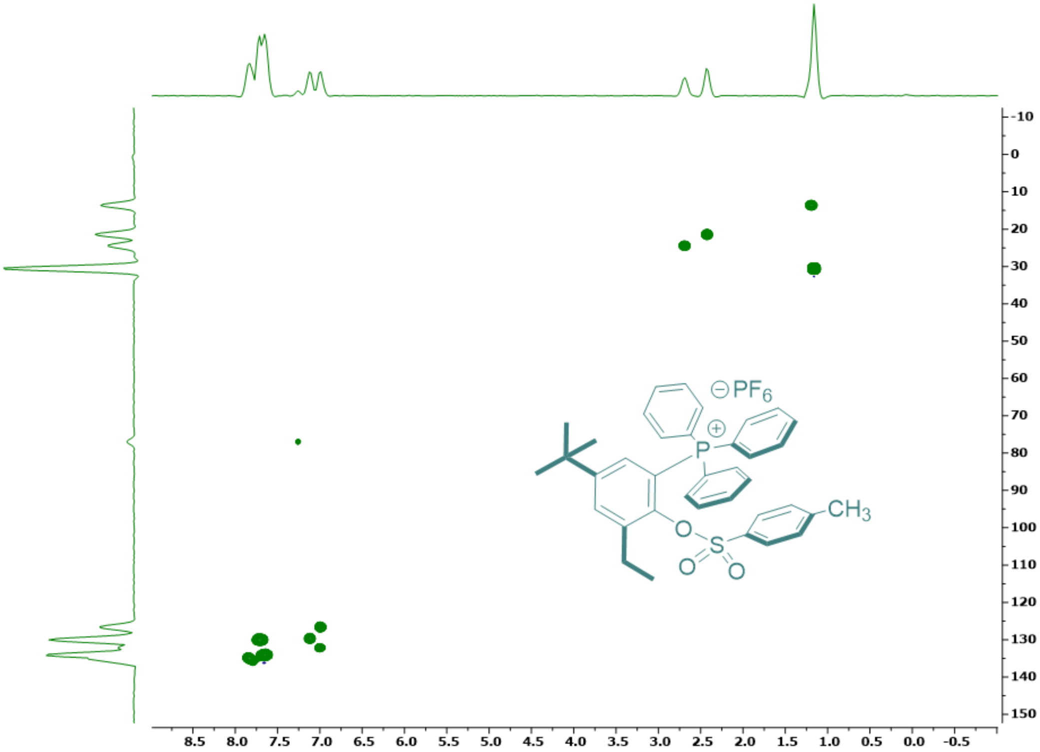


Figure S15. ^{1}H–^{13}C HSQC spectrum of 20 mM **Int2** recorded in CDCl₃ at 298 K.

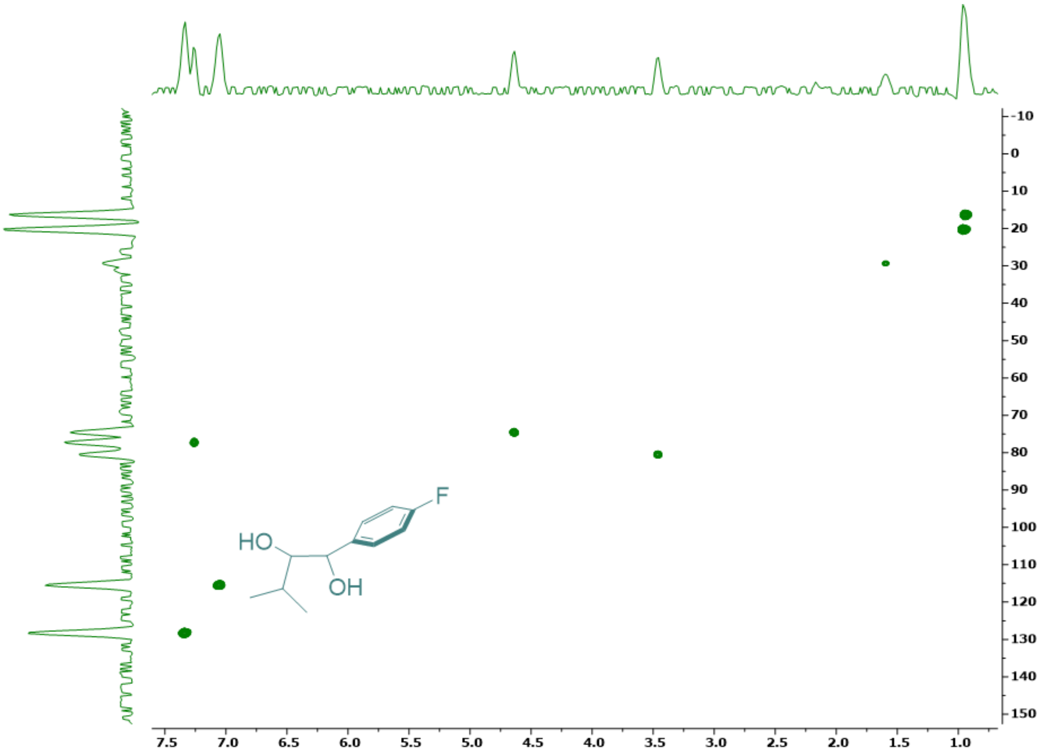


Figure S16. ^{1}H–^{13}C HSQC spectrum of 20mM **1b** recorded in CDCl₃ at 298 K.

V-III) π-Interaction Probe Experiments

V-III-1) Reduced Site-Selectivity in Non-Aromatic *Vicinal* Diols

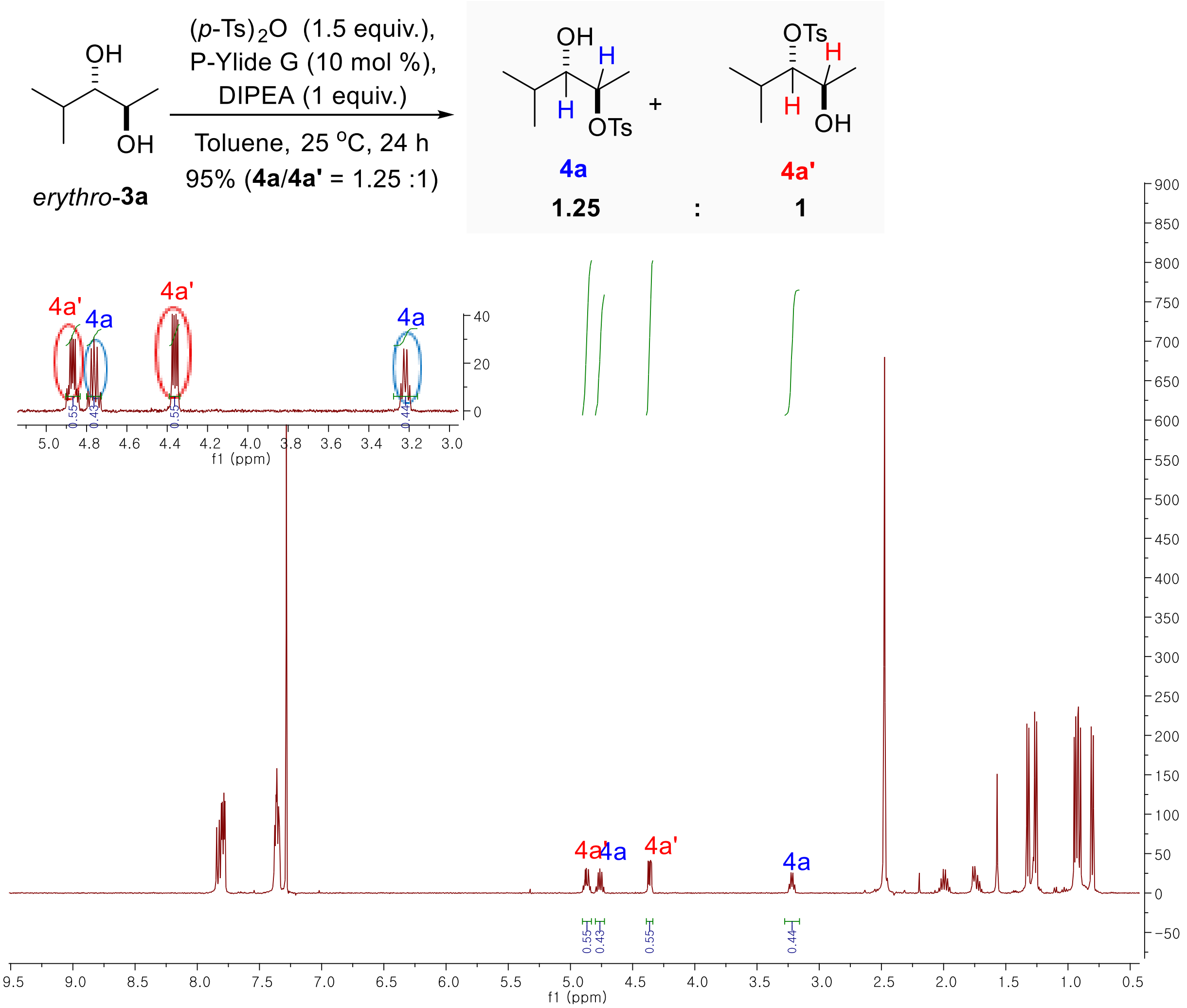
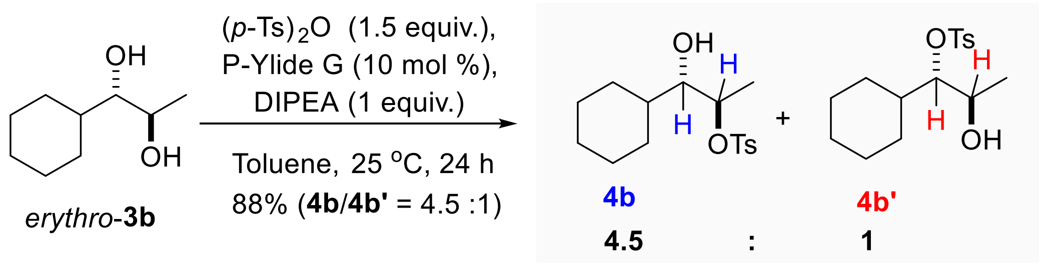


Figure S17. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of mixture of product **4a** and **4a**'.

Reactivity of non-aromatic 2°/2° vicinal diol **3a**, bearing iso-propyl and methyl substituents, was examined to probe the role of aromaticity in site-selectivity. Under the standard conditions, *threo*-**3a** afforded a mixture of regioisomeric tosylated products **4a** and **4a′** in 85% combined yield, with a ratio of **4a**/**4a′** = 1.25:1. This result indicates diminished site-selectivity in the absence of an aromatic π-interaction. The product distribution was determined by ^{1}H NMR analysis of the crude reaction mixture (400 MHz, CDCl$_3$), with diagnostic signals highlighted in the expanded region of the spectrum.



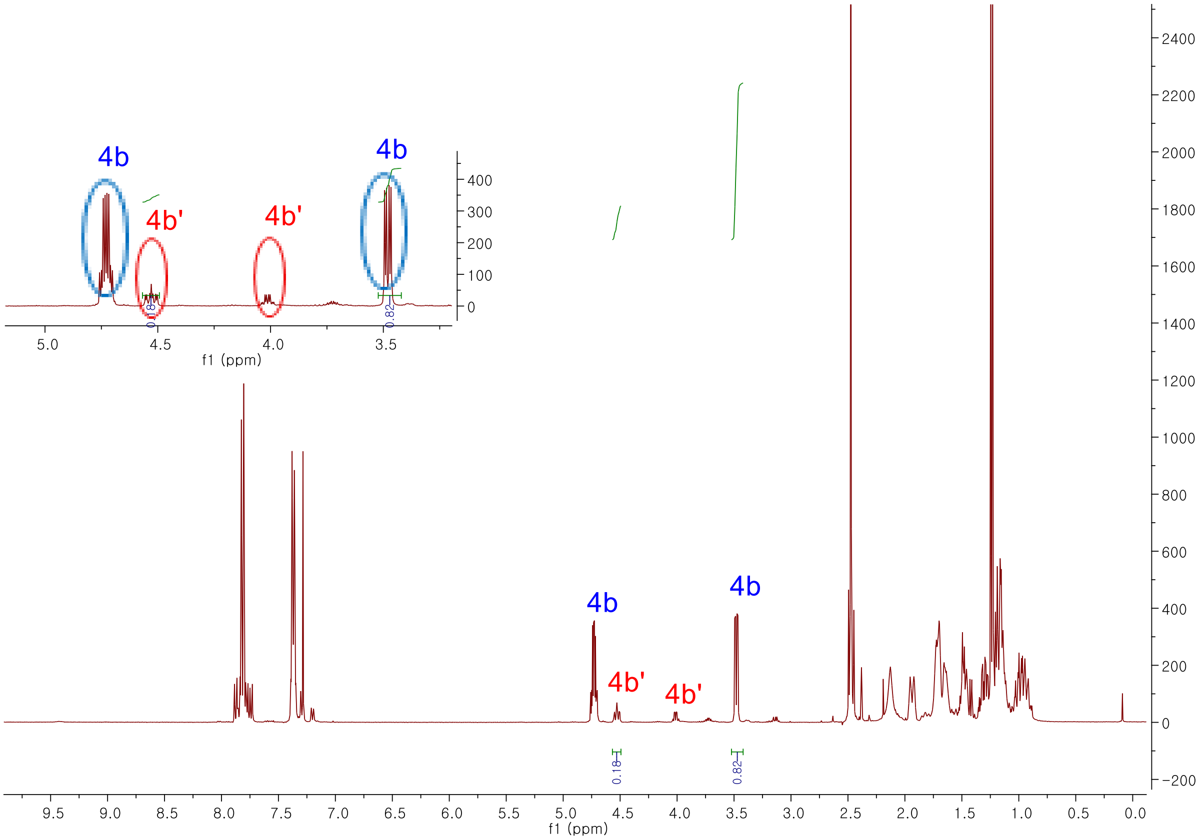
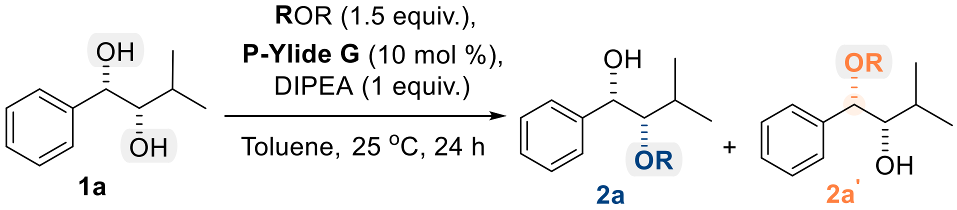


Figure S18. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of mixture of product **4b** and **4b'**.

In order to further evaluate whether aromatic π-interactions underlie the observed site-selectivity the non-aromatic 2°/2° diol ***erythro*-3b**, bearing cyclohexyl and methyl substituents were tested under standard condition which showed only modest steric bias (**4b**/**4b'** = 4.5:1). Although some degree of steric differentiation is evident, the pronounced erosion of selectivity relative to aromatic substrates indicates that steric effects alone cannot account for the high level of site discrimination. The regioisomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture (400 MHz, CDCl$_3$), and the diagnostic signals used for integration are highlighted in the expanded region of the spectrum.

V-III-2) Dependence of Regioselectivity on Electrophile Aromaticity.

Table S4. Role of electrophile aromaticity in determining regioselectivity



entry	ROR	Crude yield[a]	2a :2a'
1	Ac_2O	84%	1.17 :1
2	(*i*-PrCO)$_2$O	41%	1.3 :1
3	Ms_2O	69%	1.3 :1
4	Bz_2O	91%	13.5:1
5	(*p-Ts*)$_2$O	89%	88 :1

a) NMR yield was determined by using CH_2Br_2 as an internal standard

To investigate the influence of electrophile aromaticity on regioselectivity, a series of electrophiles (ROR) were screened under the standard reaction conditions using substrate **1a**. While aliphatic and less aromatic electrophiles such as Ac_2O, (i-PrCO)$_2$O, and Ms_2O provided low regioselectivity between products **2a** and **2a′**, aromatic electrophiles showed a significant improvement. In particular, Bz_2O increased the selectivity to 13.5:1, whereas (*p*-Ts)$_2$O exhibited the highest regioselectivity (**2a**:**2a′** = 88:1) along with high yield. These results indicate that increasing electrophile aromaticity enhances regioselective functionalization, consistent with a possible π-interaction effect in the transition state. The crude yields and regioisomeric ratios were determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard.

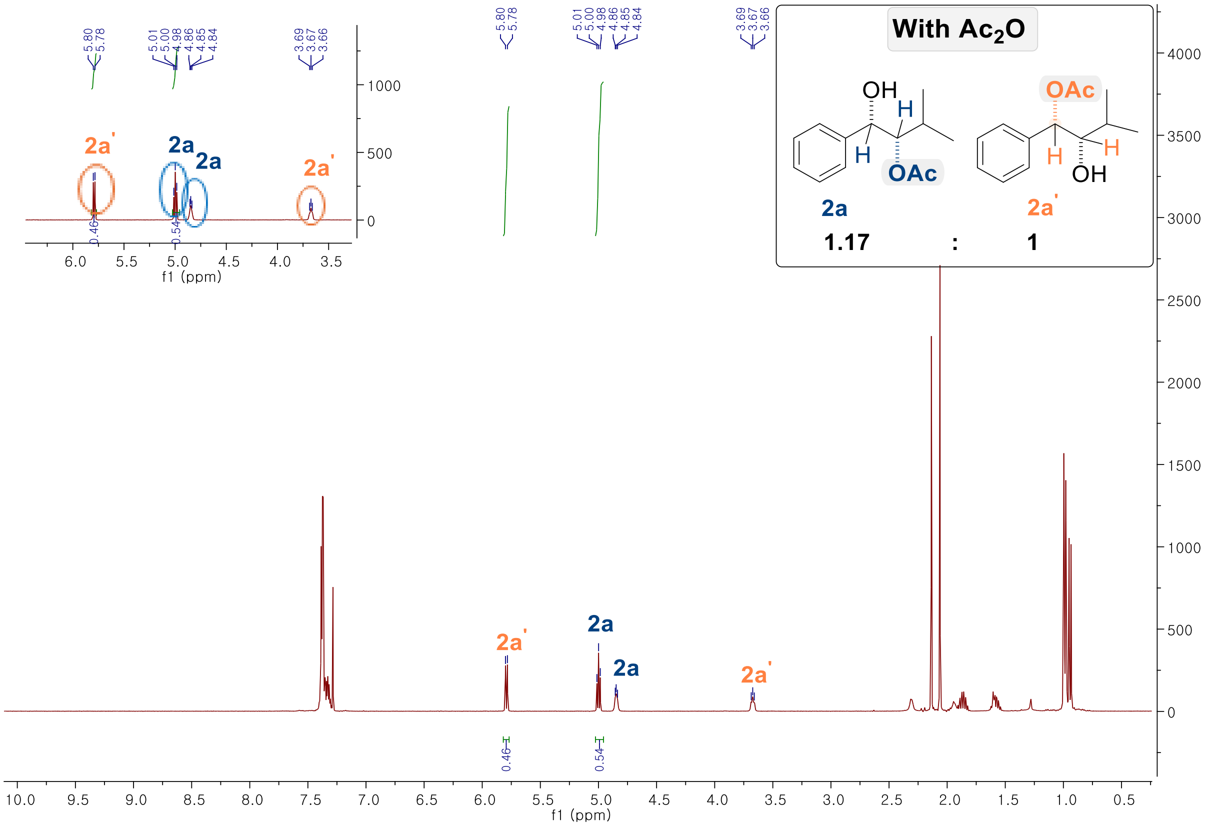


Figure S19. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of mixture of acylated product **2a** and **2a'**.

The ^{1}H NMR analysis of the crude reaction mixture obtained **using Ac₂O under** the standard conditions shows the formation of regioisomeric acylated products **2a** and **2a′** with low regioselectivity (**2a**:**2a′** = 1.17:1). The diagnostic signals corresponding to each regioisomer are highlighted in the expanded region of the spectrum and were used to determine the ratio by integration. These results indicate that acetic anhydride provides minimal differentiation between the two hydroxyl groups under the reaction conditions.

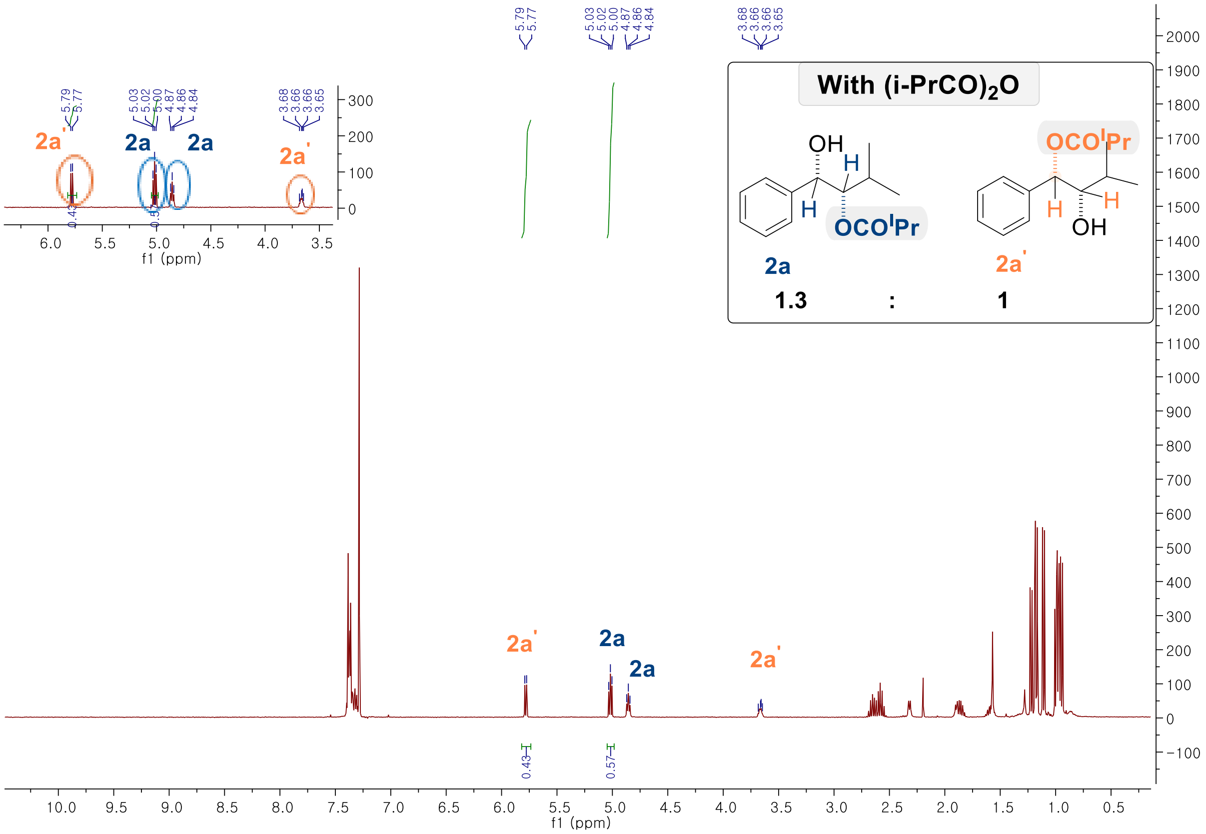


Figure S20. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of mixture of isopropylated product **2a** and **2a'**.

The ^{1}H NMR spectrum of the crude reaction mixture obtained using **(*i*-PrCO)$_2$O** under the standard conditions shows the formation of regioisomeric acylated products **2a** and **2a′** with low regioselectivity (**2a**:**2a′** = 1.3:1). The signals corresponding to each regioisomer were identified and integrated from the expanded region of the spectrum to determine the product ratio. This result indicates that the isopropyl anhydride provides no regioselective site discrimination between the two hydroxyl groups under the reaction conditions.

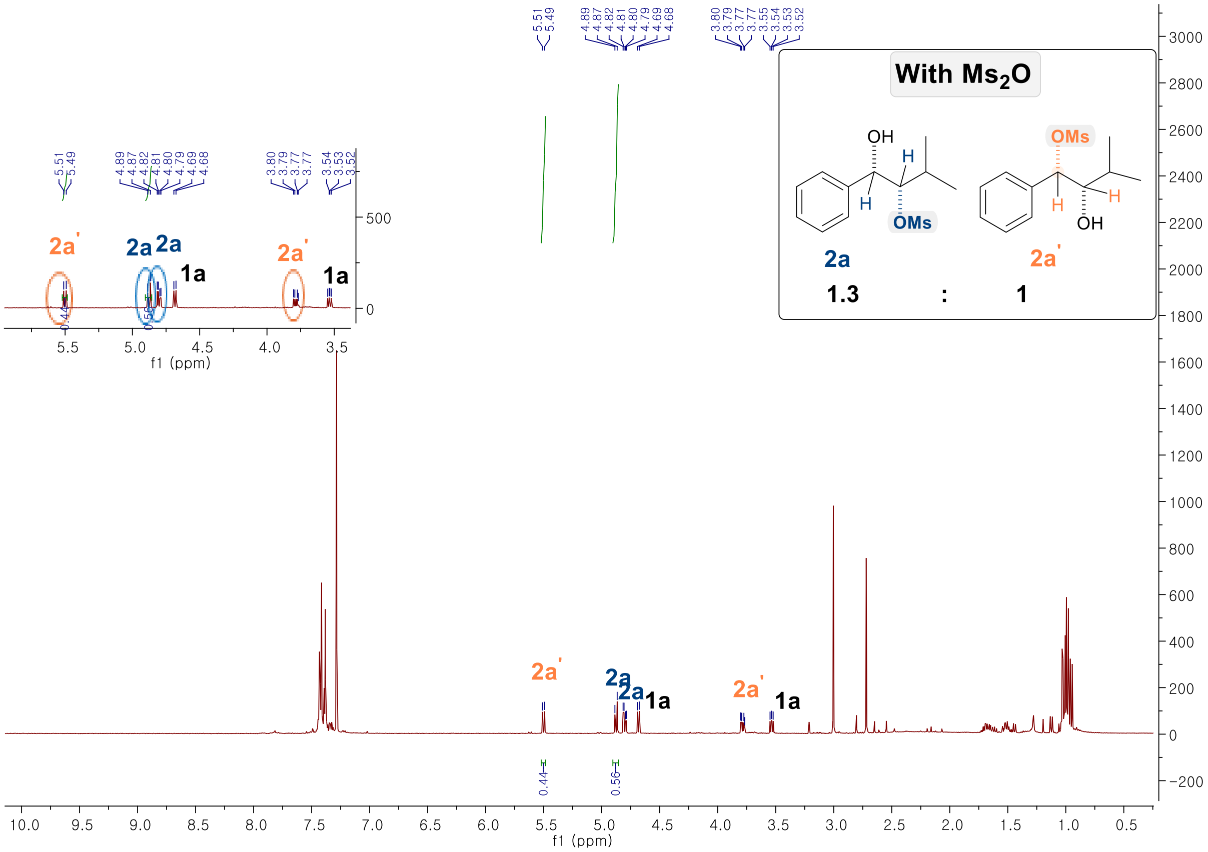


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of mixture of mesylated product **2a** and **2a'.**

The ^{1}H NMR spectrum of the crude reaction mixture obtained using mesyl anhydride **(Ms_2O)** under the standard conditions shows the formation of regioisomeric sulfonylated products **2a** and **2a′** with low regioselectivity (**2a**:**2a′** = 1.3:1). The diagnostic signals corresponding to each regioisomer were identified and integrated from the expanded region of the spectrum to determine the product ratio. This result indicates that mesyl anhydride provides almost no differentiation between the two hydroxyl groups under the reaction conditions.

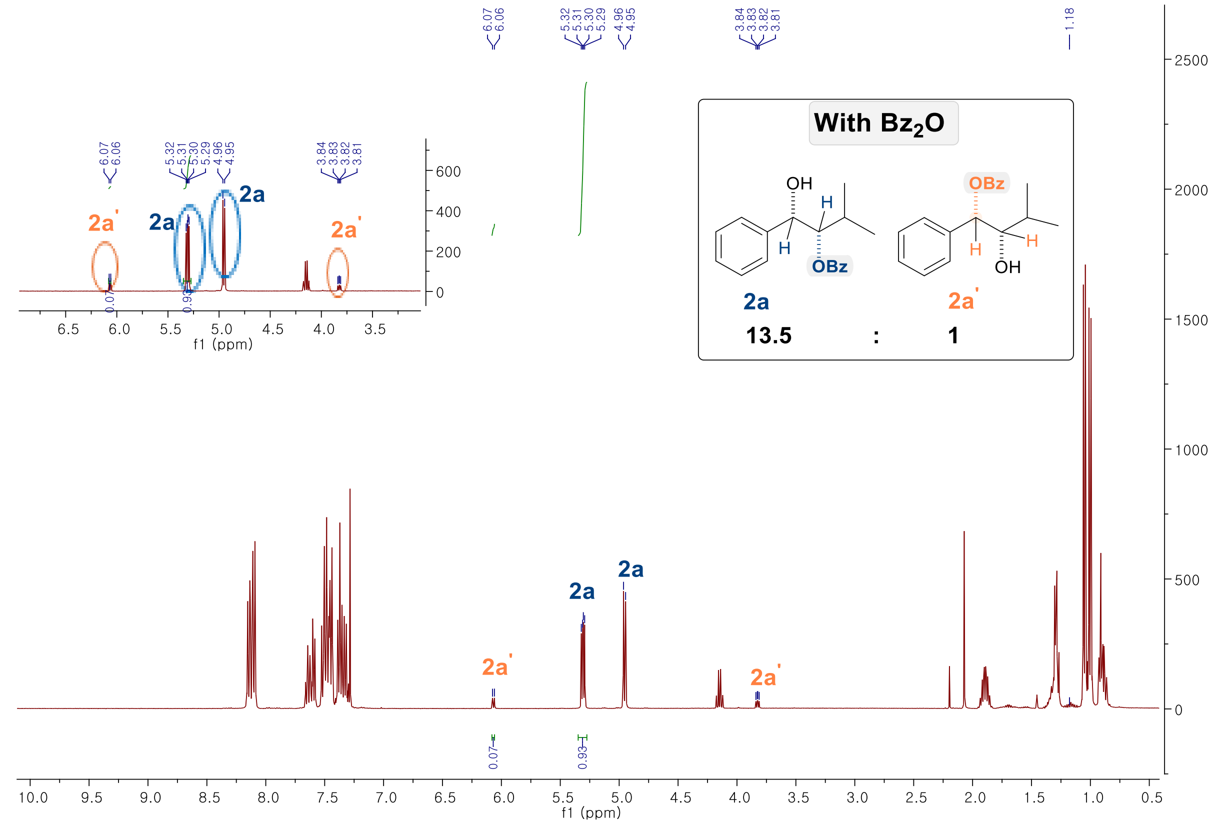


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of mixture of benzoylated product **2a** and **2a'.**

The ^{1}H NMR spectrum of the crude reaction mixture obtained using benzoic anhydride **(Bz_2O)** under the standard conditions shows the formation of regioisomeric acylated products **2a** and **2a′** with improved regioselectivity (**2a**:**2a′** = 13.5:1). The diagnostic signals corresponding to each regioisomer were identified and integrated from the expanded region of the spectrum to determine the product ratio. This result indicates that the aromatic electrophile enhances site differentiation between the two hydroxyl groups under the reaction conditions.

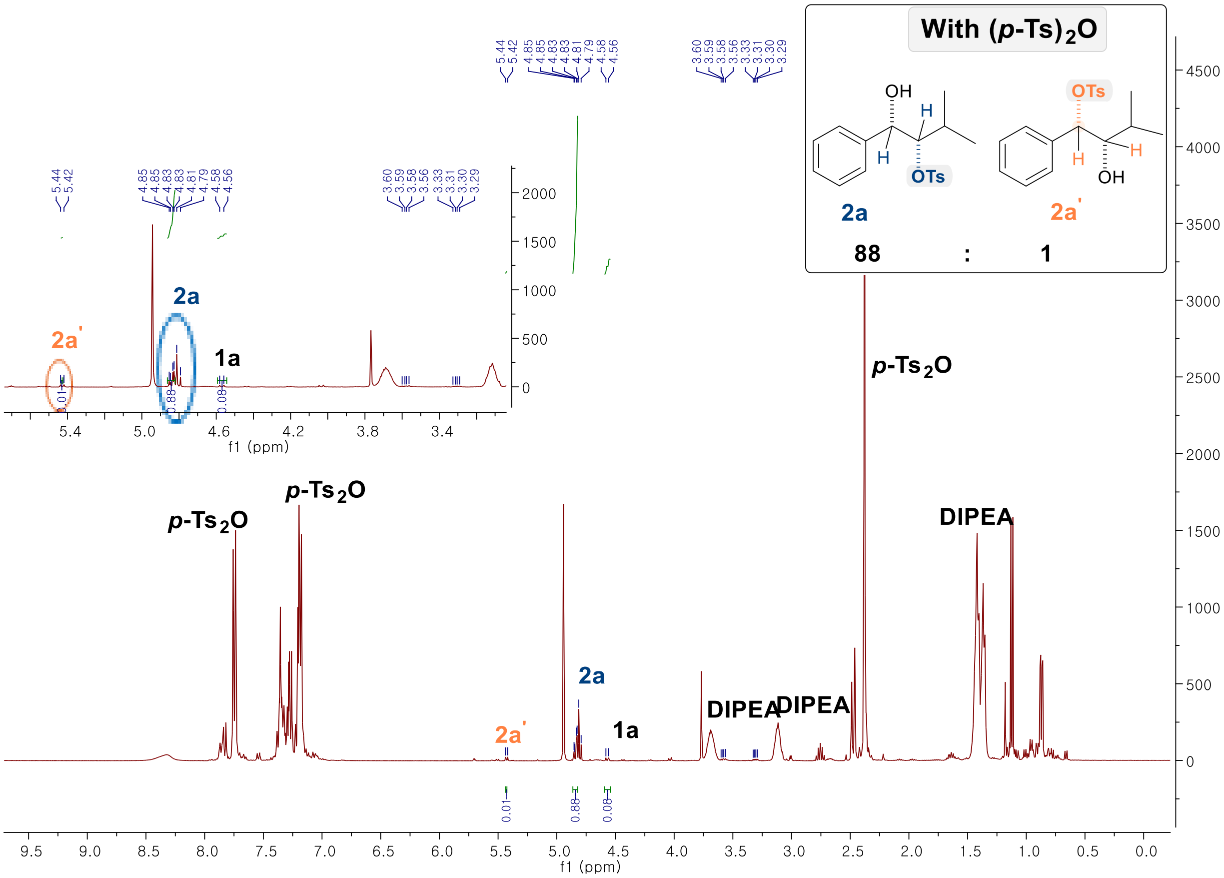


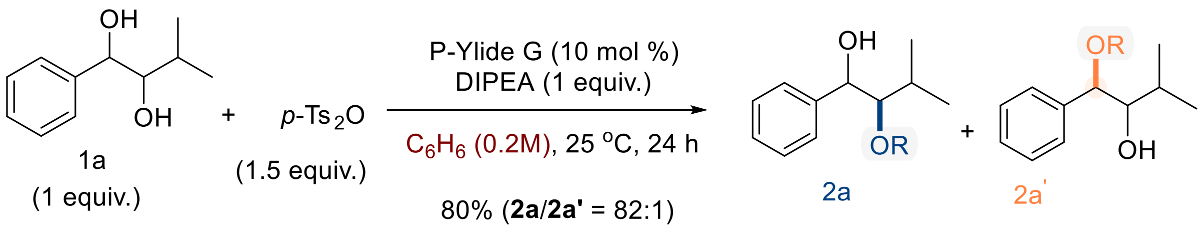
Figure S23. ^{1}H NMR (400 MHz, CDCl$_3$) of crude mixture of **2a** and **2a′** (after rotavap).

The ^{1}H NMR spectrum of the crude reaction mixture obtained using p-toluenesulfonic anhydride **((*p*-Ts)$_2$O)** under the standard conditions shows the formation of regioisomeric tosylated products **2a** and **2a′** with excellent regioselectivity (**2a**:**2a′** = 88:1). The diagnostic signals corresponding to each regioisomer were identified and integrated from the expanded region of the spectrum to determine the product ratio. This result indicates that the highly aromatic electrophile provides strong site differentiation between the two hydroxyl groups under the reaction conditions.

V-III-3) Competition Experiments Probing π–π Interactions in Site-Selective Tosylation

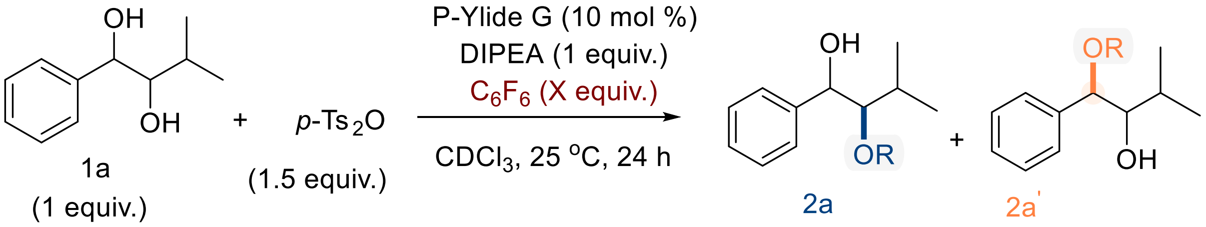
To probe the role of π–π interactions, competition experiments were performed using external aromatic additives. The reaction of the model substrate *threo*-1a was conducted under the optimized conditions, replacing toluene with benzene or hexafluorobenzene (C_6F_6) as aromatic additives. The addition of benzene (C_6H_6) had little effect on the reaction outcome under otherwise identical conditions. In contrast, increasing amounts of hexafluorobenzene (C_6F_6), a strong π-acceptor capable of engaging in donor–acceptor π–π interactions with electron-rich arenes, resulted in a gradual erosion of regioselectivity.

Experiment by using benzene as a solvent except toluene

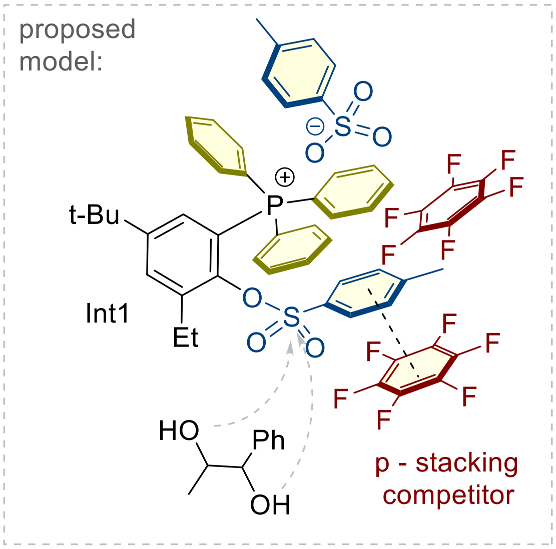


Competition experiments with hexafluorobenzene

Table S5. Effect of hexafluorobenzene loading on regioselectivity.



Entry	Inhibitor	equiv.	yield	2a/2a'
1	C_6F_6	5 equiv.	77%	8.63:1
2	C_6F_6	7 equiv.	66%	7.25:1
3	C_6F_6	10 equiv.	52%	4:1
4	C_6F_6	20 equiv.	39.5%	3:1
5	C_6F_6	30 equiv.	32.5%	2:1
6	C_6F_6	40 equiv.	32.5%	2:1



VI. Synthetic Applications

VI-I) Regioselective One-Pot Tosylation–Substitution for Benzylic Alcohol Derivatives

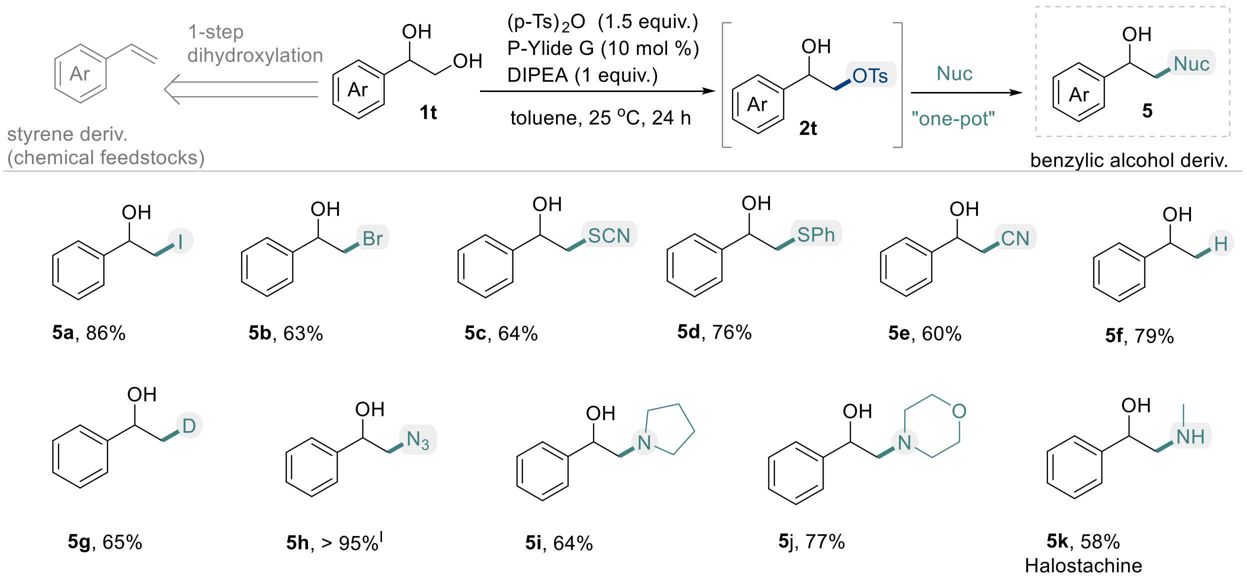


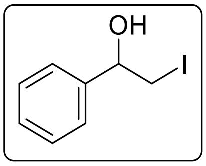
Figure S24. Diverse nucleophile incorporation via one-pot displacement of tosylate using substrate **1t**.

To demonstrate the synthetic utility of the regioselective tosylation, the resulting tosylates were subjected to substitution reactions with various external nucleophiles (**Figure. S24**). As diol **1t** is readily accessible from the chemical feedstock styrene, a sequential one-pot tosylation–substitution sequence offers an efficient approach for the diversification of benzylic alcohol frameworks. Under the optimized conditions, a broad array of nucleophiles—including I, Br, SCN, SPh, CN, hydride, deuteride, azide, and cyclic amines—were well tolerated, affording a diverse set of functionalized benzylic alcohol derivatives (**5a–5j**) in consistently moderate to high yields. Notably, reaction with methylamine furnished halostachine (**5k**), a naturally occurring sympathomimetic agent, further highlighting the modularity and synthetic versatility of this platform.

Procedure for the regioselective one-pot iodination (5a) and bromination (5b)

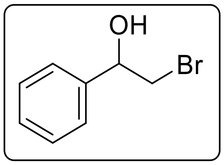
To an oven-dried screwed vial equipped with a triangular-shaped teflon stirrer bar was added diol (**1t**) (0.40 mmol, 1.0 equiv.) phosphonium ylide (**G**) (10 mol %), *p*-toluene sulfonic anhydride (0.6 mmol,1.5 equiv.), toluene (0.1 M), diisopropylethylamine (1 equiv.) and the reaction mixture was stirred at 25 ºC for 24 h. After that, remove the solvent by rota evaporator and then add the corresponding nucleophile NaI / NaBr (2.5 equiv.) and acetone (0.5 mL) and stir at 70 ºC for 12 h. After finishing the reaction, the mixture was concentrated under reduced pressure via rotavapor and extracted with water and DCM, washed with sodium thiosulfate, concentrated, and purified by flash column chromatography (eluent: n-hexane/EtOAc = 4:1) to afford product **5a/ 5b**.

2-Iodo-1-phenylethan-1-ol (5a)



Transparent liquid (86%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 4H), 7.36-7.34 (ddd, J = 5.0, 4.1, 1.5 Hz, 1H), 4.88-4.85 (dd, J = 8.8, 3.6 Hz, 1H), 3.55-3.51 (dd, J = 10.3, 3.6 Hz, 1H), 3.46-3.41 (dd, J = 10.3, 8.8 Hz, 1H), 2.45 (d, J = 15.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.12, 128.73, 128.41, 125.77, 74.07, 15.40; **IR** (CH_2Cl_2, cm^{-1}) 3364, 3029, 2916, 1452, 1261, 1173, 1053, 1025, 1001, 965, 762, 697, 643; **High Resolution MS** (EI): Calculated for $C_8H_9IO[M-H]^-$: 246.9625; Found, 246.9633. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

2-Bromo-1-phenylethan-1-ol (5b)

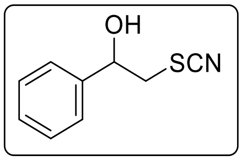


Transparent liquid (63%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 4H), 7.37 (ddd, J = 4.4, 2.4, 1.1 Hz, 1H), 4.96 (dd, J = 9.0, 3.3 Hz, 1H), 3.71 – 3.64 (m, 1H), 3.58 (dd, J = 10.5, 9.0 Hz, 1H), 2.63 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.27, 128.72, 128.51, 125.98, 73.83, 40.30; **IR** (CH_2Cl_2, cm^{-1}) 3366, 3024, 2910, 1450, 1266, 1176, 1054, 1022, 1005, 967, 764, 690, 644; **High Resolution MS** (EI): Calculated for $C_8H_9BrO[M-H]^-$: 198.9764; Found, 198.9762. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Procedure for the regioselective one-pot thiocyanation (5c)

To an oven-dried screwed vial equipped with a triangular-shaped teflon stirrer bar was added diol (**1t**) (0.40 mmol, 1.0 equiv.) phosphonium ylide (G) (10 mol %), *p*-toluene sulfonic anhydride (0.6 mmol, 1.5 equiv.), toluene (0.1 M), diisopropylethylamine (1 equiv.) and the reaction mixture was stirred at 25 °C for 24 h. After that, remove the solvent by rota evaporator and then add KSCN (4 equiv.) and CH_3CN (0.5 mL) and stirred at 70 °C for 12 h. After finishing the reaction, the mixture was concentrated under reduced pressure via rotavapor and extracted with water and DCM, washed with sodium chloride, concentrated and purified by flash column chromatography (eluent: n-hexane/EtOAc = 4:1) to afford product **5c**.

1-Phenyl-2-thiocyanatoethan-1-ol (5c)

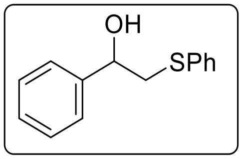


Transparent liquid (64%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 5H), 5.05 (dd, *J* = 8.7, 3.9 Hz, 1H), 3.30 (dd, *J* = 13.3, 3.9 Hz, 1H), 3.21 (dd, *J* = 13.3, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.70, 128.93, 125.86, 112.38, 72.71, 41.98; **IR** (CH_2Cl_2, cm^{-1}) 3421, 3029, 2154, 1453, 1275, 1082, 1056, 1027, 1003, 752, 698, 609; **High Resolution MS** (EI): Calculated for $C_9H_9NOS[M-H]^-$: 178.0332; Found, 178.0339. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Procedure for the regioselective one-pot nucleophile displacement with thiophenol (5d)

To an oven-dried screwed vial equipped with a triangular-shaped teflon stirrer bar was added diol (**1t**) (0.40 mmol, 1.0 equiv.) phosphonium ylide (**G**) (10 mol %), *p*-toluene sulfonic anhydride (0.6 mmol, 1.5 equiv.), toluene (0.1 M), diisopropylethylamine (1 equiv.) and the reaction mixture was stirred at 25 ºC for 24 h. After that, remove the solvent by rota evaporator. Take a separate 2 ml vial and add NaOH (2 equiv.), thiophenol (2 equiv.), and ethanol, and stir at 40 °C for 30 minutes, then add **2t** crude mixture dissolved in ethanol to it and stir at 40ºC for 14h. After finishing the reaction, the mixture was concentrated under reduced pressure via rotavapor and extracted with water and DCM, washed with sodium chloride, concentrated and purified by flash column chromatography (eluent: n-hexane/EtOAc = 4:1) to afford product **5d**.

1-Phenyl-2-(phenylthio)ethan-1-ol (5d)

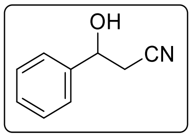


Transparent liquid (76%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.46 (dd, *J* = 5.6, 3.8 Hz, 5H), 7.40 – 7.30 (m, 20H), 7.26 (dd, *J* = 5.8, 3.6 Hz, 2H), 4.76 (dd, *J* = 9.5, 3.5 Hz, 3H), 3.36 (dd, *J* = 13.8, 3.5 Hz, 3H), 3.12 (dd, *J* = 13.8, 9.5 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 142.14, 134.86, 130.28, 129.17, 128.59, 128.03, 126.84, 125.86, 71.65, 44.10; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3389, 3061, 3026, 2919, 2851, 1584, 1479, 1275, 1261, 1053, 1024, 989, 911, 740, 691, 612; **High Resolution MS** (EI): Calculated for $C_{14}H_{14}OS[M-H]^-$: 229.0692; Found, 229.0694. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Procedure for the regioselective one-pot cyanation (5e)

To an oven-dried screwed vial equipped with a triangular-shaped teflon stirrer bar was added diol (**1t**) (0.40 mmol, 1.0 equiv.) phosphonium ylide (**G**) (10 mol %), *p*-toluene sulfonic anhydride (0.6 mmol, 1.5 equiv.), toluene (0.1 M), diisopropylethylamine (1 equiv.) and the reaction mixture was stirred at 25 ºC for 24 h. After that, remove the solvent by rota evaporator and then add NaCN (2.5 equiv.) and DMSO (0.5 mL) and stirred at 90 ºC 18 h. After finishing the reaction, the mixture was concentrated under reduced pressure via rotavapor and extracted with water and DCM, washed with sodium chloride, concentrated and purified by flash column chromatography (eluent: n-hexane/EtOAc = 4:1) to afford product **5e**.

3-Hydroxy-3-phenylpropanenitrile (5e)

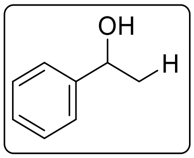


Transparent liquid (60 %, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.47 – 7.41 (m, 4H), 7.41 – 7.36 (m, 1H), 5.08 (t, J = 6.2 Hz, 1H), 2.86 – 2.75 (m, 2H), 2.36 (s, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 140.98, 128.96, 125.53, 117.19, 70.25, 27.95; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3435, 3021, 2150, 1450, 1265, 1080, 1051, 1023, 1010, 750, 695, 606; **High Resolution MS** (EI): Calculated for C$_9$H$_9$NO[M-H]$^-$: 146.0611; Found, 146.0604. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I*.

Procedure for the regioselective one-pot protonation and deutrration 5f, 5g.

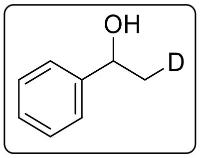
To an oven-dried screwed vial equipped with a triangular-shaped teflon stirrer bar was added diol (1t) (0.40 mmol, 1.0 equiv.) phosphonium ylide (**G**) (10 mol %), *p*-toluene sulfonic anhydride (0.6 mmol, 1.5 equiv.), toluene (0.1 M), diisopropylethylamine (1 equiv.) and the reaction mixture was stirred at 25 ºC for 24 h. After that, remove the solvent by rota evaporator. Take a separate 2 ml vial and add $LiAlH_4$/ $LiAlD_4$ (2 equiv.), diethylether, magnetic stirrer and and stir at 0 °C , then add **2t** crude mixture dissolved in diethylether to it and stir at 25 ºC for 14h. After finishing the reaction, the mixture was quenched with water and extracted with diethylether, washed with sodium chloride, concentrated and purified by flash column chromatography (eluent: n-hexane/EtOAc = 4:1) to afford product **5f / 5g.**

1-Phenylethan-1-ol (5f)



Transparent liquid (79%, 0.4 mmol scale); **^{1}H** and **^{13}C NMR spectra** is identical to those previously reported.[13]

1-Phenylethan-2-d-1-ol (5g)

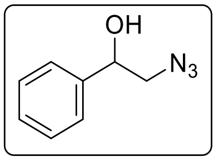


Transparent liquid (65%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 4H), 7.34 – 7.30 (m, 1H), 4.93 (t, J = 6.4 Hz, 1H), 1.79 (s, 1H), 1.55 – 1.48 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.81, 128.53, 127.51, 125.39, 70.41, 25.27 – 24.60; **IR** (CH_2Cl_2, cm^{-1}) 3357, 2933, 2855, 1723, 1602, 1452, 1275, 1261, 1089, 1059, 1026, 881, 805, 751, 698; **High Resolution MS** (EI): Calculated for $C_8H_9DO[M-H]^-$: 122.0721; Found, 122.0714. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

Procedure for the regioselective one-pot azidation (5h)

To an oven-dried screwed vial equipped with a triangular-shaped teflon stirrer bar was added diol (**1t**) (0.40 mmol, 1.0 equiv.) phosphonium ylide (**G**) (10 mol %), *p*-toluene sulfonic anhydride (0.6 mmol, 1.5 equiv.), toluene (0.1 M), diisopropylethylamine (1 equiv.) and the reaction mixture was stirred at 25 ºC for 24 h. After that, remove the solvent by rota evaporator and then add NaN_3 (2.5 equiv.) and DMF (0.5 mL) and stir at 70 ºC for 18 h. After finishing the reaction, the mixture was concentrated under reduced pressure via rotavapor and extracted with water and DCM, washed with sodium chloride, concentrated and purified by flash column chromatography (eluent: n-hexane/EtOAc = 4:1) to afford product **5h.**

2-Azido-1-phenylethan-1-ol (5h)

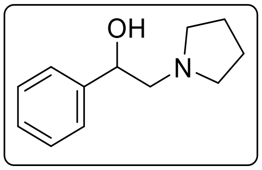


Yellow liquid (95%, 0.4 mmol scale); Prepared according to procedure **VI-V.** The ^{1}H and ^{13}C NMR spectra are identical to those previously reported. **^{1}H** and **^{13}C NMR spectra** is identical to those previously reported [14]

Procedure for the regioselective one-pot amination (5i-5k)

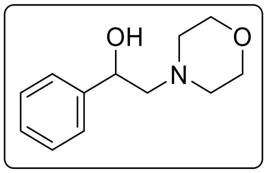
To an oven-dried screwed vial equipped with a triangular-shaped teflon stirrer bar was added diol (1x) (0.40 mmol, 1.0 equiv.) phosphonium ylide (G) (10 mol %), *p*-toluene sulfonic anhydride (0.6 mmol, 1.5 equiv.), toluene (0.1 M), diisopropylethylamine (1 equiv.) and the reaction mixture was stirred at 25 ºC for 24 h. After that, remove the solvent by rota evaporator and then add corresponding amine (3 equiv.) and DCM (0.5 mL) and stir at 50 ºC for 3 h. After finishing the reaction, the mixture was concentrated under reduced pressure via rotavapor and extracted with water and DCM, washed with sodium chloride, concentrated and purified by flash column chromatography (eluent: n-hexane/EtOAc = 4:1 to afford product **5i-k**.

1-Phenyl-2-(pyrrolidin-1-yl)ethan-1-ol (5i)



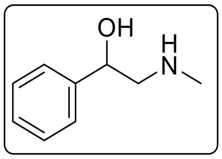
White solid (64%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 4H), 7.30 (dd, *J* = 4.0, 2.3 Hz, 1H), 4.73 (dd, *J* = 10.7, 3.3 Hz, 1H), 2.84 – 2.77 (m, 3H), 2.57 (dd, *J* = 6.8, 2.0 Hz, 2H), 2.51 (dd, *J* = 12.1, 3.3 Hz, 1H), 1.87 – 1.80 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.46, 128.31, 127.43, 125.88, 70.68, 64.09, 53.84, 23.70; **IR** (CH_2Cl_2, cm^{-1}) 3332, 3069,, 3022, 2965, 2929, 2806, 1449, 1261, 1122, 1067, 909, 880, 750, 696; **High Resolution MS** (EI): Calculated for $C_{12}H_{17}NO[M-H]^-$: 190.1237; Found, 190.1233. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

2-Morpholino-1-phenylethan-1-ol (5j)



White solid (51%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 4.79 (dd, *J* = 10.3, 3.6 Hz, 1H), 3.84 – 3.73 (m, 4H), 2.82 – 2.75 (m, 2H), 2.60 – 2.47 (m, 4H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.84, 128.42, 127.62, 125.85, 68.57, 67.04, 66.70, 53.48.; **IR** (CH_2Cl_2, cm^{-1}); 3425, 2962, 2855, 2812, 1452, 1273, 1114, 1064, 1032, 1006, 914, 867, 753, 700; **High Resolution MS** (EI): Calculated for $C_{12}H_{17}NO_2[M-H]^-$: 206.1186; Found, 206.1178. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

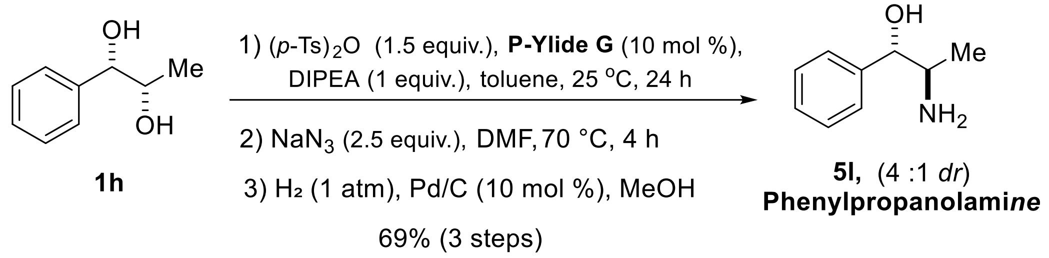
2-(Methylamino)-1-phenylethan-1-ol / Halostachine (5k)



White solid (88%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H), 7.33 – 7.29 (m, 1H), 4.75 (dd, J = 8.8, 3.7 Hz, 1H), 2.86 (dd, J = 12.1, 3.7 Hz, 1H), 2.75 (dd, J = 12.1, 8.9 Hz, 1H), 2.50 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.59, 128.39, 127.50, 125.83, 71.44, 59.22, 36.07.; **IR** (CH_2Cl_2, cm^{-1}) 3403, 3029, 2937, 2848, 2794, 1494, 1452, 1275, 1260,1050; **High Resolution MS** (EI): Calculated for $C_9H_{13}NO[M+H]^+$: 151.0992; Found, 151.0997. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

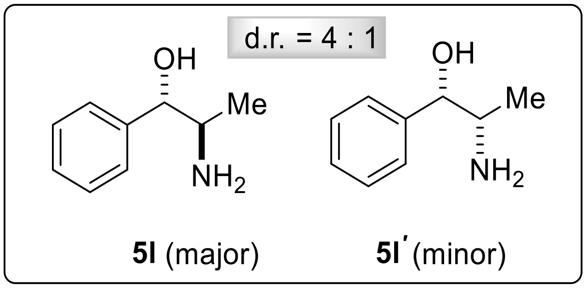
VI-II) Derivatization of Tosylates Toward Pharmaceutically Relevant Molecules.

VI-II-1) Synthesis of Phenylpropanolamine



Tosylate **2h** (prepared according to the general procedure **IV-1**) was dissolved in DMF (0.5 mL), and NaN_3 (2.5 equiv.) was added. The reaction mixture was stirred at 70 °C for 4 h. After completion of the reaction, the mixture was concentrated under reduced pressure and diluted with water, followed by extraction with DCM. The combined organic layers were washed with brine (saturated NaCl solution), dried, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent: n-hexane/EtOAc = 4:1) to afford the corresponding azide. The obtained azide was then dissolved in MeOH, and Pd/C (10 mol%) was added. The reaction mixture was stirred for 18 h at 25 °C under a hydrogen balloon atmosphere. Upon completion, the mixture was filtered through a celite pad, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: DCM/MeOH = 6:1) to afford the desired product **5l**.

Mixture of 2-amino-1-phenylpropan-1-ol / Phenylpropanolamine (5l and 5l')

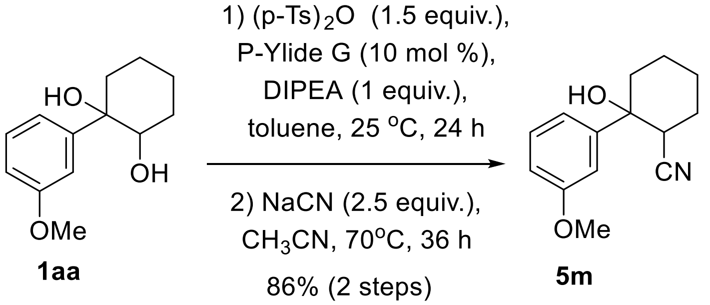


Product (69%, 0.3 mmol scale), **IR** (CH_2Cl_2, cm^{-1}) 3539, 2990, 2926, 1352, 1173, 1097, 1031, 898, 813, 748, 699, 665; **High Resolution MS (EI):** Calculated for diastereomeric mixture: $C_9H_{13}NO[M+H]^+$: 152.1070; Found, 152.1069 .

2-amino-1-phenylpropan-1-ol (5l) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 4H), 7.33 – 7.29 (m, 1H), 4.59 (d, J = 4.6 Hz, 1H), 3.32 – 3.21 (m, 1H), 2.19 (s, 2H), 0.99 (d, J = 6.5 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.19, 128.23, 127.52, 126.51, 77.24, 51.90, 18.02 . **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

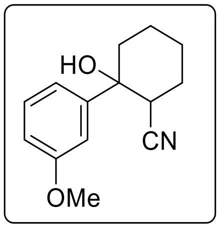
2-amino-1-phenylpropan-1-ol (5l') **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.40 – 7.37 (m, 4H), 7.32 (s, 1H), 4.28 (d, J = 6.7 Hz, 1H), 3.06 (p, J = 6.5 Hz, 1H), 2.19 (s, 2H), 1.07 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 142.57, 128.36, 127.64, 126.58, 78.56, 53.02, 20.55. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

VI-II-2) Synthesis of Tramadol Precursor



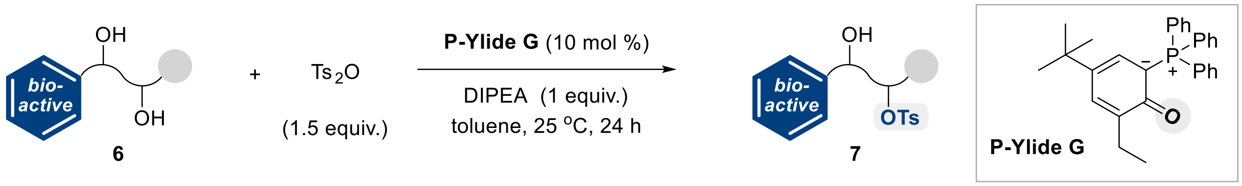
After the regioselectieve tosylation of **1aa** by following general procedure **IV-1** the resulting tosylate was treated with NaCN (2.5 equiv.) in acetonitrile and stir at 70 ºC for 36 h. After finishing the reaction was concentrated and the residue was purified by flash column chromatography on silica on silica gel (eluent: n-hexane/EtOAc = 4:1) to afford the corresponding product **5m**.

2-Hydroxy-2-(3-methoxyphenyl)cyclohexane-1-carbonitrile (5m)



Light yellow color oil (69%, 0.3 mmol scale); Prepared according to Procedure **VI-V.** The ^{1}H and ^{13}C NMR spectra are identical to those previously reported. The ^{1}H and ^{13}C NMR spectra are identical to those previously reported.**[15]**

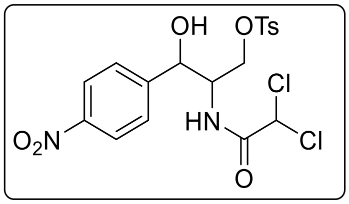
VI-III) Late-Stage Functionalization of Bioactive Diol Substrates.



General procedure for the regioselective tosylation of bioactive diol (7a-i)

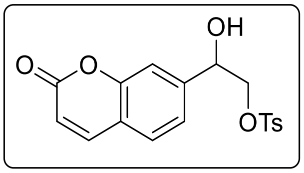
To an oven-dried screw-cap vial equipped with a triangular Teflon-coated stir bar were added diols **6a–e**, **6g–h** (0.40 mmol, 1.0 equiv.), **phosphonium ylide G** (17.53 mg, 10 mol%), p-toluenesulfonic anhydride (0.60 mmol, 1.5 equiv.), diisopropylethylamine (0.40 mmol, 1.0 equiv.), and toluene (0.1 M). The reaction mixture was stirred at 25 °C for 24 h. For diols **6f** and **6h**, *p*-toluenesulfonic anhydride (1.20 mmol, 3.0 equiv.) was used to improve the efficiency of the reaction. Upon completion of the reaction, the mixture was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (eluent: n-hexane/EtOAc = 6:1) to afford the corresponding mono-tosylated products.

2-(2,2-di-Chloroacetamido)-3-hydroxy-3-(4-nitrophenyl)propyl 4-methylbenzene sulfonate (7a) (from Chloramphenicol)



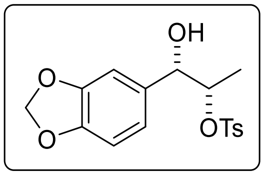
Light yellow color solid (69%, 0.3 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 – 8.17 (m, 2H), 7.87 – 7.81 (m, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.5 Hz, 1H), 5.75 (s, 1H), 5.32 (d, J = 2.6 Hz, 1H), 4.42 – 4.36 (m, 1H), 4.32 (dd, J = 10.1, 7.9 Hz, 1H), 4.09 (dd, J = 10.1, 4.7 Hz, 1H), 2.50 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.48, 147.65, 147.06, 145.86, 131.91, 130.23, 127.98, 126.80, 123.70, 69.95, 67.20, 65.87, 54.08, 21.73; **IR** (CH_2Cl_2, cm^{-1}) 3357, 2923, 2851, 2107, 1684, 1519, 1346, 1274, 1174, 1096, 984, 836, 811, 752, 702, 664; **High Resolution** MS (EI): Calculated for $C_{18}H_{18}Cl_2N_2O_7S[M-H]^-$: 475.0139; Found, 475.0135. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

2-Hydroxy-2-(2-oxo-2H-chromen-7-yl)ethyl 4-methylbenzenesulfonate (7b) (from Coumarin)



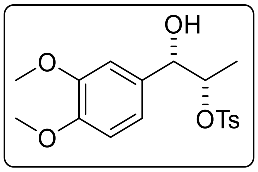
Light yellow color solid (54%, 0.3 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 9.5 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 5.0 Hz, 3H), 6.45 (d, *J* = 9.5 Hz, 1H), 5.09 (dd, *J* = 7.8, 3.4 Hz, 1H), 4.21 (dd, *J* = 10.6, 3.5 Hz, 1H), 4.09 (dd, *J* = 10.5, 7.9 Hz, 1H), 2.85 (s, 1H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 160.49, 154.12, 145.38, 142.93, 132.37, 130.02, 128.04, 122.28, 118.72, 117.02, 114.64, 73.67, 71.29, 21.71; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3503, 2919, 1729, 1620, 1353, 1261, 1174, 1100, 975, 842, 810, 751; **High Resolution** MS (EI): Calculated for C$_{18}$H$_{16}$O$_6$S[M-H]$^-$: 359.0595; Found, 359.0588. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(Benzo[d][1,3]dioxol-5-yl)-1-hydroxypropan-2-yl-4-methyl benzenesulfonate (7c) (from Isosafrole)



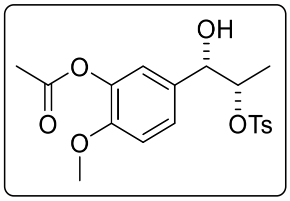
Transparent liquid (78%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.84 – 7.77 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 9.2, 2.1 Hz, 3H), 5.97 (s, 2H), 4.77 – 4.63 (m, 1H), 4.55 (d, *J* = 7.1 Hz, 1H), 2.47 (s, 3H), 2.24 (s, 1H), 1.15 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, CD$_3$OD) δ 147.44, 147.05, 144.55, 134.33, 133.76, 129.30, 127.43, 119.67, 107.33 , 106.63, 100.88 , 82.67, 74.62, 20.17, 16.32; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3510, 2983, 2933, 1515, 1260, 1232, 1173, 1160, 1137, 1025, 857, 806, 753; **High Resolution** MS (EI): Calculated for C$_{17}$H$_{18}$O$_6$S[M-H]$^-$: 349.0751; Found, 349.0751.**^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

1-(3,4-di-Methoxyphenyl)-1-hydroxypropan-2-yl 4-methylbenzenesulfonate (7d) (from Isoeugenol)



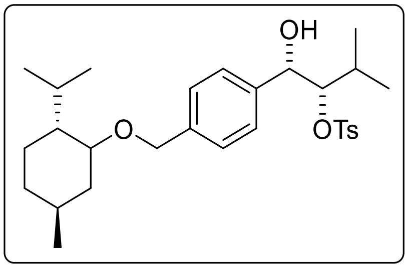
White solid (72%, 0.4 mmol scale); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.80 – 7.76 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.85 – 6.78 (m, 3H), 4.78 (p, *J* = 6.5 Hz, 1H), 4.59 (d, *J* = 7.0 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.47 (s, 3H), 1.16 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, CD$_2$Cl$_2$) δ 149.20, 144.98, 133.82, 131.61, 129.74, 127.59, 119.17, 111.05, 109.79, 83.37, 76.28, 55.69, 21.35, 17.23; **IR** (CH$_2$Cl$_2$, cm^{-1}) 3407, 2930, 1514, 1461, 1260, 1232, 1137, 1024, 912, 856, 809, 750; **High Resolution** MS (EI): Calculated for C$_{18}$H$_{22}$O$_6$S[M-H]$^-$: 365.1064; Found, 365.1065. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

5-(1-Hydroxy-2-(tosyloxy)propyl)-2-methoxyphenyl acetate (7e) (from Isovanillin)



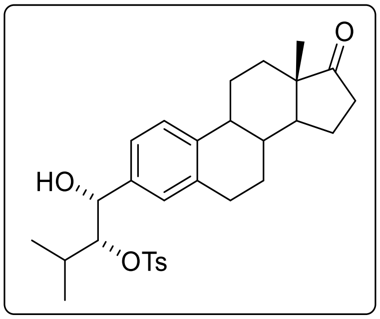
White solid (68%, 5 mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.1 Hz, 1H), 6.92 (d, J = 1.8 Hz, 1H), 6.85 (dd, J = 8.2, 1.8 Hz, 1H), 4.76 (p, J = 6.4 Hz, 1H), 4.64 (d, J = 6.5 Hz, 1H), 3.81 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H), 1.20 (d, J = 6.4 Hz, 3H); ^{13}**C NMR** (100 MHz, CD_3OD) δ 169.33, 150.69, 144.59, 139.65, 139.05, 133.46, 129.39, 127.32, 121.81, 118.21, 110.31, 82.37, 74.37, 54.65, 20.16, 19.09, 16.39; **IR** (CH_2Cl_2, cm^{-1}) 3514, 2926, 1763, 1350, 1274, 1189, 1174, 1157, 1120, 1033, 908, 750; **High Resolution** MS (EI): Calculated for $C_{19}H_{22}O_7S[M-H]^-$: 393.1013; Found, 393.1020. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

Hydroxy-1-(4-((((2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-3-methyl butan-2-yl-4-methylbenzenesulfonate (7f) (from (-)-Menthol)



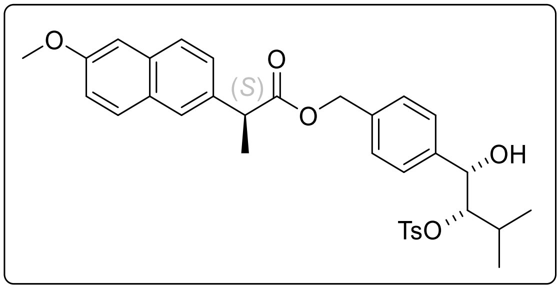
White solid (58%, 0.2mmol scale); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 4H), 7.38 – 7.30 (m, 12H), 4.82 (ddd, *J* = 19.5, 10.9, 5.3 Hz, 4H), 4.67 (d, *J* = 11.6 Hz, 2H), 4.41 (dd, *J* = 11.6, 1.9 Hz, 2H), 3.19 (td, *J* = 10.5, 4.1 Hz, 2H), 2.47 (s, 6H), 2.36 – 2.27 (m, 2H), 2.21 (d, *J* = 11.2 Hz, 2H), 1.72 –1.58 (m, 6H), 1.42 – 1.37 (m, 1H), 1.36 – 1.28 (m, 3H), 0.97 – 0.91 (m, 13H), 0.85 (d, *J* = 6.9 Hz, 12H), 0.73 (d, *J* = 6.9 Hz, 6H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 144.65, 139.5, 138.70, 134.26, 129.70, 128.23, 127.79, 127.03, 92.19, 78.93, 74.22, 70.08, 48.32, 40.33, 34.56, 31.59, 28.85, 25.54, 23.25, 22.38, 21.68, 21.03, 20.29, 16.06, 15.55; **IR** (CH_2Cl_2, cm^{-1}) 3521, 2958, 2923, 2866, 1452, 1342, 1172, 1093, 1069, 908, 874, 840, 812, 763, 749, 672; **High Resolution** MS (EI): Calculated for $C_{29}H_{42}O_5S[M-H]^-$: 501.2675; Found, 501.2679. ^{1}**H** and ^{13}**C NMR spectra** is available in the *Appendix I.*

1-Hydroxy-3-methyl-1-(-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)butan-2-yl 4-methylbenzenesulfonate (7g) (from Estrone)



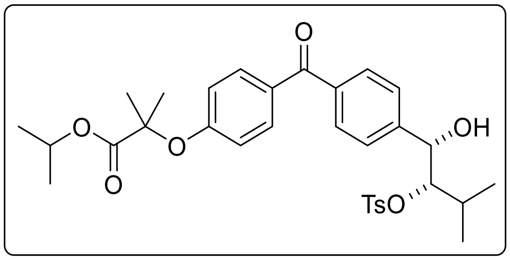
White solid (60%, 5 mmol scale); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.4, 1.9 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 2.2 Hz, 1H), 7.12 (dd, J = 8.1, 3.1 Hz, 2H), 4.89 – 4.84 (m, 1H), 4.73 (dd, J = 8.4, 1.6 Hz, 1H), 2.96 – 2.90 (m, 2H), 2.57 – 2.48 (m, 2H), 2.47 (s, 3H), 2.32 (t, J = 8.1 Hz, 1H), 2.22 – 2.09 (m, 2H), 2.06 – 1.98 (m, 2H), 1.65 (ddd, J = 10.6, 7.6, 4.7 Hz, 3H), 1.58 – 1.51 (m, 3H), 1.50 – 1.44 (m, 1H), 0.94 (d, J = 1.8 Hz, 3H), 0.88 (dd, J = 6.7, 5.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.78, 144.60, 140.15, 137.02, 134.36, 129.67, 127.78, 127.49, 125.66, 124.52, 92.13, 74.10, 50.55, 47.97, 44.40, 38.05, 35.86, 31.60, 29.38, 28.88, 26.45, 25.69, 21.65, 20.39, 15.53, 13.86; **IR** (CH_2Cl_2, cm^{-1}) 3482, 2929, 2862, 1736, 1340, 1261, 1173, 1095, 914, 847, 815, 750; **High Resolution** MS (EI): Calculated for $C_{30}H_{38}O_5S[M-H]^-$: 533.2332; Found, 533.2329. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

4-(1-Hydroxy-3-methyl-2-(tosyloxy)butyl)benzyl (2S)-2-(6-methoxynaphthalen-2-yl)propanoate (7h) (from Naproxen)



White solid (55%, 2 mmol scale); **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.75 (ddd, J = 24.6, 9.7, 5.0 Hz, 5H), 7.43 (dd, J = 8.5, 1.8 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.26 (q, J = 8.1 Hz, 4H), 7.20 – 7.15 (m, 2H), 5.19 – 5.08 (m, 2H), 4.81 – 4.73 (m, 2H), 3.98 (d, J = 7.1 Hz, 1H), 3.95 (d, J = 2.0 Hz, 3H), 2.80 (s, 1H), 2.46 (d, J = 2.7 Hz, 3H), 1.62 (d, J = 7.2 Hz, 3H), 1.60 (s, 1H), 1.30 (s, 1H), 0.92 – 0.81 (m, 6H); **^{13}C NMR** ((100 MHz, CD_3OD) δ 174.63, 157.79, 144.04, 140.92, 135.78, 135.45, 134.81, 133.91 , 129.19, 128.64, 127.26, 126.90, 126.35, 125.70, 118.63, 105.19, 91.79, 72.41, 65.66, 54.34, 45.23, 29.56 – 29.09, 22.81, 20.09, 18.84, 17.37, 16.52; **IR** (CH_2Cl_2, cm^{-1}) 3510, 2965, 2930, 1734, 1609, 1263, 1171, 1092, 908, 872, 853, 811, 735, 702, 672; **High Resolution** MS (EI): Calculated for $C_{33}H_{36}O_7S[M-H]^-$: 575.2109; Found, 575.2107. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

***iso*-Propyl 2-(4-(4-(1-hydroxy-3-methyl-2-(tosyloxy)butyl)benzoyl)phenoxy)-2-methylpropanoate (7i)** (from Fenofibrate)



White solid (56%, 0.2 mmol scale); **^{1}H NMR** (400 MHz, CD_3OD) δ 7.84 – 7.72 (m, 2H), 7.59 – 7.50 (m, 4H), 7.42 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 6.99 – 6.89 (m, 2H), 5.08 (dt, J = 12.5, 6.2 Hz, 1H), 4.95 (d, J = 4.3 Hz, 1H), 4.73 (dd, J = 5.9, 4.3 Hz, 1H), 2.37 (s, 3H), 2.06 (dq, J = 13.6, 6.9 Hz, 1H), 1.68 (s, 6H), 1.31 (s, 1H), 1.23 (d, J = 6.3 Hz, 6H), 1.06 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 195.56, 173.09, 159.84, 146.02, 144.22 , 136.88, 134.83, 131.69, 130.36, 129.27, 127.06, 126.27, 117.02, 91.75, 79.26, 72.18, 69.33 , 29.53, 24.35, 20.25 , 18.66 , 17.14; **IR** (CH_2Cl_2, cm^{-1}) 3496, 2976, 2923, 1730, 1598, 1276, 1259, 1173, 1147, 1099, 927, 802, 750, 763; **High Resolution** MS (EI): Calculated for $C_{32}H_{38}O_8S[M-H]^-$: 581.2214; Found, 581.2204. **^{1}H** and **^{13}C NMR spectra** is available in the *Appendix I.*

VII) Computational Data

All calculations were conducted using density functional theory (DFT)[16] implemented in Gaussian 09 suite of program.[17] All molecular structures were optimized by B3LYP-D3 functional[18] with 6-31G** basis set[19]. 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[20] solvation model and carried out at the same level as single-point calculations (solvent = toluene). Finally, to increase the accuracy of the integration grid, we used the int = ultrafine option for all types of calculations. Noncovalent interaction (NCI) analysis was performed using Multiwfn with a .wfn file generated from the Gaussian 09 quantum chemical package.[21] Geometry optimization and wavefunction calculations were conducted at at the SMD(toluene)-B3LYP-D3/6–311++G** level of theory.

Noncovalent Interaction Analysis of the Int2-1b Complex

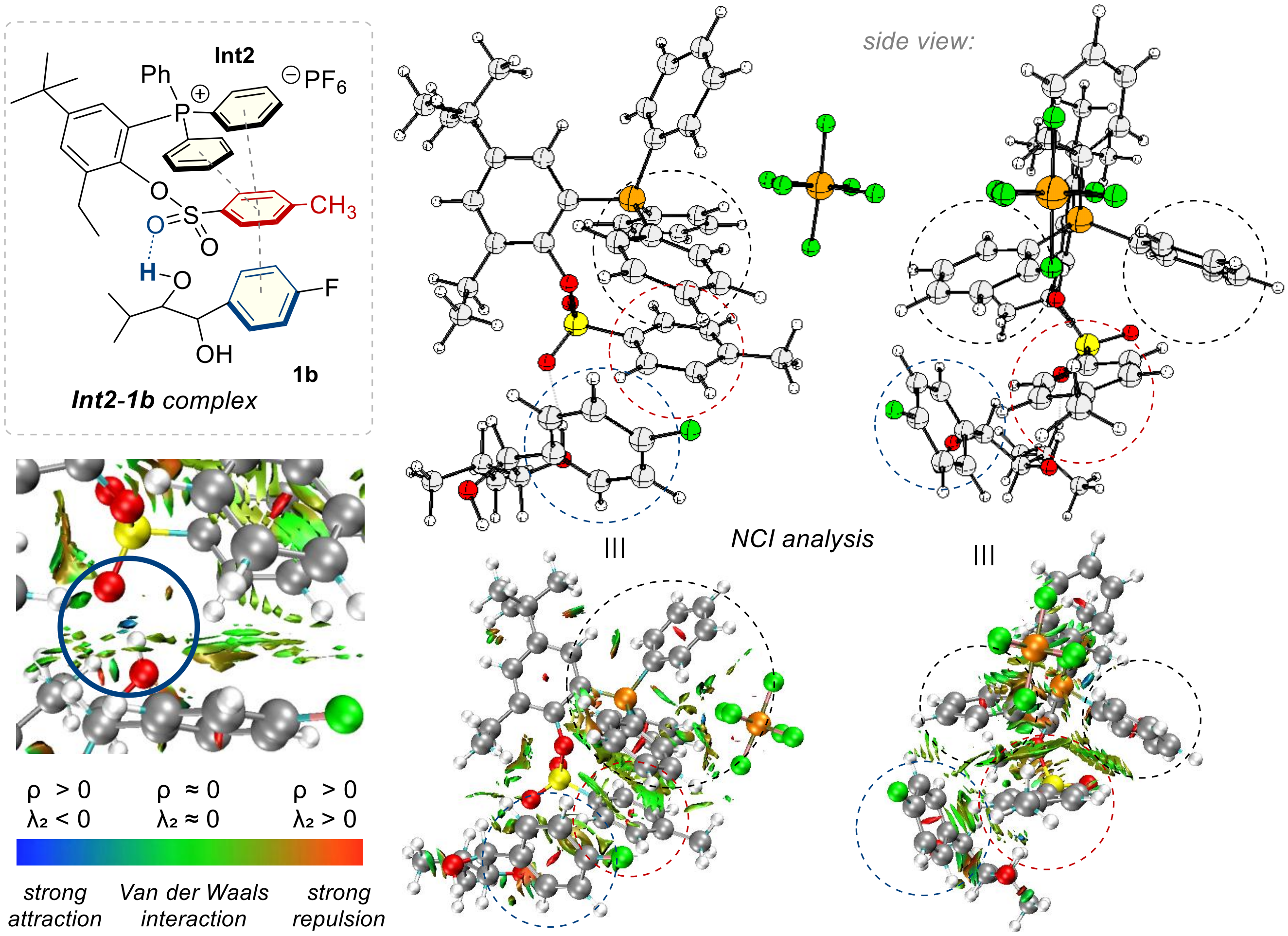


Figure 25. DFT-optimized structure and NCI analysis of the ***Int2*–1b** complex highlighting cooperative π-mediated and hydrogen-bonding interactions

To gain deeper insight into the binding mode between **Int2** and **1b**, the geometry of the **Int2–1b complex** was optimized using DFT calculations, followed by noncovalent interaction (NCI) analysis (**Figure S25**). The optimized structure preserves the characteristic umbrella-like architecture of **Int2**, in which multiple aryl groups are arranged in a convergent manner to define a confined binding environment.

The NCI analysis of this structure reveals multiple green isosurfaces distributed throughout the aryl-rich framework of **Int2**, consistent with a network of weak attractive interactions within the umbrella-like assembly. These interactions are highlighted by the dotted circles corresponding to each aromatic unit (red dotted circle and black dotted circle). Importantly, the presence of these green isosurfaces ($\mathrm{sign}(\lambda_2)\rho \approx 0$) is characteristic of dispersion-dominated attractive interactions, indicating that the umbrella-like architecture is stabilized by cooperative π-mediated contacts among the aryl groups rather than by a single dominant interaction.

Beyond these intracomplex interactions, distinct NCI features are observed in the intermolecular region between **Int2** and **1b**. In particular, green isosurfaces are clearly localized between the aryl group of **1b** and the tosyl aryl group of **Int2**, as highlighted by the corresponding dotted circles (blue dotted circle for the diol aryl group and red dotted circle for the tosyl aryl group). Similar to the intramolecular case, these isosurfaces correspond to sign(λ_2)ρ ≈ 0 and are indicative of dispersion-driven attractive interactions. Importantly, the relative orientation of the two aromatic units is consistent with an edge-to-face (T-shaped) π-interaction, rather than a parallel-stacked arrangement. The spatial localization and continuity of these NCI features support a specific π-mediated interaction between the two aromatic units, rather than nonspecific steric contact. This observation is consistent with a binding model in which the aryl substituent of **1b** directly participates in molecular recognition through interaction with the π-rich surface of **Int2**.

In addition to these π-mediated interactions, a more intense attractive region is observed between the aliphatic hydroxyl group of **1b** and a sulfonyl oxygen atom of **Int2**. As indicated by the blue solid circle, this interaction appears as a pronounced blue NCI isosurface, corresponding to a strongly attractive interaction. The position of this feature, located between the hydroxyl proton donor and the sulfonyl oxygen acceptor, together with its characteristic NCI signature, strongly suggests the presence of a hydrogen-bonding interaction. Compared to the more diffuse green isosurfaces associated with π-interactions, this localized blue feature indicates a more directional and stronger interaction that likely serves as an anchoring point within the complex.

Taken together, these results support a cooperative binding model in which the **Int2–1b complex** is stabilized by the interplay of multiple weak π-mediated interactions and a stronger hydrogen-bonding interaction. The umbrella-like arrangement of **Int2** provides a preorganized π-rich environment that engages the aryl group of **1b**, while the hydroxyl–sulfonyl interaction further reinforces the association. Such a combination of dispersed and directional interactions is likely to play a key role in substrate preorganization in solution, thereby facilitating efficient tosyl transfer.

Table S6. Cartesian Coordinates of **Int2-1b**

==================================

H	7.01498	13.82399	-2.38011
C	7.57114	12.90986	-2.54197
C	6.88991	11.72341	-2.78635
C	7.55659	10.52678	-3.01395
C	8.95224	10.5118	-2.96014
C	9.67406	11.67952	-2.67502
C	8.9632	12.87497	-2.48956
F	5.53491	11.72772	-2.76953
H	6.98597	9.62449	-3.20502
H	9.47331	9.57114	-3.08336
C	11.19382	11.75002	-2.63526
H	9.5123	13.79126	-2.29364
C	11.92672	10.4172	-2.32999
H	14.17974	8.71557	-2.47425
H	11.46853	12.46753	-1.85457
H	11.34834	11.80099	-4.58089
O	11.19395	9.61279	-1.41022
H	11.04979	10.15071	-0.61588
C	13.37126	10.62587	-1.81293
C	14.26022	11.46889	-2.73833
H	14.33562	11.00725	-3.72983
C	14.0269	9.26499	-1.5366
H	13.87798	12.48024	-2.88318
H	15.27266	11.53312	-2.32395
H	13.26815	11.15694	-0.85332
H	15.00691	9.39457	-1.06515
H	13.40001	8.65203	-0.88608
O	11.67674	12.34217	-3.8497
H	11.96536	9.83473	-3.26339
H	4.52618	13.36224	-0.9581
C	5.05121	13.41451	-0.01011
C	6.01238	14.40935	0.2054
C	6.70373	14.46641	1.40865
C	6.43913	13.5099	2.40846
C	5.46964	12.52708	2.20008
C	4.77267	12.49053	0.99121
H	6.2182	15.1493	-0.562
H	7.44568	15.24169	1.56555
H	8.48534	9.0884	7.096
H	5.20739	11.81308	2.9647
H	3.99128	11.75049	0.87418
H	6.13206	9.55336	6.42223
C	6.93242	10.2185	6.11321
C	6.62269	11.33926	5.34598
C	7.65506	12.2019	4.93491
C	8.97589	11.96072	5.33968
C	9.27057	10.83896	6.11589
C	8.25303	9.96244	6.49455
H	5.58675	11.53992	5.09903
P	7.24141	13.71624	4.01474
H	9.77954	12.62109	5.04287
H	10.29779	10.65192	6.41185
H	4.47457	14.63611	3.68129
C	4.80575	14.88919	4.67927
C	3.877	15.4049	5.58491
C	4.25893	15.68602	6.89423

C	5.56617	15.42234	7.32266
C	6.48625	14.86427	6.44251
C	6.11245	14.62008	5.1057
H	2.84858	15.52451	5.26502
H	3.53202	16.08232	7.59693
H	5.85502	15.61898	8.35066
H	7.47735	14.59542	6.79696
H	10.48317	14.21216	-0.07999
C	8.80283	14.62112	3.75125
C	9.07793	15.76376	4.51427
C	10.28328	16.4565	4.37833
C	11.19207	15.97829	3.42422
C	10.9513	14.86651	2.61003
C	9.74294	14.17852	2.8004
H	8.33021	16.1111	5.2123
C	10.62063	17.7009	5.21419
H	12.13101	16.50389	3.27791
C	11.93569	14.49543	1.52185
C	9.49524	18.05857	6.20302
C	11.91211	17.43308	6.02185
C	10.8406	18.90579	4.26982
H	9.93869	19.11346	3.68511
H	11.08397	19.80131	4.85128
H	11.66296	18.7312	3.56975
H	9.30514	17.24873	6.9154
H	9.78175	18.94299	6.77975
H	8.55715	18.29146	5.68862
H	11.78047	16.58291	6.69902
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O	10.84533	11.39472	3.08196
O	10.83679	11.67301	0.56232
H	6.15278	10.10911	-0.50215
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C	7.94537	10.71648	0.48765
C	8.67627	10.63295	1.67609
C	8.26168	9.8403	2.74797
C	7.06057	9.14866	2.63011
C	6.27022	9.24952	1.47475
H	8.28919	11.33116	-0.3337
C	4.90695	8.61158	1.42827
H	8.8531	9.78337	3.65282
H	6.71446	8.54795	3.46537
H	4.90614	7.63096	1.91387
H	4.18508	9.24274	1.96181
H	4.55249	8.49022	0.40125
F	2.76939	13.30146	2.97101
P	2.3222	12.08768	3.99194
F	0.91576	11.93326	3.21556
F	1.70793	13.19407	5.01665
F	1.95821	10.88101	5.00805
F	3.80348	12.24683	4.74806
F	3.03214	10.99728	2.95642

VIII. References

1 Toda, Y., Hashimoto, K., Mori, Y. & Suga, H. A phosphonium ylide as a ligand for [3+ 2] coupling reactions of epoxides with heterocumulenes under mild conditions. *J. Org. Chem.* **85**, 10980-10987 (2020).

2 Toda, Y., Kobayashi, T., Hirai, F., Yano, T., Oikawa, M., Sukegawa, K., Shimizu, M., Ito, F. & Suga, H. Visible-light-driven c–h imidation of arenes and heteroarenes by a phosphonium ylide organophotoredox catalyst: Application to c–h functionalization of alkenes. *J. Org. Chem.* **88**, 9574-9578 (2023).

3 Toda, Y., Sakamoto, T., Komiyama, Y., Kikuchi, A. & Suga, H. A phosphonium ylide as an ionic nucleophilic catalyst for primary hydroxyl group selective acylation of diols. *ACS Catal.* **7**, 6150-6154 (2017).

4 Toda, Y., Tanaka, K., Matsuda, R., Sakamoto, T., Katsumi, S., Shimizu, M., Ito, F. & Suga, H. A phosphonium ylide as a visible light organophotoredox catalyst. *Chem. Commun.* **57**, 3591-3594 (2021).

5 Toda, Y., Yamaguchi, R., Fuwa, S., Iwasaki, M. & Suga, H. Visible-light-driven borylation and phosphorylation of aryl halides by phosphonium ylide organophotoredox catalysis. *Chem. Commun.* **61**, 16254-16257 (2025).

6 Rong, Z.-Q., Pan, H.-J., Yan, H.-L. & Zhao, Y. Enantioselective oxidation of 1, 2-diols with quinine-derived urea organocatalyst. *Org. Lett.* **16**, 208-211 (2014).

7 Ray, R. & Matteson, D. S. Osmium tetroxide catalyzed hydroxylation of hindered olefins. *Tetrahedron Lett.* **21**, 449-450 (1980).

8 Bartoli, G., Bosco, M., Bellucci, M. C., Dalpozzo, R., Marcantoni, E. & Sambri, L. Ticl4-mediated reduction of 1, 3-diketones with bh3− pyridine complex: A highly diastereoselective method for the synthesis of s yn-1, 3-diols. *Org. Lett.* **2**, 45-47 (2000).

9 Martinelli, M. J., Vaidyanathan, R., Pawlak, J. M., Nayyar, N. K., Dhokte, U. P., Doecke, C. W., Zollars, L. M., Moher, E. D., Khau, V. V. & Košmrlj, B. Catalytic regioselective sulfonylation of α-chelatable alcohols: Scope and mechanistic insight. *J. Am. Chem. Soc.* **124**, 3578-3585 (2002).

10 Bouzide, A. & Sauvé, G. Silver (i) oxide mediated highly selective monotosylation of symmetrical diols. Application to the synthesis of polysubstituted cyclic ethers. *Org. Lett.* **4**, 2329-2332 (2002).

11 Chelouan, A., Recio, R., Alcudia, A., Khiar, N. & Fernández, I. Dmap-catalysed sulfinylation of diacetone-d-glucose: Improved method for the synthesis of enantiopure tert-butyl sulfoxides and tert-butanesulfinamides. *Eur. J. Org. Chem.* **2014**, 6935-6944 (2014).

12 Weingarten, S. & Thiem, J. Formation of lacnac mimetics employing novel donor substrates for enzymatic β1→ 4 galactosylation. *Org. Biomol. Chem.* **2**, 961-962 (2004).

13 Ledoux, A., Larini, P., Boisson, C., Monteil, V., Raynaud, J. & Lacôte, E. Polyboramines for hydrogen release: Polymers containing lewis pairs in their backbone. *Angew. Chem. Int. Ed.* **127**, 15970-15975 (2015).

14 Huang, K., Wang, H., Stepanenko, V., De Jesús, M., Torruellas, C., Correa, W. & Ortiz-Marciales, M. Chiral epoxides via borane reduction of 2-haloketones catalyzed by spiroborate ester: Application to the synthesis of optically pure 1, 2-hydroxy ethers and 1, 2-azido alcohols. *J. Org. Chem.* **76**, 1883-1886 (2011).

15 Senanayake, C. H., Jerussi, T. P., Grover, P. T., Fang, Q. K. & Currie, M. Tramadol analogs and uses thereof. **6,780,891** (2004).

16 Parr, R. G. in *Horizons of Quantum Chemistry: Proceedings of the Third International Congress of Quantum Chemistry Held at Kyoto, Japan, October 29-November 3, 1979.* 5-15 (Springer).

17 Frisch, M., Trucks, G., Schlegel, H., Scuseria, G., Robb, M., Cheeseman, J., Scalmani, G., Barone, V., Mennucci, B. & Petersson, G. Uranyl extraction by n, n-dialkylamide ligands studied by static and dynamic dft simulations. *Gaussian* **9**, 227 (2009).

18 Lee, C., Yang, W. & Parr, R. G. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785-789, doi:10.1103/PhysRevB.37.785 (1988).

19 Ditchfield, R., Hehre, W. J. & Pople, J. A. Self-consistent molecular-orbital methods. Ix. An extended gaussian-type basis for molecular-orbital studies of organic molecules. *J. Chem. Phys.* **54**, 724-728 (1971).

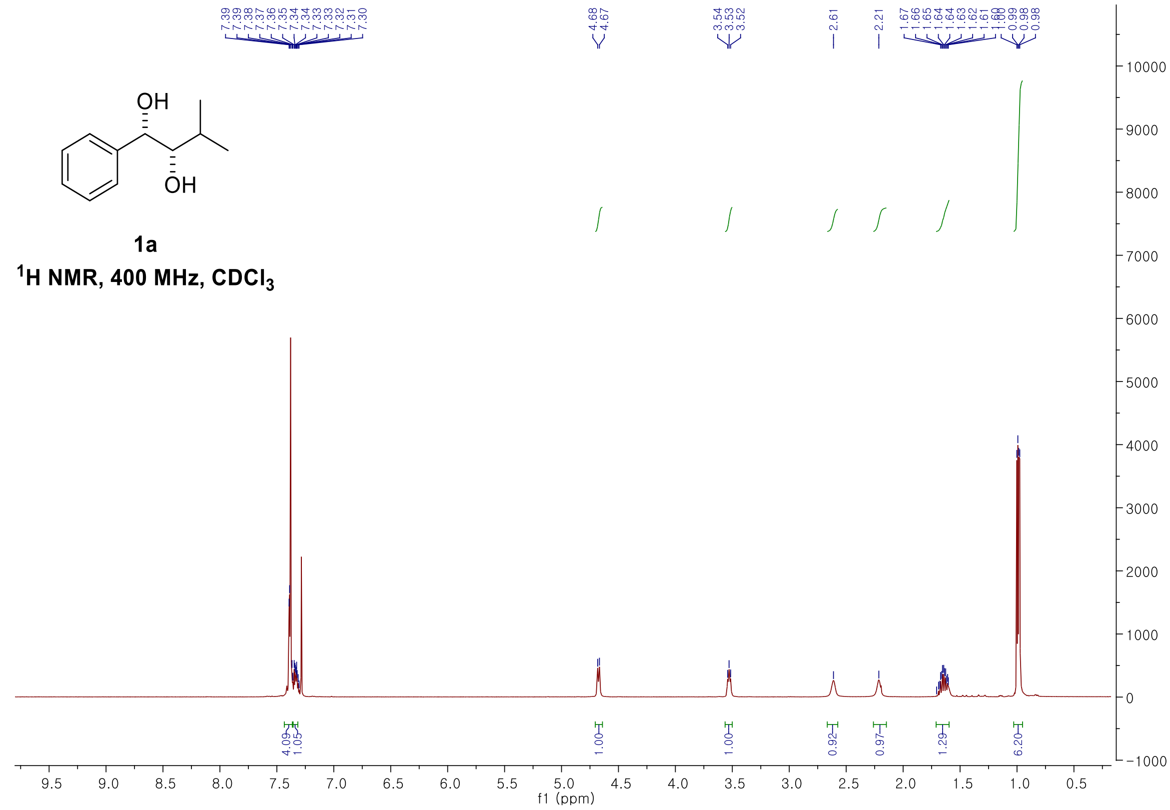
20 Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **113**, 6378-6396 (2009).

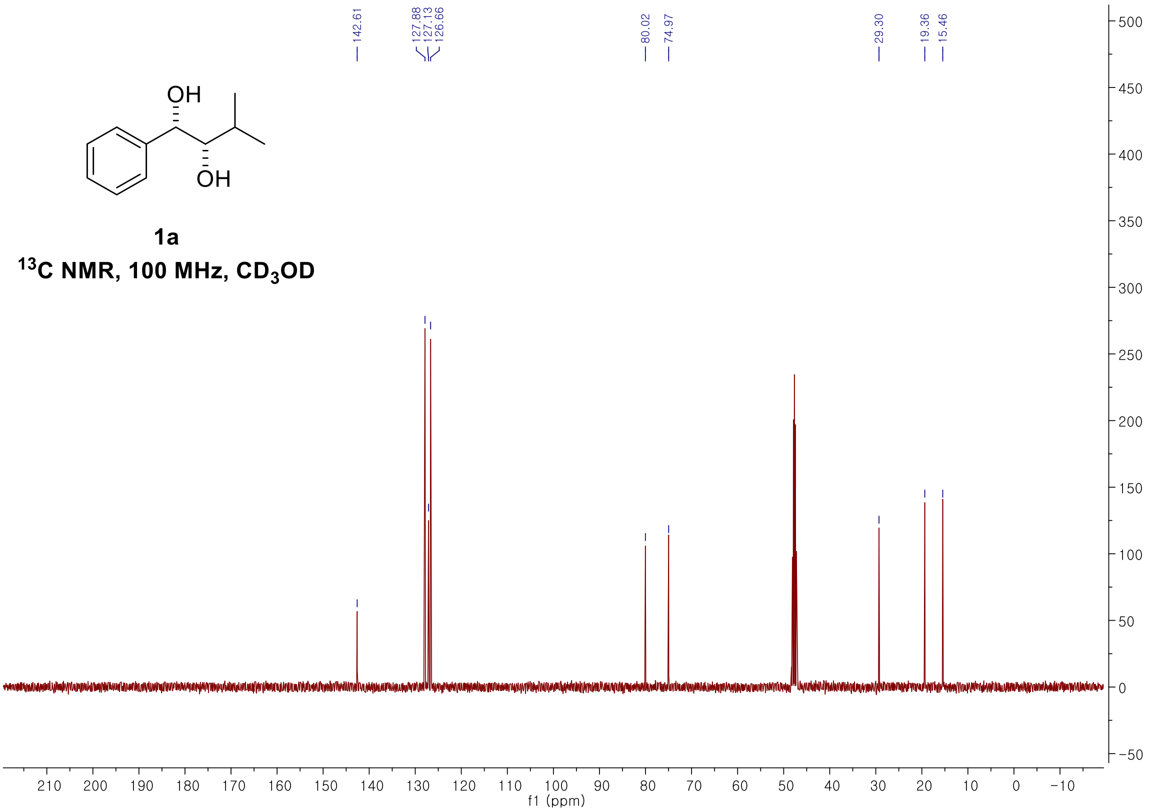
21 Lu, T. & Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580-592 (2012).

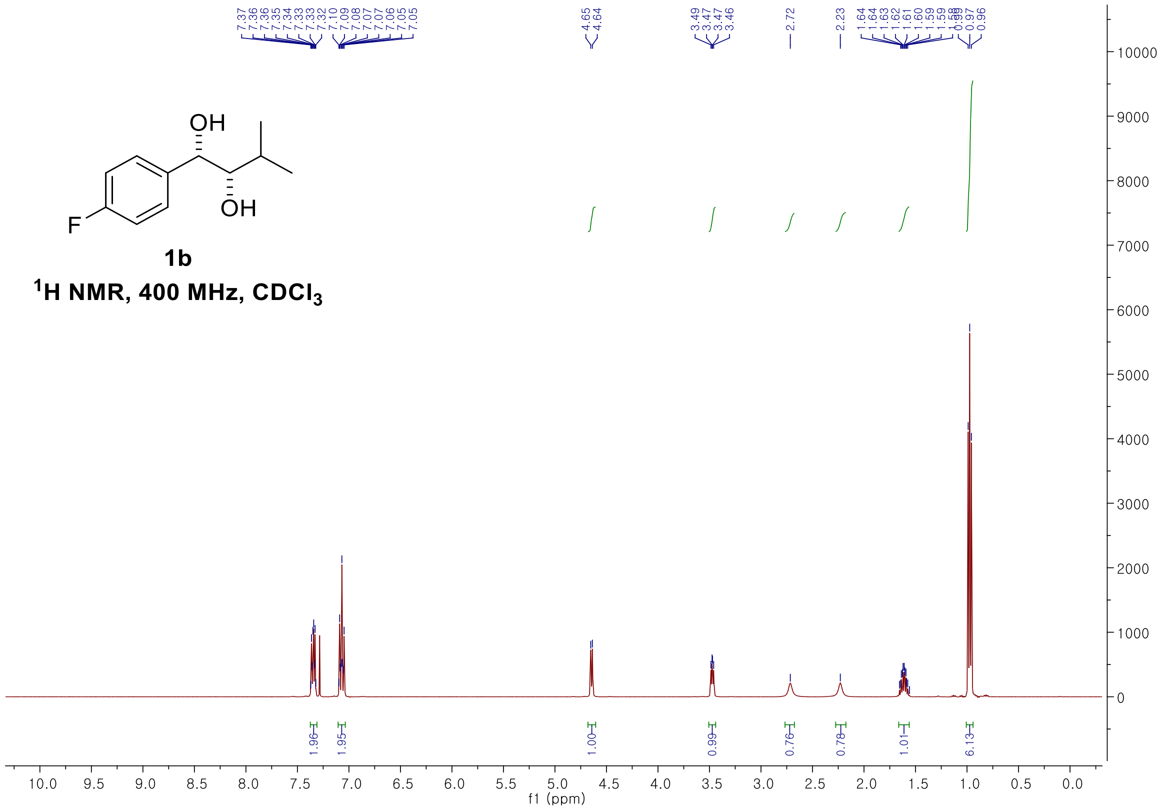
Appendix I

Spectral Copies of
^{1} H and ^{13}C NMR of Compounds

Starting Material Characterization



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7.35
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7.33
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7.32
7.10
7.09
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7.06
7.05
7.05
4.65
4.64
3.49
3.47
3.47
3.46
2.72
2.23
1.64
1.64
1.63
1.62
1.61
1.60
1.59
1.59
1.58
0.98
0.97
0.96
OH
OH
F
1b
^{1}H NMR, 400 MHz, CDCl$_3$
1.96
1.95
1.00
0.99
0.76
0.78
1.01
6.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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0.0
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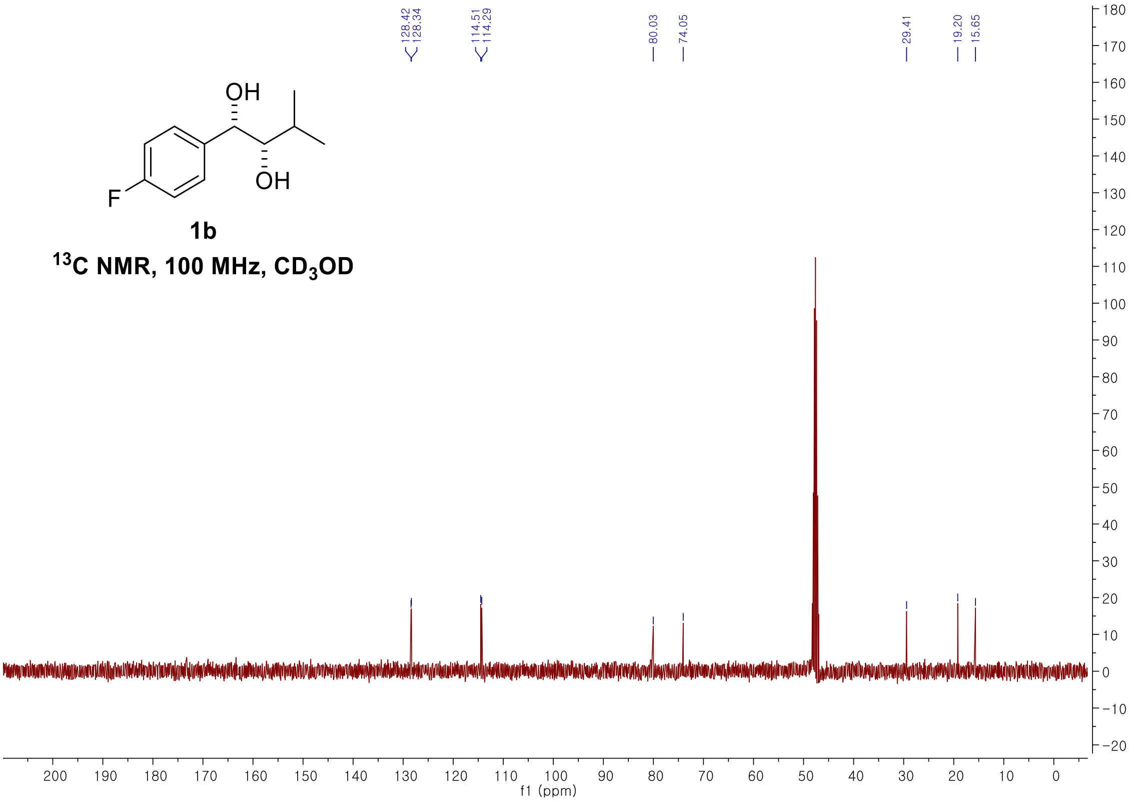
8000
7000
6000
5000
4000
3000
2000
1000
0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128.34
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80.03
74.05
29.41
19.20
15.65
OH
OH
F
1b
^{13}C NMR, 100 MHz, CD$_3$OD
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
180
170
160
150
140
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120
110
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90
80
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50
40
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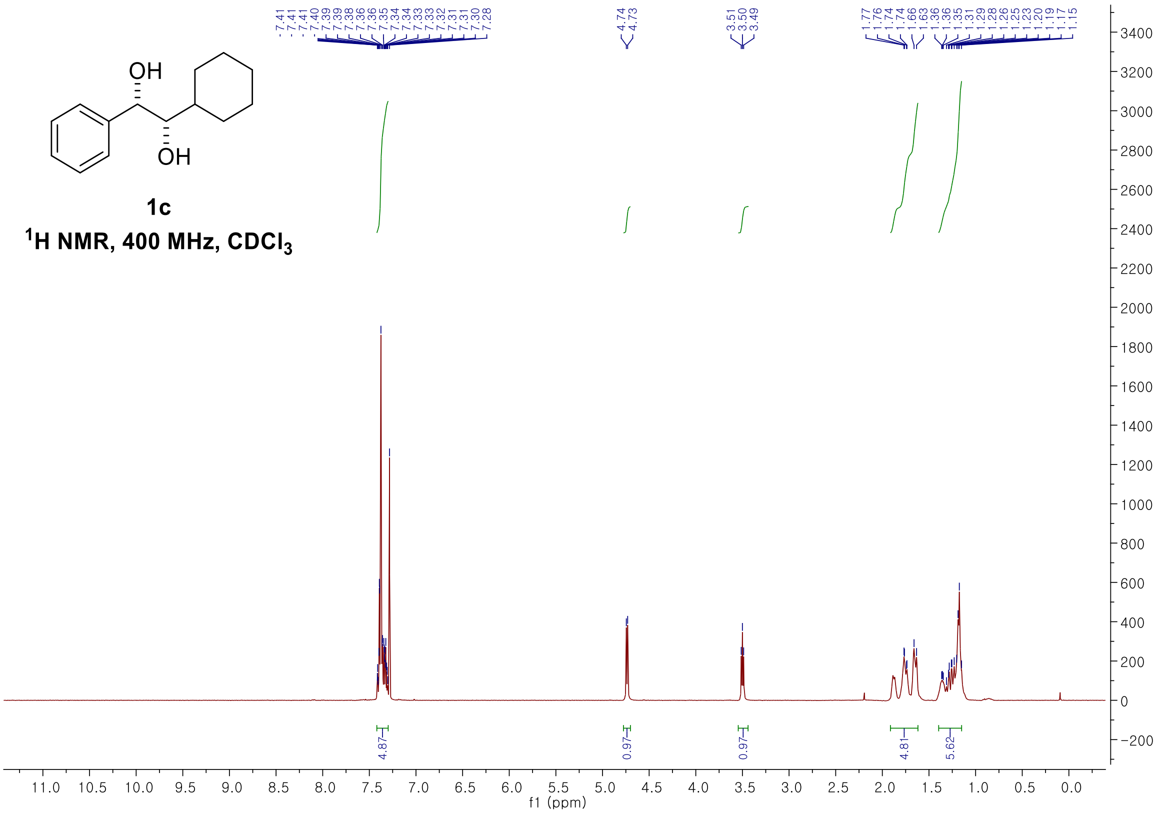
20
10
0
−10
−20



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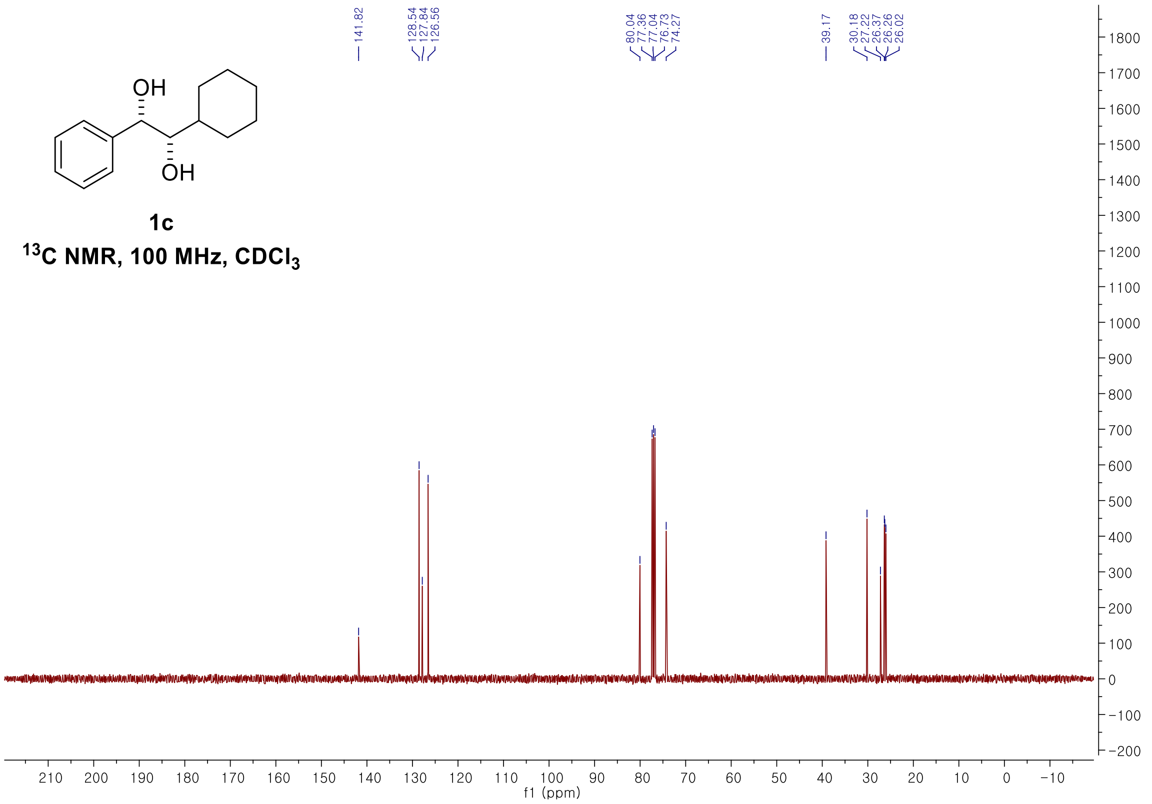

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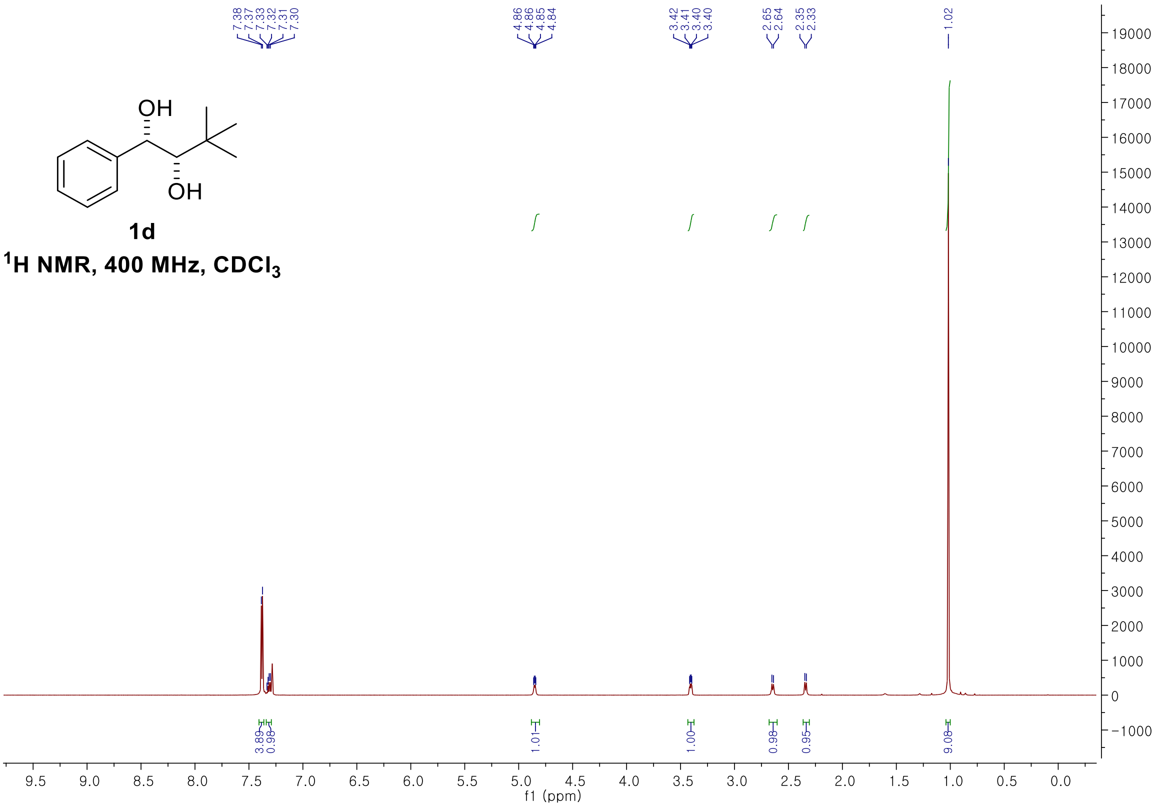

1d

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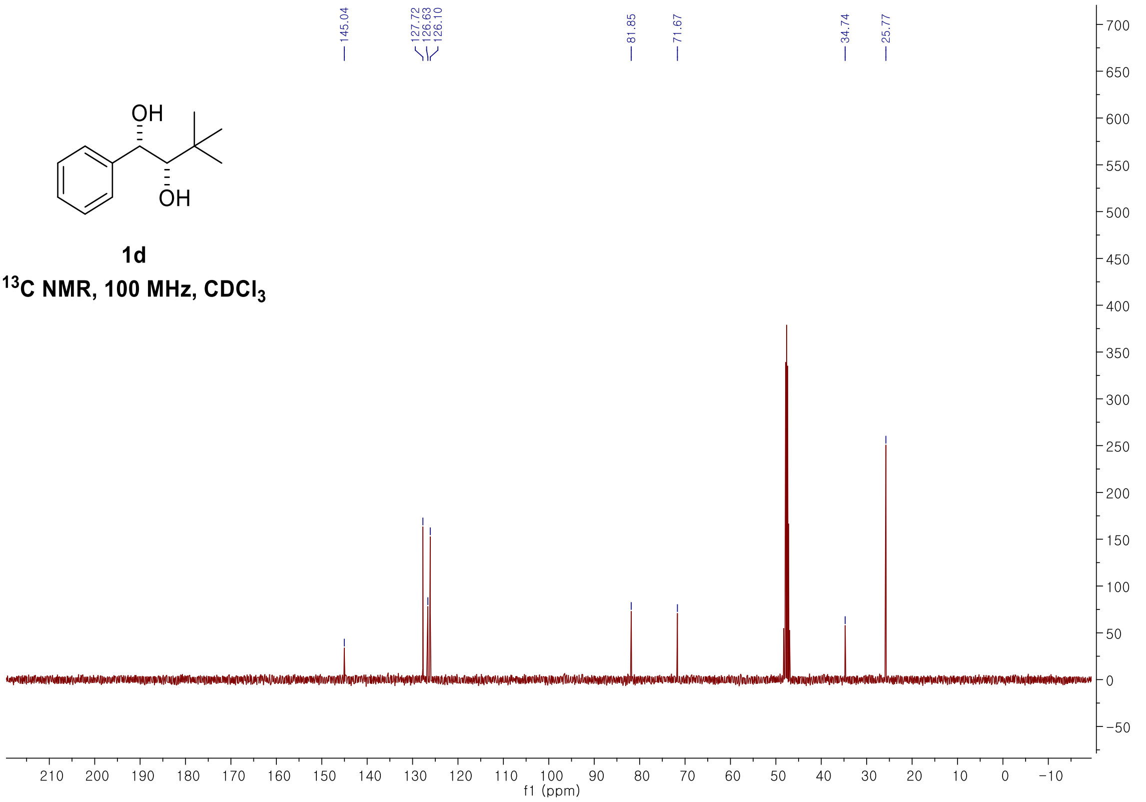

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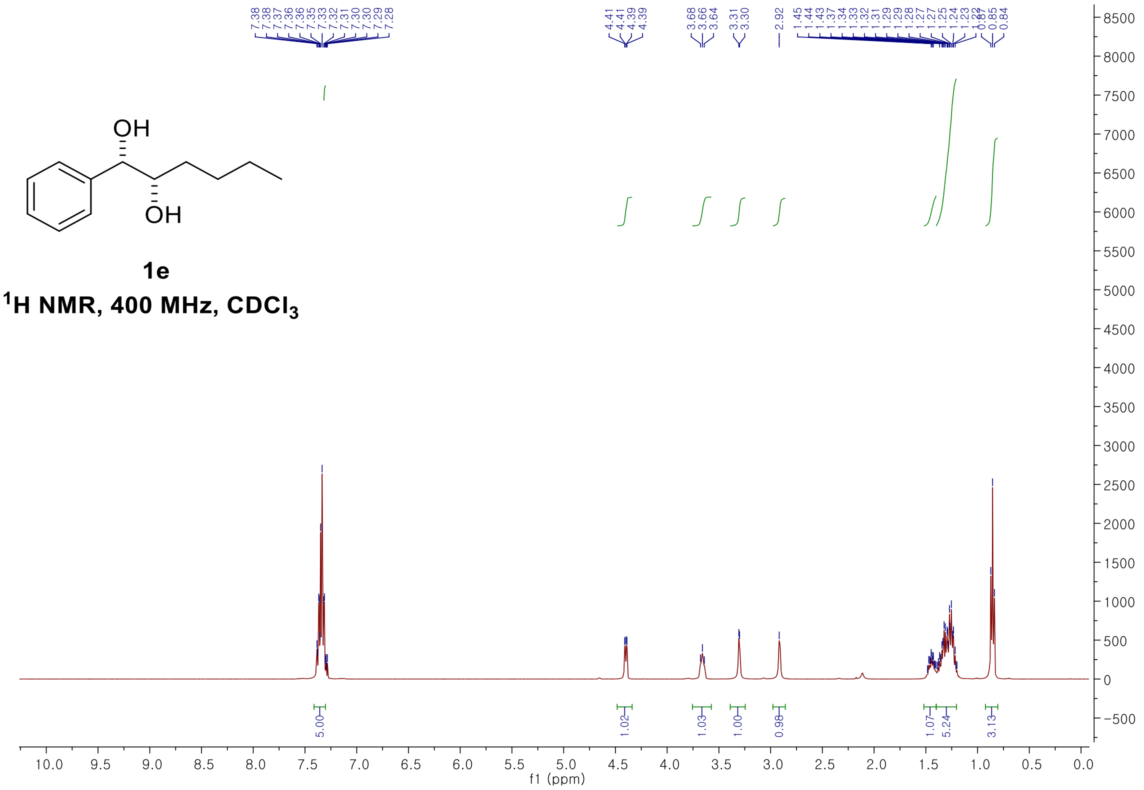

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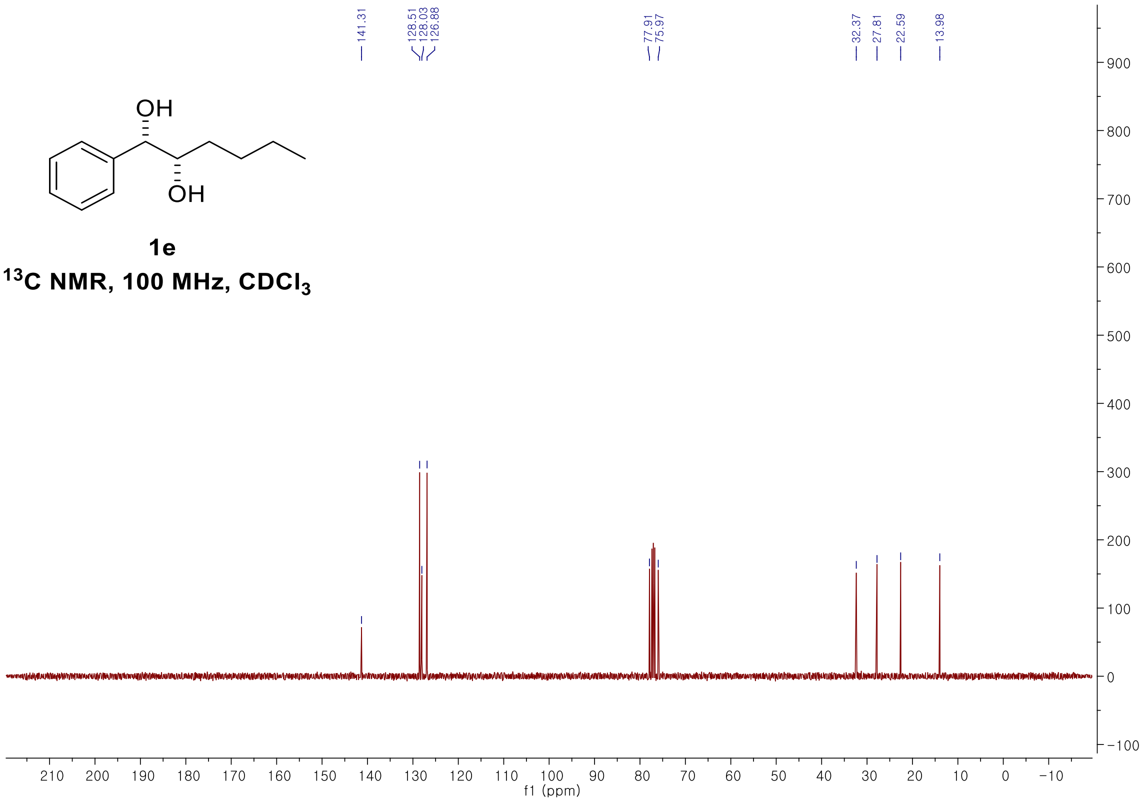
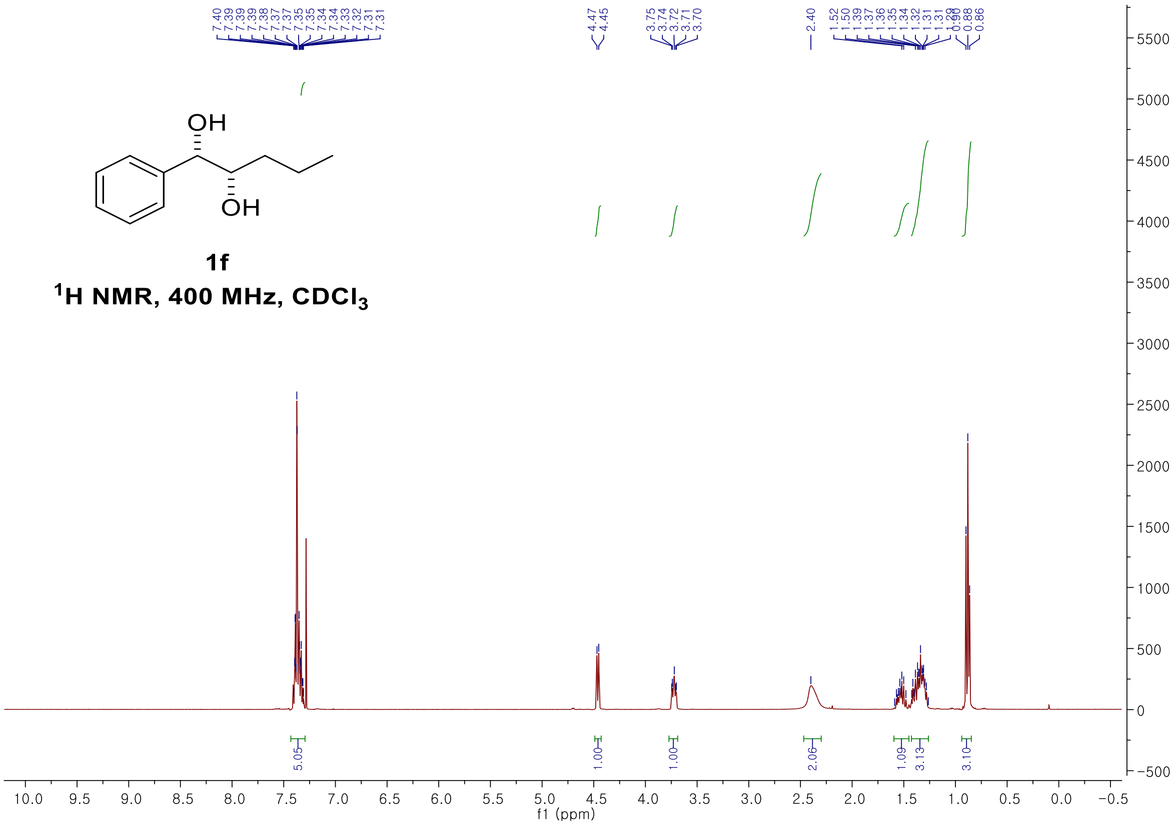


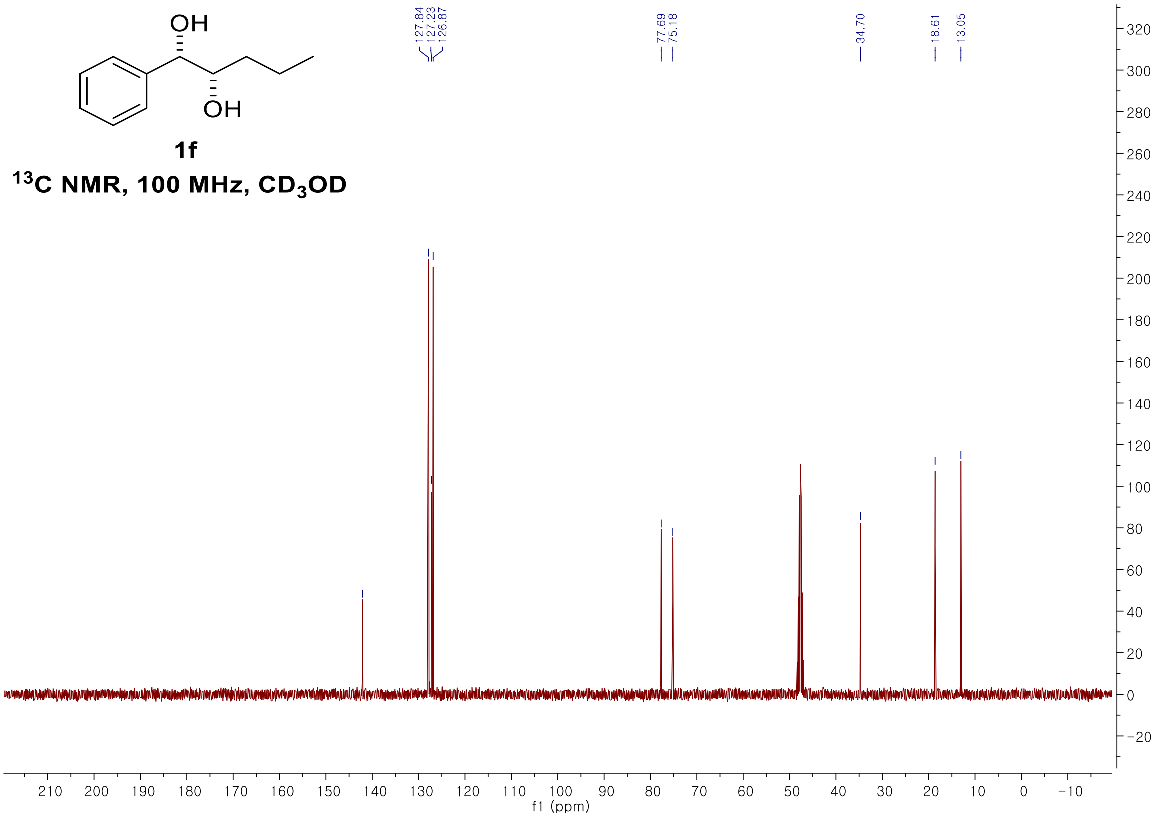
1e

^{13}C NMR, 100 MHz, CDCl$_3$



1f

^{1}H NMR, 400 MHz, CDCl$_3$



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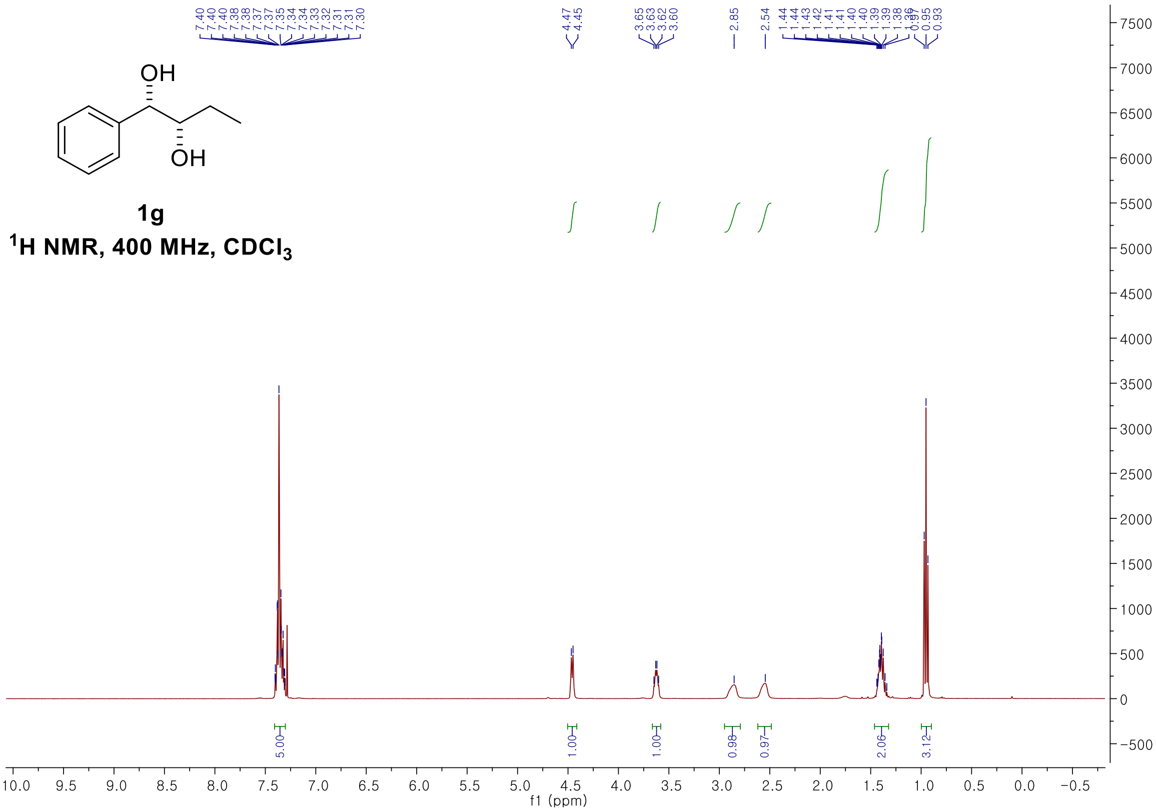

1g

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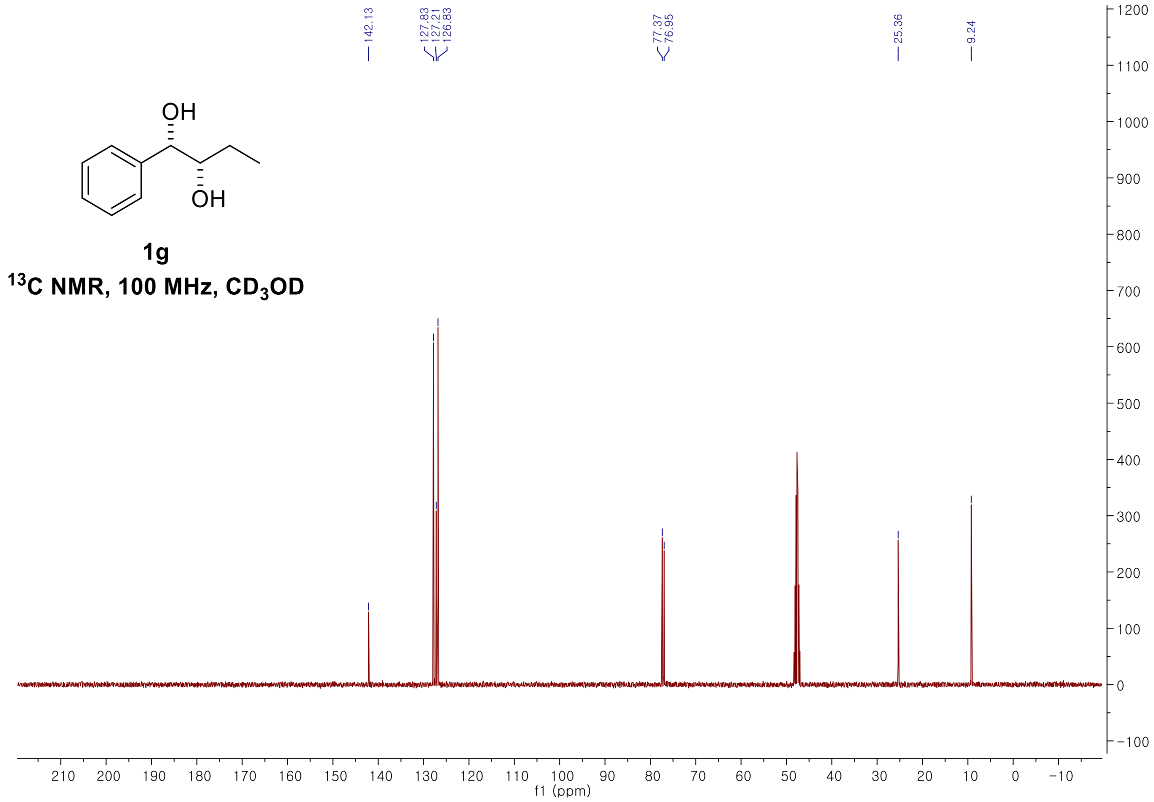

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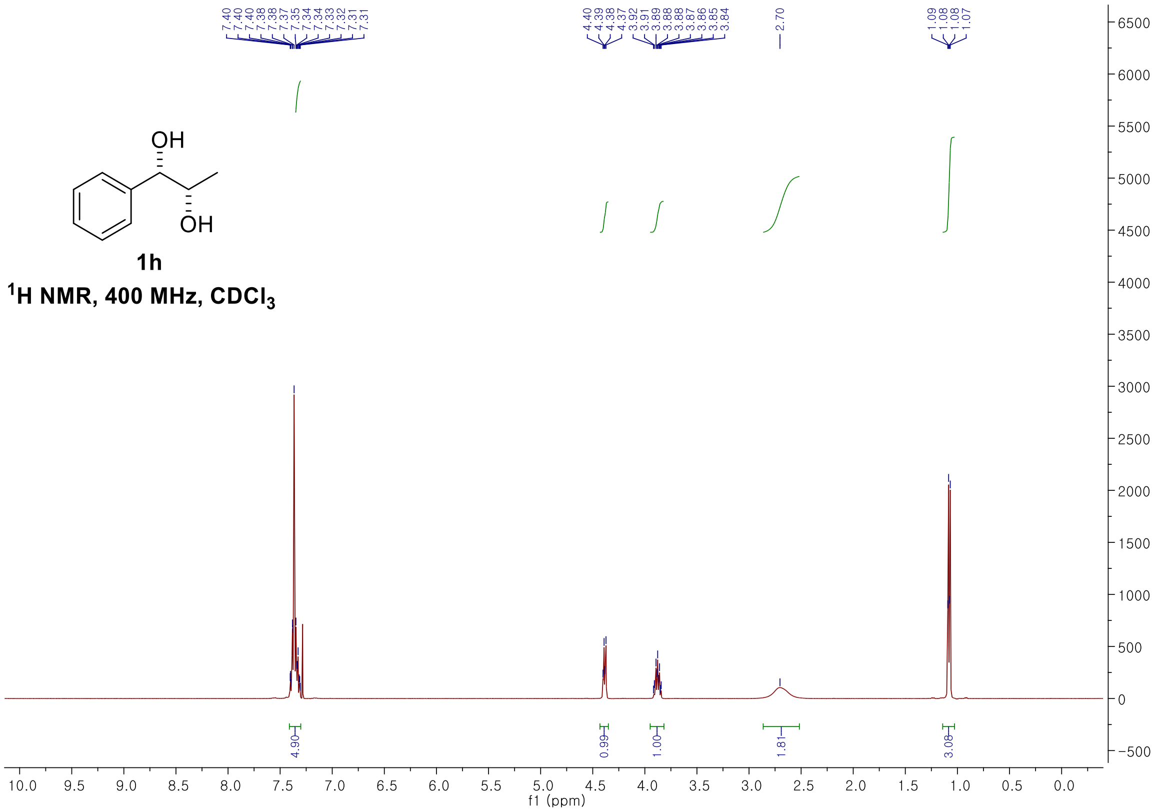

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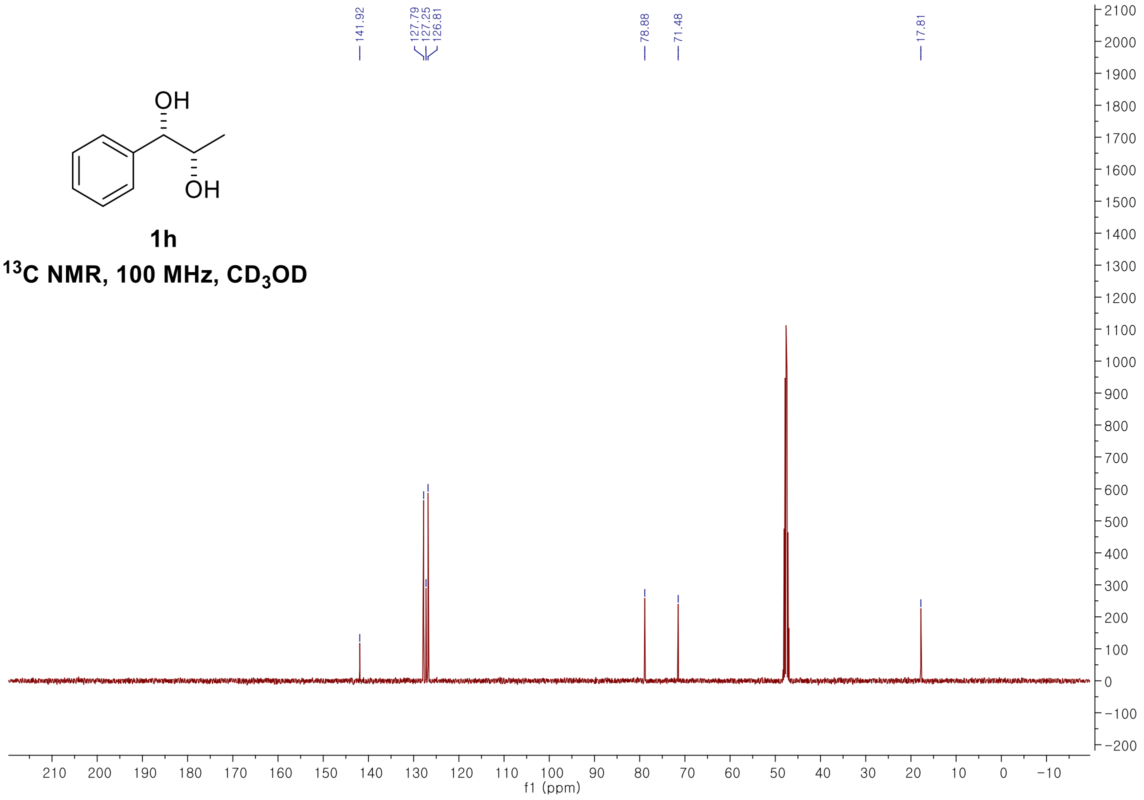

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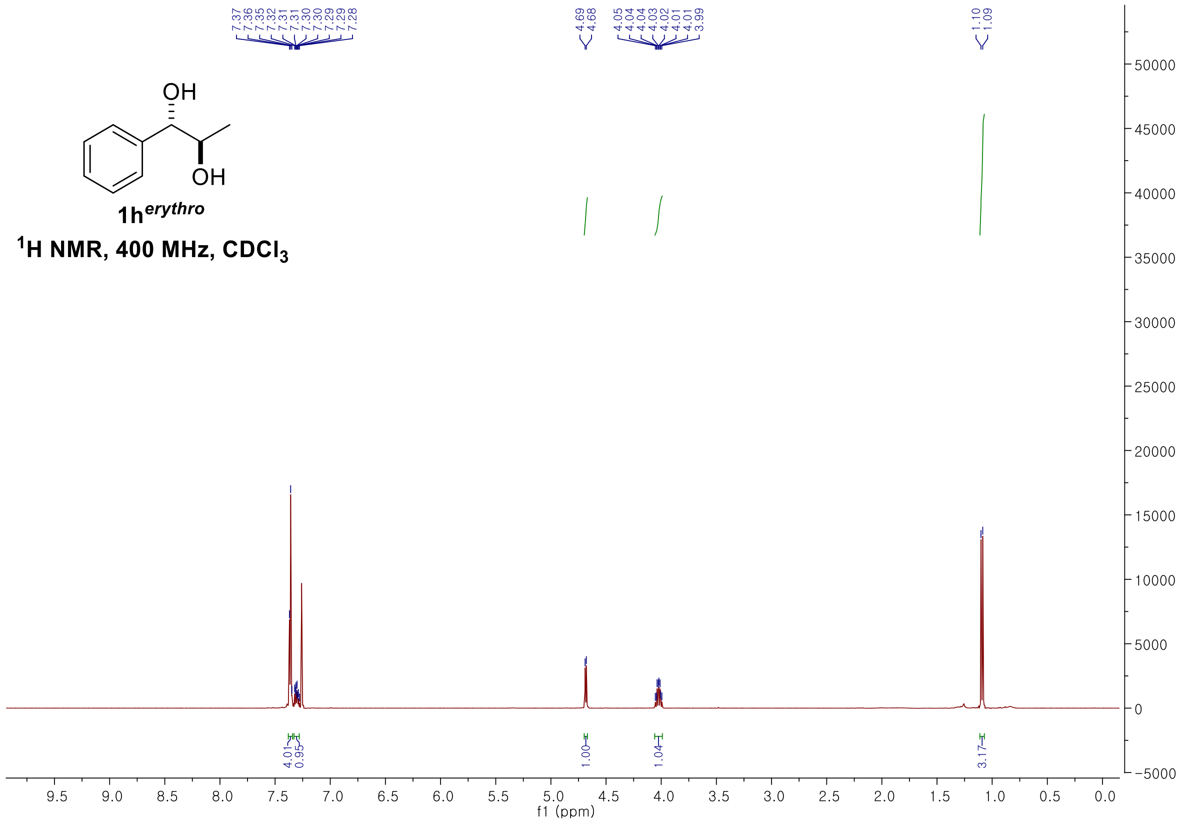
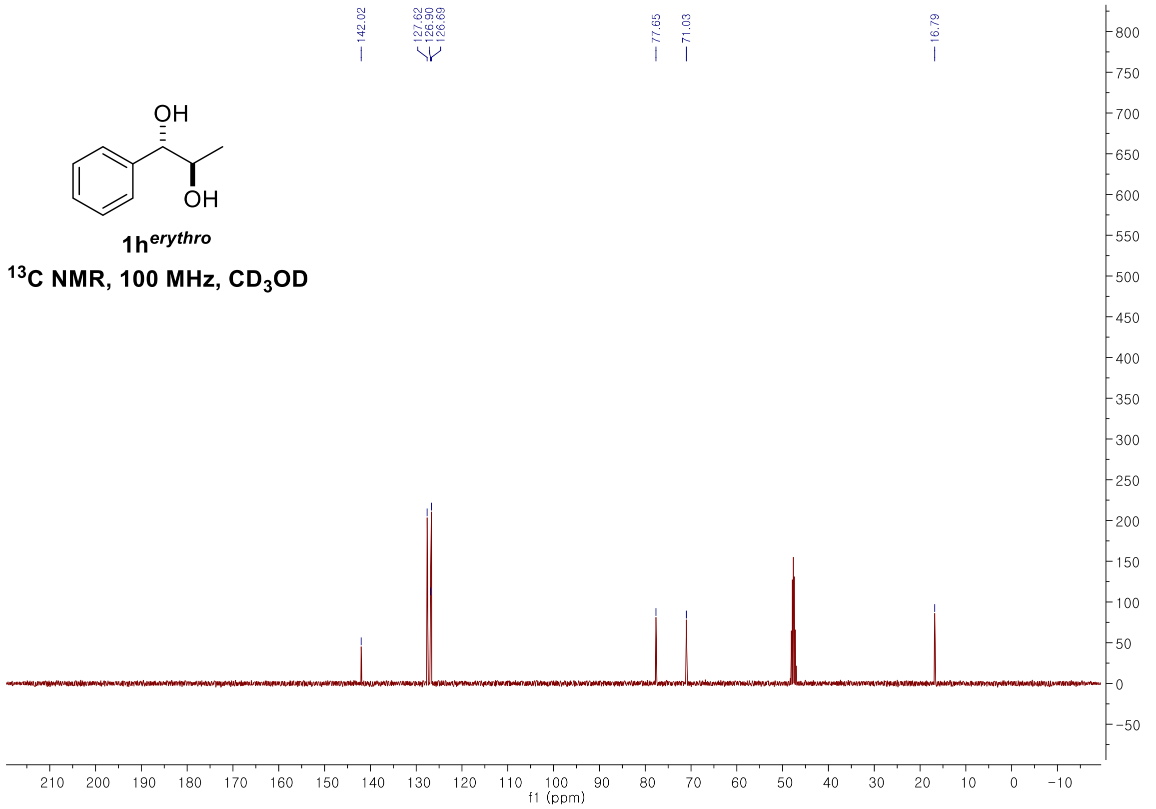
^{13}C NMR, 100 MHz, CD$_3$OD



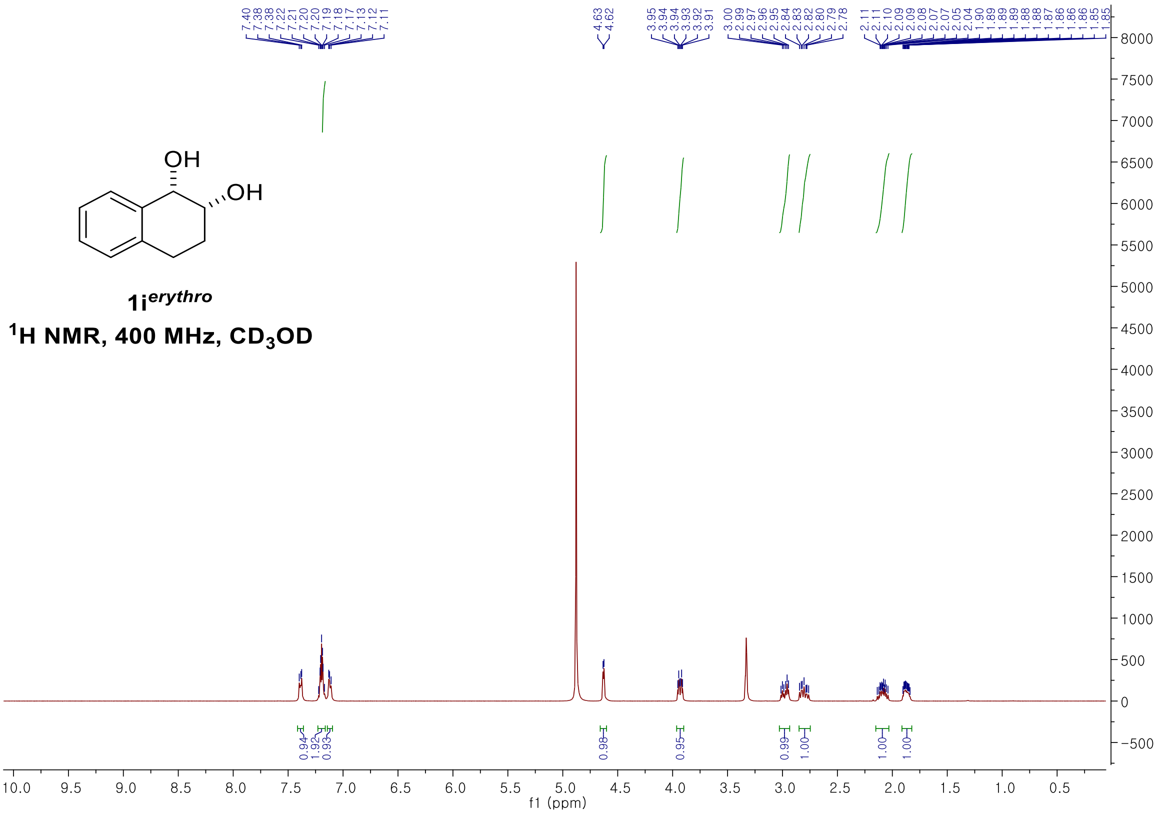
$1h^{erythro}$

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



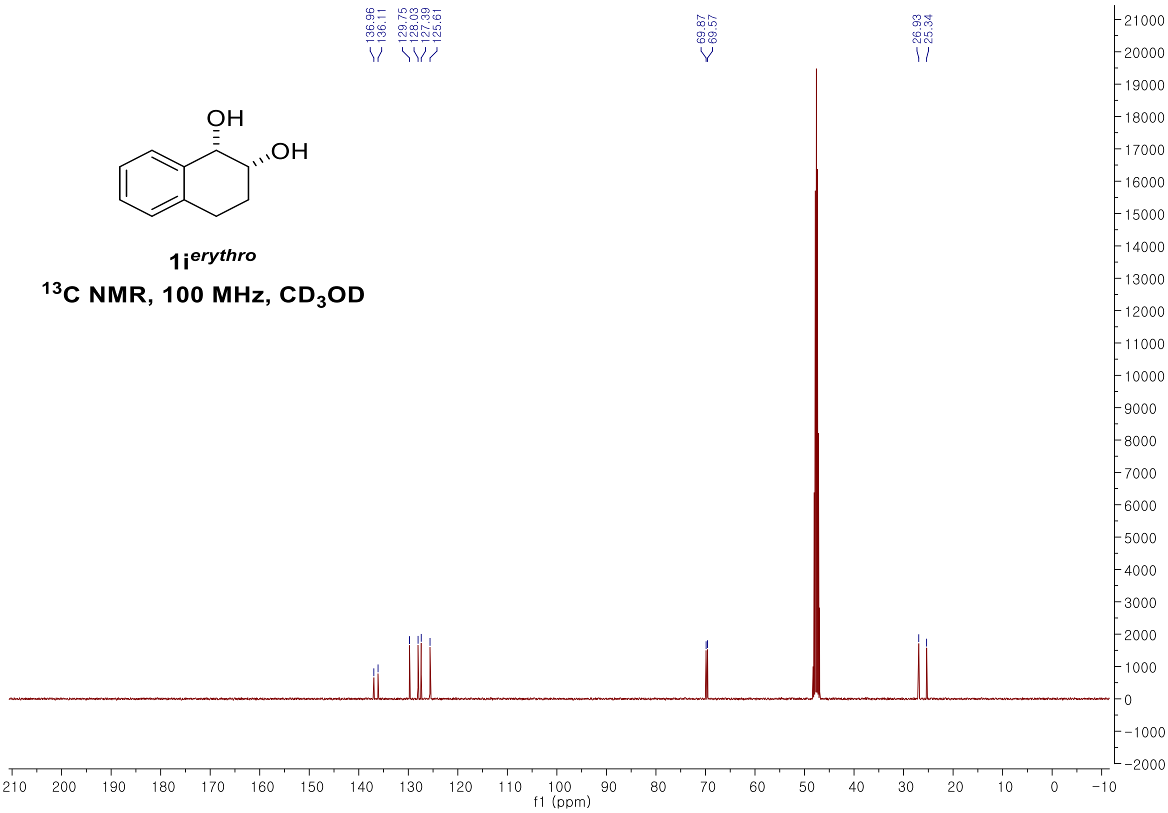
$1h^{erythro}$

^{13}C NMR, 100 MHz, CD_3OD



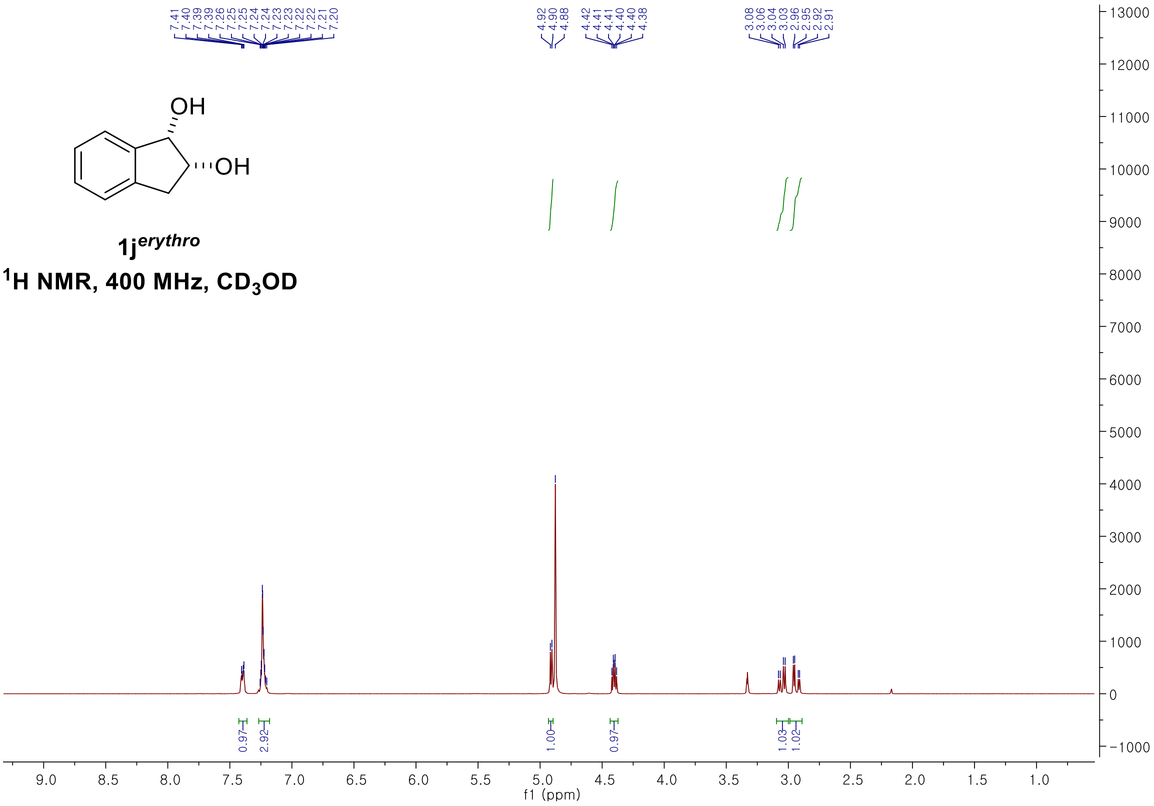
1i^{erythro}

^{1}H NMR, 400 MHz, CD$_3$OD



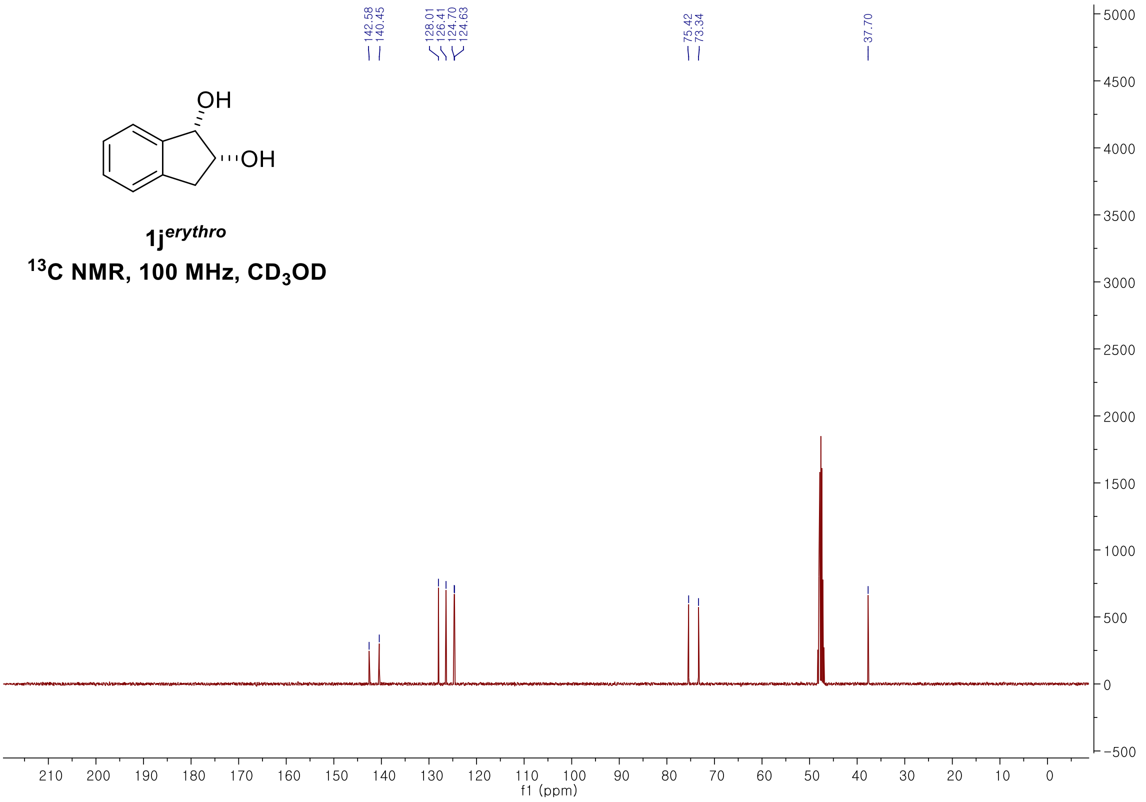
1i^{erythro}

^{13}C NMR, 100 MHz, CD$_3$OD



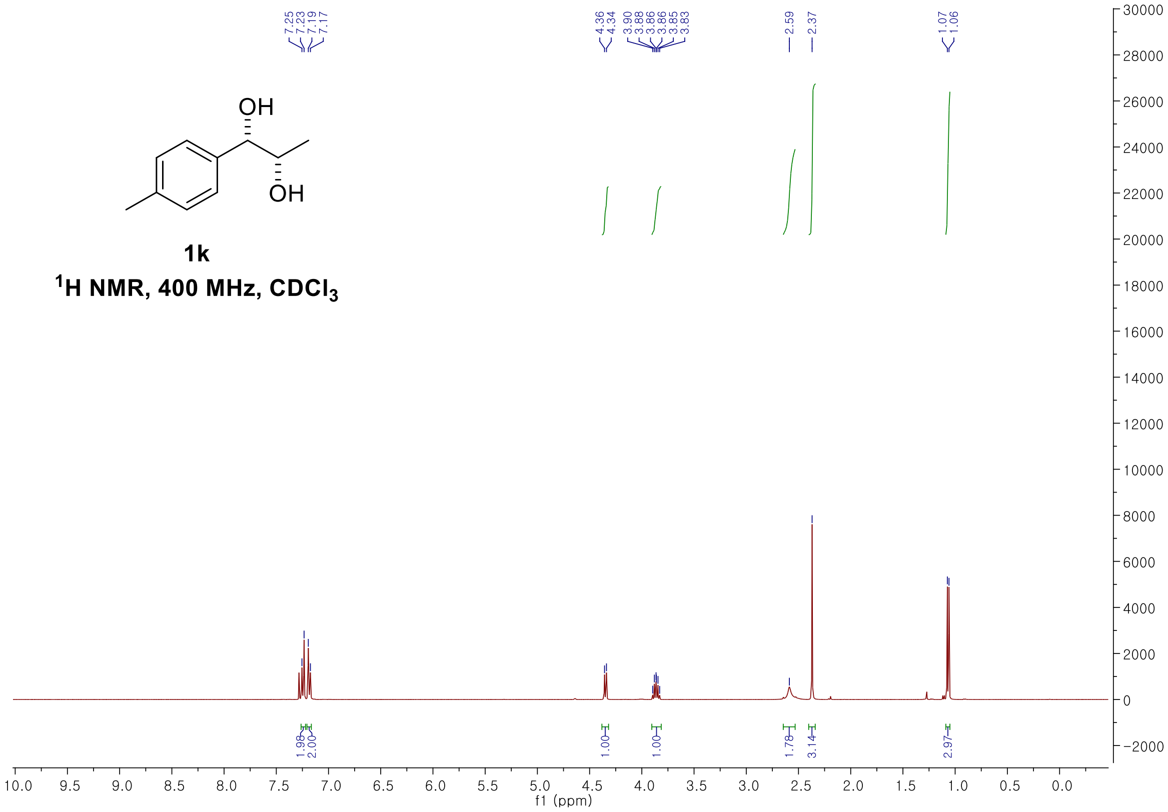
1j^{erythro}

^{1}H NMR, 400 MHz, CD_3OD



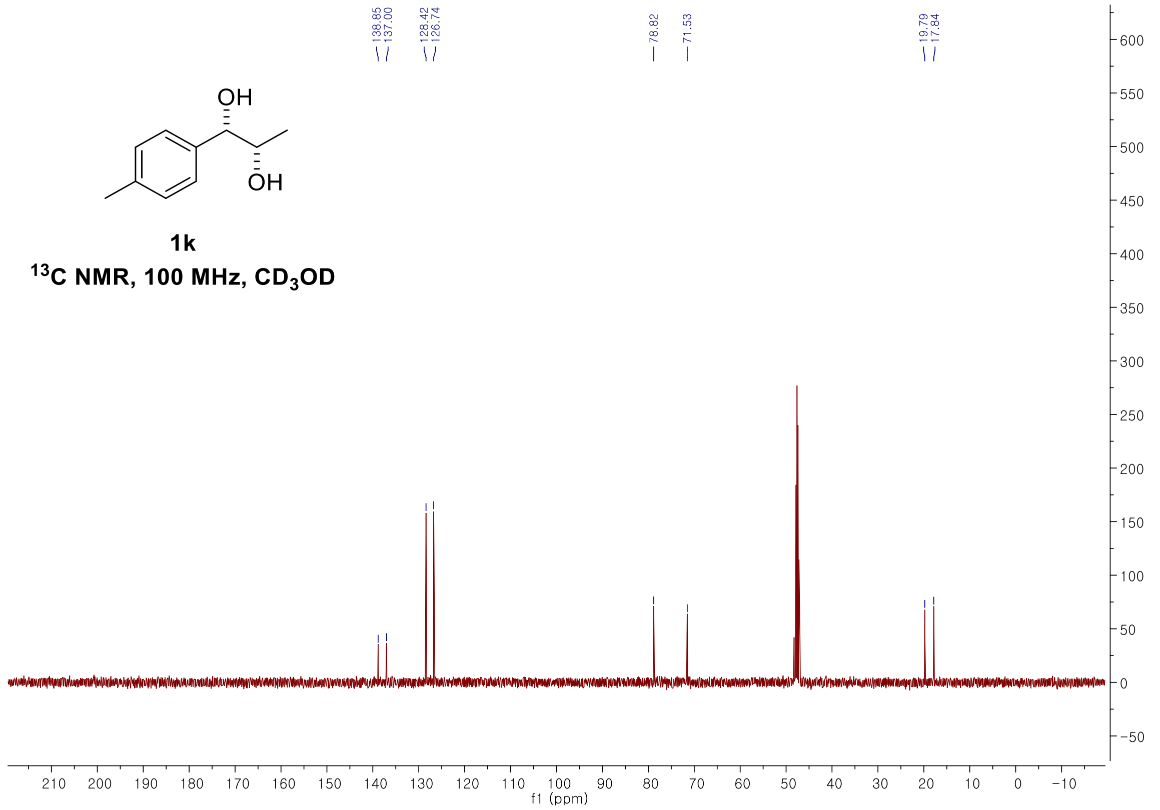
1j^{erythro}

^{13}C NMR, 100 MHz, CD_3OD



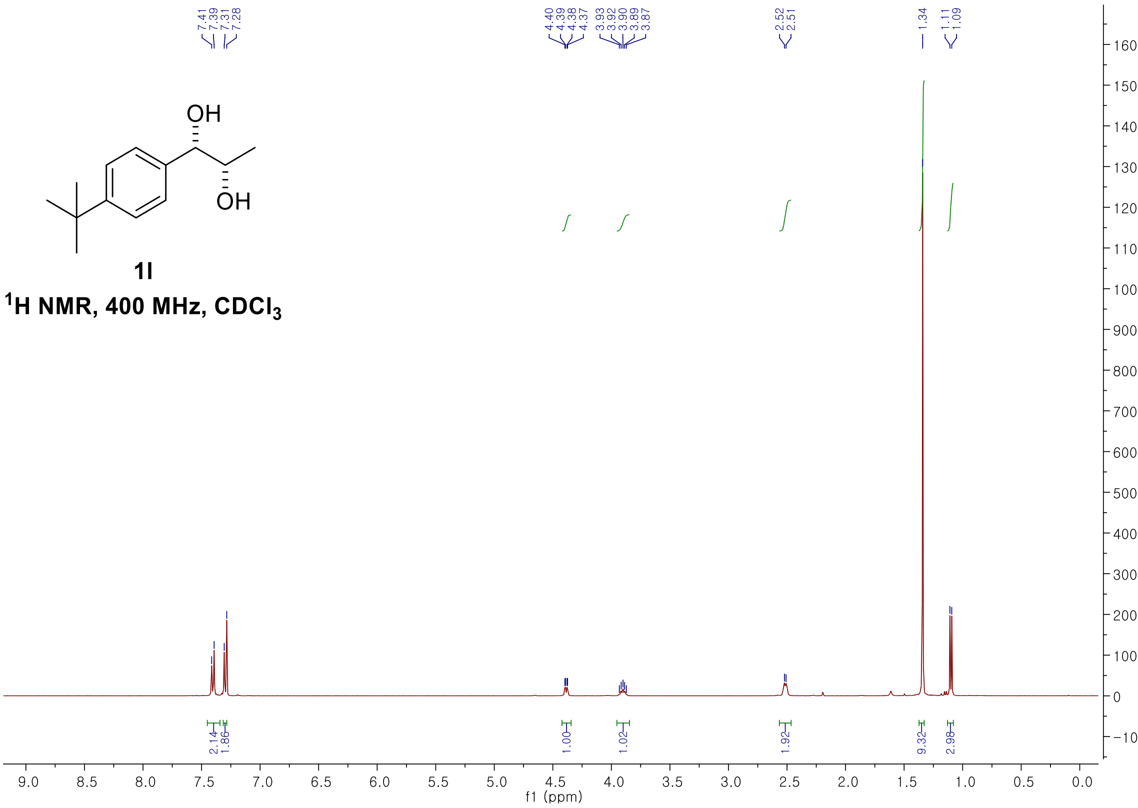
1k

^{1}H NMR, 400 MHz, CDCl$_3$



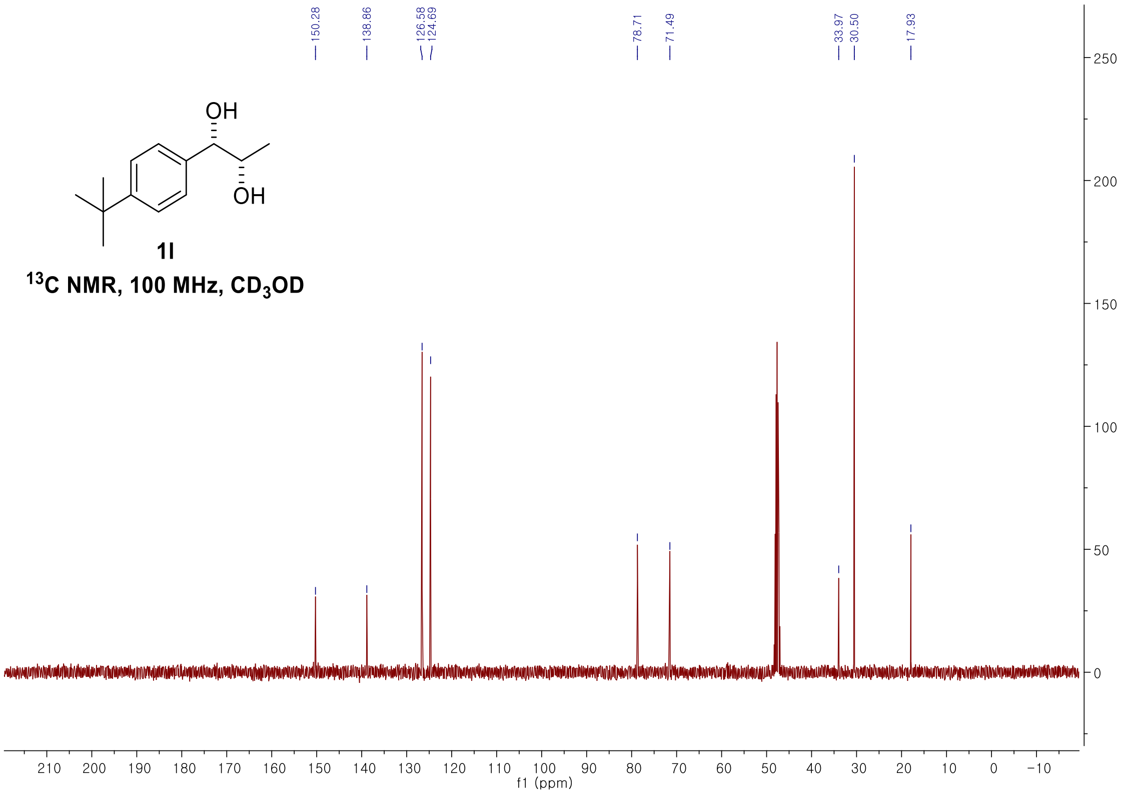
1k

^{13}C NMR, 100 MHz, CD$_3$OD



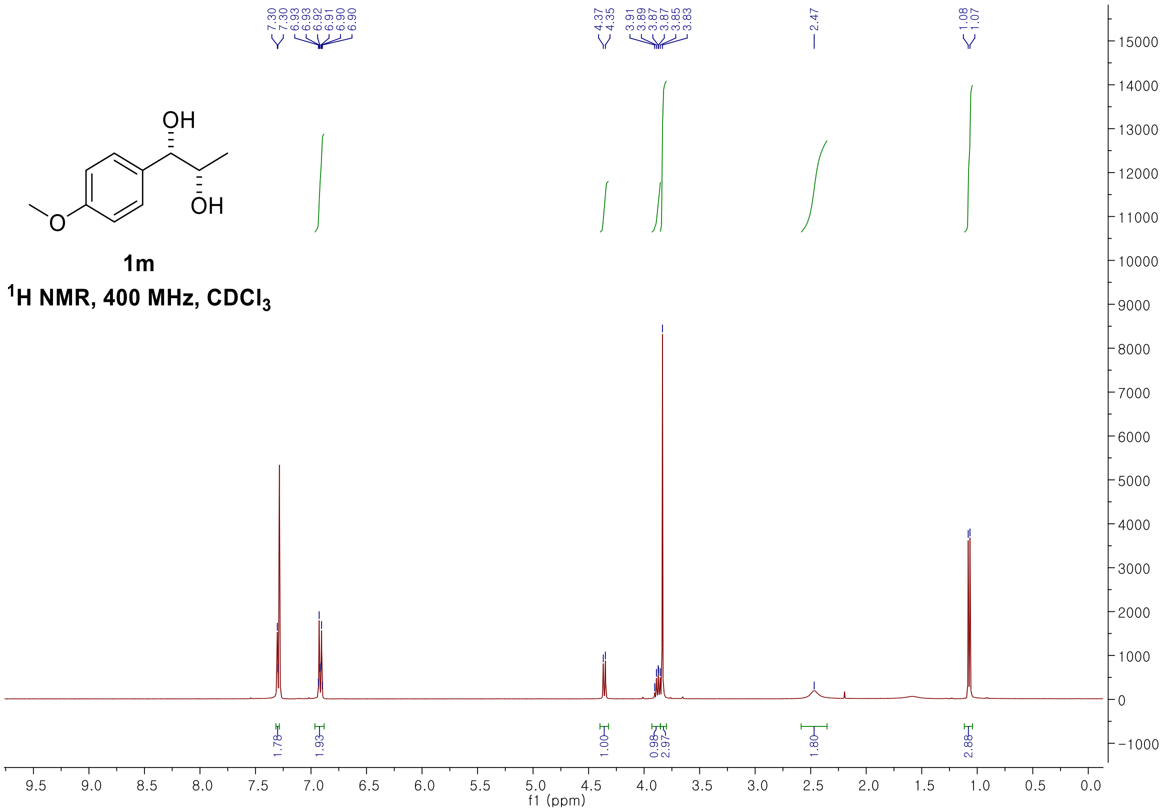
1l

^{1}H NMR, 400 MHz, CDCl$_3$



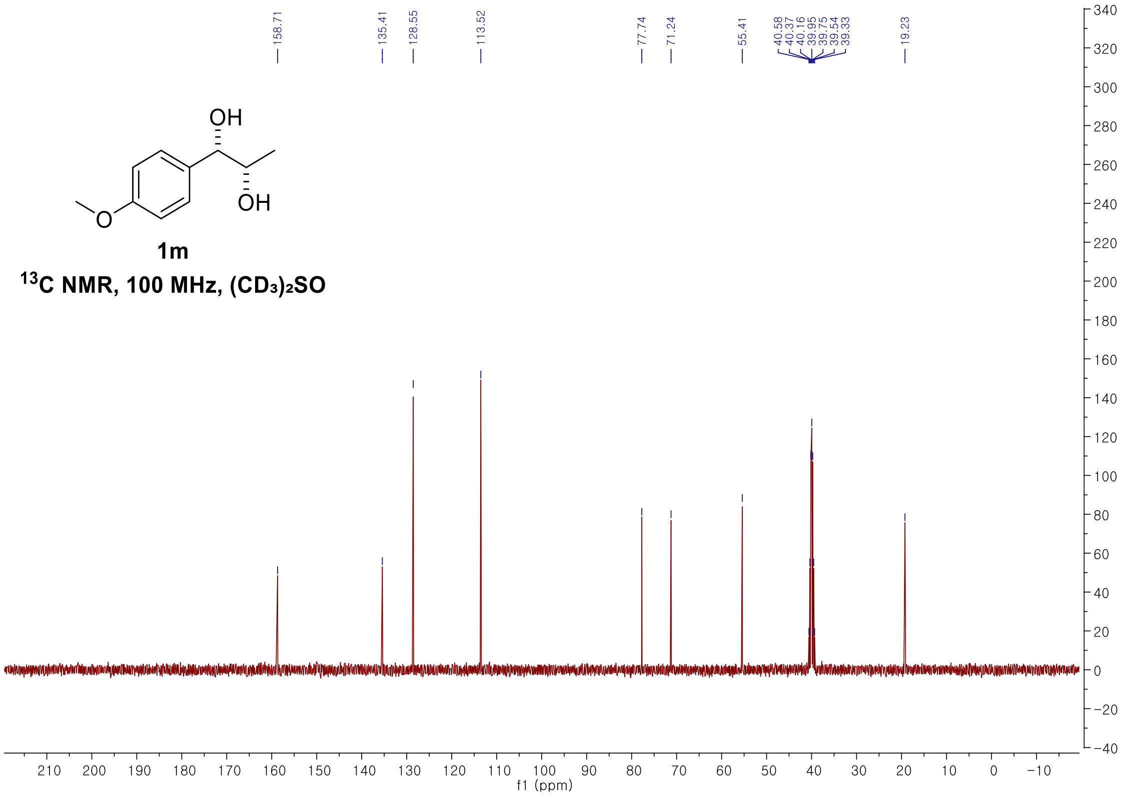
1l

^{13}C NMR, 100 MHz, CD$_3$OD



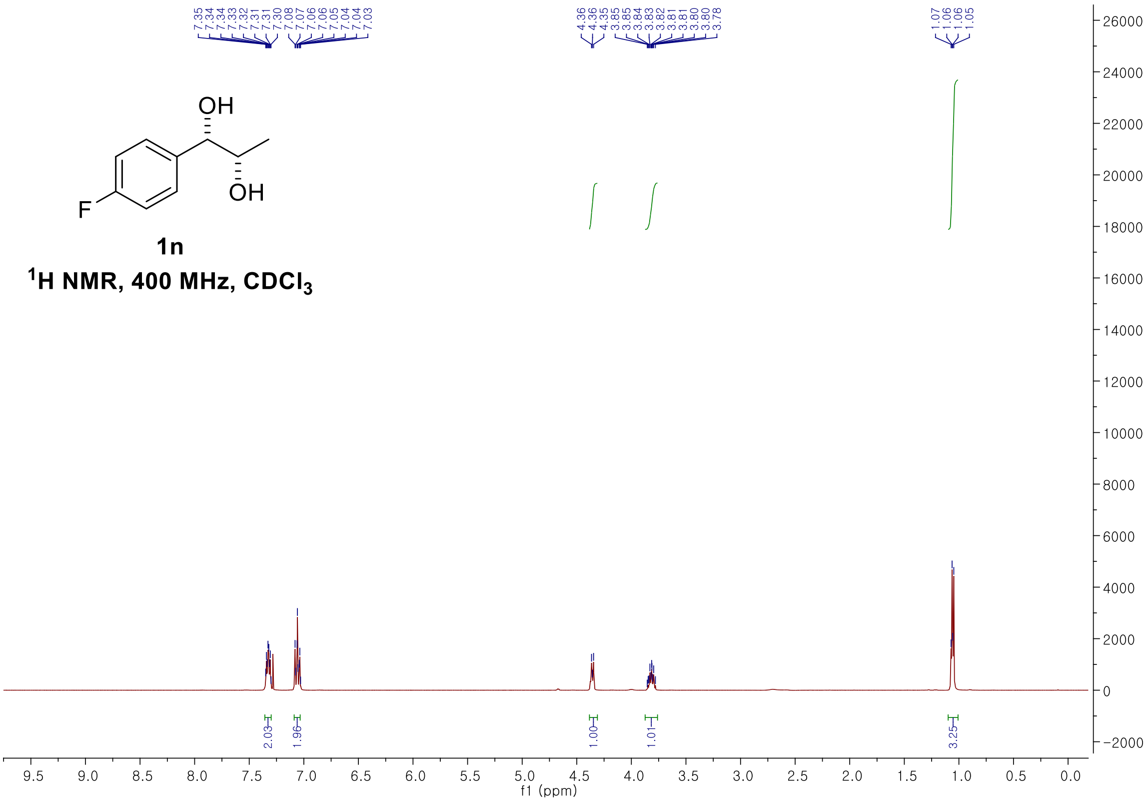
1m

^{1}H NMR, 400 MHz, CDCl$_3$



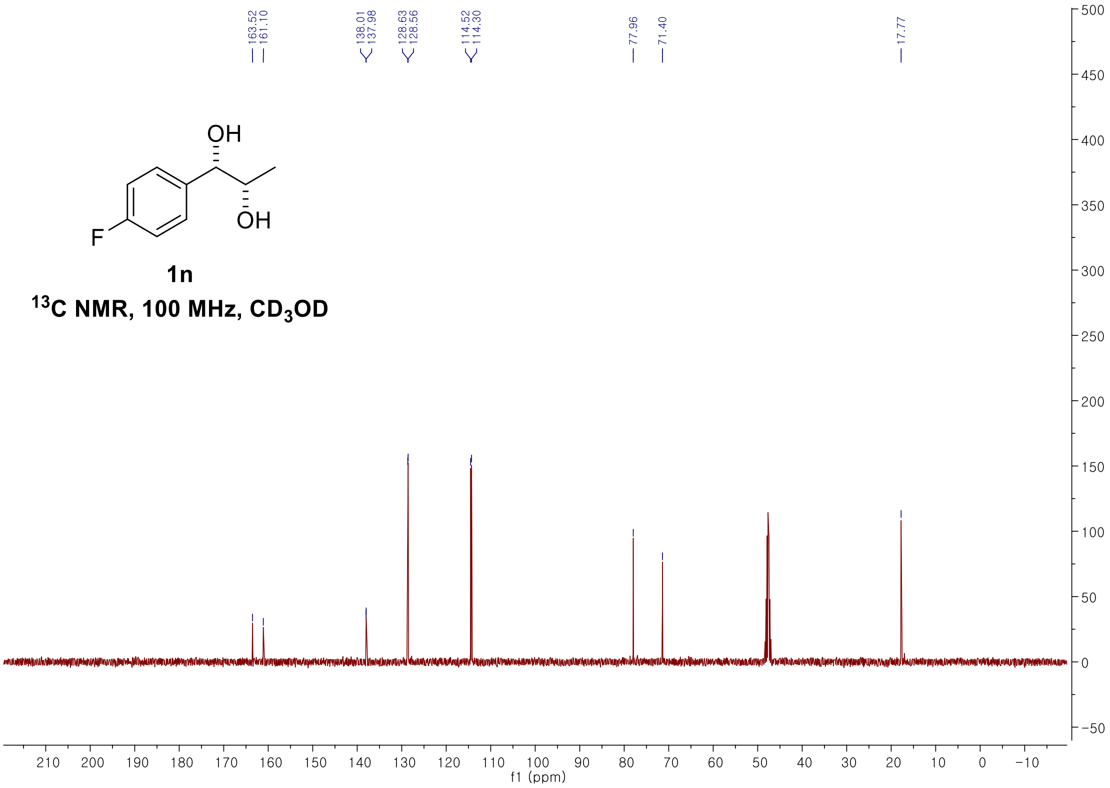
1m

^{13}C NMR, 100 MHz, $(CD_3)_2SO$



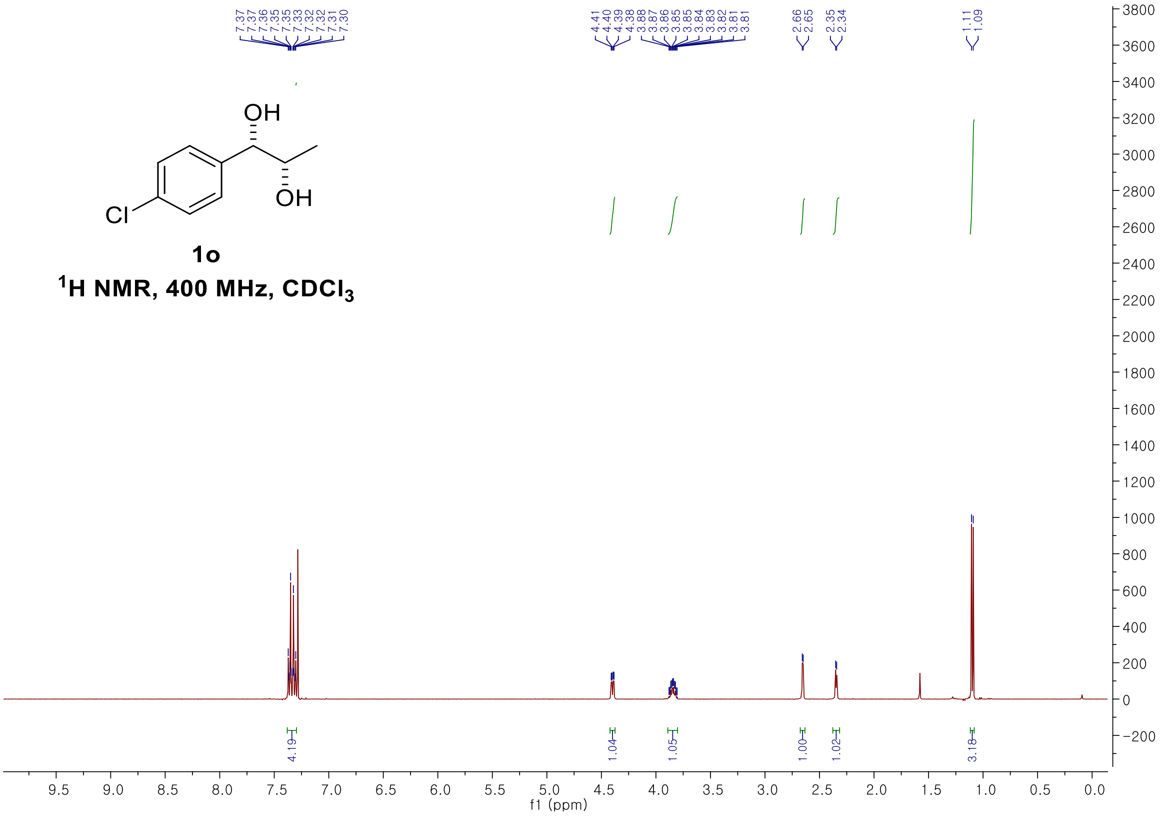
1n

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



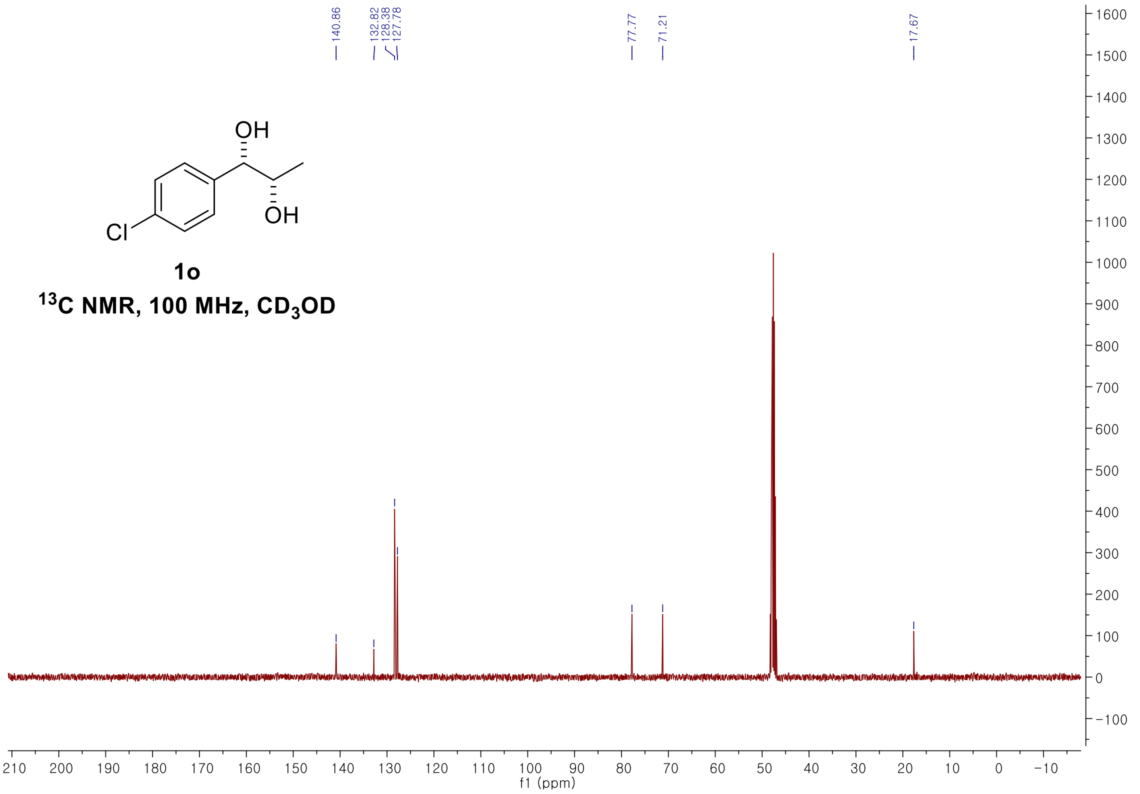
1n

^{13}C NMR, 100 MHz, CD_3OD



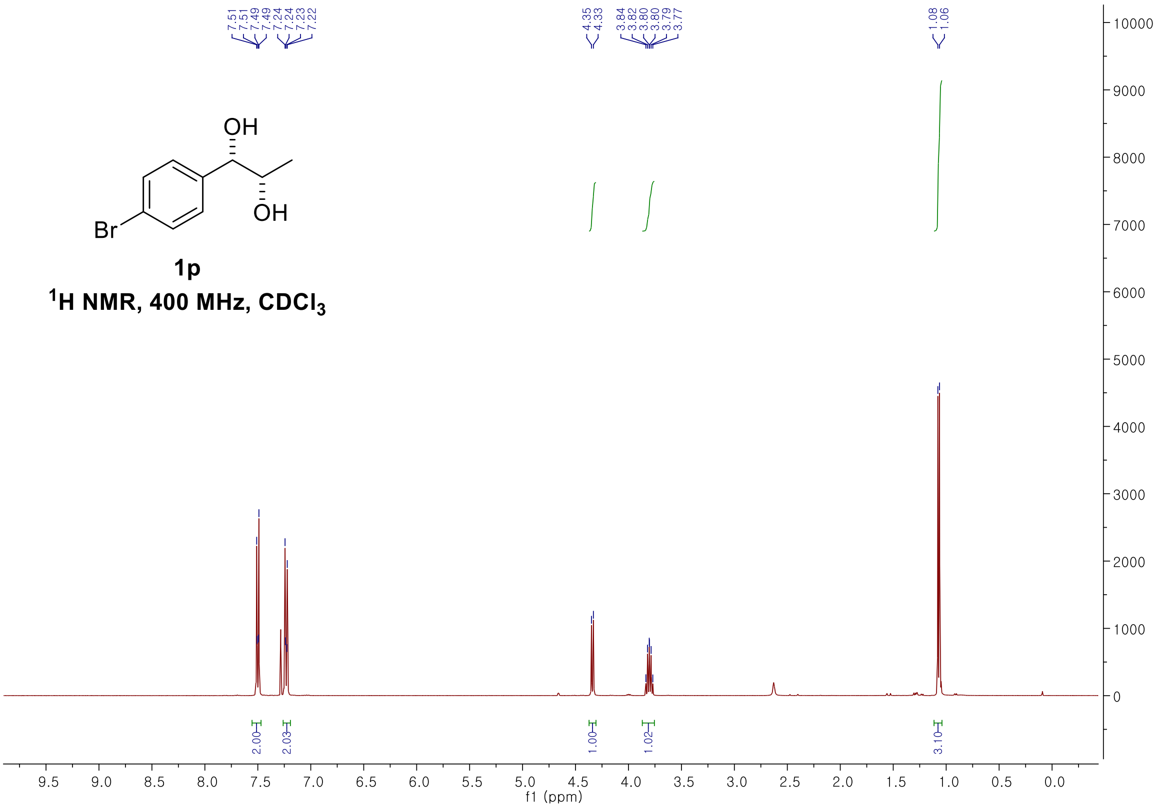
1o

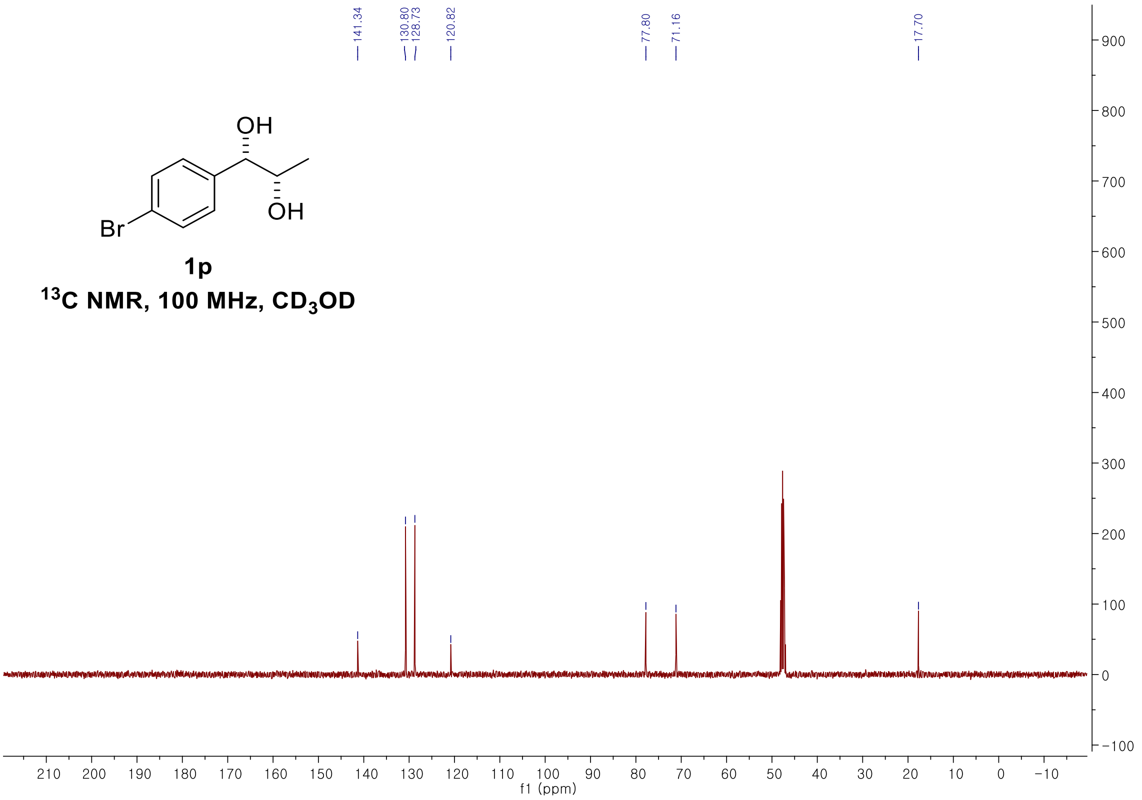
^{1}H NMR, 400 MHz, $CDCl_3$

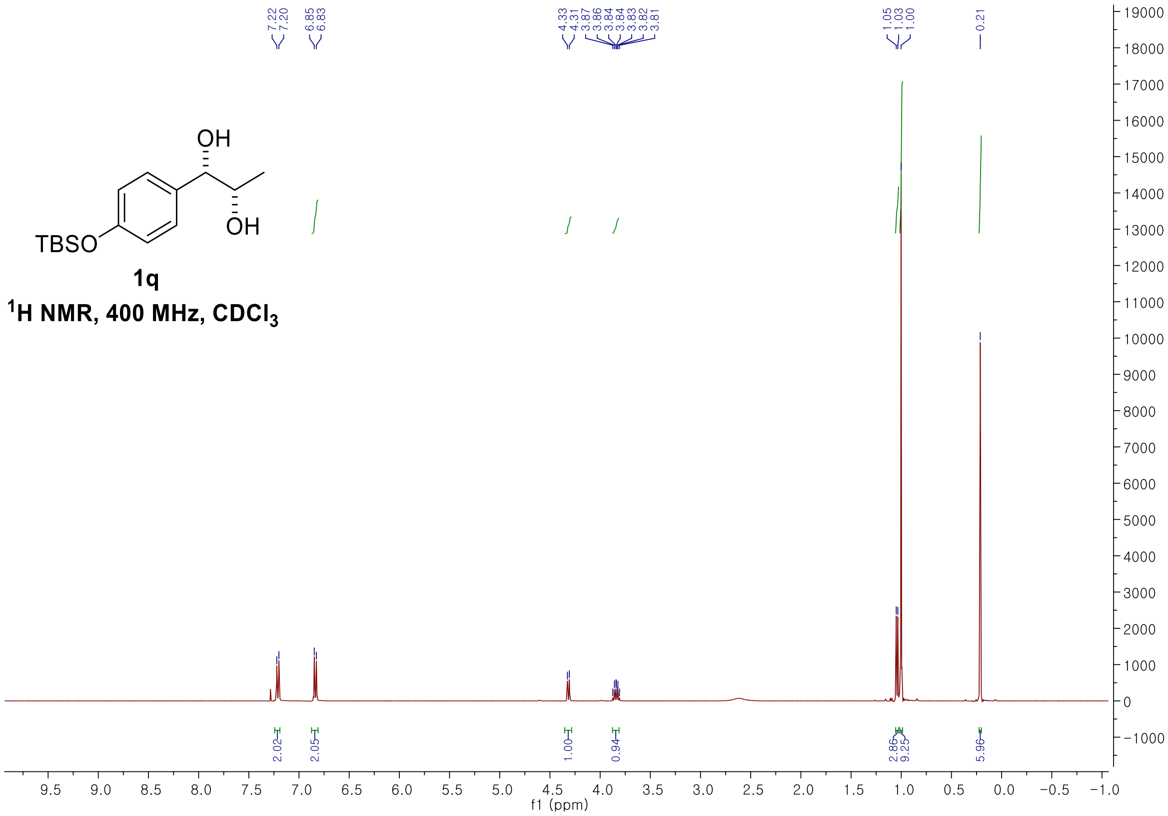


1o

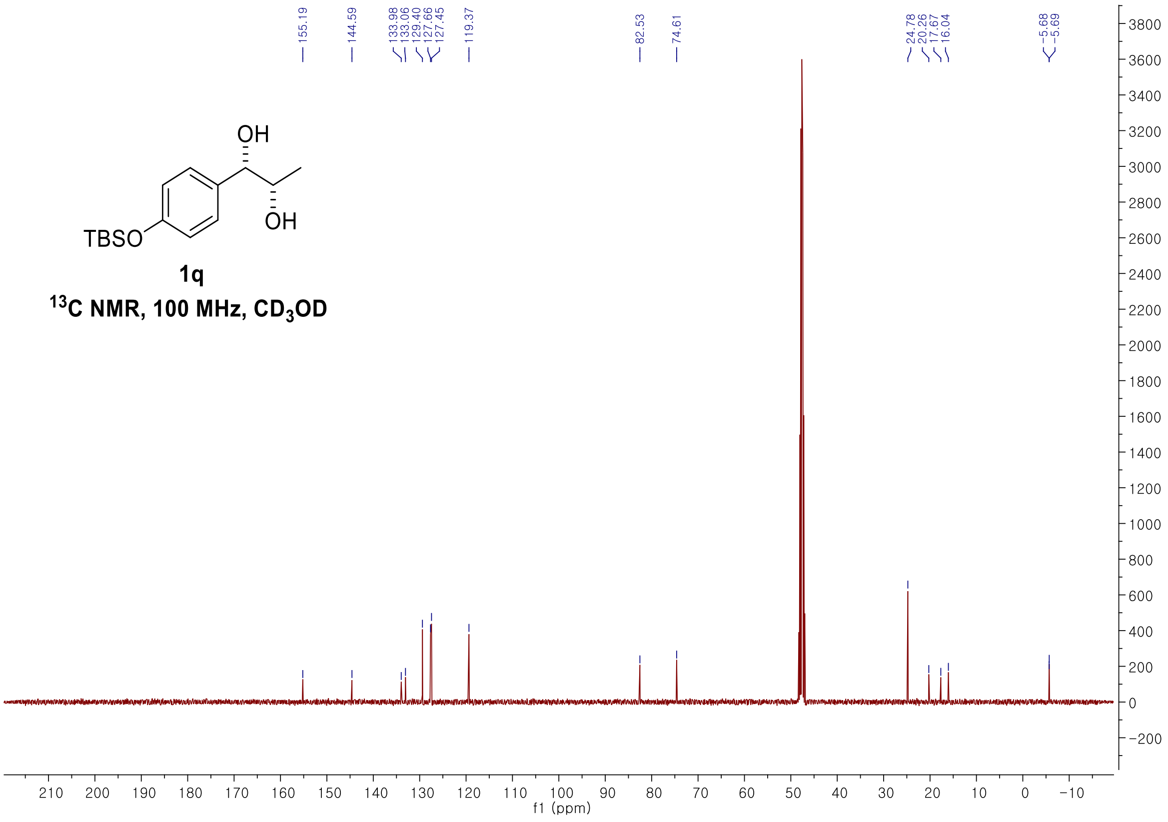
^{13}C NMR, 100 MHz, CD_3OD


7.51
7.51
7.49
7.49
7.24
7.24
7.23
7.22
4.35
4.33
3.84
3.82
3.80
3.80
3.79
3.77
1.08
1.06
OH
OH
Br
1p
^{1}H NMR, 400 MHz, CDCl$_3$
2.00
2.03
1.00
1.02
3.10
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

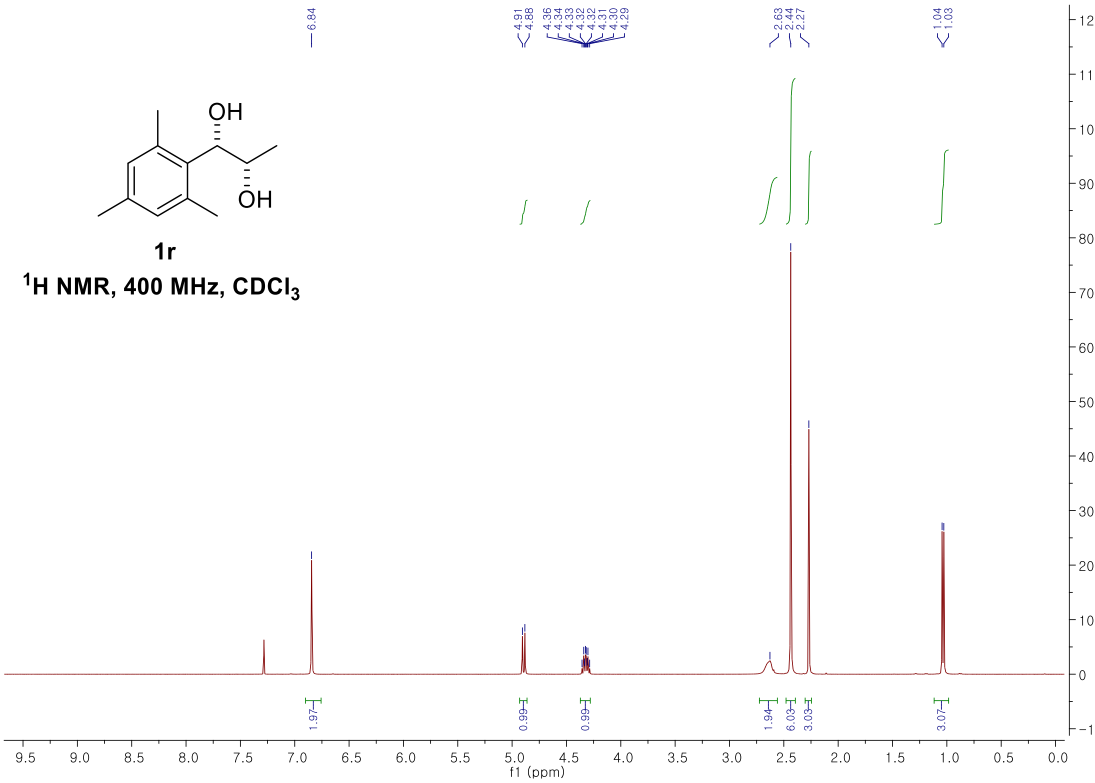

141.34
130.80
128.73
120.82
77.80
71.16
17.70
OH
OH
Br
1p
^{13}C NMR, 100 MHz, CD$_3$OD
900
800
700
600
500
400
300
200
100
0
−100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


1q

^{1}H NMR, 400 MHz, CDCl$_3$

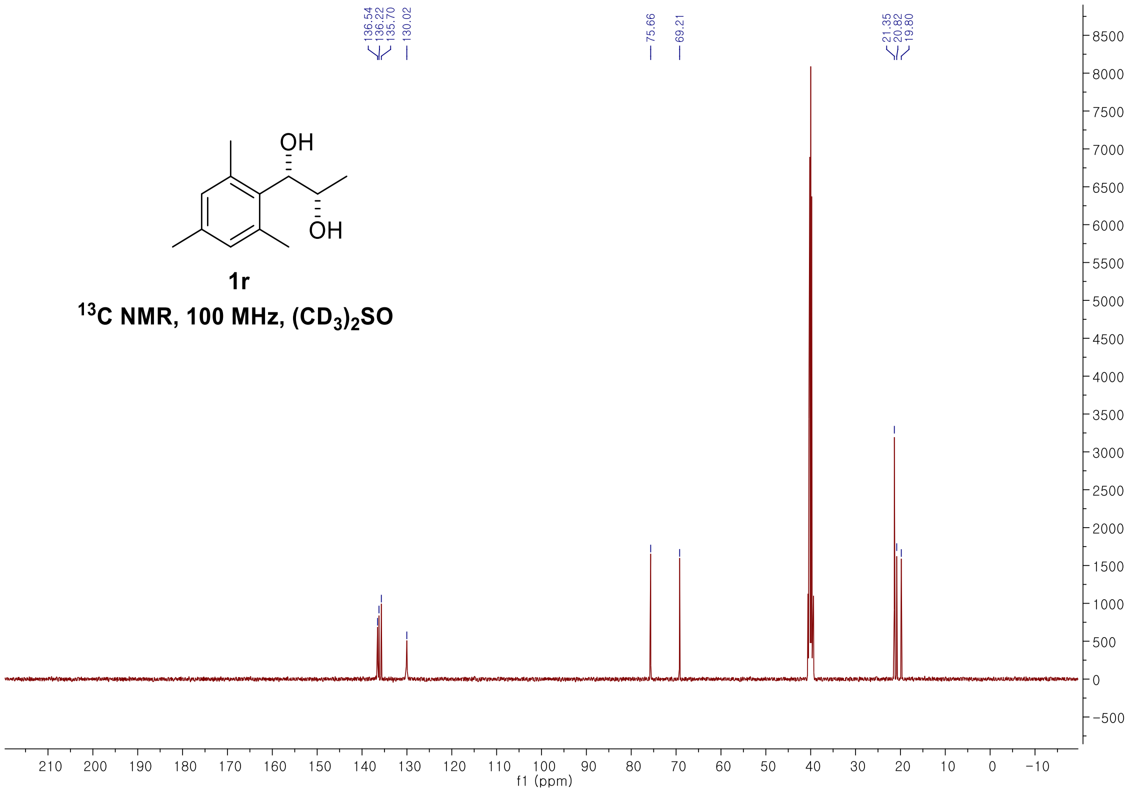

1q

^{13}C NMR, 100 MHz, CD$_3$OD



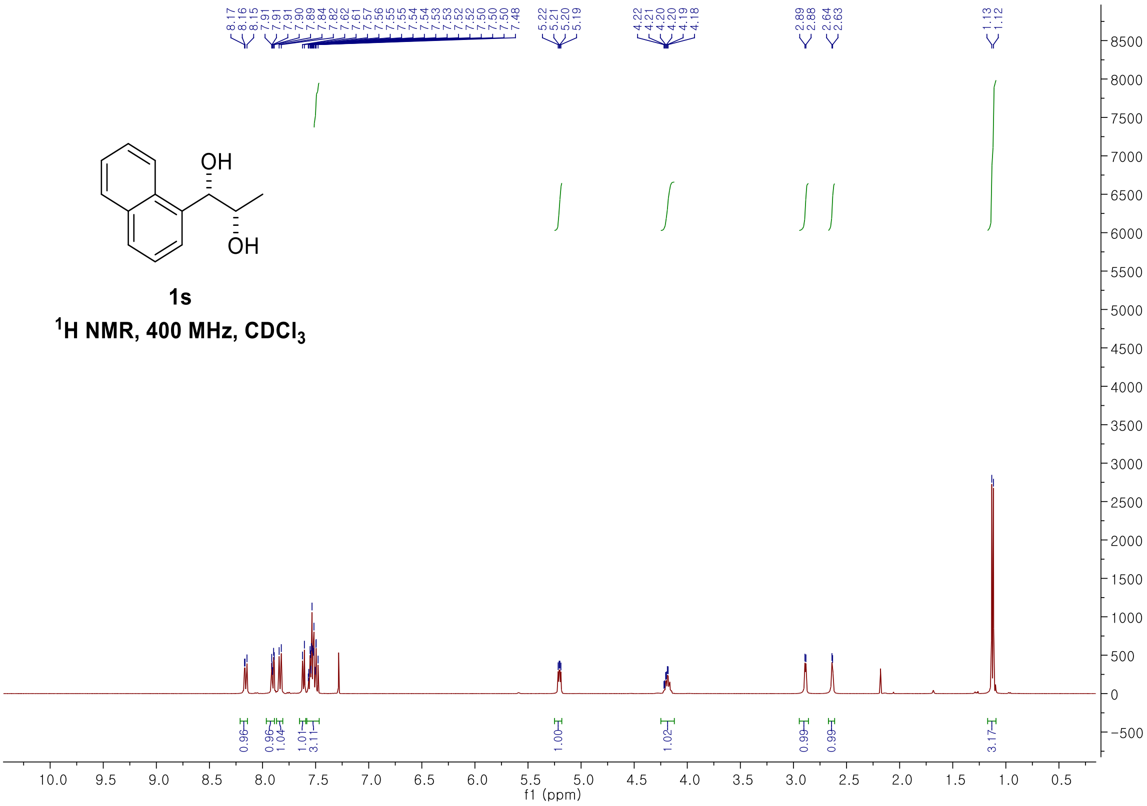
1r

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



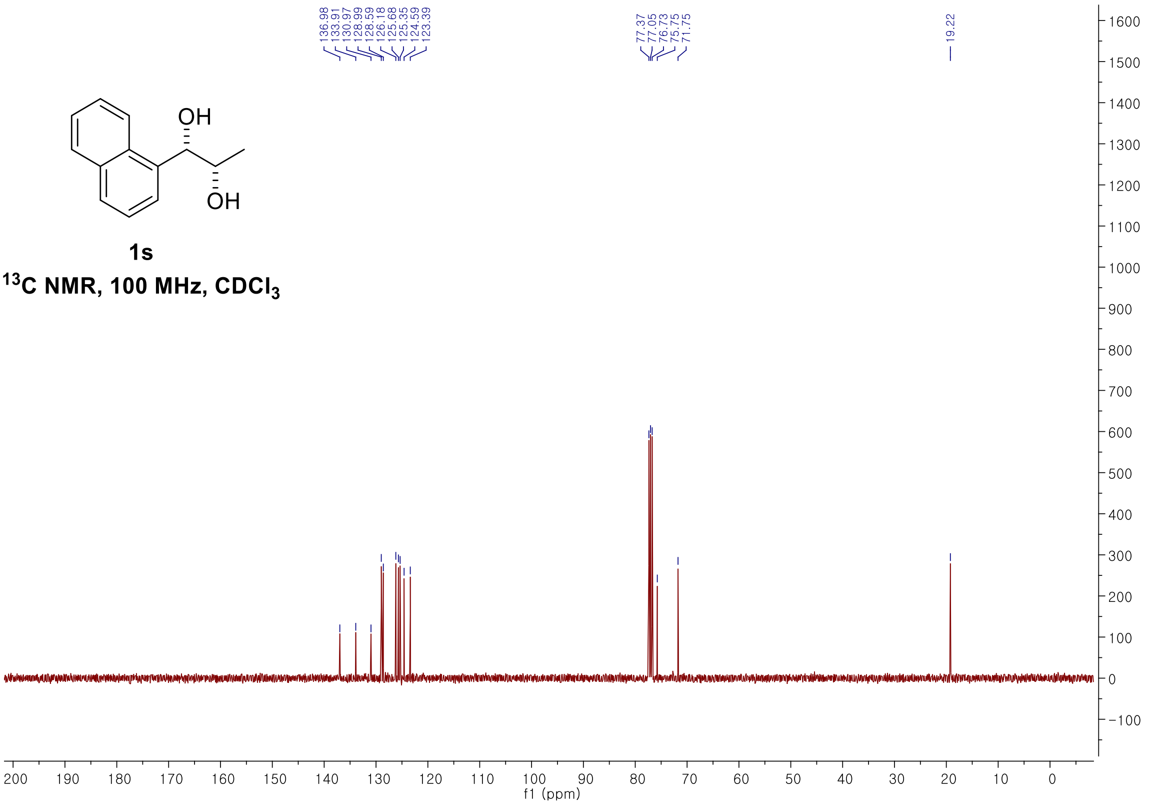
1r

^{13}C NMR, 100 MHz, $(CD_3)_2SO$



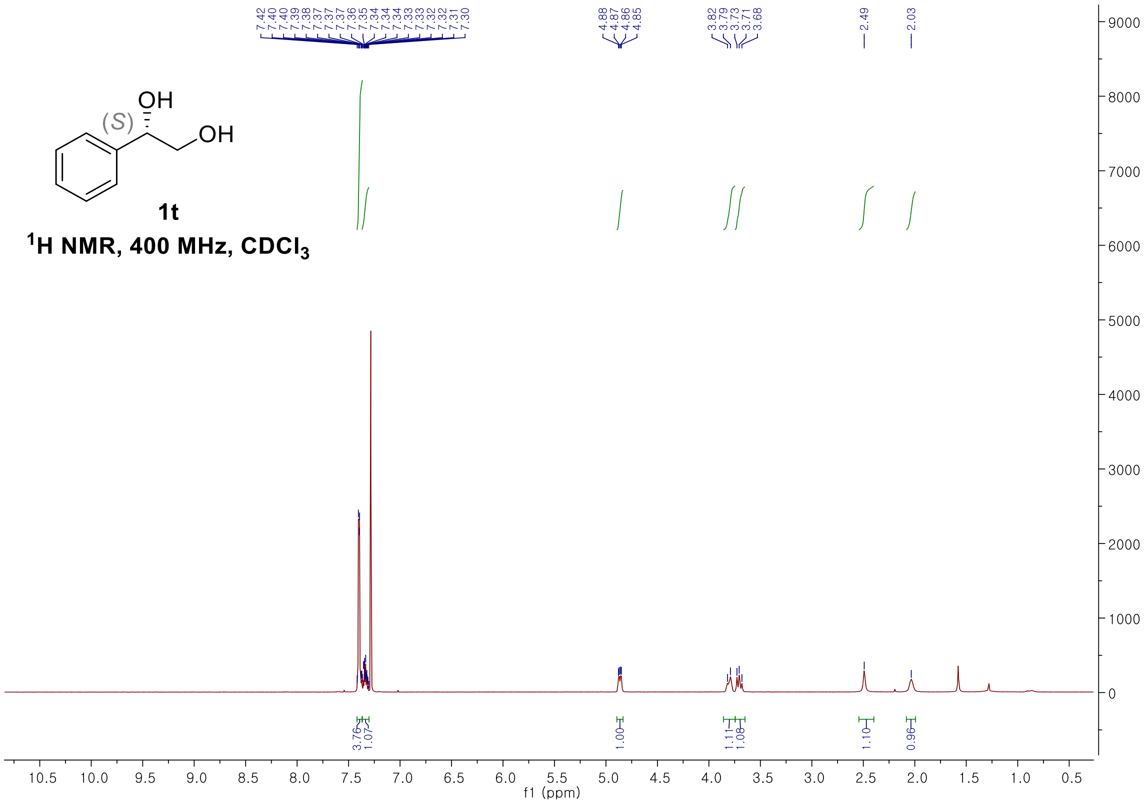
1s

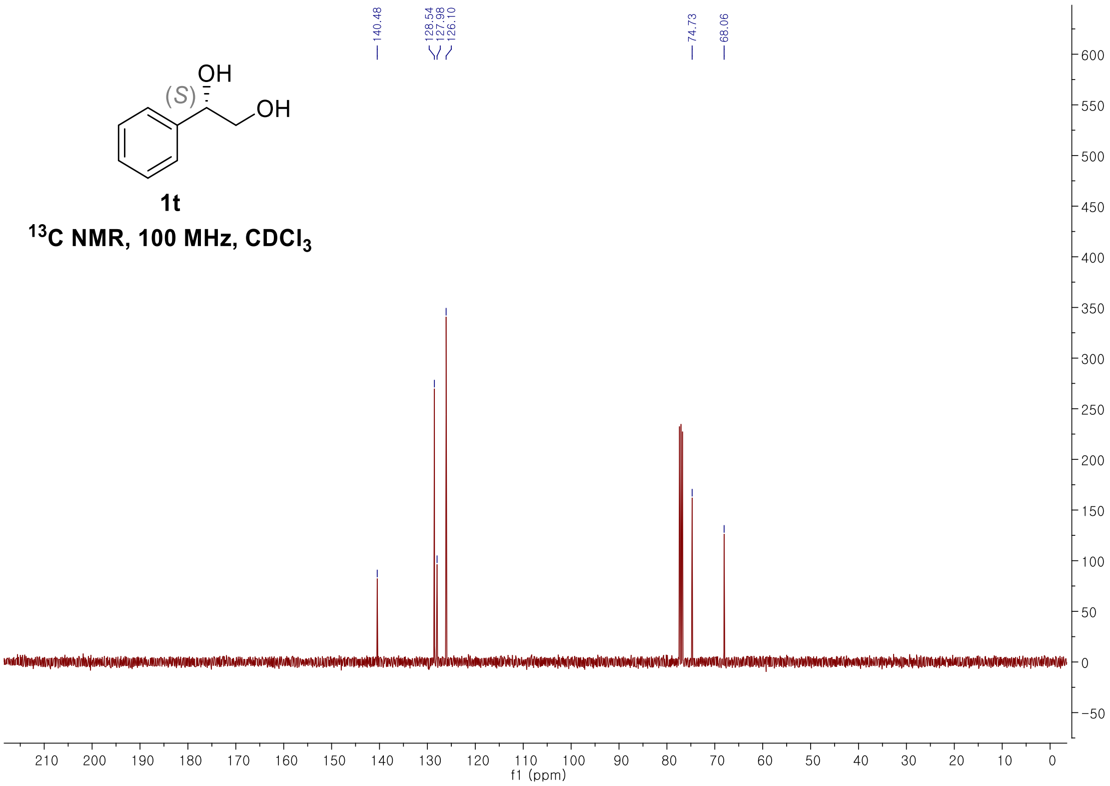
^{1}H NMR, 400 MHz, CDCl$_3$

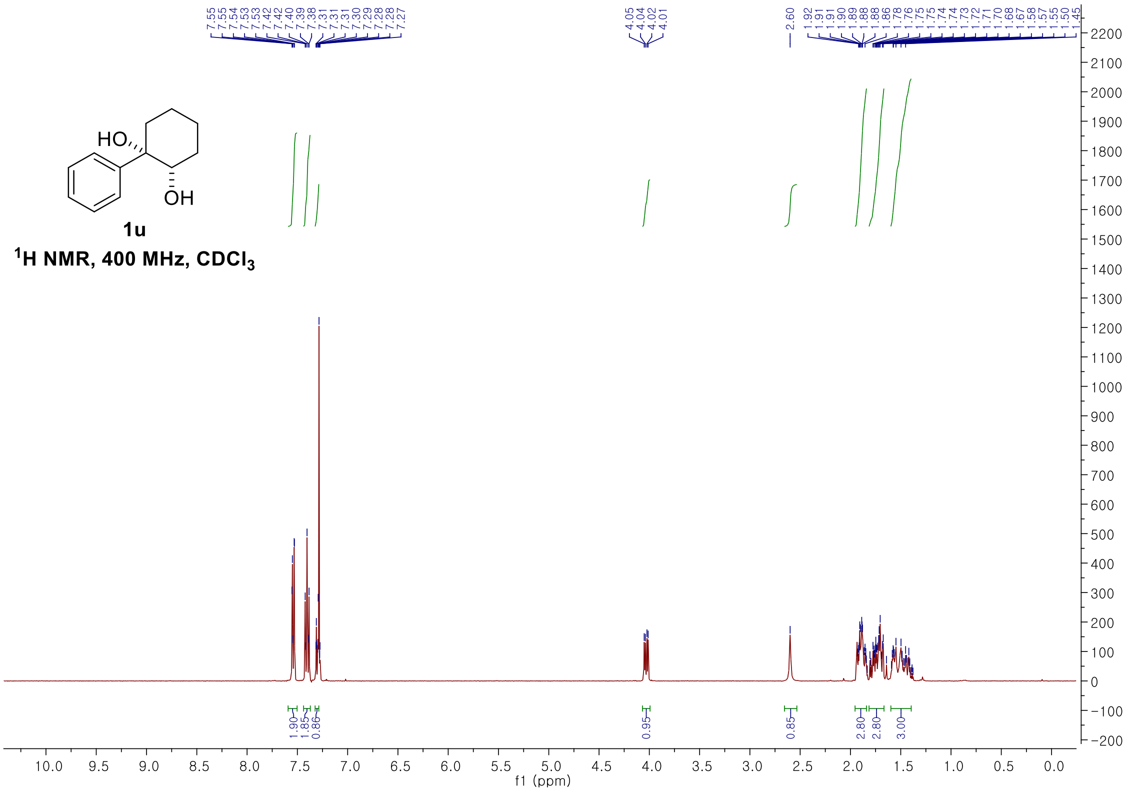


1s

^{13}C NMR, 100 MHz, CDCl$_3$

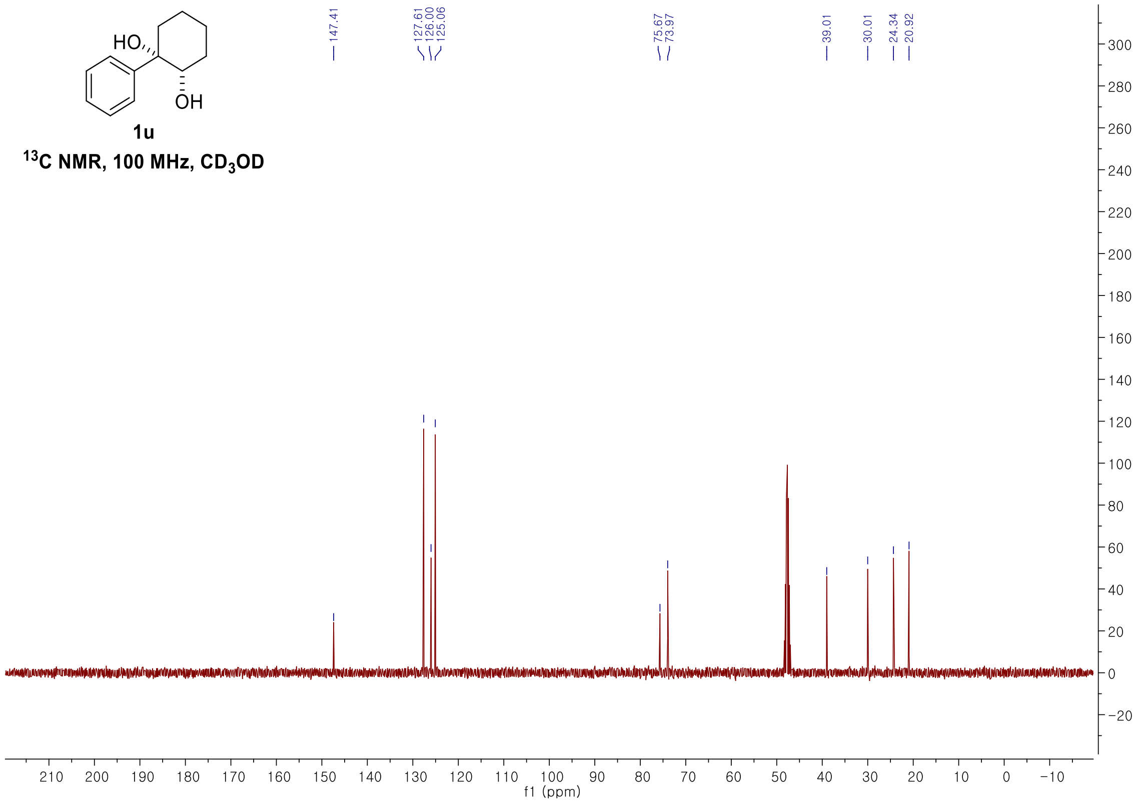

OH
(S)
OH
1t
^{1}H NMR, 400 MHz, $CDCl_3$
7.42
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
4.88
4.87
4.86
4.85
3.82
3.79
3.73
3.71
3.68
2.49
2.03
3.76
1.07
1.00
1.11
1.08
1.10
0.96
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


140.48
128.54
127.98
126.10
74.73
68.06
OH
(S)
OH
1t
^{13}C NMR, 100 MHz, $CDCl_3$
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



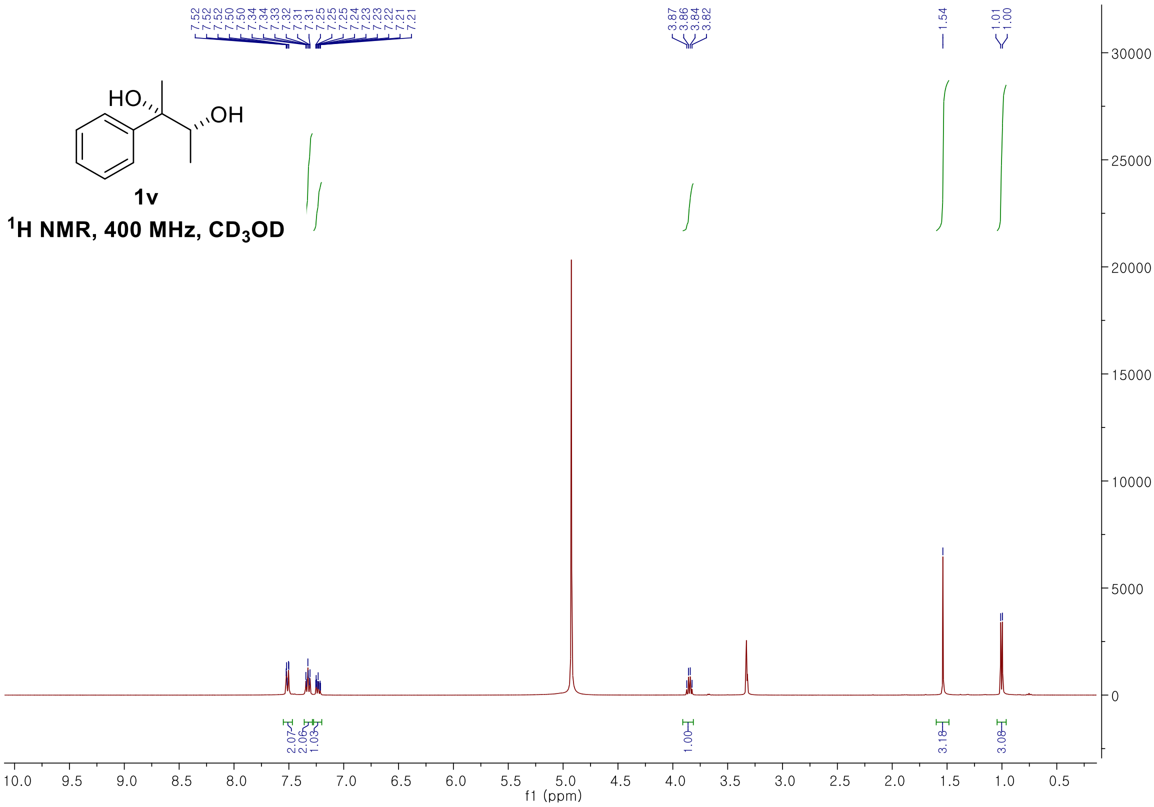
1u

^{1}H NMR, 400 MHz, CDCl$_3$



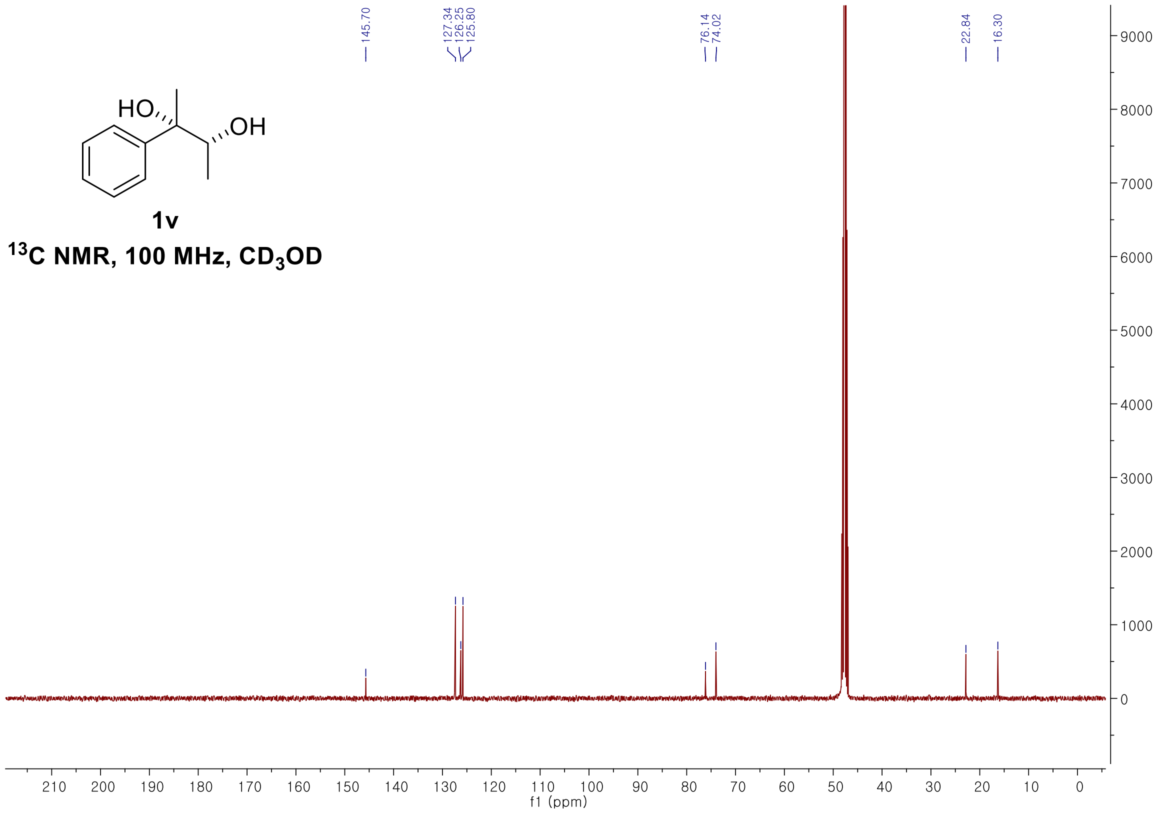
1u

^{13}C NMR, 100 MHz, CD$_3$OD



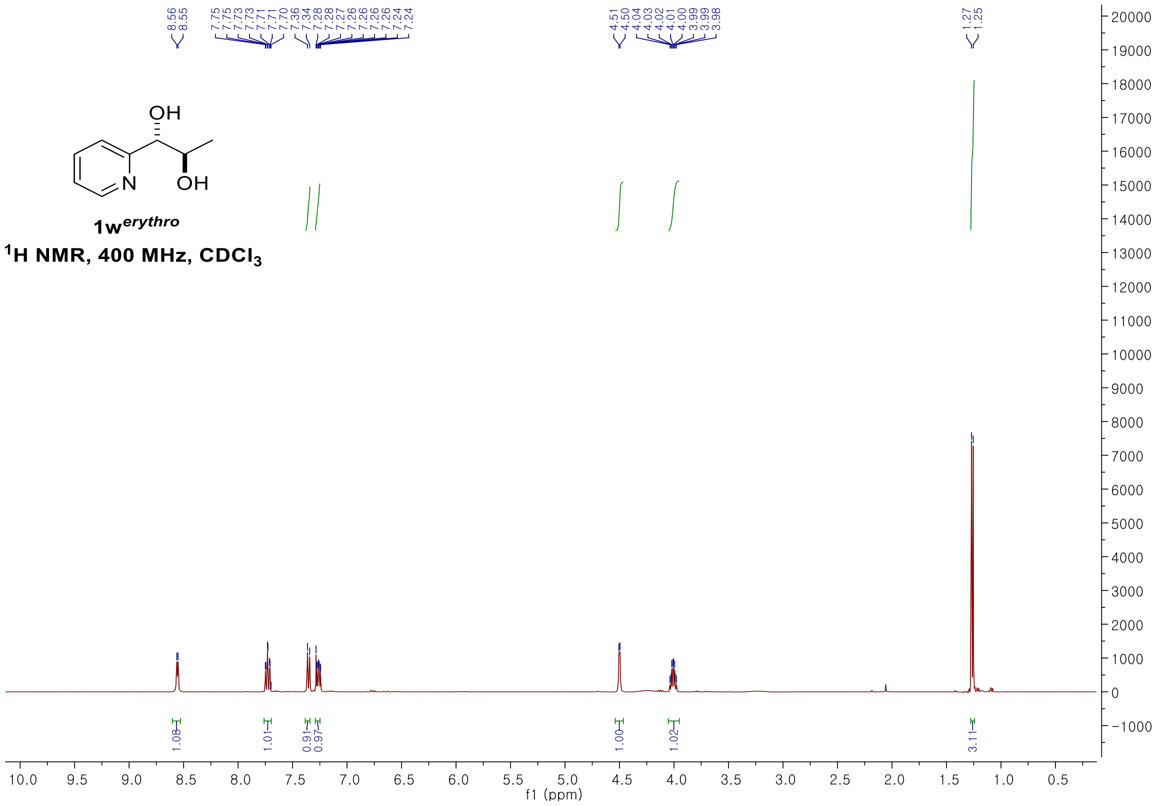
1v

^{1}H NMR, 400 MHz, CD_3OD



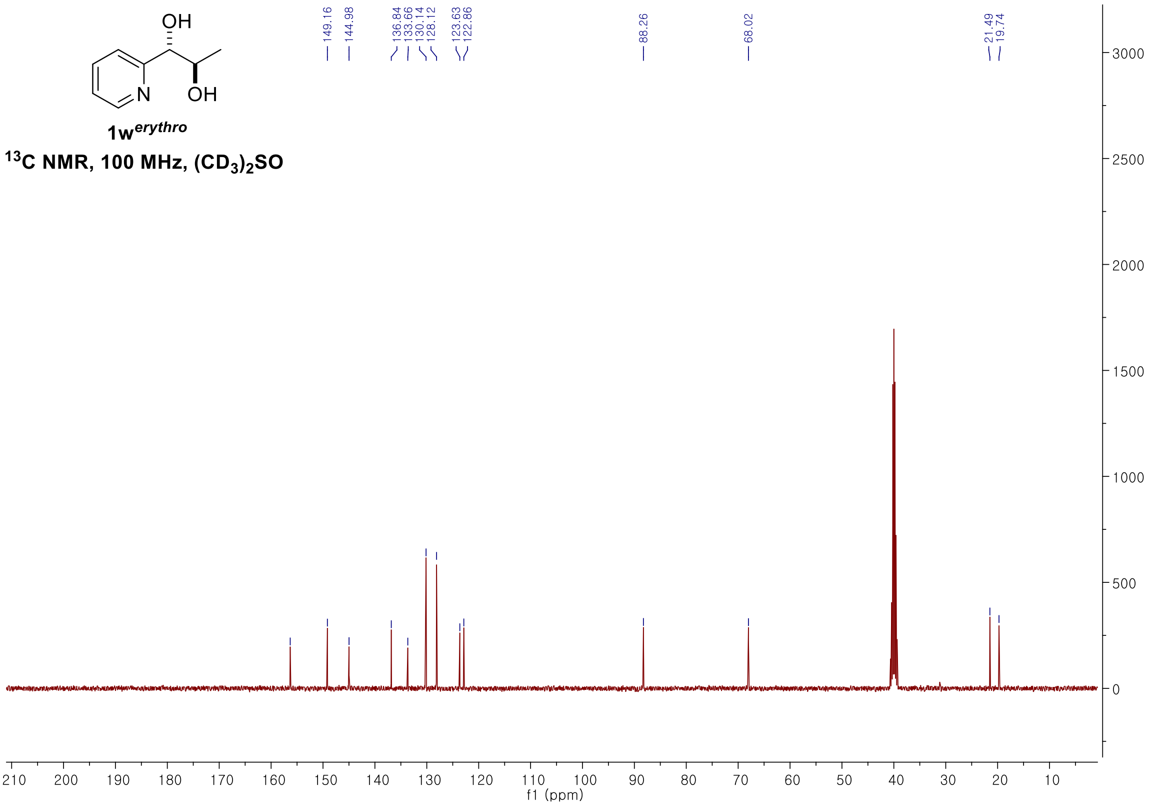
1v

^{13}C NMR, 100 MHz, CD_3OD



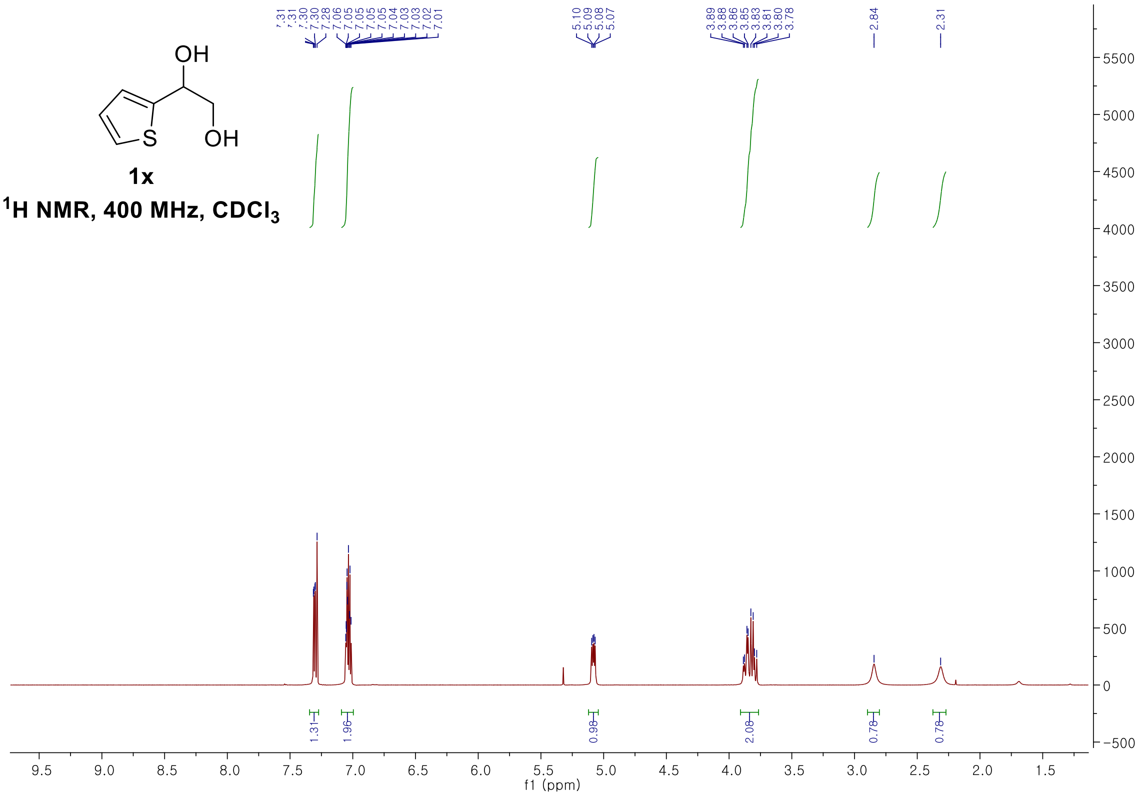
$1w^{erythro}$

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



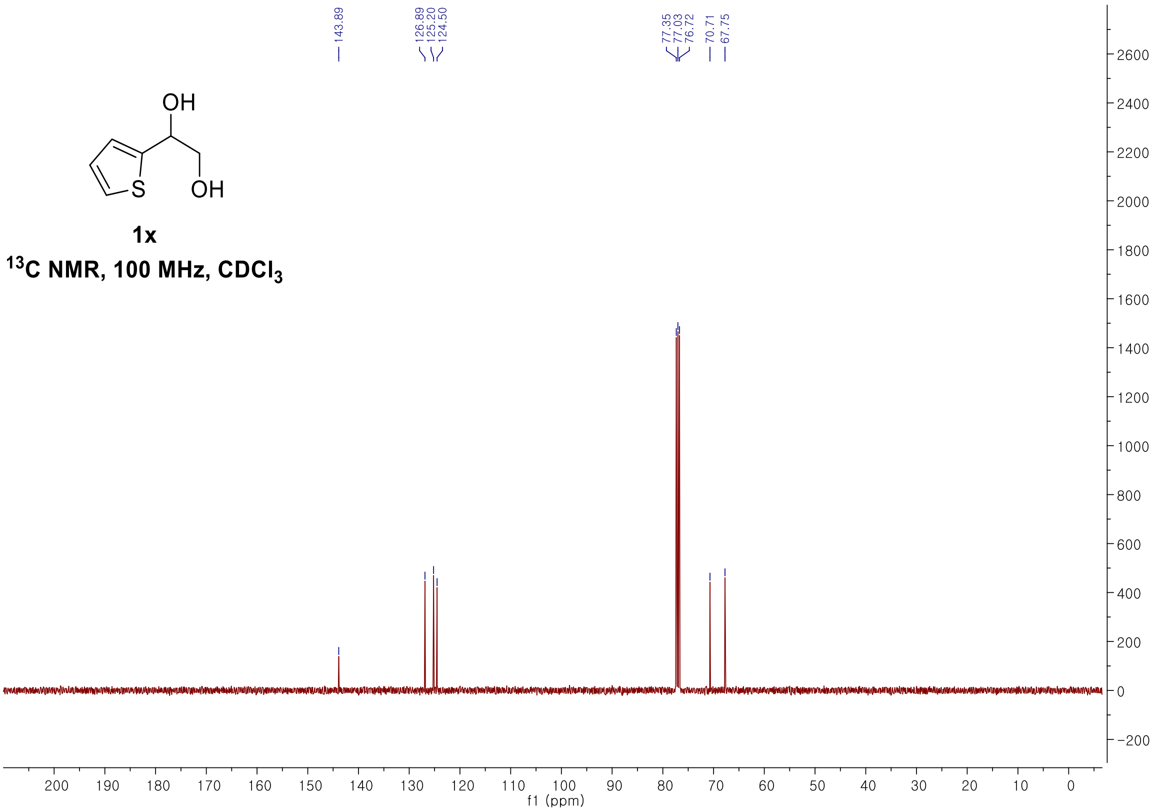
$1w^{erythro}$

^{13}C NMR, 100 MHz, $(CD_3)_2SO$



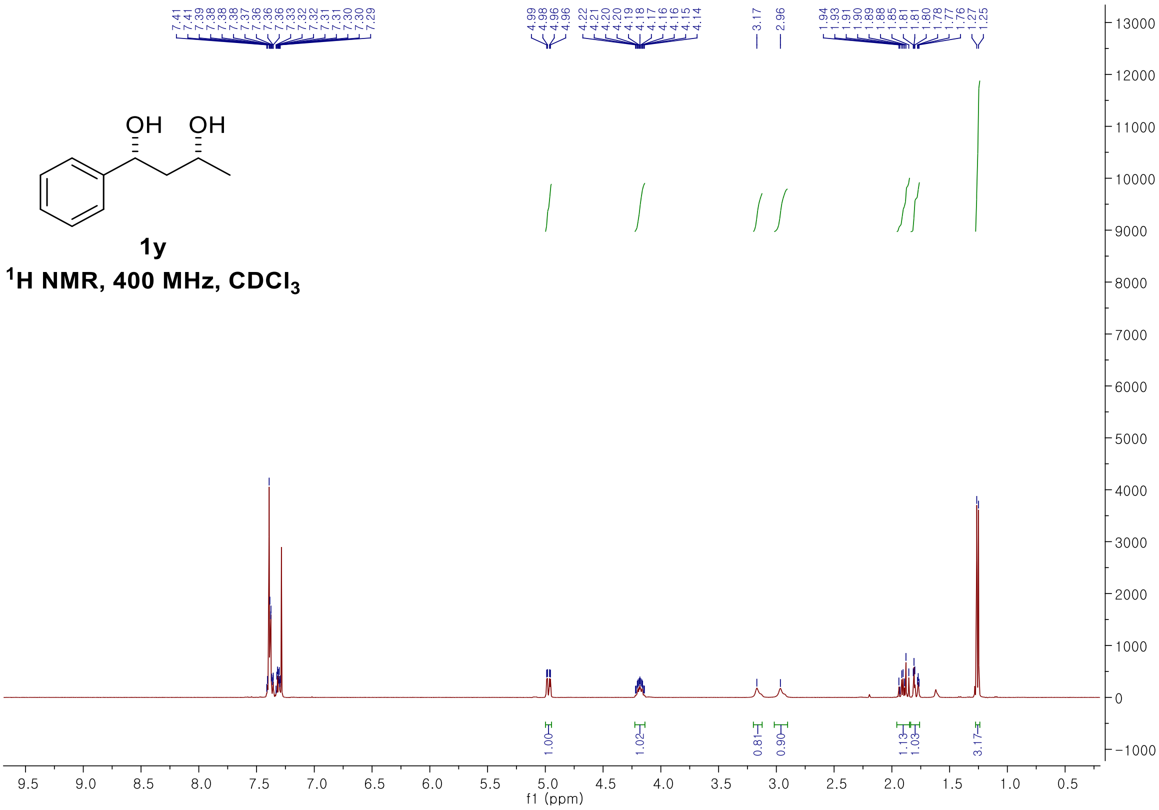
1x

^{1}H NMR, 400 MHz, CDCl$_3$

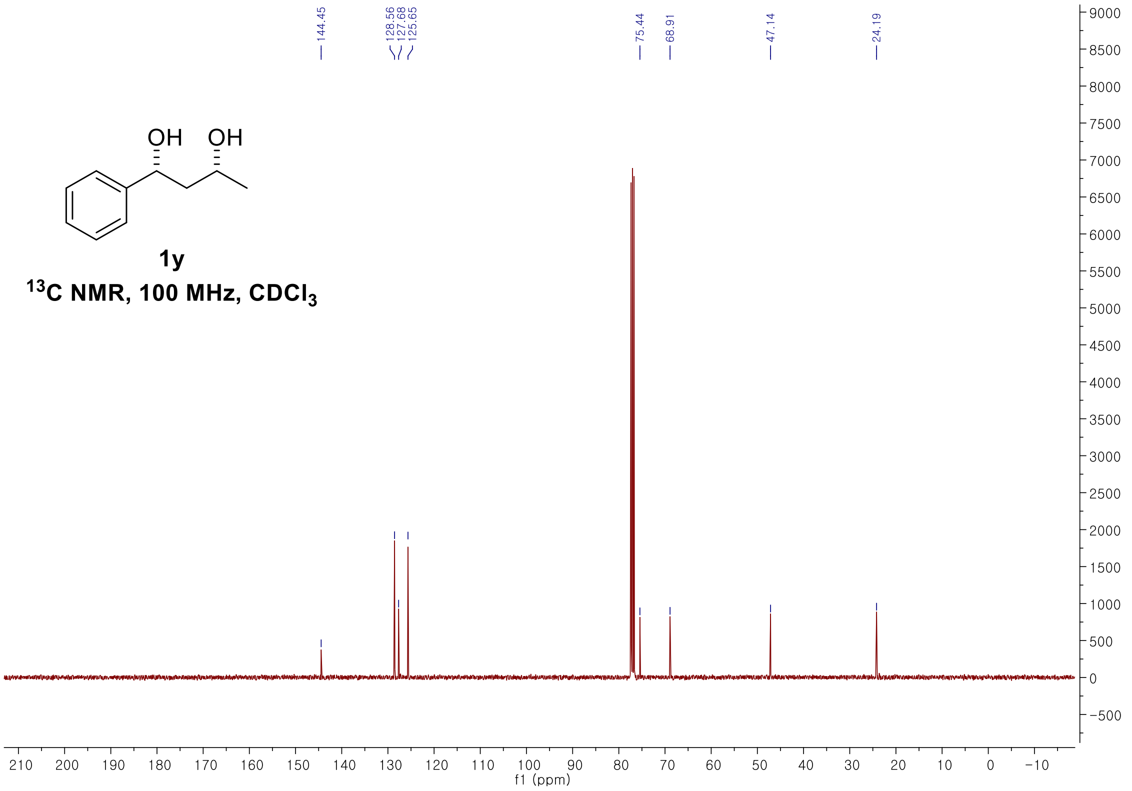


1x

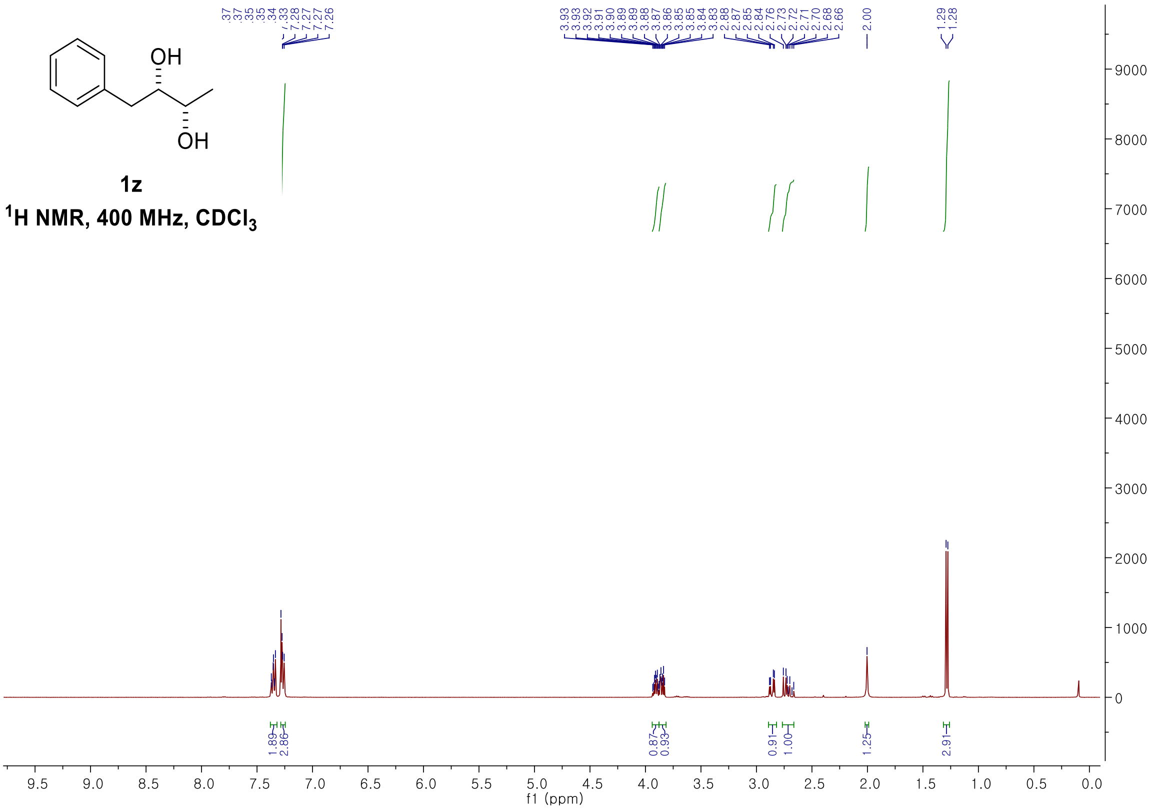
^{13}C NMR, 100 MHz, CDCl$_3$


1y

^{1}H NMR, 400 MHz, CDCl$_3$

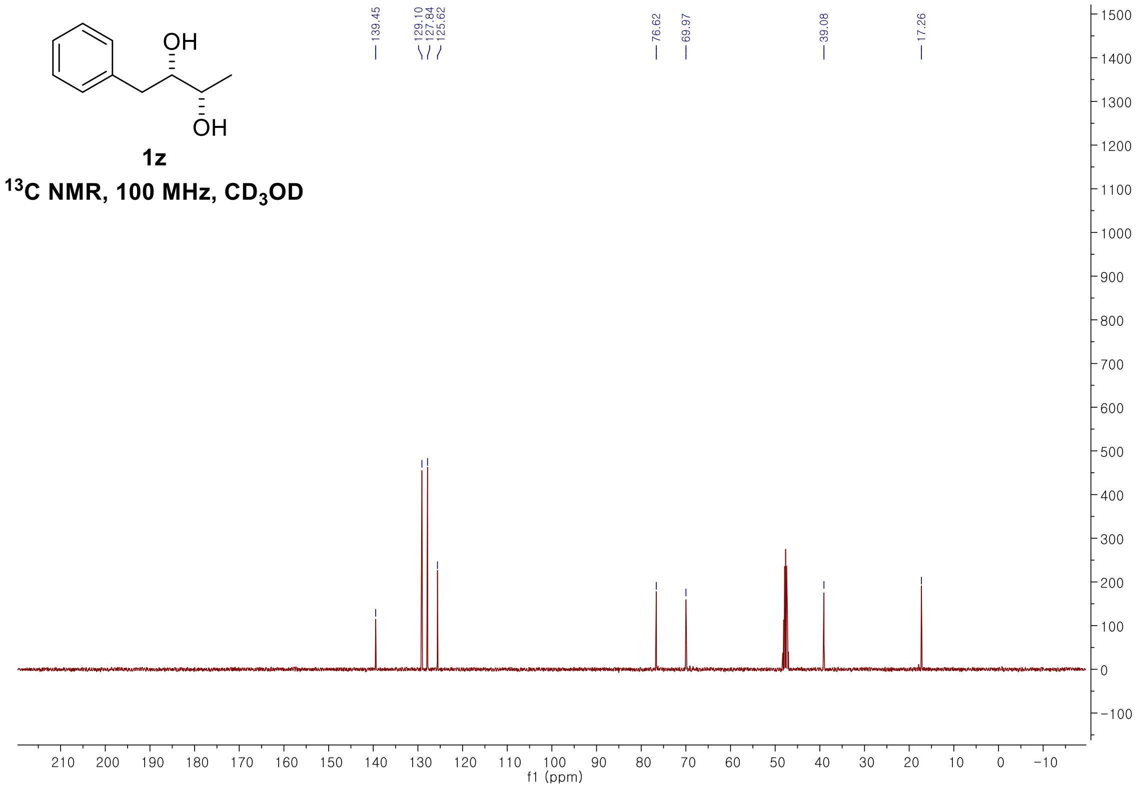

1y

^{13}C NMR, 100 MHz, CDCl$_3$



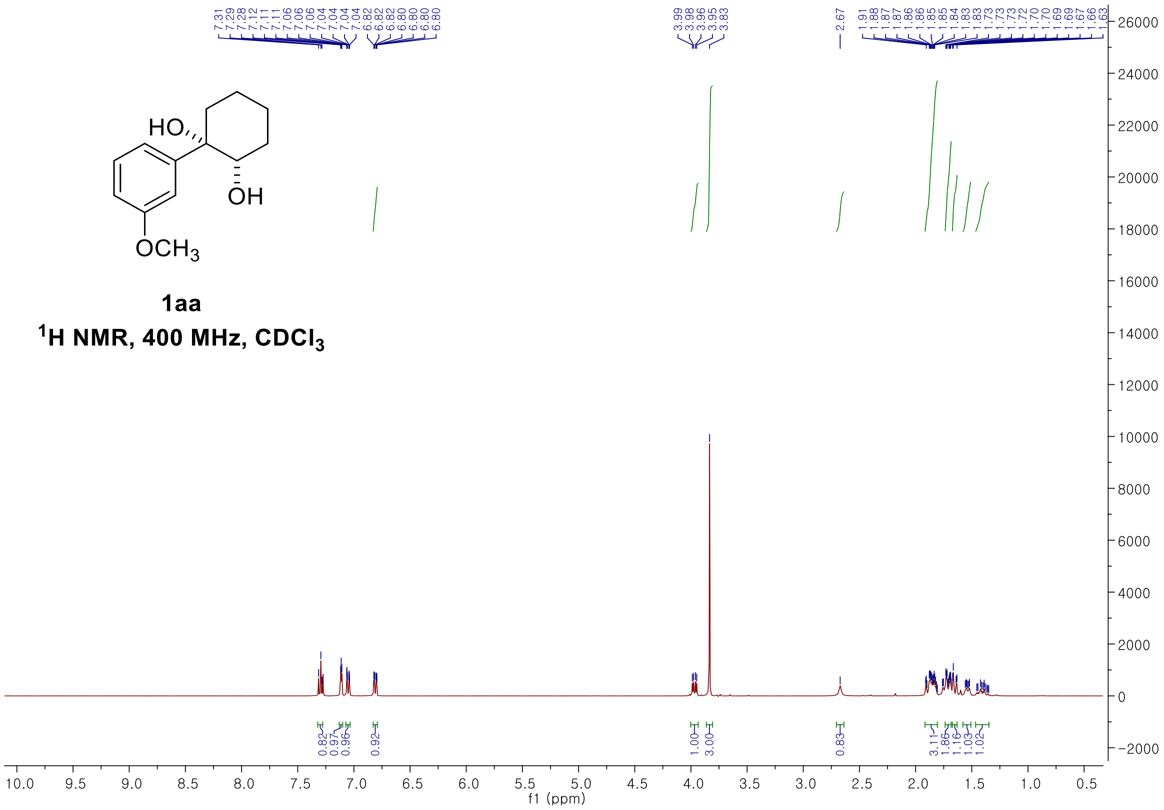
1z

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



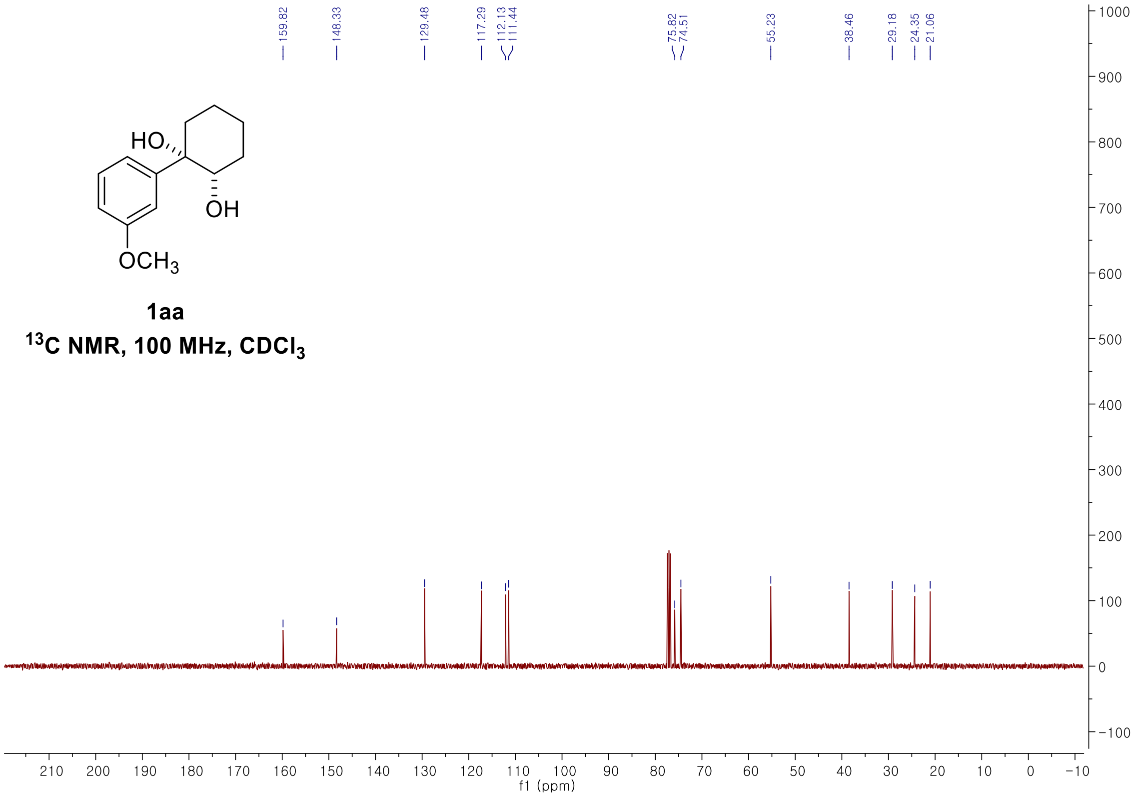
1z

^{13}C NMR, 100 MHz, CD_3OD



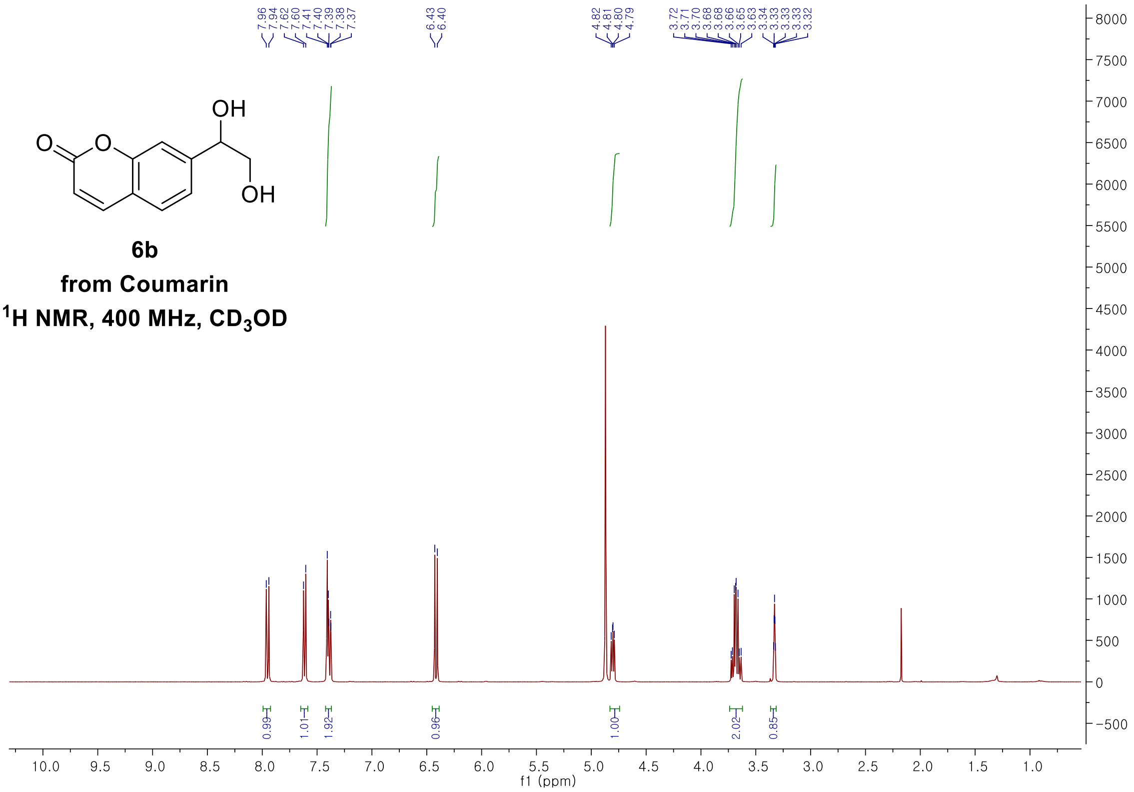
1aa

^{1}H NMR, 400 MHz, CDCl$_3$

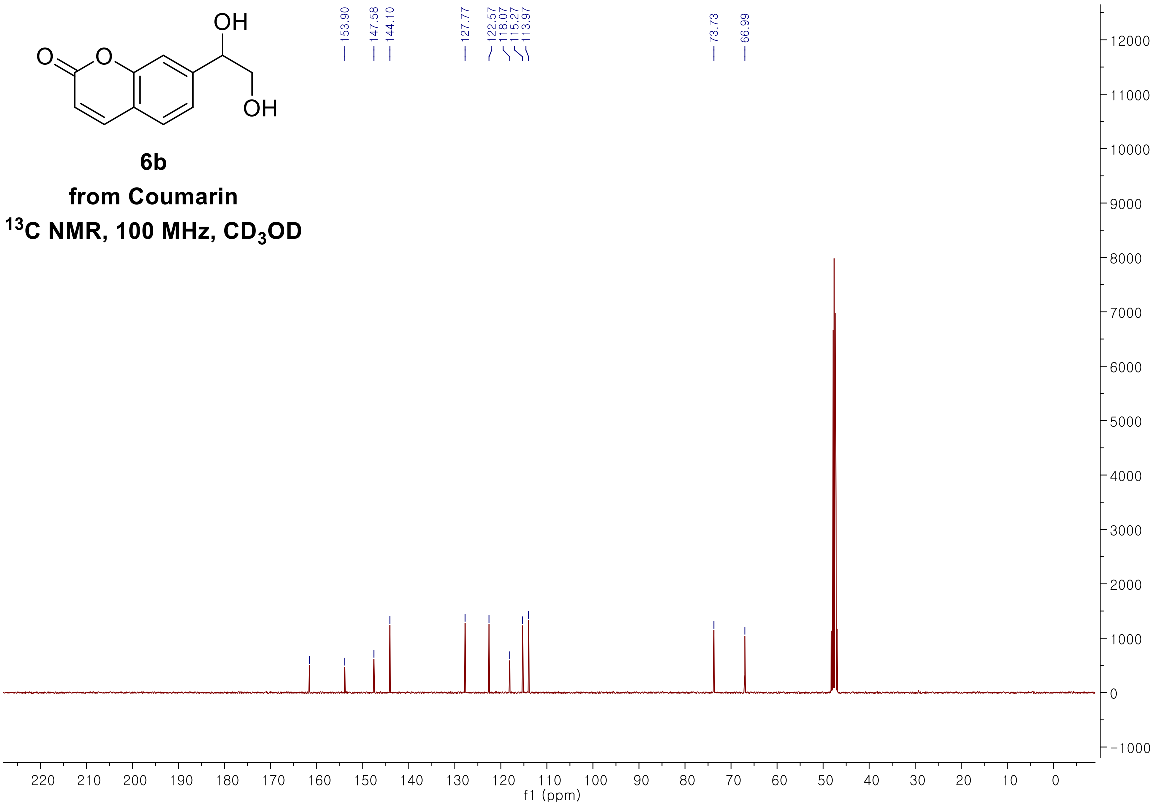


1aa

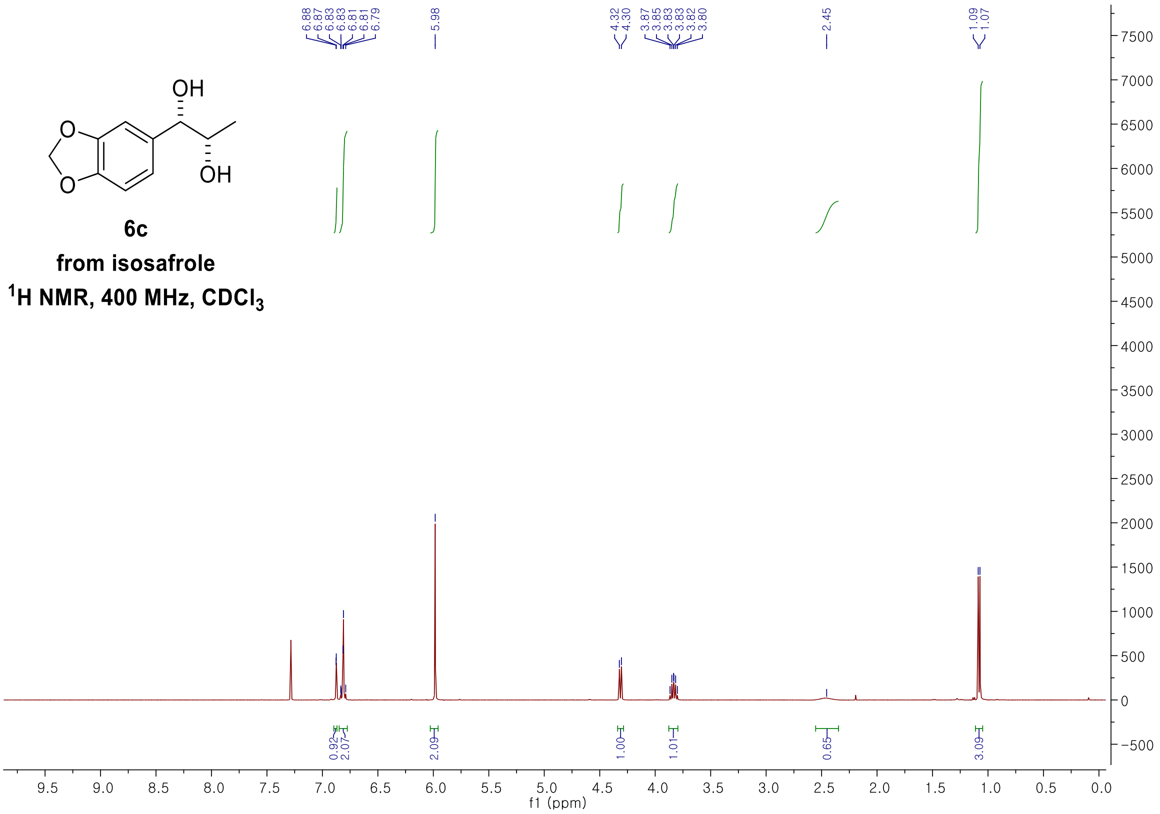
^{13}C NMR, 100 MHz, CDCl$_3$

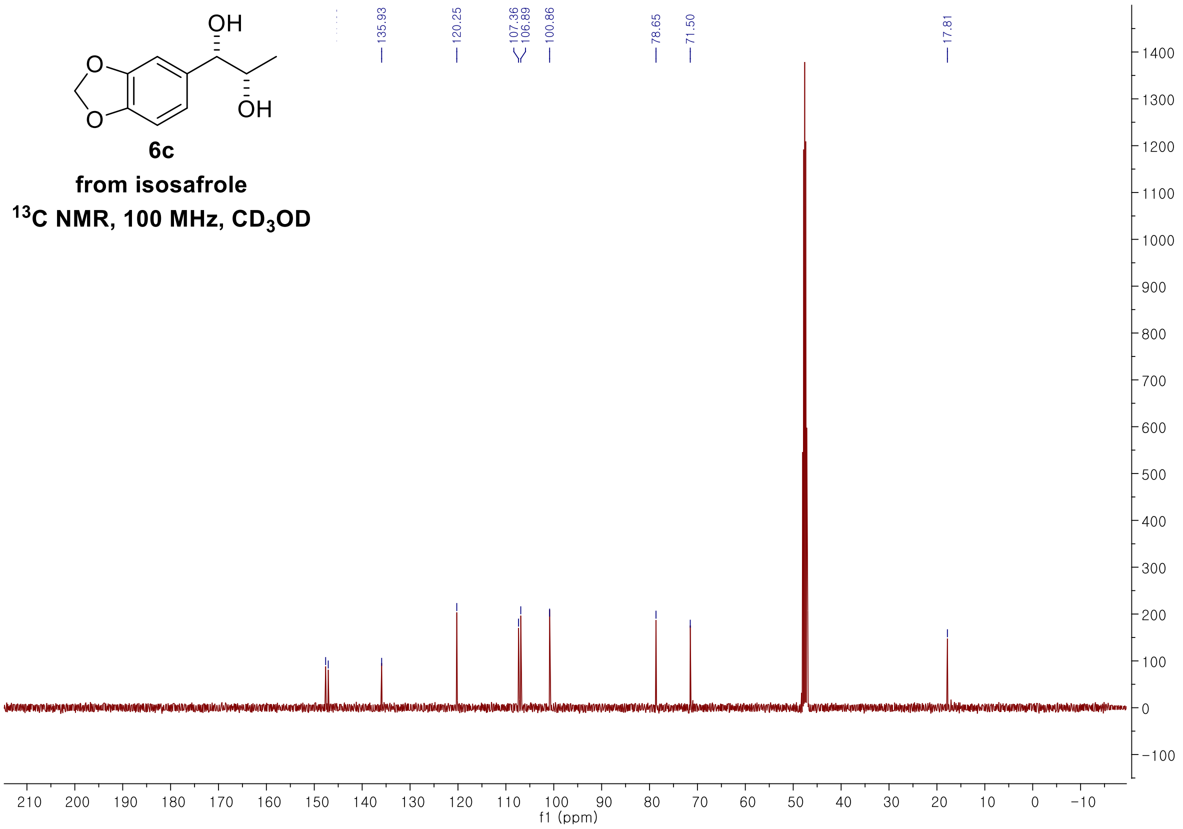


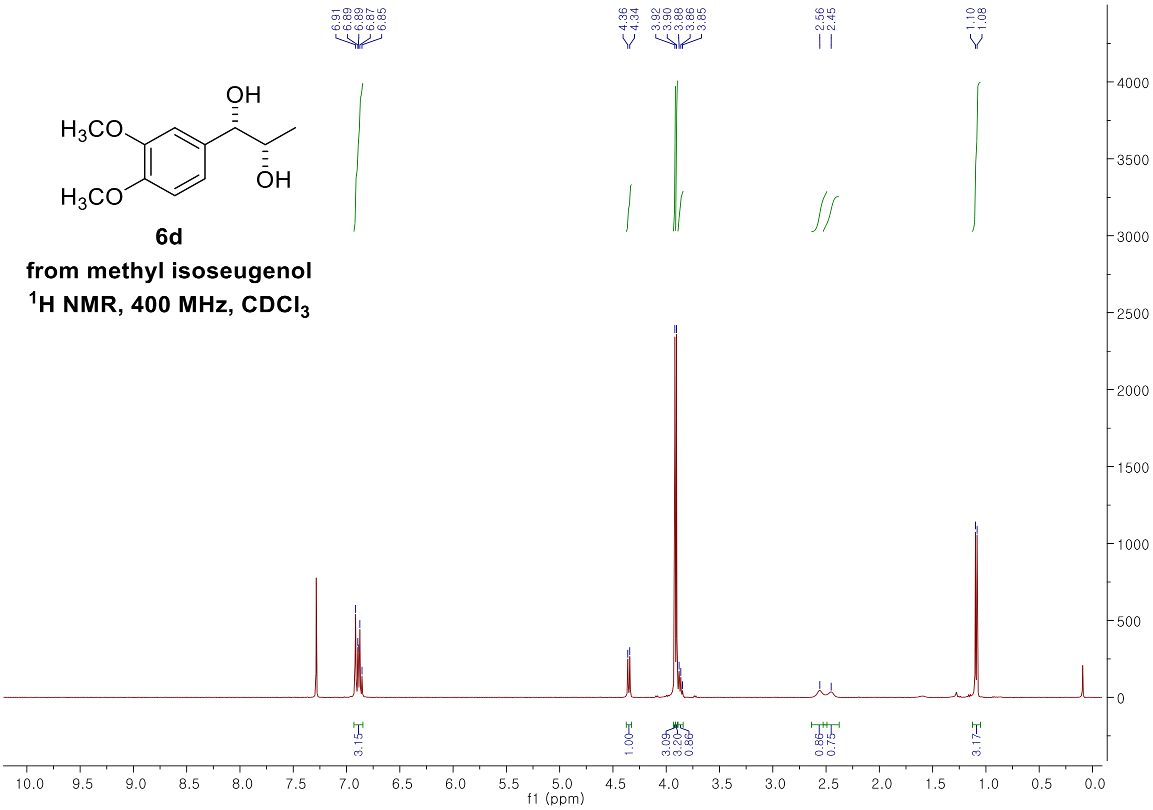
6b
from Coumarin
^{1}H NMR, 400 MHz, CD$_3$OD



6b
from Coumarin
^{13}C NMR, 100 MHz, CD$_3$OD


OH
O
O
OH
6c
from isosafrole
^{1}H NMR, 400 MHz, CDCl$_3$
6.88
6.87
6.83
6.83
6.81
6.81
6.79
5.98
4.32
4.30
3.87
3.85
3.83
3.83
3.82
3.80
2.45
1.09
1.07
0.92
2.07
2.09
1.00
1.01
0.65
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500

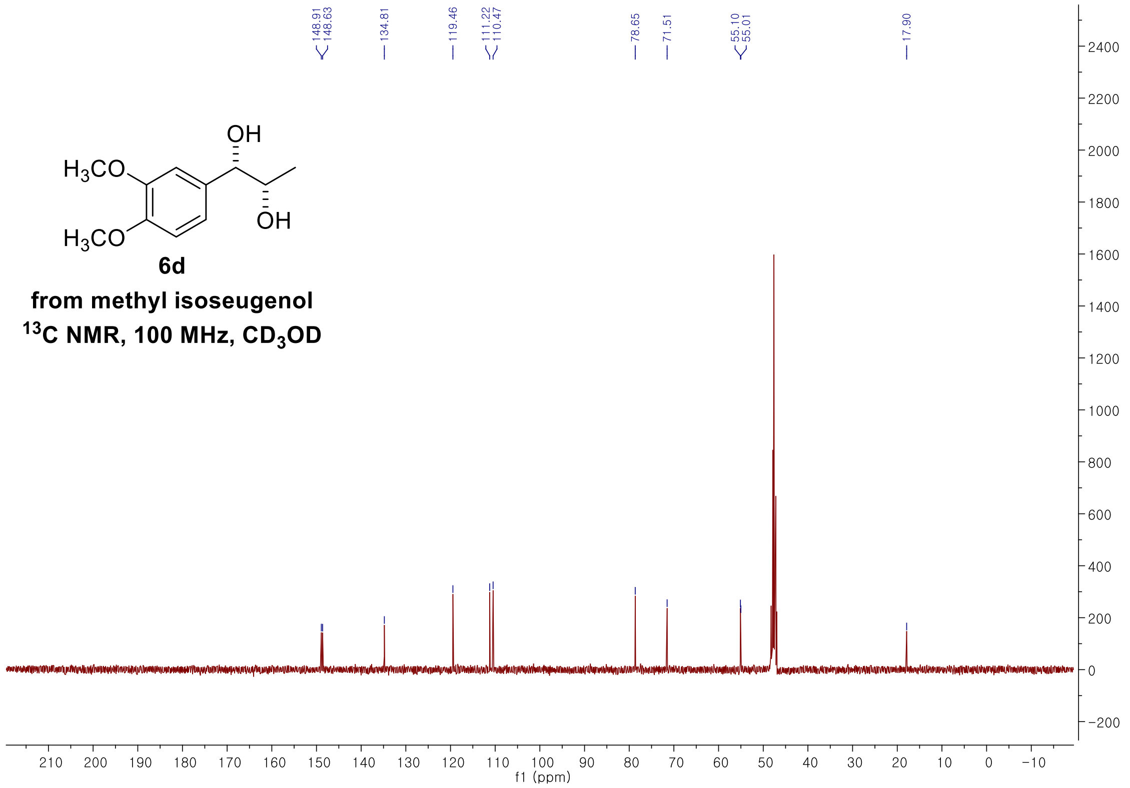

OH
O
O
OH
6c
from isosafrole
^{13}C NMR, 100 MHz, CD$_3$OD
135.93
120.25
107.36
106.89
100.86
78.65
71.50
17.81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100



6d

from methyl isoseugenol

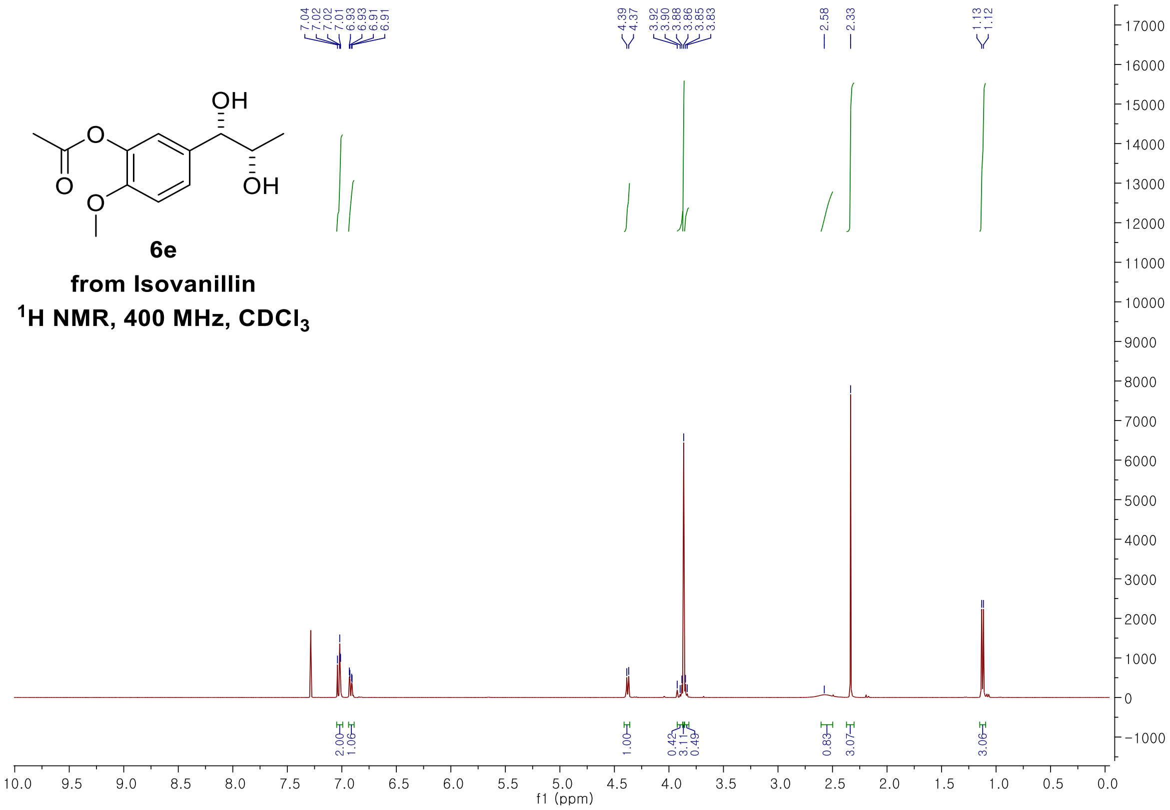
^{1}H NMR, 400 MHz, CDCl$_3$



6d

from methyl isoseugenol

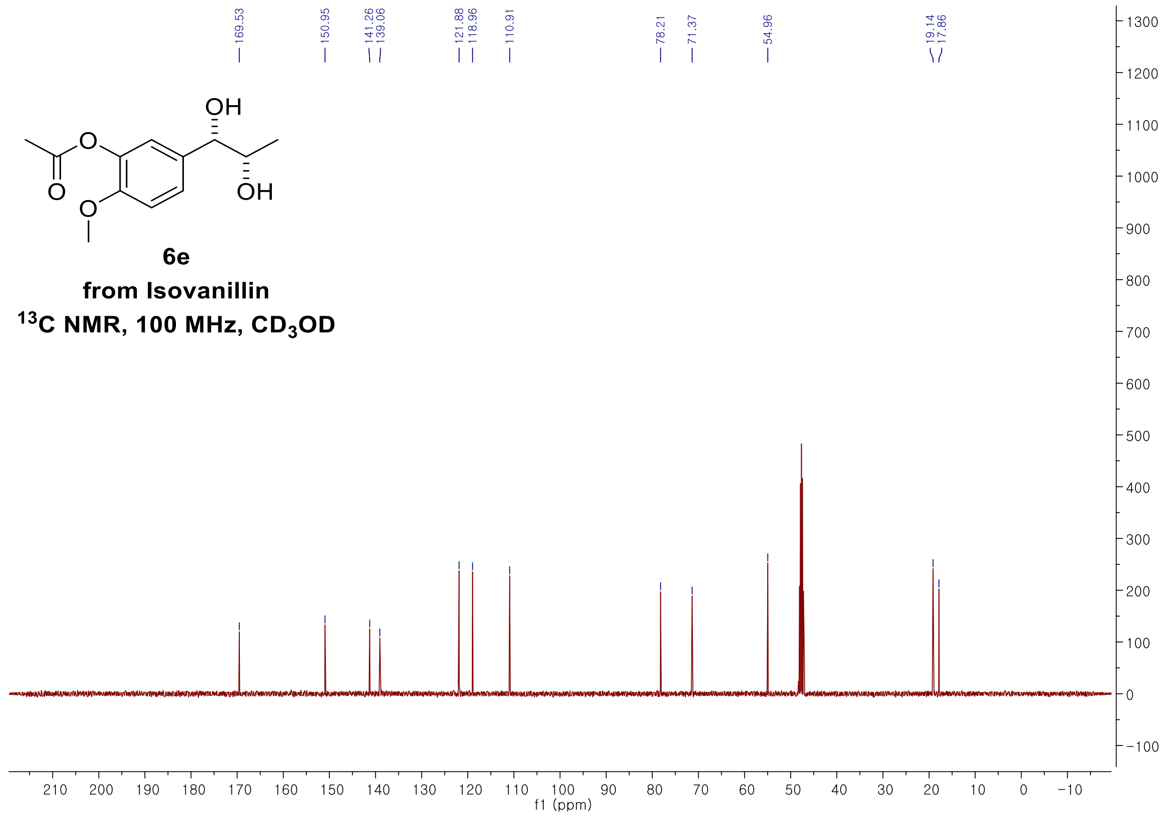
^{13}C NMR, 100 MHz, CD$_3$OD



6e

from Isovanillin

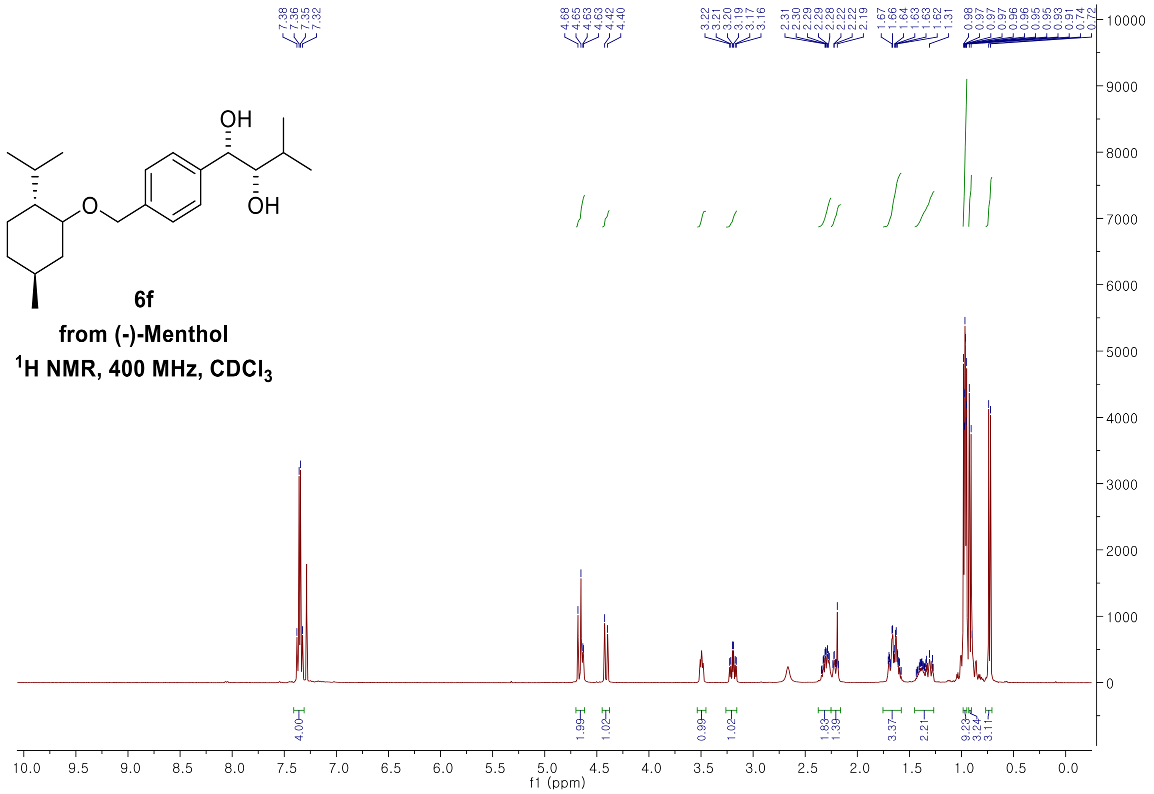
^{1}H NMR, 400 MHz, CDCl$_3$



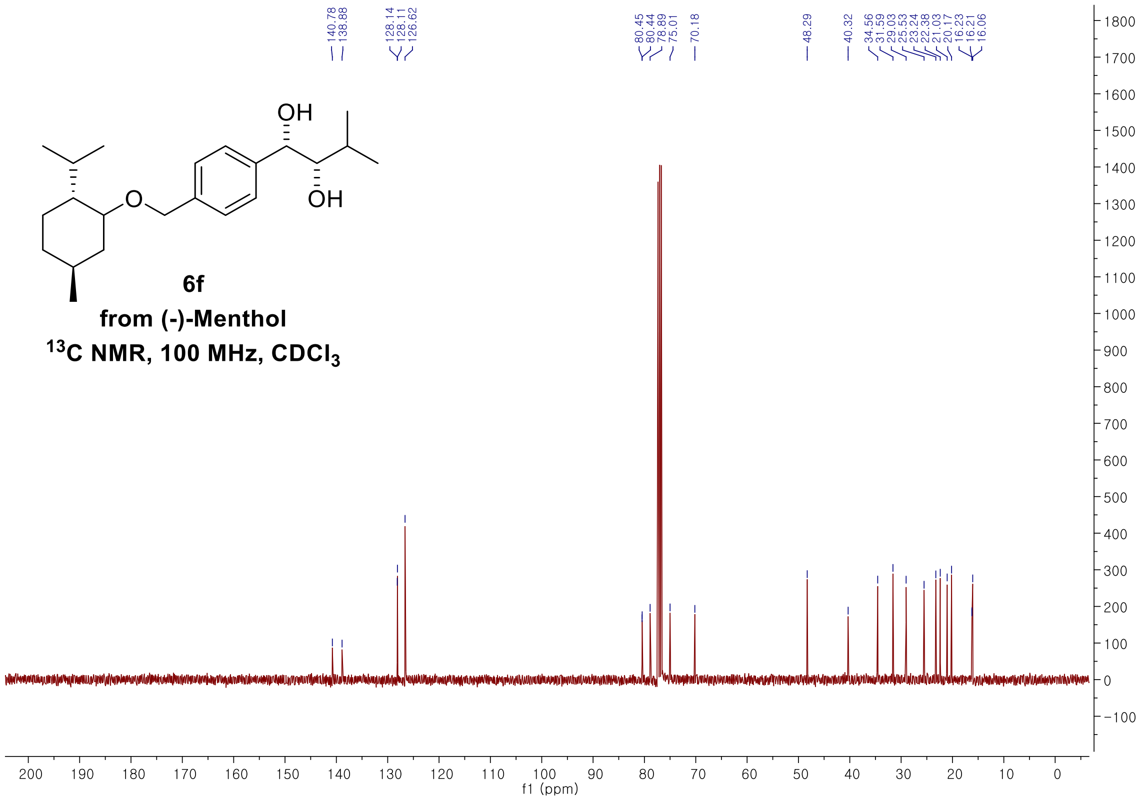
6e

from Isovanillin

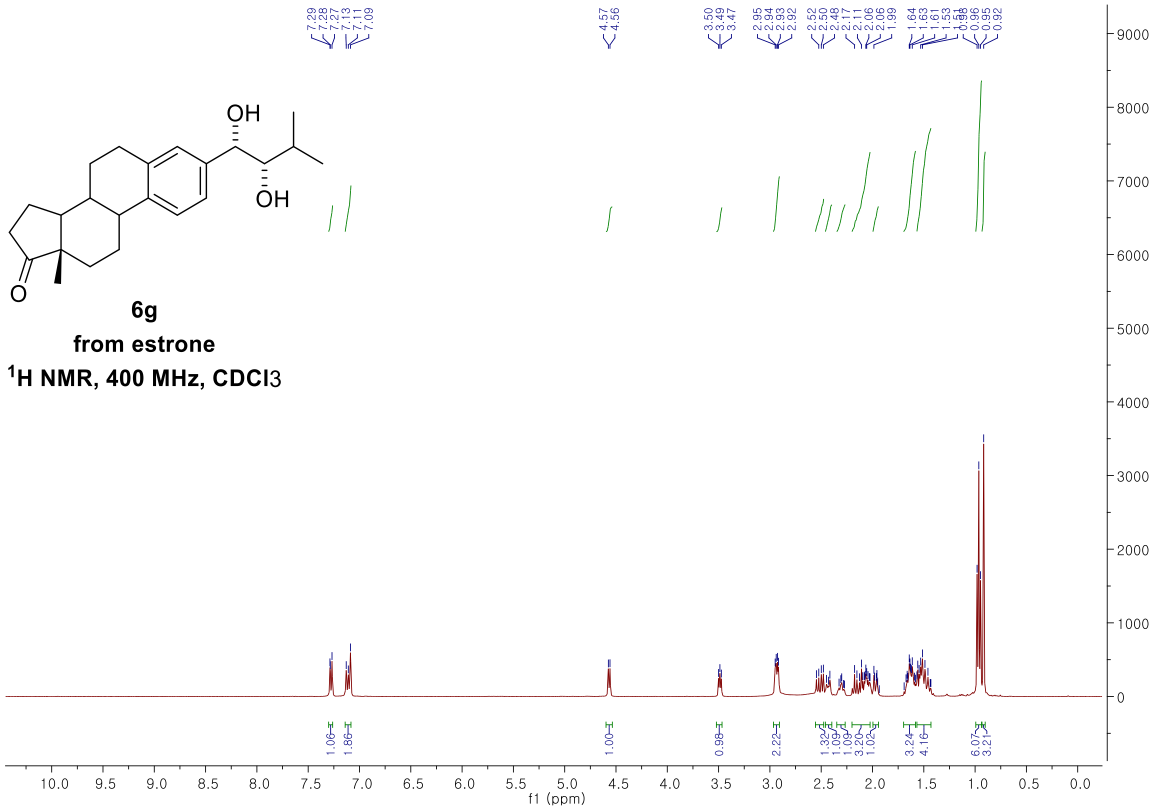
^{13}C NMR, 100 MHz, CD$_3$OD



6f
from (-)-Menthol
^{1}H NMR, 400 MHz, $CDCl_3$



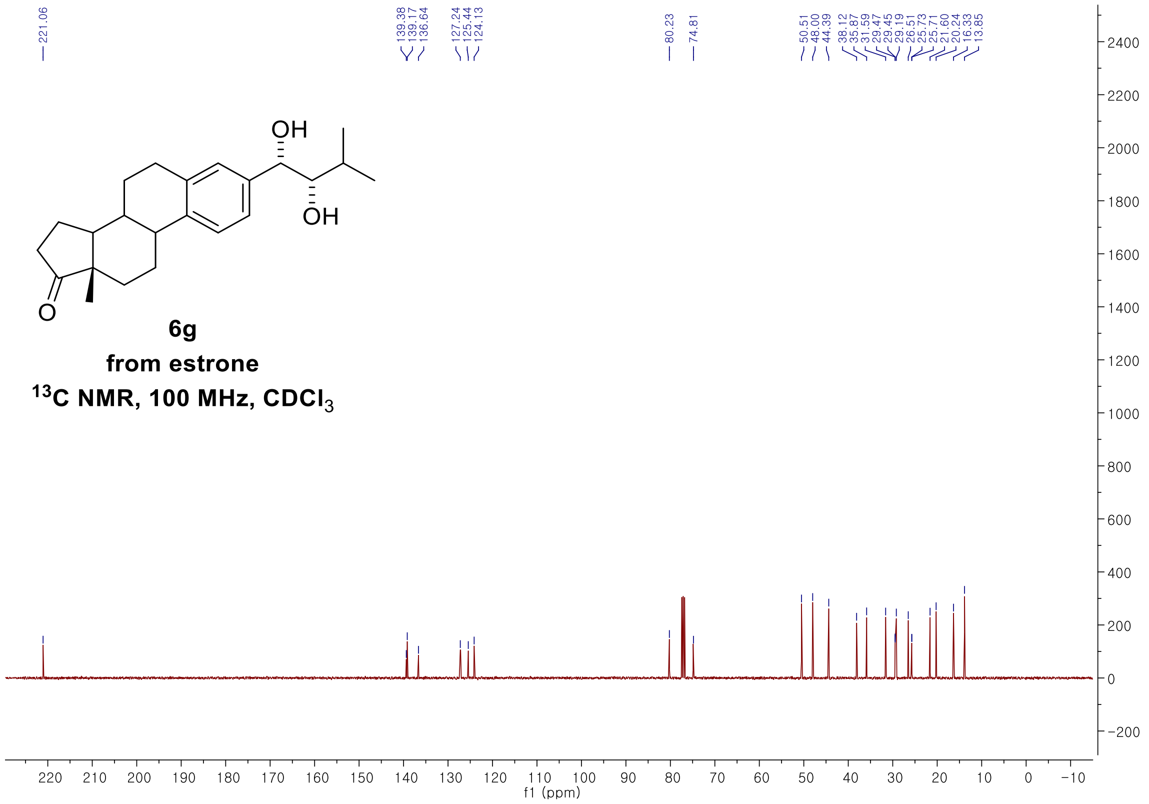
6f
from (-)-Menthol
^{13}C NMR, 100 MHz, $CDCl_3$



6g

from estrone

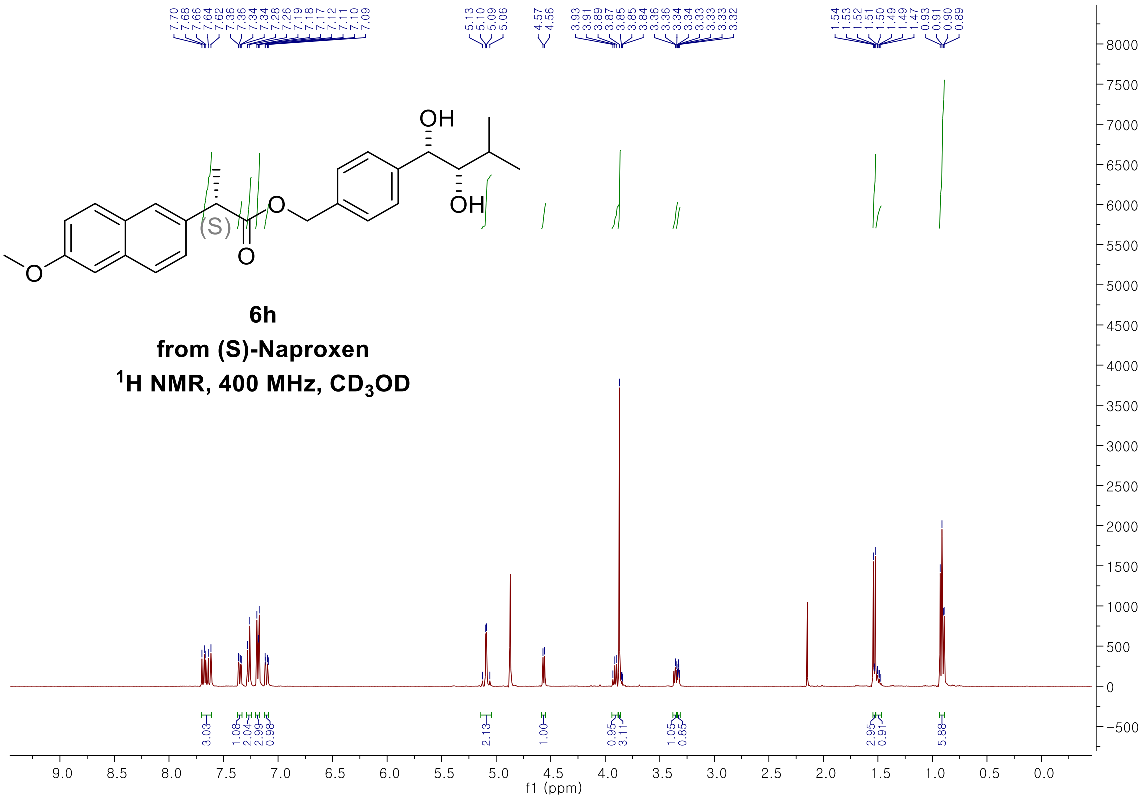
^{1}H NMR, 400 MHz, CDCl3



6g

from estrone

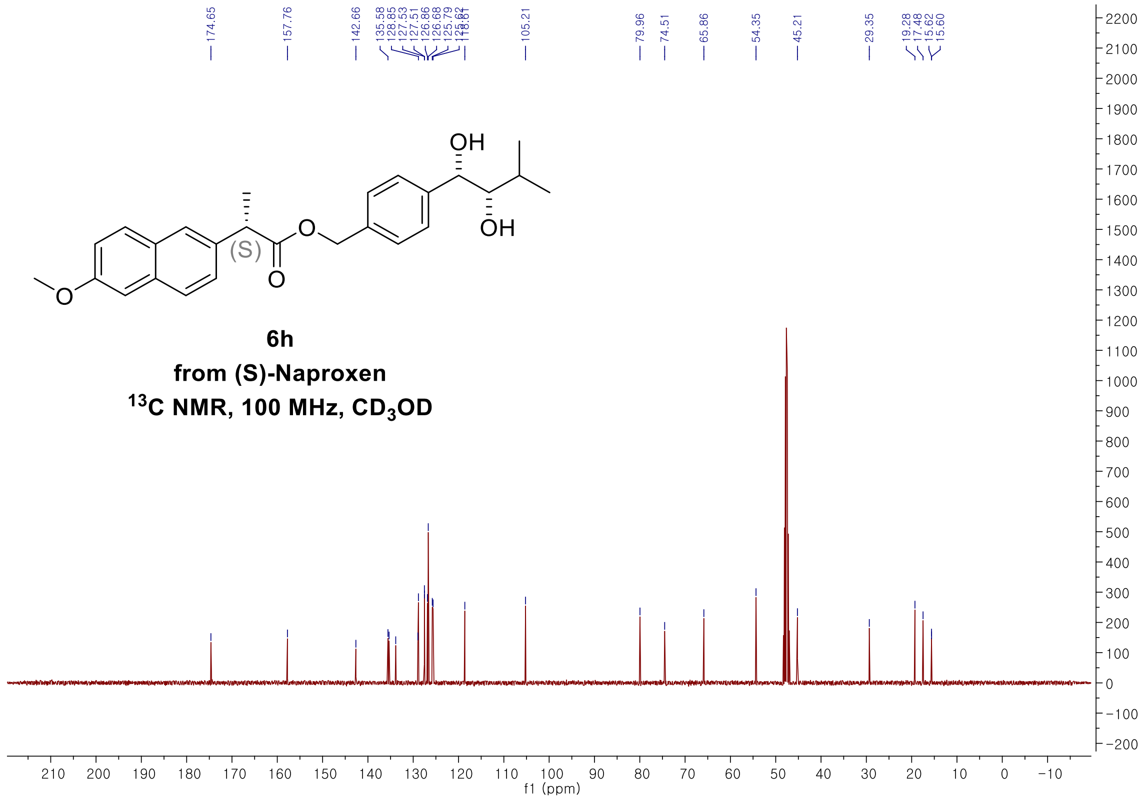
^{13}C NMR, 100 MHz, CDCl$_3$



6h

from (S)-Naproxen

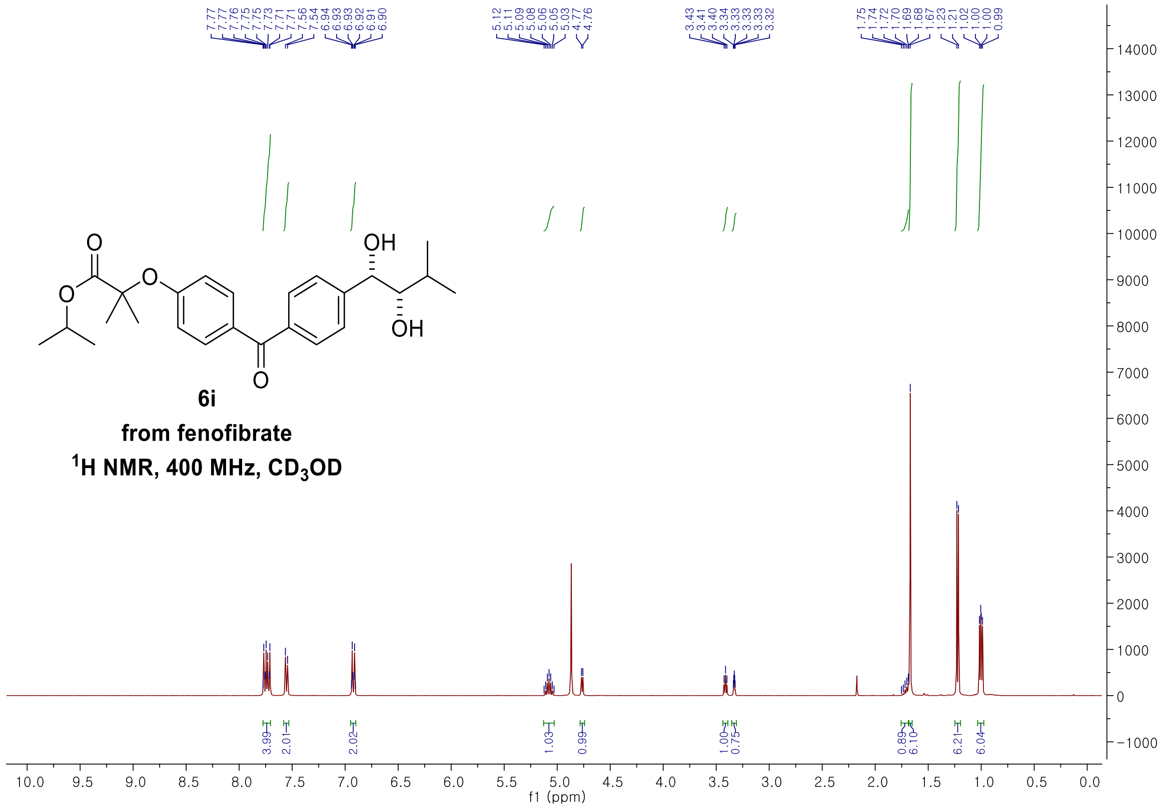
^{1}H NMR, 400 MHz, CD$_3$OD



6h

from (S)-Naproxen

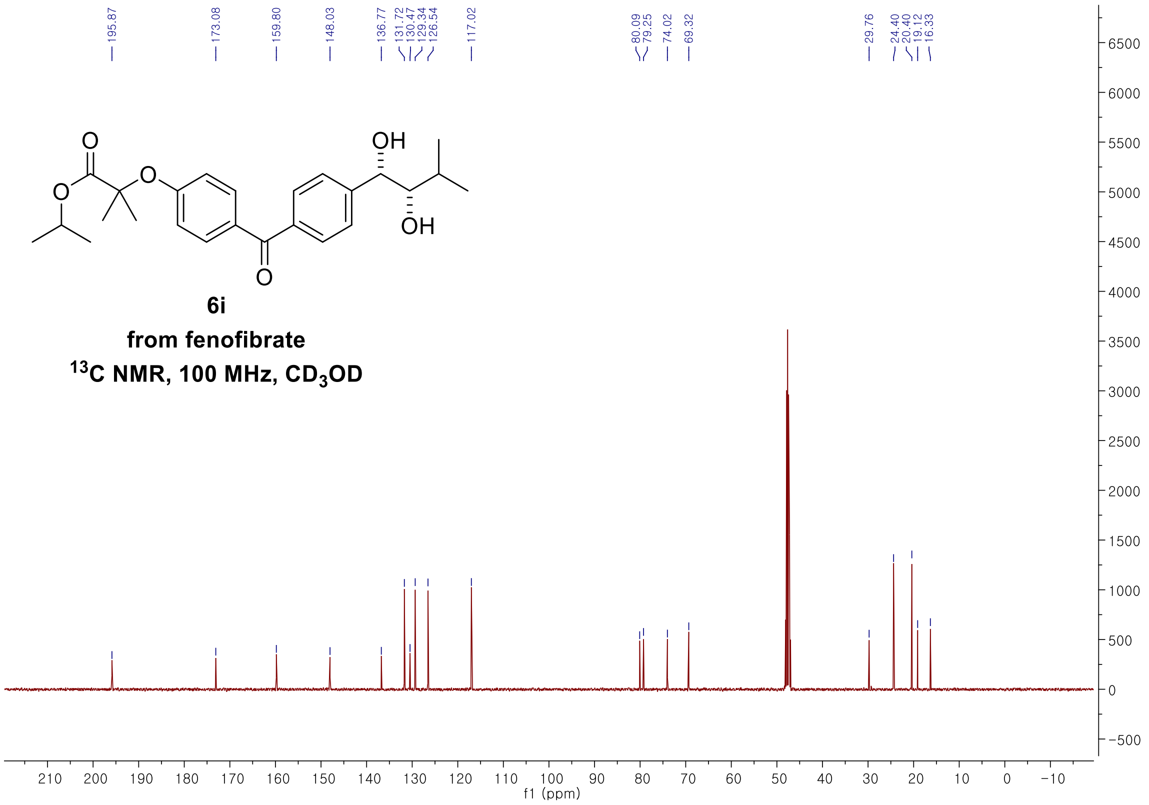
^{13}C NMR, 100 MHz, CD$_3$OD



6i

from fenofibrate

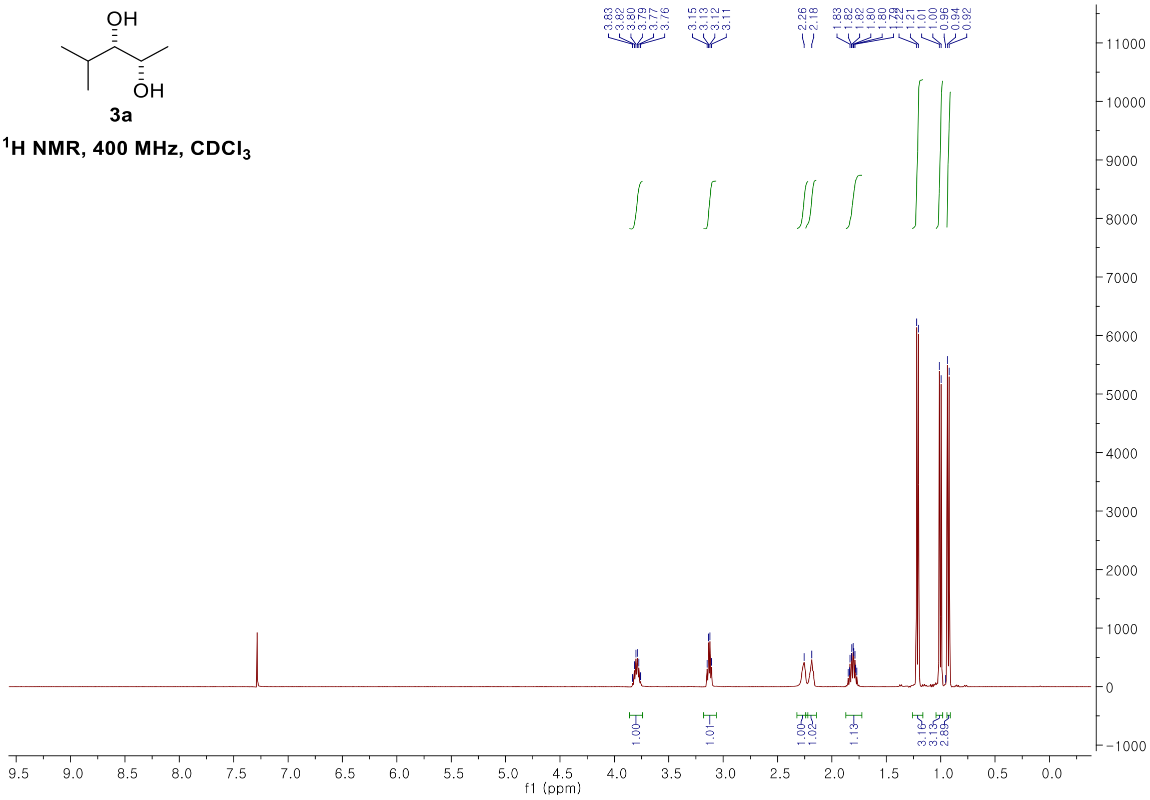
^{1}H NMR, 400 MHz, CD$_3$OD



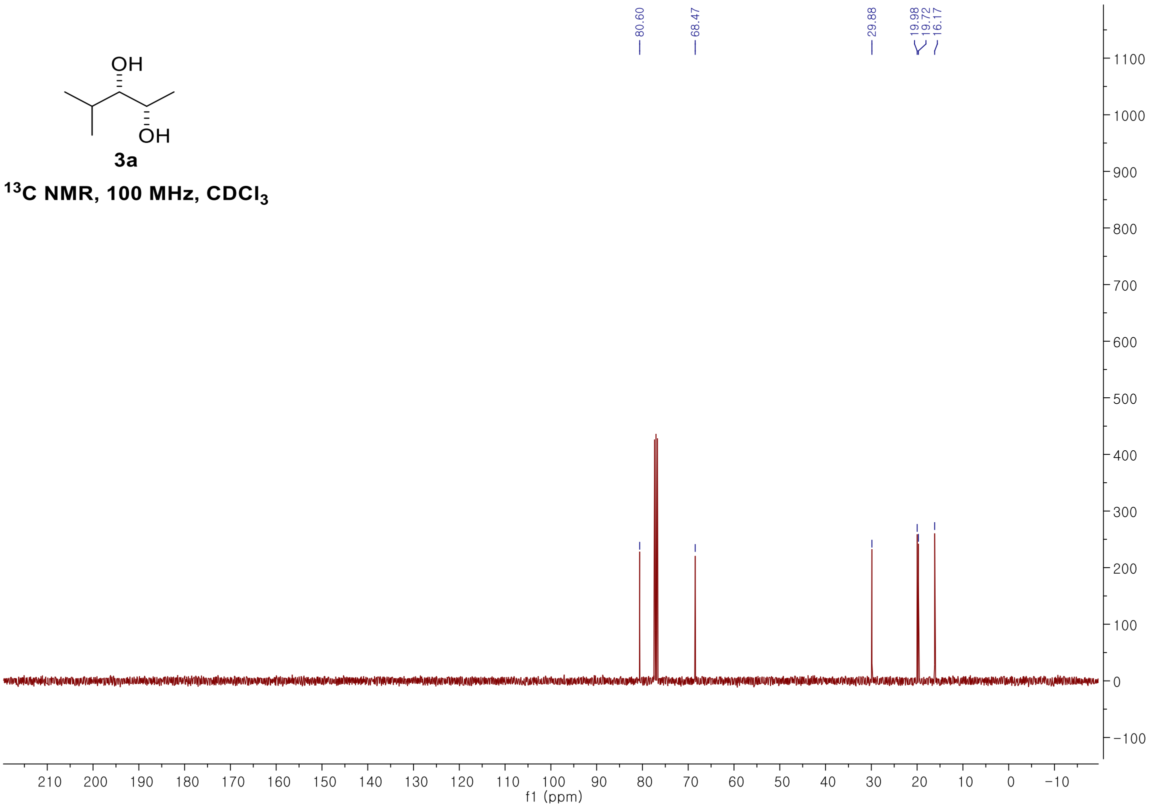
6i

from fenofibrate

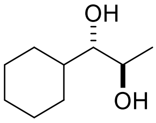
^{13}C NMR, 100 MHz, CD$_3$OD


3a

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

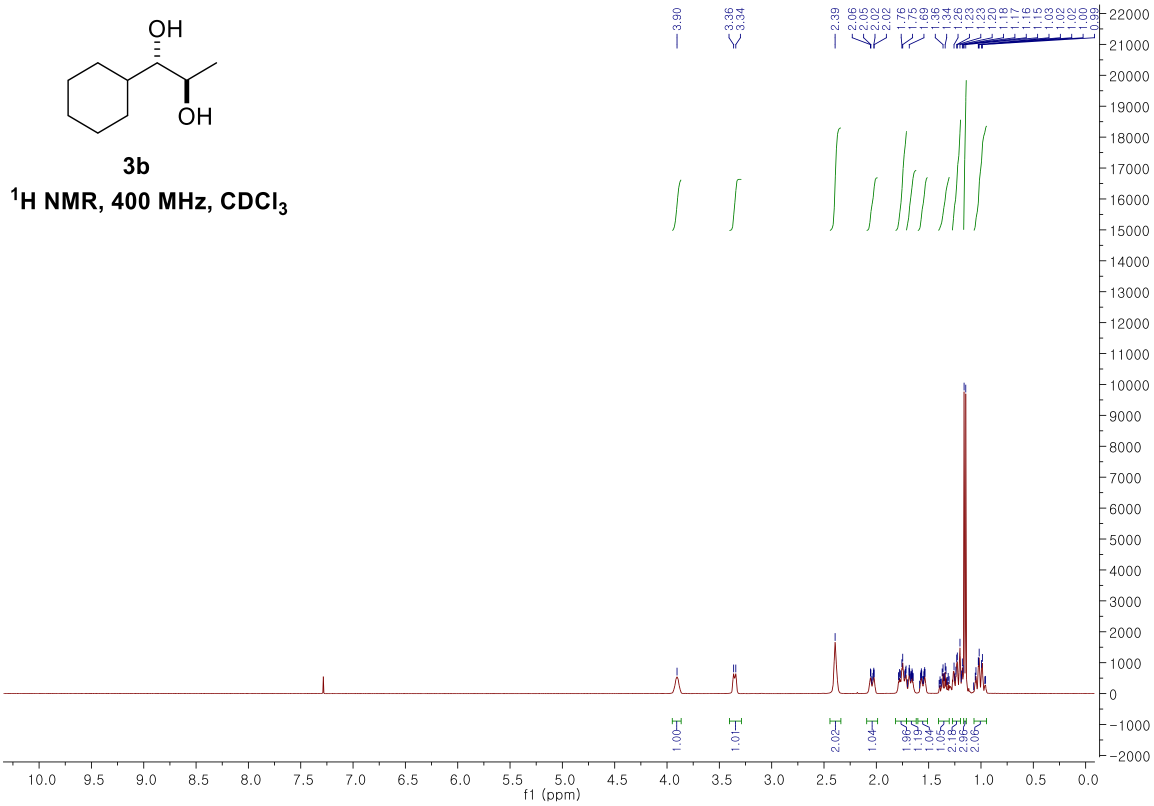

3a

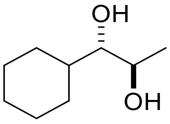
^{13}C NMR, 100 MHz, $CDCl_3$



3b

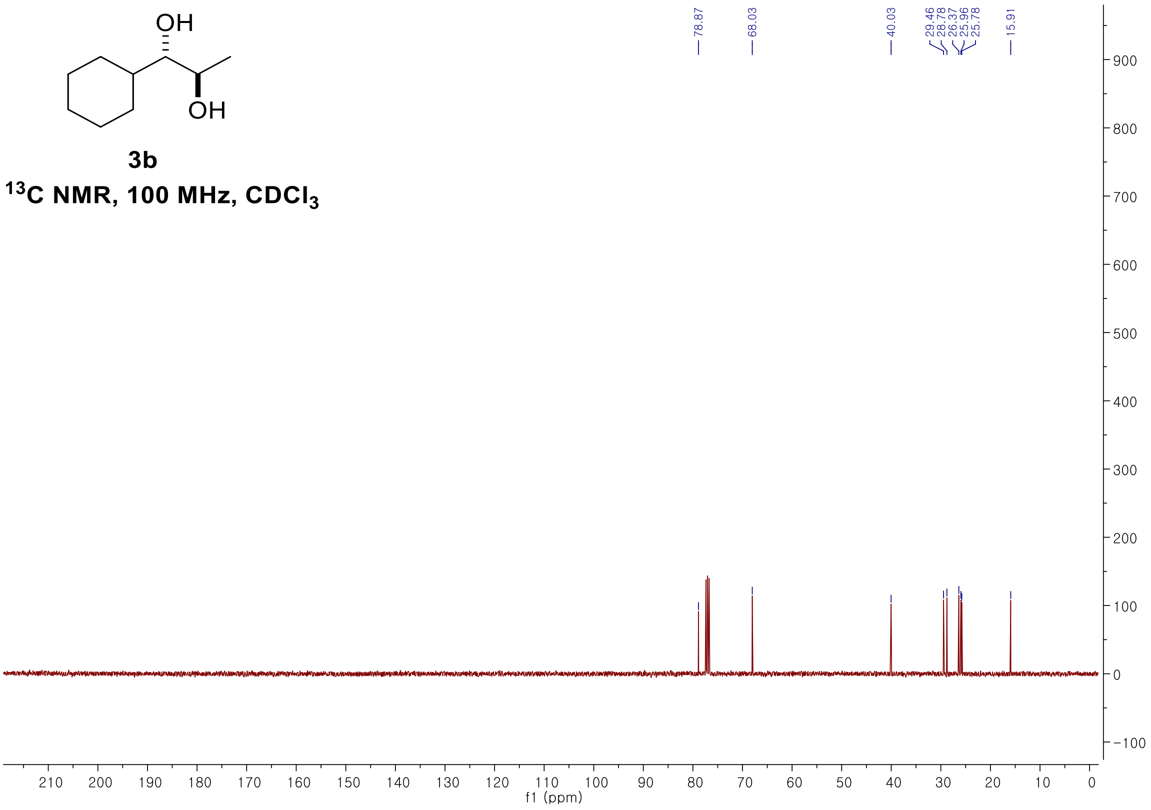
^{1}H NMR, 400 MHz, CDCl$_3$



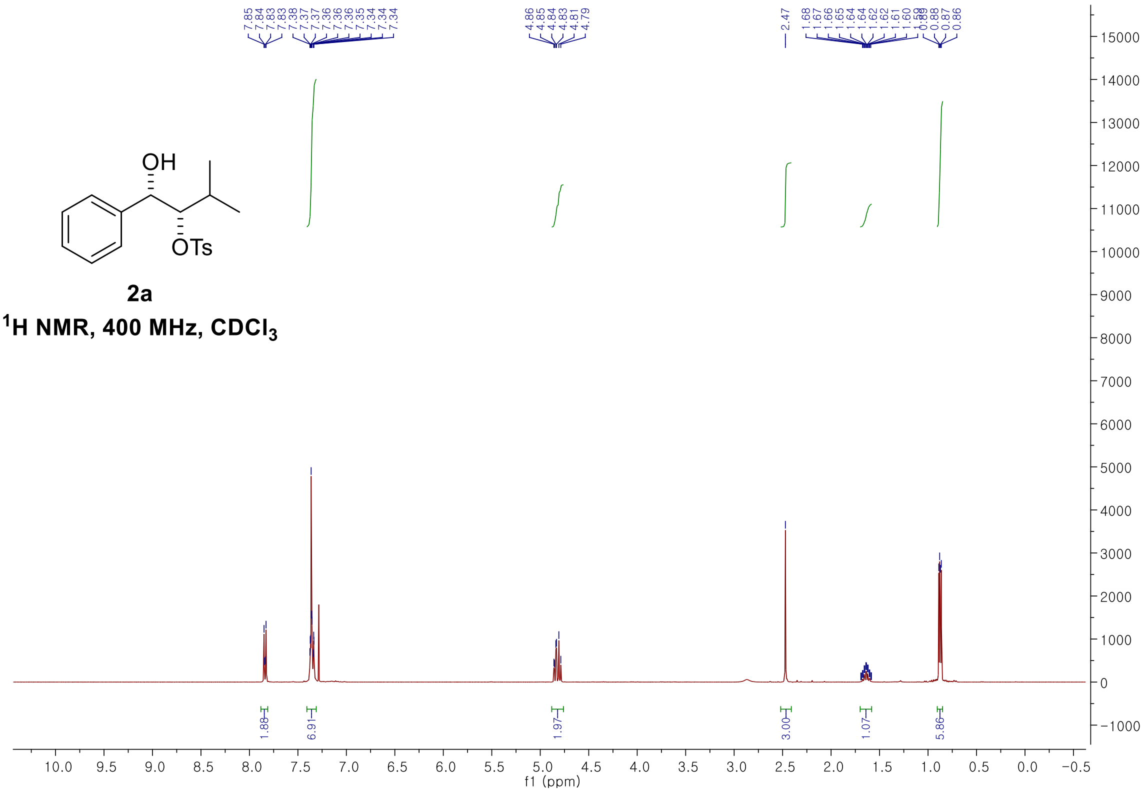


3b

^{13}C NMR, 100 MHz, CDCl$_3$

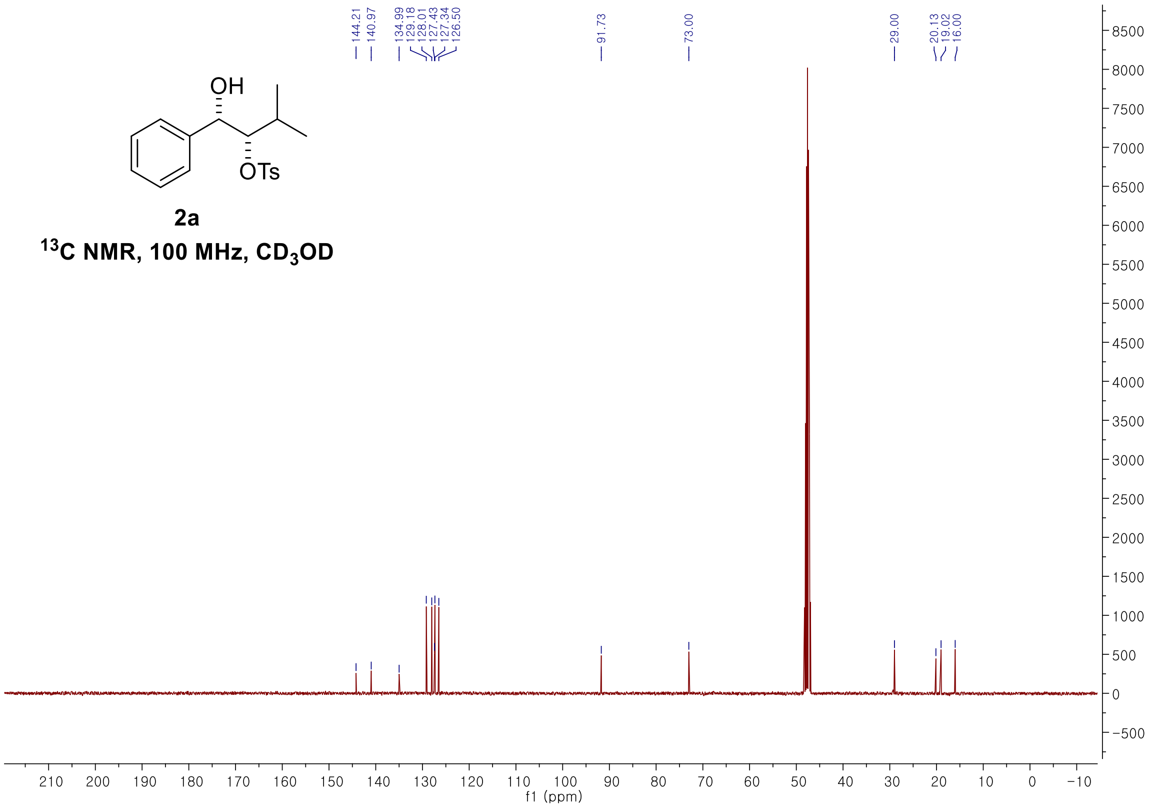


Product Characterization



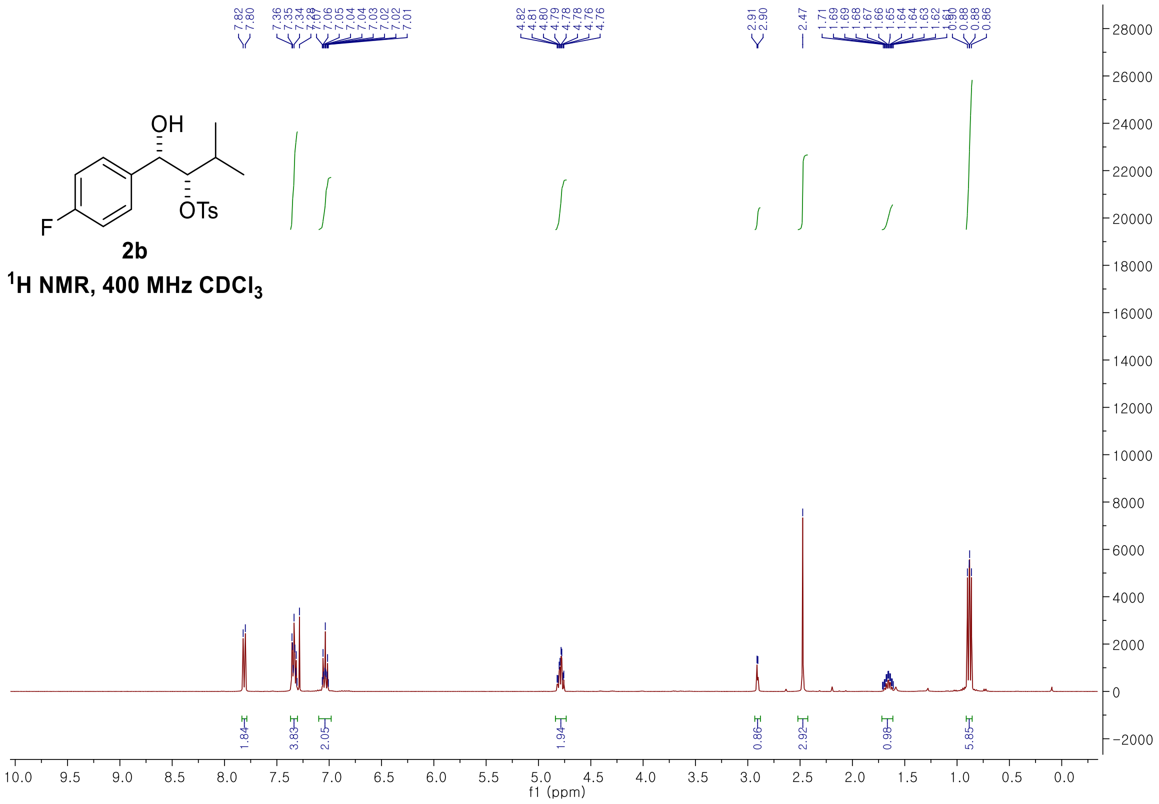
2a

^{1}H NMR, 400 MHz, CDCl$_3$



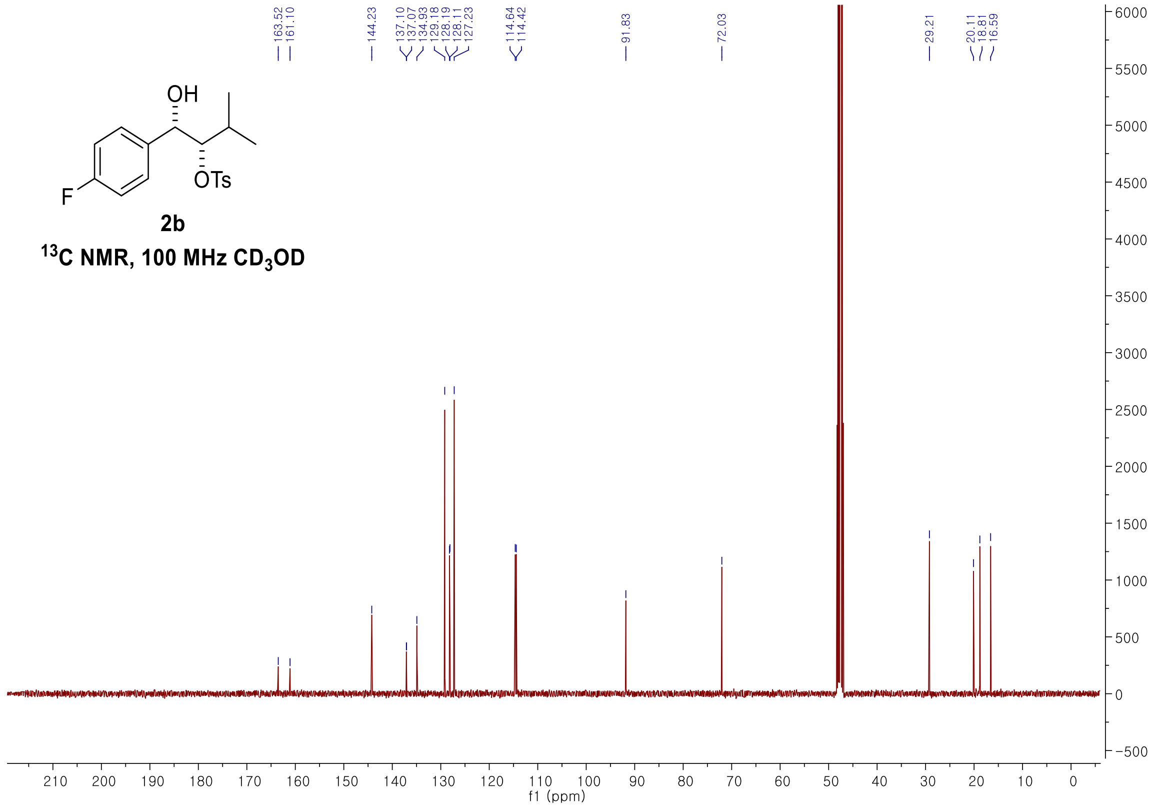
2a

^{13}C NMR, 100 MHz, CD$_3$OD



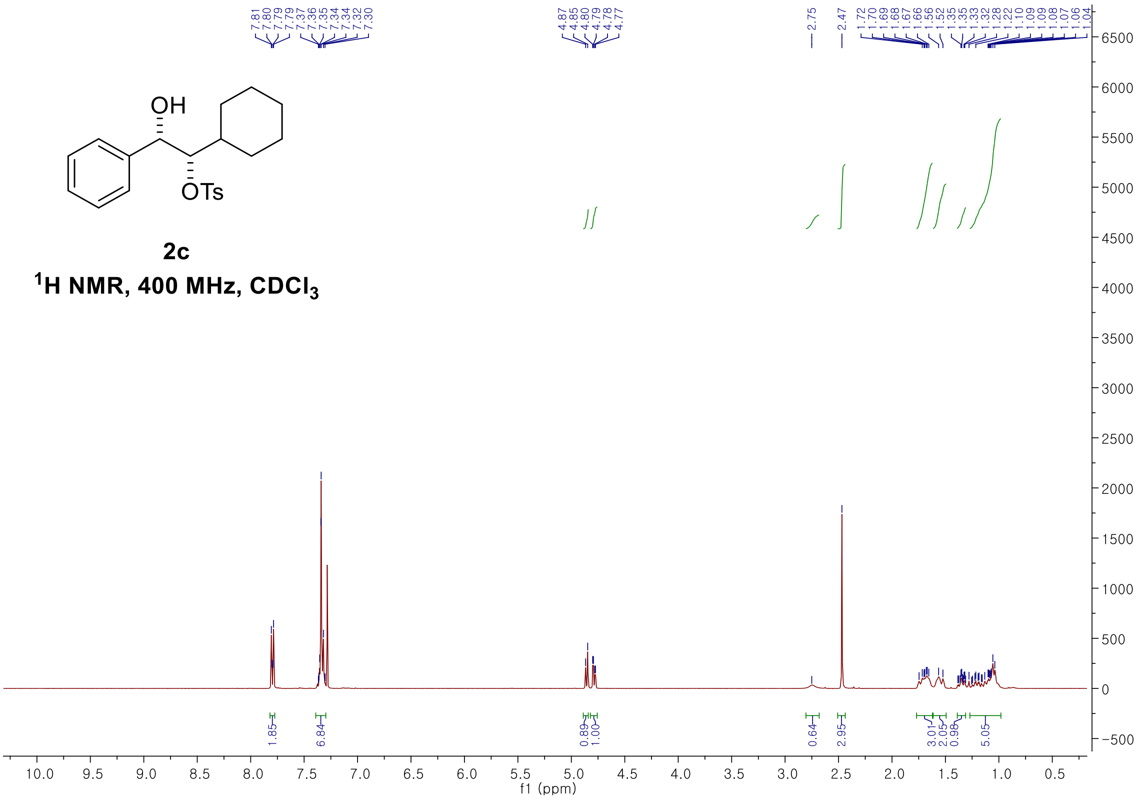
2b

^{1}H NMR, 400 MHz CDCl$_3$

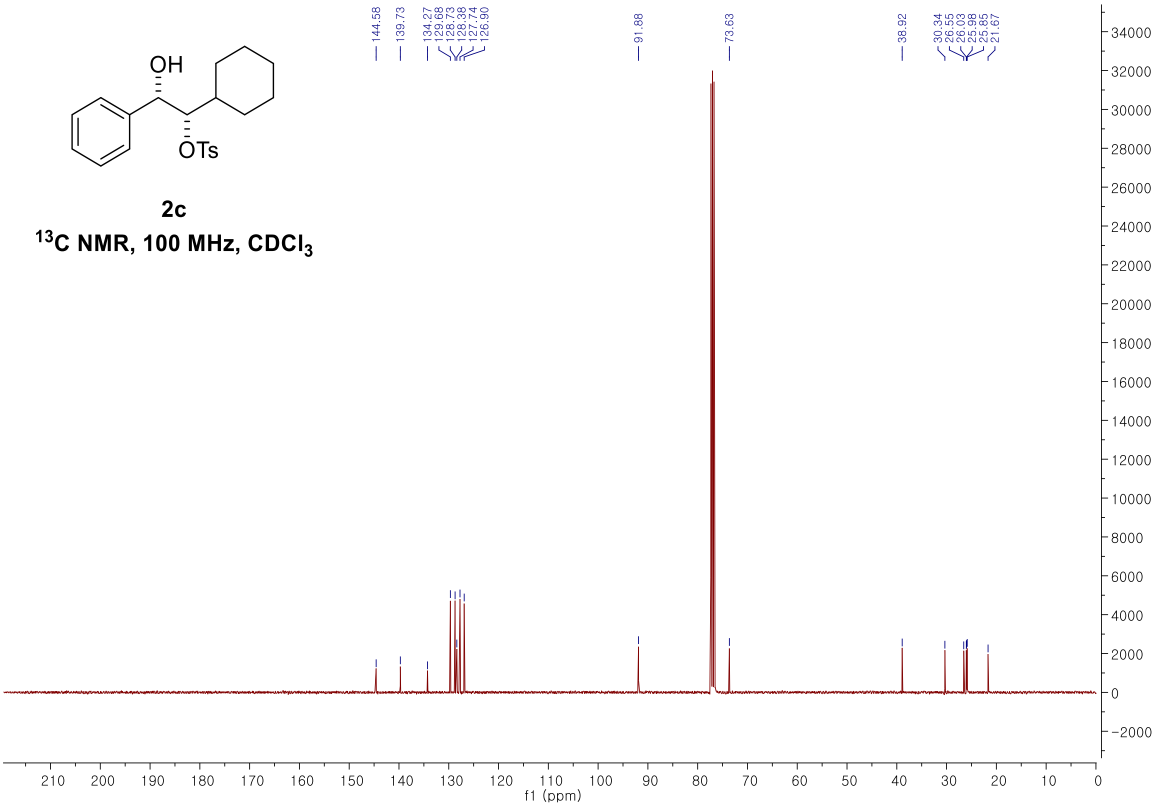


2b

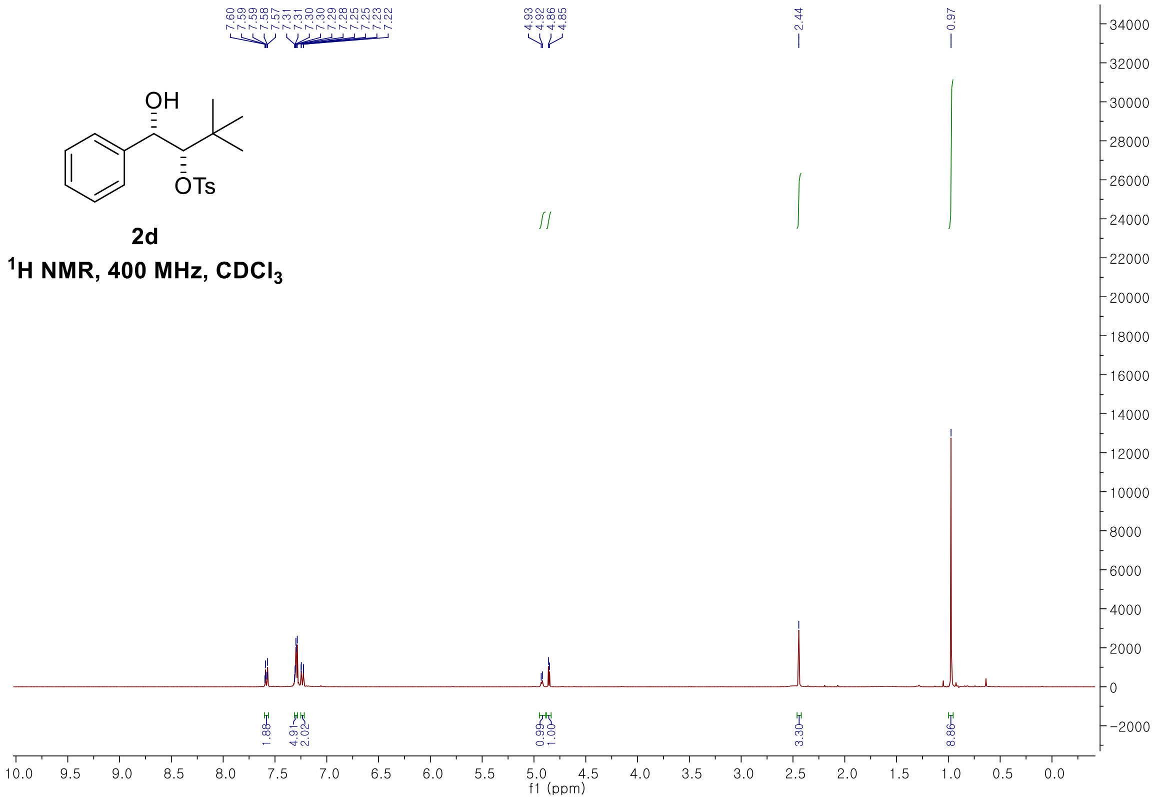
^{13}C NMR, 100 MHz CD$_3$OD



2c
^{1}H NMR, 400 MHz, $CDCl_3$

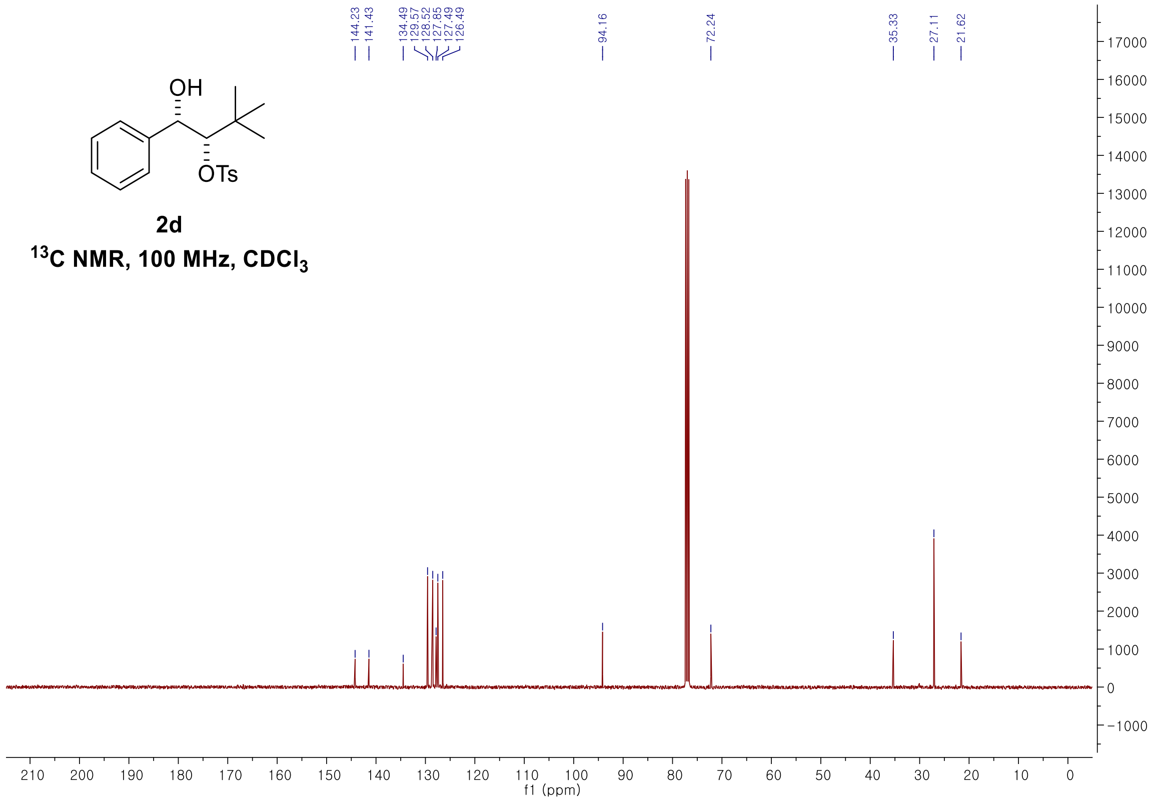


2c
^{13}C NMR, 100 MHz, $CDCl_3$



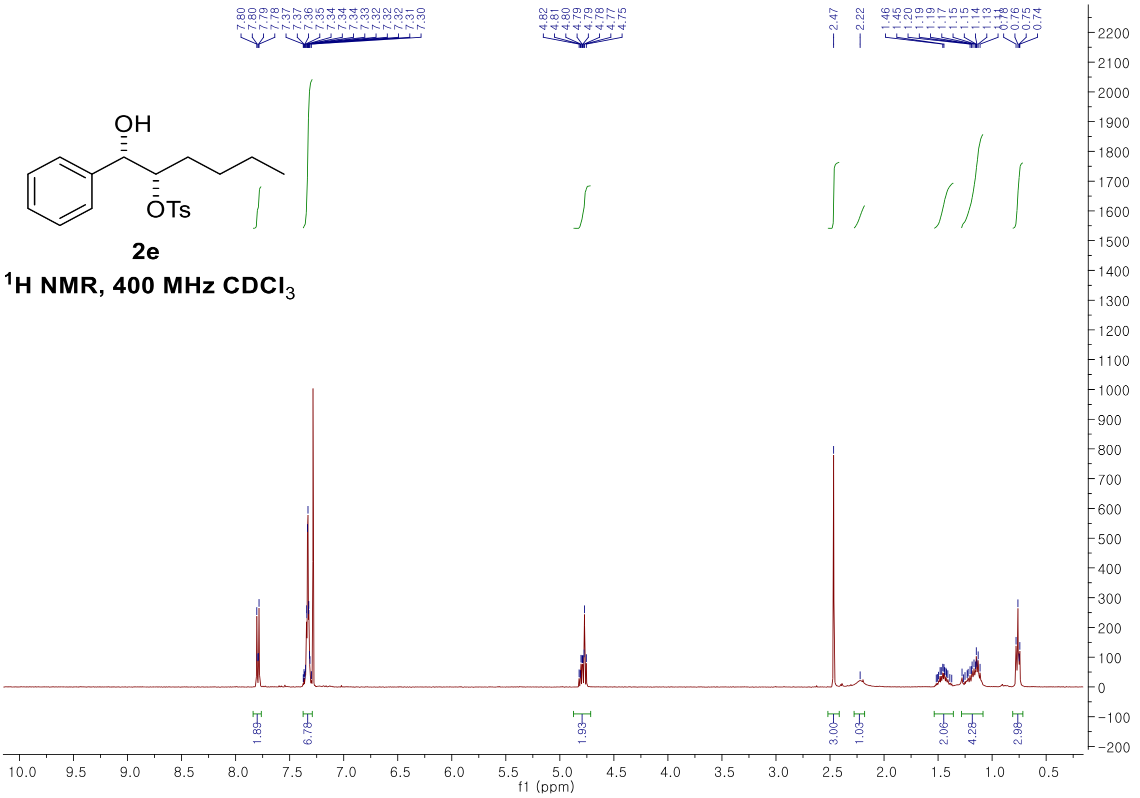
2d

^{1}H NMR, 400 MHz, CDCl$_3$



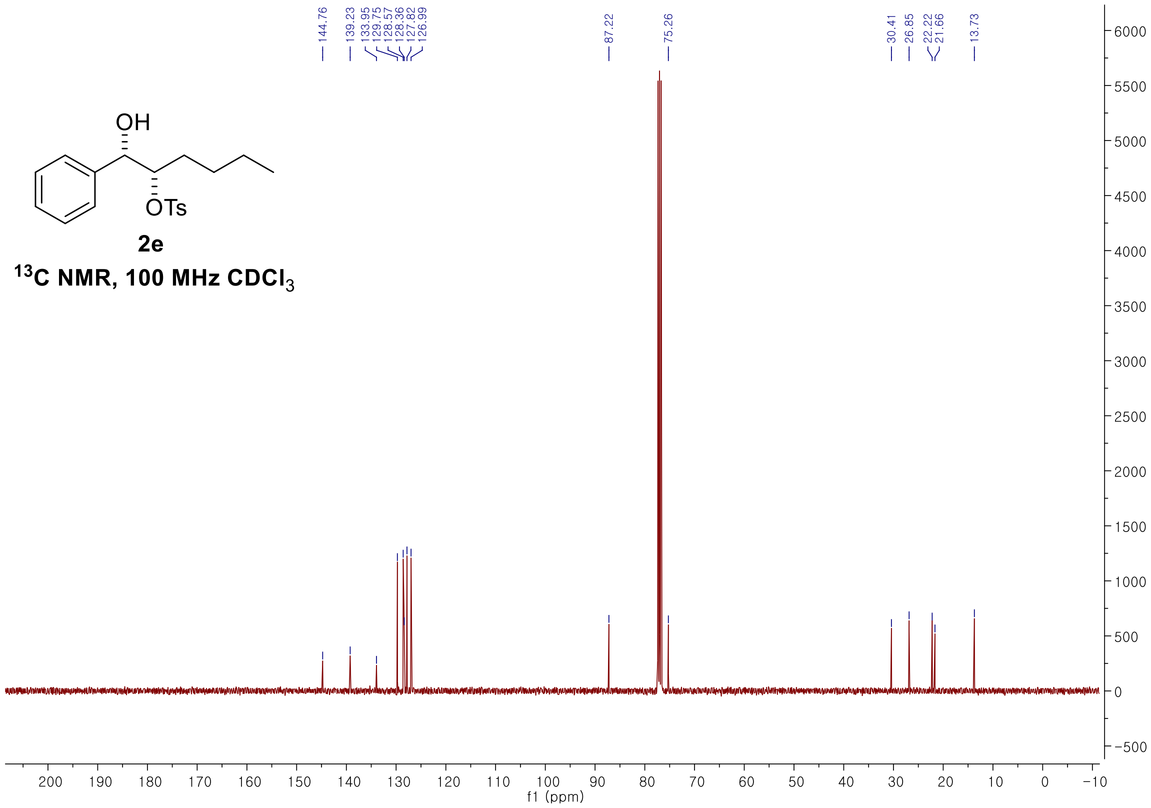
2d

^{13}C NMR, 100 MHz, CDCl$_3$



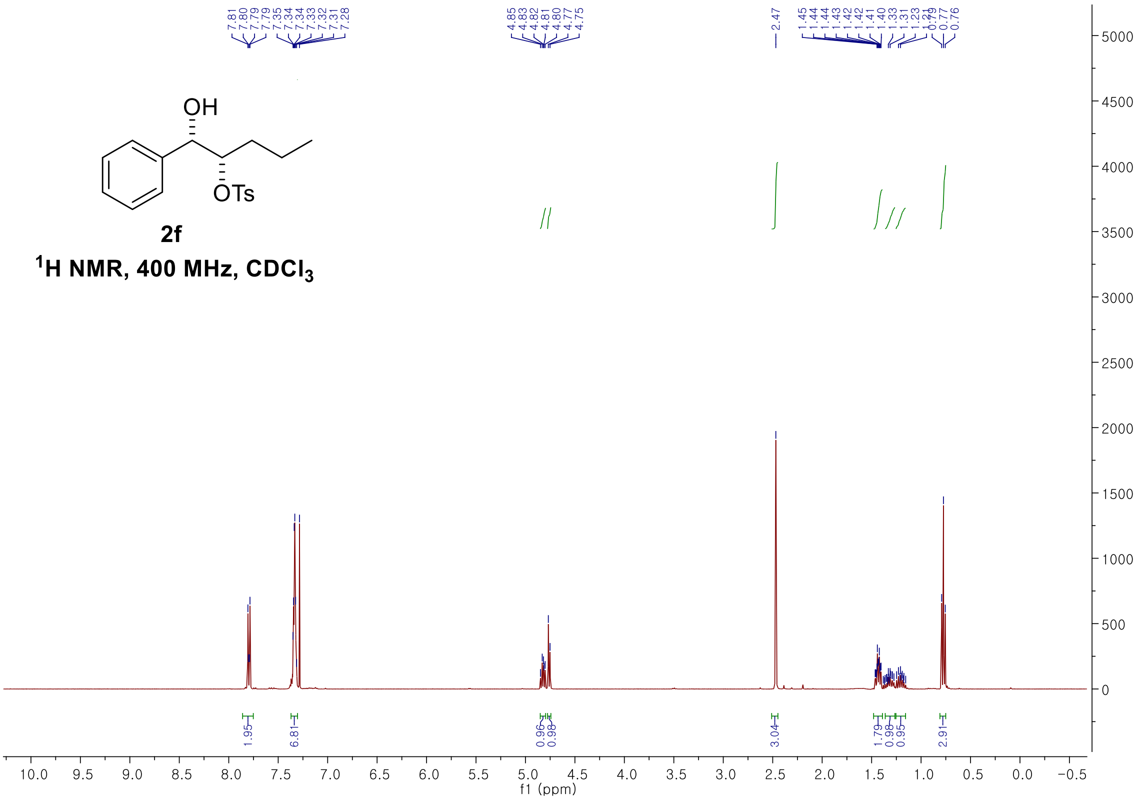
2e

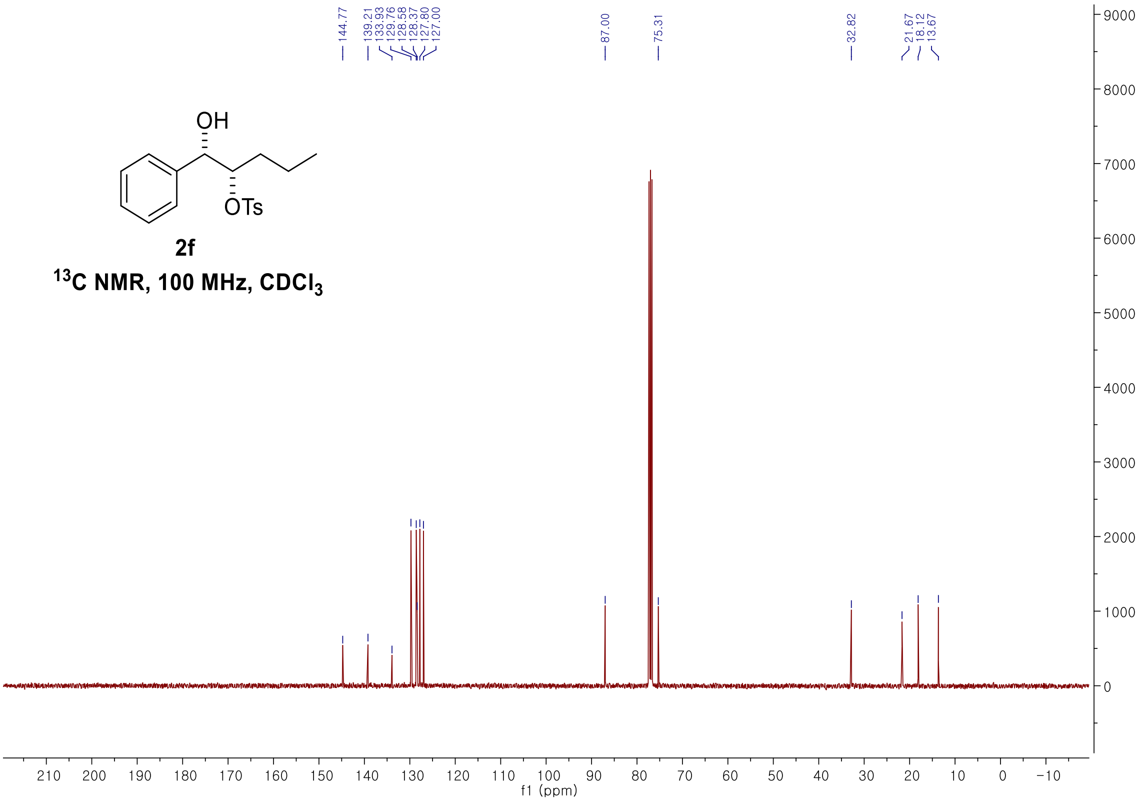
^{1}H NMR, 400 MHz CDCl$_3$

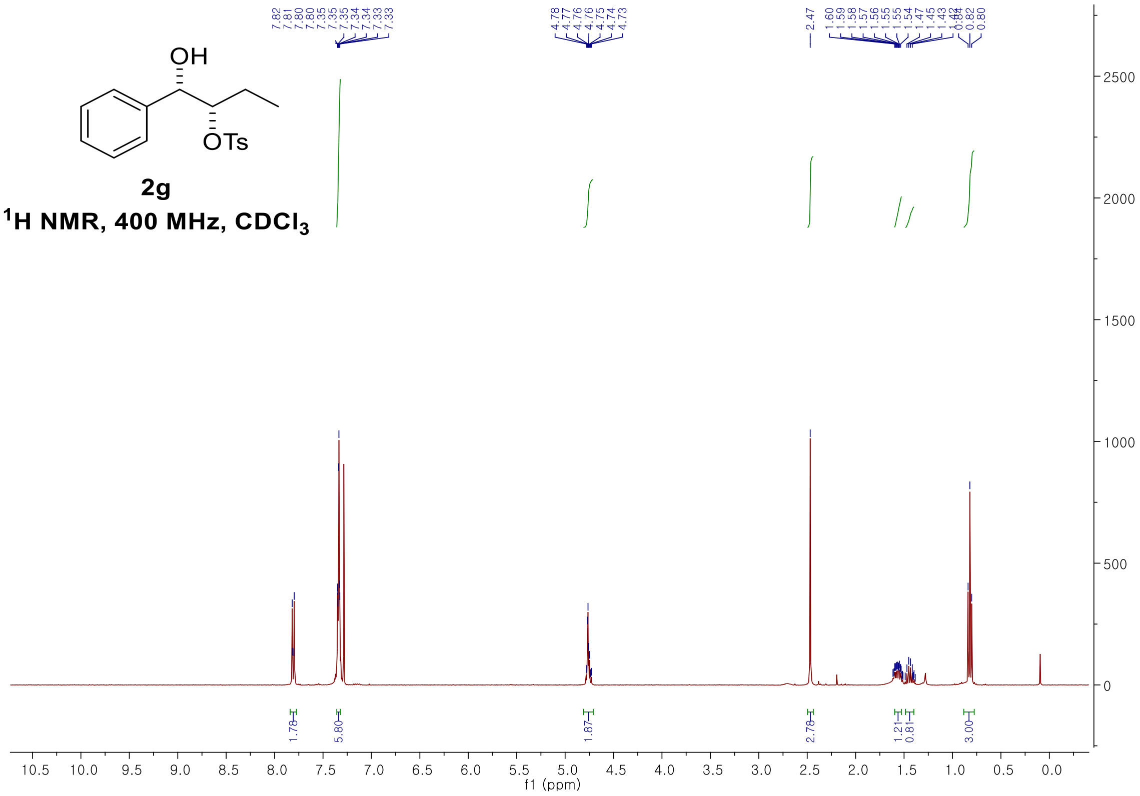


2e

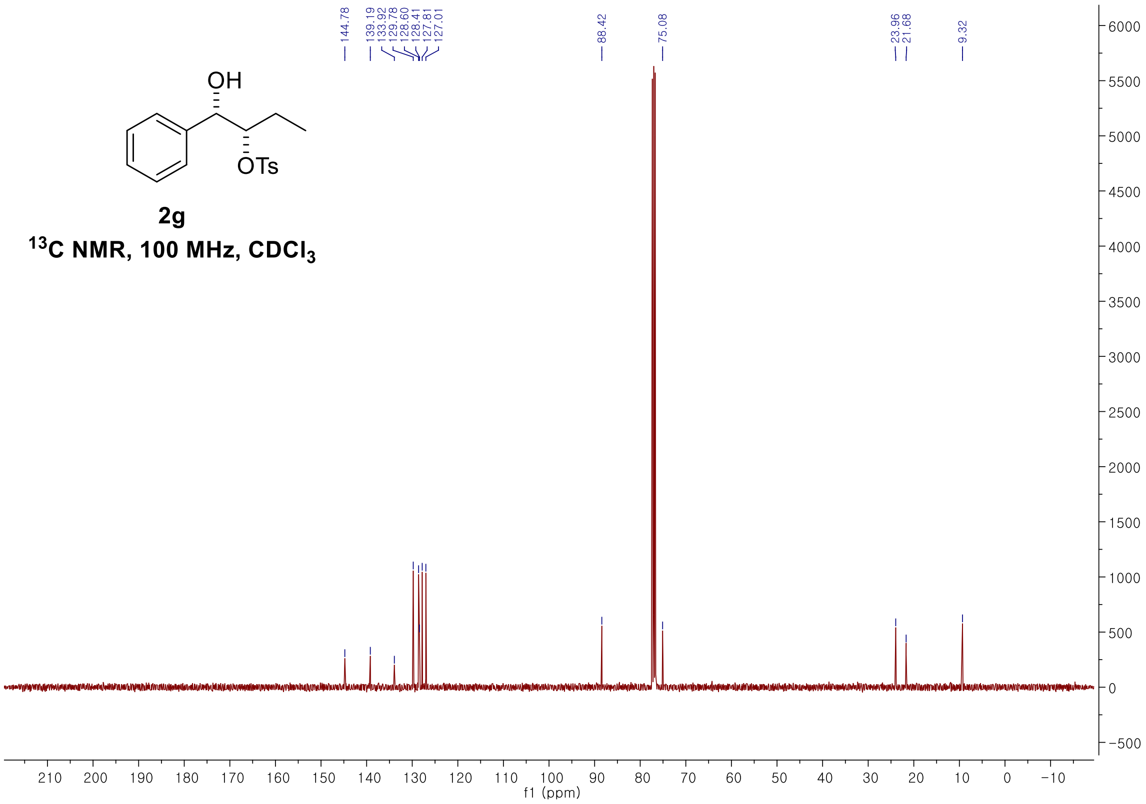
^{13}C NMR, 100 MHz CDCl$_3$


OH
OTs
2f
¹H NMR, 400 MHz, CDCl₃
7.81
7.80
7.79
7.79
7.35
7.34
7.34
7.33
7.32
7.31
7.28
4.85
4.83
4.82
4.81
4.80
4.77
4.75
2.47
1.45
1.44
1.43
1.42
1.42
1.41
1.40
1.33
1.31
1.23
1.21
0.79
0.77
0.76
1.95
6.81
0.96
0.98
3.04
1.79
0.98
0.95
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0

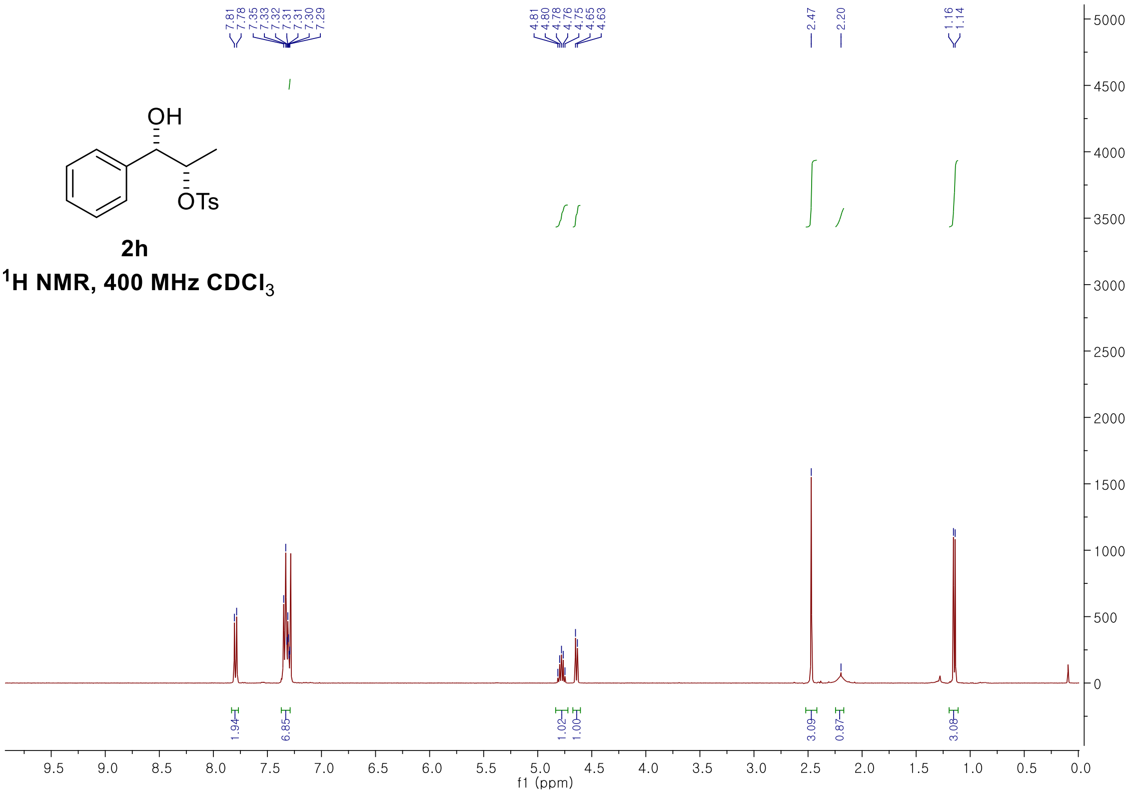

OH
OTs
2f
¹³C NMR, 100 MHz, CDCl₃
144.77
139.21
133.93
129.76
128.58
128.37
127.80
127.00
87.00
75.31
32.82
21.67
18.12
13.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
9000 8000 7000 6000 5000 4000 3000 2000 1000 0


2g

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

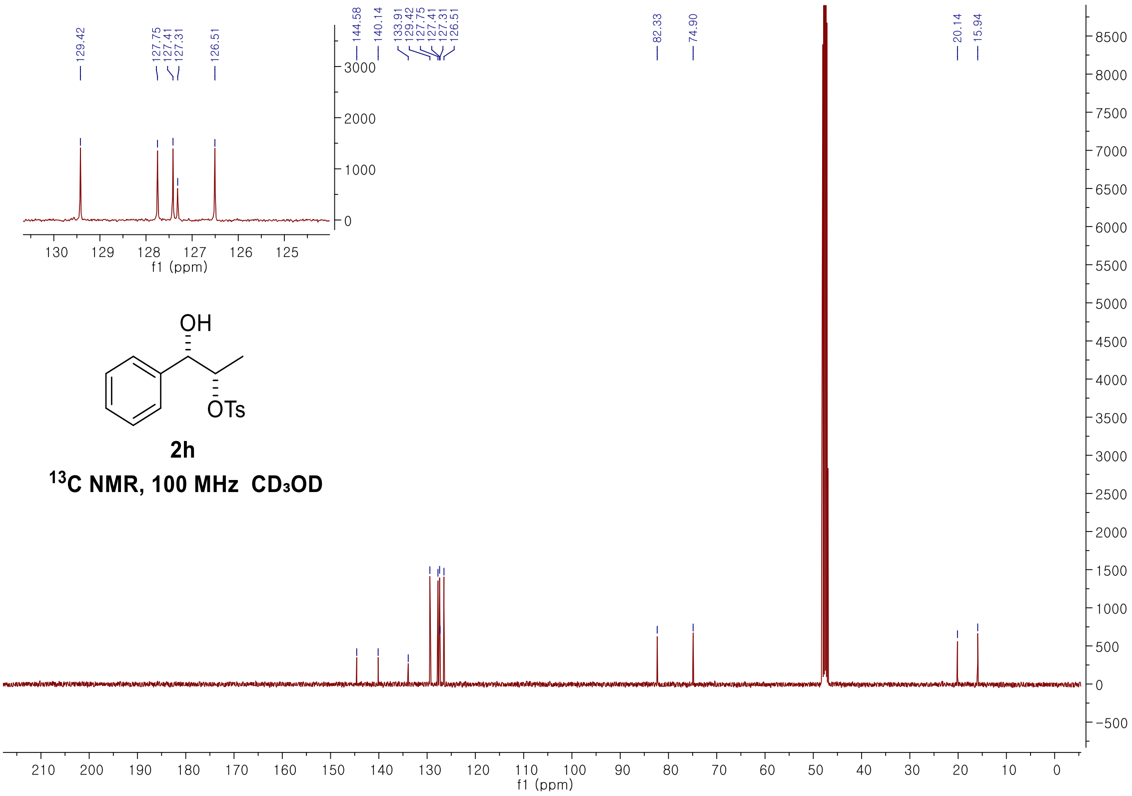

2g

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



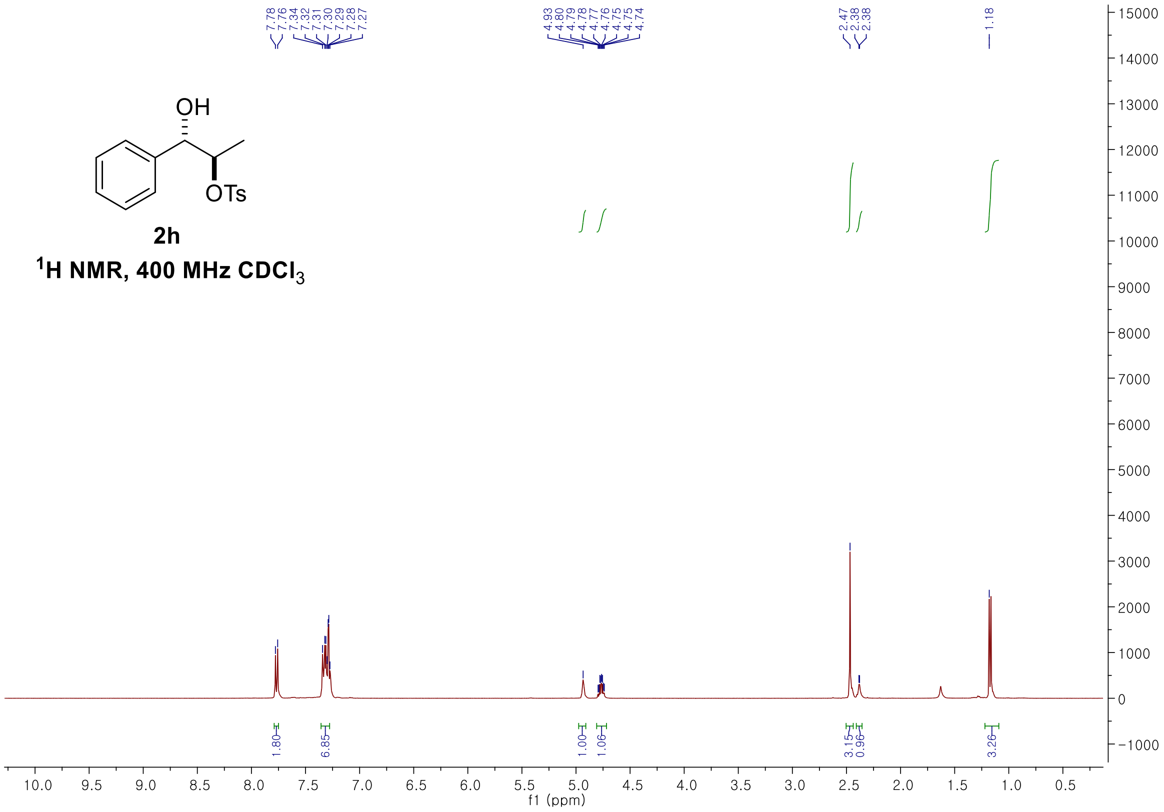
2h

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



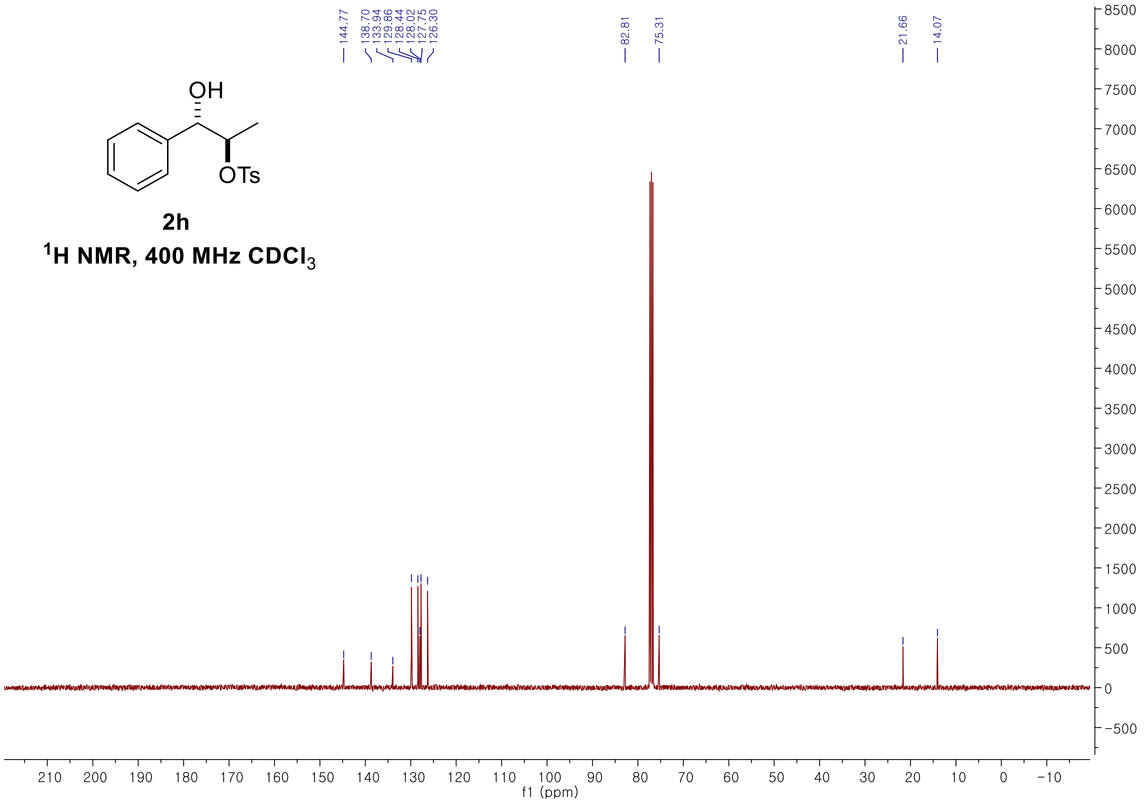
2h

^{13}C NMR, 100 MHz CD_3OD



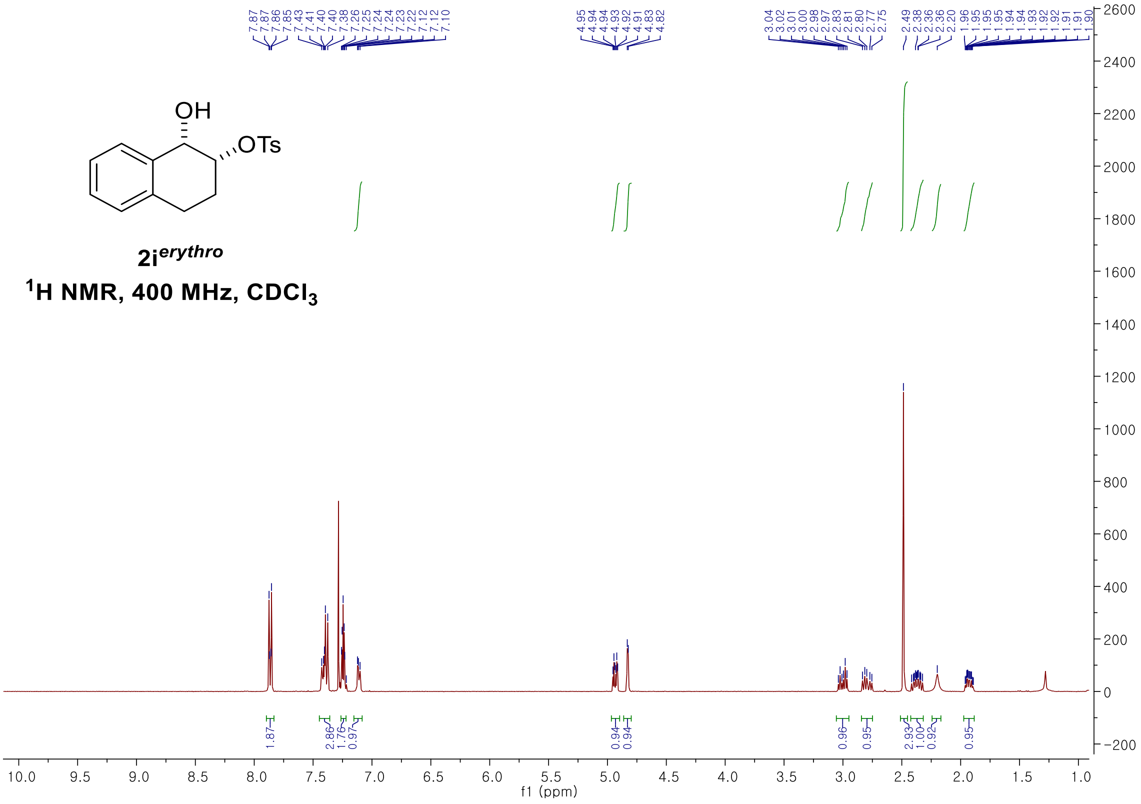
2h

^{1}H NMR, 400 MHz CDCl$_3$



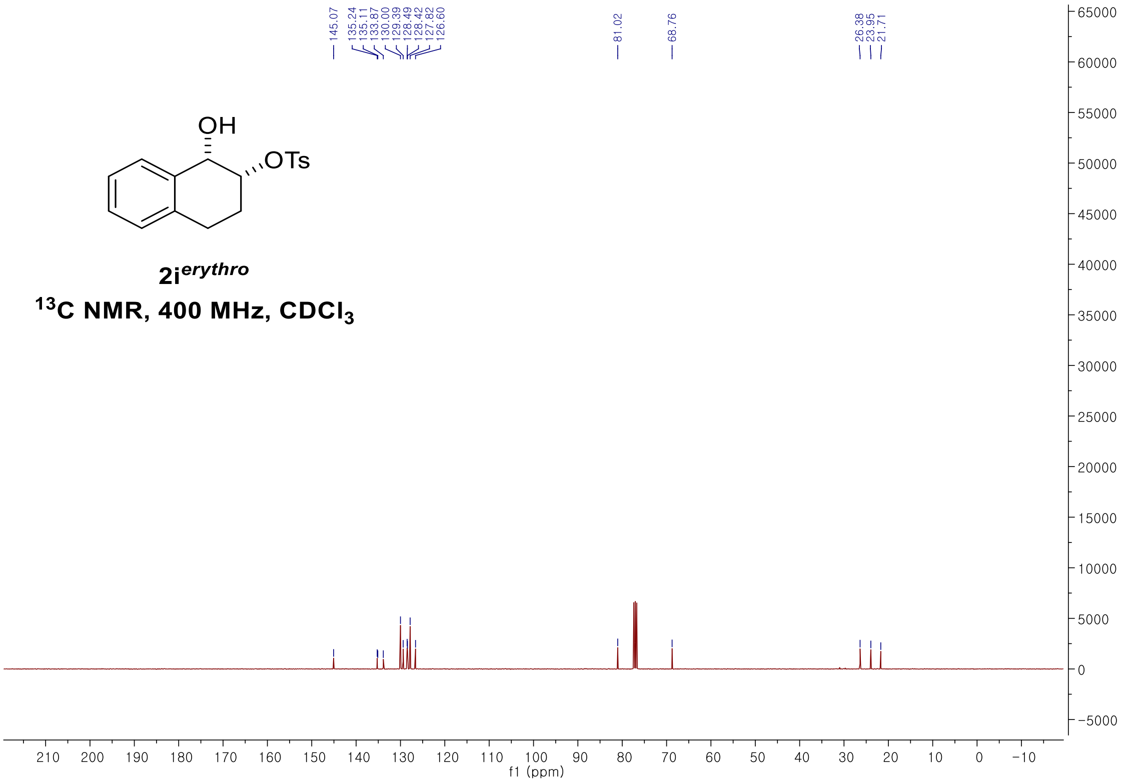
2h

^{1}H NMR, 400 MHz CDCl$_3$



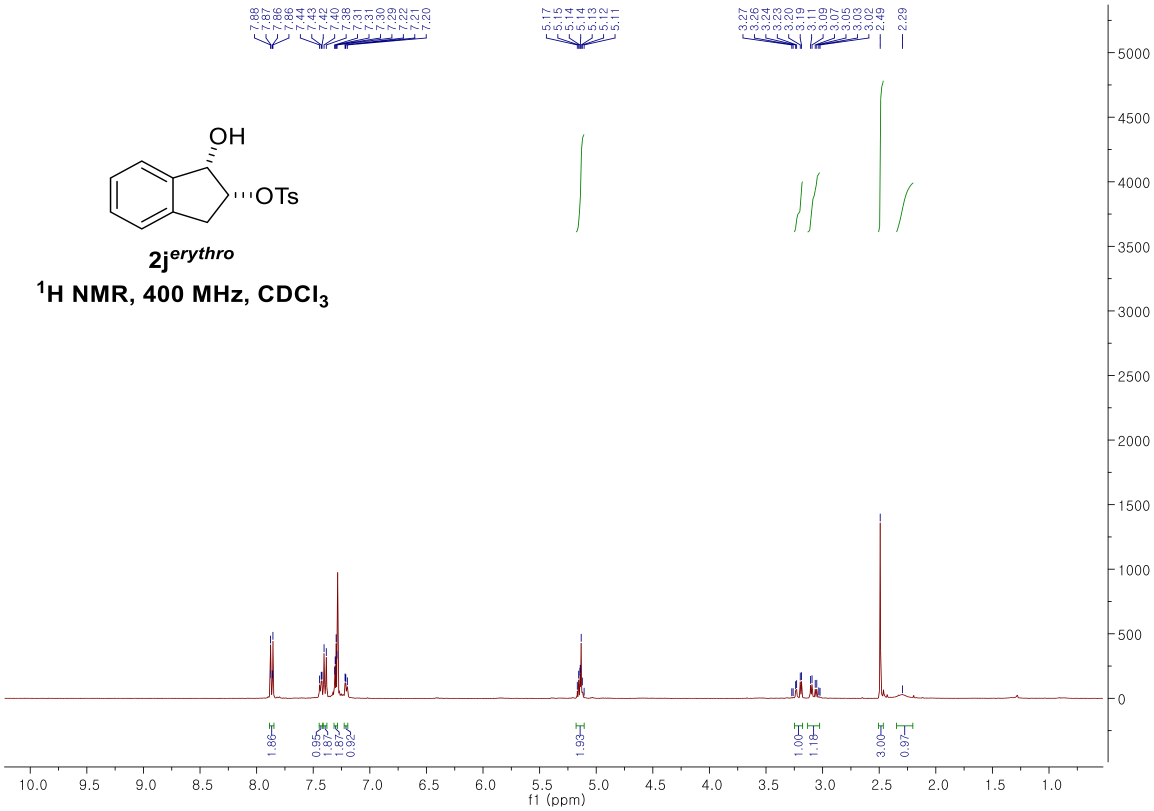
$2i^{erythro}$

^{1}H NMR, 400 MHz, CDCl$_3$



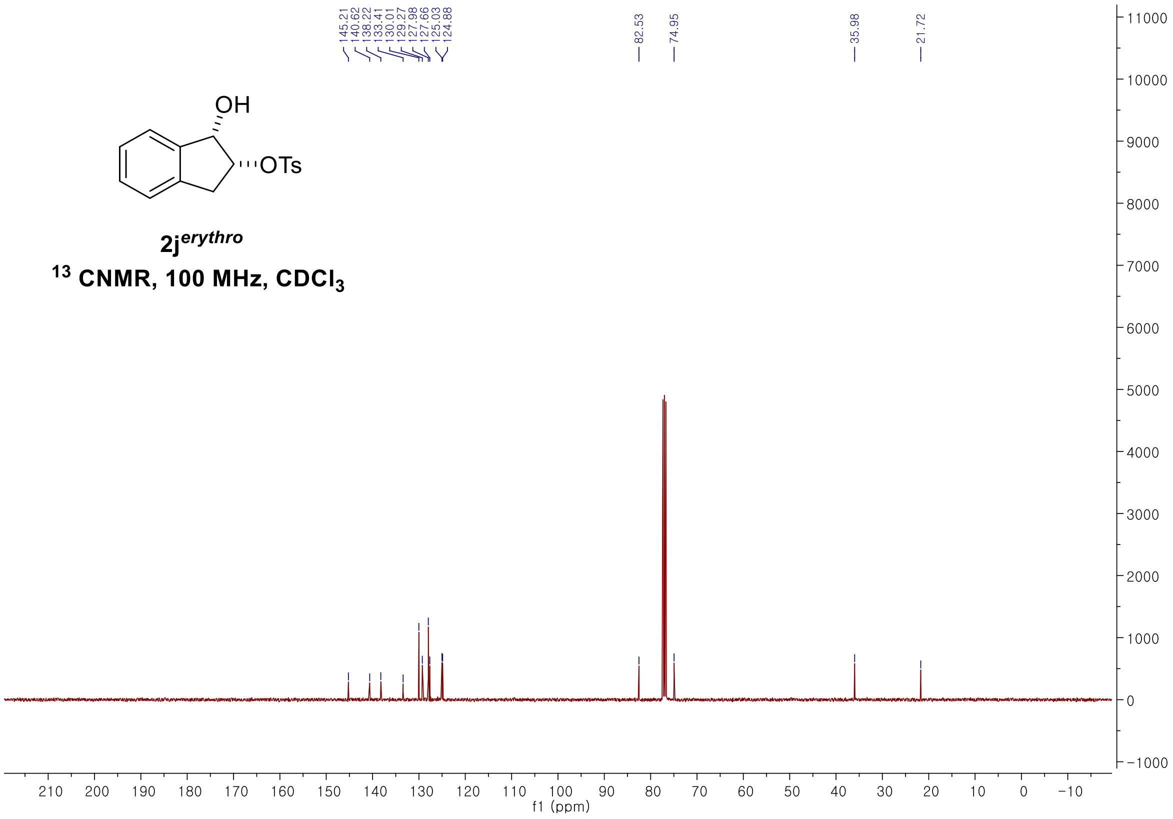
$2i^{erythro}$

^{13}C NMR, 400 MHz, CDCl$_3$



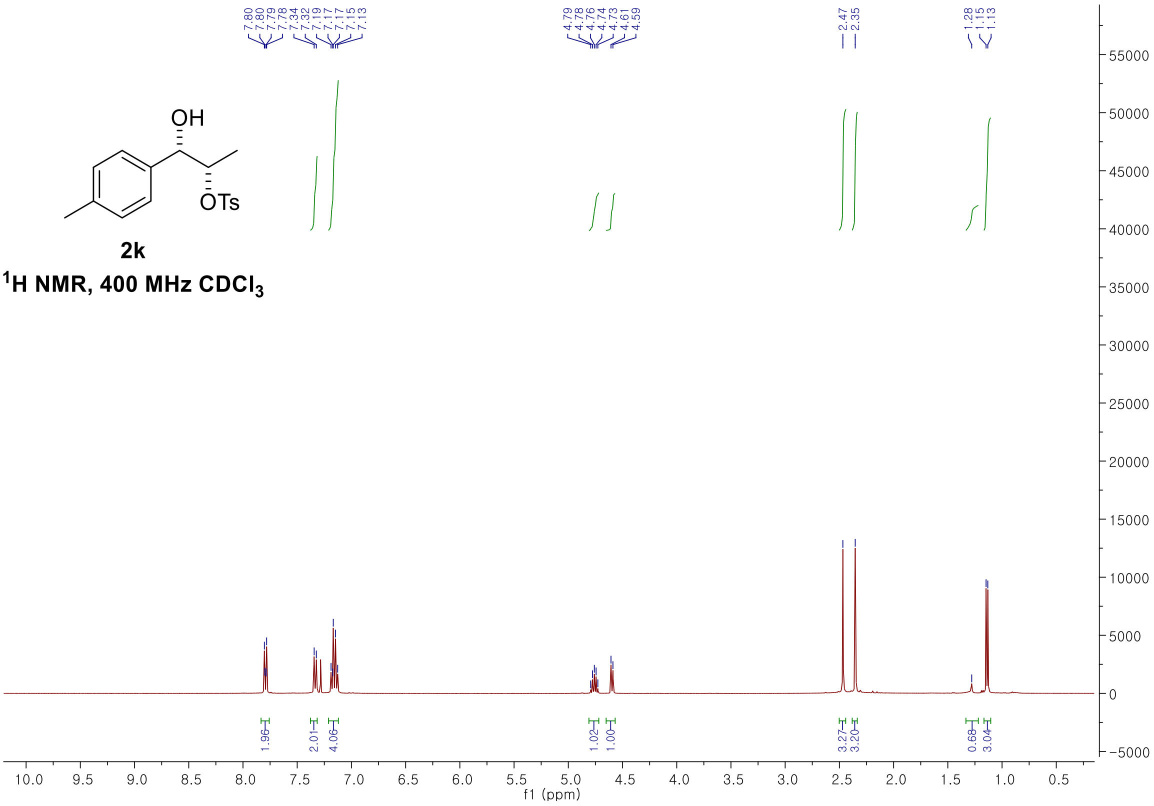
2j^{erythro}

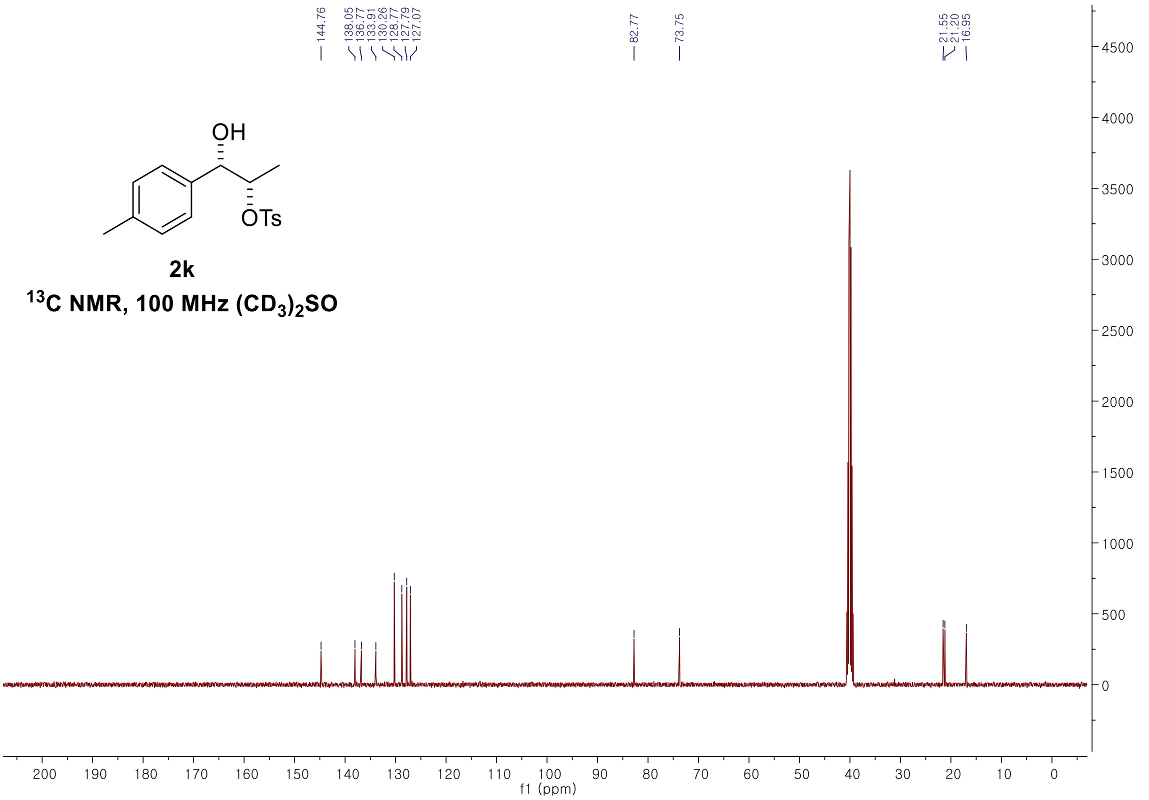
^{1}H NMR, 400 MHz, CDCl$_3$

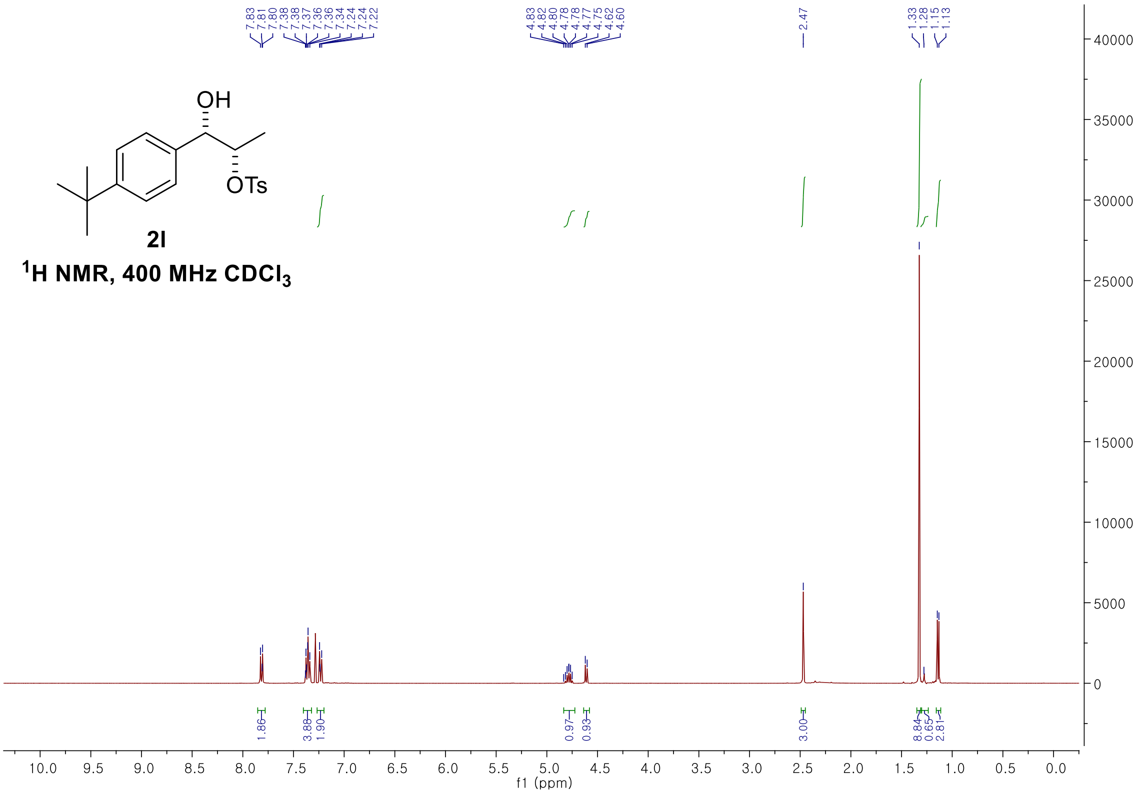


2j^{erythro}

^{13} CNMR, 100 MHz, CDCl$_3$

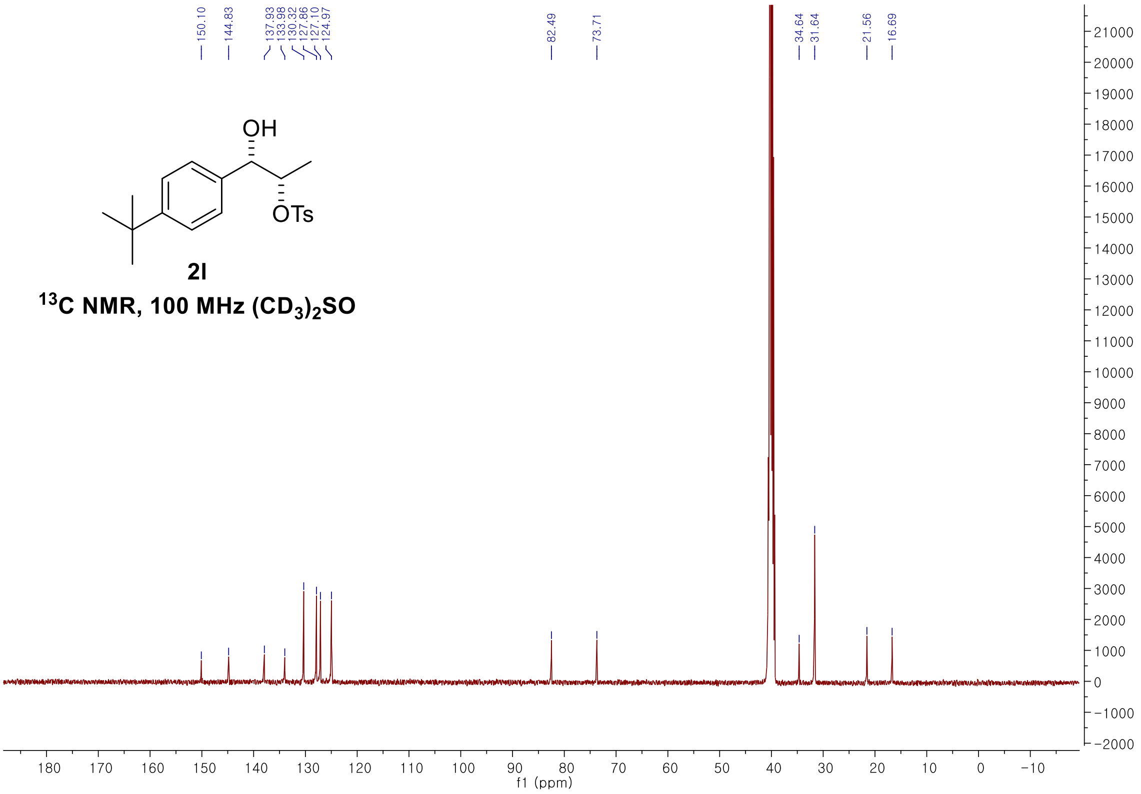

OH
OTs
2k
1H NMR, 400 MHz CDCl3
7.80
7.80
7.79
7.78
7.34
7.32
7.19
7.17
7.17
7.15
7.13
4.79
4.78
4.76
4.74
4.73
4.61
4.59
2.47
2.35
1.28
1.15
1.13
1.96
2.01
4.06
1.02
1.00
3.27
3.20
0.68
3.04
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


OH
OTs
2k
13C NMR, 100 MHz (CD3)2SO
144.76
138.05
136.77
133.91
130.26
128.77
127.79
127.07
82.77
73.75
21.55
21.20
16.95
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



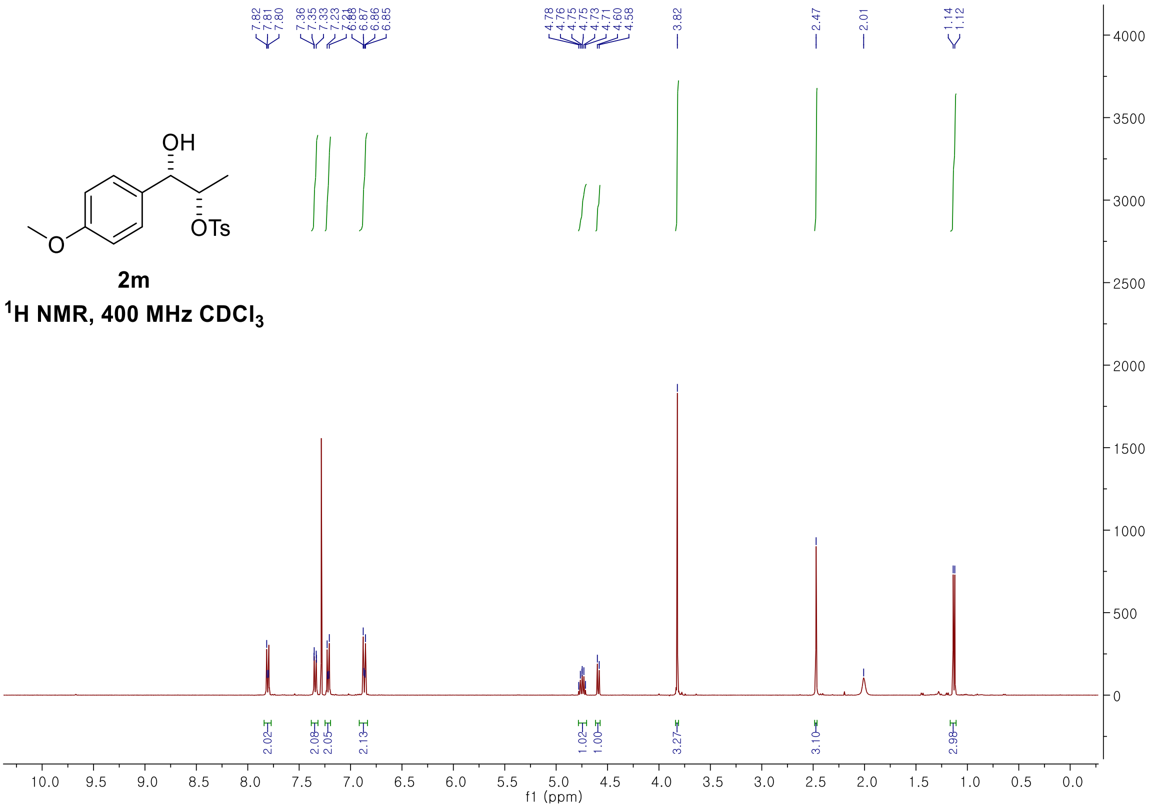
2l

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



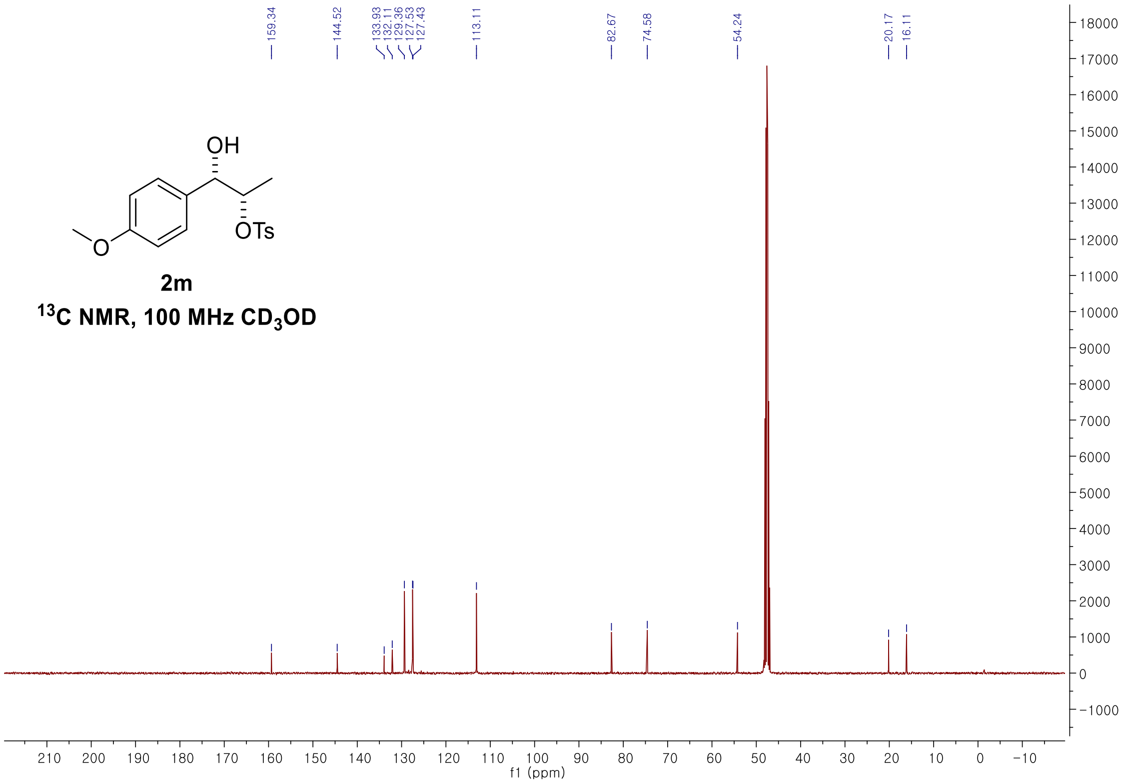
2l

^{13}C NMR, 100 MHz $(CD_3)_2SO$



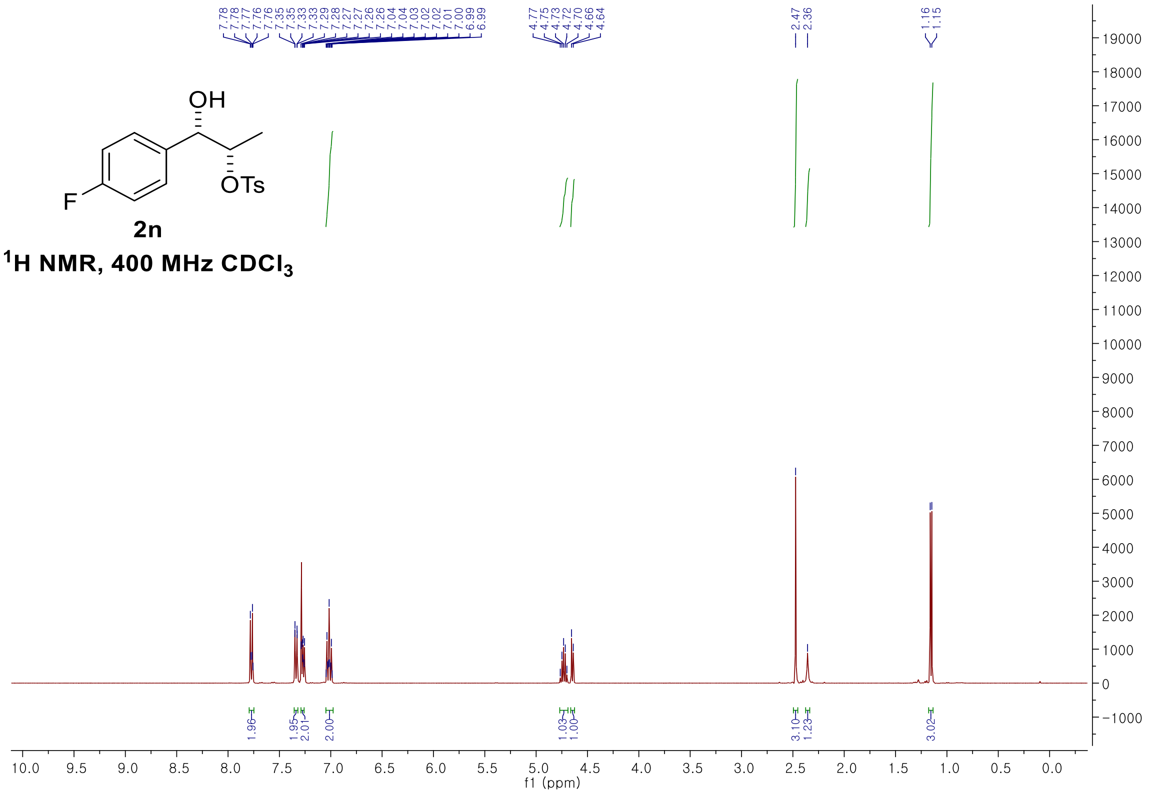
2m

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



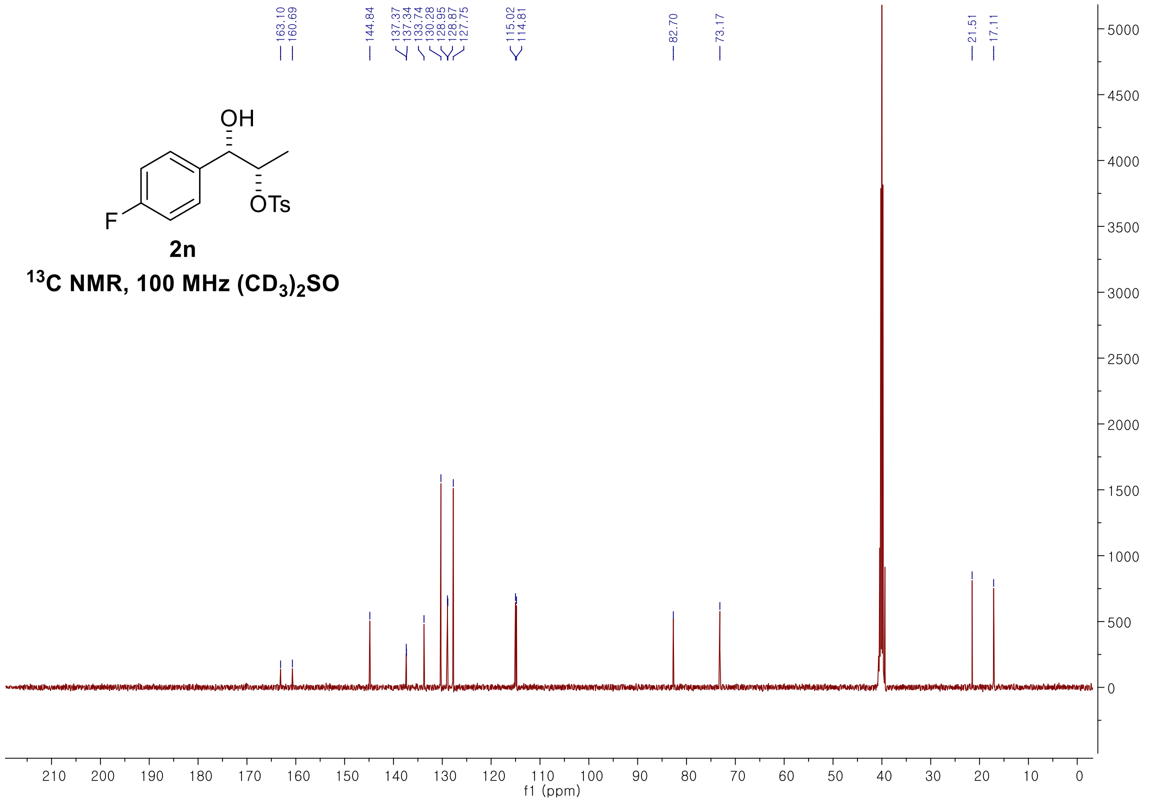
2m

^{13}C NMR, 100 MHz CD_3OD



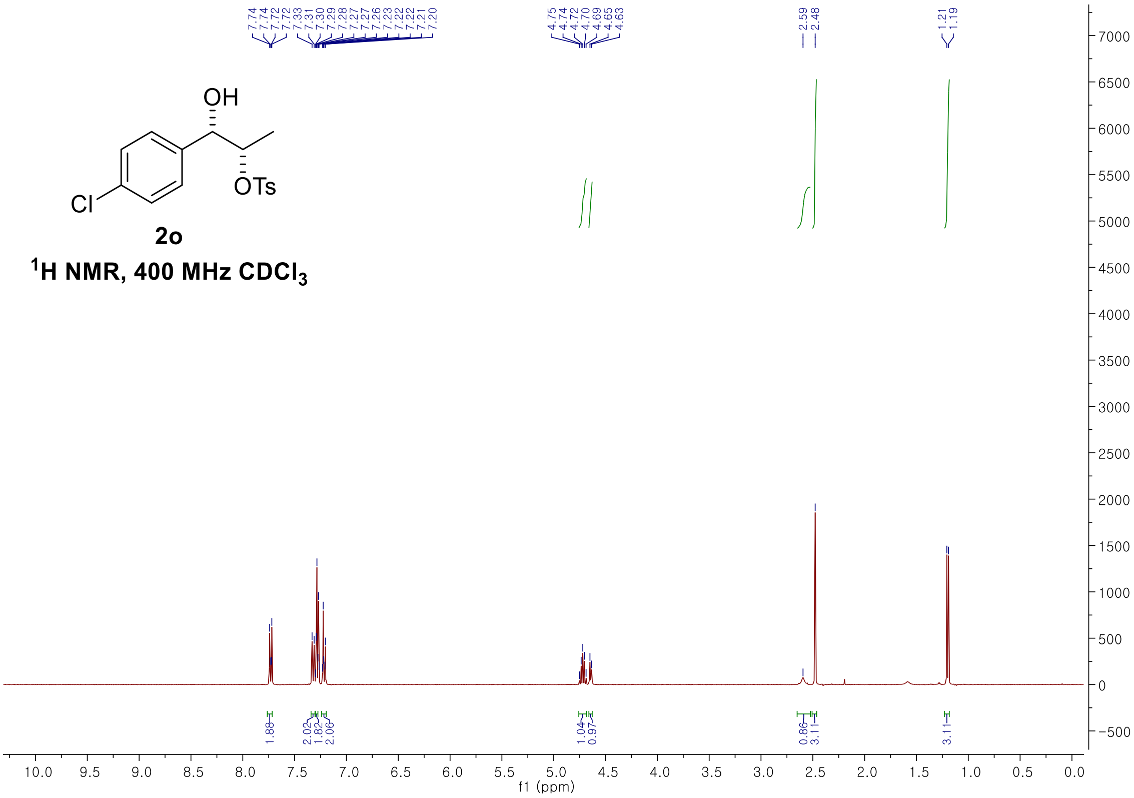
2n

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



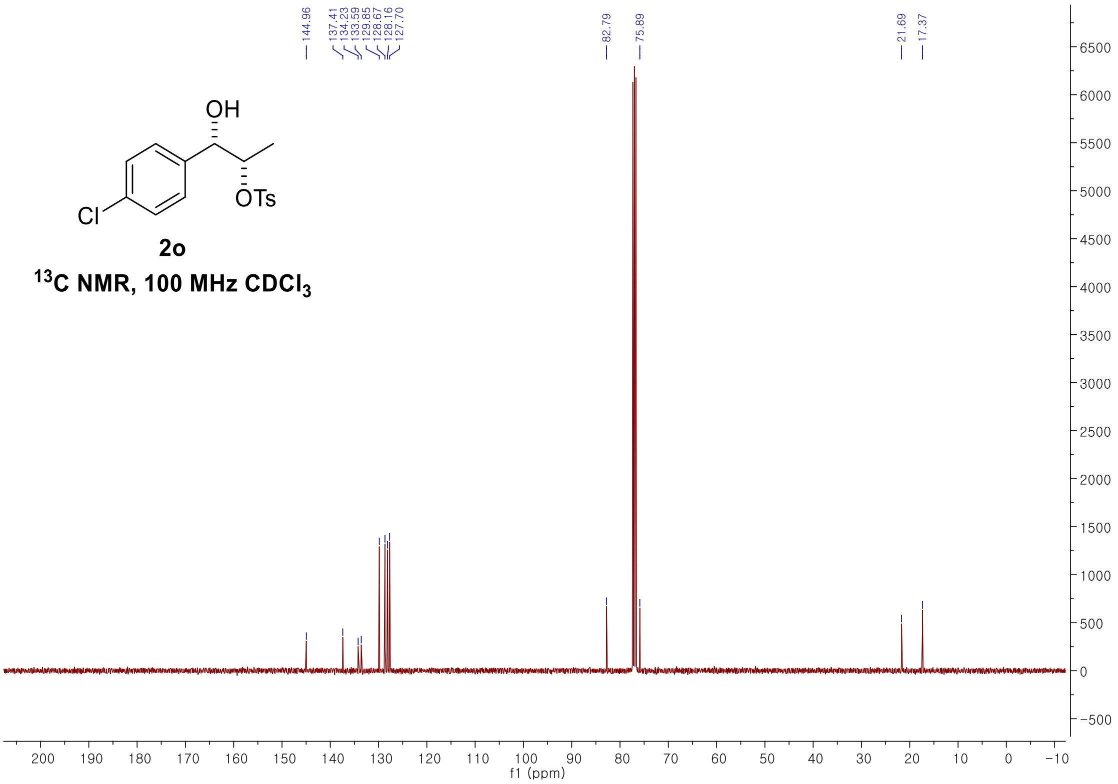
2n

^{13}C NMR, 100 MHz $(CD_3)_2SO$



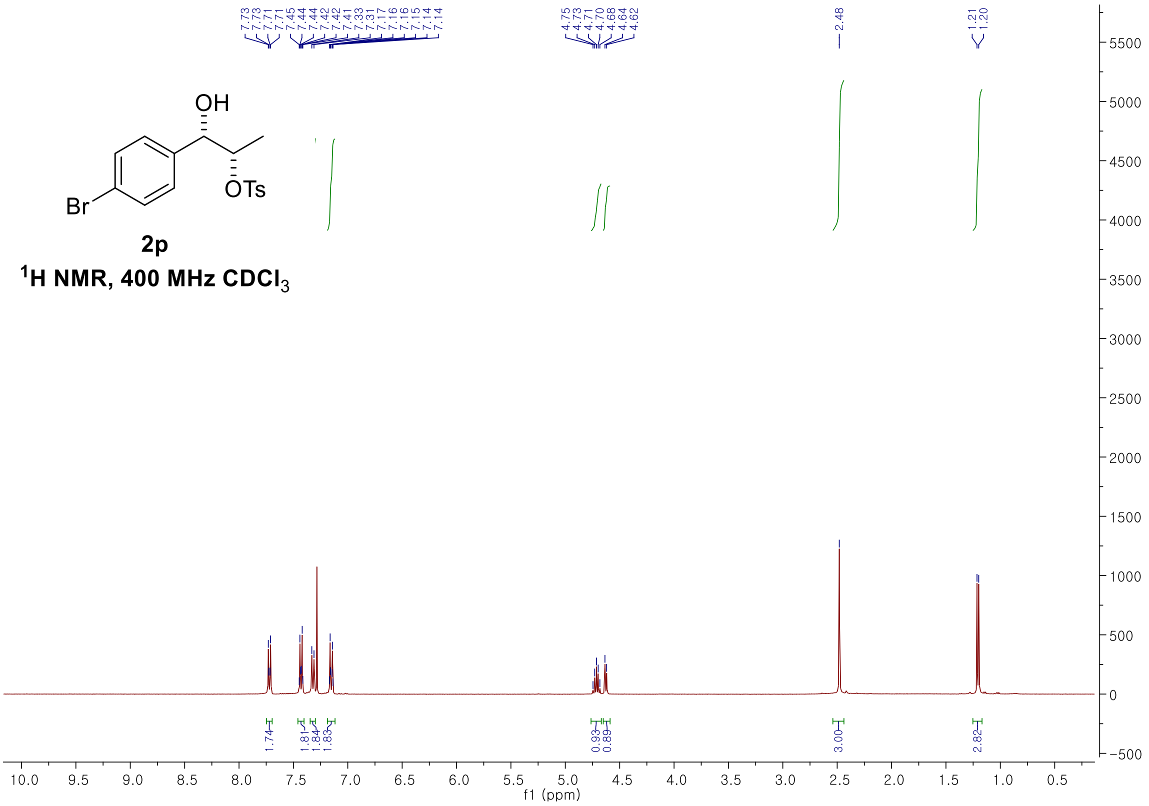
2o

^{1}H NMR, 400 MHz CDCl$_3$



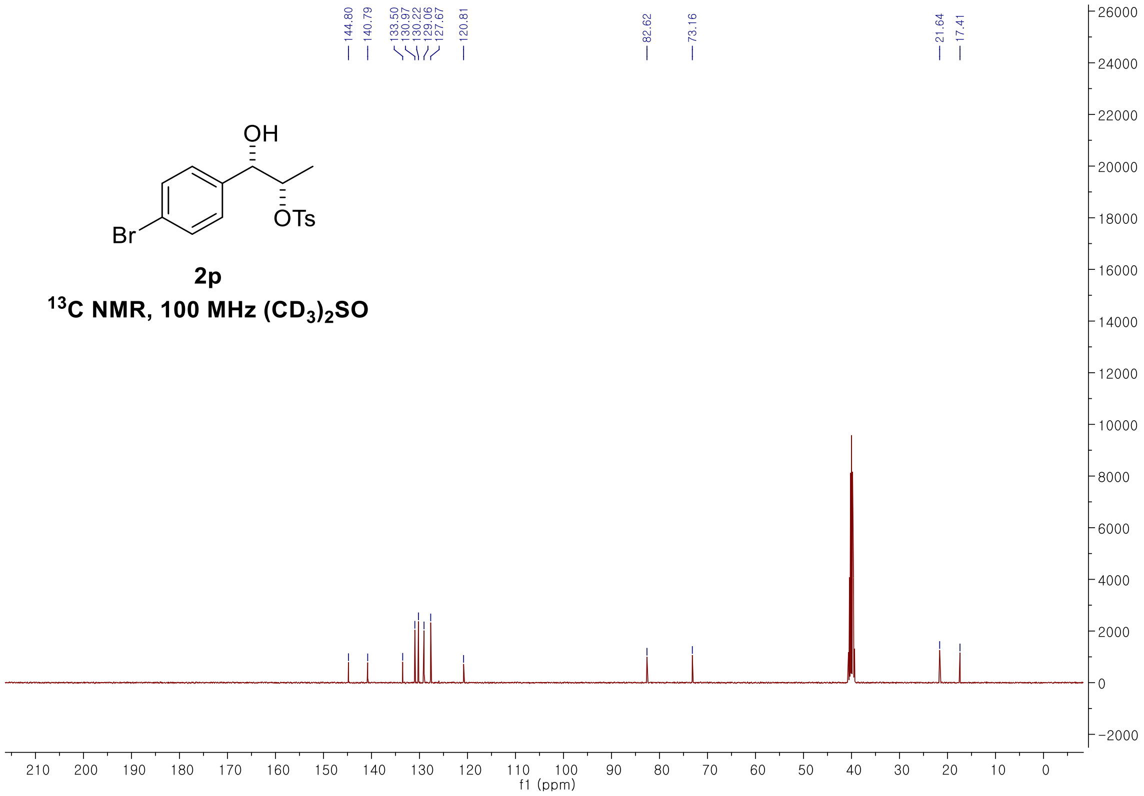
2o

^{13}C NMR, 100 MHz CDCl$_3$



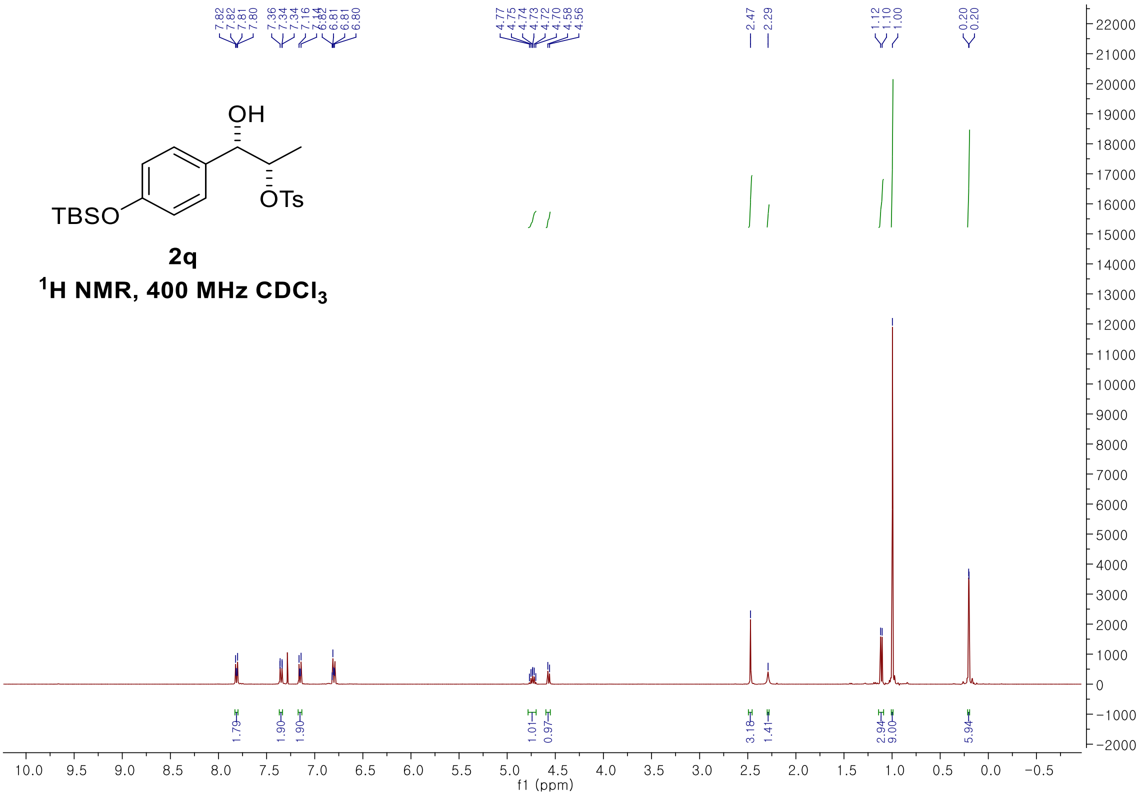
2p

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



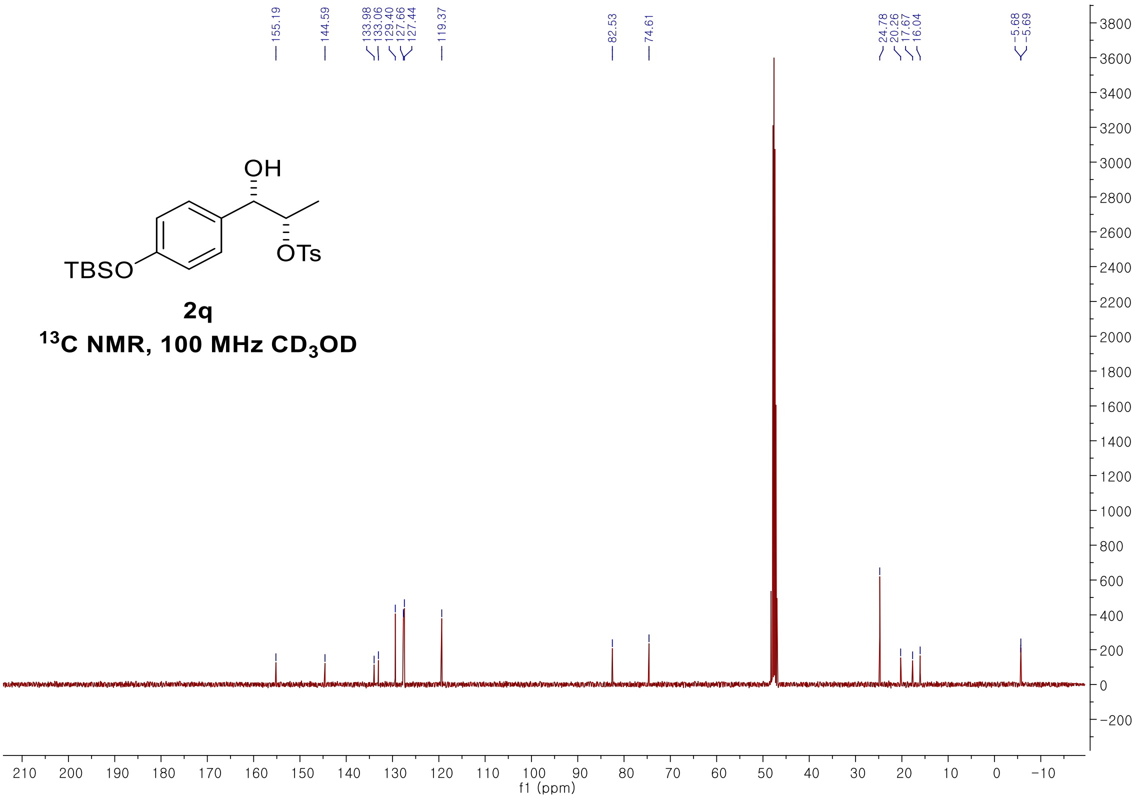
2p

^{13}C NMR, 100 MHz $(CD_3)_2SO$



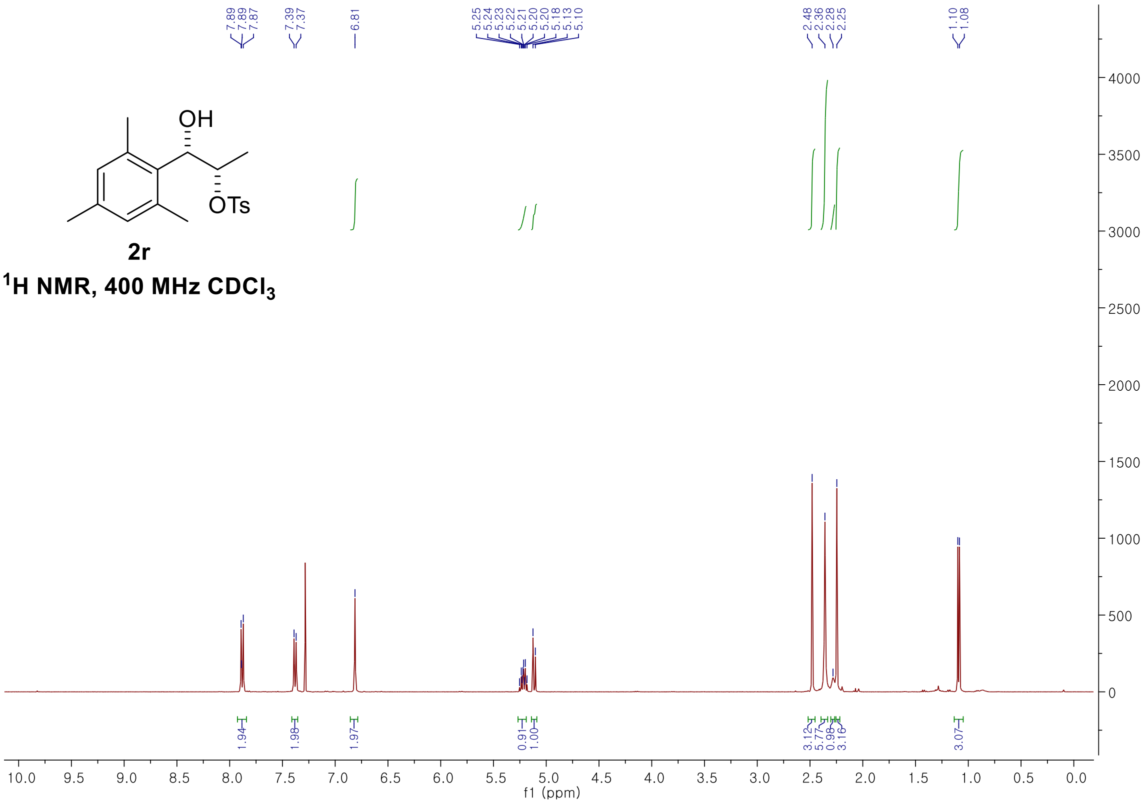
2q

^{1}H NMR, 400 MHz CDCl$_3$



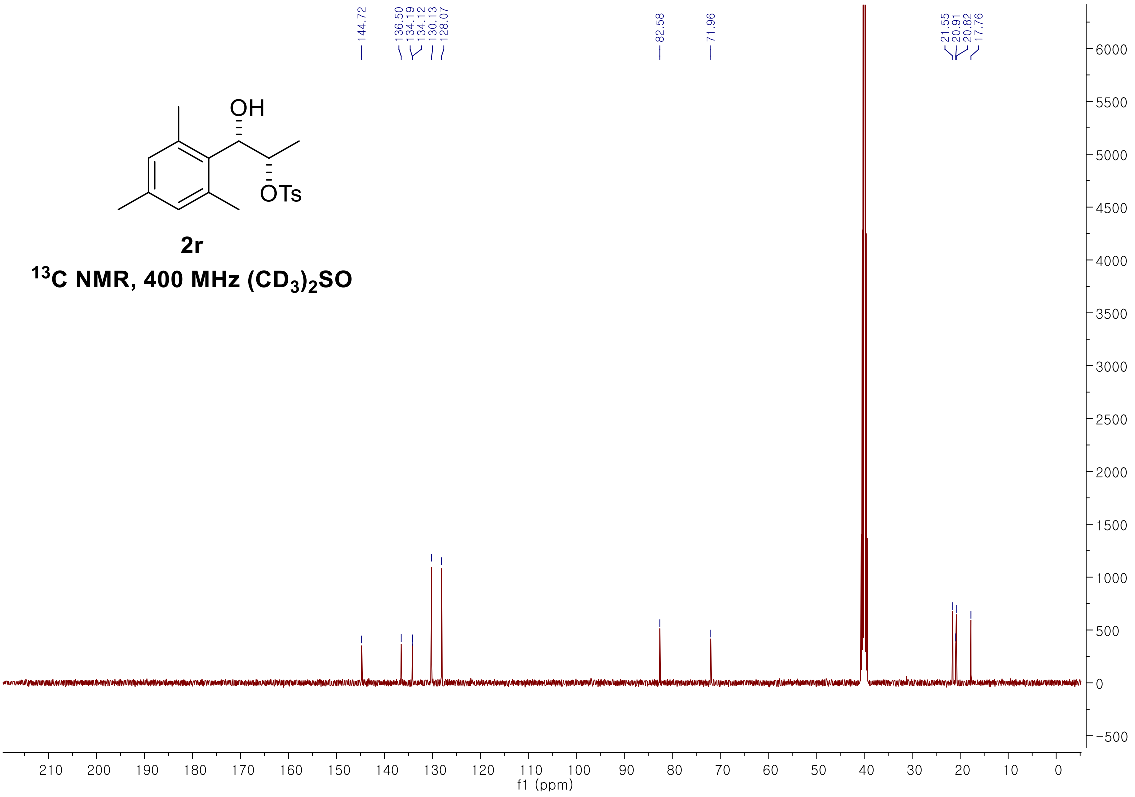
2q

^{13}C NMR, 100 MHz CD$_3$OD



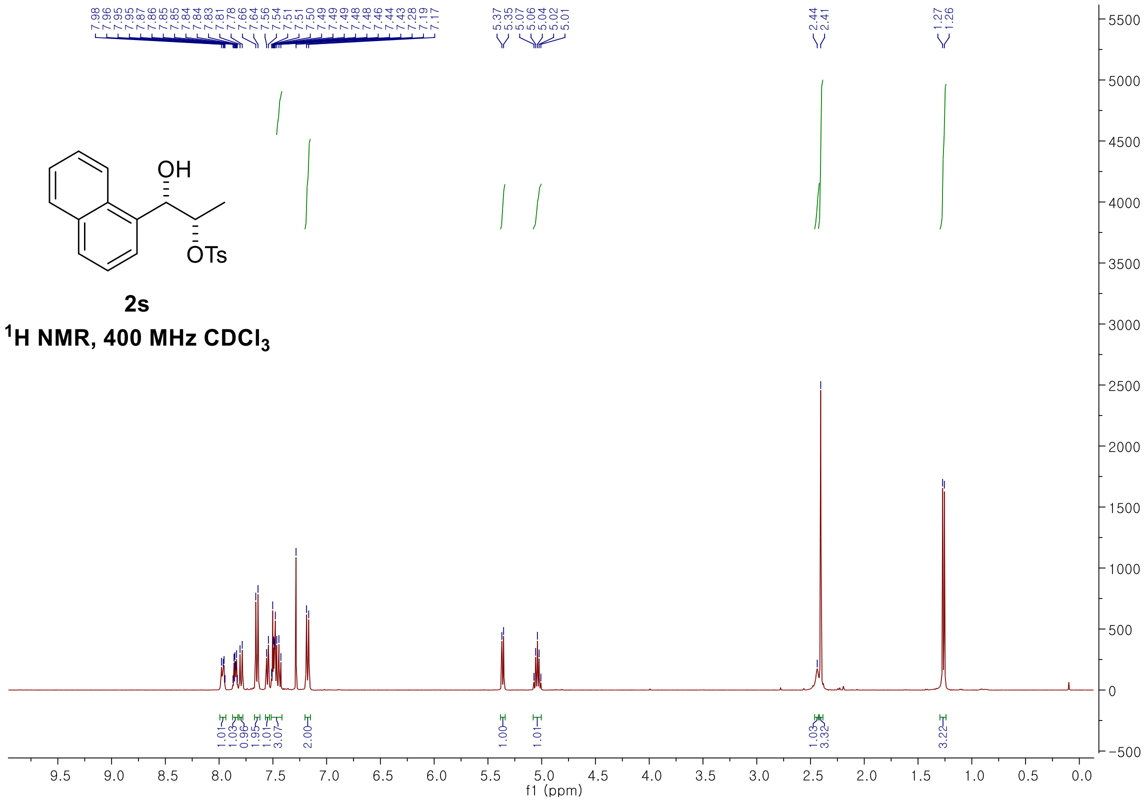
2r

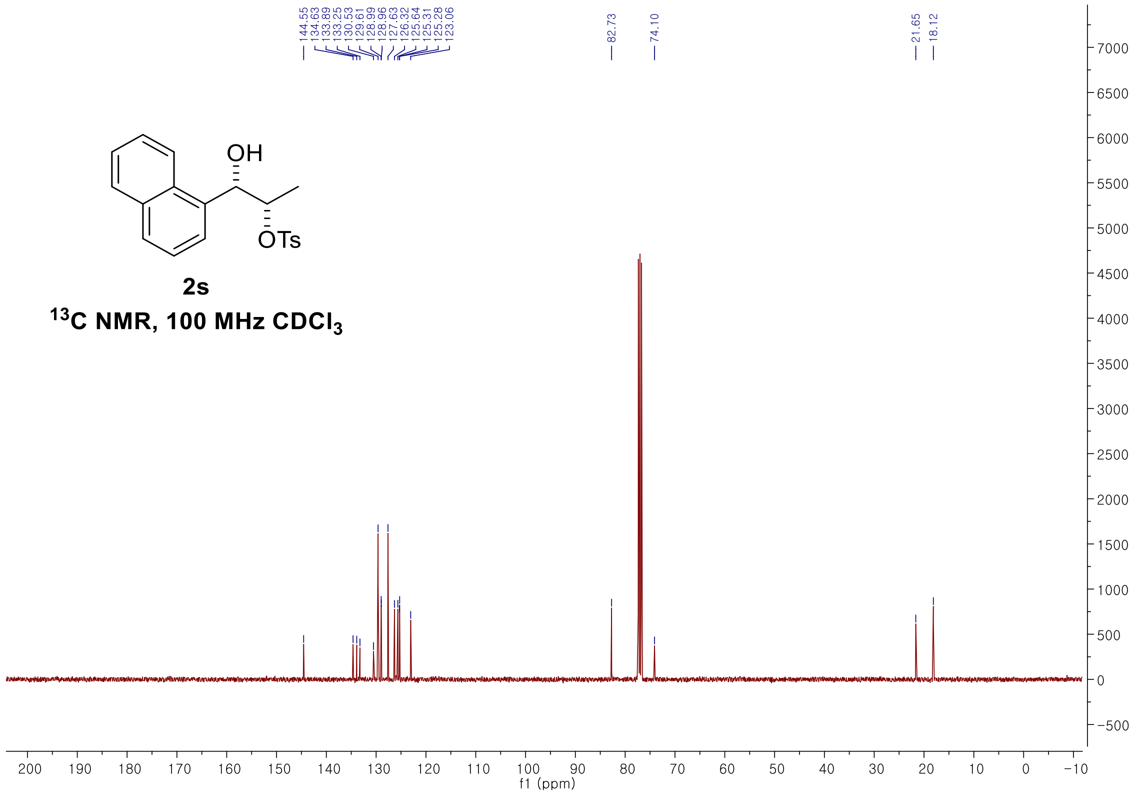
^{1}H NMR, 400 MHz $CDCl_3$

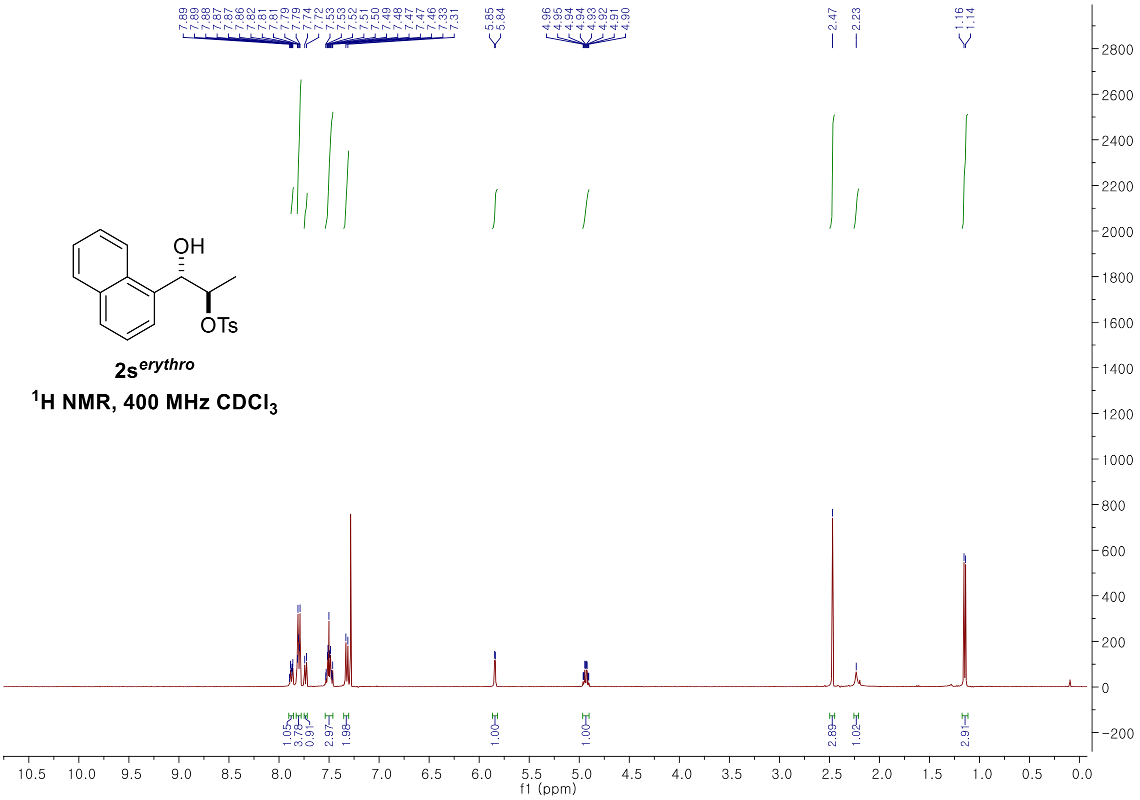


2r

^{13}C NMR, 400 MHz $(CD_3)_2SO$

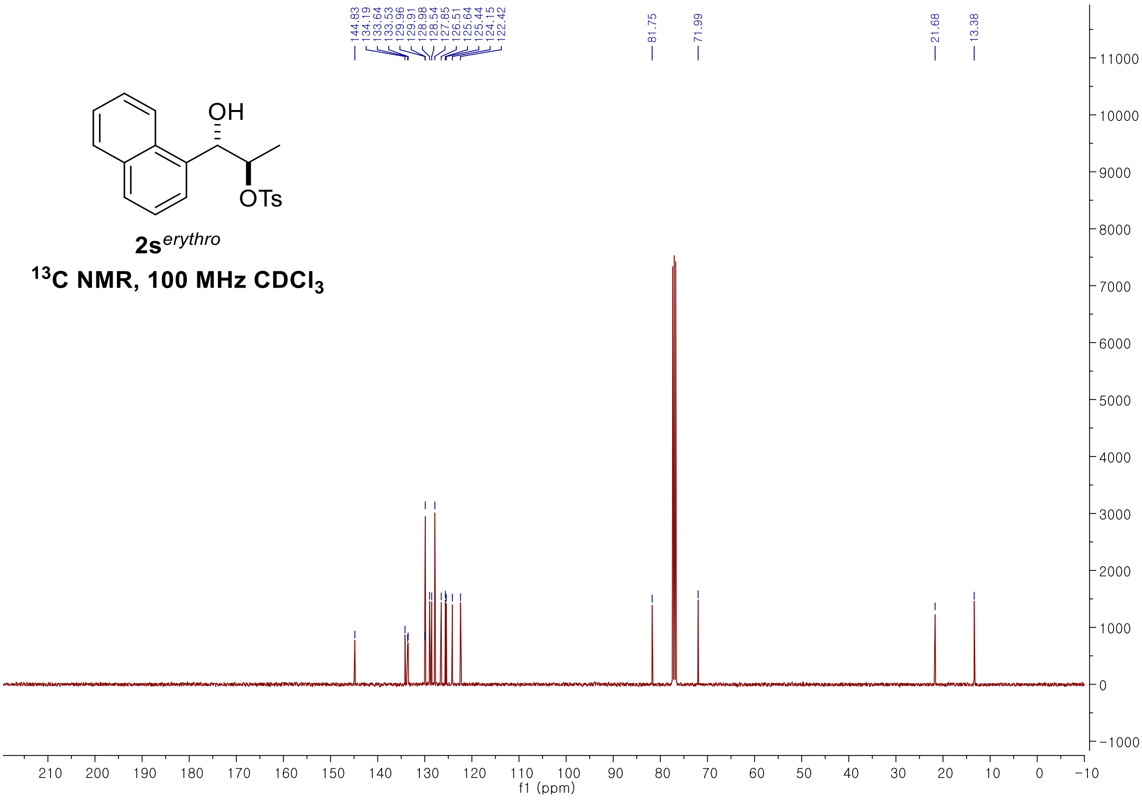

7.98
7.96
7.95
7.87
7.86
7.85
7.85
7.84
7.84
7.83
7.81
7.78
7.66
7.64
7.56
7.54
7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.46
7.44
7.43
7.28
7.19
7.17
5.37
5.35
5.07
5.06
5.04
5.02
5.01
2.44
2.41
1.27
1.26
OH
OTs
2s
^{1}H NMR, 400 MHz CDCl$_3$
1.01
1.03
0.96
1.95
1.01
3.07
2.00
1.00
1.01
1.03
3.32
3.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500


144.55
134.63
133.89
133.25
130.53
129.61
128.99
128.96
127.63
126.32
125.64
125.31
125.28
123.06
82.73
74.10
21.65
18.12
OH
OTs
2s
^{13}C NMR, 100 MHz CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500



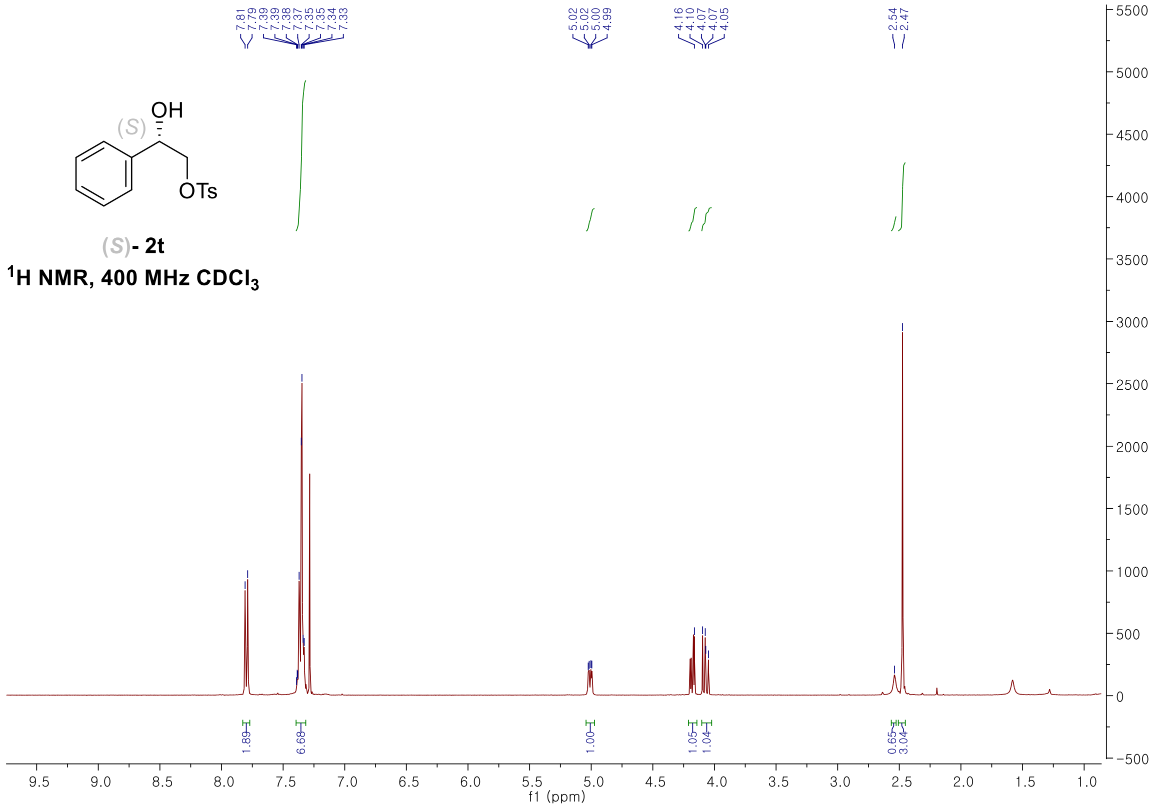
2s*erythro*

^{1}H NMR, 400 MHz CDCl$_3$



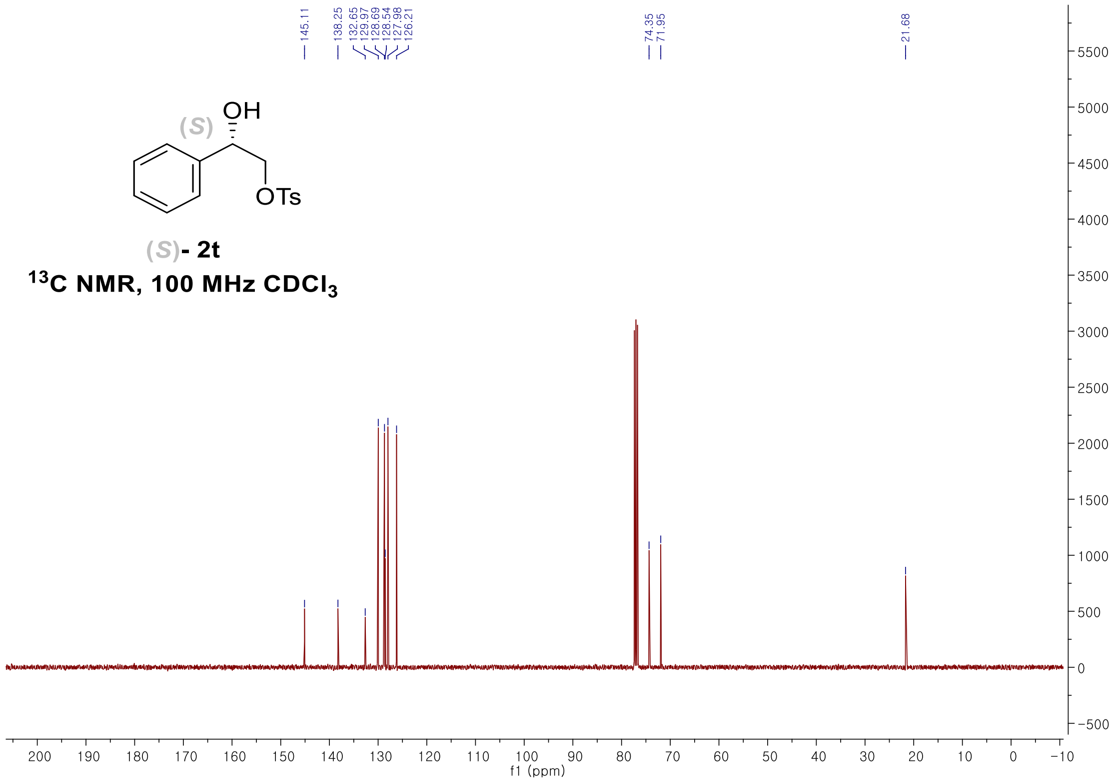
2s*erythro*

^{13}C NMR, 100 MHz CDCl$_3$



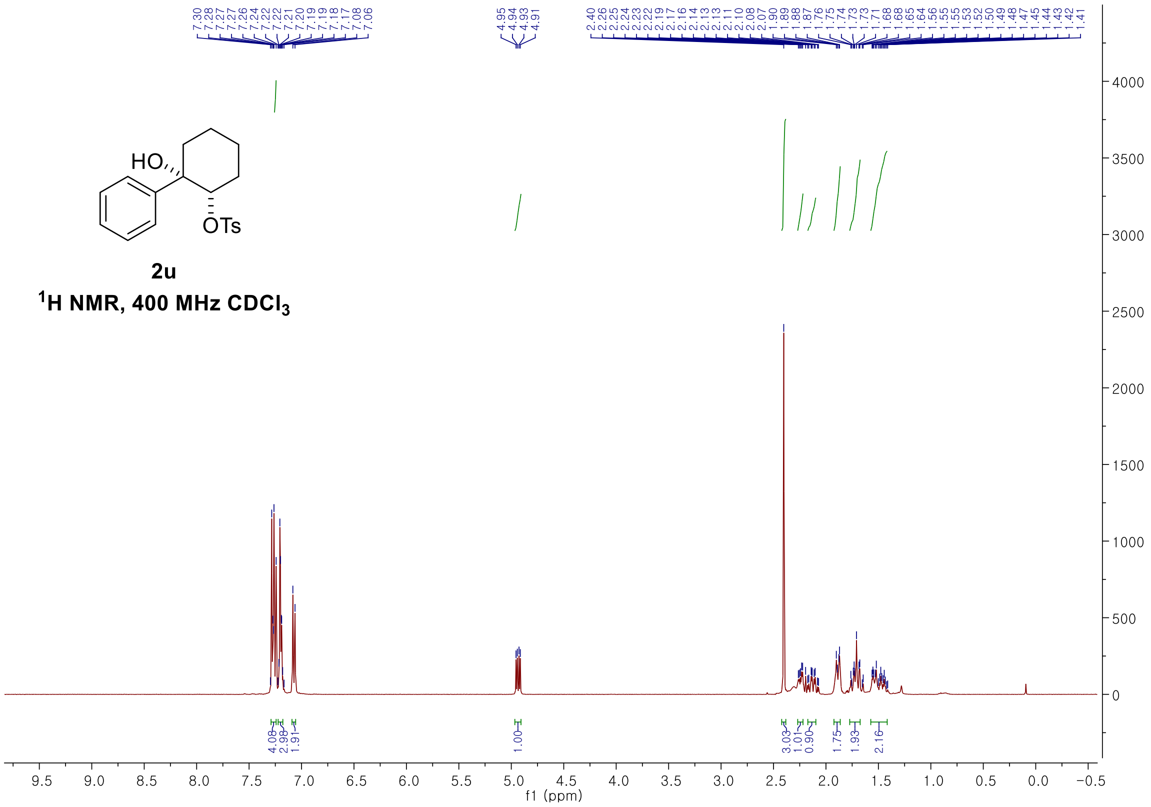
(*S*)- **2t**

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



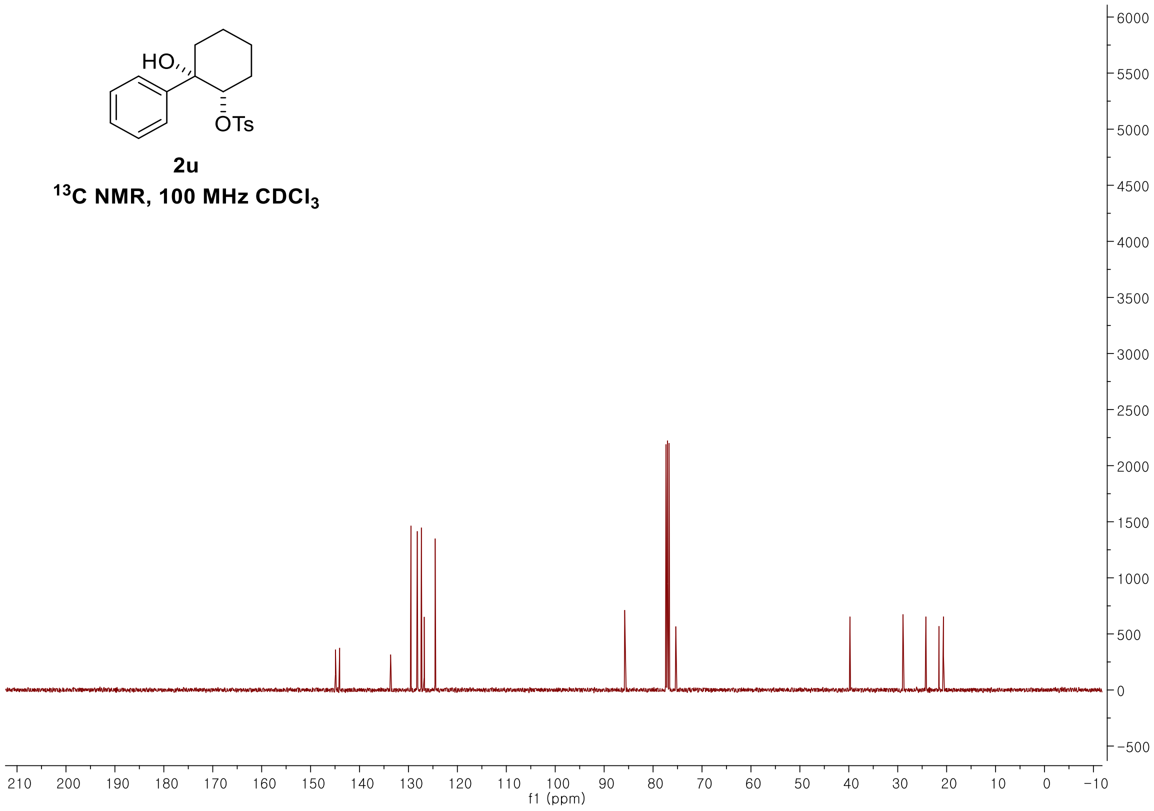
(*S*)- **2t**

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



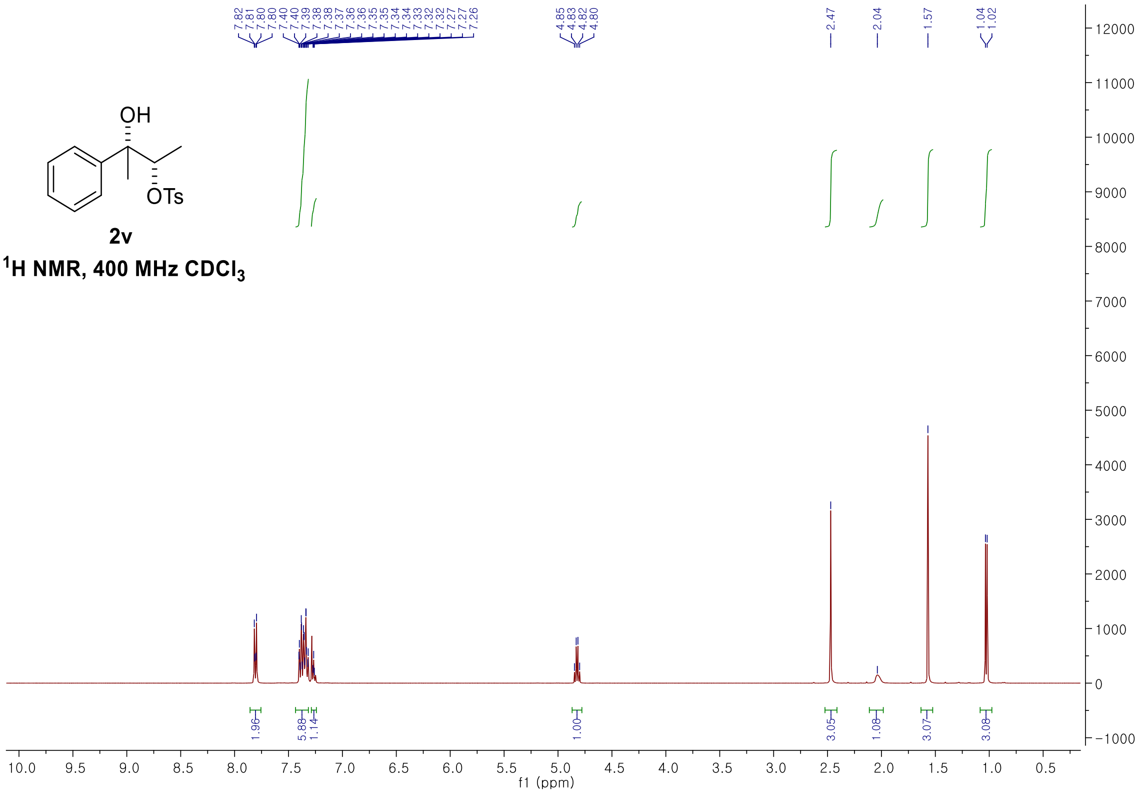
2u

^{1}H NMR, 400 MHz CDCl$_3$



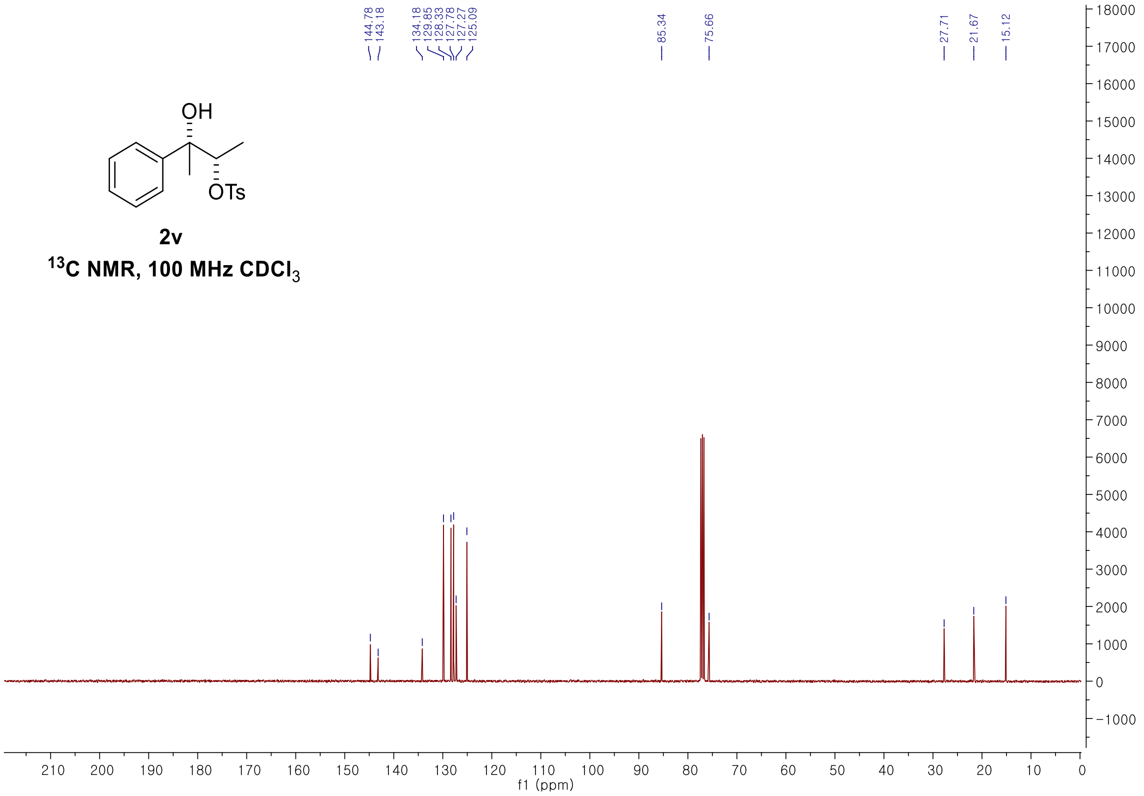
2u

^{13}C NMR, 100 MHz CDCl$_3$



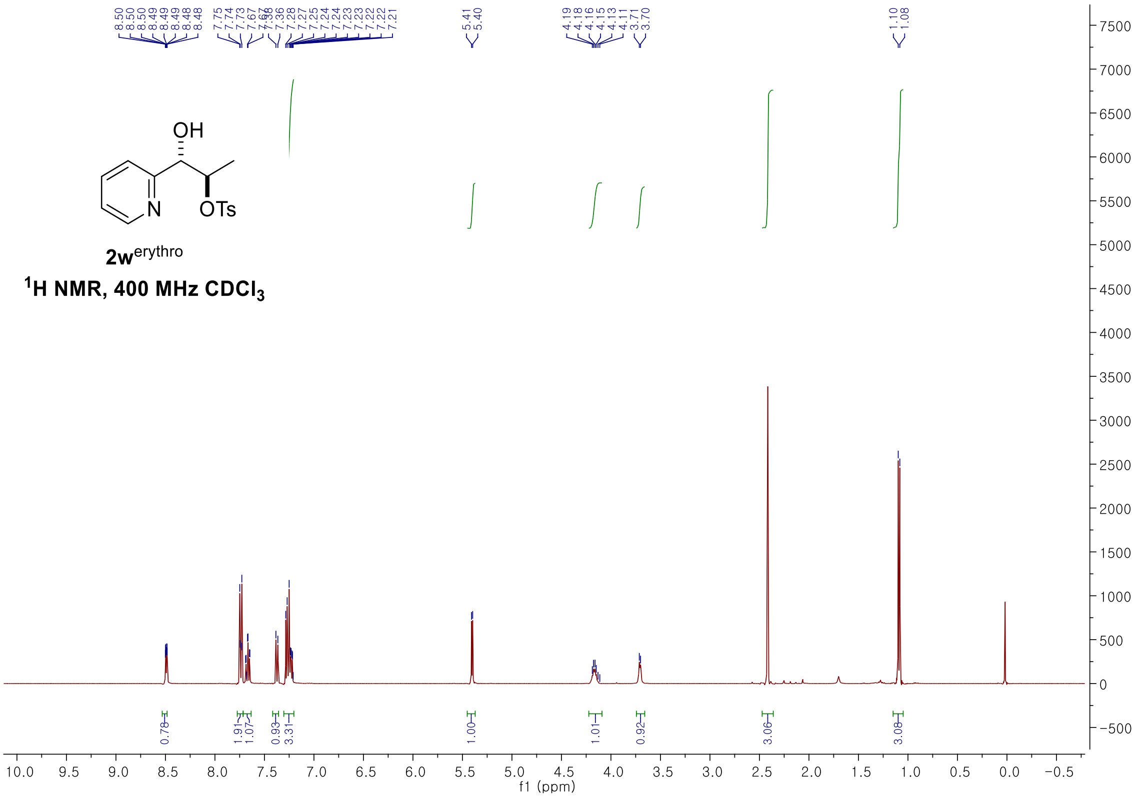
2v

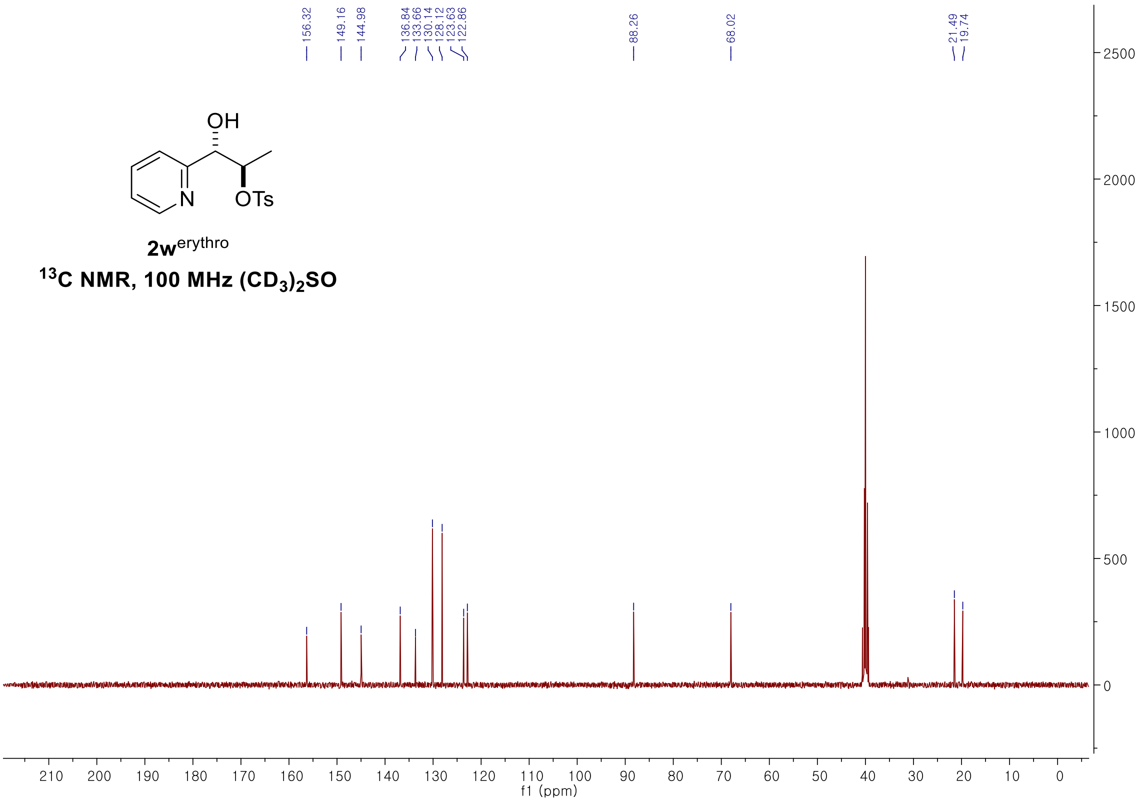
^{1}H NMR, 400 MHz CDCl$_3$

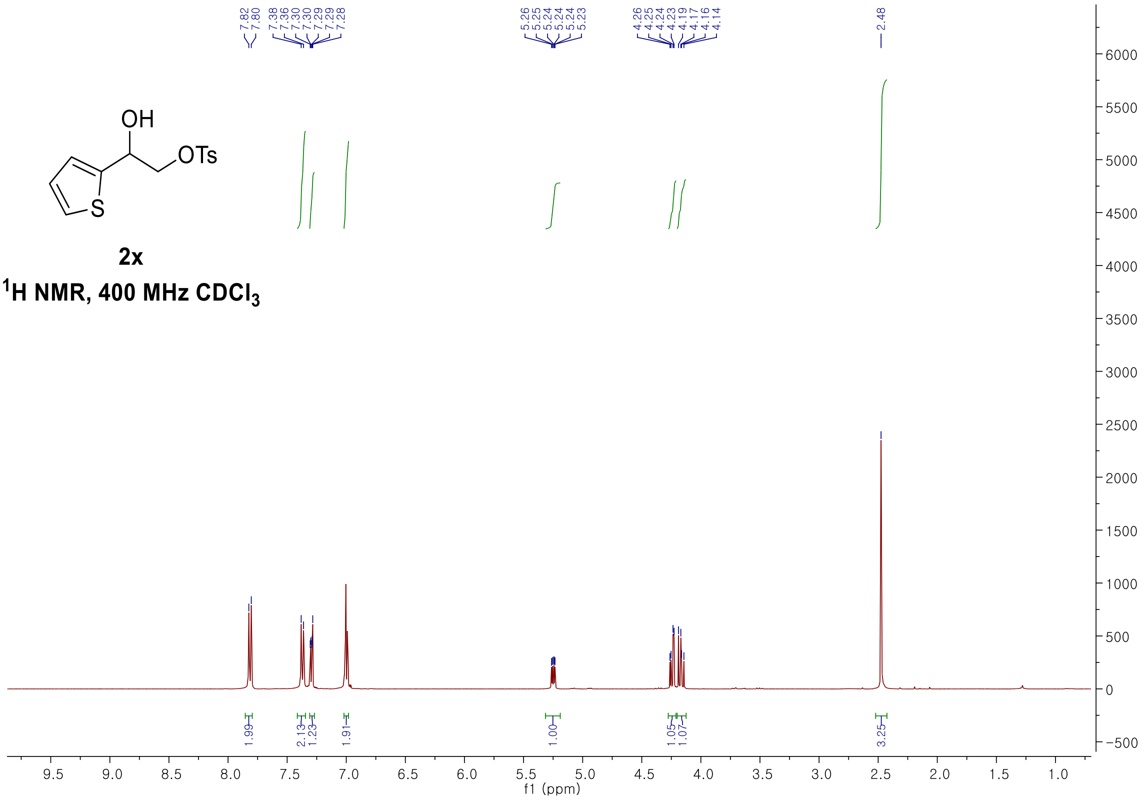


2v

^{13}C NMR, 100 MHz CDCl$_3$

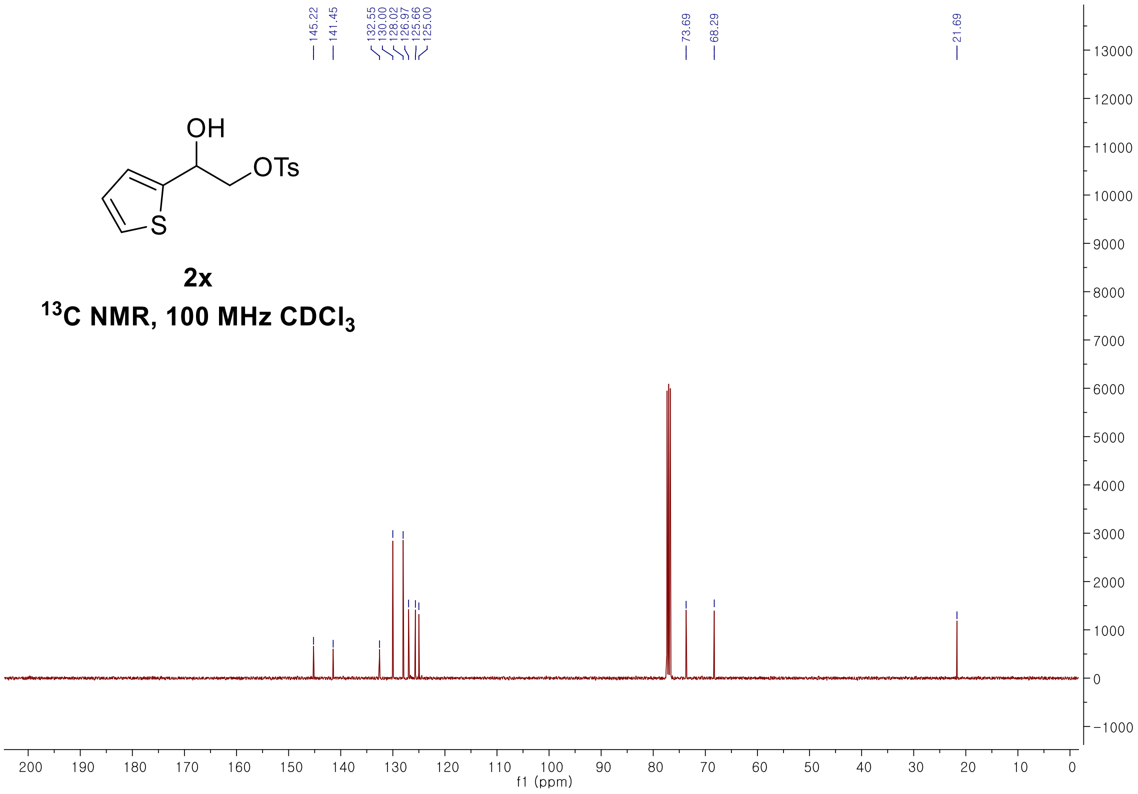

8.50
8.50
8.50
8.49
8.49
8.49
8.48
8.48
7.75
7.74
7.73
7.67
7.67
7.38
7.36
7.28
7.27
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
5.41
5.40
4.19
4.18
4.16
4.15
4.13
4.11
3.71
3.70
1.10
1.08
OH
N
OTs
2w^erythro
1H NMR, 400 MHz CDCl3
0.78
1.91
1.07
0.93
3.31
1.00
1.01
0.92
3.06
3.08
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


156.32
149.16
144.98
136.84
133.66
130.14
128.12
123.63
122.86
88.26
68.02
21.49
19.74
OH
N
OTs
2w^erythro
13C NMR, 100 MHz (CD3)2SO
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



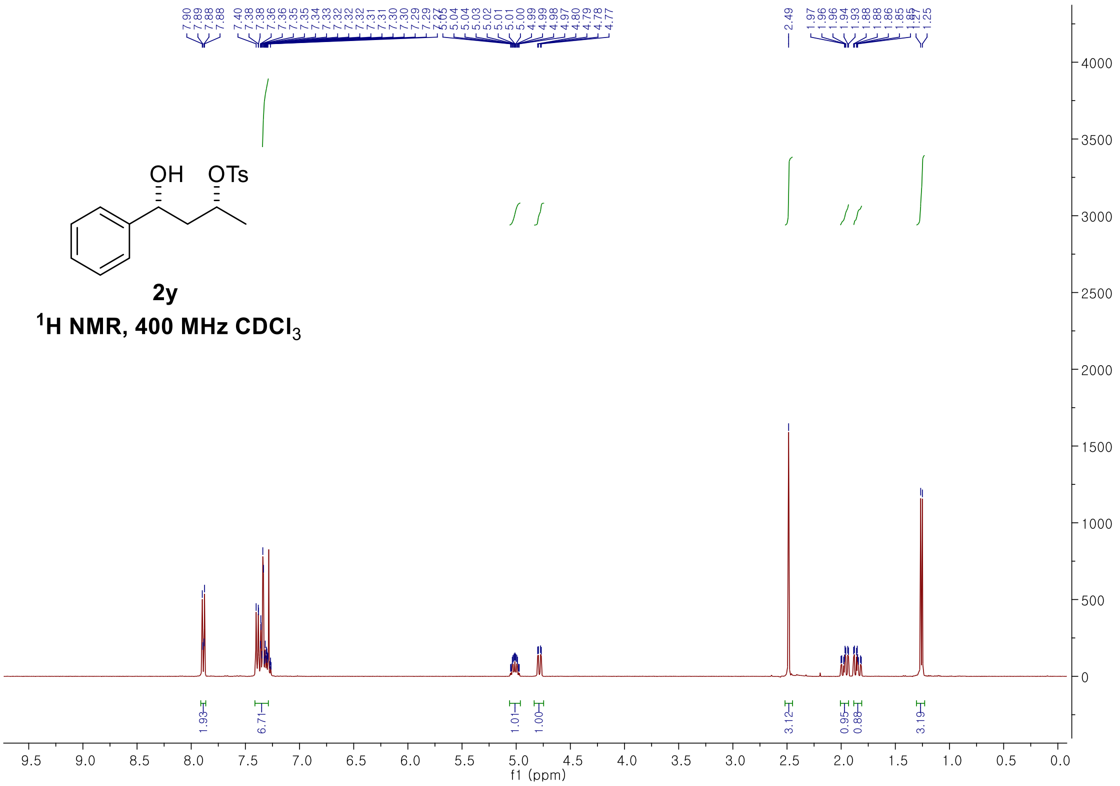
2x

^{1}H NMR, 400 MHz CDCl$_3$



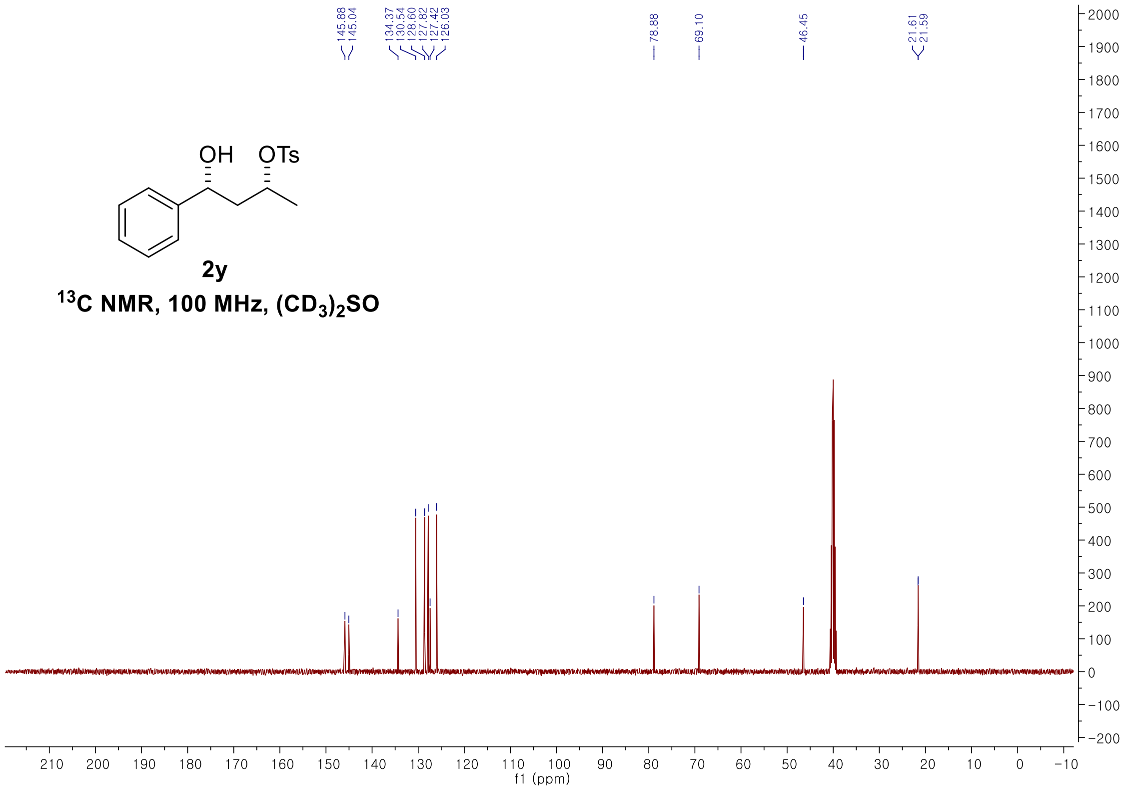
2x

^{13}C NMR, 100 MHz CDCl$_3$



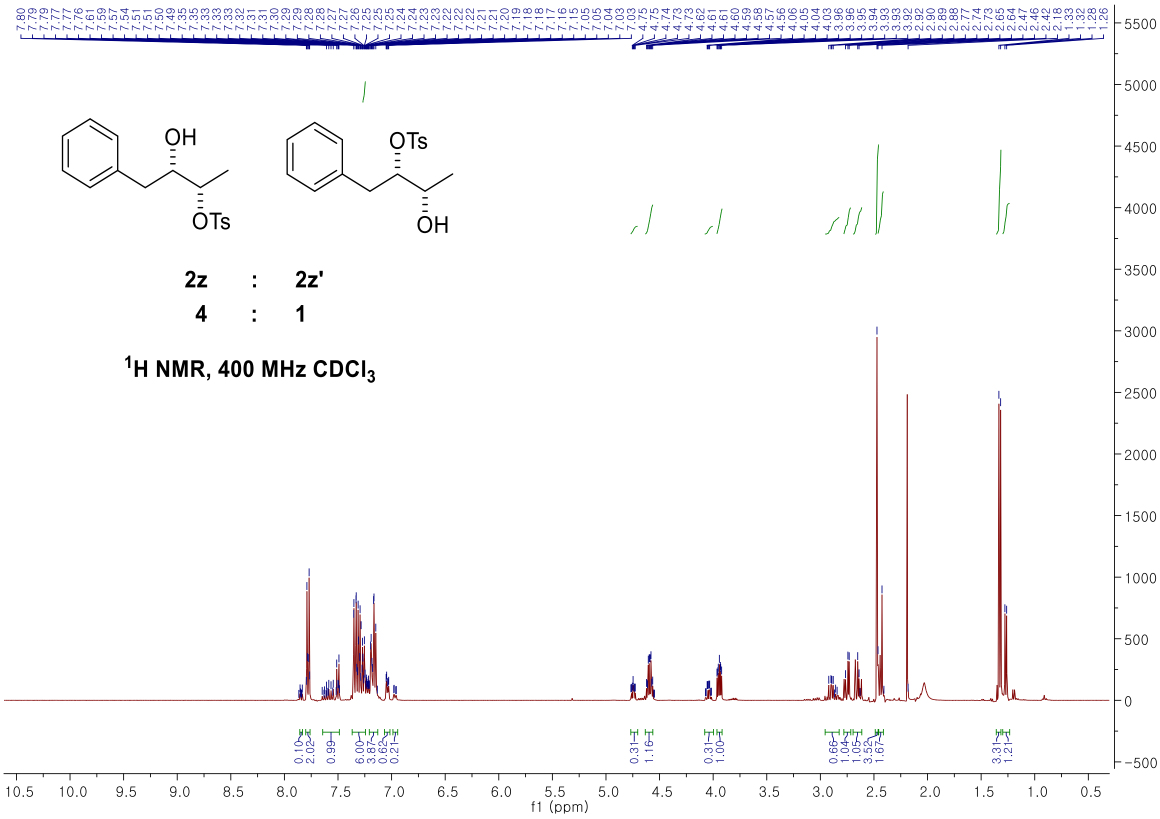
2y

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



2y

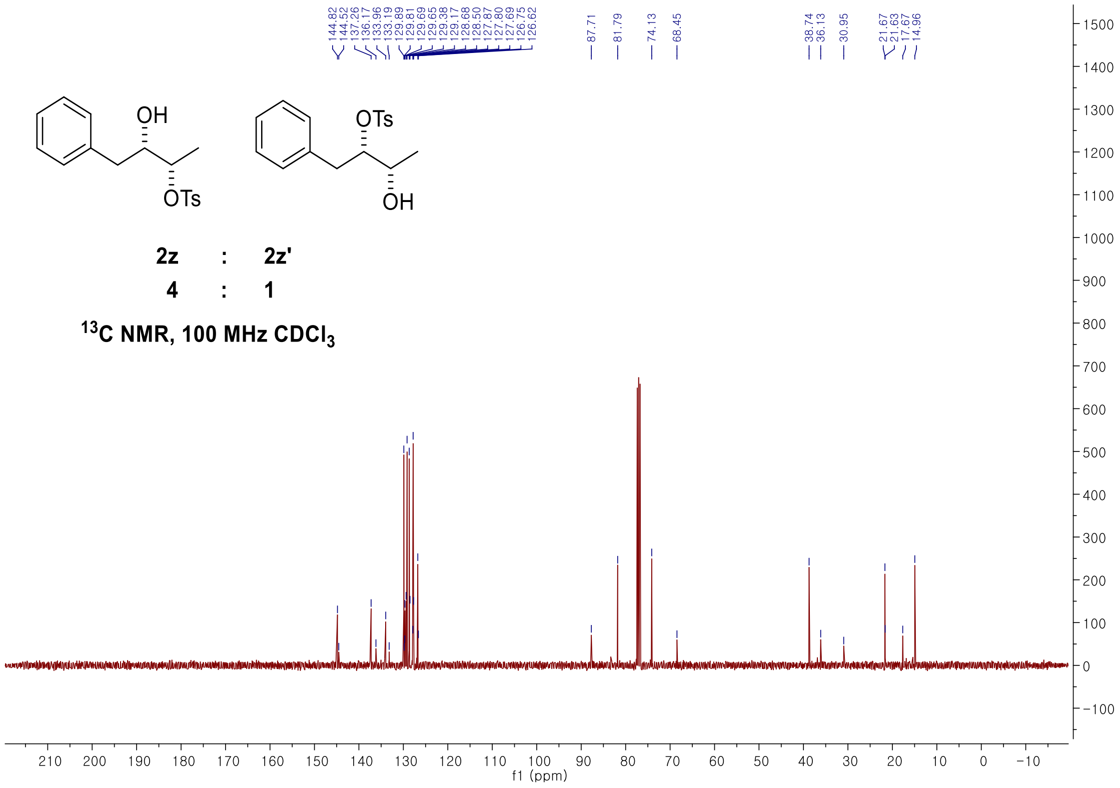
^{13}C NMR, 100 MHz, $(CD_3)_2SO$



2z : **2z'**

4 : **1**

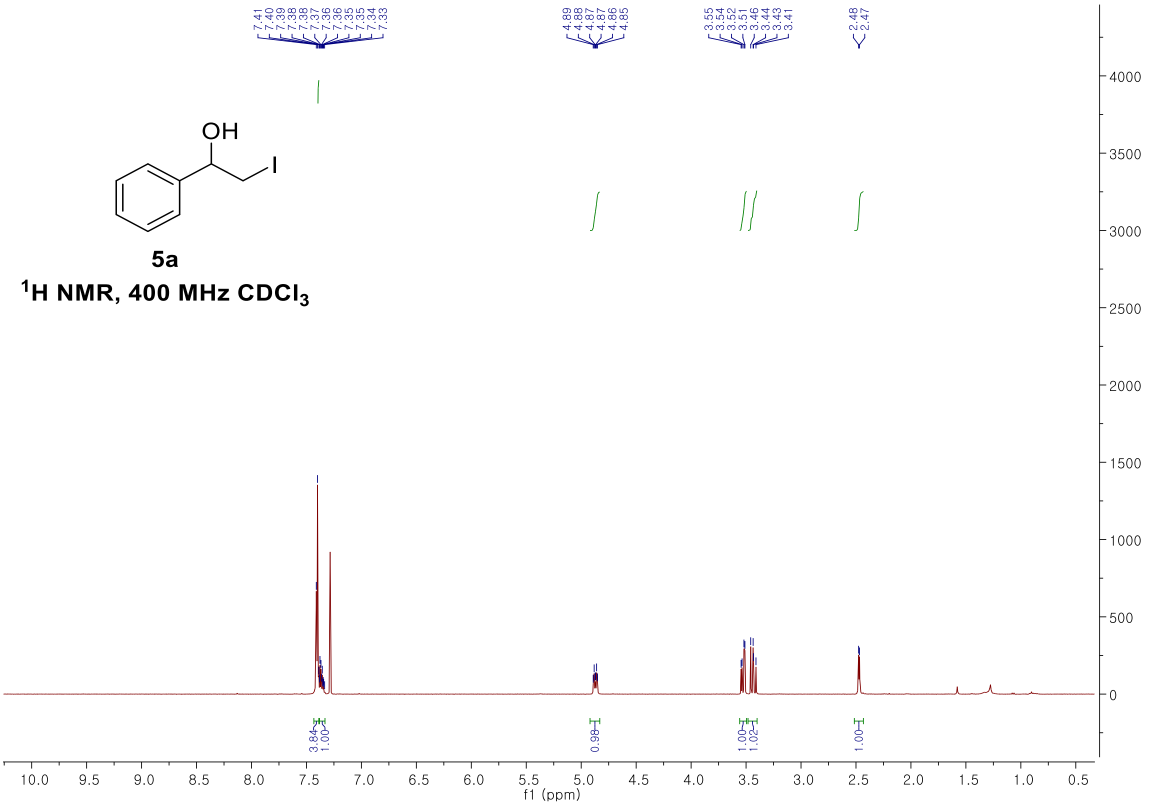
^{1}H NMR, 400 MHz CDCl$_3$

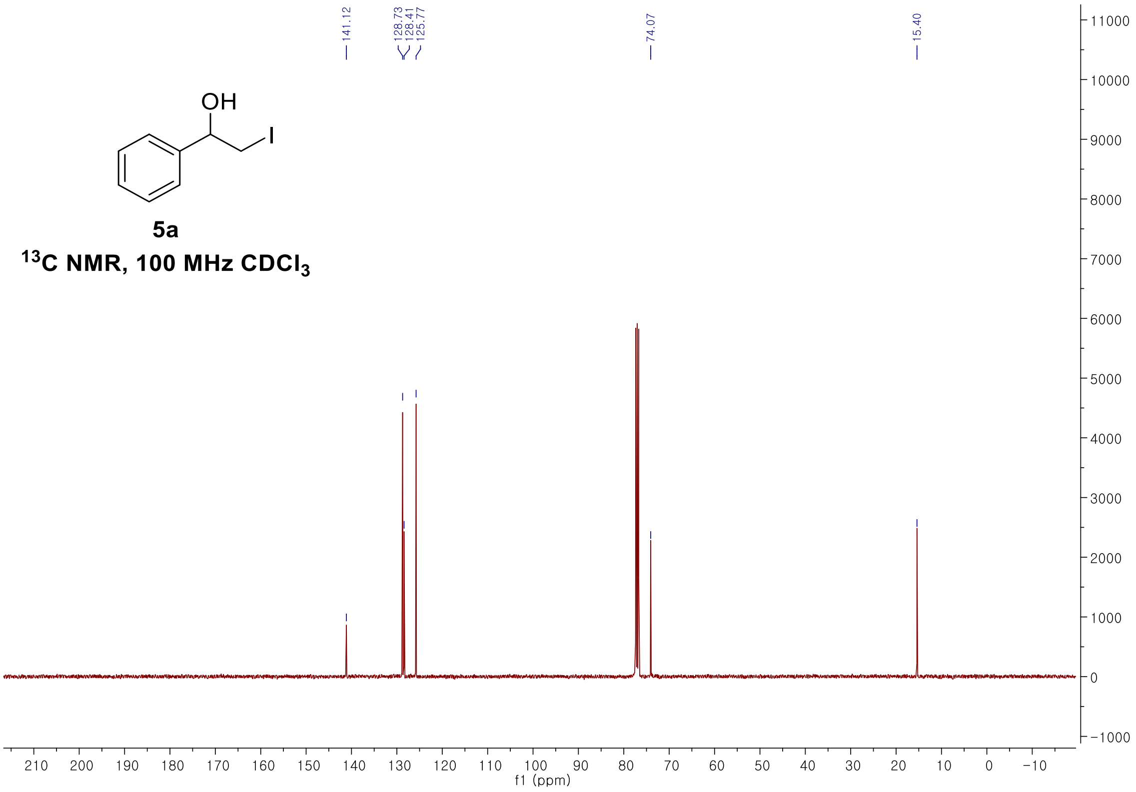


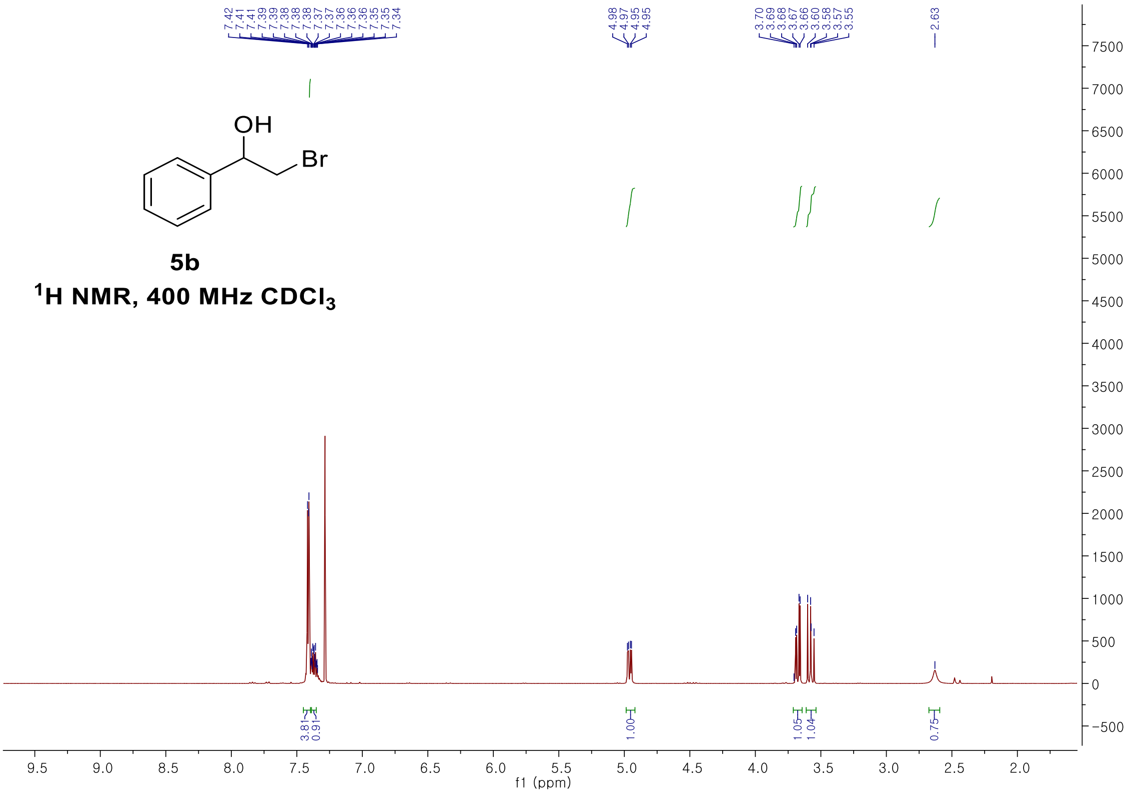
2z : **2z'**

4 : **1**

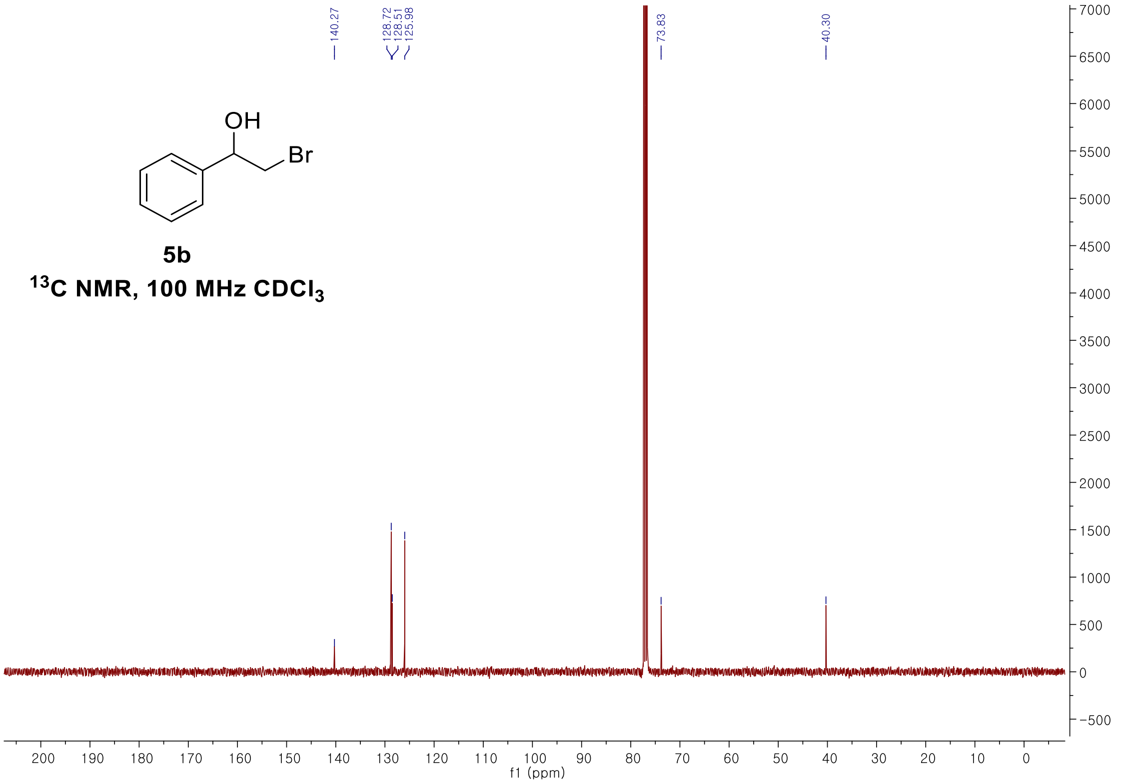
^{13}C NMR, 100 MHz CDCl$_3$


7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.33
4.89
4.88
4.87
4.87
4.86
4.85
3.55
3.54
3.52
3.51
3.46
3.44
3.43
3.41
2.48
2.47
OH
I
5a
^{1}H NMR, 400 MHz CDCl$_3$
3.84
1.00
0.98
1.00
1.02
1.00
4000
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

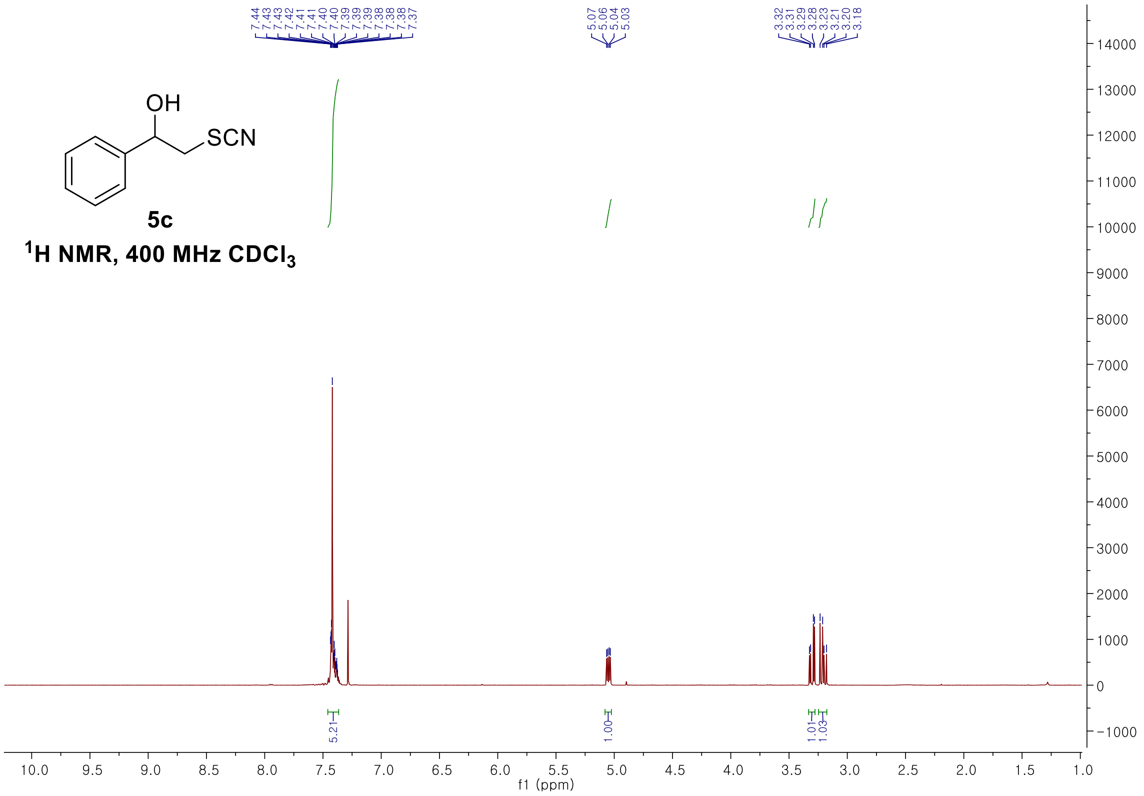

141.12
128.73
128.41
125.77
74.07
15.40
OH
I
5a
^{13}C NMR, 100 MHz CDCl$_3$
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

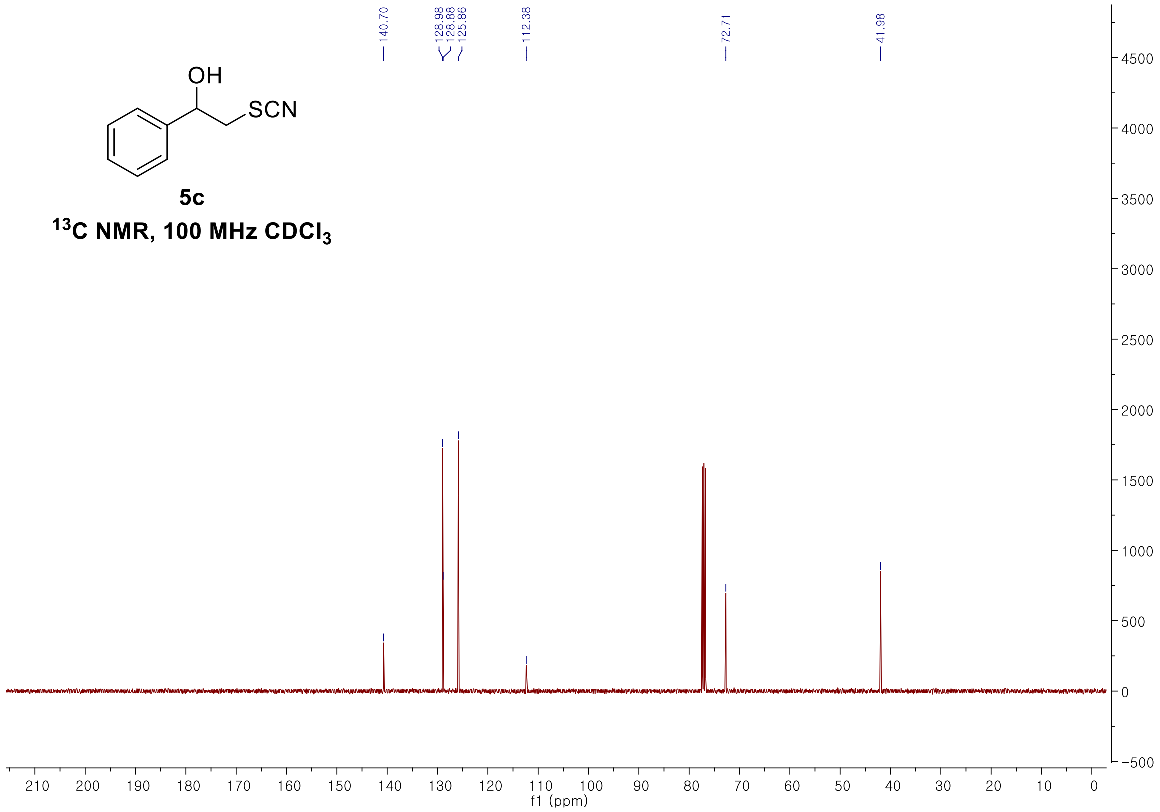

5b

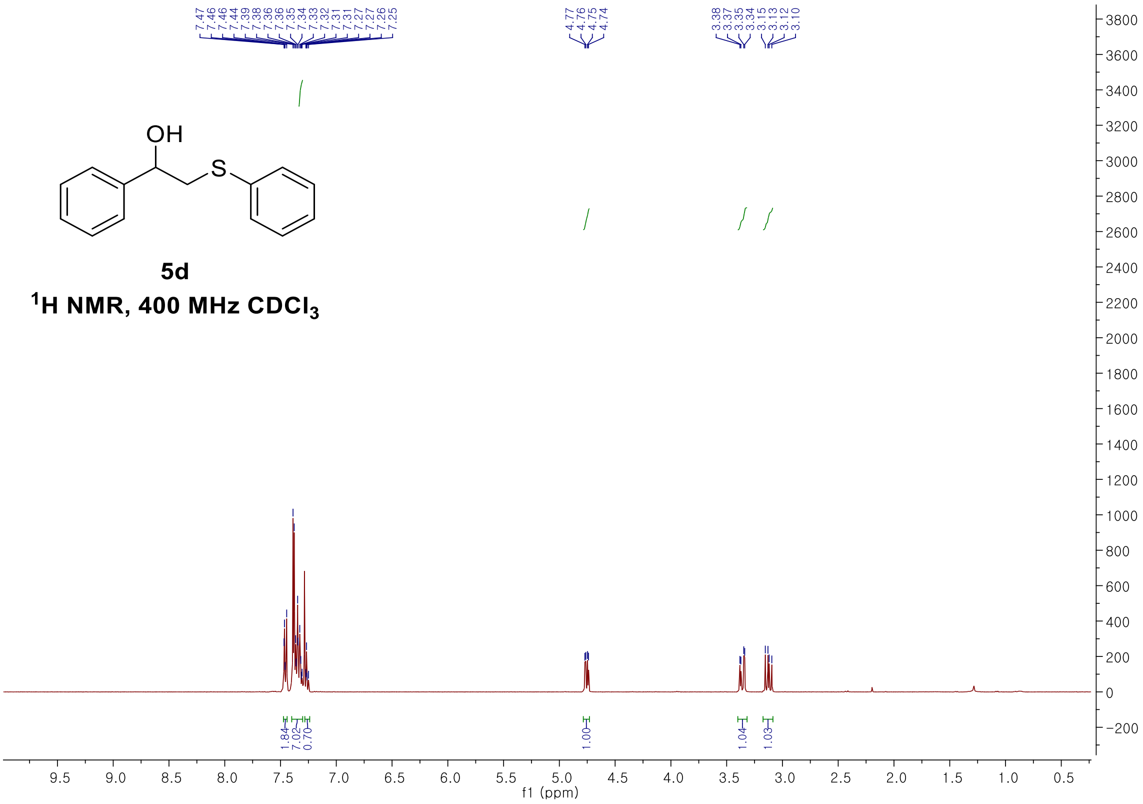
^{1}H NMR, 400 MHz CDCl$_3$


5b

^{13}C NMR, 100 MHz CDCl$_3$

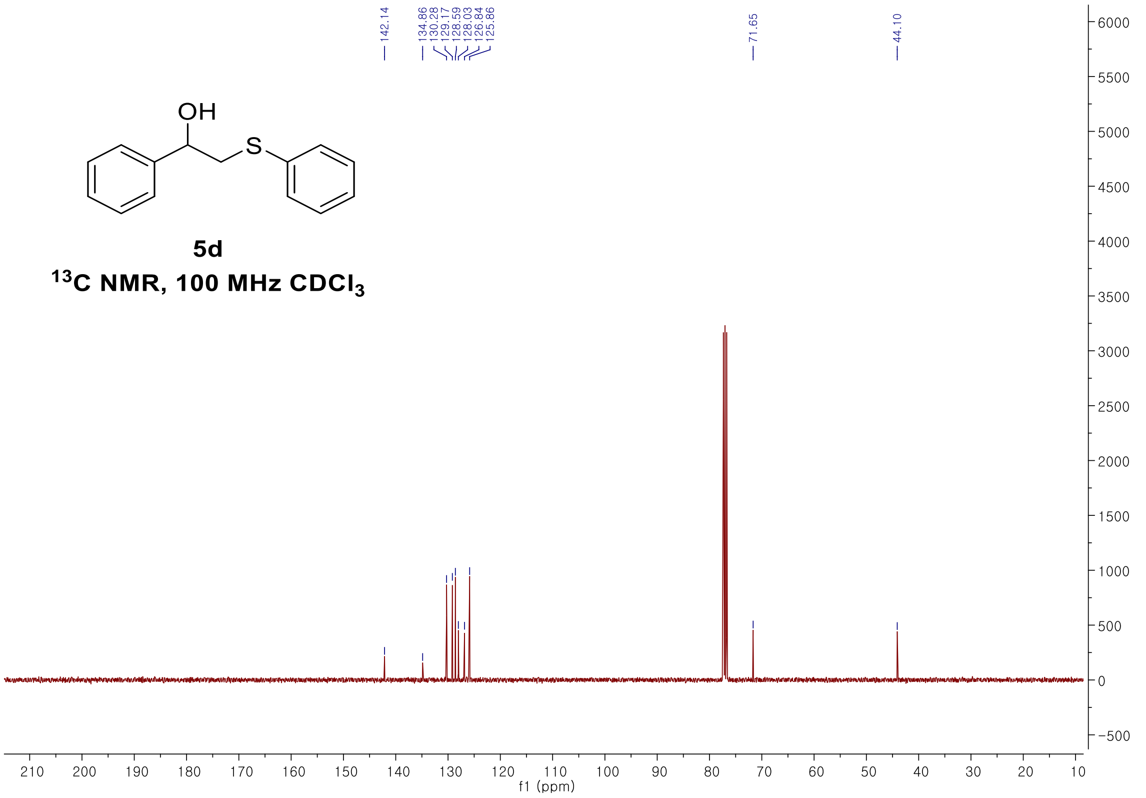

OH
SCN
5c
^{1}H NMR, 400 MHz CDCl$_3$
7.44 7.43 7.43 7.42 7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37
5.07 5.06 5.04 5.03
3.32 3.31 3.29 3.28 3.23 3.21 3.20 3.18
5.21
1.00
1.01
1.03
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000


OH
SCN
5c
^{13}C NMR, 100 MHz CDCl$_3$
140.70
128.98 128.88 125.86
112.38
72.71
41.98
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500



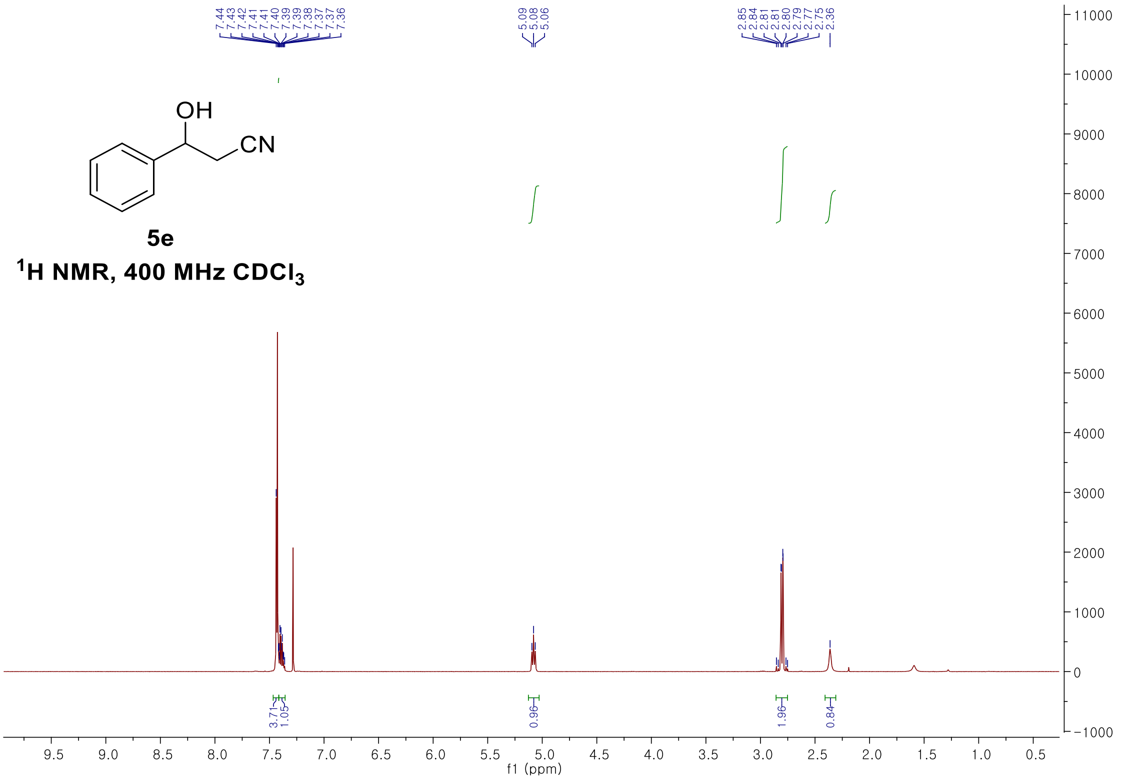
5d

^{1}H NMR, 400 MHz CDCl$_3$

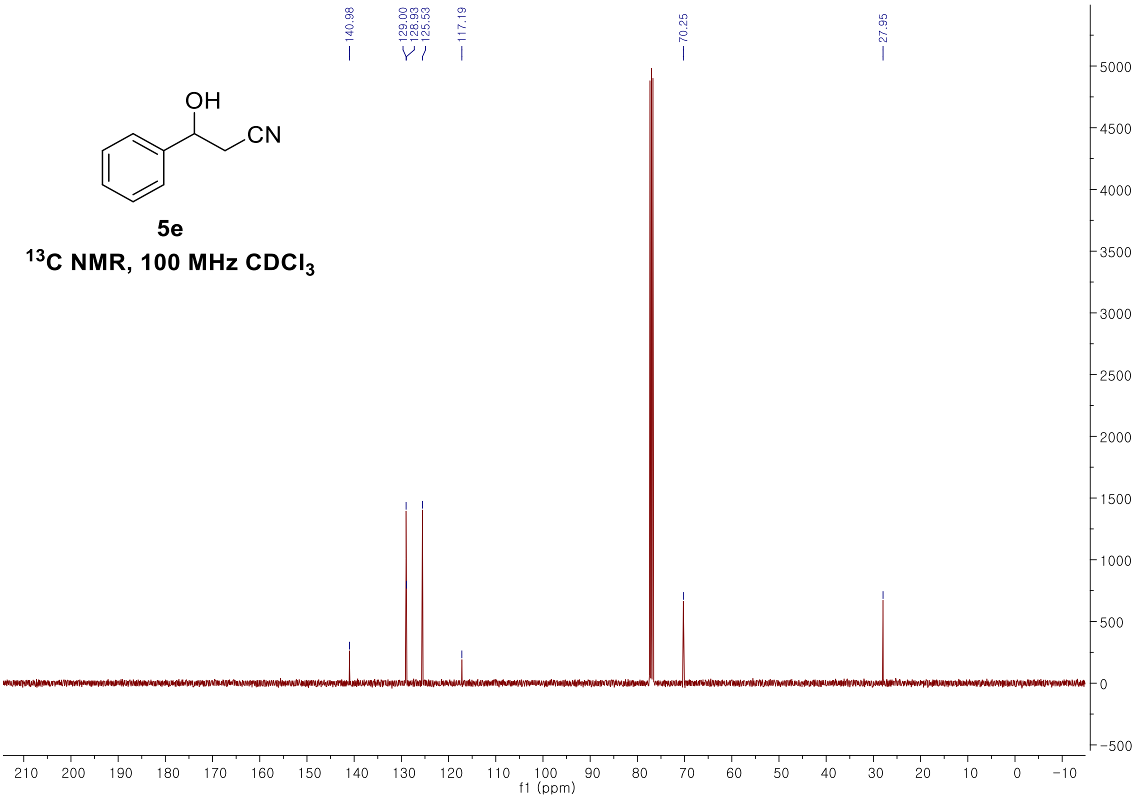


5d

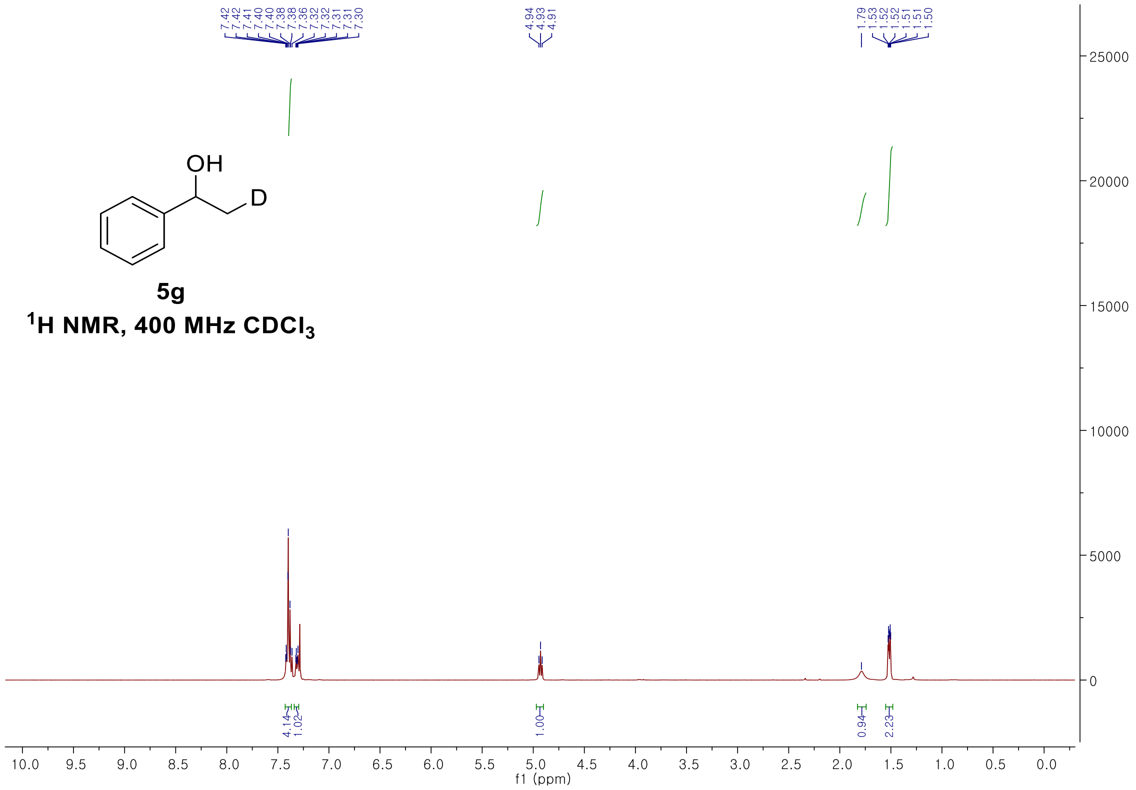
^{13}C NMR, 100 MHz CDCl$_3$

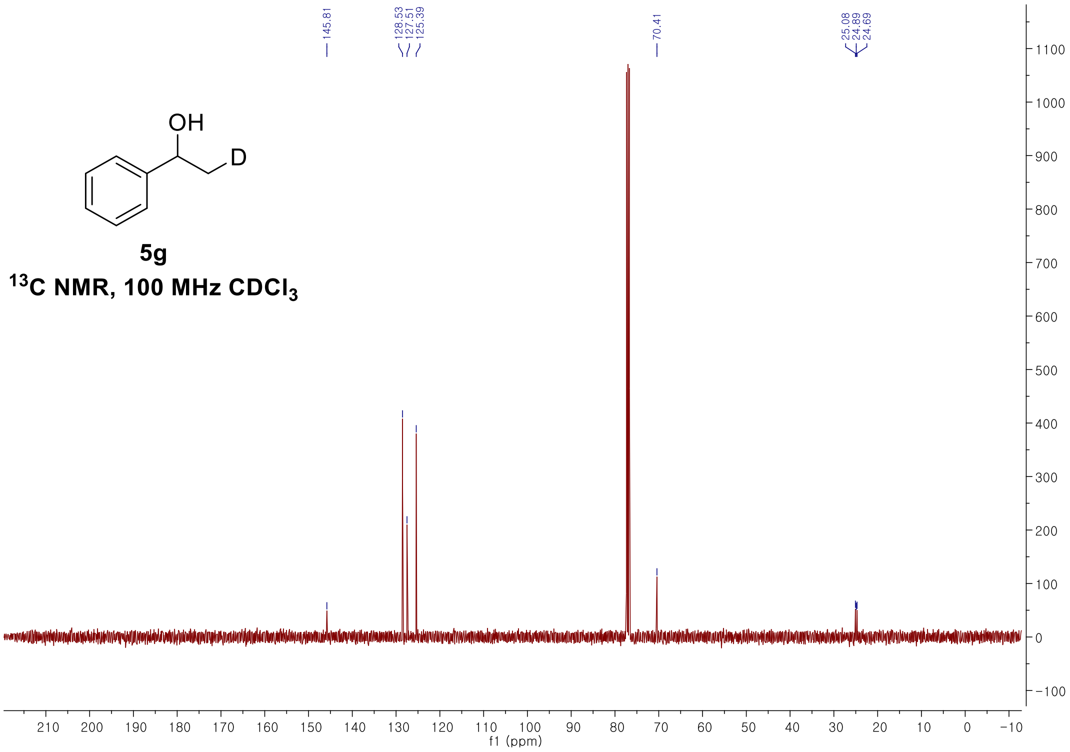

5e

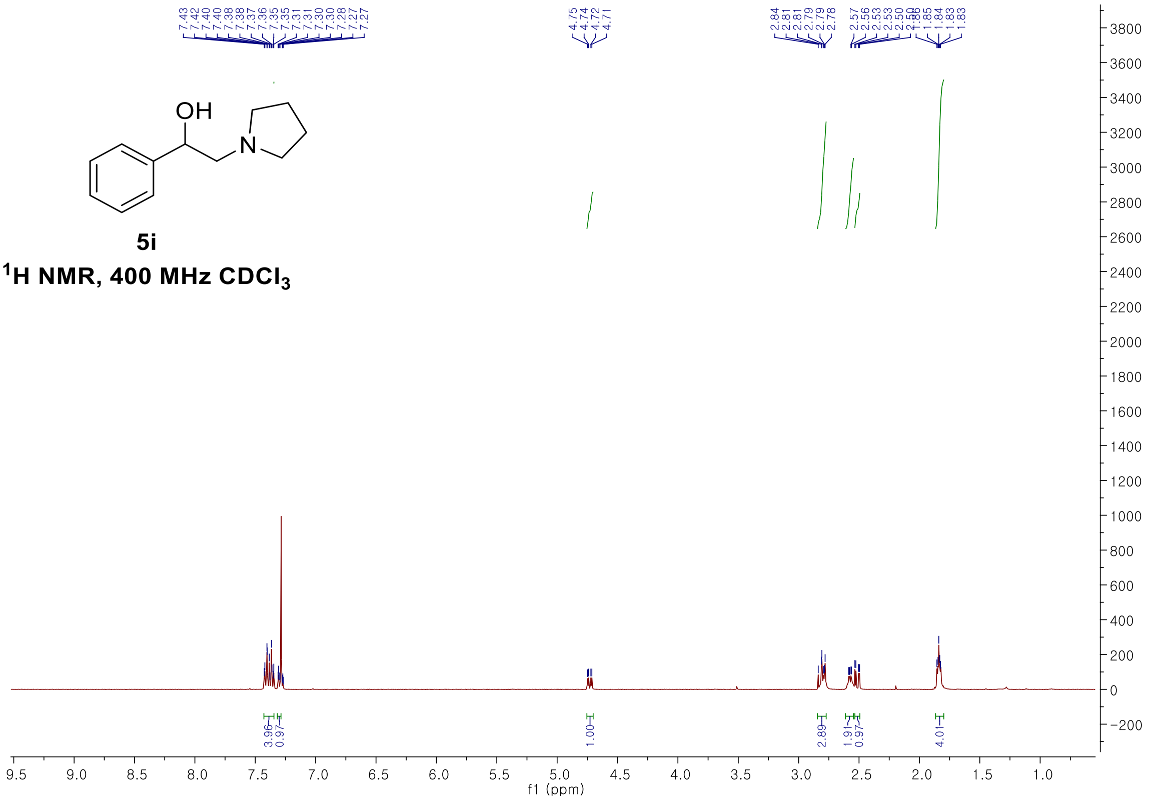
^{1}H NMR, 400 MHz $CDCl_3$


5e

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

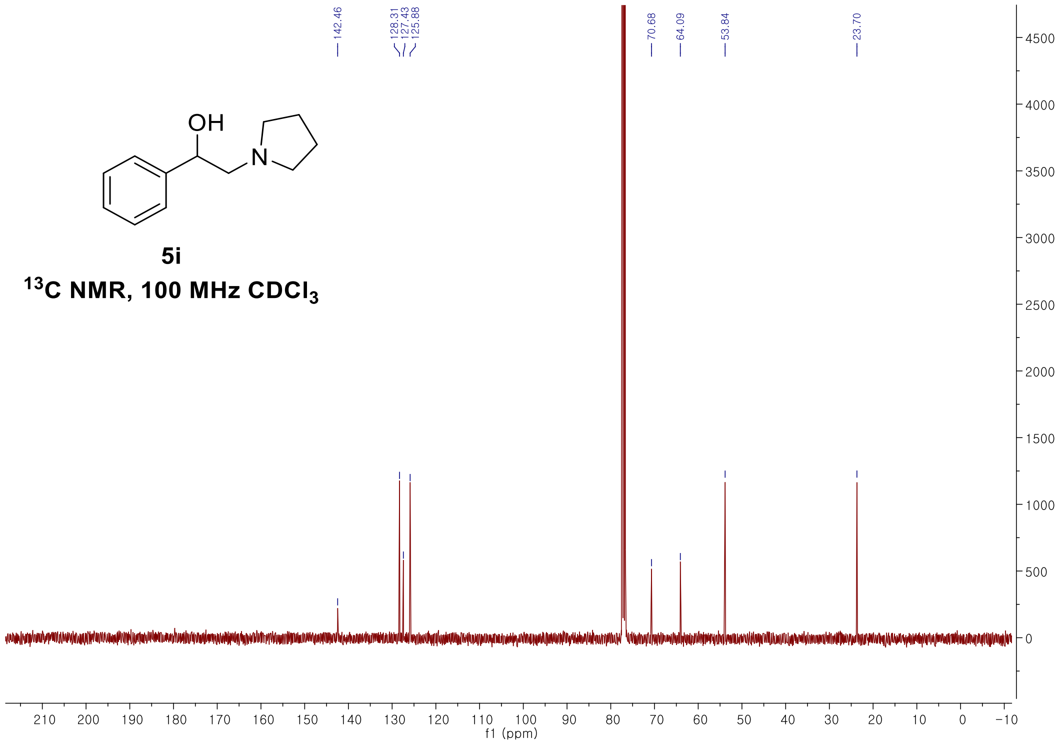

7.42
7.42
7.41
7.40
7.40
7.38
7.36
7.32
7.32
7.31
7.31
7.30
4.94
4.93
4.91
1.79
1.53
1.52
1.52
1.51
1.51
1.50
OH
D
5g
^{1}H NMR, 400 MHz CDCl$_3$
25000
20000
15000
10000
5000
0
4.14
1.02
1.00
0.94
2.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.81
128.53
127.51
125.39
70.41
25.08
24.89
24.69
OH
D
5g
^{13}C NMR, 100 MHz CDCl$_3$
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



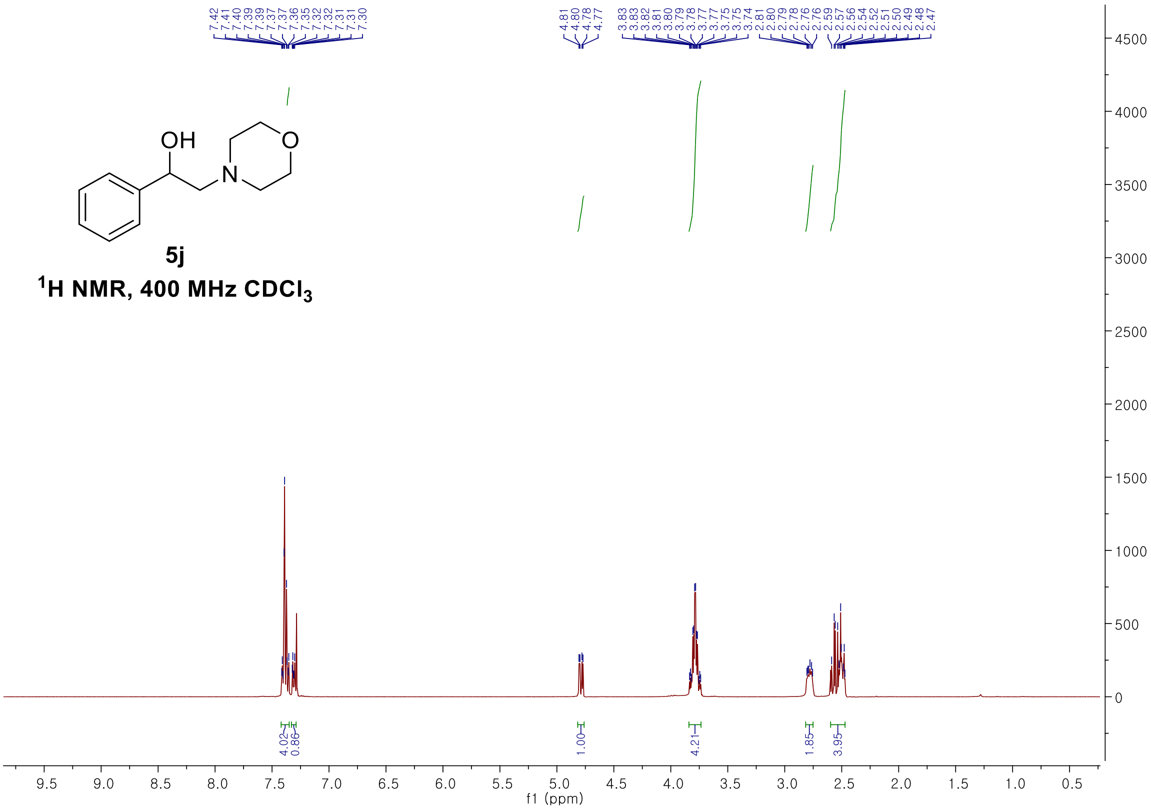
5i

^{1}H NMR, 400 MHz CDCl$_3$



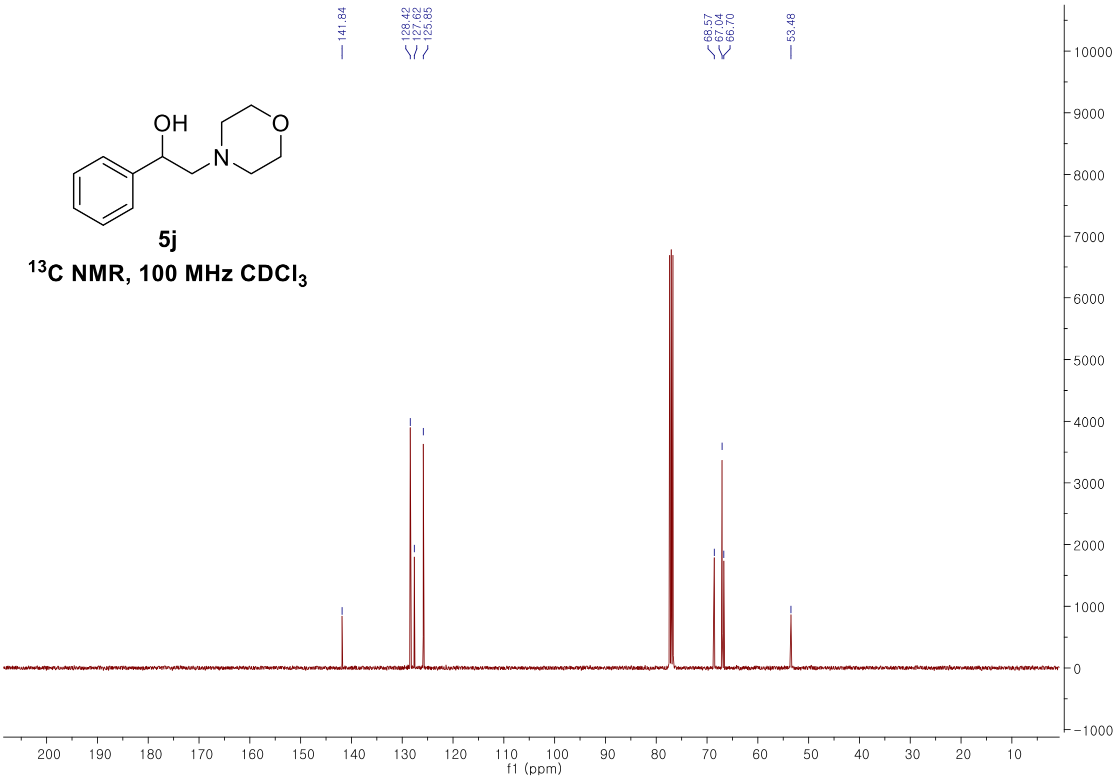
5i

^{13}C NMR, 100 MHz CDCl$_3$



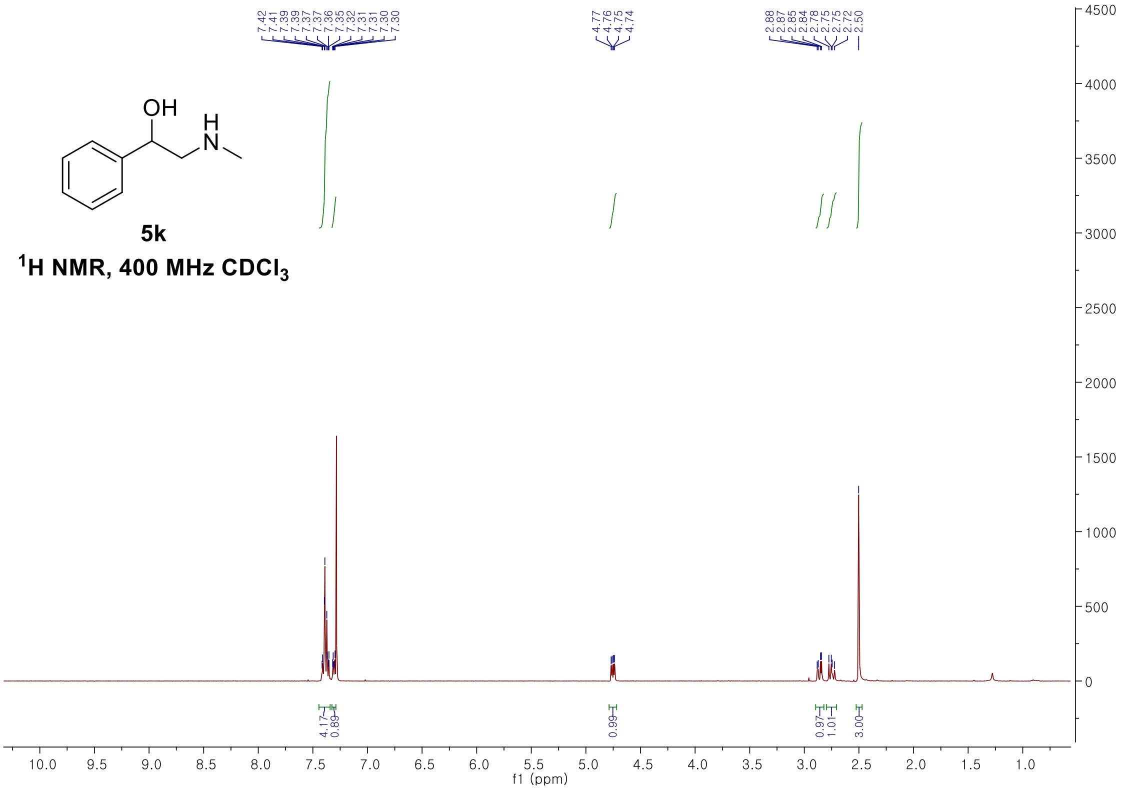
5j

^{1}H NMR, 400 MHz CDCl$_3$



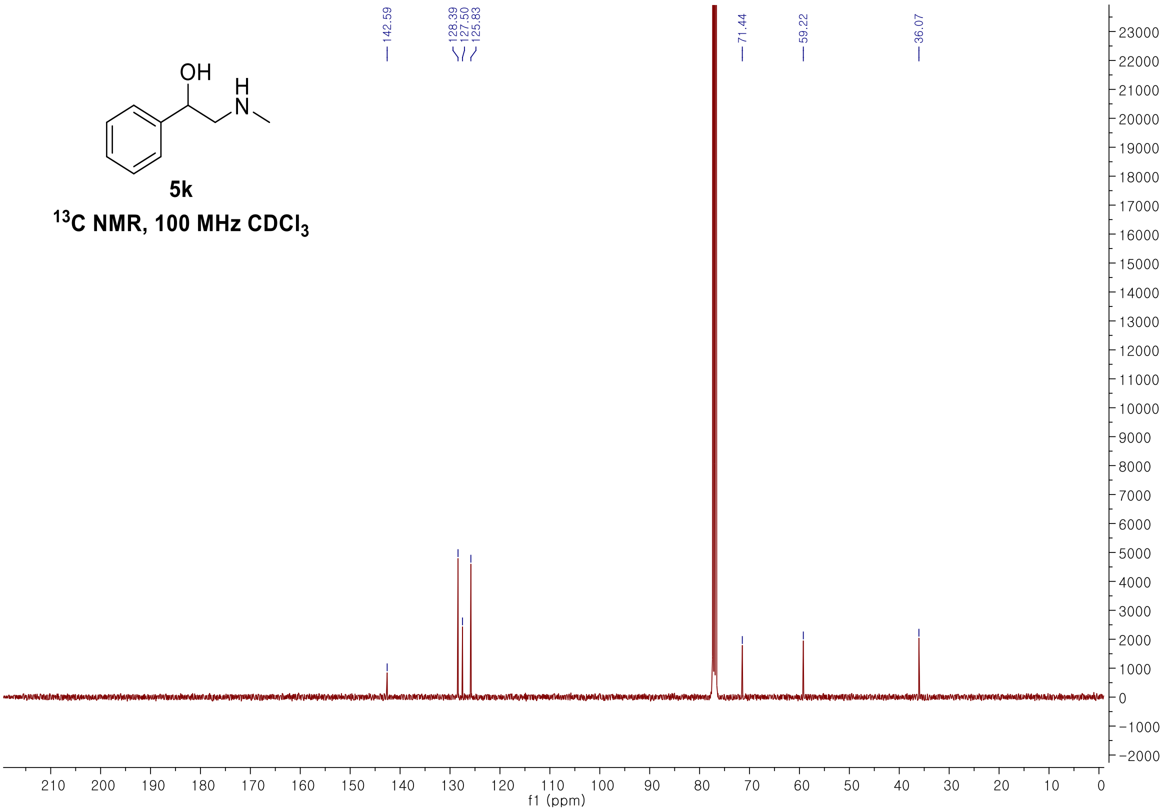
5j

^{13}C NMR, 100 MHz CDCl$_3$



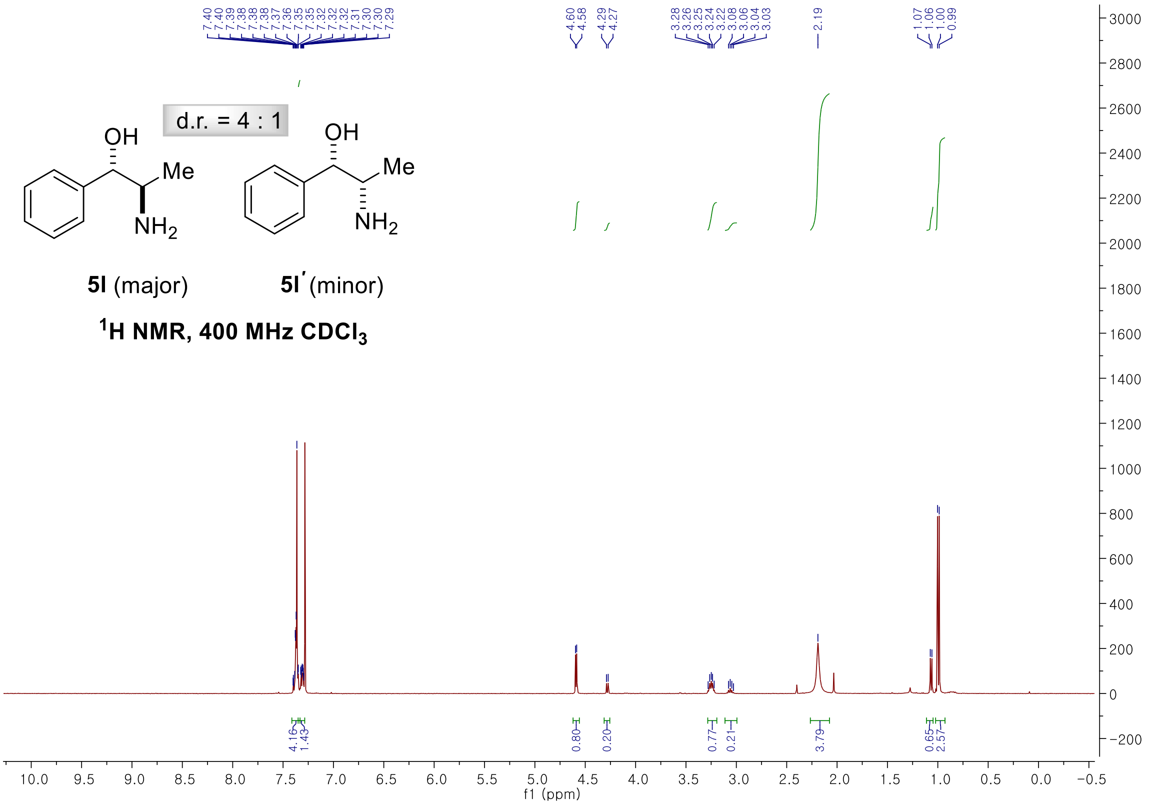
5k

^{1}H NMR, 400 MHz CDCl$_3$



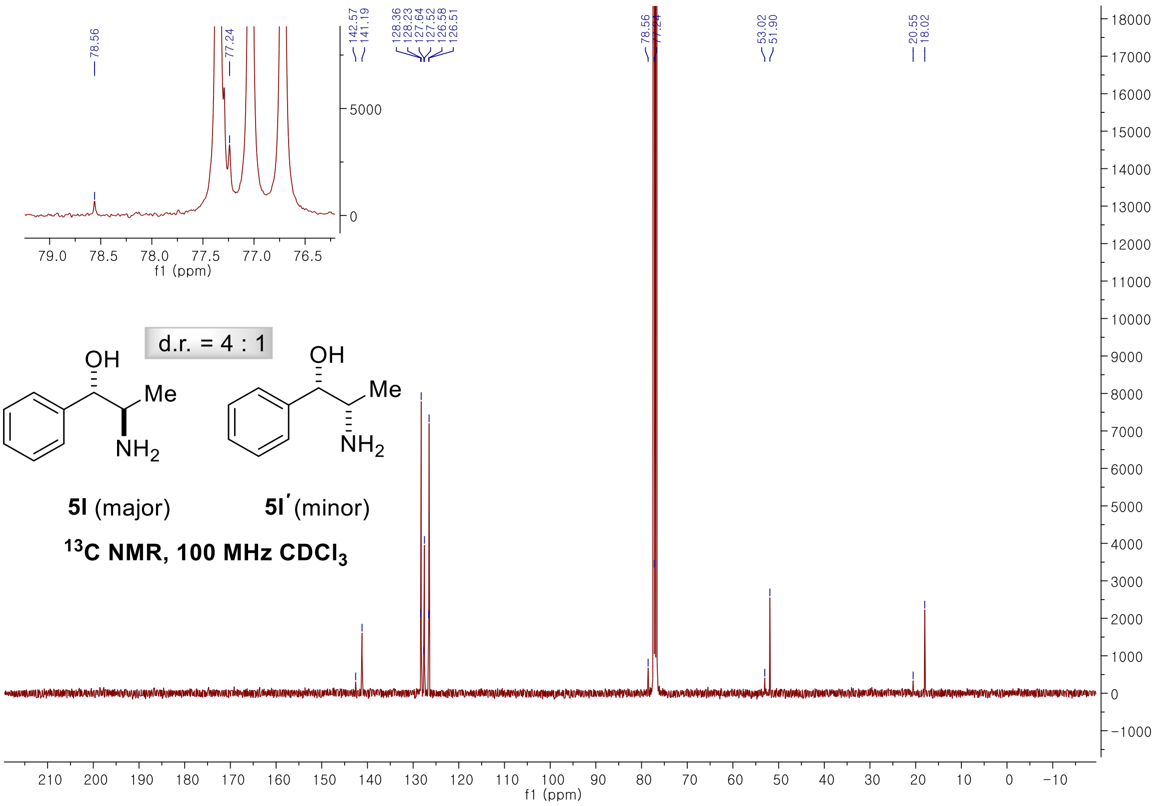
5k

^{13}C NMR, 100 MHz CDCl$_3$



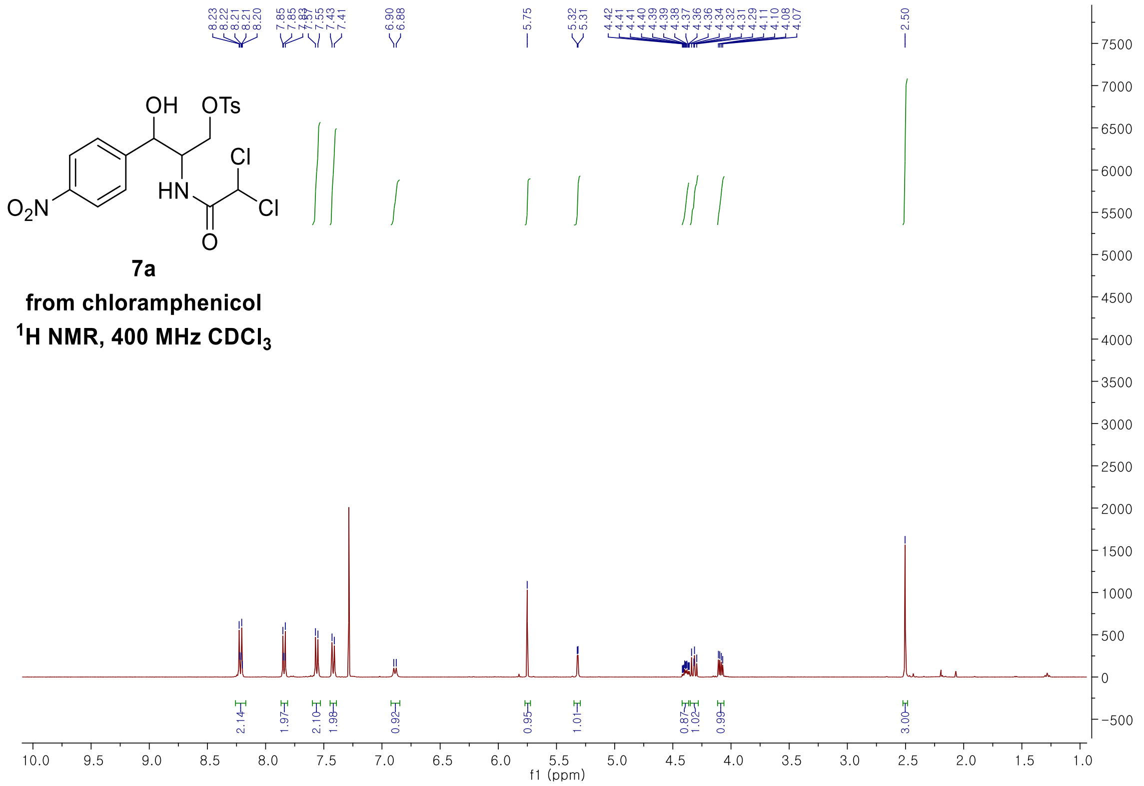
5l (major) **5l′** (minor)

^{1}H NMR, 400 MHz CDCl$_3$

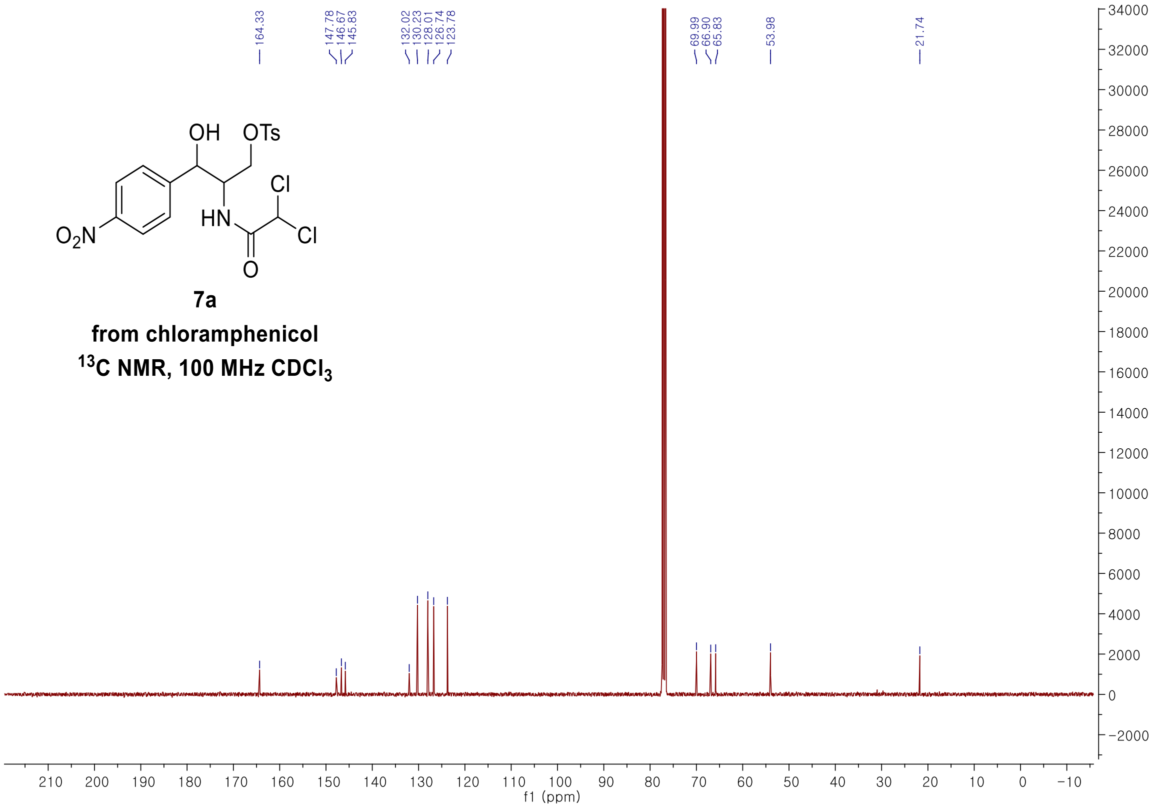


5l (major) **5l′** (minor)

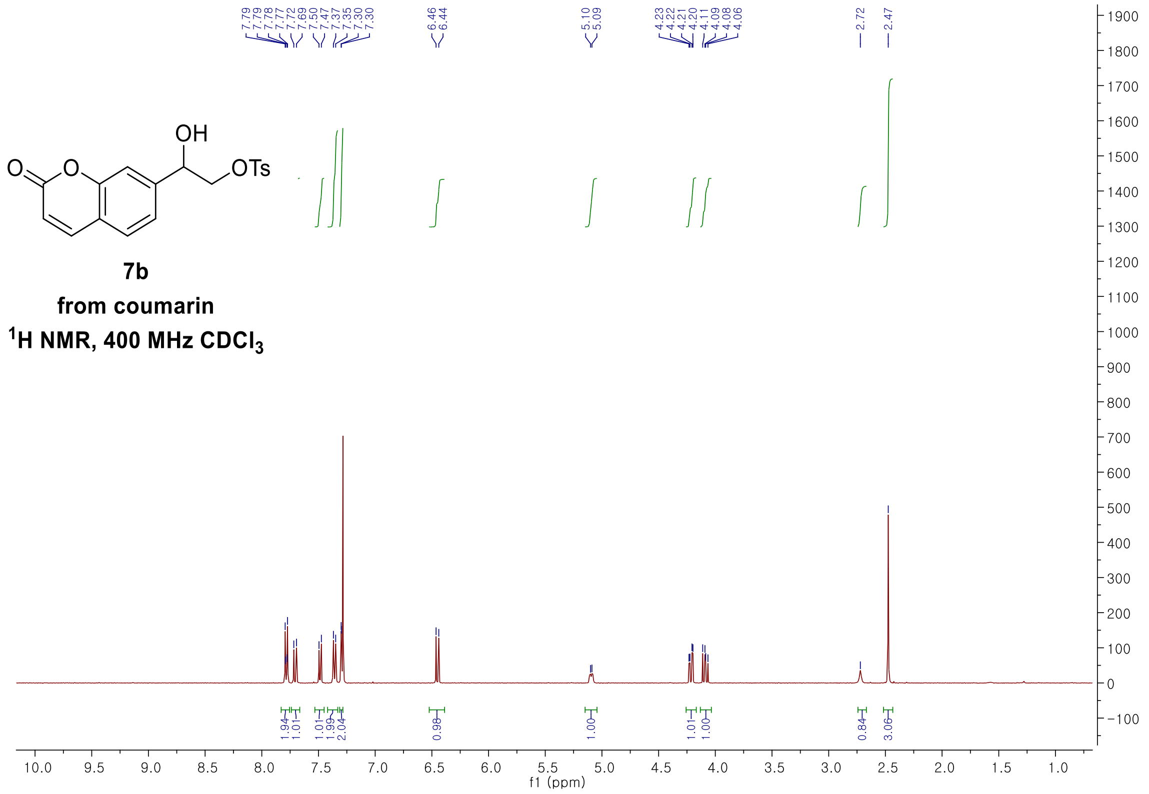
^{13}C NMR, 100 MHz CDCl$_3$



7a
from chloramphenicol
^{1}H NMR, 400 MHz $CDCl_3$



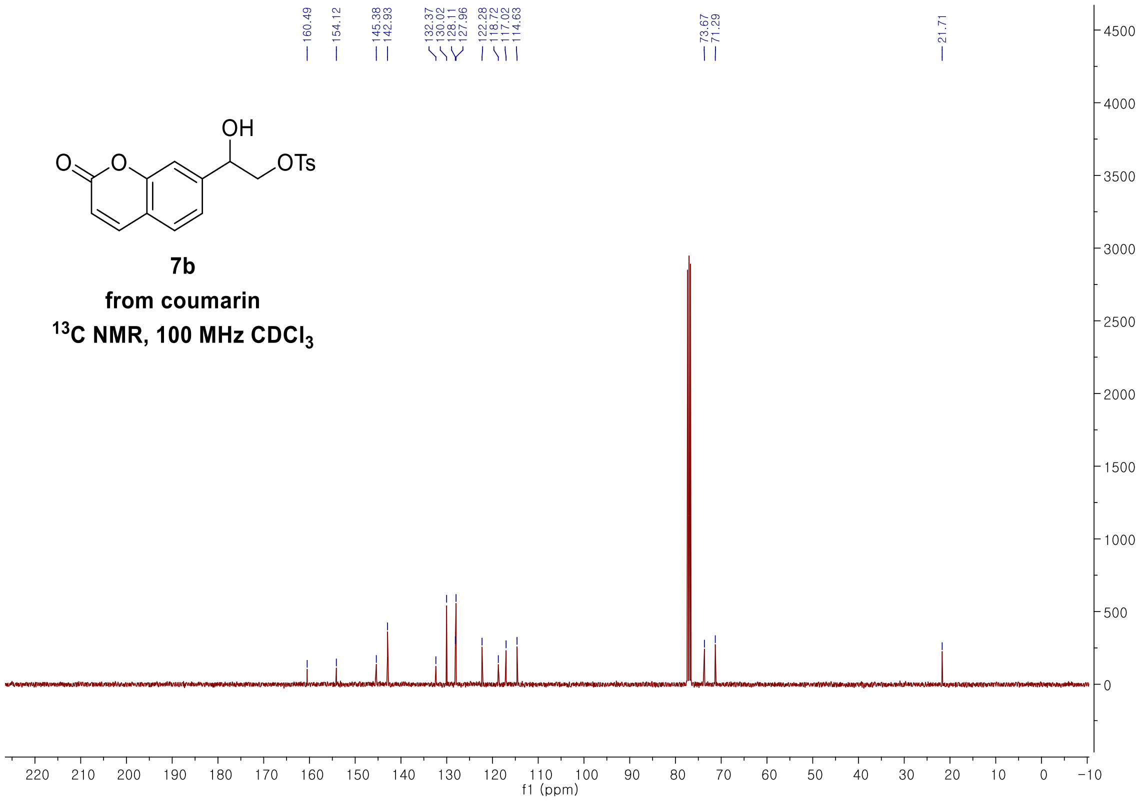
7a
from chloramphenicol
^{13}C NMR, 100 MHz $CDCl_3$



7b

from coumarin

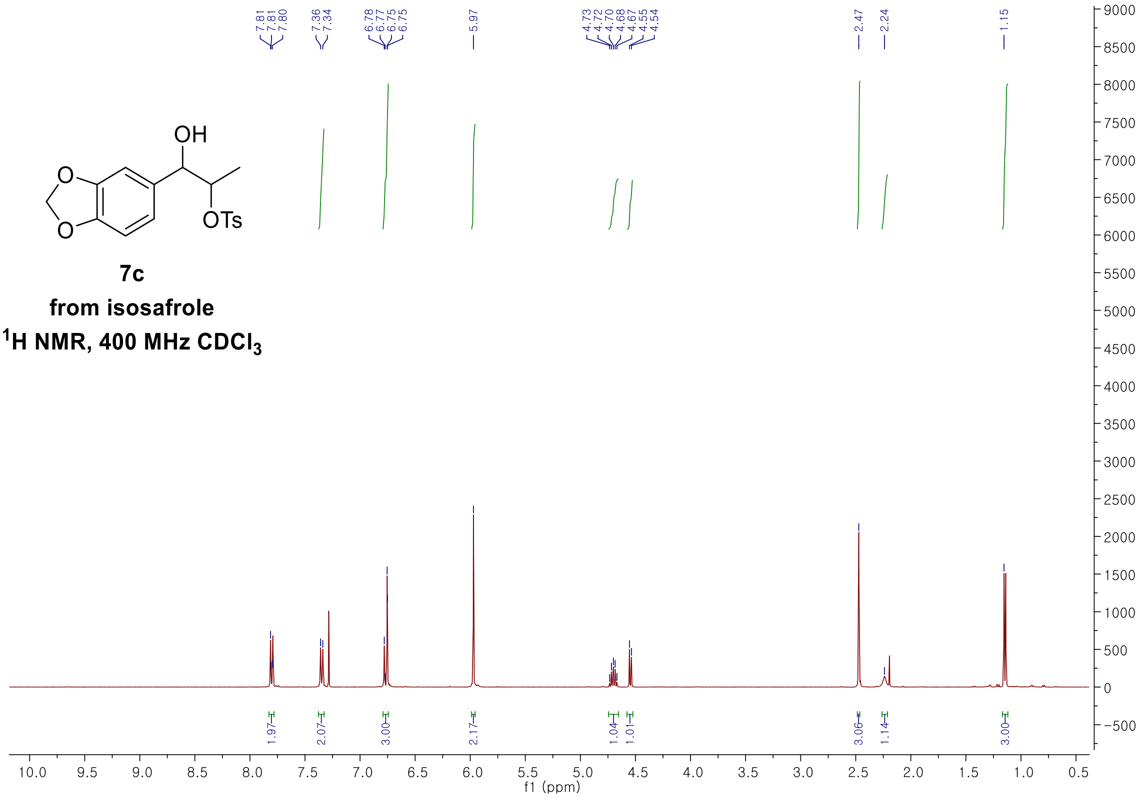
^{1}H NMR, 400 MHz CDCl$_3$



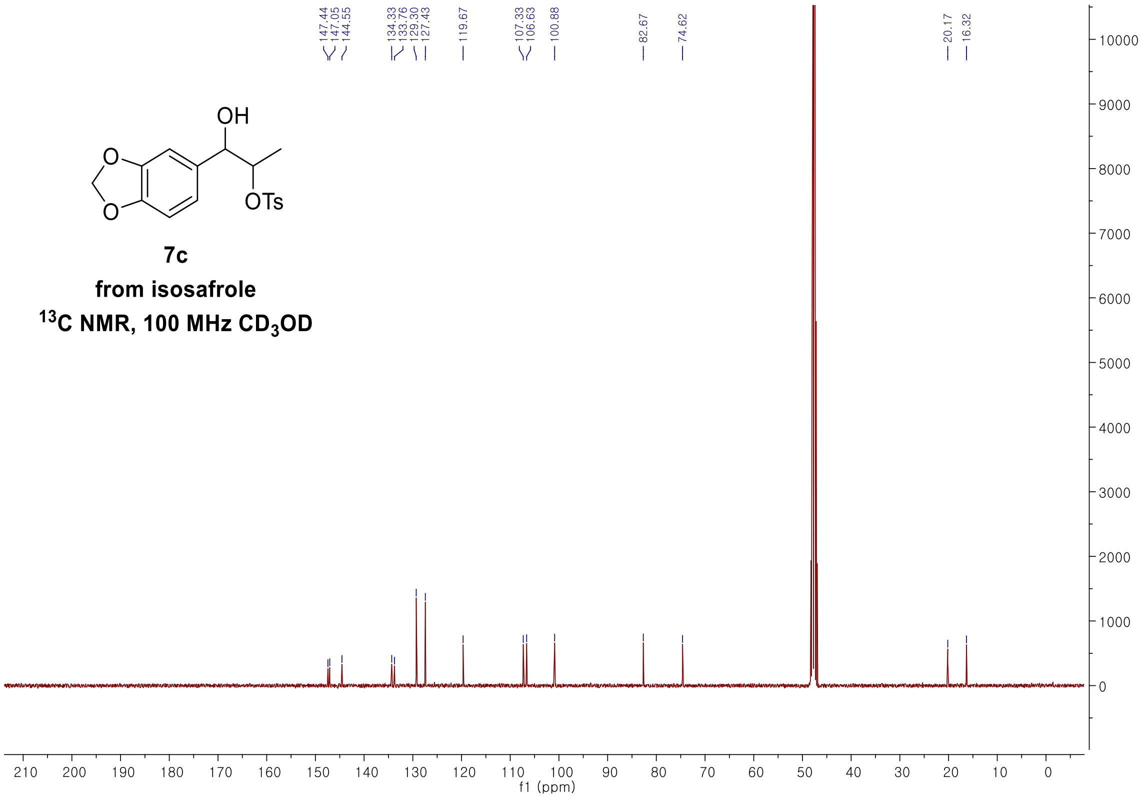
7b

from coumarin

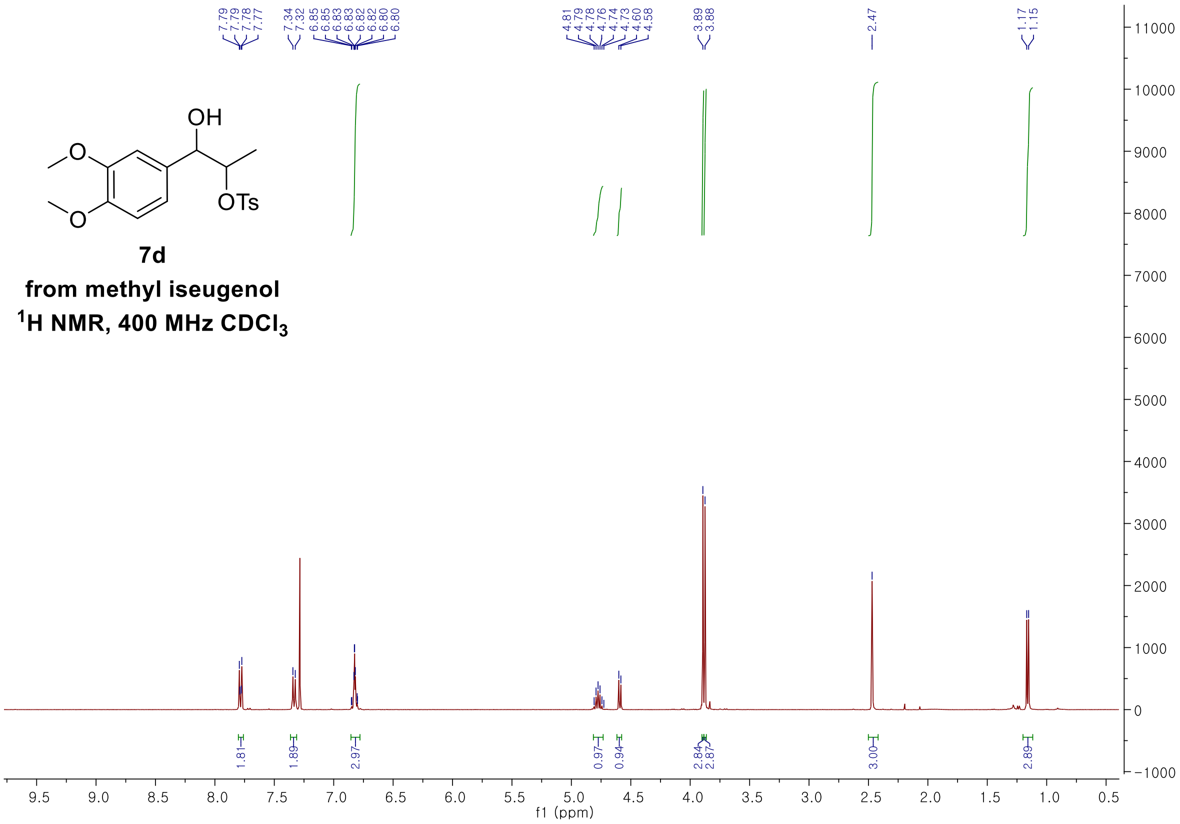
^{13}C NMR, 100 MHz CDCl$_3$



7c
from isosafrole
^{1}H NMR, 400 MHz $CDCl_3$



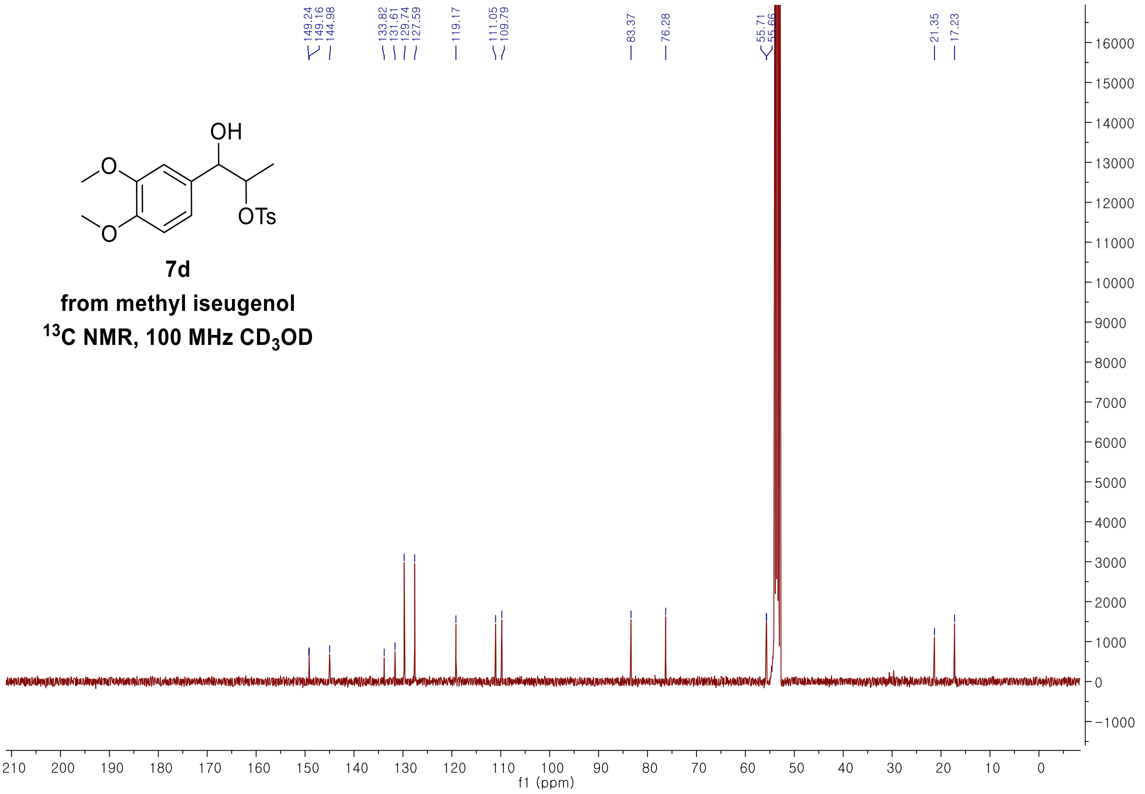
7c
from isosafrole
^{13}C NMR, 100 MHz CD_3OD



7d

from methyl iseugenol

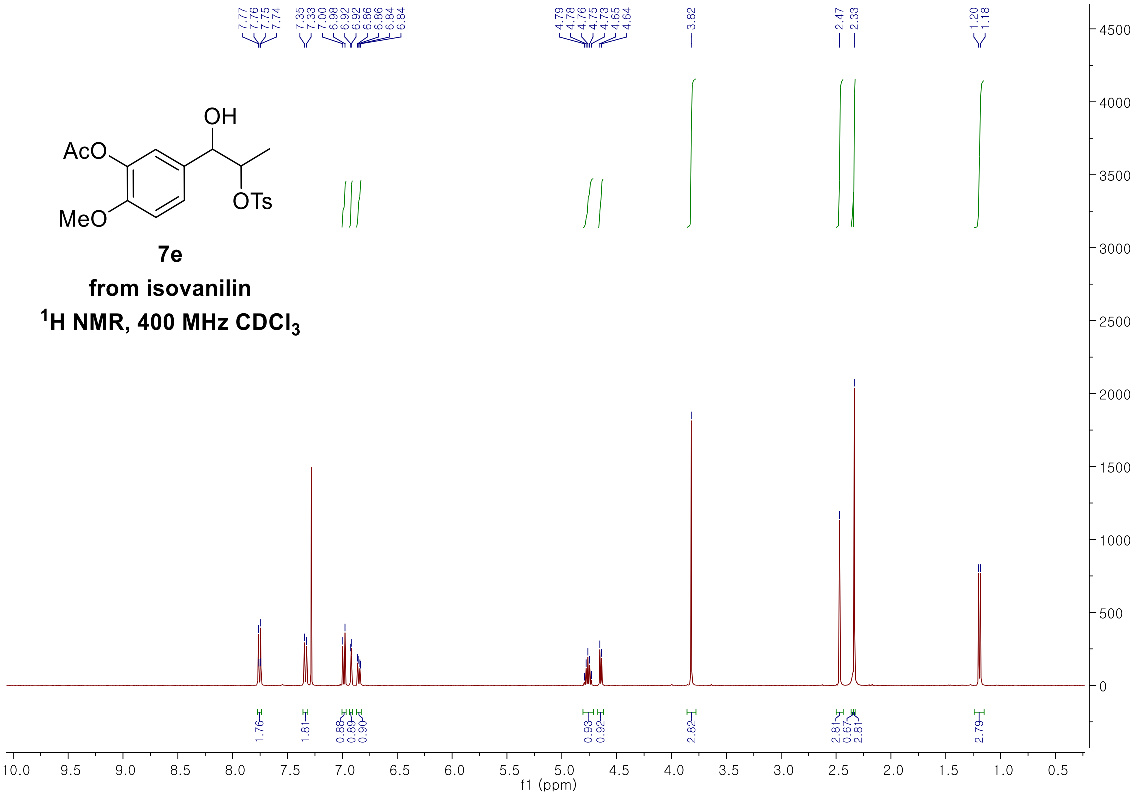
^{1}H NMR, 400 MHz $CDCl_3$

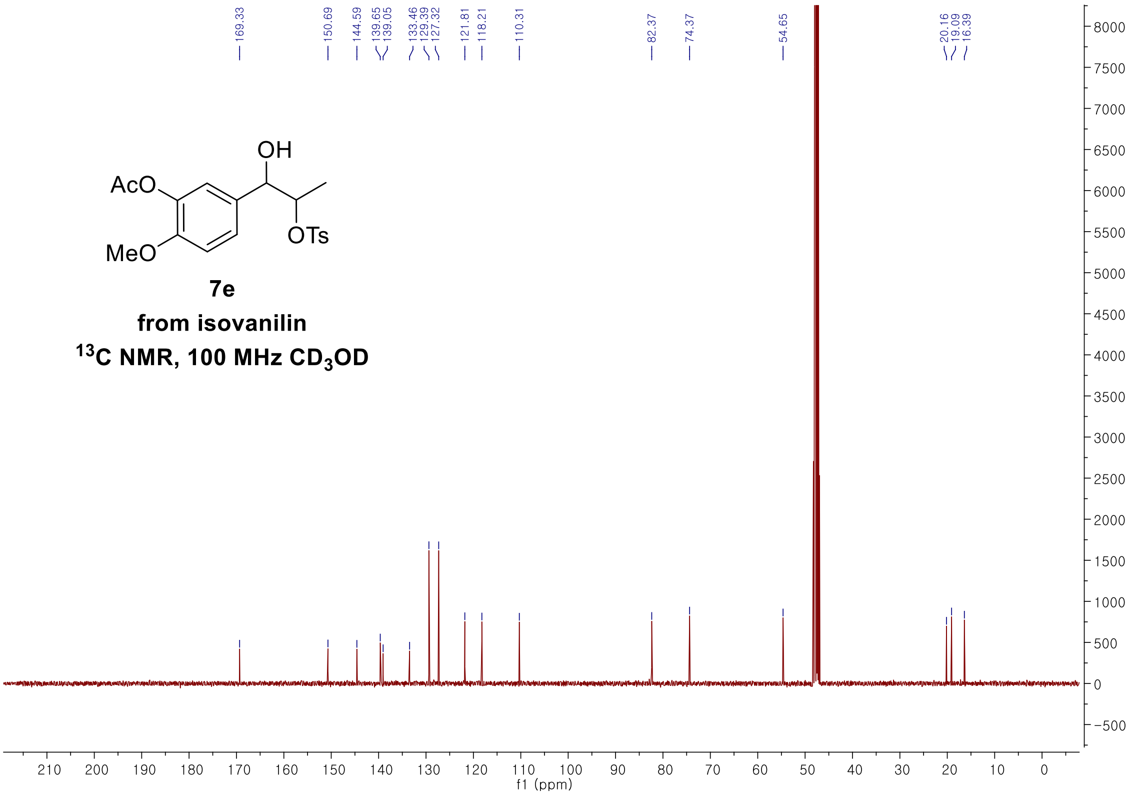


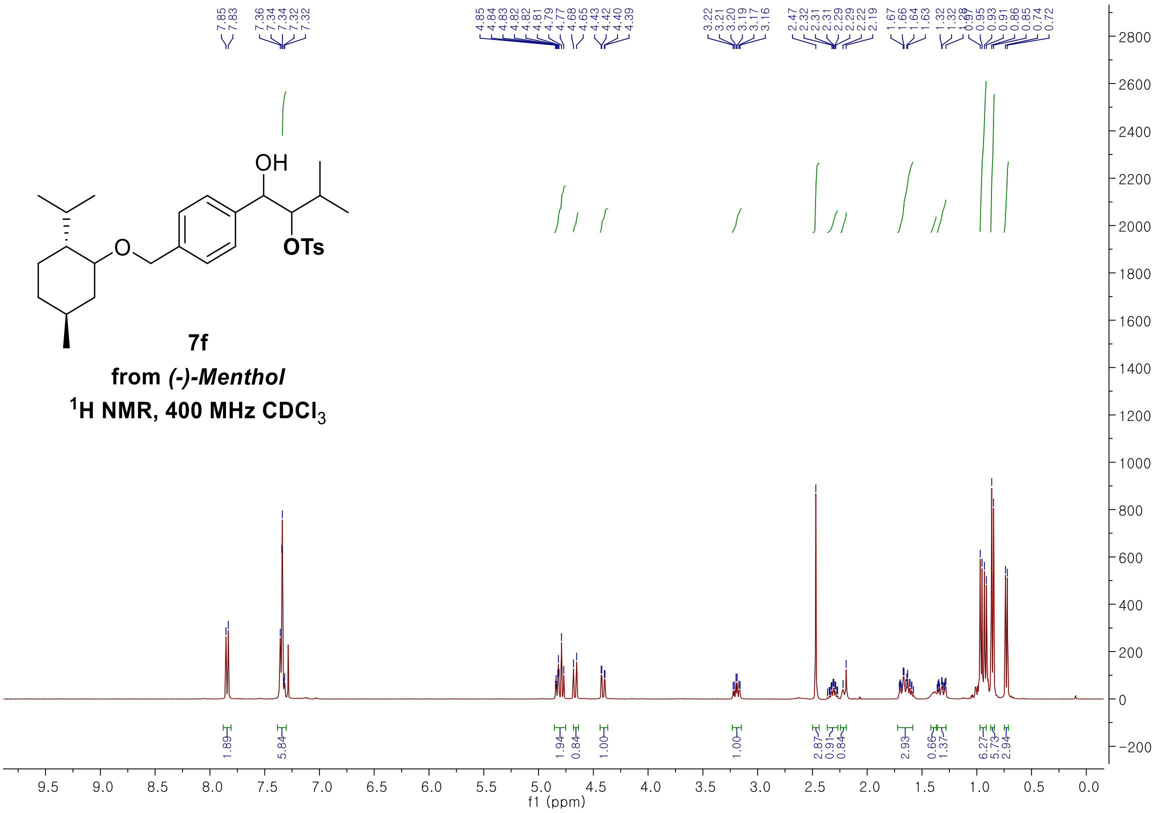
7d

from methyl iseugenol

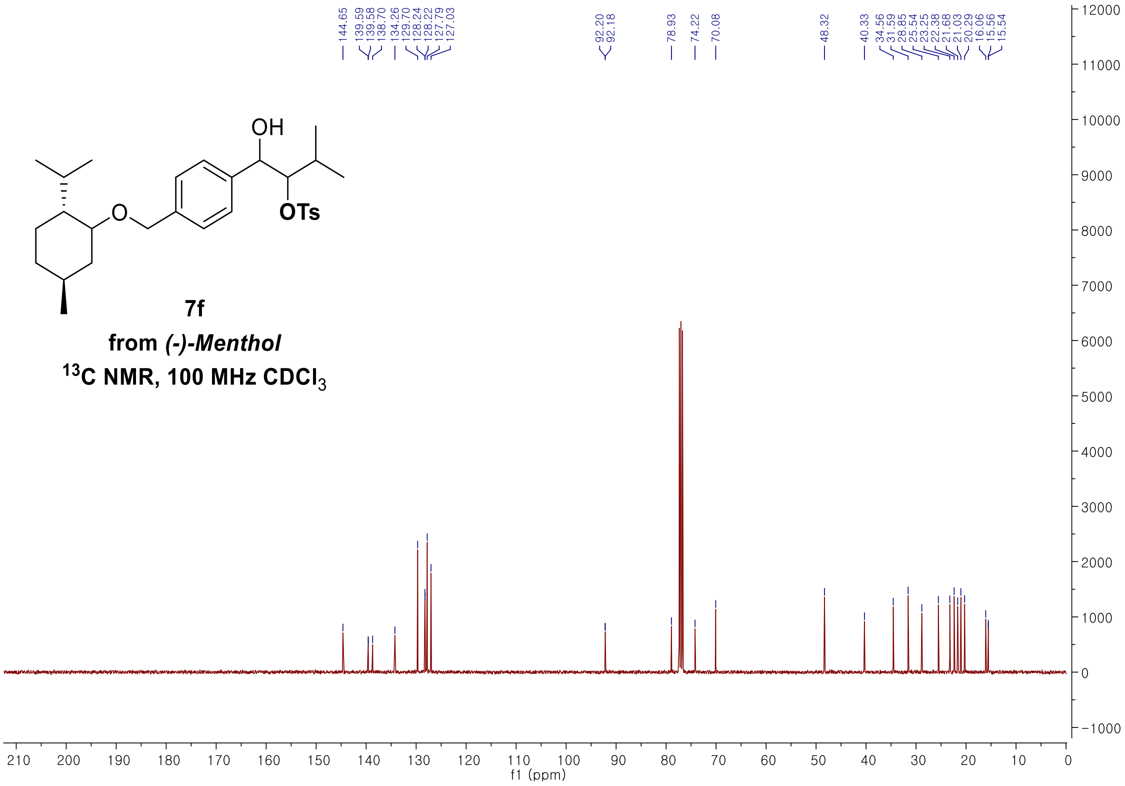
^{13}C NMR, 100 MHz CD_3OD


7.77
7.76
7.75
7.74
7.35
7.33
7.00
6.98
6.92
6.92
6.86
6.86
6.84
6.84
4.79
4.78
4.76
4.75
4.73
4.65
4.64
3.82
2.47
2.33
1.20
1.18
OH
AcO
OTs
MeO
7e
from isovanilin
^{1}H NMR, 400 MHz CDCl$_3$
1.76
1.81
0.88
0.89
0.90
0.93
0.92
2.82
2.81
0.67
2.81
2.79
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

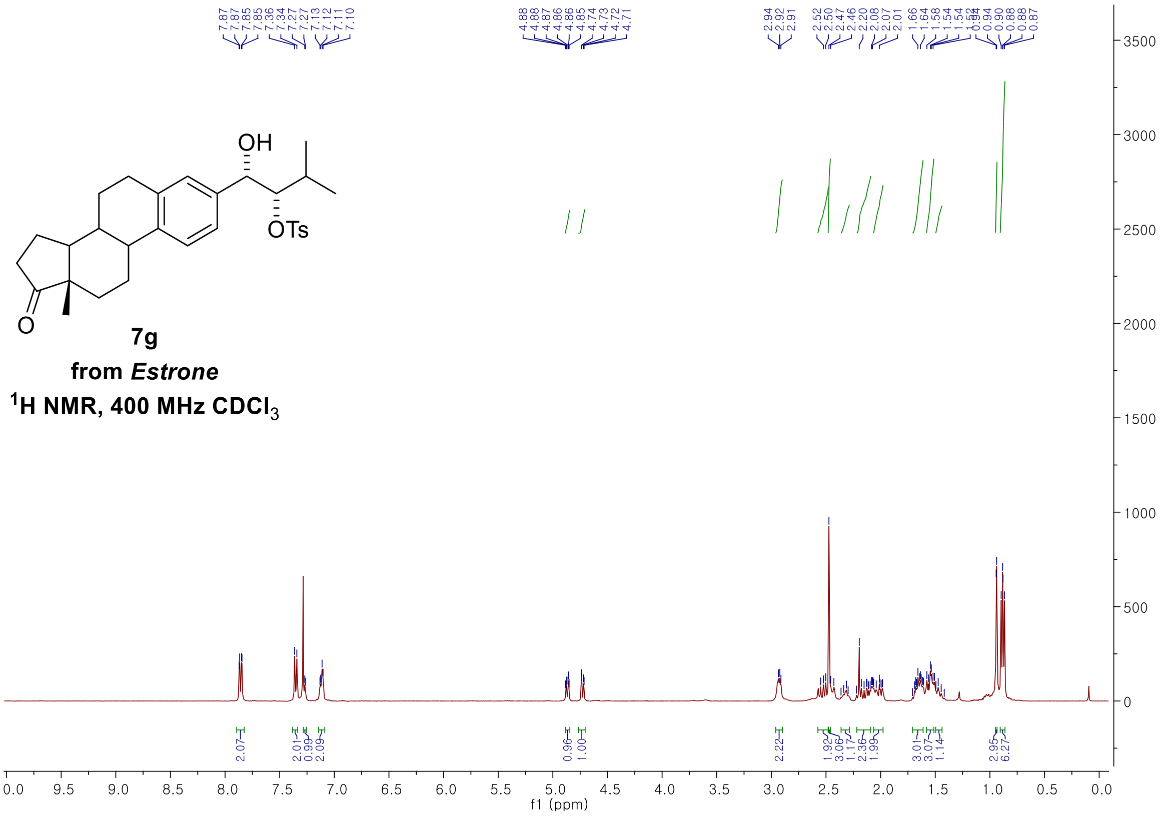

169.33
150.69
144.59
139.65
139.05
133.46
129.39
127.32
121.81
118.21
110.31
82.37
74.37
54.65
20.16
19.09
16.39
OH
AcO
OTs
MeO
7e
from isovanilin
^{13}C NMR, 100 MHz CD$_3$OD
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



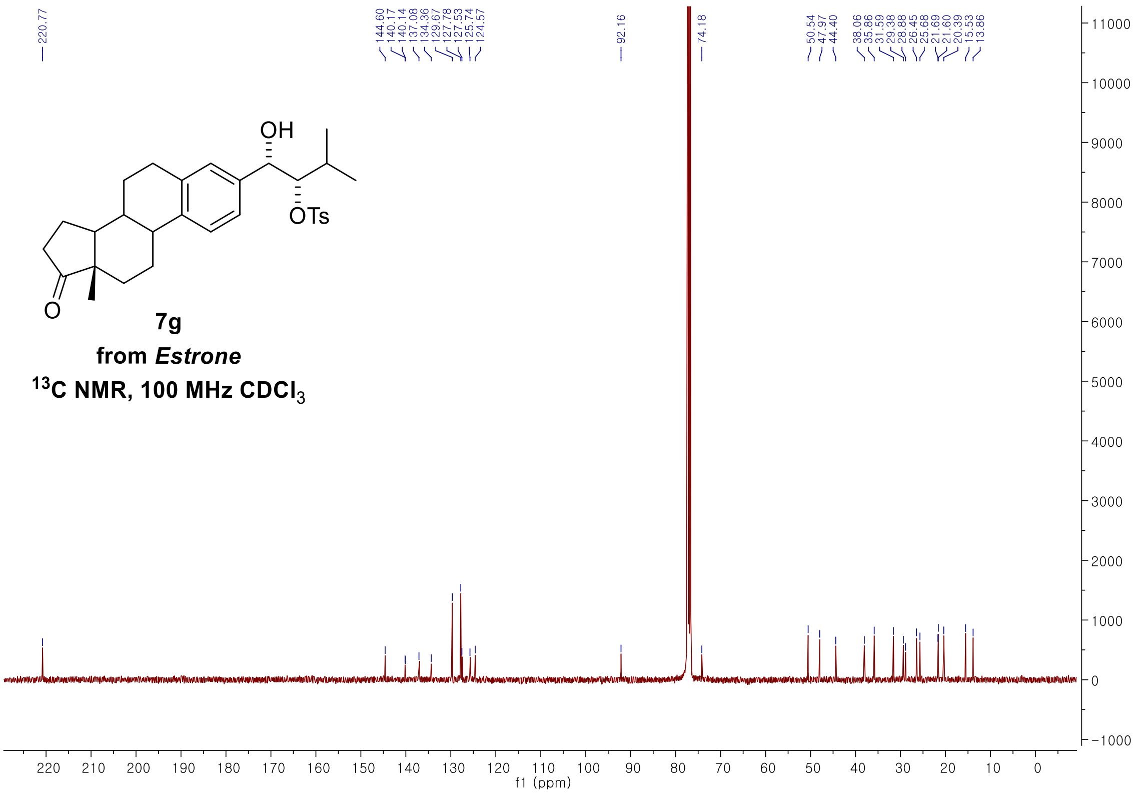
7f
from *(-)-Menthol*
^{1}H NMR, 400 MHz CDCl$_3$



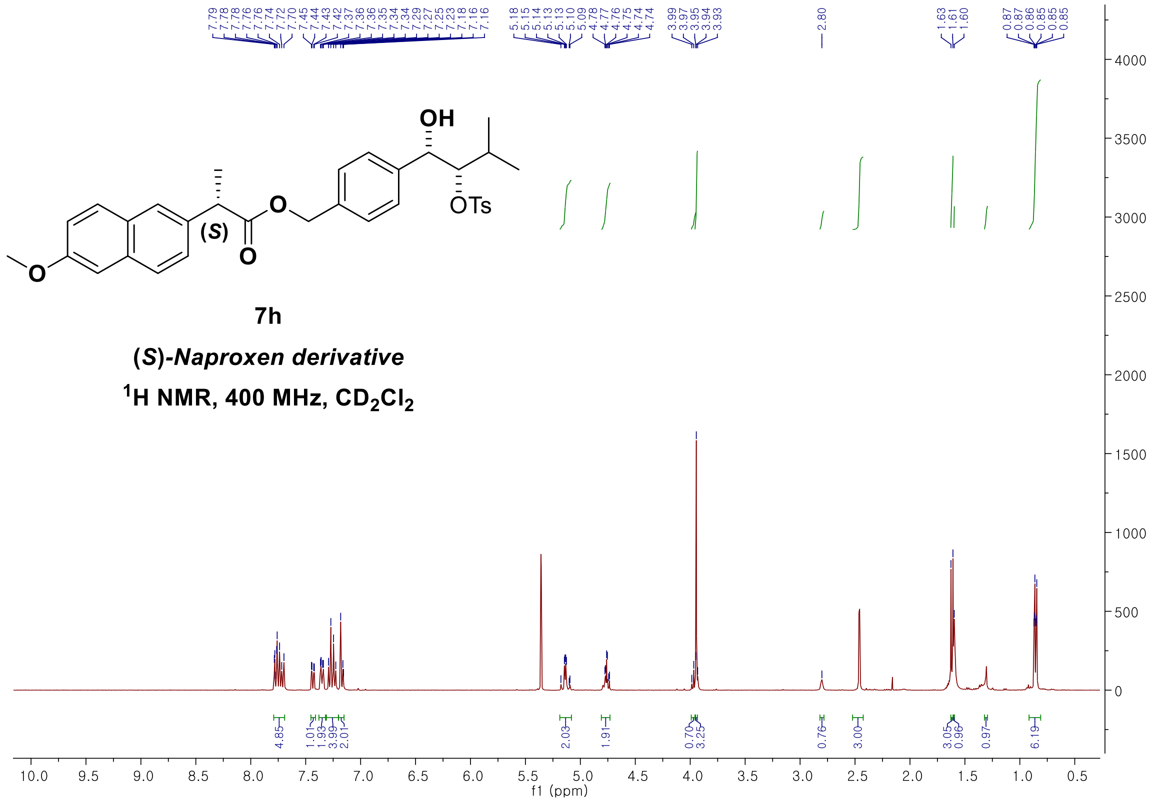
7f
from *(-)-Menthol*
^{13}C NMR, 100 MHz CDCl$_3$



7g
from *Estrone*
^{1}H NMR, 400 MHz CDCl$_3$



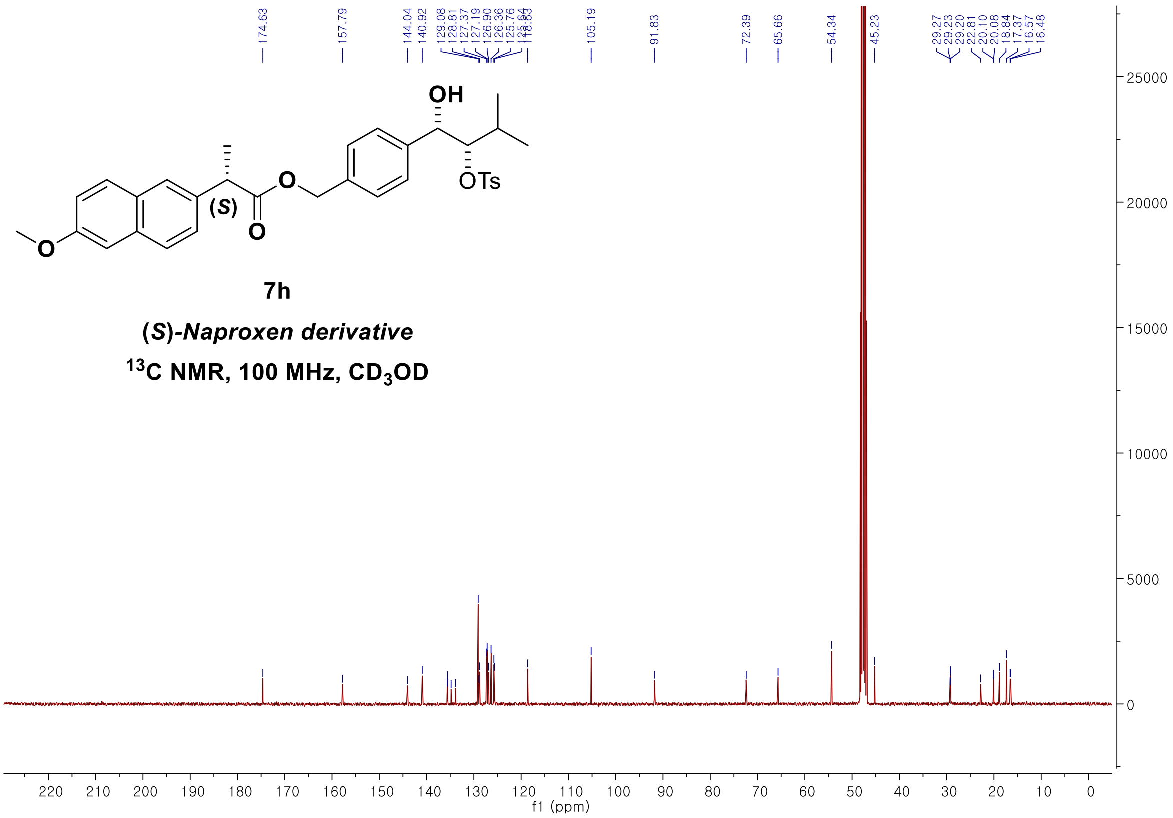
7g
from *Estrone*
^{13}C NMR, 100 MHz CDCl$_3$



7h

(S)-Naproxen derivative

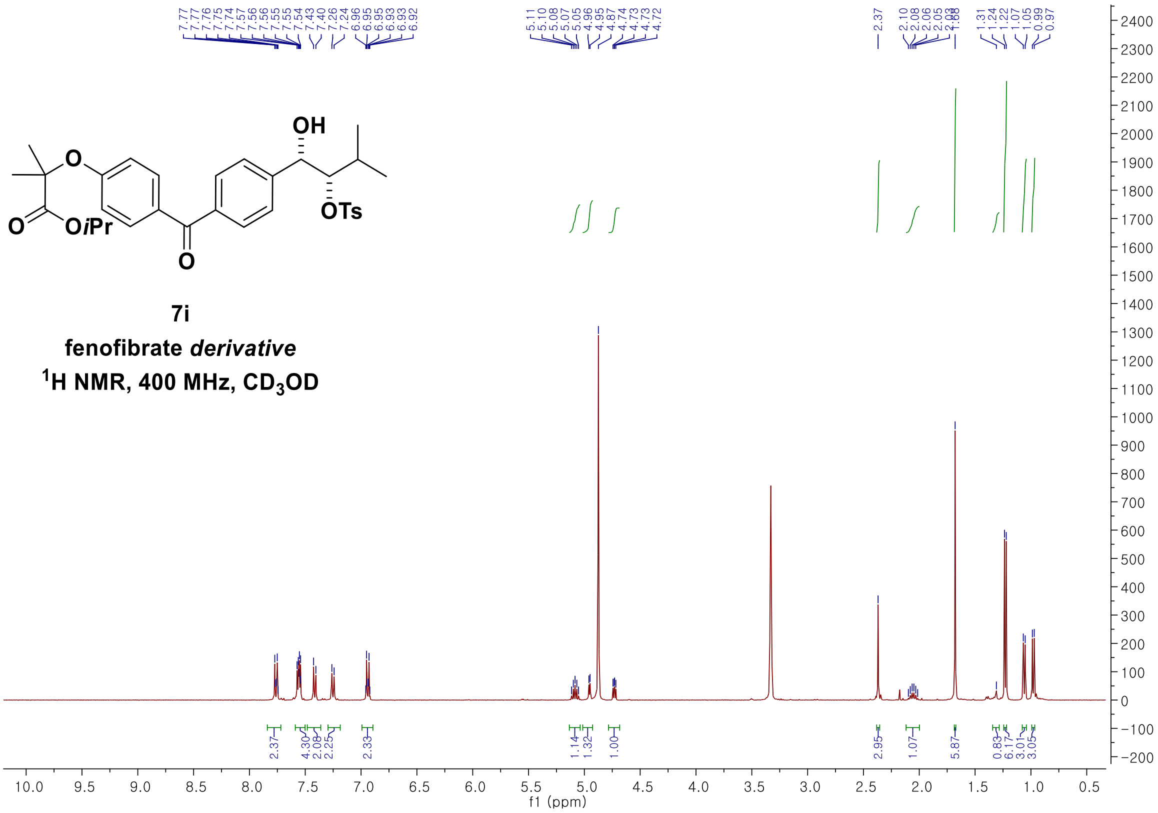
^{1}H NMR, 400 MHz, CD_2Cl_2



7h

(S)-Naproxen derivative

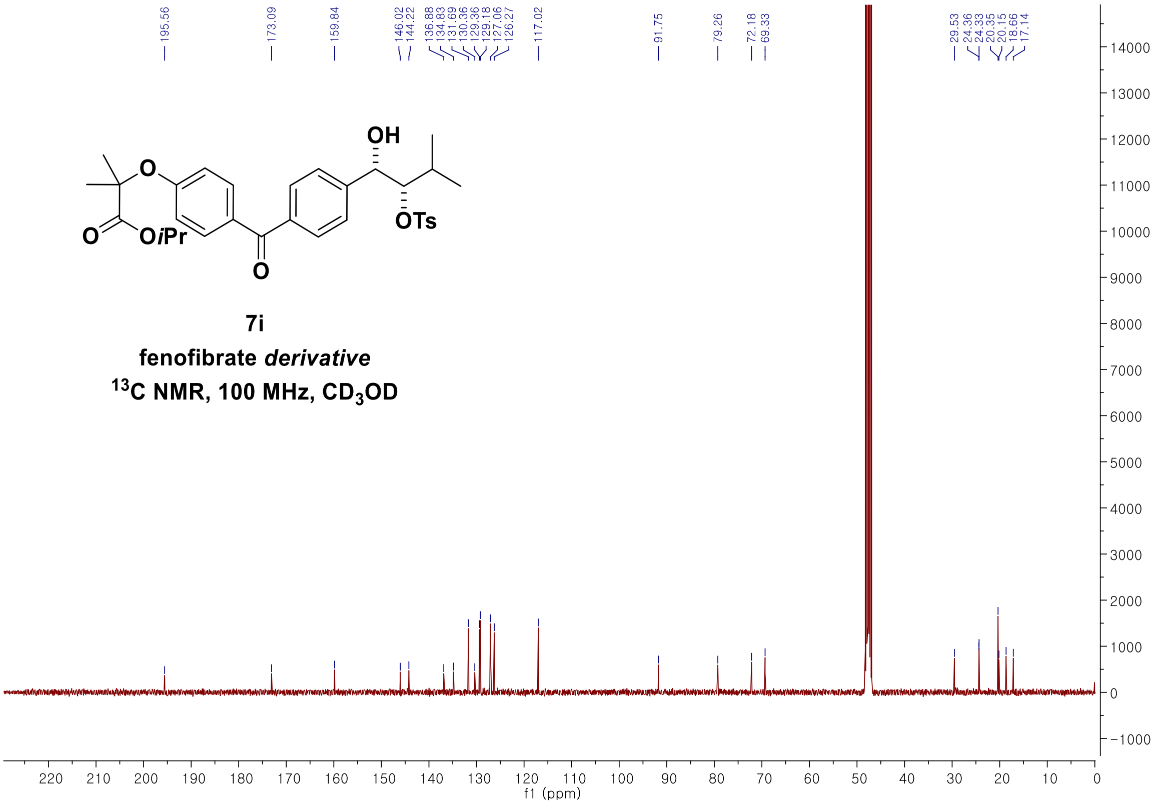
^{13}C NMR, 100 MHz, CD_3OD



7i

fenofibrate *derivative*

^{1}H NMR, 400 MHz, CD$_3$OD

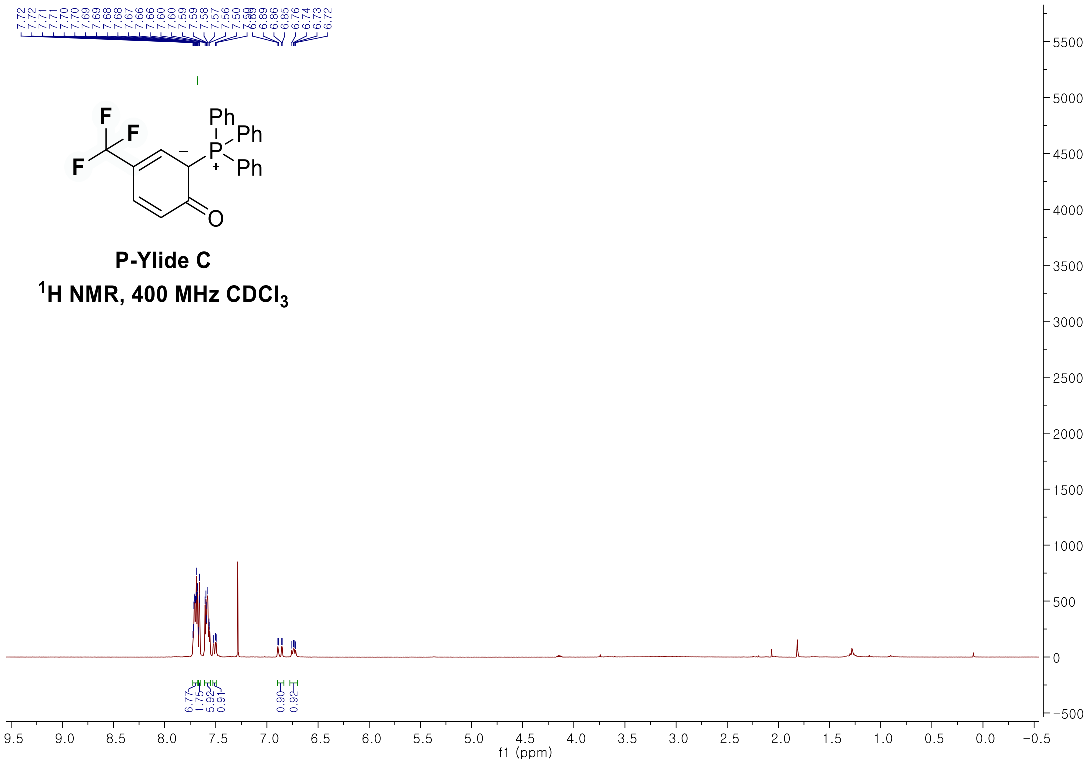


7i

fenofibrate *derivative*

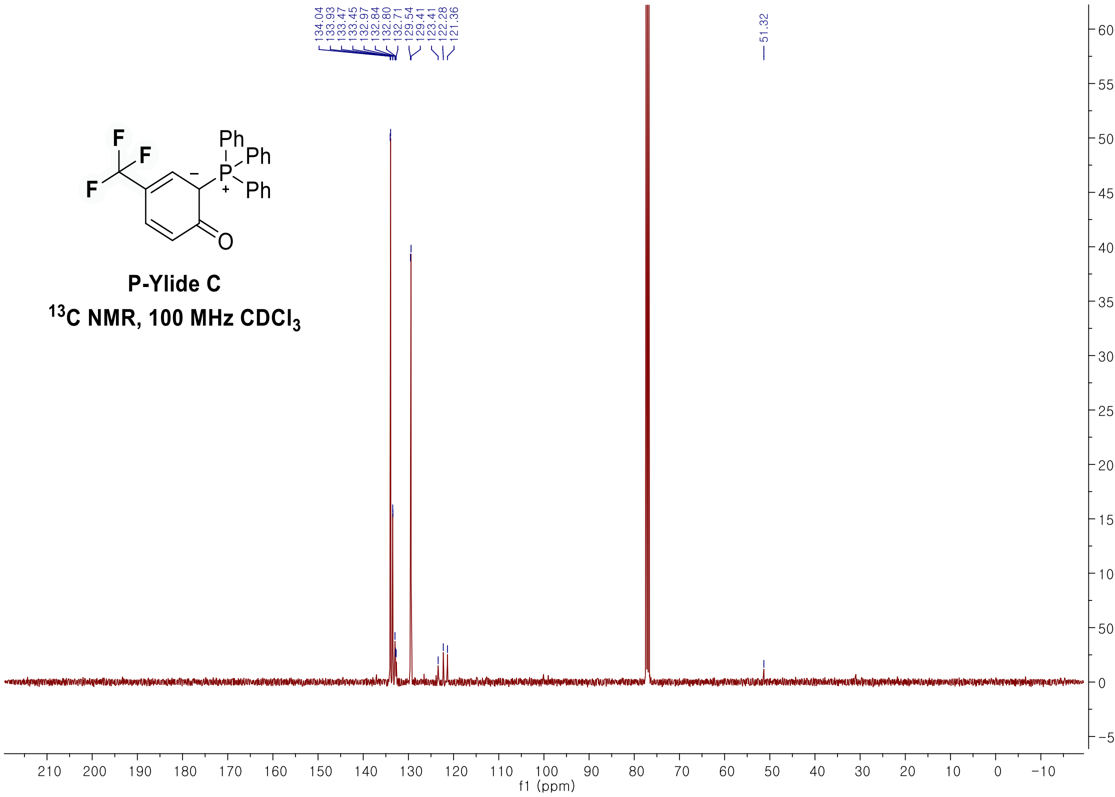
^{13}C NMR, 100 MHz, CD$_3$OD

Phosphonium ylide characterization (A-K)



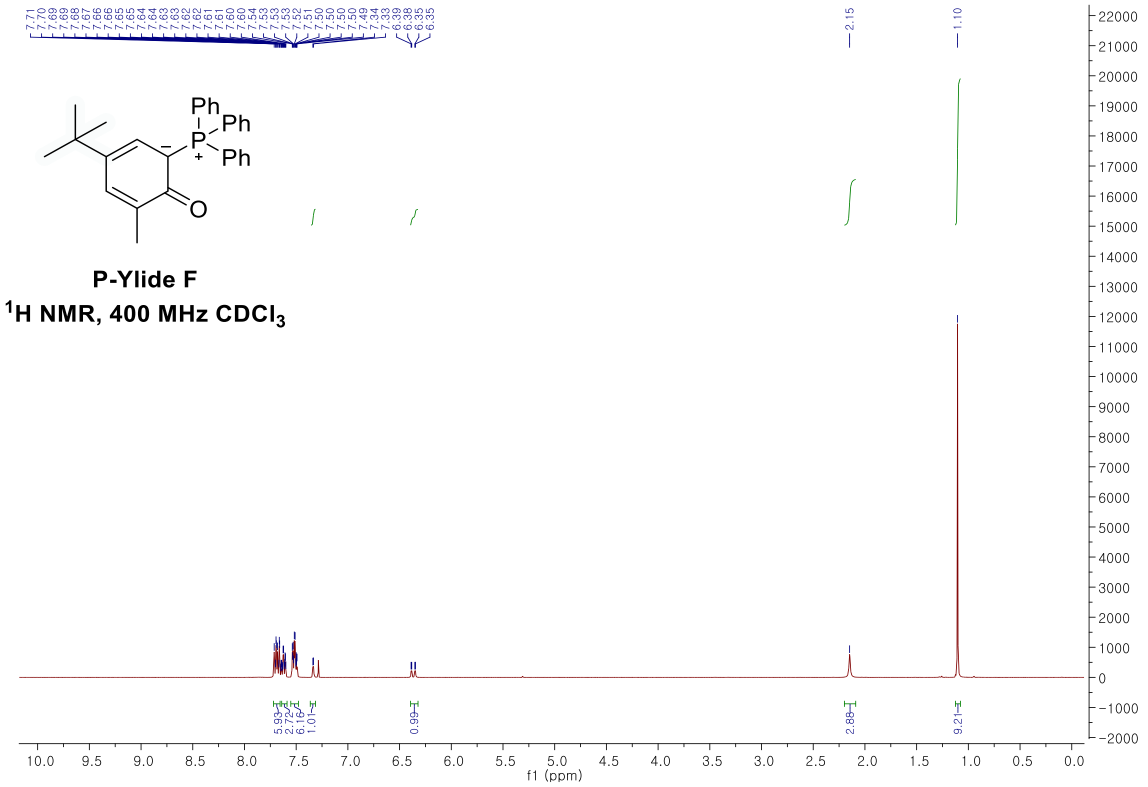
P-Ylide C

^{1}H NMR, 400 MHz CDCl$_3$



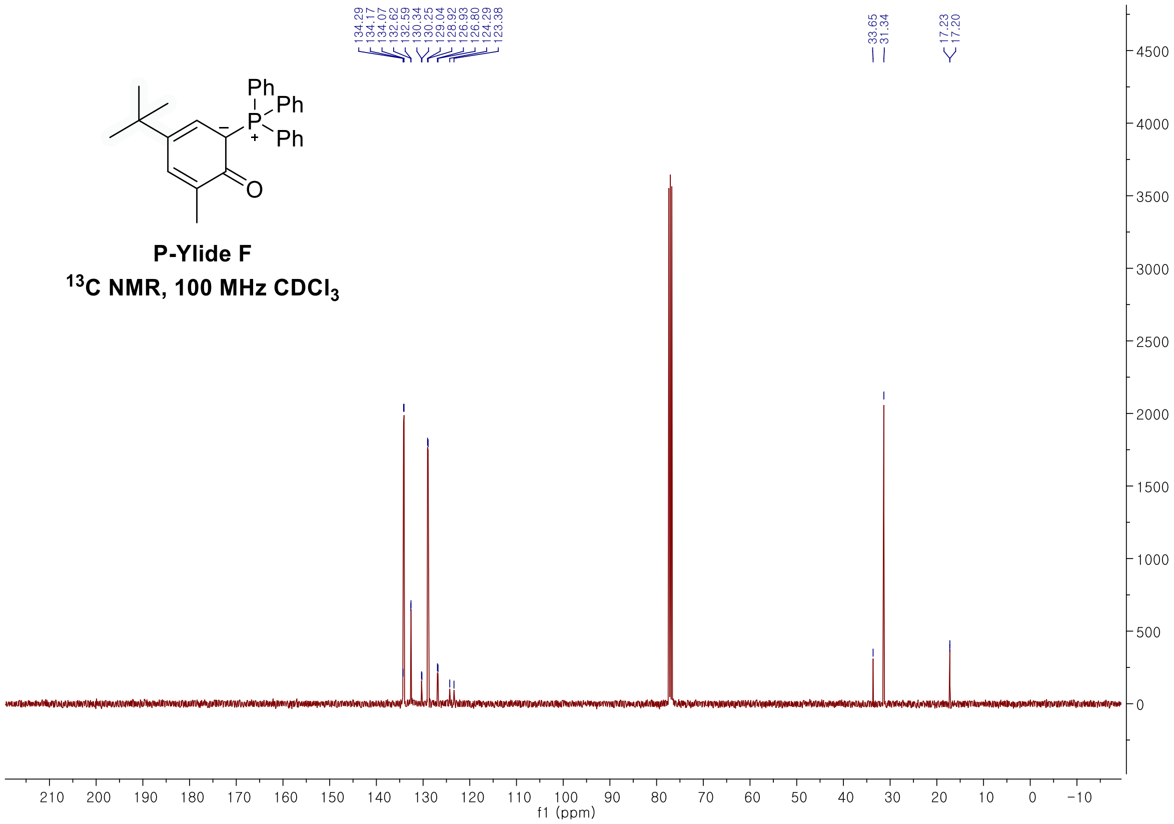
P-Ylide C

^{13}C NMR, 100 MHz CDCl$_3$



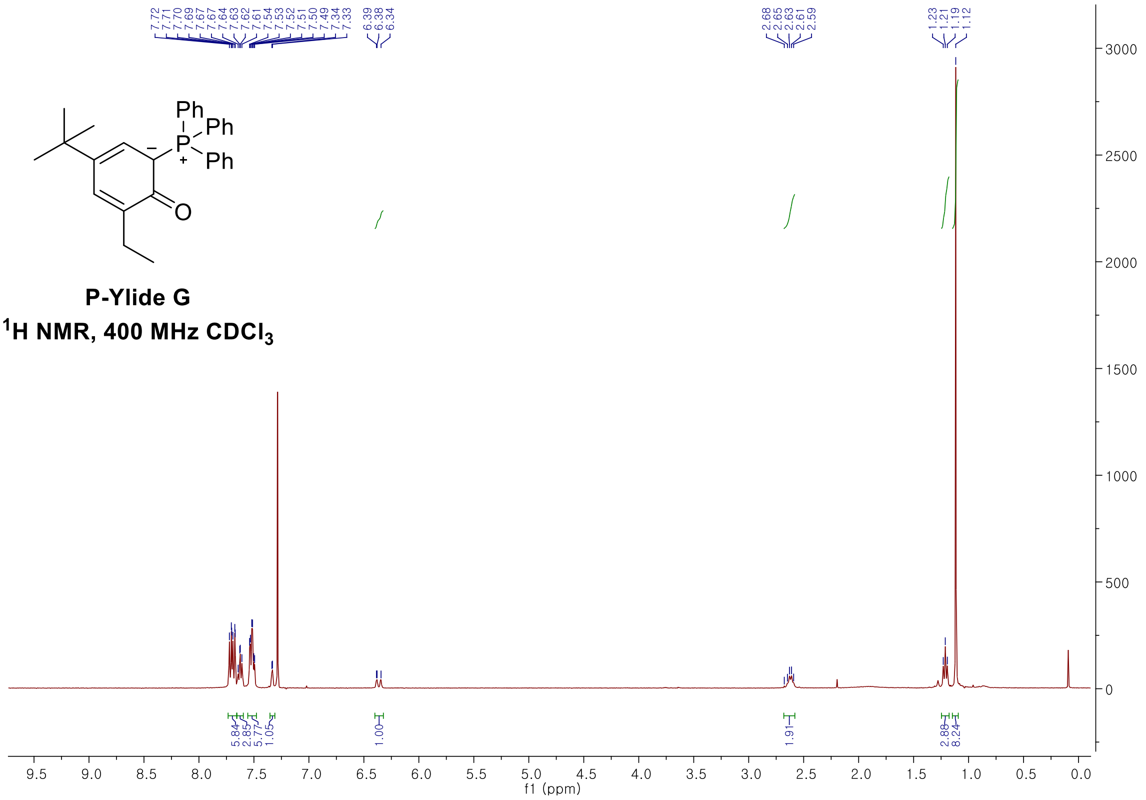
P-Ylide F

^{1}H NMR, 400 MHz CDCl$_3$



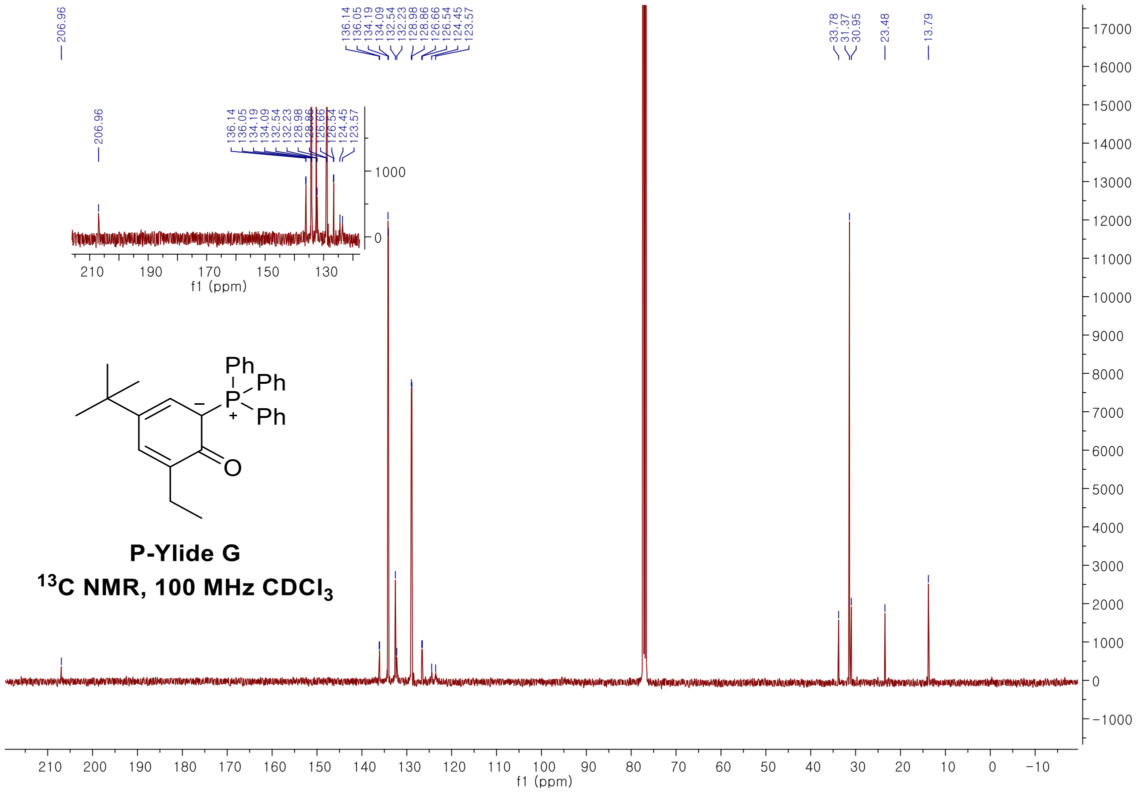
P-Ylide F

^{13}C NMR, 100 MHz CDCl$_3$



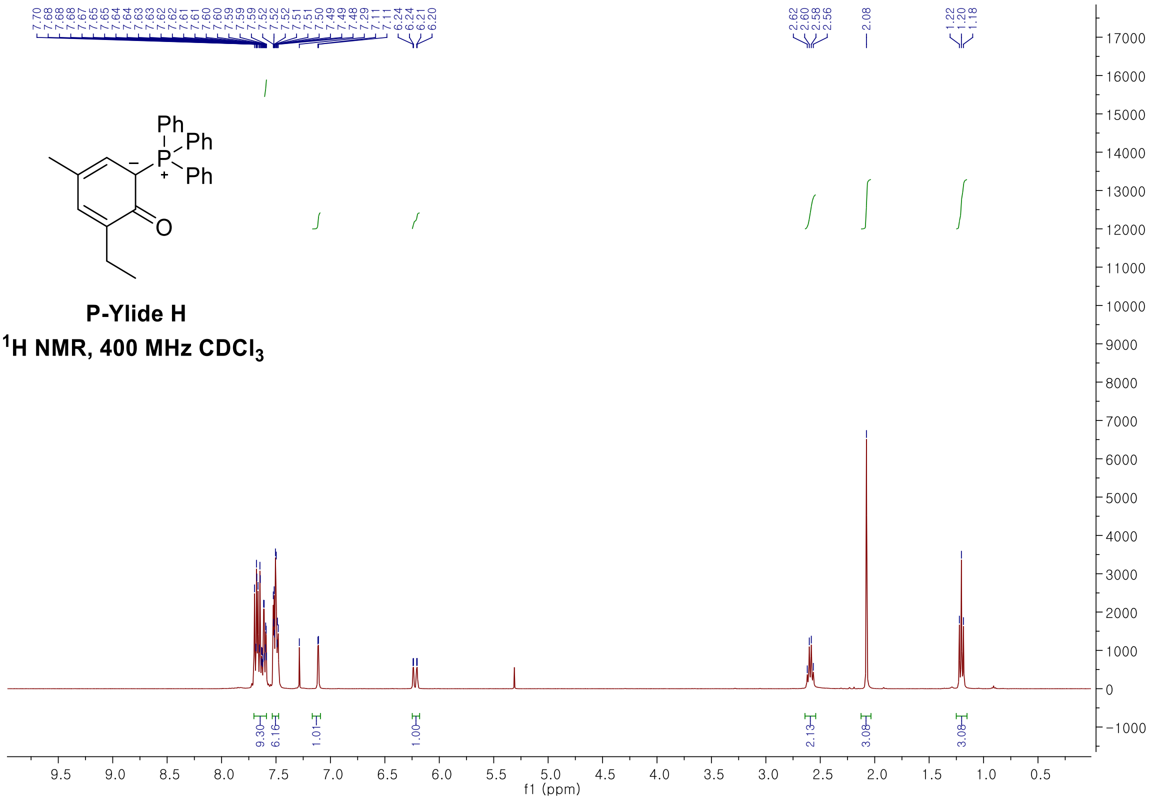
P-Ylide G

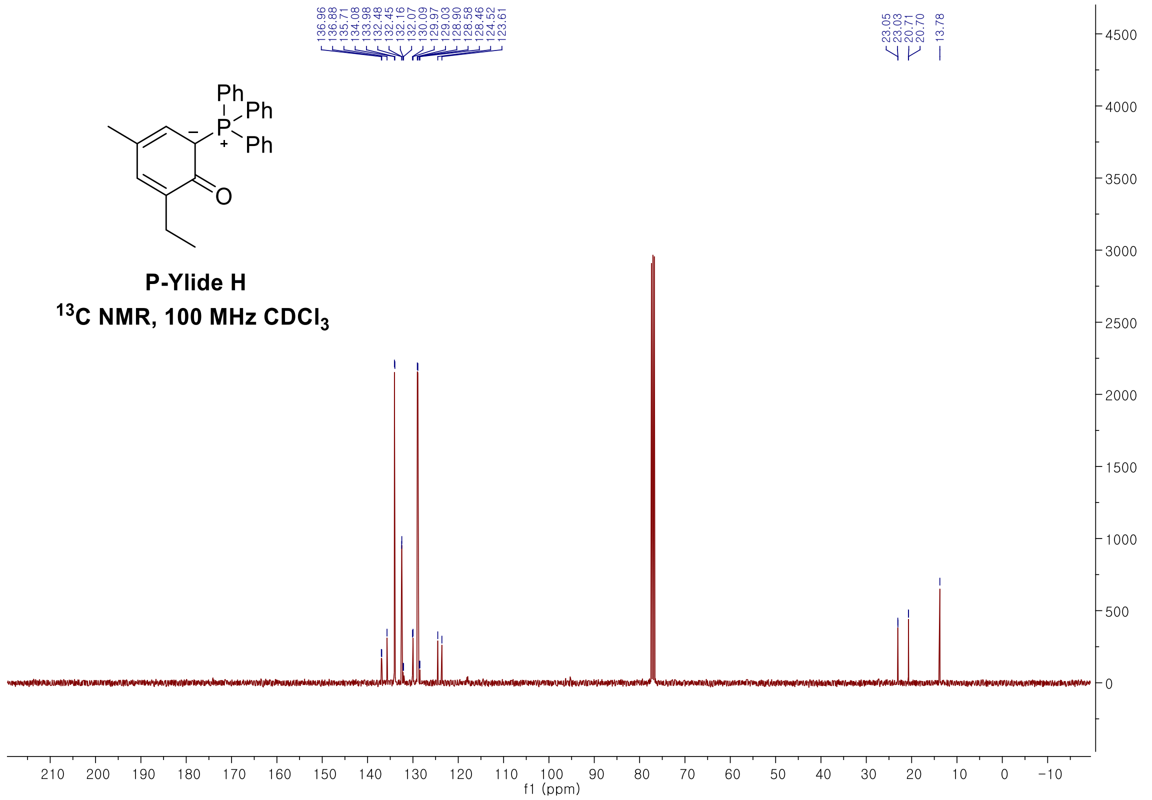
^{1}H NMR, 400 MHz CDCl$_3$

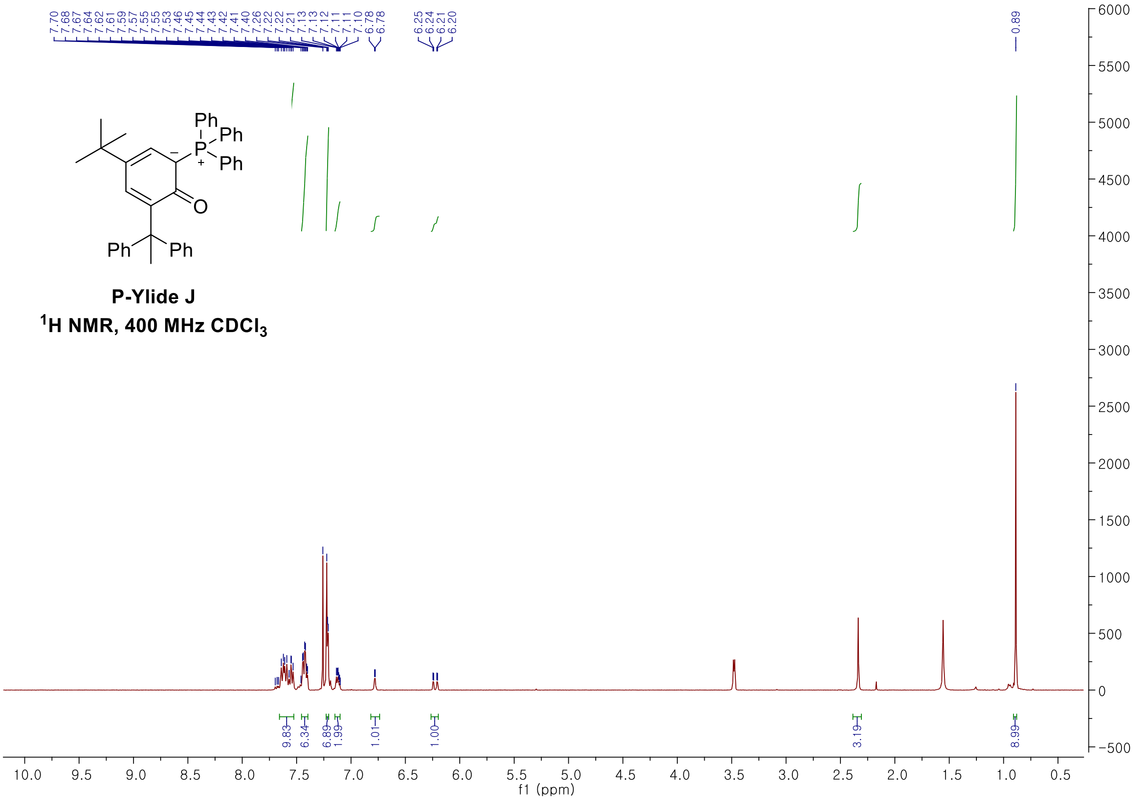


P-Ylide G

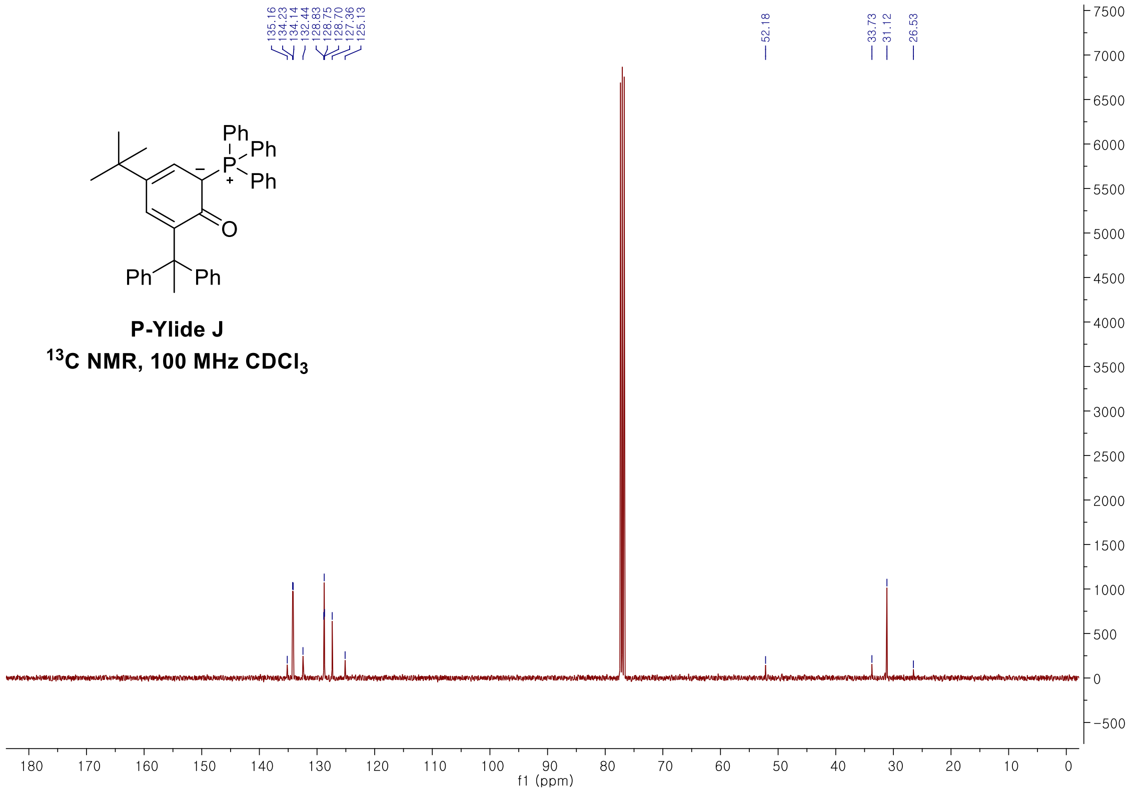
^{13}C NMR, 100 MHz CDCl$_3$


P-Ylide H
^{1}H NMR, 400 MHz CDCl$_3$

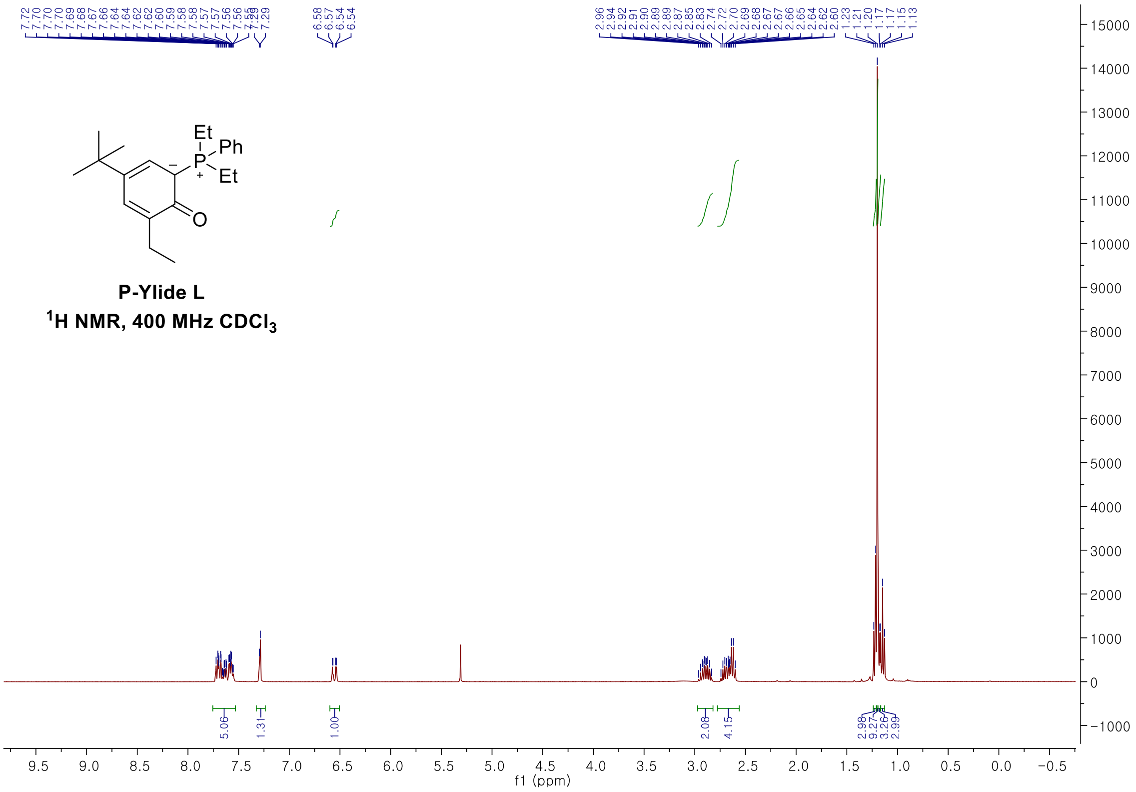

P-Ylide H
^{13}C NMR, 100 MHz CDCl$_3$



P-Ylide J
^{1}H NMR, 400 MHz CDCl$_3$

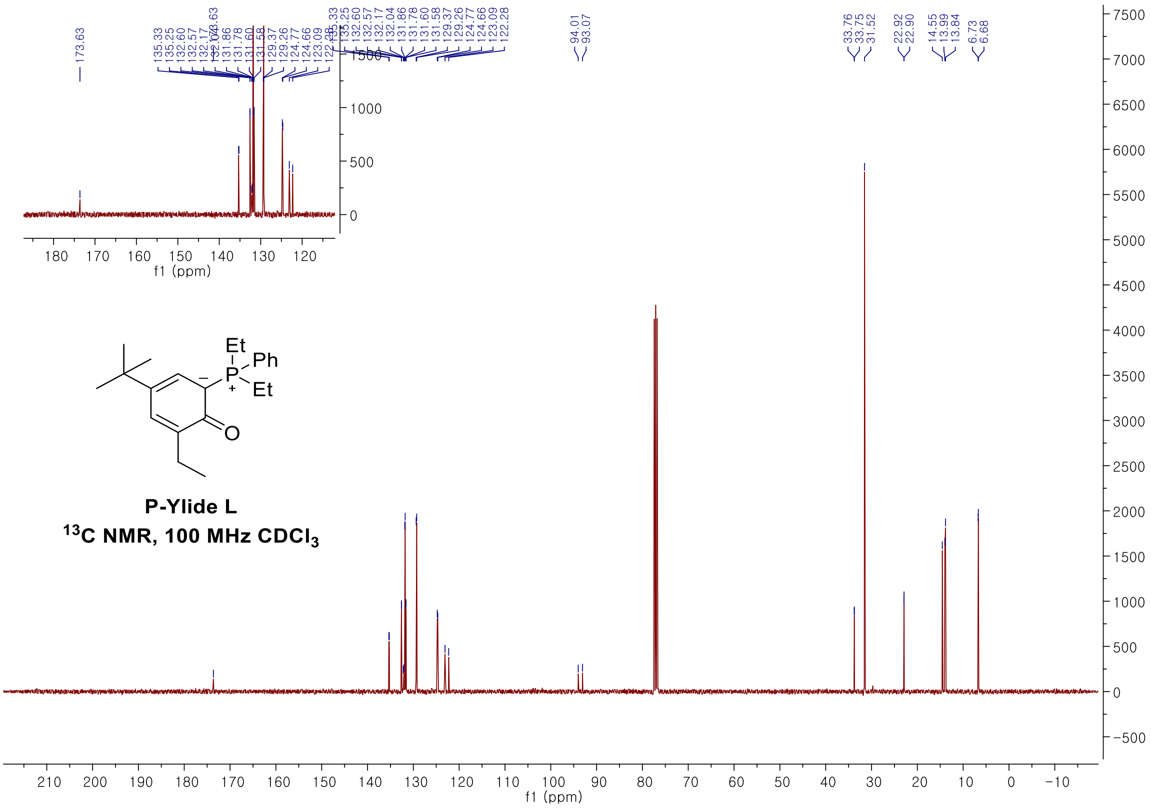


P-Ylide J
^{13}C NMR, 100 MHz CDCl$_3$



P-Ylide L

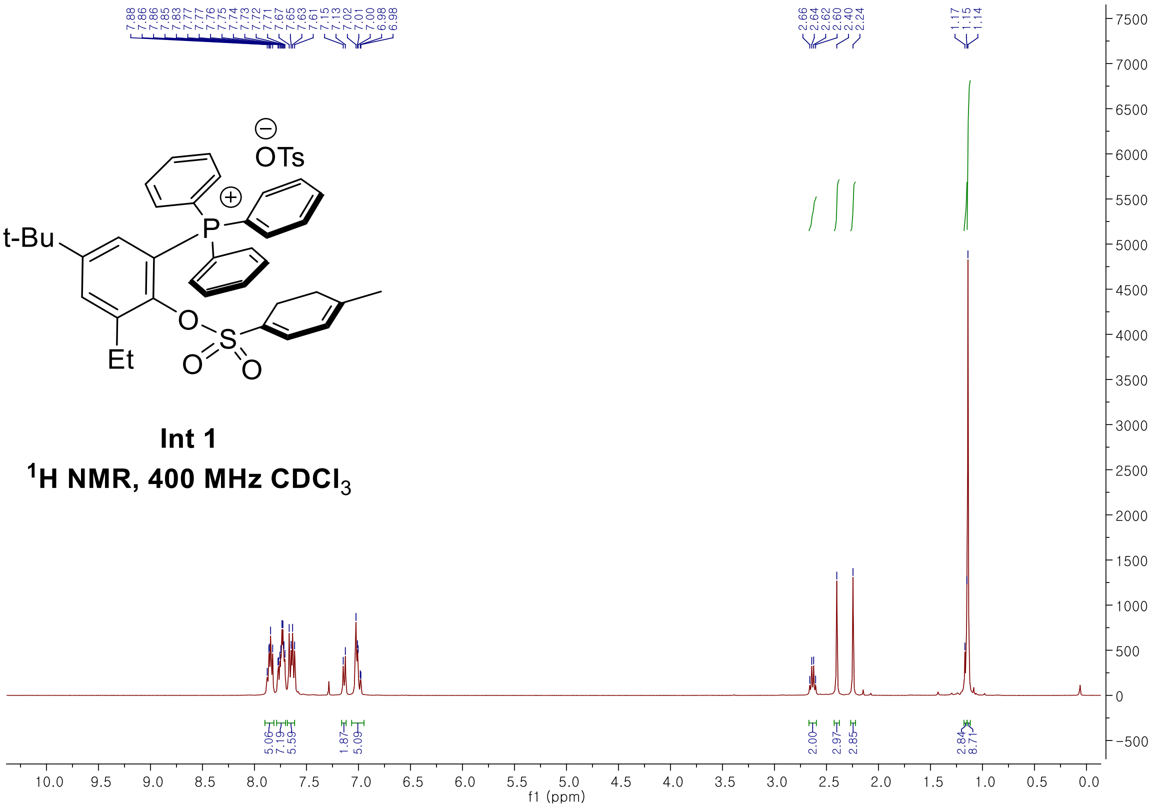
^{1}H NMR, 400 MHz $CDCl_3$



P-Ylide L

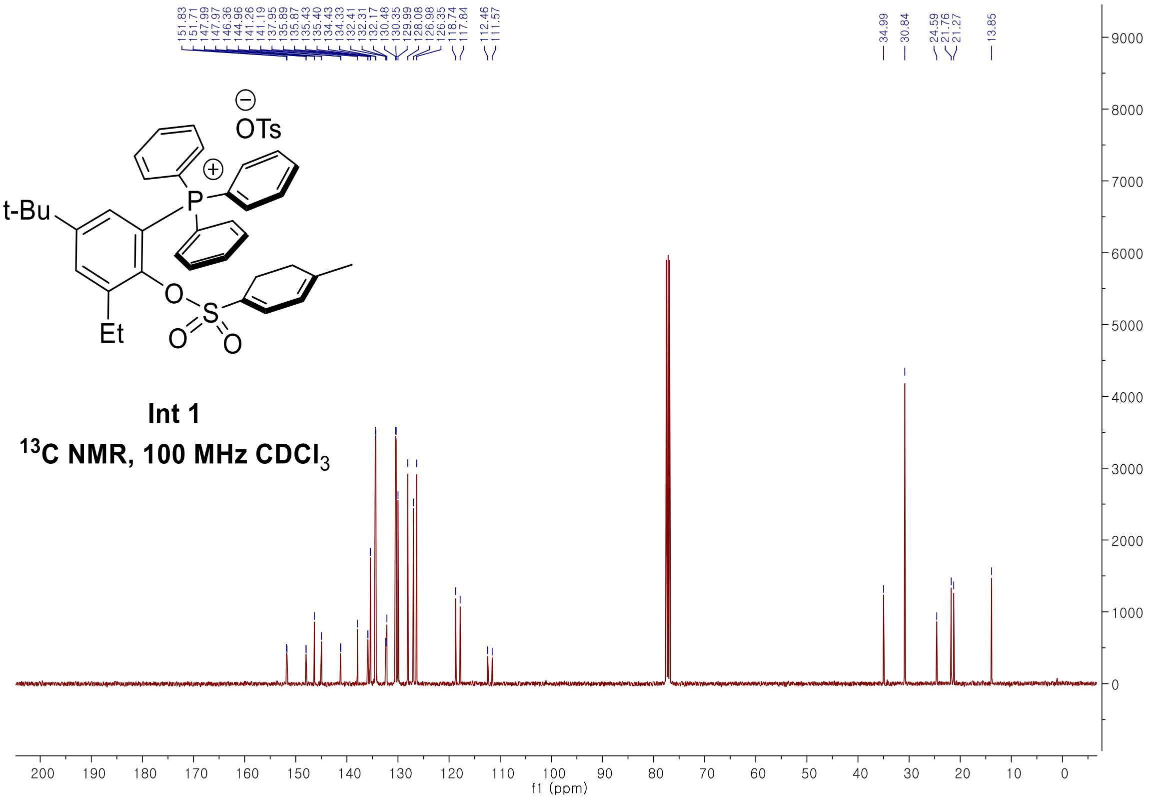
^{13}C NMR, 100 MHz $CDCl_3$

Phosphonium ylide Intermediate characterization



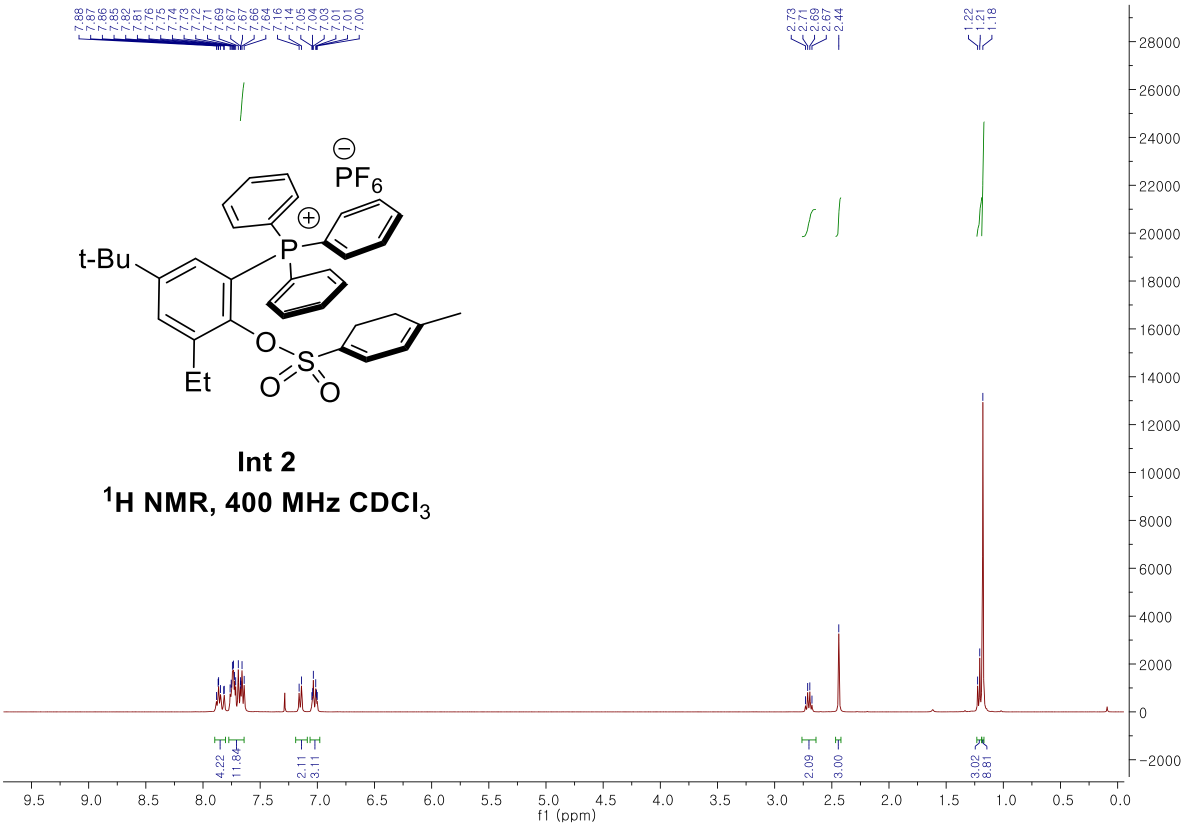
Int 1

^{1}H NMR, 400 MHz CDCl$_3$



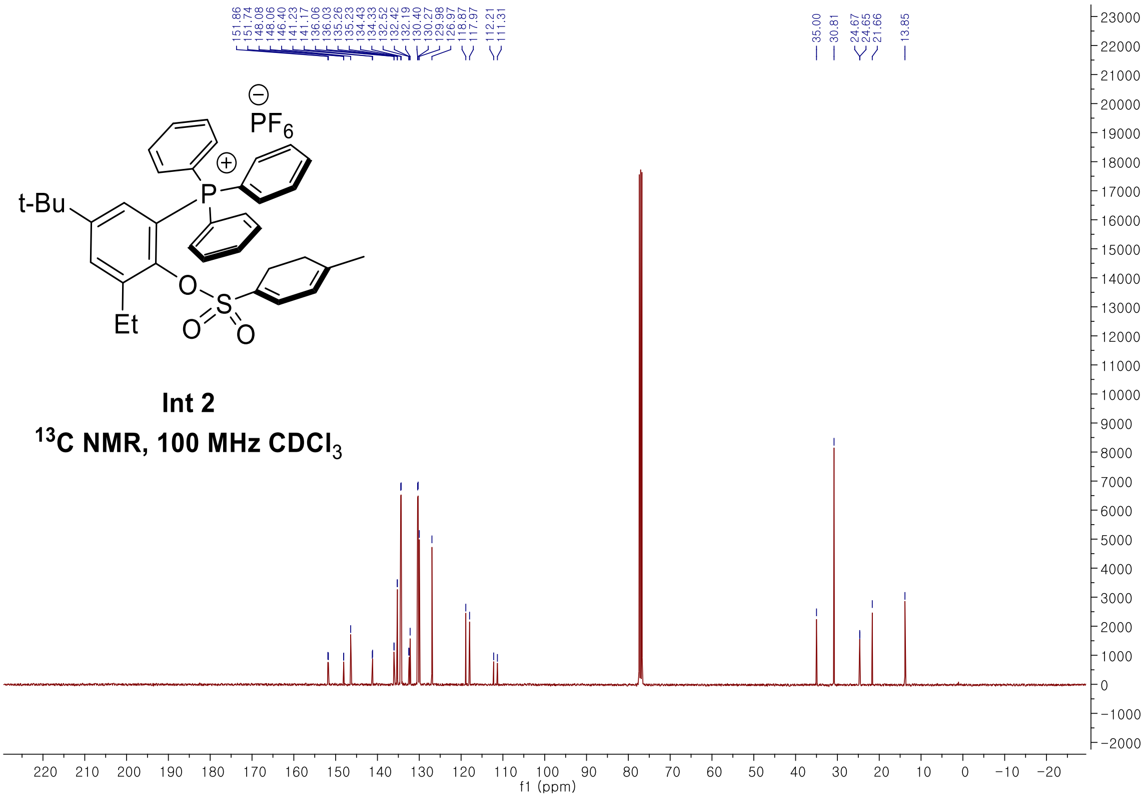
Int 1

^{13}C NMR, 100 MHz CDCl$_3$



Int 2

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



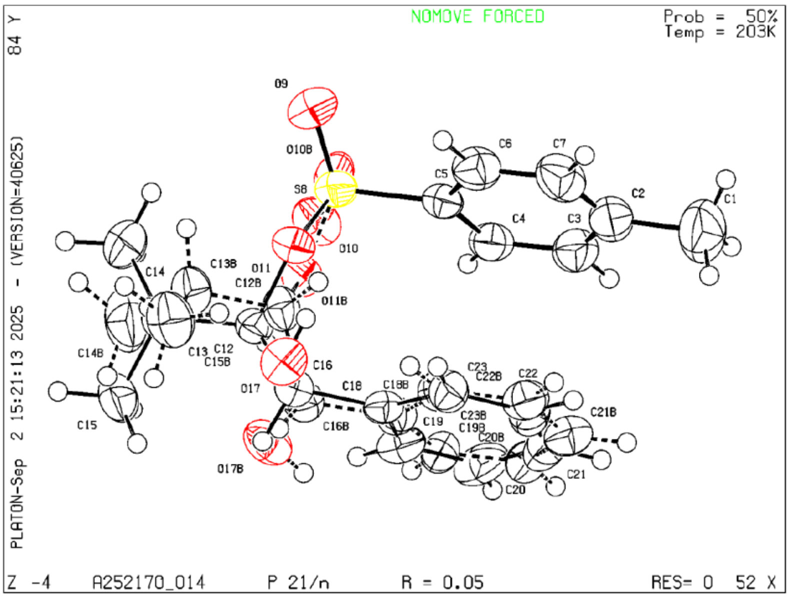
Int 2

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

Appendix II

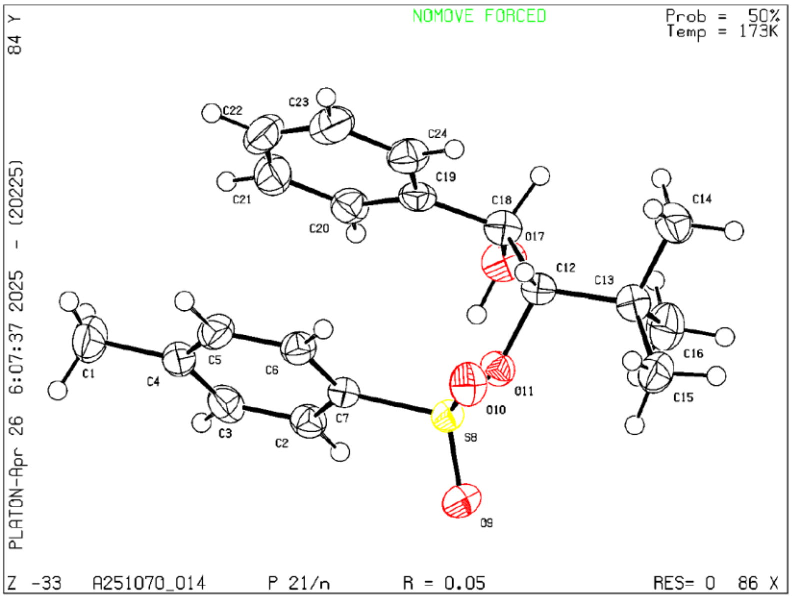
X-RAY Crystallographic structure

Crystal data and structure refinement for 2a (CCDC 2535330)



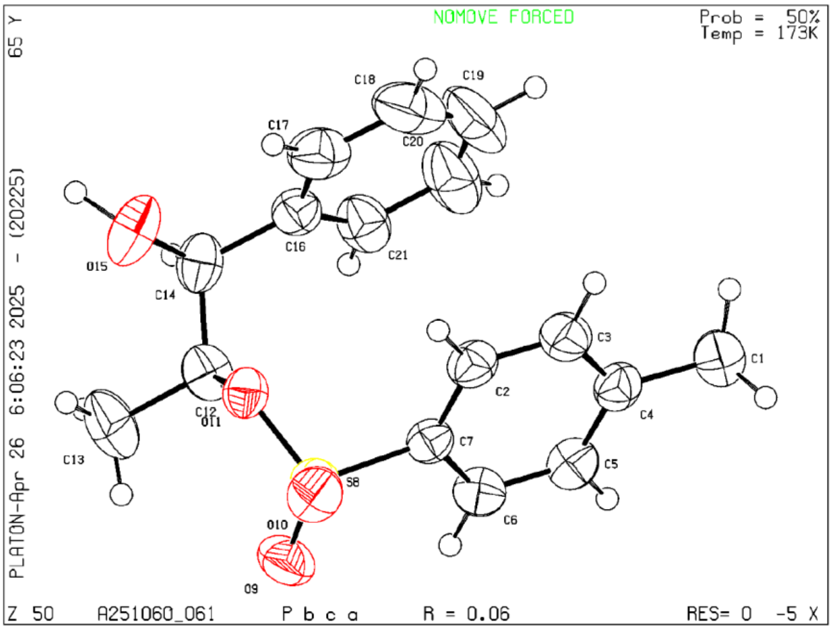
Empirical formula	$C_{18}H_{22}O_4S$	
Formula weight	334.41	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.8205(2) Å	α = 90°
	b = 18.8867(7) Å	β = 98.8445(13)°
	c = 15.8449(6) Å	γ = 90°
Volume	1721.12(11) $Å^3$	
Z	4	
Density (calculated)	1.291 Mg/m^3	
Absorption coefficient	0.205 mm^{-1}	
F(000)	712	
Crystal size	0.174 x 0.155 x 0.097 mm^3	
Theta range for data collection	2.602 to 26.037°.	
Index ranges	–7<=h<=7, –23<=k<=23, –19<=l<=16	
Reflections collected	19529	
Independent reflections	3387 [R(int) = 0.0831]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.6938	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3387 / 575 / 332	
Goodness-of-fit on F^2	1.121	
Final R indices [I>2sigma(I)]	R1 = 0.0546, wR2 = 0.1210	
R indices (all data)	R1 = 0.0813, wR2 = 0.1337	
Largest diff. peak and hole	0.298 and –0.466 e·$Å^{-3}$	

Crystal data and structure refinement for 2d (CCDC 2535331)



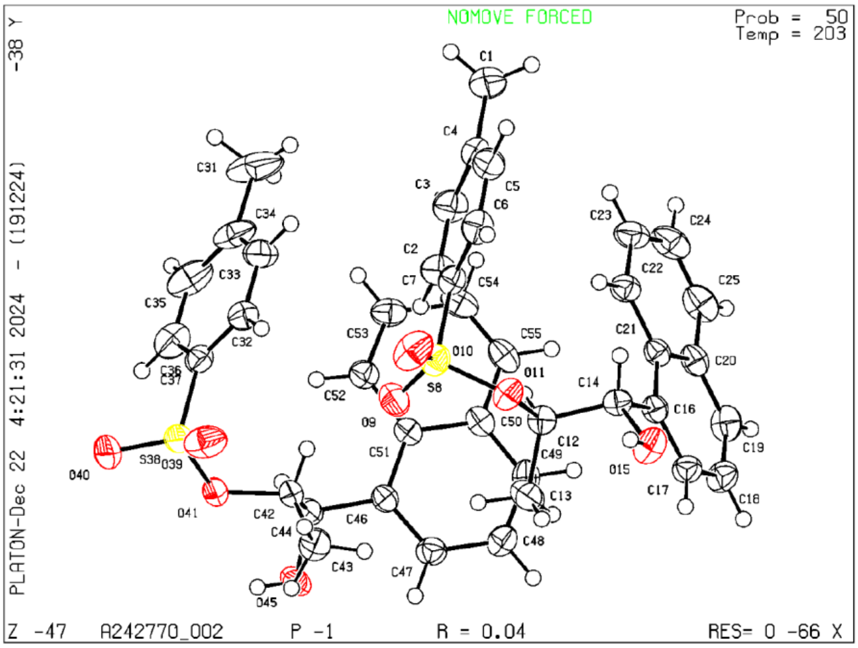
Empirical formula	$C_{19} H_{24} O_4 S$	
Formula weight	348.44	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.9208(4) Å	α = 90°
	b = 19.6966(12) Å	β = 98.269(3)°
	c = 15.4973(9) Å	γ = 90°
Volume	1788.50(19) $Å^3$	
Z	4	
Density (calculated)	1.294 Mg/m^3	
Absorption coefficient	0.200 mm^{-1}	
F(000)	744	
Crystal size	0.071 x 0.021 x 0.017 mm^3	
Theta range for data collection	2.656 to 27.028°.	
Index ranges	–7<=h<=7, –25<=k<=25, –19<=l<=19	
Reflections collected	27900	
Independent reflections	3912 [R(int) = 0.0706]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6977	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3912 / 0 / 230	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.1288	
R indices (all data)	R1 = 0.0718, wR2 = 0.1406	
Largest diff. peak and hole	0.560 and –0.417 e·$Å^{-3}$	

Crystal data and structure refinement for 2y (CCDC 2535332)



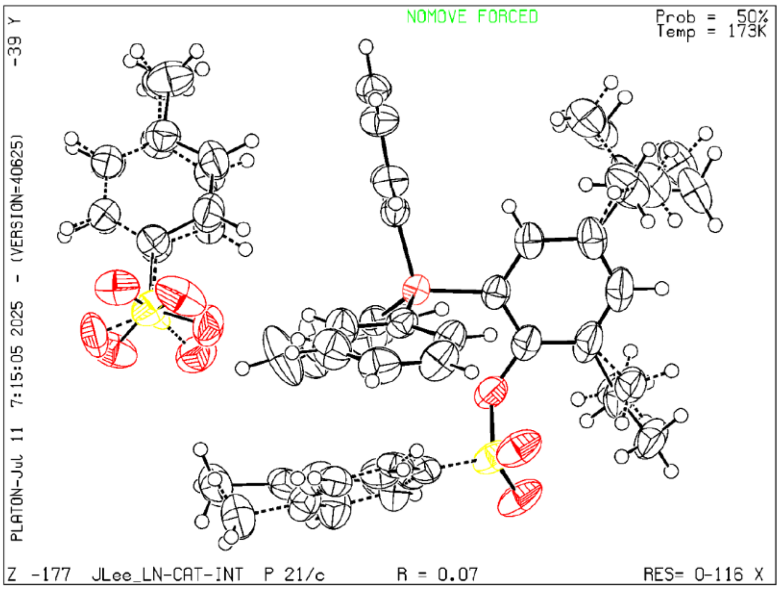
Empirical formula	$C_{16}H_{18}O_4S$	
Formula weight	306.36	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 7.0672(13) Å	α = 90°
	b = 17.385(3) Å	β = 90°
	c = 25.011(4) Å	γ = 90°
Volume	3072.9(9) Å^3	
Z	8	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.223 mm^{-1}	
F(000)	1296	
Crystal size	0.124 x 0.082 x 0.023 mm^3	
Theta range for data collection	2.481 to 25.550°.	
Index ranges	–5<=h<=8, –19<=k<=21, –26<=l<=30	
Reflections collected	15571	
Independent reflections	2852 [R(int) = 0.0980]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6288	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2852 / 0 / 198	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1368	
R indices (all data)	R1 = 0.0920, wR2 = 0.1586	
Largest diff. peak and hole	0.446 and –0.293 e·Å^{-3}	

Crystal data and structure refinement for 2s^{erythro} (CCDC 2535333)



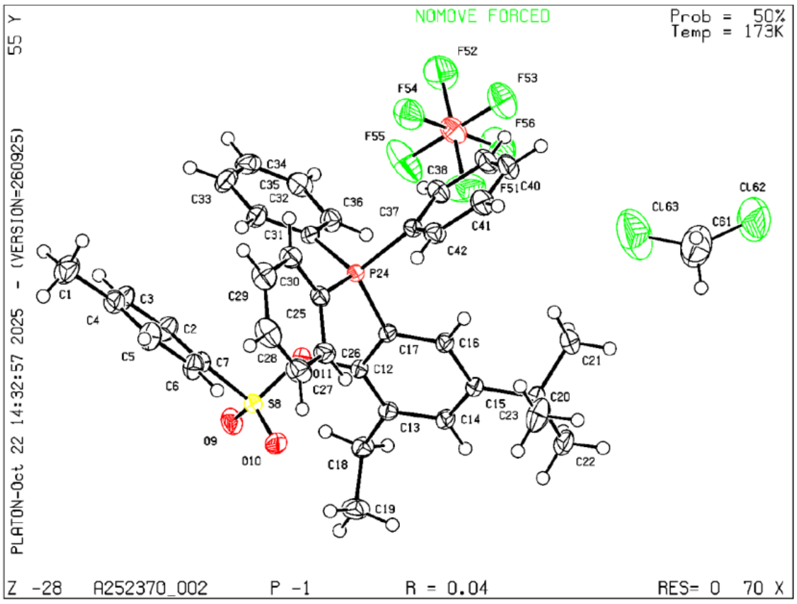
Empirical formula	$C_{20} H_{20} O_4 S$	
Formula weight	356.42	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.3551(7) Å	α = 90.974(2)°
	b = 13.3937(10) Å	β = 104.6478(19)°
	c = 13.5606(9) Å	γ = 99.278(2)°
Volume	1792.5(2) Å^3	
Z	4	
Density (calculated)	1.321 Mg/m^3	
Absorption coefficient	0.202 mm^{-1}	
F(000)	752	
Crystal size	0.118 x 0.114 x 0.092 mm^3	
Theta range for data collection	2.569 to 27.039°.	
Index ranges	–13<=h<=13, –17<=k<=17, –17<=l<=17	
Reflections collected	78311	
Independent reflections	7792 [R(int) = 0.0754]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.7145	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7792 / 0 / 473	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.0992	
R indices (all data)	R1 = 0.0547, wR2 = 0.1089	
Largest diff. peak and hole	0.267 and –0.385 e·Å^{-3}	

Crystal data and structure refinement for Int1 (CCDC 2535334)



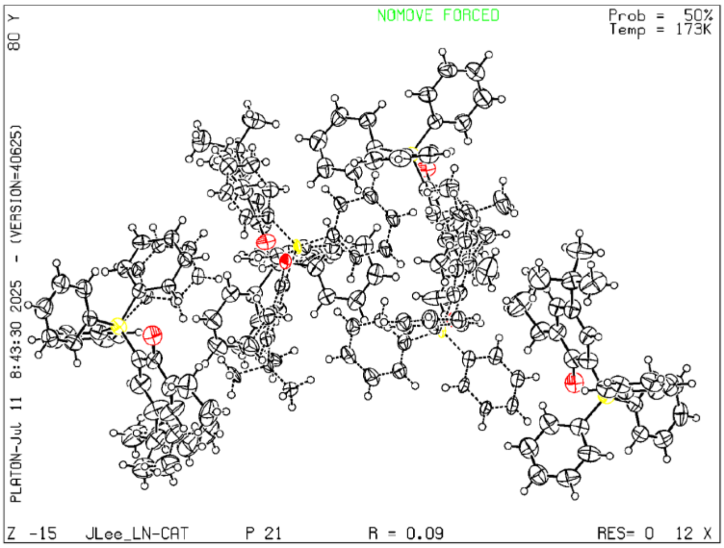
Empirical formula	$C_{44}H_{45}O_6PS_2$	
Formula weight	764.89	
Temperature	173(2) K	
Wavelength	0.700 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.6380(19) Å	α = 90°
	b = 21.446(4) Å	β = 93.38(3)°
	c = 19.101(4) Å	γ = 90°
Volume	3941.3(14) $Å^3$	
Z	4	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.212 mm^{-1}	
F(000)	1616	
Crystal size	0.085 x 0.038 x 0.034 mm^3	
Theta range for data collection	1.407 to 26.018°.	
Index ranges	–12<=h<=12, –26<=k<=26, –23<=l<=23	
Reflections collected	30994	
Independent reflections	7999 [R(int) = 0.0632]	
Completeness to theta = 24.835°	98.5 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.776	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7999 / 684 / 675	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0729, wR2 = 0.1744	
R indices (all data)	R1 = 0.0917, wR2 = 0.1859	
Extinction coefficient	0.0491(19)	
Largest diff. peak and hole	0.309 and –0.456 $e \cdot Å^{-3}$	

Crystal data and structure refinement for Int2 (CCDC 2535335)



Empirical formula	$C_{75} H_{78} Cl_2 F_{12} O_6 P_4 S_2$	
Formula weight	1562.27	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 9.1258(4) Å	α = 106.2662(15)°
	b = 13.6373(6) Å	β = 100.8964(17)°
	c = 16.0336(7) Å	γ = 97.3926(15)°
Volume	1845.75(14) $Å^3$	
Z	1	
Density (calculated)	1.406 Mg/m^3	
Absorption coefficient	0.313 mm^{-1}	
F(000)	810	
Crystal size	0.097 x 0.059 x 0.032 mm^3	
Theta range for data collection	2.316 to 30.027°.	
Index ranges	–12<=h<=12, –19<=k<=19, –22<=l<=22	
Reflections collected	91817	
Independent reflections	10745 [R(int) = 0.0561]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.7241	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10745 / 0 / 474	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.1026	
R indices (all data)	R1 = 0.0488, wR2 = 0.1092	
Largest diff. peak and hole	0.572 and –0.635 $e·Å^{-3}$	

Crystal data and structure refinement for P-ylide G (CCDC 2535336)



Empirical formula	$C_{30} H_{31} O P$	
Formula weight	438.52	
Temperature	173(2) K	
Wavelength	0.700 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.5940(19) Å	α = 90°
	b = 19.770(4) Å	β = 98.89(3)°
	c = 26.759(5) Å	γ = 90°
Volume	5014.5(18) $Å^3$	
Z	8	
Density (calculated)	1.162 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	1872	
Crystal size	0.134 x 0.023 x 0.021 mm^3	
Theta range for data collection	1.267 to 28.024°.	
Index ranges	–12<=h<=12, –26<=k<=26, –35<=l<=35	
Reflections collected	46434	
Independent reflections	24409 [R(int) = 0.1110]	
Completeness to theta = 24.835°	96.3 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.878	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24409 / 3376 / 1556	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0905, wR2 = 0.2056	
R indices (all data)	R1 = 0.1755, wR2 = 0.2526	
Absolute structure parameter	0.34(7)	
Extinction coefficient	0.033(2)	
Largest diff. peak and hole	0.430 and –0.340 e·$Å^{-3}$	