Visible Light-Promoted Dihydroxylation of Styrenes with Water and Dioxygen

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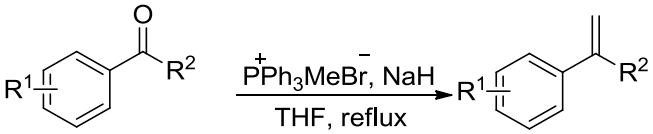
I. General Information

THF was distilled from sodium benzophenoneketyl prior to use. DCM, NEt_3 and iPr_2NEt were distilled from calcium hydride. Alcohols and MeCN was used directly. The $Acr^+MesClO_4^-$ was prepared according to the literature.[1] Unless otherwise noted, all the corresponding ketones from suppliers were used directly without further purification. NMR spectra were recorded on a Bruker-400 instrument. ^1H NMR chemical shifts were referenced tothe tetramethylsilane (0 ppm),^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$). The following abbreviations (or combinations thereof) were used to explain mμLtiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. High-resolution

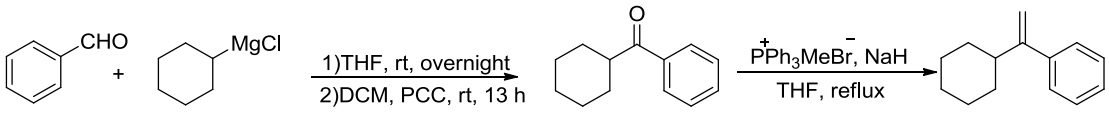
mass spectra (HRMS) were recorded on EI-TOF or ESI-TOF (electrospray ionization-time of flight). Unless noted, all the alkenes were prepared according to the general procedures using the corresponding ketones through wittig reaction.

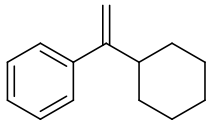
II. Procedures for Synthesis of Alkenes



A general procedure to synthesis of alkenes.

To a solution of PPh_3MeBr (36 mmol) in THF (70 mL) was added NaH (60%, 1.1 equiv.), the reaction mixture was refluxed for 1 h. Then the corresponding ketones (30 mmol) in THF (20 mL) were added dropwise at 0 ^{o}C.The mixture was refluxed overnight. When the starting material was consumed (monitored by TLC), the reaction mixture was diluted by petroleum ether and filtered through a pad of silica gel. The filtrate was concentrated to give a crude product which was distilled or purified through flash column chromatography to obtain the desired product. The known products were identical to the literature.



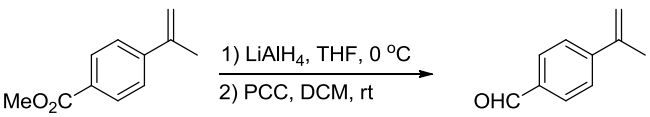


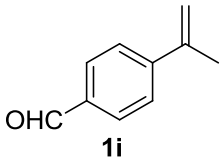
1p

(1-cyclohexylvinyl)benzene (1p). [2] To a 100 mL overdried flask, benzaldehyde (5.1 mL, 50 mmol) and THF (50 mL) were added. Cyclohexylmagnesium chloride (1.3 M in THF) (42 mL, 60 mmol) were added dropwise.Then the reaction mixture was stirred at rt overnight. The mixture was quenched by saturated NH_4Cl solution, diluted by Et_2O and filtered through a short pad of celite. The filtration was concentrated in *vacuo* to obtain the crude product which was purified by

chromatography through silica gel to obtainthe corresponding ketone (4.7545 g, 25.3 mmol，51% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.91 (m, 2H), 7.57-7.50 (m, 1H), 7.49-7.42 (m, 2H), 3.31-3.21 (m, 1H), 1.95-1.70 (m, 4H), 1.78-1.69 (m, 1H), 1.56-1.23 (m, 5H).

To a solution of PPh_3MeBr (11.17 g, 31.3 mmol) in THF (70 mL) was added NaH (60%, 1.2046 g, 30 mmol), the reaction mixture was refluxed for 1 h, the ketone (3.7094 g, 20 mmol) obtained above in THF (20 mL) were added dropwise at 0 ^{o}C and then the reaction was refluxing overnight. When the starting material was consumed (monitored by TLC), the reaction was diluted by petroleum ether and filtered through a short pad of silica gel. The filtration was concentrated and distilled to obtain the product (2.4688 g, 13.3 mmol, 67% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 5H), 5.12 (s, 1H), 5.00 (s, 1H), 2.41 (t, *J* = 11.2 Hz, 1H), 1.89-1.65 (m, 5H), 1.39-1.05 (m, 5H).

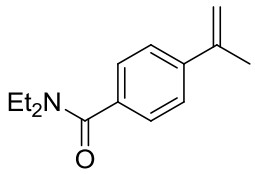




1i

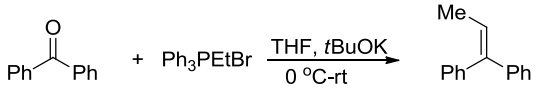
4-(prop-1-en-2-yl)benzaldehyde (1i).[3]To a over-dried flask cooled under N_2 atmosphere, methyl 4-(prop-1-en-2-yl)benzoate (1.4057 g, 8.0mmol) and THF (20 mL) were added, $LiAlH_4$ (0.1521 g, 4.0 mmol) in THF (5 mL) was added dropwise at 0^{o}C. The mixture was stirred overnight at 0 ^{o}C.NaOH (1.0 M, 4 mL) was added slowly followed by addition of H_2O (10 mL). The mixture was filtrated, and the filtration was extracted by Et_2O and the combined organic layers were dried over Na_2SO_4. After filtration, the solvent was removed and the crude product was dissolved in DCM (50 mL), PCC (1.7411 g, 8 mmol) was added and stirred overnight. The reaction mixture was monitored by TLC. When the starting material was consumed, the mixture was diluted with Et_2O and filtered through a pad of

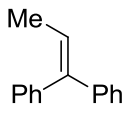
silica gel. The filtrate was condensed and the residue was purified by column chromatography to obtain **1i** (0.4413 g, 2.7 mmol, 34% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 5.51 (s, 1H), 5.26-5.23 (m, 1H), 2.19 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 147.2, 142.3, 135.3, 129.8, 126.0, 115.4, 21.6.



1j

***N,N*-diethyl-4-(prop-1-en-2-yl)benzamide (1j).** To aoverdried flask cooled under N_2, corresponding acid (649.6 mg, 4.0 mmol) and $SOCl_2$ (2.4 mL, 32.8 mmol) was added at 0 ^{o}C. Then the mixture was stirred at room temperature for 3 h. The excess $SOCl_2$ was evaporated in vacuo to obtain the crudeacyl chloride. The obtainded acyl chloride was transferred to a solution of diethylamine (1.96 mL, 19.0 mmol) in Et_2O (20 mL). The reaction mixture stirred overnight. Water was added to quench the reaction and extracted by DCM. The combined organic layers were dried by anhydrous Na_2SO_4. After filtered, the filtration was concentrated and the residue was purified by column chromatography to obtain **1j** (757.3 mg, 3.5 mmol, 87% yield) as a colorless oil.IR v2974, 1628, 1428, 1380 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.41 (s, 1H), 5.15-5.11 (m, 1H), 3.63-3.16 (m, 4H), 2.16 (s, 3H), 1.34-1.02 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 142.5, 141.9, 136.1, 126.3, 125.4, 113.2, 43.2, 39.2, 21.7, 14.2, 14.3; HRMS (EI-TOF) Calcd for $C_{14}H_{19}NO$ $[M]^{+}$:217.1467; Found 217.1468.

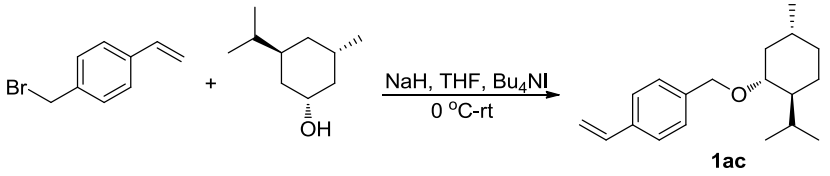


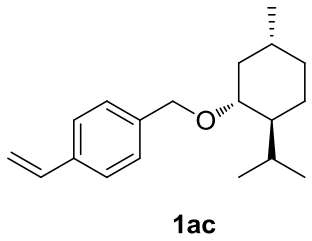


1aa

prop-1-ene-1,1-diyldibenzene (1aa). [4] To a 250 mL round flask,

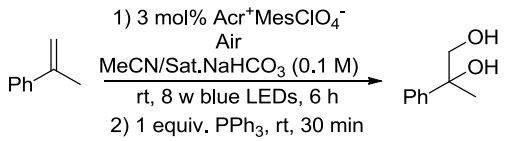
Ethyltriphenylphosphonium bromide (11.17 g, 30 mmol) and THF (100 mL) were added at room temperature. After cooled to 0 ^{o}C,*t*BuOK (3.45 g, 30 mmol) was added and the reaction mixture was stirred for 2 h. Then benzophenone (3.65 g, 20 mmol) was added and stirred at 50 ^{o}C overnight. The reaction mixture was diluted with petroleum ether and filtered through a short pad of silica gel. The filtrate was condensed and the residue was purified by column chromatography to obtain **1aa** (2.5992 g, 13.4 mmol, 67% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 2H), 7.32-7.15 (m, 8H), 6.17 (q, *J* = 7.2 Hz, 1H), 1.76 (d, *J* = 6.8 Hz, 3H).



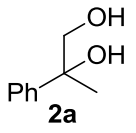


1-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-4-vinylbenzene (**1ac**). Prepared according to a similar procedure[5] using alkene (2.9560 g, 15.0 mmol), alcohol (2.5781 g, 16.5 mmol), NaH (60 wt%, 0.8806 g, 22.0 mmol), Bu_4NI (775.7 mg, 2.1 mmol) and THF (45 mL) as substrates to afford **1ac**. IR *v* 3392, 2953, 2923, 2865, 1457, 1094 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 3.16 (td, *J* = 10.8, 4.0 Hz, 1H), 2.37-2.23 (m, 1H), 2.23-2.13(m, 1H), 1.72-1.58 (m, 2H), 1.33-1.22 (m, 1H), 1.03 -0.81 (m, 10H), 0.71 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 136.7, 136.6, 128.0, 126.1, 113.5, 78.7, 70.1, 48.3, 40.3, 34.6, 31.6, 25.5, 23.2, 22.4, 21.0, 16.1; HRMS (EI-TOF) Calcd for $C_{19}H_{28}O$ $[M]^{+}$:272.2140; Found 272.2139.

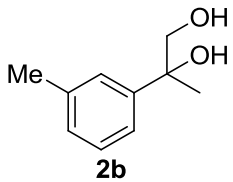
II. General procedure A for dihydroxylation of styrenes



To a 50 mL flask, $Acr^{+}MesClO_4^{-}$ (0.009 mmol), **1** (0.3 mmol),Sat.$NaHCO_3$ (0.25 mL) and MeCN (2.75 mL) were added sequently under air. The reaction mixture was irradiated by 8W blue LEDS at a distance of 10 cm for 6 h. To the flask, PPh_3 (1 equiv.) was added and stirred for 30 min at room temperature. The reaction mixture was then diluted with Et_2O and filtered through a short pad of silica using Et_2O and EA. The filtrate was concentrated *in vacuo*and purified by flash chromatography on silica gel to afford **2**.

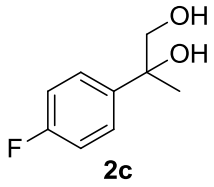


2-phenylpropane-1,2-diol (2a)[6]Prepared according to the general A procedure employing $Acr^{+}MesClO_4^{-}$ (3.7 mg, 0.009 mmol), **1a** (34.9 mg, 0.29 mmol), Sat.$NaHCO_3$ (0.25 mL), MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2a** (39.0 mg, 0.26 mmol, 87% yield) as a colourless oil using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.38-7.31 (m, 2H), 7.29-7.23 m, 1H), 3.75 (d, *J* = 11.2 Hz, 1H), 3.59 (d, *J* = 10.4 Hz, 1H), 2.97 (br s, 1H), 2.42 (br s, 1H), 1.50 (s, .3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 128.3, 127.1, 125.0, 74.8, 70.93, 25.9.



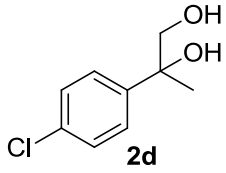
2-(m-tolyl)propane-1,2-diol (2b)[8]Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (3.8 mg, 0.009 mmol), **1b** (38.1 mg, 0.29mmol), Sat.$NaHCO_3$ (0.25 mL),MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2b**(31.5 mg, 0.19mmol, 66% yield) as a white solid using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.19 (m, 3H), 7.11-7.05 (m, 1H), 3.76 (dd, *J* = 10.8, 2.0

Hz, 1H), 3.60 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.79 (s, 1H), 2.36 (s, 3H), 2.16 (brs, 1H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 138.0, 128.3, 127.9, 125.8, 122.0, 74.8, 71.0, 26.0, 21.6.



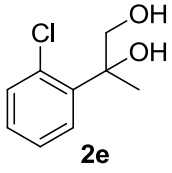
2c

2-(4-fluorophenyl)propane-1,2-diol(2c)[7] Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (4.0 mg, 0.009 mmol), **1c** (42.0 mg, 0.31 mmol), Sat.$NaHCO_3$ (0.25 mL), MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2c**(42.8 mg, 0.25 mmol, 82% yield) as a colourless oil using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.36 (m, 2H), 7.08-6.99 (m, 2H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.63-3.54 (m, 1H), 2.94 (br s, 1H), 2.37 br (s, 1H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 244.0 Hz), 140.7 (d, *J* = 3.2 Hz), 126.8 (d, *J* = 7.9 Hz), 115.09 (d, *J* = 21.1 Hz), 74.5, 70.9, 26.1 ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.92.



2d

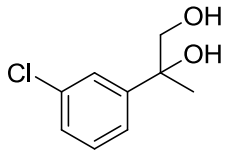
2-(4-chlorophenyl)propane-1,2-diol (2d) [8] Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.6 mg, 0.009 mmol), **1d** (48.0 mg, 0.31 mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2d**(52.5 mg, 0.28 mmol, 90% yield) as a yellow oil using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 4H), 3.70 (d, *J* = 11.2 Hz, 1H), 3.57 (d, *J* = 11.2 Hz, 1H), 3.06 (br s, 1H), 2.54 (br s, 1H), 1.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.0, 128.4, 126.6, 74.6, 70.7, 25.9.



2e

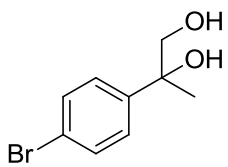
2-(2-chlorophenyl)propane-1,2-diol (2e) Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (5.9 mg, 0.015mmol), **1e** (45.9 mg,

0.30mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2e**(28.8 mg, 0.15mmol, 51% yield) as a yellow oil using PE/EA (3:1) as eluent.IR *v*3408,2928, 1466, 1431, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.35 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29 (td, *J* = 7.6, 1.6 Hz, 1H), 7.21 (td, *J* = 7.6, 2.0 Hz, 1H), 4.27 (d, *J* = 11.2 Hz, 1H), 3.81 (d, *J* = 10.8 Hz, 1H), 3.27 (s, 1H), 2.08 (brs, 1H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 131.3, 130.8, 128.8, 128.6, 127.1, 75.4, 68.1, 23.9; HRMS (EI-TOF) Calcd for C_9H_9OCl $[M-H_2O]^+$:168.0342; Found 168.0342.



2f

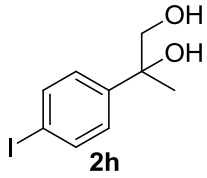
2-(3-chlorophenyl)propane-1,2-diol (2f) Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (5.9 mg, 0.015 mmol), **1f** (45.9 mg, 0.30 mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2f**(28.8 mg, 0.15 mmol, 51% yield) as a yellow oil using PE/EA (3:1) as eluent. IR *v* 3372, 2928, 2360, 1470, 1417, 1046 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.33-7.22 (m, 3H), 3.75 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.61 (dd, *J* = 10.8, 6.8 Hz, 1H), 2.82 (s, 1H), 2.13 (br s, 1H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 134.4, 129.7, 127.3, 125.6, 123.3, 74.6, 70.8, 26.0; HRMS (EI-TOF) Calcd for C_9H_9OCl $[M-H_2O]^+$:168.0342; Found 168.0339.



2g

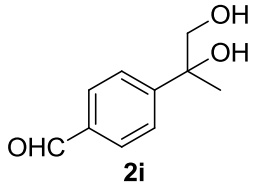
2-(4-bromophenyl)propane-1,2-diol (2g) [9] Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.9 mg, 0.009 mmol), **1g** (62.0 mg, 0.31 mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and

PPh_3(ca. 1 equiv.) to afford **2g**(63.4 mg, 0.27 mmol, 87% yield) as a yellow oil using PE/EA (3:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.70 (d, *J* = 11.2 Hz, 1H), 3.56 (dd, *J* = 10.4, 4.0 Hz, 1H), 2.98 (br s, 1H), 2.43 (br s, 1H), 1.47 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 131.4, 127.0, 121.1, 74.6, 70.7, 25.9.



2h

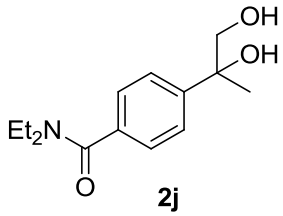
2-(4-iodophenyl)propane-1,2-diol (2h) Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.5 mg, 0.009 mmol), **1h** (73.9 mg, 0.30mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2h**(42.0 mg, 0.15mmol, 50% yield) as a yellow oil using PE/EA (2:1) as eluent. IR *v*3384, 2927, 1586, 1391, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.22-7.13 (m, 2H), 3.70 (d, *J* = 10.4 Hz, 1H), 3.63-3.51 (m, 1H), 3.01–2.69 (m, 1H), 2.45–2.01 (m, 1H), 1.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 137.4, 127.2, 92.8, 74.6, 70.7, 25.9; HRMS (EI-TOF) Calcd for $C_9H_{11}IO_2$ $[M]^+$:277.9804; Found 277.9804.



2i

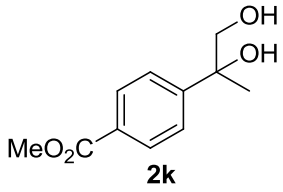
4-(1,2-dihydroxypropan-2-yl)benzaldehyde (2i) Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (4.0 mg, 0.009 mmol), **1i** (44.3 mg, 0.30mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL). and PPh_3 (ca. 1 equiv.) to afford **2i**(28.3 mg, 0.16mmol, 52% yield) as a white solid using PE/EA (1:1) as eluent. IR *v* 3409, 2924, 2856, 1695, 1608, 1216, 1045 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 3.73 (d, *J* = 10.8 Hz, 1H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.01 (brs, 1H), 2.36 (brs, 1H), 1.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

192.1, 152.2, 135.2, 129.8, 125.9, 74.9, 70.7, 26.0; HRMS (EI-TOF) Calcd for $C_{10}H_{10}O_2$ $[M-H_2O]^+$:162.0681; Found 162.0681.



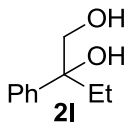
2j

4-(1,2-dihydroxypropan-2-yl)-N,N-diethylbenzamide (2j) Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.7 mg, 0.009 mmol), **1j** (66.0 mg, 0.30 mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2j**(44.1 mg, 0.18 mmol, 58% yield) as a colorless oil using DCM/MeOH (20:1) as eluent.IR *v* 3412, 2976, 2933, 1607, 1437, 1289, 1101, 1046 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.65 (s, 1H), 3.61–3.40 (m, 5H), 3.26 (d, *J* = 5.6 Hz, 2H), 1.44 (s, 3H), 1.29-1.17 (m, 3H), 1.16-1.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 146.8, 135.2, 126.0, 125.3, 74.4, 70.5, 43.3, 39.3, 25.7, 14.1, 12.8; HRMS (EI-TOF) Calcd for $C_{14}H_{21}NO_3$ $[M]^+$:251.1521; Found 251.1526.

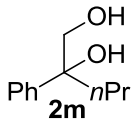


2k

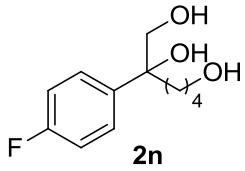
methyl 4-(1,2-dihydroxypropan-2-yl)benzoate (2k) [10] Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.9 mg, 0.009 mmol), **1k** (54.5 mg, 0.31 mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2k** (35.6 mg, 0.17 mmol, 55% yield) as a colorless oil using PE/EA (20:1) as eluent. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H), 3.78 (d, *J* = 11.2 Hz, 1H), 3.65 (d, *J* = 10.8 Hz, 1H), 3.01 (br s, 1H), 2.34 (br s, 1H), 1.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 150.3, 129.6, 128.9, 125.2, 74.9, 70.7, 52.1, 25.9.



2-phenylbutane-1,2-diol (2l)[8]Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (3.7 mg, 0.009 mmol), **1l** (40.0 mg, 0.30mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2l** (43.2 mg, 0.26mmol, 86% yield) as a colorless oil using PE/EA (4:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.31 (m, 4H), 7.29-7.22 (m, 1H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.65 (d, *J* = 10.4 Hz, 1H), 2.82 (br s, 1H), 2.24 (brs, 1H), 1.89-1.71 (m, 2H), 0.74 (t, *J* = 7.6 Hz, 31H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 128.3, 126.9, 125.6, 77.5, 70.3, 31.1, 7.4.

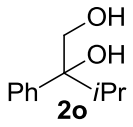


2-phenylpentane-1,2-diol (2m)[11]Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (3.9 mg, 0.009 mmol), **1m** (41.8 mg, 0.29mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2m** (42.9 mg, 0.24mmol, 83% yield) as a colorless oil using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 4H), 7.28-7.21 (m, 1H), 3.77 (dd, *J* = 11.2, 2.4 Hz, 1H), 3.63 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.93 (s, 1H), 2.32 (s, 1H), 1.81-1.63 (m, 2H), 1.37-1.21 (m, 1H), 1.11-0.95 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 128.3, 126.9, 125.5, 77.3, 70.4, 40.8, 16.3, 14.4.



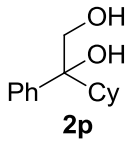
2-(4-fluorophenyl)hexane-1,2,6-triol (2n) Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (4.0 mg, 0.009 mmol), **1n** (58.8 mg, 0.30mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2n** (43.2 mg, 0.20mmol, 67% yield) as a colorless oil using PE/EA (1:1) to methanol as eluent. IR *v* 3375, 2942, 2873, 1604, 1510, 1228, 1059 cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.41-7.32 (m, 2H), 7.04 (dd, *J* = 8.8, 8.4 Hz, 2H), 3.76 (d, *J* = 11.2 Hz, 1H), 3.67 (d, *J* = 11.2 Hz, 1H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.34 (brs, 3H), 1.92-1.71 (m, 2H), 1.54-1.44 (m, 2H), 1.44-1.30 (m, 1H), 1.18-1.02 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 244.1 Hz), 139.1 (d, *J* = 3.2 Hz), 127.2 (d, *J* = 8.0 Hz), 115.2 (d, *J* = 21.1 Hz), 76.9, 70.5, 62.3, 37.9, 32.5, 19.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.08; HRMS (EI-TOF) Calcd for $C_{12}H_{13}FO$ $[M-2H_2O]^+$:192.0950; Found 192.0947.



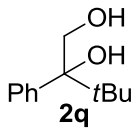
2o

3-methyl-2-phenylbutane-1,2-diol (2o)[8]Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.5 mg, 0.008mmol), **1o** (43.0 mg, 0.29mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2o** (44.9 mg, 0.25mmol, 85% yield) as a colorless oil using PE/EA (4:1)as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.30 (m, 4H), 7.29-7.21(m, 1H), 3.94 (d, *J* = 11.6Hz, 1H), 3.77 (dd, *J* = 10.8, 7.6 Hz, 1H), 2.78 (s, 1H), 2.08-1.94 (m, 1H), 1.87 (brs, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 128.1, 126.9, 126.2, 79.2, 68.2, 35.1, 17.3, 16.7.



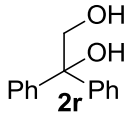
2p

1-cyclohexyl-1-phenylethane-1,2-diol (2p) [12] Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.8 mg, 0.009mmol), **1p** (54.9 mg, 0.29 mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL)and PPh_3 (ca. 1 equiv.) to afford **2p** (48.4 mg, 0.22mmol, 75% yield) as a white solid using PE/EA (5:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.31 (m, 4H), 7.30-7.23 (m, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.83 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.72 (s, 1H), 1.88-1.54 (m, 6H), 1.43 (d, *J* = 12.4 Hz, 1H), 1.29 -0.90 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 128.1, 126.9, 126.1, 79.2, 68.1, 45.5, 27.2, 26.8, 26.6, 26.4, 26.3.



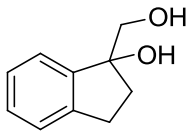
2q

3,3-dimethyl-2-phenylbutane-1,2-diol (2q) Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (3.9 mg, 0.009 mmol), **1q** (47.6 mg, 0.30mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2q** (59.7 mg, 0.30mmol, 99% yield) as a colorless oil using PE/EA (3:1) as eluent.IR *v* 3444, 2962, 2360, 1478, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.29-7.23 (m, 1H), 4.28 (d, *J* = 11.2 Hz, 1H), 3.81 (dd, *J* = 10.8, 9.6 Hz, 1H), 2.89 (br s, 1H), 1.54 (br s, 1H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 127.8, 127.6, 126.9, 80.9, 65.2, 36.7, 25.8; HRMS (EI-TOF) Calcd for $C_{12}H_{16}O$ $[M-H_2O]^+$:176.1201; Found 176.1200.



2r

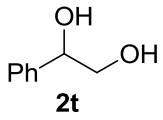
1,1-diphenylethane-1,2-diol(2r)[13]Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (4.0 mg, 0.009 mmol), **1r** (53.5 mg, 0.30 mmol), Sat.$NaHCO_3$ (0.25 mL) MeCN (2.75 mL)and PPh_3 (ca. 1 equiv.) to afford **2r** (49.1 mg, 0.23 mmol, 77% yield) as a white solid using PE/EA (3:1) as eluent. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.40 (m, 4H), 7.38-7.30 (m, 4H), 7.30-7.23 (m, 2H), 4.15 (d, *J* = 6.0 Hz, 2H), 3.23 (s, 1H), 1.95 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 128.4, 127.4, 126.4, 78.5, 69.4.



2s

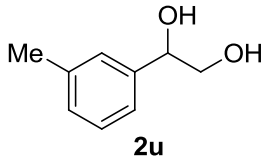
1-(hydroxymethyl)-2,3-dihydro-1H-inden-1-ol (2s)[14]Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (3.6 mg, 0.009 mmol), **1s** (44.4 mg, 0.34mmol), Sat.KH_2PO_4(0.25 mL) MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2s** (25.5 mg, 0.16mmol, 46% yield) as a white solid using PE/EA (3:1) as

eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.8 Hz, 1H), 7.31-7.21 (m, 3H), 3.73 (d, *J* = 11.2 Hz, 1H), 3.63 (d, *J* = 10.8 Hz, 1H), 3.02 (ddd, *J* = 16.0, 8.8, 3.6 Hz, 1H), 2.84 (dt, *J* = 16.0, 8.0 Hz, 1H), 2.50 (brs, 1H), 2.48-2.39 (m, 1H), 2.25 (brs, 1H), 2.06 (dt, *J* = 13.2, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 143.4, 128.8, 126.8, 125.1, 123.4, 83.7, 68.1, 37.2, 29.2.



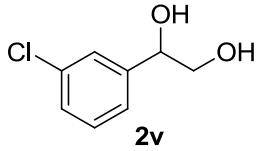
2t

1-phenylethane-1,2-diol (2t)[7]Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (3.9 mg, 0.009 mmol), **1t** (35.3 mg, 0.34mmol), Sat. $NaHCO_3$ (0.25 mL) MeCN (2.75 mL)and PPh_3 (ca. 1 equiv.) to afford **2t** (36.8 mg, 0.27mmol, 79% yield) as a yellow solid using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 5H), 4.82-4.74 (m, 1H), 3.77-3.67 (m, 1H), 3.67-3.56 (m, 1H), 3.42 (br s, 1H), 3.02 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 128.5, 127.9, 126.0, 74.7, 68.0.



2u

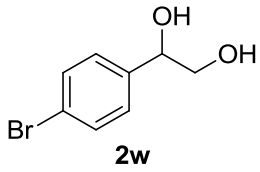
1-(m-tolyl)ethane-1,2-diol (2u)[13]Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (3.5 mg, 0.008mmol), **1u** (35.4 mg, 0.30mmol), Sat. $NaHCO_3$ (0.25 mL) MeCN (2.75 mL)and PPh_3 (ca. 1 equiv.) to afford **2u** (31.4 mg, 0.21mmol, 69% yield) as a colorless olil using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 15.2, 7.6 Hz, 1H), 7.16-7.06 (m, 3H), 4.79-4.69 (m, 1H), 3.74-3.66 (m, 1H), 3.65-3.57 (m, 1H), 3.44 (br s, 1H), 3.08 (br s, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.1, 128.7, 128.4, 126.7, 123.1, 74.7, 68.0, 21.4.



2v

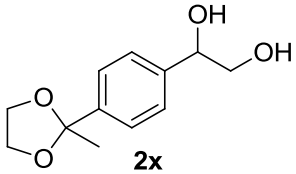
1-(3-chlorophenyl)ethane-1,2-diol (2v) [15] Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (4.0 mg, 0.009mmol),

1v(42.0 mg, 0.30mmol), Sat. $NaHCO_3$ (0.25 mL), MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2v** (25.1 mg, 0.15mmol, 48% yield) as a yellow oli using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.32-7.17 (m, 3H), 4.84-4.70 (m, 1H), 3.81-3.67 (m, 1H), 3.66-3.54 (m, 1H), 3.25 (br s, 1H), 2.62 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 134.5, 129.8, 128.1, 126.2, 124.2, 74.0, 67.8.



2w

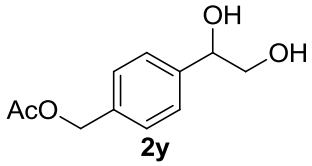
1-(4-bromophenyl)ethane-1,2-diol (2w)[7]Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.7 mg, 0.009mmol), **1w** (54.5 mg, 0.30mmol), Sat. $NaHCO_3$ (0.25 mL), MeCN (2.75 mL). and PPh_3 (ca. 1 equiv.) to afford **2w** (33.8 mg, 0.16 mmol, 52% yield) as a white solid using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.29-7.21 (m, 2H), 4.83-4.71 (m, 1H), 3.81-3.67 (m, 1H), 3.67-3.55 (m, 1H), 2.72 (s, 1H), 2.19 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 131.6, 127.8, 121.8, 74.0, 67.9.



2x

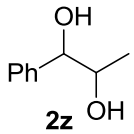
1-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)ethane-1,2-diol (2x) Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.9 mg, 0.009mmol), **1x** (60.2 mg, 0.32mmol), Sat. $NaHCO_3$ (0.25 mL),MeCN (2.75 mL)and PPh_3 (ca. 1 equiv.) to afford **2x** (51.9 mg, 0.23 mmol, 73% yield) as a white solid using PE/EA (3:2) as eluent. IR *v* 3318, 2926, 1730, 1251, 1193, 1079, 1037 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.84-4.78 (m, 1H), 4.09-3.97 (m, 1H), 3.82-3.71 (m, 3H), 3.70-3.60 (m, 1H), 2.82 (br s, 1H), 2.38

(s, 1H), 1.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 140.1, 126.0, 125.5, 108.7, 74.4, 68.0, 64.4, 27.5; HRMS (EI-TOF) Calcd for $C_{11}H_{11}O_3$ $[M-H_2O-CH_3]^+$:191.0708; Found 191.0709.



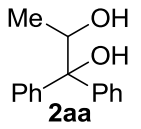
2y

4-(1,2-dihydroxyethyl)benzyl acetate (2y). Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (3.9 mg, 0.009mmol), **1y** (51.1mg, 0.29mmol), Sat. $NaHCO_3$ (0.25 mL),MeCN (2.75 mL)and PPh_3 (ca. 1 equiv.) to afford **2y**(38.6 mg, 0.18mmol, 63% yield) as a colorless oil using PE/EA (1:1) as eluent. IR *v* 3405, 2925, 1736, 1379, 1235, 1078, 1031 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 4H), 5.09 (s, 2H), 4.85-4.76 (m, 1H), 3.80-3.69 (m, 1H), 3.68-3.58 (m, 1H), 2.89 (br s, 1H), 2.42 (br s, 1H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 140.6, 135.6, 128.4, 126.3, 74.3, 68.0, 66.0, 21.0; HRMS (EI-TOF) Calcd for $C_{11}H_{12}O_3$ $[M-H_2O]^+$:192.0786; Found 192.0786.



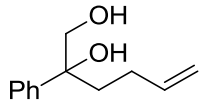
2z

1-phenylpropane-1,2-diol[6] **(2z)**Prepared according to the general procedure A employing $Acr^+MesClO_4^-$ (4.0 mg, 0.009mmol), **1z** (35.7 mg, 0.30mmol), Sat. $NaHCO_3$ (0.25 mL),MeCN (2.75 mL)and PPh_3 (ca. 1 equiv.) to afford **2z** (30.5 mg, 0.20 mmol, 66% yield, *dr*1.9/1) as a colorless oil using PE/EA (3:2) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 5H), 4.69-4.63 (m, 0.55 H), 4.36 (dd, *J* = 7.2, 1.6 Hz, 0.43 H), 4.05-3.90 (m, 0.55H), 3.89-3.80 (m, 0.44H), 2.83 (br s, 0.41H), 2.66 (br, s 0.41H), 2.58 (br s, 0.53H), 2.05 (br s, 0.52 H), 1.08 (d, *J* = 6.4 Hz, 1.64 H), 1.05 (d, *J* = 6.4 Hz, 1.33 H).



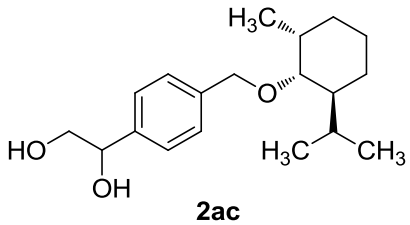
2aa

1,1-diphenylpropane-1,2-diol (2aa)[16]Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (3.9 mg, 0.009 mmol), **1aa** (60.9 mg, 0.31 mmol), Sat. $NaHCO_3$ (0.25 mL),MeCN (2.75 mL)and PPh_3 (ca. 1 equiv.) to afford **2aa** (43.3 mg, 0.19 mmol, 61% yield) as a white solid using PE/EA (5:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.38-7.22 (m, 5H), 7.22-7.14 (m, 1H), 4.86-4.73 (m, 1H), 3.05 (d, *J* = 1.2 Hz, 1H), 1.94 (s, 1H), 1.09 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 143.8, 128.6, 128.1, 127.2, 126.7, 126.2, 125.5, 79.8, 71.6, 16.6.



2ab

2-phenylhex-5-ene-1,2-diol (**2ab**). Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (4.0 mg, 0.009 mmol), **1ab** (43.6 mg, 0.27 mmol), Sat. $NaHCO_3$ (0.25 mL), MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2ab** (24.6 mg, 0.13 mmol, 46% yield) as a colorless oil using PE/EA (3:1) as eluent. IR *v* 3409, 2930, 1736, 1379, 1235, 1078, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 4H), 7.30-7.24 (m, 1H), 5.83-5.70 (m, 1H), 4.99-4.88 (m, 1H), 3.81 (d, *J* = 11.2 Hz, 1H), 3.68 (d, *J* = 11.2 Hz, 1H), 2.83 (brs, 1H), 2.13-2.02 (m, 1H), 2.02-1.76 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 138.6, 128.4, 127.1, 125.5, 114.6, 77.2, 70.6, 37.4, 27.5; HRMS (EI-TOF) Calcd for $C_{12}H_{16}O_2$ $[M+H]^+$:193.1229; Found 193.1220.

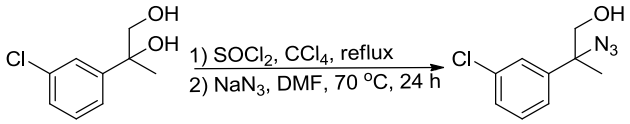


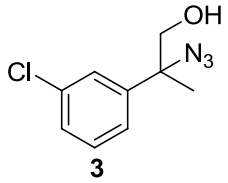
2ac

1-(4-((((1R,2S,6R)-2-isopropyl-6-methylcyclohexyl)oxy) methyl)phenyl)ethane-1,2-diol (2ac) Prepared according to the general procedure A employing $Acr^{+}MesClO_4^{-}$ (4.0 mg, 0.009mmol), **1ac** (79.5 mg, 0.29mmol), Sat. $NaHCO_3$ (0.25 mL), MeCN (2.75 mL) and PPh_3 (ca. 1 equiv.) to afford **2ac** (45.6 mg, 0.15 mmol, 51% yield) as a colorless oil using PE/EA (2:1) as

eluent.IR *v* 3389, 2952, 2923, 2867, 1456, 1077 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 4H), 4.77 (d, *J* = 6.0 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.2 Hz, 1H), 3.69 (d, *J* = 10.4 Hz, 1H), 3.64-3.53 (m, 1H), 3.17 (td, *J* = 10.8, 4.0 Hz, 1H), 2.85 (br s, 1H), 2.43 (br s, 1H), 2.33-2.23 (m, 1H), 2.18 (d, *J* = 12.0 Hz, 1H), 1.71-1.56 (m, 1H), 1.45-1.21 (m, 2H), 1.04-0.79 (m, 8H), 0.71 (d, *J* = 6.8z, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 138.8, 128.1, 126.0, 78.9, 74.4, 70.1, 68.0, 48.2, 40.3, 34.5, 31.5, 25.5, 23.2, 22.3, 21.0, 16.0; HRMS (EI-TOF) Calcd for $C_{18}H_{27}O_2$ $[M\text{-}CH_2OH]^+$:275.2011; Found 275.2012.

III. Transformations of vicinal alcohols

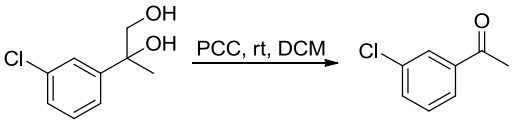


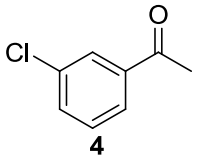


3

2-azido-2-(3-chlorophenyl)propan-1-ol (3). To a 50 mL overdried flask was added **2f** (57.5 mg, 0.31 mmol), CCl_4 (1.5 mL) and $SOCl_2$ (161 uL) under N_2 atmosphere. The mixture was refluxed for 1 h. After cooled to room temperature, the mixture was washed by saturated $NaHCO_3$ and brine. The organic phase was dried and concentrated under reduced pressure to give the crude cyclic sulfite, which was transferred to a flask containing NaN_3 (50.0 mg, 0.77 mmol) and DMF (2 mL). The reaction was refluxed overnight. After being cooled to room temperature, the reaction was quenched by diluted H_2SO_4, H_2O and saturated $NaHCO_3$. The combined organic layers was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by column chromatography using PE/EA (10:1) as eluent to afford **3** (38.8 mg, 0.18 mmol, 61% yield) as a colorless oil. IR *v* 3378, 2928, 2108, 1472, 1260, 1049 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.42-7.32 (m, 3H), 3.74 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.67 (dd, *J* = 11.2, 7.6 Hz, 1H), 2.01 (br s, 1H), 1.77 (s, 3H); ^{13}C

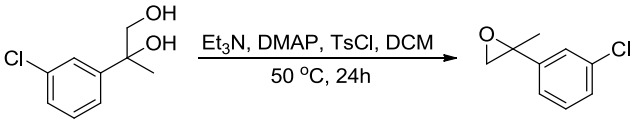
NMR (101 MHz, $CDCl_3$) δ 143.0, 134.7, 130.0, 128.1, 126.4, 124.2, 70.4, 67.3, 21.3; HRMS (ESI-TOF) Calcd for $C_9H_{11}ClN_3O$ $[M+H]^+$:212.0591; Found 212.0593.

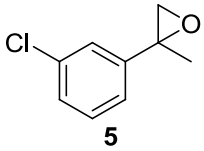




4

1-(3-chlorophenyl)ethanone (4)[17]To a 50 mL flask was added **2f** (59.5 mg, 0.32 mmol), PCC (129.3 mg, 0.6 mmol) and DCM (10 mL). The mixture was stirred overnight at room temperature. The reaction mixture was diluted with Et_2O, filtered through a short pad of silica gel, concentrated under reduced pressure and purified through column chromatography using PE/EA (20:1) to afford **4** (24.5 mg, 0.16 mmol, 51% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.60 (s, 3H).

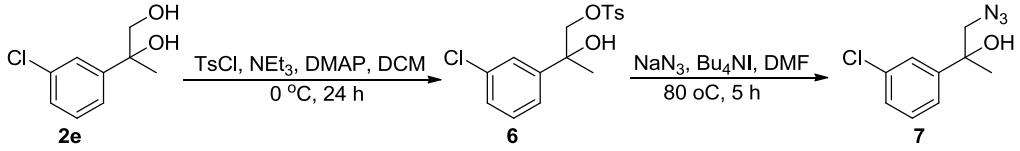




5

2-(3-chlorophenyl)-2-methyloxirane (5).[18]To a 50 mL over-dried flask, cooled under N_2 atmosphere, was added **2f** (58.8 mg, 0.31 mmol), DCM (4 mL) and NEt_3 (0.46 mL, 3.4 mmol). The mixture was cooled to 0 ^{o}C and then TsCl (70.2 mg, 0.37 mmol) and DMAP (4.9 mg, 0.04 mmol). The reaction was warmed to 50 ^{o}C and stirred for 24 h. After being cooled to room temperature, H_2O (3 mL) was added to quenched the reaction. The mixture was extracted by DCM. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated and purified by column chromatography to afford **5** (32.5 mg, 0.19 mmol, 61% yield) as a colorless oil using PE/EA (50:1) as eluent. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.30-7.22 (m, 3H), 2.97 (d, *J* = 5.6 Hz, 1H), 2.77 (d, *J* = 5.6 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 134.4, 129.6, 127.6, 125.6, 123.5, 57.0, 56.3, 21.6.



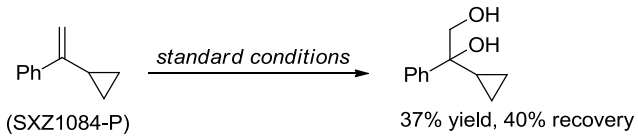
2e **6** **7**

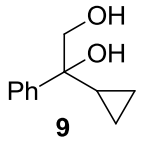
To a 50 mL over-dried flask, cooled under N_2 atmosphere, were added **2f** (55.8 mg, 0.30 mmol), DCM (3.5 mL) and NEt_3（48 uL, 0.36 mmol）. The mixture was cooled to 0 ^oC,TsCl (69.0 mg, 0.36 mmol) and DMAP (6.1 mg, 0.05 mmol) were added. Then the reaction was stirred overnight at 0 ^oC. H_2O was added to quench the the reaction and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography to afford **6** (72.5 mg, 0.21 mmol, 71% yield) as a colorless oil using PE/EA (5:1) as eluents. IR *v* 3524, 2985, 1597, 1360, 1179 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 3H), 7.23 (s, 3H), 4.07 (d, *J* = 10.0 Hz, 1H), 4.05 (d, *J* = 10.4 Hz, 1H), 2.72 (s, 1H), 2.44 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 134.3, 132.1, 129.9, 129.6, 127.8, 127.7, 125.4, 123.2, 76.3, 72.9, 26.0, 21.6; HRMS (ESI-TOF) Calcd for $C_{16}H_{18}ClO_4S$ $[M+H]^+$:341.0614; Found 341.0616.

To a 50 mL over-dried flask, cooled under N_2 atmosphere, were added **6** (71.2 mg, 0.21 mmol), DMF (2 mL), NaN_3 (48.2 mg, 0.74 mmol) and Bu_4NI (12.1 mg, 0.033 mmol). The mixture was heated to 80 ^oC and stirred overnight. After cooled to room temperature, H_2O was added and extracted with Et_2O. The combined organic layers were washed by H_2O and dried by anhydrous Na_2SO_4. After being filtered, concentrated, the reaction mixture was purified by column chromatography to afford **7** (39.8 mg, 0.19 mmol, 90% yield) as a colorless oil using PE/EA (20:1)

as eluents. IR *v* 3449, 2105, 1573, 1295 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.34-7.23 (m, 3H), 3.58 (d, *J* = 12.4 Hz, 1H), 3.44 (d, *J* = 12.4 Hz, 1H), 2.38 (s, 1H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 134.5, 129.7, 127.6, 125.4, 123.1, 74.3, 61.9, 27.1; HRMS (ESI-TOF) Calcd for $C_9H_{11}ClN_3O$ $[M+H]^+$:212.0591; Found 212.0590.

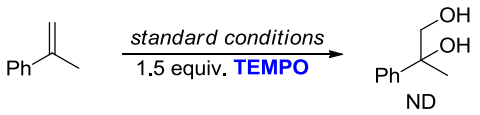
IV. Mechanistic studies





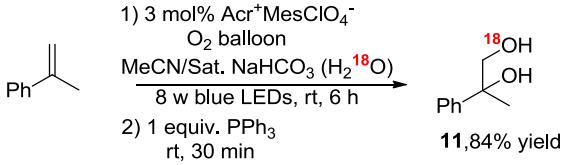
9

1-cyclopropyl-1-phenylethane-1,2-diol (9) To a 50 mL flask, $Acr^+MesClO_4^-$ (3.9 mg, 0.009 mmol), **8** (43.1 mg, 0.30mmol),Sat.$NaHCO_3$ (0.25 mL) and MeCN (2.75 mL) were added sequencely under air. The reaction mixture was irradiated by 8W blue LEDS at a distance of 10 cm for 6 h. To the flask, PPh_3 (1 equiv.) was added and stirred for 30 min at room temperature. The reaction mixture was then diluted with Et_2O and filtered through a short pad of silica using Et_2O and EA. The filtrate was concentrated *in vacuo*and purified by flash chromatography on silica gel to afford **9**(19.7 mg, 0.11 mmol, 37% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.36 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.31-7.24 (m, 1H), 3.94 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.78 (dd, *J* = 11.2, 6.8 Hz, 1H), 2.54 (s, 1H), 1.86 (br s, 1H), 1.14-1.12 (m, 1H), 0.55-.42 (m, 2H), 0.40-0.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 128.2, 127.2, 125.7, 75.1, 70.5, 18.3, 0.8, -0.2

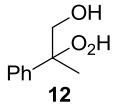


To a 50 mL flask, $Acr^{+}MesClO_4^{-}$ (3.9 mg, 0.009 mmol), **1** (34.9 mg, 0.30mmol), TEMPO (70.8 mg, 0.45 mmol), Sat.$NaHCO_3$ (0.25 mL) and MeCN (2.75 mL) were added sequencely under air. The reaction mixture was irradiated by 8W blue LEDS at a distance of 10 cm for 6 h. To the flask, PPh_3 (1 equiv.) was added and stirred for 30 min at room temperature. The reaction mixture was then diluted with Et_2O and filtered through a short pad of silica using Et_2O and EA. The filtrate was concentrated *in vacuo* and monitored by ^1H NMR spectroscopy. The results demonstrated that

No **2a** was obtained.



To a 50 mL over-dried flask, $Acr^{+}MesClO_4^{-}$ (3.7 mg, 0.009 mmol), **1** (34.9 mg, 0.3 mmol), Sat.$NaHCO_3$ (0.25 mL, $H_2{}^{18}O$) and MeCN (2.75 mL) were added sequencely under air. The reaction mixture was irradiated by 8W blue LEDS at a distance of 10 cm for 6 h. To the flask, PPh_3 (1 equiv.) was added and stirred for 30 min at room temperature. The reaction mixture was then diluted with Et_2O and filtered through a short pad of silica using Et_2O and EA. The filtrate was concentrated *in vacuo*and purified by flash chromatography on silica gel to afford **11** (38.2 mg, 0.25 mmol, 84% yield) as a colorless oil.HRMS (ESI-TOF) Calcd for $C_9H_{12}O_2$ $[M+Na]^+$:177.0777; Found 177.0772.

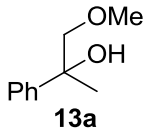


2-hydroperoxy-2-phenylpropan-1-ol (12).[19] Prepared according to the general A

procedure employing $Acr^+MesClO_4^-$ (3.9 mg, 0.009 mmol), **1a** (36.7 mg, 0.31mmol), Sat.$NaHCO_3$ (0.25 mL) and MeCN (2.75 mL). After 6h, the reaction mixture was then diluted with Et_2O and filtered through a short pad of silica using Et_2O and EA. The filtrate was concentrated *in vacuo* and purified by flash chromatography on silica gel to afford **12**(42.7 mg, 0.25mmol, 82% yield) as a colourless oil using PE/EA (2:1) as eluent.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (br s, 1H), 7.47-7.27 (m, 5H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.88 (d, *J* = 12.0 Hz, 1H), 2.61 (br s, 1H), 1.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 128.6, 127.8, 125.6, 86.2, 66.7, 21.7.

V. General Procedures B for Dioxylation of styrenes

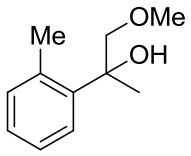
To a 50 mL flask, $Acr^+MesClO_4^-$ (0.015mmol), **1** (0.3 mmol), alcohol (0.5 mL) and MeCN (5.5 mL) were added sequencely under O_2 balloon. The reaction mixture was irradiated by 8W blue LEDS at a distance of 10 cm for 3 h. The reaction mixture was reduced by PPh_3 (0.3 mmol) stirred for 30 min at room temperaturebefore it was purified by flash chromatography on silica gel to afford **13**.



13a

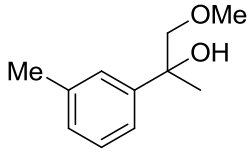
1-methoxy-2-phenylpropan-2-ol (13a) [20] **.**Prepared according to the general procedure B employing **1a** (35.8 mg, 0.30 mmol), $Acr^+MesClO_4^-$ (6.0 mg, 0.015 mmol), 4Å MS (70.7 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh_3 (78.1 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et_2O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford **13a** (31.7 mg, 0.19 mmol, 63% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.28-7.23 (m, 1H), 3.59 (d, *J* = 9.2 Hz, 1H), 3.48 (d, *J* = 9.2 Hz, 1H), 3.37 (s, 3H), 2.93 (s,

1H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 128.1, 126.9, 124.9, 80.7, 73.8, 59.3, 26.7.



13b

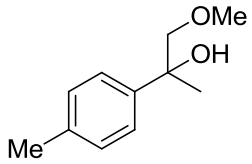
1-methoxy-2-(o-tolyl)propan-2-ol (13b). Prepared according to the general procedure B employing **the** 1-methyl-2-(prop-1-en-2-yl)benzene **13bs** (38.6 mg, 0.29 mmol), $Acr^+MesClO_4^-$ (6.4 mg, 0.015 mmol), 4Å MS (80.7 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh_3 (77.9 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et_2O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford **13b** (24.9 mg, 0.14 mmol, 47% yield) as a yellow oil. IR *v* 3460, 2928, 1455, 1108 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 1H), 7.21-7.12 (m, 3H), 3.84 (d, *J* = 9.2 Hz, 1H), 3.51 (d, *J* = 9.2 Hz, 1H), 3.42 (s, 3H), 2.92 (s, 1H), 2.56 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 136.0, 132.6, 127.2, 126.1, 125.6, 79.3, 74.9, 59.3, 25.8, 22.3; HRMS (EI-TOF) Calcd for $C_{11}H_{16}O_2$ $[M]^+$:180.1150; Found 180.1145.



13c

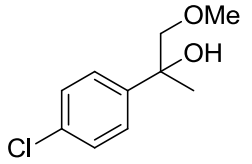
1-methoxy-2-(m-tolyl)propan-2-ol (13c). Prepared according to the general procedure B employing **1b** (38.7 mg, 0.29 mmol), $Acr^+MesClO_4^-$ (6.4 mg, 0.015 mmol), 4Å MS (75.1 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh_3 (80.6 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et_2O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford **13c** (39.7 mg, 0.22 mmol, 75% yield) as a colorless oil. IR *v* 3459, 2926, 1455, 1107 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.24 (d, *J* = 4.8 Hz, 2H), 7.10-7.04 (m, 1H), 3.58 (d,

J= 9.2 Hz, 1H), 3.47 (d, *J* = 9.2 Hz, 1H), 3.38 (s, 3H), 2.89 (s, 1H), 2.36 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 137.7, 128.1, 127.7, 125.6, 121.9, 80.7, 73.8, 59.4, 26.7, 21.6; HRMS (EI-TOF) Calcd for $C_{11}H_{16}O_2$ $[M]^+$:180.1150; Found 180.1150.



13d

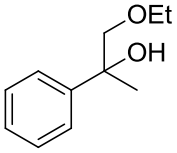
1-methoxy-2-(p-tolyl)propan-2-ol (13d). Prepared according to the general procedure B employing 1-methyl-4-(prop-1-en-2-yl)benzene**13ds** (40.4 mg, 0.30 mmol), $Acr^+MesClO_4^-$ (6.4 mg, 0.015 mmol), 4Å MS (76.4 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh_3 (77.2 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et_2O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford **13d** (33.1 mg, 0.18 mmol, 60% yield) as a colorless oil. IR *v* 3463, 2926, 1453, 1106 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.58 (d, *J* = 9.2 Hz, 1H), 3.46 (d, *J* = 9.2 Hz, 1H), 3.37 (s, 3H), 2.87 (s, 1H), 2.33 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 136.4, 128.8, 124.8, 80.7, 73.7, 59.3, 26.7, 21.0; HRMS (EI-TOF) Calcd for $C_{11}H_{16}O_2$ $[M]^+$:180.1150; Found 180.1154.



13e

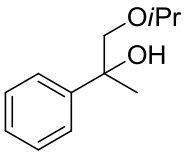
2-(4-chlorophenyl)-1-methoxypropan-2-ol (13e). Prepared according to the general procedure B employing **1d** (46.8 mg, 0.31 mmol), $Acr^+MesClO_4^-$ (6.5 mg, 0.015 mmol), 4Å MS (90.9 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh_3 (80.1 mg, 0.31 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et_2O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an

eluent to afford **13e** (47.0 mg, 0.23 mmol, 76% yield) as a colorless oil. IR *v* 3445, 2930, 1491, 1093 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 3.54 (d, *J* = 9.2 Hz, 1H), 3.45 (d, *J* = 9.2 Hz, 1H), 3.37 (s, 3H), 2.91 (s, 1H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 132.7, 128.2, 126.5, 80.5, 73.5, 59.4, 26.6; HRMS (EI-TOF) Calcd for $C_{10}H_{13}O_2Cl$ $[M]^+$:200.0604; Found 200.0606.



13f

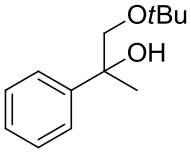
1-ethoxy-2-phenylpropan-2-ol (13f)[20]. Prepared according to the general procedure B employing **1a** (35.7 mg, 0.30 mmol), $Acr^+MesClO_4^-$ (6.3 mg, 0.015 mmol), 4Å MS (70.8 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh_3 (79.3 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et_2O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (30:1) as an eluent to afford **13f** (34.5 mg, 0.19 mmol, 63% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.34 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.25 (t, *J* = 6.4 Hz, 1H), 3.60-3.474 (m, 4H), 2.93 (s, 1H), 1.52 (s, 3H), 1.17 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 128.1, 126.8, 125.0, 78.4, 73.7, 67.0, 26.7, 15.0.



13g

1-isopropoxy-2-phenylpropan-2-ol (13g). Prepared according to the general procedure B employing **1a** (36.7 mg, 0.31 mmol), $Acr^+MesClO_4^-$ (5.8 mg, 0.014 mmol), 4Å MS (70.8 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh_3 (80.0 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et_2O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (30:1) as an eluent to afford **13g** (30.6 mg,

0.16 mmol, 51% yield) as a colorless oil. IR *v* 3455, 2974, 1449, 1372, 1127, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 3.62-3.56 (m, 1H), 3.54 (d, *J* = 8.8 Hz, 1H), 3.49 (d, *J* = 9.2 Hz, 1H), 2.98 (s, 1H), 1.52 (s, 3H), 1.15 (dd, *J* = 6.4 Hz, 3H), 1.12 (dd, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 128.0, 126.8, 125.0, 76.2, 73.6, 72.5, 26.7, 22.00, 21.97; HRMS (EI-TOF) Calcd for $C_{12}H_{18}O_2$ $[M]^+$:194.1307; Found 194.1306.



13h

1-(tert-butoxy)-2-phenylpropan-2-ol (13h). Prepared according to the general procedure B employing **1a** (36.0 mg, 0.30 mmol), $Acr^+MesClO_4^-$ (6.7 mg, 0.016 mmol), 4Å MS (71.0 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh_3 (79.7 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et_2O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford **13h** (21.1 mg, 0.10 mmol, 33% yield) as a colorless oil. IR *v* 3563, 2975, 1365, 1194, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.34 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.27-7.21 (m, 1H), 3.45 (d, *J* = 8.4 Hz, 1H), 3.41 (d, *J* = 8.8 Hz, 1H), 3.06 (s, 1H), 1.51 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 128.0, 126.7, 125.0, 73.4, 73.2, 69.8, 27.5, 26.6; HRMS (EI-TOF) Calcd for $C_{13}H_{20}O_2$ $[M]^+$:208.1463; Found 208.1459.

VII.Reference

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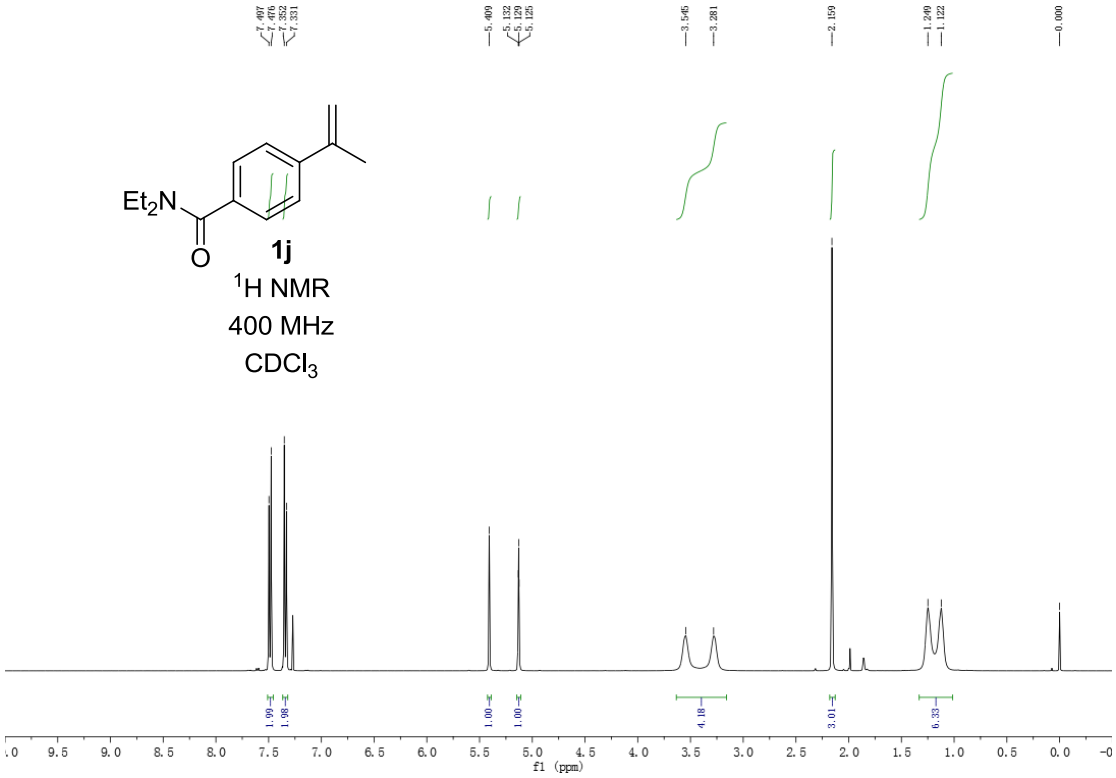
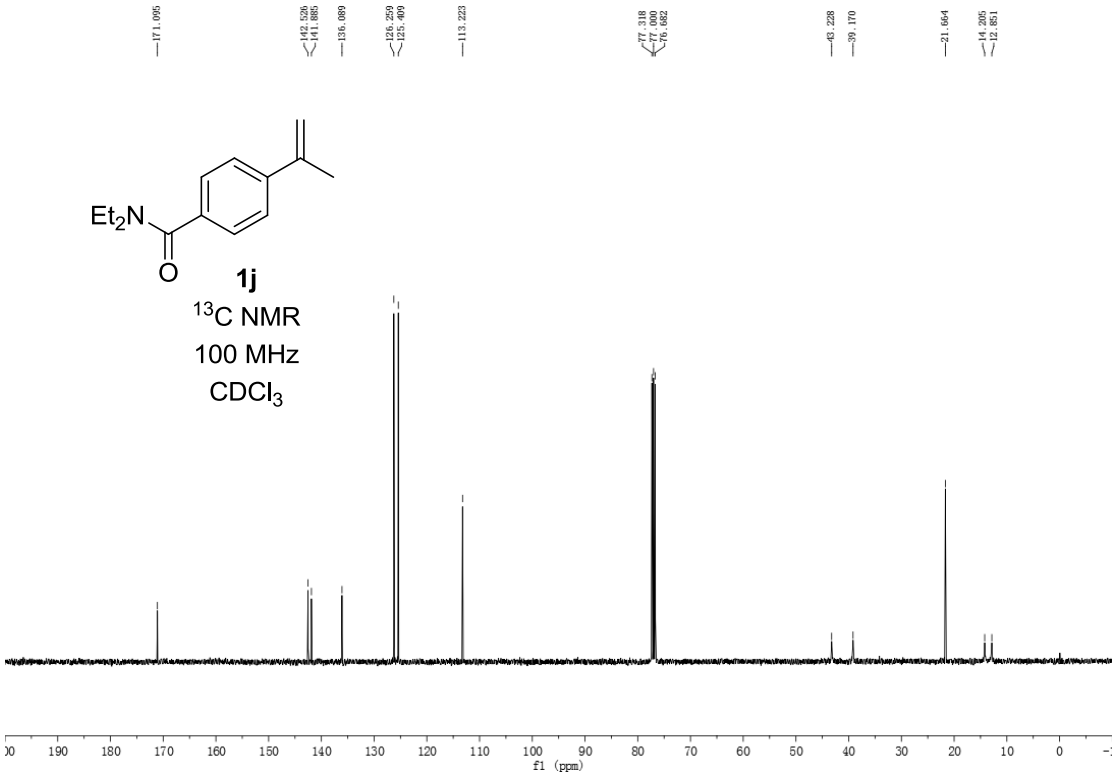
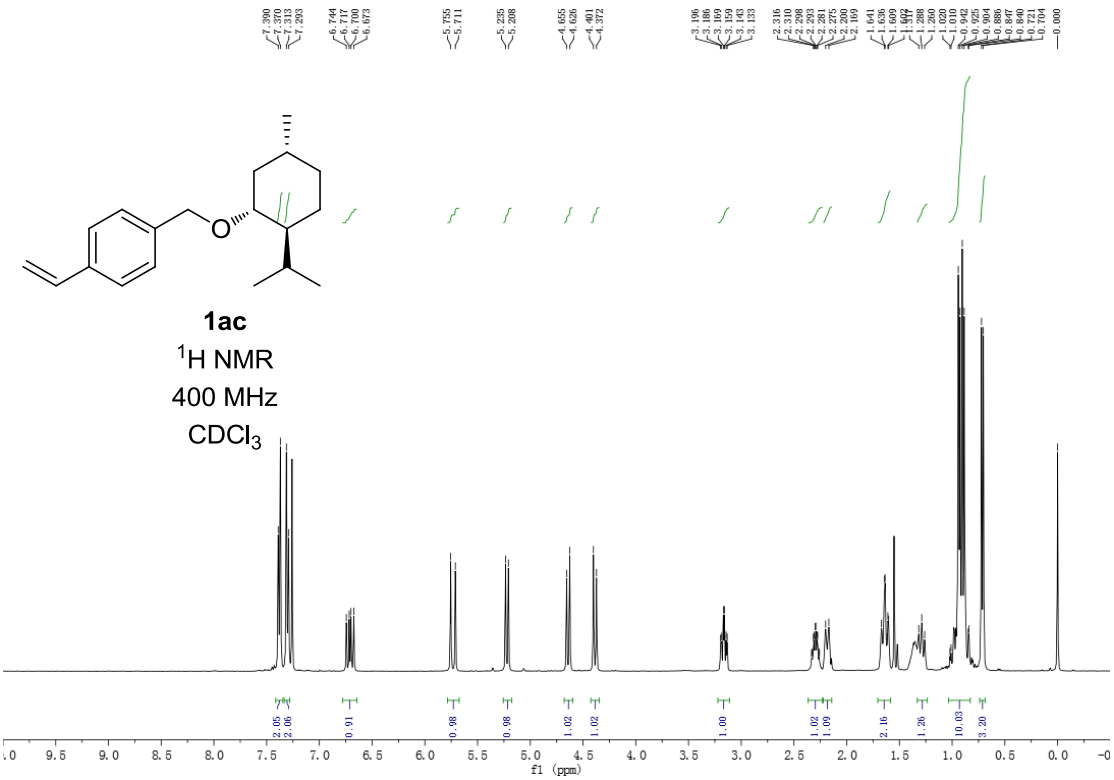
VIII. NMR Spectra



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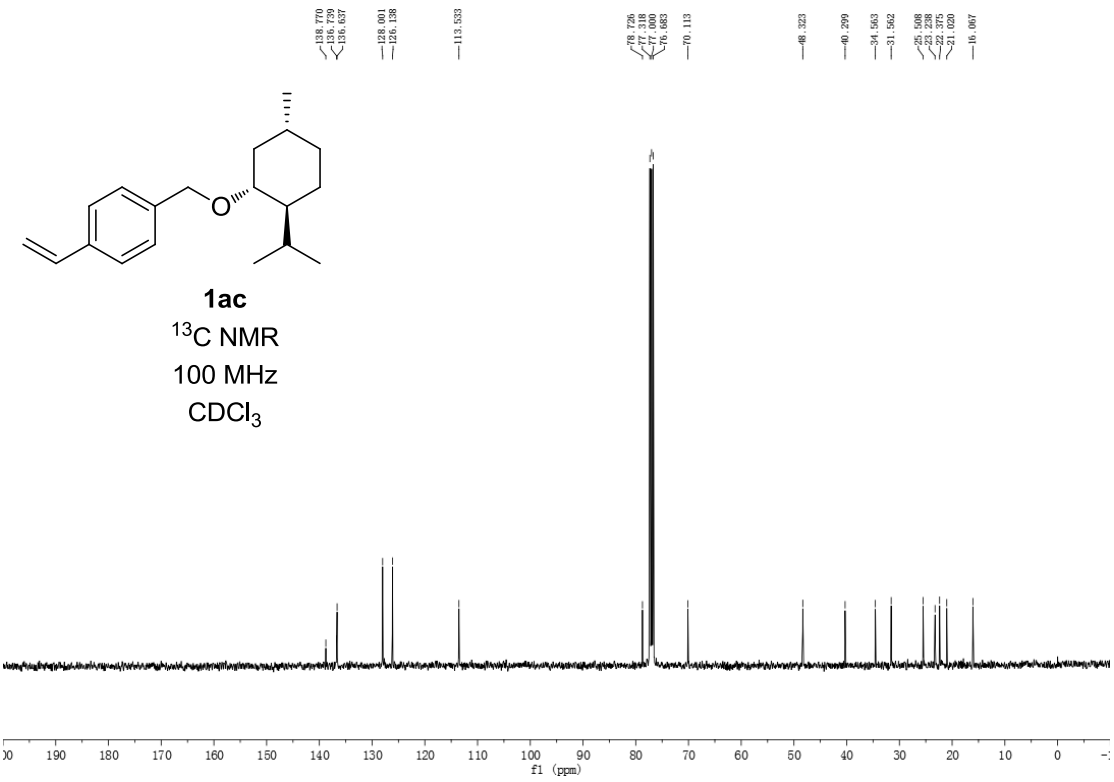
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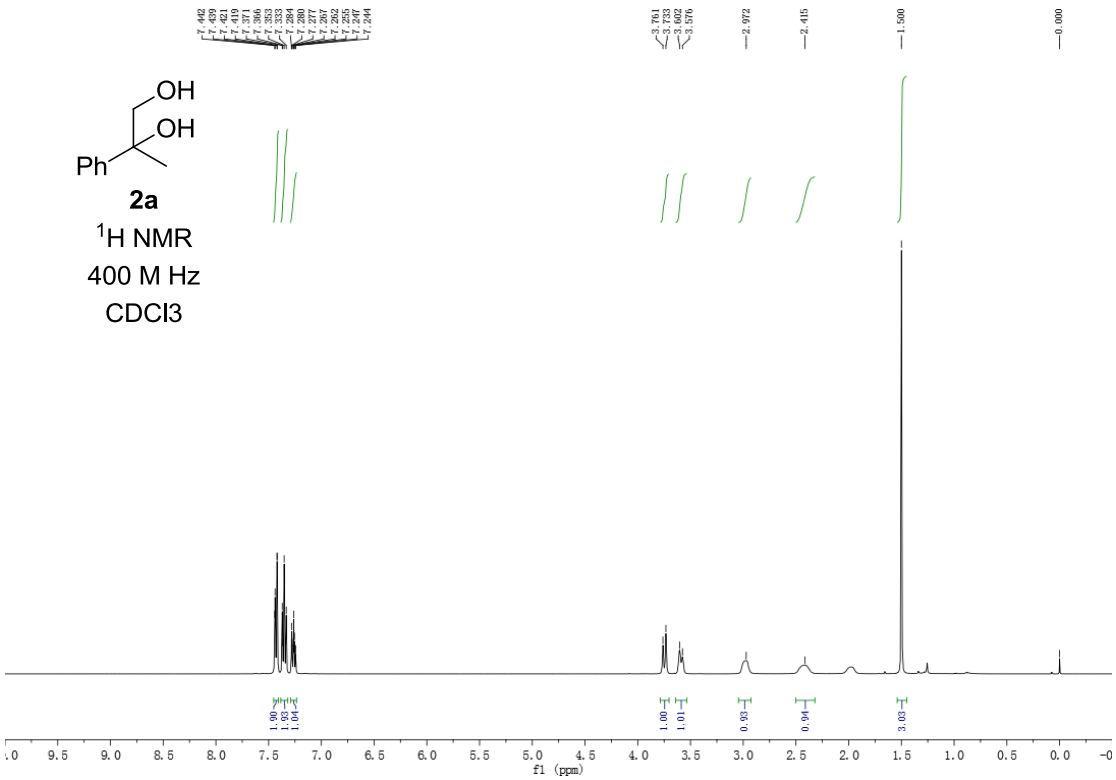
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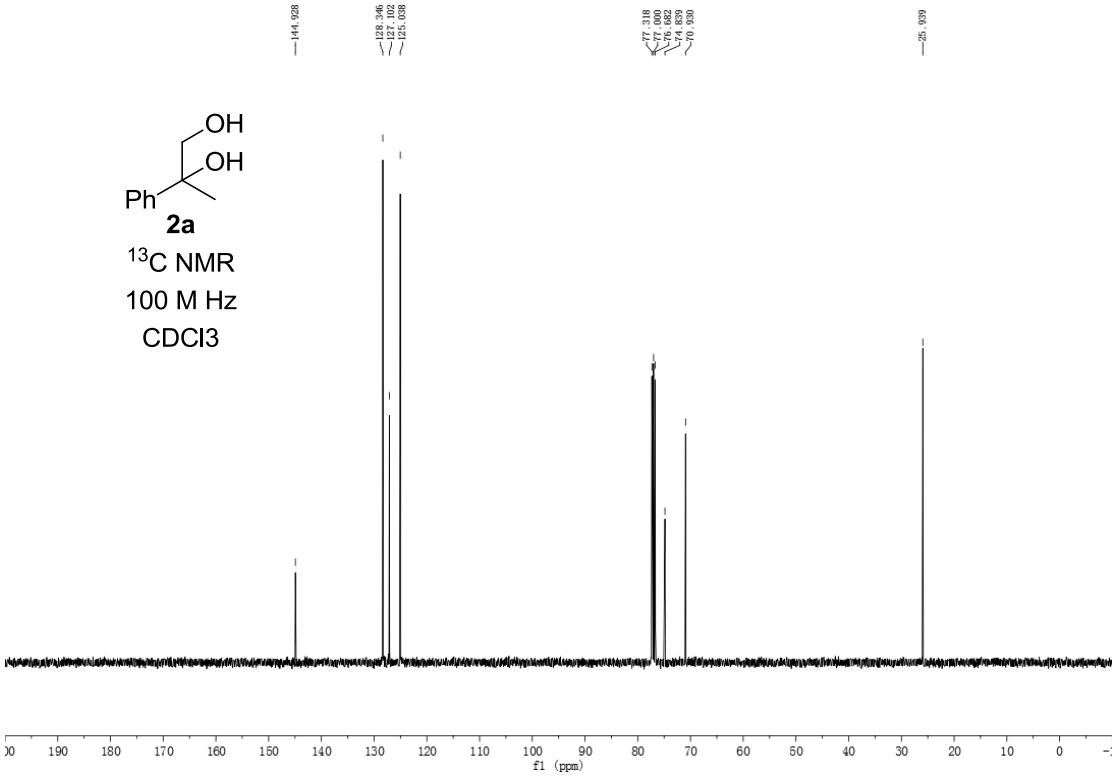
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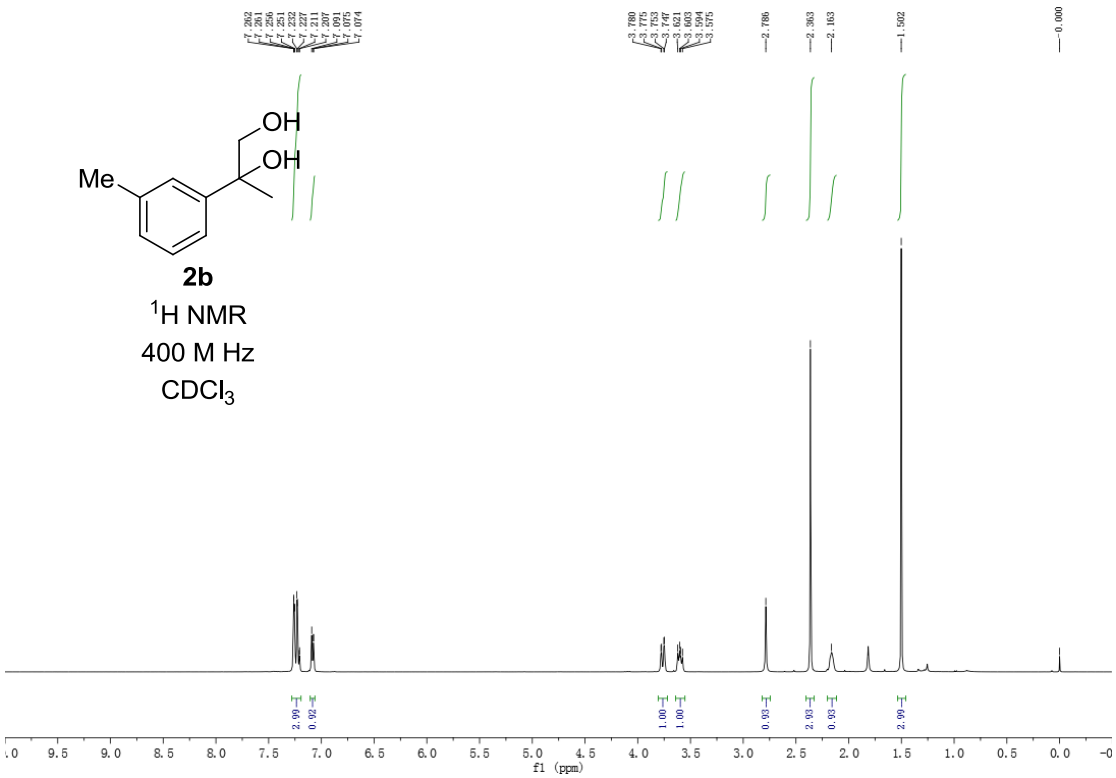
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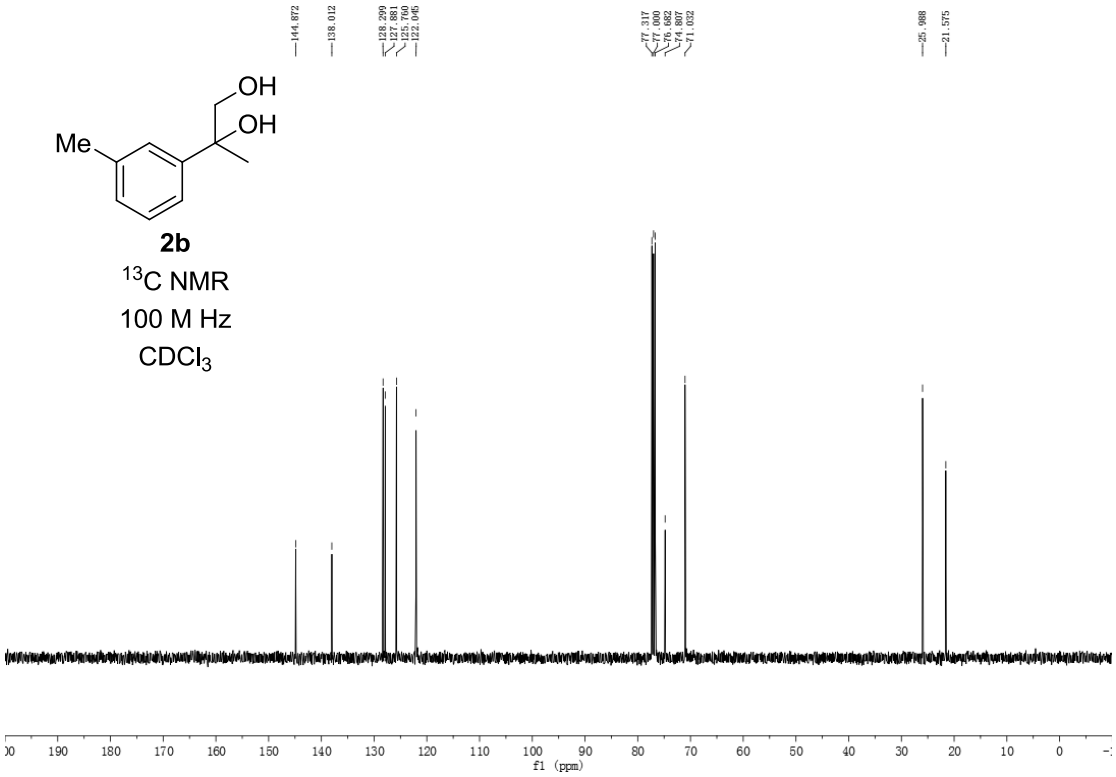
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2b
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100 M Hz
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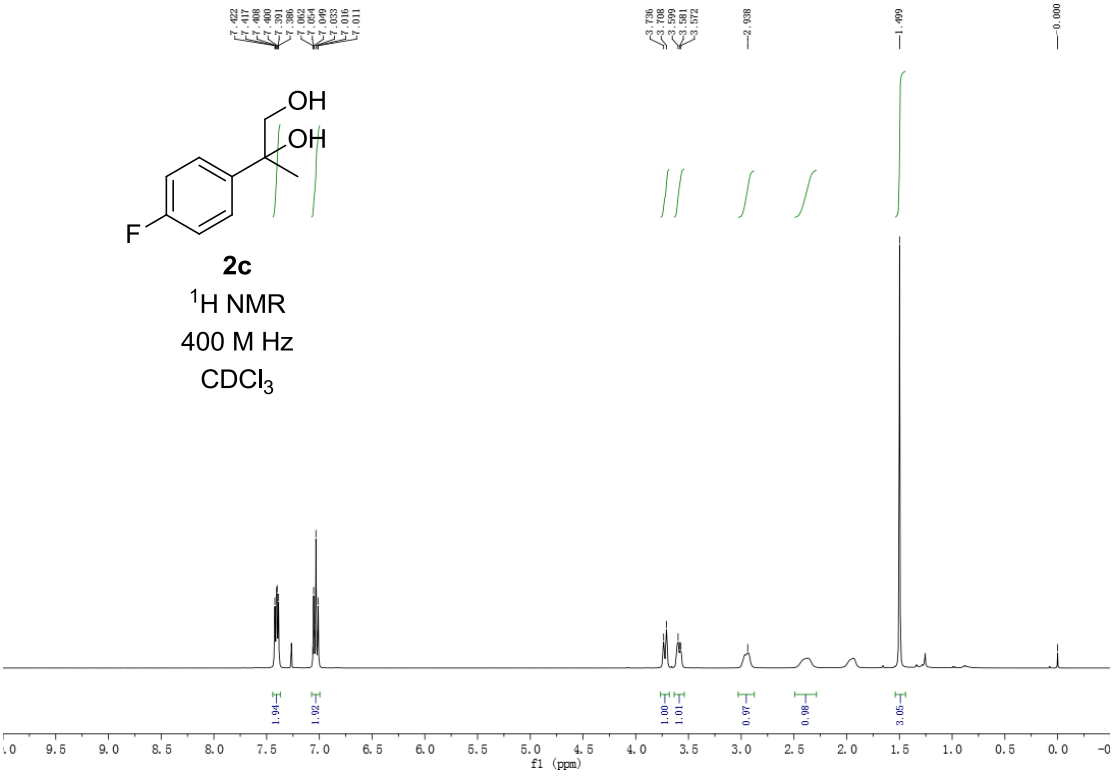
f1 (ppm)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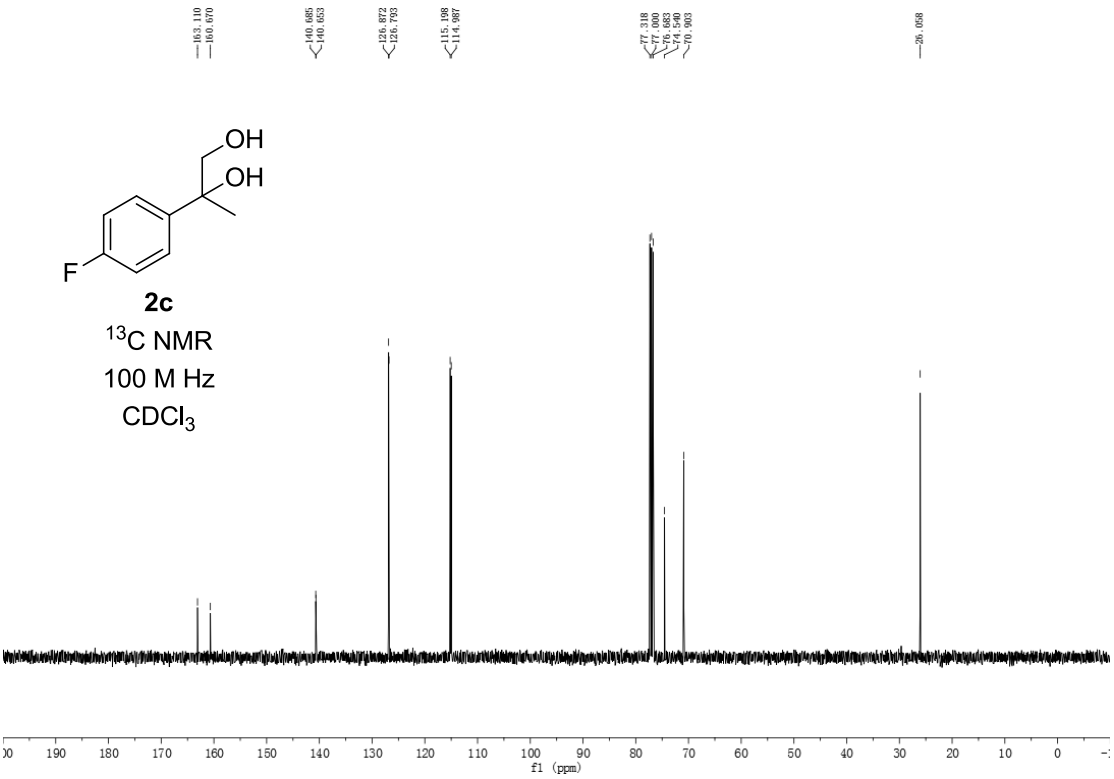
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2c
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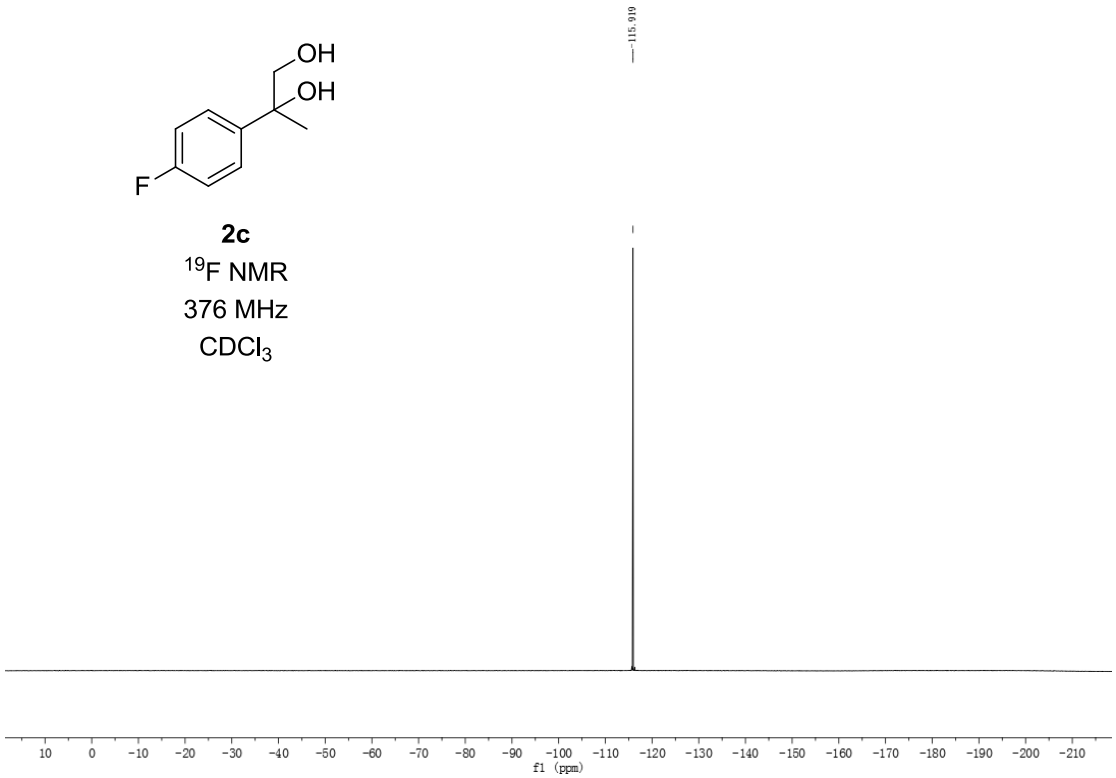
f1 (ppm)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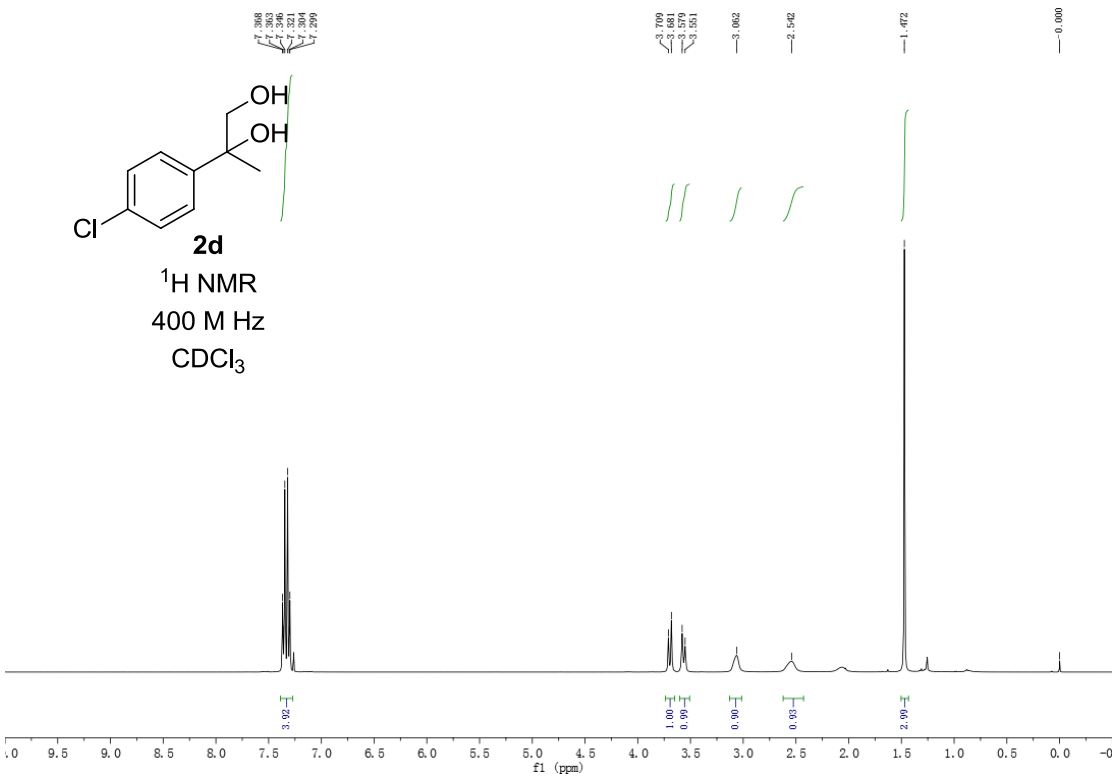
f1 (ppm)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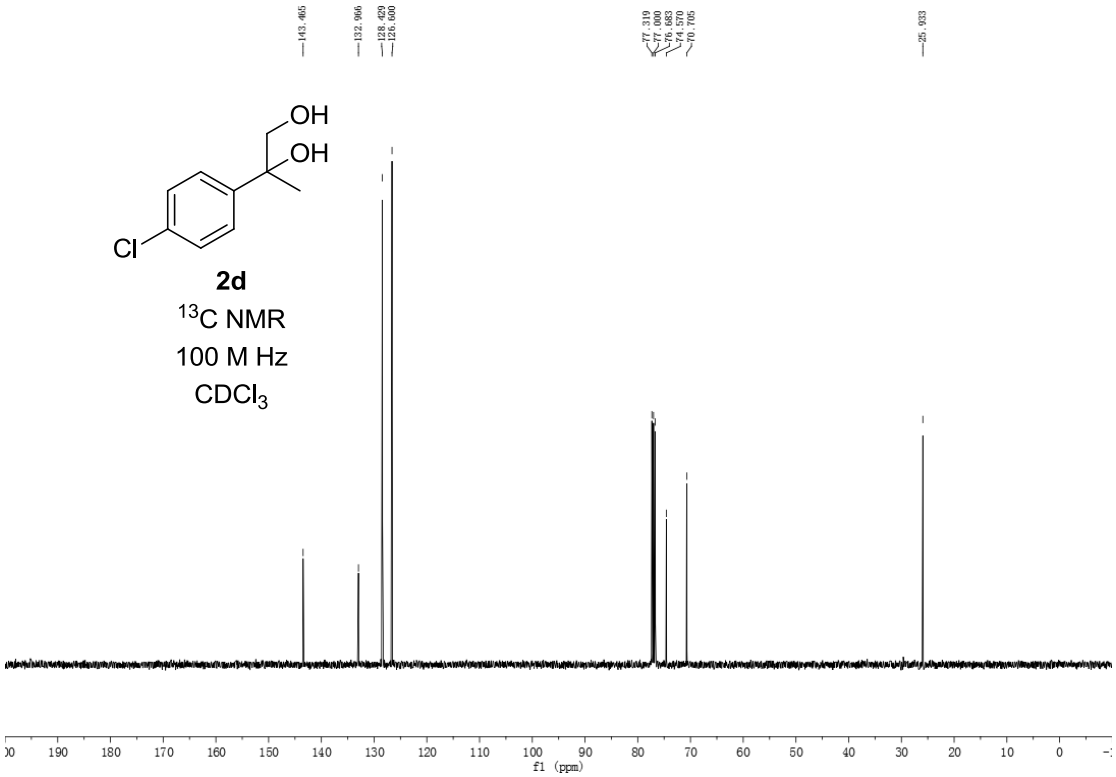
f1 (ppm)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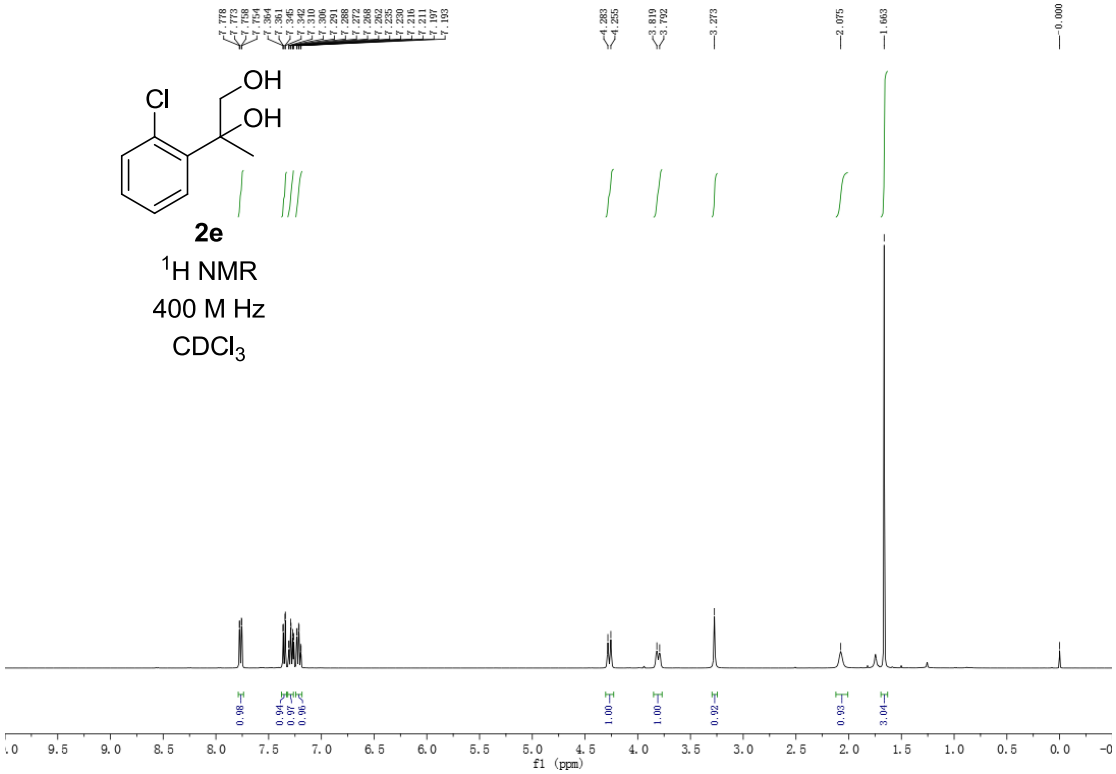
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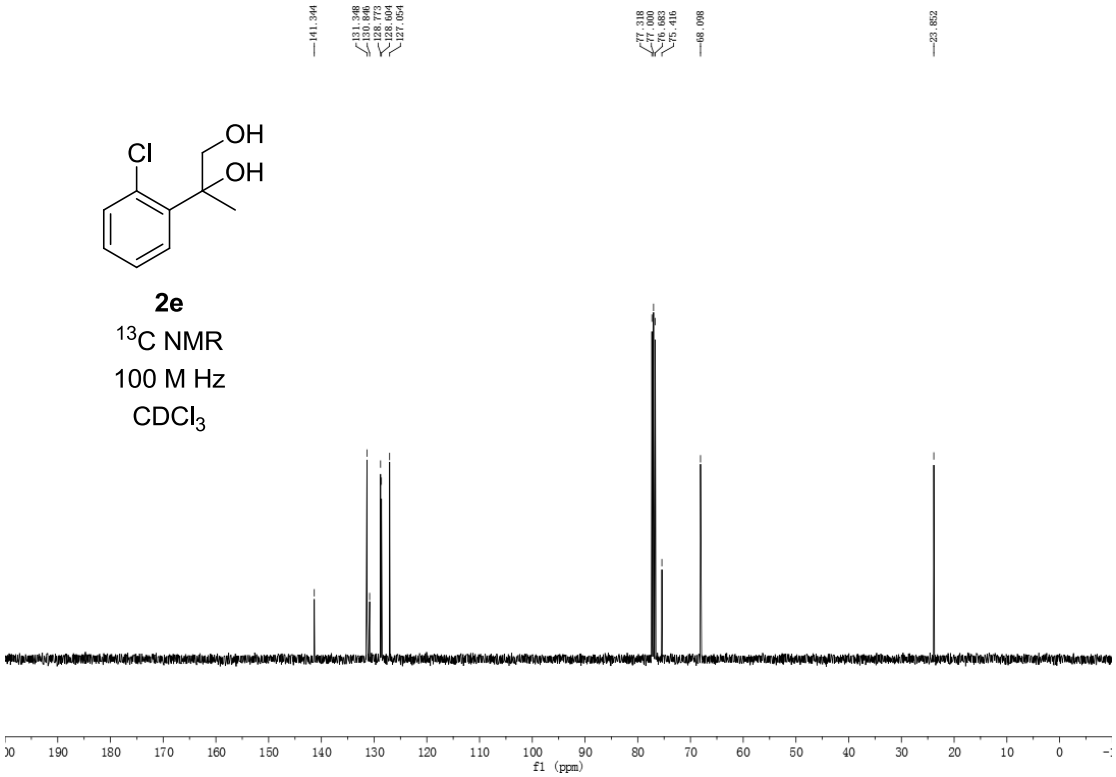
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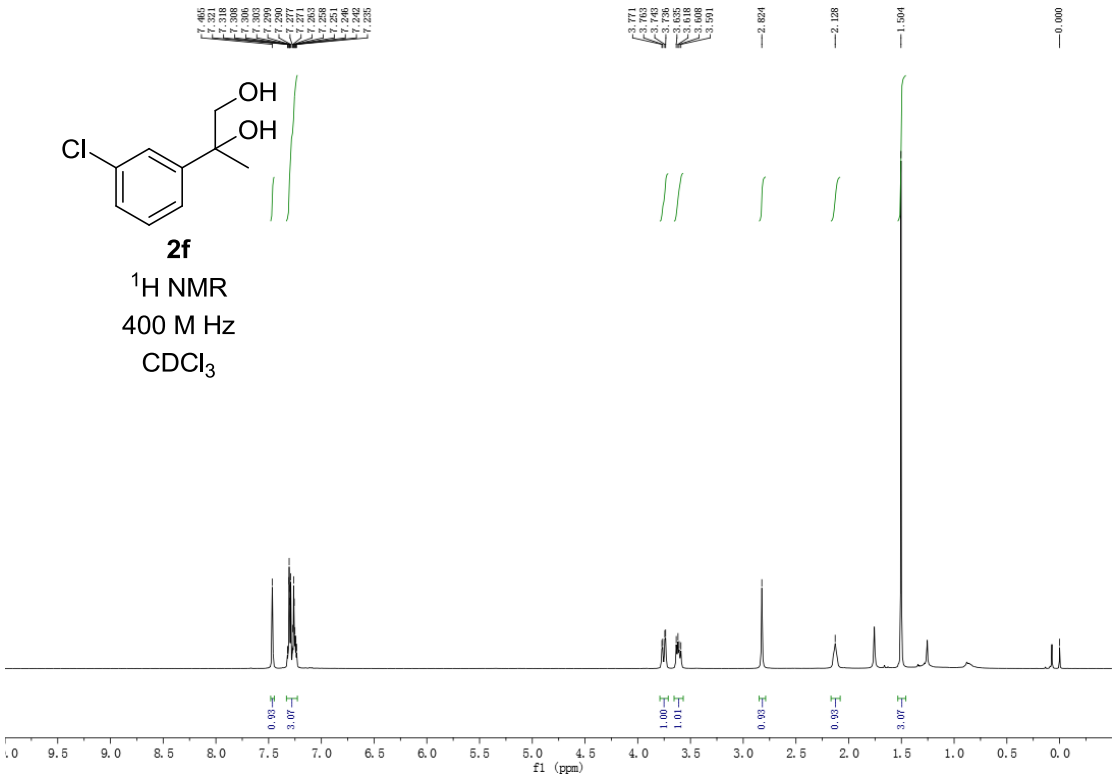
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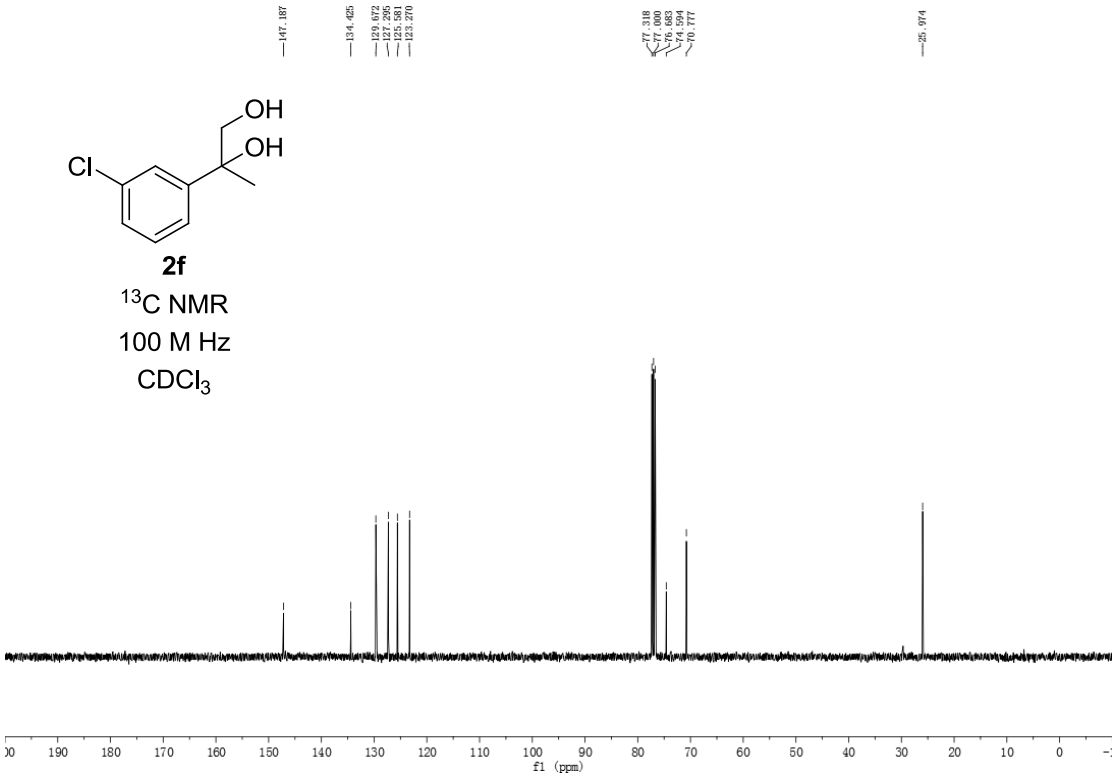
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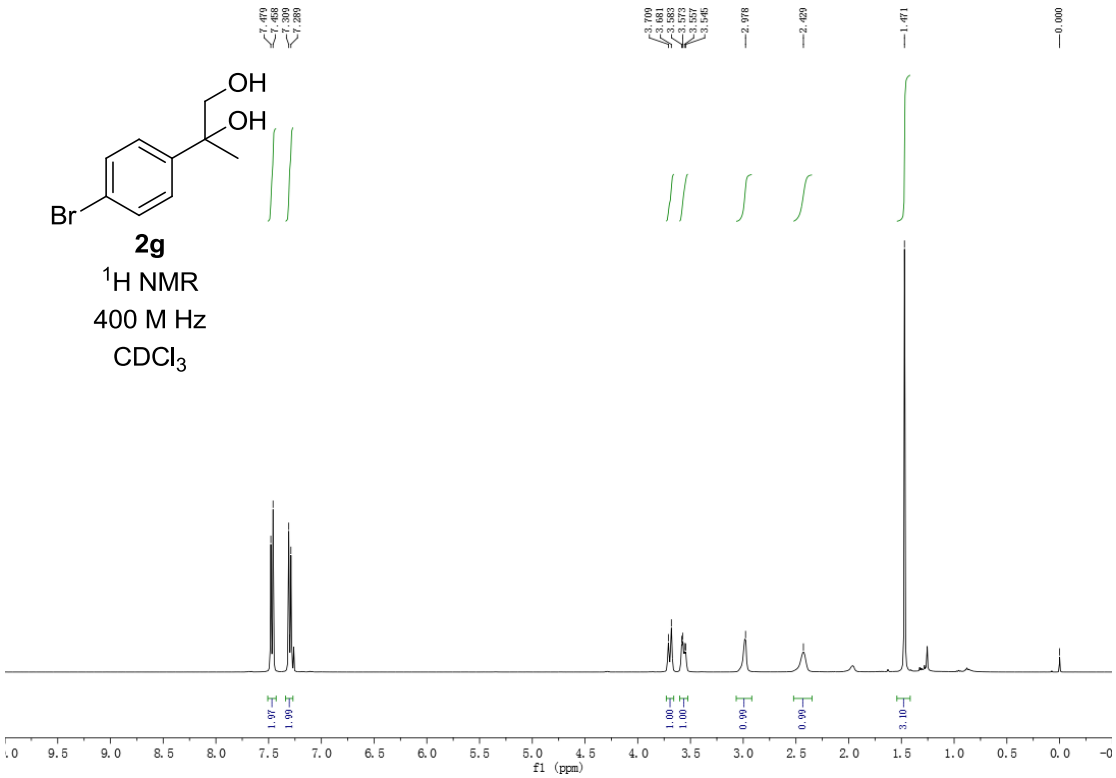
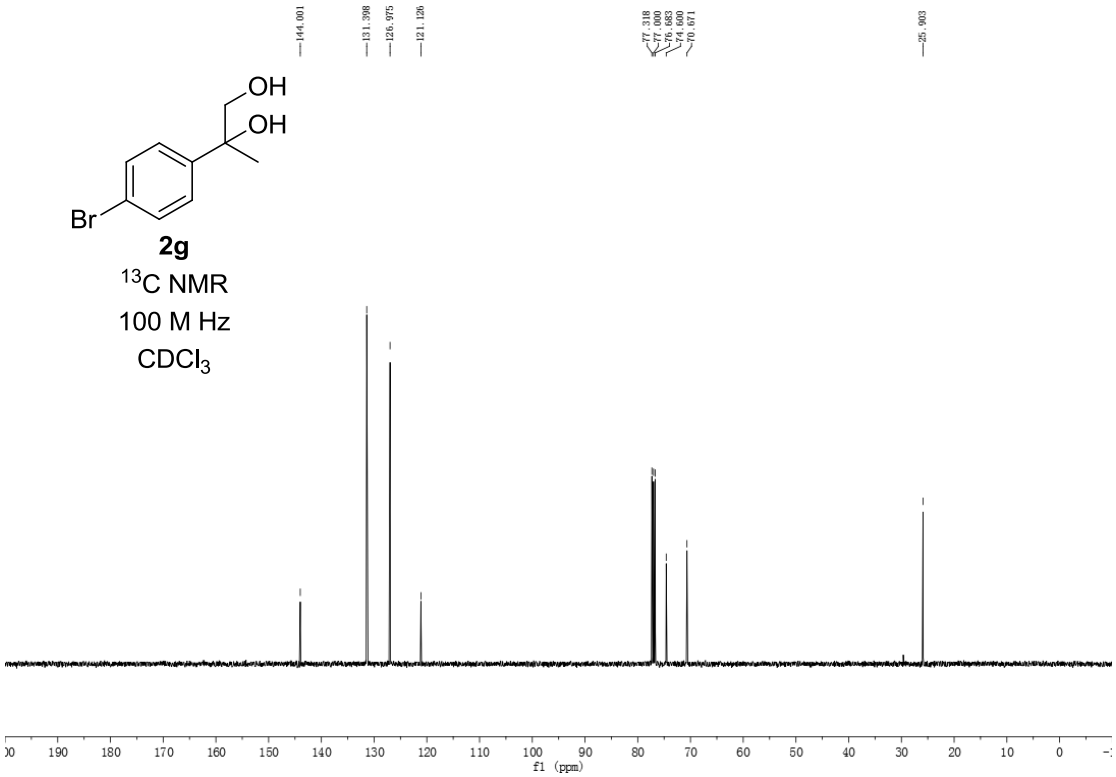
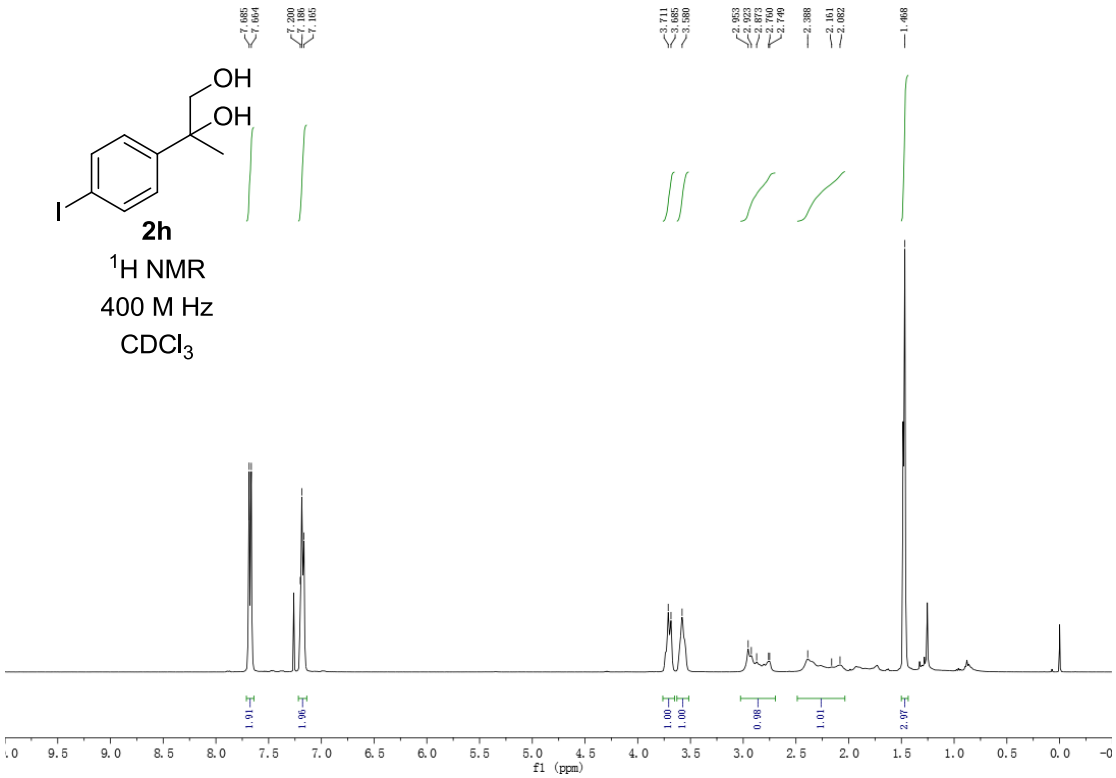
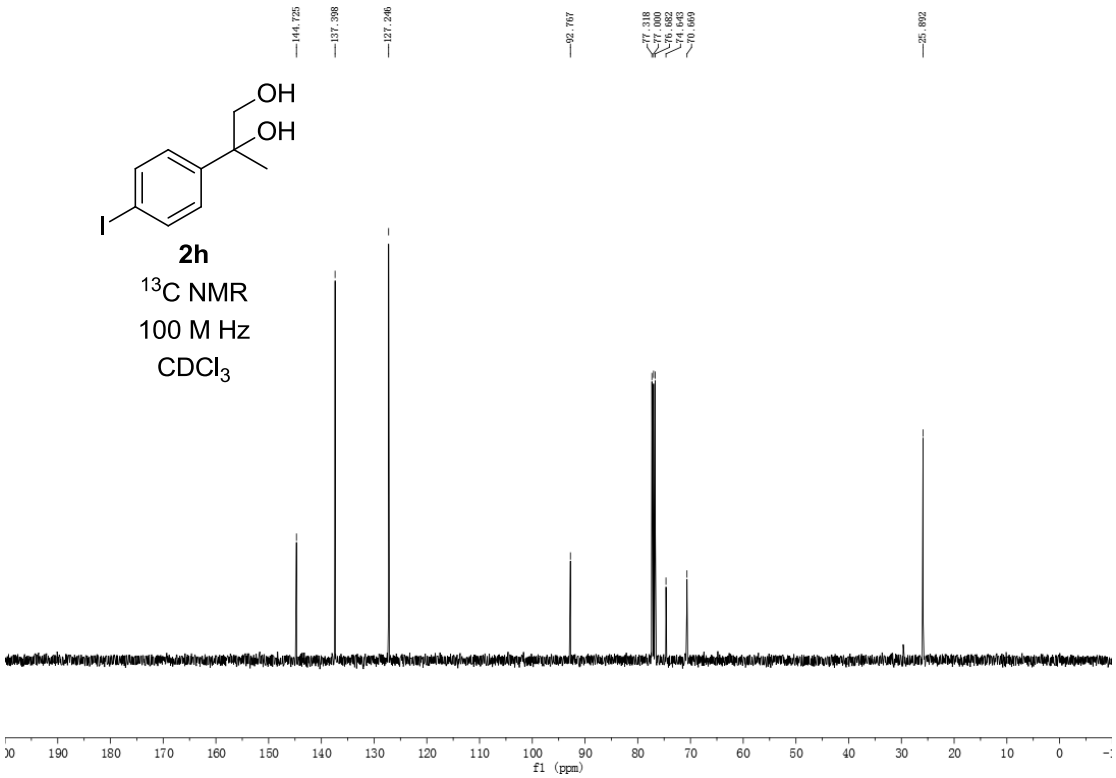
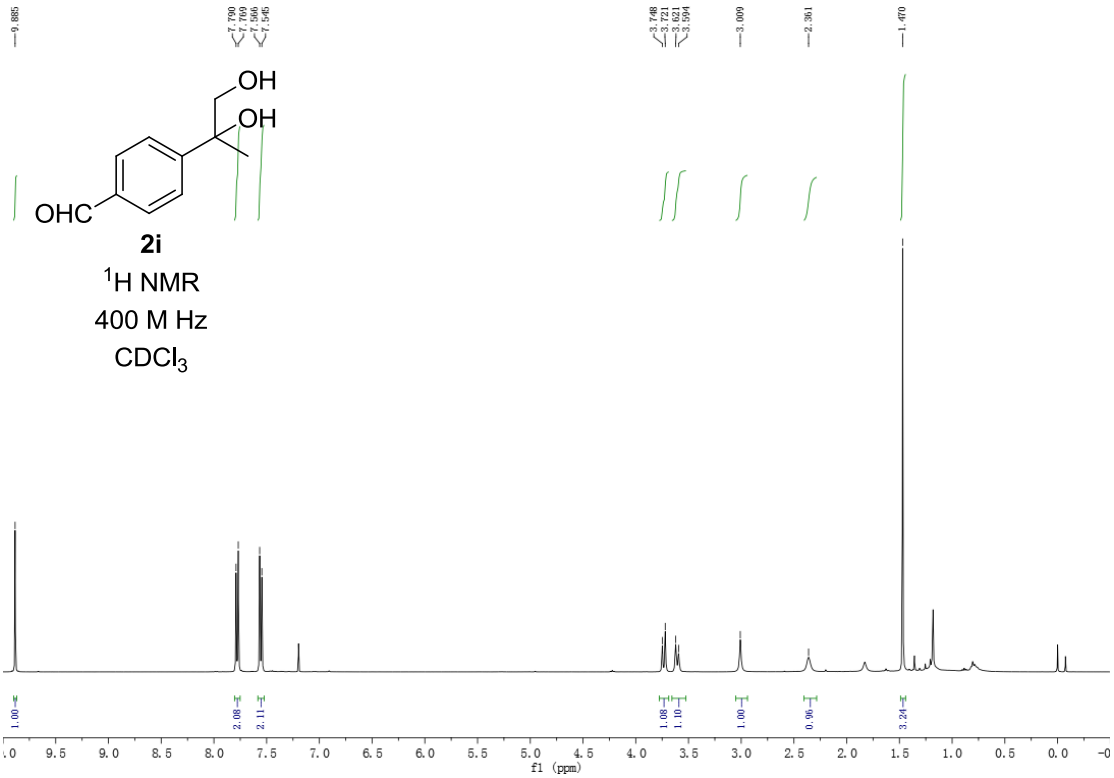
CDCl3
f1 (ppm)

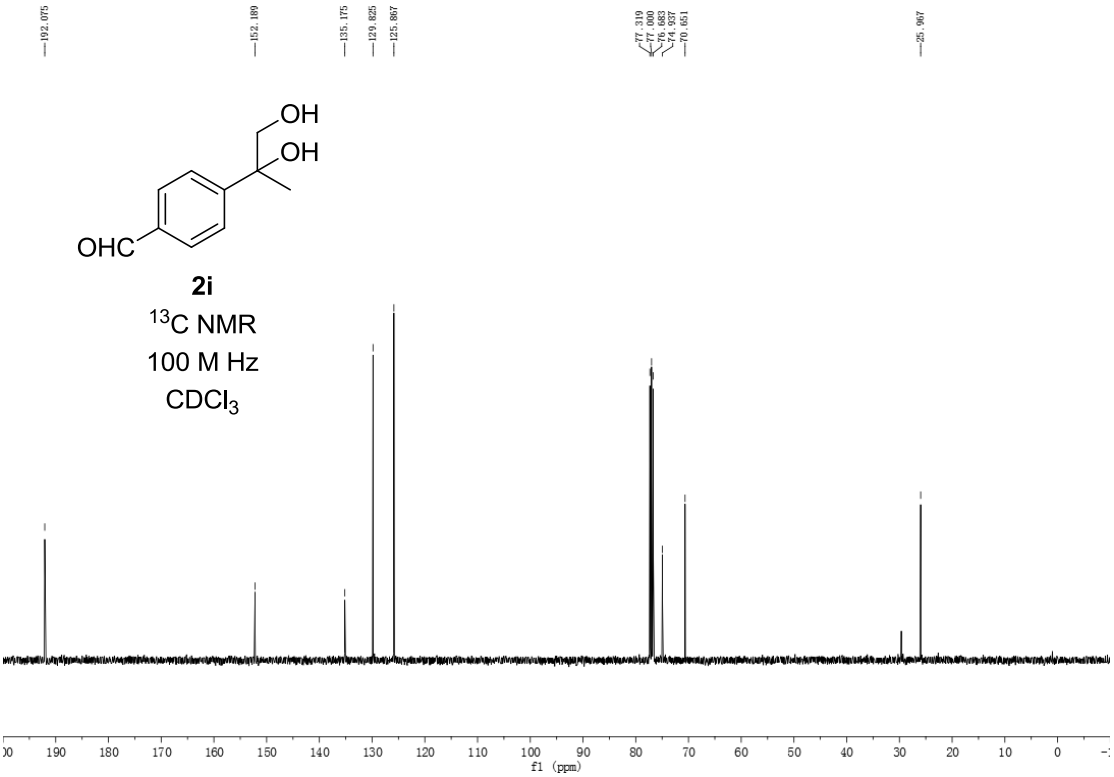

OH
OH
Br
2g
1H NMR
400 M Hz
CDCl3
f1 (ppm)

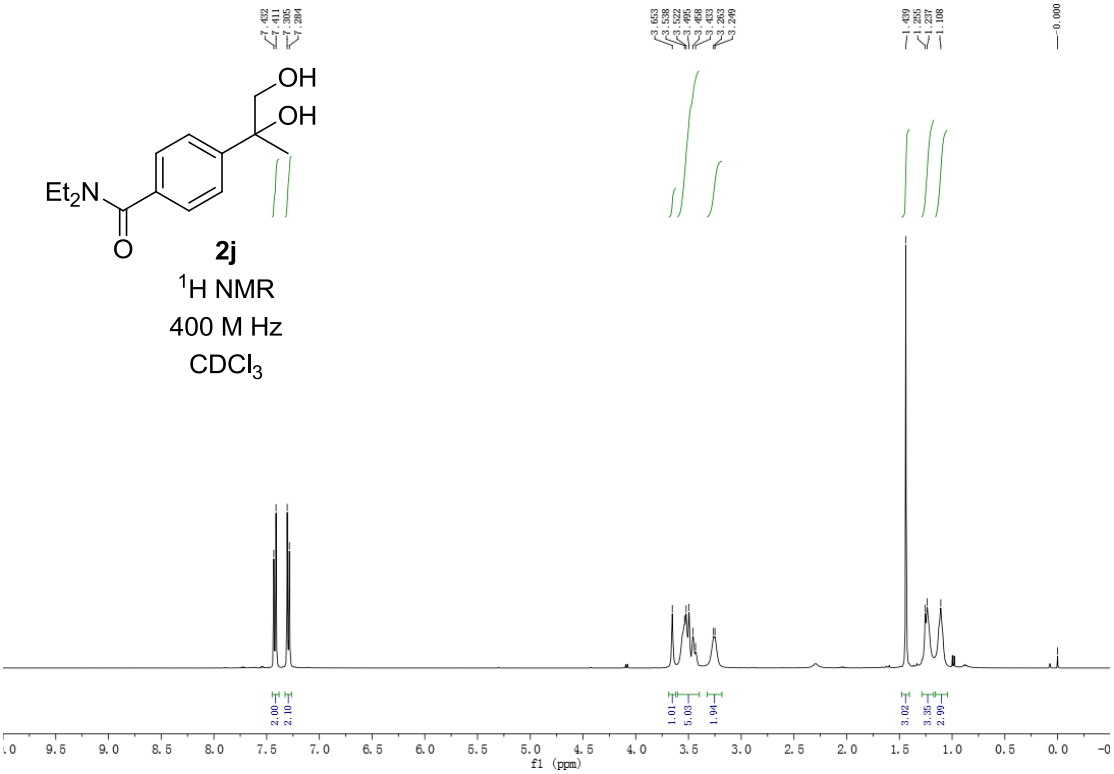

OH
OH
Br
2g
13C NMR
100 M Hz
CDCl3
f1 (ppm)

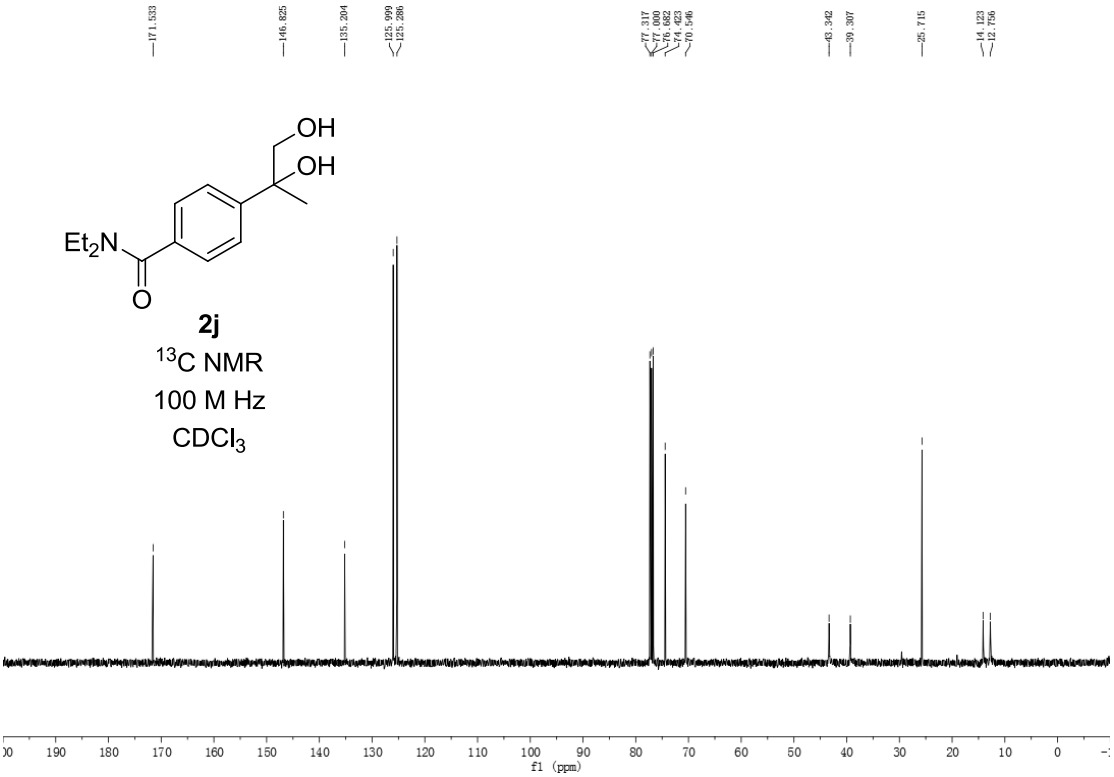

OH
OH
I
2h
1H NMR
400 M Hz
CDCl3
f1 (ppm)

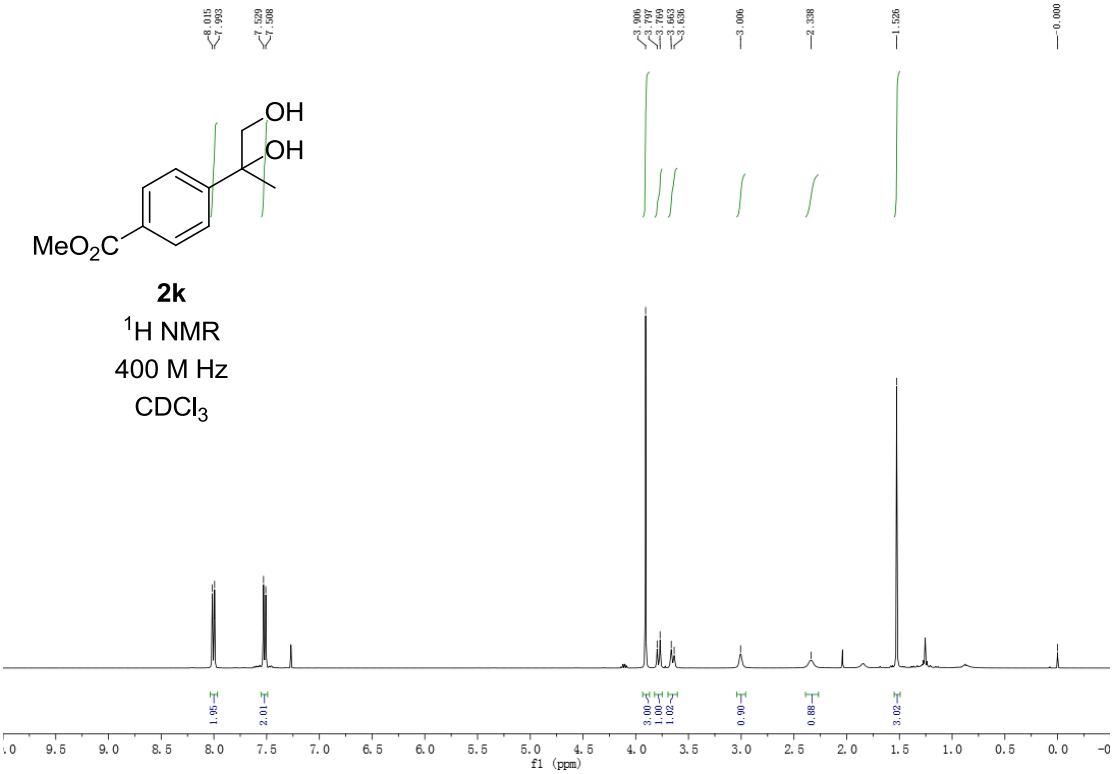

OH
OH
I
2h
13C NMR
100 M Hz
CDCl3
f1 (ppm)

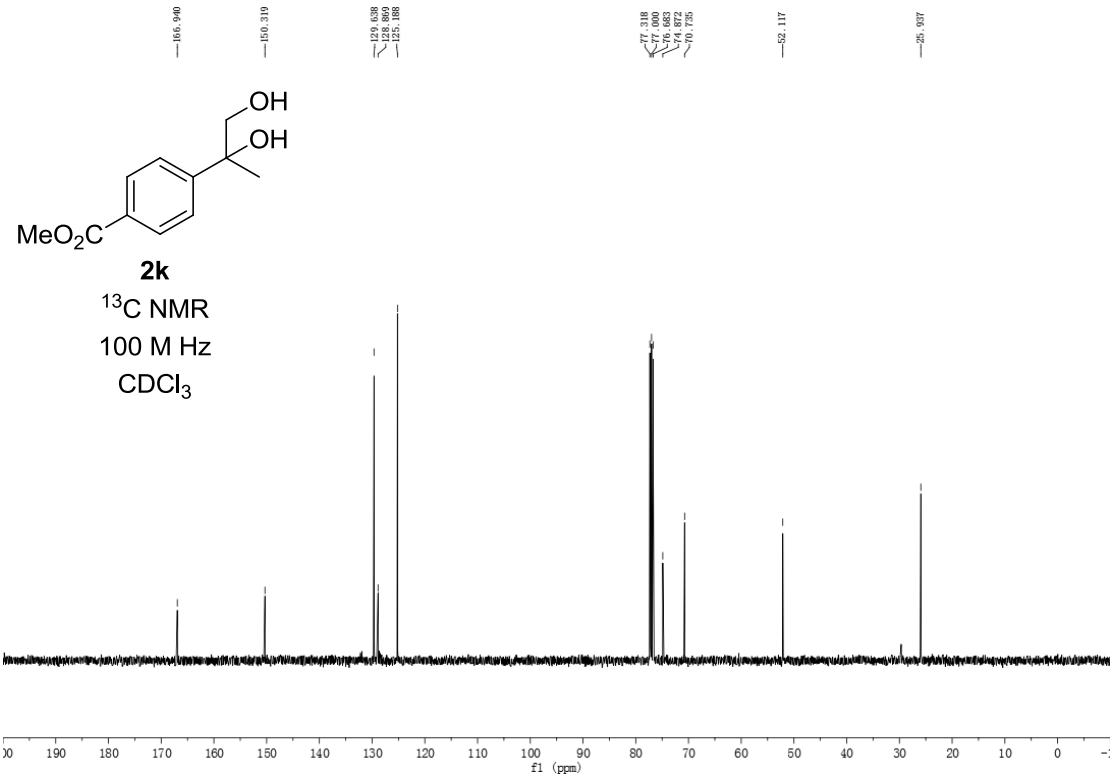

OH
OH
OHC
2i
1H NMR
400 M Hz
CDCl3
f1 (ppm)

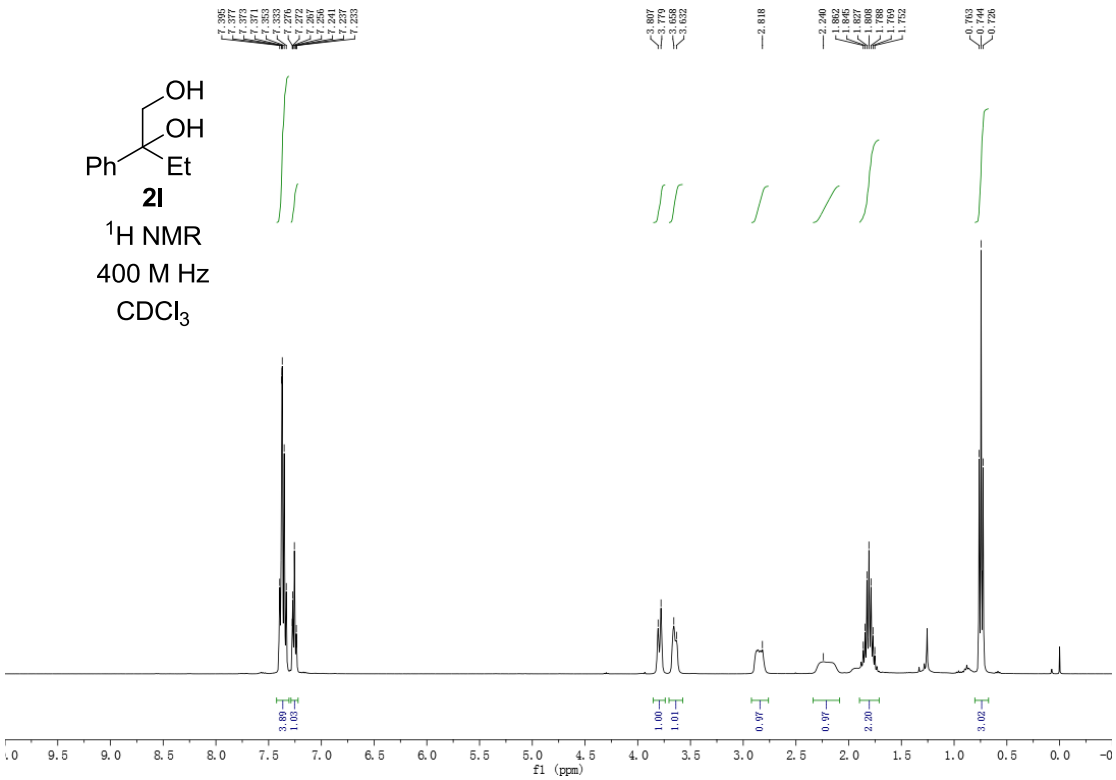

OH
OH
OHC
2i
13C NMR
100 M Hz
CDCl3
f1 (ppm)

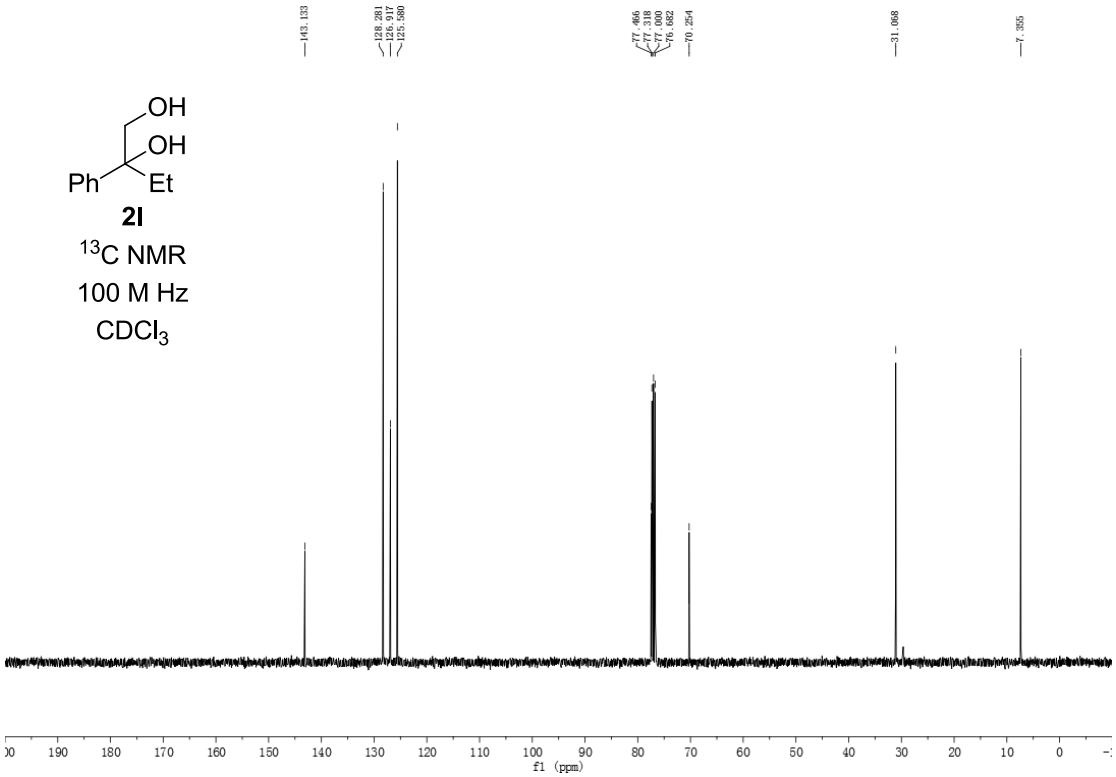

OH
OH
Et2N
O
2j
1H NMR
400 M Hz
CDCl3
f1 (ppm)

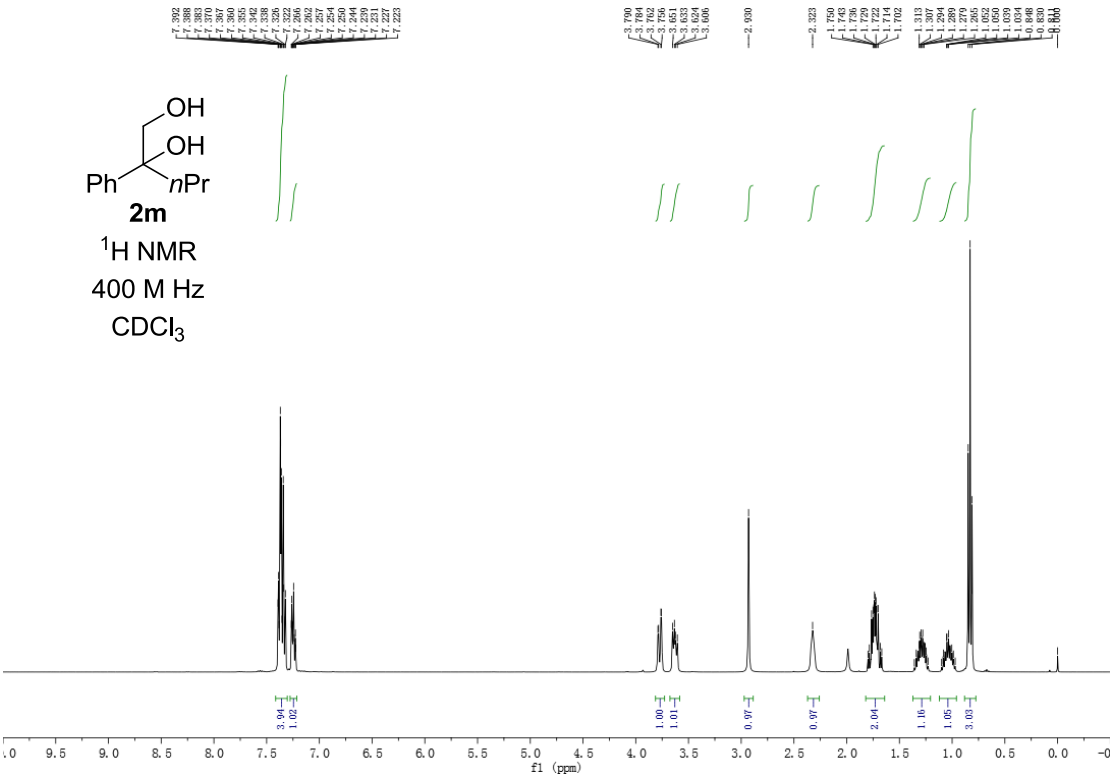

OH
OH
Et2N
O
2j
13C NMR
100 M Hz
CDCl3
f1 (ppm)

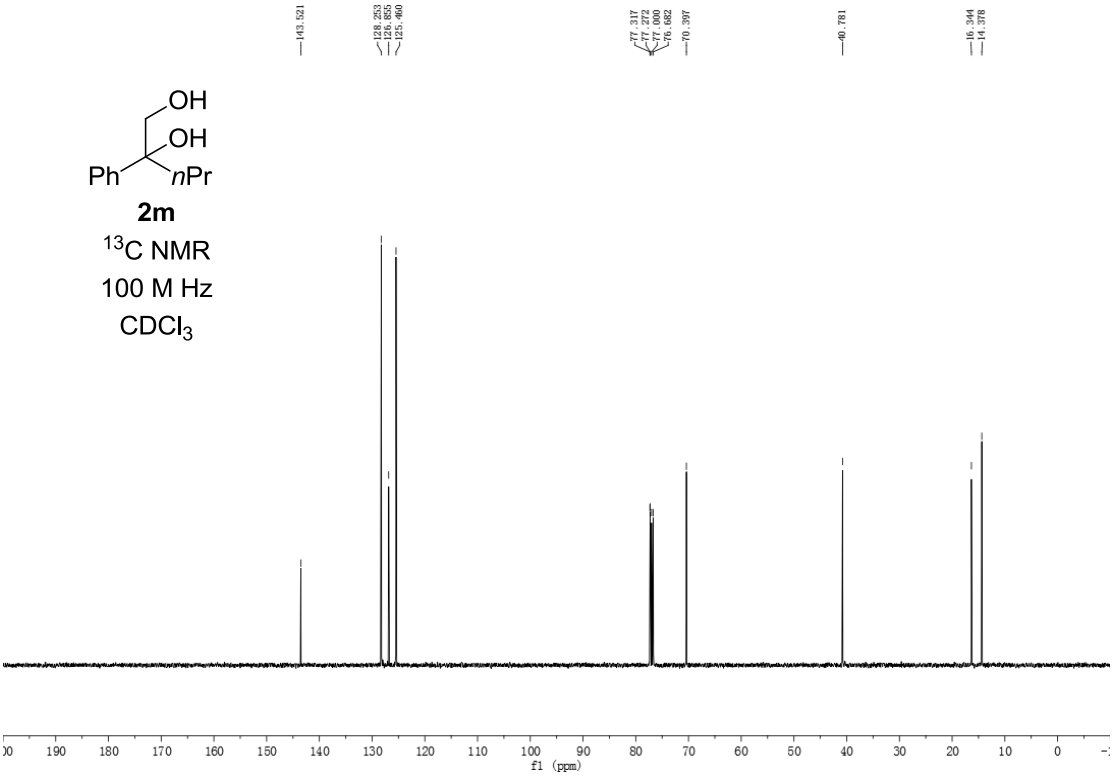

OH
OH
MeO2C
2k
1H NMR
400 M Hz
CDCl3
f1 (ppm)

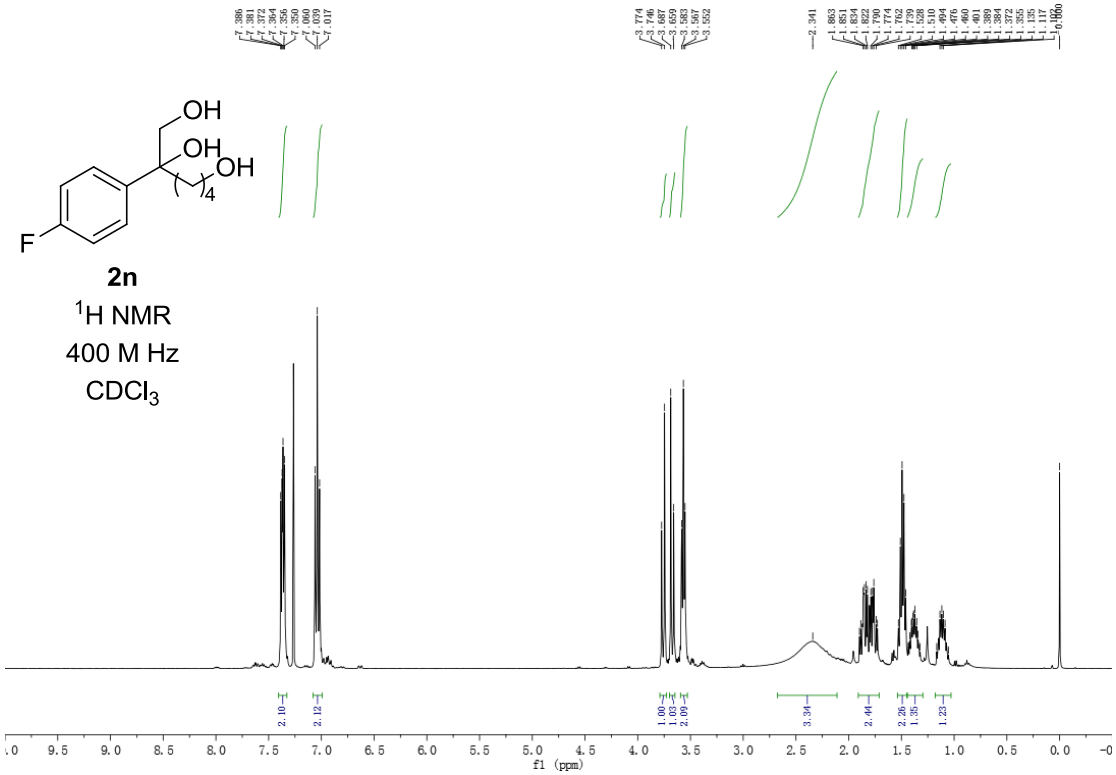

OH
OH
MeO2C
2k
13C NMR
100 M Hz
CDCl3
f1 (ppm)

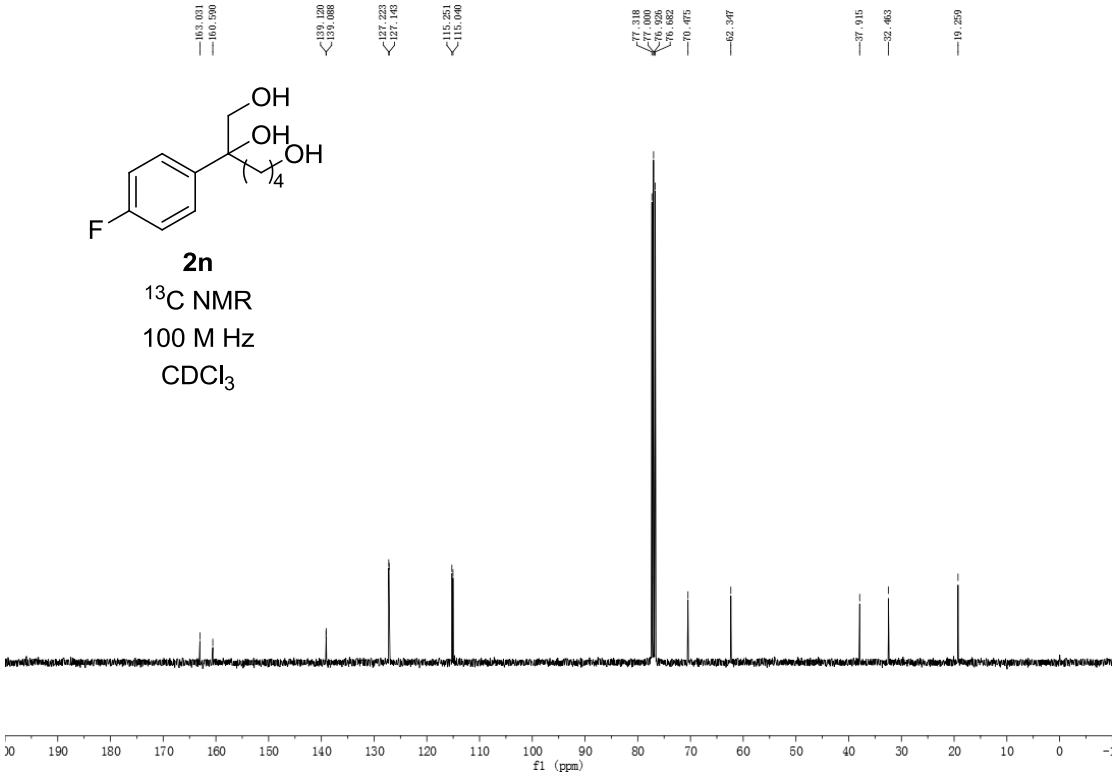

OH
OH
Ph
Et
2l
1H NMR
400 M Hz
CDCl3
f1 (ppm)

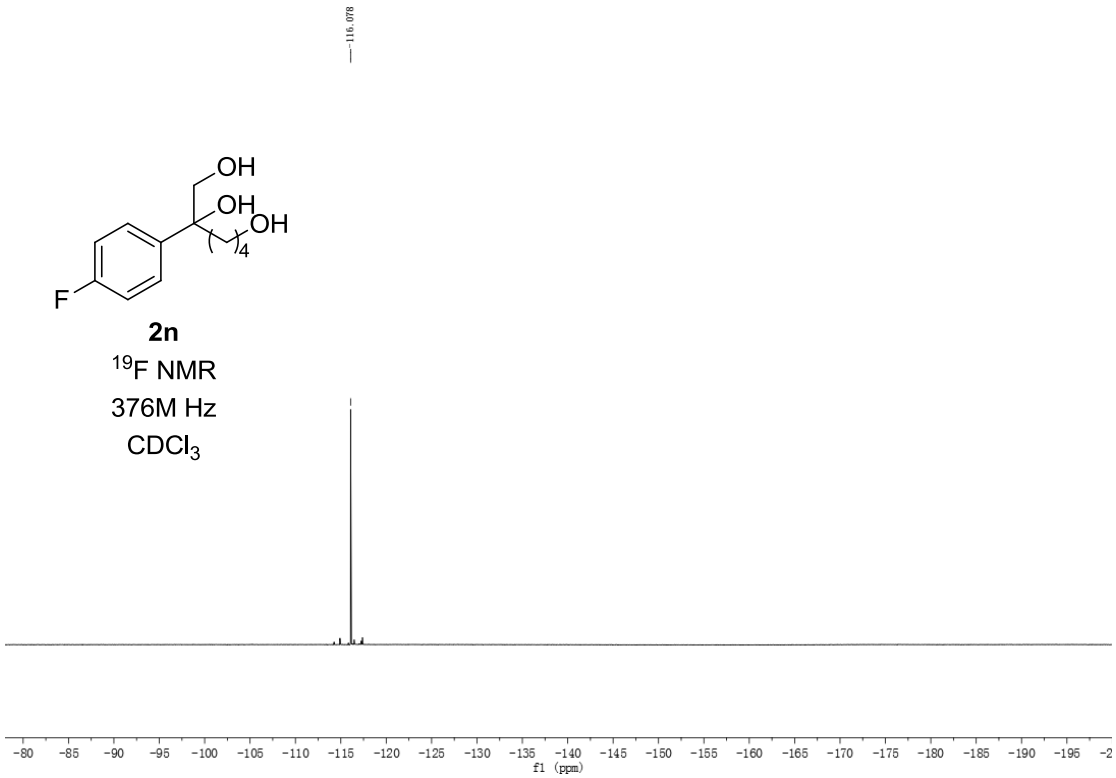

OH
OH
Ph
Et
2l
13C NMR
100 M Hz
CDCl3
f1 (ppm)

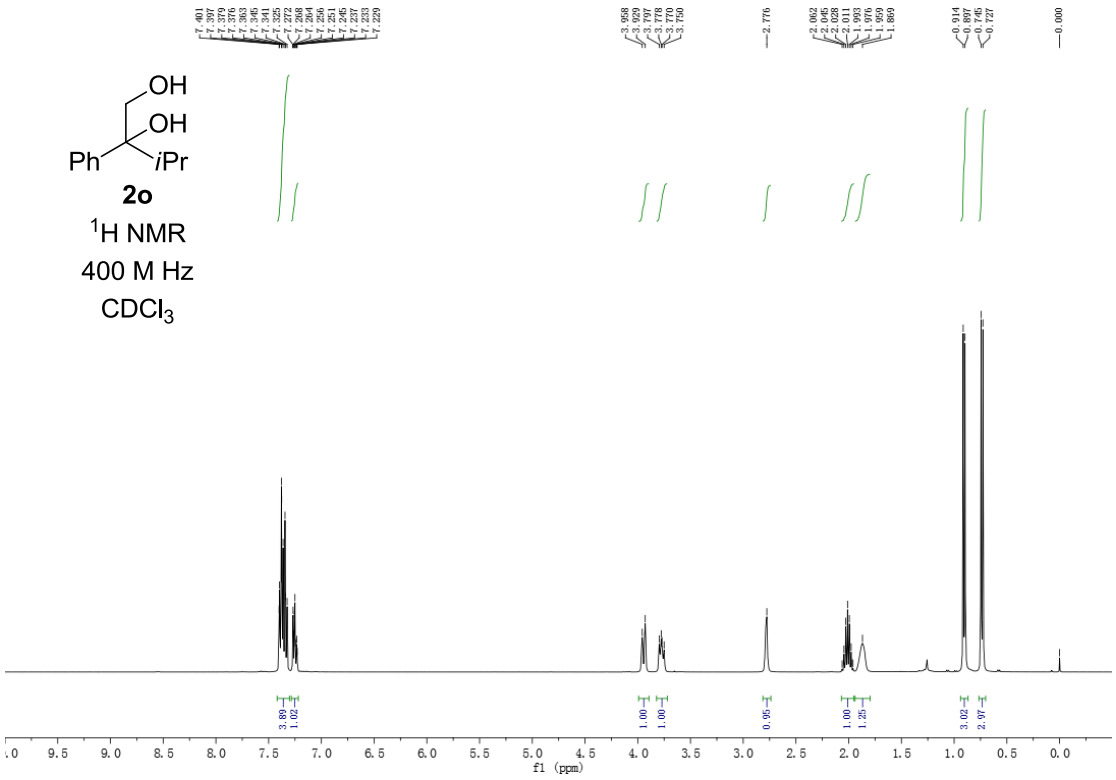

OH
OH
Ph
nPr
2m
1H NMR
400 M Hz
CDCl3
f1 (ppm)

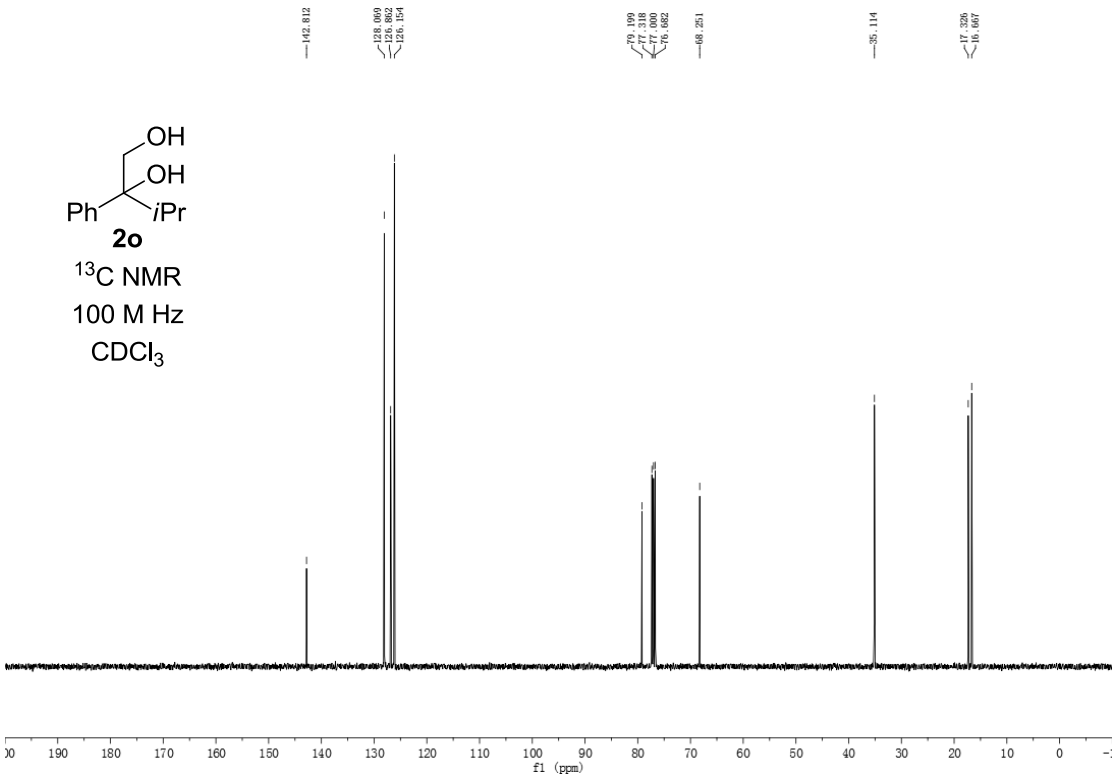

OH
OH
Ph
nPr
2m
13C NMR
100 M Hz
CDCl3
f1 (ppm)

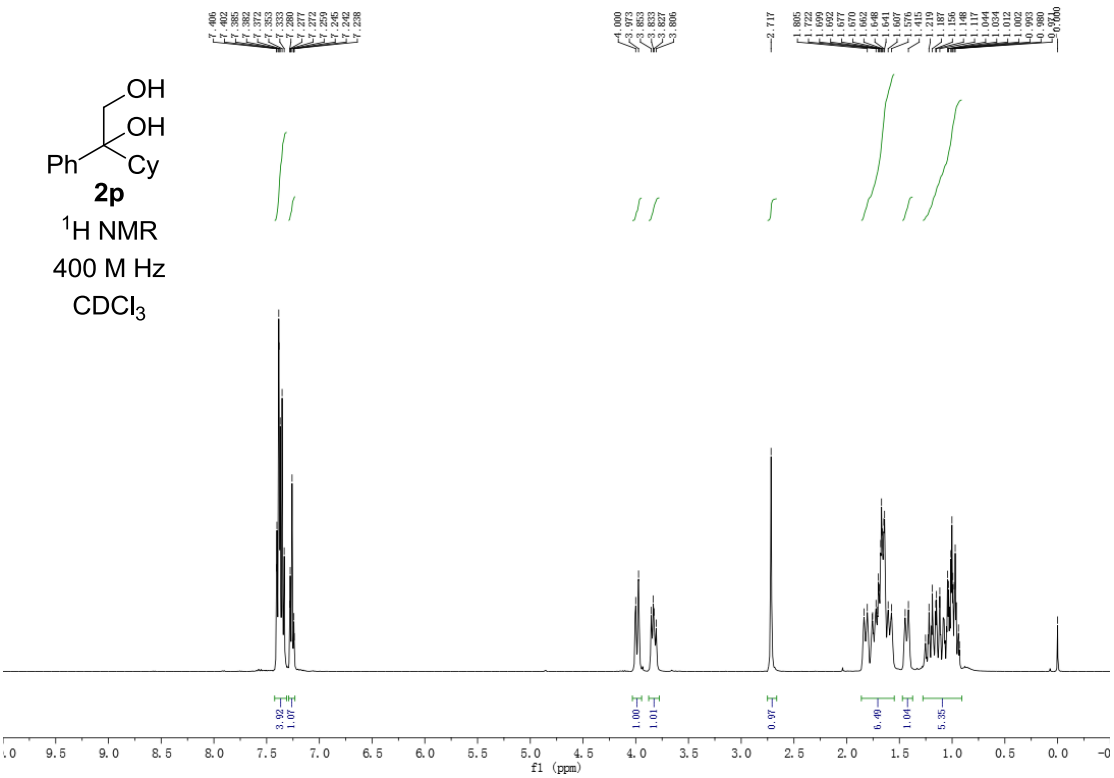

OH
OH
OH
4
F
2n
1H NMR
400 M Hz
CDCl3
f1 (ppm)

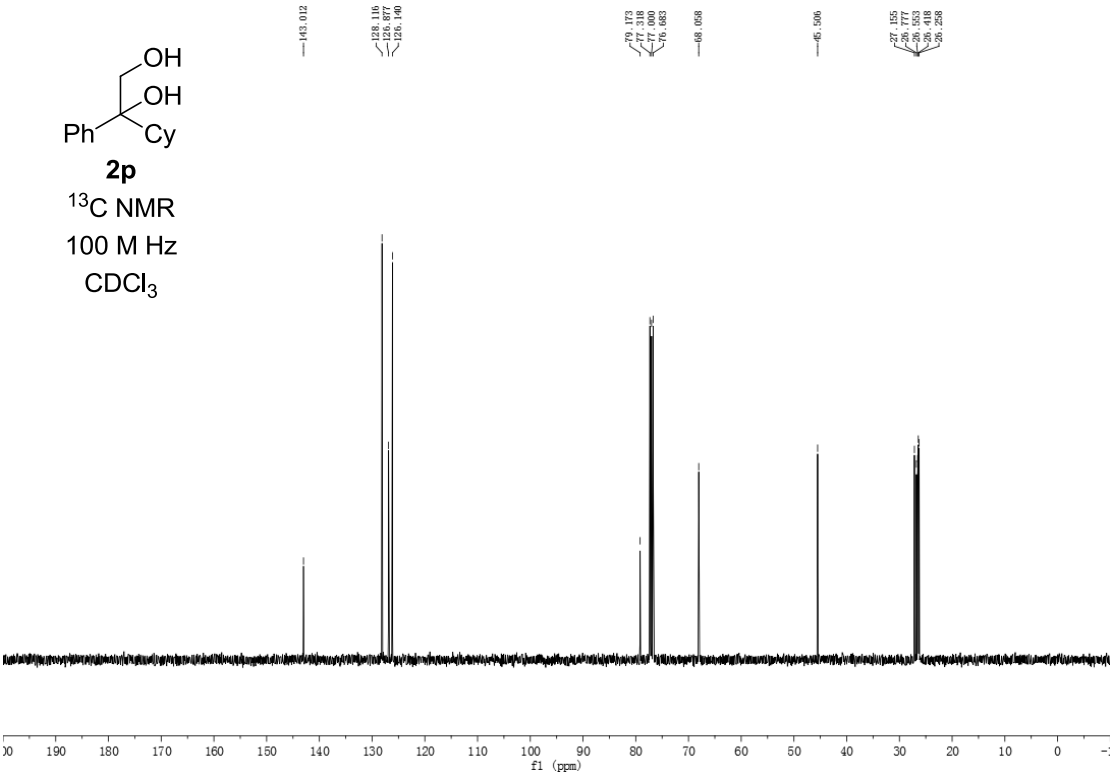

OH
OH
OH
4
F
2n
13C NMR
100 M Hz
CDCl3
f1 (ppm)

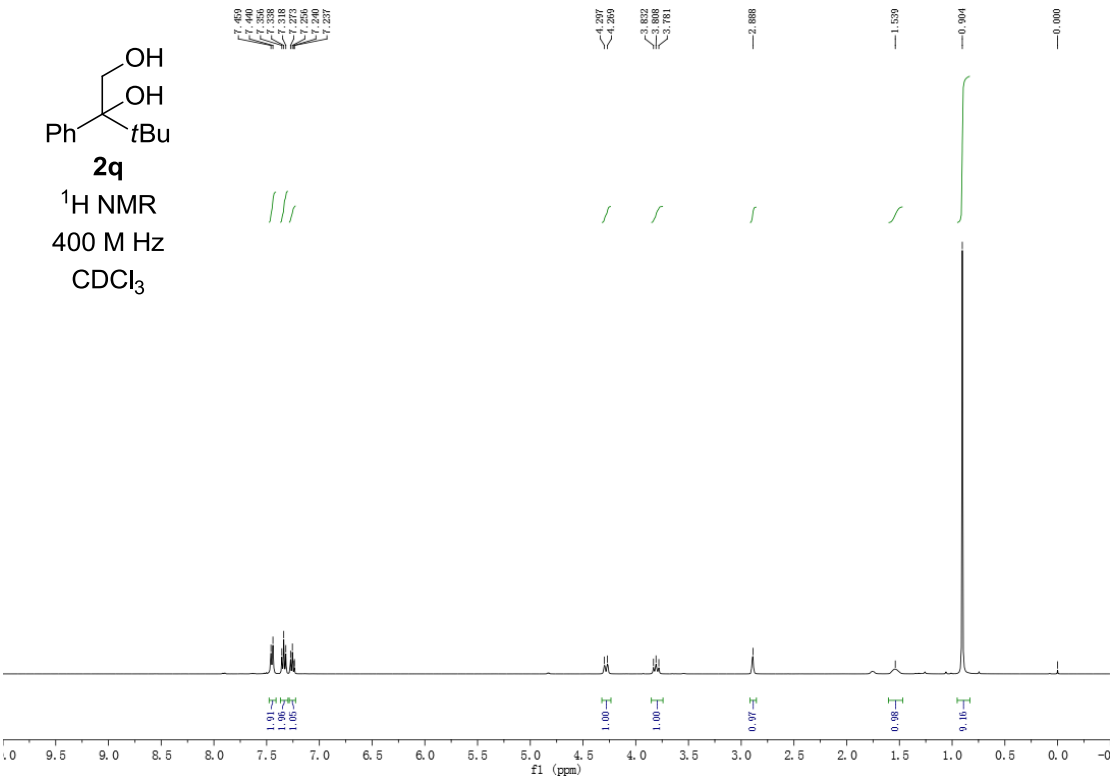

-116.078
OH
OH
OH
4
F
2n
19F NMR
376M Hz
CDCl3
-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -2
f1 (ppm)

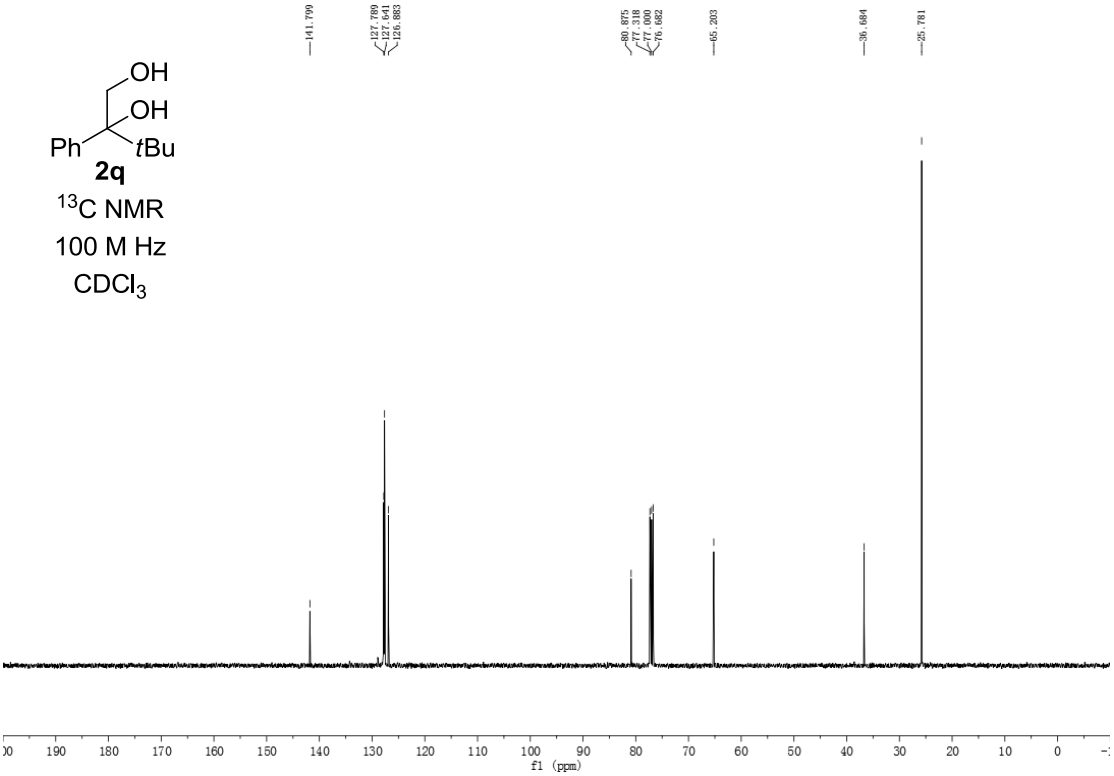

OH
OH
Ph
iPr
2o
1H NMR
400 M Hz
CDCl3
f1 (ppm)

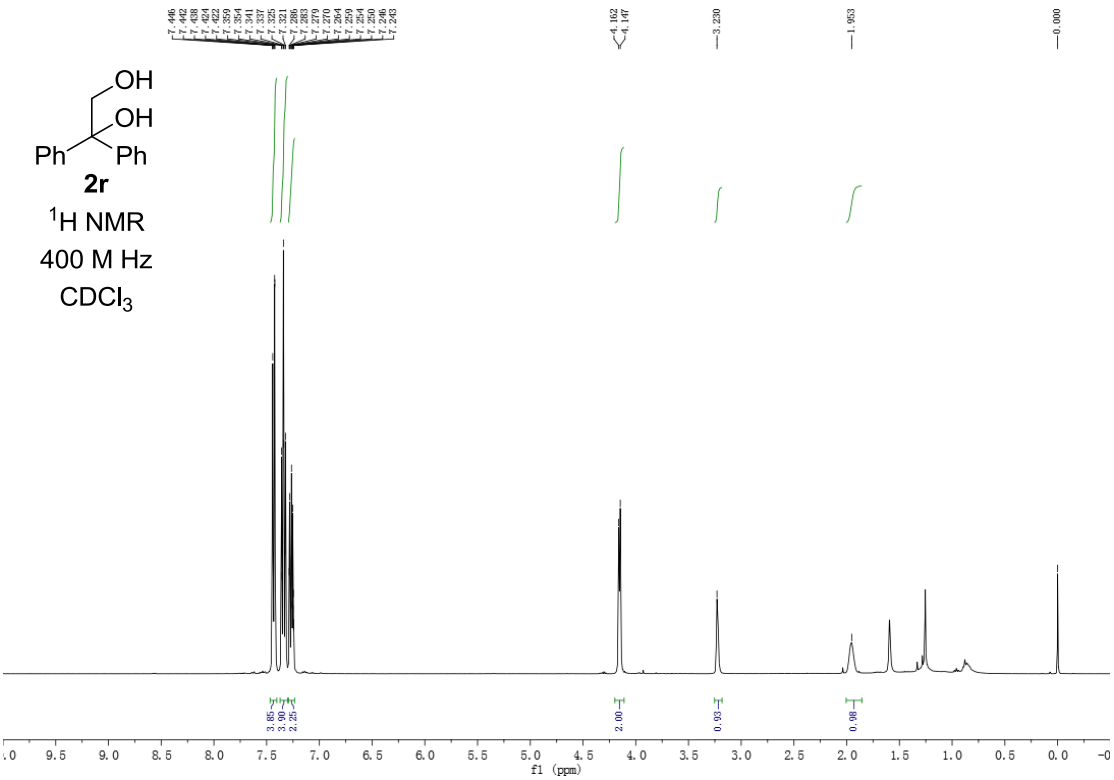

OH
OH
Ph
iPr
2o
13C NMR
100 M Hz
CDCl3
f1 (ppm)

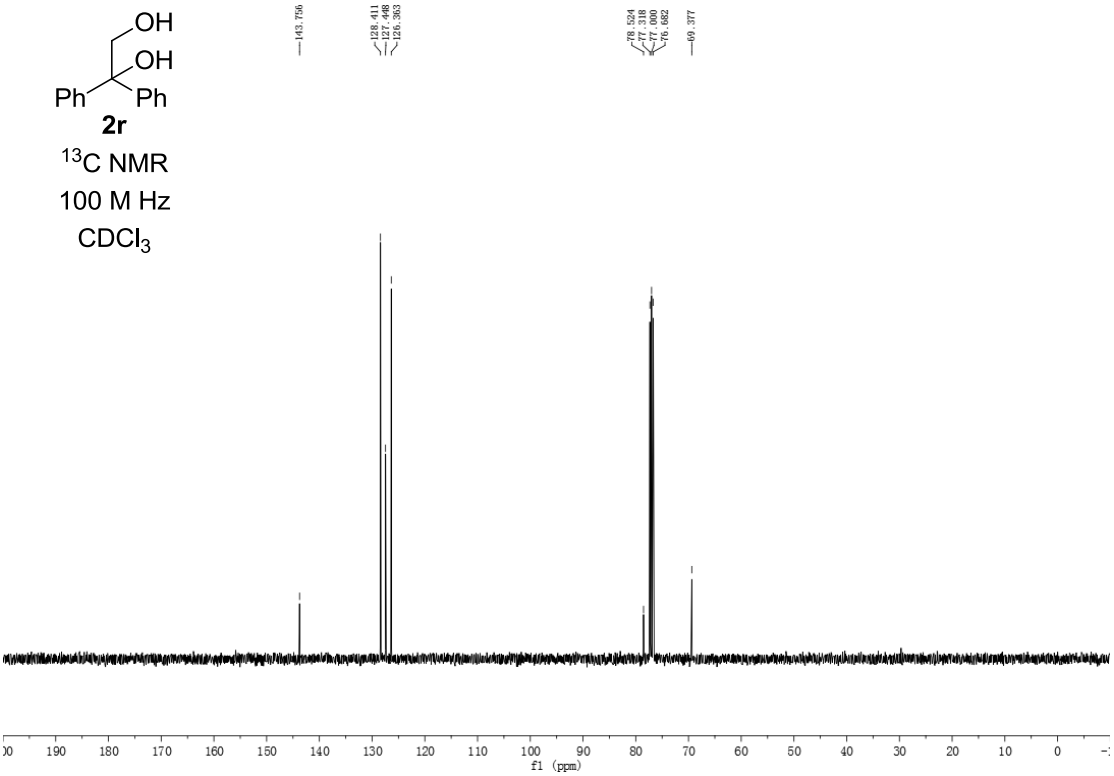

OH
OH
Ph
Cy
2p
1H NMR
400 M Hz
CDCl3
f1 (ppm)

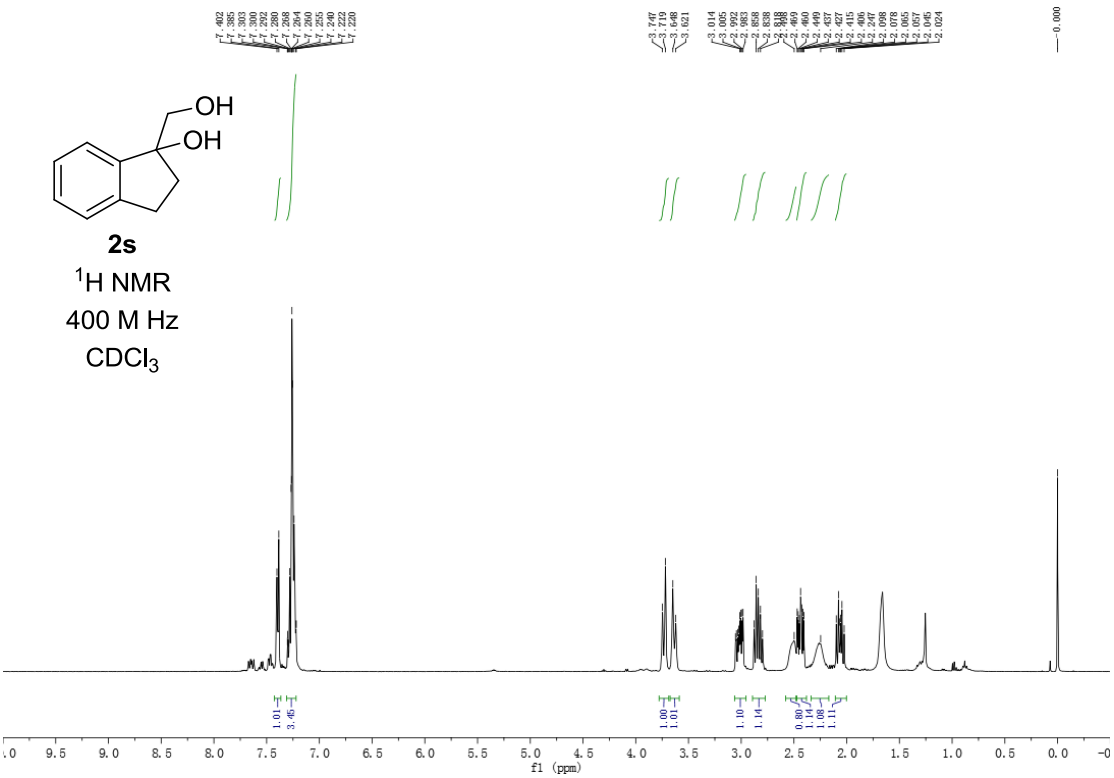

OH
OH
Ph
Cy
2p
13C NMR
100 M Hz
CDCl3
f1 (ppm)

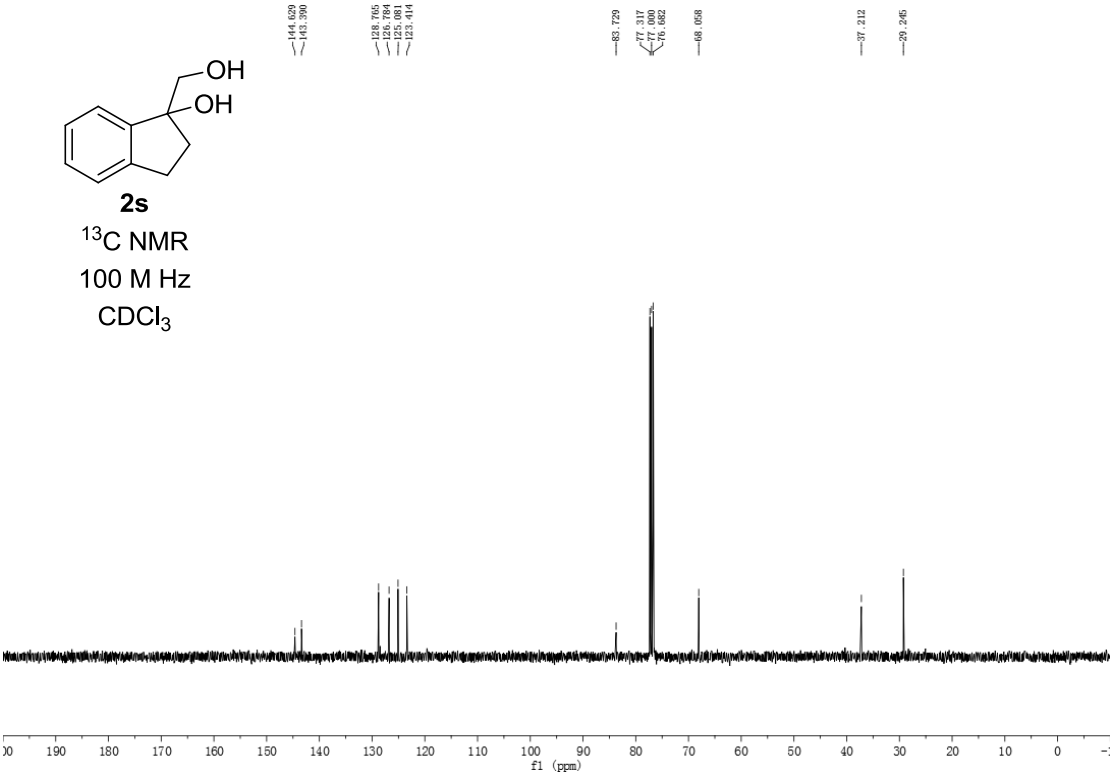

OH
OH
Ph
tBu
2q
1H NMR
400 M Hz
CDCl3
f1 (ppm)

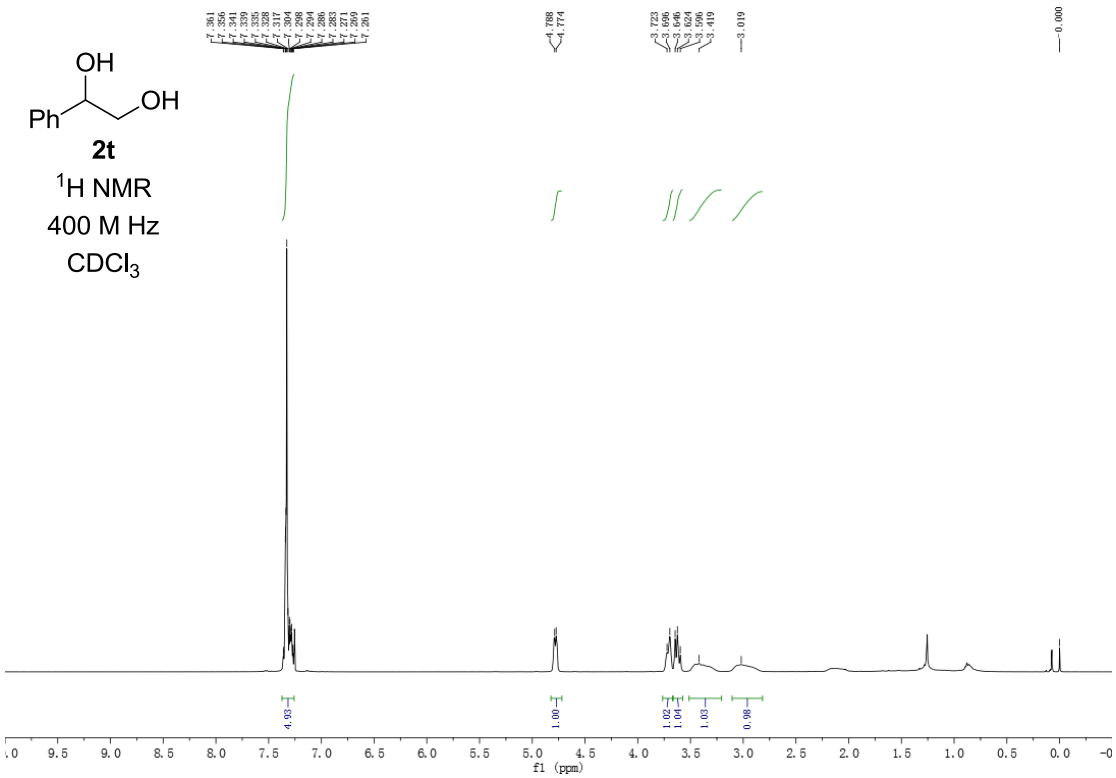

OH
OH
Ph
tBu
2q
13C NMR
100 M Hz
CDCl3
f1 (ppm)

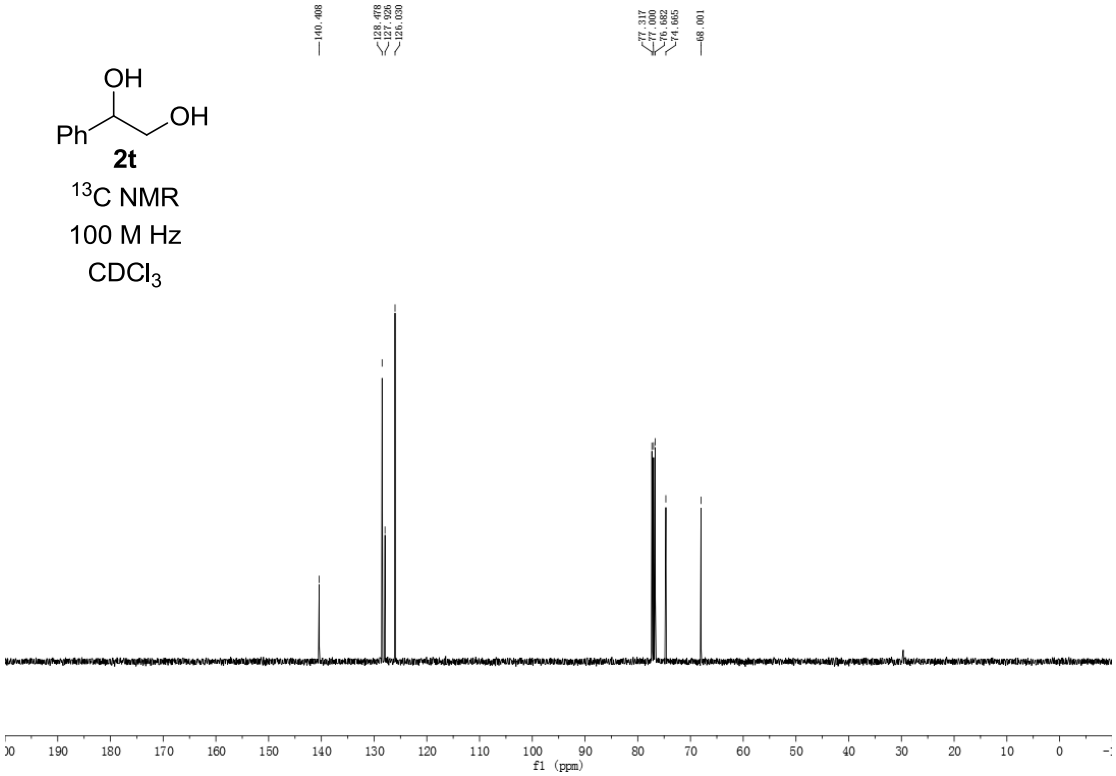

OH
OH
Ph
Ph
2r
1H NMR
400 M Hz
CDCl3
f1 (ppm)

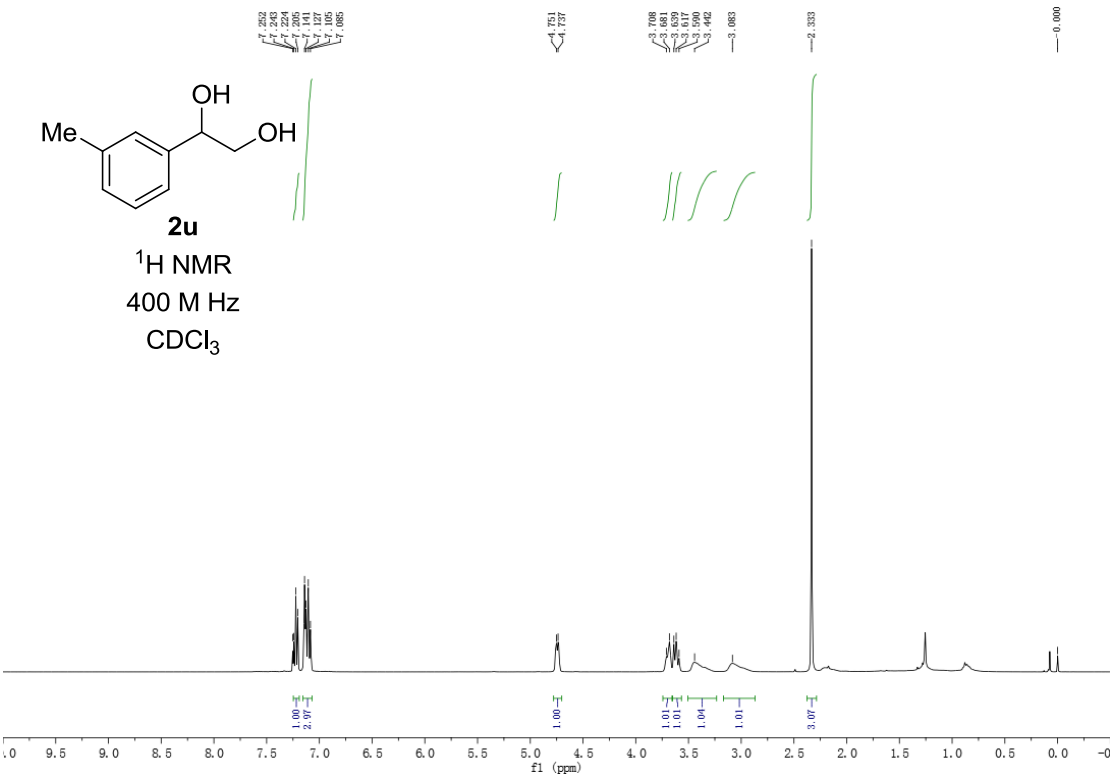

OH
OH
Ph
Ph
2r
13C NMR
100 M Hz
CDCl3
f1 (ppm)


OH
OH
2s
1H NMR
400 M Hz
CDCl3
f1 (ppm)


OH
OH
2s
13C NMR
100 M Hz
CDCl3
f1 (ppm)


OH
Ph
OH
2t
1H NMR
400 M Hz
CDCl3
f1 (ppm)


OH
Ph
OH
2t
13C NMR
100 M Hz
CDCl3
f1 (ppm)

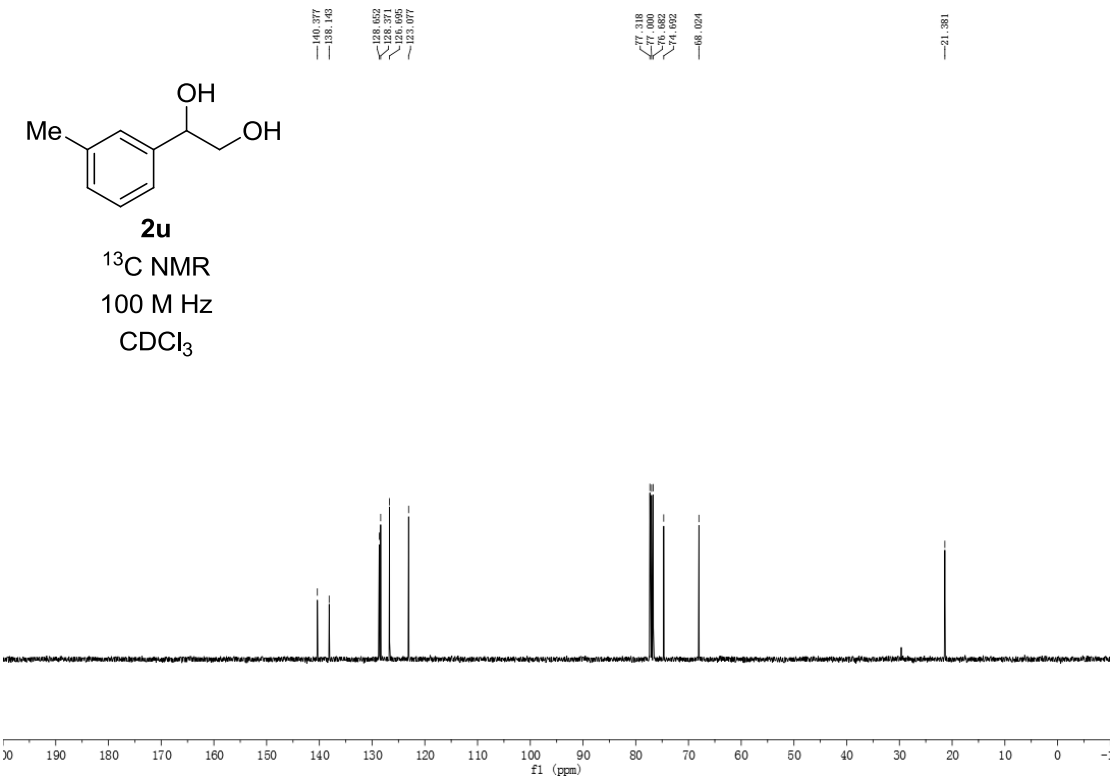


2u

^{1}H NMR

400 M Hz

$CDCl_3$

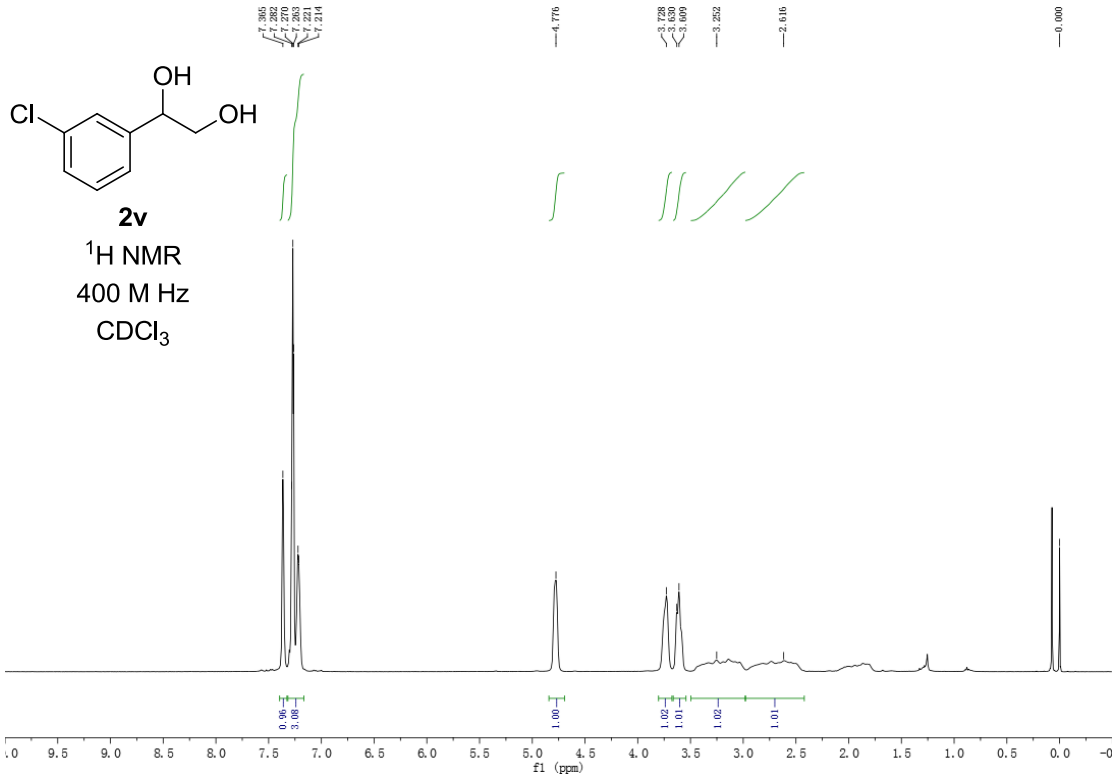


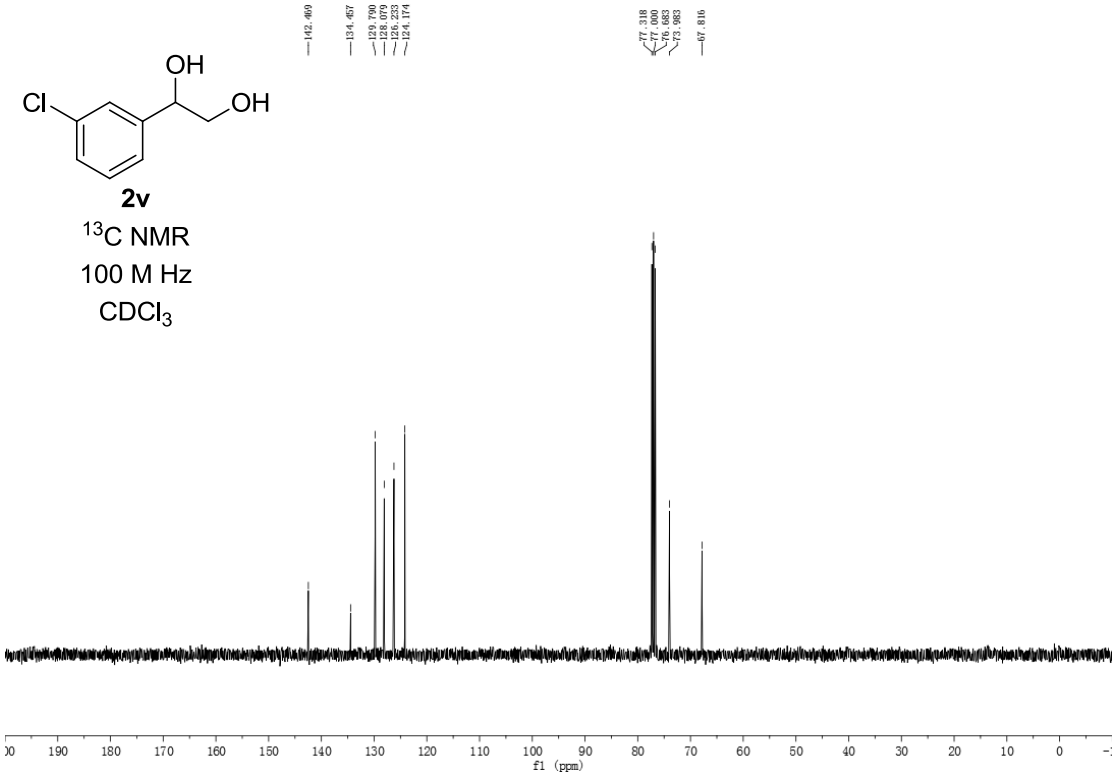
2u

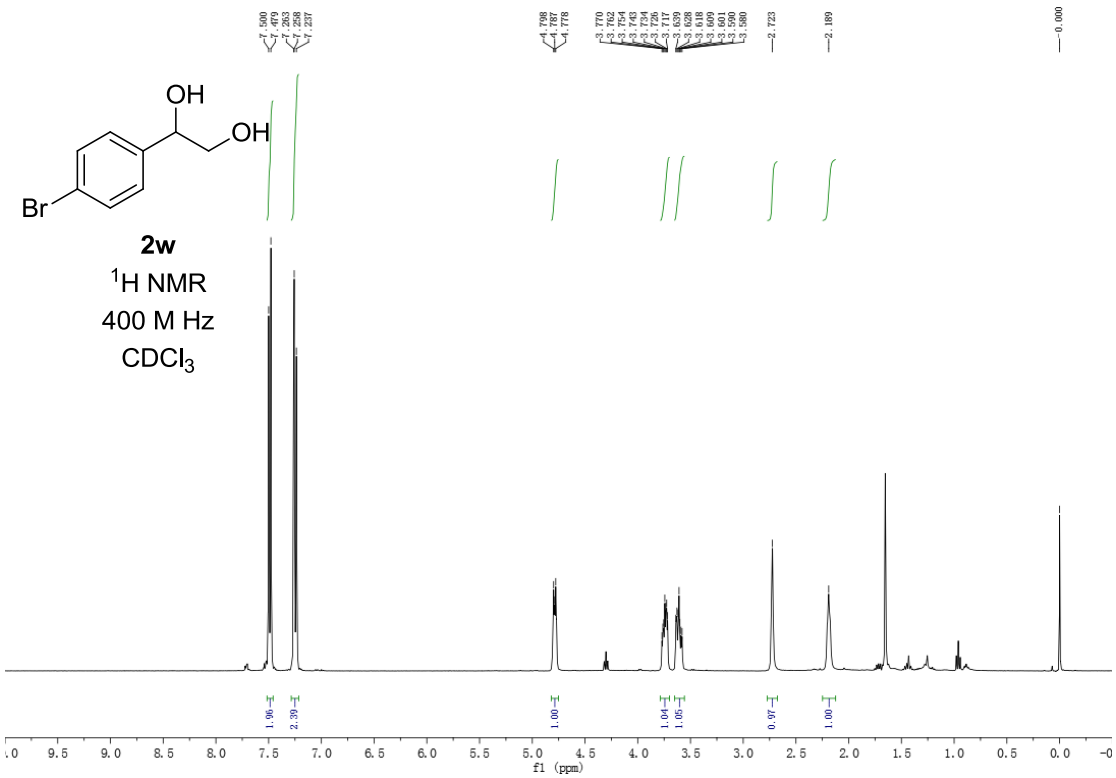
^{13}C NMR

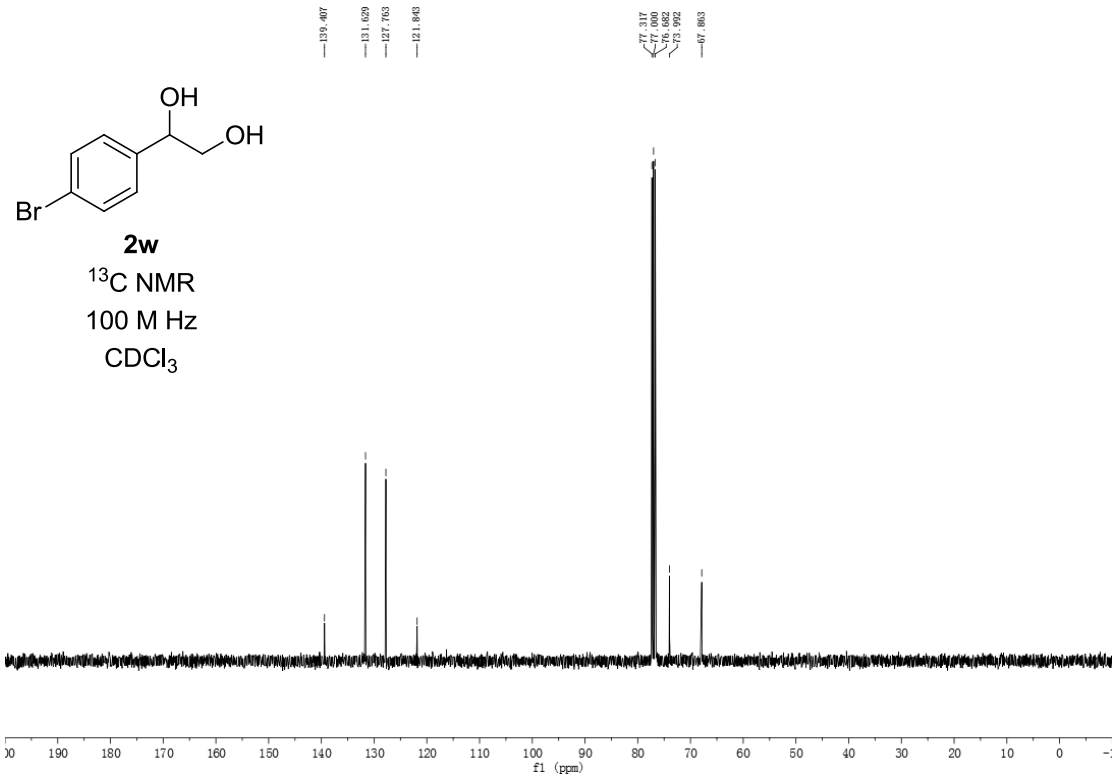
100 M Hz

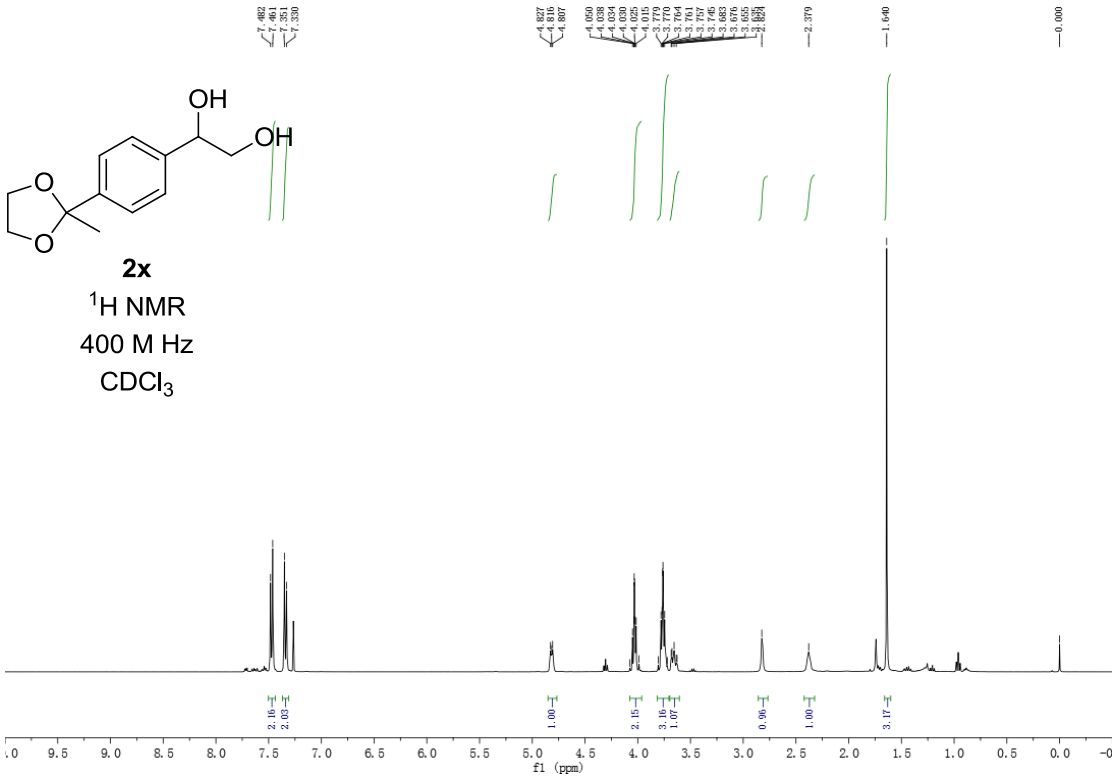
$CDCl_3$

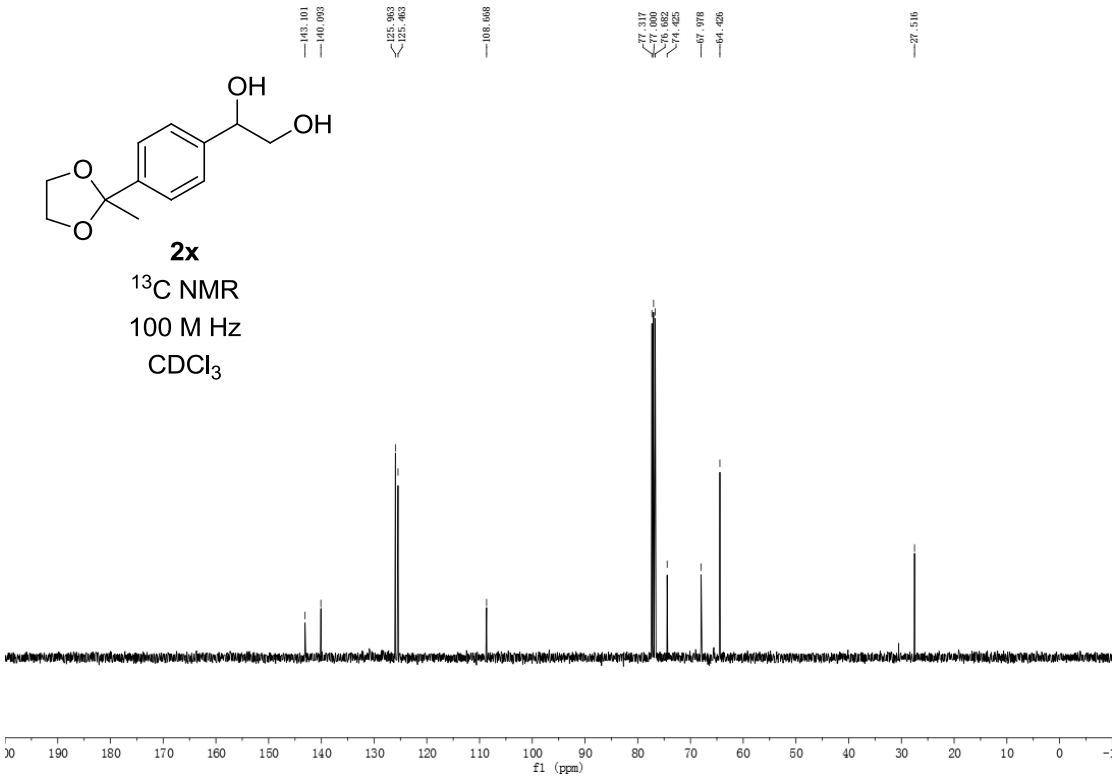

OH
Cl
OH
2v
1H NMR
400 M Hz
CDCl3
f1 (ppm)

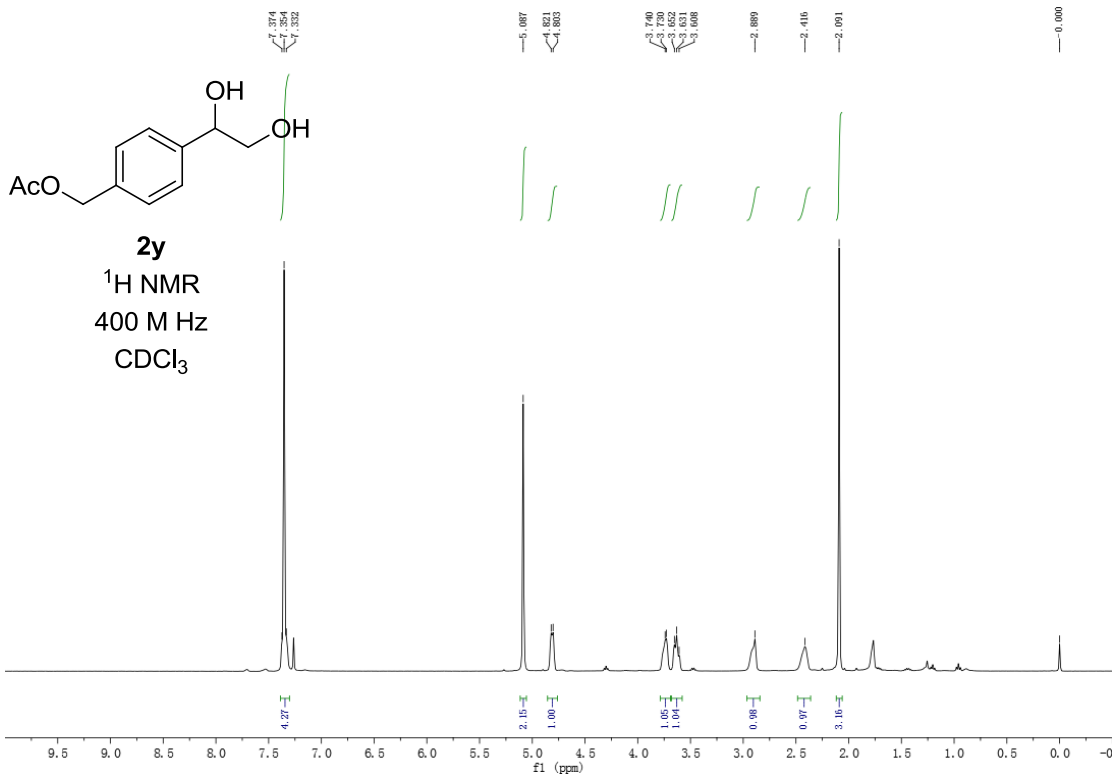

OH
Cl
OH
2v
13C NMR
100 M Hz
CDCl3
f1 (ppm)

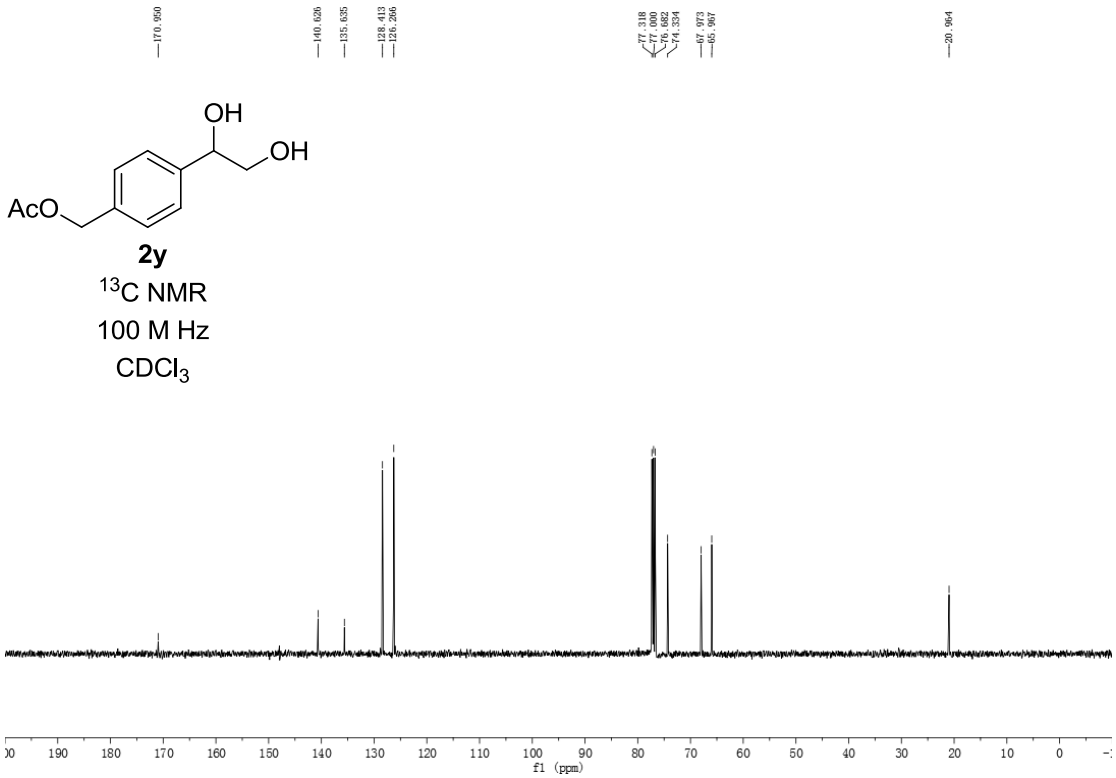

OH
OH
Br
2w
1H NMR
400 M Hz
CDCl3
f1 (ppm)

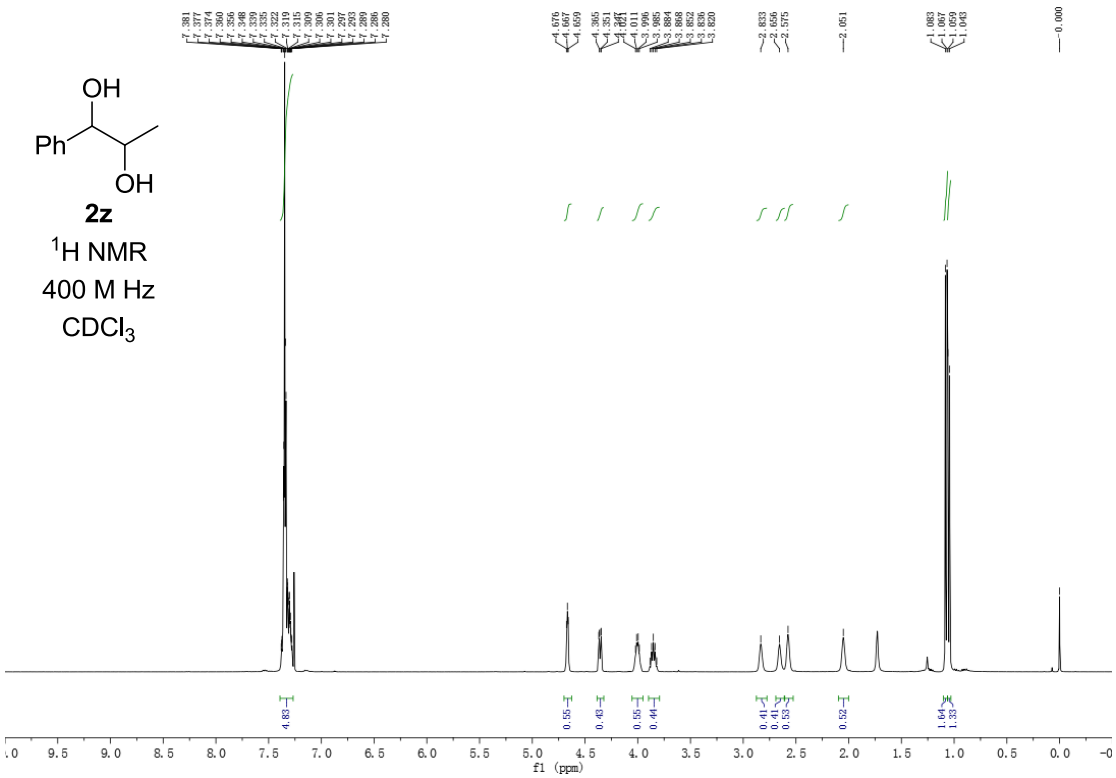

OH
OH
Br
2w
13C NMR
100 M Hz
CDCl3
f1 (ppm)

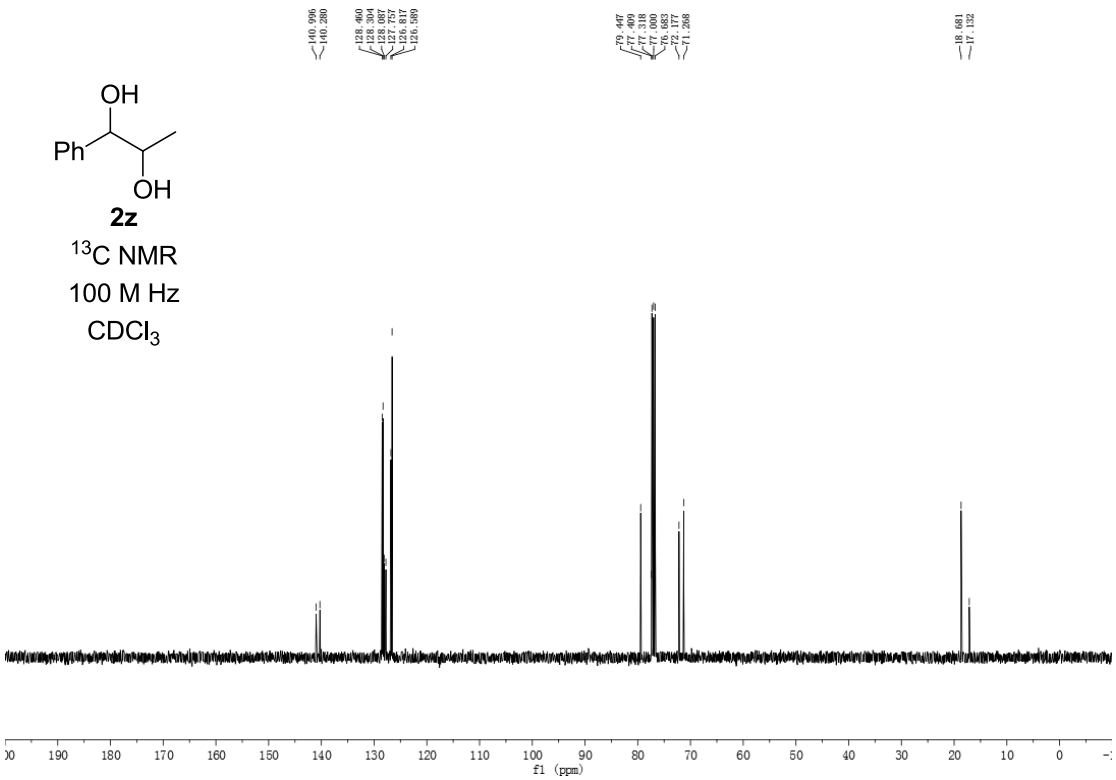

OH
OH
O
O
2x
1H NMR
400 M Hz
CDCl3
f1 (ppm)

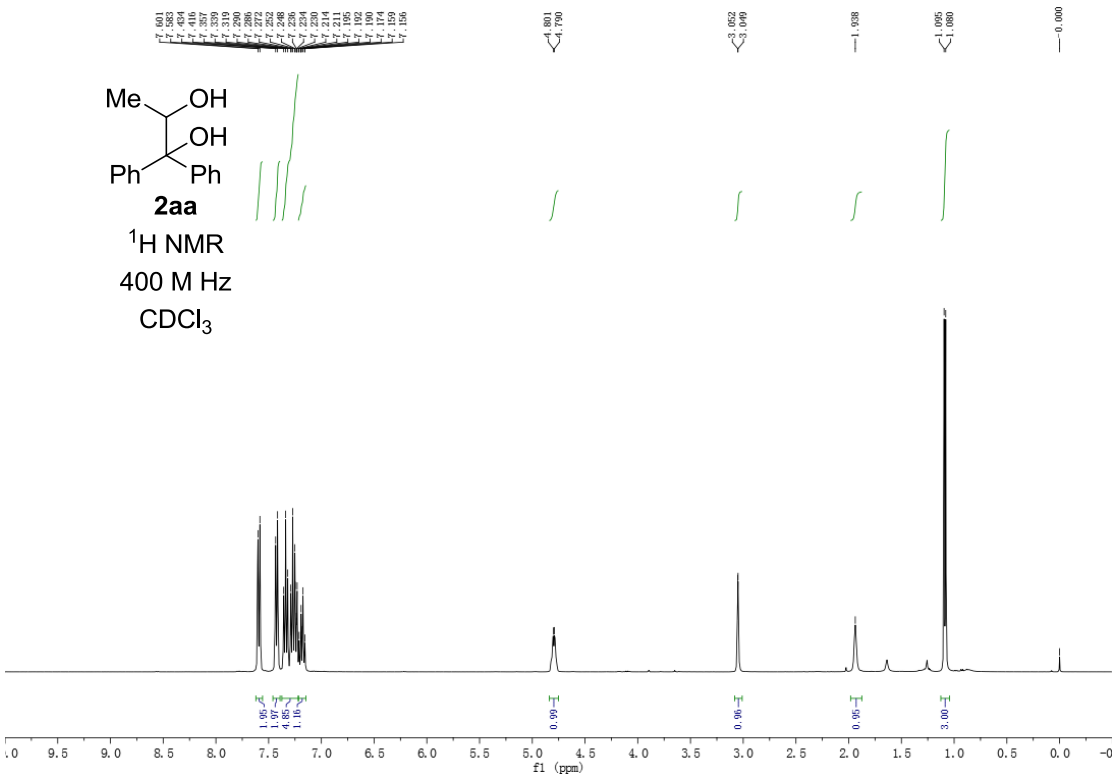

OH
OH
O
O
2x
13C NMR
100 M Hz
CDCl3
f1 (ppm)

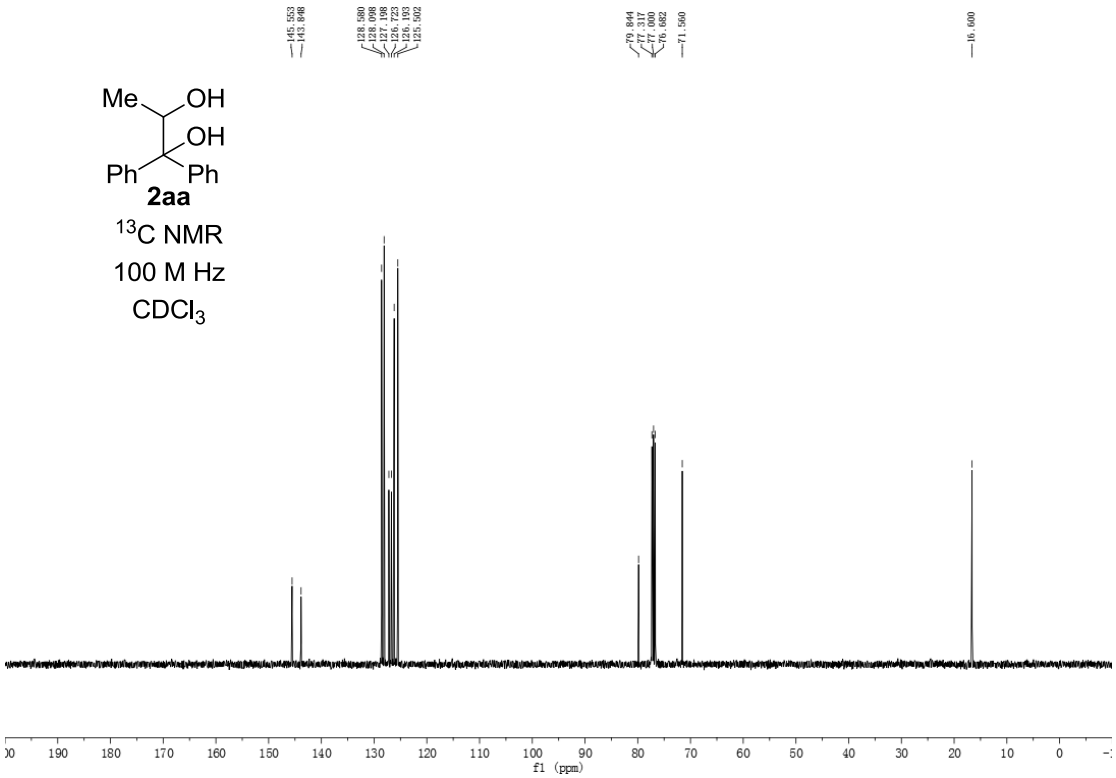

OH
OH
AcO
2y
1H NMR
400 M Hz
CDCl3
f1 (ppm)

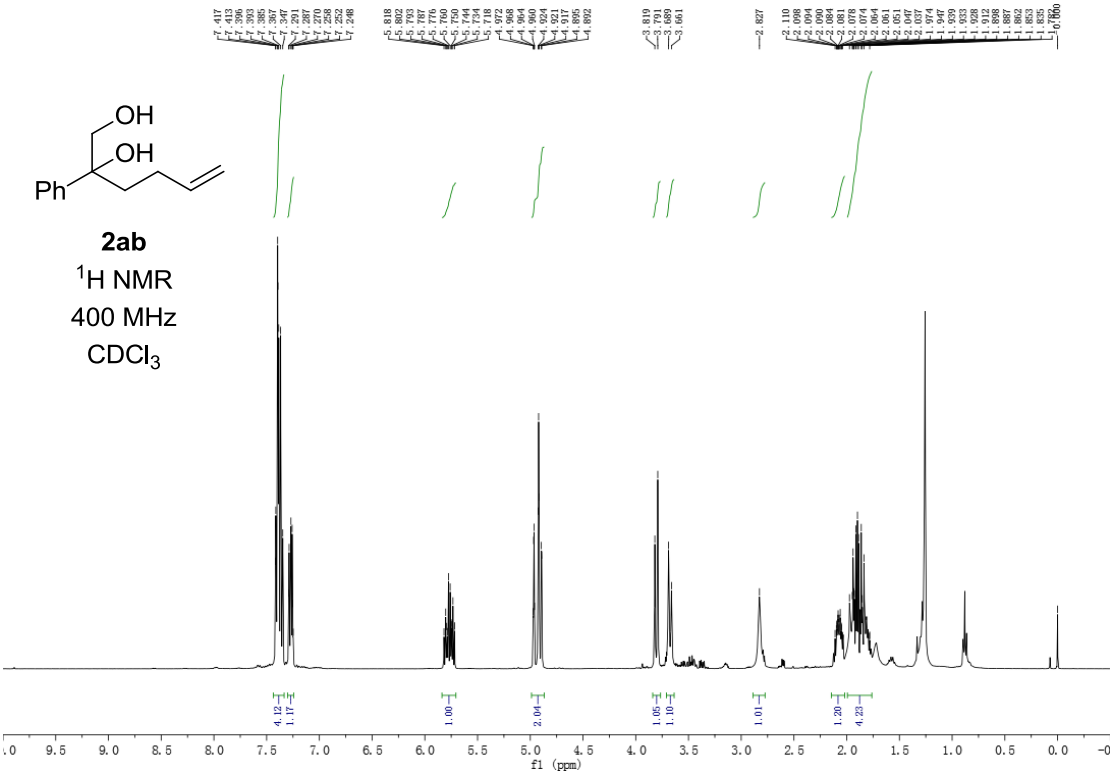

OH
OH
AcO
2y
13C NMR
100 M Hz
CDCl3
f1 (ppm)

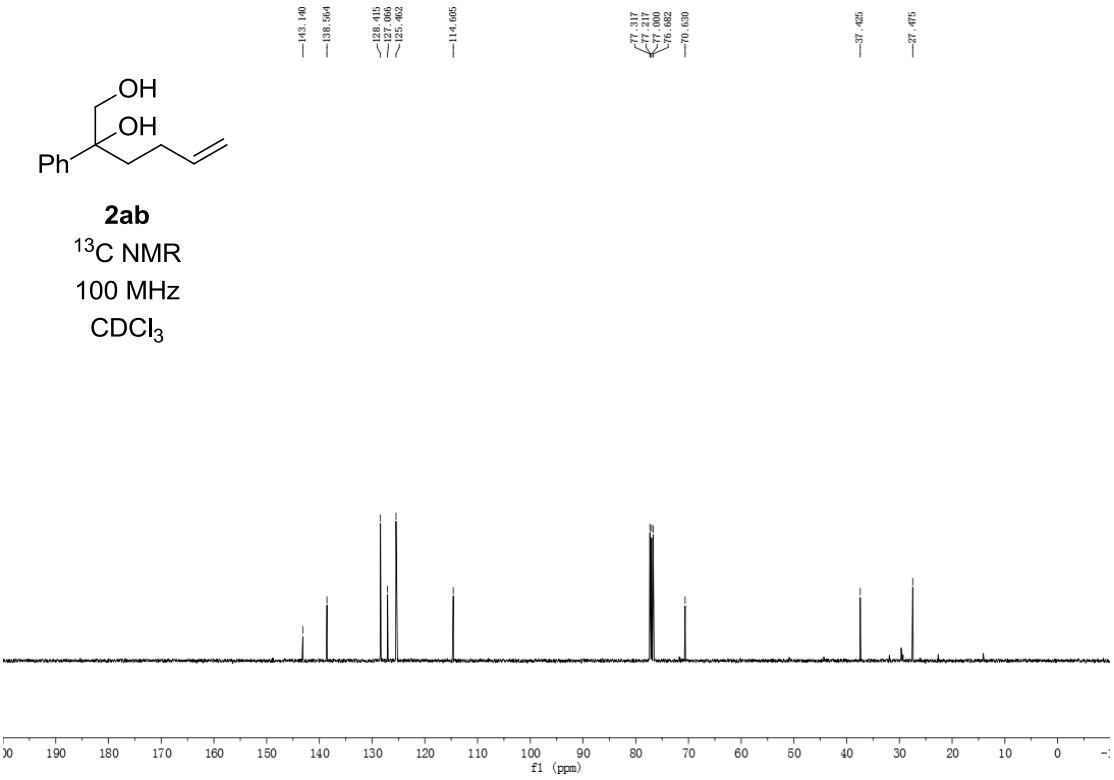

OH
Ph
OH
2z
1H NMR
400 M Hz
CDCl3
f1 (ppm)

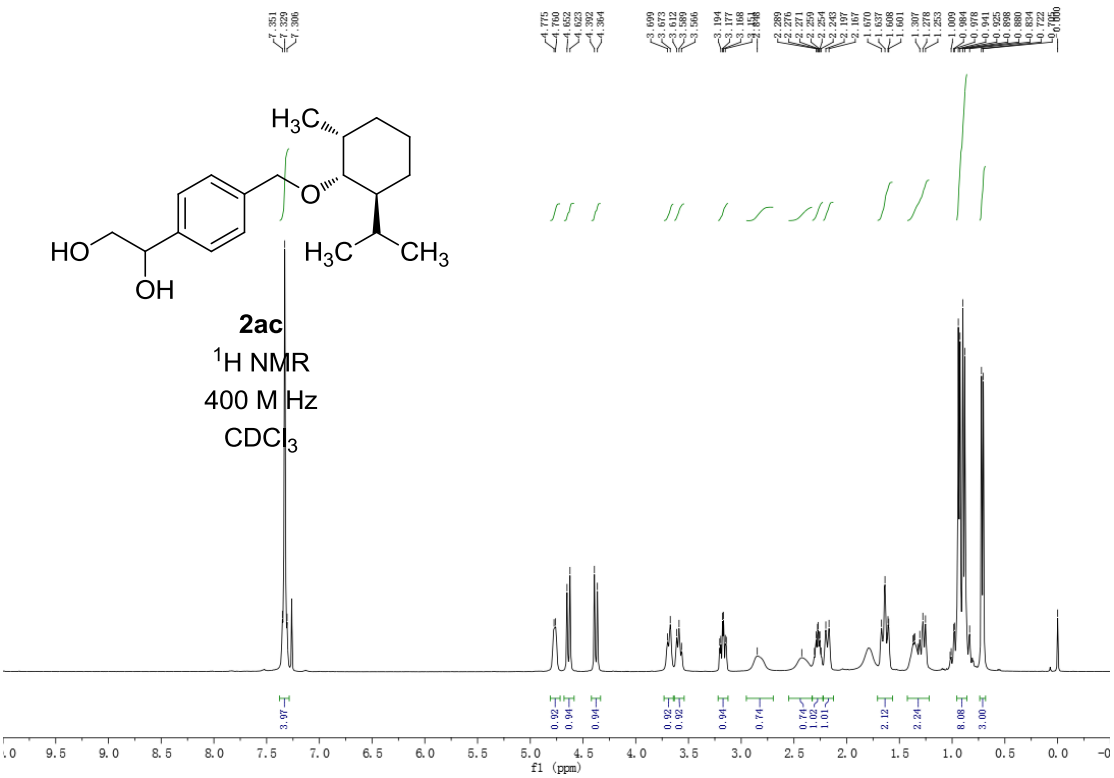

OH
Ph
OH
2z
13C NMR
100 M Hz
CDCl3
f1 (ppm)

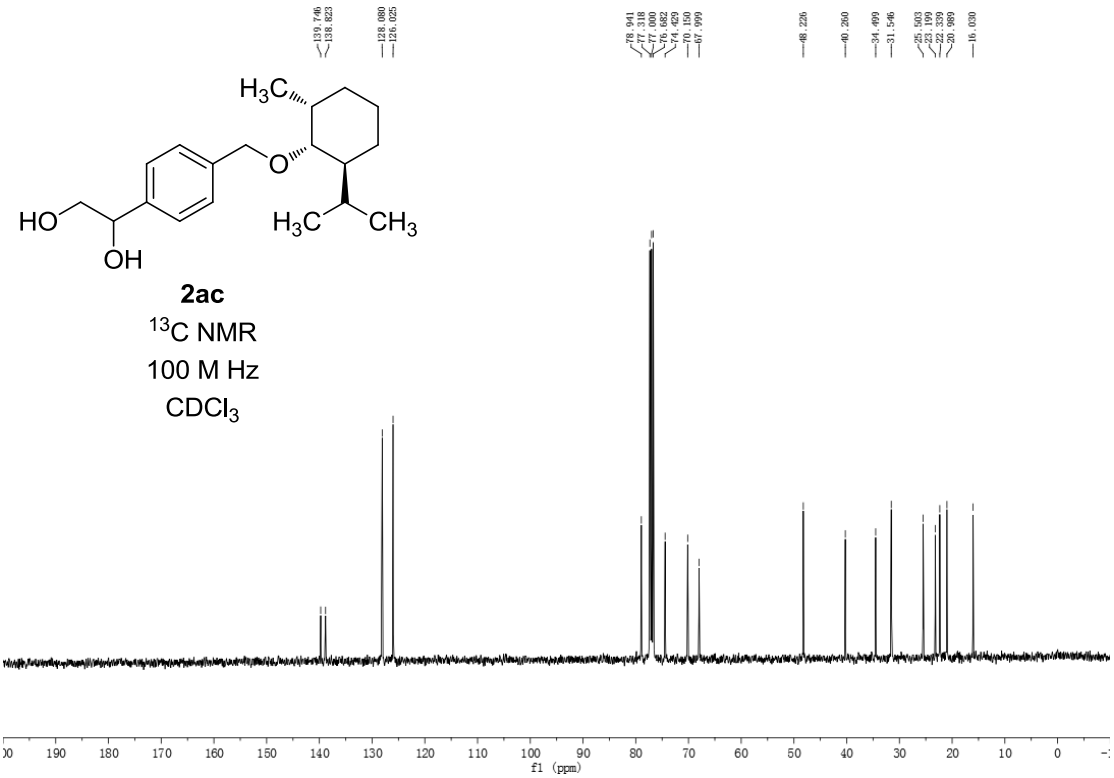

Me
OH
OH
Ph
Ph
2aa
1H NMR
400 M Hz
CDCl3
f1 (ppm)

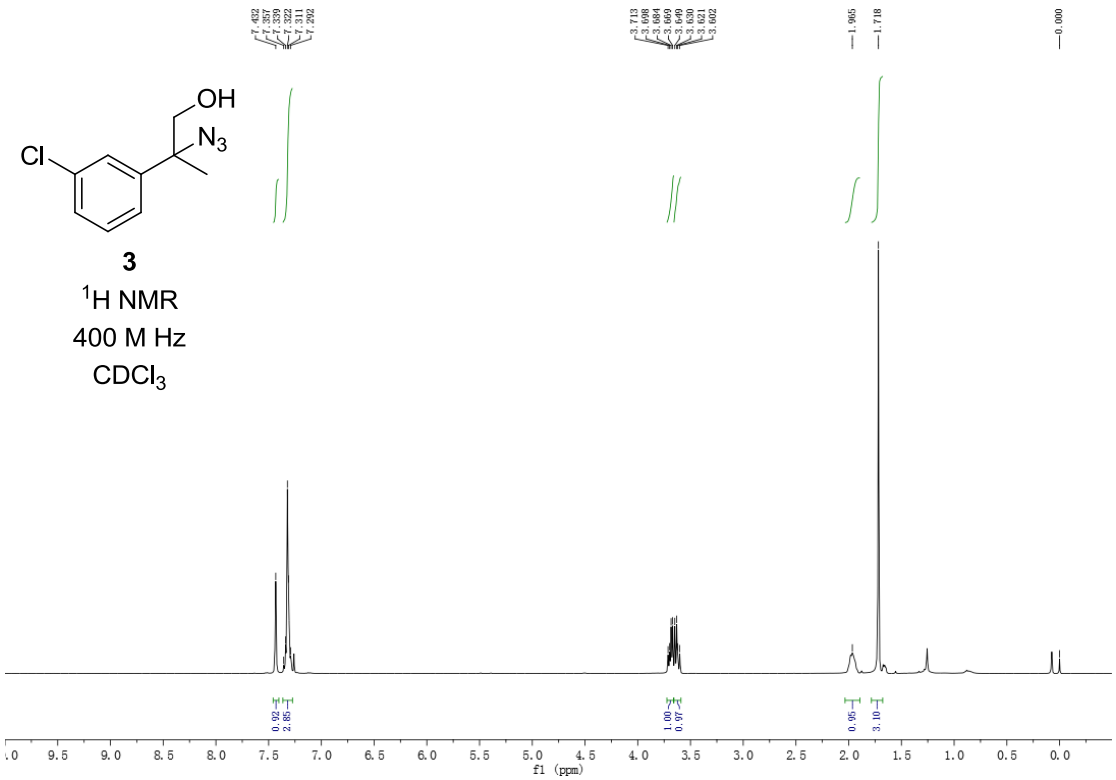

Me
OH
OH
Ph
Ph
2aa
13C NMR
100 M Hz
CDCl3
f1 (ppm)

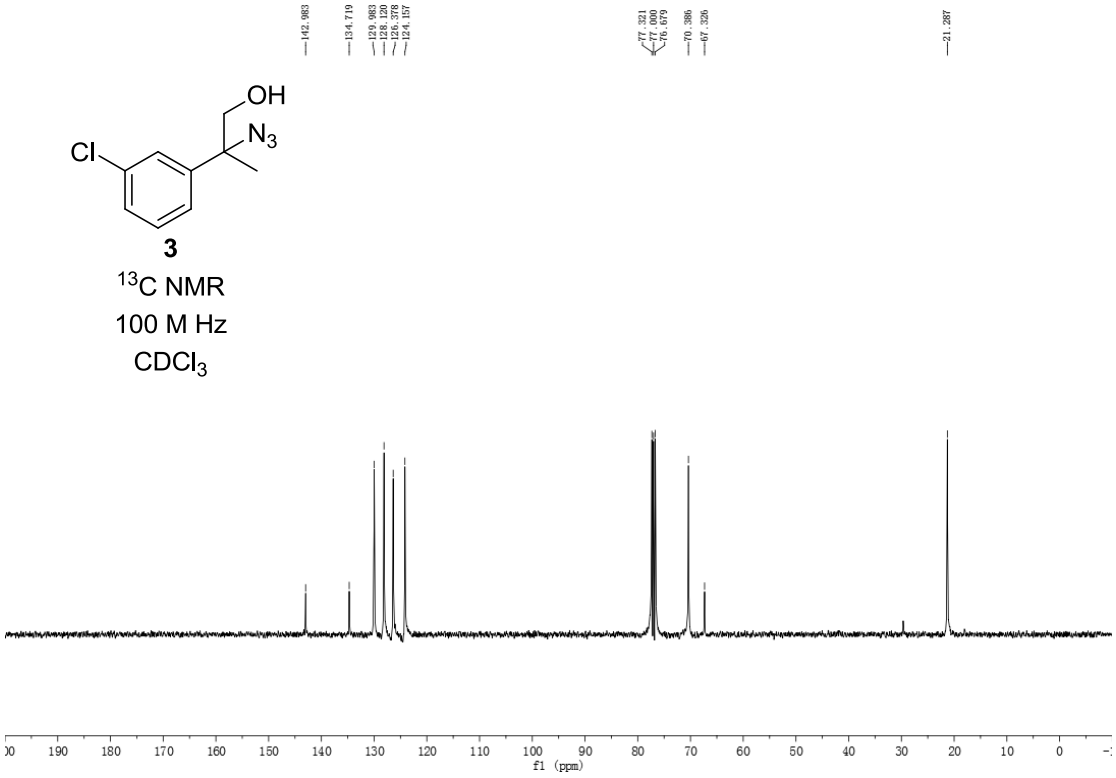

OH
OH
Ph
2ab
1H NMR
400 MHz
CDCl3
f1 (ppm)

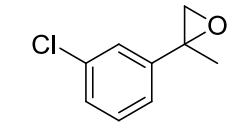

OH
OH
Ph
2ab
13C NMR
100 MHz
CDCl3
f1 (ppm)


H3C
O
HO
OH
H3C
CH3
2ac
1H NMR
400 M Hz
CDCl3
f1 (ppm)


H3C
O
HO
OH
H3C
CH3
2ac
13C NMR
100 M Hz
CDCl3
f1 (ppm)


OH
N3
Cl
3
1H NMR
400 M Hz
CDCl3
f1 (ppm)


OH
N3
Cl
3
13C NMR
100 M Hz
CDCl3
f1 (ppm)

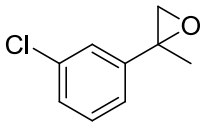


5

^{1}H NMR

400 M Hz

$CDCl_3$

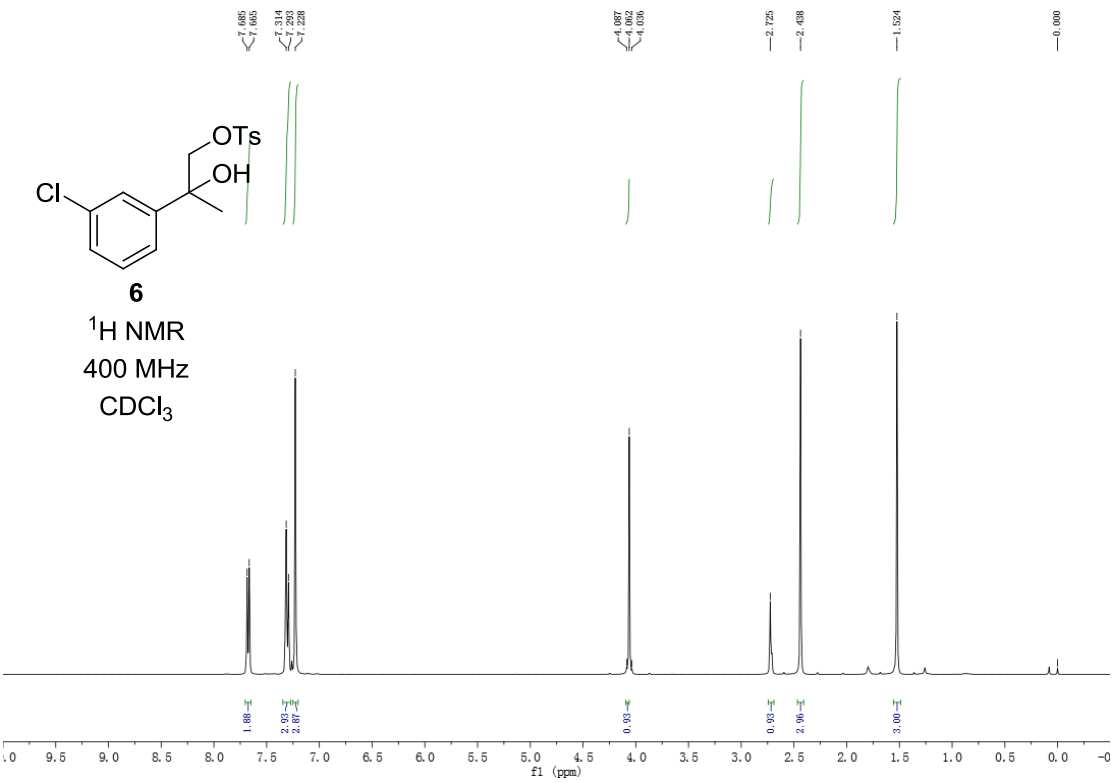


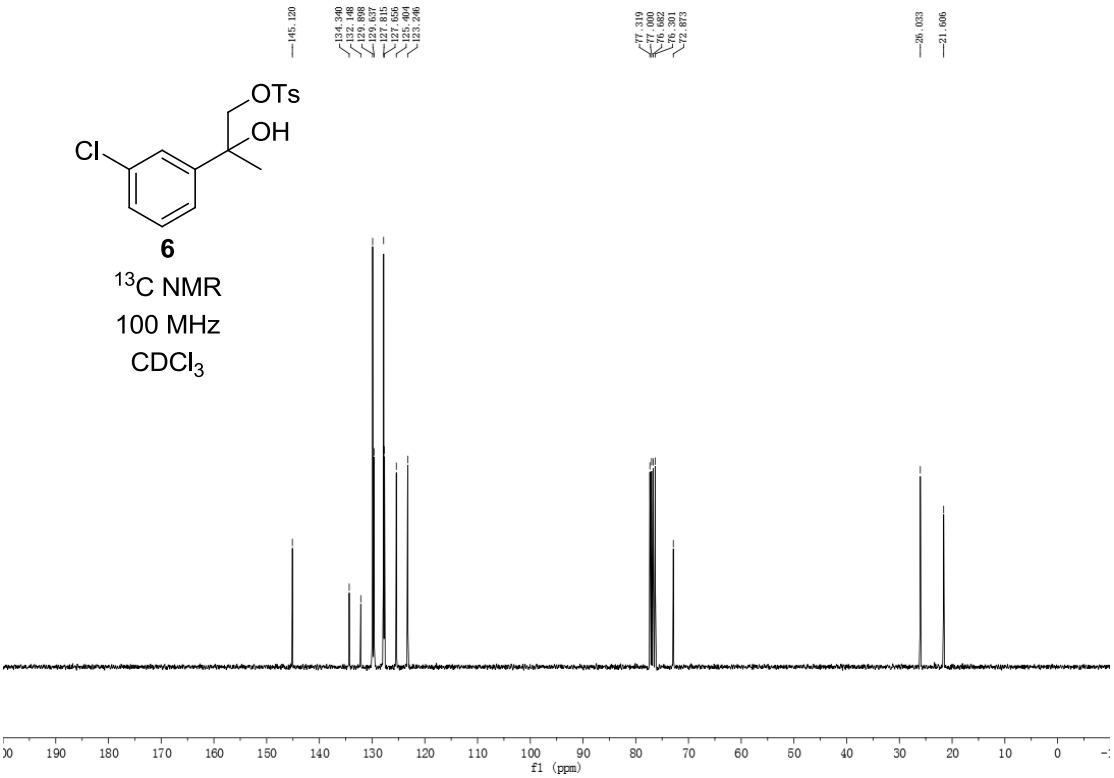
5

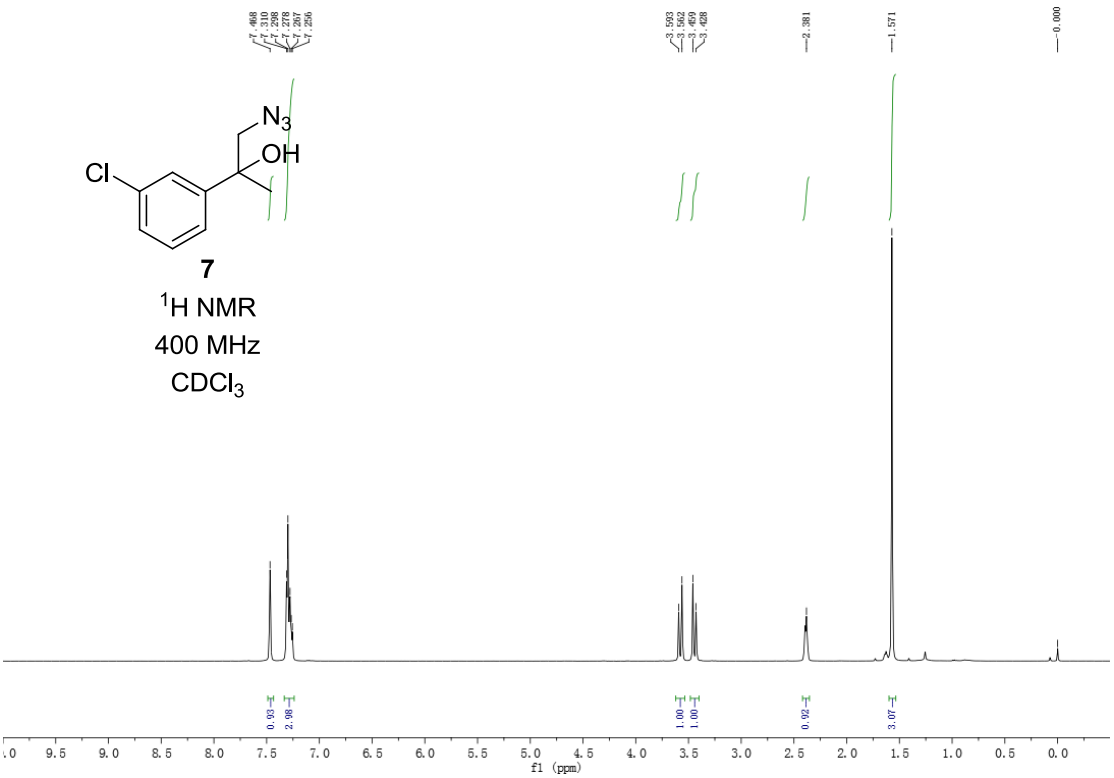
^{13}C NMR

100 M Hz

$CDCl_3$


OTs
OH
Cl
6
1H NMR
400 MHz
CDCl3
f1 (ppm)


OTs
OH
Cl
6
13C NMR
100 MHz
CDCl3
f1 (ppm)

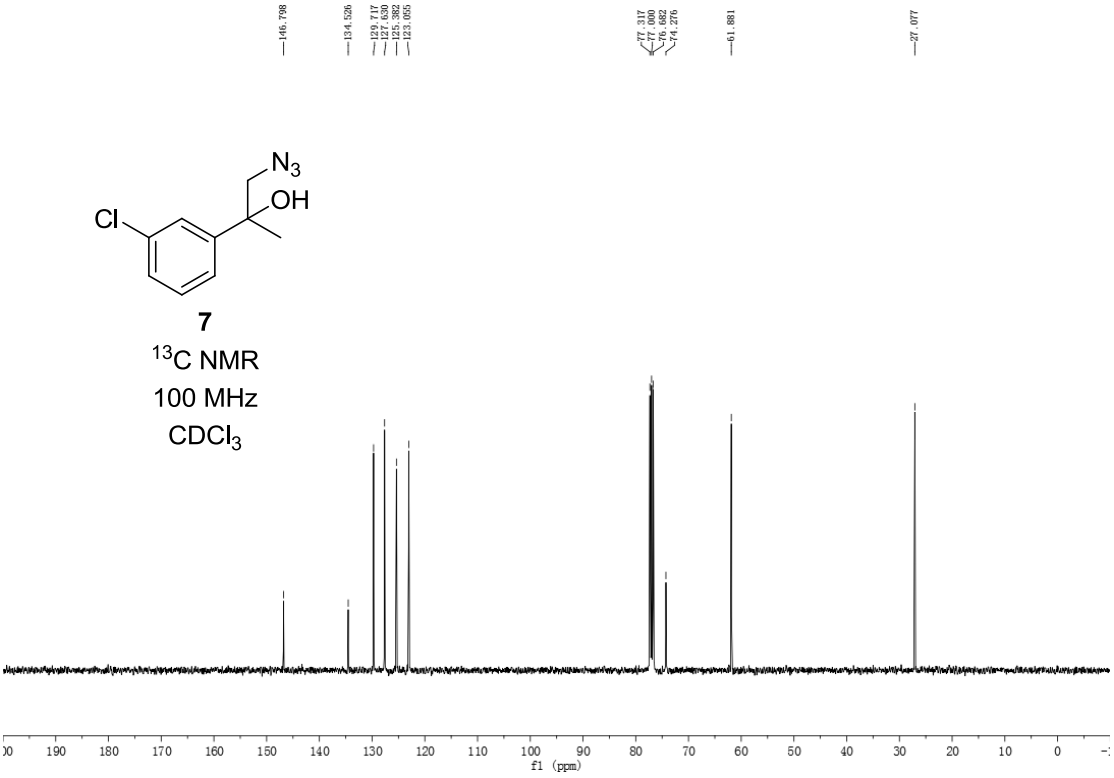


7

^{1}H NMR

400 MHz

$CDCl_3$

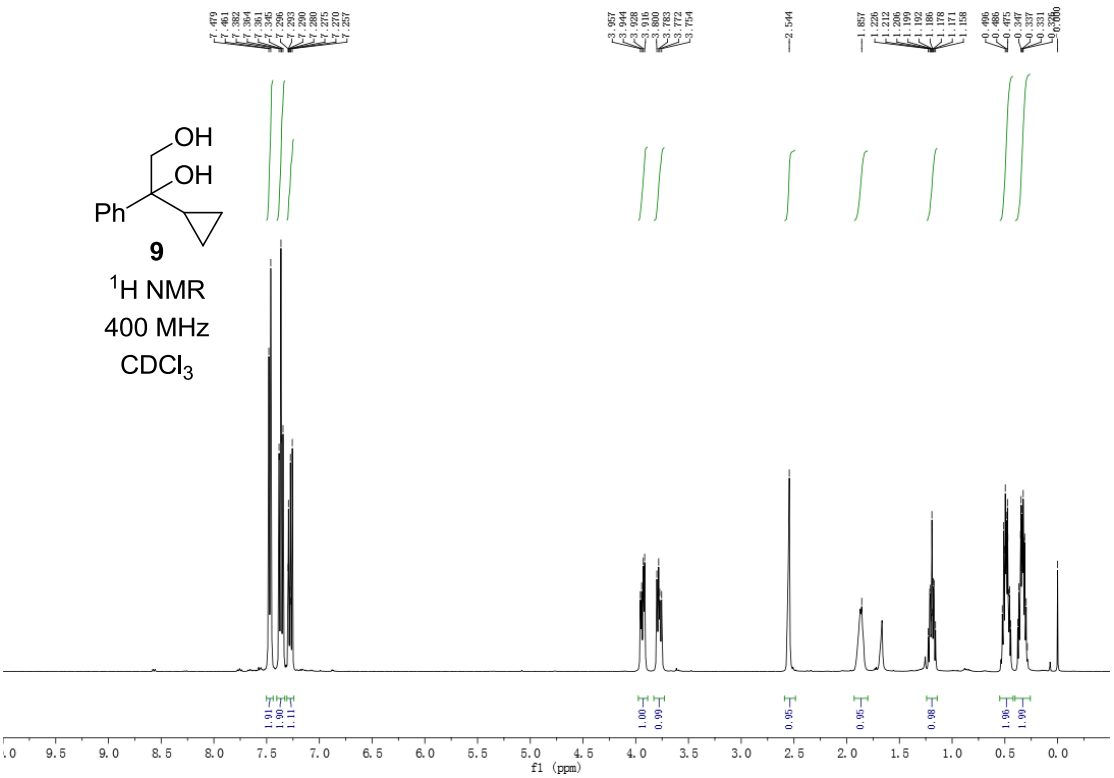


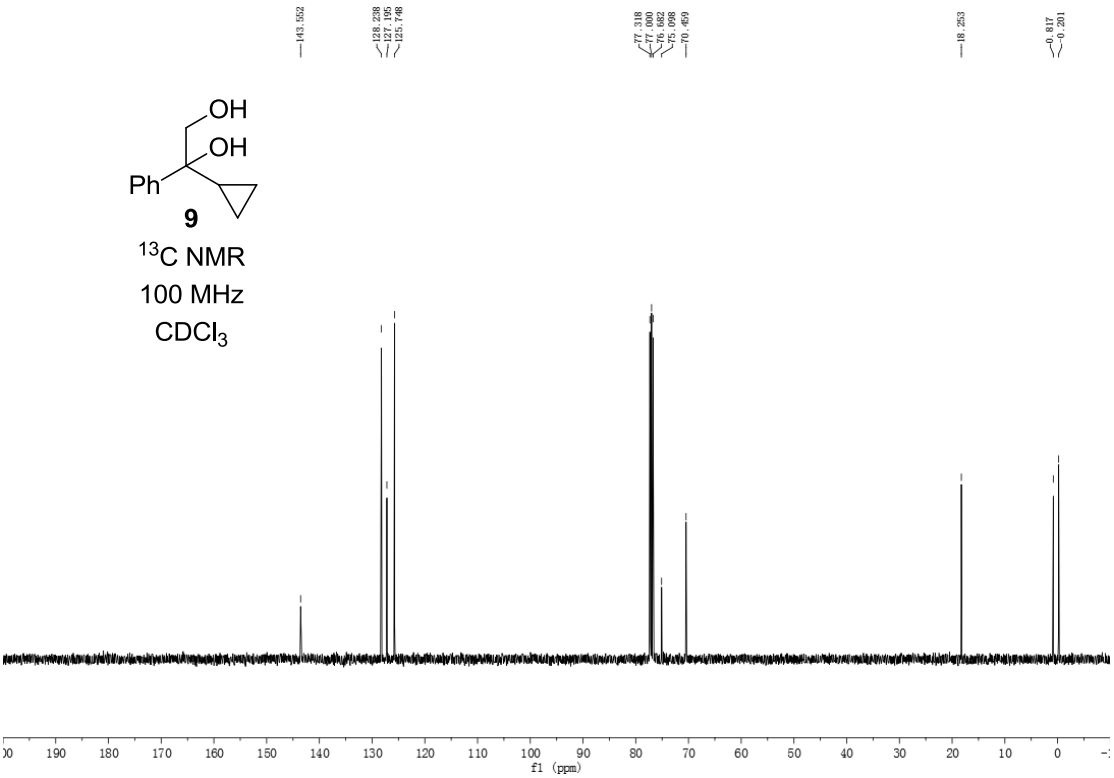
7

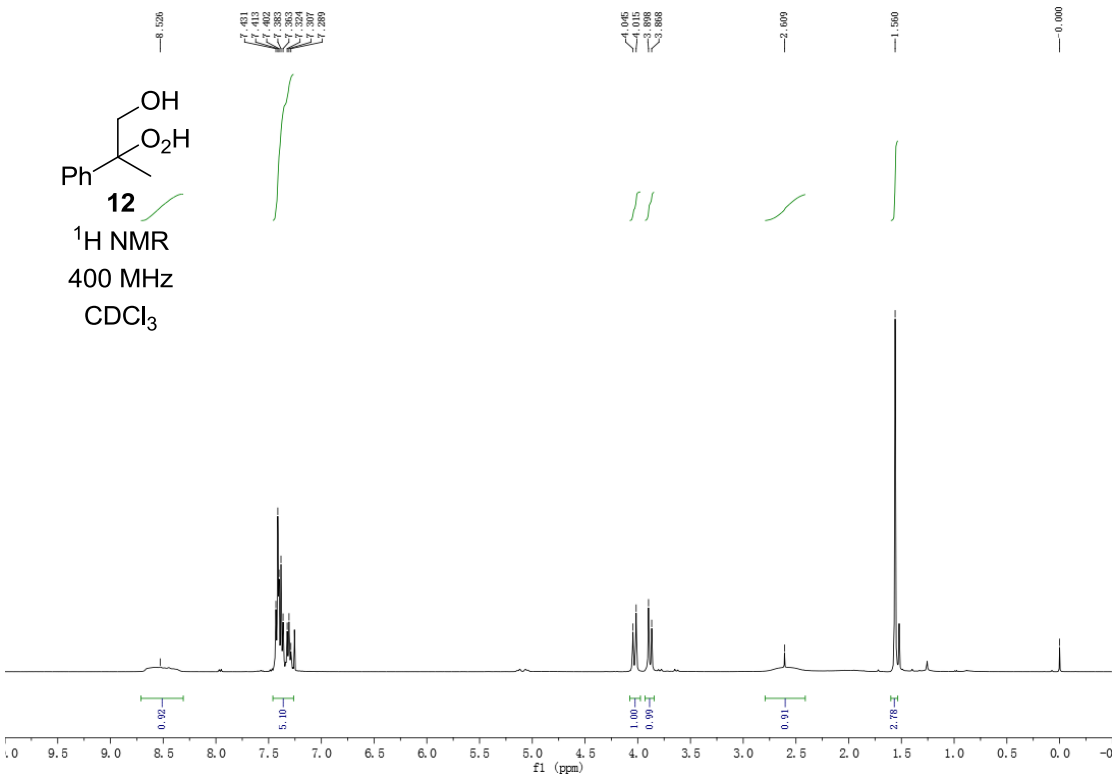
^{13}C NMR

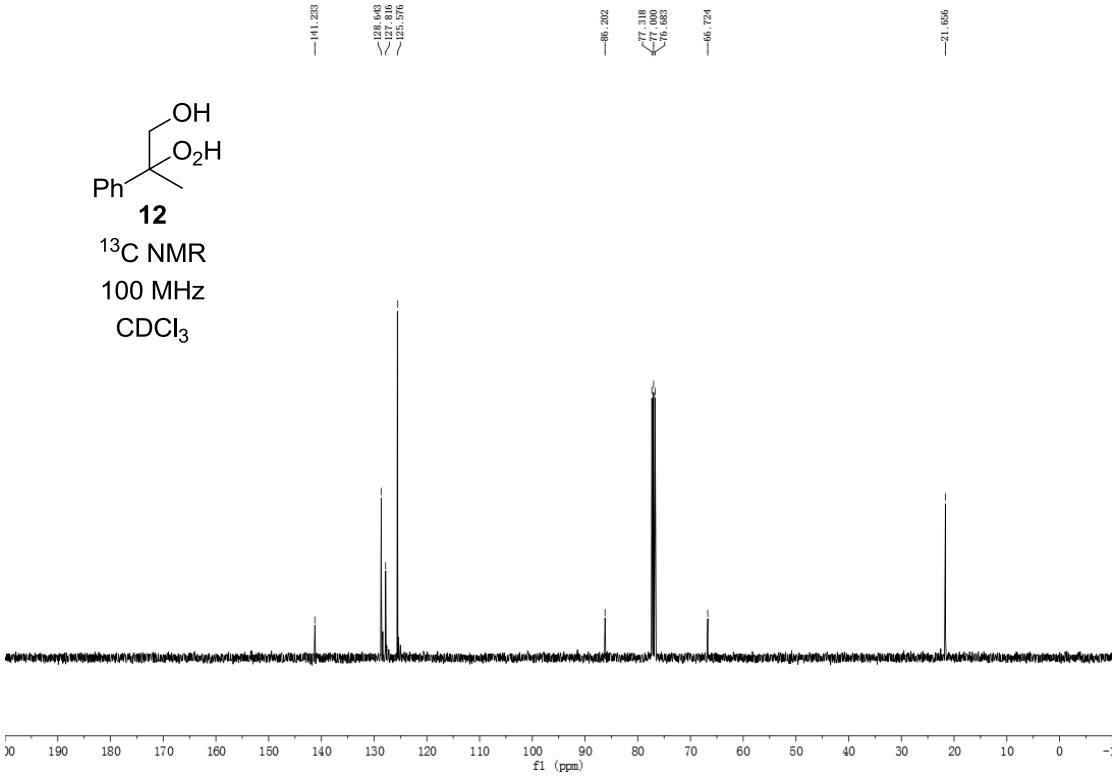
100 MHz

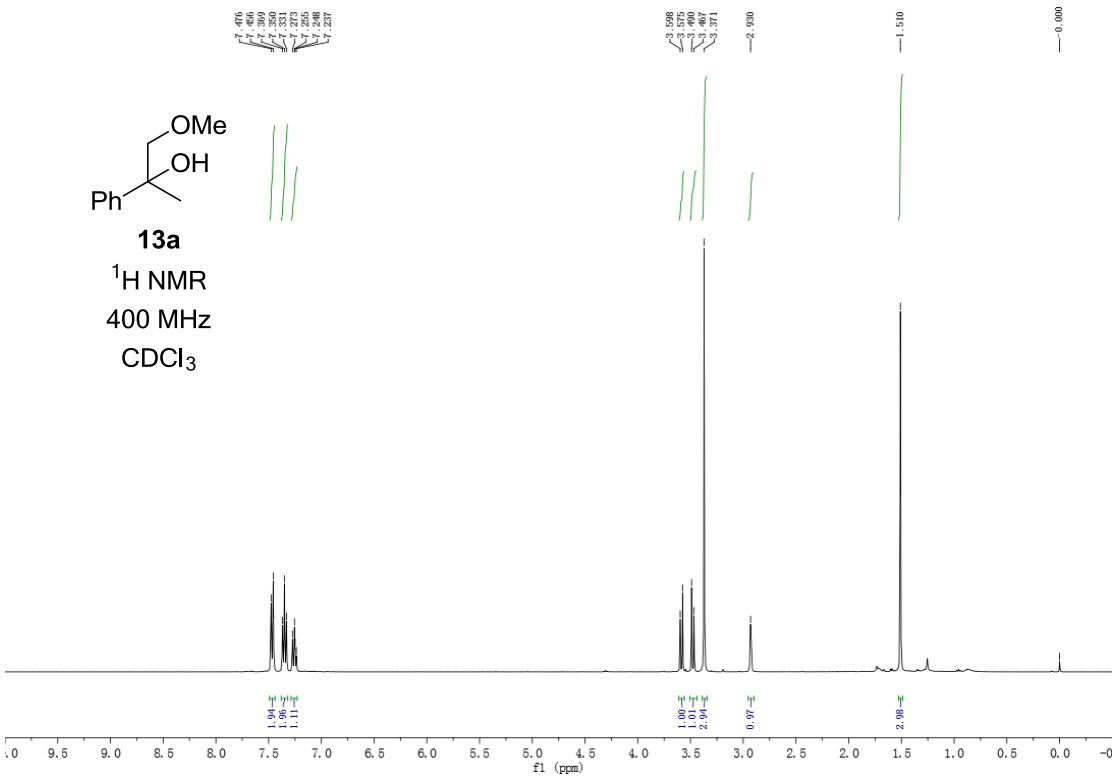
$CDCl_3$

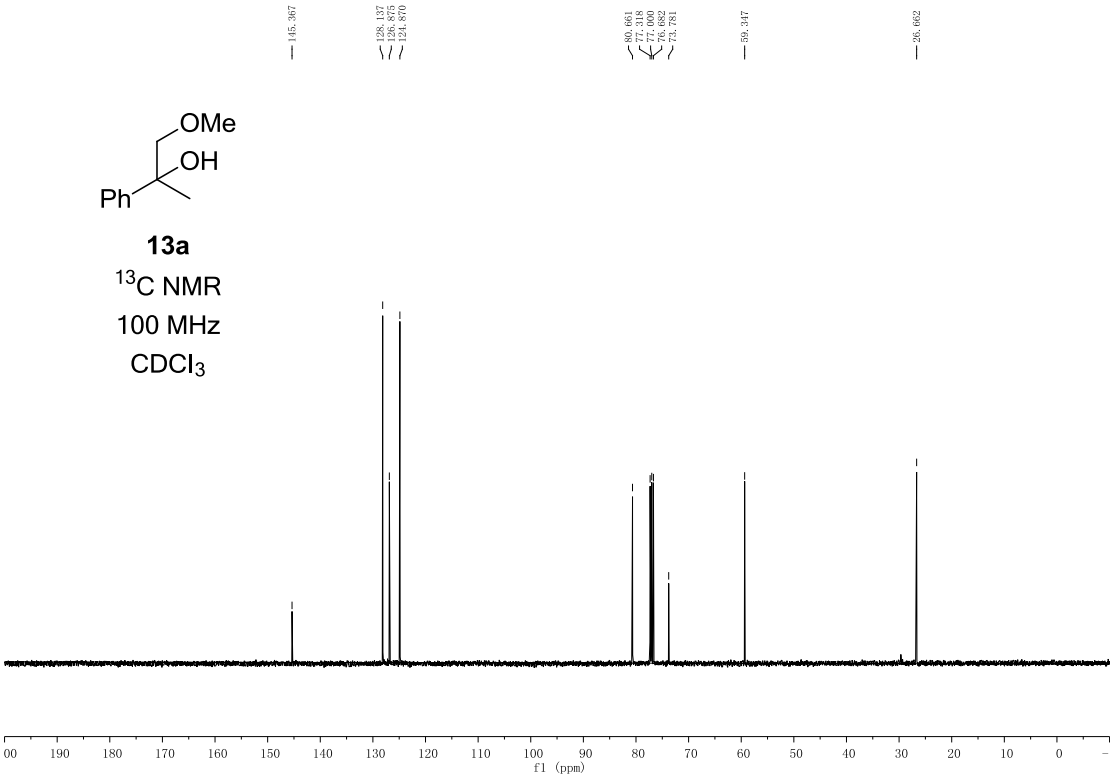

OH
OH
Ph
9
1H NMR
400 MHz
CDCl3
f1 (ppm)

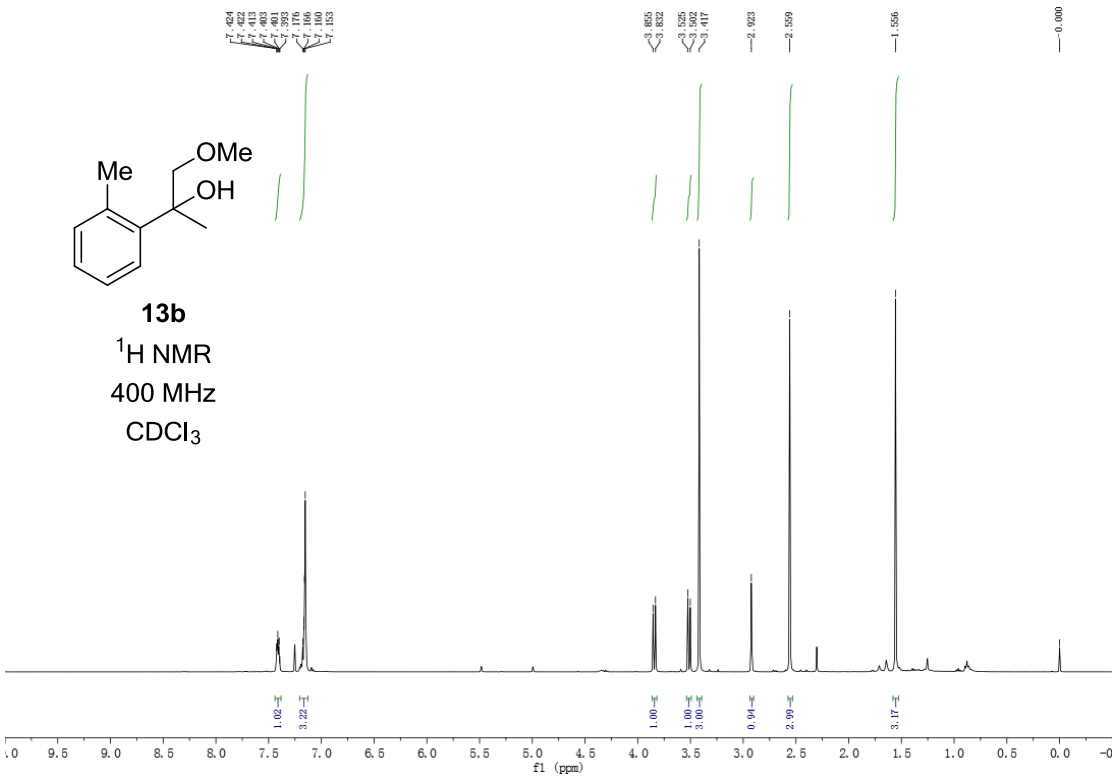

OH
OH
Ph
9
13C NMR
100 MHz
CDCl3
f1 (ppm)


OH
O2H
Ph
12
1H NMR
400 MHz
CDCl3
f1 (ppm)


OH
O2H
Ph
12
13C NMR
100 MHz
CDCl3
f1 (ppm)


OMe
OH
Ph
13a
1H NMR
400 MHz
CDCl3
f1 (ppm)


OMe
OH
Ph
13a
13C NMR
100 MHz
CDCl3
f1 (ppm)

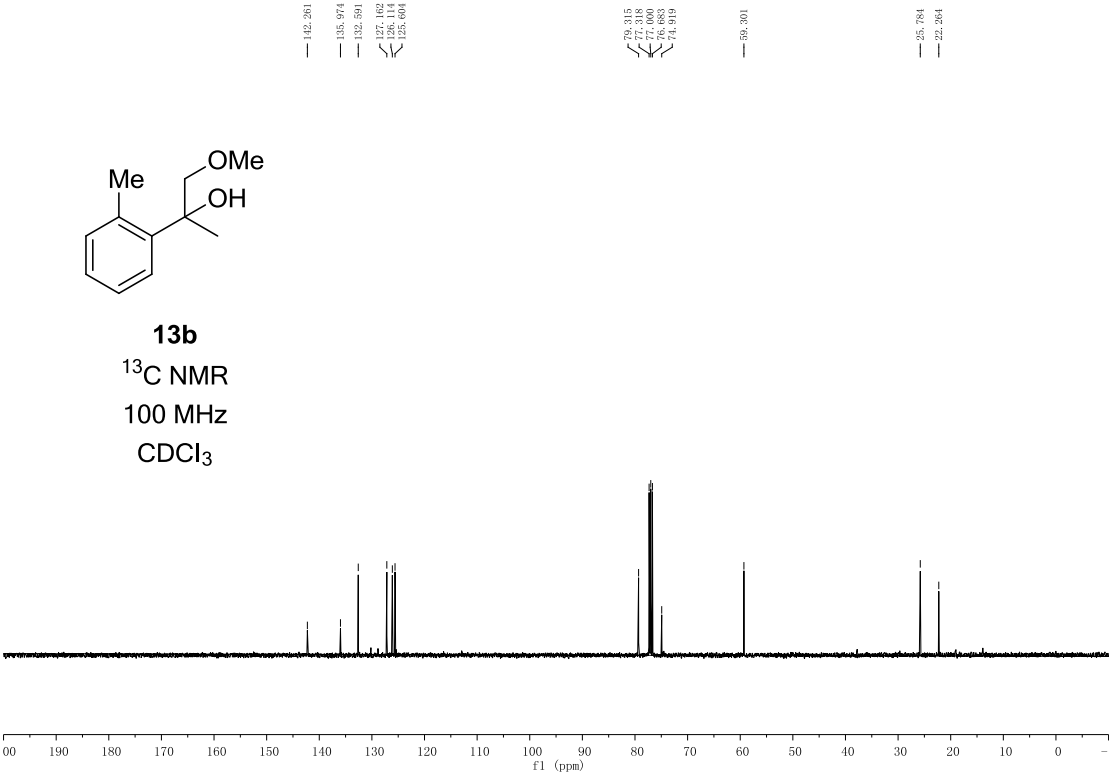


13b

^{1}H NMR

400 MHz

$CDCl_3$

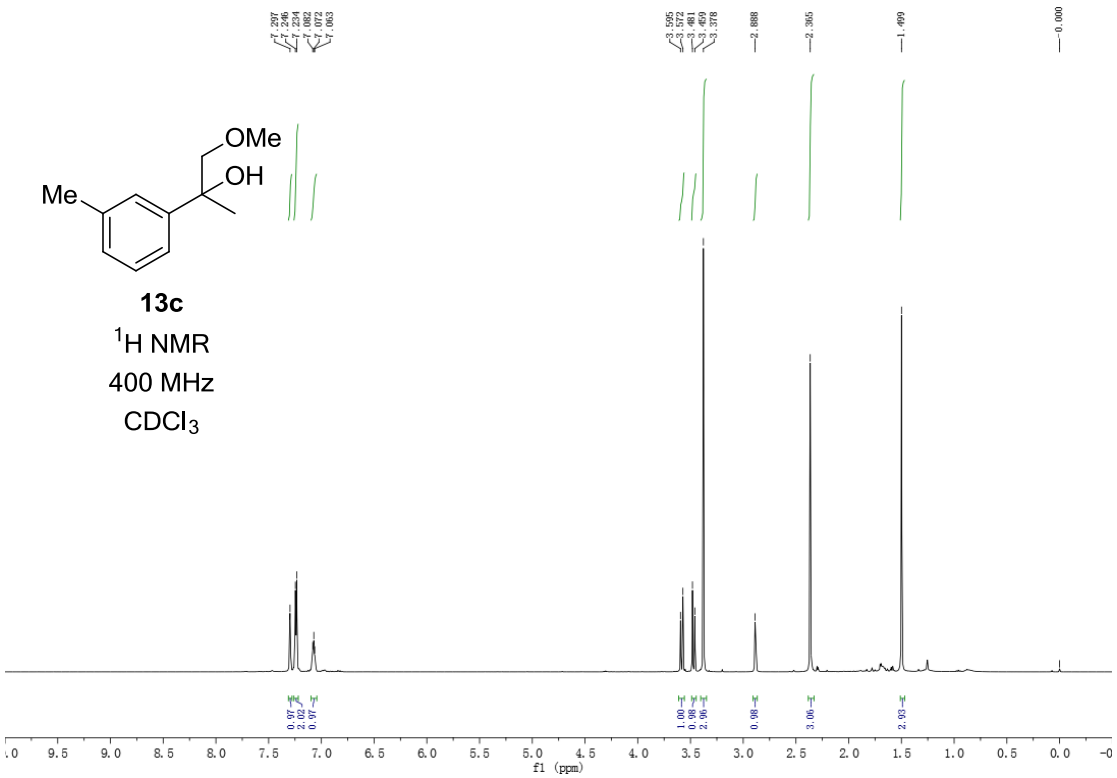


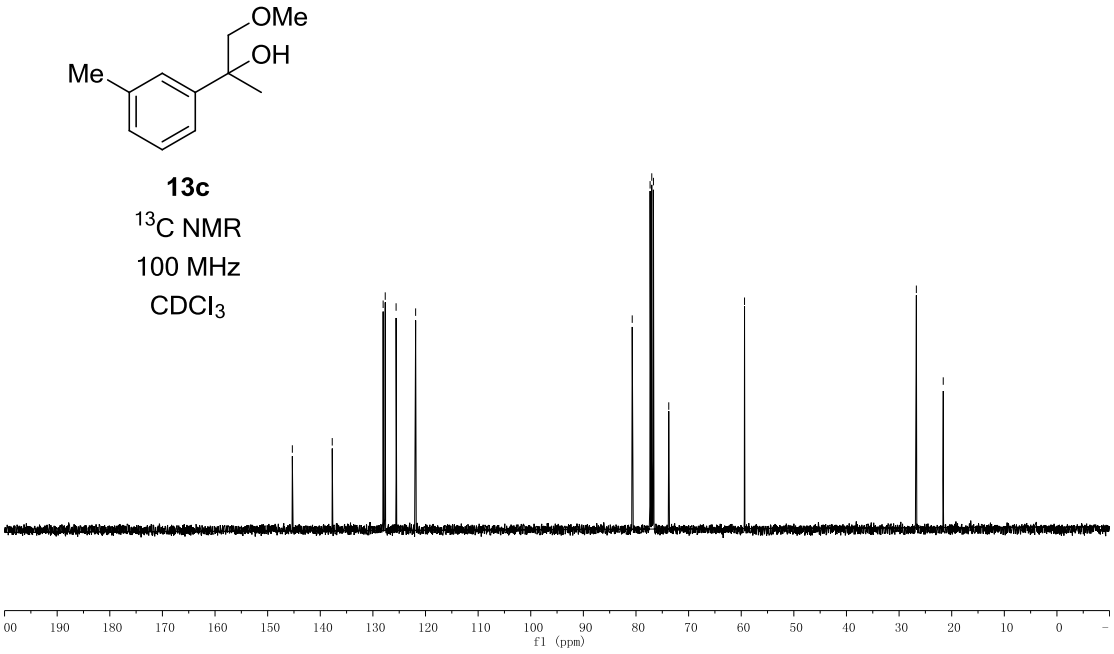
13b

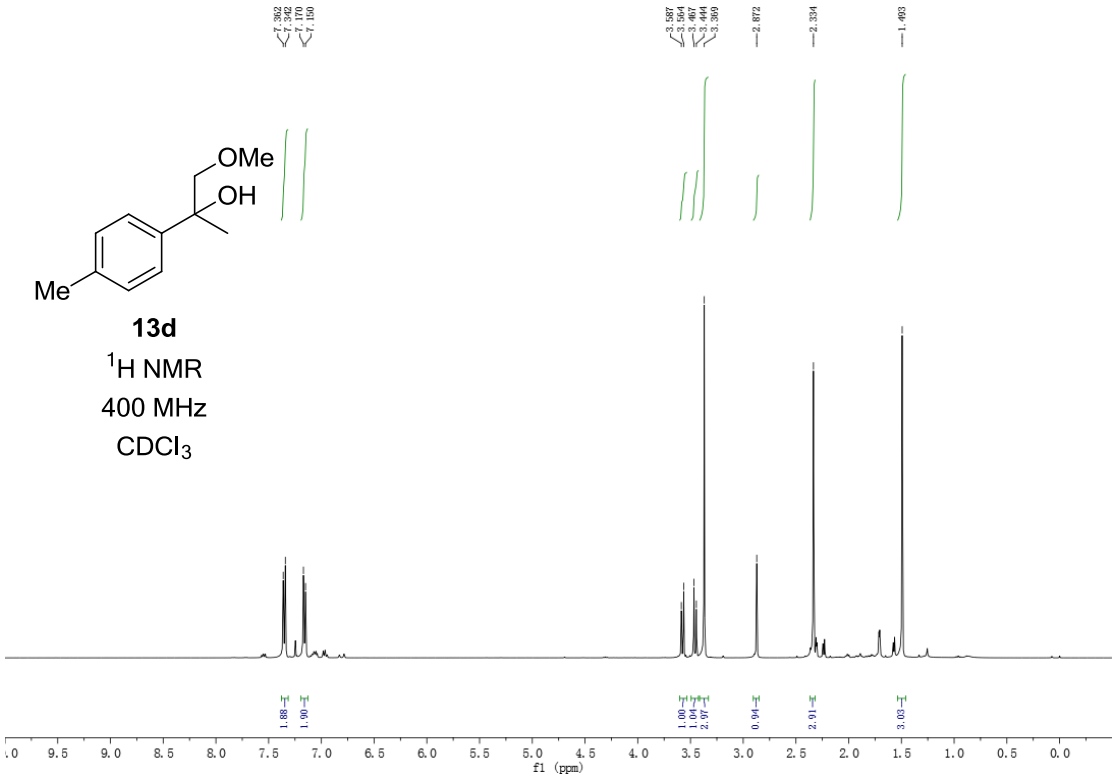
^{13}C NMR

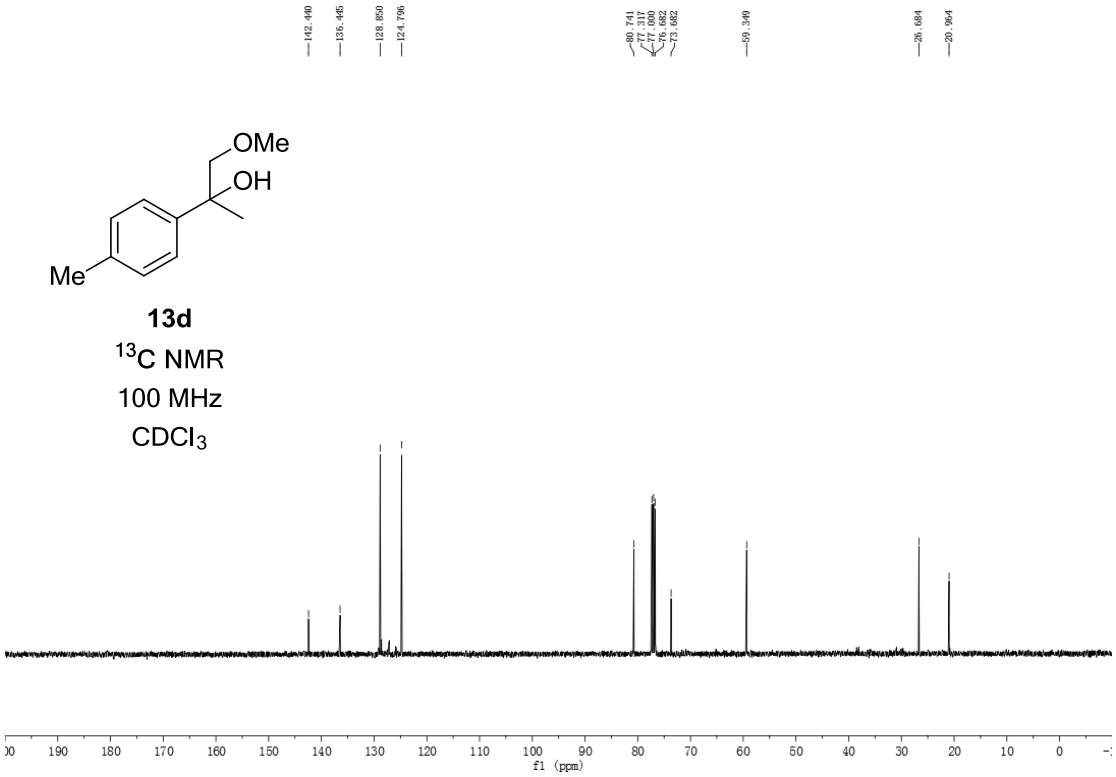
100 MHz

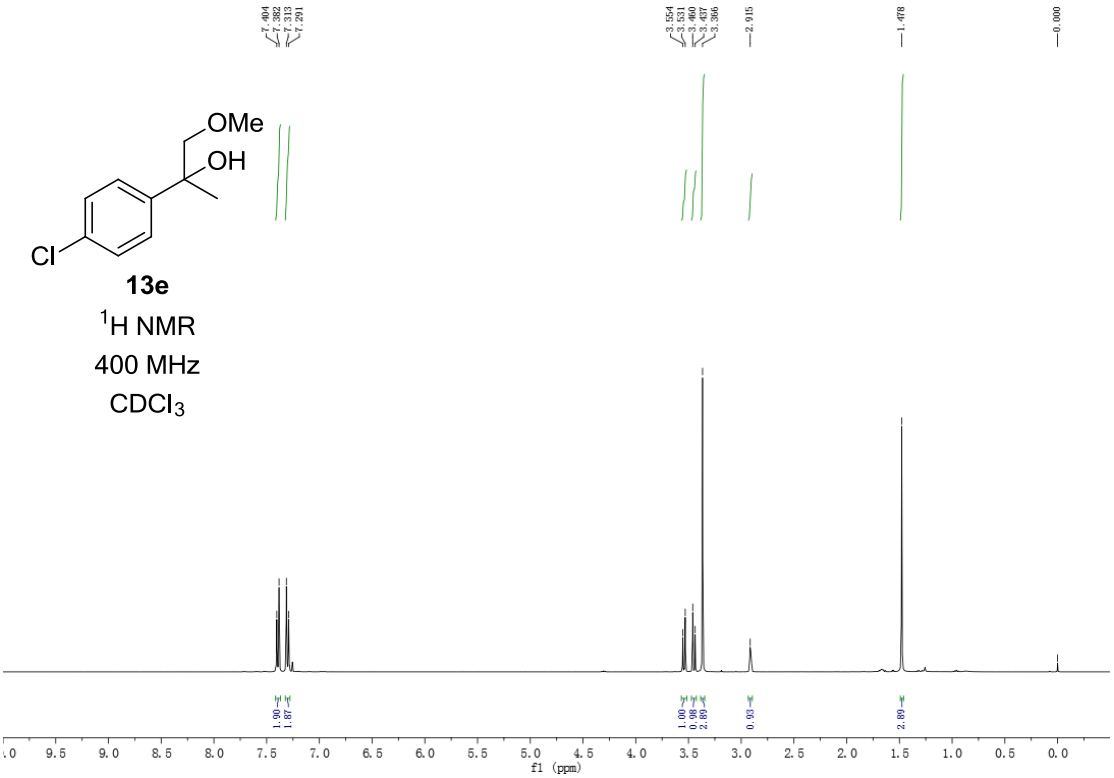
$CDCl_3$

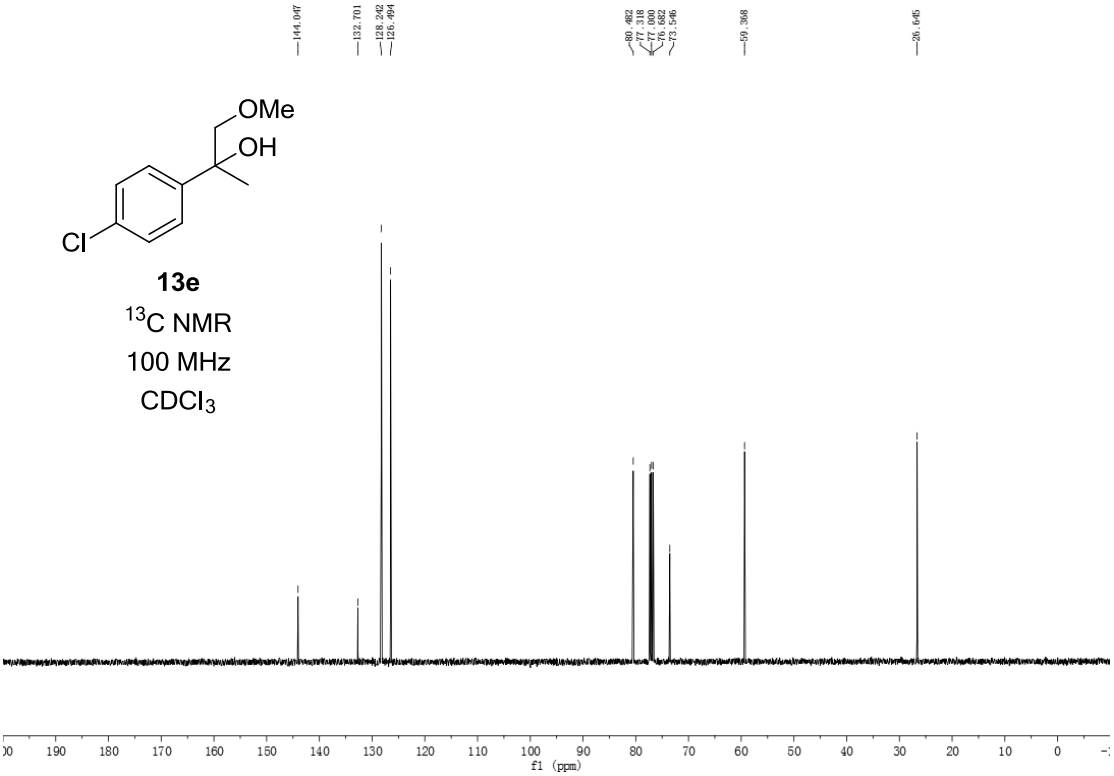

OMe
OH
Me
13c
1H NMR
400 MHz
CDCl3
f1 (ppm)

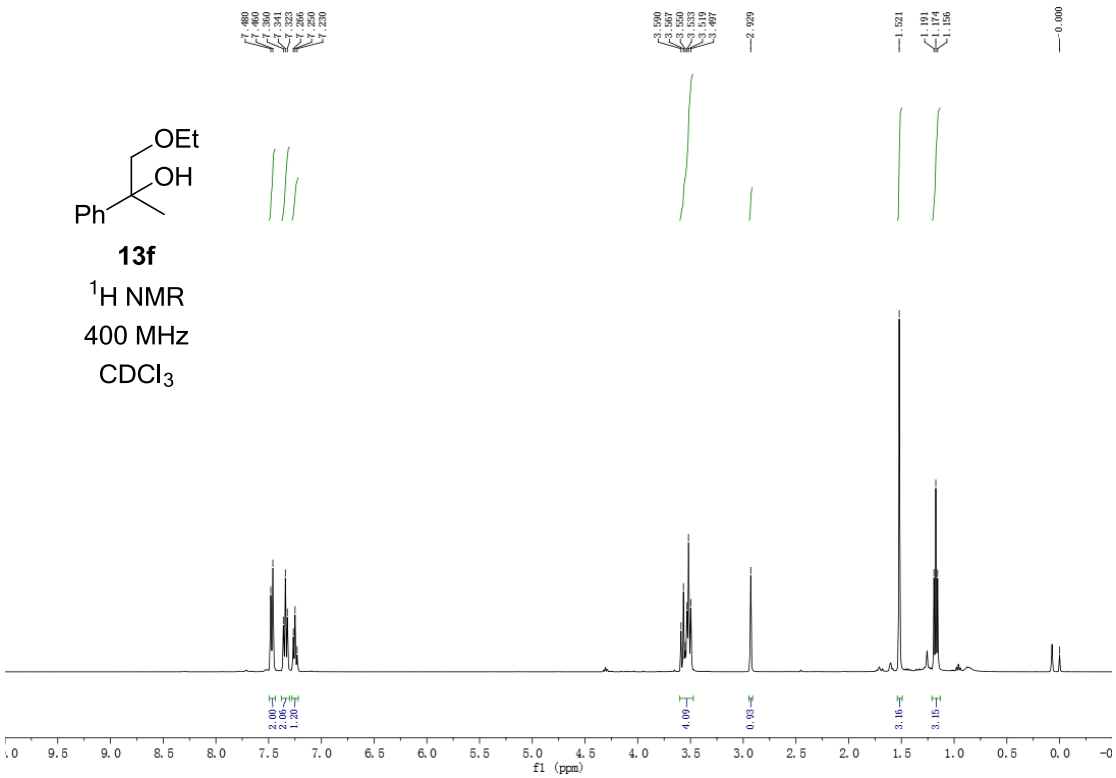

OMe
OH
Me
13c
13C NMR
100 MHz
CDCl3
f1 (ppm)

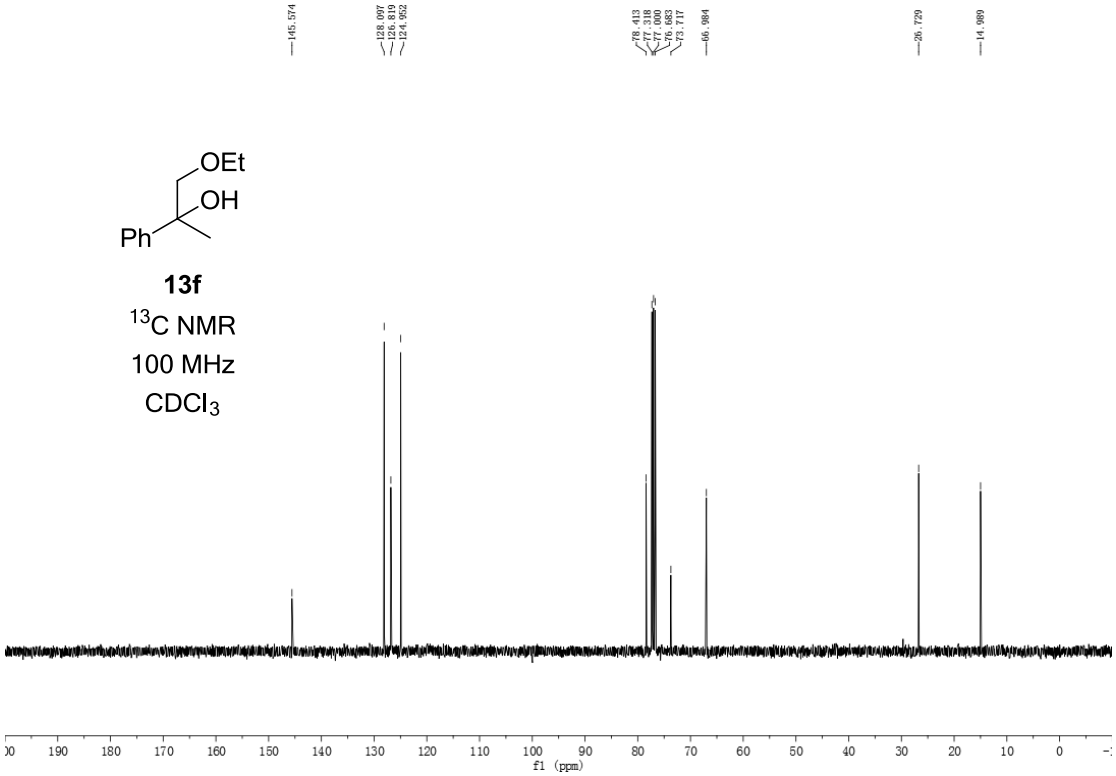

OMe
OH
Me
13d
1H NMR
400 MHz
CDCl3
f1 (ppm)

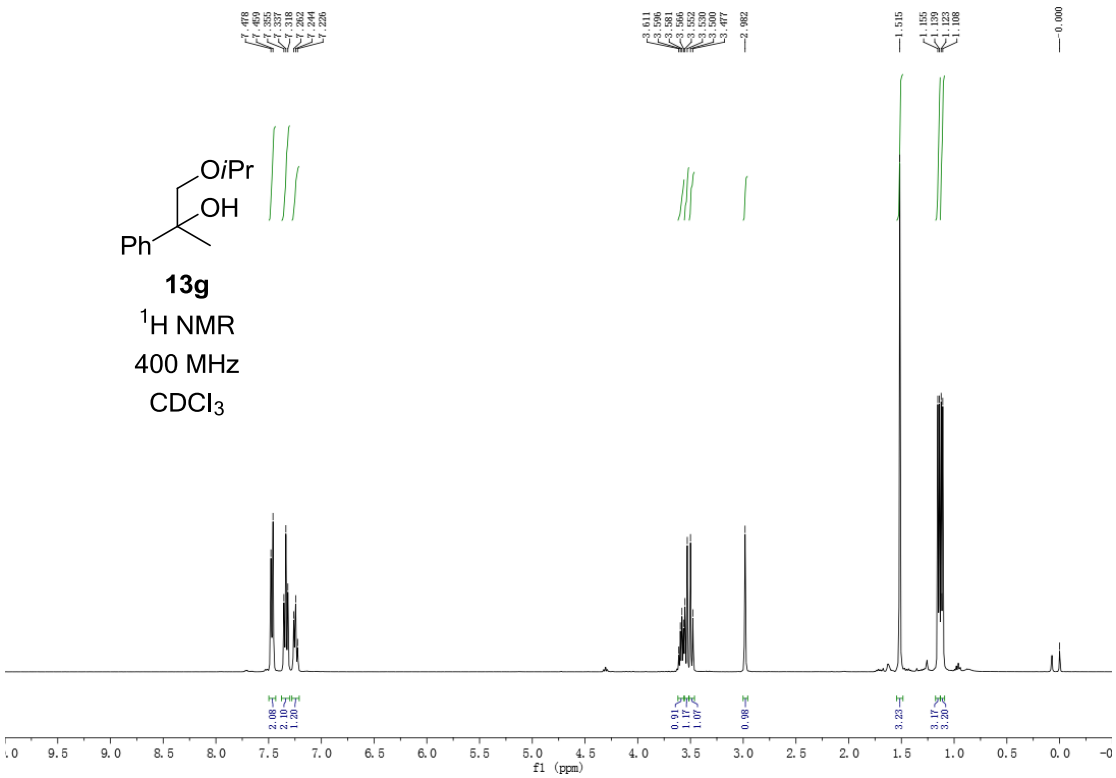

OMe
OH
Me
13d
13C NMR
100 MHz
CDCl3
f1 (ppm)

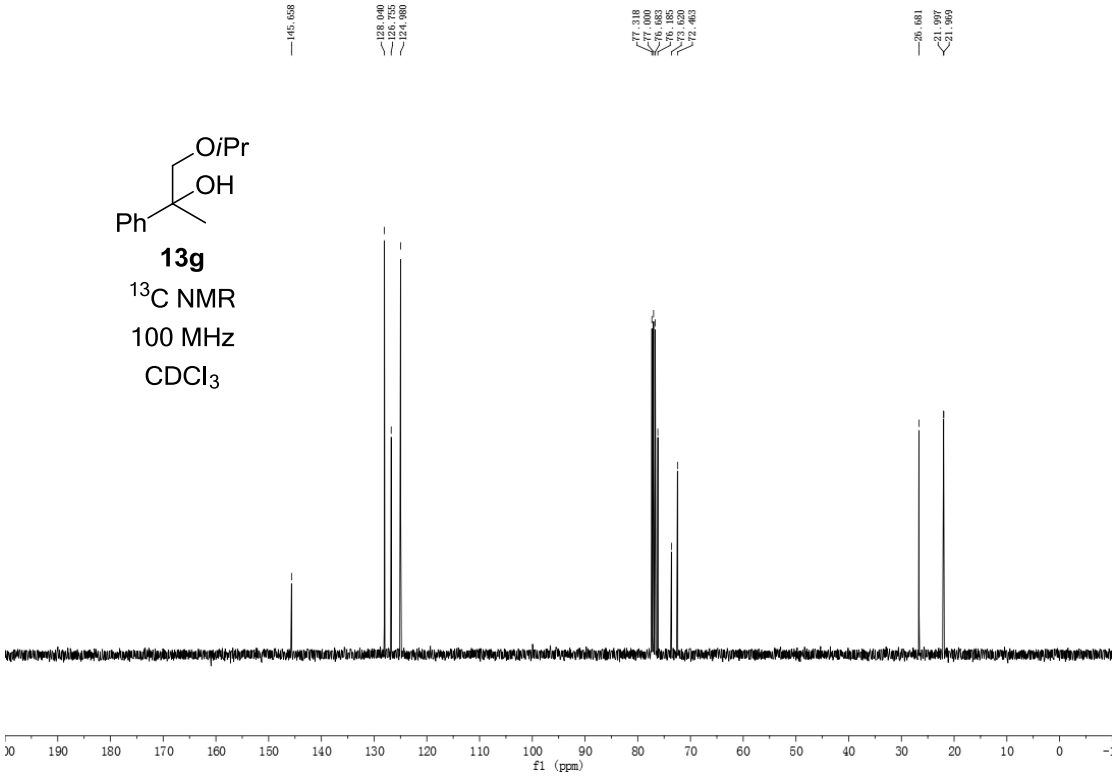

OMe
OH
Cl
13e
1H NMR
400 MHz
CDCl3
f1 (ppm)

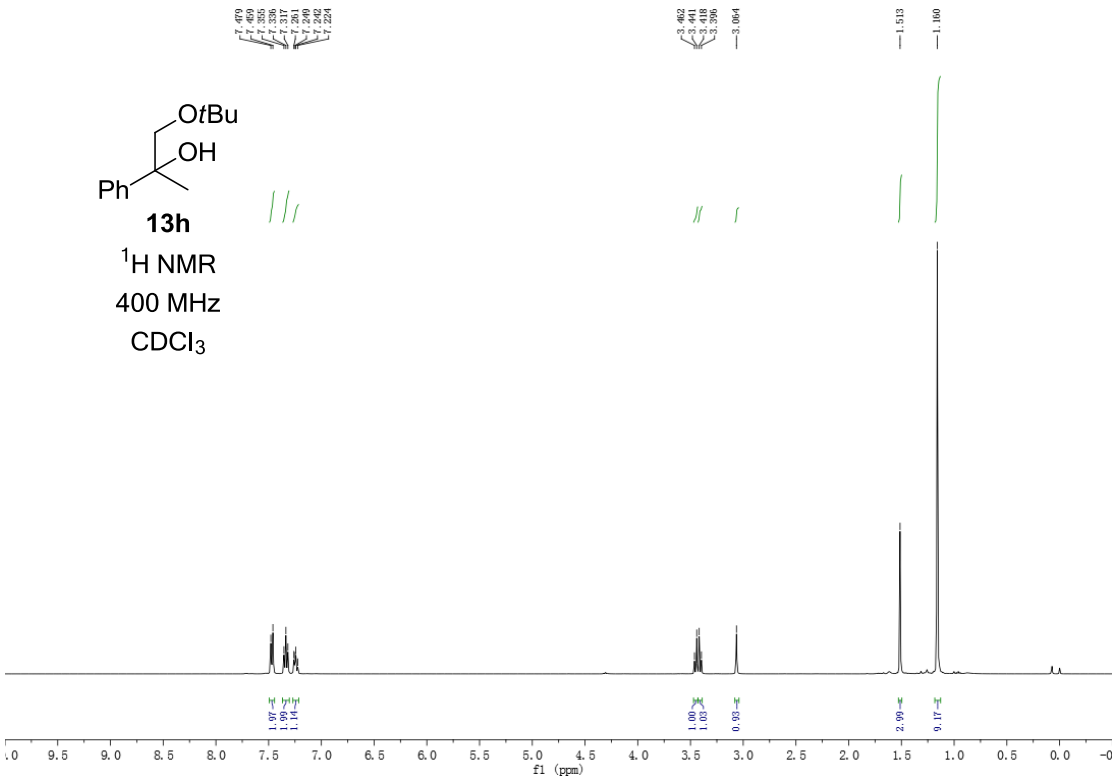

OMe
OH
Cl
13e
13C NMR
100 MHz
CDCl3
f1 (ppm)

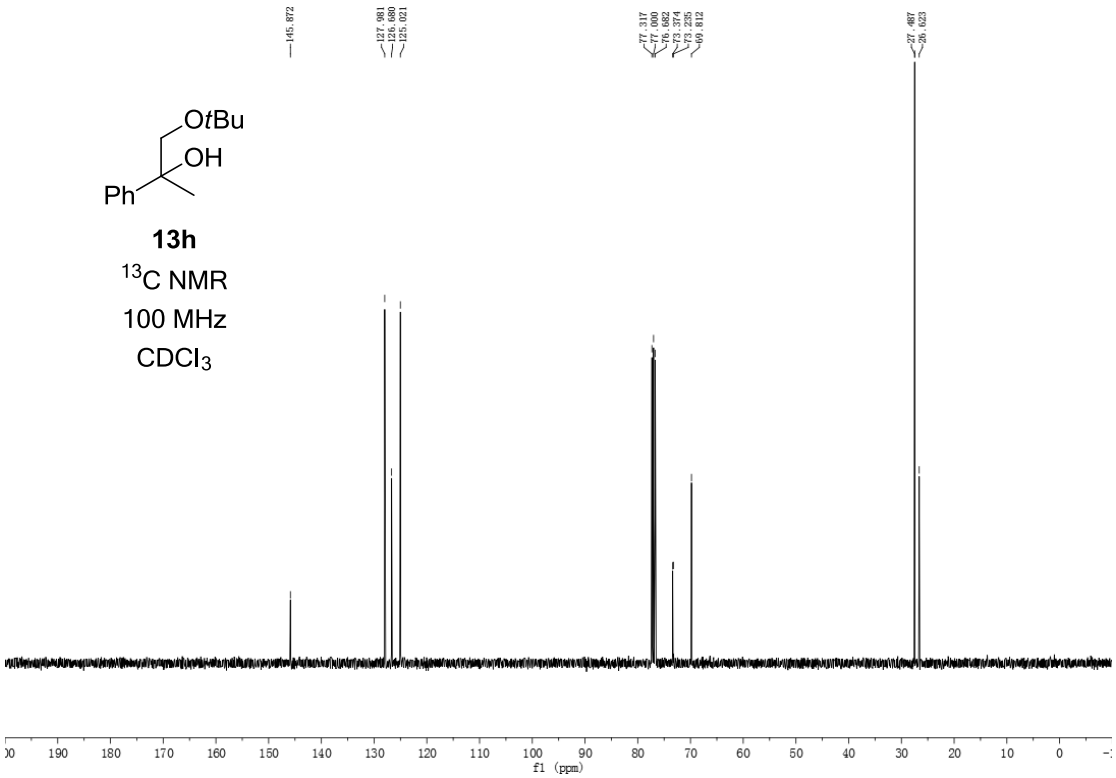

OEt
OH
Ph
13f
1H NMR
400 MHz
CDCl3
f1 (ppm)


OEt
OH
Ph
13f
13C NMR
100 MHz
CDCl3
f1 (ppm)


OiPr
OH
Ph
13g
1H NMR
400 MHz
CDCl3
f1 (ppm)


OiPr
OH
Ph
13g
13C NMR
100 MHz
CDCl3
f1 (ppm)


OtBu
OH
Ph
13h
1H NMR
400 MHz
CDCl3
f1 (ppm)


OtBu
OH
Ph
13h
13C NMR
100 MHz
CDCl3
f1 (ppm)