Supporting Information

For

Dual Photoredox and Nickel-Catalyzed Desymmetric C-O Coupling Reactions: Visible Light-Mediated Enantioselective Synthesis of 1,4-Benzodioxanes

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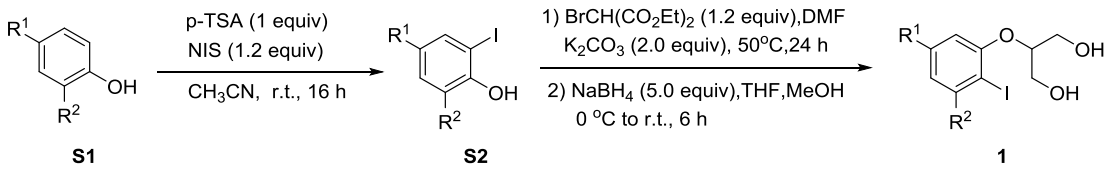
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods.[1] Flash column chromatography was performed using 200-300 mesh silica gel.[2] ^{1}H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 MHz or 600 MHz with complete proton decoupling spectrophotometers ($cdcl_3$: 77.0 ppm, d6-dmso: 39.6 ppm). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI. Enantiomeric ratio (e.r.) values were determined by chiral HPLC with chiral columns with hexane and *i*-PrOH as solvent.

2. Preparation and Spectral Data of the Substrates and Ligands

2.1 General procedure for preparation of the substrate 1.[3,4]



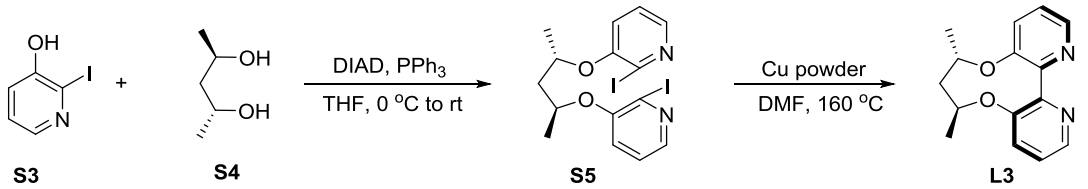
To a solution of the corresponding phenol (1.0 equiv) in CH_3CN (2 M) at room temperature was added p-TSA monohydrate (1.0 equiv). After 10 min, added NIS (1.2 equiv) to the reaction mixture. The mixture was stirred for 16 h at room temperature and quenched by addition of aqueous Na_2SO_3 solution. It was acidified by addition of aqueous HCl (1 M), the organic solvent was evaporated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica to to afford the desired product **S1 (**74-90% yields).

A mixture of **S1** (1.0 equiv) in DMF (2 M) at room temperature was added diethyl 2-bromomalonate (1.0 equiv). After 30 min, added K_2CO_3 (2.0 equiv) to the reaction mixture. The mixture was stirred at 50 °C for 24 h. Then EtOAc and H_2O were added into the mixture. The organic phase was separated. The aqueous phase was extracted

twice with EtOAc. The combined organic phase was washed with water, brine, dried over $MgSO_4$ and concentrated under reduced pressure to remove the solvent get the crude without further purification.

The crude product was dissolved in THF (2 M) at 0 ^oC, added $NaBH_4$ (4.0 equiv) and stirred at 0 ^oC for 10 min. Then added MeOH (0.8 M) slowly at 0 ^oC. After 30 mins at 0 ℃, the reaction medium was allowed to reach room temperature and stirred at room temperature for 5 hours. Until the reaction was completed, as monitored by TLC analysis, quenched by H_2O. The organic phase was separated. The aqueous phase was extracted twice with ethyl acetate. The combined organic phase was washed with brine, dried over $MgSO_4$ and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired product **1** **(**65-88% yields).

2.2 General procedure for preparation of the axially chiral 2,2'-bipyridine ligand L3[5]



S3 **S4** **S5** **L3**

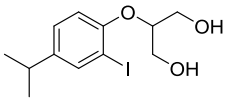
To a solution of the (2*R*,4*R*)-pentanediol (1.0 equiv), 2-iodopyridin-3-ol (2.2 equiv) and PPh_3 (2.4 equiv) in THF (4 M) at 0 ℃ was stirred for 30 min. Then slowly added diisopropylazodicarboxylate (2.4 equiv) dropwise to the reaction mixture. After addition, the reaction temperature slowly warmed up to room temperature and stirred for another 28 h. After the reaction finished, the reaction mixture was concentrated under reduced pressure to afford the yellow solid. Initial purification was carried out with recrystalization in dichloromethane/petroleum ether. The solid was filtered off and washed 3 times with petroleum ether. The solvent was evaporated and purified by column chromatography on silica to to afford the desired product **S5** in 90% yield.

To a solution of **S5** (1.0 equiv, 5 mmol) in DMF (2 M) was added added activated copper powder (10.0 equiv). Then the mixture was refluxed for 14 h. After

the reaction finished, the reaction mixture was cooled to room temperature, the solid was filtered off and washed 3 times with dichloromethane. The reaction mixture was concentrated under reduced pressure to afford the oil. Then crude was dissolved in 10 mL of dichloromethane, acidified with 4 mL hydrochloric acid (12 M) and stirred for 0.5 h. Solid sodium hydroxide was added untill pH>10 and stirred for another 0.5 h. The solid was filtered off and washed 3 times with dichloromethane. The organic layer was separated and the aqueous layer was extracted with dichloromethane washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatogramphy to give axially chiral 2,2'-bipyridine ligand **L3** as a white solid in 45% yield.

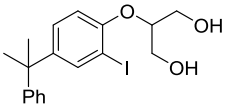
2.3 Spectral data of new compound of substrate 1 and L3

2-(2-iodo-4-isopropylphenoxy)propane-1,3-diol (1f)



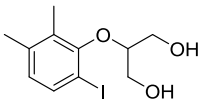
Compound **1f** was prepared above the procedure, colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.61 (d, *J* = 2.2 Hz, 1H), 7.15 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.40 – 4.36 (m, 1H), 3.97 – 3.83 (m, 4H), 2.83 (m, 1H), 2.22 (t, *J* = 6.5 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.7, 144.9, 137.2, 127.8, 115.7, 88.8, 82.0, 62.1, 33.1, 24.0. HRMS (ESI) for $C_{12}H_{17}INaO_3$ $[M+Na]^+$: calcd 359.0115, found 359.0105.

2-(2-iodo-4-(2-phenylpropan-2-yl)phenoxy)propane-1,3-diol (1g)



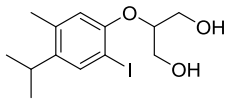
Compound **1g** was prepared above the procedure, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.64 (d, *J* = 2.4 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 7.10 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.90 (d, J = 8.6 Hz, 1H), 4.42 – 4.35 (m, 1H), 3.95 – 3.85 (m, 4H), 2.24 – 2.14 (m, 2H), 1.64 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.6, 149.9, 146.7, 137.4, 128.7, 128.1, 126.6, 125.9, 115.0, 88.5, 81.7, 62.1, 42.3, 30.8. HRMS (ESI) for $C_{18}H_{21}INaO_3$ $[M+Na]^+$: calcd 435.0428, found 435.0423.

2-(6-iodo-2,3-dimethylphenoxy)propane-1,3-diol (1l)



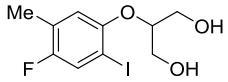
Compound **1l** was prepared above the procedure, colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.49 (s, 1H), 6.82 (s, 1H), 4.37 – 4.32 (m, 1H), 3.88 (d, J = 4.8 Hz, 4H), 2.50 – 2.42 (tm, 2H), 2.18 (d, J = 15.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.8, 139.5, 138.6, 132.8, 117.7, 84.8, 82.1, 62.0, 19.9, 18.5. HRMS (ESI) for $C_{11}H_{15}INaO_3$ $[M+Na]^+$: calcd 344.9958, found 344.9954.

2-(2-iodo-4-isopropyl-5-methylphenoxy)propane-1,3-diol (1m)



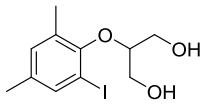
Compound **1m** was prepared above the procedure, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.55 (s, 1H), 6.81 (s, 1H), 4.40 – 4.35 (m, 1H), 3.94 – 3.85 (m, 4H), 3.06 – 2.96 (m, 1H), 2.28 (s, 3H), 2.14 (t, *J* = 6.5 Hz, 2H), 1.19 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.4, 143.3, 137.2, 135.6, 118.0, 85.7, 82.1, 62.1, 28.7, 23.2, 19.4. HRMS (ESI) for $C_{13}H_{19}INaO_3$ $[M+Na]^+$: calcd 373.0271, found 373.0269.

2-(4-fluoro-2-iodo-5-methylphenoxy)propane-1,3-diol (1n)



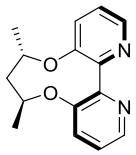
Compound **1n** was prepared above the procedure, colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) =δ 7.39 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 6.6 Hz, 1H), 4.36 – 4.29 (m, 1H), 3.89 (d, *J* = 4.2 Hz, 4H), 2.24 – 2.20 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 157.4 (d, *J* = 242.9 Hz), 153.1 (d, *J* = 27.5 Hz), 126.5 (d, *J* = 18.6 Hz), 124.7 (d, *J* = 25.9 Hz), 118.4 (d, *J* = 5.11 Hz), 84.2 (d, *J* = 8.5 Hz), 82.8, 62.1, 14.8 (d, *J* = 3.0 Hz). HRMS (ESI) for $C_{10}H_{12}FINaO_3$ $[M+Na]^+$: calcd 348.9707, found 348.9702.

2-(2-iodo-4,6-dimethylphenoxy)propane-1,3-diol (1o)



Compound **1o** was prepared above the procedure, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.45 (d, *J* = 2.2 Hz, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 4.24 – 4.19 (m, 1H), 4.04 – 3.83 (m, 4H), 2.48 (d, *J* = 6.1 Hz, 2H), 2.27 (dd, *J* = 31.5, 2.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 152.8, 137.6, 135.6, 132.99, 132.97, 131.6, 92.4, 82.1, 62.2, 20.0, 17.6.

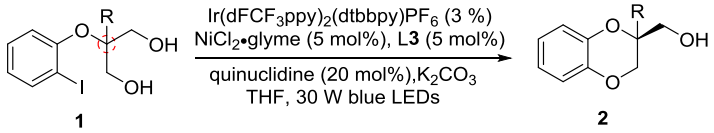
(6S,8S)-6,8-dimethyl-7,8-dihydro-6H-[1,5]dioxonino[7,6-b:8,9-b']dipyridine (L3)[5]



Compound **L3** was prepared above the procedure, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.46 (dd, *J* = 4.7, 1.4 Hz, 2H), 7.43 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.28 (dd, *J* = 8.3, 4.7 Hz, 2H), 4.67-4.60 (m, 2H), 1.96 (t, *J* = 4.2 Hz, 2H), 1.43 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.0, 149.4, 144.3, 124.8, 123.8, 75.5, 41.7, 22.6.

3. General Procedures and Characterization of the Products

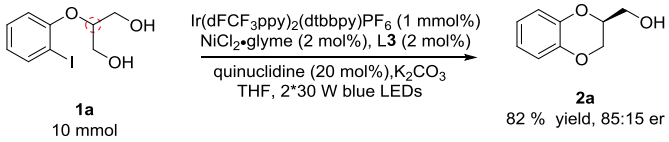
3.1 General procedure for the desymmetric C-O Coupling Reactions for the synthesis of chiral 1,4-benzodioxanes.



Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiCl_2$•glyme (0.015 mmol, 0.05 equiv) and **L3** (0.015 mmol, 0.05 equiv) and 2 mL of THF under Ar. After 0.5 h of stirring at room temperature, substrate **1**

(0.3 mmol, 1.0 equiv), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (0.009 mmol, 0.03 equiv), K_2CO_3 (0.3 mmol, 1.0 equiv) and quinuclidine (0.06 mmol, 0.2 equiv) and 1 mL of THF were added to the mixture under Ar. Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred under the irridation of 30W blue LEDs at rt about 24 h until the reaction was completed, as monitored by TLC analysis. The product was purified by flash column chromatography on silica gel to give product **2**. All the products **2** were prepared according to the above procedure.

3.2 10 Mmol-scale reaction



1a
10 mmol

2a
82 % yield, 85:15 er

Procedure: An oven-dried 200 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiCl_2$•glyme (0.2 mmol, 0.02 equiv) and **L3** (0.2 mmol, 0.02 equiv) and 50 mL of THF under Ar. After 0.5 h of stirring at room temperature, substrate **1a** (10 mmol, 1.0 equiv), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (0.01 mmol, 0.01 equiv), K_2CO_3 (10 mmol, 1.0 equiv) and quinuclidine (2 mmol, 0.2 equiv) were added to the mixture under Ar. Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred under the irridation of 2*30W blue LEDs at rt about 24 h. The product was purified by flash column chromatography on silica gel to give product **2a** in 82% yield (1.36g) and 85:15 er as a white solid.

3.3 Cyclic voltammetry profile of Ni(II)/L3 complex

In order to gain some insight into the interaction between the Ni(I) and the excited state of the photoscatalyst, we performed the CV measurements of Ni(II) complex. The result showed an irreversible reduction at -1.34 V versus Ag/AgCl in CH_3CN, we expect that the catalytic cycles are closed by SET from the highly reducing Ir-catalyst ($E^{1/2}red$ Ir^{III}/Ir^{II} = -1.37 V vs. SCE in MeCN)[6] to B, thereby reconstituting the

nickel(0) catalyst and the iridium(III) photocatalyst.

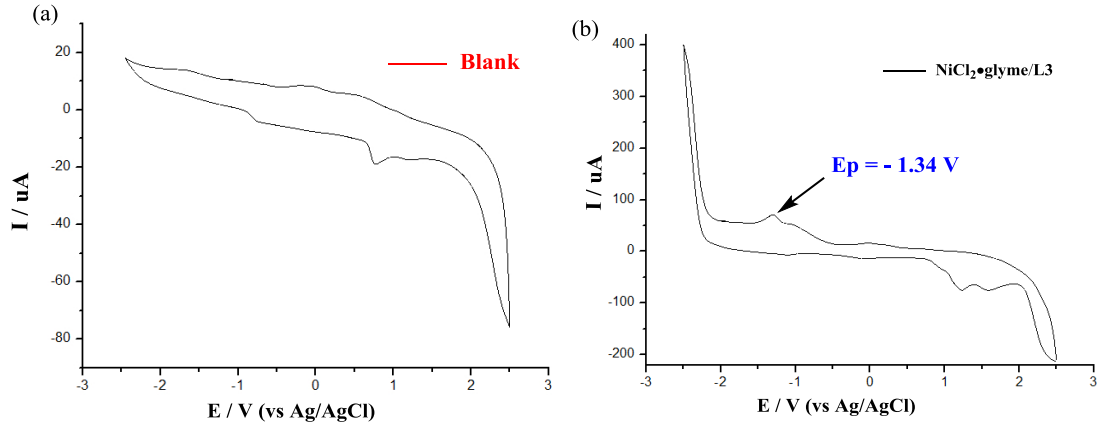
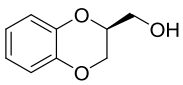


Figure S1. (a) Cyclic Voltammetry Blank Profile of CH_3CN.

(b) Cyclic Voltammetry Profile of Ni(II)/L3 Complex.

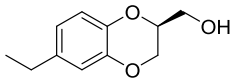
4. Characterization Data of Products

(S)-(2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2a)



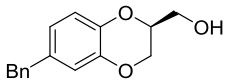
Yield of **2a**: 87% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.95 – 6.80 (m, 4H), 4.33 – 4.22 (m, 2H), 4.14 – 4.09 (m, 1H), 3.96 – 3.80 (m, 2H), 1.92 (m, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.1, 143.0, 121.63, 121.56, 117.3, 117.2, 73.4, 65.1, 61.9. 87:13 e.r., the e.r. value were determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH, 97:3 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 49.161 min, t_R (minor) = 55.460 min. $[\alpha]_D^{25}$ = -22.5 (c = 0.1, $CHCl_3$). HRMS (ESI) for $C_9H_{11}O_3$ $[M+H]^+$: calcd 167.0703, found 167.0701.

(S)-(6-ethyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2b)



Yield of **2b**: 80% as a colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.81 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.75 – 6.64 (m, 2H), 4.32 – 4.18 (m, 2H), 4.13 – 4.06 (m, 1H), 3.96 – 3.77 (m, 2H), 2.55 (m, 2H), 1.96 (t, *J* = 6.4 Hz, 1H), 1.19 (m, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.8, 140.8, 137.8, 121.0, 116.9, 116.3, 73.3, 65.2, 61.7, 28.1, 15.7. 86:14 e.r., the e.r. value were determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH, 97:3 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 34.620 min, t_R (minor) = 39.292 min. $[\alpha]_D^{25}$ = -27.4 (c = 0.2, $CHCl_3$). HRMS (ESI) for $C_{11}H_{15}O_3$ $[M+H]^+$: calcd 195.1016, found 195.1012.

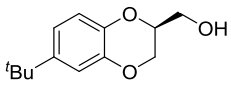
(S)-(6-benzyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2c)



Yield of **2c**: 84% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.28 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.11 (m, 3H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.75 – 6.64 (m, 2H), 4.29 – 4.20 (m, 2H), 4.08 (dd, *J*

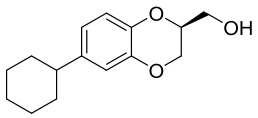
= 11.0, 7.4 Hz, 1H), 3.91 – 3.79 (m, 4H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.8, 141.20, 141.15, 134.7, 128.8, 128.4, 126.0, 122.0, 117.5, 117.1, 73.3, 65.2, 61.8, 41.2. 85.5:14.5 e.r., the e.r. value were determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 49.027 min, t_R (minor) = 34.053 min. $[\alpha]_D^{25}$ = -29.1 (c = 0.2, $CHCl_3$). HRMS (ESI) $[M+Na]^+$ calcd for $C_{16}H_{16}NaO_3$: 279.0992, found 279.0987.

(S)-(6-(tert-butyl)-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2d)



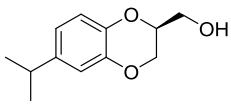
Yield of **2d**: 82% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.93 – 6.89 (m, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.84 – 6.79 (m, 1H), 4.31 – 4.19 (m, 2H), 4.13 – 4.05 (m, 1H), 3.95 – 3.77 (m, 2H), 1.89 (t, *J* = 6.4 Hz, 1H), 1.30 – 1.24 (m, 9H).6.95 – 6.80 (m, 4H), 4.33 – 4.22 (m, 2H), 4.14 – 4.09 (m, 1H), 3.96 – 3.80 (m, 2H), 1.92 (m, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.0, 142.3, 140.5, 118.6, 116.6, 114.2, 73.40, 65.2, 61.9, 34.2, 31.4. 86.5:13.5 e.r., the e.r. value were determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH, 97:3 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 29.185 min, t_R (minor) = 33.768 min. $[\alpha]_D^{25}$ = -21.5 (c = 0.1, $CHCl_3$). HRMS (ESI) for $C_{13}H_{18}NaO_3$ $[M+Na]^+$: calcd 245.1148, found 245.1148.

(S)-(6-cyclohexyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2e)



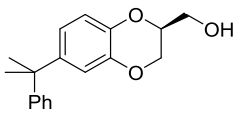
Yield of **2e**: 79% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.81 (d, *J* = 8.2 Hz, 1H), 6.77 – 6.67 (m, 2H), 4.33 – 4.18 (m, 2H), 4.09 (dd, *J* = 11.0, 7.3 Hz, 1H), 3.86 (m, 2H), 2.39 (m, 1H), 1.93 (m, 1H), 1.89 – 1.77 (m, 4H), 1.73 (d, *J* = 13.0 Hz, 1H), 1.36 (m, 4H), 1.27 – 1.18 (m, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.7, 141.9, 140.8, 120.0, 116.8, 115.2, 73.3, 65.2, 61.9, 43.8, 34.6, 26.9, 26.1. 84:16 e.r., the e.r. value were determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH, 97:3 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 32.823 min, t_R (minor) = 37.314 min. $[\alpha]_D^{25}$ = -20.62 (c = 0.1, $CHCl_3$). HRMS (ESI) $[M+Na]^+$ calcd for $C_{15}H_{20}NaO_3$: 271.1305, found 271.1302.

(S)-(6-isopropyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2f)



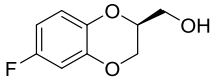
Yield of **2f**: 87% as a colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 6.85 (d, *J* = 8.2 Hz, 1H), 6.80 – 6.68 (m, 2H), 4.37 – 4.21 (m, 2H), 4.12 (dd, J = 11.0, 7.4 Hz, 1H), 3.88 (m, 2H), 2.84 (m, 1H), 2.3 – 1.981 (m, 1H), 1.23 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.7, 142.6, 140.8, 119.6, 116.9, 114.8, 73.3, 65.2, 61.9, 33.4, 24.1. 87:13 e.r., the e.r. value were determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH, 97:3 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 23.480 min, t_R (minor) = 26.594 min. $[\alpha]_D^{25}$ = -16.6 (c = 0.2, $CHCl_3$). HRMS (ESI): $[M+Na]^+$ calcd for $C_{12}H_{16}NaO_3$: 231.0992, found 231.0992.

(S)-(6-(2-phenylpropan-2-yl)-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2g)



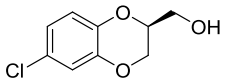
Yield of **2g**: 72% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.37 – 7.18 (m, 4H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.78 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.68 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.35 – 4.16 (m, 2H), 4.15 – 4.02 (m, 1H), 3.94 – 3.68 (m, 2H), 1.98 (d, *J* = 3.5 Hz, 1H), 1.64 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 150.5, 144.5, 142.3, 140.7, 128.0, 126.7, 125.6, 120.2, 116.6, 115.6, 73.4, 65.2, 61.8, 42.4, 30.8. 81:19 e.r., the e.r. value were determined by HPLC (Chiralpak AZ column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 17.196 min, t_R (minor) = 16.567 min. $[\alpha]_D^{25}$ = -14.2 (c = 0.2, $CHCl_3$). HRMS (ESI) for $C_{18}H_{20}NaO_3[M+Na]^+$: calcd 307.1305, found 307.1298.

(S)-(6-fluoro-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2h)



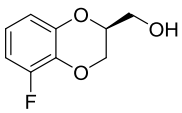
Yield of **2h**: 76% as a colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.82 (dd, *J* = 8.9, 5.4 Hz, 1H), 6.69 – 6.49 (m, 2H), 4.35 – 4.17 (m, 2H), 4.16 – 4.06 (m, 1H), 3.86 (m, 2H), 1.94 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 157.2 (d, *J* = 237.5 Hz), 143.4, (d, *J* = 12.0 Hz), 139.2 (d, *J* = 2.8 Hz), 117.5 (d, *J* = 9.5 Hz), 108.1, (d, *J* = 23.3 Hz), 104.4, (d, *J* = 26.3 Hz), 73.1, 65.3, 61.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) = -121.23. 85:15 e.r., the e.r. value were determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 33.398 min, t_R (minor) = 32.055 min. $[\alpha]_D^{25}$ = -31.0 (c = 0.2, $CHCl_3$). HRMS (ESI) for $C_9H_9FNaO_3$ $[M+Na]^+$: calcd 207.0428, found 207.0425.

(S)-(6-chloro-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2i)



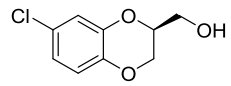
Yield of **2i**: 84% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.88 (t, *J* = 1.4 Hz, 1H), 6.80 (d, *J* = 1.4 Hz, 2H), 4.34 – 4.16 (m, 2H), 4.08 (dd, *J* = 11.3, 7.6 Hz, 1H), 3.94 – 3.77 (m, 2H), 2.15 (d, *J* = 5.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.5, 141.7, 126.0, 121.5, 118.0, 117.3, 73.4, 65.1, 61.6. 86:14 e.r., the e.r. value were determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 32.913 min, t_R (minor) = 29.389 min. $[\alpha]_D^{25}$ = -34.2 (c = 0.5, $CHCl_3$). HRMS (ESI) for $C_9H_{10}ClO_3$ $[M+H]^+$: calcd 201.0313, found 201.0316.

(S)-(5-fluoro-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2j)



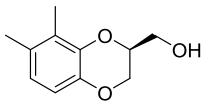
Yield of **2j**: 65% as a colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.80 – 6.72 (m, 1H), 6.72 – 6.58 (m, 2H), 4.32 (m, 2H), 4.20 – 4.12 (m, 1H), 3.93 (m, 2H), 2.12 – 1.80 (m, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.9 (d, *J* = 243.0 Hz), 144.7 (d, *J* = 3.8 Hz), 132.1 (d, *J* = 13.8 Hz), 120.0 (d, *J* = 8.8 Hz), 112.5 (d, *J* = 3.07 Hz), 108.5 (d, *J* = 18.0 Hz), 73.6, 65.2, 61.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) = -136.33. 87:13 e.r., the e.r. value were determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 °C). t_R (major) = 22.199 min, t_R (minor) = 23.878 min. $[\alpha]_D^{25}$ = -33.1 (c = 0.5, $CHCl_3$). HRMS (ESI) $[M+Na]^+$ calcd for $C_9H_9FNaO_3$: 207.0428, found 207.0423.

(S)-(7-chloro-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2k)



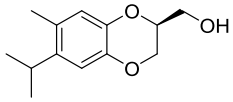
Yield of **2k**: 77% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.90 (s, 1H), 6.81 (d, *J* = 1.6 Hz, 2H), 4.33 – 4.20 (m, 2H), 4.09 (dd, *J* = 11.1, 7.3 Hz, 1H), 3.86 (m, 2H), 1.92 (m, 1H).6.95 – 6.80 (m, 4H), 4.33 – 4.22 (m, 2H), 4.14 – 4.09 (m, 1H), 3.96 – 3.80 (m, 2H), 1.92 (m, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.5, 141.9, 126.0, 121.5, 118.0, 117.4, 73.5, 65.1, 61.6. 86:14 e.r., the e.r. value were determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 ^{o}C). t_R (major) = 23.227 min, t_R (minor) = 25.178 min. $[\alpha]_D^{25}$ = -24.1 (c = 0.5, $CHCl_3$). HRMS (ESI): for $C_9H_9ClNaO_3$ $[M]^+$: calcd 223.0132, found 223.0135.

(S)-(7,8-dimethyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2l)



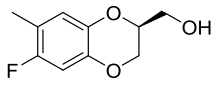
Yield of **2l**: 81% as a colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.67 (d, *J* = 5.7 Hz, 2H), 4.28 – 4.17 (m, 2H), 4.11 – 4.00 (m, 1H), 3.92 – 3.76 (m, 2H), 2.15 (s, 6H), 2.11 (d, *J* = 5.8 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 140.6, 140.4, 129.66, 129.56, 118.0, 117.9, 73.4, 65.2, 61.8, 18.96, 18.94. 87:13 e.r., the e.r. value were determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 ^{o}C). t_R (major) = 25.634 min, t_R (minor) = 29.859 min. $[\alpha]_D^{25}$ = -18.9 (c = 0.5, $CHCl_3$). HRMS (ESI) $[M+Na]^+$ calcd for $C_{11}H_{14}NaO_3$: 217.0835, found 217.0829.

(S)-(6-isopropyl-7-methyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2m)



Yield of **2m**: 66% as a colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.75 (s, 1H), 6.66 (s, 1H), 4.27 – 4.17 (m, 2H), 4.10 – 4.01 (m, 1H), 3.82 (dd, *J* = 9.8, 4.4 Hz, 2H), 3.07 – 2.93 (m, 1H), 2.49 (s, 1H), 2.21 (s, 3H), 1.17 (dd, *J* = 6.7, 1.3 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.0, 140.3, 140.1, 128.2, 118.3, 113.4, 73.4, 65.2, 61.7, 28.8, 23.3, 18.4. 83:17 e.r., the e.r. value were determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 ^{o}C). t_R (major) = 21.898 min, t_R (minor) = 15.534 min. $[\alpha]_D^{25}$ = -12.4 (c = 0.05, $CHCl_3$). HRMS (ESI) $[M+Na]^+$ calcd for $C_{13}H_{18}NaO_3$: 245.1148, found 245.1143.

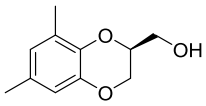
(S)-(6-fluoro-7-methyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2n)



Yield of **2n**: 68% as a colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.67 (d, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 10.1 Hz, 1H), 4.30 – 4.16 (m, 2H), 4.06 (m, 1H), 3.85 (m, 2H), 2.15 (d, *J* = 1.9 Hz, 3H), 2.13 – 2.07 (m, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.4 (d, *J* = 236.4 Hz), 141.1 (d, *J* = 11.8 Hz), 138.6 (d, *J* = 2.8 Hz), 118.6, (d, *J* = 6.0 Hz), 117.5 (d, *J* = 19.2 Hz), 103.9 (d, *J* = 27.2 Hz), 73.2, 65.2, 61.7, 13.9 (d, *J* = 3.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm) = -127.38. 80:20 e.r., the e.r. value were determined by HPLC (Chiralpak AZ column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 ^{o}C). t_R (major) = 16.255 min, t_R (minor) = 17.656 min. $[\alpha]_D^{25}$ = -12.5 (c =

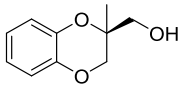
0.1, $CHCl_3$). HRMS (ESI) for $C_{10}H_{11}FNaO_3$ $[M+Na]^+$ calcd: 221.0584, found 221.0587.

(S)-(6,8-dimethyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2o)



Yield of **2o**: 78% as a clolourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.53 (s, 2H), 4.28 – 4.17 (m, 2H), 4.10 – 4.01 (m, 1H), 3.85 (m, 2H), 2.23 (d, *J* = 5.9 Hz, 1H), 2.20 (d, *J* = 1.7 Hz, 3H), 2.16 (d, *J* = 1.7 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.1, 142.5, 140.4, 134.9, 128.6, 126.8, 126.7, 120.3, 117.5, 115.7, 73.5, 65.2, 61.7. 88:12 e.r., the e.r. value were determined by HPLC (Chiralpak OD column, hexane/*i*-PrOH, 97:3 v/v, flow rate 1 mL/min, λ = 220 nm, 25 ^{o}C). t_R (major) = 21.923 min, t_R (minor) = 23.891 min. $[\alpha]_D^{25}$ = -18.6 (c = 0.05, $CHCl_3$). HRMS (ESI) $[M+H]^+$ calcd for $C_{11}H_{15}O_3$: 195.1016, found 195.1013.

(S)-(2-methyl-2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methanol (2p)



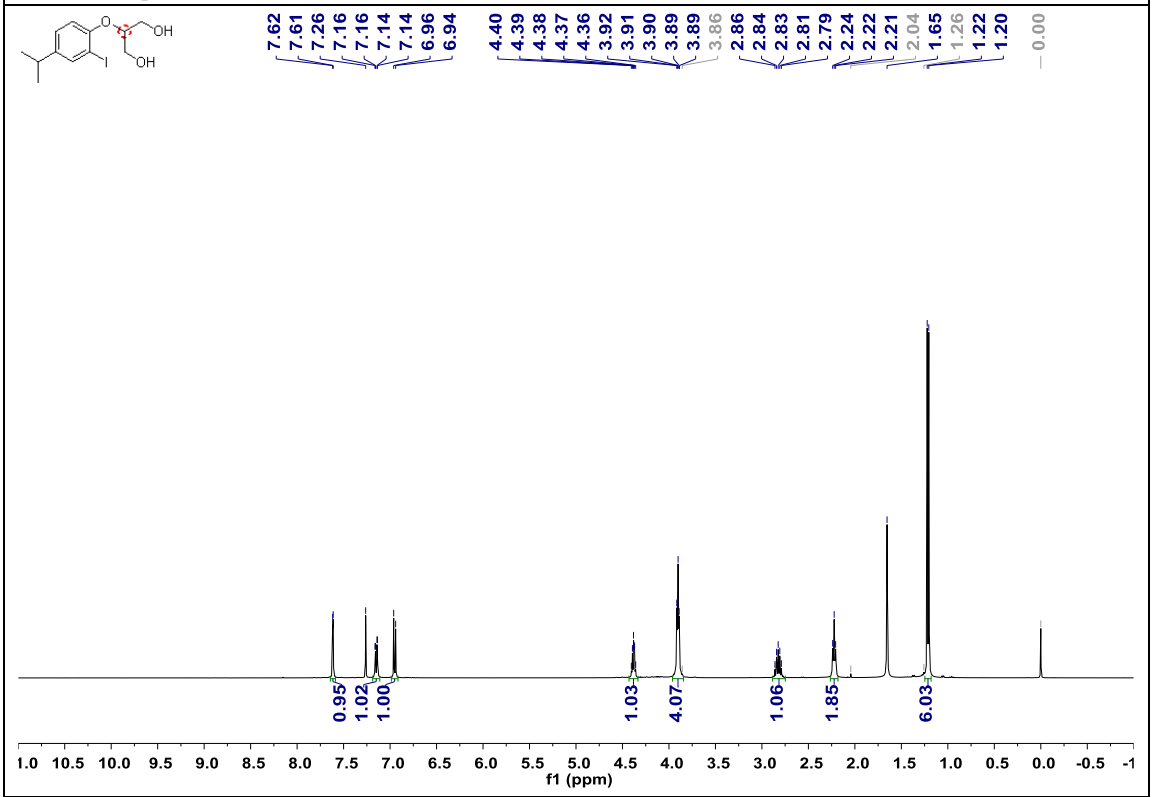
Yield of **2p**: 83% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 6.97 – 6.80 (m, 4H), 4.16 (d, *J* = 11.3 Hz, 1H), 3.91 (dd, *J* = 11.3, 1.4 Hz, 1H), 3.76 – 3.60 (m, 2H), 2.05 (d, J = 12.0 Hz, 1H), 1.32 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.31, 142.27, 121.9, 121.2, 117.5, 117.1, 74.9, 68.3, 65.3, 18.8. 70:30 e.r., the e.r. value were determined by HPLC (Chiralpak AS column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 220 nm, 25 ^{o}C). t_R (major) = 11.641 min, t_R (minor) = 9.760 min. $[\alpha]_D^{25}$ = -11.2 (c = 0.1, $CHCl_3$). HRMS (ESI) $[M+Na]^+$ calcd for $C_{10}H_{13}O_3$: 181.0859, found 181.0861.

4. References

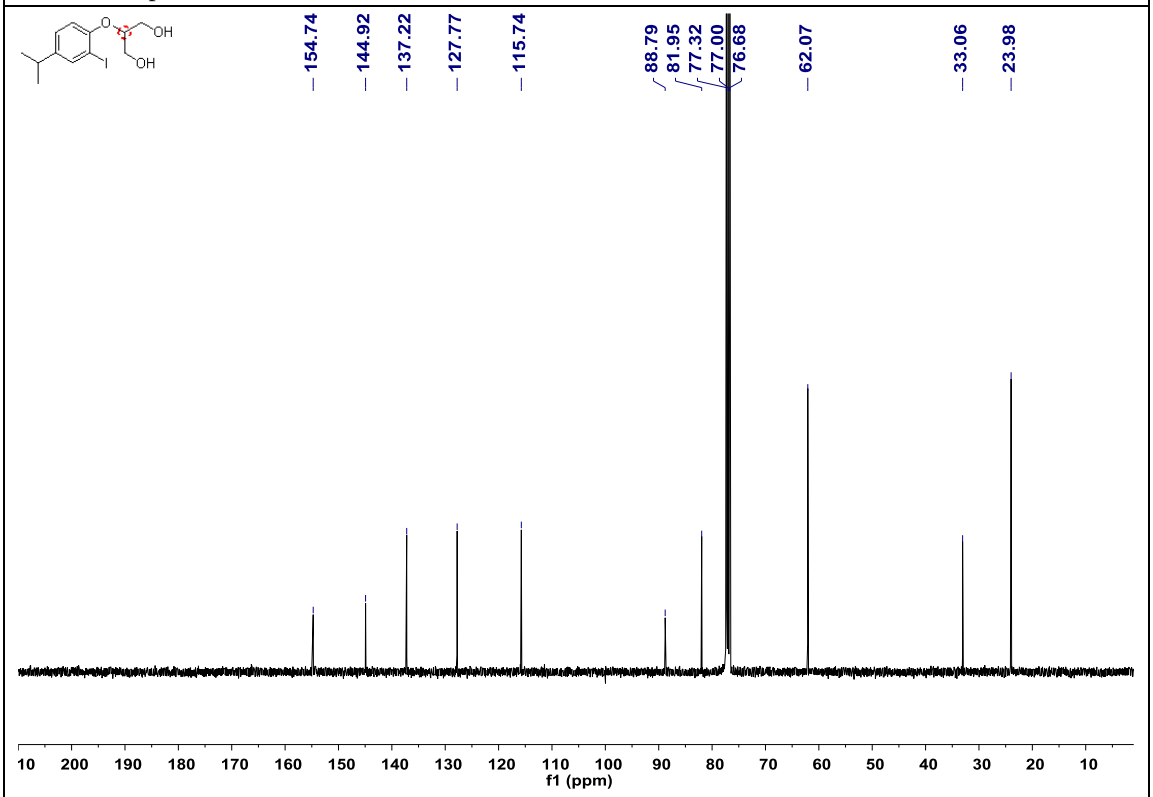
1. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals, 4th ed.*; (Pergamon Press: Oxford, 1997).
2. W.C. Still, M. Kahn and A. Mitra, *J.* Rapid Chromatographic Technique for Preparative Separations with Moderate Resolution. *J. Org. Chem*. 1987, **43**, 2923-2925.
3. B. Schmidt, M. Riemer and M. Karras, *J. Org. Chem.* 2013, **78**, 8680-8688.
4. a) W. Yang, Y. Long, S. Zhang, Y. Zeng and Q. Cai, *Org. Lett.* 2013, **15**, 3598-3601; b) W. Yang, J. Yan, Y. Long, S. Zhang, J. Liu, Y. Zeng and Q. Cai, *Org. Lett.* 2013, **15**, 6022-6025; c) N. He, Y. Huo, J. Liu, Y. Huang, S. Zhang and Q. Cai, *Org. Lett.* **2015**, *17*, 374-377; d) Y. Zhang, Q. Wang, T. Wang, H. He, W. Yang, X. Zhang and Q. Cai, *J. Org. Chem.* 2017, **82**, 1458-1463.
5. X. Gao, B. Wu, W.-X. Huang, M.-W. Chen and Y.-G. Zhou, *Angew. Chem., Int. Ed.* 2015, **54**, 11956-11960.
6. (a) M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712-5719; (b) J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, G. G. Malliaras, *J. Am. Chem. Soc.* **2004**, *126*, 2763-2767.

7. Copies of ^{1}H and ^{13}C NMR Spectra

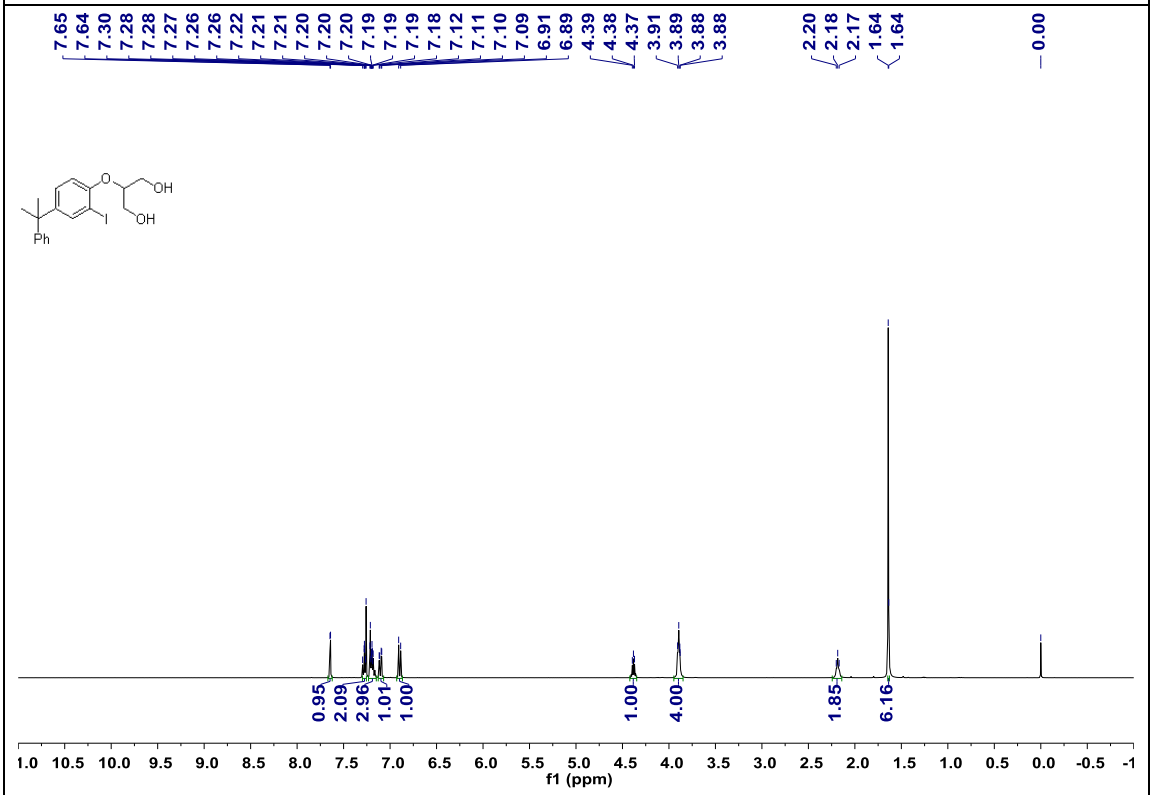
^{1}H NMR Spectrum of **1f**



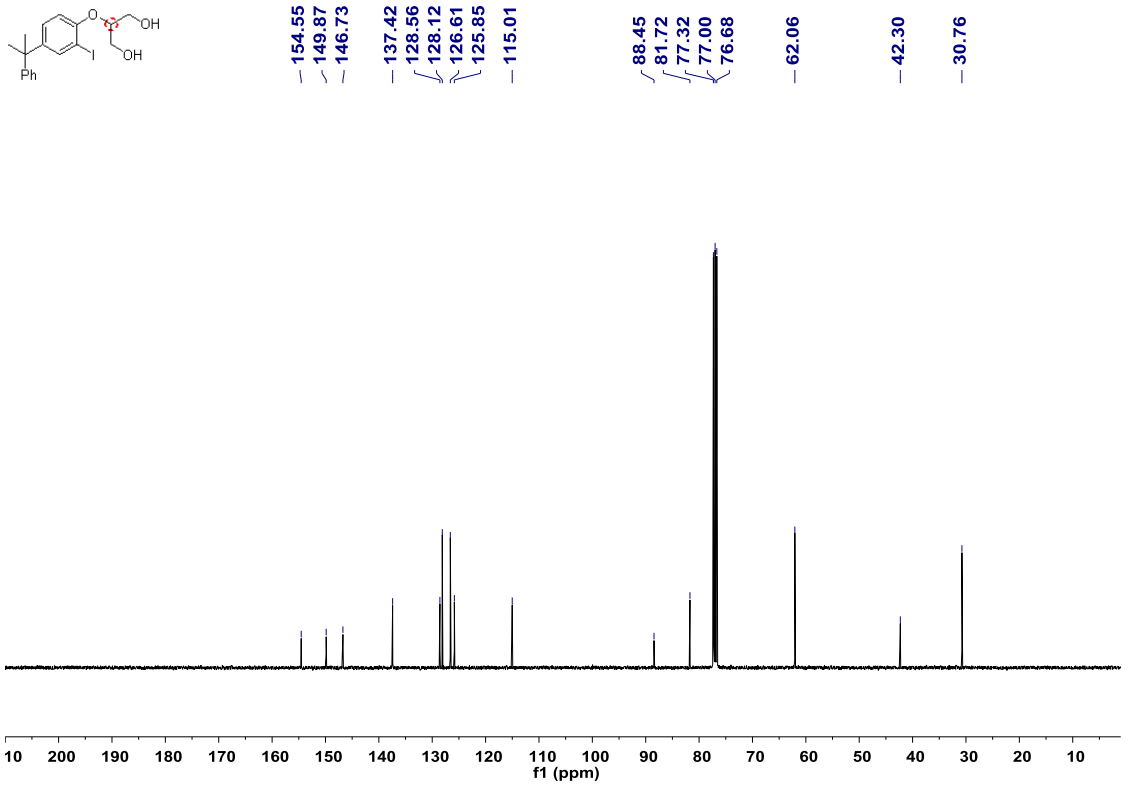
^{13}C NMR Spectrum of **1f**



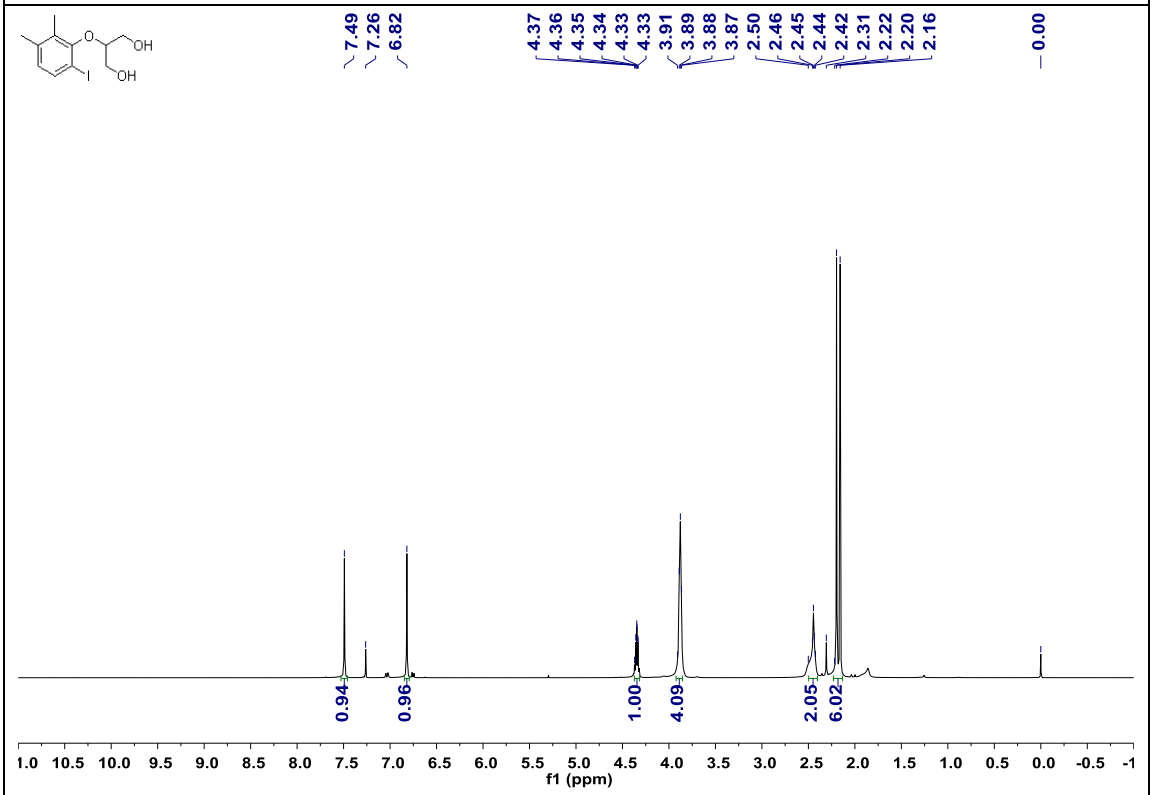
^{1}H NMR Spectrum of **1g**



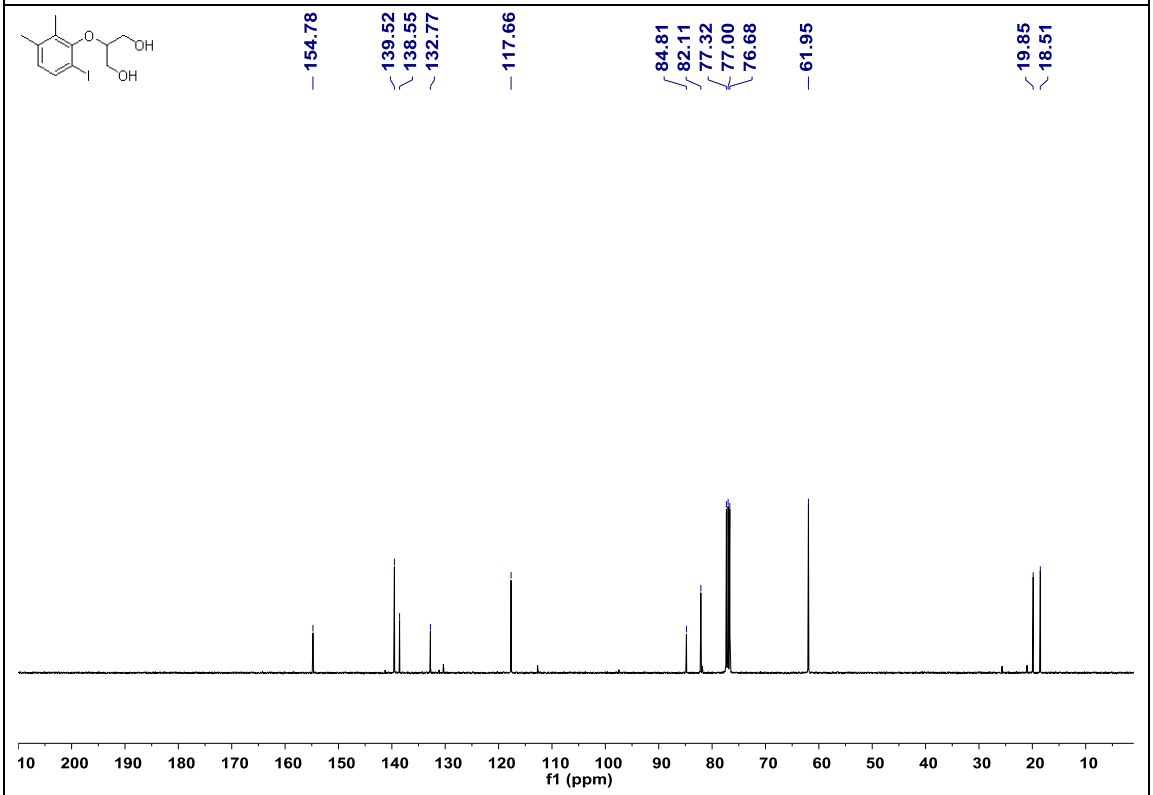
^{13}C NMR Spectrum of **1g**



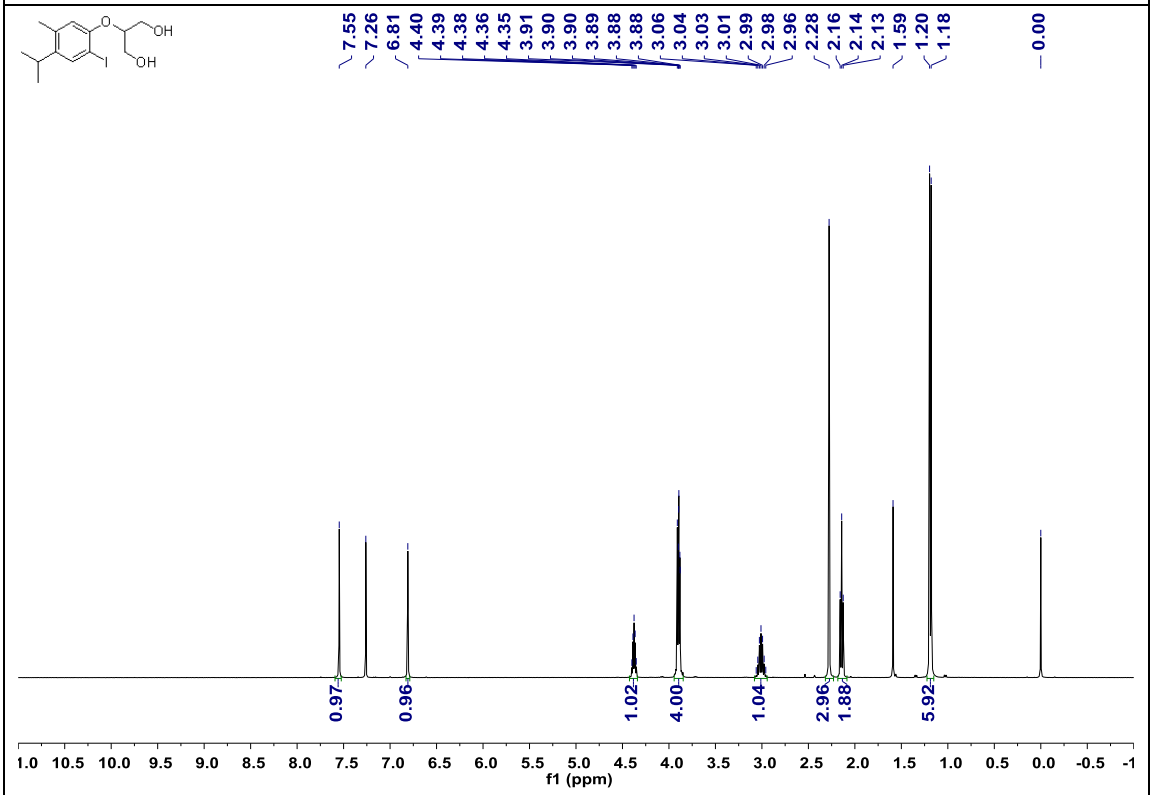
^{1}H NMR Spectrum of **1l**



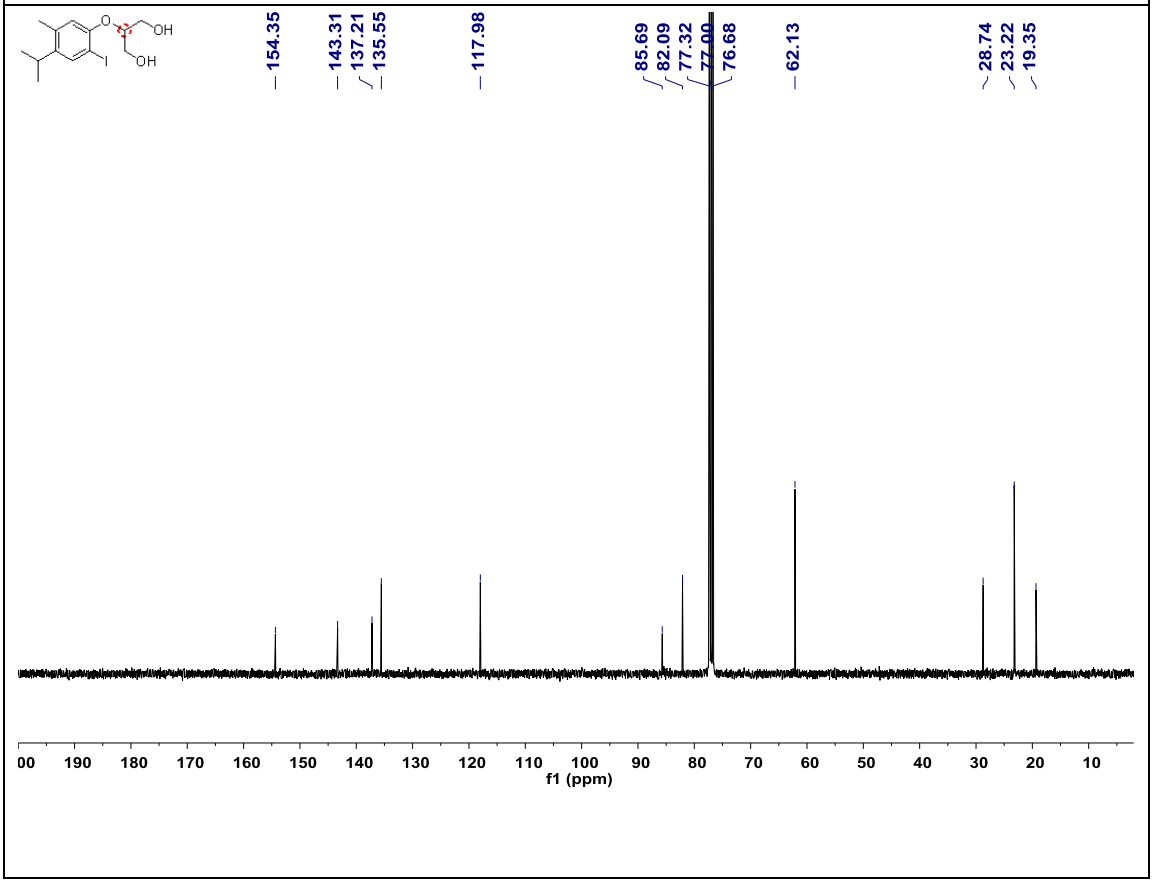
^{13}C NMR Spectrum of **1l**



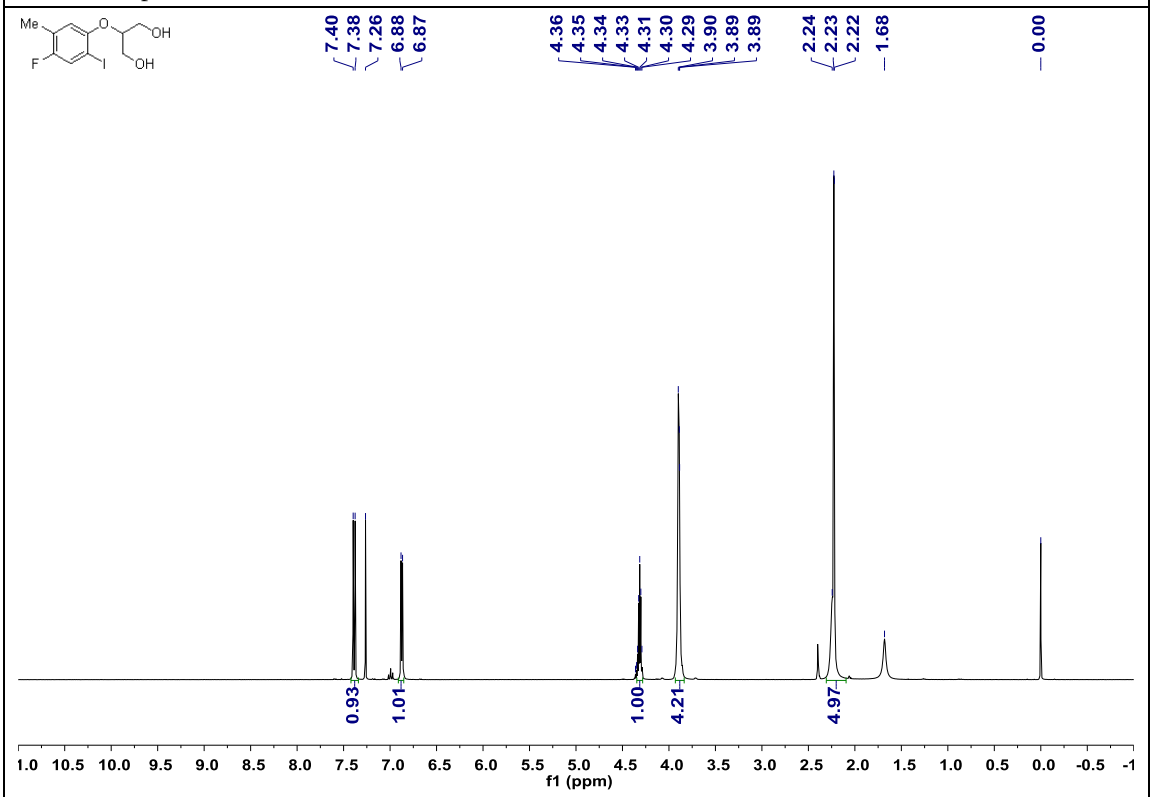
^{1}H NMR Spectrum of **1m**



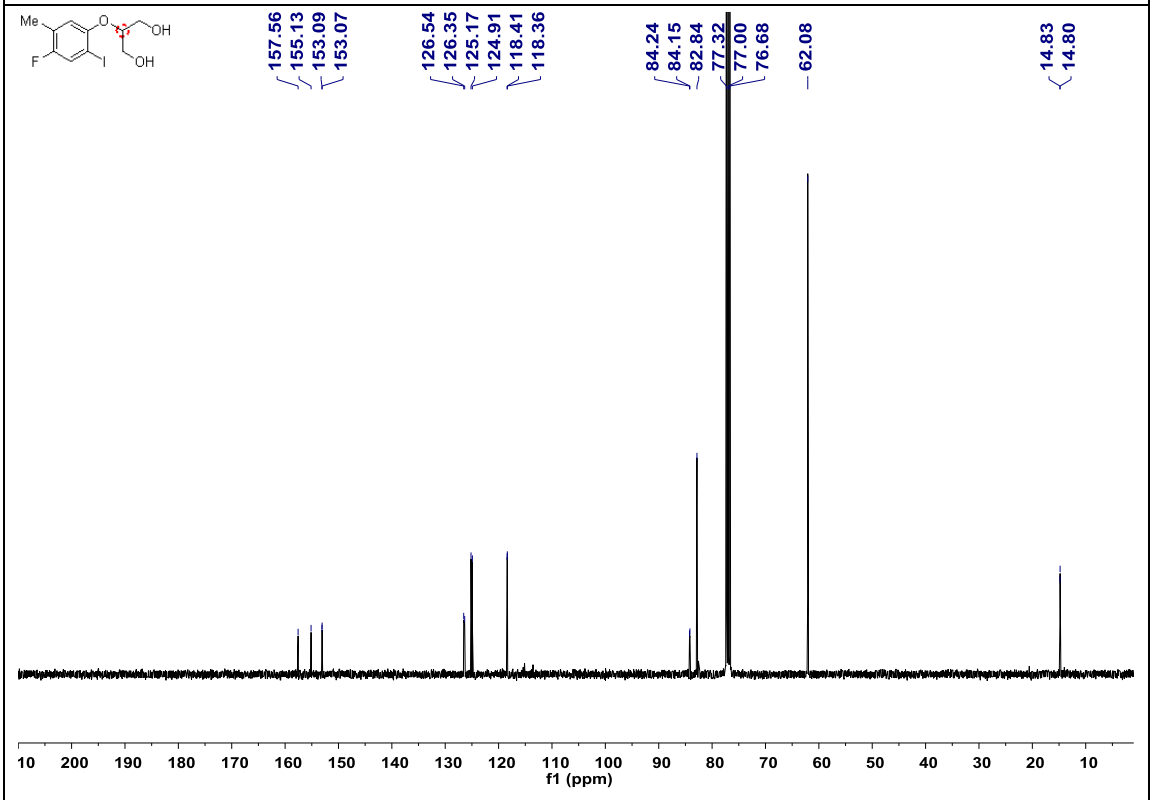
^{13}C NMR Spectrum of **1m**



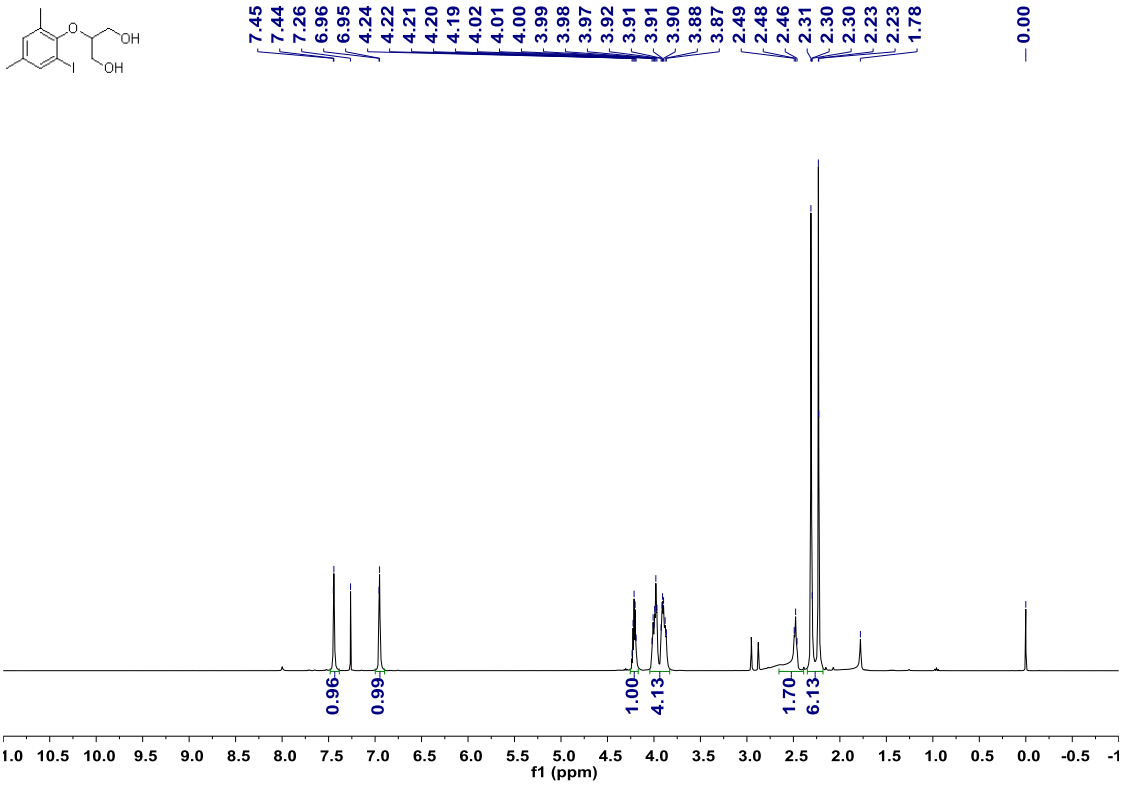
^{1}H NMR Spectrum of **1n**



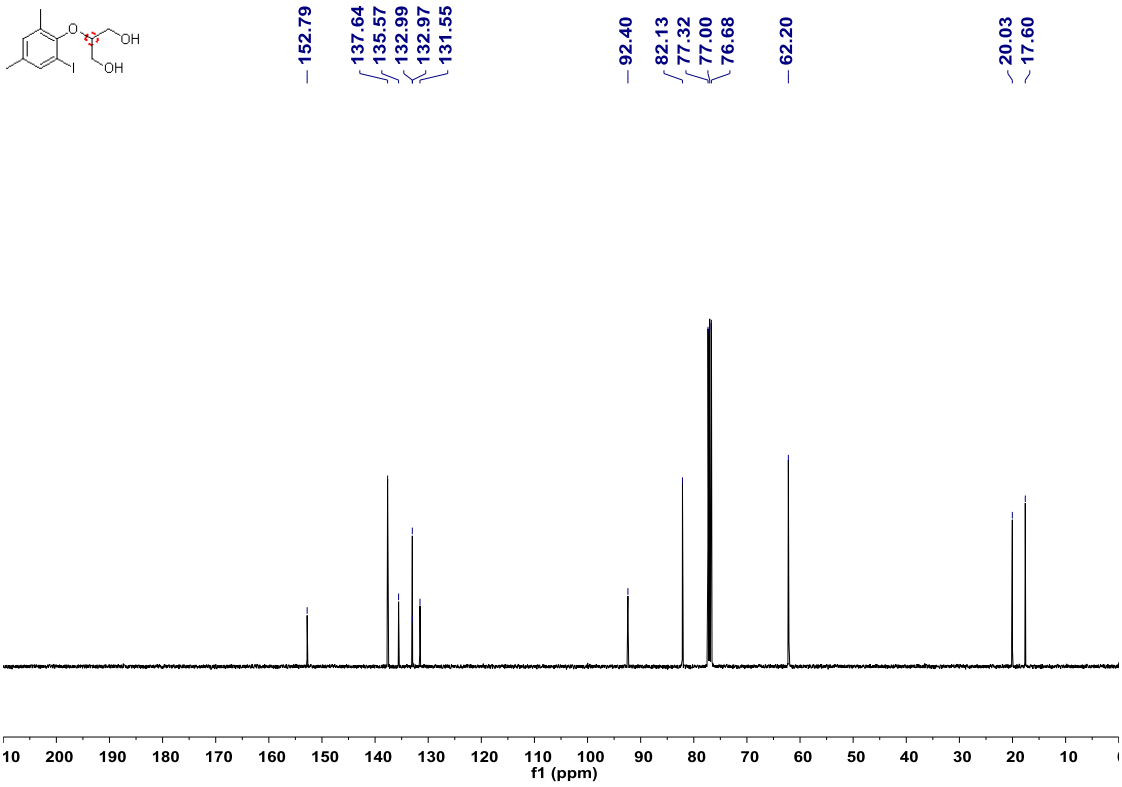
^{13}C NMR Spectrum of **1n**



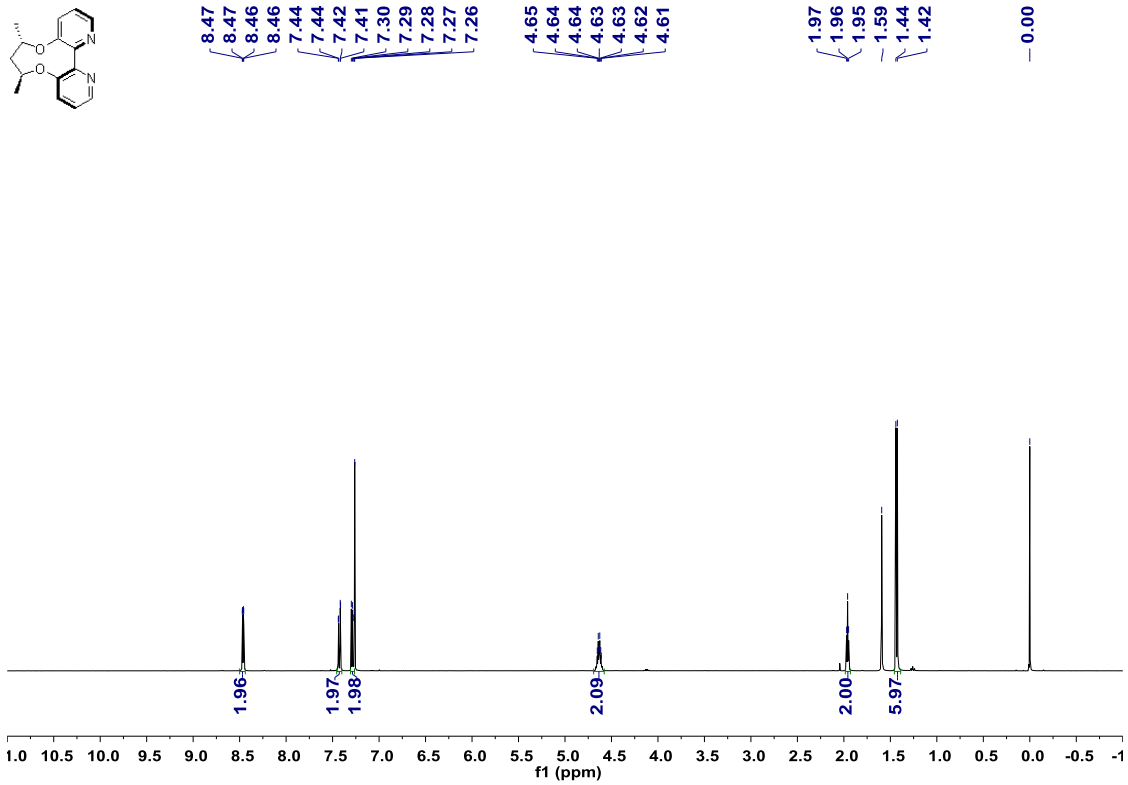
^{1}H NMR Spectrum of **1o**



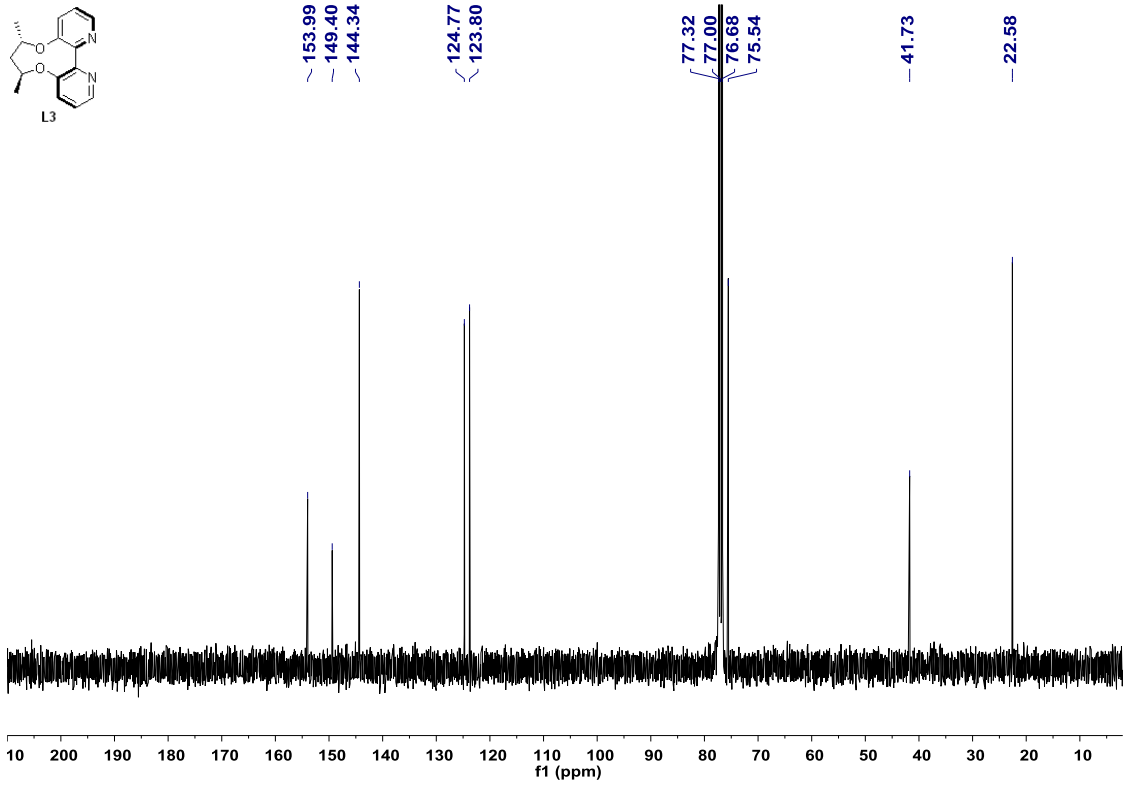
^{13}C NMR Spectrum of **1o**



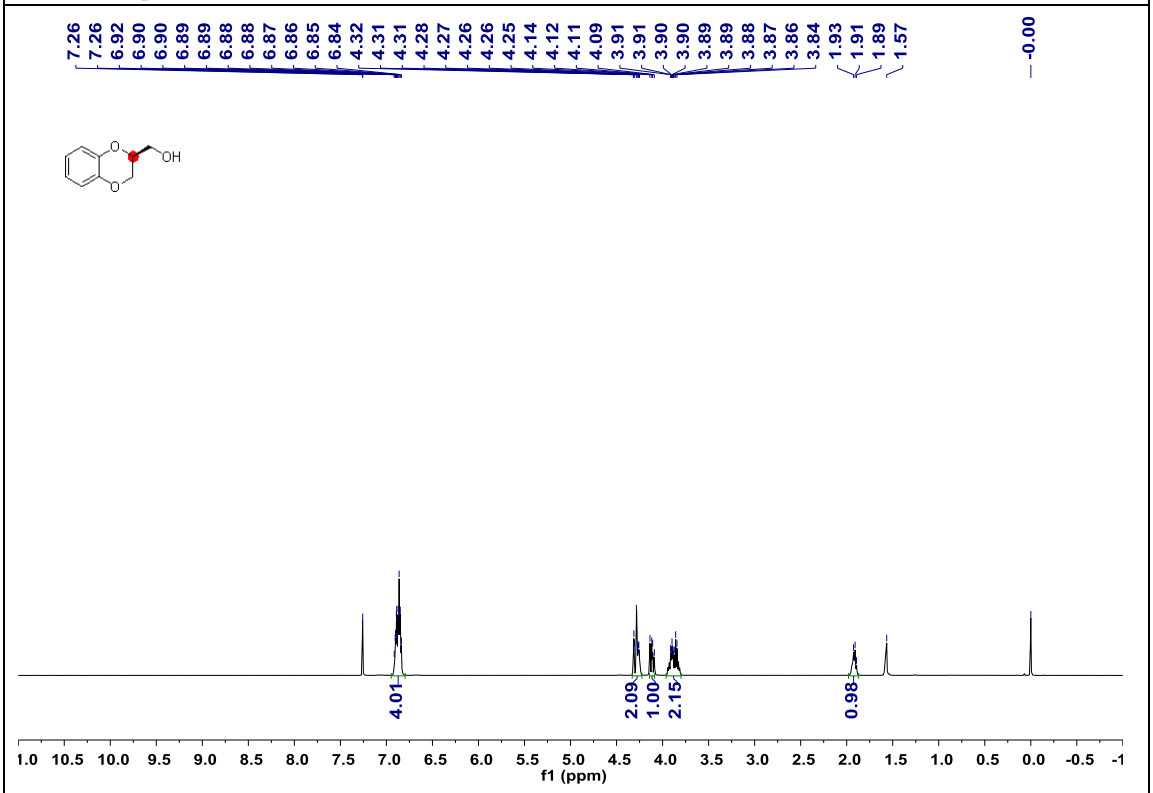
^{1}H NMR Spectrum of **L3**



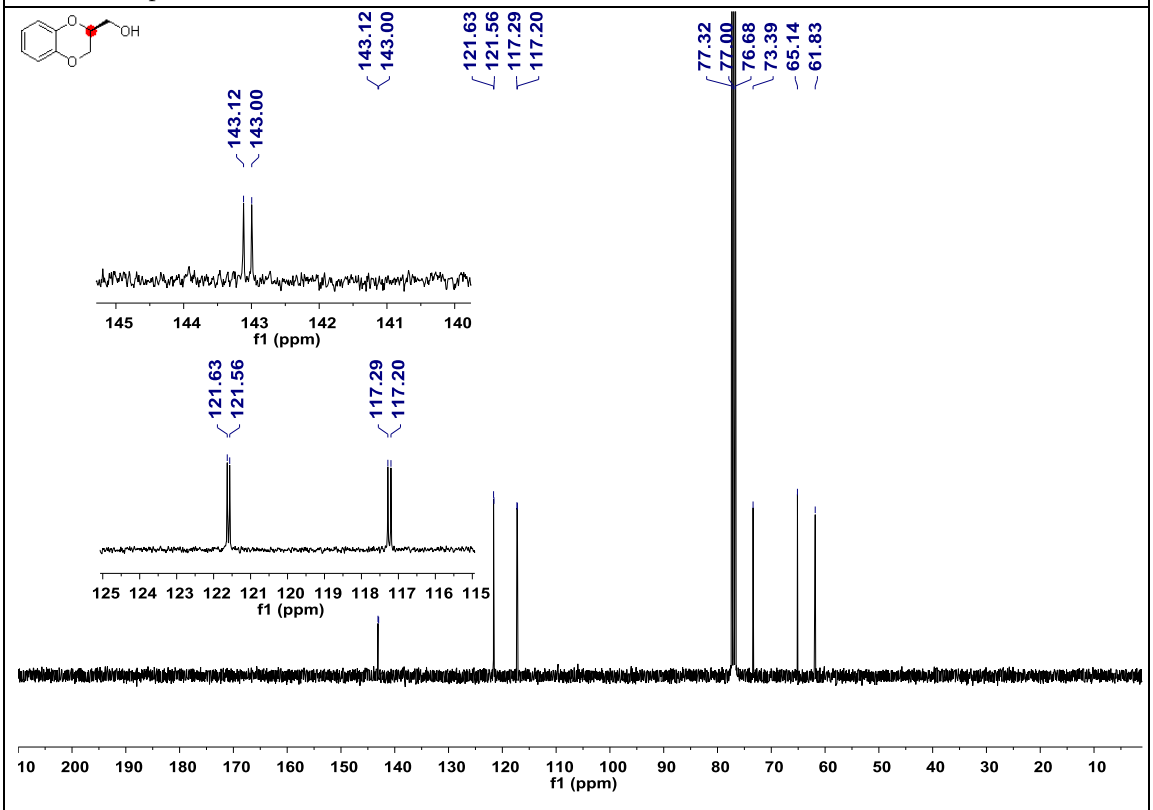
^{13}C NMR Spectrum of **L3**



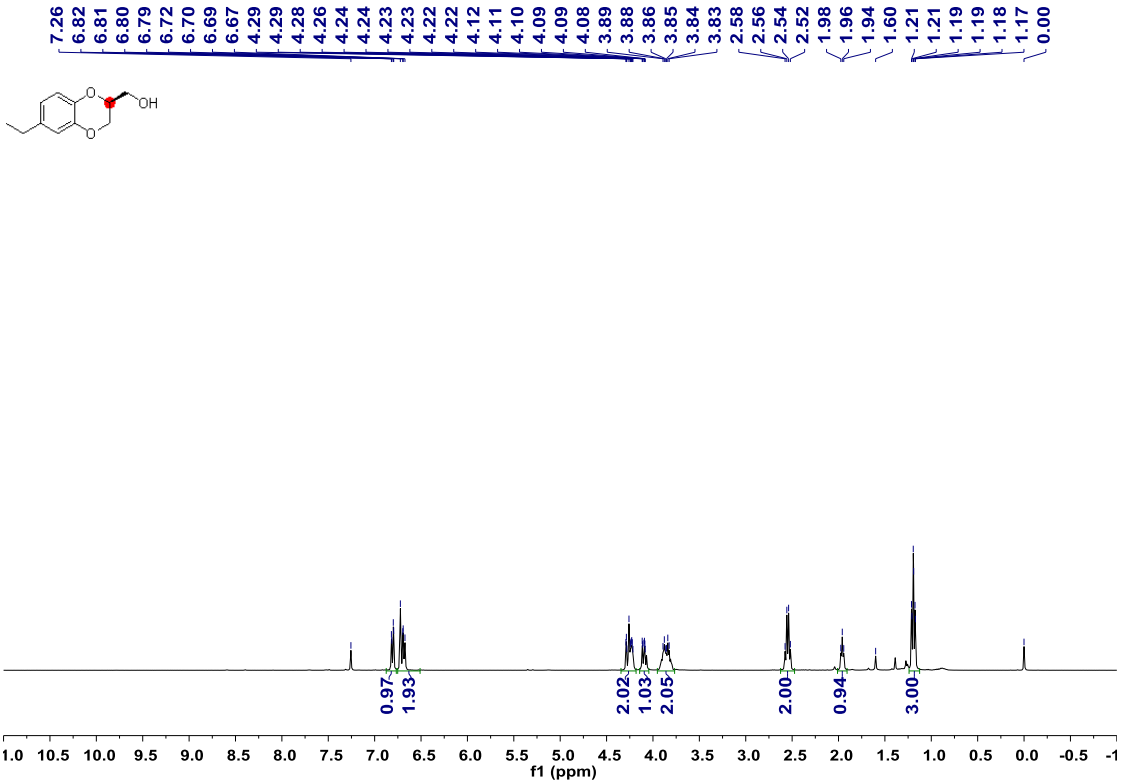
^{1}H NMR Spectrum of **2a**



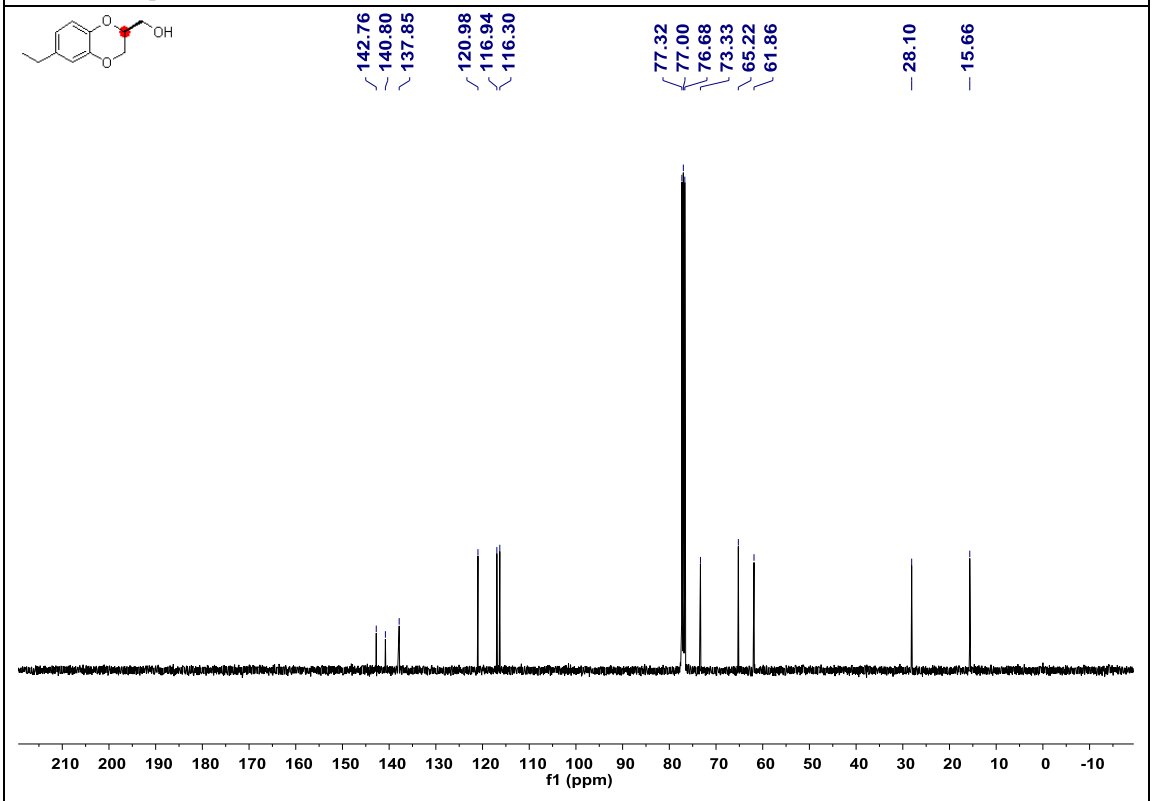
^{13}C NMR Spectrum of **2a**



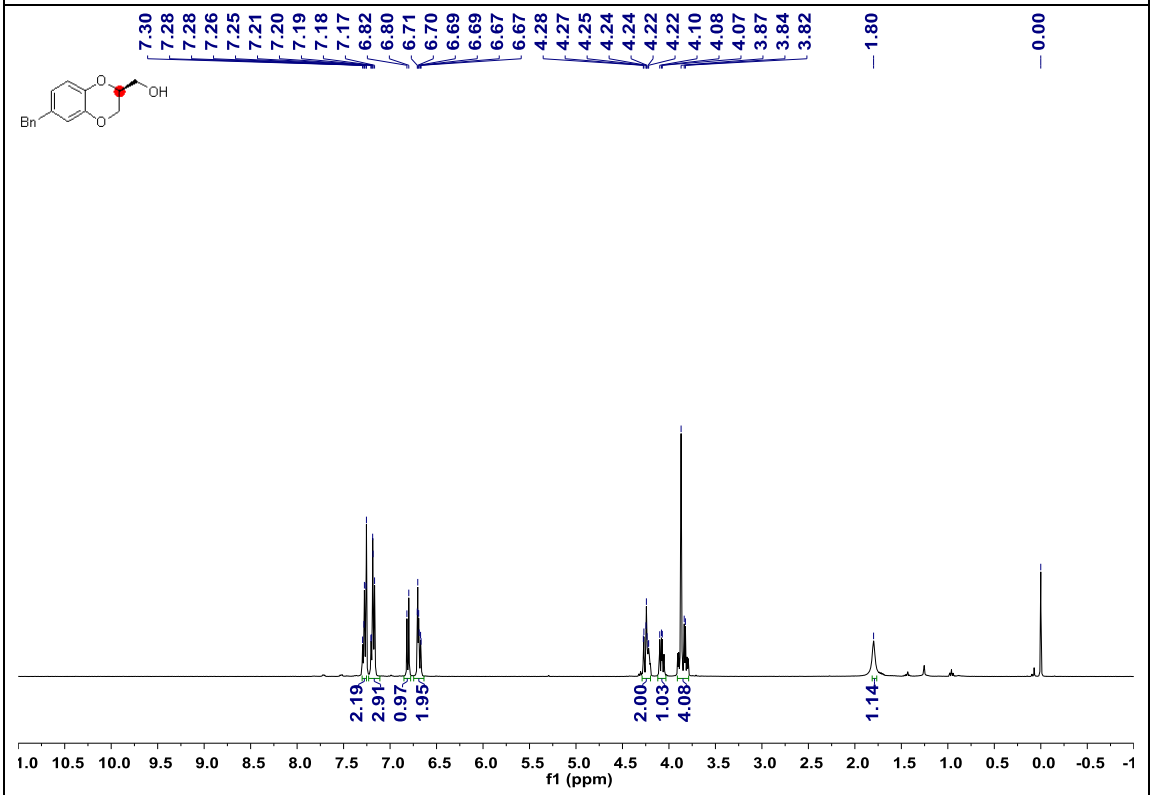
^{1}H NMR Spectrum of **2b**



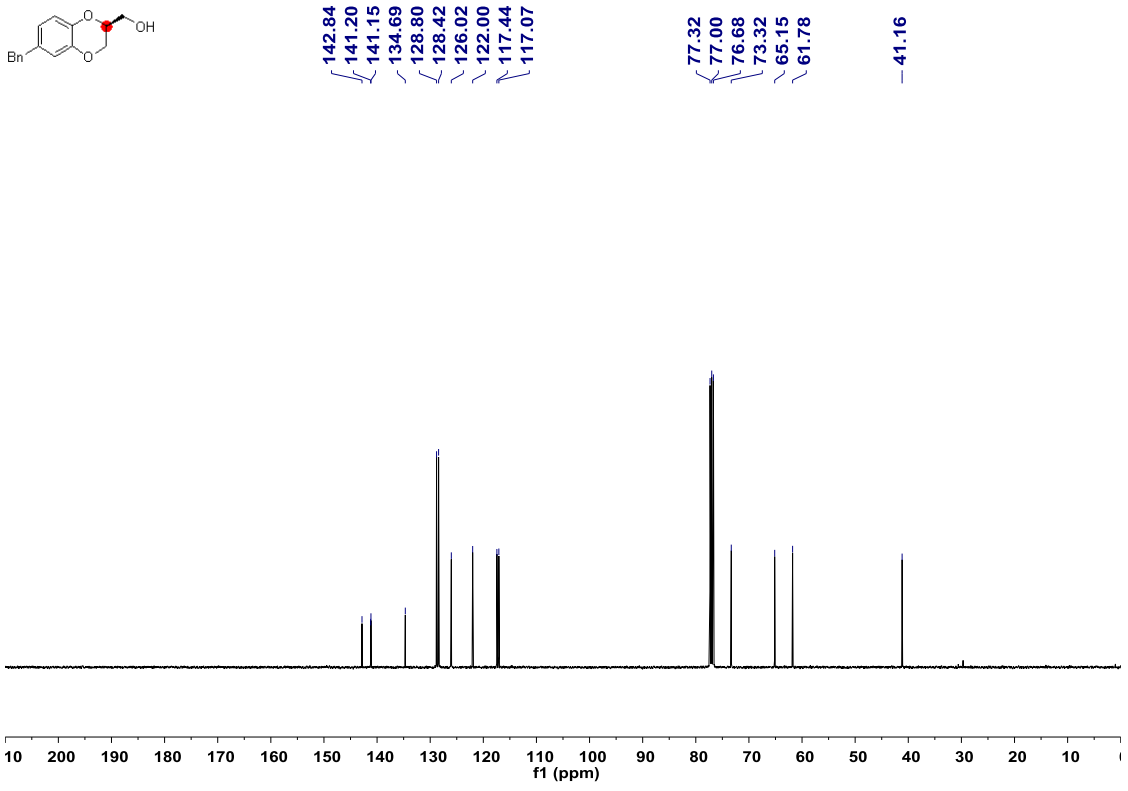
^{13}C NMR Spectrum of **2b**



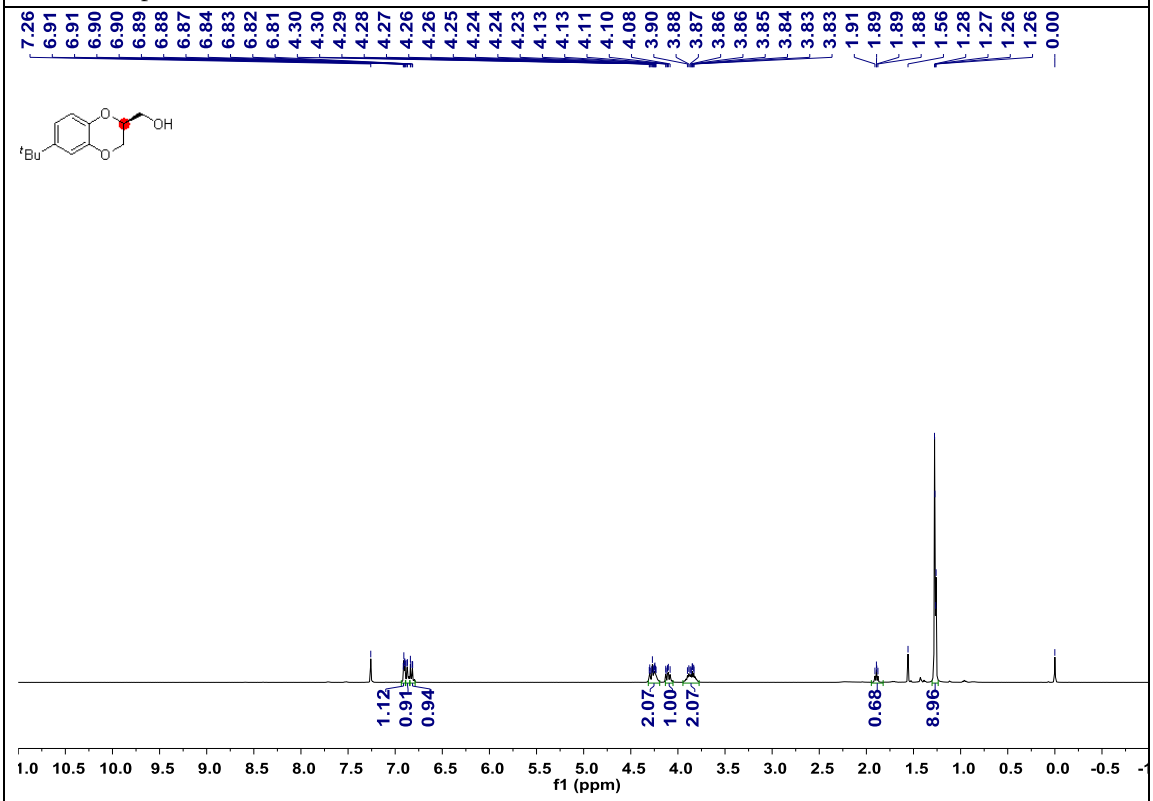
^{1}H NMR Spectrum of **2c**



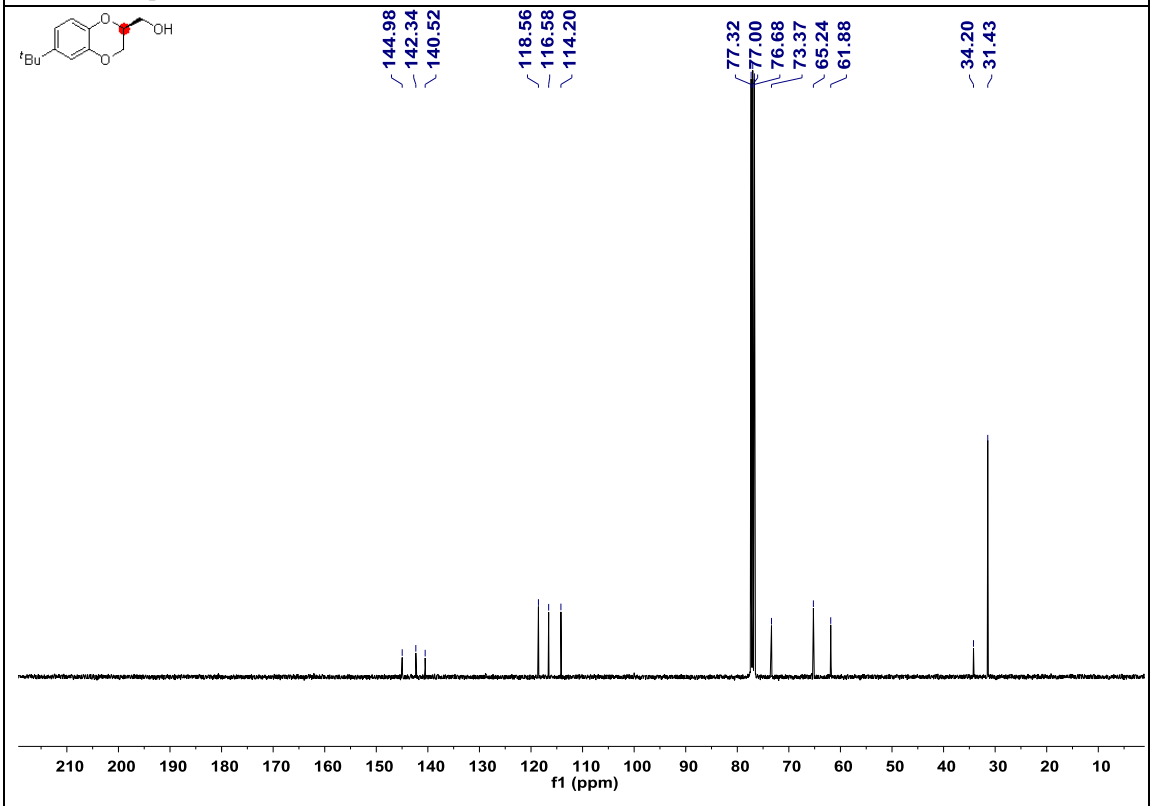
^{13}C NMR Spectrum of **2c**



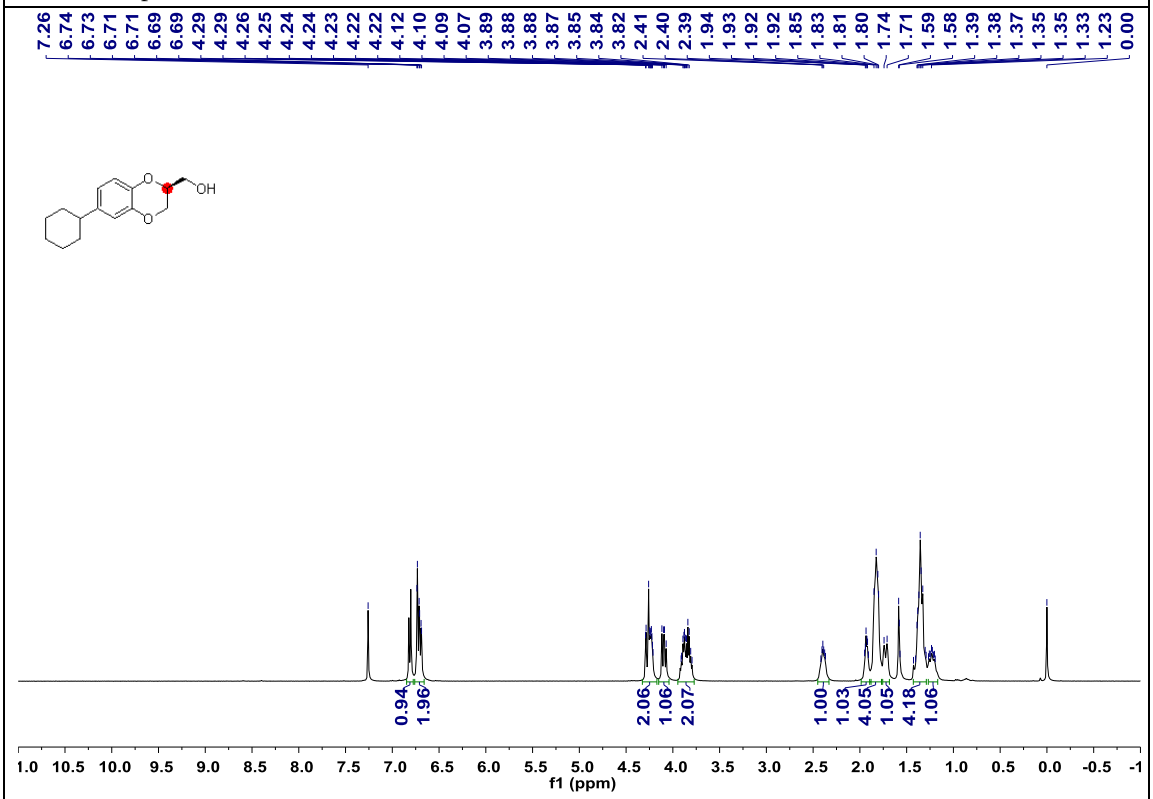
^{1}H NMR Spectrum of **2d**



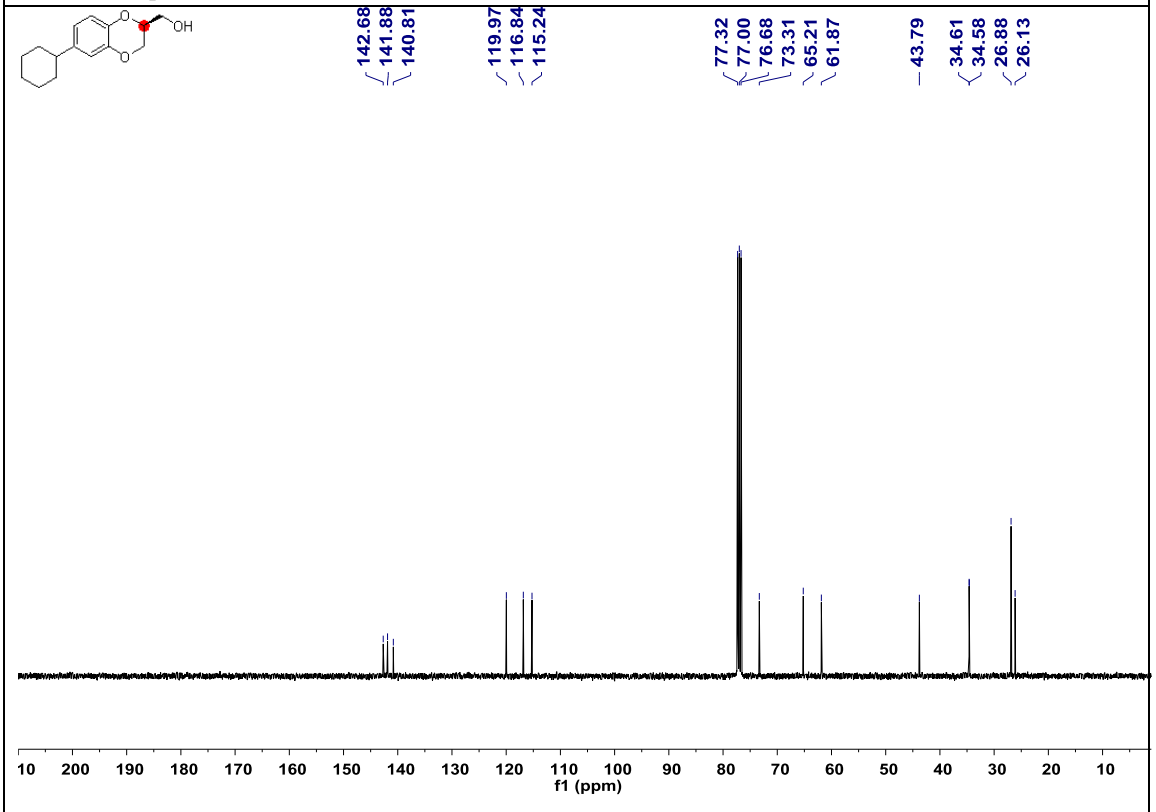
^{13}C NMR Spectrum of **2d**



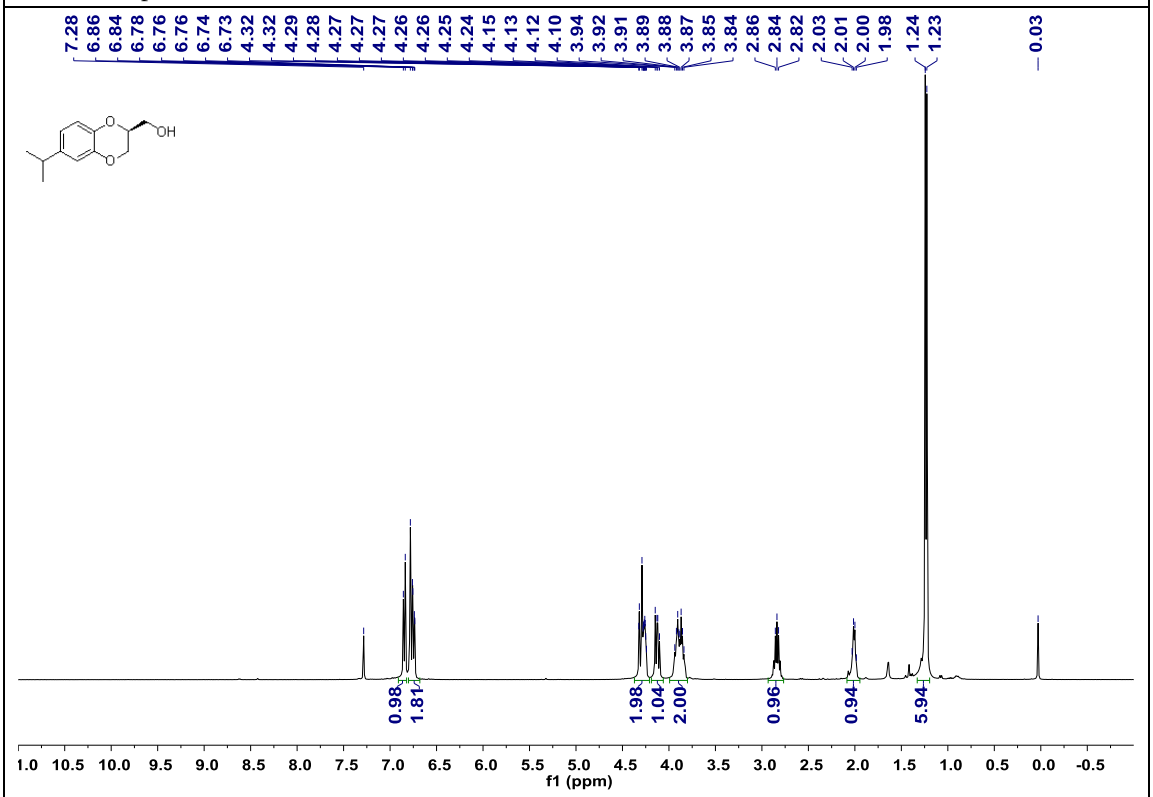
^{1}H NMR Spectrum of **2e**



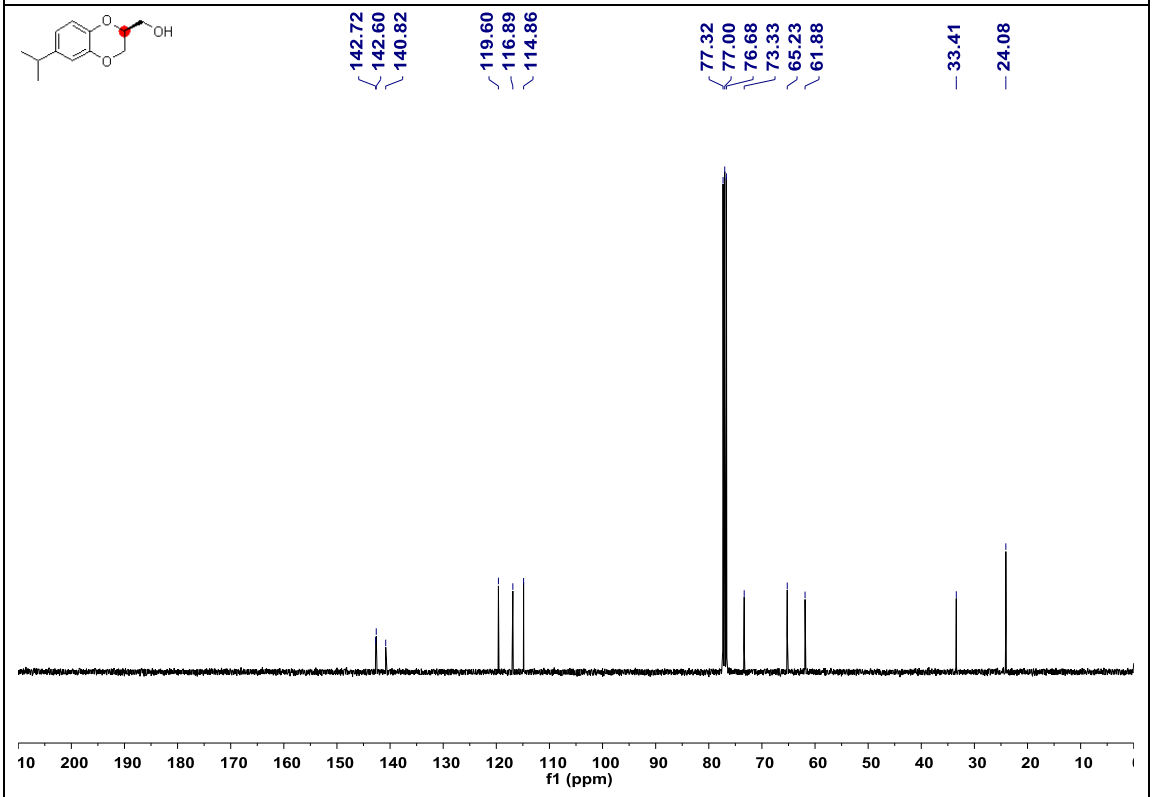
^{13}C NMR Spectrum of **2e**



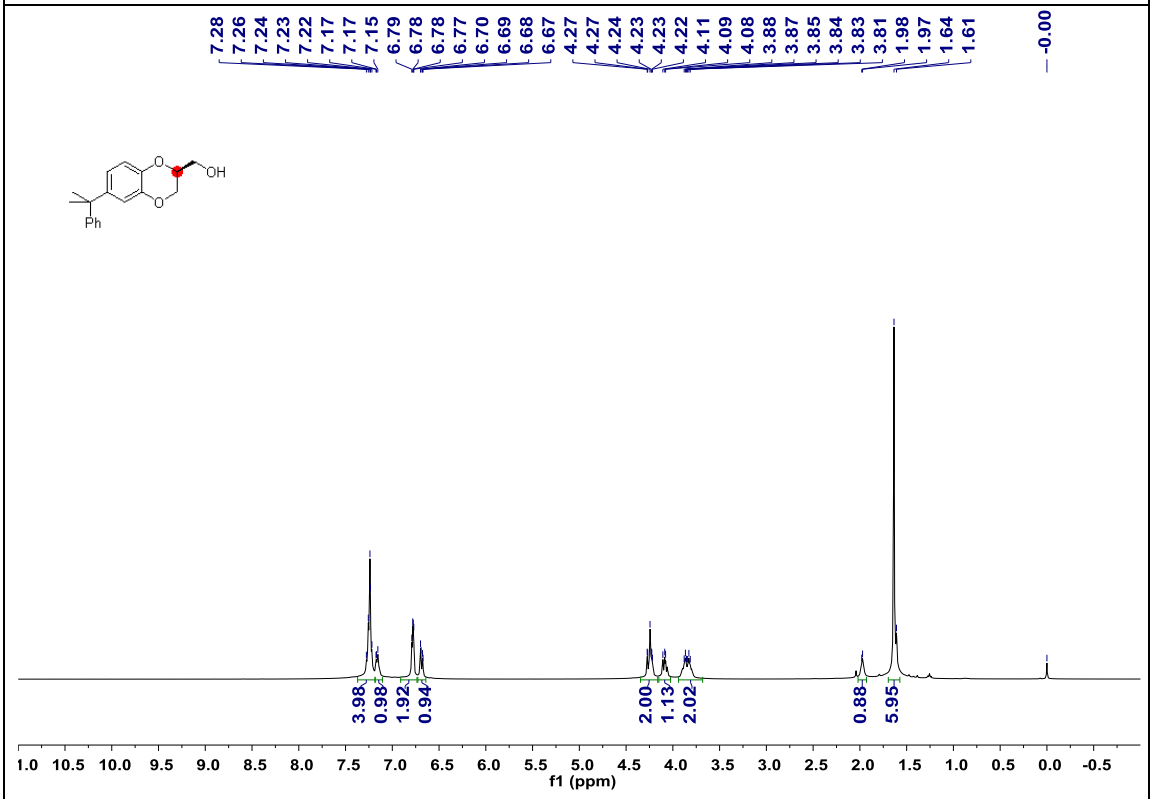
^{1}H NMR Spectrum of **2f**



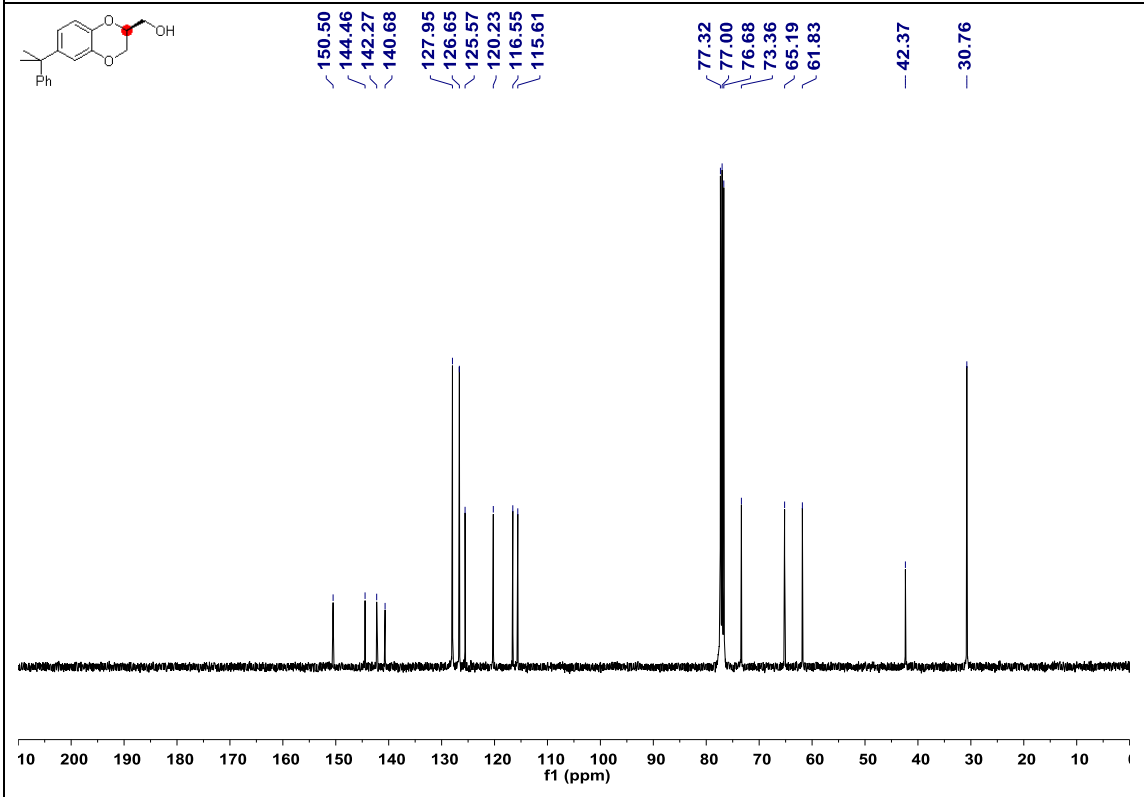
^{13}C NMR Spectrum of **2f**



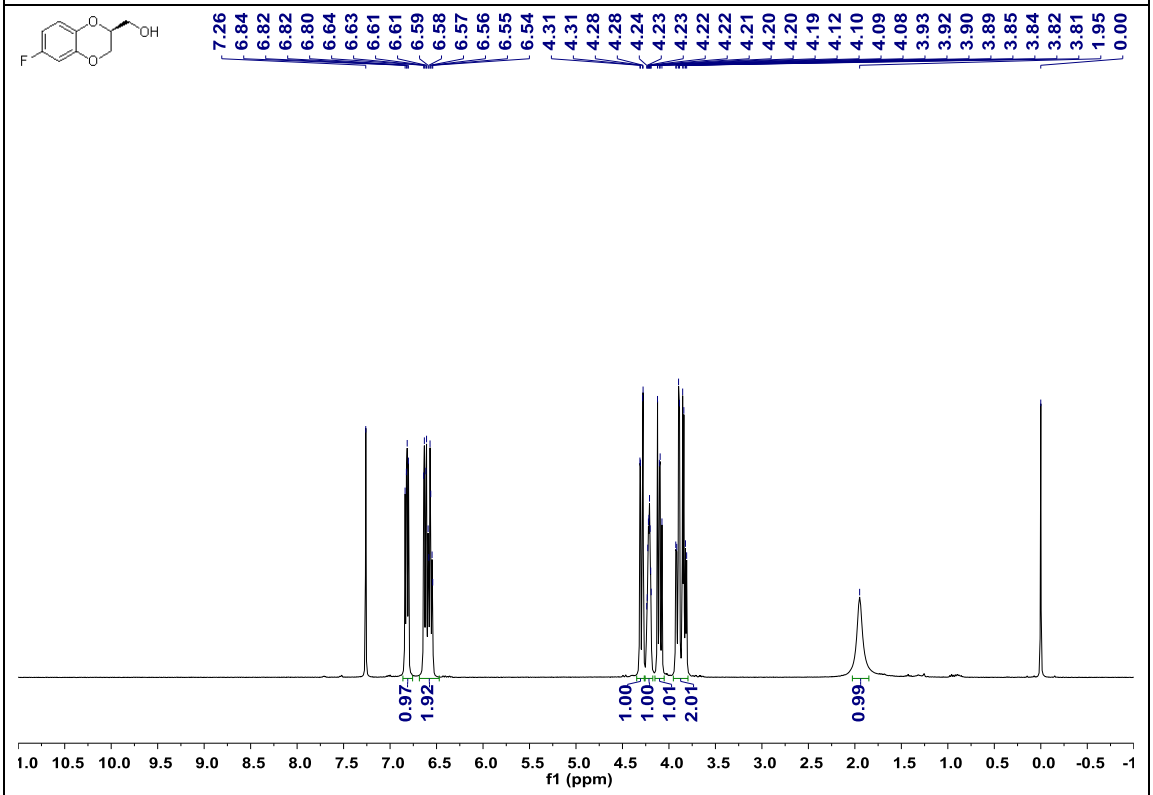
^{1}H NMR Spectrum of **2g**



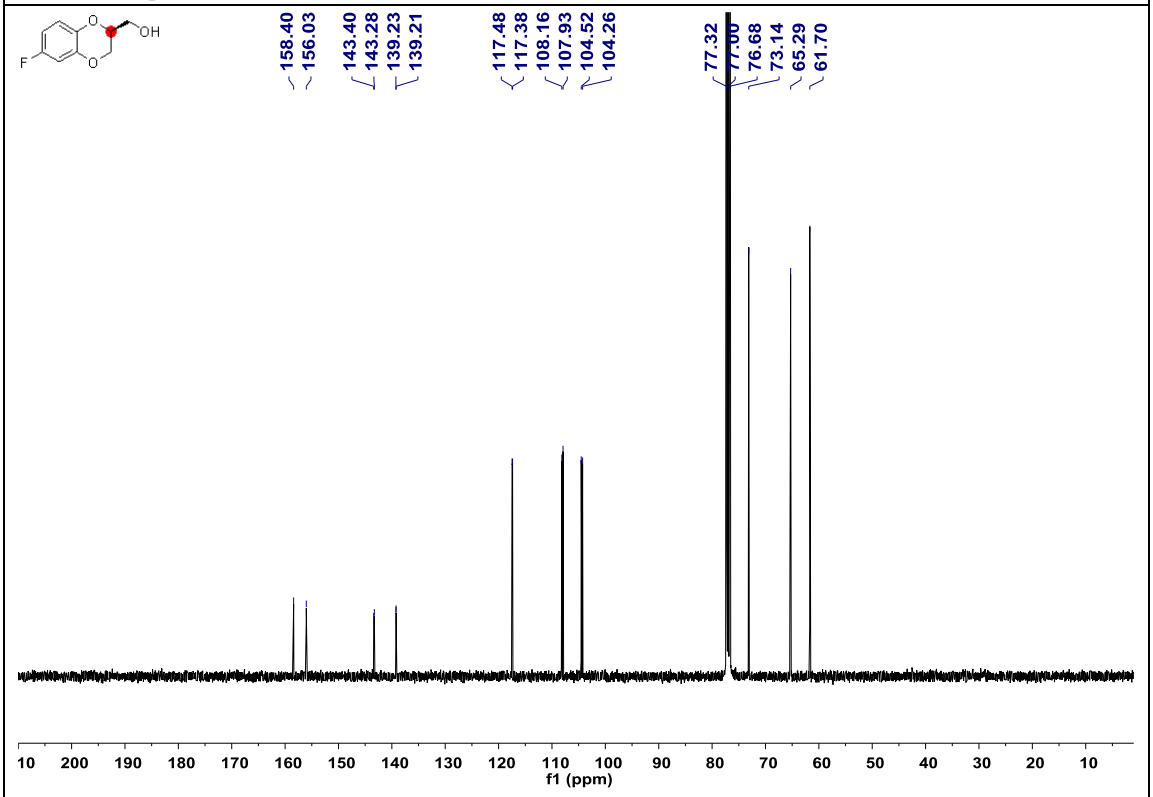
^{13}C NMR Spectrum of **2g**



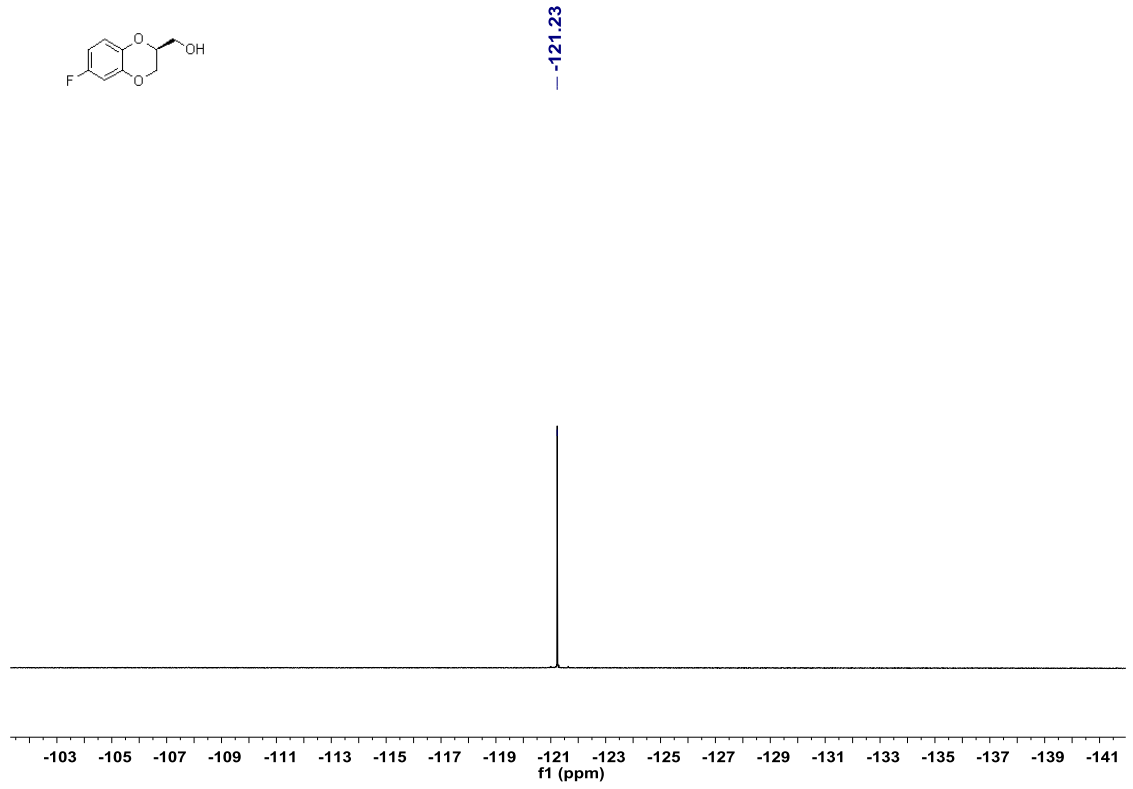
^{1}H NMR Spectrum of **2h**



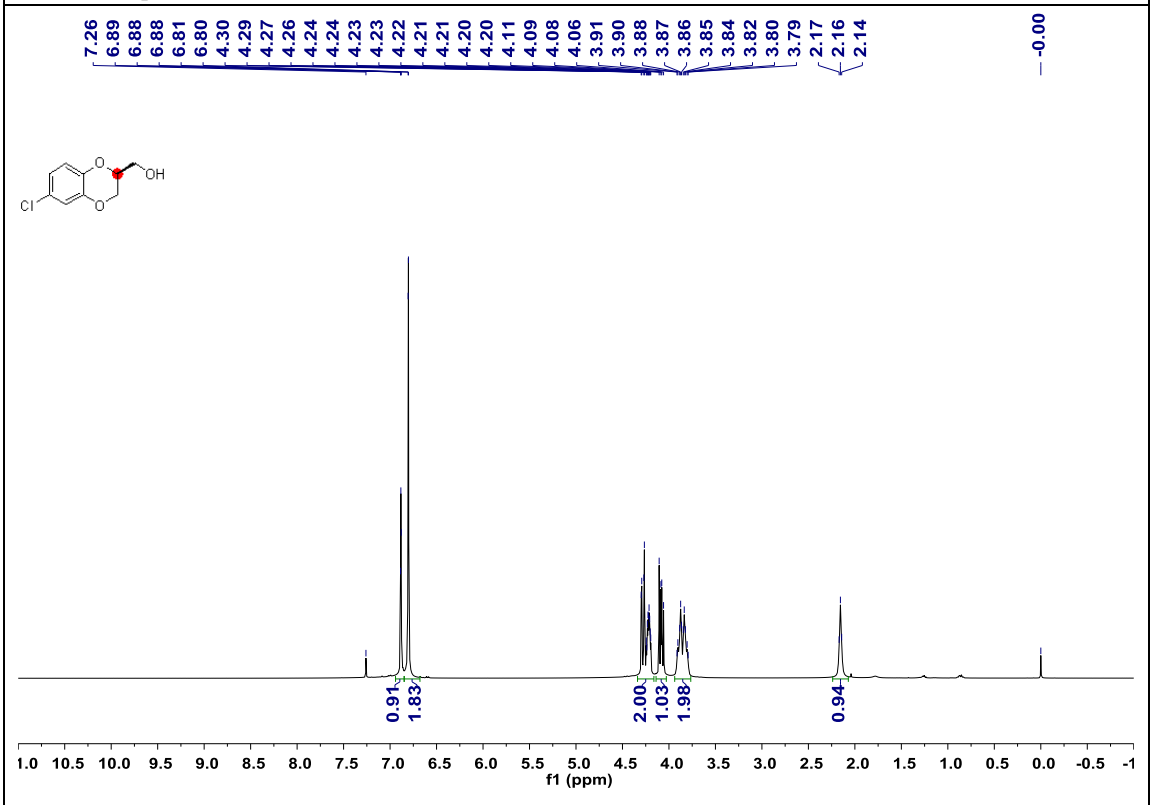
^{13}C NMR Spectrum of **2h**



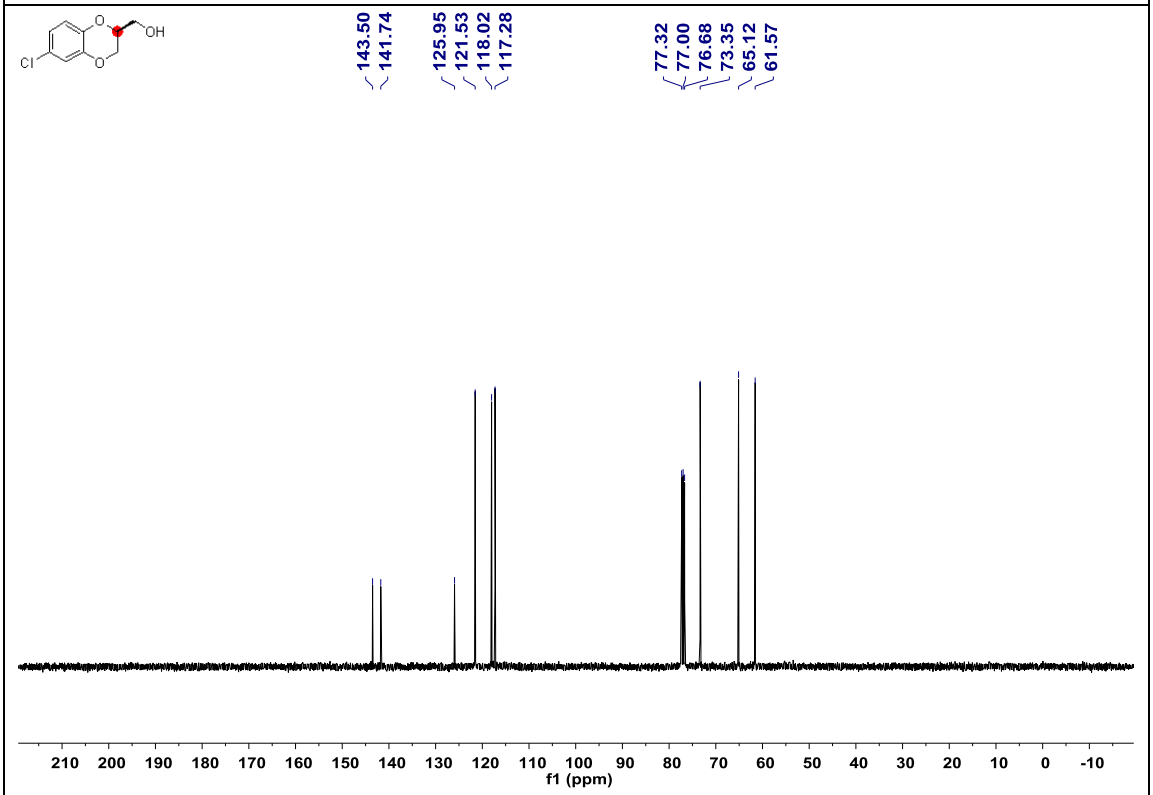
^{19}F NMR Spectrum of **2h**



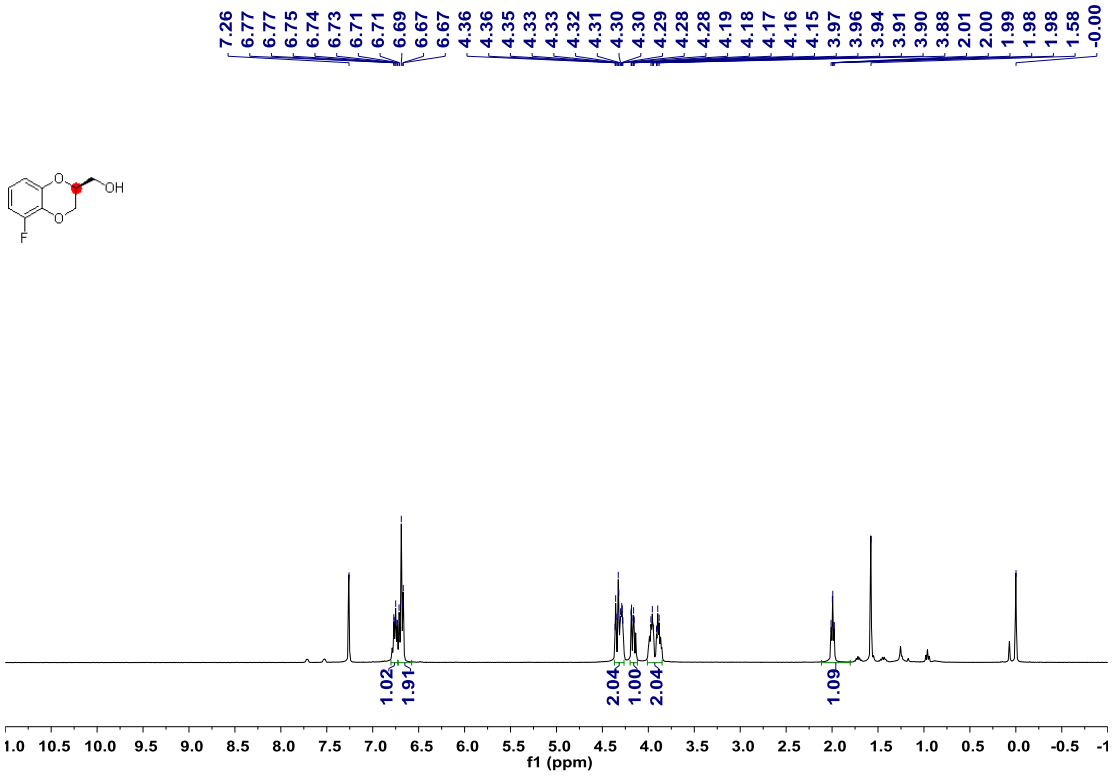
^{1}H NMR Spectrum of **2i**



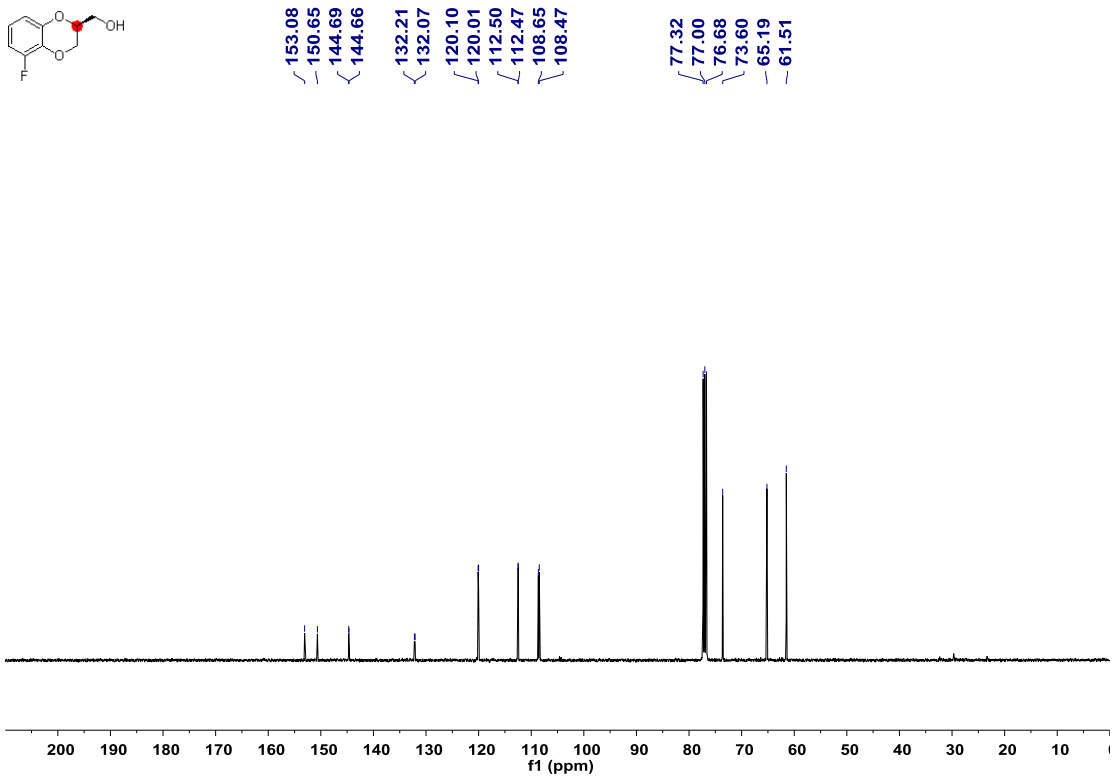
^{13}C NMR Spectrum of **2i**



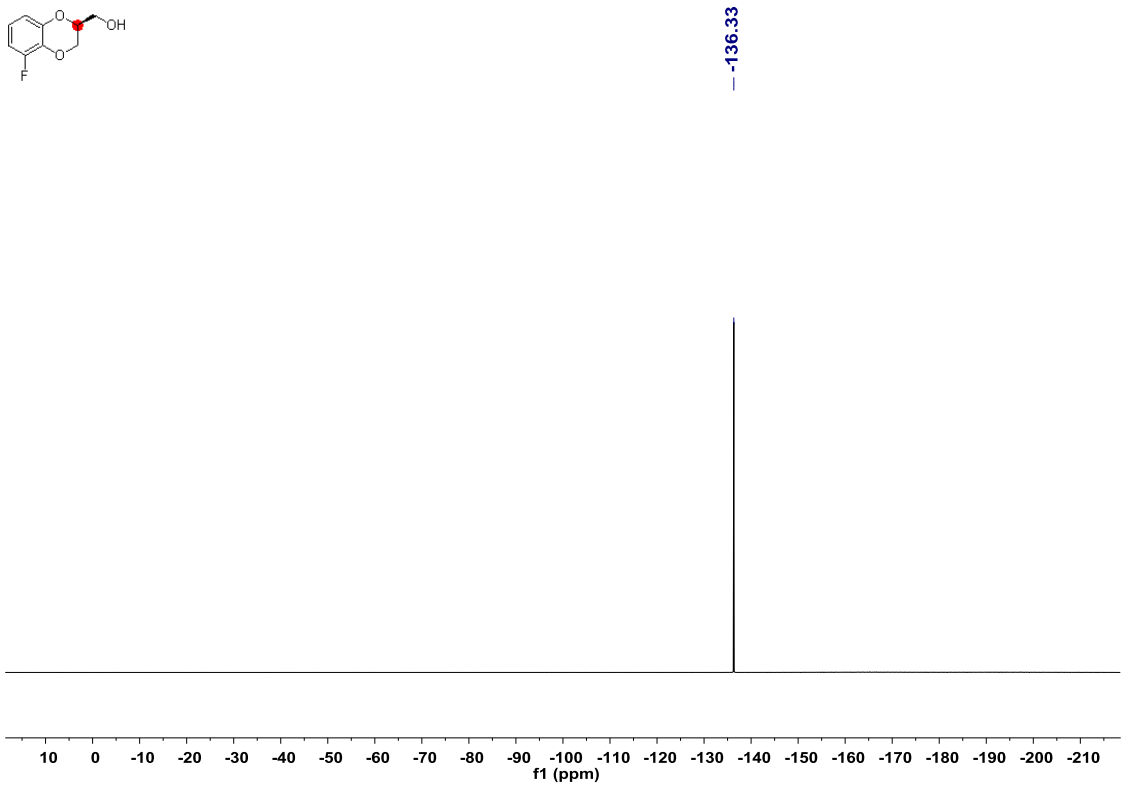
^{1}H NMR Spectrum of **2j**



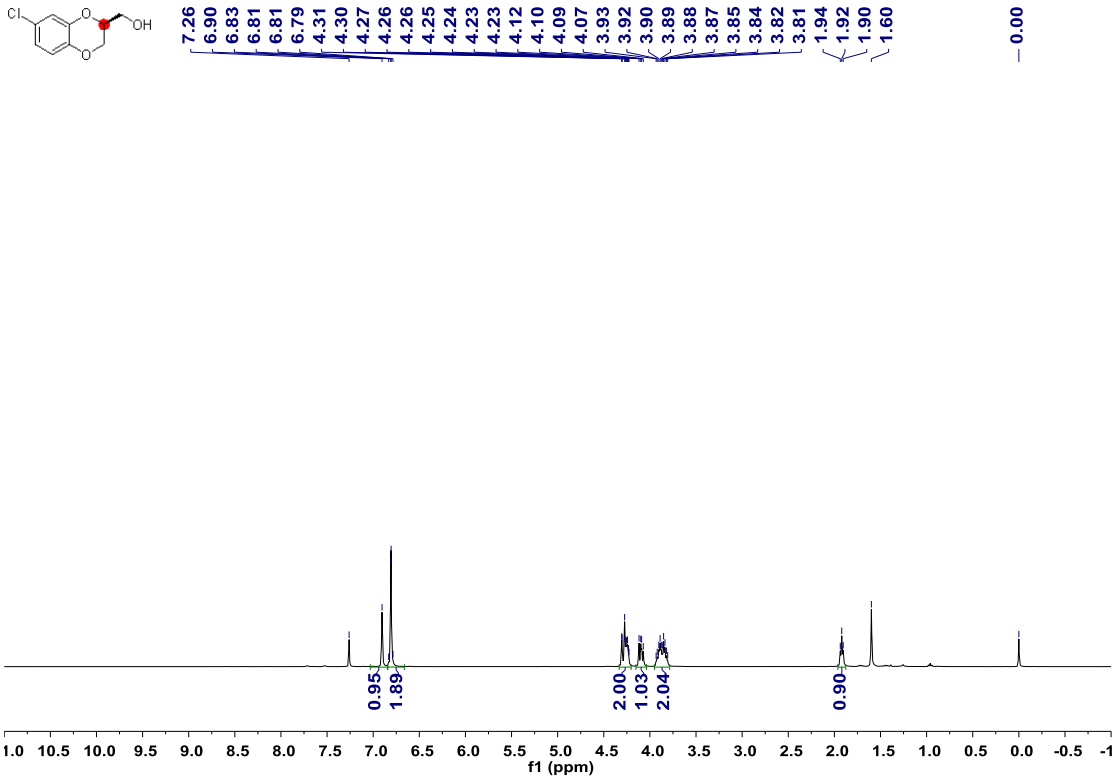
^{13}C NMR Spectrum of **2j**



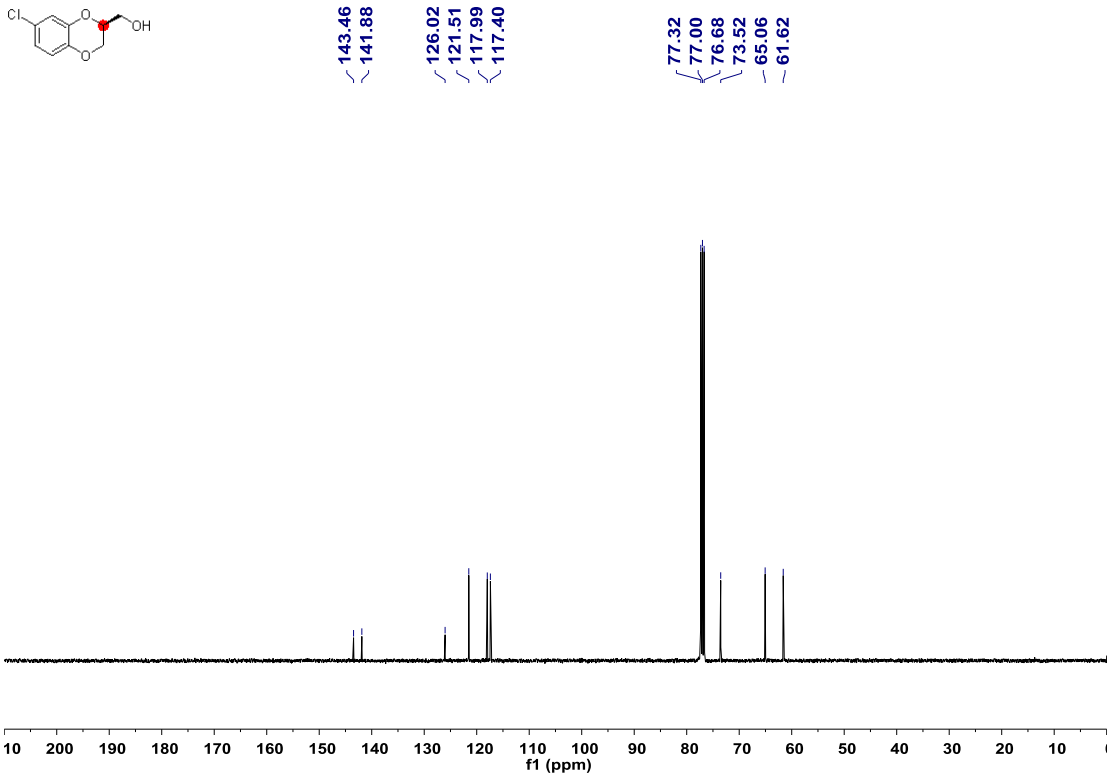
^{19}F NMR Spectrum of **2j**



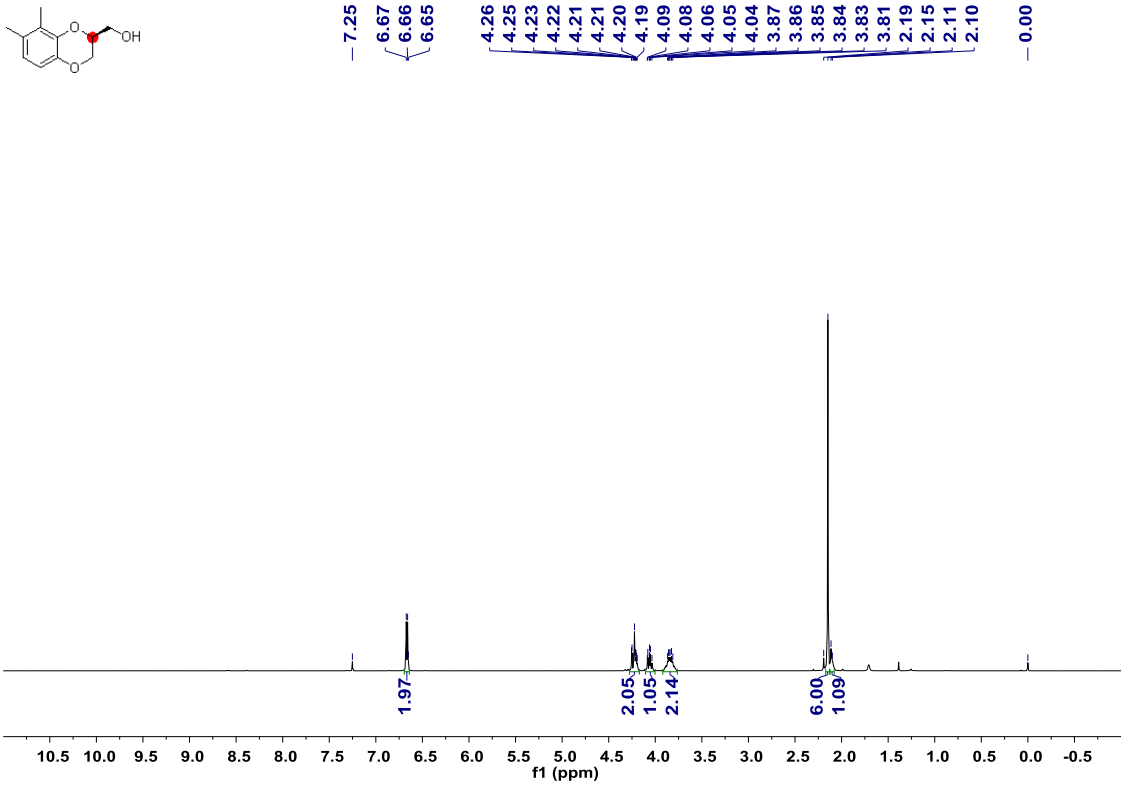
^{1}H NMR Spectrum of **2k**



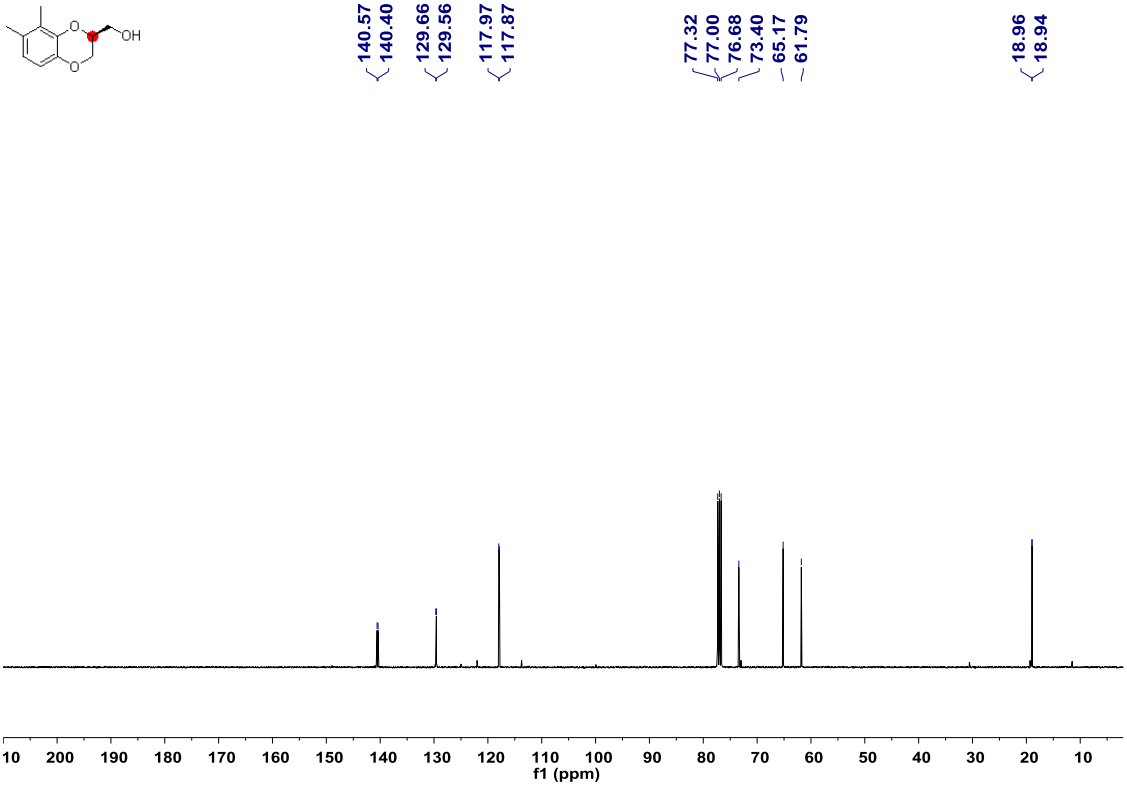
^{13}C NMR Spectrum of **2k**



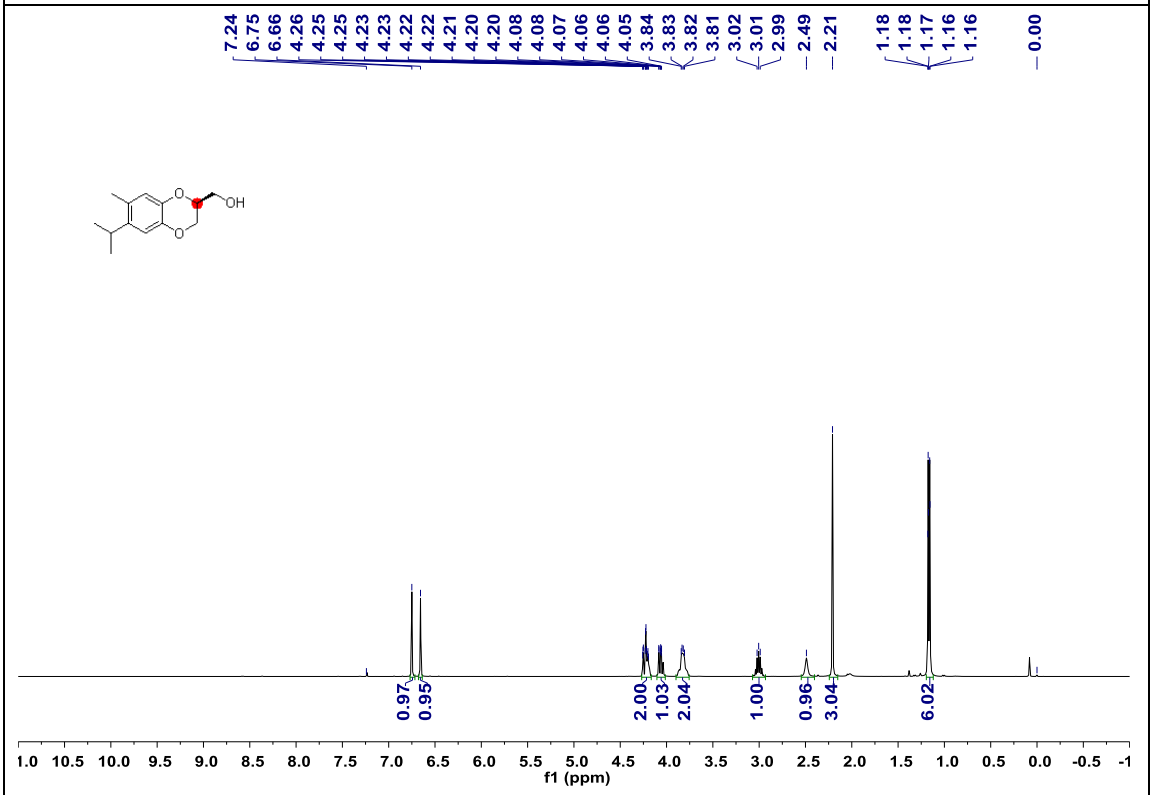
^{1}H NMR Spectrum of **2l**



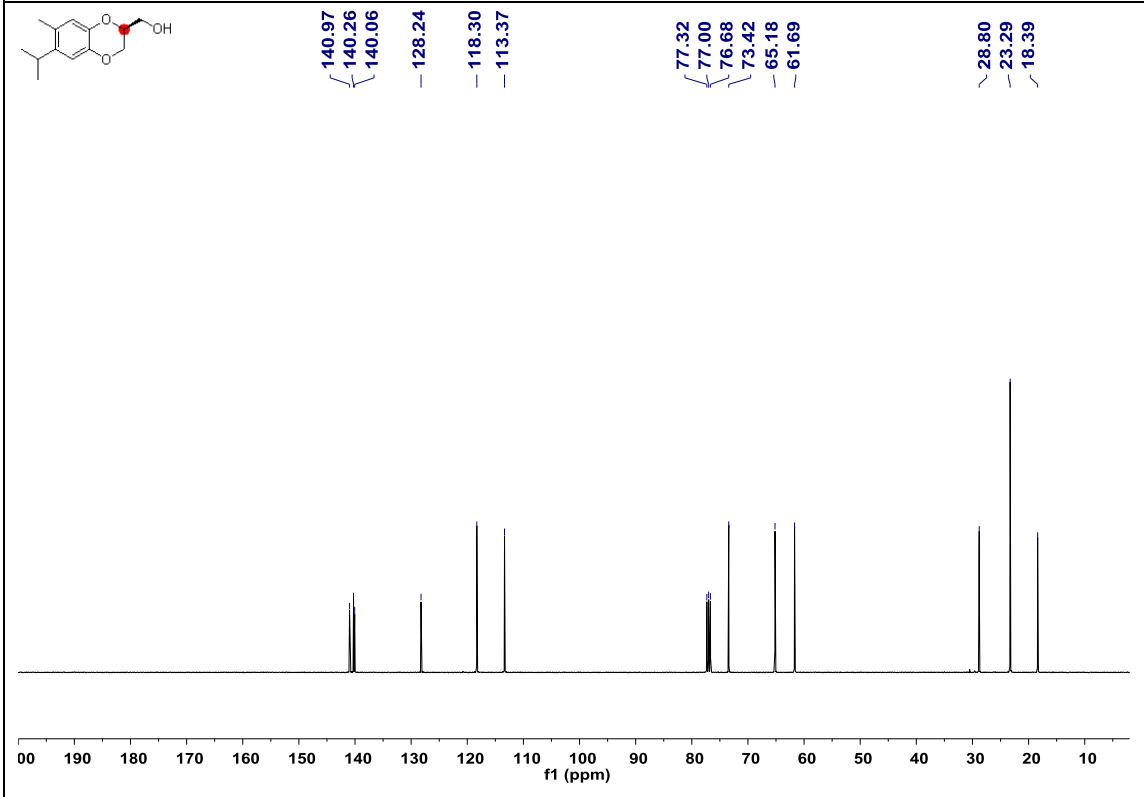
^{13}C NMR Spectrum of **2l**



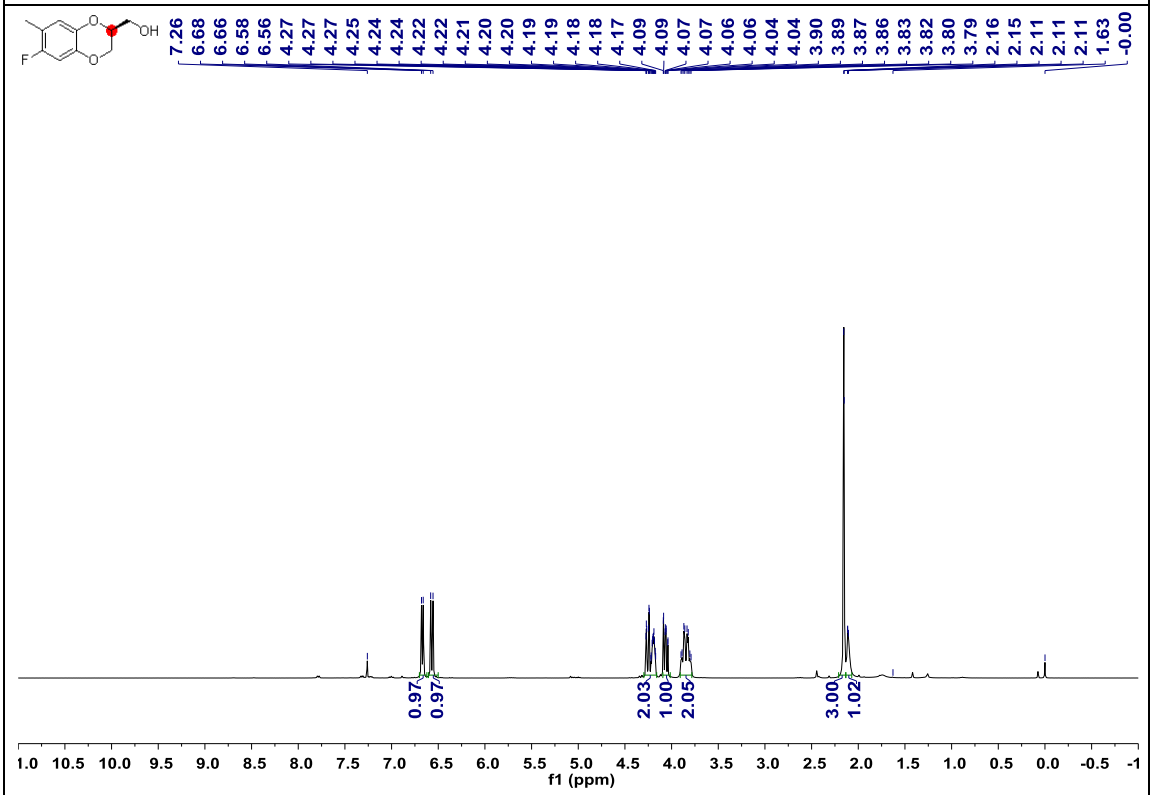
^{1}H NMR Spectrum of **2m**



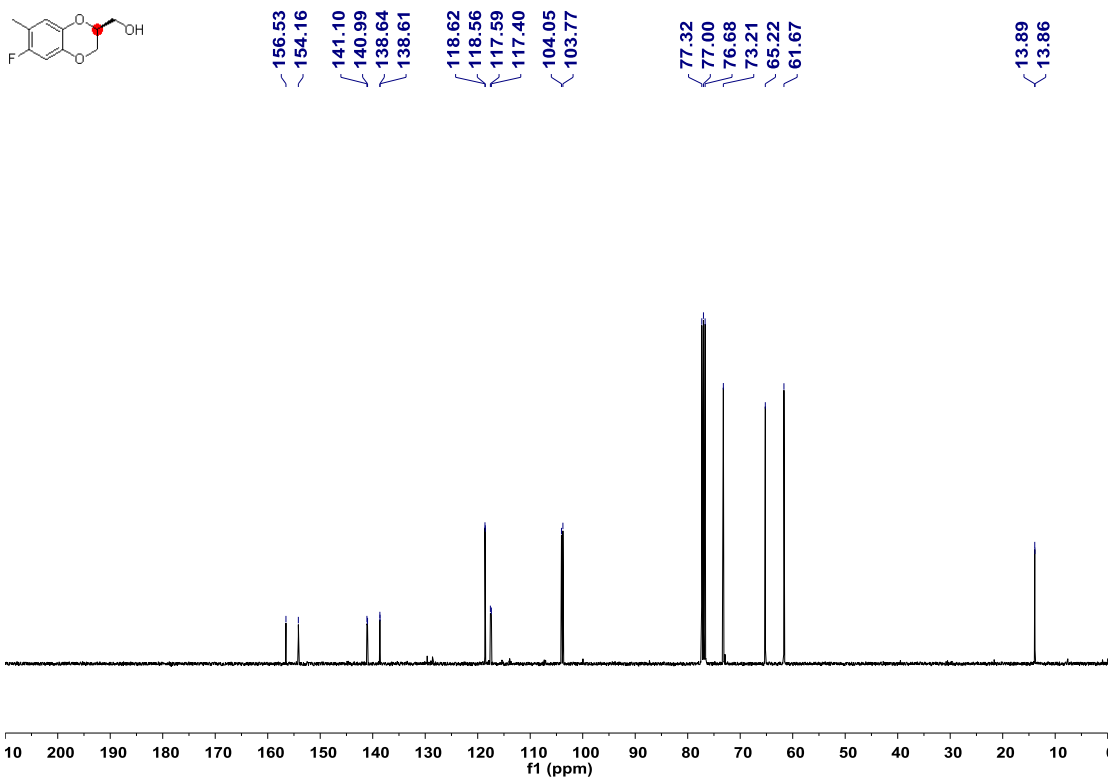
^{13}C NMR Spectrum of **2m**



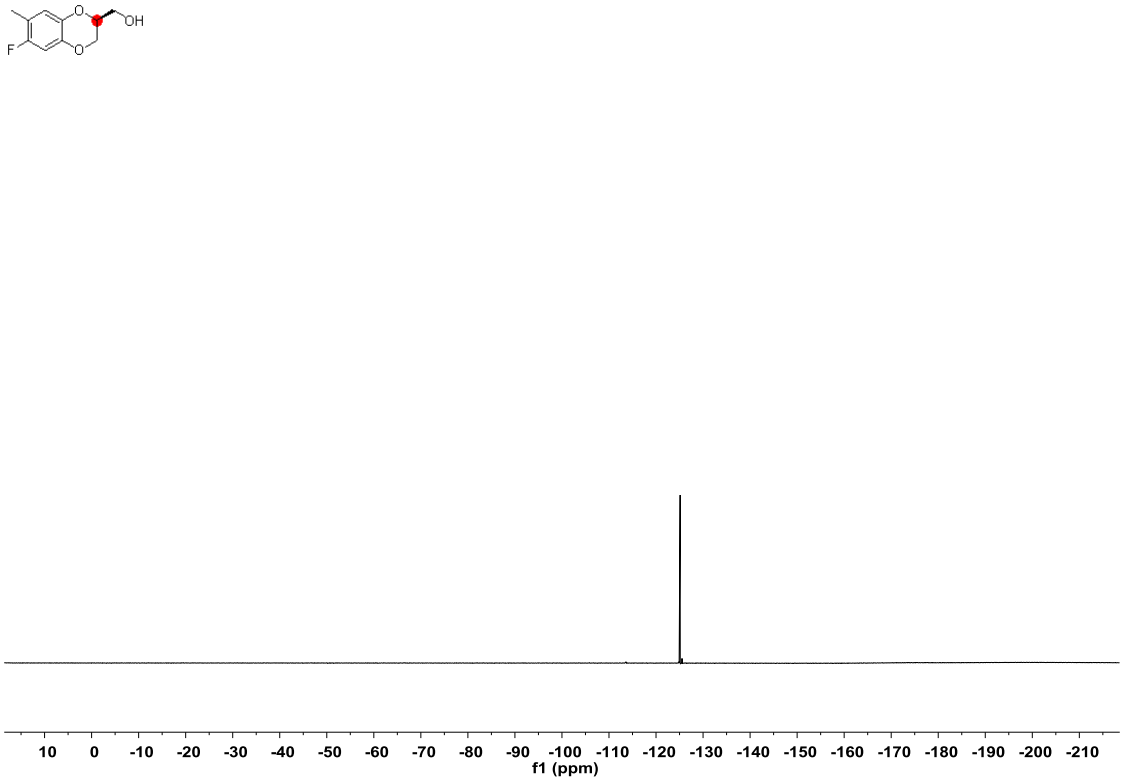
^{1}H NMR Spectrum of **2n**



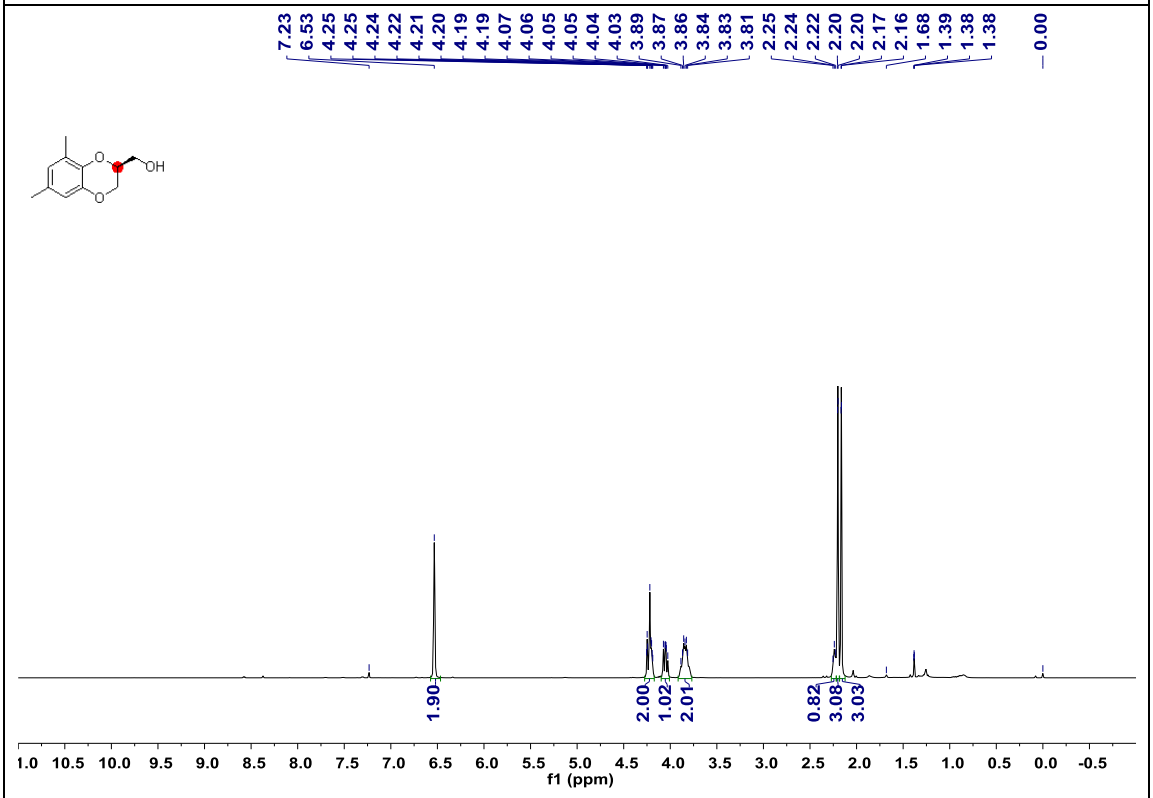
^{13}C NMR Spectrum of **2n**



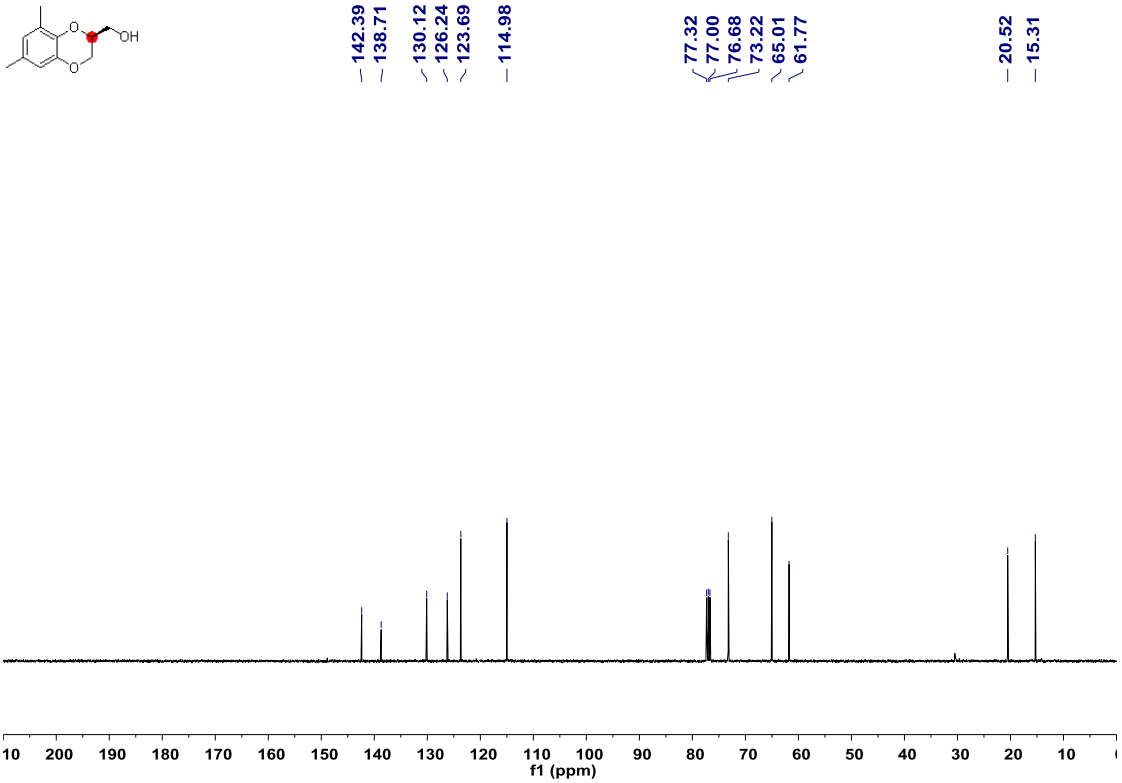
^{19}F NMR Spectrum of **2n**



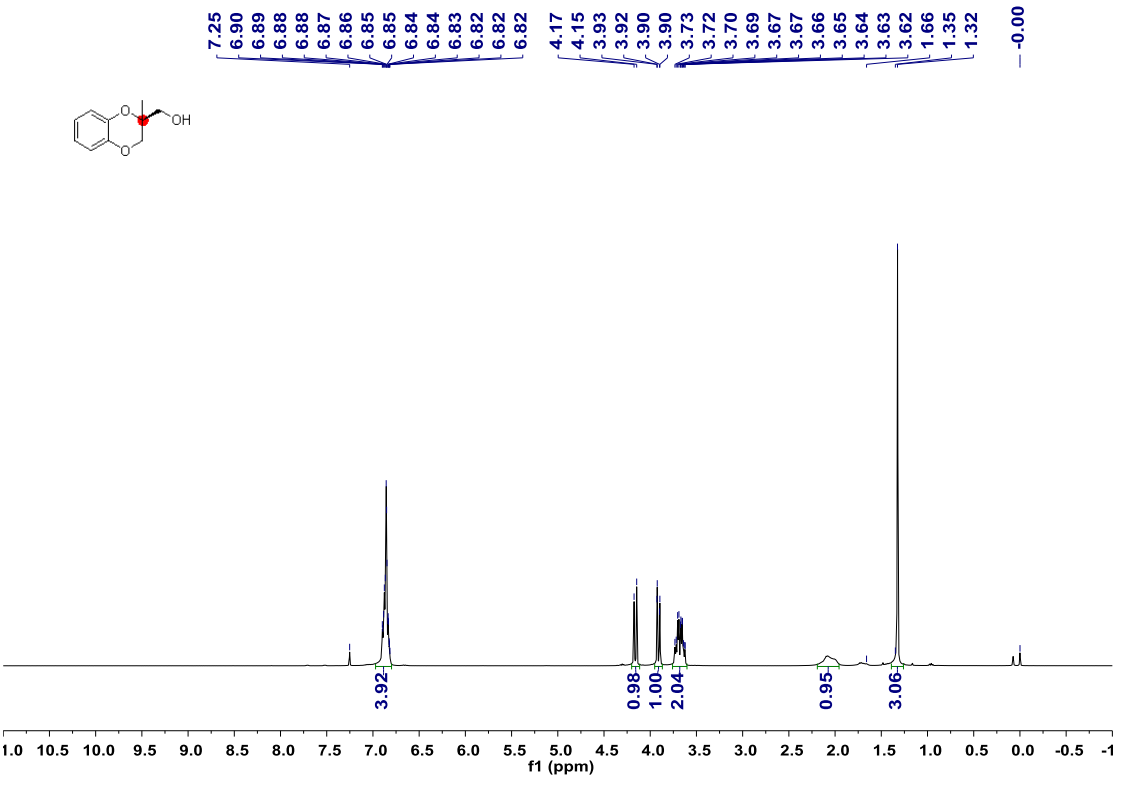
^{1}H NMR Spectrum of **2o**



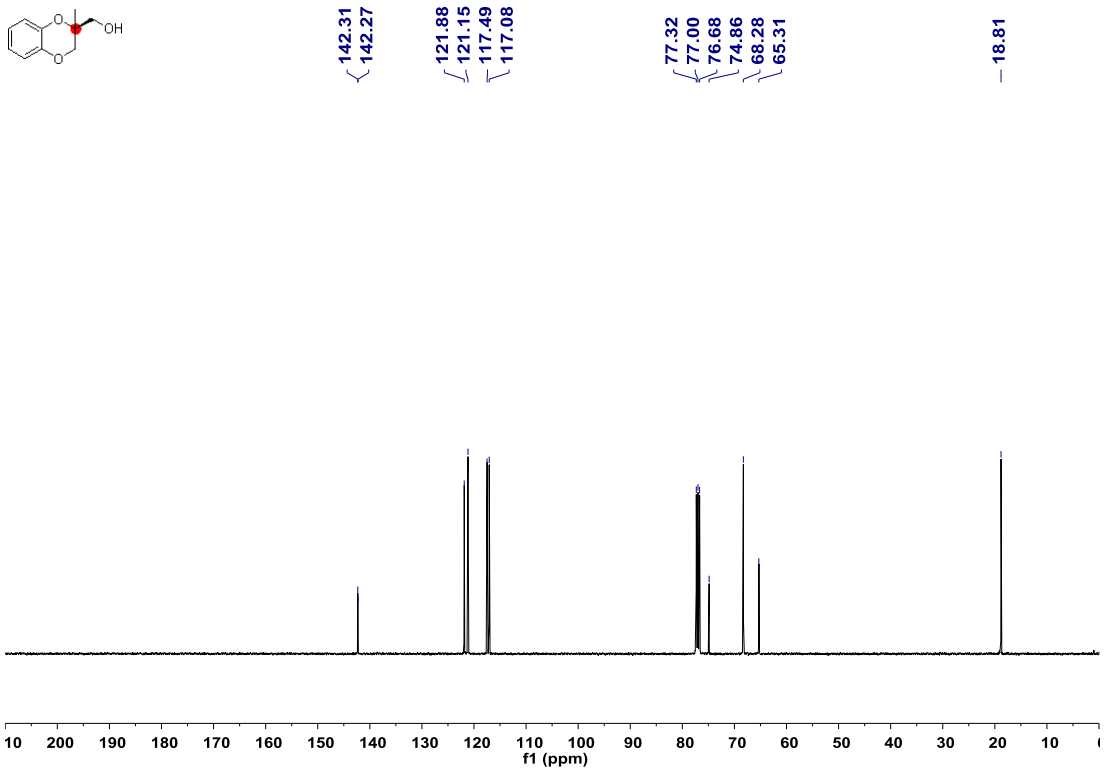
^{13}C NMR Spectrum of **2o**



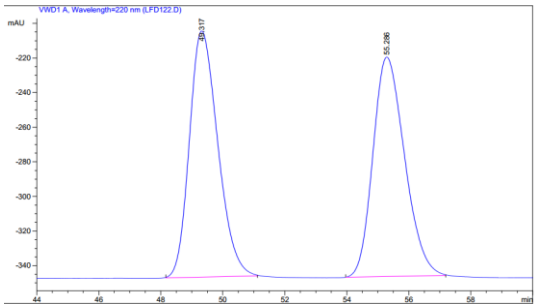
^{1}H NMR Spectrum of **2p**

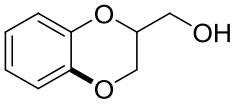


^{13}C NMR Spectrum of **2p**



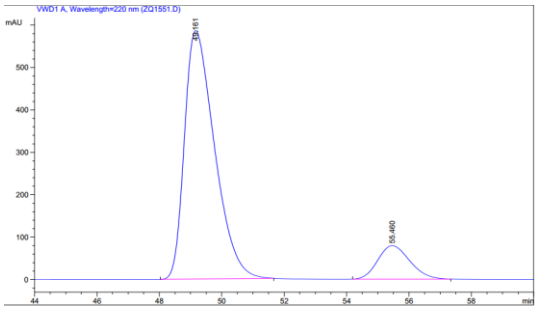
6. Copies of HPLC Chromatograms

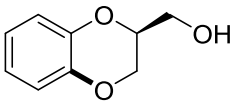




***rac*-2a**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.317	BB	0.9891	9062.58301	142.29808	50.1417
2	55.286	BB	1.1011	9011.37500	126.84747	49.8583





2a

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.161	BB	1.0187	3.91910e4	586.25153	87.3515
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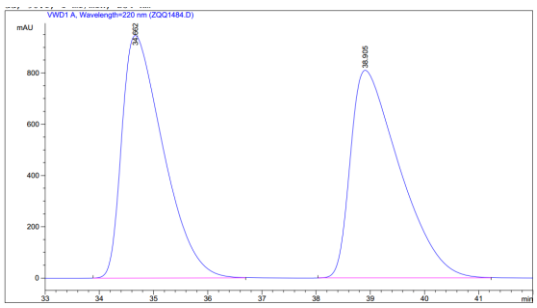
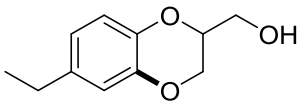
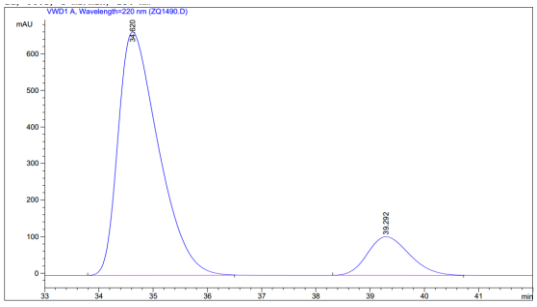
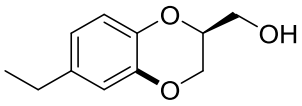




rac-2b

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.662	BB	0.8201	5.02205e4	946.29480	49.6296
2	38.905	BB	0.9495	5.09701e4	810.14673	50.3704





2b

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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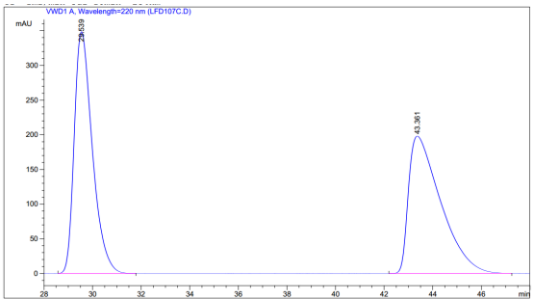
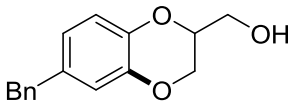
2	39.292	BB	0.8408	5729.85889	105.91169	14.3044





rac-2c

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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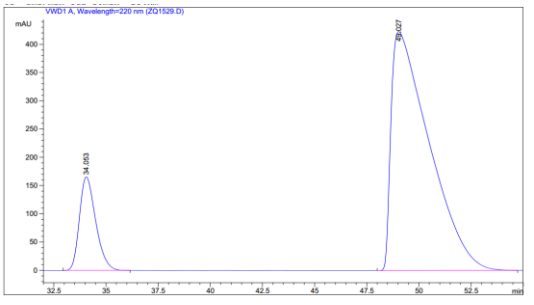
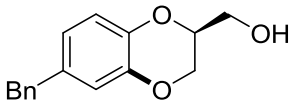
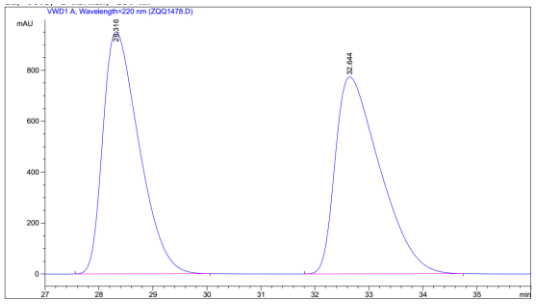
2	43.361	BB	1.3761	1.81817e4	198.17493	50.2365

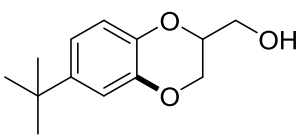




2c

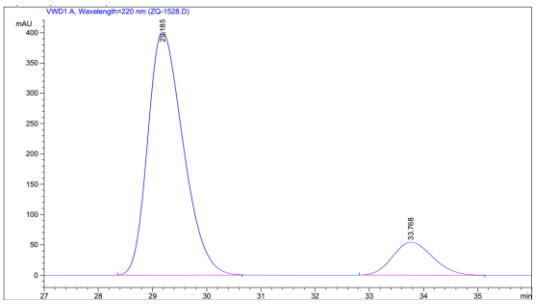
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.053	PB	0.8389	9029.60059	165.88405	14.4049
2	49.027	PB	1.8114	5.36547e4	423.12894	85.5951

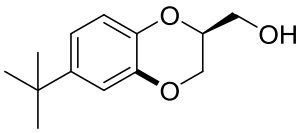




rac-2d

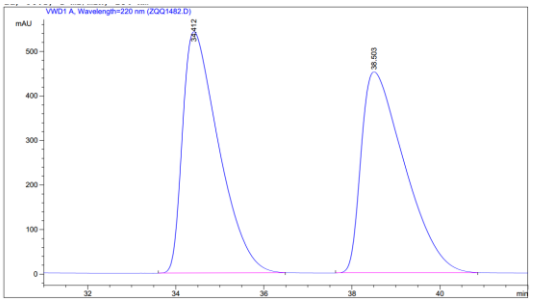
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.966	BP	0.5995	219.52844	5.67909	0.2470
2	28.316	BB	0.7103	4.41155e4	950.56213	49.6447
3	32.644	BB	0.8670	4.45274e4	773.15332	50.1082

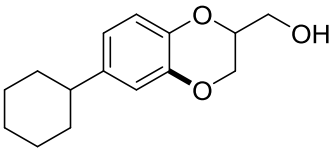




2d

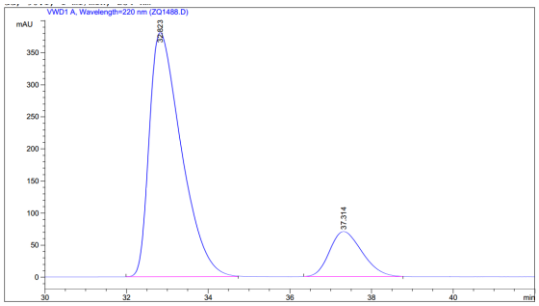
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.185	BB	0.7029	1.81671e4	401.26141	86.5405
2	33.768	BB	0.8071	2825.50024	54.64469	13.4595

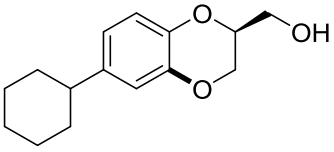




***rac*-2e**

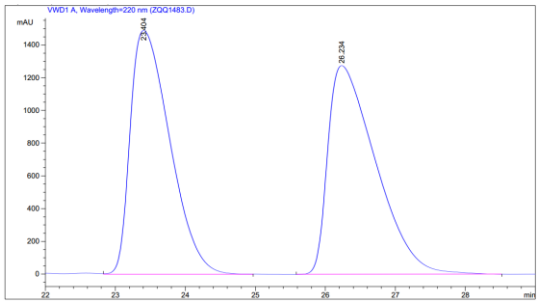
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.412	BB	0.8602	3.08973e4	541.99268	49.9484
2	38.503	BB	1.0239	3.09611e4	451.72406	50.0516

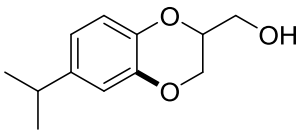




2e

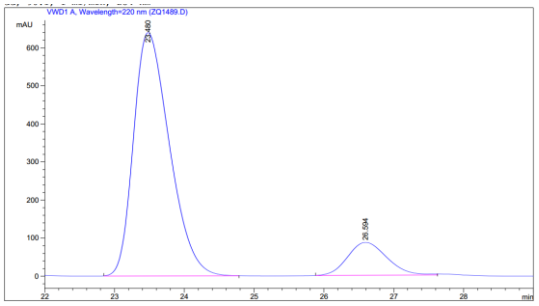
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.823	BB	0.8293	2.07000e4	380.81891	84.1565
2	37.314	BB	0.8644	3897.04272	70.38070	15.8435

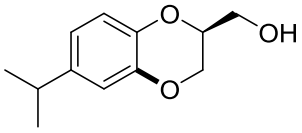




***rac*-2f**

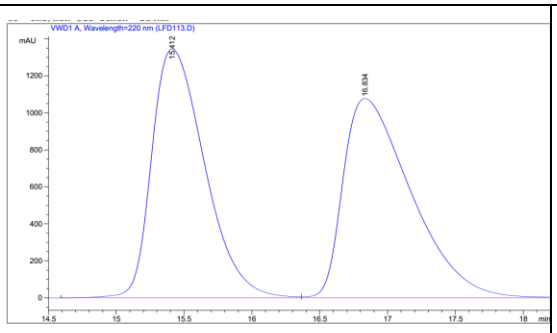
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.404	VB	0.6190	5.86070e4	1490.21375	49.1796
2	26.234	PB	0.7433	6.05624e4	1275.25403	50.8204

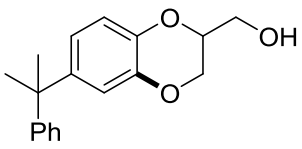




2f

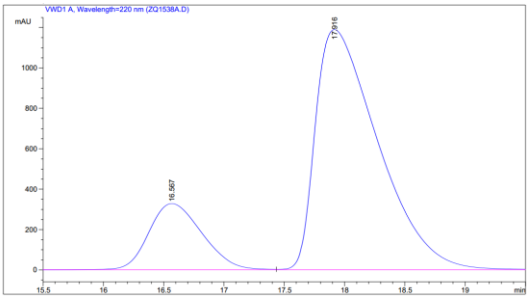
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.480	BB	0.5567	2.28448e4	639.29242	86.9951
2	26.594	BB	0.6100	3415.08008	86.87780	13.0049

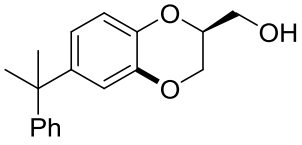




***rac*-2g**

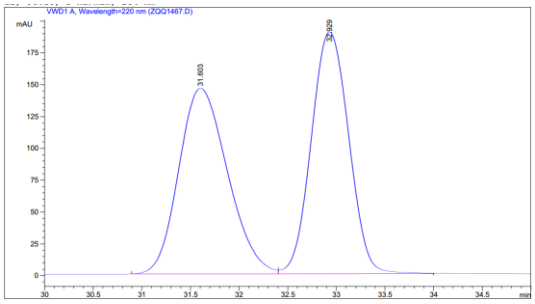
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.412	BV	0.4237	3.64289e4	1345.09607	49.2722
2	16.834	VB	0.5371	3.75051e4	1077.45691	50.7278

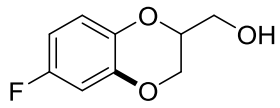




2g

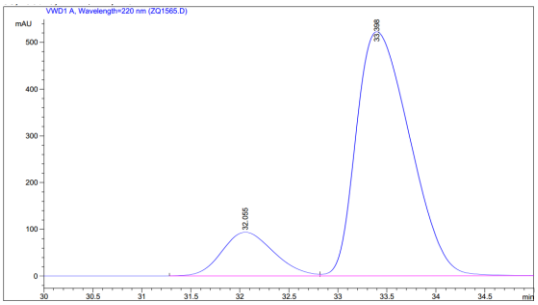
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.567	BV	0.4801	1.00634e4	328.17831	18.9482
2	17.916	VB	0.5563	4.30467e4	1189.18042	81.0518

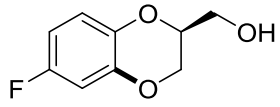




***rac*-2h**

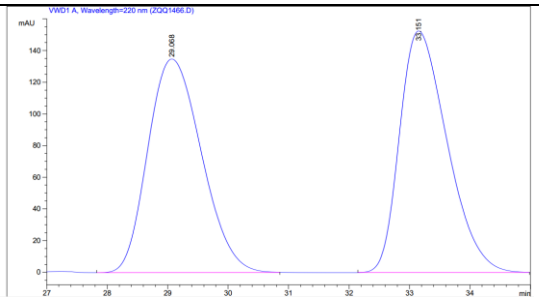
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	31.603	BV	0.5406	5086.57178	145.93790	49.9851
2	32.929	VB	0.4290	5089.60400	190.01862	50.0149

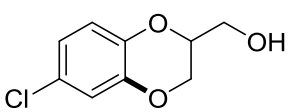




2h

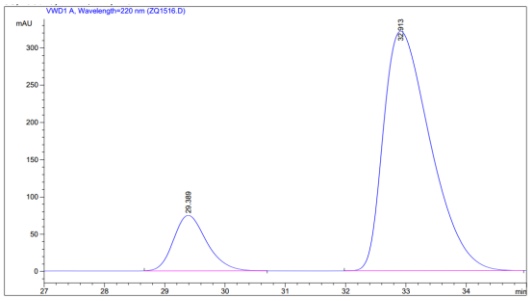
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.055	BV	0.5743	3434.88037	93.47498	14.7685
2	33.398	VB	0.6059	1.98232e4	522.20831	85.2315

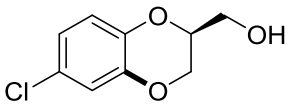




***rac*-2i**

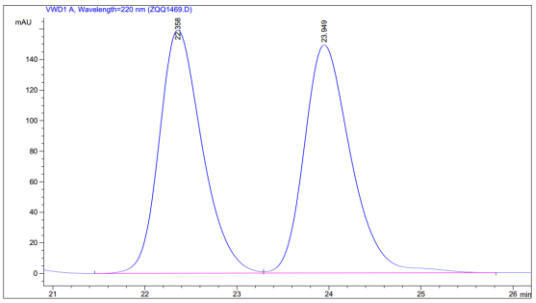
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.068	VB	0.9818	8323.45801	134.92177	49.9601
2	33.151	BBA	0.8529	8336.74316	152.59669	50.0399

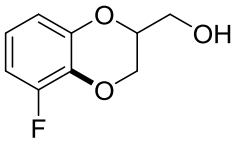




2i

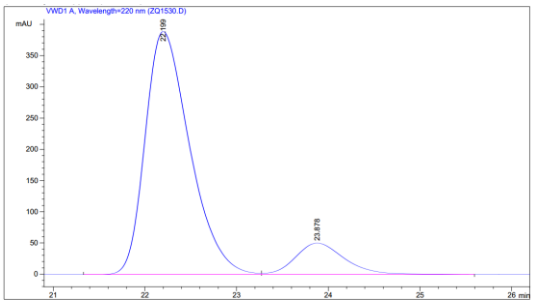
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.389	BB	0.5922	2853.76318	74.55695	14.1135
2	32.913	PB	0.8399	1.73664e4	321.47269	85.8865

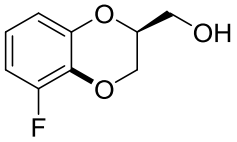




***rac*-2j**

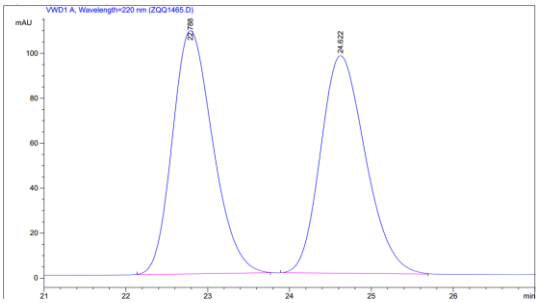
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.358	VV	0.4943	5154.86865	159.19618	49.5440
2	23.949	VP	0.5383	5249.75781	149.31653	50.4560

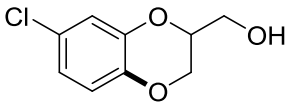




2j

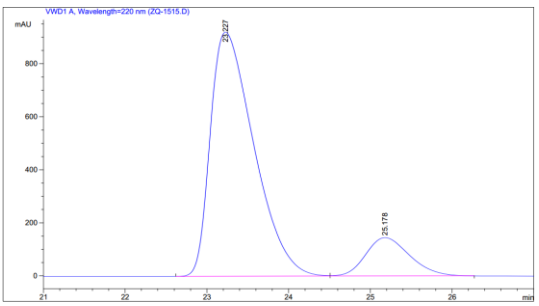
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.199	VV	0.5188	1.31299e4	389.17825	87.3602
2	23.878	VB	0.5680	1899.71753	50.38526	12.6398

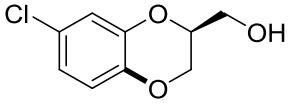




***rac*-2k**

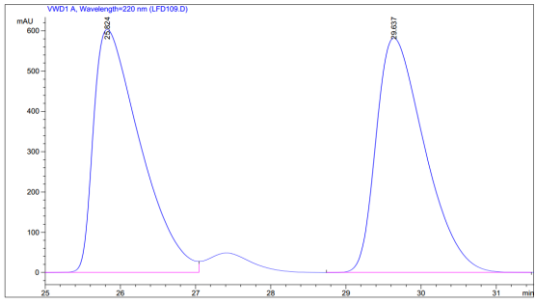
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.788	BB	0.5343	3714.28198	108.24658	50.1865
2	24.622	BB	0.5930	3686.67065	96.76699	49.8135

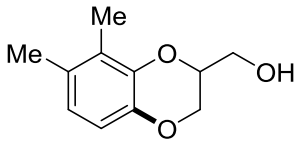




2k

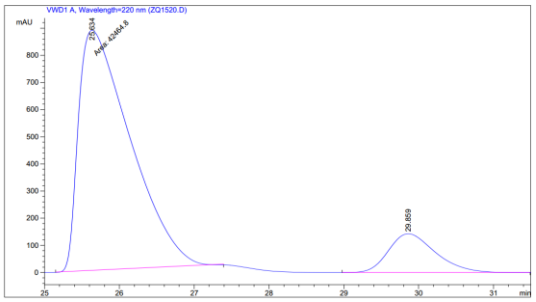
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.227	BV	0.5698	3.40664e4	921.16589	86.2458
2	25.178	VB	0.5795	5432.77051	145.09830	13.7542

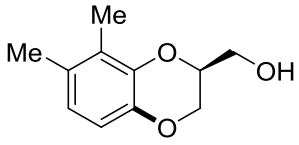




***rac*-2l**

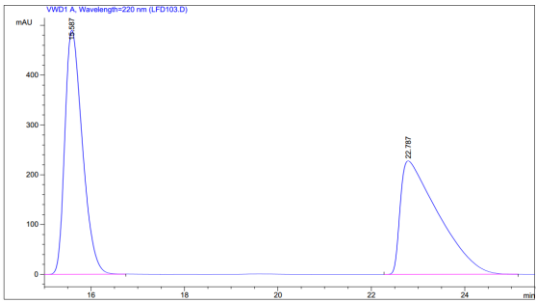
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.824	BV	0.6496	2.60682e4	603.39709	50.0029
2	29.637	VB	0.6912	2.60652e4	582.23541	49.9971

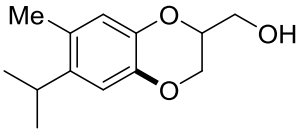




2l

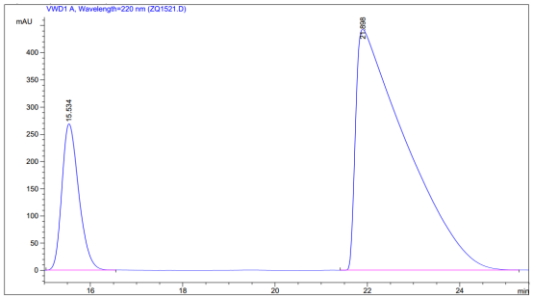
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.634	MM	0.8005	4.24648e4	884.18451	87.1894
2	29.859	BB	0.6660	6239.31201	143.06819	12.8106

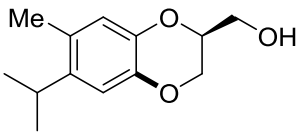




***rac*-2m**

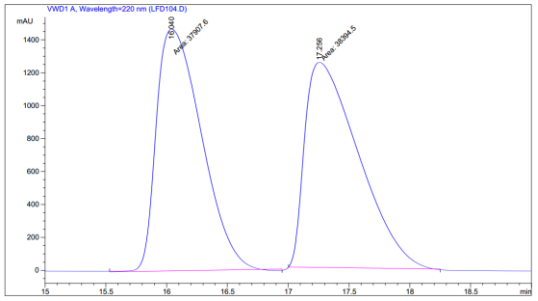
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.587	VB	0.4036	1.27999e4	490.28061	49.8321
2	22.787	BB	0.8080	1.28861e4	227.96786	50.1679

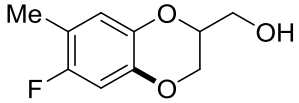




2m

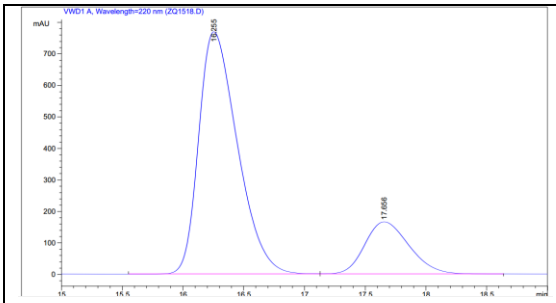
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.534	BB	0.3927	6843.04883	269.16504	16.8345
2	21.898	BB	1.0162	3.38060e4	442.65143	83.1655

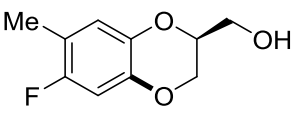




***rac*-2n**

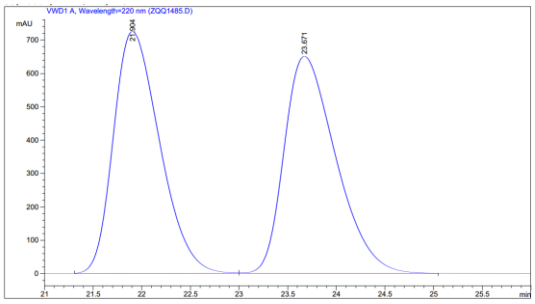
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.564	BV	0.2478	1050.81897	63.68043	49.9365
2	10.728	VB	0.2810	1053.48962	56.65486	50.0635

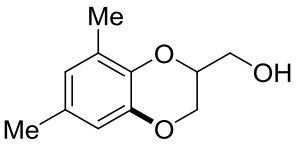




2n

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.255	VV	0.3425	1.70095e4	769.07831	80.1730
2	17.656	VB	0.3952	4206.48193	165.67117	19.8270





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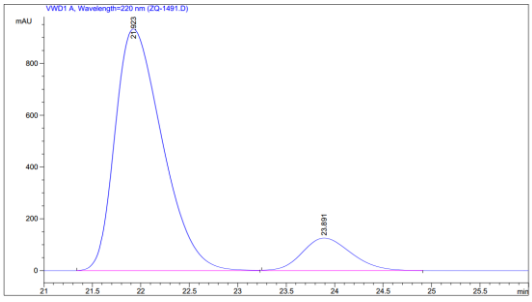
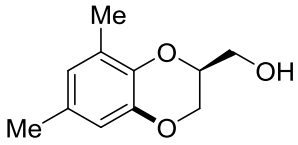
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.904	BV	0.5168	2.40088e4	726.03784	49.9346
2	23.671	VB	0.5710	2.40717e4	651.20508	50.0654





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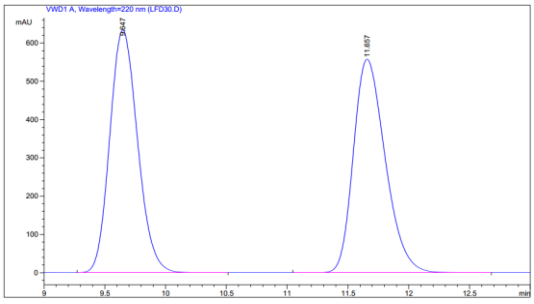
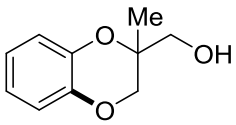
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.923	BB	0.5230	3.15917e4	933.45831	87.6752
2	23.891	BB	0.5485	4440.95020	125.87333	12.3248





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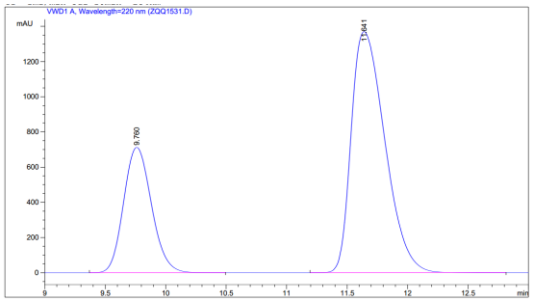
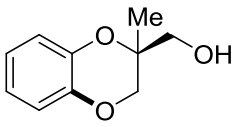
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.647	BB	0.2498	1.00899e4	633.84430	49.8829
2	11.657	BB	0.2850	1.01373e4	557.33240	50.1171





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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.760	PB	0.2508	1.13949e4	711.79749	30.0930
2	11.641	BB	0.3043	2.64708e4	1368.72083	69.9070