SUPPLEMENTAL INFORMATION

Electrochemical Ring-Opening 1,3-Dihydroxylation of Arylcyclopropanes with H2O

Jianhua Cai, Yuxi Wen, Wei Sheng, Xuejin Huang, Ye Zheng, Chunlan Song* and Jiakun Li*

College of Chemistry and Chemical Engineering, State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha, 410082, P. R. China

*E-mail: songcl@hnu.edu.cn

jkli@hnu.edu.cn

Contents

1. General information

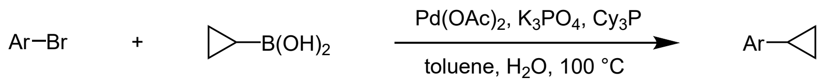
All glasswares were oven dried at 110 °C for several hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on precoated plates of Silica Gel HF254 (0.2 mm, Yantai, China). Flash chromatography columns were packed with 200 mesh silica gel in petroleum (bp. 60-90 °C) and eluted with petroleum ether/ethyl acetate. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (77.16 ppm for ^{13}C), DMSO-d_6 (2.50 ppm for ^{1}H, 39.50 ppm for ^{13}C), Methanol-d_4 (3.31 ppm for ^{1}H, 49.00 ppm for ^{13}C), and CD_3CN (1.94 ppm for ^{1}H, 118.26 ppm for ^{13}C), respectively. Data is reported as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), quartet (q), multiplet (m), and broad (br). High resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer and a Waters Micromass GCT instrument**.** Cyclic voltammograms were obtained on a Autolab PGSTAT 302N from Metrohm-Autolab (BV, Utrecht, Netherlands).

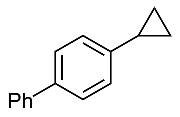
2. Preparation of starting materials

2.1 Synthesis of the cyclopropanes

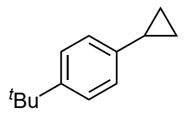
General procedure A: Suzuki coupling[1]

A three-neck (100 mL) flask equipped with a magnetic stir bar was charged with the aryl bromide (5.0 mmol, 1.0 equiv.), cyclopropylboronic acid (515.4 mg, 6.0 mmol, 1.2 equiv.), K_3PO_4 (3.18 g, 15.0 mmol, 3.0 equiv.), Cy_3P (140.2 mg, 0.5 mmol, 0.1 equiv.) and $Pd(OAc)_2$ (67.4 mg, 0.3 mmol, 0.06 equiv.). The reaction mixture was degassed via vacuum evacuation and backfilled with argon three times. Toluene (30.0 mL) and H_2O (1.0 mL) were added. The resultant mixture was heated at 100 °C until aryl halide was consumed (more than 10 h, detected by GC-MS). Next, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was diluted with ethyl acetate and H_2O. The phases were separated, and the aqueous phase was extracted with ethyl acetate, and then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the crude product purified by chromatography on silica gel.

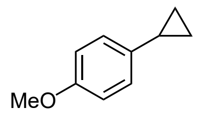




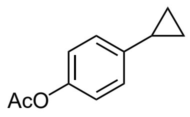
5a



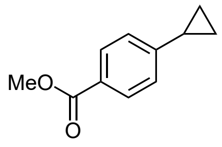
6a



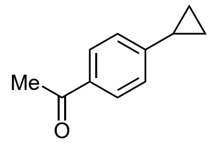
7a



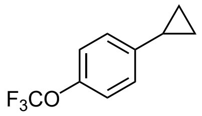
8a



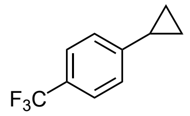
9a



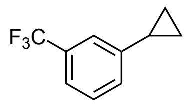
10a



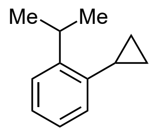
11a



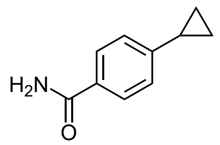
12a



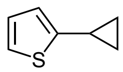
13a



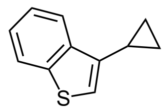
14a



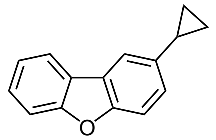
16a



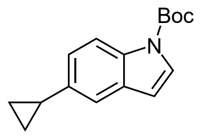
17a



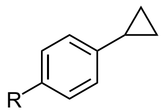
18a



19a



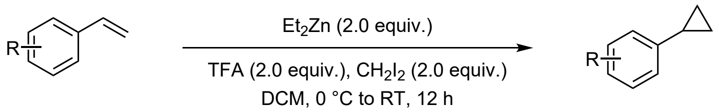
20a

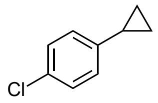


21a, R=OTf
22a, R=OTs

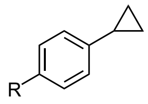
General procedure B: Simmons-Smith cyclopropanation[2]

An oven-dried round bottom flask equipped with a magnetic stir bar was added 15 mL anhydrous CH_2Cl_2 under Ar atmosphere. The solution was cooled to 0 °C in an ice bath and 10.0 mL Et_2Zn (10.0 mmol, 2.0 equiv., 1.0 M in hexanes) was added. Then a solution of trifluoroacetic acid (0.77 mL, 10.0 mmol, 2.0 equiv.) in 5 mL DCM was dripped very slowly into the reaction mixture via syringe. Upon stirring for 20 min, a solution of CH_2I_2 (0.81 mL, 10.0 mmol, 2.0 equiv.) in 5 mL DCM was added. After an additional 20 min of stirring, a solution of the respective styrene derivative (5.0 mmol, 1.0 equiv.) in 5 mL DCM was added, and the ice bath was removed. After starting styrene derivative was consumed (more than 12 h, detected by GC-MS), the reaction mixture was quenched with 1M HCl (10 mL) and the phases were separated. The aqueous layer was extracted with DCM. The combined organic layers were washed with saturated $NaHCO_3$, and brine and then dried with Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography to give the corresponding compound.

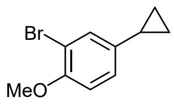




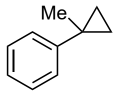
1a



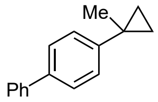
3a, R = F
4a, R = Br



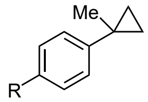
15a



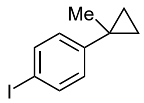
23a



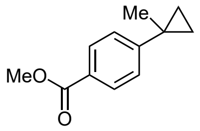
24a



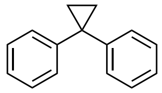
25a, R = F
26a, R = Cl
27a, R = Br



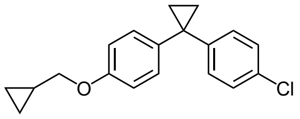
28a



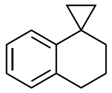
29a



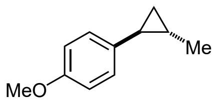
30a



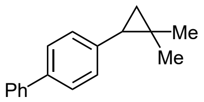
31a



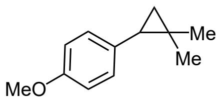
32a



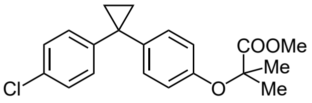
33a



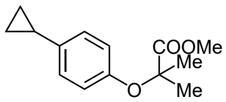
34a



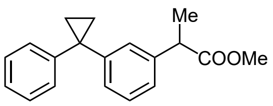
35a



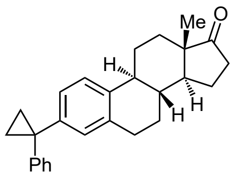
36a



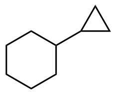
37a



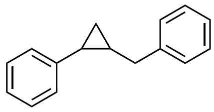
38a



44a



46a



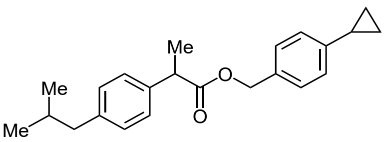
48a

General procedure C: synthesis of ester[3]

$$R^1COOH + R^2OH \xrightarrow[CH_2Cl_2,\ RT]{DCC,\ DMAP} R^1COOR^2$$

To a stirred solution of acid R^1COOH (1.0 equiv.) and *N, N'*-dicyclohexylcarbodiimide (DCC, 2.0 equiv.) in DCM (0.2 M) were added 4-(*N, N*-dimethylamino)pyridine (DMAP, 0.15 equiv.) and alcohol R^2OH (1.0 equiv.). The reaction mixture was stirred at room temperature for 24 h. After filtration, the filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to afford the desired products.

Ibuprofen derivative (39a)



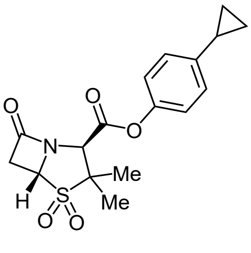
Reaction was performed in 1.0 mmol according general procedure C, affording substrate **39a** (222 mg, 0.66 mmol, 66%) as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.08 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.09 (q, *J* = 12.4 Hz, 2H), 3.81 – 3.71 (m, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 2.00 – 1.80 (m, 2H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.03 – 0.89 (m, 8H), 0.74 – 0.67 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 144.1, 140.6, 137.8, 133.2, 129.4, 128.1, 127.4, 125.8, 66.4, 45.3, 45.2, 30.3, 22.5, 18.6, 15.3, 9.4 ppm.

HRMS (ESI) calculated for $C_{23}H_{28}O_2$ $[M+Na]^+$, 359.1982; found, 359.1975.

Sulbactam derivative (40a)



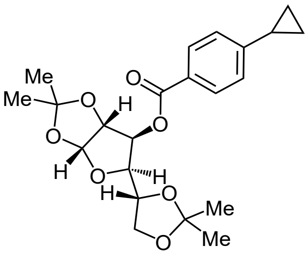
Reaction was performed in 1.5 mmol according general procedure C, affording substrate **40a** (351 mg, 1.0 mmol, 67%) as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.67 (dd, *J* = 3.6, 2.4 Hz, 1H), 4.61 (s, 1H), 3.56 – 3.43 (m, 2H), 1.96 – 1.86 (m, 1H), 1.71 (s, 3H), 1.57 (s, 3H), 1.01 – 0.94 (m, 2H), 0.71 – 0.64 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 165.8, 147.6, 142.9, 127.0, 120.8, 63.4, 63.0, 61.3, 38.6, 20.6, 18.9, 15.1, 9.5 ppm.

HRMS (ESI) calculated for $C_{17}H_{19}NO_5S$ $[M+Na]^+$, 327.0876; found,372.0876.

Diacetone-D-glucose derivative (41a)



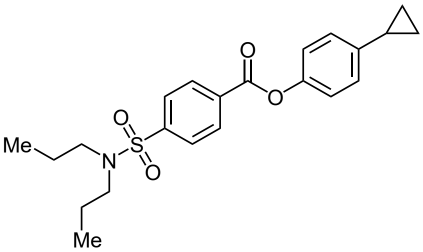
Reaction was performed in 3.0 mmol according general procedure C, affording substrate **41a** (795 mg, 1.97 mmol, 66%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 5.94 (d, J = 3.6 Hz, 1H), 5.48 (d, J = 2.0 Hz, 1H), 4.61 (d, J = 3.6 Hz, 1H), 4.40 – 4.31 (m, 2H), 4.16 – 4.04 (m, 2H), 2.00 - 1.89 (m, 1H), 1.55 (s, 3H), 1.41 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.13 – 1.00 (m, 2H), 0.81 – 0.73 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 150.9, 129.9, 126.6, 125.6, 112.5, 109.5, 105.3, 83.6, 80.1, 76.5, 72.8, 67.3, 27.0, 26.9, 26.4, 25.4, 15.9, 10.6, 10.6 ppm.

HRMS (ESI) calculated for $C_{22}H_{28}O_7$ $[M+Na]^+$, 427.1727; found, 427.1722.

Probenecid derivative (42a)



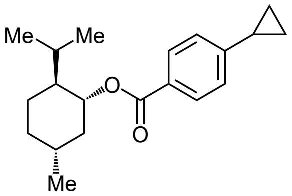
Reaction was performed in 1.27 mmol according general procedure C, affording substrate **42a** (409 mg, 1.02 mmol, 80%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.07 – 7.05 (br, 4H), 3.21 – 3.05 (m, 4H), 2.02 – 1.85 (m, 1H), 1.63 - 1.49 (m, 4H), 1.03 – 0.94 (m, 2H), 0.88 (t, J = 7.4 Hz, 6H), 0.70 (q, J = 5.3 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 148.4, 144.9, 142.1, 133.0, 130.8, 127.2, 126.9, 121.2, 50.0, 22.0, 15.1, 11.3, 9.3 ppm.

HRMS (ESI) calculated for $C_{22}H_{27}NO_4S$ [M+H]$^+$, 402.1734; found,402.1728.

DL-Menthol derivative (43a)



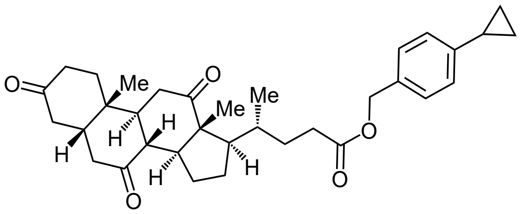
Reaction was performed in 1.85 mmol according general procedure C, affording substrate **43a** (200 mg, 0.67 mmol, 36%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 4.90 (td, *J* = 10.9, 4.4 Hz, 1H), 2.16 – 2.07 (m, 1H), 2.00 – 1.88 (m, 2H), 1.76 – 1.68(m, 2H), 1.59 – 1.48(m, 2H), 1.17 – 0.98 (m, 4H), 0.96 – 0.87 (m, 7H), 0.81 – 0.72 (m, 5H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 149.8, 129.8, 128.1, 125.4, 74.7, 47.4, 41.2, 34.5, 31.6, 26.6, 23.8, 22.2, 20.9, 16.7, 15.8, 10.3 ppm.

HRMS (ESI) calculated for $C_{20}H_{28}O_2$ [M+Na]$^+$, 323.1982; found, 323.1978.

Dehydrocholic acid derivative (45a)



Reaction was performed in 3.0 mmol according general procedure C, affording substrate **45a** (1.55 g, 2.91 mmol, 97%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 5.05 (q, *J* = 12.1 Hz, 2H), 2.97 – 2.75 (m, 3H), 2.45 – 2.18 (m, 9H), 2.16 – 2.09 (m, 2H), 2.05 – 1.91 (m, 5H), 1.91 – 1.77 (m, 3H),1.69 –1.54 (m, 2H)1.39 (s, 3H), 1.02 (s, 3H), 0.99 – 0.91 (m, 2H), 0.82 (d, *J* = 6.5 Hz, 3H), 0.73 – 0.59 (m, 2H) ppm.

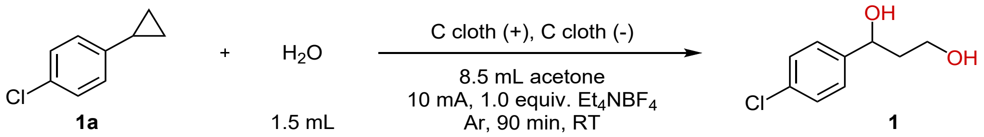
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.0, 209.1, 208.8, 174.0, 144.3, 133.2, 128.6, 125.9, 66.1, 57.0, 51.9, 49.1, 47.0, 45.8, 45.6, 45.1, 42.9, 38.7, 36.6, 36.1, 35.6, 35.4, 31.7, 30.6, 27.7, 25.3, 22.0, 18.7, 15.3, 11.9, 9.4 ppm.

HRMS (ESI) calculated for $C_{34}H_{44}O_5$ [M+Na]$^+$, 555.3081; found, 555.3081.

3. Investigation of the reaction conditions

Table 1. Reaction optimization for 1,3-dihydroxylation

After systematic examination of all the reaction parameters, it was found that diol (**1**) could be obtained in 75% isolated yield under 10 mA constant current in a simple undivided cell with carbon cloths as electrodes (Table 1, entry 1). Notably, carbon material was shown to be necessary (Table 1, entries 2-5). Among the solvent we have screened, CH_3COCH_3 was proven to be better than CH_3CN, CH_3NO_2 and DMSO (Table 1, entries 6-8). In addition, water soluble inorganic salts can also be used as electrolytes with moderate yields, such as Na_2SO_4 and $KHCO_3$ (Table 1, entries 9 and 10). Adjusting the current to 5 mA or 12 mA led to lower yields (Table 1, entries 11 and 12). The amount of H_2O has no obvious effect on the reaction (Table 1, entries 13 and 14). Finally, control experiment indicated the indispensable role of electric current (Table 1, entry 15).

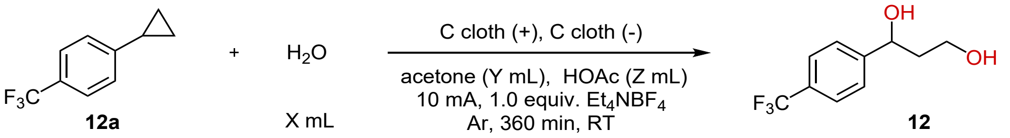


Entry	Variation from Standard Conditions[a]	Yield of **1** (%)
1	Standard conditions	78 (75[b])
2	C cloth (+), Cu (-)	69
3	C cloth (+), Pt (-)	78
4	C rode (+), Pt (-)	63
5	Pt (+), Pt (-)	trace
6	CH_3CN as the solvent	53
7	CH_3NO_2 as the solvent	30
8	DMSO as the solvent	trace
9	Na_2SO_4 as the electrolyte	39
10	$KHCO_3$ as the electrolyte	50
11	5 mA, 180 min	46
12	12 mA, 75 min	38
13	0.5 mL H_2O	75
14	1.0 mL H_2O	69

15	Without electric current, under air	n.r.

[a]Standard conditions: carbon cloth anode, carbon cloth cathode (15 mm x 15 mm x 0.3 mm), constant current = 10 mA, **1a** (0.2 mmol), Et_4NBF_4 (0.2 mmol), 1.5 mL H_2O, 8.5 mL acetone, RT, undivided cell under Ar. Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [b]Isolated yield was shown.

Table 2. Reaction optimization for electron-deficient arylcyclopropane



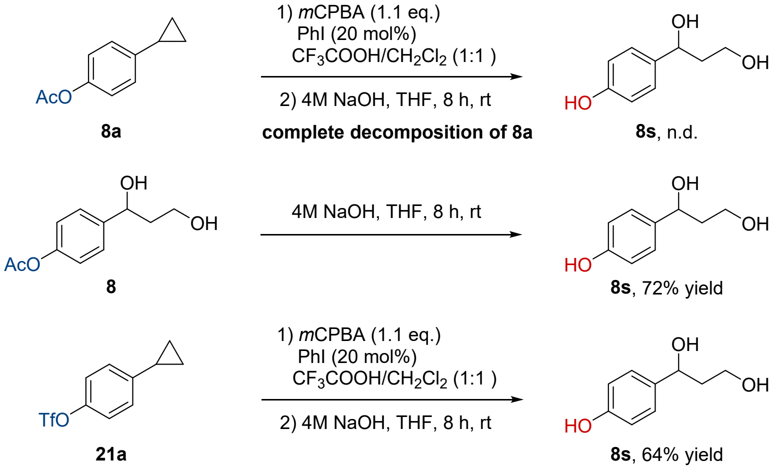
Conditions	H_2O (X mL)	Acetone (Y mL)	HOAc (Z mL)	Yield of **12** (%)
A	0.8	9.0	0.2	71
B	1.5	8.5	0.2	63
C (general conditions)	1.5	8.5	0.0	42

The controlled reaction demonstrated the significance of acetic acid in enhancing the yields of electron-deficient arylcyclopropanes, even with minimal variations in the amount of water or acetone present in the reaction system.

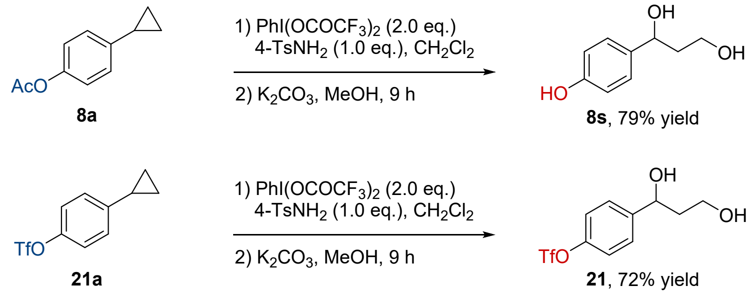
Table 3. A comparison of our method with previous methods

We have evaluated the reaction conditions for compounds **8a**, **21a**, which involve a hydrolysis step, and the results show that such substrates are not well tolerated in the ref 8 and 9.

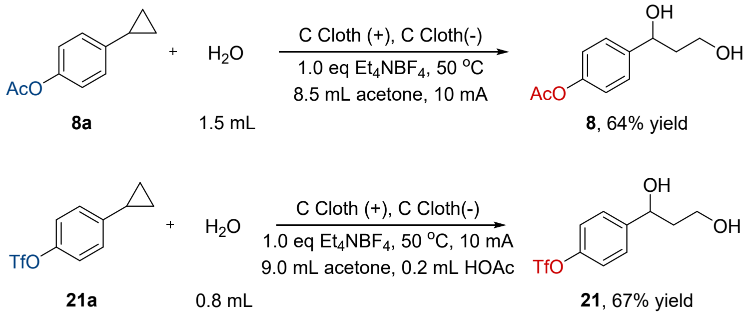
Ref. 8 method for substrates containing ester group:



Ref. 9 method for substrates containing ester group:



Our method for substrates containing ester group:



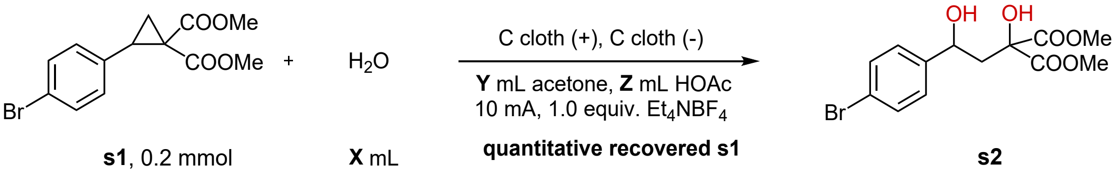
NMR Spectroscopy

^{1}H NMR of 8s (400 MHz, Methanol-d_4) δ 7.22 – 7.17 (m, 2H), 6.77 (d, J = 8.5 Hz, 2H), 4.73 (dd, J = 8.1, 5.5 Hz, 1H), 3.73 – 3.53 (m, 2H), 2.05 – 1.94 (m, 1H), 1.91 – 1.81 (m, 1H) ppm.

Table 4. Reaction of substrate scope to “push-pull”-substituted cyclopropanes

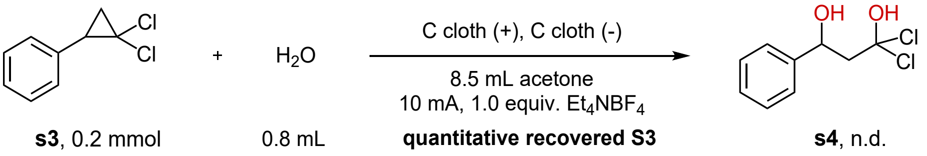
we have conducted experiments using two “push-pull” type cyclopropanes under our standard conditions as well as modified reaction conditions. However, neither of these substrates yielded 1,3-diols or β-hydroxy ketones. Instead, there was complete recovery of the starting material. Therefore, we must acknowledge that our method is not applicable for “push-pull” substituted cyclopropanes.

Substrate 1:



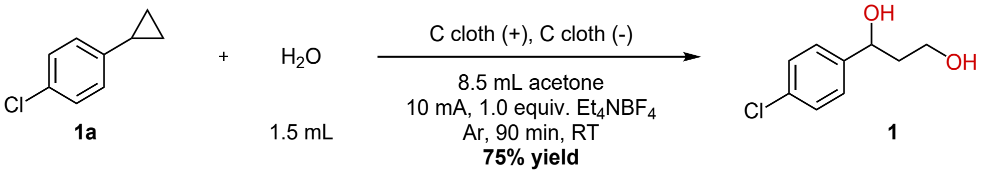
Conditions	X	Y	Z	Temp.	Yield of **s2**
A	1.5	8.5	0.0	rt	n.d.
B	1.5	8.5	0.0	50 °C	n.d.
C	0.8	9.0	0.2	50 °C	n.d.

Substrate 2:



4. Scope of the electrochemical ring-opening 1,3-dihydroxylation

1-(4-Chlorophenyl)propane-1,3-diol (1)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-chloro-4-cyclopropylbenzene **1a** (30.5 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml

H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **1** (27.9 mg, 0.149 mmol, 75%) as a pale-yellow solid. The spectra of **1** corresponded to the data reported previously.[1]

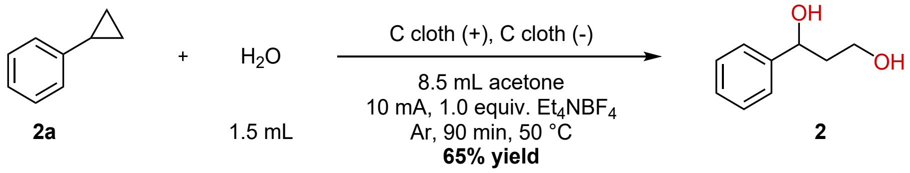
R$_f$ = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

NMR Spectroscopy:

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.28 (m, 4H), 5.29 (d, *J* = 4.4 Hz, 1H), 4.70 – 4.61 (m, 1H), 4.58 – 4.48 (m, 1H), 3.48 – 3.33 (m, 2H), 1.80 – 1.60 (m, 2H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.2, 130.9, 127.8, 127.5, 68.8, 57.7, 42.1 ppm.

1- Phenylpropane-1,3-diol (2)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, cyclopropylbenzene **2a** (23.6 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **2** (19.9 mg, 0.132 mmol, 65%) as a white solid. The spectra of **2** corresponded to the data reported previously.[1]

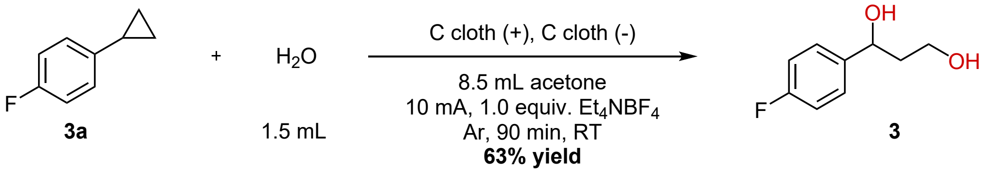
R$_f$ = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3CN) δ 7.43 – 7.30 (m, 4H), 7.29 – 7.22 (m, 1H), 4.84 – 4.73 (m, 1H), 3.73 – 3.56 (m, 3H), 2.96 (s, 1H), 1.90 – 1.74 (m, 2H) ppm.

^{13}C NMR (101 MHz, CD_3CN) δ 146.7, 129.1, 127.9, 126.6, 72.6, 60.4, 42.5 ppm.

1-(4-Fluorophenyl)propane-1,3-diol (3)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-cyclopropyl-4-fluorobenzene **3a** (27.2 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **3** (21.5 mg, 0.126 mmol, 63%) as pale-yellow oil. The spectra of **3** corresponded to the data reported previously.[1]

R_f = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

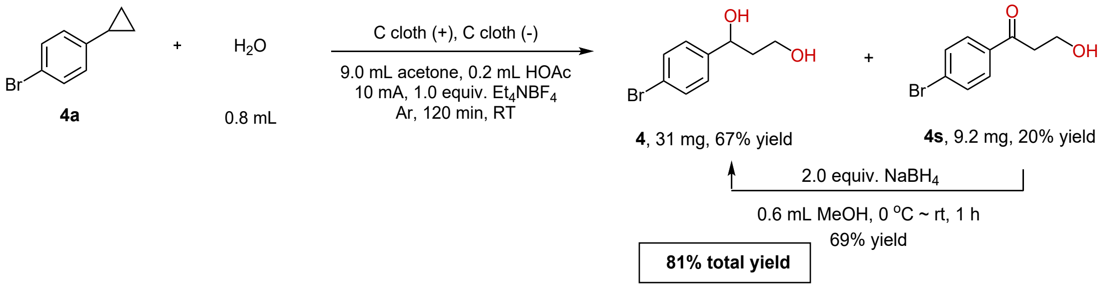
NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 7.09 – 6.97 (m, 2H), 4.93 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.91 – 3.77 (m, 2H), 3.52 – 2.43 (br, 2H), 2.03 – 1.84 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.2 Hz), 140.2 (d, *J* = 3.1 Hz), 127.4 (d, *J* = 8.1 Hz), 115.4 (d, *J* = 21.4 Hz), 73.8, 61.5, 40.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.10 – -115.18 (m) ppm.

1-(4-Bromophenyl)propane-1,3-diol (4)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via

vacuum evacuation and backfilled with argon three times. Subsequently, 1-bromo-4-cyclopropylbenzene **4a** (39.4 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 120 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **4** (31.0 mg, 0.134 mmol, 67%) as pale-yellow oil. The spectra of **4** corresponded to the data reported previously.[1]

R_f = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

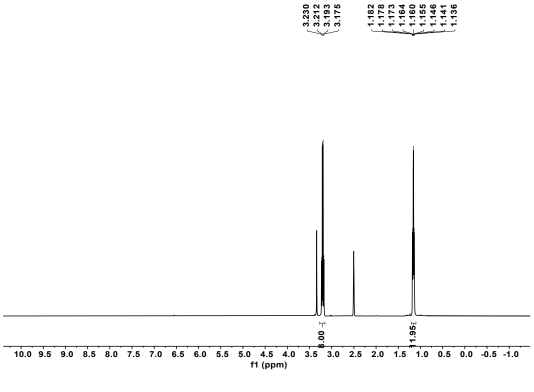
NMR Spectroscopy:

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.79 (dd, *J* = 8.4, 5.2 Hz, 1H), 3.76 – 3.64 (m, 1H), 3.64 – 3.54 (m, 1H), 2.00 – 1.78 (m, 2H) ppm.

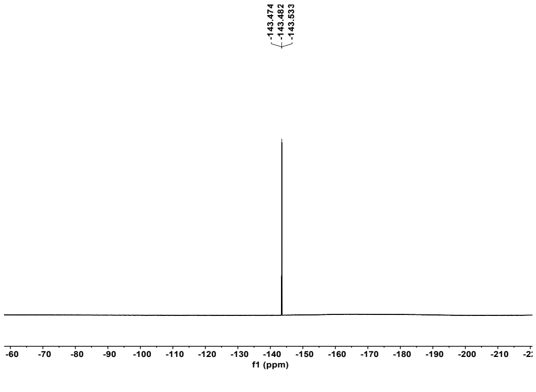
^{13}C NMR (101 MHz, Methanol-d_4) δ 145.9, 132.4, 128.9, 121.7, 71.6, 60.0, 42.7 ppm.

In addition, over-oxidation side product β-Hydroxy ketone **4s** was isolated in 20% yield, which could be further reduced to diol **4** (6.4 mg, 0.027 mmol) with 69% yield.[2] We can get a higher yield (81%) of the target product by two steps. Therefore, the reaction efficiency could be enhanced in this scenario by implementing an additional transformation. We are also pleased that the recovery of the electrolyte was successful, even in such a small-scale reaction. After extracting the aqueous solution, we were able to recycle 71% of the Et_4NBF_4 (31 mg, 0.142 mmol). This outcome provides further evidence of the practicality and feasibility of our method.

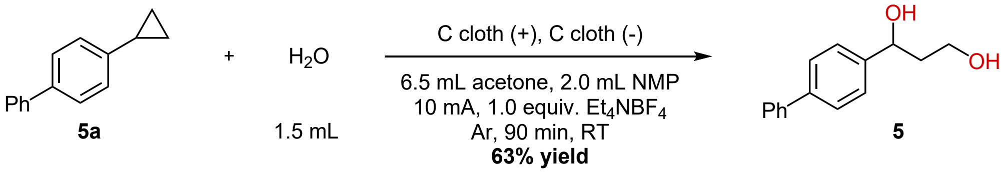
^{1}H NMR of recovered Et_4NBF_4



^{19}F NMR of recovered Et_4NBF_4



1-([1,1'-Biphenyl]-4-yl)propane-1,3-diol (5)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) and 4-cyclopropyl-1,1-biphenyl **5a** (38.9 mg, 0.20 mmol, 1.0 equiv.) were added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 6.5 Ml acetone, 1.5 Ml H_2O and 2.0 Ml NMP were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated by vacuo and then dissolve the crude product with dichloromethane and washed with saturated NH_4Cl aqueous (5 Ml × 3). The organic layers were dried over anhydrous Na_2SO_4, concentrated by vacuo. The crude product purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **5** (28.6 mg, 0.125 mmol, 63%) as a white solid.

R_f = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

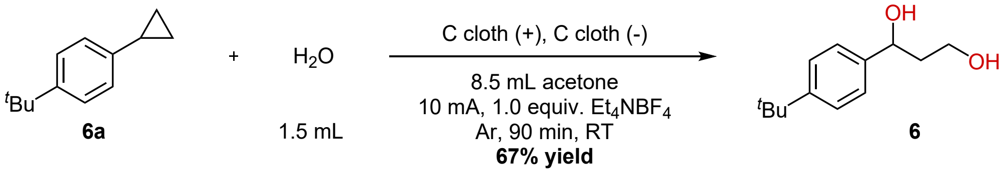
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.49 – 7.40 (m, 4H), 7.39 – 7.31 (m, 1H), 5.01 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.01 – 3.77 (m, 2H), 2.65 (br, 2H), 2.11 – 1.93 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 140.9, 140.6, 128.9, 127.4, 127.4, 127.2, 126.3, 74.2, 61.6, 40.5 ppm.

HRMS GC-EI (m/z) calculated for $C_{15}H_{16}O_2$ $[M]^+$, 228.1145; found, 228.1149.

1-(4-(tert-Butyl)phenyl)propane-1,3-diol (6)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-(tert-butyl)-4-cyclopropylbenzene **6a** (34.9 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **6** (28.0 mg, 0.134 mmol, 67%) as a pale-yellow solid. The spectra of **6** corresponded to the data reported previously.[1]

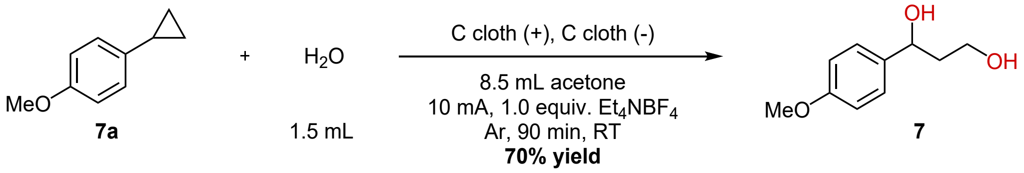
R_f = 0.40 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 4.95 – 4.88 (m, 1H), 3.87 – 3.79 (m, 2H), 2.81 – 2.71 (br, 1H), 2.70 – 2.61 (br, 1H), 2.09 – 1.86 (m, 2H), 1.32 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 141.4, 125.5, 125.5, 74.1, 61.5, 40.5, 34.6, 31.5 ppm.

1-(4-Methoxyphenyl)propane-1,3-diol (7)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-cyclopropyl-4-methoxybenzene **7a** (29.6 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **7** (25.5 mg, 0.140 mmol, 70%) as a white solid. The spectra of **7** corresponded to the data reported previously.[5]

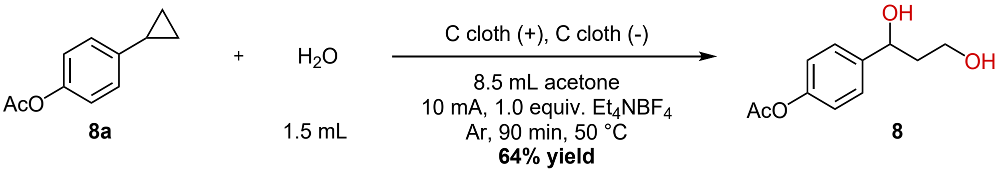
R*f* = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.74 (dd, *J* = 8.0, 5.6 Hz, 1H), 3.77 (s, 3H), 3.70 – 3.53 (m, 2H), 2.04 – 1.92 (m, 1H), 1.90 – 1.78 (m, 1H) ppm.

^{13}C NMR (101 MHz, Methanol-*d*$_4$) δ 160.4, 138.3, 128.2, 114.7, 72.0, 60.2, 55.7, 42.7 ppm.

1-(4-Acetyloxyphenyl)propane-1,3-diol (8)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 4-cyclopropylphenyl acetate **8a** (35.2 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **8** (26.8 mg, 0.127 mmol, 64%) as a white solid.

R*f* = 0.20 (petroleum ether/ethyl acetate 1 :1, v/v).

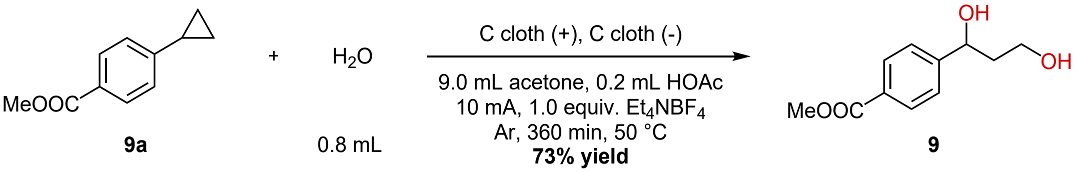
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 7.08 – 7.01 (m, 2H), 4.92 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.88 – 3.74 (m, 2H), 2.75 (br, 2H), 2.29 (s, 3H), 2.02 – 1.83 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 150.0, 142.2, 126.9, 121.7, 73.8, 61.4, 40.5, 21.2 ppm.

HRMS (ESI) calculated for $C_{11}H_{14}O_4$, $[M+Na]^+$, 233.0784; found, 233.0778.

1-(4-Carbomethoxyphenyl)propane-1,3-diol (9)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 4-cyclopropylbenzoate **9a** (35.2 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 360 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **9** (30.5 mg, 0.145 mmol, 73%) as a pale-yellow solid. The spectra of **9** corresponded to the data reported previously.[6]

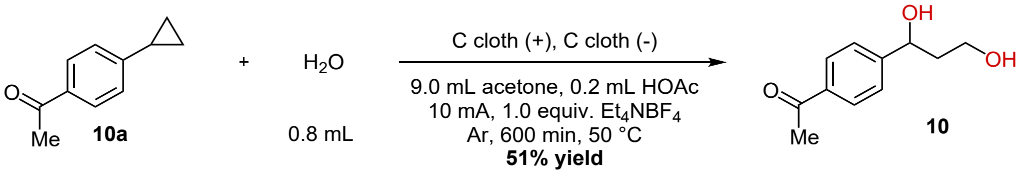
R_f = 0.30 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 4.98 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.89 (s, 3H), 3.85 – 3.77 (m, 2H), 2.00 – 1.84 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 149.7, 129.9, 129.3, 125.7, 73.7, 61.2, 52.2, 40.4 ppm.

1-(4-Acetylphenyl)propane-1,3-diol (10)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4

(43.4 mg, 0.20 mmol, 1.0 equiv.) and 1-(4-cyclopropylphenyl)e than-1-one **10a** (32.0 mg, 0.20 mmol, 1.0 equiv.) were added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 600 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **10** (19.8 mg, 0.102 mmol, 51%) as a white solid.

R$_f$ = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

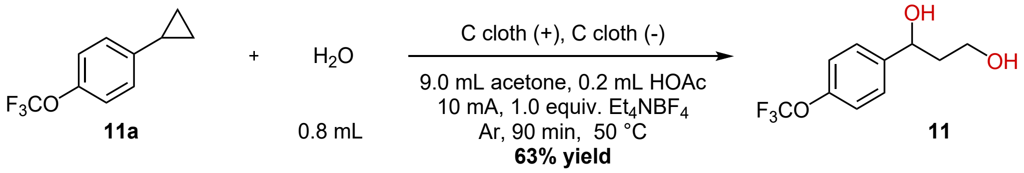
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 5.06 – 4.99 (m, 1H), 3.87 (t, *J* = 5.2 Hz, 2H), 3.49 (br, 1H), 2.59 (s, 3H), 2.01 – 1.92 (m, 2H), 1.80 (br, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 149.9, 136.4, 128.7, 125.9, 73.8, 61.4, 40.4, 26.8 ppm.

HRMS (ESI) calculated for $C_{11}H_{14}O_3$ $[M+Na]^+$, 217.0835; found, 217.0829.

1-(4-Trifluoromethoxyphenyl)propane-1,3-diol (11)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-cyclopropyl-4-(trifluoromethoxy)benzene **11a** (40.4 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **11** (29.7 mg, 0.126

mmol, 63%) as pale-yellow oil. The spectra of **11** corresponded to the data reported previously.[7]

R$_f$ = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

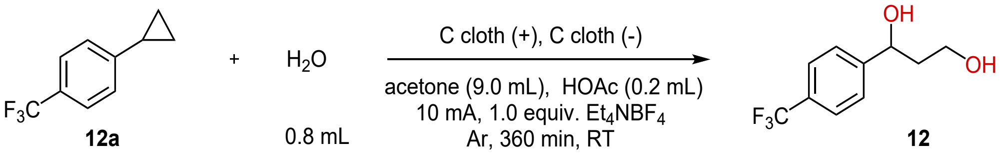
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.97 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.92 – 3.80 (m, 2H), 3.26 (br, 1H), 2.31 (br, 1H), 2.03 – 1.88 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 143.1, 127.2 ,121.13, 120.6 (q, *J* =257.8 Hz), 73.7, 61.5, 40.5 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.90 ppm.

1-(4-Trifluoromethylphenyl)propane-1,3-diol (12)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-cyclopropyl-3-(trifluoromethyl)benzene **12a** (37.2 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 360 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **12** (31.4 mg, 0.143 mmol, 71%) as pale-yellow oil. The spectra of **12** corresponded to the data reported previously.[1]

R$_f$ = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

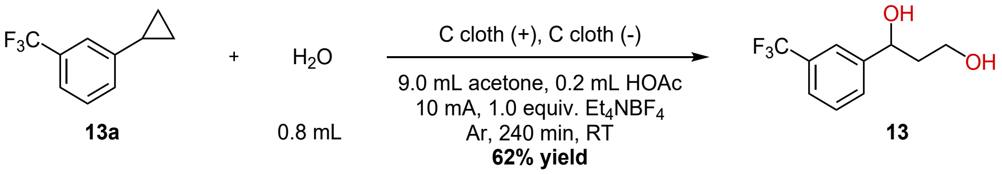
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 5.08 – 4.93 (m, 1H), 3.97 – 3.79 (m, 2H), 3.60 (br, 1H), 2.68 (br, 1H), 1.96 – 1.89 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 129.8 (q, *J* = 32.4 Hz), 126.03, 125.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.9 Hz), 73.7, 61.4, 40.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.46 ppm.

1-(3-Trifluoromethylphenyl)propane-1,3-diol (13)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-cyclopropyl-3-(trifluoromethyl)benzene **13a** (37.2 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 240 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **13** (27.3 mg, 0.124 mmol, 62%) as pale-yellow oil. The spectra of **13** corresponded to the data reported previously. [1]

R*f* = 0.30 (petroleum ether/ethyl acetate 1:1, v/v).

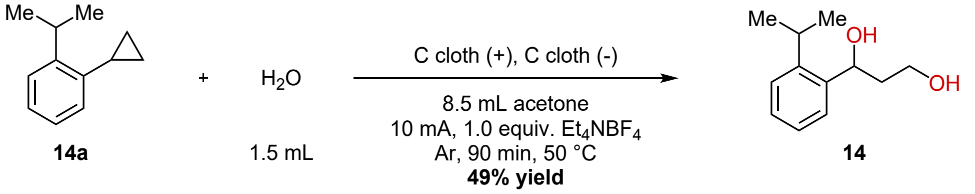
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.57 – 7.51 (m, 2H), 7.49 – 7.43 (m, 1H), 5.05 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.93 – 3.83 (m, 2H), 2.58 (br, 2H), 2.05 – 1.89 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 131.0 (q, *J* = 32.3 Hz), 129.1, 129.0, 124.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 273.3 Hz), 122.6 (q, *J* = 3.8 Hz), 73.7, 61.4, 40.5 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.60 ppm.

1-(2-Isopropylphenyl)propane-1,3-diol (14)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-cyclopropyl-2-isopropylbenzene **14a** (32.1 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **14** (19.0 mg, 0.098 mmol, 49%) as pale-yellow oil.

R_f = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

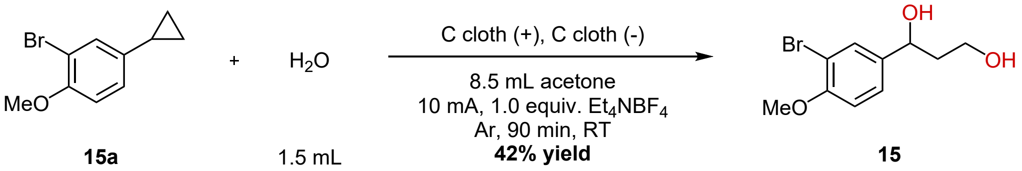
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 1H), 7.32 – 7.18 (m, 3H), 5.31 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.88 (t, *J* = 5.2 Hz, 2H), 3.28 – 3.13 (m, 1H), 2.70 (br, 2H), 2.06 – 1.82 (m, 2H), 1.33 – 1.21 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 141.0, 127.8, 126.2, 125.6, 125.5, 70.3, 61.8, 40.4, 28.2, 24.7, 23.9 ppm.

HRMS (ESI) calculated for $C_{12}H_{18}O_2$ $[M+Na]^+$, 217.1199; found, 217.1199.

1-(3-Bromo-4-methoxyphenyl)propane-1,3-diol (15)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 2-bromo-4-

cyclopropyl-1-methoxybenzene **15a** (45.4 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **15** (22.0 mg, 0.084 mmol, 42%) as colorless oil. The spectra of **15** corresponded to the data reported previously.[8]

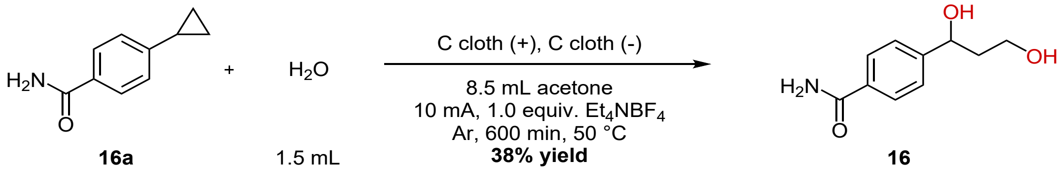
R*f* = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.91 – 4.80 (m, 1H), 3.87 (s, 3H), 3.84 – 3.75(m, 2H), 3.17 – 2.50 (m, 2H), 2.03 – 1.80 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 138.1, 130.8, 125.9, 111.9, 111.7, 73.2, 61.4, 56.4, 40.4 ppm.

1-(4-Carbamoylphenyl)propane-1,3-diol (16)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) and 4-cyclopropylbenzamide **16a** (32.2 mg, 0.20 mmol, 1.0 equiv.) were added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 600 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **16** (15.0 mg, 0.077 mmol, 38%) as a pale-yellow solid.

R*f* = 0.10 (petroleum ether/ethyl acetate 1:1, v/v).

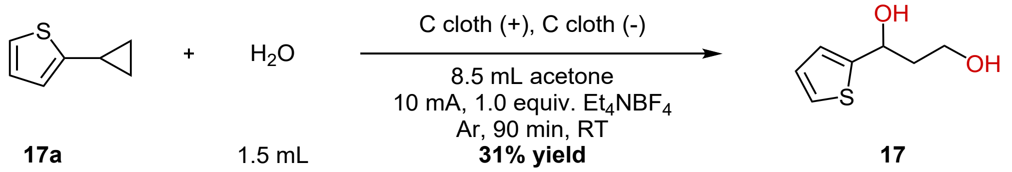
NMR Spectroscopy

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.26 (s, 1H), 5.31 (d, J = 4.4 Hz, 1H), 4.74 – 4.67 (m, 1H), 4.57 (t, J = 4.8 Hz, 1H), 3.44 – 3.37 (m, 2H), 1.81 – 1.65 (m, 2H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.3, 149.9, 132.7, 127.5, 125.7, 69.5, 58.1, 42.4 ppm.

HRMS (ESI) calculated for $C_{10}H_{13}NO_3$ [M+H]$^+$, 196.0968; found, 196.0959.

1-(Thiophen-2-yl) propane-1,3-diol (17)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 2-cyclopropylthiophene **17a** (24.8 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **17** (9.8 mg, 0.062 mmol, 31%) as pale-yellow oil.

R$_f$ = 0.30 (petroleum ether/ethyl acetate 1:1, v/v).

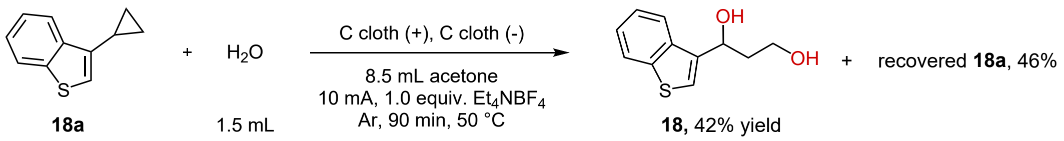
NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.04 – 6.93 (m, 2H), 5.23 (dd, J = 8.8, 4.3 Hz, 1H), 3.97 – 3.84 (m, 2H), 2.16 – 2.05 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 126.9, 124.8, 123.6, 70.2, 61.4, 40.9 ppm.

HRMS (ESI) calculated for C_7H_8S [M+Na]$^+$, 181.0294; found, 181.0296.

1-(Benzo[*b*]thiophen-3-yl)propane-1,3-diol (18)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 2-cyclopropylbenzo[b]thiophene **18a** (34.9 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **18** (17.5 mg, 0.084 mmol, 42%) as pale-yellow oil. **18a** (16.1 mg, 0.092 mmol) was recovered in 46% yield

R_f = 0.20 (petroleum ether/ethyl acetate 1 :1, v/v).

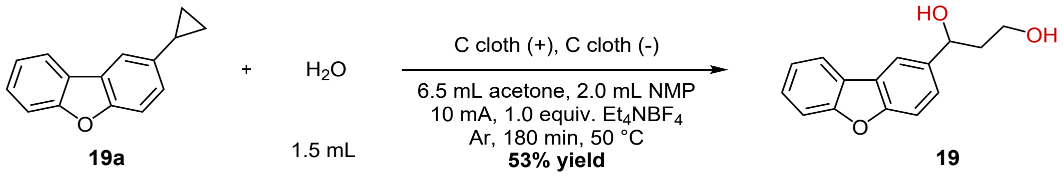
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 2H), 7.42 (s, 1H), 7.40 – 7.32 (m, 2H), 5.37 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.01 – 3.86 (m, 2H), 3.19 – 2.96 (br, 1H), 2.25 – 2.09 (m, 2H), 1.86 – 1.57 (br, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 139.4, 137.1, 124.6, 124.2, 123.1, 122.3, 122.2, 70.0, 61.6, 38.7 ppm.

HRMS GC-EI (m/z) calculated for $C_{11}H_{12}O_2S$ $[M]^+$, 208.0553; found, 208.0550.

1-(Dibenzo[*b,d*]furan-2-yl)propane-1,3-diol (19)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) and 2-cyclopropyldibenzo[*b,d*]furan **19a** (41.7 mg, 0.20 mmol, 1.0 equiv.) were added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 6.5 Ml acetone, 1.5

Ml H_2O and 2.0 Ml NMP were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 180 min. When the reaction finished, the reaction mixture was concentrated by vacuo and then dissolve the crude product with dichloromethane and washed with saturated NH_4Cl aqueous (5 Ml×3). The organic layers were dried over anhydrous Na_2SO_4, concentrated by vacuo. The crude product purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **19** (25.5 mg, 0.105 mmol, 53%) as a white solid.

R*f* = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

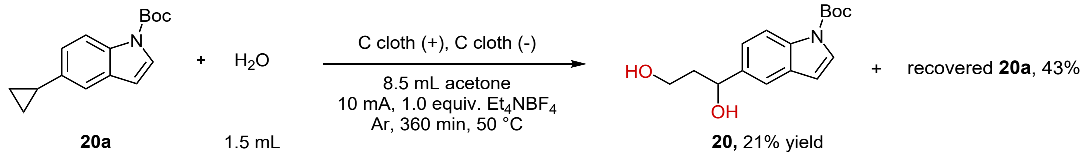
NMR Spectroscopy.

^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 8.17 – 7.94 (m, 2H), 7.77 – 7.38 (m, 4H), 7.36 – 7.23 (m, 1H), 5.14 – 4.95 (m, 1H), 3.96 – 3.54 (m, 2H), 2.24 – 1.84 (m, 2H) ppm.

^{13}C NMR (101 MHz, Methanol-*d*$_4$) δ 157.9, 156.8, 141.4, 128.3, 126.5, 125.4, 125.3, 123.9, 121.7, 119.1, 112.5, 112.2, 72.4, 60.2, 43.1 ppm.

HRMS (ESI) calculated for $C_{15}H_{14}O_3$ $[M+Na]^+$, 265.0835; found, 265.0832.

tert-Butyl 5-(1,3-dihydroxypropyl)-1*H*-indole-1-carboxylate (20)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, *tert*-butyl 5-cyclopropyl-1*H*-indole-1-carboxylate **20a** (51.5 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 360 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **20** (12.2 mg , 0.042 mmol, 21%) as pale-yellow oil. **20a** (22.2 mg , 0.086 mmol) was recovered in 43% yield.

Rf = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

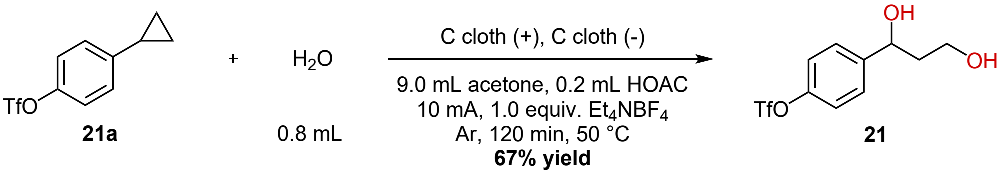
NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 1H), 7.64 – 7.53 (m, 2H), 7.35 – 7.29 (m, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 5.08 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.88 (t, *J* = 5.6 Hz, 2H), 2.70 – 2.58 (br, 1H), 2.12 – 2.06 (m, 1H), 2.02 – 1.95 (m, 1H), 1.67 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 139.0, 130.9, 126.6, 122.2, 118.1, 115.4, 107.5, 83.9, 74.8, 61.7, 41.0, 28.4 ppm.

HRMS (ESI) calculated for $C_{16}H_{21}NO_4$ $[M+H]^+$, 292.1543; found, 292.1542.

4-(1,3-Dihydroxypropyl)phenyl trifluoromethanesulfonate (21)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 4-cyclopropylphenyl trifluoromethanesulfonate **21a** (53.3 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 120 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **21** (40.2 mg, 0.134 mmol, 67%) as a white solid.

R*f* = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

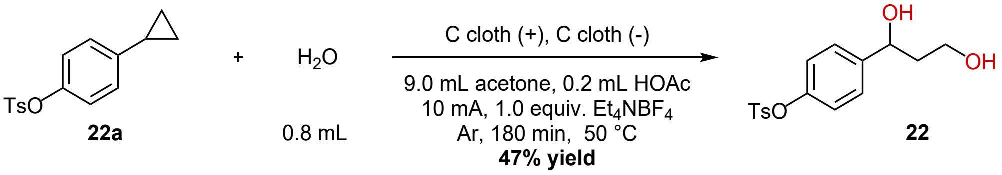
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 4.89 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.84 – 3.68 (m, 2H), 3.46 – 2.08 (m, 2H), 1.93 – 1.75 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 145.0, 127.6, 121.5, 118.8 (q, *J* = 324.2 Hz), 73.5, 61.4, 40.5 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.89 ppm.

HRMS (ESI) calculated for $C_{10}H_{11}F_3O_5S$ $[M+Na]^+$, 323.0171; found, 323.0168.

1-(4-Tosyloxyphenyl)propane-1,3-diol (22)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 4-methylbenzenesulfonate **22a** (57.7 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 180 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **22** (30.1 mg, 0.093 mmol, 47%) as a white solid.

R*f* = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

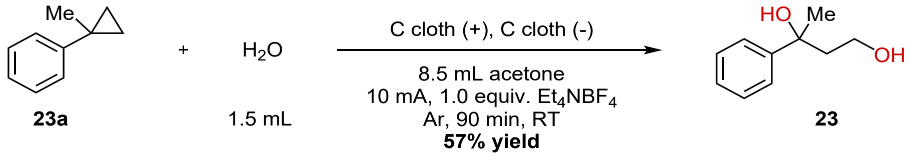
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.23 (m, 4H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.90 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.87 – 3.72 (m, 2H), 3.08 – 2.61 (br, 2H), 2.44 (s, 3H), 1.96 – 1.79 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 145.5, 143.5, 132.5, 129.9, 128.6, 127.0, 122.4, 73.6, 61.4, 40.5, 21.8 ppm.

HRMS (ESI) calculated for $C_{16}H_{18}O_5S$ $[M+Na]^+$, 345.0767; found, 345.0759.

3-Phenylbutane-1,3-diol (23)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via

vacuum evacuation and backfilled with argon three times. Subsequently, (1-methylcyclopropyl)benzene **23a** (26.4 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (2:1, v/v) to afford **23** (19.1 mg, 0.115 mmol, 57%) as colorless oil. The spectra of **23** corresponded to the data reported previously.[9]

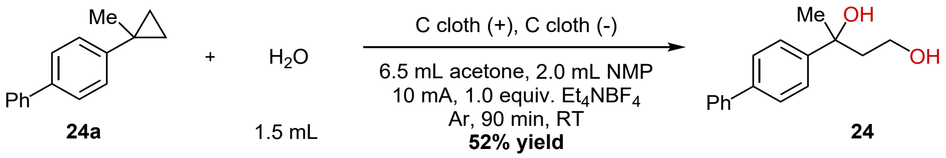
R_f = 0.30 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.31 – 7.23 (m, 2H), 7.21 – 7.12 (m, 1H), 3.75 – 3.63 (m, 1H), 3.54 – 3.42 (m, 1H), 2.77 (br, 2H), 2.09 – 1.89 (m, 2H), 1.50 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 128.4, 126.7, 124.9, 76.0, 60.5, 44.1, 31.1 ppm.

3-([1,1’-Biphenyl]-4-yl)butane-1,3-diol (24)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) and 4-(1-methylcyclopropyl)-1,1’-biphenyl **24a** (41.7 mg, 0.20 mmol, 1.0 equiv.) were added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 6.5 Ml acetone, 1.5 Ml H_2O and 2.0 Ml NMP were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated by vacuo and then dissolve the crude product with dichloromethane and washed with saturated NH_4Cl aqueous (5 Ml × 3). The organic layers were dried over anhydrous Na_2SO_4, concentrated by vacuo. The crude product purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **24** (25.0 mg, 0.103 mmol, 52%) as a white solid.

R$_f$ = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

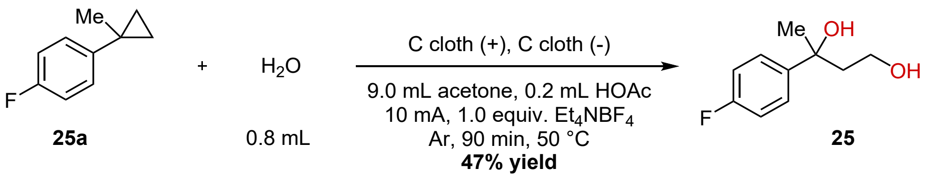
NMR Spectroscopy

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.65 – 7.55 (m, 4H), 7.54 – 7.48 (m, 2H), 7.43 – 7.37 (m, 2H), 7.33 – 7.27 (m, 1H), 3.68 – 3.46 (m, 2H), 2.09 (t, *J* = 7.2 Hz, 2H), 1.57 (s, 3H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 148.4, 142.2, 140.5, 129.8, 128.2, 127.9, 127.6, 126.4, 75.1, 59.9, 46.4, 30.8 ppm.

HRMS (ESI) calculated for $C_{16}H_{18}O_2$ [M+Na]$^+$, 265.1199; found, 265.1194.

3-(4-Fluorophenyl)butane-1,3-diol (25)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-fluoro-4-(1-methylcyclopropyl)benzene **25a** (30.0 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1, v/v) to afford **25** (17.4 mg, 0.094 mmol, 47%) as pale-yellow oil.

R$_f$ = 0.40 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

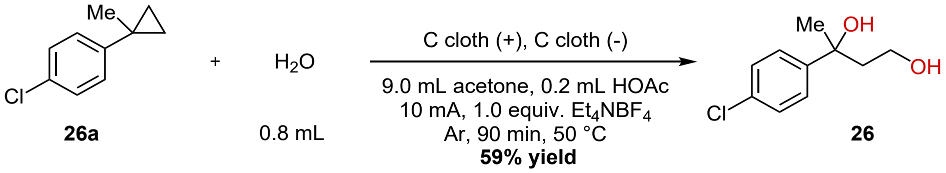
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.06 – 6.95 (m, 2H), 3.93 – 3.73 (m, 2H), 3.61 – 3.49 (m, 1H), 2.67 (br, 1H), 2.14 – 1.94 (m, 2H), 1.55 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (d, *J* = 245.6 Hz), 143.4(d, *J* = 3.0 Hz), 126.6 (d, *J* = 8.0 Hz), 115.0 (d, *J* = 21.2 Hz), 75.7, 60.4, 44.0, 31.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.95 – -117.05 (m) ppm.

HRMS GC-EI (m/z) calculated for $C_{10}H_{13}FO_2$ $[M]^+$, 184.0894; found, 184.0894.

3-(4-Chlorophenyl)butane-1,3-diol (26)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-chloro-4-(1-methylcyclopropyl)benzene **26a** (33.3 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1, v/v) to afford **26** (23.7 mg, 0.118 mmol, 59%) as pale-yellow oil. The spectra of **26** corresponded to the data reported previously.[10]

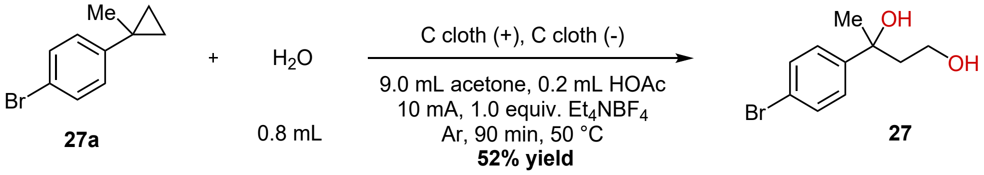
R_f = 0.40 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 4H), 3.96 (br, 1H), 3.80 – 3.72 (m, 1H), 3.61 – 3.49 (m, 1H), 2.72 (br, 1H), 2.13 – 2.03 (m,1H), 2.02 – 1.93 (m, 1H), 1.53 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 132.5, 128.4, 126.5, 75.7, 60.3, 43.8, 31.0 ppm.

3-(4-Bromophenyl)butane-1,3-diol (27)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via

vacuum evacuation and backfilled with argon three times. Subsequently, 1-bromo-4-(1-methylcyclopropyl)benzene **27a** (42.2 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1, v/v) to afford **27** (25.2 mg, 0.103 mmol, 52%) as colorless oil. The spectra of **27** corresponded to the data reported previously.[11]

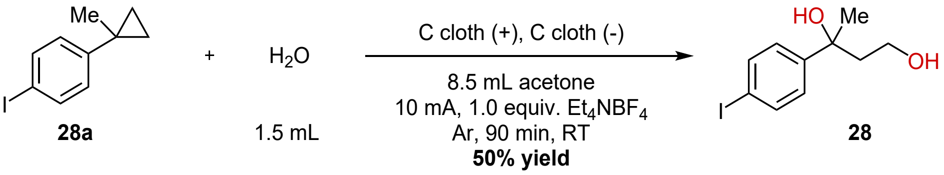
R_f = 0.40 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 3.81 – 3.70 (m, 1H), 3.58 – 3.47 (m, 1H), 2.13 – 2.03 (m, 1H), 2.01 – 1.92 (m, 1H), 1.53 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 131.4, 126.9, 120.6, 75.8, 60.3, 43.7, 31.0 ppm.

3-(4-Iodophenyl)butane-1,3-diol (28)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-iodo-4-(1-methylcyclopropyl)benzene **28a** (51.6 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1, v/v) to afford **28** (29.0 mg, 0.099 mmol, 50%) as pale-yellow oil.

R_f = 0.40 (petroleum ether/ethyl acetate 1:1, v/v).

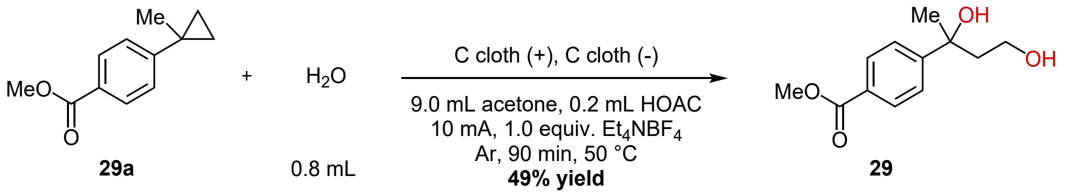
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 3.81 – 3.71 (m, 1H), 3.59 – 3.47 (m, 1H), 2.14 – 2.03 (m, 1H), 2.01 – 1.92 (m, 1H), 1.52 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 137.4, 127.2, 92.2, 75.8, 60.3, 43.7, 31.0 ppm.

HRMS GC-EI (m/z) calculated for $C_{10}H_{13}IO_2$ $[M]^+$, 291.9955; found, 291.9951.

3-(4-Carbomethoxyphenyl)butane-1,3-diol (29)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, methyl 4-(1-methylcyclopropyl)benzoate **29a** (38.1 mg, 0.2 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **29** (22.2 mg, 0.099 mmol, 49%) as a white solid.

R_f = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

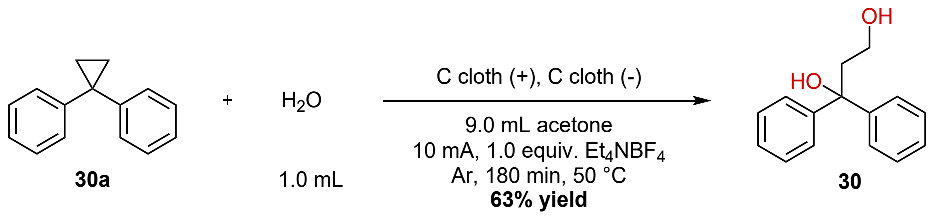
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 4.20 (br, 1H), 3.89 (s, 3H), 3.80 – 3.71 (m, 1H), 3.56 – 3.45 (m, 1H), 3.05 – 2.66 (s, 1H), 2.16 – 2.08 (m, 1H), 2.05 – 1.98 (m, 1H), 1.55 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 153.0, 129.7, 128.5, 125.1, 76.0, 60.3, 52.2, 43.7, 30.9 ppm.

HRMS (ESI) calculated for $C_{12}H_{16}O_4$ $[M+Na]^+$, 247.0941; found, 247.0941.

1,1-Diphenylpropane-1,3-diol (30)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1,1-diphenylcyclopropane **30a** (38.9 mg, 0.20 mmol, 1.0 equiv.), 9 Ml acetone and 1 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 180 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1, v/v) to afford **30** (28.6 mg, 0.125 mmol, 63%) as a pale-yellow soild. The spectra of **30** corresponded to the data reported previously.[12]

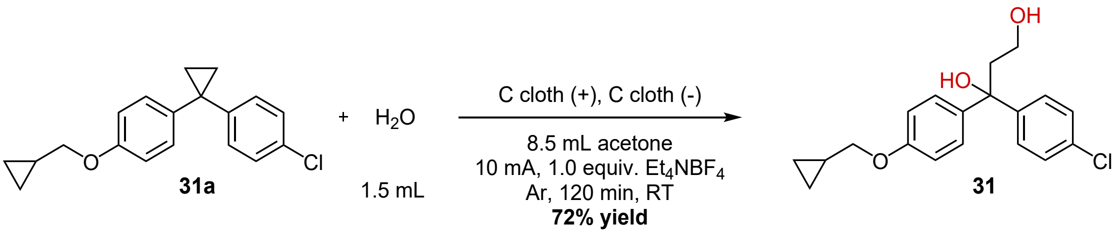
R*f* = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

NMR Spectroscopy

^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 7.46 – 7.38 (m, 4H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.21 – 7.14 (m, 2H), 3.60 (t, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H) ppm.

^{13}C NMR (101 MHz, Methanol-*d*$_4$) δ 148.6, 129.0, 127.6, 127.1, 78.8, 60.1, 44.1 ppm.

1-(4-Chlorophenyl)-1-(4-(cyclopropylmethoxy)phenyl)propane-1,3-diol (31)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-chloro-4-(1-

(4-(Cyclopropylmethoxy)phenyl)cyclopropyl)benzene **31a** (59.8 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 120 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1, v/v) to afford **31** (47.9 mg, 0.144 mmol, 72%) as pale-yellow oil.

R*f* = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

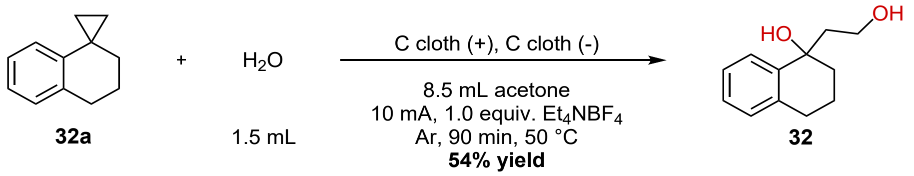
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.30 – 7.23 (m, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.13 (br, 1H), 3.78 (d, *J* = 6.8 Hz, 2H), 3.75 – 3.64 (m, 2H), 2.68 – 2.26 (m, 3H), 1.30 – 1.19 (m, 1H), 0.69 – 0.57 (m, 2H), 0.40 – 0.27 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 145.7, 138.6, 132.8, 128.4, 127.6, 127.3, 114.5, 78.9, 72.9, 60.5, 42.2, 10.4, 3.3 ppm.

HRMS (ESI) calculated for $C_{19}H_{21}ClO_3$ $[M+Na]^+$, 355.1071; found, 355.1063.

1-(2-Hydroxyethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (32)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 3’,4’-dihydro-2’H-spiro[cyclopropane-1,1’-naphthalene] **32a** (31.6 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (2:1, v/v) to afford **32** (20.9 mg, 0.109 mmol, 54%) as pale-yellow oil.

R*f* = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

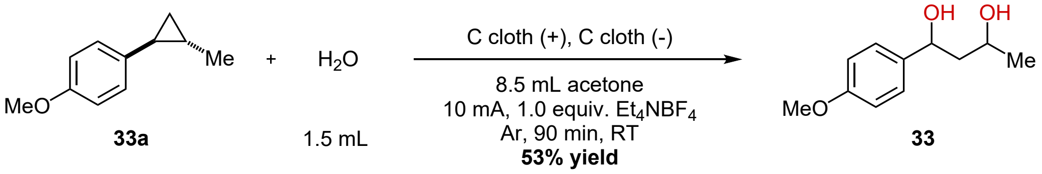
NMR Spectroscopy

^{1}**H NMR** (400 MHz, Methanol-d_4) δ 7.54 (d, J = 7.6 Hz, 1H), 7.23 – 7.09 (m, 2H), 7.07 – 7.01 (m, 1H), 3.76 – 3.57 (m, 2H), 2.86 – 2.67 (m, 2H), 2.15 – 1.99 (m, 3H), 1.97 – 1.76 (m, 3H) ppm.

^{13}**C NMR** (101 MHz, Methanol-d_4) δ 143.4, 137.7, 129.8, 127.9, 127.6, 127.0, 73.0, 59.6, 45.3, 37.4, 30.7, 20.9 ppm.

HRMS (ESI) calculated for $C_{16}H_{12}O_2$ $[M+Na]^+$, 215.1043; found, 215.1043.

1-(4-Methoxyphenyl)butane-1,3-diol (33)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-methoxy-4-((1S,2S)-2-methylcyclopropyl)benzene **33a** (32.5 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **33** (***cis-33**,* 12.7 mg, 0.064 mmol, 32%; ***trans-33**,* 8.3 mg, 0.042 mmol, 21%. 1.5:1 d.r., based on isolated yield) as a white solid. The spectra of **33** corresponded to the data reported previously.[13, 14]

R$_f$ = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

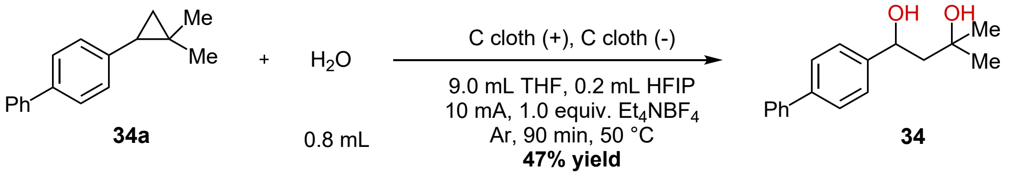
***cis*-31:** ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 4.88 (dd, J = 10.0, 2.8 Hz, 1H), 4.18 – 4.05 (m, 1H), 3.80 (s, 3H), 2.93 (br, 2H), 1.92 – 1.68 (m, 2H), 1.21 (d, J = 6.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 136.9, 127.1, 114.1, 75.1, 68.9, 55.4, 47.2, 24.2 ppm.

***Trans*-31: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.99 (dd, *J* = 8.0, 3.6 Hz, 1H), 4.12 – 4.01 (m, 1H), 3.80 (s, 3H), 2.65 (br, 2H), 1.93 – 1.75 (m, 2H), 1.23 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 136.8, 127.0, 114.0, 71.5, 65.6, 55.4, 46.3, 23.6 ppm.

1-([1,1'-Biphenyl]-4-yl)-3-methylbutane-1,3-diol (34)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, cyclopropane-1,1-diyldibenzene **34a** (44.5 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml THF, 0.8 Ml H_2O and 0.2 Ml HFIP were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **34** (24.3 mg, 0.095 mmol, 47%) as a white solid.

R_f = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

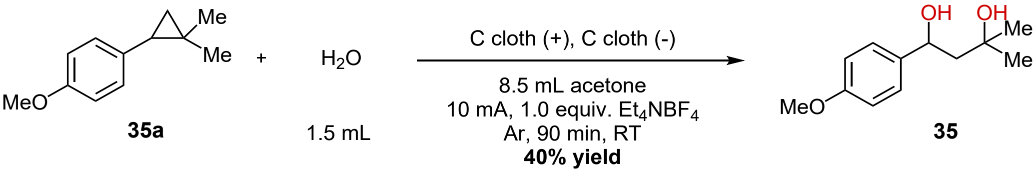
NMR Spectroscopy

^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 7.63 – 7.55 (m, 4H), 7.47 – 7.38 (m, 4H), 7.34 – 7.27 (m, 1H), 5.04 (dd, *J* = 10.0, 2.8 Hz, 1H), 1.94 (dd, *J* = 14.4, 10.4 Hz, 1H), 1.77 (dd, *J* = 14.4, 2.8 Hz, 1H), 1.37 (s, 3H), 1.27 (s, 3H) ppm.

^{13}C NMR (101 MHz, Methanol-*d*$_4$) δ 146.1, 142.2, 141.4, 129.8, 128.2, 127.9, 127.9, 127.3, 72.6, 72.0, 51.9, 30.9, 28.8 ppm.

HRMS (ESI) calculated for $C_{17}H_{20}O_2$ $[M+Na]^+$, 279.1356; found, 279.1352.

1-(4-Methoxyphenyl)-3-methylbutane-1,3-diol (35)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-(2,2-dimethylcyclopropyl)-4-methoxybenzene **35a** (35.3 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (2:1, v/v) to afford **35** (17.0 mg, 0.081 mmol, 40%) as pale-yellow oil.

R*f* = 0.30 (petroleum ether/ethyl acetate 2:1, v/v).

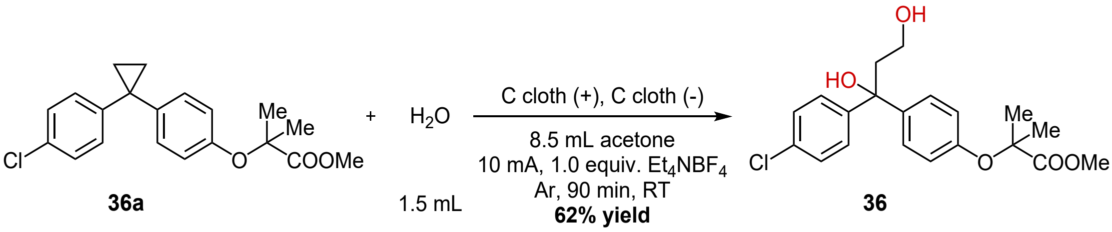
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.02 (dd, *J* = 11.0, 1.8 Hz, 1H), 3.80 (s, 3H), 1.97 (dd, *J* = 14.8, 11.2 Hz, 1H), 1.65 (dd, *J* = 14.6, 2.2 Hz, 1H), 1.42 (s, 3H), 1.27 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 137.1, 127.0, 114.0, 72.1, 71.7, 55.4, 50.5, 32.0, 27.8 ppm.

HRMS (ESI) calculated for $C_{12}H_{18}O_3$, $[M+Na]^+$, 233.1148; found, 233.1152.

Fenofibrate derivative-1,3-diol (36)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (4

3.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, fenofibrate derivative **36a** (69.0 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1, v/v) to afford **36** (47.0 mg, 0.124 mmol, 62%) as pale-yellow oil.

R*f* = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

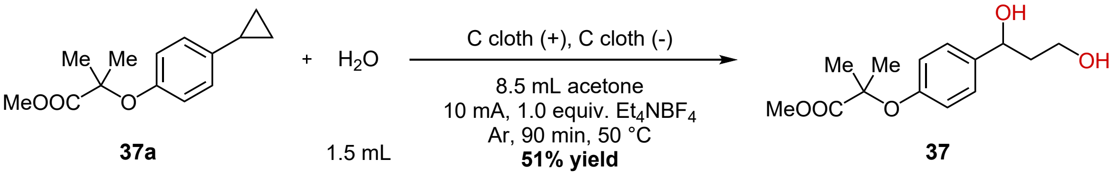
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.29 – 7.21 (m, 4H), 6.80 – 6.72 (m, 2H), 3.74 (s, 3H), 3.73 – 3.63 (m, 2H), 2.53 – 2.38 (m, 2H), 1.57 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 154.5, 145.4, 140.2, 132.8, 128.4, 127.6, 127.1, 118.9, 79.2, 78.8, 60.4, 52.6, 42.1, 25.5 ppm.

HRMS (ESI) calculated for $C_{20}H_{23}ClO_5$ $[M+Na]^+$, 401.1126; found, 401.1121.

Ciprofibrate derivative-1,3-diol (37)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, ciprofibrate derivative **37a** (46.9 mg, 0.20 mmol, 1.0 equiv.) 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **37** (27.5 mg, 0.102 mmol, 51%) as pale-yellow oil.

R$_f$ = 0.20 (petroleum ether/ethyl acetate 1:1, v/v)

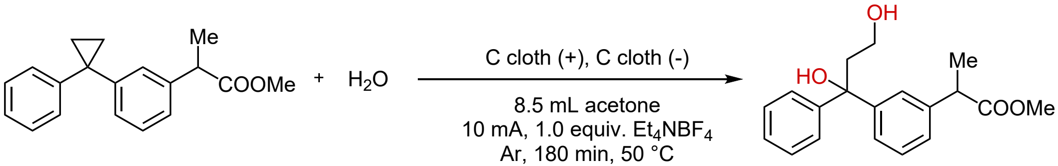
NMR Spectroscopy

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.75 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.75 (s, 3H), 3.71 – 3.53 (m, 2H), 2.02 – 1.79 (m, 2H), 1.55 (s, 6H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 176.2, 155.9, 140.4, 127.9, 120.4, 80.4, 71.9, 60.1, 52.9, 42.6, 25.7 ppm.

HRMS (ESI) calculated for $C_{14}H_{20}O_5$ $[M+Na]^+$, 291.1203; found, 291.1201.

Ketoprofen derivative-1,3-diol (38)



38a 1.5 mL **45% yield** **38**

In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, ketoprofen derivative **38a** (56.1 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 180 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1, v/v) to afford **38** (28.4 mg, 0.09 mmol, 45%) as pale-yellow oil.

R$_f$ = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

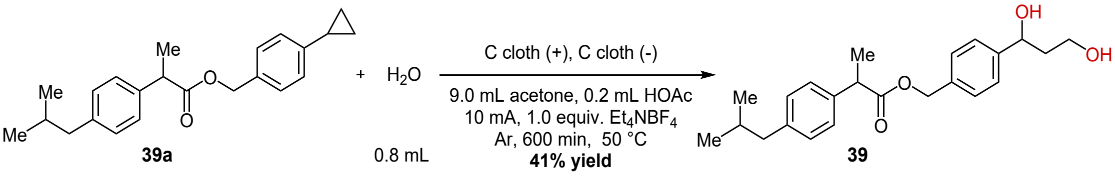
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 3H), 7.35 – 7.28 (m, 2H), 7.28 – 7.22 (m, 3H), 7.20 – 7.14 (m, 1H), 3.80 – 3.67(m, 3H), 3.62 (s, 3H), 2.55 (t, *J* = 5.4 Hz, 2H), 1.47 (dd, *J* = 7.2, 2.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2(9), 175.2(7), 147.2, 146.6, 140.6, 128.6, 128.4, 127.1, 126.1(1), 126.1(9), 126.0(3), 126.0(0), 125.5, 125.4, 125.1, 79.4, 60.5, 52.1, 45.7, 45.6, 42.3, 18.8, 18.7 ppm.

HRMS GC-EI (m/z) calculated for $C_{19}H_{22}O_4$ $[M]^+$, 314.1513; found, 314.1513.

Ibuprofen derivative-1,3-diol (39)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, ibuprofen derivative **39a** (67.3 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 600 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **39** (30.4 mg, 0.082 mmol, 41%) as pale-yellow oil.

R*f* = 0.30 (petroleum ether/ethyl acetate 1:1, v/v).

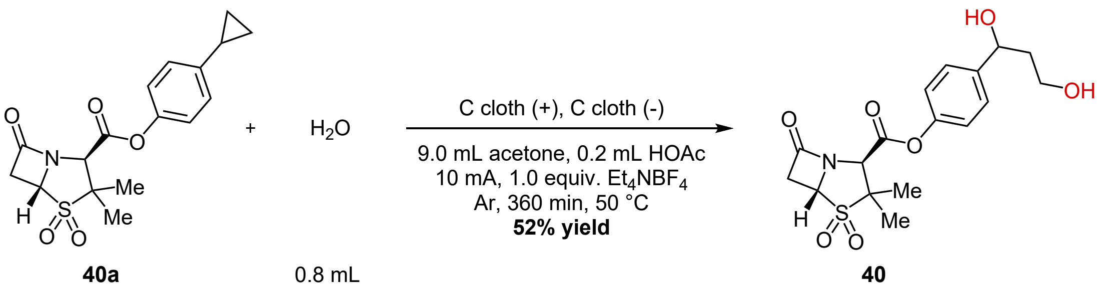
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.16 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.13 – 5.03 (m, 2H), 4.93 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.88 – 3.80 (m, 2H), 3.74 (q, *J* = 7.2 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 2.08 – 1.70 (m, 3H), 1.50 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 144.3, 140.7, 137.7, 135.5, 129.4, 128.0, 127.3, 125.9, 74.1, 66.2, 61.5, 45.2, 45.1, 40.5, 30.3, 22.5, 18.5 ppm.

HRMS (ESI) calculated for $C_{23}H_{30}O_4$ $[M+Na]^+$, 393.2036; found, 393.2035.

Sulbactam derivative-1,3-diol (40)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, sulbactam derivative **40a** (69.9 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 360 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (2:1, v/v) to afford **40** (40.0 mg, 0.104 mmol, 52%) as colorless oil.

R*f* = 0.30 (petroleum ether/ethyl acetate 2:1, v/v).

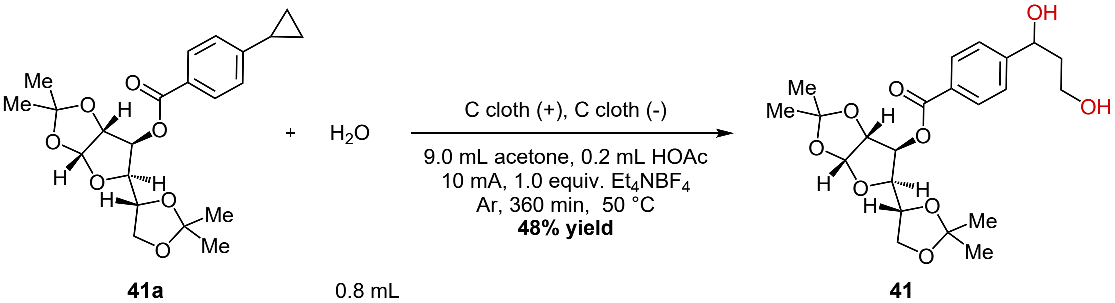
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.93 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.67 (dd, *J* = 3.8, 1.8 Hz, 1H), 4.62 (s, 1H), 3.89 – 3.74 (m, 2H), 3.55-3.41 (m, 3H), 2.75 (br, 1H), 2.01 – 1.83 (m, 2H), 1.70 (s, 3H), 1.56 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 165.8, 149.0, 143.2, 127.2, 121.0, 73.4, 63.3, 63.0, 61.3, 61.3, 40.5, 38.5, 20.6, 18.8 ppm.

HRMS (ESI) calculated for $C_{17}H_{21}NO_7S$ $[M+Na]^+$, 406.0931; found, 406.0923.

Diacetone-D-glucose derivative-1,3-diol (41)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, diacetone-D-glucose derivative **41a** (80.9 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 360 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **41** (42.0 mg, 0.096 mmol, 48%) as a white solid.

R_f = 0.20 (petroleum ether/ethyl acetate 1:1, v/v).

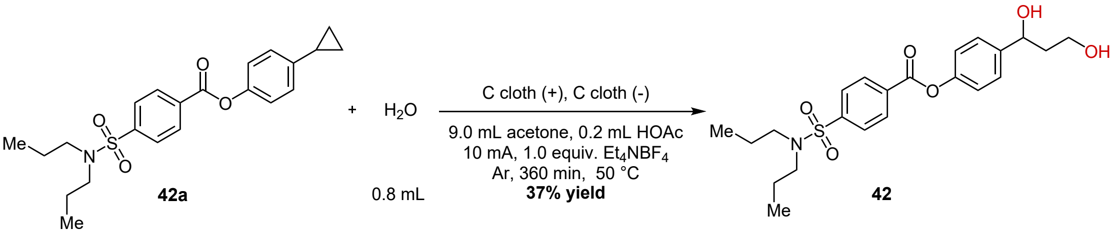
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 5.93 (d, J = 3.6 Hz, 1H), 5.47 (d, J = 2.0 Hz, 1H), 5.01 (t, J = 6.0 Hz, 1H), 4.61 (d, J = 3.6 Hz, 1H), 4.38 – 4.28 (m, 2H), 4.11 – 4.05 (m, 2H), 3.84 (t, J = 5.4 Hz, 2H), 3.69 (br, 1H), 2.77 (br, 1H), 1.96 – 1.88 (m, 2H), 1.54 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H), 1.24 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.5, 130.0, 128.7, 125.9, 112.5, 109.5, 105.3, 83.5, 80.1, 76.8, 73.5, 72.7, 67.3, 61.1, 40.5, 26.9, 26.8, 26.3, 25.3 ppm.

HRMS (ESI) calculated for $C_{22}H_{30}O_9$ $[M+H]^+$, 439.1963; found, 439.1956.

Probenecid derivative-1,3-diol (42)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et4NBF4 (43.4 mg, 0.20 mmol, 1.0 equiv.) and probenecid derivative **42a** (80.3 mg, 0.20 mmol, 1.0 equiv.) were added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 360 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **42** (32.5 mg, 0.08 mmol, 37%) as a white solid.

R*f* = 0.20 (petroleum ether/ethyl acetate 1:1, v/v)

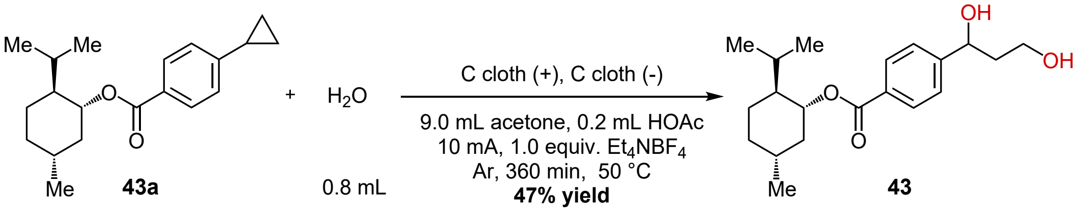
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.99 (dd, *J* = 8.6, 3.8 Hz, 1H), 3.94 – 3.81 (m, 2H), 3.19 – 3.05 (m, 4H), 2.06 – 1.88 (m, 2H), 1.61 – 1.50 (m, 4H), 0.88 (t, *J* = 7.6 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 149.9, 145.0, 142.7, 132.9, 130.9, 127.3, 127.1, 121.6, 73.9, 61.5, 50.1, 40.6, 22.1, 11.3 ppm.

HRMS (ESI) calculated for $C_{22}H_{29}NO_6S$ $[M+Na]^+$, 458.1608; found, 458.1606.

DL-Menthol derivative-1,3-diol (43)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et4NBF4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, DL-menthol derivative **43a** (60.1 mg, 0.20 mmol, 1.0 equiv.), 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 360 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **43** (31.5 mg, 0.094 mmol, 47%) as colorless oil.

R_f = 0.30 (petroleum ether/ethyl acetate 1:1, v/v).

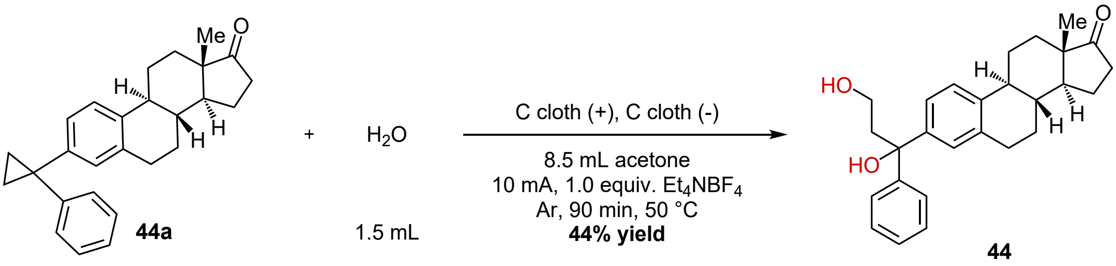
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.00 (dd, *J* = 7.4, 4.6 Hz, 1H), 4.90 (td, *J* = 10.8, 4.4 Hz, 1H), 3.93 – 3.78 (m, 2H), 3.71 (br, 1H), 2.93 (br, 1H), 2.12 – 2.15 (m, 1H), 1.98 – 1.89 (m, 3H), 1.75 – 1.67 (m, 2H), 1.62 – 1.47 (m, 2H), 1.15 – 1.03 (m, 2H), 0.96 – 0.87 (m, 7H), 0.77 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 149.5, 130.0, 129.9, 125.6, 75.0, 73.8, 61.3, 47.3, 41.1, 40.4, 34.4, 31.5, 26.6, 23.7, 22.2, 20.9, 16.6 ppm.

HRMS (ESI) calculated for $C_{20}H_{30}O_4$ $[M+Na]^+$, 357.2036; found, 357.2033.

Estrone derivative-1,3-diol (44)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (32.6 mg, 0.15 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, estrone derivative **44a** (55.6 mg, 0.15 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1, v/v) to afford **44** (26.7 mg, 0.066 mmol, 44%) as pale-yellow oil.

R_f = 0.30 (petroleum ether/ethyl acetate 3:1, v/v).

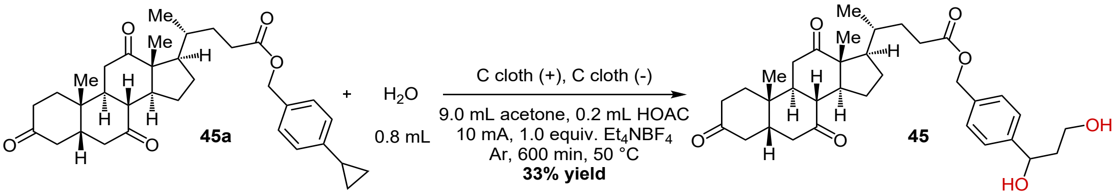
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.09 (m, 4H), 4.06 (br, 1H), 3.86 – 3.63 (m, 2H), 2.93 – 2.79 (m, 2H), 2.56 – 2.45 (m, 3H), 2.42 – 2.35 (m, 1H), 2.30 – 2.22 (m, 1H), 2.19 – 2.10 (m, 1H), 2.00 – 1.90 (m, 2H), 1.68 – 1.37 (m, 8H), 0.89 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.2, 146.8, 144.3, 138.5(0), 138.5(8), 136.4(4), 136.4(0), 128.3, 126.9, 126.6, 126.5, 126.0, 125.3(9), 125.3(6), 123.5(3), 123.5(5), 79.2(4), 79.2(2), 60.5, 50.6, 48.1, 44.4, 42.2, 38.2, 36.0, 31.7, 29.7, 26.7, 25.7, 21.7, 14.0 ppm.

HRMS GC-EI (m/z) calculated for $C_{27}H_{32}O_3$ $[M]^+$, 404.2346; found, 404.2347.

Dehydrocholic acid derivative-1,3-diol (45)



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) and dehydrocholic acid derivative **45a** (106.5 mg, 0.20 mmol, 1.0 equiv.) were added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 9.0 Ml acetone, 0.8 Ml H_2O and 0.2 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 600 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **45** (37.0 mg, 0.065mmol, 33%) as a white solid.

R_f = 0.15 (petroleum ether/ethyl acetate 1:1, v/v).

NMR Spectroscopy

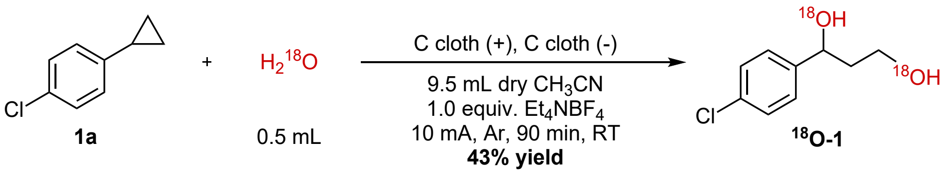
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 5.13 – 5.00 (m, 2H), 4.94 (dd, *J* = 8.6, 3.8 Hz, 1H), 3.89 – 3.76 (m, 2H), 3.26 (br, 1H), 2.94 – 2.76 (m, 3H), 2.47 – 2.37 (m, 1H), 2.36 – 2.15 (m, 8H), 2.14 – 2.08 (m, 2H), 2.03 – 1.90 (m, 6H), 1.86 – 1.76 (m, 2H), 1.64 – 1.53 (m, 1H), 1.38 (s, 3H), 1.31 – 1.15 (m, 4H), 1.03 (s, 3H), 0.81 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.2, 209.4, 209.0, 174.0, 144.6, 135.4, 128.5, 125.9, 73.9, 66.0, 61.4, 57.0, 51.8, 49.1, 46.9, 45.7, 45.6, 45.1, 42.9, 40.6, 38.7, 36.6, 36.1, 35.5, 35.3, 31.6, 30.5, 27.7, 25.2, 22.0, 18.7, 11.9 ppm.

HRMS (ESI) calculated for $C_{34}H_{46}O_7$ $[M+Na]^+$, 589.3136; found, 589.3135.

5. Mechanistic studies

^{18}O-Labeling experiment



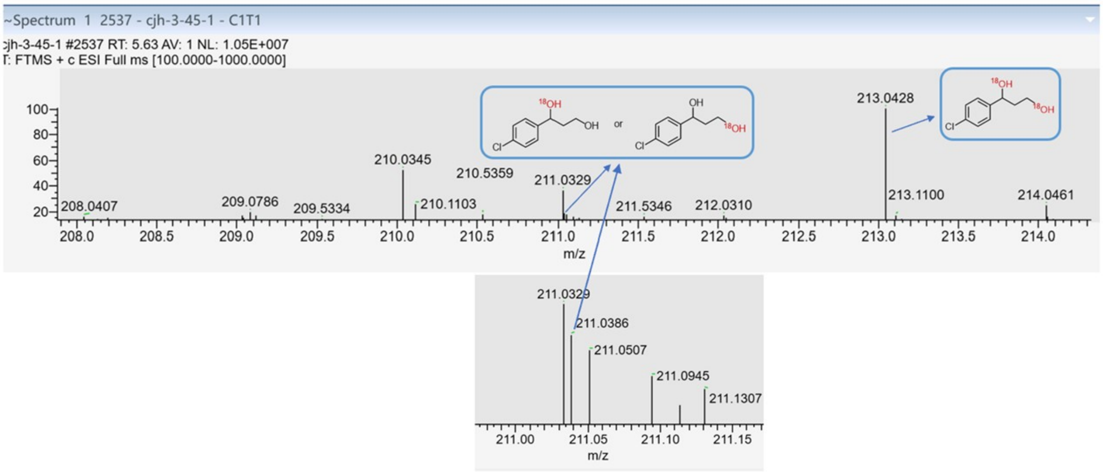
In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-chloro-4-cyclopropylbenzene **1a** (30.5 mg, 0.20 mmol, 1.0 equiv.), 9.5 Ml dry CH_3CN and 0.5 Ml $H_2{}^{18}O$ were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with ethyl acetate to afford **^{18}O-1** (16.4 mg, 0.086 mmol, 43%) as a pale-yellow solid. This result clearly indicated the hydroxyl groups were transformed from H_2O.

NMR Spectroscopy:

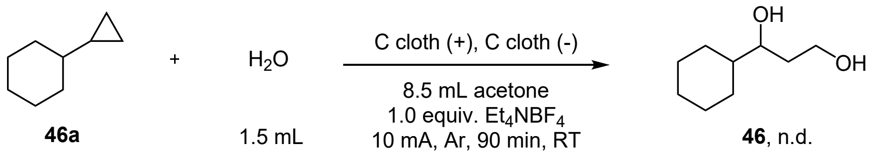
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 4.94 (dd, *J* = 8.4, 3.8 Hz, 1H), 3.92 – 3.79 (m, 2H), 3.38 – 3.02 (br, 1H), 2.64 – 2.27 (br, 1H), 1.98 – 1.85 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 133.3, 128.8, 127.2, 73.8, 61.5, 40.5 ppm.

HRMS (ESI) calculated for $C_9H_{11}Cl^{18}O_2$ $[M+Na]^+$, 213.0425; found, 213.0428.



Control experiment



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, cyclopropylcyclohexane **46a** (24.8 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. The reaction system was monitored by TLC and NMR, and no desired product **46** could be detected.

Cyclic voltammetry studies

Cyclic voltammograms were performed in a three-electrode cell under nitrogen at room temperature. The working electrode was a Pt electrode, the counter electrode was a graphite rod. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 10 Ml CH_3CN containing 100 Mm Et_4NBF_4 was tested as blank background. 20 Mm Substrate, 100 Mm Et_4NBF_4 and 10 Ml CH_3CN were contained in the electrochemical cell in all experiments. The scan rate was 100 Mv/s.

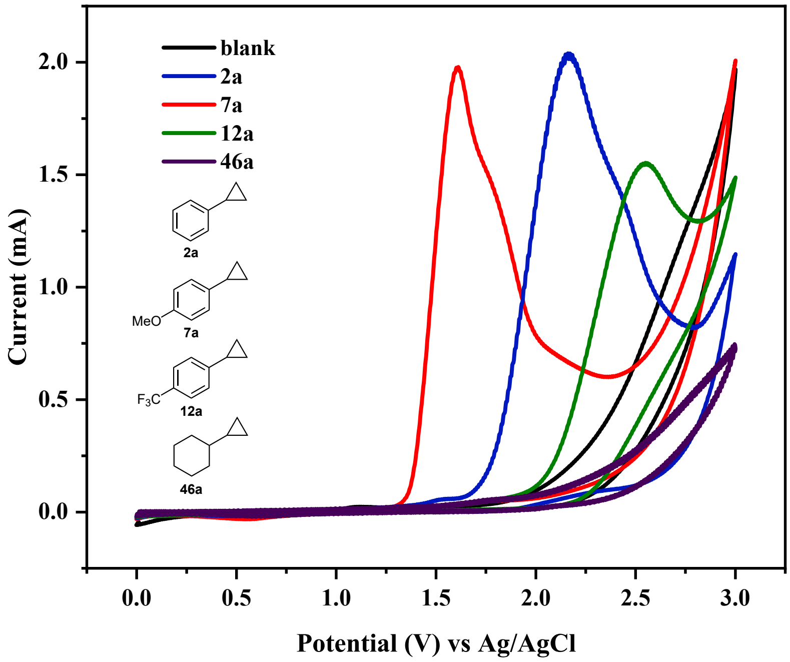


Figure S1. CV of **2a**, **7a**, **12a** and **46a**

Cyclic voltammograms at 100 Mv/s in CH_3CN. The black line is Et_4NBF_4 (100 Mm). The blue line is **2a** (20 Mm) + Et_4NBF_4 (100 Mm), ($E_{p/2}$ = 1.94 V). The red line is **7a** (20 Mm) + Et_4NBF_4 (100 Mm), ($E_{p/2}$ = 1.47 V). The green line is **12a** (20 Mm) + Et_4NBF_4 (100 Mm), ($E_{p/2}$ = 2.27 V). The purple line is **46a** (20 Mm) + Et_4NBF_4 (100 Mm).

Cyclic voltammetry experiments showed that **46a** has a high oxidation potential and no oxidation peak can be observed under 3 V. In comparison, arylcyclopropanes **2a**, **7a** and **12a** all gave obvious oxidative peak. These results illustrated that aromatic system was essential for the anodic oxidation of cyclopropanes.

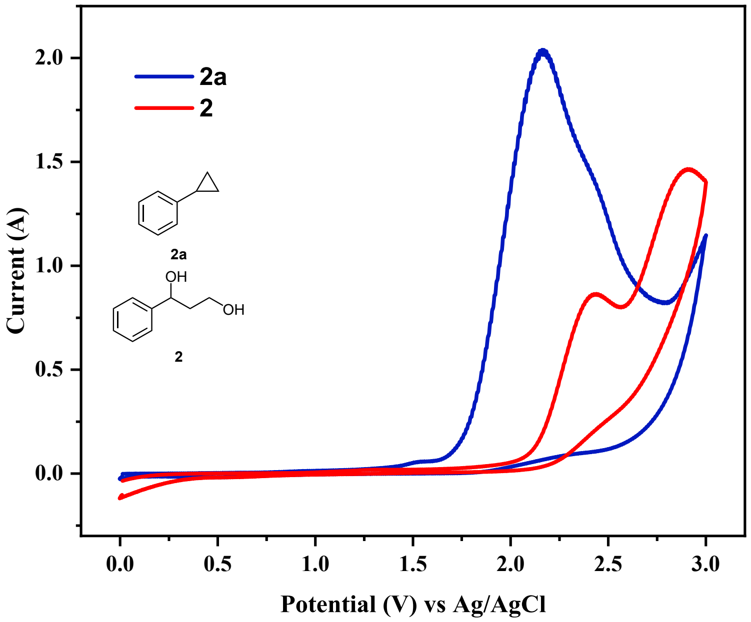


Figure S2. CV of **2a** and **2**

Cyclic voltammograms at 100 Mv/s in CH_3CN. The blue line is **2a** (20 Mm) + Et_4NBF_4 (100 Mm), ($E_{p/2}$ = 1.94 V). The red line is **2** (20 Mm) + Et_4NBF_4 (100 Mm), ($E_{p/2}$ = 2.24 V).

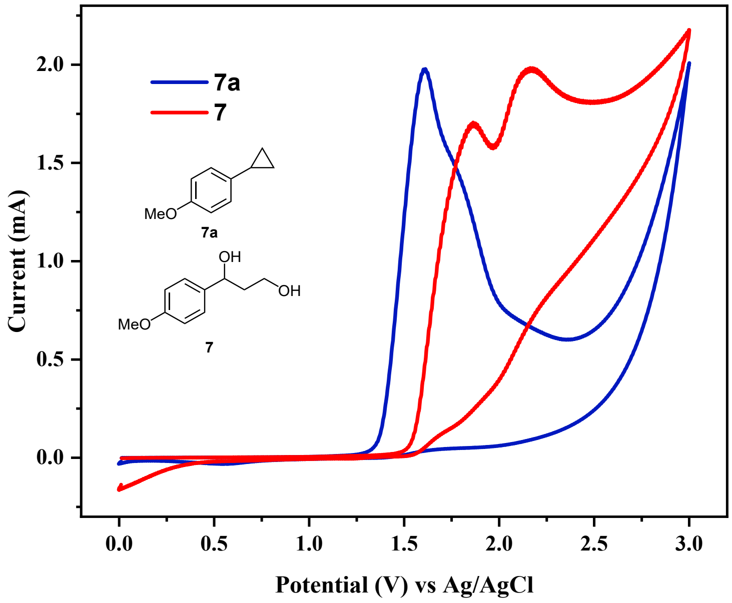
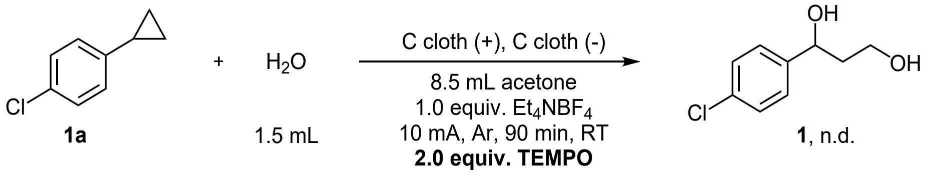


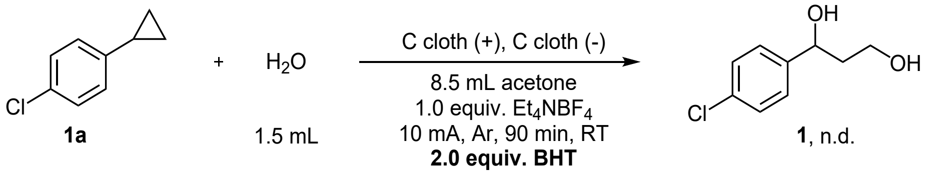
Figure S3. CV of **7a** and **7**

Cyclic voltammograms at 100 Mv/s in CH_3CN.The blue line is **7a** (20 Mm) + Et_4NBF_4 (100 Mm), ($E_{p/2}$ = 1.47 V). The red line is **7** (20 Mm) + Et_4NBF_4 (100 Mm), ($E_{p/2}$ = 1.65 V).

Radical inhibition experiments

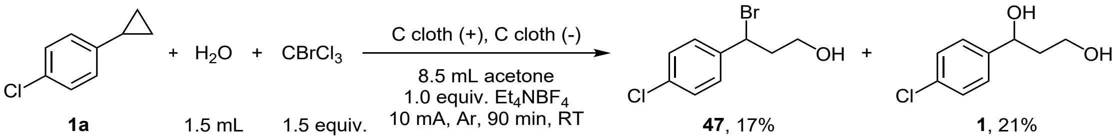


In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-chloro-4-cyclopropylbenzene **1a** (30.4 mg, 0.20 mmol, 1.0 equiv.), TEMPO (62.5 mg, 0.40 mmol, 2.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. The reaction system was monitored by TLC and NMR, and no desired product **1** could be detected.



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-chloro-4-cyclopropylbenzene **1a** (30.4 mg, 0.20 mmol, 1.0 equiv.), BHT (220.4 mg, 0.40 mmol, 2.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. The reaction system was monitored by TLC and NMR, and no desired product **1** could be detected.

Radical trapping experiment



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, 1-chloro-4-cyclopropylbenzene **1a** (30.5 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone, 1.5 Ml H_2O and $CBrCl_3$ (59.5 mg, 0.30 mmol, 1.5 equiv.) were added. Then the electrolysis system was stirred at a constant current of 10 Ma at room temperature for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1, v/v) to afford **47** (8.3 mg, 0.034 mmol, 17%) as yellow oil and **1** (8.0 mg, 0.042 mmol, 21%) as a pale-yellow solid. Radical trapping experiment provided solid evidence for the formation of the putative benzyl radical.

R_f = 0.20 (petroleum ether/ethyl acetate 10:1, v/v, **47**).

R_f = 0.20 (petroleum ether/ethyl acetate 1:1, v/v, **1**).

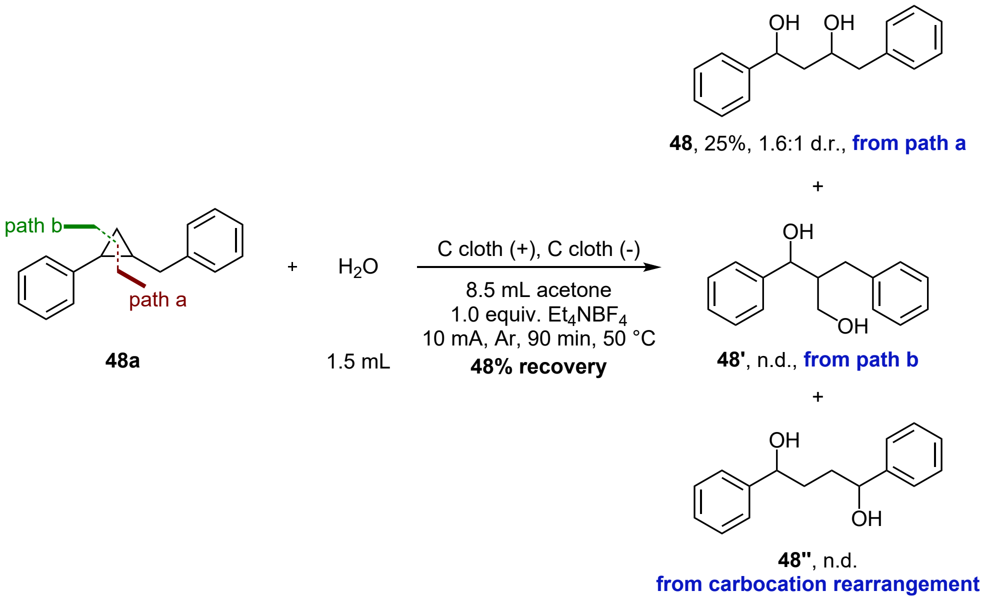
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 5.19 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.89 – 3.81 (m, 1H), 3.77 – 3.70 (m, 1H), 2.51 – 2.41 (m, 1H), 2.34 – 2.24 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 134.4, 129.1, 128.9, 60.7, 50.8, 42.3 ppm.

HRMS GC-EI (m/z) calculated for $C_9H_{10}BrClO$ $[M]^+$, 247.9598; found, 247.9598.

Selective ring-opening experiment



In an oven-dried undivided three-necked bottle (30 Ml) equipped with a stir bar, and two carbon cloths (15 mm × 15 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (43.4 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, (2-benzylcyclopropyl)benzene **48a** (41.7 mg, 0.20 mmol, 1.0 equiv.), 8.5 Ml acetone and 1.5 Ml H_2O were added. Then the electrolysis system was stirred at a constant current of 10 Ma at 50 °C for 90 min. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to afford **48** (12.3 mg, 0.156 mmol, 25%, 1.6:1 d.r., based on NMR) as yellow oil.[15, 116] And the product **48'** and **48''** were not be produced. Cyclopropane substrate was recovered in 48% yield.

R_f = 0.20 (petroleum ether/ethyl acetate 3:1, v/v).

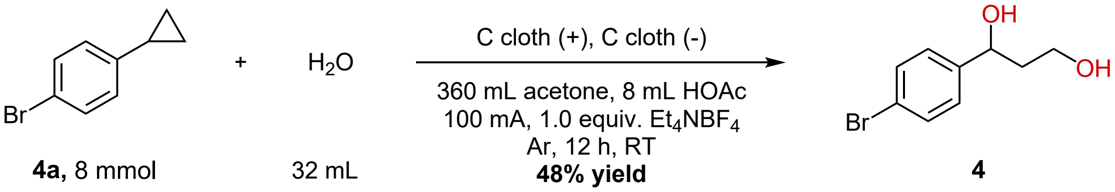
NMR Spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 16.24H), 5.08 (dd, *J* = 8.0, 3.2 Hz, 1H, *trans*-1,3-diol), 4.92 (dd, *J* = 9.2, 3.6 Hz, 0.61H, *cis*-1,3-diol), 4.22 – 4.03 (m, 1.63H), 2.86 – 2.76 (m, 3.30H), 2.03 – 1.82 (m, 3.34H) ppm.

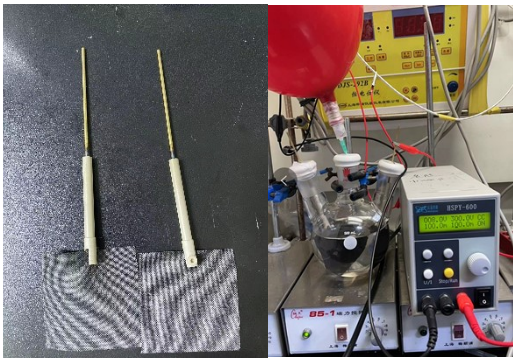
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 144.5, 129.6, 129.5, 128.8, 128.6, 128.6, 127.8, 127.5, 126.8, 126.8, 125.9, 125.7, 75.2, 73.7, 71.7, 70.1, 45.0, 44.7, 44.4, 44.1 ppm.

HRMS GC-EI (m/z) calculated for $C_{16}H_{18}O_2$ $[M]^+$, 242.1301; found, 242.1305.

6. Gram scale reactions



In an oven-dried three-necked bottle (500 Ml) equipped with a stir bar, and two carbon cloths (50 mm × 50 mm × 0.3 mm) as the anode and cathode. Et_4NBF_4 (1.74 g, 8 mmol, 1.0 equiv.) was added. The reaction system was degassed via vacuum evacuation and backfilled with argon three times. Subsequently, **4a** (1.58 g, 8 mmol), 360 Ml acetone, 32 Ml H_2O and 8.0 Ml HOAc were added. Then the electrolysis system was stirred at a constant current of 100 Ma at room temperature for 12 hours. When the reaction finished, the reaction mixture was concentrated in vacuo, and purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (1:1, v/v) to give the product **4** as yellow oil (48% yield, 0.89 g).



7. References

1. Gieuw, M. H.; Ke, Z.; Yeung, Y.-Y. Lewis Base-Promoted Ring-Opening 1,3-Dioxygenation of Unactivated Cyclopropanes Using a Hypervalent Iodine Reagent. *Angew. Chem. Int. Ed.* **2018**, *57*, 3782-3786.

2. Petzold, D.; Singh, P.; Almqvist, F.; König, B. Visible‐Light‐Mediated Synthesis of β‐Chloro Ketones from Aryl Cyclopropanes. *Angew. Chem. Int. Ed.* **2019**, *58*, 8577-8580.

3. Cheng, Y. Y.; Yu, J. X.; Lei, T.; Hou, H. Y.; Chen, B.; Tung, C. H.; Wu, L. Z. Direct 1,2‐Dicarbonylation of Alkenes towards 1,4‐Diketones via Photocatalysis. *Angew. Chem. Int. Ed.* **2021**, *60*, 26822-26828.

4. Zhai, S.; Qiu, S.; Yang, S.; Gao, X.; Feng, X.; Yun, C.; Han, N.; Niu, Y.; Wang, J.; Zhai, H., Facile access to β-hydroxyl ketones via a cobalt-catalyzed ring-opening/hydroxylation cascade of cyclopropanols. *Chinese Chemical Letters* **2023,** 34.

5. Kumar, M.; Shah, B. A.; Taneja, S. C. Tandem Catalysis by Lipase in a Vinyl Acetate-Mediated Cross-Aldol Reaction. *Adv. Synth. Catal.* **2011**, *353*, 1207-1212.

6. Kim, J.; De Castro, K. A.; Lim, M.; Rhee, H. Reduction of Aromatic and Aliphatic Keto Esters Using Sodium Borohydride/MeOH at Room Temperature: A Thorough Investigation. *Tetrahedron Lett.* **2010**, *66*, 3995-4001.

7. Cherian, J.; Choi, I.; Nayyar, A.; Manjunatha, U. H.; Mukherjee, T.; Lee, Y. S.; Boshoff, H. I.; Singh, R.; Ha, Y. H.; Goodwin, M.; Lakshminarayana, S. B.; Niyomrattanakit, P.; Jiricek, J.; Ravindran, S.; Dick, T.; Keller, T. H.; Dartois, V.; Barry, C. E. Structure–Activity Relationships of Antitubercular Nitroimidazoles. 3. Exploration of the Linker and Lipophilic Tail of ((*S*)-2-Nitro-6,7-dihydro-5H-imidazo[2,1-*b*][1,3]oxazin-6-yl)-(4-trifluoromethoxybenzyl)amine (6-Amino PA-824). *J. Med. Chem.* **2011**, *54*, 5639-5659.

8. K. Raja R.; Michael C. M.; Bheemarao G. U.; Jorge E. Gómez-Galeno.; Jay D.; Kristin O.; Zhili S.; William C.; Timothy J. C.; James M. F.; Serge H. B.; Paul D. van P. and Mark D. E. Pradefovir: A Prodrug That Targets Adefovir to the Liver for the Treatment of Hepatitis B. *J. Med. Chem.* **2008,** *51,* 666–676.

9. Kim, J. H.; Čorić, I.; Palumbo, C.; List, B. Resolution of Diols via Catalytic Asymmetric Acetalization. *J. Am. Chem. Soc.* **2015**, *137*, 1778-1781.

10. Brioche, J. One-Pot Synthesis of Tertiary Alkyl Fluorides From Methyl Oxalates by Radical Deoxyfluorination Under Photoredox Catalysis. *Tetrahedron Lett.* **2018**, *59*, 4387-4391.

11. Han, W.-B.; Wu, Y. Facile Perhydrolysis of Oxetanes Catalyzed by Molybdenum Species. *Org. Lett.* **2014**, *16*, 5706-5709.

12. Zhu, Y.; Zhang, Z.; Jin, R.; Liu, J.; Liu, G.; Han, B.; Jiao, N. DMSO‐Enabled Selective Radical O−H Activation of 1,3(4)‐Diols. *Angew. Chem. Int. Ed.* **2020**, *59*, 19851-19856.

13. Solé, C.; Tatla, A.; Mata, J. A.; Whiting, A.; Gulyás, H.; Fernández, E. Catalytic 1,3-Difunctionalisation of Organic Backbones through a Highly Stereoselective, One-Pot, Boron Conjugate-Addition/Reduction/Oxidation Process. *Chem. Eur. J.* **2011,** *17*, 14248-14257.

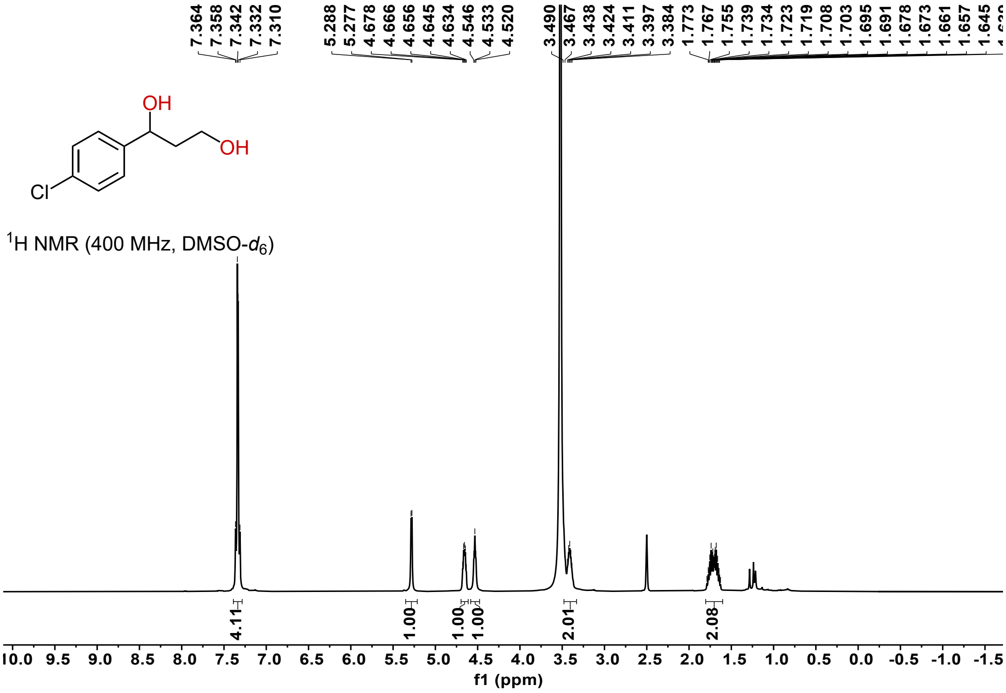
14. Yuanda H.; Hiep H. N.; William R. S.; and Junha J. Ligand-Controlled, Norbornene-Mediated, Regio- and Diastereoselective Rhodium-Catalyzed Intramolecular Alkene Hydrosilylation Reactions. *Org. Lett.* **2013**, *15*, 3412-3415.

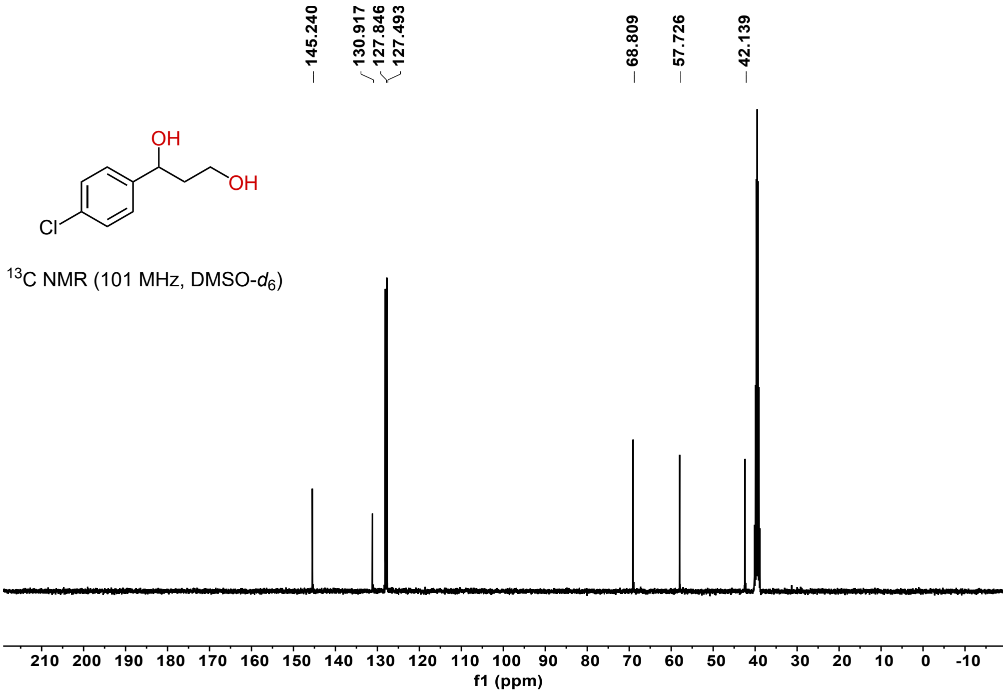
15. Pan, L.; Zheng, L.; Chen, Y.; Ke, Z.; Yeung, Y. Y., A Mechanochemical, Catalyst‐Free Cascade Synthesis of 1,3‐Diols and 1,4‐Iodoalcohols Using Styrenes and Hypervalent Iodine Reagents. *Angew. Chem. Int. Ed.* **2022**, 61, e2022079. DOI：10.1002/anie.202207926.

16. Chatla N., M. Rama R., Max H. and George W. K. Diastereoselective Reduction of β-Hydroxyketones with Amineboranes in the presence of Lithium Perchlorate. *Tetrahedron Lett.* **1997***, 36,* 7705-7708*.*

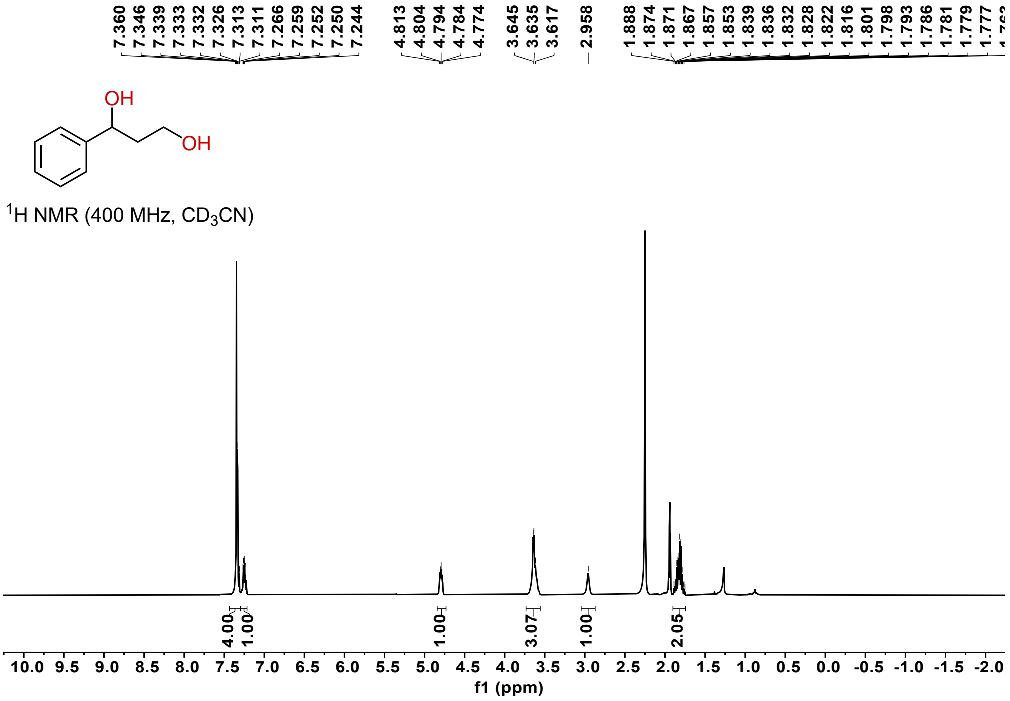
8. NMR spectra of products

1-(4-Chlorophenyl)propane-1,3-diol (1)

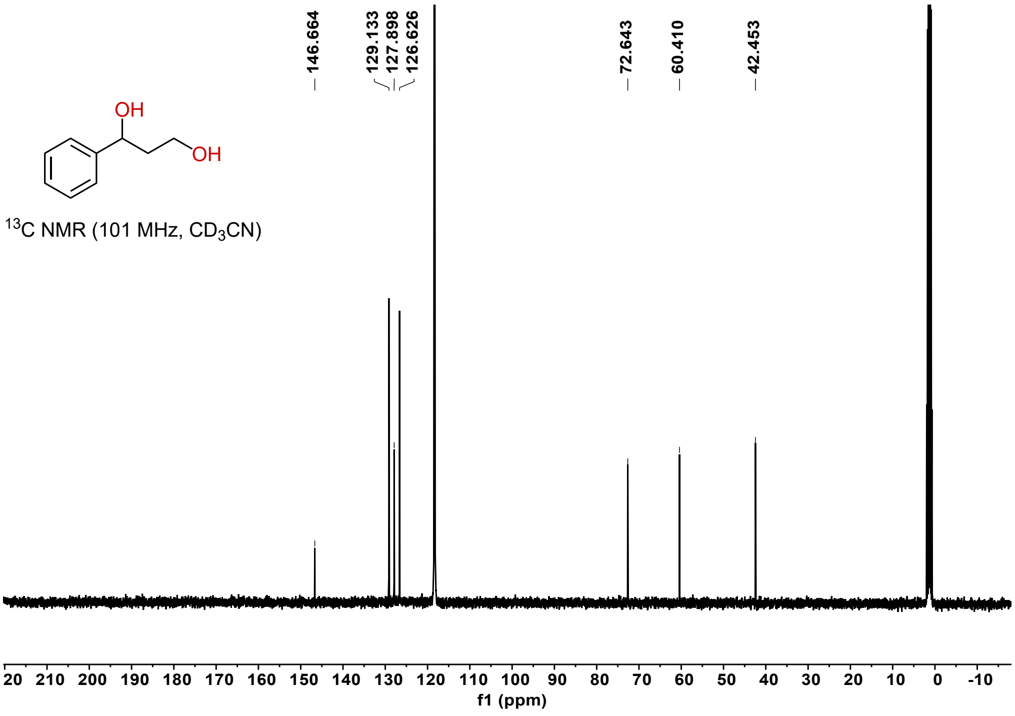

^{1}H NMR (400 MHz, DMSO-d_6)


^{13}C NMR (101 MHz, DMSO-d_6)

1-Phenylpropane-1,3-diol (2)

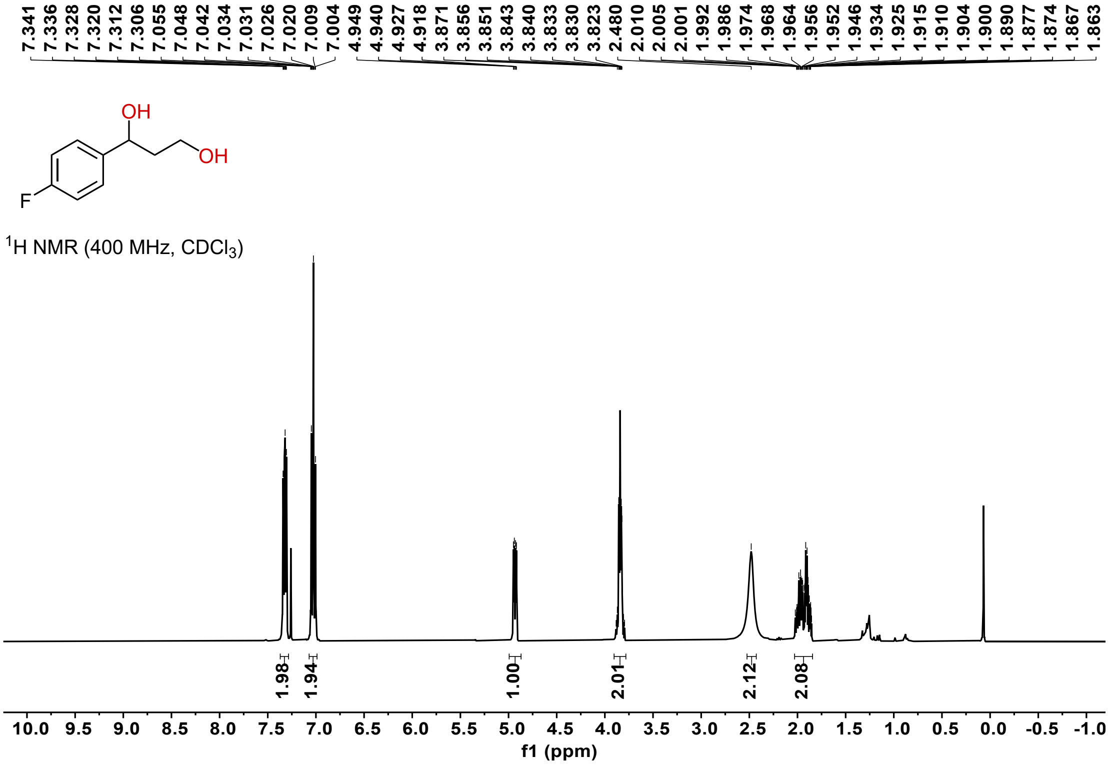


^{1}H NMR (400 MHz, CD_3CN)

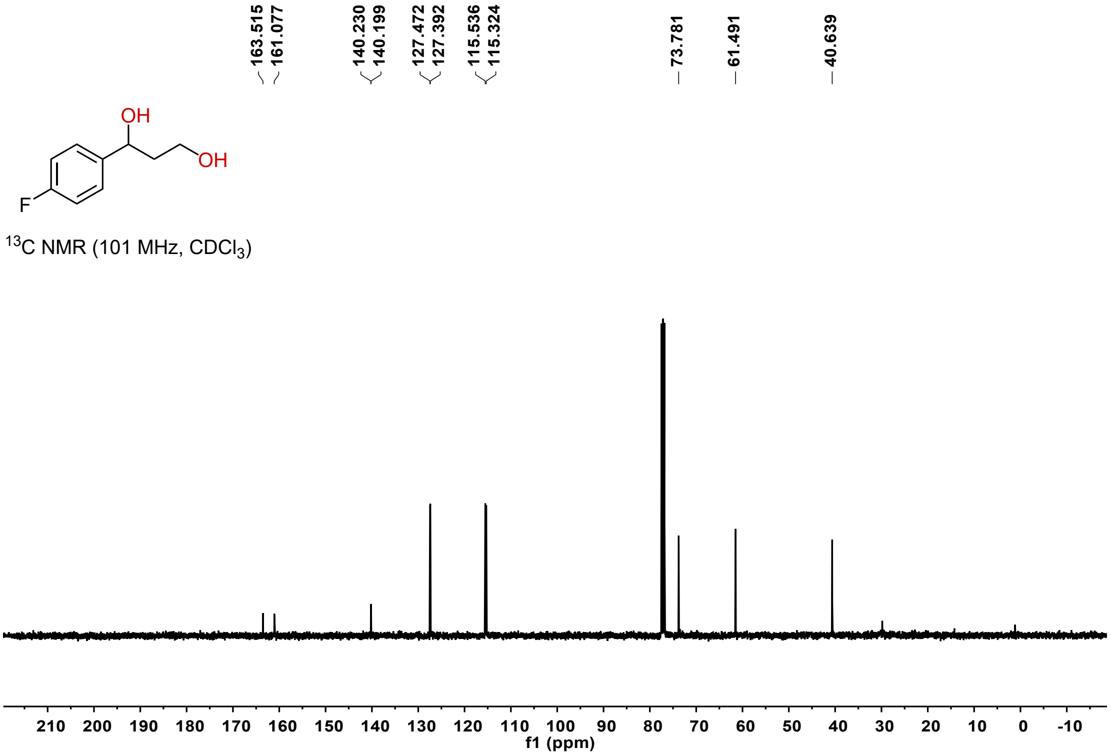


^{13}C NMR (101 MHz, CD_3CN)

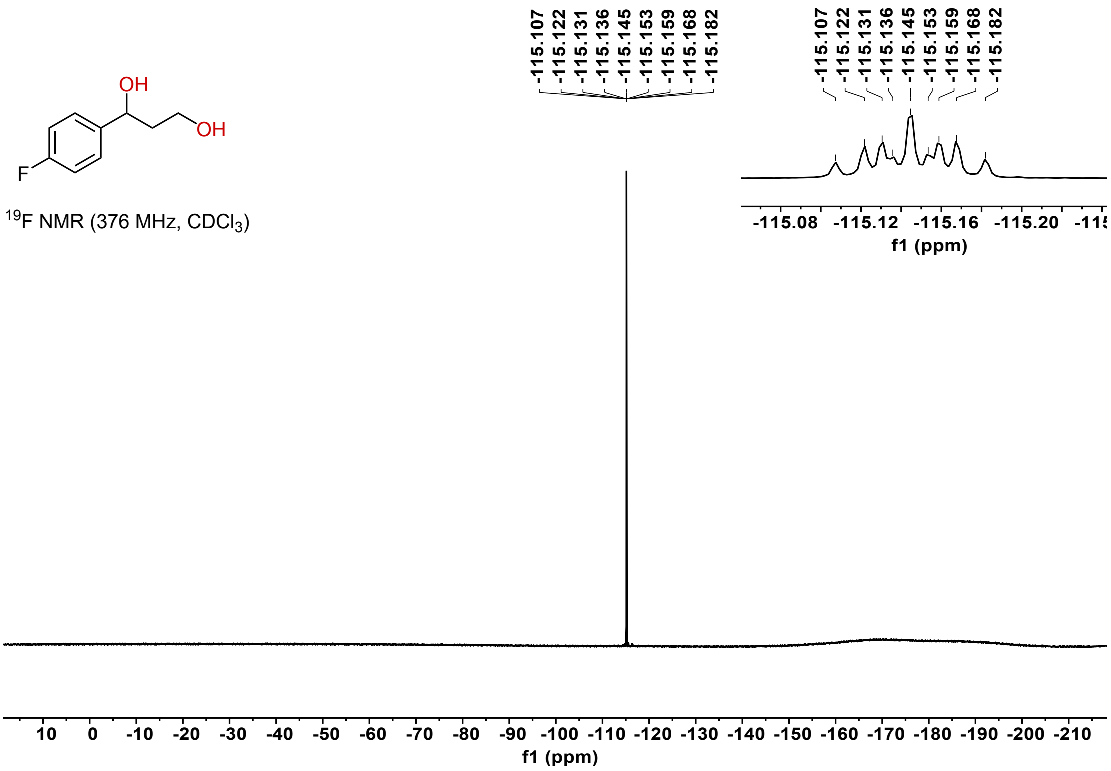
1-(4-Fluorophenyl)propane-1,3-diol (3)



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

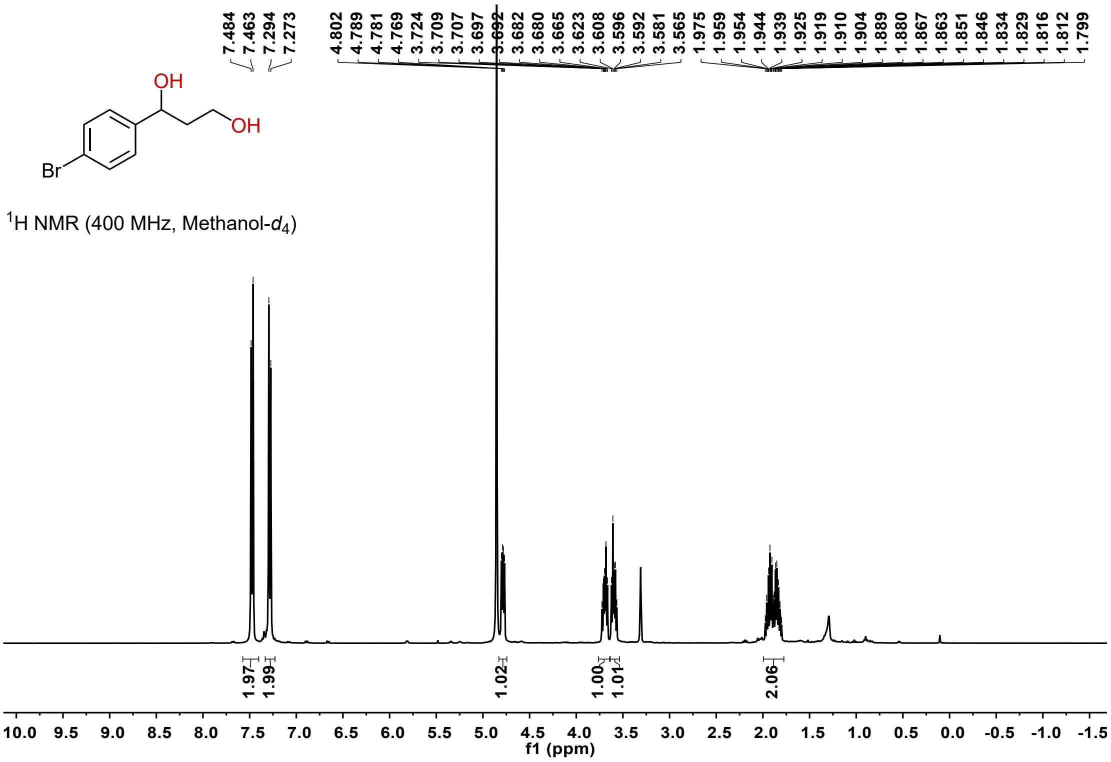


^{13}C NMR (101 MHz, CDCl$_3$)

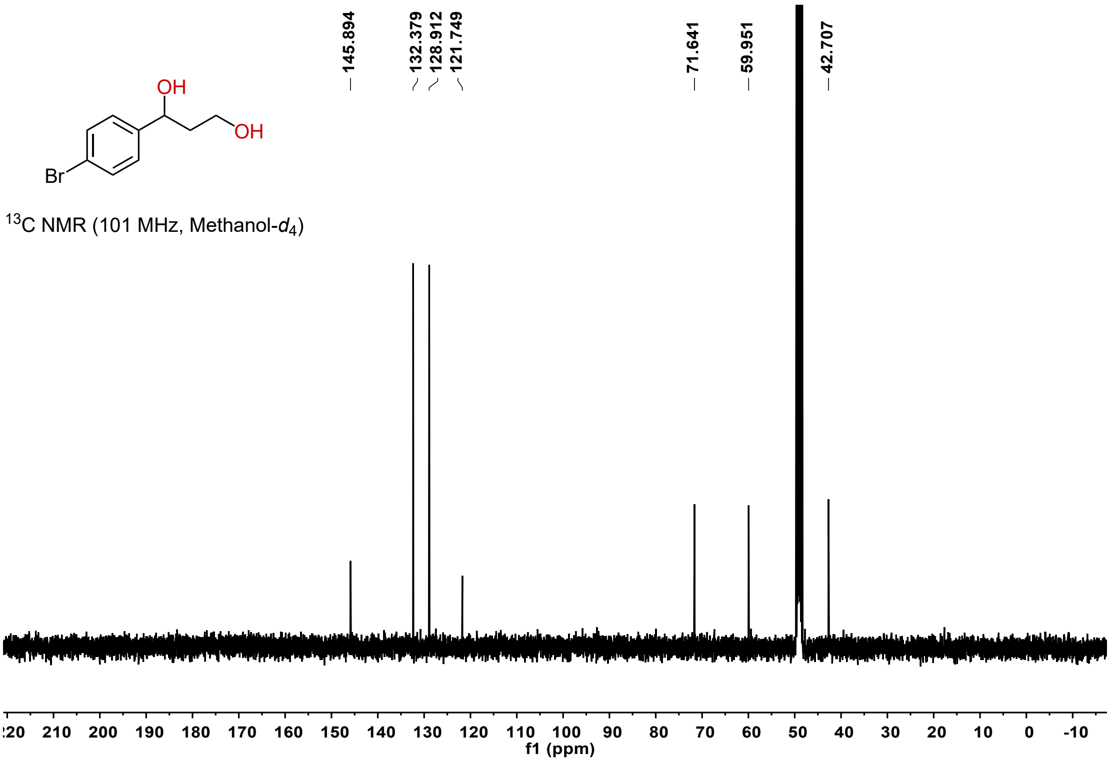


^{19}F NMR (376 MHz, CDCl$_3$)

1-(4-Bromophenyl)propane-1,3-diol (4)

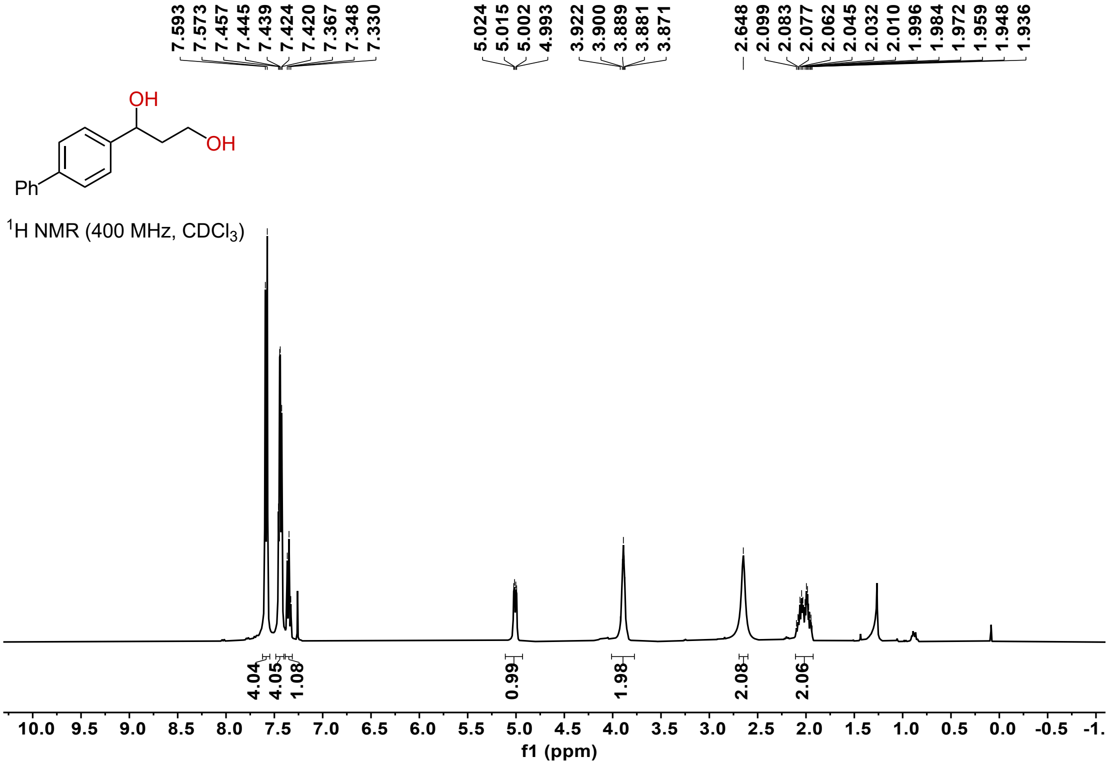


^{1}H NMR (400 MHz, Methanol-d_4)

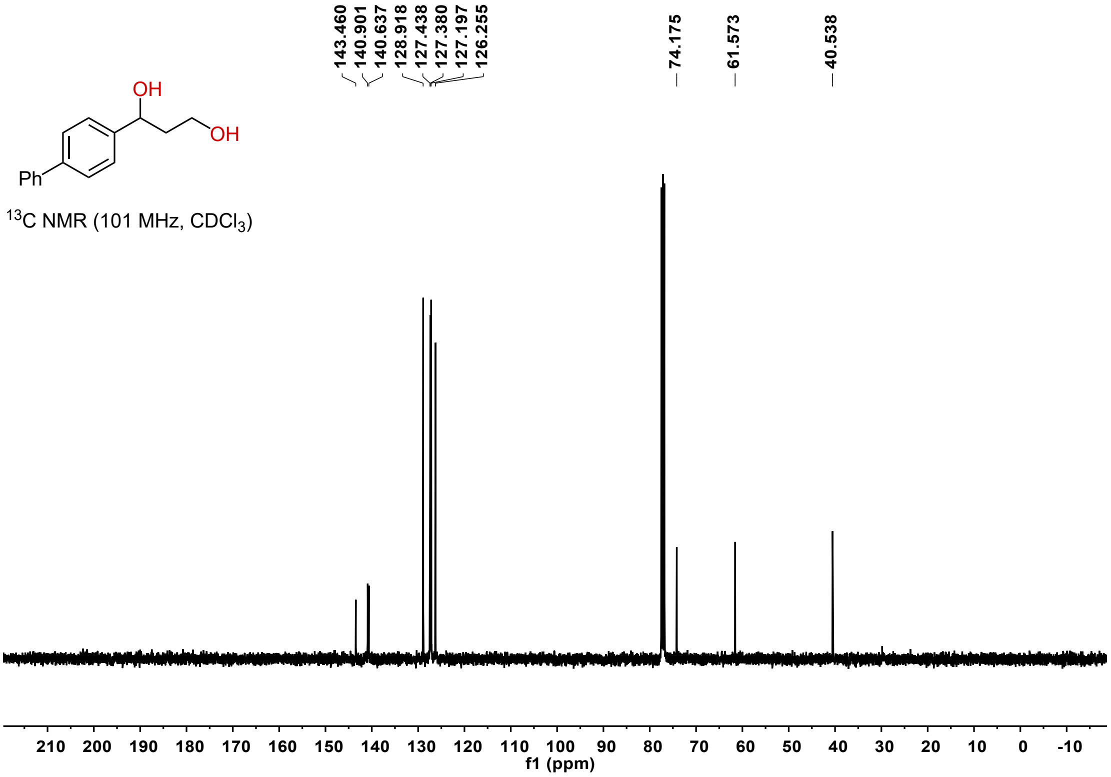


^{13}C NMR (101 MHz, Methanol-d_4)

1-([1,1’-Biphenyl]-4-yl)propane-1,3-diol (5)

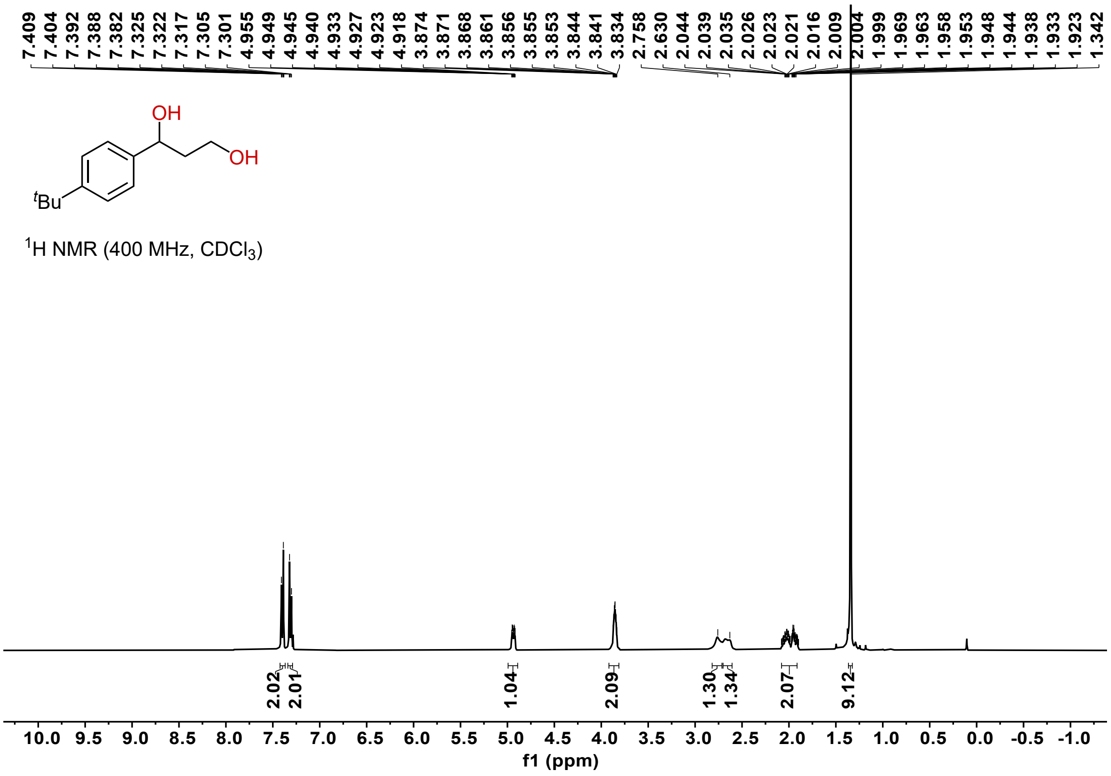


^{1}H NMR (400 MHz, $CDCl_3$)

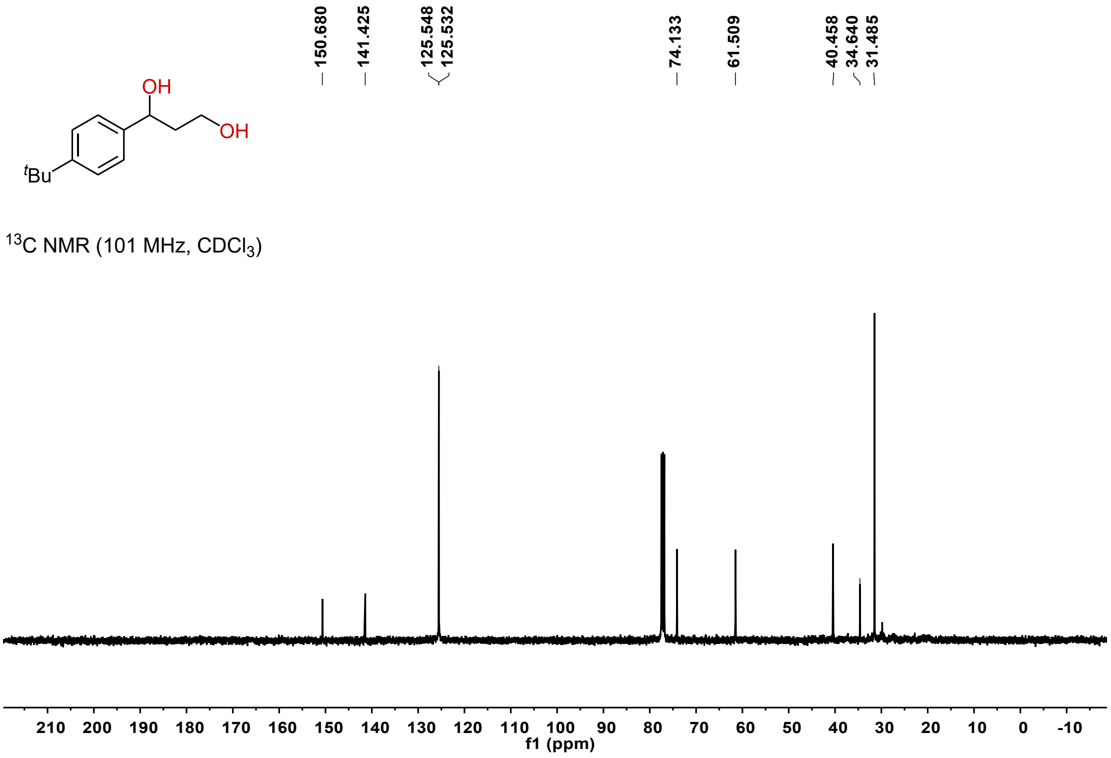


^{13}C NMR (101 MHz, $CDCl_3$)

1-(4-(tert-Butyl)phenyl)propane-1,3-diol (6)

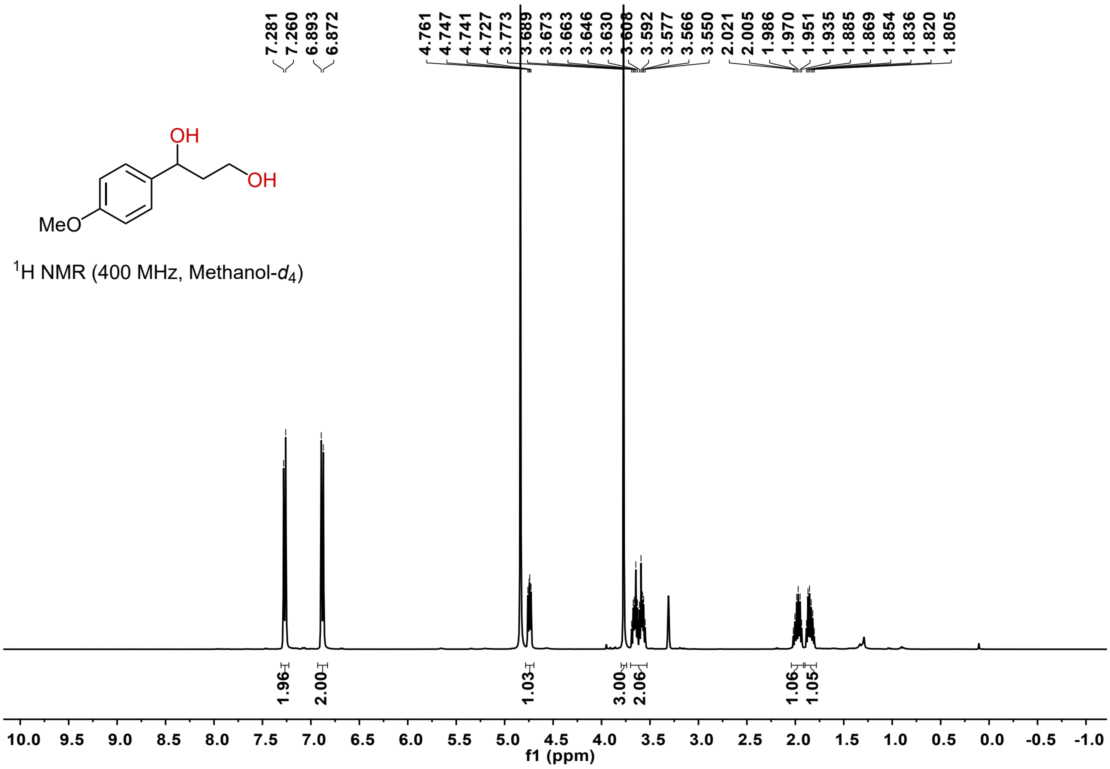


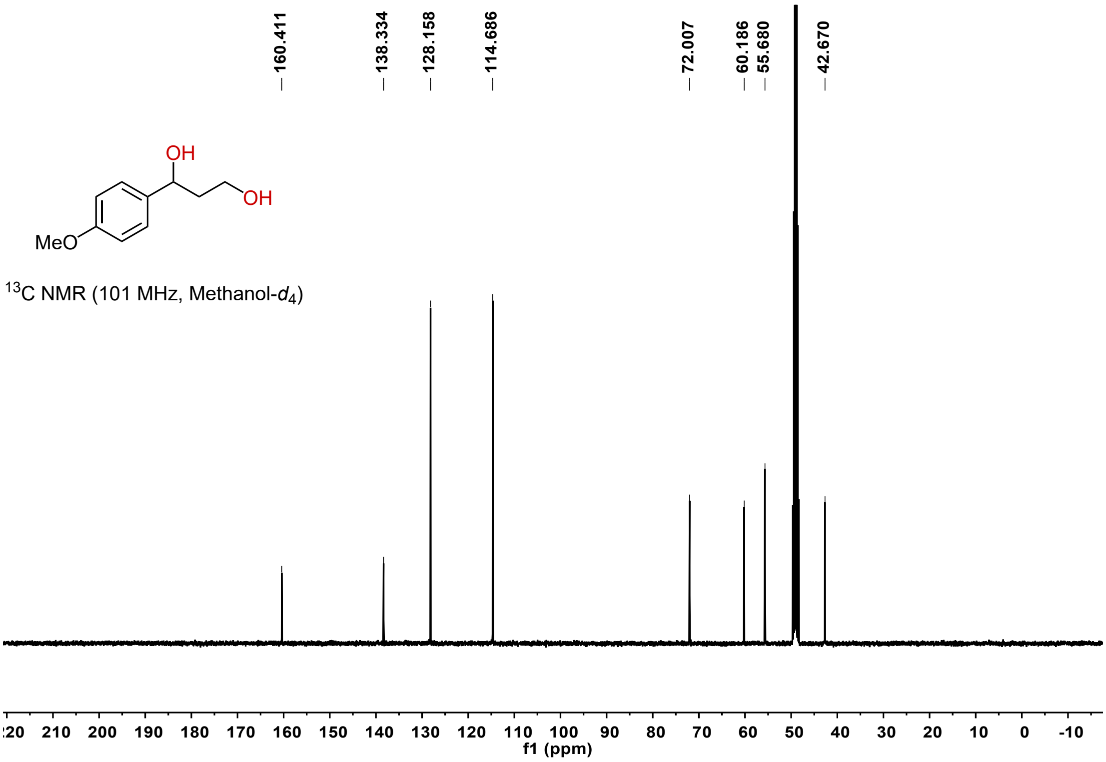
^{1}H NMR (400 MHz, CDCl$_3$)



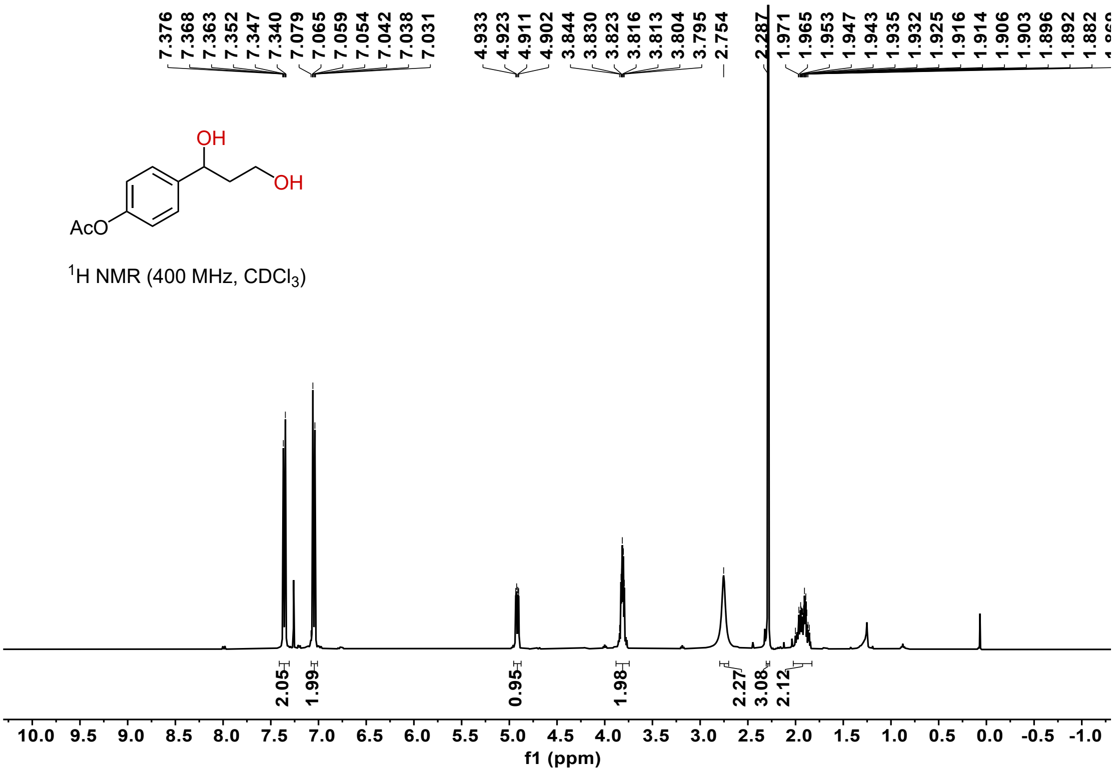
^{13}C NMR (101 MHz, CDCl$_3$)

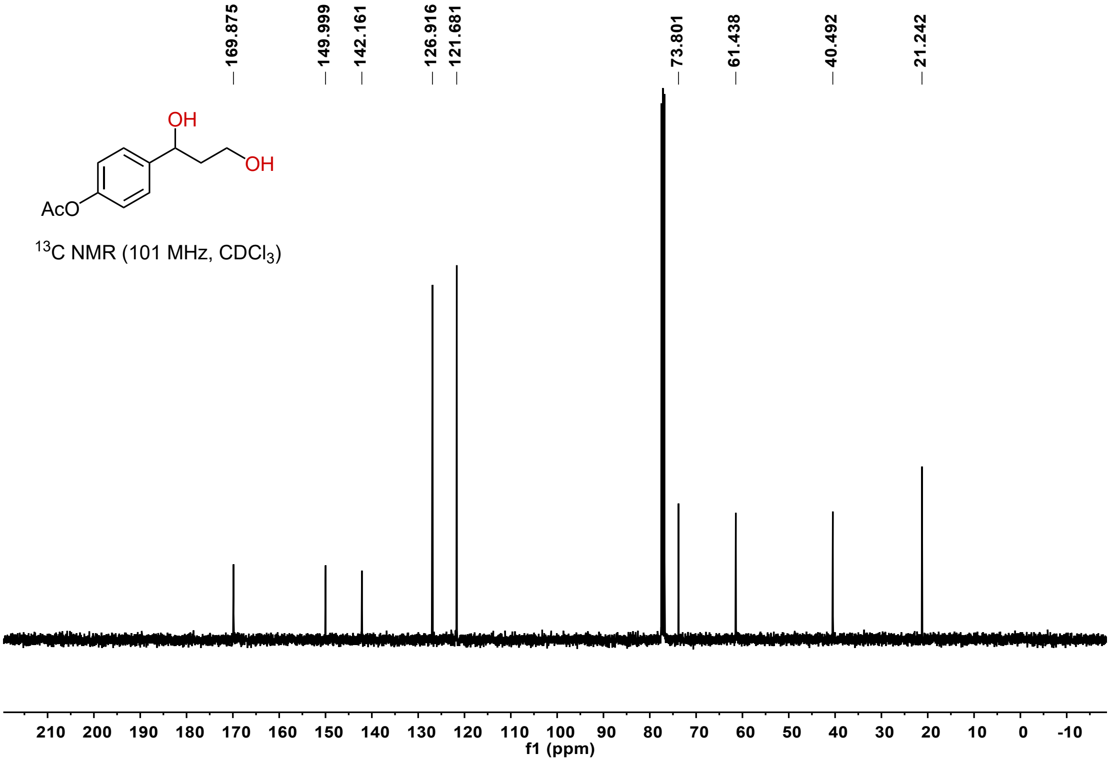
1-(4-Methoxyphenyl)propane-1,3-diol (7)



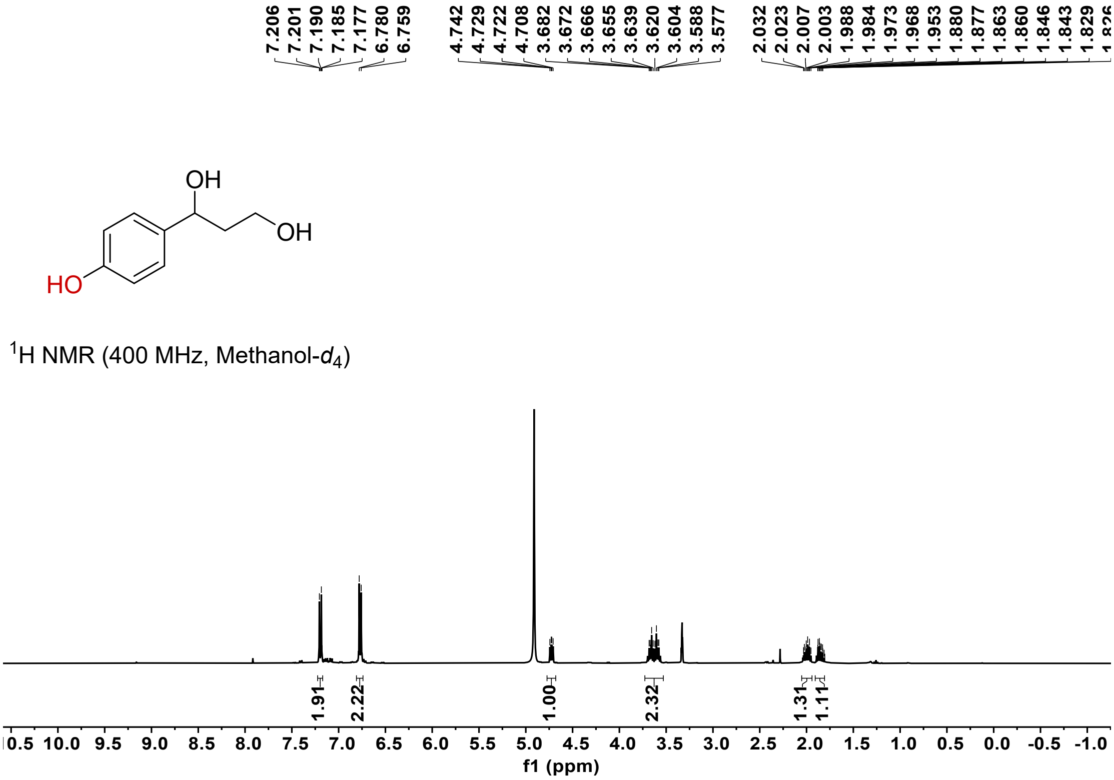


1-(4-Acetyloxyphenyl)propane-1,3-diol (8)



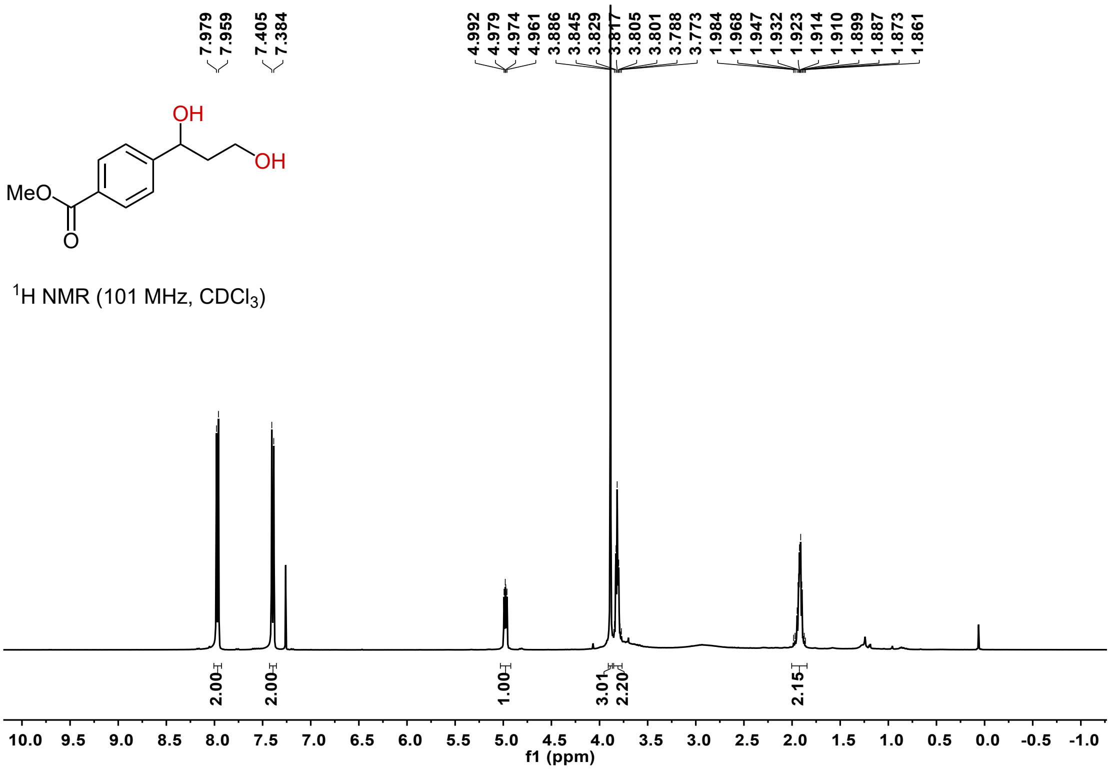


1-(4-hydroxyphenyl)propane-1,3-diol (8s)

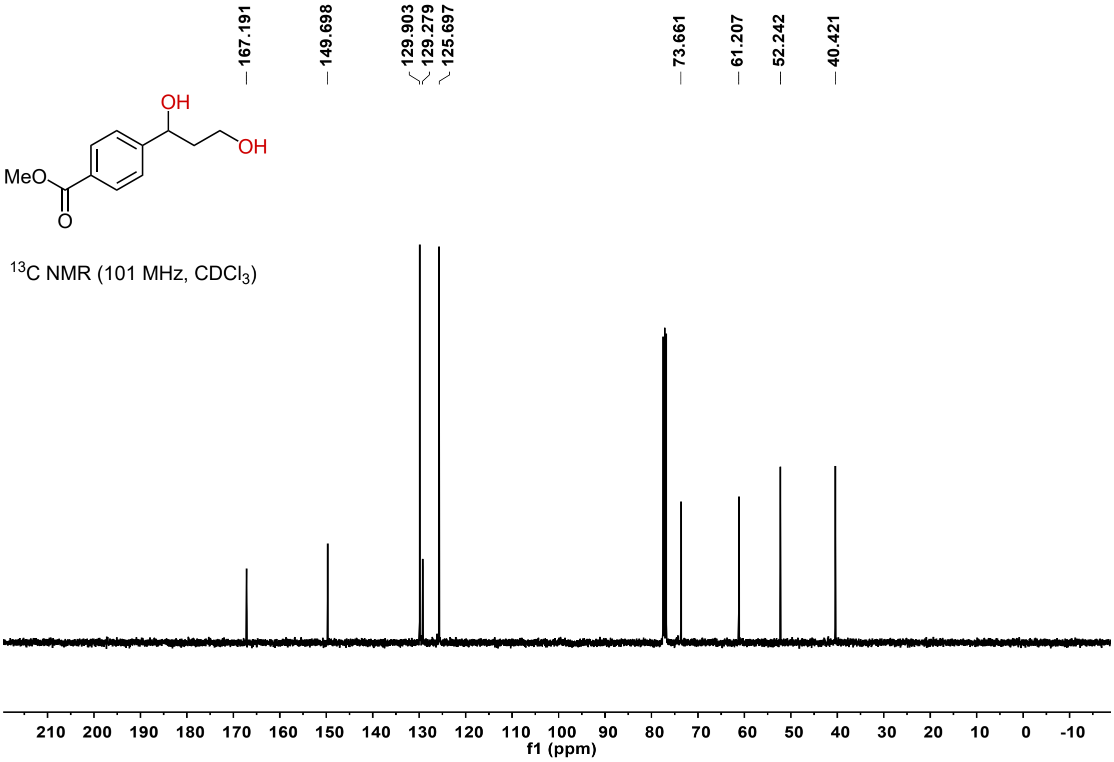


^{1}H NMR (400 MHz, Methanol-d_4)

1-(4-Carbomethoxyphenyl)propane-1,3-diol (9)

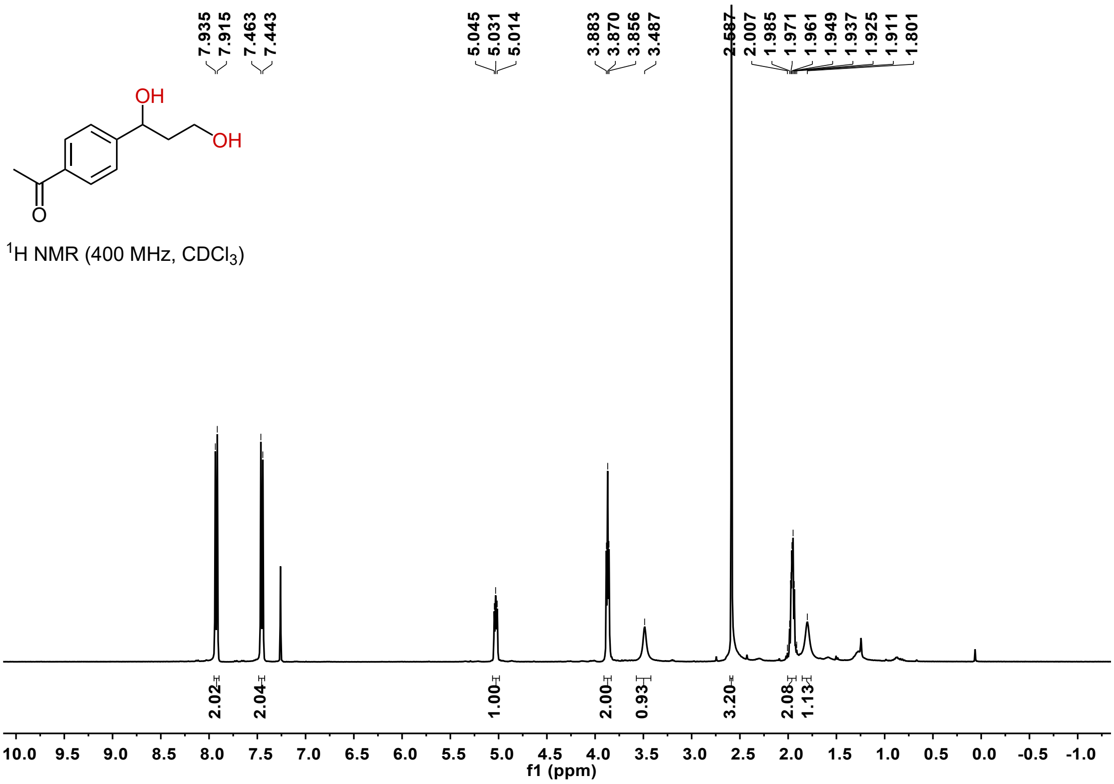


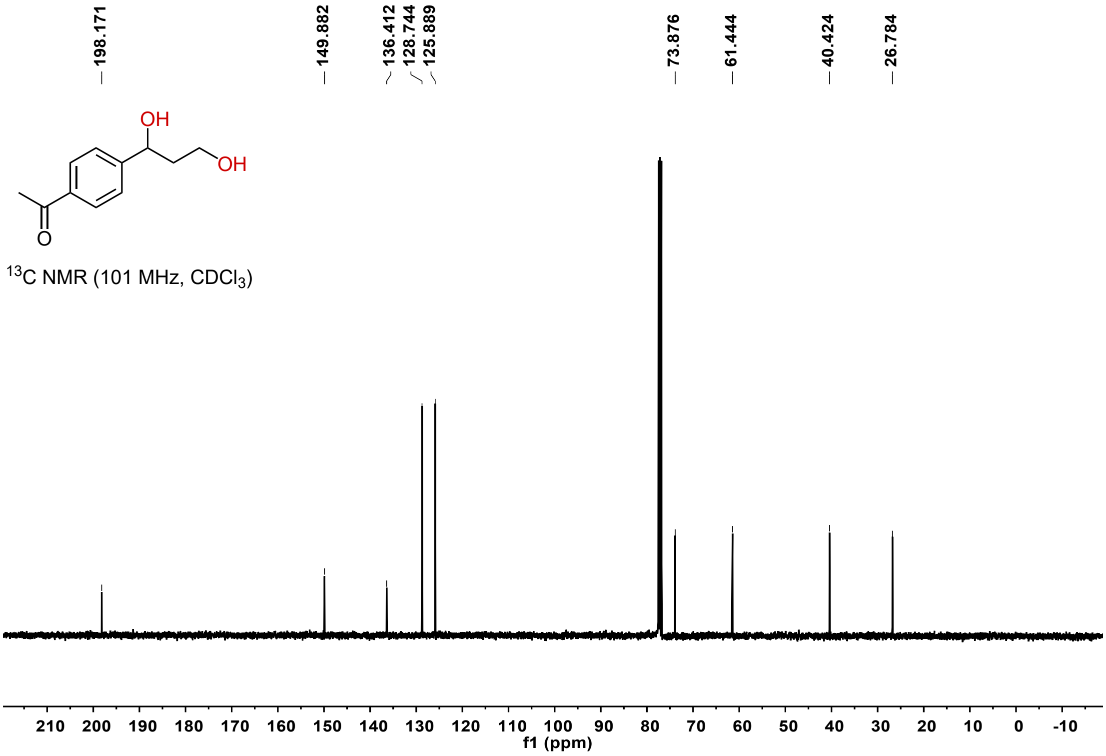
^{1}H NMR (101 MHz, $CDCl_3$)



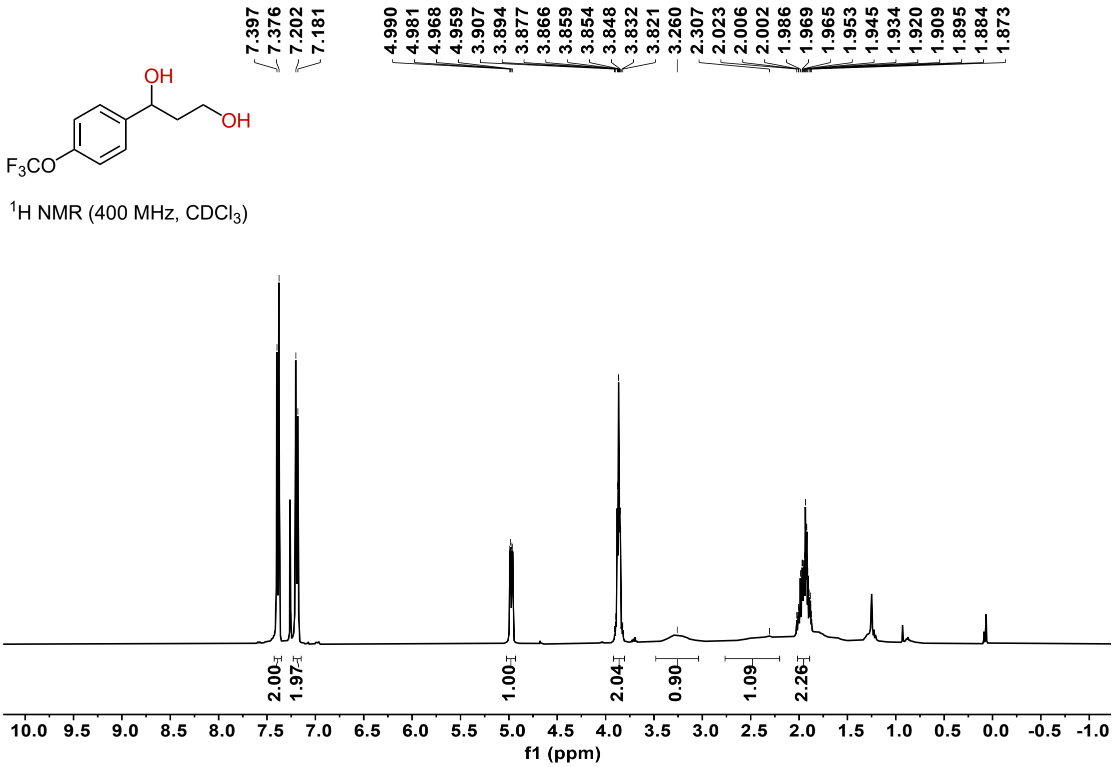
^{13}C NMR (101 MHz, $CDCl_3$)

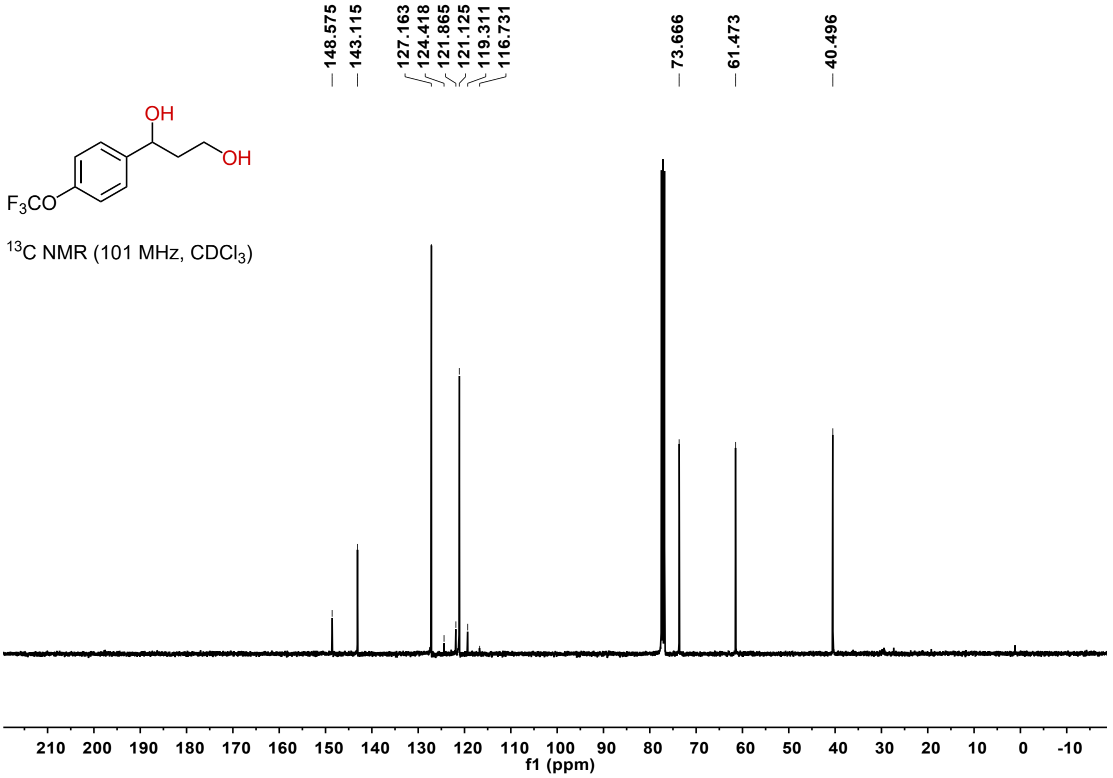
1-(4-Acetylphenyl)propane-1,3-diol (10)

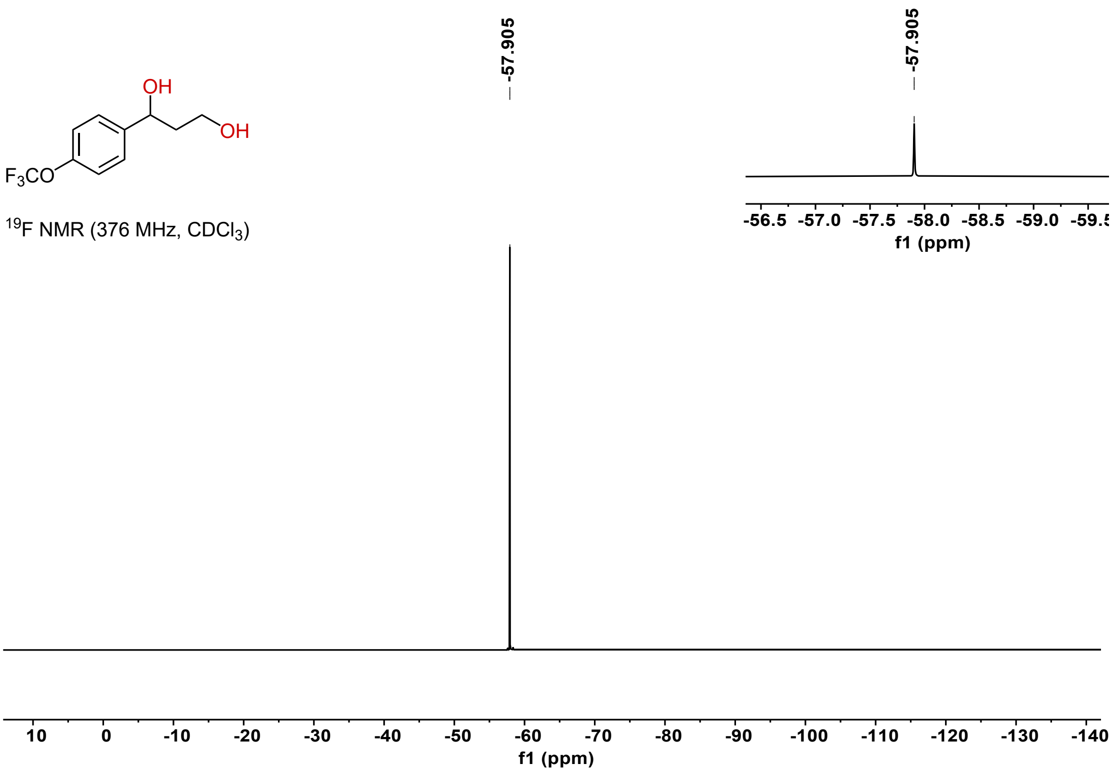




1-(4-Trifluoromethoxyphenyl)propane-1,3-diol (11)

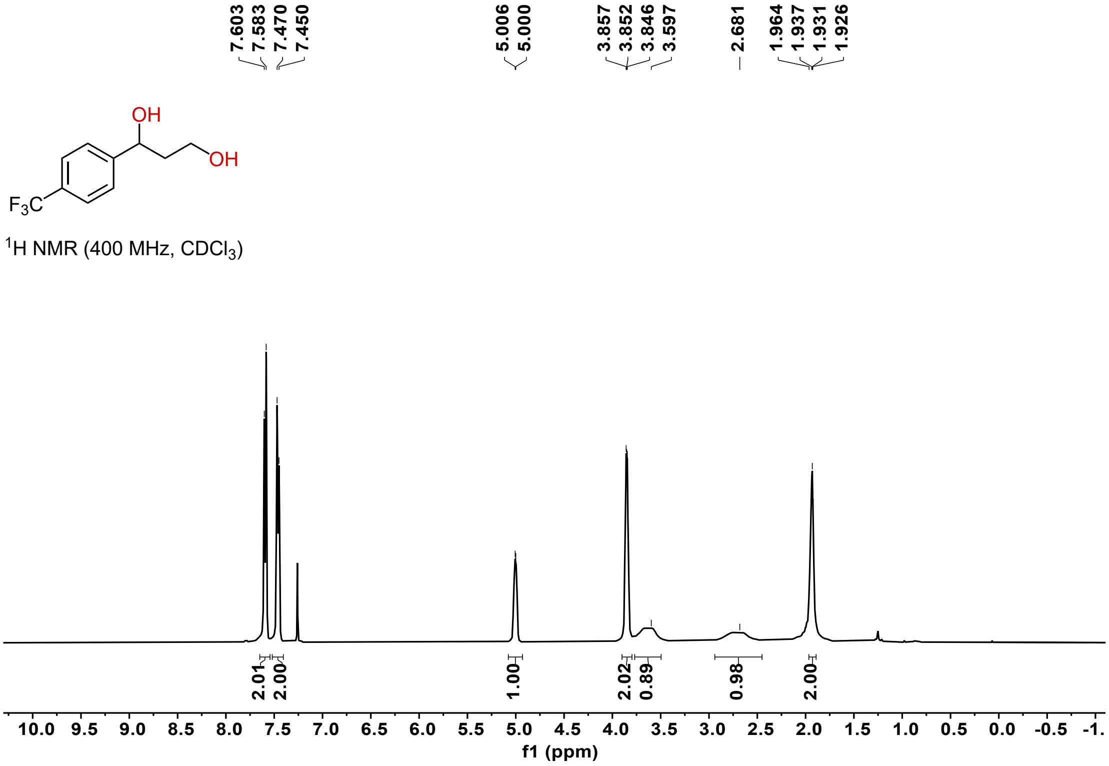




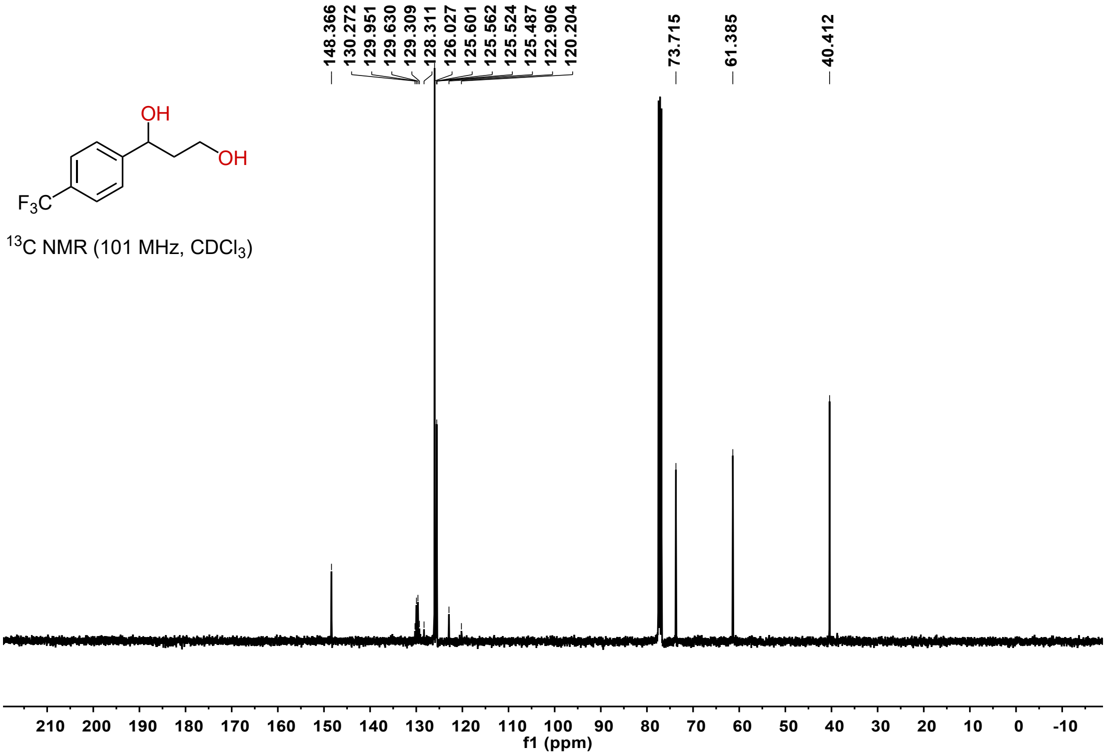


^{19}F NMR (376 MHz, $CDCl_3$)

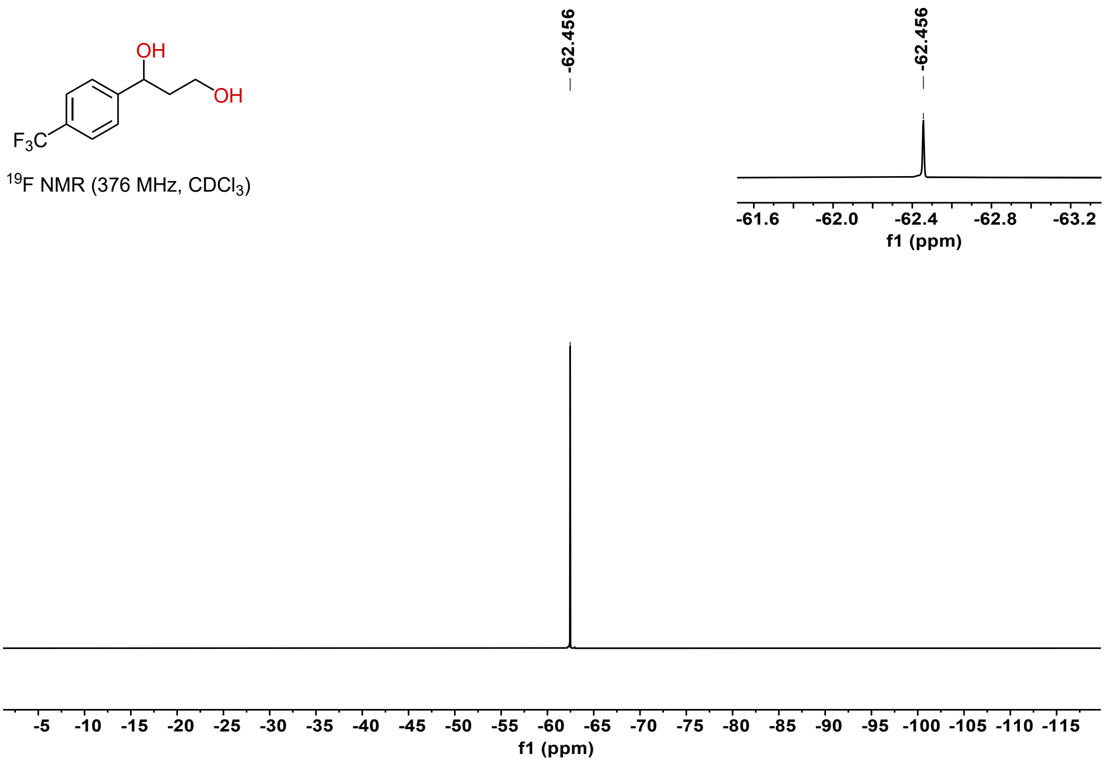
1-(4-Trifluoromethylphenyl)propane-1,3-diol (12)



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

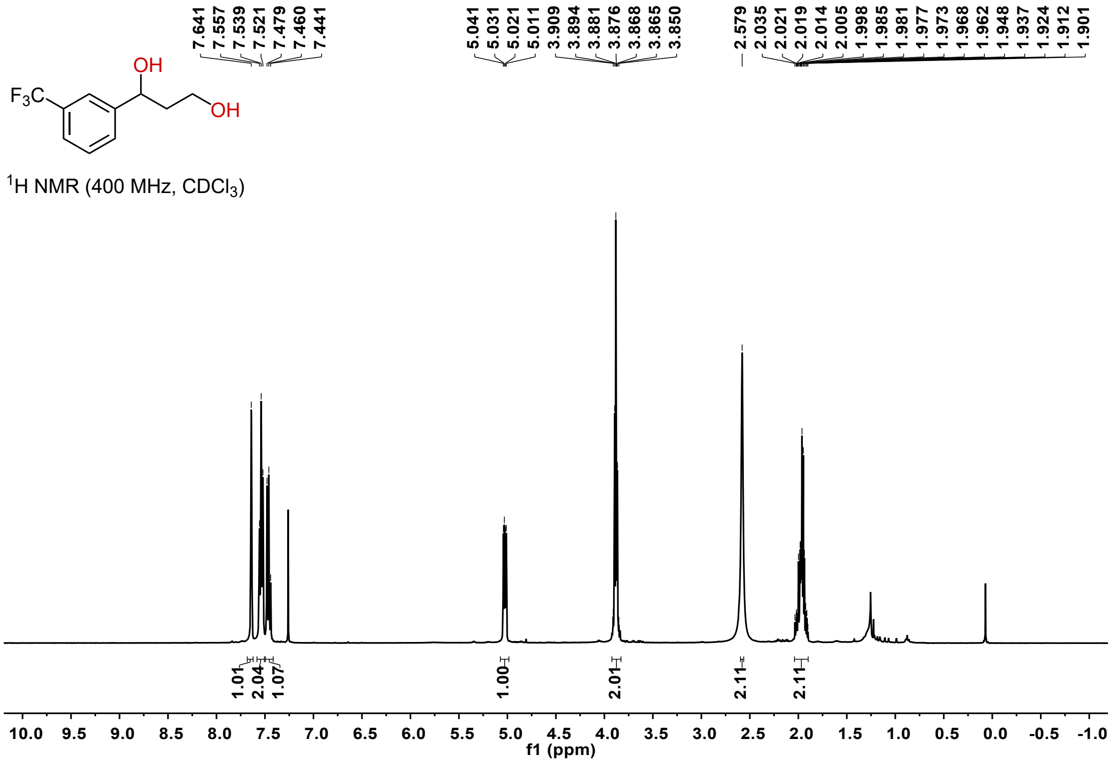


^{13}C NMR (101 MHz, CDCl$_3$)

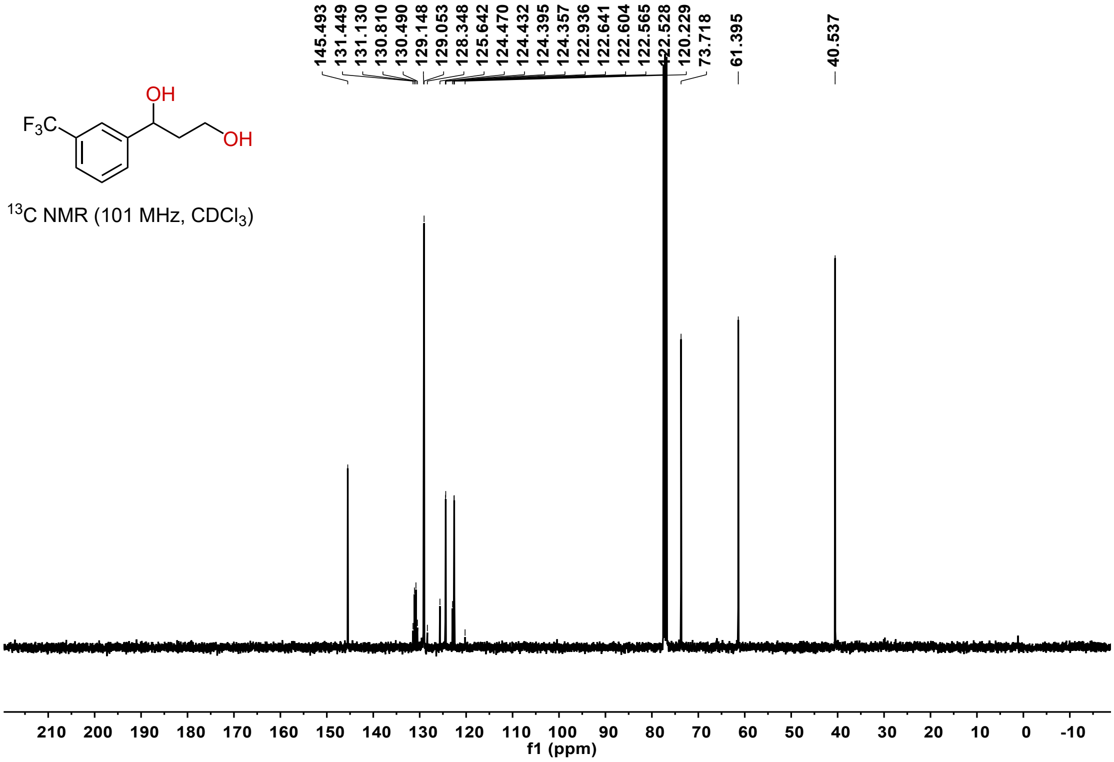


^{19}F NMR (376 MHz, $CDCl_3$)

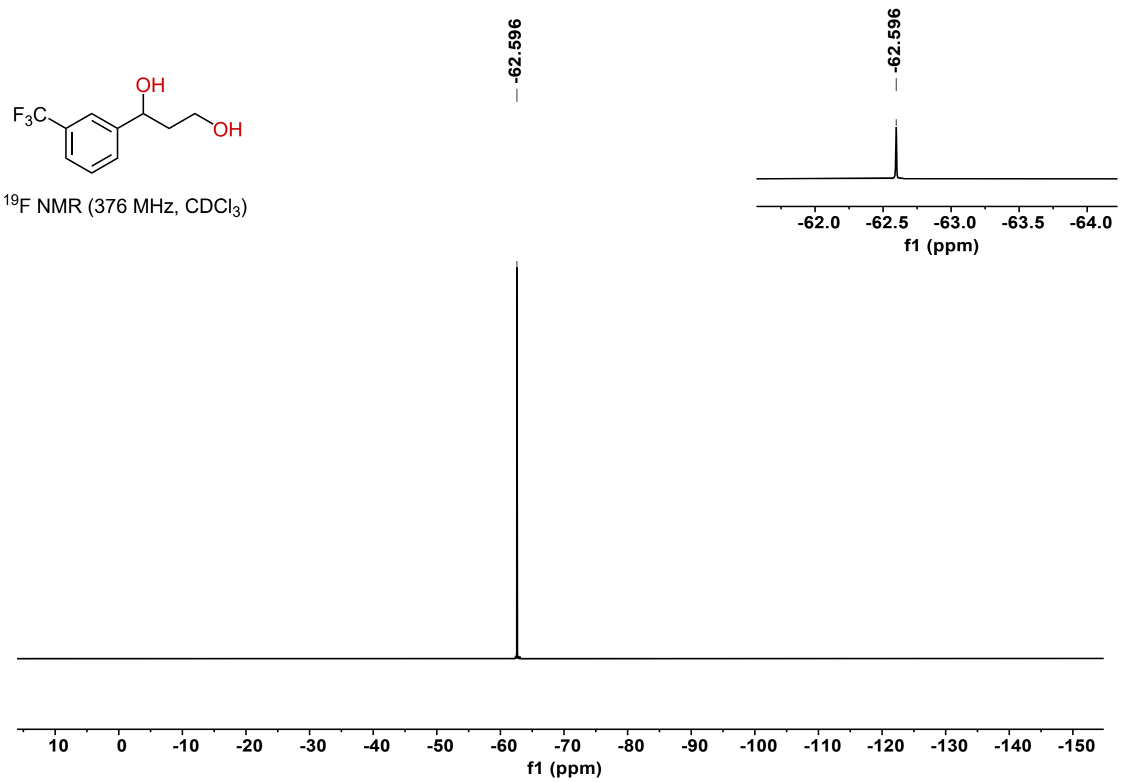
1-(3-Trifluoromethylphenyl)propane-1,3-diol (13)



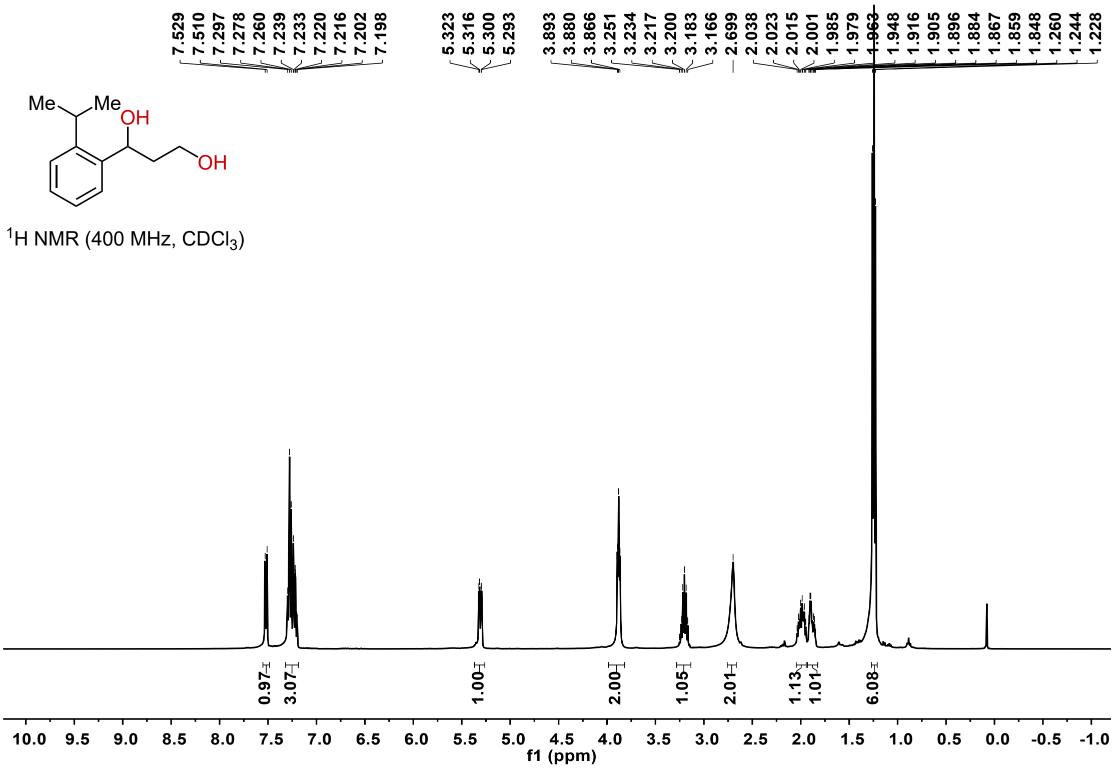
^{1}H NMR (400 MHz, CDCl$_3$)



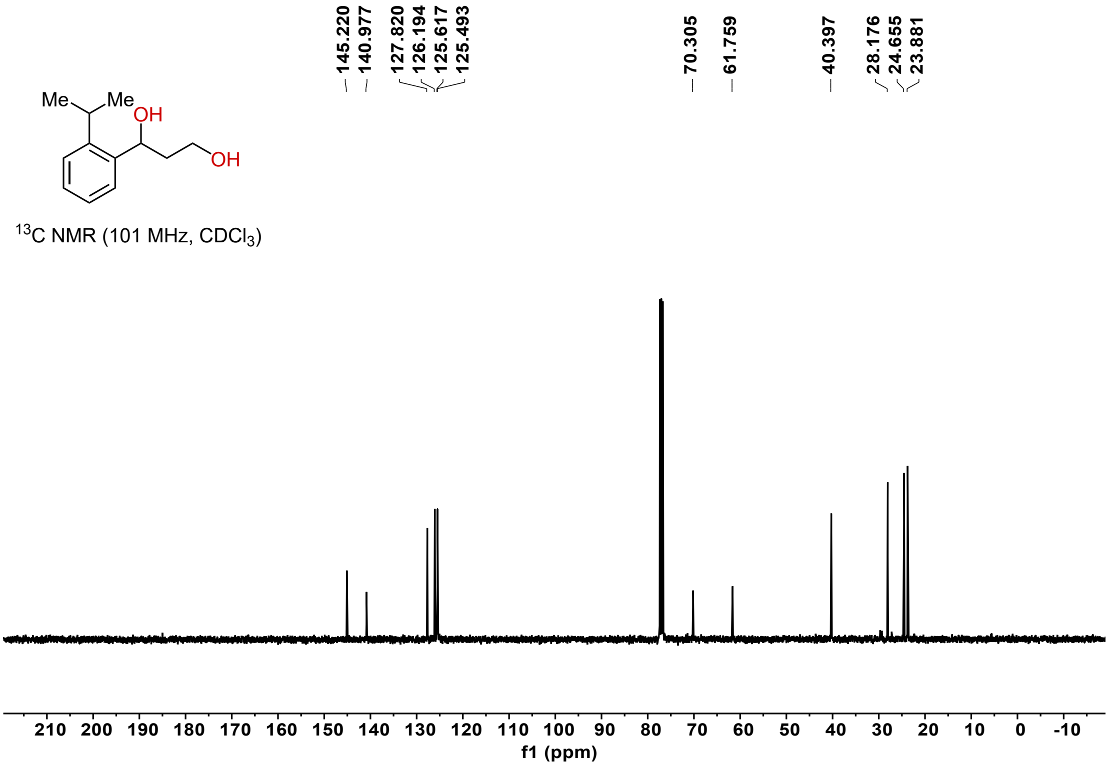
^{13}C NMR (101 MHz, CDCl$_3$)


F3C
OH
OH
19F NMR (376 MHz, CDCl3)
-62.596
-62.596
-62.0 -62.5 -63.0 -63.5 -64.0
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

1-(2-Isopropylphenyl)propane-1,3-diol (14)

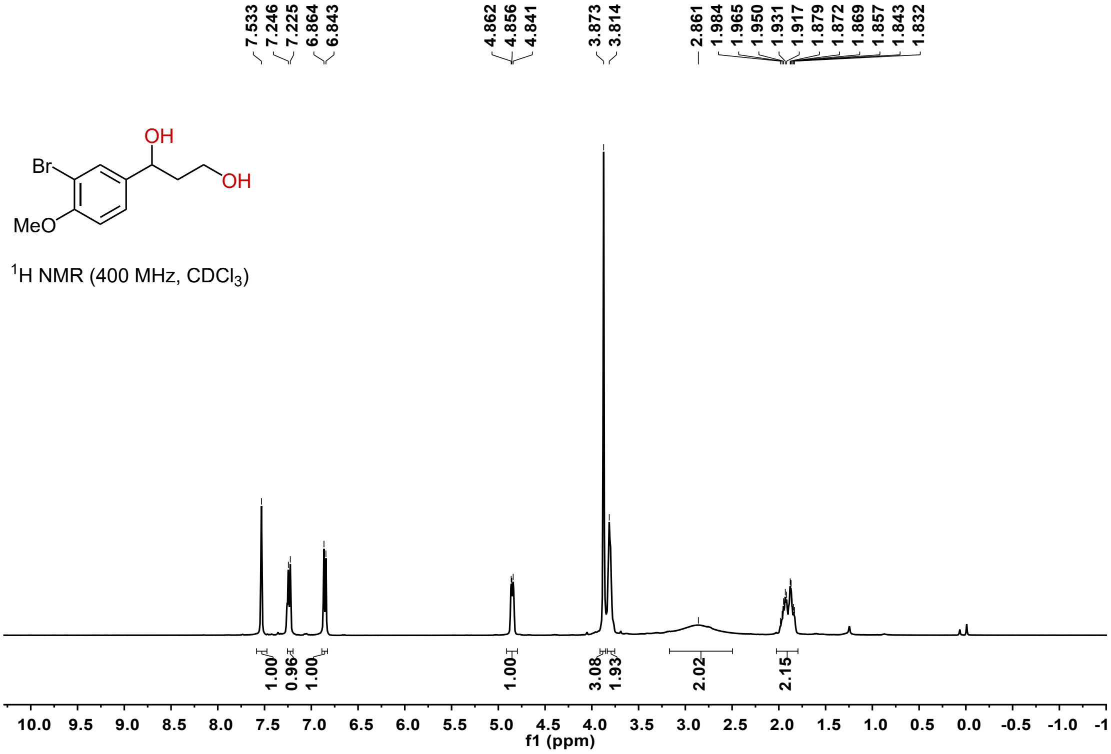


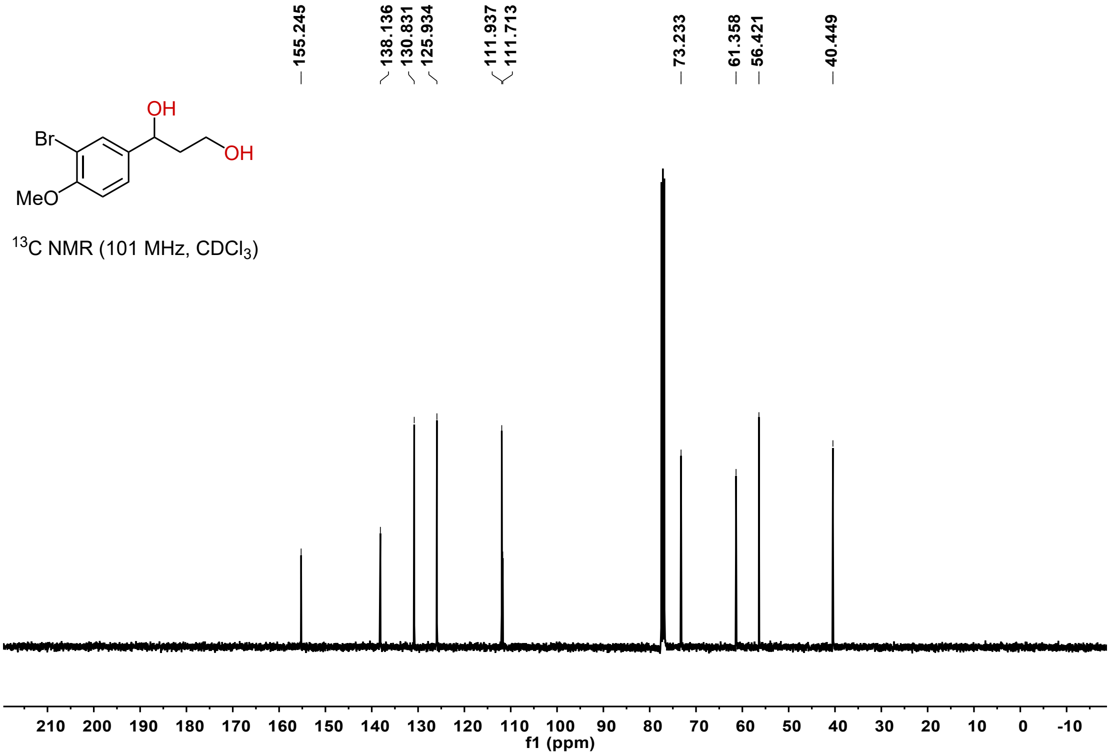
^{1}H NMR (400 MHz, CDCl$_3$)



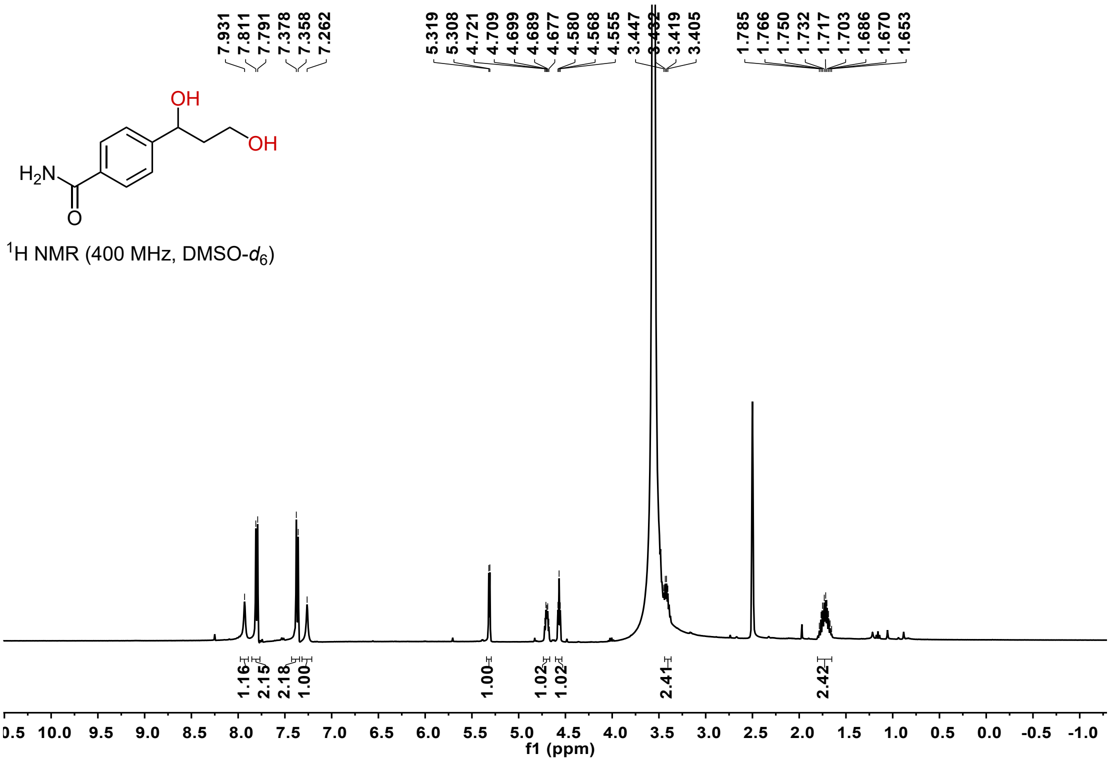
^{13}C NMR (101 MHz, CDCl$_3$)

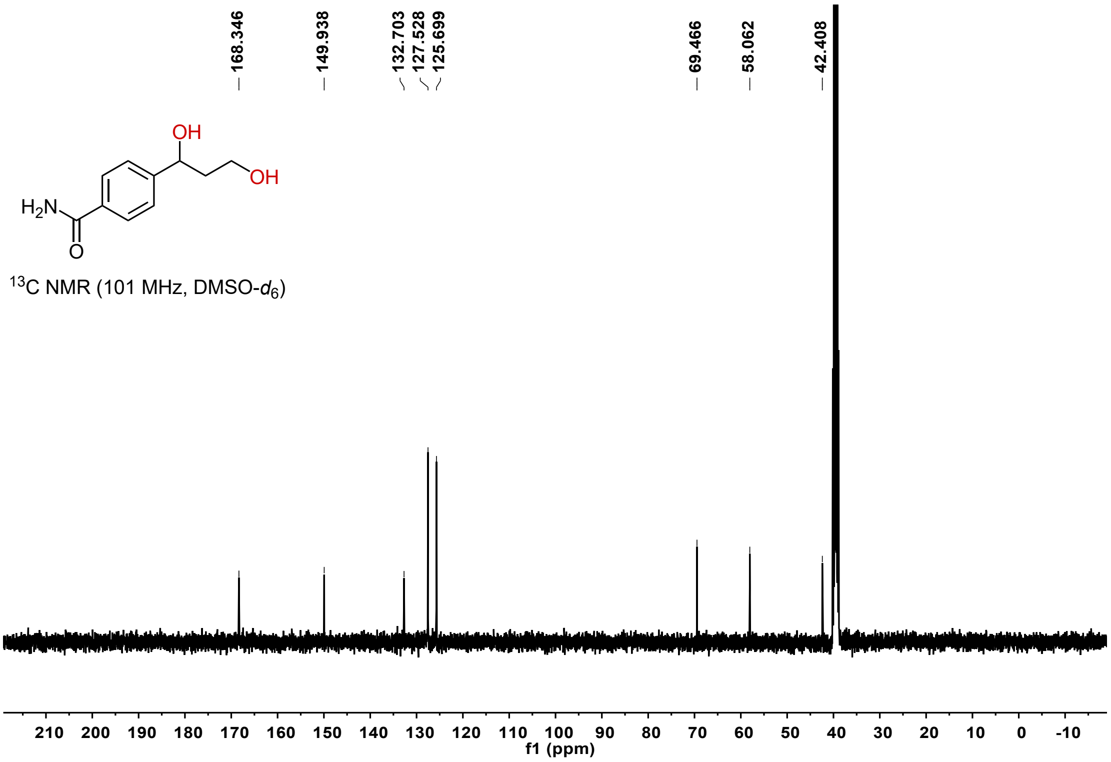
1-(3-Bromo-4-methoxyphenyl)propane-1,3-diol (15)



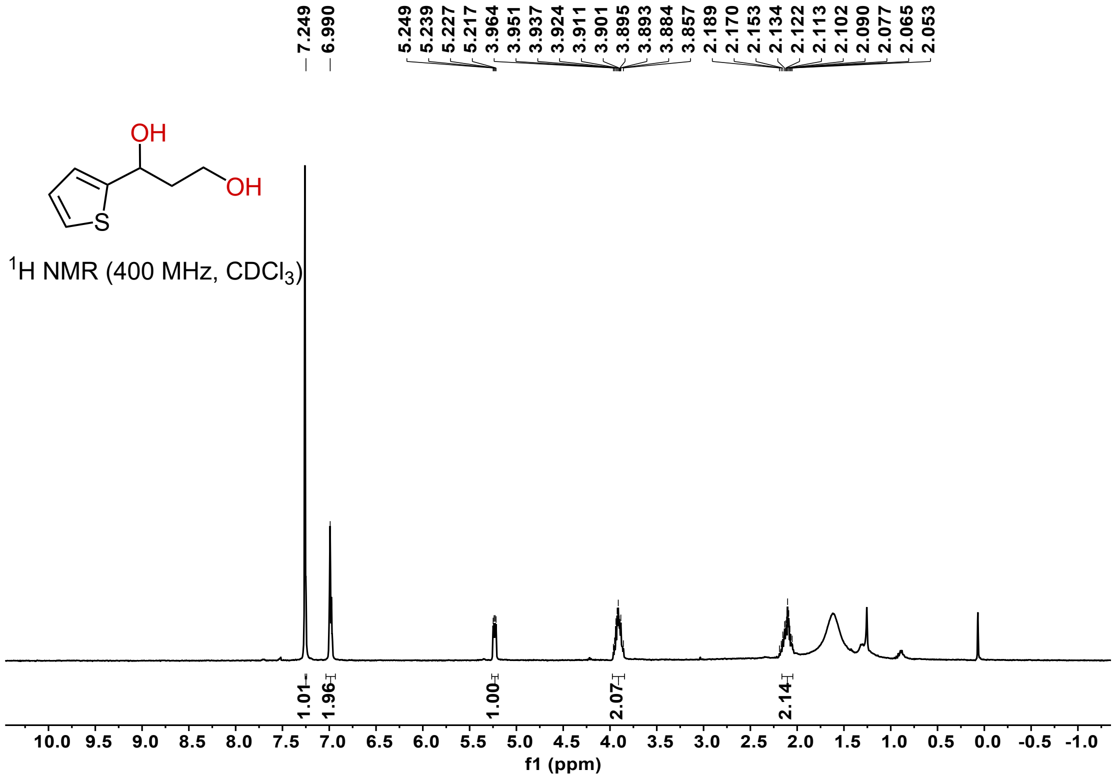


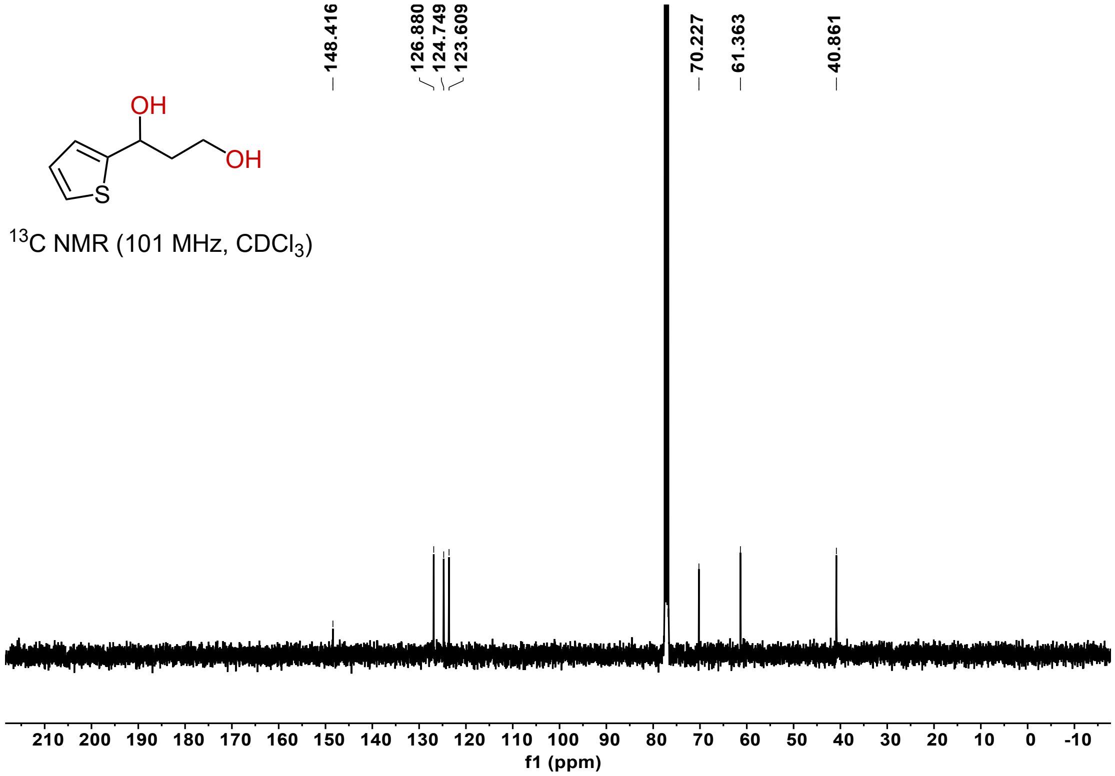
1-(4-Carbamoylphenyl)propane-1,3-diol (16)



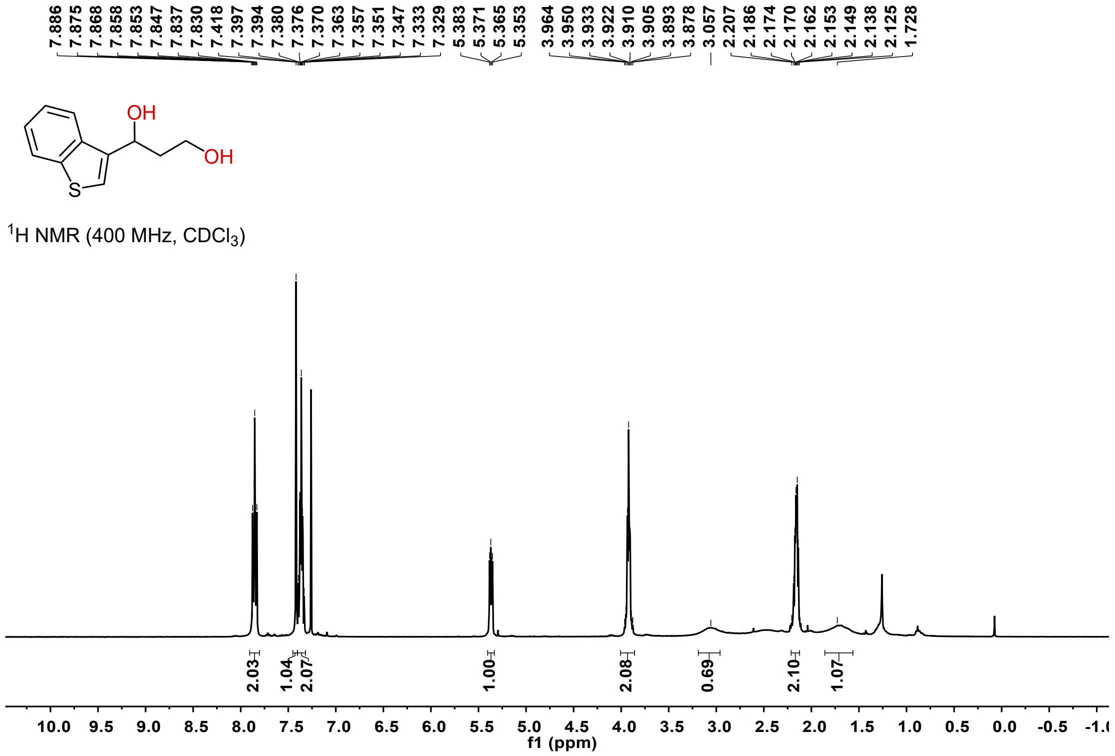


1-(Thiophen-2-yl) propane-1,3-diol (17)

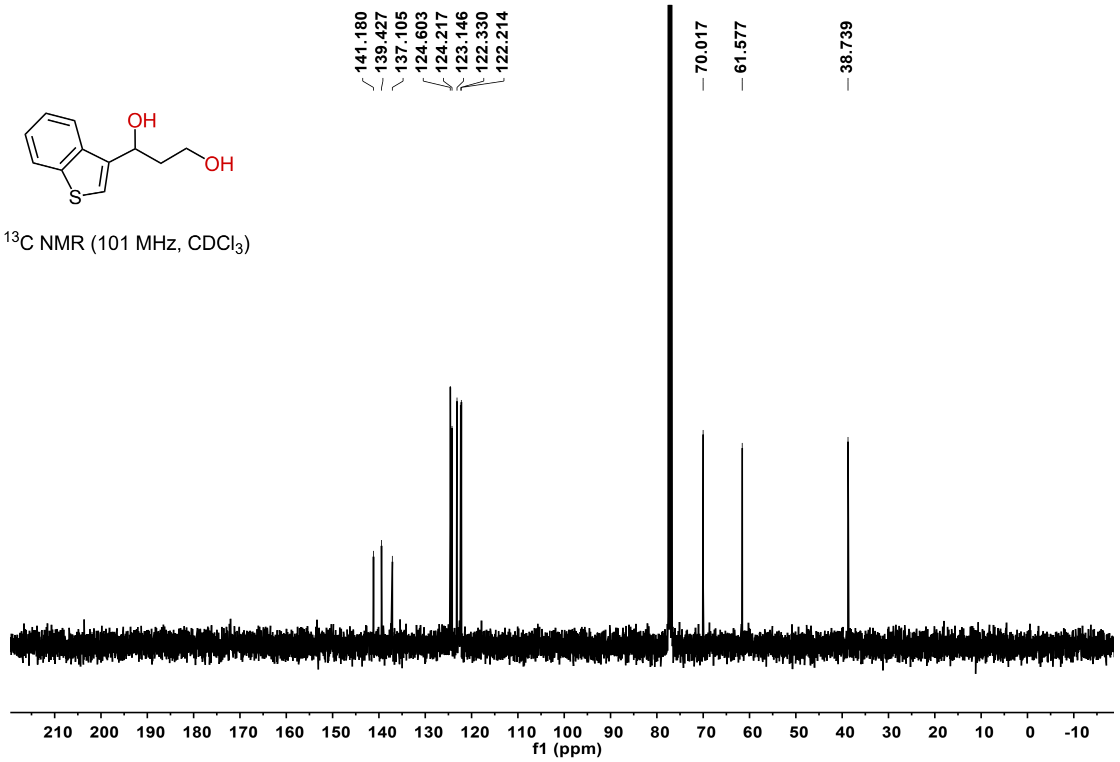




1-(Benzo[*b*]thiophen-3-yl)propane-1,3-diol (18)

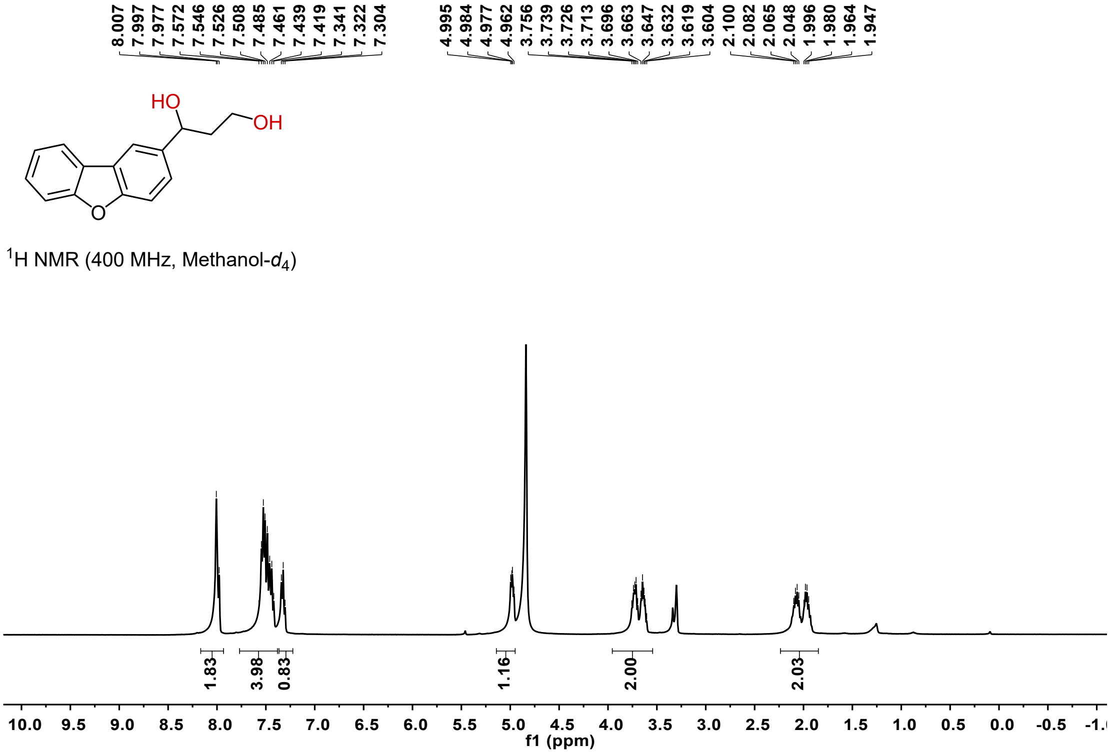


^{1}H NMR (400 MHz, CDCl$_3$)

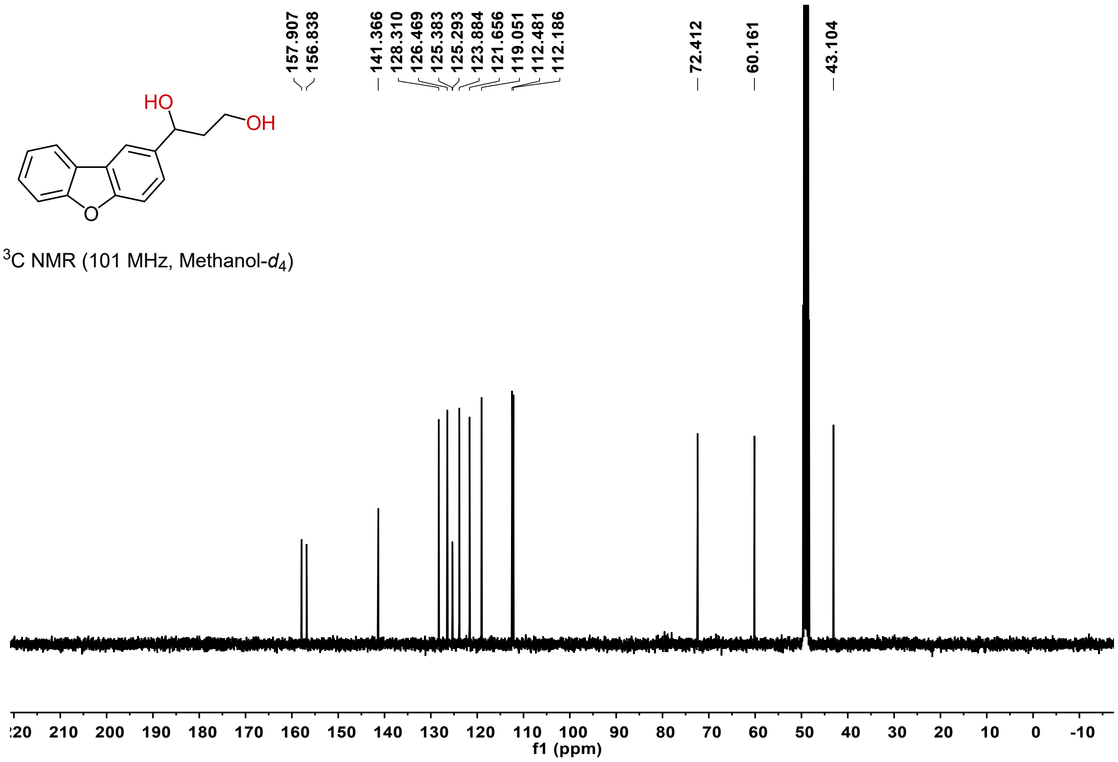


^{13}C NMR (101 MHz, CDCl$_3$)

1-(Dibenzo[*b*,*d*]furan-2-yl)propane-1,3-diol (19)

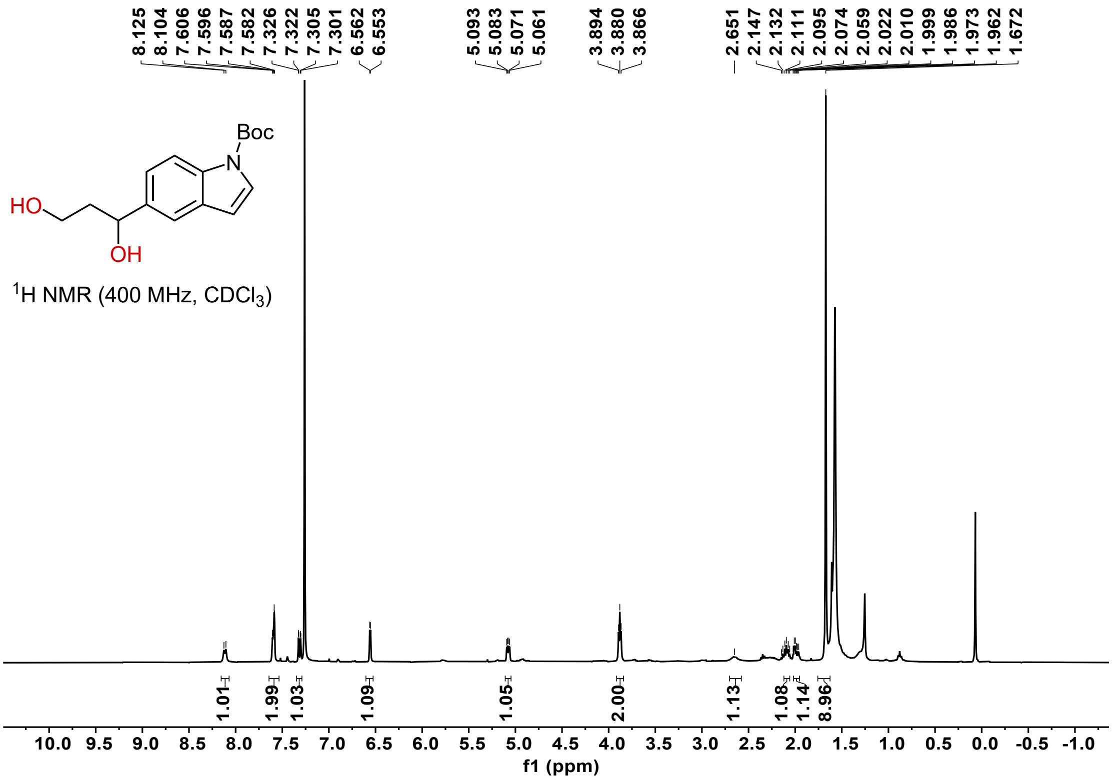


^{1}H NMR (400 MHz, Methanol-d_4)

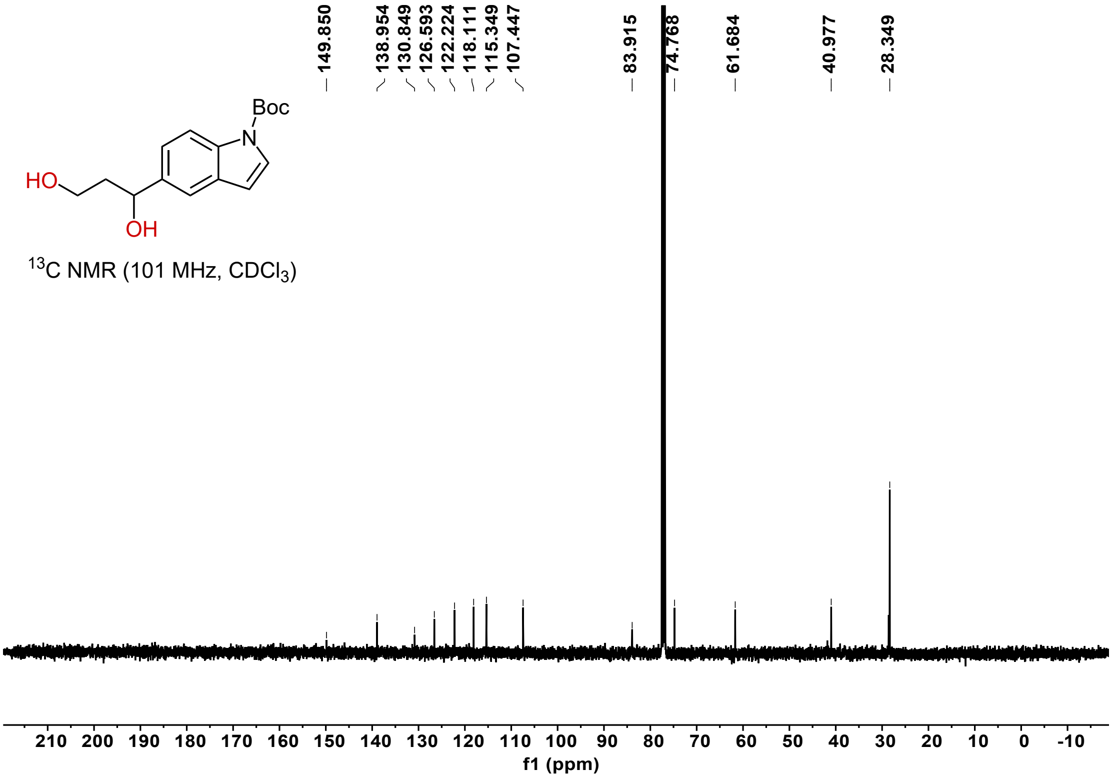


^{13}C NMR (101 MHz, Methanol-d_4)

tert-Butyl 5-(1,3-dihydroxypropyl)-1*H*-indole-1-carboxylate (20)

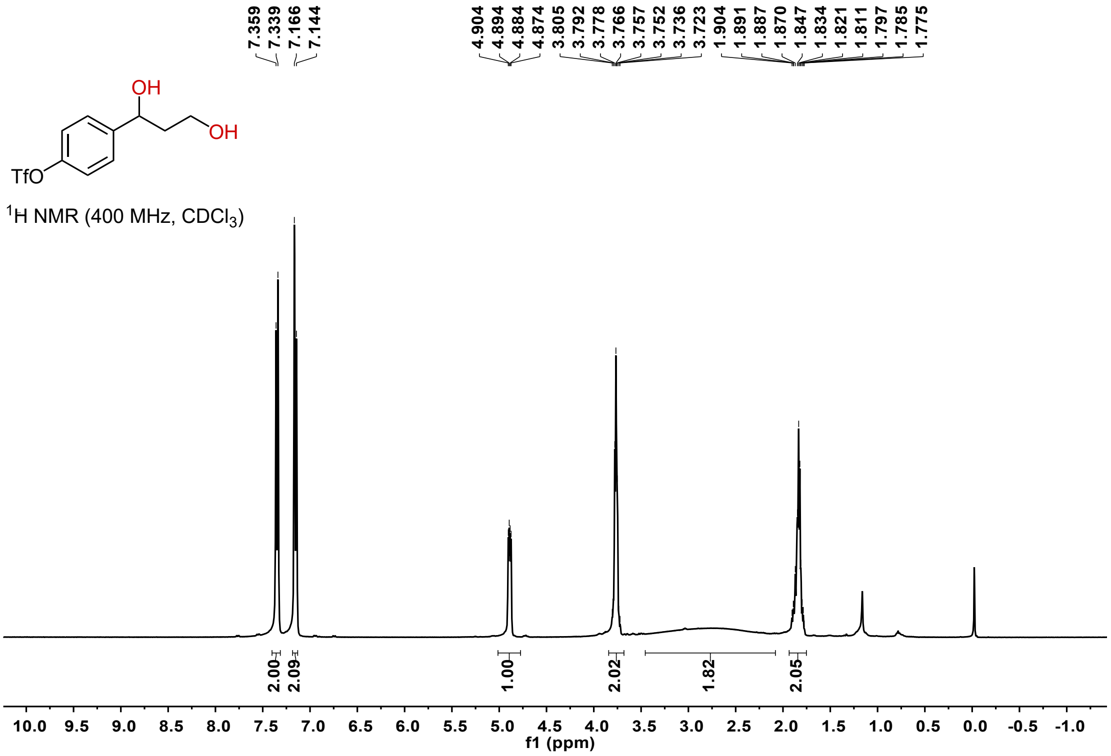


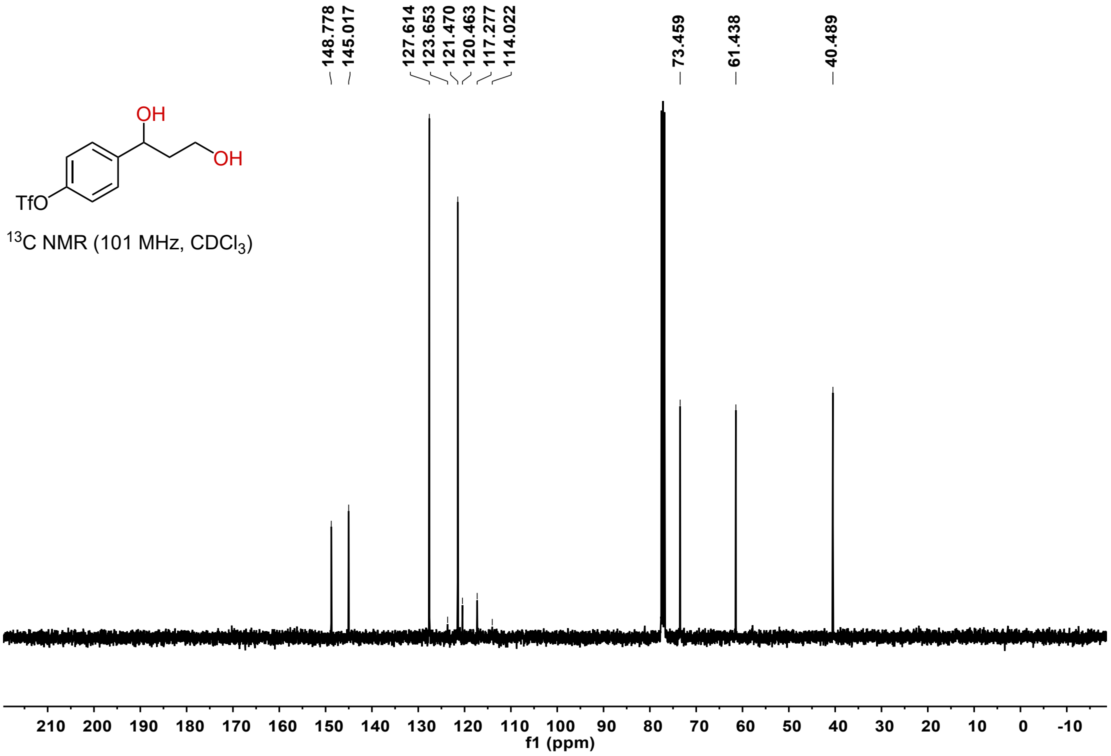
^{1}H NMR (400 MHz, $CDCl_3$)

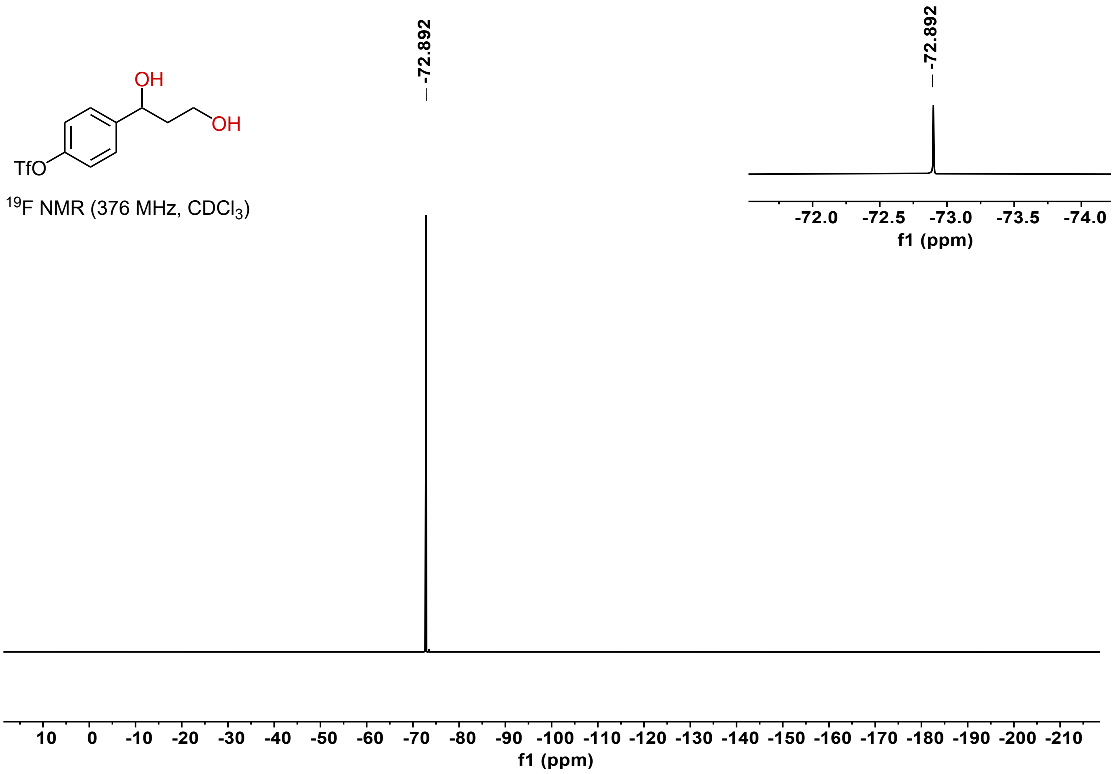


^{13}C NMR (101 MHz, $CDCl_3$)

4-(1,3-Dihydroxypropyl)phenyl trifluoromethanesulfonate (21)

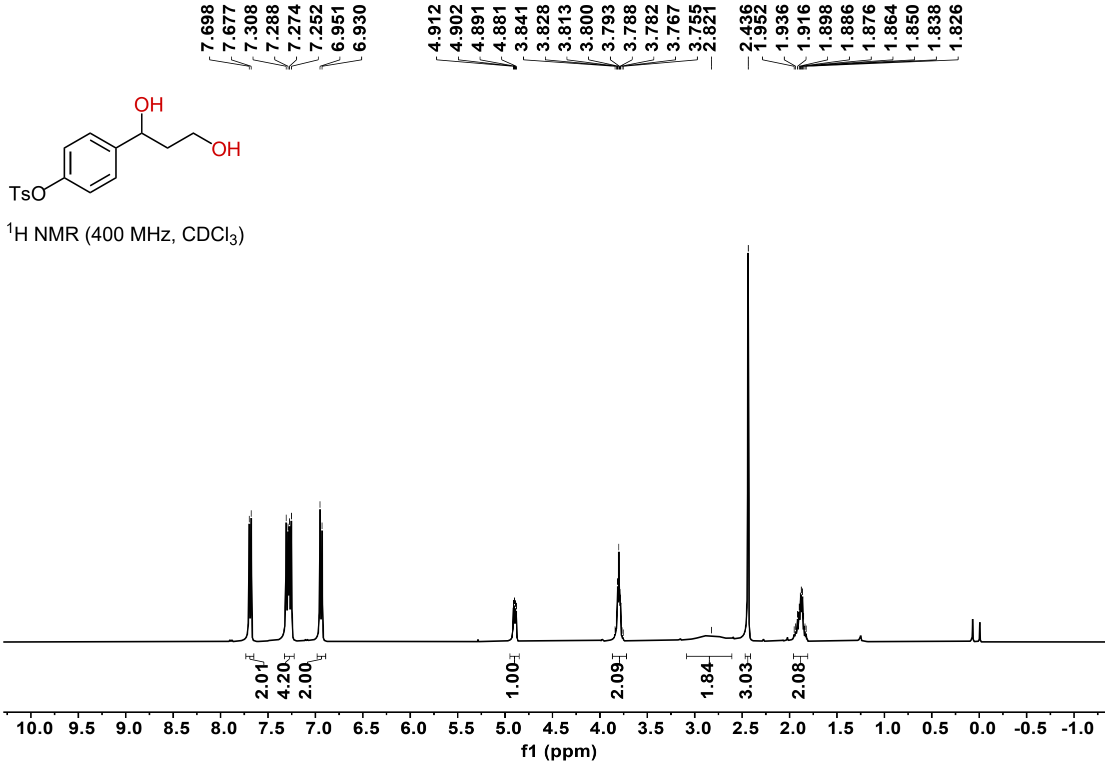




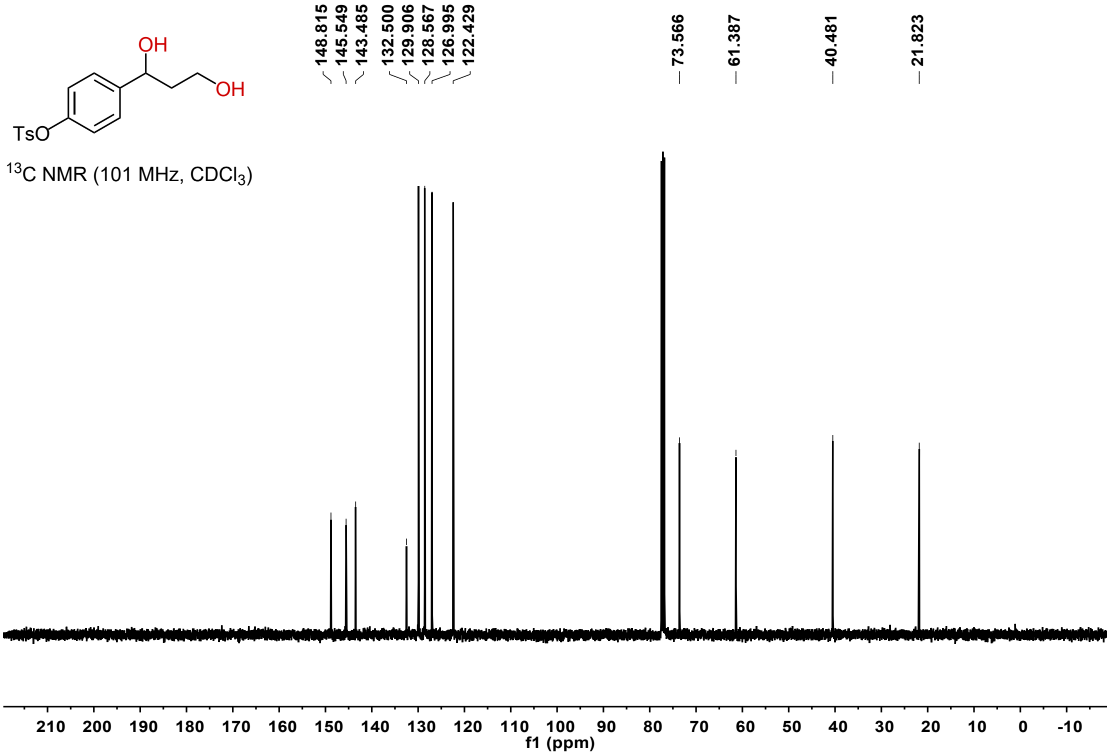


^{19}F NMR (376 MHz, $CDCl_3$)

1-(4-Tosyloxyphenyl)propane-1,3-diol (22)

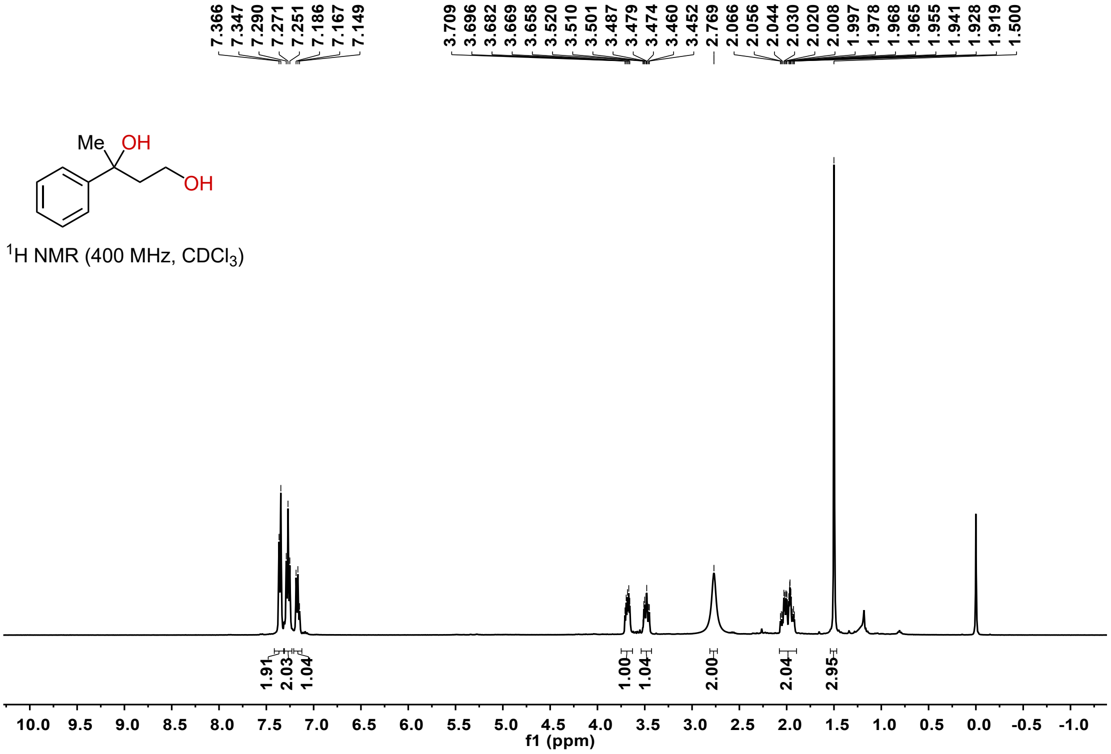


^{1}H NMR (400 MHz, CDCl$_3$)

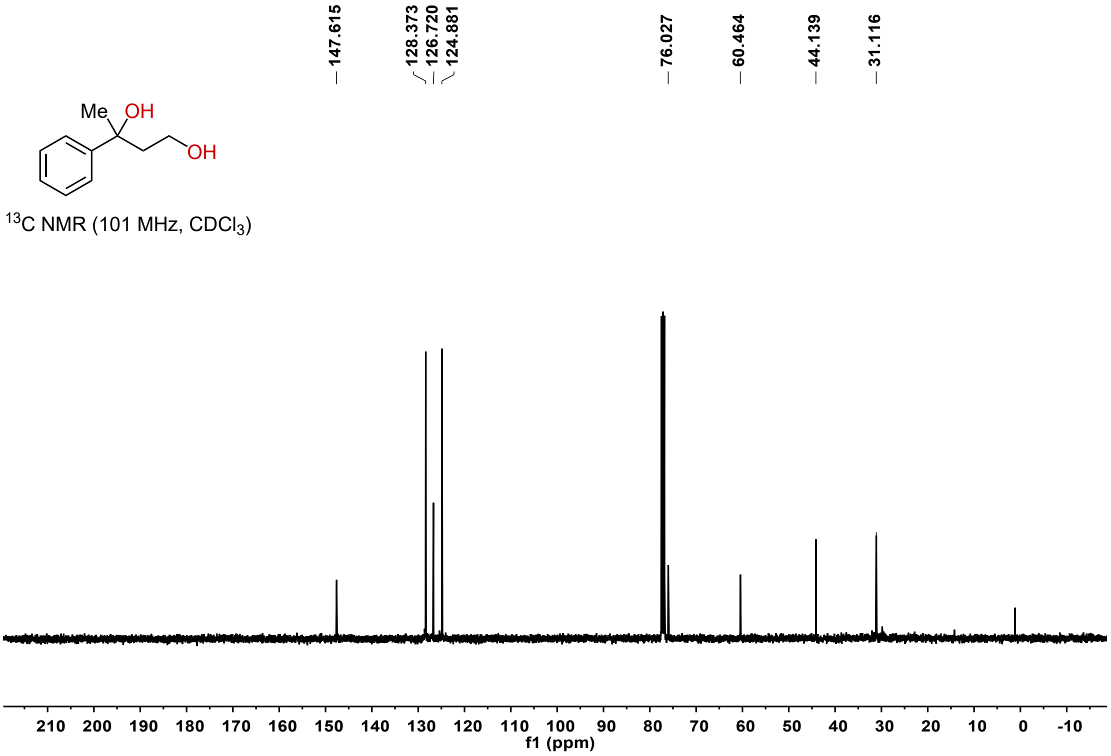


^{13}C NMR (101 MHz, CDCl$_3$)

3-Phenylbutane-1,3-diol (23)

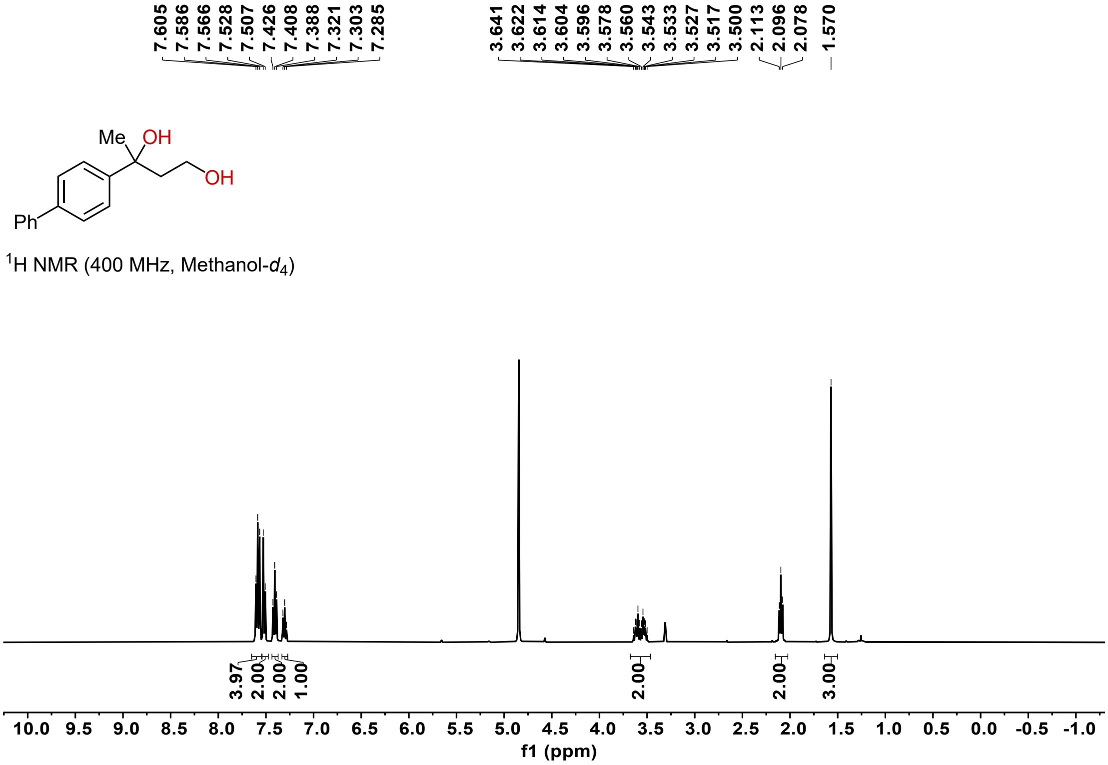


^{1}H NMR (400 MHz, CDCl$_3$)

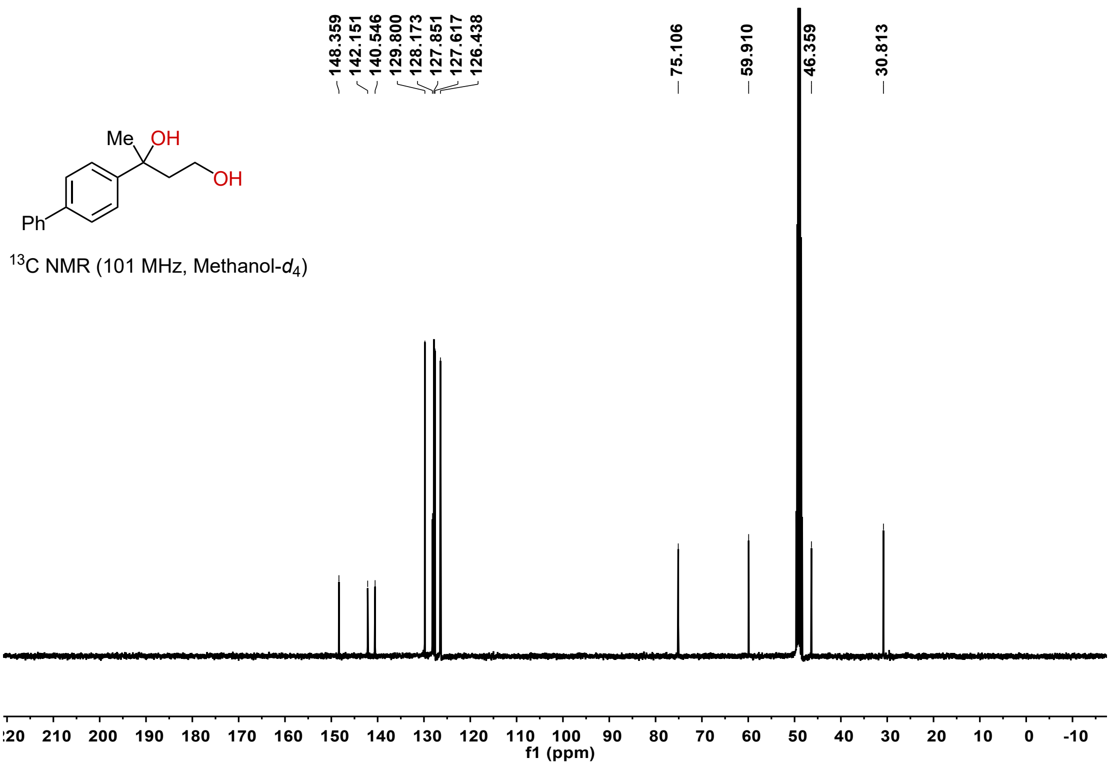


^{13}C NMR (101 MHz, CDCl$_3$)

3-([1,1'-Biphenyl]-4-yl)butane-1,3-diol (24)

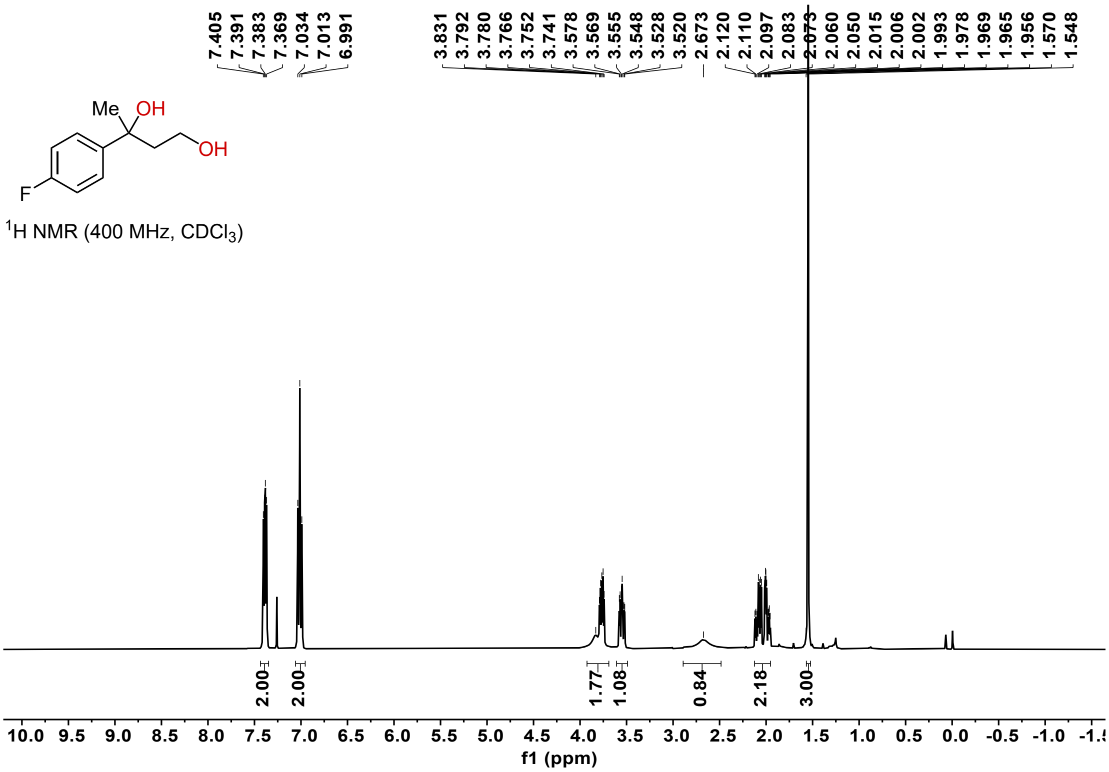


^{1}H NMR (400 MHz, Methanol-d_4)

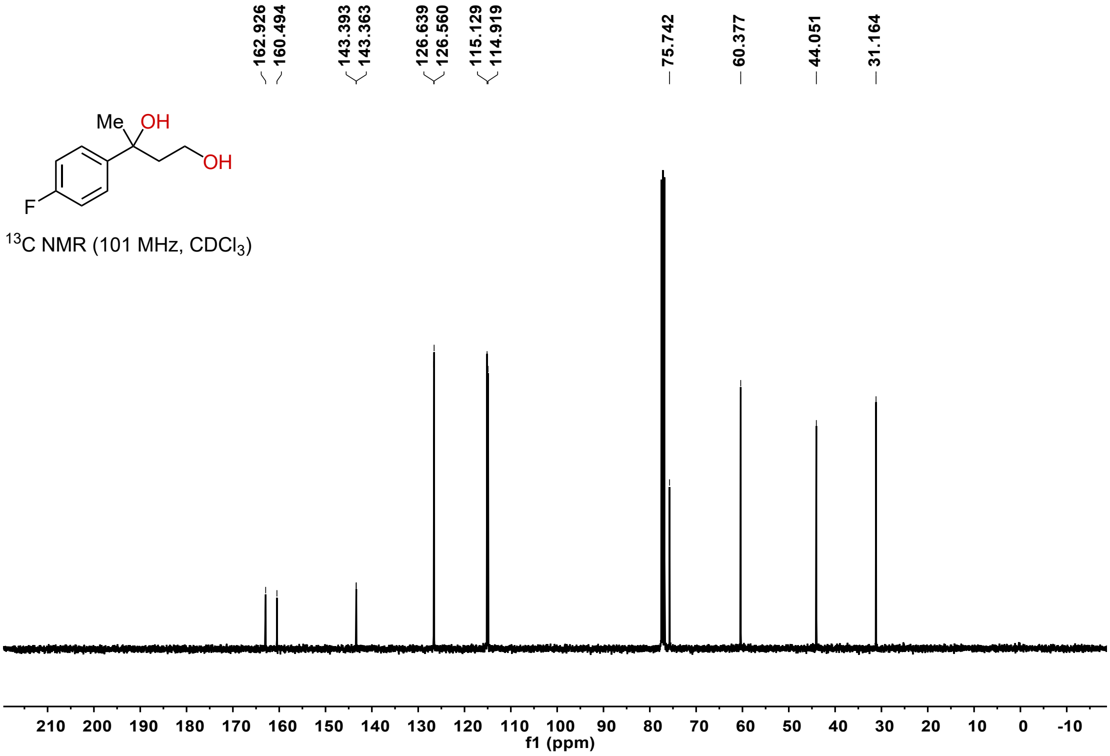


^{13}C NMR (101 MHz, Methanol-d_4)

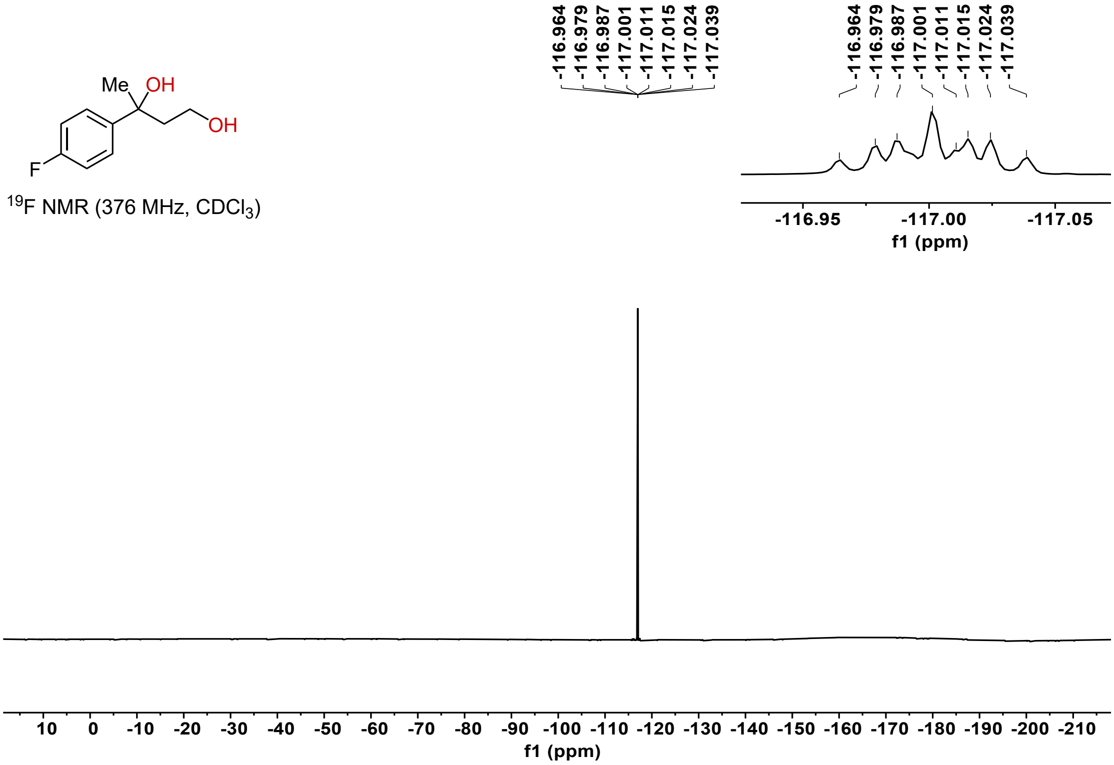
3-(4-Fluorophenyl)butane-1,3-diol (25)



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

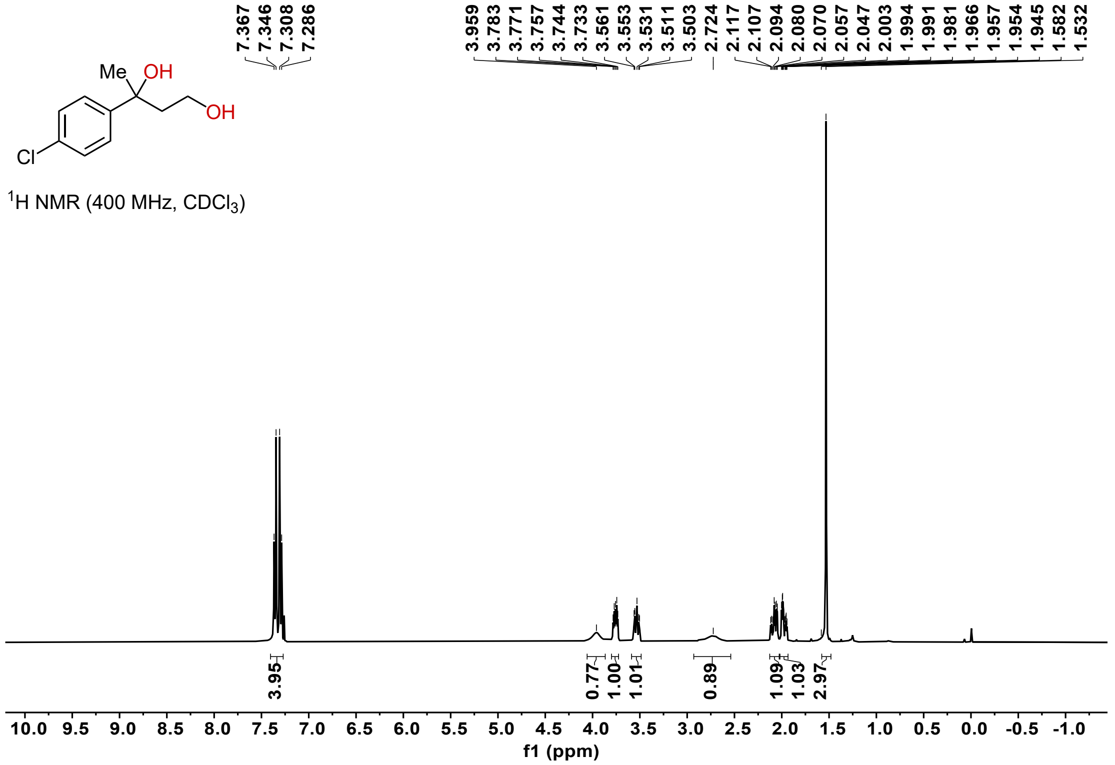


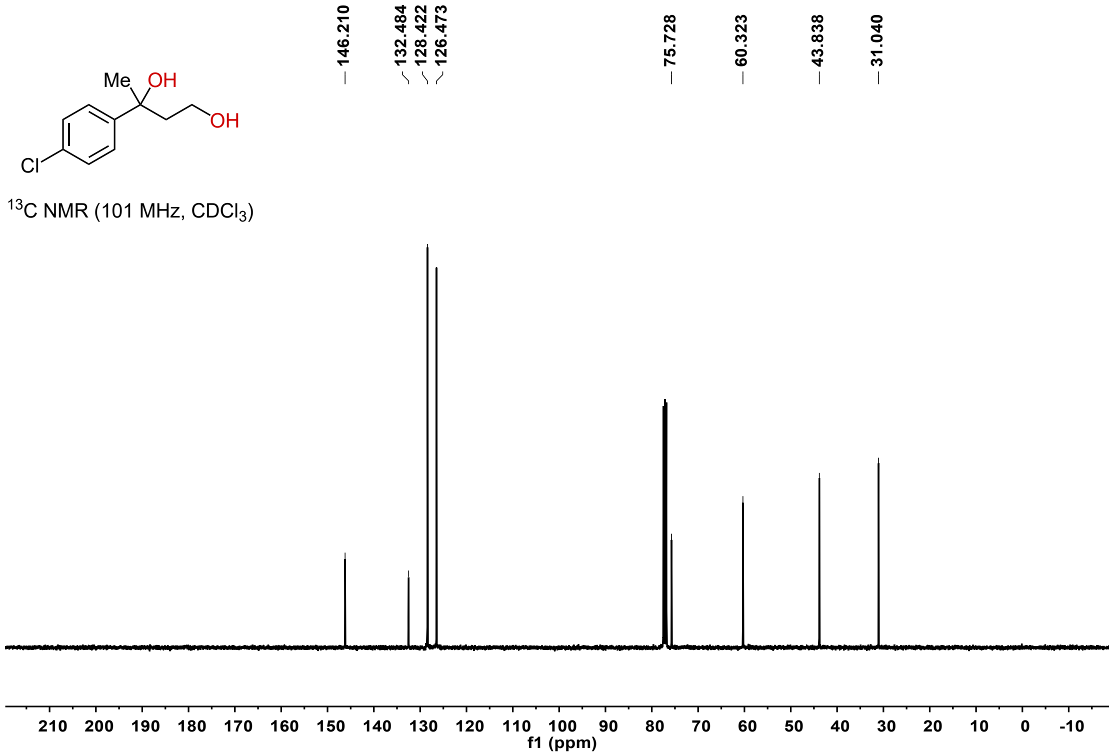
^{13}C NMR (101 MHz, $CDCl_3$)



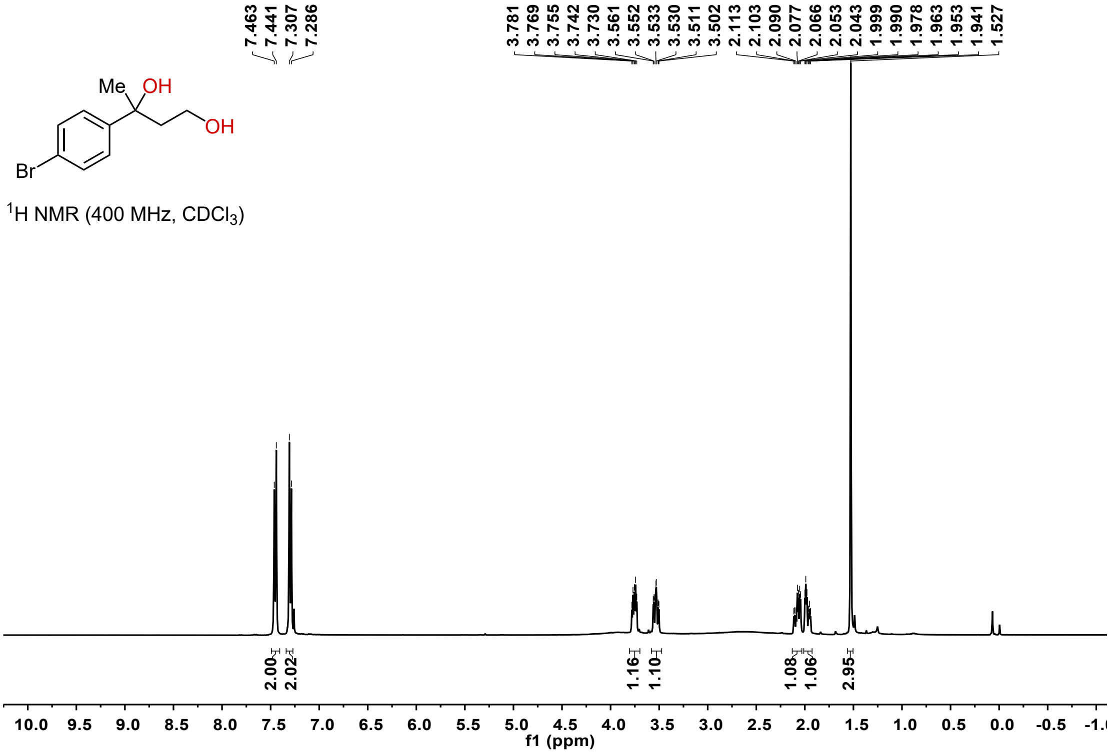
^{19}F NMR (376 MHz, $CDCl_3$)

3-(4-Chlorophenyl)butane-1,3-diol (26)

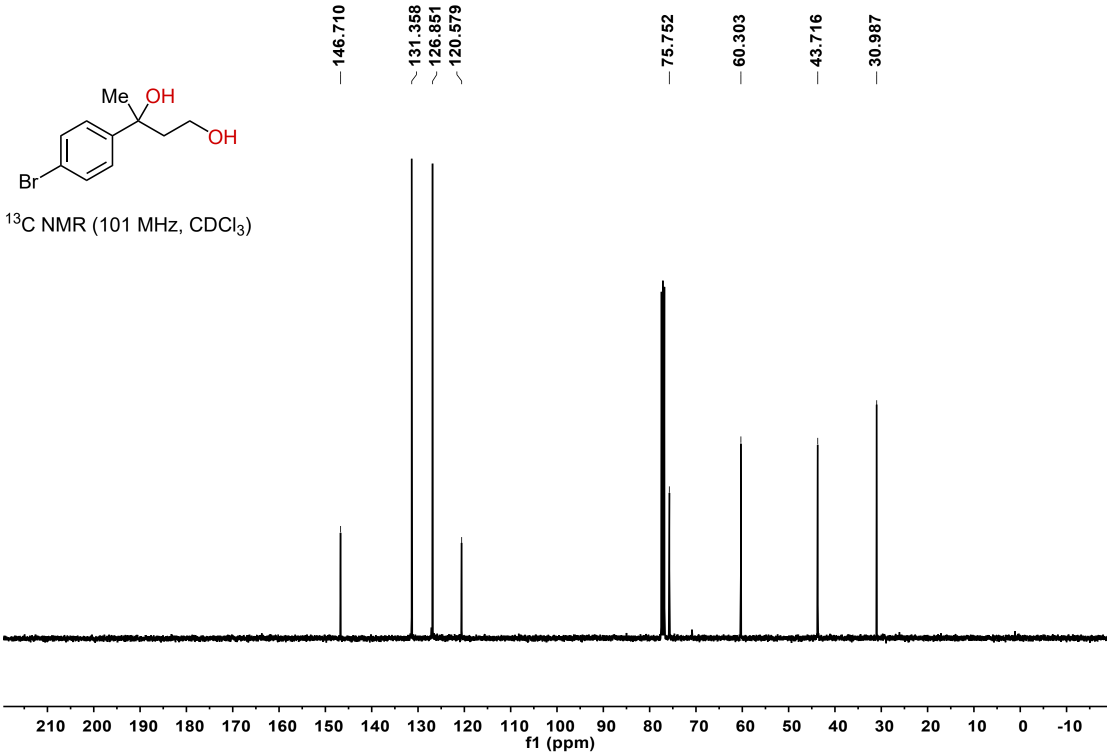




3-(4-Bromophenyl)butane-1,3-diol (27)

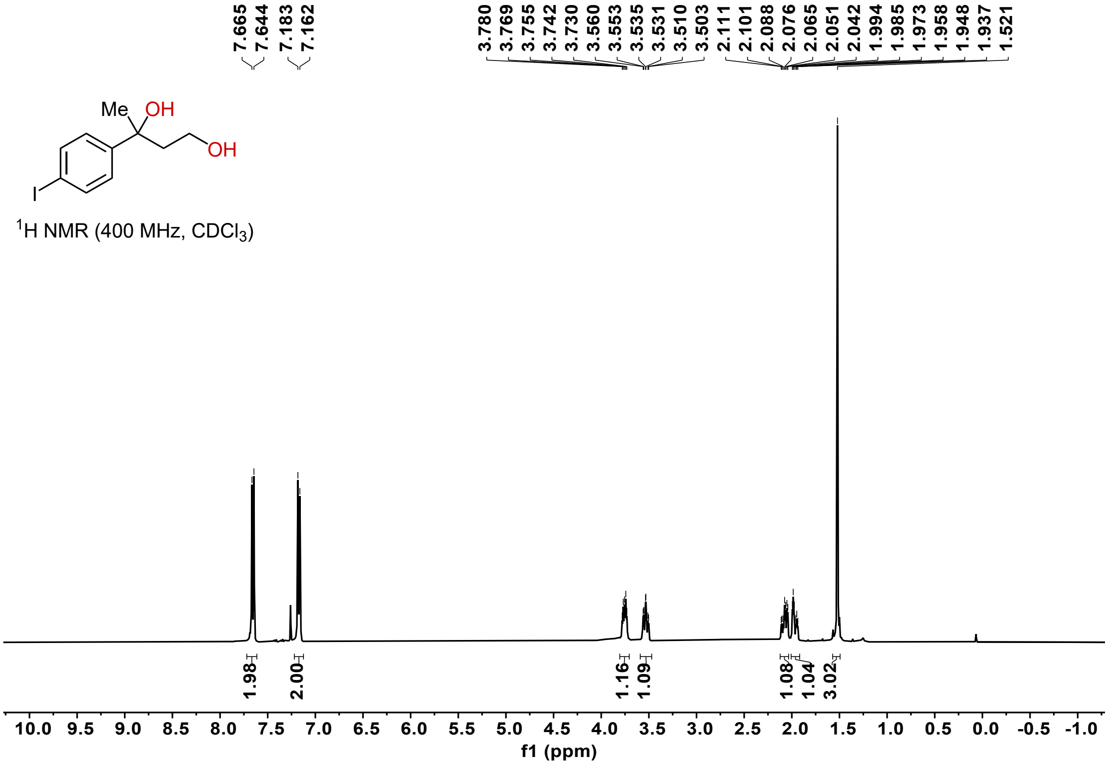


^{1}H NMR (400 MHz, $CDCl_3$)

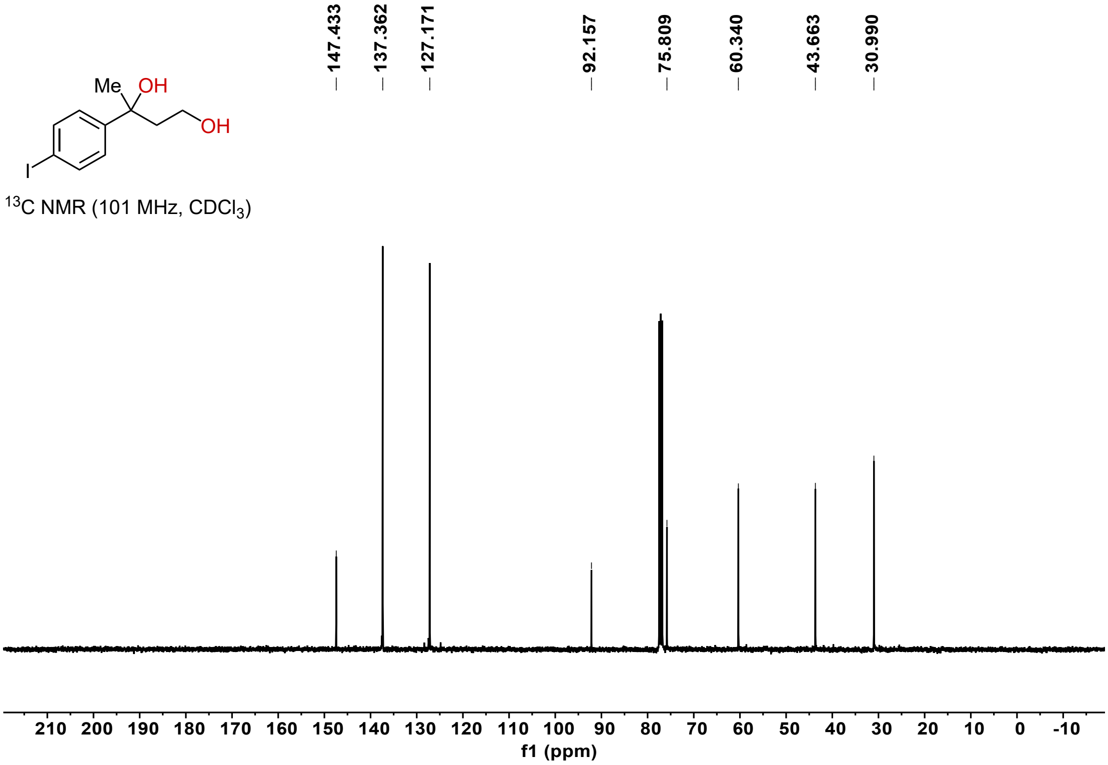


^{13}C NMR (101 MHz, $CDCl_3$)

3-(4-Iodophenyl)butane-1,3-diol (28)

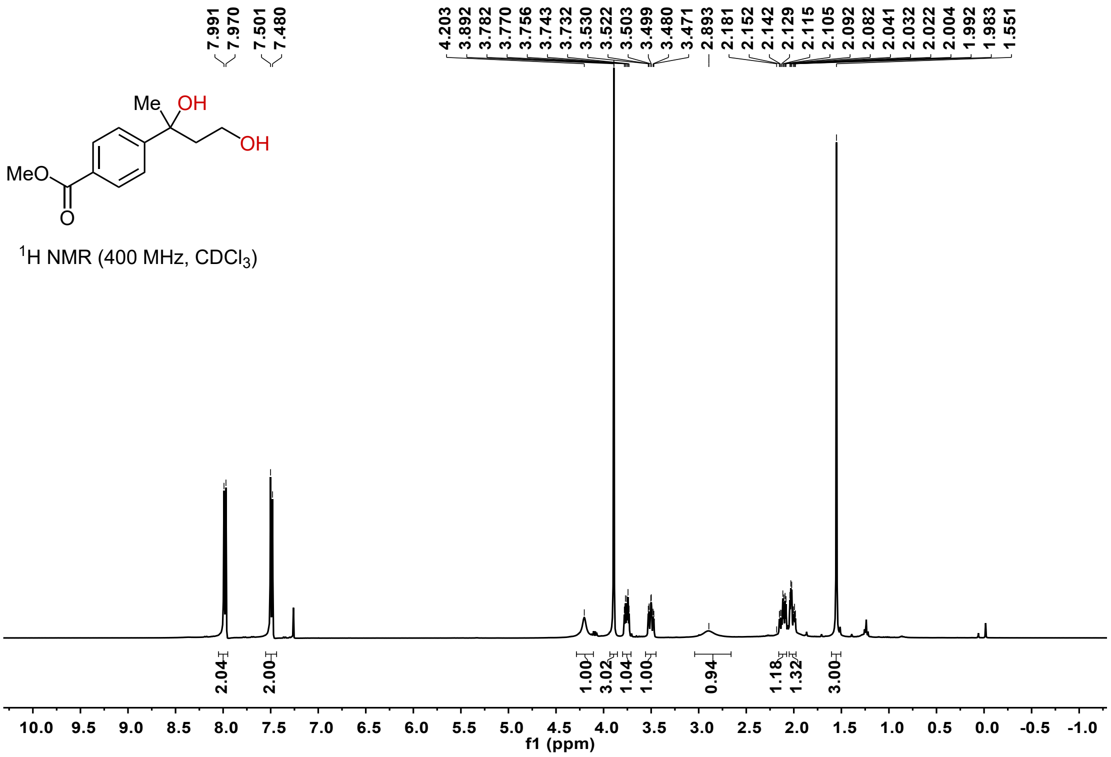


^{1}H NMR (400 MHz, CDCl$_3$)

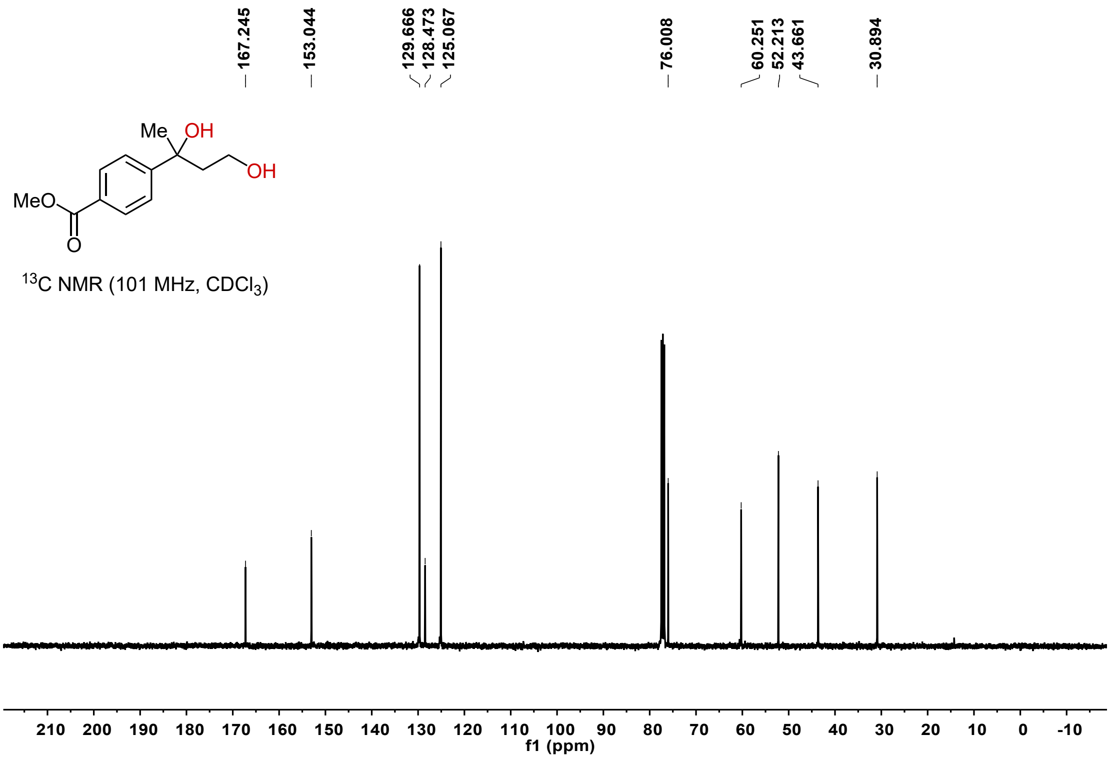


^{13}C NMR (101 MHz, CDCl$_3$)

3-(4-Carbomethoxyphenyl)butane-1,3-diol (29)

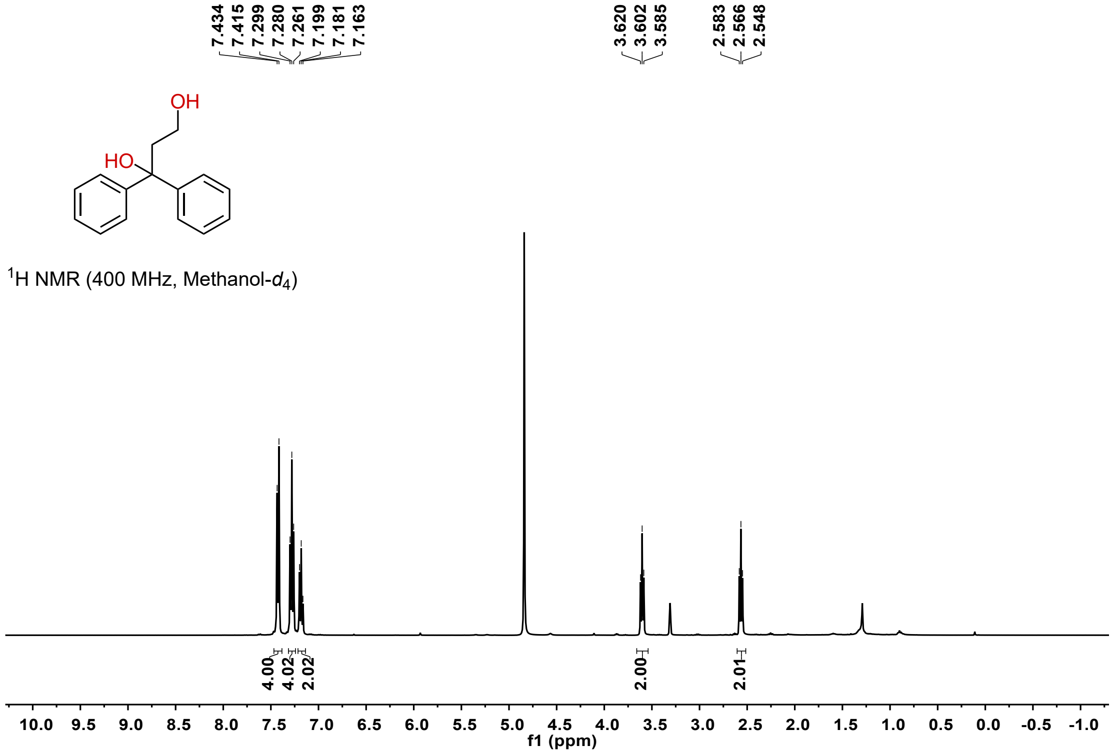


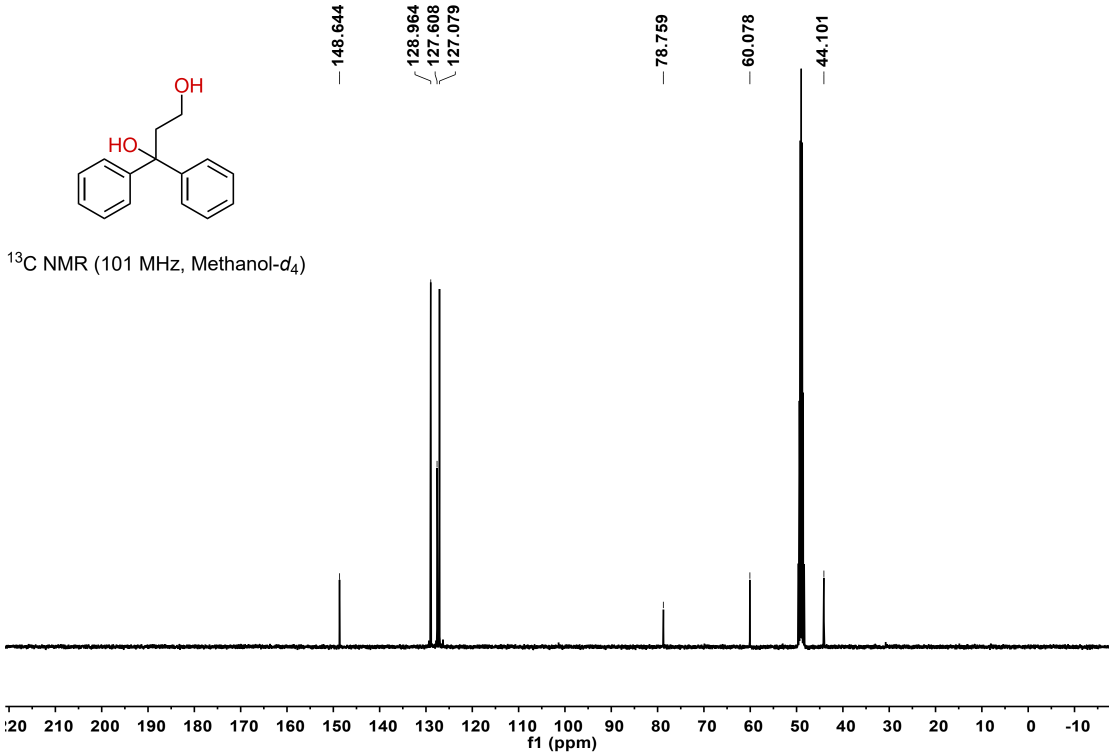
^{1}H NMR (400 MHz, CDCl$_3$)



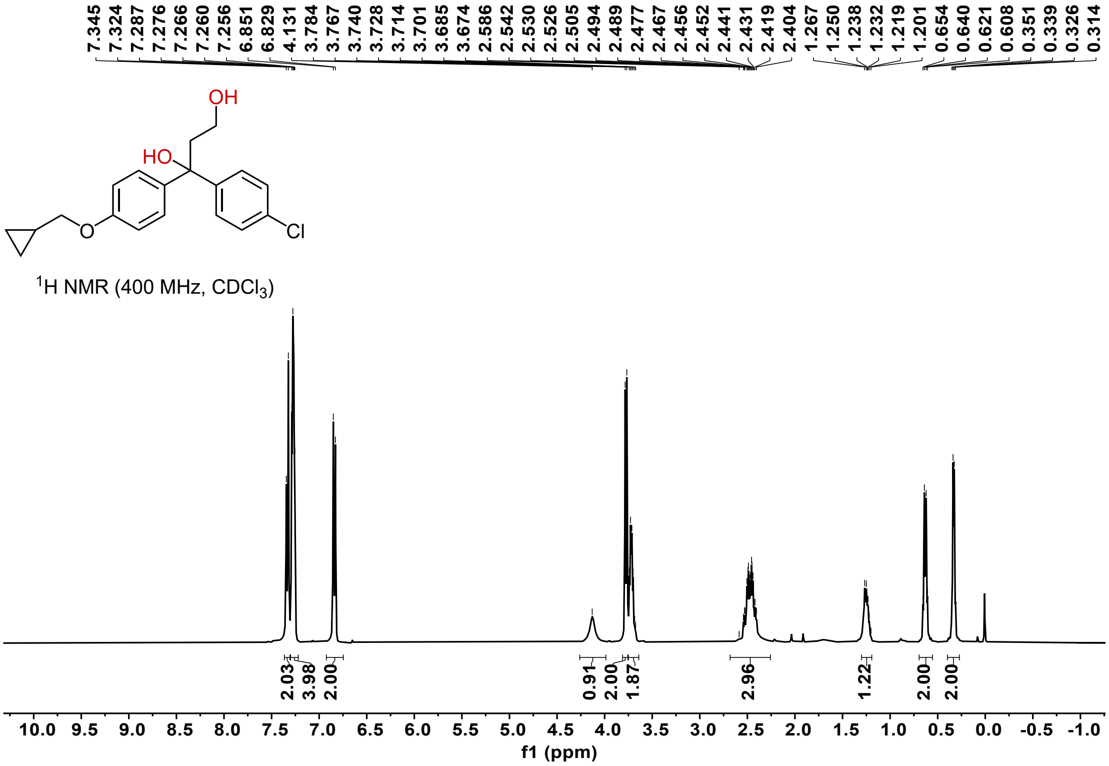
^{13}C NMR (101 MHz, CDCl$_3$)

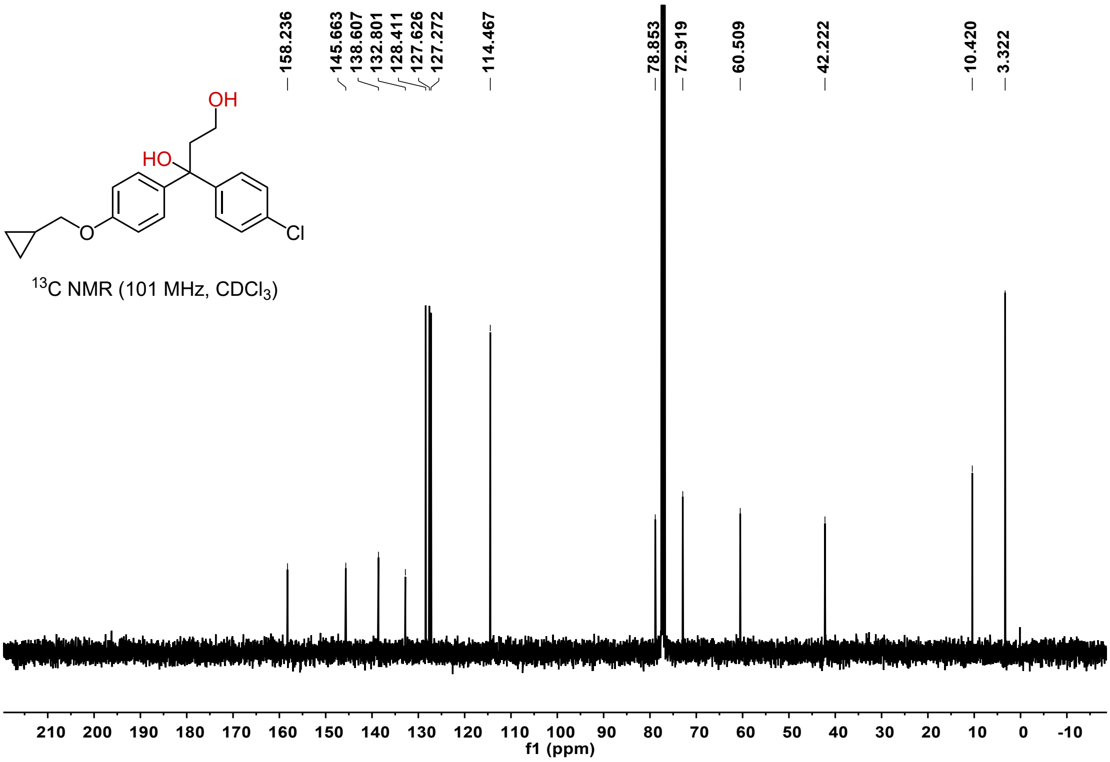
1,1-Diphenylpropane-1,3-diol (30)



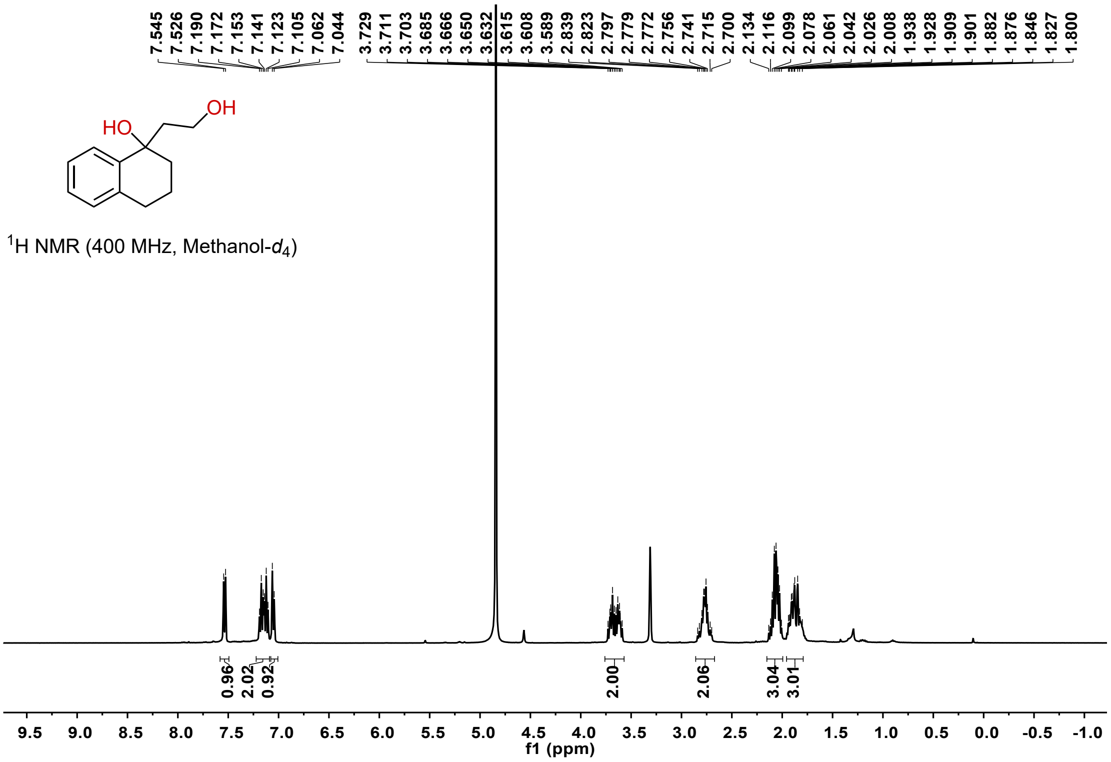


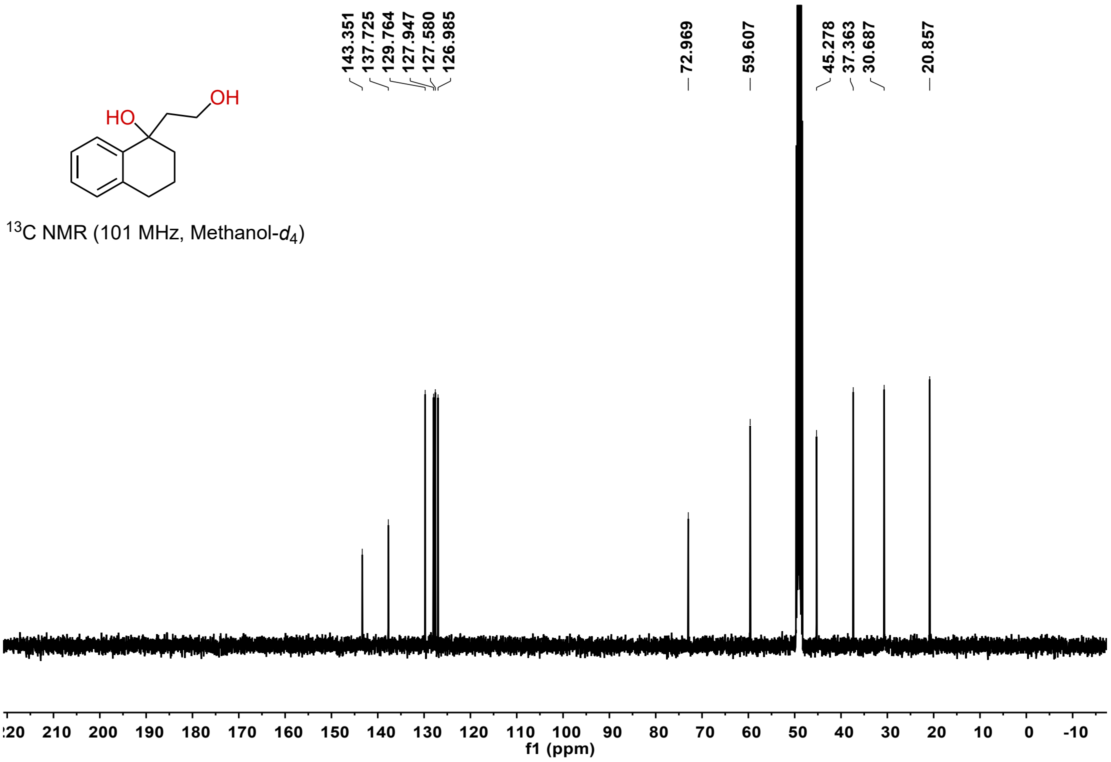
1-(4-Chlorophenyl)-1-(4-(cyclopropylmethoxy)phenyl)propane-1,3-diol (31)



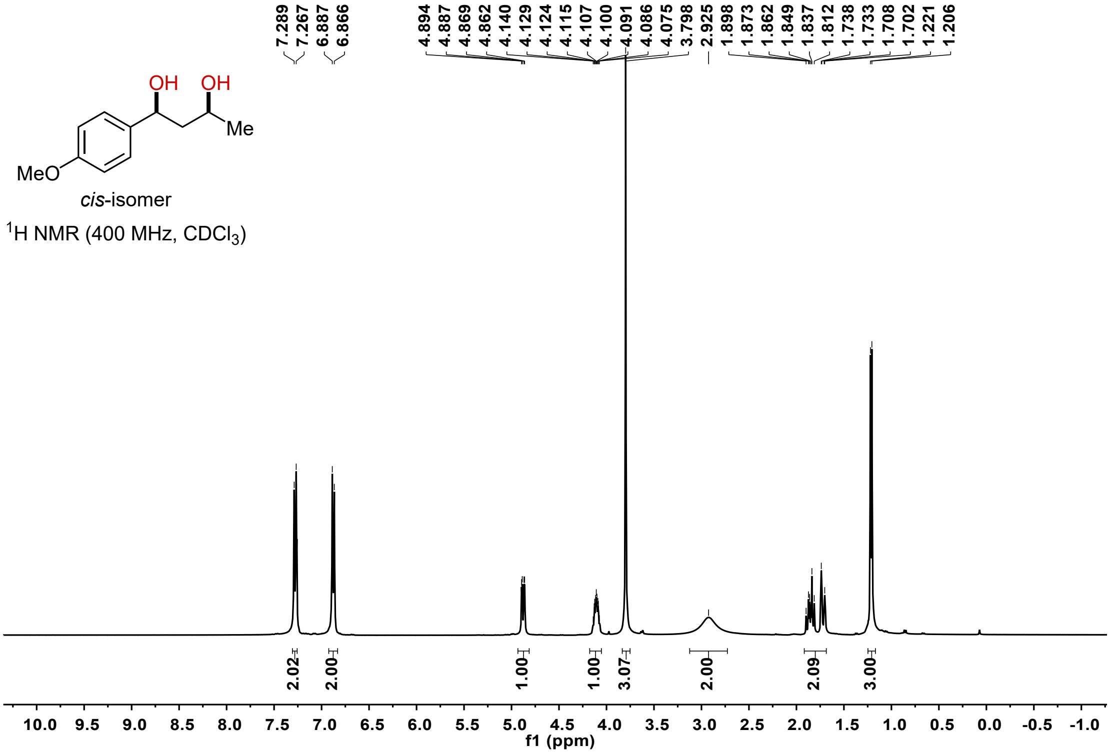


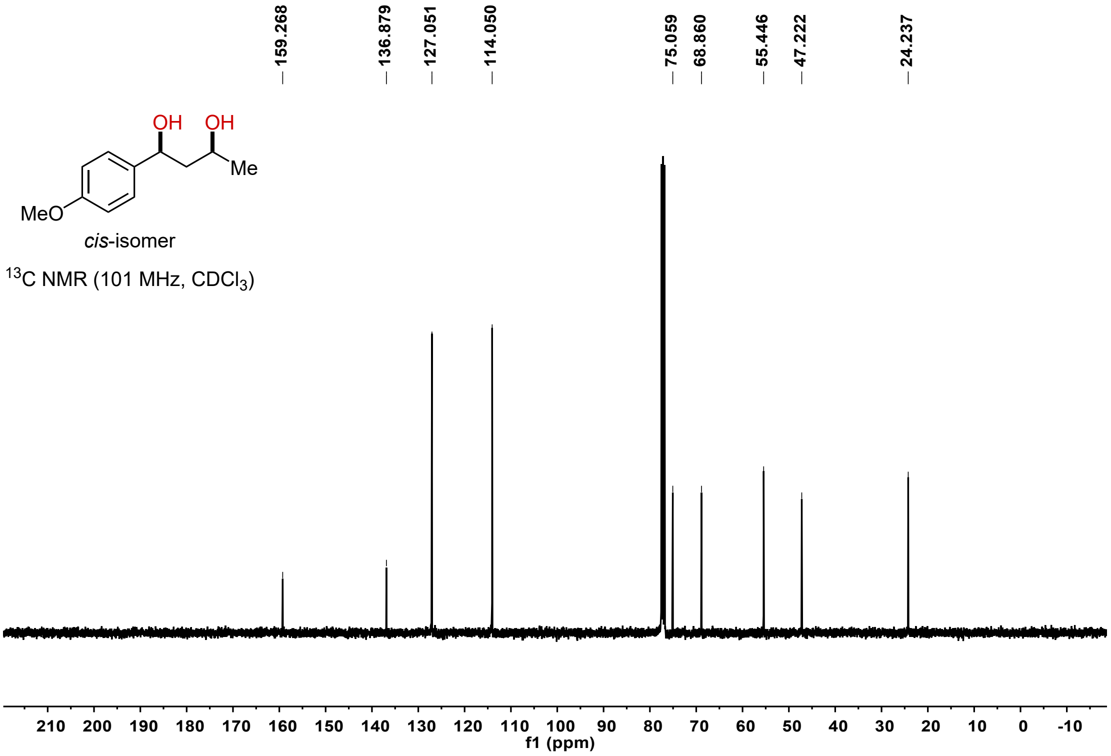
1-(2-Hydroxyethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (32)

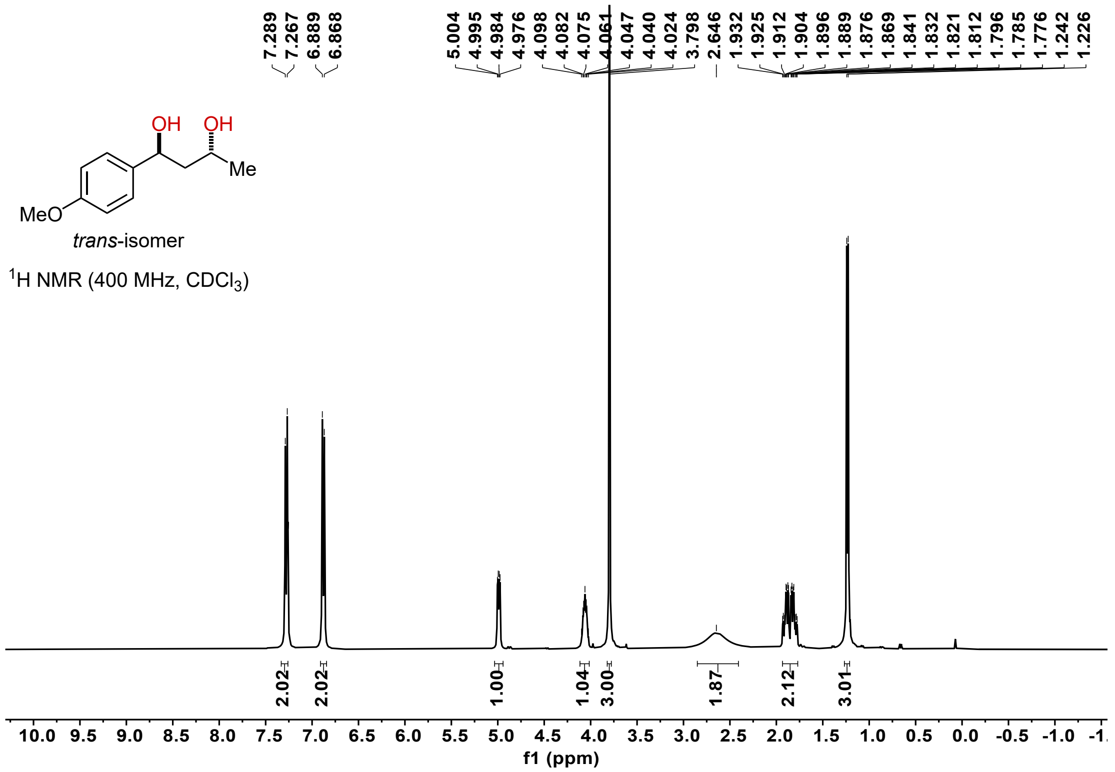




1-(4-Methoxyphenyl)butane-1,3-diol (33)

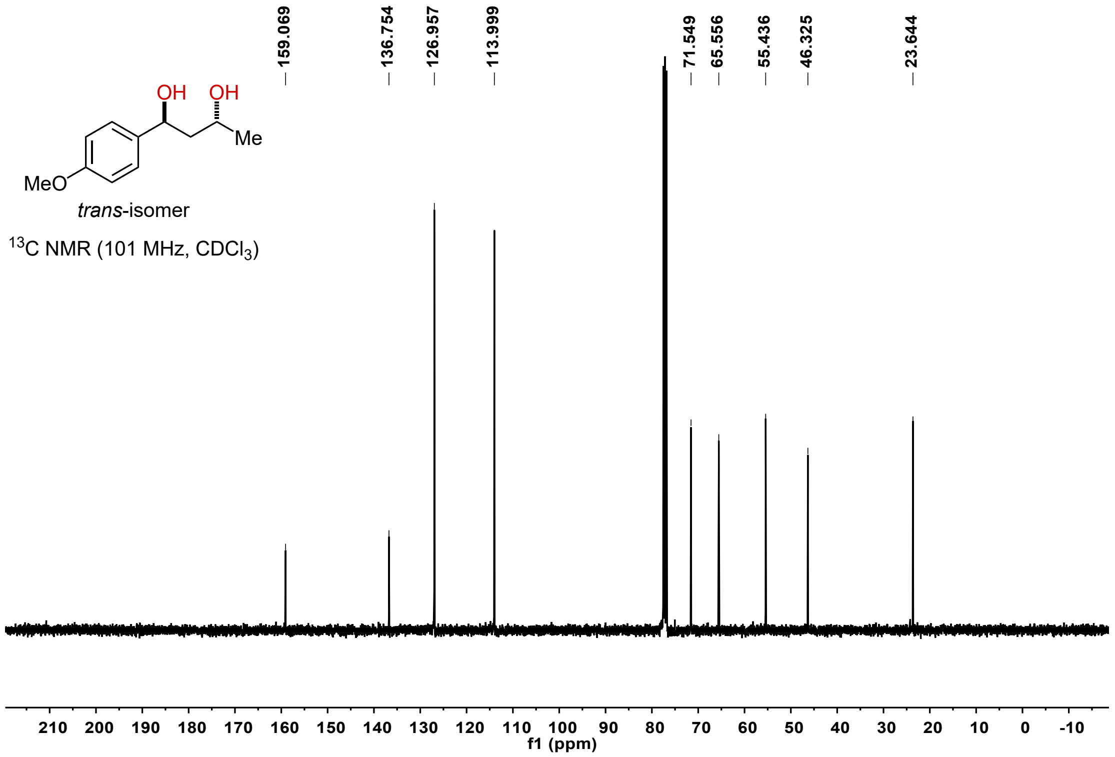






trans-isomer

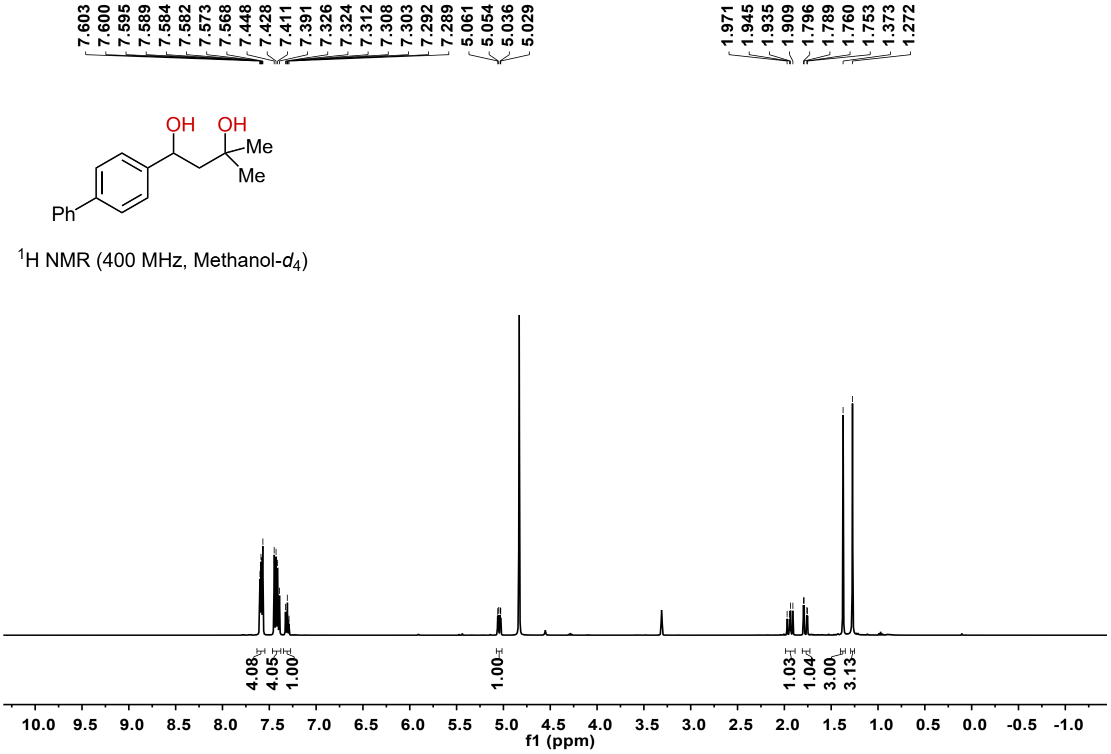
^{1}H NMR (400 MHz, $CDCl_3$)



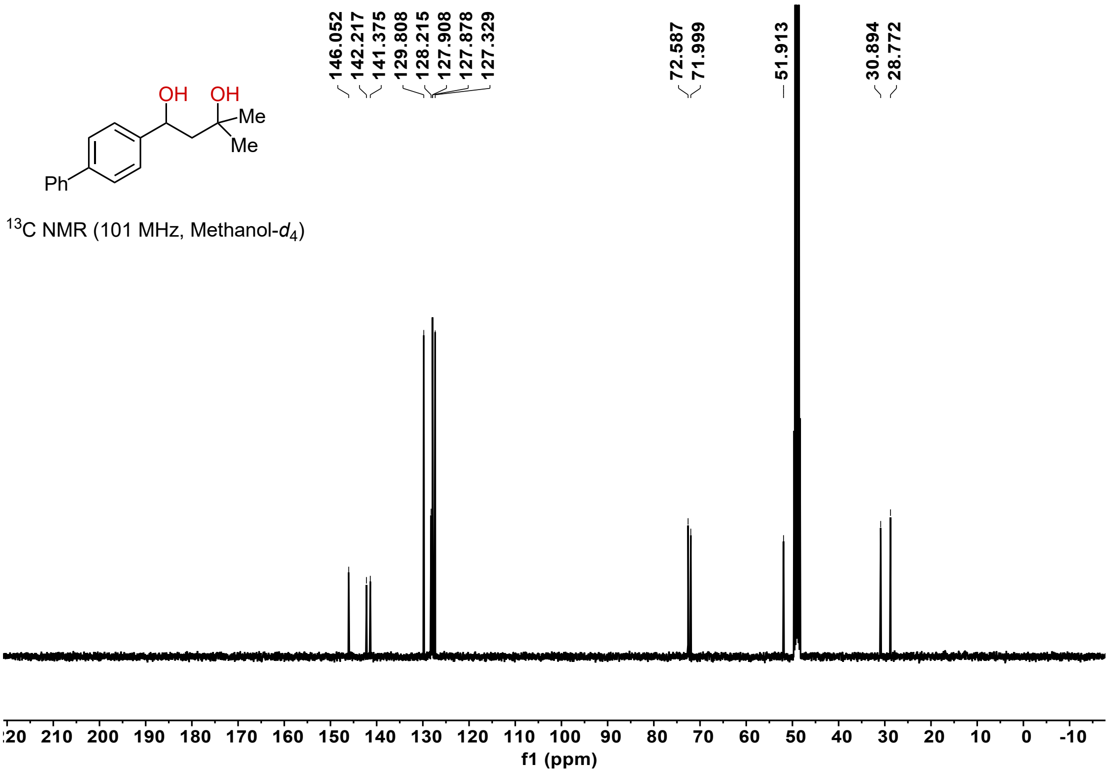
trans-isomer

^{13}C NMR (101 MHz, $CDCl_3$)

1-([1,1'-Biphenyl]-4-yl)-3-methylbutane-1,3-diol (34)

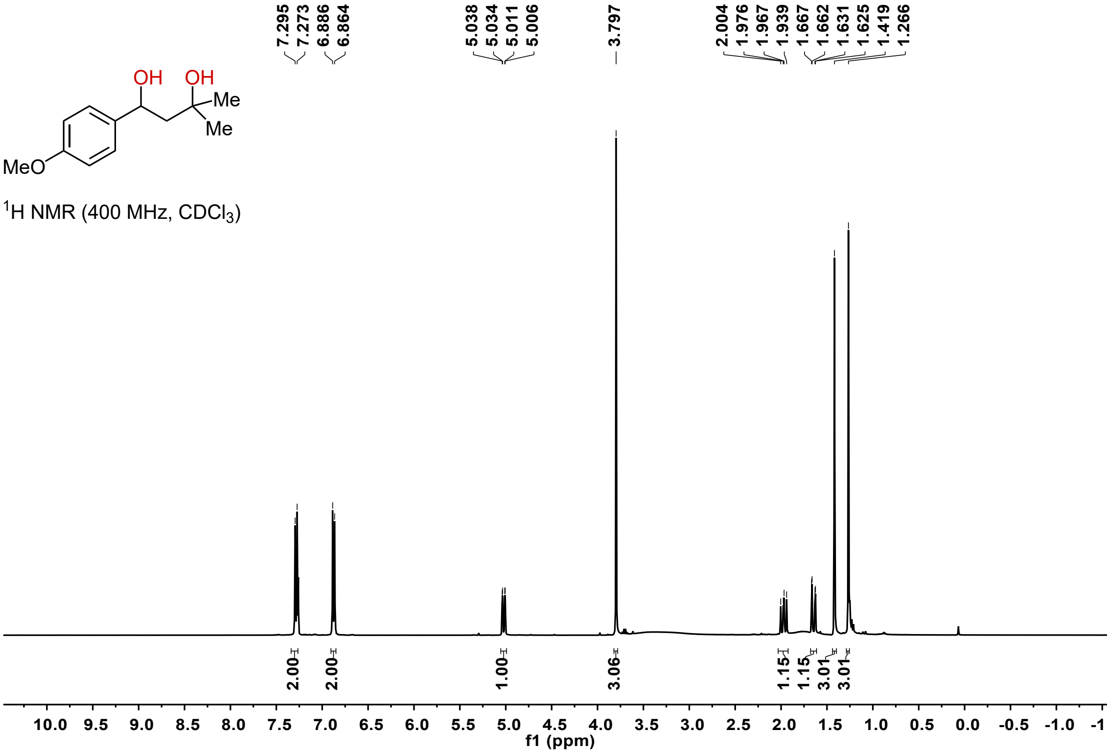


^{1}H NMR (400 MHz, Methanol-d_4)

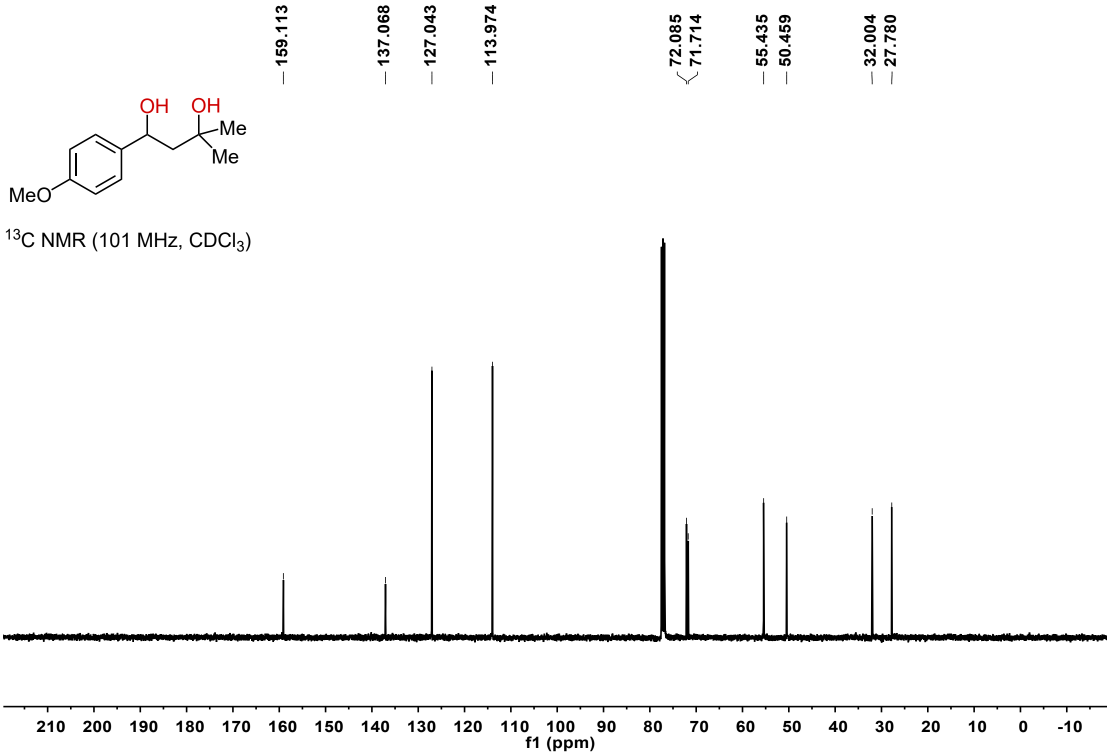


^{13}C NMR (101 MHz, Methanol-d_4)

1-(4-Methoxyphenyl)-3-methylbutane-1,3-diol (35)

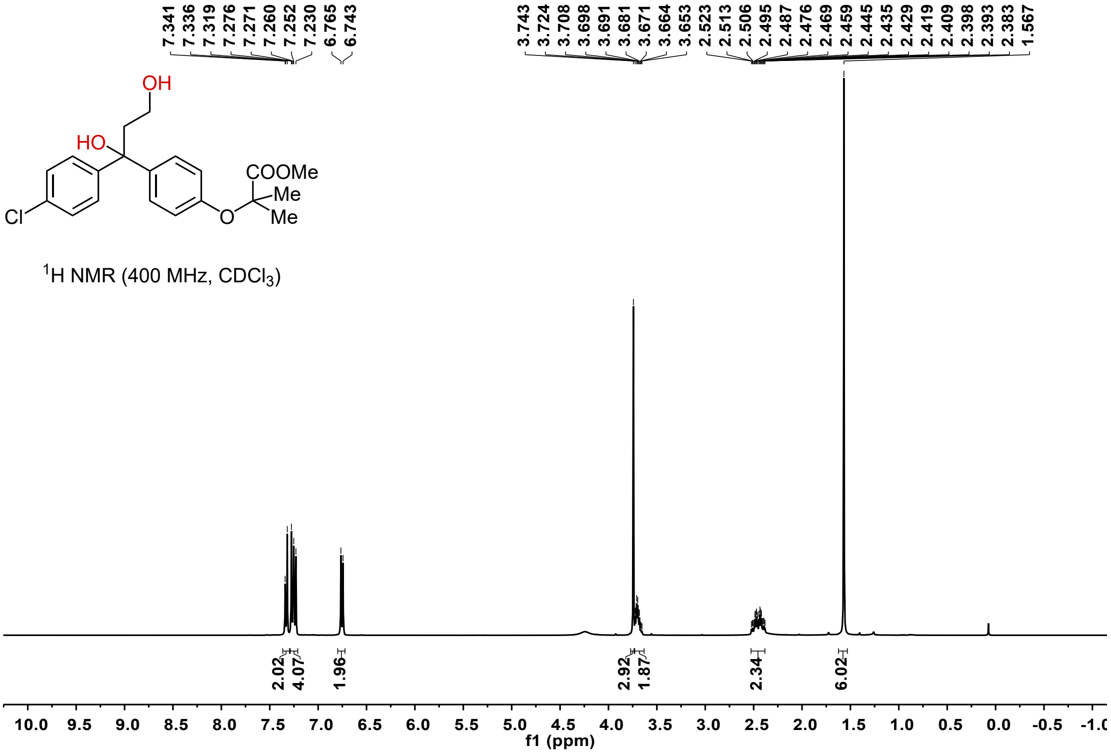


^{1}H NMR (400 MHz, CDCl$_3$)

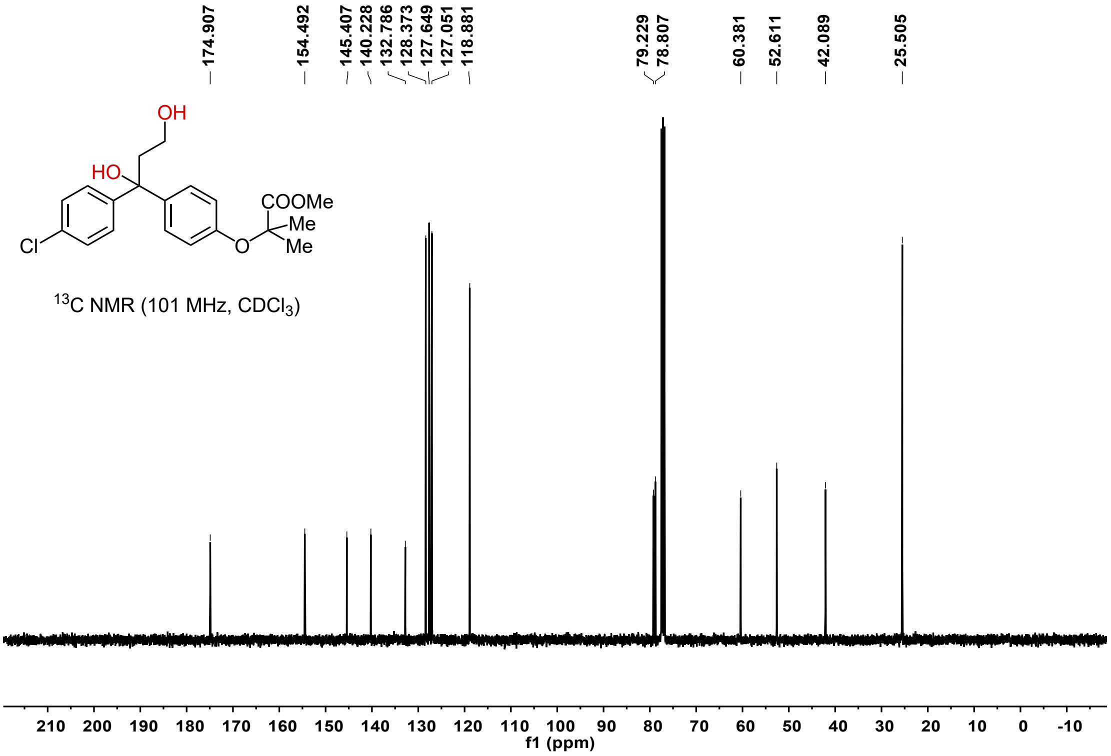


^{13}C NMR (101 MHz, CDCl$_3$)

Fenofibrate derivative-1,3-diol (36)

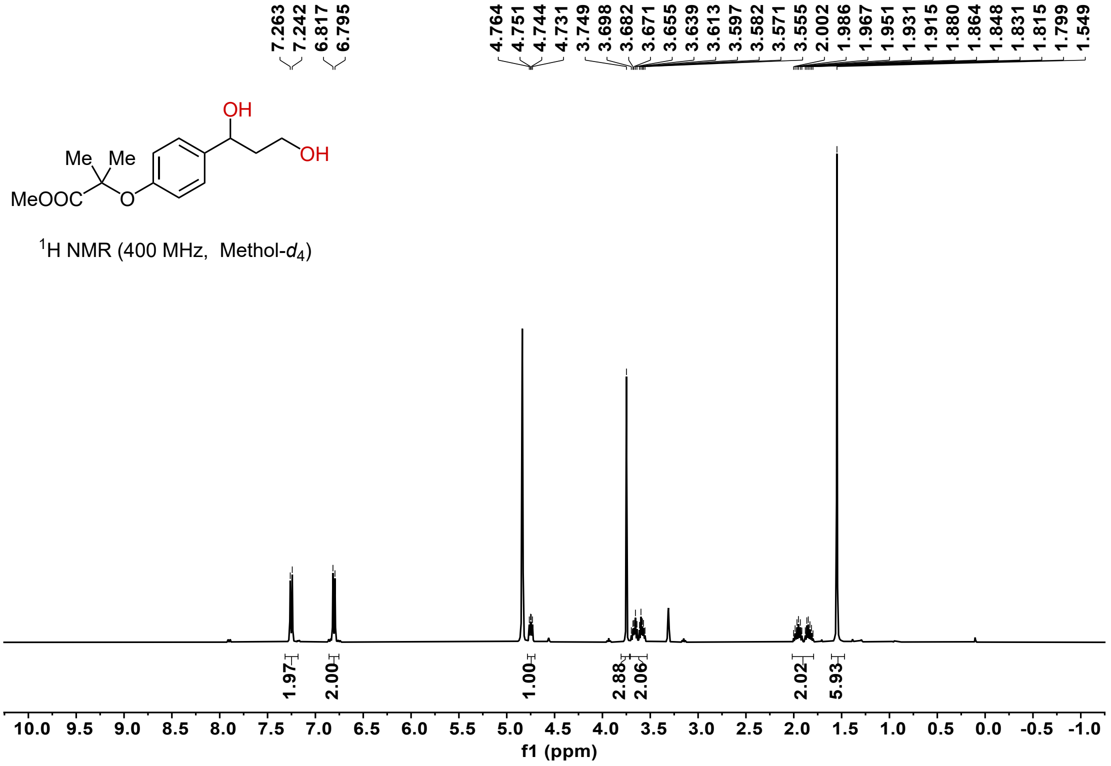


^{1}H NMR (400 MHz, CDCl$_3$)

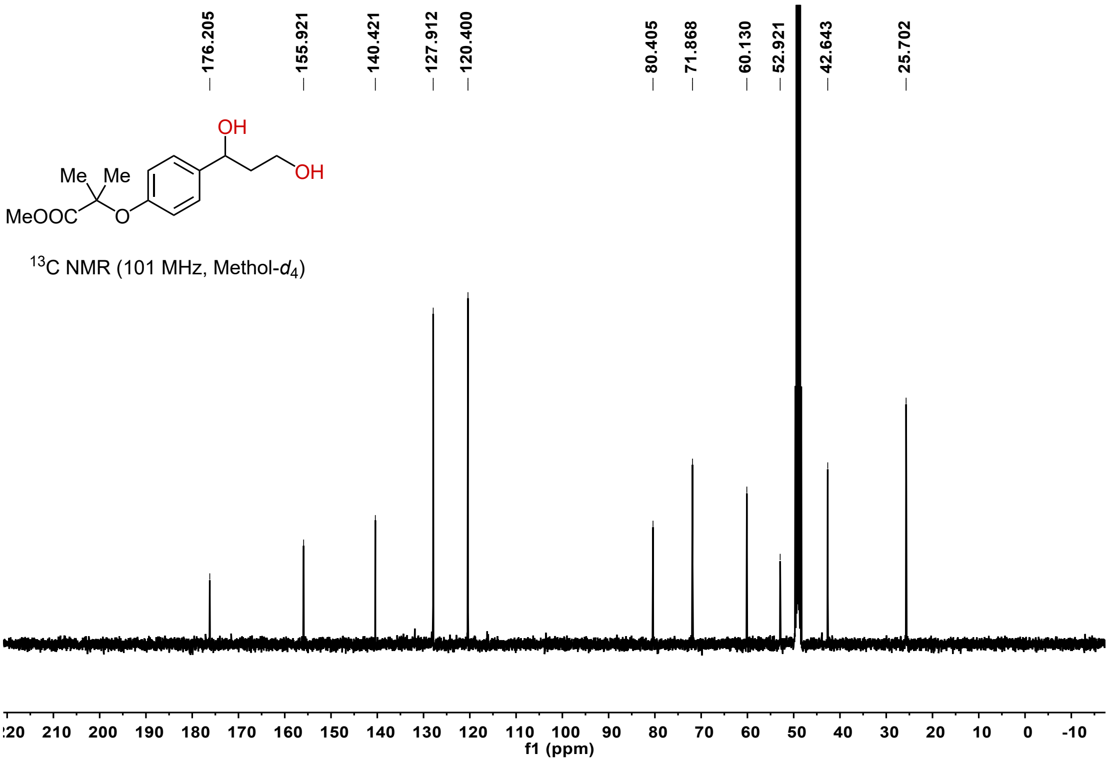


^{13}C NMR (101 MHz, CDCl$_3$)

Ciprofibrate derivative-1,3-diol (37)

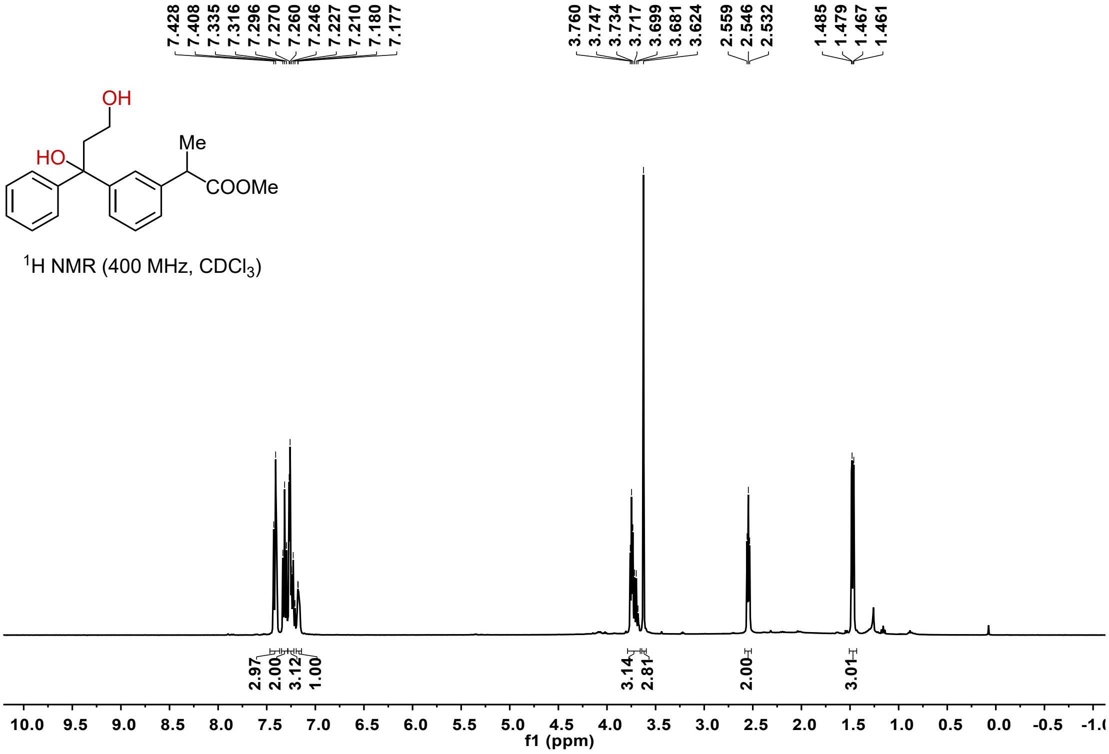


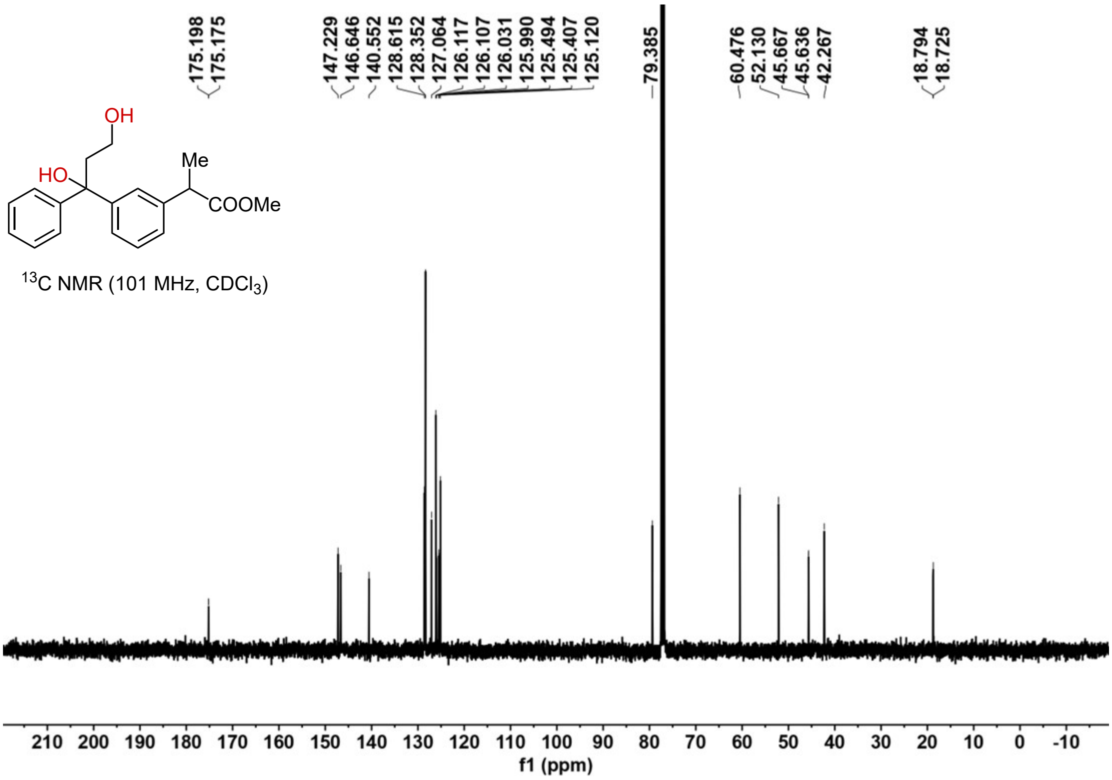
^{1}H NMR (400 MHz, Methol-d_4)



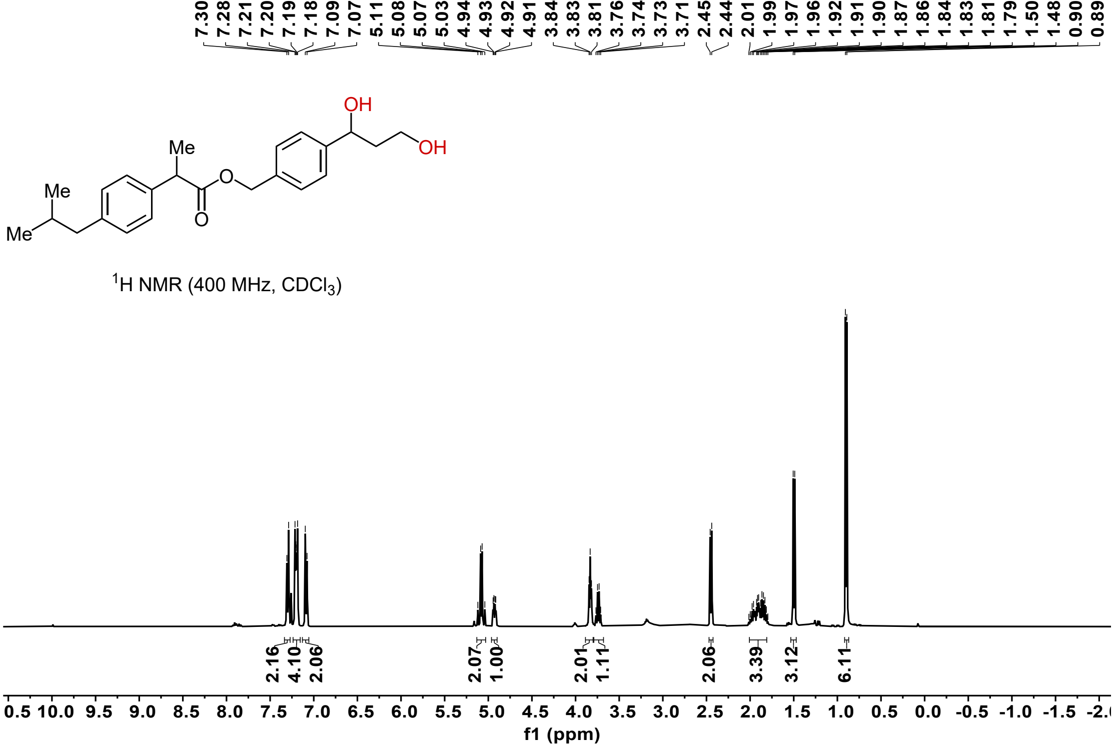
^{13}C NMR (101 MHz, Methol-d_4)

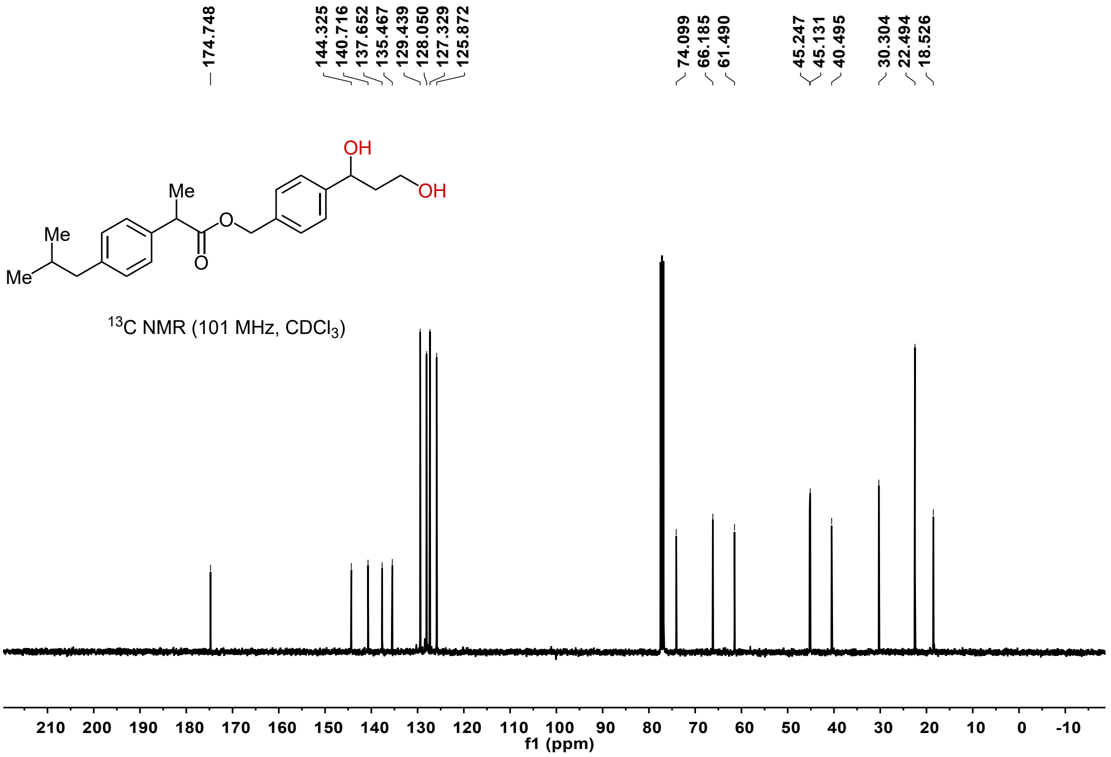
Ketoprofen derivative-1,3-diol (38)



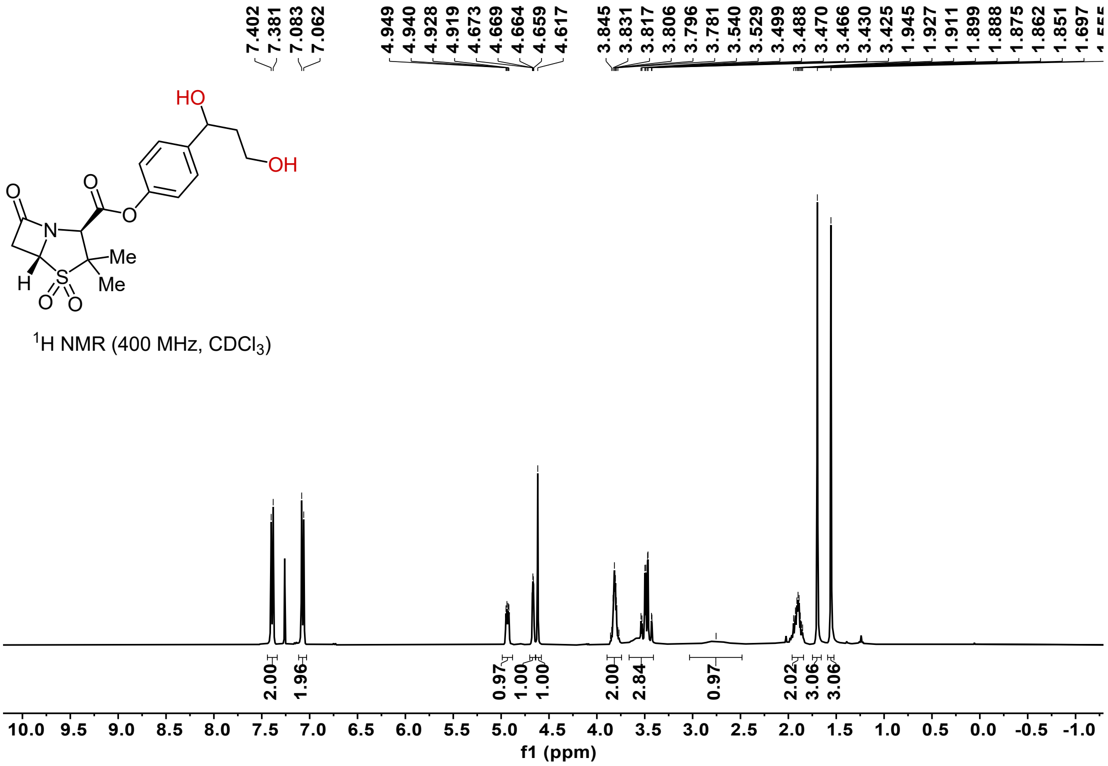


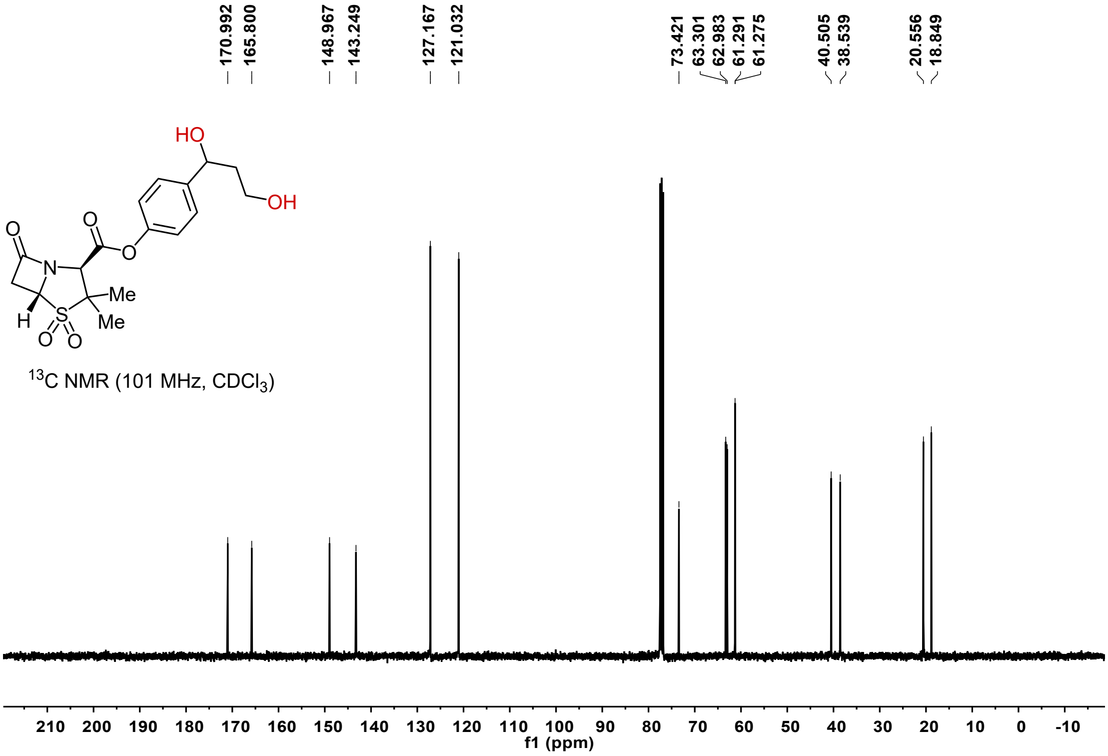
Ibuprofen derivative-1,3-diol (39)



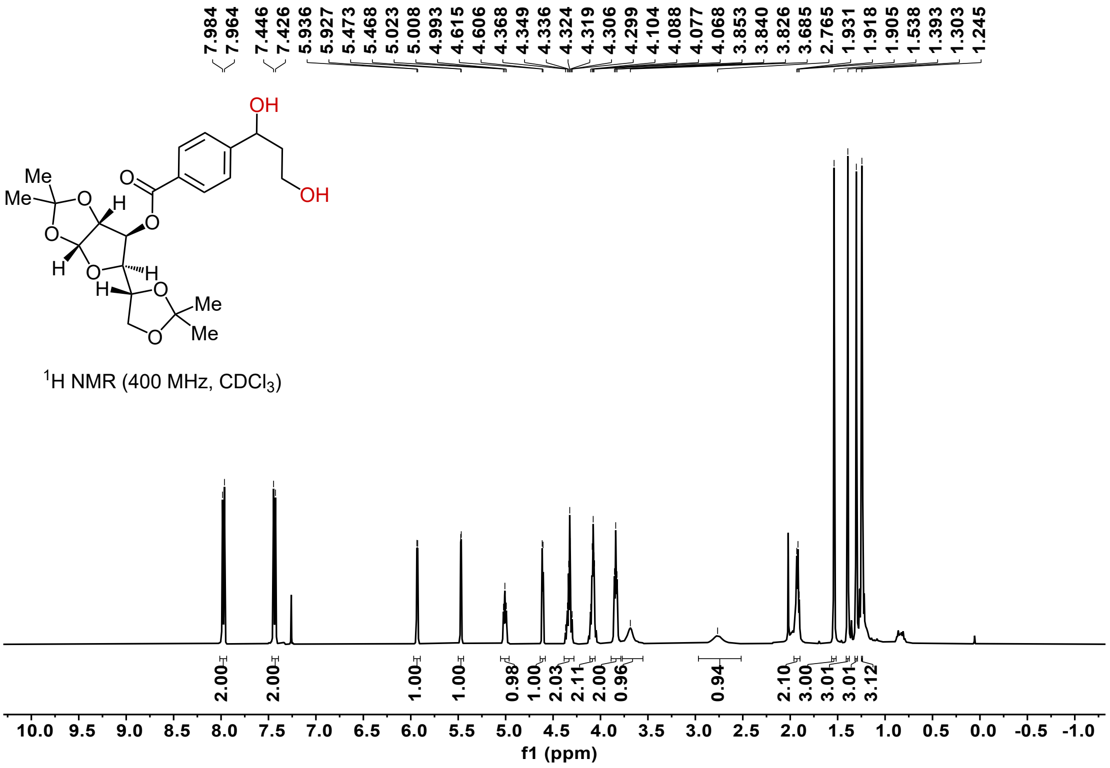


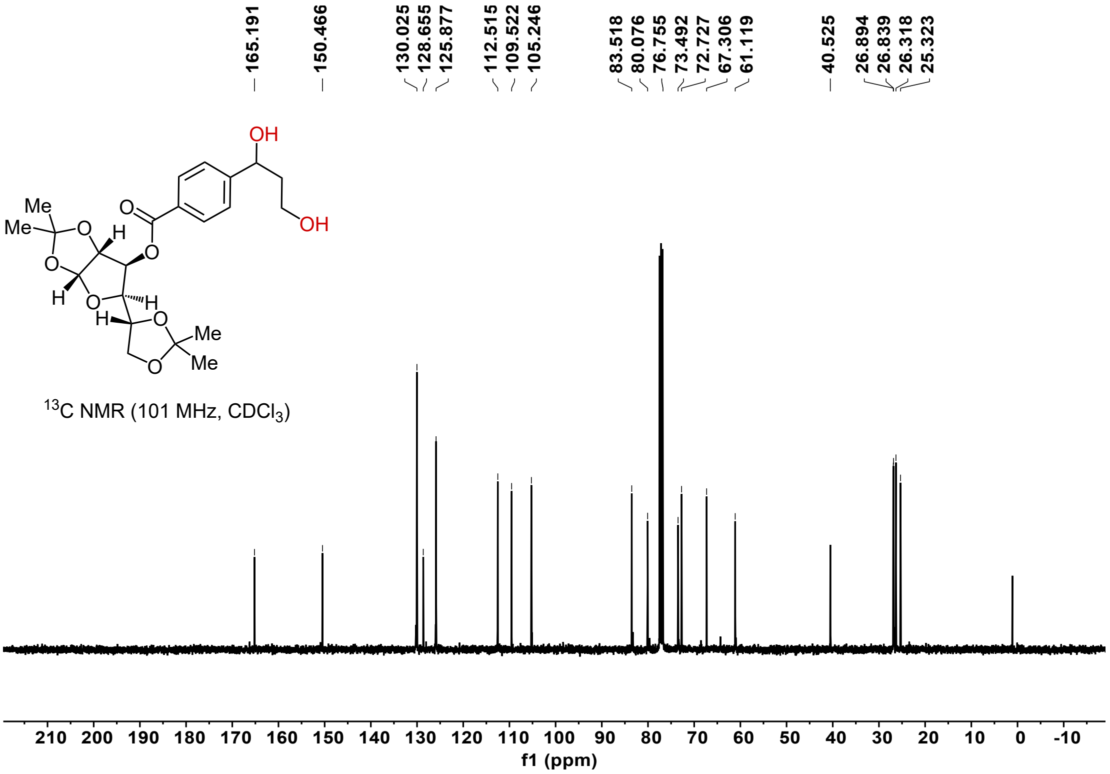
Sulbactam derivative-1,3-diol (40)



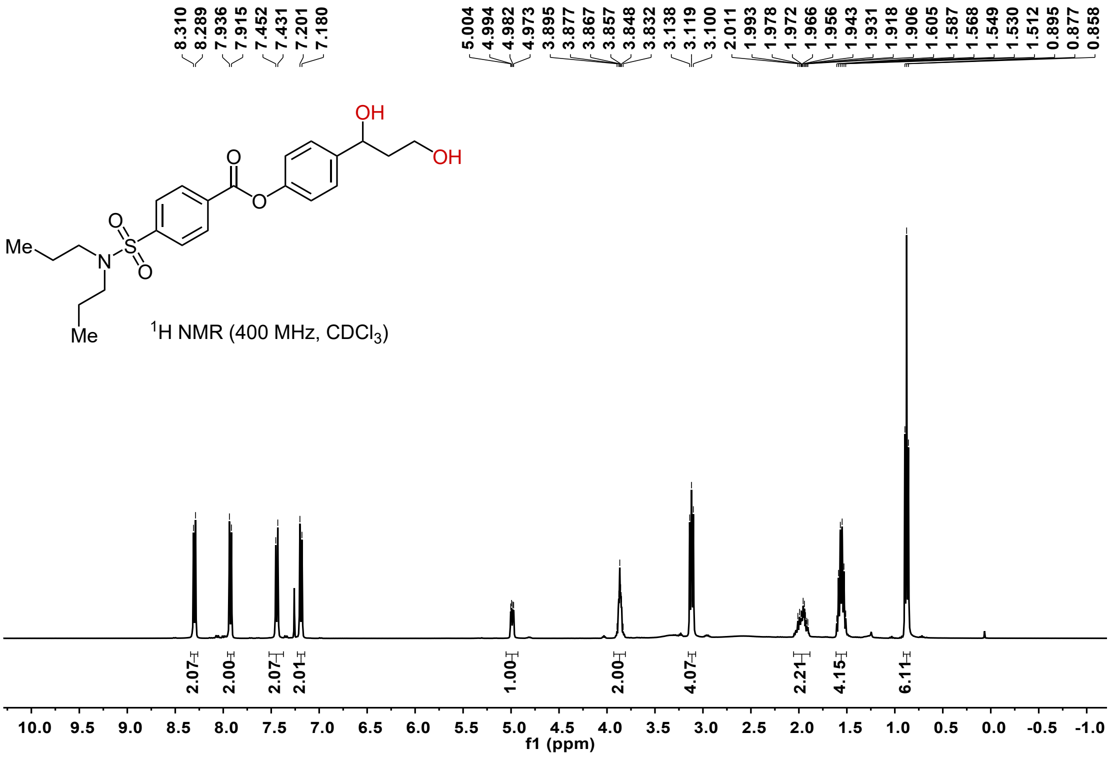


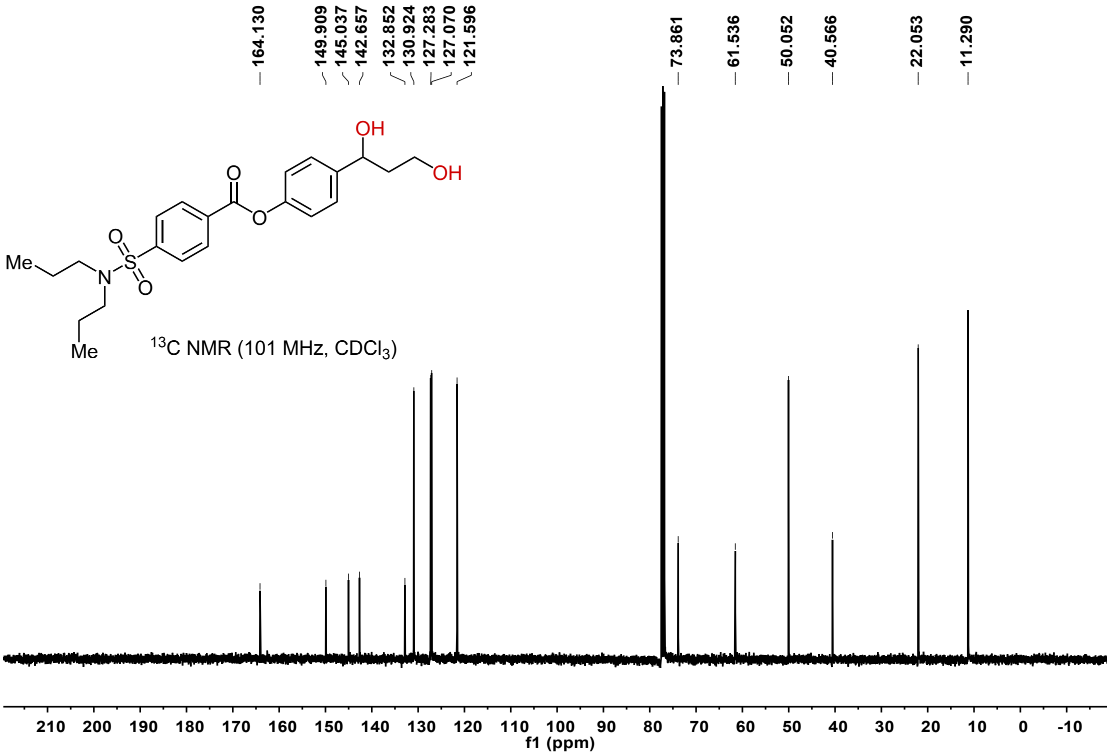
Diacetone-D-glucose derivative-1,3-diol (41)



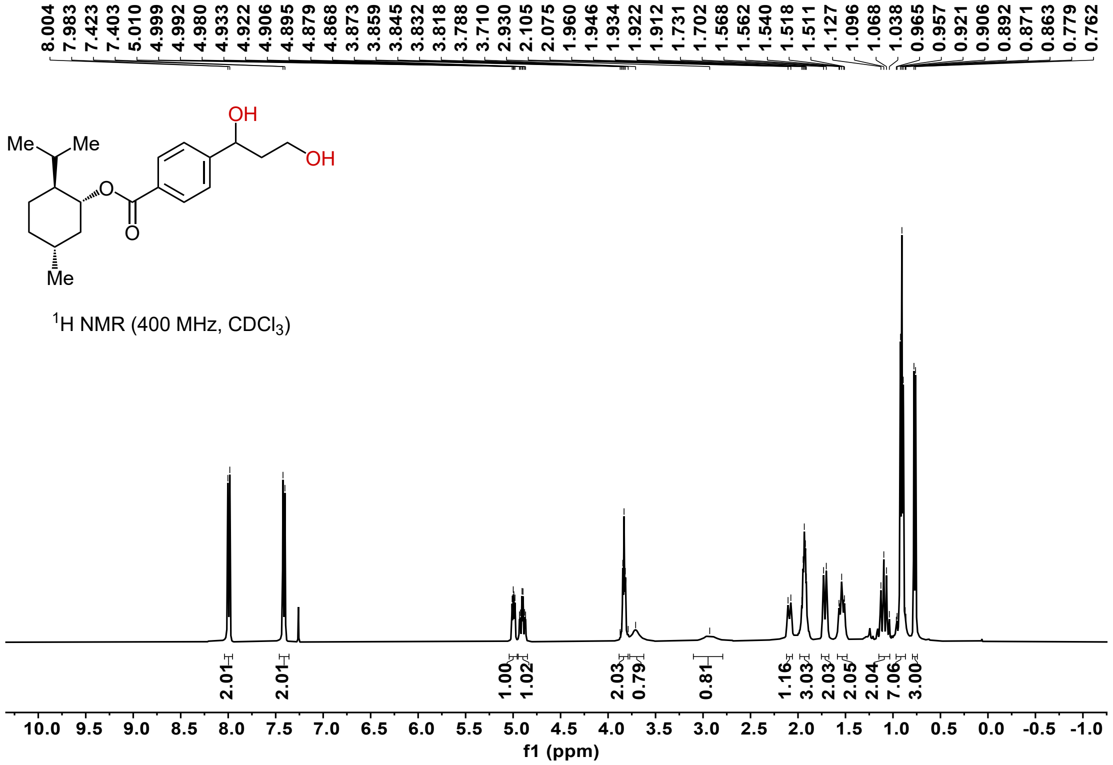


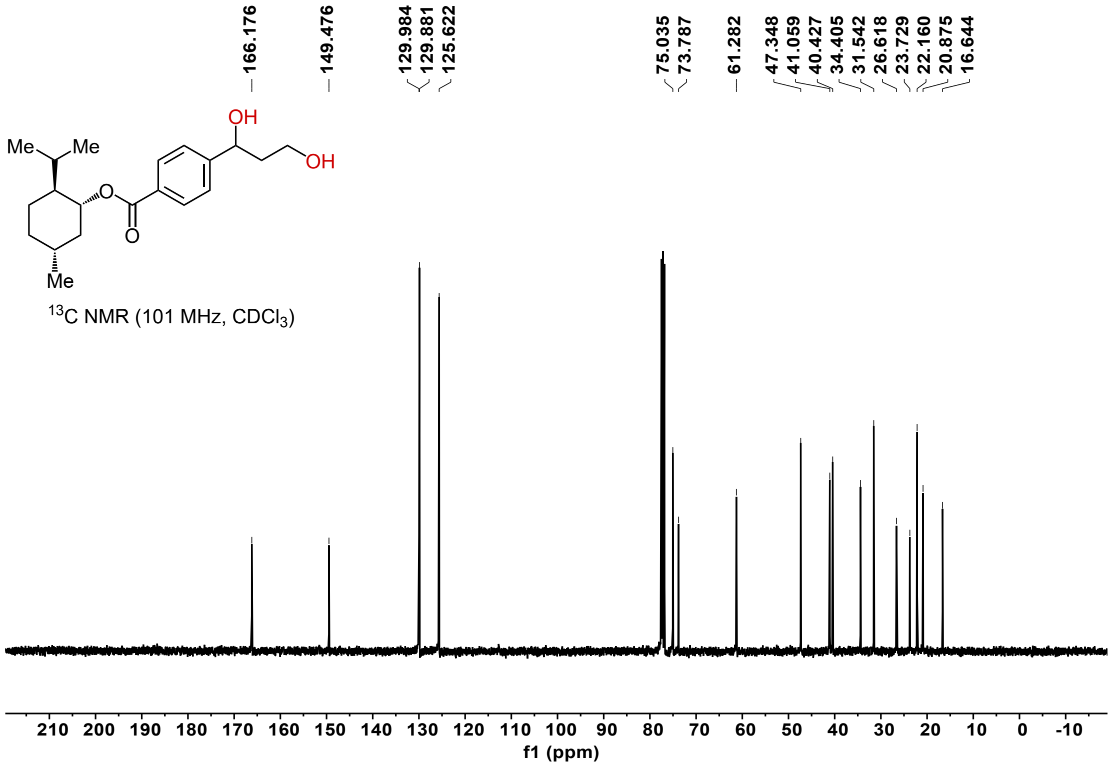
Probenecid derivative-1,3-diol (42)



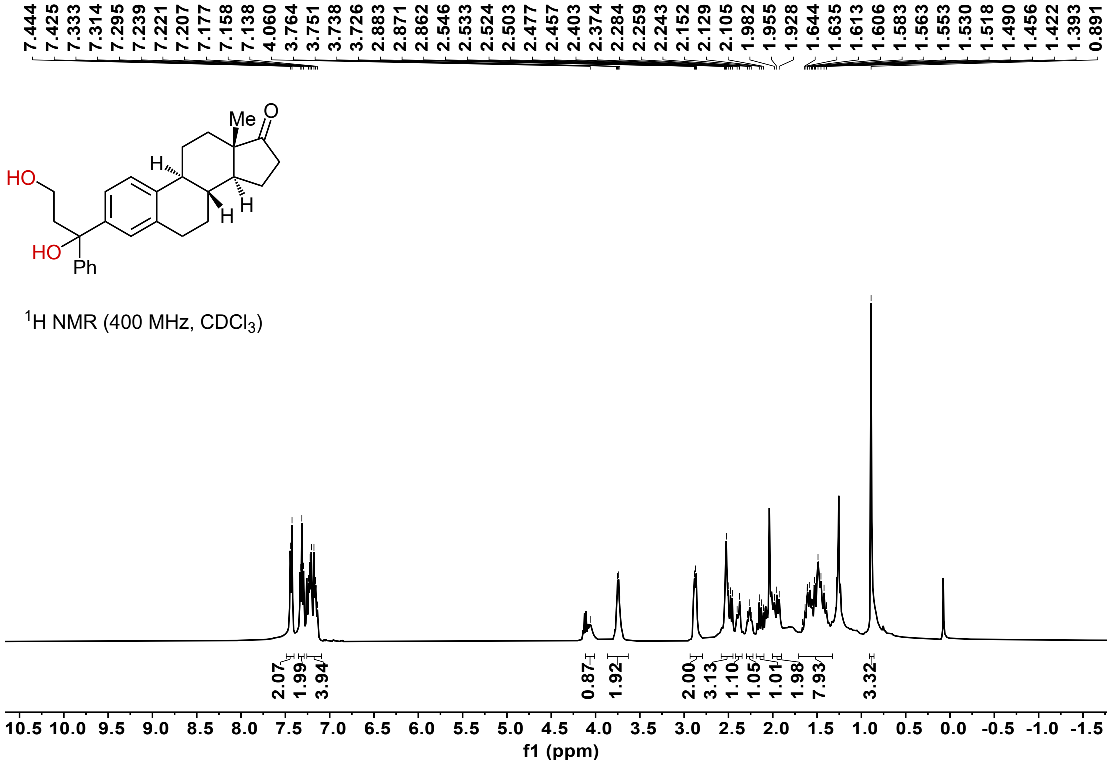


DL-Menthol derivative-1,3-diol (43)

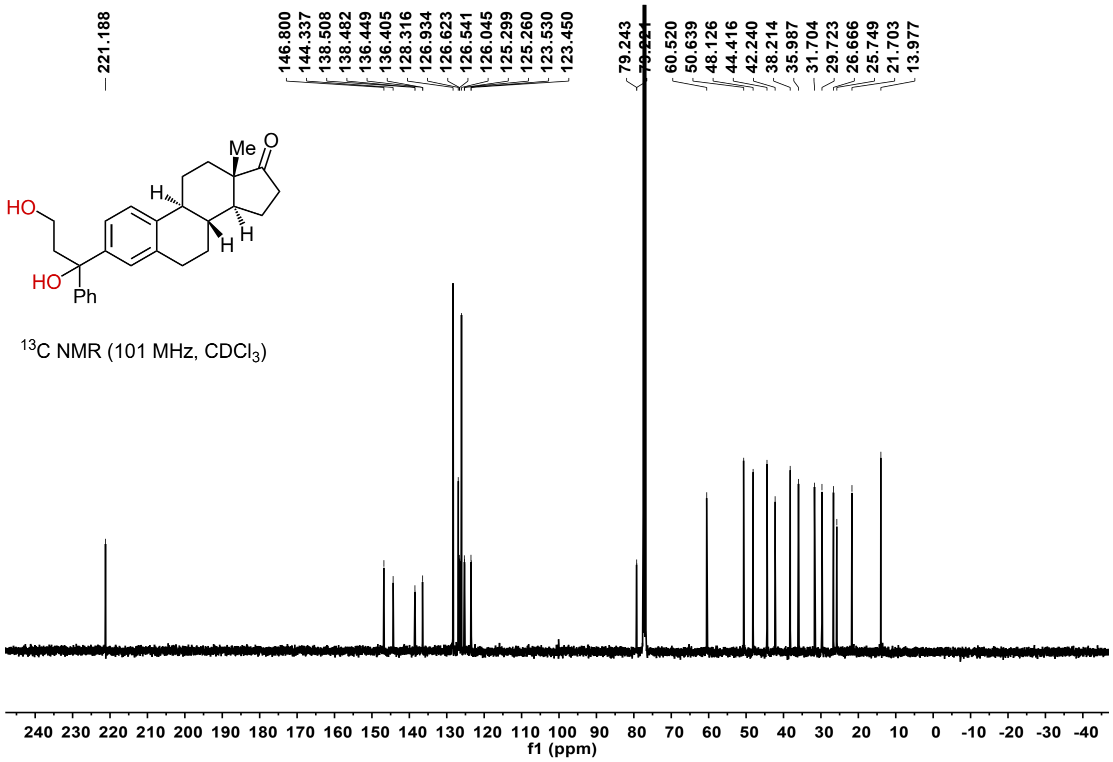




Estrone derivative-1,3-diol (44)

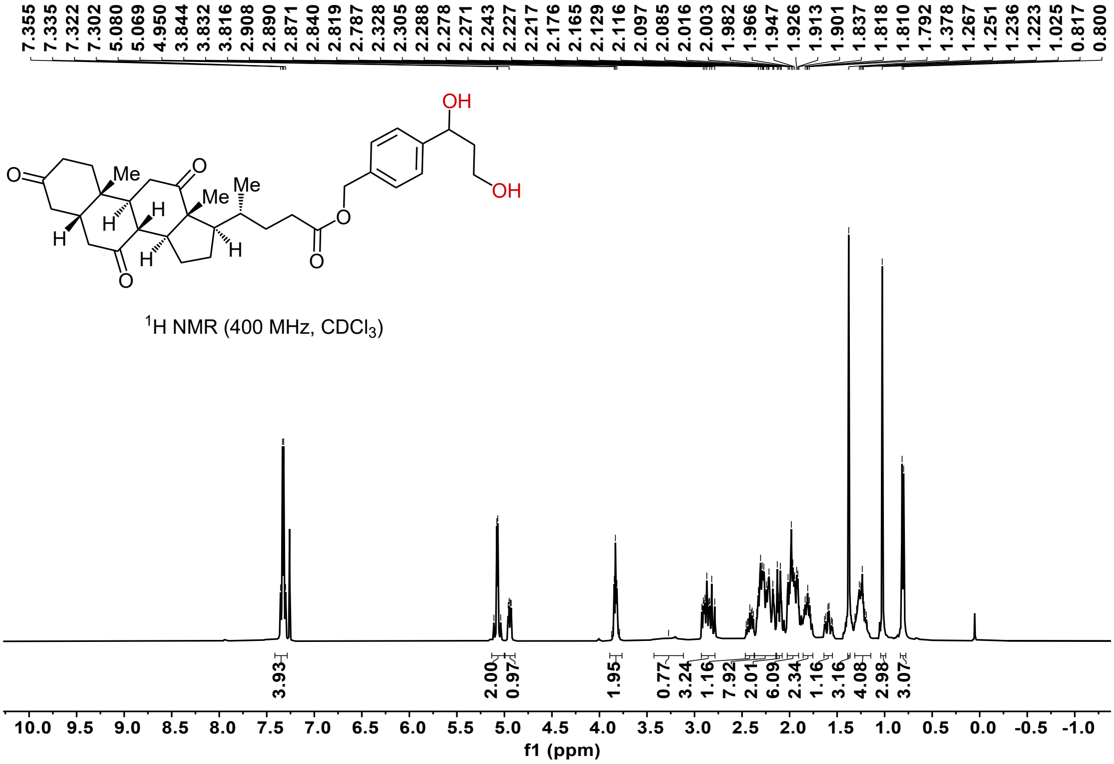


^{1}H NMR (400 MHz, CDCl$_3$)

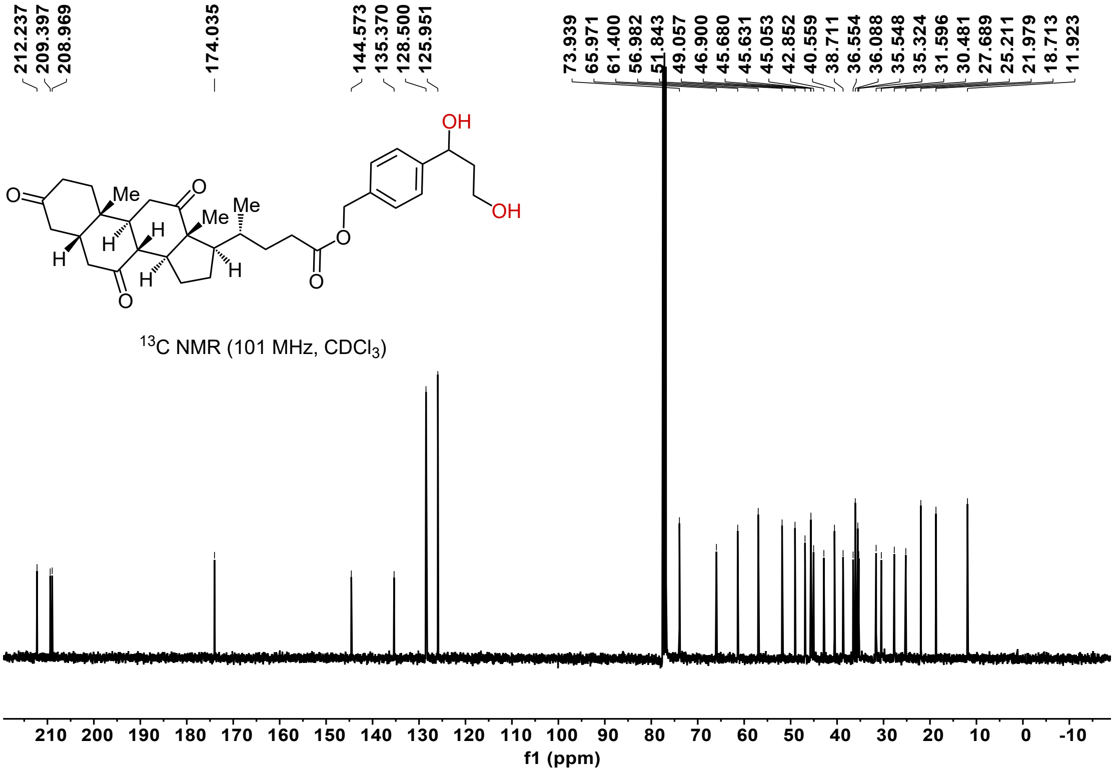


^{13}C NMR (101 MHz, CDCl$_3$)

Dehydrocholic acid derivative-1,3-diol (45)

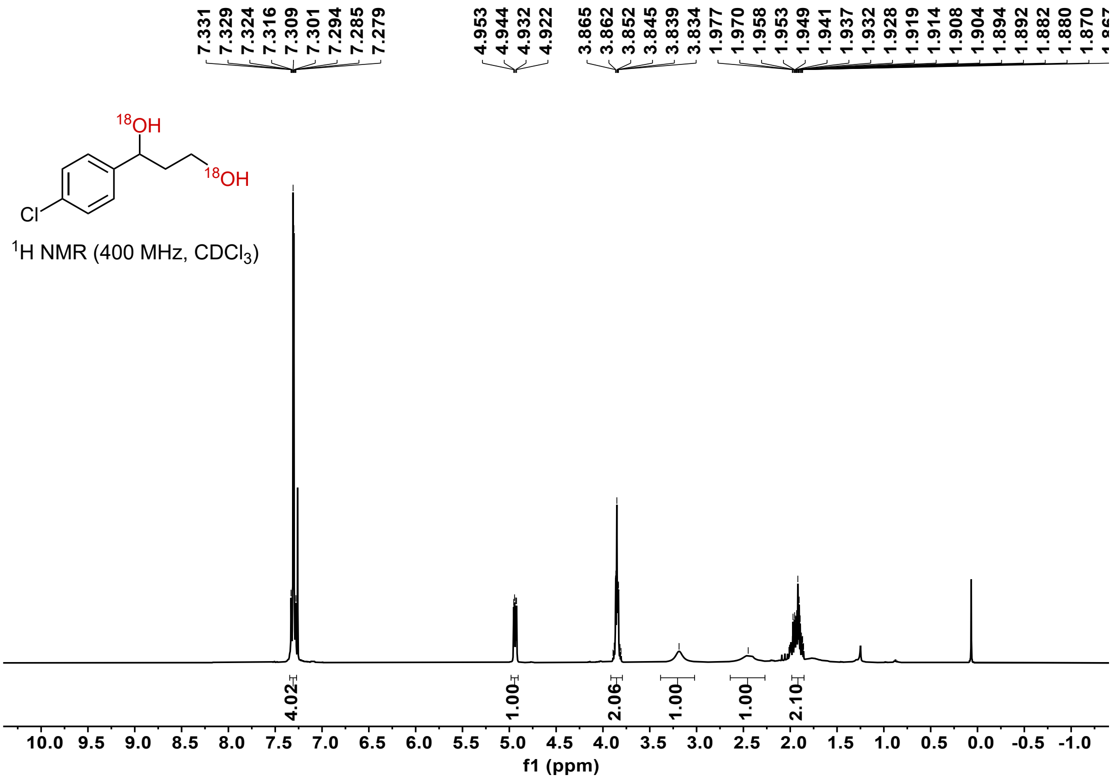


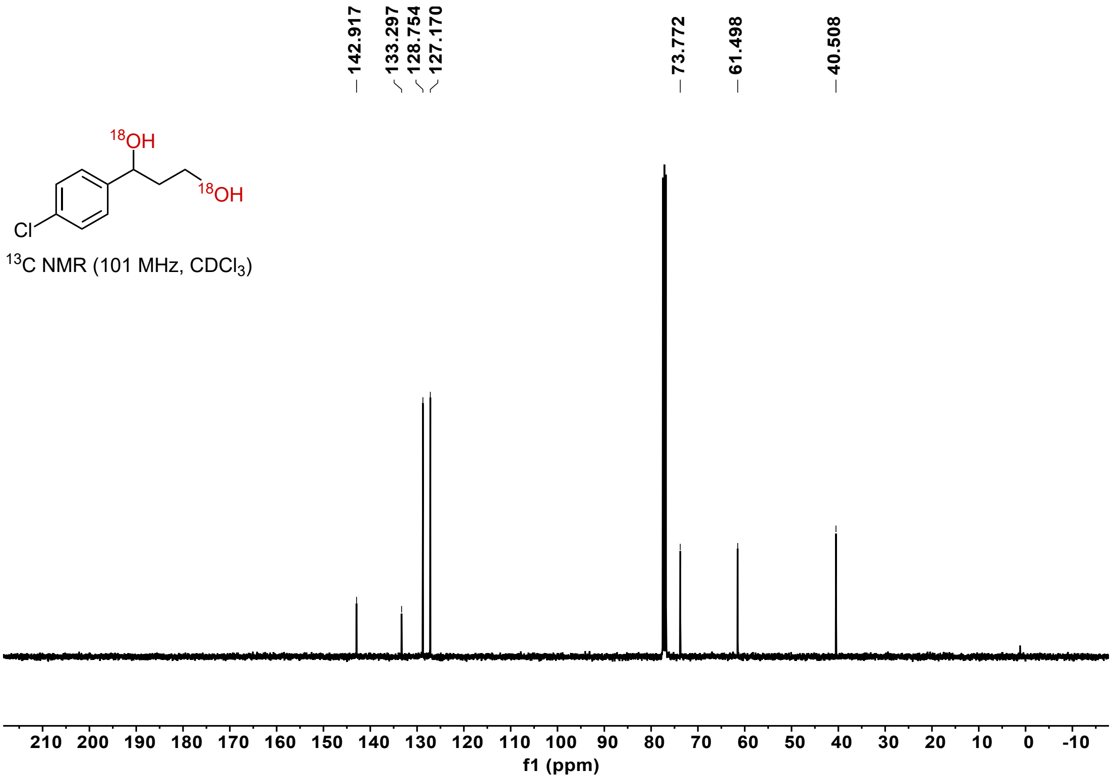
^{1}H NMR (400 MHz, $CDCl_3$)



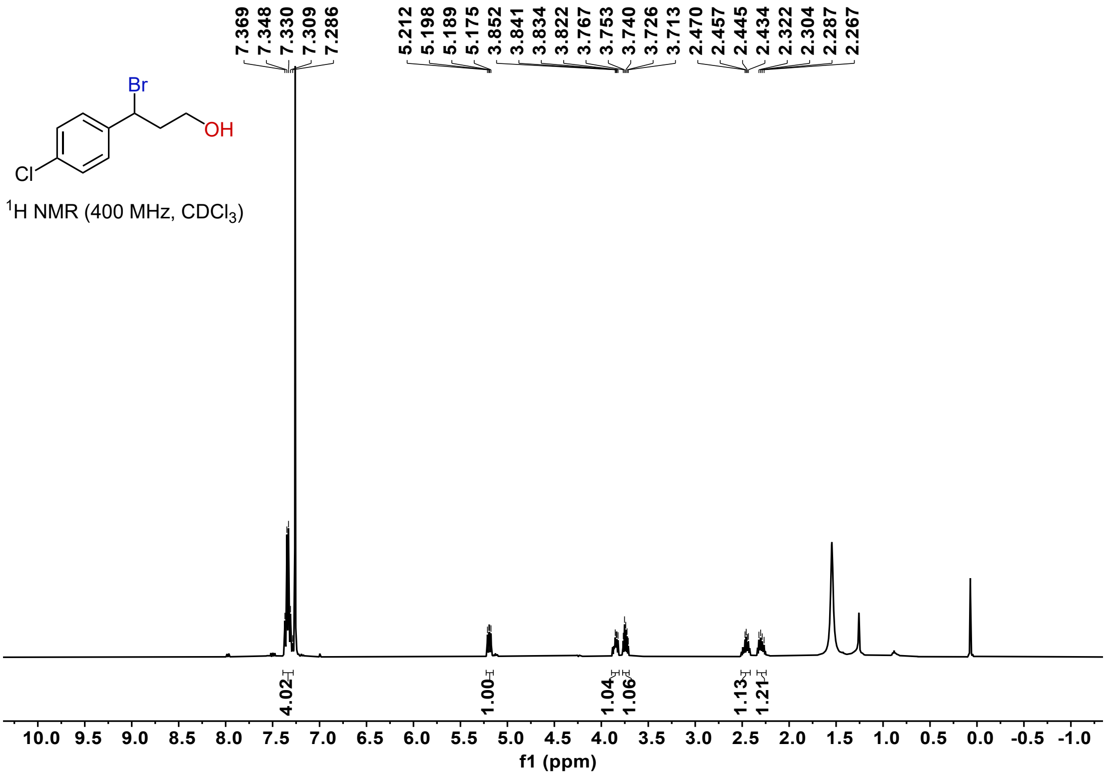
^{13}C NMR (101 MHz, $CDCl_3$)

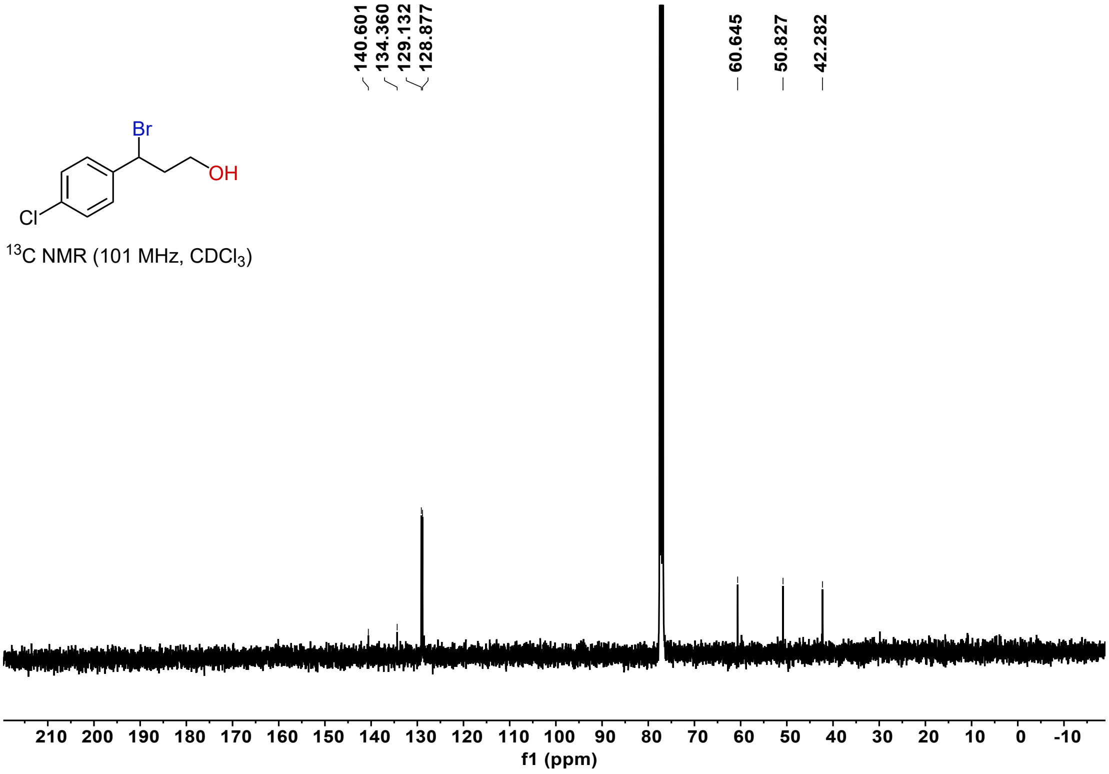
1-(4-Chlorophenyl)propane-1,3-diol-$^{18}O_2$ (^{18}O-1)



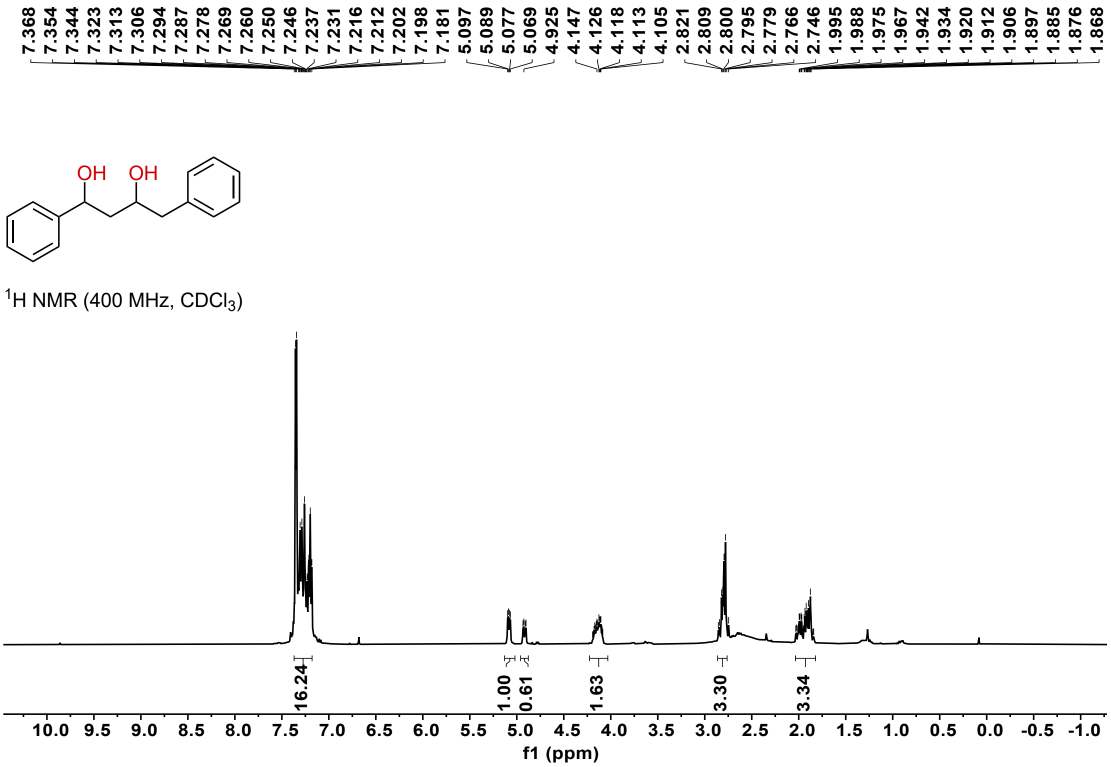


3-Bromo-3-(4-chlorophenyl)propan-1-ol (47)

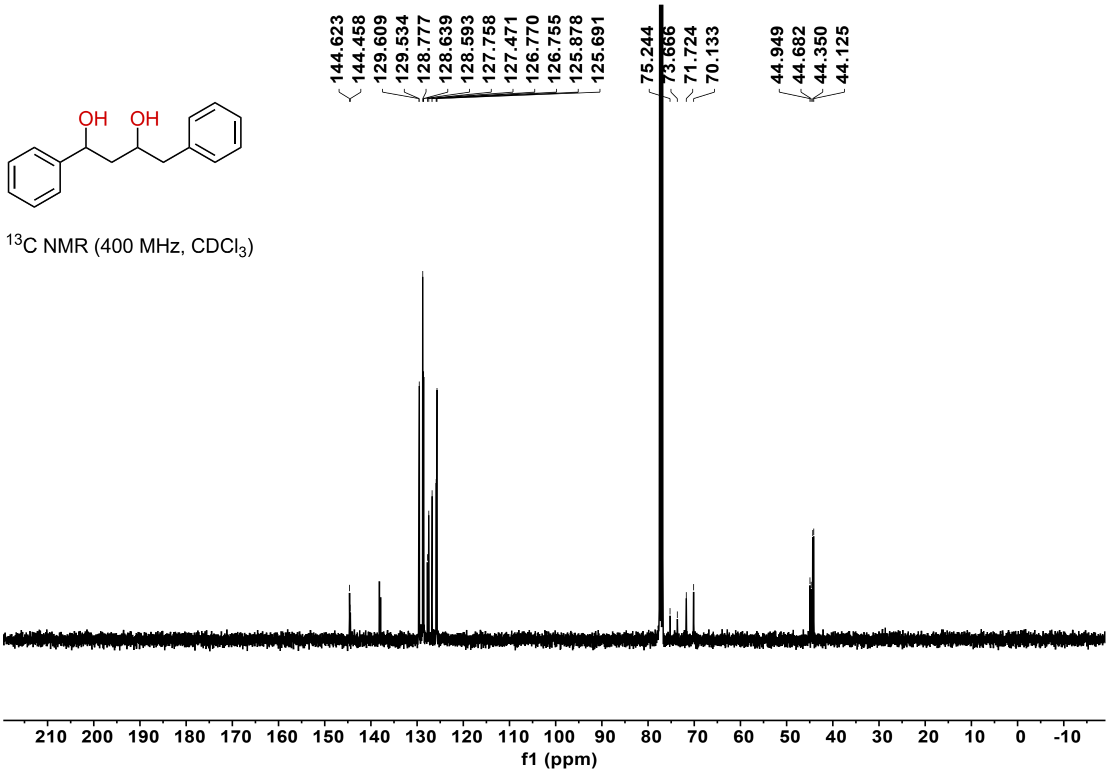




1,4-Diphenylbutane-1,3-diol (48)



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



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