

## Supporting information

# Multiple Mechanisms Mapped in Aryl Alkyl Ether Cleavage via Aqueous Electrocatalytic Hydrogenation (ECH) over Skeletal Nickel

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### Table of Contents

General Experimental Details .....	S2
Preparation of Ni Plating Solution .....	S3
Preparation of pH 7 Phosphate Buffer and pH 8 Borate Buffer .....	S3
Skeletal Nickel Cathode Electrode Preparation .....	S3
Water splitting CoP Anode Electrode Preparation .....	S4
General Procedure of Electro-Catalyzed Hydrogenation.....	S4
Volatile Products Evaporation Accounts for Major Loss of the Mass Balance.....	S5
Evaporation and Extraction Efficiency from Different Co-Solvent .....	S5
Applied example of Evaporation/Extraction Correction to Quantified Yield .....	S9
Full ECH Kinetic Measurements of Direct Competitions .....	S10
Full ECH Kinetic Results for 2-phenylethanol ( <b>7</b> ) .....	S11
Full ECH Kinetic Results for 2-(2-phenylethoxy)phenol ( <b>6</b> ) .....	S11
Full ECH Kinetic Results for 1-phenyl-2-phenoxyethane ( <b>8</b> ) .....	S12
Full ECH Kinetic Results for 2-phenoxy-1-phenylpropanone ( <b>19</b> ).....	S12
Full ECH Kinetic Results for 1-methoxy-4-(2-phenylethoxy)benzene ( <b>16</b> ) .....	S13
Full ECH Kinetic Results for 1-methoxy-2-(2-phenylethoxy)benzene ( <b>15</b> ) .....	S13
Full ECH Kinetic Results for (1-methoxy-2-phenoxyethyl)benzene ( <b>17</b> ).....	S14
Full ECH Kinetic Results for 1-methoxy-4-(2-phenoxyethyl)benzene ( <b>13</b> ) .....	S14
Full ECH Kinetic Results for 1-methoxy-2-(2-phenoxyethyl)benzene ( <b>14</b> ) .....	S15
Full ECH Kinetic Results for 1-methyl-4-(2-phenoxyethyl)benzene ( <b>11</b> ) .....	S15
Full ECH Kinetic Results for 1-methyl-2-(2-phenoxyethyl)benzene ( <b>12</b> ) .....	S16
Full ECH Kinetic Results for 2-(phenoxypropyl)benzene ( <b>18</b> ).....	S16
Full ECH Kinetic Results for 1-(4-methoxyphenyl)-2-phenoxyethanone ( <b>20</b> ) .....	S17
Full ECH Kinetic Results for 1-(4-methylphenyl)-2-phenoxyethanone ( <b>21</b> ) .....	S17
General Experimental Procedure for H/D Isotope Exchange of $\beta$ -O-4 Aryl Ethers.....	S18
MS Fitting Method of H/D Isotope Labeling Experiment .....	S18
Fitting Result % D <sub>n</sub> in the Kinetic H/D Exchange of 2-phenoxyacetophenone .....	S21
H/D Exchange Mass Spectra and NMR Spectra of 2-phenoxyacetophenone (Ketone $\beta$ -O-4) .....	S22
Fitting Results (Washed and Non-Washed Trials) %D <sub>n</sub> in the Kinetic H/D Exchange of 2-Phenoxy-1-phenylethanol (Alcohol $\beta$ -O-4).....	S24
H/D Exchange MS and NMR Spectra of 2-phenoxy-1-phenylethanol (Alcohol $\beta$ -O-4) .....	S24

Fitting Results %D <sub>n</sub> in Kinetic H/D Exchange of 2-phenoxy-1-phenylethane (CH <sub>2</sub> β-O-4).....	S27
H/D Exchange Mass Spectra and NMR Spectra of 2-phenoxy-1-phenylethane (CH <sub>2</sub> β-O-4).....	S28
Cathodic Reduction of 2-phenoxyacetophenone via RVC Electrode.....	S30
NMR Spectra of 2,3-diphenylbutane-2,3-diol from Cathodic Reduction Experiments Using RVC Cathode .....	S31
ECH Co-Solvent Studies using 10% v/v of Each Co-solvent.....	S32
Dimer Synthesis Procedures .....	S32
Cartesian coordinates (Angstroms) and total energies (Hartrees) for compounds <b>1, 2, 8, 10, 18, 19</b> , and their respective C-O fragmentation products.....	S41
NMR Spectra of Synthesized Dimer Model .....	S52
References.....	S39

## General Experimental Details

Chemicals were tested for purity using <sup>1</sup>H NMR prior to use. Aluminum-nickel alloy purum (Al:Ni 50:50 by weight) was purchased from Sigma-Aldrich; Nickel strip 22x127 mm was purchased from Science Company; Nickel(II) chloride hexahydrate 99.3% (metals basis) was purchased from Alfa Aesar; Potassium tetraborate tetrahydrate ≥99.5% was purchased from Sigma-Aldrich; Boric acid (Granular) 99.5% was purchased from J. T. Baker; Potassium carbonate, sodium hydride (60% in mineral oil) and potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>) were purchased from Jade Scientific; Potassium phosphate dibasic (K<sub>2</sub>HPO<sub>4</sub>) and ammonium chloride ≥99.5% were purchased from Columbus Chemical Industries, Inc; Ammonium hydroxide (28~30% NH<sub>3</sub>) was purchased from Mallinckrodt Chemicals; Sodium hydroxide was purchased from Jade Scientific; Phenol 99+%, 4-methoxyphenol (98+%), 4-ethylanisole 98+%, p-cresol 99%, cyclohexyl ethyl ketone 99%, 2-methyl-1-phenyl-1-propanol 98%, 1,2-cyclohexanediol (cis+trans) 98%, iodomethane 99% stabilized with copper, cyclohexyl ethyl ketone 99%, cyclohexyl methyl ketone 95% and 1-cyclohexyl-1-propanol 97% were purchased from Alfa Aesar; Acetophenone 99%, 1-phenylethanol 98%, ethylbenzene anhydrous 99.8%, cyclohexanol, methyllithium solution (1.6 M in diethyl ether), 4-ethyltoluene ≥95%, propylbenzene 98%, 4-methoxyphenethyl bromide 97%, 4-methylphenethyl bromide 97%, 4-methoxyacetophenone 99%, 4-methylacetophenone 95%, 2-phenoxyethanol ≥99%, isobutyrophenone 97%, isobutylbenzene 99%, 1-phenyl-2-propanol 98%, 2-methylphenethyl bromide 97%, 2-ethyltoluene 99%, 1,10-phenanthroline >99%, 2,3-diphenyl-2,3-butanediol, 1-phenyl-1-propanol ≥97% and propiophenone 99% were purchased from Sigma-Aldrich; Guaiacol 99+% was purchased from Acros Organics; Nafion membrane 117 was purchased from Fuel Cell Store; *N,N*-dimethylformamide 99.9%, tetrahydrofuran (THF) >99.9% and pentane HPLC grade 99.7% were purchased from Fisher Chemical; Hexane 98.5% was purchased from VWR Chemicals; Isopropyl Alcohol ≥99.5% was purchased from VWR Analytical; Dichloromethane ≥99.5% (40-150 ppm amylene as stabilizer), methanol ≥99.8%, ethyl acetate ≥99.5% and 1,4-dioxane ≥99.0% were purchased from Sigma-Aldrich. All other solvents were purchased from commercial suppliers and used without further purification.

Duocel<sup>®</sup> reticulated vitreous carbon foam (100 Pores Per Inch) was purchased from ERG materials & aerospace.

Column chromatography purification of reaction mixtures was performed using Silicycle (Quebec City, Canada) SiliaFlash P60 silica gel (40-63 μm). Thin layer chromatography (TLC) analysis of reaction mixtures was performed using Sigma Aldrich (St. Louis, MO) plastic silica gel 60 F-254 plates and the bands were visualized using UV light (254 nm) or by staining with KMnO<sub>4</sub>.

Nuclear magnetic resonance (NMR) spectra were acquired on Agilent 500/54 premium shielded instruments at the Michigan State University, NMR facility.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ( $\text{CHCl}_3$ ;  $\delta\text{H} = 7.26$  ppm). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. GC-MS analyses were performed on an Agilent 7890A GC/ single quadrupole mass spectrometer with 5975C inert XL MSD (Agilent, Santa Clara, CA) equipped with Agilent J&W VF-5ms column (30 m x 0.25 mm x 0.25 mm) (Agilent, Santa Clara, CA). GC-MS yields were determined based on external standards with prepared concentrations (0.25 mM - 4 mM) to form a 5-point calibration curve for each corresponding compound. Each GC-MS analysis sequence included a freshly prepared external standard sequence.

### **Preparation of Ni Plating Solution**

To a 1 L volumetric flask, 213 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 30 g of  $\text{NH}_4\text{Cl}$  were added, 500 mL of deionized water was added, following by the addition of 200 mL (28~30%  $\text{NH}_3$ )  $\text{NH}_4\text{OH}$  solution to keep the plating bath pH between 9-10. Addition of deionized water was continued to make a total volume of 1 L plating solution. The prepared plating solution was transferred into a 1.2 L glass bottle and stored in nitrogen glove bag. Preparation of Ni plating solution followed our previously reported procedure.<sup>1</sup>

### **Preparation of pH 7 Phosphate Buffer and pH 8 Borate Buffer**

#### pH 8 Borate Buffer (0.1 M):

To a 500 mL volumetric flask, 3.00 g of  $\text{H}_3\text{BO}_3$  (0.097 M) and 1.00 g of  $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$  (0.0066 M) was added, the chosen water/co-solvent mixture (most commonly 2:1 v/v  $\text{H}_2\text{O}/\text{IPA}$ ) was added to make a buffer with 500 mL total volume, measured pH; if needed, KOH was added to adjust pH to 8.

#### pH 7 Phosphate Buffer (0.1 M):

To a 1 L volumetric flask, 5.30 g of  $\text{KH}_2\text{PO}_4$  (0.039 M) and 10.8 g of  $\text{K}_2\text{HPO}_4$  (0.062 M) was added, deionized water was added to make a buffer solution with 1 L total volume.

### **Skeletal Nickel Cathode Electrode Preparation**

To obtain the maximum surface area of the skeletal nickel contains most potential active site, the cathode was prepared by Lessard's<sup>2</sup> and Lam's<sup>1</sup> methods with small modifications, using a square mesh of stainless steel undergoing nickel electroplating to trap the aluminum-nickel (1:1) powder. About 1.5 g of Aluminum-nickel (1:1) alloy purum was placed in 50 ml of nickel-ammonia plating solution with stirring at 350 rpm, to result in a heterogeneous suspension. A square of stainless steel 314 screen (50 mesh, 2.5 x 2.5 cm) that connected to the cathode was positioned facing parallel to a plain nickel bar as a sacrificial anode. Application of electrical current allows direct deposition of nickel on the mesh to trap the nickel-aluminum powder during the reduction of nickel ions. The plating current was maintained at 0.6 A to for approximately 1~2 hours, and the cathode was turned 180° every 30 minutes to ensure even deposition of the nickel-aluminum particles on both sides. The plated skeletal nickel cathode was then activated in 30 wt% NaOH solution at 75 °C for 6 hours to etch out the aluminum. After the etching process, the activated

skeletal Ni electrode was washed with deionized water to wash off the surface base and stored in different organic solvents for a minimum of 24 hours before the next use.

IPA treated Catalyst (Low Surface Oxide Storage): The fresh activated skeletal nickel cathode prepared as described above was stored in pure 2-propanol under nitrogen for a minimum of 24 hours before the next use.

Acetone treated Catalyst (Surface H Discharged Storage): The fresh activated skeletal nickel cathode prepared as described above was stored in pure acetone under nitrogen for a minimum of 24 hours before the next use.

### **Water splitting CoP Anode Electrode Preparation**

The Kanan-Nocera<sup>3</sup> cobalt phosphate (Co-P) water splitting anode electrode was formed in-situ during the electro-catalytic process before the injection of the organic substrate in cathode half-cell. A flat square stainless steel (8 mesh, 12 cm x 4 cm) rolled up cylinder shape with a cross-section of 2.5 cm x 2.5 cm that will be immersed in the electrolyte was placed in the anode half-cell in 30 ml of 0.1 M potassium phosphate buffer with 30 mg of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . After dissolving the  $\text{Co}(\text{NO}_3)_2$  into the potassium phosphate buffer a small amount of precipitate was formed, due to the low solubility of  $\text{Co}_3(\text{PO}_4)_2$  ( $K_{\text{sp}} = 10^{-35}$ ).<sup>3</sup> Under the electrical current, the deposition of Co-P coats onto the stainless-steel surface as a black thin coating, which can enable oxygen evolution and proton production via water oxidation. Note that after application of potential and current, the  $\text{Co}_3(\text{PO}_4)_2$  precipitate gradually dissolved, presumably due to the continuous oxidation of  $\text{Co}^{2+}$  ions.

### **General Procedure for Electrocatalytic Hydrogenation**

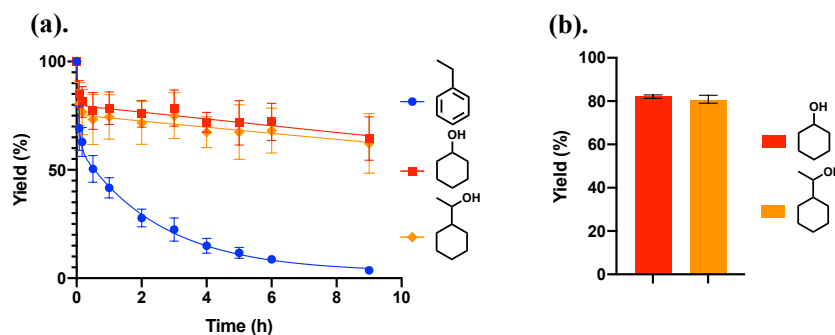
The hydrogenation of all aryl ether substrates followed a similar procedure. A two divided half cells were separated by a Nafion 117 membrane. The cathode half-cell was equipped with a water condenser to prevent evaporative loss of the buffer solution. The Skeletal Ni cathode was placed in the cathode side with 20 mL of 0.1 M pH 8 potassium borate buffer with the addition of 8 mL 2-propanol as co-solvent. A small stir bar was also placed inside the cathode half-cell (stirring at 300 rpm). An additional 2 ml of 2-propanol was used to dissolve the weighed aryl ether substrate (0.25 mmol) in a 4-mL glass vial, in preparation for its addition to the cathode solution. Depending on the aryl ether substrate, warming the vial to 60 °C was sometimes needed to ensure complete dissolution of the corresponding aryl ether. The Co-P coated stainless steel anode was placed in 30 mL of 0.1 M pH 7 potassium phosphate buffer. The entire set up was placed in a water bath where the temperature was maintained at 60 °C. The divided cell containing both electrodes was equilibrated for 30 mins to obtain a constant current at 50 mA (current density 8 mA/cm<sup>2</sup>). The vial with the 2 mL of 2-propanol with the aryl ether substrate was added into the cathode solution and hydrogenated for 9 hours at 60 °C under ambient pressure.

#### Quantitative Analysis Preparation:

At each desired time point 0.25 mL of cathode solution was syringed into a 1.7 mL conical vial for extraction. To extract the organics, 3 drops of diluted HCl solution were added to the conical vial to acidify the cathode solution following by the addition of 3 drops of saturated NaCl solution, 1 mL of dichloromethane (DCM) was added, the conical vial was vortexed, and the bottom DCM layer was carefully pipetted into a GC vial. The sample was analyzed through GC-MS, and quantified with the calibration curves of the corresponding external standard of each compound.

## Volatile Products Evaporation Accounts for Major Loss in the Mass Balance

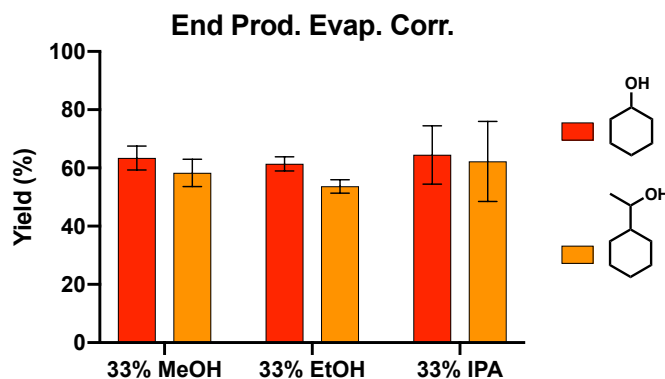
In situ formation of surface H creates a potentially powerful hydrogenation method; however, water reduction also generates a large amount of hydrogen gas. Under ambient pressure and with an open system, volatile and water insoluble products such as alkylbenzenes were sparged by this bubbling, making them hard to capture, causing incomplete mass balance. Meanwhile, to ensure the homogeneity for kinetic measurements of water insoluble ether substrates, 33% v/v isopropanol was used, which resulted in extraction losses of alcohol end products.



**Figure S1.** (a) Kinetic evaporation curves of ethylbenzene, cyclohexanol and 1-cyclohexylethanol (non-reducible products) under standard ECH condition, 60 °C, 50 mA, 2-propanol treated catalyst with 33% 2-propanol as co-solvent. (b) Extraction efficiency of cyclohexanol and 1-cyclohexylethanol in pH 8 borate buffer with 33% 2-propanol. Analytical sample preparation is the same as in the above described analysis section.

In the evaporation curves Figure S1a, ethylbenzene (low water solubility) almost completely evaporated after 9 hours of ECH. Cyclohexanol and 1-cyclohexylethanol suffered less evaporation loss in this period (~20%), but the extraction process of both alcohols caused ~20% loss (Figure S1b). The evaporation curves and extraction efficiency of cyclohexanol and 1-cyclohexylethanol were used to correct the yields in the ECH kinetics. The correction process is described below. However, due to its fast evaporation, the ethylbenzene correction is unable to be applied in the kinetic data, because the rate of evaporation is faster than the rate of formation. Therefore, the actual yields of ethylbenzene were larger than the reported numbers.

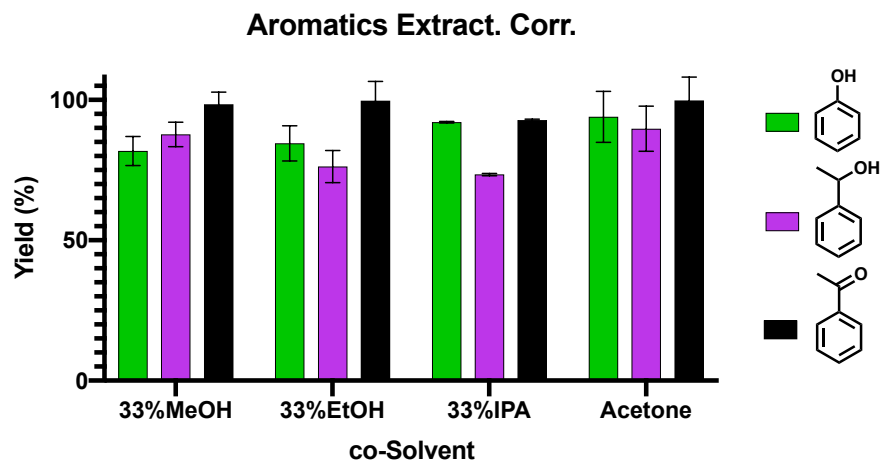
### End Product Evaporation in Different Co-solvent:



**Figure S2.** Cyclohexanol and 1-cyclohexylethanol evaporation efficiencies in different co-solvent (33% v/v) mixtures after 9 hours of ECH at 60 °C with 2-propanol treated electrode under 50 mA.

In the co-solvent studies, methanol and ethanol were also used as co-solvents (Figure 10), the ECH in both alcohols also generate the aromatic reduction products cyclohexanol and 1-cyclohexylethanol. Evaporation correction of both product in 33% v/v methanol and ethanol were also performed to correct the corresponding quantified yields (Figure S2).

### Aromatic Intermediates Extraction Efficiency in Different co-Solvents:

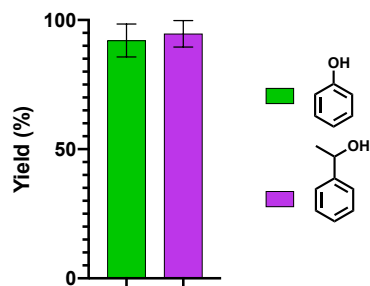


**Figure S3.** Extraction efficiency of aromatic intermediates phenol, 1-phenylethanol and acetophenone in different co-solvents (33% v/v). Standard deviations shown are from triplicate measurements.

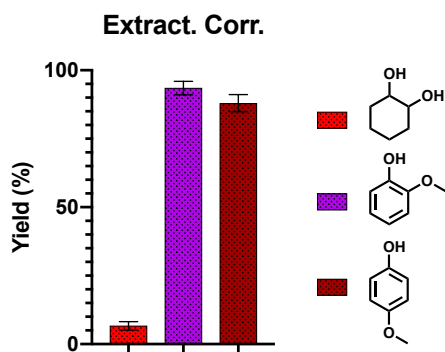
For the three reducible aromatic intermediates, phenol, 1-phenylethanol and acetophenone, only extraction corrections were performed to the quantified yield. Phenol and acetophenone both could be efficiently extracted out of the buffer mixture. However, in 33% v/v ethanol and isopropanol the extraction efficiency of 1-phenylethanol is lower. Repeated extraction corrections were performed to confirm the lower extraction efficiency of 1-phenylethanol in the dual solvent system; the standard deviations are shown in figure S3. The lower extraction efficiency of 1-phenylethanol is likely due to the high content of organic

co-solvent, since 1-phenylethanol can be efficiently extracted out of the pure buffer system as shown in figure S4.

**Aromatics Extract. Corr. (100% borate buffer)**



**Figure S4.** Extraction efficiency of phenol and 1-phenylethanol for 100% pH 8 borate buffer. Note, acetophenone is not soluble in 100% borate buffer.



**Figure S5.** Extraction efficiency of 1,2-dihydroxycyclohexane, 2-methoxyphenol and 4-methoxyphenol in 33% v/v IPA borate buffer solution.

The extraction efficiencies of the aromatic intermediates were used to correct the yields of the intermediates in the kinetic data as described in the example below. The extraction solvent is dichloromethane as described in the quantitative analysis section above.

## Evaporation and Extraction Correction Application

### General Information:

- Due to the low solubility and high vapor pressure of alkylbenzene products in the aqueous system, the rate of evaporation is faster than the rate of formation. Therefore, the quantified yield of all alkylbenzene had no correction, the actual yield should be higher than the reported numbers.

- No yield correction for all the  $\beta$ -O-4 aryl ethers as their volatility is low and extraction efficiency is high. The reported numbers were the GC quantified numbers.
- For reducible aromatic intermediates, such as phenol, 1-phenylethanol and acetophenone, the quantified GC yield is only corrected for extraction loss.
- For non-reducible end products, such as cyclohexanol and 1-cyclohexylethanol, the quantified GC yield is corrected by evaporation curves, which included the extraction loss.

Extraction Correction:

$$Yield (reported) = \frac{Yield (quantified)}{Extraction Efficiency} \quad [1]$$

Example: Phenol Sample at 9 hours (S6)

$$Yield (reported) = \frac{Yield (quantified)}{Extraction Efficiency} = \frac{26\%}{0.92} = 28\%$$

- Extraction Efficiency of phenol in 33% v/v IPA buffer mixtures is 0.92 (Figure S3)

Evaporation Correction:

$$Yield (reported) = \frac{Yield (quantified)}{Evaporation Efficiency} \quad [2]$$

Example: Cyclohexanol Data Point at 9 h (S6)

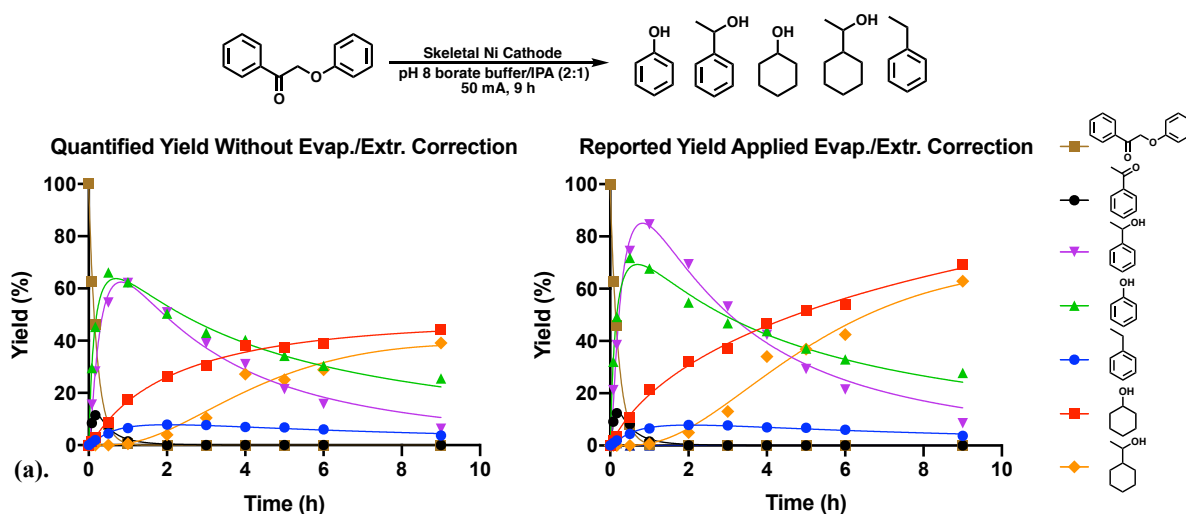
$$Yield (reported) = \frac{Yield (quantified)}{Evaporation Efficiency} = \frac{44\%}{0.64} = 69\%$$

- Evaporation Efficiency of Cyclohexanol after 9 hour ECH at 50 mA is 0.64 (Figure S1a)

## Kinetic Measurement Yield Correction Example: ECH of Ketone $\beta$ -O-4

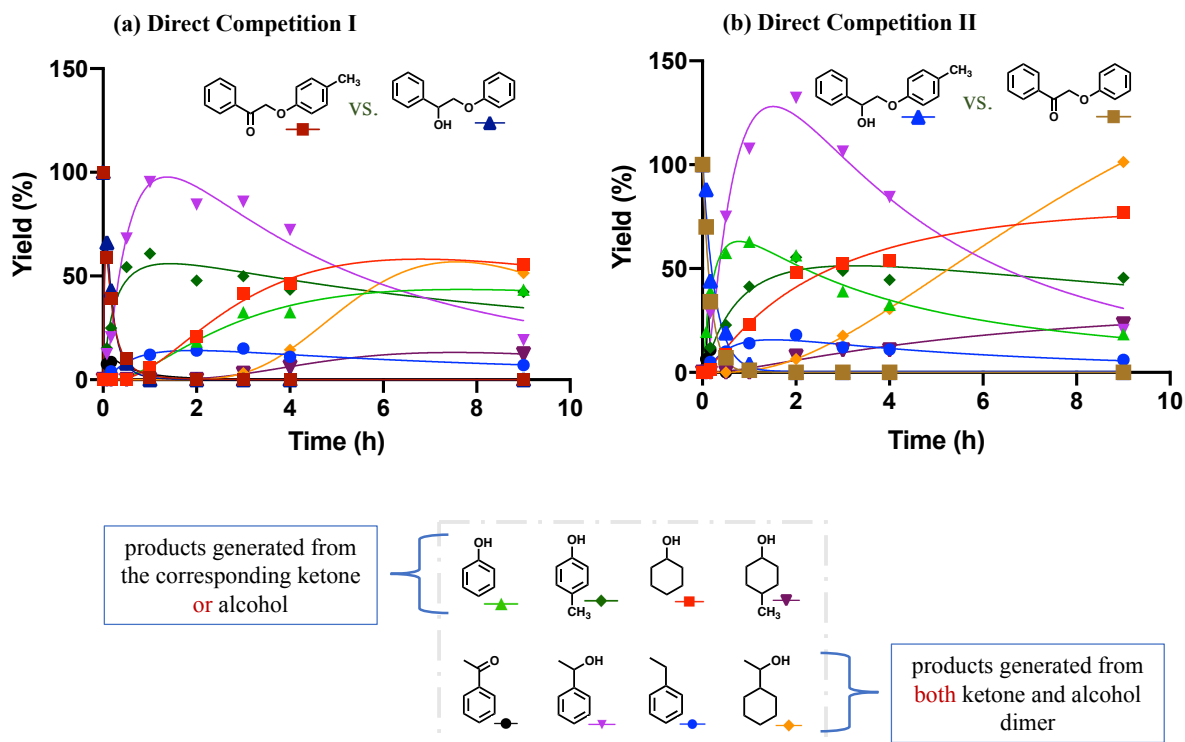
Figure S6 is an example of yield correction by evaporation and extraction efficiency of the corresponding products. The applied corrections only influence the yield values, not the kinetic reduction results. Both S6a and S6b have the same kinetic pattern; the ketone dimer undergoes direct cleavage to become the corresponding aromatic monomer first. Phenol competes with 1-phenylethanol in aromatic reduction, with formation of cyclohexanol faster than 1-cyclohexylethanol, as already observed in the quantified figure S6a. But without the extraction correction, the build up and decay of 1-phenylethanol looks similar to that of phenol, which is not matched with the ring reduction products.

As reported in S3, the extraction efficiency of 1-phenylethanol is lower than that of phenol in 33% v/v 2-propanol. After the applied extraction correction, the reported formation and decay of 1-phenylethanol is consistent with the slower formation of 1-cyclohexylethanol.



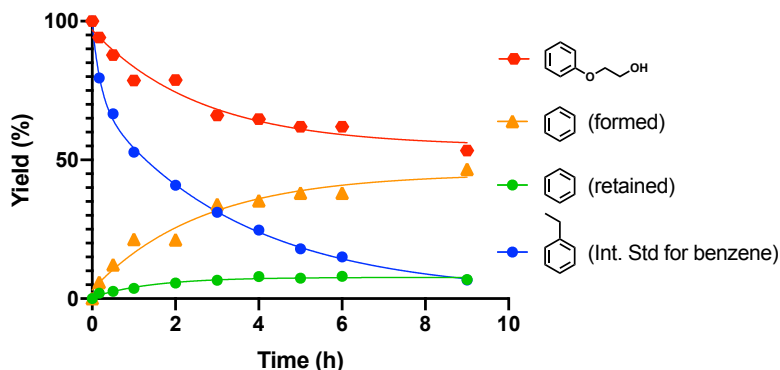
**Figure S6.** (a) ECH kinetic measurements of 2-phenoxyacetophenone, quantified yields without any correction. (b) ECH kinetic measurements of 2-phenoxyacetophenone, reported yields with evaporation/extraction corrections. ECH performed at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA.

## Full ECH Kinetic Measurements for Direct Competitions



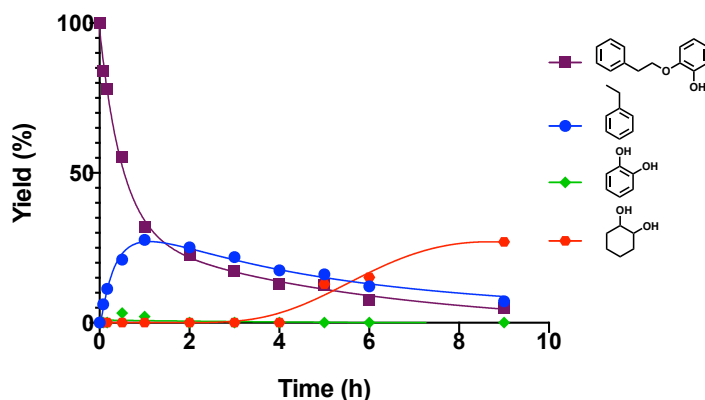
**Figure S7.** (a) Full kinetic measurement of direct competition of methyl labeled ketone model and unlabeled alcohol model. (b) Full kinetic measurement of direct competition of unlabeled ketone model and methyl labeled alcohol model. ECH performed at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA.

## Full ECH Kinetic Results for 2-phenylethanol (7)



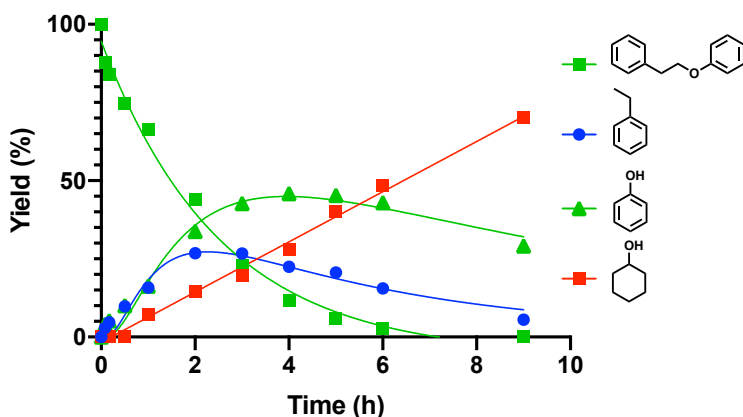
**Figure S8.** ECH measurement of 2-phenylethanol at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. Note, ethylbenzene is used as the internal evaporation correction of benzene, but the evaporation rate of ethylbenzene is faster than the formation rate of benzene, thus cannot applied the correction. The amount of benzene that was detected and quantified by GC-MS was near 8% (green circles). The benzene that was formed (orange triangles) is from the subtraction of the remaining starting material 2-phenylethanol (red hexagons), no other product was observed. Though the ethylene glycol by product was expected, its high water solubility prevents its effective analysis in the organic extracts from these reactions.

## Full ECH Kinetic Results for 2-(2-phenylethoxy)phenol (6)



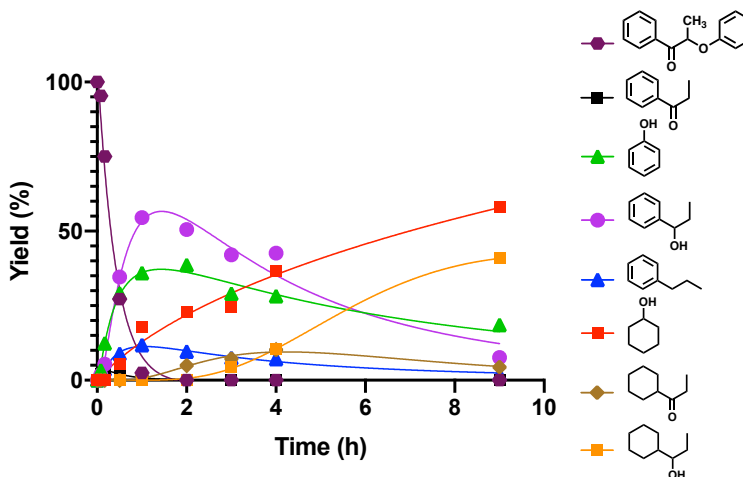
**Figure S9.** ECH measurement of 2-(2-phenylethoxy)phenol at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. 1,2-dihydroxycyclohexane yield was corrected by extraction losses (S5). No yield corrections were applied for the dimer 2-(2-phenylethoxy)phenol, ethylbenzene and catechol. The formed amount of catechol and ethylbenzene were higher than the reported numbers. Note, two different extraction solvents (dichloromethane and ethyl acetate) were used, 2-(2-phenylethoxy)phenol, ethylbenzene and 1,2-dihydroxycyclohexane were quantified from the dichloromethane extraction. Due to the high solubility of catechol in the aqueous buffer mixture, ethyl acetate extraction only captured trace amounts of catechol. Both extractions were performed according to the standard procedure described in the analyzation section.

### Full ECH Kinetic Results for 1-phenyl-2-phenoxyethane (8)



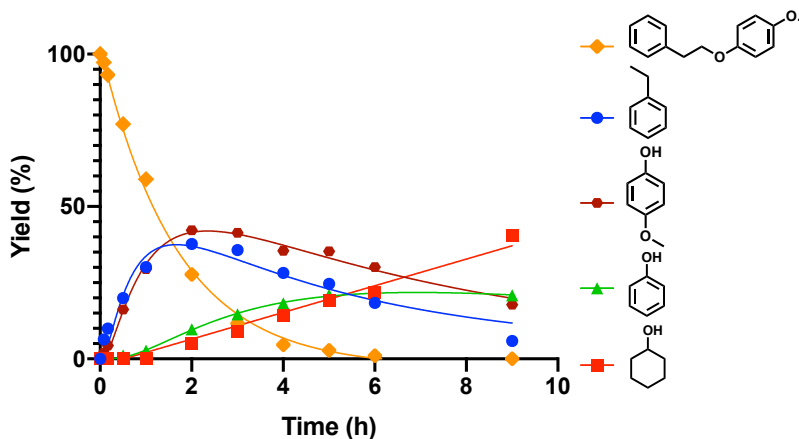
**Figure S10.** ECH measurement of 1-phenyl-2-phenoxyethane at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation (S1a). No yield corrections were applied on 2-phenoxy-1-phenyl ethane and ethylbenzene.

### Full ECH Kinetic Results for 2-phenoxy-1-phenylpropanone (19)



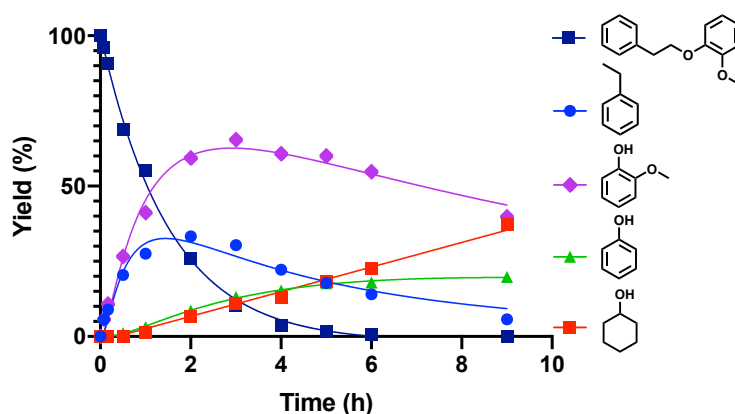
**Figure S11.** ECH measurement of 2-phenoxy-1-phenylpropanone at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation (S1a). The yield of 1-phenylpropanone was corrected using the extraction efficiency of acetophenone (S3). The yield of 1-phenylpropanol was corrected using the extraction efficiency of 1-phenylethanol (S3). The yield of 1-cyclohexylpropanol was corrected using the evaporation curve of 1-cyclohexylethanol (S1a). No yield correction was applied on 2-phenoxy-1-phenylpropanone and propylbenzene.

### Full ECH Kinetic Results of 1-methoxy-4-(2-phenylethoxy)benzene (16)



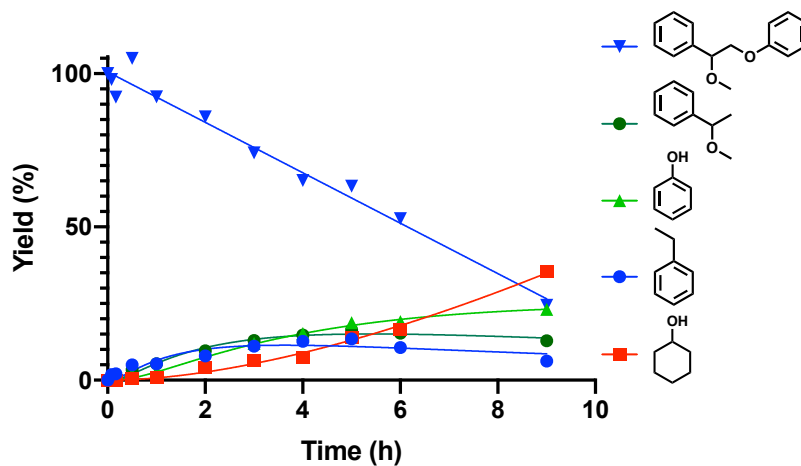
**Figure S12.** ECH measurement of 1-methoxy-4-(2-phenylethoxy)benzene at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation (S1a). The yield of 4-methoxyphenol was corrected for the extraction losses (S5). No yield correction was applied on 1-methoxy-4-(2-phenylethoxy)benzene and ethylbenzene.

### Full ECH Kinetic Results of 1-methoxy-2-(2-phenylethoxy)benzene (15)



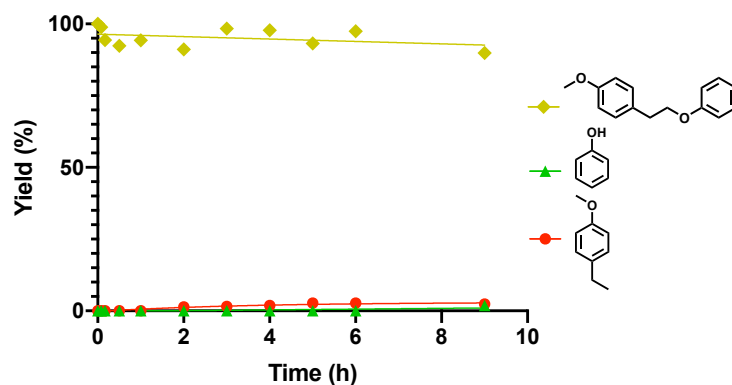
**Figure S13.** ECH measurement of 1-methoxy-2-(2-phenylethoxy)benzene at standard conditions, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation (S1a). The yield of 2-methoxyphenol was corrected for the extraction losses (S5). No yield correction was applied on 1-methoxy-2-(2-phenylethoxy)benzene and ethylbenzene.

### Full ECH Kinetic Results of (1-methoxy-2-phenoxyethyl)benzene (17)



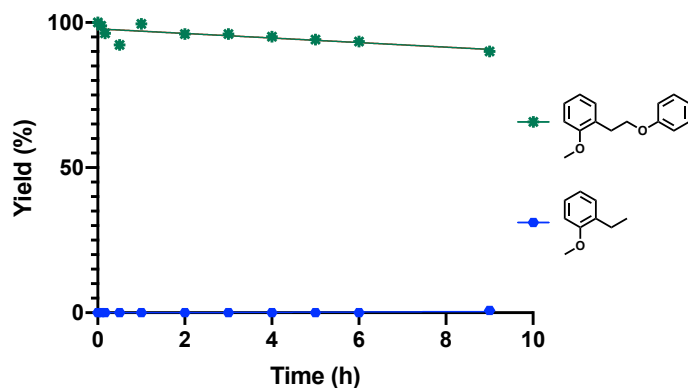
**Figure S14.** ECH measurement of 2-methoxy-1-phenylethanol at standard conditions, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation losses (S1a). No yield corrections were applied on 2-methoxy-1-phenylethanol, 1-methoxyphenylethanol and ethylbenzene.

### Full ECH Kinetic Results for 1-methoxy-4-(2-phenoxyethyl)benzene (13)



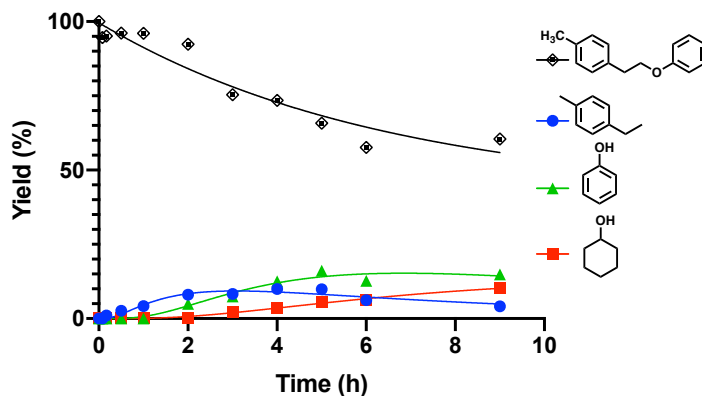
**Figure S15.** ECH measurement of 1-methoxy-4-(2-phenoxyethyl)benzene at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. Less than 3% cleavage product was observed. No yield corrections were applied in the substrate and products.

### Full ECH Kinetic Results for 1-methoxy-2-(2-phenoxyethyl)benzene (14)



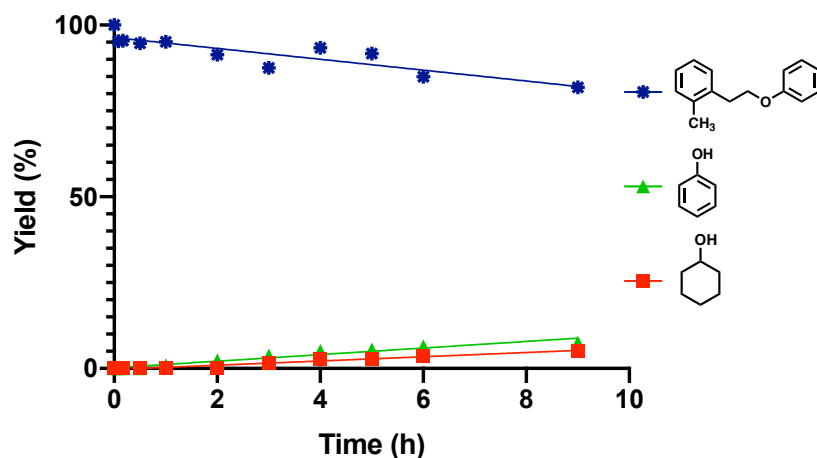
**Figure S16.** ECH measurement of 1-methoxy-2-(2-phenoxyethyl)benzene at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. Less than 2% cleavage product was observed. No yield corrections were applied in the substrate and products.

### Full ECH Kinetic Results for 1-methyl-4-(2-phenoxyethyl)benzene (11)



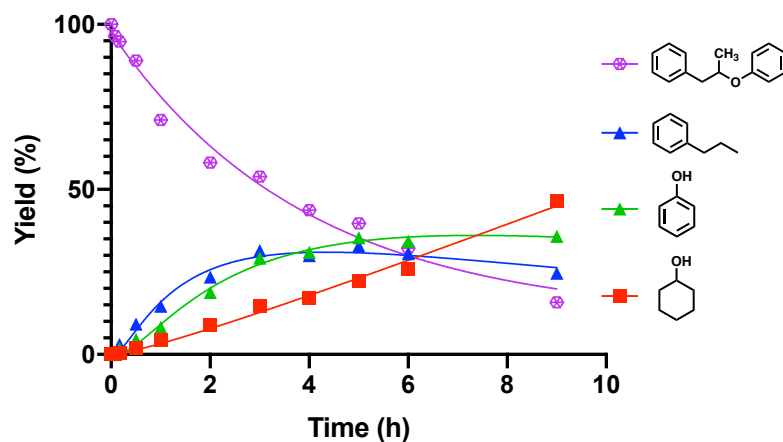
**Figure S17.** ECH measurement of 1-methyl-4-(2-phenoxyethyl)benzene at standard conditions, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation losses (S1a). No yield corrections were applied on 4-ethyltoluene and substrate.

### Full ECH Kinetic Results for 1-methyl-2-(2-phenoxyethyl)benzene (12)



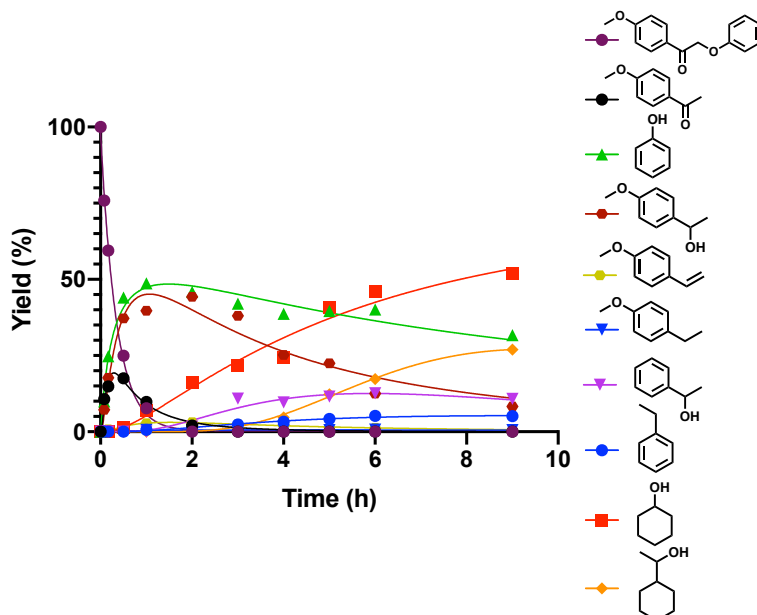
**Figure S18.** ECH measurement of 1-methyl-2-(2-phenoxyethyl)benzene at standard conditions, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation losses (S1a). No yield correction was applied on substrate.

### Full ECH Kinetic Results for 2-(phenoxypropyl)benzene (18)



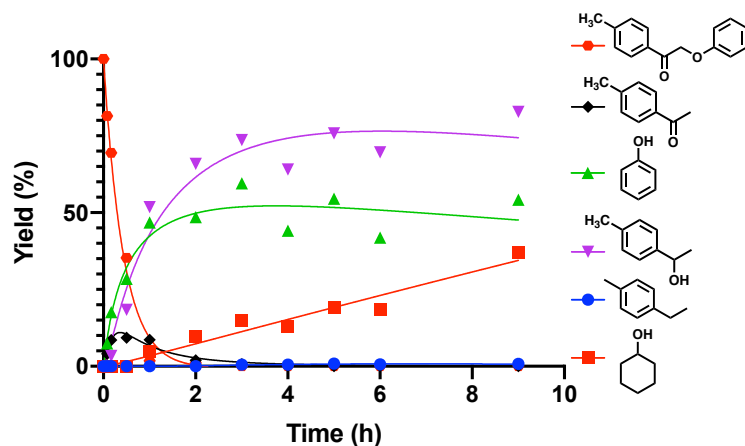
**Figure S19.** ECH measurement of 2-(phenoxypropyl)benzene at standard conditions, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation losses (S1a). No yield corrections were applied on propylbenzene and substrate.

## Full ECH Kinetic Results for 1-(4-methoxyphenyl)-2-phenoxyethanone (20)



**Figure S20.** ECH measurement of 1-(4-methoxyphenyl)-2-phenoxyethanone at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol and 1-phenylethanol were corrected for extraction losses (S3). The yield of cyclohexanol and 1-cyclohexylethanol were corrected for evaporation losses (S1a). The yield of 4-methoxyacetophenone was corrected using the extraction efficiency of acetophenone (S3). The yield of 4-methoxyphenylethanol was corrected using the extraction efficiency of 1-phenylethanol (S3). No yield correction was applied on 1-(4-methoxyphenyl)-2-phenoxyethanone, ethylbenzene, 4-methoxystyrene and 4-ethylanisole.

## Full ECH Kinetic Results for 1-(4-methylphenyl)-2-phenoxyethanone (21)



**Figure S21.** ECH measurement of 1-(4-methylphenyl)-2-phenoxyethanone at standard condition, 50 mA, 60 °C and IPA treated electrode with 33% v/v IPA. The yield of phenol was corrected for extraction losses (S3). The yield of cyclohexanol was corrected for evaporation losses (S1). The yield of 4-methylacetophenone was corrected using the extraction efficiency of acetophenone (S3). The yield of 4-

methylphenylethanol was corrected using the extraction efficiency of 1-phenylethanol (S3). No yield correction was applied on 1-(4-methylphenyl)-2-phenoxyethanone and 4-ethyltoluene.

## General Experimental Procedure of H/D Isotope Exchange of $\beta$ -O-4 Aryl Ethers

The H/D isotope exchange experiments of all aryl ether substrates followed a similar procedure. A cylinder shaped one compartment cell was equipped with a small stir bar and a rubber stopper with a stainless steel metal clip. The acetone treated skeletal Ni catalyst (same size and preparation as the electrode) was hung on the metal clip and placed inside the one compartment cell, positioned high enough to avoid contact with the stirrer. 20 mL of D<sub>2</sub>O with the addition of 8 mL 2-propanol (non-deuterated) was charged inside the cell. As with the ECH studies, another 2 mL of 2-propanol was used to dissolve the weighed aryl ether substrate (0.25 mmol) in a 4-mL glass vial, before it was added to the D<sub>2</sub>O solution. The entire set up was placed in a water bath where the temperature was maintained at 60 °C. The skeletal Ni catalyst was allowed to react with the D<sub>2</sub>O/2-propanol mixture for 1 hour, and then the vial with 2 mL of 2-propanol with the aryl ether substrate was added into the D<sub>2</sub>O solution and allowed to exchange for 9 hours at 60 °C under ambient pressure. No current was applied in the exchange experiments to avoid conversion to downstream reduced products.

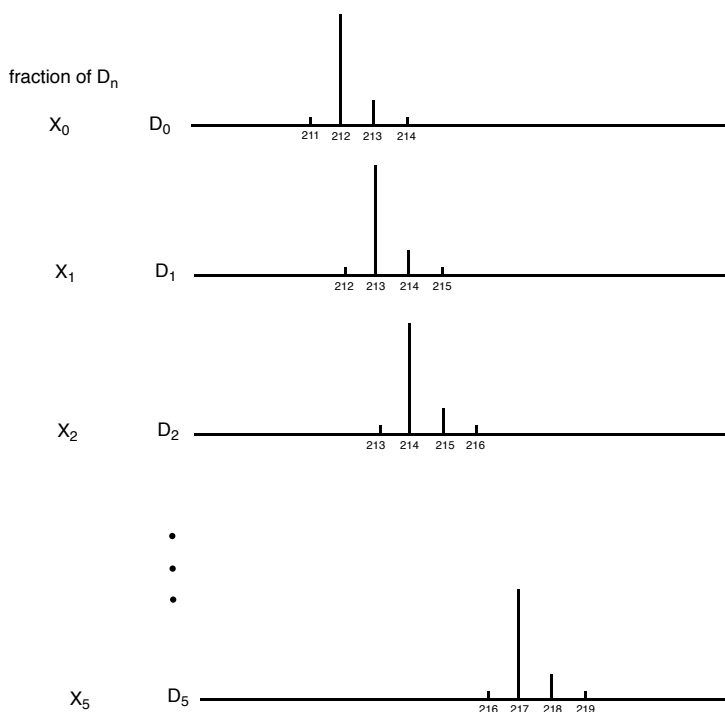
### Quantitative Analysis Preparation:

At each desired time point 0.25 mL of D<sub>2</sub>O solution was syringed into a 1.7 mL conical vial and analyzed by GC-MS as described earlier.

Note, an extra step was needed to accurately assess the amount of deuterium that was incorporated in the alcohol  $\beta$ -O-4 aryl ether, because the H/D exchange on –OH functional groups happens instantaneously. The H/D exchange measurement of alcohol 2-phenoxy-1-phenylethanol was sampled twice at each time point, and two different extractions were conducted at each time point. One is normally extracted with 1 mL of dichloromethane and then inject into the GC-MS for quantification. The other one is first extracted with 1 mL of dichloromethane, then the dichloromethane extract was washed with 1 mL of deionized non-deuterated water to make sure there was no D on the –OH functional group, followed by injection on GC-MS. Both non-washed and washed exchange kinetics were analyzed.

## MS Fitting Method of H/D Isotope Labeling Experiment

The total ion abundance of different mass fragments after H/D exchange was provided by GC-MS. However, GC-MS only gives the total ion mass chromatogram of each measurement. The total ion mass chromatogram represents a mixture of D<sub>n</sub> dimer isotopomers. The intensity of each measured ion fragment is also a combination of the intensities of the same mass fragment from different D<sub>n</sub> incorporated aryl ether dimer. Therefore, to determine the % abundance of D<sub>n</sub> in the exchange results, the proportion of D<sub>n</sub> in each mixture is defined as fraction coefficient X<sub>n</sub> (n = 0,1,2,3...n). The sum of the products of fraction coefficient X<sub>n</sub> times peak fragment intensity I<sub>n</sub> should be the total intensity of the corresponding peak in the total ion chromatogram. Meanwhile, the relative fragmentation pattern of different D labeled aryl ethers should not change, only the peak value will shift by one for each H that was replaced by D incorporated inside the compound (Figure S22).



**Figure S22.** As the numbers of D labels in the compound increase, the mass fragmentation pattern and intensity remains the same; only the peak's  $m/z$  value will shift. Fractional coefficients  $X_n$  were used as the proportions of  $D_n$  in the total ion mixture.

Excel solver was used to fit the corresponding fraction  $X_n$  of  $D_n$  in the total ion mixture. Below is an example of the solver fitting method of 2-phenoxyacetophenone H/D exchange at 10 min.

As presented in **table S1**, column 2 is the intensity distribution of unlabeled 2-phenoxyacetophenone fragments (parent). Column 3 is the intensity distribution of the D labeled mixture (labeled). The fitted intensity of each ion was calculated by the below **equation 3** and tabulated in column 4-9, where fraction coefficient  $X_n$  is tabulated in column 2 (row 11-17). The values of the fractional coefficients  $X_n$  were found through excel solver as presented in **equation 5** in giving the minimum value of the sum of the square errors. The square error is calculated by **equation 4** and tabulated in column 10, where the smaller the deviation, the closer the fitted intensity to the actual labeled intensity. Based on solved  $X_n$ , the percent abundance of  $D_n$  is plotted.

$$\%Ion Intensity_{fitted} = X_n * \%Ion Intensity_{parent} \quad [3]$$

$$Square Error = \left( \sum_0^5 \%Ion Intensity_{fitted} - \%Ion Intensity_{labeled} \right)^2 \quad [4]$$

$$Solver : \left[ minimize \sum_0^5 Square error = by Varying X_n \right] \quad [5]$$

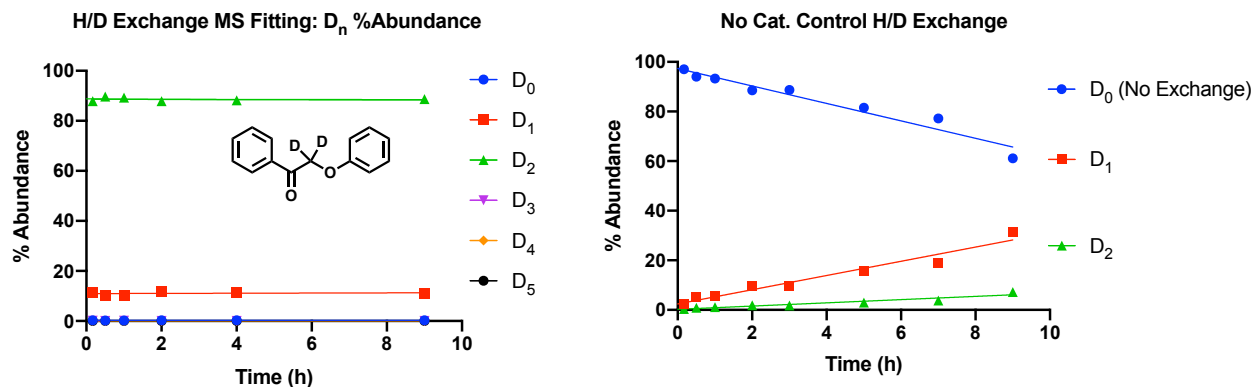
$$\%Abundance (D_n) = \frac{X_n}{\sum_0^5 X_n} * 100 \quad [6]$$

**Table S1. Ketone Model 2-Phenoxyacetophenone H/D Exchange MS Fitting at 10 min**

mass frag. (m/z)	MS Intensity (parent)	MS Intensity (labeled)	Fitted Int. X <sub>0</sub> *Parent	Fitted Int. X <sub>1</sub> *Parent	Fitted Int. X <sub>2</sub> *Parent	Fitted Int. X <sub>3</sub> *Parent	Fitted Int. X <sub>4</sub> *Parent	Fit. I. X <sub>5</sub> *P	Square Error
210.079	0.01	0	3.79E-05						1.44063E-09
210.983	0.03	0	0.000113867	0.001354892					2.15725E-06
212.094	25.2	0.11	0.095648138	0.004064677	0.010285769				2.00621E-12
213.1	3.9	3.46	0.014802688	3.414328793	0.030857306	1.12217E-05			7.09511E-17
214.1	0.37	26.45	0.001404358	0.528408027	25.92013672	3.36652E-05	1.22961E-05		2.43227E-11
215.1	0.03	4.09	0.000113867	0.050131018	4.011449731	0.028278796	3.68883E-05	0	1.06079E-10
216.1	0	0.42	0	0.004064677	0.380573436	0.00437648	0.03098620	0	6.31821E-13
217.053	0	0.03	0	0	0.030857306	0.000415205	0.00479548	0	3.68205E-05
Deuterium number (D <sub>n</sub> )	Fraction Coefficient X <sub>n</sub>	% Abundance							Sum of Square Errors
D0	0.00379556	0.32435148							2.15883E-06
D1	0.13548923	11.5782975							
D2	1.02857685	87.8975264							
D3	0.00112217	0.09589595							
D4	0.00122961	0.10507701							
D5	0	0							

Analogous analyses applied to the fragments with NMR evidence (below) confirm the assigned locations of the D labels.

## Fitted Result of $D_n$ in the Kinetic H/D Exchange Experiments of 2-Phenoxyacetophenone



**Figure S23.** Plotted %Abundance of  $D_n$  of 2-phenoxyacetophenone in 2:1  $D_2O$ /IPA with exchange catalyzed by acetone treated skeletal nickel. Quantitation of the H/D exchange was determined by GC-MS. The location of the exchange is determined by mass fragmentation and NMR evidence in the section below. Control experiment shows results with catalyst omitted.

## H/D Exchange Mass Spectra and NMR Spectra of 2-phenoxyacetophenone (Ketone $\beta$ -O-4)

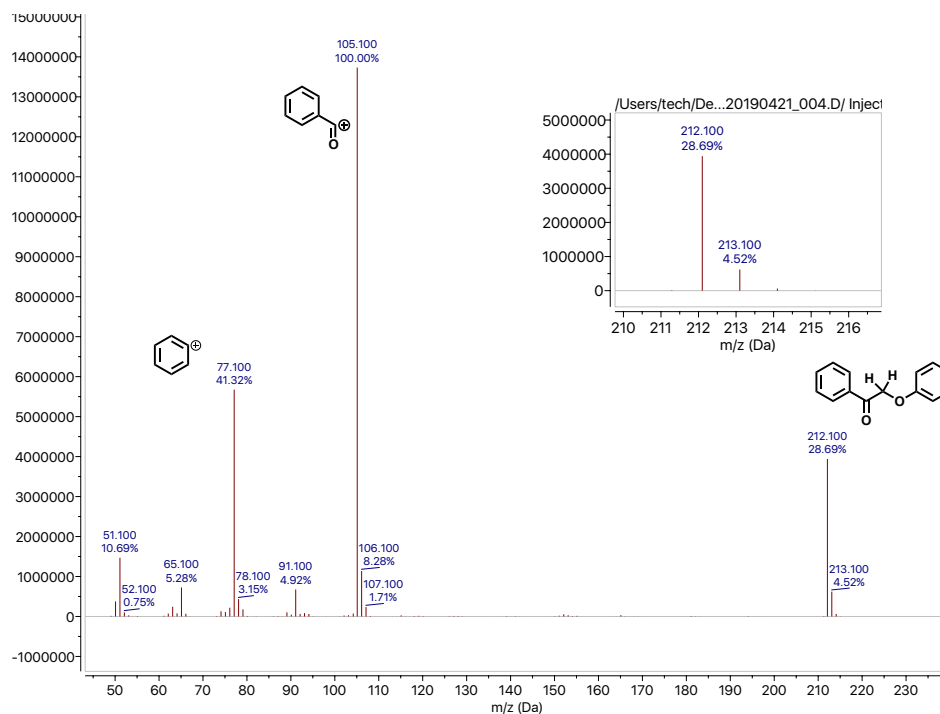


Figure S24. Mass Spectra of unlabeled 2-phenoxyacetophenone without exchange.

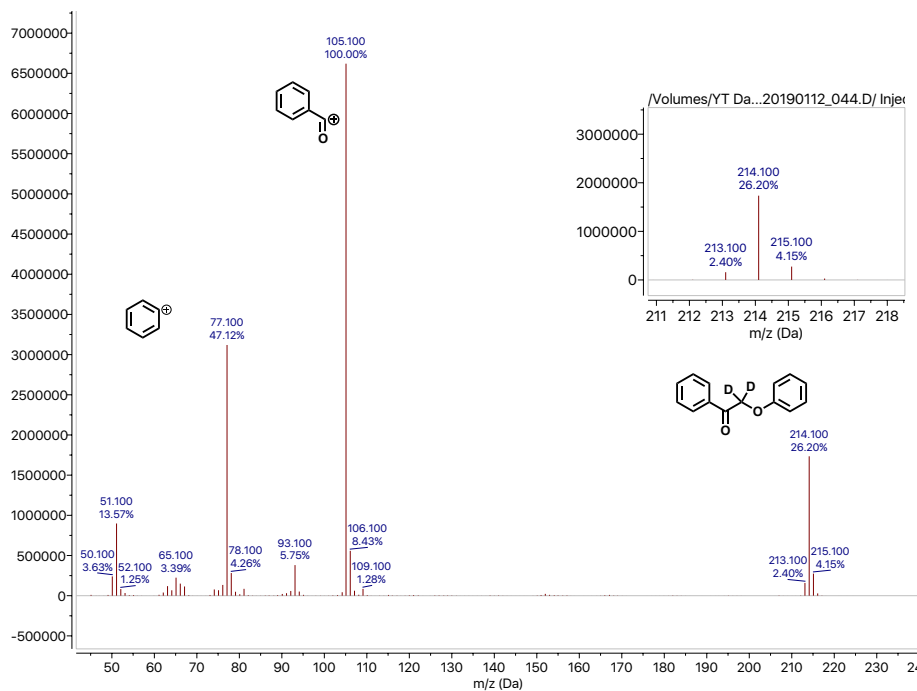
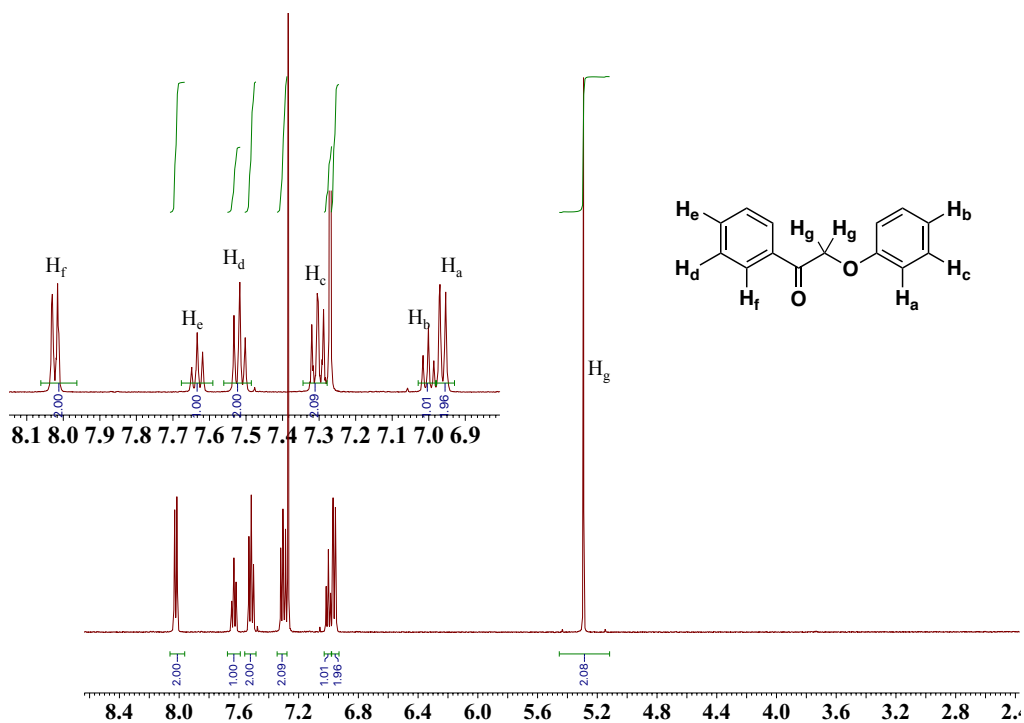
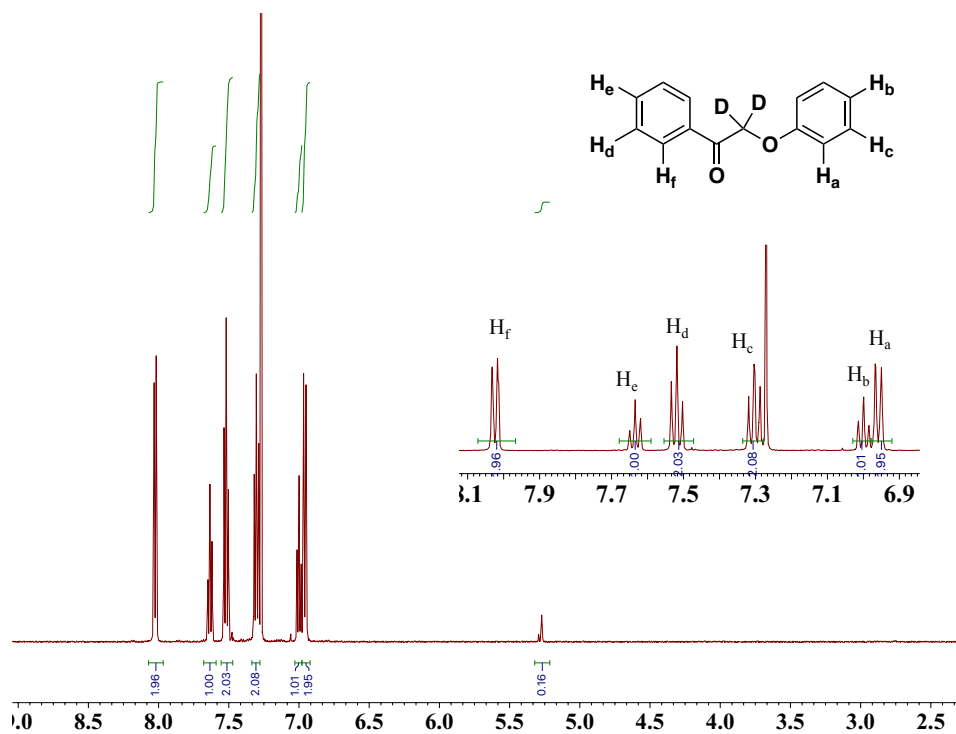


Figure S25. Mass Spectra of labeled 2-phenoxyacetophenone after 10 mins exchange. Notice, compared with the unlabeled parent mass, the major fragment 105 (PhCO<sup>+</sup>) was remained the same, which indicated the exchange happened on the lost fragment. The exchange location is further confirmed by NMR.

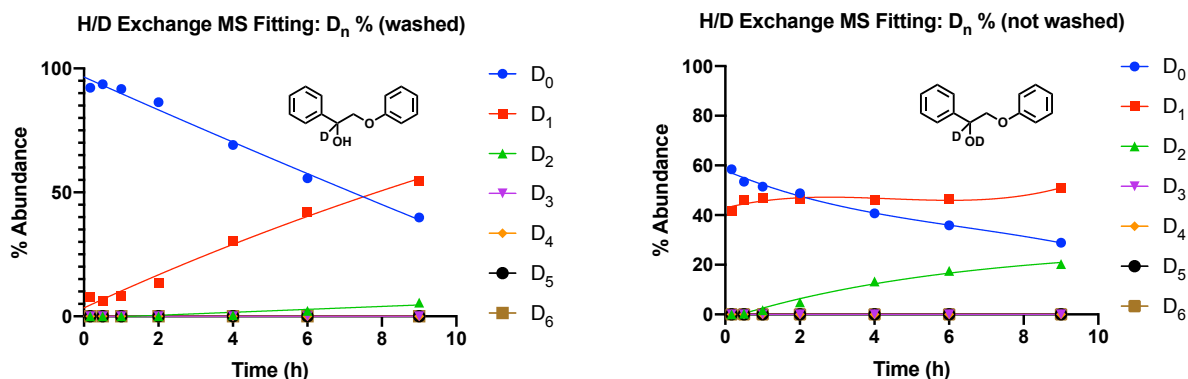


**Figure S26.** NMR Spectra of unlabeled 2-phenoxyacetophenone without exchange. Spectral data are in accordance with those previously reported.<sup>4</sup> Synthesis is described below.



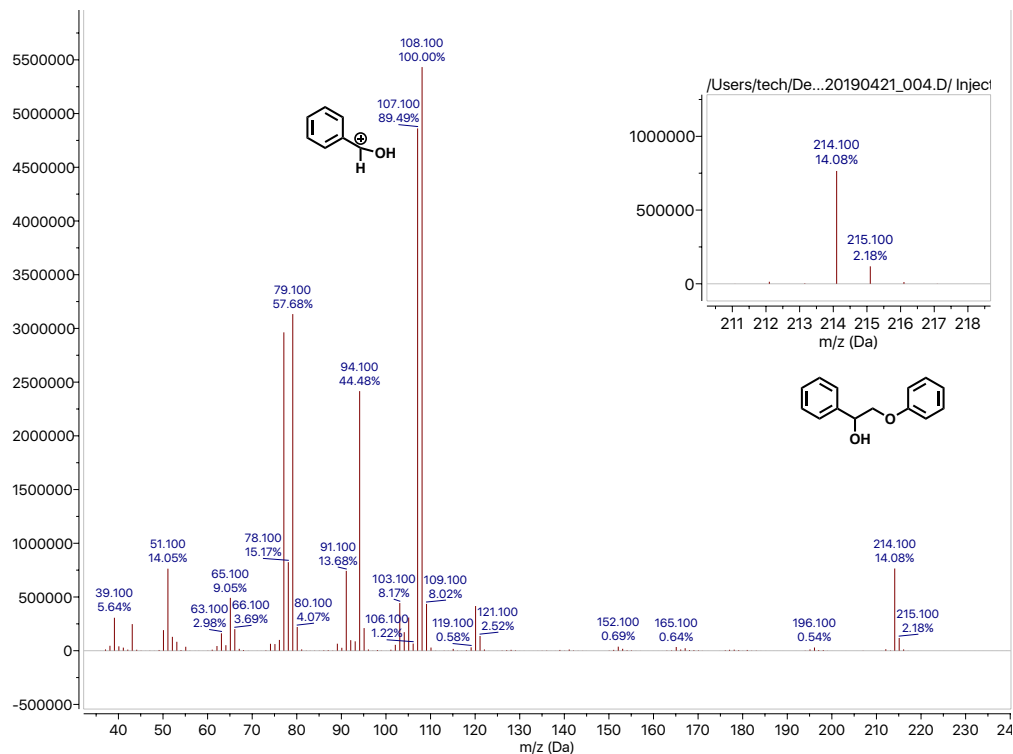
**Figure S27.** NMR Spectra of labeled 2-phenoxyacetophenone after exchange for 10 mins. As indicated in the spectra, only beta C-H were exchange, which matched up with the fitted MS % abundance where D<sub>2</sub> is the major numbers of the D incorporation.

## Fitted Results of $D_n$ in the Kinetic H/D Exchange Experiment of 2-phenoxy-1-phenyl ethanol

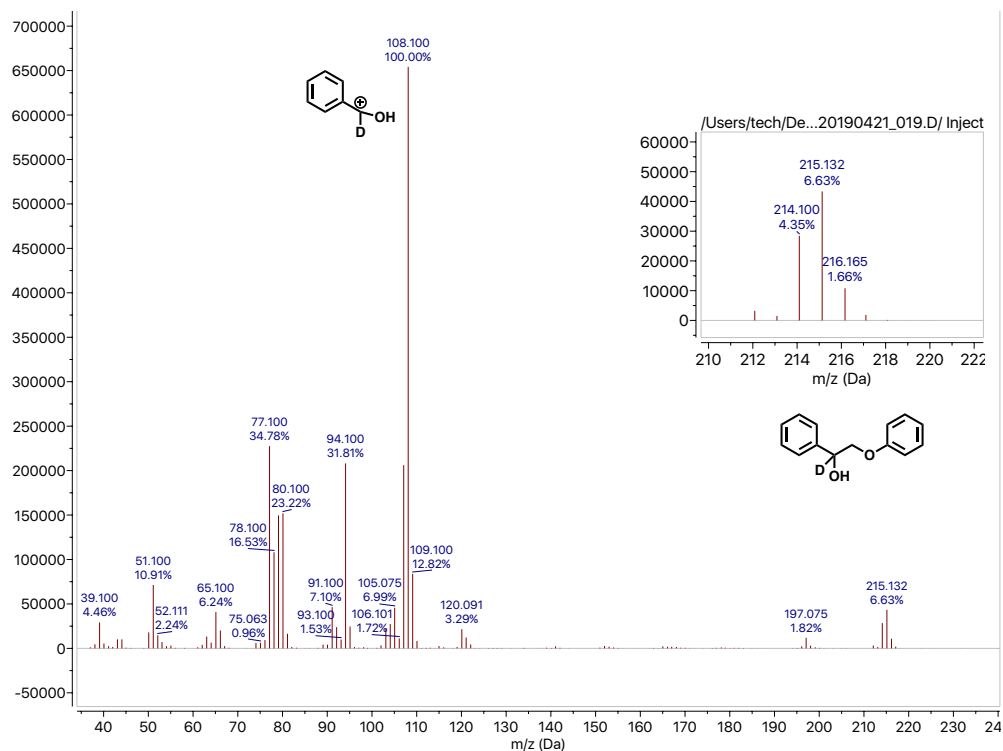


**Figure S28.** Plotted %Abundance of  $D_n$  of 2-phenoxy-1-phenylethanol both washed and non-washed trials. The D incorporated on the alcohol functional group is easy to lose in the analytical sample preparation process. To proper counting the number of D incorporated on the aryl ether, washed trials were performed to remove the D on -OH. The quantitative exchange result was determined by GC-MS. The location of the exchange is determined by mass fragmentation and NMR evidence in the section below.

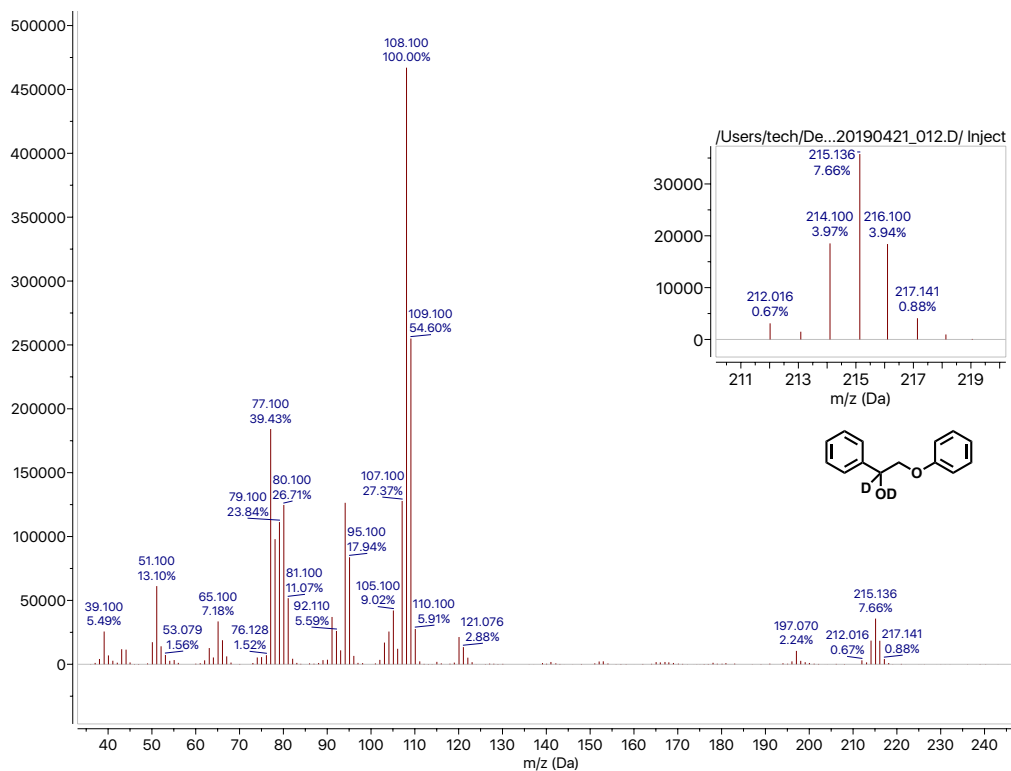
## H/D Exchange Mass Spectra and NMR Spectra of 2-phenoxy-1-phenylethanol (alcohol $\beta$ -O-4)



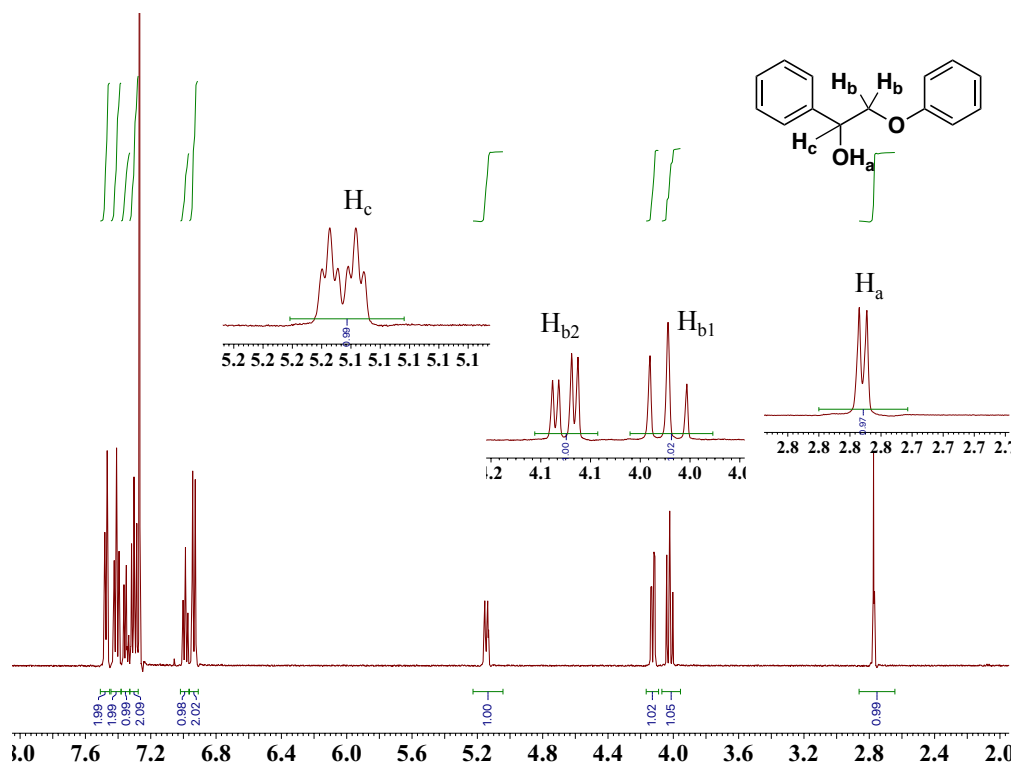
**Figure S29.** Mass Spectra of unlabeled 2-phenoxy-1-phenylethanol without exchange.



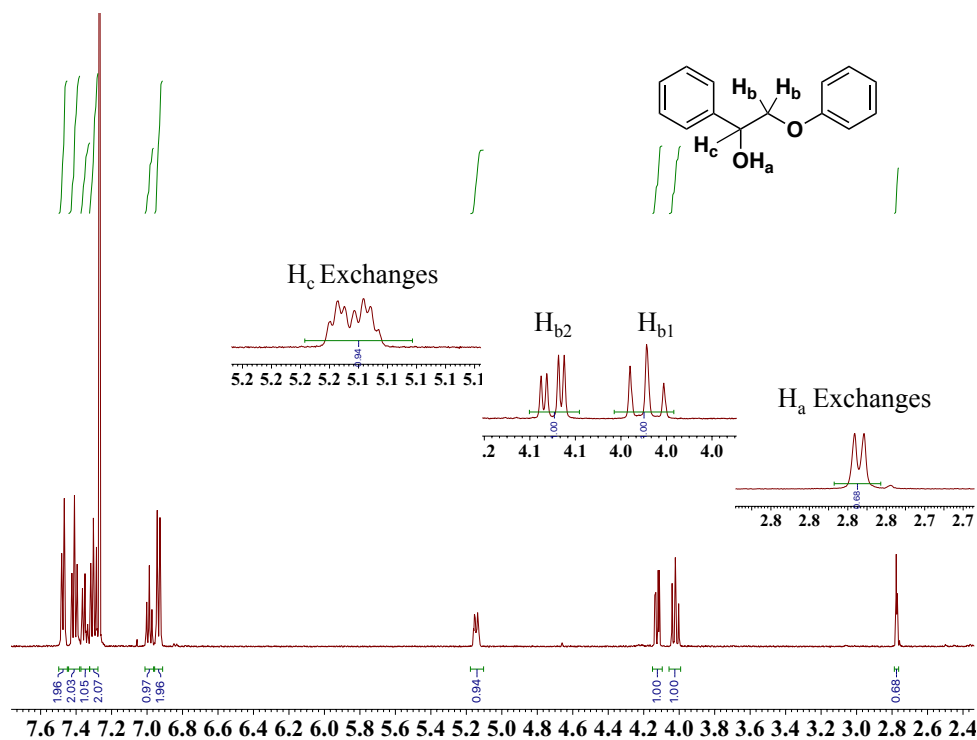
**Figure S30.** Mass Spectra of 2-phenoxy-1-phenylethanol after 9-hour H/D isotope exchange. Analytical sample **washed** with DI water to remove the D on alcohol -OH functional group. The exchange location is further confirmed by NMR.



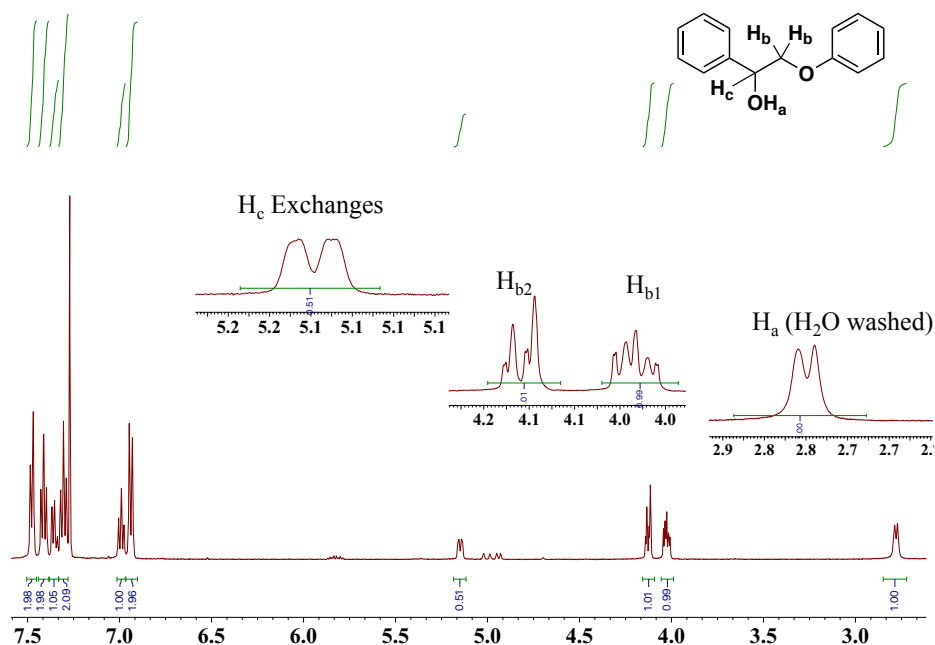
**Figure S31.** Mass Spectra of 2-phenoxy-1-phenylethanol after 9-hour H/D isotope exchange. Analytical sample **not** washed. The exchange location is further confirmed by NMR.



**Figure S32.** NMR Spectra of unlabeled 2-phenoxy-1-phenylethanol without exchange. Spectral data are in accordance with those previously reported.<sup>4</sup> Synthesis is described below.

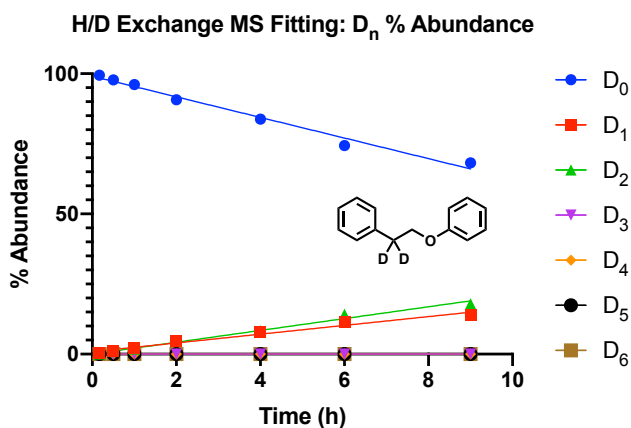


**Figure S33.** NMR Spectra of 2-phenoxy-1-phenyl ethanol after H/D isotope exchange for 30 mins at 60 °C, the -OD exchange ( $H_a$ ) varies during the NMR sample preparation. The -OH and  $\alpha$  C-H start to exchange.

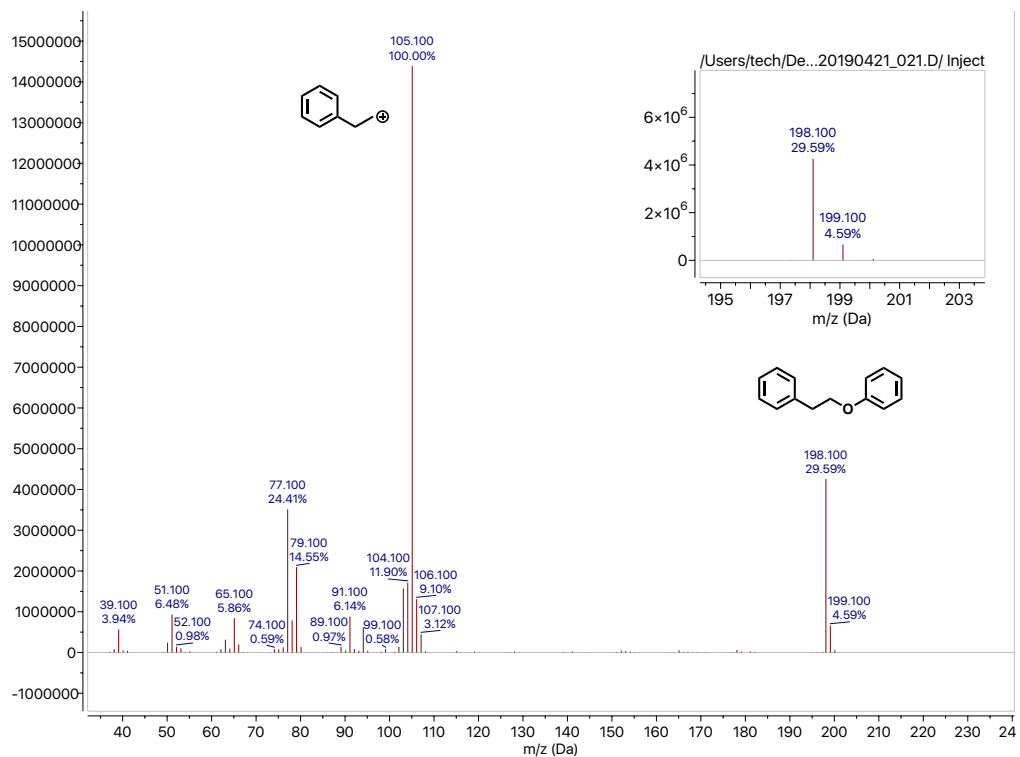


**Figure S34.** NMR Spectra of 2-phenoxy-1-phenylethanol after H/D isotope exchange for 9 hours at 60 °C (sample was extracted and washed with H<sub>2</sub>O), the -OD exchange (H<sub>a</sub>) was removed. Approximately half of the α (H<sub>c</sub>) were exchanged, which matched up with the fitted MS % abundance.

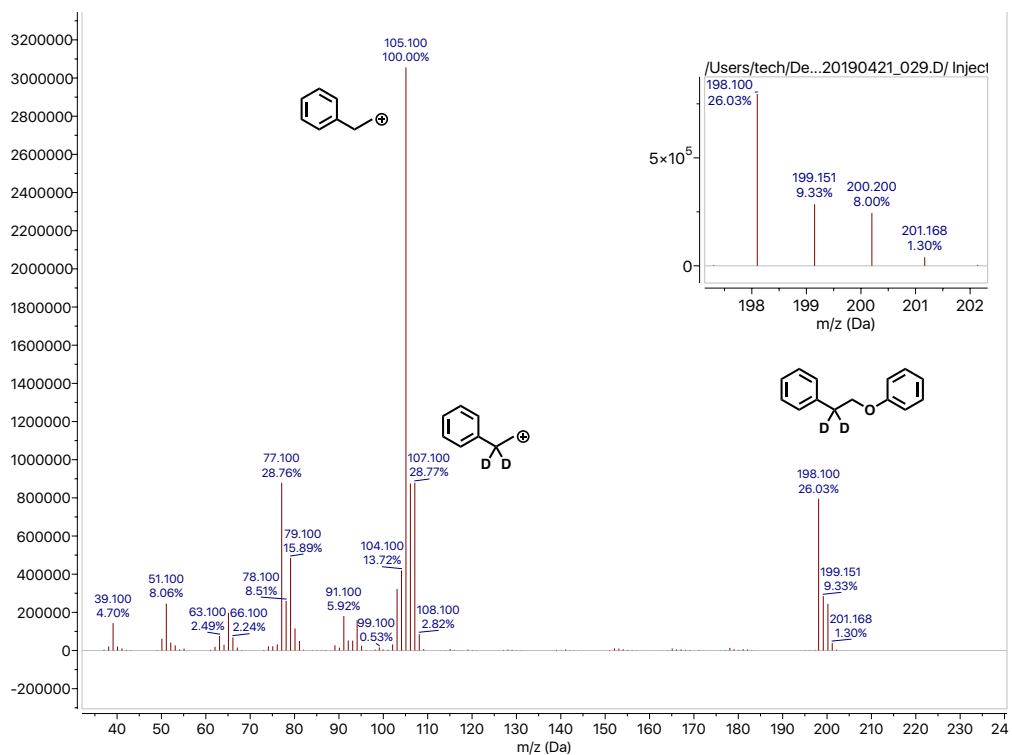
### Fitted Result of D<sub>n</sub> in the Kinetic H/D Exchange Experiments of 1-Phenyl-2-phenoxyethane



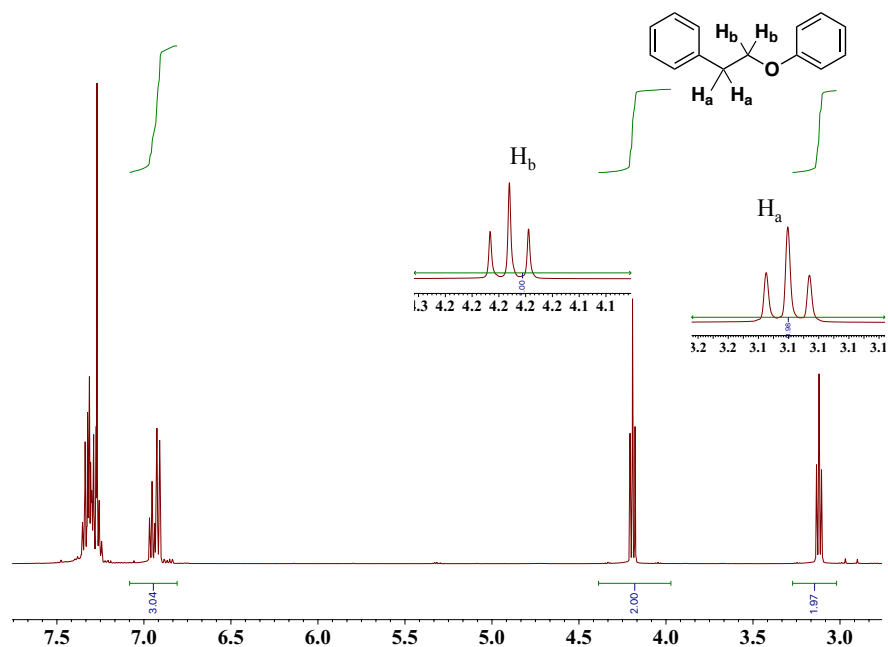
**Figure S35.** Plotted %Abundance of D<sub>n</sub> of 2-phenoxy-1-phenylethane. The quantitative exchange result was determined by GC-MS. The location of the exchange is determined by mass fragmentation and NMR evidence in the below section.



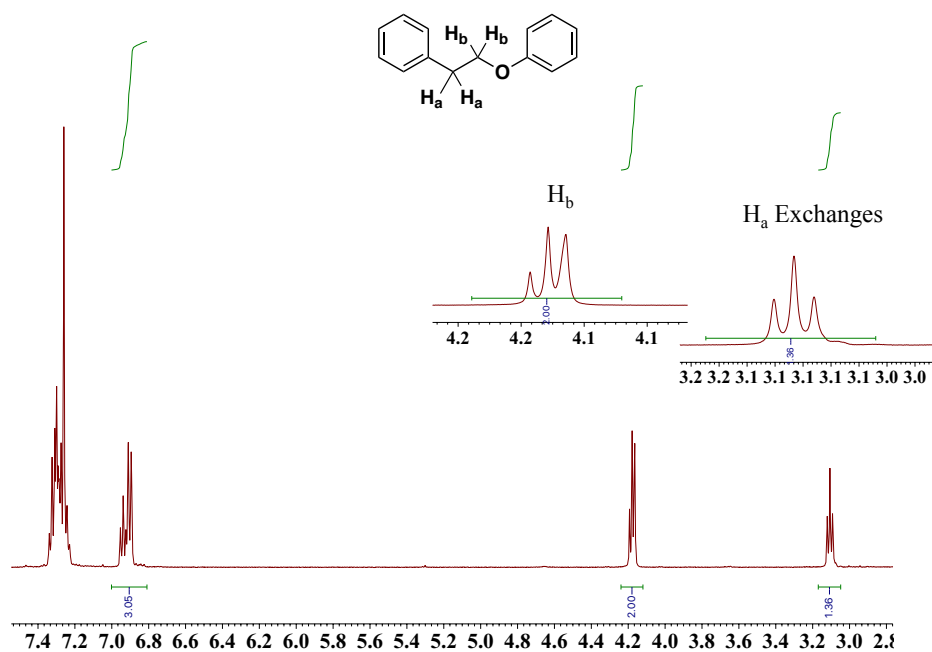
**Figure S36.** Mass Spectra of unlabeled 2-phenoxy-1-phenyl ethane without exchange.



**Figure S37.** Mass Spectra of labeled 2-phenoxy-1-phenylethane after 9-hour exchange. Increases in m/z 199 and 200 are seen, with both ions showing similar intensities. The exchange location is further confirmed by NMR.

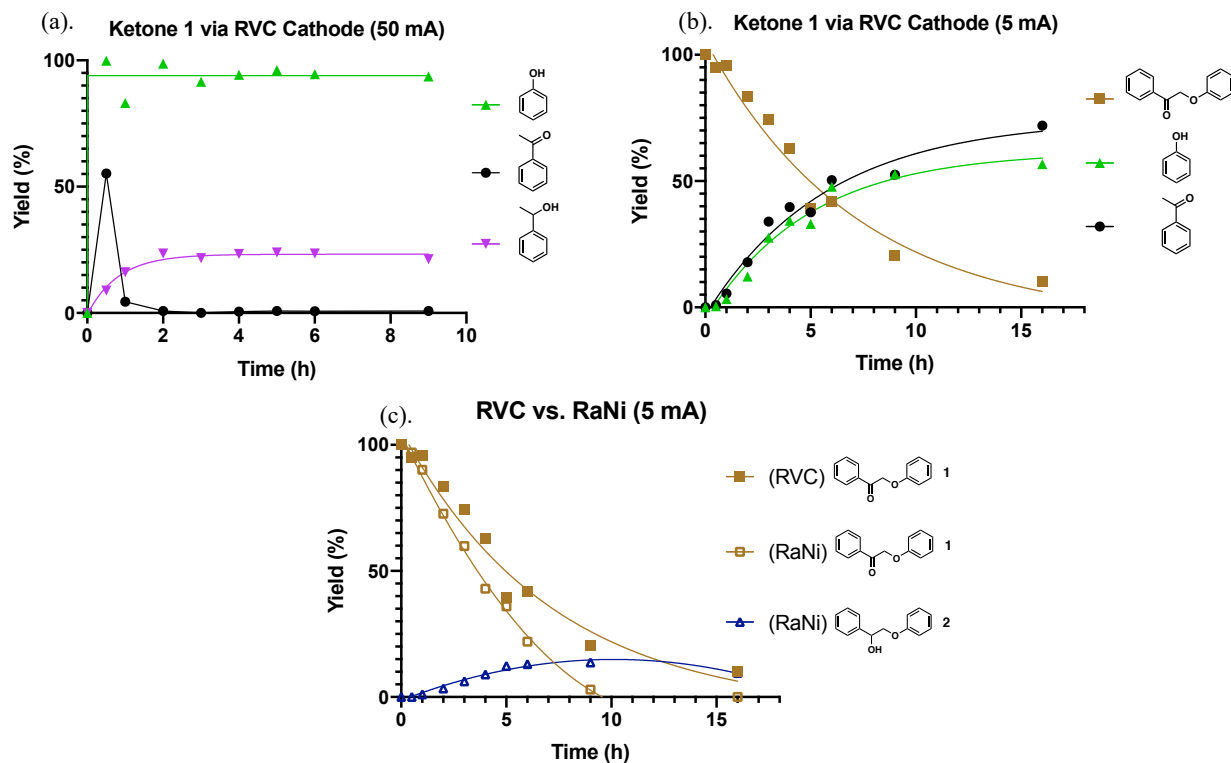


**Figure S38.** NMR Spectra of unlabeled 2-phenoxy-1-phenylethane without exchange. Spectral data are in accordance with those previously reported.<sup>4</sup> Synthesis is described below.



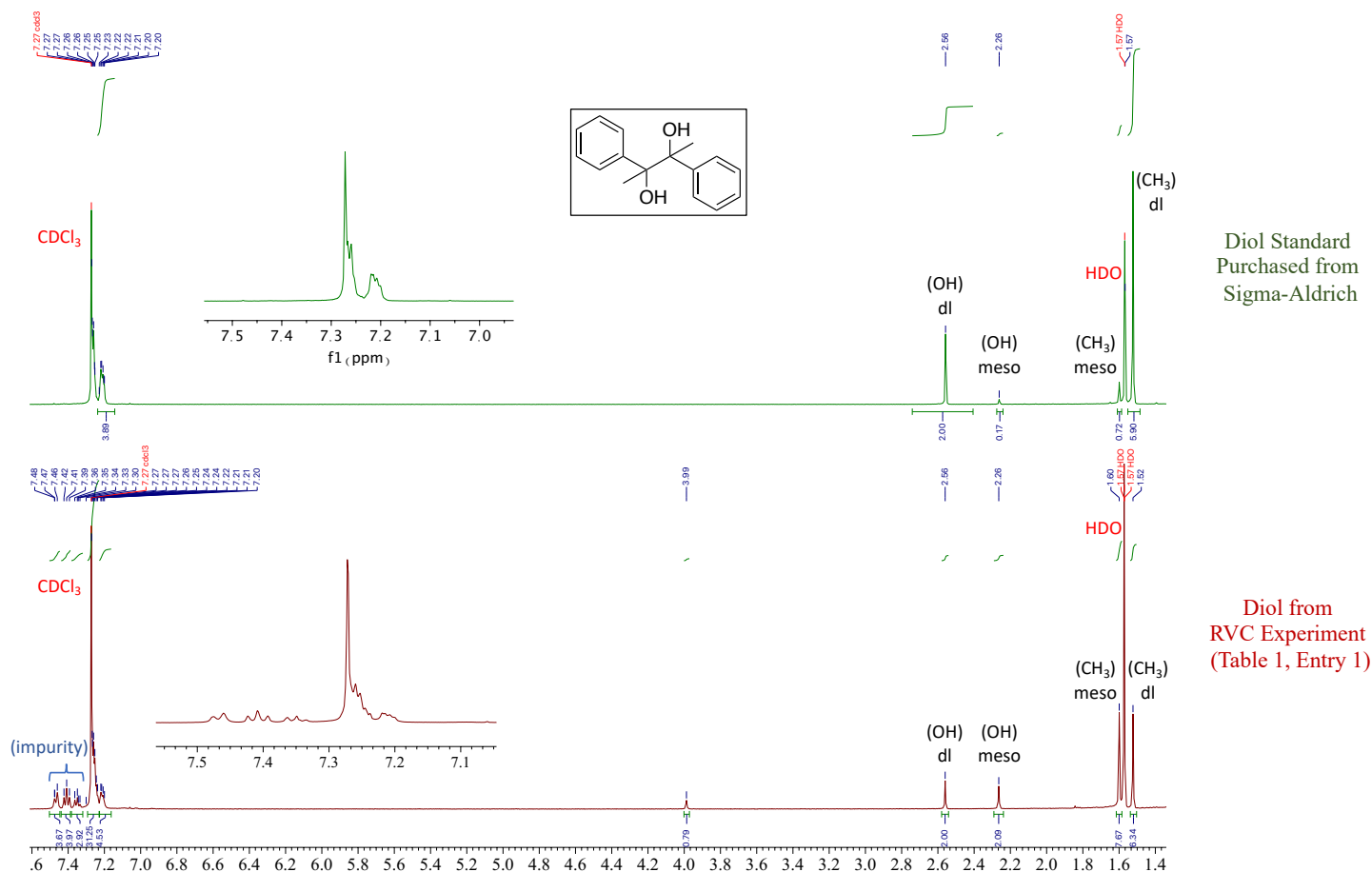
**Figure S39.** NMR Spectra of labeled 2-phenoxy-1-phenylethane after 9-hour H/D exchange. As indicated in the spectra, only  $\alpha$  C-H were exchanged, which matched up with the fitted MS % abundance where  $D_2$  is the maximum number of the D incorporated in 2-phenoxy-1-phenylethane.

### Cathodic Reduction 2-phenoxyacetophenone Ketone **1** via RVC Electrode @ (5 and 50 mA)



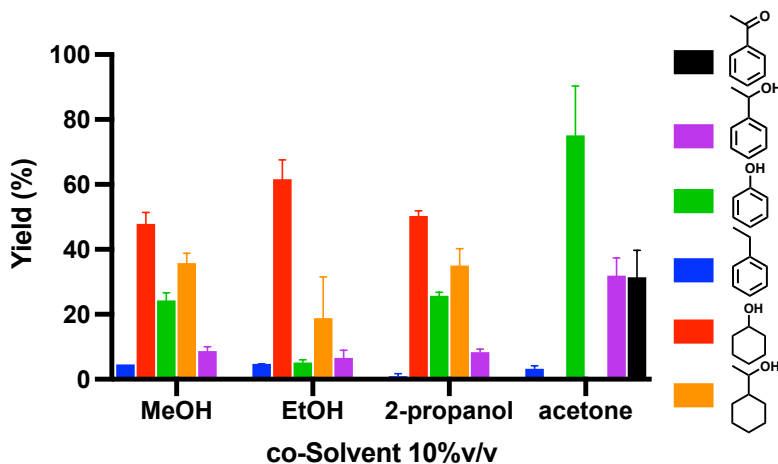
**Figure S40.** (a) Full kinetic measurement of cathodic reduction of ketone **1** using RVC electrode at 50 mA (Table 1, Entry 1). (b) Full kinetic measurement of cathodic reduction of ketone **1** using RVC electrode at 5 mA (Table 1, Entry 3). (c) Ketone **1** cleavage rate comparison between RVC electrode and Ni electrode at 5 mA (for full kinetic data of Ni electrode @ 5 mA, see Figure 3c). Cathodic reductions were performed at the same standard conditions as the Ni ECH experiments: 50 or 5 mA, 60 °C with 33% v/v IPA.

**2,3-diphenylbutane-2,3-diol from Cathodic Reduction Experiment Using RVC Cathode  
(Table 1, Entry 1)**



**Figure S41.** NMR Spectra of 2,3-diphenylbutane-2,3-diol; standard spectra of diol purchased from Sigma-Aldrich with mixtures of meso and dl diastereomers as labeled (Green Spectra). 2,3-diphenylbutane-2,3-diol from cathodic reduction at 50 mA using RVC electrode (Red Spectra), both meso and dl were formed in the radical dimerization process with approximately 1:1 ratio. Spectral data are also in accordance with those previously reported.<sup>5</sup> A small amount of unknown aromatic impurity accompanied the material isolated by column chromatography. Beside the cleavage product phenol, compounds in the red spectra are the largest spot in the thin-layer chromatography (Hexane/EtOAc 4:1).

## ECH of Co-Solvent Studies using 10% v/v of Each Co-solvent



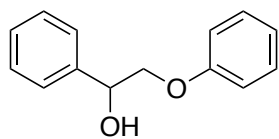
**Figure S42.** Co-solvent influence on electro-catalyzed hydrogenation (ECH). Reaction conditions: isopropyl alcohol treated Ni electrode, constant current at 50 mA, co-solvent content 10% by volume, mixed with 90% pH 8 borate buffer. ECH for 9 hours at 60 °C. No product yield correction was applied in 10% by volume co-solvent studies, the actual yield may be larger than the reported numbers here due to extraction/evaporation losses.

## Dimer Synthesis Procedures

**2-bromo-1-phenylethanone:** This compound was prepared following a literature procedure with modification.<sup>4</sup> Acetophenone (6.0 g, 50 mmol) was added into 70 mL of  $\text{CHCl}_3$  in a 250 mL round bottom flask. To this mixture, bromine (8.4 g, 52.5 mmol) dissolved in another 70 mL of  $\text{CHCl}_3$  was added dropwise over 2 hours at room temperature. After the completion of the reaction, the reaction mixture was washed with saturated  $\text{Na}_2\text{S}_2\text{O}_3$  and brine solution. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuo. The crude product was directly carried to the next step without purification.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.99 (dd,  $J = 8.3, 1.4$  Hz, 2H), 7.67 – 7.58 (m, 1H), 7.56 – 7.47 (m, 2H), 4.47 (s, 2H). Spectral data are consistent with those reported in the literature.<sup>6</sup>

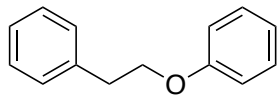
**2-phenoxyacetophenone (1):** This compound was prepared following a literature procedure.<sup>4</sup> Potassium carbonate (5.23 g, 37.8 mmol) and phenol (3.55 g, 37.8 mmol) were stirred in acetone (75 mL) at room temperature for 30 minutes. 2-bromo-1-phenylethanone (5 g, 25.2) dissolved in another 75 mL of acetone was added dropwise to the mixture and stirred overnight at room temperature. The reaction was filtered, and dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuo. The solids were recrystallized from ethanol producing a white crystal (3.96 g) in 75% yield.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.02 (dd,  $J = 8.4, 1.3$  Hz, 2H), 7.66 – 7.61 (m, 1H), 7.52 (dd,  $J = 8.4, 7.1$  Hz, 2H), 7.33 – 7.28 (m, 2H), 7.00 (tt,  $J = 7.4, 1.1$  Hz, 1H), 6.96 (dt,  $J = 7.8, 1.0$  Hz, 2H), 5.29 (s, 2H). Spectral data are consistent with those reported in the literature.<sup>4</sup>

**2-phenoxy-1-phenylethan-1-ol (2):** This compound was prepared following a literature procedure.<sup>4</sup> 2-



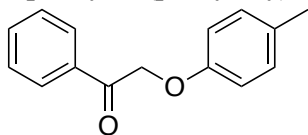
phenoxyacetophenone (2.25 g, 10.6 mmol) was added to MeOH (80 mL). To this mixture, NaBH<sub>4</sub> (0.6 g, 15.9 mmol) was added in small portions and stirred overnight at RT. After the completion of the reaction, saturated NH<sub>4</sub>Cl (100 mL) solution was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with deionized water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum, giving 97% yield of the pure product (2.2 g). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.46 (m, 2H), 7.44 – 7.38 (m, 2H), 7.38 – 7.33 (m, 1H), 7.33 – 7.28 (m, 2H), 6.99 (tt, *J* = 7.5, 1.1 Hz, 1H), 6.95 – 6.91 (m, 2H), 5.15 (dt, *J* = 8.9, 2.8 Hz, 1H), 4.13 (dd, *J* = 9.5, 3.1 Hz, 1H), 4.02 (t, *J* = 9.3 Hz, 1H), 2.77 (d, *J* = 2.4 Hz, 1H). Spectral data are in accordance with those previously reported.<sup>4</sup>

**1-phenyl-2-phenoxyethane (8):** This compound was prepared following a literature procedure with

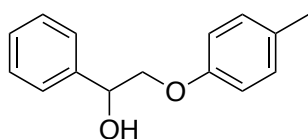


modification.<sup>4</sup> Potassium carbonate (3.6 g, 26.0 mmol) and phenol (2.45 g, 26.0 mmol) were stirred in DMF (45 mL) at room temperature for 30 minutes. 2-bromo-1-phenylethane (3.7 g, 20.0 mmol) was added dropwise to the mixture and stirred overnight at room temperature. After the completion of the reaction, cold water was added into the reaction mixture. The aqueous mixture was extracted with diethylether (2×60 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Pentane/DCM, 4:1) to give 2-phenoxy-1-phenylethane as an oil (0.97 g) in 24% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.23 (m, 7H), 6.95 (td, *J* = 7.3, 1.1 Hz, 1H), 6.92 (dt, *J* = 7.9, 1.0 Hz, 2H), 4.19 (t, *J* = 7.1 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H). Spectral data are in accordance with those previously reported.<sup>4</sup>

**1-phenyl-2-(*p*-tolylloxy)ethan-1-one (3):** This compound was prepared following a literature procedure.<sup>7</sup>

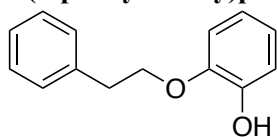


A 250 mL round bottom flask connected with a dropping funnel was charged with *p*-cresol (6.5 g, 60 mmol) and K<sub>2</sub>CO<sub>3</sub> (11 g, 79 mmol) in acetone (50 mL) and stirred at room temperature. To this solution, 2-bromoacetophenone (7.9 g, 40 mmol) in acetone (50 mL) was added dropwise at room temperature. The resulting suspension was stirred at room temperature overnight; the suspension was filtered and concentrated *in vacuo*. The crude product was purified by column chromatography using EtOAc/hexane (1:9) to give 1-phenyl-2-(*p*-tolylloxy)ethan-1-one as a white solid (4.8 g) in 53% yield after solvent removal. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.69 – 7.58 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.13 – 7.05 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.26 (s, 2H), 2.29 (s, 3H). Spectral data are in accordance with those previously reported.<sup>7</sup>

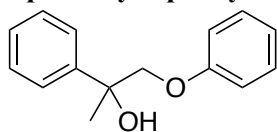


**1-phenyl-2-(*p*-tolylloxy)ethanol (4):** This compound was prepared following a literature procedure.<sup>4</sup> 1-phenyl-2-(*p*-tolylloxy)ethan-1-one (0.87 g, 3.84 mmol) was added to MeOH (40 mL). To this mixture, NaBH<sub>4</sub> (0.5 g, 13.2 mmol) was added in small portions and stirred overnight at RT. After the completion of the reaction, saturated NH<sub>4</sub>Cl (100 mL) solution was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with deionized water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The crude product was purified by column chromatography using EtOAc /hexane (1:4) to give 1-phenyl-2-(*p*-tolylloxy)ethanol as a white solid (0.59 g) in 67% yield after solvent removal. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.45 (m, 2H), 7.40 (ddd, *J* = 7.7, 6.3, 1.3 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.14 – 7.06 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.13 (dd, *J* = 9.0, 3.1 Hz, 1H), 4.10 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.99 (t, *J* = 9.3 Hz, 1H), 2.30 (s, 3H). Spectral data are in accordance with those previously reported.<sup>7</sup>

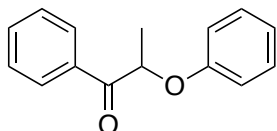
**2-(2-phenylethoxy)phenol (6):** Potassium carbonate (1.6 g, 11.6 mmol) and catechol (1.27 g, 11.5 mmol) were stirred in DMF (45 mL) at 90 °C for 30 minutes. 2-bromo-1-phenylethane (1.85 g, 10.0 mmol) was added dropwise to the mixture and stirred overnight at 90 °C. After the completion of the reaction, cold water was added into the reaction mixture. The aqueous mixture was extracted with diethylether (2×60 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Hexane/EtOAc, 9:1) to give 2-(2-phenylethoxy)phenol as an oil (0.39 g) in 18% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.24 (m, 3H), 6.87 (m, *J* = 22.0, 18.0, 7.6, 1.8 Hz, 4H), 5.48 (s, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.13 (t, *J* = 6.8 Hz, 2H). Spectral data are in accordance with those previously reported.<sup>8</sup>



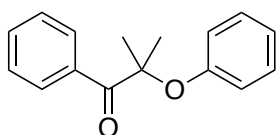
**1-phenoxy-2-phenyl-2-propanol (9):** This compound was prepared following a literature procedure.<sup>4</sup> To a stirring solution of 2-phenoxyacetophenone (0.5 g, 2.36 mmol) in anhydrous THF (15 mL), 2 mL of methyllithium (0.6 M in Et<sub>2</sub>O) was added dropwise at 0 °C, under argon. The reaction mixture was stirred for 10 hours where the temperature slowly warmed up to room temperature. The reaction was quenched with saturated ammonium chloride solution (15 mL). The aqueous layer was extracted with diethylether (3×20 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (pentane/DCM 7:3) to give 1-phenoxy-2-phenyl-2-propanol (0.192 g) in 36% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2H), 7.39 (ddd, *J* = 8.1, 6.9, 1.8 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.00 – 6.95 (m, 1H), 6.93 – 6.89 (m, 2H), 4.13 (dd, *J* = 9.0, 1.8 Hz, 1H), 4.04 (dd, *J* = 9.0, 1.8 Hz, 1H), 2.82 (d, *J* = 1.8 Hz, 1H), 1.68 (d, *J* = 1.8 Hz, 3H). Spectral data are consistent with those reported in the literature.<sup>4</sup>



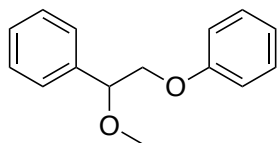
**2-phenoxy-1-phenylpropan-1-one (19):** To a stirring solution of sodium hydride (0.226 g, 5.6 mmol, 60% in mineral oil) in anhydrous THF (20 mL), 2-phenoxyacetophenone (1.0 g, 4.71 mmol) in anhydrous THF (20 mL) was added in two portions at 0 °C, under argon. The reaction mixture was stirred for 20 min. Methyl iodide (0.32 mL, 5.6 mmol) was added dropwise at 0 °C, and the solution was warmed to room temperature. The reaction mixture was monitored by TLC. The mixture was quenched by slow addition of water (30 mL) and extracted with diethylether (2×30 mL). The combined organic extracts were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to give a crude oil. The oil was purified by column chromatography (pentane/DCM, 1:1) to give 2-phenoxy-1-phenyl-1-propanone as white solid (0.57 g) in 54% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.14 – 8.04 (m, 2H), 7.68 – 7.55 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.94 (t, *J* = 7.4, 1.0 Hz, 1H), 6.88 (d, *J* = 7.3, 1.0 Hz, 2H), 5.49 (q, *J* = 6.9 Hz, 1H), 1.72 (d, *J* = 6.9, 0.7 Hz, 3H). Spectral data are in accordance with those previously reported.<sup>9</sup>



**2-methyl-2-phenoxy-1-phenylpropan-1-one (10):** This compound was prepared following a literature procedure.<sup>4</sup> To a stirring solution of sodium hydride (0.47 g, 11.7 mmol, 60% in mineral oil) in anhydrous THF (20 mL), 2-phenoxyacetophenone (1.0 g, 4.71 mmol) in anhydrous THF (20 mL) was added in two portions at 0 °C, under argon. The reaction mixture was stirred for 20 min. Methyl iodide (0.63 mL, 9.9 mmol) was added dropwise at 0 °C, and the solution was warmed to room temperature. The reaction mixture was monitored by TLC. The mixture was quenched by slow addition of water (30 mL) and extracted with diethyl ether (2×30 mL). The combined organic extracts were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to give a crude oil. The oil was purified by column chromatography (pentane/DCM, 4:1) to give 2-methyl-2-phenoxy-1-phenylpropan-1-one as white solid (0.5 g) in 44% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.38 – 8.24 (m, 2H),

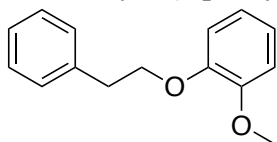


7.49 (t,  $J = 7.2$ , 1.3 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.18 – 7.11 (m, 2H), 6.89 (t,  $J = 7.3$ , 1.1 Hz, 1H), 6.79 – 6.74 (m, 2H), 1.70 (s, 6H). Spectral data are in accordance with those previously reported.<sup>4</sup>

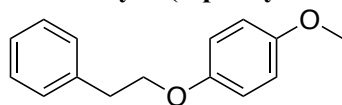


**(1-methoxy-2-phenoxyethyl)benzene (17):** This compound was prepared following a literature procedure.<sup>4</sup> To a stirring solution of sodium hydride (0.14 g, 3.5 mmol, 60% in mineral oil) in anhydrous THF (10 mL), 2-phenoxy-1-phenylethanol (0.5 g, 2.33 mmol) in anhydrous THF (10 mL) was added in two portions at 0 °C, under argon. The resulting suspension was stirred at 0 °C for 1 h. Then iodomethane (0.174 mL, 2.80 mmol) was added dropwise. The reaction mixture was monitored by TLC. The reaction was quenched with saturated ammonium chloride solution. The aqueous layer was extracted with diethylether (2×30 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography, first with pentane to remove the mineral oil followed by (pentane/DCM 4:1) to give (1-methoxy-2-phenoxyethyl)benzene as an oil (0.39 g) in 75% yield after solvent removal. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.41 (d,  $J = 4.4$  Hz, 4H), 7.38 – 7.33 (m, 1H), 7.30 – 7.24 (m, 2H), 6.97 – 6.89 (m, 3H), 4.60 (dd,  $J = 8.0$ , 3.6 Hz, 1H), 4.18 (dd,  $J = 10.2$ , 8.0 Hz, 1H), 4.01 (dd,  $J = 10.3$ , 3.6 Hz, 1H), 3.37 (s, 3H). Spectral data are in accordance with those previously reported.<sup>4</sup>

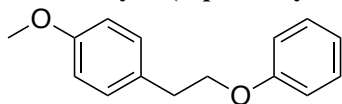
**1-methoxy-2-(2-phenylethoxy)benzene (15):** This compound was prepared following a literature procedure with modification.<sup>4</sup> Potassium carbonate (3.37 g, 24.4 mmol) and guaiacol (3.00 g, 24.2 mmol) were stirred in DMF (60 mL) at room temperature for 30 minutes. 2-bromo-1-phenylethane (3.00 g, 16.2 mmol) was added dropwise to the mixture and stirred overnight at room temperature. After the completion of the reaction, cold water was added into the reaction mixture. The aqueous mixture was extracted with diethylether (2×60 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Pentane/DCM, 4:1) to give 1-methoxy-2-(2-phenylethoxy)benzene as an oil (0.89 g) in 25% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 4H), 7.26 (d,  $J = 9.3$  Hz, 1H), 6.98 – 6.87 (m, 4H), 4.23 (dd,  $J = 8.1$ , 7.3 Hz, 2H), 3.88 (s, 3H), 3.18 (t,  $J = 7.7$  Hz, 2H). Spectral data are in accordance with those previously reported.<sup>10</sup>



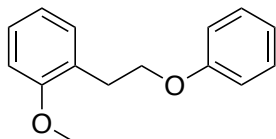
**1-methoxy-4-(2-phenylethoxy)benzene (16):** This compound was prepared following a literature procedure with modification.<sup>4</sup> Potassium carbonate (3.37 g, 24.4 mmol) and 4-methoxyphenol (3.00 g, 24.2 mmol) were stirred in DMF (60 mL) at room temperature for 30 minutes. 2-phenethyl bromide (3.00 g, 16.2 mmol) was added dropwise to the mixture and stirred overnight at room temperature. After the completion of the reaction, cold water was added into the reaction mixture. The aqueous mixture was extracted with diethylether (2×60 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Pentane/DCM, 4:1) to give 1-methoxy-4-(2-phenylethoxy)benzene as a white solid (0.94 g) in 26% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.20 (m, 5H), 6.87 – 6.80 (m, 4H), 4.14 (t,  $J = 7.2$  Hz, 2H), 3.77 (s, 3H), 3.09 (t,  $J = 7.2$  Hz, 2H). Spectral data are in accordance with those previously reported.<sup>11</sup>



**1-methoxy-4-(2-phenoxyethyl)benzene (13):** This compound was prepared following a literature procedure with modification.<sup>4</sup> Potassium carbonate (0.96 g, 6.95 mmol) and phenol (0.66 g, 7.00 mmol) were stirred in DMF (30 mL) at room temperature for 30 minutes. 2-(4-methoxyphenyl)ethyl bromide (1.00 g, 4.65 mmol) was added dropwise to the mixture and stirred overnight at

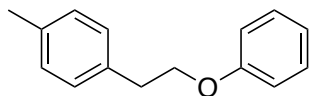


room temperature. After the completion of the reaction, cold water was added into the reaction mixture. The aqueous mixture was extracted with diethylether (2×30 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Pentane/DCM, 4:1) to give 1-methoxy-4-(2-phenoxyethyl)benzene as an oil (0.28 g) in 27% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 6.94 (td, *J* = 7.3, 1.2 Hz, 1H), 6.91 (dd, *J* = 7.6, 1.2 Hz, 2H), 6.87 (dd, *J* = 8.6, 1.4 Hz, 2H), 4.14 (t, *J* = 7.2, 1.3 Hz, 2H), 3.81 (s, *J* = 1.4 Hz, 3H), 3.05 (t, *J* = 7.2, 1.3 Hz, 2H). Spectral data are in accordance with those previously reported.<sup>12</sup>

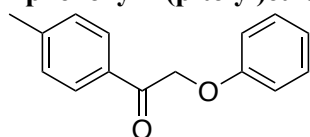


**1-methoxy-2-(2-phenoxyethyl)benzene (14):** This compound was prepared following a literature procedure with modification.<sup>4</sup> Potassium carbonate (0.64 g, 4.63 mmol) and phenol (0.44 g, 4.67 mmol) were stirred in DMF (30 mL) at room temperature for 30 minutes. 2-(2-methoxyphenyl)ethyl bromide (0.5 g, 2.32 mmol) was added dropwise to the mixture and stirred overnight at room temperature. After the completion of the reaction, cold water was added into the reaction mixture. The aqueous mixture was extracted with diethylether (2×30 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Pentane/DCM, 4:1) to give 1-methoxy-2-(2-phenoxyethyl)benzene as an oil (0.15 g) in 28% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.22 (m, 4H), 6.98 – 6.90 (m, 4H), 6.90 – 6.87 (m, 1H), 4.17 (t, *J* = 7.4 Hz, 2H), 3.86 (s, 3H), 3.13 (t, *J* = 7.4 Hz, 2H). Spectral data are in accordance with those previously reported.<sup>12</sup>

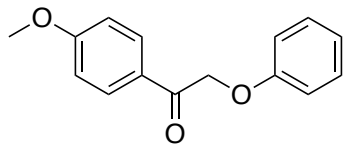
**1-methyl-4-(2-phenoxyethyl)benzene (11):** This compound was prepared following a literature procedure with modification.<sup>4</sup> Potassium carbonate (1.04 g, 7.53 mmol) and phenol (0.71 g, 7.54 mmol) were stirred in DMF (30 mL) at room temperature for 30 minutes. 4-methylphenethyl bromide (1.00 g, 5.02 mmol) was added dropwise to the mixture and stirred overnight at room temperature. After the completion of the reaction, cold water was added into the reaction mixture. The aqueous mixture was extracted with pentane (2×30 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Pentane/DCM, 4:1) to give 1- as an oil (0.41 g) in 39% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.94 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.92 – 6.89 (m, 2H), 4.16 (t, *J* = 7.2, 1.2 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.35 (s, 3H). Spectral data are in accordance with those previously reported.<sup>13</sup>



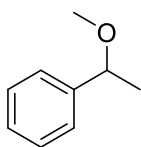
**2-phenoxy-1-(*p*-tolyl)ethan-1-one (21):** This compound was prepared according to literature procedure.<sup>7</sup> 2-bromo-1-(*p*-tolyl)ethan-1-one (2.15 g, 10.1 mmol) was added to a mixture of potassium carbonate (2.07 g, 15.07 mmol) and phenol (0.95 g, 10.1 mmol) in acetone (15 mL). The mixture was stirred at room temperature overnight. The reaction was filtered; the solvent was removed by rotary evaporation and the resulting solid was re-dissolved in EtOAc/diethyl ether and washed with brine. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, rotary evaporated, and then recrystallized from 2-propanol forming a white crystal (0.59 g) in 26% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.27 (m, 4H), 7.02 – 6.96 (m, 1H), 6.95 (dt, *J* = 7.8, 1.0 Hz, 2H), 5.25 (s, 2H), 2.43 (s, 3H). Spectral data are in accordance with those previously reported.<sup>14</sup>



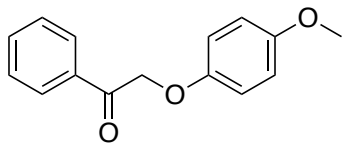
**1-(4-methoxyphenyl)-2-phenoxyethan-1-one (20):** This compound was prepared according to literature procedure.<sup>7</sup> Potassium carbonate (5.2 g, 37.7 mmol) and phenol (3.5 g, 37.2 mmol) were stirred in acetone (75 mL) at room temperature for 30 minutes. 2-bromo-1-(4-methoxyphenyl)ethan-1-one (7 g, 30.6 mmol) was added to the mixture and stirred overnight at room temperature. The reaction was filtered, the solvent removed by rotary evaporation, and the resulting solid dissolved in EtOAc. The EtOAc was washed with water (20 mL) and brine (20 mL), and it was then dried with Na<sub>2</sub>SO<sub>4</sub>. The remaining EtOAc was rotary evaporated and pumped on overnight. The solids were recrystallized from ethanol producing a white crystal (7.77 g) in 93% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.01 – 6.91 (m, 5H), 5.22 (s, 2H), 3.89 (s, 3H). Spectral data are in accordance with those previously reported.<sup>7</sup>



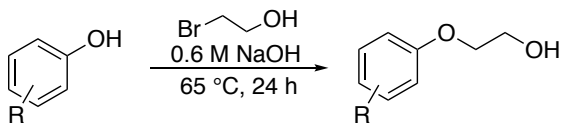
**(1-methoxyethyl)benzene:** This compound was prepared following a literature procedure. To a stirring solution of NaH (2 g, 49.2 mmol, 60% in mineral oil) in anhydrous THF (40 mL), 1-phenylethanol (3 g, 24.6 mmol) in anhydrous THF (40 mL) was added under argon in two portions at 0 °C. The resulting suspension was stirred at 0 °C for 1 h. Then iodomethane (2.3 mL, 36.9 mmol) was added dropwise, and the reaction mixture was monitored by TLC. The reaction was quenched with saturated NH<sub>4</sub>Cl solution. The aqueous layer was extracted with diethylether (2×80 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The crude product was purified by column chromatography (100% pentane) and dried via rotary evaporation to give (1-methoxyethyl)benzene as an oil (2.36 g) in 71% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 4.31 (q, *J* = 6.5 Hz, 1H), 3.24 (s, 3H), 1.45 (d, *J* = 6.5 Hz, 3H). Spectral data are in accordance with those previously reported.<sup>15</sup>



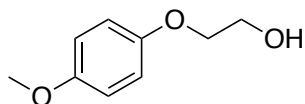
**2-(4-methoxyphenoxy)-1-phenylethan-1-one:** This compound was prepared following a literature procedure.<sup>7</sup> A 250 mL round bottom flask connected with a dropping funnel was charged with 4-methoxyphenol (0.3 g, 2.25 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.5 g, 3.6 mmol) in acetone (20 mL) and stirred at room temperature. To this solution, 2-bromoacetophenone (0.3 g, 1.5 mmol) in acetone (20 mL) was added dropwise at room temperature. The resulting suspension was stirred at room temperature overnight; the suspension was filtered and concentrated *in vacuo*. The crude product was purified by column chromatography using 100% dichloromethane to give 2-(4-methoxyphenoxy)-1-phenylethan-1-one as a white solid (0.24 g) in 66% yield after solvent removal. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.08 – 7.92 (m, 2H), 7.66 – 7.58 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 6.93 – 6.87 (m, 2H), 6.86 – 6.80 (m, 2H), 5.23 (s, 2H), 3.76 (s, 3H). Spectral data are in accordance with those previously reported.<sup>7</sup>



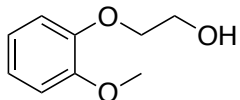
**General Procedure for synthesis of substituted 2-phenylethanols.** A 250 mL round bottom flask equipped with a water condenser was charged with substituted phenol (0.02 mol) in 40 mL NaOH aqueous solution (0.6 M). The mixture was allowed to stir at 65 °C for 15 mins. To this stirring mixture, 2-bromoethanol (0.01 mol) was added. The reaction mixture was stirred at 65 °C overnight. After the completion of the reaction. The aqueous reaction mixture was extracted with dichloromethane (2x40 mL) and washed with 0.6 M NaOH solution (2x40 mL). The combined organic was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo* giving pure product. This reaction was conducted following a literature procedure.<sup>16</sup>



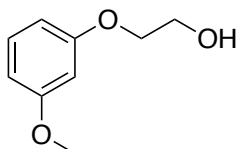
**2-(4-methoxyphenoxy)ethanol:** White solid (0.78 g, 47% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 6.90 – 6.81 (m, 4H), 4.04 (dd, *J* = 5.2, 3.8 Hz, 2H), 3.98 – 3.91 (m, 2H), 3.77 (s, 3H), 2.03 (t, *J* = 6.3 Hz, 1H). Spectral data are in accordance with those previously reported.<sup>16</sup>



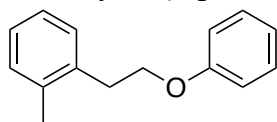
**2-(2-methoxyphenoxy)ethanol:** Colorless oil (0.51 g, 30% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.04 – 6.81 (m, 4H), 4.17 – 4.08 (m, 2H), 3.96 – 3.90 (m, 2H), 3.87 (s, 3H). Spectral data are in accordance with those previously reported.<sup>16</sup>



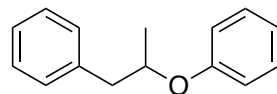
**2-(3-methoxyphenoxy)ethanol:** Colorless oil (0.83 g, 50% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 8.2 Hz, 1H), 6.55 – 6.51 (m, 2H), 6.49 (t, *J* = 2.3 Hz, 1H), 4.14 – 4.03 (m, 2H), 3.99 – 3.90 (m, 2H), 3.79 (s, 3H). Spectral data are in accordance with those previously reported.<sup>16</sup>



**1-methyl-2-(2-phenoxyethyl)benzene (12):** This compound was prepared following a literature procedure with modification.<sup>4</sup> Potassium carbonate (2.08 g, 15.06 mmol) and phenol (0.995 g, 10.54 mmol) were stirred in DMF (30 mL) at room temperature for 30 minutes. 2-methylphenethyl bromide (2.00 g, 10.04 mmol) was added dropwise to the mixture and stirred overnight at room temperature. After the completion of the reaction, cold water was added into the reaction mixture. The aqueous mixture was extracted with pentane (2×30 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Pentane/DCM, 4:1) to give 1-methyl-2-(2-phenoxyethyl)benzene as an oil (0.36 g) in 17% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.18 (t, *J* = 4.7, 2.6 Hz, 3H), 6.96 (t, *J* = 7.4, 1.0 Hz, 1H), 6.94 – 6.90 (m, 2H), 4.16 (t, *J* = 7.4 Hz, 2H), 3.13 (t, *J* = 7.4 Hz, 2H), 2.39 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 158.77, 136.53, 136.26, 130.34, 129.54, 129.48, 126.69, 126.12, 120.72, 114.48, 67.60, 33.07, 19.52.



**(2-phenoxypropyl)benzene (18):** This compound was prepared following a literature procedure with modification.<sup>17</sup> A 100 mL round bottom flask equipped with a water condenser was charged with cesium carbonate (9.6 g, 29.4 mmol), iodobenzene (3 g, 14.7 mmol), 1,10-phenanthroline (0.53 g, 2.94 mmol, 20 mol%), copper(I) iodide (0.28 g, 1.47 mmol, 10 mol%), 1-phenylpropan-2-ol (2.01 g, 14.7 mmol) and 40 mL of toluene. The reaction mixture was reflux under N<sub>2</sub> for 48 hours. The aqueous mixture was extracted with pentane (2×50 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (Pentane/DCM, 4:1) to give (2-phenoxypropyl)benzene as an oil (1.06 g) in 34% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.18 (m, 7H), 6.97 – 6.87 (m, 3H), 4.59 (h, *J* = 6.2 Hz, 1H), 3.12 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.83 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.31 (dd, *J* = 6.1, 0.7 Hz, 3H). Spectral data are in accordance with those previously reported.<sup>18</sup>



## Reference:

1. Lam, C. H.; Lowe, C. B.; Li, Z. L.; Longe, K. N.; Rayburn, J. T.; Caldwell, M. A.; Houdek, C. E.; Maguire, J. B.; Saffron, C. M.; Miller, D. J.; Jackson, J. E., Electrocatalytic upgrading of model lignin monomers with earth abundant metal electrodes. *Green Chemistry* **2015**, *17* (1), 601-609.
2. Cyr, A.; Chiltz, F.; Jeanson, P.; Martel, A.; Brossard, L.; Lessard, J.; Menard, H., Electrocatalytic hydrogenation of lignin models at Raney nickel and palladium-based electrodes. *Canadian Journal of Chemistry* **2000**, *78* (3), 307-315.
3. Kanan, M. W.; Nocera, D. G., In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co<sup>2+</sup>. *Science* **2008**, *321* (5892), 1072-1075.
4. Galkin, M. V.; Dahlstrand, C.; Samec, J. S. M., Mild and Robust Redox-Neutral Pd/C-Catalyzed Lignol -O-4 Bond Cleavage Through a Low-Energy-Barrier Pathway. *ChemSuschem* **2015**, *8* (13), 2187-2192.
5. Steiner, A.; Williams, J. D.; Rincon, J. A.; de Frutos, O.; Mateos, C.; Kappe, C. O., Implementing Hydrogen Atom Transfer (HAT) Catalysis for Rapid and Selective Reductive Photoredox Transformations in Continuous Flow. *European Journal of Organic Chemistry* **2019**, *2019* (33), 5807-5811.
6. Chen, J. Z.; Liu, D. L.; Butt, N.; Li, C.; Fan, D. Y.; Liu, Y. G.; Zhang, W. B., Palladium-Catalyzed Asymmetric Hydrogenation of alpha-Acyloxy-1-arylethanones. *Angewandte Chemie-International Edition* **2013**, *52* (44), 11632-11636.
7. Cao, Y.; Wang, N.; He, X.; Li, H. R.; He, L. N., Photocatalytic Oxidation and Subsequent Hydrogenolysis of Lignin beta-O-4 Models to Aromatics Promoted by In Situ Carbonic Acid. *Acs Sustainable Chemistry & Engineering* **2018**, *6* (11), 15032-15039.
8. Sang, D. Y.; Tian, J.; Tu, X. D.; He, Z. J.; Yao, M., Cleavage of Catechol Monoalkyl Ethers by Aluminum Triiodide-Dimethyl Sulfoxide. *Synthesis-Stuttgart* **2019**, *51* (3), 704-712.
9. Fabbri, C.; Bietti, M.; Lanzalunga, O., Generation and reactivity of ketyl radicals with lignin related structures. On the importance of the ketyl pathway in the photoyellowing of lignin containing pulps and papers. *Journal of Organic Chemistry* **2005**, *70* (7), 2720-2728.
10. Sawatzky, R. S.; Hargreaves, B. K. V.; Stradiotto, M., A Comparative Ancillary Ligand Survey in Palladium-Catalyzed C-O Cross-Coupling of Primary and Secondary Aliphatic Alcohols. *European Journal of Organic Chemistry* **2016**, (14), 2444-2449.
11. Vaxelaire, C.; Souquet, F.; Lannou, M. I.; Ardisson, J.; Royer, J., Anodic Oxidation: An Attractive Alternative to CAN-Mediated Cleavage of para-Methoxyphenyl Ethers. *European Journal of Organic Chemistry* **2009**, (19), 3138-3140.
12. Fleury-Bregeot, N.; Pisset, M.; Beaumard, F.; Colornbel, V.; Oehlich, D.; Rombouts, F.; Molander, G. A., Suzuki-Miyaura Cross-Coupling of Potassium Alkoxyethyltrifluoroborates: Access to Aryl/Heteroarylethoxy Motifs. *Journal of Organic Chemistry* **2012**, *77* (22), 10399-10408.
13. Vechorkin, O.; Proust, V.; Hu, X. L., Functional Group Tolerant Kumada-Corriu-Tamao Coupling of Nonactivated Alkyl Halides with Aryl and Heteroaryl Nucleophiles: Catalysis by a Nickel Pincer Complex Permits the Coupling of Functionalized Grignard Reagents. *Journal of the American Chemical Society* **2009**, *131* (28), 9756-9766.
14. Enthaler, S.; Spilker, B.; Erre, G.; Junge, K.; Tse, M. K.; Beller, M., Biomimetic transfer hydrogenation of 2-alkoxy- and 2-aryloxyketones with iron-porphyrin catalysts. *Tetrahedron* **2008**, *64* (17), 3867-3876.

15. Shah, S. T. A.; Singh, S.; Guiry, P. J., A Novel, Chemoselective and Efficient Microwave-Assisted Deprotection of Silyl Ethers with Selectfluor. *Journal of Organic Chemistry* **2009**, *74* (5), 2179-2182.
16. Hu, Z. P.; Zhang, S. S.; Zhou, W. C.; Ma, X.; Xiang, G. Y., Synthesis and antibacterial activity of 3-benzylamide derivatives as FtsZ inhibitors. *Bioorganic & Medicinal Chemistry Letters* **2017**, *27* (8), 1854-1858.
17. Wolter, M.; Nordmann, G.; Job, G. E.; Buchwald, S. L., Copper-catalyzed coupling of aryl iodides with aliphatic alcohols. *Organic Letters* **2002**, *4* (6), 973-976.
18. Simon, M. O.; Girard, S. A.; Li, C. J., Catalytic Aerobic Synthesis of Aromatic Ethers from Non-Aromatic Precursors. *Angewandte Chemie-International Edition* **2012**, *51* (30), 7537-7540.

Cartesian coordinates (Angstroms) and total energies (Hartrees) for compounds **1, 2, 8, 10, 18, 19**, and their respective C-O fragmentation products as computed at the wB97X-V/6-311+G(2df,2p)[6-311G\*] level of theory (**Derived C-O bond dissociation energies are shown in Footnote [44]**).

Computations were performed using Spartan '18, v. 1.4.1 WaveFunction, Inc. Irvine, CA, 92612.

**wB97X-V/6-311+G(2df,2p)[6-311G\*] Energy calculations**

Methylated 2-phenoxyketones	E(H)	BDE (kJ/mol)
Compound <b>1</b>	-691.161466	262.4
Compound <b>19</b>	-730.482658	251.9
Compound <b>10</b>	-769.801815	250.3
<hr/>		
Substituted 2-phenoxy ethanes		
Compound <b>2</b>	-692.373197	315.0
Compound <b>8</b>	-617.149885	309.1
Compound <b>18</b>	-656.469608	303.7
<hr/>		
Radical fragments		
Phenoxy_radical (from all species above)	-306.826718	
Acetophenone-2-yl_radical (from <b>1</b> )	-384.234801	
Propiophenone-2-yl_radical (from <b>19</b> )	-423.559981	
2-Methylpropiophenone-2-yl (from <b>10</b> )	-462.879756	
1-phenylethanol-2-yl_radical (from <b>2</b> )	-385.426496	
2-Phenylethyl_radical (from <b>8</b> )	-310.205428	
1-Phenyl-2-propyl_radical (from <b>18</b> )	-349.527229	

Compound 1

Total energy = -691.161466

H1	2.100330476	3.365344846	-1.779425741
C2	1.115732132	2.944167287	-1.953982005
C3	-1.414029120	1.845520040	-2.337334662
C4	0.613648415	2.017297625	-1.034078054
C5	0.362494744	3.312443133	-3.059899787
C6	-0.904749137	2.763834444	-3.251478090
C7	-0.657436000	1.468162925	-1.233365712
H8	0.759499850	4.028790364	-3.772663046
H9	-1.496094493	3.052910428	-4.115473130
H10	-1.055113772	0.738488866	-0.537211627
H11	-2.401109543	1.418566946	-2.485655443
C12	1.457316447	1.690913341	0.152831427
C13	0.995258369	0.613125744	1.132902627
H14	1.803590846	0.461550150	1.856446845
H15	0.102117024	0.973624614	1.667983551
O16	0.708241149	-0.568340728	0.420191426
C17	0.199533193	-1.628809081	1.109455970
C18	-0.865920875	-3.905195561	2.321621611
C19	-0.148025549	-2.737774159	0.332577504
C20	0.017717407	-1.656178507	2.491397439
C21	-0.516575887	-2.800079316	3.085972010
C22	-0.676491338	-3.866531279	0.939193131
H23	0.006835553	-2.688033254	-0.740242305
H24	0.289908512	-0.809592842	3.111466203
H25	-0.655038370	-2.817185988	4.163023736
H26	-0.943842460	-4.723862506	0.328526625
H27	-1.280012116	-4.790162550	2.793945721
O28	2.482214546	2.297005015	0.393273779

## Compound 2

Total energy = -692.373197

H1	-0.333529540	2.799269203	-1.777007095
C2	0.284489993	3.077786558	-0.930236807
C3	1.908837407	3.766773433	1.223733744
C4	1.146251593	2.127774777	-0.383654255
C5	0.238830093	4.365641042	-0.404799355
C6	1.046729579	4.712469529	0.674622636
C7	1.959136768	2.481613229	0.693796260
H8	-0.430421805	5.101608551	-0.840888768
H9	1.009963775	5.718031614	1.083123709
H10	2.642502748	1.747934877	1.116656018
H11	2.547953481	4.031940888	2.060823138
C12	1.156481567	0.708788525	-0.902716259
H13	2.176895095	0.299504023	-0.827518612
C14	0.239564551	-0.160109709	-0.043771669
H15	0.601056096	-0.204234908	0.991846777
H16	-0.775406438	0.259510414	-0.053721284
O17	0.249707384	-1.445303879	-0.640050540
C18	-0.587085253	-2.405226996	-0.155685446
C19	-2.226910128	-4.503315653	0.680665507
C20	-0.597235732	-3.610785945	-0.862119421
C21	-1.393539415	-2.247054285	0.970590937
C22	-2.209316446	-3.303017910	1.378351671
C23	-1.413363941	-4.650283167	-0.443367471
H24	0.041445329	-3.708711985	-1.733974194
H25	-1.394061698	-1.321178023	1.534384285
H26	-2.835470946	-3.174554819	2.256317333
H27	-1.416425190	-5.582821548	-0.999924819
H28	-2.865753230	-5.317988361	1.005958284
O29	0.714161236	0.681394444	-2.239681397
H30	0.514513067	-0.245453920	-2.431752908

## Compound 8

Total energy = -617.149885

H1	-0.526508975	2.143390597	-2.534585299
C2	-0.249537949	1.200740217	-3.001288400
C3	0.453778280	-1.203451539	-4.201943934
C4	-0.611371735	0.000001248	-2.386627426
C5	0.453776646	1.203450317	-4.201947183
C6	0.807713462	-0.000001243	-4.805707153
C7	-0.249536331	-1.200738929	-3.001285195
H8	0.722541846	2.146801072	-4.668262671
H9	1.354437999	-0.000002112	-5.743965533
H10	-0.526506177	-2.143388414	-2.534579512
H11	0.722544781	-2.146803248	-4.668256764
C12	-1.325855001	0.000002474	-1.056748919
C13	-0.326051730	0.000000822	0.093591605
H14	0.318338169	-0.889080052	0.035150508
H15	0.318338533	0.889081515	0.035152429
O16	-1.059759097	-0.000000522	1.301582011
C17	-0.372792635	-0.000000698	2.474012019
C18	0.843145074	-0.000000816	4.991978832
C19	-1.154813714	-0.000001546	3.633941497
C20	1.019123892	-0.000000077	2.575376210
C21	1.614283940	-0.000000089	3.837534225
C22	-0.547970025	-0.000001602	4.880229773
H23	-2.234899879	-0.000002109	3.529207062
H24	1.645968981	0.000000436	1.691077921
H25	2.698322402	0.000000513	3.907303693
H26	-1.166041731	-0.000002228	5.773452635
H27	1.315978524	-0.000000810	5.968810591
H28	-1.968322475	0.881800899	-0.961601375
H29	-1.968325078	-0.881794074	-0.961601648

## Compound 10

Total energy = -769.801815

H1	3.226928145	-1.512331872	0.047696636
C2	2.270182312	-1.999828892	-0.104890597
C3	-0.204287212	-3.210277977	-0.469358824
C4	1.112549099	-1.349951312	0.341292272
C5	2.192296337	-3.238645538	-0.724685961
C6	0.952299268	-3.847500335	-0.907527459
C7	-0.129781782	-1.967631179	0.150981340
H8	3.097822493	-3.731424303	-1.065302084
H9	0.888164766	-4.817121437	-1.392612930
H10	-1.039028822	-1.476608979	0.473810337
H11	-1.172760704	-3.679131512	-0.613981748
C12	1.310603008	-0.020675115	1.010202420
C13	0.127395430	0.760027397	1.638042691
O14	-1.068934791	0.710472481	0.856205489
C15	-1.135178633	1.218656759	-0.410489003
C16	-1.546676246	2.160071193	-3.011772887
C17	-2.430257494	1.335492222	-0.921727742
C18	-0.043201321	1.571013978	-1.204396227
C19	-0.261615220	2.041344333	-2.498581427
C20	-2.631412063	1.801494016	-2.212918457
H21	-3.264189815	1.055650508	-0.286178453
H22	0.973768339	1.487643524	-0.841151244
H23	0.595590504	2.313278484	-3.107392924
H24	-3.643818570	1.887655505	-2.596677303
H25	-1.703868842	2.527303979	-4.020777165
O26	2.431575158	0.435409468	1.140712068
C27	0.514670254	2.207070655	1.938726934
H28	1.379019052	2.237010984	2.603702716
H29	-0.332778161	2.701544957	2.422150221
H30	0.769682490	2.761798703	1.033612605
C31	-0.240021308	0.037366729	2.940405713
H32	0.615751044	0.039052369	3.621369163
H33	-0.536234146	-0.997782664	2.754075389
H34	-1.074252569	0.559552872	3.417436441

## Compound 18

Total energy = -656.469608

H1	-0.983215939	2.502835096	-1.262558980
C2	-0.125653055	2.937612394	-0.753536552
C3	2.065514211	4.059655852	0.529846269
C4	1.024803596	2.165543200	-0.570353744
C5	-0.184221198	4.251516228	-0.301455010
C6	0.913091290	4.816930531	0.343092725
C7	2.118507127	2.744464048	0.075790224
H8	-1.085991043	4.836616797	-0.456679238
H9	0.870980989	5.843466182	0.694662602
H10	3.021749147	2.157448637	0.224055038
H11	2.927610397	4.493590094	1.028013124
C12	1.053292569	0.728852205	-1.031871355
C13	0.310461582	-0.209076571	-0.073446585
H14	-0.714897951	0.168095877	0.043770545
O15	0.277615430	-1.471367385	-0.733708249
C16	-0.642497468	-2.405709452	-0.378302487
C17	-2.457132341	-4.472226865	0.151034310
C18	-0.558047872	-3.617794344	-1.072506984
C19	-1.638046050	-2.232930211	0.586318557
C20	-2.536444222	-3.269591112	0.839911170
C21	-1.458508836	-4.638331595	-0.809298265
H22	0.222497588	-3.730518243	-1.817891647
H23	-1.726919235	-1.309258457	1.146334646
H24	-3.305841698	-3.123904940	1.592866496
H25	-1.380878616	-5.571968875	-1.358973388
H26	-3.161216750	-5.271909703	0.357341576
C27	0.989410008	-0.326138609	1.285747037
H28	2.021973420	-0.666772338	1.154649607
H29	0.473726780	-1.044995513	1.928110149
H30	1.002550049	0.643878568	1.791103779
H31	0.580505760	0.637418741	-2.015708019
H32	2.085222332	0.374569763	-1.136357351

## Compound 19

Total energy = -730.482658

H1	-1.133647642	0.573717638	-0.197985561
C2	-0.935719153	1.281929131	-0.995276120
C3	-0.474281787	3.086362394	-3.069939452
C4	0.319222001	1.887555296	-1.125046410
C5	-1.951289434	1.581147009	-1.896078757
C6	-1.721808149	2.479866633	-2.934347857
C7	0.538635698	2.794186677	-2.167316151
H8	-2.922839284	1.109050839	-1.787913484
H9	-2.516325654	2.708501018	-3.638704377
H10	1.514842684	3.260540145	-2.249392564
H11	-0.294655143	3.788697509	-3.878214026
C12	1.447582374	1.642781124	-0.174562479
C13	1.284944801	0.550757300	0.897877404
H14	0.409306028	0.824994058	1.504534663
O15	1.018566669	-0.650223313	0.186419077
C16	0.221549680	-1.605338603	0.741716884
C17	-1.427245595	-3.666890453	1.658174967
C18	-0.163985537	-2.634460510	-0.122911096
C19	-0.217269137	-1.608205936	2.066406540
C20	-1.041662922	-2.641811282	2.511534049
C21	-0.979826067	-3.656751337	0.336347822
H22	0.186565630	-2.604215480	-1.149180047
H23	0.082249635	-0.831972923	2.761317132
H24	-1.376646674	-2.638676086	3.544648715
H25	-1.273355450	-4.450410228	-0.344404436
H26	-2.066951924	-4.467402041	2.015434991
O27	2.467389446	2.299701437	-0.221857076
C28	2.519336911	0.420075854	1.771479672
H29	3.392238902	0.202352031	1.152440437
H30	2.388097380	-0.388636989	2.495680090
H31	2.706981713	1.352779089	2.309117450

## Phenoxy radical

Total energy = -306.826718

O1	0.000000000	0.000000000	2.668486877
C2	0.000000000	0.000000000	1.418932253
C3	0.000000000	0.000000000	-1.407800763
C4	1.238105481	0.000000000	0.661497081
C5	-1.238105481	0.000000000	0.661497081
C6	-1.223435312	0.000000000	-0.712570288
C7	1.223435312	0.000000000	-0.712570288
H8	2.163265886	0.000000000	1.228763056
H9	-2.163265886	0.000000000	1.228763056
H10	-2.154937258	0.000000000	-1.270749037
H11	2.154937258	0.000000000	-1.270749037
H12	0.000000000	0.000000000	-2.493499991

## Acetophenone-2-yl\_radical

Total energy = -384.234801

H1	0.353625490	0.740509281	-2.184053711
C2	0.236261921	0.847311148	-1.110860707
C3	-0.042397143	1.063518237	1.648431760
C4	0.069778314	-0.308017487	-0.341785502
C5	0.251090157	2.098645716	-0.508877728
C6	0.110588968	2.209170409	0.873004956
C7	-0.065307567	-0.189534820	1.044209809
H8	0.374367304	2.989913276	-1.116612613
H9	0.124445712	3.186892050	1.345410573
H10	-0.168273512	-1.072124424	1.668186813
H11	-0.141644303	1.144250710	2.726630405
C12	0.065147059	-1.627681539	-1.056640943
C13	-0.404569098	-2.816393509	-0.396358405
H14	-0.356824911	-3.746494717	-0.950903214
H15	-0.846258944	-2.820134650	0.593328442
O16	0.439970551	-1.699829680	-2.233109935

## Propiophenone-2-yl radical

Total energy = -423.559981

H1	0.916748468	1.043841007	-2.075873170
C2	0.493514414	1.363126723	-1.129251301
C3	-0.560867743	2.129488630	1.327993225
C4	0.176380959	0.386310870	-0.180935044
C5	0.271355304	2.707228810	-0.858911972
C6	-0.258199082	3.093687779	0.370803429
C7	-0.347645047	0.782206106	1.052815148
H8	0.513670118	3.456431934	-1.606622470
H9	-0.429554782	4.144580581	0.584630231
H10	-0.569898125	0.046375926	1.819968291
H11	-0.960155032	2.426067856	2.293247312
C12	0.445034187	-1.047131996	-0.538151294
C13	-0.227274678	-2.102625273	0.178665871
H14	-0.981516667	-1.856177418	0.920248624
O15	1.214821079	-1.316272620	-1.468591733
C16	0.033257237	-3.532055003	-0.118911818
H17	-0.875221307	-4.022136656	-0.494831304
H18	0.323811686	-4.073378859	0.790993163
H19	0.821739011	-3.629568396	-0.867285188

## 2-Methylpropiophenone-2-yl radical

Total energy = -462.879756

H1	0.415102228	1.469493714	-2.305835045
C2	0.516754085	1.671885716	-1.244397833
C3	0.693753587	2.190132055	1.483244801
C4	-0.031888967	0.765415382	-0.333499842
C5	1.171940264	2.811924175	-0.795884242
C6	1.263041218	3.072485283	0.569894896
C7	0.052618996	1.039615316	1.033503092
H8	1.605680235	3.503634783	-1.511880502
H9	1.769948581	3.966437861	0.920999456
H10	-0.404902396	0.365397582	1.752077166
H11	0.744146709	2.399160799	2.547688468
C12	-0.767055373	-0.427446269	-0.876586304
C13	-0.681996348	-1.721458557	-0.230113077
O14	-1.429938171	-0.297310396	-1.914402721
C15	-1.582588311	-2.810481092	-0.708459713
H16	-2.366899970	-2.419322283	-1.357056357
H17	-2.029738731	-3.341998837	0.141598289
H18	-1.008711970	-3.557641984	-1.275681001
C19	0.325242586	-2.082201607	0.814731717

H20	1.129225528	-1.349392416	0.907334119
H21	0.767583389	-3.059175466	0.581977529
H22	-0.151317168	-2.189153760	1.800747104

## 2-Phenylethyl\_radical

Total energy = -310.205428

H1	0.305667995	2.143623706	-0.153831580
C2	0.195100918	1.200522085	0.376683279
C3	-0.082619261	-1.202886361	1.740507592
C4	0.339500228	0.000000000	-0.321398633
C5	-0.082619261	1.202886362	1.740507592
C6	-0.222701767	0.000000000	2.427302332
C7	0.195100917	-1.200522084	0.376683278
H8	-0.186450118	2.146679211	2.268274623
H9	-0.436861307	0.000000000	3.491906602
H10	0.305667995	-2.143623706	-0.153831583
H11	-0.186450119	-2.146679209	2.268274622
C12	0.599596650	0.000000000	-1.822132175
C13	-0.683345082	0.000000000	-2.590296136
H14	-1.226007067	-0.928247310	-2.740977084
H15	-1.226007070	0.928247309	-2.740977085
H16	1.196213174	0.882246830	-2.083347822
H17	1.196213175	-0.882246830	-2.083347821

## 1-Phenyl-2-propyl\_radical

Total energy = -349.527229

H1	-0.784157944	1.037313755	-2.086898338
C2	-0.341350293	1.235734815	-1.113400922
C3	0.785024161	1.749875326	1.372375735
C4	0.405920934	0.237221367	-0.484923774
C5	-0.522152878	2.477354655	-0.511484374
C6	0.040612708	2.738296630	0.735464216
C7	0.965582076	0.510005634	0.764980092
H8	-1.101402322	3.243851581	-1.018520663
H9	-0.098064568	3.707205425	1.205818432
H10	1.552422705	-0.257015493	1.265403661
H11	1.231210066	1.944868174	2.343454453
C12	0.552495053	-1.139041641	-1.118240290
C13	-0.584446636	-2.037303435	-0.732389459
H14	-1.490831548	-1.996098978	-1.332126444
C15	-0.665495642	-2.600756232	0.644799184

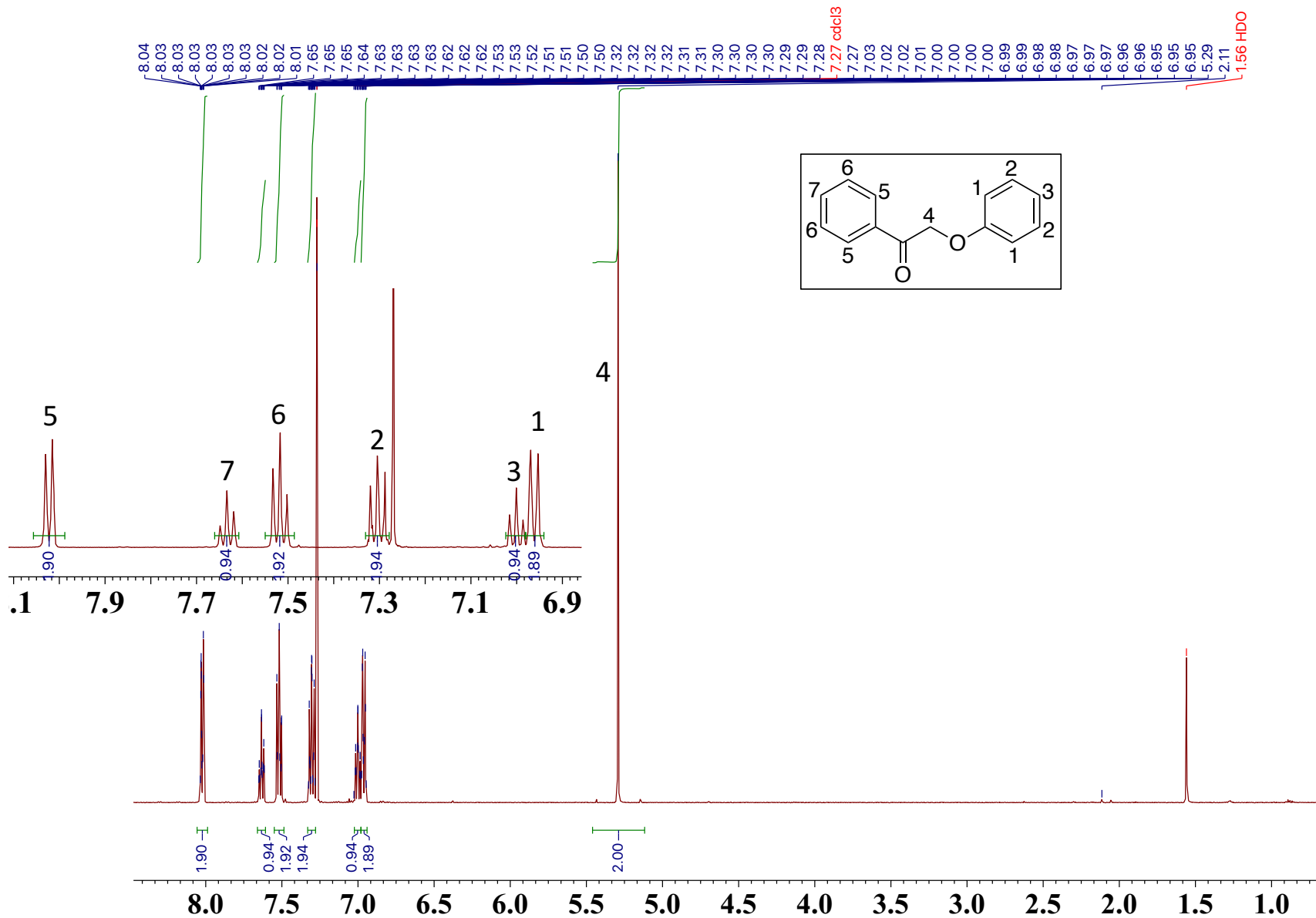
H16	0.299281870	-3.019478909	0.961859575
H17	-1.421161150	-3.388973906	0.718555875
H18	-0.927228502	-1.826189818	1.385601071
H19	0.600110960	-1.035047064	-2.208268189
H20	1.503630951	-1.581821885	-0.792059842

### 1-phenylethanol-2-yl Radical

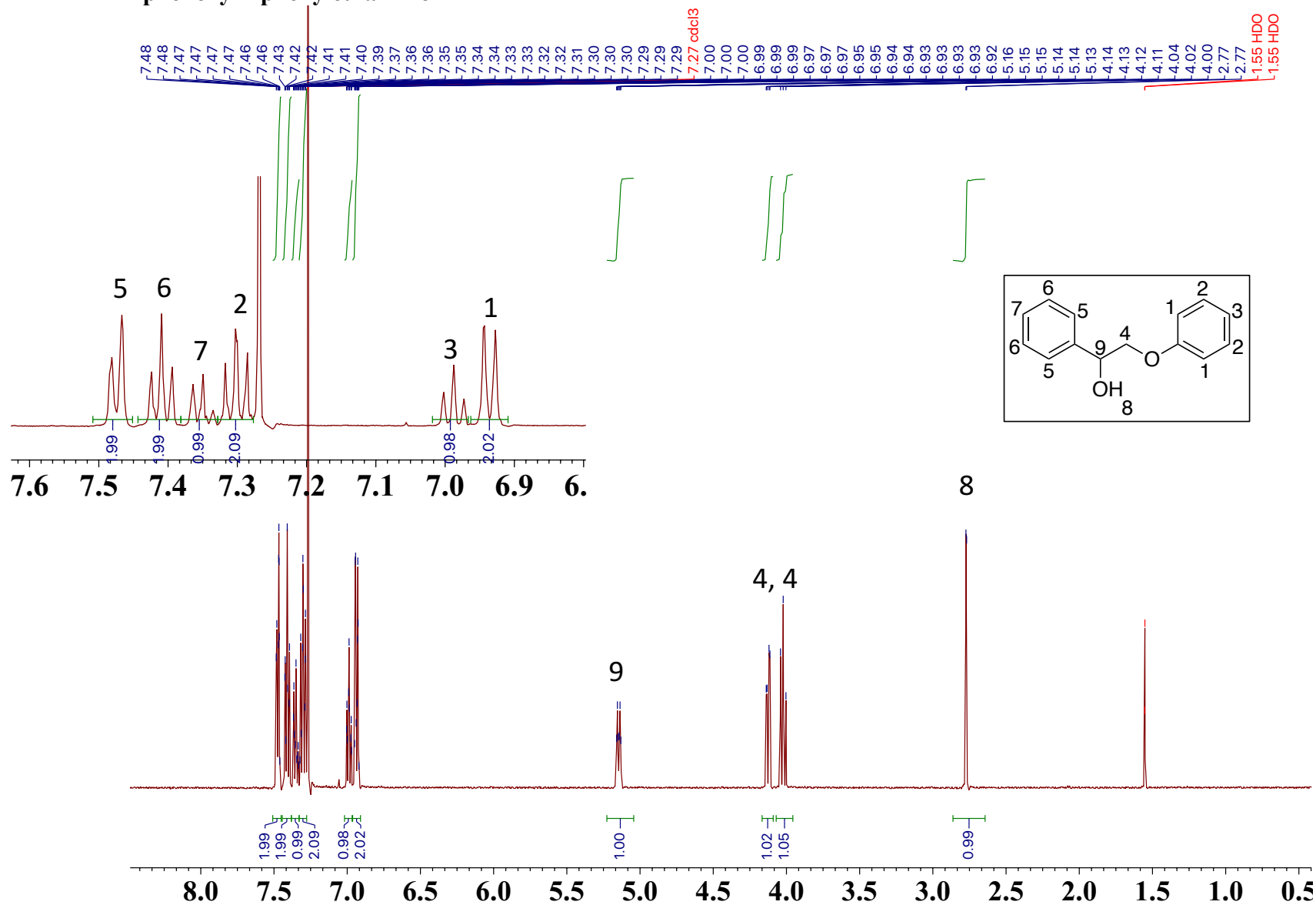
Total energy = -385.426496

H1	-0.675960298	0.728408852	-1.784799227
C2	-0.314997616	0.859907519	-0.768740788
C3	0.624032207	1.170361774	1.832712729
C4	0.189663152	-0.246145037	-0.080370728
C5	-0.345909495	2.111138324	-0.162238794
C6	0.121593918	2.269075338	1.141127191
C7	0.659991528	-0.080717004	1.222168682
H8	-0.737049547	2.965884467	-0.706588518
H9	0.096683174	3.246051785	1.614645622
H10	1.060547427	-0.936301186	1.761810335
H11	0.996103025	1.288130588	2.846400968
C12	0.183108118	-1.625291329	-0.739159335
H13	0.924124895	-2.252352851	-0.213765363
C14	-1.165259659	-2.241611266	-0.605012330
H15	-1.492151611	-2.611616680	0.360211700
H16	-1.898782868	-2.068948261	-1.385272154
O17	0.486530148	-1.553378099	-2.120410805
H18	1.287733502	-1.022596933	-2.212719184

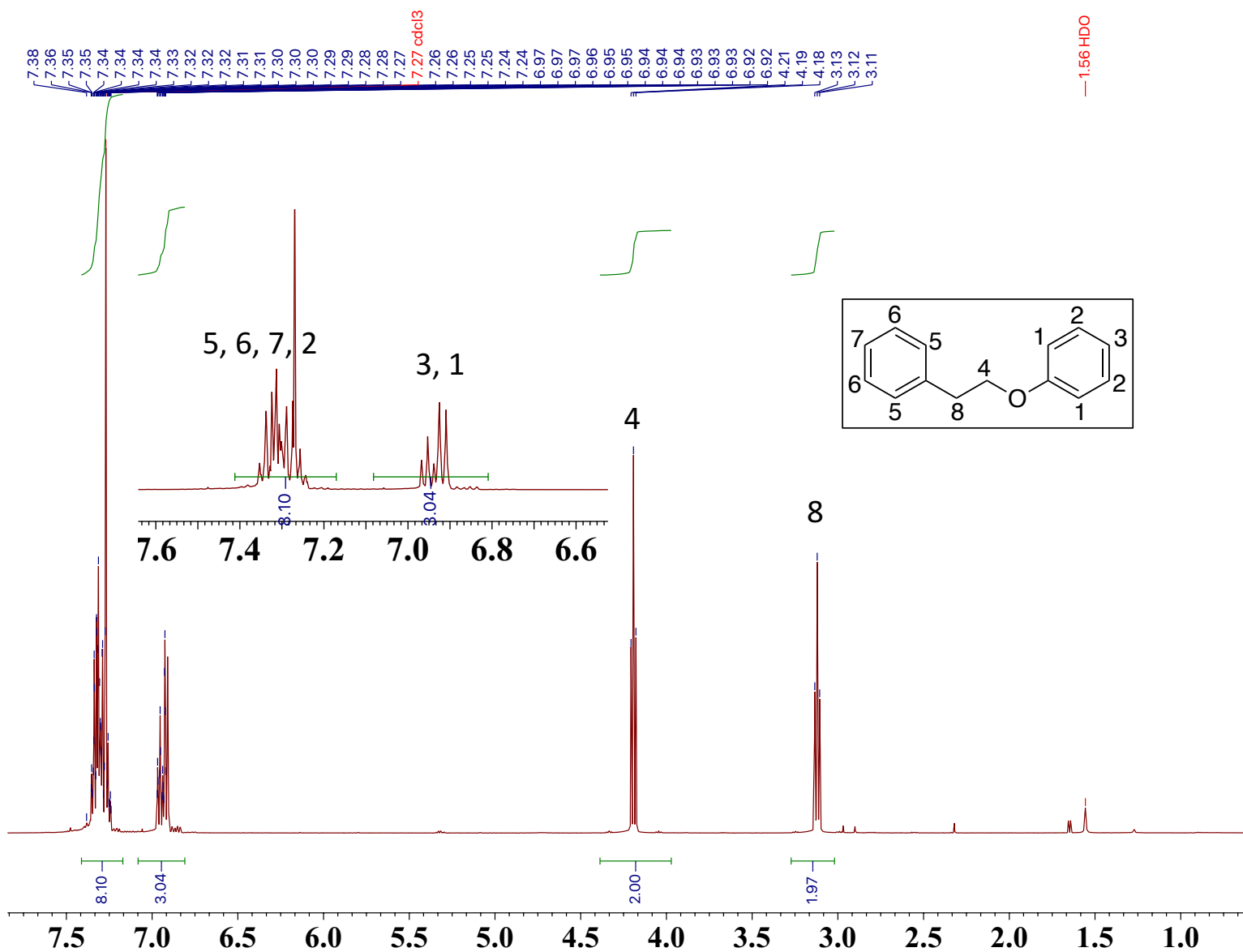
# <sup>1</sup>H NMR of 2-phenoxyacetophenone



<sup>1</sup>H NMR of 2-phenoxy-1-phenylethan-1-ol

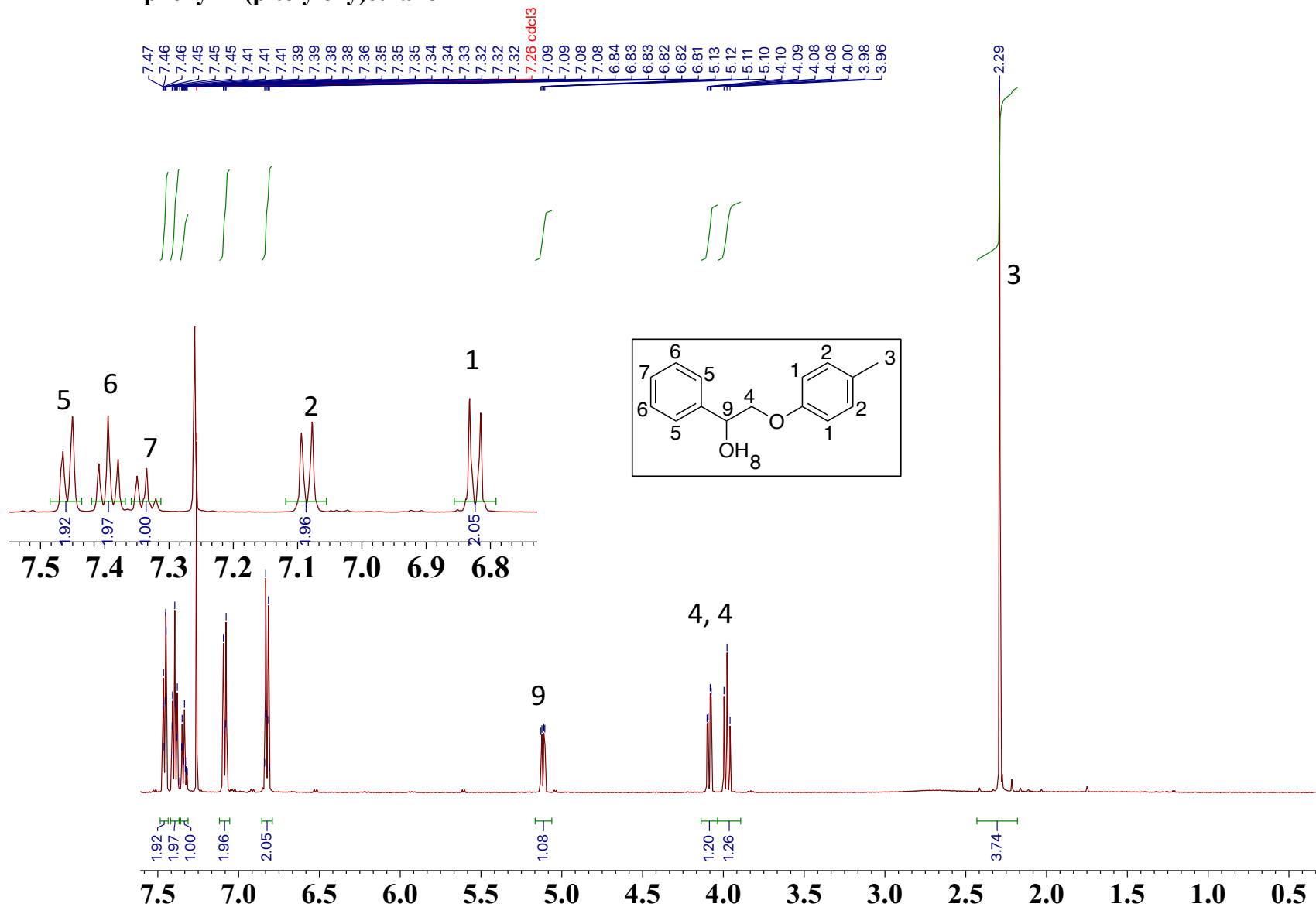


<sup>1</sup>H NMR of 2-phenoxy-1-phenylethane

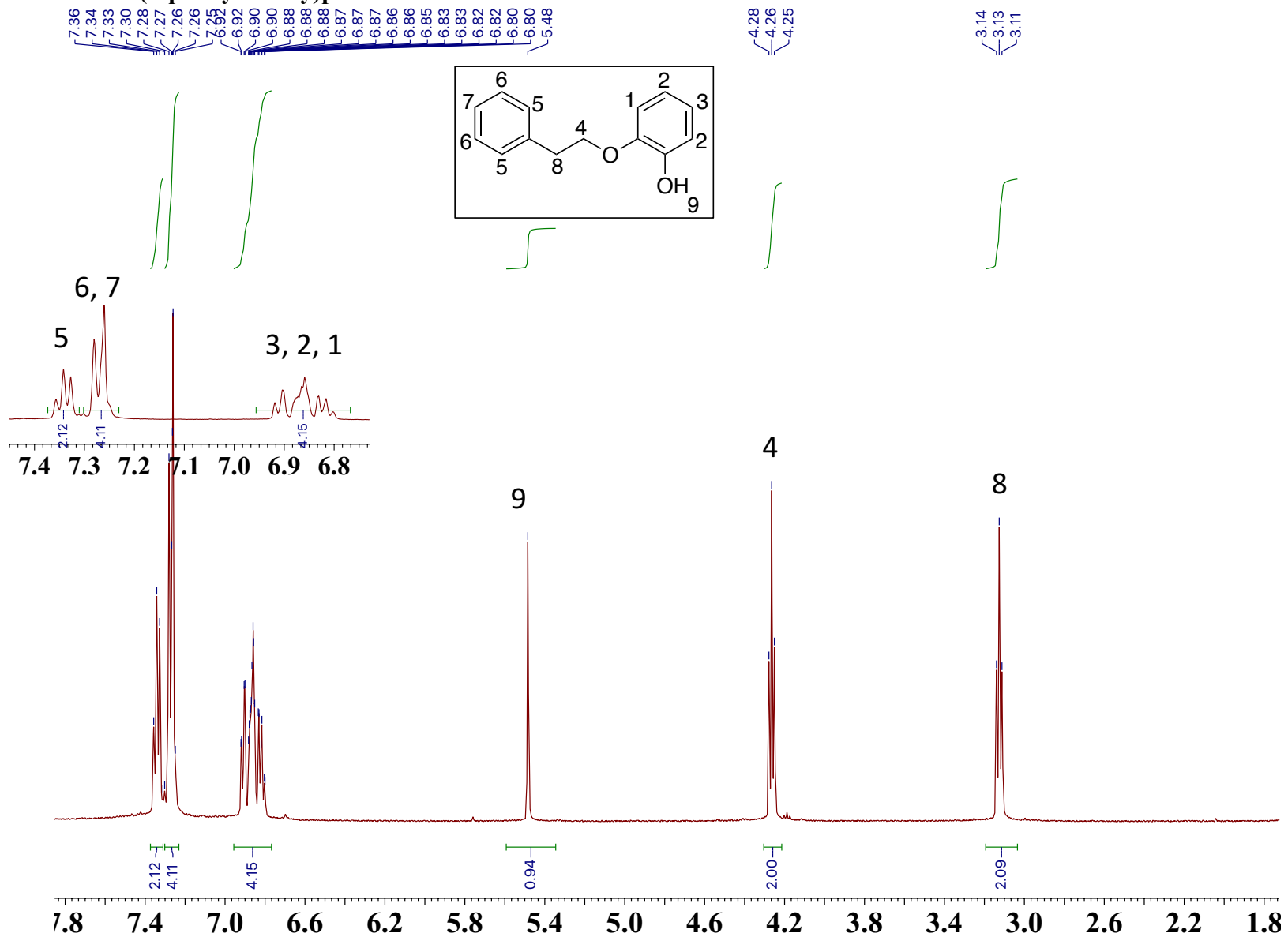




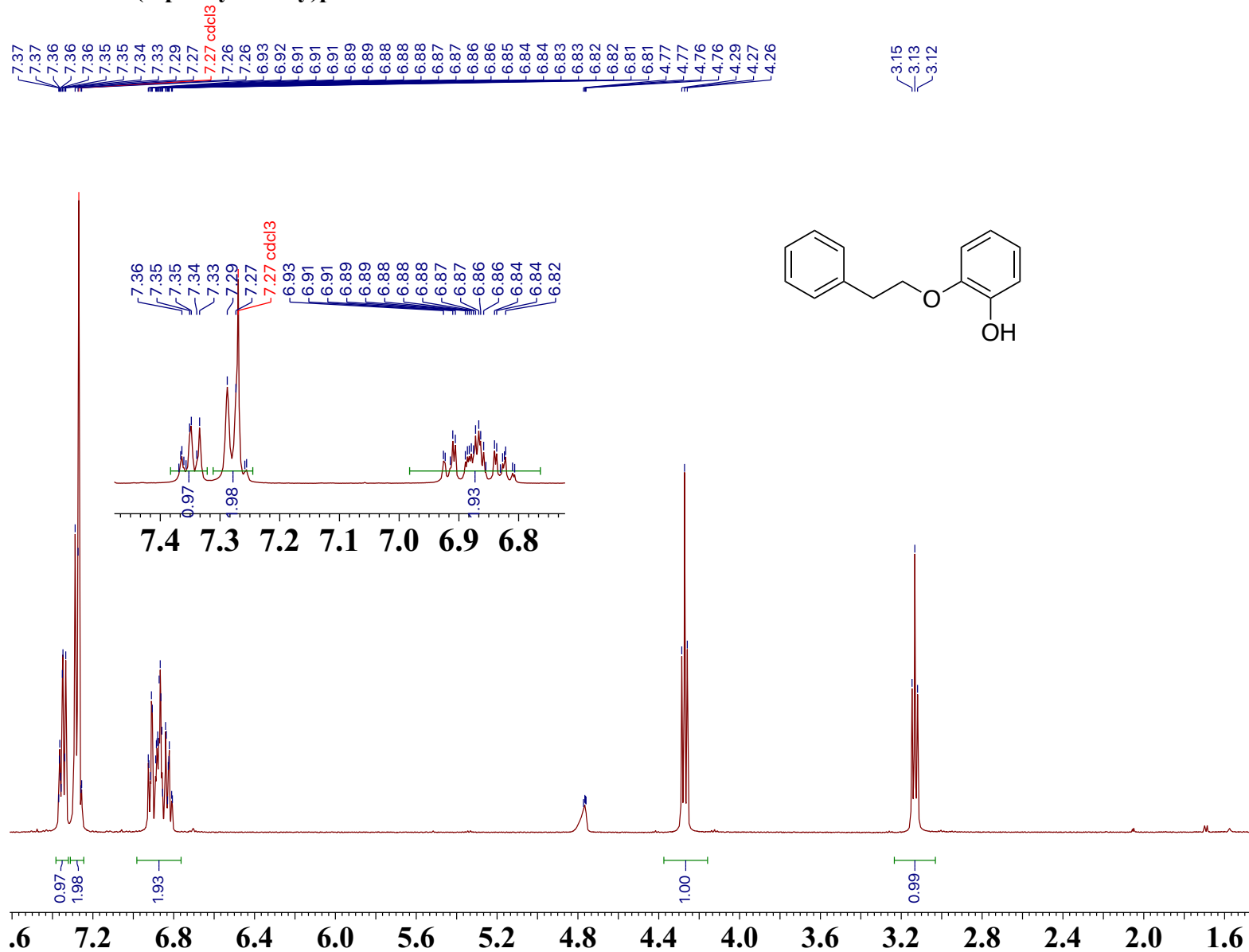
<sup>1</sup>H NMR of 1-phenyl-2-(p-tolyloxy)ethanol



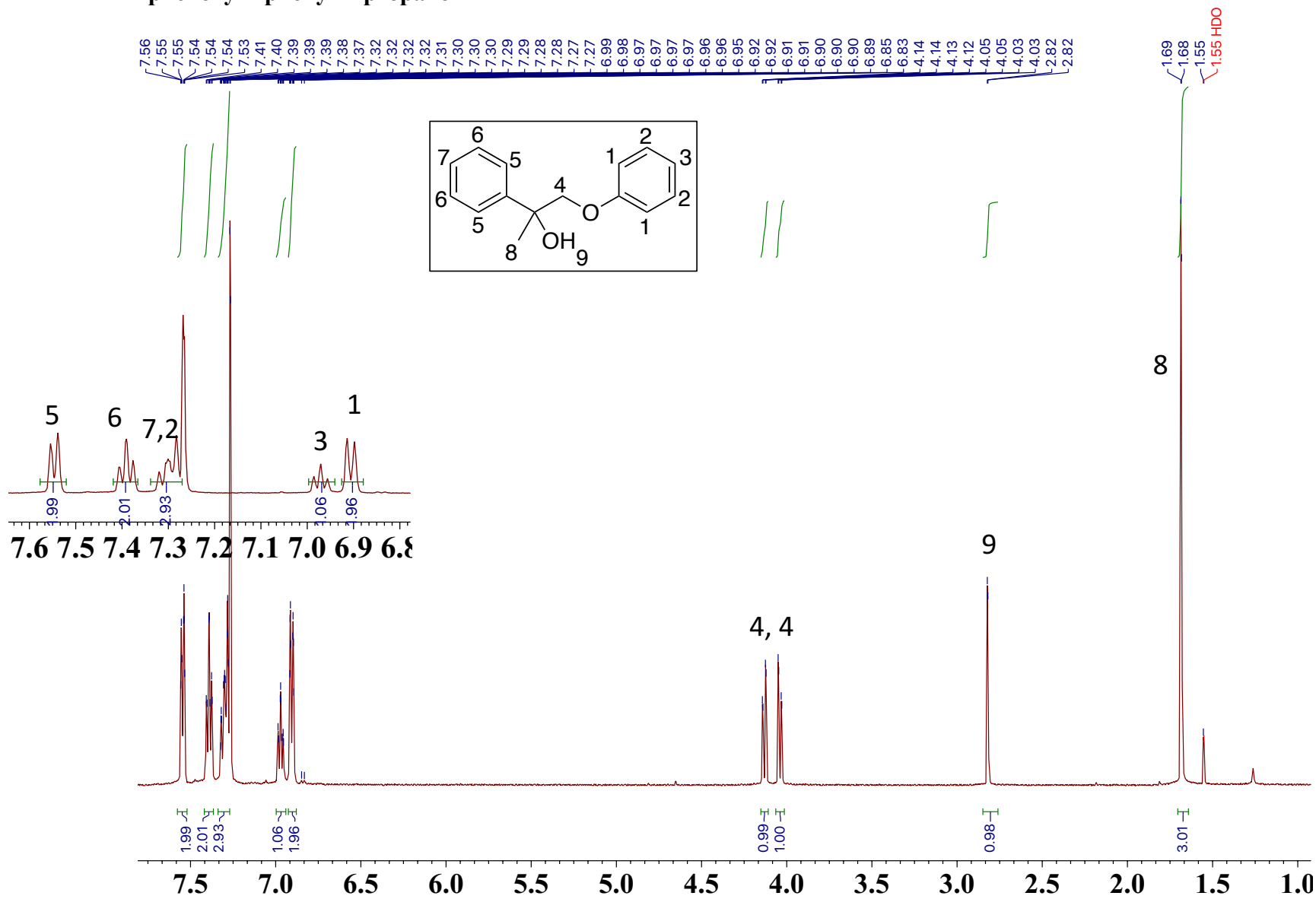
# <sup>1</sup>H NMR of 2-(2-phenylethoxy)phenol



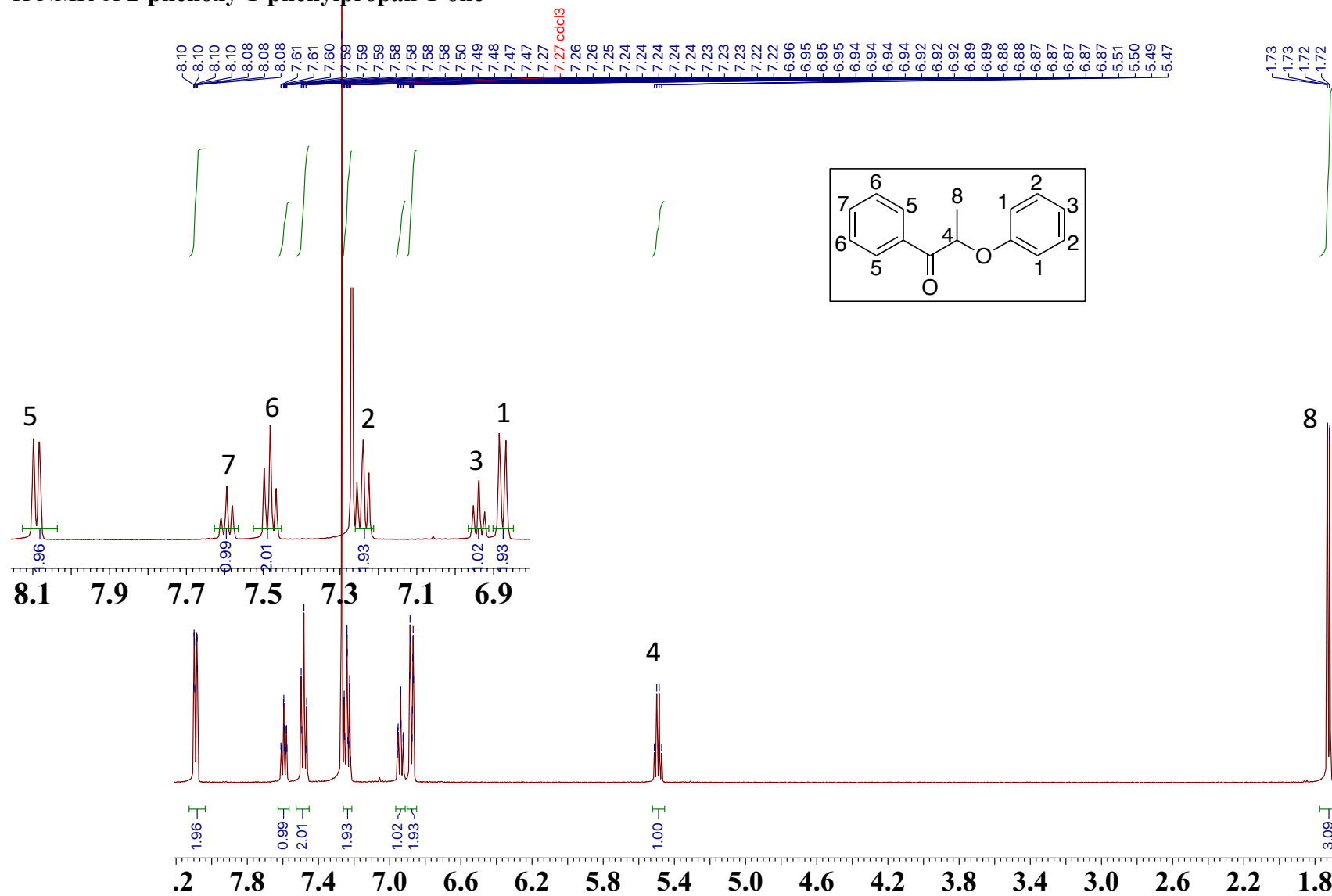
<sup>1</sup>H NMR of 2-(2-phenylethoxy)phenol D<sub>2</sub>O shaken



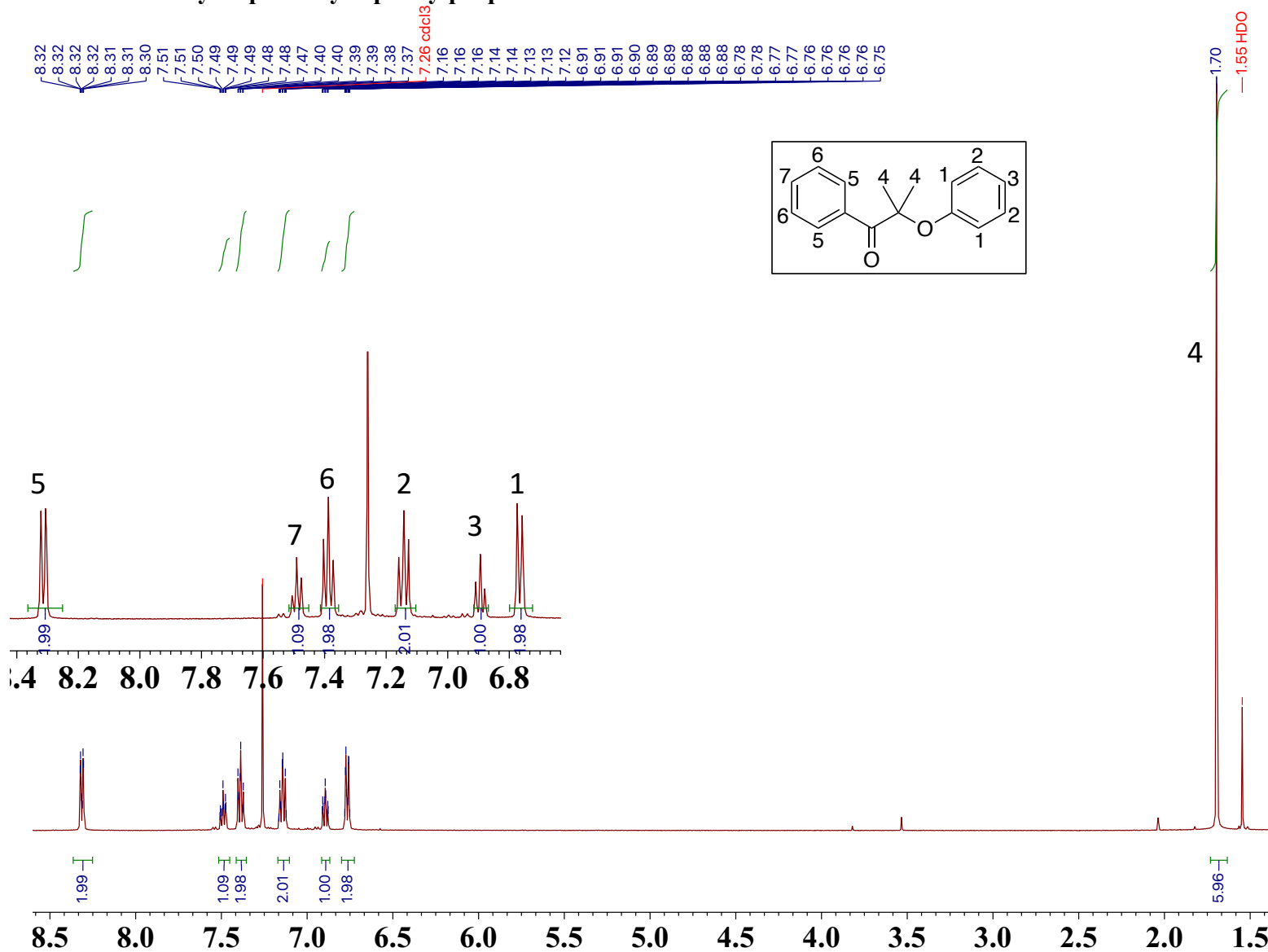
<sup>1</sup>H NMR of 1-phenoxy-2-phenyl-2-propanol



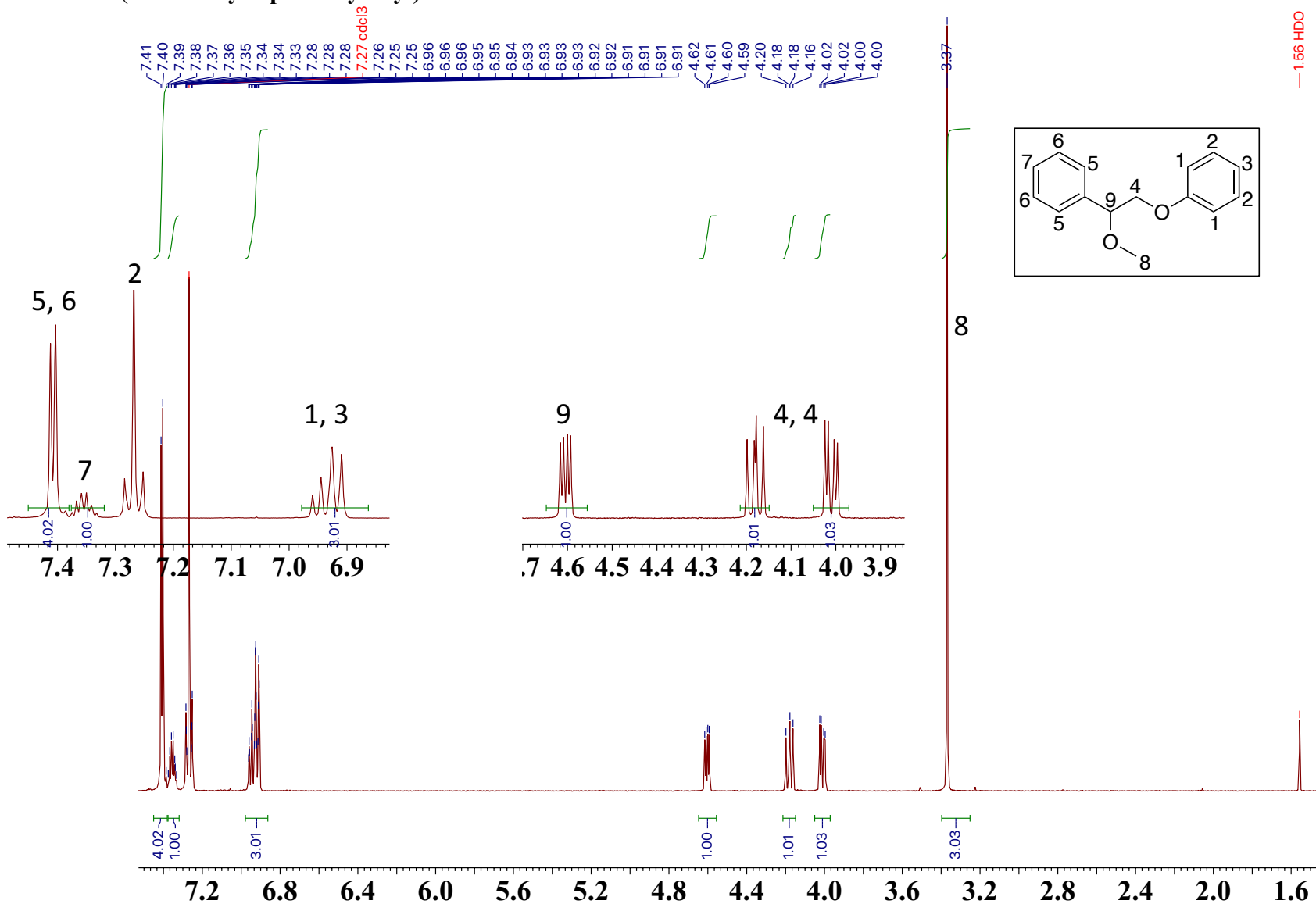
<sup>1</sup>H NMR of 2-phenoxy-1-phenylpropan-1-one



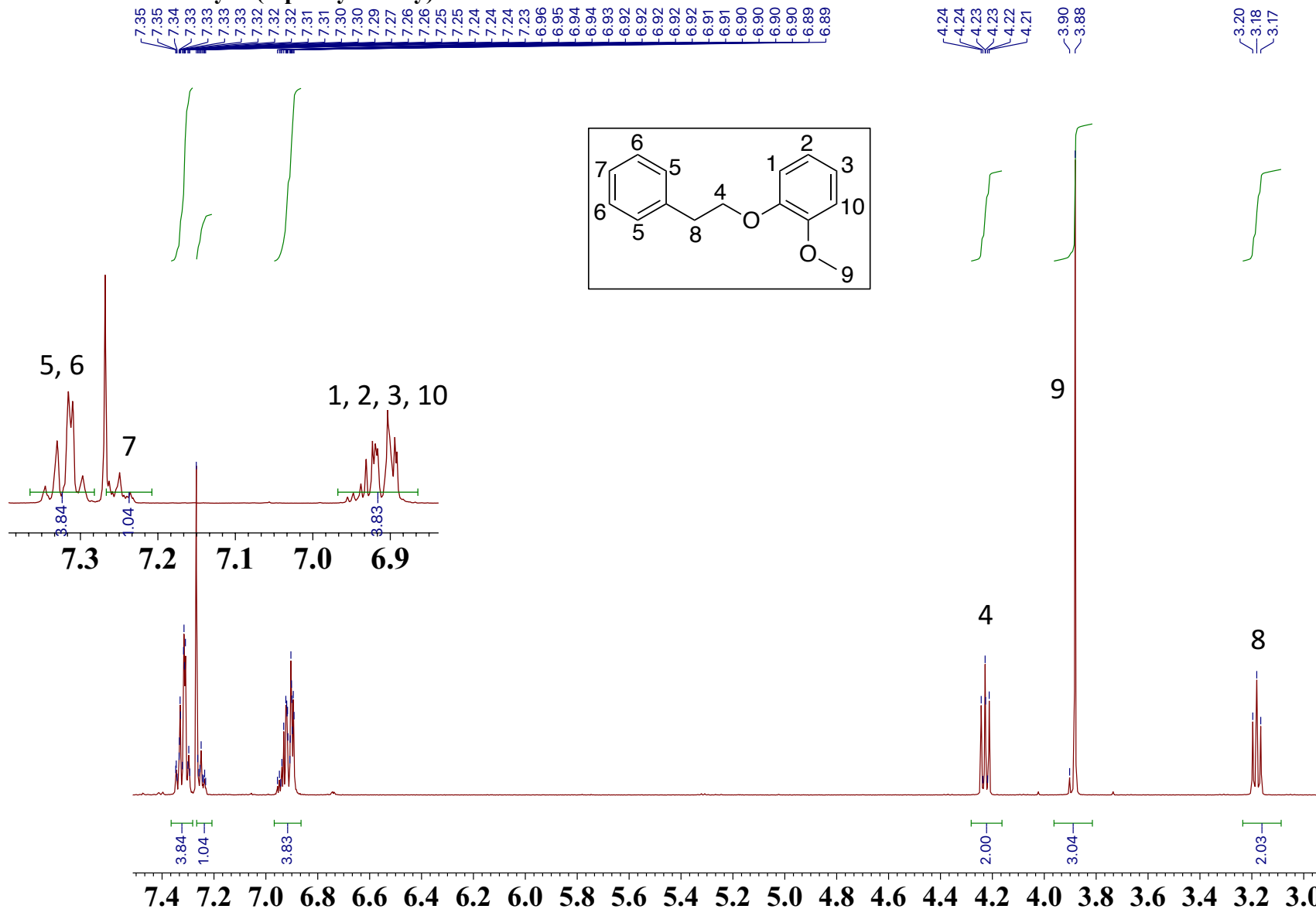
# <sup>1</sup>H NMR of 2-methyl-2-phenoxy-1-phenylpropan-1-one



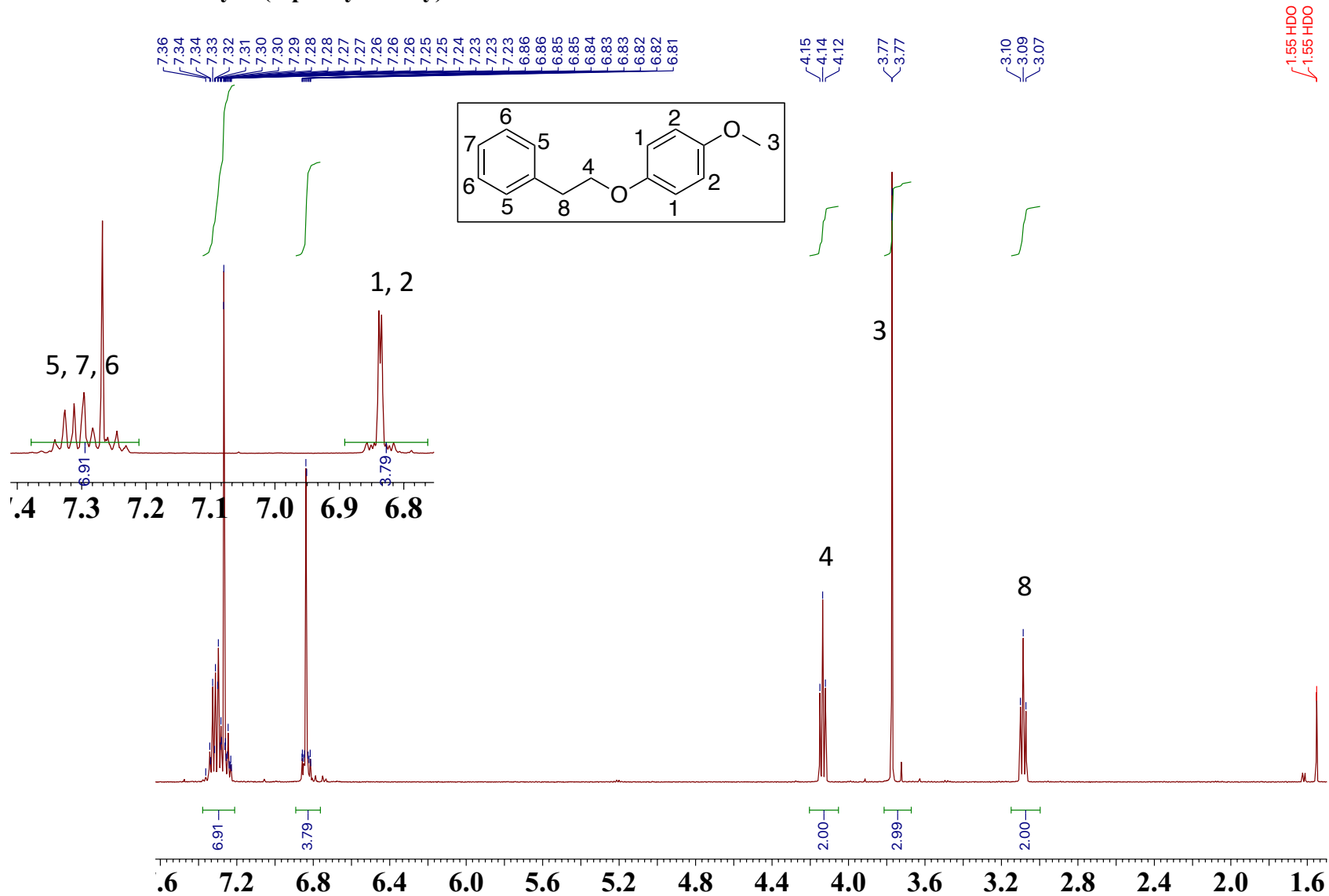
<sup>1</sup>H NMR of (1-methoxy-2-phenoxyethyl)benzene



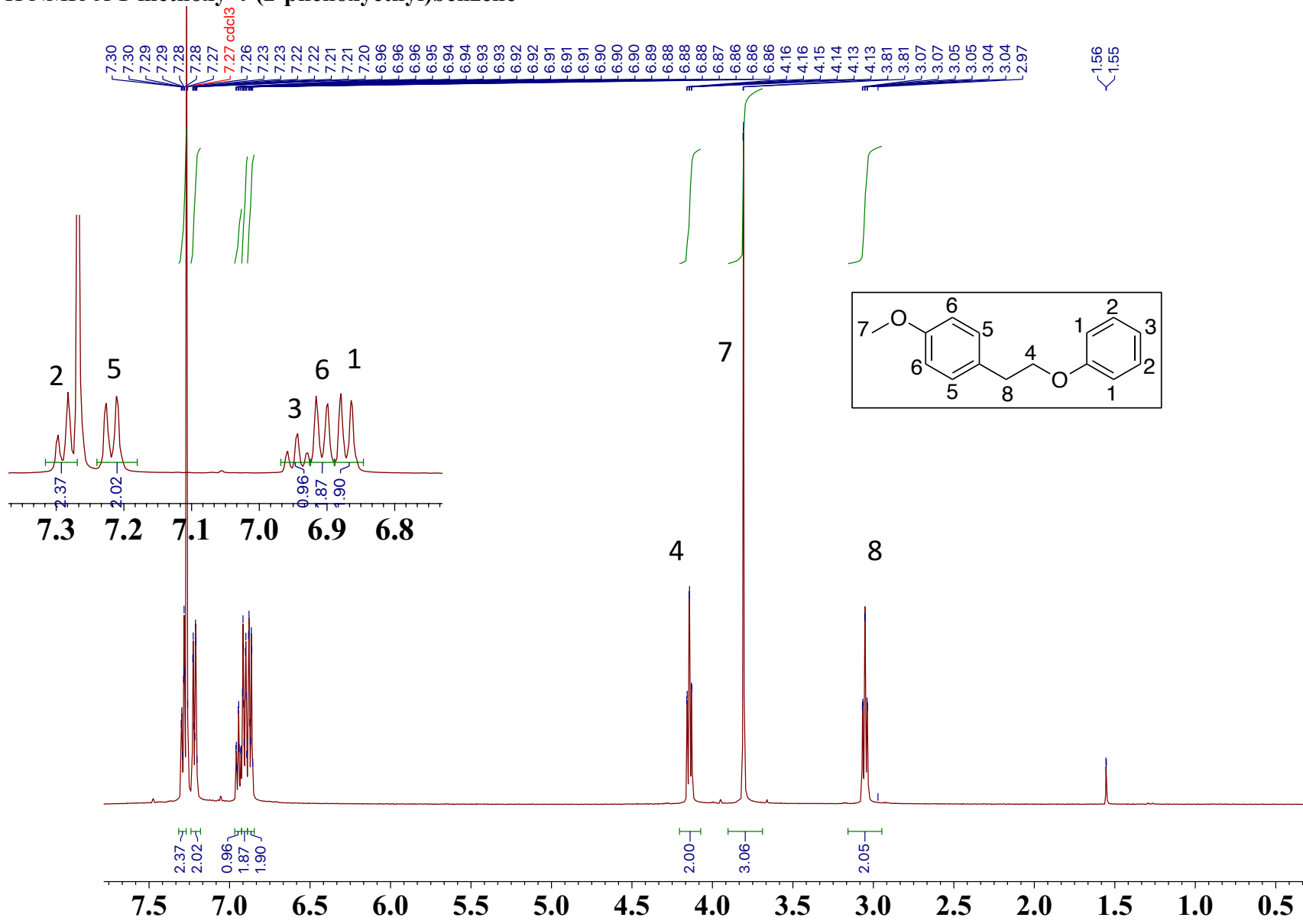
<sup>1</sup>H NMR of 1-methoxy-2-(2-phenylethoxy)benzene



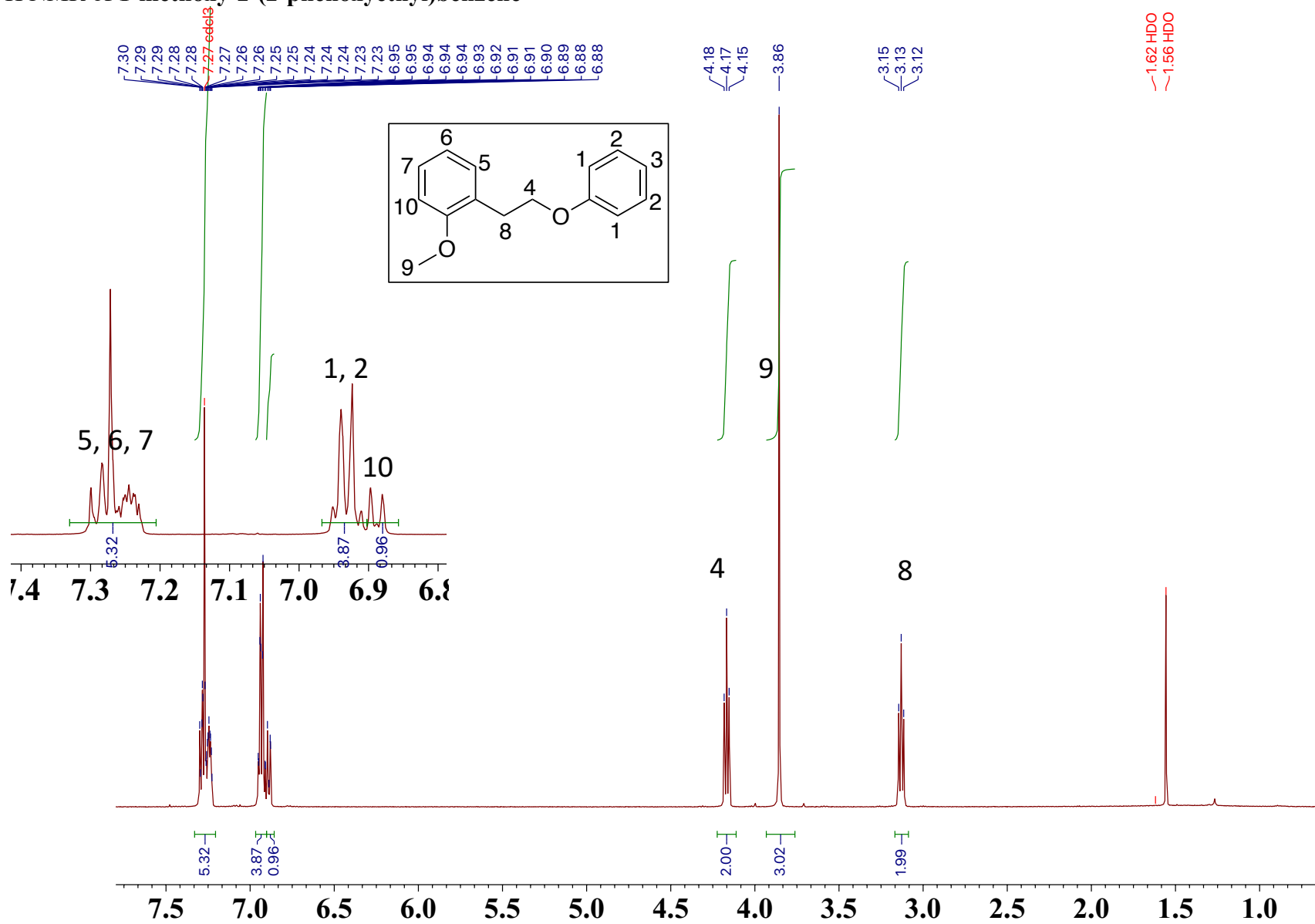
<sup>1</sup>H NMR of 1-methoxy-4-(2-phenylethoxy)benzene



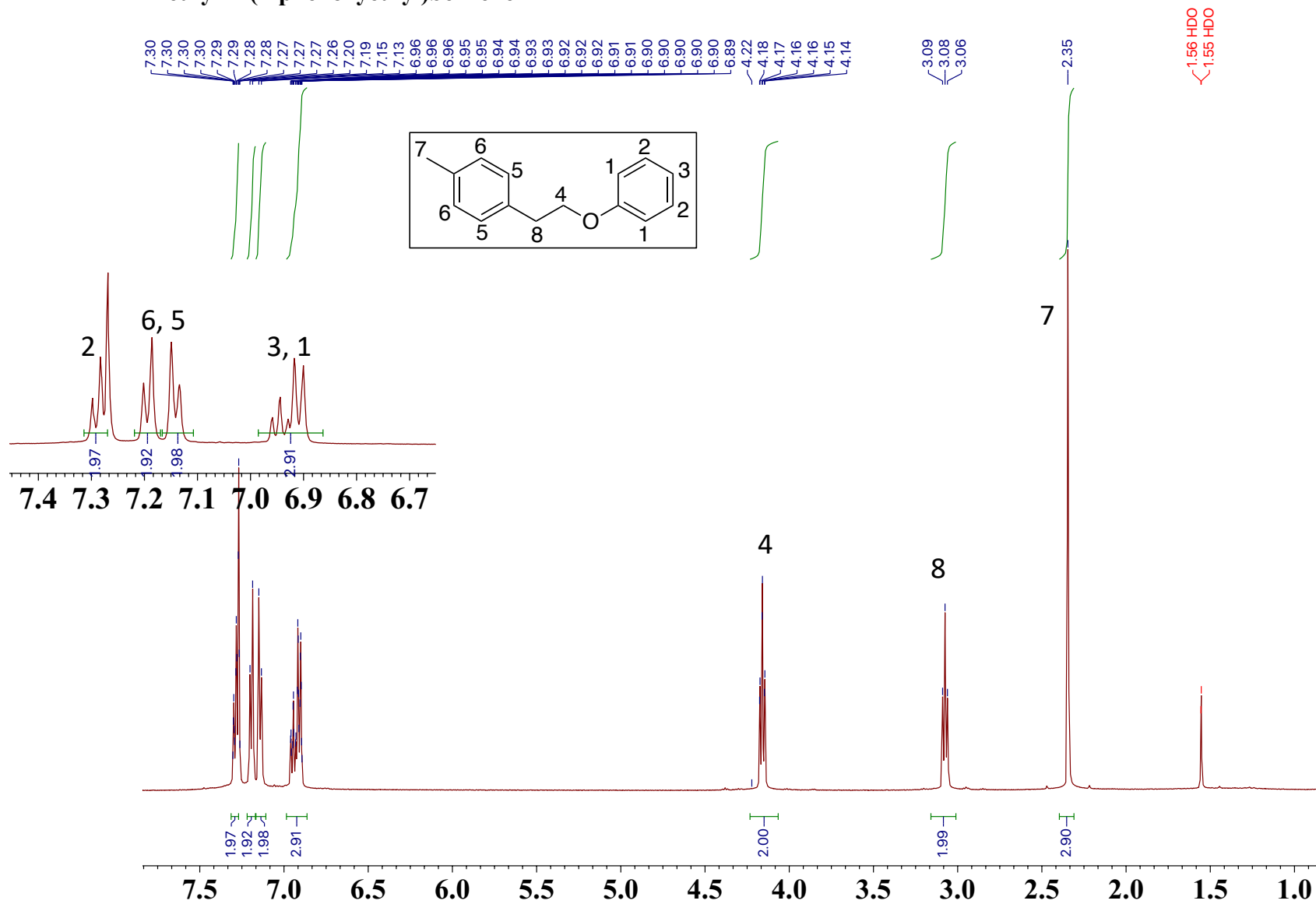
<sup>1</sup>H NMR of 1-methoxy-4-(2-phenoxyethyl)benzene



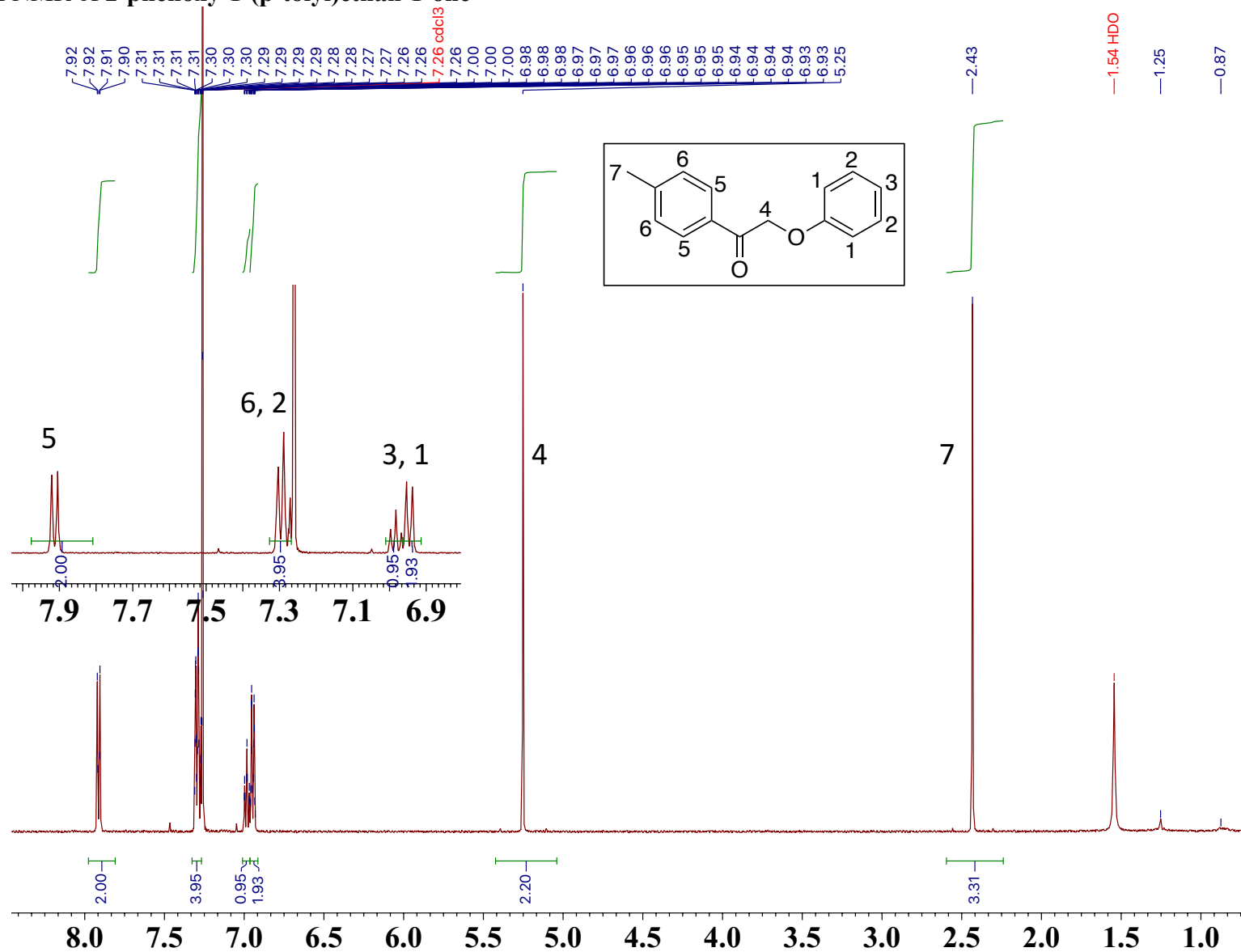
<sup>1</sup>H NMR of 1-methoxy-2-(2-phenoxyethyl)benzene



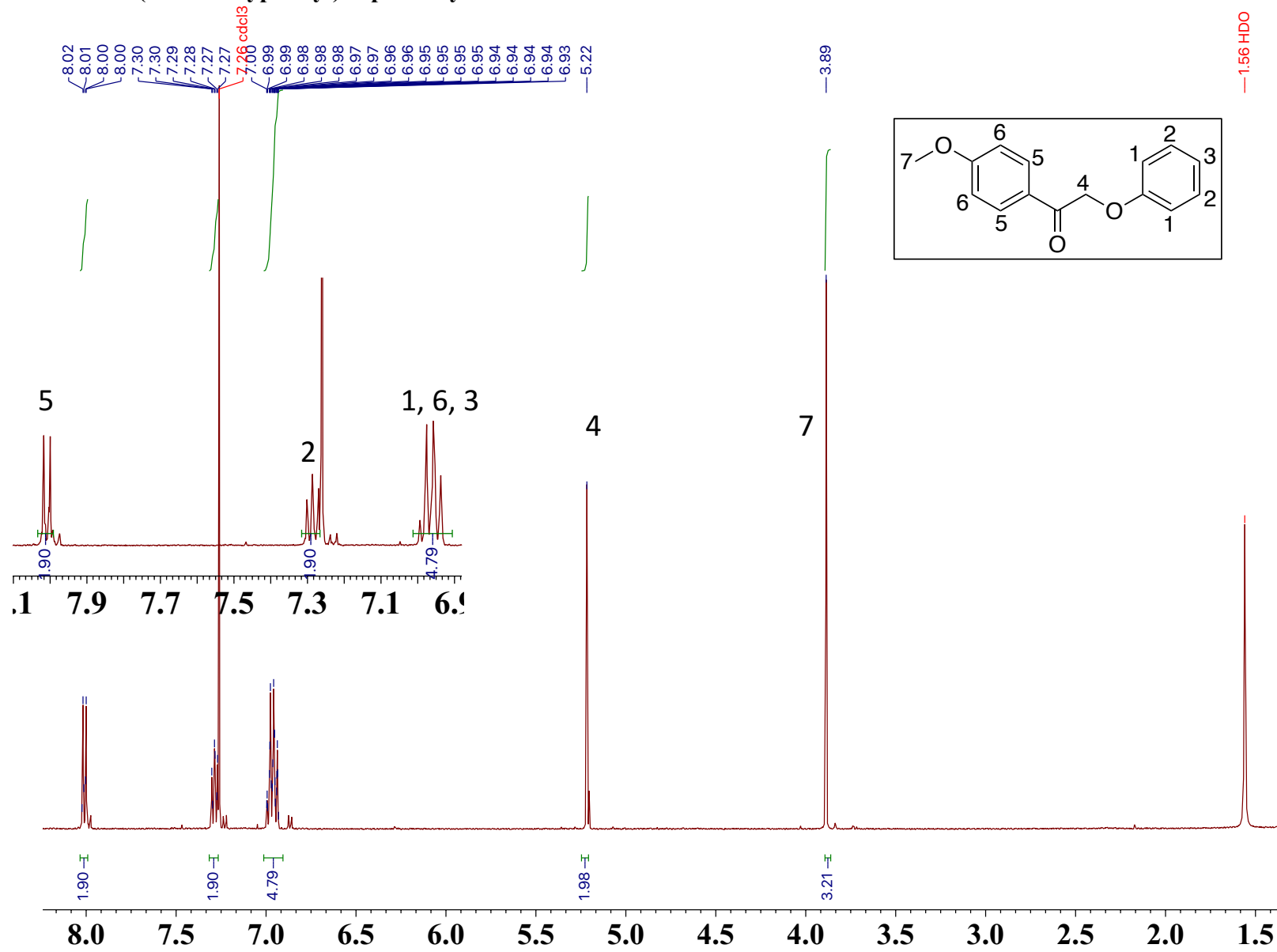
<sup>1</sup>H NMR of 1-methyl-4-(2-phenoxyethyl)benzene



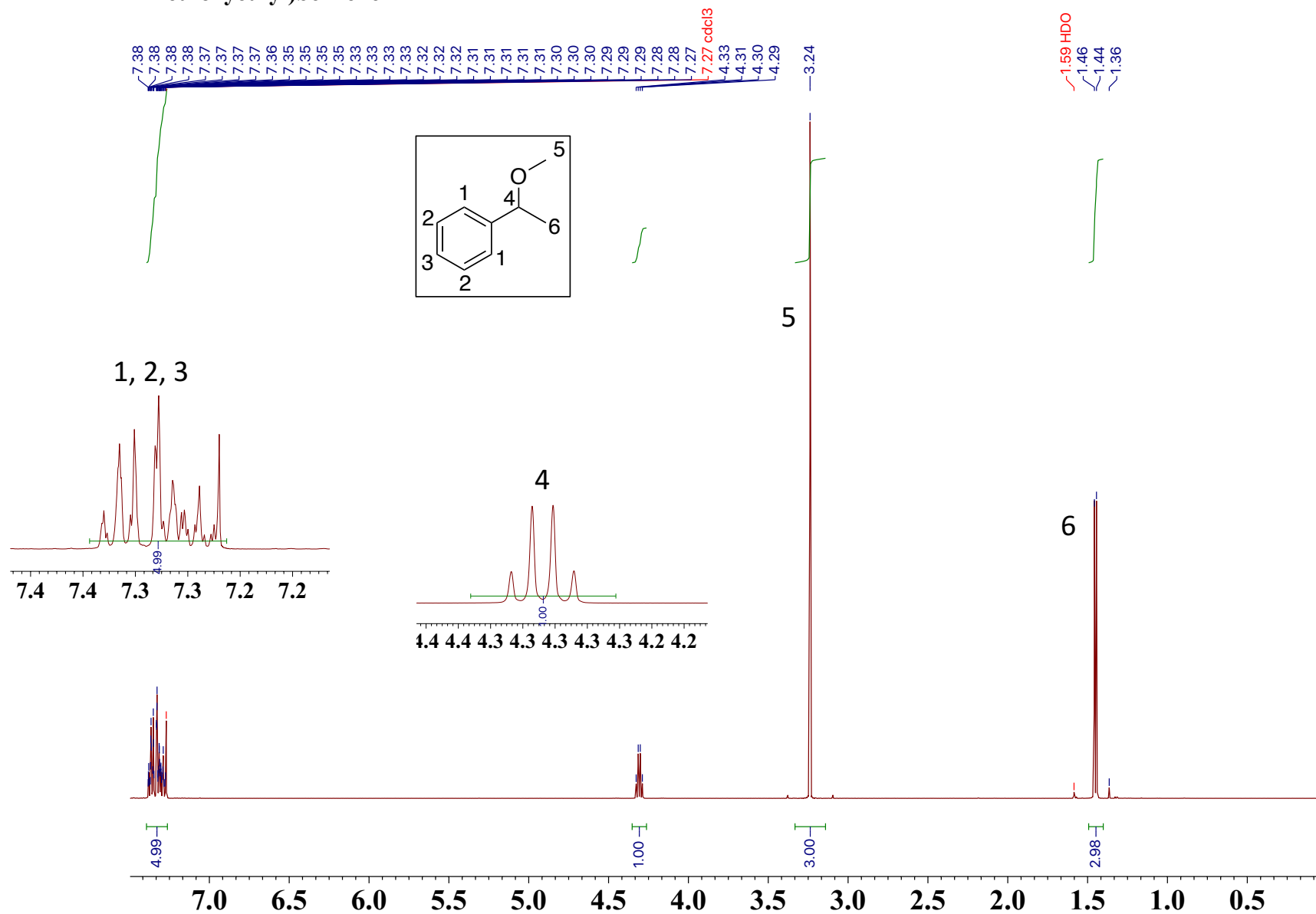
<sup>1</sup>H NMR of 2-phenoxy-1-(p-tolyl)ethan-1-one



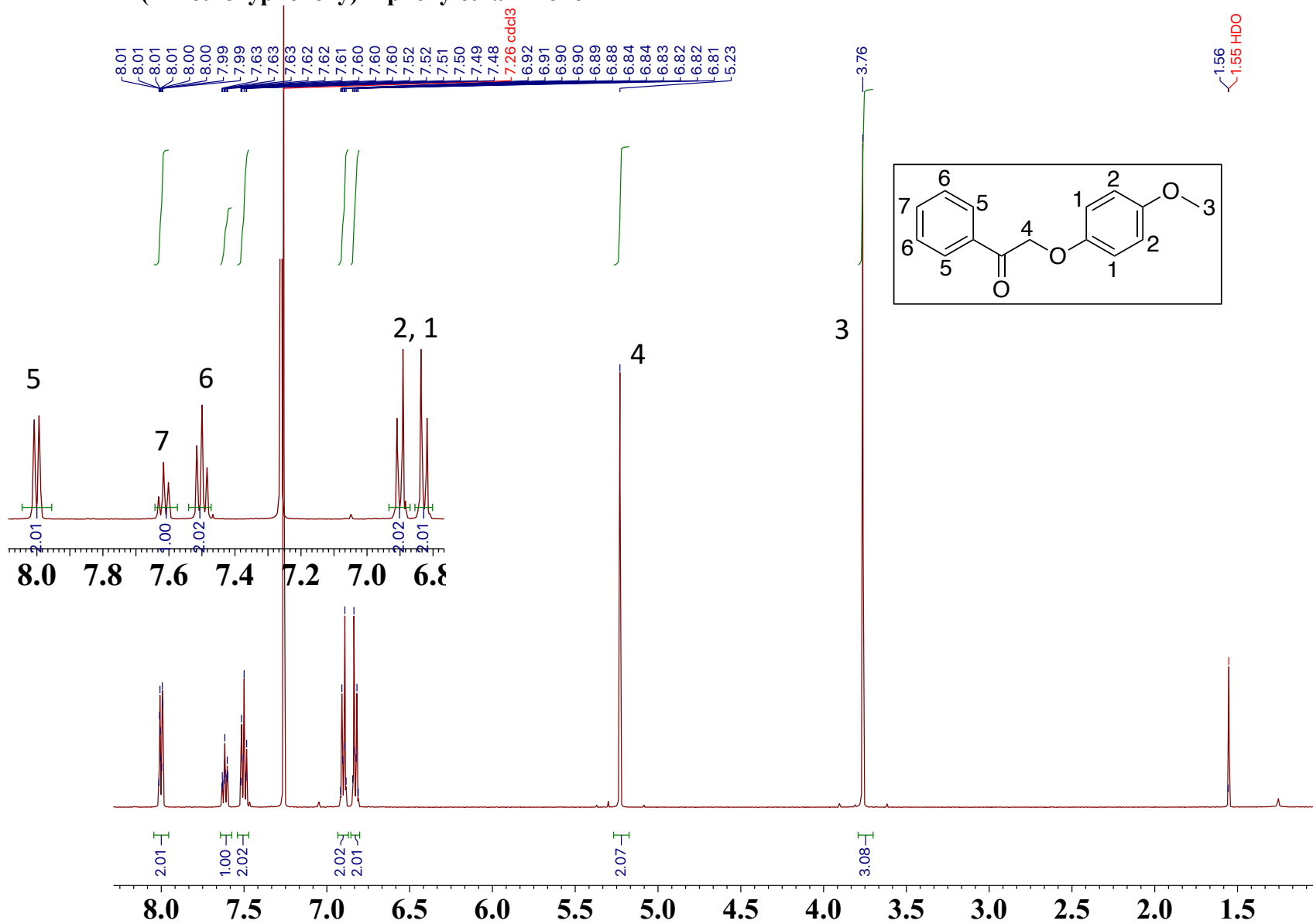
<sup>1</sup>H NMR of 1-(4-methoxyphenyl)-2-phenoxyethan-1-one



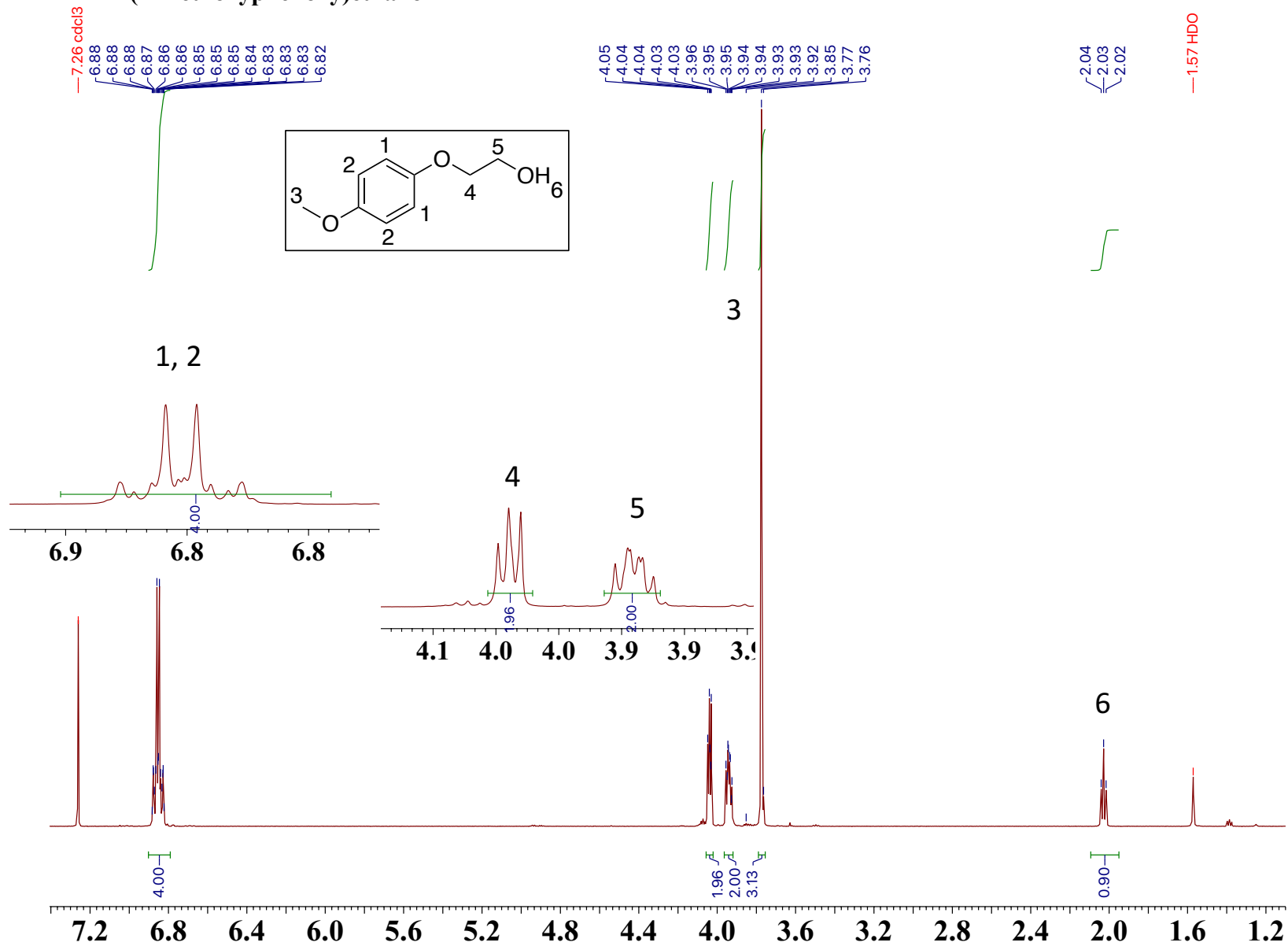
<sup>1</sup>H NMR of 1-methoxyethyl)benzene



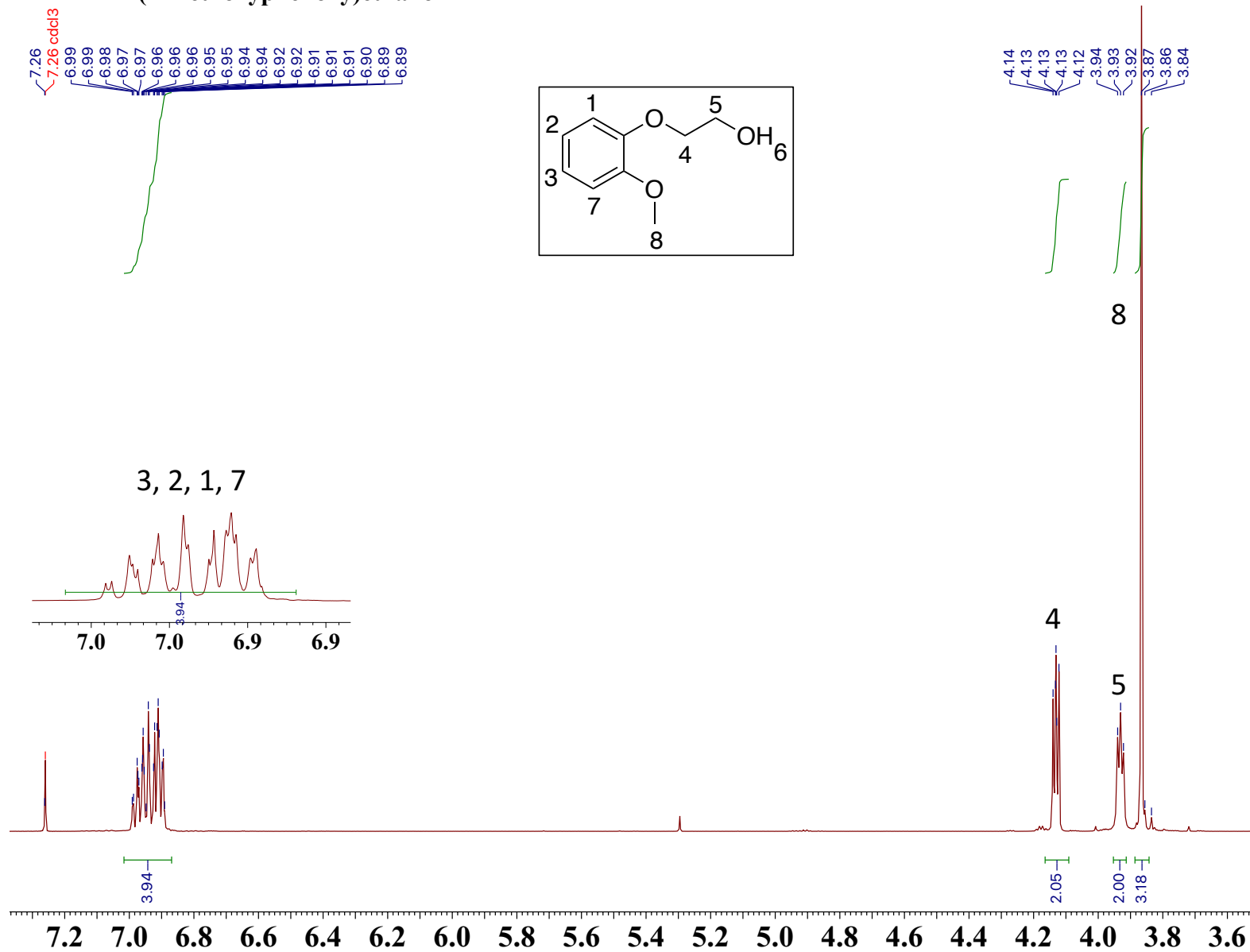
<sup>1</sup>H NMR of 2-(4-methoxyphenoxy)-1-phenylethan-1-one



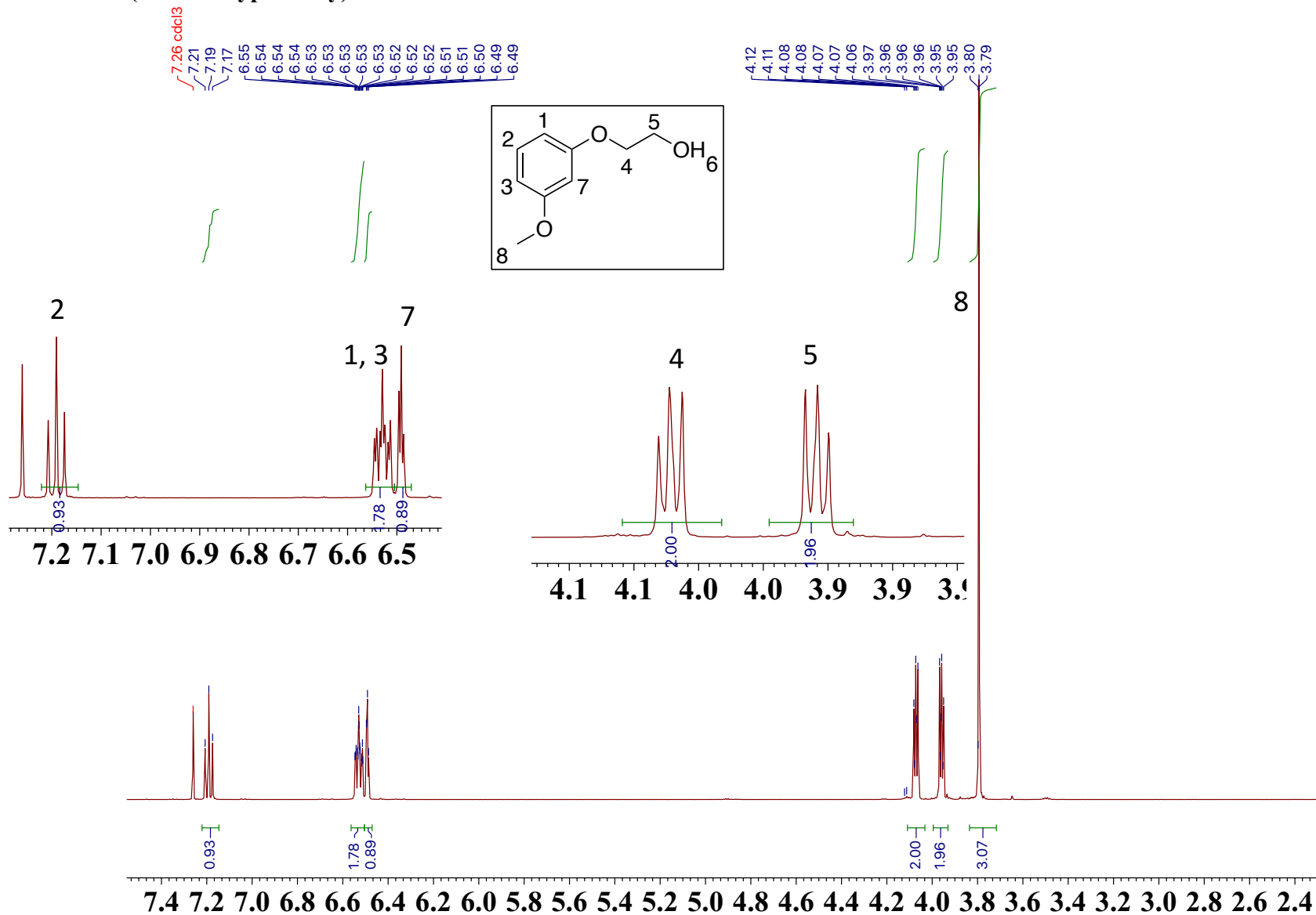
# <sup>1</sup>H NMR of 2-(4-methoxyphenoxy)ethanol



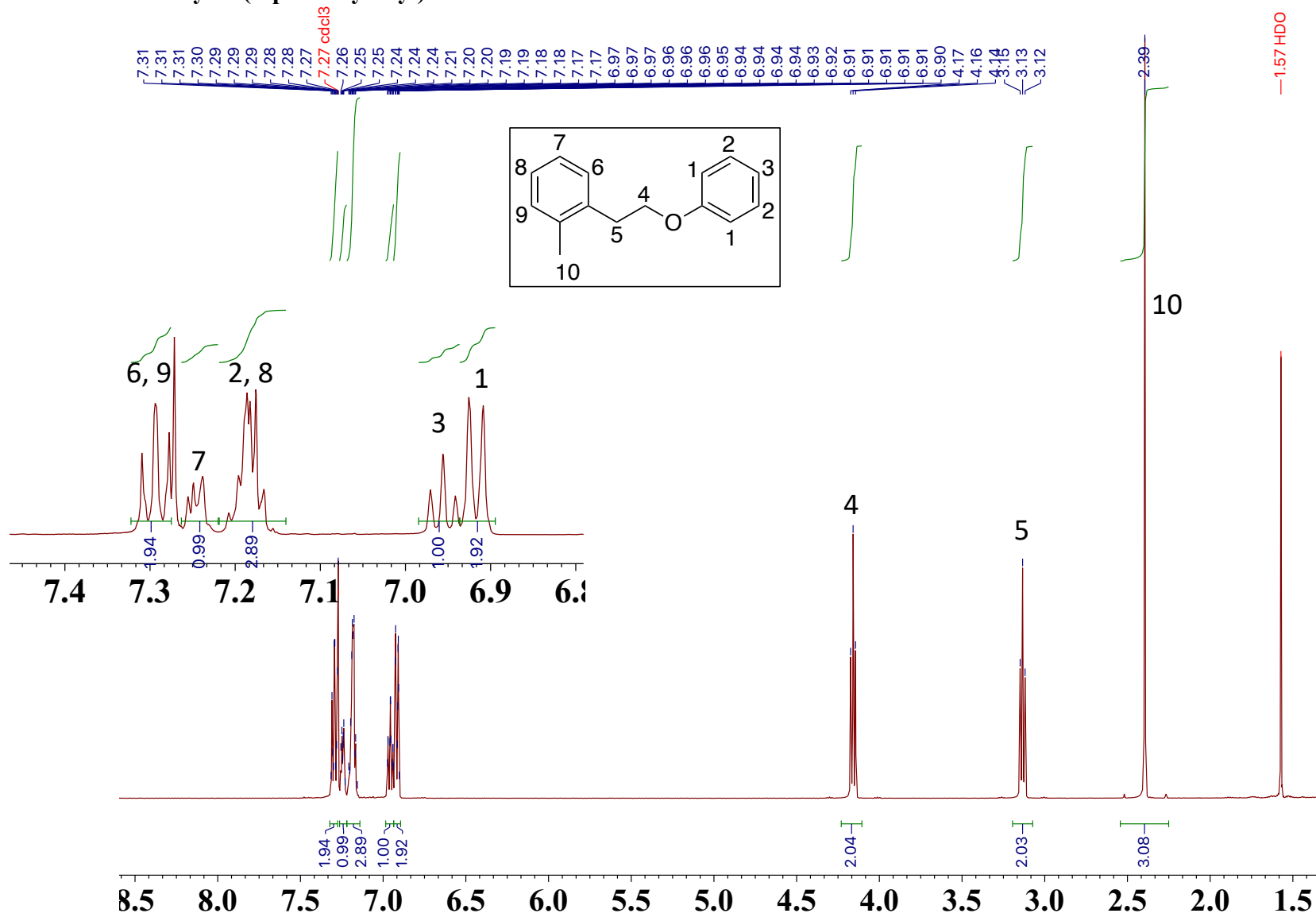
# <sup>1</sup>H NMR of 2-(2-methoxyphenoxy)ethanol



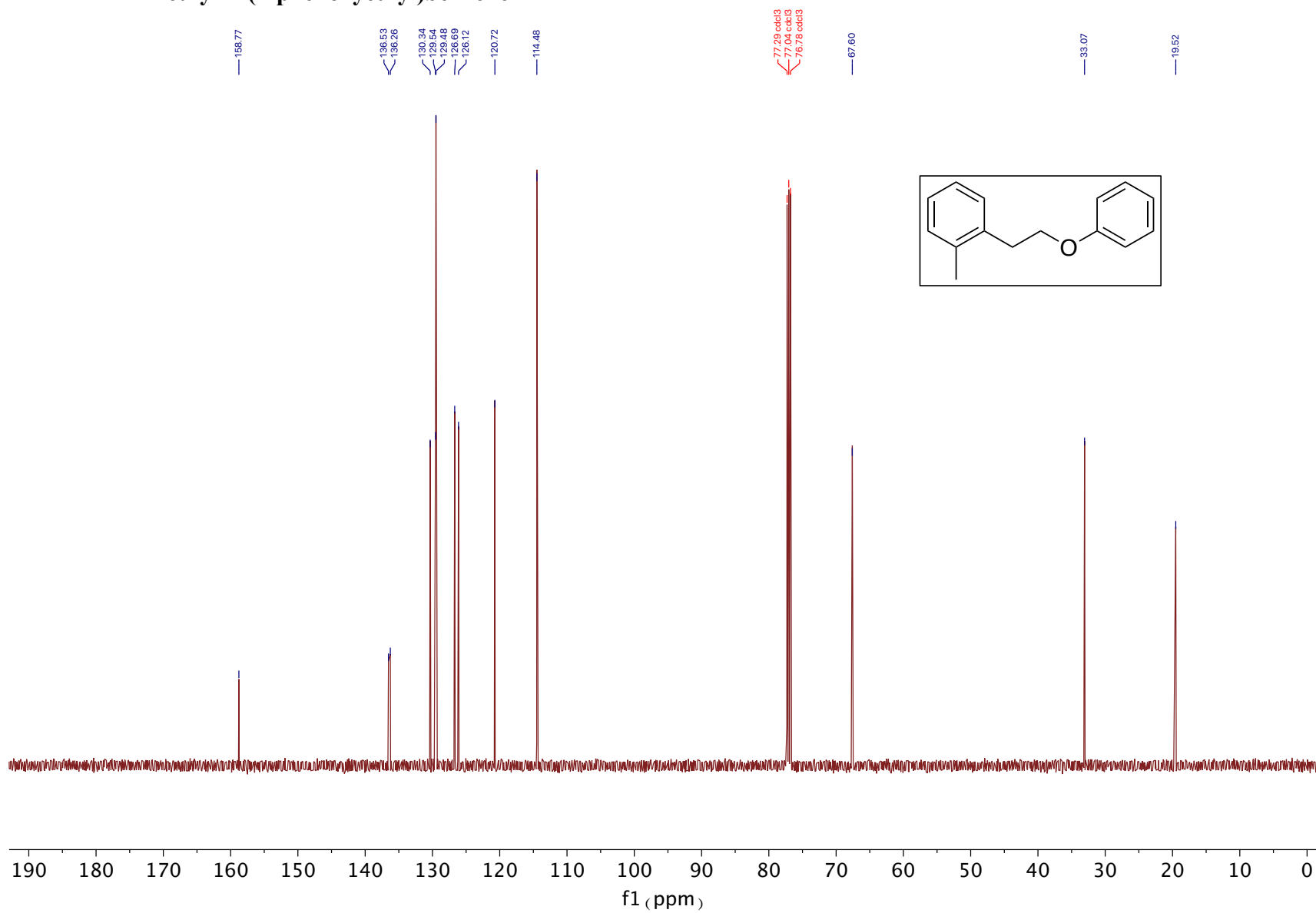
# <sup>1</sup>H NMR of 2-(3-methoxyphenoxy)ethanol



<sup>1</sup>H NMR of 1-methyl-2-(2-phenoxyethyl)benzene



<sup>13</sup>C NMR of 1-methyl-2-(2-phenoxyethyl)benzene



<sup>1</sup>H NMR of (2-phenoxypropyl)benzene

