

Benzoic Acid Resin (BAR): A Heterogeneous Redox Organocatalyst for Continuous Flow Synthesis of Benzoquinones from β -O-4 Lignin Models

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Supporting Information

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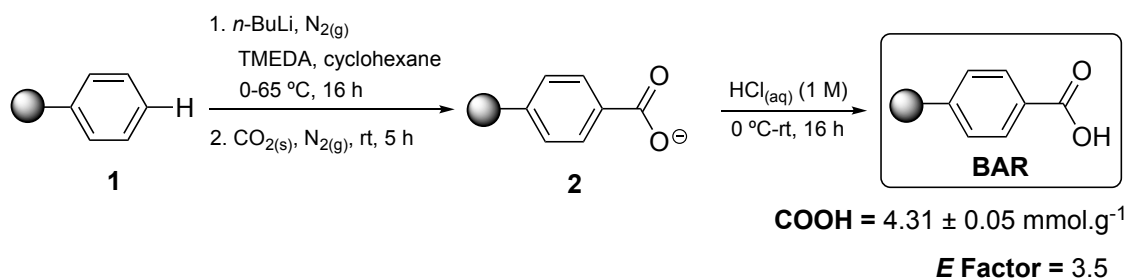
General

Chemicals: Starting materials were purchased from Sigma-Aldrich[®] and used without further purification. Solvents were purified by standard procedures.¹

Analytical Methods: The reaction outcomes were analyzed by Merck[®] Thin Layer Chromatography Silica Gel 60 F₂₅₄, visualized with UV light and revealed with vanillin solution in H₂SO_{4(aq)} followed by heating. Conversions were analyzed by GC-FID, GC-MS and ¹H NMR analysis. The GC-17A (Shimadzu[®]) chromatograph with flame ionization detector (FID), equipped with Agilent[®] HP-5 capillary column was used. The GC-FID conditions were: injector = 260°C; detector = 280°C; pressure = 100 kPa. The column temperature range was 40 °C to 115 °C at 10 °C/min. GC-MSQP2010SE (Shimadzu[®]) with low-resolution electron impact (EI, 70 eV) chromatograph, equipped with a Restek[®] Rtx-5MS capillary column, was also employed. The GC-MS conditions were: injector = 260°C; detector = 280°C; pressure = 100 kPa. The column temperature range was 40 °C to 115 °C at 10 °C/min and hold time = 15 min). Varian[®] INOVA (300 MHz) and Bruker[®] Avance III (300 MHz) spectrometers were used in the NMR characterizations. The chemical shifts of ¹H and ¹³C NMR spectra were referenced either to tetramethylsilane as internal standard (¹H NMR: CDCl₃ at δ 7.26 ppm and acetone-d₆ at δ 2.05 ppm) or deuterated solvent (¹³C NMR = CDCl₃ at δ 77.16 ppm and acetone-d₆ at δ 29.92 ppm and δ 206.25 ppm). High-resolution mass spectra were obtained on a Bruker[®] Daltonics MicroToF spectrometer using electrospray ionization–time of flight (ESI-TOF) techniques. The melting points were determined with a BÜCHI[®] B-545 apparatus. Scanning Electron Microscopy (SEM) images were obtained using a JEOL[®] JSM 7401F field emission gun electron microscope. Samples were prepared by the conductive double-sided carbon tape technique. All experiments described in this study were carried out at least in sextuplicate.

Synthesis and Characterization of the Benzoic Acid Resin (BAR)

Scheme S1



Considering solvent recycle, the *E* Factor value was calculated as follows: Obtained mass of **BAR** = 2.49 g; Mass of reagents = 9.25 g (1.97 g of TMEDA + 1.54 g of *n*-BuLi + 3.00 g of $\text{CO}_2(\text{s})$ + 2.74 g of HCl); Amount of poly(styrene-co-divinylbenzene) **1** = 2.00 g.

$$E \text{ Factor} = (2.00 + 9.25 - 2.49)/2.49 = 3.5$$

Resin **1** and **BAR** were also characterized by SEM (Figure S1).

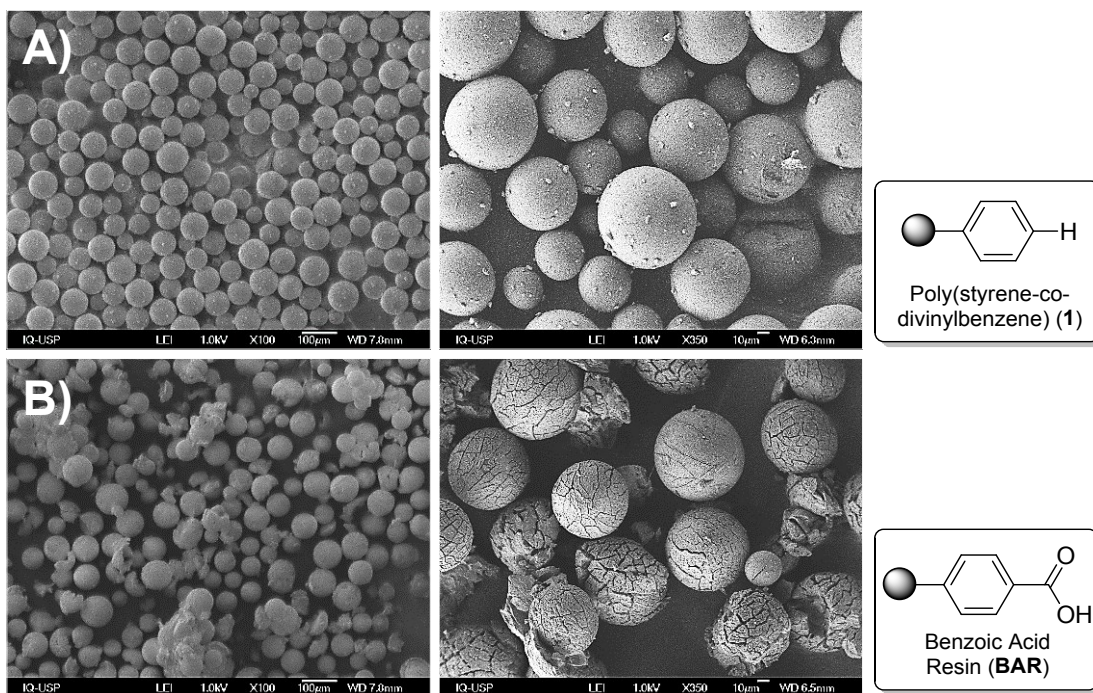


Figure S1: SEM images of **1** (A) and **BAR** (B) at x100 and x350 magnifications.

Assembly for Continuous Flow Oxidations of β -O-4 Lignin Models Mediated by BAR

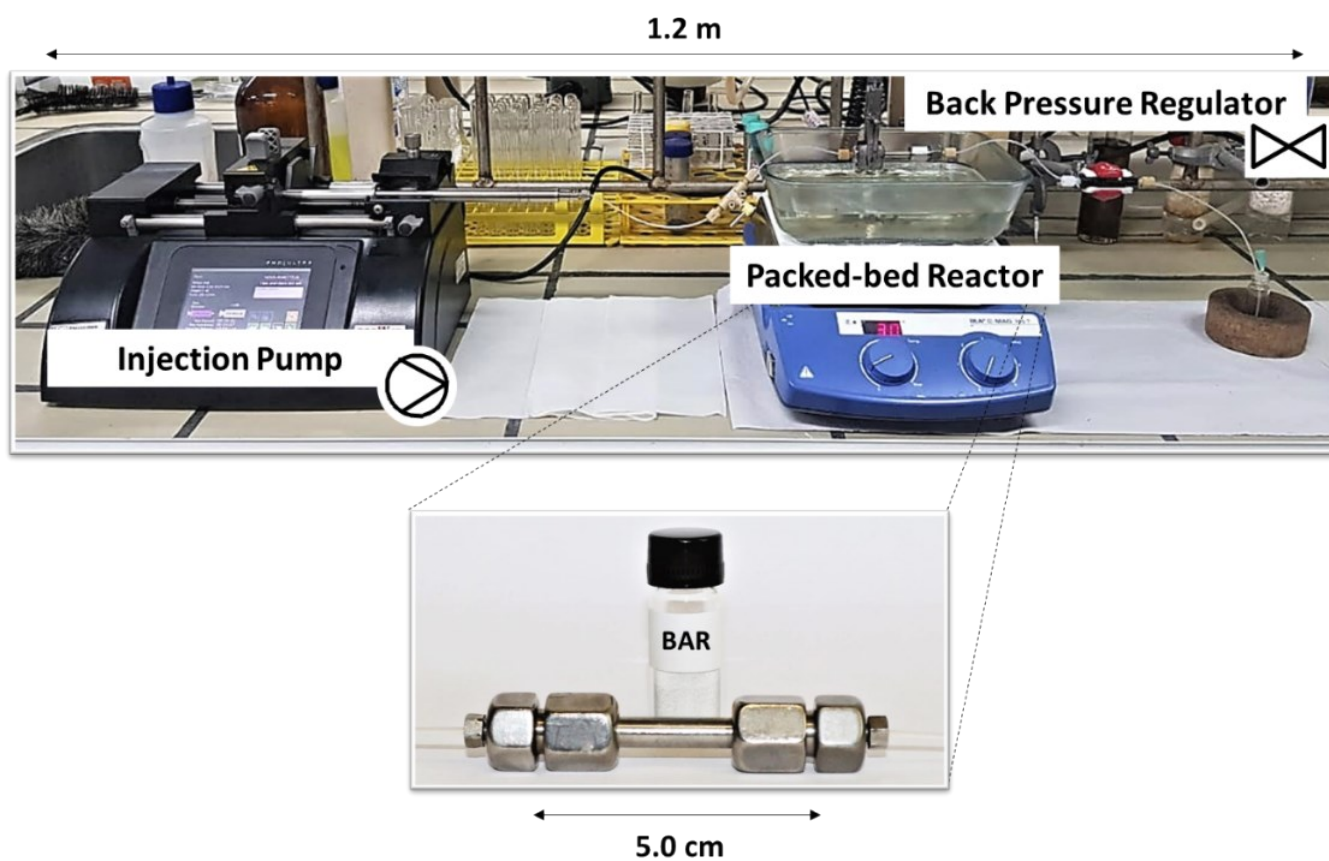
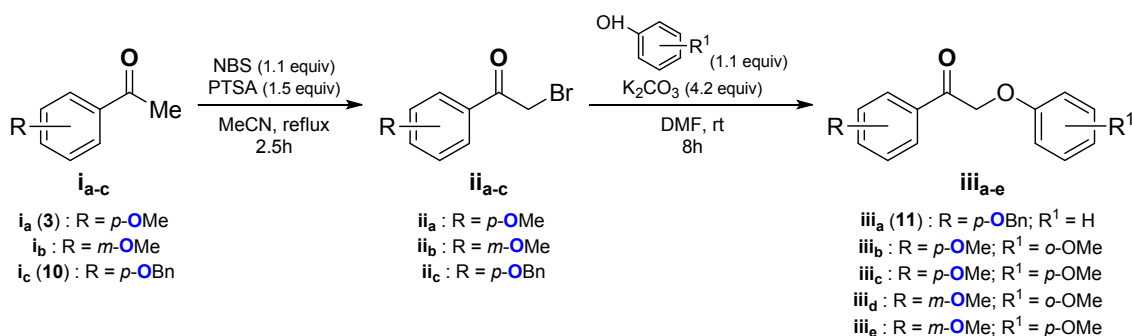


Figure S2: Assembly for the continuous flow system mediated by **BAR**.

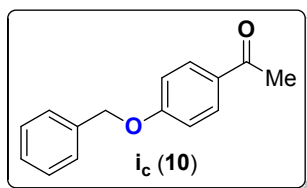
Synthesis of the β -O-4 Lignin Models

The synthesis and characterization of the ether-substituted α -phenoxyacetophenones (**iii_{a-e}**) from ether-substituted acetophenones (**i_{a-c}**) was published by our group (Scheme S2).²

Scheme S2²



1-(4-(benzyloxy)phenyl)ethanone (i_c, 10): white powder.



¹H NMR (300 MHz, CDCl₃): δ = 7.94 (d, *J* = 8.8 Hz, 2H), 7.44–7.34 (m, 5H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 2H), 2.55 (s, 3H) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 196.9, 162.8, 136.2, 130.7 (2C), 128.8 (2C), 128.4, 127.6 (2C), 114.7 (2C), 70.3, 26.5

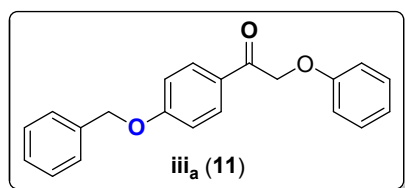
ppm.

mp (°C): 90-91 (lit.⁴ 89-90).

R_f: 0.72 (3:7 EtOAc/hexanes).

#CAS: 54696-05-8.

1-(4-(benzyloxy)phenyl)-2-phenoxyethanone (iii_a, 11): beige solid.



¹H NMR (300 MHz, CDCl₃): δ = 7.99 (d, *J* = 8.9 Hz, 2H), 7.42–7.25 (m, 7H), 7.04–6.92 (m, 5H), 5.19 (s, 2H), 5.13 (s, 2H) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 193.2, 163.3, 158.2, 136.1, 130.7 (2C), 129.7 (2C), 128.8 (2C), 128.4,

127.9, 127.6 (2C), 121.7, 115.0 (2C), 114.9 (2C), 70.8, 70.3 ppm.

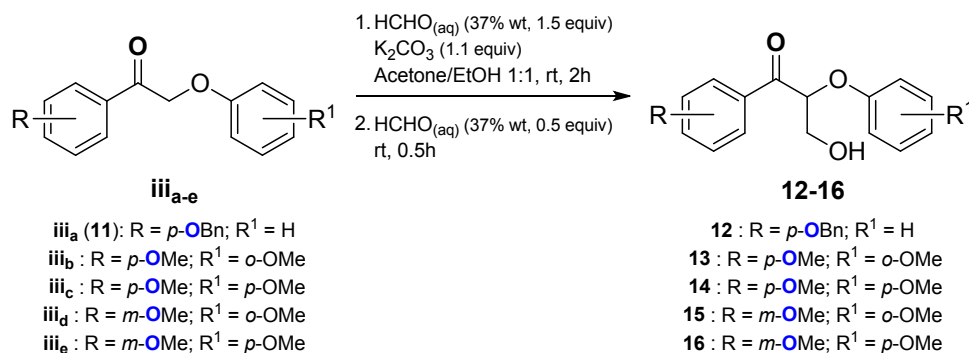
mp (°C): 111-112.

R_f: 0.66 (3:7 CH₂Cl₂/hexanes).

#CAS: 2173138-44-6.

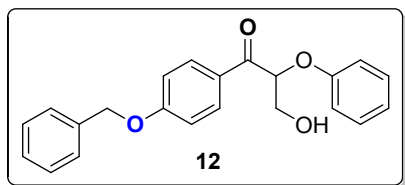
For the synthesis of the ether-substituted α,α -(hydroxymethyl)phenoxyacetophenones **12-16**, a slightly modified procedure for the aldol addition between formaldehyde (HCHO) and **iii_{a-e}** (Scheme S3), previously described for Magallanes *et al.*³, was employed.

Scheme S3³



Substrates **iii_{a-e}** (7.00 mmol) were solubilized in 50 mL of a mixture of acetone and ethanol (1:1). Potassium carbonate (1.06 g, 7.70 mmol) was added and the reaction mixture was left stirring for 5 minutes. Then, formalin (aqueous, 37% wt, 830 μ L, 10.5 mmol) was added, stirred for 2 h at room temperature. The reaction mixture was analyzed by TLC. Due to the presence of starting material, formalin (37% wt, 275 μ L, 3.50 mmol) was added once again. After 30 min, the solvent was evaporated under reduced pressure, and water (50 mL) and CHCl₃ (50 mL) were added to the flask. The aqueous layer was washed with CHCl₃ (3 x 25 mL). The combined organic layers were washed with water, brine, and then dried over anhydrous MgSO₄. The organic layer was concentrated and purified by column chromatography (EtOAc/hexanes).

1-(4-(benzyloxy)phenyl)-3-hydroxy-2-phenoxypropan-1-one (12): yield = 91% (2.20 g), pearl-white solid.



¹H NMR (300 MHz, CDCl₃): δ = 8.05 (d, *J* = 5.4 Hz, 2H), 7.41–7.35 (m, 5H), 7.24 (dd, *J* = 4.5 Hz, *J* = 5.4 Hz, 2H), 7.01 (d, *J* = 5.4 Hz, 2H), 6.96 (t, *J* = 4.5 Hz, 1H), 6.89 (d, *J* = 4.5 Hz, 2H), 5.49 (dd, *J* = 2.4 Hz, *J* = 3.9 Hz, 1H), 5.13 (s, 1H), 4.17–4.07 (m, 2H), 2.38 (dd, *J* = 3.6 Hz, *J* = 4.5 Hz, 1H) ppm.
¹³C NMR (75 MHz, CDCl₃): δ = 195.1, 163.5, 157.4, 136.1, 131.4 (2C), 129.8 (2C), 128.9 (2C), 128.5, 128.0, 127.6 (2C), 122.0, 115.4 (2C), 115.1 (2C), 81.2, 70.4, 63.5 ppm.

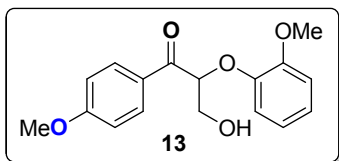
mp (°C): 107-109.

R_f: 0.41 (5:5 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + H]⁺ calc. for C₂₂H₂₁O₄: 349.1440, found: 349.1433.

#CAS: 2183492-22-8.

3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (13): yield = 83% (1.76 g), pale-yellow syrup.



¹H NMR (300 MHz, acetone-*d*₆): δ = 8.15 (d, *J* = 8.8 Hz, 2H), 7.08–6.76 (m, 6H), 5.51 (t, *J* = 5.6 Hz, 1H), 4.07–4.045.13 (m, 2H), 3.90 (s, 3H), 3.79 (s, 3H), 2.82–2.79 (m, 1H) ppm.

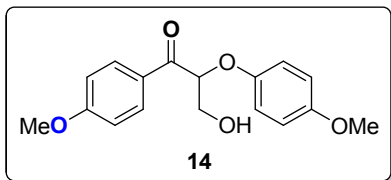
¹³C NMR (75 MHz, acetone-*d*₆): δ = 196.1, 164.8, 151.3, 148.6, 132.1 (2C), 129.7, 123.3, 121.7, 117.5, 114.7 (2C), 113.9, 84.3, 64.1, 56.3, 56.0 ppm.

***R*_f:** 0.39 (4:6 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + H]⁺ calc. for C₁₇H₁₉O₅: 303.1233, found: 303.1231.

#CAS: 92409-23-9.

3-hydroxy-2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (14): yield = 87% (1.84 g), colorless crystals.



¹H NMR (300 MHz, acetone-*d*₆): δ = 8.13 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 5.4 Hz, 2H), 6.89 (d, *J* = 5.4 Hz, 2H), 5.48 (d, *J* = 5.5 Hz, 1H), 4.23 (dd, *J* = 5.5 Hz, *J* = 5.5 Hz, 2H), 3.96 (s, 3H), 3.80

(s, 3H), 2.85 (bs, 1H) ppm.

¹³C NMR (75 MHz, acetone-*d*₆): δ = 196.3, 164.9, 155.3, 153.0, 132.0 (2C), 129.5, 117.3 (2C), 115.4 (2C), 114.8 (2C), 83.6, 64.0, 56.1, 55.8 ppm.

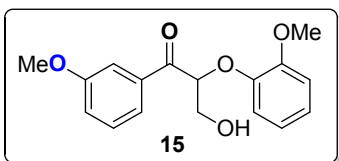
mp (°C): 94-96 (lit.⁵ 93-96).

***R*_f:** 0.34 (4:6 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + H]⁺ calc. for C₁₇H₁₉O₅: 303.1233, found: 303.1239.

#CAS: 2093366-73-3.

3-hydroxy-2-(2-methoxyphenoxy)-1-(3-methoxyphenyl)propan-1-one (15): yield = 90% (1.90 g), non-crystalline beige solid.



¹H NMR (300 MHz, acetone-*d*₆): δ = 7.72 (ddd, *J* = 1.2 Hz, *J* = 0.9 Hz, *J* = 1.5 Hz, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 1.5 Hz, *J* = 2.7 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 1H), 7.19 (ddd, *J* = 0.9 Hz, *J* = 0.9 Hz, *J* = 2.7 Hz, *J* = 8.1 Hz, 1H), 6.96–6.89 (m, 3H), 6.82–6.79 (m, 1H), 5.59–5.56 (m, 1H), 4.09–4.05 (m, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 2.81 (bs, 1H) ppm.

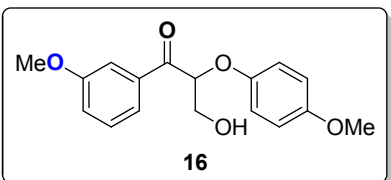
¹³C NMR (75 MHz, acetone-*d*₆): δ = 197.6, 160.8, 151.2, 148.5, 138.1, 130.6, 123.4, 122.0, 121.6, 120.3, 117.6, 114.2, 113.8, 84.2, 64.0, 56.2, 55.8 ppm.

***R*_f:** 0.40 (4:6 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + H]⁺ calc. for C₁₇H₁₉O₅: 303.1233, found: 303.1245.

#CAS: 20730-76-1.

3-hydroxy-2-(4-methoxyphenoxy)-1-(3-methoxyphenyl)propan-1-one (16): yield = 86% (1.82 g), white powder.



¹H NMR (300 MHz, acetone-*d*₆): δ = 7.65 (ddd, *J* = 1.1 Hz, *J* = 0.9 Hz, *J* = 1.5 Hz, *J* = 7.7 Hz, 1H), 7.55 (dd, *J*

= 1.5 Hz, $J = 2.7$ Hz, 1H), 7.47 (t, $J = 8.0$ Hz, 1H), 7.23 (ddd, $J = 0.9$ Hz, $J = 1.1$ Hz, $J = 2.7$ Hz, $J = 7.9$ Hz, 1H), 6.94–6.83 (m, 4H), 5.64 (t, $J = 5.4$ Hz, 1H), 4.15–4.10 (m, 2H), 3.87 (s, 3H), 3.73 (s, 3H), 2.85 (bs, 1H) ppm.

^{13}C NMR (75 MHz, acetone- d_6): $\delta = 197.4, 160.9, 155.3, 153.0, 137.9, 130.4, 123.6, 120.0, 117.8, 115.1$ (2C), 114.6 (2C), 84.5, 64.1, 55.9, 55.7 ppm.

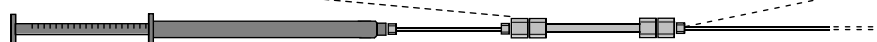
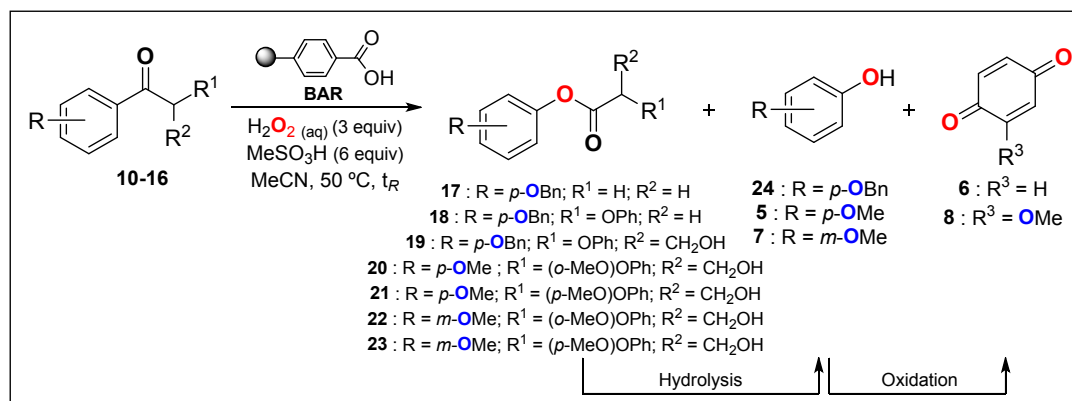
mp ($^{\circ}\text{C}$): 90-93.

R_f : 0.42 (4:6 AcOEt/hexanes).

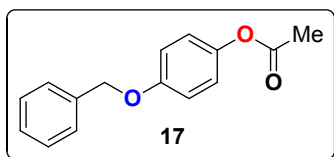
HRMS (ESI-TOF): m/z $[\text{M} + \text{H}]^+$ calc. for $\text{C}_{17}\text{H}_{19}\text{O}_5$: 303.1233, found: 303.1247.

NMR data for the Products (Table 3, Scheme S4)

Scheme S4



4-(benzyloxy)phenyl acetate (17): yield for Entry 1, Table 3 = 16% (34.2 mg, 0.14 mmol), colorless crystals.



¹H NMR (300 MHz, CDCl₃): δ = 7.44–7.34 (m, 4H), 7.31 (ddd, *J* = 1.5 Hz, *J* = 1.5 Hz, *J* = 2.1 Hz, *J* = 9.0 Hz, 1H), 7.02–6.94 (m, 4H), 5.04 (s, 2H), 2.28 (s, 3H) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 170.0, 156.7, 144.6, 137.0, 128.8 (2C), 128.2, 127.6 (2C), 122.5 (2C), 115.6 (2C), 70.6, 21.2 ppm.

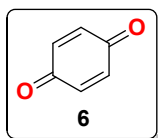
mp (°C): 111–112 (lit.⁶ 100–111).

R_f: 0.67 (5:5 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + H]⁺ calc. for C₁₅H₁₅O₃: 243.1021, found: 243.1015.

#CAS: 6311-66-6.

1,4-benzoquinone (6): yield for Entry 6, Table 3 = 89% (56.2 mg, 0.52 mmol), neon-yellow crystals.



¹H NMR (300 MHz, CDCl₃): δ = 6.79 (s, 4H) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 187.1 (2C), 136.4 (4C) ppm.

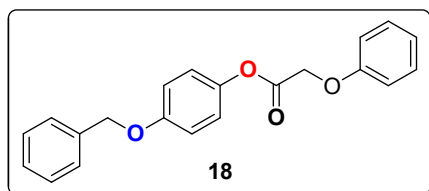
mp (°C): 112–115 (lit.⁷ 115–116).

R_f: 0.91 (6:4 AcOEt/hexanes).

MS (EI⁺): *m/z* (relative intensity) 108 (M⁺, 89), 54 (100).

#CAS: 106-51-4.

4-(benzyloxy)phenyl 2-phenoxyacetate (18): yield for Entry 3, Table 3 = 22% (64.8 mg, 0.19 mmol), pale-yellow solid.



¹H NMR (300 MHz, CDCl₃): δ = 7.43–7.30 (m, 7H), 7.04–6.94 (m, 7H), 5.05 (s, 2H), 5.13 (s, 2H), 4.86 (s, 2H) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 168.0, 157.9, 156.8, 143.9, 136.8, 129.8 (2C), 128.8 (2C), 128.2,

127.6 (2C), 122.2 (2C), 122.1, 115.7 (2C), 114.9 (2C), 70.6, 65.6 ppm.

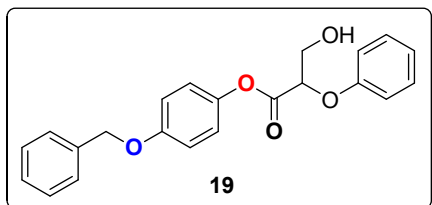
mp (°C): 124-127.

R_f: 0.59 (5:5 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + Na]⁺ calc. for C₂₁H₁₈O₄Na: 357.1103, found: 357.1099.

#CAS: 686311-24-0.

4-(benzyloxy)phenyl 3-hydroxy-2-phenoxypropanoate (19): yield for Entry 5, Table 3 = 8% (16.7 mg, 0.04 mmol), beige solid.



¹H NMR (300 MHz, CDCl₃): δ = 7.42–7.22 (m, 7H), 7.0–6.88 (m, 7H), 5.10 (s, 2H), 4.95 (dd, *J* = 5.7 Hz, *J* = 5.8 Hz, 1H), 4.22–4.16 (m, 2H), 2.33 (bs, 1H) ppm.

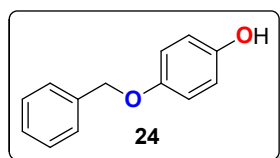
¹³C NMR (75 MHz, CDCl₃): δ = 168.9, 158.1, 156.9, 144.5, 135.1 (2C), 130.0 (2C), 128.3, 127.7 (2C), 122.5, 122.4 (2C), 115.8 (2C), 115.0 (2C), 89.5, 70.5, 63.4 ppm.

mp (°C): 137-139.

R_f: 0.62 (6:4 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + Na]⁺ calc. for C₂₂H₂₀O₅Na: 387.1209, found: 387.1218.

4-benzyloxyphenol (24): Table 3, conjoined traces (8.5 mg),



white powder.

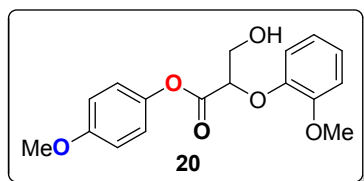
¹H NMR (300 MHz, CDCl₃): δ = 7.42–7.29 (m, 5H), 6.85 (d, *J* = 5.4 Hz, 2H), 6.75 (d, *J* = 5.4 Hz, 2H), 5.82 (bs, 1H), 4.99 (s, 2H) ppm.

m.p. (°C): 120-122 (lit.⁶ 121-122).

R_f: 0.12 (6:4 AcOEt/hexanes).

#CAS: 103-16-2.

4-methoxyphenyl 3-hydroxy-2-(2-methoxyphenoxy)propanoate (20): yield for Entry 6, Table 3 = 9% (16.5 mg, 0.05 mmol), opaque white crystals.



¹H NMR (300 MHz, CDCl₃): δ = 7.26–6.76 (m, 8H), 4.88 (dd, *J* = 3.9 Hz, *J* = 6.3 Hz, 1H), 4.19 (ddd, *J* = 6.3 Hz, *J* = 3.9 Hz, *J* = 11.7 Hz, *J* = 26.1 Hz, 2H), 3.86 (s, 3H), 3.75

(s, 3H), 3.30 (bs, 1H) ppm.

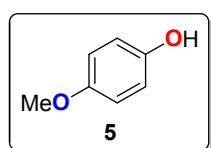
¹³C NMR (75 MHz, CDCl₃): δ = 168.6, 150.1, 147.4, 143.8, 143.3, 123.1, 122.0 (2C), 120.9, 115.6, 114.9 (2C), 112.6, 81.0, 67.3, 56.0, 55.6 ppm.

mp (°C): 146-149.

R_f: 0.70 (6:4 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + H]⁺ calc. for C₁₇H₁₉O₆: 319.1182, found: 319.1190.

4-methoxyphenol (5): Table 3, conjoined traces (6.5 mg), off white powder.



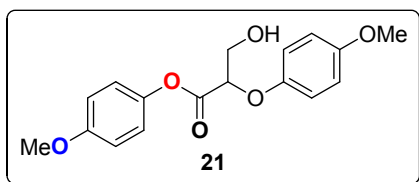
¹H NMR (300 MHz, CDCl₃): δ = 6.81–6.75 (m, 4H), 4.60 (bs, 1H), 3.76 (s, 3H) ppm.

mp (°C): 56-57 (lit.⁸ 54-56).

R_f : 0.16 (6:4 AcOEt/hexanes).

#CAS: 150-76-5.

4-methoxyphenyl 3-hydroxy-2-(4-methoxyphenoxy)propanoate (21): yield for Entry



7, Table 3 = 8% (14.6 mg, 0.05 mmol), white powder.

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 7.02 (d, J = 9.0 Hz, 2H), 6.95–6.82 (m, 6H), 4.89 (dd, J = 4.5 Hz, J = 5.1 Hz, 1H), 4.22 (ddd, J = 5.1 Hz, J = 4.5 Hz, J = 12.0 Hz, J = 14.1 Hz, 2H), 5.13 (s, 2H), 3.76 (s, 6H), 2.70

(bs, 1H) ppm.

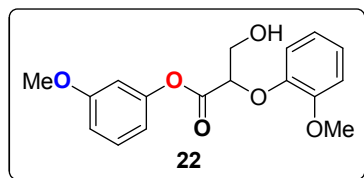
$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ = 168.9, 157.7, 155.2, 151.6, 143.8, 122.2 (2C), 117.2 (2C), 114.9 (2C), 114.6 (2C), 79.1, 63.6, 55.7, 55.6 ppm.

mp ($^\circ\text{C}$): 150-152.

R_f : 0.72 (6:4 AcOEt/hexanes).

HRMS (ESI-TOF): m/z [$\text{M} + \text{H}$] $^+$ calc. for $\text{C}_{17}\text{H}_{19}\text{O}_6$: 319.1182, found: 319.1196.

3-methoxyphenyl 3-hydroxy-2-(2-methoxyphenoxy)propanoate (22): yield for Entry



8, Table 3 = 11% (20.0 mg, 0.06 mmol), yellow oil.

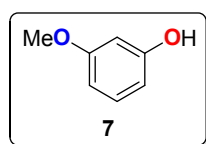
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 7.21 (t, J = 5.6 Hz, 1H), 7.01–6.77 (m, 7H), 4.89 (dd, J = 3.9 Hz, J = 6.3 Hz, 1H), 4.08 (ddd, J = 6.3 Hz, J = 3.9 Hz, J = 11.7 Hz, J = 27.3 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 3.16 (bs, 1H) ppm.

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ = 169.1, 160.4, 151.9, 147.2, 143.6, 130.0, 123.2, 120.6, 116.0, 114.2, 112.7, 111.3, 107.5, 83.0, 68.1, 56.0, 55.6 ppm.

R_f : 0.75 (6:4 AcOEt/hexanes).

HRMS (ESI-TOF): m/z [$\text{M} + \text{H}$] $^+$ calc. for $\text{C}_{17}\text{H}_{19}\text{O}_6$: 319.1182, found: 319.1177.

3-methoxyphenol (7): Table 3, conjoined traces (6.2 mg), deep-brown liquid.

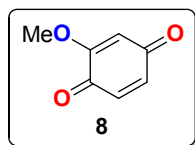


$^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 7.14 (t, J = 5.8 Hz, 1H), 6.54–6.44 (m, 3H), 5.56 (bs, 1H), 3.78 (s, 3H) ppm.

R_f : 0.15 (6:4 AcOEt/hexanes).

#CAS: 150-19-6.

2-methoxycyclohexa-2,5-diene-1,4-dione (8): yield for Entry 8, Table 3 = 84% (56.2 mg, 0.52 mmol), beige powder.



$^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 6.71 (m, 2H), 5.95 (m, 1H), 3.74 (s, 3H) ppm.

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ = 187.4, 181.5, 158.6, 137.0, 134.3, 107.5, 56.2 ppm.

mp ($^\circ\text{C}$): 144-145 (lit.⁹ 144-146).

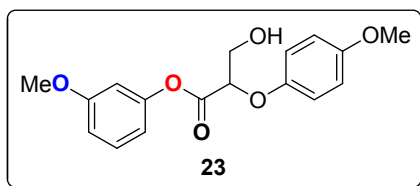
R_f : 0.88 (6:4 AcOEt/hexanes).

MS (EI^+): m/z (relative intensity) 138 (M^+ , 53), 108 (68), 69 (100).

#CAS: 2880-58-2.

3-methoxyphenyl 3-hydroxy-2-(4-methoxyphenoxy)propanoate (23): yield for Entry 9, Table 3 = 10% (18.4 mg, 0.06 mmol), pale-yellow non-crystalline solid.

¹H NMR (300 MHz, CDCl₃): δ = 7.20 (t, *J* = 5.7 Hz, 1H), 7.00–6.83 (m, 7H), 4.90 (dd, *J* = 4.5 Hz, *J* = 5.1 Hz, 1H), 4.04 (ddd, *J* = 5.1 Hz, *J* = 4.5 Hz, *J* = 11.7 Hz, *J* = 15.0 Hz, 2H), 3.83 (s, 3H), 3.75 (s, 3H), 2.93 (bs, 1H) ppm.



¹³C NMR (75 MHz, CDCl₃): δ = 169.0, 160.2, 152.1, 151.2, 145.9, 129.9, 115.2 (2C), 114.7 (2C), 113.8,

111.7, 107.2, 80.5, 68.0, 55.7, 55.6 ppm.

***R_f*:** 0.73 (6:4 AcOEt/hexanes).

HRMS (ESI-TOF): *m/z* [M + H]⁺ calc. for C₁₇H₁₉O₆: 319.1182, found: 319.1185.

At the end of this study, after approximately 700 reactions showing the same catalytic activity, **BAR** was unloaded from the packed-bed reactor and analyzed by SEM (Figure S3).

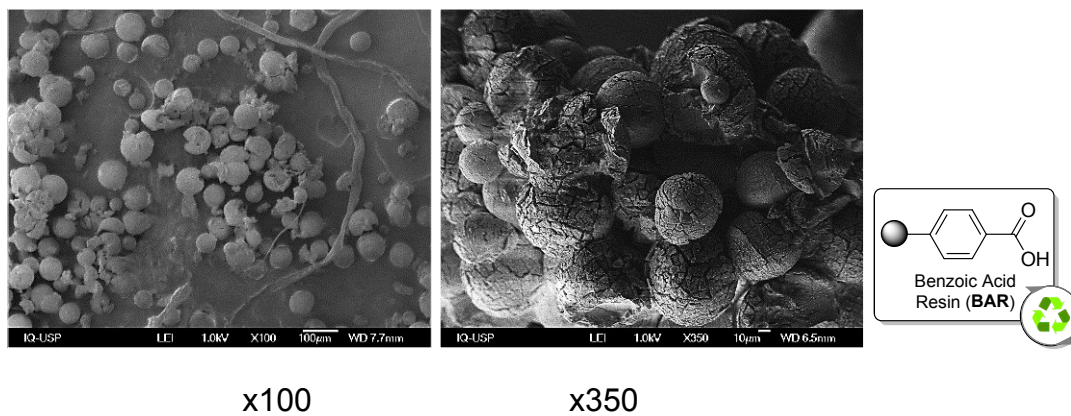


Figure S3: SEM images of recycled **BAR** at x100 and x350 magnifications.

Considering solvent recycle, the *E* Factor was calculated as follows: Obtained mass of products = 72.7 mg (56.2 mg of **6** + 16.5 mg of **20**); Mass of reagents = 1008.3 mg (60.7 mg of H₂O₂ + 342.8 mg of MeSO₃H + 604.8 mg of NaHCO₃); Amount of the starting material **13** = 179.7 mg.

$$E \text{ Factor} = (179.7 + 1008.3 - 72.7)/72.7 = 15.3.$$

Experimental

- [1] D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 2nd ed. Oxford: Pergamon Press; 1989.
- [2] W. C. C. Santos, K. A. Dias, L. P. Santos, C. M. Kisukuri, T. S. Rodrigues, R. S. Geonmonond, P. H. C. Camargo and L. H. Andrade, *Adv. Synth. Catal.*, 2018, **360**, 1376–1383.
- [3] G. Magallanes, M. D. Kärkäs, I. Bosque, S. Lee, S. Maldonado and C. R. J. Stephenson, *ACS Catal.*, 2019, **9**, 2252–2260.
- [4] C. -F. Lin, J. -S. Yang, C. -Y. Chang, S. -C. Kuo, M. -R. Lee and L. -J. Huang, *Bioorg. Med. Chem.*, 2005, **13**, 1537–1544.
- [5] A. C. Lindsay, S. Kudo and J. Sperry, *Org. Biomol. Chem.*, 2019, **17**, 7408–7415.
- [6] G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 1955, 1404–1407.
- [7] A. A. Zagulyaeva, C. T. Banek, M. S. Yusubov and Viktor V. Zhdanki, *Org. Lett.*, 2010, **12**, 4644–4647.
- [8] H. Yang, Y. Li, M. Jiang, J. Wang and H. Fu, *Chem. Eur. J.*, 2011, **17**, 5652–5660.
- [9] F. Derikvand, F. Bigi, R. Maggi, C. G. Piscopo and G. Sartori, *J. Catal.*, 2010, **271**, 99–103.

NMR Spectra of the β -O-4 Lignin Models and Products (Table 3)

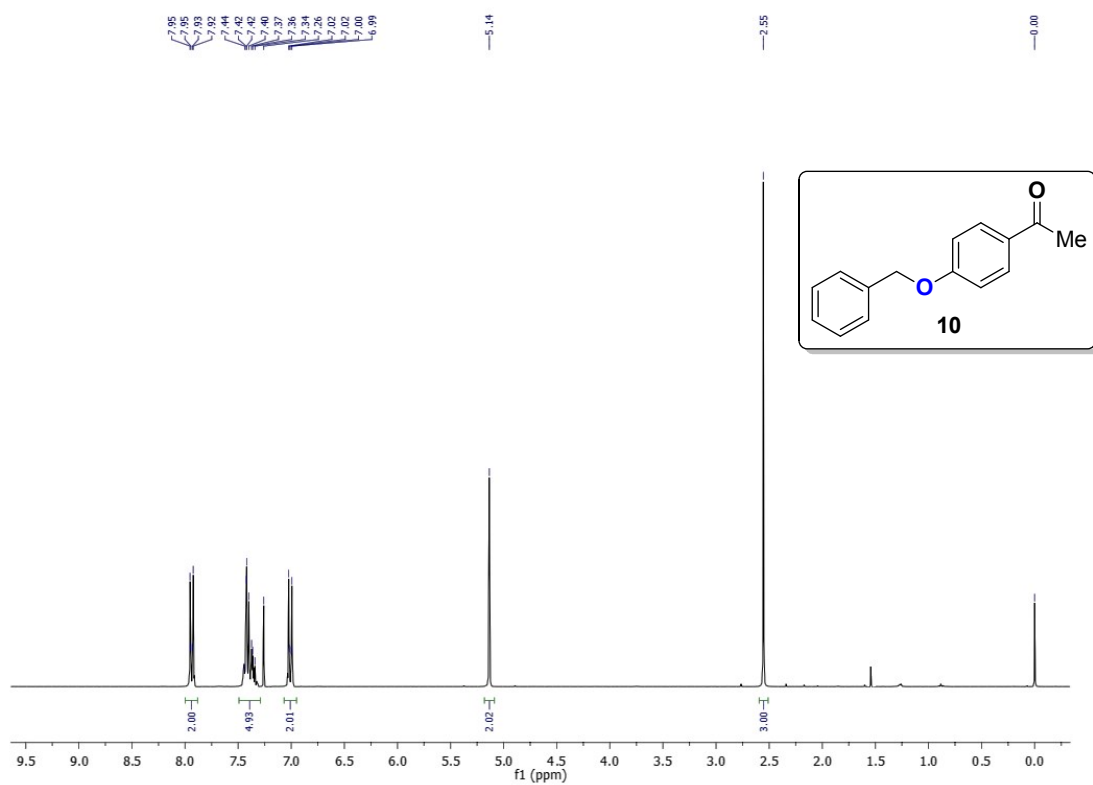


Figure S4. ^1H NMR Spectrum of **10** (300 MHz, CDCl_3).

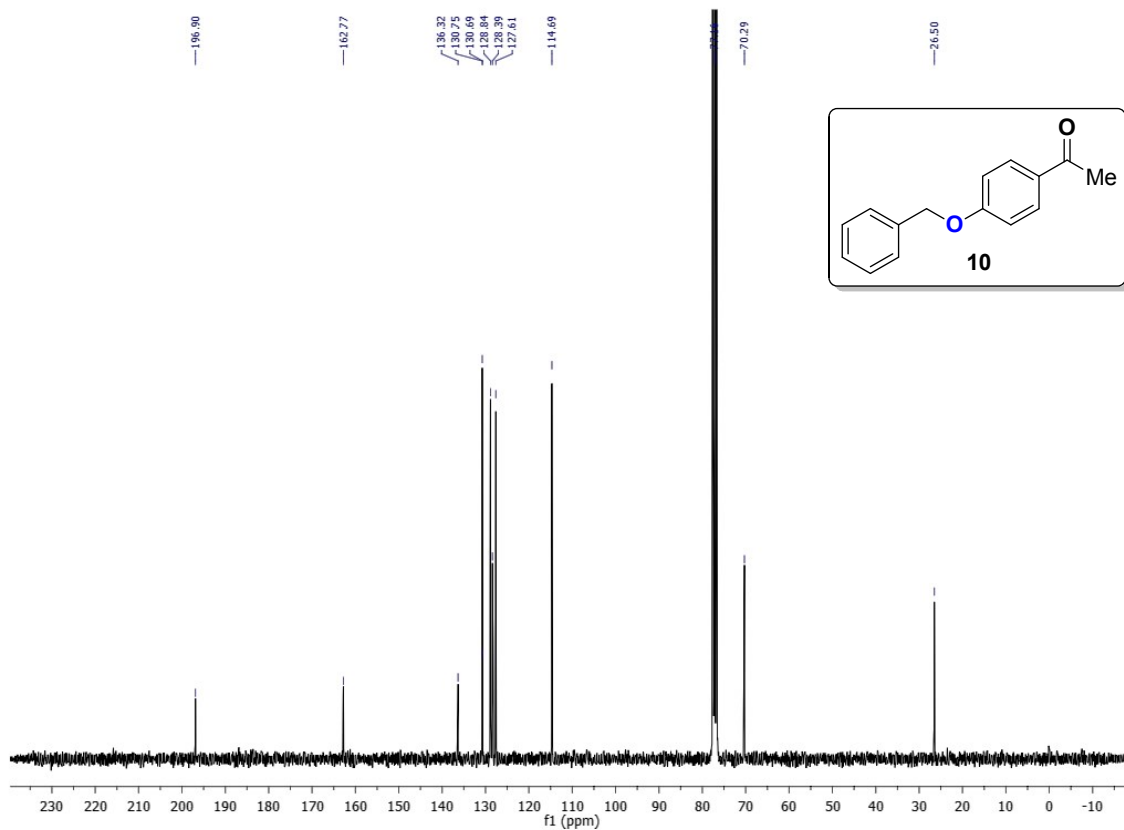


Figure S5. ^{13}C NMR Spectrum of **10** (75 MHz, CDCl_3).

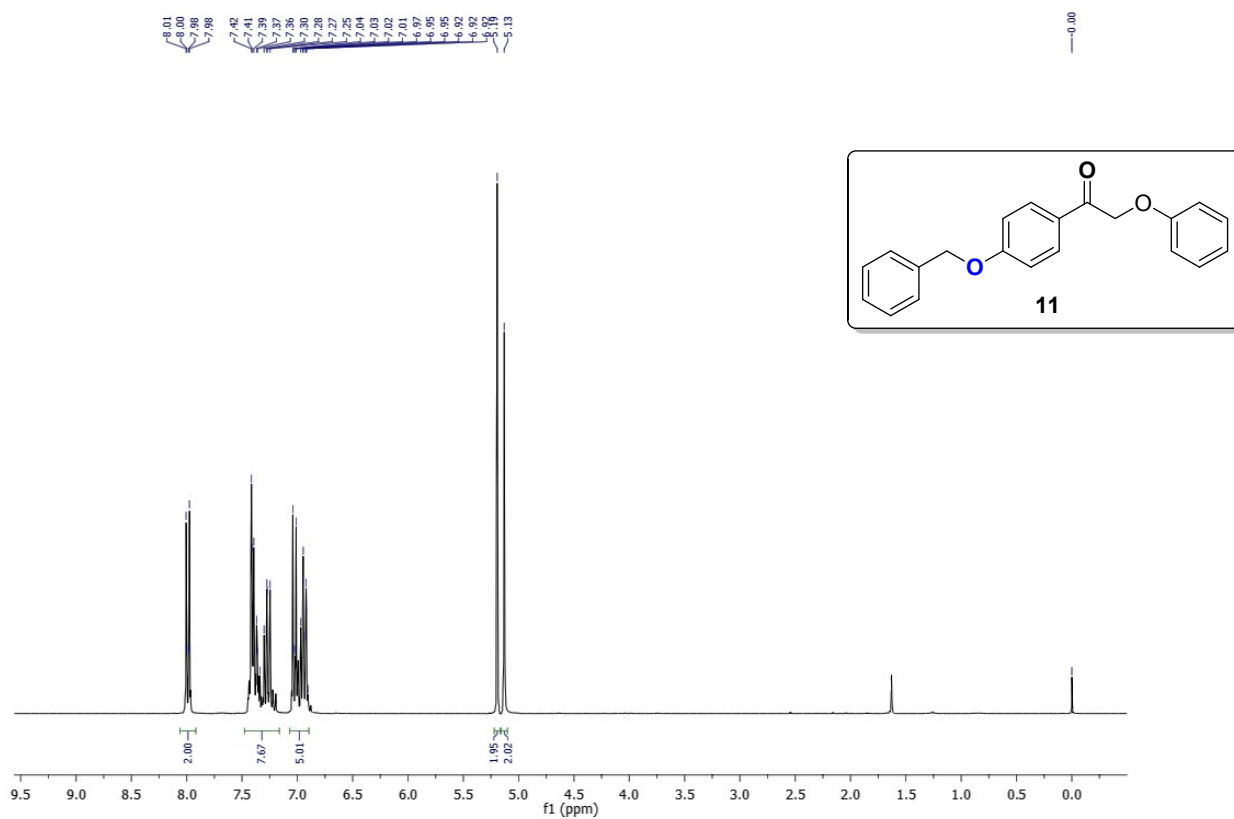


Figure S6. ¹H NMR Spectrum of **11** (300 MHz, CDCl₃).

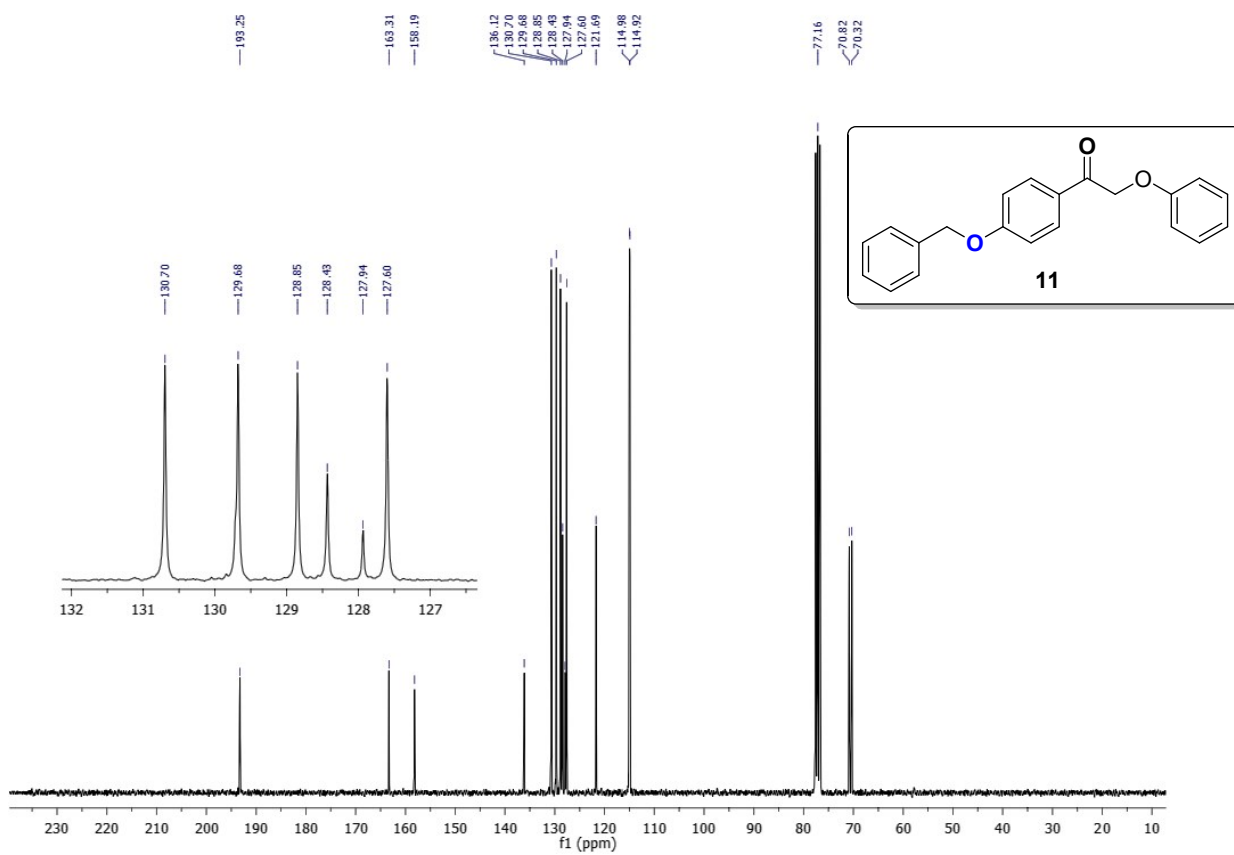


Figure S7. ¹³C NMR Spectrum of **11** (75 MHz, CDCl₃).

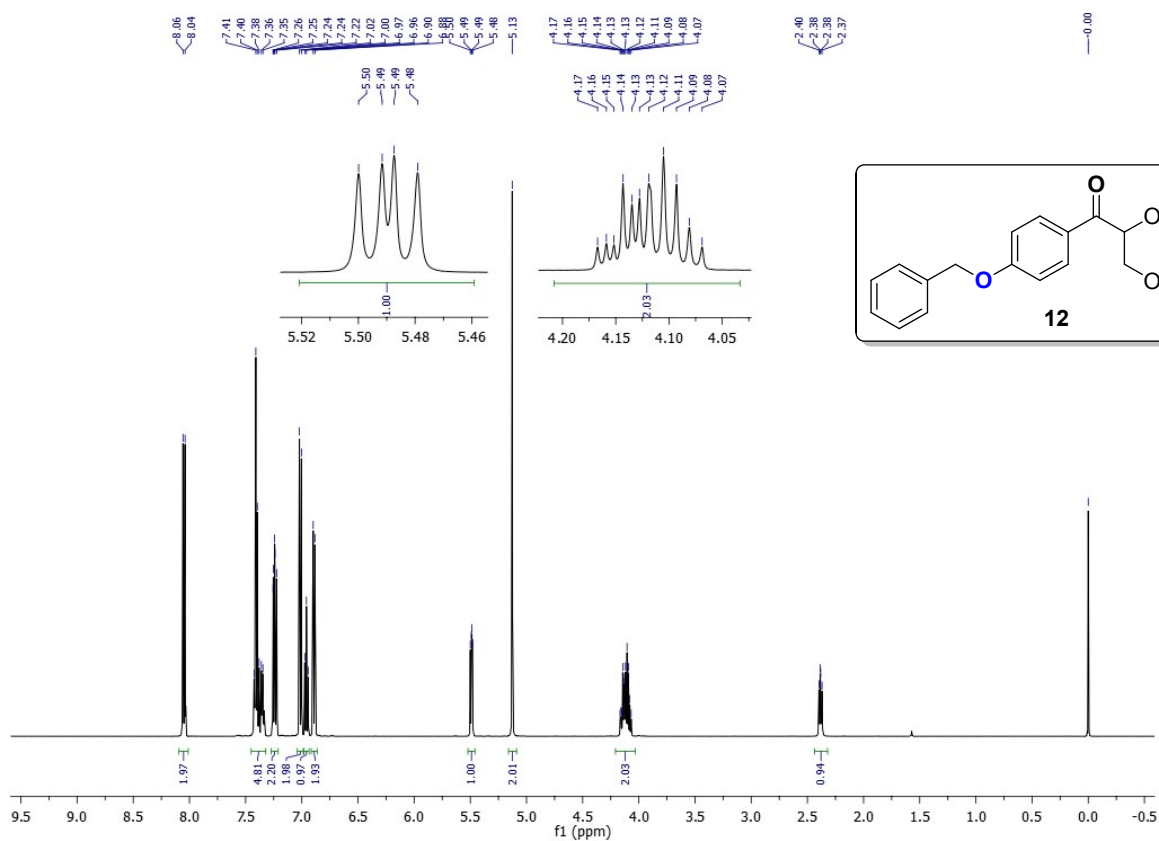


Figure S8. ¹H NMR Spectrum of **12** (300 MHz, CDCl₃).

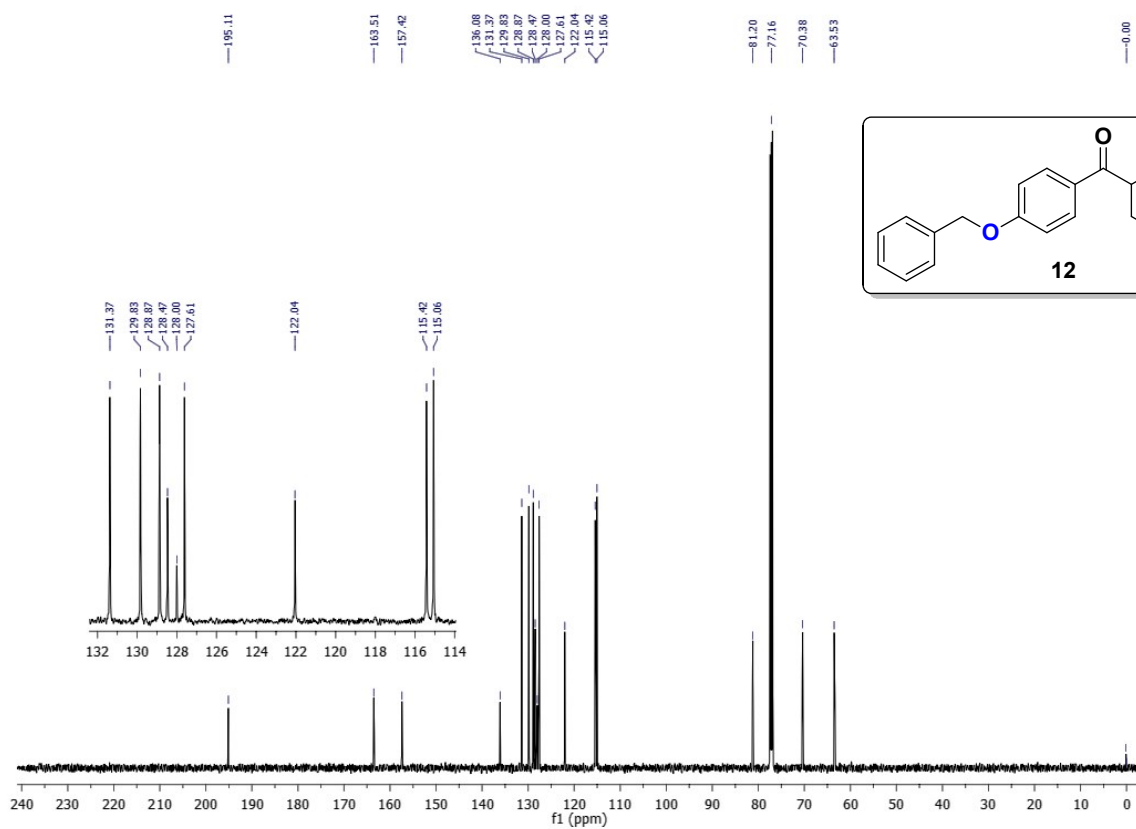


Figure S9. ¹³C NMR Spectrum of **12** (75 MHz, CDCl₃).

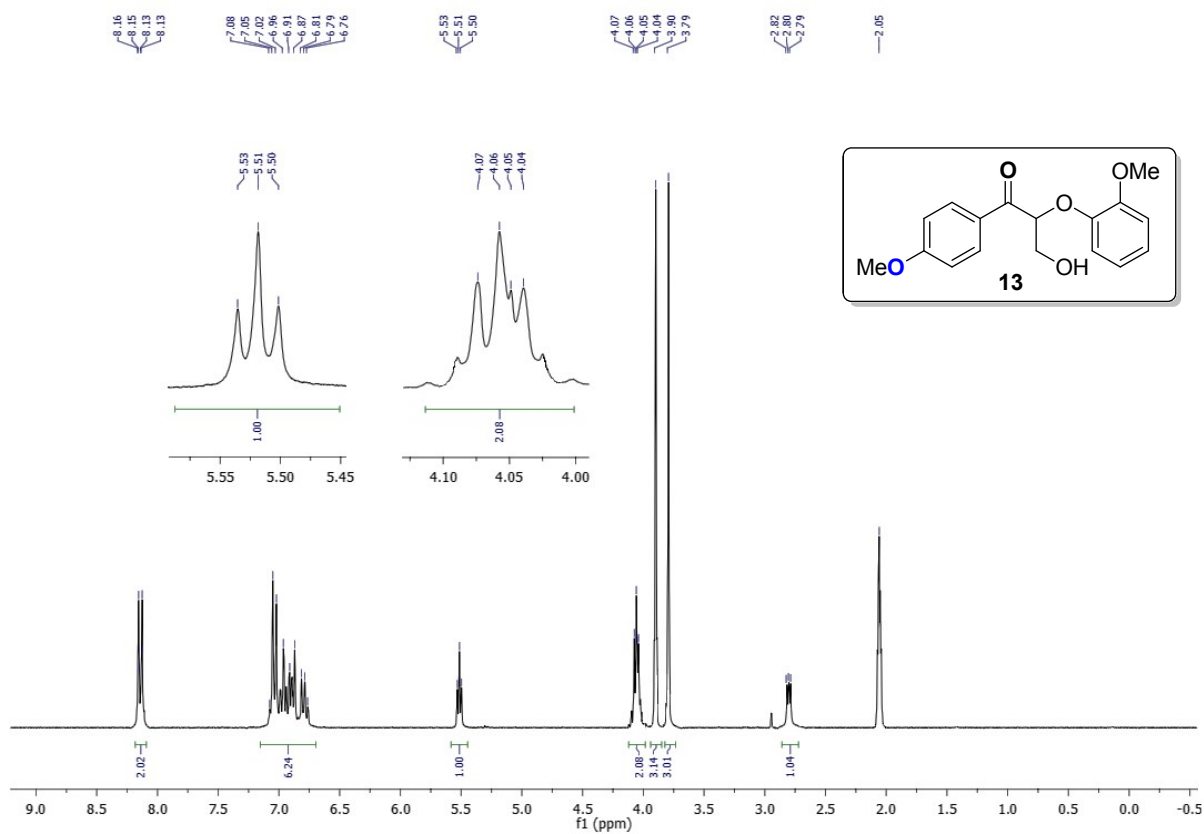


Figure S10. ¹H NMR Spectrum of **13** (300 MHz, acetone-d₆).

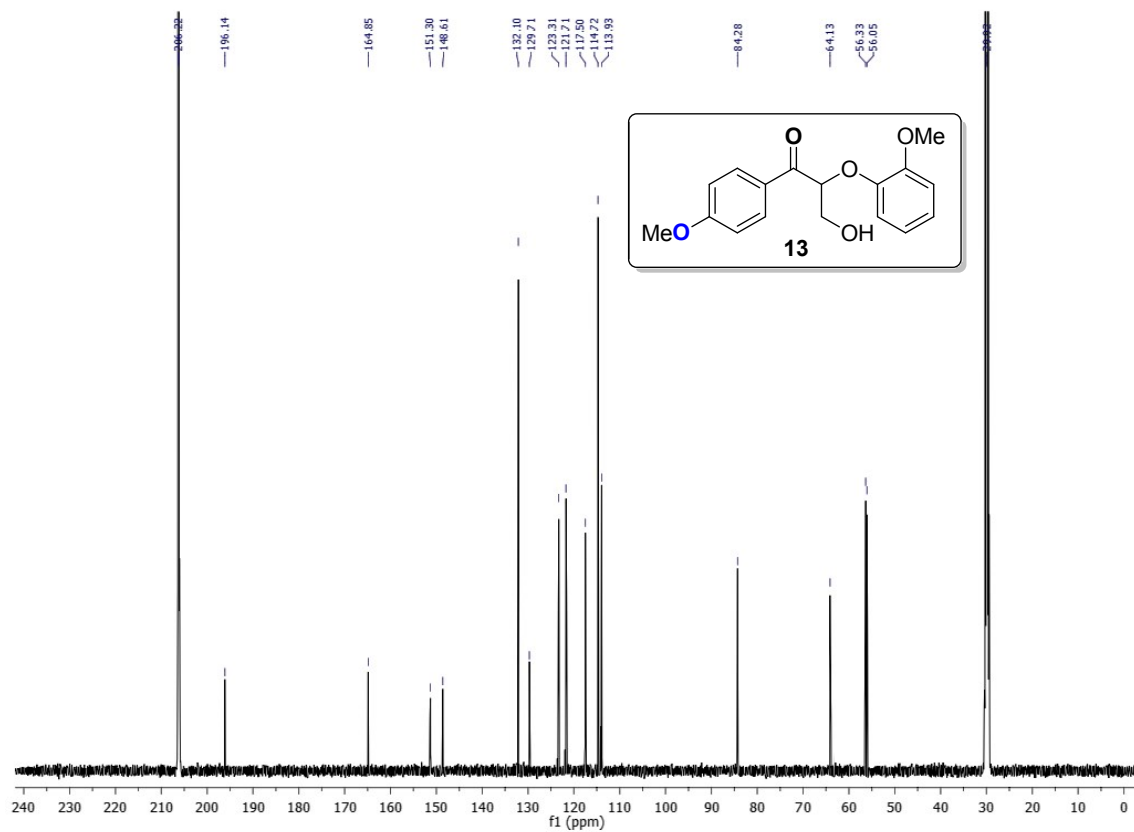


Figure S11. ¹³C NMR Spectrum of **13** (75 MHz, acetone-d₆).

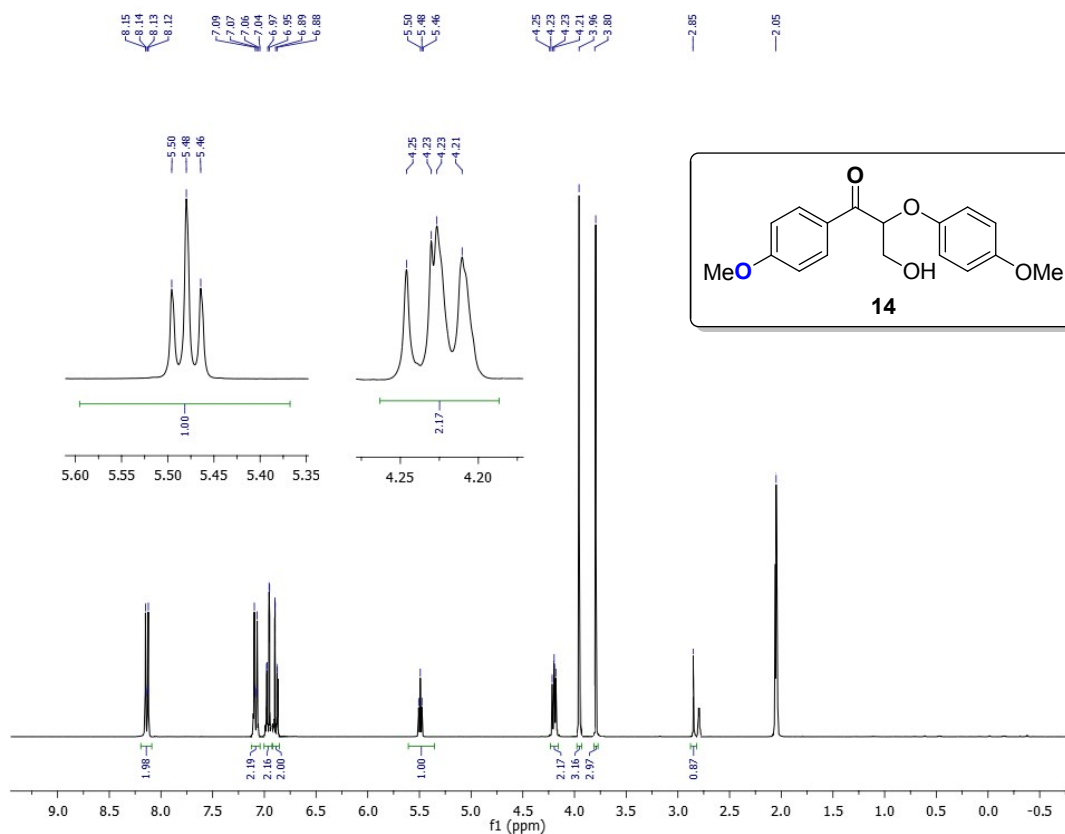


Figure S12. ¹H NMR Spectrum of **14** (300 MHz, acetone-d₆).

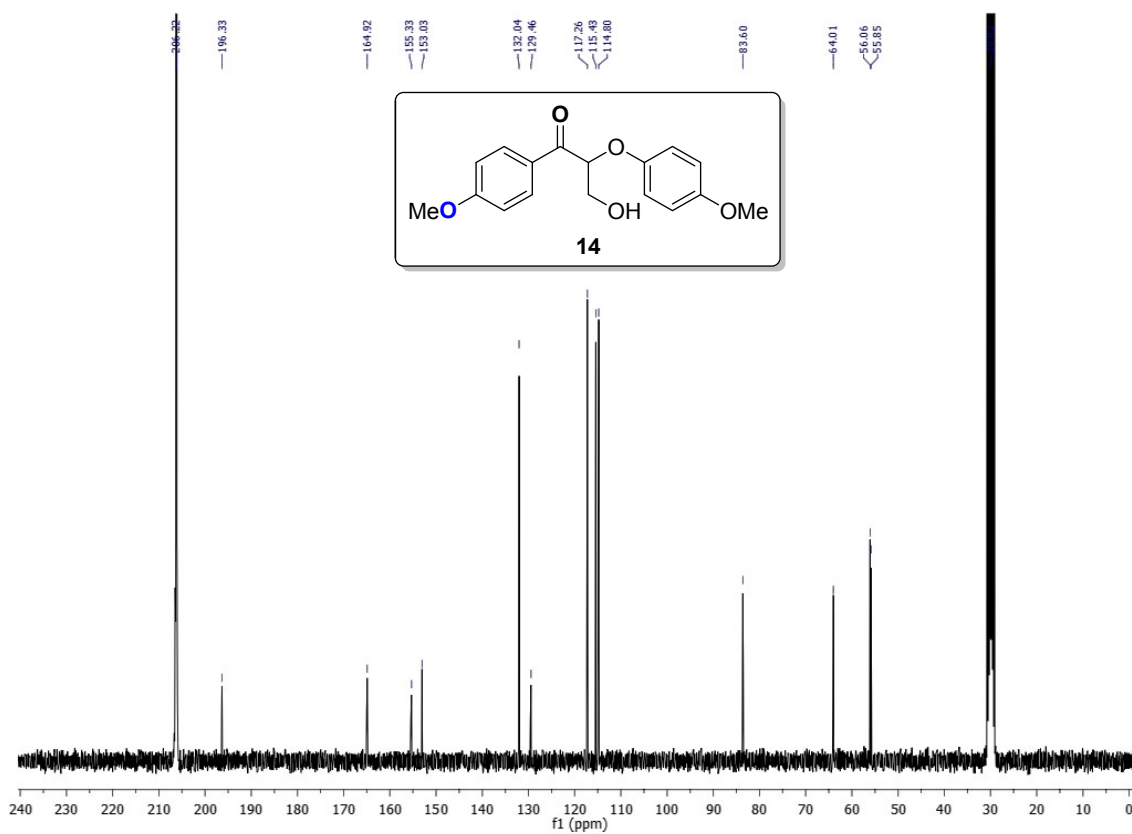


Figure S13. ¹³C NMR Spectrum of **14** (75 MHz, acetone-d₆).

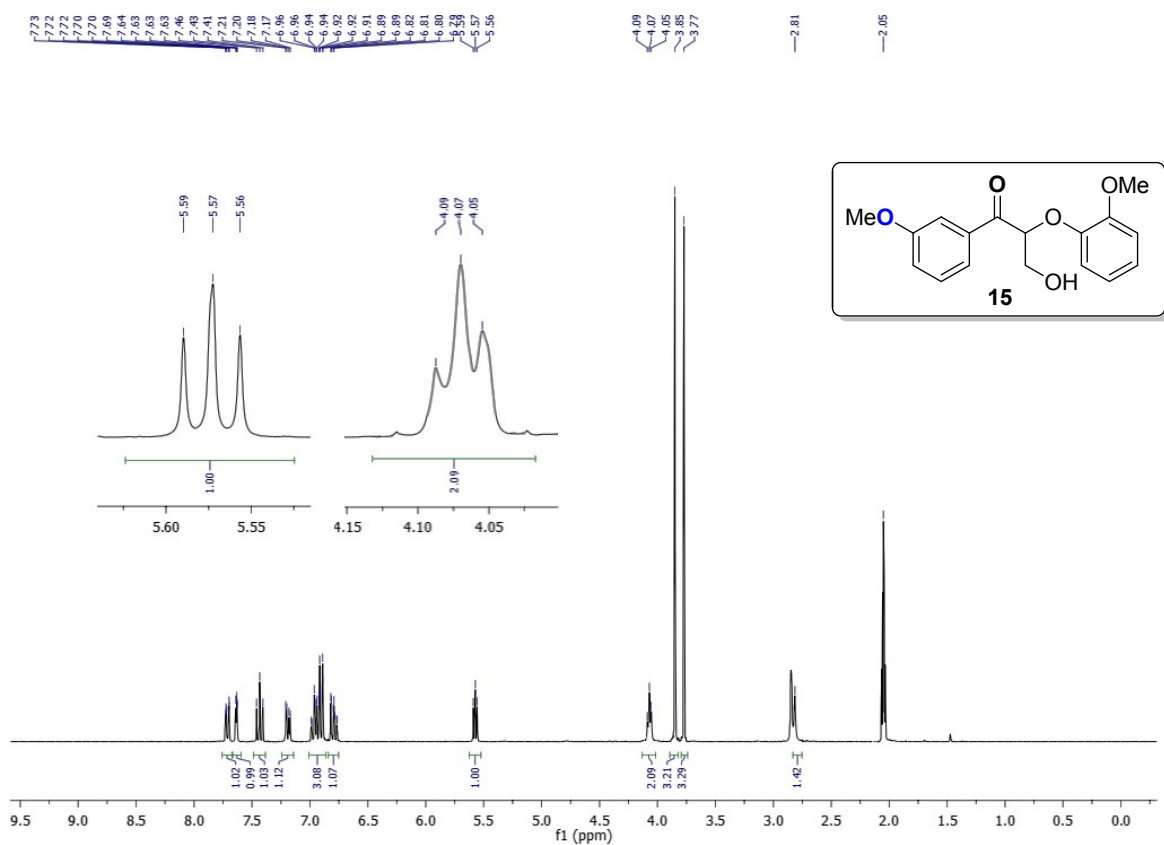


Figure S14. ¹H NMR Spectrum of **15** (300 MHz, acetone-d₆).

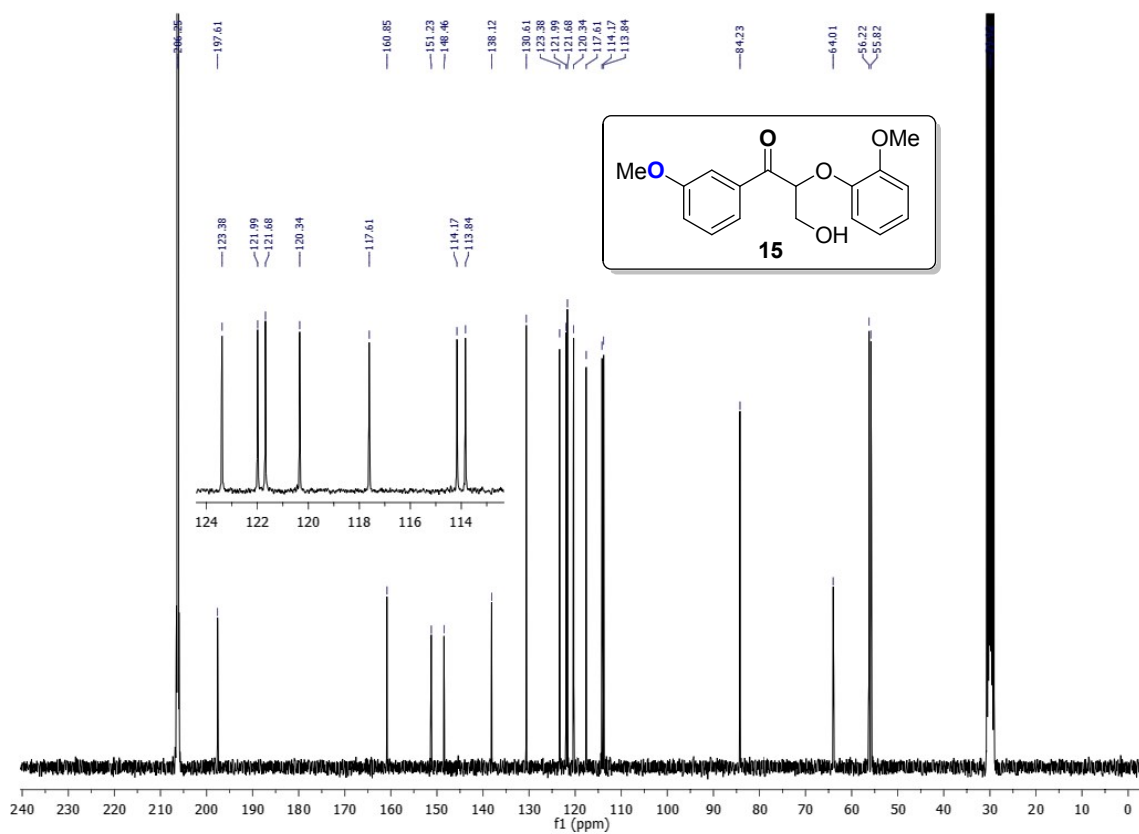


Figure S15. ¹³C NMR Spectrum of **15** (75 MHz, acetone-d₆).

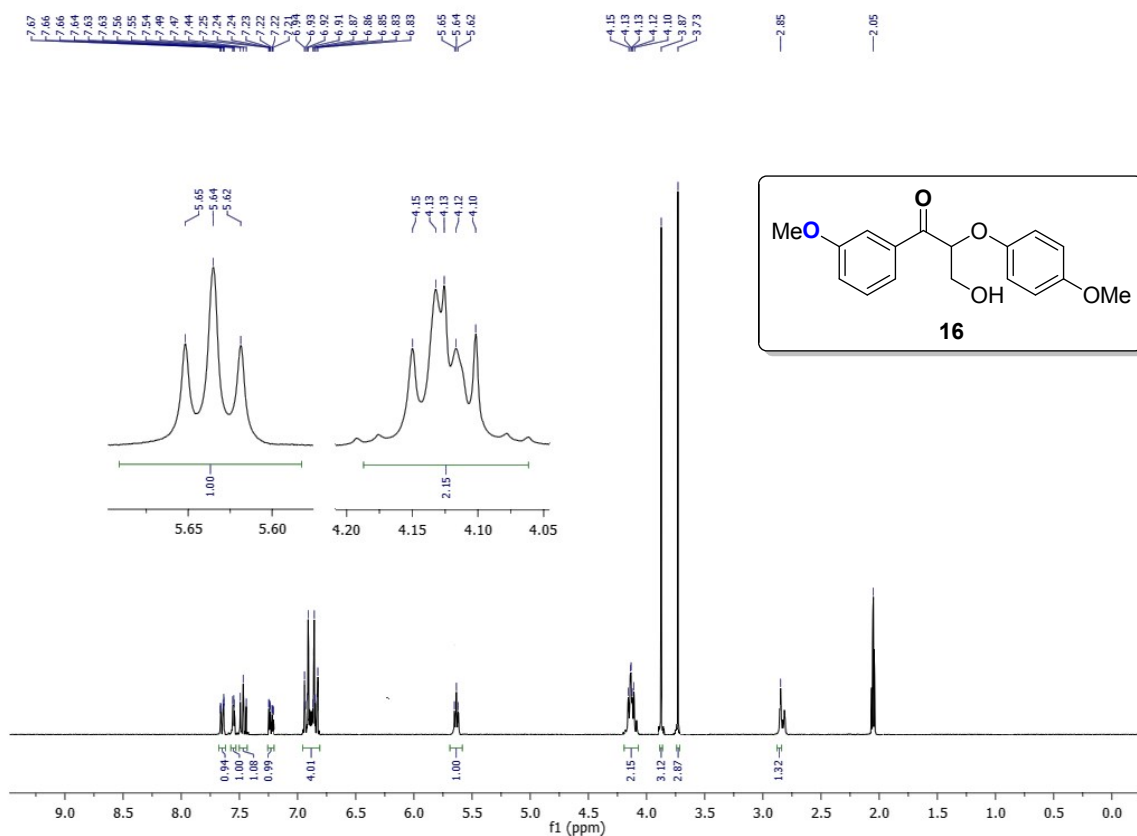


Figure S16. ¹H NMR Spectrum of **16** (300 MHz, acetone-d₆).

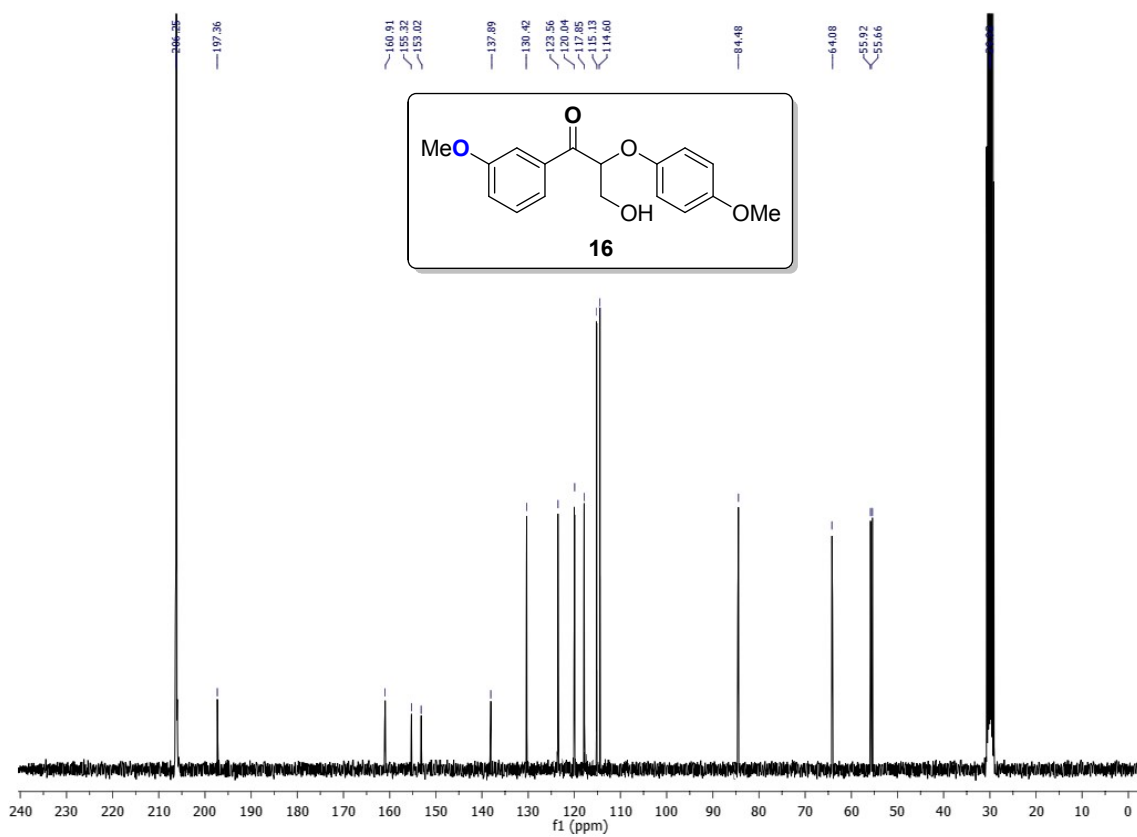


Figure S17. ¹³C NMR Spectrum of **16** (75 MHz, acetone-d₆).

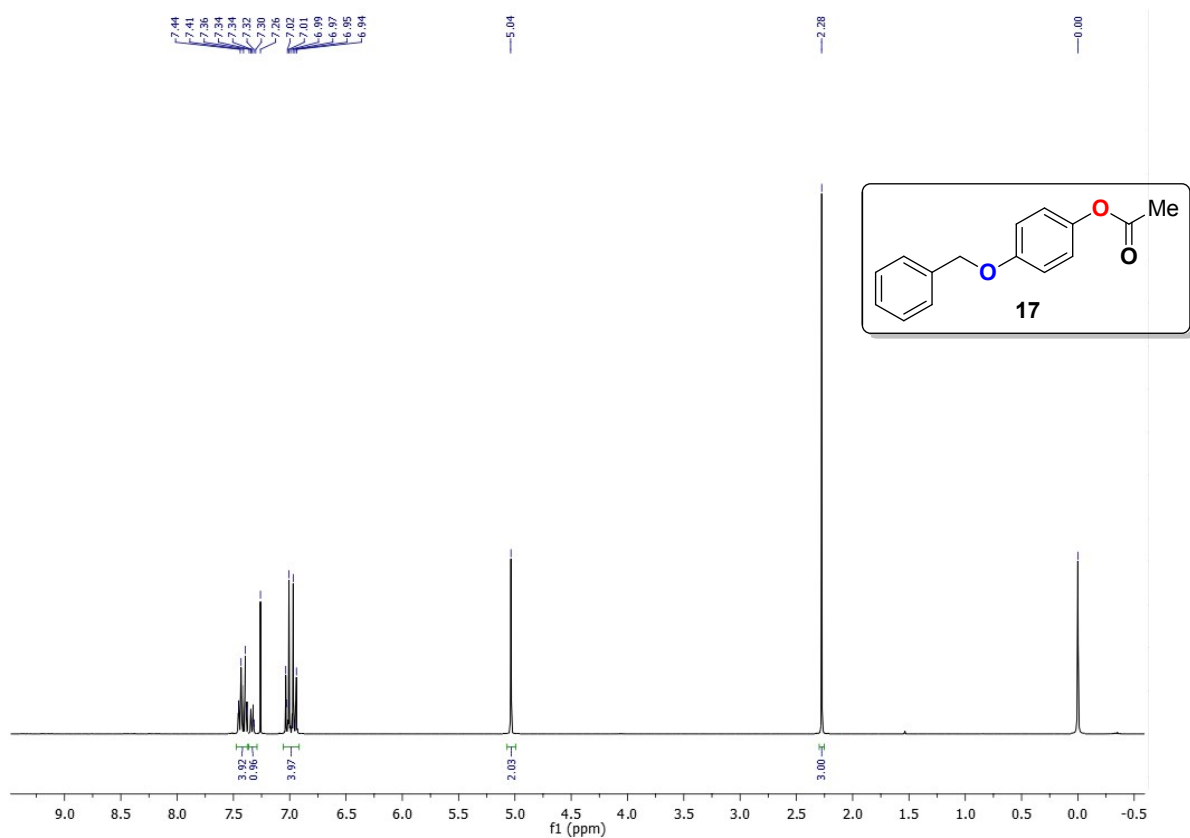


Figure S18. ^1H NMR Spectrum of 17 (300 MHz, CDCl_3).

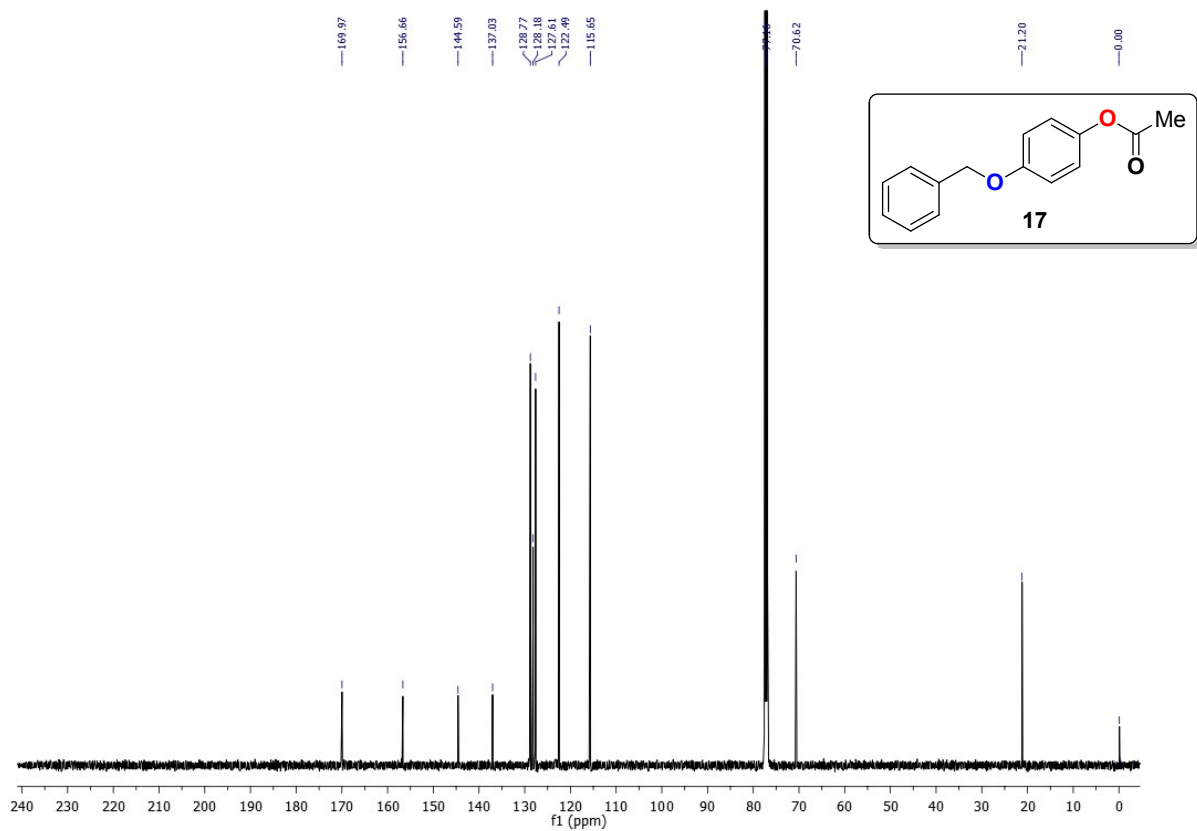


Figure S19. ^{13}C NMR Spectrum of 17 (75 MHz, CDCl_3).

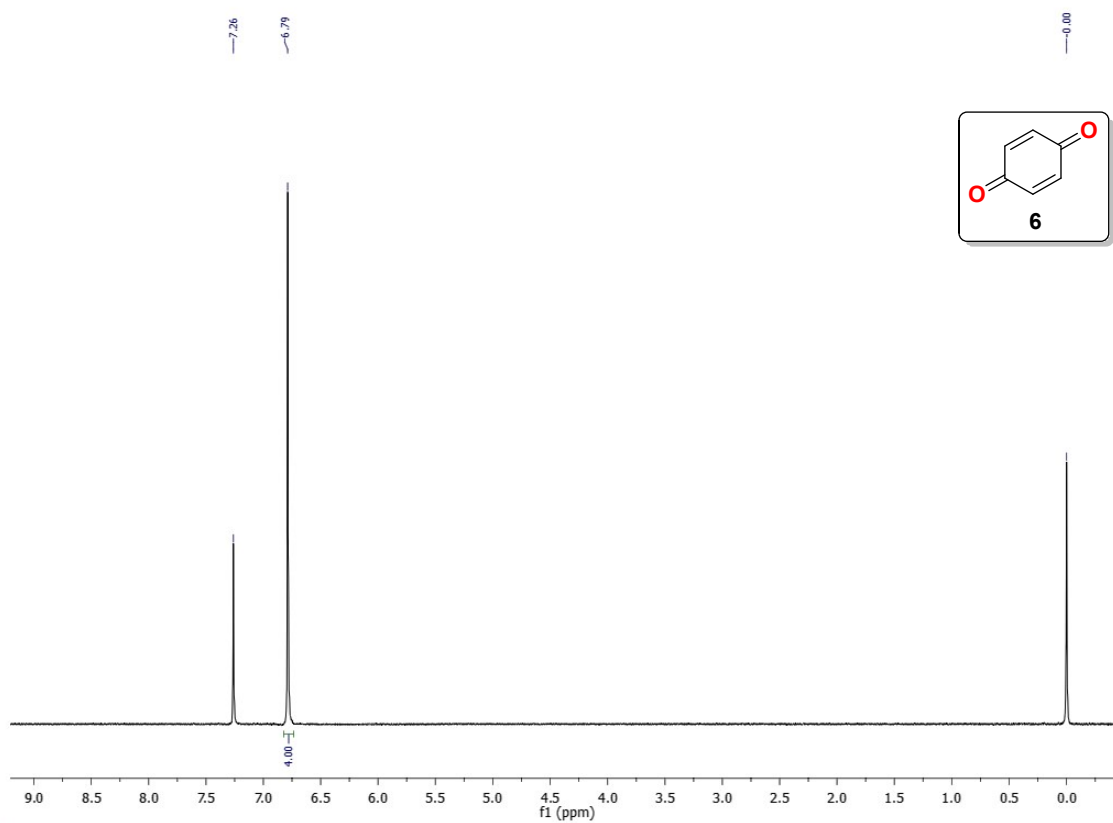


Figure S20. ^1H NMR Spectrum of **6** (300 MHz, CDCl_3).

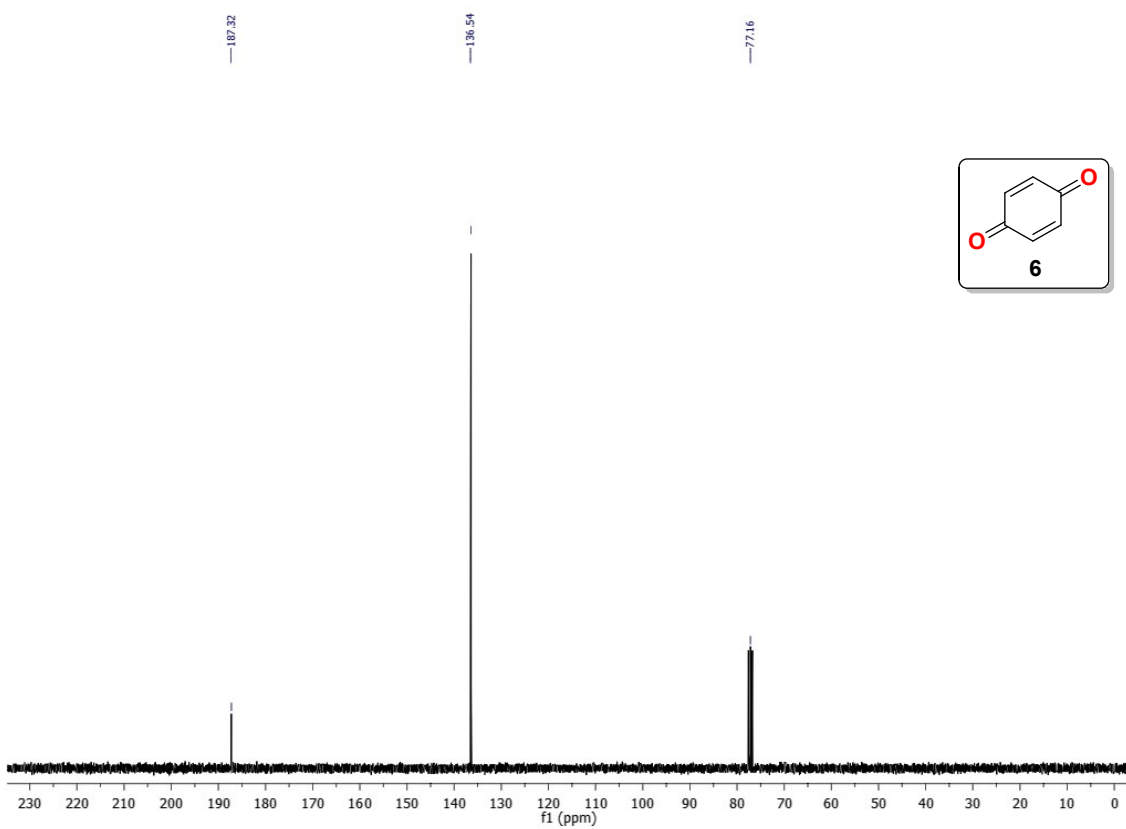


Figure S21. ^{13}C NMR Spectrum of **6** (75 MHz, CDCl_3).

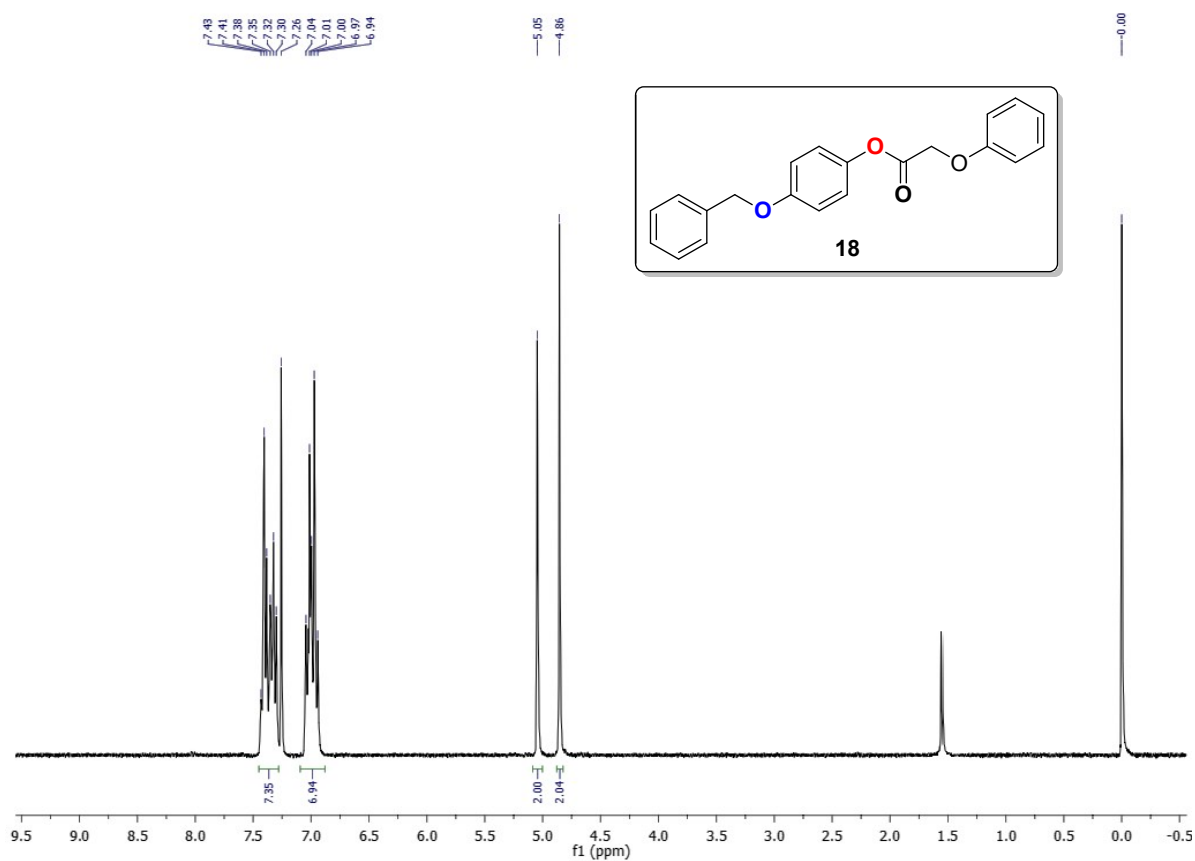


Figure S22. ¹H NMR Spectrum of **18** (300 MHz, CDCl₃).

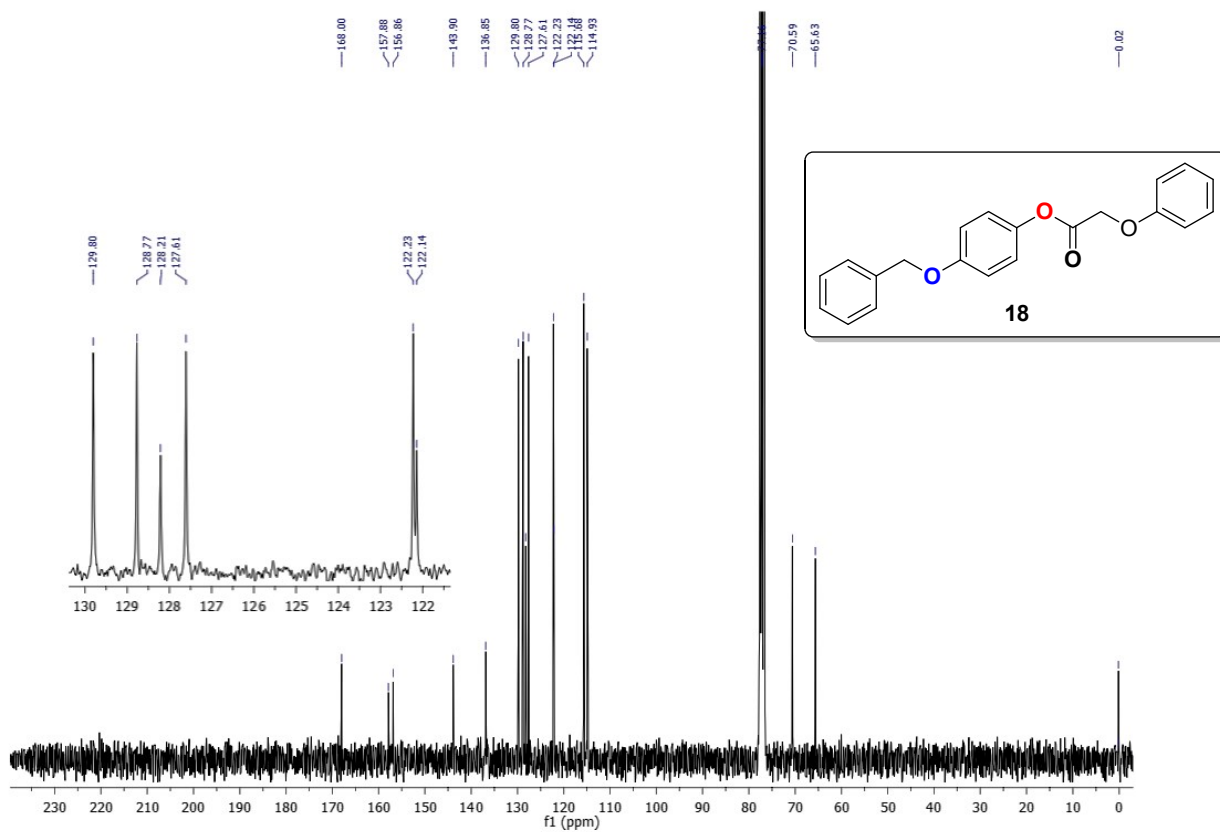
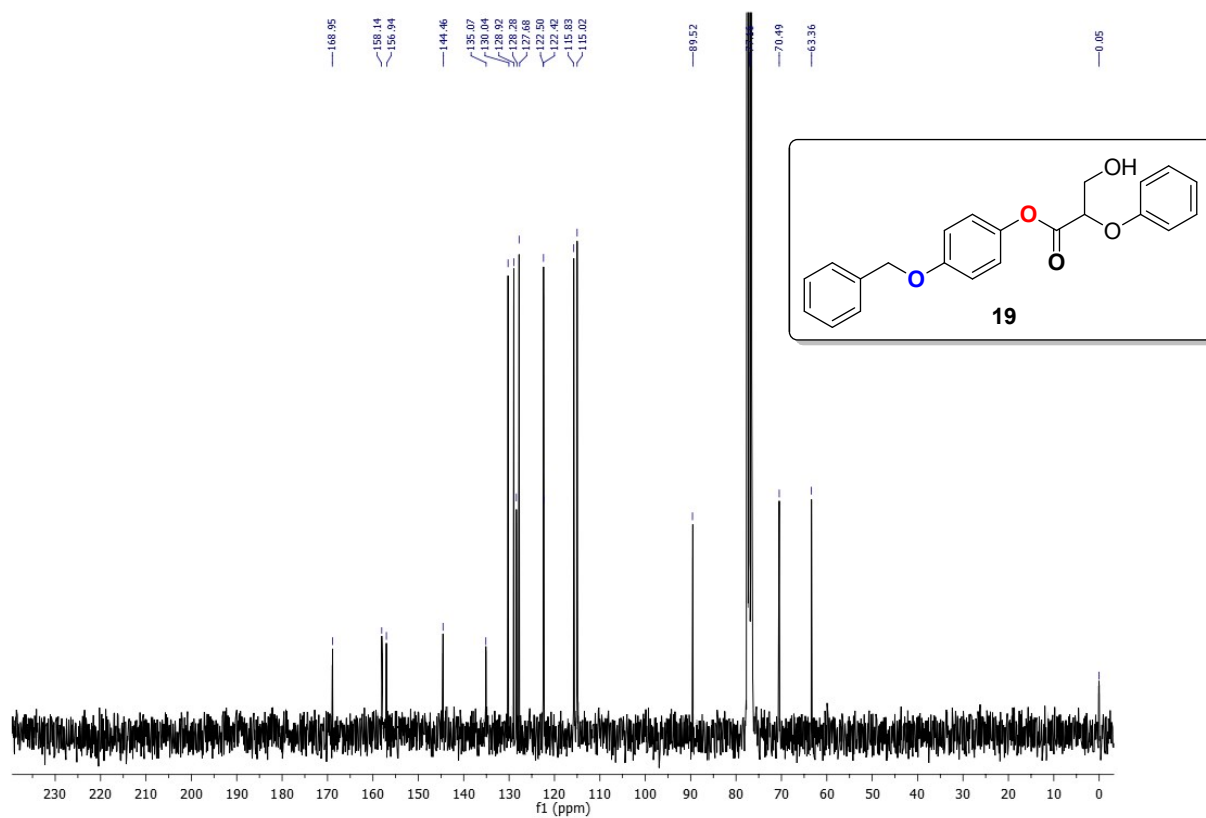
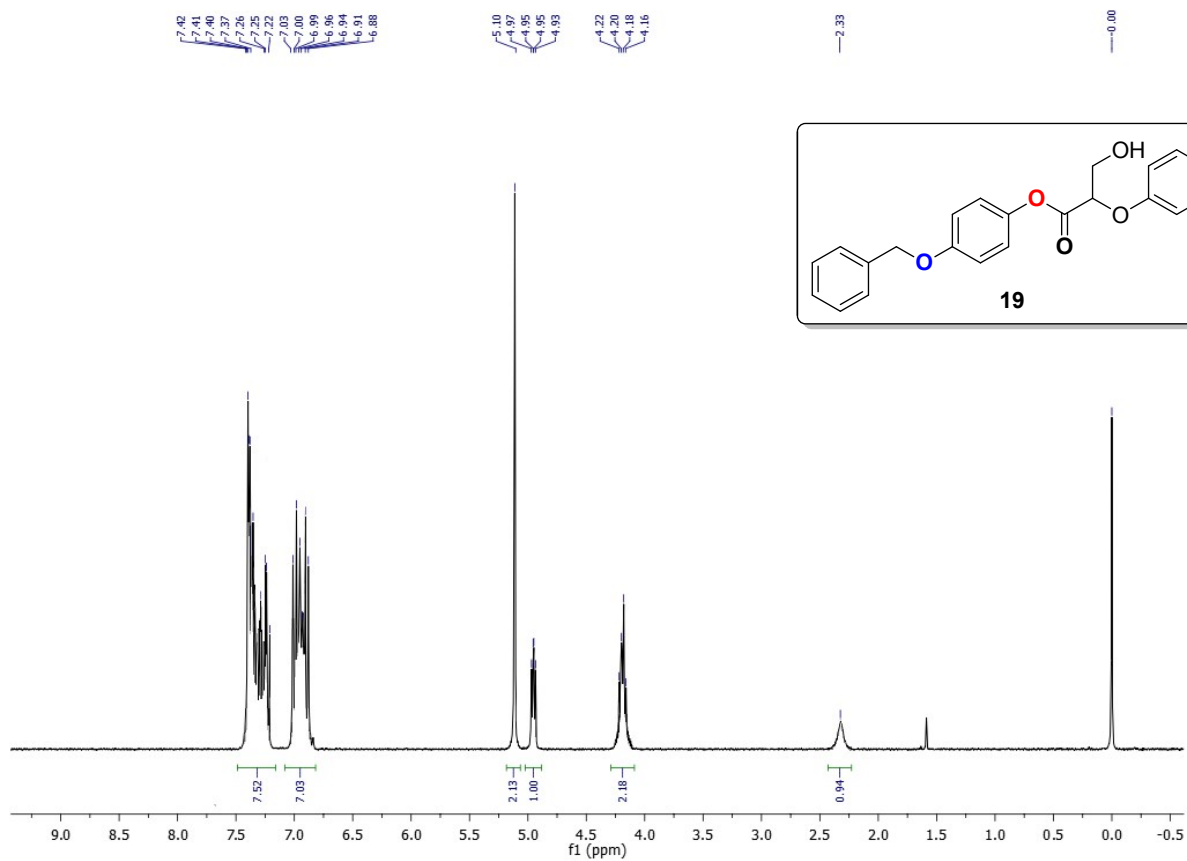


Figure S23. ¹³C NMR Spectrum of **18** (75 MHz, CDCl₃).



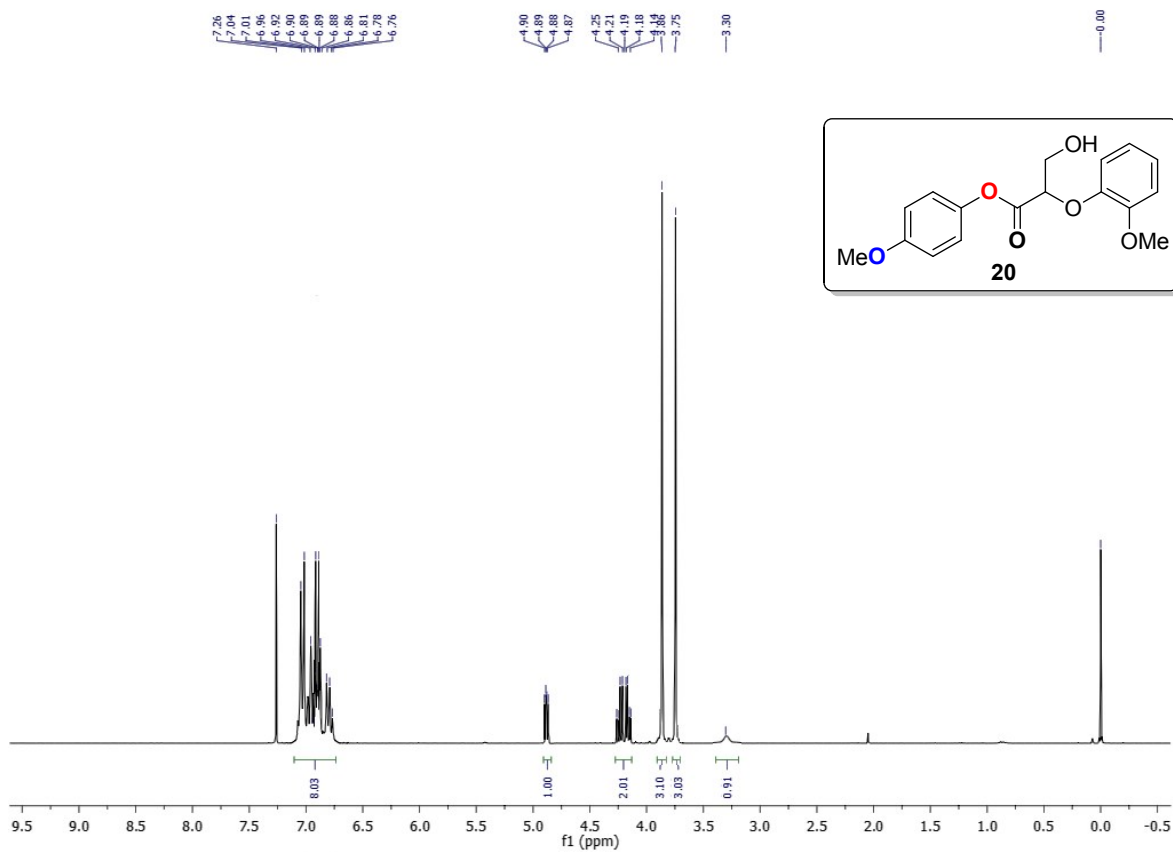


Figure S26. ¹H NMR Spectrum of **20** (300 MHz, CDCl₃).

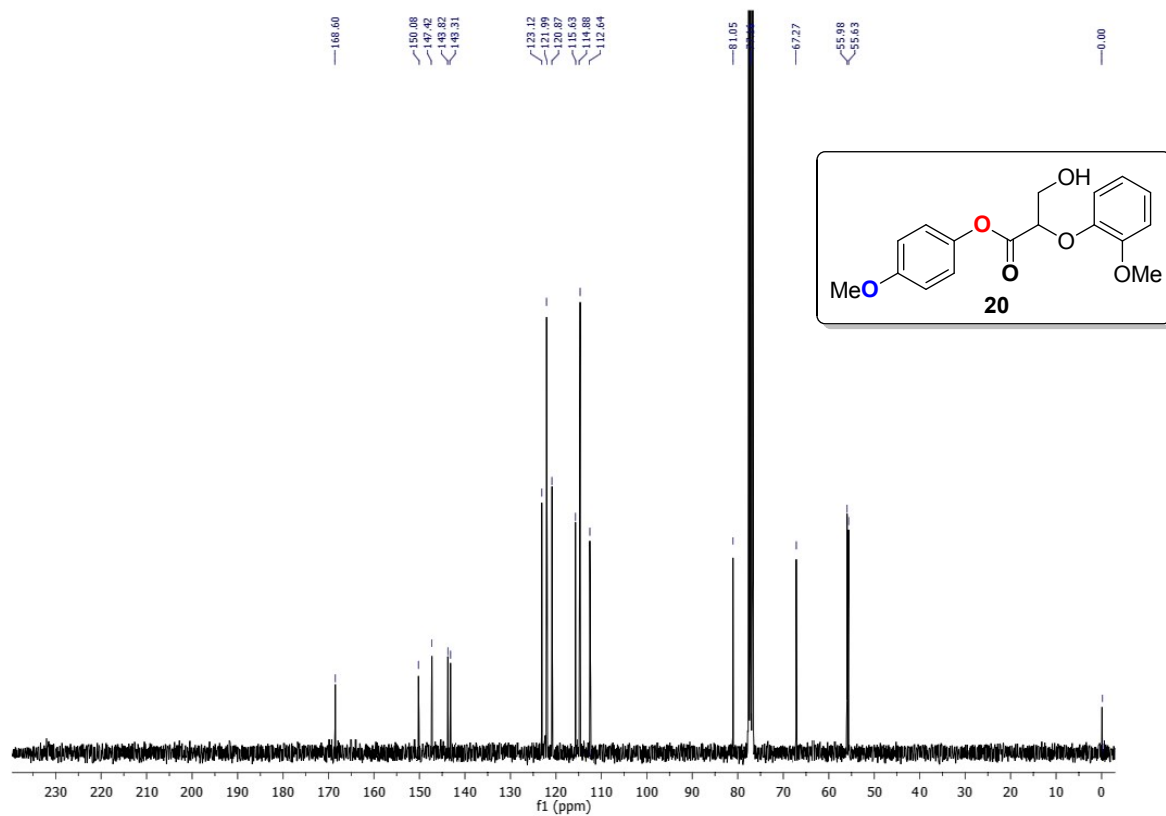


Figure S27. ¹³C NMR Spectrum of **20** (75 MHz, CDCl₃).

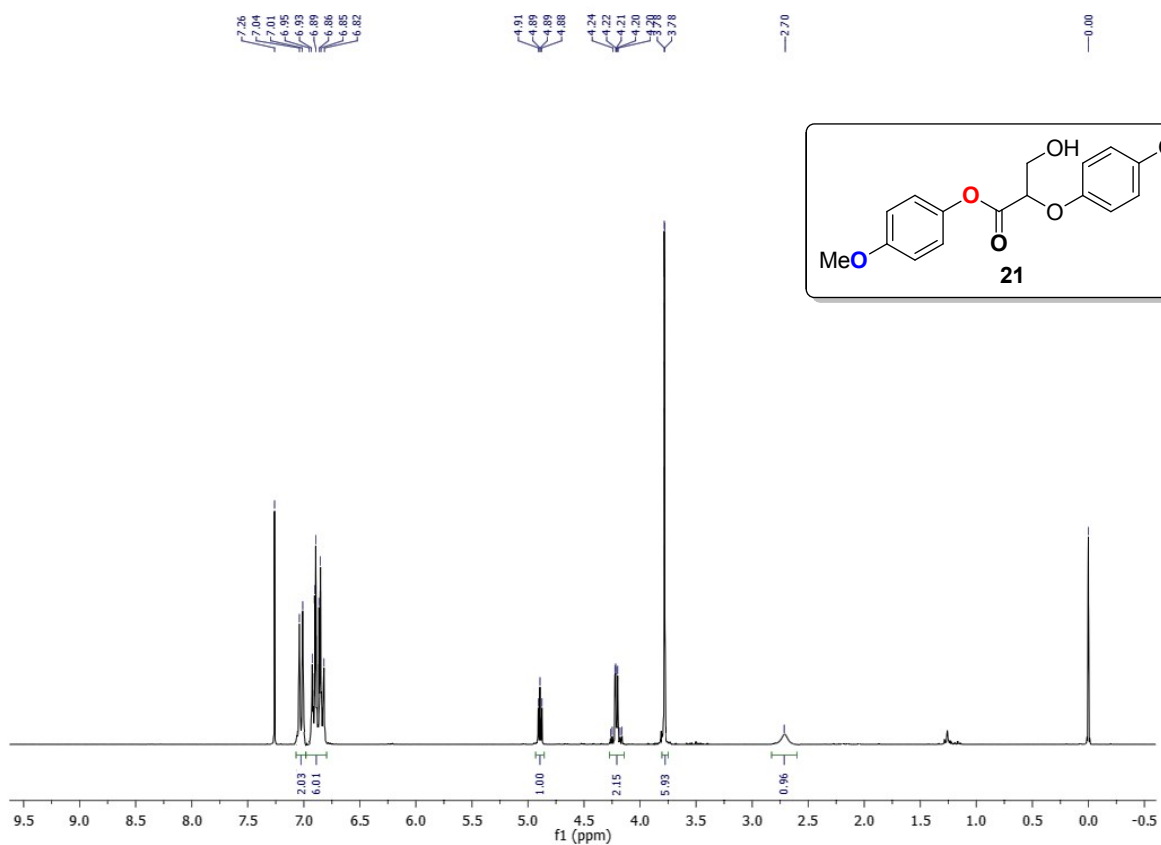


Figure S28. ¹H NMR Spectrum of **21** (300 MHz, CDCl₃).

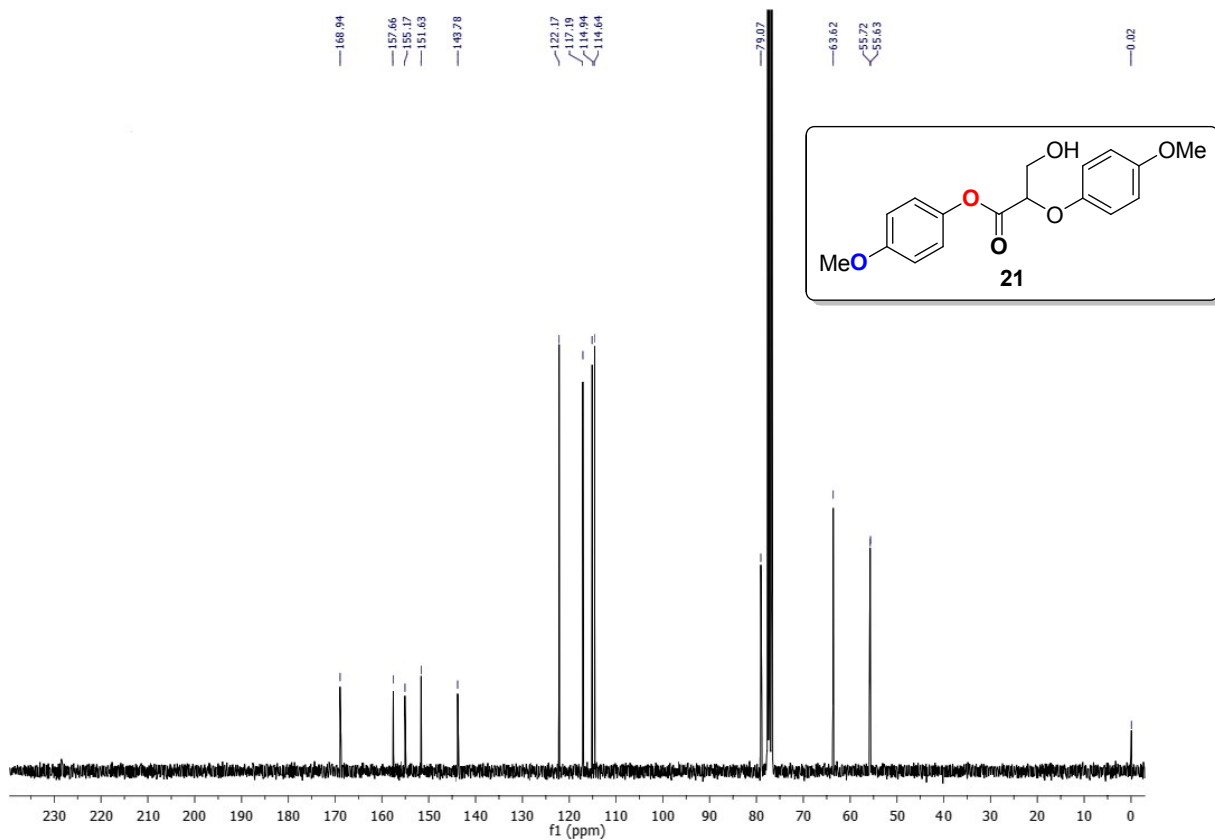


Figure S29. ¹³C NMR Spectrum of **21** (75 MHz, CDCl₃).

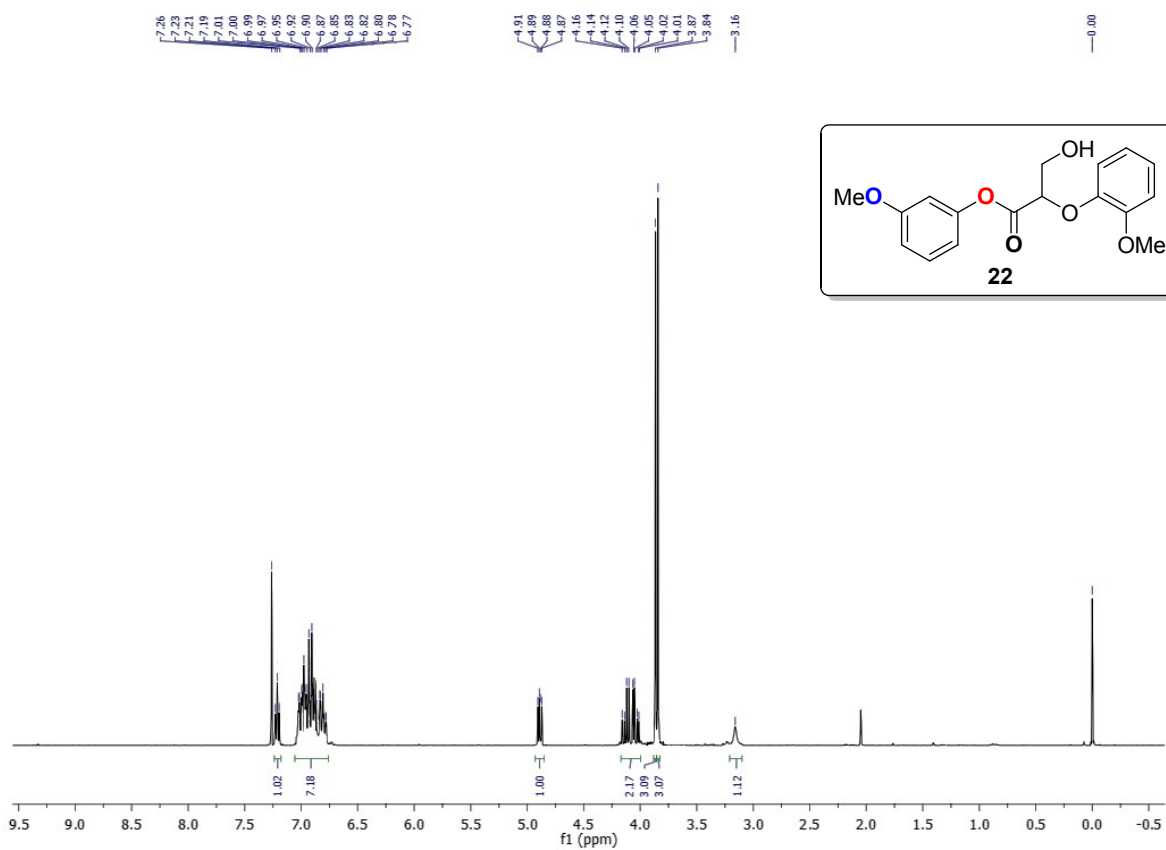


Figure S30. ¹H NMR Spectrum of **22** (300 MHz, CDCl₃).

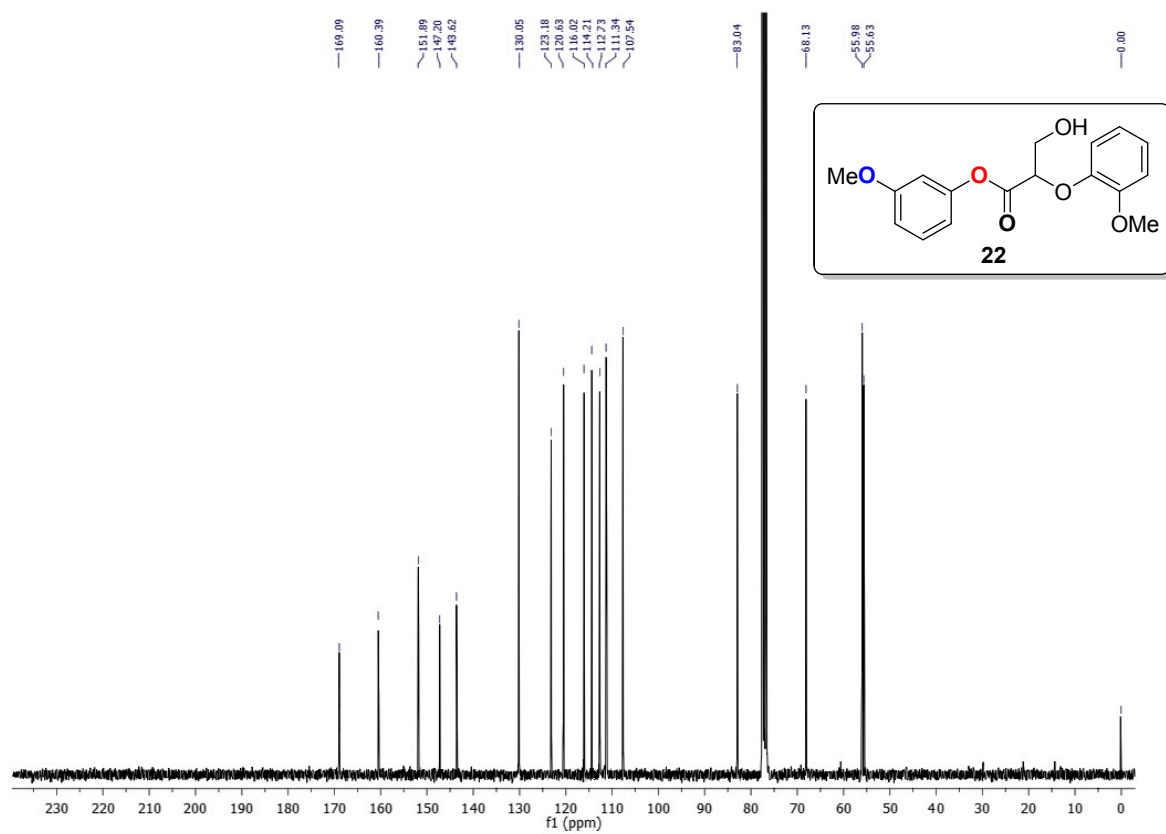


Figure S31. ¹³C NMR Spectrum of **22** (75 MHz, CDCl₃).

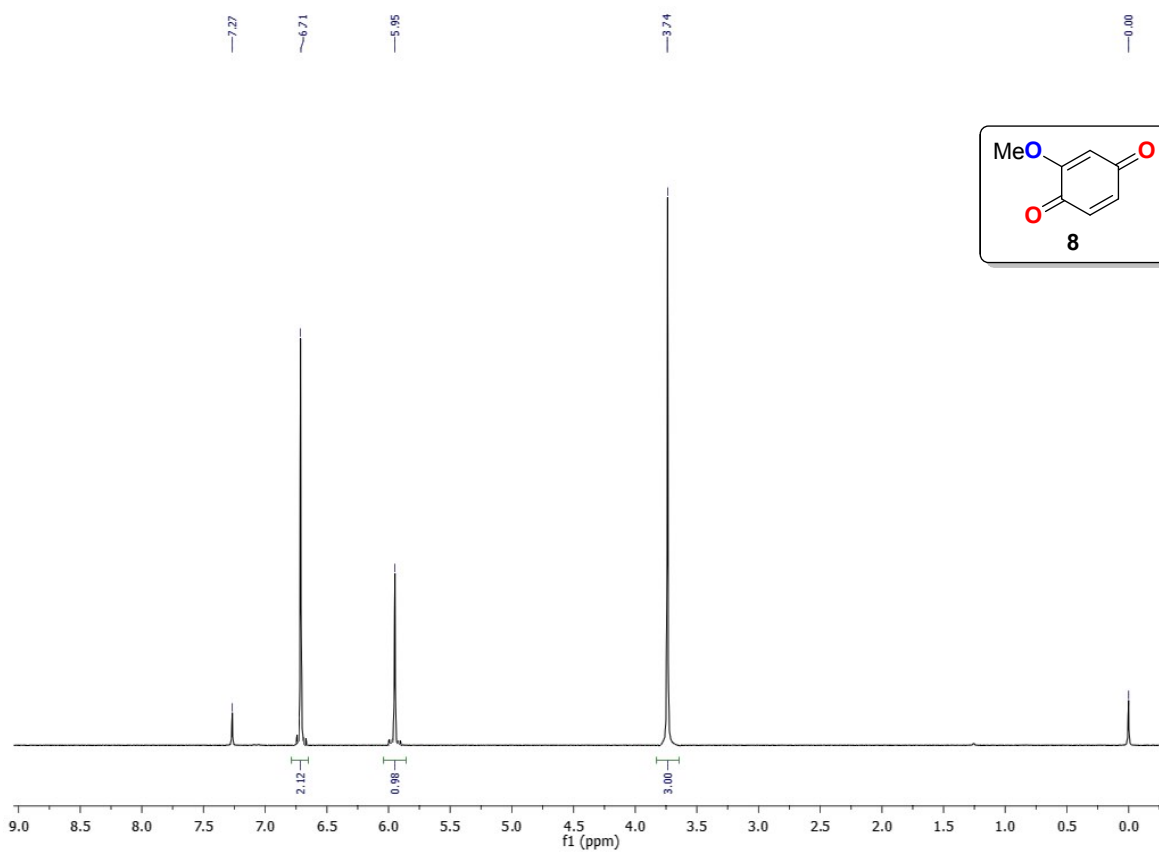


Figure S32. ¹H NMR Spectrum of **8** (300 MHz, CDCl₃).

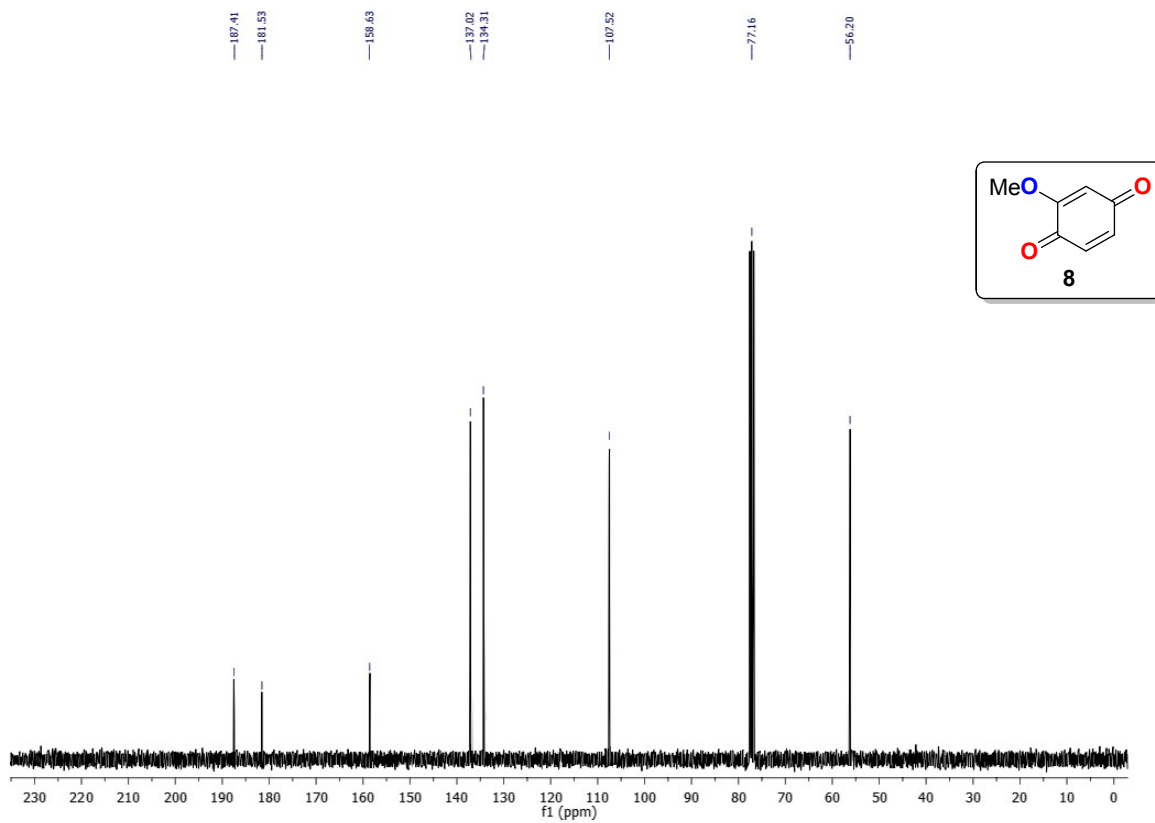


Figure S33. ¹³C NMR Spectrum of **8** (75 MHz, CDCl₃).

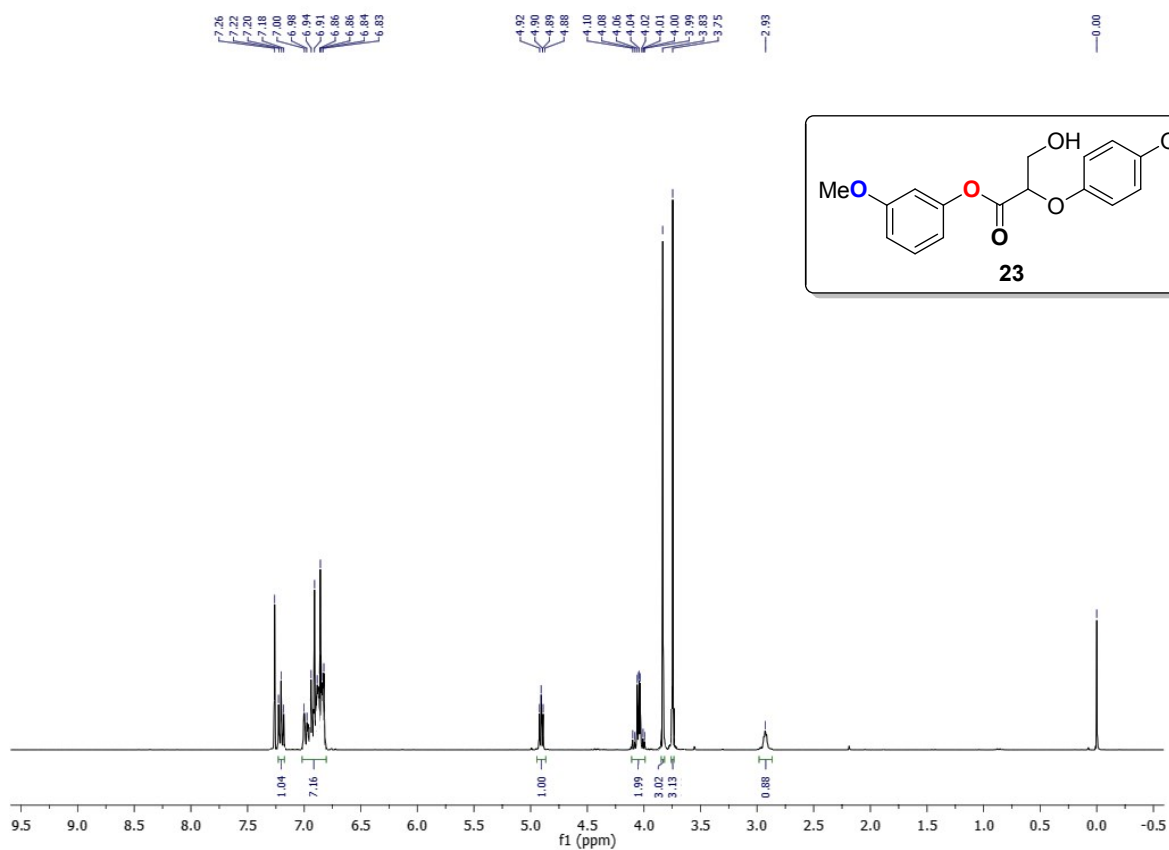


Figure S34. ^1H NMR Spectrum of **23** (300 MHz, CDCl_3).

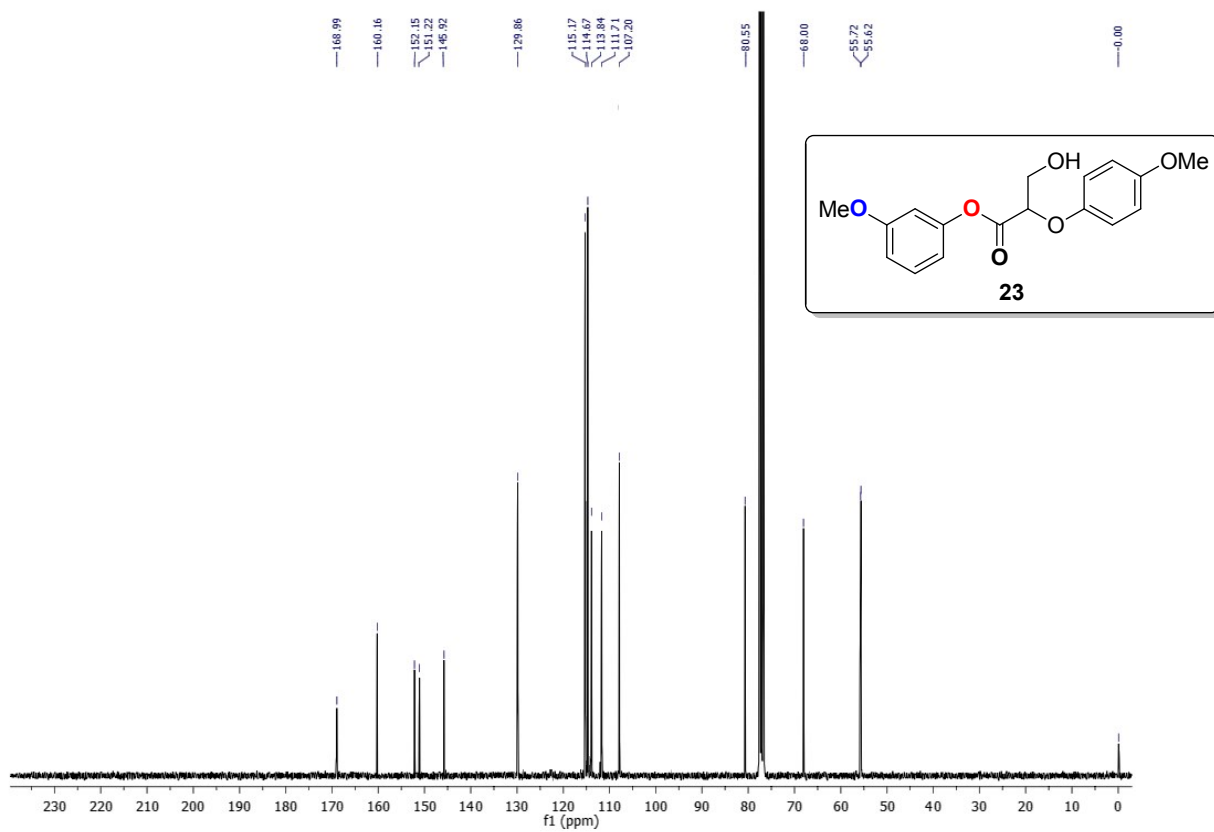


Figure S35. ^{13}C NMR Spectrum of **23** (75 MHz, CDCl_3).

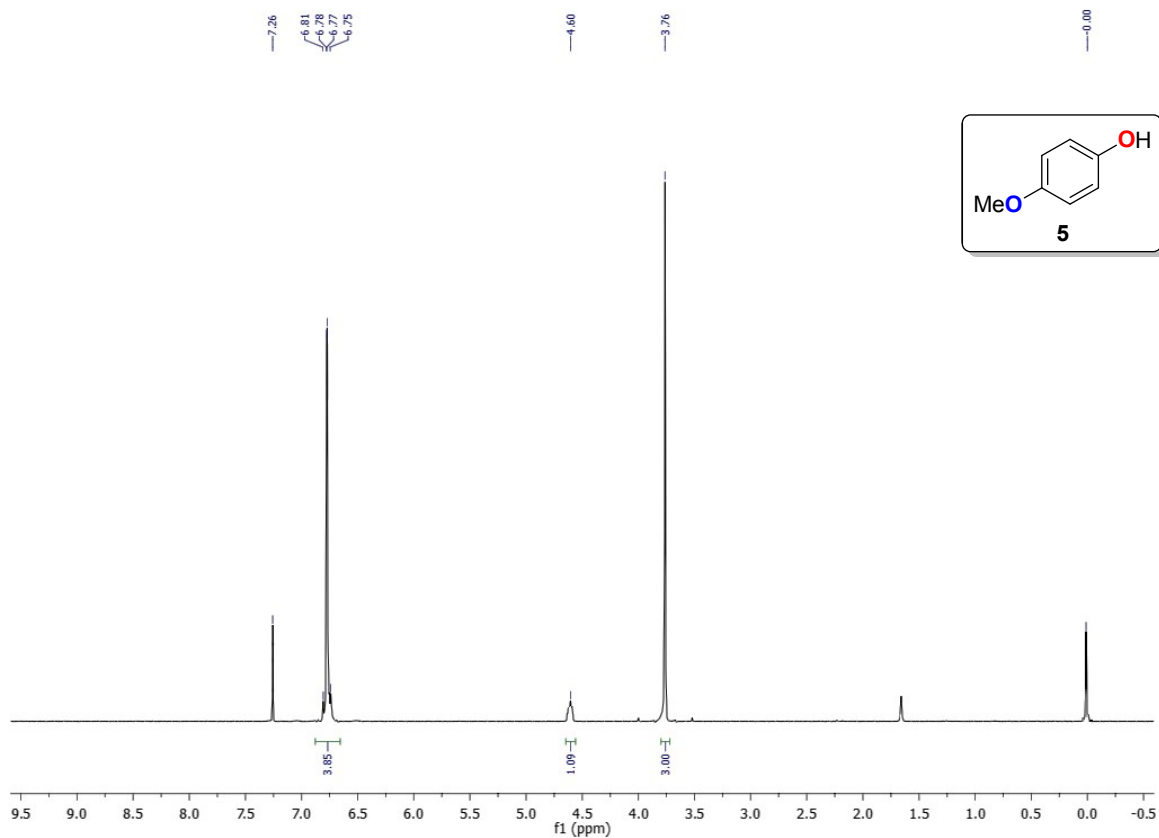


Figure S36. ^1H NMR Spectrum of **5** (300 MHz, CDCl_3).

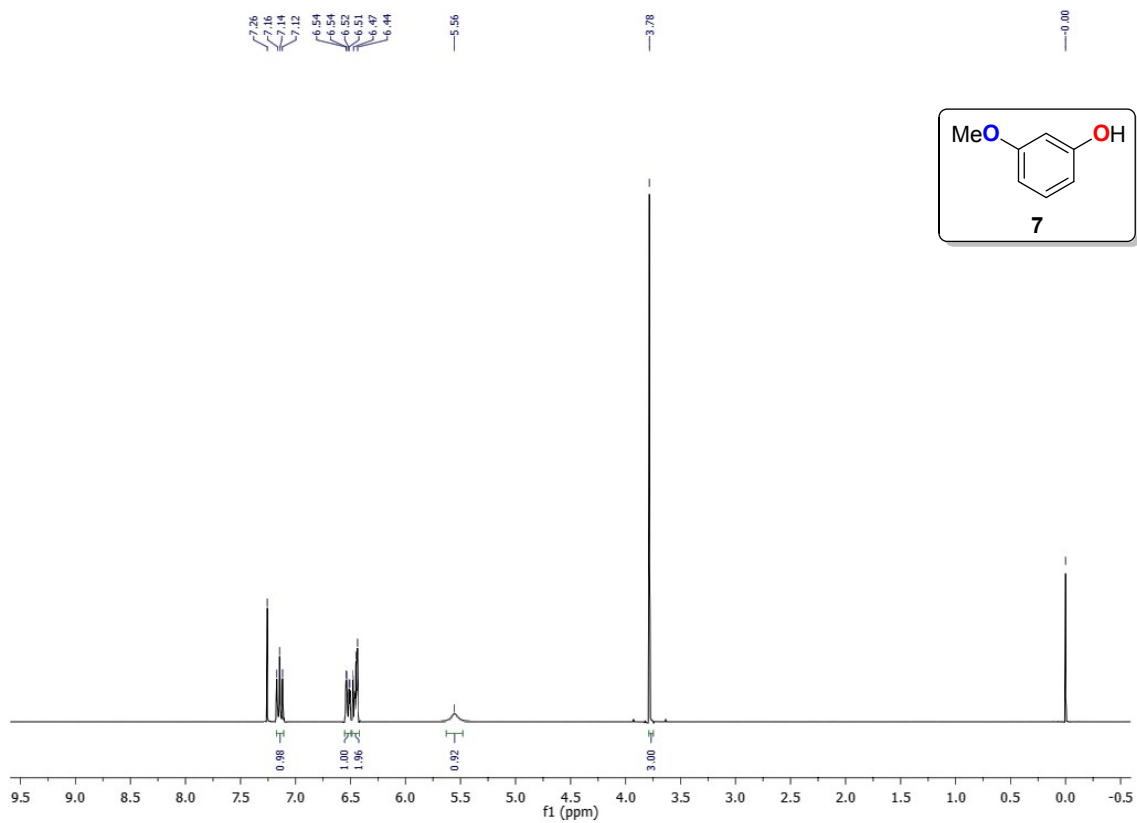


Figure S37. ^1H NMR Spectrum of **7** (300 MHz, CDCl_3).

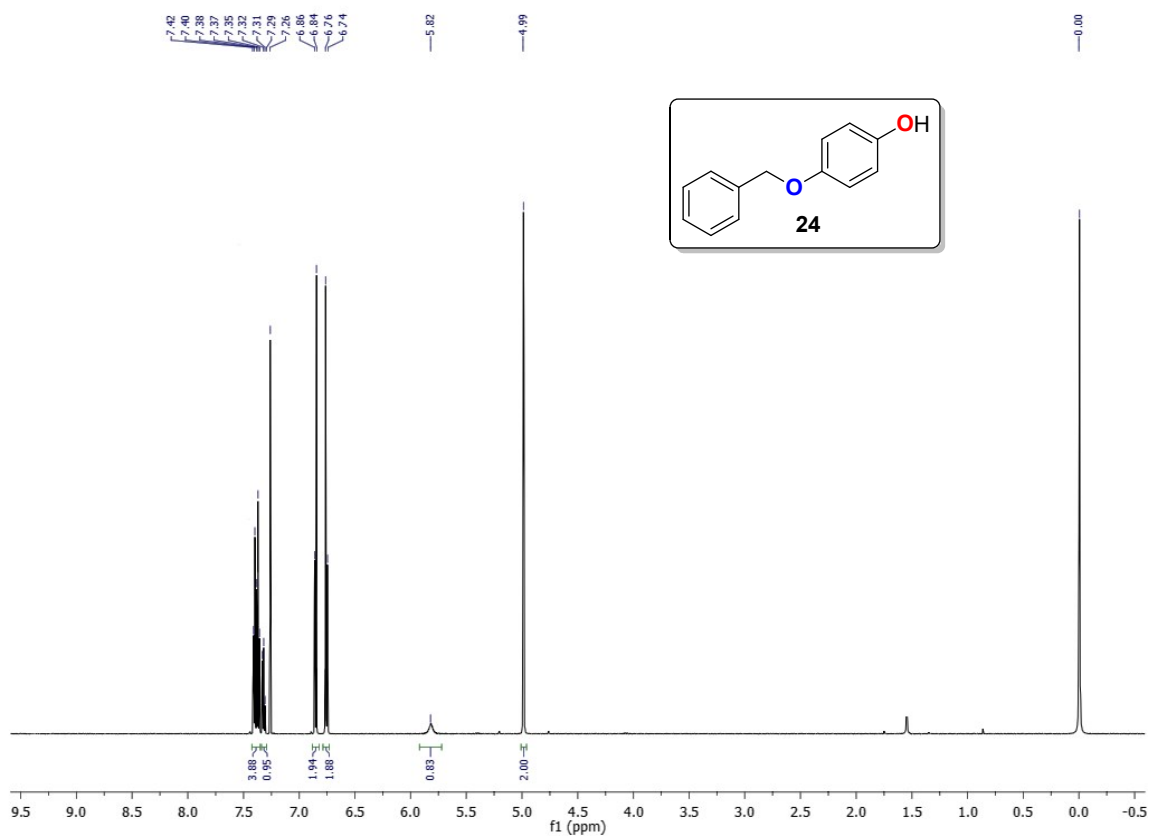


Figure S39. ^1H NMR Spectrum of **24** (300 MHz, CDCl_3).