Catalytic C-O Bond Cleavage of 2-Aryloxy-1-arylethanols and Its Application to the Depolymerization of Lignin Related Polymers

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Supporting Information (23 pages)

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1. General Experimental

Unless otherwise noted, reactions and manipulations were carried out under inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres inert atmosphere glove box at ambient temperature. ^{1}H and ^{13}C{^{1}H} spectra were recorded on Bruker AVB-400, AVQ-400, AV-500, or AV-600 spectrometers. All NMR chemical shifts are reported as δ in parts per million (ppm) relative to the residual solvent signal. IR spectra were measured neat on a Nicolet iS10 FT-IR spectrometer with a diamond attenuated total reflective (ATR) accessory. Peak intensities are reported as broad (b), weak (w), medium (m), or strong (s). Only peaks in the functional group region (4000–1300 cm–1) are reported. Mass spectral data were obtained at the QB3 Mass Spectrometry Facility operated by the College of Chemistry, University of California, Berkeley. Fast atom bombardment mass spectra were recorded on a Micromass ZAB2-EQ magnetic sector instrument. Electron impact (EI) mass spectra were recorded on a Micromass ProSpec magnetic sector instrument equipped with an EI source. Low-resolution gas chromatography/mass spectrometry (GC-MS) was performed on a Varian 3800 gas chromatograph equipped with a Varian 320 triple-quad mass selective detector. Gel permeation chromatography was performed on Polymer Laboratories GPC 50 Plus equipped with two 300 mm Resipore 3 Å columns using refractive index detection (elution conditions: 1 mL/min THF/0.25% BHT @ 30 ℃). All reagents were used as received from commercial suppliers unless otherwise noted. Xylenes were purchased as an isomeric mixture from Aldrich. Toluene was passed

through a column of activated alumina (type A2, size 12 x 32, Purify Co.) under nitrogen pressure and sparged with nitrogen before use. Xylenes and toluene-d_8 were degassed/dried by distillation from CaH_2 under an inert atmosphere. 1,4-dioxane was degassed/dried by vacuum transfer from sodium metal with benzophenone indicator.

2. Substrate preparation.

Substrate preparation was not performed using a glovebox. All reactions were carried out in oven-dried, nitrogen-flushed glassware. 2-Aryloxy-1-phenethanols **2a**-**2e** were prepared in a two-step sequence from the corresponding phenol and 2-bromoacetophenone according to the method of Franz and co-workers.[1] The sequence began with a base promoted etherification to yield the 2-aryloxyacetophenones **4a**-**4e** followed by sodium borohydride reduction. Polymer **3** was prepared in a three-step sequence according to the procedure of Ubukata and co-workers.[2] The sequence began with the radical bromination of 4'-hydroxyacetophenone. A base promoted condensation of 4'-hydroxy-2-bromoacetophenone yielded poly(4'-hydroxyacetophenone) and global reduction using sodium borohydride yielded **3**.

Representative Procedure: 2-(2-methoxyphenyl)oxy-1-phenethanol (2b). Step 1: A round bottom flask equipped with a reflux condenser was charged with 2-bromoacetophenone (11.8 g, 59.4 mmol), potassium carbonate (12.3 g, 89.1 mmol), guaiacol (8.2 mL, 74.2 mmol), and acetone (250 mL). The resulting suspension was stirred and heated to reflux for 3 h, after which it was filtered through Celite and concentrated in vacuo. The resulting solid was crystallized from ethanol to give 10.6 g of 2-(2-methoxyphenyl)oxy-acetophenone (**4b**) as white crystals (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.99-6.81 (m, 4H), 5.33 (s, 2H), 3.86 (s, 3H). Step 2: A round bottom flask was charged with **4b** (1.50 g, 6.19 mmol), tetrahydrofuran (28 mL), and water (7 mL). Sodium borohydride (469 mg, 12.4 mmol) was added portion-wise to maintain a gentle evolution of gas over 5 minutes, after which the reaction mixture was stirred for 3 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (50 mL) and then the reaction mixture was diluted with water (50 mL). The aqueous portion was extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give 1.20 g of **2b** as a white solid (79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 7.3 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.06 - 7.02 (m, 1H), 6.99 -6.90 (m, 3H), 5.16 (d, J = 9.3 Hz, 1H), 4.22 (dd, J = 10.1, 2.9 Hz, 1H), 4.03 (t, J = 9.7 Hz, 1H), 3.91 (s, 3H), 3.70 (d, J = 1.7 Hz, 1H); ^{13}C{^{1}H} (126 MHz, $CDCl_3$) δ 150.2, 148.0, 139.6, 128.5,

[1] Kandanarachchi, P. H.; Autrey, T.; Franz, J. A. *J. Org. Chem.* **2002**, *23,* 7937-7945.
[2] Kishimoto, T.; Uraki, Y.; Ubukata, M. *Org. Biomol. Chem.* **2005**, *6*, 1067-1073.

128.0, 126.3, 122.6, 121.1, 116.1, 112.1, 76.3, 72.4, 55.9; HRMS (ESI) Exact mass calcd for $C_{15}H_{16}O_3Na$ $[M+Na]^+$: 267.0997, found: 267.0992 m/z.

2-phenoxy-1-phenethanol (2a). Step1: Using the representative procedure, 2-phenoxyacetophenone (**4a**) was prepared from phenol (5.90 g, 62.7 mmol) and 2-bromoacetophenone (10.0 g, 50.2 mmol) as 10.1 g of a white amorphous solid (95%). ^{1}H NMR (400 MHz, d_8-PhMe) δ 7.74 (d, J = 8.4 Hz, 2H), 7.14 - 7.02 (m, 5H), 6.82 - 6.79 (m, 3H), 4.64 (s, 2H). Step 2: Using the representative procedure, compound **2a** was prepared from **4a** (2.00 g, 9.42 mmol) as 1.78 g of a white amorphous solid (88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.4 Hz, 2H), 7.42 (t, J = 7.4 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 5.16 (d, J = 8.9 Hz, 1H), 4.14 (dd, J = 9.6, 3.1 Hz, 1H), 4.04 (t, J = 9.3 Hz, 1H), 2.81 (d, J = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.4, 139.7, 129.6, 128.6, 128.2, 126.3, 121.3, 114.7, 73.3, 72.6. Data are consistent with previously reported data.[1]

2-(2,6-dimethoxyphenyl)oxy-1-phenethanol (2c). Step1: Using the representative procedure, 2-(2,6-dimethoxyphenyl)oxy-acetophenone (**4c**) was prepared from 2,6-dimethoxyphenol (2.50 g, 12.6 mmol) and 2-bromoacetophenone (2.46 g, 15.7 mmol) as 2.10 g of a yellow crystalline solid (86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 2H), 7.62 - 7.57 (t, J = 7.7 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.03 (t, J = 8.4 Hz, 1H), 6.59 (d, J = 8.4 Hz, 2H), 5.22 (s, 2H), 3.82 (s, 6H). Step 2: Using the representative procedure, compound **2c** was prepared from **4c** (1.00 g, 4.13 mmol). Recrystallization from boiling ethanol yielded 1.92 g of **2c** as a white amorphous solid (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.09 (t, J = 8.4 Hz, 1H), 6.67 (d, J = 8.4 Hz, 2H), 5.02 (d, J = 9.9 Hz, 1H), 4.61 (d, J = 1.4 Hz, 1H), 4.48 (dd, J = 10.9, 2.7 Hz, 1H), 3.93 (s, 6H), 3.79 (dd, J = 10.0, 10.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.3, 139.5, 136.8, 128.4, 127.7, 126.4, 124.2, 105.2, 80.1, 72.5, 56.1; HRMS (ESI) Exact mass calcd for $C_{16}H_{18}O_4Na$ $[M+Na]^+$: 297.1100, found: 297.1097 m/z.

2-phenoxy-1-(4-methoxyphenyl)-ethanol (2d). Step1: Using the representative procedure, 2-phenoxy-4'-methoxyacetophenone (**4d**) was prepared from phenol (2.57 g, 27.3 mmol) and 2-bromo-4'-methoxyacetophenone (5.00 g, 21.8 mmol) as 4.26 g of a white amorphous solid (81%). ^{1}H NMR (400 MHz, d_8-PhMe) δ 7.81 (d, J = 6.8 Hz, 2H), 7.14 - 7.07 (m, 3H), 6.87 - 6.80 (m, 3H), 6.61 - 6.58 (m, 2 H), 4.70 (s, 2H), 3.24 (s, 3H). Step 2: Using the representative procedure, compound **2d** was prepared from **4d** (2.10 g, 10.7 mmol) to yield 950 mg of a white amorphous solid (95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.4 Hz, 2H), 6.98 (d, J = 8.6 Hz, 4H), 5.11 (dt, J = 5.9, 2.7 Hz, 1H), 4.11 (dd, J = 9.6, 3.4 Hz, 1H), 4.06 (dd, J = 9.1, 9.3 Hz, 1H), 3.86 (s, 3H), 3.07 (d, J = 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.5, 158.5, 132.0, 129.6, 127.7, 121.3, 114.7, 114.0, 73.3, 72.2, 55.4 ; HRMS (ESI) Exact mass calcd for $C_{15}H_{16}O_3Na$ $[M+Na]^+$: 267.0994, found: 267.0994 m/z.

2-(2-methoxyphenyl)oxy-1-(3,4-dimethoxyphenyl)-ethanol (2e). Step1: Using the representative procedure, 2-(2-methoxyphenyl)oxy-3',4'-dimethoxyacetophenone (**4e**) was prepared from 2-methoxyphenol (3.40 g, 27.4 mmol) and 2-bromo-3',4'-dimethoxyacetophenone (5.96 g, 22.0 mmol) as 4.01 g of a white amorphous solid (60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.97 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.93 (dd, *J* = 10.5, 4.6 Hz, 2H), 6.88 - 6.88 (m, 2H), 5.32 (s, 2H), 3.96 (s, 3H) 3.94 (s, 3H), 3.90 (s, 3H). Step 2: Using the representative procedure, compound **2e** was prepared from **4e** (4.00 g, 13.2 mmol). Recrystallization from boiling ethanol yielded 2.40 g of a white crystalline solid (60%).[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 - 7.01 (m, 2H), 6.98 - 6.93 (m, 4H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.09 (d, *J* = 9.2 Hz, 1H), 4.19 (dd, *J* = 10.0, 1.9 Hz, 1H), 4.01 (t, *J* = 9.7 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 6H), 3.57 (s, 1H); ^{13}C{^{1}H} (126 MHz, $CDCl_3$) δ 150.1, 149.1, 148.7, 148.0, 132.2, 122.5, 121.1, 118.6, 115.9, 112.0, 111.0, 109.4, 76.3, 72.1, 56.0, 55.9, 55.8. Data are consistent with previously reported data.[4]

Poly(4'-hydroxy-1-phenethanol) (3). Prepared from 4'-hydroxyacetophenone using the procedure reported by Ubukata and co-workers.[2] GPC data were collected on the per-acylated polymer as described by the same authors. All other data were collected for the unmodified polymer. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.33 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 7.5 Hz, 2H), 5.52 (bs, 1H), 4.85 (bs, 1H), 3.96 (bs, 1H), 1.28 (d, *J* = 5.5 Hz, terminal CH_3); GPC (acylated) M_n – 4288, M_w – 7045, PD – 1.64; IR (cm^{-1}) 3376 (b), 2916 (w), 2855 (w), 1608 (m), 1506 (s). Data are consistent with previously reported data.[2]

Synthesis of 2-methoxy-1-phenoxy-1-phenylethane (8). A round bottom flask was charged with 2-phenoxy-1-phenylethanol (505 mg, 2.35 mmol) and tetrahydrofuran (12 mL). The resulting solution was cooled to 0 ºC and sodium hydride (94 mg, 60 wt% in mineral oil, 2.35 mmol) was added in one portion. The resulting suspension was stirred at 0 ºC for 1.5 h after which iodomethane (0.15 mL, 2.47 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred overnight, and the reaction was quenched with half-saturated aqueous sodium bicarbonate solution. The aqueous layer was extracted twice with ethyl acetate. The combined organic extracts were washed twice with brine, dried over $MgSO_4$, filtered, concentrated *in vacuo*, and purified by silica gel chromatography (gradient elution, 5-12% EtOAc in hexanes) yielding **8** as 534 mg of a yellow oil (99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.32 (m, 5H), 7.27 (t, *J* = 8.0 Hz, 2H), 6.97-6.90 (m, 3H), 4.61 (dd, *J* = 3.6, 7.9 Hz, 1H), 4.19 (dd, *J* = 8.0, 10.3 Hz, 1H), 4.02 (dd, *J* = 3.6, 10.3 Hz, 1H); ^{13}C{^{1}H}

[3] Residual amounts of CH_2Cl_2, or ethanol, were found to be deleterious to the ruthenium-catalyzed reaction. Recrystallization from mesitylene can also be used to purify the 2-aryloxy-1-arylethanol derivatives and remove these impurities.

[4] Schultz, T. P.; Fisher, T. H. *Holzforschung* **2002**, *6,* 592-594.

NMR (125 MHz, $CDCl_3$) δ 158.8, 138.7, 129.6, 128.8, 128.4, 127.2, 121.1, 114.9, 82.4, 72.4, 57.4; HRMS (FAB) Exact mass calcd for $C_{15}H_{16}O_2$ $[M]^+$: 228.1150, found 228.1152.

3. Disproportionation/Depolymerization Conditions

Disproportionation procedure for 2a-2e. In a glovebox, 2-aryloxy-1-phenethanol (1.00 mmol), $RuH_2(CO)(PPh_3)_3$ (0.01 mmol), and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (0.01 mmol) were diluted in anhydrous xylenes (2.50 mL). The reaction mixture was sealed in a 10 mL Biotage Microwave reaction vial with an aluminum crimp-top. The sealed vial was heated to 135 °C for 4 h. The reaction mixture was cooled to room temperature and the acetophenone product was obtained by silica gel chromatography of the crude reaction mixture (gradient elution, 7-60% EtOAc in hexanes).

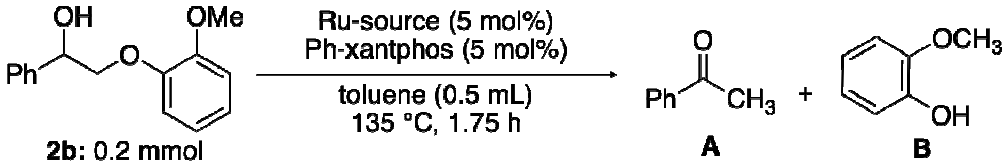
Depolymerization procedure for 3. Poly(4'-hydroxy-1-phenethanol) (20 mg, 0.15 mmol), $RuH_2(CO)(PPh_3)_3$ (6.9 mg, 7.5 μmol), and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (4.3 mg, 7.5 μmol) were diluted in anhydrous 1,4-dioxane (0.50 mL). The reaction mixture was sealed in a 10 mL Biotage Microwave reaction vial with an aluminum crimp-top. The sealed vial was heated to 175 °C for 3 h.[5] The reaction mixture was then cooled to room temperature and the crude reaction mixture was purified by silica gel chromatography (gradient elution, 7-60% EtOAc in hexanes) to yield 4'-hydroxyacetophenone as a white solid (20 mg, 99%).

4. Reaction Optimization.

General Procedure. The reaction media for Tables S1 and S2 were prepared as stock solutions (Solution-1) of **2b** (976 mg, 4.00 mmol) and 1,2,4,5-tetramethylbenzene (268 mg, 2.00 mmol)[6] prepared in a volumetric flask (10.00 mL) using toluene as the diluent. The reaction media for Tables S4, S6, and S7 were prepared as stock solutions (Solution-2) of **2b** (976 mg, 4.00 mmol) and 1,2,4,5-tetramethylbenzene (268 mg, 2.00 mmol) prepared in a volumetric flask (10.00 mL) using xylenes as the diluent. Preparations of reaction mixtures using these media were performed in a glovebox. Once prepared, each individual reaction mixture was sealed in a 10 mL Biotage Microwave reaction vial with an aluminum crimp-top. The sealed vial was then heated to the reported temperature for the reported time and allowed to cool to ambient temperature. An analytical sample was prepared for each sample by diluting an aliquot of the reaction mixture (25 μL) in acetone (2.00 mL). All samples were analyzed for acetophenone (**A**) and guaiacol (**B**) by GC-MS and quantitated against the internal standard.

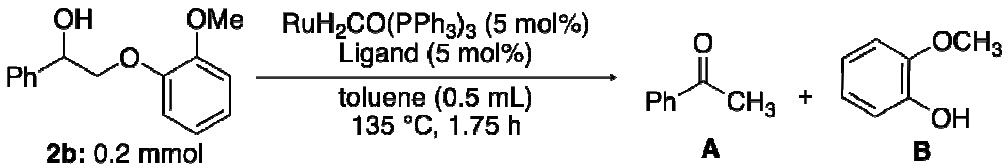
[5] Heating the polymer without catalyst at 150 °C for 3 h resulted in no observed formation of depolymerization products.
[6] Internal standard.

Table S1. **Variation of ruthenium source.** A stock solution (Solution-3) of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (29 mg, 0.050 mmol) was prepared using Solution-1 as the diluent (2.500 mL). The reactions were prepared by diluting the ruthenium source (0.01 mmol) in Solution-3 (0.500 mL).



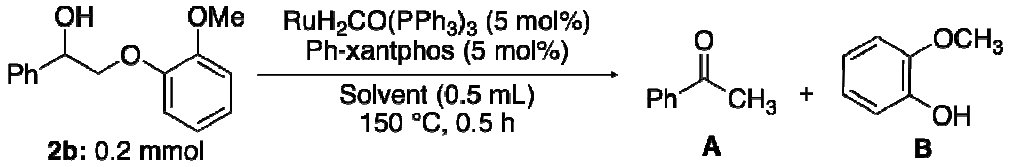
Entry	Ru-source	Yield (%) A	B
1	none	0	0
2	$RuH_2(CO)(PPh_3)_3$	>99	>99
3	$RuHCl(CO)(PPh_3)_3$	0	0
4	$Ru(CF_3CO_2)_2(CO)(PPh_3)_3$	0	0
5	$RuH(CF_3CO_2)(CO)(PPh_3)_3$	0	0
6	$RuH_2(PPh_3)_4$	36	38
7	$Ru_3(CO)_{12}$	0	0
8	$Ru(methallyl)_2(cod)$	13	10

Table S2. **Variation of wide-bite angle ligand.** A stock solution (Solution-4) of $RuH_2(CO)(PPh_3)_3$ (46 mg, 0.050 mmol) was prepared using Solution-1 (2.500 mL) as the diluent. The reactions reported in Table S2 were prepared by diluting the ligand (0.01 mmol) in Solution-4 (0.500 mL).



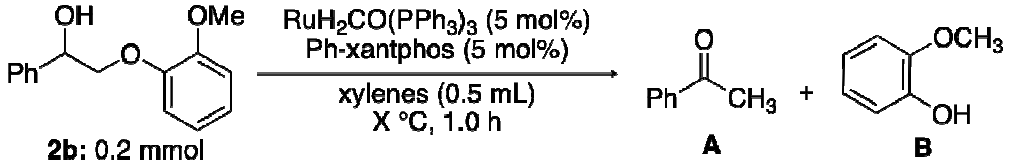
Entry	Ligands	Yield (%) A	B
1	DPE-phos	0	0
2	Ph-Xantphos	73	73
3	Et-Xantphos	32	34
4	DBF-phos	2	0

Table S3. **Variation of solvent.** Each entry was prepared by diluting **2b** (48.8 mg, 0.20 mmol), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.100 mmol), $RuH_2(CO)(PPh_3)_3$ (9.2 mg, 0.010 mmol), and bis(diphenylphosphino)-9,9-dimethylxanthene (5.8 mg, 0.010 mmol) in the reported solvent (0.500 mL). The reaction was run at 150 °C so that all solvents were heated above their respective boiling points at atmospheric pressure.



Entry	Solvent (bp @ 1 atm)	Yield (%) A	B
1	xylenes (138-144 °C)	87	84
2	toluene (115 °C)	67	62
3	1,4-dioxane (101 °C)	71	65
4	tetrahydrofuran (66 °C)	72	69
5	*tert*-butanol (82 °C)	77	75
6	acetonitrile (82 °C)	0	2

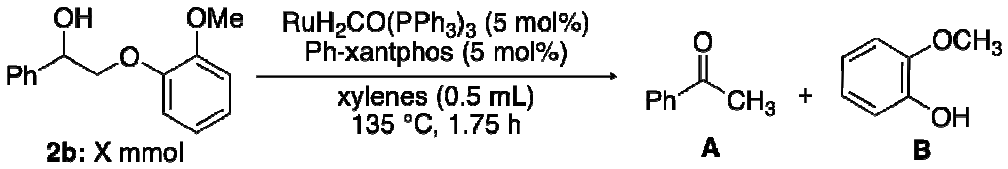
Table S4. **Variation of temperature.** A stock solution (Solution-5) was prepared by diluting $RuH_2(CO)(PPh_3)_3$ (46 mg, 0.050 mmol) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (29 mg, 0.050 mmol) in Solution-2 (2.500 mL). Each entry was prepared by transferring Solution-5 (0.500 mL) to the reaction vessel. [7]



Entry	Reaction Temp (°C)	Yield (%) A	B
1	100	4	3
2	125	46	43
3	150	83	83
4	175	86	84

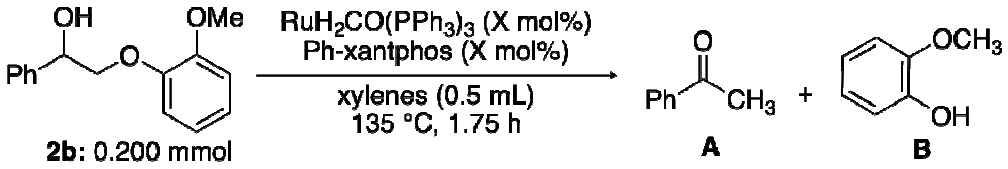
[7] 135 °C was chosen as it is with the boiling point range of xylenes.

Table S5. **Variation of absolute concentration.** A stock solution (Solution-6) was prepared by diluting $RuH_2(CO)(PPh_3)_3$ (46 mg, 0.050 mmol) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (29 mg, 0.050 mmol) in Solution-2 (2.500 mL). A second stock solution (Solution-7) was prepared with 1,2,4,5-tetramethylbenzene (134 mg, 1.00 mmol) in a volumetric flask (5.000 mL) using xylenes as the diluent. The entries in Table S5 were prepared by dilution of a given volume of Solution-6 with Solution-7 to volume (0.5 mL) as follows: Entry 1 – Solution 6 (75 μL, 0.030 mmol **2b**), Entry 2 – (150 μL, 0.060 mmol 2a), Entry 3 – (300 μL, 0.150 mmol **2b**). Entry 4 was prepared by dissolving **2b** (24.4 mg, 0.100 mmol) in Solution 6 (500 μL).[8]



Entry	[**2b**]	Yield (%) **A**	**B**
1	0.06	43	38
2	0.12	61	60
3	0.30	77	81
4	0.60	93	>99

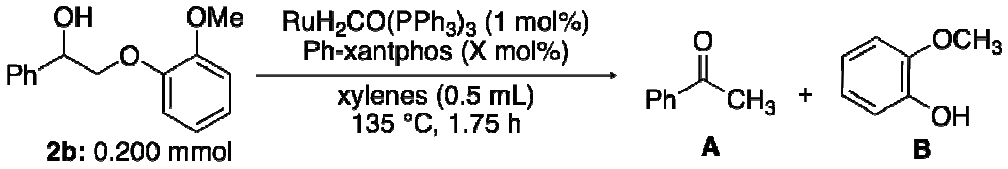
Table S6. **Variation of catalyst loading.** The entries in Table S6 were prepared by diluting $RuH_2(CO)(PPh_3)_3$ and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (1:1) in Solution-2 (0.500 mL) as follows: Entry 1 - $RuH_2(CO)(PPh_3)_3$ (18.4 mg, 0.020 mmol), Entry 2 - $RuH_2(CO)(PPh_3)_3$ (9.2 mg, 0.010 mmol), Entry 3 - $RuH_2(CO)(PPh_3)_3$ (1.8 mg, 5.0 μmol), Entry 4 - $RuH_2(CO)(PPh_3)_3$ (1.8 mg, 5.0 μmol) in Solution-2 (1.00 mL).



Entry	Cat. Loading (mol%)	Yield (%) **A**	**B**
1	X = 10	87	89
2	X = 5.0	83	85
3	X = 1.0	87	87
4	X = 0.5	85	87

[8] 0.4 M was chosen as the best concentration as it is the highest concentration that results in a homogeneous reaction mixture at ambient temperature.

Table S7. **Variation of ligand stoichiometry.** A stock solution (Solution-8) was prepared by diluting $RuH_2(CO)(PPh_3)_3$ (46 mg, 0.050 mmol) in Solution-2 (2.500 mL). The reactions reported in Table S6 were prepared with 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene diluted in Solution-8 (0.500 mL) as follows: Entry 1 – 2.3 mg, 2.0 μmol, Entry 2 – 4.6 mg, 4.0 μmol, Entry 3 – 11.5 mg, 10.0 μmol.



Entry	Ligand:$RuH_2(CO)(PPh_3)_3$	Yield (%) A	B
1	1:1	67	71
2	2:1	72	75
3	5:1	66	68

5. Mechanistic Experiments

Control reaction showing the necessity of a free hydroxyl group for successful disproportionation. An NMR tube was charged with $RuH_2(CO)(PPh_3)_3$ (7.3 mg, 0.008 mmol), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (4.6 mg, 0.008 mmol), **2b** (9.8 mg, 0.040 mmol), toluene-d_8 (350 μL), and a glass capillary containing 4-trifluoromethylpyridine. The NMR tube was sealed under vacuum and heated at 135 ºC for 18 min, after which 33% conversion of **2b**, 26% yield of acetophenone, and 7% yield of guaiacol were observed by ^{1}H NMR. The NMR tube was then opened and a solution of **8** (150 μL, 800 mM in toluene-d_8, 0.120 mmol) was added. The NMR tube was sealed under vacuum, heated at 135 ºC, and monitored periodically *via* ^{1}H NMR. After 3.45 h of heating, quantitative conversion of **2b** to acetophenone and guaiacol and less than 5% decomposition of **8** were observed. No phenol was detected by GC/MS analysis of the reaction mixture. The diagnostic resonances used to determine yields by comparison to the external standard are as follows: ^{1}H NMR (600 MHz, toluene-d_8) 2-guaiacoxy-1-phenylethanol – δ 4.98 (d, J = 9.0 Hz, 1H), 3.89 (dd, J = 3.0, 9.6 Hz, 1H), 3.56 (s, 1H); 2-guaiacoxyacetophenone – δ 4.80 (s, 2H); acetophenone – δ 2.14 (s, 3H); guaiacol – δ 5.57 (s, 1H), 3.20 (s, 3H); 2-methoxy-1-phenoxy-1-phenylethane – δ 4.41 (dd, J = 3.9, 7.6 Hz, 1H), 4.03 (dd, J = 7.8, 9.9 Hz, 1H), 3.16 (s, 3H). The diagnostic resonance of the 4-trifluoromethylpyridine external standard is as follows: ^{1}H NMR (600 MHz, neat): δ 8.82 (d, J = 4.8 Hz, 2H).

Disproportionation of 2a in the presence of radical trap 2,6-di-*tert*-butyl-4-methylphenol. A solution of **2a** (200 μL, 200 mM in toluene-d_8, 0.040 mmol) and a solution containing $RuH_2(CO)(PPh_3)_3$ and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (50 μL, 32 mM in both, 0.0016 mmol of both) were combined in an NMR tube with 2,6-di-*tert*-butyl-4-methylphenol (35 mg, 0.160 mmol), toluene-d_8

(150 µL), and a glass capillary containing 4-trifluoromethylpyridine. The NMR tube was sealed under vacuum, heated at 135 ºC, and monitored periodically *via* ^{1}H NMR. After 15 h of heating, complete consumption of **2a** was observed. The approximate half-life of the reaction was 2 h. The diagnostic resonances used to determine yields by comparison to the external standard are as listed above for the disproportionation of **2b** in the presence of **8**. A control reaction was carried out in an identical fashion omitting the addition of 2,6-di-*tert*-butyl-4-methylphenol and proceeded with an approximate half-life of 2 h.

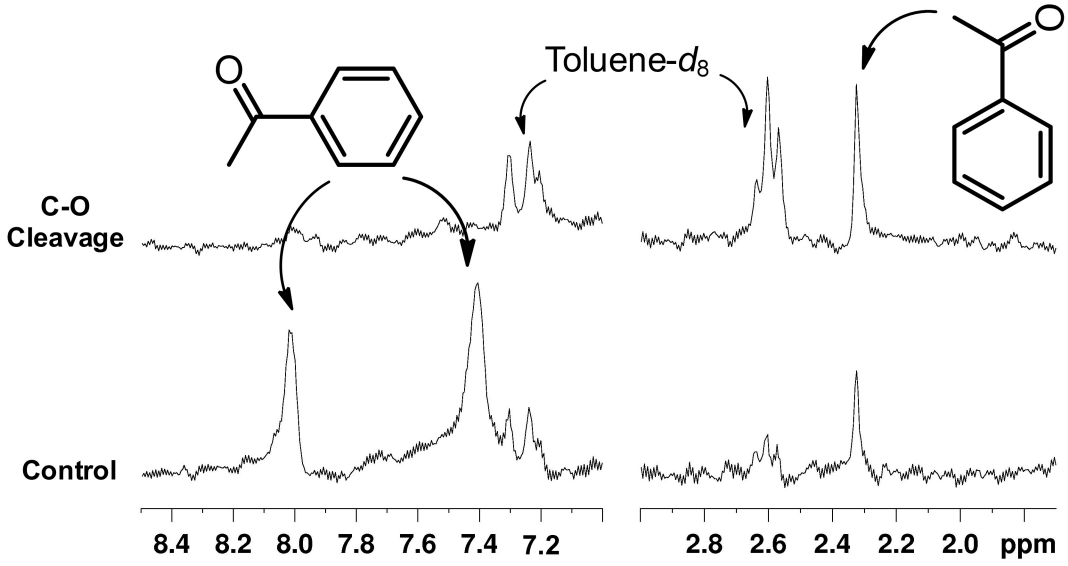
Hydrosilylation of 4a. To an NMR tube containing **4a** (34 mg, 0.16 mmol) was added a solution containing $RuH_2(CO)(PPh_3)_3$ and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (50 µL, 32 mM in both, 0.0016 mmol of both), tri-*iso*-propylsilane (49 µL, 0.24 mmol), and a glass capillary containing 4-trifluoromethylpyridine. The NMR tube was sealed under vacuum and heated at 135 ºC for 6 h, after which quantitative conversion of phenoxyacetophenone and 89% yield of acetophenone were observed by ^{1}H NMR. The diagnostic resonances used to determine yields by comparison to the external standard are as follows: ^{1}H NMR (400 MHz, toluene-d_8): 2-phenoxyacetophenone – δ 4.66 (s, 2H) ; acetophenone – δ 2.14 (s, 3H) . The diagnostic resonance of the 4-trifluoromethylpyridine external standard is as follows: ^{1}H NMR (600 MHz, neat): δ 8.82 (d, J = 4.8 Hz, 2H) .

Deuterium tracer experiment in the hydrosilylation of 4a. An NMR tube was charged with $RuH_2(CO)(PPh_3)_3$ (7.3 mg, 0.008 mmol), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (4.6 mg, 0.008 mmol), 2-phenoxyacetophenone (34.0 mg, 0.160 mmol), triethylsilyl deuteride (30.6 µL, 0.192 mmol, 97% D), and toluene-d_8 (400 µL). The NMR tube was sealed under vacuum, heated at 125 ºC, and monitored periodically *via* ^{1}H NMR, which after 50 min indicated 79% conversion of **4a**. A control reaction was carried out in an identical fashion, charging the NMR tube with acetophenone (18.7 µL, 0.160 mmol) instead of 2-phenoxyacetophenone. The isotopic distributions of the molecular ion of acetophenone obtained from this experiment were measured *via* GC/MS analysis of the crude reaction mixtures and integration of the mass spectral signals of 120, 121, 122, 123, 124, and 125 m/z in the region ±1 minutes of the acetophenone retention time (Table S8). ^{2}H NMR spectra were obtained by concentrating the reaction mixtures *in vacuo*, dissolving the residues in CD_2Cl_2 and analyzing the resulting solutions on an AVB-400 spectrometer (Figure S1).

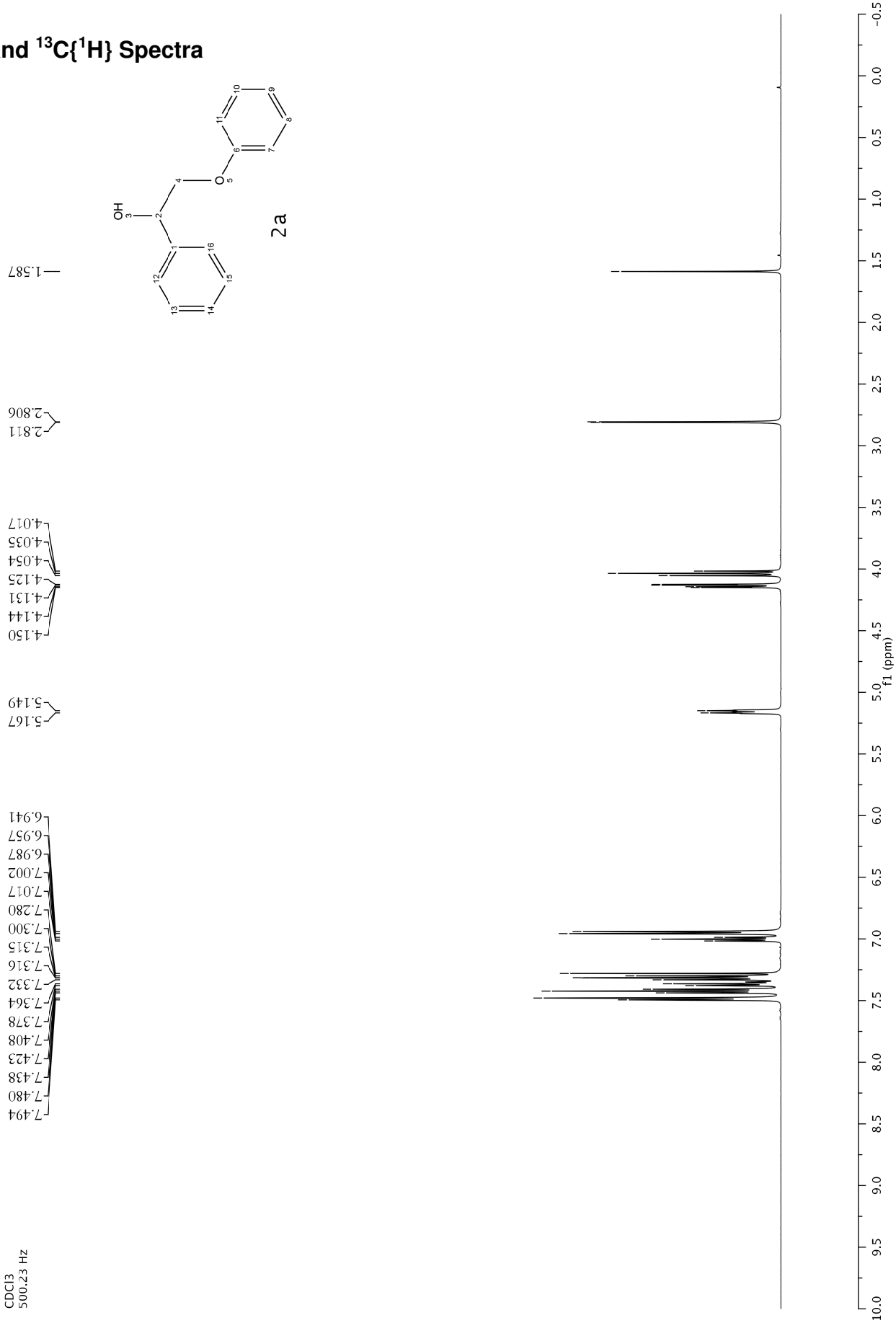
Table S8. Relative intensities of the acetophenone (MW = 120 m/z) molecular ions, corrected for ^{13}C and normalized to 120 m/z, as determined by GC/MS analysis. Standard deviation in parentheses.

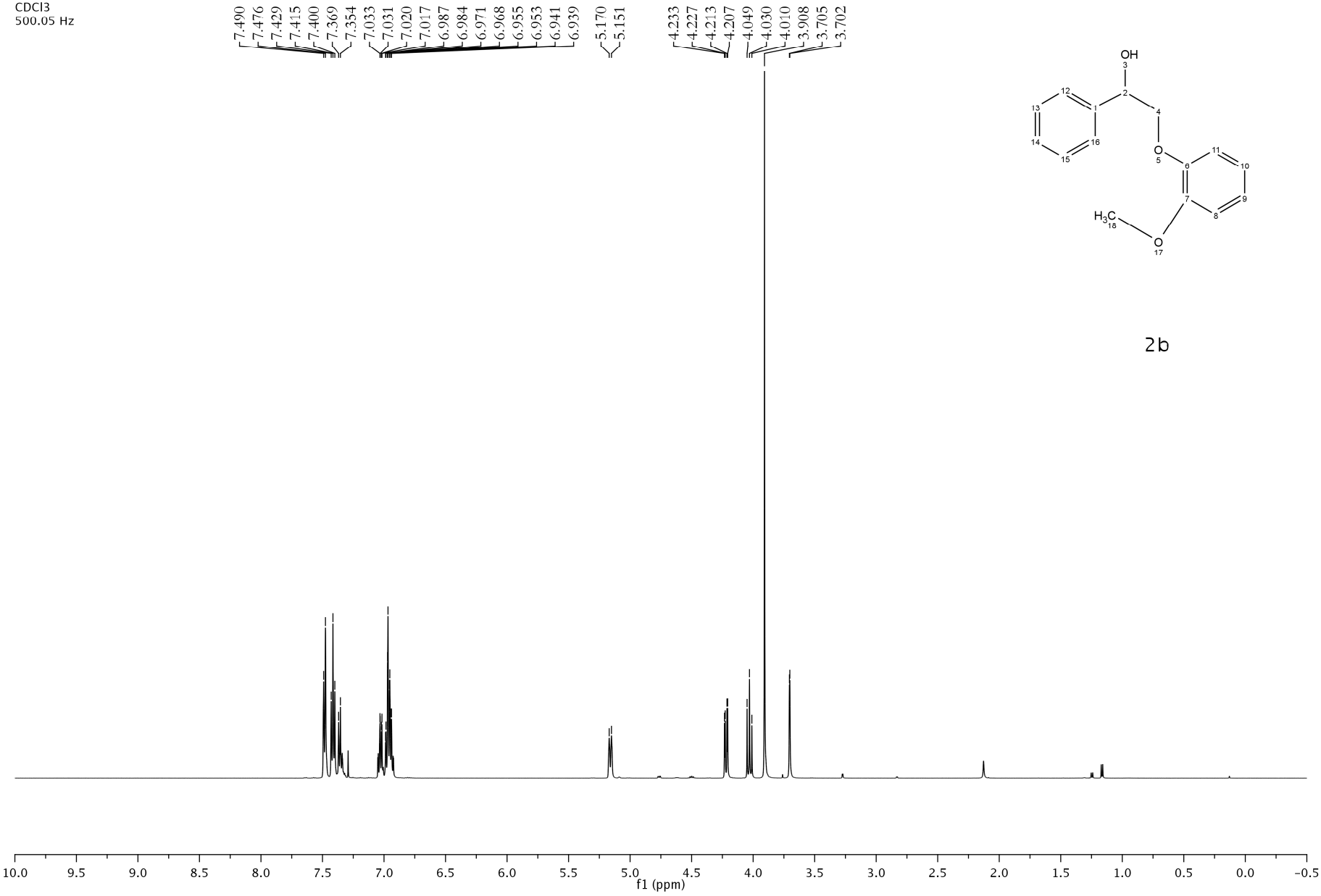
	Relative Intensity	
Ion	**C-O Cleavage**	**Control**
120	100(0)	100(0)
121	85.7(6)	15.8(5)
122	16.6(5)	7.1(1)
123	10.4(8)	2.3(1)
124	6.7(4)	0.3(3)
125	0.9(3)	0.0(1)

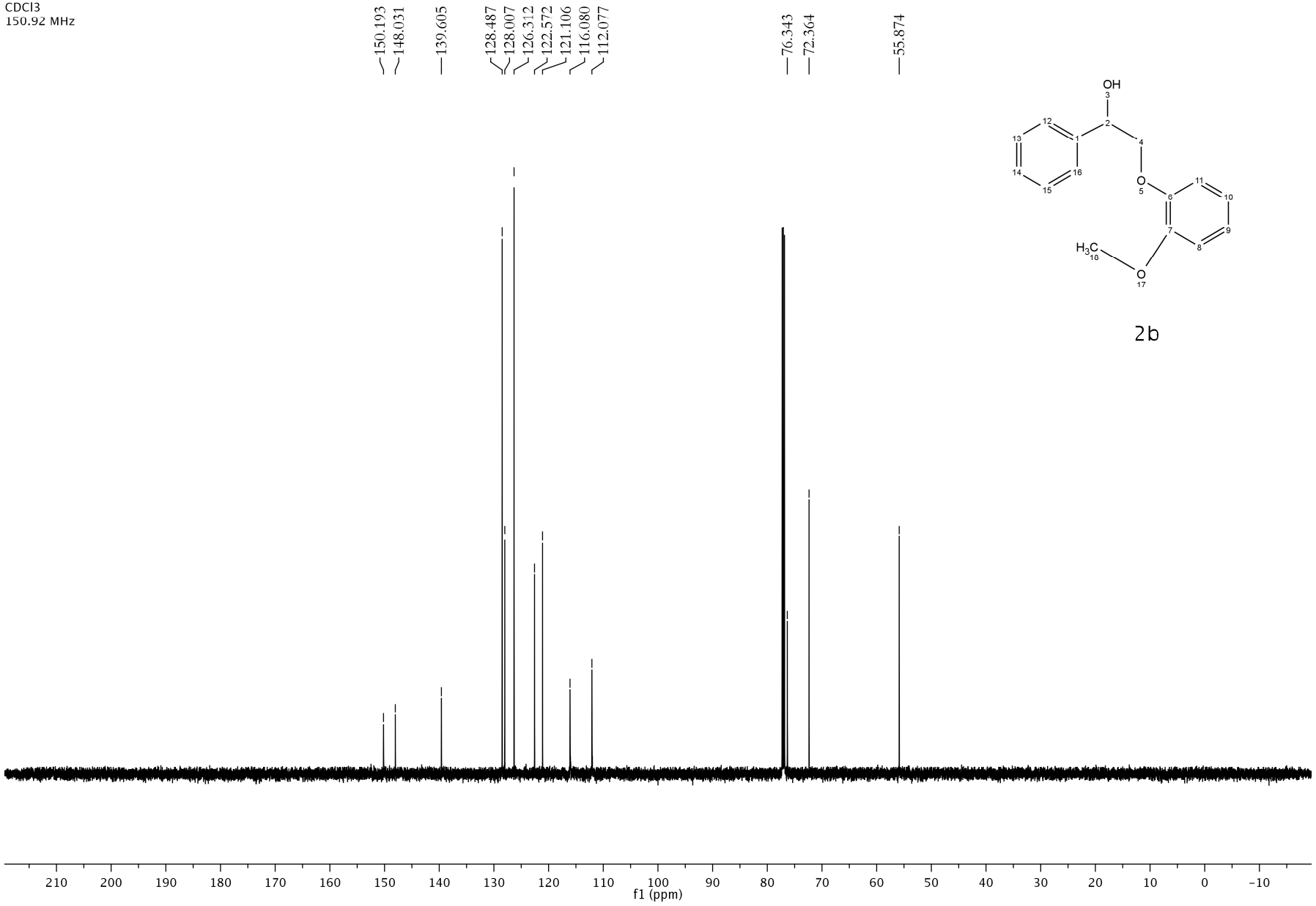
Figure S1. ^{2}H NMR spectra of the C-O bond cleavage (top) and control (bottom).



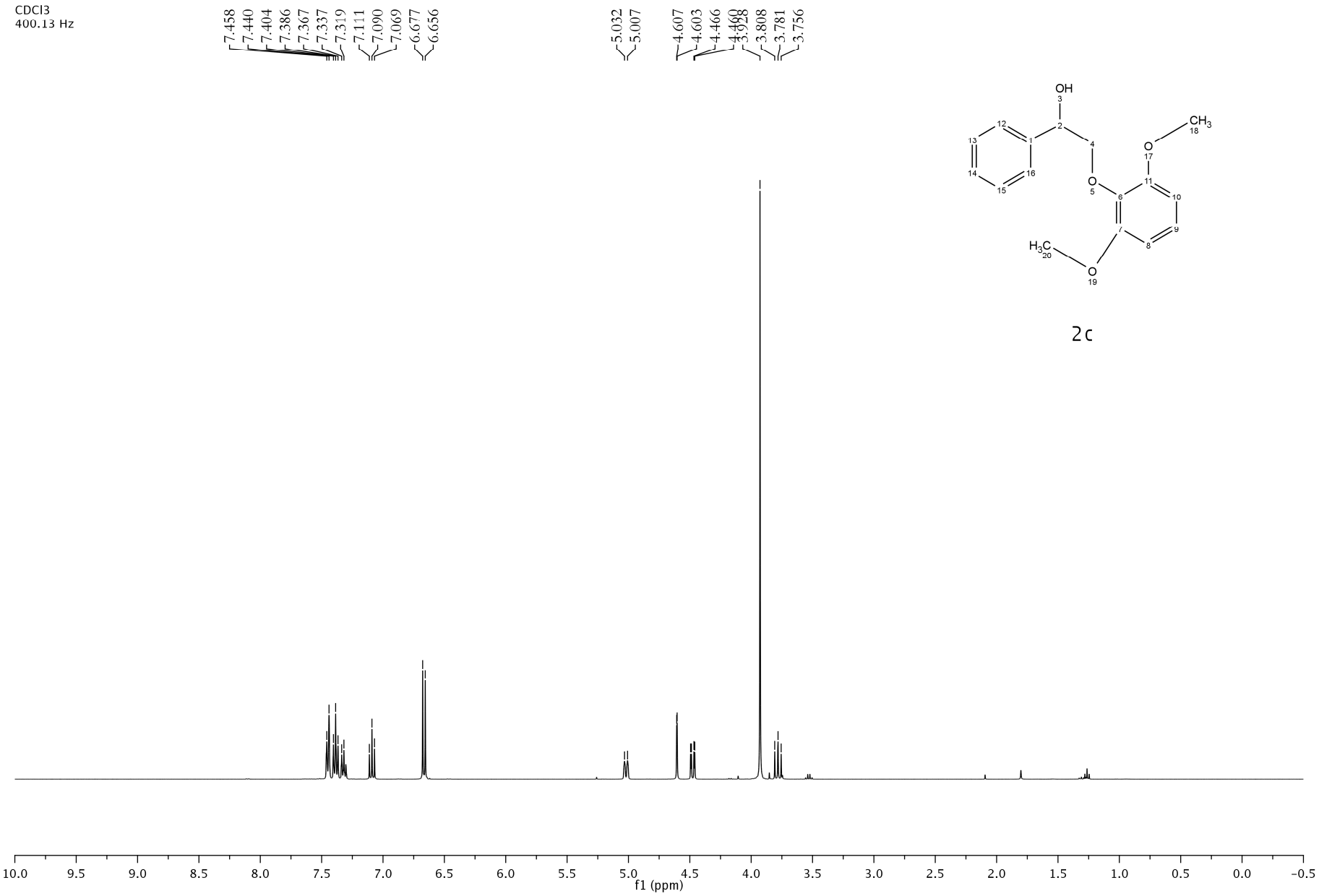
6. ^{1}H and $^{13}C\{^{1}H\}$ Spectra




CDCl3
500.05 Hz
7.490
7.476
7.429
7.415
7.400
7.369
7.354
7.033
7.031
7.020
7.017
6.987
6.984
6.971
6.968
6.955
6.953
6.941
6.939
5.170
5.151
4.233
4.227
4.213
4.207
4.049
4.030
4.010
3.908
3.705
3.702
OH
3
2
1
12
13
14
15
16
4
O
5
6
11
10
9
8
7
H3C
18
O
17
2b
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


CDCl3
150.92 MHz
150.193
148.031
139.605
128.487
128.007
126.312
122.572
121.106
116.080
112.077
76.343
72.364
55.874
OH
3
2
1
12
13
14
15
16
4
O
5
6
11
10
9
8
7
H_3C
18
O
17
f1 (ppm)

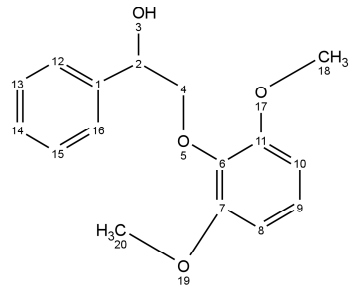
2b


CDCl3
400.13 Hz
7.458
7.440
7.404
7.386
7.367
7.337
7.319
7.111
7.090
7.069
6.677
6.656
5.032
5.007
4.607
4.603
4.466
4.460
3.928
3.808
3.781
3.756
OH
CH3
O
O
H3C
O
f1 (ppm)

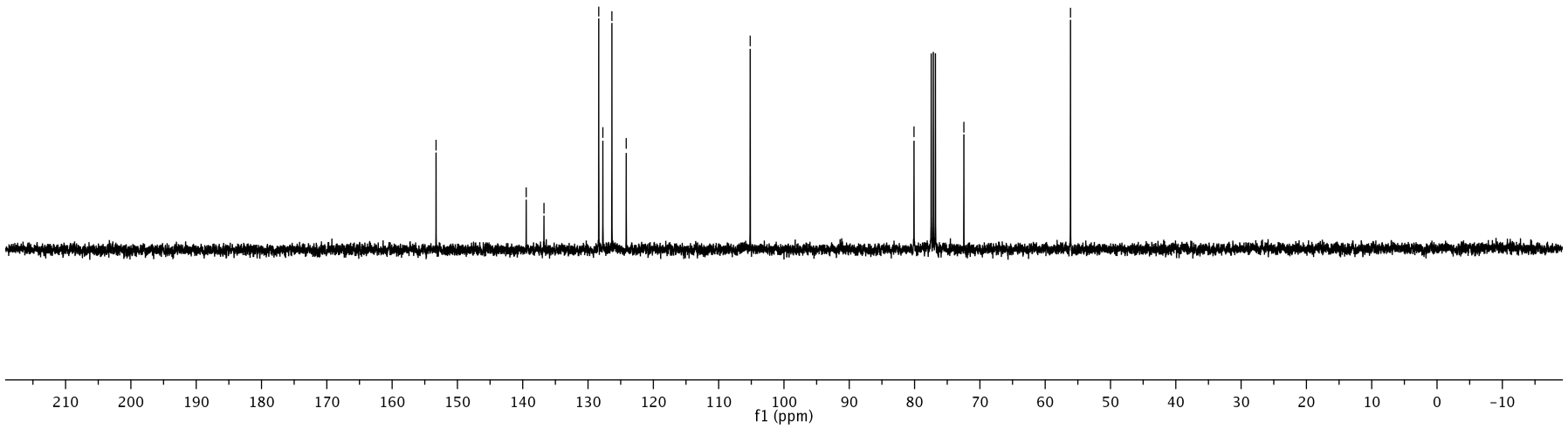
2c

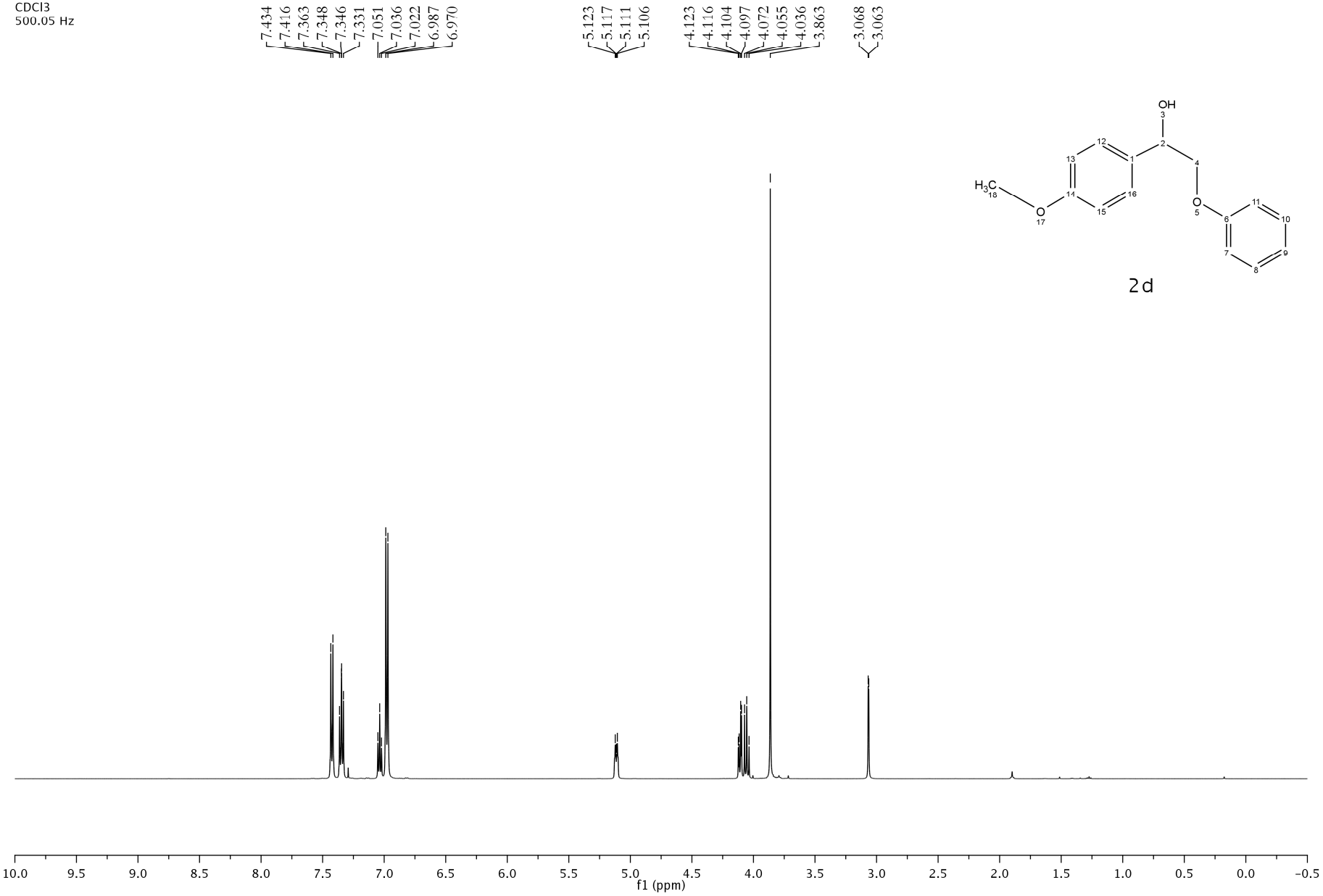
CDCl3
100.61 Hz

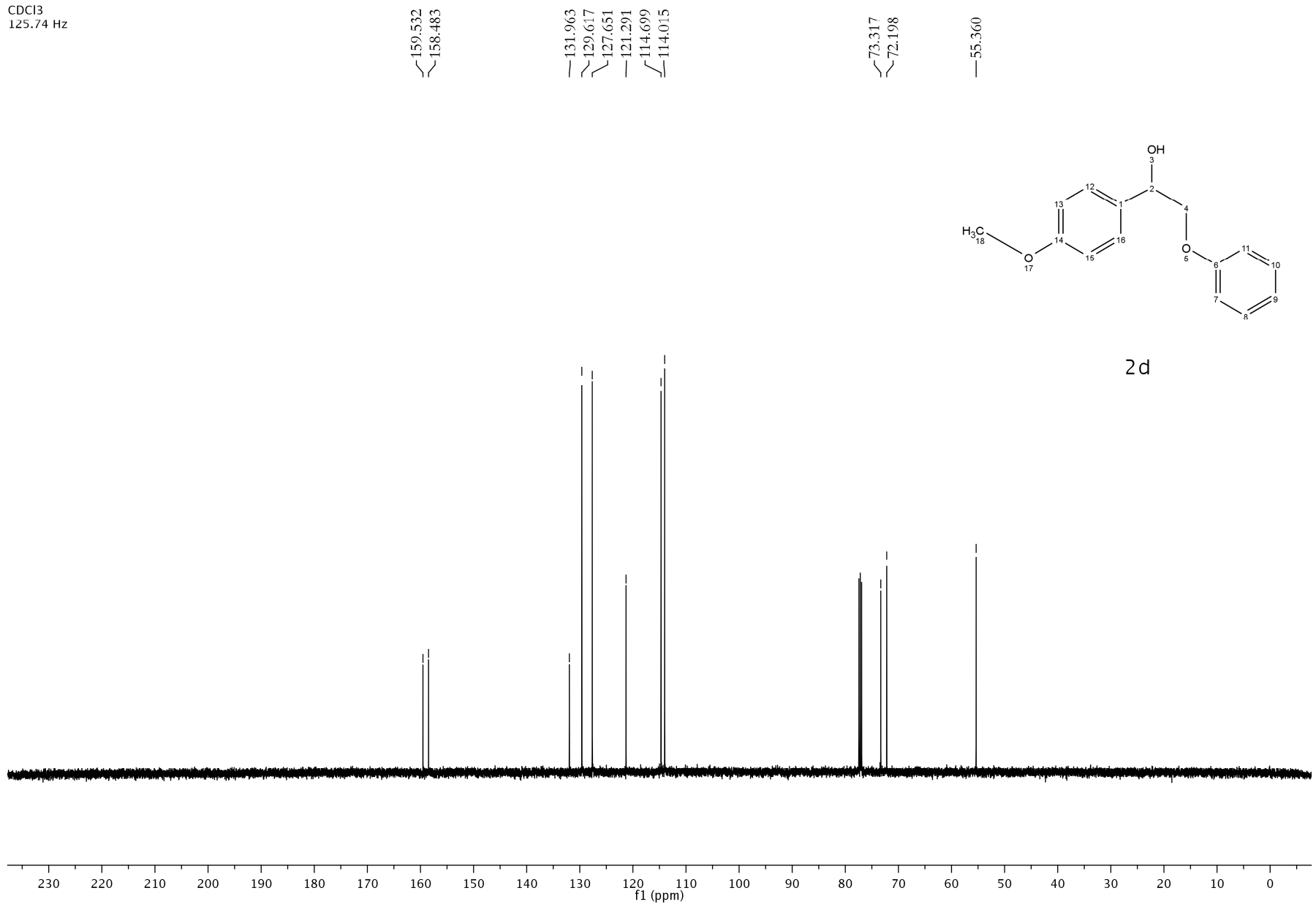
153.274
139.467
136.748
128.361
127.731
126.347
124.155
105.170
80.087
72.451
56.124

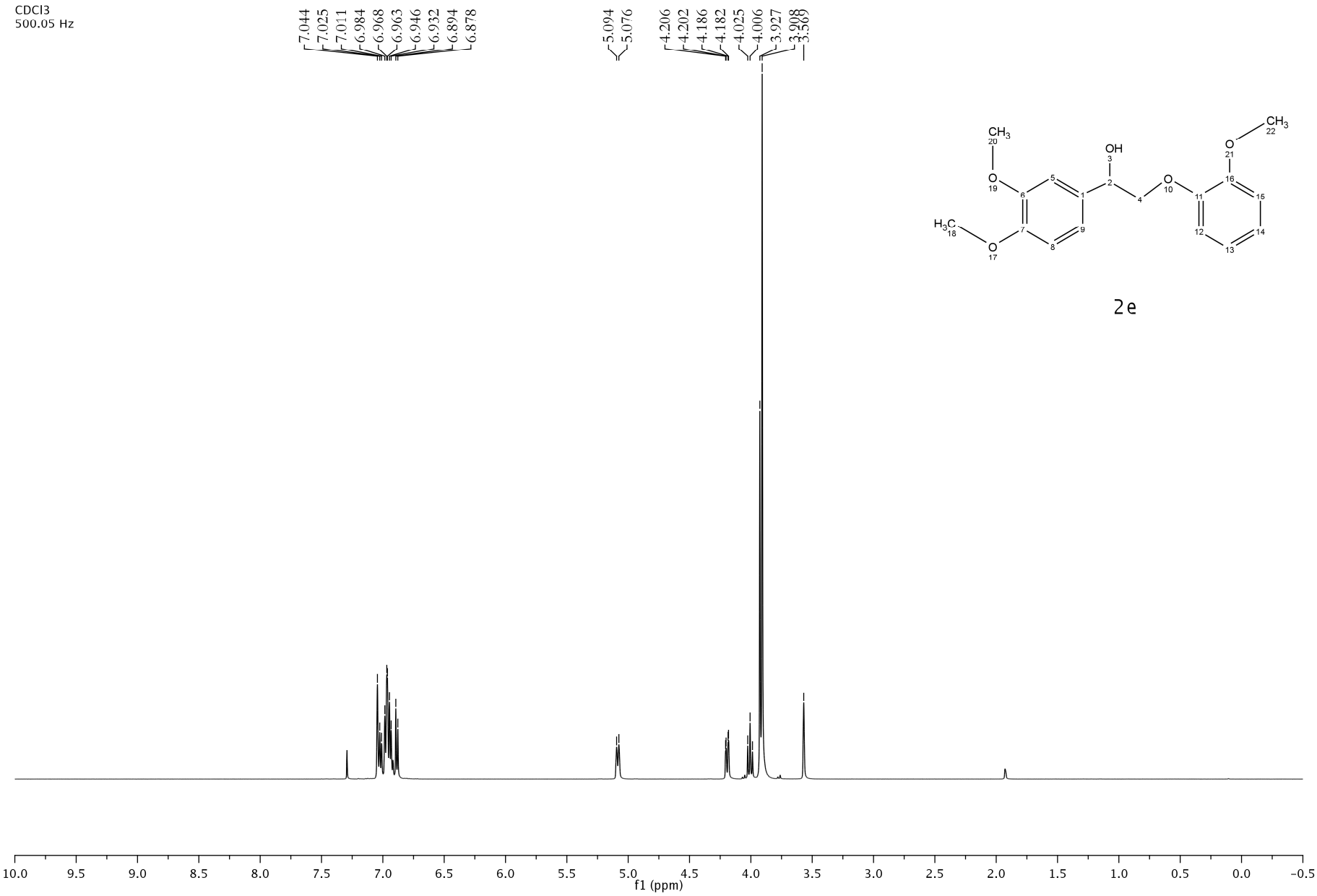


2c



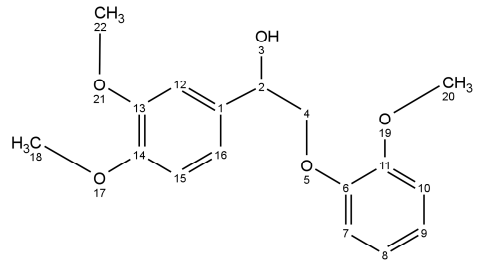

CDCl3
500.05 Hz
7.434
7.416
7.363
7.348
7.346
7.331
7.051
7.036
7.022
6.987
6.970
5.123
5.117
5.111
5.106
4.123
4.116
4.104
4.097
4.072
4.055
4.036
3.863
3.068
3.063
OH
3
2
1
12
13
4
H3C
18
14
16
O
17
15
O
5
6
11
10
7
9
8
2d
f1 (ppm)


CDCl3
125.74 Hz
159.532
158.483
131.963
129.617
127.651
121.291
114.699
114.015
73.317
72.198
55.360
OH
3
2
1
12
13
4
H_3C
18
14
16
15
O
17
O
5
6
11
10
7
9
8
2d
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CDCl3
500.05 Hz
7.044
7.025
7.011
6.984
6.968
6.963
6.946
6.932
6.894
6.878
5.094
5.076
4.206
4.202
4.186
4.182
4.025
4.006
3.927
3.908
3.369
f1 (ppm)
2e

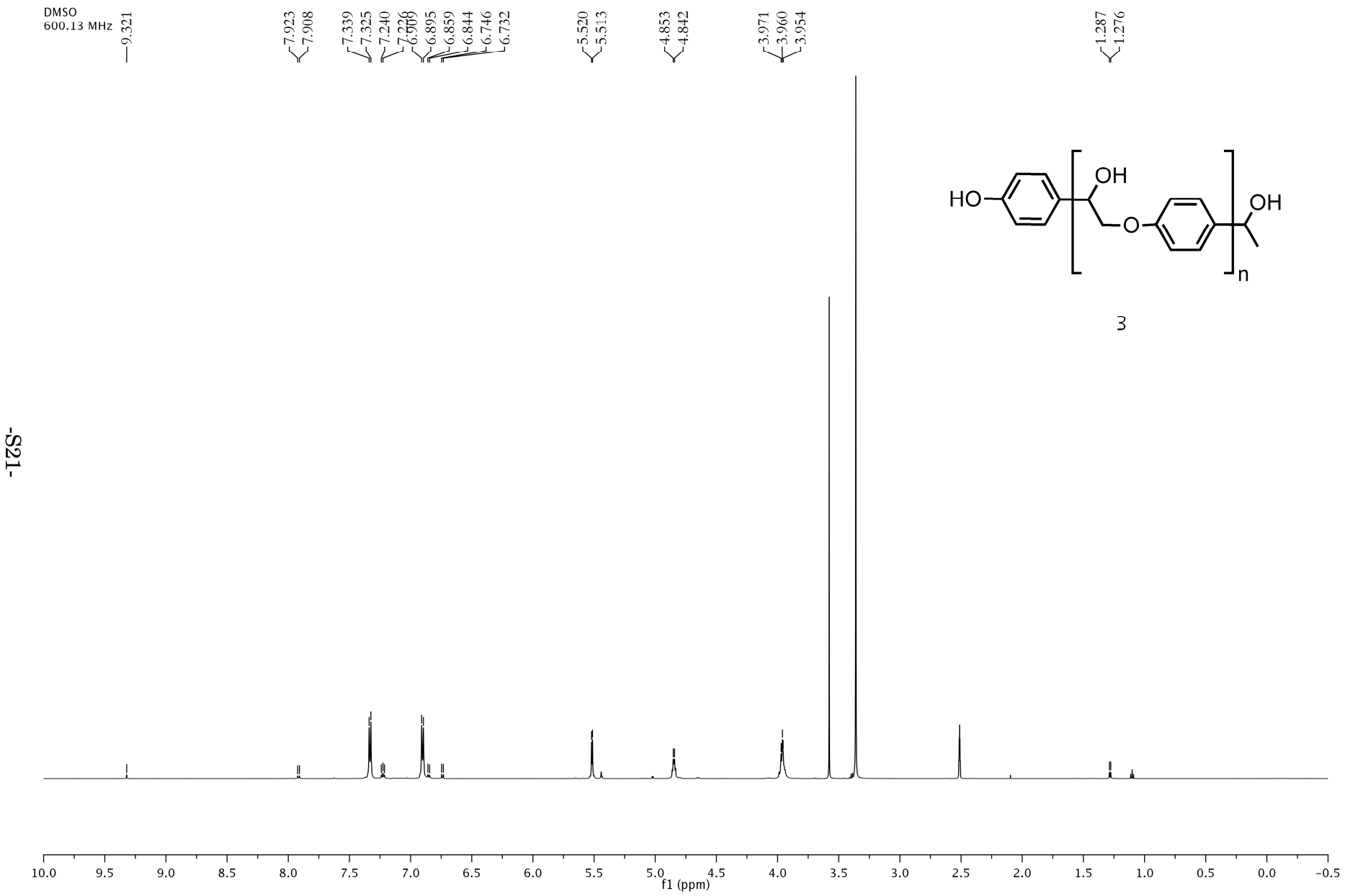
CDCl3
125.75 Hz

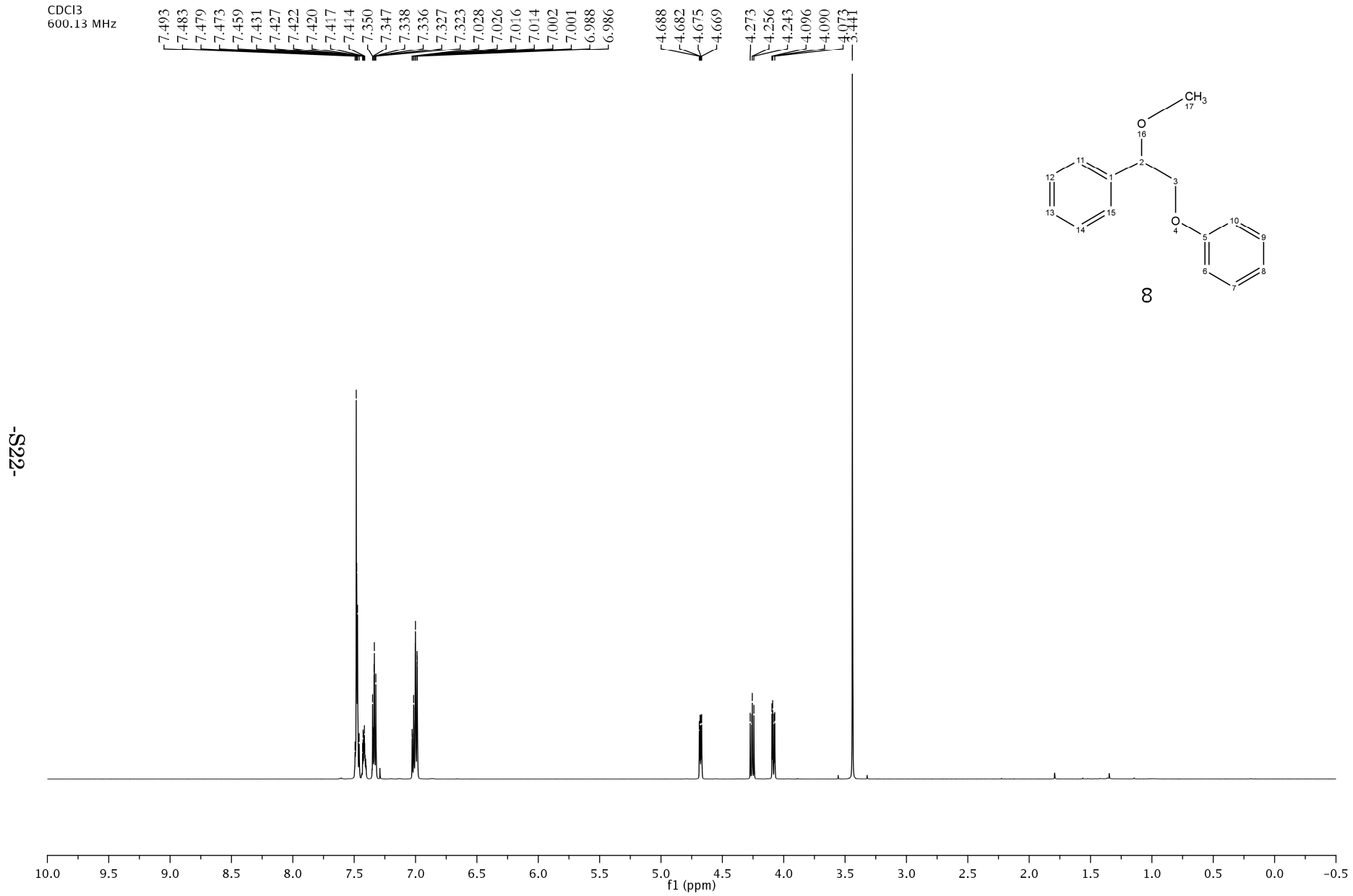
150.101
149.059
148.731
147.985
132.190
122.519
121.079
118.621
115.938
111.952
110.988
109.357
72.120
55.948
55.882
55.834



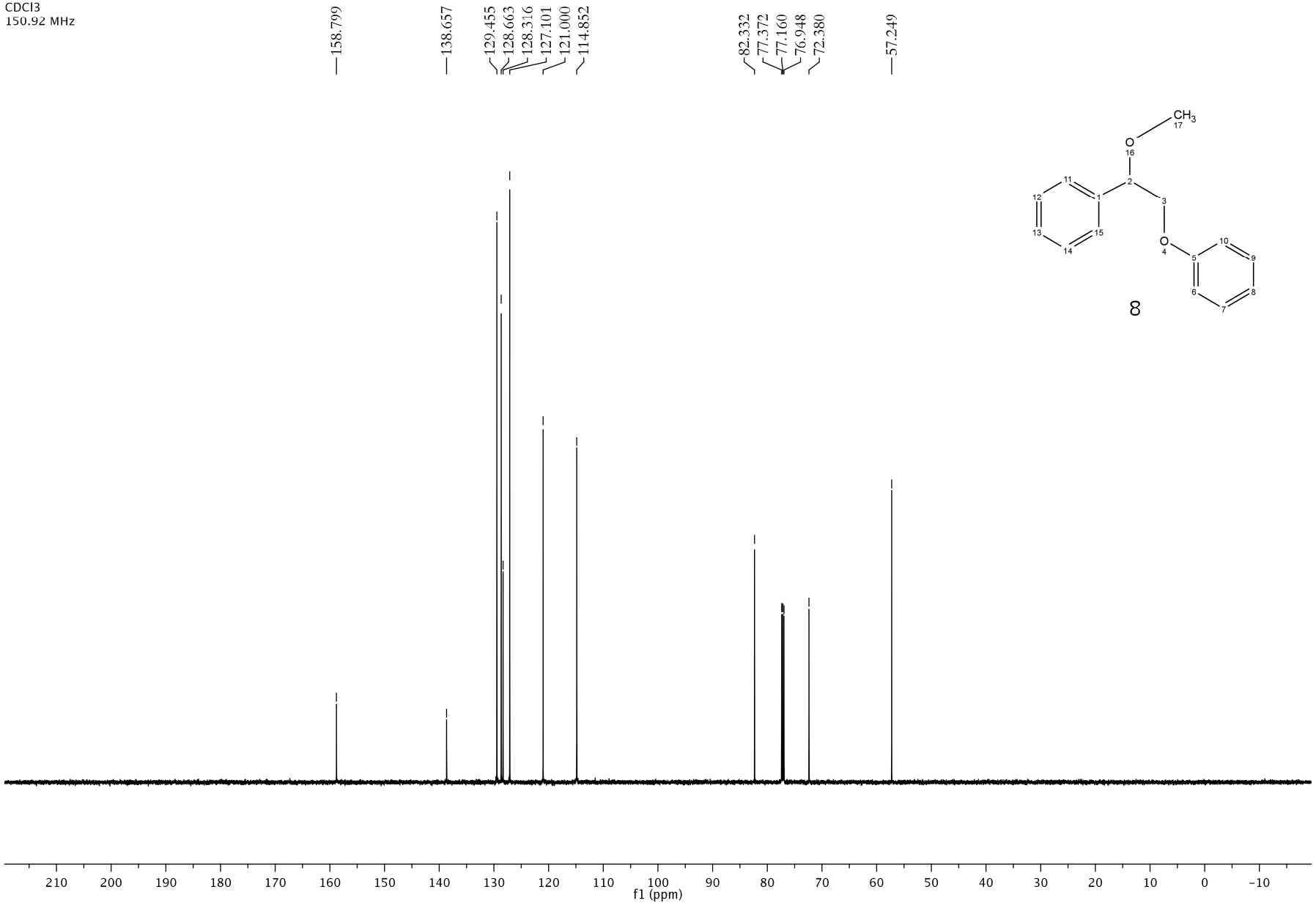
2e

f1 (ppm)


DMSO
600.13 MHz
9.321
7.923
7.908
7.339
7.325
7.240
7.226
6.900
6.895
6.859
6.844
6.746
6.732
5.520
5.513
4.853
4.842
3.971
3.960
3.954
1.287
1.276
HO
OH
O
OH
n
3
f1 (ppm)


CDCl3
600.13 MHz
7.493
7.483
7.479
7.473
7.459
7.431
7.427
7.422
7.420
7.417
7.414
7.350
7.347
7.338
7.336
7.327
7.323
7.028
7.026
7.016
7.014
7.002
7.001
6.988
6.986
4.688
4.682
4.675
4.669
4.273
4.256
4.243
4.096
4.090
4.073
3.441
f1 (ppm)

8


CDCl3
150.92 MHz
158.799
138.657
129.455
128.663
128.316
127.101
121.000
114.852
82.332
77.372
77.160
76.948
72.380
57.249
f1 (ppm)

8