Supporting Information

Transition-metal-free Access to Benzyl Ethers via Aerobic Cross Dehydrogenative Coupling of Benzylic C(sp^3)–H with Alcohols

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1. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification. Unless otherwise specified, all other reagents were purchased from Acros, Aldrich, Fisher, Adamas-beta Co. Ltd. or TCI and used without further purification. ^{1}H NMR spectra was recorded at 400 MHz and 600 MHz, ^{13}C NMR spectra was recorded at 100 MHz and 150 MHz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ 77.00 ppm) as internal reference. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Chromatography was carried out with silica gel (200-300 mesh) using mixtures of petroleum ether (b.p. 60-80 ºC) and ethyl acetate as eluents. Mass Spectra were obtained from the mass spectrometry facility of East China University of Science and Technology.

2. General procedure for the preparation of substrates

2.1 General procedure A (1b as an example): [1]

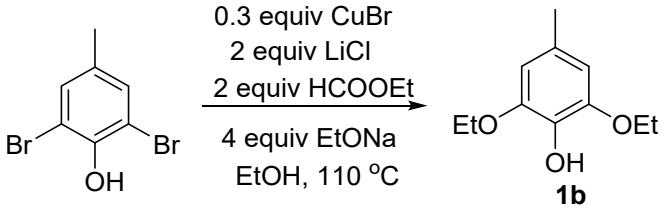
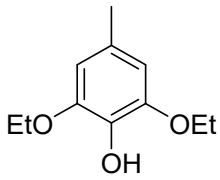
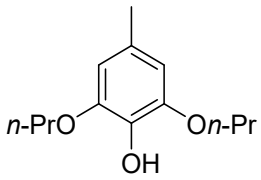


Figure S1. The synthesis of **1b**

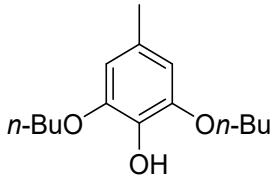
To a solution of EtONa in EtOH [freshly prepared from metallic Na (0.18 g, 8.0 mmol) and EtOH (8 mL)], LiCl (0.17 g, 4.0 mmol), 2,6-dibromo-4-methylphenol (0.53 g, 2.0 mmol), CuBr (0.09 g, 0.6 mmol) and HCOOEt (0.30 g, 4.0 mmol) were added. The mixture was stirred at room temperature for 15 min, and then it was heated at 110 °C. After the completion of the reaction monitored by thin-layer chromatography (TLC), the mixture was stirred open to the air for 0.5 h at room temperature. Then the mixture was evaporated under reduced pressure to recover the EtOH solvent and give a residue. 10 mL MTBE and dilute 10 mL 1M hydrochloric acid were added to the residue. The organic phase was separated, and the aqueous phase was extracted with MTBE (3×10 mL), then dried over Na_2SO_4. After that, the solvent was removed under reduced pressure. The obtained residue was purified by column chromatography (Petroleum ether/EtOAc = 40:1) on silica gel to give the desired product.



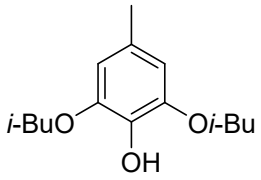
2,6-Diethoxy-4-methylphenol (1b),[1] yellow solid, purification by flash column chromatography (eluent: PE/EA = 40/1), 0.32 g (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.37 (s, 2H), 5.38 (s, 1H), 4.09 (q, J = 7.2 Hz, 4H), 2.27 (s, 3H), 1.43 (t, J = 6.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.1, 132.8, 128.5, 106.7, 64.6, 21.6, 15.0.



4-Methyl-2,6-dipropoxyphenol (1c), [1] yellow solid, purification by flash column chromatography (eluent: PE/EA = 40/1), 0.36 g (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38 (s, 2H), 5.37 (s, 1H), 3.98 (t, *J* = 6.8 Hz, 4H), 2.27 (s, 3H), 1.88 – 1.79 (m, 4H), 1.03 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.2, 133.0, 128.5, 106.8, 70.8, 22.6, 21.5, 10.4.



2,6-Dibutoxy-4-methylphenol (1d), yellow solid, purification by flash column chromatography (eluent: PE/EA = 40/1), 0.39 g (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38 (s, 2H), 5.35 (s, 1H), 4.02 (t, *J* = 6.8 Hz, 4H), 2.27 (s, 3H), 1.83 – 1.76 (m, 4H), 1.54 – 1.44 (m, 4H), 0.97 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.3, 133.0, 128.5, 106.8, 69.0, 31.4, 21.6, 19.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{24}O_3Na$ 275.1623; Found 275.1617.



2,6-Diisobutoxy-4-methylphenol (1e), yellow solid, purification by flash column chromatography (eluent: PE/EA = 50/1), 0.37 g (74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.37 (s, 2H), 5.34 (s, 1H), 3.77 (d, *J* = 6.8 Hz, 4H), 2.26 (s, 3H), 2.18 – 2.08 (m, 2H), 1.03 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.4, 133.0, 128.5, 106.9, 75.7, 28.3, 21.5, 19.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{24}O_3Na$ 275.1623; Found 275.1616.

2.2 General procedure B (1f as an example): [1]

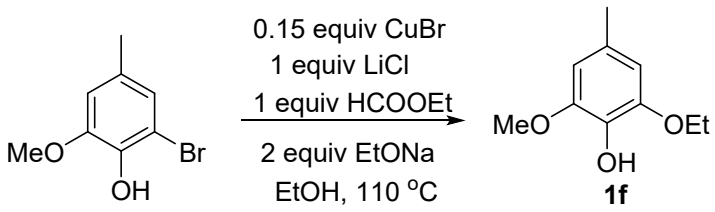
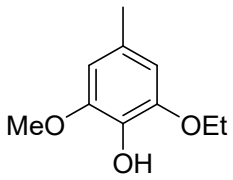
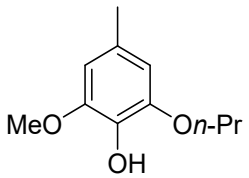


Figure S2. The synthesis of **1f**

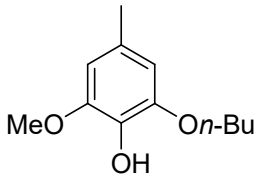
To a solution of EtONa in EtOH [freshly prepared from metallic Na (0.14 g, 6.0 mmol) and ROH (6 mL)], LiCl (0.13 g, 3.0 mmol), 2-bromo-6-methoxy-4-methylphenol (0.65 g, 3.0 mmol), CuBr (0.06 g, 0.45 mmol) and HCOOEt (3.0 mmol) were added. The mixture was stirred at room temperature for 15 min, and then it was heated at 110 °C for 8 h. After the completion of the reaction monitored by thin-layer chromatography (TLC), the mixture was stirred open to the air for 0.5 h at room temperature. Then the mixture was evaporated under reduced pressure to recover the EtOH solvent and give a residue. 10 mL MTBE and dilute 10 mL 1M hydrochloric acid were added to the residue. The organic phase was separated, and the aqueous phase was extracted with MTBE (3×10 mL), then dried over Na_2SO_4. After that, the solvent was removed under reduced pressure. The obtained residue was purified by column chromatography (Petroleum ether/EtOAc = 20:1) on silica gel to give the desired product.



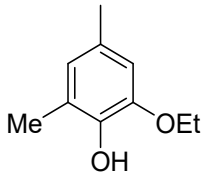
2-Ethoxy-6-methoxy-4-methylphenol (1f),[1] yellow oil, purification by flash column chromatography (eluent: PE/EA = 20/1), 0.49 g (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38 (s, 2H), 5.40 (s, 1H), 4.08 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 2.28 (s, 3H), 1.42 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 146.1, 132.7, 128.7, 106.7, 105.7, 64.7, 56.2, 21.6, 15.0.



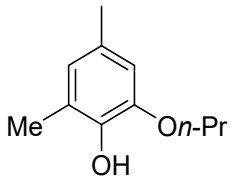
2-Methoxy-4-methyl-6-propoxyphenol (1g),[2] yellow solid, purification by flash column chromatography (eluent: PE/EA = 20/1), 0.52 g (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.39 (s, 2H), 5.35 (s, 1H), 3.98 (t, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 2.28 (s, 3H), 1.88 – 1.79 (m, 2H), 1.04 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 146.2, 132.7, 128.7, 106.7, 105.7, 70.8, 56.2, 22.7, 21.6, 10.5.



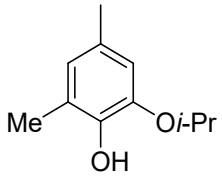
2-Butoxy-6-methoxy-4-methylphenol (1h), yellow solid, purification by flash column chromatography (eluent: PE/EA = 20/1), 0.54 g (85% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.39 (s, 2H), 5.36 (s, 1H), 4.02 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 2.28 (s, 3H), 1.81 – 1.78 (m, 2H), 1.51 – 1.47 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.9, 146.2, 132.7, 128.7, 106.6, 105.7, 69.0, 56.2, 31.4, 21.6, 19.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_3Na$ 233.1154; Found 233.1145.



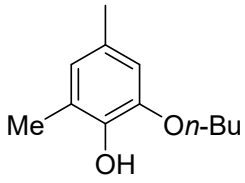
2-Ethoxy-4,6-dimethylphenol (1i), yellow solid, purification by flash column chromatography (eluent: PE/EA = 30/1), 0.43 g (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (s, 1H), 6.53 (s, 1H), 5.57 (s, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 2.23 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.2, 141.5, 128.4, 123.3, 123.2, 110.0, 64.4, 21.0, 15.4, 15.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}O_2Na$ 189.0891; Found 189.0890.



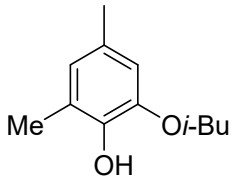
2,4-Dimethyl-6-propoxyphenol (1j), yellow oil, purification by flash column chromatography (eluent: PE/EA = 30/1), 0.46 g (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (s, 1H), 6.55 (s, 1H), 5.60 (s, 1H), 3.98 (t, J = 6.8 Hz, 2H), 2.27 (s, 3H), 2.25 (s, 3H), 1.89 – 1.80 (m, 2H), 1.06 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.3, 141.5, 128.4, 123.3, 123.2, 110.0, 70.4, 22.6, 21.0, 15.4, 10.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_2Na$ 203.1048; Found 203.1048.



2-Isopropoxy-4,6-dimethylphenol (1k), yellow oil, purification by flash column chromatography (eluent: PE/EA = 30/1), 0.37 g (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 2H), 5.64 (s, 1H), 4.59 – 4.50 (m, 1H), 2.25 (s, 3H), 2.23 (s, 3H), 1.36 (d, J = 6.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.9, 142.4, 128.3, 123.5, 123.4, 111.7, 71.5, 22.2, 21.0, 15.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_2Na$ 203.1048; Found 203.1050.



2-Butoxy-4,6-dimethylphenol (1l),[1] yellow oil, purification by flash column chromatography (eluent: PE/EA = 30/1), 0.49 g (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (s, 1H), 6.54 (s, 1H), 5.57 (s, 1H), 4.02 (t, J = 6.8 Hz, 2H), 2.26 (s, 3H), 2.23 (s, 3H), 1.83 – 1.73 (m, 2H), 1.55 – 1.45 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.3, 141.5, 128.4, 123.3, 123.2, 110.0, 68.6, 31.3, 21.0, 19.3, 15.4, 13.9.



2-Isobutoxy-4,6-dimethylphenol (1m), yellow oil, purification by flash column chromatography (eluent: PE/EA = 30/1), 0.40 g (69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (s, 1H), 6.55 (s, 1H), 5.58 (s, 1H), 3.79 (d, J = 6.8 Hz, 2H), 2.27 (s, 3H), 2.25 (s, 3H), 2.18 – 2.08 (m, 1H), 1.05 (d, J = 6.4 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.3, 140.4, 127.4, 122.3, 122.2, 108.9, 74.1, 27.2, 20.0, 18.2, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}O_2$ 195.1385; Found 195.1385.

2.3 General procedure C (1n as an example): [2]

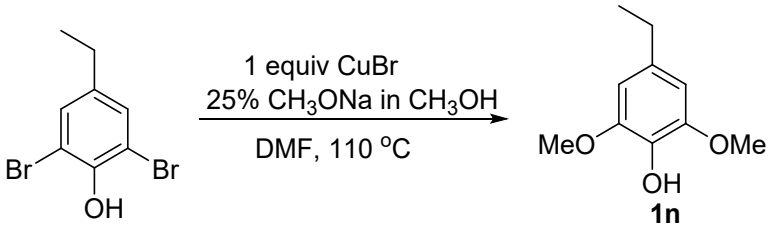
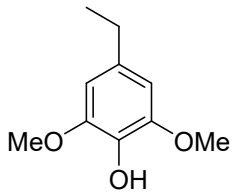
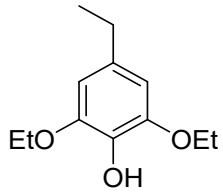


Figure S3. The synthesis of **1n**

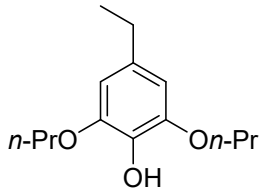
To a 25% solution of CH_3ONa in CH_3OH (21 mL, 0.09 mol) was added a suspension of CuBr (429 mg, 3.0 mmol) in DMF (10 mL) and stirred at room temperature for 1 h. After the solution became blue, the mixture was added in small portions to a solution of 2,6-dibromo-4-ethylphenol (0.84 g, 3.0 mmol) in DMF (6 mL) at 110 °C and stirred at this temperature. When the reaction finished monitored by TLC, the mixture was cooled to room temperature and acidified with 2 M HCl solution. Methanol was evaporated under reduced pressure and the residue was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and evaporated under vacuum. The obtained residue was purified by column chromatography (Petroleum ether/EtOAc = 20:1) to give the desired product.



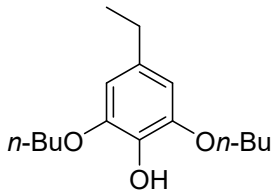
4-Ethyl-2,6-dimethoxyphenol (1n),[3] yellow solid, purification by flash column chromatography (eluent: PE/EA = 20/1), 0.38 g (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42 (s, 2H), 5.41 (s, 1H), 3.87 (s, 6H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 135.4, 132.6, 104.4, 56.2, 29.1, 15.9.



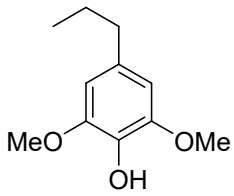
2,6-Diethoxy-4-ethylphenol (1o), yellow solid, purification by flash column chromatography (eluent: PE/EA = 20/1), 0.45 g (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (s, 2H), 5.39 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 4H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.44 (t, *J* = 6.8 Hz, 6H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 135.2, 133.2, 105.6, 64.7, 29.0, 15.9, 15.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_3Na$ 233.1154; Found 233.1158.



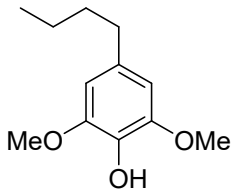
4-Ethyl-2,6-dipropoxyphenol (1p), white solid, purification by flash column chromatography (eluent: PE/EA = 20/1), 0.49 g (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (s, 2H), 5.37 (s, 1H), 3.99 (t, *J* = 6.8 Hz, 4H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.87 – 1.80 (m, 4H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 135.2, 133.3, 105.7, 70.8, 29.0, 22.7, 16.0, 10.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{22}O_3Na$ 261.1467; Found 261.1461.



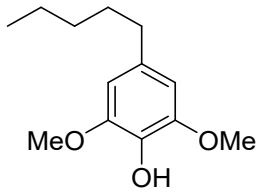
2,6-Dibutoxy-4-ethylphenol (1q), white solid, purification by flash column chromatography (eluent: PE/EA = 20/1), 0.53 g (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (s, 2H), 5.35 (s, 1H), 4.03 (t, *J* = 6.8 Hz, 4H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.83 – 1.76 (m, 4H), 1.54 – 1.45 (m, 4H), 1.21 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 135.2, 133.3, 105.7, 69.0, 31.4, 29.0, 19.2, 15.9, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{26}O_3Na$ 289.1780; Found 289.1778.



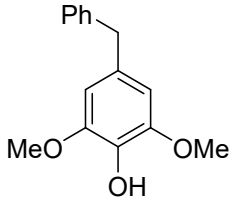
2,6-Dimethoxy-4-propylphenol (1t),[4] yellow solid, purification by flash column chromatography (eluent: PE/EA = 8/1), 0.57 g (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.39 (s, 2H), 4.67 (s, 1H), 3.84 (s, 6H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.56 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 133.8, 132.7, 105.1, 56.2, 38.3, 24.8, 13.8.



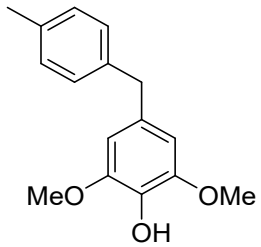
4-Butyl-2,6-dimethoxyphenol (1u), yellow oil, purification by flash column chromatography (eluent: PE/EA = 8/1), 0.60 g (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (s, 2H), 5.40 (s, 1H), 3.86 (s, 6H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.40 – 1.31 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 134.0, 132.7, 105.0, 56.2, 35.9, 34.0, 22.4, 14.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_3Na$ 233.1154; Found 233.1156.



2,6-Dimethoxy-4-pentylphenol (1v), yellow oil, purification by flash column chromatography (eluent: PE/EA = 8/1), 0.62 g (93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (s, 2H), 5.39 (s, 1H), 3.86 (s, 6H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.37 – 1.29 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 134.1, 132.7, 105.0, 56.2, 36.2, 31.5, 31.4, 22.6, 14.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_3Na$ 247.1310; Found 247.1306.

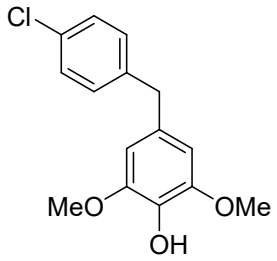


4-Benzyl-2,6-dimethoxyphenol (1w), yellow solid, purification by flash column chromatography (eluent: PE/EA = 6/1), 0.43 g (59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 –7.17 (m, 5H), 6.41 (s, 2H), 5.38 (s, 1H), 3.91 (s, 2H), 3.84 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 141.3, 133.1, 132.1, 128.7, 128.5, 126.1, 105.7, 56.3, 42.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{16}O_3Na$ 267.0997; Found 267.1000.

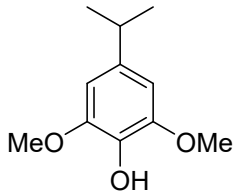


2,6-Dimethoxy-4-(4-methylbenzyl)phenol (1x), white solid, purification by flash column chromatography (eluent: PE/EA = 6/1), 0.46 g (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 – 7.06 (m, 4H), 6.41 (s, 2H), 5.37 (s, 1H), 3.87 (s, 2H), 3.84 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 138.2, 135.6, 133.0, 132.4,

129.1, 128.6, 105.6, 56.3, 41.6, 21.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}O_3Na$ 281.1154; Found 281.1151.



4-(4-Chlorobenzyl)-2,6-dimethoxyphenol (1y), yellow solid, purification by flash column chromatography (eluent: PE/EA = 6/1), 0.53 g (64% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.17 (s, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.54 (s, 2H), 3.87 (s, 2H), 3.76 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.5, 141.4, 134.4, 131.1, 130.9, 130.8, 128.7, 106.7, 56.4, 40.8. RMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{15}O_3NaCl$ 301.0607; Found 301.0600.



4-Isopropyl-2,6-dimethoxyphenol (1z), yellow oil, purification by flash column chromatography (eluent: PE/EA = 30/1), 0.39 g (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (s, 2H), 5.38 (s, 1H), 3.89 (s, 6H), 2.88 – 2.78(m, 1H), 1.23 (d, J = 6.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.8, 140.2, 132.7, 103.0, 56.2, 34.3, 24.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_3Na$ 219.0997; Found 219.0995.

2.4 General procedure D (1r as an example): [2]

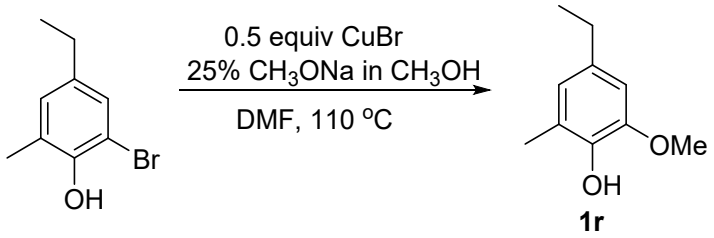
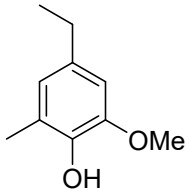
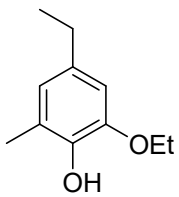


Figure S4. The synthesis of **1r**

To a 25% solution of CH_3ONa in CH_3OH (11 mL, 0.05 mol) was added a suspension of CuBr (215 mg, 1.5 mmol) in DMF (5 mL) and stirred at room temperature for 1 h. After the solution became blue, the mixture was added in small portions to a solution of 2-bromo-4-ethyl-6-methylphenol (0.65 g, 3.0 mmol) in DMF (6 mL) at 110 °C and stirred at this temperature. When the reaction finished monitored by TLC, the mixture was cooled to room temperature and acidified with 2 M HCl solution. Methanol was evaporated under reduced pressure and the residue was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and evaporated under vacuum. The obtained residue was purified by column chromatography (Petroleum ether/EtOAc = 80:1) to give the desired product.



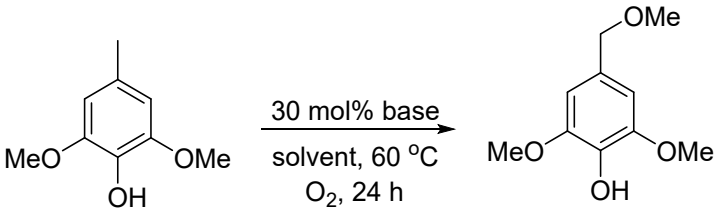
4-Ethyl-2-methoxy-6-methylphenol (1r), brown oil, purification by flash column chromatography (eluent: PE/EA = 80/1), 0.40 g (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (s, 1H), 6.62 (s, 1H), 5.65 (s, 1H), 3.90 (s, 3H), 2.61 (q, J = 7.6 Hz, 2H), 2.30 (s, 3H), 1.30 – 1.25 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 141.7, 135.3, 123.5, 122.3, 108.0, 56.0, 28.6, 16.1, 15.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}O_2Na$ 189.0891; Found 189.0889.



2-Ethoxy-4-ethyl-6-methylphenol (1s), brown oil, purification by flash column chromatography (eluent: PE/EA = 80/1), 0.43 g (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 1H), 6.54 (s, 1H), 5.62 (s, 1H), 4.06 (q, *J* = 6.8 Hz, 2H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.23 (s, 3H), 1.40 (t, *J* = 6.8 Hz, 3H), 1.19 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 141.8, 135.2, 123.5, 122.2, 109.0, 64.5, 28.6, 16.1, 15.5, 15.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_2Na$ 203.1048; Found 203.1049.

3. Optimization of alkoxylation reactions of benzylic C(sp^3)–H Bond

Table S1. Optimization of reaction conditions by employing **1a** as substrate[a]



1a **2a**

Entry	Base	Solvent	Yield of **2a**[b]/%
1[c]	KO*t*Bu	MeOH	42
2[c]	KO*t*Bu	toluene : MeOH= 4:1	40
3[c]	KO*t*Bu	DMSO : MeOH= 4:1	-
4[d]	KO*t*Bu	MeOH	51
5[e]	KO*t*Bu	MeOH	72
6	**KO*t*Bu**	**MeOH**	**78**
7[f]	KO*t*Bu	MeOH	67
8[g]	KO*t*Bu	MeOH	65
9	LiO*t*Bu	MeOH	41
10	NaO*t*Bu	MeOH	47
11	LiOH	MeOH	66
12	NaOH	MeOH	68
13	CsOH	MeOH	74
14	KOH	MeOH	72
15	$KHCO_3$	MeOH	57
16	$NaHCO_3$	MeOH	43

17	CH_3OK	MeOH	69
18	K_2CO_3	MeOH	70
19	DBU	MeOH	29
20	TBD	MeOH	25
21	DABCO	MeOH	16
22[h]	KO*t*Bu	MeOH	40
23[i]	KO*t*Bu	MeOH	71

[a] Unless specified, substrate **1a** (0.3 mmol) and base (0.09 mmol) in 2 mL MeOH was stirred for 24 h under O_2 balloon atmosphere. [b] Isolated yield. [c] 2 equiv base was used. [d] 0.5 equiv base was used. [e] The reaction was carried out with 15 h. [f] The reaction was carried out under aerobic atmosphere. [g] The reaction was carried out under N_2 atmosphere.

4. Synthesis of benzyl ethers via direct alkoxylation of benzylic C(sp^3)–H

4.1 Typical procedure A for preparing products (2a as an example):

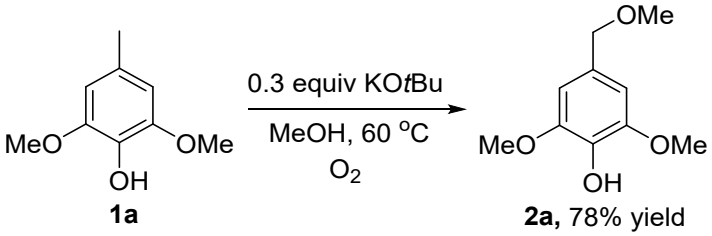
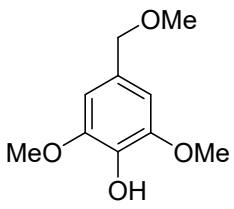
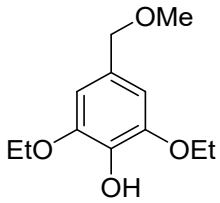


Figure S5. The synthesis of **2a**

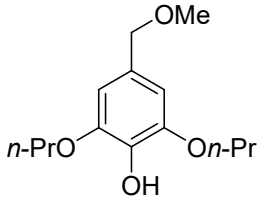
Substrate **1a** (50 mg, 0.3 mmol) was dissolved in 2 mL MeOH. KO*t*Bu (10 mg, 0.09 mmol) was added into the solution and stirred at 60 °C under oxygen balloon (1 bar). When the reaction finished in 24 h monitored by TLC, the mixture was concentrated in vacuo to recover MeOH and give a residue. Then the resulting residue was purified by flash chromatography over silica gel (Petroleum ether/EtOAc = 5:1) to give **2a** as a yellow solid (46 mg, 78% yield).



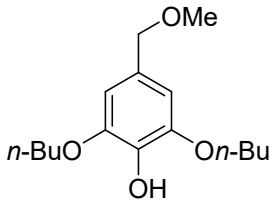
2,6-Dimethoxy-4-(methoxymethyl)phenol (2a), [5] yellow oil, purification by flash column chromatography (eluent: PE/EA = 5/1), 46 mg (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (s, 2H), 5.57 (s, 1H), 4.37 (s, 2H), 3.88 (s, 6H), 3.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 134.2, 129.2, 104.6, 75.0, 57.9, 56.3.



2,6-Diethoxy-4-(methoxymethyl)phenol (2b), yellow solid, purification by flash column chromatography (eluent: PE/EA = 5/1), 56 mg (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (s, 2H), 5.56 (s, 1H), 4.34 (s, 2H), 4.11 (q, J = 7.2 Hz, 4H), 3.35 (s, 3H), 1.43 (t, J = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.3, 134.8, 129.0, 105.8, 75.0, 64.8, 57.8, 15.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_4Na$ 249.1103; Found 249.1099.

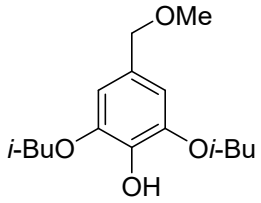


4-(Methoxymethyl)-2,6-dipropoxyphenol (2c), yellow solid, purification by flash column chromatography (eluent: PE/EA = 6/1), 52 mg (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (s, 2H), 5.53 (s, 1H), 4.34 (s, 2H), 4.00 (t, J = 6.8 Hz, 4H), 3.36 (s, 3H), 1.88 - 1.79 (m, 4H), 1.03 (t, J = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.5, 134.9, 129.0, 105.9, 75.0, 70.9, 57.9, 22.6, 10.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{22}O_4Na$ 277.1416; Found 277.1412.

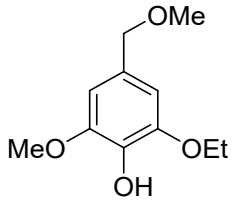


2,6-Dibutoxy-4-(methoxymethyl)phenol (2d), yellow oil, purification by flash column chromatography (eluent: PE/EA = 6/1), 58 mg (69% yield). ^{1}H NMR (400

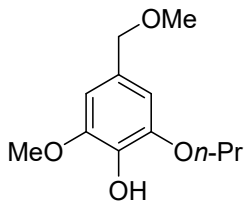
MHz, $CDCl_3$): δ 6.48 (s, 2H), 5.46 (s, 1H), 4.28 (s, 2H), 3.97 (t, *J* = 6.8 Hz, 4H), 3.29 (s, 3H), 1.76 - 1.69 (m, 4H), 1.46 -1.37 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.4, 133.8, 128.0, 104.8, 74.0, 68.0, 56.8, 30.3, 18.2, 12.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{26}O_4Na$ 305.1729; Found 305.1728.



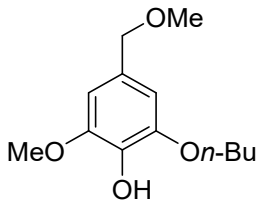
2,6-Diisobutoxy-4-(methoxymethyl)phenol (2e), yellow solid, purification by flash column chromatography (eluent: PE/EA = 6/1), 55 mg (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.47 (s, 2H), 5.43 (s, 1H), 4.27 (s, 2H), 3.73 (d, *J* = 6.4 Hz, 4H), 3.29 (s, 3H), 2.11 - 2.01 (m, 2H), 0.96 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.6, 134.9, 129.0, 106.0, 75.8, 75.0, 57.9, 28.3, 19.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{26}O_4Na$ 305.1729; Found 305.1726.



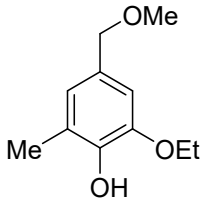
2-Ethoxy-6-methoxy-4-(methoxymethyl)phenol (2f), yellow solid, purification by flash column chromatography (eluent: PE/EA = 5/1), 46 mg (73% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.18 (s, 1H), 6.56 (s, 1H), 6.55 (s, 1H), 4.28 (s, 2H), 3.99 (q, *J* = 6.8 Hz, 2H), 3.75 (s, 3H), 3.25 (s, 3H), 1.31 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 148.0, 147.0, 135.3, 128.2, 106.8, 105.3, 74.1, 64.3, 57.2, 56.0, 15.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_4Na$ 235.0946; Found 235.0944.



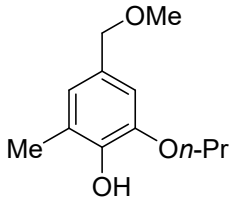
2-Methoxy-4-(methoxymethyl)-6-propoxyphenol (2g), yellow solid, purification by flash column chromatography (eluent: PE/EA = 5/1), 43 mg (63% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.15 (s, 1H), 6.55 (s, 1H), 6.54 (s, 1H), 4.27 (s, 2H), 3.89 (t, J = 6.8 Hz, 2H), 3.75 (s, 3H), 3.25 (s, 3H), 1.76-1.67 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 148.4, 147.5, 135.6, 128.6, 107.1, 105.6, 74.4, 70.7, 57.6, 56.3, 22.7, 10.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_4Na$ 249.1103; Found 249.1104.



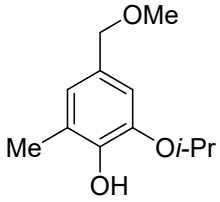
2-Butoxy-6-methoxy-4-(methoxymethyl)phenol (2h), yellow solid, purification by flash column chromatography (eluent: PE/EA = 5/1), 43 mg (60% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.14 (s, 1H), 6.55 (s, 2H), 4.27 (s, 2H), 3.93 (t, J = 6.4 Hz, 2H), 3.75 (s, 3H), 3.25 (s, 3H), 1.72 – 1.65 (m, 2H), 1.49 – 1.39 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 153.1, 152.2, 140.3, 133.3, 111.8, 110.3, 79.2, 73.5, 62.3, 61.1, 36.2, 23.9, 19.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_4Na$ 263.1259; Found 263.1263.



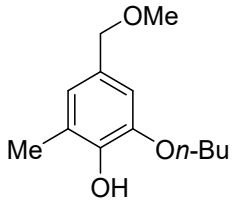
2-Ethoxy-4-(methoxymethyl)-6-methylphenol (2i), yellow oil, purification by flash column chromatography (eluent: PE/EA = 5/1), 32 mg (55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 6.70 (s, 1H), 5.75 (s, 1H), 4.33 (s, 2H), 4.11 (q, J = 6.8 Hz, 2H), 3.35 (s, 3H), 2.24 (s, 3H), 1.43 (t, J = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.4, 143.4, 128.9, 123.5, 122.9, 109.0, 74.9, 64.6, 57.8, 15.4, 15.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_3Na$ 219.0997; Found 219.0992.



4-(Methoxymethyl)-2-methyl-6-propoxyphenol (2j), yellow solid, purification by flash column chromatography (eluent: PE/EA = 6/1), 38 mg (61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 (s, 1H), 6.70 (s, 1H), 5.75 (s, 1H), 4.33 (s, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 3.35 (s, 3H), 2.25 (s, 3H), 1.86 - 1.81 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.6, 143.4, 128.9, 123.4, 122.9, 109.0, 74.9, 70.5, 57.8, 22.6, 15.4, 10.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_3Na$ 233.1154; Found 233.1148.

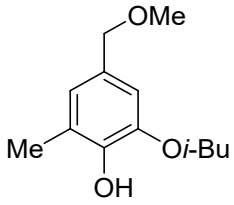


2-Isopropoxy-4-(methoxymethyl)-6-methylphenol (2k), yellow oil, purification by flash column chromatography (eluent: PE/EA = 7/1), 36 mg (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (s, 1H), 6.69 (s, 1H), 5.79 (s, 1H), 4.62 - 4.53 (m, 1H), 4.33 (s, 2H), 3.35 (s, 3H), 2.24 (s, 3H), 1.35 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.3, 144.2, 128.9, 123.6, 122.9, 110.6, 74.9, 71.7, 57.8, 22.3, 15.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_3Na$ 233.1154; Found 233.1155.

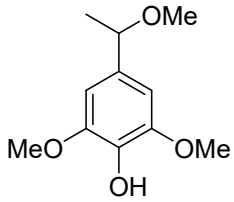


2-Butoxy-4-(methoxymethyl)-6-methylphenol (2l), yellow oil, purification by flash column chromatography (eluent: PE/EA = 7/1), 42 mg (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 (s, 1H), 6.70 (s, 1H), 5.75 (s, 1H), 4.33 (s, 2H), 4.03 (t, *J* = 6.8 Hz, 2H), 3.35 (s, 3H), 2.24 (s, 3H), 1.82 - 1.75 (m, 2H), 1.53 - 1.44 (m, 2H), 0.98 (t, *J*

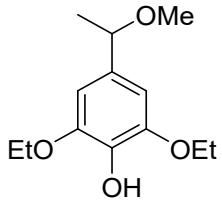
= 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.6, 143.4, 128.9, 123.4, 122.8, 108.9, 74.9, 68.7, 57.8, 31.3, 19.2, 15.4, 13.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_3Na$ 247.1310; Found 247.1304.



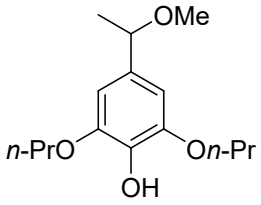
2-Isobutoxy-4-(methoxymethyl)-6-methylphenol (2m), yellow oil, purification by flash column chromatography (eluent: PE/EA = 7/1), 37 mg (55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 6.70 (s, 1H), 5.71 (s, 1H), 4.33 (s, 2H), 3.81 (d, *J* = 6.8 Hz, 2H), 3.36 (s, 3H), 2.25 (s, 3H), 2.17 - 2.07 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 142.4, 127.9, 122.4, 121.8, 107.9, 74.3, 73.9, 56.8, 27.2, 18.2, 14.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_3Na$ 247.1310; Found 247.1306.



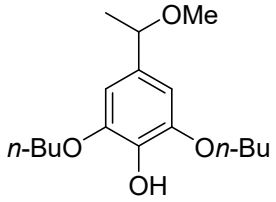
2,6-Dimethoxy-4-(1-methoxyethyl)phenol (2n), yellow solid, purification by flash column chromatography (eluent: PE/EA = 5/1), 39 mg (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.53 (s, 2H), 5.52 (s, 1H), 4.19 (q, *J* = 6.4 Hz, 1H), 3.88 (s, 6H), 3.21 (s, 3H), 1.41 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.1, 134.7, 133.9, 102.7, 79.9, 56.4, 56.3, 24.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_4Na$ 235.0946; Found 235.0942.



2,6-Diethoxy-4-(1-methoxyethyl)phenol (2o), yellow solid, purification by flash column chromatography (eluent: PE/EA = 5/1), 50 mg (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.51 (s, 2H), 5.53 (s, 1H), 4.18– 4.08 (m, 5H), 3.19 (s, 3H), 1.44 – 1.38 (m, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.3, 133.5, 133.4, 102.8, 78.8, 63.7, 55.3, 23.0, 14.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_4Na$ 263.1259; Found 263.1255.

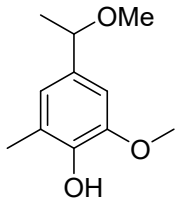


4-(1-Methoxyethyl)-2,6-dipropoxyphenol (2p), yellow solid, purification by flash column chromatography (eluent: PE/EA = 5/1), 48 mg (60% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.52 (s, 2H), 5.47 (s, 1H), 4.17 (q, J = 6.6 Hz, 1H), 4.01 (t, J = 6.6 Hz, 4H), 3.21 (s, 3H), 1.88 – 1.82 (m, 4H), 1.41 (d, J = 6.6 Hz, 3H), 1.04 (t, J = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.5, 134.5, 134.4, 103.9, 79.9, 70.8, 56.3, 24.1, 22.6, 10.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{24}O_4Na$ 291.1572; Found 291.1576.

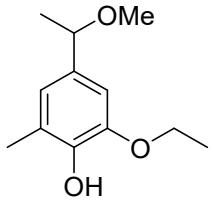


2,6-Dibutoxy-4-(1-methoxyethyl)phenol (2q), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 54 mg (61% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.51 (s, 2H), 5.47 (s, 1H), 4.17 (q, J = 6.6 Hz, 1H), 4.04 (t, J = 7.2 Hz, 4H), 3.20 (s, 3H), 1.82 – 1.77 (m, 4H), 1.52 – 1.47 (m, 4H), 1.40 (d, J = 6.6 Hz, 3H), 0.97 (t, J = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.5, 134.5, 134.4, 103.9,

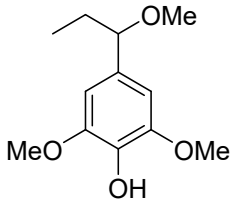
79.9, 69.1, 56.3, 31.4, 24.1, 19.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{28}O_4Na$ 319.1885; Found 319.1888.



2-Methoxy-4-(1-methoxyethyl)-6-methylphenol (2r), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 35 mg (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 6.67 (s, 1H), 5.68 (s, 1H), 4.18 (q, *J* = 6.4 Hz, 1H), 3.89 (s, 3H), 3.21 (s, 3H), 2.25 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 143.0, 134.4, 123.4, 121.3, 105.7, 79.6, 56.3, 56.0, 23.9, 15.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{17}O_3$ 197.1178; Found 197.1174.

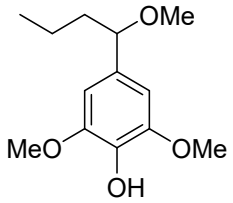


2-Ethoxy-4-(1-methoxyethyl)-6-methylphenol (2s), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 37 mg (58% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.69 (s, 1H), 6.65 (s, 1H), 5.72 (s, 1H), 4.17 (q, *J* = 6.0 Hz, 1H), 4.12 (q, *J* = 6.6 Hz, 2H), 3.20 (s, 3H), 2.25 (s, 3H), 1.44 (t, *J* = 6.6 Hz, 3H), 1.41 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.6, 143.1, 134.3, 123.3, 121.2, 106.6, 79.6, 64.5, 56.3, 24.0, 15.6, 15.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_3Na$ 233.1154; Found 233.1153.

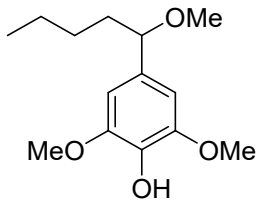


2,6-Dimethoxy-4-(1-methoxypropyl)phenol (2t), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 41 mg (61% yield). ^{1}H NMR (600

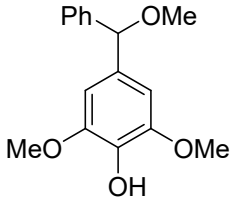
MHz, $CDCl_3$): δ 6.50 (s, 2H), 5.50 (s, 1H), 3.90 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 6H), 3.20 (s, 3H), 1.84 – 1.76 (m, 1H), 1.66 – 1.57 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 133.9, 133.4, 103.2, 85.8, 56.6, 56.3, 31.0, 10.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_4Na$ 249.1103; Found 249.1098.



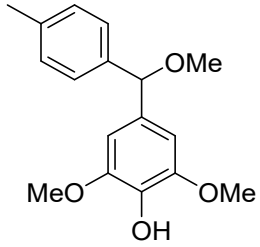
2,6-Dimethoxy-4-(1-methoxybutyl)phenol (2u), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 55 mg (76% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 6.44 (s, 2H), 5.46 (s, 1H), 3.91 (t, *J* = 7.2 Hz, 1H), 3.81 (s, 6H), 3.12 (s, 3H), 1.73 – 1.67 (m,1H), 1.52 – 1.46 (m, 1H), 1.37 – 1.28 (m, 1H), 1.23 – 1.14 (m, 1H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.0, 132.8, 132.7, 102.1, 83.1, 55.5, 55.2, 39.4, 18.1, 13.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_4Na$ 263.1259; Found 263.1259.



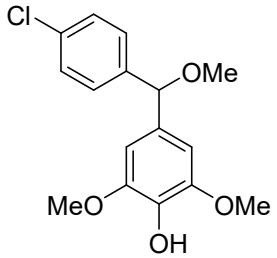
2,6-Dimethoxy-4-(1-methoxypentyl)phenol (2v), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 52 mg (68% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 6.50 (s, 2H), 5.49 (s, 1H), 3.96 (t, *J* = 6.6 Hz, 1H), 3.88 (s, 6H), 3.19 (s, 3H), 1.81 – 1.75 (m, 1H), 1.61 – 1.55 (m, 1H), 1.39 – 1.17 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 133.9, 133.8, 103.2, 84.5, 56.5, 56.3, 38.0, 28.1, 22.6, 14.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{22}O_4Na$ 277.1416; Found 277.1412.



2,6-Dimethoxy-4-(methoxy(phenyl)methyl)phenol (2w), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 61 mg (74% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 – 7.30 (m, 4H), 7.25 – 7.23(m, 1H), 6.57 (s, 2H), 5.52 (s, 1H), 5.15 (s, 1H), 3.83 (s, 6H), 3.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 142.1, 134.1, 133.1, 128.4, 127.5, 126.9, 103.8, 85.5, 57.0, 56.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}O_4Na$ 297.1103; Found 297.1103.

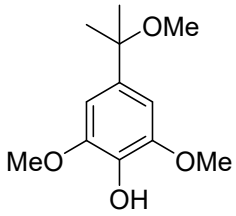


2,6-Dimethoxy-4-(methoxy(p-tolyl)methyl)phenol (2x), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 54 mg (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.57 (s, 2H), 5.46 (s, 1H), 5.13 (s, 1H), 3.86 (s, 6H), 3.37 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 139.1, 137.2, 133.9, 133.4, 129.1, 126.8, 103.6, 85.3, 57.0, 56.3, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_4Na$ 311.1259; Found 311.1260.



4-((4-Chlorophenyl)(methoxy)methyl)-2,6-dimethoxyphenol (2y), yellow solid, purification by flash column chromatography (eluent: PE/EA = 7/1), 53 mg (57% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.25 (m, 4H), 6.53 (s, 2H), 5.50 (s, 1H), 5.12 (s, 1H), 3.86 (s, 6H), 3.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.1, 140.7,

134.2, 133.2, 132.6, 128.5, 128.2, 103.7, 84.7, 57.0, 56.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{17}O_4NaCl$ 331.0713; Found 331.0704.



2,6-Dimethoxy-4-(2-methoxypropan-2-yl)phenol (2z), yellow oil, purification by flash column chromatography (eluent: PE/EA = 7/1), 20 mg (29% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (s, 2H), 5.48 (s, 1H), 3.90 (s, 6H), 3.07 (s, 3H), 1.52 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.7, 136.2, 132.5, 101.8, 55.3, 49.6, 27.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_4Na$ 249.1103; Found 249.1104.

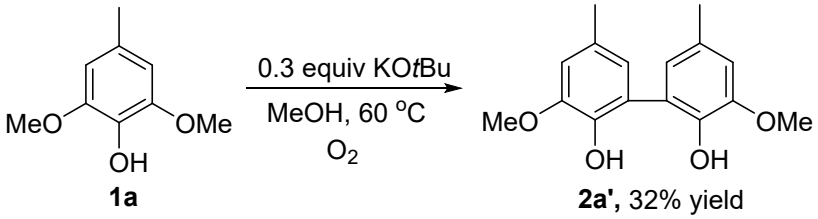
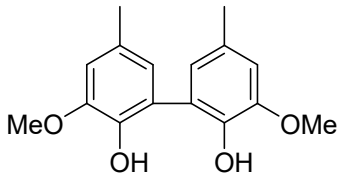


Figure S6. The dimer formation of **1a**



3,3'-Dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (2a'),[6] brown solid, purification by flash column chromatography (eluent: CH_2Cl_2/MeOH = 30:1), 13 mg (32% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (s, 2H), 6.72 (s, 2H), 6.00 (s, 2H), 3.91 (s, 6H), 2.33 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 140.3, 129.6, 124.3, 123.4, 111.3, 56.0, 21.2.

4.2 Typical procedure B for preparing products (3b as an example):

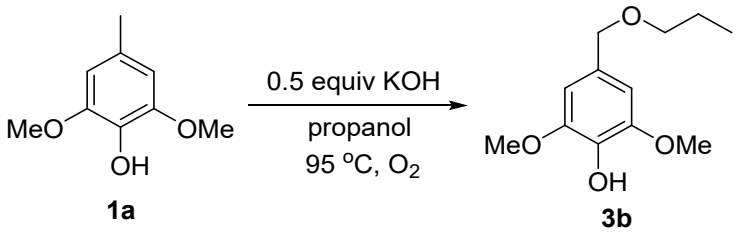
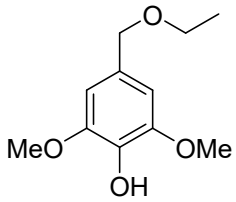


Figure S7. The synthesis of **3b**

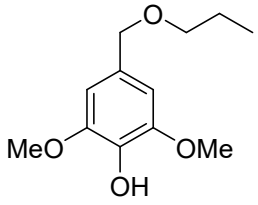
Substrate **1a** (50 mg, 0.3 mmol) was dissolved in 2 mL propanol. KOH (8 mg, 0.15 mmol) was added into the solution and stirred at 95 °C under oxygen balloon (1 bar). When the reaction finished in 48 h monitored by TLC, the mixture was concentrated in vacuo to recover propanol and give a residue. Then the resulting residue was purified by flash chromatography over silica gel (Petroleum ether/EtOAc = 5:1) to give **3b** as a yellow oil (34 mg, 50% yield).

The reaction of synthesizing **3a** was carried out at 65 °C.

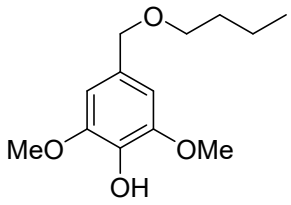
The reaction of synthesizing **3m** was carried out in MeCN and 10 equiv alcohol was used.



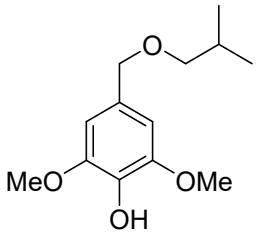
4-(Ethoxymethyl)-2,6-dimethoxyphenol (3a), yellow oil, purification by flash column chromatography (eluent: PE/EA = 5/1), 34 mg (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (s, 2H), 4.41 (s, 2H), 3.88 (s, 6H), 3.52 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.9, 134.1, 129.5, 104.5, 73.0, 65.5, 56.2, 15.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_4Na$ 235.0946; Found 235.0936.



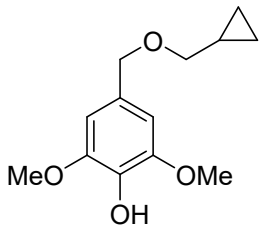
2,6-Dimethoxy-4-(propoxymethyl)phenol (3b), yellow oil, purification by flash column chromatography (eluent: PE/EA = 5/1), 34 mg (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (s, 2H), 5.49 (s, 1H), 4.42 (s, 2H), 3.89 (s, 6H), 3.42 (t, *J* = 6.8 Hz, 2H), 1.68 – 1.59 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 134.1, 129.8, 104.5, 73.1, 72.0, 56.3, 23.0, 10.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_4Na$ 249.1103; Found 249.1102.



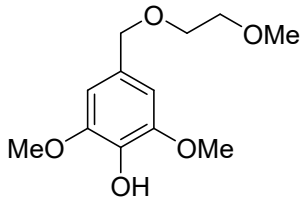
4-(Butoxymethyl)-2,6-dimethoxyphenol (3c), yellow oil, purification by flash column chromatography (eluent: PE/EA = 6/1), 33 mg (46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (s, 2H), 5.51 (s, 1H), 4.41 (s, 2H), 3.88 (s, 6H), 3.45 (t, *J* = 6.8 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.44 – 1.35 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 134.1, 129.8, 104.5, 73.2, 70.1, 56.23, 31.8, 19.4, 14.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_4Na$ 263.1259; Found 263.1251.



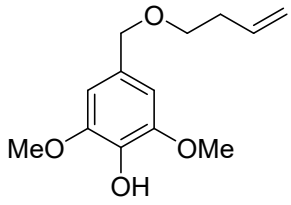
4-(Isobutoxymethyl)-2,6-dimethoxyphenol (3d), yellow oil, purification by flash column chromatography (eluent: PE/EA = 6/1), 30 mg (41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (s, 2H), 5.50 (s, 1H), 4.42 (s, 2H), 3.88 (s, 6H), 3.21 (d, *J* = 6.4 Hz, 2H), 1.95 – 1.85 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.1, 134.1, 130.0, 104.5, 77.2, 73.3, 56.4, 28.6, 19.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_4Na$ 263.1259; Found 263.1253.



4-((Cyclopropylmethoxy)methyl)-2,6-dimethoxyphenol (3e), yellow oil, purification by flash column chromatography (eluent: PE/EA = 5/1), 38 mg (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (s, 2H), 5.51 (s, 1H), 4.45 (s, 2H), 3.88 (s, 6H), 3.28 (d, *J* = 7.2 Hz, 2H), 1.13 – 1.05 (m, 1H), 0.56 – 0.52 (m, 2H), 0.21 – 0.18 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.0, 133.1, 128.6, 103.5, 73.8, 71.8, 55.2, 9.6, 2.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}O_4Na$ 261.1103; Found 261.1096.

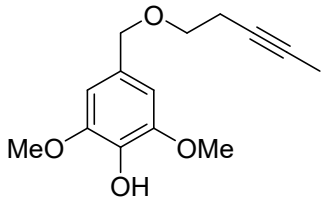


2,6-Dimethoxy-4-((2-methoxyethoxy)methyl)phenol (3f), yellow oil, purification by flash column chromatography (eluent: PE/EA = 7/1), 37 mg (51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60 (s, 2H), 5.52 (s, 1H), 4.49 (s, 2H), 3.89 (s, 6H), 3.63 – 3.56 (m, 4H), 3.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 134.2, 129.2, 104.7, 73.6, 72.0, 69.0, 59.1, 56.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_5Na$ 265.1052; Found 265.1046.

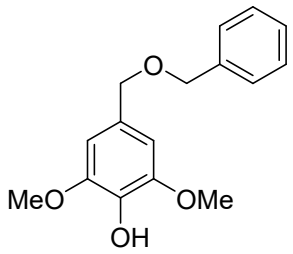


4-((But-3-en-1-yloxy)methyl)-2,6-dimethoxyphenol (3g), yellow oil, purification by flash column chromatography (eluent: PE/EA = 7/1), 34 mg (47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (s, 2H), 5.89 – 5.79 (m, 1H), 5.51 (s, 1H), 5.13 – 5.08 (m, 1H), 5.06 - 5.03 (m, 1H), 4.43 (s, 2H), 3.89 (s, 6H), 3.51 (t, *J* = 6.8 Hz, 2H), 2.41 – 2.35 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.9, 135.2, 134.1, 129.4, 116.4, 104.5, 73.1,

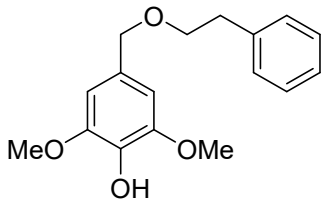
69.4, 56.2, 34.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}O_4Na$ 261.1103; Found 261.1100.



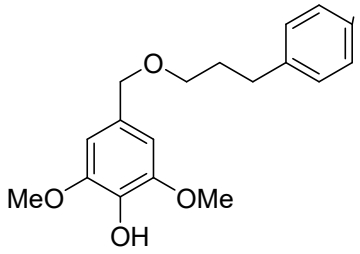
2,6-Dimethoxy-4-((pent-3-yn-1-yloxy)methyl)phenol (3h), yellow oil, purification by flash column chromatography (eluent: PE/EA = 7/1), 32 mg (42% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.59 (s, 2H), 5.51 (s, 1H), 4.47 (s, 2H), 3.90 (s, 6H), 3.54 (t, J = 6.8 Hz, 2H), 2.46 – 2.43 (m, 2H), 1.79 (t, J = 2.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 134.2, 129.2, 104.6, 76.7, 75.9, 73.2, 68.6, 56.3, 20.2, 3.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_4Na$ 273.1103; Found 273.1097.



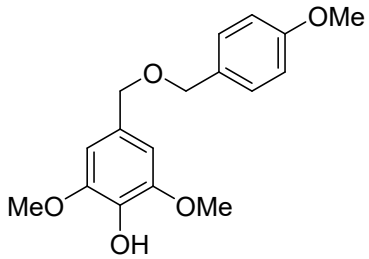
4-((Benzyloxy)methyl)-2,6-dimethoxyphenol (3i), yellow oil, purification by flash column chromatography (eluent: PE/EA = 10/1), 35 mg (42% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.26 (m, 5H), 6.58 (s, 2H), 5.53 (s, 1H), 4.50 (s, 2H), 4.49 (s, 2H), 3.89 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 138.2, 134.2, 129.3, 128.4, 127.9, 127.7, 104.7, 72.4, 71.9, 56.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}O_4Na$ 297.1103; Found 297.1100.



2,6-Dimethoxy-4-(phenethoxymethyl)phenol (3j), yellow oil, purification by flash column chromatography (eluent: PE/EA = 8/1), 37 mg (43% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.19 (m, 5H), 6.52 (s, 2H), 5.48 (s, 1H), 4.44 (s, 2H), 3.85 (s, 6H), 3.69 (t, *J* = 6.8 Hz, 2H), 2.93 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 139.0, 134.0, 129.5, 129.0, 128.3, 126.2, 104.4, 73.2, 71.0, 56.2, 36.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_4Na$ 311.1259; Found 311.1256.

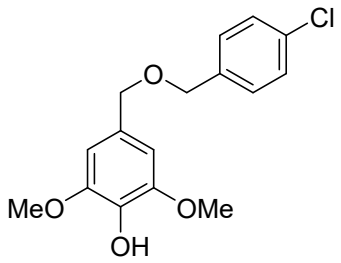


2,6-Dimethoxy-4-((3-(p-tolyl)propoxy)methyl)phenol (3k), yellow oil, purification by flash column chromatography (eluent: PE/EA = 12/1), 46 mg (51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 2H), 7.21 – 7.16 (m, 3H), 6.59 (s, 2H), 5.52 (s, 1H), 4.43 (s, 2H), 3.89 (s, 6H), 3.48 (t, *J* = 6.4 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 1.98 – 1.91 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 141.9, 134.1, 129.6, 128.5, 128.3, 125.8, 104.6, 73.2, 69.4, 56.3, 32.4, 31.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_4Na$ 339.1572; Found 339.1569.

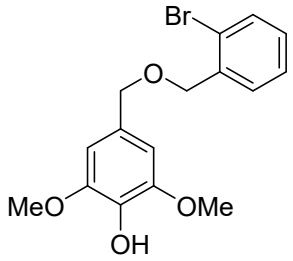


2,6-Dimethoxy-4-(((4-methoxybenzyl)oxy)methyl)phenol (3l), yellow oil, purification by flash column chromatography (eluent: PE/EA = 10/1), 38 mg (42% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.59 (s, 2H), 4.48 (s, 2H), 4.44 (s, 2H), 3.89 (s, 6H), 3.81 (s, 3H). ^{13}C NMR (150

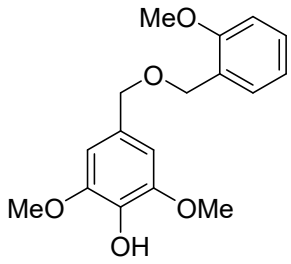
MHz, $CDCl_3$): δ 159.2, 147.0, 134.2, 130.3, 129.5, 129.4, 113.8, 104.7, 72.1, 71.6, 56.3, 55.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_5Na$ 327.1208; Found 327.1204.



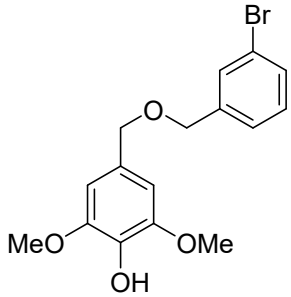
4-(((4-Chlorobenzyl)oxy)methyl)-2,6-dimethoxyphenol (3m), yellow oil, purification by flash column chromatography (eluent: PE/EA = 10/1), 45 mg (49% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 4H), 6.58 (s, 2H), 5.53 (s, 1H), 4.50 (s, 2H), 4.46 (s, 2H), 3.89 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 136.7, 134.3, 133.4, 129.2, 129.0, 128.6, 104.7, 72.5, 71.1, 56.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{17}O_4NaCl$ 331.0713; Found 331.0708.



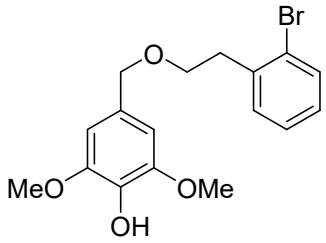
4-(((2-Bromobenzyl)oxy)methyl)-2,6-dimethoxyphenol (3n), yellow oil, purification by flash column chromatography (eluent: PE/EA = 8/1), 50 mg (47% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 6.64 (s, 2H), 5.52 (s, 1H), 4.61 (s, 2H), 4.55 (s, 2H), 3.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 137.6, 134.3, 132.6, 129.4, 129.1, 129.0, 127.4, 123.0, 104.8, 73.0, 71.4, 56.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{17}O_4BrNa$ 375.0208; Found 375.0209.



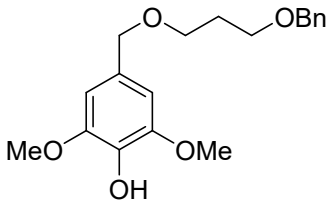
2,6-Dimethoxy-4-(((2-methoxybenzyl)oxy)methyl)phenol (3o), yellow oil, purification by flash column chromatography (eluent: PE/EA = 8/1), 42 mg (46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.62 (s, 2H), 5.49 (s, 1H), 4.59 (s, 2H), 4.52 (s, 2H), 3.89 (s, 6H), 3.83 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.2, 145.9, 133.1, 128.7, 128.1, 127.7, 125.6, 119.4, 109.2, 103.6, 71.6, 65.8, 55.3, 54.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_5Na$ 3727.1208; Found 327.1209.



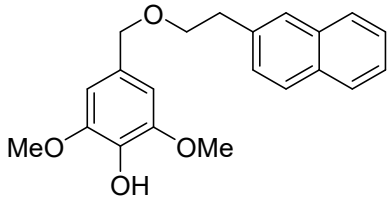
4-(((3-Bromobenzyl)oxy)methyl)-2,6-dimethoxyphenol (3p), yellow oil, purification by flash column chromatography (eluent: PE/EA = 8/1), 53 mg (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.20 (m, 2H), 6.59 (s, 2H), 5.54 (s, 1H), 4.50 (s, 2H), 4.47 (s, 2H), 3.90 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.1, 140.7, 134.4, 130.8, 130.7, 130.0, 128.9, 126.3, 122.6, 104.8, 72.7, 71.0, 56.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{17}O_4BrNa$ 375.0208; Found 375.0208.



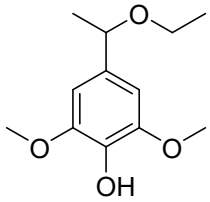
4-((2-Bromophenethoxy)methyl)-2,6-dimethoxyphenol (3q), yellow oil, purification by flash column chromatography (eluent: PE/EA = 8/1), 49 mg (45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.53 (s, 2H), 5.48 (s, 1H), 4.46 (s, 2H), 3.87 (s, 6H), 3.70 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 138.2, 134.1, 132.8, 131.2, 129.4, 128.0, 127.3, 124.7, 104.3, 73.1, 69.1, 56.3, 36.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{19}O_4NaBr$ 389.0364; Found 389.0358.



4-((3-(Benzyloxy)propoxy)methyl)-2,6-dimethoxyphenol (3r), yellow oil, purification by flash column chromatography (eluent: PE/EA = 15/1), 43 mg (43% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.28 (m, 5H), 6.56 (s, 2H), 5.49 (s, 1H), 4.50 (s, 2H), 4.41 (s, 2H), 3.87 (s, 6H), 3.61 – 3.57 (m, 4H), 1.97 – 1.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 138.5, 134.1, 129.6, 128.4, 127.6, 127.5, 104.6, 73.3, 73.0, 67.4, 67.2, 56.3, 30.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_5Na$ 355.1521; Found 355.1520.



2,6-Dimethoxy-4-((2-(naphthalen-2-yl)ethoxy)methyl)phenol (3s), yellow oil, purification by flash column chromatography (eluent: PE/EA = 15/1), 45 mg (44% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.42 – 7.38 (m, 2H), 6.51 (s, 2H), 5.47 (s, 1H), 4.46 (s, 2H), 3.85 – 3.81 (m, 8H), 3.42 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 134.9, 134.1, 133.8, 132.1, 129.4, 128.8, 127.1, 126.9, 125.9, 125.6, 125.5, 123.7, 104.4, 73.3, 70.4, 56.2, 33.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}O_4Na$ 361.1416; Found 361.1415.



4-(1-Ethoxyethyl)-2,6-dimethoxyphenol (3t), yellow oil, purification by flash column chromatography (eluent: PE/EA = 5/1), 21 mg (31% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (s, 2H), 5.47 (s, 1H), 4.31 (q, *J* = 6.4 Hz, 1H), 3.89 (s, 6H), 3.40 – 3.30 (m, 2H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 135.5, 133.8, 102.6, 78.0, 63.8, 56.3, 24.4, 15.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_4Na$ 249.1103; Found 249.1094.

4.3 Typical procedure for preparing benzyl trideuteromethoxylation product

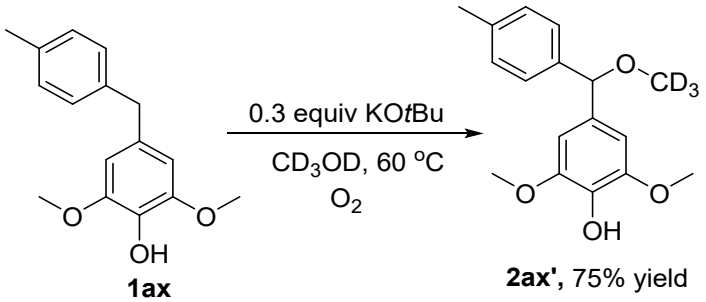
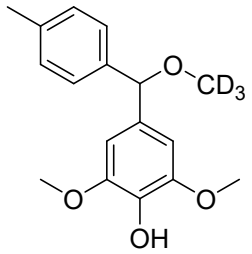


Figure S8. The synthesis of **2ax'**

Substrate **1ax** (77 mg, 0.3 mmol) was dissolved in 2 mL CD_3OD. KO*t*Bu (10 mg, 0.09 mmol) was added into the solution and stirred at 60 °C under oxygen balloon (1 bar). When the reaction finished in 24 h monitored by TLC, the mixture was

concentrated in vacuo to recover CD_3OD and give a residue. Then the resulting residue was purified by flash chromatography over silica gel (Petroleum ether/EtOAc = 7:1) to give **2ax'** as a yellow solid (65 mg, 75% yield).



2,6-Dimethoxy-4-((methoxy-d3)(p-tolyl)methyl)phenol (2ax'), yellow oil, purification by flash column chromatography (eluent: PE/EA = 7/1), 65 mg (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 2H), 5.46 (s, 1H), 5.13 (s, 1H), 3.86 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 139.1, 137.1, 133.9, 133.4, 129.1, 126.8, 103.6, 85.2, 56.3, 56.0 (m), 21.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}D_3O_4Na$ 314.1448; Found 314.1441.

5. Applications

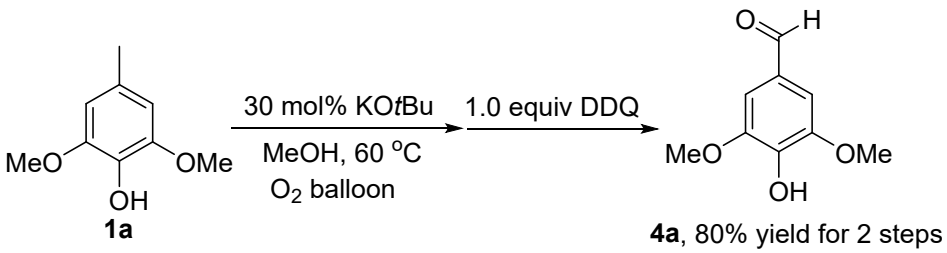
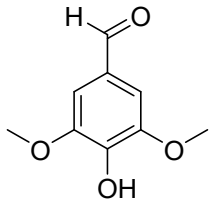


Figure S9. The synthesis of **4a**

To a solution of substrate **1a** (50 mg, 0.3 mmol) in 2 mL MeOH, KO*t*Bu (10 mg, 0.09 mmol) was added. The mixture was stirred at 60 °C under oxygen balloon (1 bar). When the reaction finished in 24 h monitored by TLC, DDQ (68 mg, 0.3 mmol) was added to the reaction solution and stirred at 60 °C for 12 h. After that, the mixture was concentrated in vacuo to recover MeOH and give a residue. Then the resulting residue was purified by flash chromatography over silica gel (Petroleum ether/ EtOAc = 2:1)

to give **2a** as a white solid (44 mg, 80% yield for 2 steps).



4-Hydroxy-3,5-dimethoxybenzaldehyde (4a), white solid, purification by flash column chromatography (eluent: PE/EA = 2/1), 44 mg (80% yield for 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.16 (s, 2H), 6.07 (s, 1H), 3.98 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.8, 147.4, 140.8, 128.4, 106.7, 56.5.[6]

6. Gram-scale reaction

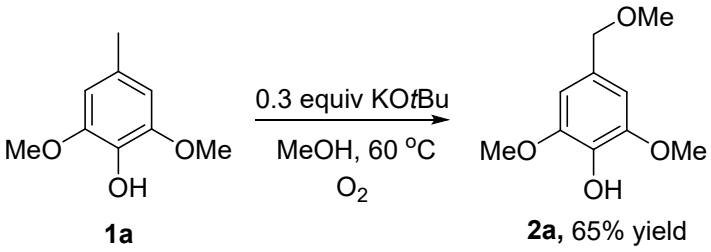


Figure S10. Gram-scale reaction

Under O_2 atmosphere, substrate **1a** (1.01 g, 6 mmol) was dissolved in MeOH (20 mL). Then KO*t*Bu (201 mg, 1.8 mmol) was added to the solution. The reaction mixture was stirred at 60 °C under O_2 atmosphere. After the reaction was completed in 24 h monitored by TLC, the reaction was quenched with 150 mL H_2O. Then the mixture was concentrated in vacuo to recover MeOH and give a residue. The resulting residue was purified by flash chromatography over silica gel (Petroleum ether/ EtOAc = 4:1) to give **2a** as a yellow solid (0.77 g, 65% yield).

7. Mechanistic Study

7.1 TEMPO as additive

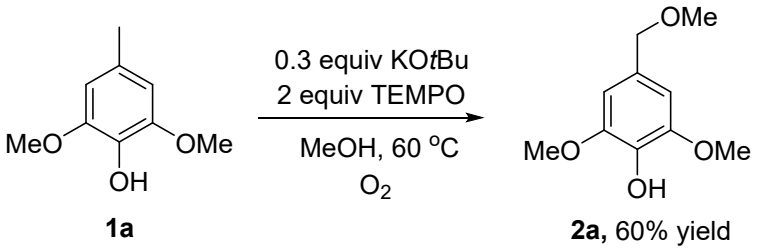


Figure S11. The reaction of **1a** with TEMPO.

KO*t*Bu (10 mg, 0.09 mmol) was added into a mixture of substrate **1ba** (50 mg, 0.3 mmol) and TEMPO (94 mg, 0.6 mmol) in MeOH (2 mL). Then the reaction mixture was stirred at 60 °C under O_2 atmosphere for 24 h. MeOH was evaporated under reduced pressure after the mixture was cooled to room temperature. Then he resulting residue was purified by flash chromatography over silica gel (Petroleum ether/ EtOAc = 4:1) to give **2a** as a yellow solid (36 mg, 60% yield).

7.2 Ethene-1,1-diyldibenzene as additive

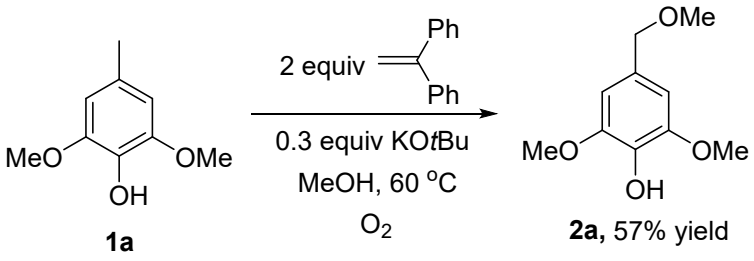


Figure S12. The reaction of **1a** with ethene-1,1-diyldibenzene.

KO*t*Bu (10 mg, 0.09 mmol) was added into a mixture of substrate **1ba** (50 mg, 0.3 mmol) and ethene-1,1-diyldibenzene (108 mg, 0.6 mmol) in MeOH (2 mL). Then the reaction mixture was stirred at 60 °C under O_2 atmosphere. When the reaction proceeded in 24 h, the mixture evaporated under reduced pressure. The resulting residue was purified by flash chromatography over silica gel (Petroleum ether/ EtOAc = 4:1) to give **2a** as a yellow solid (34 mg, 57% yield).

7.3 EPR experiments

The first oven-dried schlenk tube equipped with a stir bar was loaded with MeOH (2 mL), and KO*t*Bu (10 mg, 0.09 mmol). The second and the third oven-dried schlenk

tube with a stir bar was loaded with MeOH (2 mL), and KO*t*Bu (10 mg, 0.09 mmol), and 2,6-dimethoxy-4-methylphenol **1a** (50 mg, 0.3 mmol). The three mixtures were stirred under standard condition for 10 h. And the two solutions were analyzed by EPR respectively.

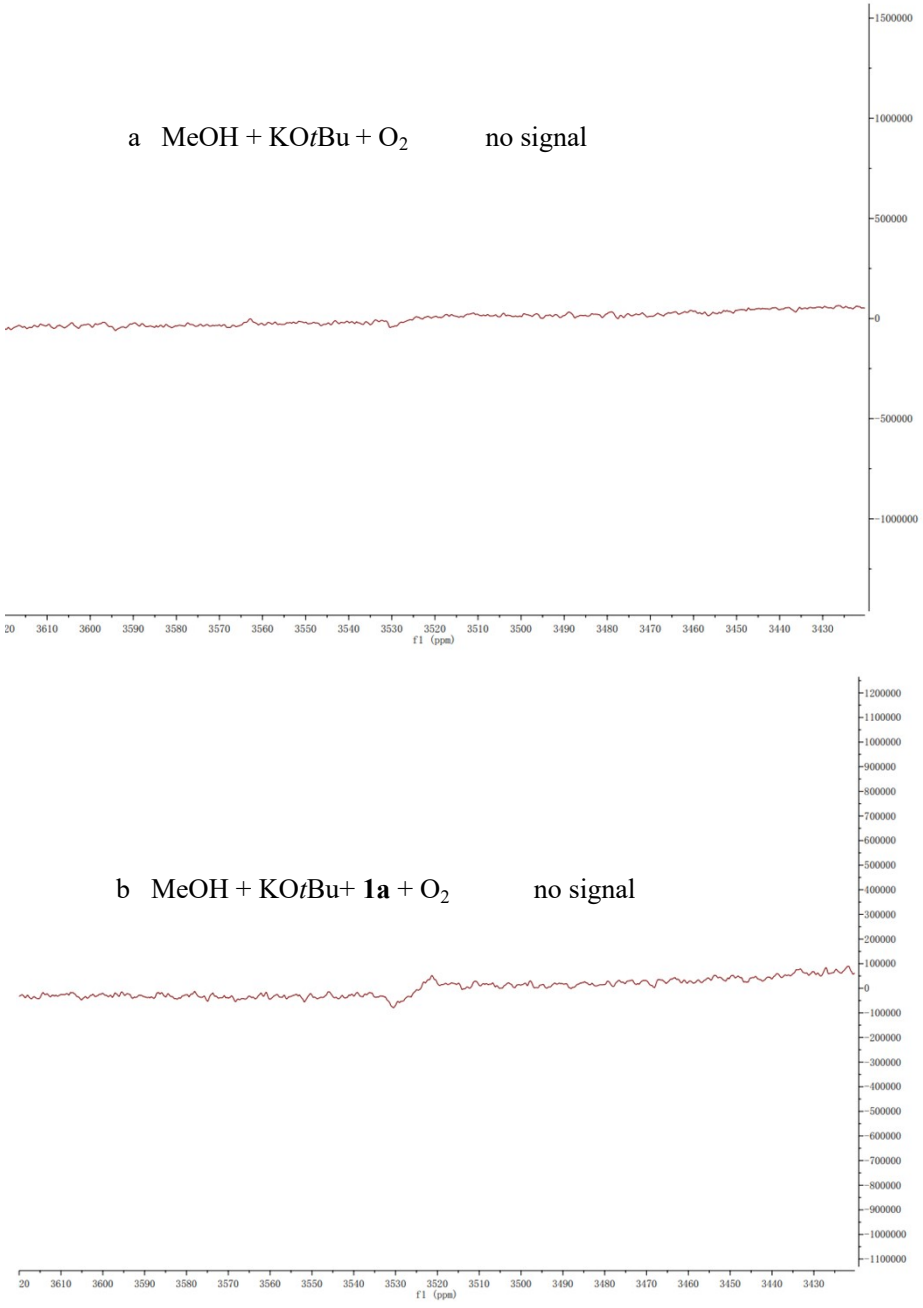
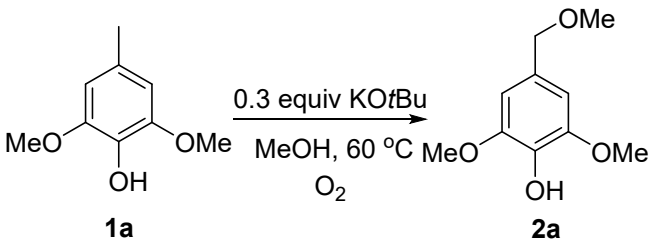


Figure S13. The EPR spectrum.

7.4 The changes of substrate 1a and methoxylated products 2a with time



1a **2a**

m (**1a**)	s (**1a**)	m (Mesitylene)	s (Mesitylene)	s (**1a**)/s (Mesitylene)	m (**1a**)/m (Mesitylene)
0	0	0	0	0	0
15.5	508.80	30.6	1809.50	0.2812	0.5065
20.6	740.26	30.4	1818.33	0.4071	0.6776
30.8	1169.99	29.8	2004.46	0.5837	1.0336
45.9	1686.38	32.6	2085.24	0.8087	1.4080

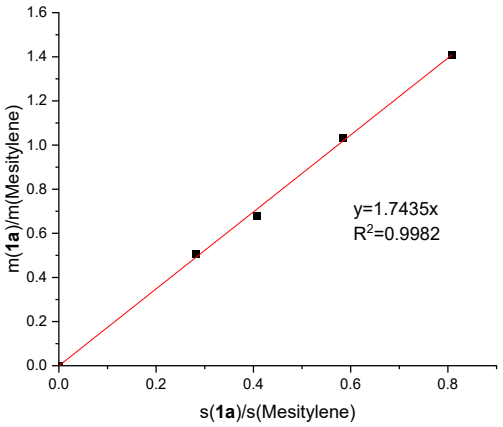


Figure S14 Standard curve of **1a**

m (**2a**)	s (**2a**)	m (Mesitylene)	s (Mesitylene)	s (**2a**)/s (Mesitylene)	m (**2a**)/m (Mesitylene)
0	0	0	0	0	0
17.2	496.30	30.6	1809.50	0.2743	0.5621
21.1	638.98	30.4	1818.33	0.3498	0.6941
30.5	990.38	29.8	2004.46	0.4941	1.0235
45.4	1420.15	32.6	2085.24	0.6810	1.3926

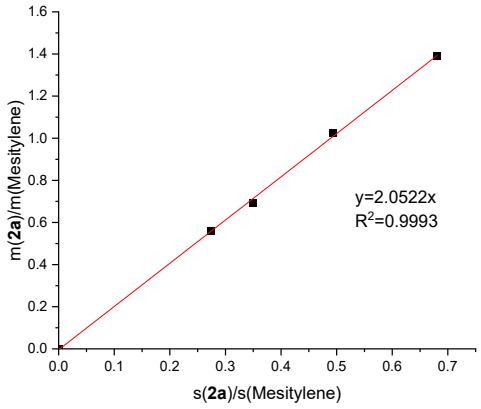


Figure S15 Standard curve of **2a**.

Each of oven-dried flasks equipped with a stir bar was loaded with MeOH (2 mL), KO*t*Bu (10 mg, 0.09 mmol)and substrate **1a** (50 mg, 0.3 mmol). Then the reaction mixtures were stirred at 60 °C under O_2 atmosphere. The mixtures proceeded in 1 h, 2 h, 3.5 h, 4 h, 5 h, 10 h, 15 h and 20 h respectively. The mixtures were analyzed by GC for quantitative study.

7.5 The study of reaction kinetics mechanism

([S] = [C_A/C_{A0}])

Time (h)	[S]	ln[S]	1/[S]
0	1.00000	0.00000	1.00000
1	0.83228	-0.18359	1.20152
2	0.77118	-0.25984	1.29672
3.5	0.65544	-0.42245	1.52570
4	0.63796	-0.44948	1.56750
5	0.44821	-0.80248	2.23108
10	0.23088	-1.46587	4.33132
15	0.17609	-1.73678	5.67901
20	0.07213	-2.62922	13.86301

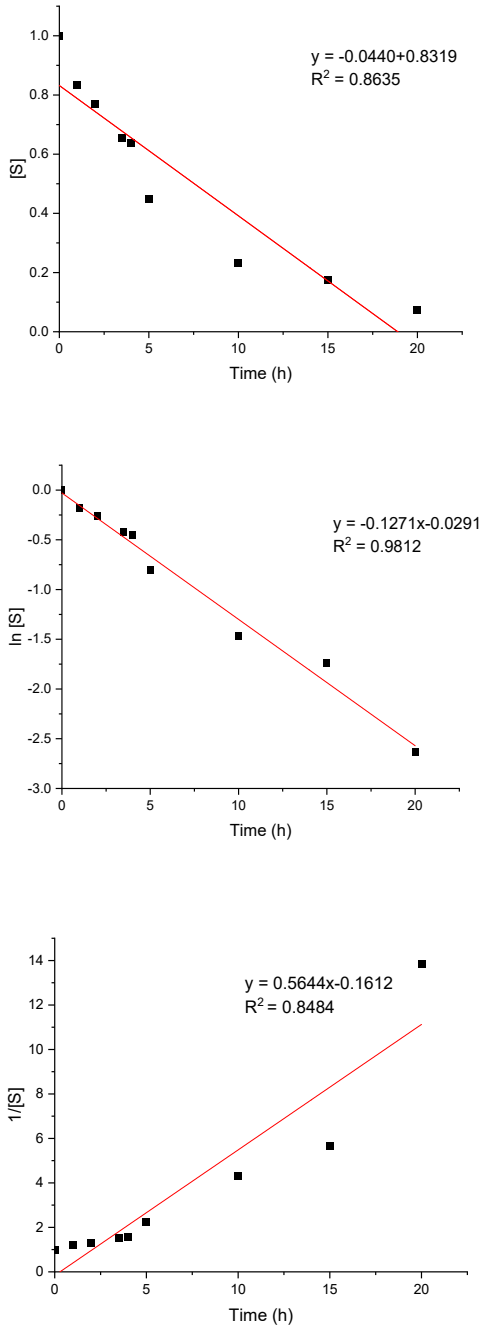


Figure S16 Reaction rate curve of **1a**.

7.6 HPLC method and results

The detection of H_2O_2 was worked on an Agilent 1260 Infinity equipped with a DAD-3000 diode array detector high performance liquid chromatography (HPLC). The separation was conducted using Agilent Zorbax C18 (4.6 x 250 mm) column. The mobile phase consisted of 0.1% phosphoric acid in water (A) and methanol (B) in a

gradient elution programmed as follows: 0–5 min, maintain at 8% B; 5–18 min, linear gradient from 8% to 60% B; 18–22 min, linear gradient from 60% to 8% B. The solvent flow rate was 0.3 mL/min and the column oven temperature was 35 °C. The analysis was carried out within the wavelength interval of 190-400 nm and the optimal wavelength value for the detection of H_2O_2 was 210 nm. The identification of compounds was carried out by comparing the retention time with the commercially available reference compound.

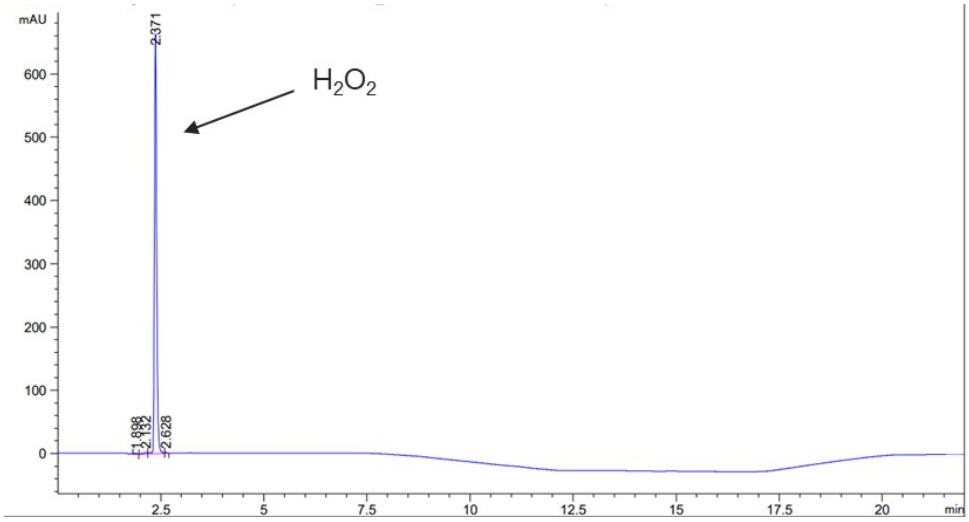


Figure S17 HPLC spectra of hydrogen peroxide

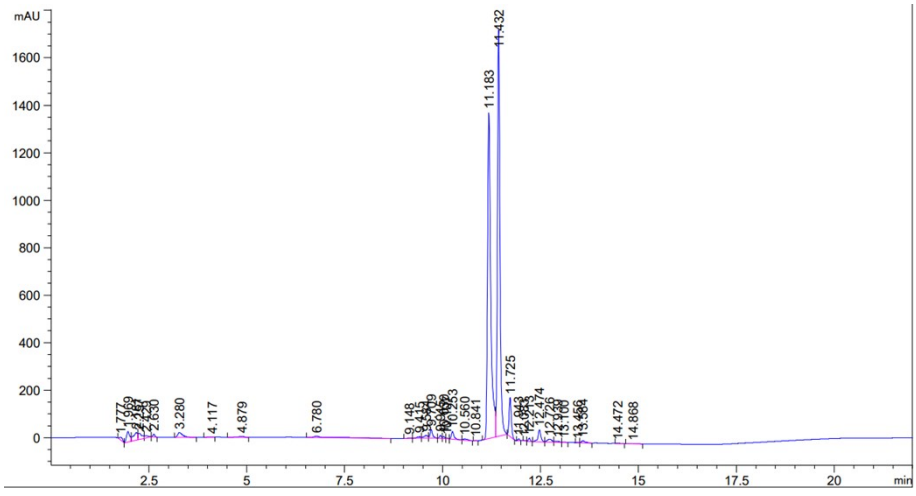


Figure S18 HPLC spectra of reaction solution

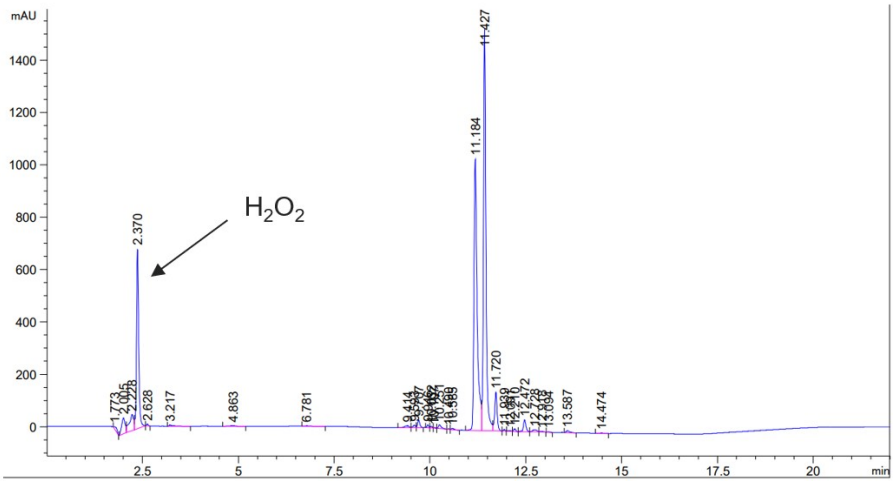


Figure S19 HPLC spectra of the mixture with hydrogen peroxide added after the reaction

7.7 The procedure for preparing VII' and the corresponding methoxylated product 2w

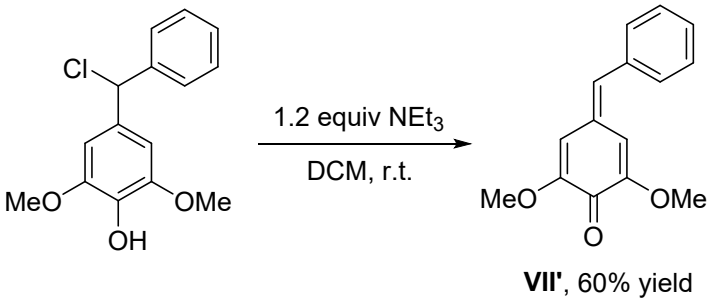
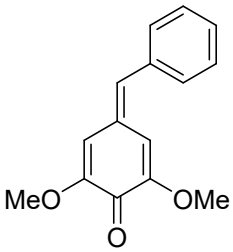


Figure S20. The synthesis of **VII'**

4-(Chloro(phenyl)methyl)-2,6-dimethoxyphenol (1.11 g, 4.0 mmol) was dissolved in 25 mL dry DCM under N_2 atmosphere and NEt_3 (490 mg, 4.8 mmol) was added. After the reaction finished in 2 h monitored by TLC, diethyl ether was added. The resulting precipitate was filtered off and dried under reduced pressure. The desired product was obtained as a yellow solid (581 mg, 60% yield).[7]



4-Benzylidene-2,6-dimethoxycyclohexa-2,5-dien-1-one (VII'), yellow solid, 581 mg (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.43 (m, 4H), 7.42 – 7.36 (m, 1H), 7.16 (s, 1H), 6.86 (d, *J* = 1.6 Hz, 1H), 6.41 (d, *J* = 1.6 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.4, 153.6, 152.1, 140.8, 136.1, 130.2, 130.1, 129.0, 128.9, 112.7, 105.6, 55.64, 55.61. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{14}O_3$ 242.0943; Found 242.0946.

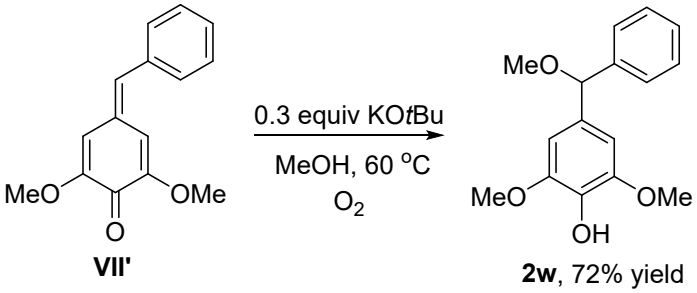


Figure S21. The synthesis of **2w** from **VII'**

KO*t*Bu (10 mg, 0.09 mmol) was added into a mixture of 4-benzylidene-2,6-dimethoxycyclohexa-2,5-dien-1-one (73 mg, 0.3 mmol) in MeOH (2 mL). The reaction mixture was stirred at 60 °C under O_2 atmosphere. The mixture was evaporated under reduced pressure after 3 h. The resulting residue was purified by flash chromatography over silica gel (Petroleum ether/ EtOAc = 7:1) to give **2w** as a yellow solid (59 mg, 72% yield).

8. Reference

[1] Y. Guo, X.-M. Fan, M. Nie, H.-W. Liu, D.-H. Liao, X.-D. Pan, Y.-F. Ji, *Eur. J. Org. Chem.*, 2015, **21**, 4744–4755.

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[4] J. Wang, T. Wang, H. Du, N. Chen, *J. Org. Chem.*, 2023, **88**, 12572−12584.

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1248-1254.

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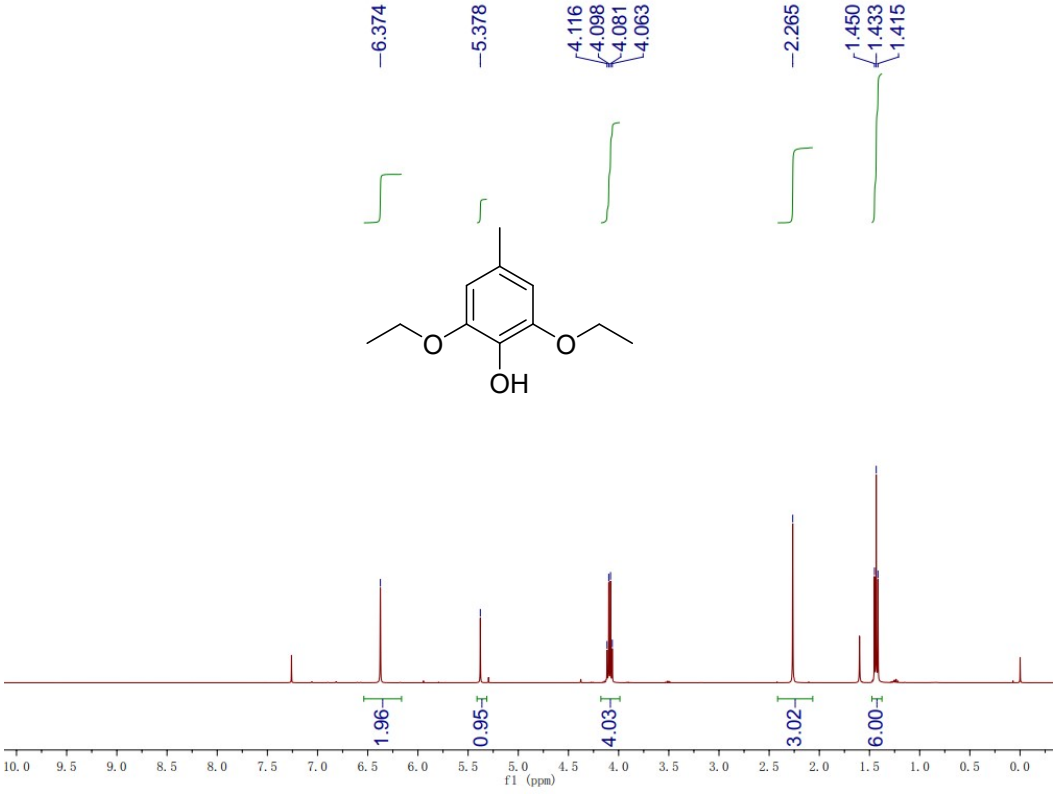
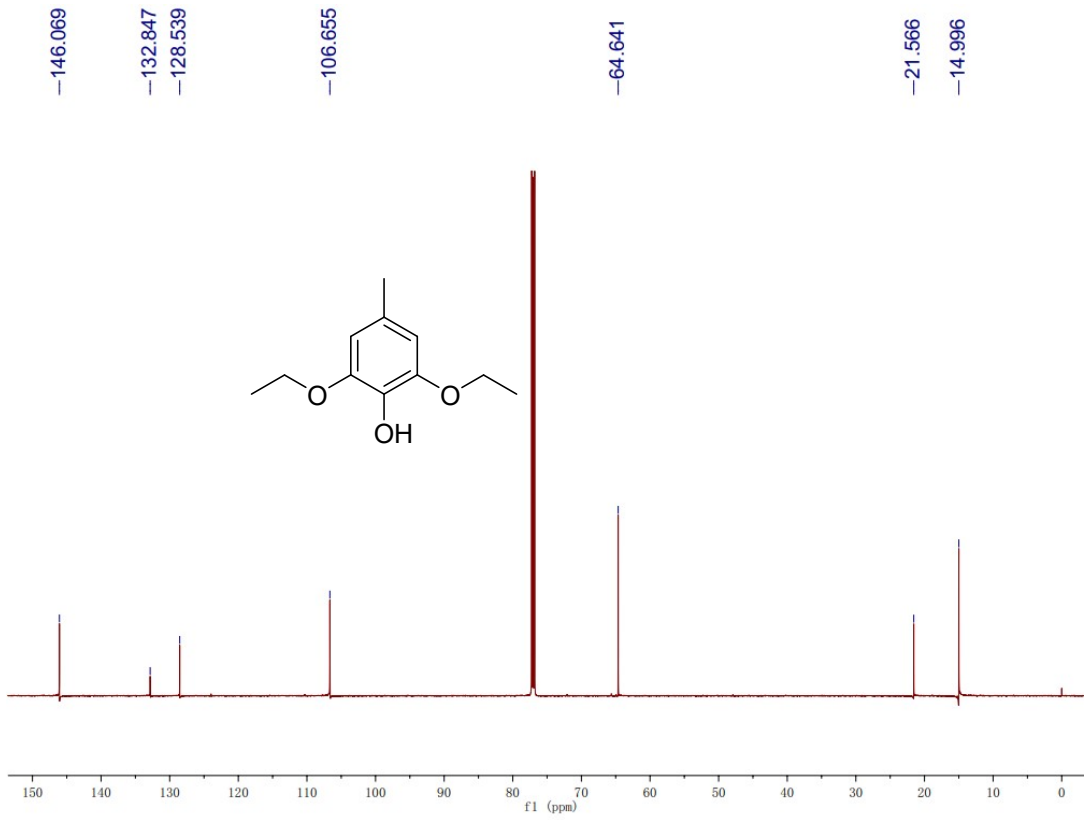
9. ^{1}H and ^{13}C-NMR Spectra Data

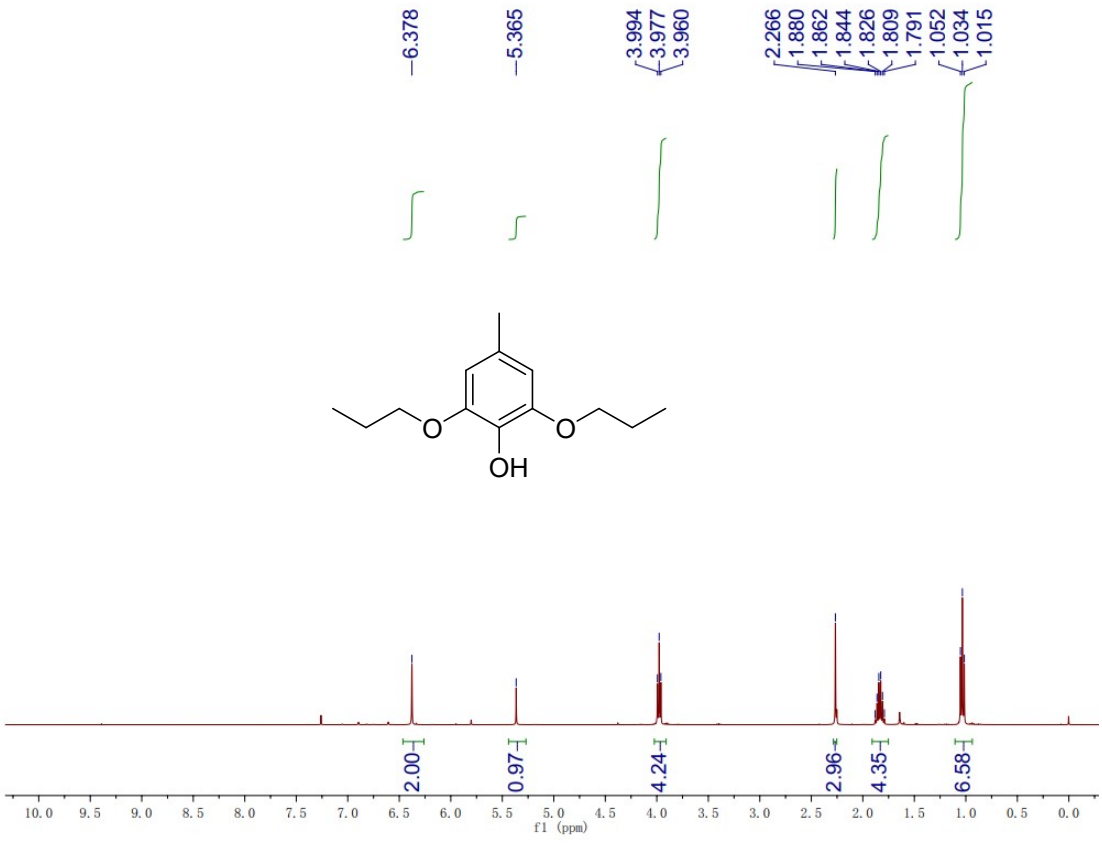
2,6-Diethoxy-4-methylphenol (1b) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



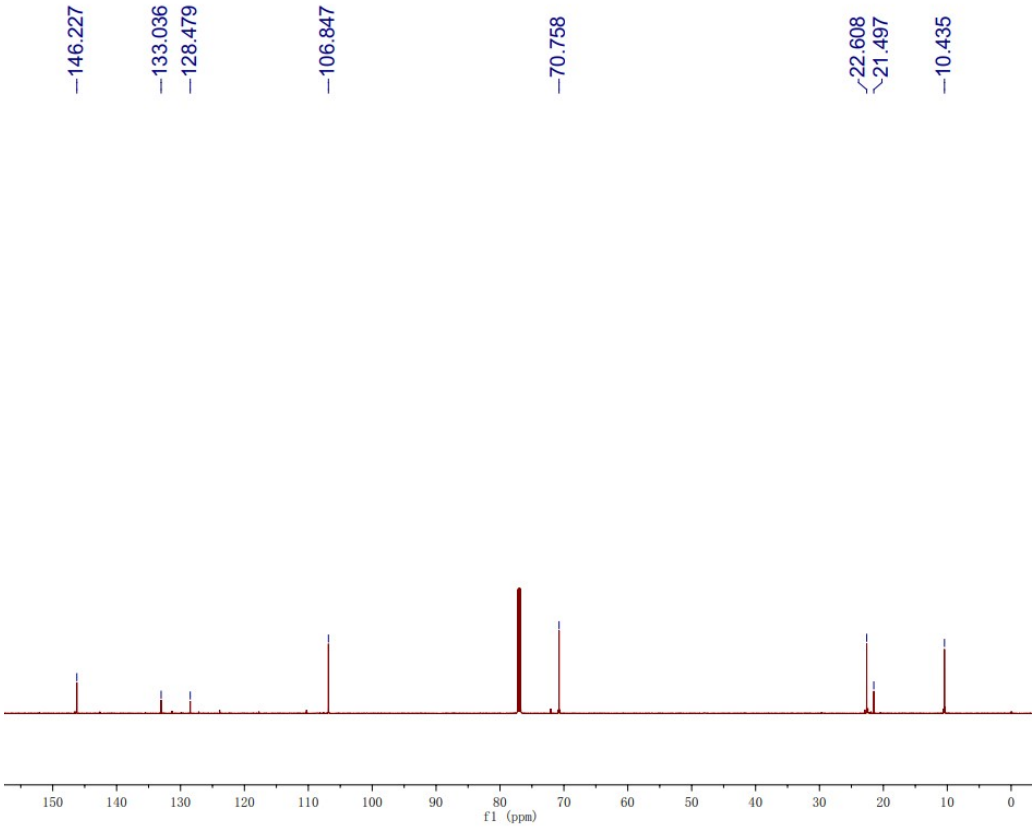
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



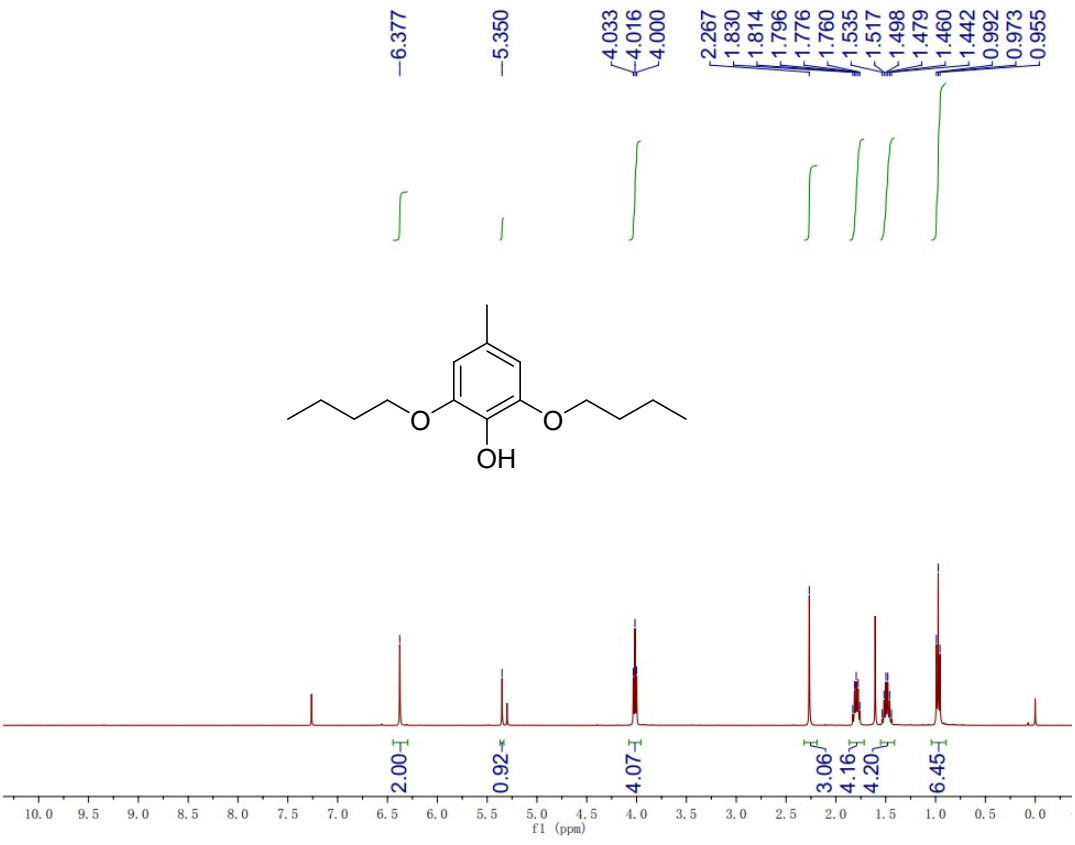
4-Methyl-2,6-dipropoxyphenol (1c) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



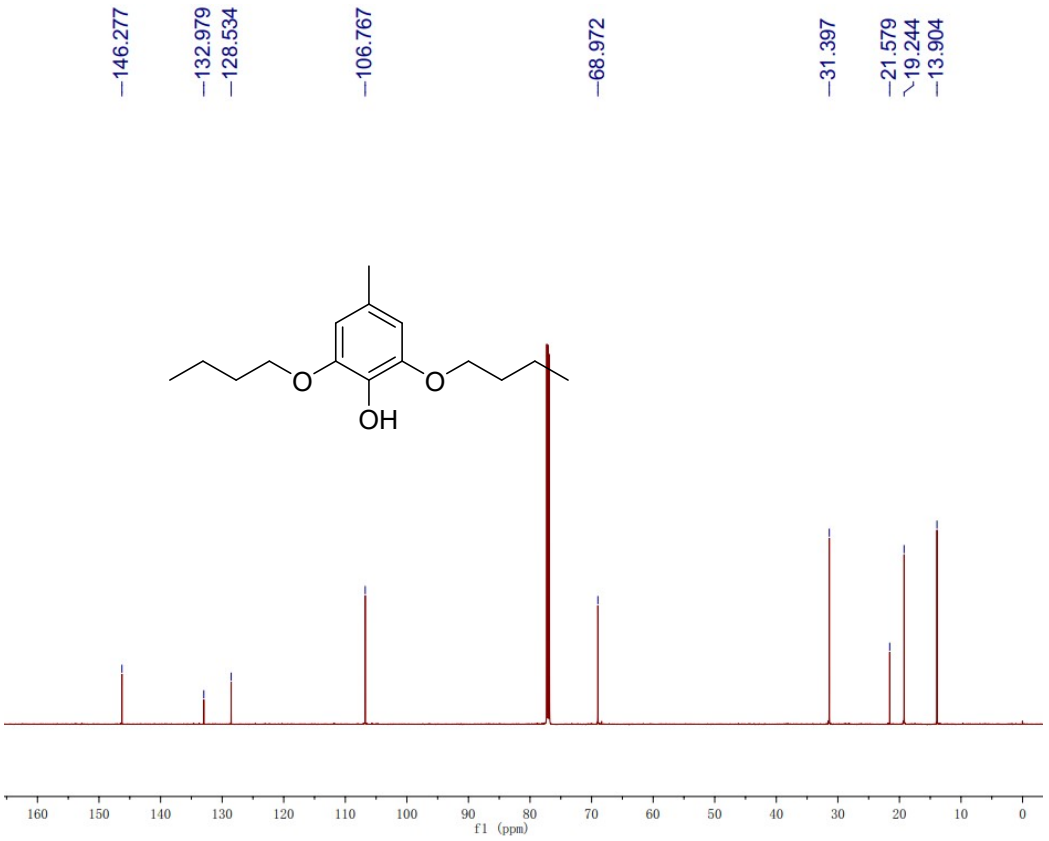
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



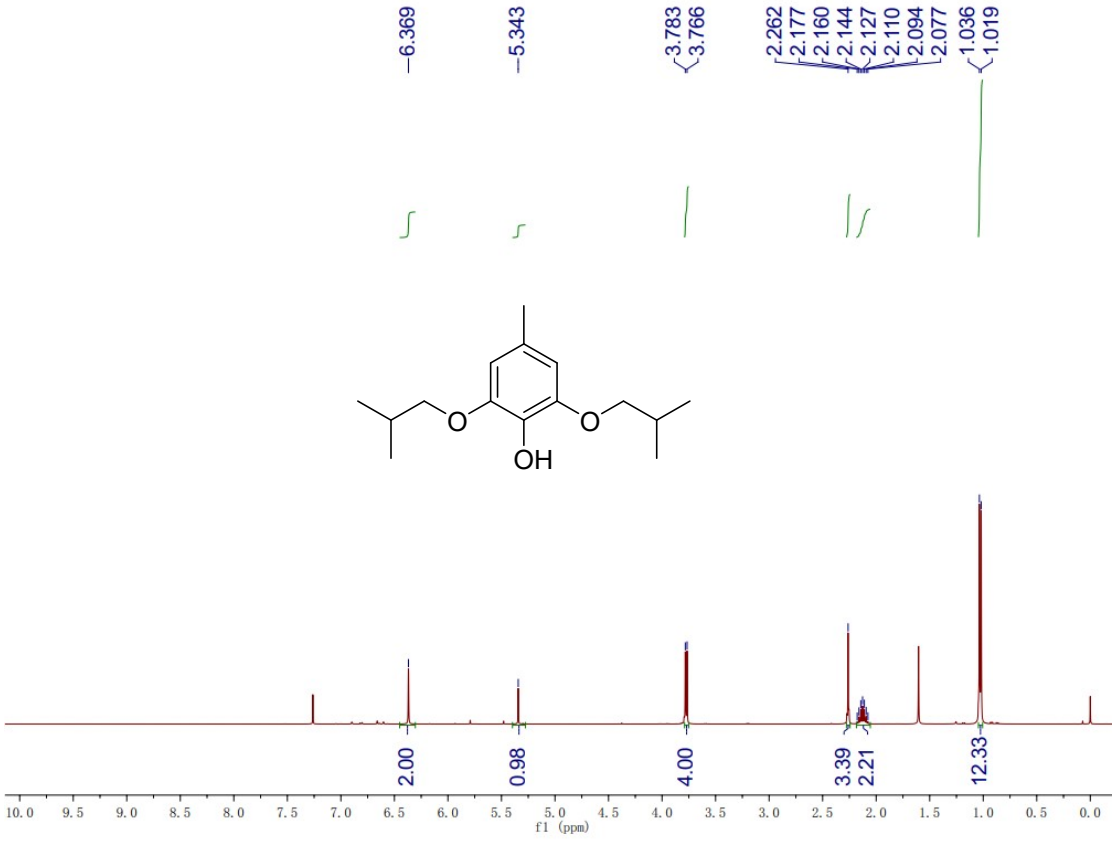
2,6-Dibutoxy-4-methylphenol (1d) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



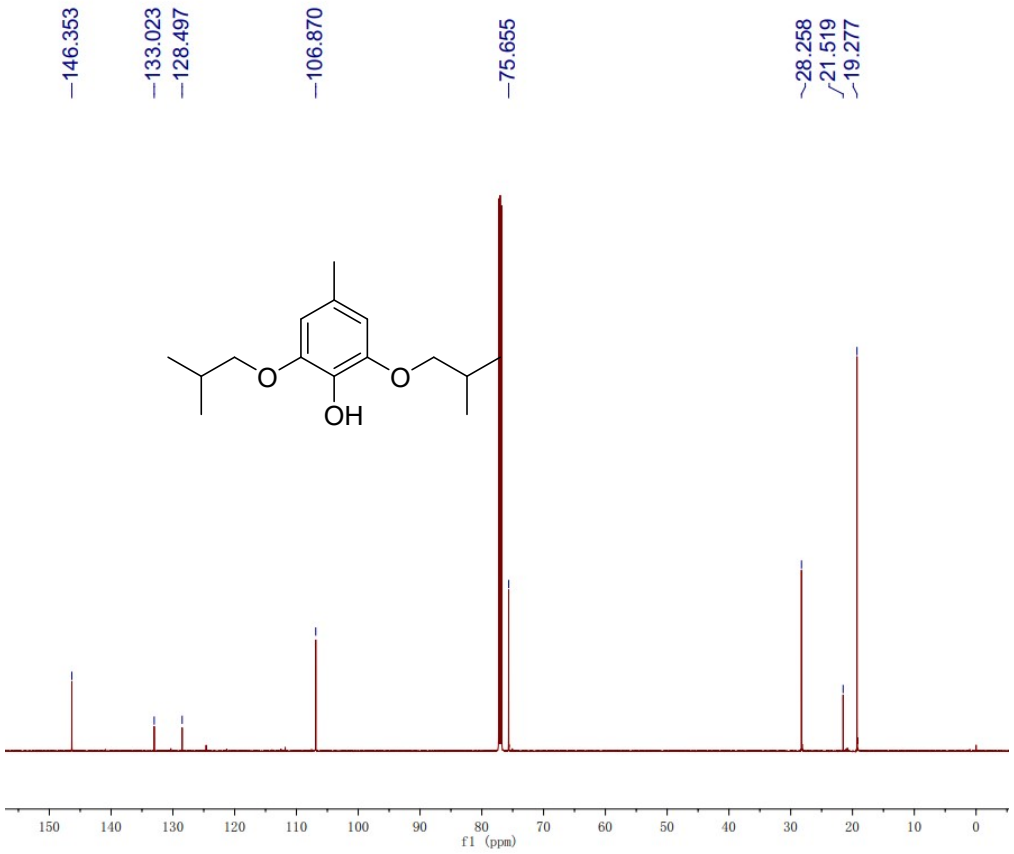
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



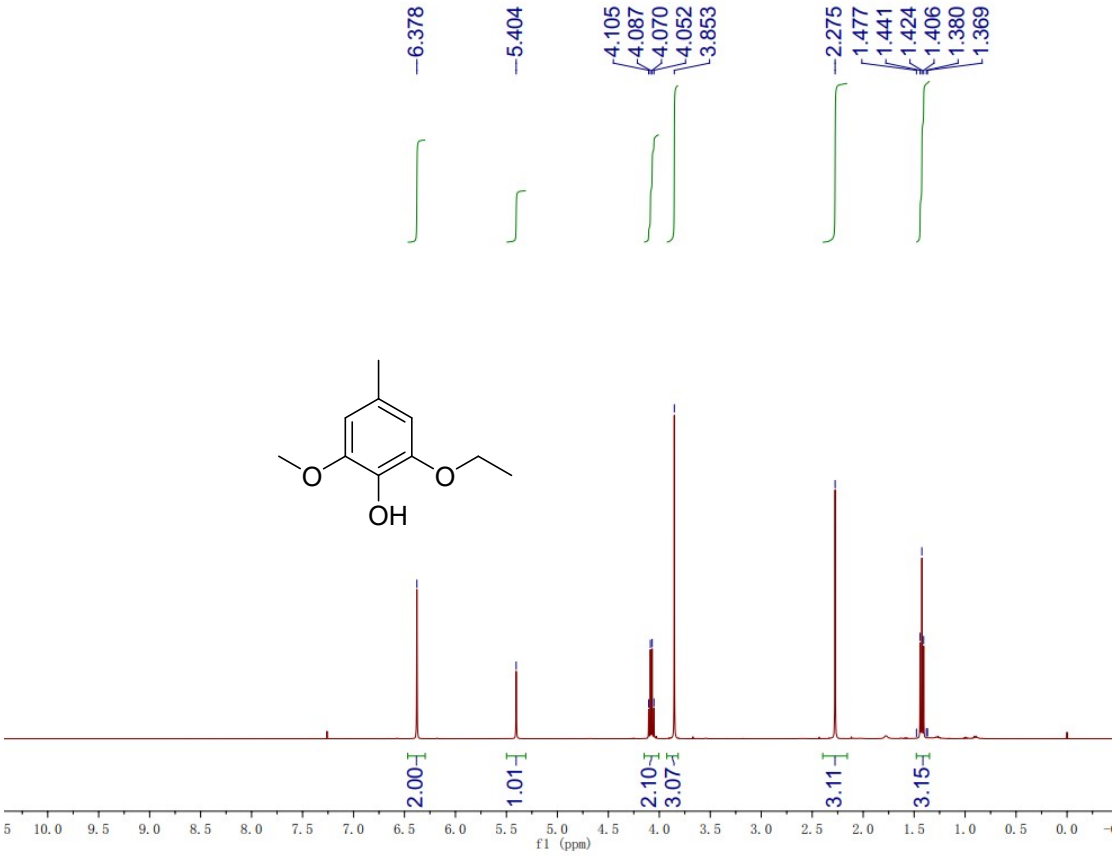
2,6-Diisobutoxy-4-methylphenol (1e) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



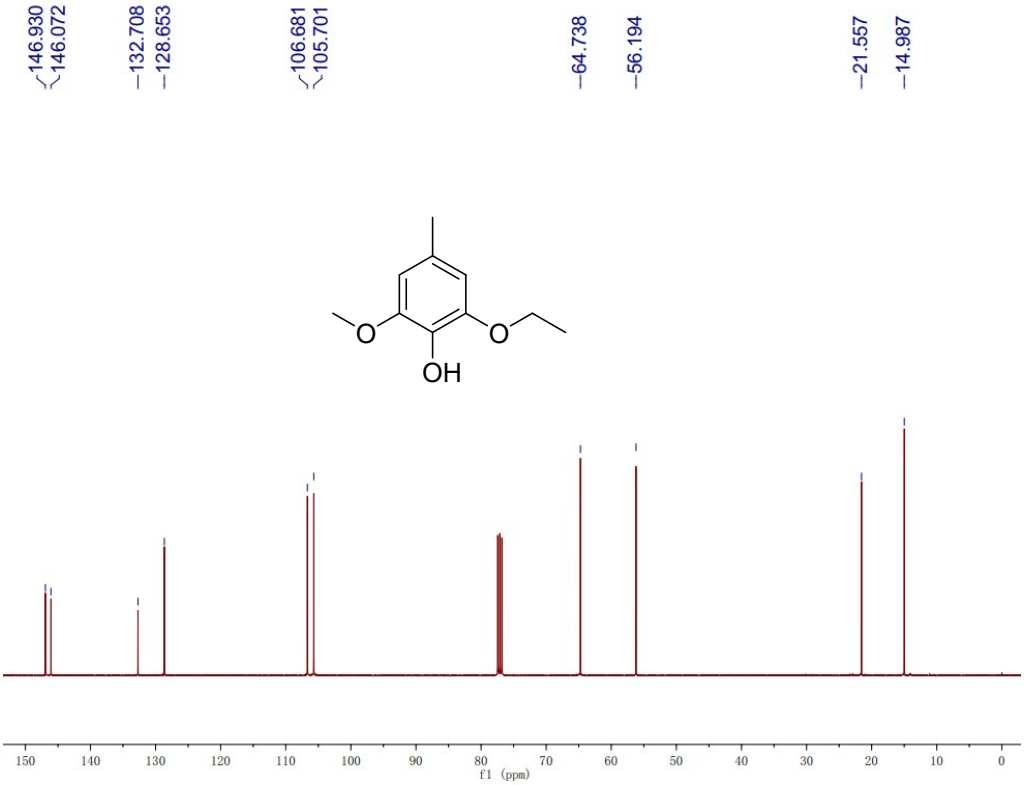
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



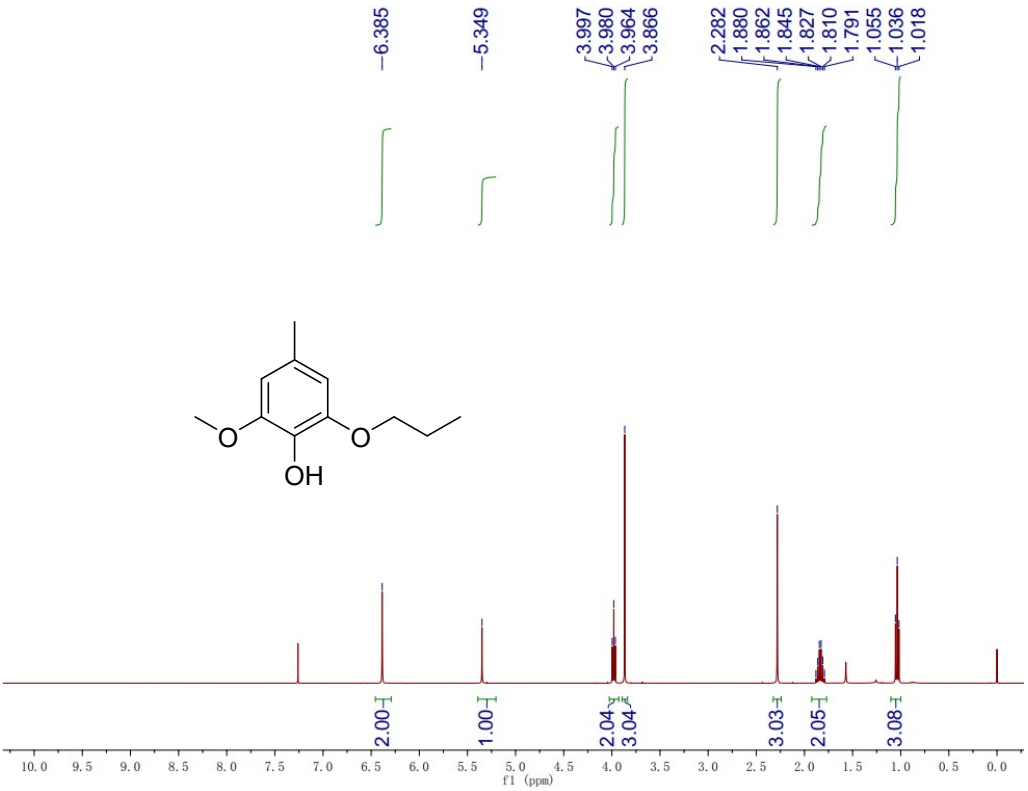
2-Ethoxy-6-methoxy-4-methylphenol (1f) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



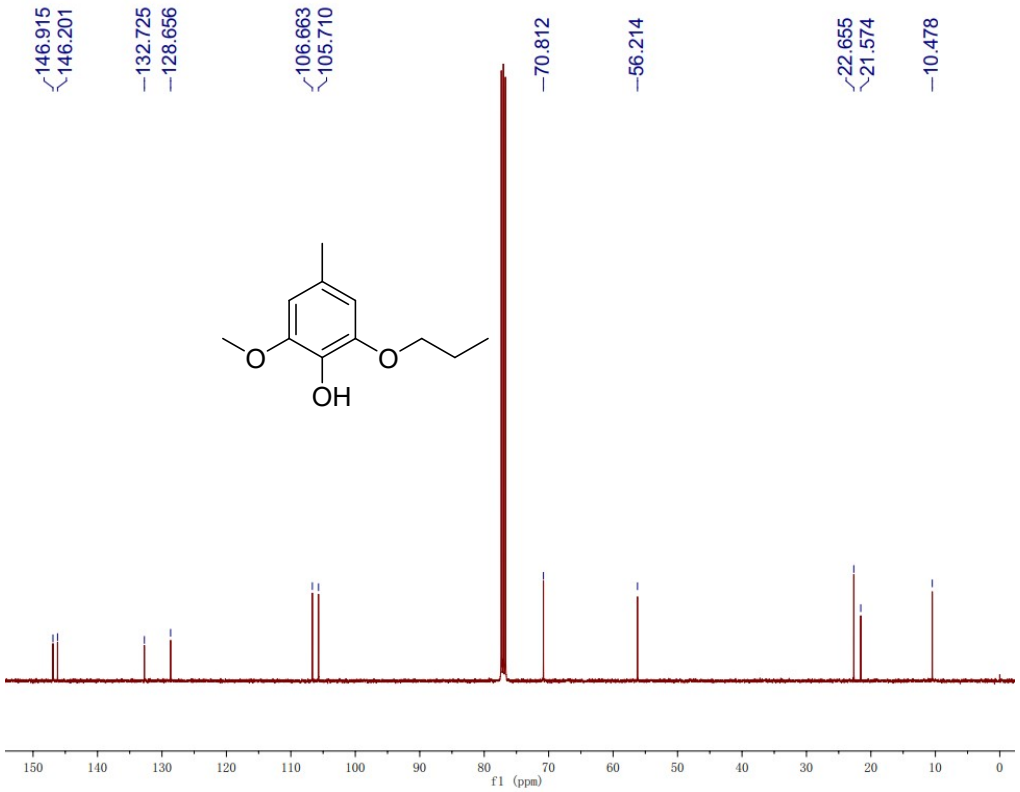
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



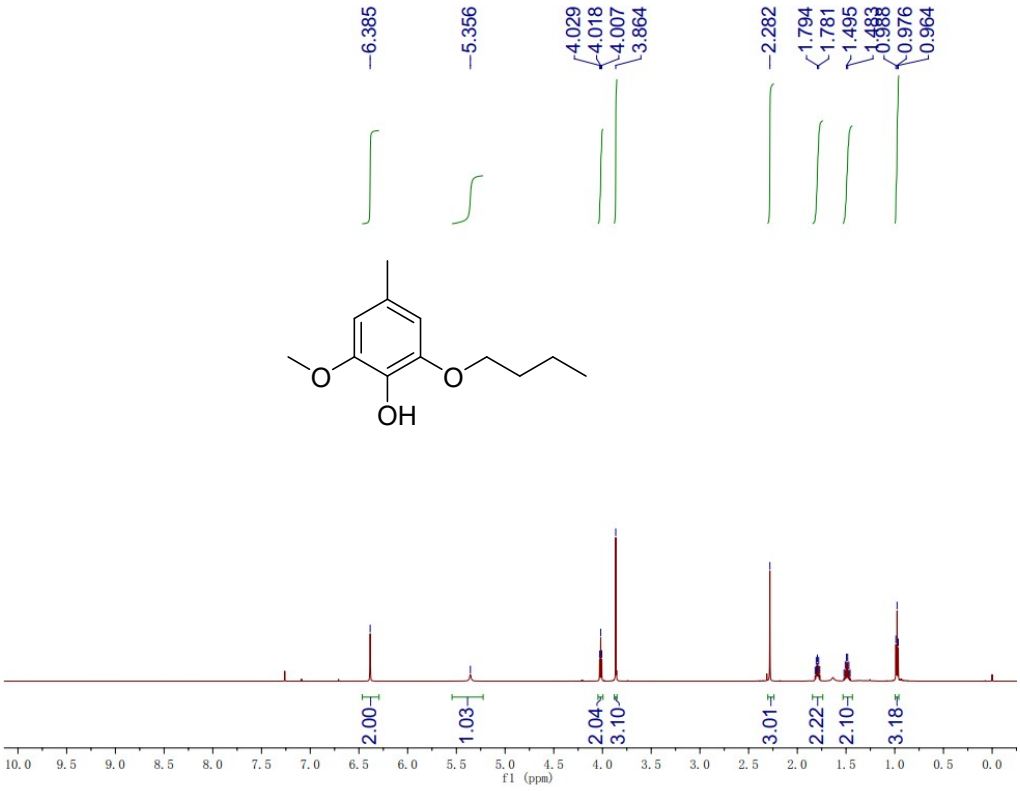
2-Methoxy-4-methyl-6-propoxyphenol (1g) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



2-Butoxy-6-methoxy-4-methylphenol (1h) [^{1}H_NMR_600 MHz_($CDCl_3$: 7.26 ppm)]



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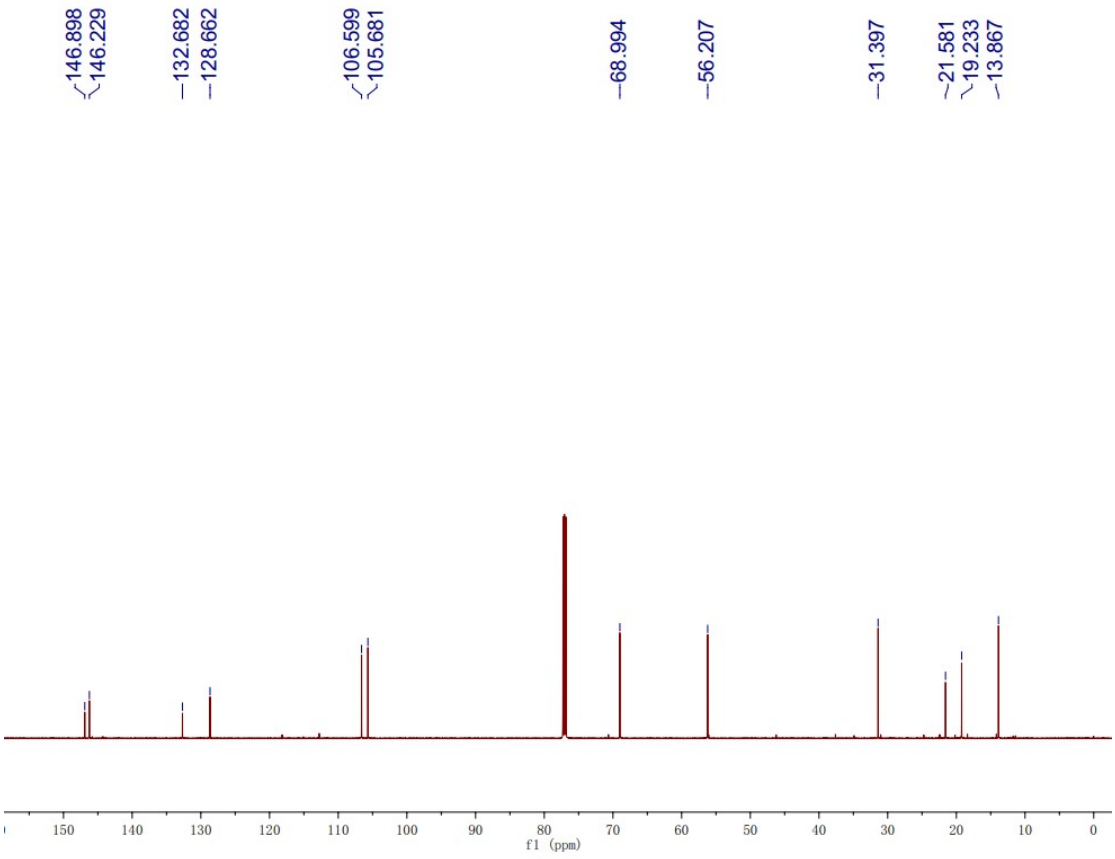
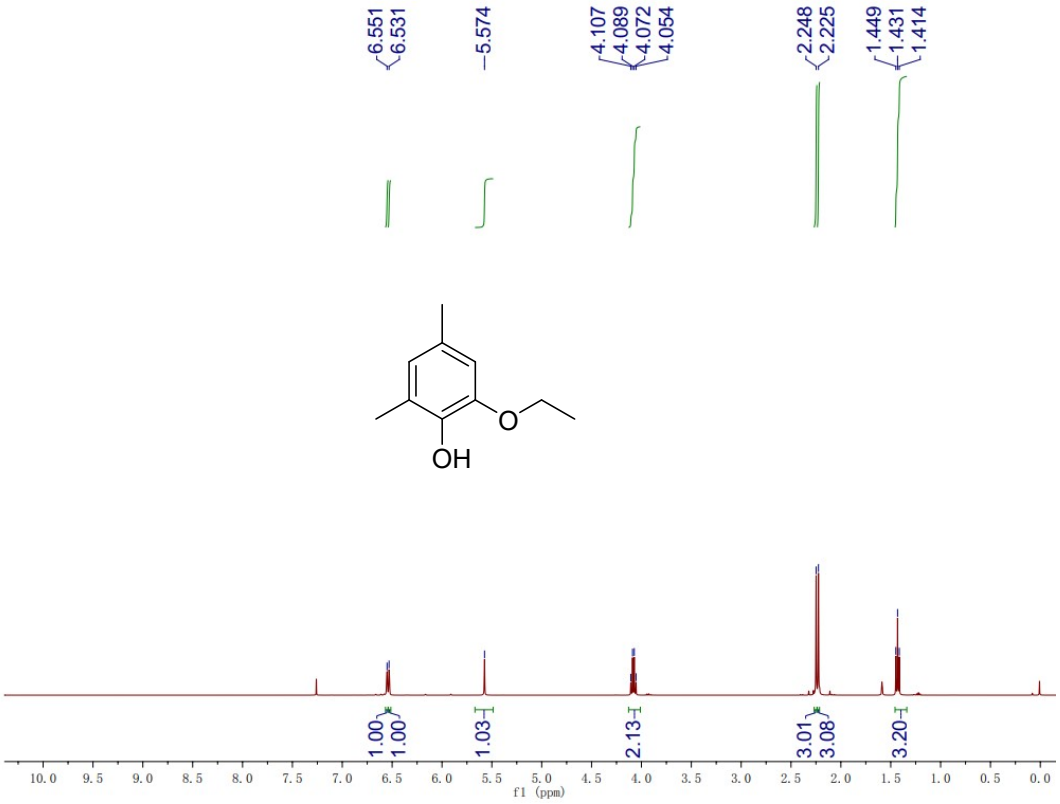
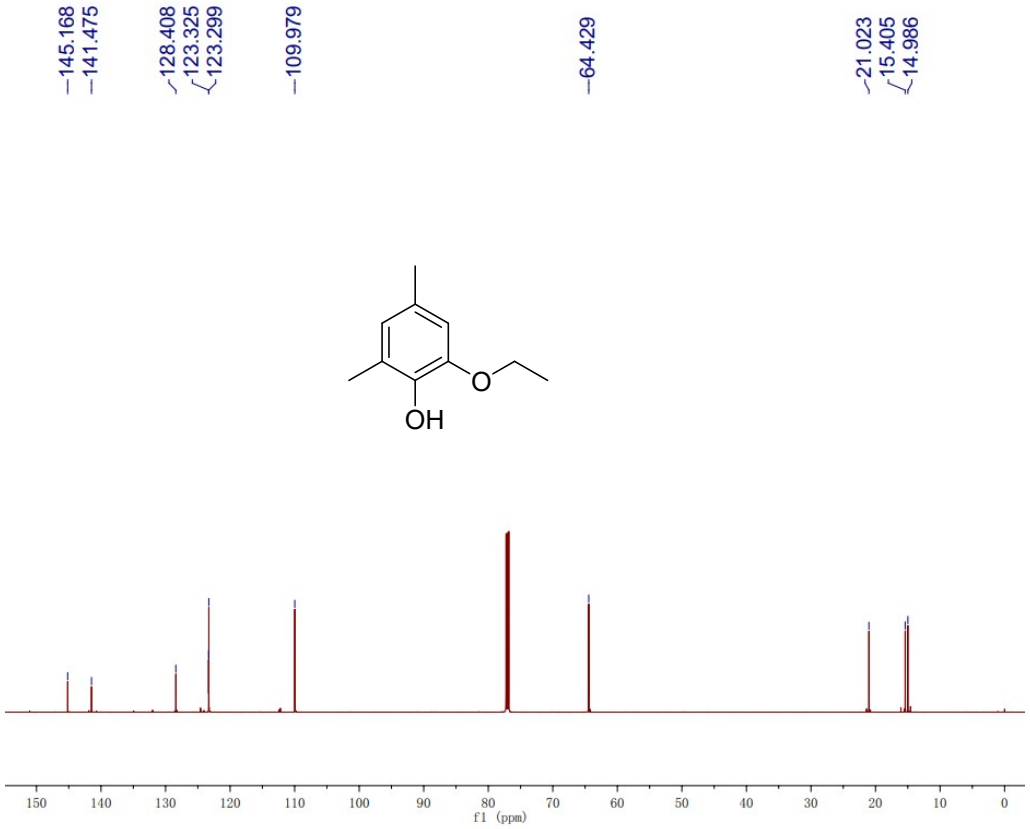


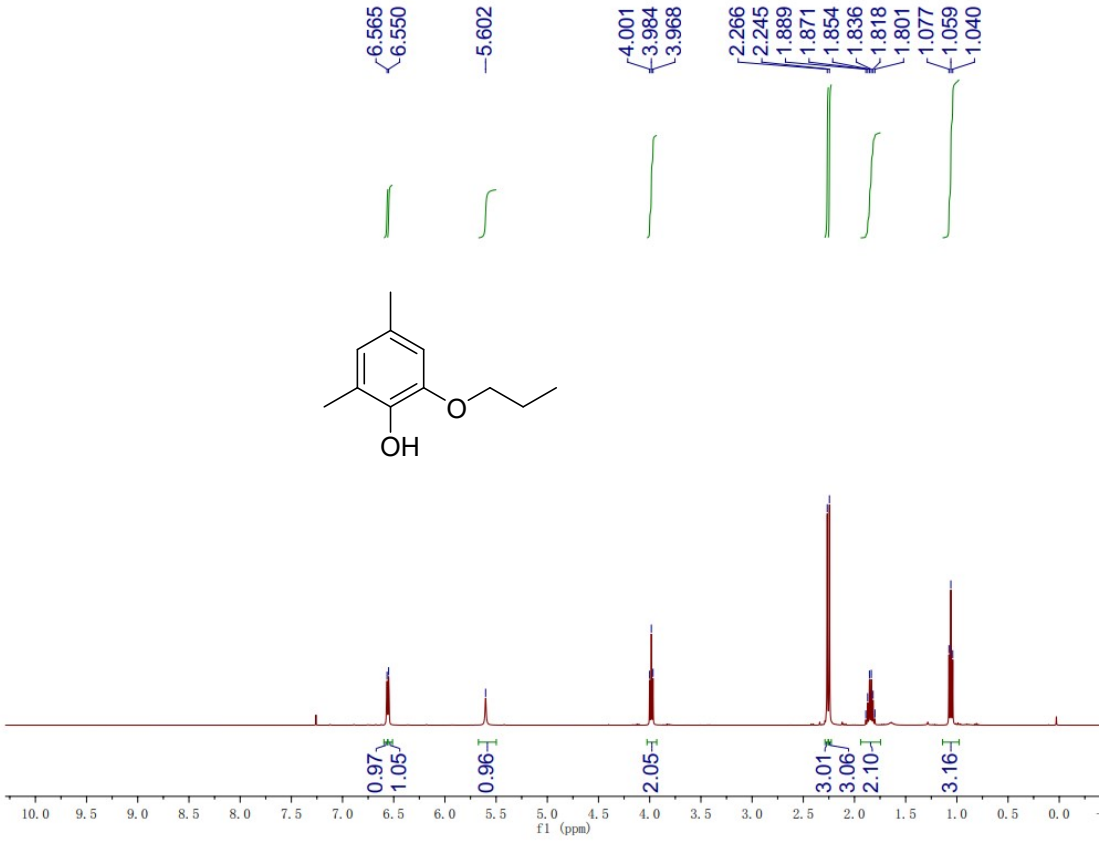
2-Ethoxy-4,6-dimethylphenol (1i) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



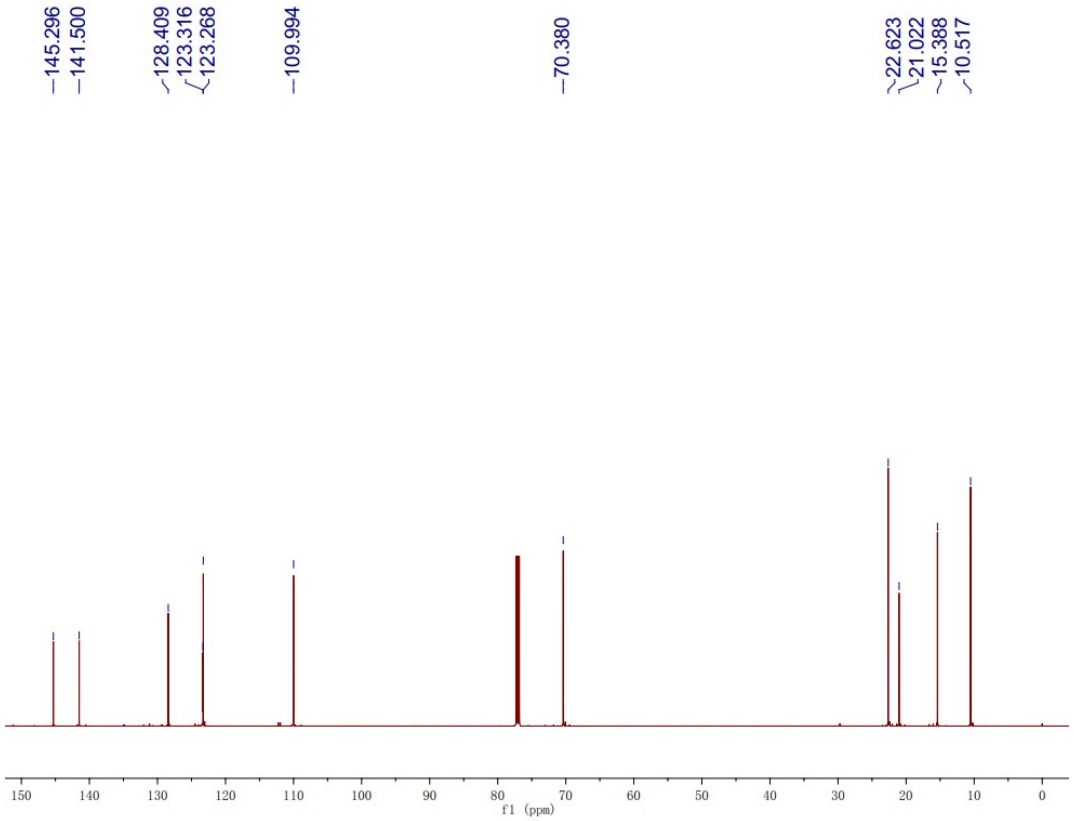
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



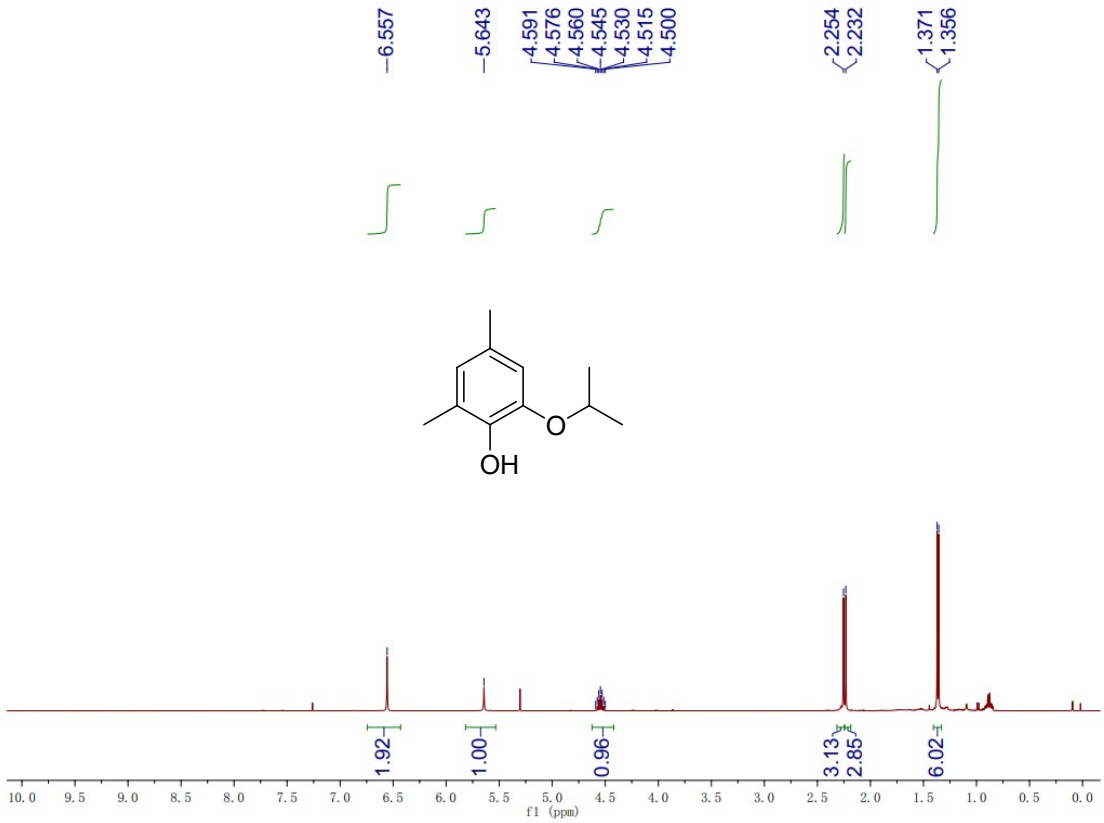
2,4-Dimethyl-6-propoxyphenol (1j) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



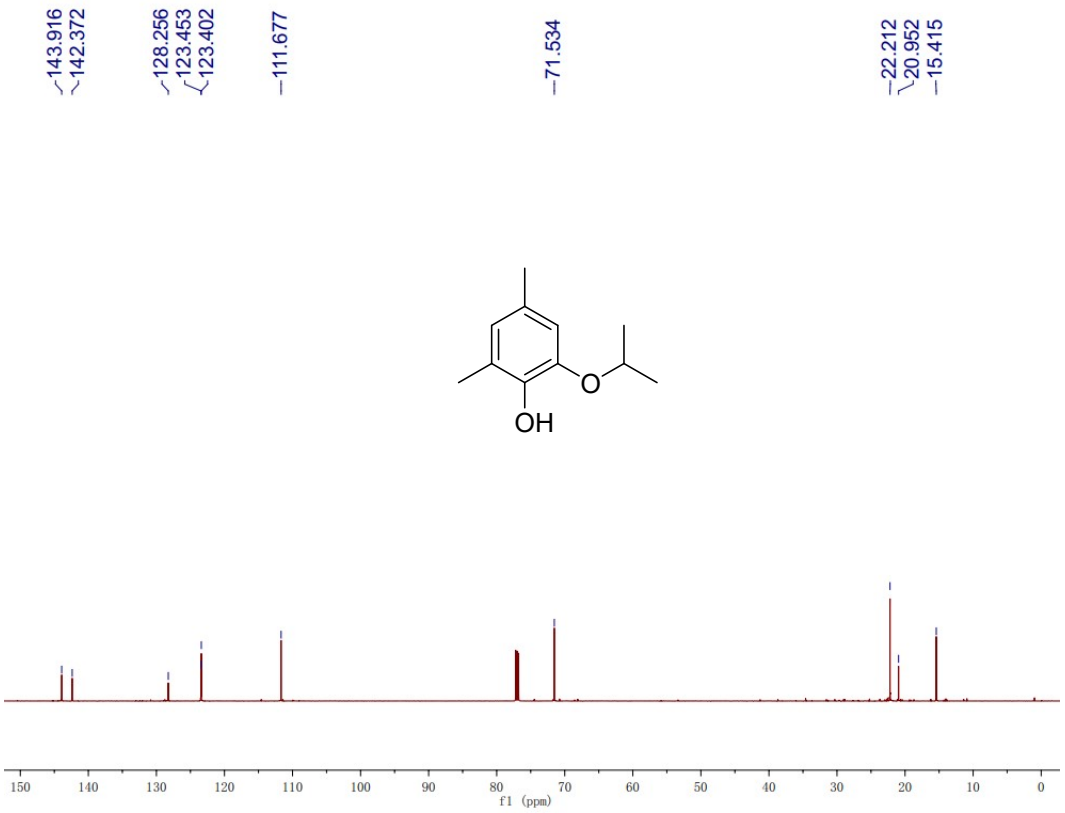
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



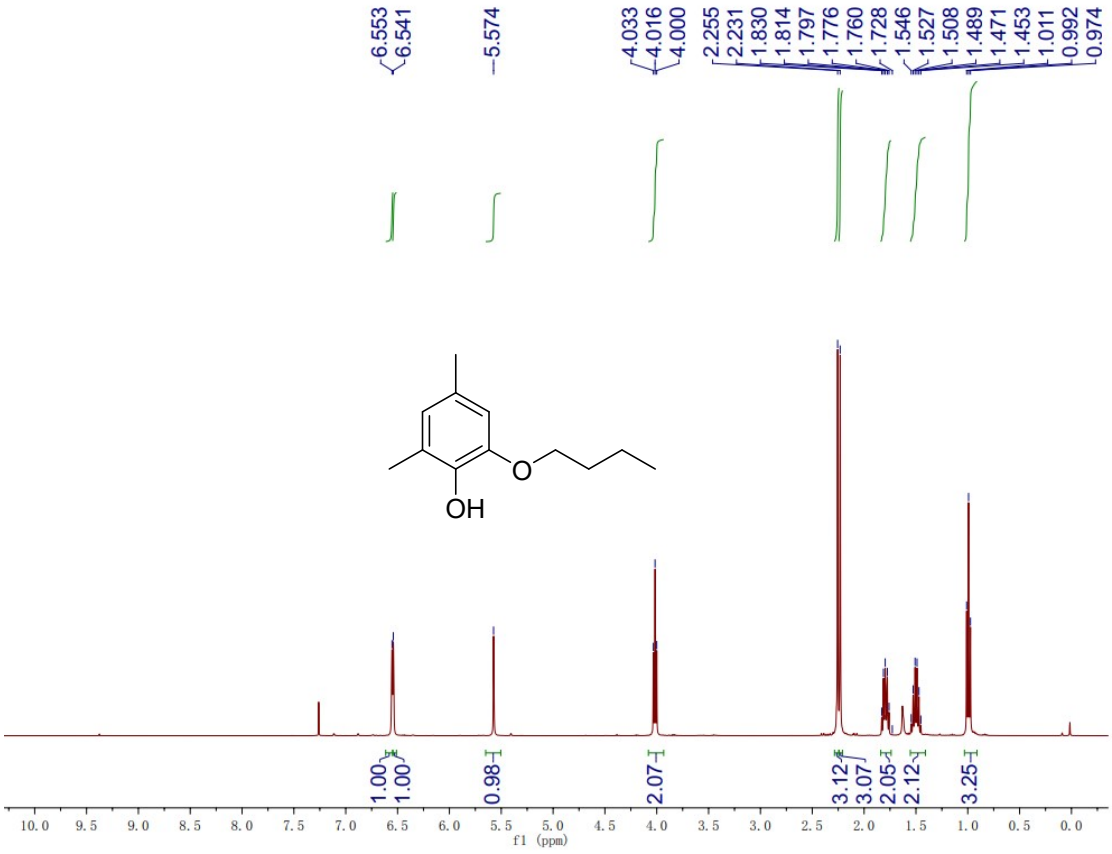
2-Isopropoxy-4,6-dimethylphenol (1k) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]

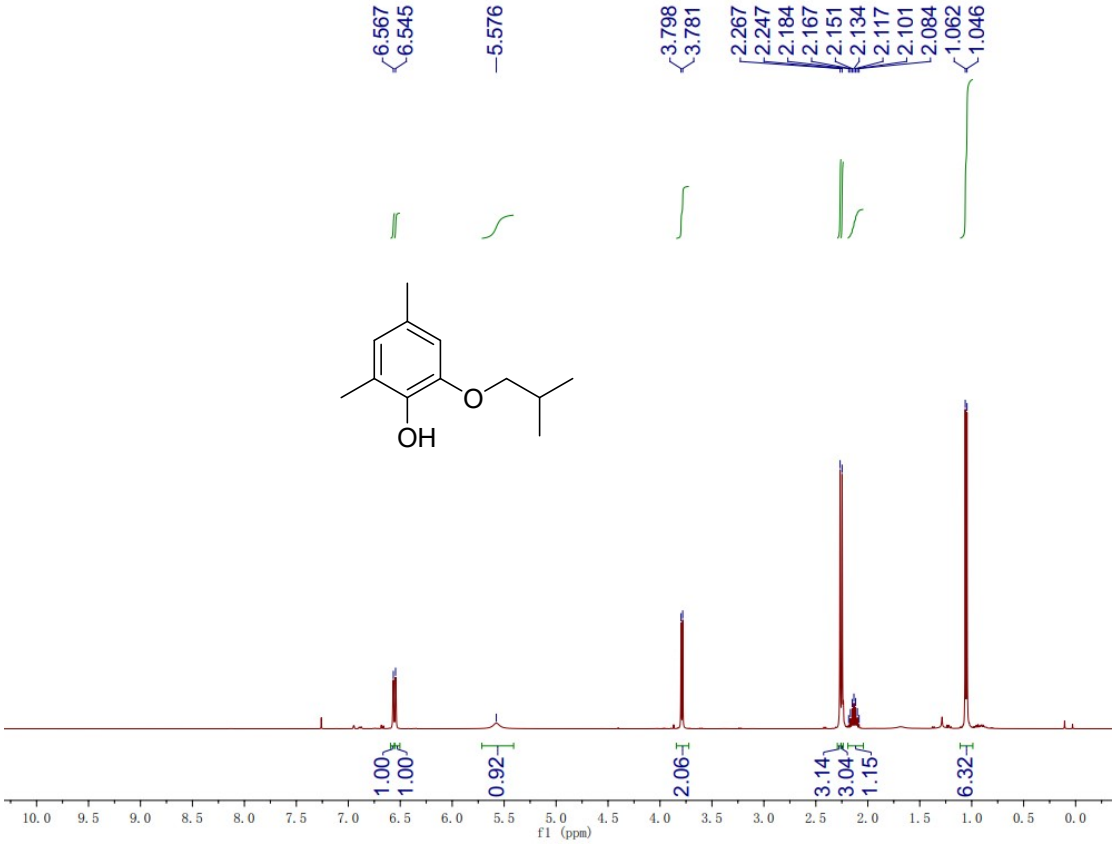


2-Butoxy-4,6-dimethylphenol (1l) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]

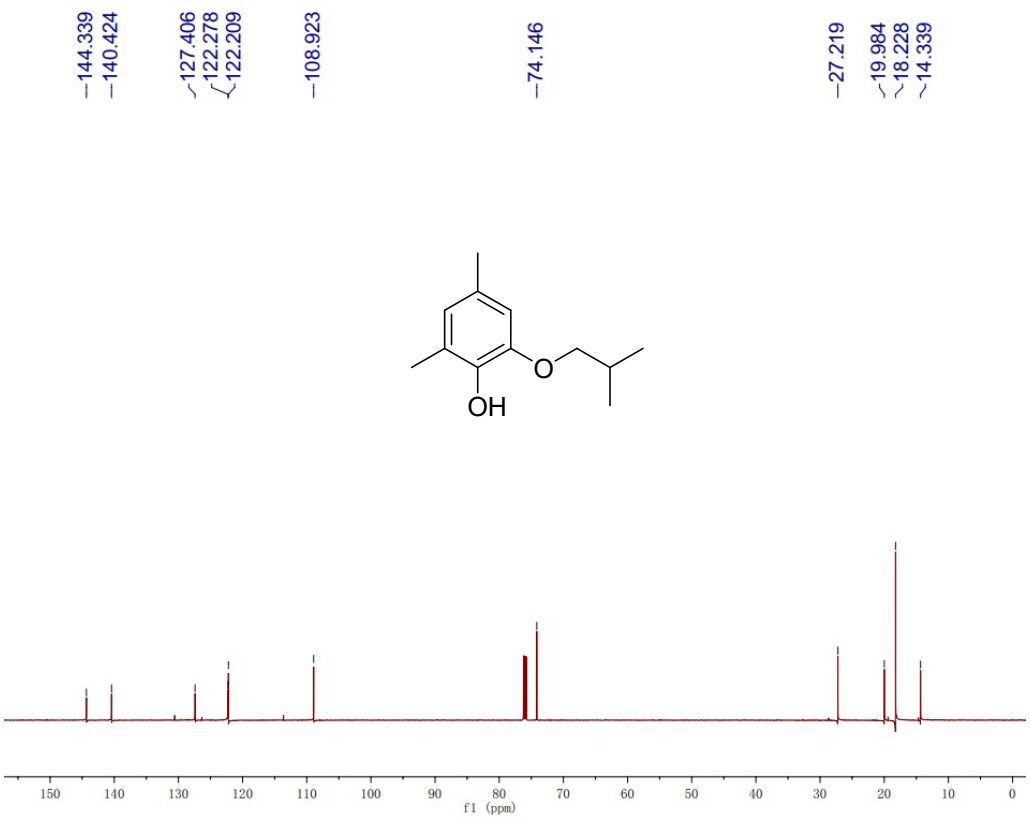


[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]

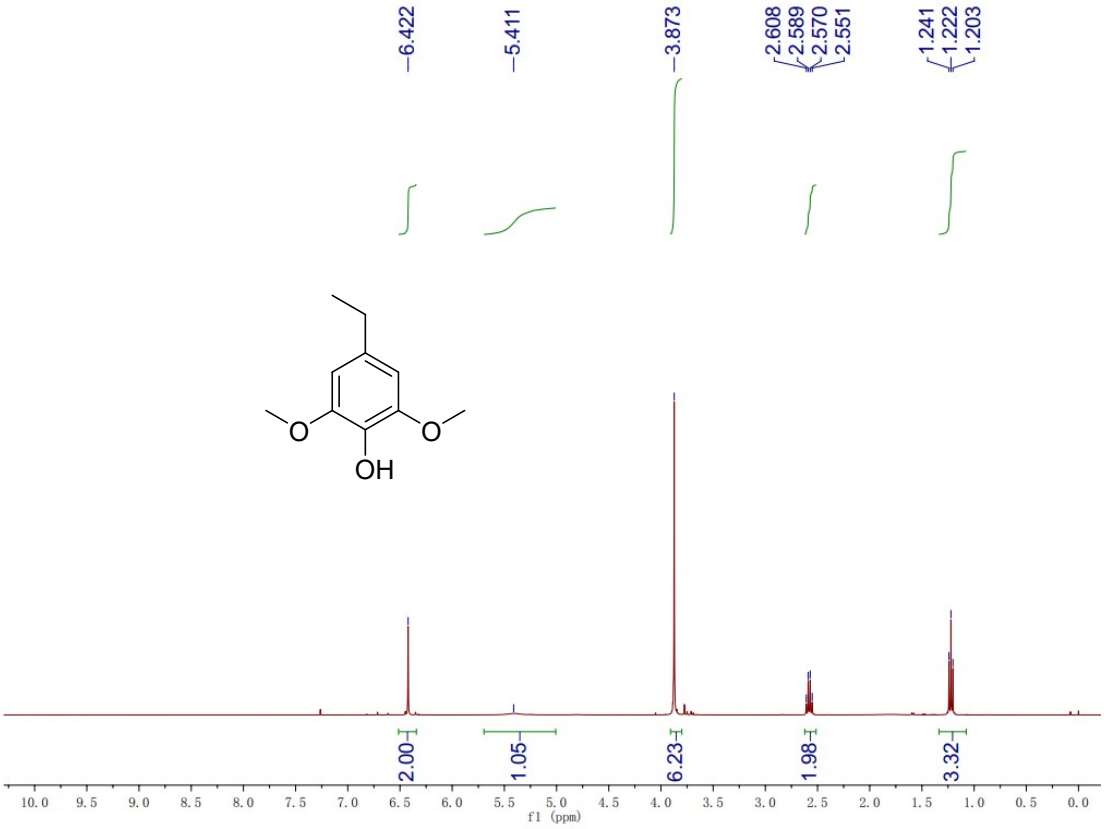
2-Isobutoxy-4,6-dimethylphenol (1m) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



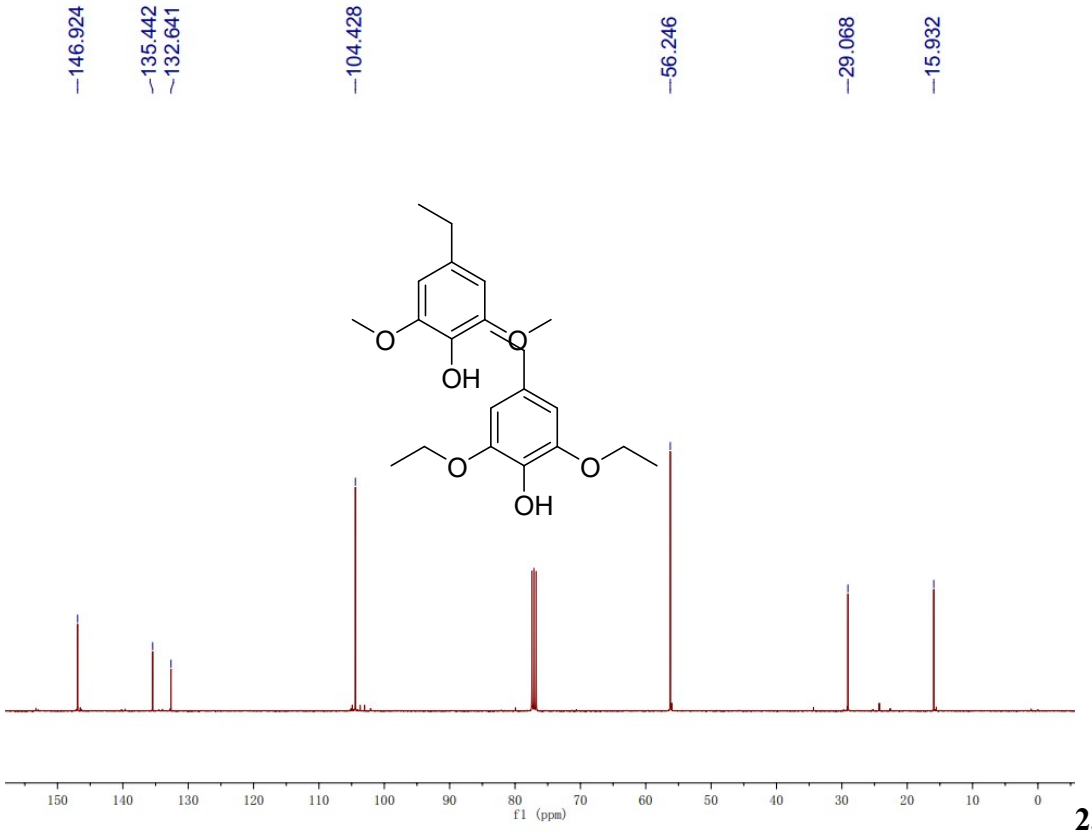
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



Ethyl-2,6-dimethoxyphenol (1n) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]

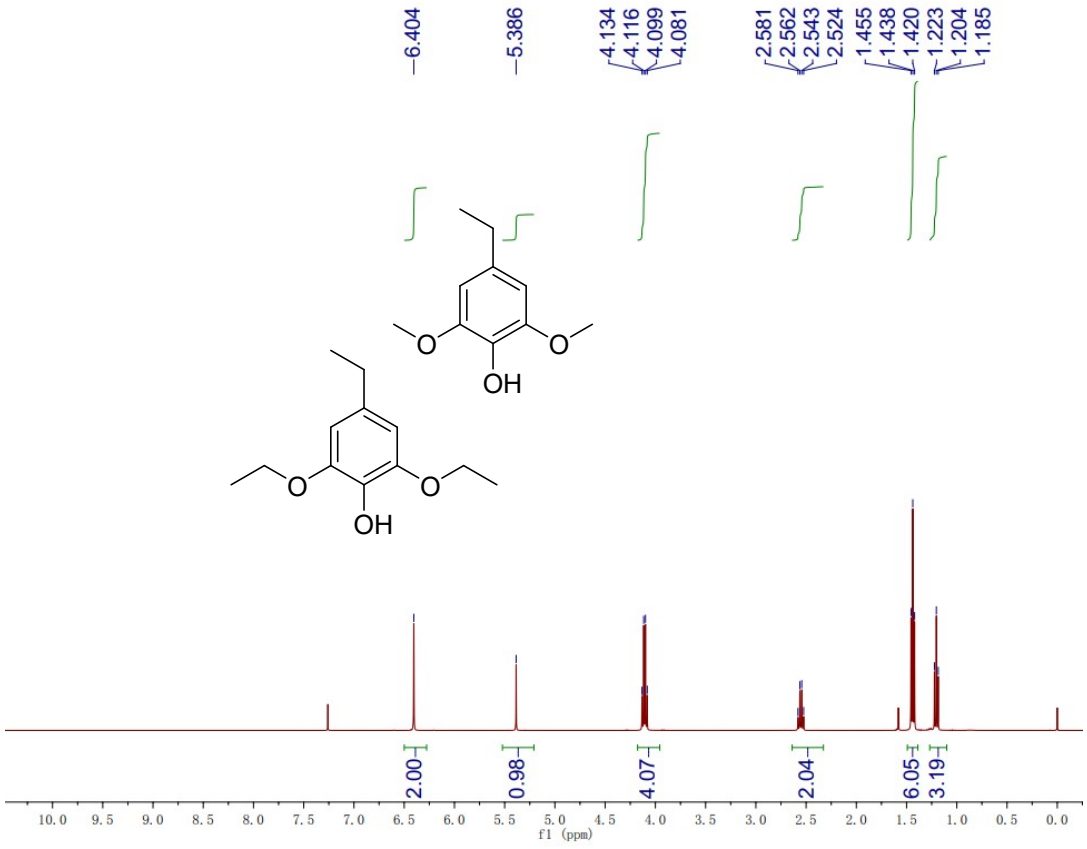


[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]

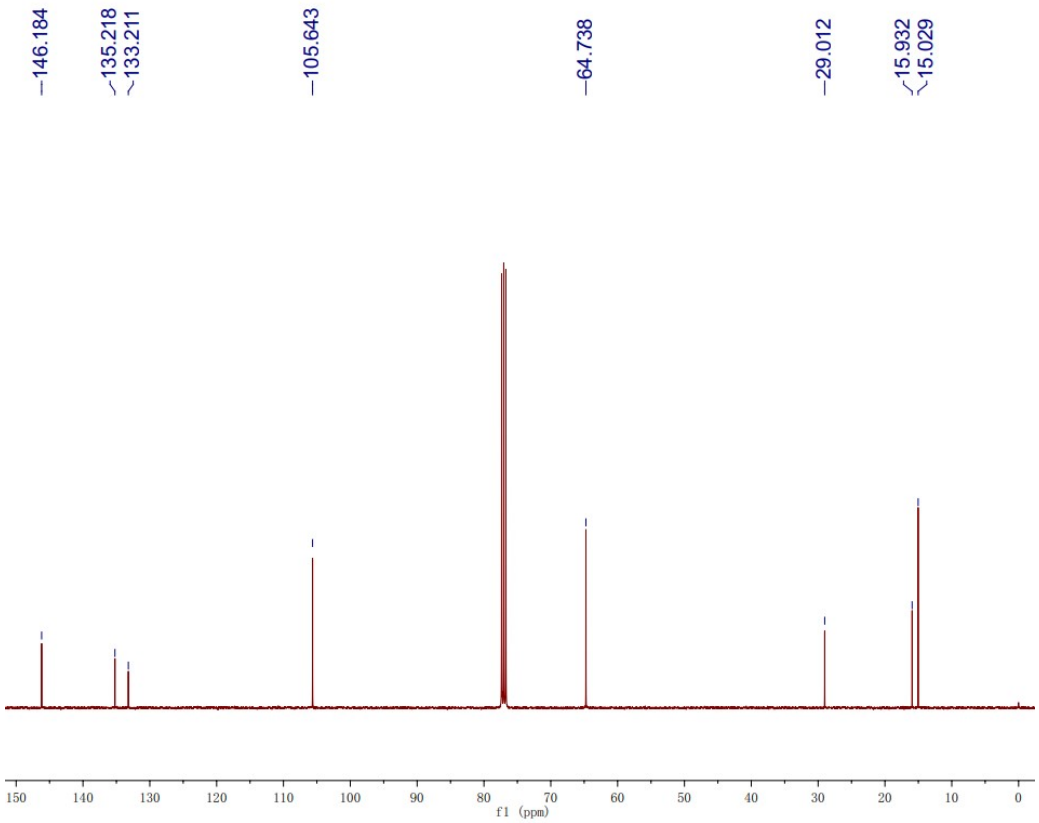


2,

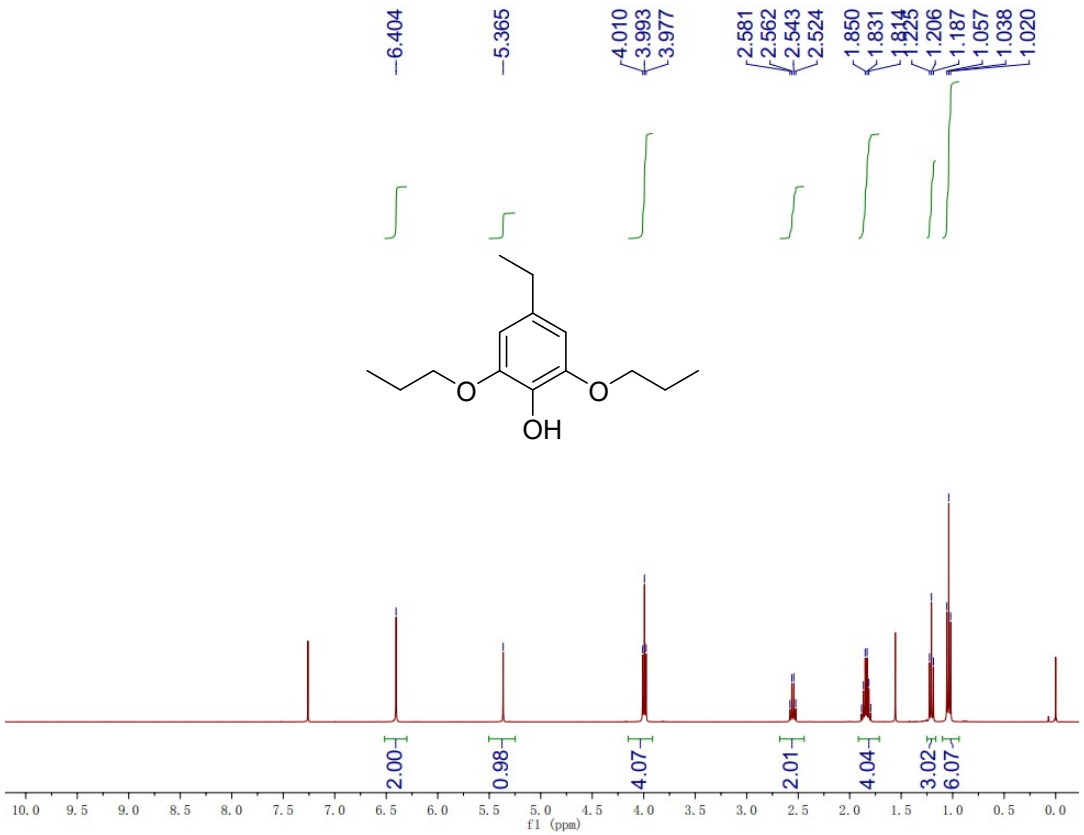
6-Diethoxy-4-ethylphenol (1o) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



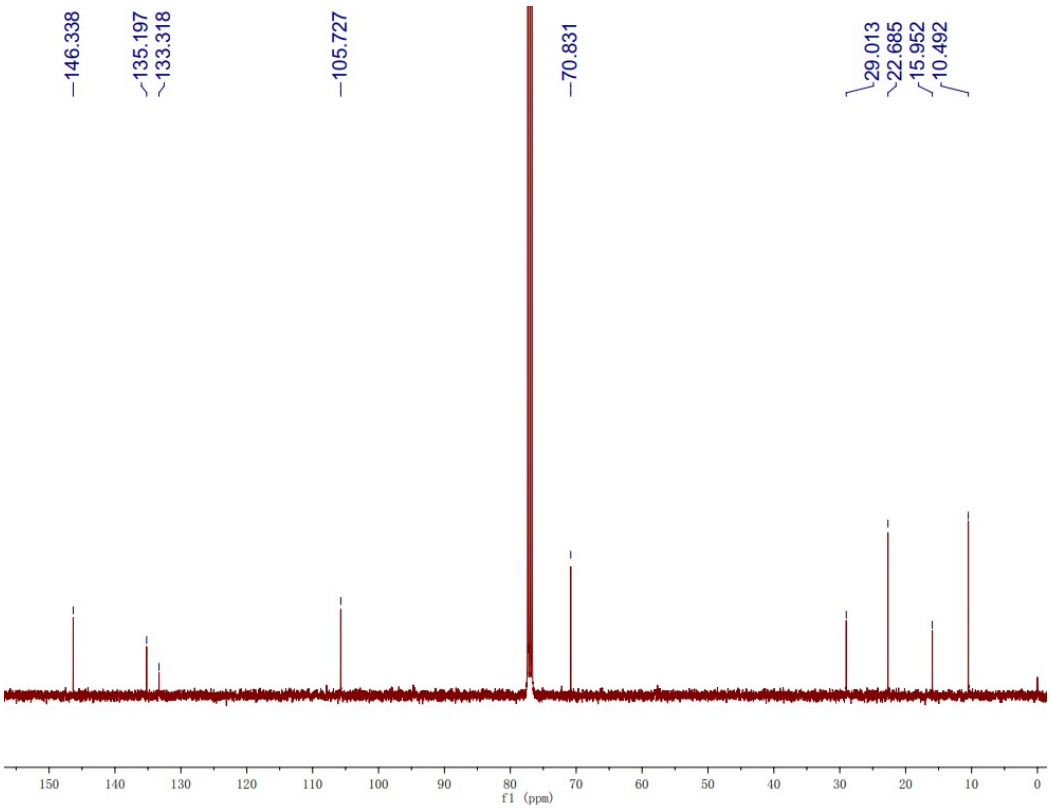
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



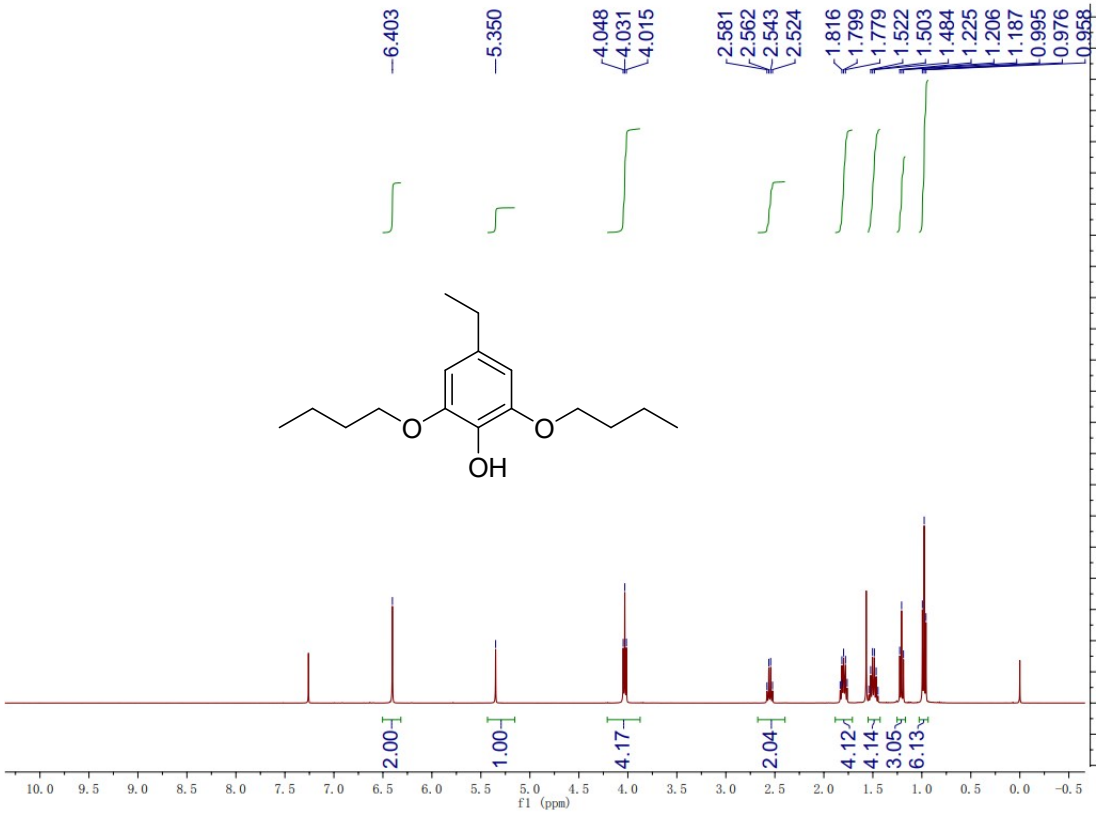
4-Ethyl-2,6-dipropoxyphenol (1p) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



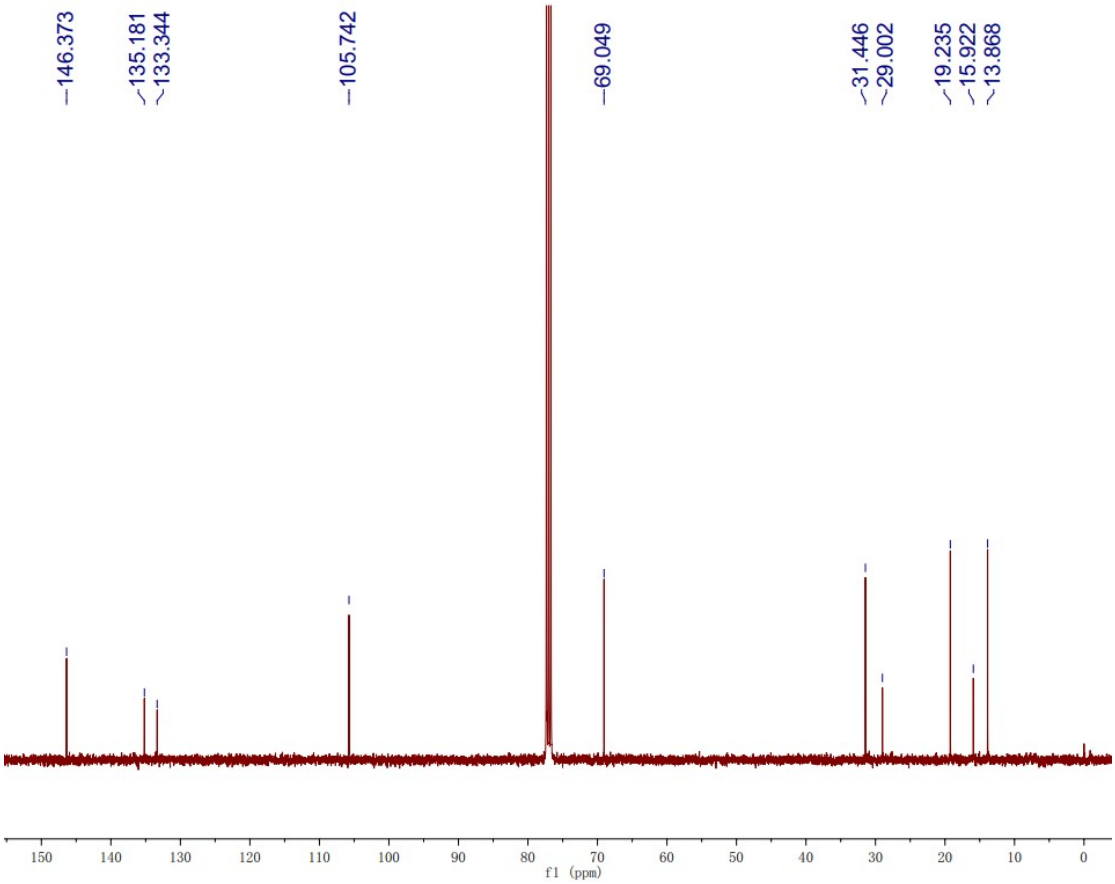
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



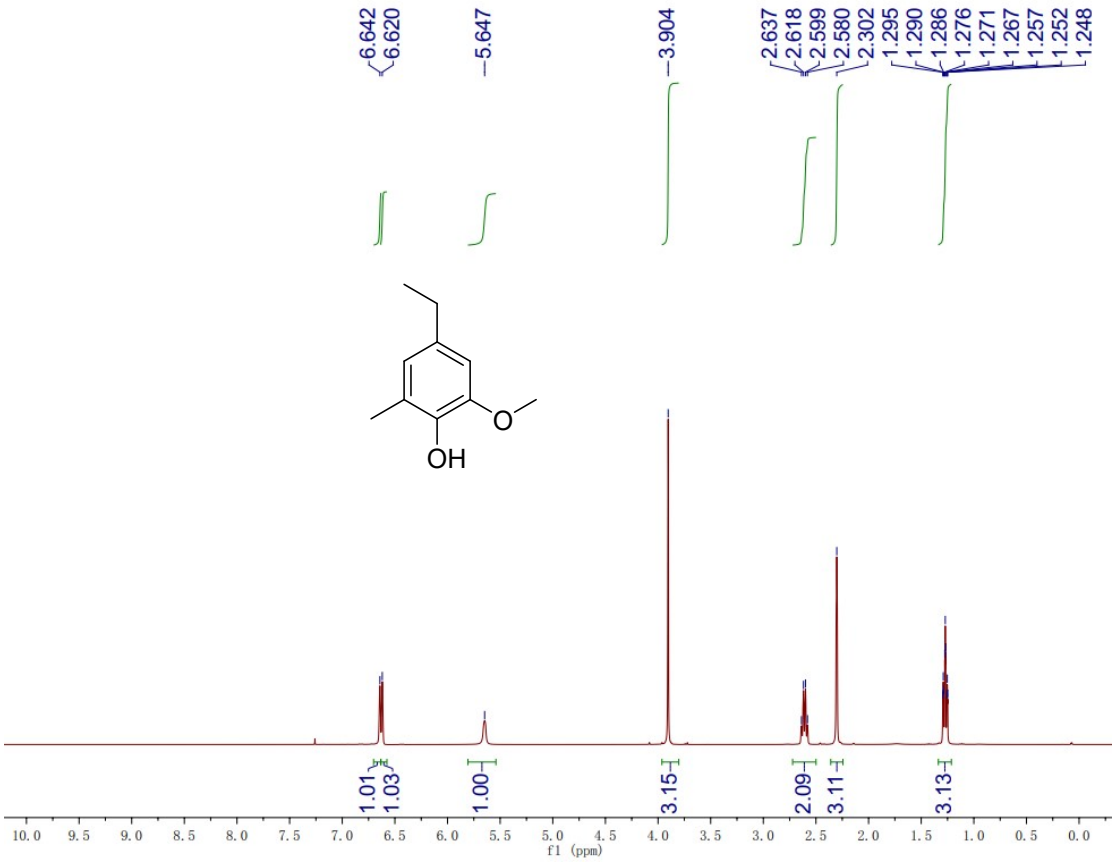
2,6-Dibutoxy-4-ethylphenol (1q) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



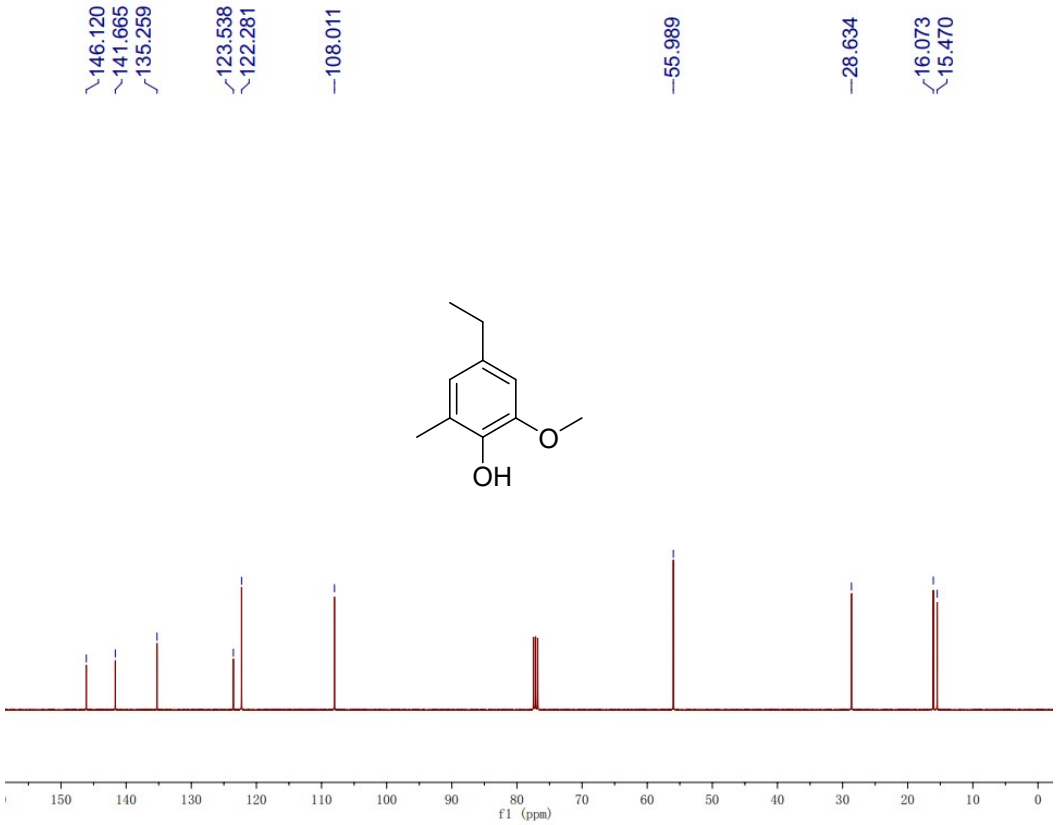
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



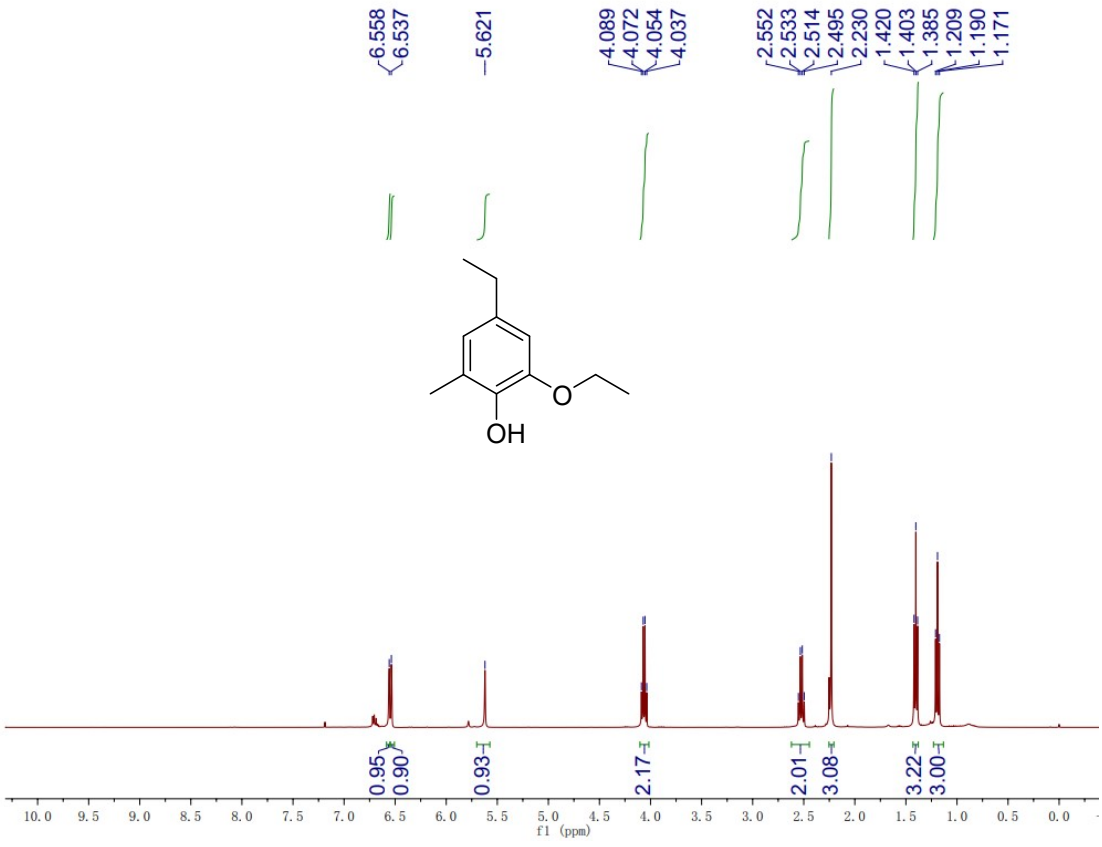
4-Ethyl-2-methoxy-6-methylphenol (1r) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



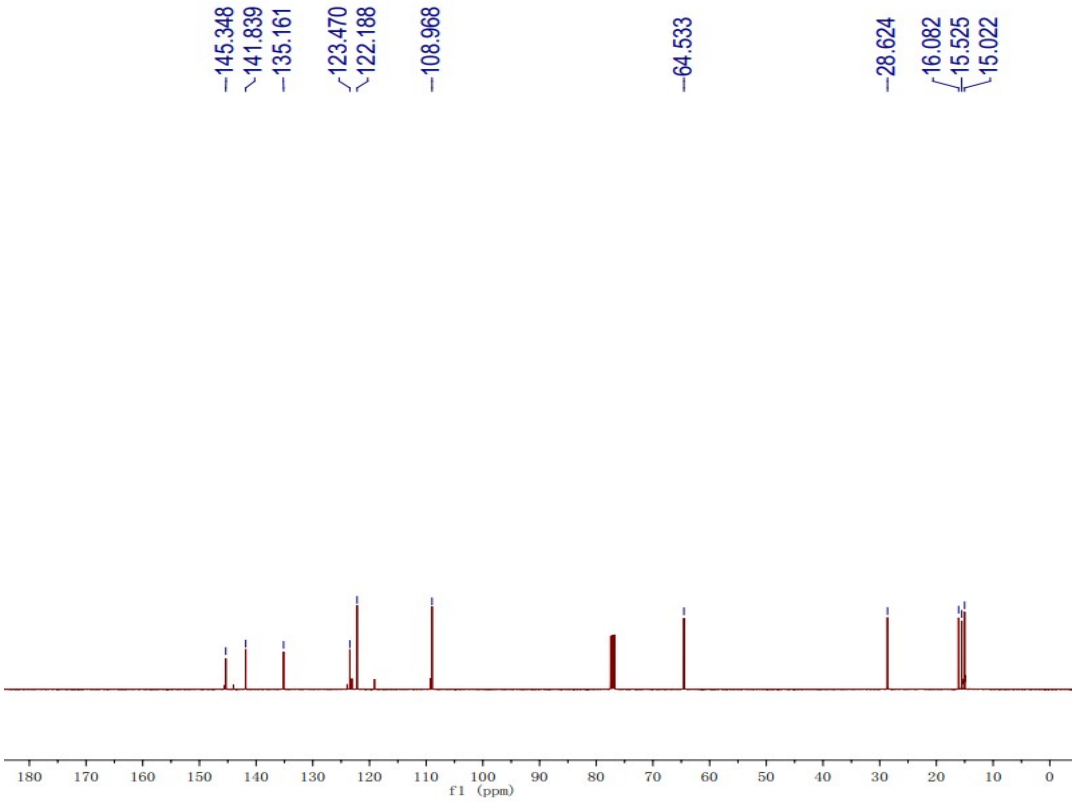
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



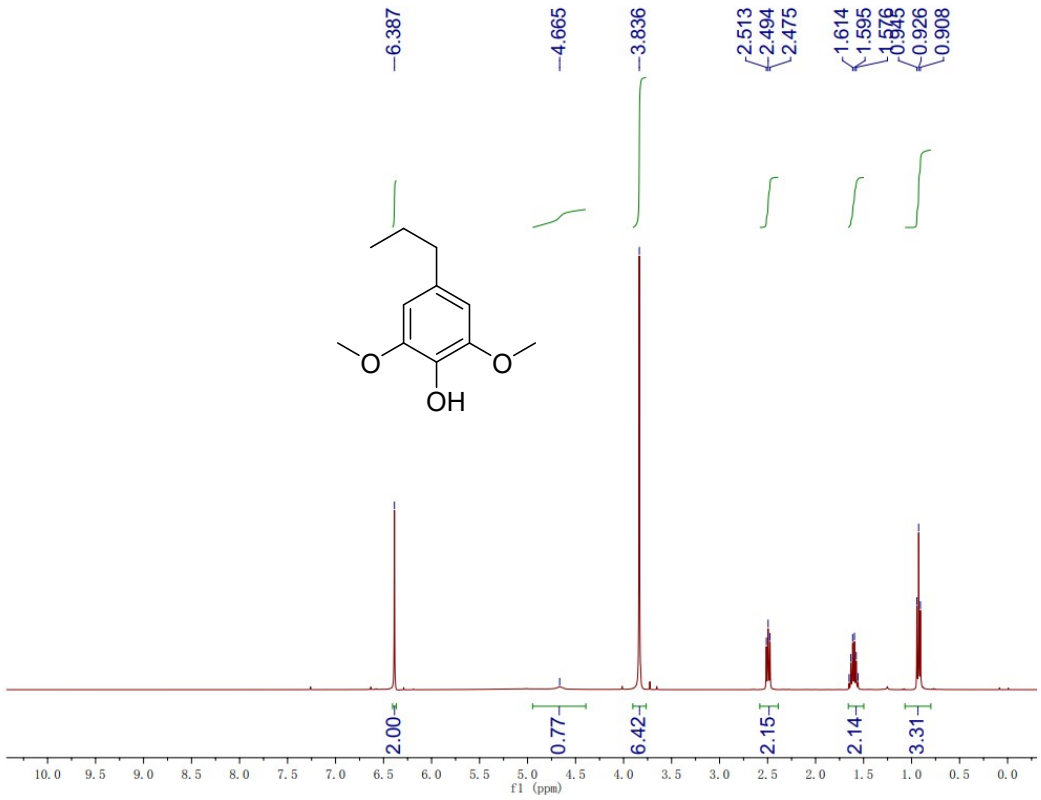
2-Ethoxy-4-ethyl-6-methylphenol (1s) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



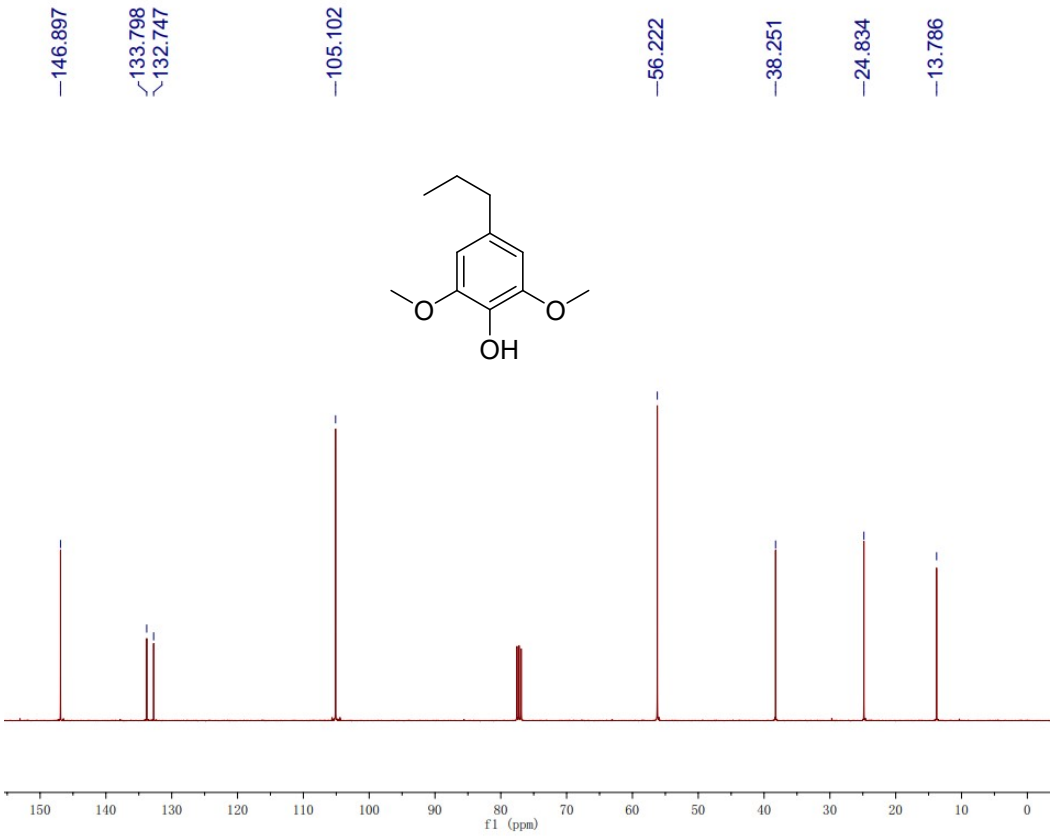
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



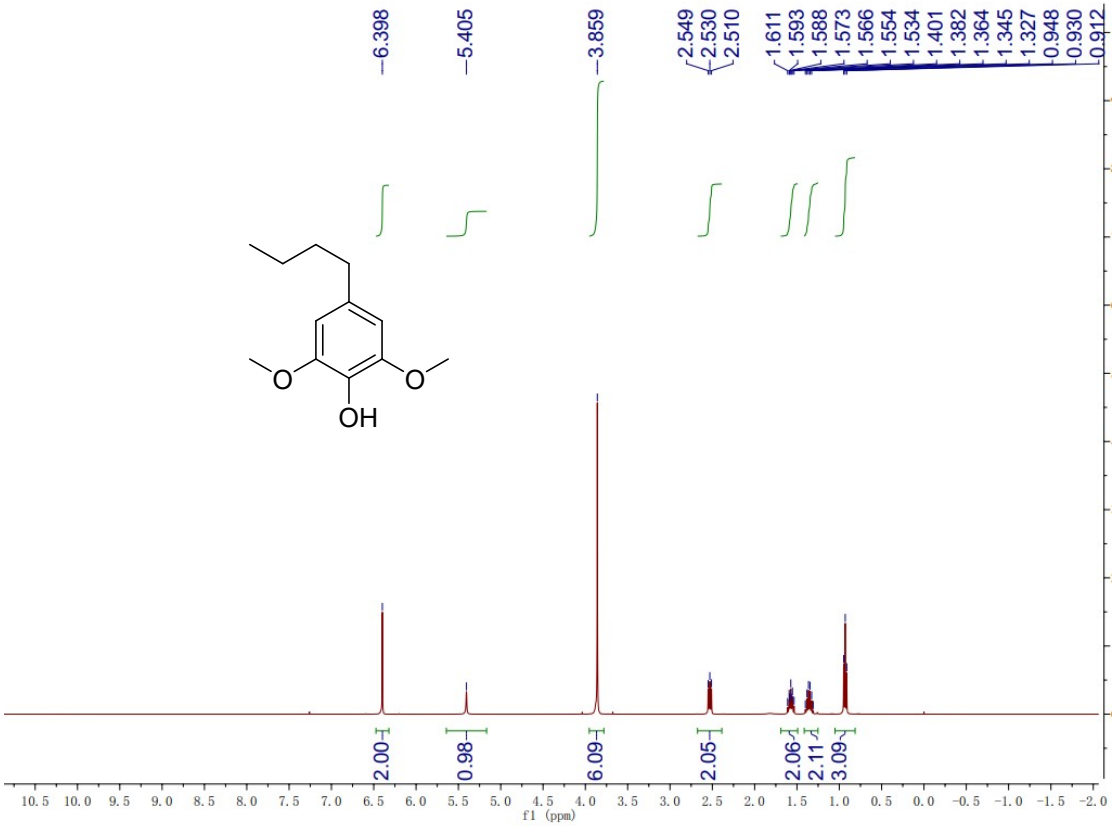
2,6-Dimethoxy-4-propylphenol (1t) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



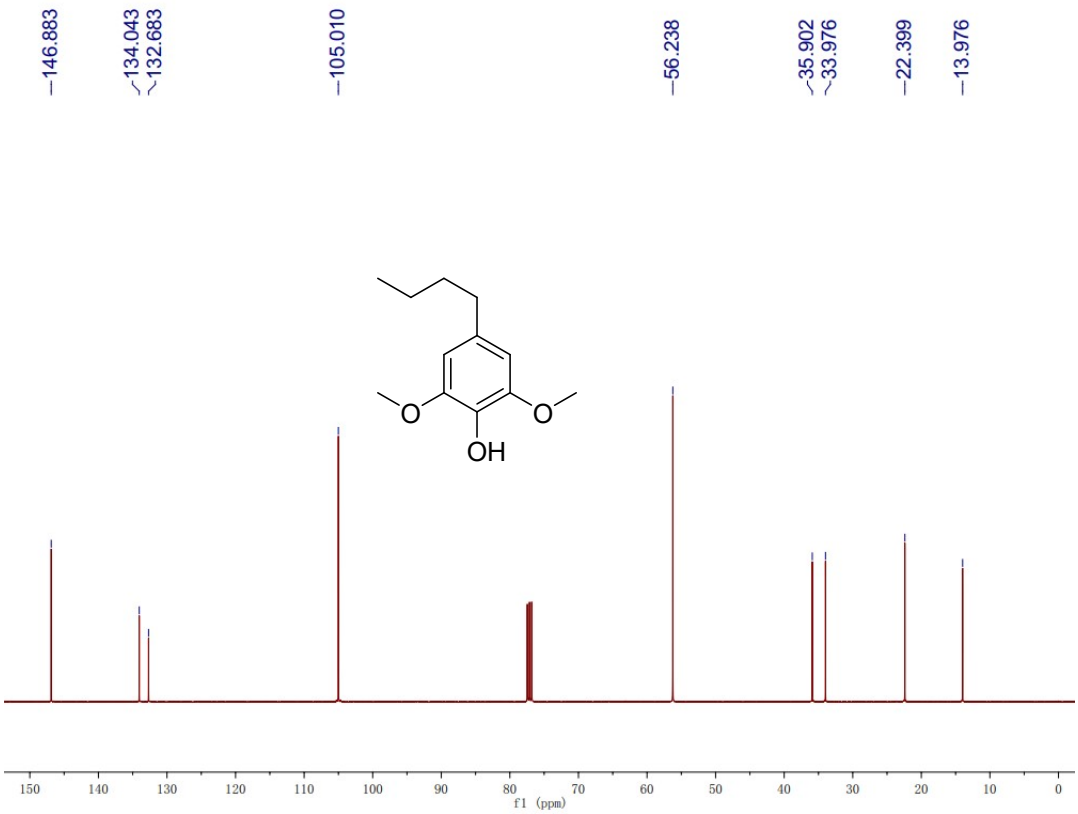
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



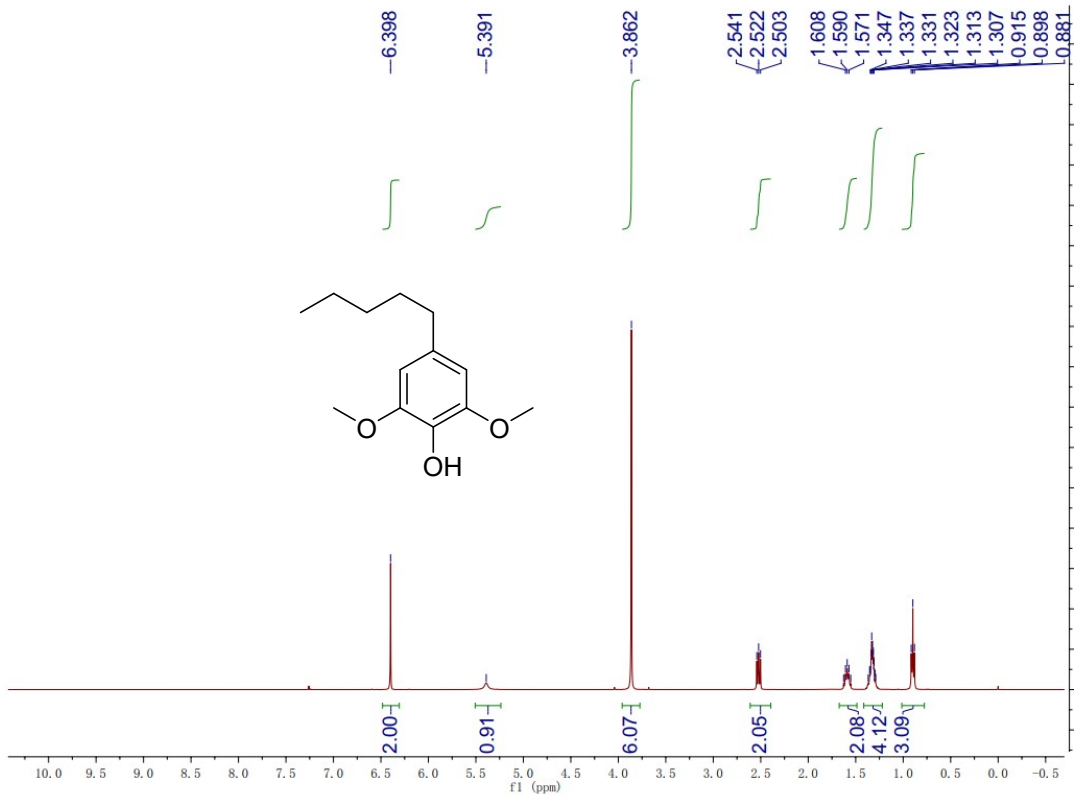
4-Butyl-2,6-dimethoxyphenol (1u) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



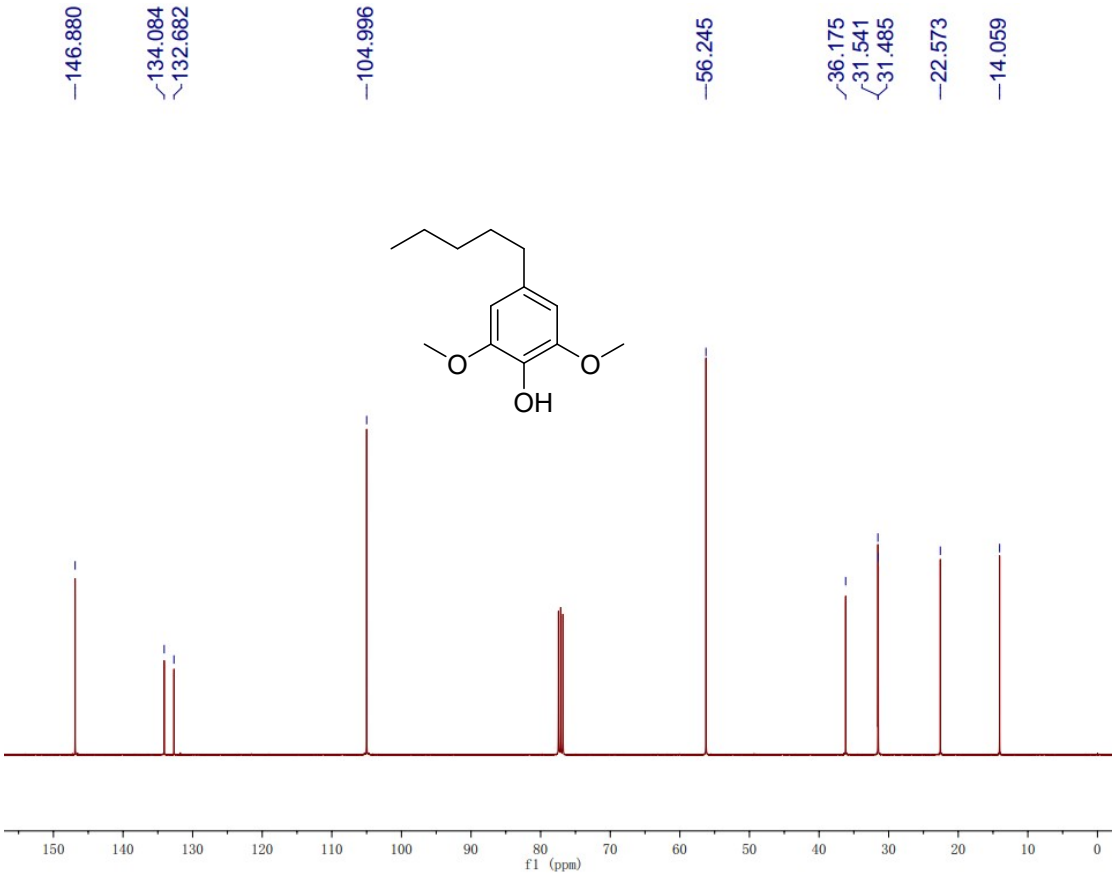
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



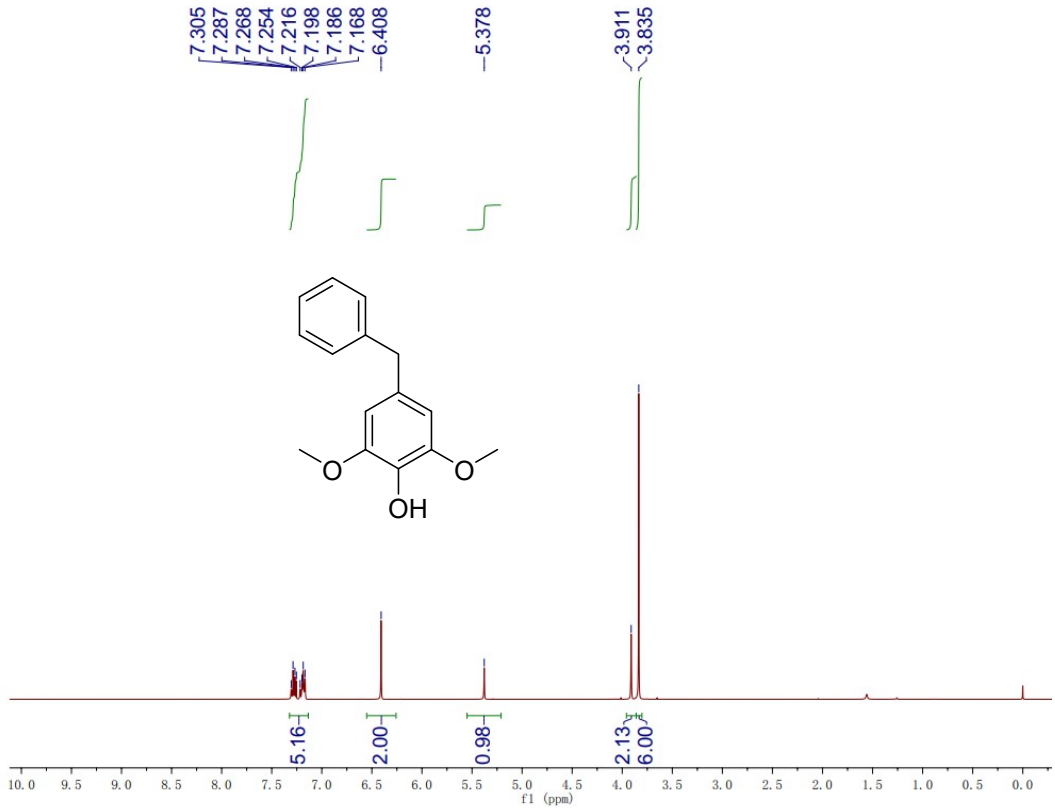
2,6-Dimethoxy-4-pentylphenol (1v) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



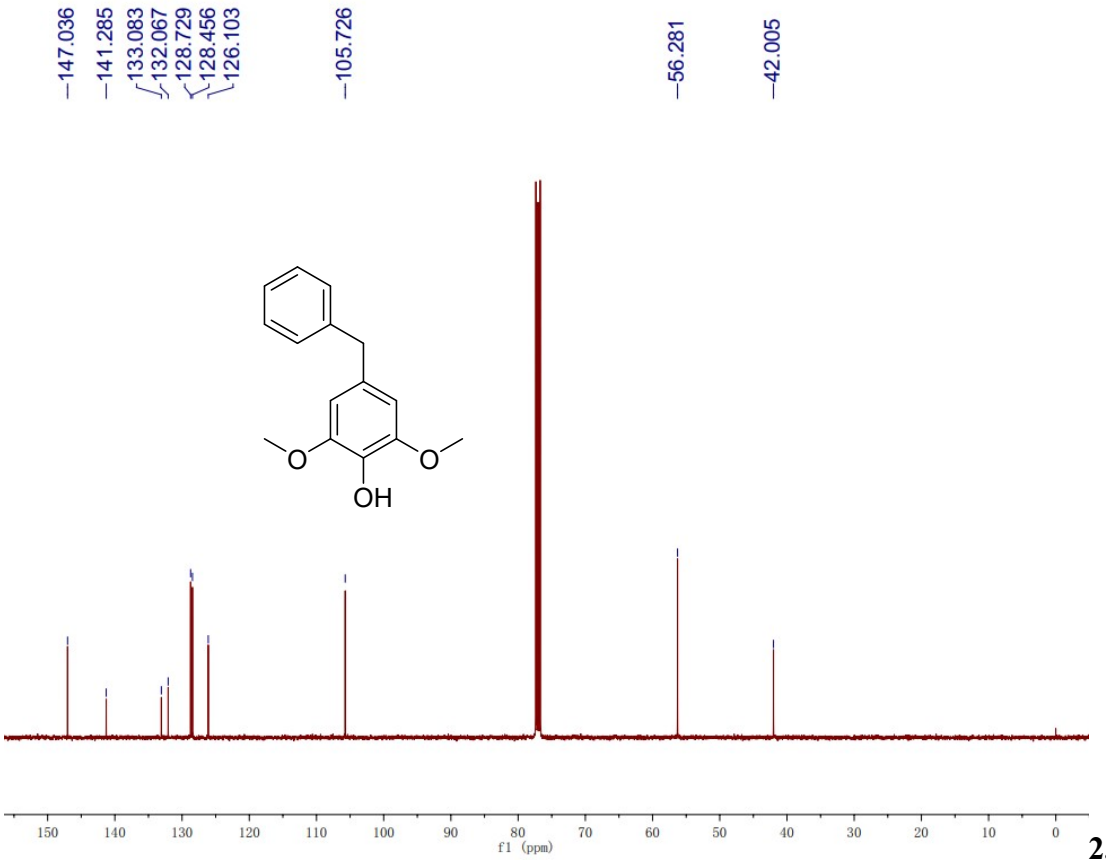
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



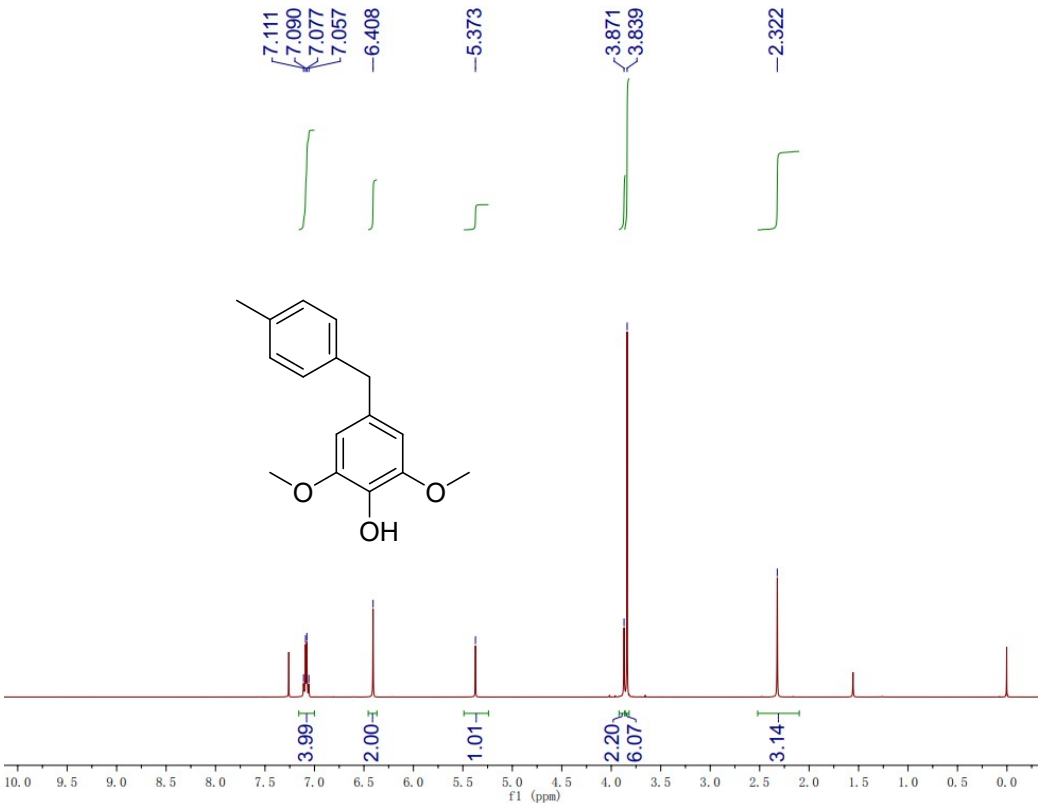
4-Benzyl-2,6-dimethoxyphenol (1w) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



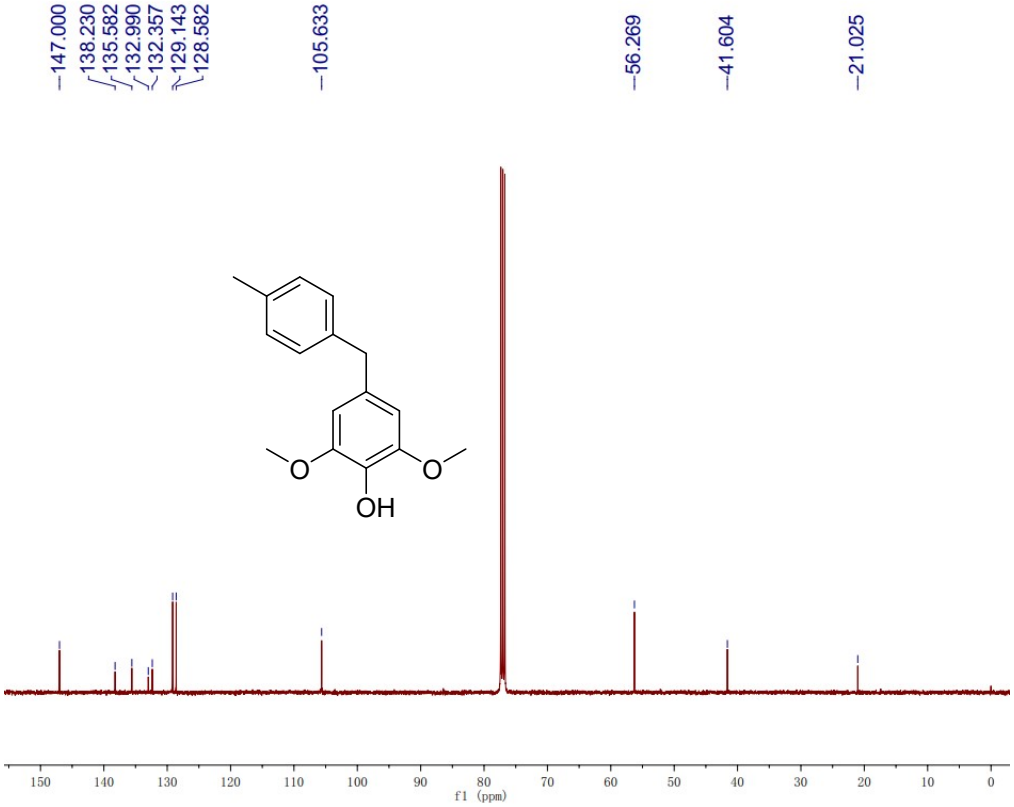
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



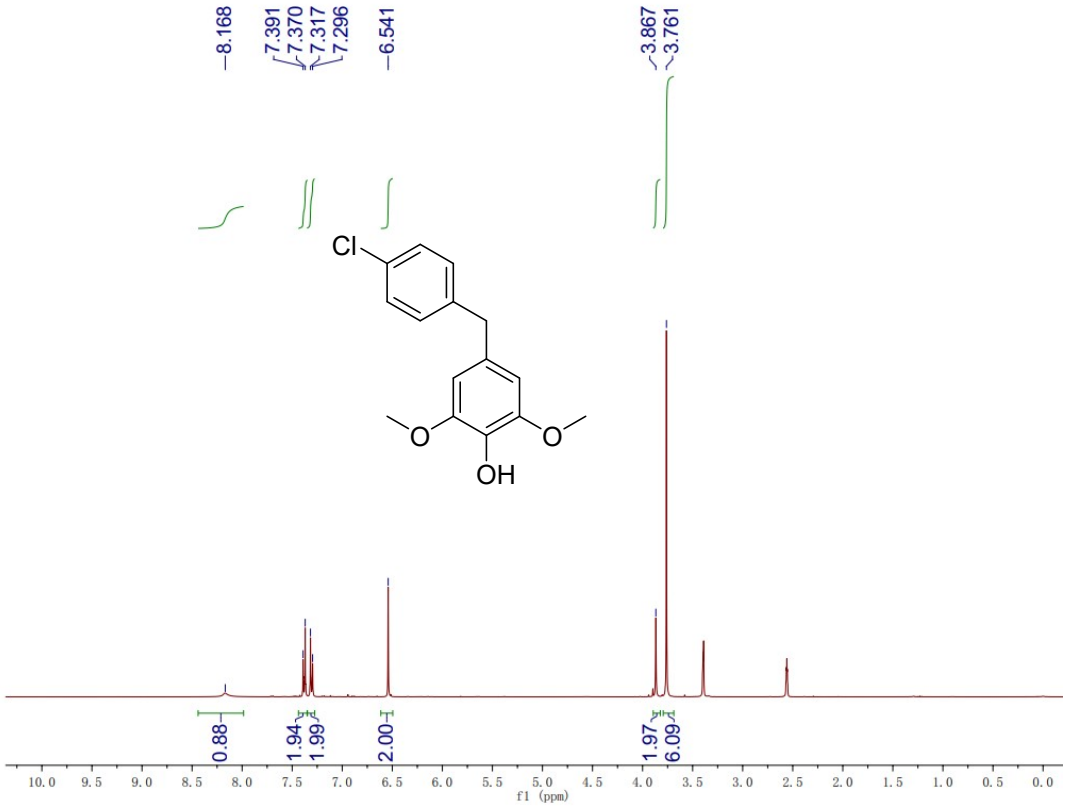
2,6-Dimethoxy-4-(4-methylbenzyl)phenol (1x) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



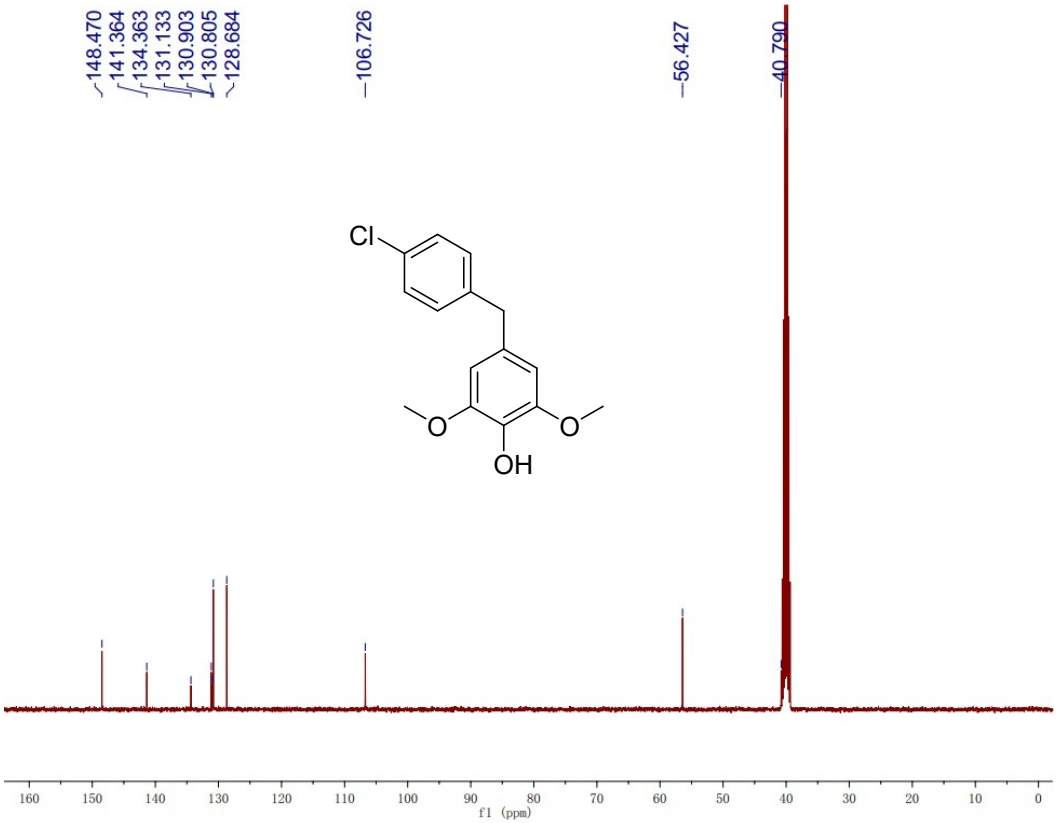
[^{13}C_NMR_100 MHz_(CDCl$_3$: 77.00 ppm)]



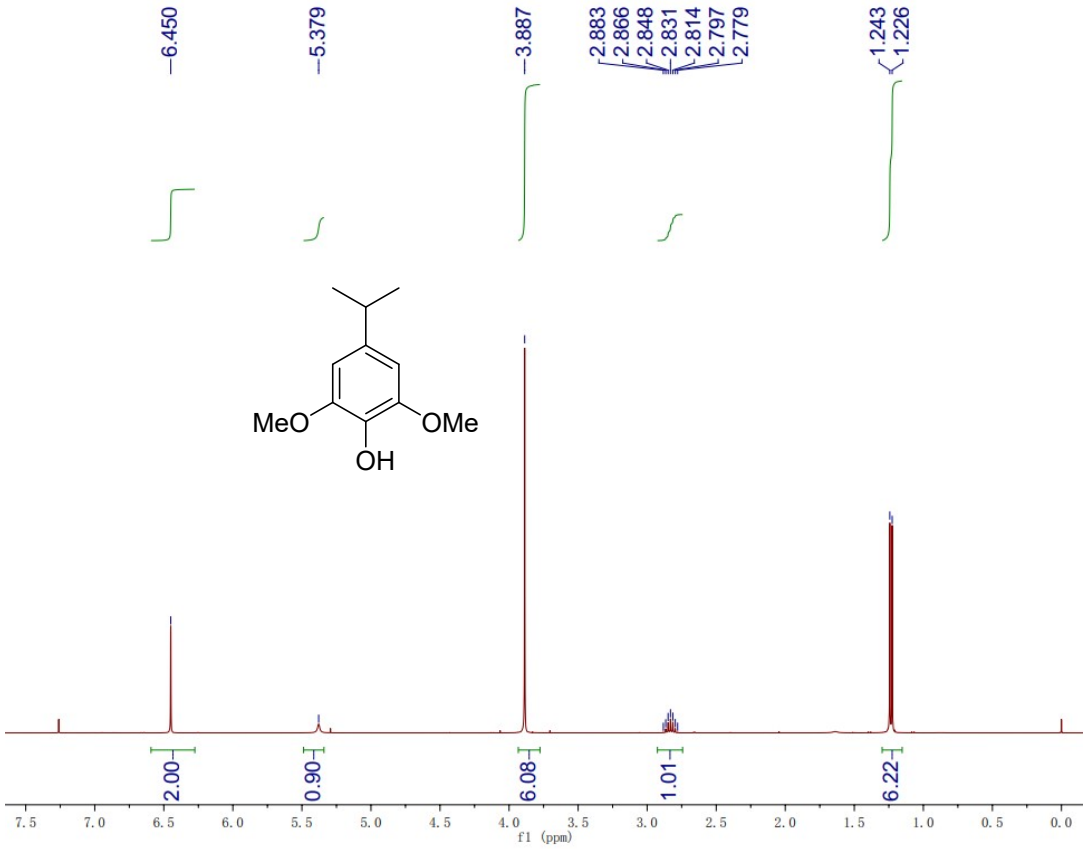
4-(4-Chlorobenzyl)-2,6-dimethoxyphenol (1y) [^{1}H_NMR_400 MHz_(DMSO-d_6: 2.50 ppm)]



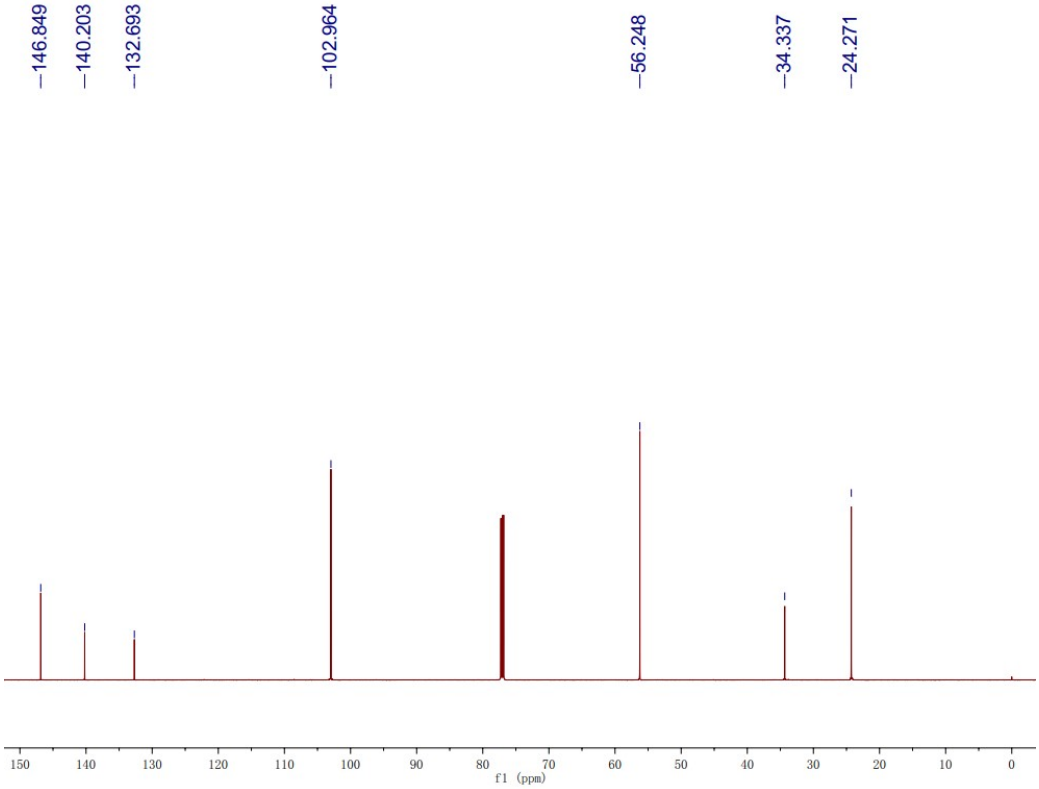
[^{13}C_NMR_100 MHz_(DMSO-d_6: 39.52 ppm)]



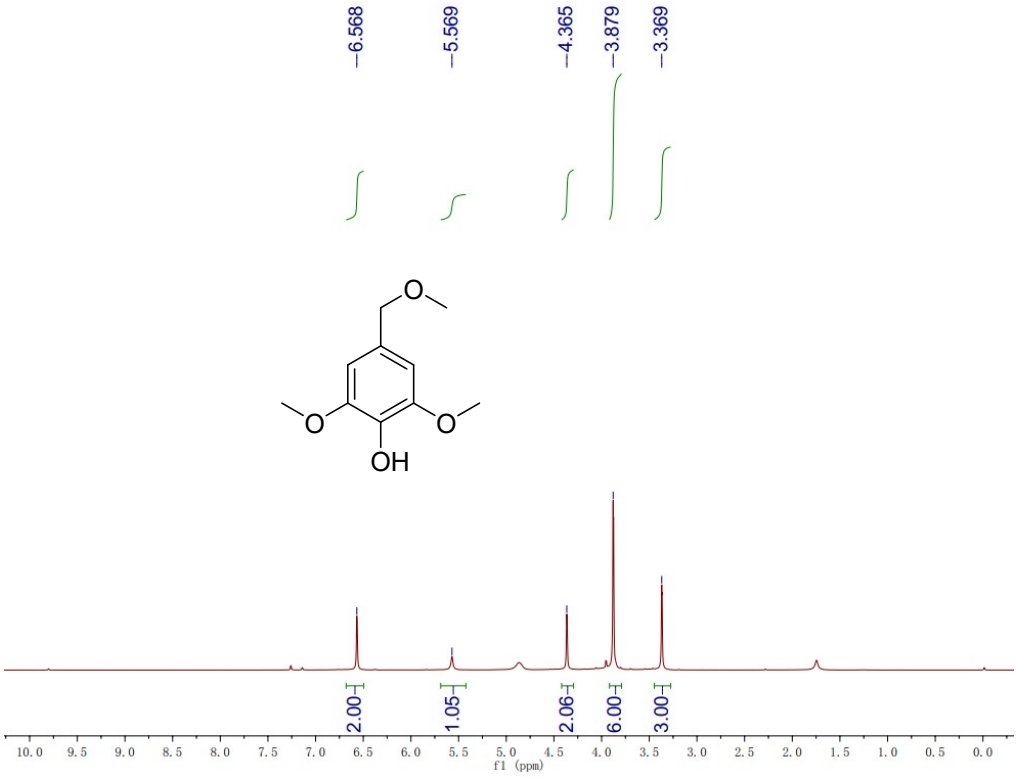
4-Isopropyl-2,6-dimethoxyphenol (1z) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



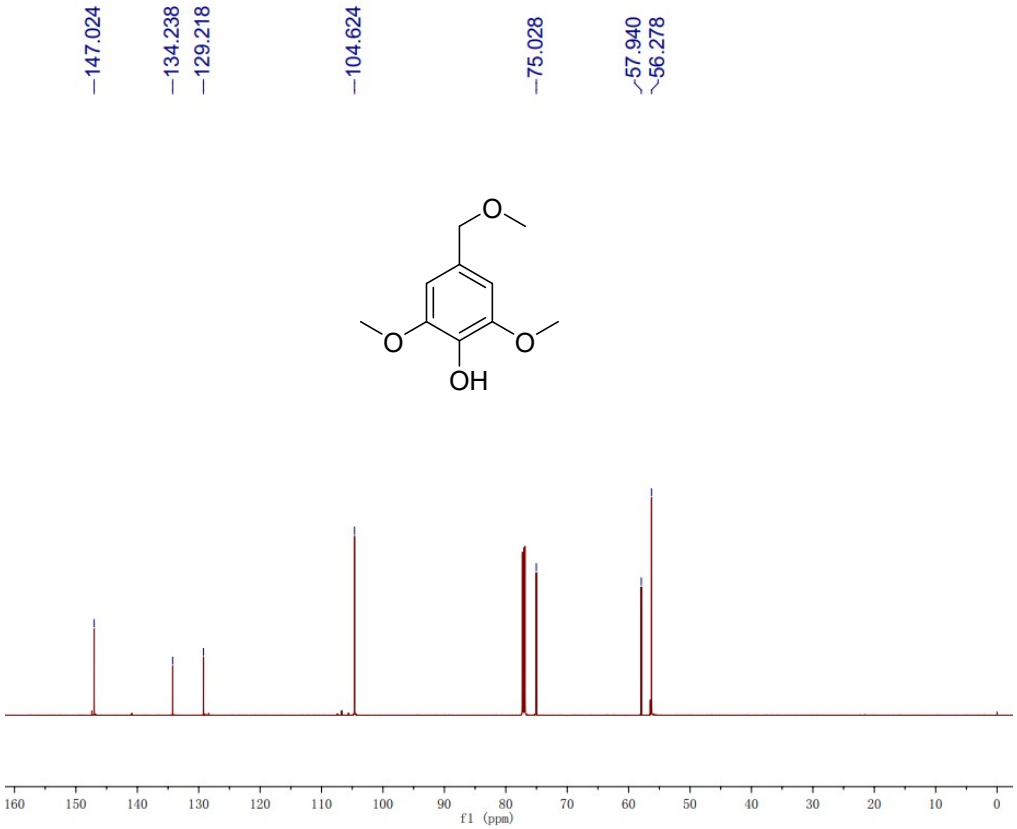
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



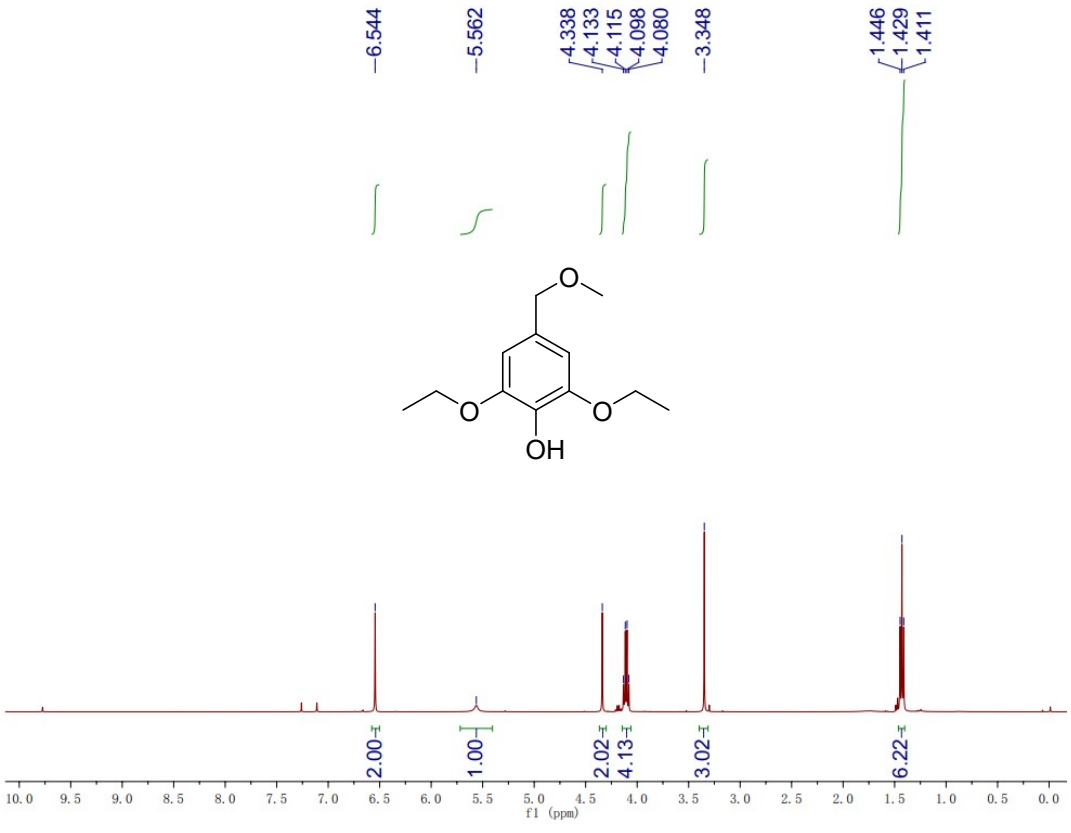
2,6-Dimethoxy-4-(methoxymethyl)phenol (2a) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



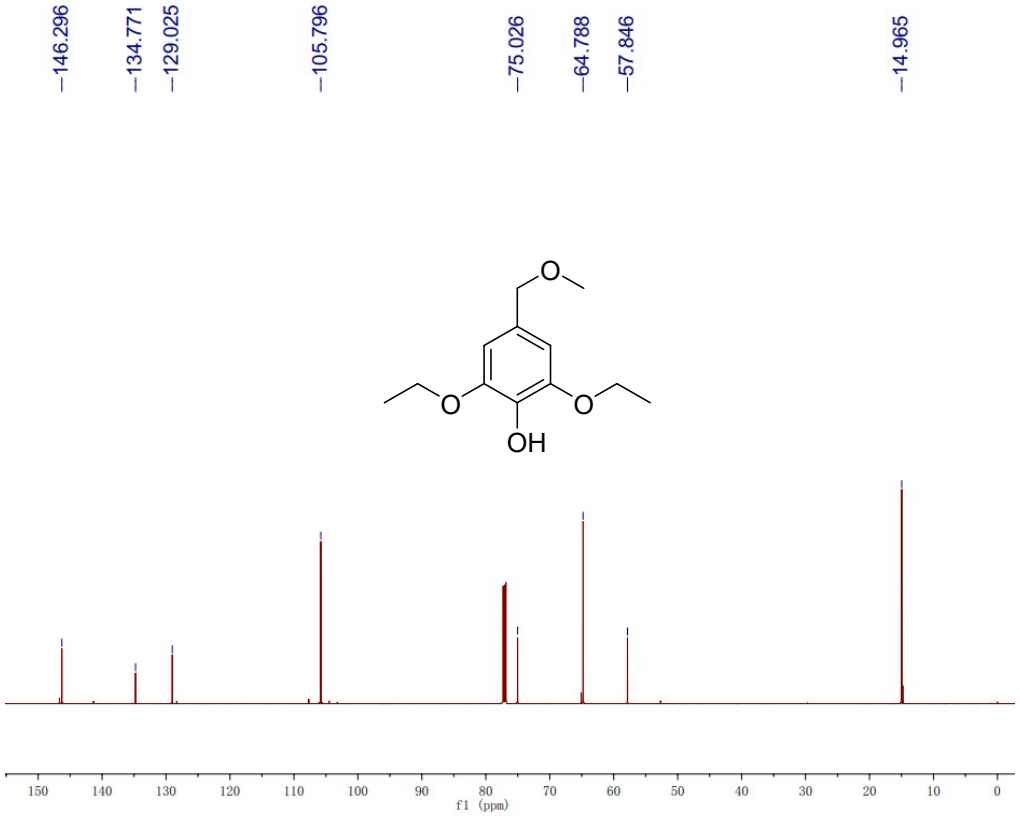
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



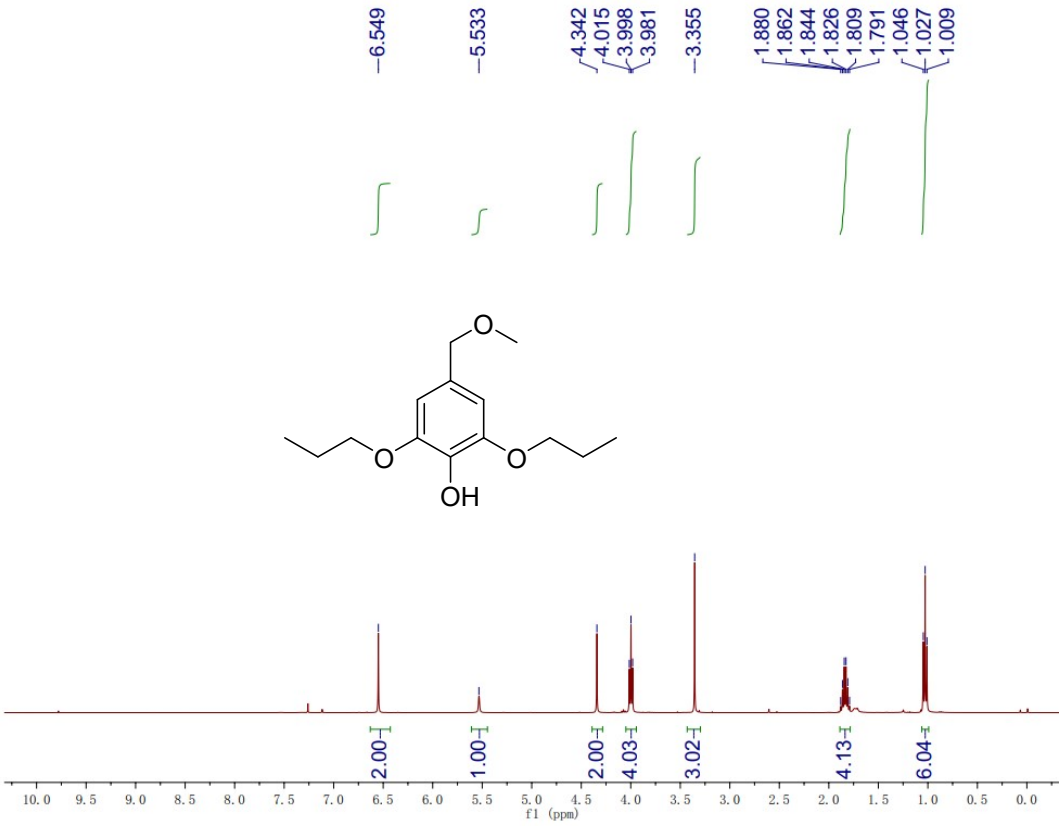
2,6-Diethoxy-4-(methoxymethyl)phenol (2b) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



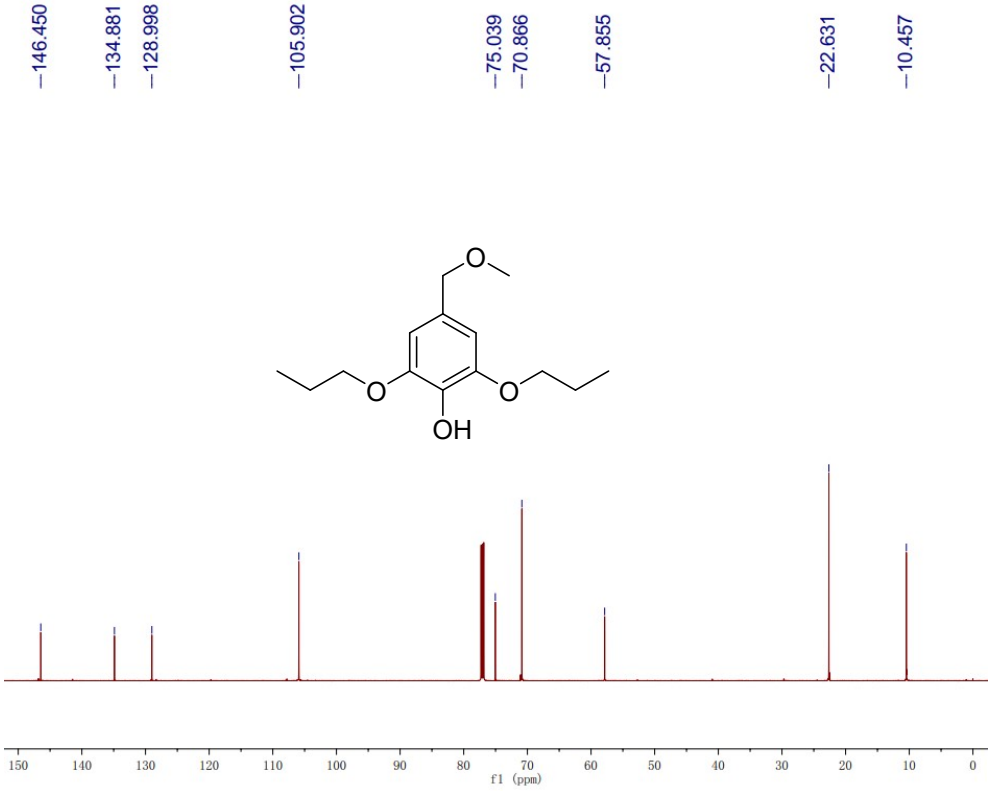
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



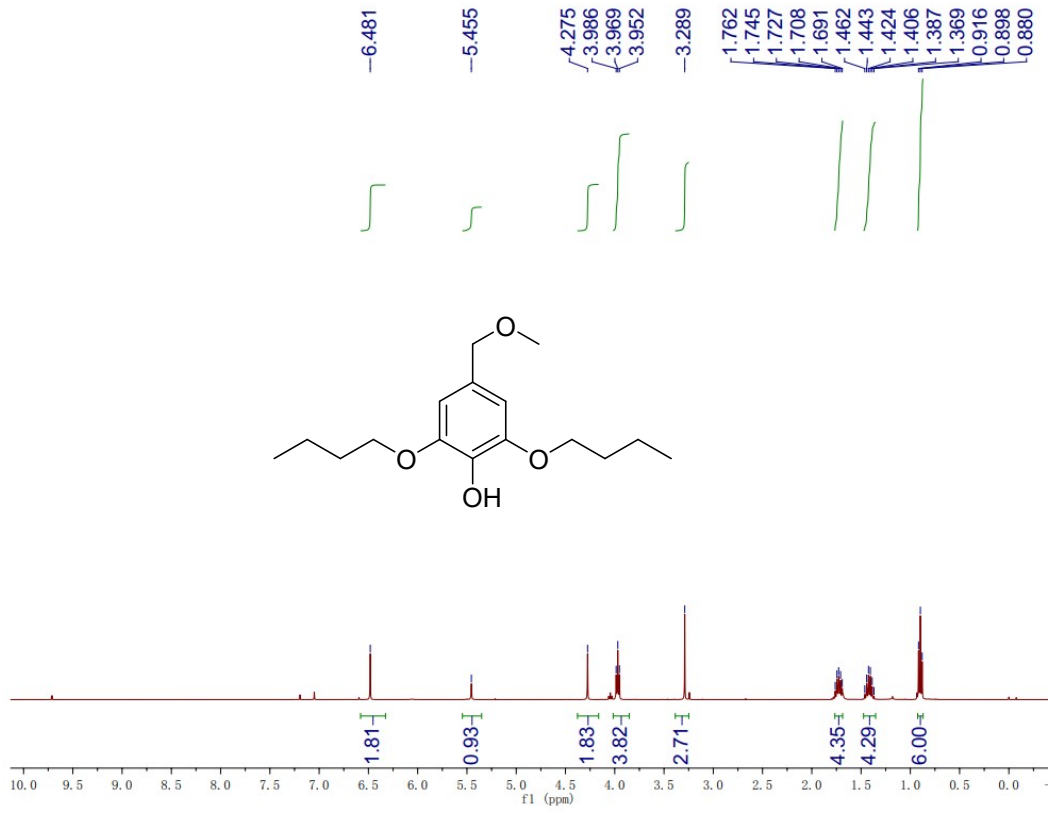
4-(Methoxymethyl)-2,6-dipropoxyphenol (2c) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



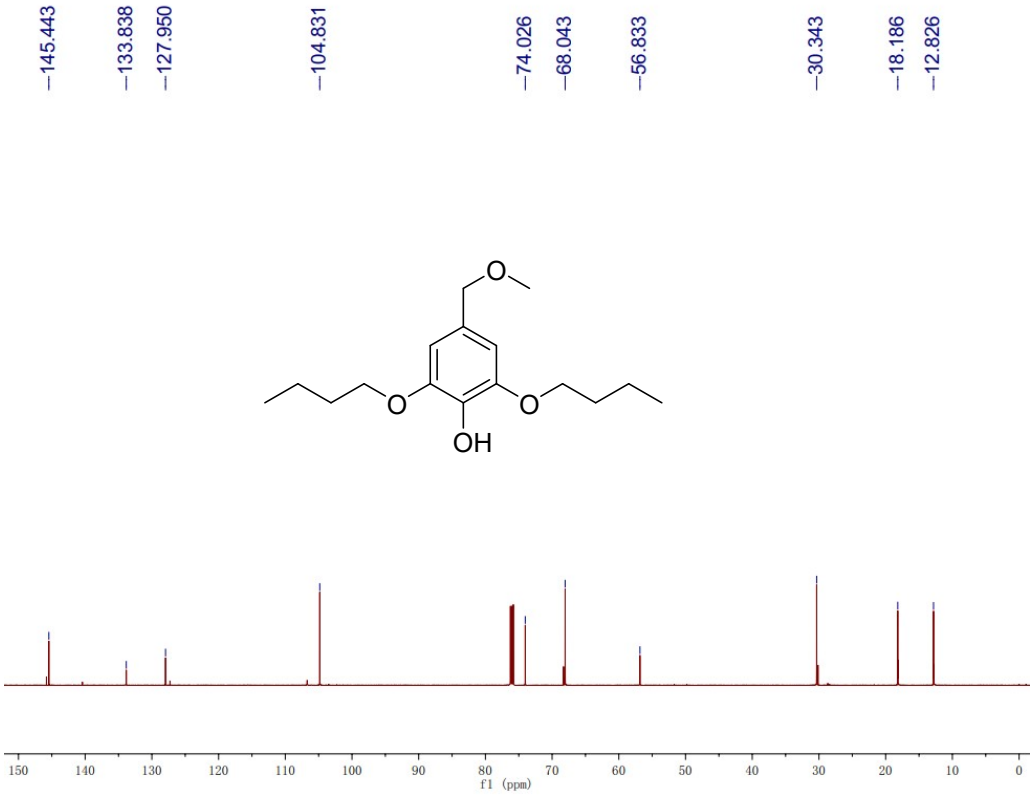
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



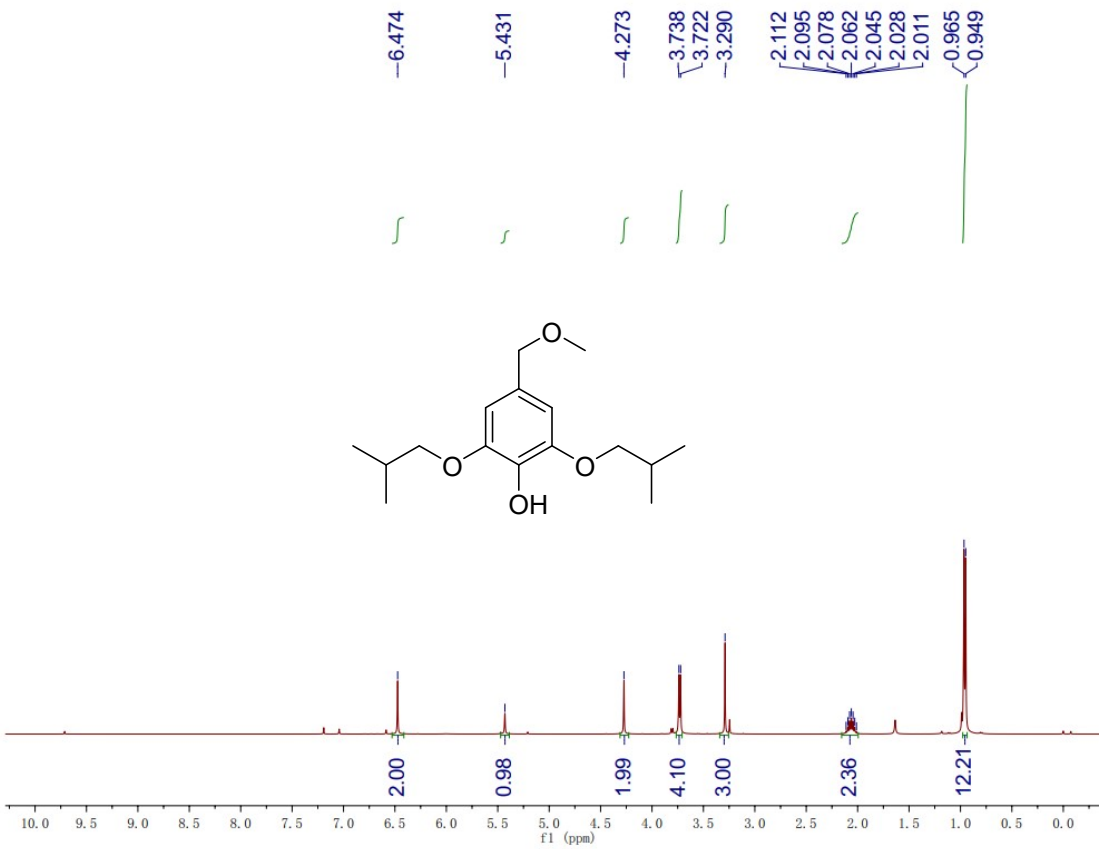
2,6-Dibutoxy-4-(methoxymethyl)phenol (2d) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



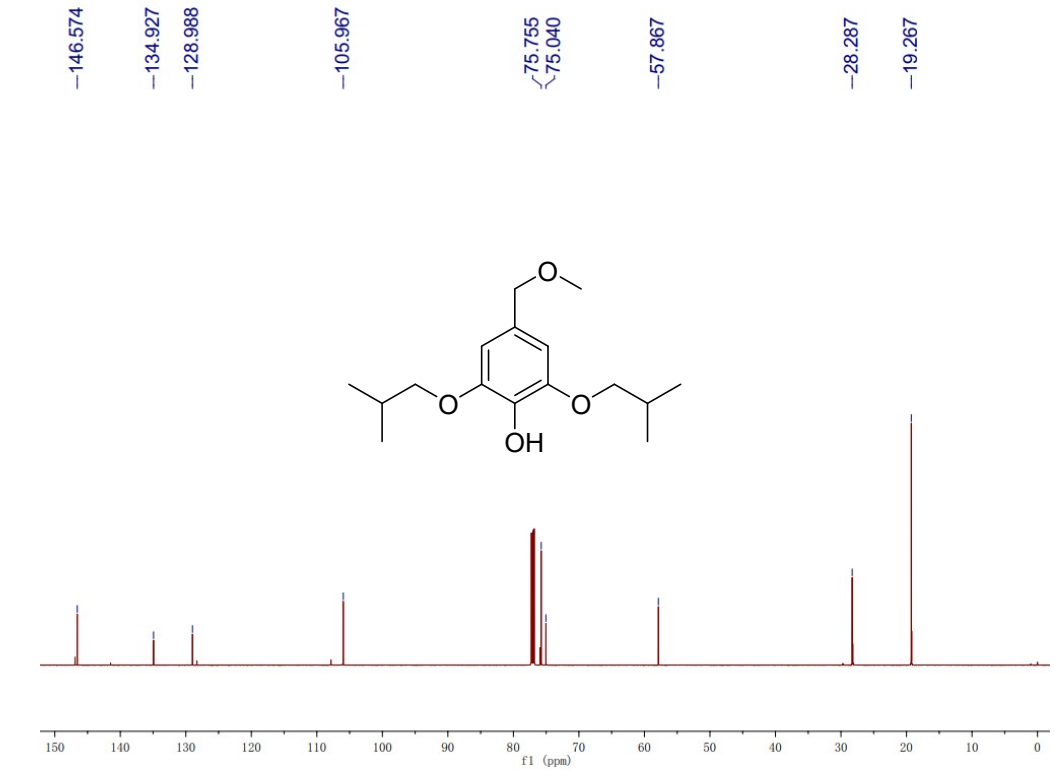
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



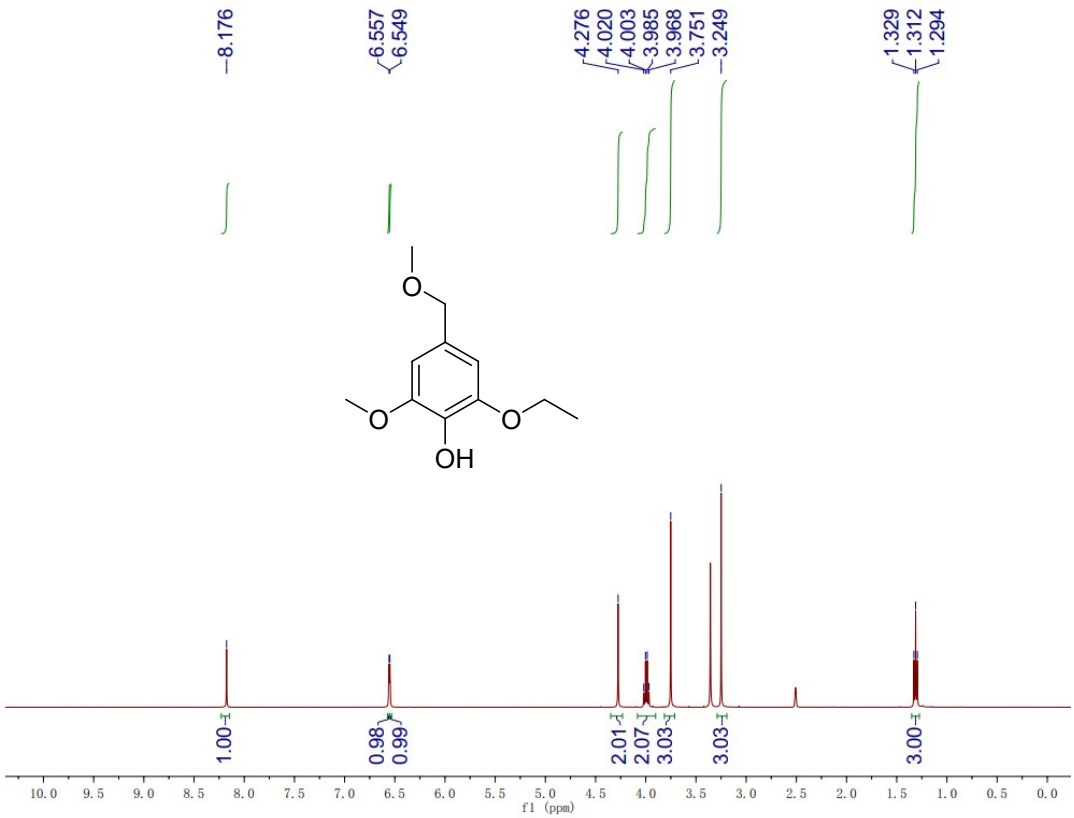
2,6-Diisobutoxy-4-(methoxymethyl)phenol (2e) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



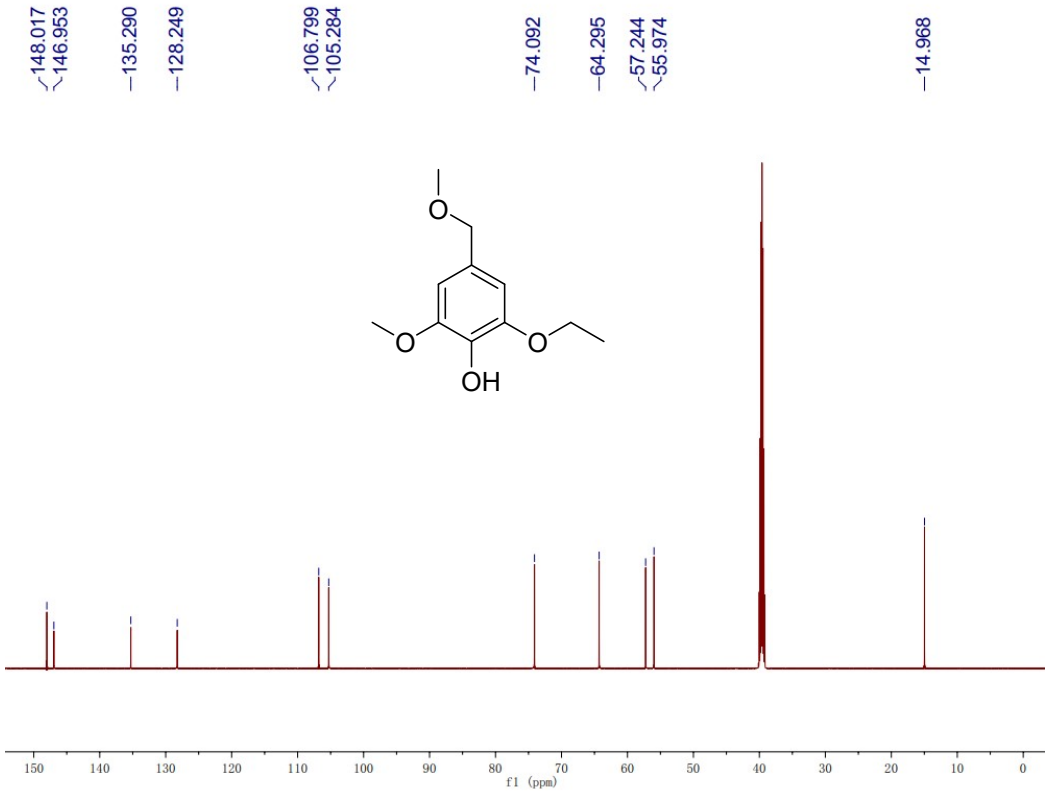
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



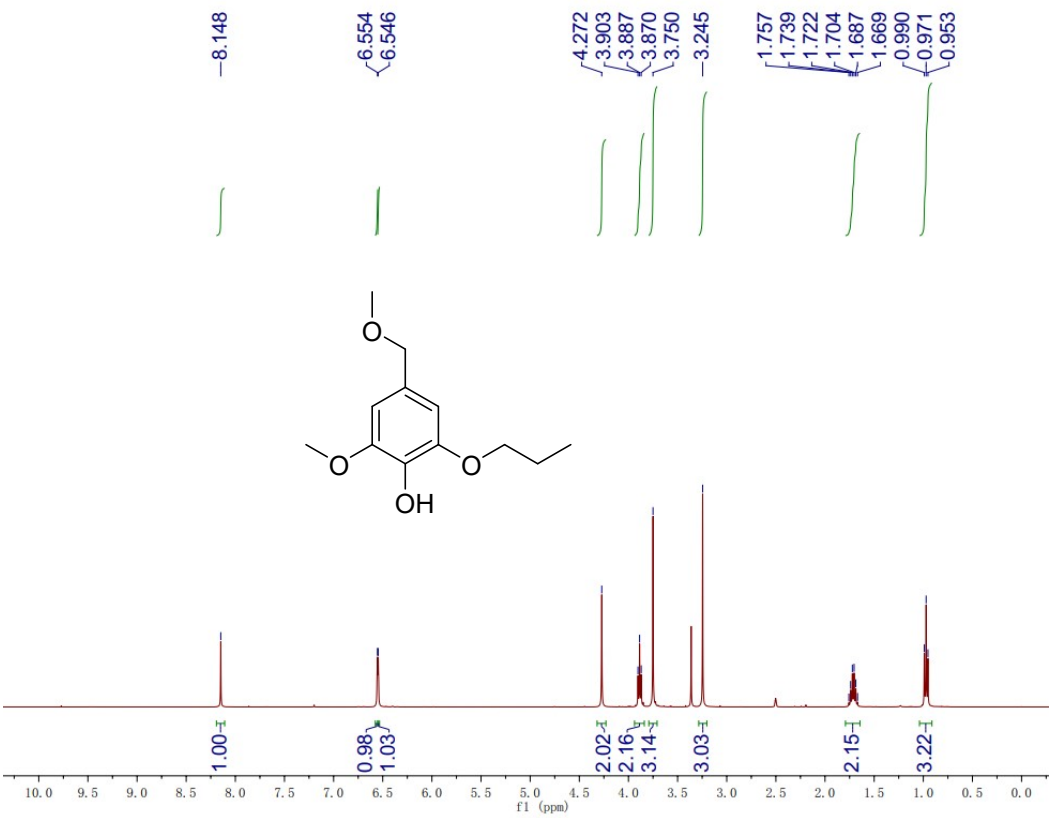
2-Ethoxy-6-methoxy-4-(methoxymethyl)phenol (2f) [^{1}H_NMR_400 MHz_(DMSO-d_6: 2.50 ppm)]



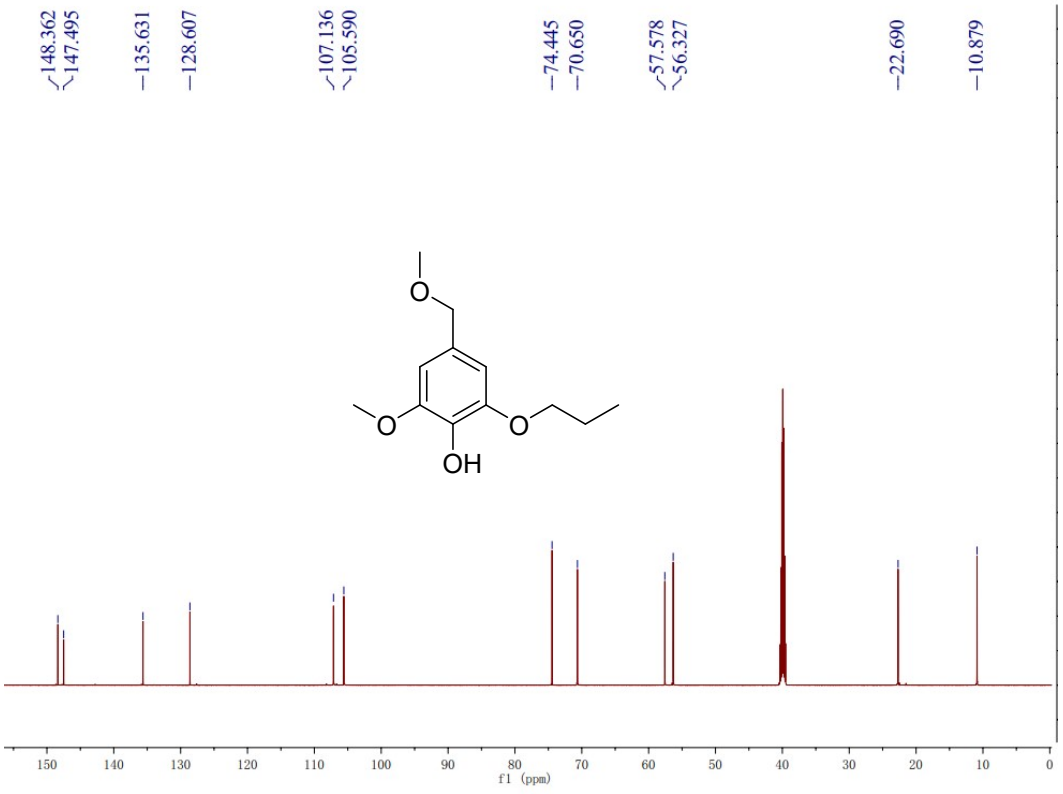
[^{13}C_NMR_150 MHz_(DMSO-d_6: 39.52 ppm)]



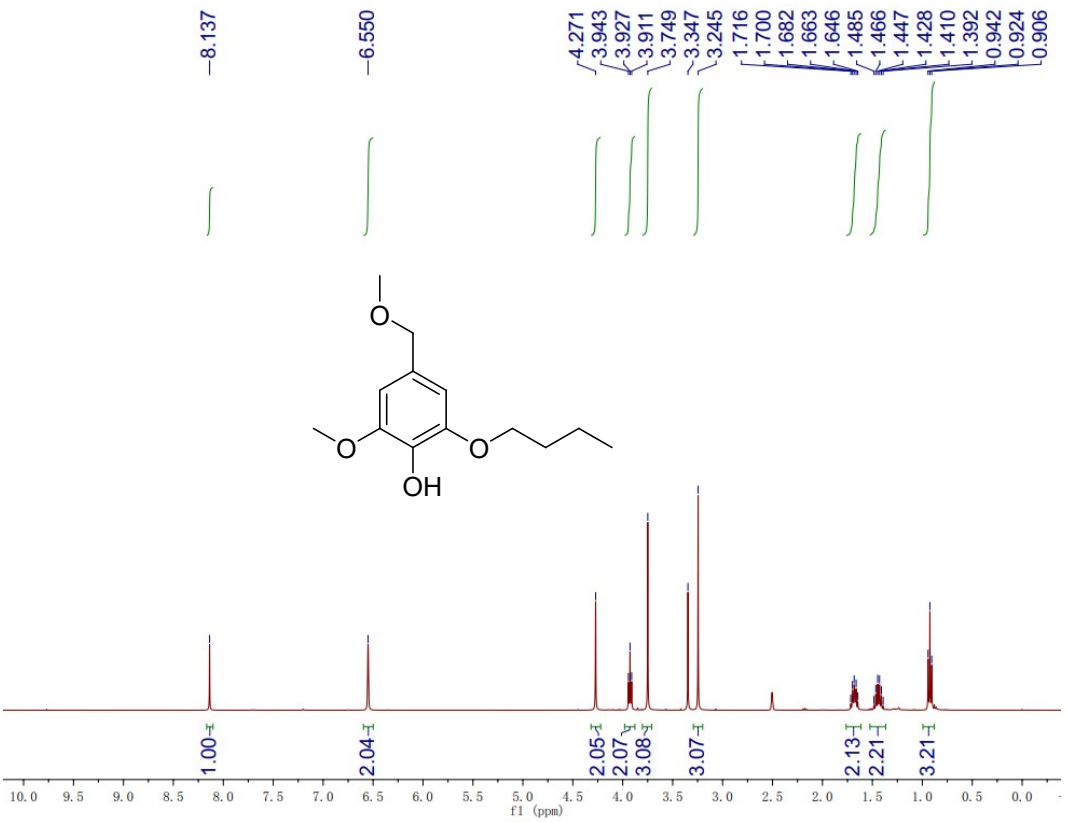
2-Methoxy-4-(methoxymethyl)-6-propoxyphenol (2g) [^{1}H_NMR_400 MHz_(DMSO-d_6: 2.50 ppm)]



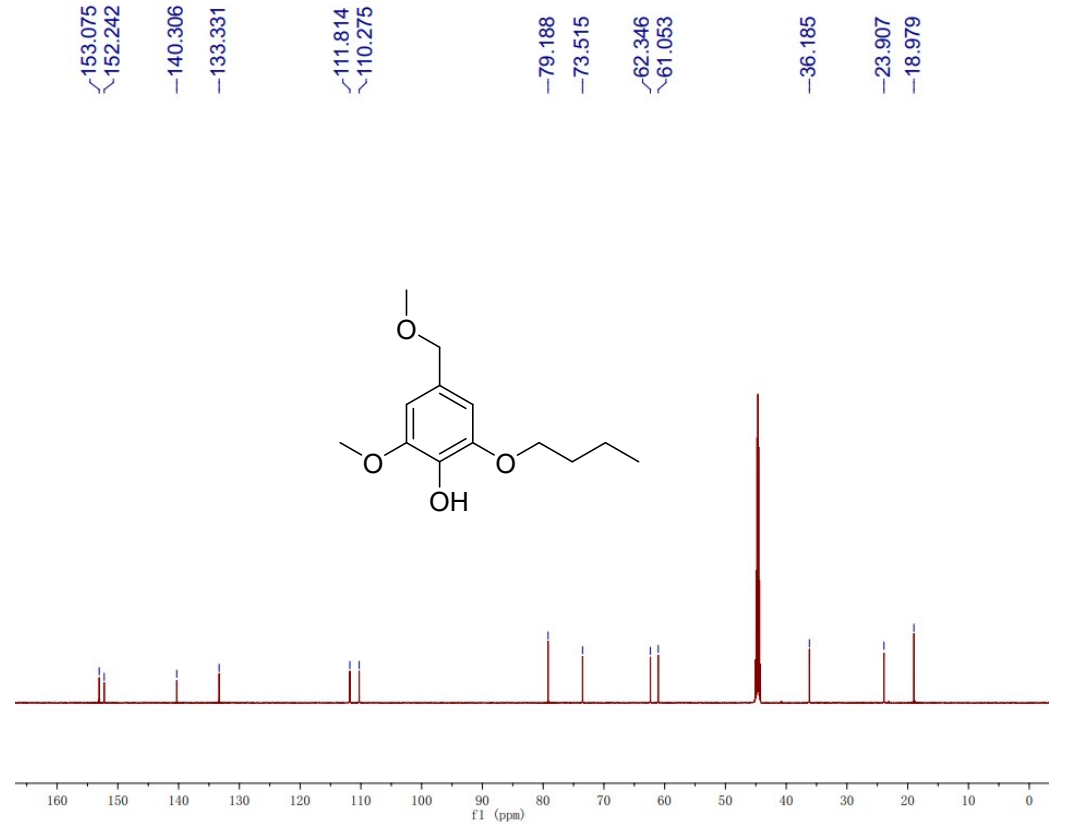
[^{13}C_NMR_150 MHz_(DMSO-d_6: 39.52 ppm)]



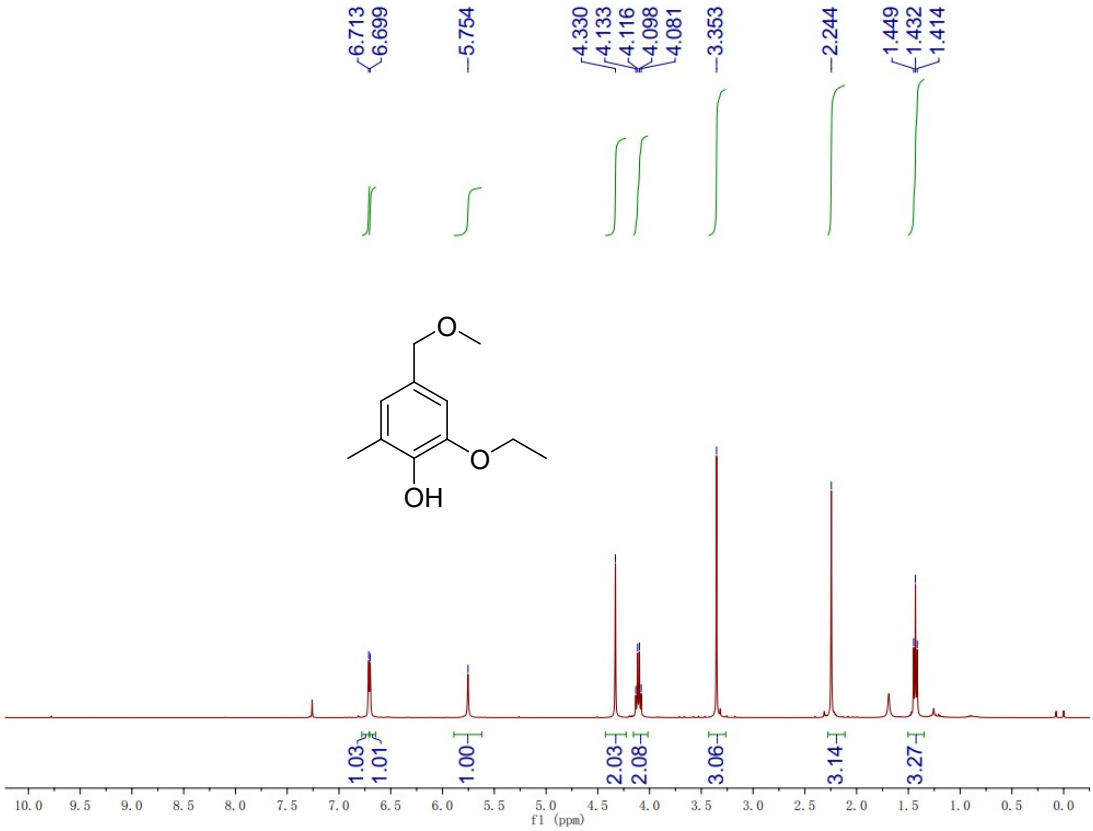
2-Butoxy-6-methoxy-4-(methoxymethyl)phenol (2h) [^{1}H_NMR_400 MHz_(DMSO-d_6: 2.50 ppm)]



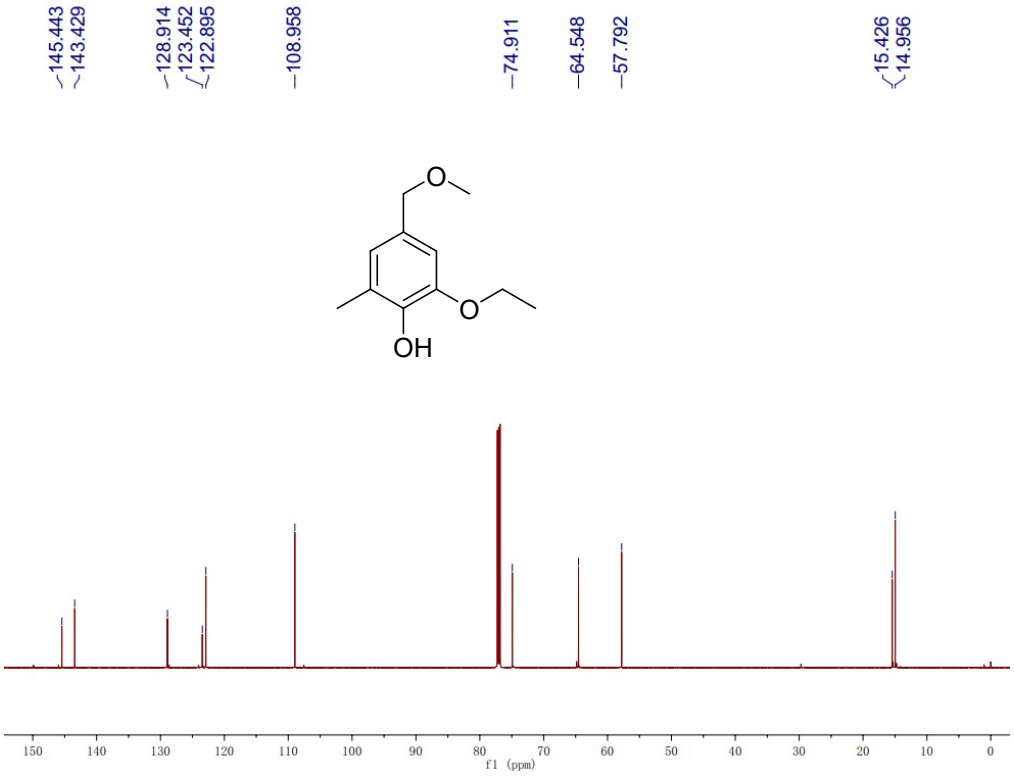
[^{13}C_NMR_150 MHz_(DMSO-d_6: 39.52 ppm)]



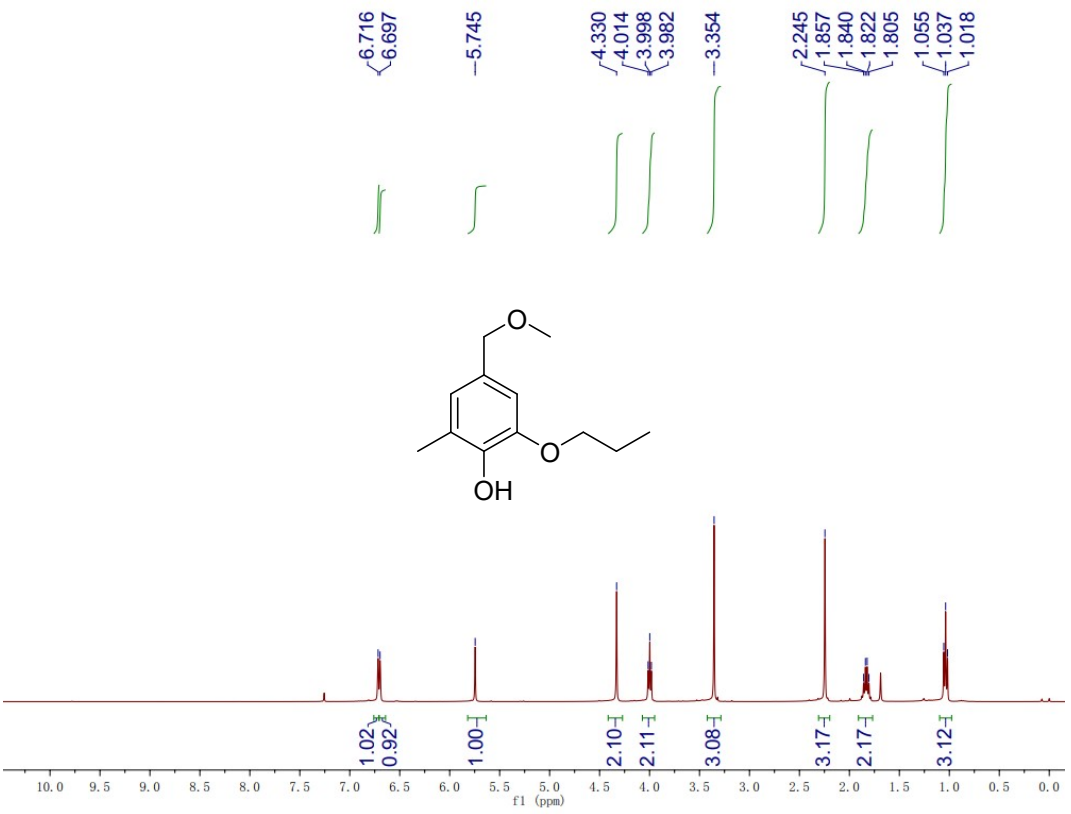
2-Ethoxy-4-(methoxymethyl)-6-methylphenol (2i) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



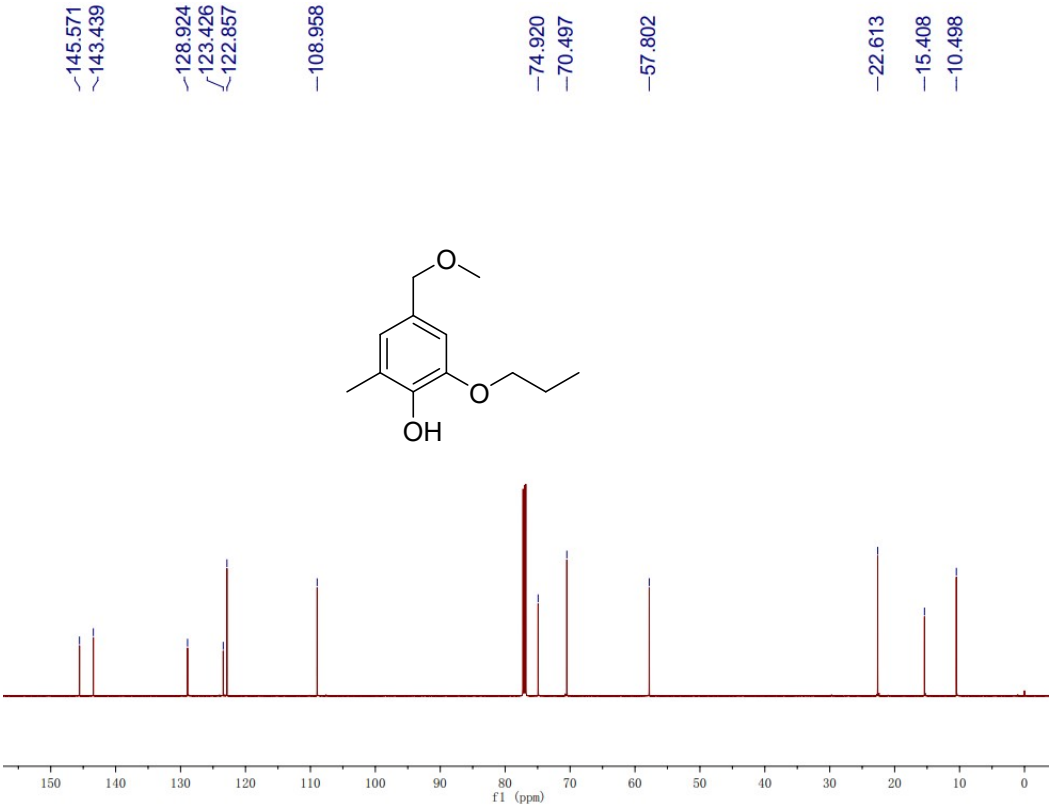
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



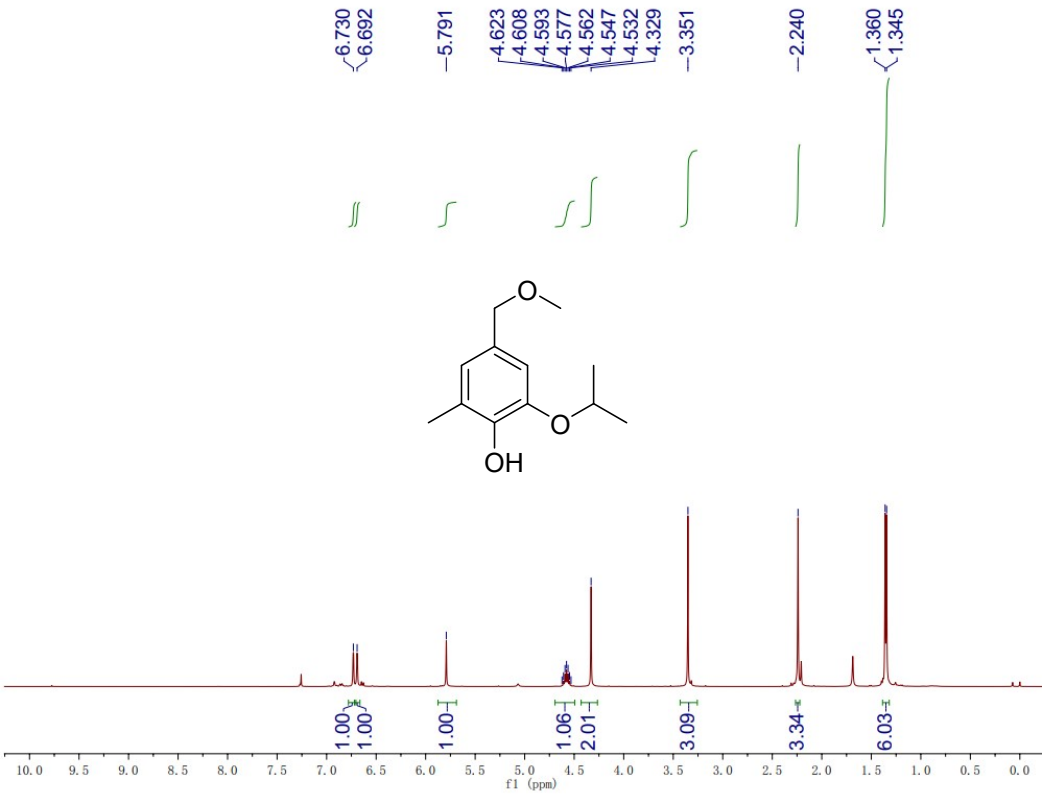
4-(Methoxymethyl)-2-methyl-6-propoxyphenol (2j) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



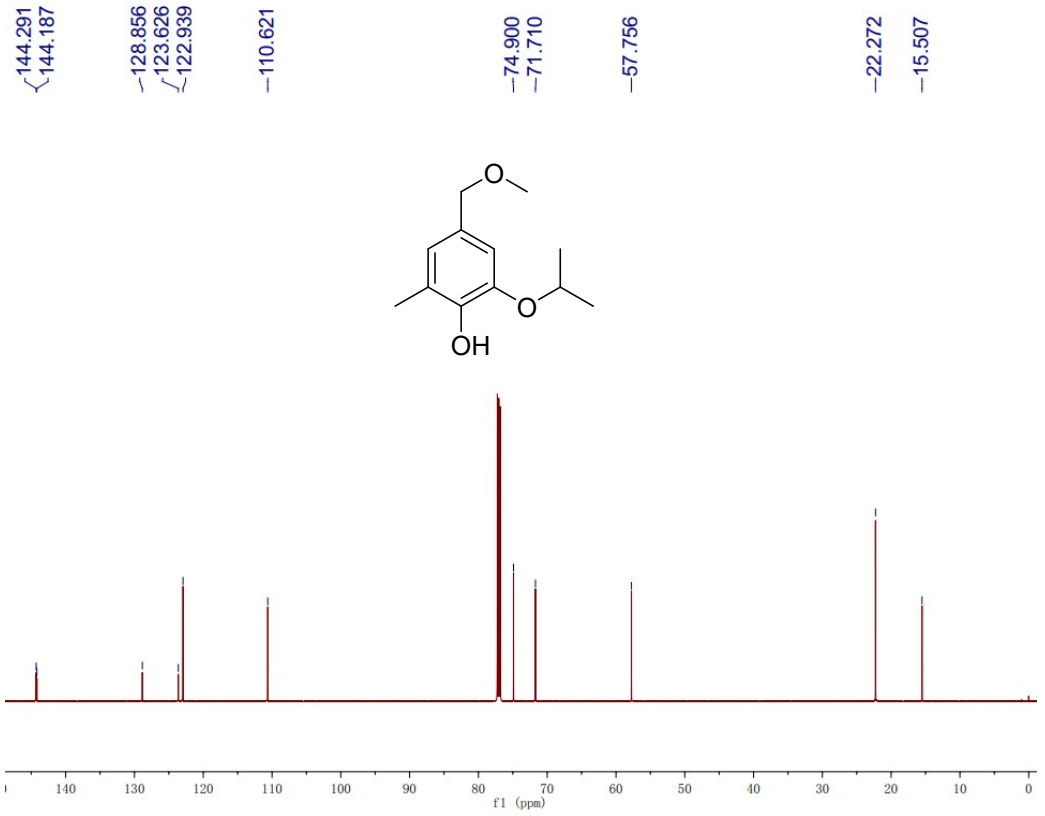
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



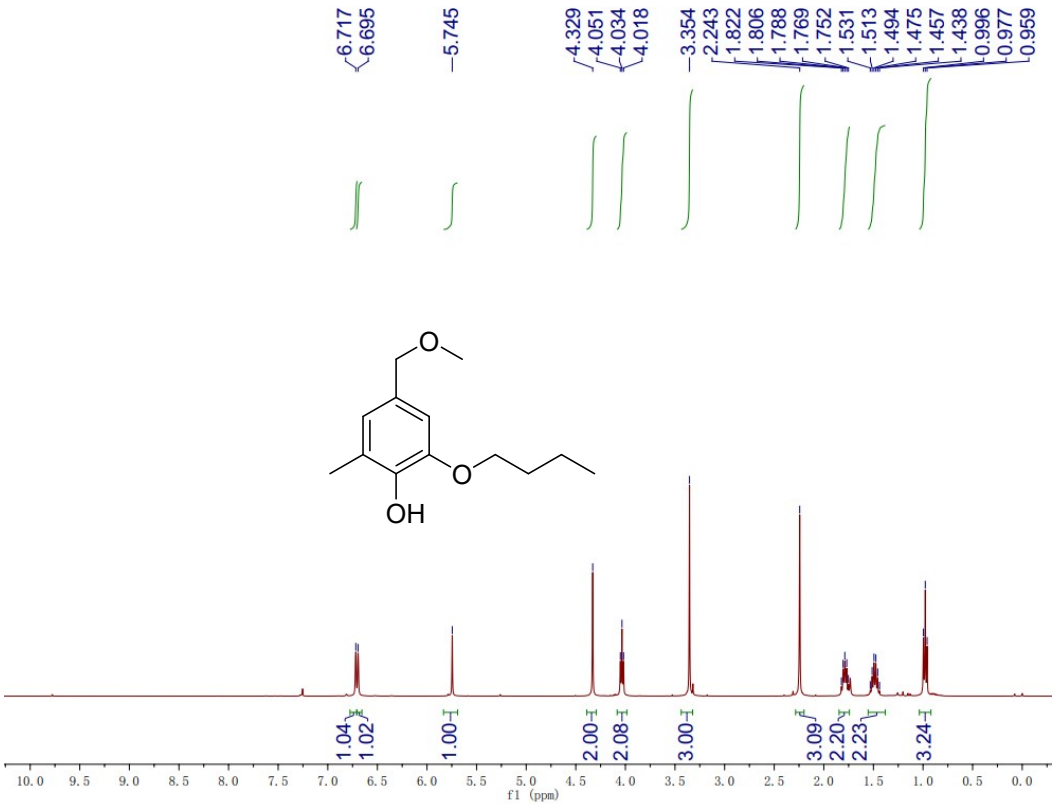
2-Isopropoxy-4-(methoxymethyl)-6-methylphenol (2k) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



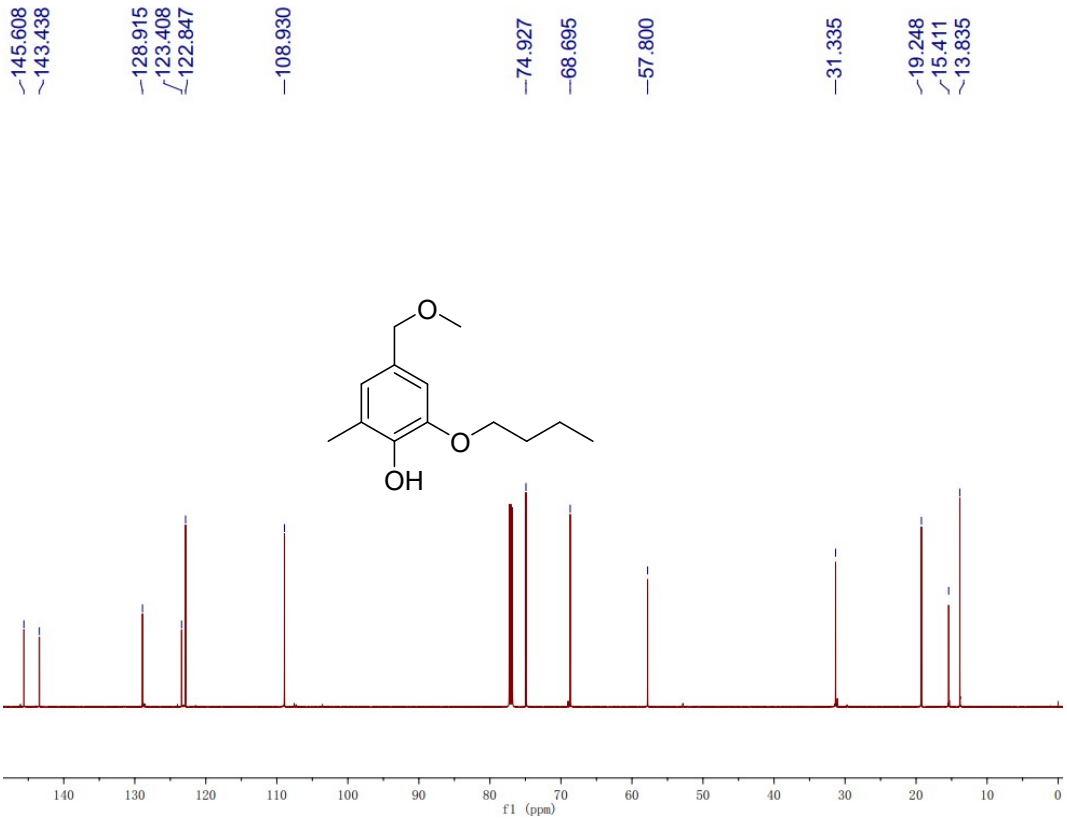
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



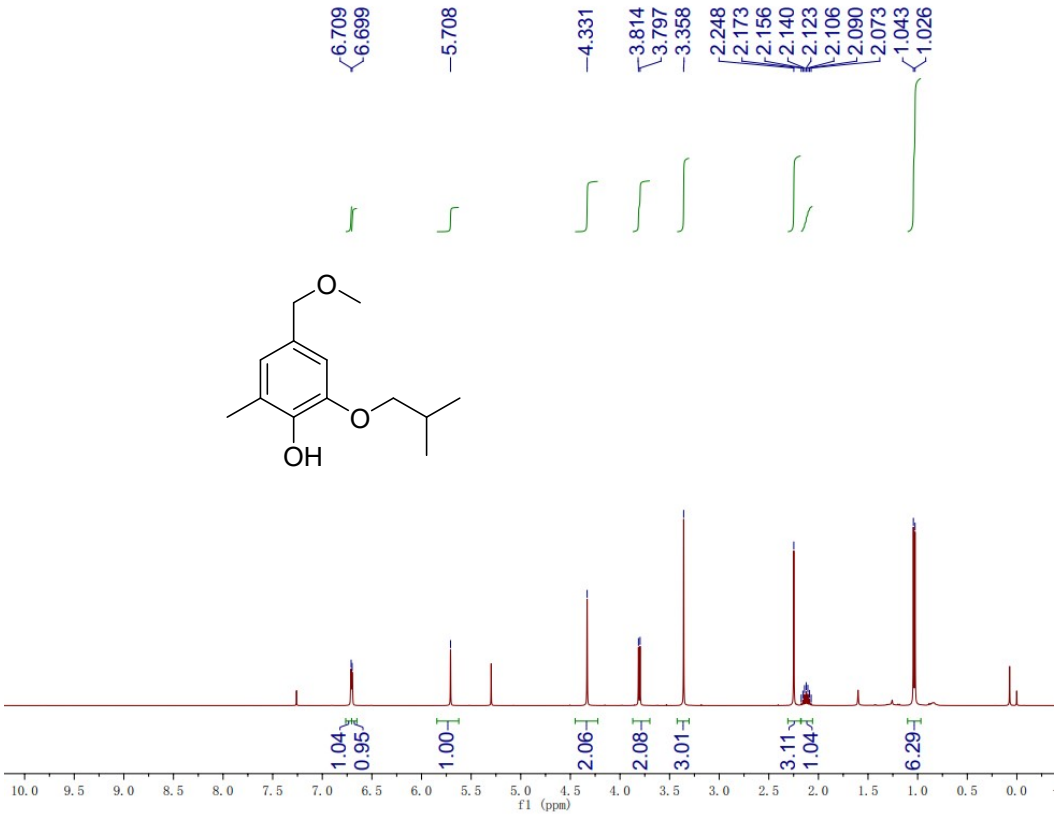
2-Butoxy-4-(methoxymethyl)-6-methylphenol (2l) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



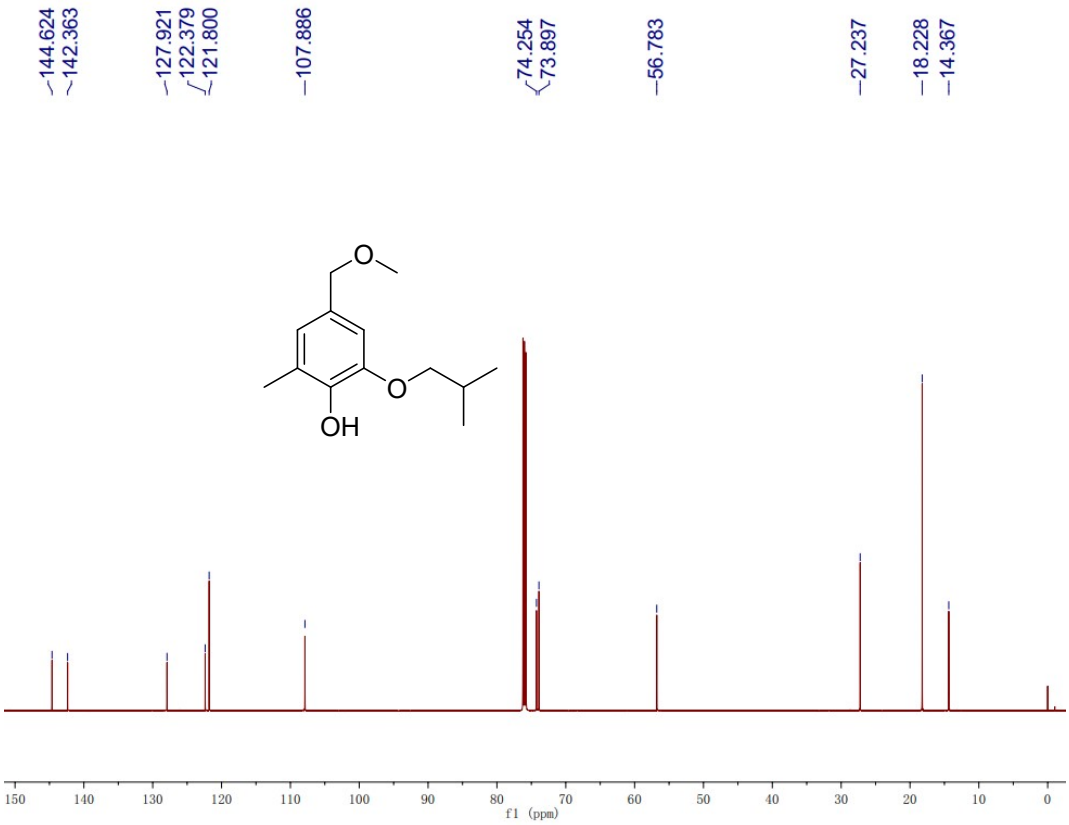
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



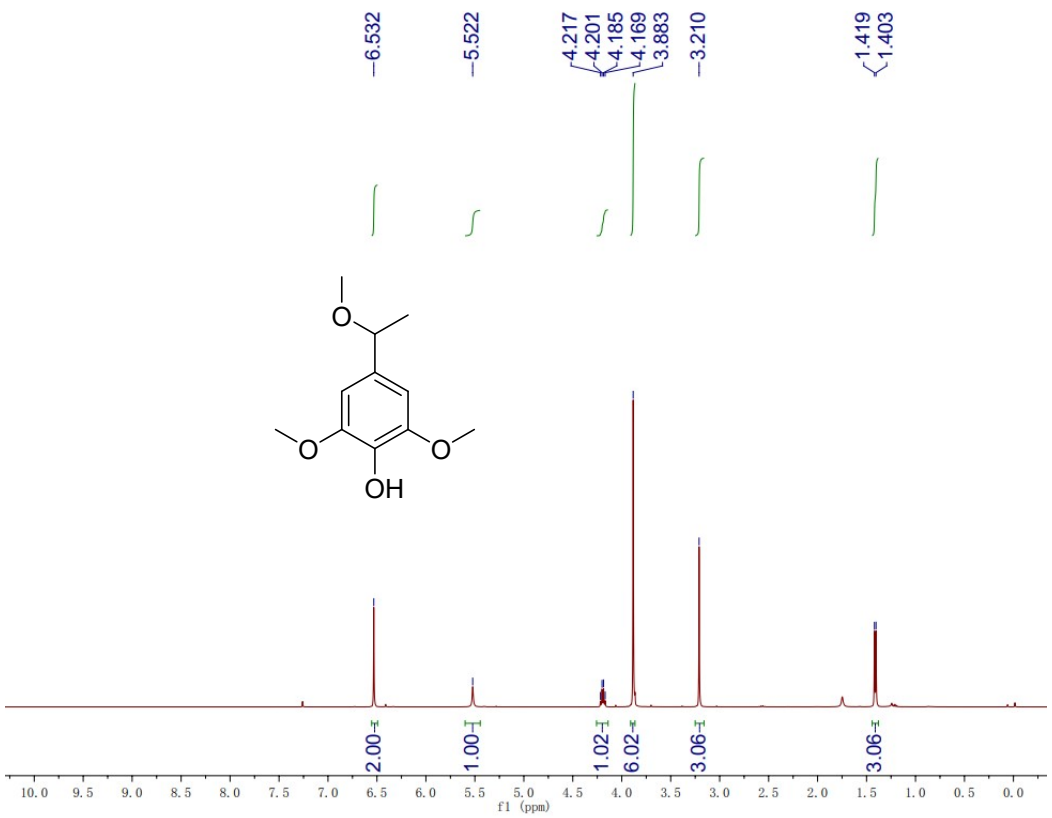
2-Isobutoxy-4-(methoxymethyl)-6-methylphenol (2m) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



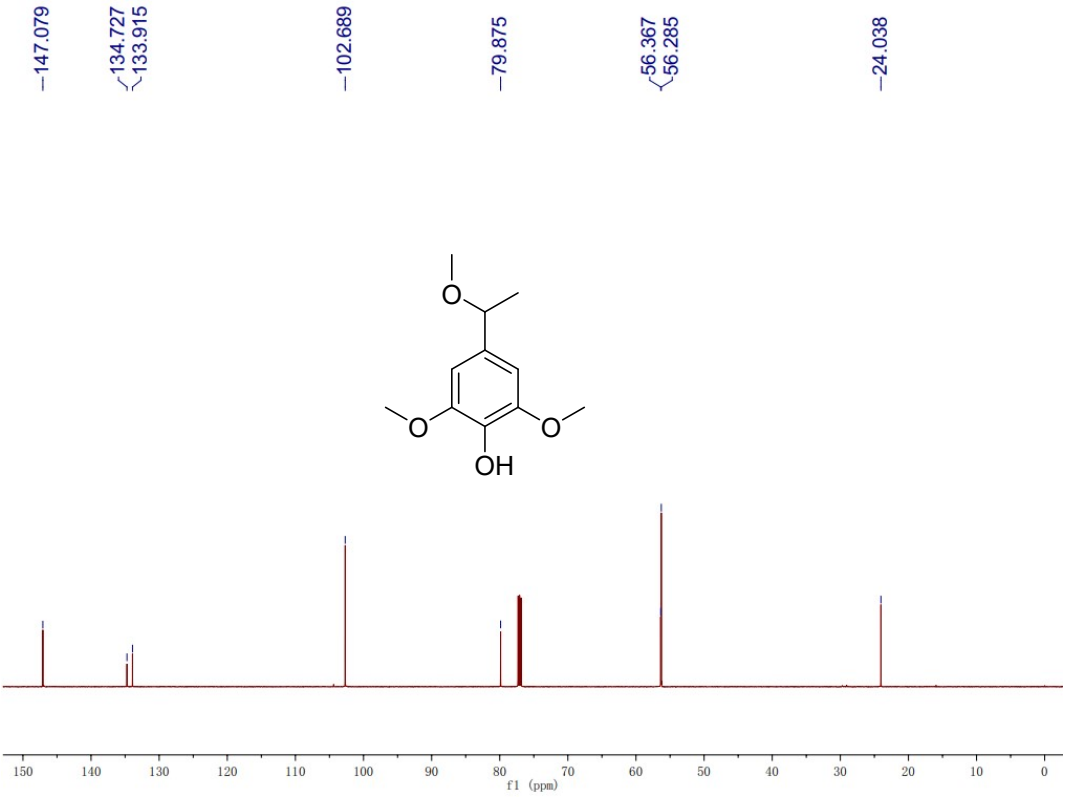
[^{13}C_NMR_150 MHz_(CDCl$_3$: 77.00 ppm)]



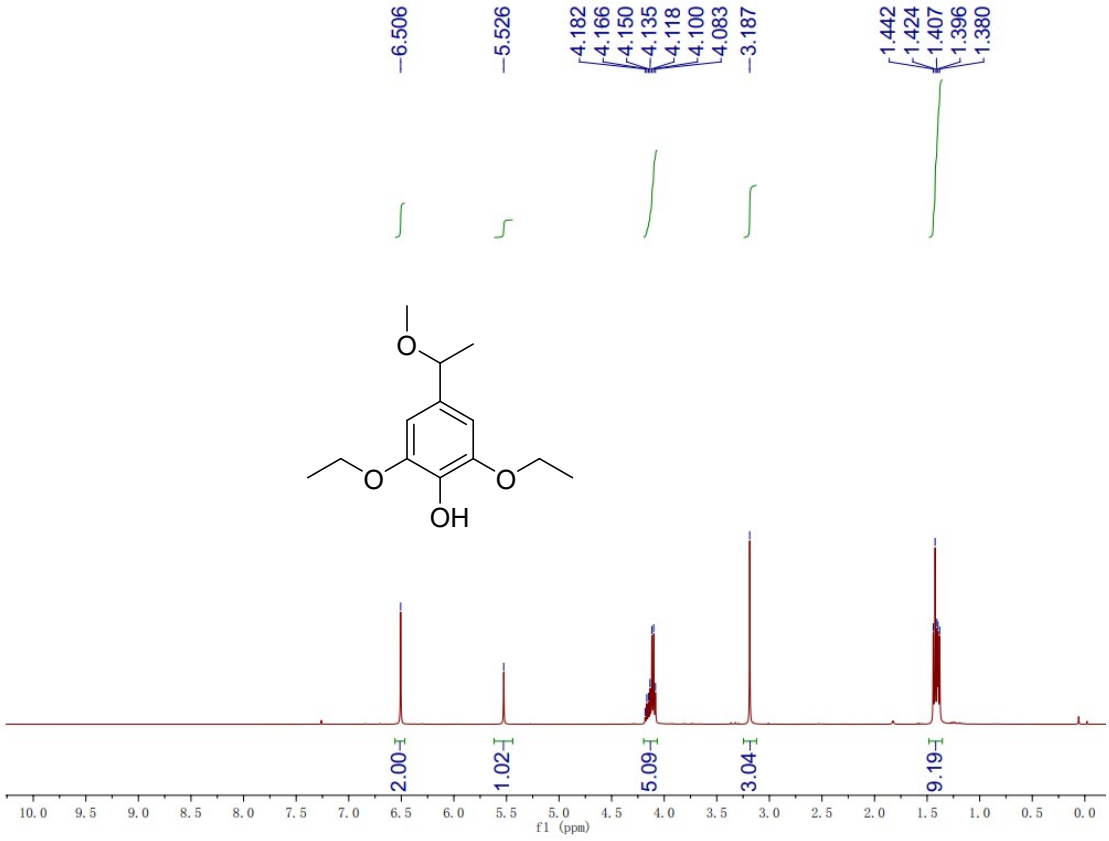
2,6-Dimethoxy-4-(1-methoxyethyl)phenol (2n) [^{1}H_NMR_400 MHz_(CDCl$_3$: 7.26 ppm)]



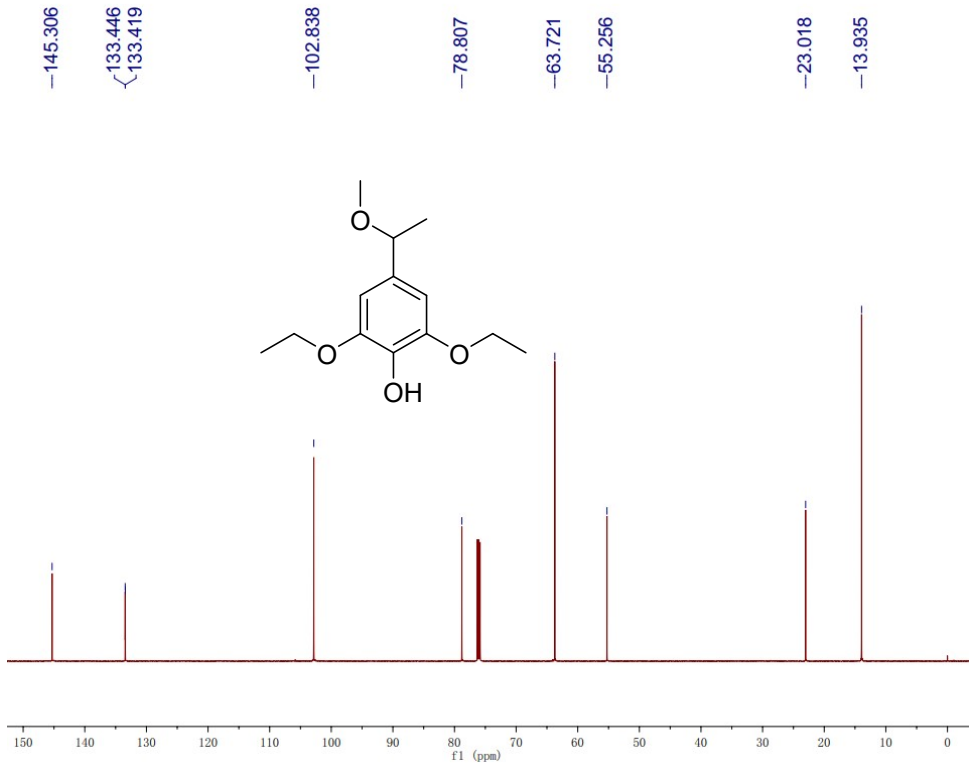
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



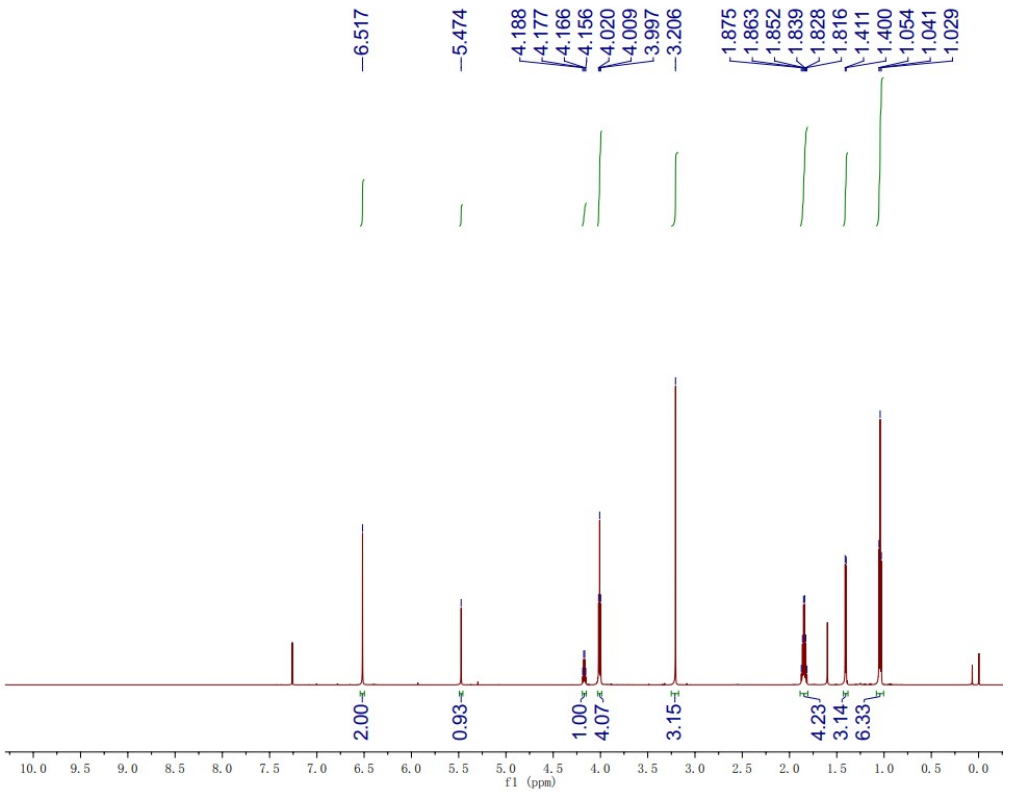
2,6-Diethoxy-4-(1-methoxyethyl)phenol (2o) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



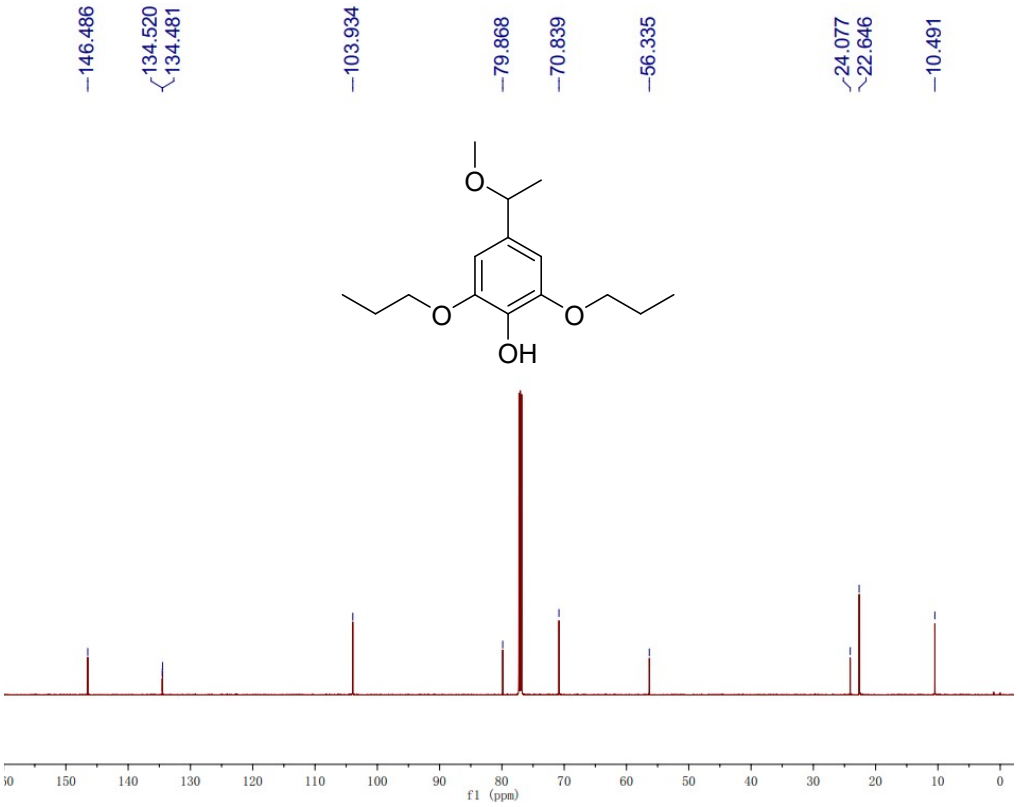
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



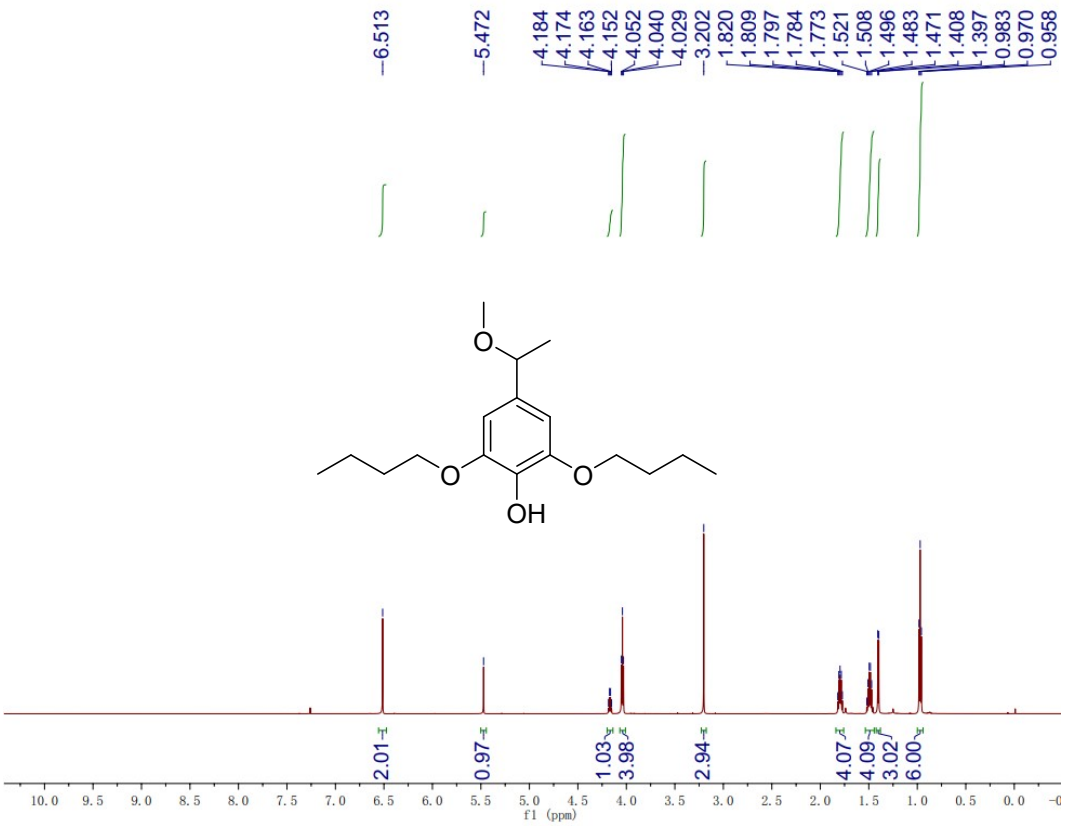
4-(1-Methoxyethyl)-2,6-dipropoxyphenol (2p) [^{1}H_NMR_600 MHz_($CDCl_3$: 7.26 ppm)]



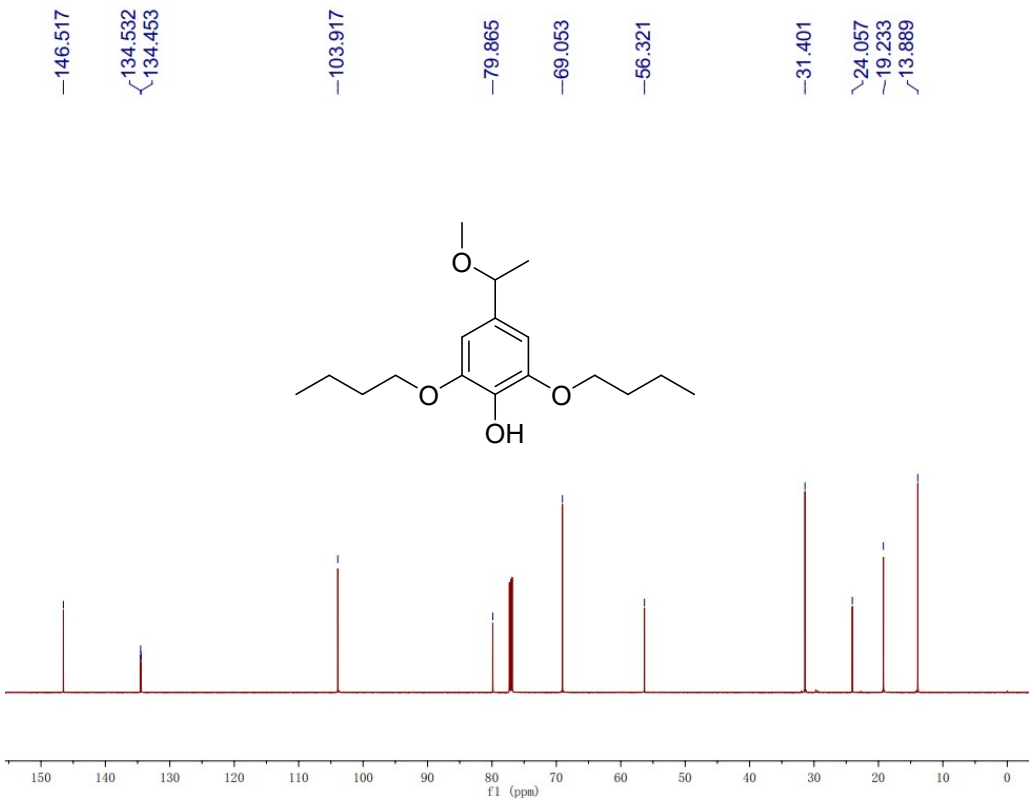
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



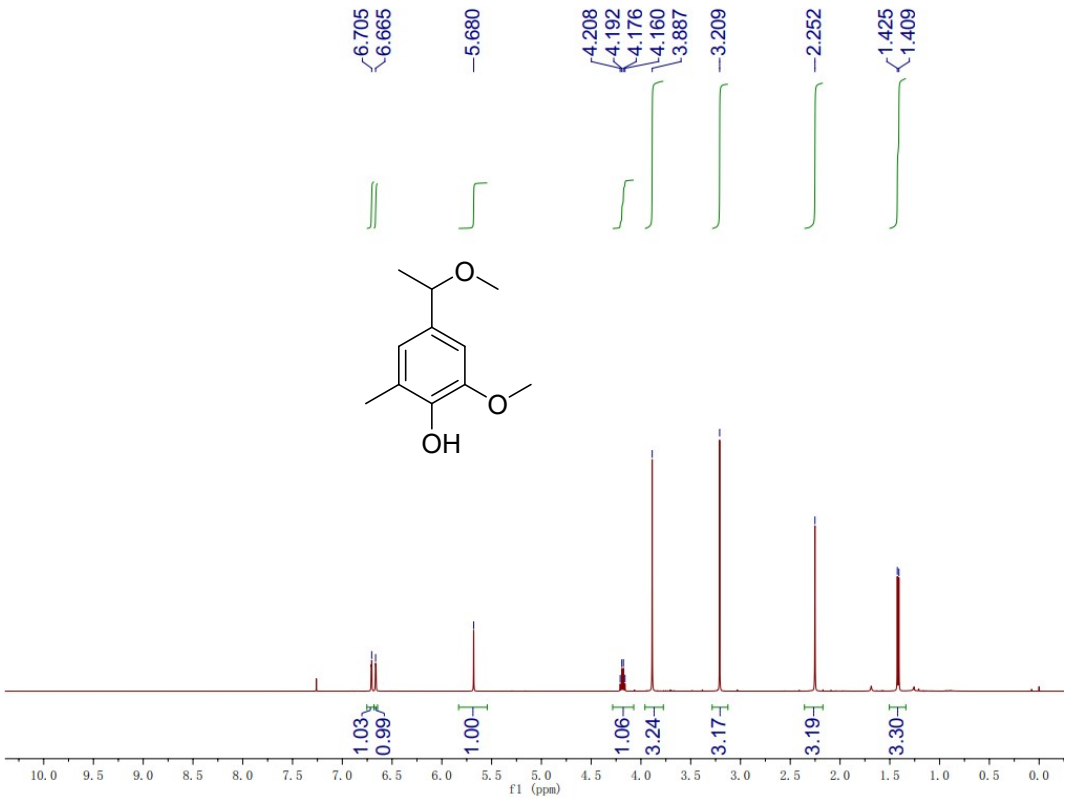
2,6-Dibutoxy-4-(1-methoxyethyl)phenol (2q) [^{1}H_NMR_600 MHz_($CDCl_3$: 7.26 ppm)]



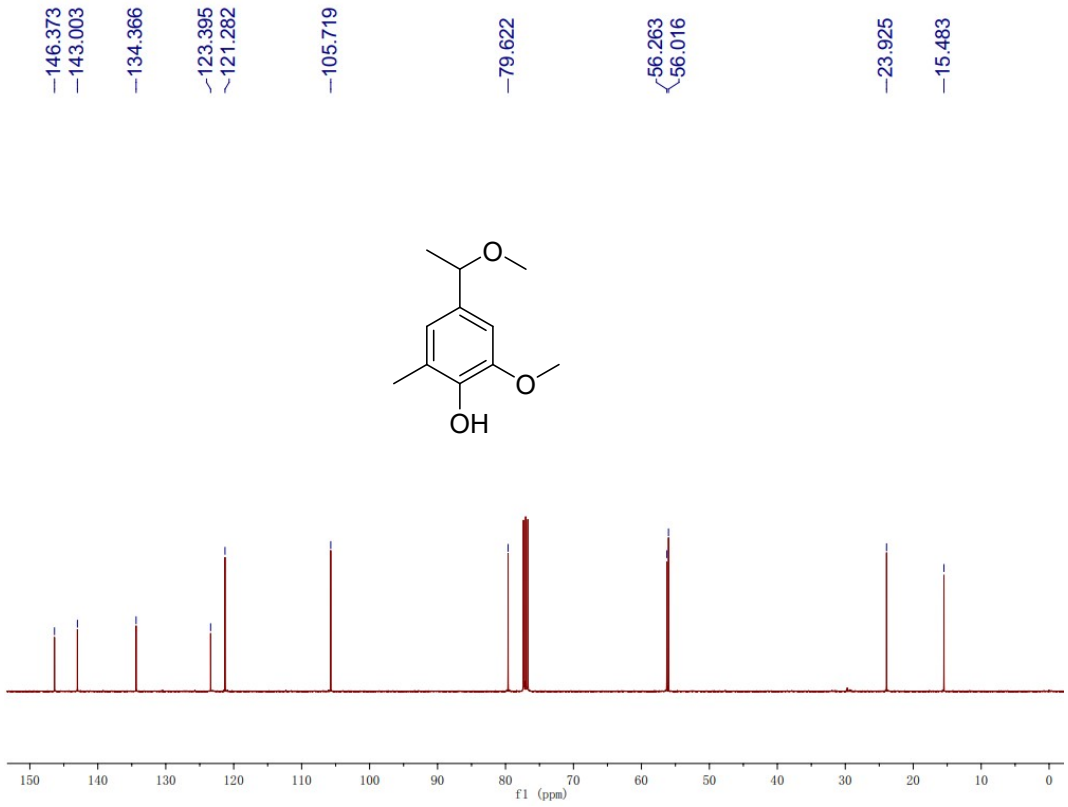
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



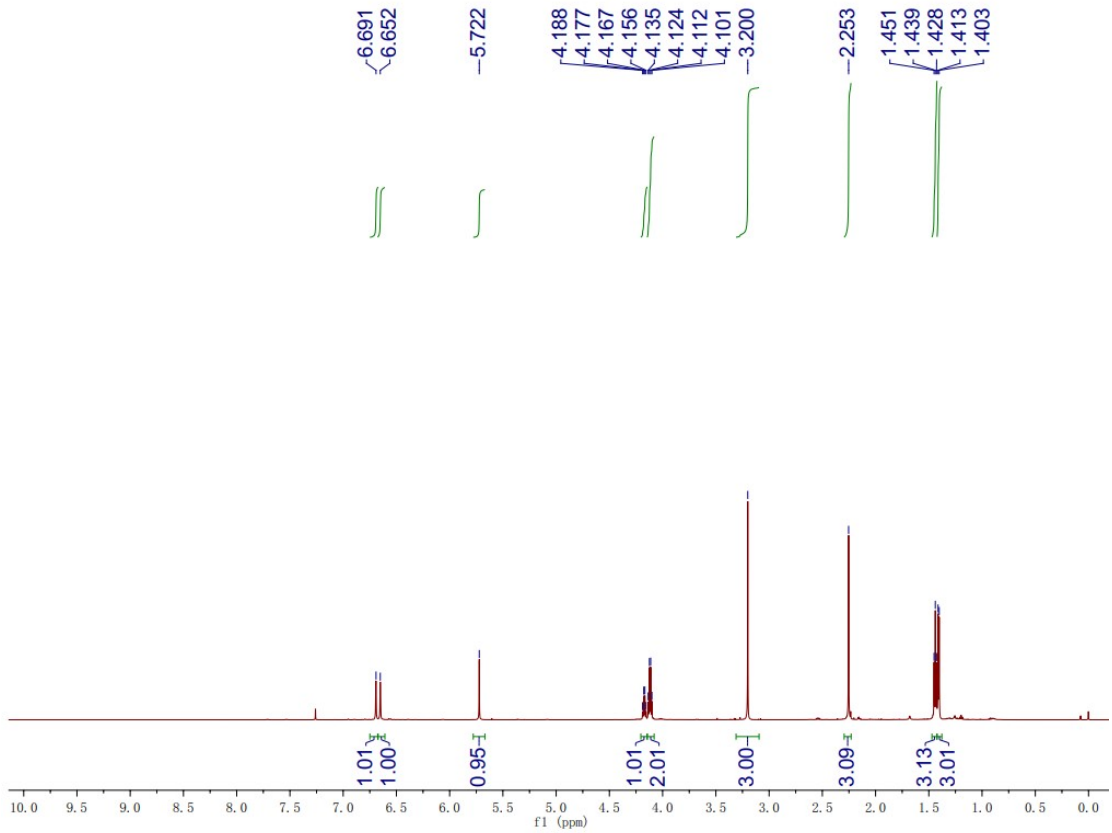
2-Methoxy-4-(1-methoxyethyl)-6-methylphenol (2r) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



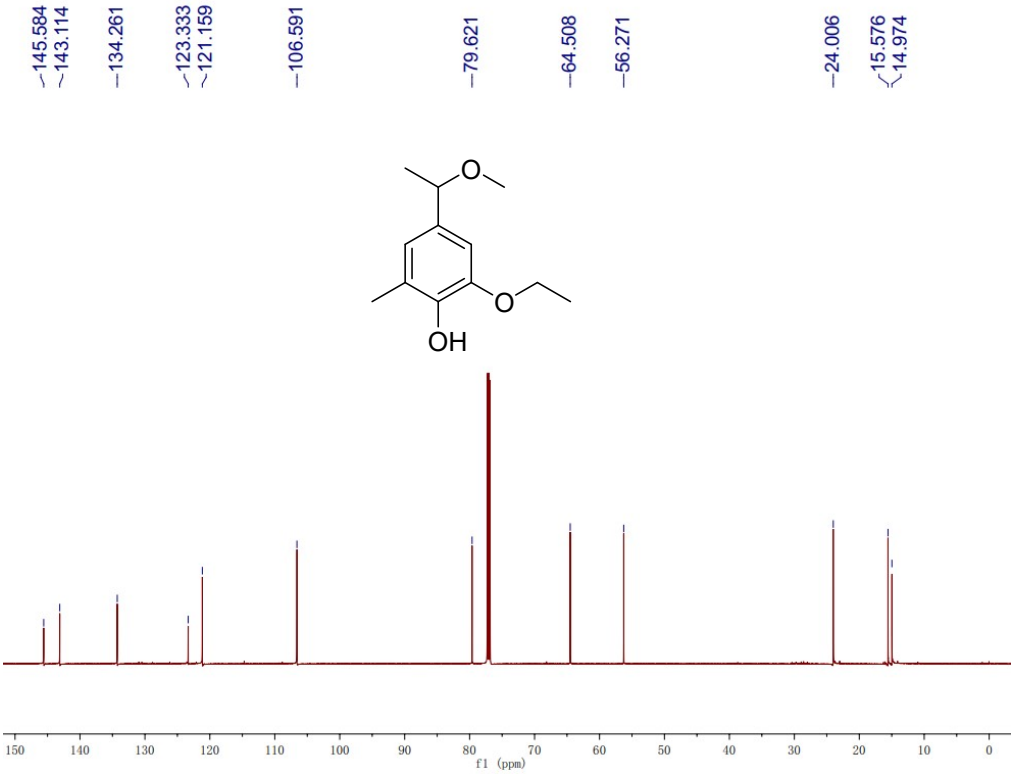
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



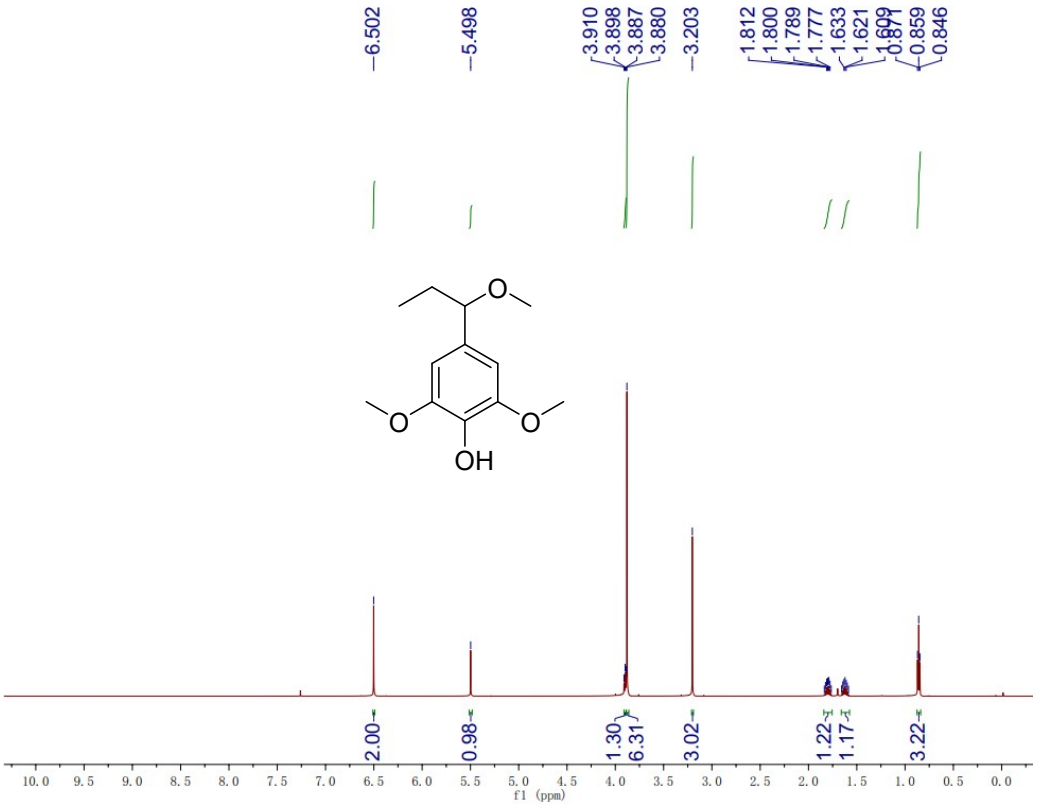
2-Ethoxy-4-(1-methoxyethyl)-6-methylphenol (2s) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



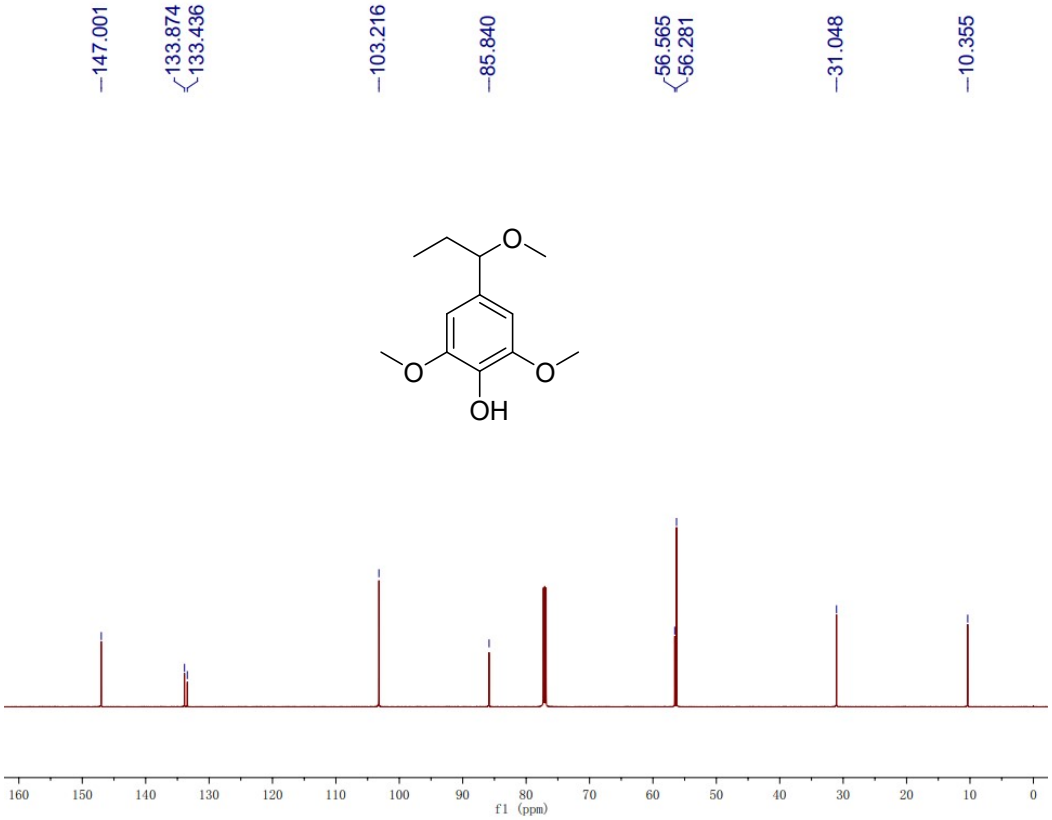
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



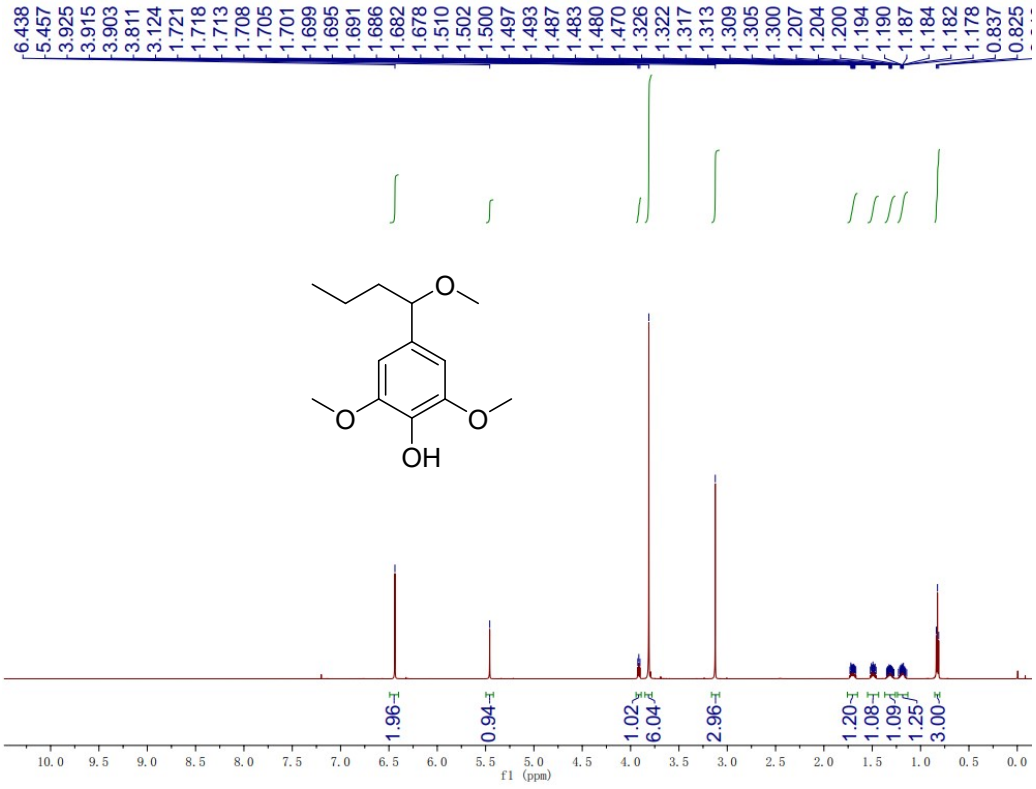
2,6-Dimethoxy-4-(1-methoxypropyl)phenol (2t) [^{1}H_NMR_600 MHz_($CDCl_3$: 7.26 ppm)]



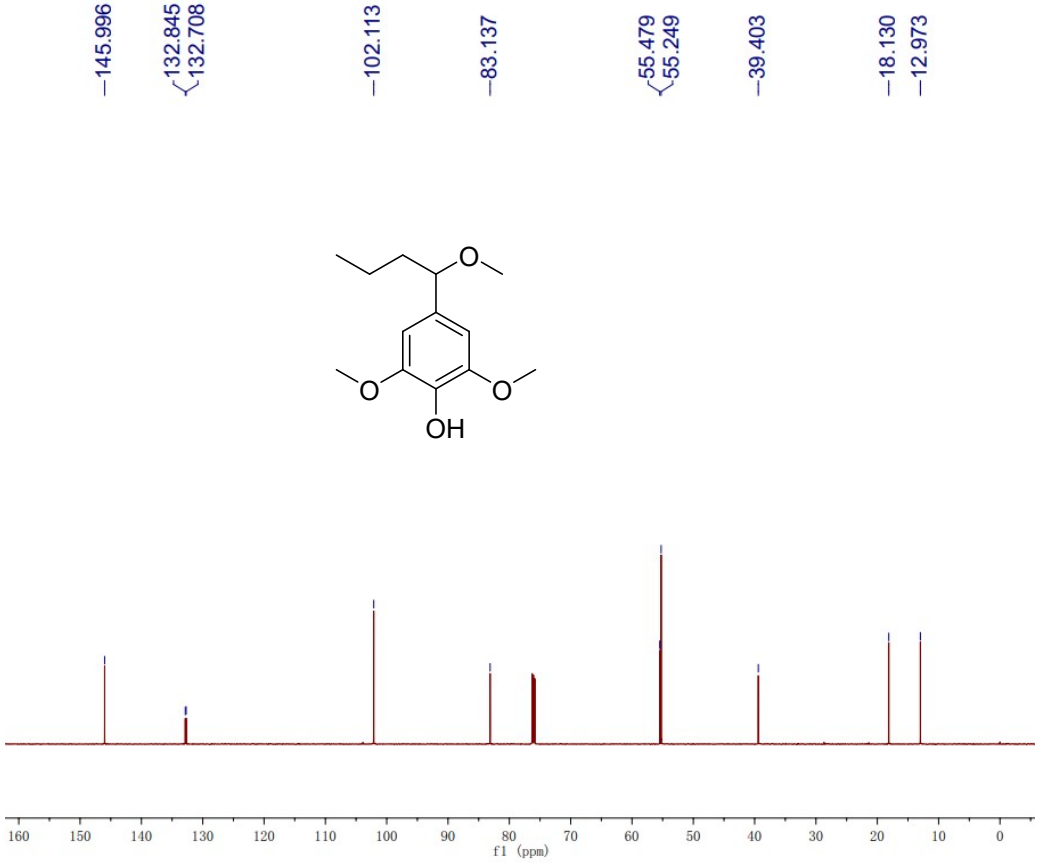
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



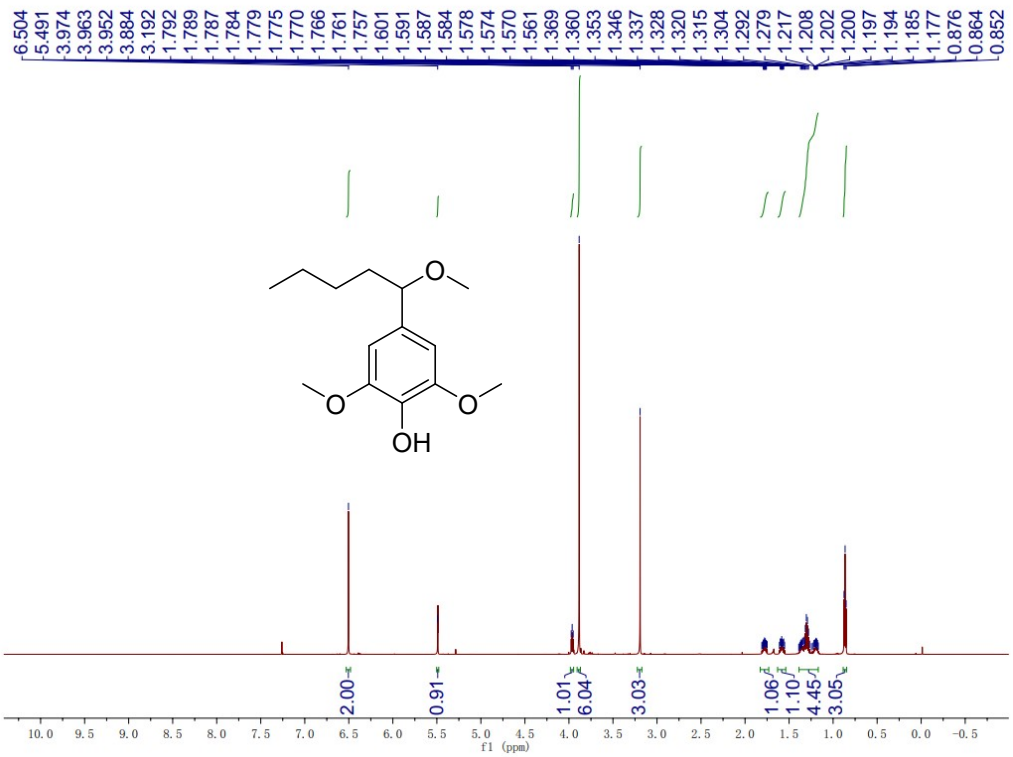
2,6-Dimethoxy-4-(1-methoxybutyl)phenol (2u) [^{1}H_NMR_600 MHz_($CDCl_3$: 7.26 ppm)]



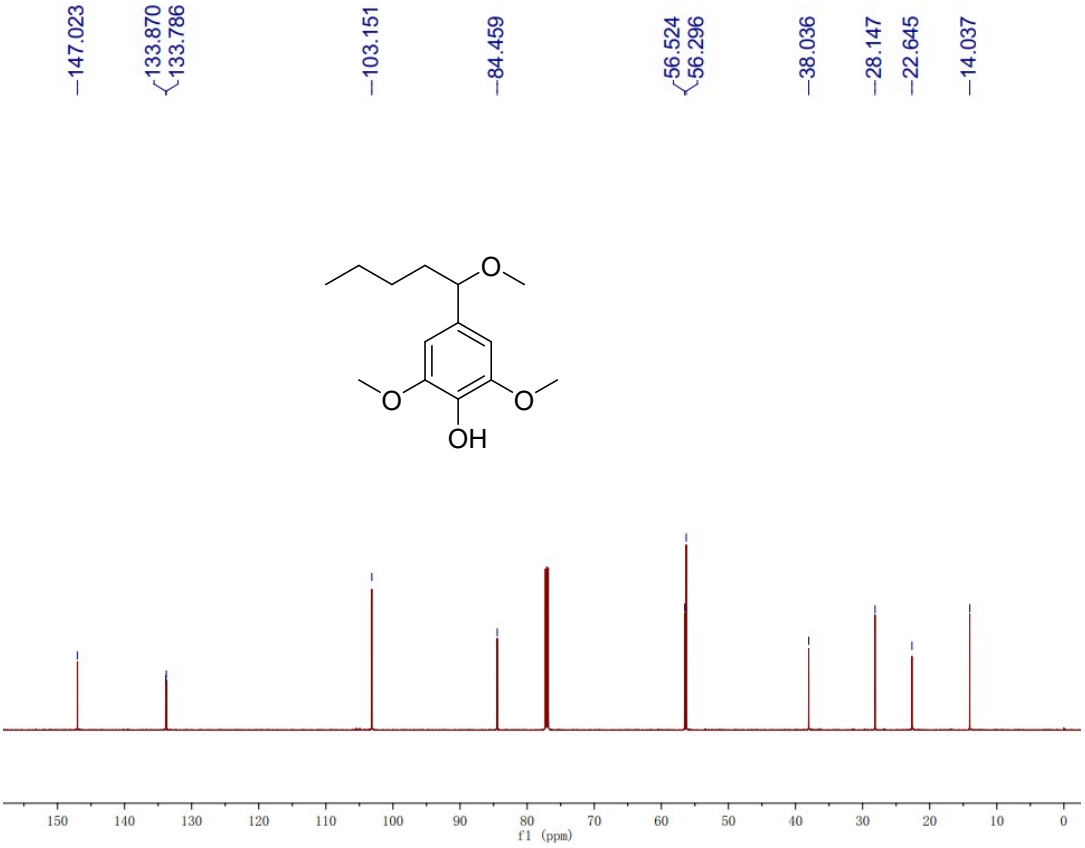
[^{13}C_NMR_150 MHz_(CDCl$_3$: 77.00 ppm)]



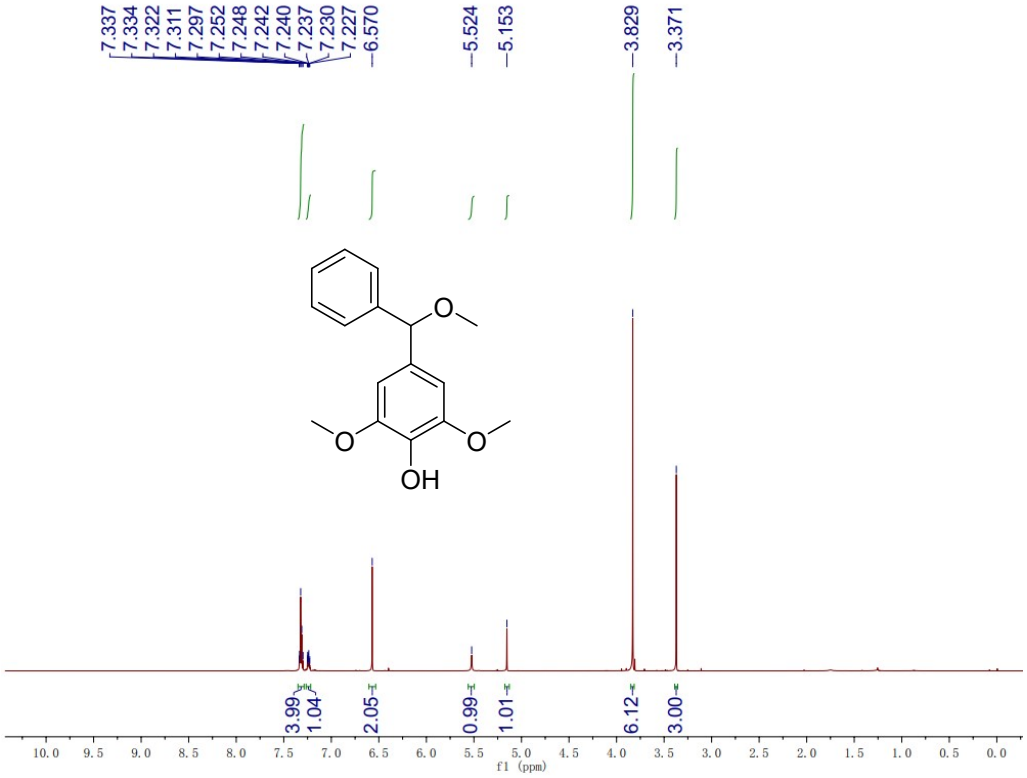
2,6-Dimethoxy-4-(1-methoxypentyl)phenol (2v) [^{1}H_NMR_600 MHz_(CDCl$_3$: 7.26 ppm)]



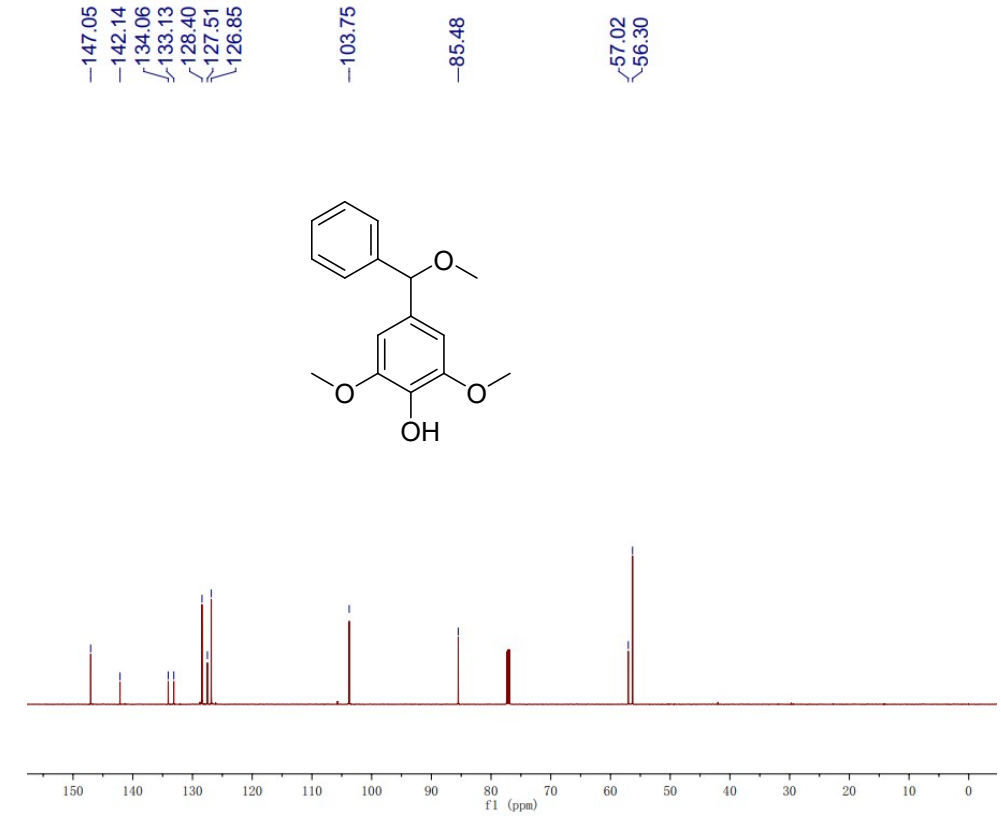
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



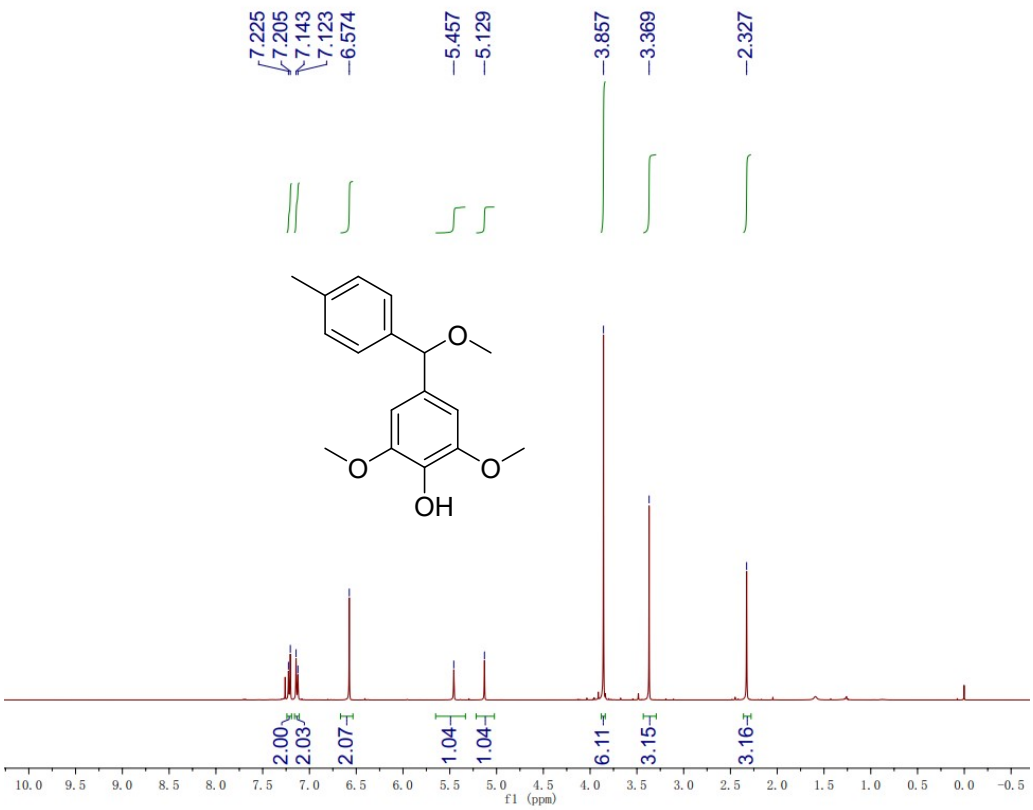
2,6-Dimethoxy-4-(methoxy(phenyl)methyl)phenol (2w) [^{1}H_NMR_600 MHz_($CDCl_3$: 7.26 ppm)]



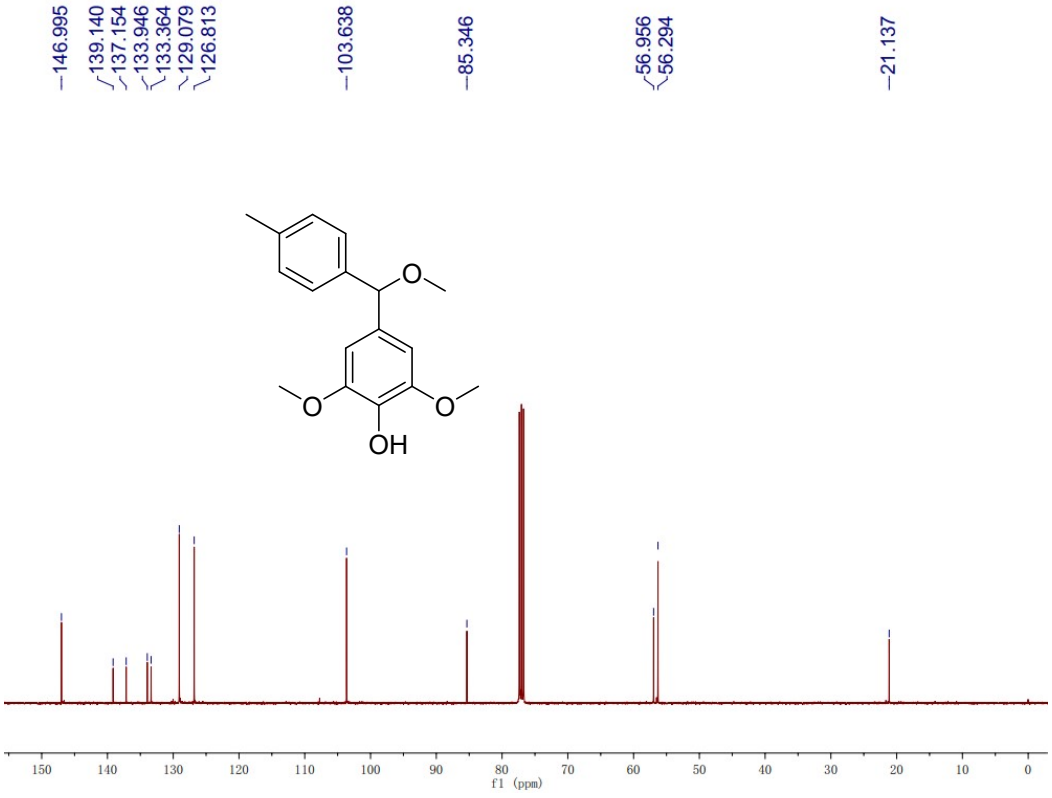
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



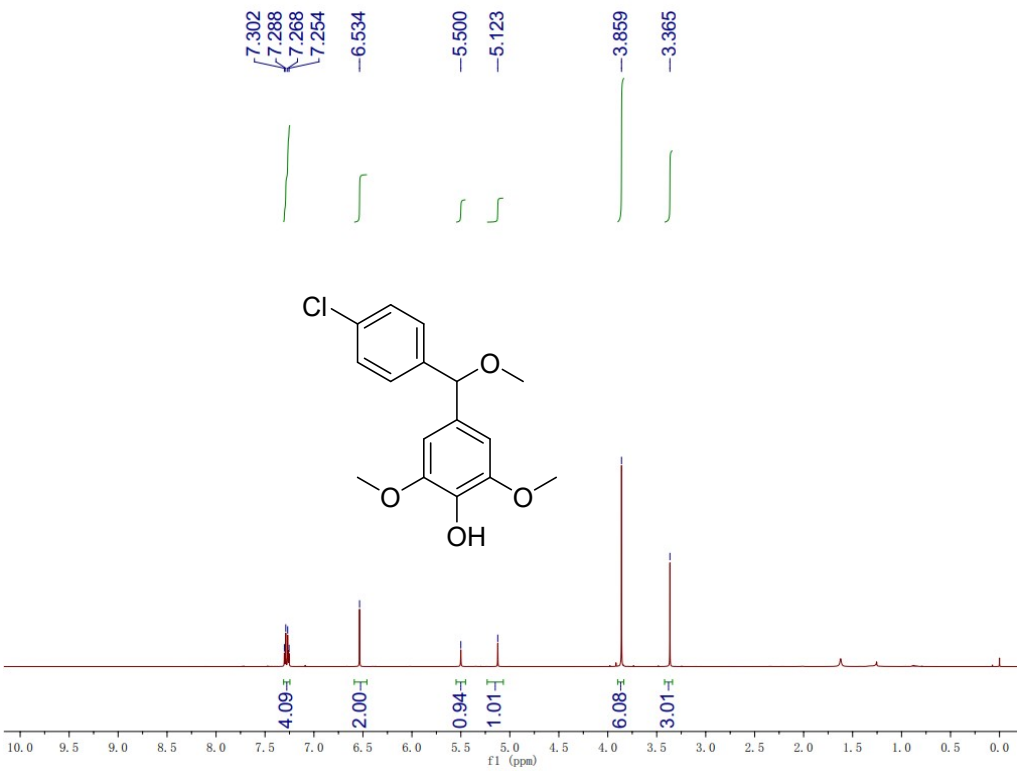
2,6-Dimethoxy-4-(methoxy(p-tolyl)methyl)phenol (2x) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



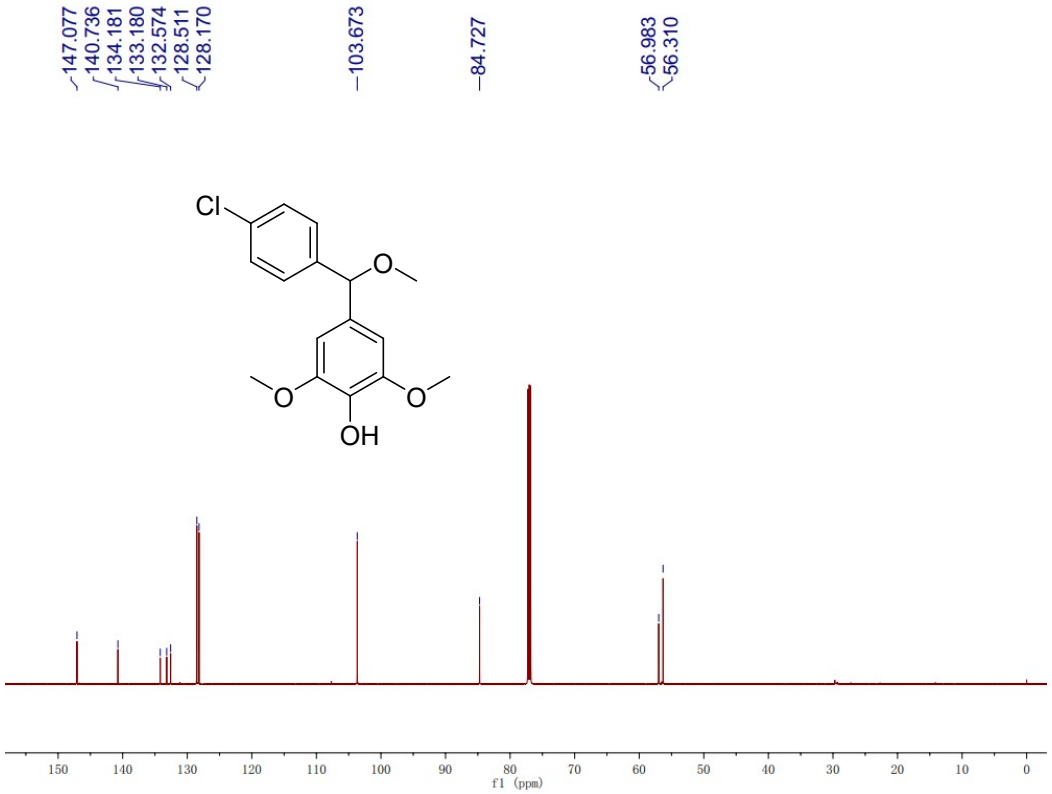
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



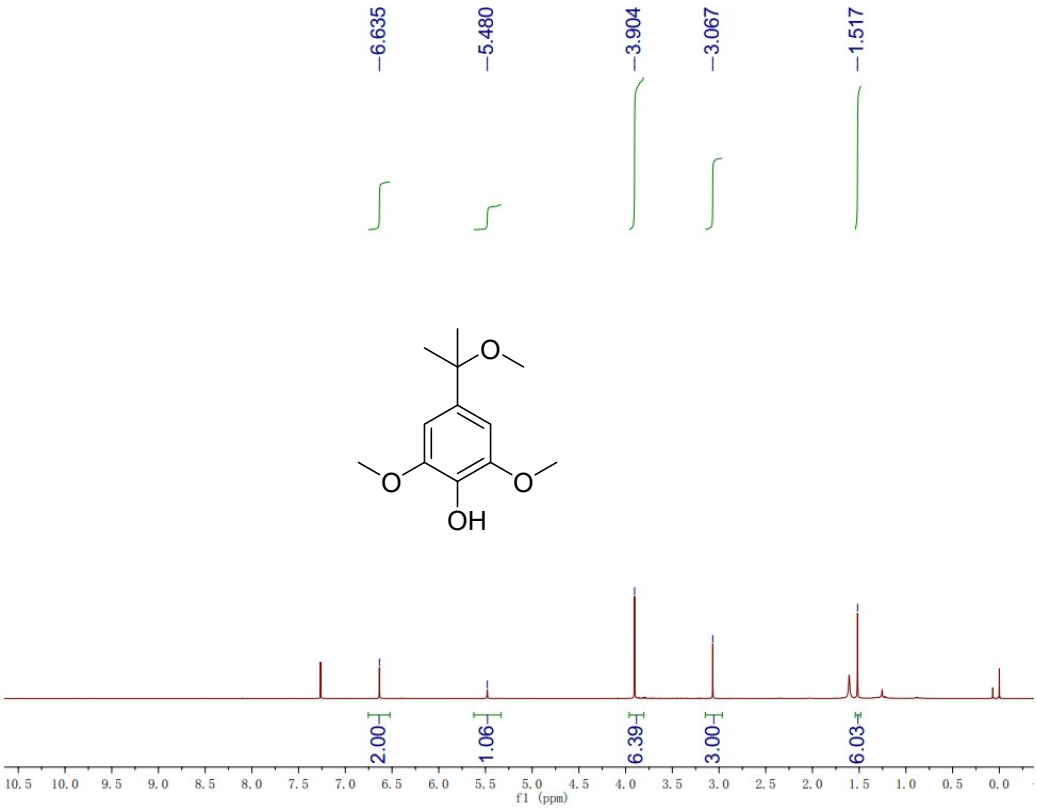
4-((4-Chlorophenyl)(methoxy)methyl)-2,6-dimethoxyphenol (2y) [^{1}H_NMR_600 MHz_($CDCl_3$: 7.26 ppm)]



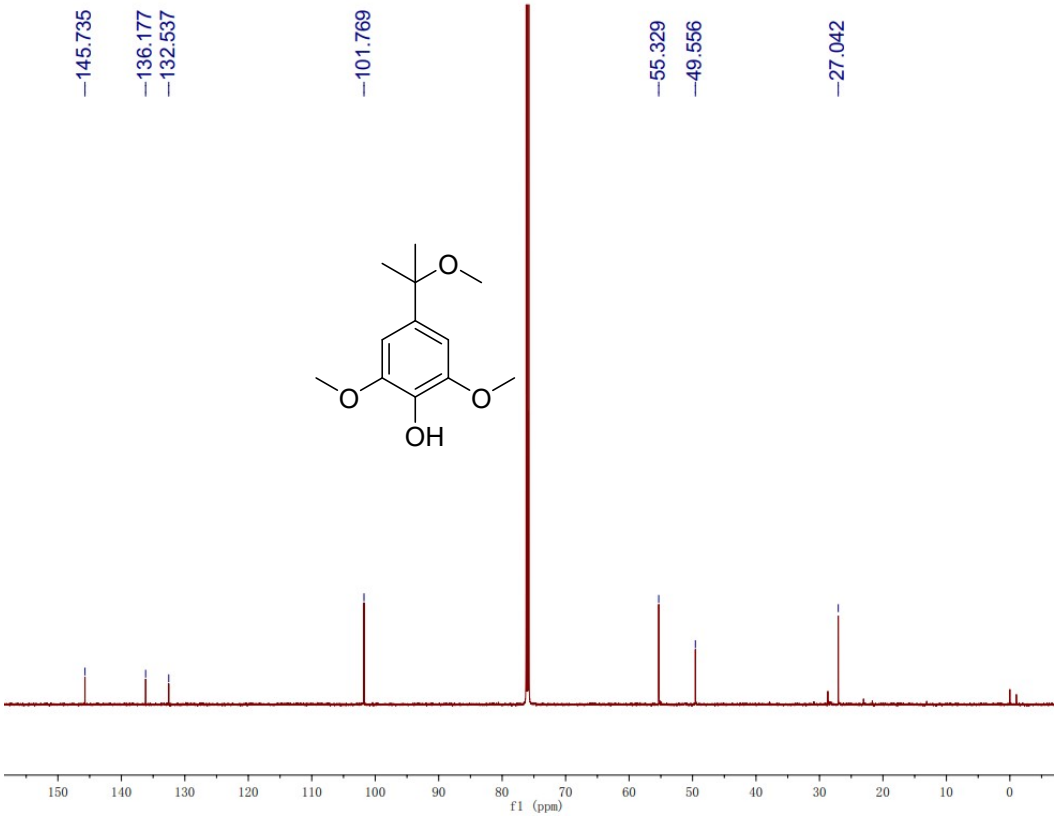
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



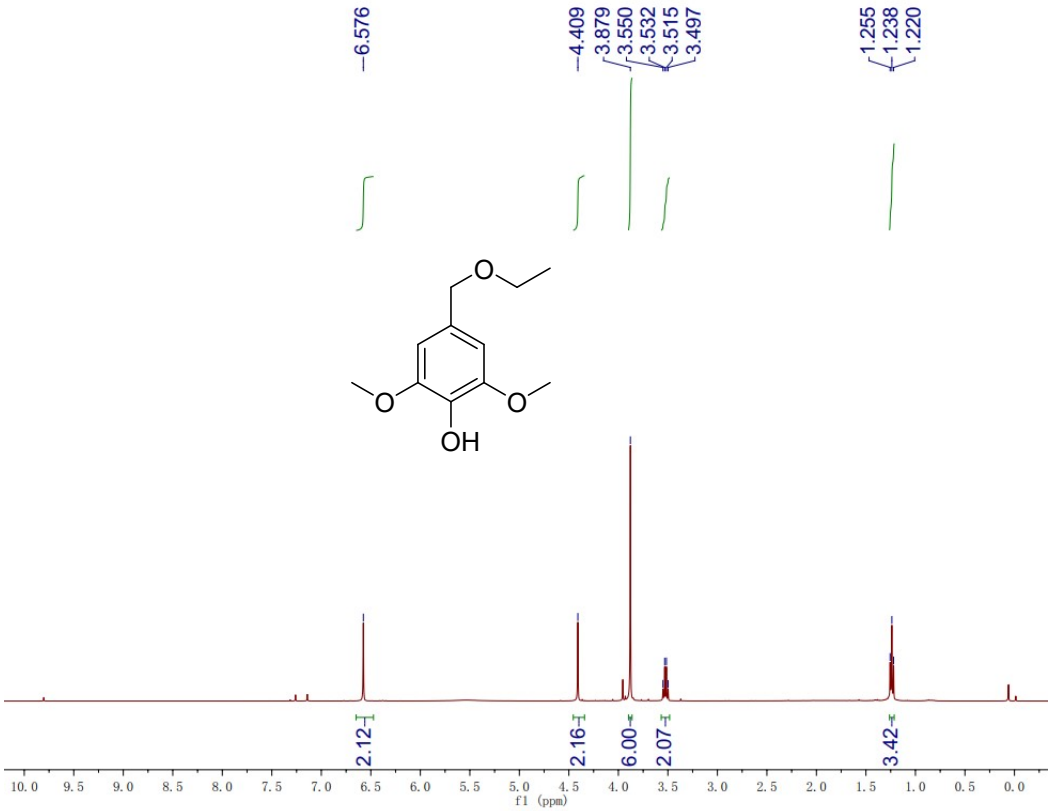
2,6-Dimethoxy-4-(2-methoxypropan-2-yl)phenol (2z) [^{1}H_NMR_600 MHz_($CDCl_3$: 7.26 ppm)]



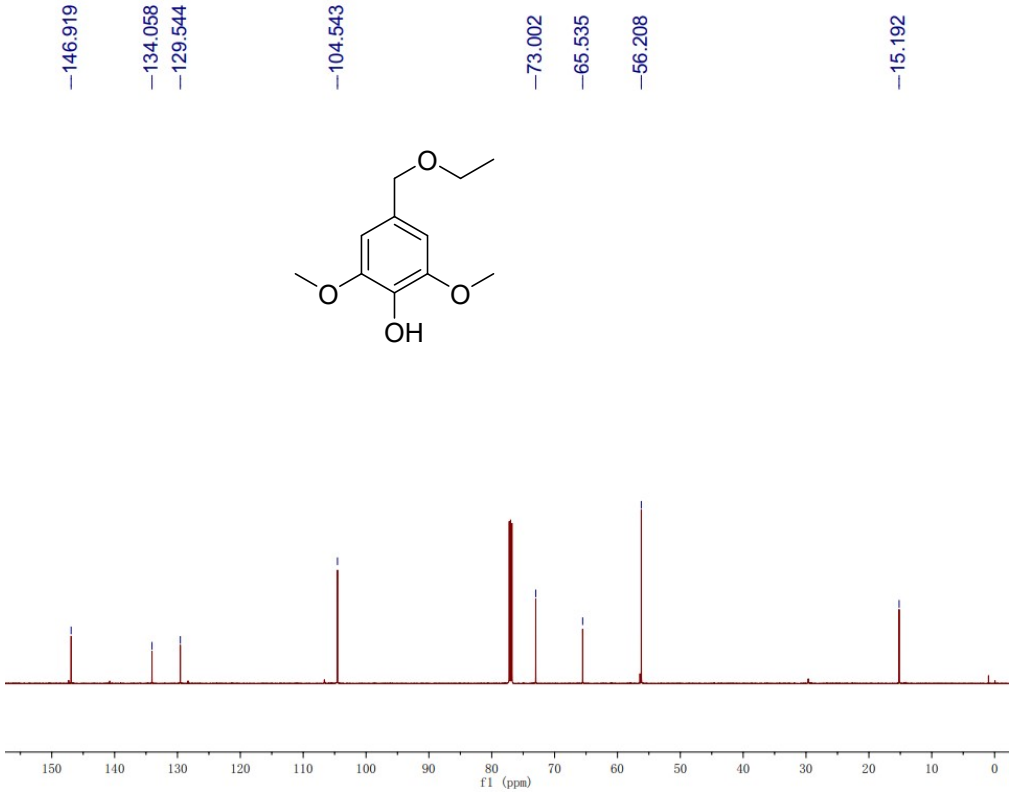
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



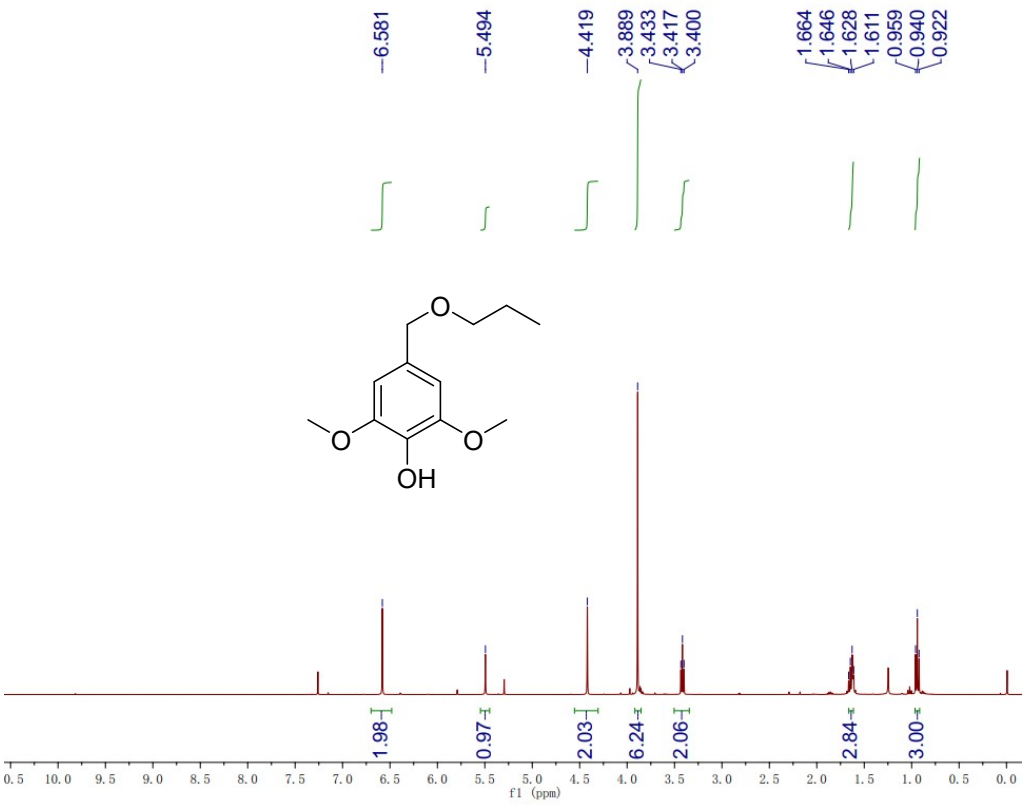
4-(Ethoxymethyl)-2,6-dimethoxyphenol (3a) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



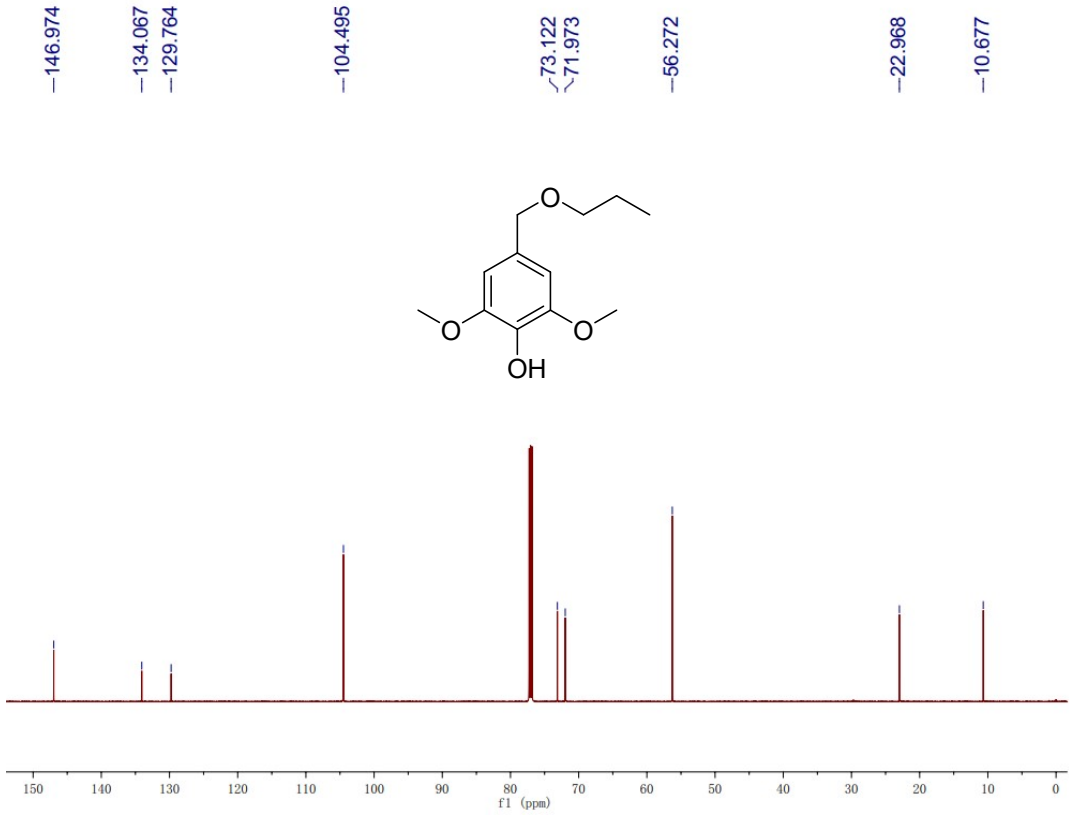
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



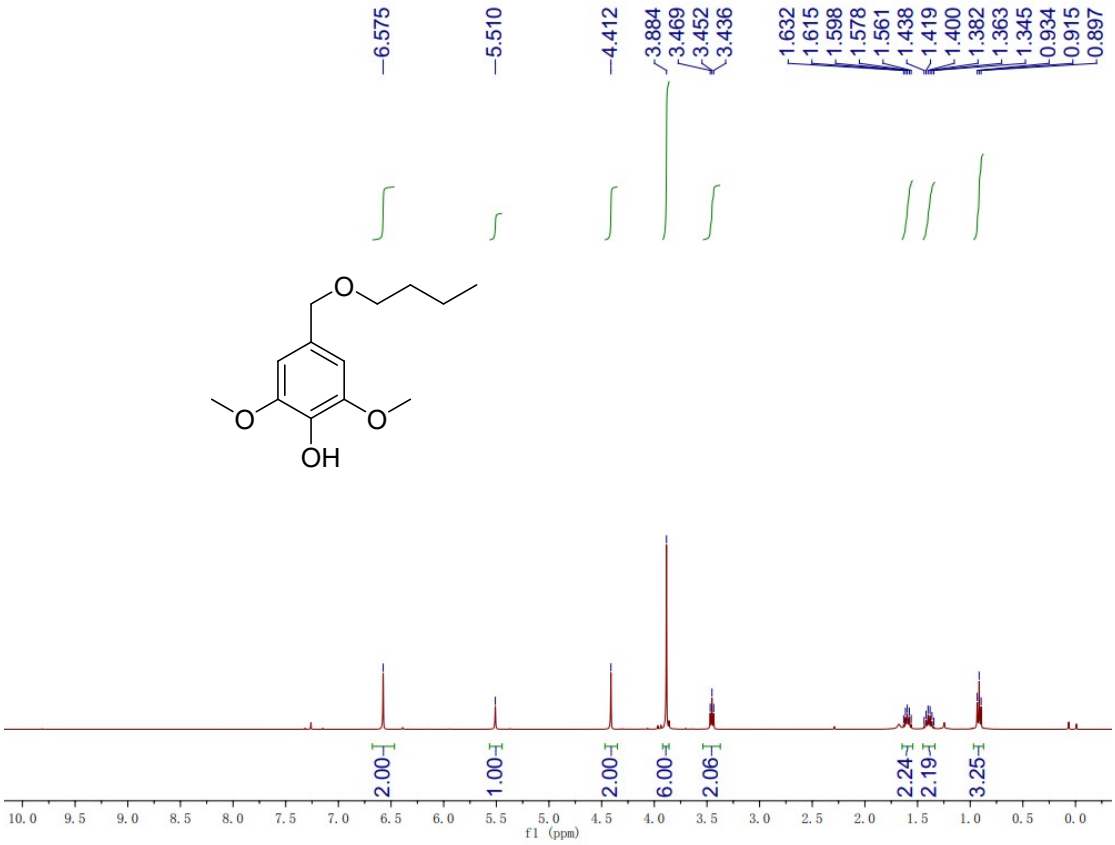
2,6-Dimethoxy-4-(propoxymethyl)phenol (3b) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



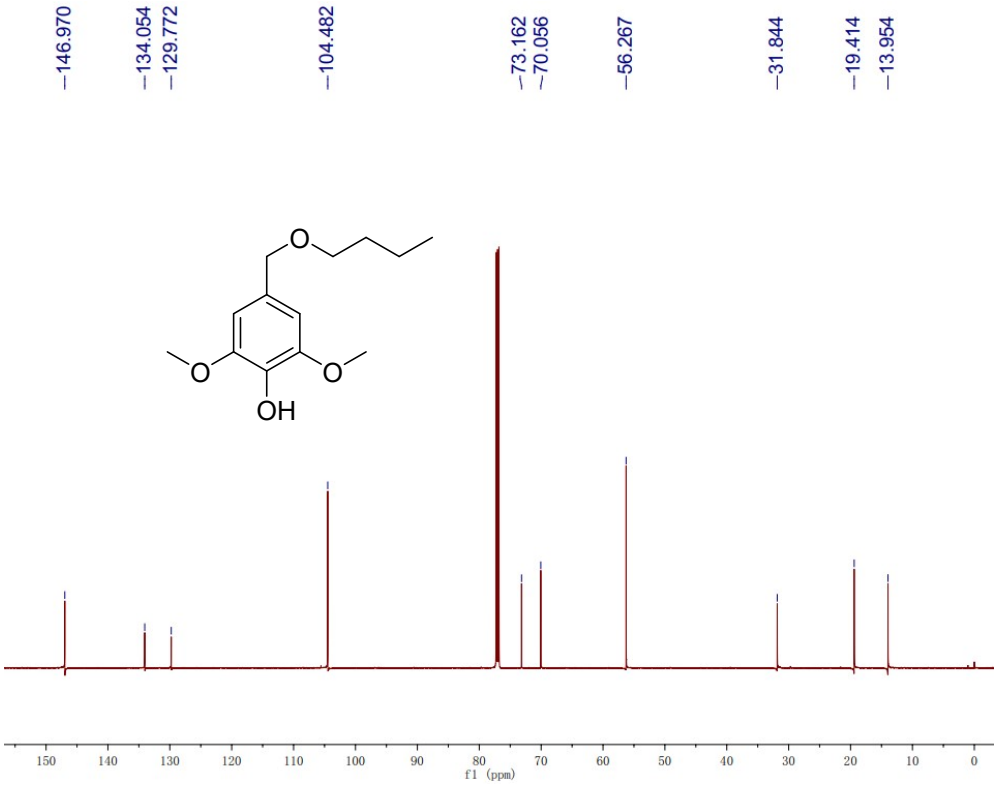
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



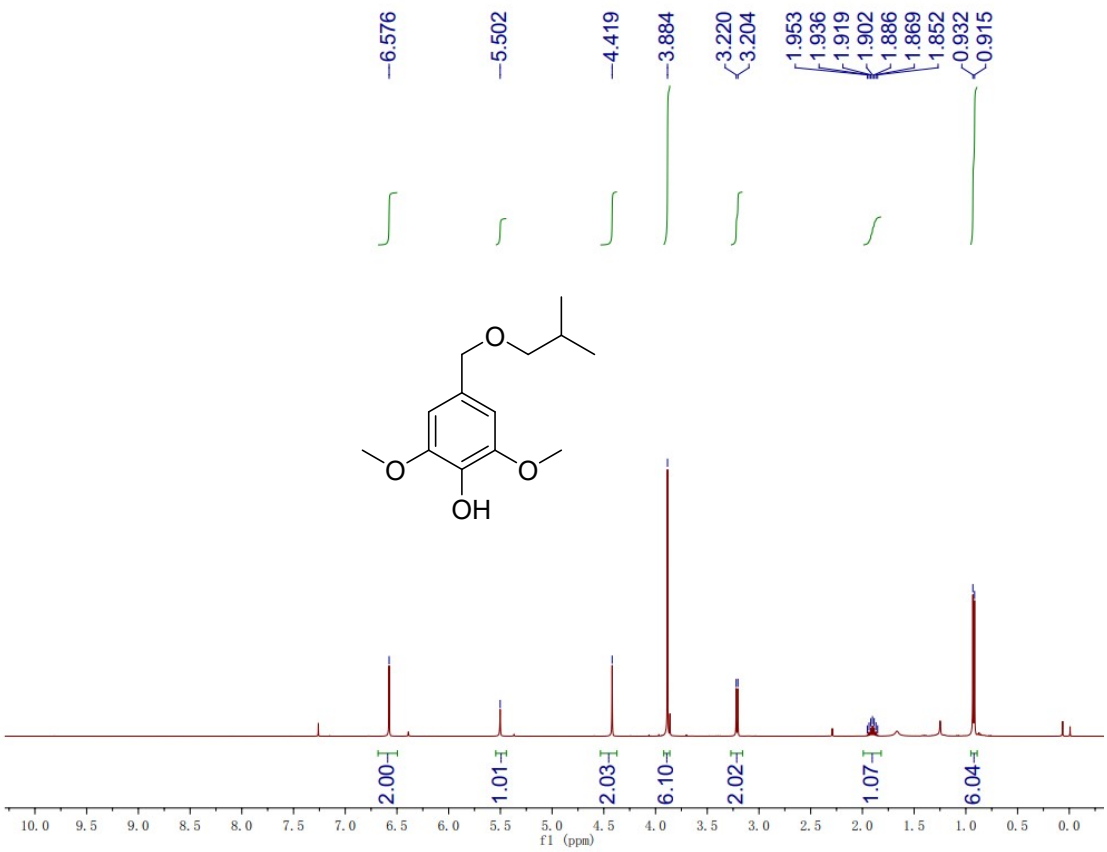
4-(Butoxymethyl)-2,6-dimethoxyphenol (3c) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



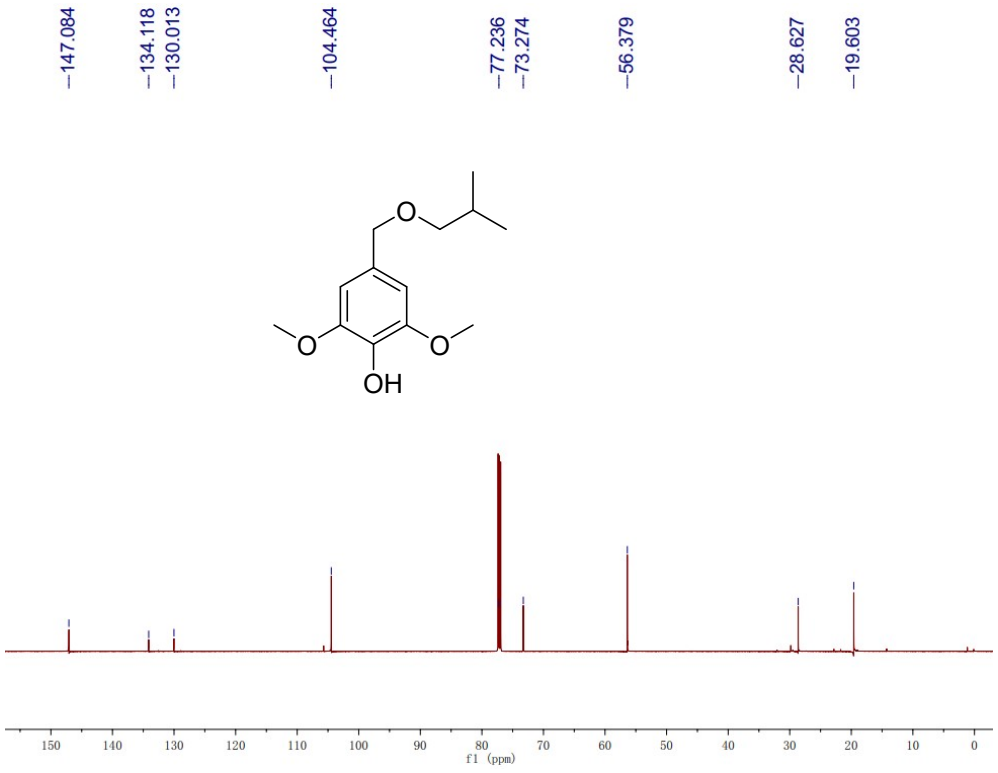
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



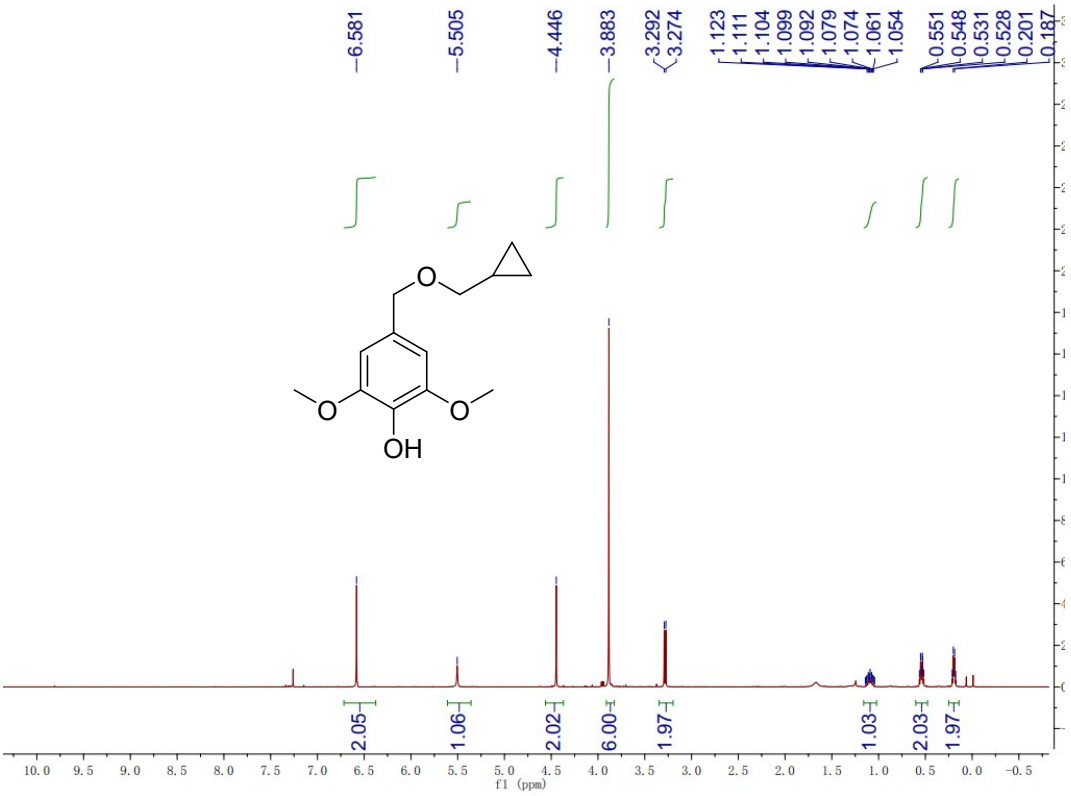
4-(Isobutoxymethyl)-2,6-dimethoxyphenol (3d) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



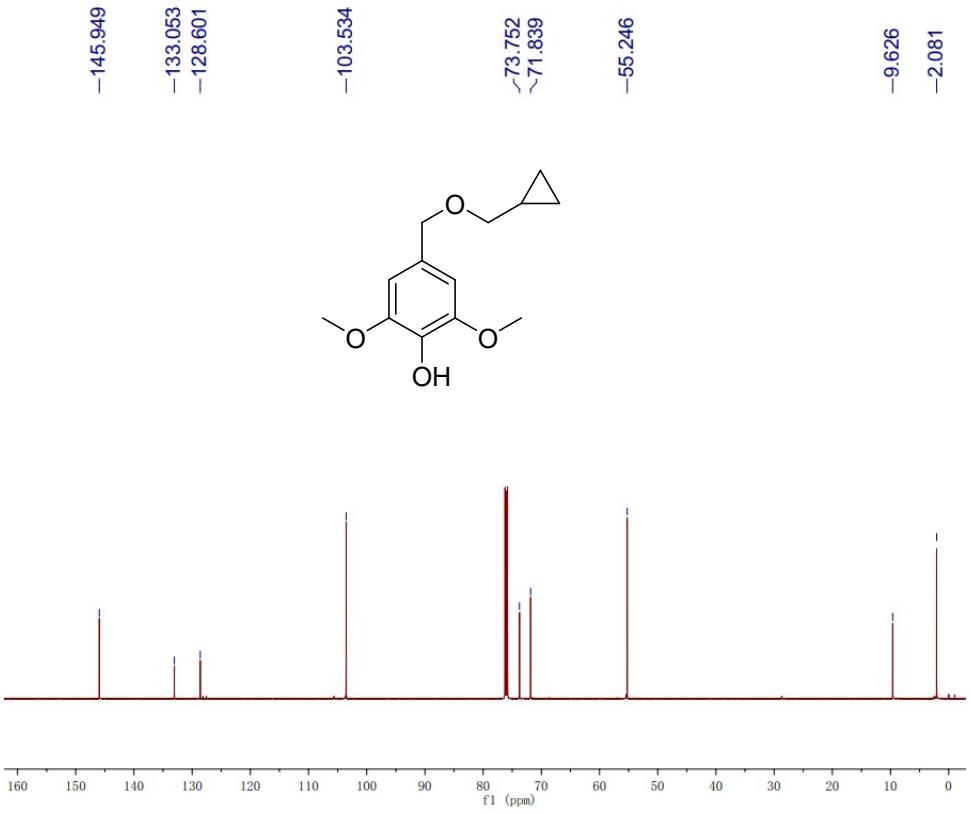
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



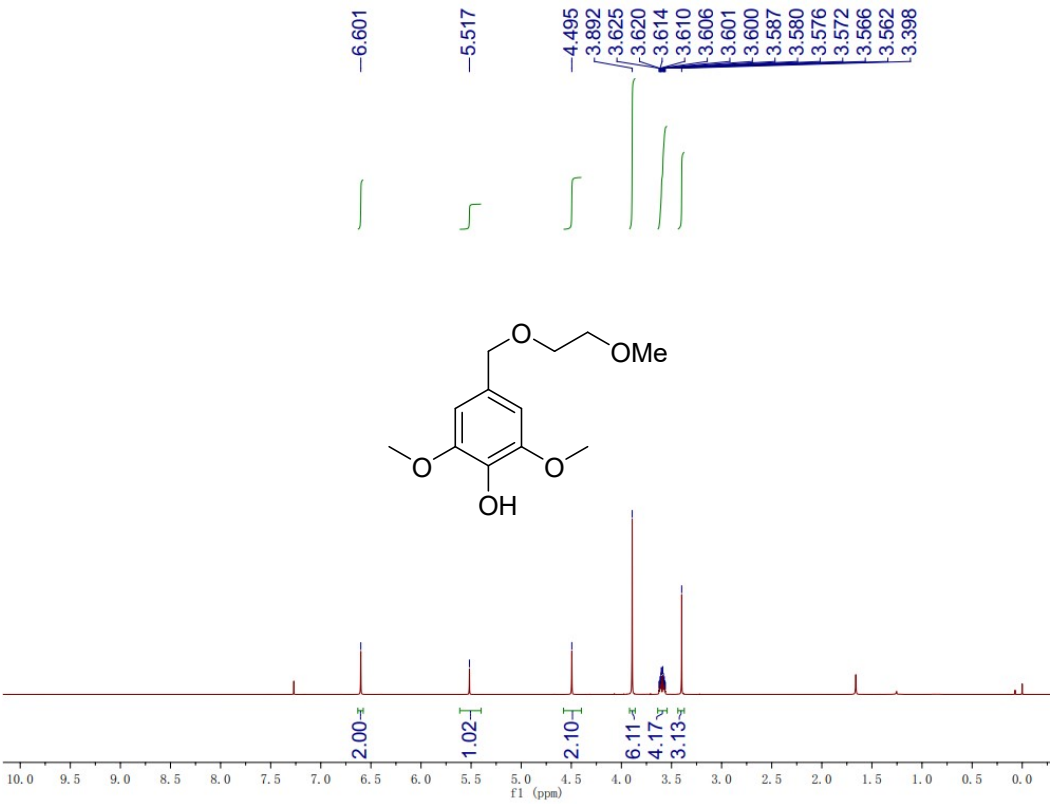
4-((Cyclopropylmethoxy)methyl)-2,6-dimethoxyphenol (3e) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



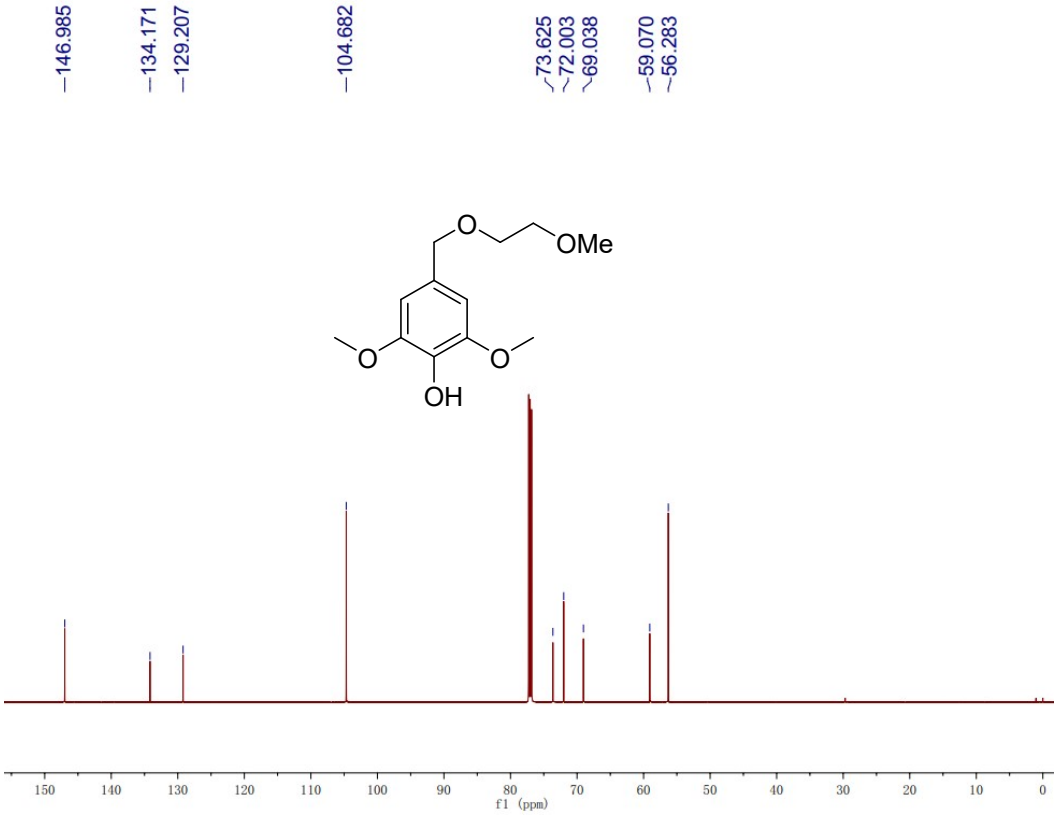
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



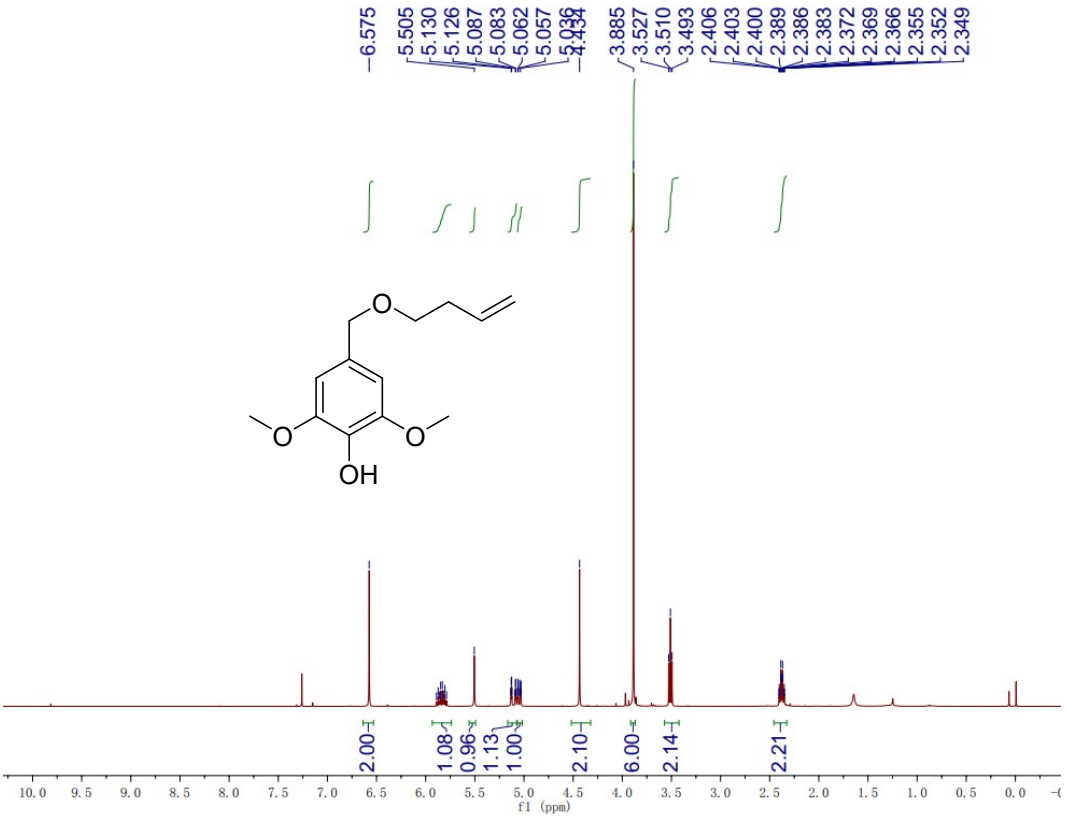
2,6-Dimethoxy-4-((2-methoxyethoxy)methyl)phenol (3f) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



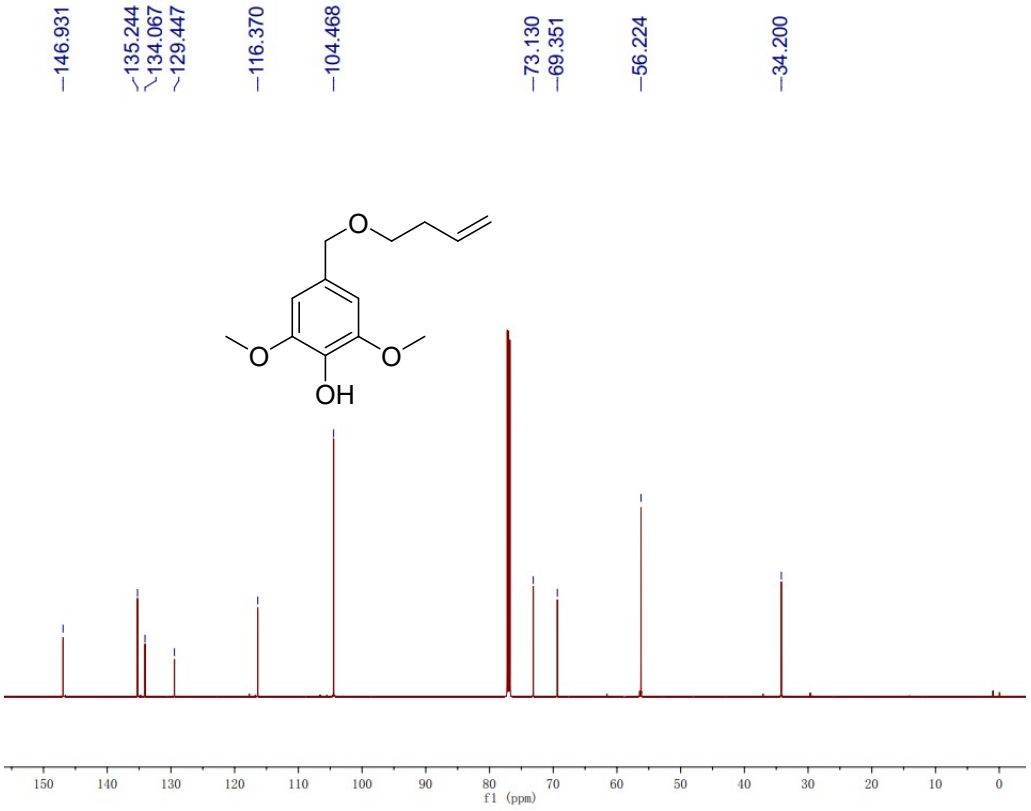
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



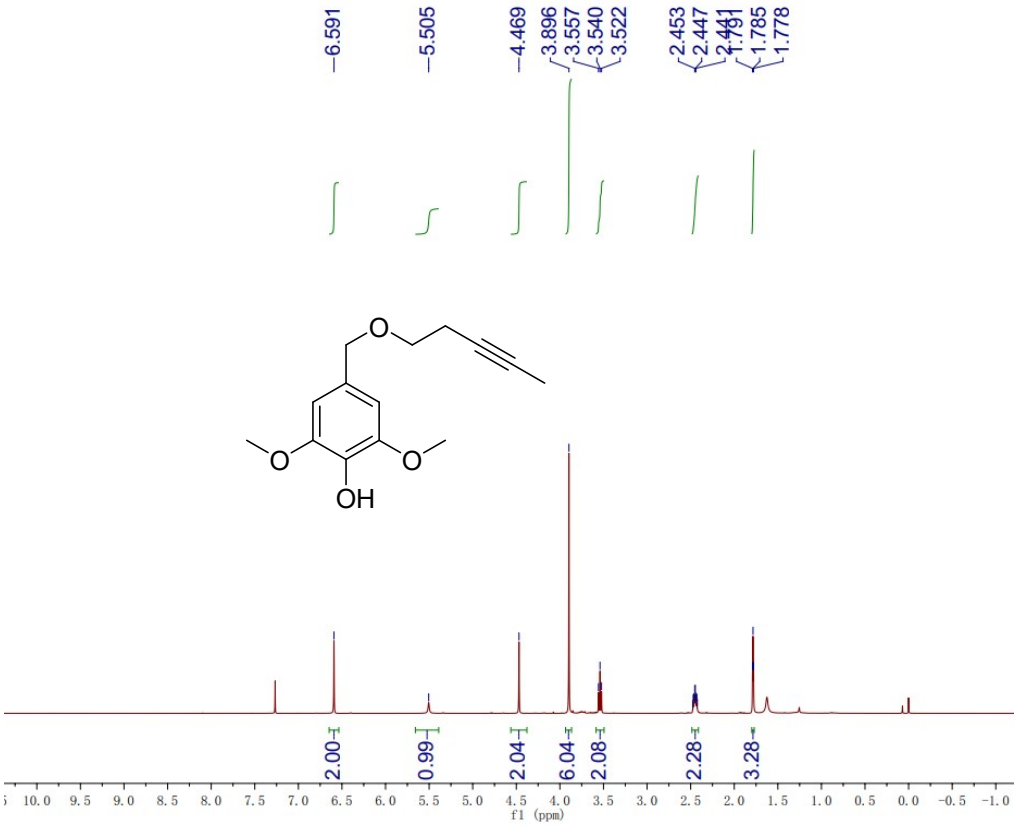
4-((But-3-en-1-yloxy)methyl)-2,6-dimethoxyphenol (3g) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



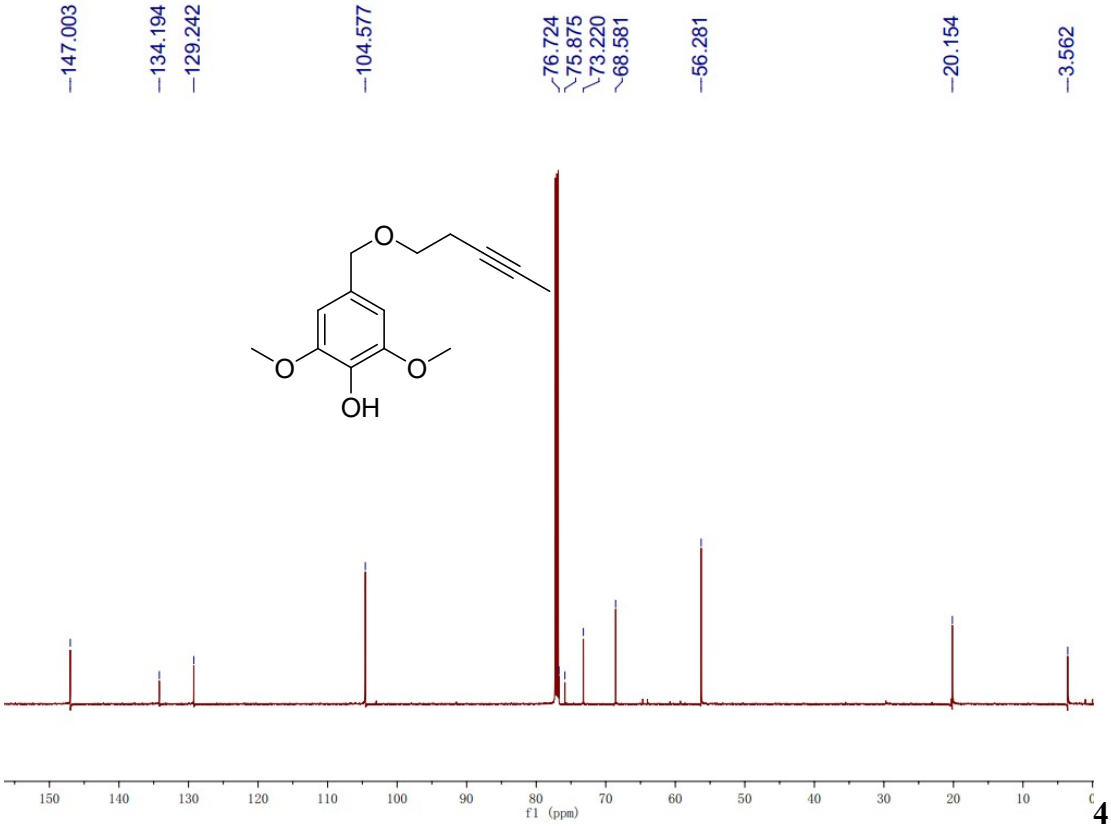
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



2,6-Dimethoxy-4-((pent-3-yn-1-yloxy)methyl)phenol (3h) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



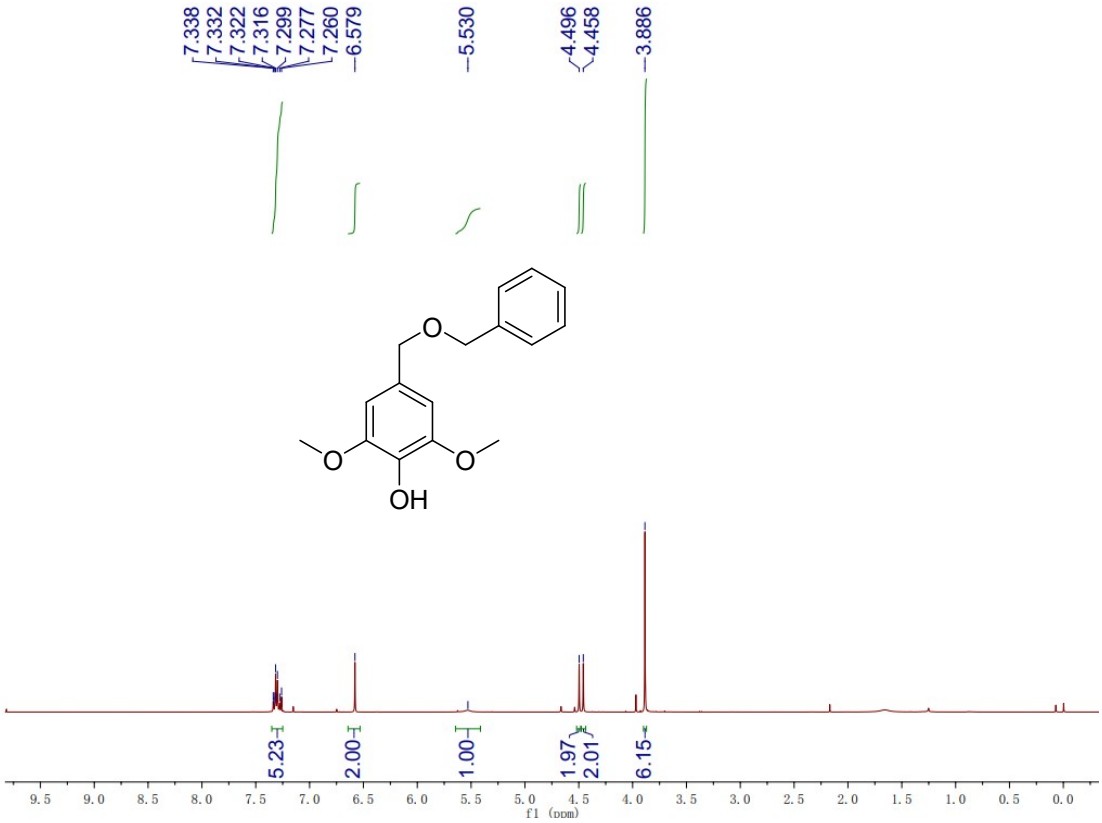
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



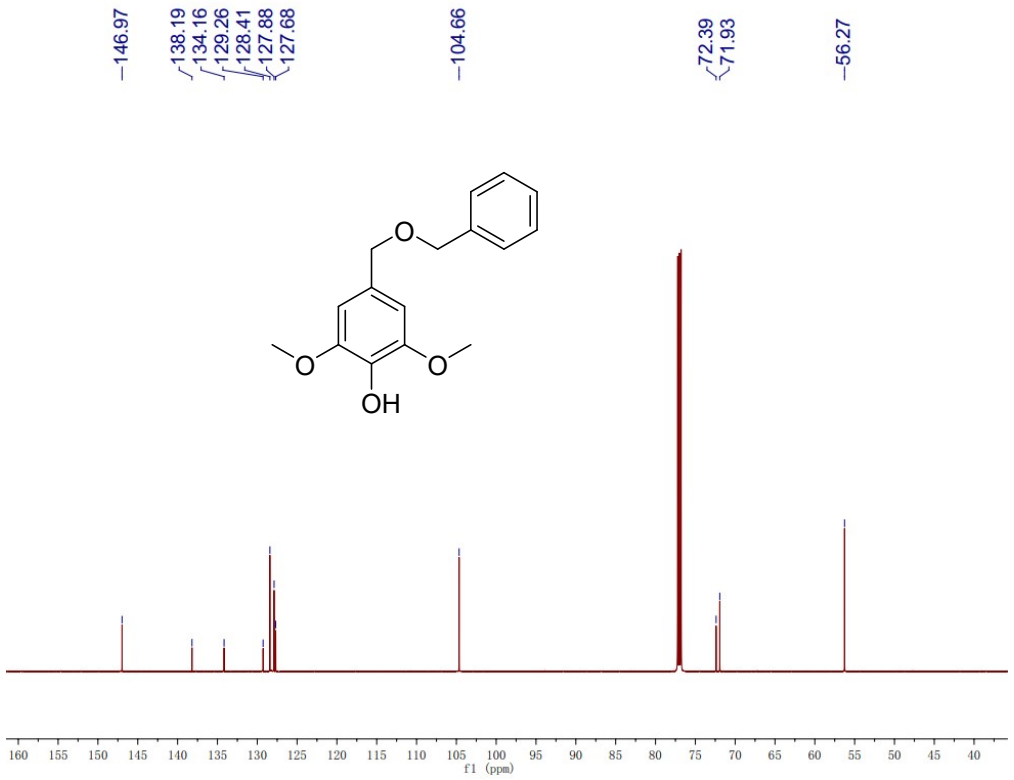
4

-((Benzyloxy)methyl)-2,6-dimethoxyphenol (3i) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26

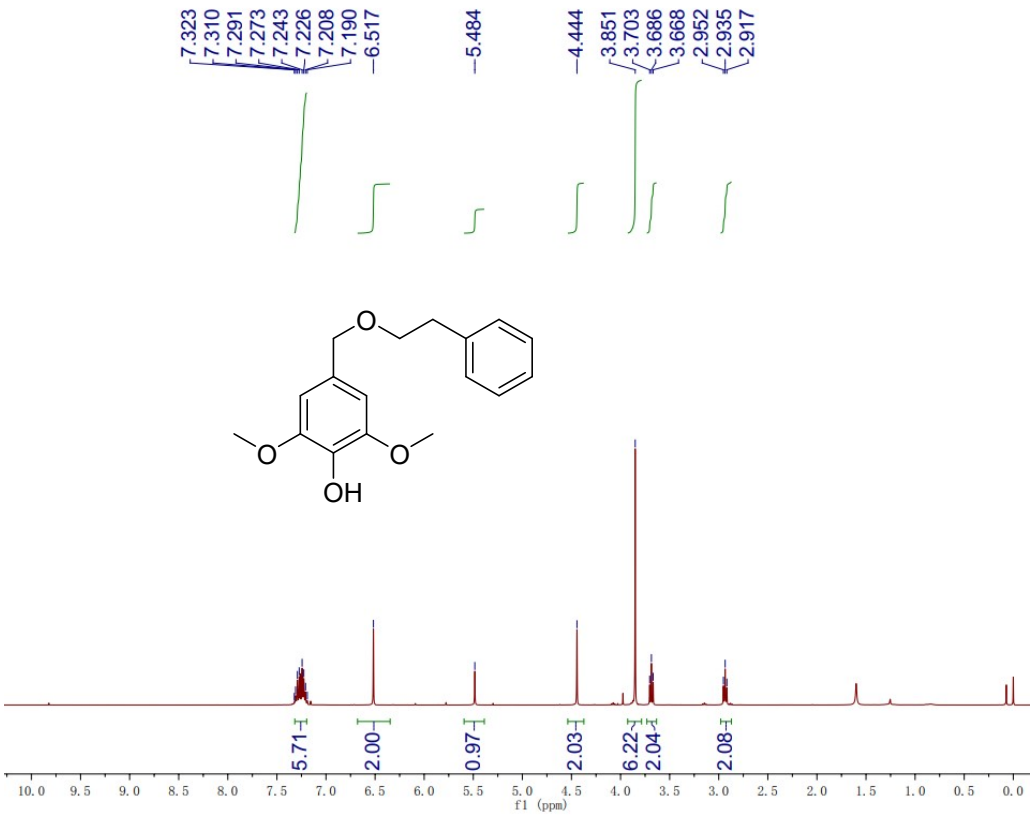
ppm)]



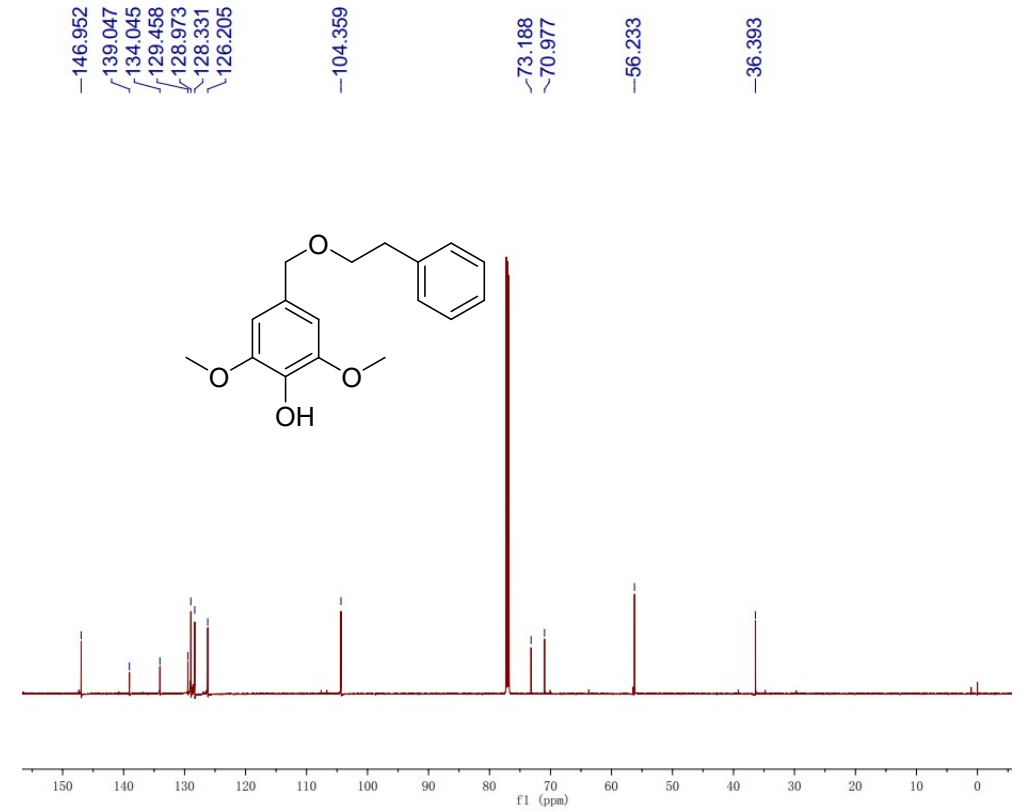
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



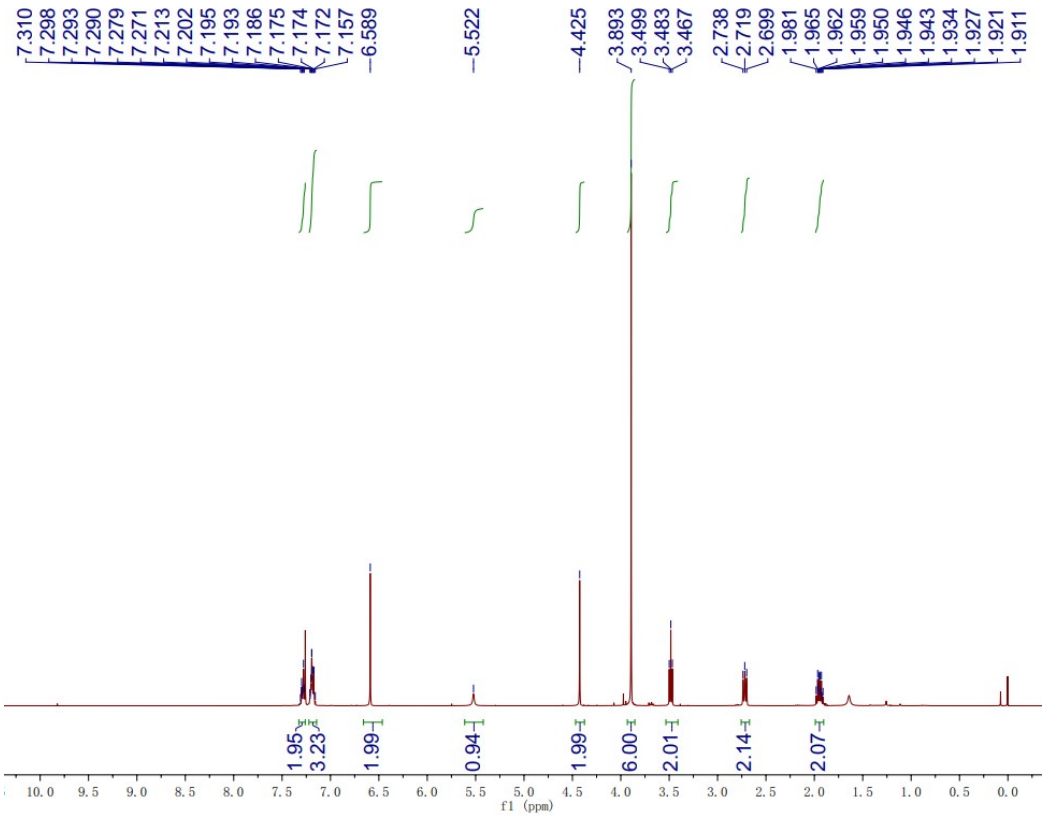
2,6-Dimethoxy-4-(phenethoxymethyl)phenol (3j) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



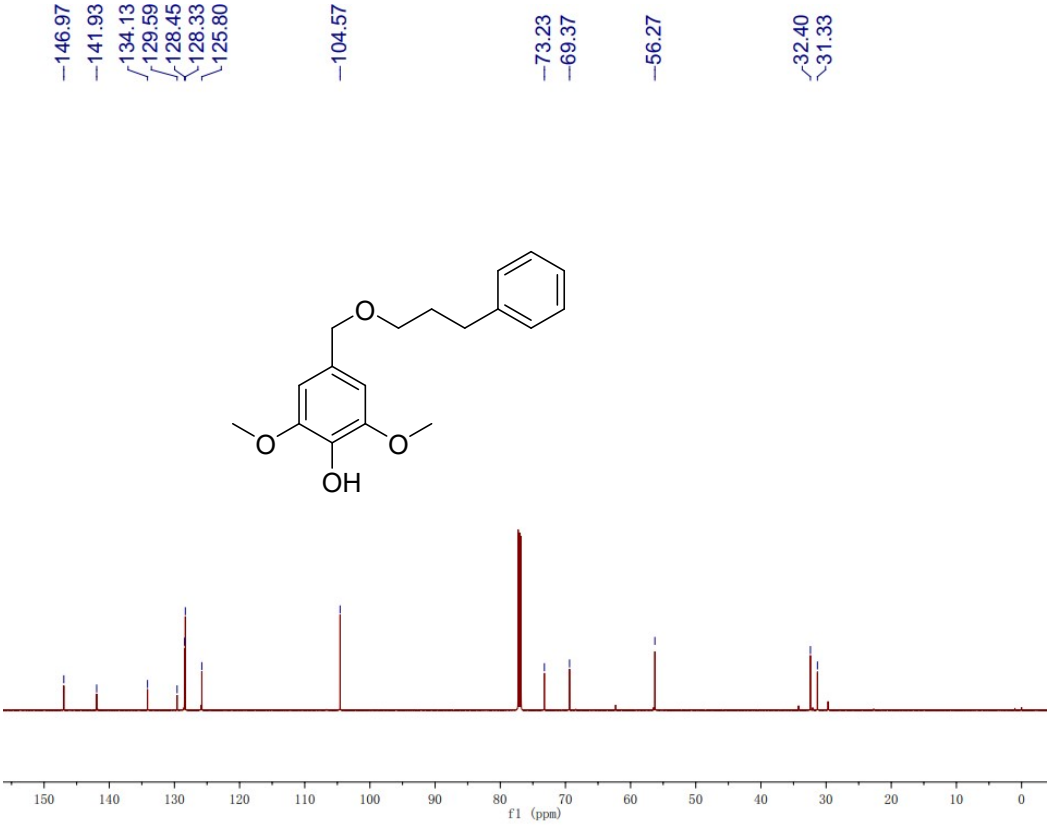
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



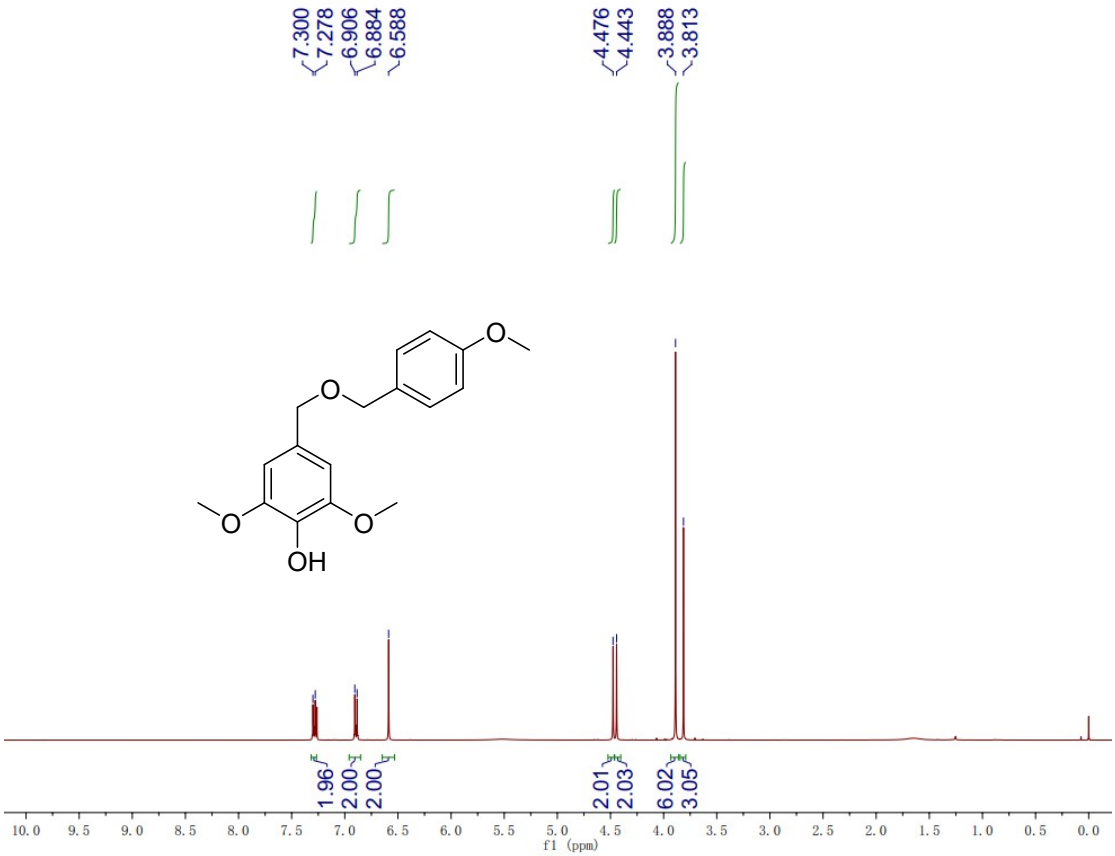
2,6-Dimethoxy-4-((3-(p-tolyl)propoxy)methyl)phenol (3k) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



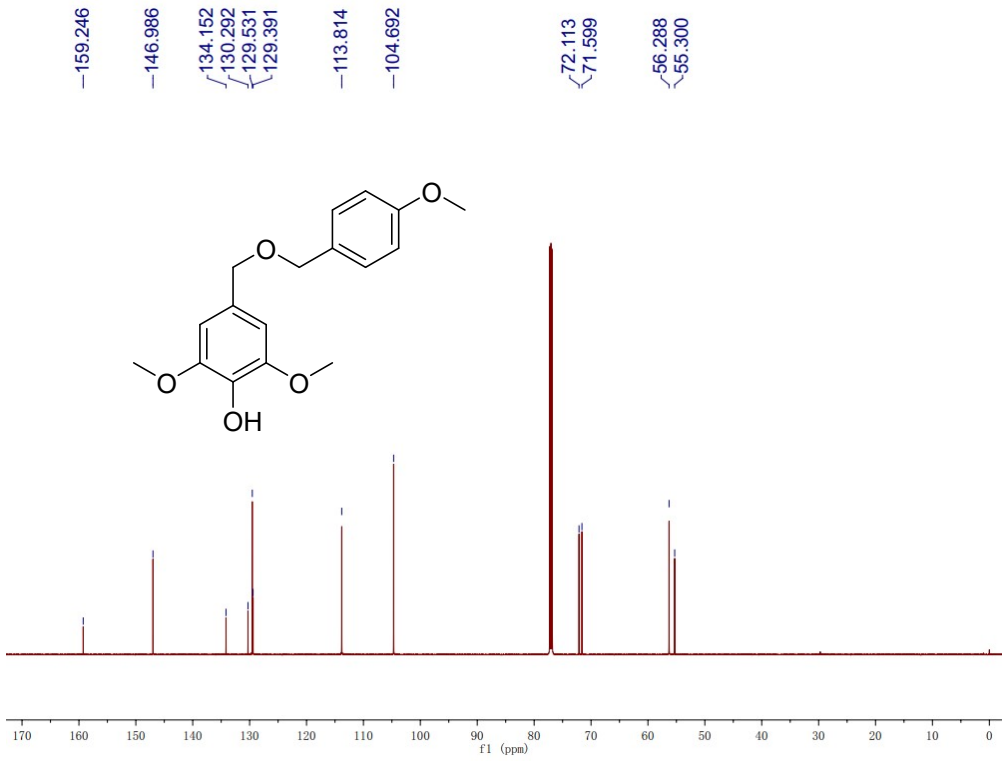
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



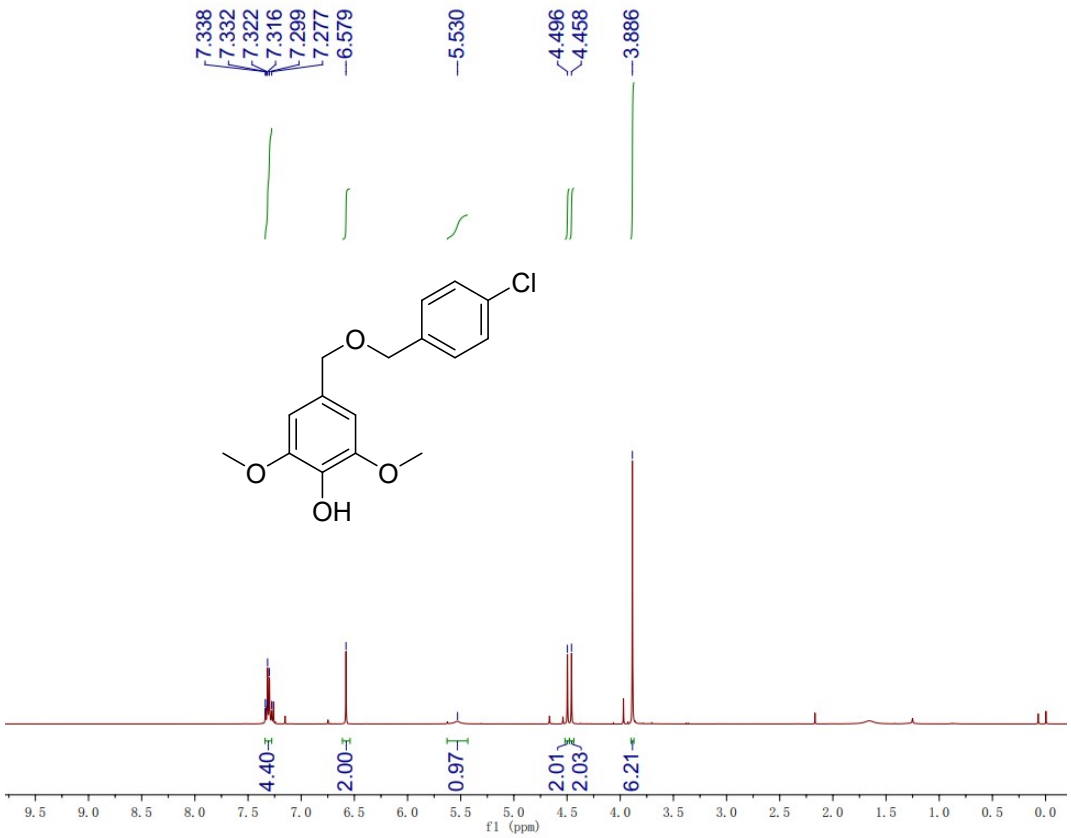
2,6-Dimethoxy-4-(((4-methoxybenzyl)oxy)methyl)phenol (3l) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



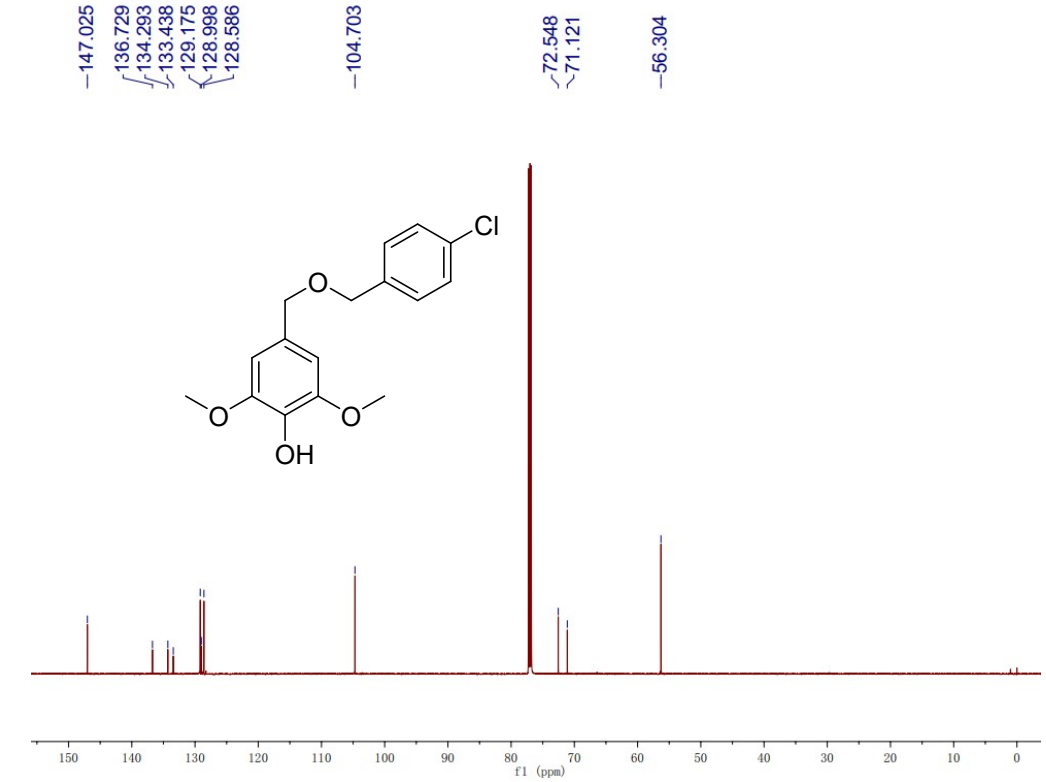
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



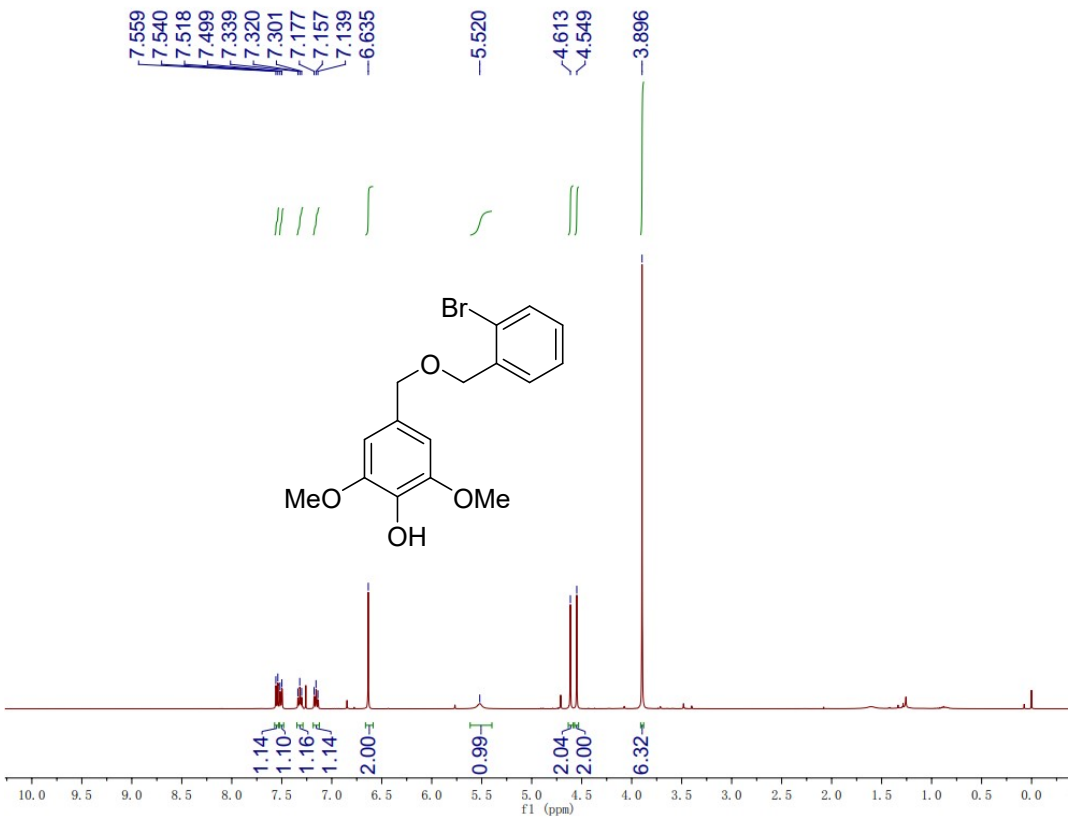
4-(((4-Chlorobenzyl)oxy)methyl)-2,6-dimethoxyphenol (3m) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



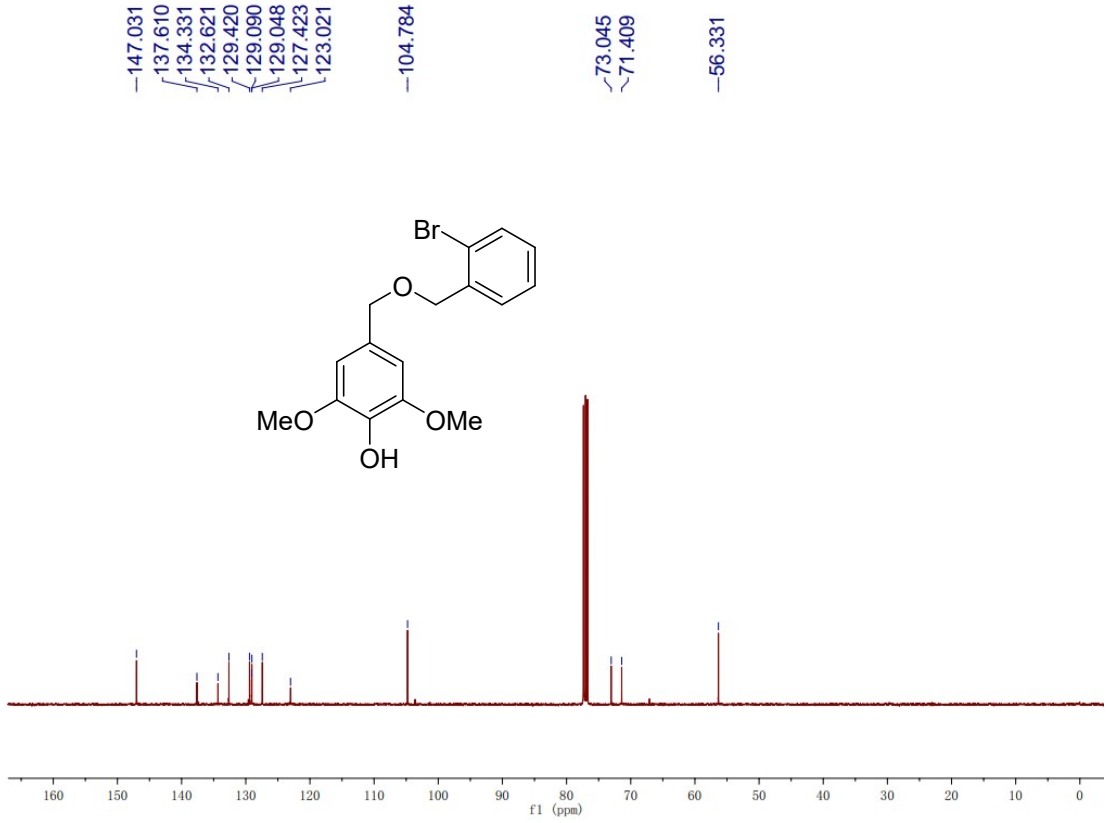
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



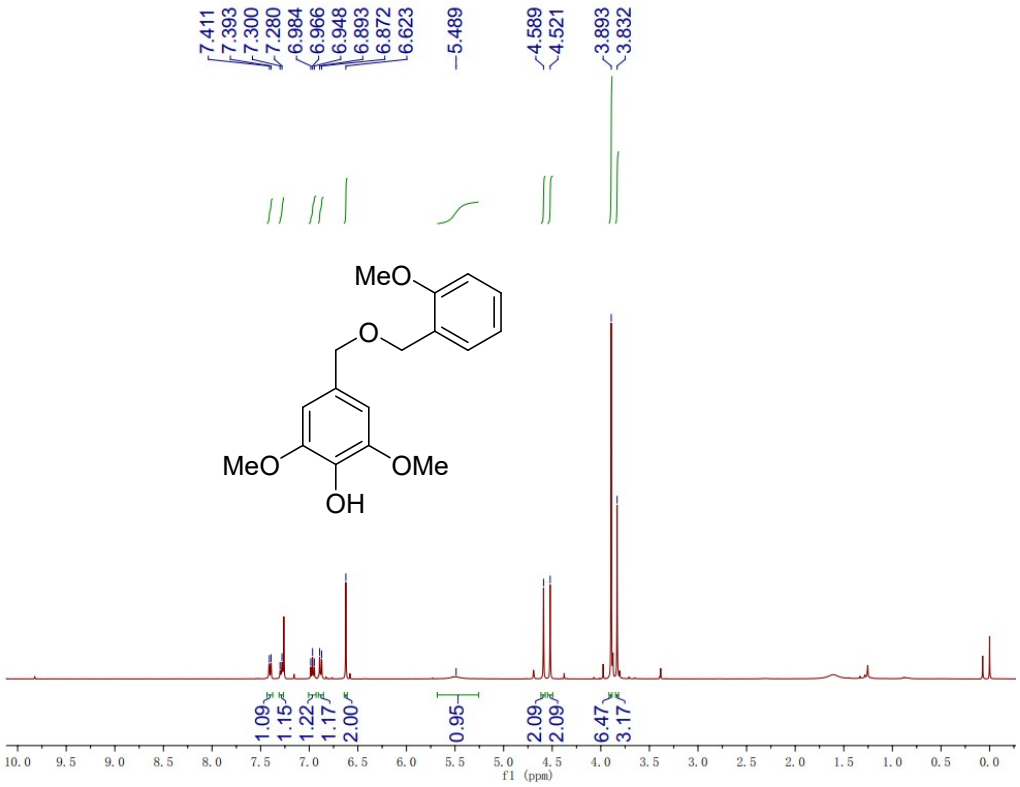
4-(((2-Bromobenzyl)oxy)methyl)-2,6-dimethoxyphenol (3n) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



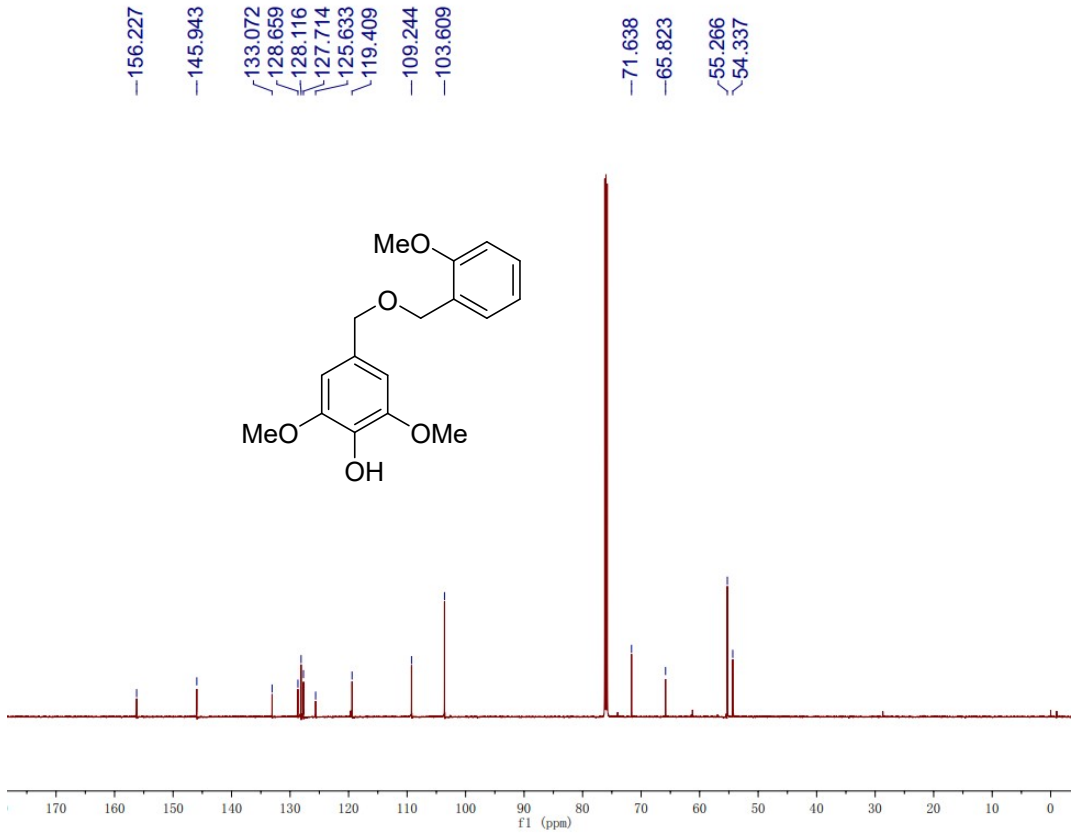
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



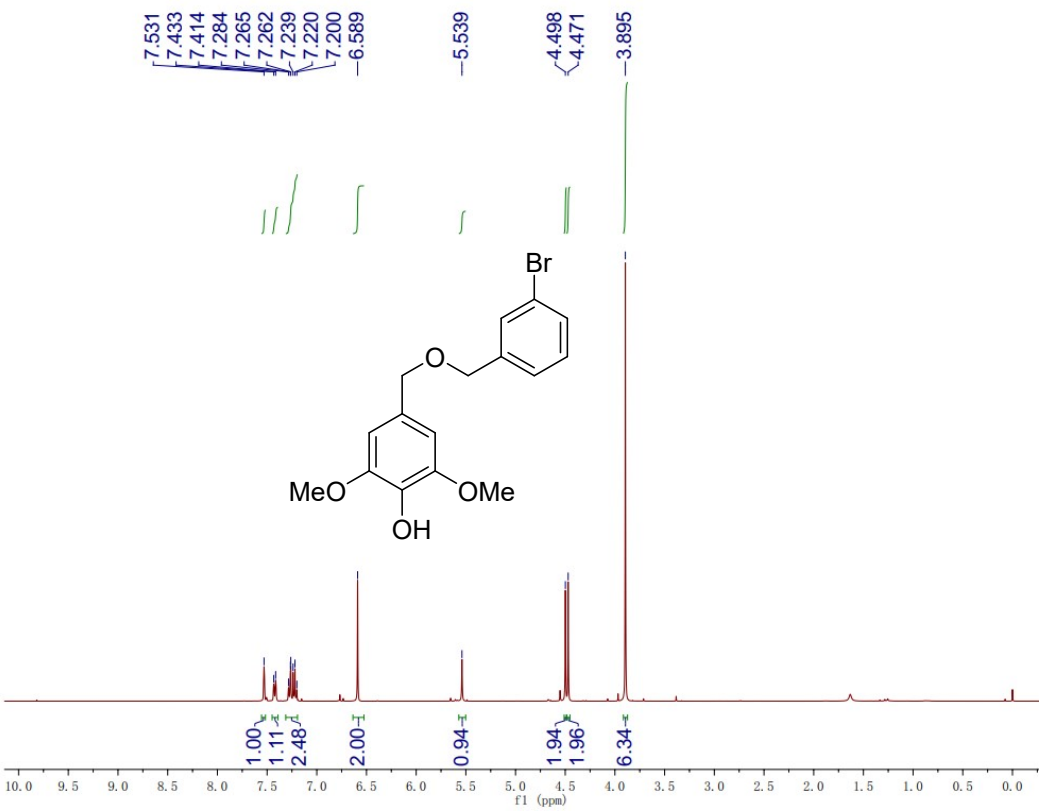
2,6-Dimethoxy-4-(((2-methoxybenzyl)oxy)methyl)phenol (3o) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



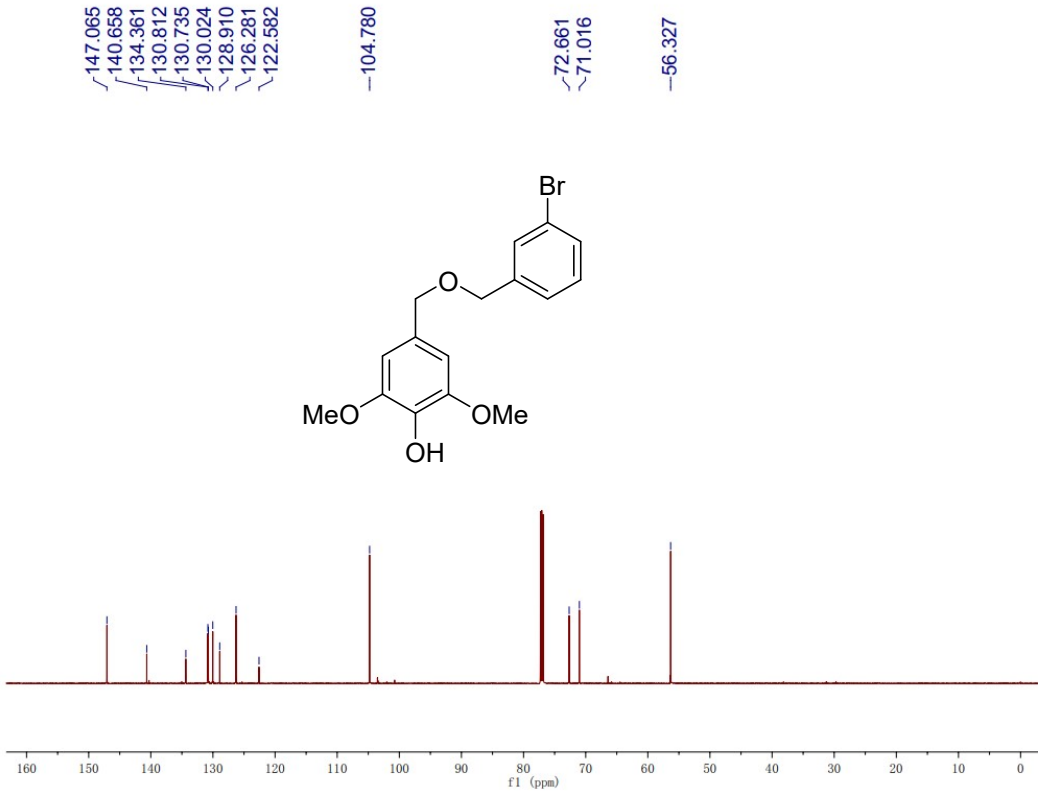
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



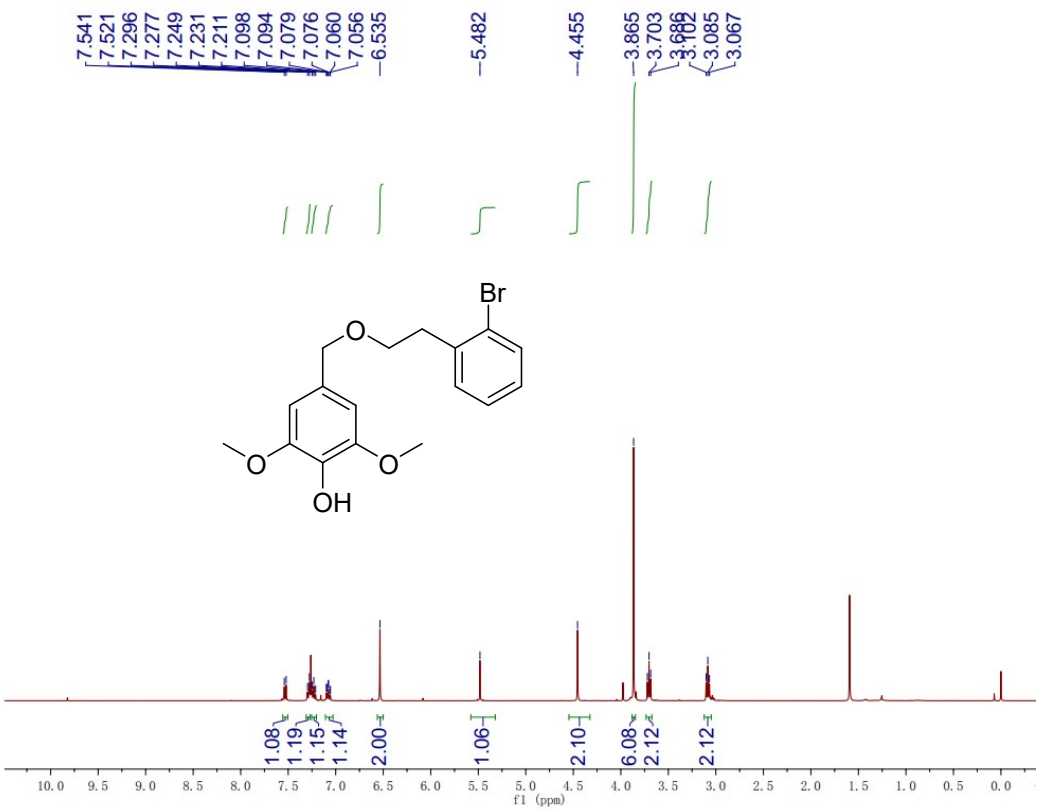
4-(((3-Bromobenzyl)oxy)methyl)-2,6-dimethoxyphenol (3p) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



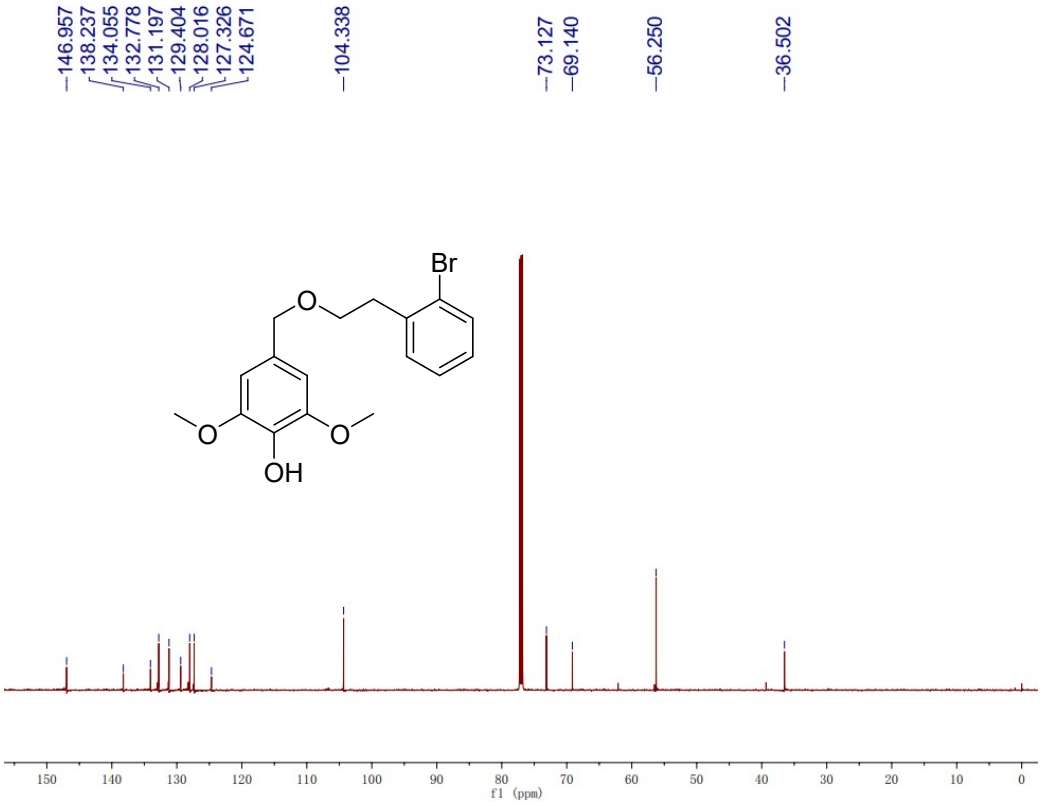
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



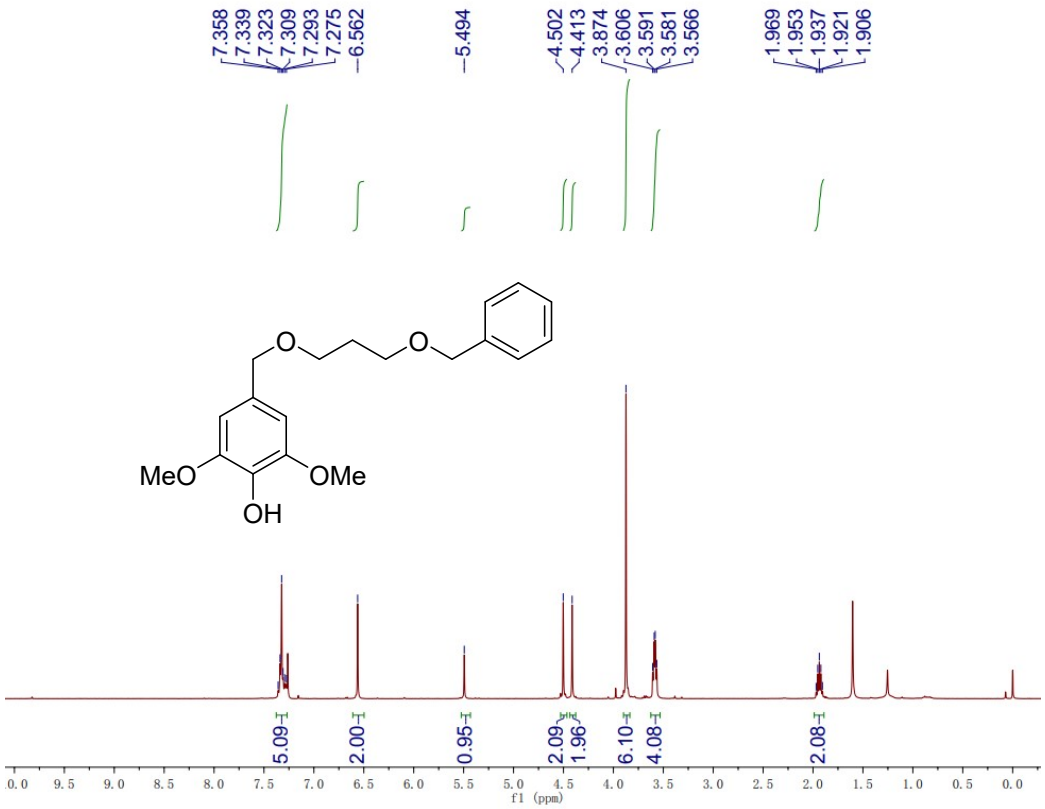
4-((2-Bromophenethoxy)methyl)-2,6-dimethoxyphenol (3q) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



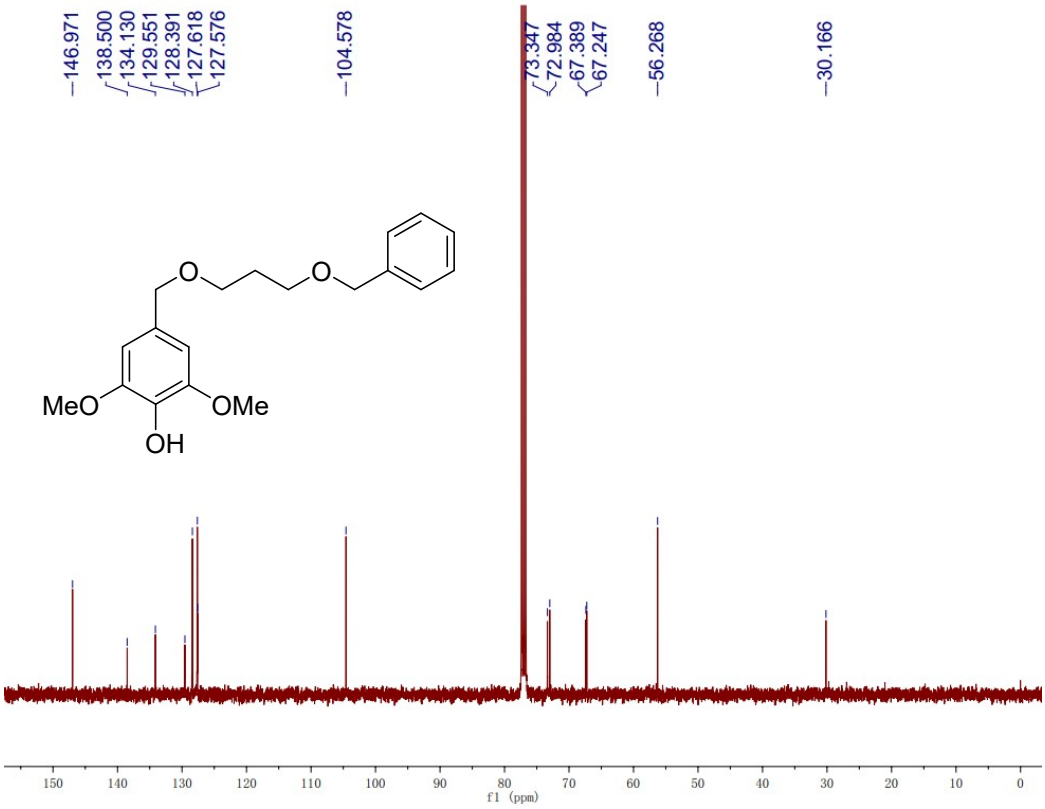
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



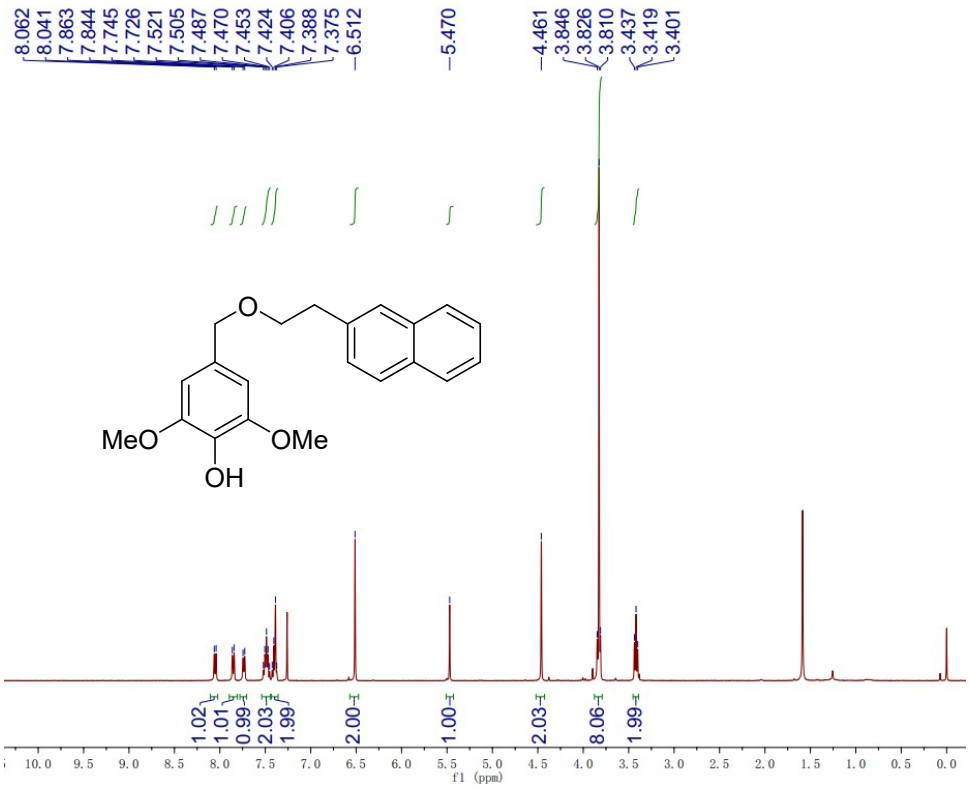
4-((3-(Benzyloxy)propoxy)methyl)-2,6-dimethoxyphenol (3r) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



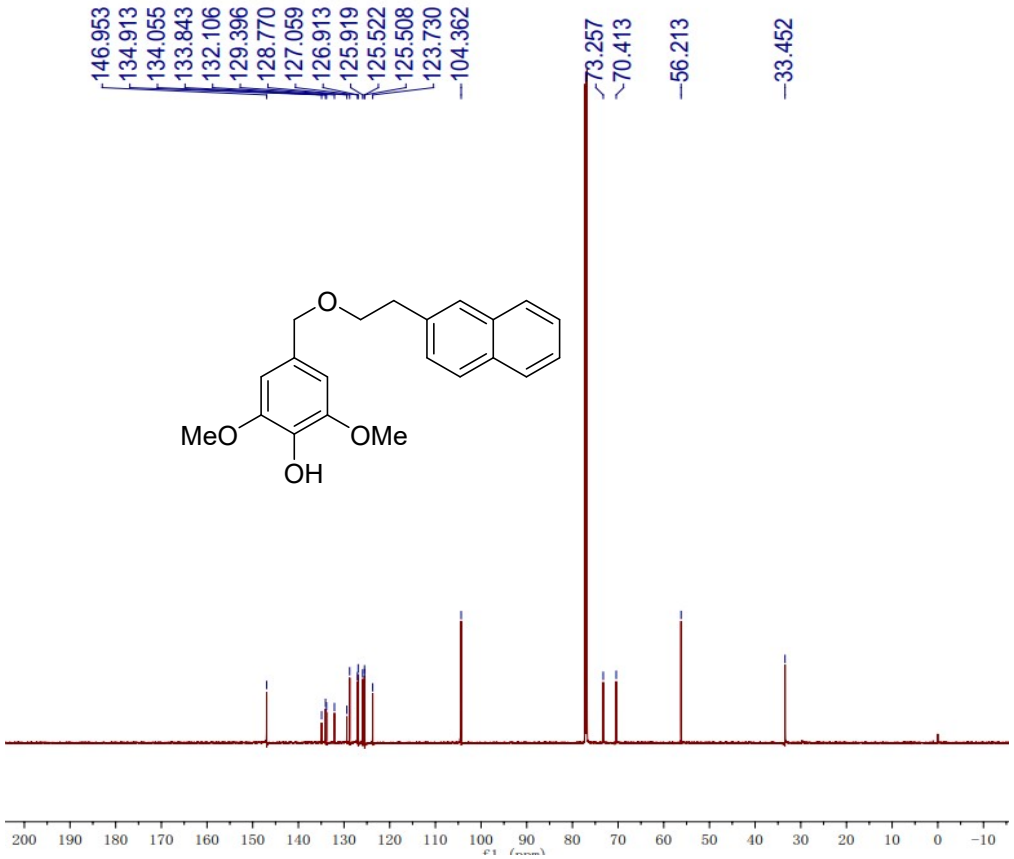
[^{13}C_NMR_100 MHz_($CDCl_3$: 77.00 ppm)]



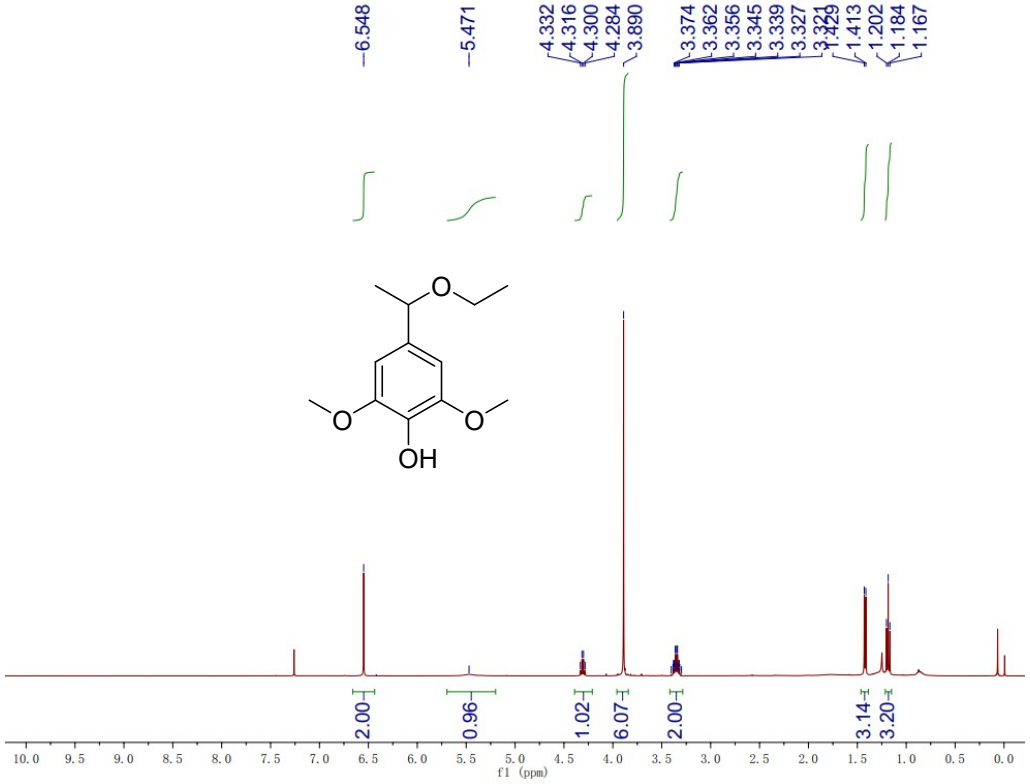
2,6-Dimethoxy-4-((2-(naphthalen-2-yl)ethoxy)methyl)phenol (3s) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



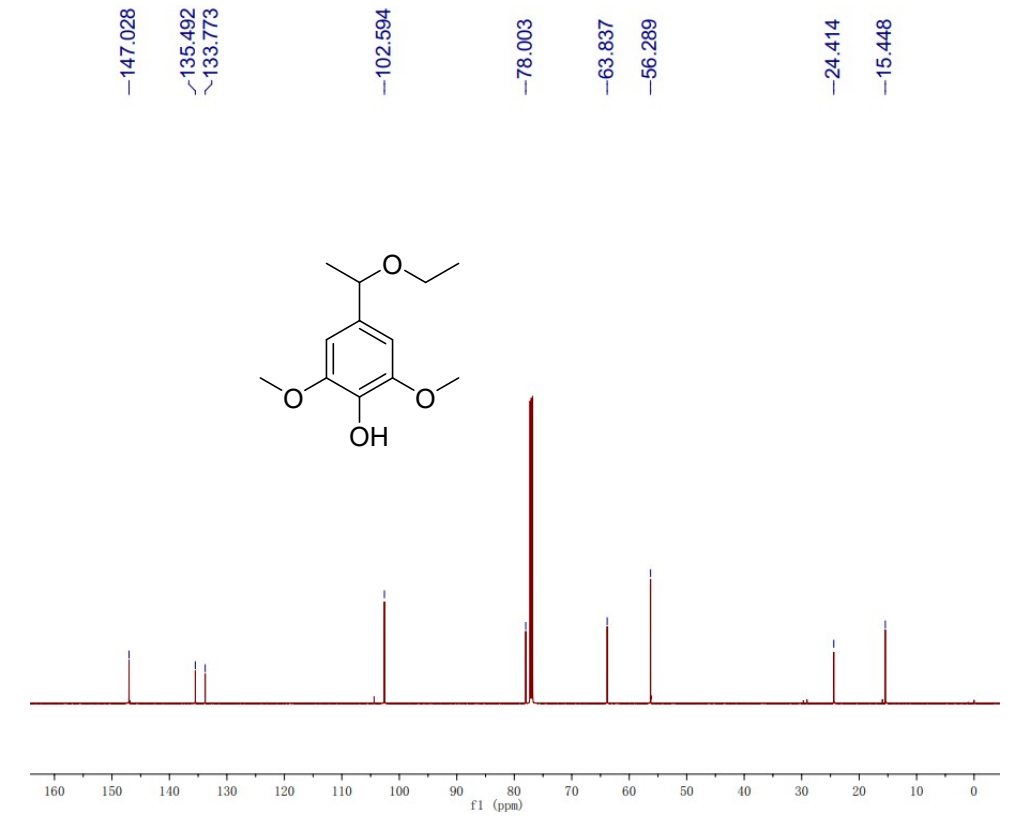
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



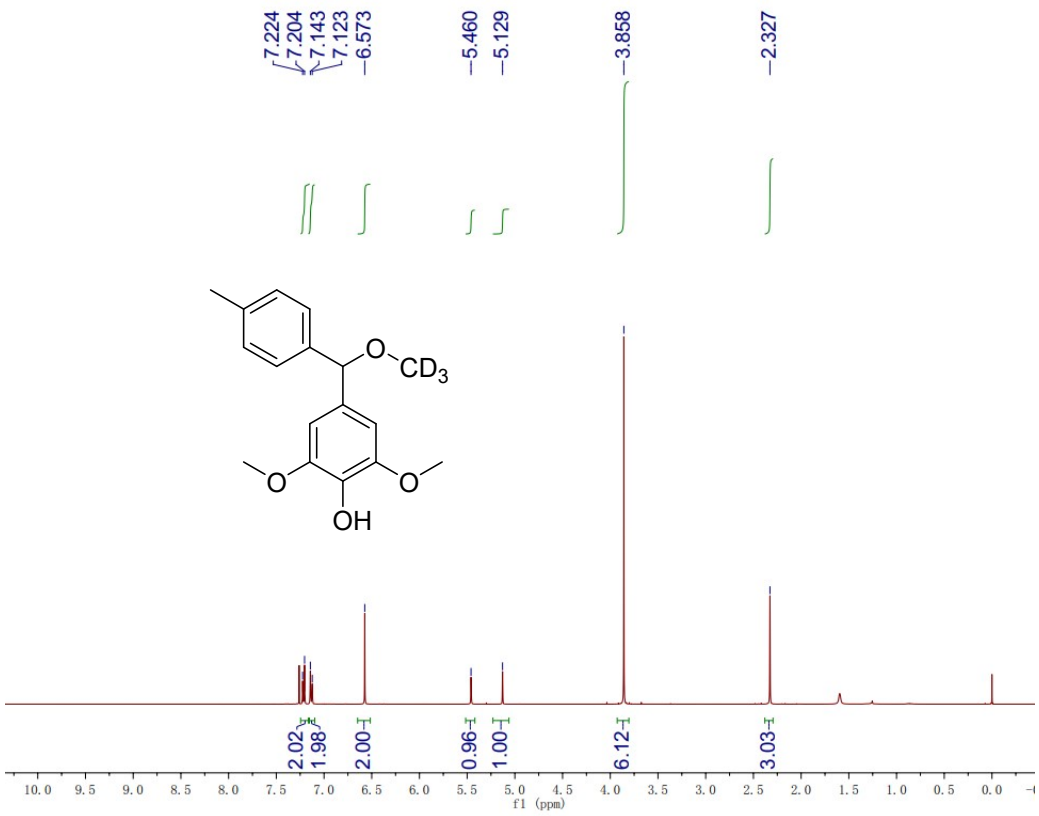
4-(1-Ethoxyethyl)-2,6-dimethoxyphenol (3t) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



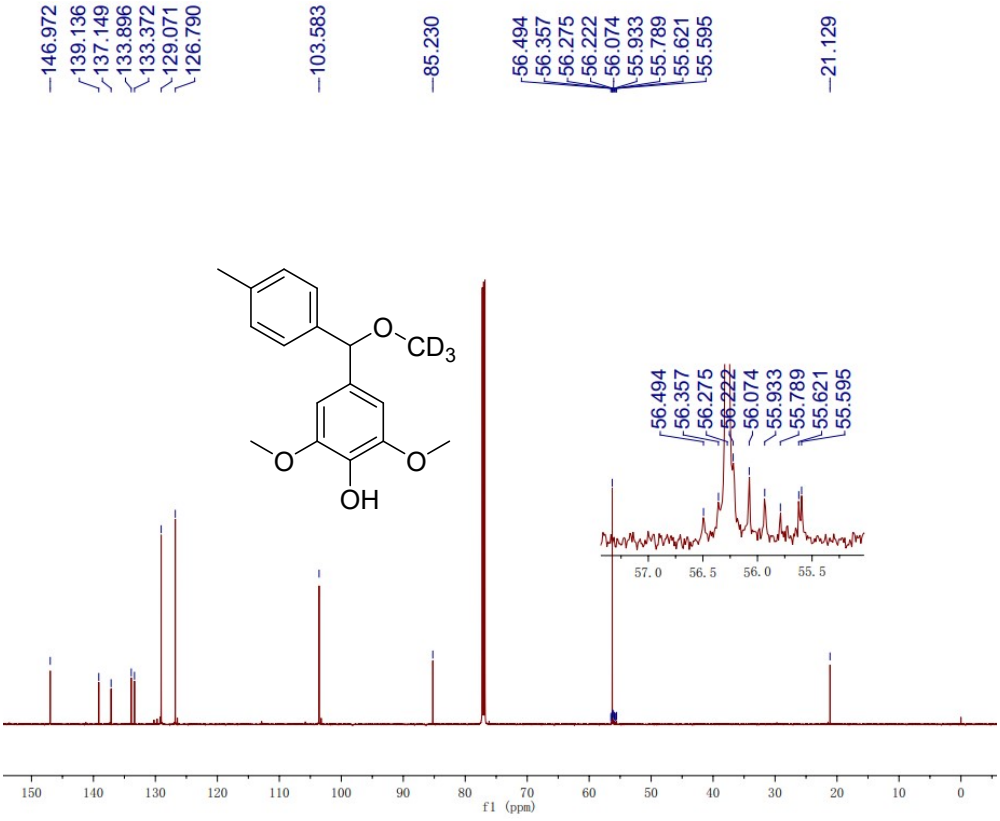
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



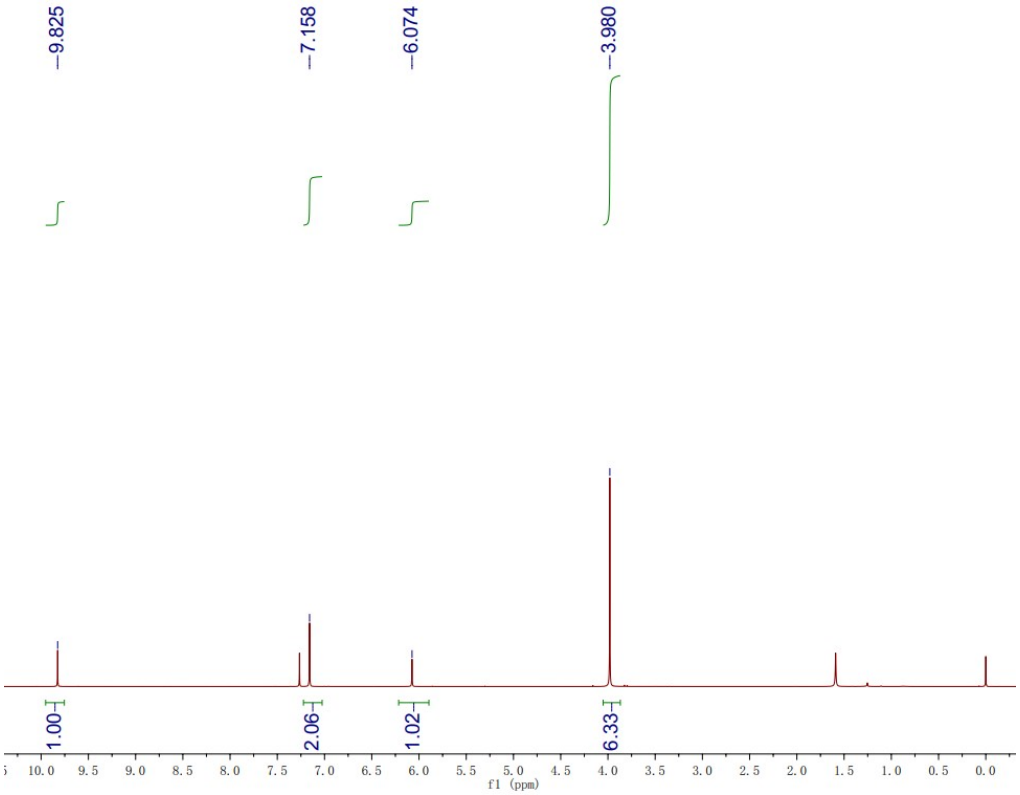
2,6-Dimethoxy-4-((methoxy-d3)(p-tolyl)methyl)phenol (2ax') [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



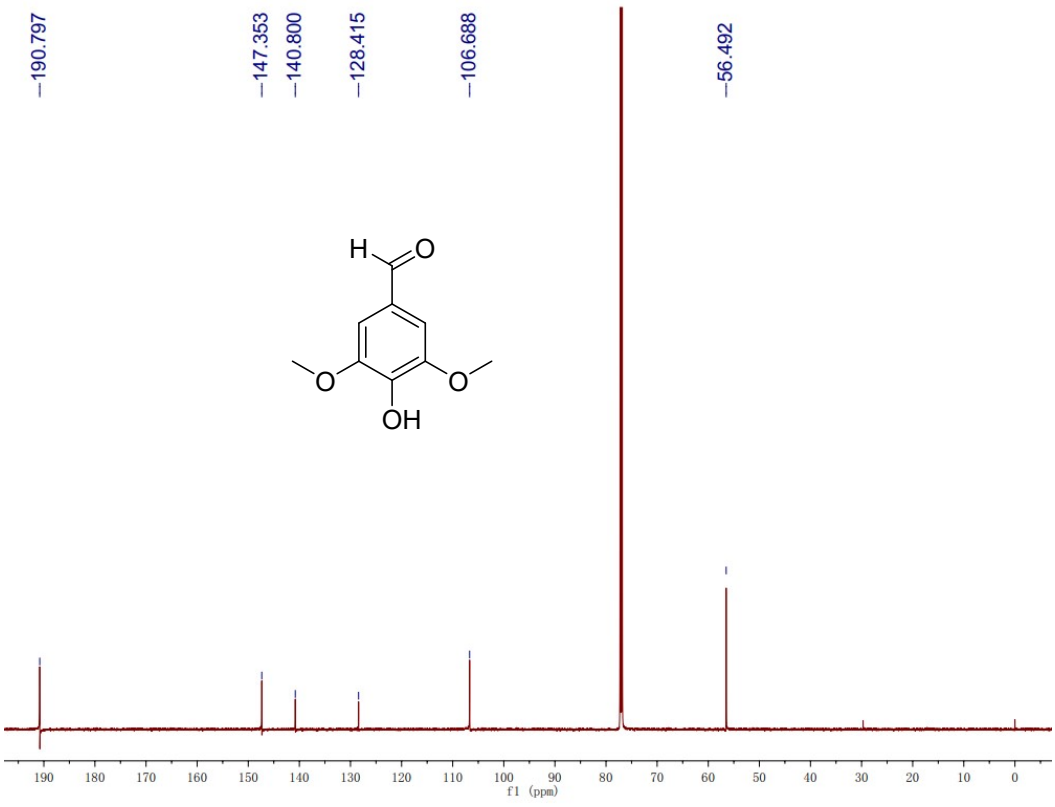
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



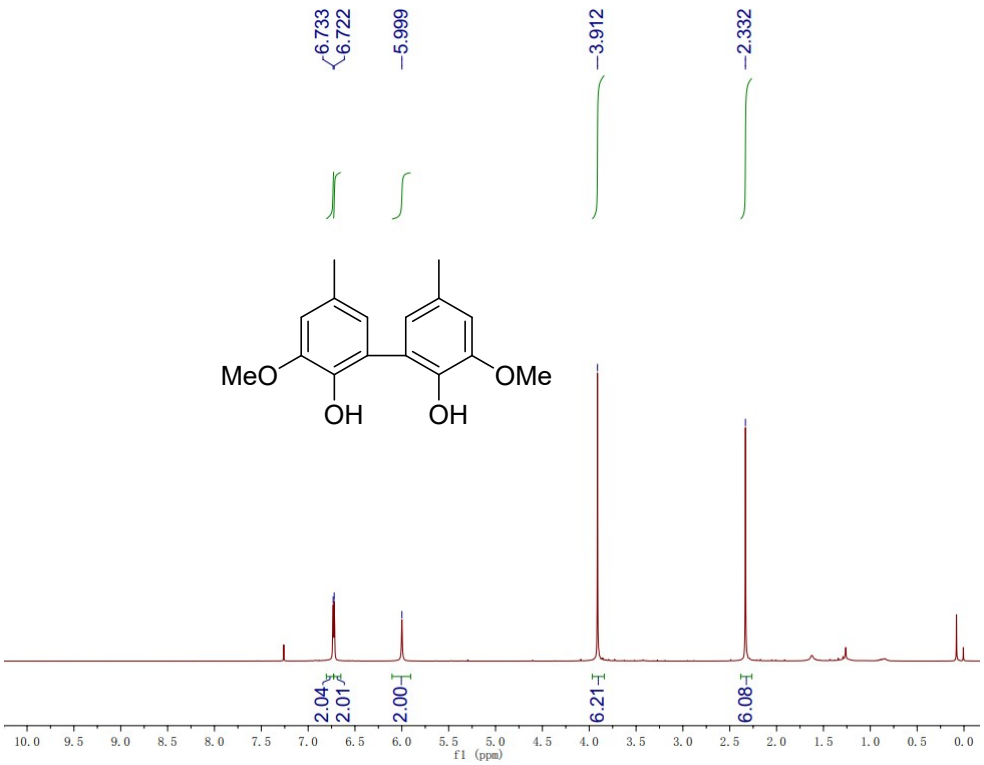
4-Hydroxy-3,5-dimethoxybenzaldehyde (4a) [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



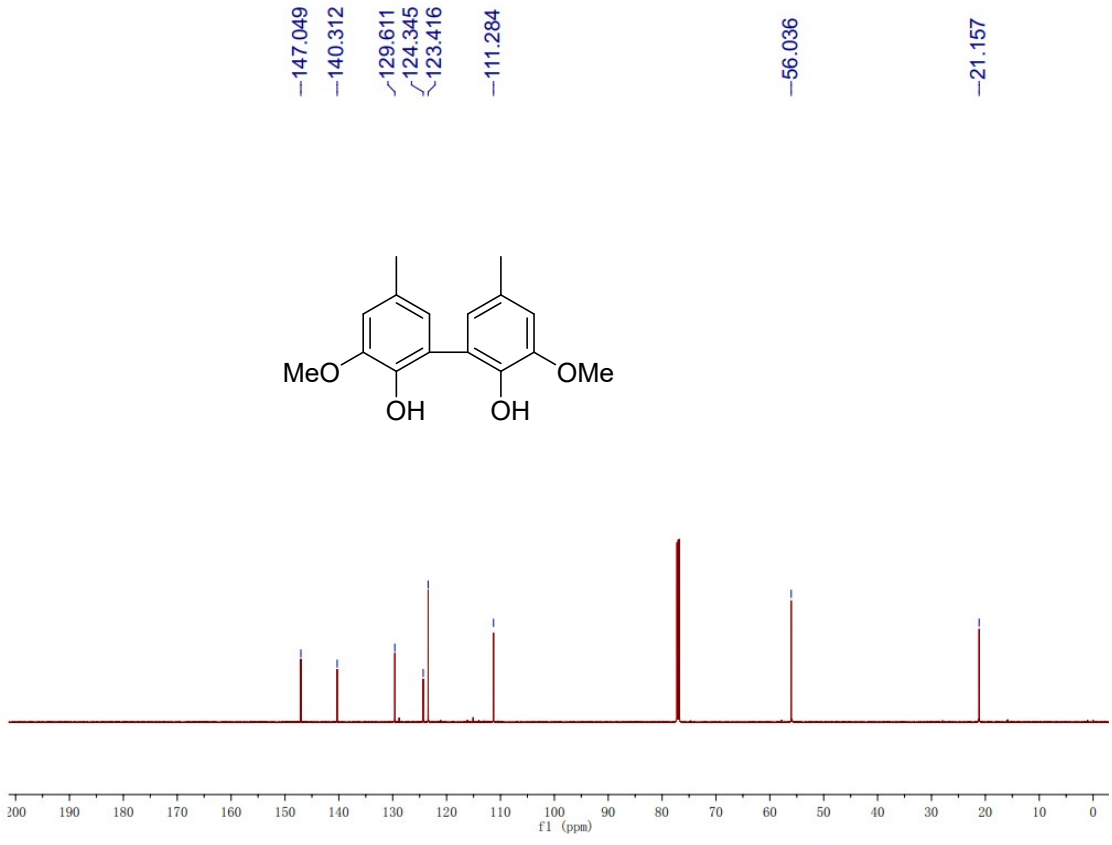
[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



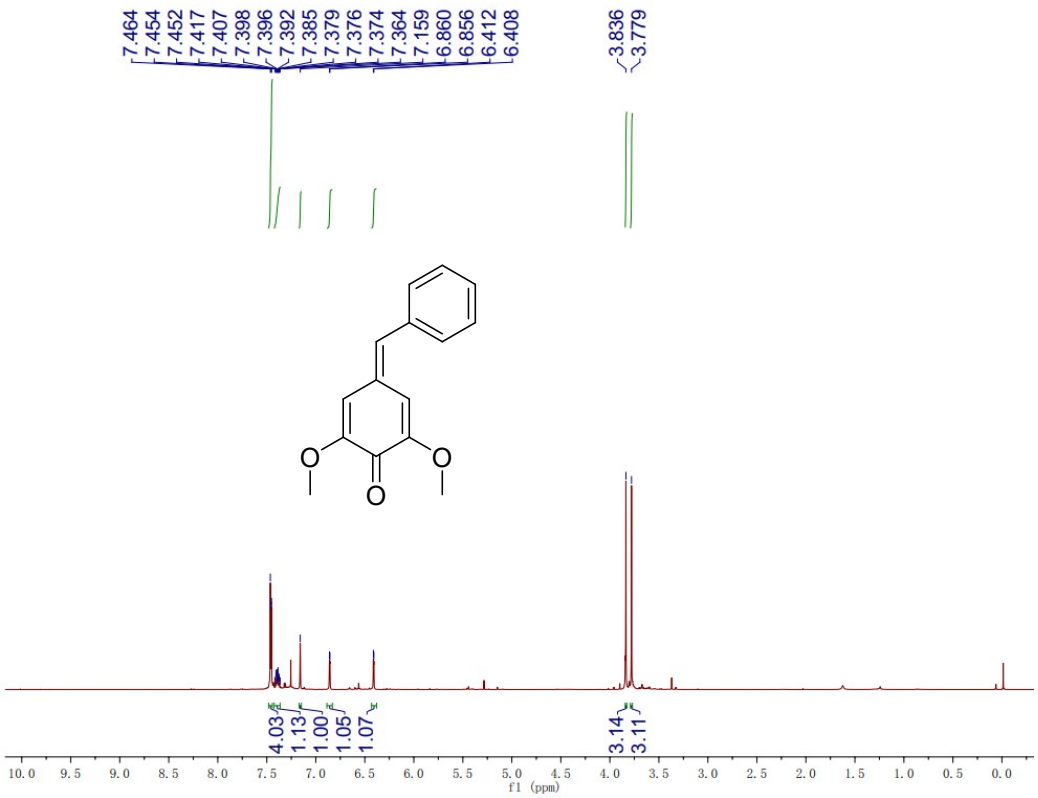
3,3'-Dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (2a') [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]



4-Benzylidene-2,6-dimethoxycyclohexa-2,5-dien-1-one (VII') [^{1}H_NMR_400 MHz_($CDCl_3$: 7.26 ppm)]



[^{13}C_NMR_150 MHz_($CDCl_3$: 77.00 ppm)]