Supplementary Information

Transition-metal-free, conversion of lignin model compounds to high-value aromatics: scope and chemoselectivity

Tae Woo Lee and Jung Woon Yang*

Department of Energy Science, Sungkyunkwan University, Suwon 16419, South Korea.

E-mail: jwyang@skku.edu (J. W. Yang), Tel: +82-31-299-4276

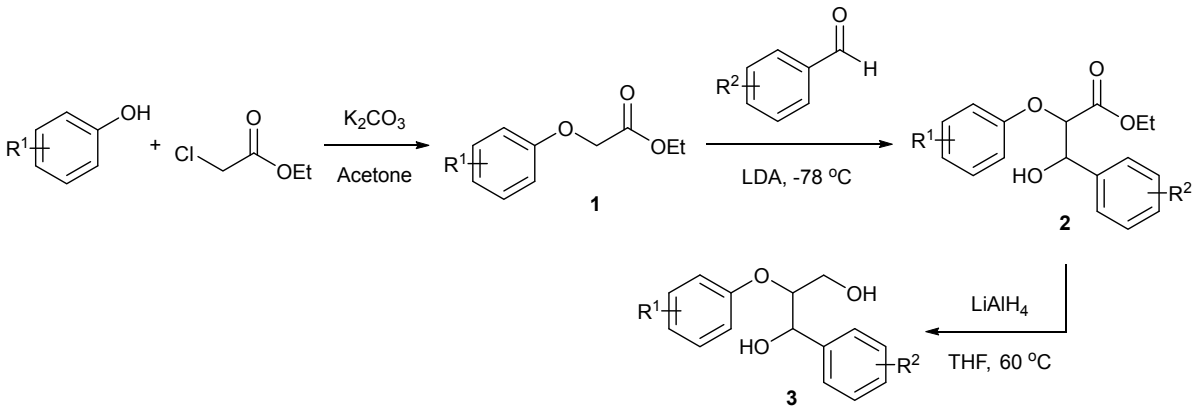
Contents

General Remarks

Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254}. ^{1}H NMR spectra were recorded on a Varian at 500 MHz in $CDCl_3$ (δ 7.26 ppm) or Acetone-d_6 (δ 2.05 ppm), ^{13}C NMR spectral measurements were performed at 126 MHz using $CDCl_3$ (δ 77.16 ppm) or Acetone-d_6 (δ 29.84 ppm). The terms m, s, d, t, and q. represent multiplet, singlet, doublet, triplet, and quadruplet, respectively. Commercial grade reagents and solvents were used without further purification. Mass analysis was performed using on a Gas Chromatography High Resolution Mass Spectrometer JMS-700(JEOL, Japan), 6890 Series (Agilent, USA). FT-IR spectrum was performed on a VERTEX 70(Bruker) IR spectrometer in the range of 1000–4000 cm^{-1}. Melting points were determined using a melting point apparatus.

Procedure A – Preparation of Lignin β-O-4 Model Compounds

All dimeric lignin model compounds (**1a-1v**) were prepared according to the previously reported procedures.[1-2]

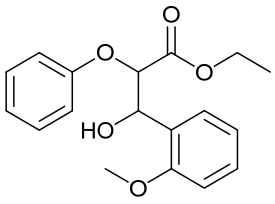


A mixture of K_2CO_3 (8.29 g, 0.060 mol), phenol (4.70 g, 0.050 mol), and acetone (200 mL) was heated to reflux for 30 minutes. Ethylchloroacetate (5.35 mL, 0.050 mol) was then added dropwise with a syringe, over 5 min, and the reaction mixture was kept under reflux for 12 h. After cooling the solution down to room temperature, the crude mixture was filtered over celite and the filtrate was evaporated under reduced pressure. The resulting slightly pinkish oil was then dissolved in diethyl ether (100 mL) and washed with an aqueous NaOH solution (10% w/w, 3 × 25 mL), water (25 mL) and brine (25 mL). After drying over $MgSO_4$, the organic phase was filtered and evaporated under reduced pressure, to yield ethyl 2-phenoxyacetate (**1**; 6.21 g, 69 %) as colorless oil.

A solution of *n*-BuLi in hexanes (7.3 mL, 1.6 M, 11.5 mmol) was added dropwise over 20 min to a solution of diisopropylamine (1.11 g, 11 mmol) in THF (25 mL), at 0 °C. After 20 min at 0 °C the solution turned pale yellow. The resulting mixture was cooled down to –78 °C, and a solution of ethyl-2-phenoxyacetate (1.80 g, 10 mmol) in THF (30 mL) was then added over a period of 1 h. Benzaldehyde (1.02 g, 9.57 mmol) in THF (30 mL) was added over 30 min at –78 °C and the solution was stirred for 90 min at –78 °C, prior to the addition of distilled water (60 mL). The aqueous phase was then extracted with ethyl acetate (3 × 80 mL). The combined organic phases were washed with a 1 N aqueous HCl solution (80 mL), water (80 mL), brine (80 mL), and then dried over $MgSO_4$. The yellowish crude oil (2.4 g), was obtained after removal of the volatiles under reduced pressure. The residue was purified by column chromatography with hexanes:ethyl acetate (5:1 to 1:1) as an eluent. After solvent evaporation, ethyl 3-hydroxy-2-phenoxy-3-phenylpropanoate (**2**) was obtained as a yellowish oil (1.67 g, 58%). No attempt was made to separate the diastereomers mixture.

A suspension of $LiAlH_4$ (331.6 mg, 8.7 mmol) in THF (9 mL) was stirred at 0 °C under argon, and a THF (12 mL) solution of ethyl-3-hydroxy-2-phenoxy-3-phenylpropanoate (**2**; 1 g, 3.5 mmol) was added dropwise over 20 min. When gas evolution ended, the mixture was warmed to 60 °C for 3 h. After cooling to 0 °C, the mixture was quenched by adding Glaubler's Salt ($Na_2SO_4 \cdot 10H_2O$) carefully until hydrogen evolution is no longer evident, then add some more. The mixture was then stirred for 15 min at ambient temperature. The suspension was filtered through celite, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane) to afford the corresponding lignin model compound [2-phenoxy-1-phenylpropane-1,3-diol (**3**); 769 mg, 90 %] as a white solid.

Characterization Data for Starting Materials

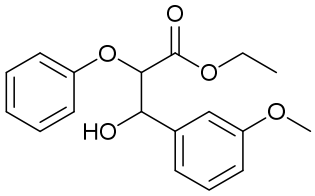


Ethyl 3-hydroxy-3-(2-methoxyphenyl)-2-phenoxypropanoate: The title compound was synthesized according to general procedure A. Pale yellow oil; yield = 42.5%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.47–7.42 (m, 1H both diastereomers), 7.30–7.23 (m, 3H both diastereomers), 7.01–6.92 (m, 2H both diastereomers), 6.91–6.79 (m, 3H both diastereomers) ppm,
Major δ 5.38 (t, J = 5.8 Hz, 1H), 5.01 (d, J = 5.3 Hz, 1H), 4.11–4.04 (m, 2H), 3.87 (s, 3H), 3.41 (d, J = 6.3 Hz, 1H), 1.08 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.46 (dd, J = 7.5, 4.8 Hz, 1H), 4.91 (d, J = 4.8 Hz, 1H), 4.16–4.11 (m, 2H), 3.85 (s, 3H), 3.20 (d, J = 7.5 Hz, 1H), 1.13 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.43, 157.46, 156.47, 129.51, 129.13, 128.16, 126.60, 121.83, 120.75, 115.38, 110.33, 78.91, 71.52, 61.13, 55.39, 13.94 ppm.
Minor δ 169.64, 157.92, 156.49, 129.44, 129.24, 128.08, 126.95, 121.89, 120.78, 115.55, 110.37, 80.18, 71.15, 61.36, 55.42, 13.97 ppm.

HRMS (FAB+) m/z: ($[M+H]^+$) calcd for $C_{18}H_{20}O_5$ 316.1311, found 316.1316.
IR: 3516, 2983, 2838, 1750, 1599, 1493, 1239, 1190, 1026 cm^{-1}.



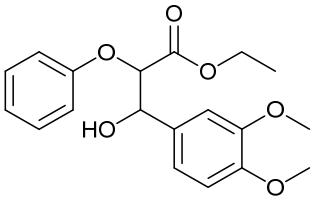
Ethyl 3-hydroxy-3-(3-methoxyphenyl)-2-phenoxypropanoate phe-nolxypropanoate: The title compound was synthesized according to general procedure A. Pale yellow oil; yield = 57%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.30–7.21 (m, 3H both diastereomers), 7.07–6.94 (m, 3H both diastereomers), 6.89–6.82 (m, 3H both diastereomers) ppm,
Major δ 5.23–5.18 (m, 1H), 4.77 (d, J = 5.8 Hz, 1H), 4.20–4.12 (m, 2H), 3.80 (s, 3H), 2.88 (d, J = 4.4 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.14 (t, J = 5.2 Hz, 1H), 4.72 (d, J = 5.4 Hz, 1H), 4.12–4.06 (m, 2H), 3.81 (s, 3H), 2.99 (d, J = 5.1 Hz, 1H), 1.10 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

Major δ 169.48, 159.66, 157.42, 140.65, 129.56, 129.39, 122.14, 118.98, 115.50, 113.96, 112.16, 80.73, 74.17, 61.48, 55.27, 13.99 ppm.
Minor δ 169.33, 159.75, 157.50, 140.06, 129.63, 129.49, 122.27, 119.03, 115.50, 114.16, 112.22, 81.64, 74.77, 61.53, 55.28, 13.92 ppm.

HRMS (FAB+) *m*/*z*: ([M+H]$^+$) calcd for $C_{18}H_{20}O_5$: 316.1389, found 317.1390.
IR: 3489, 2924, 2850, 1740, 1598, 1493, 1230, 1191, 1041cm^{-1}

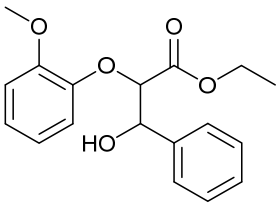


Ethyl 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-phenoxypropanoate: The title compound was synthesized according to general procedure A. Pale yellow oil; yield = 63%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.28–7.19 (m, 2H both diastereomers), 7.03–6.91 (m, 3H both diastereomers), 6.90–6.79 (m, 3H both diastereomers) ppm,
Major δ 5.13 (dd, J = 5.9, 3.9 Hz, 1H), 4.73 (d, J = 5.9 Hz, 1H), 4.22–4.12 (m, 2H), 3.85 (s, 3H), 3.85 (s, 3H), 3.08 (d, J = 3.9 Hz, 1H), 1.16 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.11–5.08 (m, 1H), 4.69 (d, J = 5.7 Hz, 1H), 4.12–4.03 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.16 (d, J = 4.4 Hz, 1H), 1.08 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.83, 157.51, 148.93, 148.84, 131.90, 129.55, 122.10, 119.19, 115.49, 110.86, 109.83, 80.92, 74.01, 61.48, 55.89, 55.87, 14.05 ppm.
Minor δ 169.47, 157.56, 149.13, 149.00, 131.00, 129.63, 122.24, 119.33, 115.47, 110.86, 109.93, 81.85, 74.65, 61.48, 55.91, 55.89, 13.96 ppm.

HRMS (FAB+) *m*/*z*: ([M+H]$^+$) calcd for $C_{19}H_{22}O_6$: 346.1416, found 346.1423
IR: 3508, 2935, 2839, 1738, 1596, 1517, 1494, 1264, 1234, 1027cm^{-1}



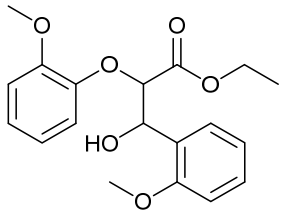
Ethyl 3-hydroxy-2-(2-methoxyphenoxy)-3-phenylpropanoate: The title compound was synthesized according to general procedure A. Colorless oil; yield = 53.4%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.48–7.39 (m, 2H both diastereomers), 7.37–7.26 (m, 3H both diastereomers), 7.04–7.01 (m, 1H both diastereomers), 6.95–6.90 (m, 2H both

diastereomers), 6.86–6.82 (m, 1H both diastereomers) ppm,
Major δ 5.21 (m, 1H), 4.76 (d, J = 4.7 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.85–3.81 (m, 1H), 1.11 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.11 (d, J = 7.1 Hz, 1H), 4.52 (d, J = 7.1 Hz, 1H), 4.06–3.99 (m, 2H), 3.87–3.85 (m, 1H), 3.86 (s, 3H), 1.02 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.16, 150.79, 147.20, 138.98, 128.18, 128.05, 126.84, 124.16, 121.14, 119.52, 112.37, 84.20, 74.04, 61.20, 55.90, 13.98 ppm.
Minor δ 169.35, 150.81, 147.30, 138.08, 128.45, 128.34, 127.10, 124.05, 121.05, 118.69, 112.32, 85.63, 75.19, 61.20, 55.82, 13.83 ppm.

HRMS (FAB+) m/z: ($[M+H]^+$) calcd for $C_{18}H_{20}O_5$: 317.1389, found 317.1390.
IR: 3504, 2984, 2838, 1750, 1599, 1493, 1239, 1190, 1026cm^{-1}.

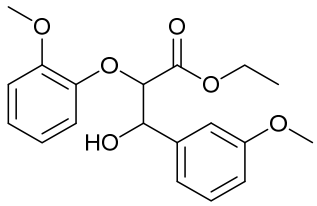


Ethyl 3-hydroxy-2-(2-methoxyphenoxy)-3-(2-methoxyphenyl)-propanoate: The title compound was synthesized according to general procedure A. Colorless oil; yield = 38.4%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.31–7.23 (m, 1H), 7.18–7.09 (m, 1H), 7.01–6.96 (m, 2H), 6.89–6.82 (m, 1H), 6.57–6.50 (m, 1H), 6.48–6.41 (m, 2H) ppm,
Major δ 5.22–5.16 (m, 1H), 4.76 (d, J = 5.8 Hz, 1H), 4.23–4.11 (m, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 2.87 (d, J = 4.4 Hz, 1H), 1.15 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.13 (t, J = 5.2 Hz, 1H), 4.71 (d, J = 5.5 Hz, 1H), 4.12–4.06 (m, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 2.97 (d, J = 5.0 Hz, 1H), 1.10 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.41, 160.82, 159.67, 158.61, 140.63, 129.97, 129.40, 118.96, 113.96, 112.11, 107.99, 107.25, 102.00, 80.70, 74.15, 61.49, 55.29, 55.27, 14.00 ppm.
Minor δ 169.26, 160.86, 159.76, 158.69, 140.01, 130.04, 129.50, 119.03, 114.17, 112.22, 108.07, 107.25, 102.01, 81.62, 74.75, 61.54, 55.29, 55.27, 13.93 ppm.

HRMS (FAB+) m/z: ($[M+H]^+$) calcd for $C_{19}H_{22}O_6$: 347.1495, found 347.1498.
IR: 3485, 2938, 2836, 1742, 1602, 1492, 1285, 1198, 1154, 1041cm^{-1}.

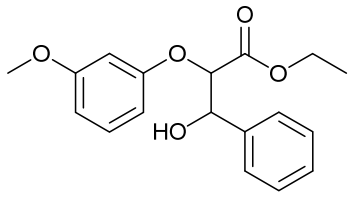


Ethyl 3-hydroxy-2-(2-methoxyphenoxy)-3-(3-methoxyphenyl) propaneate: The title compound was synthesized according to general procedure A. Pale yellow oil; yield = 38.4%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.27–7.22 (m, 1H both diastereomers), 7.06–6.99 (m, 3H both diastereomers), 6.99–6.88 (m, 2H both diastereomers), 6.87–6.80 (m, 2H both diastereomers) ppm,
Major δ 5.22–5.15 (m, 1H), 4.75 (d, J = 4.8 Hz, 1H), 4.17–4.10 (m, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 3.81–3.79 (m, 1H), 1.13 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.09 (dd, J = 7.0, 3.3 Hz, 1H), 4.51 (d, J = 7.0 Hz, 1H), 4.09–4.02 (m, 2H), 3.86 (s, 3H), 3.87–3.84 (m, 1H), 3.79 (s, 3H), 1.06 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.15, 159.53, 150.74, 147.18, 140.61, 129.18, 124.10, 121.13, 119.33, 119.15, 113.77, 112.36, 112.33, 84.03, 73.96, 61.23, 55.89, 55.21, 14.02 ppm.
Minor δ 169.36, 159.68, 150.46, 147.30, 139.72, 129.33, 123.99, 121.05, 119.41, 118.52, 114.25, 112.33, 112.31, 85.46, 75.04, 61.23, 55.82, 55.25, 13.89 ppm.

HRMS (FAB+) *m*/*z*: ([M+H]$^+$) calcd for $C_{19}H_{22}O_6$: 346.1416, found 346.1415.
IR: 3484, 2941, 2837, 1744, 1595, 1502, 1460, 1255, 1178, 1041cm^{-1}.



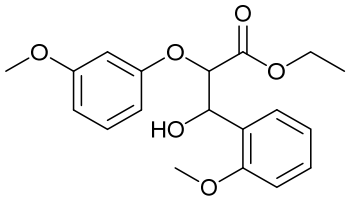
Ethyl 3-hydroxy-2-(3-methoxyphenoxy)-3-phenylpropanoate: The title compound was synthesized according to general procedure A. Pale yellow oil; yield = 64.1%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.44 (m, 2H both diastereomers), 7.41–7.28 (m, 3H both diastereomers), 7.17–7.10 (m, 1H both diastereomers), 6.59–6.50 (m, 1H both diastereomers), 6.47–6.42 (m, 2H both diastereomers) ppm,
Major δ 5.26–5.18 (m, 1H), 4.77 (d, J = 5.7 Hz, 1H), 4.21–4.10 (m, 2H), 3.74 (s, 3H), 2.89 (d, J = 4.4 Hz, 1H), 1.13 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.15 (t, J = 5.3 Hz, 1H), 4.71 (d, J = 5.7 Hz, 1H), 4.11–4.02 (m, 2H), 3.75 (s, 3H), 2.99 (d, J = 4.9 Hz, 1H), 1.06 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

Major δ 169.34, 160.82, 158.63, 138.99, 129.97, 128.38, 128.34, 126.64, 108.00, 107.26, 102.01, 80.76, 74.23, 61.48, 55.29, 13.98 ppm.
Minor δ 169.26, 160.86, 158.69, 138.35, 130.04, 128.54, 128.49, 126.80, 108.08, 107.23, 102.01, 81.70, 74.90, 61.50, 55.33, 13.89 ppm.

HRMS (FAB+) *m*/*z*: ([M+H]$^+$) calcd for $C_{18}H_{20}O_5$: 317.1389, found 317.1386.
IR: 3486, 2921, 2838, 1740, 1602, 1492, 1285, 1198, 1154, 1040cm^{-1}.

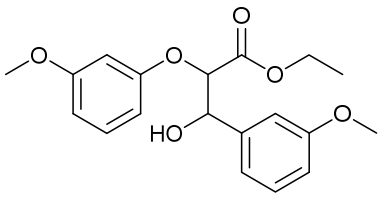


Ethyl 3-hydroxy-2-(3-methoxyphenoxy)-3-(2-methoxyphenyl)-propanoate: The title compound was synthesized according to general procedure A. Pale yellow oil; yield = 49.4%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.48–7.40 (m, 1H both diastereomers), 7.32–7.25 (m, 1H both diastereomers), 7.19–7.04 (m, 1H both diastereomers), 7.00–6.95 (m, 1H both diastereomers), 6.94–6.84 (m, 1H both diastereomers), 6.58–6.46 (m, 2H both diastereomers), 6.42–6.33 (m, 1H both diastereomers) ppm,
Major δ 5.44 (dd, J = 7.4, 4.8 Hz, 1H), 4.90 (d, J = 4.8 Hz, 1H), 4.17–4.09 (m, 2H), 3.85 (s, 3H), 3.72 (s, 3H), 3.20 (d, J = 7.4 Hz, 1H), 1.13 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.38 (t, J = 5.8 Hz, 1H), 5.00 (d, J = 5.2 Hz, 1H), 4.10–4.03 (m, 2H), 3.87 (s, 3H), 3.75 (s, 3H), 3.40 (d, J = 6.3 Hz, 1H), 1.08 (t, J = 6.9 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.58, 160.74, 159.15, 156.52, 129.84, 129.27, 128.12, 126.91, 120.80, 110.38, 107.77, 107.35, 102.08, 80.19, 71.20, 61.37, 55.44, 55.26, 13.98 ppm.
Minor δ 169.35, 160.82, 159.65, 156.46, 129.93, 129.14, 128.10, 126.58, 120.75, 110.33, 107.61, 107.20, 101.92, 78.85, 71.41, 61.15, 55.39, 55.29, 13.96 ppm.

HRMS (FAB+) *m*/*z*: ([M+H]$^+$) calcd for $C_{19}H_{22}O_6$: 346.1416, found 346.1412.
IR: 3492, 2937, 2837, 1751, 1602, 1492, 1286, 1240, 1198, 1153, 1049cm^{-1}.

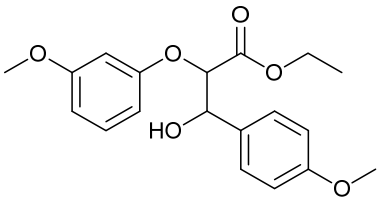


Ethyl 3-hydroxy-2-(3-methoxyphenoxy)-3-(3-methoxyphenyl)propanoate: The title compound was synthesized according to general procedure A. Yellow oil; yield = 59.1%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.27–7.24 (m, 1H both diastereomers), 7.19–7.08 (m, 1H both diastereomers), 7.05–6.96 (m, 2H both diastereomers), 6.90–6.80 (m, 1H both diastereomers), 6.55–6.51 (m, 1H both diastereomers), 6.46–6.42 (m, 2H both diastereomers) ppm,
Major δ 5.22–5.15 (m, 1H), 4.75 (d, J = 5.8 Hz, 1H), 4.22–4.11 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 3.04 (d, J = 4.3 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.12 (t, J = 5.1 Hz, 1H), 4.70 (d, J = 5.5 Hz, 1H), 4.12–4.05 (m, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 3.10 (d, J = 4.9 Hz, 1H), 1.09 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.50, 160.79, 159.62, 158.59, 140.71, 129.99, 129.40, 118.98, 113.94, 112.09, 107.96, 107.19, 101.93, 80.69, 74.12, 61.53, 55.29, 55.27, 14.03 ppm.
Minor δ 169.33, 160.83, 159.72, 158.69, 140.04, 130.05, 129.51, 119.05, 114.17, 112.19, 108.04, 107.19, 101.97, 81.61, 74.75, 61.57, 55.29, 55.27, 13.95 ppm.

HRMS (FAB+) m/z: ($[M+H]^+$) calcd for $C_{19}H_{22}O_6$: 347.1495, found 347.1490.
IR: 3486, 2933, 2837, 1741, 1602, 1492, 1284, 1198, 1154, 1041 cm^{-1}.

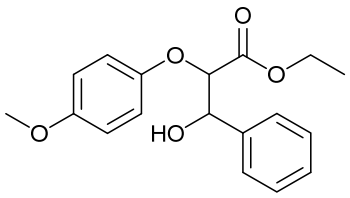


Ethyl 3-hydroxy-2-(3-methoxyphenoxy)-3-(4-methoxyphenyl)propanoate: The title compound was synthesized according to general procedure A. Yellow oil; yield = 63.8%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.41–7.32 (m, 2H both diastereomers), 7.17–7.08 (m, 1H both diastereomers), 6.93–6.84 (m, 2H both diastereomers), 6.60–6.38 (m, 3H both diastereomers) ppm,
Major δ 5.14 (dd, J = 5.4, 4.5 Hz, 1H), 4.73 (d, J = 5.9 Hz, 1H), 4.22–4.11 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 2.89 (d, J = 4.5 Hz, 1H), 1.15 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.10–5.06 (m, 1H), 4.68 (d, J = 5.9 Hz, 1H), 4.12–4.01 (m, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.01 (d, J = 4.4 Hz, 1H), 1.07 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.62, 160.80, 159.59, 158.71, 131.29, 129.95, 127.96, 113.78, 107.95, 107.28, 102.02, 80.85, 73.87, 61.47, 55.30, 55.28, 14.05 ppm.
Minor δ 169.32, 160.87, 159.77, 158.73, 130.40, 130.05, 128.16, 113.87, 108.04, 107.20, 101.98, 81.81, 74.49, 61.45, 55.30, 55.28, 13.94 ppm.

HRMS (FAB+) m/z: ($[M+H]^+$) calcd for $C_{19}H_{22}O_6$: 347.1495, found 347.1494.
IR: 3478, 2938, 2837, 1742, 1604, 1514, 1492, 1270, 1198, 1153, 1033cm^{-1}.

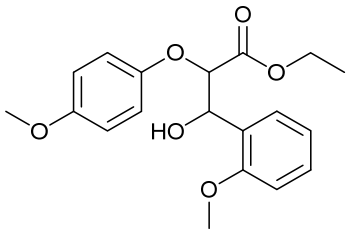


Ethyl 3-hydroxy-2-(4-methoxyphenoxy)-3-phenylpropanoate: The title compound was synthesized according to general procedure A. Pale yellow oil; yield = 66.4%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.46–7.42 (m, 2H both diastereomers), 7.38–7.26 (m, 3H both diastereomers), 6.83–6.72 (m, 4H both diastereomers)ppm,
Major δ 5.19–5.16 (m, 1H), 4.67 (d, J = 5.9 Hz, 1H), 4.20–4.09 (m, 2H), 3.72 (s, 3H), 3.04 (d, J = 4.4 Hz, 1H), 1.12 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.13 (t, J = 4.9 Hz, 1H), 4.61 (d, J = 5.6 Hz, 1H), 4.09–4.02 (m, 2H), 3.73 (s, 3H), 3.12 (d, J = 4.9 Hz, 1H), 1.06 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.79, 154.88, 151.66, 139.20, 128.34, 128.28, 126.71, 117.10, 114.63, 82.11, 74.21, 61.40, 55.64, 13.99 ppm.
Minor δ 169.58, 154.98, 151.70, 138.57, 128.56, 128.46, 126.79, 117.11, 114.69, 83.09, 74.94, 61.42, 55.64, 13.90 ppm.

HRMS (FAB+) *m/z*: ([M+H]$^+$) calcd for $C_{18}H_{20}O_5$: 316.1311, found 316.1313.
IR: 3458, 2934, 2835, 1741, 1506, 1455, 1292, 1224, 1032cm^{-1}.



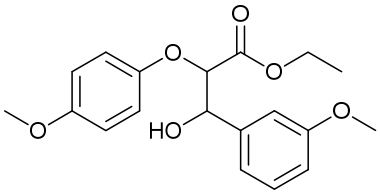
Ethyl 3-hydroxy-2-(4-methoxyphenoxy)-3-(2-methoxyphenyl)-propanoate: The title compound was synthesized according to general procedure A. Yellow oil; yield = 48.3%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.44 (m, 1H), 7.32–7.24 (m, 1H), 7.03–6.94 (m, 1H), 6.92–6.67 (m, 5H) ppm,
Major δ 5.44 (dd, J = 7.4, 4.7 Hz, 1H), 4.80 (d, J = 4.7 Hz, 1H), 4.17–4.11 (m, 2H), 3.84 (s, 3H), 3.72 (s, 3H), 3.23 (d, J = 7.4 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.36 (t, J = 5.8 Hz, 1H), 4.91 (d, J = 5.4 Hz, 1H), 4.13–4.04 (m, 2H), 3.86 (s, 3H), 3.74 (s, 3H), 3.43 (t, J = 4.7 Hz, 1H), 1.08 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

Major δ 169.93, 156.44, 154.73, 152.23, 129.18, 128.08, 127.21, 120.77, 117.19, 114.54, 110.36, 81.55, 71.04, 61.30, 55.62, 55.42, 14.01 ppm.
Minor δ 169.66, 156.49, 154.68, 151.66, 129.09, 128.13, 126.80, 120.73, 116.86, 114.61, 110.35, 80.13, 71.38, 61.06, 55.66, 55.40, 13.97 ppm.

HRMS (FAB+) *m*/*z*: ([M+H]$^+$) calcd for $C_{19}H_{22}O_6$: 346.1416, found 346.1420.
IR: 3491, 2954, 2837, 1748, 1507, 1464, 1287, 1239, 1077, 1029 cm^{-1}.

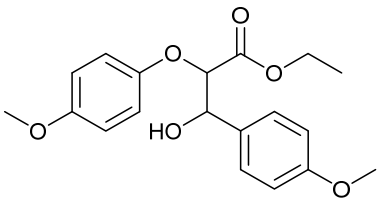


Ethyl 3-hydroxy-2-(4-methoxyphenoxy)-3-(3-methoxyphenyl)propanoate: The title compound was synthesized according to general procedure A. Yellow oil; yield = 68.8%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.28–7.25(m, 1H), 7.03–6.98(m, 2H), 6.89–6.82 (m, 1H), 6.82–6.73 (m, 4H) ppm,
Major δ 5.19–5.13 (m, 1H), 4.66 (d, J = 5.9 Hz, 1H), 4.20–4.11 (m, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 2.98 (t, J = 4.2 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.11 (t, J = 5.2 Hz, 1H), 4.61 (d, J = 5.4 Hz, 1H), 4.12–4.07 (m, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 3.09–3.01 (m, 1H), 1.10 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.75, 159.65, 154.89, 151.65, 140.84, 129.35, 119.03, 117.09, 114.63, 113.92, 112.17, 82.04, 74.13, 61.40, 55.65, 55.26, 14.00 ppm.
Minor δ 169.57, 159.74, 154.99, 151.71, 140.26, 129.46, 119.03, 117.13, 114.69, 114.10, 112.21, 83.01, 74.79, 61.44, 55.65, 55.28, 13.94 ppm.

HRMS (FAB+) *m*/*z*: ([M+H]$^+$) calcd for $C_{19}H_{22}O_6$: 346.1416, found 346.1414.
IR: 3493, 3002, 2837, 1739, 1601, 1507, 1226, 1038 cm^{-1}.



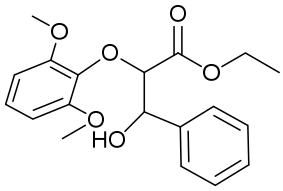
Ethyl 3-hydroxy-2-(4-methoxyphenoxy)-3-(4-methoxyphenyl)propanoate: The title compound was synthesized according to general procedure A. Pale yellow oil; yield = 60.1%; No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.40–7.32 (m, 2H both diastereomers), 6.91–6.86 (m, 2H both diastereomers), 6.85–6.74 (m, 4H both diastereomers) ppm,

Major δ 5.12 (d, J = 6.0 Hz, 1H), 4.64 (d, J = 6.0 Hz, 1H), 4.21–4.10 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 2.89 (br, 1H), 1.16 (t, J = 7.1 Hz, 3H) ppm.
Minor δ 5.07 (d, J = 5.9 Hz, 1H), 4.58 (d, J = 5.9 Hz, 1H), 4.10–4.01 (m, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 3.03 (br, 1H), 1.07 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)
Major δ 169.91, 159.55, 154.83, 151.72, 131.39, 127.98, 117.09, 114.59, 113.74, 82.14, 73.84, 61.38, 55.63, 55.27, 14.04 ppm.
Minor δ 169.58, 159.72, 154.94, 151.68, 130.53, 128.12, 117.03, 114.68, 113.84, 83.13, 74.53, 61.36, 55.64, 55.29, 13.94 ppm.

HRMS (FAB+) m/z: ([M+H]$^+$) calcd for $C_{19}H_{22}O_6$: 346.1416, found 346.1419.
IR: 3468, 2936, 2836, 1741, 1612, 1507, 1225, 1180, 1032 cm^{-1}.



Ethyl 2-(2,6-dimethoxyphenoxy)-3-hydroxy-3-phenylpropanoate: The title compound was synthesized according to general procedure A. Yellow oil; yield = 52.9%.

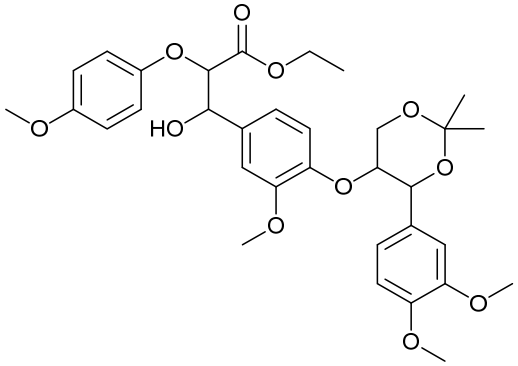
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.42–7.40 (m, 2H), 7.35–7.30 (m, 2H), 7.27 (m, 1H), 7.04 (t, J = 8.4 Hz, 1H), 6.60 (d, J = 8.4 Hz, 2H), 5.01 (dd, J = 7.2, 3.8 Hz, 1H), 4.74 (d, J = 3.8 Hz, 1H), 4.67 (d, J = 7.2 Hz, 1H), 4.12–3.96 (m, 2H), 3.85 (s, 6H), 1.01 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 168.62, 152.88, 138.82, 136.09, 128.07, 127.73, 126.62, 124.44, 105.33, 85.73, 73.62, 60.67, 56.17, 13.94 ppm.

HRMS (FAB+) m/z: ([M+H]$^+$) calcd for $C_{19}H_{22}O_6$: 347.1495, found 347.1501.
IR: 3475, 2941, 2841, 1749, 1599, 1479, 1297, 1256, 1111, 1031 cm^{-1}.

Synthesis of Lignin Model Compound (Trimer 21 – Scheme 4)

The trimeric lignin model compound was prepared following the same procedure in the literature.[3]

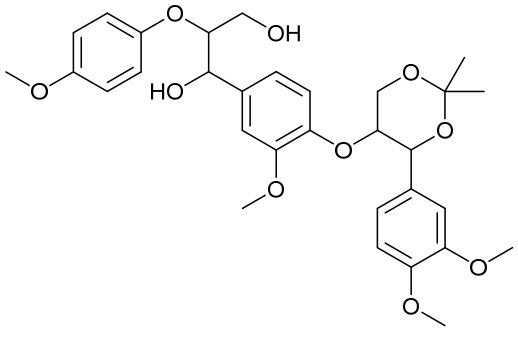


Ethyl 3-(4-((4-(3,4-dimethoxyphenyl)-2,2-dimethyl-1,3-dioxan-5-yl)oxy)-3-methoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propanoate: The title compound was synthesized according to reference. [3] White sticky semi-solid; mp = 50.2–51.2 °C; yield = 69% (unoptimized). No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.17 (m, 1H), 6.99–6.91 (m, 2H), 6.82–6.71 (m, 6H), 6.49–6.41 (m, 1H), 5.10–5.00 (m, 2H), 4.58–4.49 (m, 1H), 4.18–4.02 (m, 5H), 3.86 (m, 6H), 3.76–3.70 (m, 6H), 2.89 (m, 1H), 1.61 (s,3H), 1.58 (s, 3H), 1.16–1.04 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 169.89, 154.86, 151.68, 151.27, 148.72, 148.50, 147.43, 134.05, 131.18, 119.65, 119.38, 119.25, 117.11, 117.04, 114.60, 111.67, 111.62, 111.04, 110.60, 99.33, 82.00, 74.94, 73.90, 73.17, 62.48, 61.40, 56.15, 55.95, 55.87, 55.64, 29.10, 19.24, 14.04 ppm.

HRMS (FAB+) *m*/*z*: ([M+H]$^{+}$) calcd for $C_{33}H_{40}O_{11}$: 612.2571, found 612.2579
IR: 3478, 2992, 2836, 1742, 1507, 1465, 1420, 1380, 1266, 1231, 1197, 1085 cm^{-1}.



1-(4-((4-(3,4-Dimethoxyphenyl)-2,2-dimethyl-1,3-dioxan-5-yl)oxy)-3-methoxyphenyl)-2-(4-methoxyphenoxy)propane-1,3-diol: The title compound was synthesized according to reference.[3] White sticky semi-solid; mp = 54.1–55.6 °C; yield = 94.4% (unoptimized). No attempt was made to separate the diastereomers mixture.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.06–7.00(m, 2H), 6.92–6.68 (m, 7H), 6.48–6.44(m, 1H), 4.95–4.87 (m, 2H), 4.21–4.09 (m, 3H), 4.04–3.97(m, 1H), 3.88–3.69 (m, 13H), 3.64–3.43 (m, 1H), 2.80–2.62 (m, 1H), 2.14–1.71 (m, 1H), 1.64 (s, 3H), 1.51 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 154.80, 151.97, 150.45, 148.81, 148.68, 148.65, 134.93, 131.77, 119.83, 118.57, 118.28, 118.09, 117.22, 114.81, 114.72, 110.90, 110.60, 110.11, 99.50, 84.48, 83.38, 74.59, 73.65, 62.84, 61.28, 55.93, 55.85, 55.80, 55.66, 28.54, 19.67 ppm.

HRMS (FAB+) *m*/*z*: ($[M+H]^+$) calcd for $C_{31}H_{38}O_{10}$: 570.2465, found 570.2473
IR: 3510, 2939, 2836, 1506, 1465, 1420, 1379, 1270, 1222, 1161, 1140, 1031 cm^{-1}.

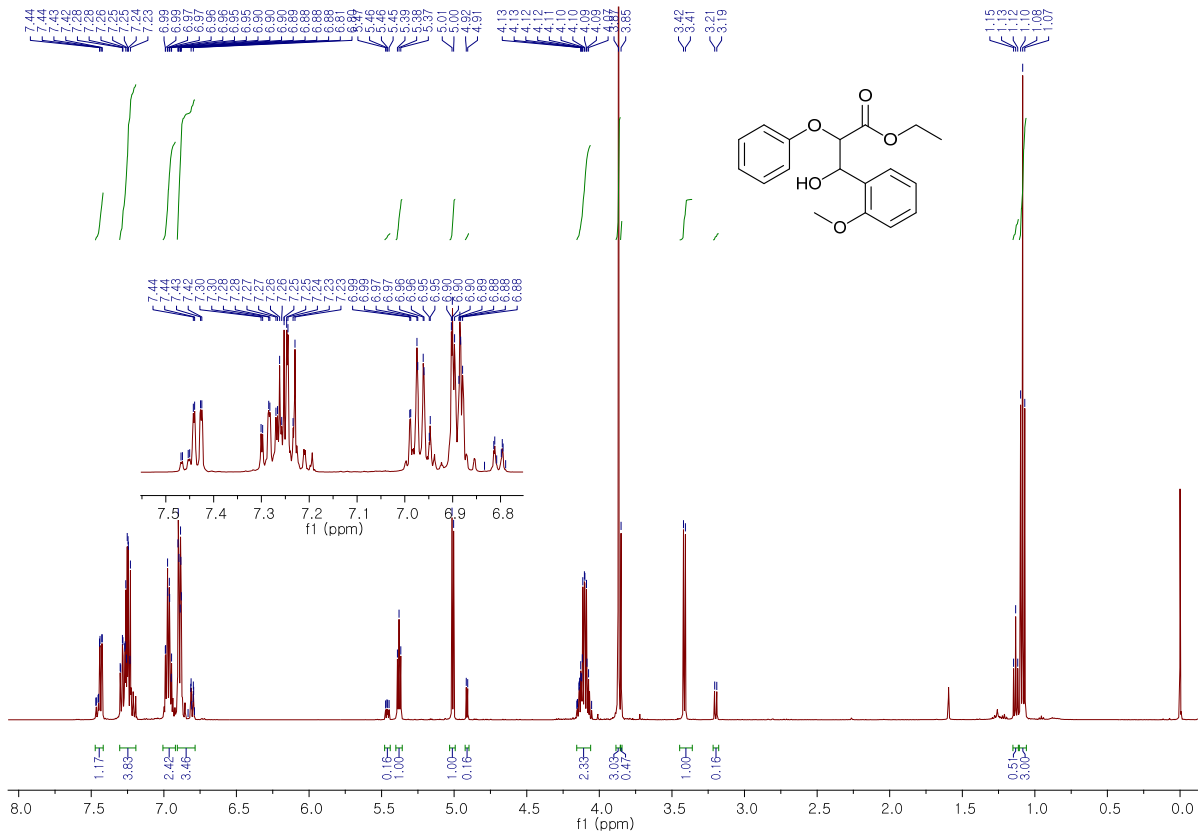
References

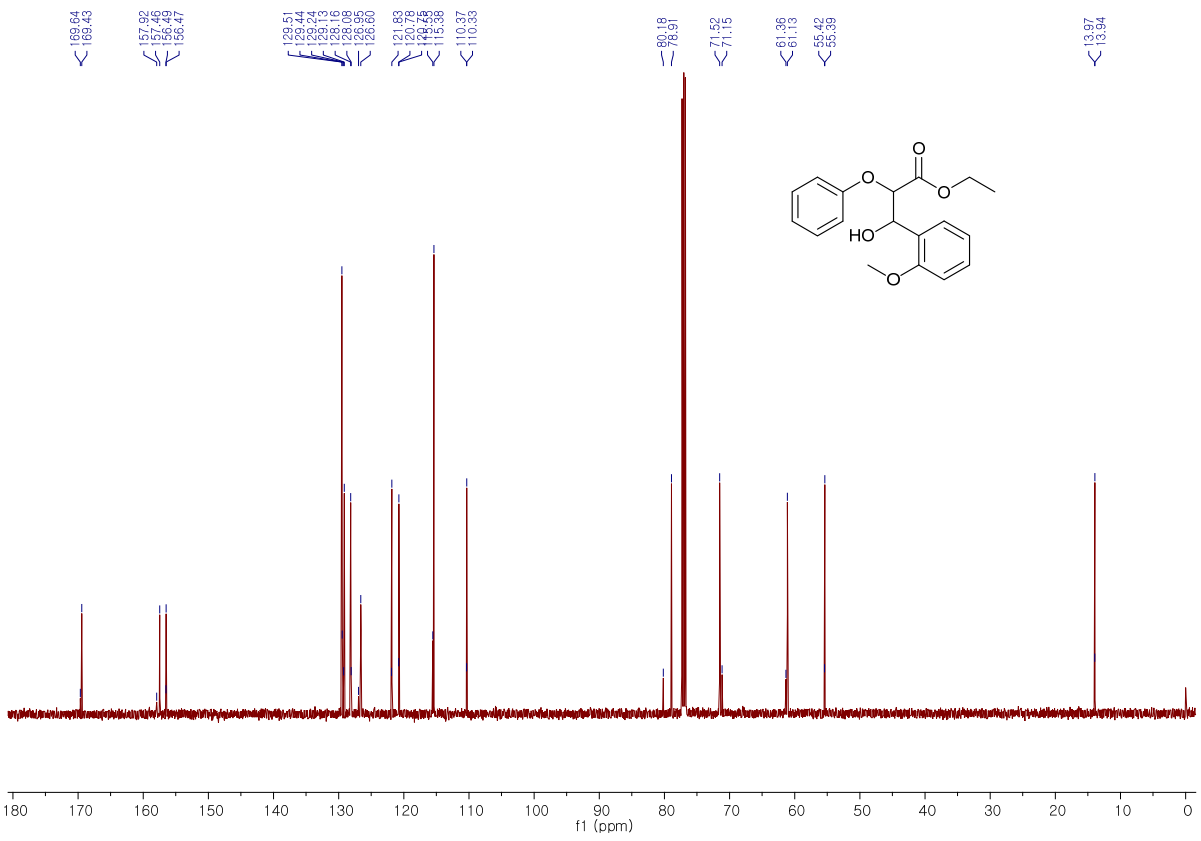
[1] E. Feghali, T. Cantat, *Chem. Commun.,* 2014, **50,** 862.

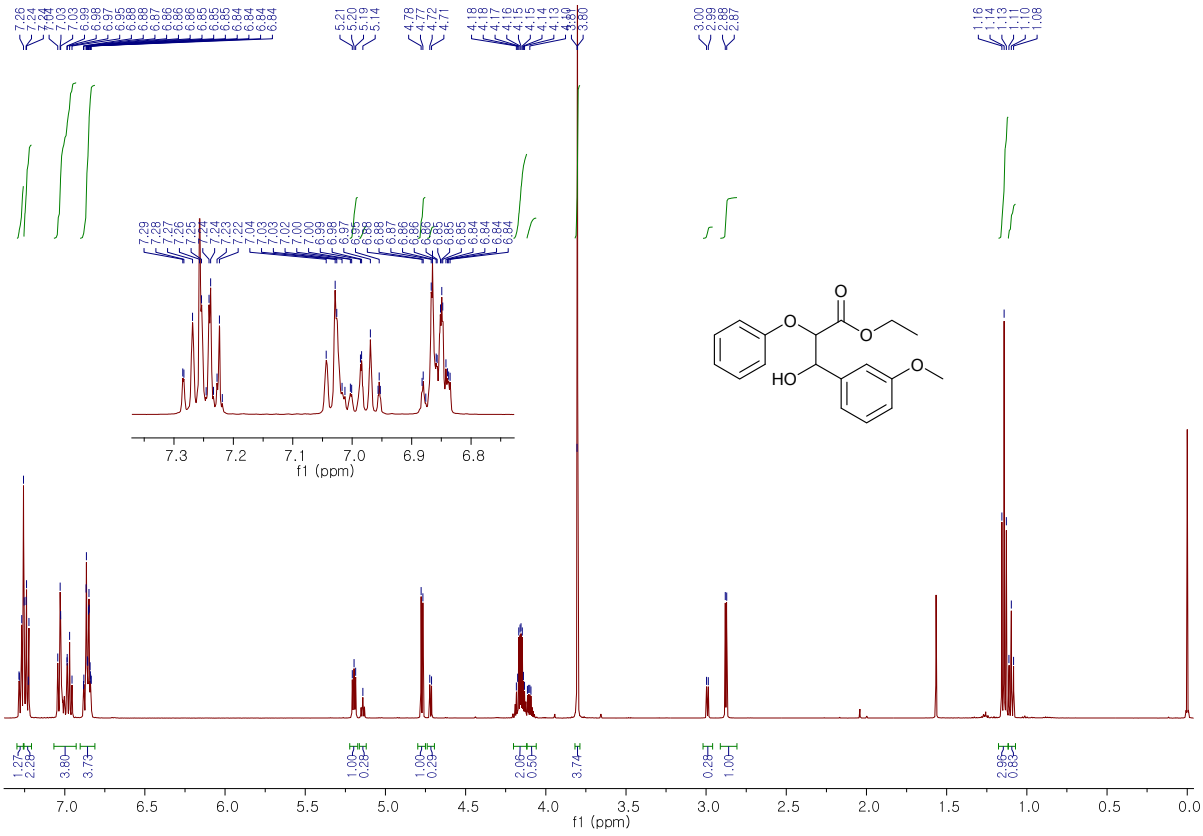
[2] D. W. Cho, J. A. Latham, H. J. Park, U. C. Yoon, P. Langan, D. Dunaway-Mariano and P. S. Mariano, *J. Org. Chem.*, 2011, **76**, 2840.

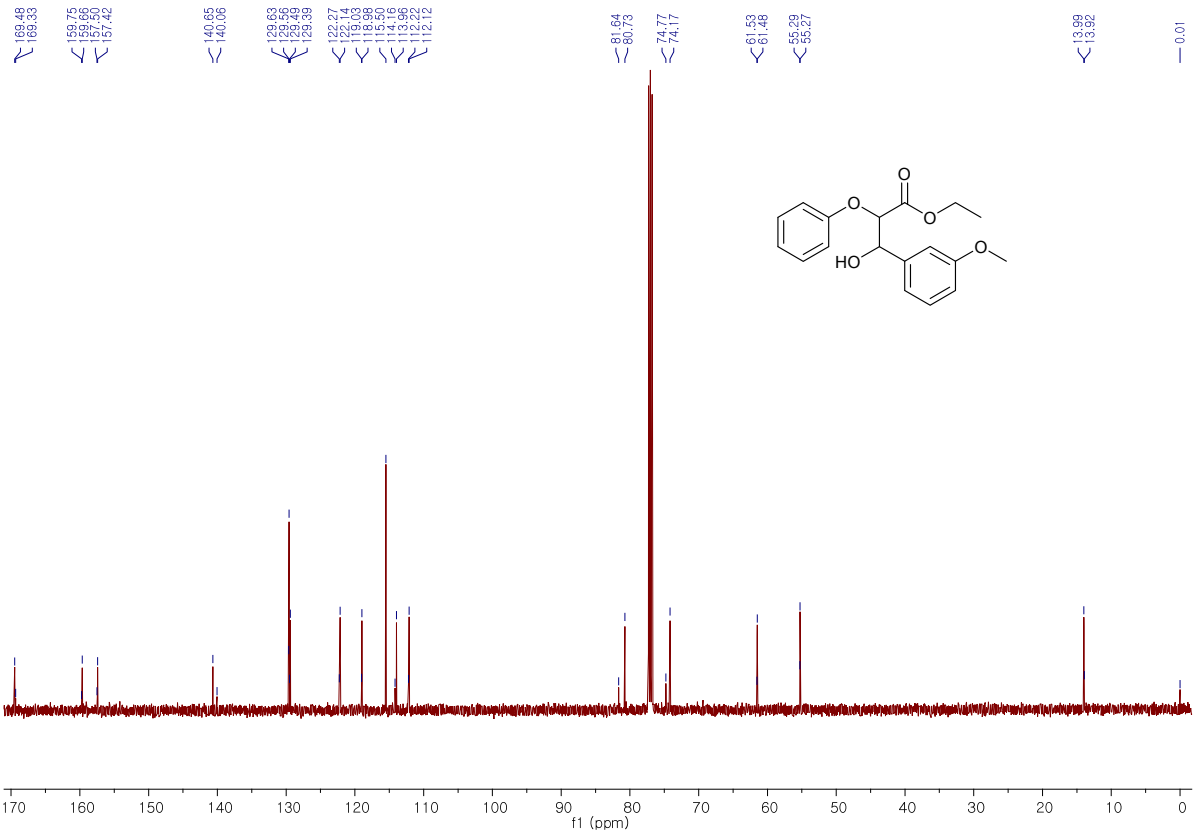
[3] E. Baciocchi, C. Fabbri and O. Lanzalunga, *J. Org. Chem.*, 2003, **68**, 9061.

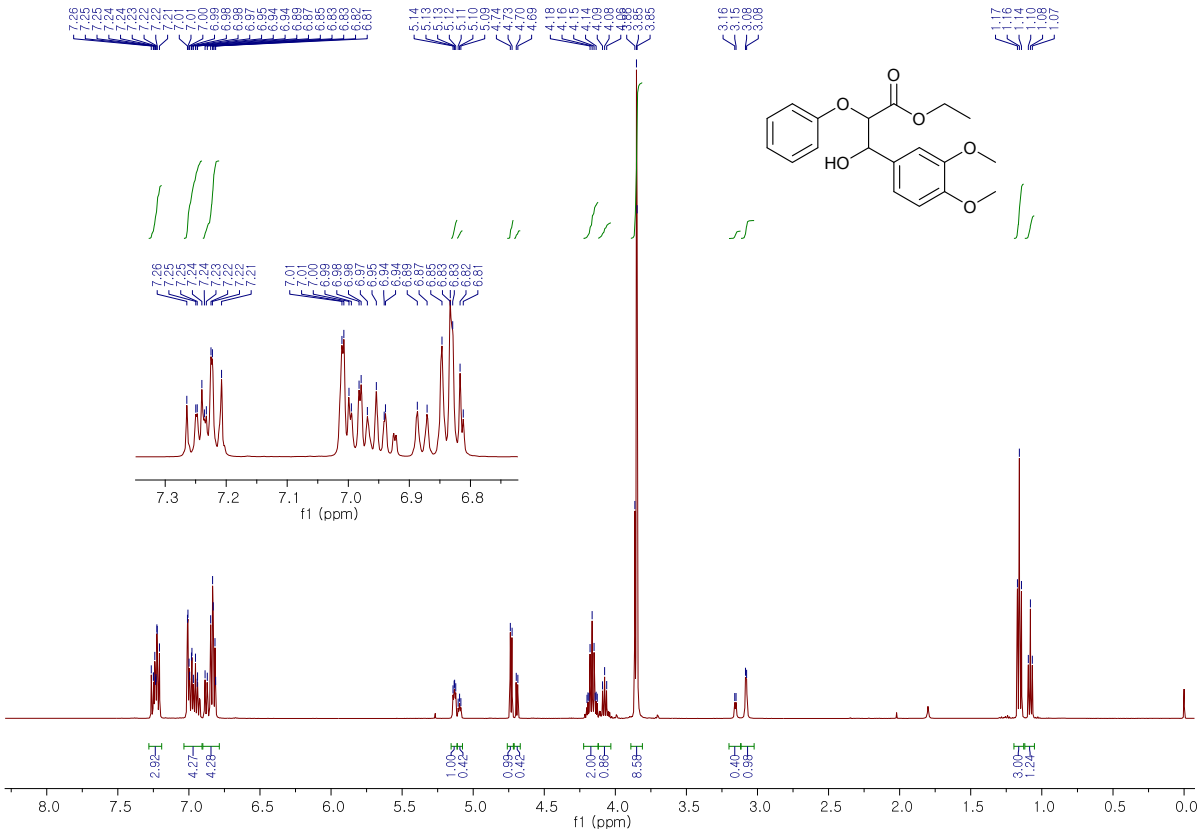
^{1}H NMR and ^{13}C NMR Spectra of Materials

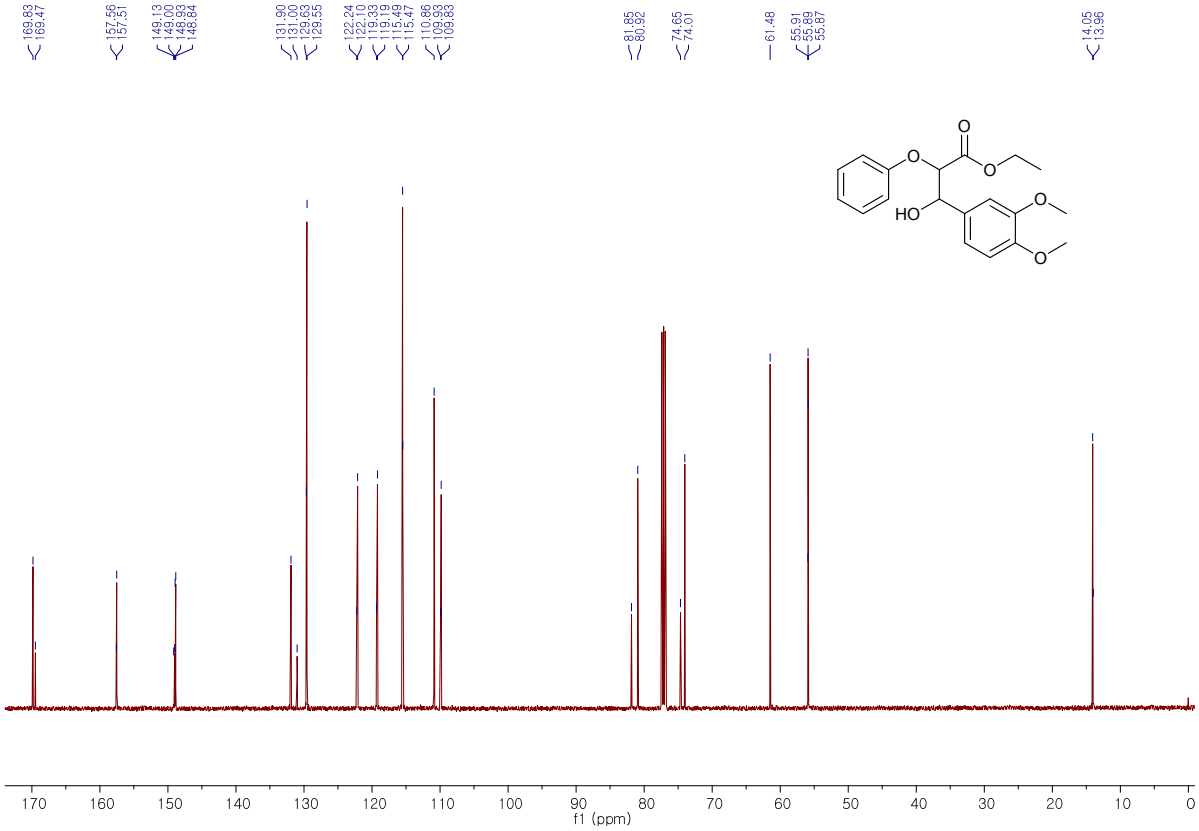


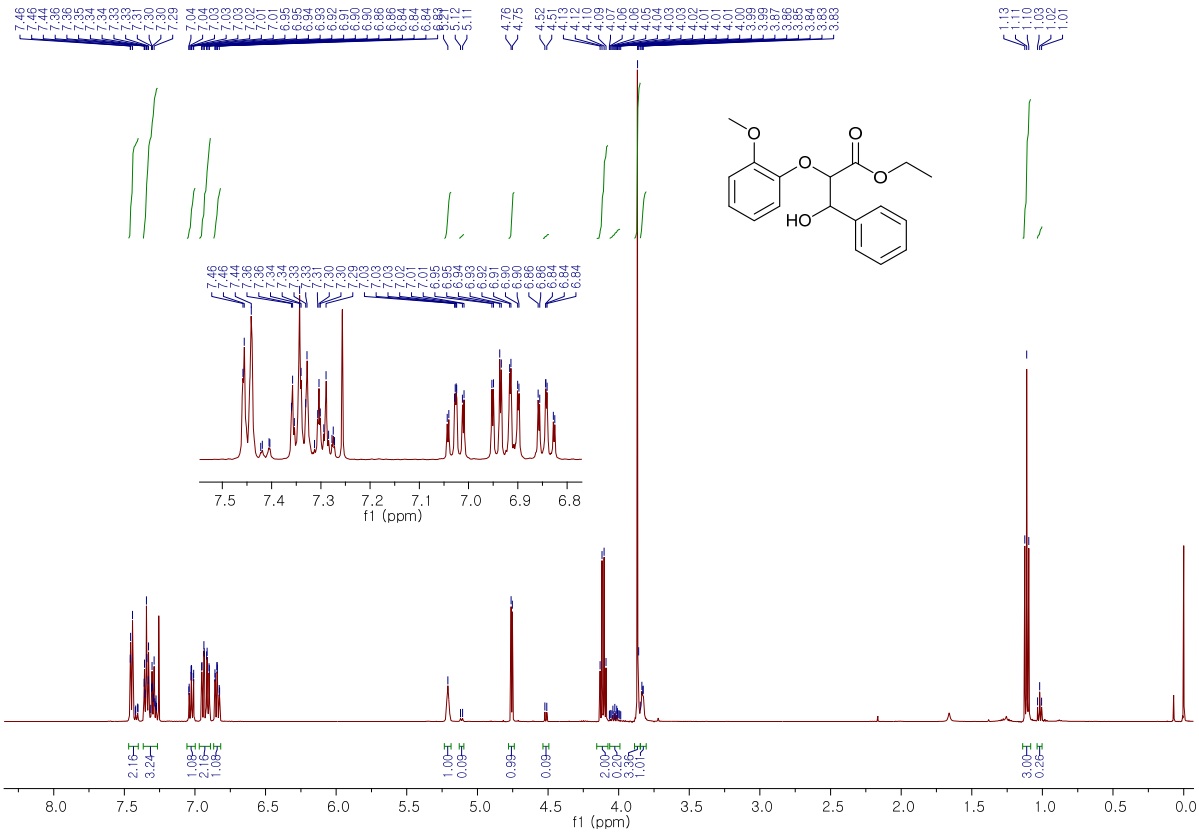


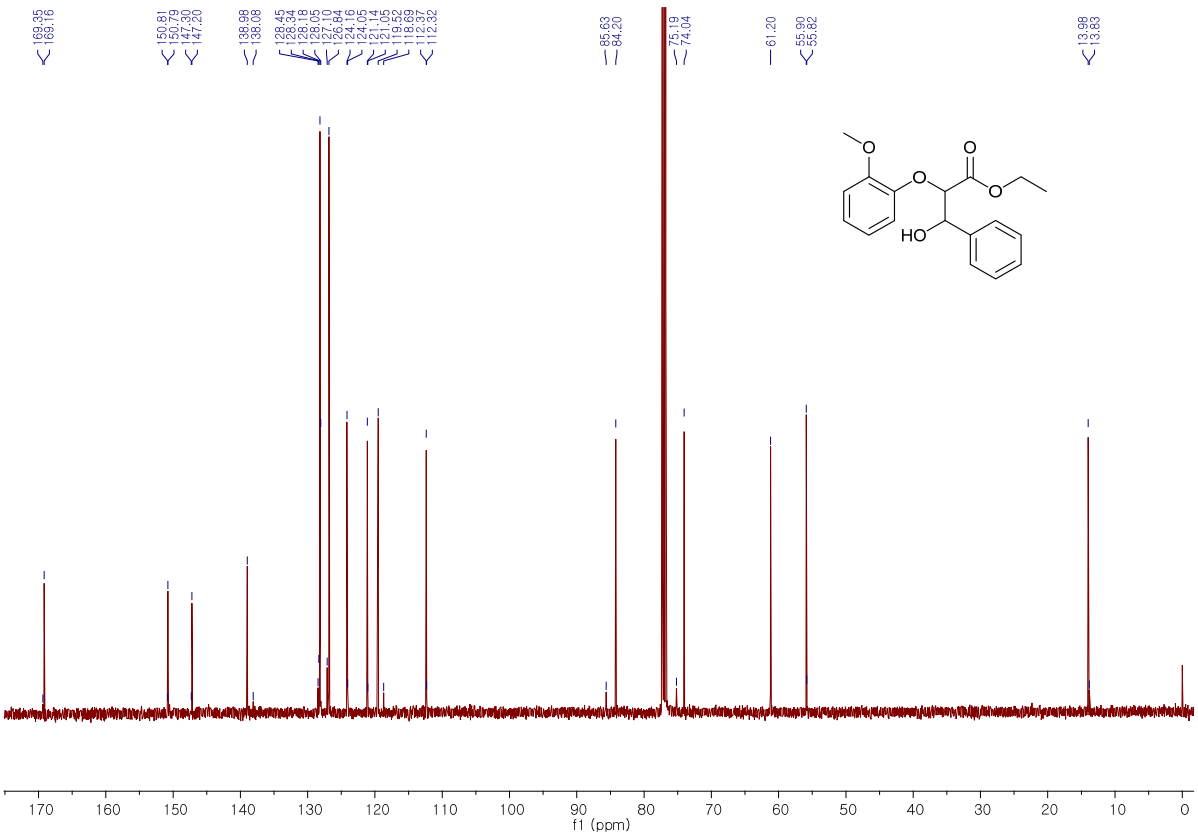

f1 (ppm)

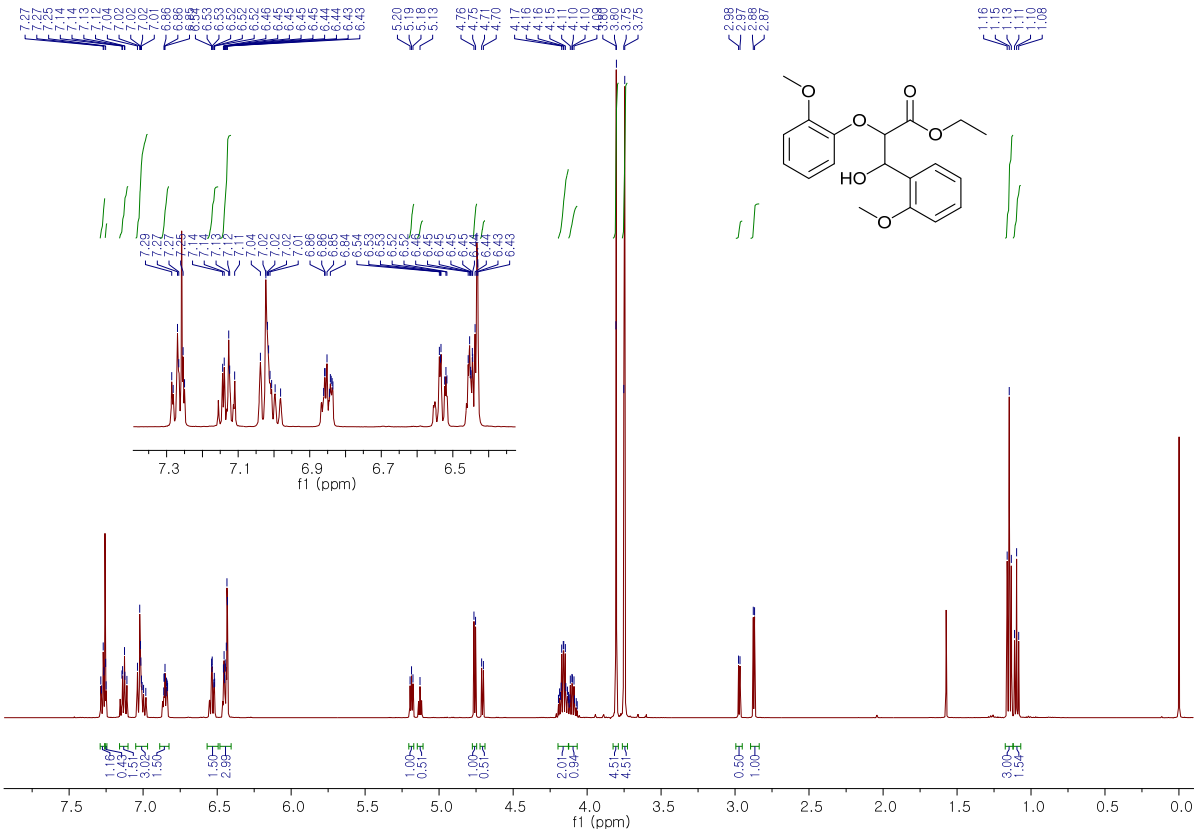

f1 (ppm)

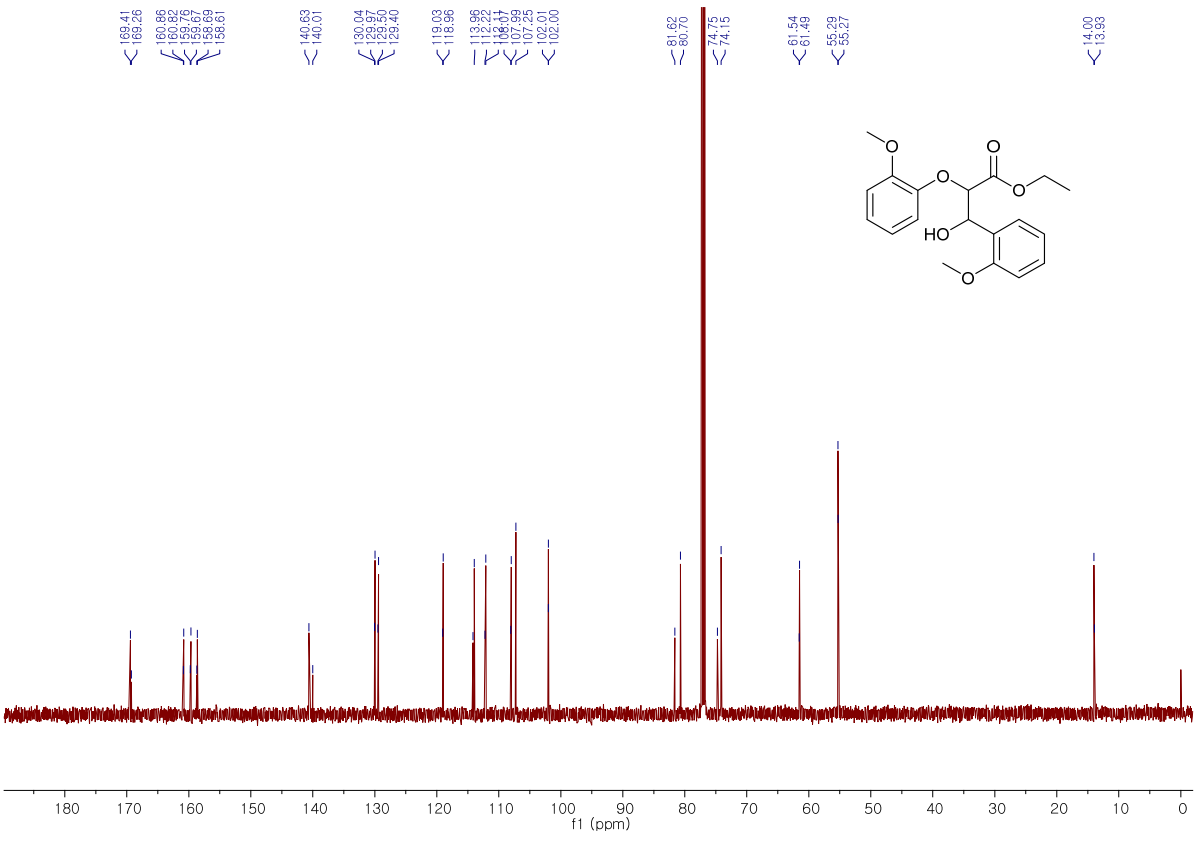

f1 (ppm)

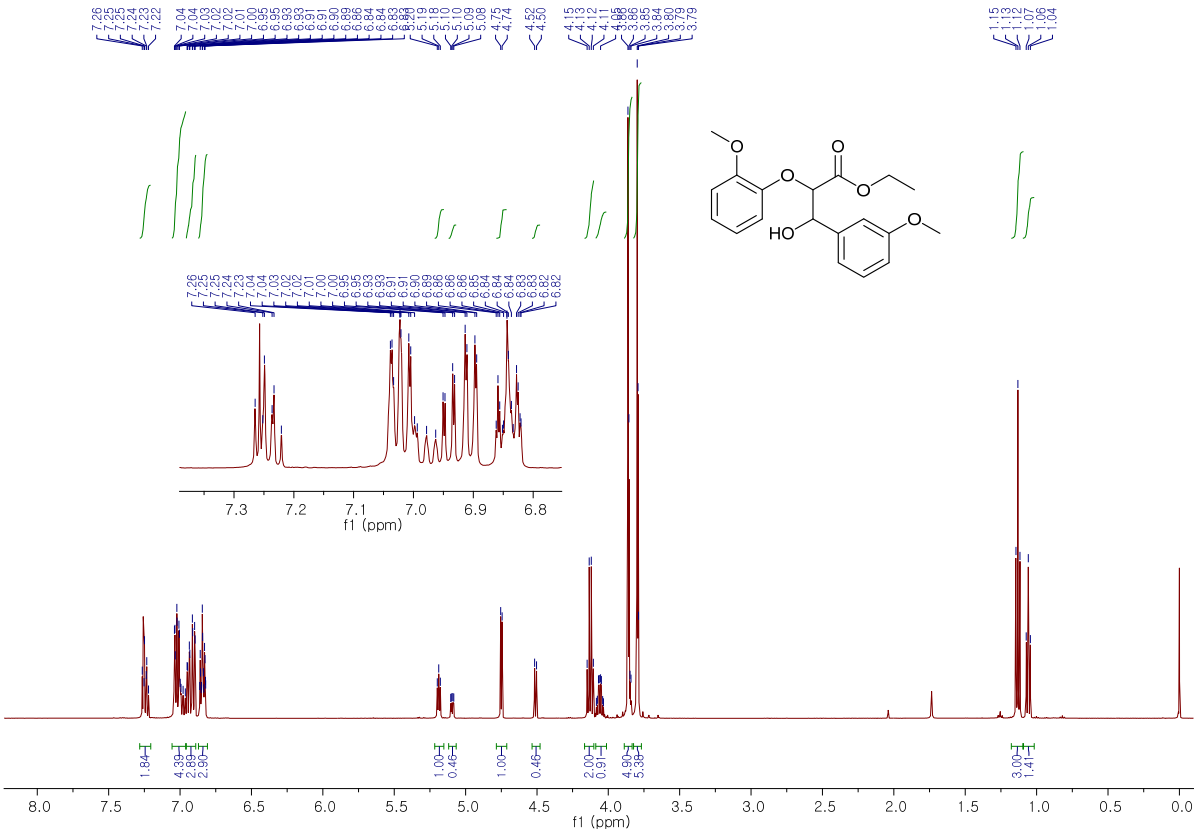

f1 (ppm)

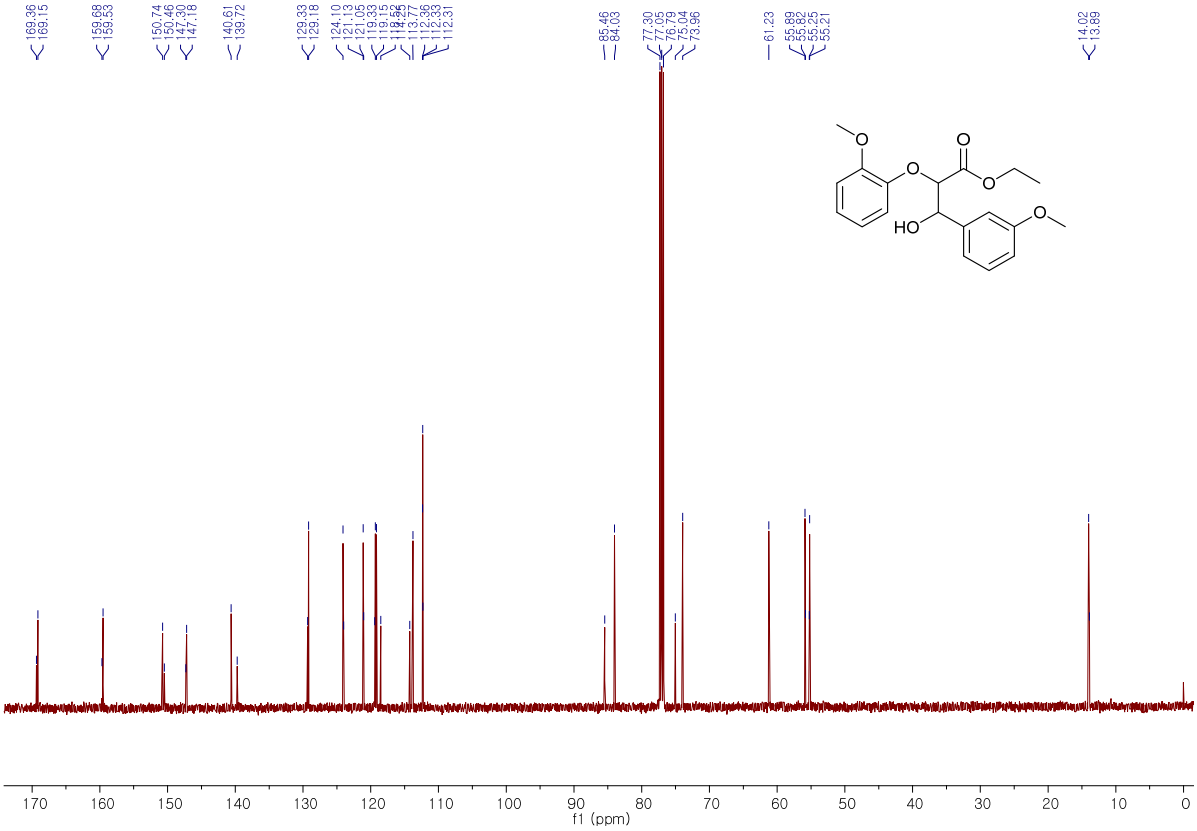

f1 (ppm)

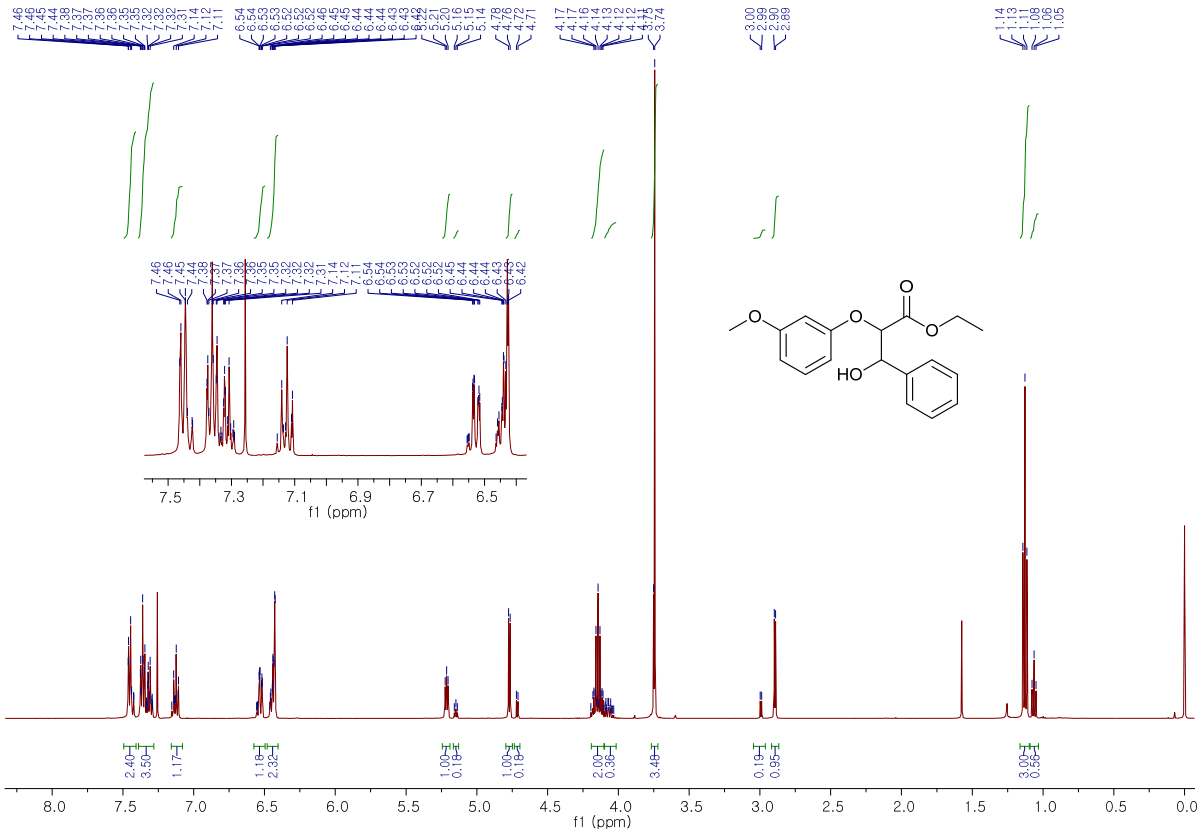

f1 (ppm)

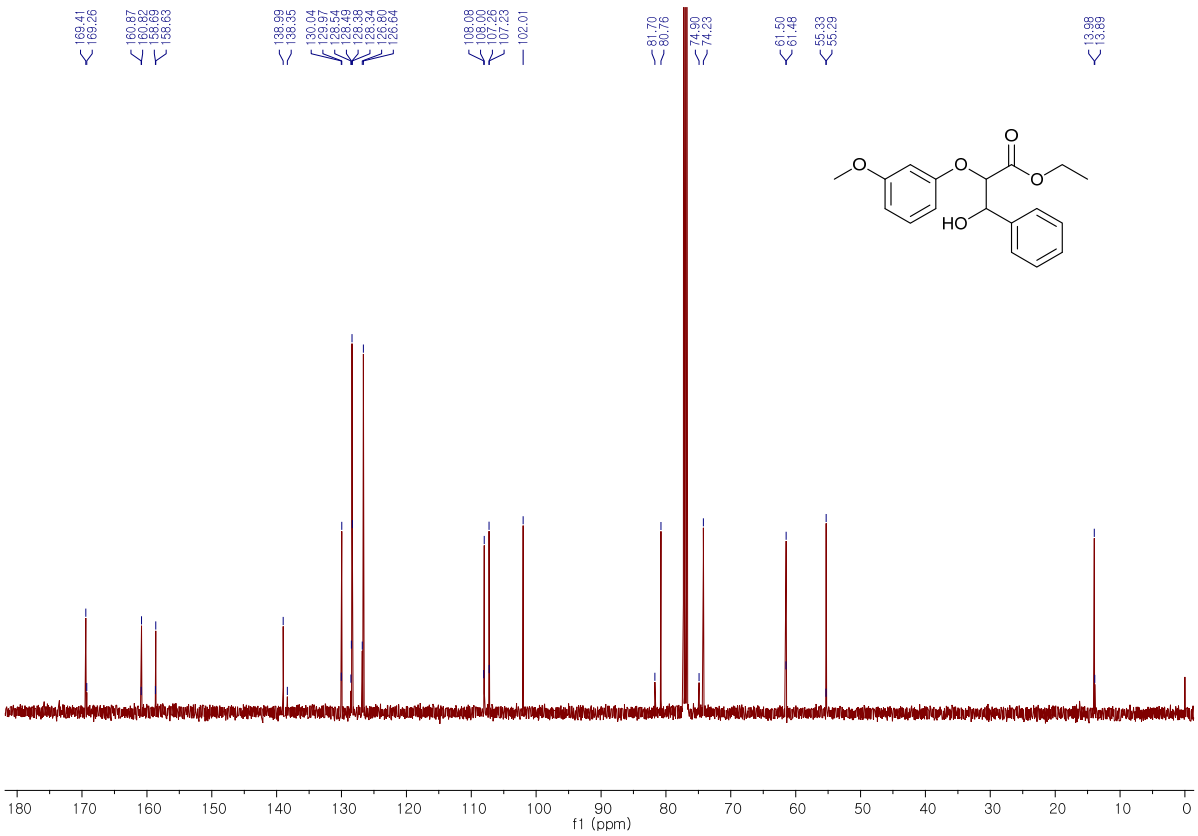

f1 (ppm)

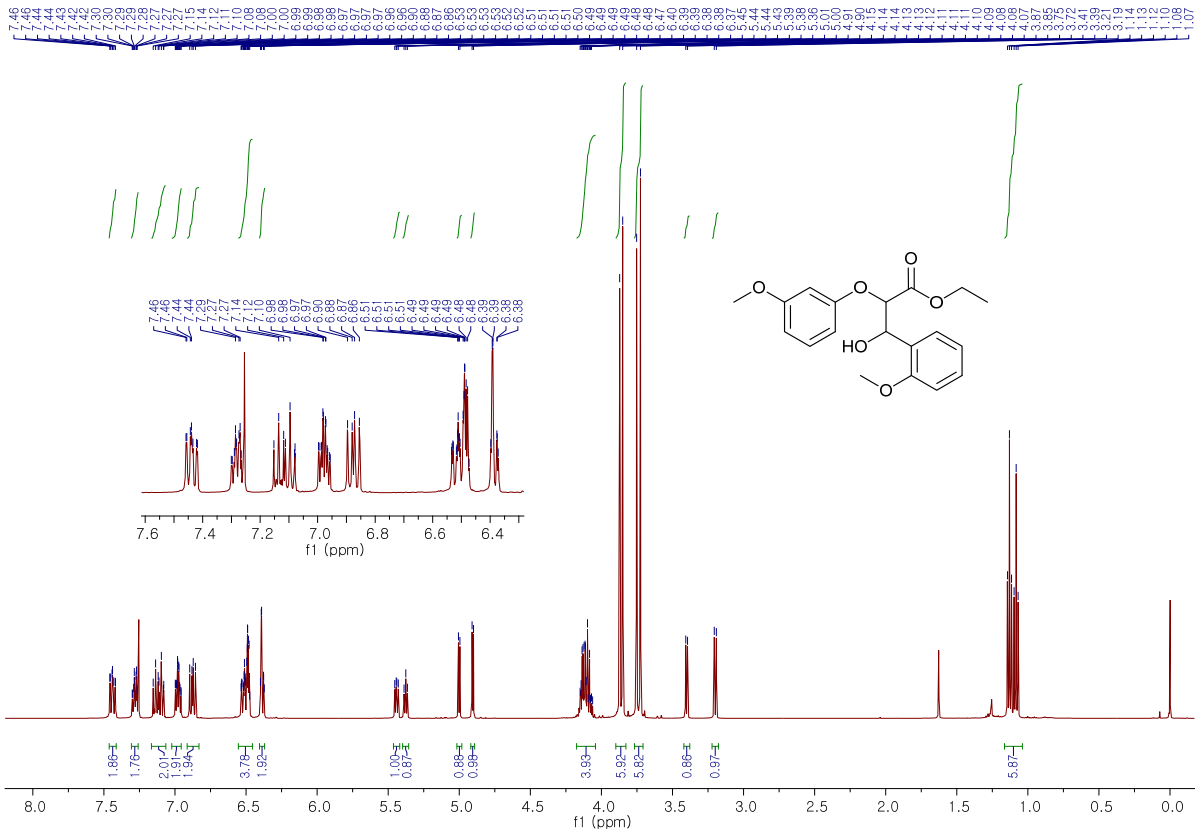

f1 (ppm)

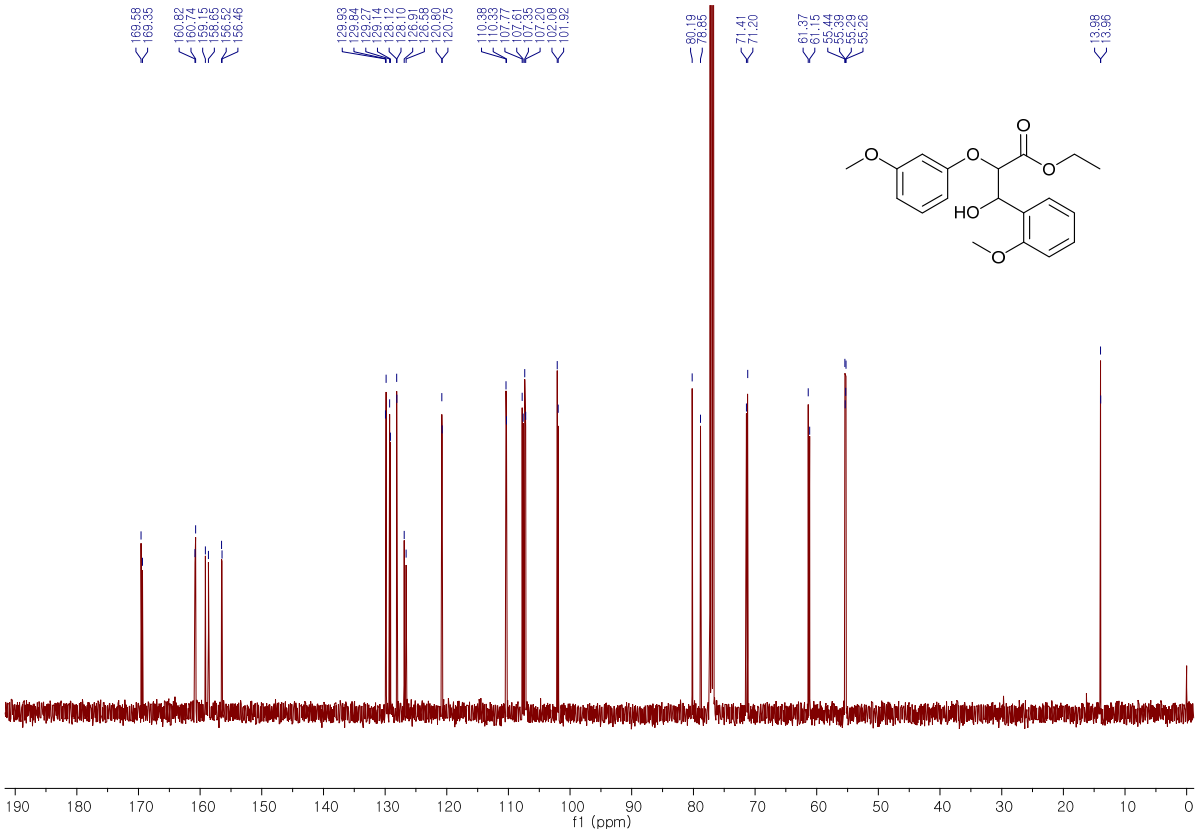

f1 (ppm)

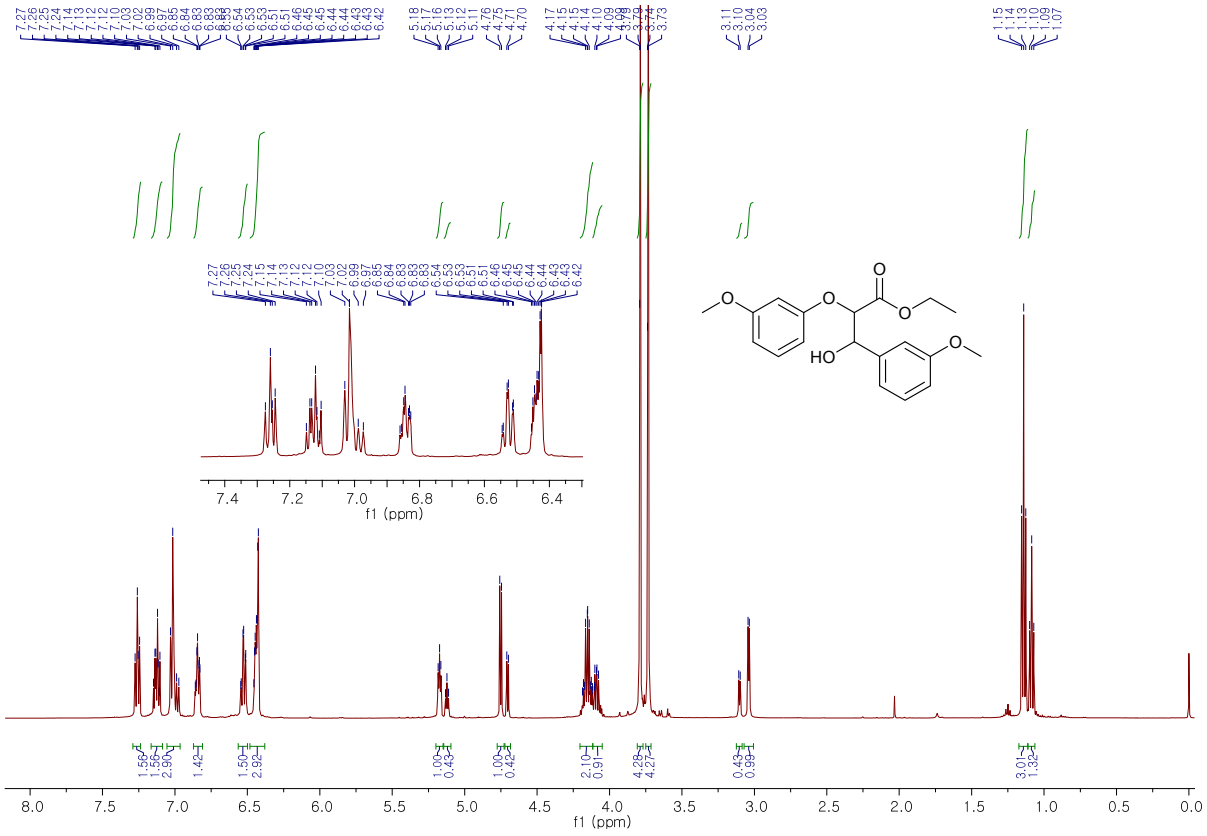

f1 (ppm)

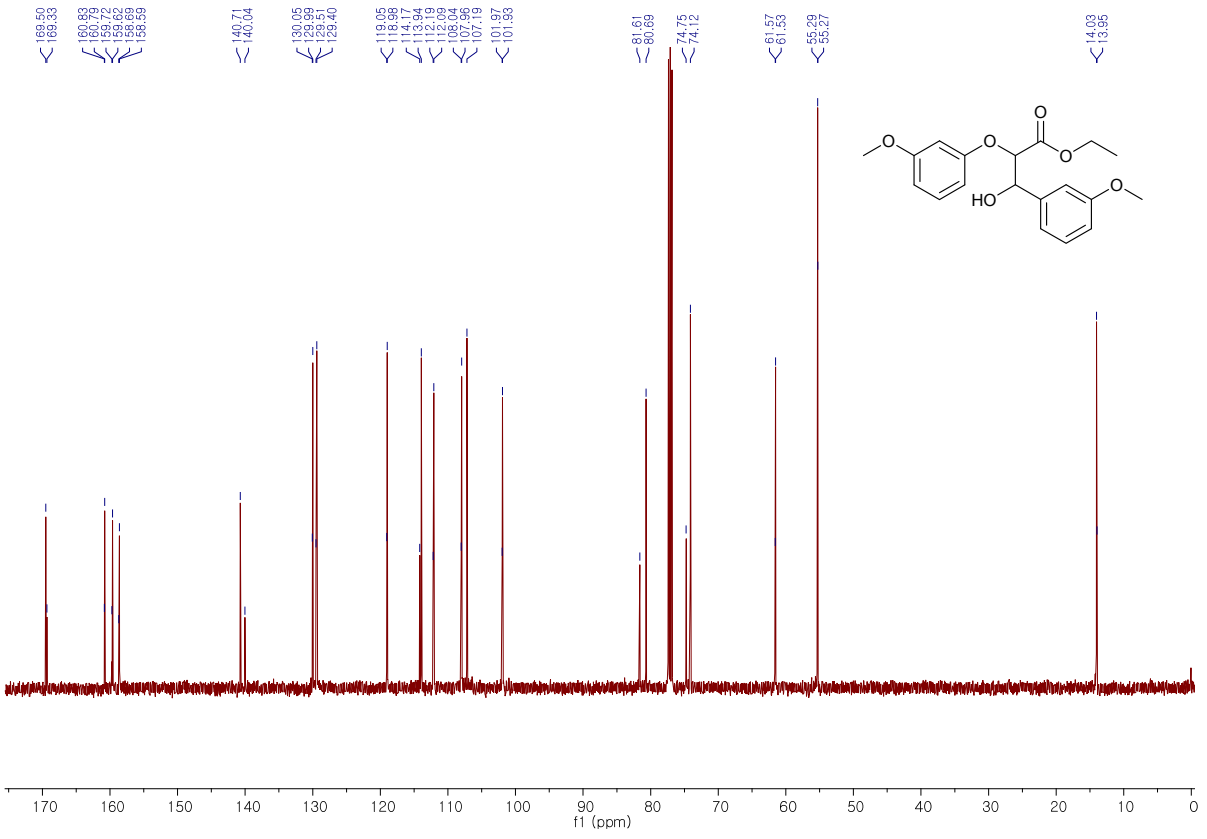

f1 (ppm)

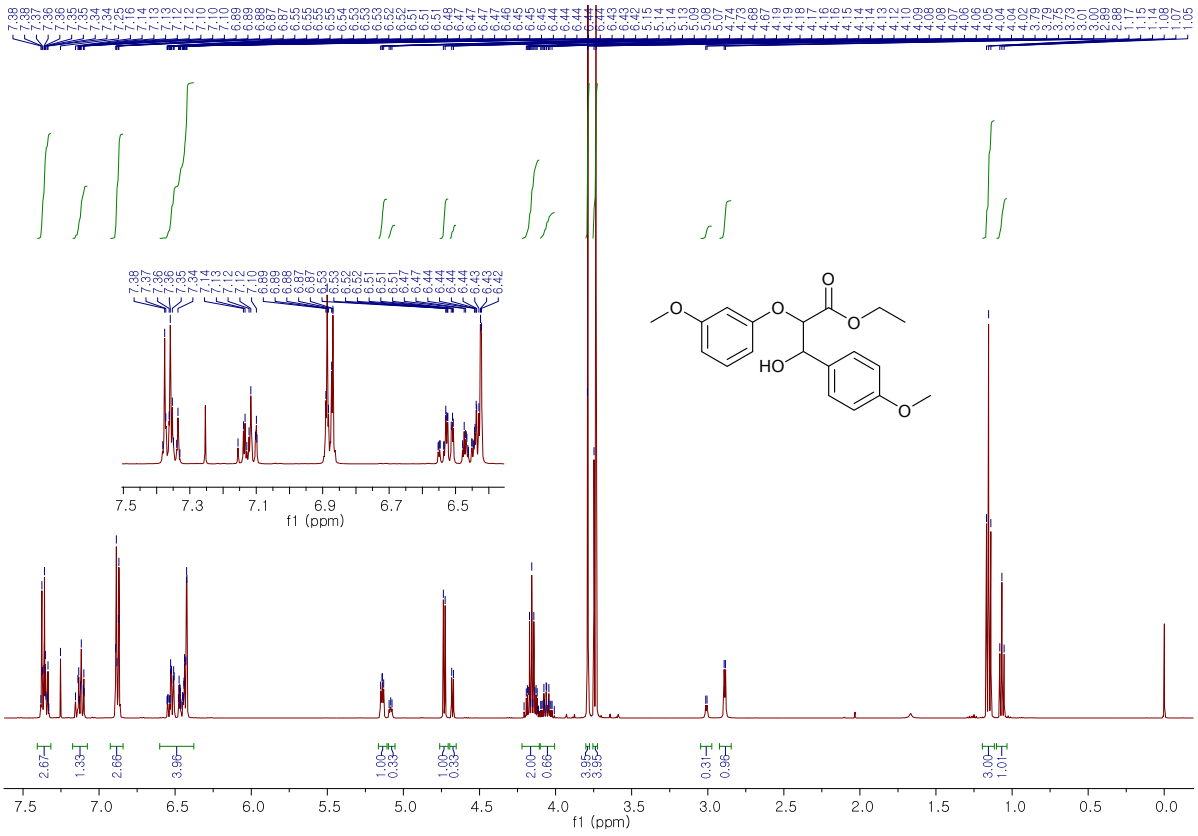

f1 (ppm)

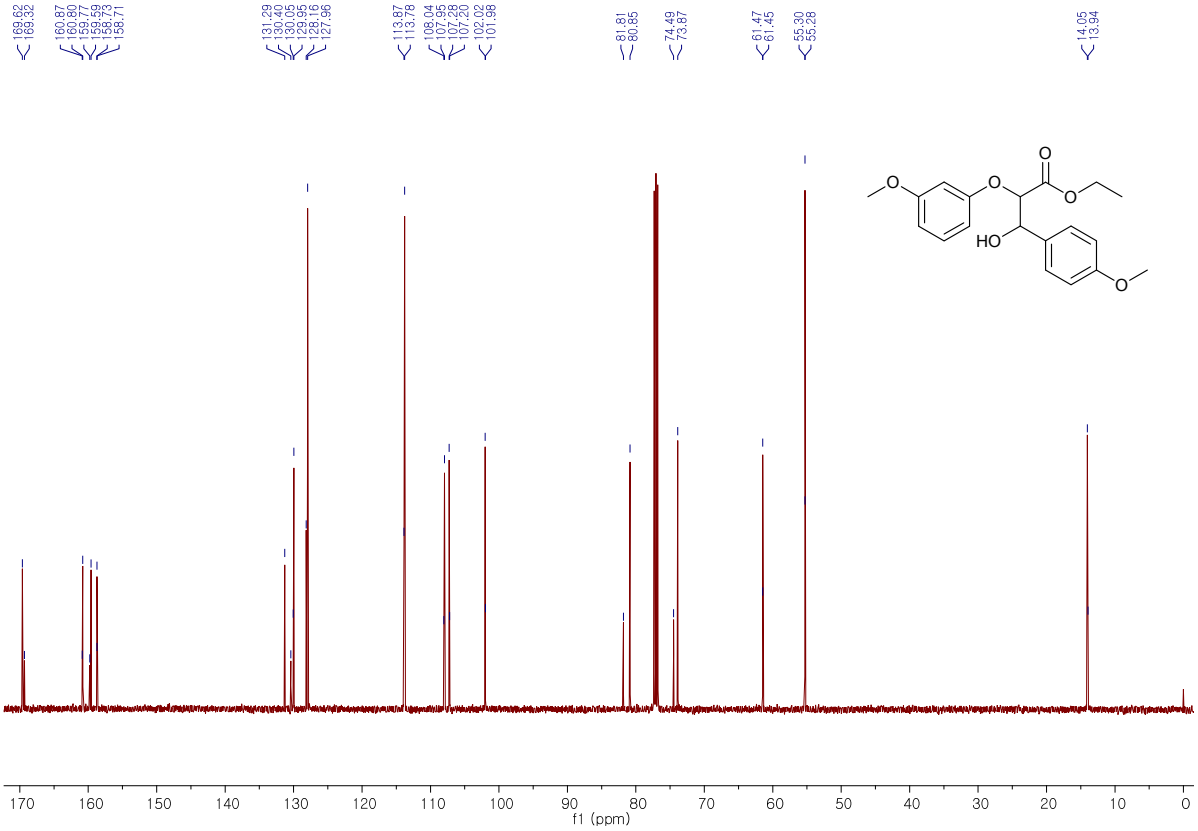

f1 (ppm)
HO

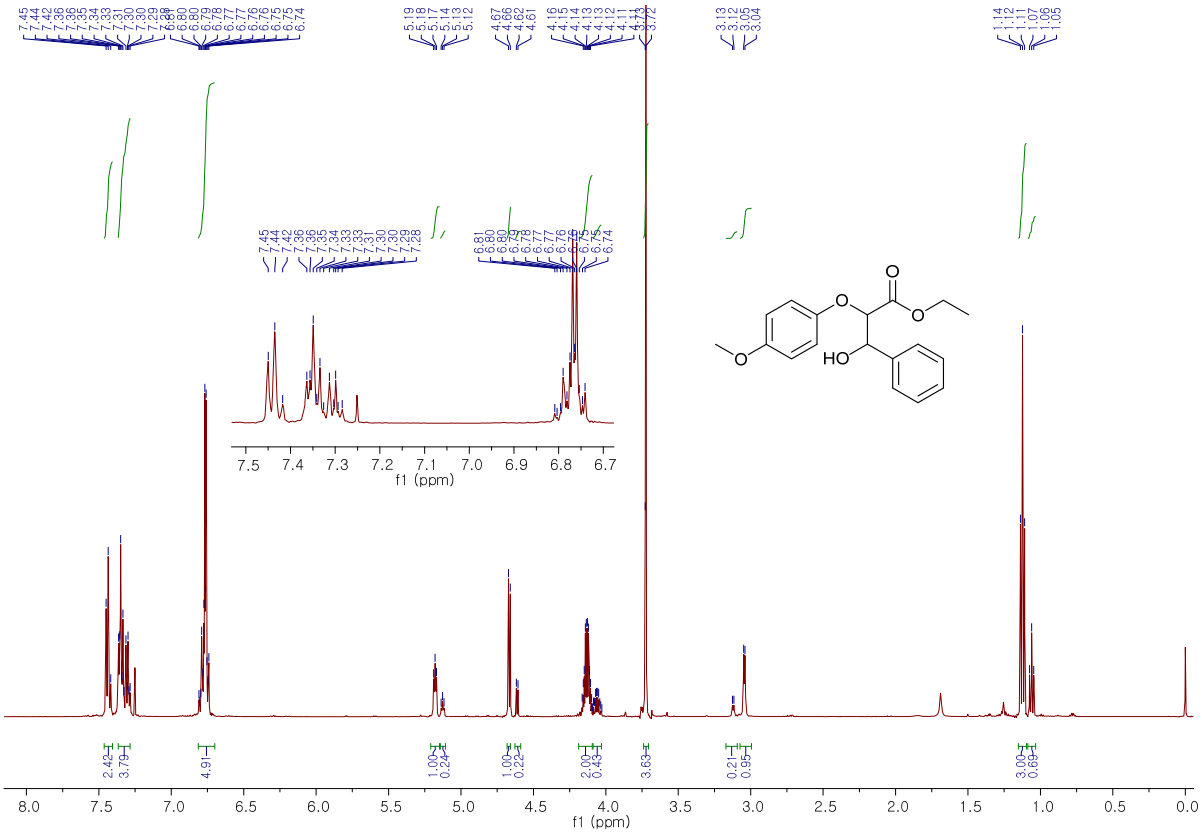

f1 (ppm)
HO

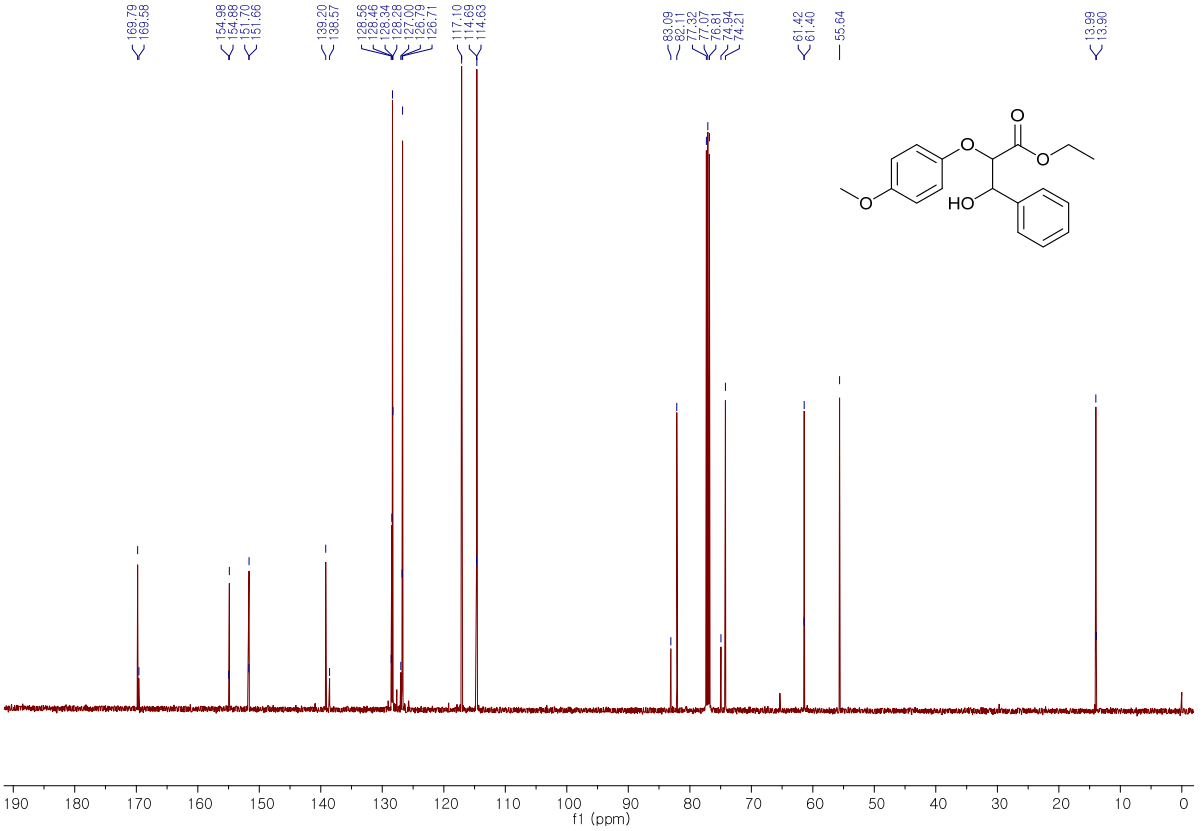

f1 (ppm)
HO

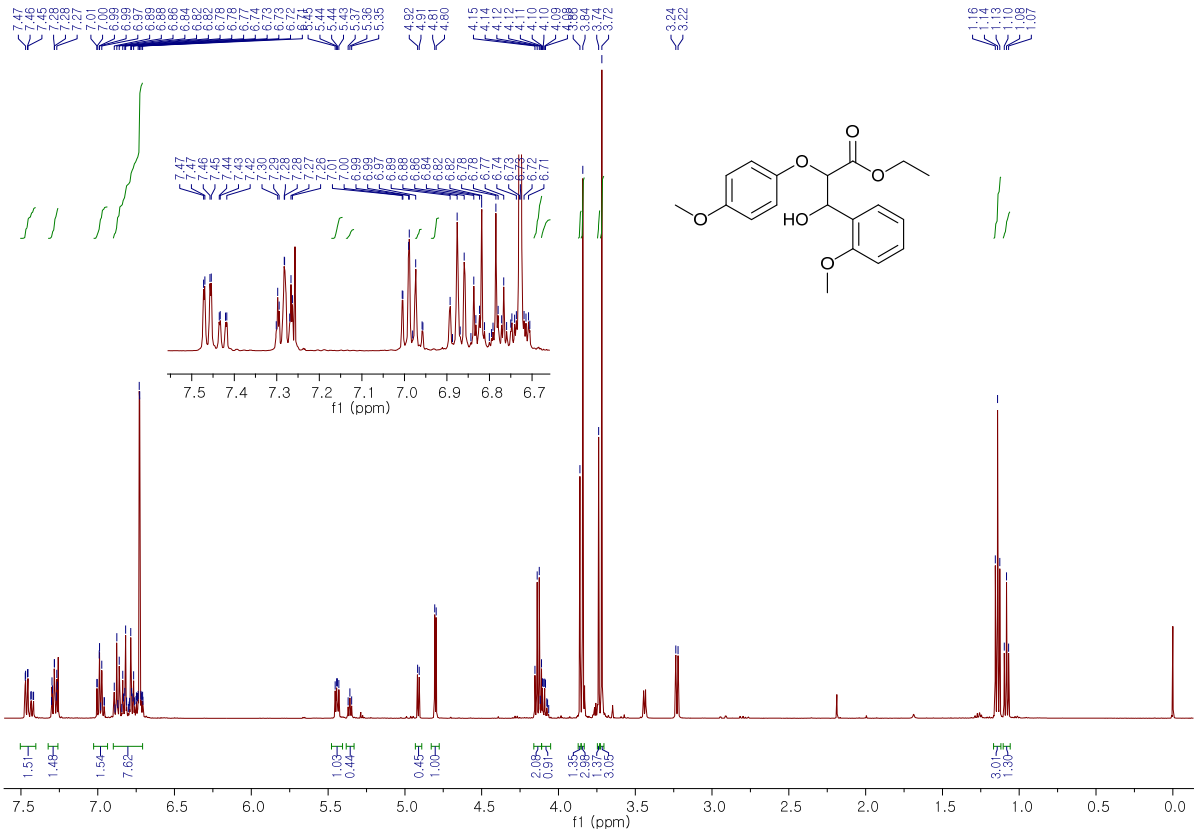

f1 (ppm)
HO

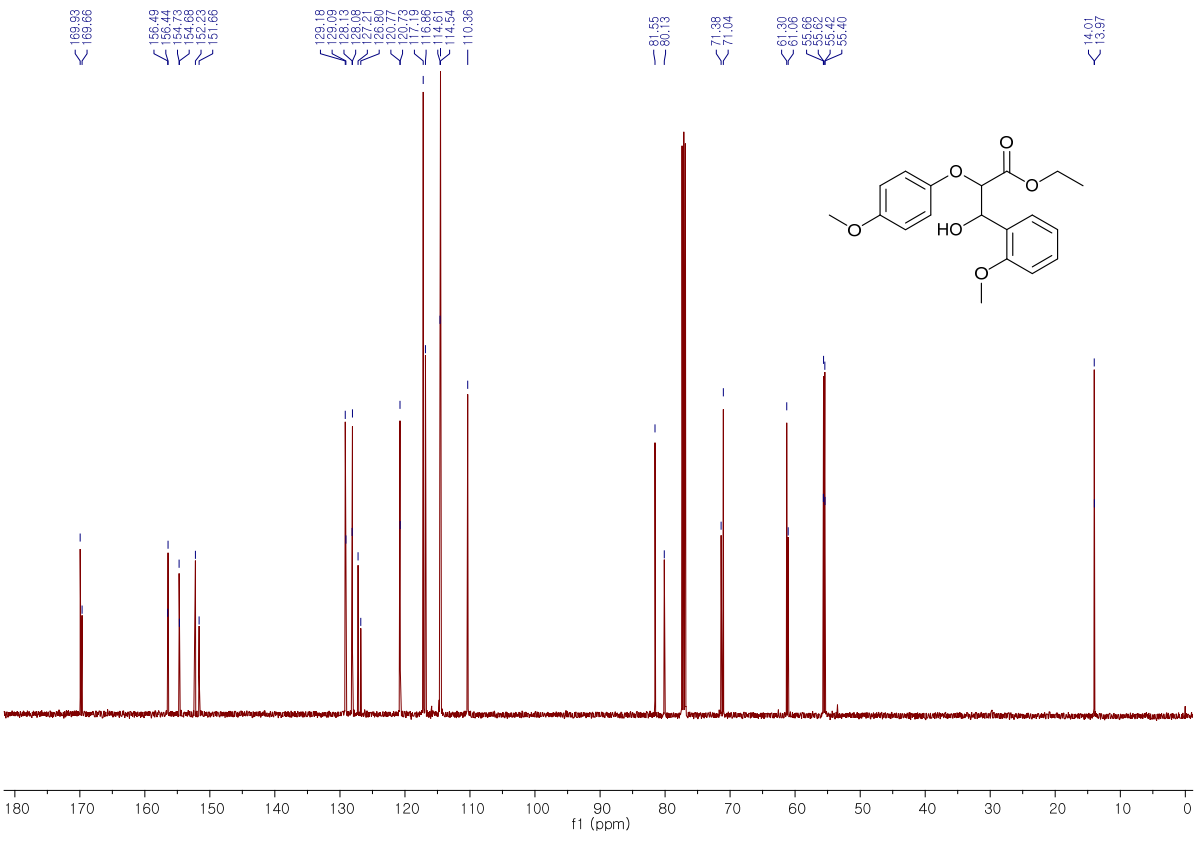

f1 (ppm)
HO

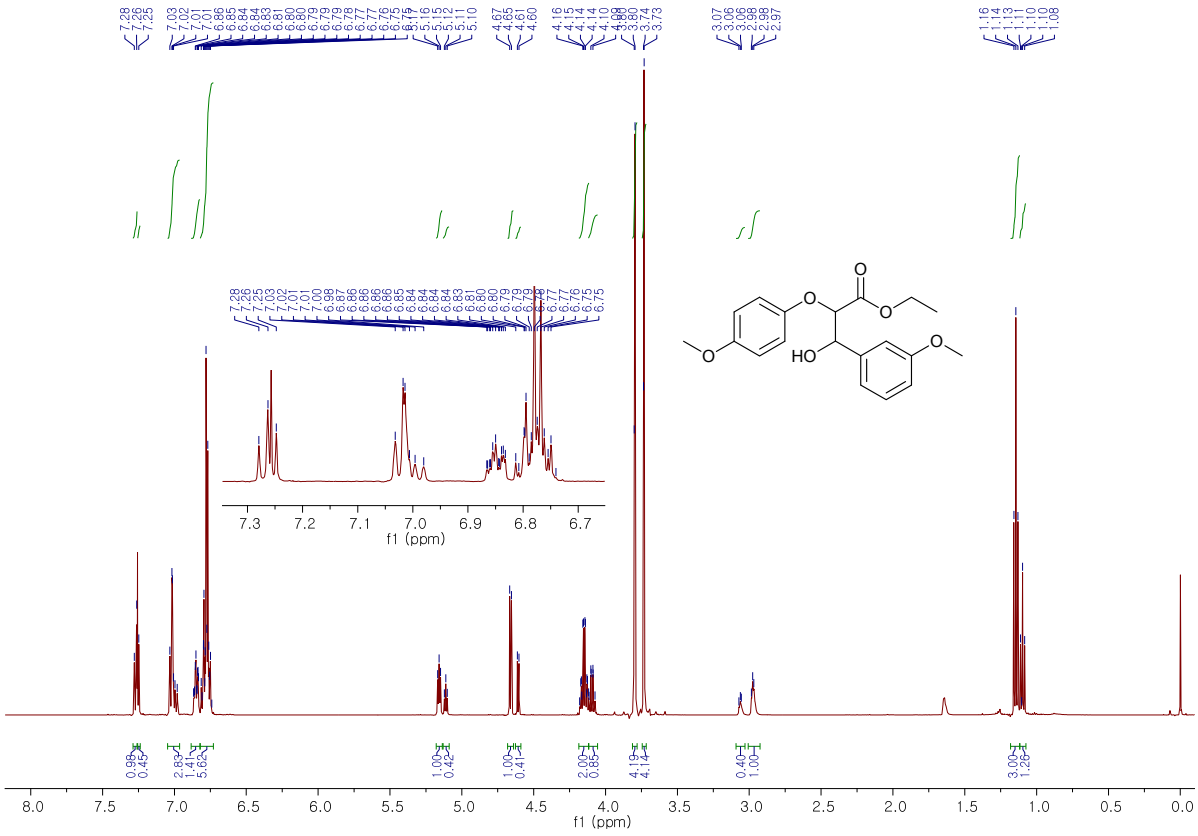

f1 (ppm)
HO

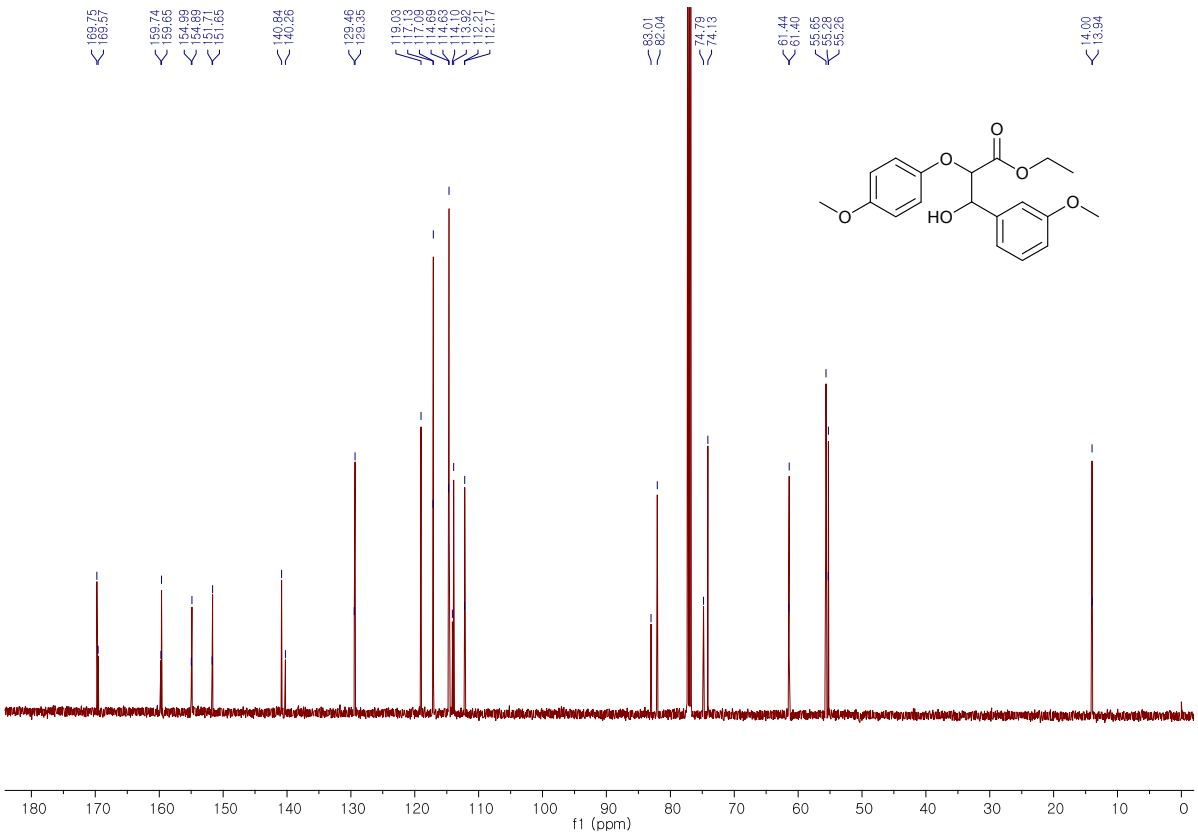

f1 (ppm)
HO

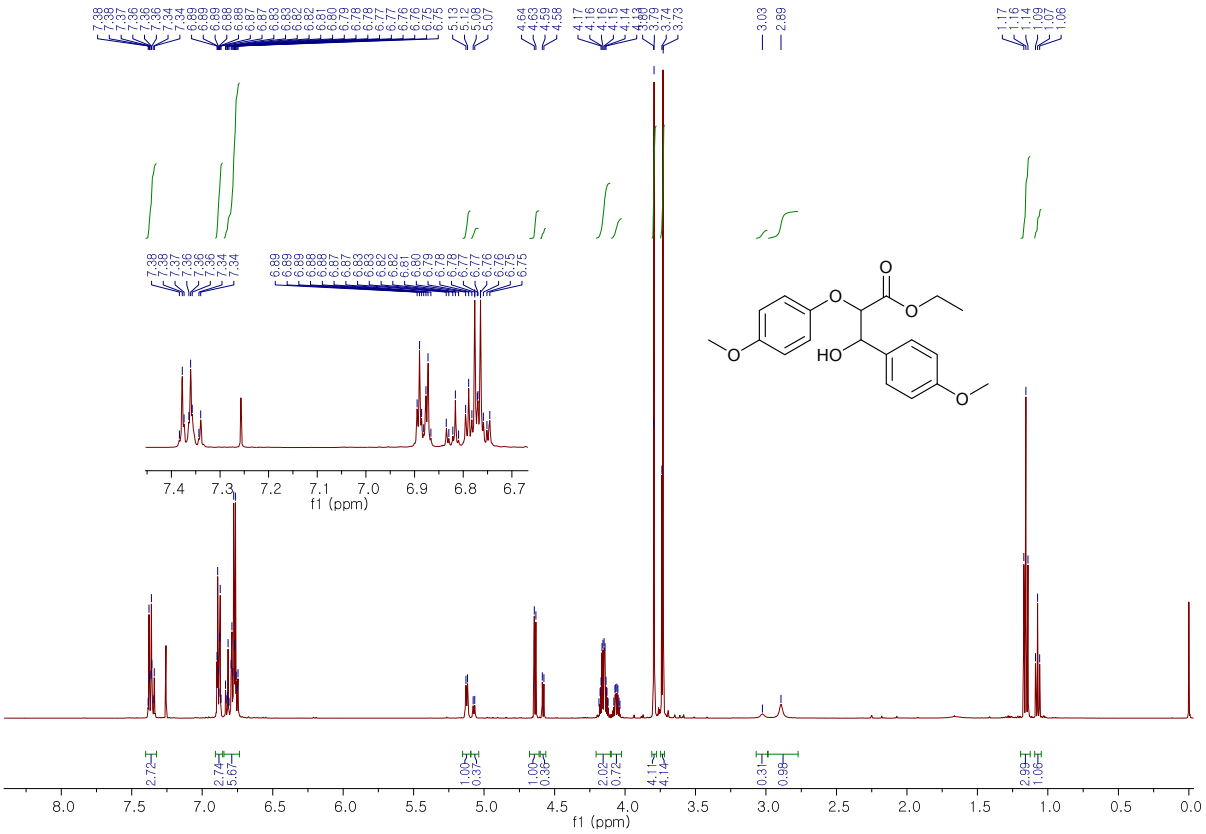

f1 (ppm)
HO

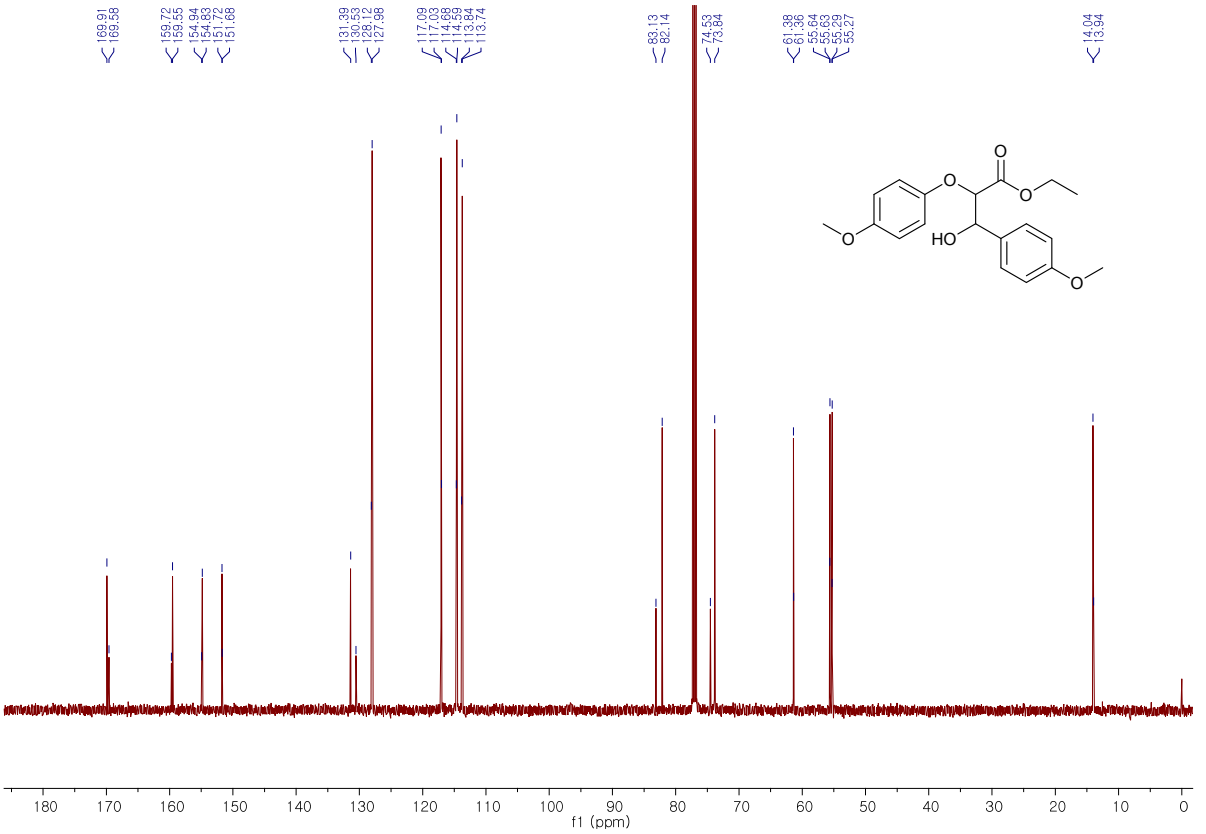

7.47
7.46
7.45
7.44
7.43
7.42
7.30
7.29
7.28
7.27
7.26
7.01
7.00
6.99
6.97
6.89
6.88
6.86
6.84
6.82
6.78
6.77
6.74
6.73
6.72
6.71
5.44
5.43
5.37
5.36
5.35
4.92
4.91
4.81
4.80
4.15
4.14
4.12
4.11
4.10
4.09
3.88
3.84
3.74
3.72
3.24
3.22
1.16
1.14
1.13
1.10
1.08
1.07
HO
1.51
1.48
1.54
7.62
1.03
0.44
0.45
1.00
2.08
0.91
1.35
2.37
3.05
3.01
1.30
f1 (ppm)

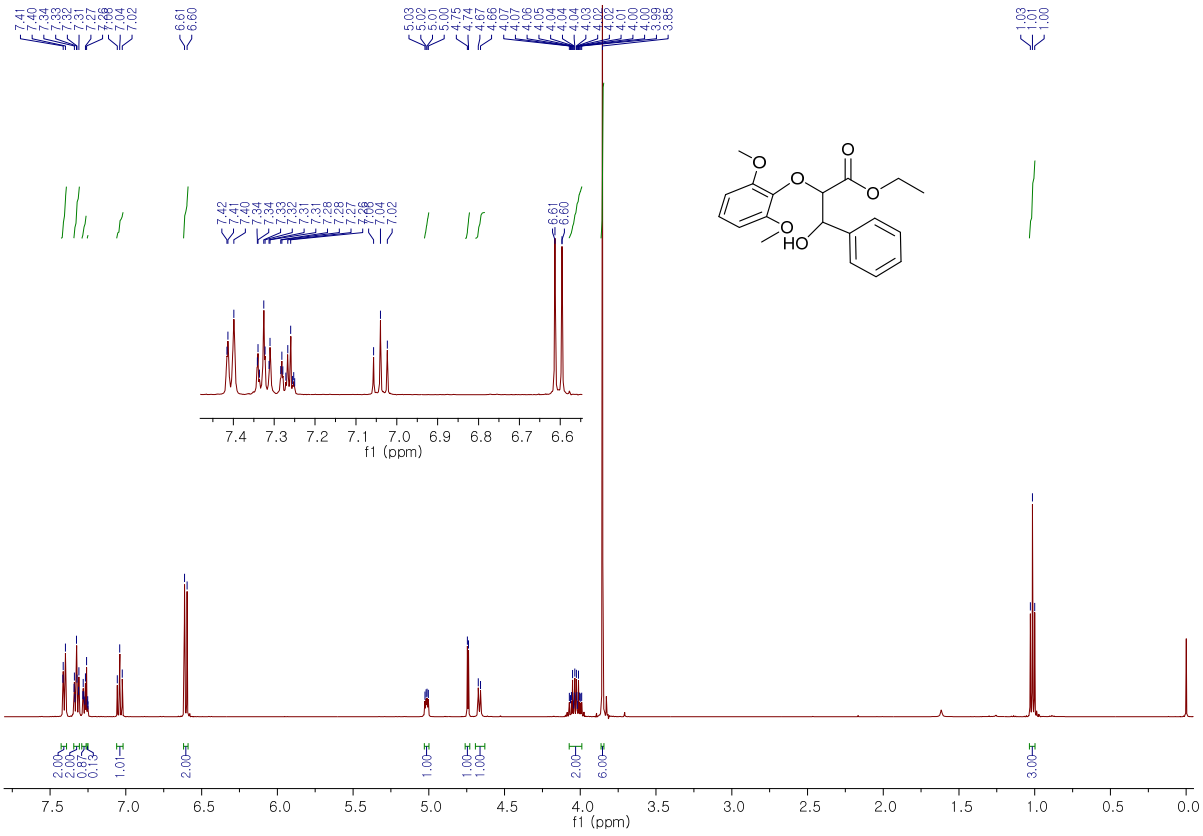

169.93
169.66
156.49
156.44
154.73
154.68
152.23
151.66
129.18
129.08
128.13
128.08
127.21
126.80
120.77
117.19
116.86
114.61
114.54
110.36
81.55
80.13
71.38
71.04
61.30
61.06
55.66
55.62
55.42
55.40
14.01
13.97
HO
f1 (ppm)

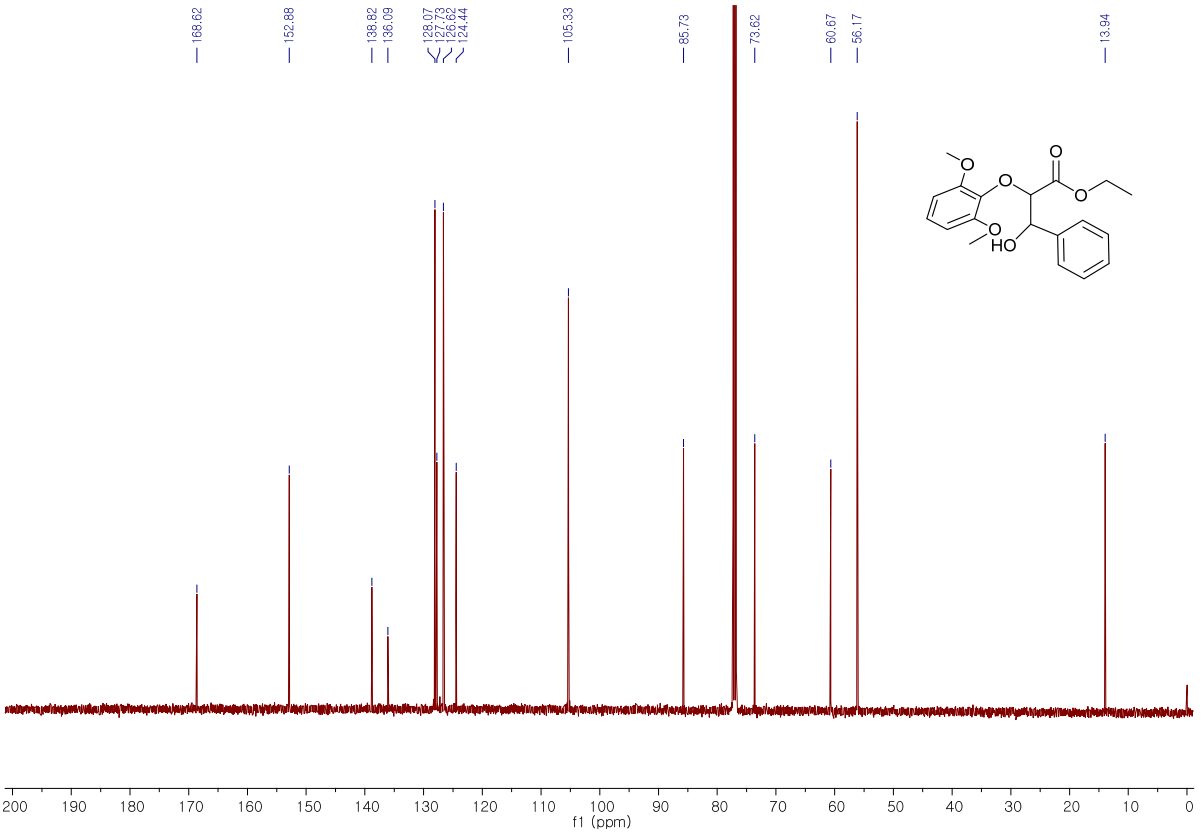

f1 (ppm)

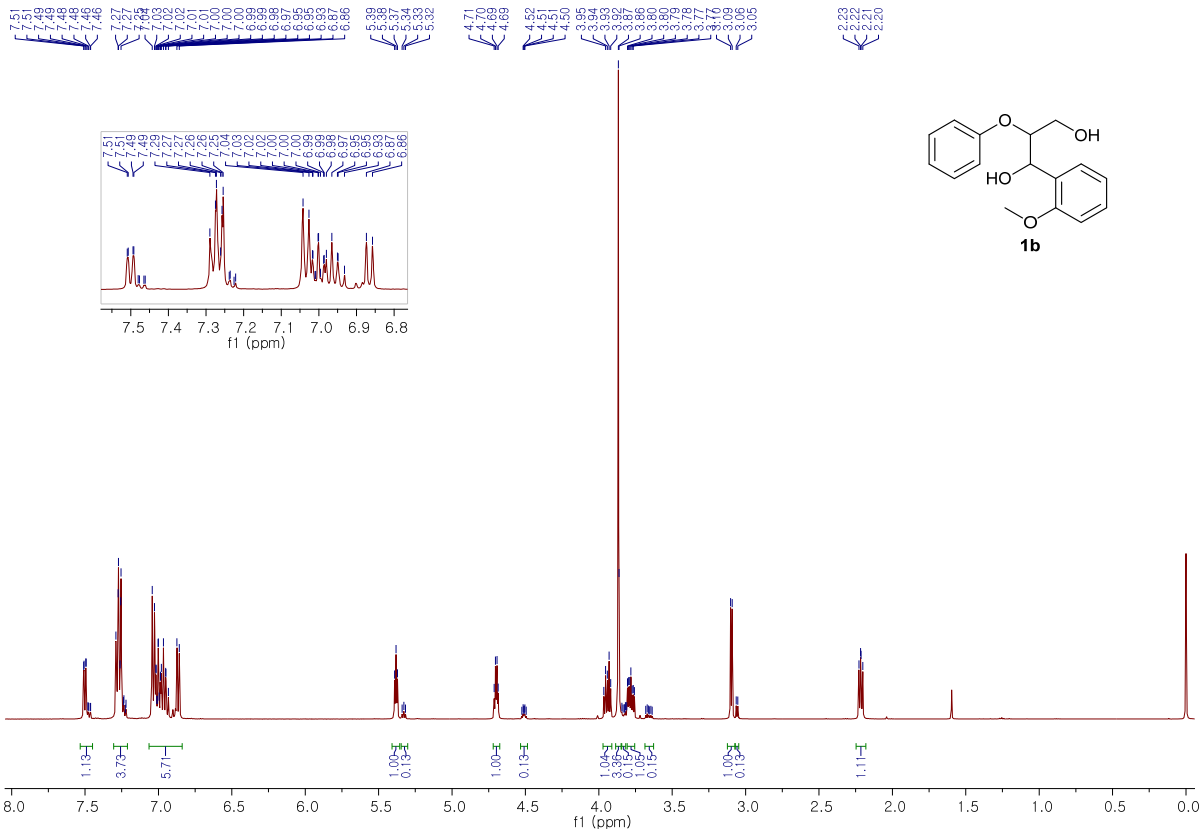

f1 (ppm)

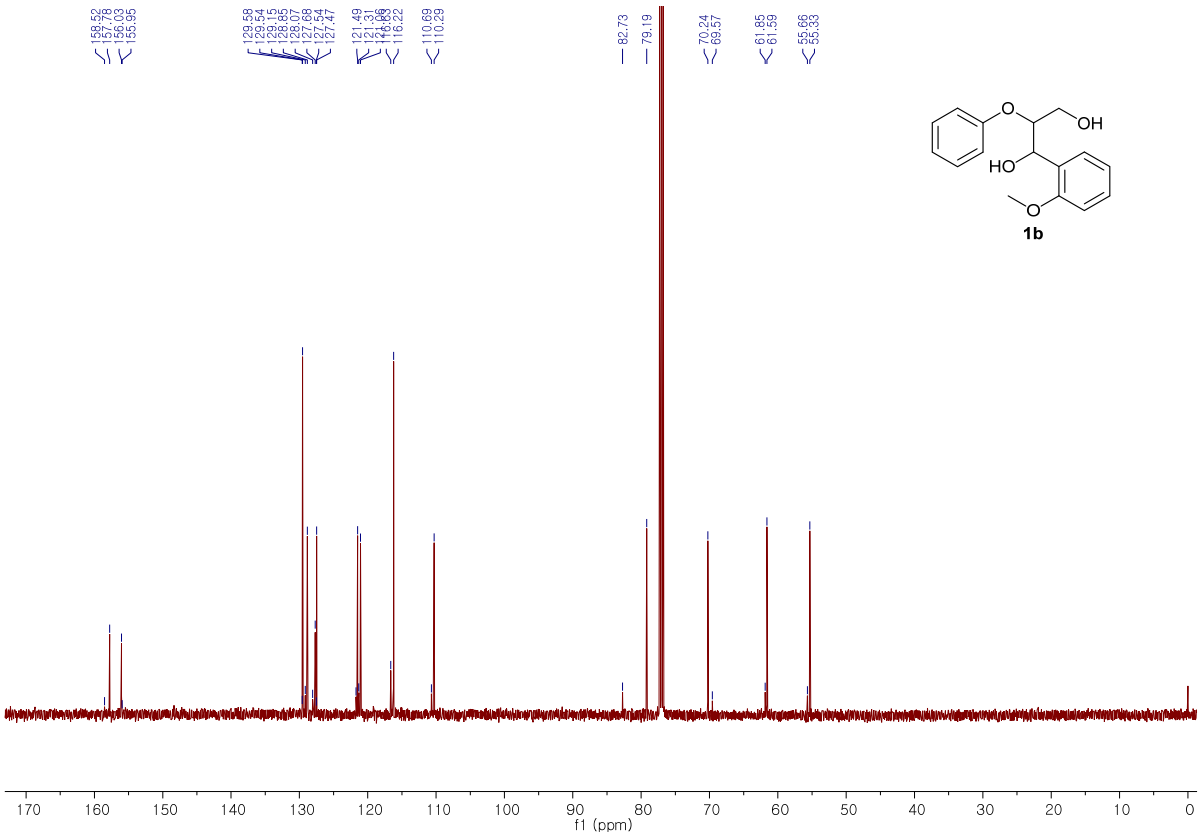

f1 (ppm)
HO

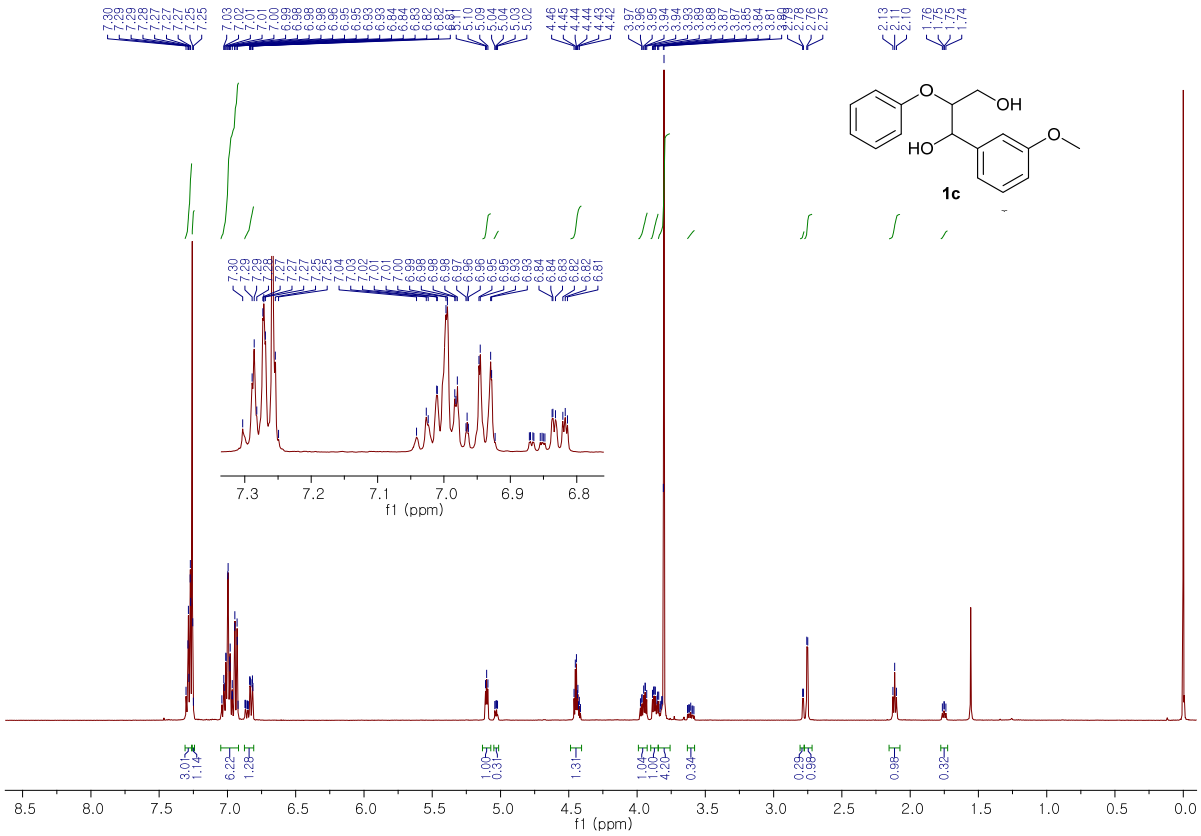

f1 (ppm)
HO

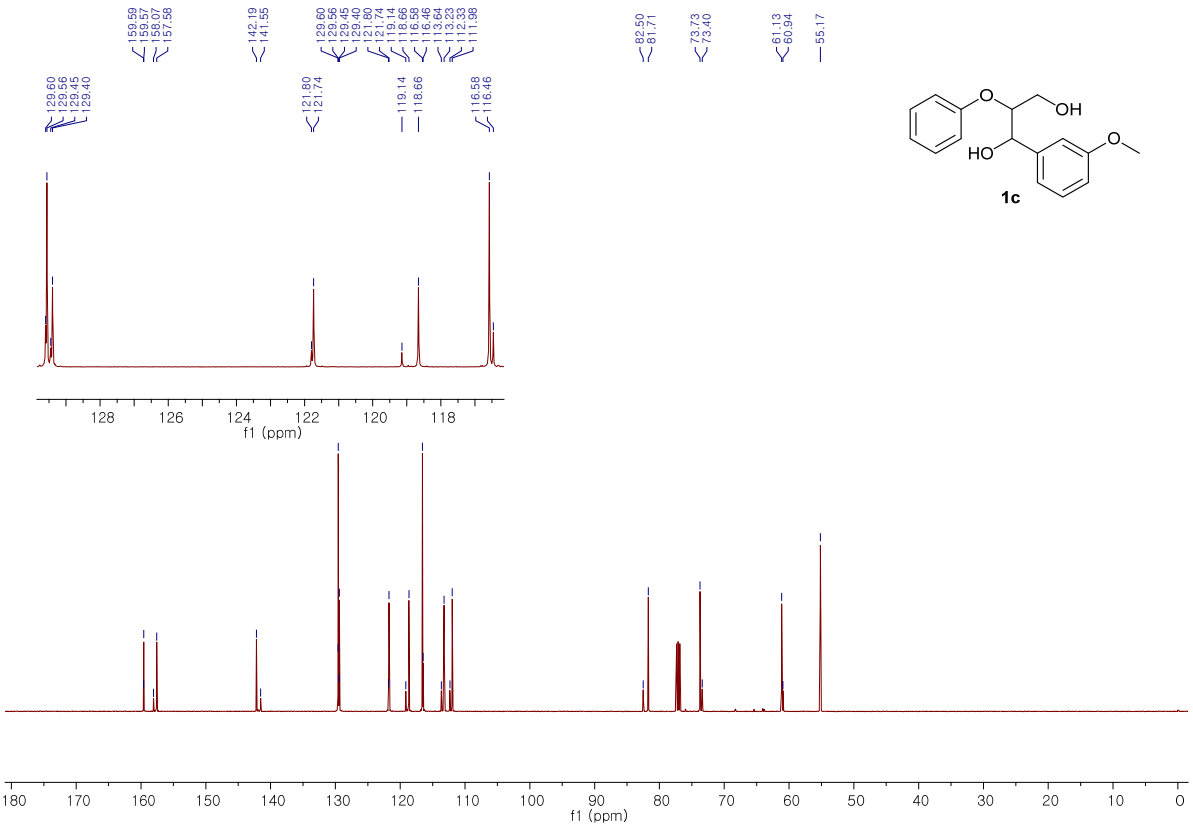

7.41
7.40
7.34
7.33
7.32
7.31
7.27
7.68
7.04
7.02
6.61
6.60
5.03
5.02
5.01
5.00
4.75
4.74
4.67
4.66
4.07
4.06
4.05
4.04
4.04
4.03
4.02
4.01
4.00
4.00
3.89
3.85
1.03
1.01
1.00
2.00
2.00
0.87
0.19
1.01
2.00
1.00
1.00
1.00
2.00
6.00
3.00
f1 (ppm)
HO

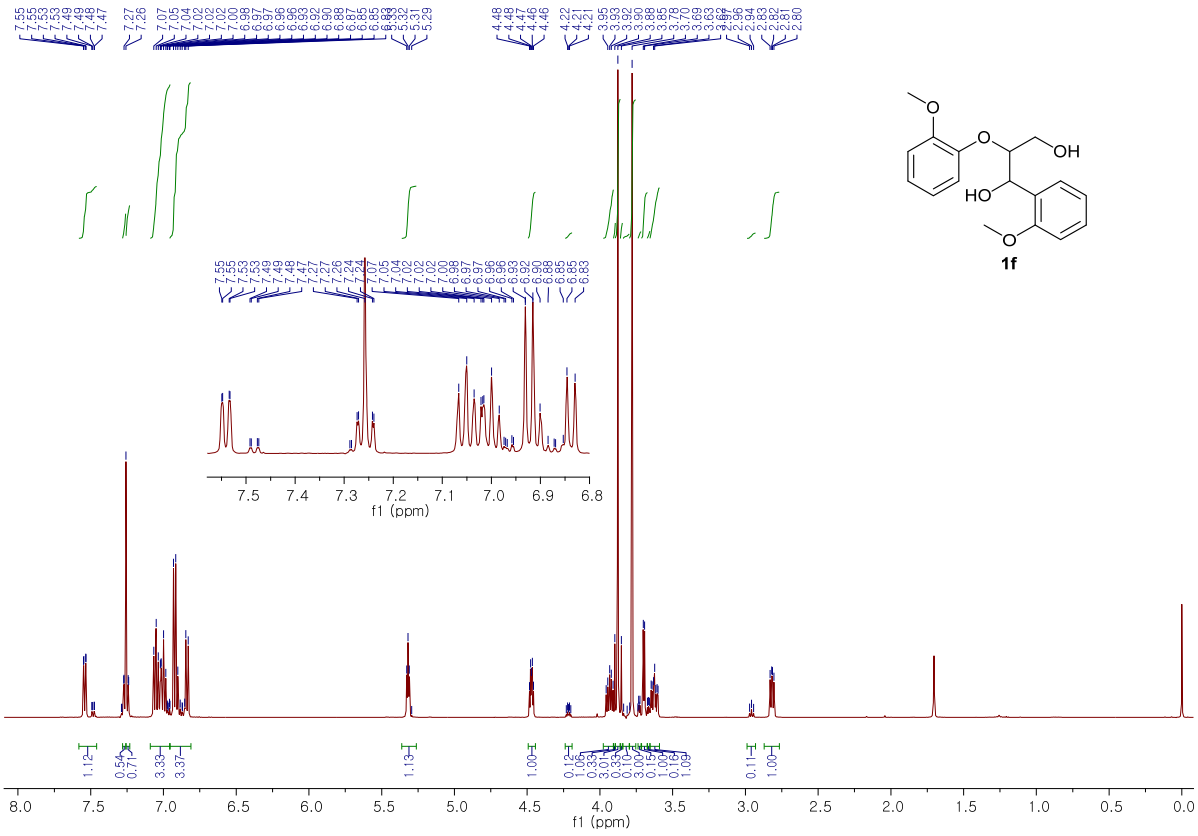

168.62
152.88
138.82
136.09
128.07
127.73
126.62
124.44
105.33
85.73
73.62
60.67
56.17
13.94
f1 (ppm)
HO

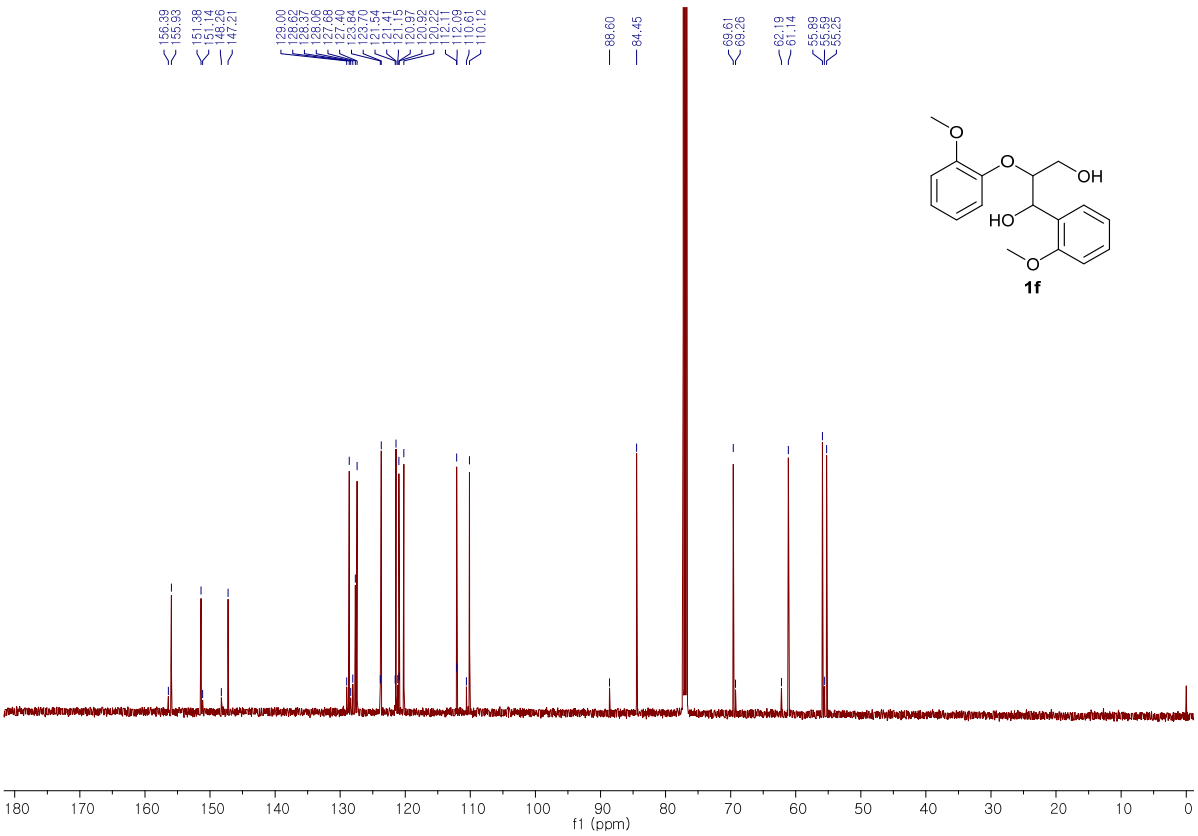

OH
HO
O
1b
f1 (ppm)

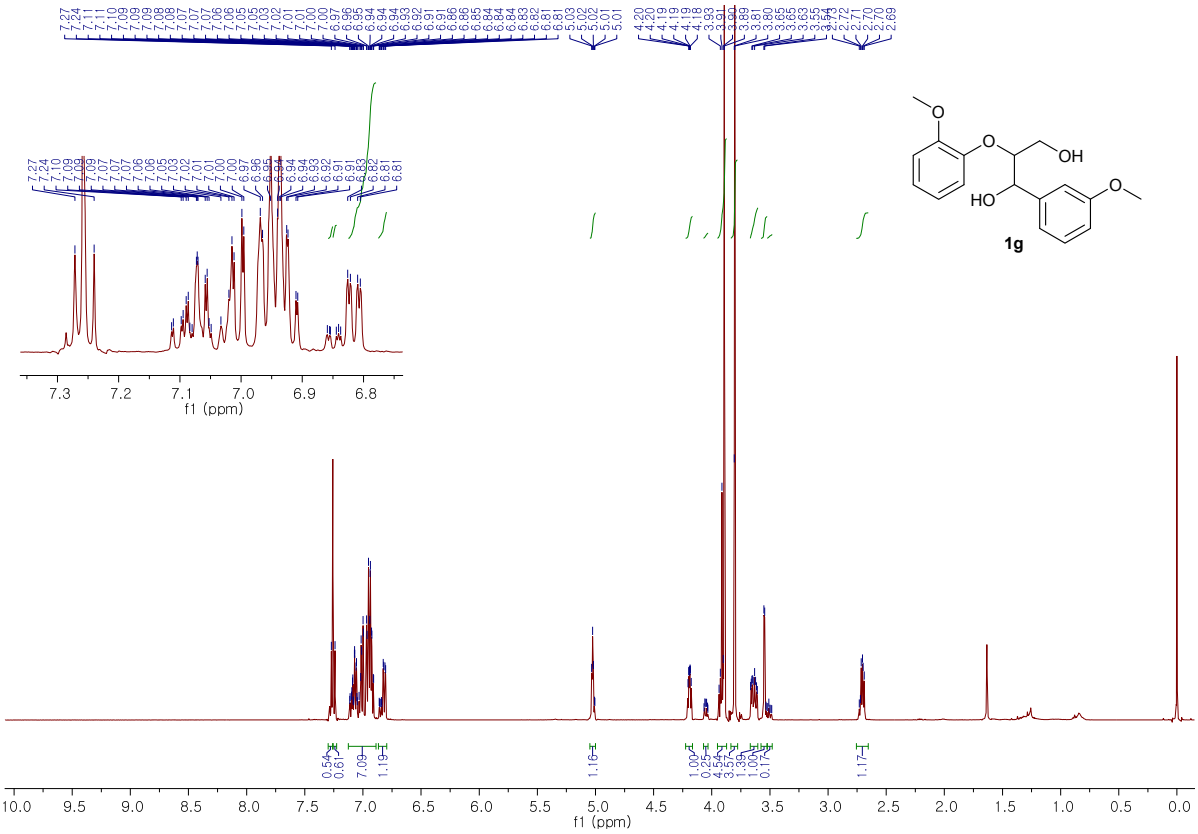

OH
HO
O
1b
f1 (ppm)

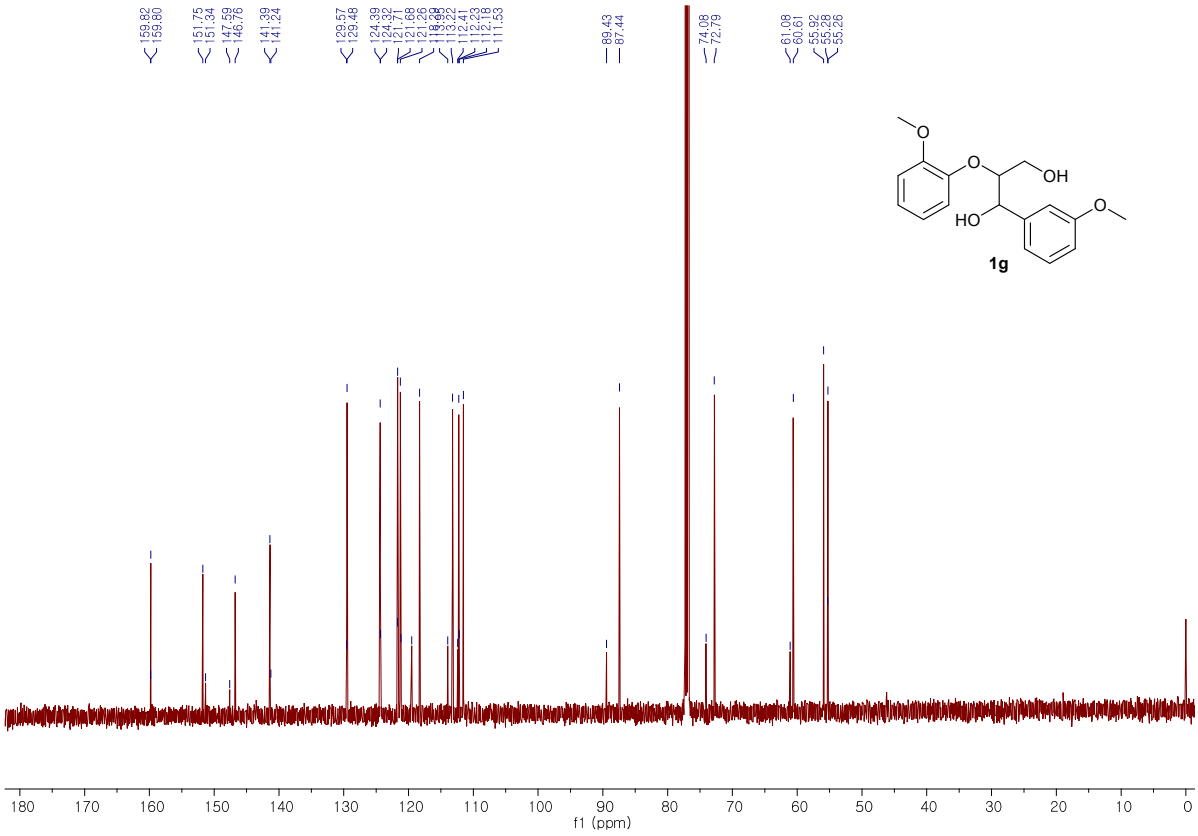

OH
HO
O
O
1c
f1 (ppm)

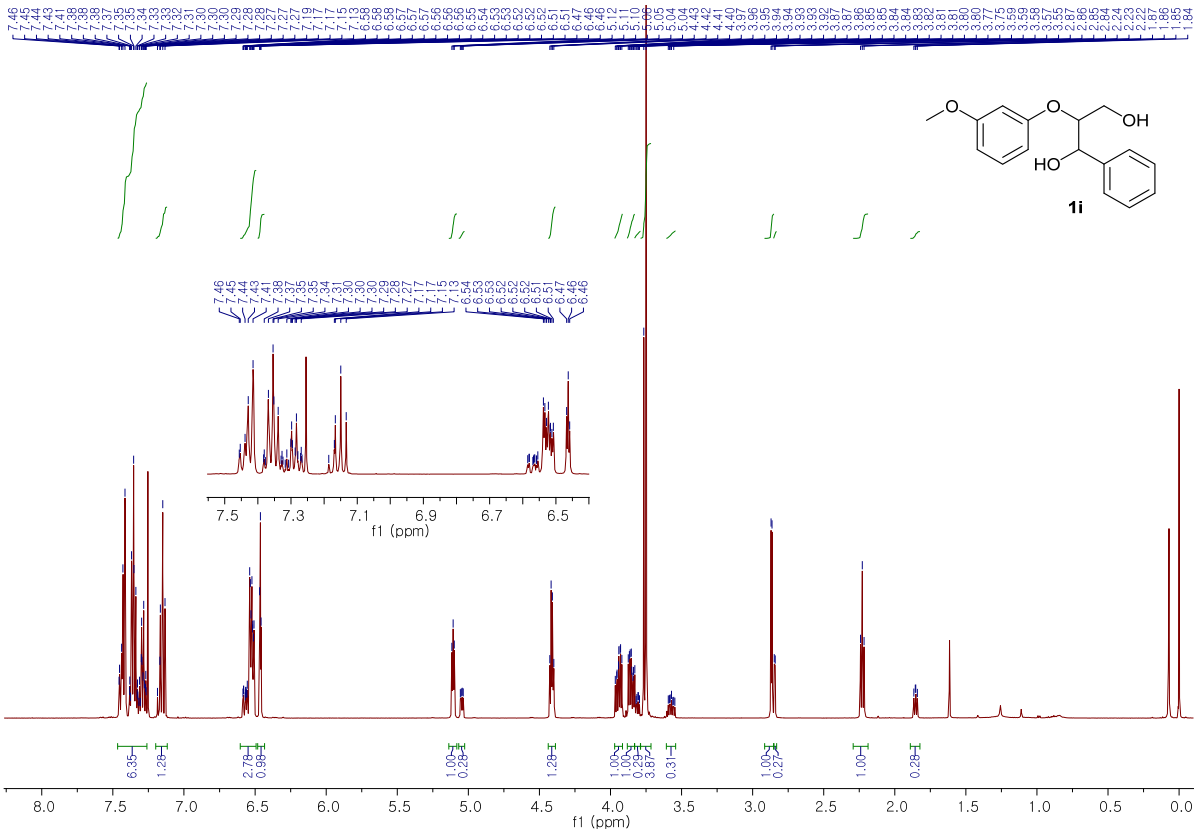

OH
HO
O
O
1c
f1 (ppm)

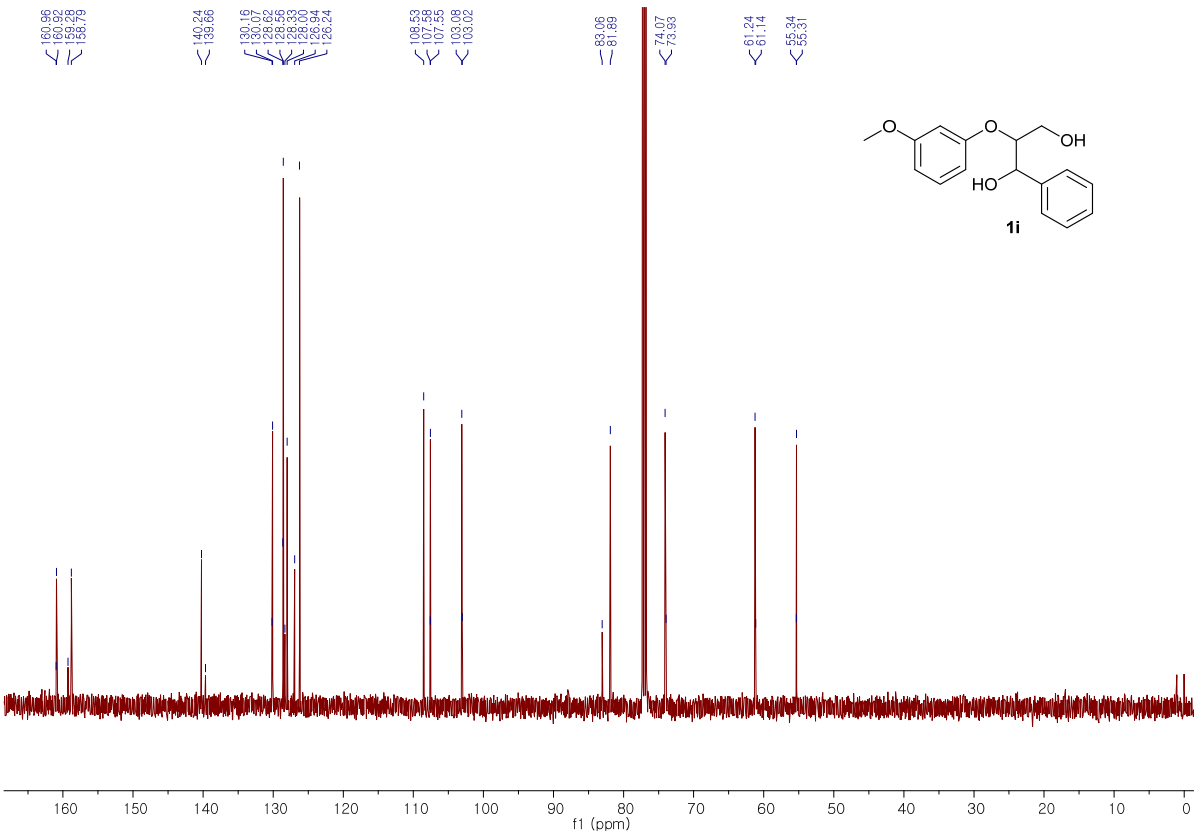

OH
HO
1f
f1 (ppm)

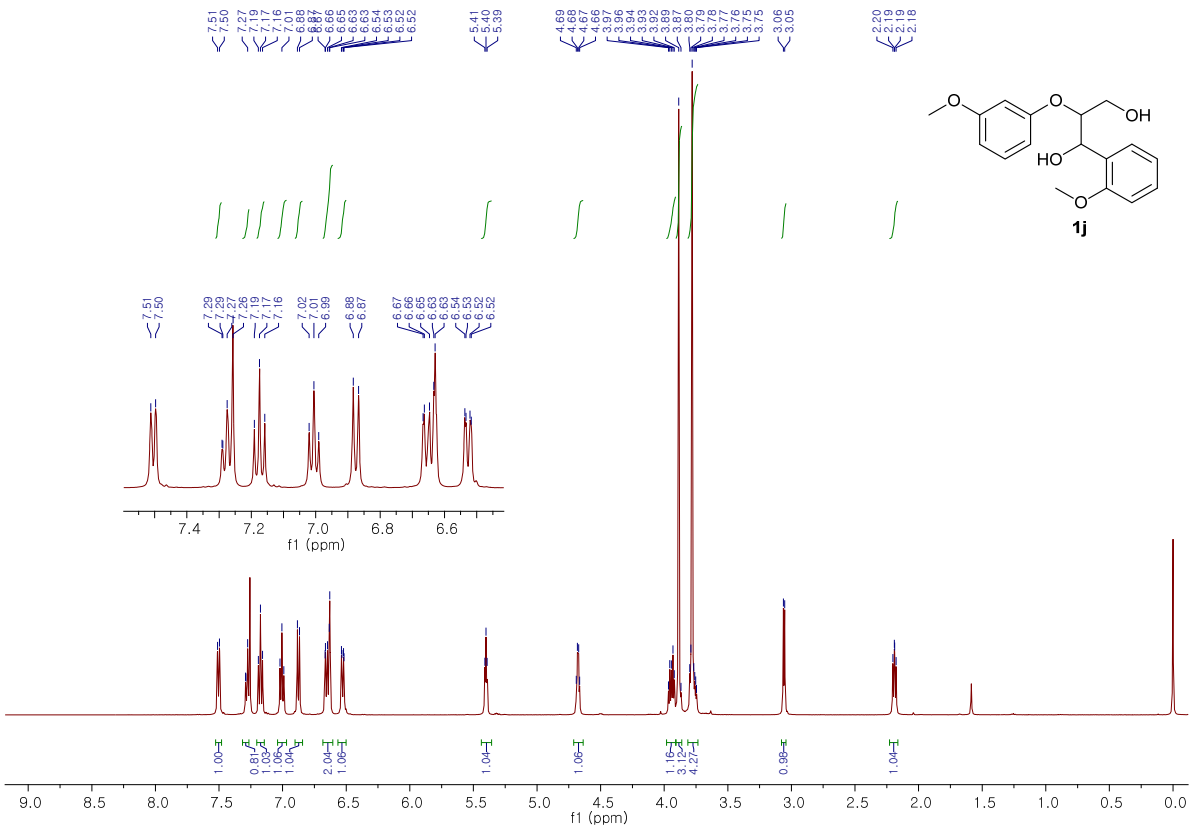

OH
HO
1f
f1 (ppm)

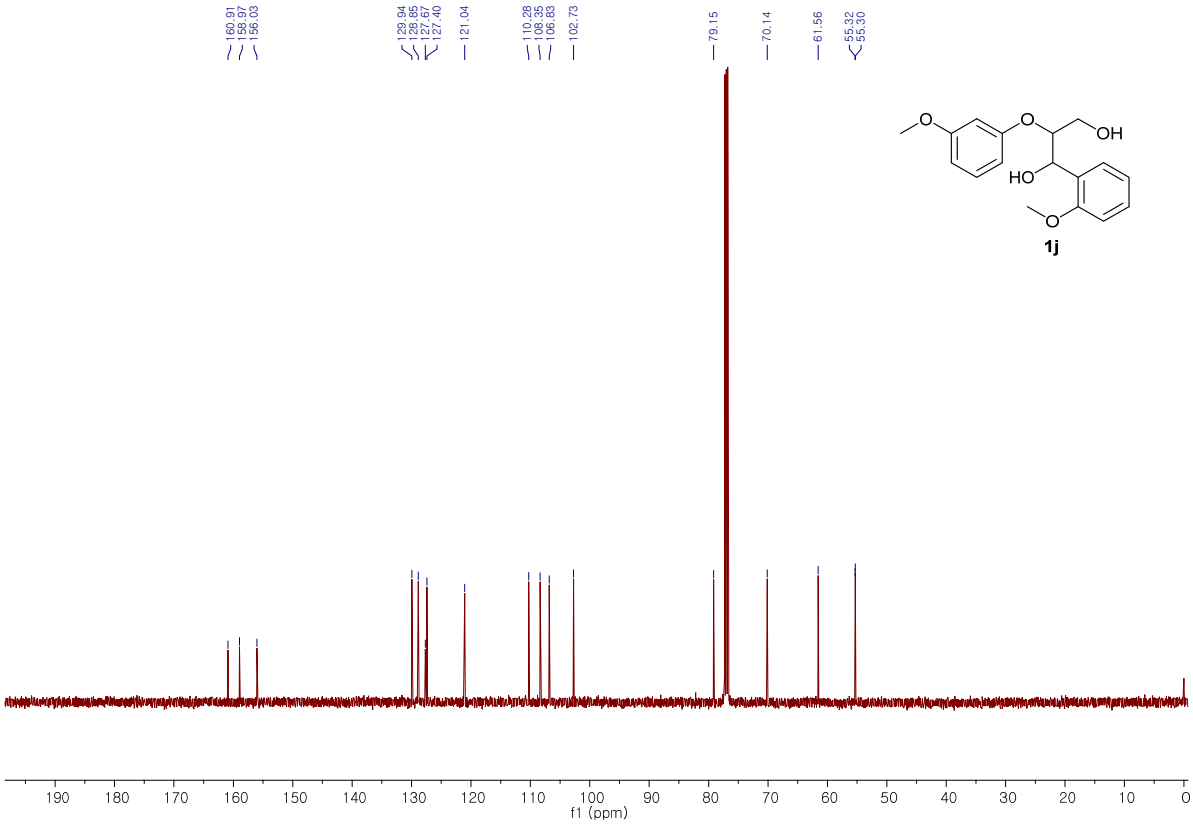

f1 (ppm)
1g

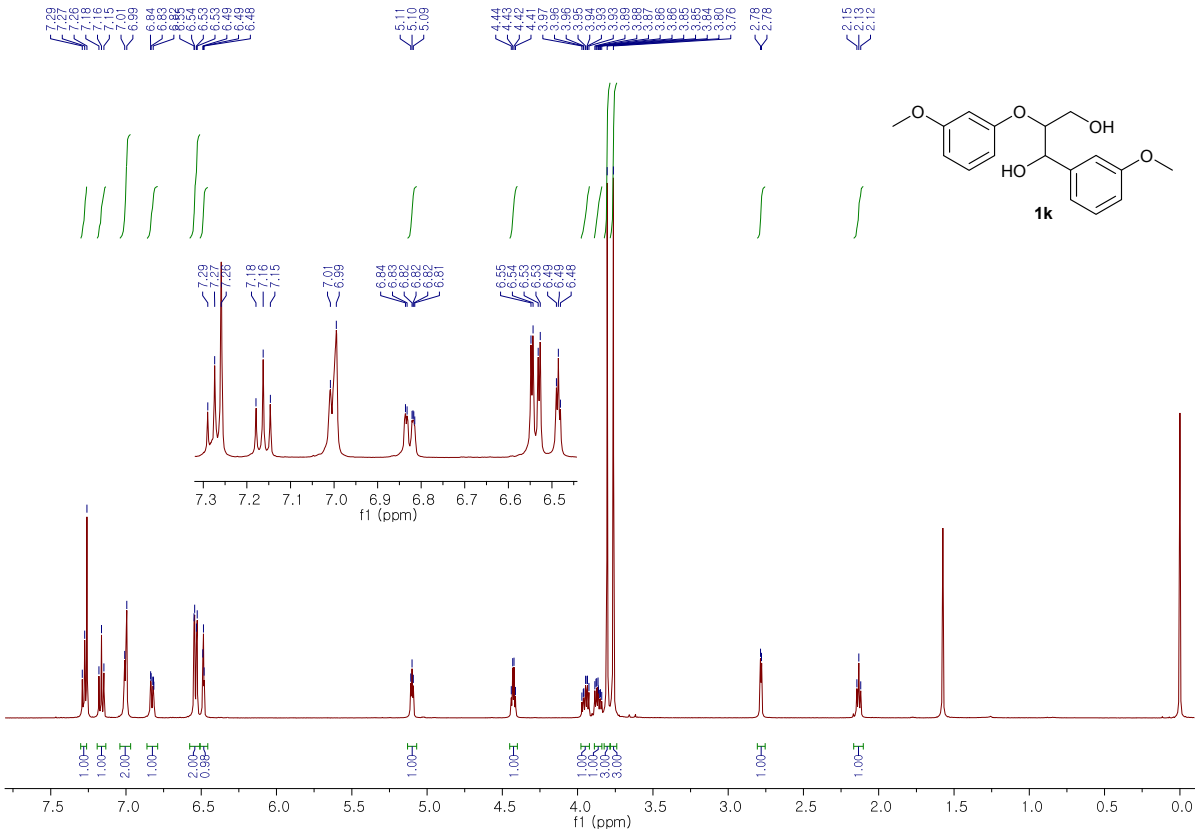

f1 (ppm)
1g

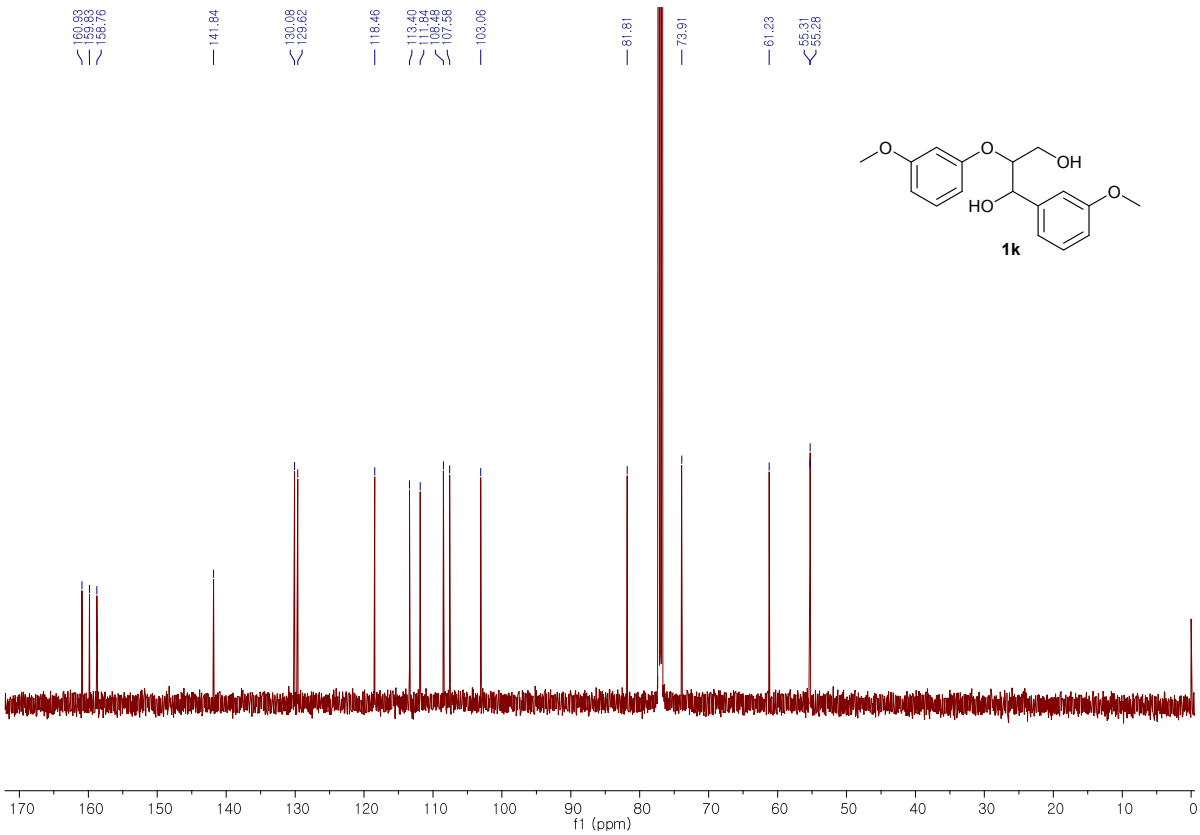

1i
f1 (ppm)

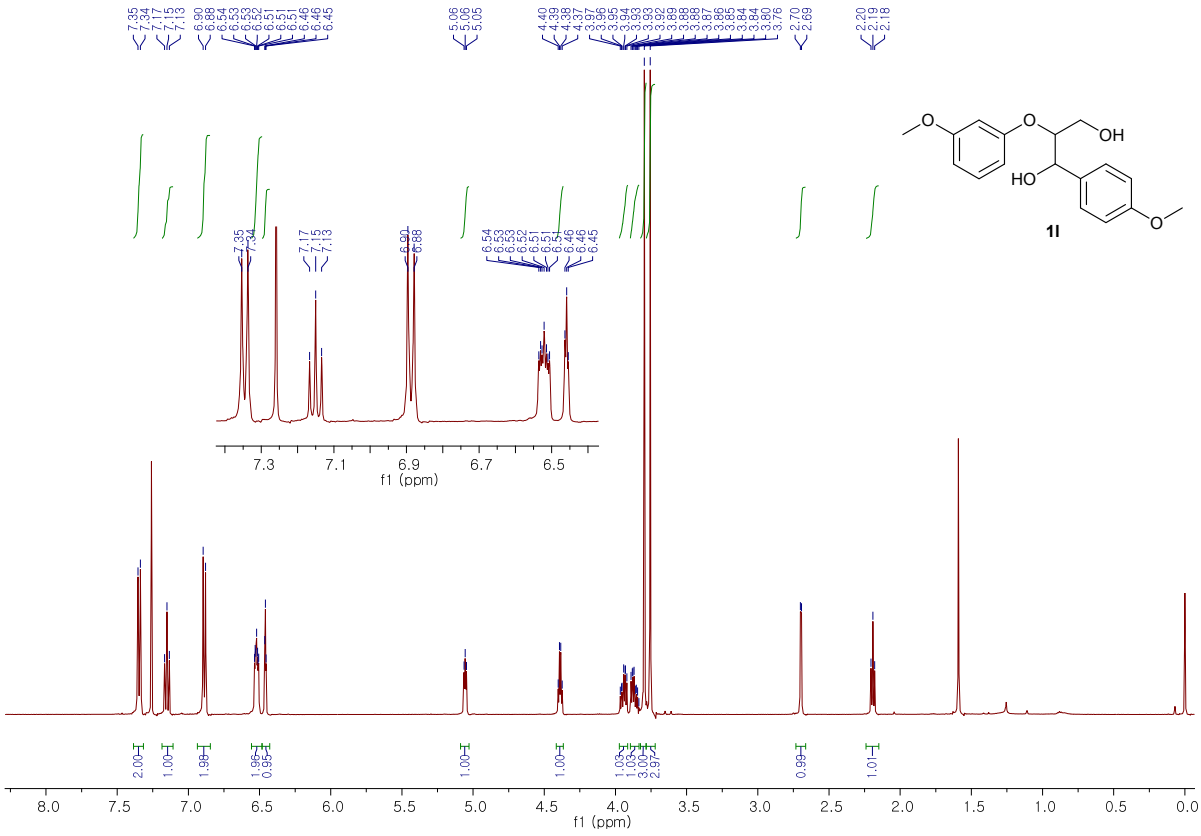

1i
f1 (ppm)

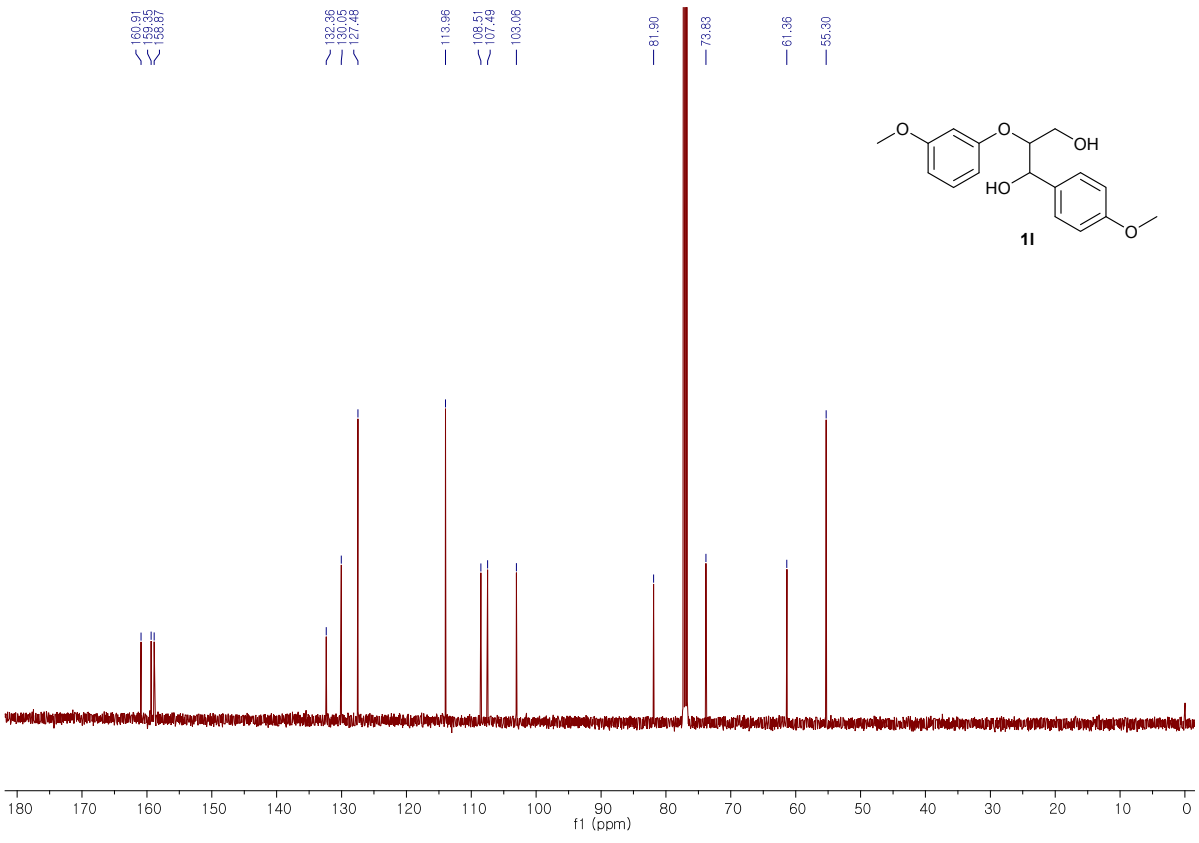

1j
f1 (ppm)

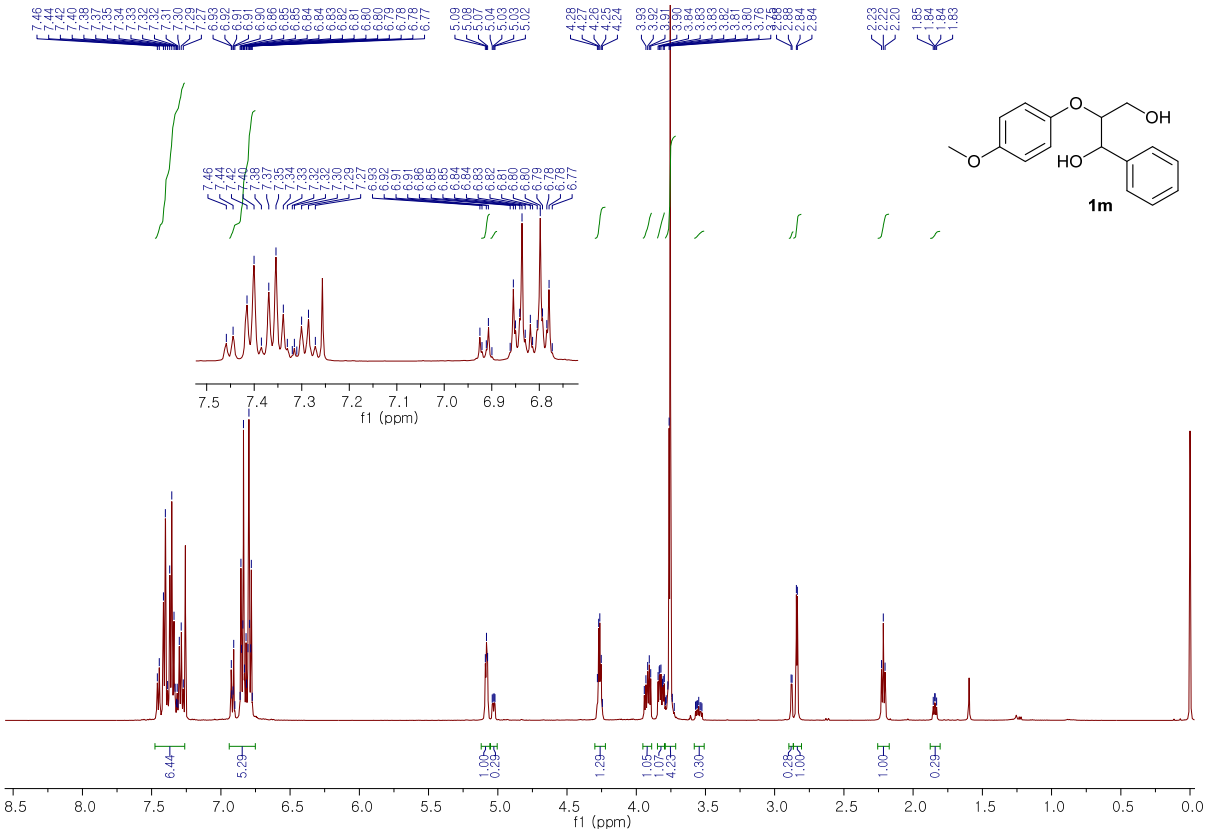

1j
f1 (ppm)

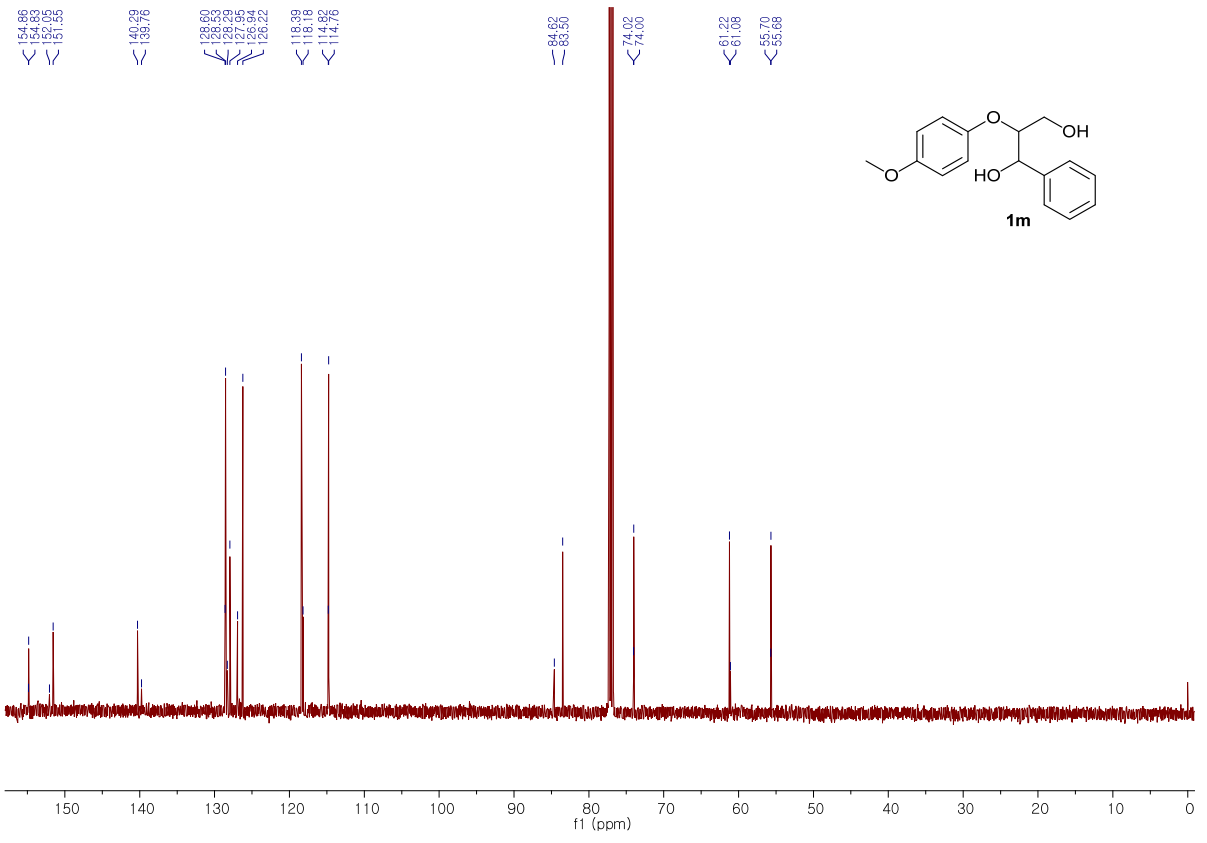

1k
f1 (ppm)

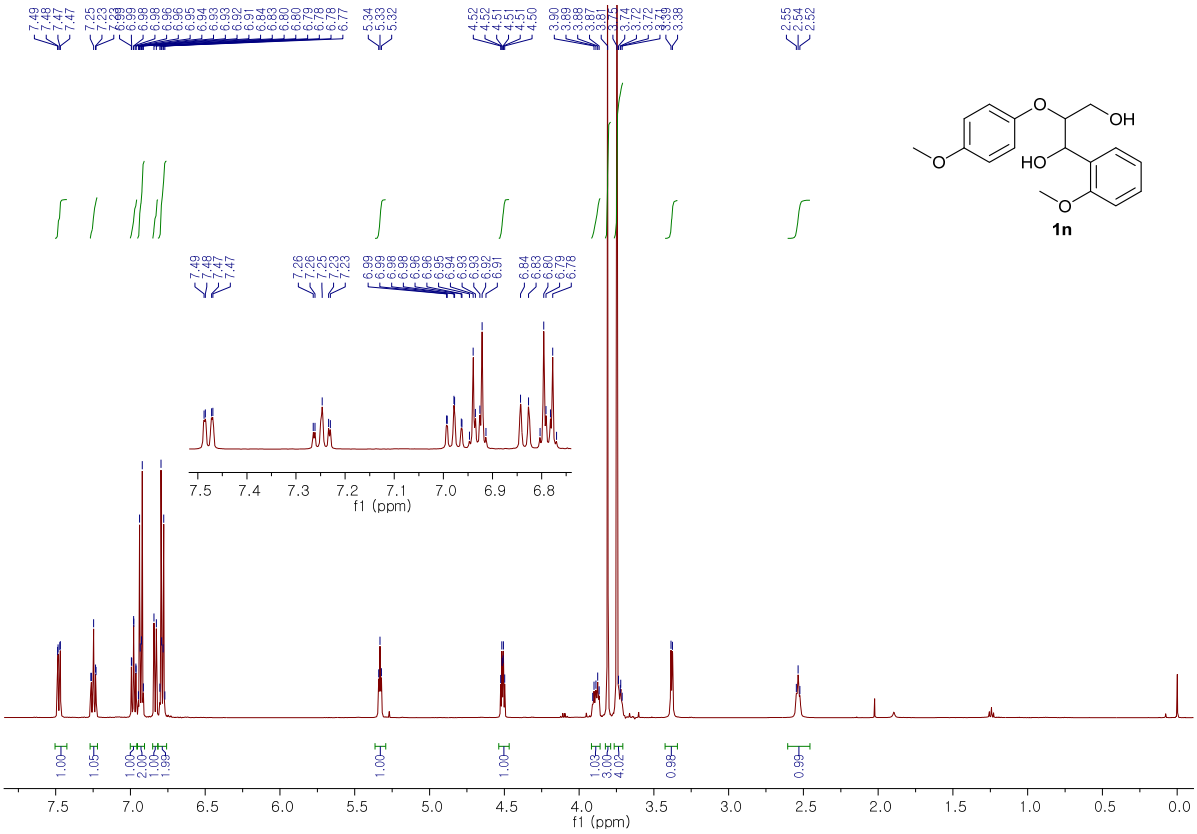

1k
f1 (ppm)

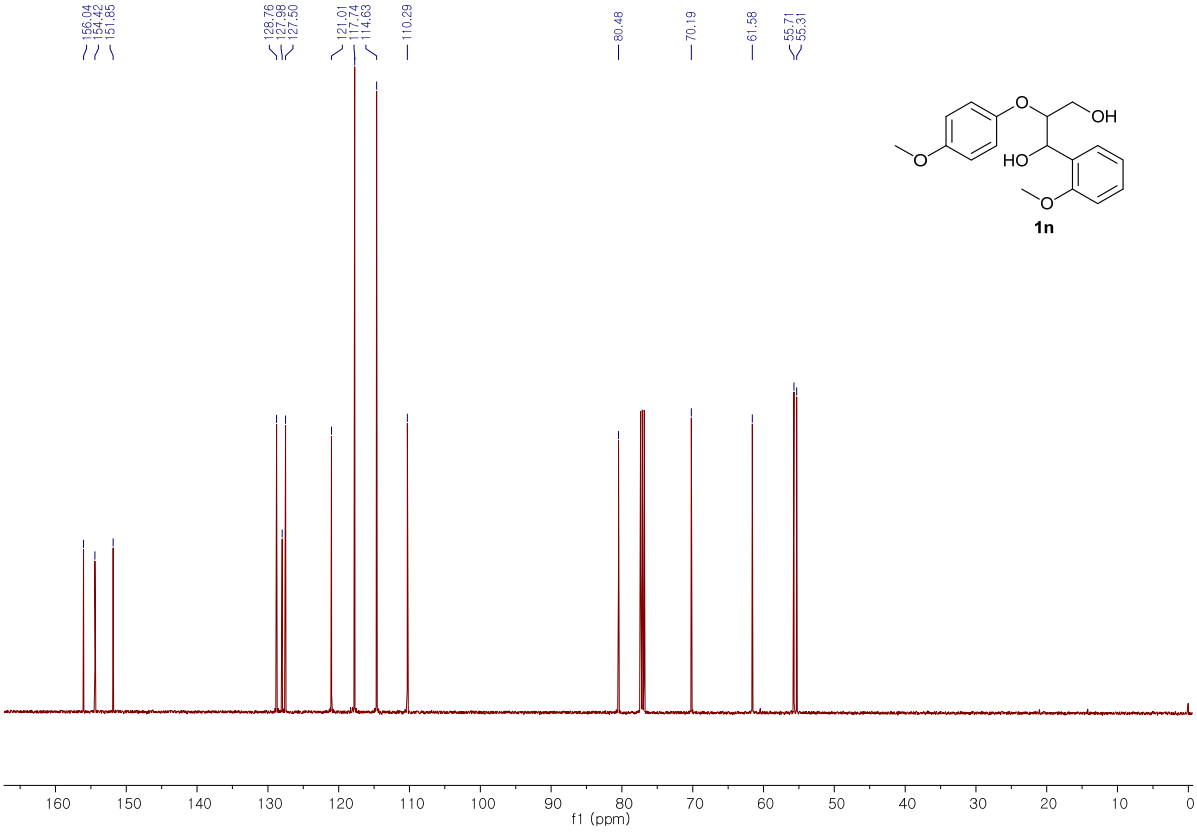

7.35
7.34
7.17
7.15
7.13
6.90
6.88
6.54
6.53
6.52
6.51
6.51
6.46
6.45
5.06
5.06
5.05
4.40
4.39
4.38
4.37
3.97
3.96
3.95
3.94
3.93
3.93
3.92
3.89
3.88
3.88
3.87
3.86
3.85
3.84
3.84
3.80
3.76
2.70
2.69
2.20
2.19
2.18
OH
HO
O
O
O
1l
f1 (ppm)
2.00
1.00
1.98
1.96
0.95
1.00
1.00
1.03
1.03
3.07
2.97
0.99
1.01

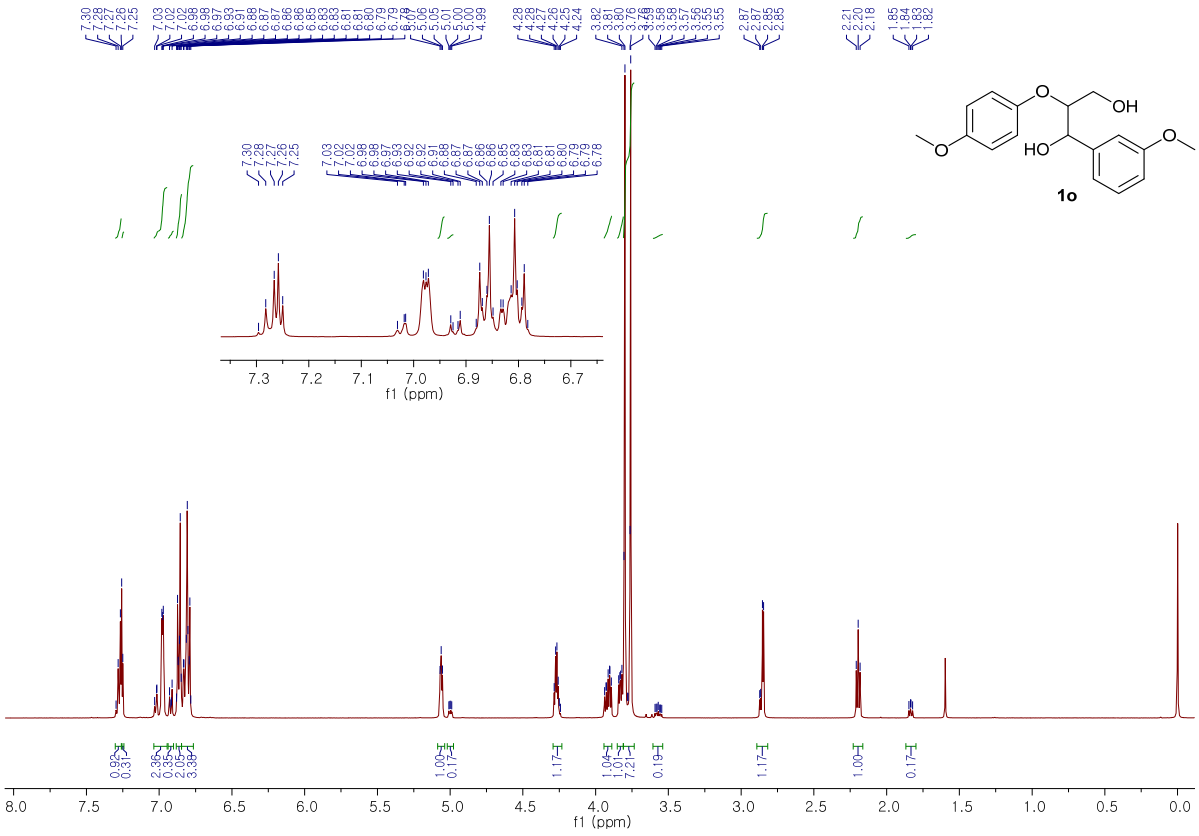

160.91
159.35
158.87
132.36
130.05
127.48
113.96
108.51
107.49
103.06
81.90
73.83
61.36
55.30
OH
HO
O
O
O
1l
f1 (ppm)

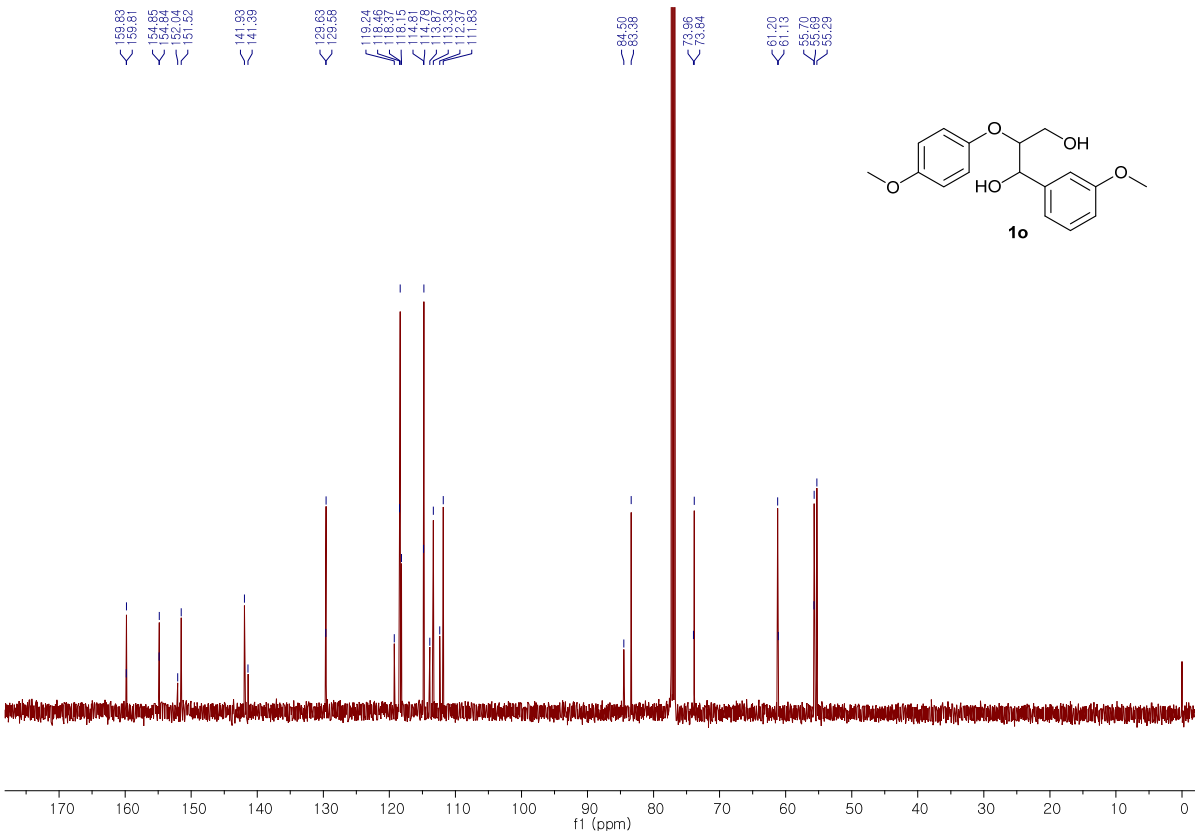

1m
f1 (ppm)

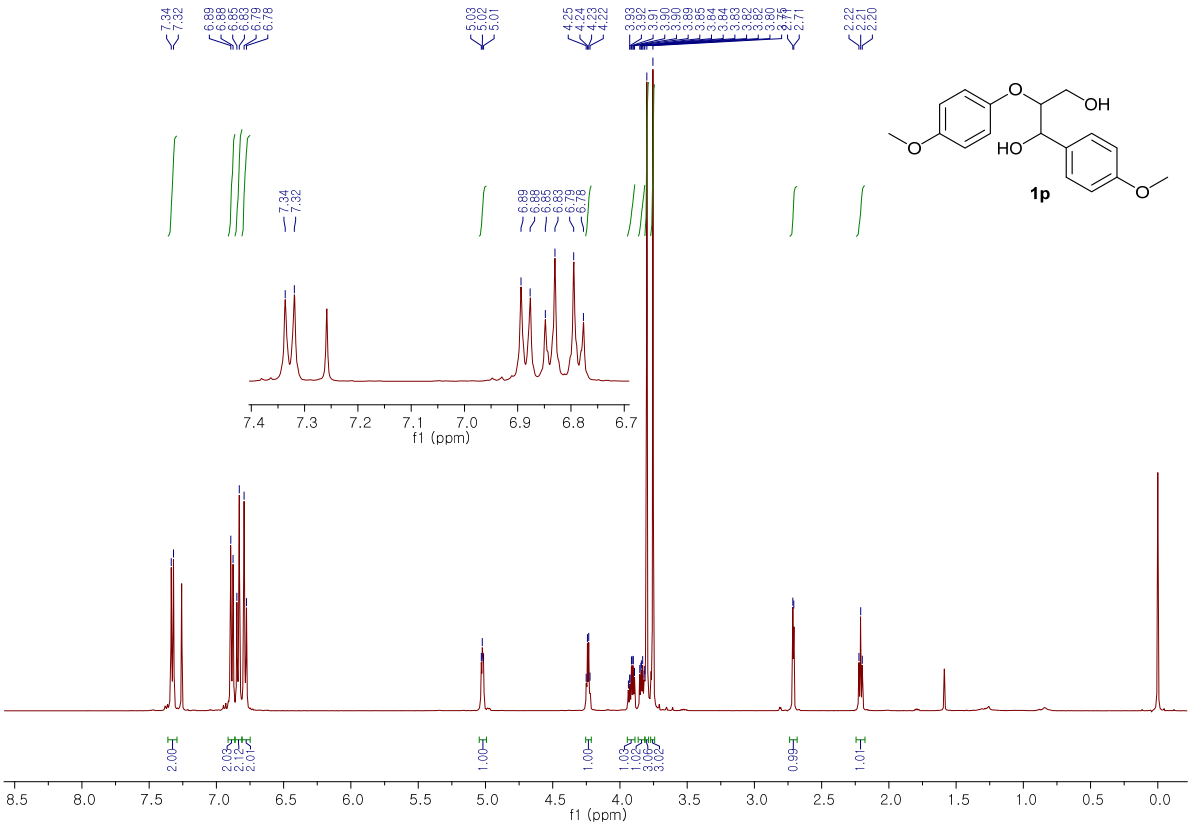

1m
f1 (ppm)

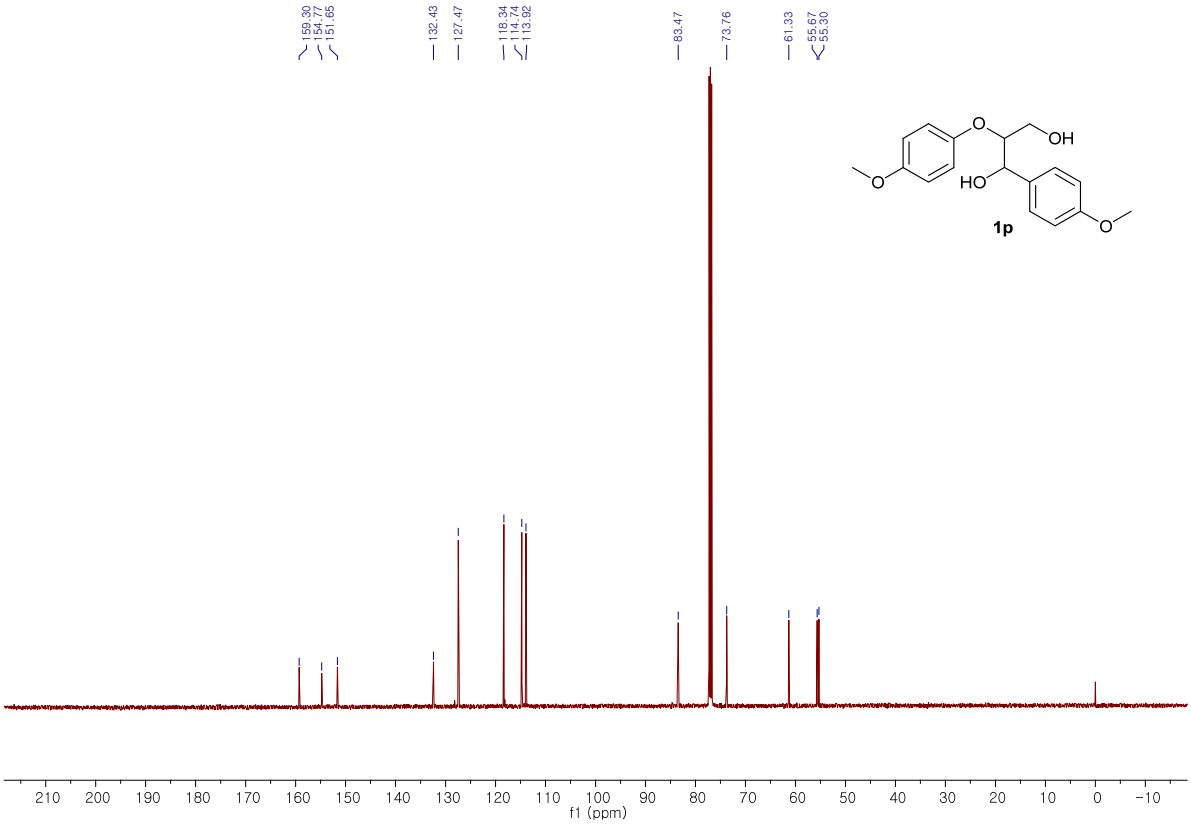

7.49
7.48
7.47
7.47
7.25
7.23
6.99
6.98
6.96
6.95
6.94
6.93
6.92
6.91
6.84
6.83
6.80
6.79
6.78
6.77
5.34
5.33
5.32
4.52
4.52
4.51
4.51
4.51
4.50
3.90
3.89
3.88
3.87
3.74
3.72
3.72
3.39
3.38
2.55
2.54
2.52
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00
1.05
1.00
2.00
1.00
1.99
1.00
1.00
1.03
3.00
4.02
0.98
0.99
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
OH
HO
O
O
1n

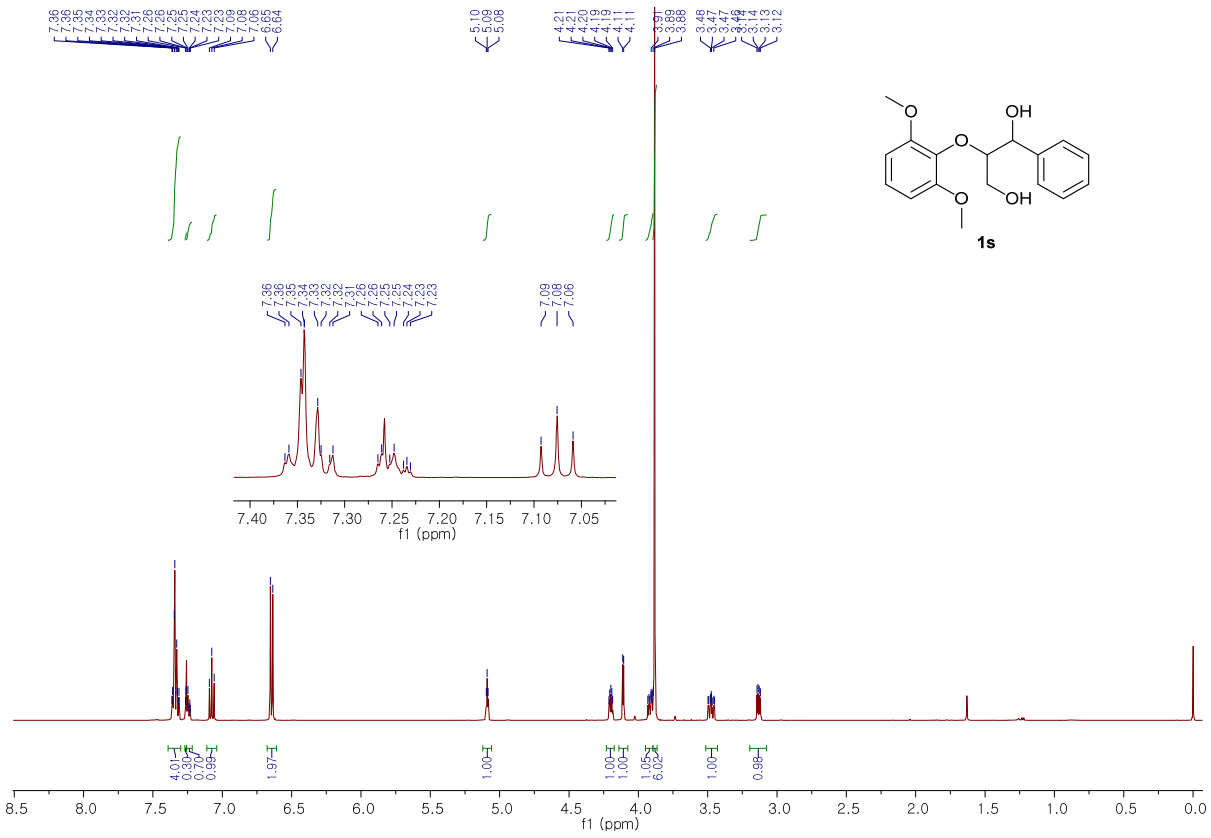

156.04
154.42
151.85
128.76
127.98
127.50
121.01
117.74
114.63
110.29
80.48
70.19
61.58
55.71
55.31
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
OH
HO
O
O
1n

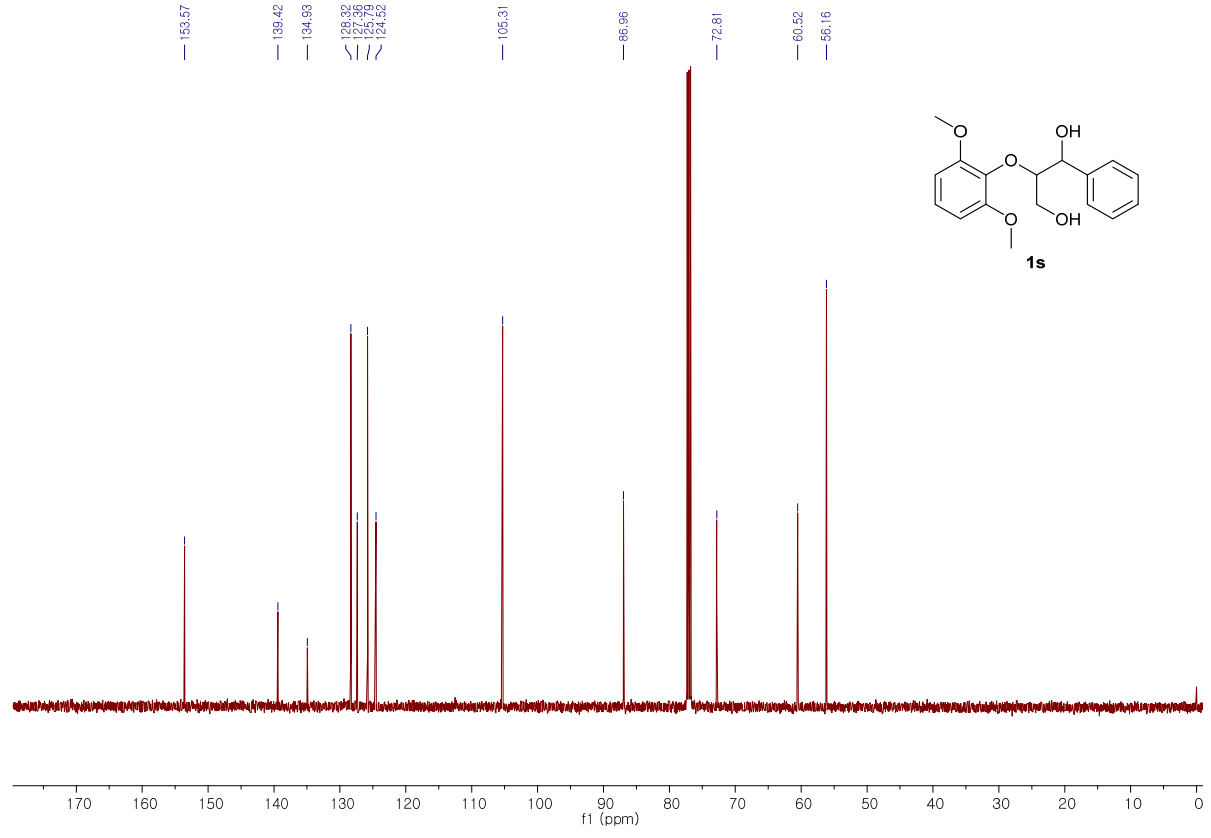

OH
HO
O
O
1o
f1 (ppm)

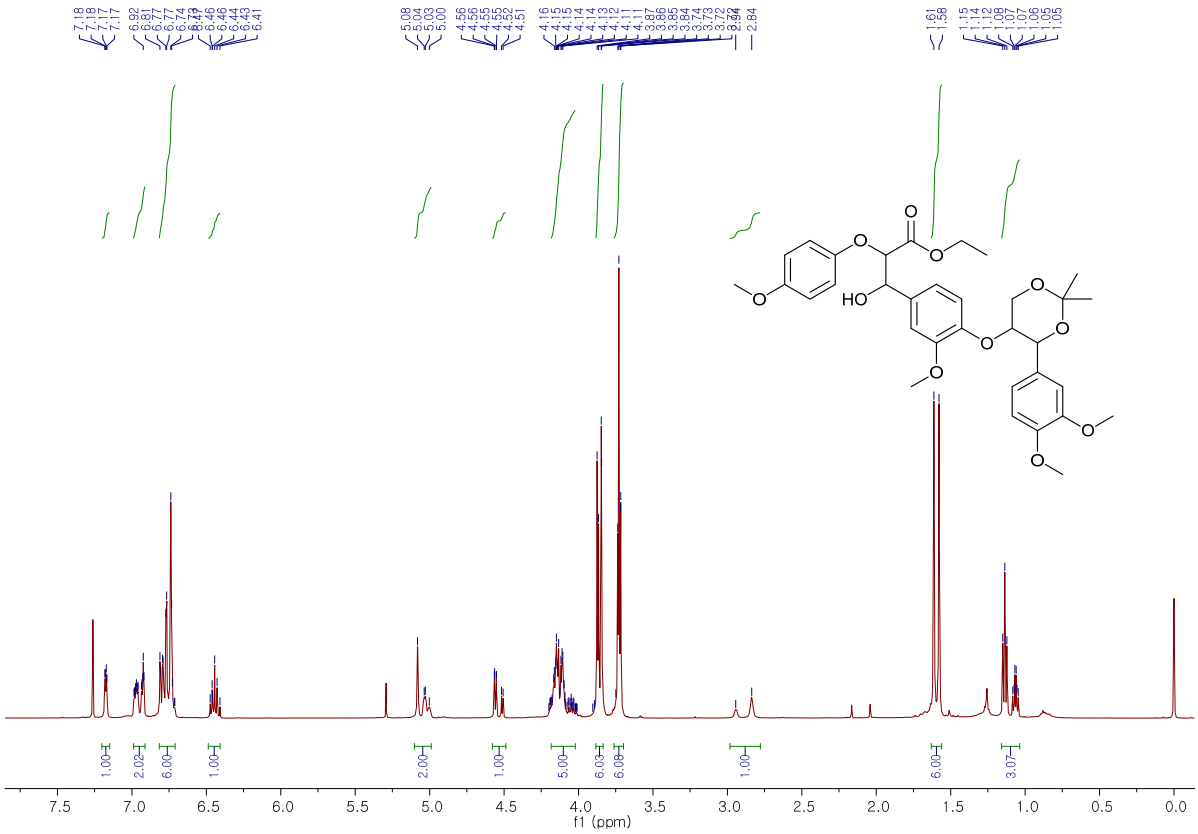

OH
HO
O
O
1o
f1 (ppm)

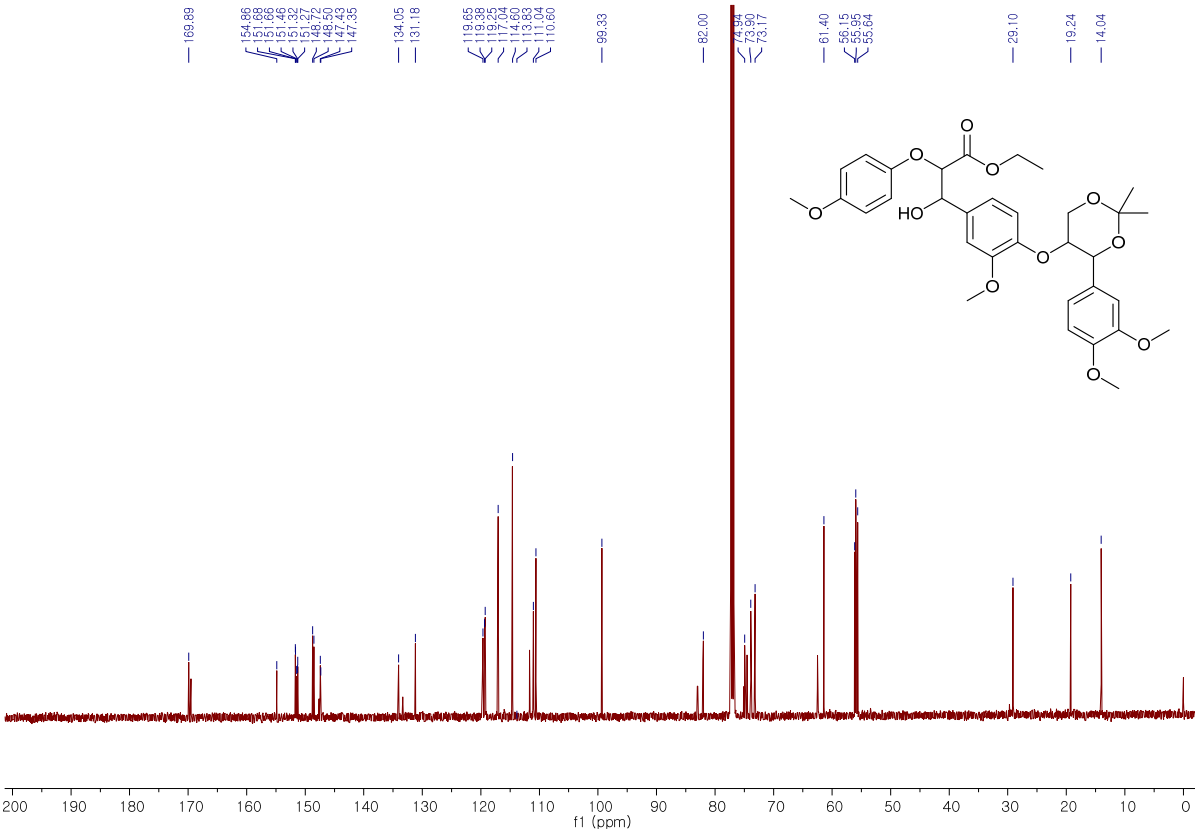

7.34
7.32
6.89
6.88
6.85
6.83
6.79
6.78
5.03
5.02
5.01
4.25
4.24
4.23
4.22
3.93
3.92
3.91
3.90
3.89
3.85
3.84
3.83
3.82
3.81
3.80
2.75
2.71
2.22
2.21
2.20
OH
HO
O
O
1p
f1 (ppm)
f1 (ppm)

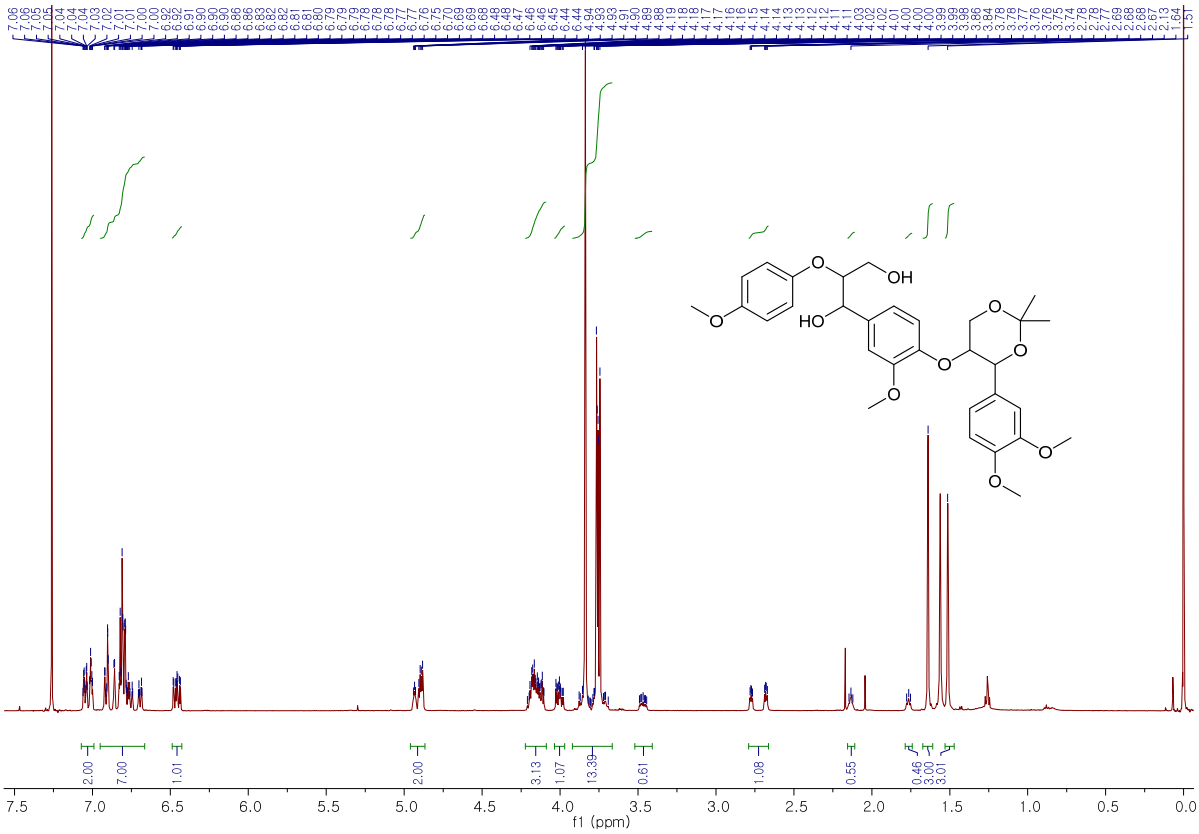

159.30
154.77
151.65
132.43
127.47
118.34
114.74
113.92
83.47
73.76
61.33
55.67
55.30
OH
HO
O
O
1p
f1 (ppm)

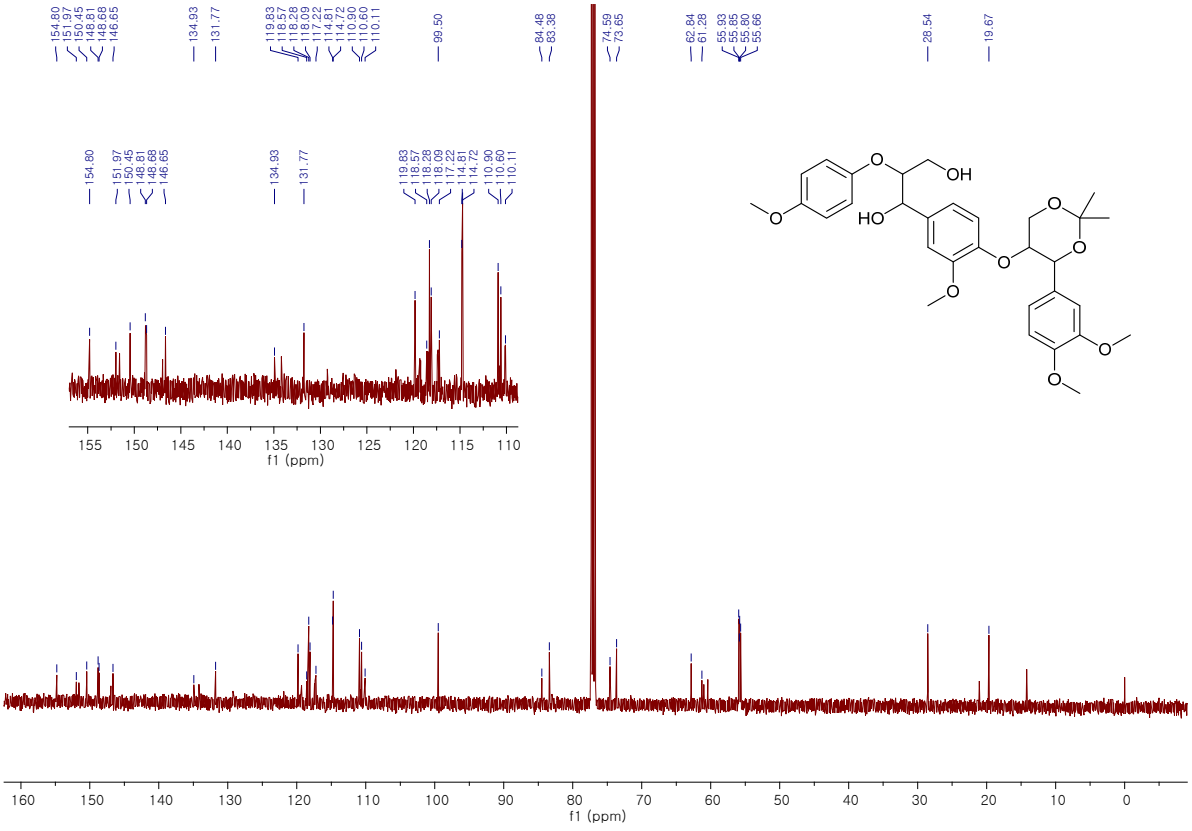

7.36
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.26
7.25
7.25
7.24
7.23
7.23
7.09
7.08
7.06
6.65
6.64
5.10
5.09
5.08
4.21
4.21
4.20
4.19
4.19
4.11
4.11
3.91
3.89
3.88
3.48
3.47
3.47
3.46
3.14
3.13
3.12
OH
OH
1s
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)
4.01
1.30
0.70
0.99
1.97
1.00
1.00
1.05
6.02
1.00
0.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

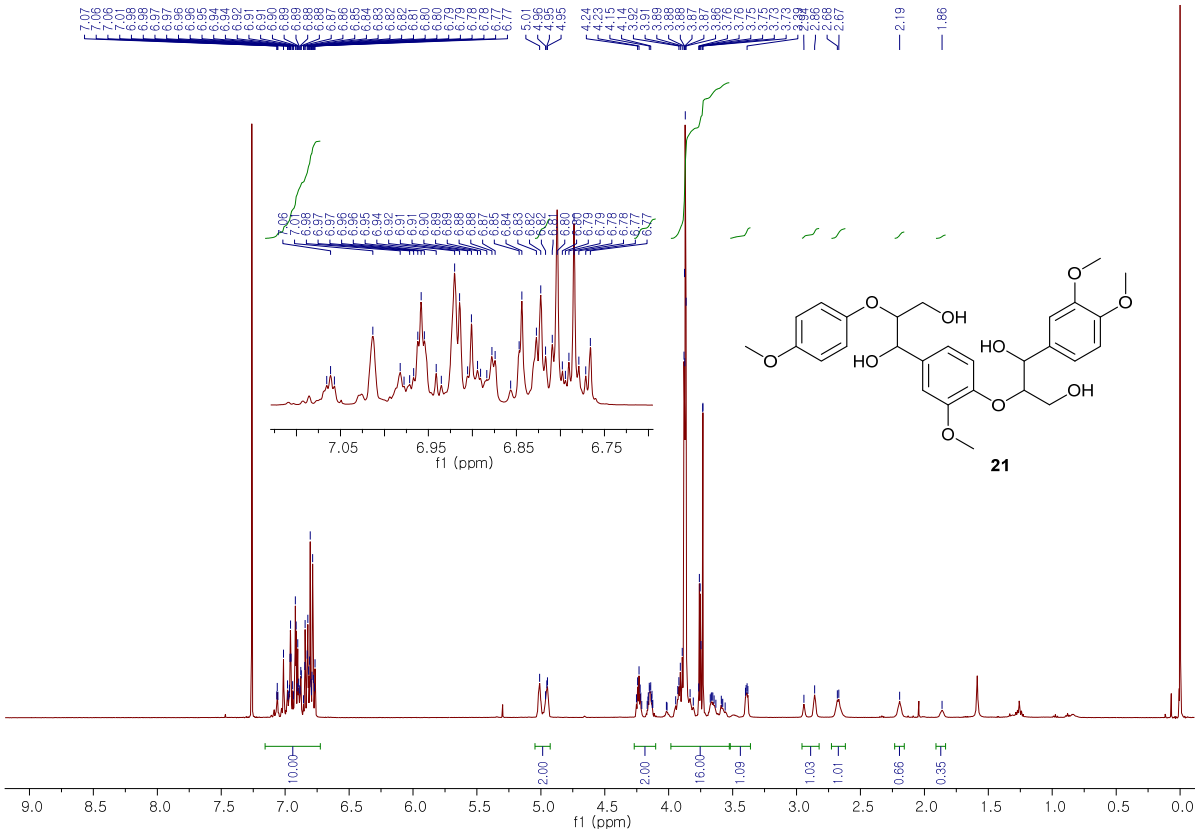

153.57
139.42
134.93
128.32
127.96
125.79
124.52
105.31
86.96
72.81
60.52
56.16
OH
OH
1s
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

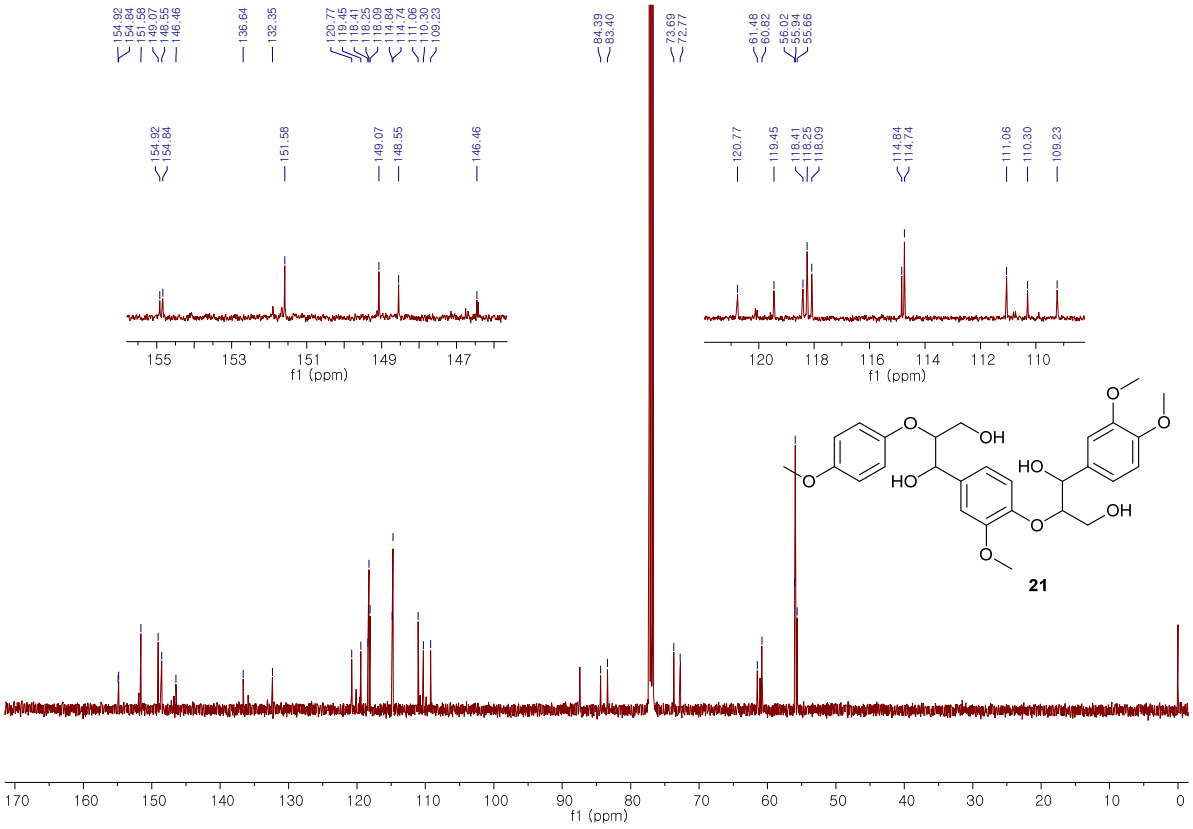

f1 (ppm)


f1 (ppm)

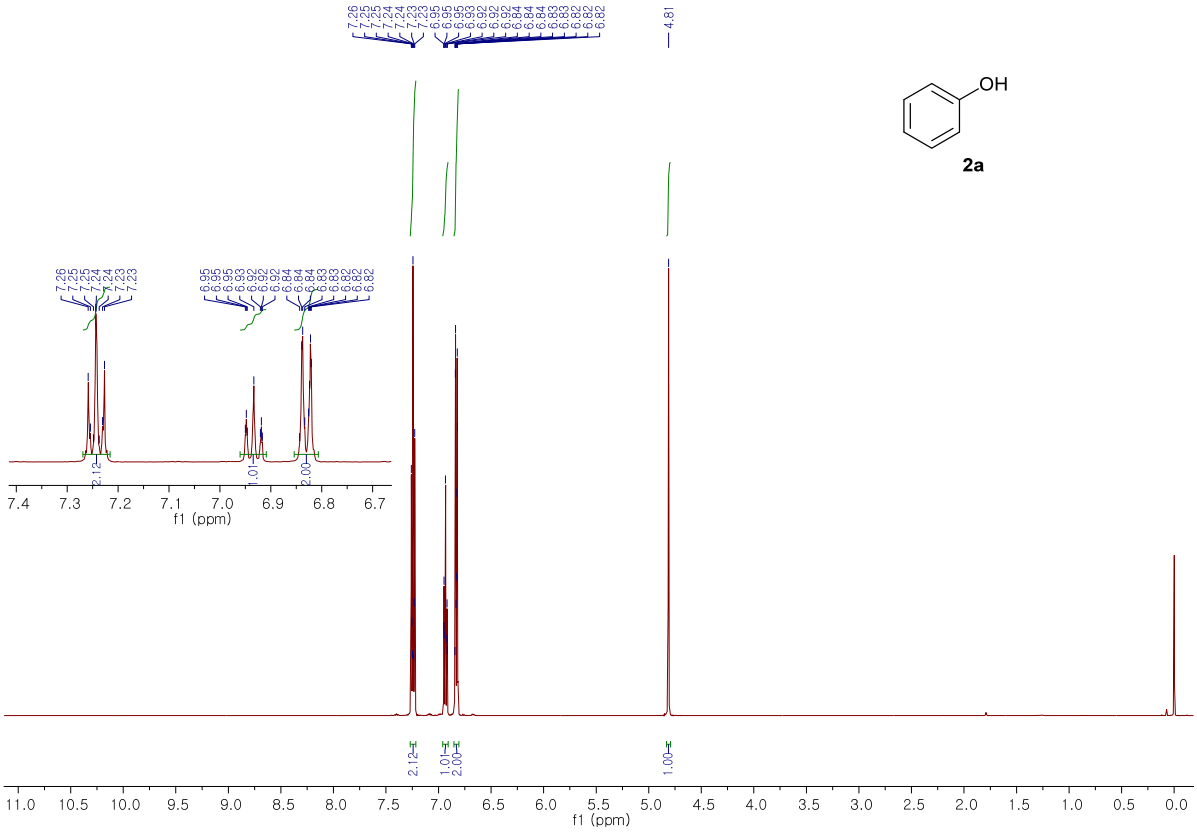

OH
HO
O
f1 (ppm)

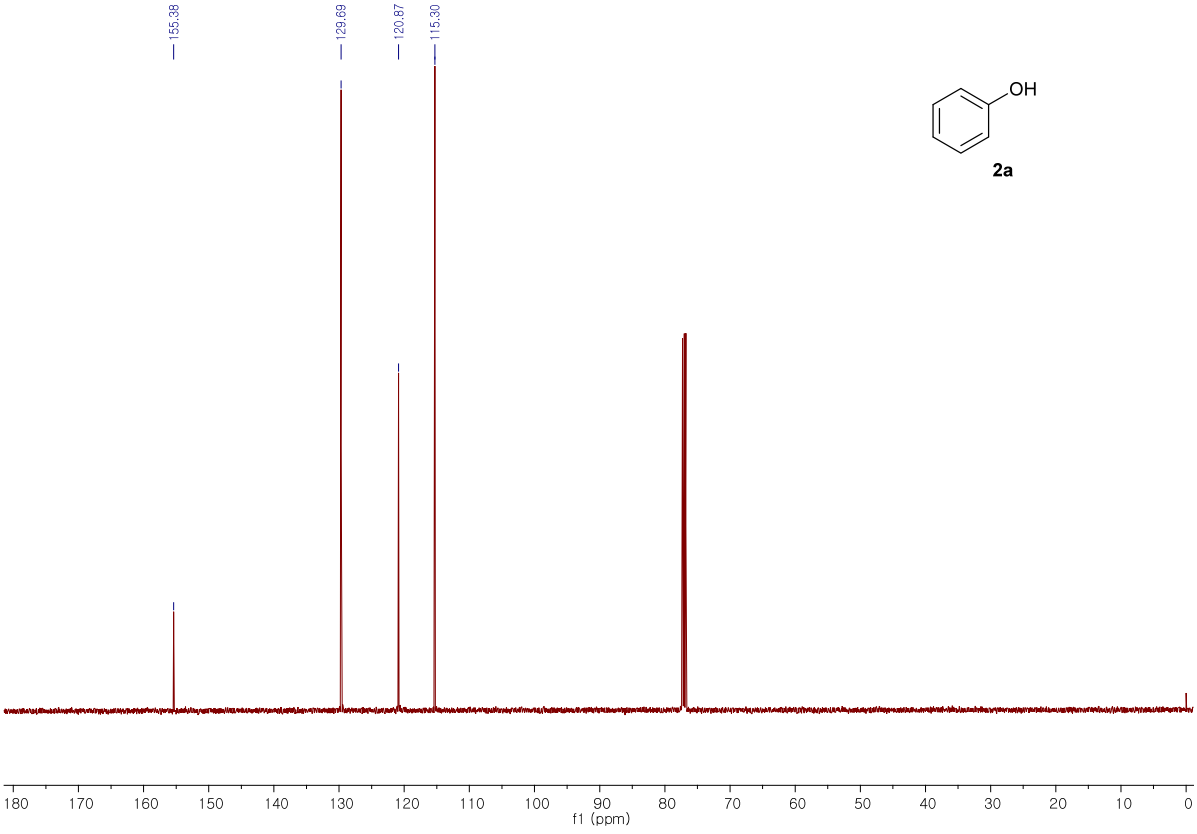

OH
HO
O
f1 (ppm)

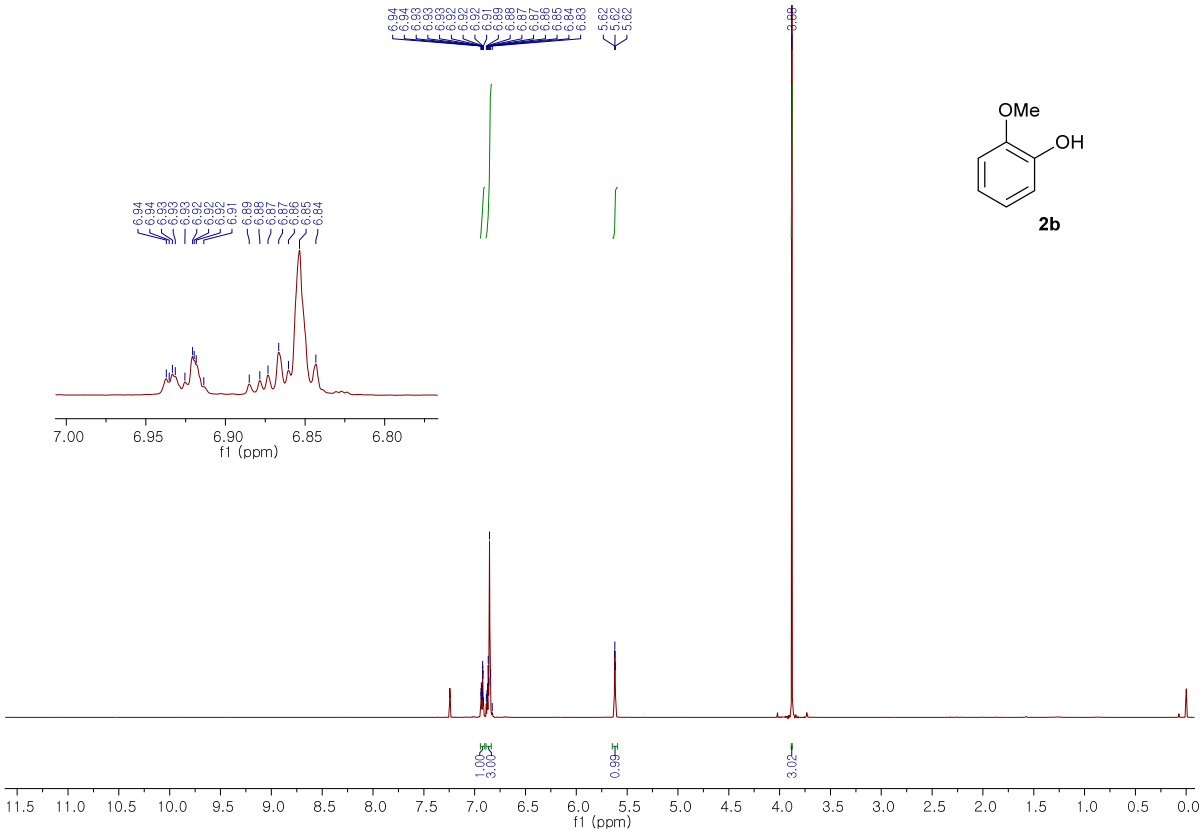

f1 (ppm)
21

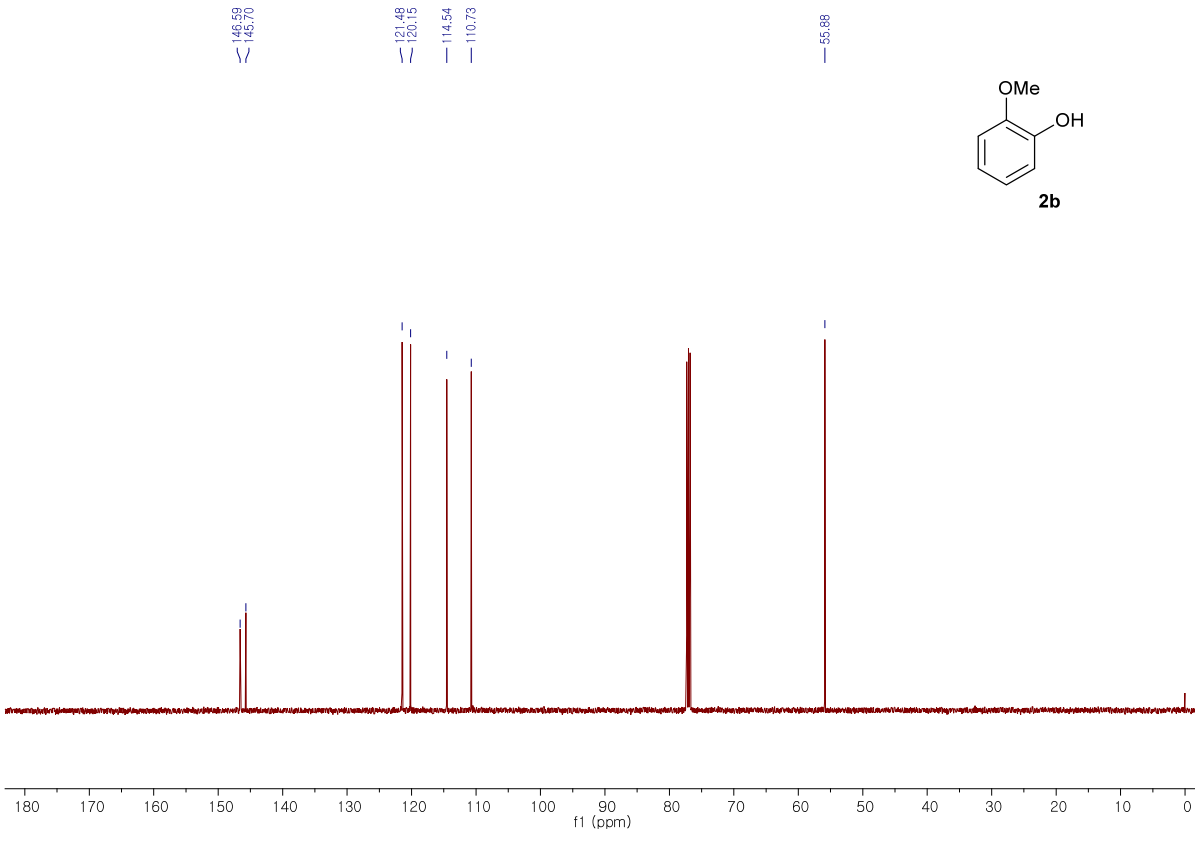

f1 (ppm)
21

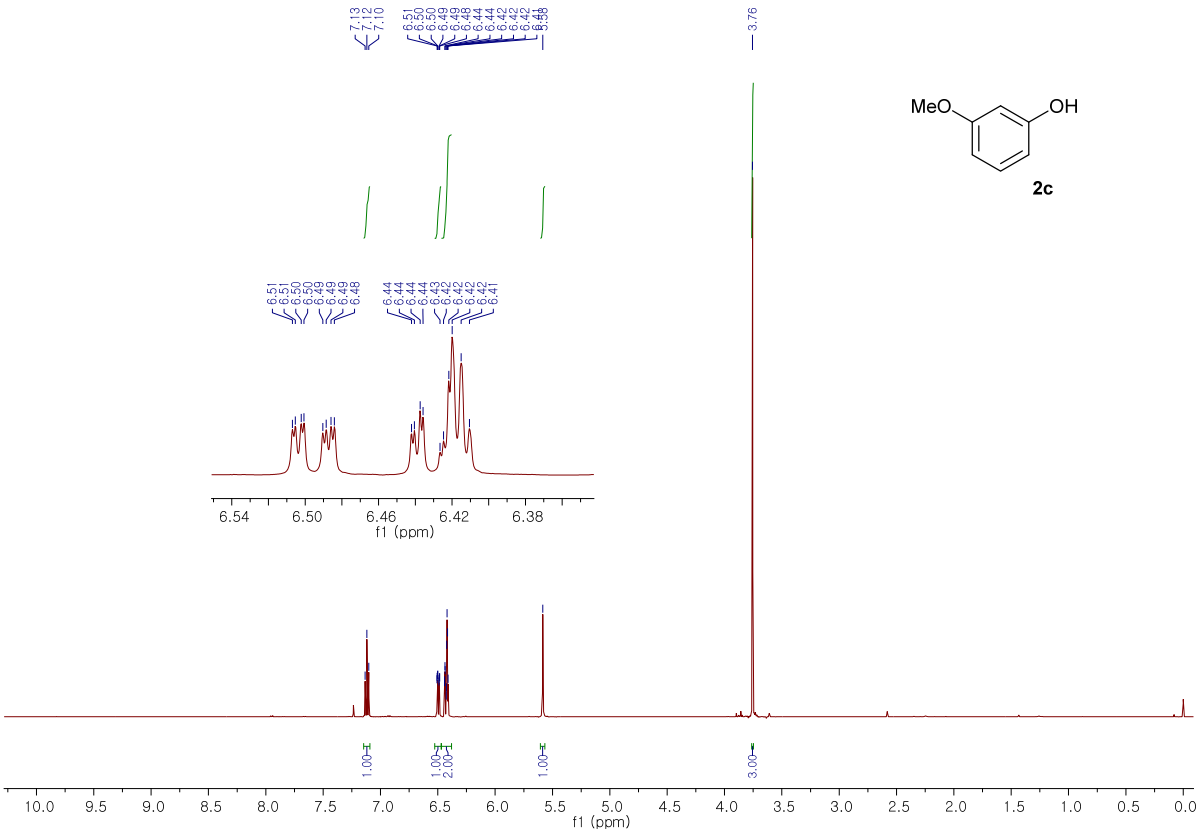
^{1}H NMR and ^{13}C NMR Spectra of Products

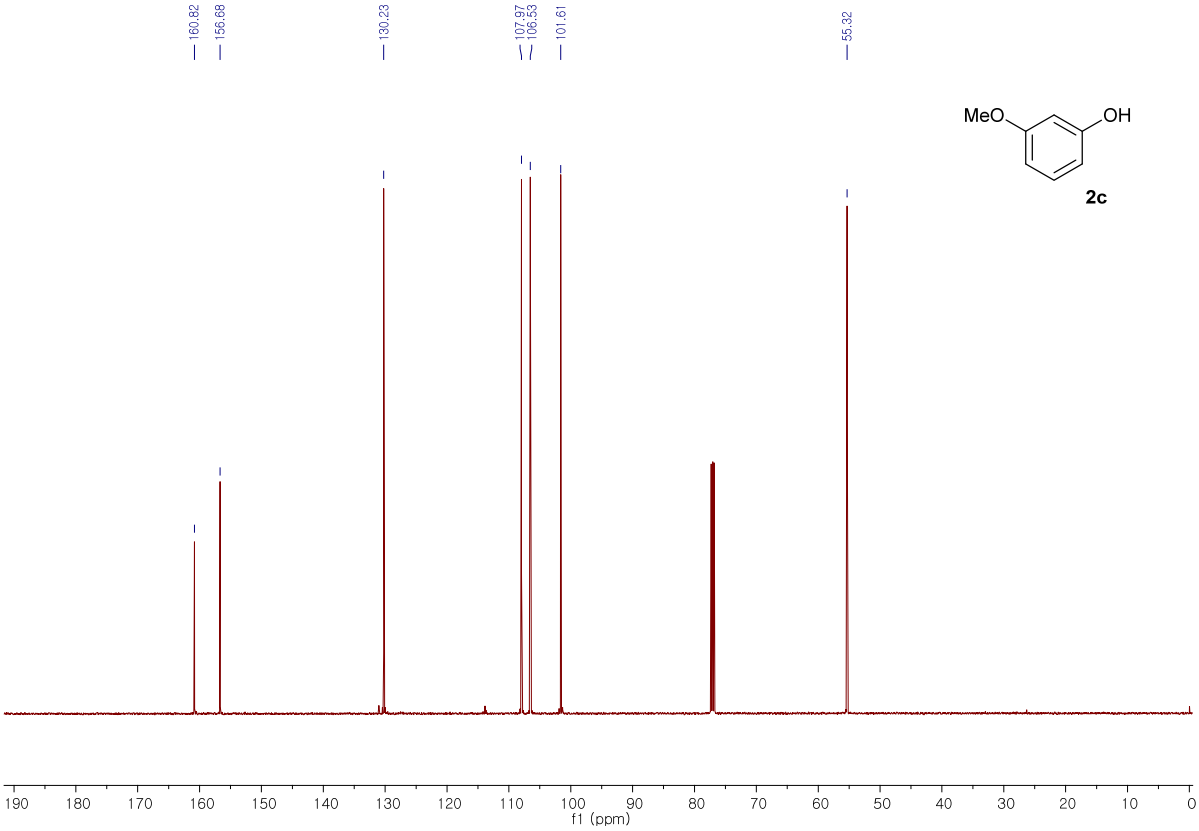


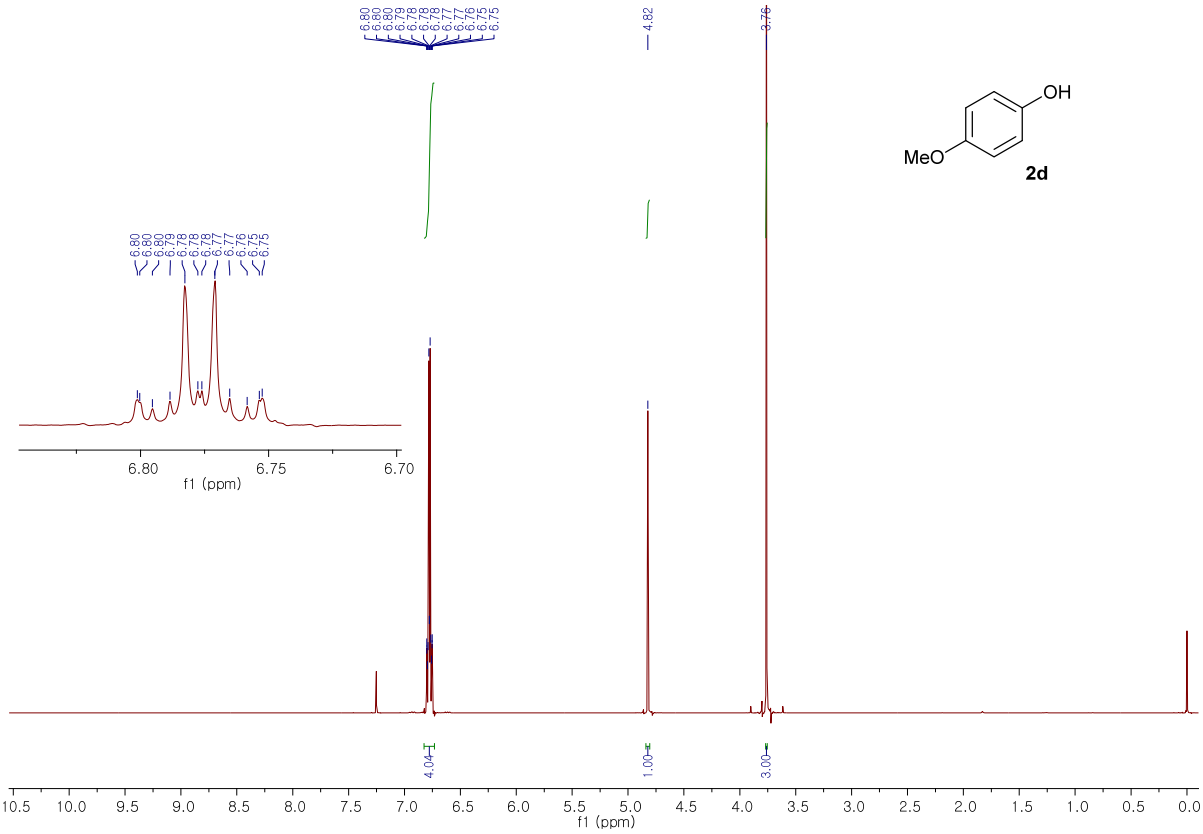


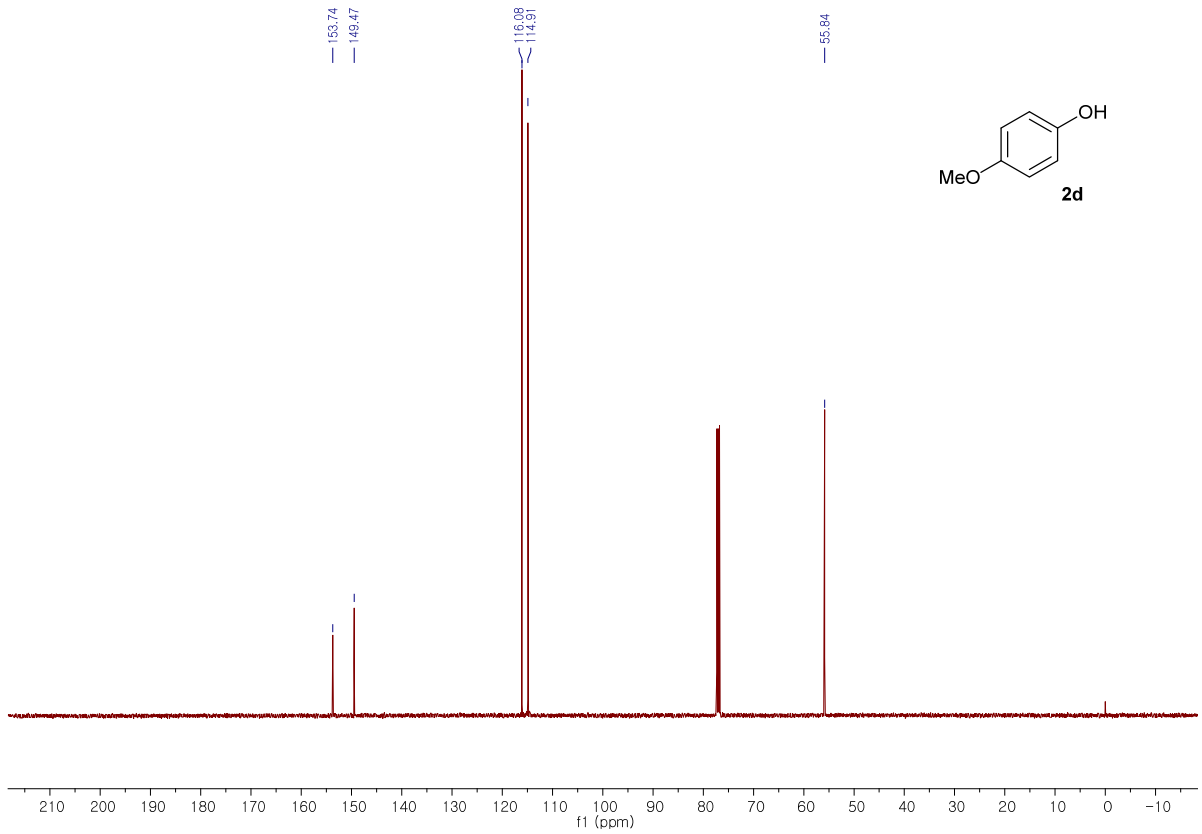

OMe
OH
2b
f1 (ppm)

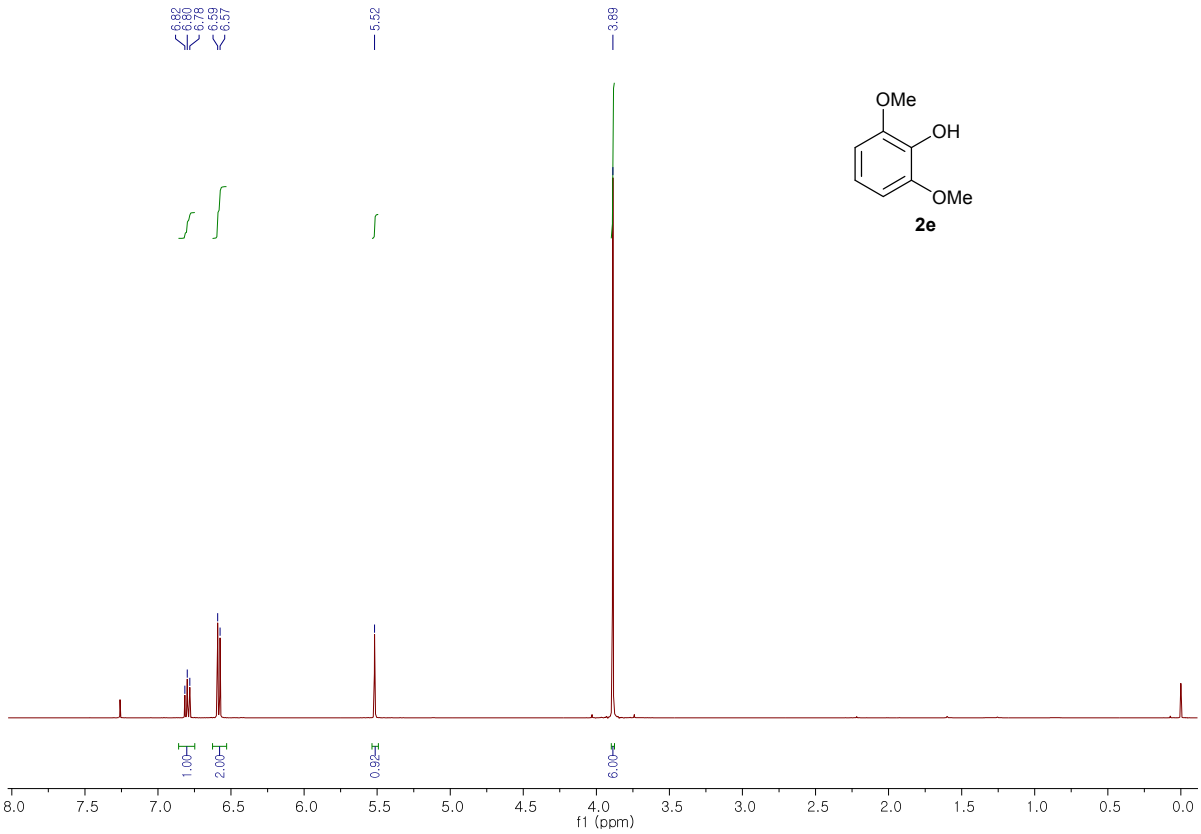

OMe
OH
2b
f1 (ppm)

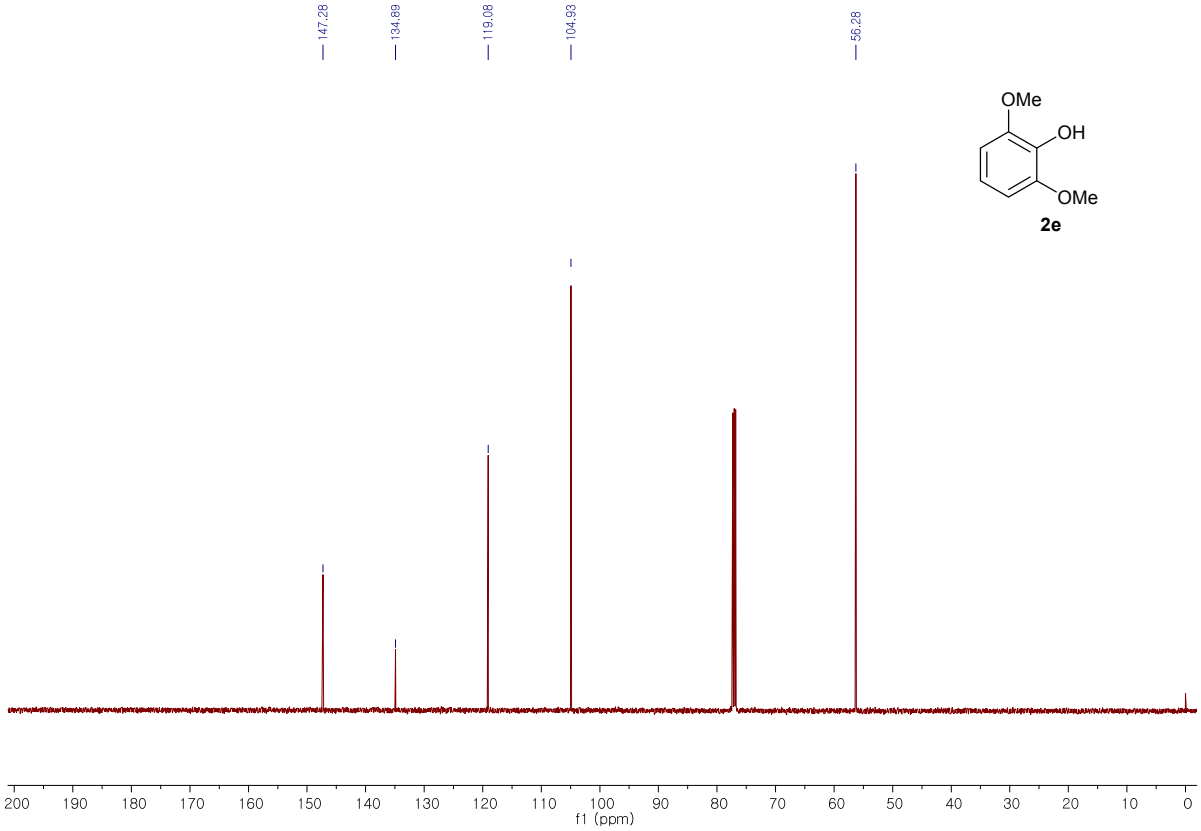

7.13
7.12
7.10
6.51
6.50
6.50
6.49
6.49
6.48
6.44
6.44
6.42
6.42
6.41
6.38
3.76
MeO
OH
2c
6.54
6.50
6.46
6.42
6.38
f1 (ppm)
1.00
1.00
2.00
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

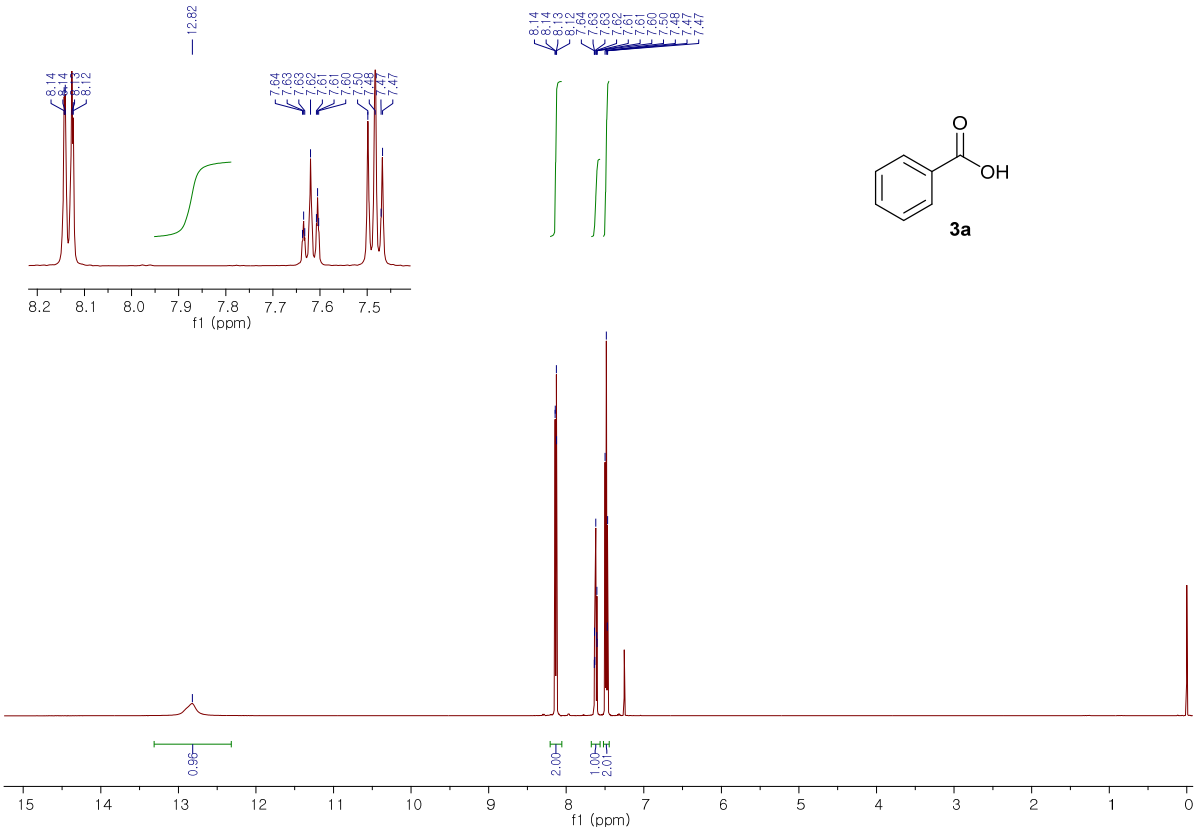

160.82
156.68
130.23
107.97
106.53
101.61
55.32
MeO
OH
2c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

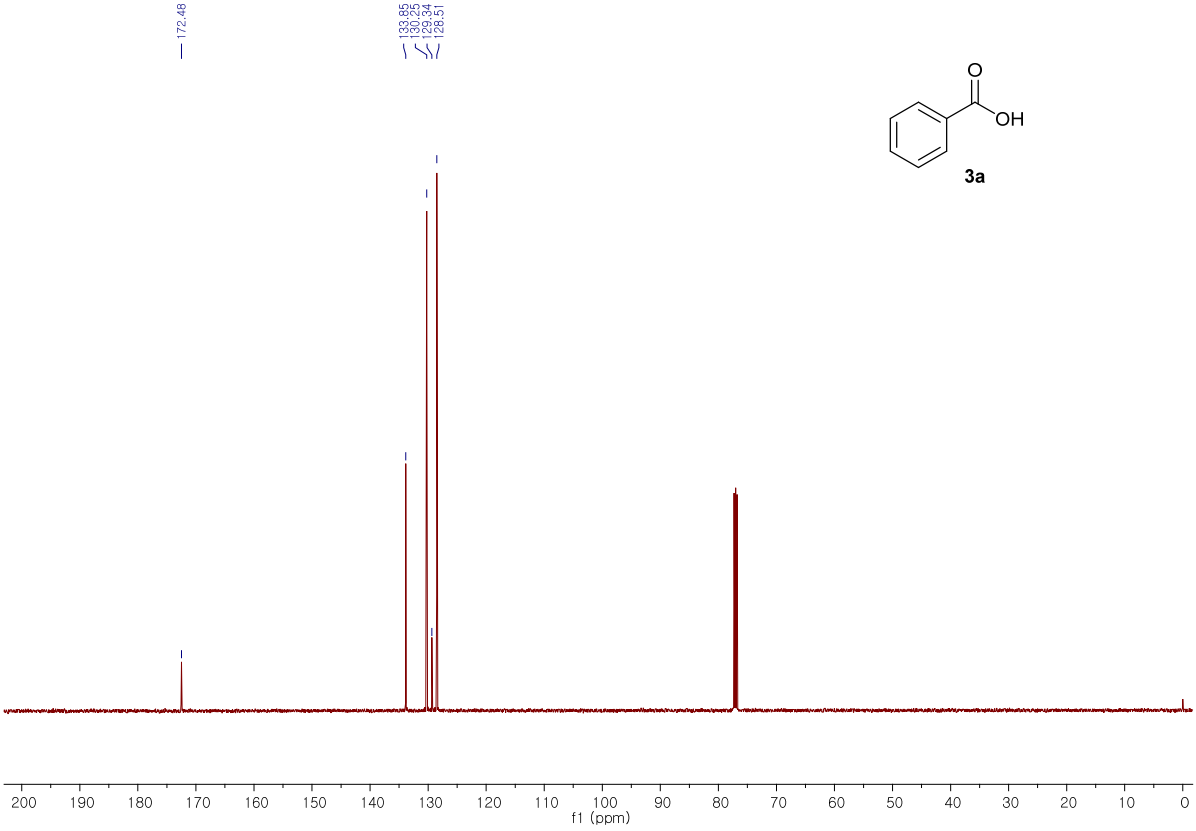

6.80
6.80
6.80
6.79
6.78
6.78
6.78
6.77
6.77
6.76
6.75
6.75
4.82
3.76
OH
MeO
2d
4.04
1.00
3.00
f1 (ppm)

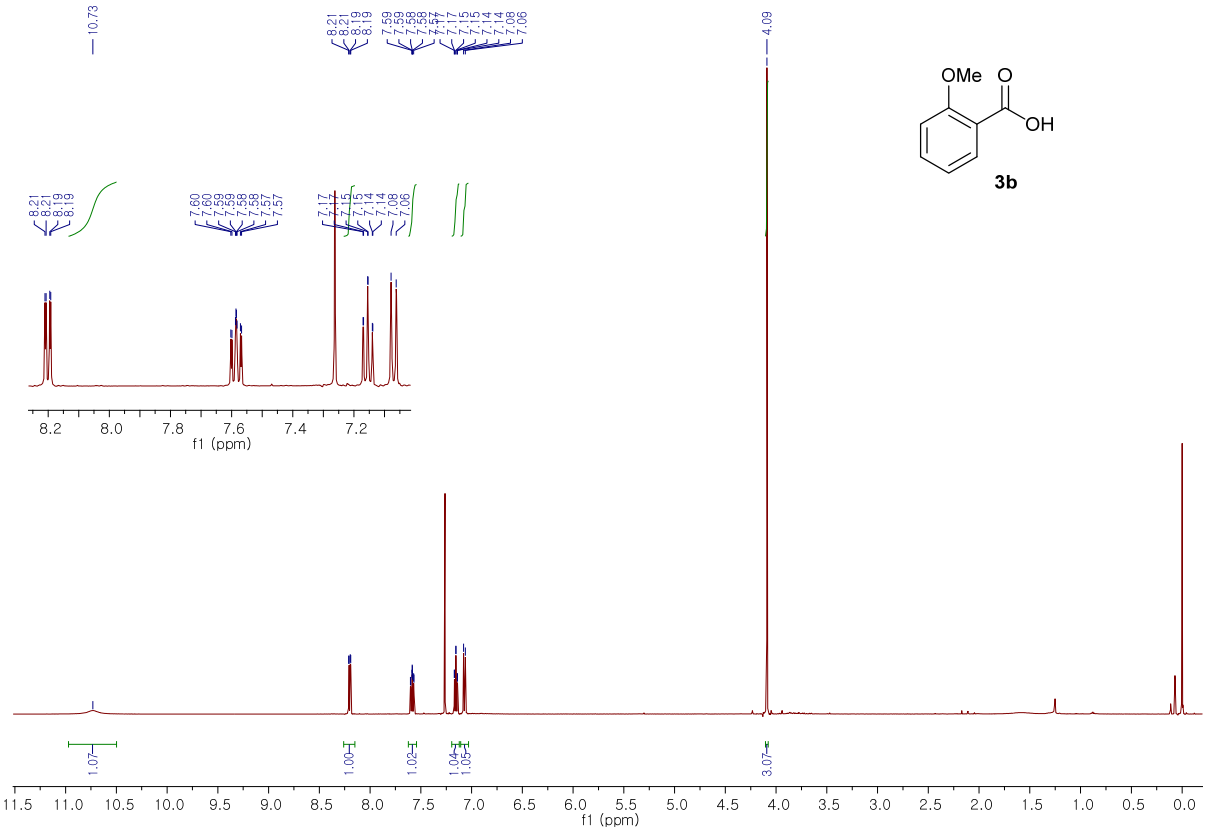

153.74
149.47
116.08
114.91
55.84
OH
MeO
2d
f1 (ppm)

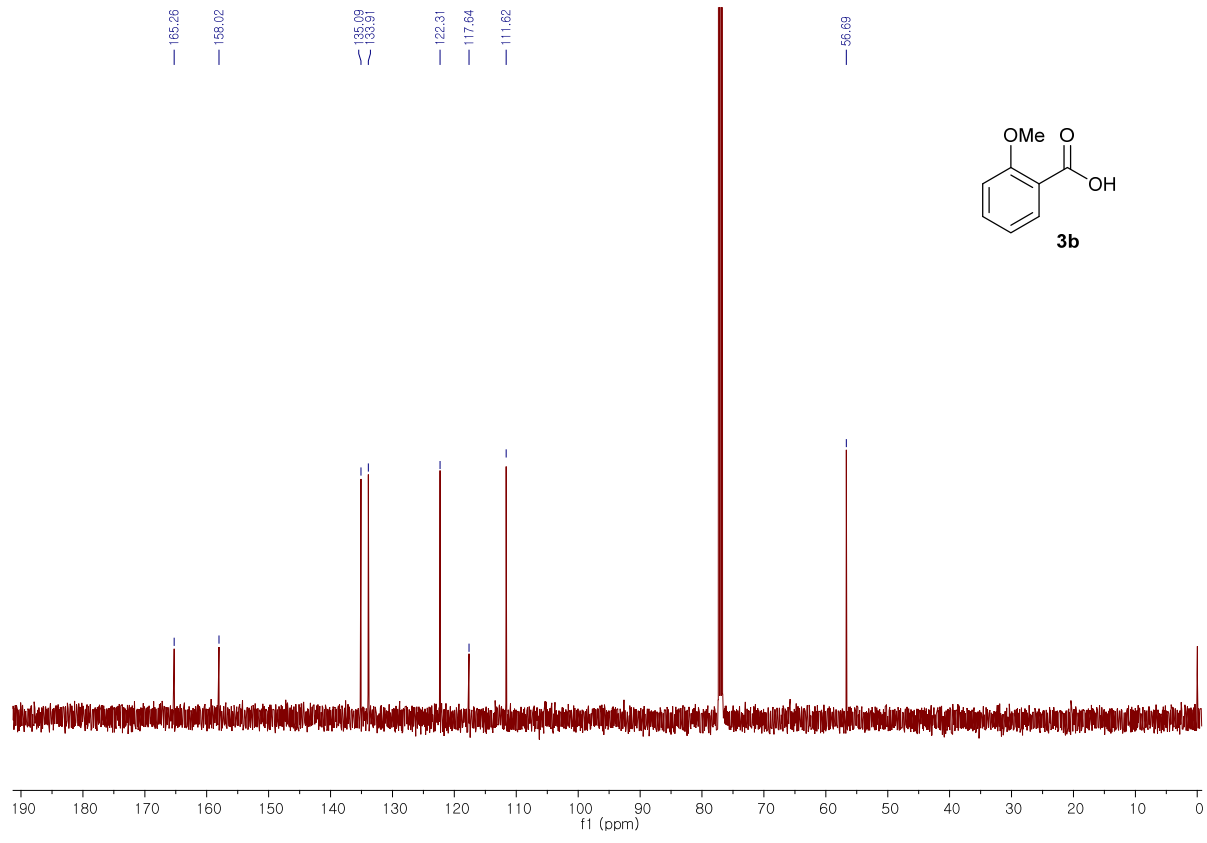

6.82
6.80
6.78
6.59
6.57
5.52
3.89
OMe
OH
OMe
2e
1.00
2.00
0.92
6.00
f1 (ppm)

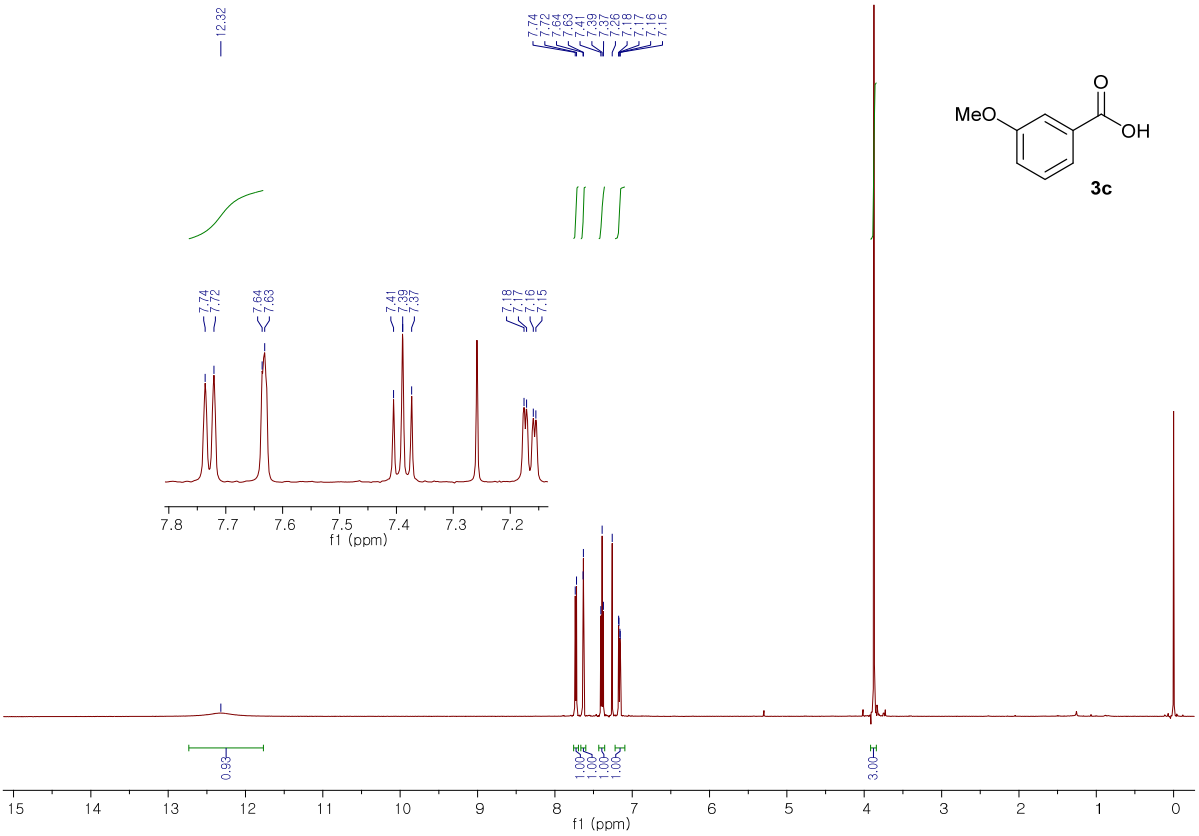

147.28
134.89
119.08
104.93
56.28
OMe
OH
OMe
2e
f1 (ppm)

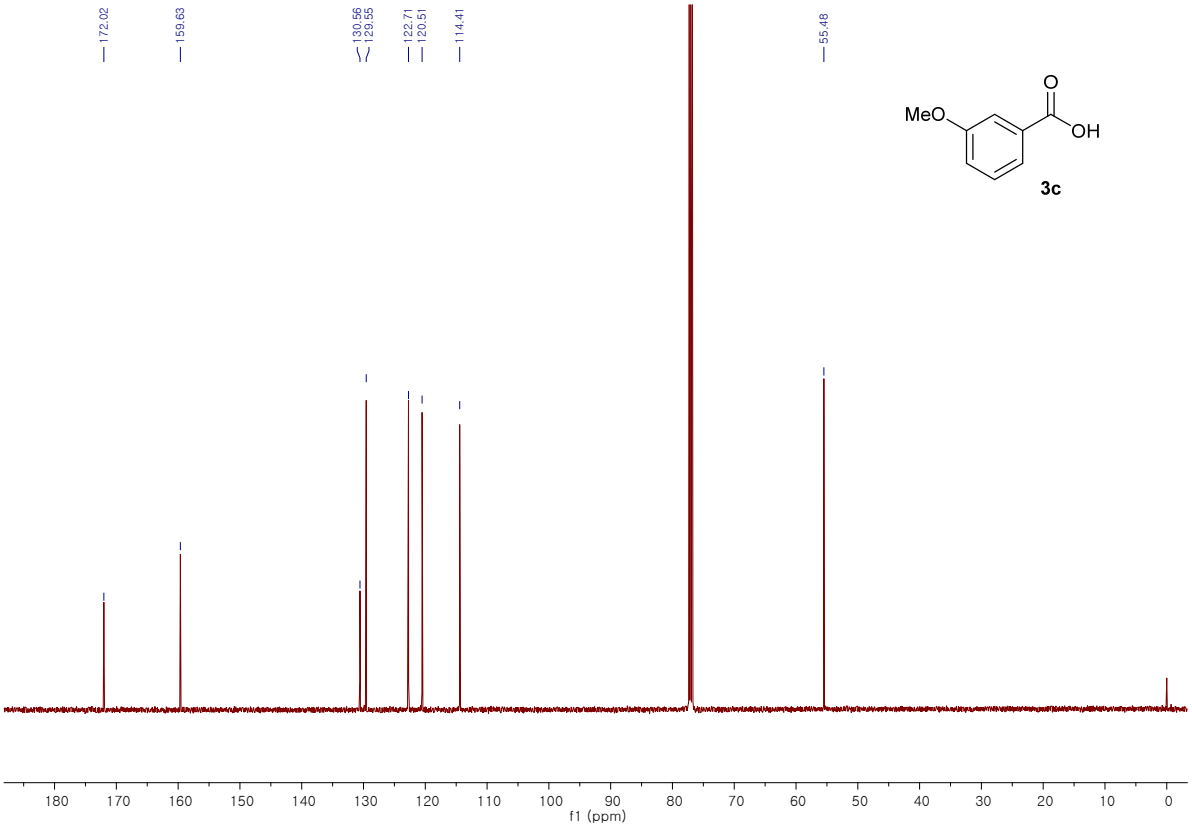

12.82
8.14
8.14
8.13
8.12
7.64
7.63
7.63
7.62
7.61
7.61
7.60
7.50
7.48
7.47
7.47
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5
f1 (ppm)
O
OH
3a
0.96
2.00
1.00
2.01
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

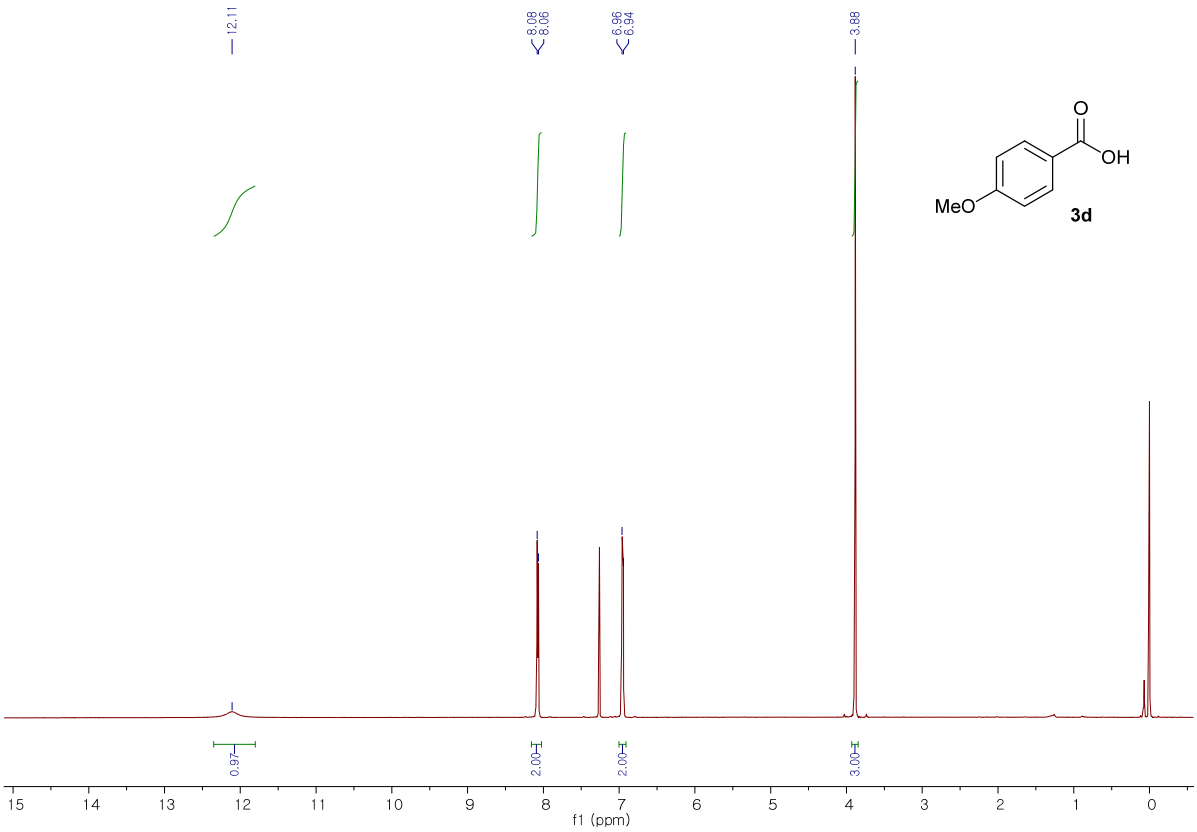

172.48
133.85
130.25
129.34
128.51
O
OH
3a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

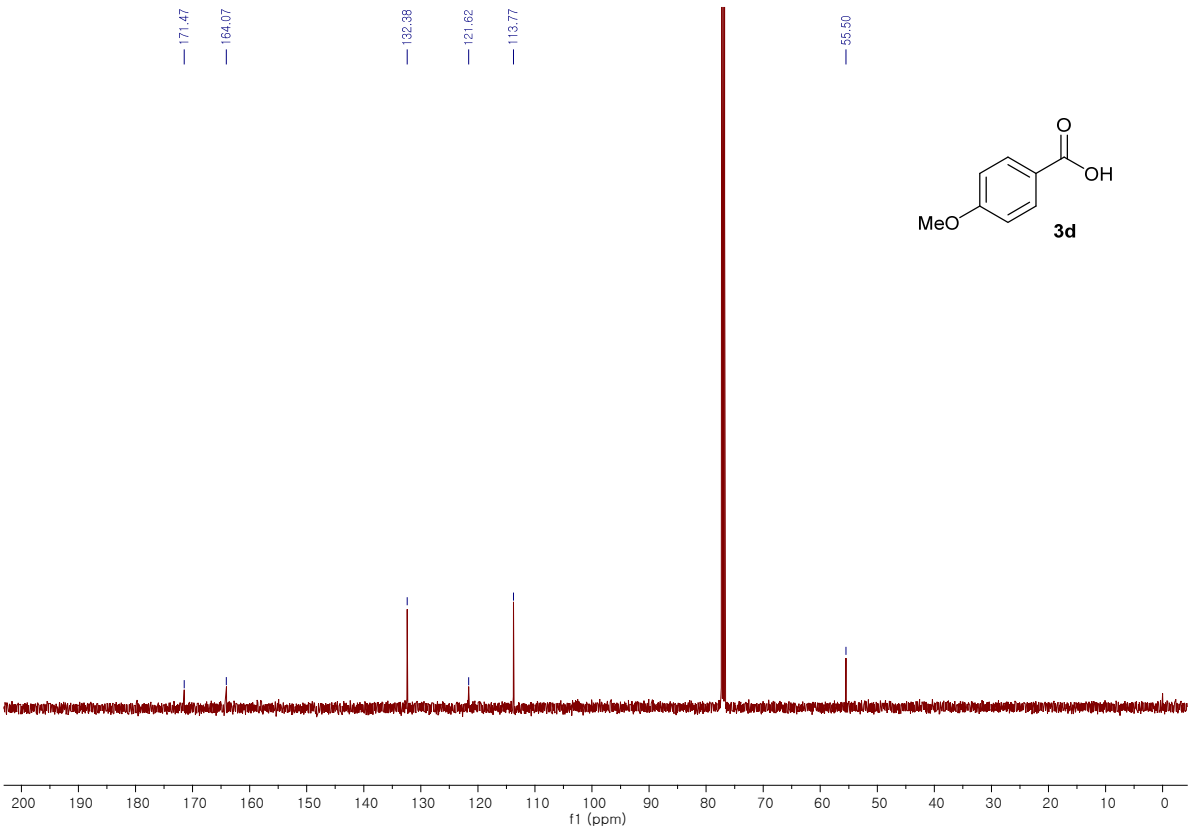

10.73
8.21
8.21
8.19
8.19
7.59
7.59
7.58
7.58
7.57
7.57
7.17
7.17
7.15
7.15
7.14
7.14
7.08
7.08
7.06
4.09
OMe
O
OH
3b
f1 (ppm)
1.07
1.00
1.02
1.04
1.05
3.07

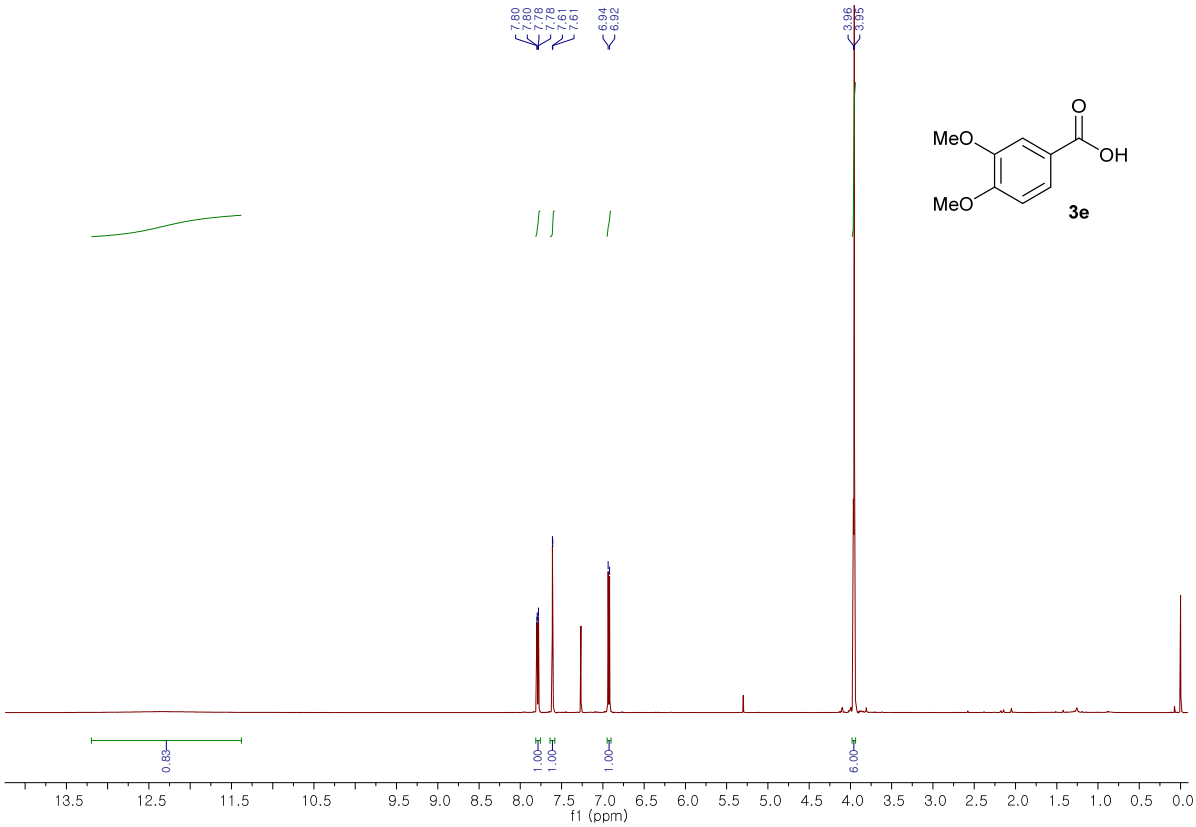

165.26
158.02
135.09
133.91
122.31
117.64
111.62
56.69
OMe
O
OH
3b
f1 (ppm)

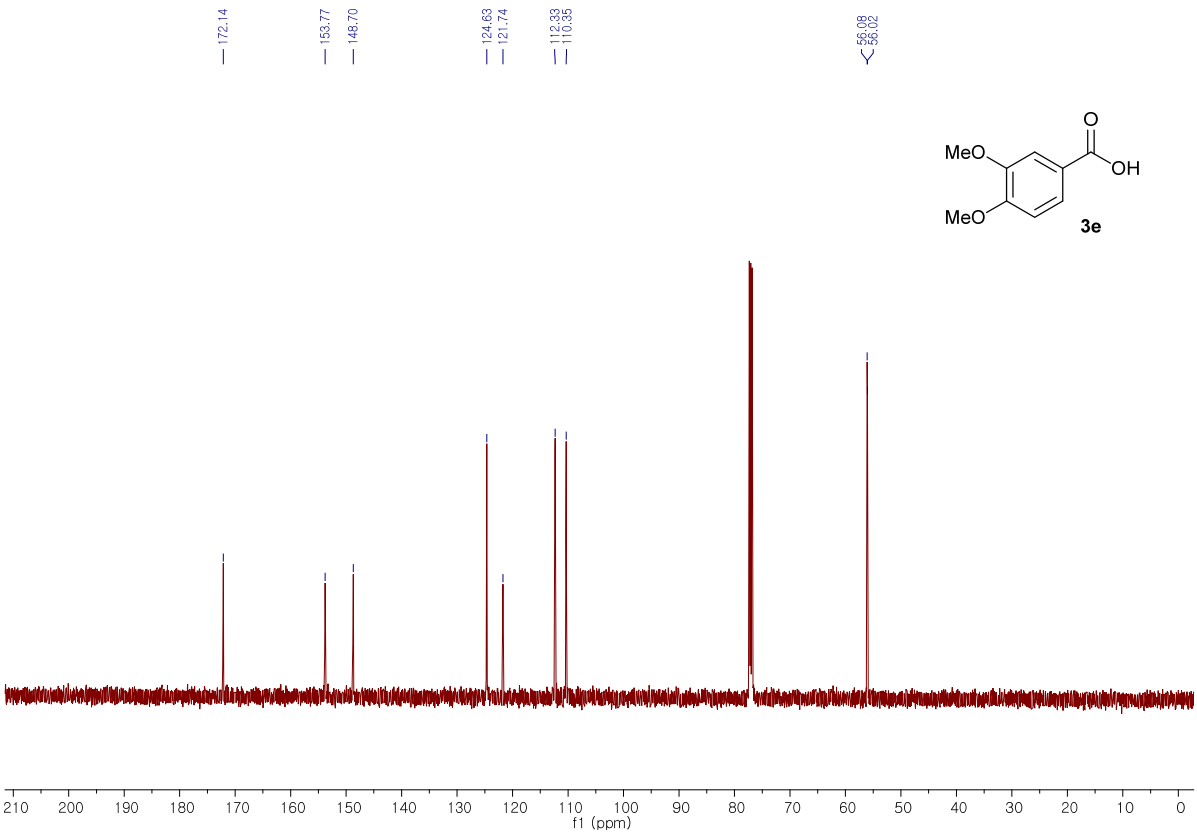

12.32
7.74
7.72
7.64
7.63
7.41
7.39
7.37
7.26
7.18
7.17
7.16
7.15
MeO
O
OH
3c
0.93
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

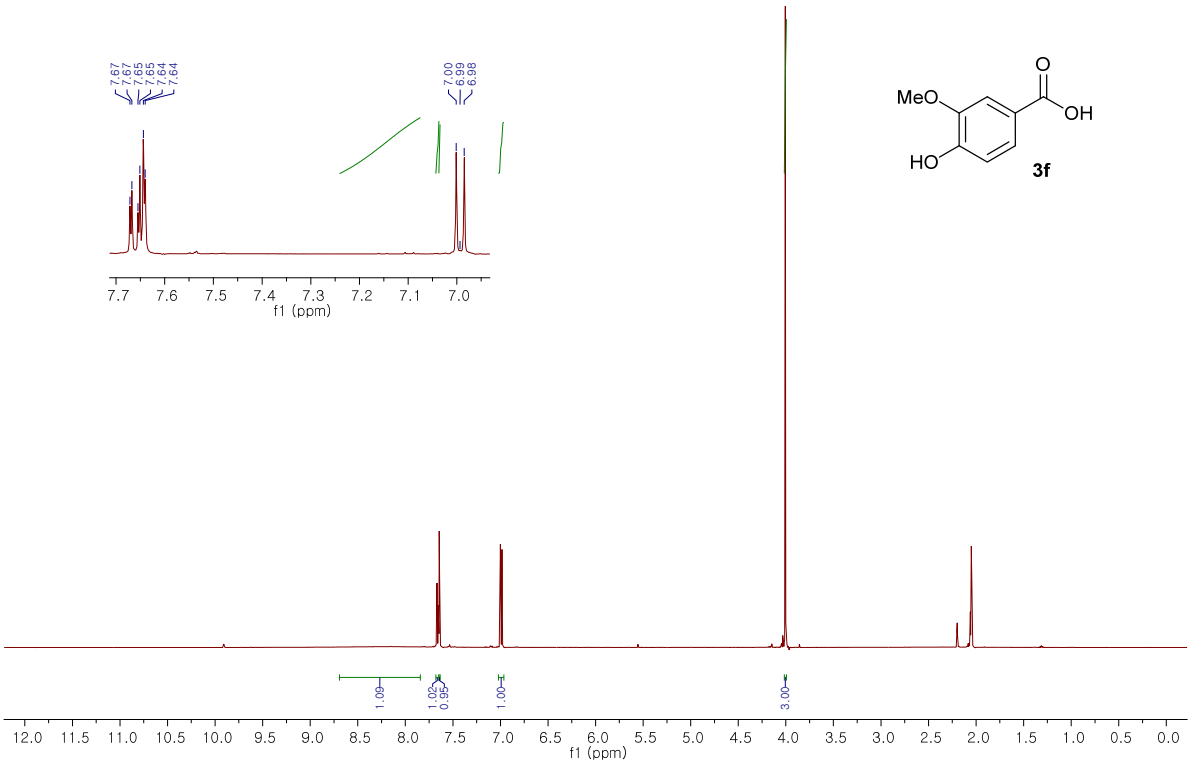

172.02
159.63
130.56
129.55
122.71
120.51
114.41
55.48
MeO
O
OH
3c
f1 (ppm)

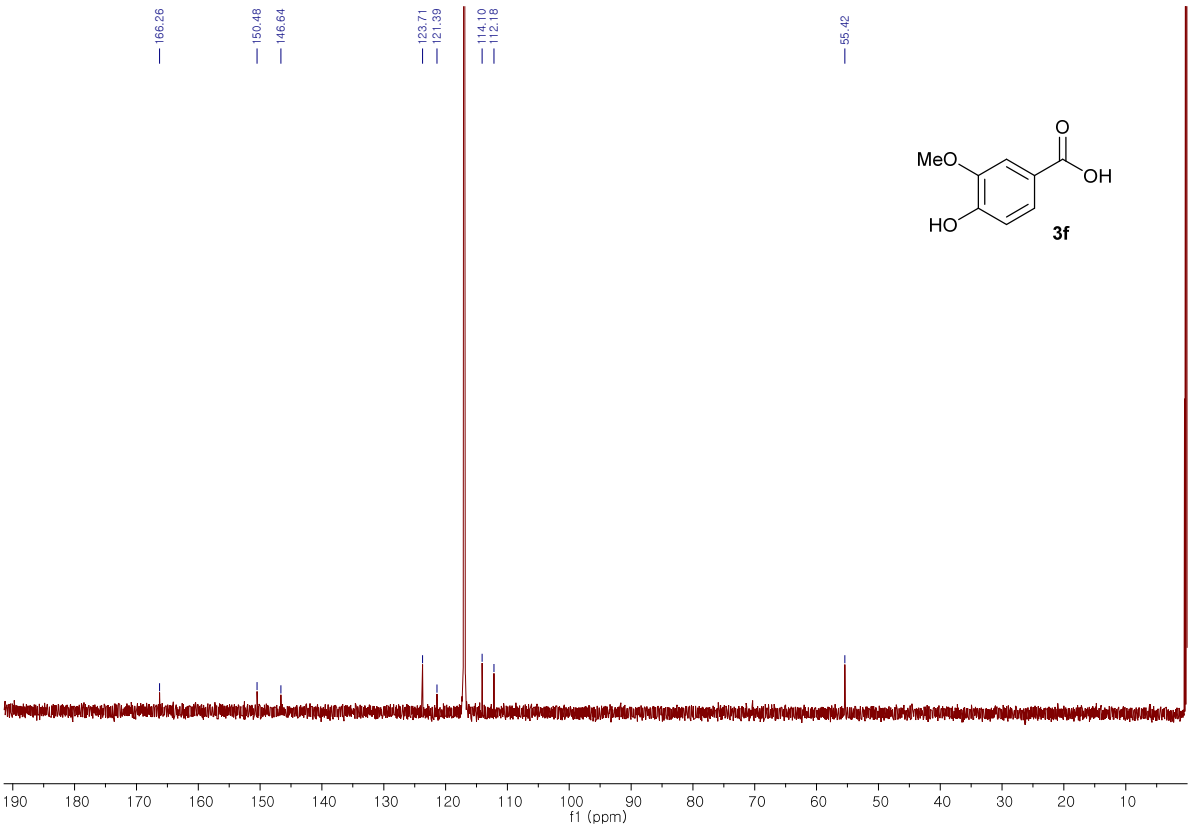

12.11
8.08
8.06
6.96
6.94
3.88
O
OH
MeO
3d
0.97
2.00
2.00
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

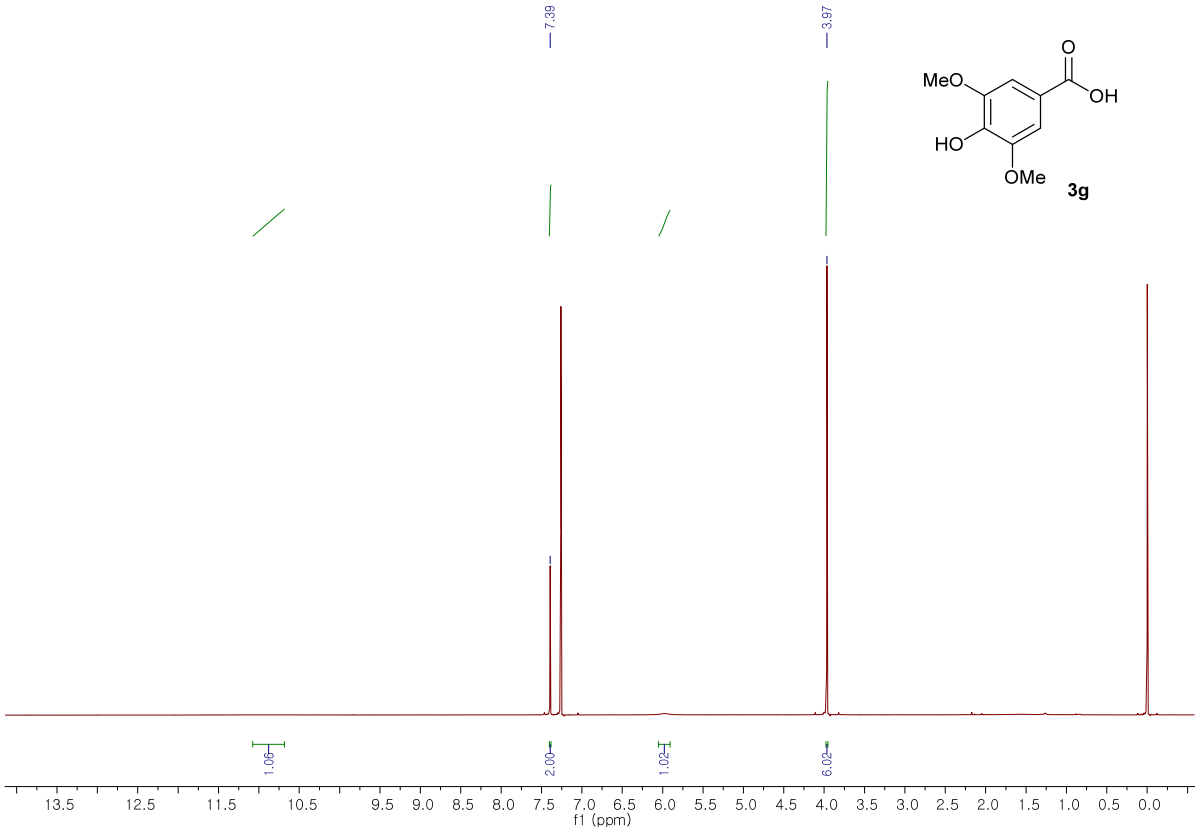

171.47
164.07
132.38
121.62
113.77
55.50
O
OH
MeO
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

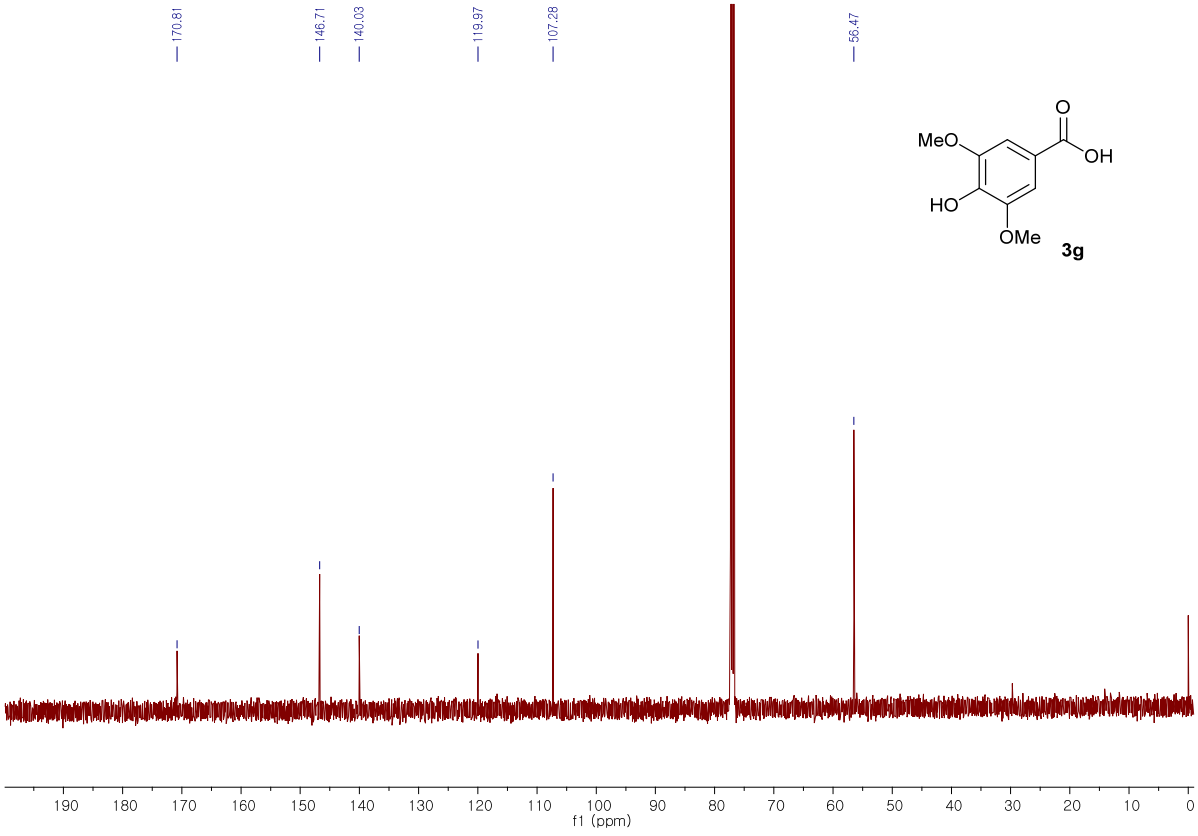

7.80
7.80
7.78
7.78
7.61
7.61
6.94
6.92
3.96
3.95
MeO
MeO
O
OH
3e
0.83
1.00
1.00
1.00
6.00
f1 (ppm)

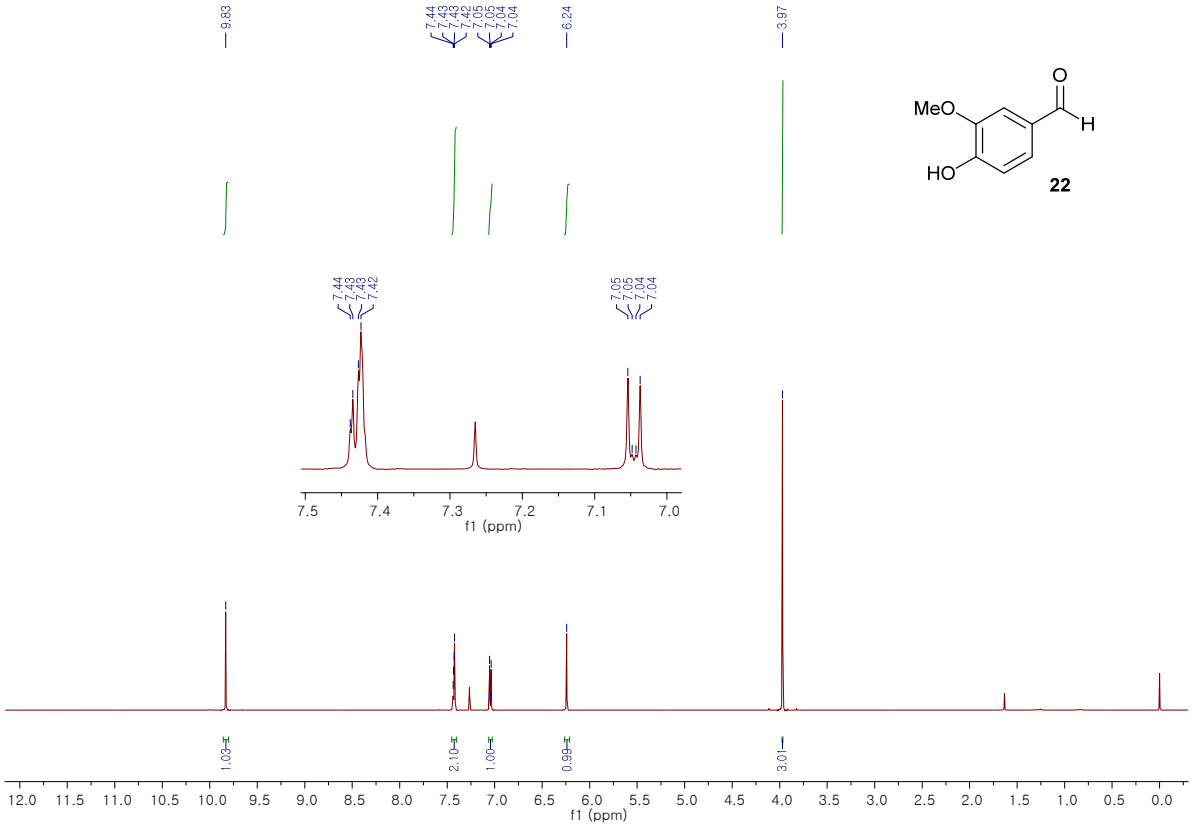

172.14
153.77
148.70
124.63
121.74
112.33
110.35
56.08
56.02
MeO
MeO
O
OH
3e
f1 (ppm)

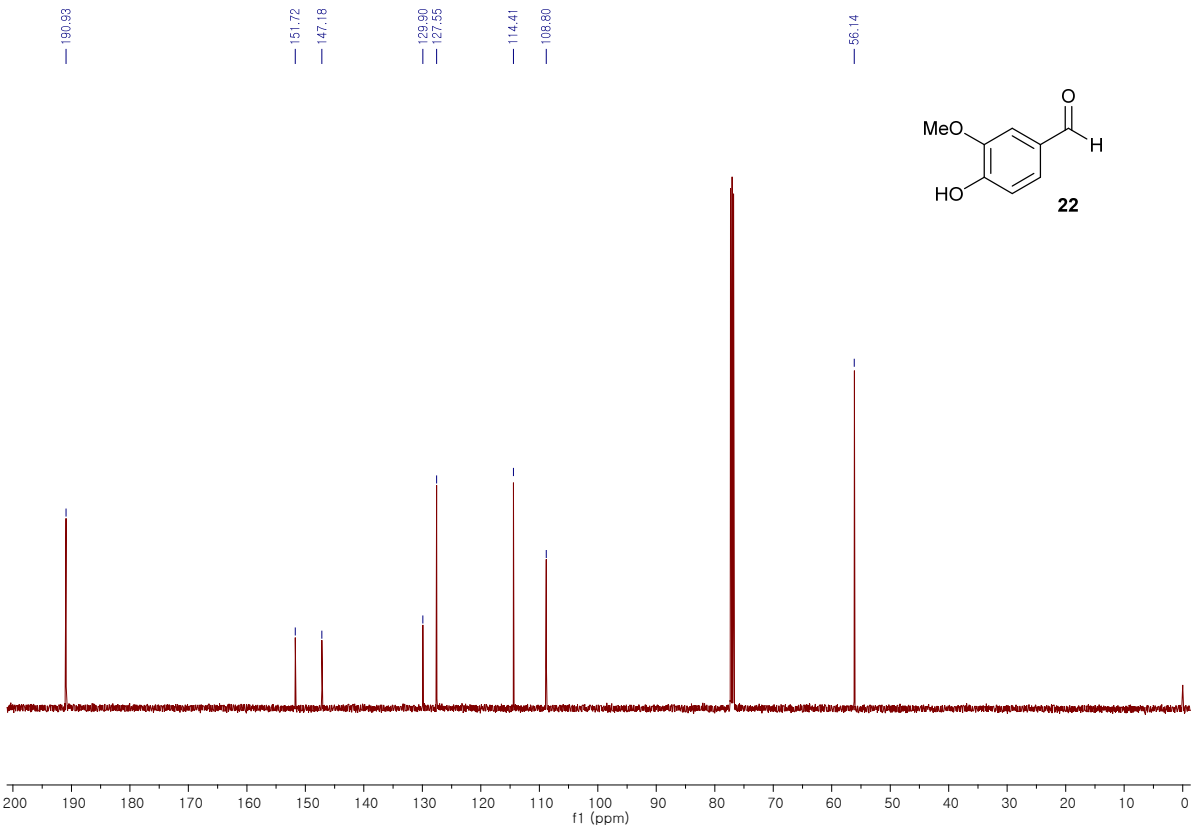

7.67
7.67
7.65
7.65
7.64
7.64
7.00
6.99
6.98
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
MeO
OH
HO
O
3f
1.09
1.02
0.95
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

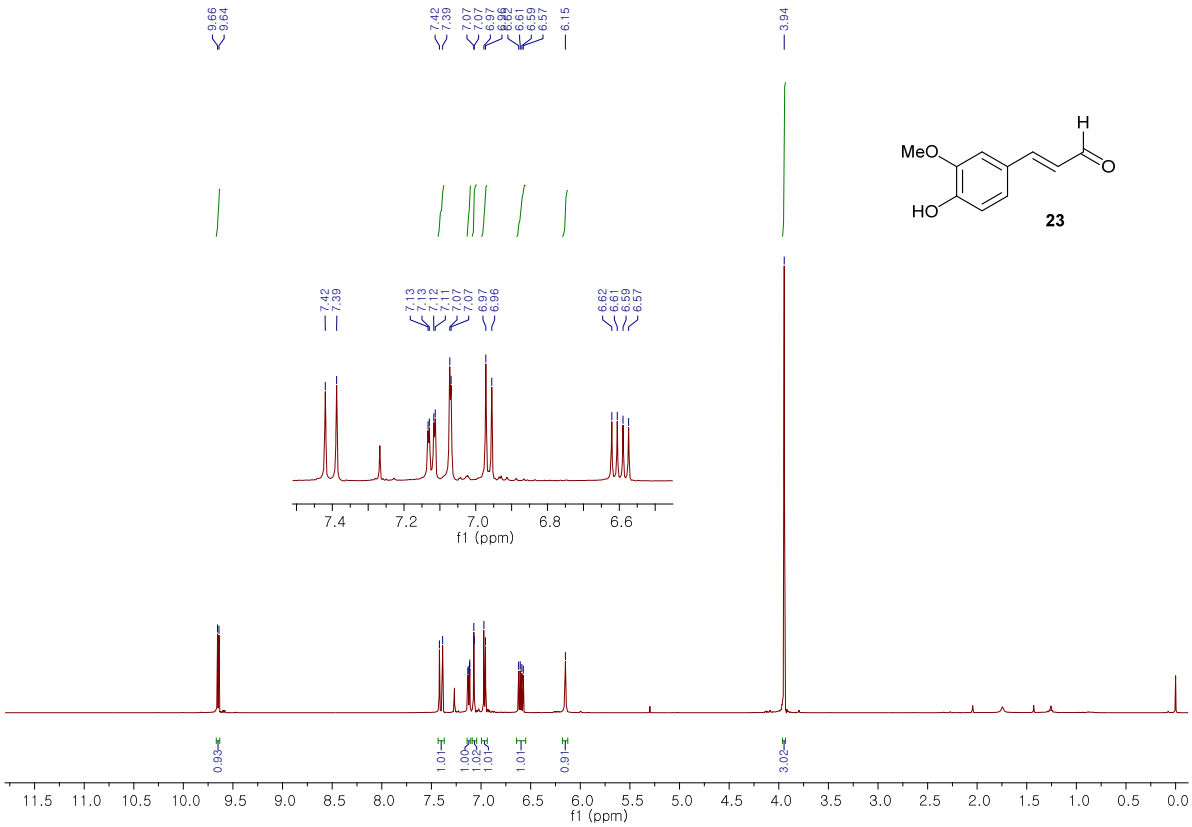

166.26
150.48
146.64
123.71
121.39
114.10
112.18
55.42
MeO
OH
HO
O
3f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

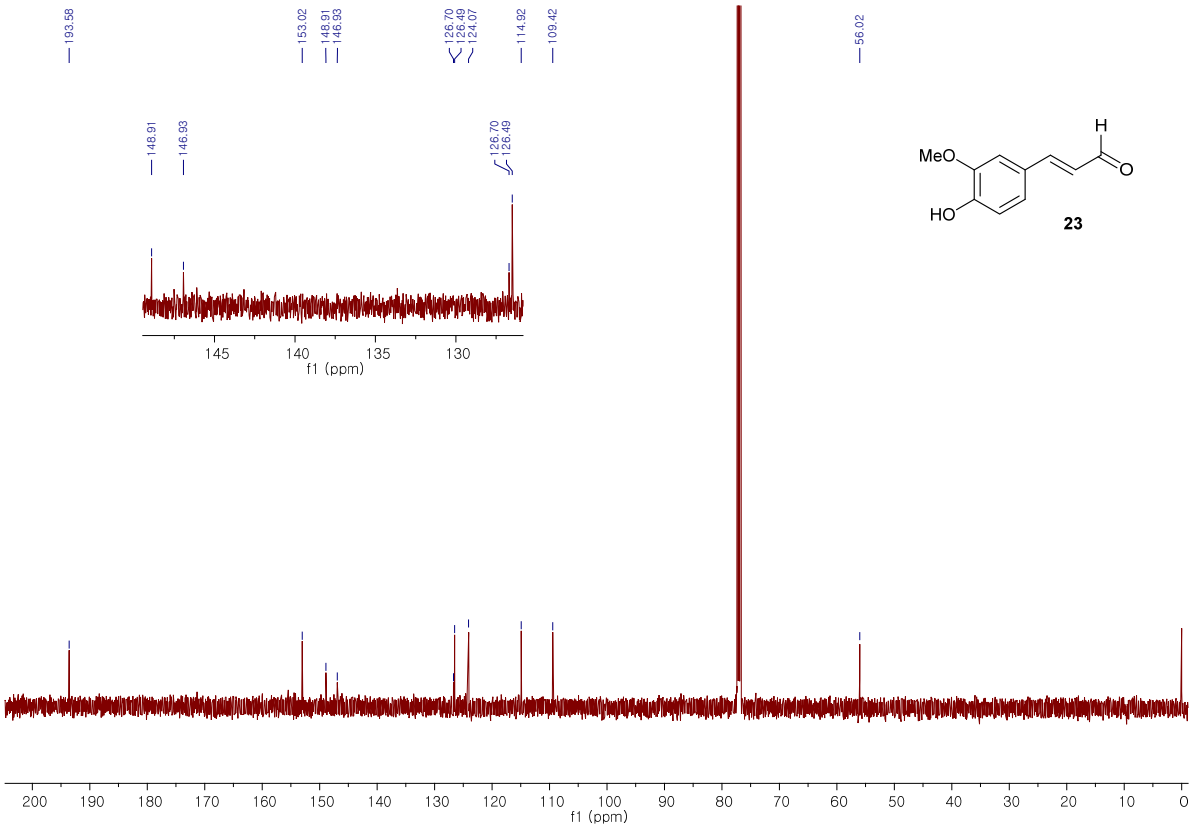

7.39
3.97
MeO
OH
HO
OMe
3g
1.06
2.00
1.02
6.02
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.81
146.71
140.03
119.97
107.28
56.47
MeO
OH
HO
OMe
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.83
7.44
7.43
7.42
7.05
7.04
6.24
3.97
MeO
HO
O
H
22
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
1.03
2.10
1.00
0.99
3.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


190.93
151.72
147.18
129.90
127.55
114.41
108.80
56.14
MeO
HO
O
H
22
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.66
9.64
7.42
7.39
7.07
7.07
6.97
6.96
6.61
6.59
6.57
6.15
3.94
MeO
HO
H
O
23
7.13
7.12
7.11
6.62
6.61
6.59
6.57
f1 (ppm)
0.93
1.01
1.00
1.02
1.01
1.01
0.91
3.02


193.58
153.02
148.91
146.93
126.70
126.49
124.07
114.92
109.42
56.02
MeO
HO
H
O
23
f1 (ppm)