Supporting Information (spectra copies) for

Base-Promoted Addition of DMA with 1,1-diarylethylenes: Application to a Total Synthesis of (-)-Sacidumlignan B

Zhen-Biao Luo, Ya-Wen Wang, Yu Peng*

State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China

pengyu@lzu.edu.cn

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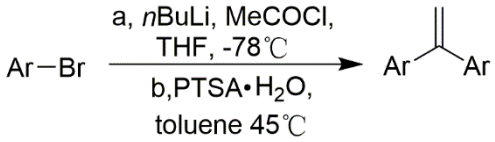
General Experimental Section

For product purification by flash column chromatography, silica gel (200~300 mesh) and petroleum ether (bp. 60~90 °C) are used. All solvents were purified and dried by standard techniques, and distilled prior to use. All experiments were conducted under an argon or nitrogen atmosphere in oven-dried or flame-dried glassware with magnetic stirring, unless otherwise specified. All organic extracts were dried over Na_2SO_4 or $MgSO_4$, unless otherwise noted. IR spectra were recorded on a Nicolet FT-170SX spectrometer as liquid film. ^1H NMR and ^{13}C NMR spectra were taken on Bruker AM-400, AM-600 and Varian mercury 300 MHz spectrometer with TMS as an internal standard and $CDCl_3$ as solvent unless otherwise noted. EI−MS was obtained on GC/MS QP-2010 SE, and ESI−MS was obtained on Bruker esquire 6000 spectrometer. HRMS were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer with ESI and APCI positive or negative ion mode. Melting points were measured on Kofler hot stage and are uncorrected.

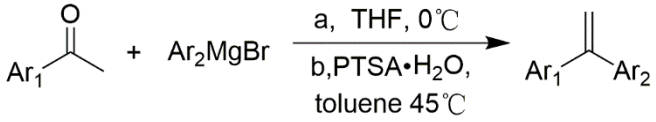
The following chemicals were purchased and used as received: NaHMDS (2.0 M, in THF), DMA (99.8%, Superdry, with molecular sieves). 1,1-diarylpropenes can be synthesized from corresponding arylbromides.

General Procedure 1: The Synthesis of 1,1-diarylethylenes



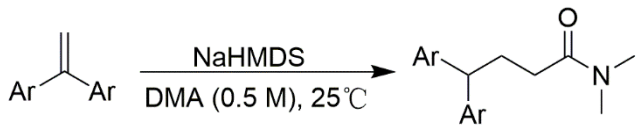
In a 50 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with arylbromide (3.2 mmol) in THF (10 mL) was added dropwise a solution of *n*-BuLi in hexane (3.2 mmol, 2.0 mL, 1.6 M) at –78℃. The reaction mixture was stirred at this temperature for another 0.5 h followed by the addition of acetyl chloride (1.5 mmol, 118 mg). The resulting mixture was stirred at –78℃ for additional 1.0 h, warmed up to room temperature for 5 h. After quenching with aqueous saturated NH_4Cl (3.0 mL), the reaction mixture was extracted with ethyl acetate, the combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude tertiary alcohol product was dissolved in toluene (5 mL) followed by addition of PTSA•H_2O (0.5 mmol, 95 mg). The mixture was heated to 45℃ for 6 h, then cooled down to room temperature, evaporated. Purification by flash column chromatography on 200-300 mesh silica gel afforded 1,1-diarylethylenes.

General Procedure 2: The Synthesis of 1,1-diarylethylenes



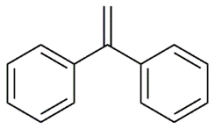
In a 50 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with aryl ketone (2.0 mmol) in THF (8 mL) was added dropwise a solution of ArMgBr in THF (2.0 mmol, 2.0 mL, 1.0 M) at 0℃. The reaction mixture was stirred at this temperature for another 0.5 h, warmed up to room temperature for 4.0 h. After quenching with aqueous saturated NH_4Cl (1 mL), the reaction mixture was extracted with ethyl acetate, the combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude tertiary alcohol product was dissolved in toluene (5 mL) followed by addition of PTSA•H_2O (0.5 mmol, 95 mg). The mixture was heated to 45℃ for 6 h, then cooled down to room temperature, evaporated. Purification by flash column chromatography on 200-300 mesh silica gel afforded 1,1-diarylethylenes.

General Procedure 3: The Synthesis of N, N-dimethyl-4,4-diarylbutanamides



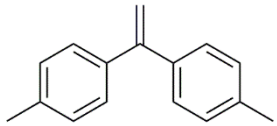
In a 25 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with 1,1-diarylethylenes (1.0 mmol, 1.0 eq) in DMA (2.0 mL) at room temperature, followed by the addition of NaHMDS (1.5 mmol, 1.5 eq, 2.0 M) in THF. The reaction was allowed to stir further stirred for 3.0 h and quenched by the addition of saturated aqueous NH_4Cl (1.5 mL). The crude residue was diluted with EtOAc (50 mL) and washed with water (5 × 5 mL) and brine (5 mL), dried over Na_2SO_4. The crude residue was purified through flash column chromatography on 200-300 mesh afforded N, N-dimethyl-4,4-diarylbutanamides.

Characterization Data for substrates and products



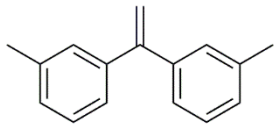
ethene-1,1-diyldibenzene (1a)[1, 2, 4]

Physical state: white solid; **Mp.** 41–43 °C; **TLC:** R_f = 0.58 (petroleum ether/EtOAc = 50 : 1); **IR (film)**: ν_{max} = 3409, 3058, 3030, 2925, 1722, 1657, 1598, 1577, 1492, 1447, 1318, 1277, 1152, 1072, 1028, 941, 919, 762, 698, 638 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.41 (s, 10 H), 5.54 (d, J = 2.8 Hz, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.0, 141.4, 128.2, 128.1, 127.7, 114.3 ppm.



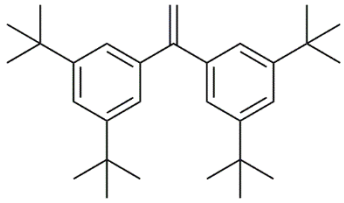
4,4'-(ethene-1,1-diyl)bis(methylbenzene) (1b)[1,2,4]

Physical state: white solid; **Mp.** 51–53 °C; **TLC:** R_f = 0.52 (petroleum ether/EtOAc = 20 : 1); **IR (film)**: ν_{max} = 3408, 3027, 2951, 2922, 2868, 1725, 1655, 1608, 1511, 1450, 1407, 1313, 1293, 1278, 1177, 1071, 1020, 927, 822, 750, 579 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.24–7.22 (m, 4H), 7.13–7.11 (m, 4H), 5.37 (s, 2H), 2.35 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 149.7, 138.8, 137.4, 128.8, 128.1, 112.9, 21.1 ppm.



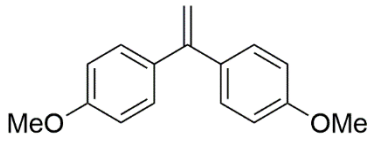
3,3'-(ethene-1,1-diyl)bis(methylbenzene) (1c)[2]

Physical state: colorless oil; **TLC:** R_f = 0.52 (petroleum ether/EtOAc = 20 : 1); **IR (film)**: ν_{max} = 3430, 3018, 2923, 2867, 1648, 1510, 1455, 1409, 1397, 1265, 1139, 809, 733, 554 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.20–7.10 (m, 8H), 5.41 (s, 2H), 2.32 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.2, 141.6, 137.6, 128.9, 128.4, 128.0, 125.4, 114.0, 21.4 ppm.



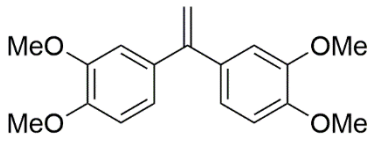
5,5'-(ethene-1,1-diyl)bis(1,3-di-tert-butylbenzene) (1d)

Physical state: white solid; **Mp.** 78–80 °C; **TLC:** R_f = 0.52 (petroleum ether/EtOAc = 20 : 1); **IR (film)**: ν_{max} = 3433, 2923, 2857, 1635, 1459, 1101, 1025, 700, 608 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.38–7.37 (m, 2H), 7.22–7.21 (m, 4H), 5.48 (s, 2H), 1.31 (s, 36H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.3, 150.1, 140.3, 122.7, 121.5, 112.9, 34.8, 31.5 ppm. **HRMS (ESI)**: calcd. for $C_{30}H_{44}^+$ $[M+K]^+$: 443.3075, found: 443.3078.



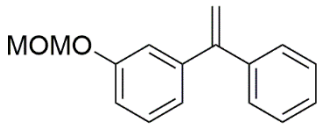
4,4'-(ethene-1,1-diyl)bis(methoxybenzene) (1e)[3]

Physical state: white solid; **Mp.** 135–137 °C; **TLC:** R_f = 0.31 (petroleum ether/EtOAc = 10 : 1); **IR (film)**: ν_{max} = 3422, 3053, 2954, 2926, 2854, 1647, 1606, 1574, 1510, 1463, 1377, 1293, 1264, 1251, 1182, 1168, 1151 1116, 1027, 896, 840, 740, 705, 506 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 4H), 6.88–6.85 (m, 4H), 5.30 (s, 2H), 3.83 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 159.2, 148.9, 134.3, 129.4, 113.4, 111.7, 55.3 ppm.



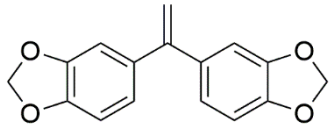
4,4'-(ethene-1,1-diyl)bis(1,2-dimethoxybenzene) (1f)

Physical state: white solid; **Mp.** 87–89 °C; **TLC:** R_f = 0.31 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3538, 3470, 3058, 3000, 2956, 2934, 2908, 2835,1724, 1642, 1600, 1579, 1513, 1463, 1415, 1337, 1310, 1253, 1220, 1173, 1140, 1125, 1026, 936, 891, 862, 813, 767, 734, 701, 683, 614, 579 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.94–6.83 (m, 6H), 5.34 (s, 2H), 3.90 (s, 6H), 3.84 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 149.2, 148.6, 148.3, 134.2, 120.8, 111.9, 111.2, 110.5, 55.7, 55.7 ppm. **HRMS (ESI)**: calcd. for $C_{18}H_{20}O_4^+$ $[M+H]^+$: 301.1434, found: 301.1433.



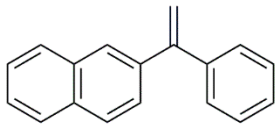
1-(methoxymethoxy)-3-(1-phenylvinyl)benzene (1g)

Physical state: colorless oil; **TLC:** R_f = 0.32 (petroleum ether/EtOAc = 20 : 1); **IR (film)**: ν_{max} = 3409, 3056, 2955, 2926, 2851, 1599, 1575, 1485, 1462, 1444, 1324, 1266, 1226, 1199, 1153, 1080, 1017, 992, 923, 901, 778, 739, 700, 590 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.35–7.22 (m, 6H), 7.03–6.95 (m, 3H), 5.46 (dd, J = 1.2, 4.4 Hz, 2H), 5.16 (s, 2H), 3.47 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.1, 149.7, 143.0, 141.2, 129.1, 128.2, 128.1, 127.7, 122.0, 116.4, 115.3, 114.5, 94.5, 56.0 ppm. **HRMS (ESI)**: calcd. for $C_{16}H_{16}O_2^+$ $[M+H]^+$: 241.1223, found: 241.1225.



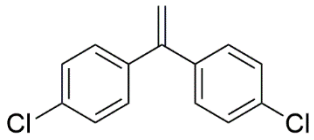
5,5'-(ethene-1,1-diyl)bis(benzo[d][1,3]dioxole) (1h)

Physical state: white solid; **Mp.** 106–108 °C; **TLC:** R_f = 0.43 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3405, 3075, 2956, 2899, 2778, 1735, 1726, 1648, 1601, 1502, 1487, 1442, 1351, 1304, 1240, 1226, 1103, 1075, 1039, 937, 905, 867, 815, 784, 759, 738, 672, 560, 525 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.82–6.75 (m, 6H), 5.95 (s, 4H), 5.27 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 149.2, 147.4, 147.2, 135.8, 122.0, 112.5, 108.7, 107.9, 101.0 ppm. **HRMS (ESI)**: calcd. for $C_{16}H_{12}O_4^+$ $[M+H]^+$: 269.0808, found: 269.0811.



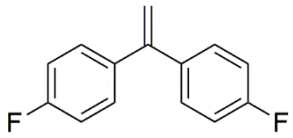
2-(1-phenylvinyl)naphthalene (1i)[1,4]

Physical state: white solid; **Mp.** 56–58 °C; **TLC:** R_f = 0.51 (petroleum ether/EtOAc = 20 : 1); **IR (film)**: ν_{max} = 3404, 3056, 2955, 2925, 2853, 1735, 1655, 1627, 1598, 1492, 1465, 1446, 1287, 1236, 1118, 1026, 897, 860, 820, 778, 749, 713, 698, 474 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84–7.78 (m, 4H), 7.49–7.33 (m, 8H), 5.57 (d, J = 16.4 Hz, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.0, 141.5, 138.9, 133.3, 133.0, 128.4, 128.2, 128.1, 127.8, 127.7, 127.6, 127.3, 126.4, 126.2, 126.0, 114.8 ppm.



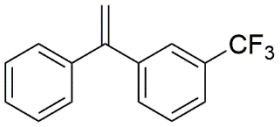
4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (1j)[2, 3]

Physical state: white solid; **Mp.** 83–85 °C; **TLC:** R_f = 0.51 (petroleum ether/EtOAc = 20 : 1); **IR (film)**: ν_{max} = 3404, 3097, 3081, 2954, 2924, 1914, 1817, 1670, 1607, 1590, 1489, 1398, 1322, 1106, 1093, 1011, 907, 836, 725, 611, 513, 488, 440 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.31–7.29 (m, 4H), 7.24–7.22 (m, 4H), 5.44 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 147.9, 139.4, 133.8, 129.4, 128.4, 115.1 ppm.



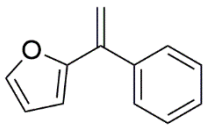
4,4'-(ethene-1,1-diyl)bis(fluorobenzene) (1k)[2, 3]

Physical state: white solid; **Mp.** 45–47 °C; **TLC:** R_f = 0.51 (petroleum ether/EtOAc = 20 : 1); **IR (film)**: ν_{max} = 3404, 3047, 2954, 2925, 1661, 1602, 1509, 1324, 1226, 1156, 1098, 901, 840, 775, 554, 533 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 4H), 7.04–6.99 (m, 4H), 5.38 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 163.8, 161.3, 148.0, 137.3 (d, J = 4.0 Hz, 1C), 129.8, 129.7, 115.2, 115.0, 114.1 ppm.



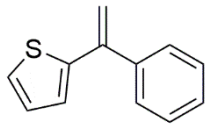
1-(1-phenylvinyl)-3-(trifluoromethyl)benzene (1l)[4]

Physical state: colorless oil; **TLC:** R_f = 0.45 (petroleum ether/EtOAc = 20 : 1); **IR (film)**: ν_{max} = 3399, 3059, 3029, 2956, 2926, 1615, 1494, 1442, 1338, 1319, 1305, 1266, 1168, 1127, 1073, 903, 807, 777, 721, 699, 656, 592 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.62–7.56 (m, 2H), 7.51–7.42 (m, 2H), 7.36–7.30 (m, 5H), 5.55 (s, 1H), 5.50 (s, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 148.9, 142.3, 140.6, 131.6, 130.7 (q, J = 32, 64 Hz, 1C), 128.7, 128.4, 128.2, 125.5, 125.0 (q, J = 4.0, 8.0 Hz, 1C), 124.5 (q, J = 4.0, 7.0 Hz, 1C), 122.8, 115.7 ppm.



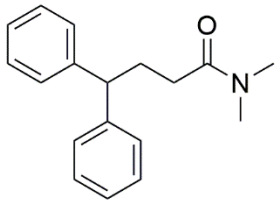
2-(1-phenylvinyl)furan (1m)[1c]

Physical state: yellow solid; **Mp.** 37–39 °C; **TLC:** R_f = 0.43 (petroleum ether/EtOAc = 10 : 1); **IR (film)**: ν_{max} = 3408, 3058, 3028, 2955, 2925, 2854, 1774, 1727, 1686, 1647, 1598, 1493, 1462, 1448, 1377, 1265, 1125, 1072, 1020, 886, 759, 737, 699, 596 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 3H), 7.38–7.34 (m, 3H), 6.38 (dd, J = 2.0, 3.6 Hz, 1H), 6.19 (d, J = 3.2 Hz, 1H), 5.75 (d, J = 1.2 Hz, 1H), 5.22 (d, J = 1.2 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.0, 142.4, 139.5, 139.2, 128.3, 128.2, 128.0, 112.0, 111.2, 109.1 ppm. **HRMS (ESI)**: calcd. for $C_{12}H_{10}O^+$ $[M+H]^+$: 171.0804, found: 171.0809.



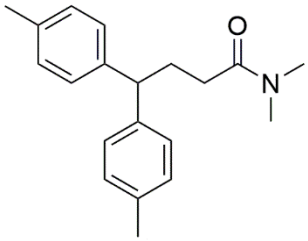
2-(1-phenylvinyl)thiophene (1n)[1c]

Physical state: yellow solid; **Mp.** 49–51 °C; **TLC:** R_f = 0.41 (petroleum ether/EtOAc = 10 : 1); **IR (film)**: ν_{max} = 3397, 3063, 2955, 2925, 2869, 2853, 1728, 1688, 1638, 1604, 1492, 1459, 1377, 1263, 1123, 1097, 1072, 1024, 800, 774, 741, 698 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 2H), 7.37–7.34 (m, 3H), 7.23–7.21 (m, 1H), 6.98–6.95 (m, 1H), 6.91–6.89 (m, 1H), 5.58 (s, 1H), 5.24 (s, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 144.8, 143.4, 141.1, 128.3, 128.2, 128.1, 127.3, 126.5, 125.0, 113.6 ppm.



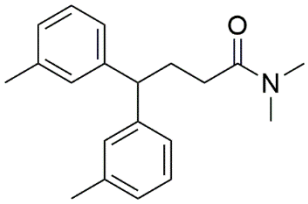
N,N-dimethyl-4,4-diphenylbutanamide (2a)

Physical state: white solid; **Mp.** 81–83 °C; **TLC:** R_f = 0.33 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3431, 2955, 2923, 2853, 2102, 1637, 1492, 1449, 1399, 1309, 1095, 1027, 740, 701, 610 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 8H), 7.19–7.15 (m, 2H), 3.97 (t, J = 8.0 Hz, 1H), 2.92 (s, 3H), 2.83 (s, 3H), 2.43–2.38 (m, 2H), 2.27–2.23 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.6, 144.5, 128.4, 127.8, 126.2, 50.5, 37.1, 35.3, 31.5, 30.7 ppm. **HRMS (ESI)**: calcd. for $C_{18}H_{21}NO^+$ $[M+H]^+$: 268.1696, found: 268.1689.



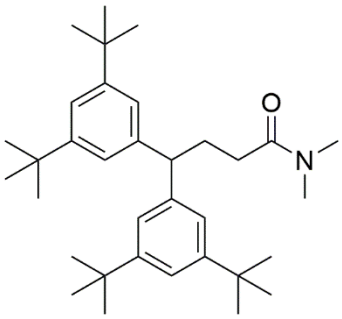
N,N-dimethyl-4,4-di-p-tolylbutanamide (2b)

Physical state: white solid; **Mp.** 71–73 °C; **TLC:** R_f = 0.35 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3411, 3018, 2923, 2869, 1647, 1510, 1452, 1397, 1265, 1139, 1047, 1021, 809, 734, 554 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.14–7.12 (m, 4H), 7.08–7.06 (m, 4H), 3.87 (t, J = 7.6 Hz, 1H), 2.91 (s, 3H), 2.82 (s, 3H), 2.39–2.33 (m, 2H), 2.28 (s, 6H), 2.25–2.22 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.7, 141.7, 135.5, 129.1, 127.6, 49.7, 37.1, 35.3, 31.6, 30.8, 20.9 ppm. **HRMS (ESI)**: calcd. for $C_{20}H_{25}NO^+$ $[M+H]^+$: 296.2009, found: 296.2001.



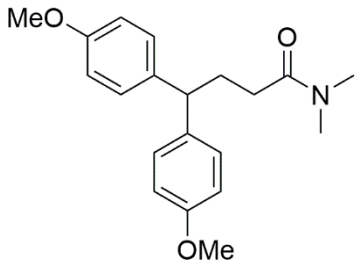
N,N-dimethyl-4,4-di-m-tolylbutanamide (2c)

Physical state: white solid; **Mp.** 40–42 °C; **TLC:** R_f = 0.35 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3435, 3021, 2924, 2868, 1648, 1604, 1587, 1488, 1457, 1397, 1265, 1138, 1097, 1054, 783, 753, 723, 703 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.17–7.13 (m, 2H), 7.06–7.04 (m, 4H), 6.98–6.96 (m, 2H), 3.87 (t, J = 7.6 Hz, 1H), 2.91 (s, 3H), 2.82 (s, 3H), 2.40–2.35 (m, 2H), 2.29 (s, 6H), 2.25–2.21 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.7, 144.5, 137.9, 128.6, 128.2, 168.9, 124.7, 50.4, 37.0, 35.3, 31.5, 30.7, 21.4 ppm. **HRMS (ESI)**: calcd. for $C_{20}H_{25}NO^+$ $[M+H]^+$: 296.2009, found: 296.2001.



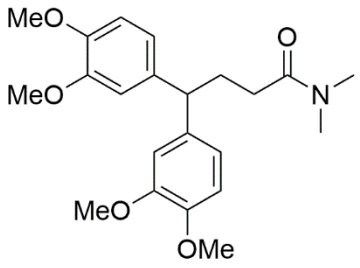
4,4-bis(3,5-di-tert-butylphenyl)-N,N-dimethylbutanamide (2d)

Physical state: white solid; **Mp.** 83–85 °C; **TLC:** R_f = 0.37 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3412, 3056, 2961, 2905, 2867, 1650, 1596, 1477, 1460, 1393, 1362, 1264, 1248, 1200, 1136, 1079, 896, 875, 726, 713 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.23–7.22 (m, 2H), 7.14–7.13 (m, 4H) 3.92 (t, J = 8.0 Hz, 1H), 2.91 (s, 3H), 2.79 (s, 3H), 2.41–2.36 (m, 2H), 2.27–2.23 (m, 2H), 1.29 (s, 36H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 173.1, 150.3, 143.4, 122.2, 119.9, 51.9, 37.2, 35.3, 34.8, 32.2, 32.0, 31.5 ppm. **HRMS (ESI)**: calcd. for $C_{34}H_{53}NO^+$ $[M+H]^+$: 492.4200, found: 492.4201.



4,4-bis(4-methoxyphenyl)-N,N-dimethylbutanamide (2e)

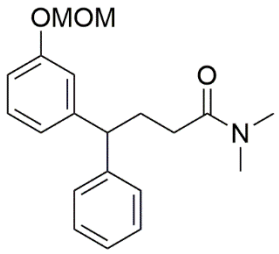
Physical state: colorless oil; **TLC:** R_f = 0.34 (petroleum ether/EtOAc = 2 : 1); **IR (film)**: ν_{max} = 3409, 2954, 2925, 2869, 2852, 1640, 1610, 1582, 1510, 1462, 1398, 1378, 1301, 1247, 1177, 1144, 1112, 1089, 1034, 828, 737, 701, 556 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.16–7.14 (m, 4H), 6.82–6.80 (m, 4H), 3.87 (t, J = 7.6 Hz, 1H), 3.77 (s, 6H), 2.92 (s, 3H), 2.84 (s, 3H), 2.36–2.30 (m, 2H), 2.25–2.21 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.7, 157.8, 137.0, 128.7, 113.8, 55.2, 48.8, 37.1, 35.3, 31.6, 31.1 ppm. **HRMS (ESI)**: calcd. for $C_{20}H_{25}NO_3^+$ $[M+H]^+$: 328.1907, found: 328.1912.



4,4-bis(3,4-dimethoxyphenyl)-N,N-dimethylbutanamide (2f)

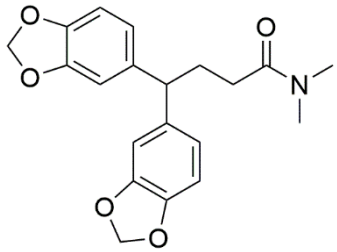
Physical state: colorless oil; **TLC:** R_f = 0.28 (petroleum ether/EtOAc = 1 : 1); **IR (film)**: ν_{max} = 3463, 3055, 2998, 2934, 2835, 1722, 1640, 1606, 1590, 1513, 1463, 1415, 1399, 1331, 1258, 1236, 1185, 1141, 1027, 915, 856, 807, 763, 733, 701, 649 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.80 (s, 4H), 6.75 (s, 2H), 3.88 (t, J = 8.0 Hz, 1H), 3.85 (s, 6H), 3.84 (s, 6H), 2.93 (s, 3H), 2.86 (s, 3H), 2.38–2.32 (m, 2H), 2.27–2.23 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.7, 148.8, 147.3, 137.3, 119.5, 111.0, 110.9, 55.8, 49.6, 37.1, 35.3, 31.5, 31.0 ppm. **HRMS (ESI)**: calcd. for $C_{20}H_{29}NO_5^+$ $[M+H]^+$: 388.2118,

found: 388.2117.



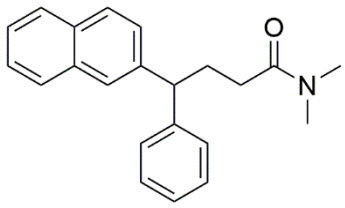
4-(3-(methoxymethoxy)phenyl)-N,N-dimethyl-4-phenylbutanamide (2g)

Physical state: colorless oil; **TLC:** R_f = 0.46 (petroleum ether/EtOAc = 2 : 1); **IR (film)**: ν_{max} = 3439, 3055, 3026, 2953, 2929, 1644, 1608, 1597, 1584, 1488, 1450, 1399, 1265, 1247, 1150, 1079, 1015, 992, 923, 787, 734, 702 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 4H), 7.21–7.15 (m, 2H), 6.92–6.85 (m, 3H), 5.13 (s, 2H), 3.94 (t, J = 8.0 Hz, 1H), 3.46 (s, 3H), 2.92 (s, 3H), 2.83 (s, 3H), 2.41–2.36 (m, 2H), 2.27–2.23 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.6, 157.4, 146.2, 144.3, 129.4, 128.5, 127.8, 126.2, 121.4, 116.2, 113.7, 94.5, 56.0, 50.5, 37.1, 35.3, 31.5, 30.7 ppm. **HRMS (ESI)**: calcd. for $C_{20}H_{25}NO_3^+$ $[M+H]^+$: 328.1907, found: 328.1909.



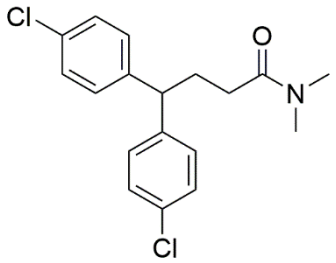
4,4-bis(benzo[d][1,3]dioxol-5-yl)-N,N-dimethylbutanamide (2h)

Physical state: white solid; **Mp.** 116–118 °C; **TLC:** R_f = 0.31 (petroleum ether/EtOAc = 2 : 1); **IR (film)**: ν_{max} = 3409, 2953, 2925, 1641, 1502, 1486, 1439, 1398, 1242, 1185, 1141, 1125, 1097, 1038, 931, 864, 807, 735 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.71 (s, 6H), 5.89 (s, 4H), 3.81 (t, J = 7.6 Hz, 1H), 2.92 (s, 3H), 2.85 (s, 3H), 2.30–2.21 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.5, 147.7, 145.9, 138.7, 120.6, 108.1, 100.8, 49.8, 37.1, 35.4, 31.4, 30.9 ppm. **HRMS (ESI)**: calcd. for $C_{20}H_{21}NO_5^+$ $[M+H]^+$: 356.1492, found: 356.1483.



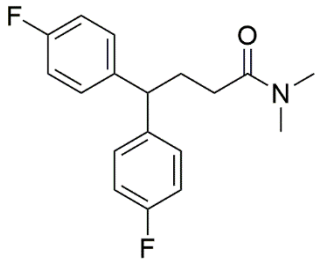
N,N-dimethyl-4-(naphthalen-2-yl)-4-phenylbutanamide (2i)

Physical state: colorless oil; **TLC:** R_f = 0.29 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3432, 3054, 3025, 2932, 1722, 1645, 1599, 1504, 1493, 1452, 1397, 1350, 1265, 1140, 1080, 1059, 951, 895, 858, 819, 746, 702, 556, 478 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78–7.70 (m, 4H), 7.44–7.32 (m, 3H), 7.30–7.23 (m, 4H), 7.17–7.13 (m, 1H), 4.13 (t, J = 7.6 Hz, 1H), 2.88 (s, 3H), 2.74 (s, 3H), 2.56–2.45 (m, 2H), 2.28–2.24 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.4, 144.3, 141.8, 133.4, 132.1, 128.4, 128.0, 127.9, 127.6, 127.4, 126.6, 126.2, 125.9, 125.8, 125.3, 50.4, 35.9, 35.2, 31.3, 30.4 ppm. **HRMS (ESI)**: calcd. for $C_{22}H_{23}NO^+$ $[M+H]^+$: 318.1852, found: 318.1855.



4,4-bis(4-chlorophenyl)-N,N-dimethylbutanamide (2j)

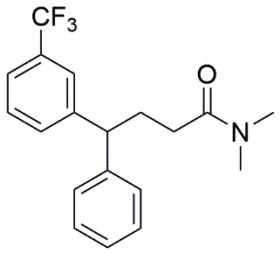
Physical state: white solid; **Mp.** 62–64 °C; **TLC:** R_f = 0.32 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3303, 2956, 2924, 2856, 1778, 1630, 1490, 1460, 1415, 1399, 1267, 1211, 1177, 1091, 1077, 1012, 845, 826, 812, 624, 602, 529 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.25–7.23 (m, 4H), 7.16–7.14 (m, 4H), 3.96 (t, J = 7.6 Hz, 1H), 2.92 (s, 3H), 2.84 (s, 3H), 2.37–2.32 (m, 2H), 2.23–2.20 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.0, 142.5, 132.1, 129.1, 128.6, 49.0, 37.0, 35.3, 31.0, 30.4 ppm. **HRMS (ESI)**: calcd. for $C_{18}H_{19}Cl_2NO^+$ $[M+Na]^+$: 358.0736, found: 358.0740.



4,4-bis(4-fluorophenyl)-N,N-dimethylbutanamide (2k)

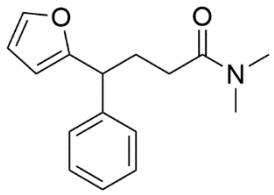
Physical state: colorless oil; **TLC:** R_f = 0.32 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3409, 3044, 2926, 1640, 1603, 1507, 1411, 1400, 1223, 1158, 1100, 1080, 1014, 833, 576, 551 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.20–7.16 (m, 4H), 6.99–6.94 (m, 4H), 3.97 (t, J = 7.6 Hz, 1H), 2.92 (s, 3H), 2.84 (s, 3H), 2.37–2.32 (m, 2H), 2.24–2.20 (m,

2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.3, 162.6, 160.1, 140.0 (d, J = 4.0 Hz, 2C), 129.2, 129.1, 115.4, 115.2, 48.9, 37.0, 35.3, 31.1, 30.9 ppm. **HRMS (ESI)**: calcd. for $C_{18}H_{19}F_2NO^+$ $[M+H]^+$: 304.1507 found: 304.1499.



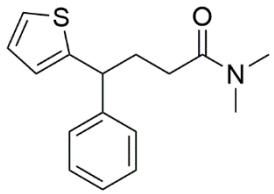
N,N-dimethyl-4-phenyl-4-(3-(trifluoromethyl)phenyl)butanamide (2l)

Physical state: colorless oil; **TLC:** R_f = 0.32 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3410, 3060, 3027, 2927, 1646, 1493, 1449, 1399, 1328, 1265, 1163, 1123, 1098, 1075, 899, 803, 705 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.45–7.36 (m, 3H), 7.32–7.28 (m, 2H), 7.26–7.19 (m, 3H), 4.06 (t, J = 8.0 Hz, 1H), 2.92 (s, 3H), 2.83 (s, 3H), 2.45–2.39 (m, 2H), 2.26–2.22 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.2, 145.6, 143.4, 131.2, 130.7 (q, J = 19.0, 63.0 Hz, 1C), 128.9, 128.7, 127.9, 126.6, 126.1, 125.5, 124.5 (q, J = 3.0, 7.0 Hz, 1C), 123.1 (q, J = 4.0, 8.0 Hz, 1C), 122.8, 50.2, 37.0, 35.3, 31.1, 30.6 ppm. **HRMS (ESI)**: calcd. for $C_{19}H_{20}F_3NO^+$ $[M+H]^+$: 336.1570, found: 336.1572.



4-(furan-2-yl)-N,N-dimethyl-4-phenylbutanamide (2m)

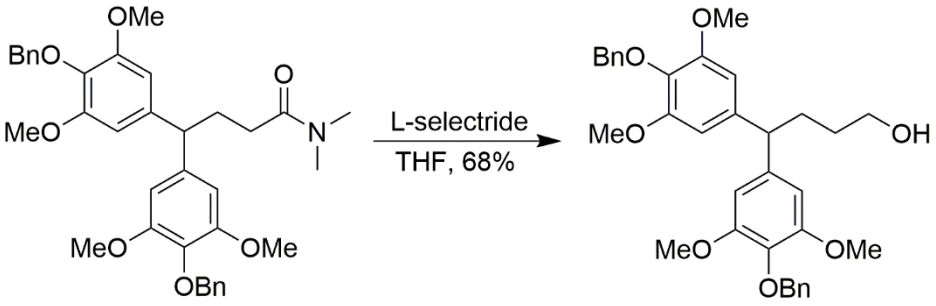
Physical state: yellow oil; **TLC:** R_f = 0.46 (petroleum ether/EtOAc = 2 : 1); **IR (film)**: ν_{max} = 3428, 3112, 3027, 2929, 1719, 1645, 1493, 1453, 1399, 1352, 1265, 1145, 1080, 1010, 922, 803, 734, 701, 599, 532 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.32–7.28 (m, 3H), 7.25–7.21 (m, 3H), 6.29 (q, J = 2.0, 3.2 Hz, 1H), 6.11 (d, J = 3.2 Hz, 1H), 4.02 (t, J = 7.6 Hz, 1H), 2.92 (s, 3H), 2.85 (s, 3H), 2.48–2.38 (m, 1H), 2.28–2.21 (m, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.4, 157.4, 142.3, 141.5, 128.5, 127.8, 126.7, 110.0, 105.6, 44.5, 37.1, 35.4, 31.1, 30.0 ppm. **HRMS (ESI)**: calcd. for $C_{16}H_{19}NO_2^+$ $[M+H]^+$: 258.1489, found: 258.1490.



N,N-dimethyl-4-phenyl-4-(thiophen-2-yl)butanamide (2n)

Physical state: yellow solid; **Mp.** 76–78 °C; **TLC:** R_f = 0.41 (petroleum ether/EtOAc = 2 : 1); **IR (film)**: ν_{max} = 3452, 3062, 3026, 2927, 1644, 1493, 1452, 1398, 1265, 1142, 1078, 1060, 1032, 852, 826, 700, 536 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.32–7.26 (m, 4H), 7.23–7.19 (m, 1H), 7.14–7.13 (m, 1H), 6.92–6.85 (m, 2H), 4.22 (t, J = 7.6 Hz, 1H), 2.92 (s, 3H), 2.83 (s, 3H), 2.52–2.33 (m, 2H), 2.32–2.20 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.3, 148.8, 144.0, 128.5, 127.6, 126.6, 126.5, 123.9, 123.6, 46.0, 37.0, 35.3, 32.4, 31.2 ppm. **HRMS (ESI)**: calcd. for $C_{16}H_{19}NOS^+$ $[M+H]^+$: 274.1260, found: 274.1262.

General Procedure 4: The Synthesis of 4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl) butan-1-amine (3)

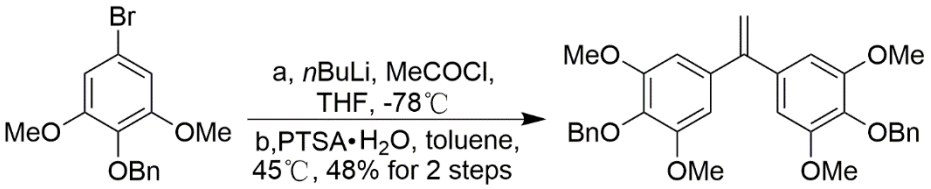


2o **3c**

In a 10 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with 4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-N,N-dimethylbutanamide-anhydrous (**2o**) (180 mg, 0.3 mmol, 1.0 eq) in THF (1.0 mL) cooled to 0 °C, followed by the addition of L-selectride (0.6 mmol, 2.0 eq, 1.0 M) in THF (0.6 mL). the mixture further stirred for 12 h and quenched by the addition of saturated aqueous NH_4Cl (1.0 mL), the crude residue was diluted with EtOAc (80 mL), and washed with water (3 × 6 mL) and brine (6 mL), dried over Na_2SO_4. The crude residue was purified by flash column chromatography (petroleum ether: EtOAc = 4 : 1) on silica gel to afford the desired **3** (114 mg, 68% yield). **Physical state:** colorless oil; **TLC:** R_f = 0.31 (petroleum ether/EtOAc = 1 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48–7.47 (m, 4H), 7.34–7.27 (m, 6H), 6.44 (s, 4H), 4.98 (s, 4H), 3.78 (s, 13H), 3.66 (t, J = 6.4 Hz, 2H), 2.08–2.02 (m, 2H), 1.58–1.50 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.3,

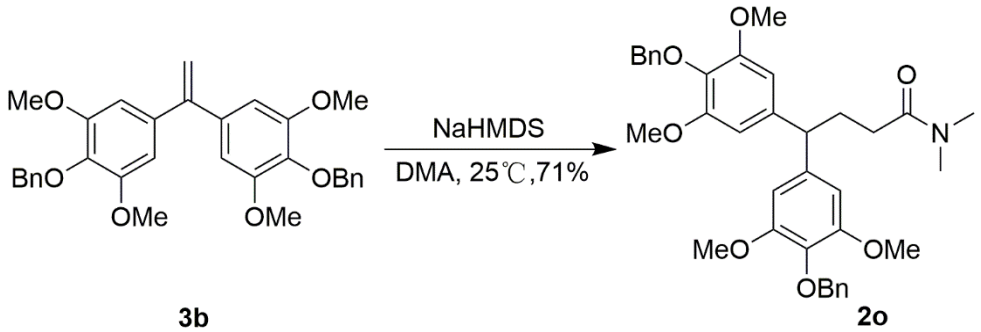
140.5, 137.9, 135.5, 128.4, 128.0, 127.7, 105.1, 74.9, 62.8, 56.2, 51.5, 32.3, 31.3 ppm. **HRMS (ESI)**: calcd. for $C_{34}H_{38}O_7^+$ $[M+Na]^+$: 581.2510, found: 581.2512.

Total Synthesis of (-)-Sacidumlignan B



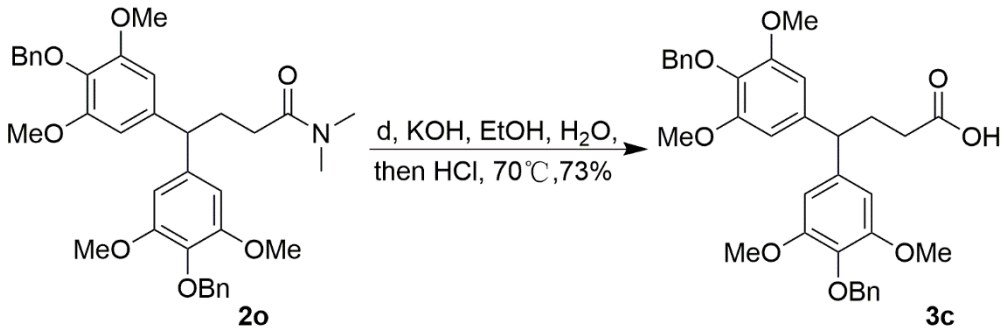
3a **3b**

In a 250 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with arylbromide (**3a**) (16.1 g, 50.0 mmol, 1.0 eq) in THF (80 mL) was added dropwise a solution of *n*-BuLi in hexane (33.0 mL, 53.0 mmol, 1.06 eq, 1.6 M) at –78℃. The reaction mixture was stirred at this temperature for another 0.5 h followed by the addition of acetyl chloride (1.57 g, 20.0 mmol, 0.4 eq). The resulting mixture was stirred at –78℃ for additional 1.0 h, warmed up to room temperature for 8 h. After quenching with aqueous saturated NH_4Cl (3 mL), the reaction mixture was extracted with ethyl acetate (200 mL), the combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude tertiary alcohol product was dissolved in toluene (5 mL) followed by addition of PTSA• H_2O (1.90 g, 10.0 mmol, 0.2 eq). The mixture was heated to 45℃ for 5 h, then cooled down to room temperature, evaporated. Purification by flash column chromatography (petroleum ether : ethyl acetate = 10 : 1 → 4 : 1) on 200-300 mesh silica gel afforded 5,5'-(ethene-1,1-diyl)bis(2-(benzyloxy)-1,3-dimethoxybenzene) (**3b**) (6.1 g, 48% yield). **Physical state:** colorless oil; **TLC:** R_f = 0.43 (petroleum ether/EtOAc = 4 : 1); **IR (film)**: ν_{max} = 3400, 3057, 2959, 2930, 2859, 1654, 1581, 1500, 1461, 1413, 1335, 1265, 1237, 1214, 1176, 1129, 1027, 912, 896, 846, 738, 700 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 4H), 7.36–7.25 (m, 6H), 6.55 (s, 4H), 5.40 (s, 2H), 5.06 (s, 4H), 3.78 (s, 12H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.1, 150.0, 137.8, 136.9, 136.8, 128.4, 128.1, 127.7, 113.2, 105.7, 74.9, 56.1 ppm. **HRMS (ESI)**: calcd. for $C_{32}H_{32}O_6^+$ $[M+Na]^+$: 535.2091, found: 535.2084.



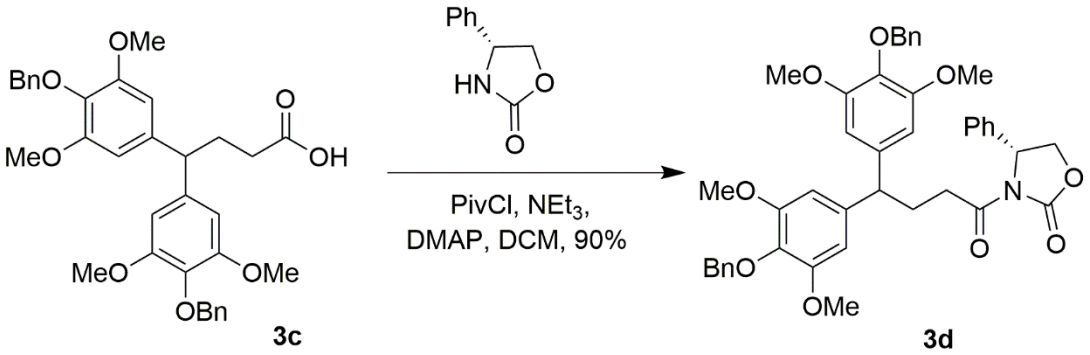
3b **2o**

In a 50 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with 5,5'-(ethene-1,1-diyl)bis(2-(benzyloxy)-1,3-dimethoxybenzene) (**3b**) (10.0 mmol, 5.12 g, 1.0 eq) in DMA (20.0 mL) at room temperature, followed by the addition of NaHMDS (7.0 mL, 15.0 mmol, 1.5 eq, 2.0 M) in THF. The reaction was allowed to stir for 3.0 h and quenched by the addition of aqueous saturated NH_4Cl (1.5 mL). The crude residue was diluted with EtOAc (150 mL) and washed with water (5 × 15 mL) and brine (15 mL), dried over Na_2SO_4. The crude residue was purified through flash column chromatography (petroleum ether : ethyl acetate = 4 : 1 → 1 : 1) on 200-300 mesh afforded 4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-N,N-dimethylbutan- amide (**2o**) (4.26 g, 71% yield). **Physical state:** yellow oil; **TLC:** R_f = 0.36 (petroleum ether/EtOAc = 1 : 2); **IR (film)**: ν_{max} = 3403, 3055, 2927, 2854, 1638, 1590, 1460, 1421, 1265, 1129, 739, 704 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48–7.47 (m, 4H), 7.34–7.27 (m, 6H), 6.45 (s, 4H), 4.99 (s, 4H), 3.85 (t, J = 7.6 Hz, 1H), 3.78 (s, 12H), 2.94 (s, 3H), 2.84 (s, 3H), 2.36–2.30 (m, 2H), 2.25–2.22 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.6, 153.3, 140.0, 137.9, 135.3, 128.4, 128.0, 127.7, 105.0, 74.9, 56.1, 50.1, 37.1, 35.4, 31.3, 31.1 ppm. **HRMS (ESI)**: calcd. for $C_{36}H_{41}NO_7^+$ $[M+Na]^+$: 622.2775, found: 622.2769.

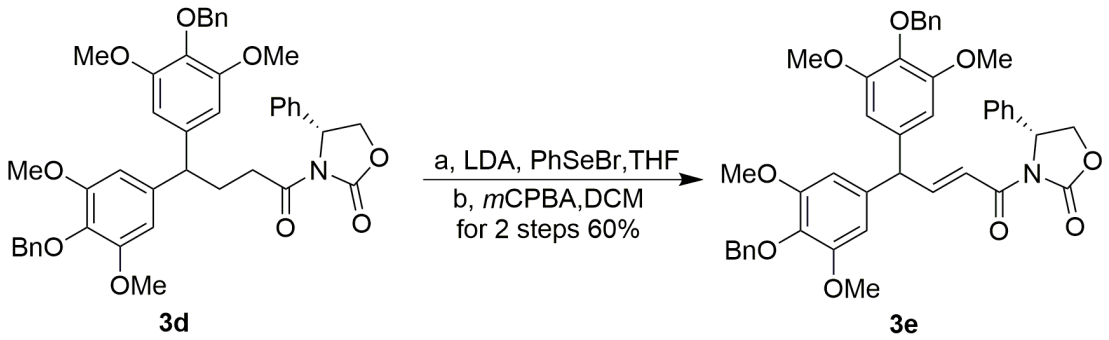


In a 50 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with 4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-N,N-dimethylbutan-amide (**2o**) (4.8 g, 8.0 mmol, 1.0 eq) in ethanol/H_2O = 4 : 1 (20 mL) was added KOH (2.25 g, 40.0 mmol, 5.0 eq) at room temperature, warmed up to 70℃ for 7 d. the combined organic phases were concentrated in vacuo, followed by the addition of 1 N aqueous HCl. The reaction mixture was extracted with ethyl acetate (80 mL), and washed with water (3 × 5 mL) and brine (5 mL) dried over Na_2SO_4. Purification by flash column chromatography (petroleum ether: ethyl acetate = 4 : 1 → 2 : 1) on 200-300 mesh silica gel afforded 4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-butanoic acid (**3c**) (3.34 g, 73% yield). **Physical state:** colorless oil; **TLC:** R_f = 0.36 (petroleum ether/EtOAc = 1 : 1); **IR (film)**: ν_{max} = 3402, 3056, 2957, 2929, 2871, 1589, 1501, 1460, 1420, 1376, 1326, 1265, 1241, 1186, 1129, 1027, 738, 700 cm^{-1}; **^{1}H NMR** (400 MHz,

$CDCl_3$): δ = 7.48–7.46 (m, 4H), 7.34–7.27 (m, 6H), 6.43 (s, 4H), 4.98 (s, 4H), 3.78 (s, 13H), 2.32 (s, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 178.5, 153.5, 139.4, 137.9, 135.7, 128.4, 128.1, 127.7, 105.1, 74.9, 56.2, 50.7, 32.3, 30.7 ppm. **HRMS (ESI)**: calcd. for $C_{34}H_{36}O_8^+$ $[M+H]^+$: 573.2483, found: 573.2492.

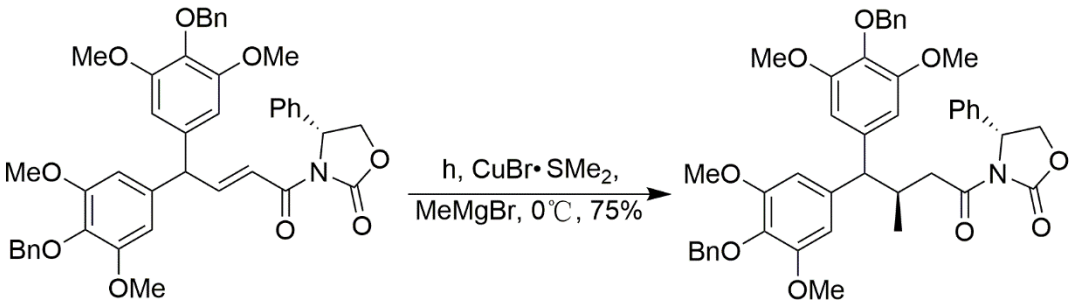


In a 50 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with 4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-butanoic acid (**3c**) (1.72 g, 3.0 mmol, 1.0 eq) in dichloromethane (20 mL) was added triethyl amine (727 mg, 7.2 mmol, 2.4 eq) and pivaloyl chloride (370 mg, 3.6 mmol, 1.2 eq) at room temperature and stirred for 3 h at the same temperature. To the above reaction mixture (*R*)-4-Phenyl-2-oxazolidione (267 g, 1.74 mol) and DMAP (40 mg) were added and heated to 35℃. The reaction mixture was maintained for 8 h at 35℃. After cooling to room temperature water (1.0 mL) was added, the reaction mixture was extracted with ethyl acetate (80 mL), and washed with water (3 × 5 mL) and brine (5 mL) dried over Na_2SO_4. Purification by flash column chromatography (petroleum ether : ethyl acetate = 4 : 1 → 2 : 1) on 200-300 mesh silica gel afforded (*R*)-3-(4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)butanoyl)-4-phenyloxazolidin-2-one (**3d**) (1.93 g, 90% yield). **Physical state:** yellow oil; **TLC:** R_f = 0.36 (petroleum ether/EtOAc = 2 : 1); $[\alpha]^{25}_D$ = –49 (c 1.0, acetone); **IR (film)**: ν_{max} = 3365, 3057, 2959, 2930, 2872, 1779, 1721, 1589, 1501, 1458, 1420, 1383, 1327, 1265, 1242, 1218, 1129, 1076, 1041, 1027, 738, 701 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48–7.46 (m, 4H), 7.39–7.27 (m, 11H), 6.43 (s, 2H), 6.42 (s, 2H), 5.32 (dd, *J* = 3.6, 8.8 Hz, 1H), 4.98 (s, 2H), 4.97 (s, 2H), 4.64 (t, *J* = 9.2 Hz, 1H), 4.24 (dd, *J* = 3.6, 8.8 Hz, 1H), 3.83 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 6H), 3.76 (s, 6H), 3.08–3.00 (m, 1H), 2.90–2.82 (m, 1H), 2.30 (dd, *J* = 7.6, 15.2 Hz, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.5, 153.6, 153.3, 153.2, 139.7, 139.5, 139.1, 137.9, 137.8, 135.3, 135.2, 129.2, 128.7, 128.4, 128.3, 128.1, 127.7, 127.7, 125.8, 104.9, 104.8, 74.9, 69.9, 57.5, 56.1, 50.8, 34.1, 30.3 ppm. **HRMS (ESI)**: calcd. for $C_{43}H_{43}NO_9^+$ $[M+Na]^+$: 740.2830, found: 740.2849.



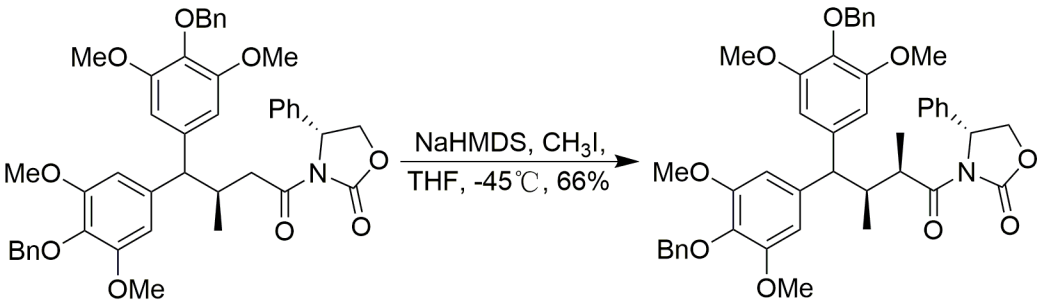
3d **3e**

In a 250 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with (*R*)-3-(4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)butanoyl)-4-phenyl-oxazolidin-2-one (**3d**) (1.43 g, 2.0 mmol, 1.0 eq) in THF (5 mL) was added dropwise a solution of LDA in THF (5 mL, 2.4 mmol, 1.2 eq) at –78℃. The reaction mixture was stirred at this temperature for another 1.0 h followed by the addition of phenylselenyl bromide (566 mg, 2.4 mmol, 1.2 eq). The resulting mixture was stirred at –78℃ for additional 0.5 h, warmed up to room temperature for 8 h. After quenching with aqueous saturated NH_4Cl, the reaction mixture was extracted with ethyl acetate, the combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was dissolved in DCM (5 mL) followed by addition of *m*CPBA (259 mg, 1.5 mmol, 0.75 equiv) at room temperature for 15 min. the reaction mixture was extracted with DCM (80 mL), and washed with water (3 × 5 mL) and brine (5 mL) dried over Na_2SO_4. Purification by flash column chromatography (petroleum ether : ethyl acetate = 4 : 1 → 2 : 1) on 200-300 mesh silica gel afforded (*R*,E)-3-(4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)but-2-enoyl)-4-phenyloxazolidin-2-one (**3e**) (855 mg, 60% yield). **Physical state:** yellow oil; **TLC:** R_f = 0.35 (petroleum ether/EtOAc = 2: 1); $[\alpha]^{25}_D$ = –36 (c 1.0, acetone); **IR (film)**: ν_{max} = 3370, 3058, 3032, 2956, 2926, 2870, 2854, 1779, 1688, 1631, 1589, 1501, 1459, 1419, 1378, 1327, 1264, 1240, 1195, 1127, 1015, 984, 913, 895, 837, 738, 698 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48–7.46 (m, 4H), 7.41–7.28 (m, 13H), 6.37 (s, 2H), 6.36 (s, 2H), 5.48 (dd, *J* = 4.0, 8.8 Hz, 1H), 4.99 (s, 2H), 4.98 (s, 2H), 4.77 (d, *J* = 8.4 Hz, 1H), 4.71 (t, *J* = 8.8 Hz, 1H), 4.31 (dd, *J* = 4.0, 9.2 Hz, 1H), 3.75 (s, 12H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 164.6, 153.6, 153.5, 153.5, 150.7, 138.8, 137.7, 136.9, 136.8, 135.8, 135.7, 129.1, 128.8, 128.4, 128.1, 127.7, 126.1, 121.6, 105.6, 105.5, 74.9, 70.0, 57.8, 56.1, 54.0 ppm. **HRMS (ESI)**: calcd. for $C_{43}H_{41}NO_9^+$ $[M+H]^+$: 716.2854, found: 716.2863.



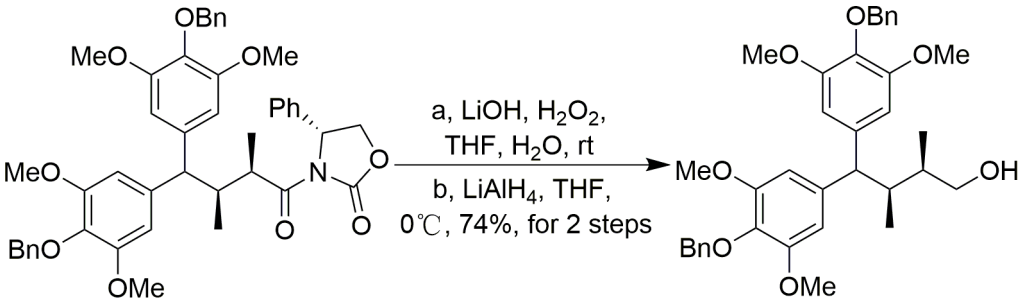
3e **3f**

In a 25 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with CuBr•SMe_2 (206 mg, 1.0 mmol, 2.0 eq) in THF : SMe_2 (3 : 1) (4.0 mL) at –45℃ for additional 10 min, warmed up to 0℃ for 0.5 h, followed by the addition of (*R,E*)-3-(4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)but-2-enoyl)-4-phenylo-xazolidin-2-one (**3e**) (365 mg, 0.5 mmol) in THF (2 mL) at –45℃. The reaction was allowed to stir for 20 min, warmed up to room temperature for 8 h, and quenched by the addition of aqueous saturated NH_4Cl (1.5 mL). The crude residue was diluted with EtOAc (50 mL) and washed with water (3 × 5 mL) and brine (5 mL), dried over Na_2SO_4. The crude residue was purified through flash column chromatography (petroleum ether : ethyl acetate = 4 : 1 → 2 : 1) on 200-300 mesh afforded (*R*)-3-((*R*)-4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-3-methylbutan-oyl)-4-phenyloxazolidin-2-one (**3f**) (278 mg, 75% yield). **Physical state:** yellow oil; **TLC:** R_f = 0.36 (petroleum ether/EtOAc = 2 : 1); $[\alpha]^{25}_D$ = –31 (c 1.0, acetone); **IR (film)**: ν_{max} = 3396, 3056, 2959, 2928, 2872, 2855, 1781, 1701, 1590, 1500, 1459, 1421, 1383, 1325, 1265, 1243, 1189, 1130, 1076, 738, 700 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48–7.45 (m, 4H), 7.34–7.25 (m, 9H), 7.21–7.20 (m, 2H), 6.53 (s, 2H), 6.51 (s, 2H), 5.08 (dd, *J* = 3.2, 8.8 Hz, 1H), 4.97–4.95 (m, 4H), 4.53 (t, *J* = 8.8 Hz, 1H), 4.14 (dd, *J* = 3.2, 8.8 Hz, 1H), 3.83 (s, 6H), 3.80 (s, 6H), 3.45 (d, *J* = 11.2 Hz, 1H), 3.25 (dd, *J* = 6.0, 16.4 Hz, 1H), 3.00–2.93 (m, 1H), 2.67 (dd, *J* = 6.4, 16.4 Hz, 1H), 0.86 (d, *J* = 6.4, Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.3, 153.6, 153.4, 153.0, 139.4, 139.3, 139.0, 137.9, 135.4, 135.3, 129.0, 128.5, 128.3, 128.3, 128.1, 128.0, 127.7, 127.6, 125.8, 105.4, 104.9, 75.0, 74.9, 69.7, 59.7, 57.6, 56.1, 56.0, 40.3, 34.6, 19.9 ppm. **HRMS (ESI)**: calcd. for $C_{44}H_{45}NO_9^+$ $[M+Na]^+$: 754.2987, found: 754.2995.



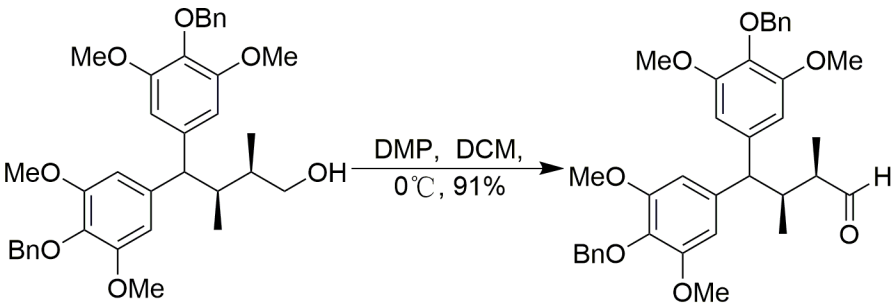
3f **3g**

In a 25 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with (*R*)-3-((*R*)-4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-3-methyl-butanyl)-4-phenyloxazolidin-2-one (**3f**) (365 mg, 0.5 mmol, 1.0 eq) in THF (2.0 mL) at -45℃, followed by the addition of NaHMDS (0.37 mL, 0.75 mmol, 1.5 eq, 2.0 M) in THF. The reaction mixture was stirred at this temperature for another 1.0 h followed by the addition of methyl iodide (106 mg, 0.75 mmol, 1.5 eq). The reaction was allowed to stir for 20 min, warmed up to room temperature for 8 h and quenched by the addition of aqueous saturated NH_4Cl (1.0 mL). The crude residue was diluted with EtOAc (50 mL) and washed with water (3 × 5 mL) and brine (5 mL), dried over Na_2SO_4. The crude residue was purified through flash column chromatography (petroleum ether : ethyl acetate = 4 : 1 → 2 : 1) on 200-300 mesh afforded (4*R*)-3-((3*S*)-4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-2,3-dimethylbutanoyl)-4-phenyloxazolidin-2-one (**3g**) (dr = 94 : 6) (245 mg, 66% yield). **Physical state:** yellow oil; **TLC:** R_f = 0.36 (petroleum ether/EtOAc = 2 : 1); $[\alpha]^{25}_D$ = –28 (c 1.0, acetone); **IR (film)**: ν_{max} = 3400, 3056, 2957, 2925, 2854, 1777, 1701, 1590, 1494, 1460, 1421, 1378, 1324, 1264, 1198, 1131, 1076, 1027, 740, 703 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.49–7.47 (m, 4H), 7.34–7.25 (m, 9H), 7.14–7.12 (m, 2H), 6.56 (s, 4H), 5.01–4.91 (m, 4H), 4.79 (dd, *J* = 2.8, 8.8 Hz, 1H), 4.47 (t, *J* = 8.8 Hz, 1H), 4.04 (dd, *J* = 2.4, 8.8 Hz, 1H), 3.88 (s, 6H), 3.83 (s, 7H), 3.41 (d, *J* = 10.8 Hz, 1H), 3.04–2.94 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.4, Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 176.4, 153.4, 153.1, 152.5, 140.0, 139.6, 138.3, 137.9, 137.8, 135.4, 135.0, 128.9, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6,125.5, 106.5, 105.0, 75.0, 74.9, 69.7, 60.8, 57.6, 56.2, 55.8, 40.8, 37.9, 16.4, 15.5 ppm. **HRMS (ESI)**: calcd. for $C_{45}H_{47}NO_9^+$ $[M+Na]^+$: 768.3143, found: 768.3149.



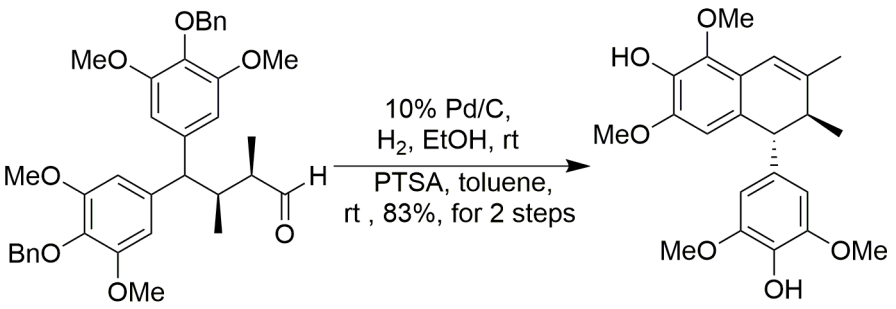
3g **3h**

In a 25 mL round-bottom flask equipped with stir bar under H2 (1 atm) atmosphere was charged with (4*R*)-3-((3*S*)-4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-2,3-dimethyl- butanoyl)-4-phenyloxazolidin-2-one (**3g**) (150 mg, 0.2 mmol, 1.0 eq) in THF : water (4:1, 1.9 mL) (2 mL) was added d added 30% aqueous H_2O_2 (0.3 mL), followed by the addition of 0.5 M aqueous LiOH (3.0 mL) at 0℃. After 30 min, the mixture was stirred at room temperature for 10 h. After dilution with water, the aqueous layer was acidified by the addition of 1 N aqueous HCl and extracted with EtOAc. The reaction mixture was extracted with ethyl acetate, the combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was dissolved in THF (2 mL) followed by addition of LAH (259 mg, 1.5 mmol, 0.75 equiv) at 0℃ for 15 min. the reaction mixture was extracted with EtOAc (30 mL), and washed with water (3 × 3 mL) and brine (3 mL) dried over Na_2SO_4. Purification by flash column chromatography (petroleum ether : ethyl acetate = 2 : 1 → 1 : 1) on 200-300 mesh silica gel afforded (3*S*)-4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-2,3-dimethylbutan-1-ol (**3h**) (87 mg, 74% yield). **Physical state:** colorless oil; **TLC:** R_f = 0.32 (petroleum ether/EtOAc = 1 : 1); $[\alpha]^{25}_D$ = –26 (c 1.0, acetone); **IR (film)**: ν_{max} = 3437, 3061, 3031, 2957, 2925, 2871, 1590, 1501, 1458, 1420, 1377, 1324, 1377, 1324, 1264, 1242, 1219, 1187, 1128, 1029, 1015, 987, 912, 847, 737, 698, 601, 529 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48–7.45 (m, 4H), 7.34–7.27 (m, 6H), 6.55 (s, 2H), 6.51 (s, 2H), 4.97 (s, 2H), 4.96 (s, 2H), 3.81 (s, 12H), 3.50–3.47 (m, 3H), 2.60–2.56 (m, 1H), 1.76–1.68 (m, 1H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.68 (d, *J* = 6.8, Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.4, 153.3, 128.4, 128.3, 128.0, 127.7, 105.1, 74.9, 66.8, 57.1, 56.2, 36.1, 36.0, 11.8, 9.8 ppm. **HRMS (ESI)**: calcd. for $C_{36}H_{42}O_7^+$ $[M+H]^+$: 587.3003, found: 587.3015.



3h **3i**

In a 25 mL round-bottom flask equipped with stir bar under Ar atmosphere was charged with (3*S*)-4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-2,3-dimethylbu-tan-1-ol (3h) (59 mg, 0.1 mmol, 1.0 eq) in DCM (2.0 mL) at 0℃, followed by the addition of DMP (64 mg, 0.15 mmol, 1.5 eq). The reaction mixture was stirred at this temperature for another 2.0 h. The crude residue was diluted with DCM (30 mL) and washed with water (3 × 3 mL) and brine (3 mL), dried over Na_2SO_4. The crude residue was purified through flash column chromatography (petroleum ether : ethyl acetate = 4 : 1 → 2 : 1) on 200-300 mesh afforded (3*S*)-4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-2,3-dimethylbutanal (3i) (53 mg, 91% yield). **Physical state:** colorless oil; **TLC:** R_f = 0.55 (petroleum ether/EtOAc = 1 : 1); $[\alpha]^{25}_D$ = –26 (c 1.0, acetone); **IR (film)**: ν_{max} = 3409, 3062, 3030, 2958, 2930, 2872, 2838, 1721, 1589, 1501, 1456, 1420, 1376, 1326, 1242, 1220, 1187, 1130, 1012, 914, 847, 735, 697 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.65 (s, 1H), 7.71–7.45 (m, 4H), 7.35–7.27 (m, 6H), 6.54 (s, 2H), 6.53 (s, 2H), 4.97 (s, 4H), 3.83 (s, 6H), 3.82 (s, 6H), 3.51 (d, *J* = 11.6 Hz, 1H), 2.97–2.92 (m, 1H), 2.38–2.32 (m, 1H), 1.07 (d, *J* = 7.2, Hz, 3H), 0.71 (d, *J* = 6.4, Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 205.3, 153.7, 153.5, 139.0, 138.9, 137.8, 137.7, 135.8, 135.6, 128.4, 128.3, 128.0, 127.7, 105.0, 104.8, 74.9, 56.7, 56.2, 56.2, 47.9, 35.8, 13.7, 6.7 ppm. **HRMS (ESI)**: calcd. for $C_{36}H_{40}O_7^+$ $[M+H]^+$: 585.2847, found: 585.2836.

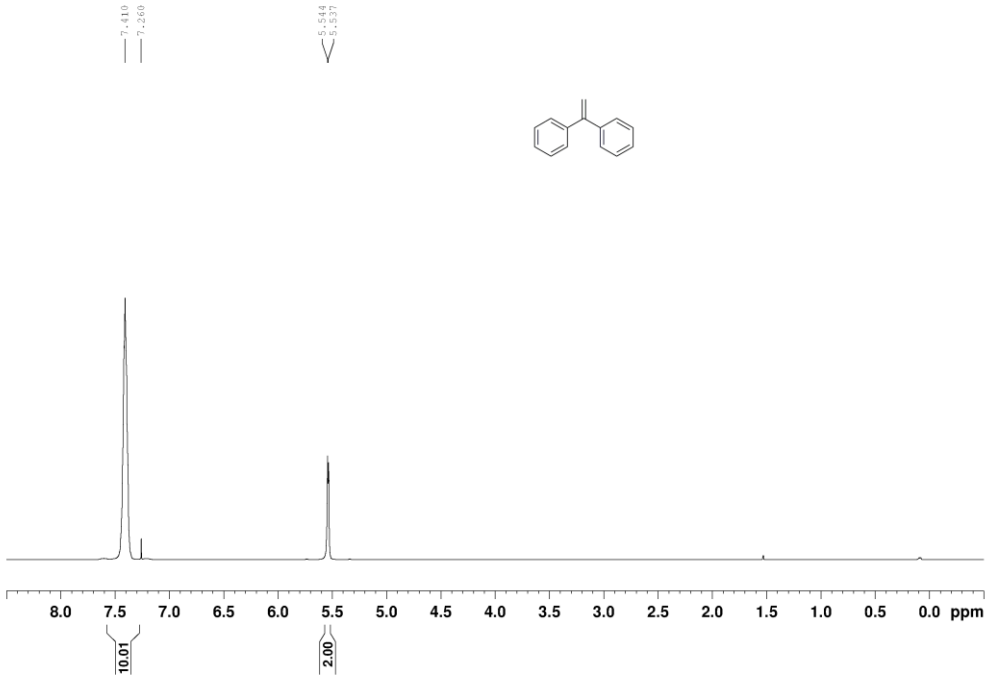


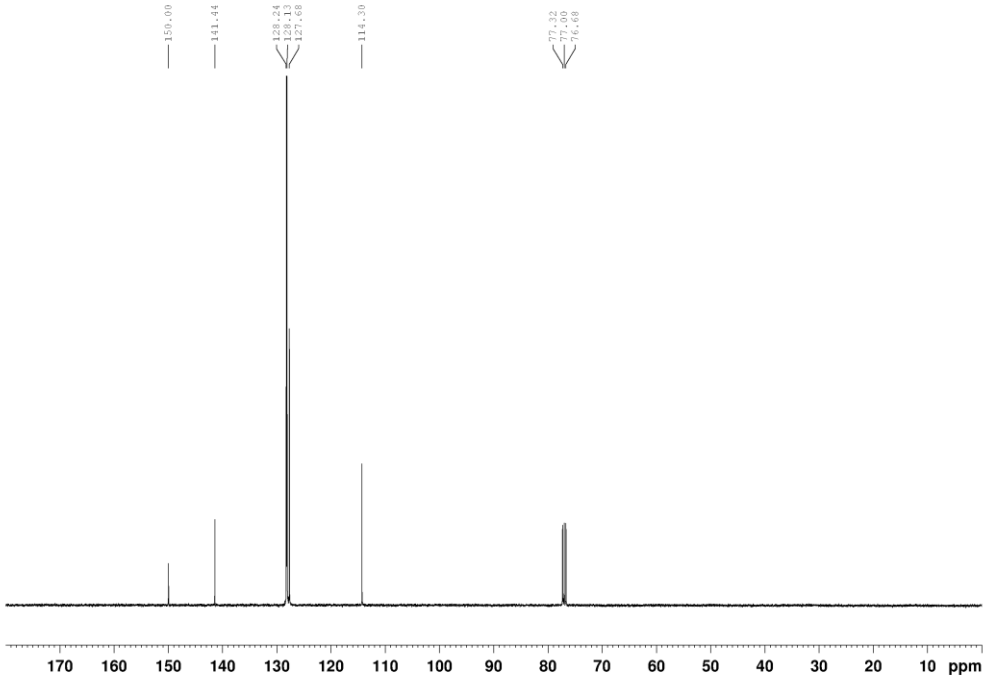
3i **3j**

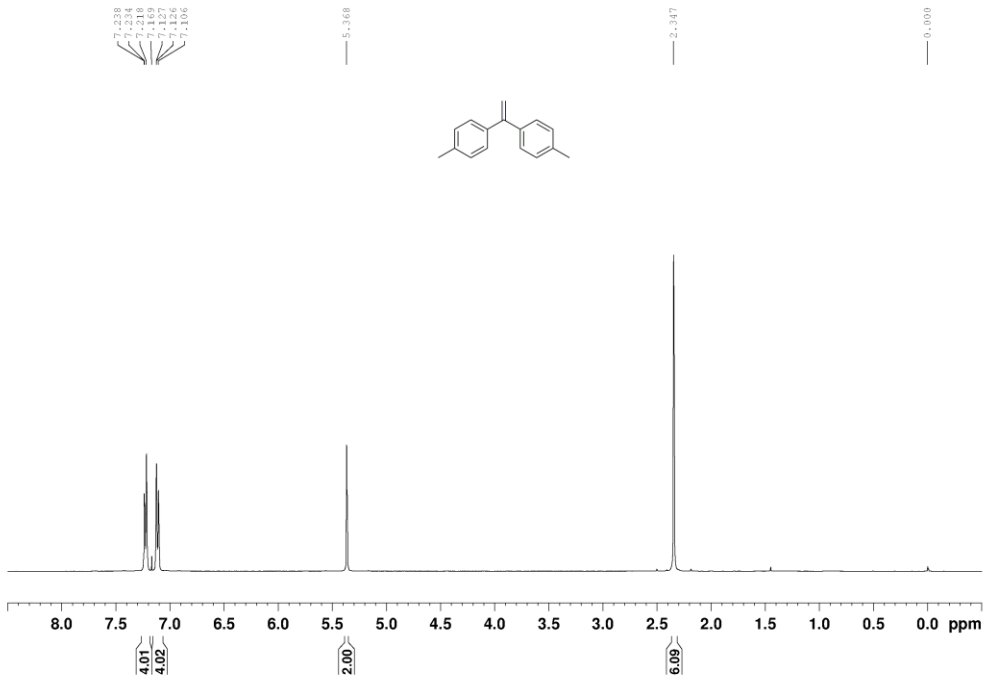
In a 10 mL round-bottom flask equipped with stir bar under Ar atmosphere was

charged with (4*R*)-3-((3*S*)-4,4-bis(4-(benzyloxy)-3,5-dimethoxyphenyl)-2,3-dim-ethyl-butanoyl)-4-phenyloxazolidin-2-one (3g) (29 mg, 0.05 mmol, 1.0 eq) in EtOH (1.0 mL) followed by the addition of Pd/C (10.0 mg) at room temperature for 5 h. The reaction mixture was filtered and concentrated in vacuo. he crude tertiary alcohol product was dissolved in toluene (5 mL) followed by addition of PTSA• H_2O (5.0 mg, 0.025 mmol, 0.5 eq) at room temperature for 2 h. Purification by flash column chromatography (petroleum ether : ethyl acetate = 6 : 1 → 4 : 1) on 200-300 mesh silica gel afforded (-)-Sacidumlignan B (3j) (16 mg, 83% yield). **Physical state:** colorless solid; **Mp.** 128–130 °C; **TLC:** R_f = 0.31 (petroleum ether/EtOAc = 2 : 1); $[\alpha]^{25}_D$ = –29 (c 0.6, acetone); **IR (film)**: ν_{max} = 3436, 3049, 2959, 2934, 2840, 1612, 1516, 1496, 1460, 1424, 1360, 1320, 1304, 1267, 1242, 1214, 1114, 1098, 1065, 1036, 932, 912, 888, 852, 767, 735, 701, 666, 582 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.45 (s, 1H), 6.35 (s, 1H), 6.30 (s, 2H), 5.43 (s, 1H), 5.34 (s, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H), 3.61 (d, *J* = 3.2 Hz, 1H), 2.40–2.34 (m, 1H), 1.82 (s, 3H), 1.07 (d, *J* = 6.8, Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 146.7, 145.9, 142.4, 139.1, 137.0, 136.6, 132.9, 126.7, 120.8, 114.9, 108.0, 104.3, 61.2, 56.1, 51.7, 41.9, 22.5, 18.7 ppm. **^{1}H NMR** (400 MHz, acetone-d_6): δ = 7.28 (s, 1H), 6.93 (s, 1H), 6.49 (s, 1H), 6.46 (d, *J* = 1.2 Hz, 1H), 6.42 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.70 (s, 6H), 3.66 (d, *J* = 2.8 Hz, 1H), 2.40 (dq, J = 2.8, 6.8, 9.6 Hz, 1H), 1.82 (d, *J* = 0.8, Hz, 3H), 1.05 (d, *J* = 6.8, Hz, 3H) ppm; **^{13}C NMR** (100 MHz, acetone-d_6): δ = 148.5, 148.0, 144.2, 139.3, 139.0, 137.3, 135.3, 127.4, 121.6, 116.3, 109.6, 106.2, 61.1, 56.7, 52.2, 42.7, 22.9, 19.1 ppm. **HRMS (ESI)**: calcd. for $C_{22}H_{26}O_6^+$ $[M+H]^+$: 387.1802, found: 387.1801.

Copies of the ^{1}H and ^{13}C NMR Spectra



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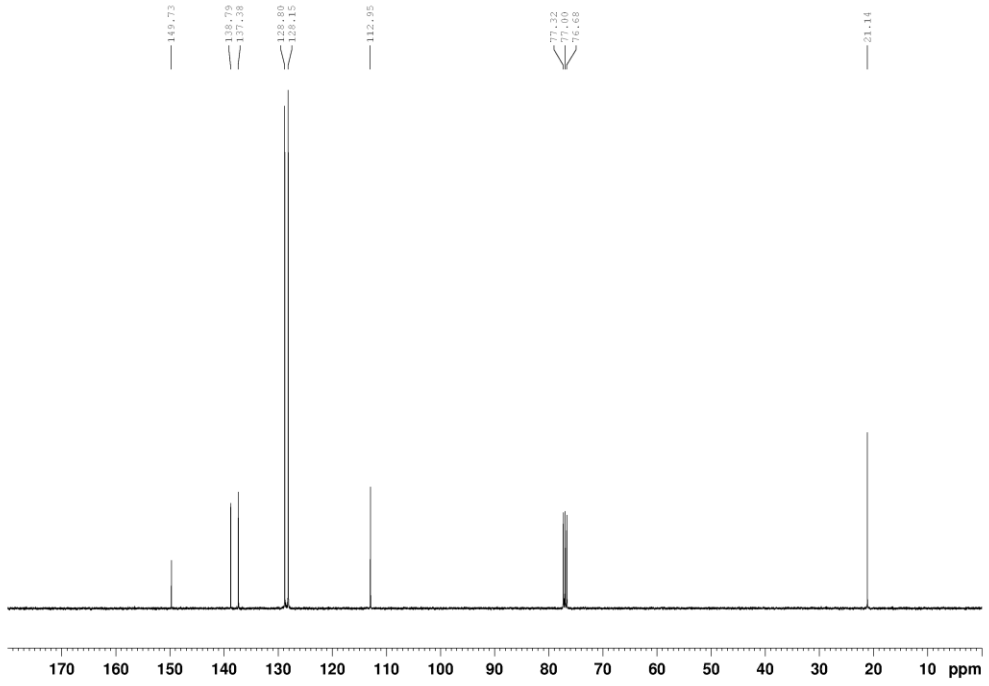
7.234
7.218
7.169
7.127
7.126
7.106
5.368
2.347
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.01
4.02
2.00
6.09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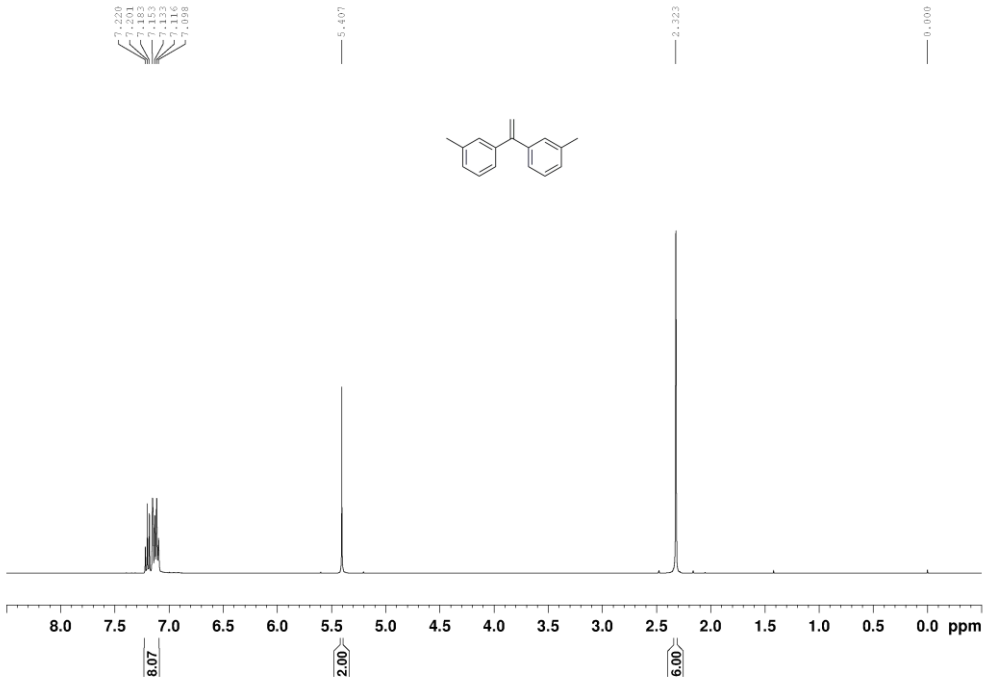
138.79
137.38
128.80
128.15
112.95
77.32
77.00
76.68
21.14
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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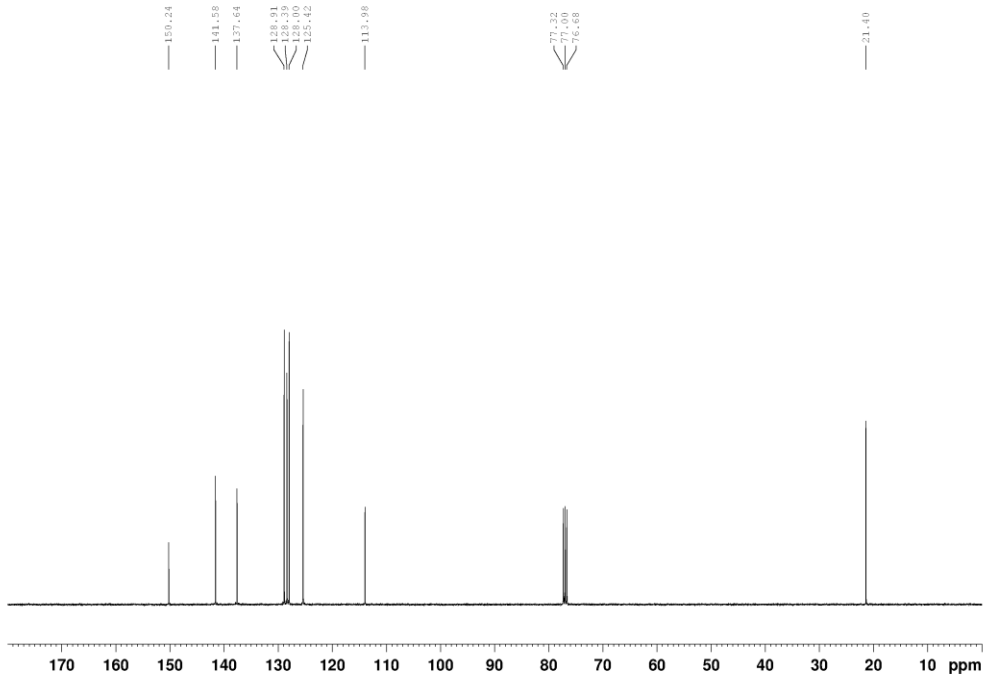
7.201
7.183
7.153
7.133
7.116
7.098
5.407
2.323
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
8.07
2.00
6.00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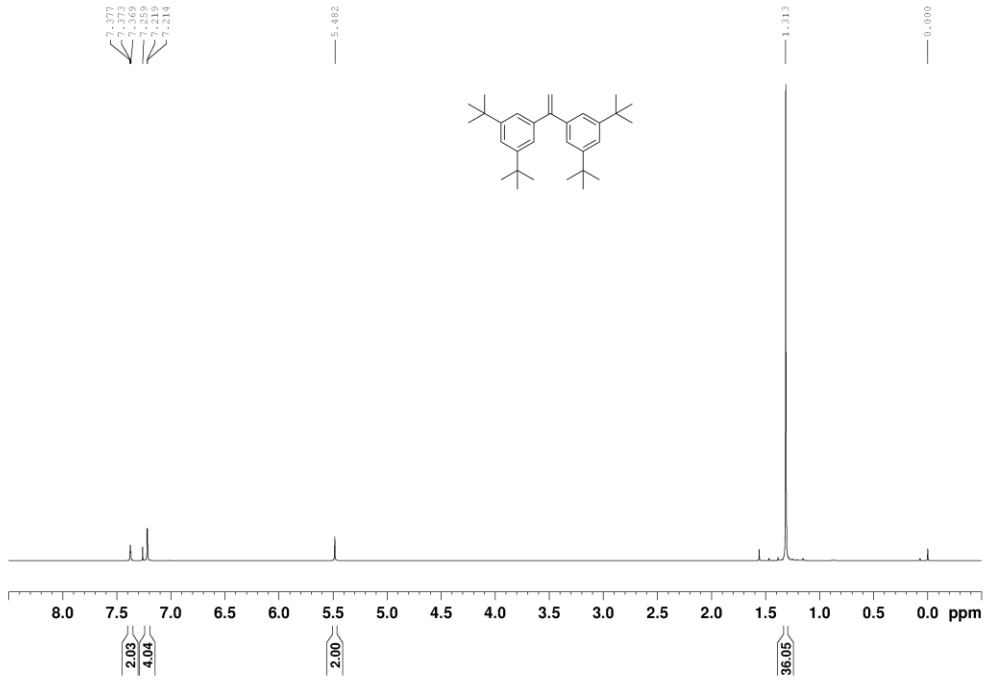
141.58
137.64
128.91
128.39
128.00
125.42
113.98
77.32
77.00
76.68
21.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.373
7.368
7.259
7.219
7.214
5.482
1.313
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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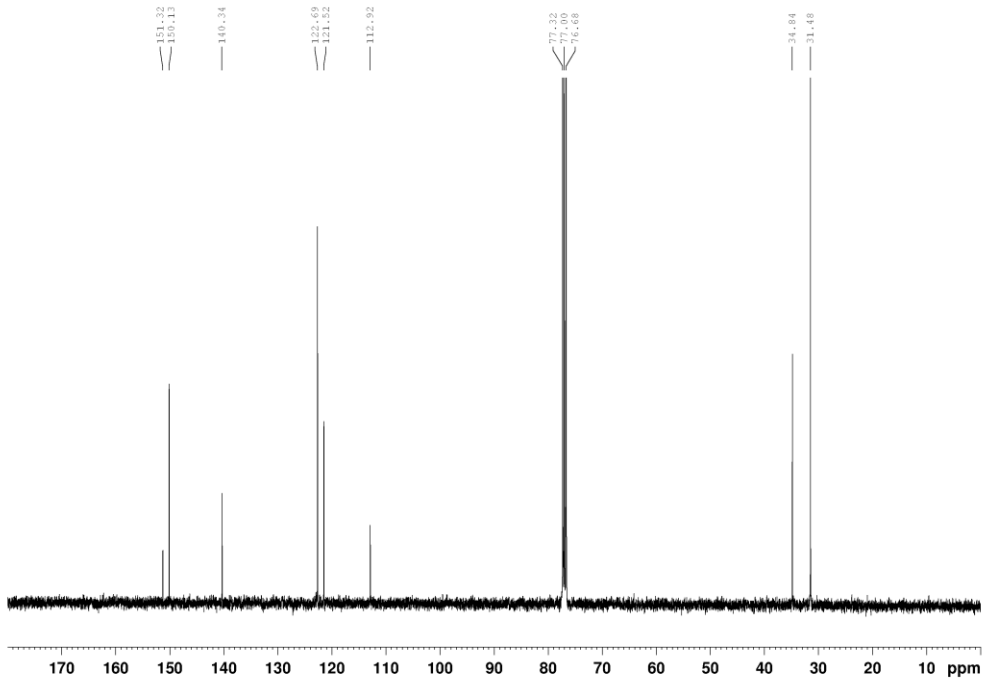
4.04
2.00
36.05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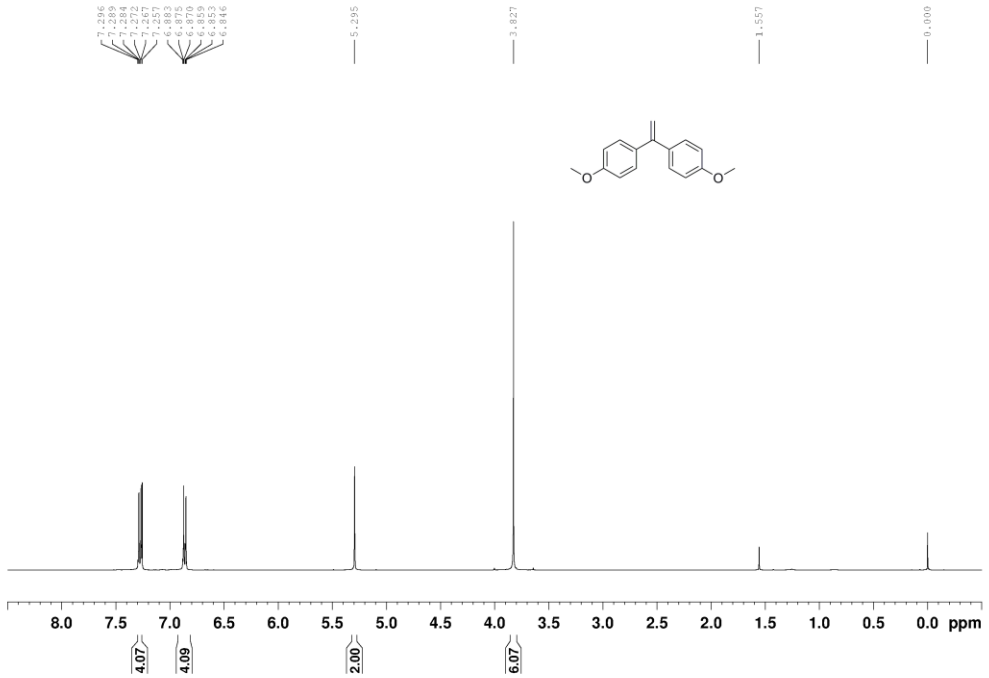
150.13
140.34
122.69
121.52
112.92
77.32
77.00
76.68
34.84
31.48
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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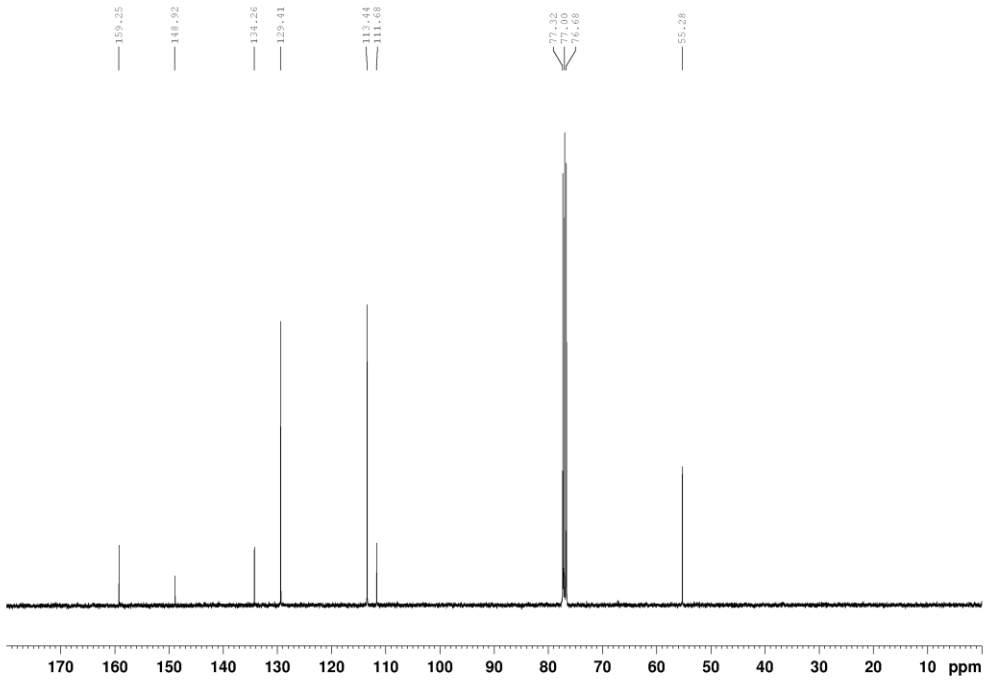
7.284
7.272
7.267
7.257
6.883
6.875
6.870
6.859
6.853
6.846
5.295
3.827
1.557
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.07
4.09
2.00
6.07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148.92
134.26
129.41
113.44
111.68
77.32
77.00
76.68
55.28
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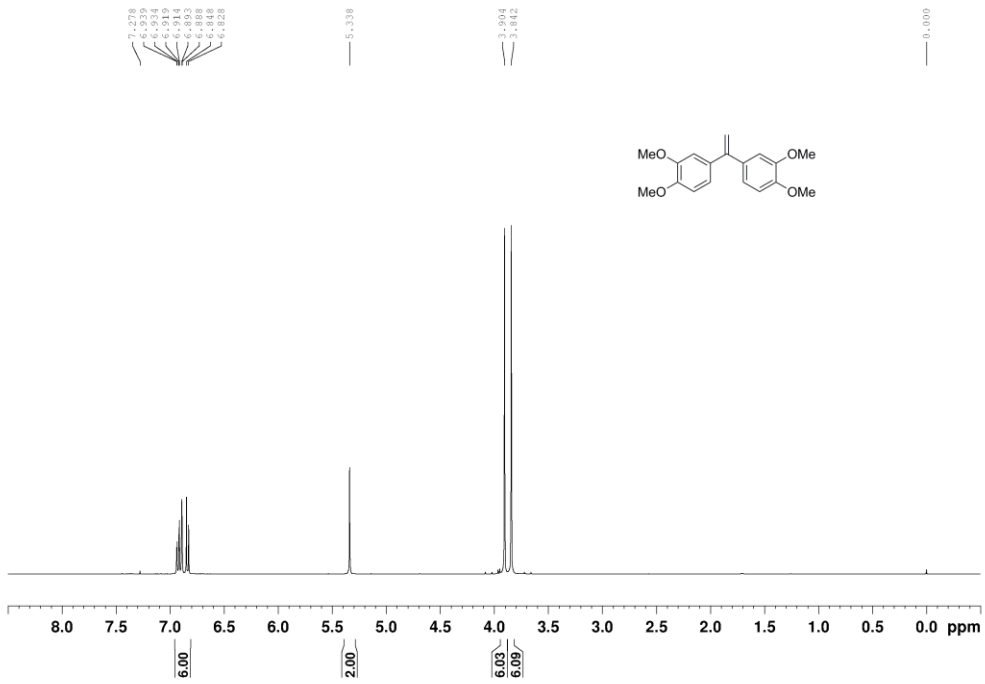
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6.939
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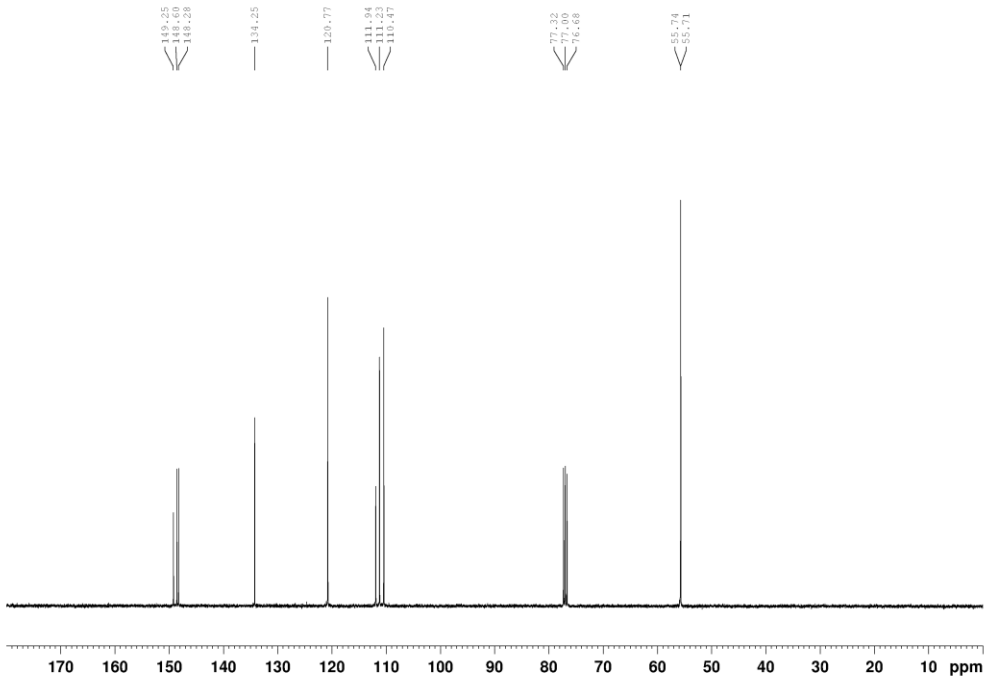
6.919
6.914
6.895
6.888
6.848
6.828
5.338
3.904
3.842
0.000
MeO
MeO
OMe
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.00
2.00
6.03
6.09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134.25
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110.47
77.32
77.00
76.68
55.74
55.71
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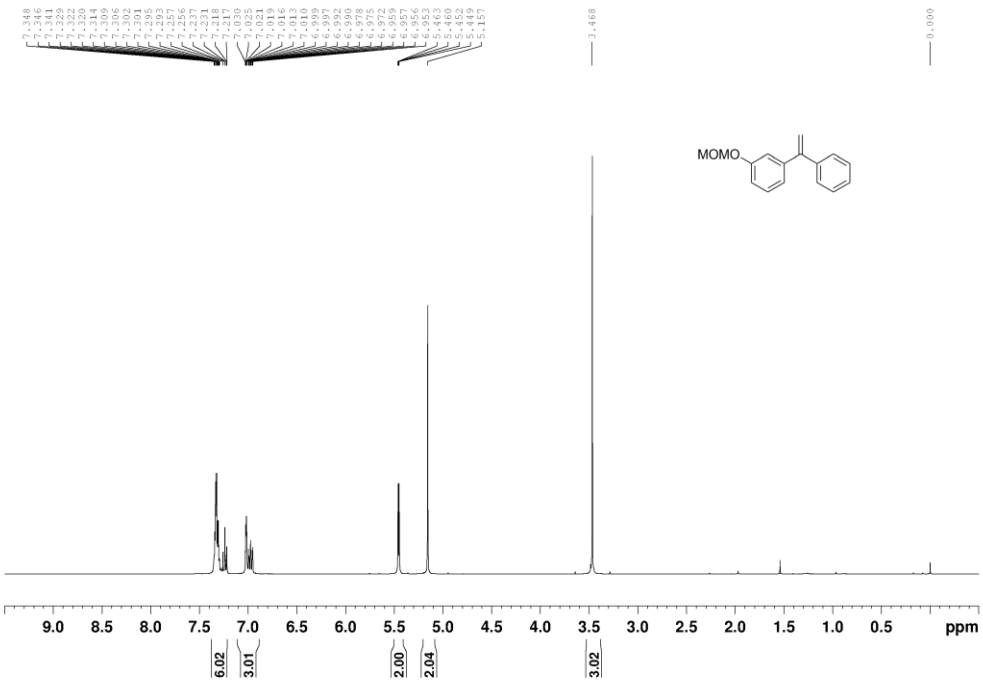
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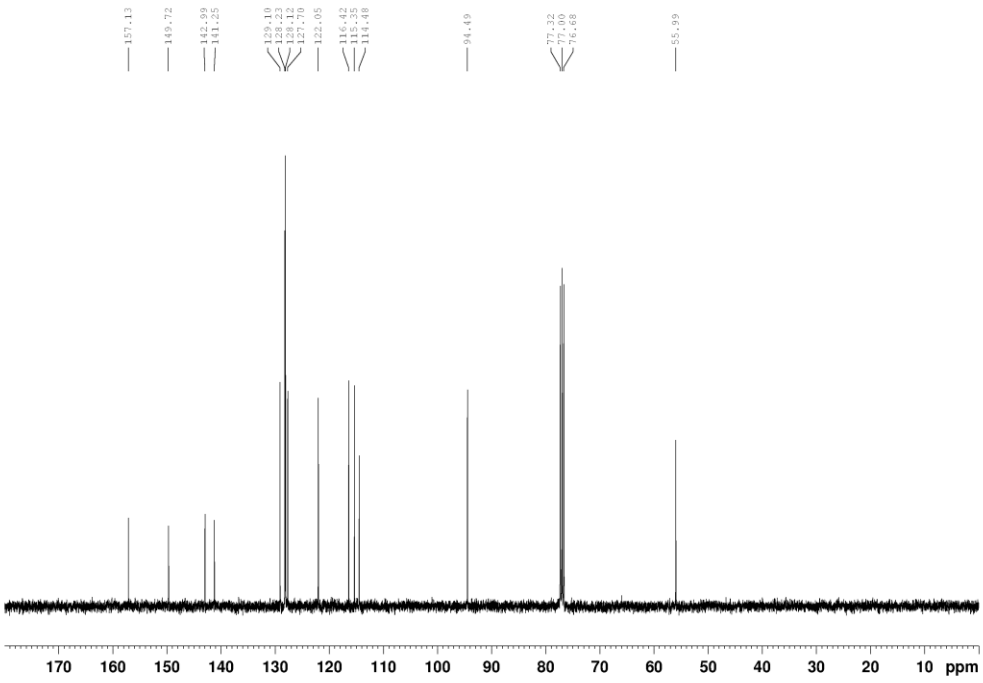
7.329
7.322
7.320
7.314
7.309
7.306
7.302
7.301
7.295
7.263
7.257
7.256
7.237
7.231
7.218
7.217
7.030
7.025
7.021
7.018
7.016
7.013
7.010
6.999
6.997
6.992
6.990
6.978
6.975
6.972
6.959
6.957
6.956
6.953
6.463
5.460
5.452
5.449
5.157
3.468
0.000
MOMO
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
6.02
3.01
2.00
2.04
3.02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149.72
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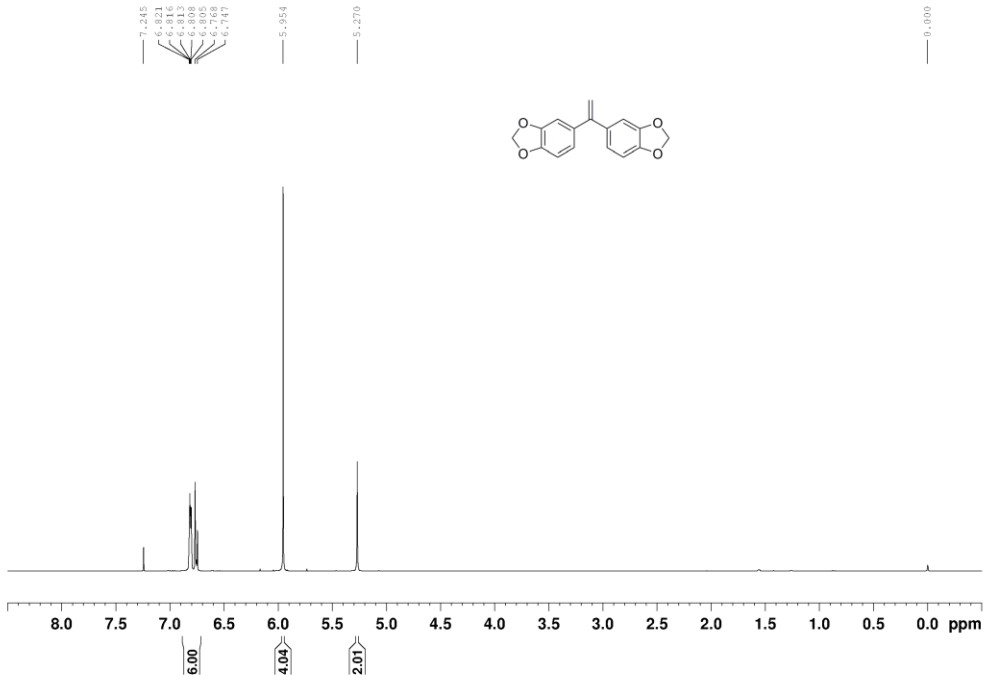
141.25
129.10
128.23
128.12
127.70
122.05
116.42
115.55
114.48
94.49
77.32
77.00
76.68
55.99
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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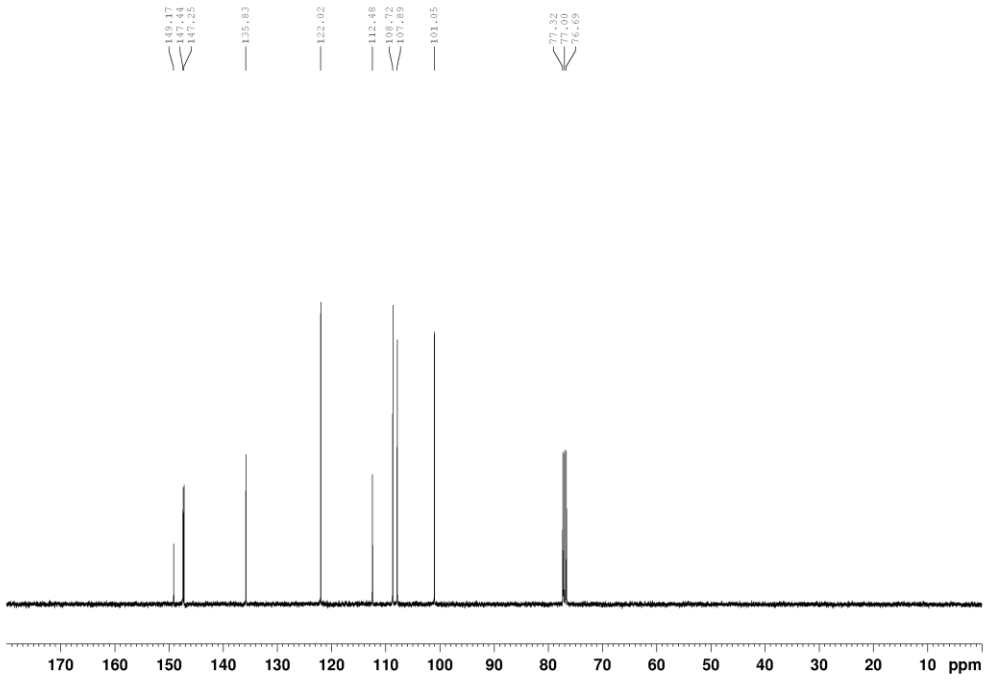
6.821
6.816
6.813
6.808
6.805
6.768
6.747
5.954
5.270
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.00
4.04
2.01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147.25
135.83
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108.72
107.89
101.05
77.32
77.00
76.69
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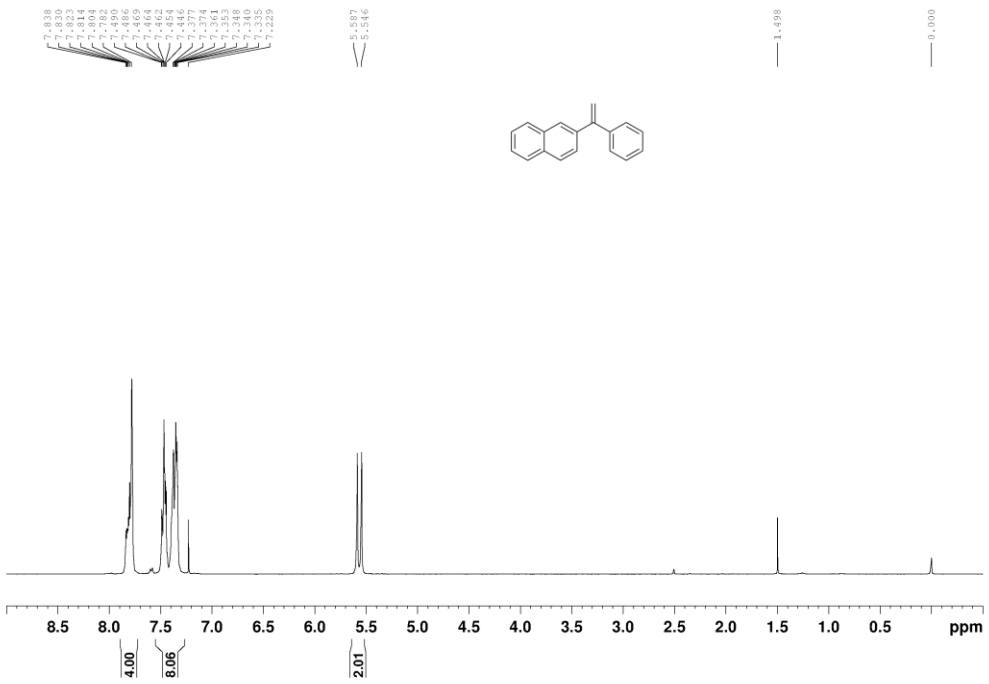
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7.830
7.823
7.814
7.804
7.794
7.782
7.490
7.486
7.469
7.464
7.462
7.454
7.446
7.377
7.374
7.361
7.353
7.348
7.340
7.335
7.229
5.587
5.546
1.498
0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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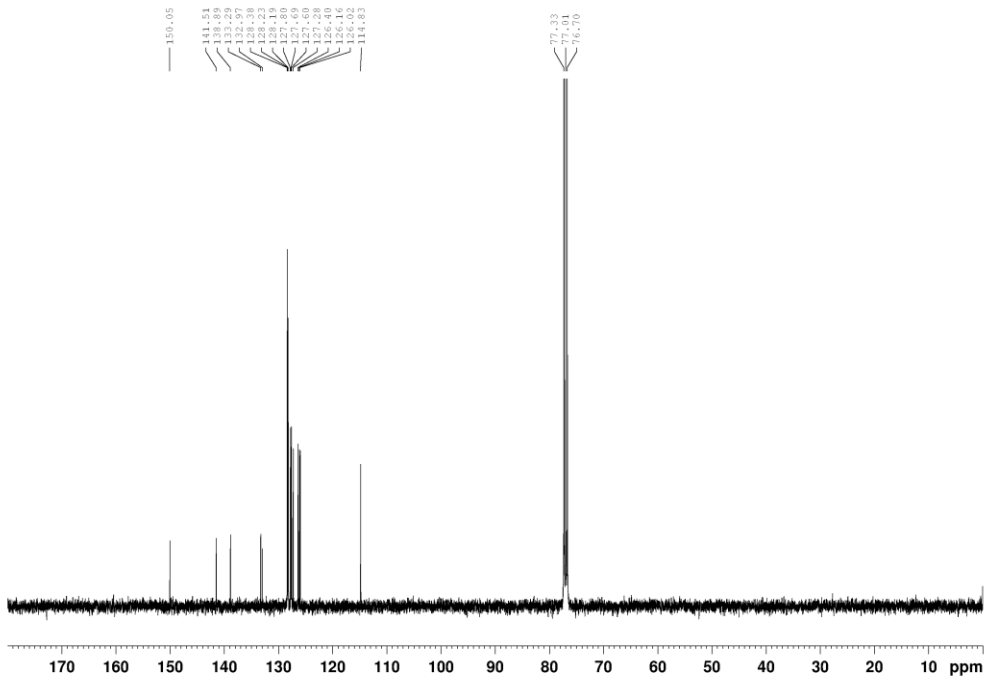
8.06
2.01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132.97
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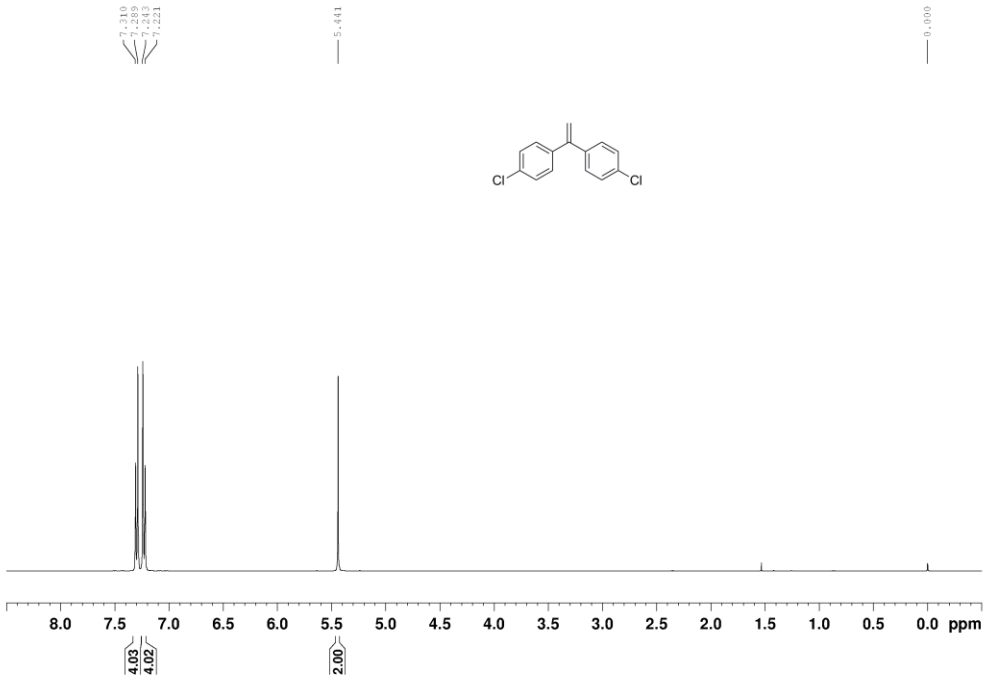
128.23
128.19
127.80
127.69
127.60
127.28
127.00
126.16
126.02
114.83
77.33
77.01
76.70
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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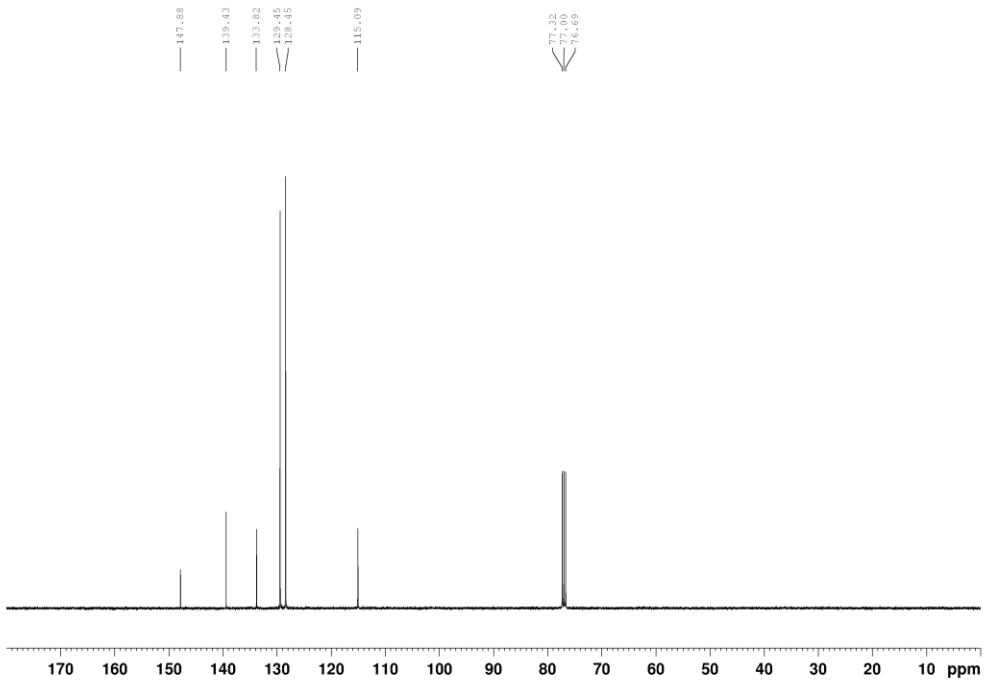
7.303
7.283
7.265
7.221
5.441
0.000
Cl
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
4.03
4.02
2.00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128.45
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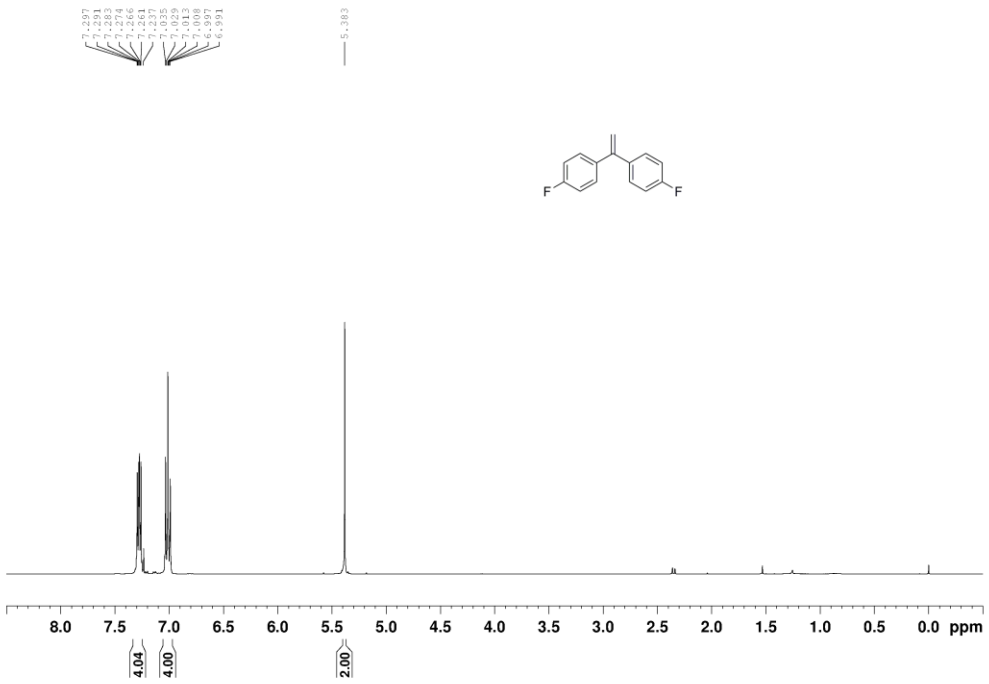
77.32
77.00
76.69
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.013
7.008
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6.991
5.383
F
F
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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0.5
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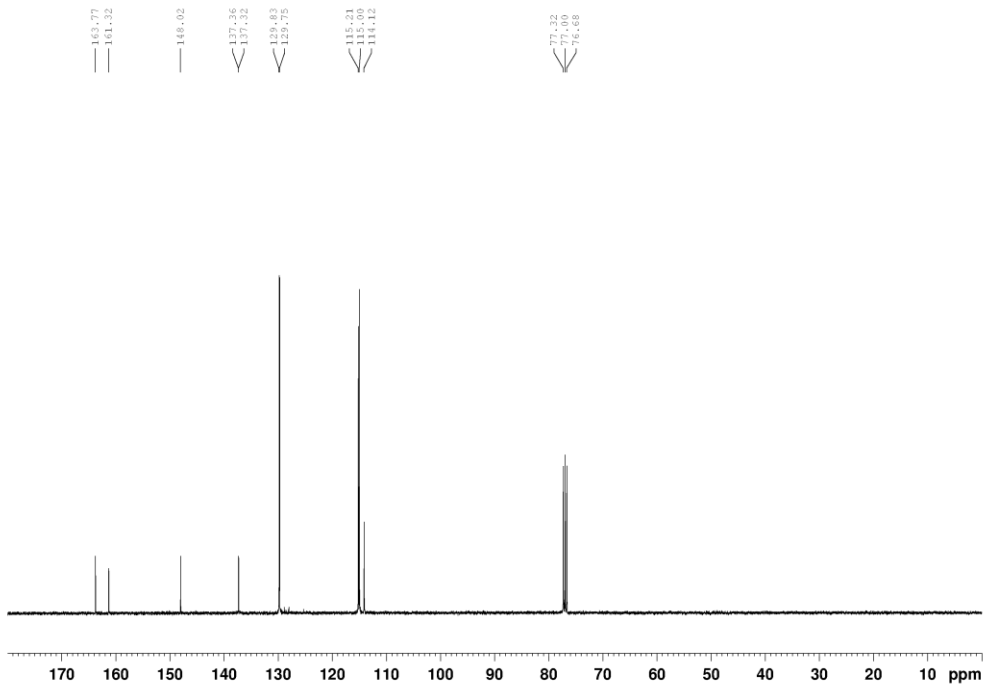
4.00
2.00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129.75
115.21
115.09
114.96
114.12
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77.00
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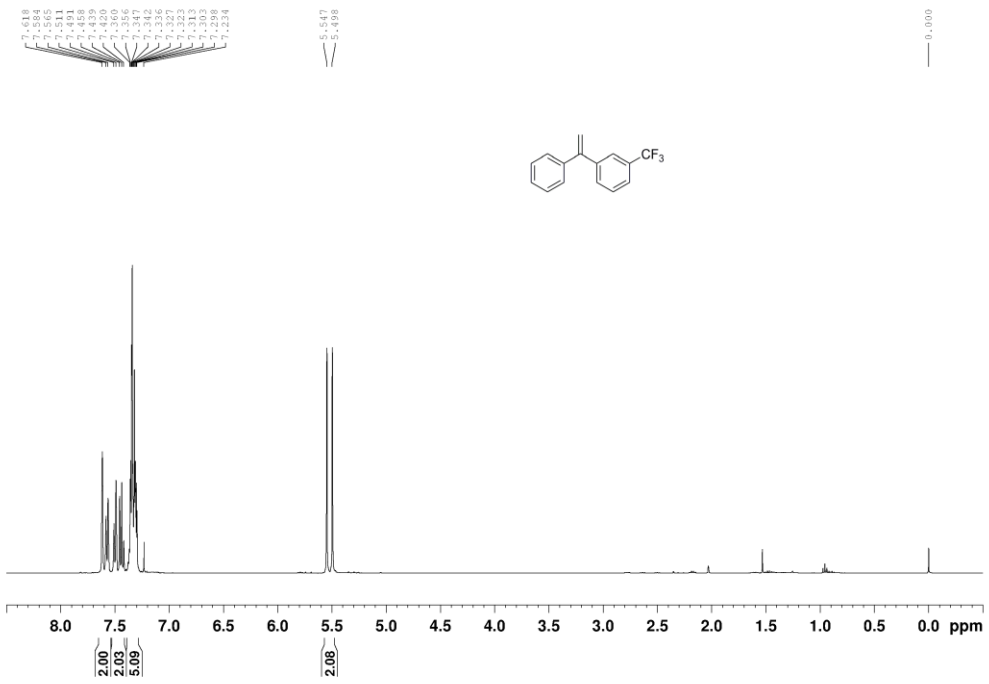
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.336
7.327
7.323
7.313
7.303
7.298
7.234
5.547
5.498
0.000
CF3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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1.0
0.5
0.0 ppm
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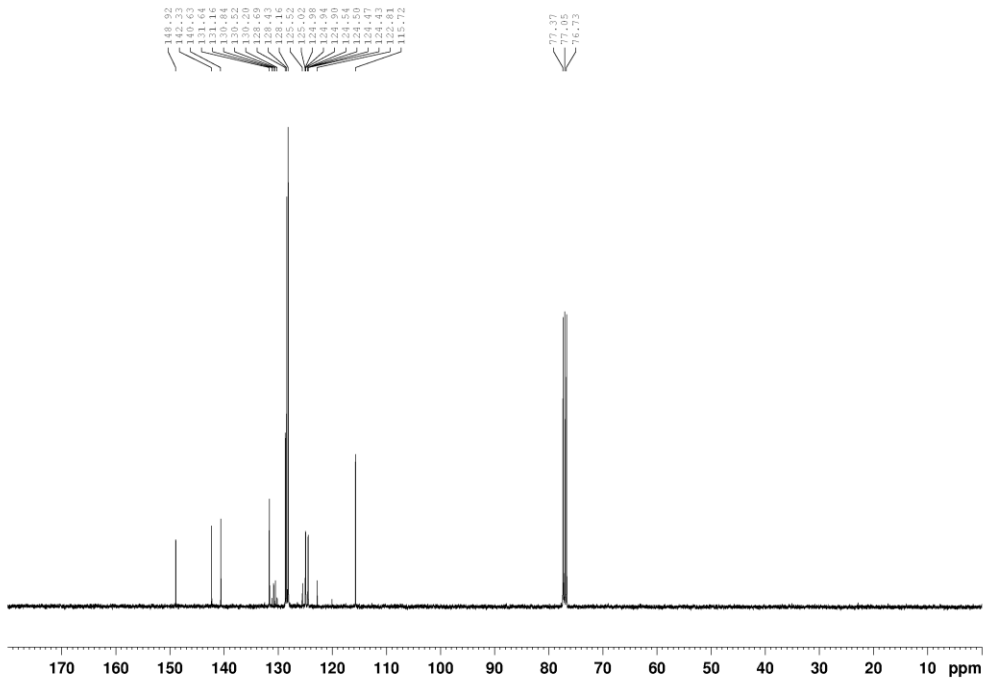
2.03
5.09
2.08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124.90
124.54
124.50
124.47
124.43
122.81
115.72
77.37
77.05
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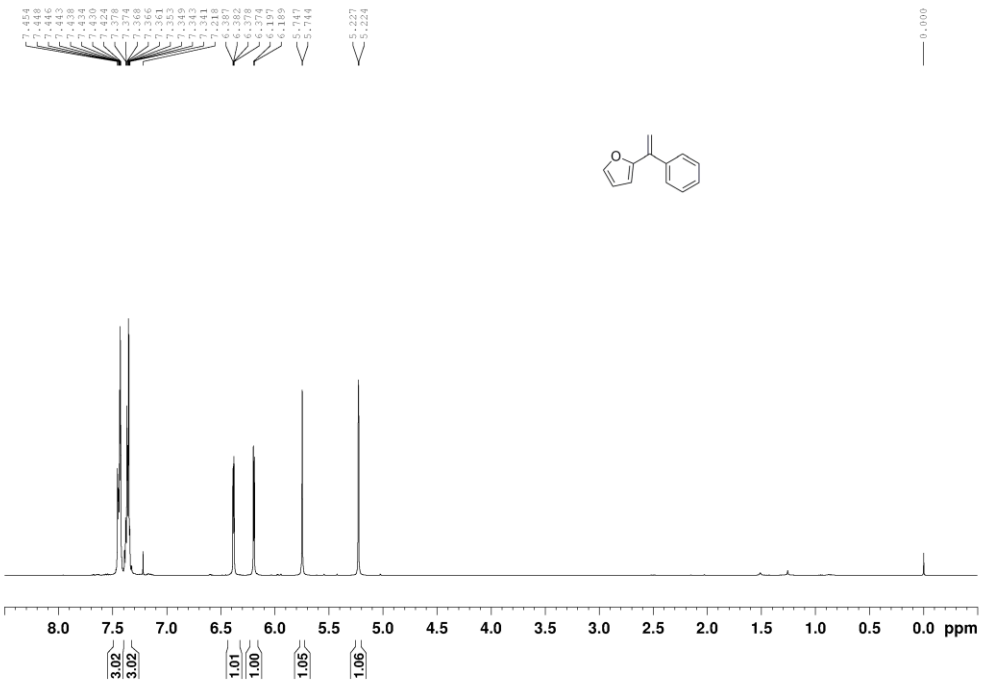
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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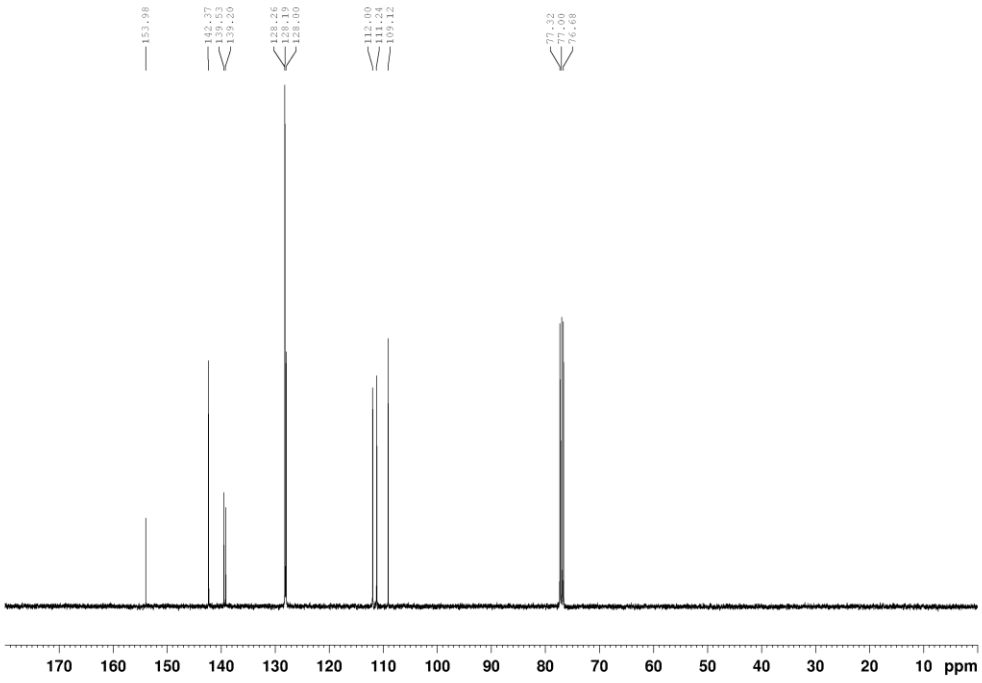
7.363
7.353
7.349
7.343
7.341
7.338
6.387
6.382
6.378
6.374
6.370
6.189
5.747
5.744
5.227
5.224
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.02
3.02
1.01
1.00
1.05
1.06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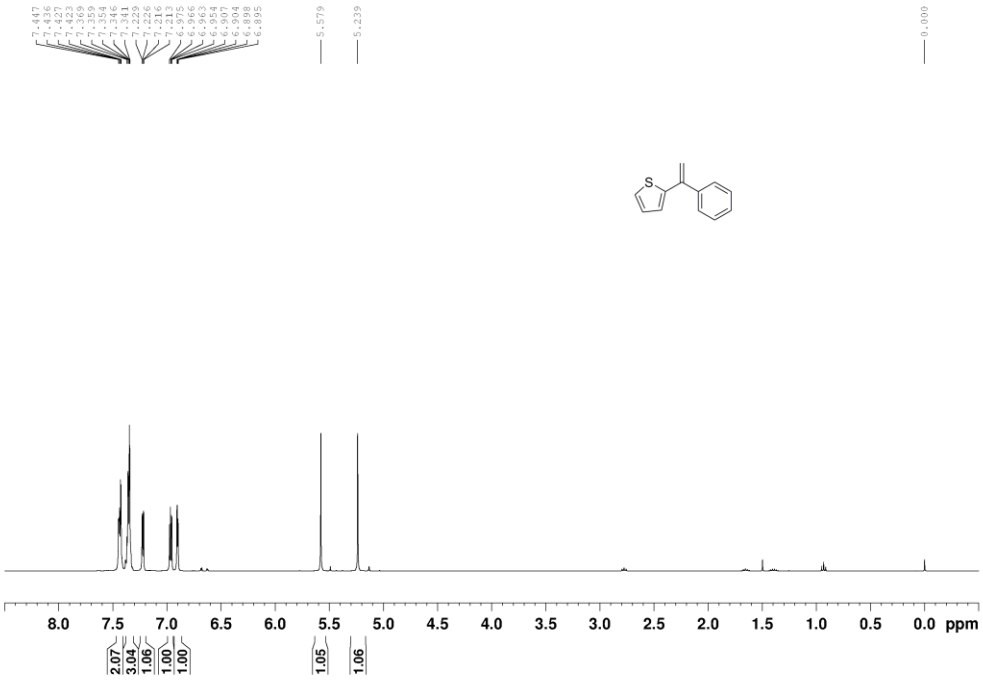
128.19
128.00
112.00
111.24
109.12
77.32
77.00
76.68
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.229
7.226
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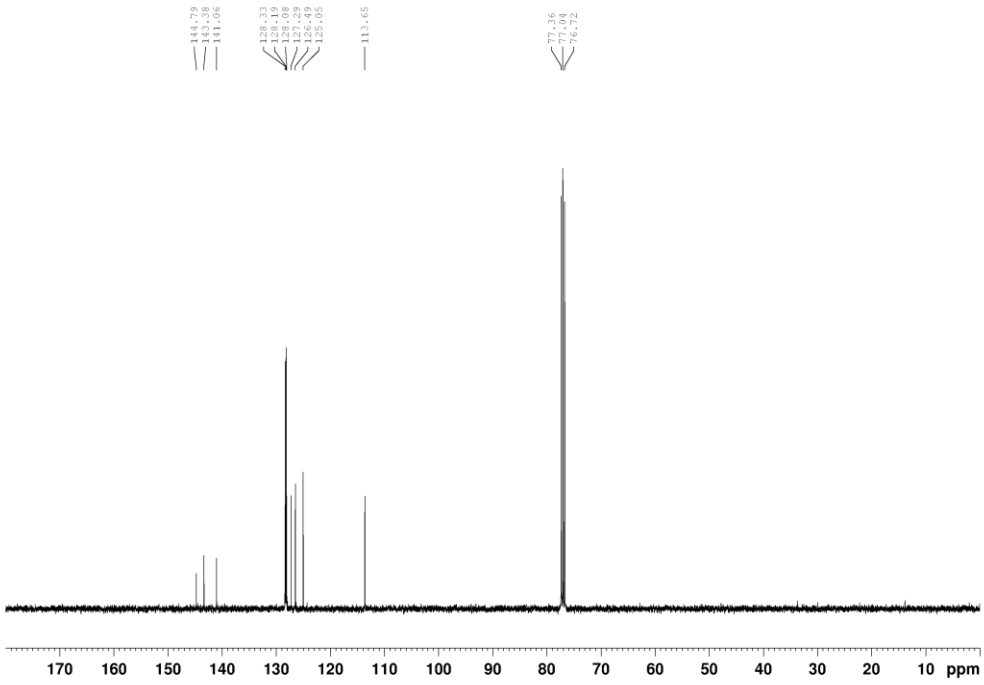
6.975
6.966
6.963
6.954
6.907
6.904
6.898
6.895
5.579
5.239
0.000
S
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.07
3.04
1.06
1.00
1.00
1.05
1.06


144.79
143.38
141.06
128.33
128.19
128.08
127.29
126.49
125.05
113.65
77.36
77.04
76.72
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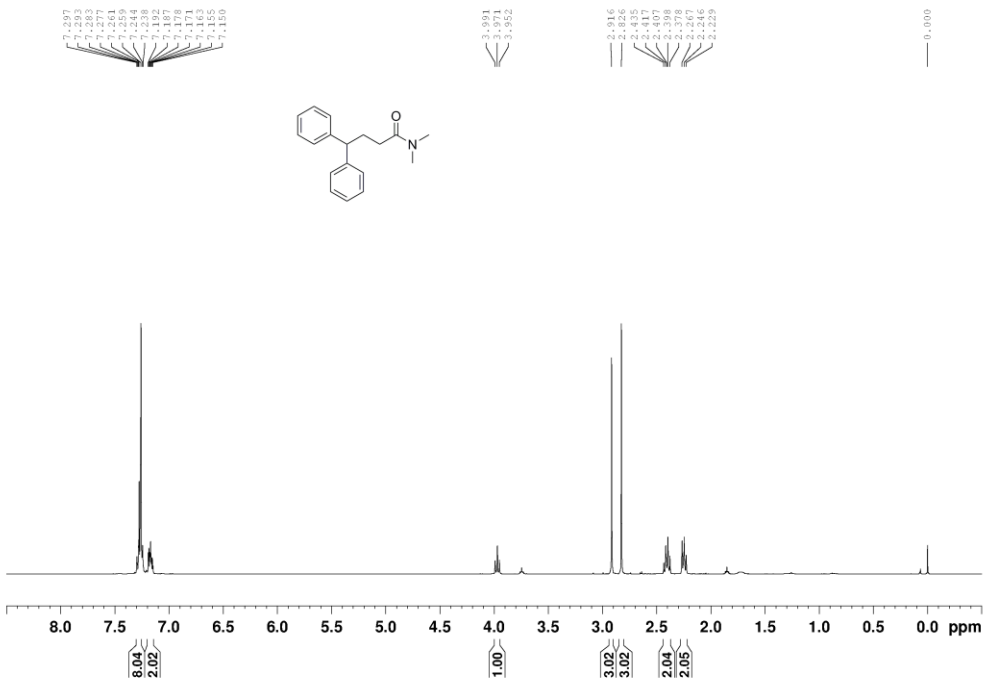
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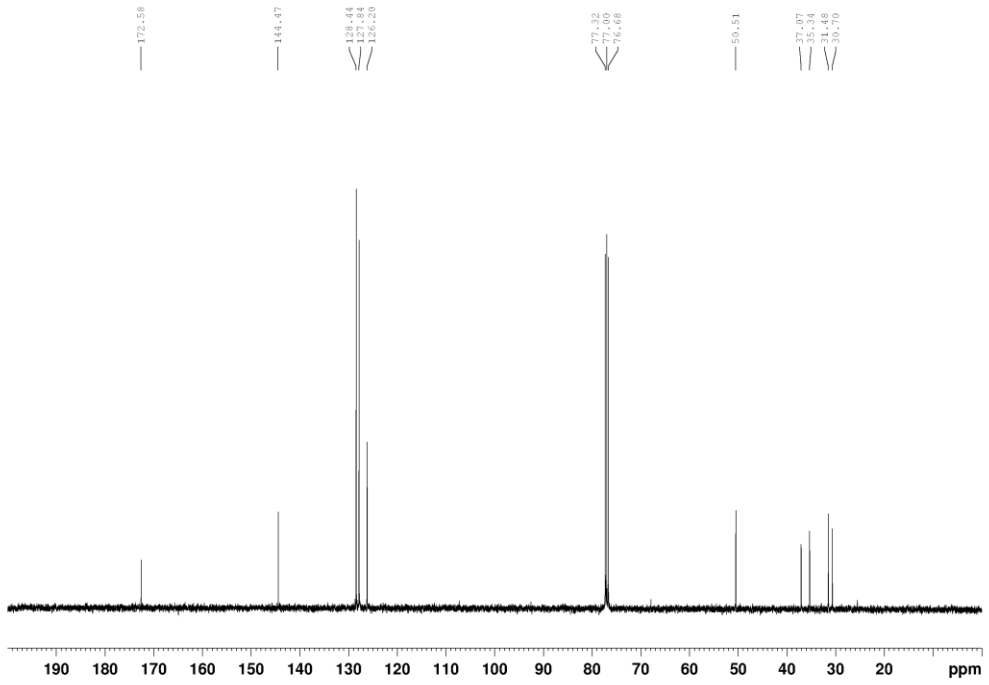
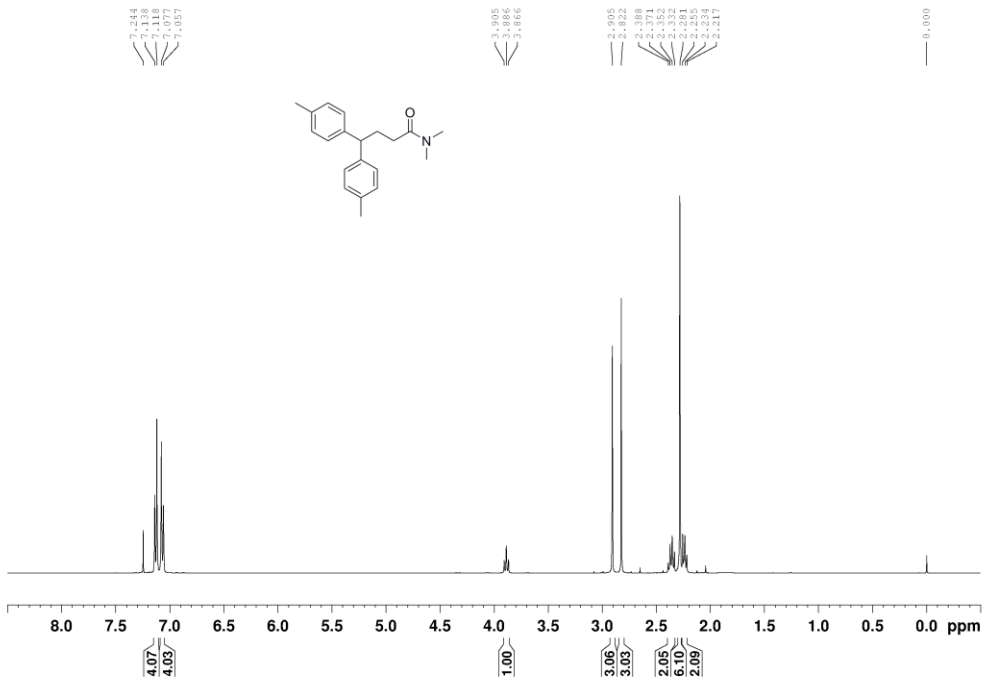
7.283
7.277
7.261
7.259
7.244
7.238
7.192
7.187
7.178
7.171
7.163
7.155
7.150
3.991
3.971
3.952
2.916
2.826
2.435
2.417
2.407
2.398
2.378
2.267
2.246
2.229
0.000
O
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
8.04
2.02
1.00
3.02
3.02
2.04
2.05


172.58
144.47
128.44
127.84
126.20
77.32
77.00
76.68
50.51
37.07
35.34
31.48
30.70
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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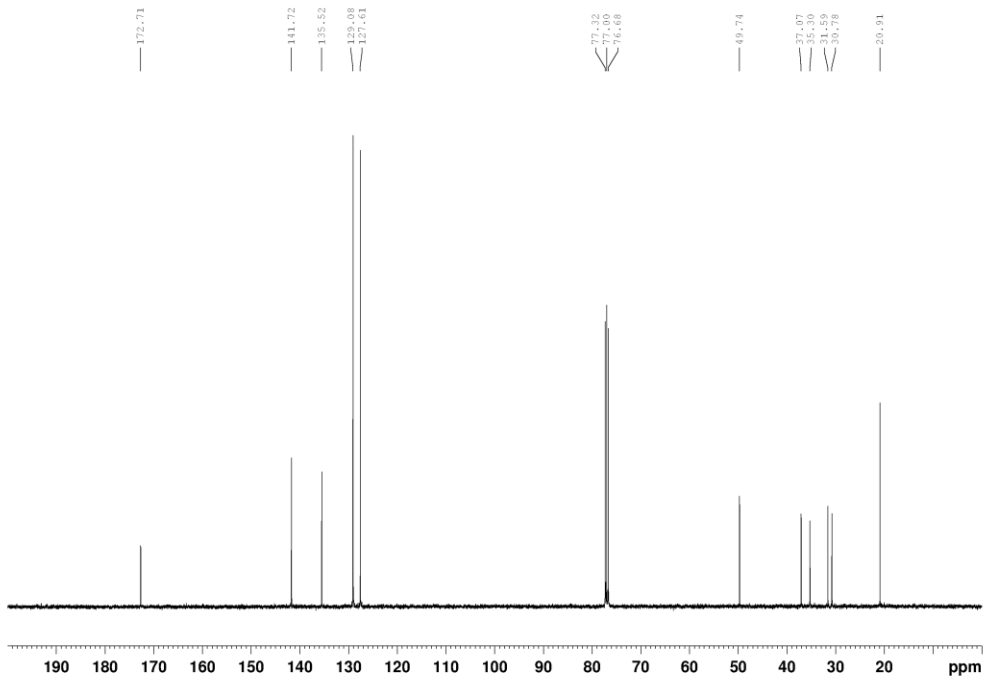
7.138
7.118
7.077
7.057
3.905
3.886
3.866
2.905
2.902
2.900
2.371
2.352
2.332
2.281
2.255
2.234
2.217
0.000
O
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.07
4.03
1.00
3.06
3.03
2.05
6.10
2.09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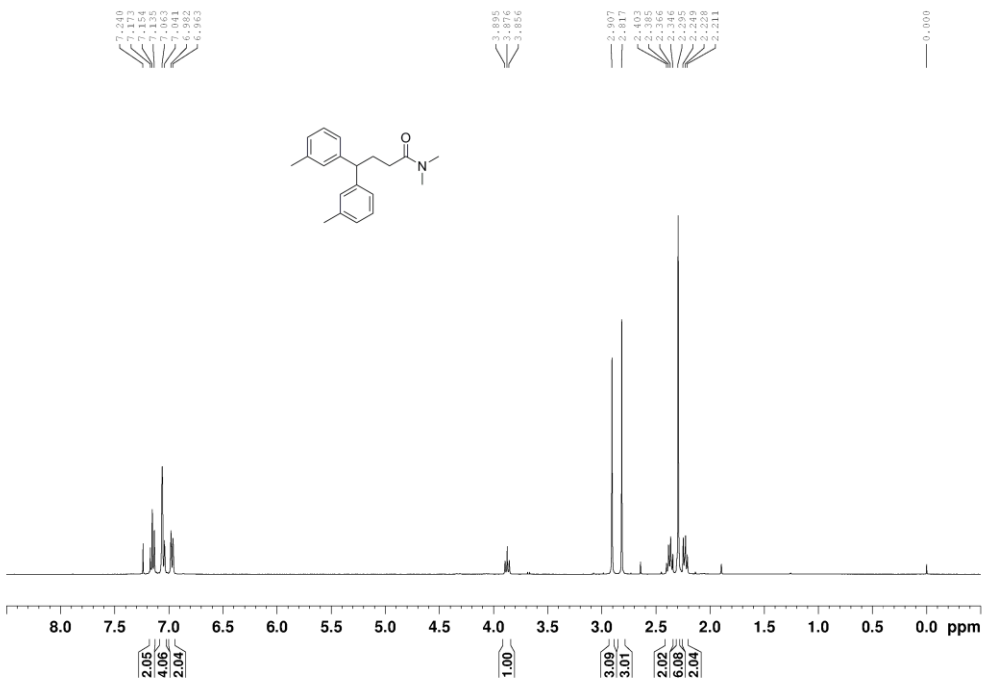
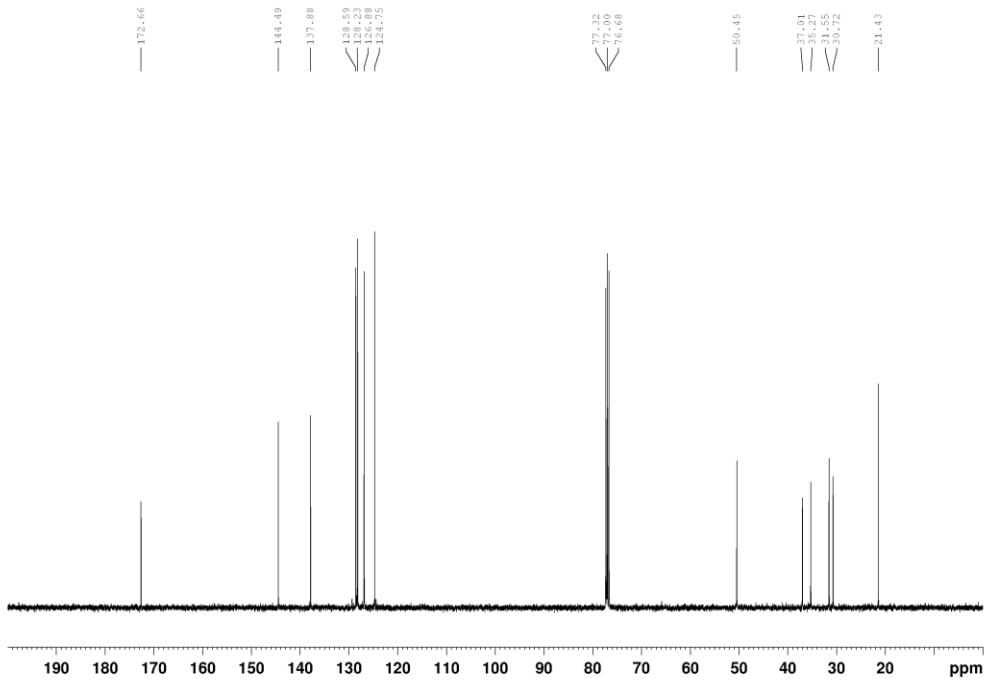
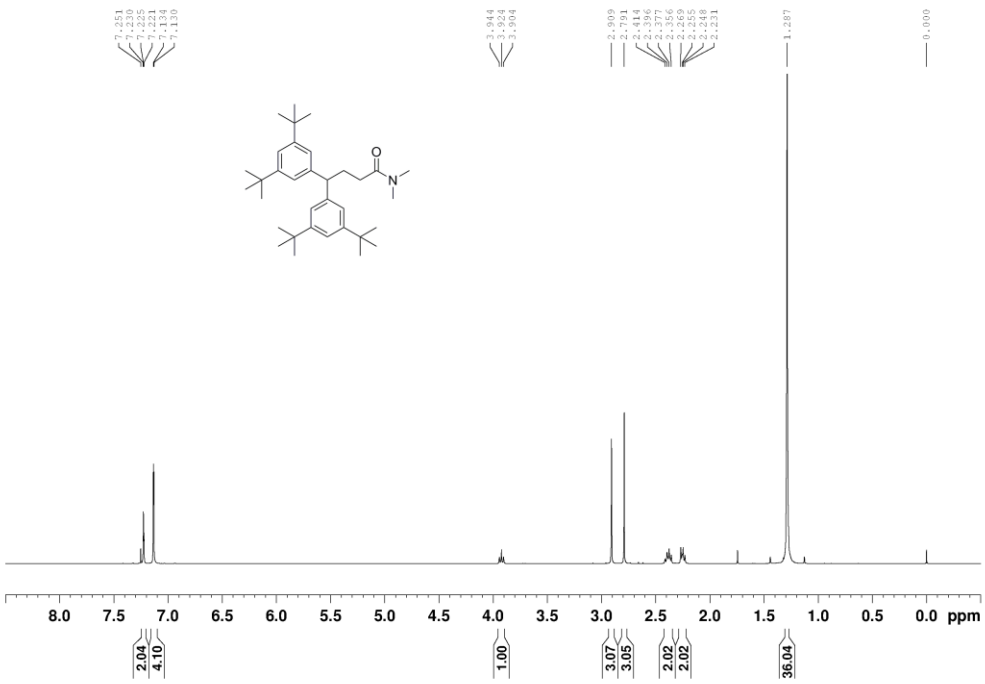
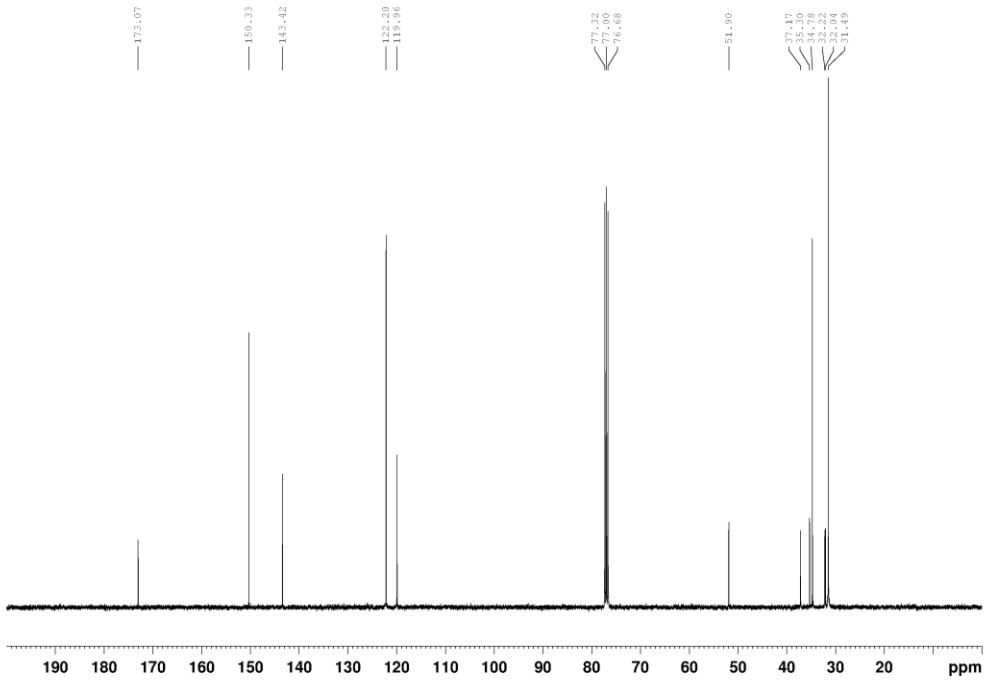
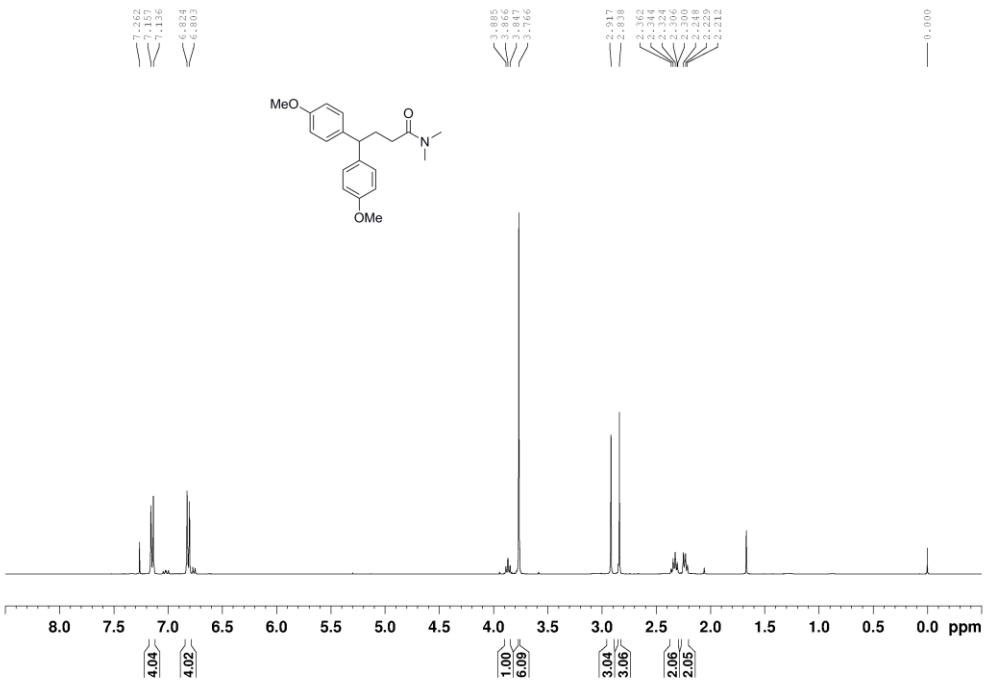
141.72
135.52
129.08
127.61
77.32
77.00
76.68
49.74
37.07
35.30
31.59
30.78
20.91
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

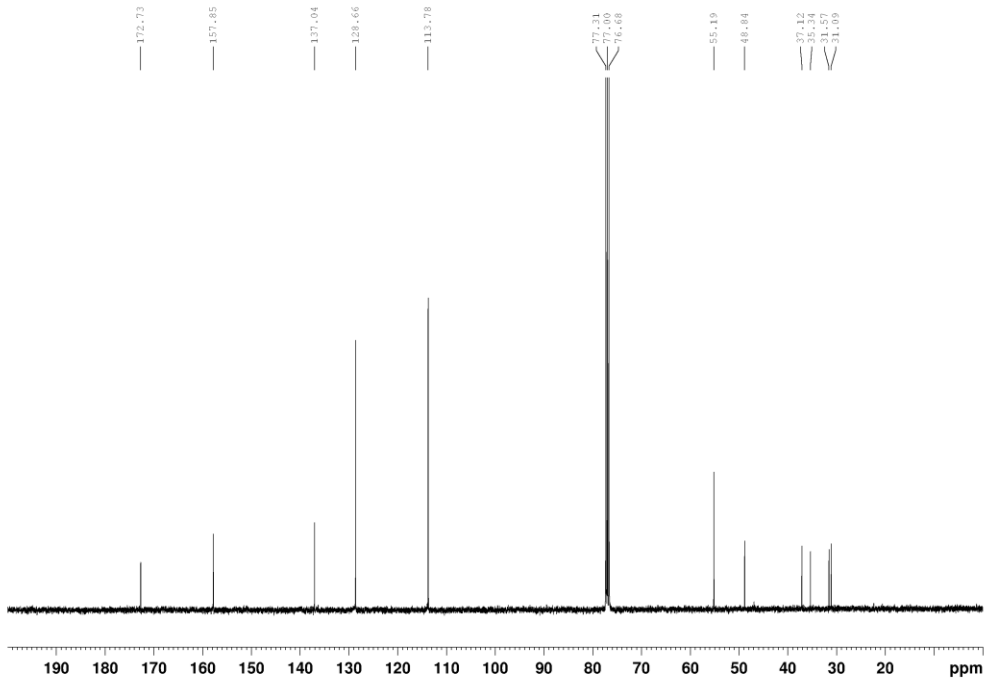

7.240
7.173
7.154
7.135
7.063
7.041
6.982
6.963
3.895
3.876
3.856
2.907
2.817
2.403
2.385
2.366
2.346
2.295
2.248
2.228
2.211
0.000
O
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05
4.06
2.04
1.00
3.09
3.01
2.02
6.08
2.04

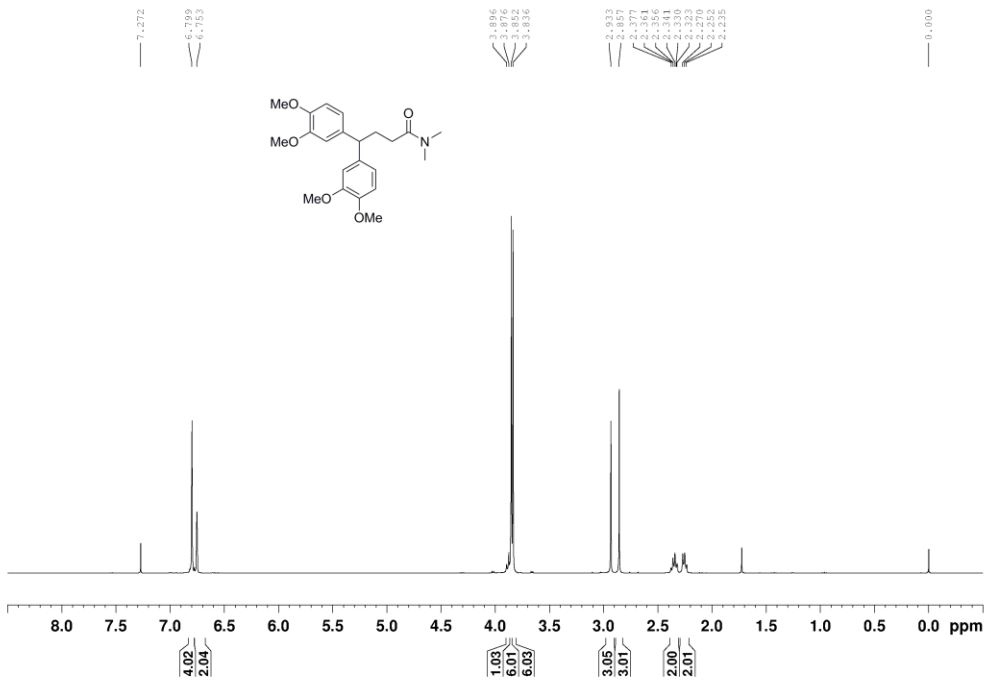

172.66
144.49
137.88
128.59
128.23
126.88
124.75
77.32
77.00
76.68
50.45
37.01
35.27
31.55
30.72
21.43
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

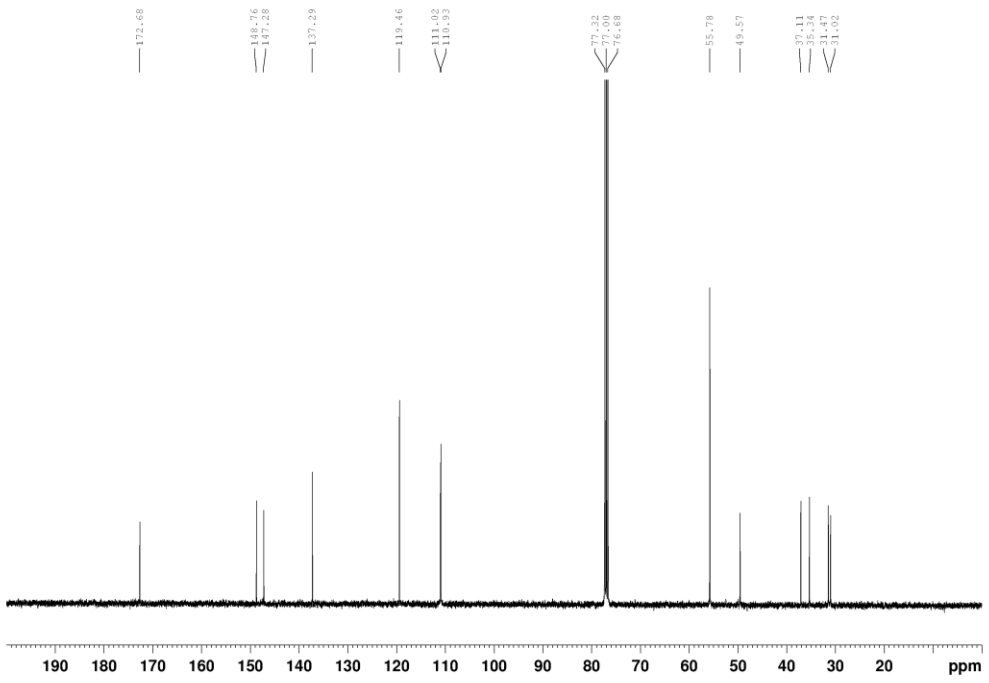

7.251
7.230
7.225
7.221
7.134
7.130
3.944
3.924
3.904
2.909
2.791
2.414
2.396
2.377
2.356
2.269
2.255
2.248
2.231
1.287
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.04
4.10
1.00
3.07
3.05
2.02
2.02
36.04


173.07
150.33
143.42
122.20
119.96
77.32
77.00
76.68
51.90
37.17
35.30
34.78
32.22
32.04
31.49
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.462
7.157
7.136
6.824
6.803
3.885
3.866
3.847
3.766
2.917
2.838
2.362
2.344
2.324
2.306
2.300
2.248
2.229
2.212
0.000
MeO
O
N
OMe
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 ppm
4.04
4.02
1.00
6.09
3.04
3.06
2.06
2.05


172.73
157.85
137.04
128.66
113.78
77.31
77.00
76.68
55.19
48.84
37.12
35.34
31.57
31.09
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.272
6.799
6.753
3.896
3.876
3.852
3.836
2.933
2.857
2.377
2.361
2.356
2.341
2.330
2.323
2.270
2.252
2.235
0.000
MeO
MeO
MeO
OMe
O
N
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 ppm
4.02
2.04
1.03
6.01
6.03
3.05
3.01
2.00
2.01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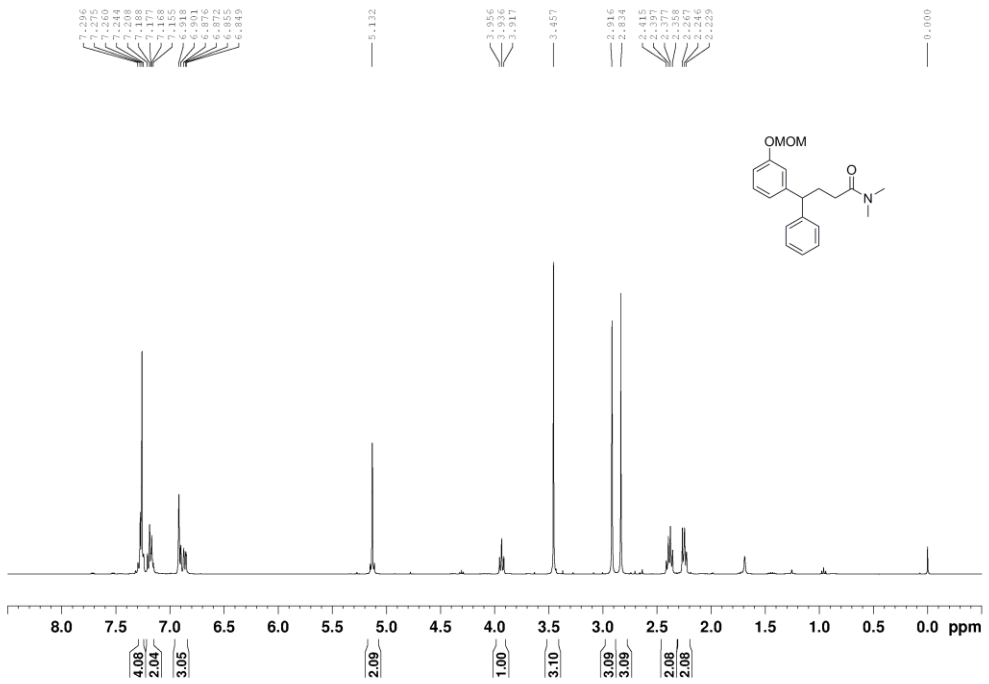
148.76
147.28
137.29
119.46
111.02
110.93
77.32
77.00
76.68
55.78
49.57
37.11
35.34
31.47
31.02
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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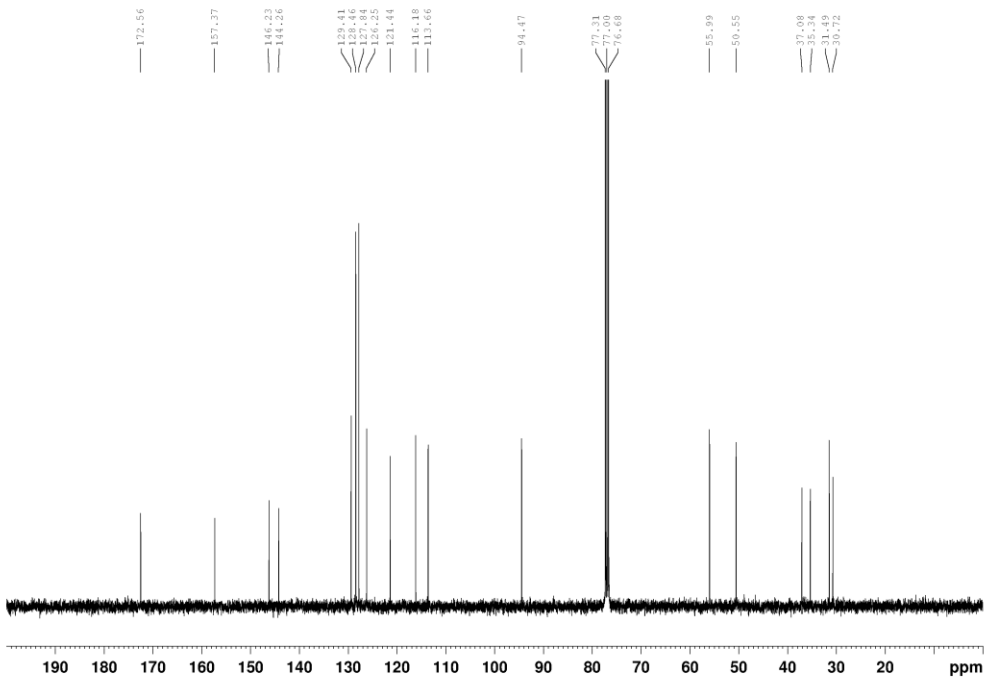
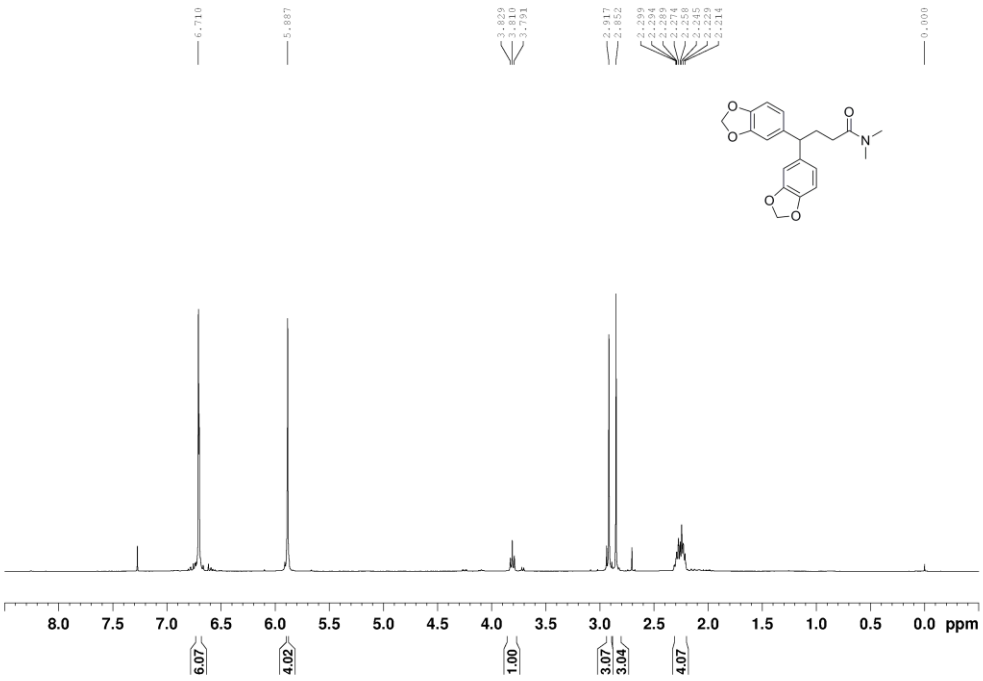
7.275
7.265
7.244
7.208
7.188
7.177
7.168
7.155
6.918
6.901
6.876
6.872
6.855
6.849
5.132
3.956
3.936
3.917
3.457
2.916
2.834
2.415
2.397
2.377
2.358
2.267
2.246
2.229
0.000
OMOM
O
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.06
2.04
3.05
2.09
1.00
3.10
3.09
3.09
2.08
2.08


172.56
157.37
146.23
144.26
129.41
128.46
127.84
126.25
121.44
116.18
113.66
94.47
77.31
77.00
76.68
55.99
50.55
37.08
35.34
31.49
30.72
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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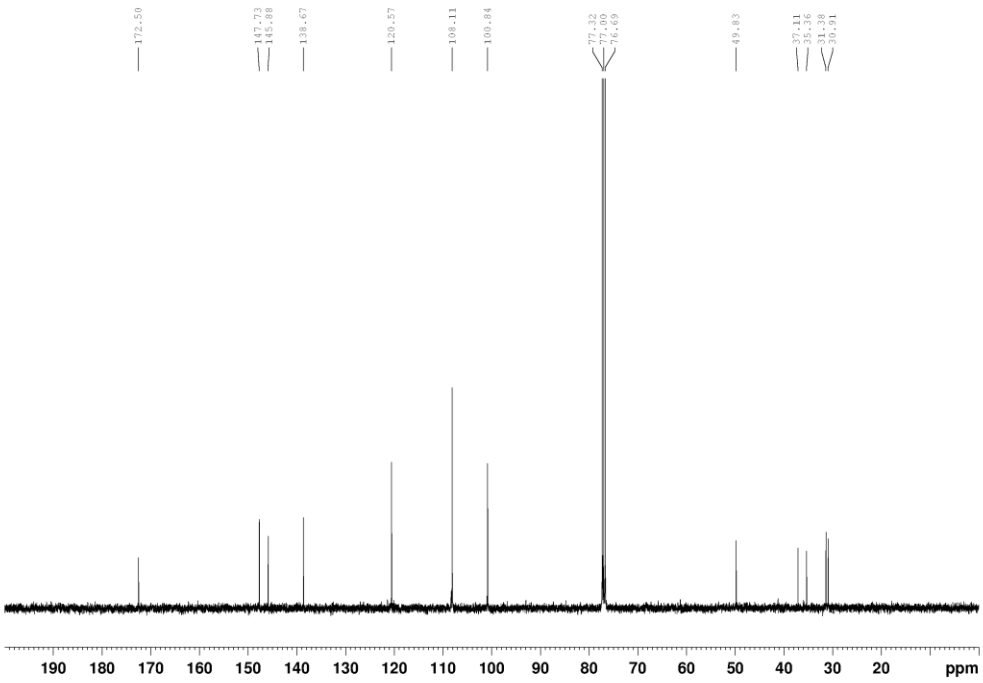
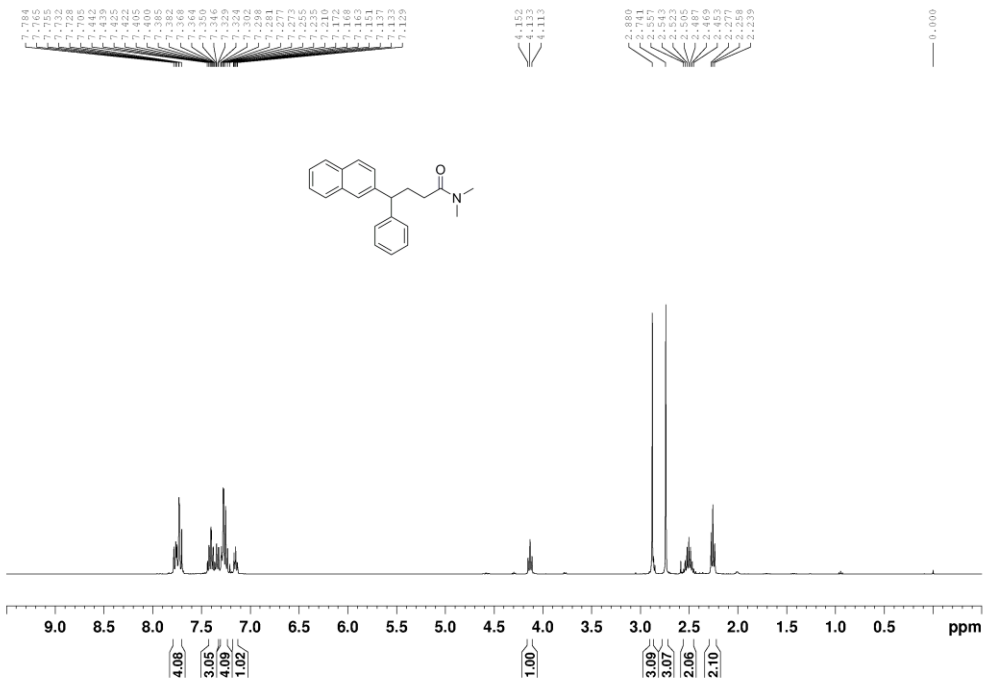
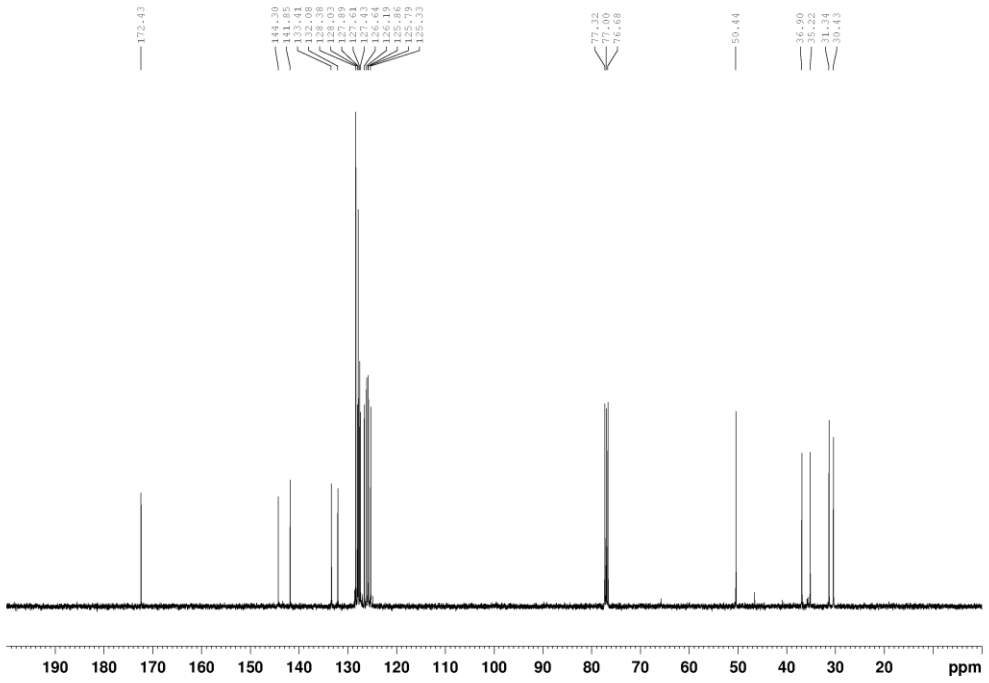
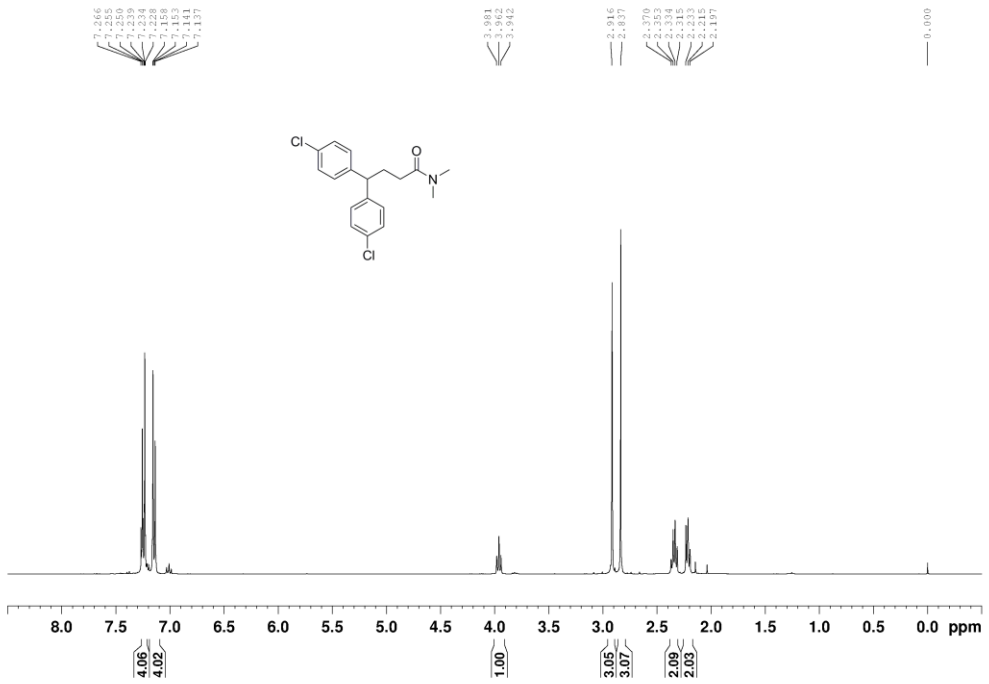
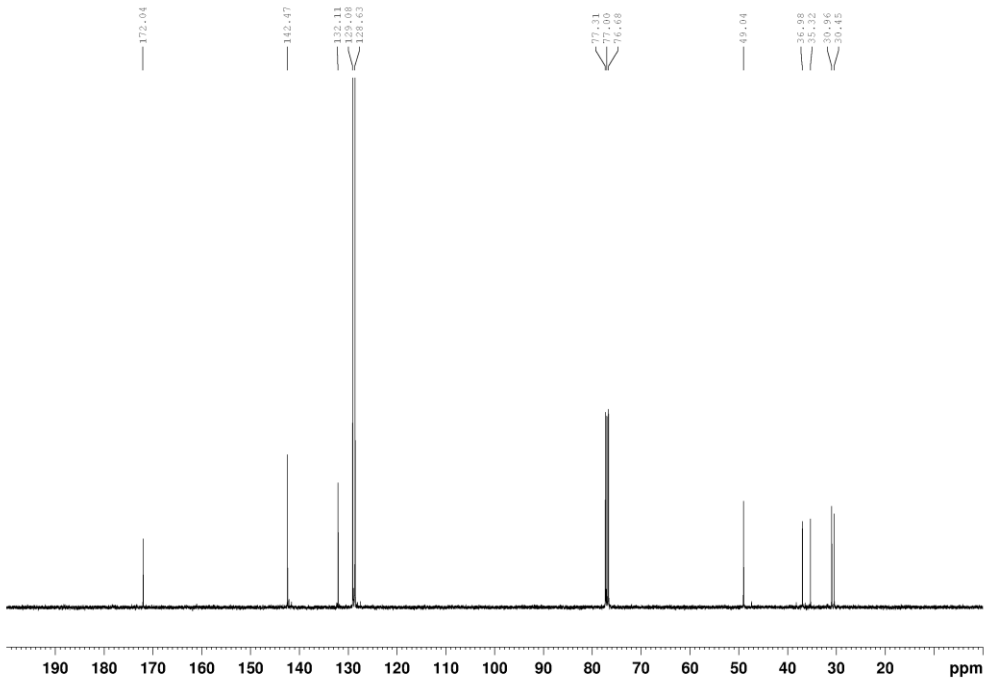
5.887
3.829
3.810
3.791
2.917
2.852
2.299
2.294
2.289
2.274
2.258
2.245
2.229
2.214
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.07
4.02
1.00
3.07
3.04
4.07

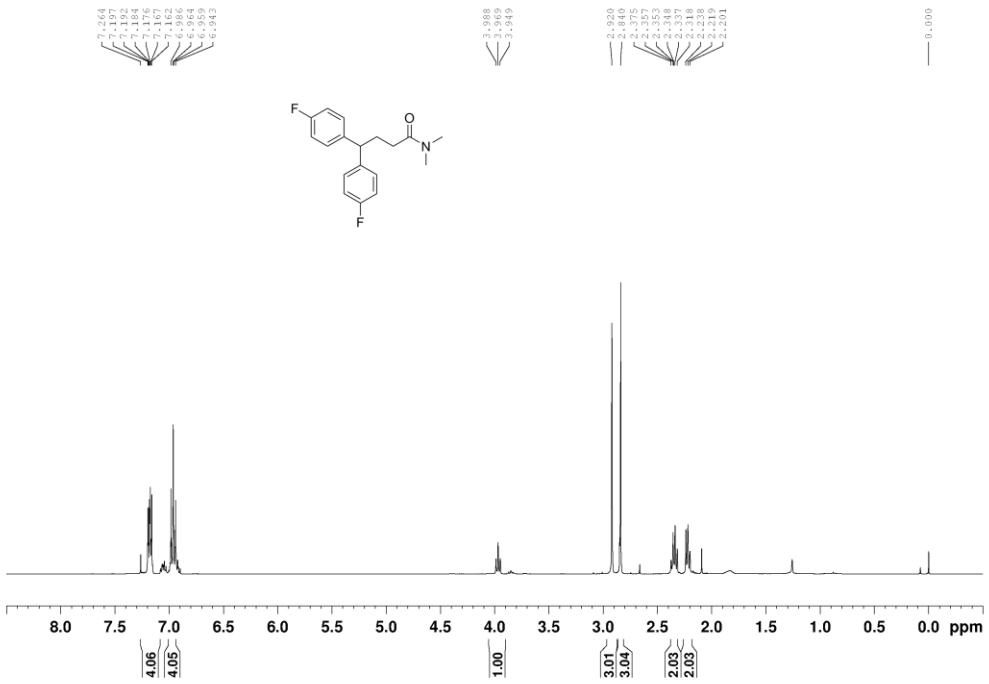

172.50
147.73
145.88
138.67
120.57
108.11
100.84
77.32
77.06
76.69
49.83
37.11
35.36
31.38
30.91
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm






7.266
7.255
7.250
7.239
7.234
7.228
7.158
7.153
7.141
7.137
3.981
3.962
3.942
2.916
2.897
2.370
2.353
2.334
2.315
2.233
2.215
2.197
0.000
Cl
O
N
Cl
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 ppm
4.06
4.02
1.00
3.05
3.07
2.09
2.03


172.04
142.47
132.11
129.08
128.63
77.31
77.00
76.68
49.04
36.98
35.32
30.96
30.45
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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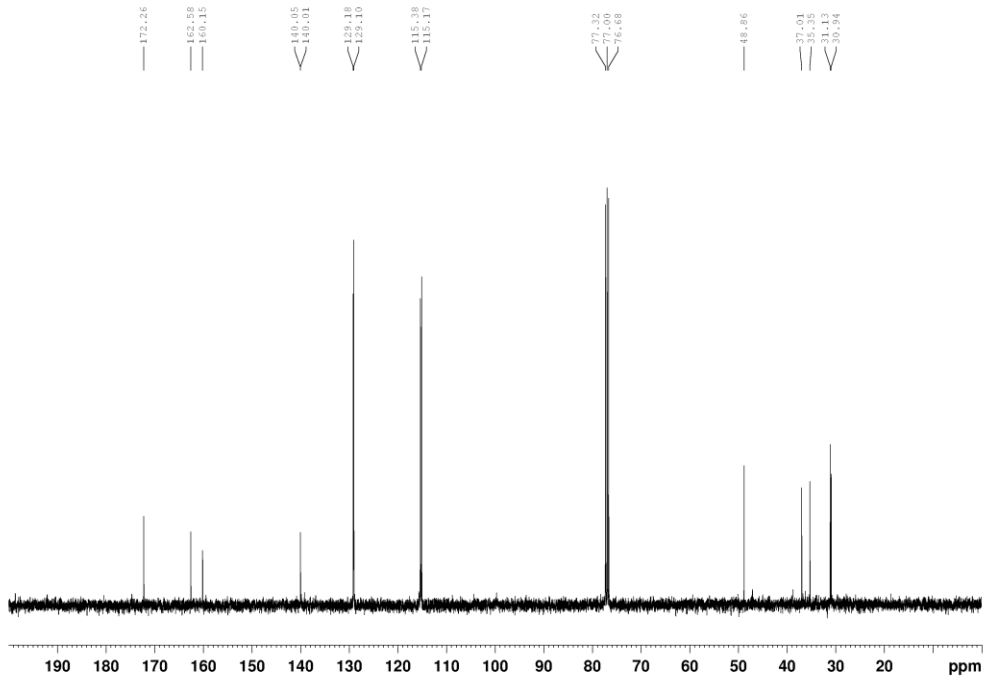
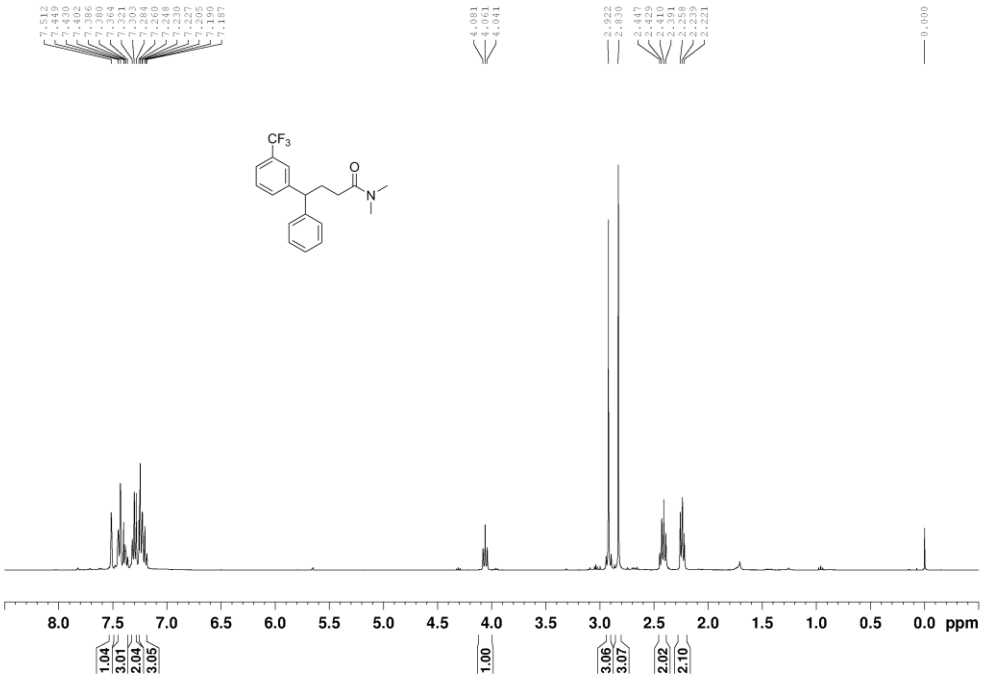
7.197
7.192
7.184
7.176
7.167
7.162
6.986
6.964
6.959
6.943
3.988
3.969
3.949
2.920
2.840
2.375
2.357
2.353
2.348
2.337
2.318
2.238
2.219
2.201
0.000
F
O
N
F
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.06
4.05
1.00
3.01
3.04
2.03
2.03


172.26
162.58
160.15
140.05
140.01
129.18
129.10
115.38
115.17
77.32
77.00
76.68
48.86
37.01
35.35
31.13
30.94
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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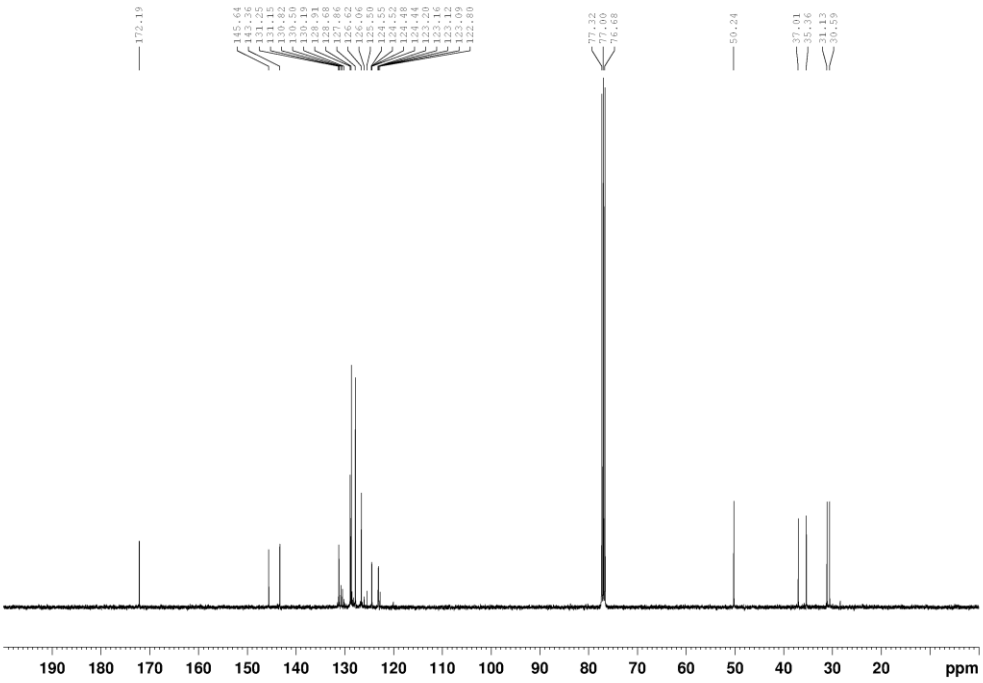
7.430
7.402
7.386
7.380
7.364
7.321
7.303
7.284
7.260
7.248
7.230
7.227
7.205
7.190
7.187
4.081
4.061
4.041
2.922
2.830
2.447
2.428
2.410
2.391
2.258
2.239
2.221
0.000
CF3
O
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.04
3.01
2.04
3.05
1.00
3.06
3.07
2.02
2.10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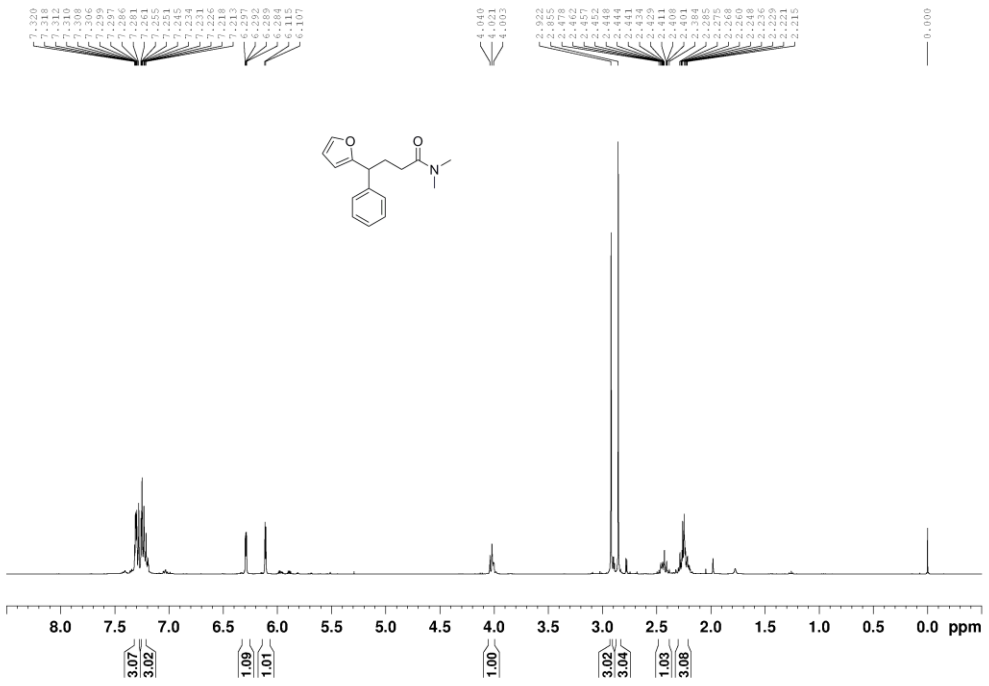
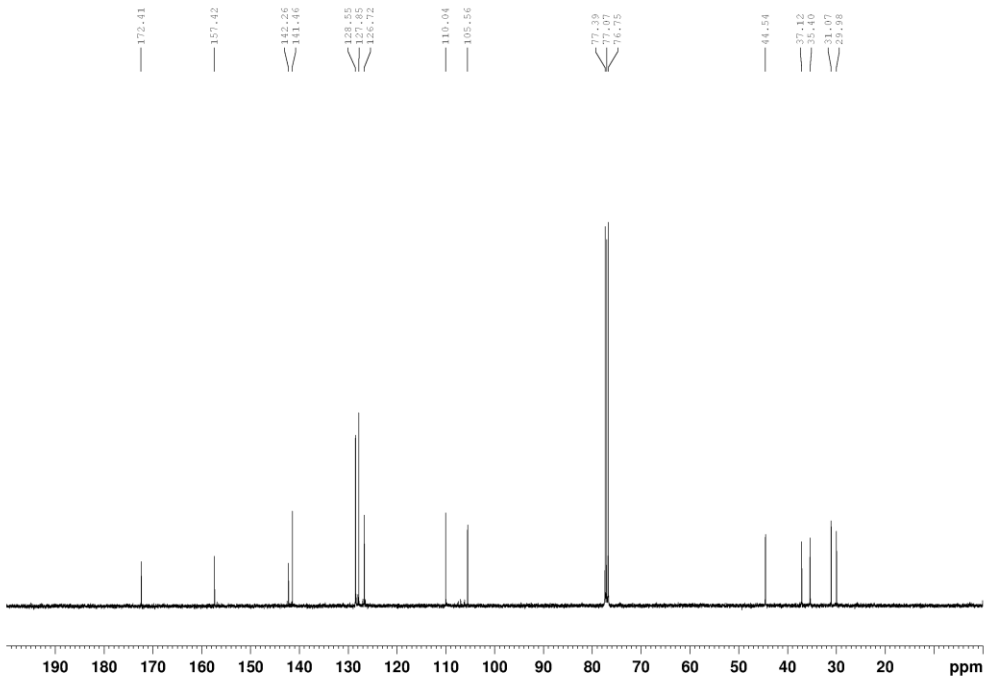
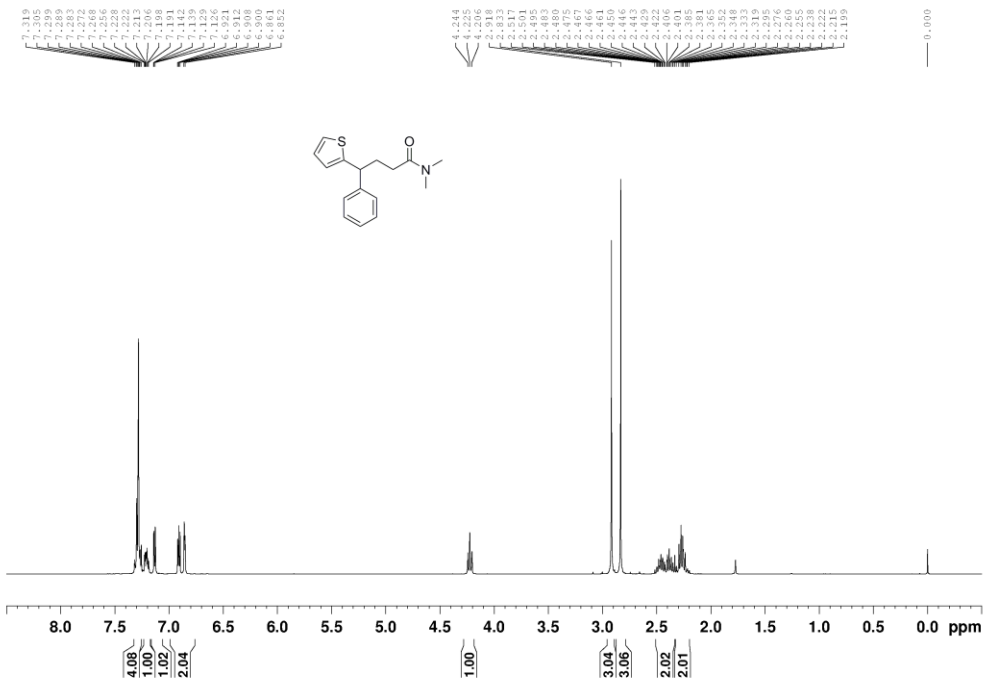
145.64
143.36
131.25
131.15
130.82
130.59
130.19
128.91
128.88
127.86
126.62
126.06
125.59
124.55
124.52
124.48
124.44
123.38
123.16
123.12
123.09
122.80
77.32
77.00
76.68
50.24
37.01
35.36
31.13
30.59
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



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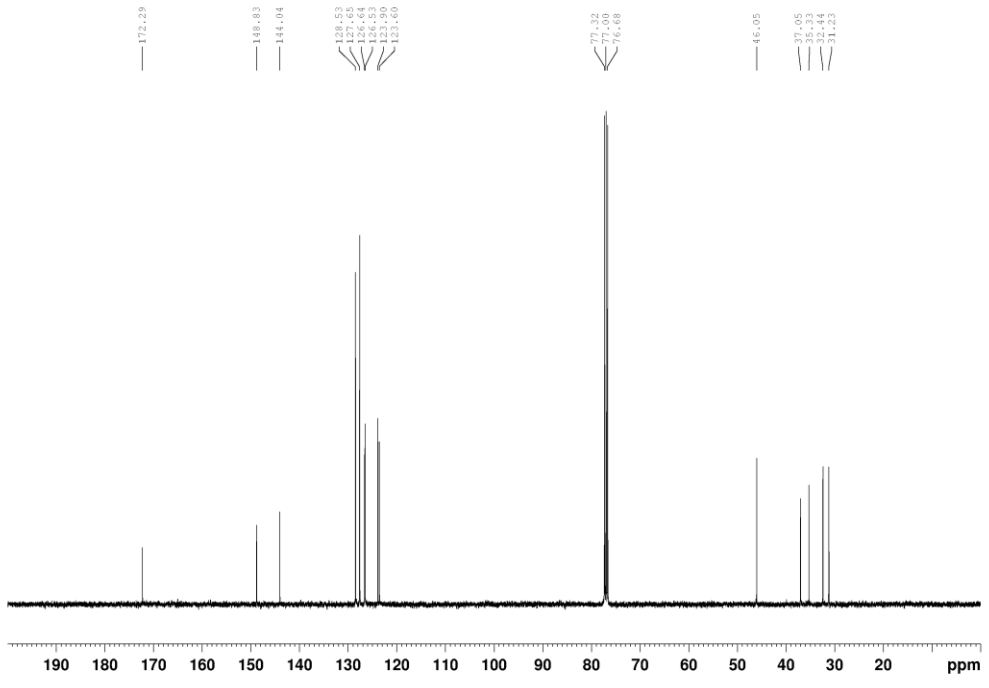
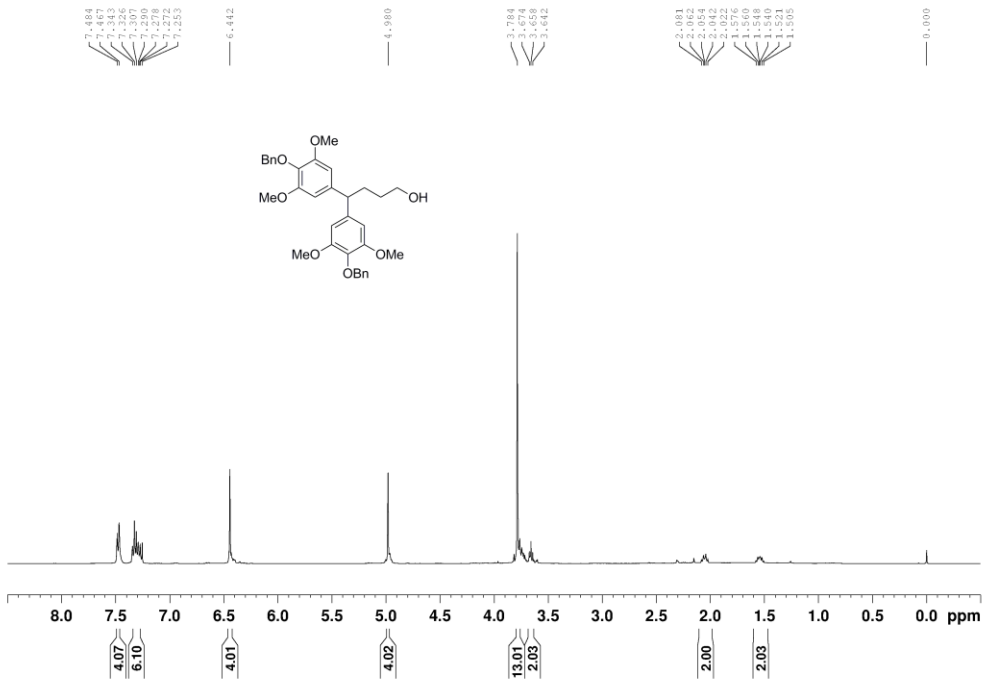
7.305
7.289
7.283
7.272
7.268
7.250
7.228
7.222
7.213
7.206
7.198
7.191
7.142
7.139
7.128
7.126
6.921
6.908
6.900
6.861
6.852
4.244
4.225
4.206
2.918
2.893
2.517
2.501
2.495
2.483
2.480
2.475
2.467
2.466
2.461
2.450
2.446
2.443
2.429
2.422
2.406
2.401
2.385
2.381
2.365
2.352
2.348
2.333
2.319
2.295
2.276
2.260
2.255
2.238
2.222
2.215
2.199
0.000
S
O
N
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 ppm
4.08
1.00
1.02
2.04
1.00
3.04
3.06
2.02
2.01


172.29
148.83
144.04
128.53
127.65
126.64
126.33
125.90
123.60
77.32
77.00
76.68
46.05
37.05
35.33
32.44
31.23
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.467
7.343
7.326
7.300
7.290
7.278
7.272
7.253
6.442
4.980
3.784
3.674
3.658
3.642
2.081
2.062
2.054
2.042
2.022
1.576
1.560
1.548
1.540
1.521
1.505
0.000
OMe
BnO
MeO
OH
MeO
OMe
OBn
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 ppm
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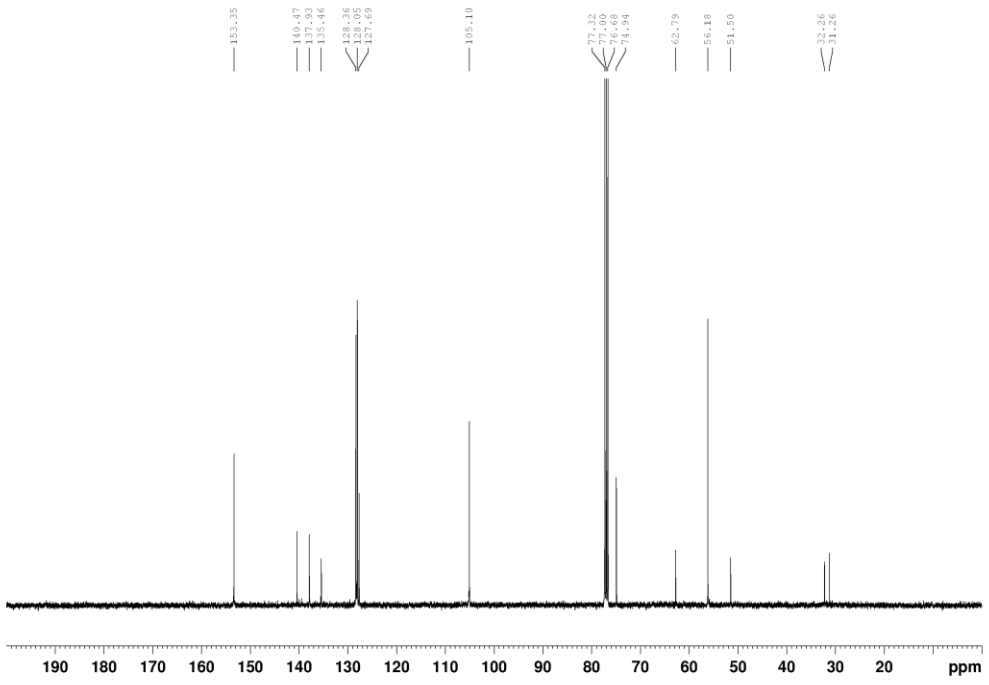
6.10
4.01
4.02
13.01
2.03
2.00
2.03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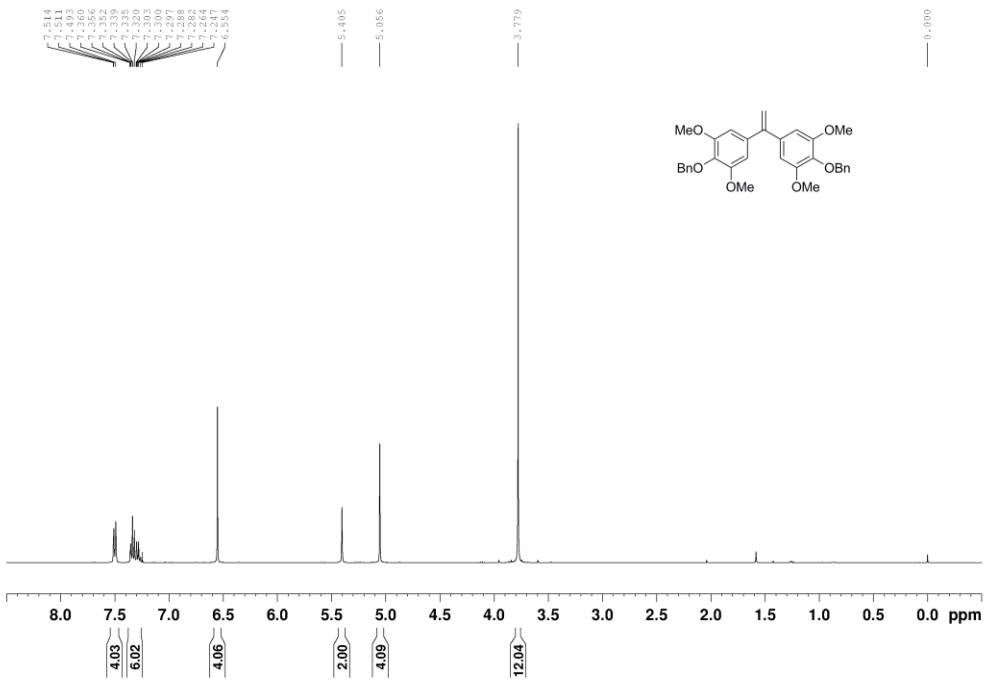
140.47
137.93
135.46
128.56
128.05
127.69
105.10
77.32
77.00
76.68
74.94
62.79
56.18
51.50
32.26
31.26
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.493
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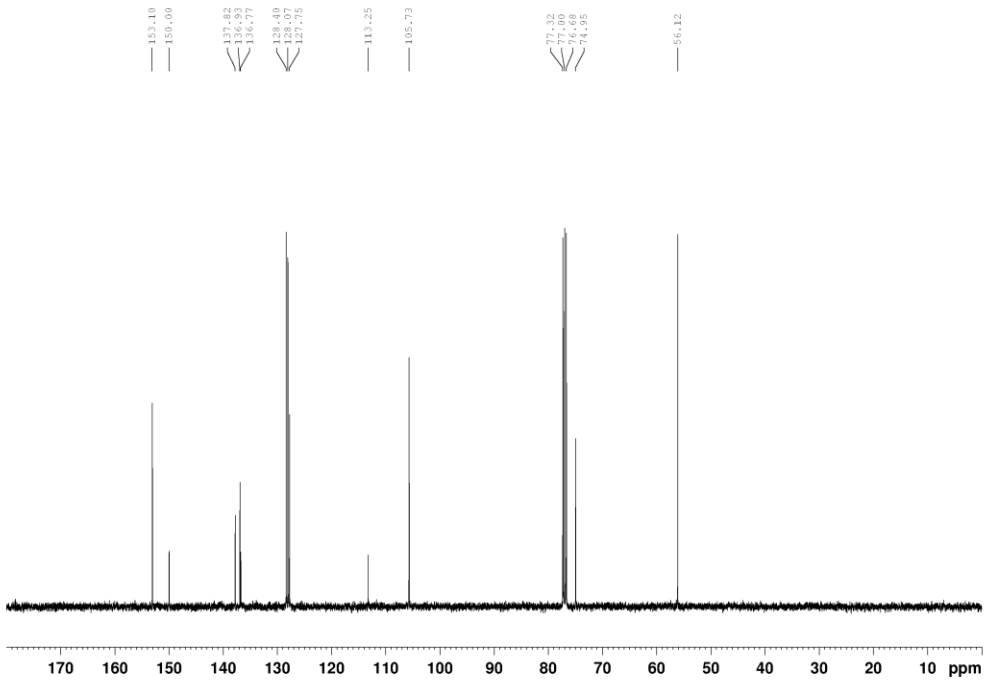
7.352
7.339
7.335
7.320
7.303
7.300
7.297
7.288
7.282
7.264
7.247
6.554
5.405
5.056
3.779
0.000
MeO
OMe
BnO
OBn
OMe
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.03
6.02
4.06
2.00
4.09
12.04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150.00
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136.77
128.49
128.07
127.75
113.25
105.73
77.32
77.00
76.68
74.95
56.12
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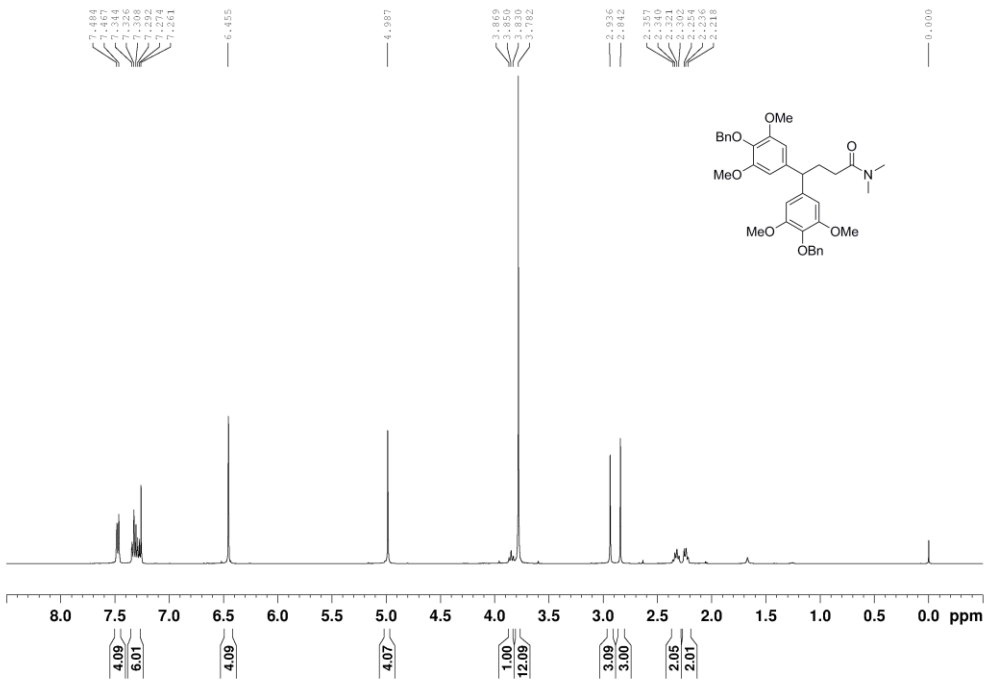
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7.344
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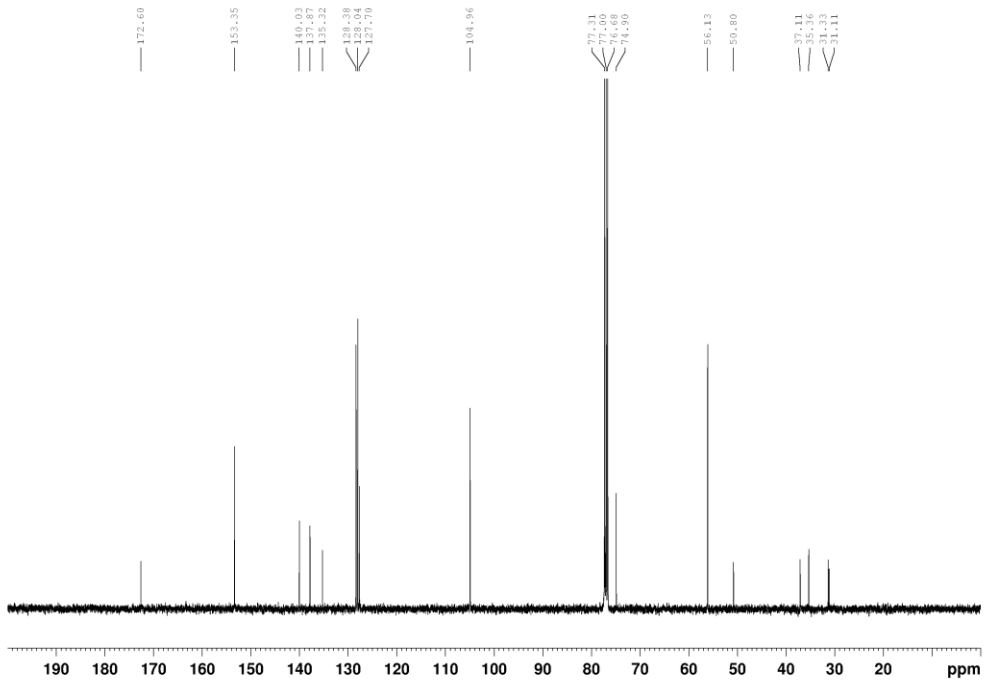
7.308
7.292
7.274
7.261
6.455
4.987
3.869
3.850
3.830
3.782
2.936
2.842
2.357
2.340
2.321
2.302
2.294
2.236
2.218
0.000
OMe
BnO
MeO
O
N
MeO
OMe
OBn
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.09
6.01
4.09
4.07
1.00
12.09
3.09
3.00
2.05
2.01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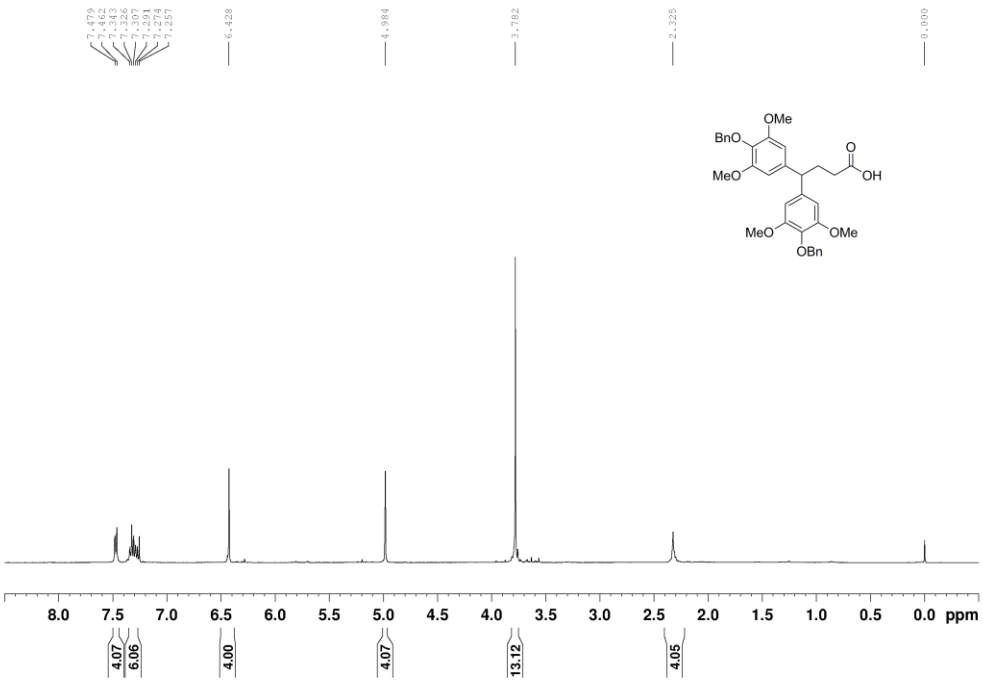
153.35
140.03
137.87
135.32
128.38
128.04
127.70
104.96
77.31
77.00
76.68
74.90
56.13
50.80
37.11
35.36
31.33
31.11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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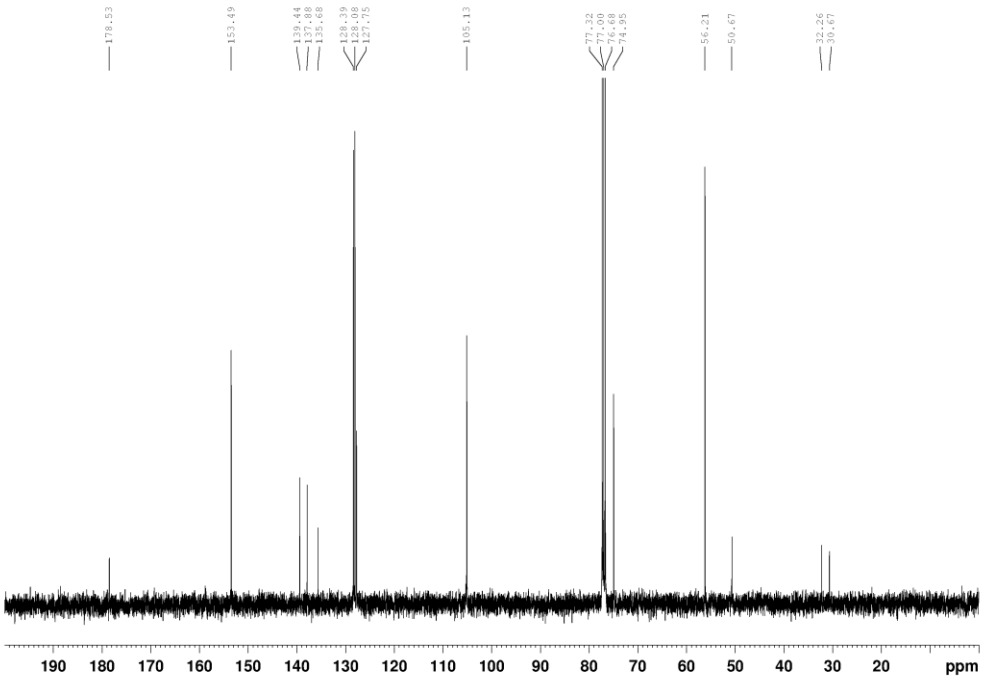
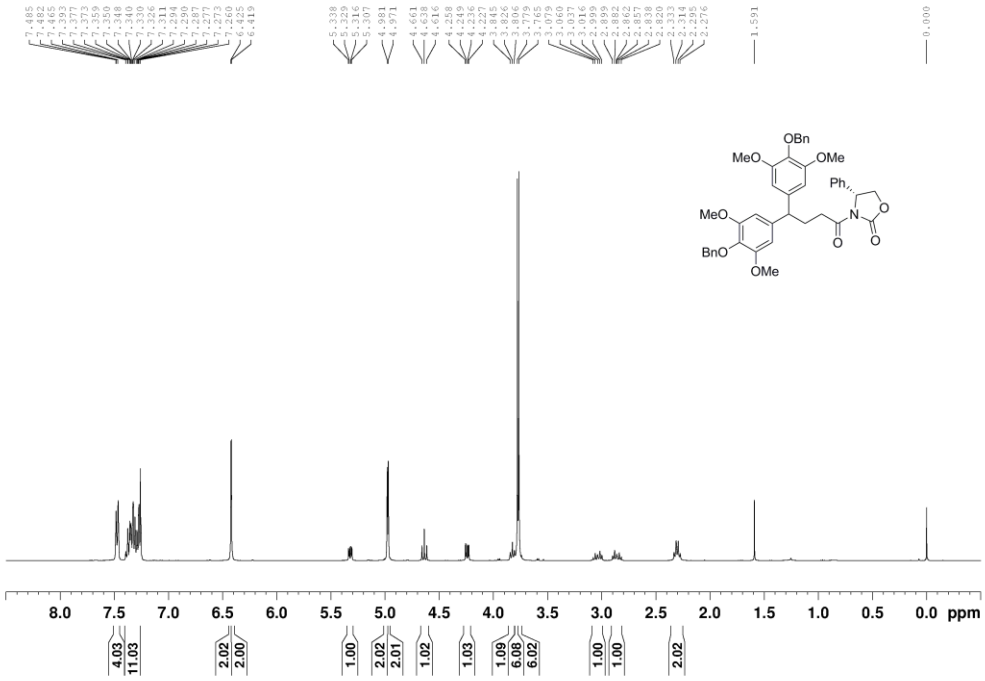
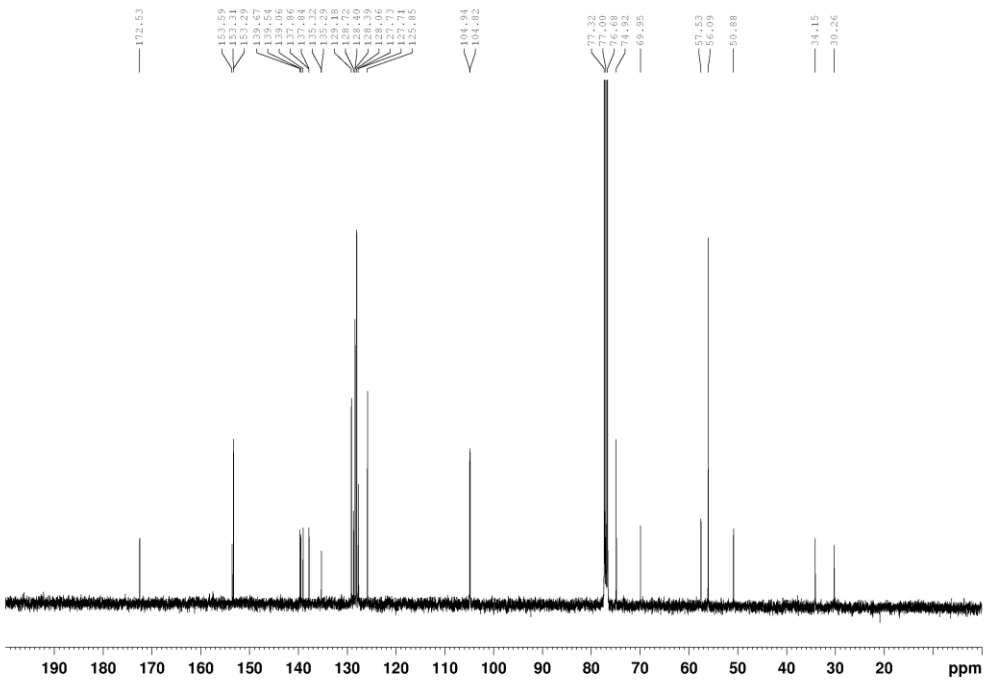
7.462
7.343
7.326
7.307
7.294
7.274
7.257
6.428
4.984
3.782
2.325
0.000
OMe
BnO
MeO
O
OH
MeO
OMe
OBn
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.07
6.06
4.00
4.07
13.12
4.05


178.53
153.49
139.44
137.88
135.68
128.39
128.08
127.75
105.13
77.32
77.00
76.68
74.95
56.21
50.67
32.26
30.67
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


OBn
MeO
OMe
Ph
MeO
BnO
OMe
N
O
O
O
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 ppm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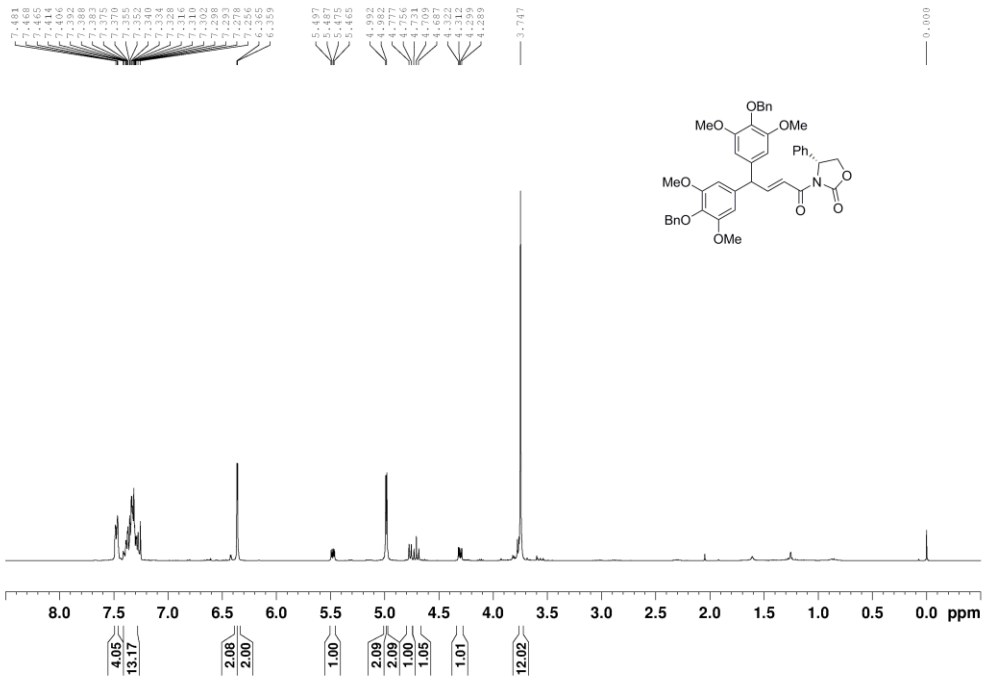
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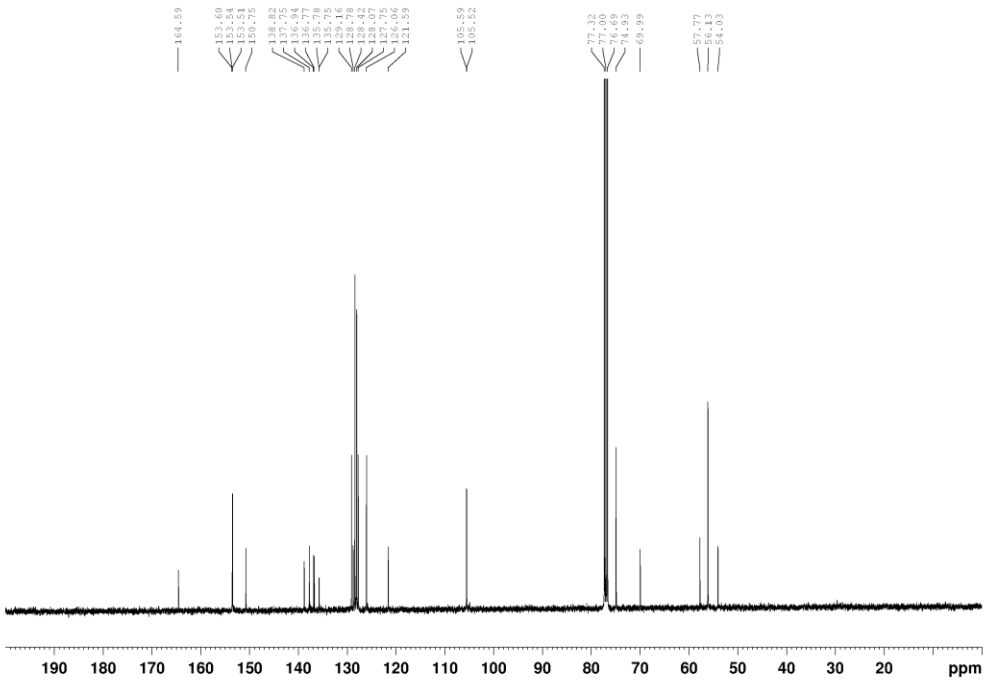
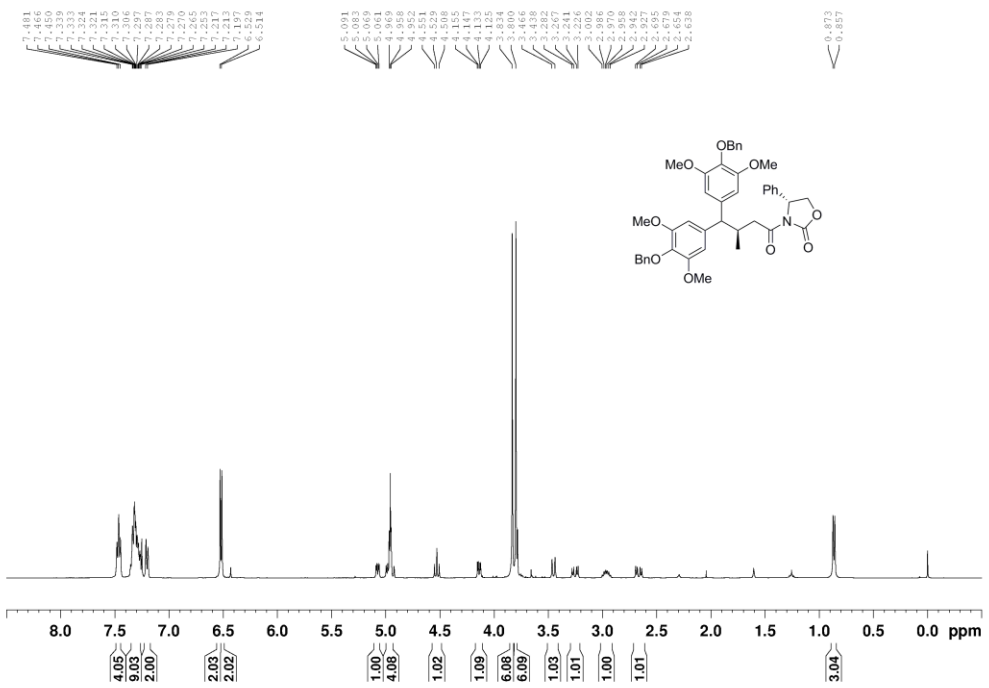
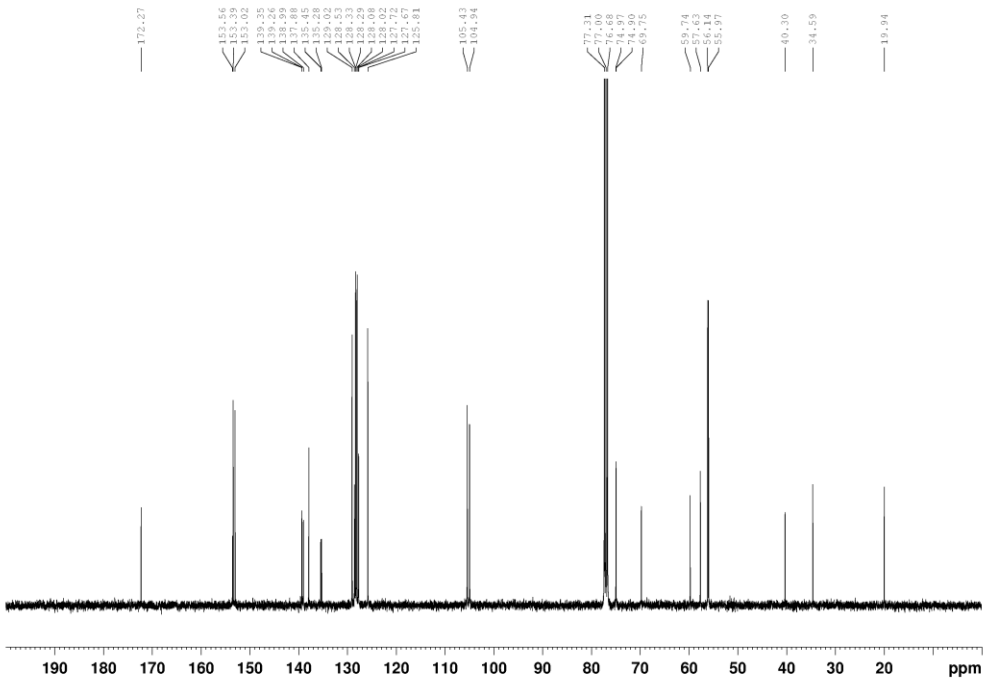
7.383
7.375
7.370
7.355
7.352
7.340
7.334
7.328
7.316
7.310
7.298
7.293
7.278
7.256
7.255
6.359
5.497
5.487
5.475
5.465
4.992
4.982
4.777
4.756
4.731
4.709
4.687
4.322
4.312
4.299
4.289
3.747
0.000
OBn
MeO
OMe
Ph
MeO
N
O
O
O
BnO
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.05
13.17
2.08
2.00
1.00
2.09
2.09
1.00
1.05
1.01
12.02


164.59
153.60
153.54
153.51
150.75
138.82
137.75
136.94
136.77
135.78
135.75
129.16
128.78
128.42
128.27
127.95
126.06
121.59
105.59
105.52
77.32
77.00
76.69
74.93
69.99
57.77
56.13
56.03
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


OBn
MeO
OMe
Ph
MeO
BnO
OMe
N
O
O
O
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 ppm
4.05 9.03 2.00 2.03 2.02 1.00 4.08 1.02 1.09 6.08 6.09 1.03 1.01 1.00 1.01 3.04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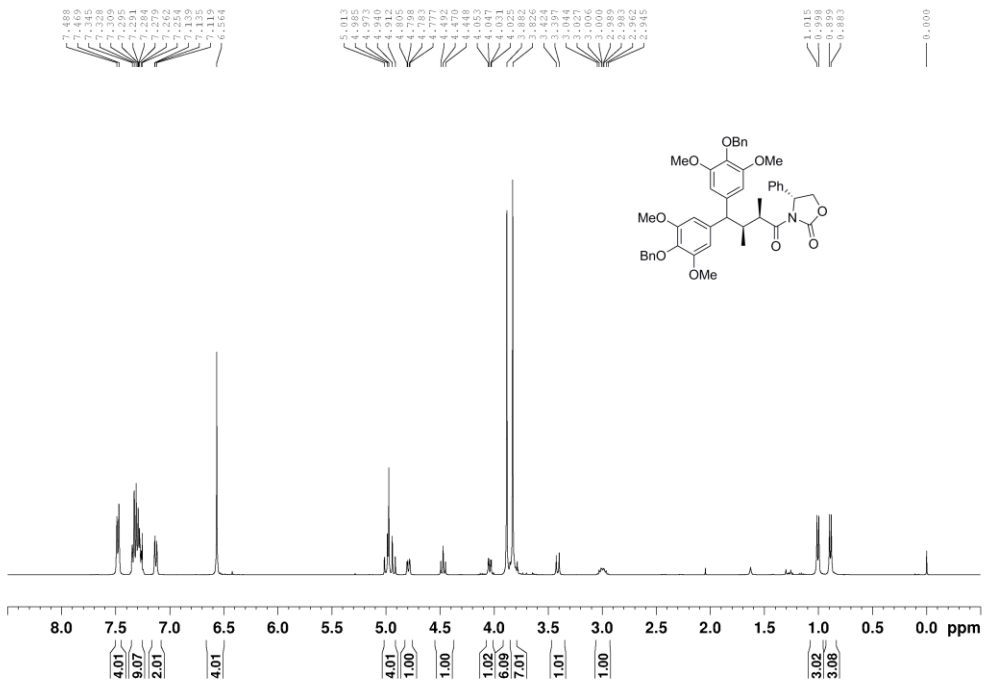
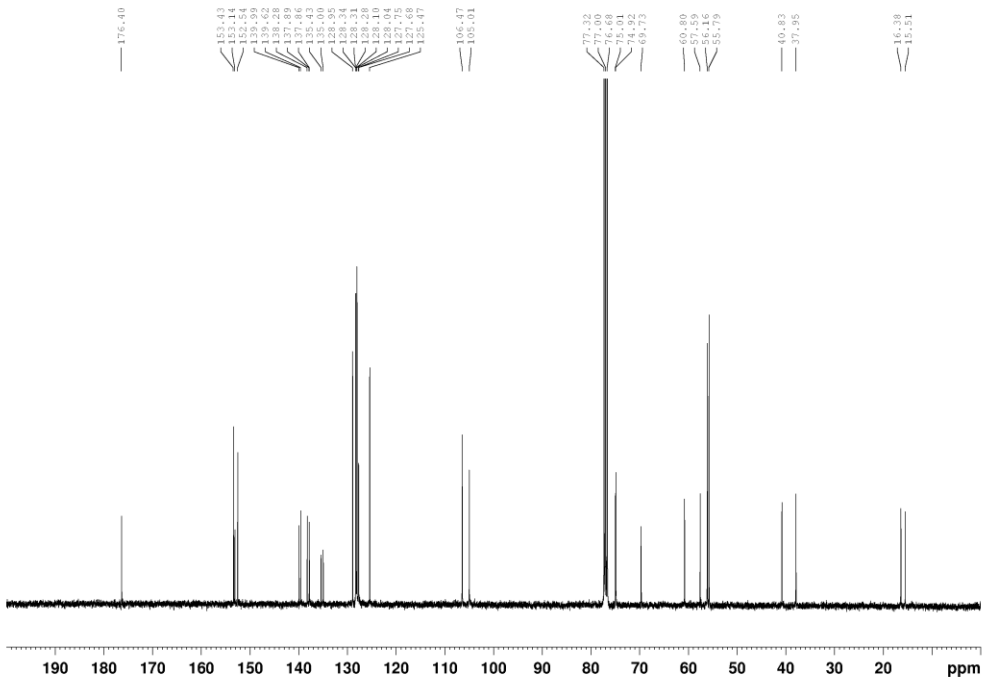

OBn
MeO
OMe
Ph
MeO
BnO
OMe
O
N
O
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.01 9.07 2.01 4.01 4.01 1.00 1.00 1.02 6.09 7.01 1.01 1.00 3.02 3.08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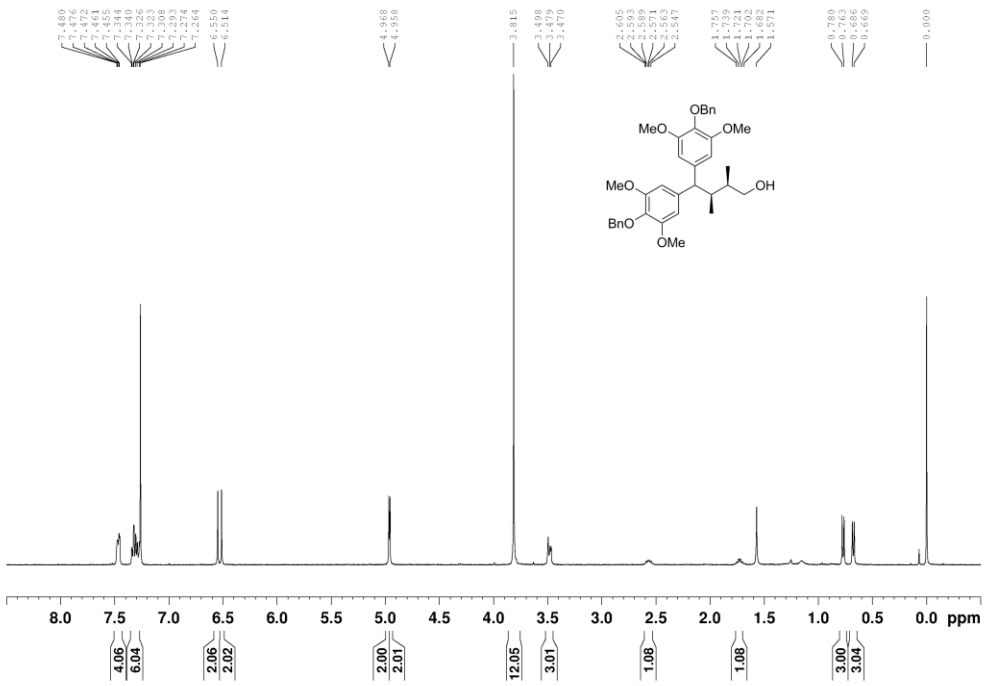
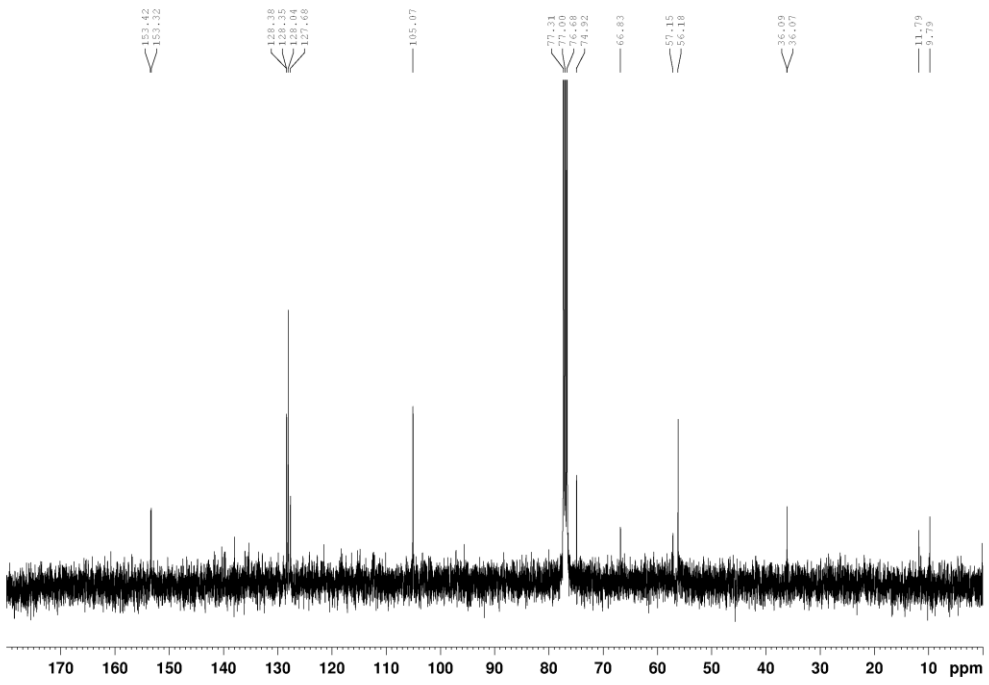

7.480
7.476
7.472
7.461
7.455
7.348
7.340
7.326
7.323
7.308
7.293
7.274
7.264
6.550
6.514
4.968
4.958
3.815
3.498
3.479
3.470
2.605
2.593
2.589
2.571
2.560
2.547
1.757
1.739
1.721
1.702
1.682
1.571
0.780
0.763
0.686
0.669
0.000
OBn
MeO
OMe
MeO
OH
BnO
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
4.06
6.04
2.06
2.02
2.00
2.01
12.05
3.01
1.08
1.08
3.00
3.04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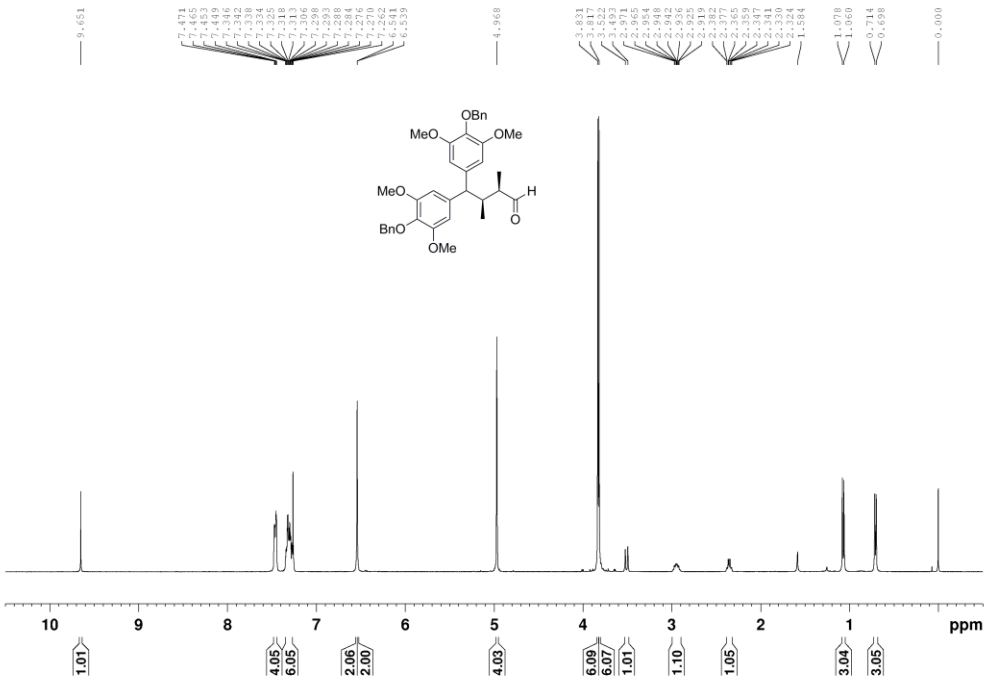
153.32
128.38
128.35
128.04
127.68
105.07
77.31
77.00
76.68
74.92
66.83
57.15
56.10
36.09
36.07
11.79
9.79
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.453
7.449
7.346
7.342
7.338
7.334
7.325
7.320
7.318
7.313
7.206
7.200
7.198
7.293
7.288
7.284
7.276
7.270
7.262
6.541
6.539
4.968
3.831
3.817
3.522
3.493
3.471
2.961
2.954
2.948
2.942
2.936
2.925
2.919
2.382
2.377
2.365
2.359
2.347
2.341
2.330
2.324
1.584
1.078
1.060
0.714
0.698
0.000
OBn
MeO
OMe
MeO
H
O
BnO
OMe
10
9
8
7
6
5
4
3
2
1
ppm
1.01
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2.00
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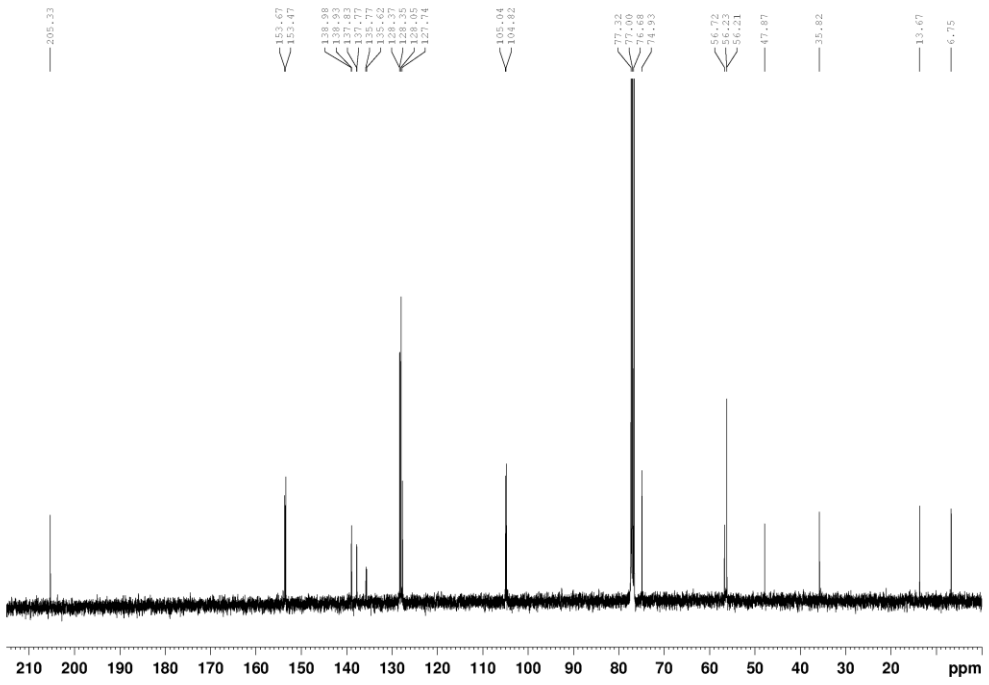
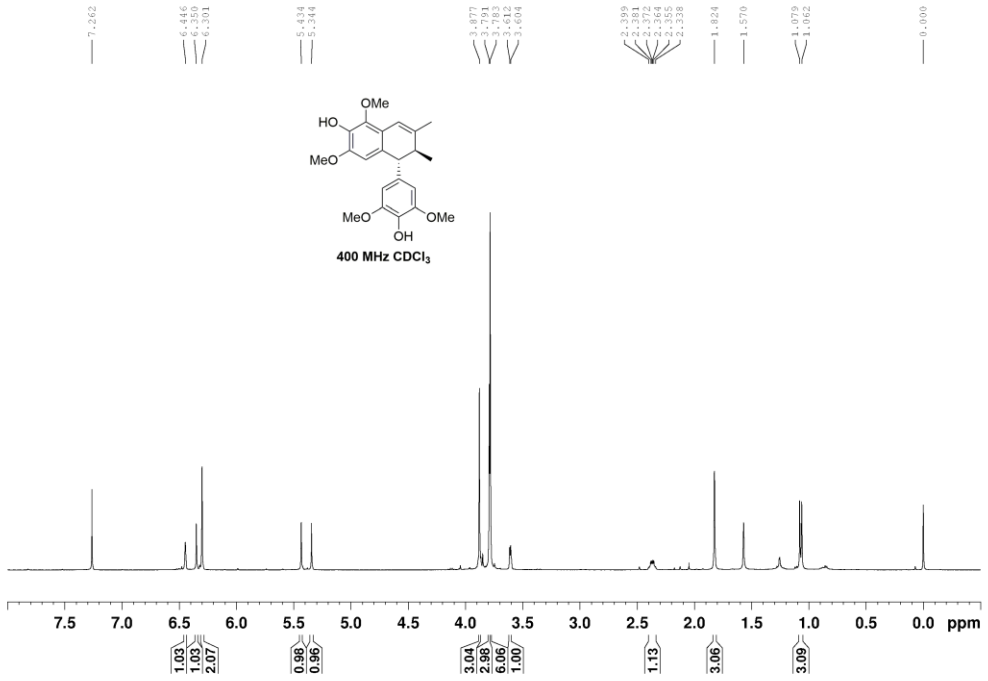
6.07
1.01
1.10
1.05
3.04
3.05


205.33
153.67
153.47
138.98
138.93
137.83
137.77
135.62
128.37
128.35
128.15
127.74
105.04
104.82
77.32
77.00
76.68
74.93
56.72
56.23
56.21
47.87
35.82
13.67
6.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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5.344
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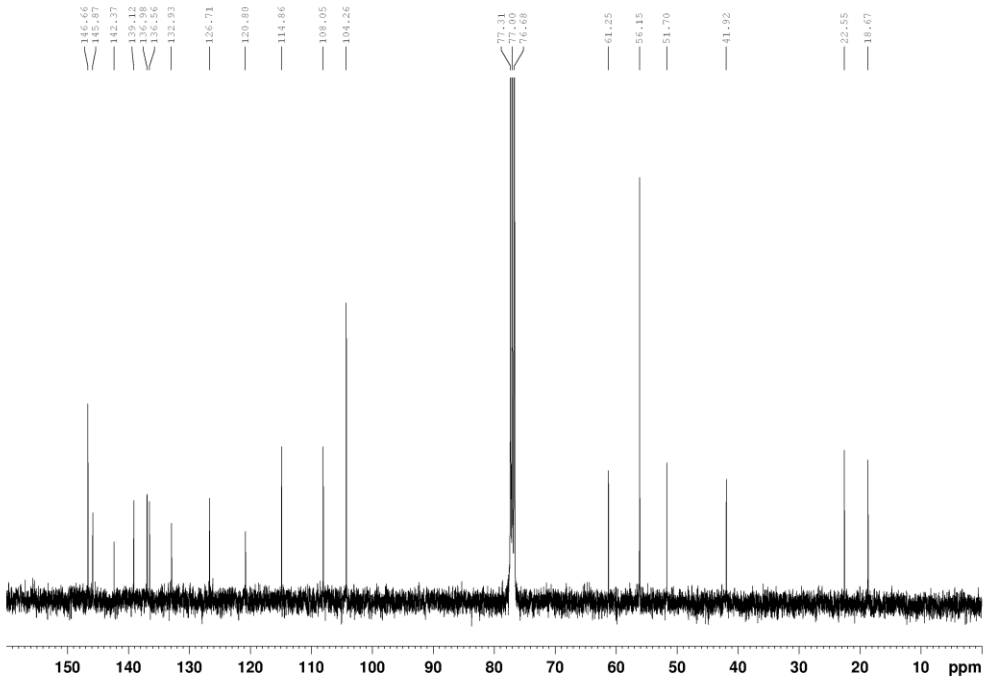
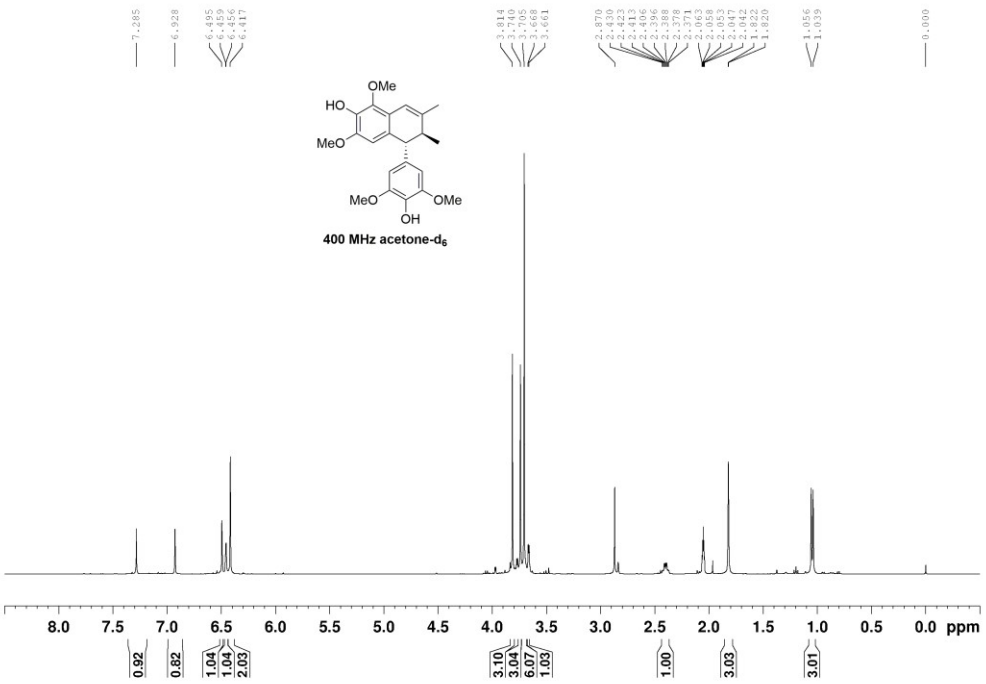
3.631
3.583
3.612
3.604
2.399
2.381
2.372
2.364
2.355
2.338
1.824
1.570
1.079
1.062
0.000
OMe
HO
MeO
MeO
OMe
OH
400 MHz CDCl3
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.03 1.03 2.07 0.98 0.96 3.04 2.98 6.06 1.00 1.13 3.06 3.09


146.66
145.87
142.37
139.12
136.98
136.56
132.93
126.71
120.80
114.86
108.05
104.26
77.31
77.06
76.68
61.25
56.15
51.70
41.92
22.55
18.67
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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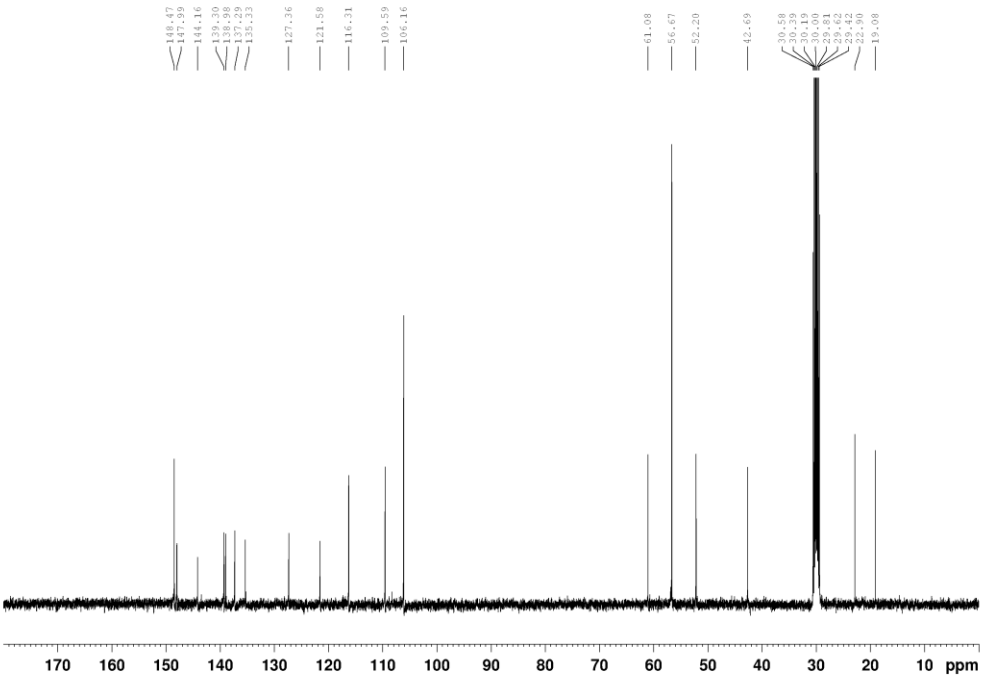
6.495
6.459
6.456
6.417
3.814
3.740
3.705
3.668
3.661
2.870
2.430
2.423
2.413
2.406
2.396
2.388
2.378
2.371
2.063
2.058
2.053
2.047
2.042
1.822
1.820
1.056
1.039
0.000
OMe
HO
MeO
MeO
OMe
OH
400 MHz acetone-d6
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.92
0.82
1.04
1.04
2.03
3.10
3.04
6.07
1.03
1.00
3.03
3.01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138.98
137.29
135.33
127.36
121.58
116.31
109.59
106.16
61.08
56.67
52.20
42.69
30.58
30.39
30.19
30.00
29.81
29.62
29.42
22.90
19.08
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

References

(1) (a) J. Tang, D. Hackenberger and L. J. Goossen, *Angew. Chem. Int. Ed.*, 2016, **55**, 11296; (b) A. Gonzalez-de-Castro and J. Xiao, *J. Am. Chem. Soc.* 2015, **137**, 8206; (c) C. Lei, Y. J. Yip, and J. S. Zhou, *J. Am. Chem. Soc.* 2017, **139**, 6086; (d) C. Wan, R. Song and J. Li, *Org. Lett.* 2019, **21**, 2800.

(2) S. Xu, Y. Gao, R. Chen, K. Wang, Y. Zhang and J. Wang, *Chem. Commun.,* 2016, **52**, 4478.

(3) (a) C. Chatalova-Sazepin, Q. Wang, G. M. Sammis and J. Zhu, *Angew. Chem. Int. Ed.*, 2015, **54**, 5443; (b) J. C. L. Walker and M. Oestreich, *Org. Lett.*, 2018, **20**, 6411.

(4) Y. Zou, L. Qin, X. Ren, Y. Lu, Y. Li and J. Zhou, *Chem. Eur. J.* 2013, **19**, 3504.