Supporting Information

Metal-Free C-H Cross Coupling Toward Oxygenated Naphthalene-Benzene Linked Biaryls

Toshifumi Dohi,[†] Motoki Ito,[†,‡] Itsuki Itani,[†] Nobutaka Yamaoka,[†] Koji Morimoto,[†] Hiromichi Fujioka,[‡] and Yasuyuki Kita[†,*]

[†]*College of Pharmaceutical Sciences, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga, 525-8577, Japan*

[‡]*Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamaka-oka, Suita, Osaka, 565-0871, Japan*

E-mail: kita@ph.ritsumei.ac.jp

1. General Information

Melting point (mp) was measured by Stuart® melting point apparatus SMP3 AC input 100 V. ^{1}H and ^{13}C NMR spectra were collected on JEOL JMN-300 (300 MHz) or 400 (400 MHz) spectrometers using $CDCl_3$ or DMSO as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, □) relative to tetramethylsilane (□ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: □ = 7.24 ppm, DMSO: δ = 2.54 ppm). Data are reported as follows: chemical shift in ppm (□), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: □ = 77.0 ppm, DMSO: δ = 40.5). Infrared spectra (IR) were recorded on a JASCO FT/IR-4200 spectrometer; absorptions are reported in reciprocal centimeters. High Resolution Mass measurement and Elemental Analysis were performed by the Elemental Analysis Section of Osaka University and the Elemental Analysis Section of Osaka University of Pharmaceutical Sciences. Column chromatography was carried out on Merk Sillica Gel 60 (230-400 mesh) eluting with ethyl acetate and hexane. Thin-layer chromatography (TLC) was performed on Merk Silica Gel F_{254} plates (0.25 mm). The spots and bands were detected by UV light of irradiation (254, 365 nm).

2. Materials

Hypervalent iodine reagents, $PhI(OCOCF_3)_2$ (PIFA) and $C_6F_5I(OCOCF_3)_2$ (FPIFA), are commercially available. 4-$CF_3C_6F_4I(OCOCF_3)_2$[1)] and other iodine(III) compounds[2)] were prepared by the reported methods in literatures. Naphthalene ethers (**1b**, **1c**, **1e**, and **1f**) and phenyl ethers (**2c**, **2d**, **2g,** and **2i**) were obtained from corresponding phenols, alcohol, and amine by typical protection methods. Naphthalene **1g** was synthesized from 5,8-dimethoxy-1-naphthol[3)] by using the reported three step functional group conversions of hydroxyl group to bromide.[4)] Naphthalene **1h** was synthesized from 4-methoxy-8-benzyloxy-1-naphthol[5)] by protection of the hydroxyl group using isopropyl bromide, followed by debenzylation with H_2-Pd/C and silyletherification. Phenyl ether **2e** was prepared by Sonogashira coupling between 1-bromo-3,5-dimethoxybenzene and

1-hexyne.[6] Unless otherwise indicated, all other reagents and solvents were obtained from commercial suppliers and used as received.

3. Oxidative Cross Coupling of Aromatic Ethers 1 and 2

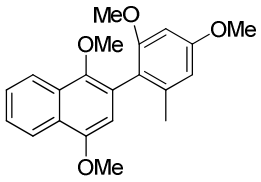
3.1 General Procedure for the Cross Coupling of Aromatic Ethers 1 and 2

Under the nitrogen atmosphere, to a stirred solution of naphthalene ethers **1** (0.20 mmol, 1 equiv.) and phenyl ethers **2** (0.40 mmol, 2 equiv.) in CH_2Cl_2 (2 mL) was added $BF_3{\cdot}Et_2O$ (50 μL, 0.40 mmol, 2 equiv.) and then FPIFA (104 mg, 0.20 mmol, 1 equiv.) at -40 °C. The reaction mixture was stirred for additional 3 to 6 hours at the same temperature. After the reaction completion was checked by TLC, saturated $NaHCO_3$ aq. was added to the reaction mixture, and the aqueous phase was extracted with CH_2Cl_2 twice. The combined extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residue was purified by column chromatography on silica-gel to give the pure cross coupling biaryls **3**.

The reactions of all the substrates in Table 2, Schemes 2 and 3, were conducted using PIFA to give inferior results in terms of the yield of the cross coupling products **3** and homocoupling product formations. Other Lewis acids used in our previous works[7)-9)] showed disappointing results in terms of product yield.

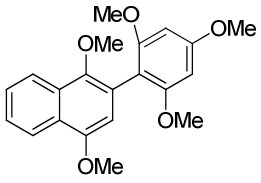
3.2 Chemical Data of the Cross Coupling Products 3

2-(2,4-Dimethoxy-6-methylphenyl)-1,4-dimethoxynaphthalene (3aa)



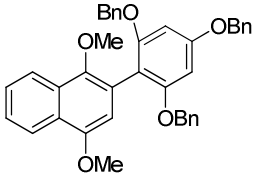
Colorless solid; mp:123-126 °C,^{1}H NMR (300 MHz, $CDCl_3$): δ 2.08 (s, 3H), 3.56 (s, 3H), 3.72 (s, 3H), 3.87 (s, 3H), 3.93 (s, 3H), 6.46 (d, *J* = 2.4 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.53 (s, 1H), 7.48-7.55 (m, 2H), 8.12 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.25 (dd, *J* = 7.5, 1.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5, 55.2, 55.5, 55.6, 61.0, 96.1, 106.2, 107.4, 120.4, 122.1, 122.2, 125.2, 125.3, 126.0, 126.2, 128.8, 139.2, 147.3, 151.1, 158.1, 159.8 ppm; IR (KBr): 2999, 2953, 1604, 1498, 1458, 1415, 1388, 1363, 1330, 1319, 1269, 1220, 1199, 1159, 1141, 1101, 1070, 1051, 999, 972, 829, 771, 715 cm^{-1}; *Anal*. calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55, found: C, 74.33; H, 6.60.

1,4-Dimethoxy-2-(2,4,6-trimethoxyphenyl)naphthalene (3ab)



Colorless solid; mp: 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (s, 3H), 3.74 (s, 3H), 3.90 (s, 6H), 3.96 (s, 3H), 6.30 (s, 2H), 6.61 (s, 1H), 7.45-7.54 (m, 2H), 8.14 (dd, *J* = 7.6, 0.7 Hz, 1H), 8.26 (dd, *J* = 7.6, 0.7 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 55.5, 55.9, 61.2, 90.8, 108.0, 109.5, 122.1, 122.2, 122.6, 125.0, 126.0, 126.1, 128.7, 147.9, 150.9, 158.7, 160.9 ppm; IR (KBr): 2937, 2837, 1606, 1504, 1454, 1415, 1365, 1334, 1222, 1203, 1157, 1126, 1101, 1070, 1037, 999, 970, 948, 844, 812, 771, 567 cm^{-1}; *Anal*. calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26, found: C, 71.04; H, 6.26.

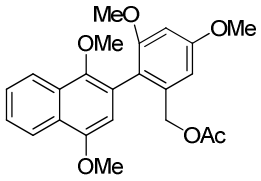
1,4-Dimethoxy-2-[2,4,6-tris(benzyloxy)phenyl]naphthalene (3ac)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 3H), 3.79 (s, 3H), 4.93 (s, 6H), 6.31 (s, 2H), 6.60 (s, 1H), 7.09-7.11 (m, 10H), 7.25-7.44 (m, 7H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 61.3, 70.2,

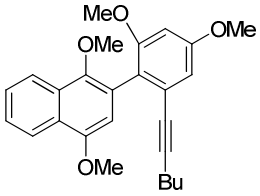
70.4, 94.1, 108.3, 111.2, 122.1, 122.2, 122.5, 125.0, 125.9, 126.0, 126.7, 127.4, 127.6, 128.1, 128.2, 128.6, 128.8, 136.7, 137.2, 148.2, 150.8, 157.7, 159.8 ppm; IR (KBr): 3030, 2933, 1953, 1874, 1815, 1604, 1504, 1433, 1365, 1219, 1159, 1116, 1066, 1028, 999, 972, 904, 844, 810, 771, 698, 665, 634, 561 cm^{-1}; HRMS (FAB): calcd for $C_{39}H_{34}O_5$ $[M]^+$: 582.2406, found: 582.2419.

2-(1,4-Dimethoxy-2-naphthalenyl)-3,5-dimethoxybenzyl acetate (3ad)



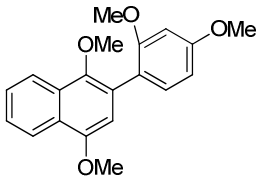
Colorless amorphous; ^1H NMR (400 MHz, $CDCl_3$): δ 1.98 (s, 3H), 3.54 (s, 3H), 3.74 (s, 3H), 3.89 (s, 3H), 3.93 (s, 3H), 4.84 (d, *J* = 12.8 Hz, 1H), 4.98 (d, *J* = 12.8 Hz, 1H), 6.56-6.58 (m, 2H), 6.68 (d, *J* = 2.4 Hz, 1H), 7.47-7.55 (m, 2H), 8.10 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.25 (dd, *J* = 8.0, 1.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 55.9, 56.2, 56.4, 61.7, 65.0, 98.8, 104.9, 107.8, 120.4, 122.7, 122.8, 124.2, 126.0, 126.8, 126.9, 129.3, 137.4, 148.0, 151.8, 158.8, 160.9, 171.1 ppm; IR (KBr): 3070, 2998, 2938, 2839, 2072, 1961, 1804, 1738, 1606, 1497, 1458, 1320, 1224, 1159, 1102, 1070, 1034, 997, 970, 928, 836, 770, 717, 675, 657, 642, 632, 600, 560 cm^{-1}; HRMS (FAB): calcd for $C_{23}H_{24}O_6$ $[M]^+$: 396.1573, found: 396.1567.

2-[2-(Hex-1-yn-1-yl)-4,6-dimethoxyphenyl]-1,4-dimethoxynaphthalene (3ae)



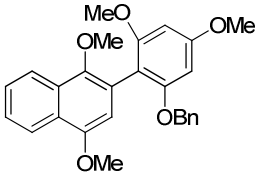
Colorless solid; mp: 110-113 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 0.43 (t, *J* = 7.2 Hz, 3H), 0.77-0.85 (m, 2H), 1.02-1.08 (m, 2H), 2.08 (t, *J* = 7.6 Hz, 2H), 3.58 (s, 3H), 3.71 (s, 3H), 3.84, (s, 3H), 3.93 (s, 3H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.60 (s, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 7.43-7.51 (m, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.1, 18.9, 21.3, 30.3, 55.4 55.6, 55.9, 61.4, 79.9, 93.8, 99.2, 107.3, 107.5, 122.1, 122.2, 123.9, 125.0, 125.4, 125.7, 126.0, 126.2, 128.7, 147.7, 151.0, 158.2, 159.7 ppm; IR (KBr): 3068, 2934, 2839, 2227, 1955, 1734, 1666, 1598, 1458, 1365, 1279, 1202, 1160, 1102, 999, 973, 938, 834, 770, 719, 660, 599, 575 cm^{-1}; HRMS (FAB): calcd for $C_{26}H_{28}O_4$ $[M]^+$: 404.1998, found: 404.1990.

2-(2,4-Dimethoxyphenyl)-1,4-dimethoxynaphthalene (3af)[10)]



Colorless solid; mp: 123-125 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 3.56 (s, 3H), 3.79 (s, 3H), 3.88 (s, 3H), 3.96 (s, 3H), 6.59-6.63 (m, 2H), 6.72 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.47-7.53 (m, 2H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 55.6, 55.7, 61.2, 98.9, 104.3, 107.4, 120.5, 122.0, 122.1, 125.2, 125.9, 126.3, 126.4, 128.8, 132.0, 147.2, 150.9, 157.8, 160.4 ppm; IR (KBr): 2935, 1610, 1508, 1458, 1415, 1390, 1365, 1303, 1257, 1224, 1207, 1159, 1126, 1101, 1064, 1035, 769 cm^{-1}; *Anal*. calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21, found: C, 73.91; H, 6.27.

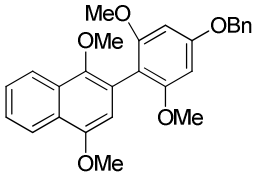
2-[2-(Benzyloxy)-4,6-dimethoxyphenyl]-1,4-dimethoxynaphthalene (3ag)



Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 3.59 (s, 3H), 3.73 (s, 3H), 3.83 (s, 3H), 3.90 (s, 3H), 5.03 (s, 2H), 6.27 (s, 1H), 6.28 (s, 1H), 6.61 (s, 1H), 7.16-7.17 (m, 5H), 7.46-7.50 (m, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 55.6, 56.0, 61.3, 70.4, 91.3, 92.6, 108.1, 110.3, 122.1, 122.2, 122.6, 125.0, 126.0, 126.1, 126.7, 127.4, 128.2, 128.8, 137.3, 148.1, 150.9, 157.6, 158.8, 160.8 ppm; IR (KBr): 2933, 2842, 1587,

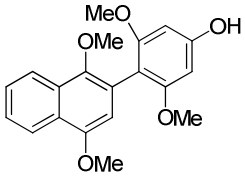
1503, 1459, 1417, 1365, 1335, 1226, 1158, 1122, 1072, 1000, 814, 770, 741, 697, 656, 639, 614, 593, 581, 553, 546, 527, 514 cm^{-1}; HRMS (FAB): calcd for $C_{27}H_{26}O_5$ $[M]^+$: 430.1780, found: 430.1779.

2-[4-(Benzyloxy)-2,6-dimethoxyphenyl]-1,4-dimethoxynaphthalene (3'ag)



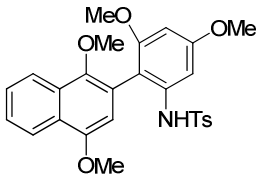
Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 3.60 (s, 3H), 3.71 (s, 6H), 3.94 (s, 3H), 5.14 (s, 2H), 6.36 (s, 2H), 6.58 (s, 1H), 7.36-7.52 (m, 7H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 56.0, 61.3, 70.3, 91.7, 108.0, 109.7, 122.1, 122.2, 122.6, 125.1, 126.0, 126.1, 127.7, 128.1, 128.6, 128.7, 136.8, 147.9, 151.0, 158.7, 160.2 ppm; IR (KBr): 3065, 2999, 2935, 2838, 2247, 2156, 2070, 1957, 1822, 1585, 1504, 1458, 1414, 1365, 1334, 1225, 1126, 1065, 1028, 999, 972, 844, 810, 741, 700, 654, 581, 507 cm^{-1}.

4-(1,4-Dimethoxy-2-naphthalenyl)-3,5-dimethoxyphenol (3'ah, sole product)



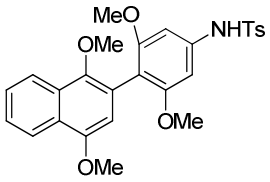
Colorless solid; mp: 223-224 °C; ^1H NMR (400 MHz, DMSO): δ 3.47 (s, 3H), 3.58 (s, 6H), 3.85 (s, 3H), 6.18 (s, 2H), 6.52 (s, 1H), 7.47-7.55 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 9.61 (brs, 1H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 55.3, 55.7, 60.6, 92.0, 106.8, 108.7, 121.7, 121.9, 123.6, 125.1, 125.2, 126.2, 128.2, 147.4, 150.2, 158.2, 158.8 ppm; IR (KBr): 3334, 2937, 2840, 1956, 1596, 1504, 1458, 1366, 1221, 1160, 996, 847, 816, 770, 750, 725, 711, 692, 681, 670, 651, 625, 599 cm^{-1}; HRMS (FAB): calcd for $C_{20}H_{20}O_5$ $[M]^+$: 340.1311, found: 340.1315.

***N*-[2-(1,4-Dimethoxy-2-naphthalenyl)-3,5-dimethoxyphenyl]-4-methylbenzenesulfonamide (3ai, minor product)**



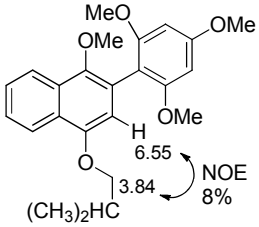
Colorless solid; ^1H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 3.48 (s, 3H), 3.66 (s, 3H), 3.71 (s, 3H), 3.89 (s, 3H), 5.87 (s, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.49-7.57 (m, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H) ppm.

***N*-[4-(1,4-Dimethoxy-2-naphthalenyl)-3,5-dimethoxyphenyl]-4-methylbenzenesulfonamide (3'ai, major product)**



Colorless solid; mp: 193-196 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.49 (s, 3H), 3.59 (s, 6H), 3.90 (s, 3H), 6.38 (s, 2H), 6.48 (s, 1H), 6.80 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.42-7.50 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 55.6, 55.9, 61.2, 97.4, 105.5, 107.3, 113.3, 122.1, 122.2, 125.2, 126.1, 126.2, 127.5, 128.6, 129.7, 136.1, 137.7, 144.1, 147.5, 151.1, 158.4 ppm; IR (KBr): 3562, 3254, 3069, 2938, 2840, 2252, 1594, 1459, 1393, 1365, 1330, 1288, 1227, 1157, 1126, 1101, 1061, 1004, 970, 912, 814, 733, 662, 543 cm^{-1}; HRMS (FAB): calcd for $C_{27}H_{27}NO_6S$ $[M]^+$: 493.1559, found: 493.1556.

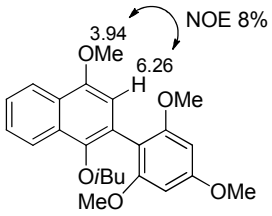
4-Isobutoxy-1-methoxy-2-(2,4,6-trimethoxyphenyl)naphthalene (3bb)



Colorless solid; mp: 120-123 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 6.8 Hz, 6H), 2.18-2.25 (m, 1H), 3.60 (s, 3H), 3.73, (s, 6H), 3.84 (d, *J* = 6.4 Hz, 2H), 3.89 (s,

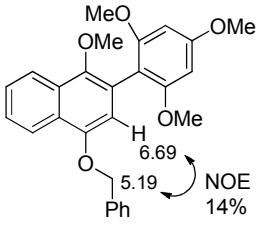
3H), 6.28 (s, 2H), 6.55 (s, 1H), 7.44-7.52 (m, 2H), 8.12 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.30 (dd, *J* = 8.0, 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 28.4, 55.3, 55.9, 61.3, 74.3, 90.7, 108.5, 109.5, 122.2, 122.3, 122.7, 124.9, 125.9, 126.2, 128.7, 147.6, 150.5, 158.7, 160.9 ppm; IR (KBr): 3070, 2957, 2838, 2251, 2156, 2077, 1956, 1586, 1504, 1457, 1416, 1390, 1363, 1335, 1225, 1156, 1126, 1098, 1070, 1039, 1003, 950, 911, 840, 812, 770, 730, 665, 584, 574, 561, 550, 537, 527 cm^{-1}; HRMS (FAB): calcd for $C_{24}H_{28}O_5$ $[M]^+$: 396.1937, found: 396.1936.

1-Isobutoxy-4-methoxy-2-(2,4,6-trimethoxyphenyl)naphthalene (3'bb)



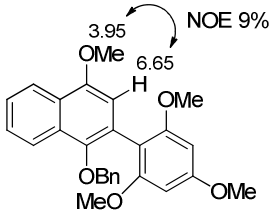
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76 (d, *J* = 6.8 Hz, 6H), 1.81-1.88 (m, 1H), 3.43 (d, *J* = 6.4 Hz, 2H), 3.73 (s, 6H), 3.89 (s, 3H), 3.94 (s, 3H), 6.26 (s, 2H), 6.61 (s, 1H), 7.42-7.50 (m, 2H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 28.9, 55.4, 55.5, 55.9, 80.3, 90.7, 108.1, 109.8, 122.1, 122.3, 122.7, 124.9, 125.8, 126.0, 129.1, 147.1, 150.7, 158.8, 160.9 ppm; IR (KBr): 3069, 2999, 2954, 2871, 2838, 2249, 2079, 1956, 1586, 1504, 1456, 1414, 1379, 1358, 1335, 1268, 1225, 1178, 1126, 1068, 1006, 950, 911, 845, 811, 770, 735, 650, 574 cm^{-1}; HRMS (FAB): calcd for $C_{24}H_{28}O_5$ $[M]^+$: 396.1937, found: 396.1938.

4-(Benzyloxy)-1-methoxy-2-(2,4,6-trimethoxyphenyl)naphthalene (3cb)



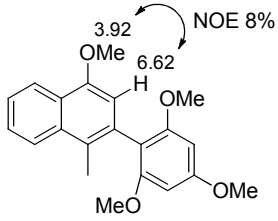
Colorless solid; mp: 53-55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (s, 3H), 3.71 (s, 6H), 3.89 (s, 3H), 5.19 (s, 2H), 6.28 (s, 2H), 6.69 (s, 1H), 7.34-7.54 (m, 7H), 8.15 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 55.9, 61.3, 70.1, 90.8, 109.4, 109.5, 122.2, 122.4, 122.6, 125.1, 126.1, 126.3, 127.5, 127.7, 128.4, 128.8, 137.5, 148.1, 150.1, 158.7, 161.0 ppm; IR (KBr): 3068, 2994, 2936, 2837, 2072, 1955, 1585, 1504, 1456, 1415, 1362, 1268, 1226, 1156, 1126, 1095, 1070, 1038, 997, 950, 919, 851, 811, 769, 736, 697, 655, 637, 601, 558, 546, 520 cm^{-1}; HRMS (FAB): calcd for $C_{27}H_{26}O_5$ $[M]^+$: 430.1780, found: 430.1777.

1-(Benzyloxy)-4-methoxy-2-(2,4,6-trimethoxyphenyl)naphthalene (3'cb)



Colorless solid; mp: 47-50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 6H), 3.88 (s, 3H), 3.95 (s, 3H), 4.67 (s, 2H), 6.27 (s, 2H), 6.65 (s, 1H), 7.10-7.12 (m, 2H), 7.23-7.26 (m, 3H), 7.44-7.47 (m, 2H), 8.12 (d, *J* = 9.2 Hz, 1H), 8.24 (d, *J* = 9.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 55.5, 55.9, 75.8, 90.8, 108.0, 109.5, 122.1, 122.3, 123.0, 125.0, 125.9, 126.0, 127.5, 128.0, 128.1, 129.1, 138.0, 146.9, 151.1, 158.8, 161.1 ppm; IR (KBr): 3066, 2999, 2936, 2836, 1953, 1586, 1504, 1455, 1414, 1388, 1355, 1268, 1225, 1157, 1124, 1102, 1067, 1038, 995, 951, 922, 849, 813, 769, 699, 661, 645, 629, 586, 558, 531, 510 cm^{-1}.

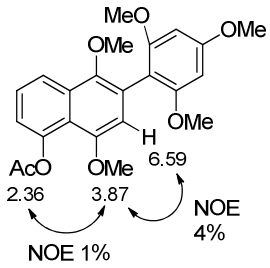
1-Methoxy-4-methyl-2-(2,4,6-trimethoxyphenyl)naphthalene (3'db, sole product)



Colorless solid; mp: 171-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 3.69 (s, 6H), 3.88 (s, 3H), 3.92 (s, 3H), 6.26 (s, 2H), 6.62 (s, 1H), 7.43 (td, *J* = 6.8, 1.2 Hz, 1H), 7.51 (td, *J* = 6.8, 1.2 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.27 (dd, *J* = 8.0, 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 55.4, 55.5, 55.9, 90.8, 107.9, 112.8,

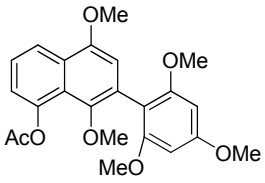
122.3, 124.3, 124.4, 125.2, 125.4, 125.9, 130.7, 133.6, 152.8, 158.5, 161.8 ppm; IR (KBr): 2999, 2937, 1606, 1585, 1502, 1458, 1413, 1382, 1332, 1224, 1203, 1157, 1141, 1126, 1101, 1060, 1037, 964, 812, 761, 638 cm^{-1}; *Anal*. calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55, found: C, 74.38; H, 6.55.

5,8-Dimethoxy-6-(2,4,6-trimethoxyphenyl)naphthalen-1-yl acetate
(3eb, major product)



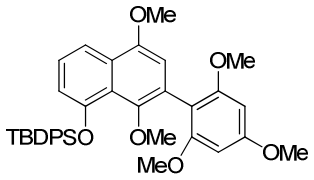
Light yellow solid; mp: 141-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 3.55 (s, 3H), 3.70 (s, 6H), 3.84 (s, 3H), 3.87 (s, 3H), 6.24 (s, 2H), 6.59 (s, 1H), 7.05 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.42 (dd, *J* = 8.4, 7.2 Hz, 1H), 8.04 (dd, *J* = 8.4, 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 55.4, 55.9, 56.3, 61.2, 90.8, 109.0, 110.7, 119.2, 119.4, 121.0, 123.7, 125.6, 131.3, 146.7, 148.2, 150.6, 158.7, 161.1, 170.5 ppm; IR (KBr): 3003, 2937, 2841, 1761, 1606, 1504, 1456, 1436, 1413, 1367, 1334, 1220, 1157, 1126, 1066, 1037, 1018, 977, 952, 912, 877, 813, 767, 742, 648, 590, 538 cm^{-1}; HRMS (FAB): calcd for $C_{23}H_{24}O_7$ $[M]^+$: 412.1522, found: 412.1521.

5,8-Dimethoxy-7-(2,4,6-trimethoxyphenyl)naphthalen-1-yl acetate
(3'eb, minor product)



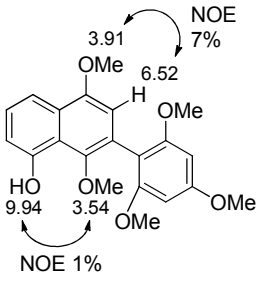
Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 3.45 (s, 3H), 3.72 (s, 6H), 3.88 (s, 3H), 3.93 (s, 3H), 6.26 (s, 2H), 6.63 (s, 1H), 7.12 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.40 (dd, *J* = 8.4, 7.2 Hz, 1H), 8.18 (dd, *J* = 8.4, 1.2 Hz, 1H) ppm.

***tert*-Butyl{[5,8-dimethoxy-7-(2,4,6-trimethoxyphenyl)naphthalen-1-yl]oxy}**
diphenylsilane (3'fb, sole product)



Light yellow solid; mp: 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (s, 9H), 3.53 (s, 3H), 3.78 (s, 6H), 3.91 (s, 3H), 3.93 (s, 3H), 6.31 (s, 2H), 6.50 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.68 (s, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 7.32-7.42 (m, 6H), 7.76-7.81 (m, 5H) ppm; ^{13}CNMR(100 MHz, $CDCl_3$): δ 19.7, 26.6, 55.3, 55.6, 56.0, 61.8, 91.0, 108.6, 110.5, 115.2, 116.5, 122.1, 123.7, 124.6, 127.6, 128.8, 129.6, 133.6, 135.6, 148.9, 150.6, 151.6, 158.9, 160.7 ppm; IR (KBr): 3071, 2998, 2935, 2857, 2246, 1960, 1824, 1606, 1504, 1465, 1414, 1369, 1336, 1271, 1225, 1204, 1148, 1126, 1062, 988, 941, 910, 811, 737, 701, 648, 612, 522, 500 cm^{-1}; HRMS (FAB): calcd for $C_{37}H_{40}O_6Si$ $[M]^+$: 608.2594, found: 608.2596.

The regioselectivity was determined by measurement of NOE interaction after deprotection of the TBDPS group.

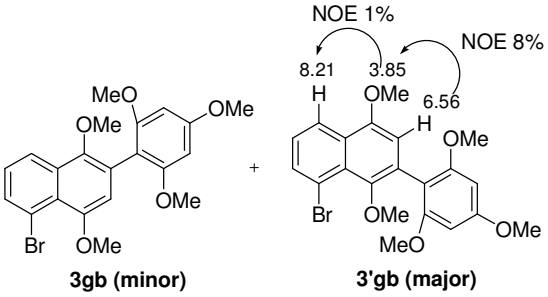


5,8-Dimethoxy-7-(2,4,6-trimethoxyphenyl)naphthalen-1-ol

Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.54 (s, 3H), 3.73 (s, 6H), 3.88 (s, 3H), 3.91 (s, 3H), 6.26 (s, 2H), 6.52 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 9.94 (s, 1H) ppm.

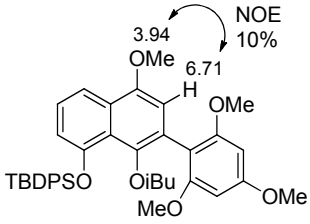
5-Bromo-1,4-dimethoxy-2-(2,4,6-trimethoxyphenyl) naphthalene (3gb, minor product) and

8-Bromo-1,4-dimethoxy-2-(2,4,6-trimethoxyphenyl) naphthalene (3'gb, major product)



Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (s, 3H, for **3'gb**), 3.48 (s, 3H, for **3gb**), 3.65-3.86 (12H, for **3gb**, and 12H, for 3'**gb**), 6.19 (2H, for **3gb**, and 2H, for **3'gb**), 6.56 (s, 1H, for **3'gb**), 6.64 (s, 1H, for **3gb**), 7.12-7.17 (1H, for **3gb**, and 1H, for **3'gb**), 7.69 (dd, *J* = 7.6, 1.2 Hz, 1H, for **3gb**), 7.74 (dd, *J* = 7.6, 1.2 Hz, 1H, for **3'gb**), 8.06 (dd, *J* = 8.4, 1.2 Hz, 1H, for **3gb**), 8.21 (dd, *J* = 8.4, 1.2 Hz, 1H, for **3'gb**) ppm; IR (KBr): 3003, 2937, 2839, 1606, 1496, 1463, 1409, 1363, 1224, 1205, 1184, 1161, 1126, 1087, 1062, 1039, 1004, 974, 950, 912, 850, 819, 742, 650, 549 cm^{-1}.

tert-Butyl{[8-isobutoxy-5-methoxy-7-(2,4,6-trimethoxyphenyl)naphthalen-1-yl]oxy}diphenylsilane (3'hb, sole product)

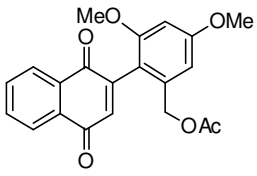


Colorless amorphous; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.47 (d, *J* = 6.4 Hz, 6H), 1.11 (s, 9H), 1.69-1.72 (m, 1H), 3.49 (d, *J* = 7.2 Hz, 2H), 3.79 (s, 6H), 3.90 (s, 3H), 3.94 (s, 3H), 6.30 (s, 2H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 7.34-7.43 (m, 6H), 7.79-7.81 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 19.9, 27.1, 27.7, 55.4, 55.5, 55.8, 82.1, 90.7, 108.6, 111.0, 115.3, 116.6, 122.5, 123.5, 124.4, 127.5, 128.7, 129.6, 134.0, 135.6, 148.4, 150.2, 151.6, 158.9, 160.8 ppm; IR (KBr): 3071, 3050, 2999, 2954, 2859, 2247, 1962, 1825, 1587, 1503, 1465, 1415, 1368, 1266, 1224, 1127, 1056, 1008, 939, 909, 848, 810, 766, 736, 708, 654, 611, 525 cm^{-1}; HRMS (FAB): calcd for $C_{40}H_{46}O_6Si$ $[M]^+$: 650.3064, found: 650.3066.

4. Elaboration of the Biaryl 3ad

To a stirred solution of the biaryl **3ad** (288 mg, 0.73 mmol) in CH_3CN (15 mL) was added aqueous solution of cerium(IV) ammonium nitrate (1.0 g, 1.83 mmol in 7.5 mL H_2O) dropwise at room temperature. After 30 minutes, the mixture was diluted with the water and AcOEt. The aqueous phase was extracted with AcOEt, and the combined organic phase was washed by brine. The extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residue was purified by column chromatography on silica-gel (hexane/AcOEt = 4/1) to give a pure quinone compound **4** (207 mg, 78%).

2-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-3,5-dimethoxybenzyl acetate (4)

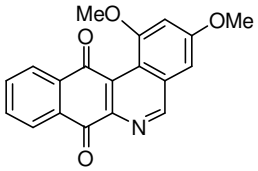


Yellow solid; mp: 150-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (s, 3H), 3.70 (s, 3H) 3.84 (s, 3H), 4.83 (d, *J* = 12.4 Hz, 1H), 5.00 (d, *J* = 12.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 6.90 (s, 1H), 7.74-7.76 (m, 2H), 8.10-8.12 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 55.3, 55.8, 64.1, 98.5, 105.9, 115.7, 126.0, 126.8, 132.1, 132.2, 133.5, 133.6, 135.8, 138.1, 146.4, 158.2, 161.2, 170.2, 183.7, 184.8 ppm; IR (KBr): 3074, 3007, 2945, 2840, 1740, 1665, 1602, 1463, 1324, 1302, 1253, 1228, 1157, 1064, 1028, 934, 841, 781, 751, 725, 704, 681, 633, 594, 546, 506 cm^{-1}; HRMS (FAB): calcd for $C_{21}H_{18}O_6$ $[M]^+$: 366.1103, found: 366.1104.

The quinone **4** (159 mg, 0.43 mmol), NH_4Cl (465 mg, 8.69 mmol), and AcONa (713 mg, 8.69 mmol) were dissolved in ethanol (13 mL), and refluxed for 24 hours. After the reaction completion was monitored by TLC, the reaction mixture was cooled to room temperature. Water was added to the solution and then it was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and evaporated to dryness. The crude reaction mixture was dissolved in MeOH (5 mL), to which 10 M NaOH aq. (2 mL) was added dropwise. After stirring for 24 hours, the solution was neutralized with 1 M HCl aq., and the aqueous phase was extracted by CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated by evaporation. The crude residue was purified by column chromatography on silica-gel (hexane/AcOEt = 1/1) to give an intermediate **5** (79 mg, 53% from **4**)

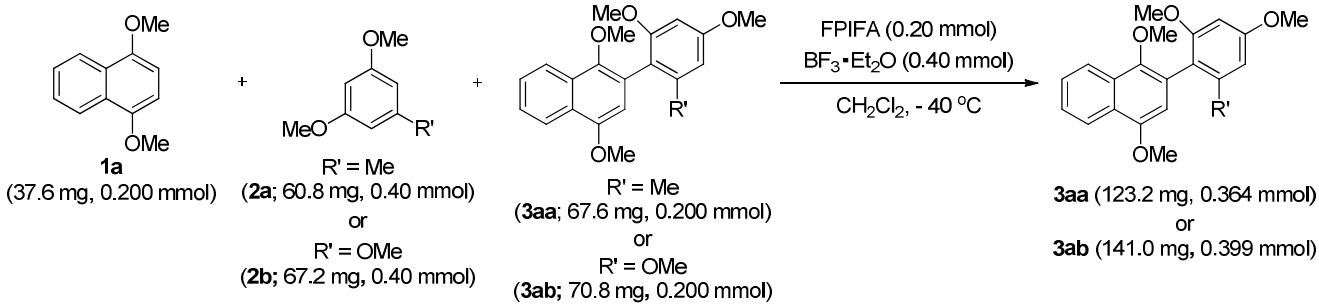
To a stirred solution of the quinine **5** (75 mg, 0.22 mmol) in CH_2Cl_2 (2 mL) was added Dess-Martin periodinane (234 mg, 0.55 mmol) and water (50 μL) at 0 °C. The solution was refluxed for additional 8 hours. The reaction mixture was cooled to room temperature, and diluted with CH_2Cl_2 and water. The aqueous phase was extracted by CH_2Cl_2, and the combined organic layer was dried over Na_2SO_4. After evaporation of the solvent, the crude residue was purified by column chromatography on silica-gel (hexane/AcOEt = 1/1 to 1/5) to give a target pure tetracyclic compound **6** (68 mg, 97%).

1,3-Dimethoxybenzo[b]phenanthridine-7,12-dione (6)



Yellow solid; 223-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96 (s, 3H), 3.98 (s, 3H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 7.72-7.77 (m, 2H), 8.07 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.28 (dd, *J* = 7.6, 1.6 Hz, 1H), 9.31 (s, 1H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 55.9, 56.3, 98.7, 105.5, 119.4, 126.2, 127.1, 131.3, 132.1, 133.2, 133.4, 134.0, 136.1, 143.4, 155.7, 157.9, 162.3, 181.8, 185.4 ppm; IR (KBr): 3328, 3012, 2933, 2856, 1674, 1606, 1466, 1410, 1382, 1284, 1216, 1164, 1050, 1000, 946, 838, 789, 770, 722, 690, 668, 638, 559, 534 cm^{-1}; HRMS (FAB): calcd for $C_{19}H_{13}O_4N$ $[M+H]^+$: 320.0917, found: 320.0927.

5. Cross-Over Experiments



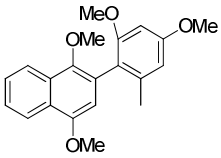
Under the nitrogen atmosphere, naphthalene ether **1a** (37.6 mg, 0.200 mmol), phenyl ethers **2a** (60.8 mg, 0.40 mmol) or **2b** (67.2 mg, 0.40 mmol), and biaryls **3aa** (67.6 mg, 0.200 mmol) or **3ab** (70.8 mg, 0.200 mmol) were dissolved in CH_2Cl_2 (2 mL). BF_3·Et_2O (50 μL, 0.40 mmol) and FPIFA (104.0 mg, 0.200 mmol) were added to the mixture at -40 °C. The solution was stirred for additional 3 hours at the same temperature where the reaction completion was checked by TLC. Saturated $NaHCO_3$ aq. was added to the reaction mixture, and the aqueous

phase was extracted with CH_2Cl_2 twice. The combined extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residue was purified by column chromatography on silica-gel (hexane/ AcOEt = 4/1) to give the pure biaryl **3aa** (123.2 mg, 0.364 mmol) or **3ab** (141.0 mg, 0.399 mmol).

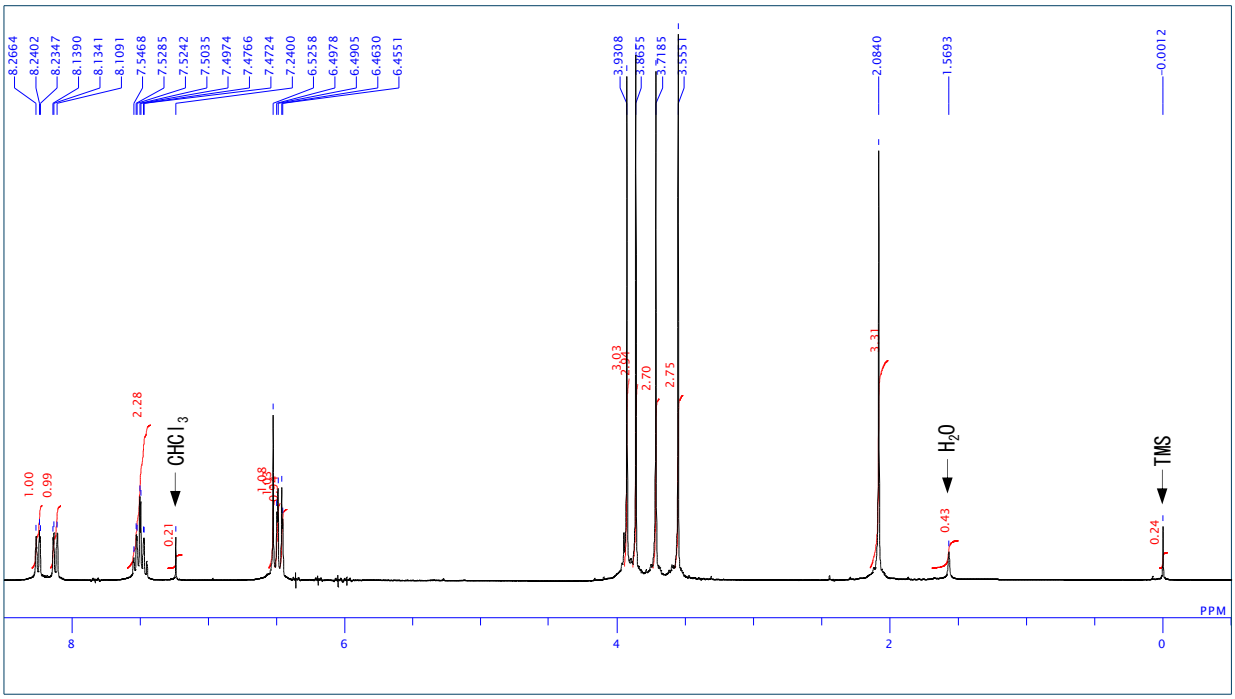
6. References

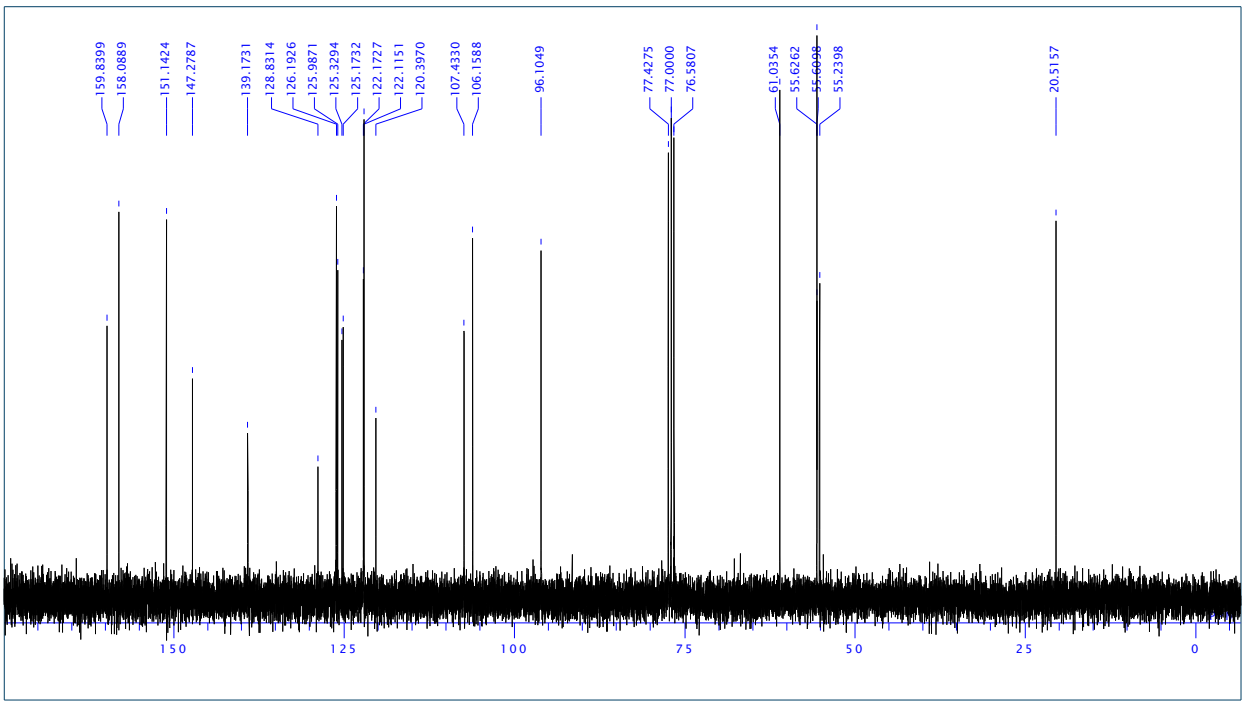
1) Schaefer, S.; Wirth, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 2786.
2) McKillop, A.; Kemp, D. *Tetrahedron* **1989**, *45*, 3299.
3) Peng, F.; Fan, B.; Shao, Z.; Pu, X.; Li, P.; Zhang, H. *Synthesis* **2008**, 3043.
4) Thompson, A. L. S.; Kabalka, G. W.; Akula, M. R.; Hoffman, J. W. *Synthesis* **2005**, 547.
5) Brimble, M. A.; Brenstrum, T. J. *J. Chem. Soc., Perkin Trans.* **2001**, 1612.
6) Singh, R.; Just, G. *J. Org. Chem.* **1989**, *54*, 4453.
7) Kita, Y.; Gyoten, M.; Ohtsubo, M.; Tohma, H.; Takada, T. *Chem. Commun*. **1996**, 1481; Takada, T.; Arisawa, M.; Gyoten, M.; Hamada, R.; Tohma, H.; Kita, Y. *J. Org. Chem.* **1998**, *63*, 7698; Hamamoto, H.; Anilkumar, G.; Tohma, H.; Kita, Y. *Chem. Eur. J*. **2002**, *8*, 5377.
8) Arisawa, M.; Utsumi, S.; Nakajima, M.; Ramesh, N. G.; Tohma, H.; Kita, Y. *Chem. Commun.* **1999**, 469; Tohma, H.; Morioka, H.; Takizawa, S.; Arisawa, M.; Kita, Y. *Tetrahedron* **2001**, *57*, 345; Tohma, H.; Iwata, M.; Maegawa, T.; Kita, Y. *Tetrahedron Lett.* **2002**, *8*, 5377.
9) Kita, Y.; Morimoto, K.; Ito, M.; Ogawa, C.; Goto, A.; Dohi, T. *J. Am. Chem. Soc.* **2009**, *131*, 1668; Morimoto, K.; Yamaoka, N.; Ogawa, C.; Nakae, T.; Fujioka, H.; Dohi, T.; Kita, Y. *Org. Lett.* **2010***, 12,* 3804.
10) Högberg, H.–E. *Acta Chem. Scand*. **1973**, *27*, 2559.

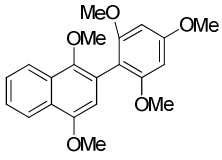
7. Spectrum Chart of the Product



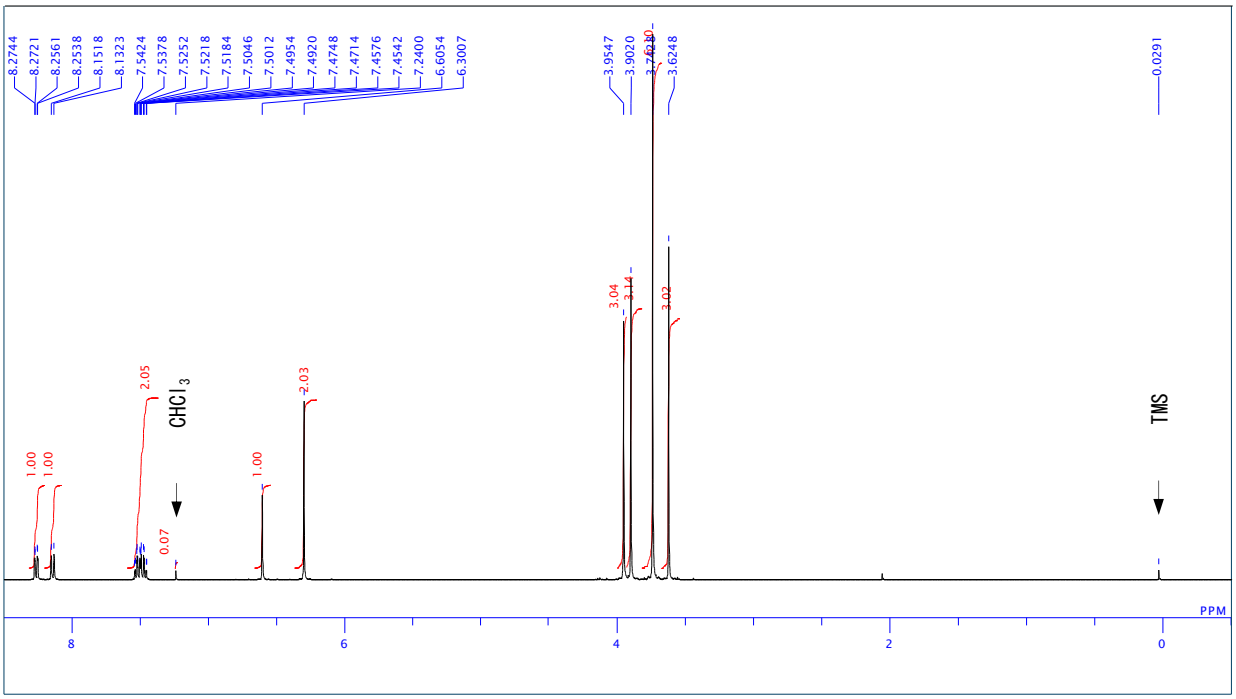
3aa

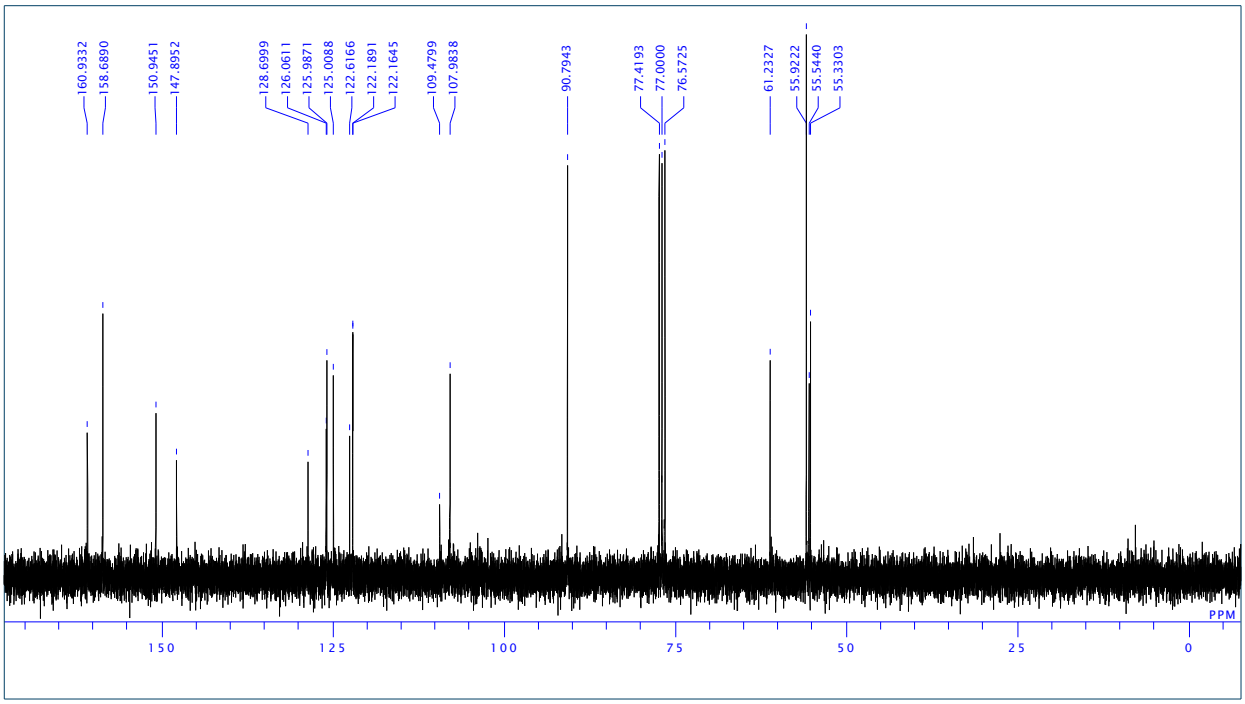


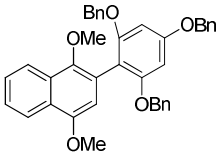



MeO
OMe
OMe
OMe
OMe
OMe

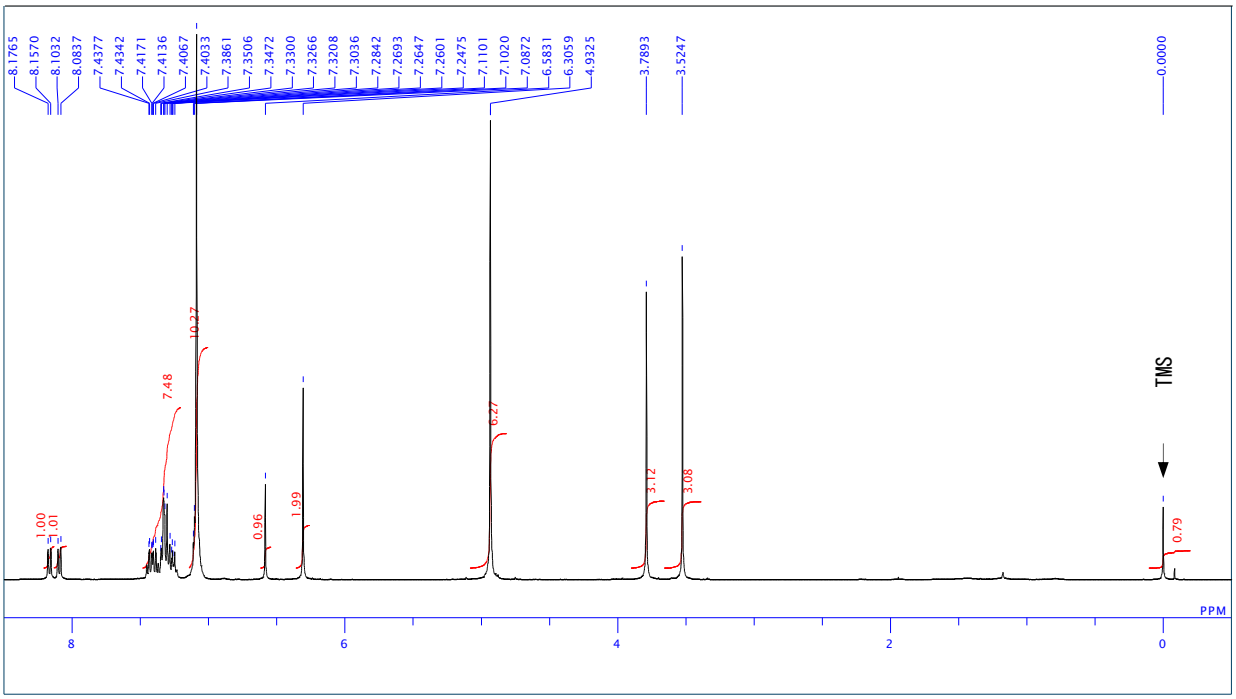
3ab

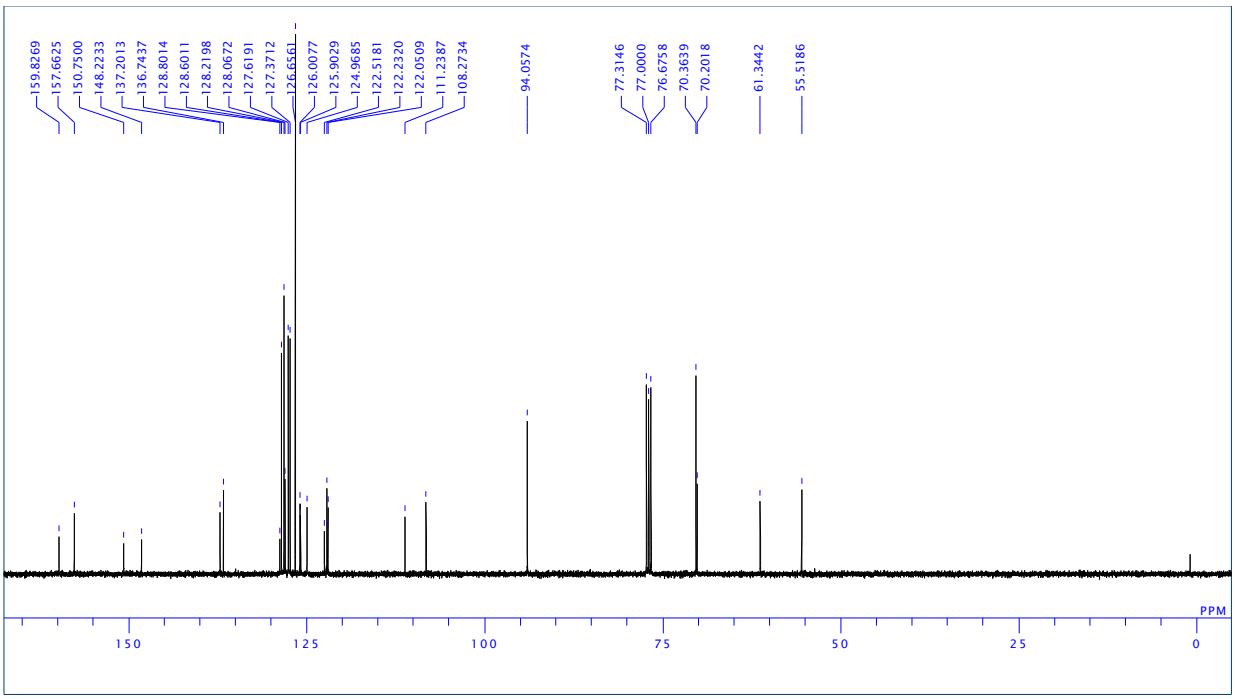

8.2744
8.2721
8.2561
8.2538
8.1518
8.1323
7.5424
7.5378
7.5252
7.5218
7.5184
7.5046
7.5012
7.4954
7.4920
7.4748
7.4714
7.4576
7.4542
7.2400
6.6054
6.3007
3.9547
3.9020
3.7630
3.6248
0.0291
1.00
1.00
2.05
CHCl3
0.07
1.00
2.03
3.04
3.14
3.02
TMS
PPM
8
6
4
2
0

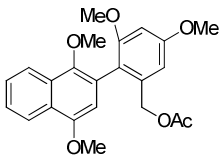

160.9332
158.6890
150.9451
147.8952
128.6999
126.0611
125.9871
125.0088
122.6166
122.1891
122.1645
109.4799
107.9838
90.7943
77.4193
77.0000
76.5725
61.2327
55.9222
55.5440
55.3303
PPM
150
125
100
75
50
25
0


BnO
OMe
OBn
OBn
OMe

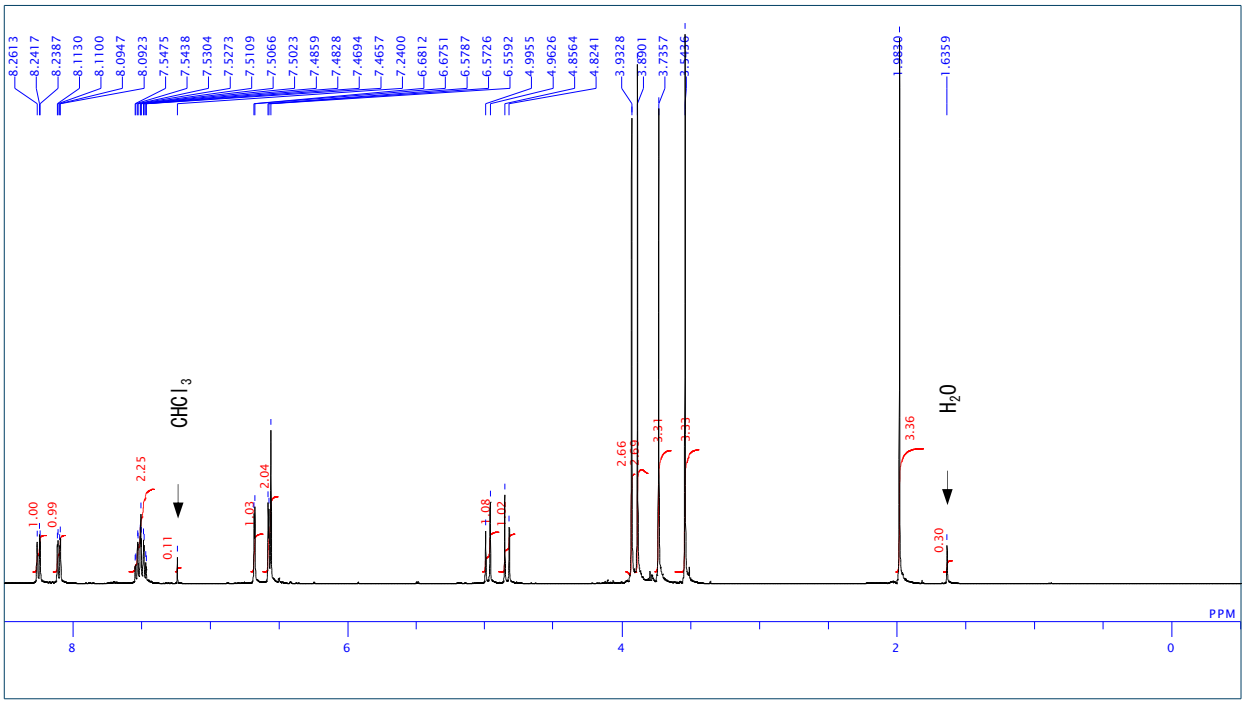
3ac

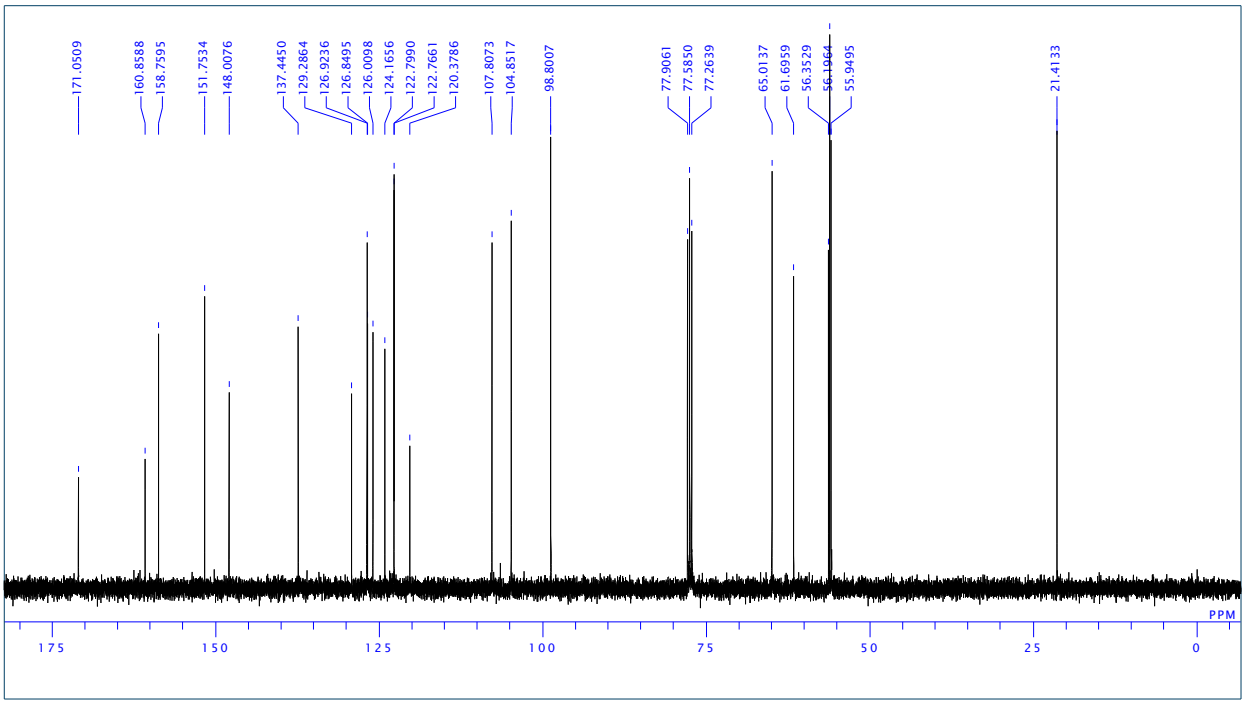

8.1765
8.1570
8.1032
8.0837
7.4377
7.4342
7.4171
7.4136
7.4067
7.4033
7.3861
7.3506
7.3472
7.3300
7.3266
7.3208
7.3036
7.2842
7.2693
7.2647
7.2601
7.2475
7.1101
7.1020
7.0872
6.5831
6.3059
4.9325
3.7893
3.5247
0.0000
TMS
1.00
1.01
7.48
10.27
0.96
1.99
6.27
3.12
3.08
0.79
PPM
8
6
4
2
0

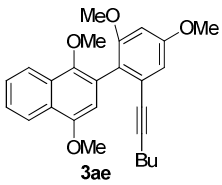

159.8269
157.6625
150.7500
148.2233
137.2013
136.7437
128.8014
128.6011
128.2198
128.0672
127.6191
127.3712
126.6561
126.0077
125.9029
124.9685
122.5181
122.2320
122.0509
111.2387
108.2734
94.0574
77.3146
77.0000
76.6758
70.3639
70.2018
61.3442
55.5186
PPM
150
125
100
75
50
25
0


MeO
OMe
OMe
OAc
OMe

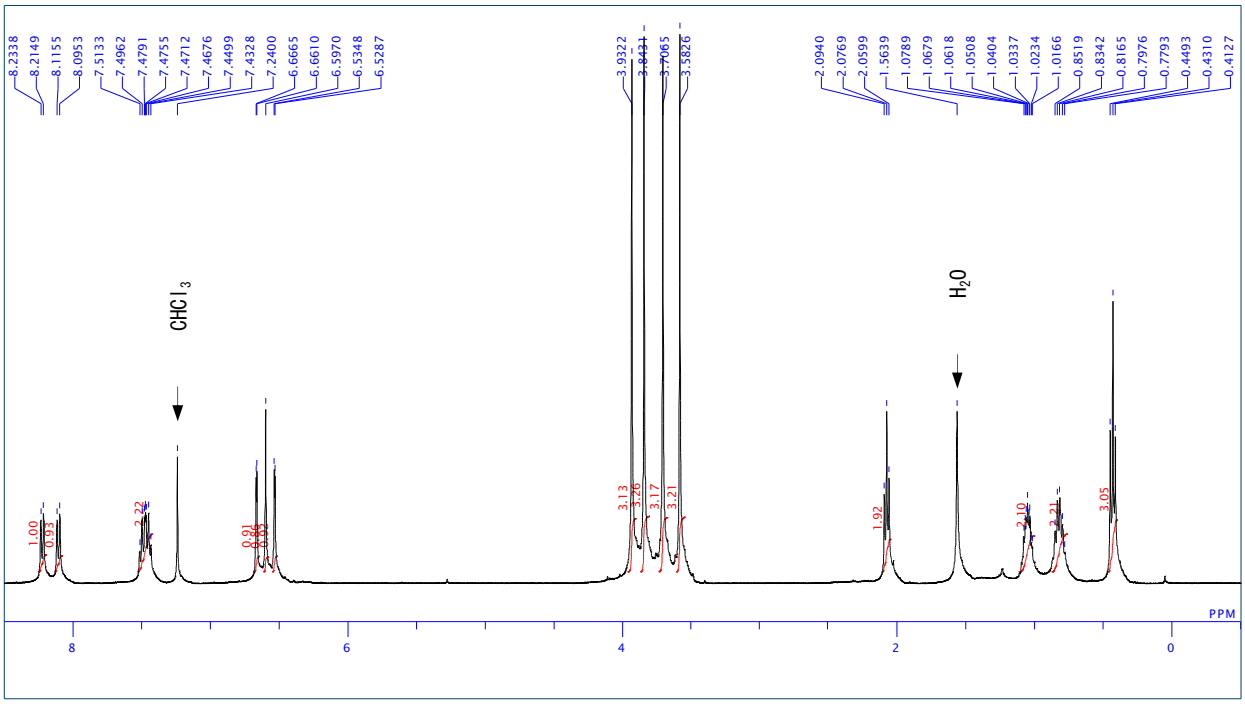
3ad

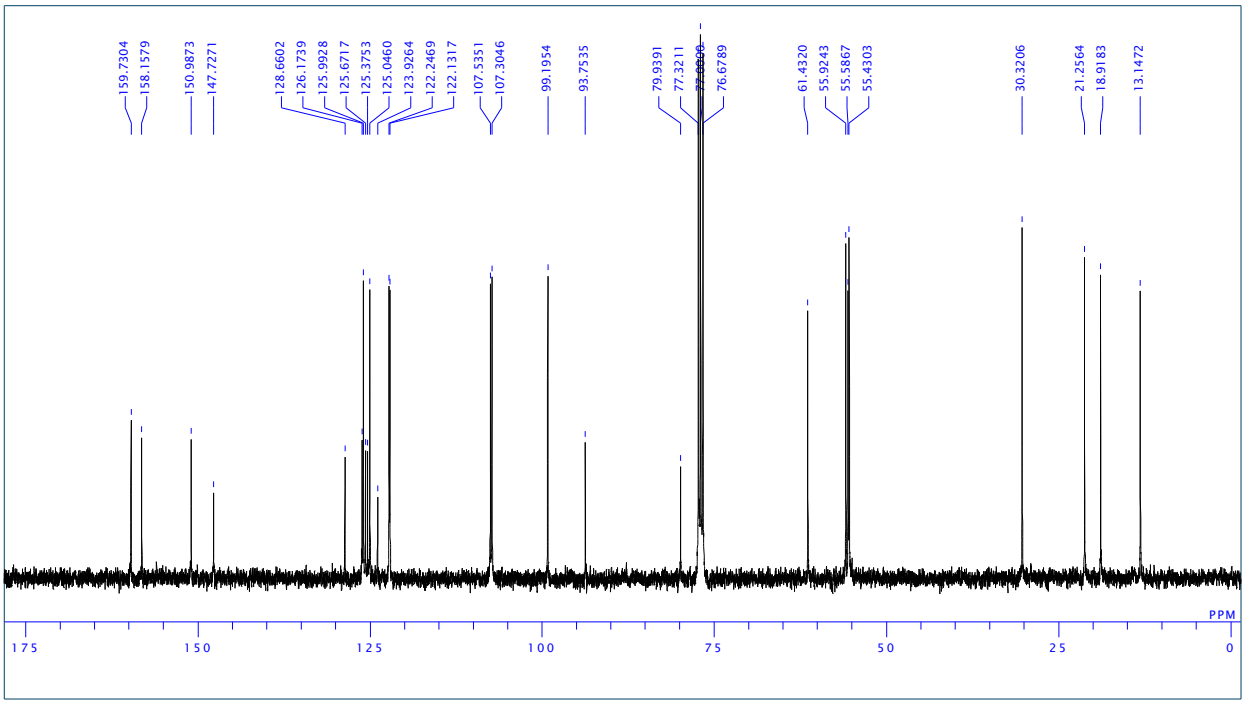

8.2613
8.2417
8.2387
8.1130
8.1100
8.0947
8.0923
7.5475
7.5438
7.5304
7.5273
7.5109
7.5066
7.5023
7.4859
7.4828
7.4694
7.4657
7.2400
6.6812
6.6751
6.5787
6.5726
6.5592
4.9955
4.9626
4.8564
4.8241
3.9328
3.8901
3.7357
3.5436
1.9839
1.6359
CHCl3
H2O
1.00
0.99
2.25
0.11
1.03
2.04
1.08
1.02
2.66
2.69
3.31
3.33
3.36
0.30
PPM
8
6
4
2
0

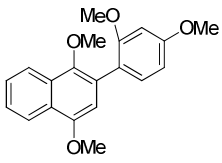

171.0509
160.8588
158.7595
151.7534
148.0076
137.4450
129.2864
126.9236
126.8495
126.0098
124.1656
122.7990
122.7661
120.3786
107.8073
104.8517
98.8007
77.9061
77.5850
77.2639
65.0137
61.6959
56.3529
56.1964
55.9495
21.4133
PPM
175
150
125
100
75
50
25
0



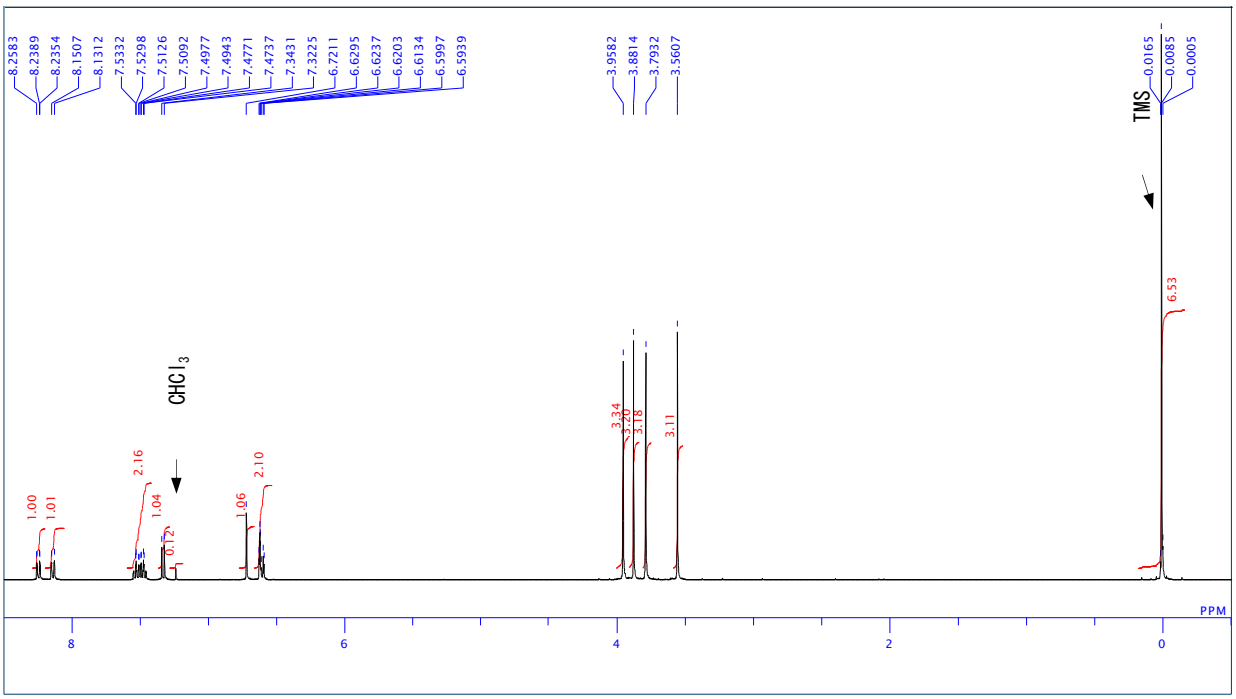
3ae

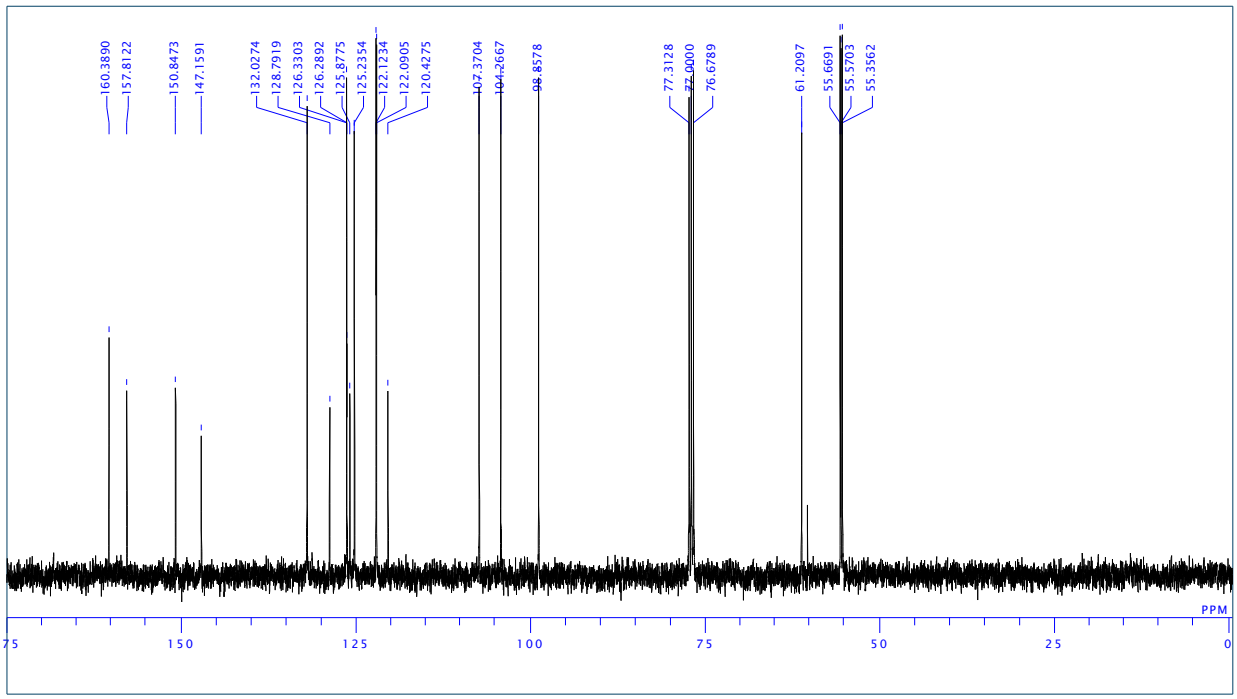


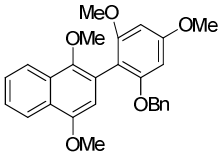



MeO
OMe
OMe
OMe

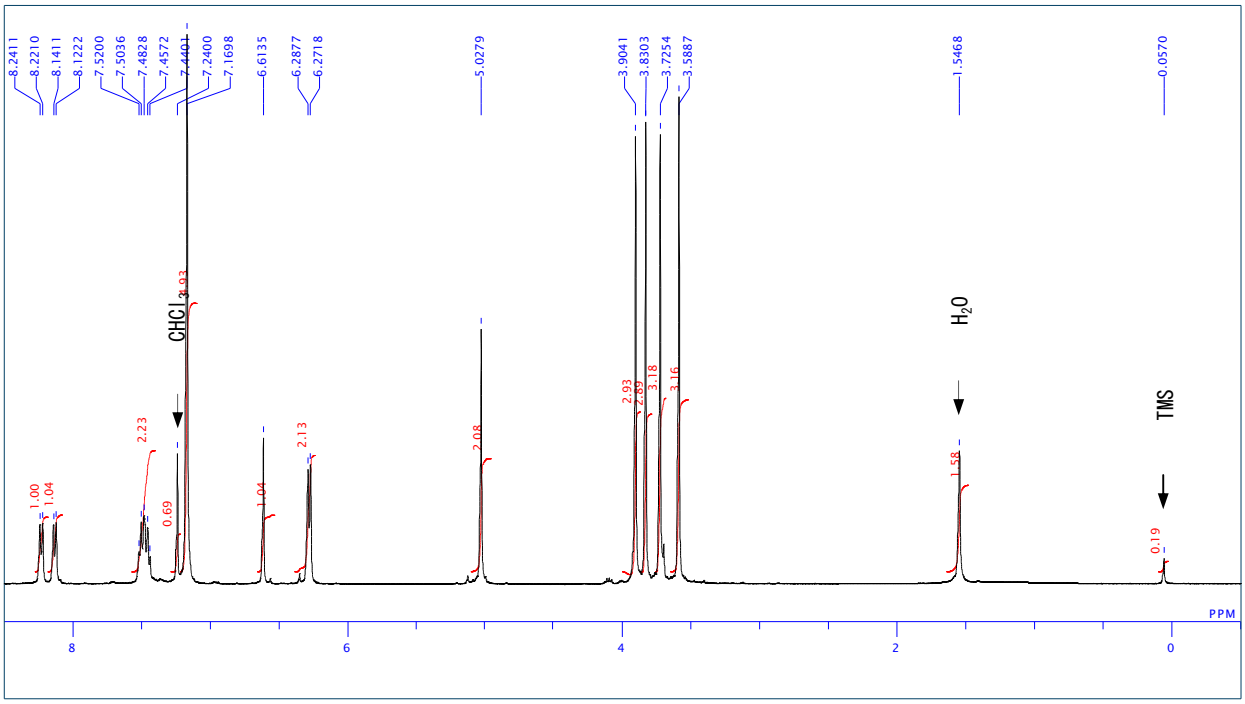
3af

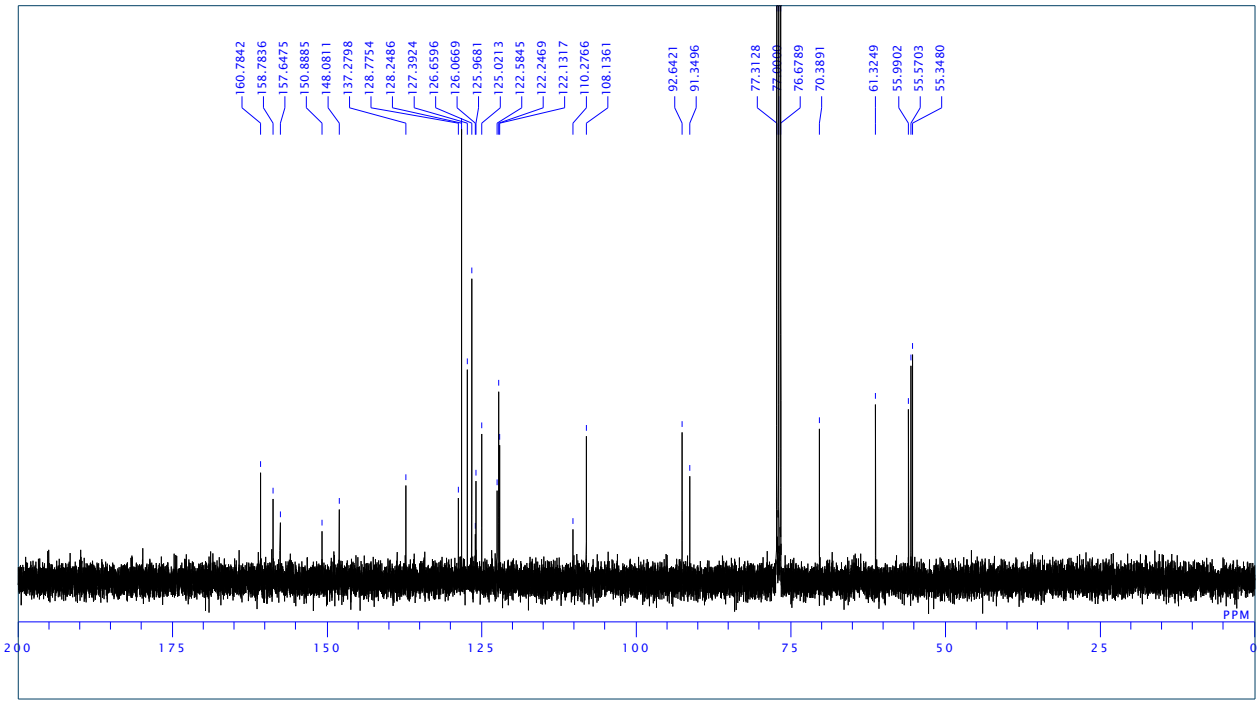

8.2583
8.2389
8.2354
8.1507
8.1312
7.5332
7.5298
7.5126
7.5092
7.4977
7.4943
7.4771
7.4737
7.3431
7.3225
7.2211
6.6295
6.6237
6.6203
6.6134
6.5997
6.5939
3.9582
3.8814
3.7932
3.5607
0.0165
0.0085
0.0005
TMS
6.53
3.34
3.20
3.18
3.11
2.16
2.10
1.06
1.04
1.00
1.01
0.12
CHCl3
PPM
8
6
4
2
0

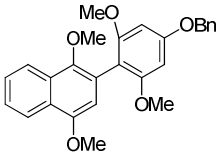

160.3890
157.8122
150.8473
147.1591
132.0274
128.7919
126.3303
126.2892
125.8775
125.2354
122.1234
122.0905
120.4275
107.3704
104.2667
98.8578
77.3128
77.0000
76.6789
61.2097
55.6691
55.5703
55.3562
PPM
175
150
125
100
75
50
25
0



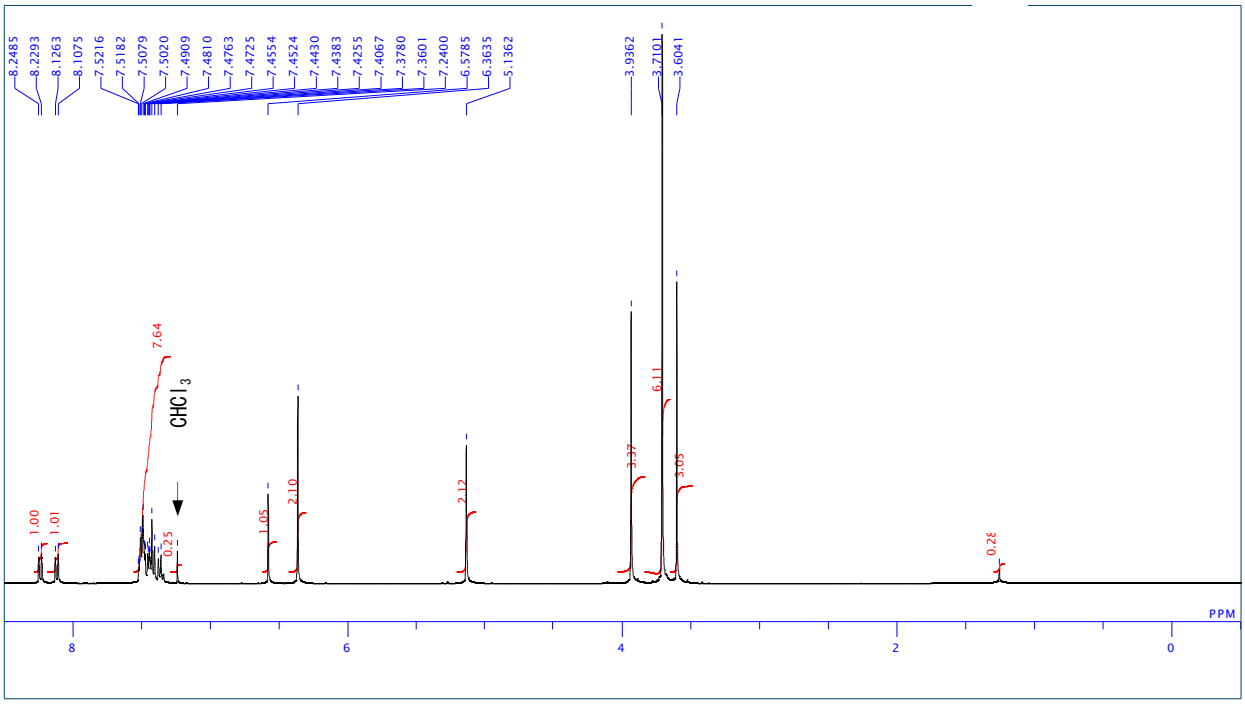
3ag (major product)

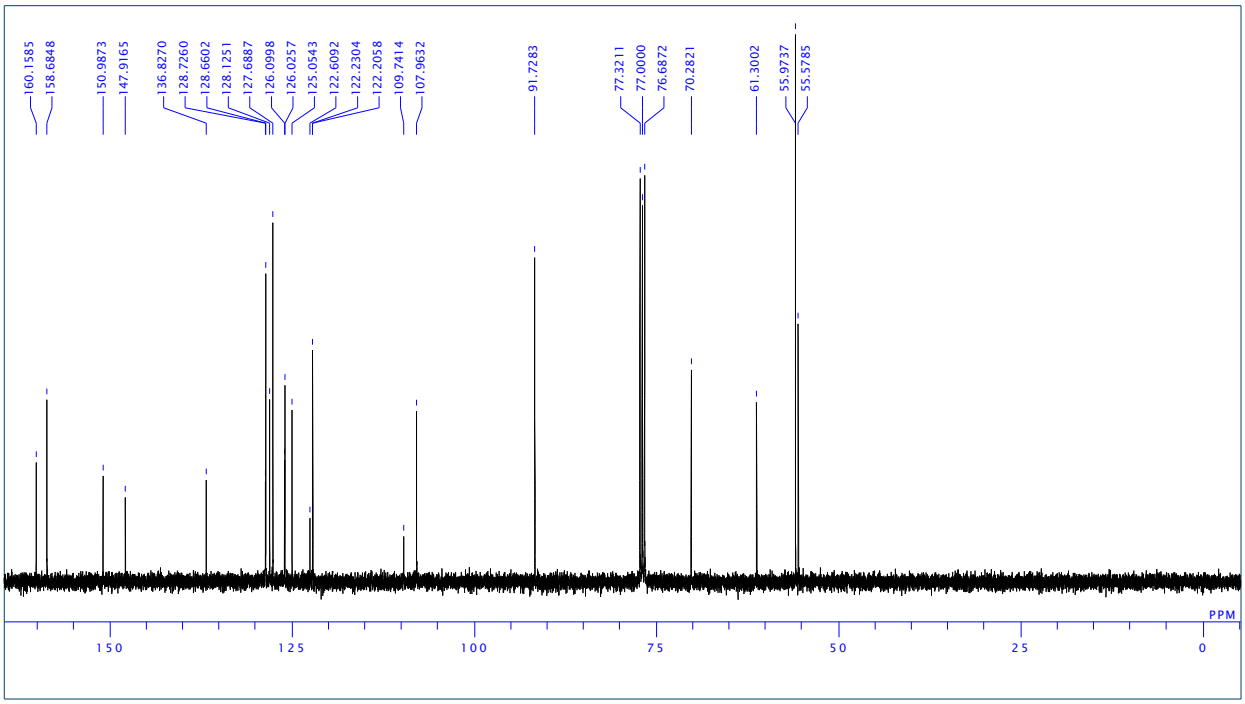


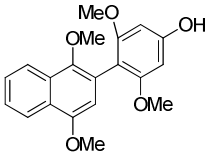




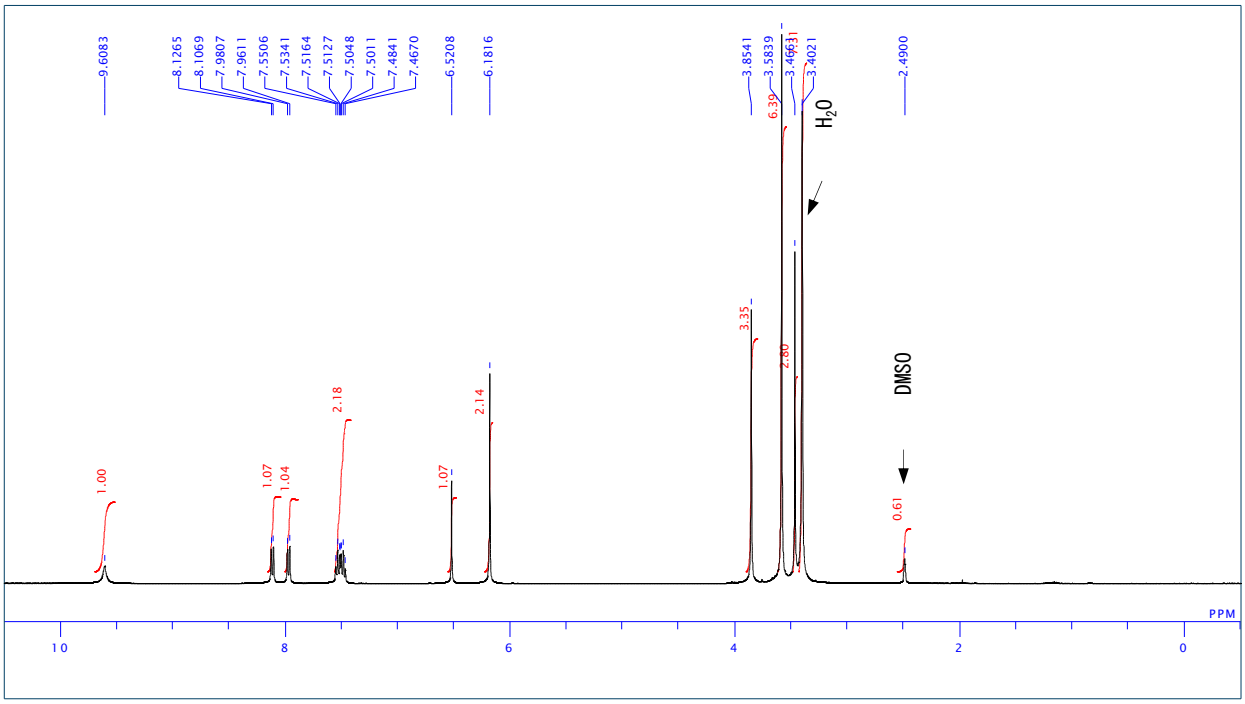
3'ag (minor product)

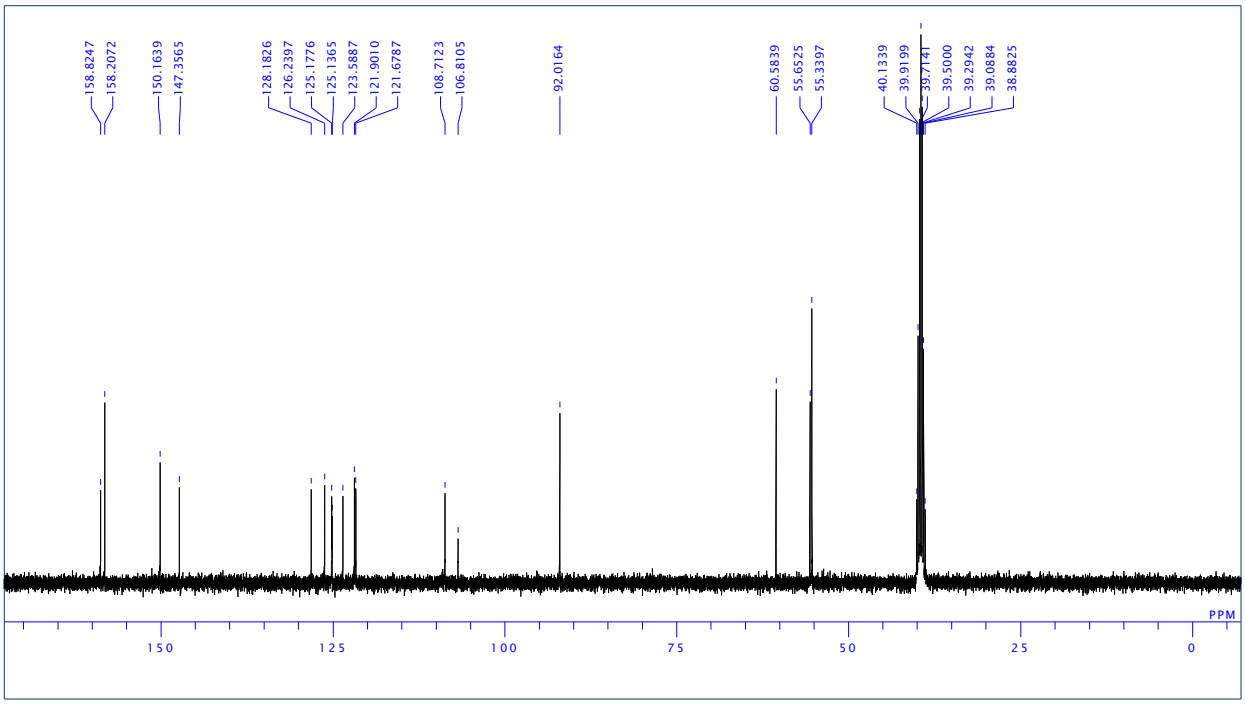


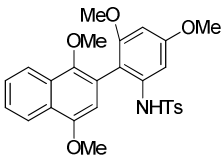




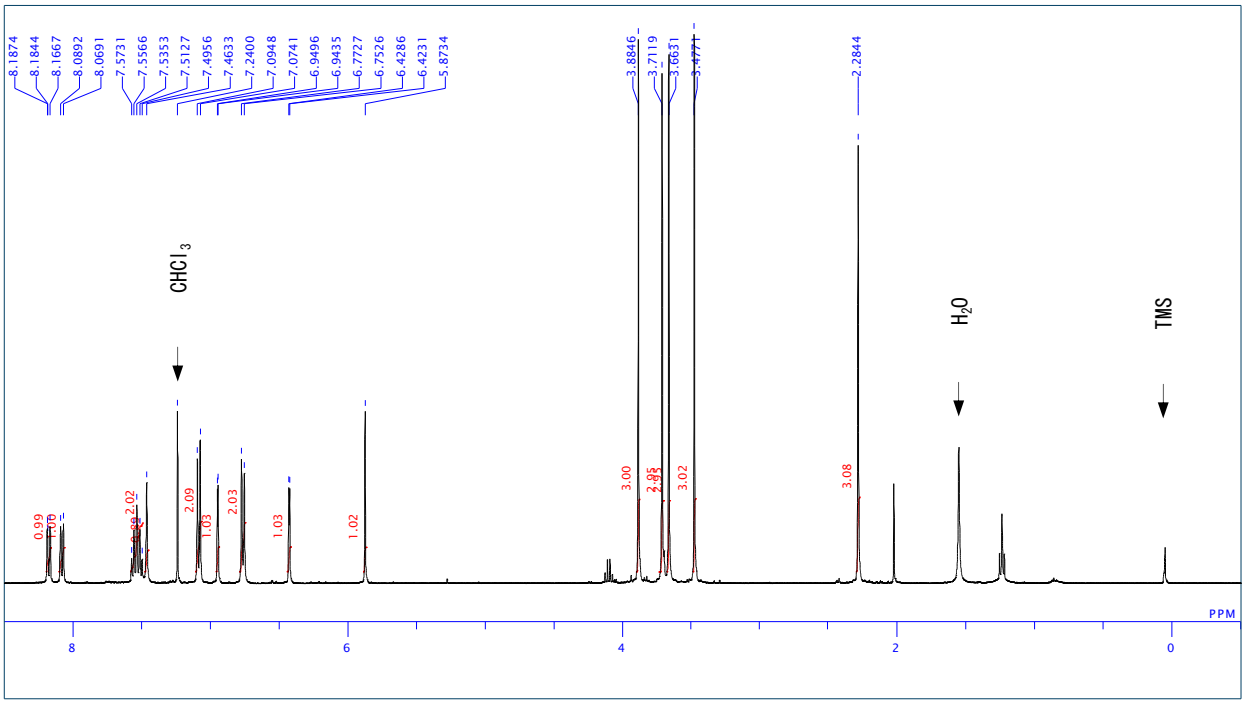
3'ah (sole product)

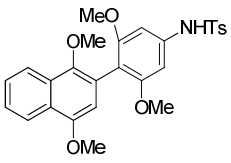




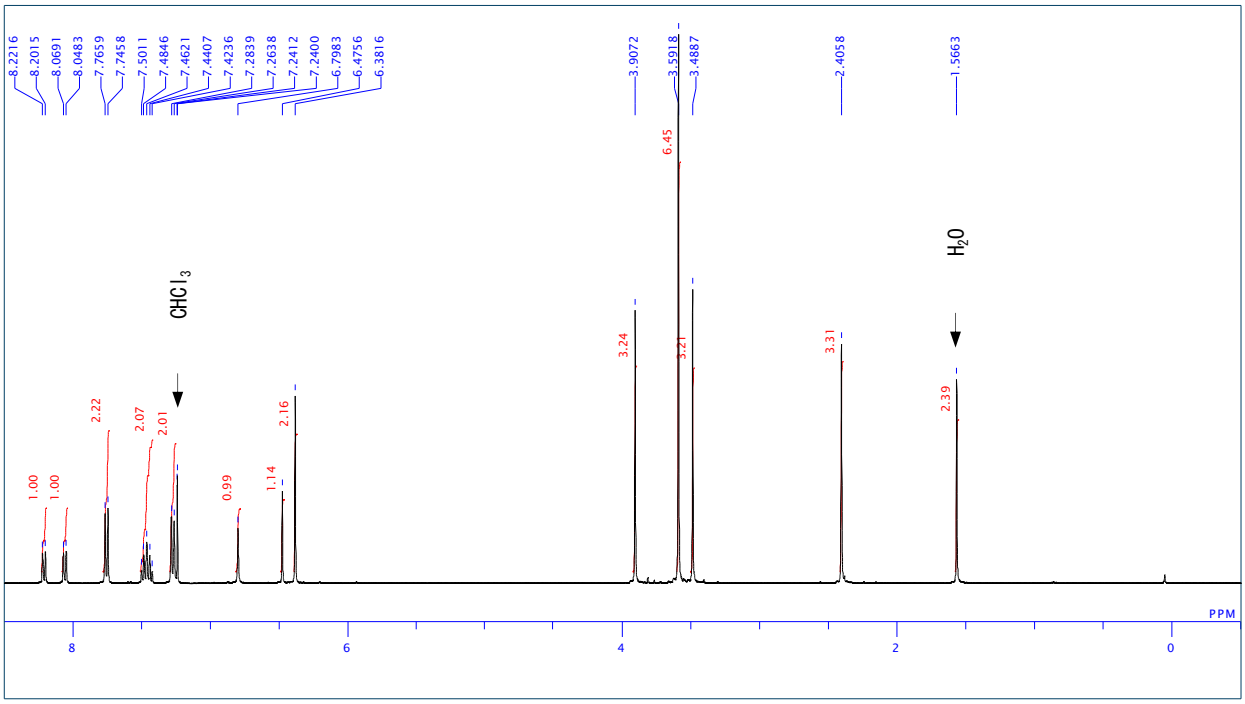


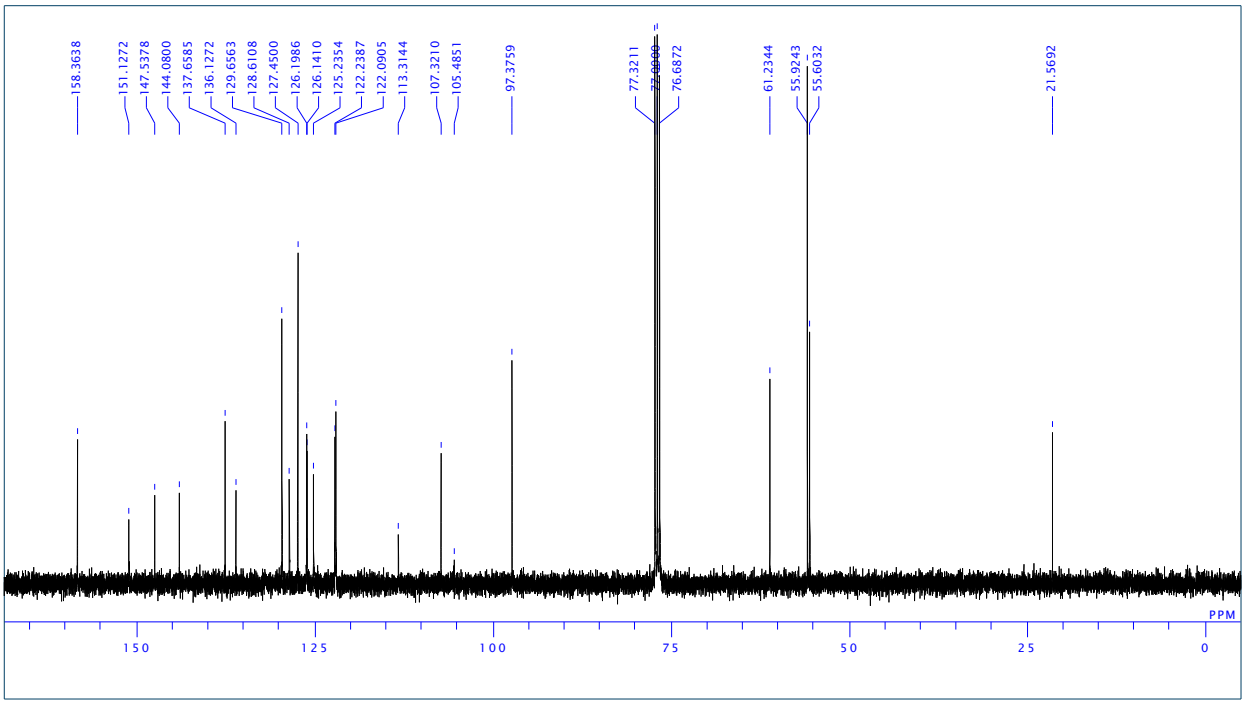
3ai (minor product)

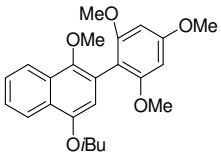




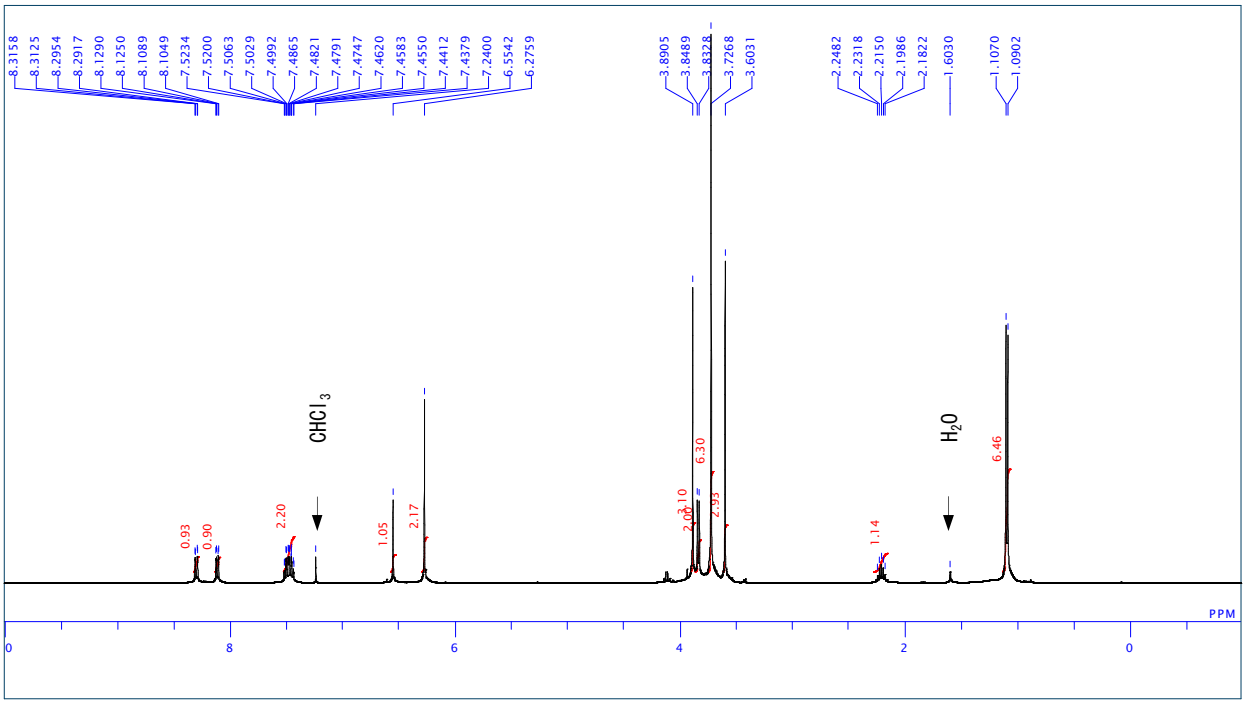
3'ai (major product)

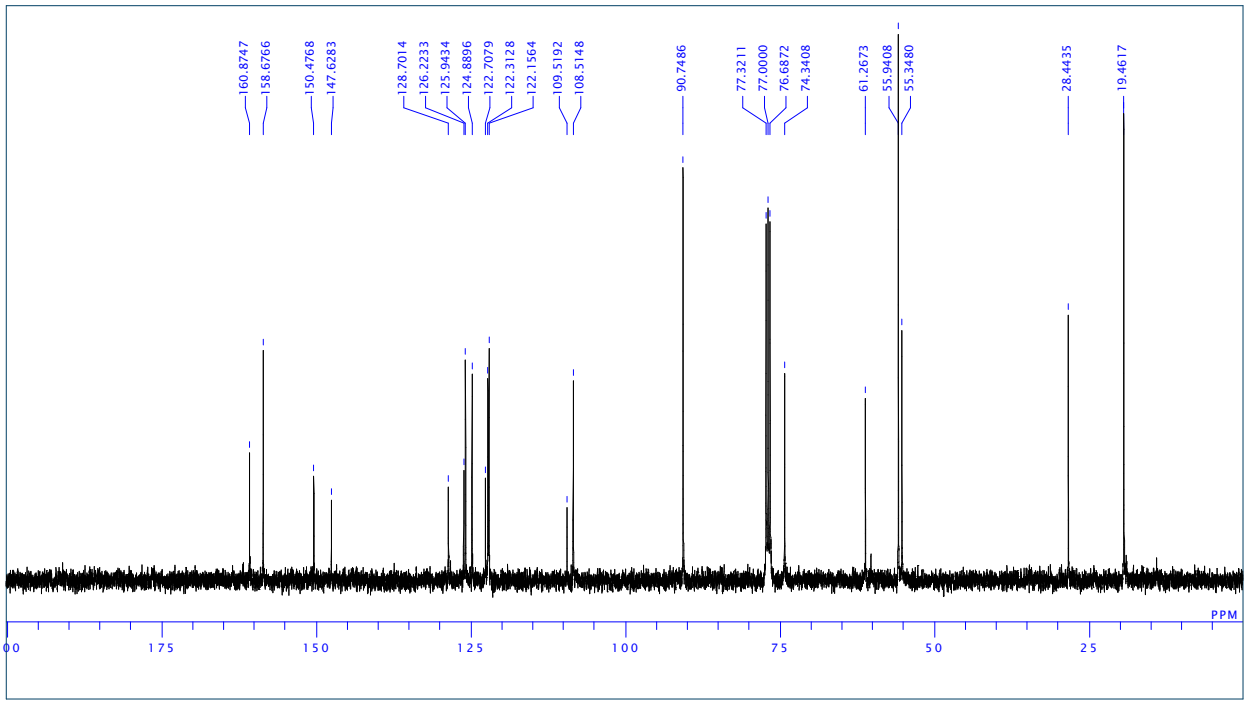


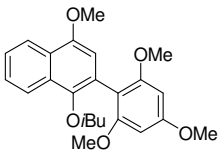



MeO
OMe
OMe
OMe
O*i*Bu

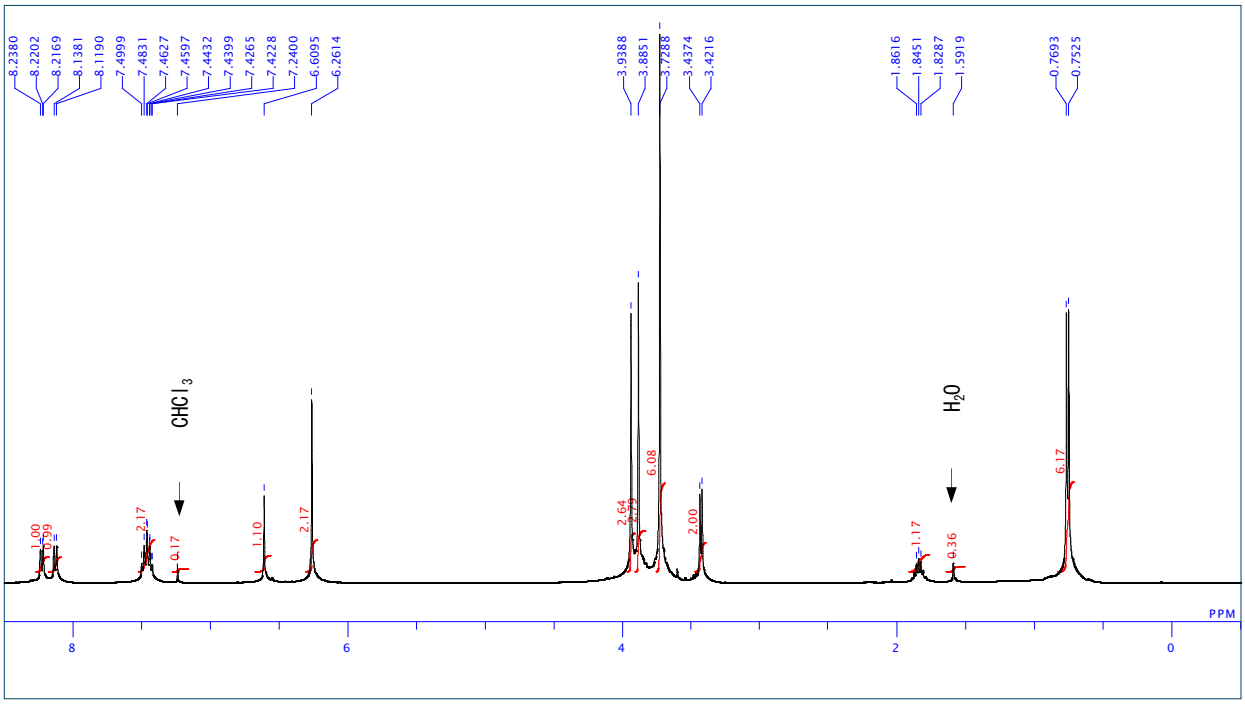
3bb

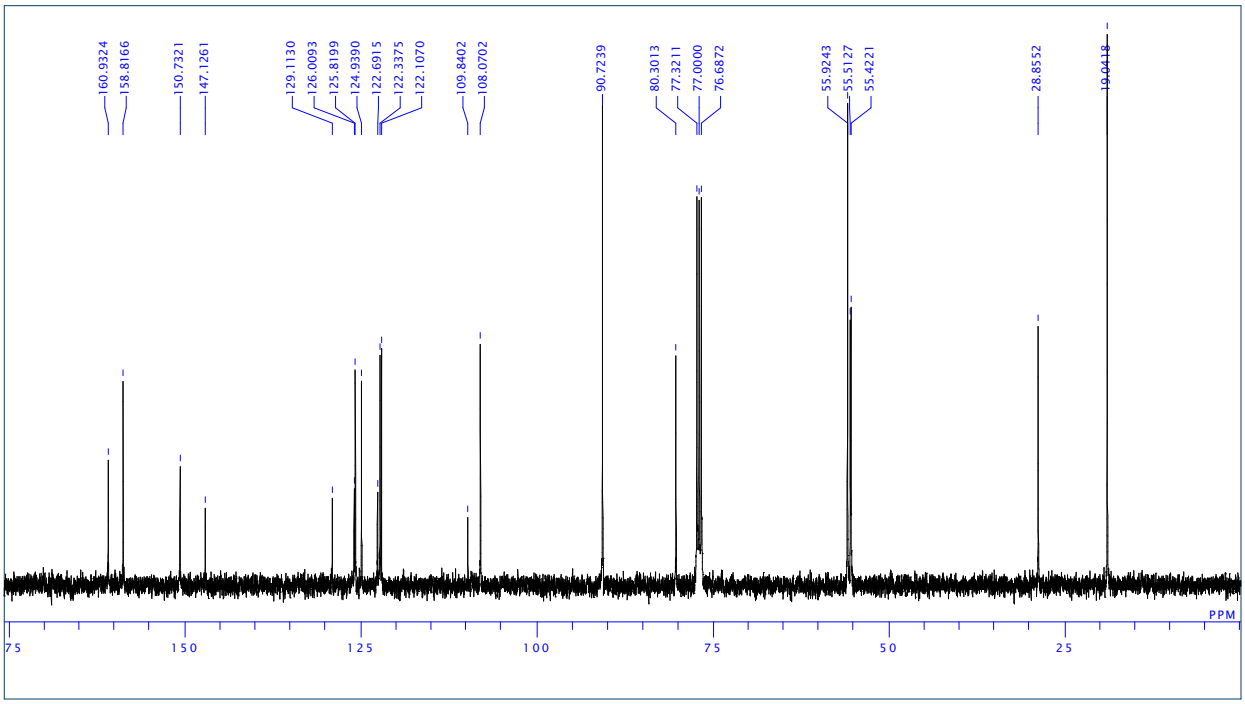

8.3158
8.3125
8.2954
8.2917
8.1290
8.1250
8.1089
8.1049
7.5234
7.5200
7.5063
7.5029
7.4992
7.4865
7.4821
7.4791
7.4747
7.4620
7.4583
7.4550
7.4412
7.4379
7.2400
6.5542
6.2759
3.8905
3.8489
3.8328
3.7268
3.6031
2.2482
2.2318
2.2150
2.1986
2.1822
1.6030
1.1070
1.0902
CHCl3
H2O
0.93
0.90
2.20
1.05
2.17
3.10
2.00
6.30
2.93
1.14
6.46
PPM
10
8
6
4
2
0

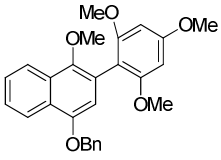

160.8747
158.6766
150.4768
147.6283
128.7014
126.2233
125.9434
124.8896
122.7079
122.3128
122.1564
109.5192
108.5148
90.7486
77.3211
77.0000
76.6872
74.3408
61.2673
55.9408
55.3480
28.4435
19.4617
PPM
200
175
150
125
100
75
50
25


OMe
OMe
OiBu
MeO
OMe

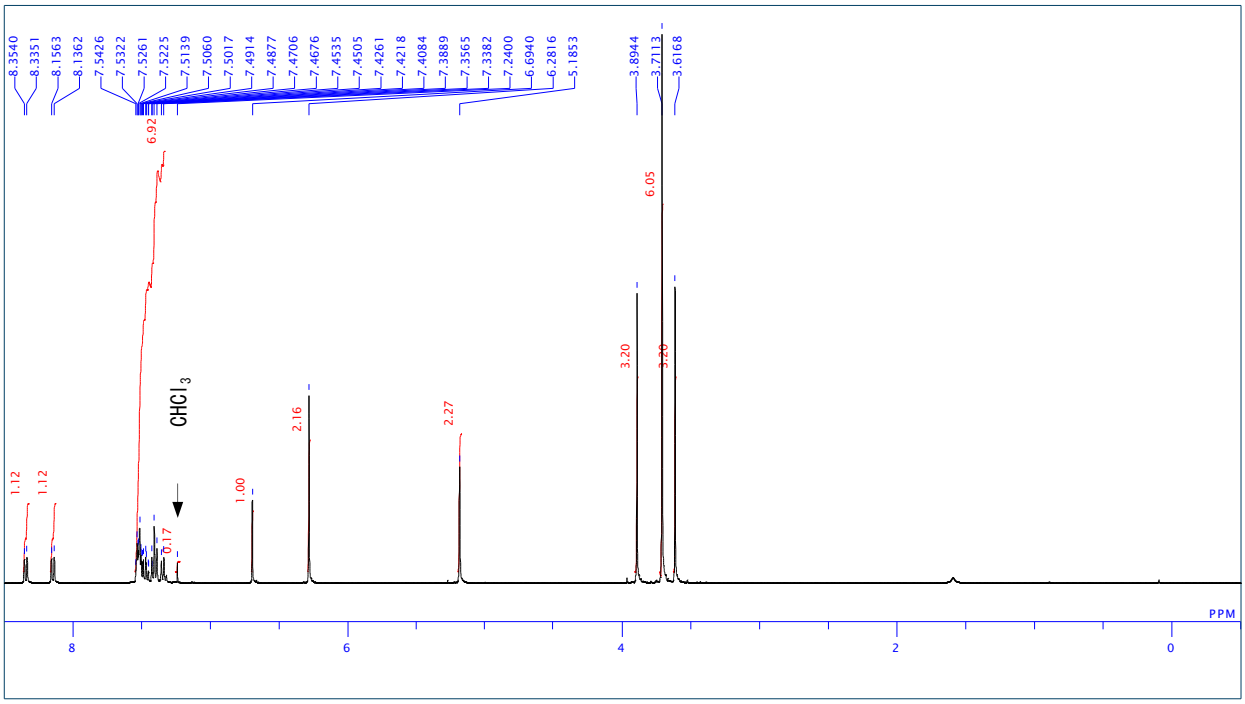
3'bb

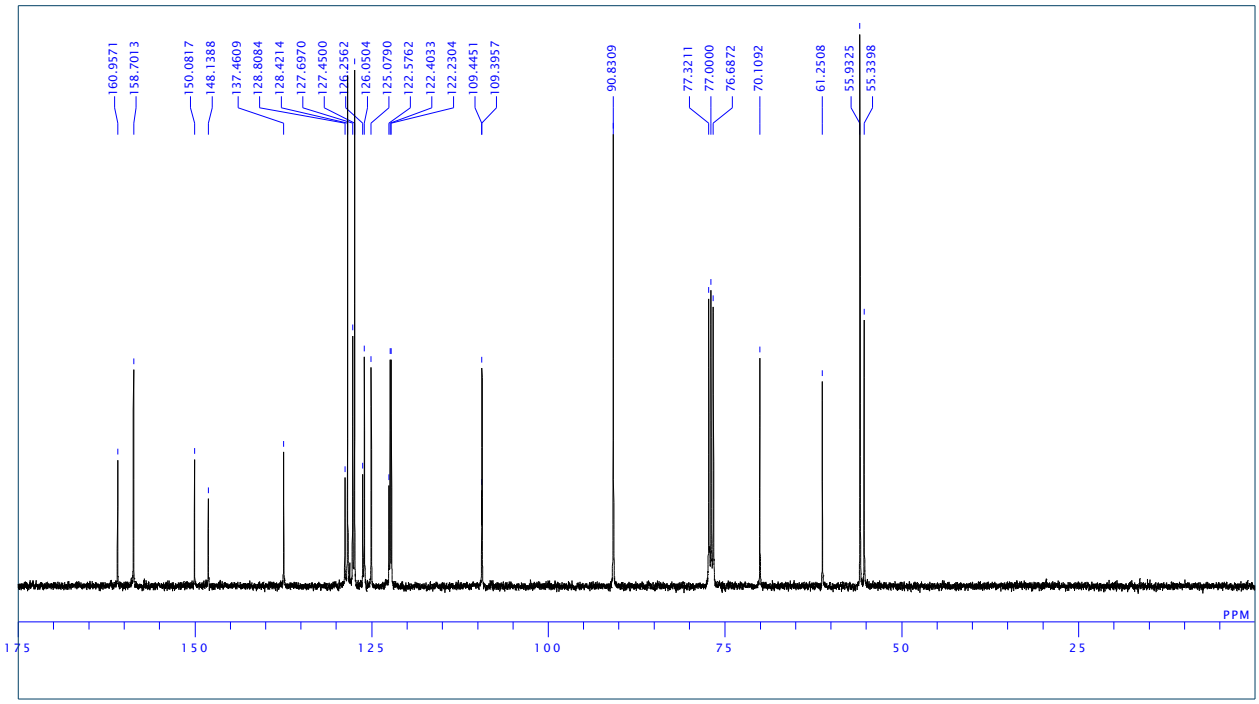

8.2380
8.2202
8.2169
8.1381
8.1190
7.4999
7.4831
7.4627
7.4597
7.4432
7.4399
7.4265
7.4228
7.2400
6.6095
6.2614
3.9388
3.8851
3.7288
3.4374
3.4216
1.8616
1.8451
1.8287
1.5919
0.7693
0.7525
CHCl3
H2O
PPM

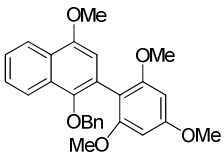

160.9324
158.8166
150.7321
147.1261
129.1130
126.0093
125.8199
124.9390
122.6915
122.3375
122.1070
109.8402
108.0702
90.7239
80.3013
77.3211
77.0000
76.6872
55.9243
55.5127
55.4221
28.8552
19.0418
PPM



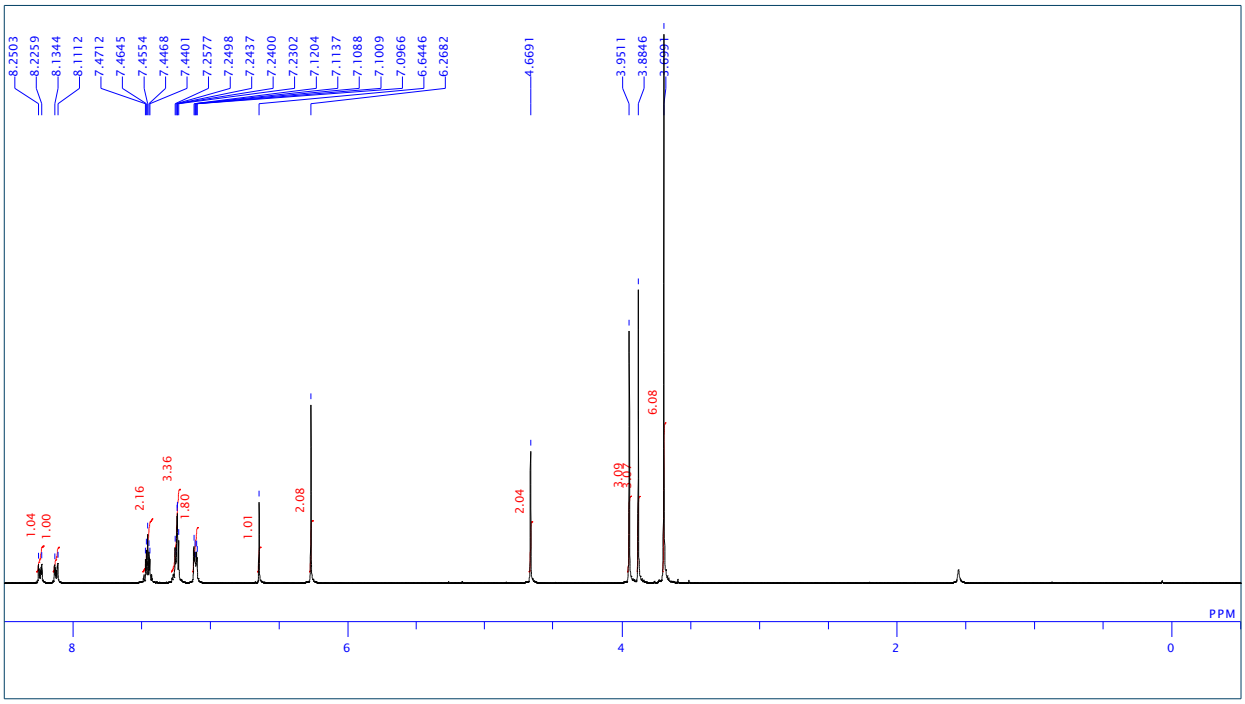
3cb (major product)

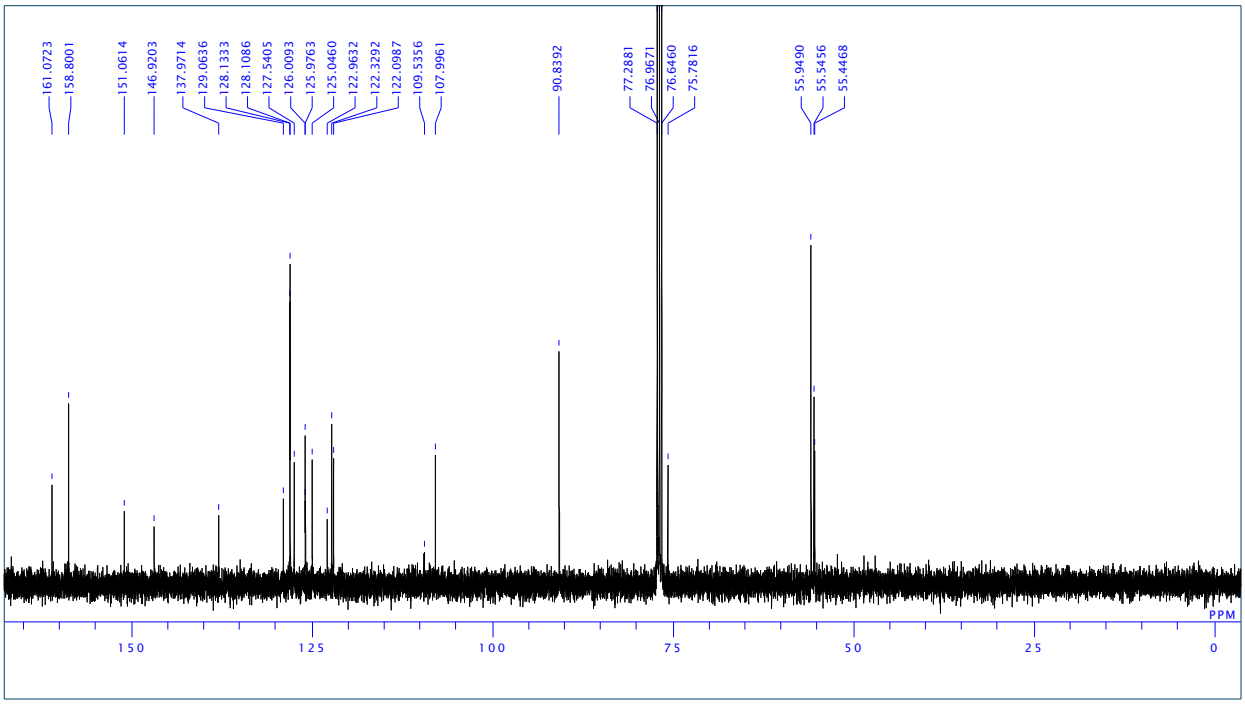


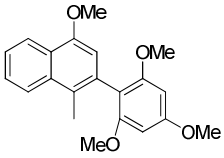




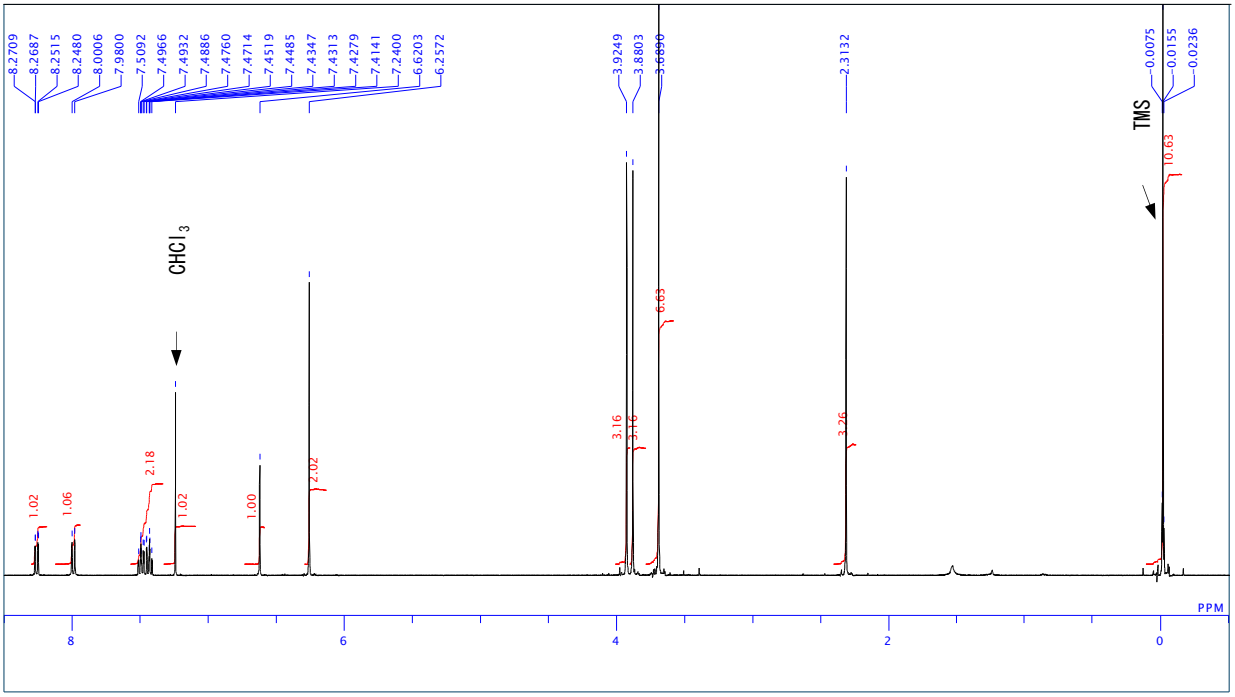
3'cb (minor product)

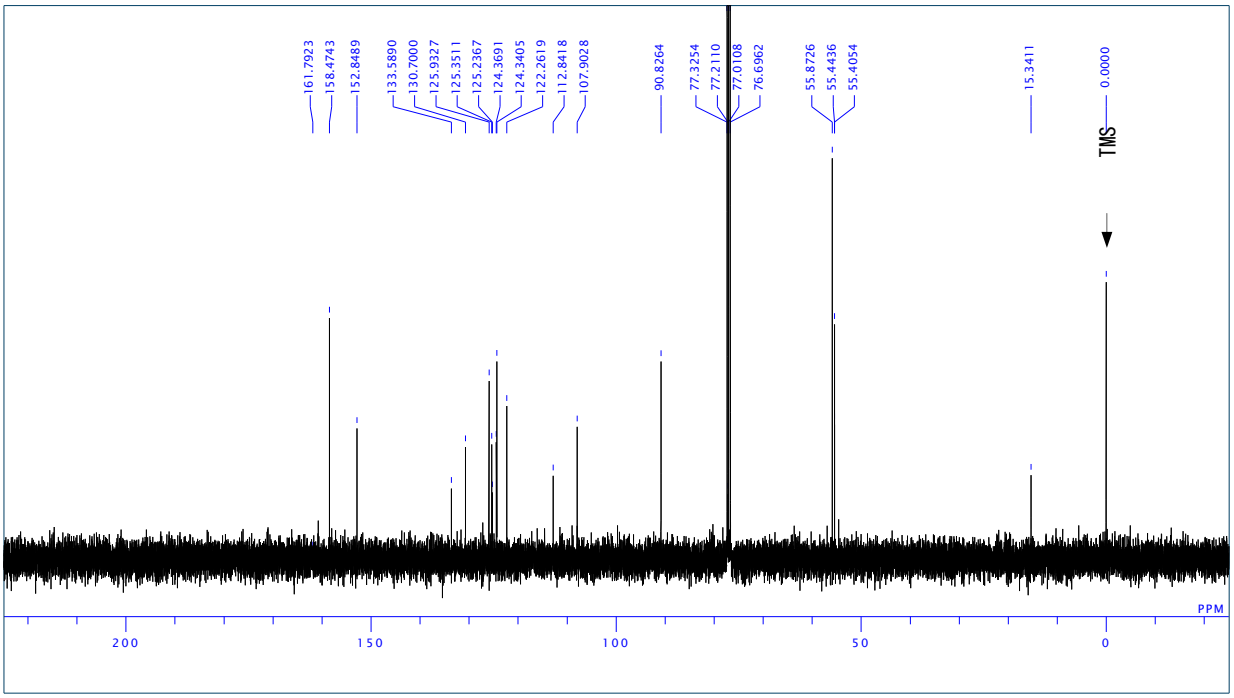


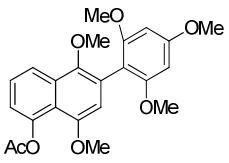




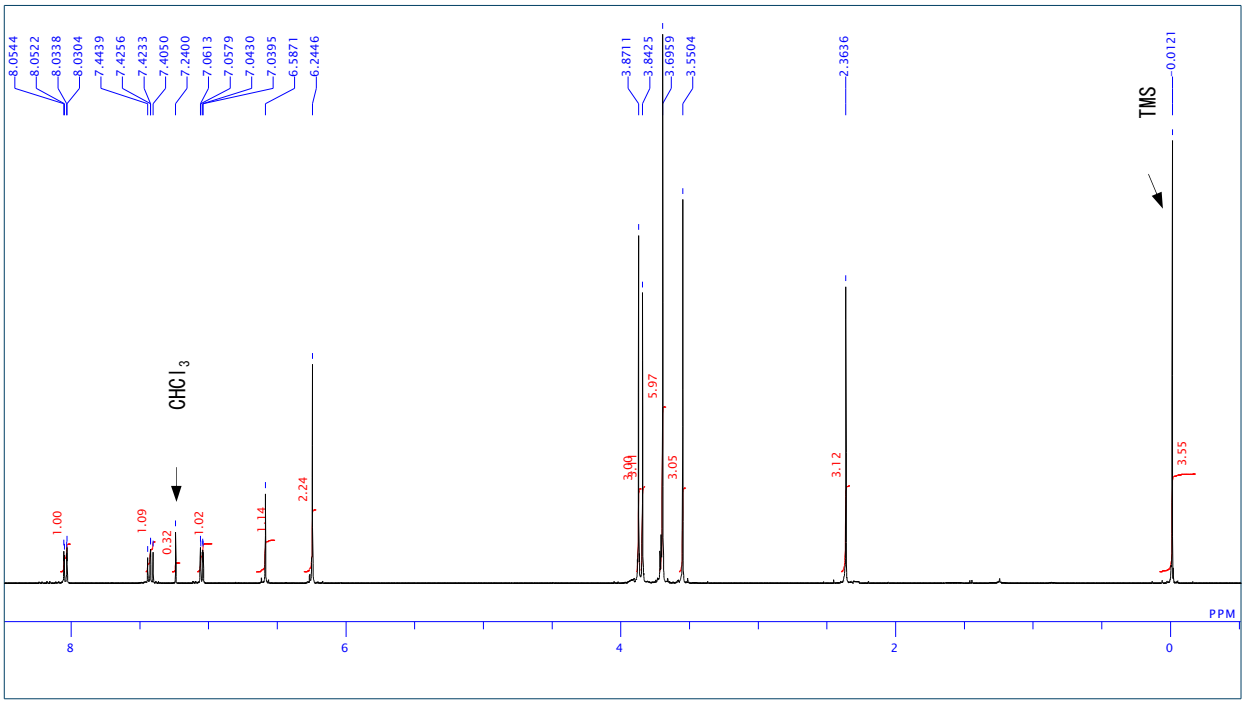
3'db (sole product)

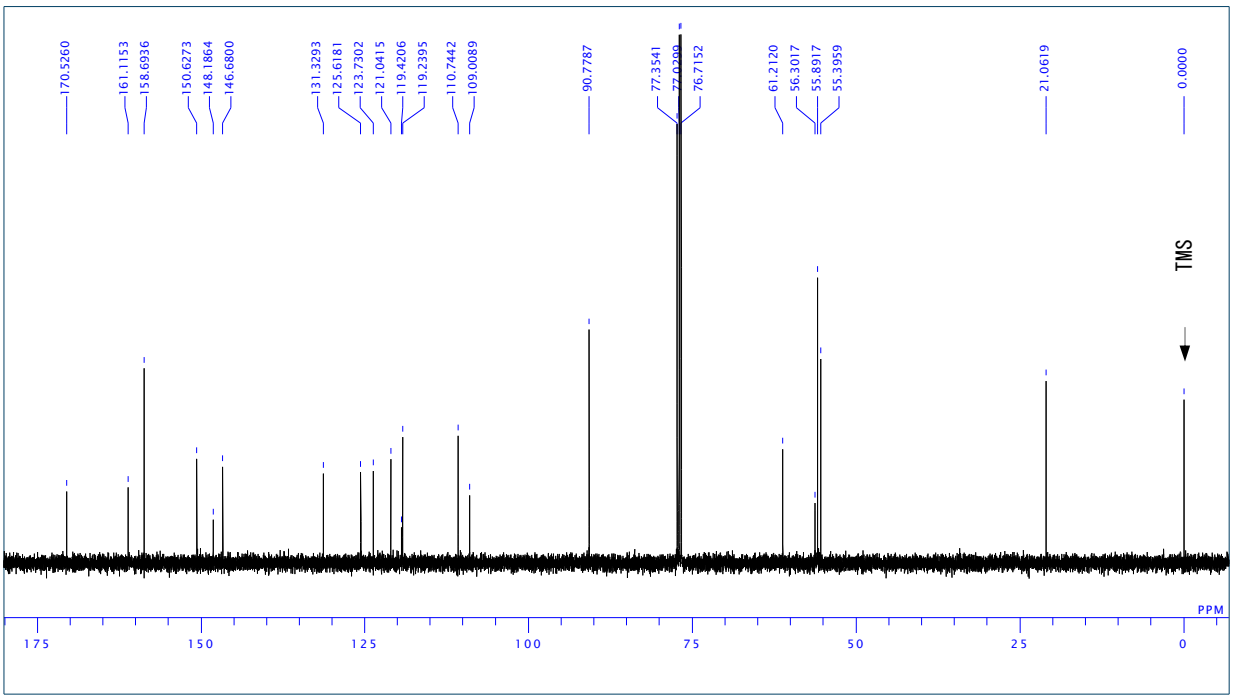


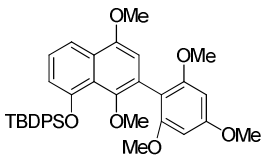




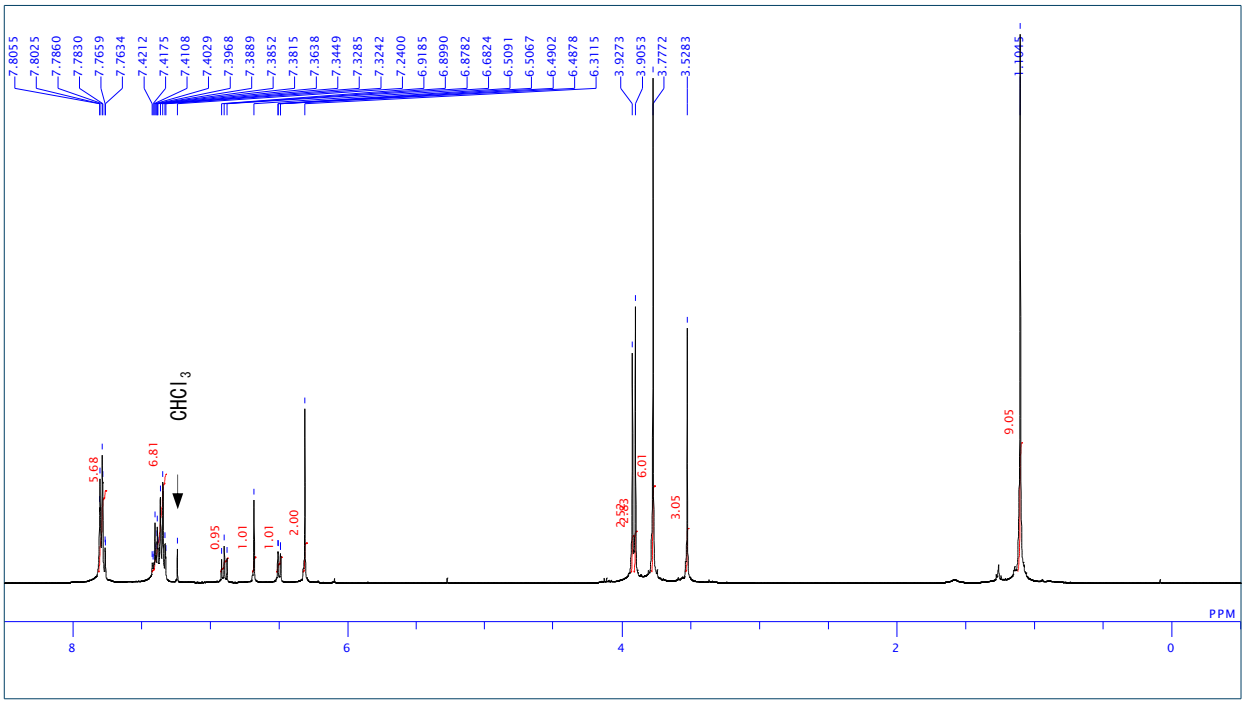
3eb (major product)

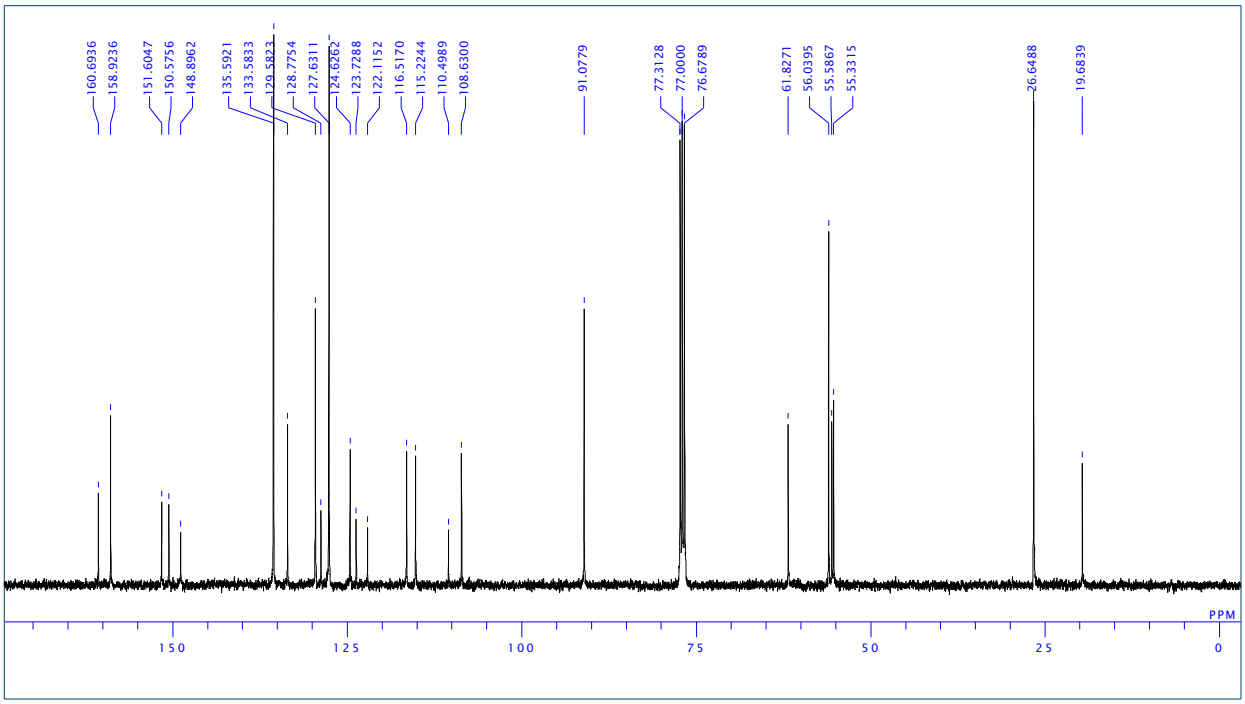


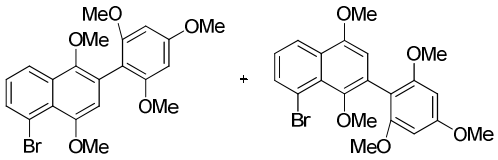




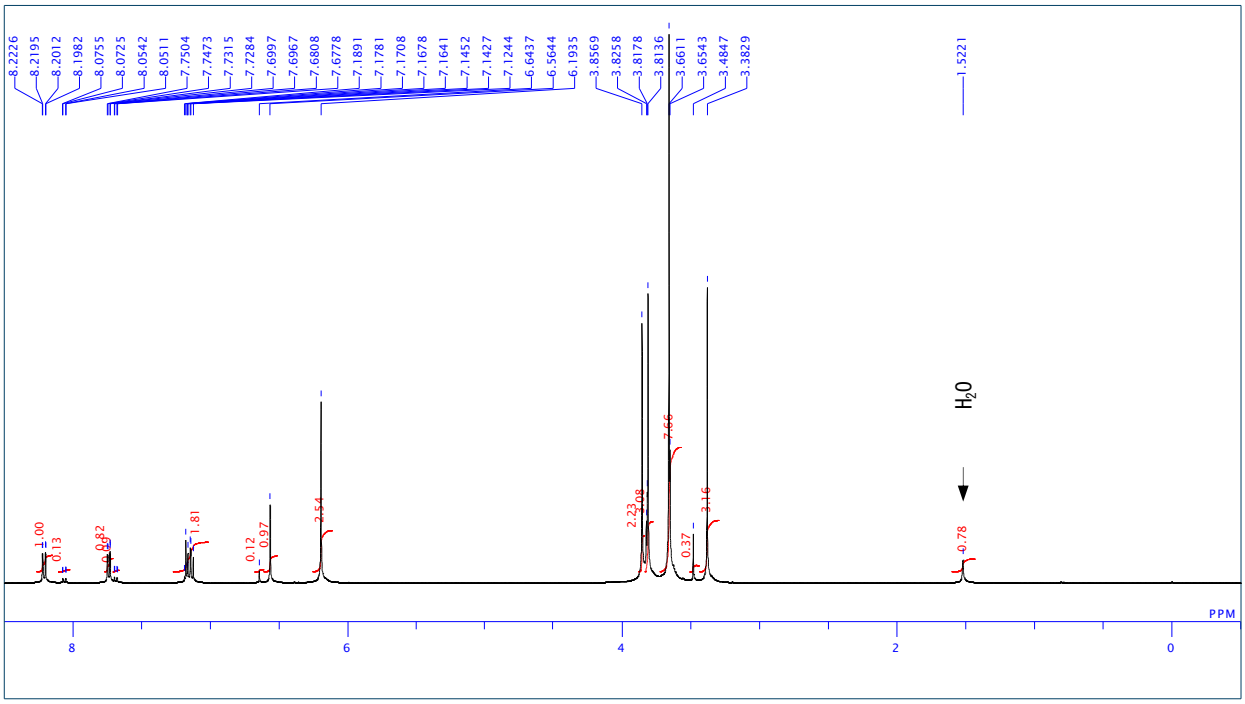
3'fb (sole product)

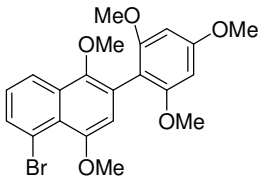






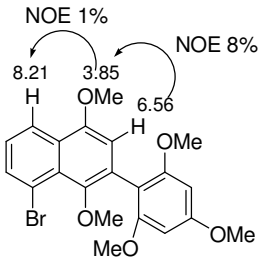
3gb (minor product) 3'gb (major product)





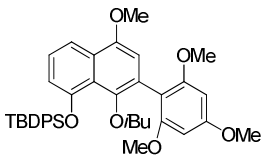
3gb (minor)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48 (s, 3H), 3.65-3.86 (m, 12H), 6.19 (s, 2H), 6.64 (s, 1H), 7.12-7.17 (m, 1H), 7.69 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.06 (dd, *J* = 8.4, 1.2 Hz, 1H) ppm.

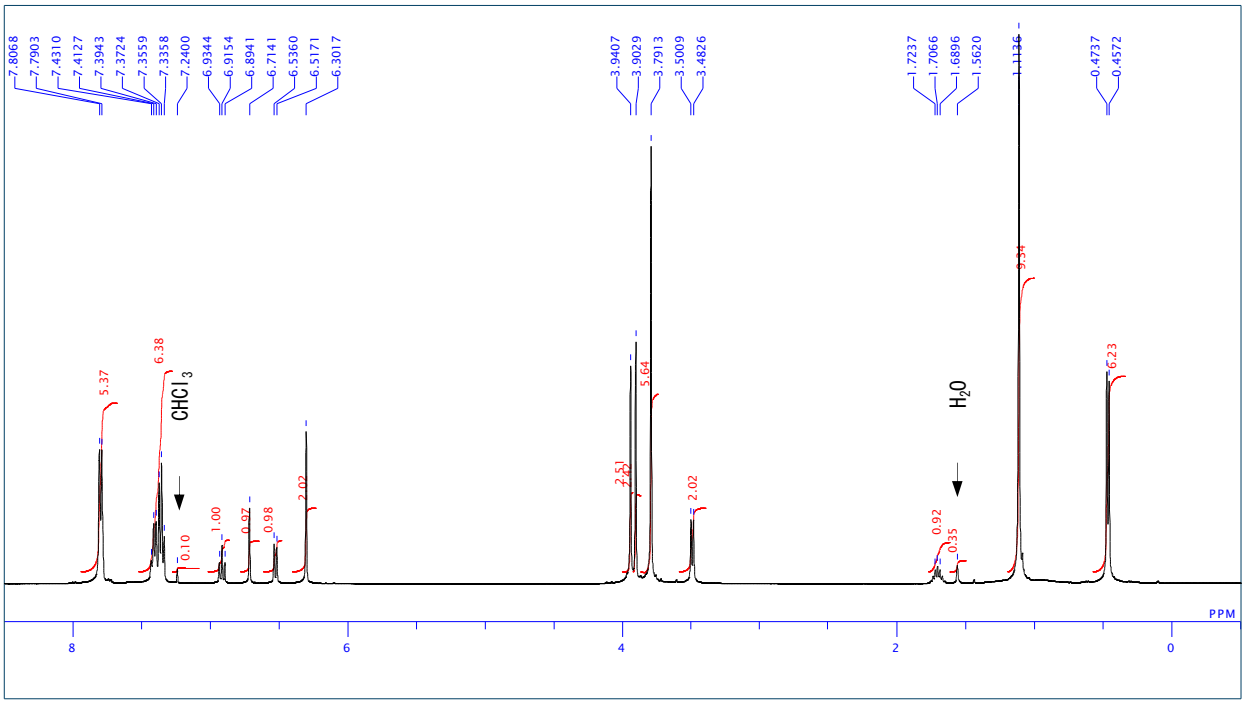


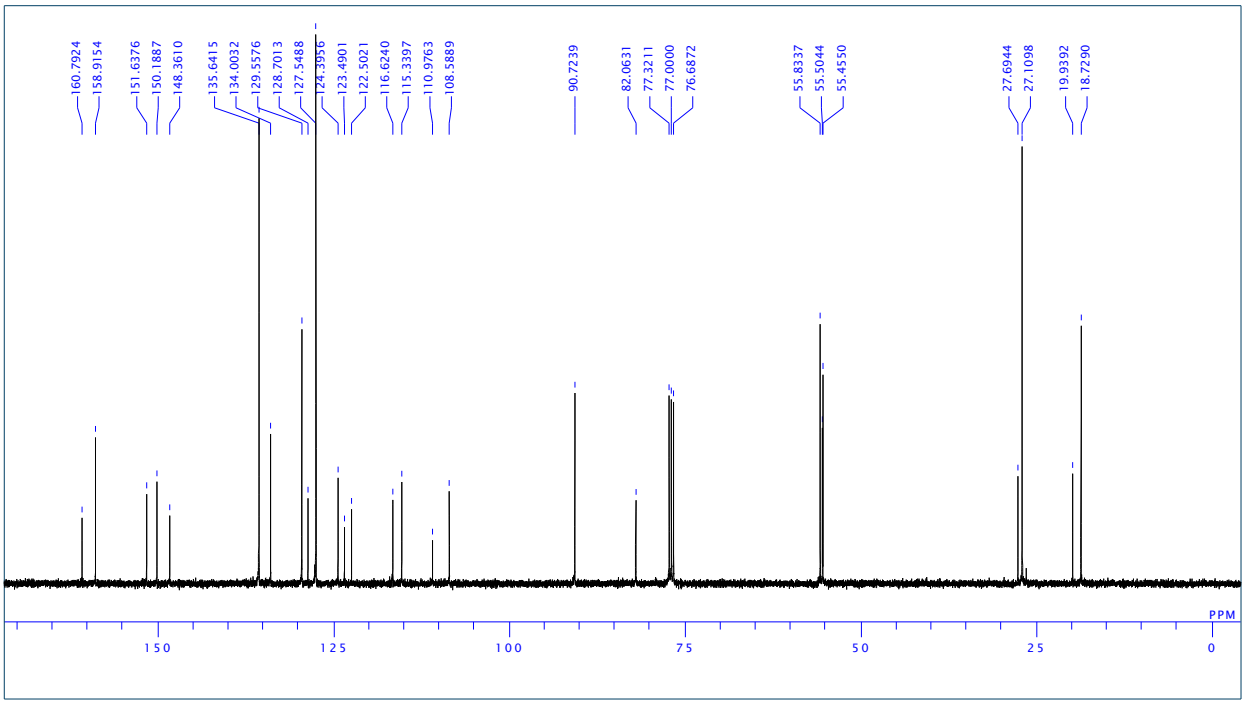
3'gb (major)

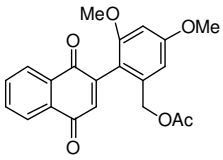
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (s, 3H), 3.65-3.86 (m, 12H), 6.19 (s, 2H), 6.56 (s, 1H), 7.12-7.17 (m, 1H), 7.74 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.21 (dd, *J* = 8.4, 1.2 Hz, 1H) ppm.



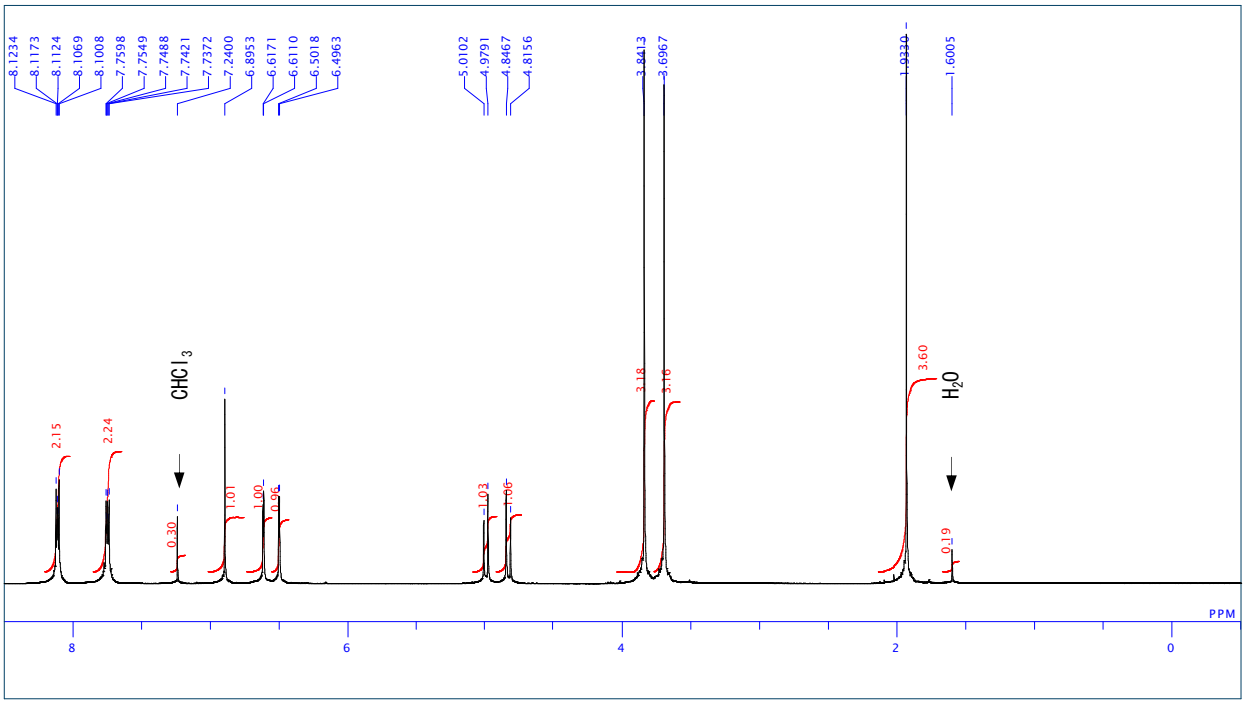
3'hb (sole product)

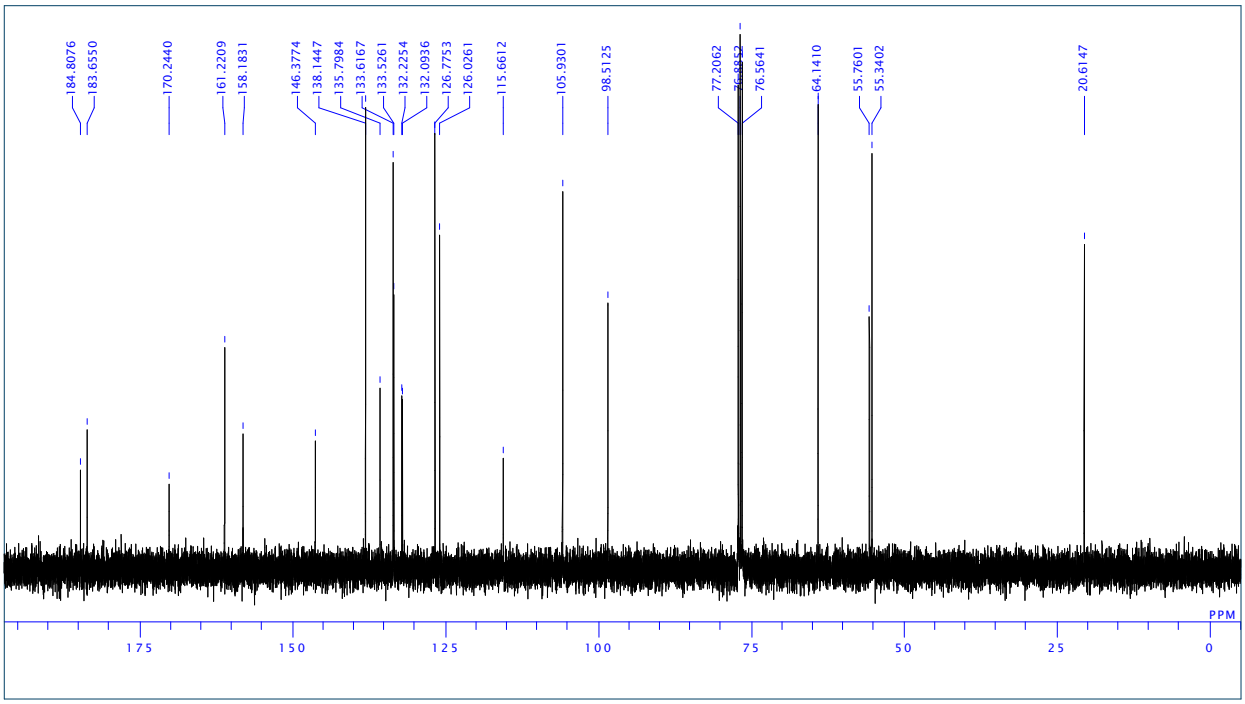


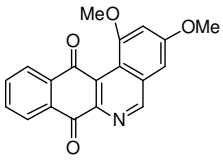



MeO
OMe
O
OAc
O

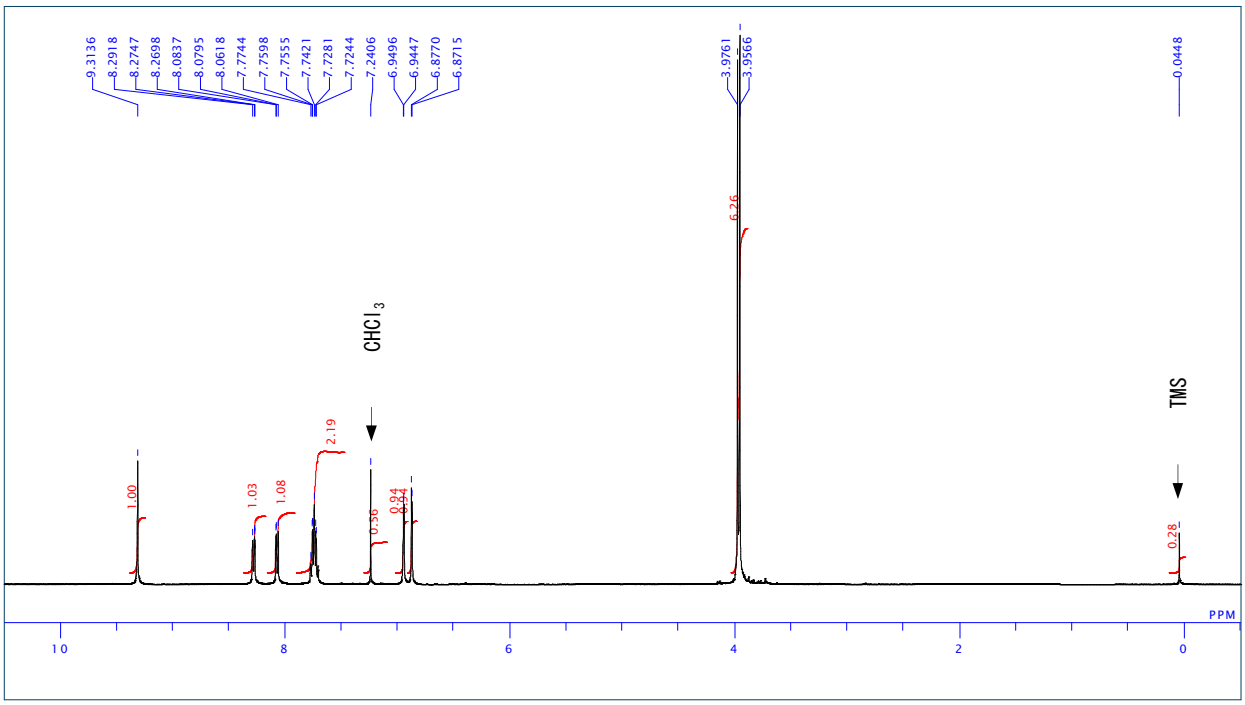
4

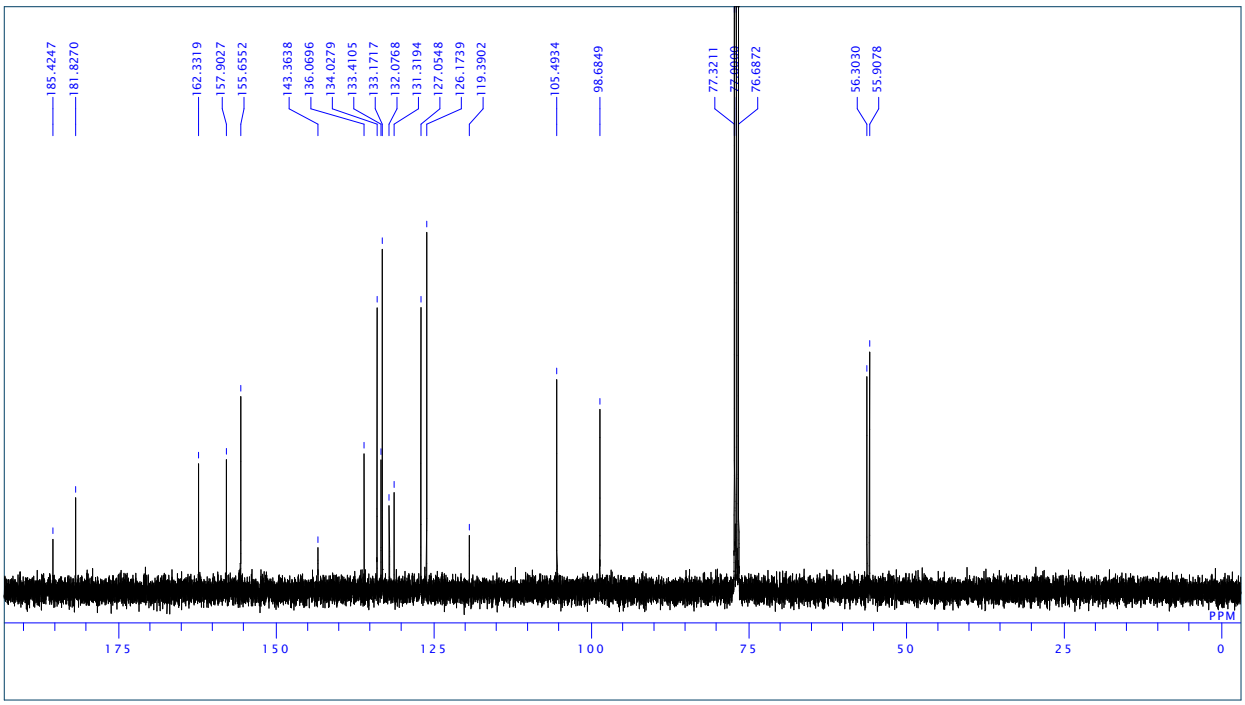

8.1234
8.1173
8.1124
8.1069
8.1008
7.7598
7.7549
7.7488
7.7421
7.7372
7.2400
6.8953
6.6171
6.6110
6.5018
6.4963
5.0102
4.9791
4.8467
4.8156
3.8413
3.6967
1.9330
1.6005
CHCl3
H2O
2.15
2.24
0.30
1.01
1.00
0.96
1.03
1.06
3.18
3.16
3.60
0.19
PPM
8
6
4
2
0


184.8076
183.6550
170.2440
161.2209
158.1831
146.3774
138.1447
135.7984
133.6167
133.5261
132.2254
132.0936
126.7753
126.0261
115.6612
105.9301
98.5125
77.2062
76.8852
76.5641
64.1410
55.7601
55.3402
20.6147
PPM
175
150
125
100
75
50
25
0


MeO
OMe
O
O
N
O

6


9.3136
8.2918
8.2747
8.2698
8.0837
8.0795
8.0618
7.7744
7.7598
7.7555
7.7421
7.7281
7.7244
7.2406
6.9496
6.9447
6.8770
6.8715
3.9761
3.9566
0.0448
6.26
CHCl3
TMS
2.19
1.00
1.03
1.08
0.56
0.94
0.94
0.28
PPM
10
8
6
4
2
0


185.4247
181.8270
162.3319
157.9027
155.6552
143.3638
136.0696
134.0279
133.4105
133.1717
132.0768
131.3194
127.0548
126.1739
119.3902
105.4934
98.6849
77.3211
77.0000
76.6872
56.3030
55.9078
PPM
175
150
125
100
75
50
25
0