SUPPORTING INFORMATION

Single-step synthesis of 3-hydroxycarbazoles by annulation of electron-rich anilines and quinones

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Experimental section

Unless stated otherwise, the carbazole formation reactions were performed under an ambient atmosphere of nitrogen in 20 mL vials sealed by Teflon-lined caps and wrapped in aluminum foil. All solvents and commercially obtained reagents were used as received, unless specified otherwise. Anilines **1a**, **1b** and **1h** were synthesized via a reductive amination protocol according to a literature procedure.[1] Compound **1e** was prepared via a palladium-catalyzed amination by following a literature procedure.[2] Thin-layer chromatography (TLC) was conducted with EMD silica gel 60 F254 pre-coated plates and visualized using UV light (254 nm). Flash column chromatography was performed with pre-packed RediSep silica gel columns on a CombiFlash ISCO system using gradient EtOAc (or CH_2Cl_2) in hexanes, or MeOH in CH_2Cl_2 as eluent and detected with both 254 and 280 nm wavelengths. Analytical HPLC analyses were performed with an Agilent 1290 Infinity Series HPLC instrument. ^{1}H NMR spectra were recorded on a Bruker 300 (at 300 MHz) or 400 (at 400 MHz) and are reported relative to the residual solvent peak (δ 7.26 for $CDCl_3$, 2.50 for DMSO-d_6). ^{13}C NMR spectra were recorded on a Bruker 300 (at 75 MHz) or 400 (at 101 MHz) and are reported relative to the residual solvent peak (δ 77.0 for $CDCl_3$, 39.5 for DMSO-d_6). Melting points are uncorrected and were recorded on a Büchi Melting Point B-540 apparatus. IR spectra were recorded on a Bruker Alpha Platinum-ATR spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS data were obtained on a LTQ Orbitrap Discovery (Thermo Fisher Scientific) at Genentech, Inc.

Preparation of starting material

N,4-Dibenzyl-3,5-dimethoxyaniline (1i). To a mixture of 3,5-dimethoxyaniline (5.0 g, 33 mmol) and benzaldehyde (3.8 g, 1.1 equiv) in CH_2Cl_2 (50 mL) was added TFA (7.5 g, 2.0 equiv) at 0−10 °C. The resulting solution was stirred at 0−10 °C for 30 min and triethylsilane (7.5 g, 2.0 equiv) was added dropwise. The mixture was warmed to 20−25 °C and stirred for 3 h. The resulting white solid was filtered, washed with heptane (10 mL), dried under vacuum to give 4-benzyl-3,5-dimethoxyaniline (2.3 g, 29%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.21 − 7.17 (m, 2H), 7.13 − 7.08 (m, 3H), 6.32 (s, 2H), 3.73 (s, 6H). To a solution of 4-benzyl-3,5-dimethoxyaniline (2.1 g, 8.6 mmol) in MeOH (30 mL) was added benzaldehyde (2.1 g, 20 mmol, 2.3 equiv) at 0−10 °C. The resulting solution was stirred at 0−10 °C for 30 min and $NaBH(OAc)_3$ (3.5 g, 16.5 mmol, 2.0 equiv) was added portion-wise at 0−10 °C and then stirred for 2 h. The reaction mixture was quenched with satd aq NH_4Cl solution (20 mL), concentrated to remove MeOH and extracted with EtOAc (20 mL, ×2). The combined organic layers were washed with satd aq $NaHCO_3$ (20 mL), water (20 mL) and concentrated to afford an oil. The oil was crystallized from EtOAc/heptane (1/10) to give **1i** as an off-white solid (1.9 g, 66%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 − 7.30 (m, 4H), 7.22 − 7.06 (m, 5H), 6.18 (t, J = 5.6 Hz, 1H), 5.91 (s, 2H), 4.26 (d, J = 5.6 Hz, 2H), 3.62 (s, 6H).

General procedure for the formation of 3-hydroxycarbazoles

To a 20 mL vial with a stir bar was added aniline (**1**, 1.0 mmol) and toluene (3.2 mL). The mixture was stirred to obtain a homogeneous solution. Then quinone (**2**, 1.1 equiv) and acetic acid (0.8 mL) were added. The mixture was vacuumed, back-filled with nitrogen (×3), stirred at room temperature and monitored by HPLC. Upon reaction completion based on HPLC analysis (> 95% conversion), the reaction mixture was concentrated and the residue was purified by silica gel column chromatography using appropriate eluent to give the desired product carbazole **3**.

9-Benzyl-5,7-dimethoxy-9H-carbazol-3-ol (3a). *N*-Benzyl-3,5-dimethoxyaniline[1] (**1a**, 243 mg, 1.0 mmol) and benzoquinone (**2a**, 172 mg, 1.1 mmol) were employed. The reaction was purified using 30−80% CH_2Cl_2 in hexanes. Compound **3a** was obtained as an off-white solid (220 mg, 66%); mp 158−160 °C; FTIR (thin film, cm^{-1}) 3502, 3352, 2842, 1631, 1264; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.82 (s, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.18 − 7.22 (m, 4H), 7.08 − 7.11 (m, 2H), 6.68 − 6.70 (m, 2H), 6.52 (s, 1H), 6.27 (d, J = 1.8 Hz, 1H), 5.46 (s, 2H), 3.93 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.9, 156.0, 150.9, 142.8, 138.0, 133.4, 128.4, 127.0, 126.7, 122.5, 115.6, 112.2, 109.1, 106.7, 105.0, 90.2, 86.1, 55.5, 55.4, 45.6, 39.4; HRMS (ESI+) calculated for $C_{21}H_{19}NO_3$ ([M +

H]$^+$), 334.1438; found, 334.1433. A reaction employing **1a** (1.0 g) and **2a** (0.71 g) afforded compound **3a** (0.90 g) in a same 66% yield after purification.

5,7-Dimethoxy-9-(4-methoxybenzyl)-9H-carbazol-3-ol (3b). 3,5-Dimethoxy-*N*-(4-methoxybenzyl)aniline[1] (**1b**, 273 mg, 1.0 mmol) and benzoquinone (**2a**, 119 mg, 1.1 mmol) were employed. The reaction was purified using 35−100% CH_2Cl_2 in hexanes. Compound **3b** was obtained as an off-white solid (211 mg, 58%); mp 185−186 °C; FTIR (thin film, cm^{-1}) 3388, 2966, 2932, 2842, 1456; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.85 (s, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.26 (d, J = 8.6 Hz, 1H), 7.10 (d, J = 8.7 Hz, 2H), 6.91 – 6.78 (m, 3H), 6.78 – 6.63 (m, 2H), 6.30 (d, J = 1.8 Hz, 1H), 5.41 (s, 2H), 3.97 (s, 3H), 3.82 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.8, 158.3, 156.0, 150.9, 142.7, 133.3, 130.0, 128.1, 122.5, 113.8, 112.1, 109.2, 106.7, 105.0, 90.1, 86.1, 55.5 55.4, 55.0, 45.1; HRMS (ESI+) calculated for $C_{22}H_{21}NO_4$ ([M + H]$^+$), 364.1543; found, 364.1534.

9-Allyl-5,7-dimethoxy-9H-carbazol-3-ol (3c). *N*-Allyl-3,5-dimethoxyaniline[3] (**1c,** 193 mg, 1.0 mmol) and benzoquinone (**2a**, 119 mg, 1.1 mmol) were employed. The reaction was purified using 30−80% CH_2Cl_2 in hexanes. Compound **3c** was obtained as a white solid (205 mg, 72%); mp 136−139 °C; FTIR (thin film, cm^{-1}) 3229, 2924, 2840, 1590, 1462; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.80 (s, 1H), 7.42 (d, J = 2.4 Hz, 1H), 7.19 (d, J = 8.7, 1H), 6.72 (dd, J = 8.6, 2.5 Hz, 1H), 6.58 (d, J = 1.9 Hz, 1H), 6.25 (d, J = 1.8 Hz, 1H), 5.93 (ddt, J = 17.0, 10.2, 5.0, 1H), 5.05 (dd, J = 10.3, 1.6 Hz, 1H), 4.90 (dd, J = 17.1, 1.7 Hz, 1H), 4.83 (d, J = 5.2 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.8, 156.0, 142.5, 133.3, 1m33.2, 122.3, 116.1, 112.1, 108.9, 106.7, 105.0, 90.1, 85.9, 55.5, 55.4, 44.7; HRMS (ESI+) calculated for $C_{17}H_{17}NO_3$ ([M + H]$^+$), 284.1281; found, 284.1284.

5,7-Dimethoxy-9-propyl-1H-carbazol-3-ol (3d). 3,5-Dimethoxy-*N*-propylaniline[4] (**1d**, 195 mg, 1.0 mmol) and benzoquinone (**2a**, 119 mg, 1.1 mmol) were employed. The reaction was purified using 0−25% EtOAc in hexanes. Compound **3d** was obtained as a pale yellow solid (255 mg, 89%); mp 121−123 °C; FTIR (thin film, cm^{-1}) 3364, 2960, 2933, 2842, 1630; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 2.6 Hz, 1H), 7.15 (d, J = 8.6 Hz, 1H), 6.89 (dd, J = 8.6, 2.6 Hz, 1H), 6.42 (d, J = 1.9 Hz, 1H), 6.26 (d, J = 1.9 Hz, 1H), 4.69 (s, 1H), 4.13 (t, J = 7.1 Hz, 2H), 3.99 (s, 3H), 3.91 (s, 3H), 1.85 (q, J = 7.3 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 156.8, 149.1, 143.2, 134.9, 123.0, 111.9, 108.3, 107.7, 105.9, 90.0, 85.3, 77.5, 77.0, 76.6, 55.7, 55.4, 44.8, 22.3, 11.8. HRMS (ESI+) calculated for $C_{17}H_{19}NO_3$ ([M + H]$^+$), 286.1438; found, 286.1438.

9-Benzyl-6-ethyl-5,7-dimethoxy-9H-carbazol-3-ol (3h). *N*-Benzyl-4-ethyl-3,5-dimethoxyaniline (**1h**, 271 mg, 1.0 mmol) and benzoquinone (**2a**, 119 mg, 1.1 mmol) were employed. The reaction was purified using 0−25% EtOAc in hexanes. Compound **3h** was obtained as a pale yellow oil (108 mg, 30%); FTIR (thin film, cm^{-1}) 3331, 2957, 2925, 2852, 1451; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 2.5 Hz, 1H), 7.27 (d, J = 6.7 Hz, 2H), 7.24 – 7.08 (m, 4H), 6.90 – 6.81 (m, 1H), 6.54 (s, 1H), 5.38 (s, 2H), 4.51 (s, 1H), 4.01 (s, 3H), 3.83 (s, 3H), 2.80 (q, J = 7.4 Hz, 2H), 1.21 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 154.0, 149.4, 141.8, 137.3, 135.4, 128.7, 127.4, 126.4, 122.5, 117.8, 112.6, 108.8, 107.7, 87.8, 61.1, 55.8, 46.9, 29.6, 16.8, 15.0. HRMS (ESI+) calculated for $C_{23}H_{23}NO_3$ ([M + H]$^+$), 362.1751; found, 362.1750.

6,9-Dibenzyl-5,7-dimethoxy-9H-carbazol-3-ol (3i). *N*,4-Dibenzyl-3,5-dimethoxyaniline (**1i**, 333 mg, 1.0 mmol) and benzoquinone (**2a**, 119 mg, 1.1 mmol) were employed. The reaction was purified using 0−20% EtOAc in hexanes. Compound **3i** was obtained as a yellow solid (90 mg, 21%); mp 213−214 °C; FTIR (thin film, cm^{-1}) 3437, 2997, 2921, 2836, 1613; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 2.5 Hz, 1H), 7.32 – 7.25 (m, 5H), 7.24 – 7.06 (m, 6H), 6.86 (dd, J = 8.6, 2.5 Hz, 1H), 6.57 (s, 1H), 5.39 (s, 2H), 4.49 (s, 1H), 4.16 (s, 2H), 3.90 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 154.6, 149.5, 142.4, 137.2, 135.4, 128.7, 128.4, 127.9, 127.4, 126.4, 125.3, 122.4, 114.5, 112.7, 109.5, 108.9, 107.8, 88.0, 60.9, 55.9, 47.0, 29.2, one carbon missing possibly due to overlap. HRMS (ESI+) calculated for $C_{28}H_{25}NO_3$ ([M + H]$^+$), 424.1907; found, 424.1911.

9-Benzyl-7-methoxy-5-methyl-9H-carbazol-3-ol (3j) and 9-Benzyl-5-methoxy-7-methyl-9H-carbazol-3-ol (3j'). *N*-Benzyl-3-methoxy-5-methylaniline (**1i**, 227 mg, 1.0 mmol) and benzoquinone (**2a**, 119 mg, 1.1 mmol) were

employed. The reaction was purified using 0−30% EtOAc in hexanes. A 1:1 mixture of compounds **3j** and **3j'** were obtained as a yellow oil (80 mg, 25%); FTIR (thin film, cm^{-1}) 3231, 3033, 2915, 2853, 1453; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.5 Hz, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.27 (d, *J* = 2.6 Hz, 1H), 7.24 – 7.18 (m, 4H), 7.11 (td, *J* = 8.8, 3.9 Hz, 5H), 6.87 (ddd, *J* = 8.6, 4.2, 2.5 Hz, 2H), 6.74 (s, 1H), 6.66 – 6.58 (m, 2H), 6.46 (s, 1H), 5.40 (s, 4H), 4.45 (d, J = 3.5 Hz, 2H), 4.05 (s, 3H), 3.83 (s, 3H), 2.80 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 149.3, 149.2, 144.5, 143.2, 143.0, 137.5, 137.3, 137.2, 136.0, 135.1, 134.6, 132.5, 130.1, 128.7, 128.7, 127.34, 127.25, 126.4, 126.3, 124.6, 123.2, 113.0, 112.4, 109.0, 108.8, 108.7, 108.4, 107.7, 102.1, 101.7, 90.9, 55.5, 55.3, 52.8, 46.7, 22.5, 20.6. HRMS (ESI+) calculated for $C_{21}H_{19}NO_2$ ($[M + H]^+$), 318.1489; found, 318.1487.

9-Benzyl-5,7-dimethoxy-2-methyl-9H-carbazol-3-ol (3k) and 9-benzyl-5,7-dimethoxy-1-methyl-9H-carbazol-3-ol (3k'). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and 2-methylbenzoquinone (**2b**, 134 mg, 1.1 mmol) were employed. The reaction was purified using 80−100% CH_2Cl_2 in hexanes. Compounds **3k** was obtained as an off-white solid (102 mg, 29%); mp 202−204 °C; FTIR (thin film, cm^{-1}) 3540, 3447, 2932, 2844, 1585; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.26 (d, *J* = 6.6 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 6.98 (s, 1H), 6.32 (dd, *J* = 34.6, 1.8 Hz, 2H), 5.36 (s, 2H), 4.44 (s, 1H), 4.02 (s, 3H), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 156.5, 148.0, 143.1, 137.4, 135.2, 128.7, 127.3, 126.3, 121.3, 120.9, 109.6, 107.6, 106.4, 90.5, 85.9, 55.7, 55.4, 46.8, 16.7. HRMS (ESI+) calculated for $C_{22}H_{21}NO_3$ ($[M + H]^+$), 348.1594; found, 348.1594. Compounds **3k'** was obtained as an off-white solid (70 mg, 20%); mp 197−199 °C; FTIR (thin film, cm^{-1}) 3344, 2913, 2831, 1597, 1448; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.6 Hz, 1H), 7.26 (s, 1H), 7.24 – 7.17 (m, 2H), 6.99 (s, 2H), 6.58 (d, *J* = 2.6 Hz, 1H), 6.30 (dd, *J* = 14.3, 1.8 Hz, 2H), 5.61 (s, 2H), 4.41 (s, 1H), 4.02 (s, 3H), 3.80 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 156.7, 149.2, 144.4, 138.9, 133.7, 128.8, 127.1, 125.5, 124.3, 120.4, 115.5, 106.5, 105.6, 90.7, 85.7, 55.6, 55.4, 48.5, 19.4. HRMS (ESI+) calculated for $C_{22}H_{21}NO_3$ ($[M + H]^+$), 348.1594; found, 348.1593. The structures of **3k** and **3k'** were also confirmed by NOESY spectra.

9-Benzyl-2-(tert-butyl)-5,7-dimethoxy-9H-carbazol-3-ol (3l). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and 2-*tert*-butylbenzoquinone (**2c**, 181 mg, 1.1 mmol) were employed. The reaction was purified using 40−50% CH_2Cl_2 in hexanes. Compound **3l** was obtained as a purple solid (167 mg, 43%); mp 177−180 °C; FTIR (thin film, cm^{-1}) 3461, 3000, 2967, 2840, 1606; ^1H NMR (300 MHz, DMSO-d_6) δ 8.89 (s, 1H), 7.51 (d, *J* = 2.5 Hz, 1H), 7.21 – 6.99 (m, 3H), 6.84 (d, *J* = 2.6 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.7 Hz, 2H), 6.44 (d, *J* = 1.8 Hz, 1H), 6.27 (d, *J* = 1.8 Hz, 1H), 5.87 (s, 2H), 3.96 (s, 3H), 3.68 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.3, 155.6, 150.7, 144.6, 138.5, 135.0, 132.2, 128.3, 126.5, 125.9, 125.7, 111.7, 106.7, 105.2, 90.6, 88.4, 55.4, 55.3, 50.5, 34.2, 31.7. HRMS (ESI+) calculated for $C_{25}H_{27}NO_3$ ($[M + H]^+$), 390.2064; found, 390.2078.

9-Benzyl-5,7-dimethoxy-2-phenyl-9H-carbazol-3-ol (3m). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and 2-phenylbenzoquinone (**2d**, 203 mg, 1.1 mmol) were employed. The reaction was purified using 0−10% MeOH in CH_2Cl_2. Compound **3m** was obtained as an off-white foam (190 mg, 47%); FTIR (thin film, cm^{-1}) 3523, 3325, 2934, 2839, 1590; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.6 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.17 (d, *J* = 4.4 Hz, 4H), 7.12 – 7.03 (m, 3H), 6.64 (d, *J* = 2.6 Hz, 1H), 6.58 – 6.45 (m, 2H), 6.28 (dd, *J* = 17.7, 1.8 Hz, 2H), 4.97 (s, 2H), 4.49 (s, 1H), 4.05 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 156.8, 148.8, 144.9, 139.7, 137.8, 132.2, 129.6, 128.1, 127.6, 127.1, 126.6, 126.2, 125.7, 124.9, 115.0, 107.0, 106.5, 90.9, 86.3, 55.6, 55.4, 48.2. HRMS (ESI+) calculated for $C_{27}H_{23}NO_3$ ($[M + H]^+$), 410.1751; found, 410.1752.

9-Benzyl-2,5,7-trimethoxy-9H-carbazol-3-ol (3n). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and 2-methoxybenzoquinone (**2e**, 152 mg, 1.1 mmol) were employed. The reaction was purified using 60% CH_2Cl_2 in hexanes. Compound **3n** was obtained as a pale purple solid (229 mg, 63%); mp 181−182 °C; FTIR (thin film, cm^{-1}) 3471, 2935, 2843, 1615, 1452; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 0.9 Hz, 1H), 7.25 (tdd, *J* = 2.9, 1.9, 0.8 Hz, 4H), 7.17 – 6.90 (m, 2H), 6.71 (s, 1H), 6.38 (d, *J* = 1.8 Hz, 1H), 6.30 (d, *J* = 1.7 Hz, 1H), 5.38 (s, 2H), 4.02 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 156.0, 144.9, 142.5, 140.3, 137.2, 134.1, 128.8,

127.4, 126.3, 115.6, 107.1, 106.5, 91.7, 90.5, 85.7, 56.3, 55.7, 55.4, 46.8; HRMS (ESI+) calculated for $C_{22}H_{21}NO_4$ ($[M + H]^+$), 364.1543; found, 364.1542.

9-Benzyl-5,7-dimethoxy-1,2-dimethyl-9H-carbazol-3-ol (3o). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and 2,3-dimethylbenzoquinone (**2f**, 150 mg, 1.1 mmol) were employed. The reaction was purified using 0−20% CH_2Cl_2 in hexanes. Compound **3o** was obtained as a yellow solid (198 mg, 55%); mp 209−210 °C; FTIR (thin film, cm^{-1}) 3421, 2937, 2842, 1627, 1437; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 7.08 (d, J = 6.9 Hz, 2H), 6.29 (d, J = 8.5 Hz, 2H), 5.60 (s, 2H), 4.46 (s, 1H), 4.02 (s, 3H), 3.79 (s, 3H), 2.46 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 156.4, 147.9, 144.8, 139.0, 134.6, 128.8, 127.0, 125.7, 121.7, 120.3, 119.3, 106.5, 105.2, 90.7, 86.0, 55.6, 55.4, 49.3, 14.8, 12.2. HRMS (ESI+) calculated for $C_{23}H_{23}NO_4$ ($[M + H]^+$), 378.1700; found, 378.1684.

9-Benzyl-1,2,5,7-tetramethoxy-9H-carbazol-3-ol (3p). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and 2,3-dimethoxybenzoquinone (**2g**, 185 mg, 1.1 mmol) were employed. The reaction was purified using CH_2Cl_2. Compound **3p** was obtained as an off-white solid (210 mg, 53%); mp 148−149 °C; FTIR (thin film, cm^{-1}) 3378, 2934, 2839, 1633, 1421; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.24 – 7.14 (m, 3H), 7.07 (d, J = 7.3 Hz, 2H), 6.33 (s, 1H), 6.27 (s, 1H), 5.68 (s, 2H), 5.41 (s, 1H), 4.00 (s, 3H), 3.93 (s, 3H), 3.79 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 156.5, 143.9, 143.6, 138.8, 138.5, 137.7, 128.5, 126.8, 126.5, 126.0, 119.9, 106.7, 102.3, 90.7, 85.8, 61.0, 61.0, 55.6, 55.4, 48.3. HRMS (ESI+) calculated for $C_{23}H_{23}NO_5$ ($[M + H]^+$), 394.1649; found, 394.1647.

11-Benzyl-7,9-dimethoxy-11H-benzo[a]carbazol-5-ol (3q). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and naphthalene-1,4-dione (**2h**, 240 mg, 1.1 mmol) were employed. The reaction was purified using 50−70% CH_2Cl_2 in hexanes. Compound **3q** was obtained as a tan solid (173 mg, 45%); mp 200−202 °C; FTIR (thin film, cm^{-1}) 3396, 3001, 2930, 2836, 1584; ^1H NMR (400 MHz, DMSO-d_6) δ 9.55 (s, 1H), 8.36 – 8.17 (m, 2H), 7.79 (s, 1H), 7.40 – 7.32 (m, 2H), 7.32 – 7.24 (m, 2H), 7.22 – 7.14 (m, 1H), 7.09 (dd, J = 7.1, 1.7 Hz, 2H), 6.78 (d, J = 1.9 Hz, 1H), 6.42 (d, J = 1.8 Hz, 1H), 6.00 (d, J = 2.5 Hz, 2H), 4.04 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.9, 156.3, 147.4, 143.4, 138.8, 129.1, 127.5, 127.4, 126.4, 125.8, 124.1, 123.7, 123.1, 122.3, 121.6, 119.2, 106.7, 103.2, 91.8, 86.8, 56.1, 56.0, 49.3. HRMS (ESI+) calculated for $C_{25}H_{21}NO_3$ ($[M + H]^+$), 384.1594; found, 384.1588. *2-(benzyl(3,5-dimethoxyphenyl)amino)-2,3-dihydronaphthalene-1,4-dione (6).* Compound **6** was obtained as a yellow solid (70 mg, 17%); mp 137−138 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 – 8.01 (m, 2H), 7.79 – 7.66 (m, 2H), 7.44 – 7.23 (m, 6H), 5.88 (s, 2H), 4.76 (dd, J = 11.4, 6.2 Hz, 1H), 4.34 (s, 2H), 3.64 (s, 6H), 3.03 (dd, J = 16.3, 6.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 196.1, 158.7, 149.4, 139.2, 135.8, 135.7, 133.8, 133.4, 128.7, 127.6, 127.4, 127.3, 126.2, 104.9, 89.7, 55.4, 48.5, 43.6, 42.6. HRMS (ESI+) calculated for $C_{25}H_{23}NO_4$ ($[M + H]^+$), 402.1700; found, 402.1700.

11-Benzyl-7,9-dimethoxy-2,3-dimethyl-11H-benzo[a]carbazol-5-ol (3r). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and 6,7-dimethylnaphthalene-1,4-dione (**2i**, 205 mg, 1.1 mmol) were employed. The reaction was purified using 0−50% CH_2Cl_2 in hexanes. Compound **3r** was obtained as a light brown solid (223 mg, 54%); mp 218−220 °C; FTIR (thin film, cm^{-1}) 3383, 2936, 2842, 1622, 1580; ^1H NMR (400 MHz, DMSO-d_6) δ 9.36 (s, 1H), 8.01 (d, J = 11.9 Hz, 2H), 7.66 (s, 1H), 7.33 – 7.24 (m, 2H), 7.24 – 7.15 (m, 1H), 7.15 – 7.03 (m, 2H), 6.80 (d, J = 1.8 Hz, 1H), 6.40 (d, J = 1.8 Hz, 1H), 5.97 (s, 2H), 4.02 (s, 3H), 3.83 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.7, 156.1, 146.9, 143.3, 139.1, 134.6, 132.1, 129.5, 129.1, 127.4, 127.3, 126.4, 123.4, 122.9, 121.8, 121.1, 118.5, 102.3, 91.7, 86.7, 56.1, 56.0, 49.3, 20.5, 20.1. HRMS (ESI+) calculated for $C_{27}H_{25}NO_3$ ($[M + H]^+$), 412.1907; found, 412.1899.

11-Benzyl-1,4,7,9-tetramethoxy-11H-benzo[a]carbazol-5-ol (3s). *N*-Benzyl-3,5-dimethoxyaniline (**1a**, 243 mg, 1.0 mmol) and 5,8-dimethoxynaphthalene-1,4-dione (**2j**, 205 mg, 1.1 mmol) were employed. The reaction was purified

using 0−80% CH_2Cl_2 in hexanes. Compound **3s** was obtained as a light brown solid (248 mg, 56%); mp 177−179 °C; FTIR (thin film, cm^{-1}) 3372, 2943, 2839, 1609, 1401; ^1H NMR (300 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.89 (s, 1H), 7.46 – 7.31 (m, 4H), 7.26 (d, *J* = 6.2 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 6.28 (dd, *J* = 24.7, 1.9 Hz, 2H), 5.41 (s, 2H), 4.04 (s, 6H), 3.71 (s, 3H), 3.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 156.3, 150.7, 149.5, 148.7, 147.2, 140.2, 130.3, 128.3, 126.2, 126.2, 123.2, 116.2, 114.5, 107.6, 105.9, 103.4, 103.2, 91.4, 88.1, 77.4, 77.0, 76.6, 56.8, 55.6, 55.4, 55.0, 54.7. HRMS (ESI+) calculated for $C_{27}H_{25}NO_5$ ($[M + H]^+$), 444.1805; found, 444.1809.

References

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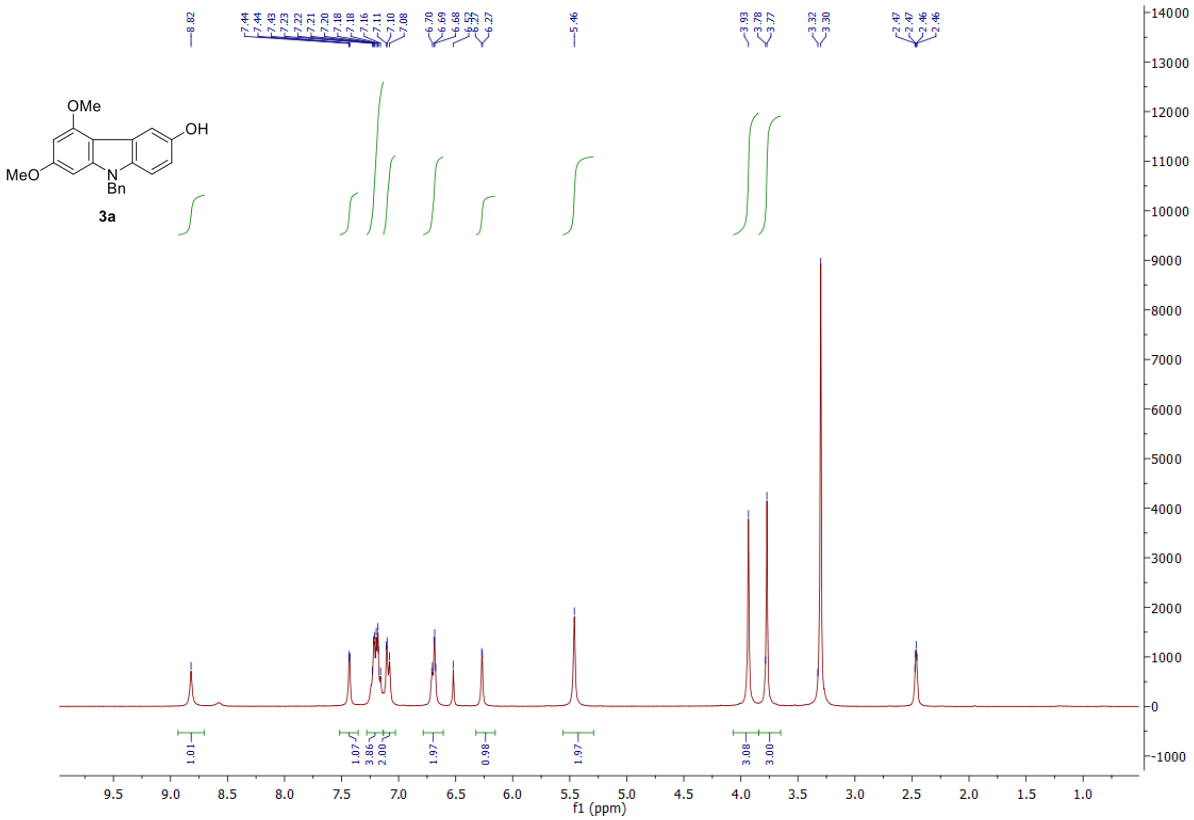
4. Razzuk, A.; Biehl, E. R. *J. Org. Chem.* **1987**, *52*, 2619.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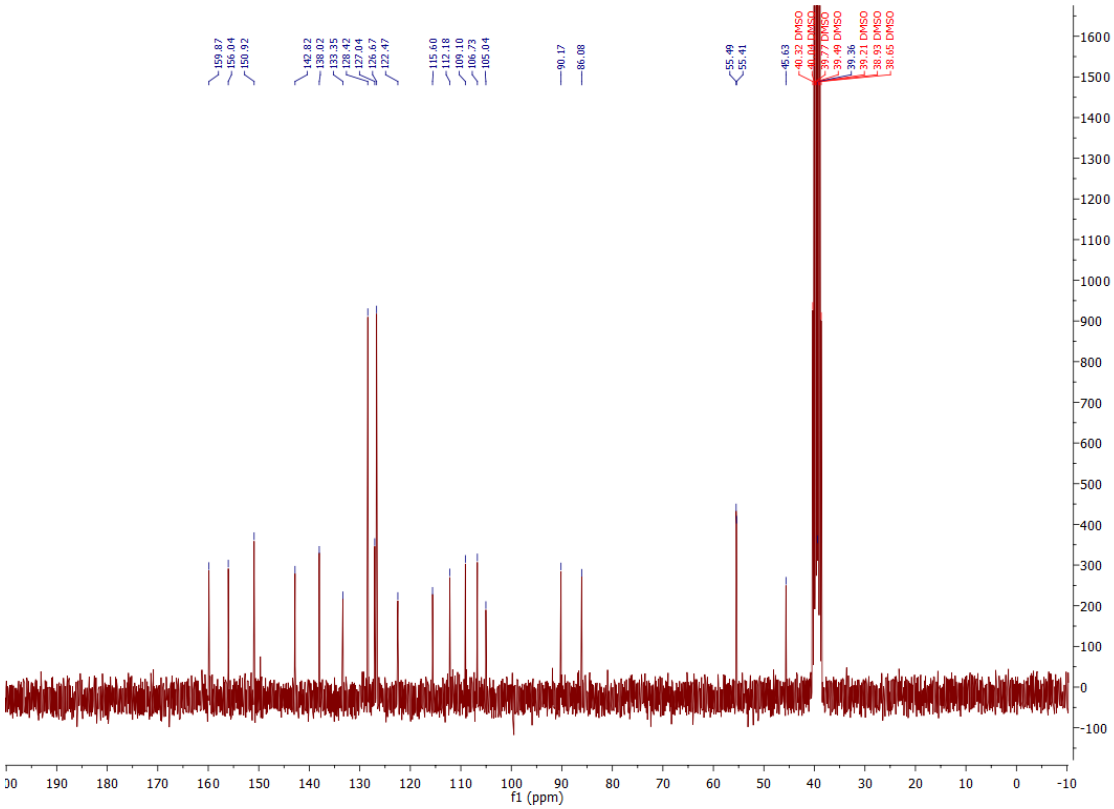
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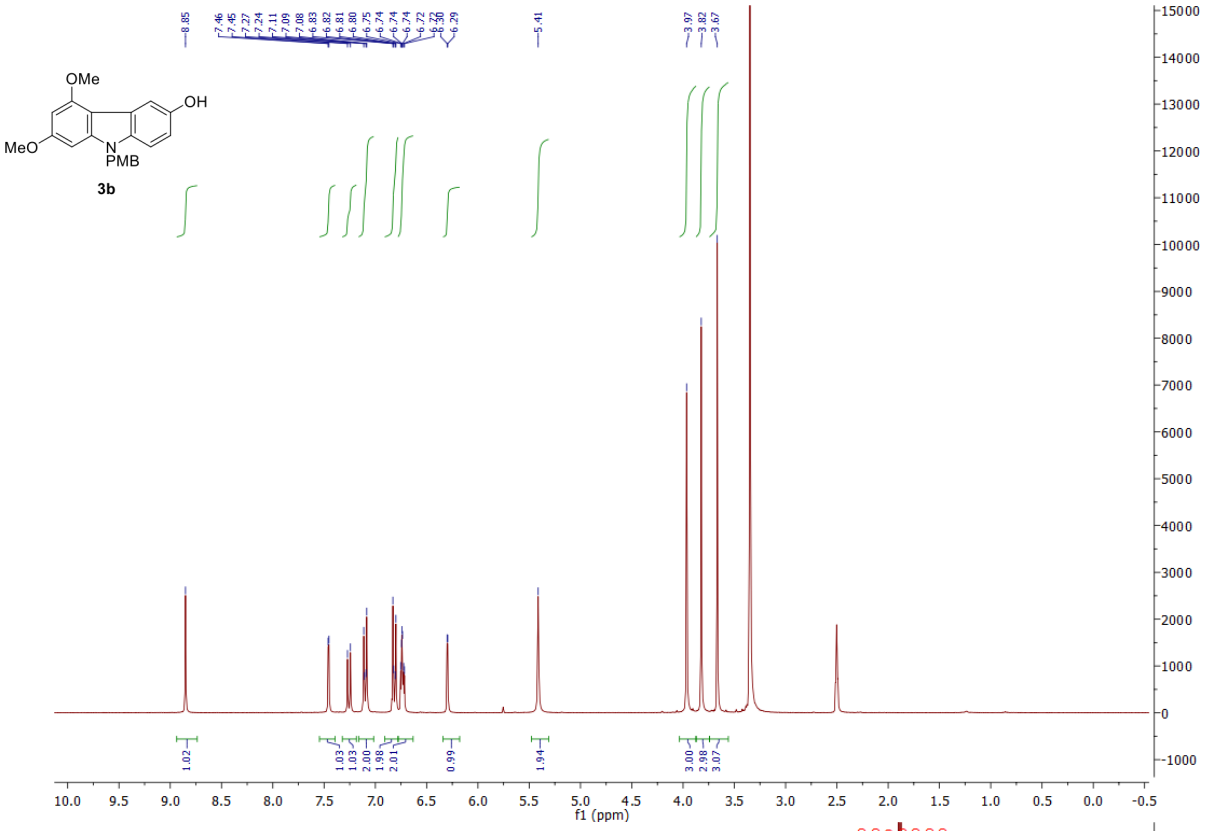
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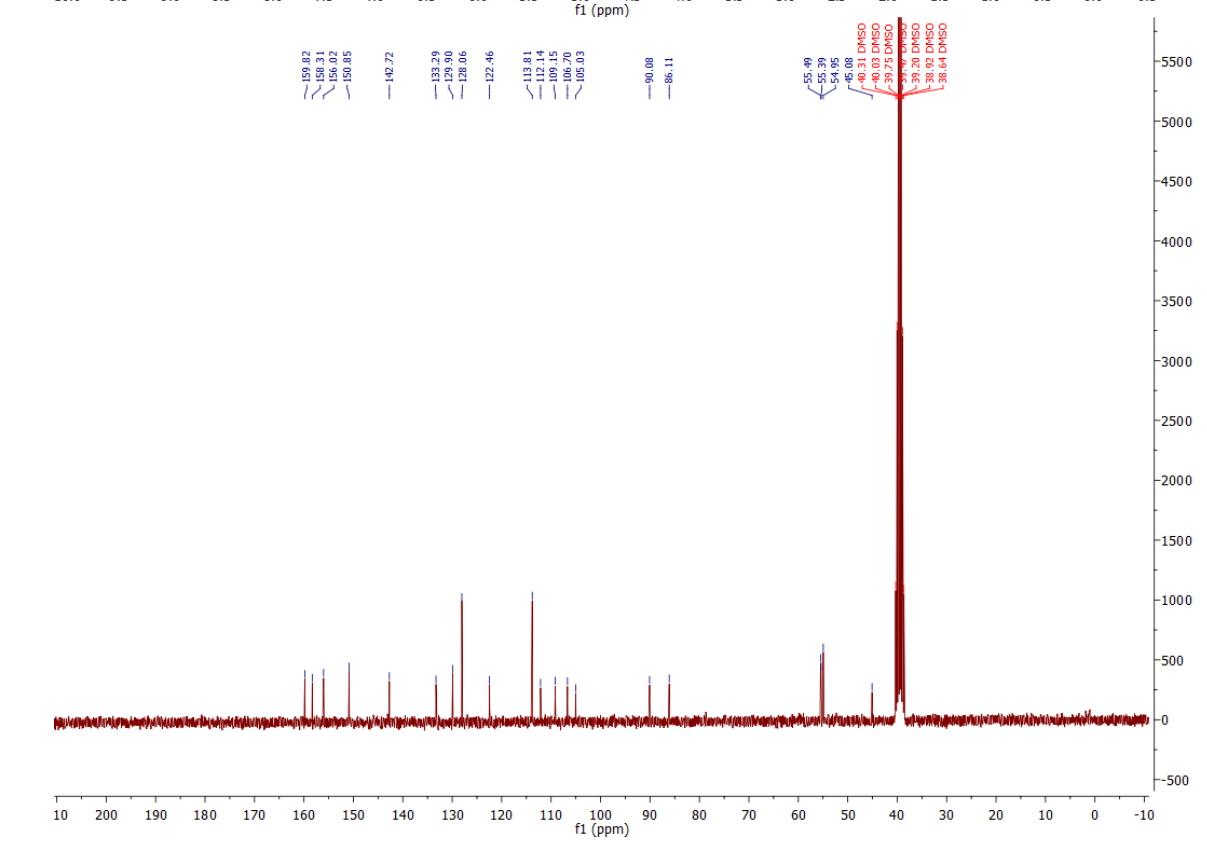
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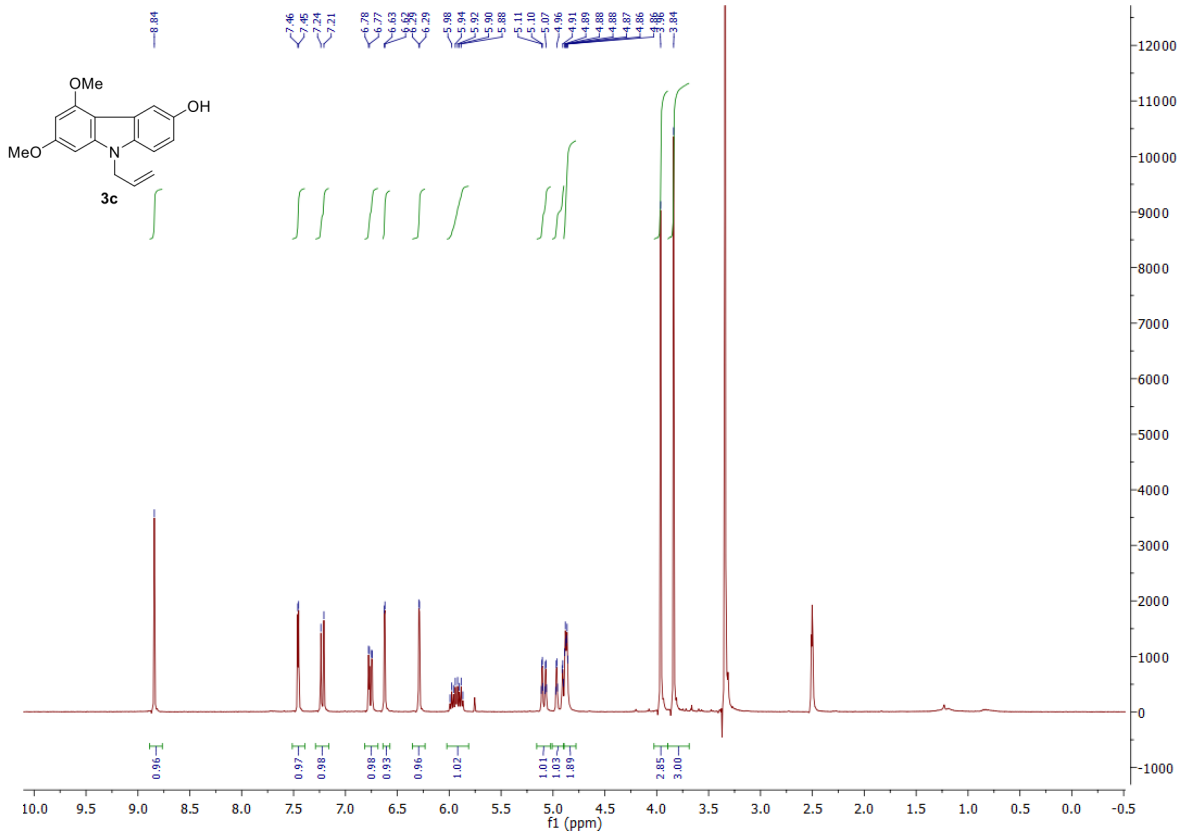
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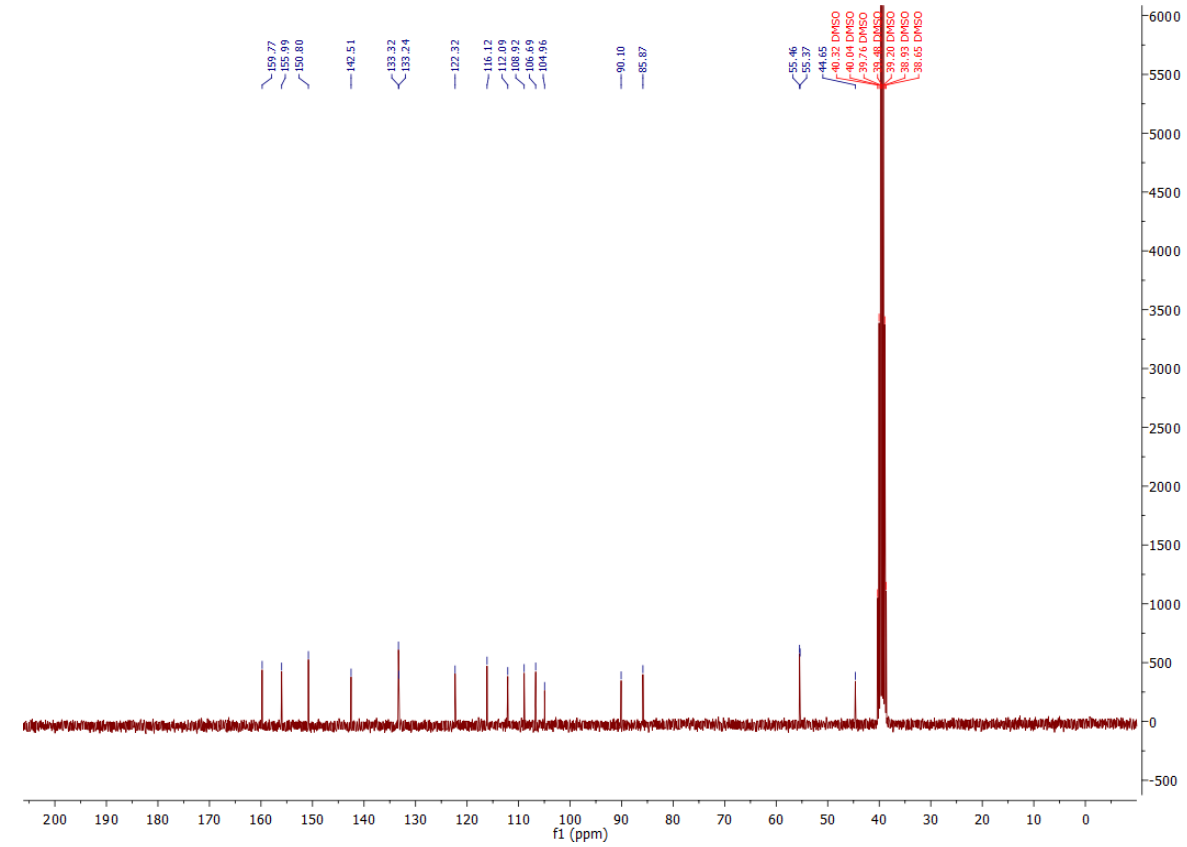
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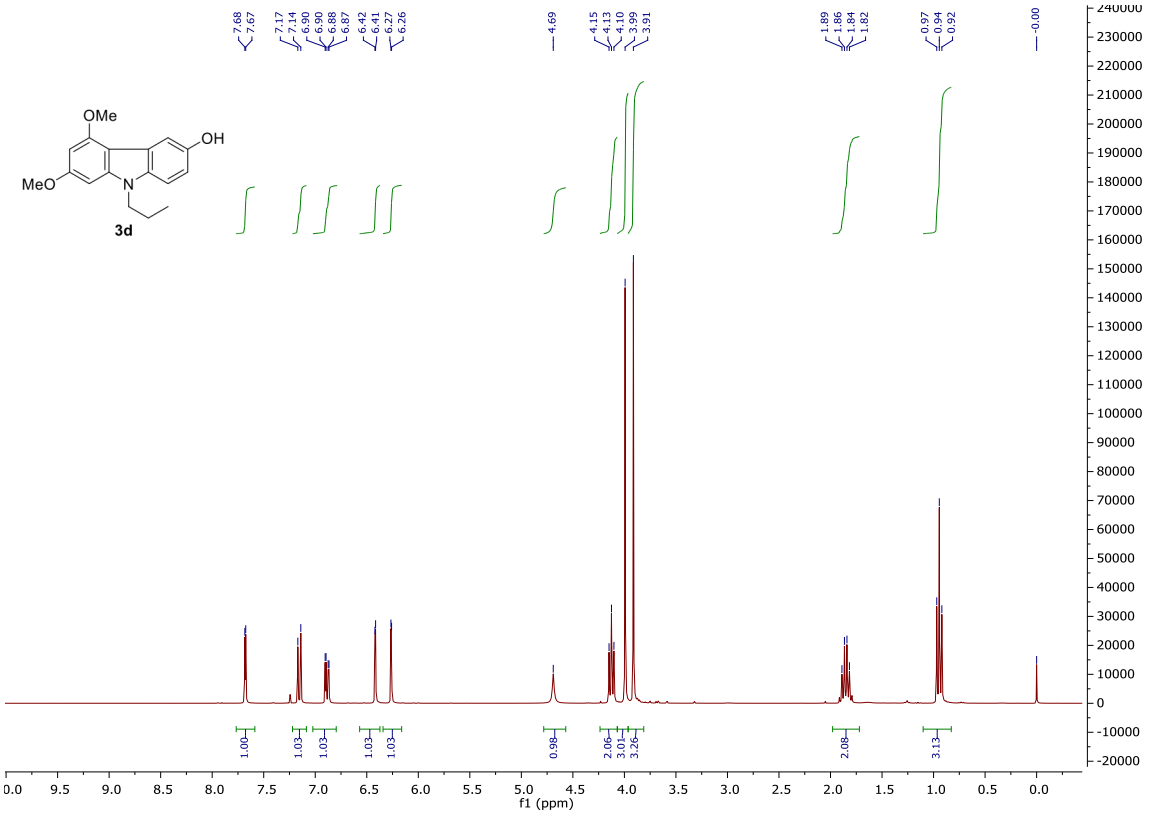
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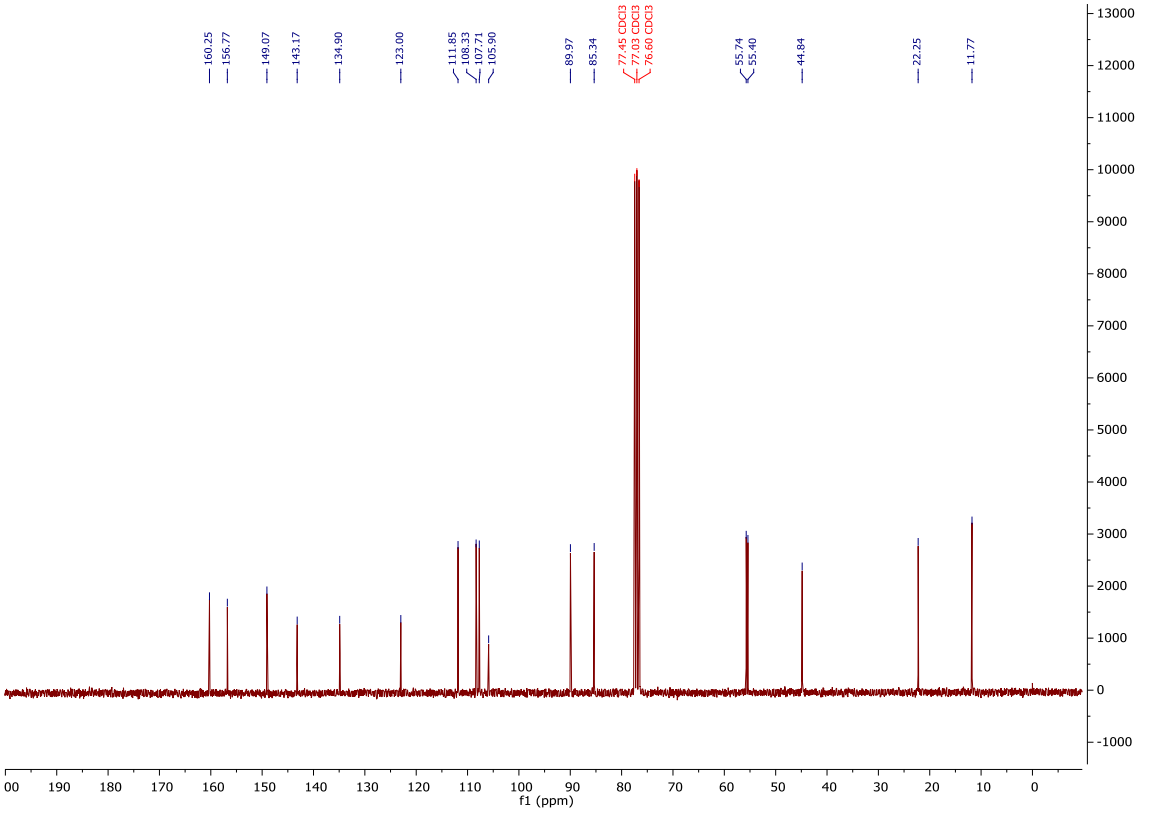
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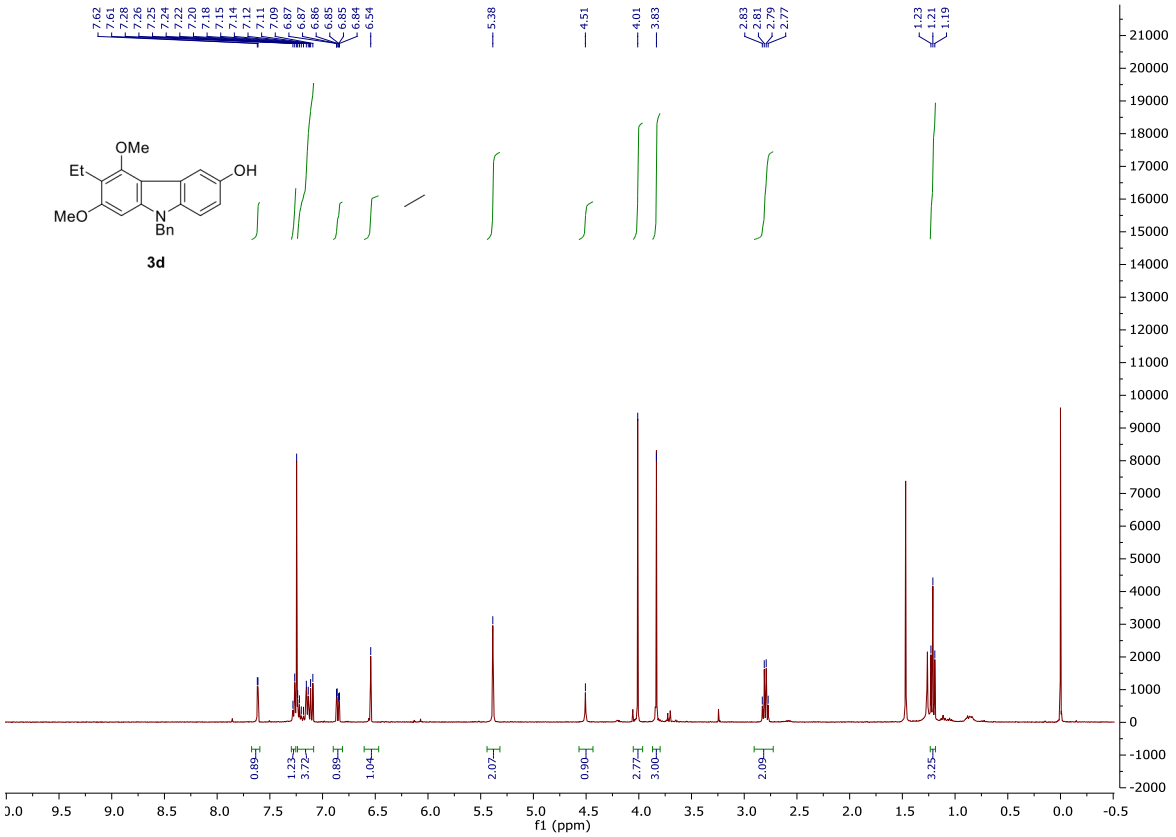
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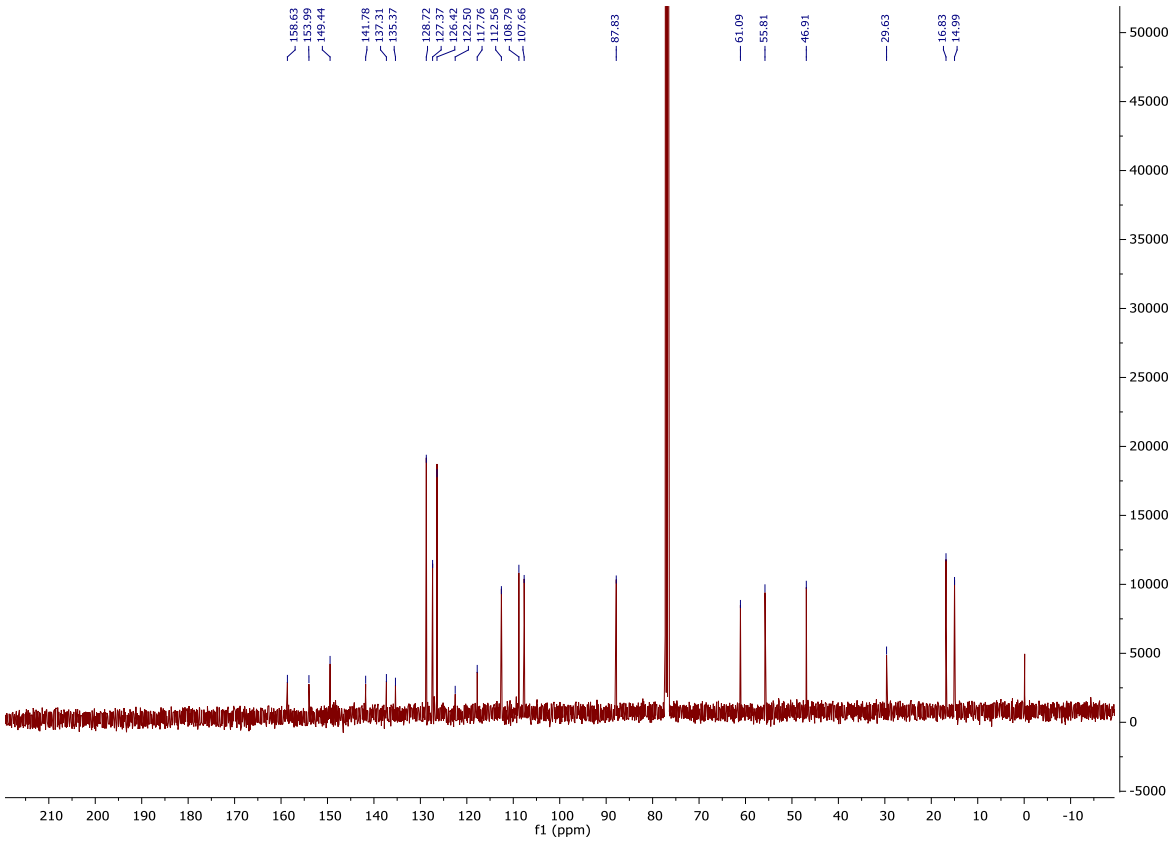
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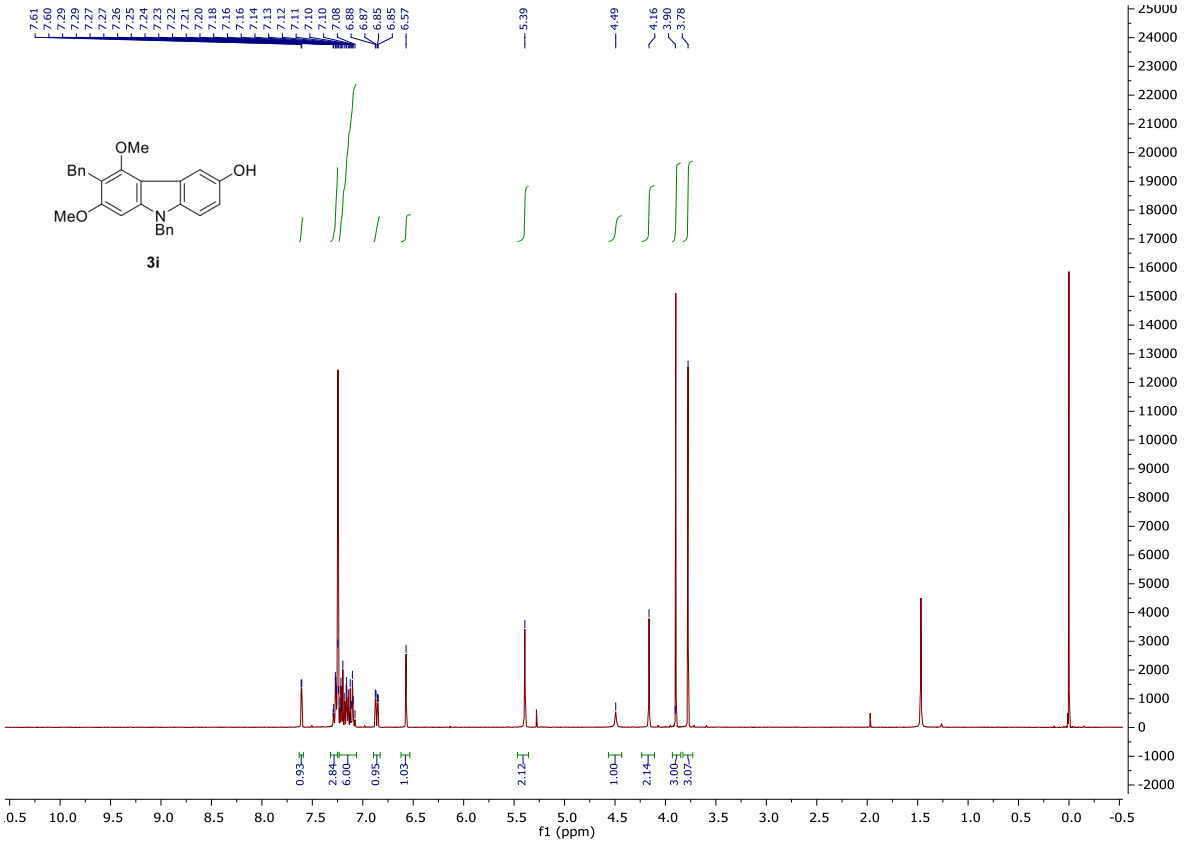
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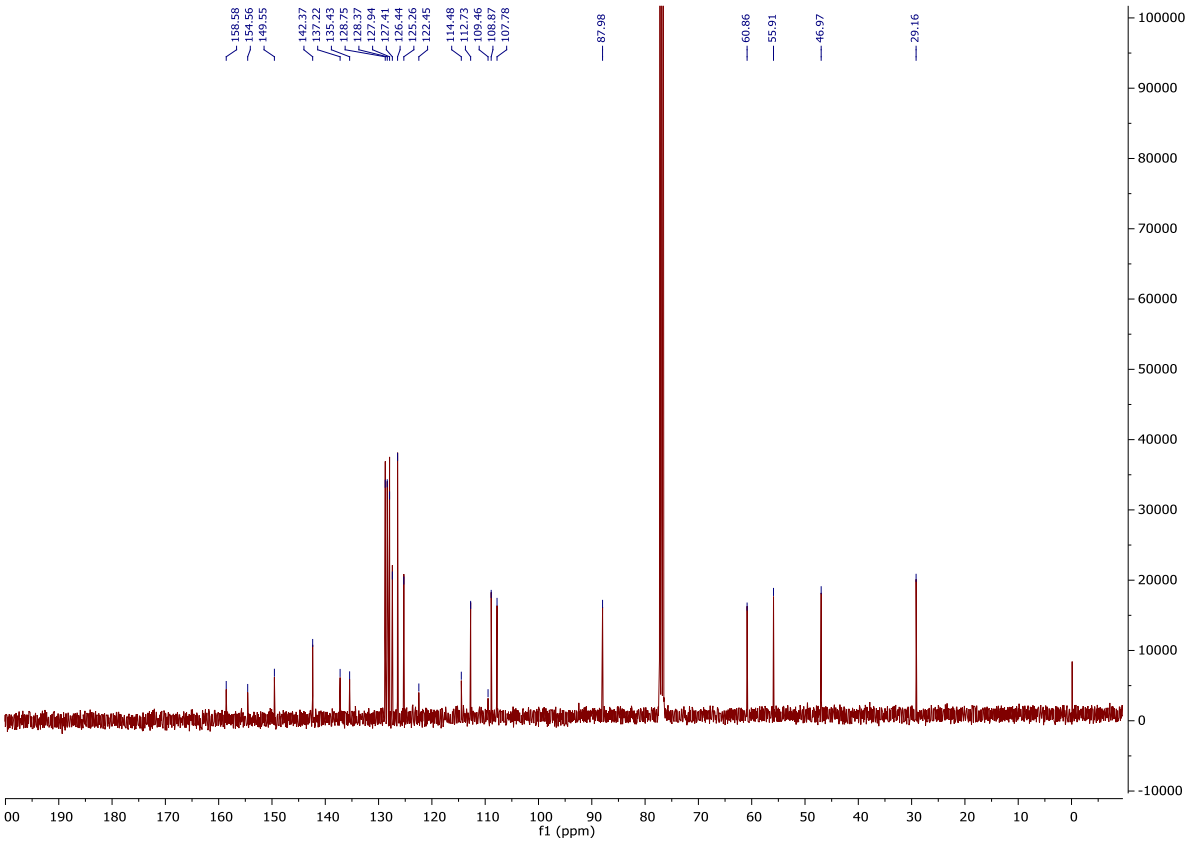
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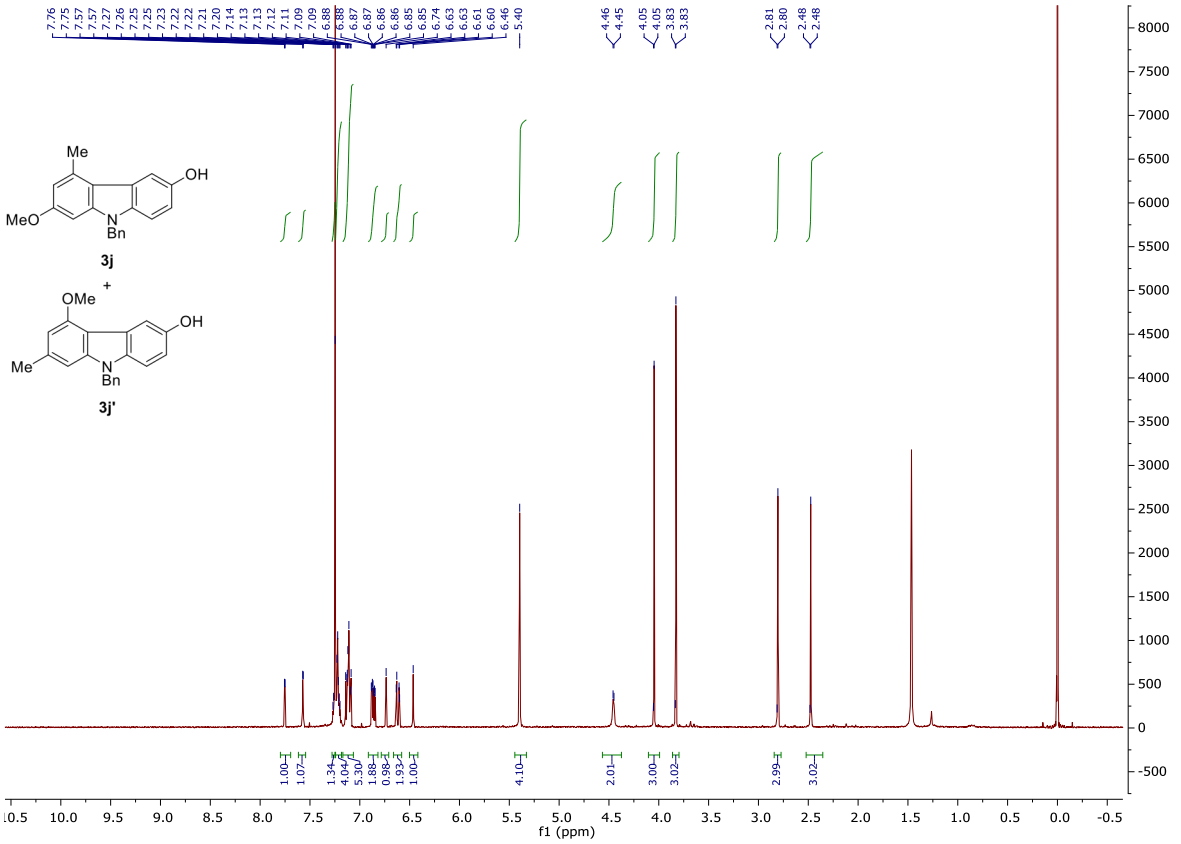
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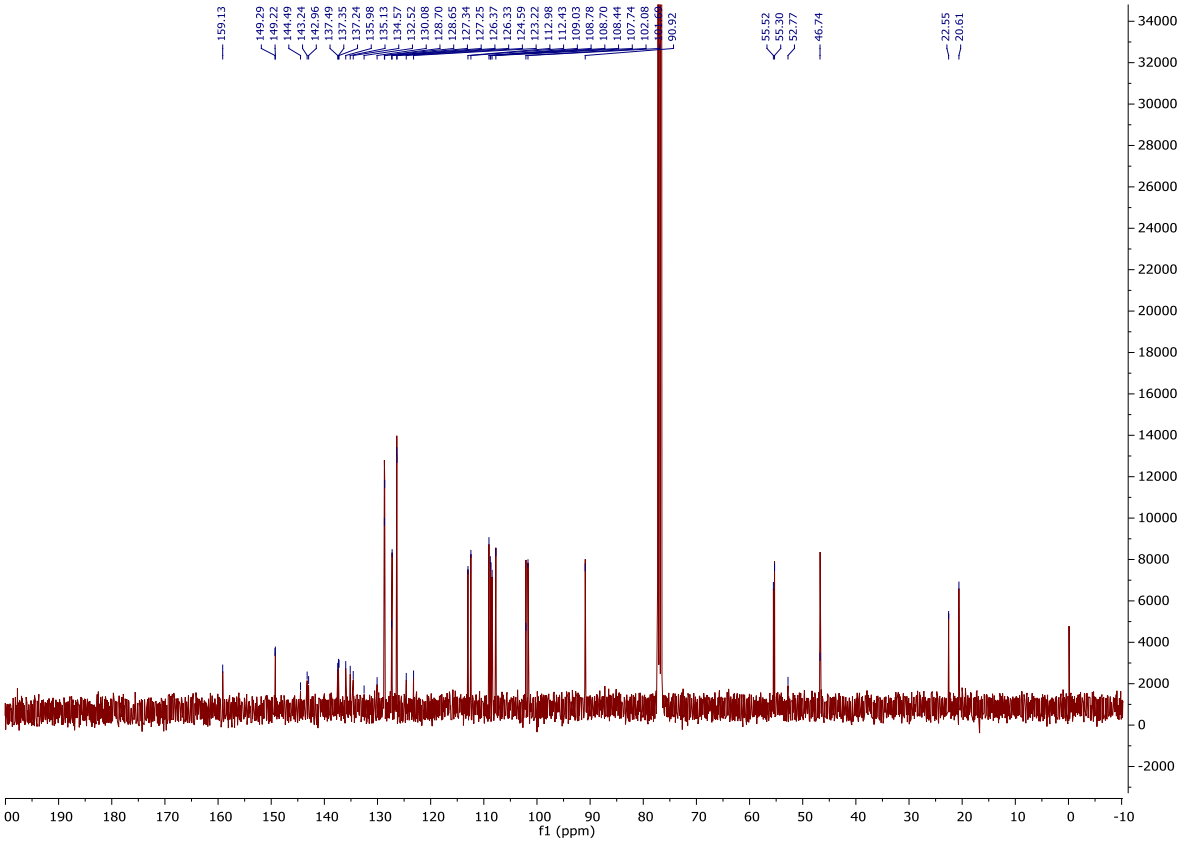
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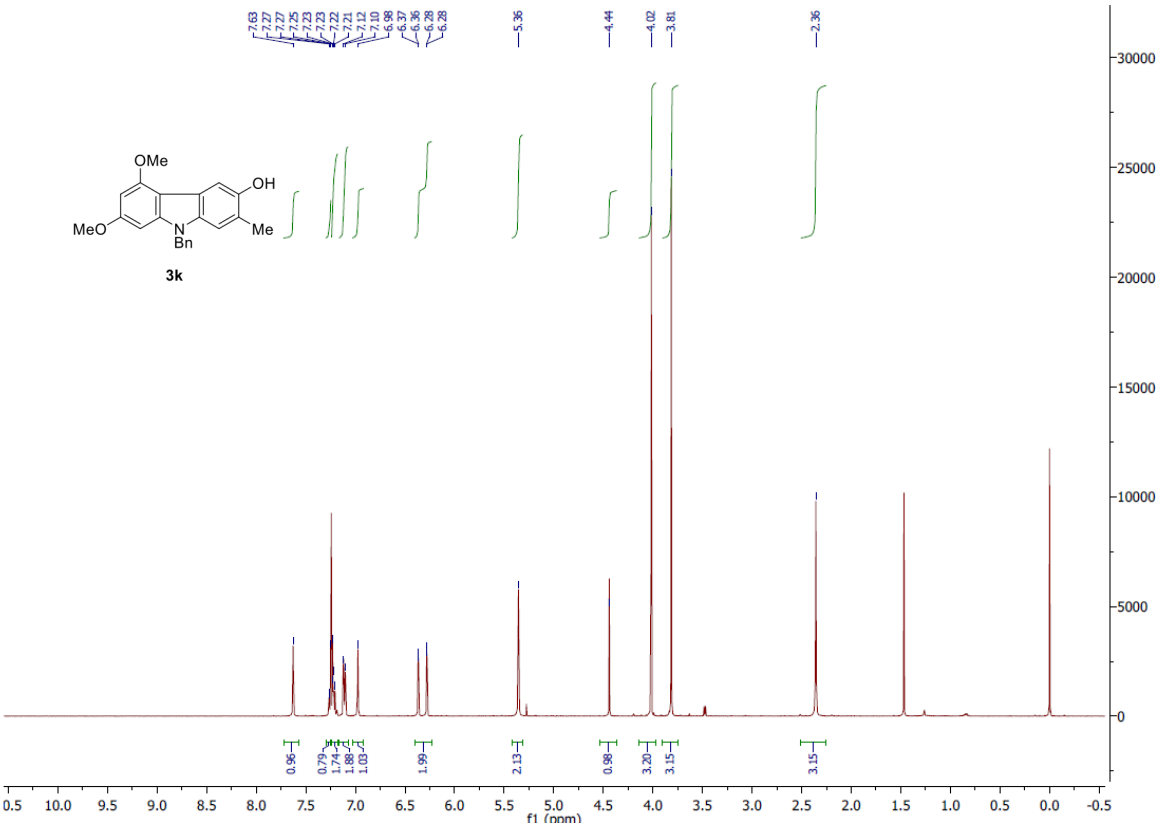
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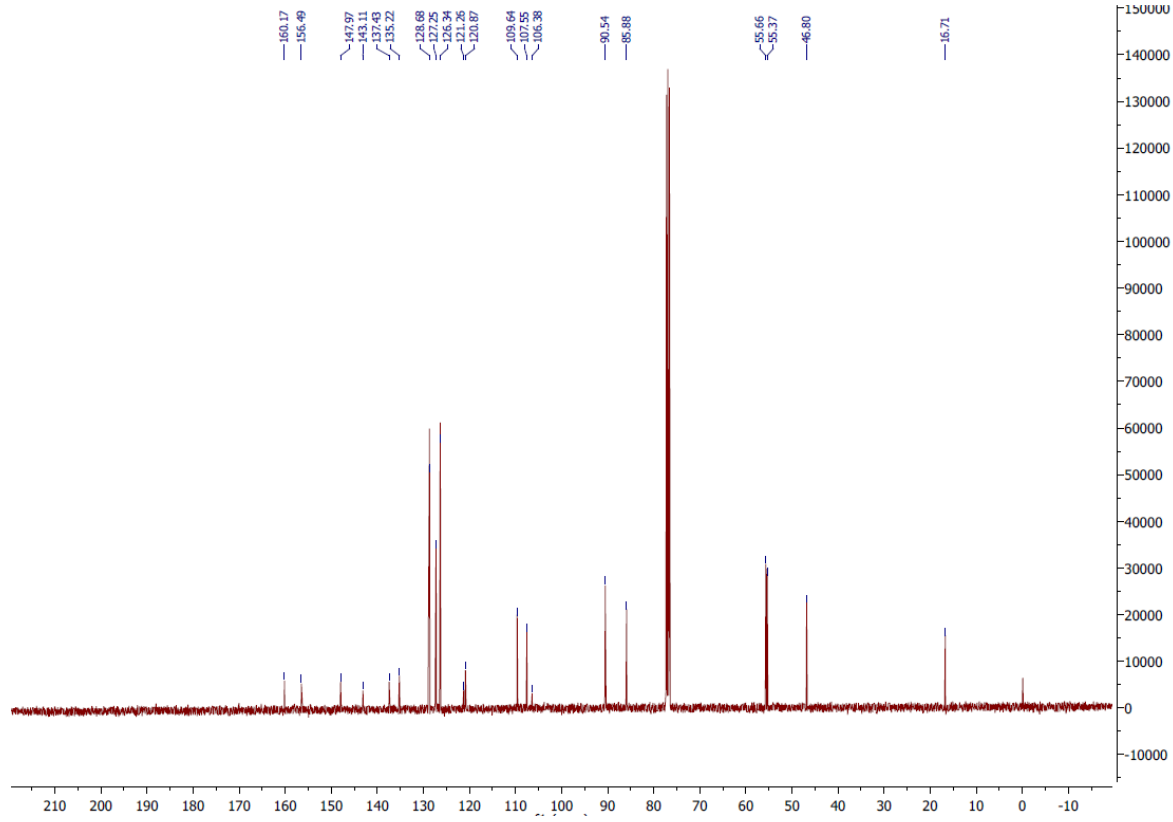
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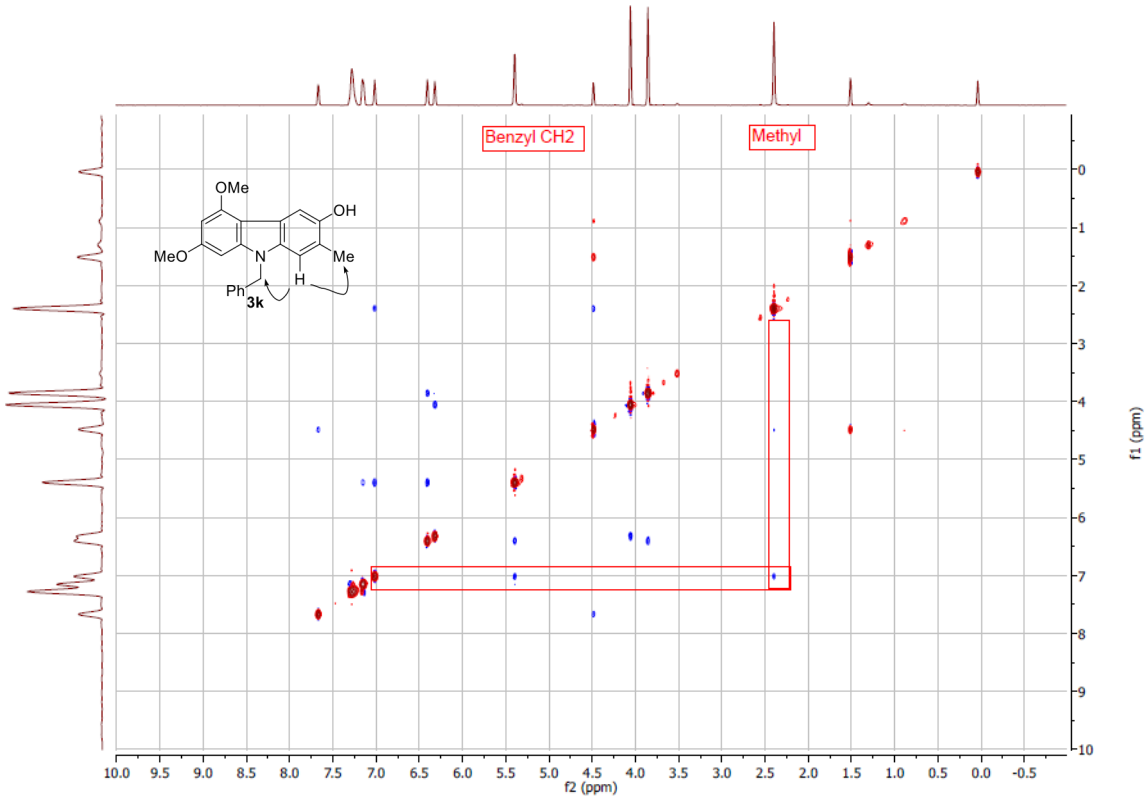
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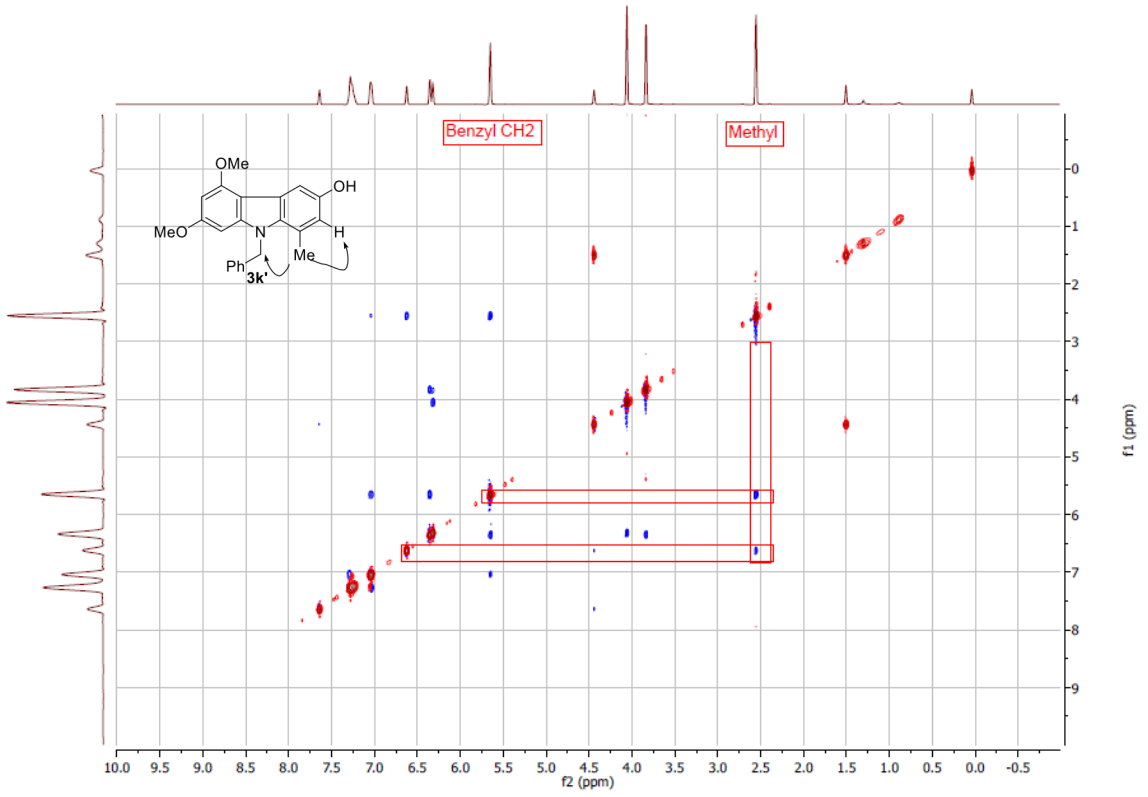
f1 (ppm)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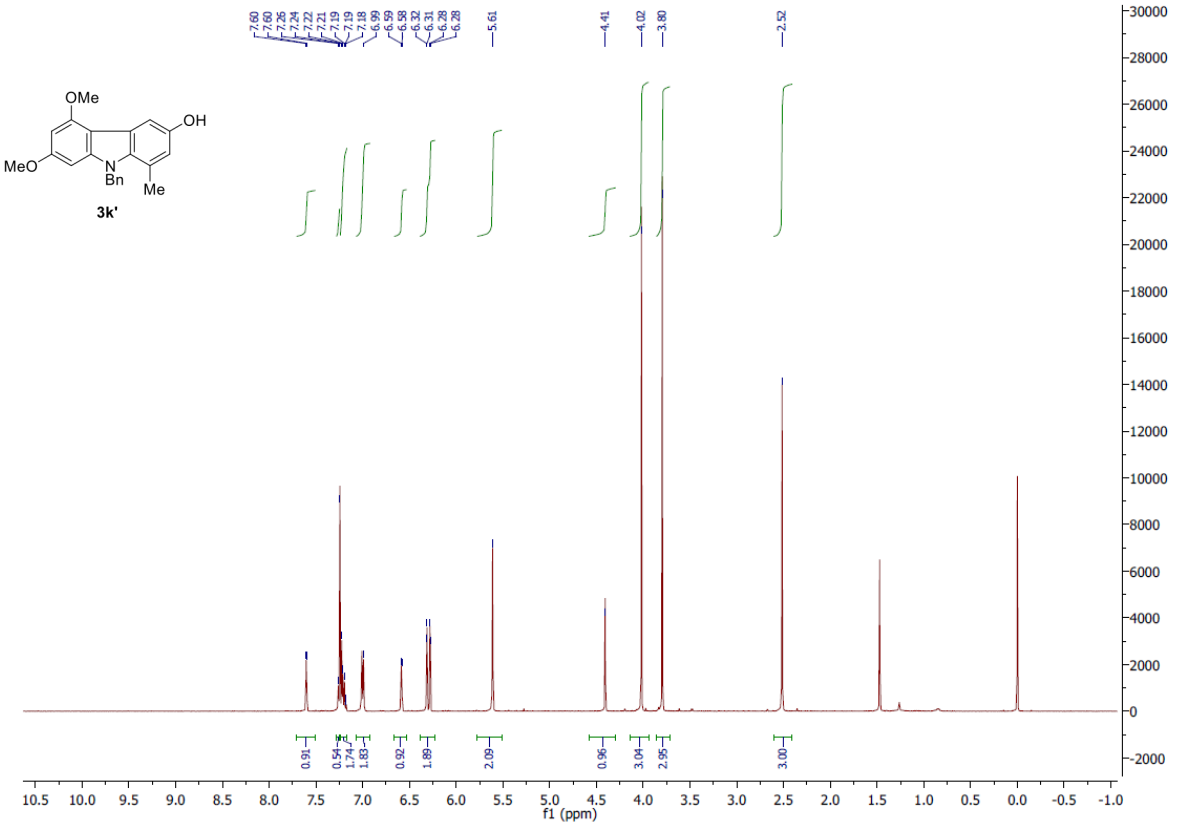
f1 (ppm)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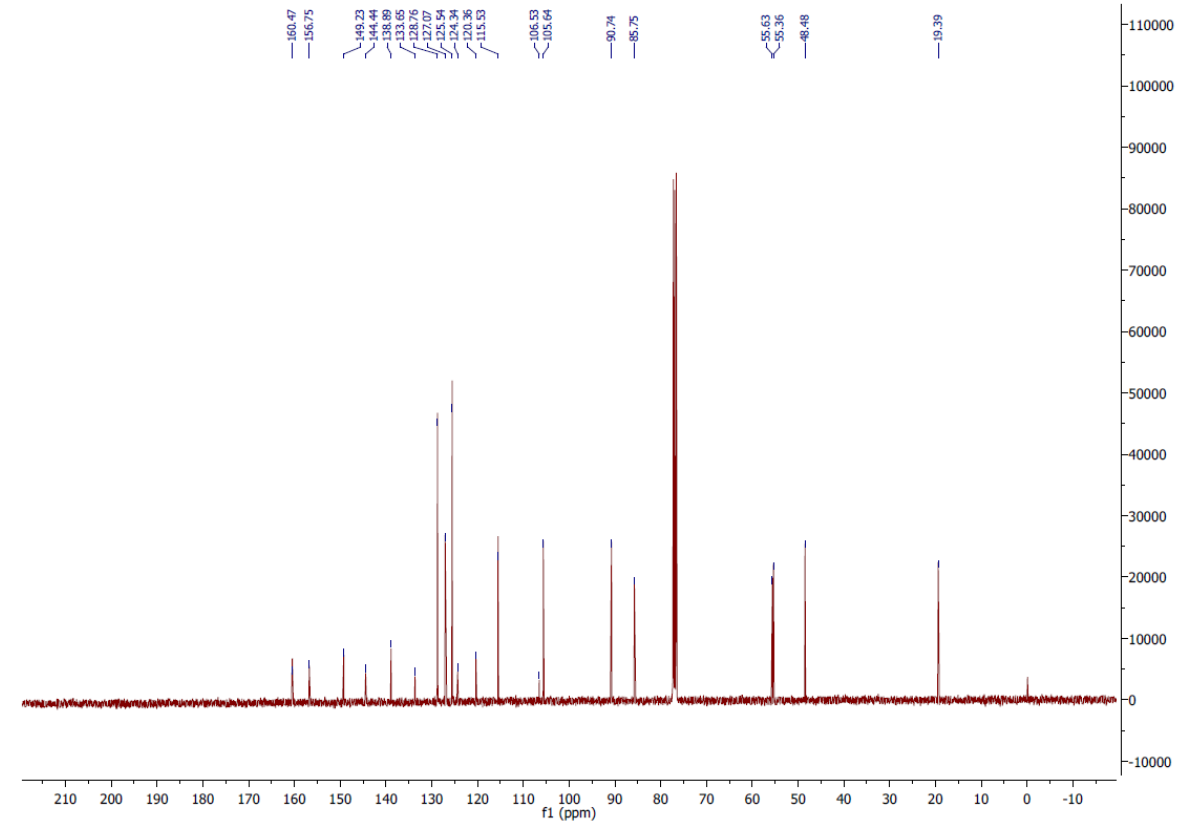
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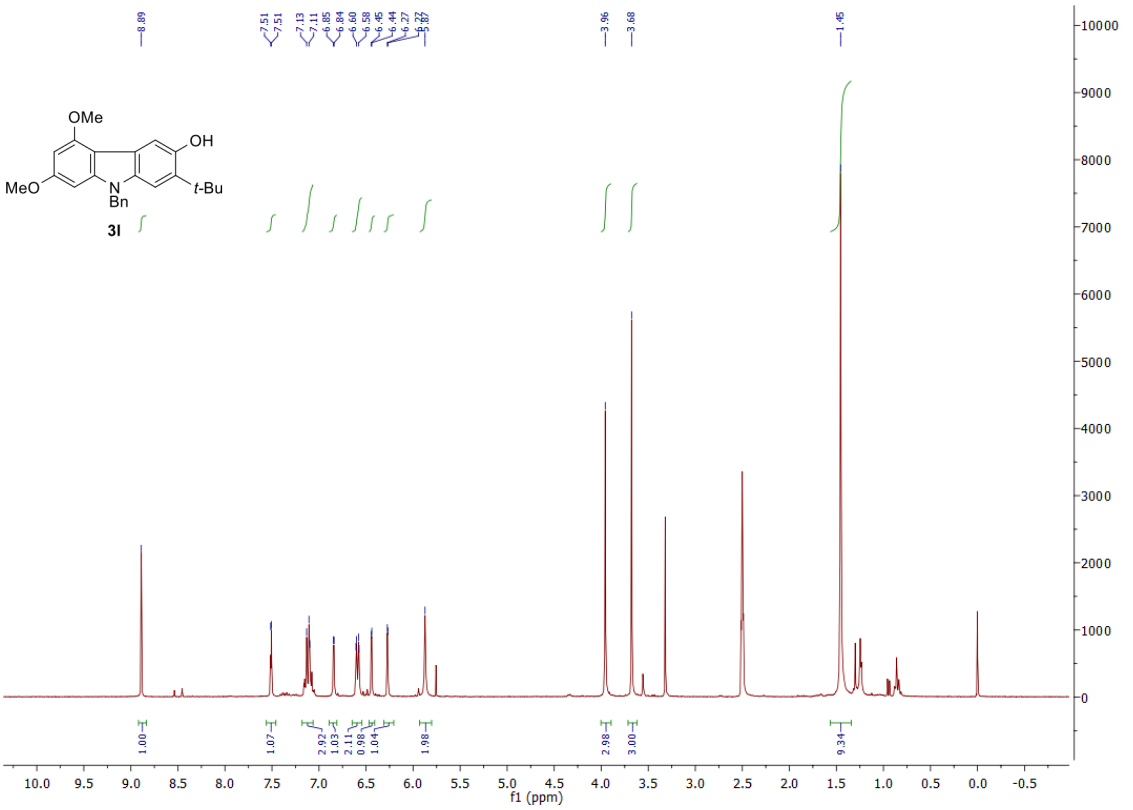
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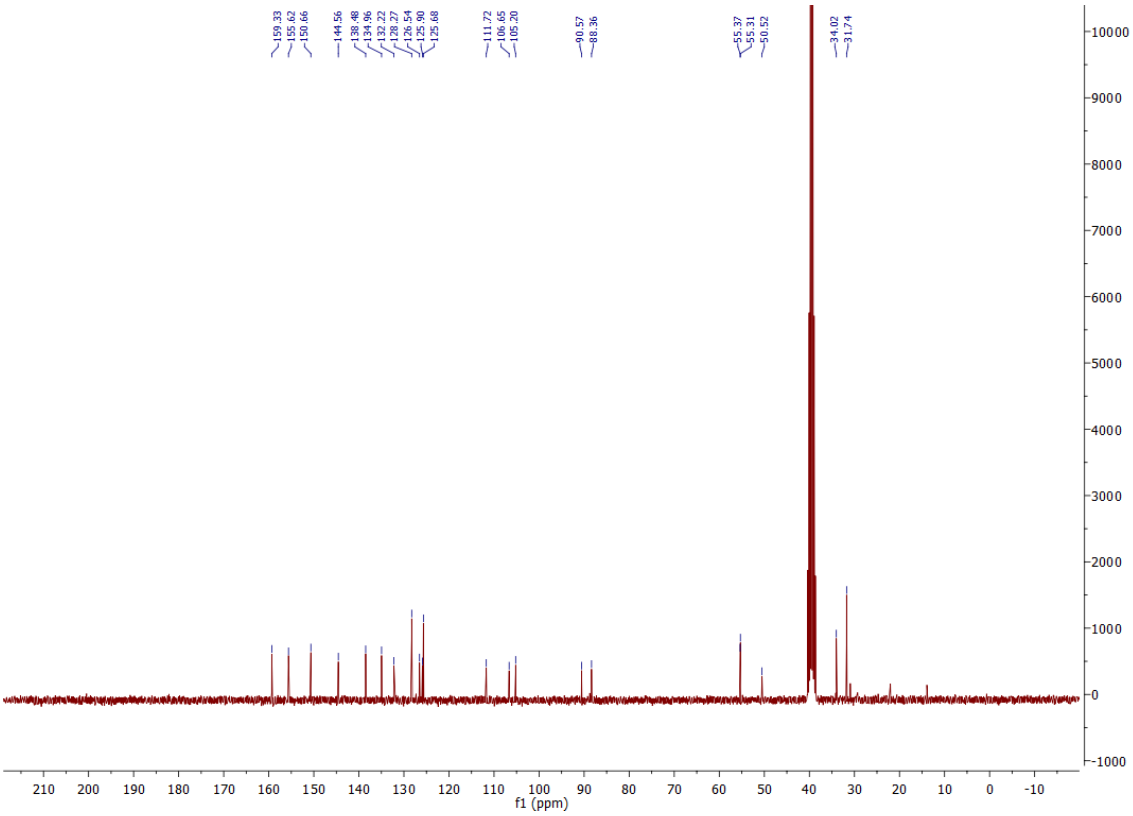
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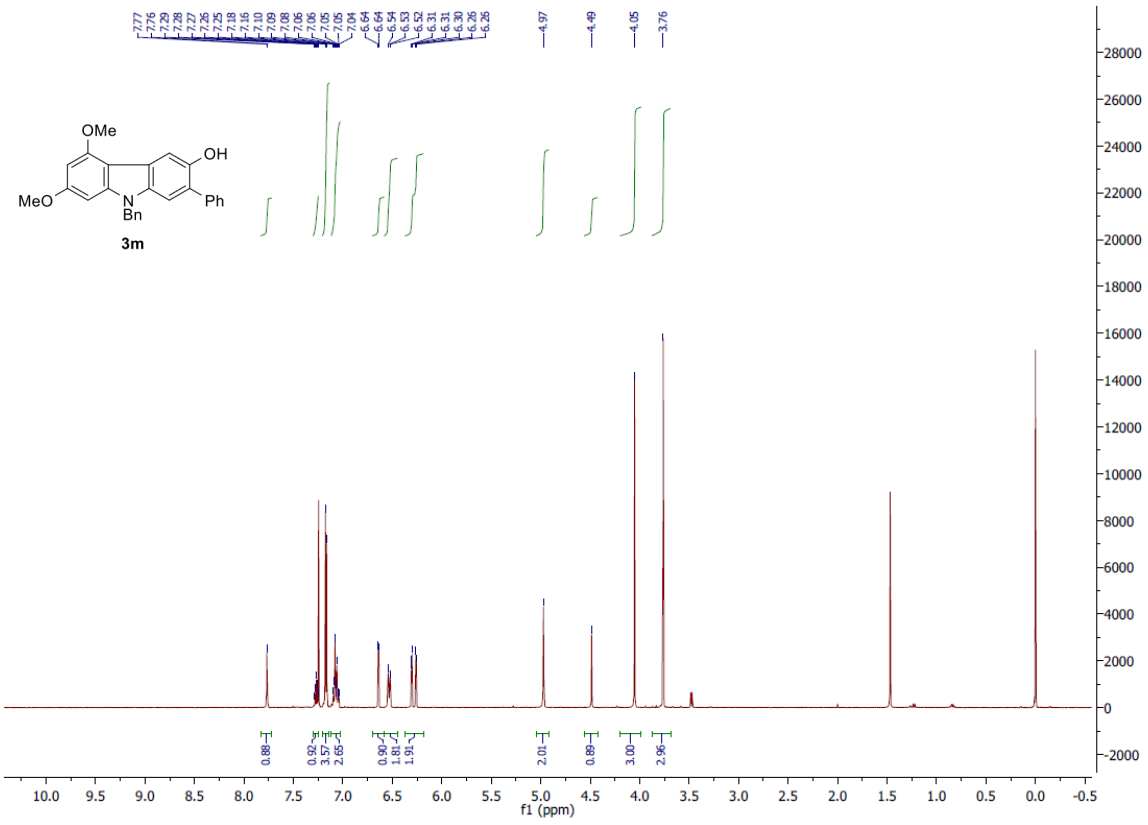
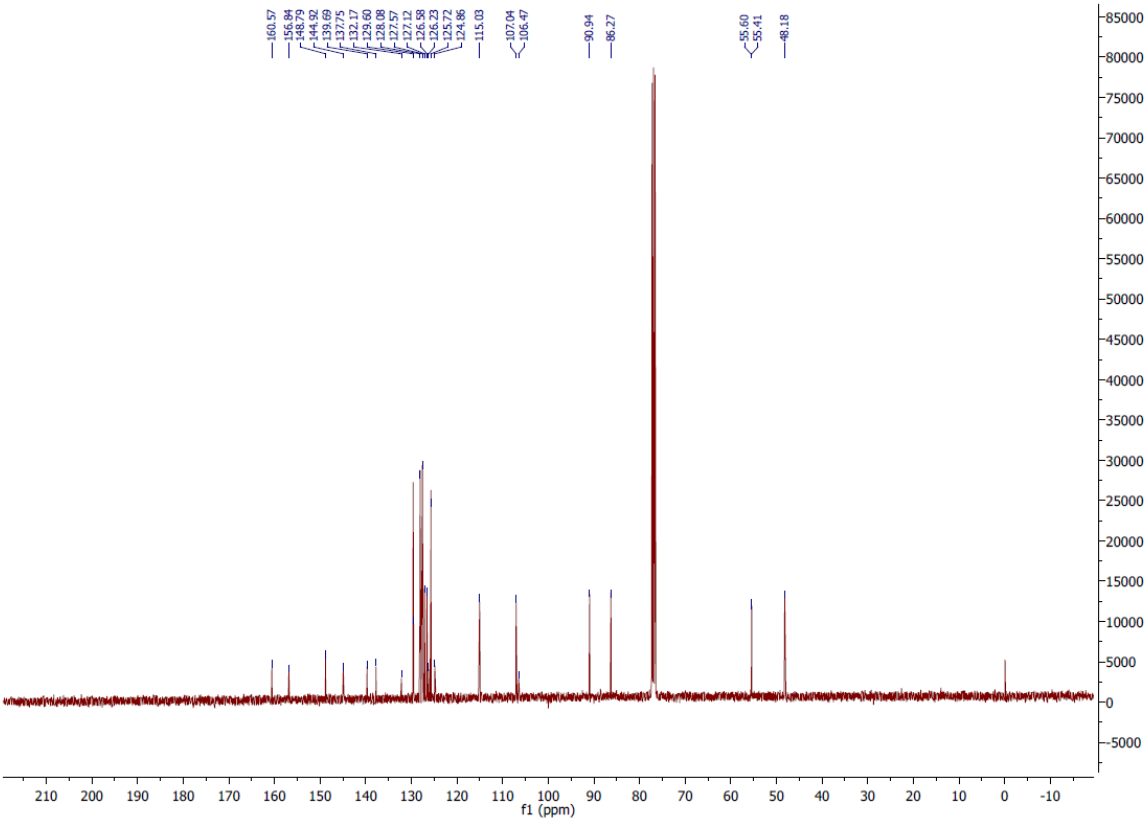
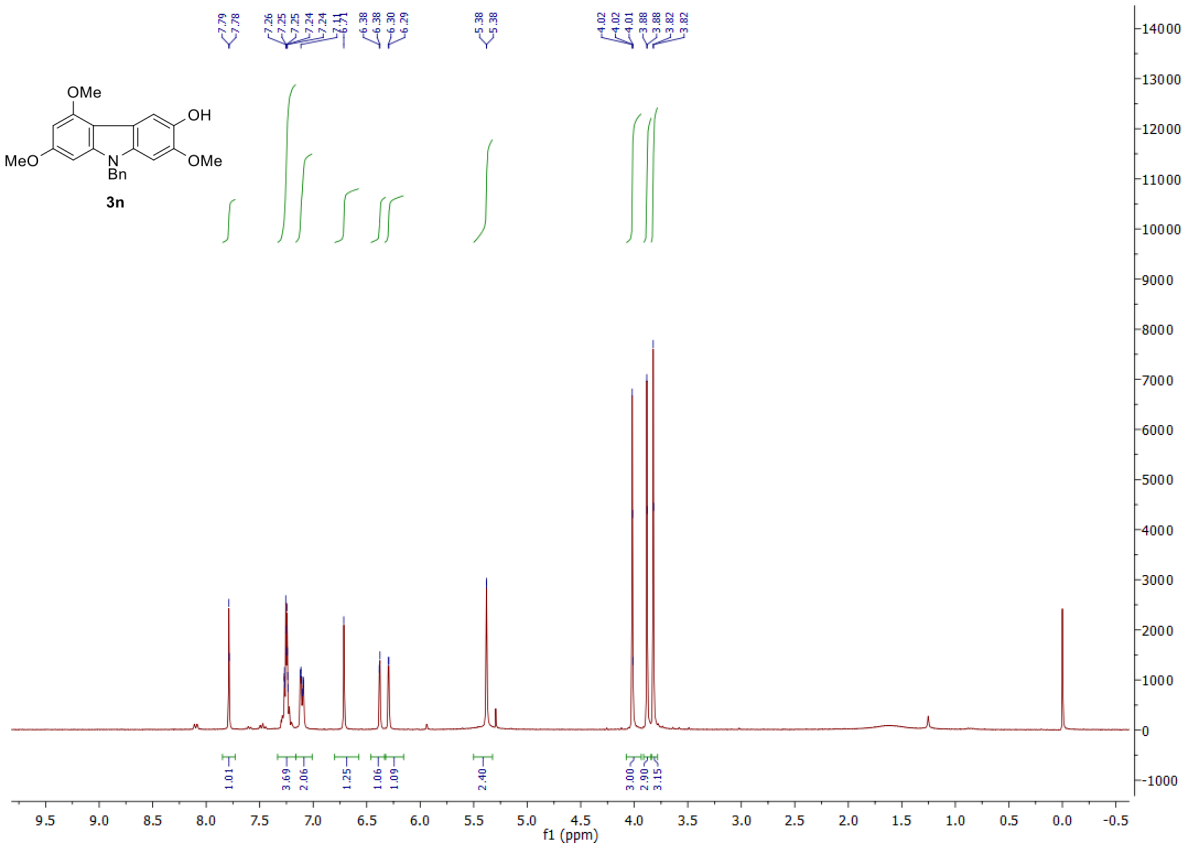
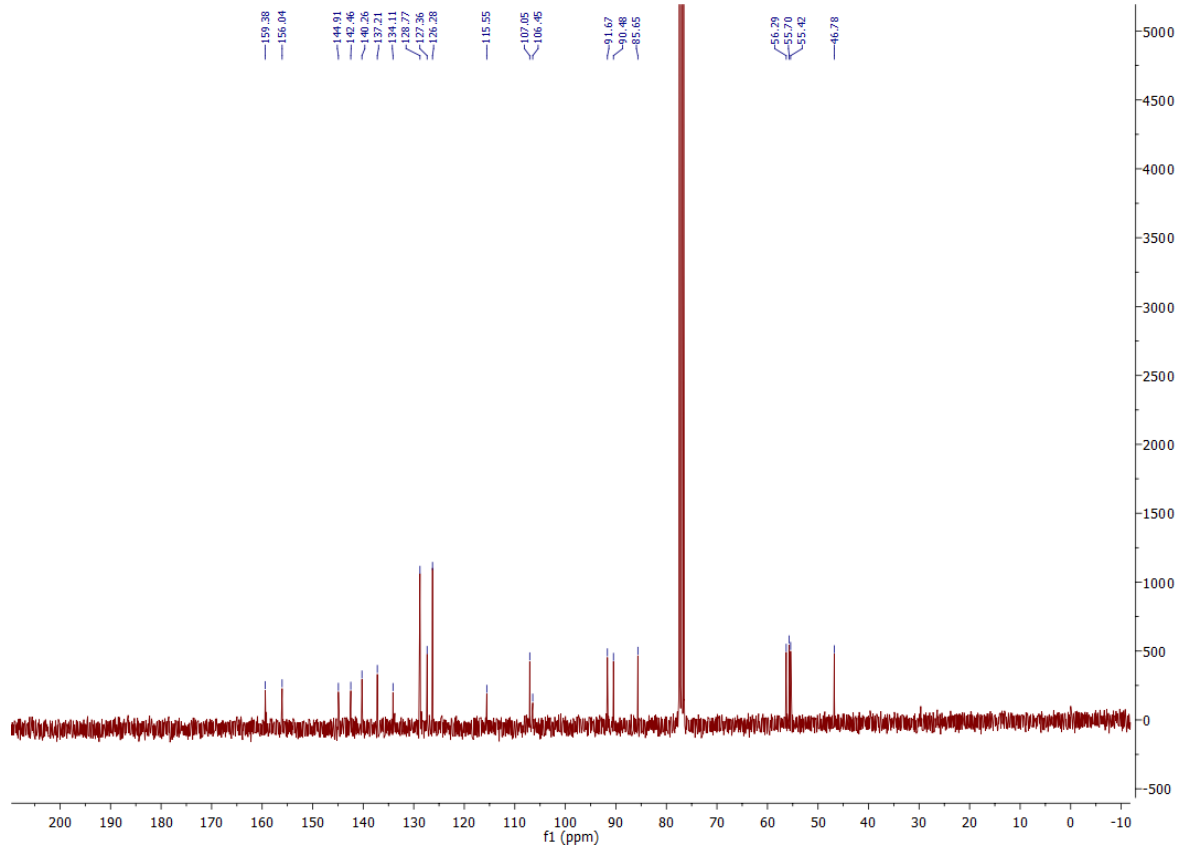
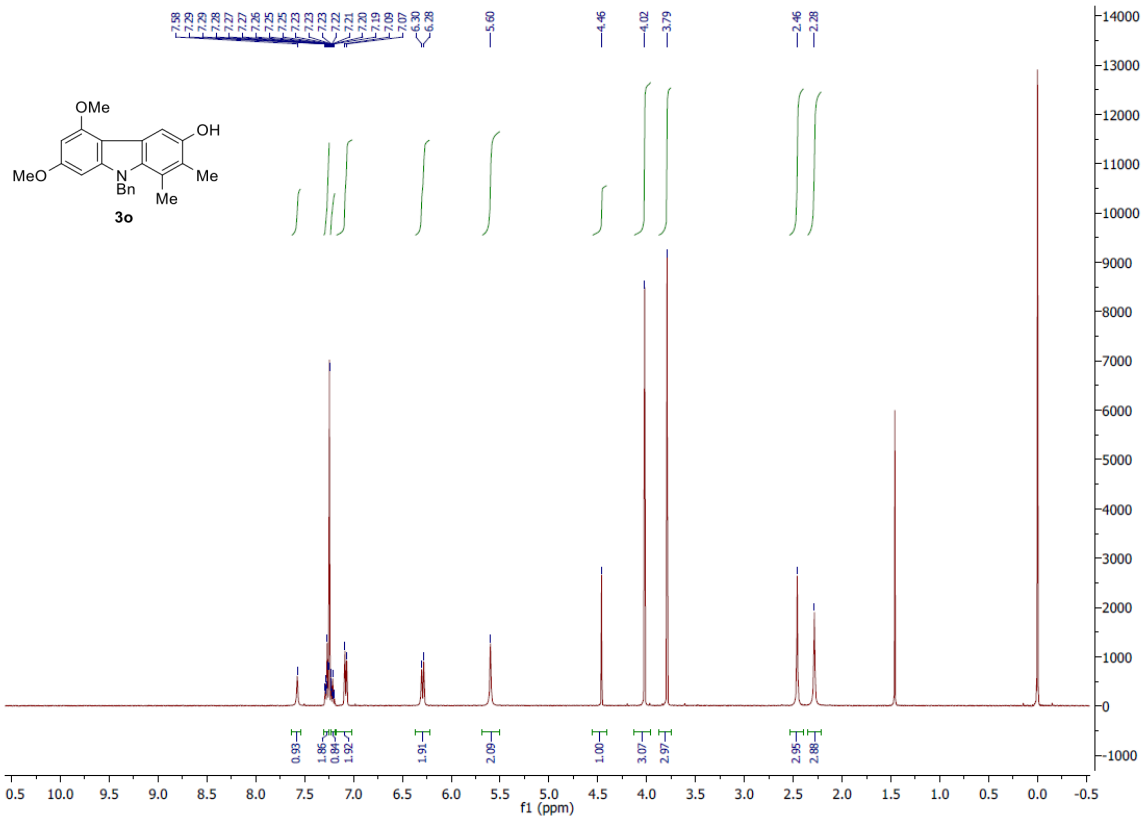
31.74
f1 (ppm)

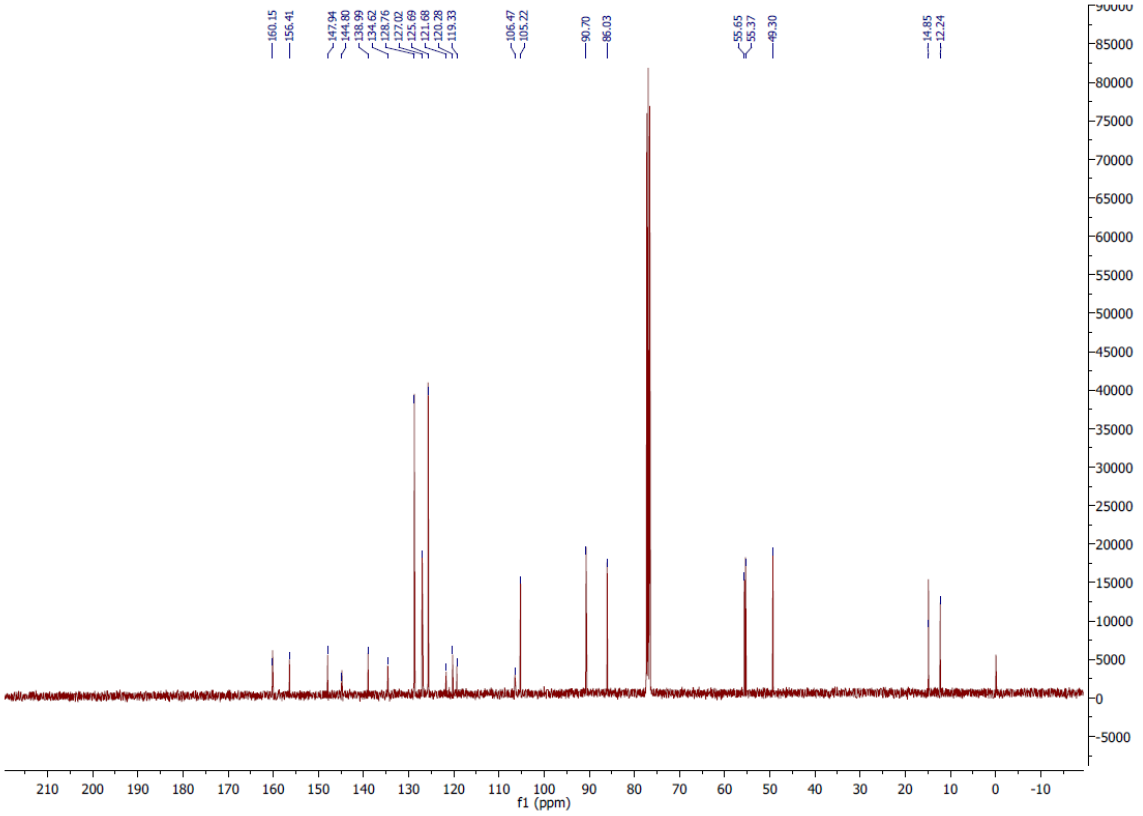

OMe
OH
MeO
N
Bn
Ph
3m
7.77
7.76
7.29
7.28
7.27
7.26
7.25
7.18
7.16
7.10
7.09
7.08
7.06
7.06
7.05
7.05
7.04
6.64
6.64
6.54
6.53
6.52
6.31
6.31
6.30
6.26
6.26
4.97
4.49
4.05
3.76
0.88
0.92
3.57
2.65
0.90
1.81
1.91
2.01
0.89
3.00
2.96
f1 (ppm)

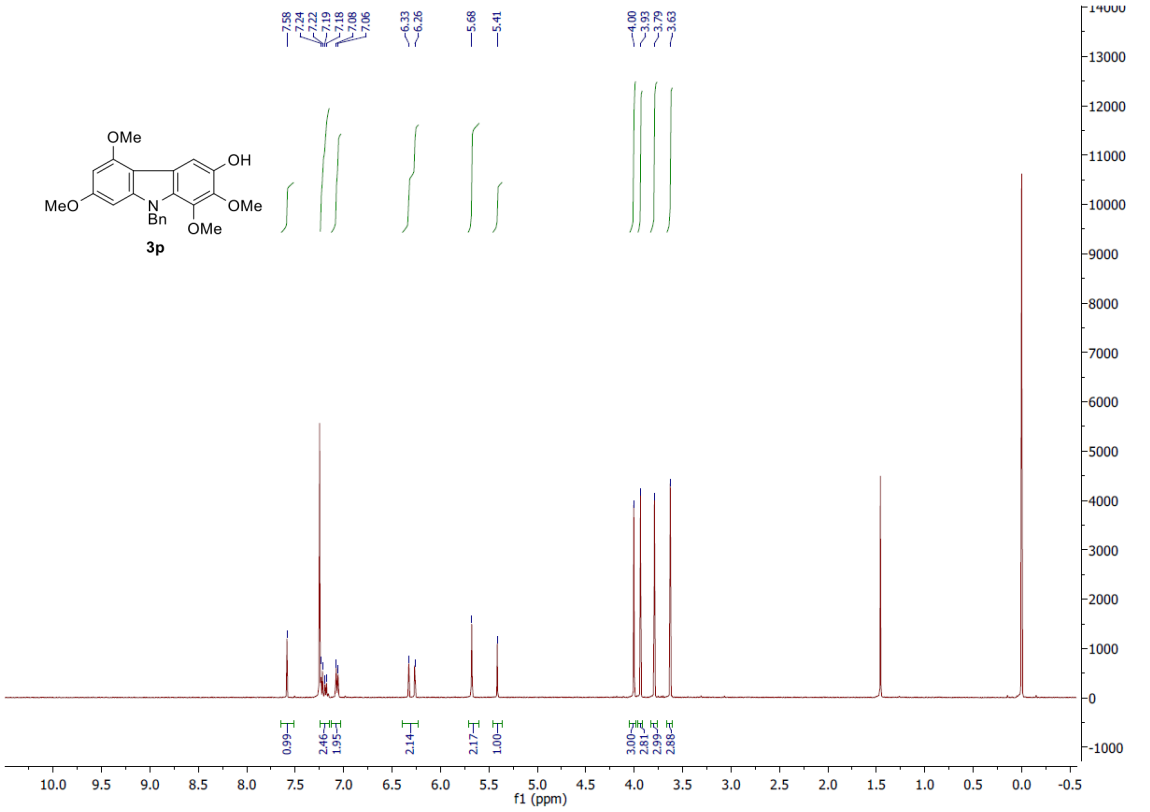

160.57
156.84
148.79
144.92
139.69
137.75
132.17
129.60
128.08
127.57
127.12
126.58
126.23
125.72
124.86
115.03
107.04
106.47
90.94
86.27
55.60
55.41
48.18
f1 (ppm)

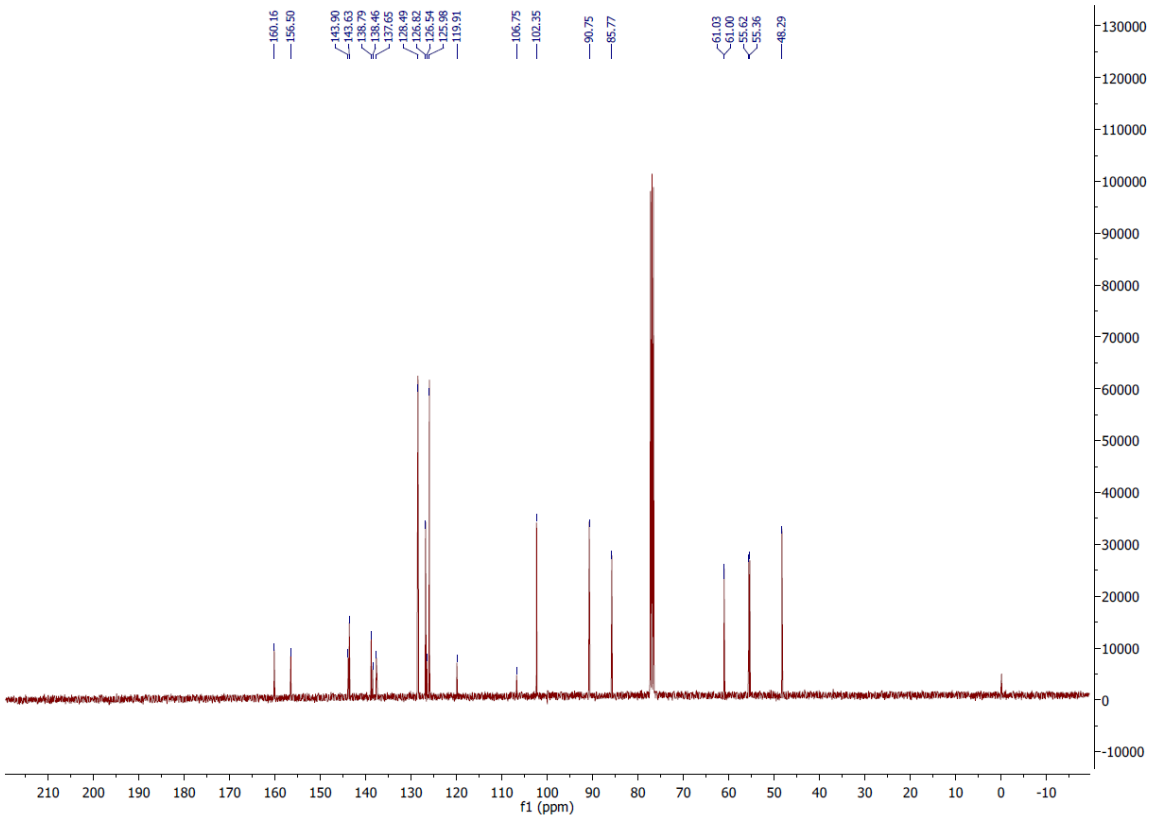

OMe
OH
MeO
OMe
N
Bn
3n
f1 (ppm)

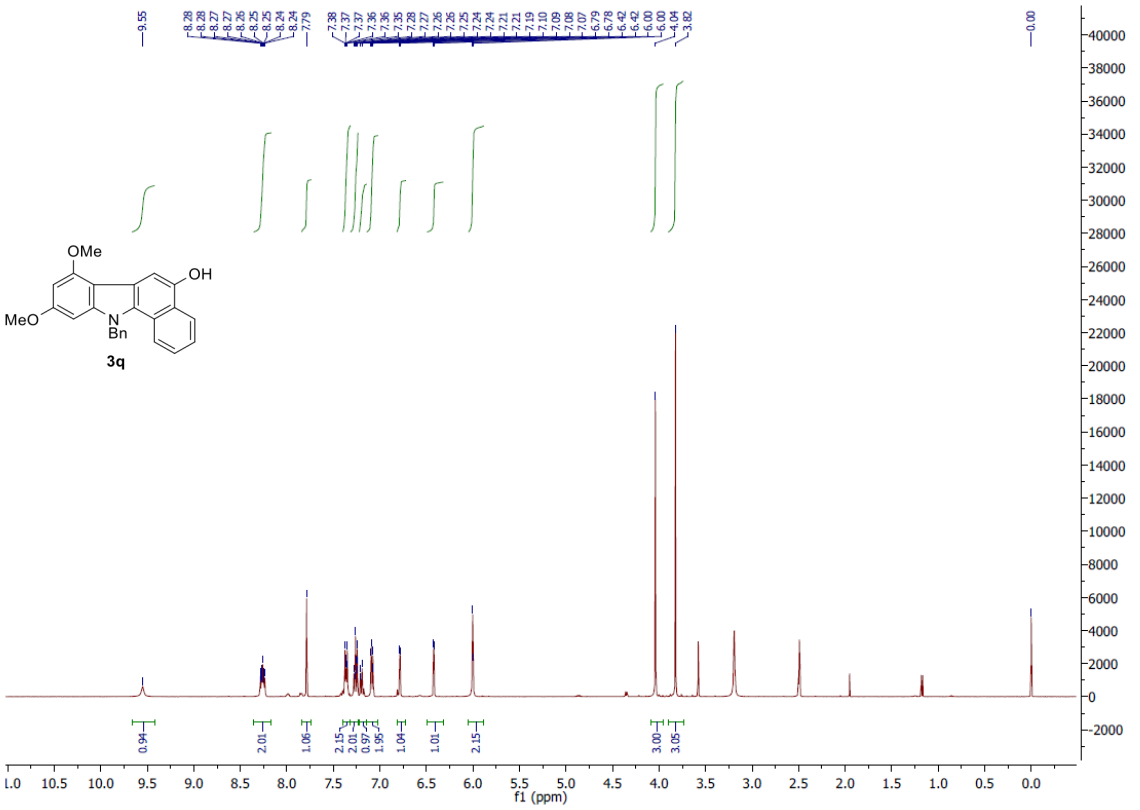

f1 (ppm)

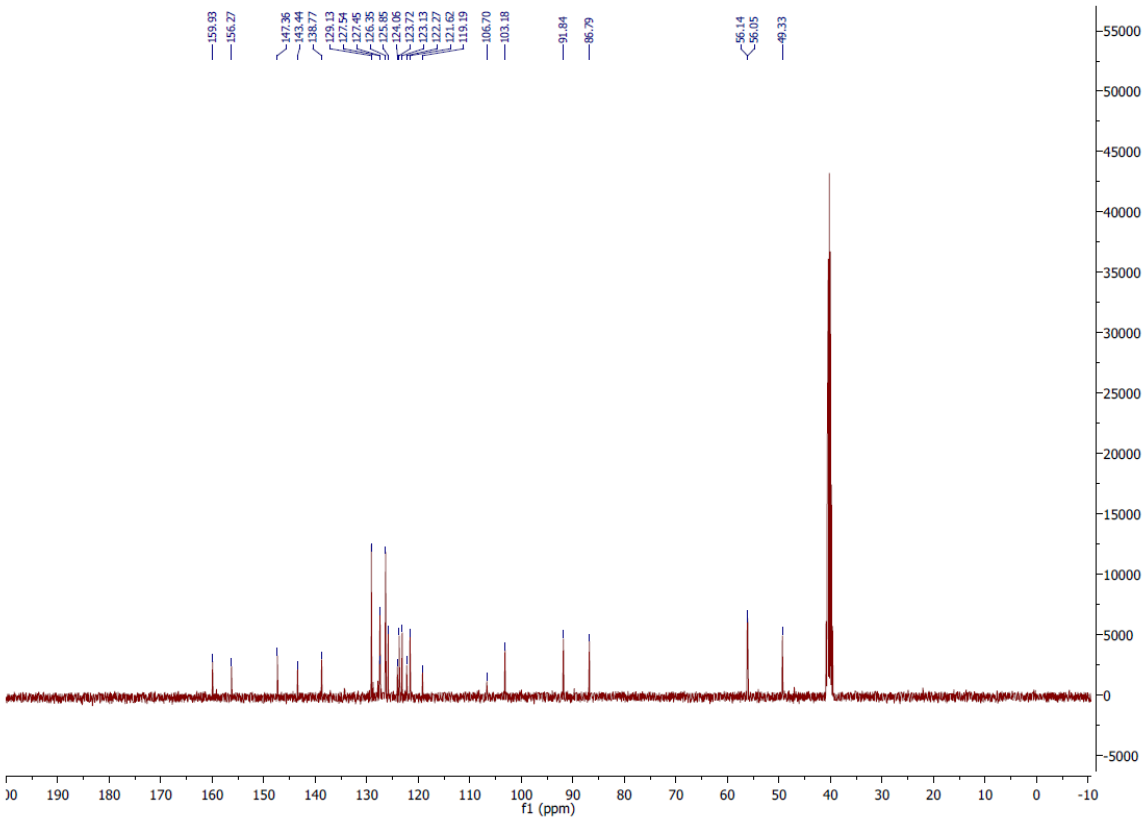

OMe
OH
MeO
N
Bn
Me
Me
3o
7.58
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.23
7.23
7.22
7.21
7.20
7.19
7.09
7.07
6.30
6.28
5.60
4.46
4.02
3.79
2.46
2.28
0.93
1.86
0.84
1.92
1.91
2.09
1.00
3.07
2.97
2.95
2.88
f1 (ppm)

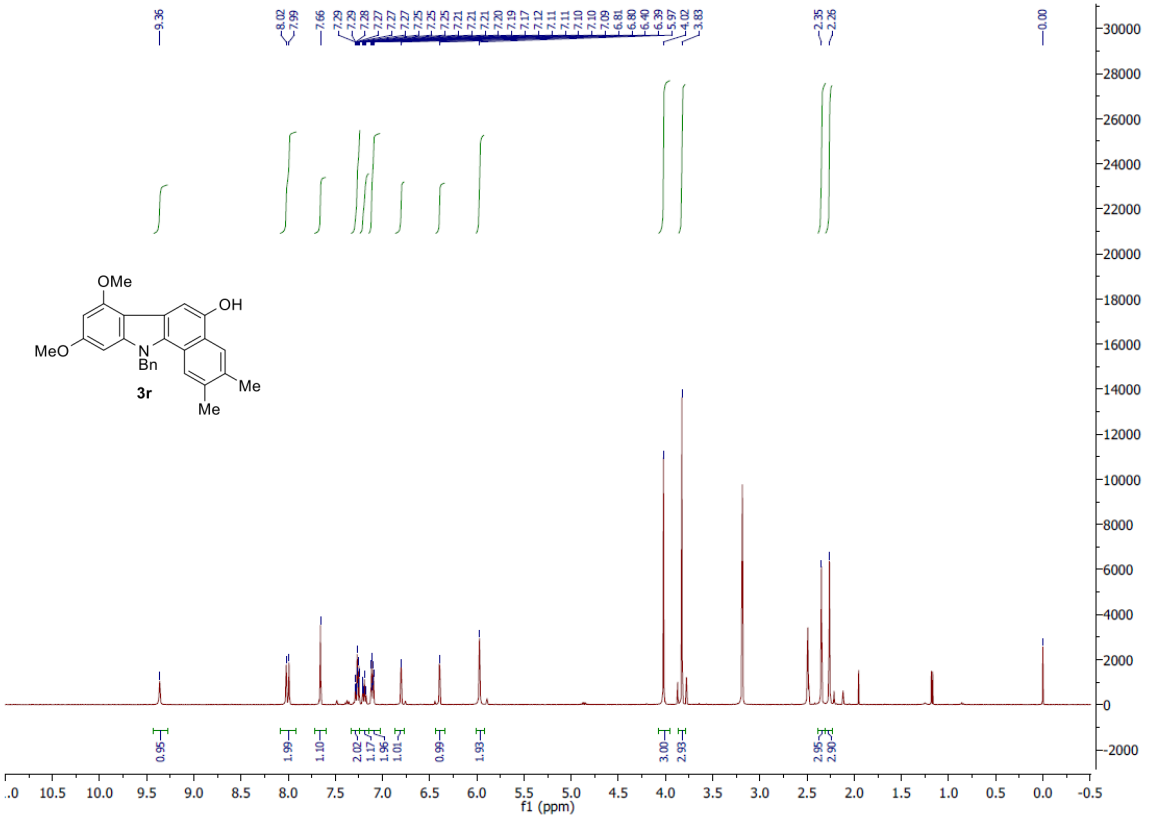

160.15
156.41
147.94
144.80
138.99
134.62
128.76
127.02
125.69
121.68
121.28
119.33
106.47
105.22
90.70
86.03
55.65
55.37
49.30
14.85
12.24
f1 (ppm)

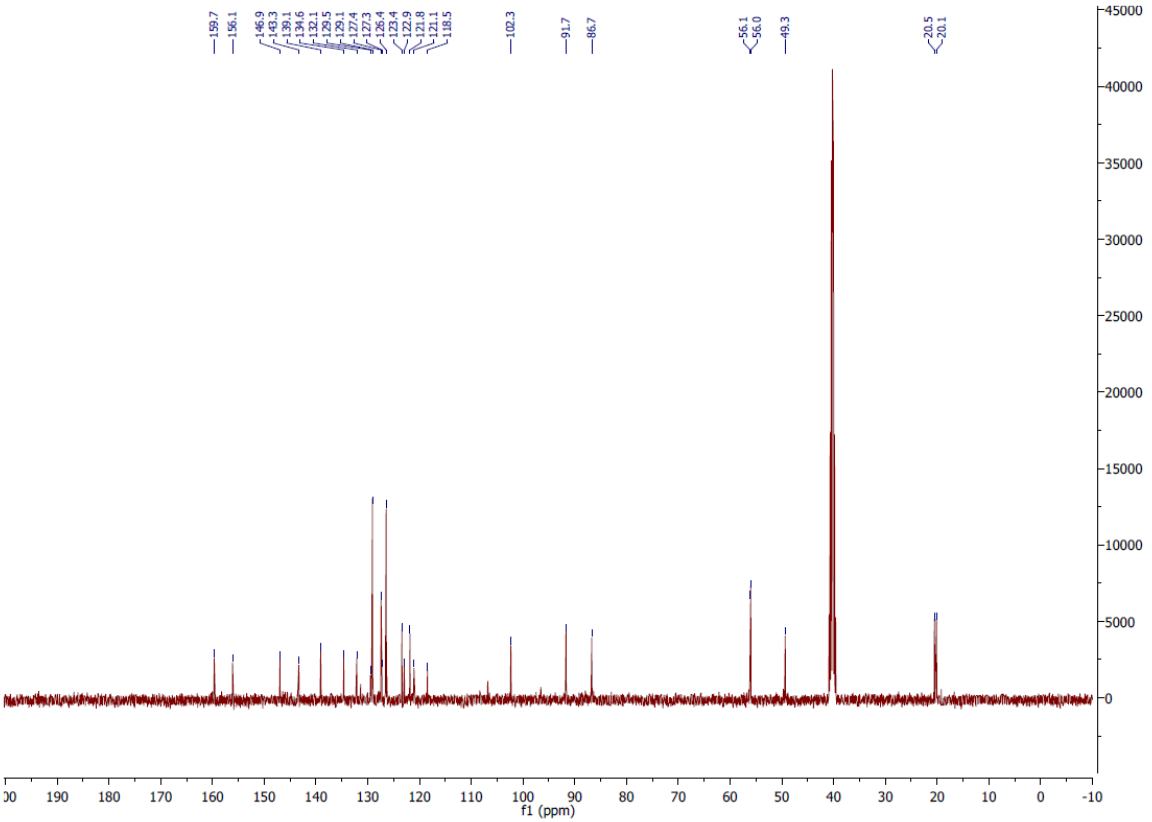

OMe
OH
MeO
N
Bn
OMe
OMe
3p
7.58
7.24
7.22
7.19
7.18
7.08
7.06
6.33
6.26
5.68
5.41
4.00
3.93
3.79
3.63
0.99
2.46
1.95
2.14
2.17
1.00
3.00
2.81
2.99
2.88
f1 (ppm)

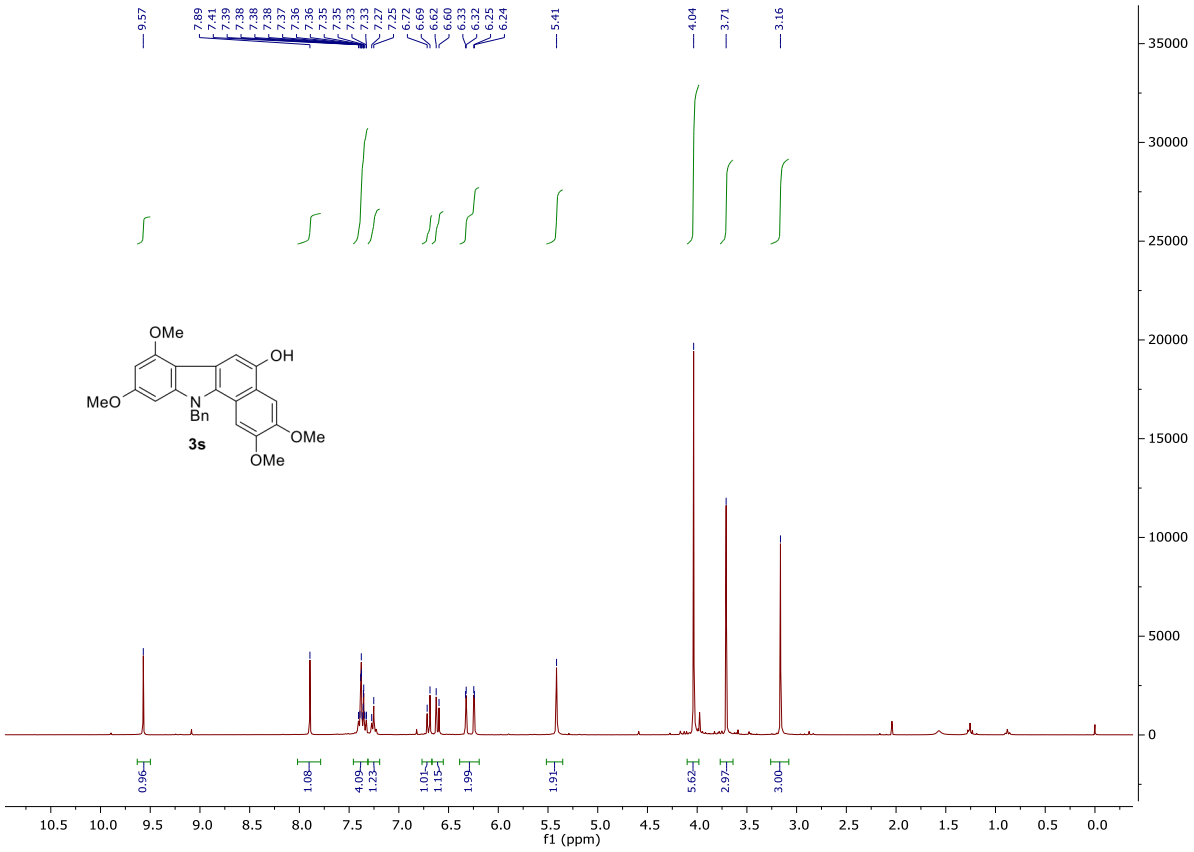

160.16
156.50
143.90
143.63
138.79
138.46
137.65
128.49
126.82
126.54
125.98
119.91
106.75
102.35
90.75
85.77
61.03
61.00
55.62
55.36
48.29
f1 (ppm)

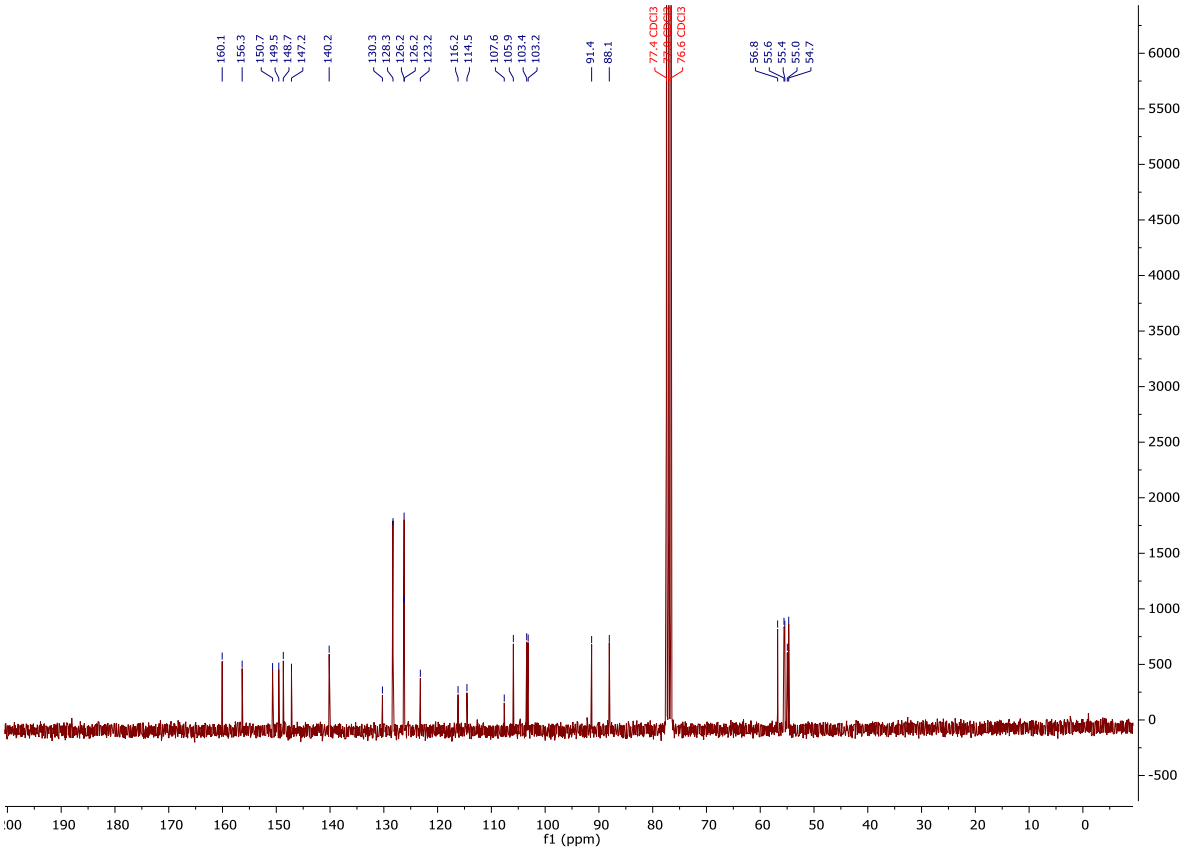

OMe
OH
MeO
N
Bn
3q
f1 (ppm)

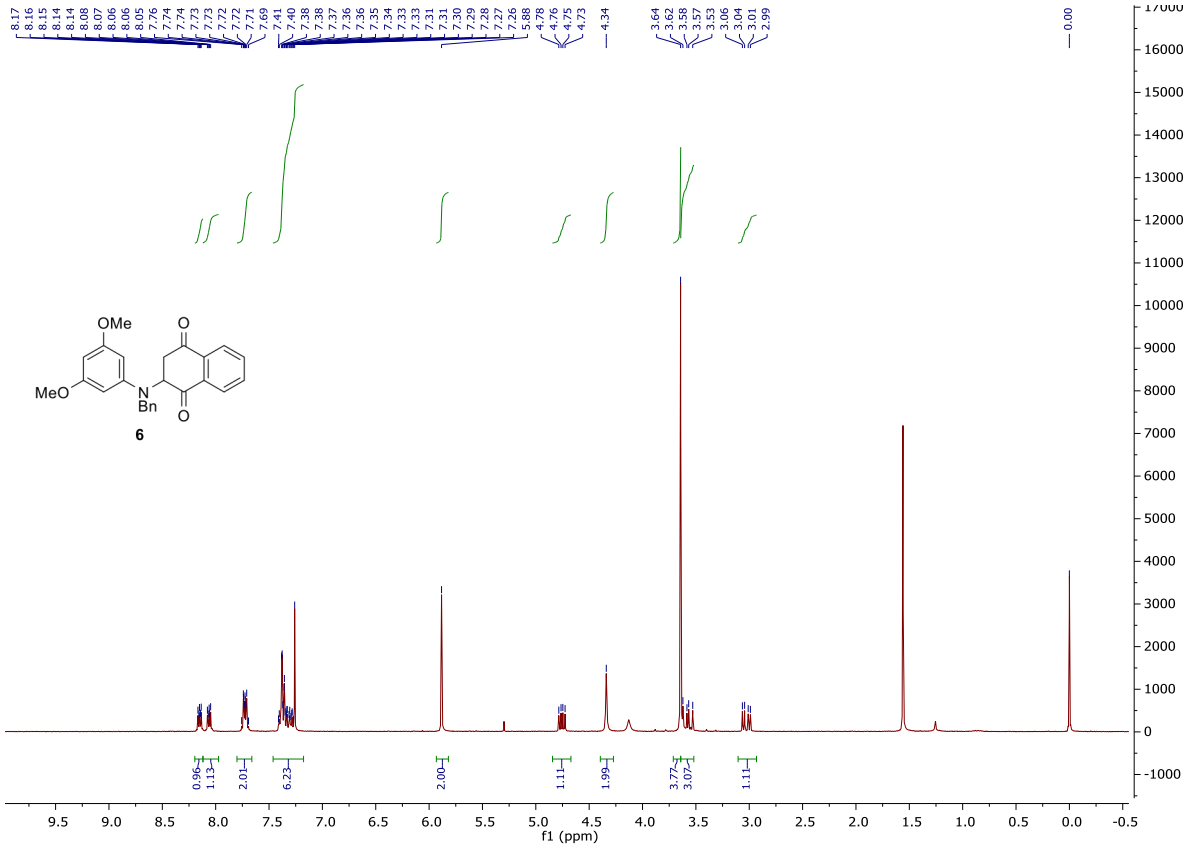

f1 (ppm)

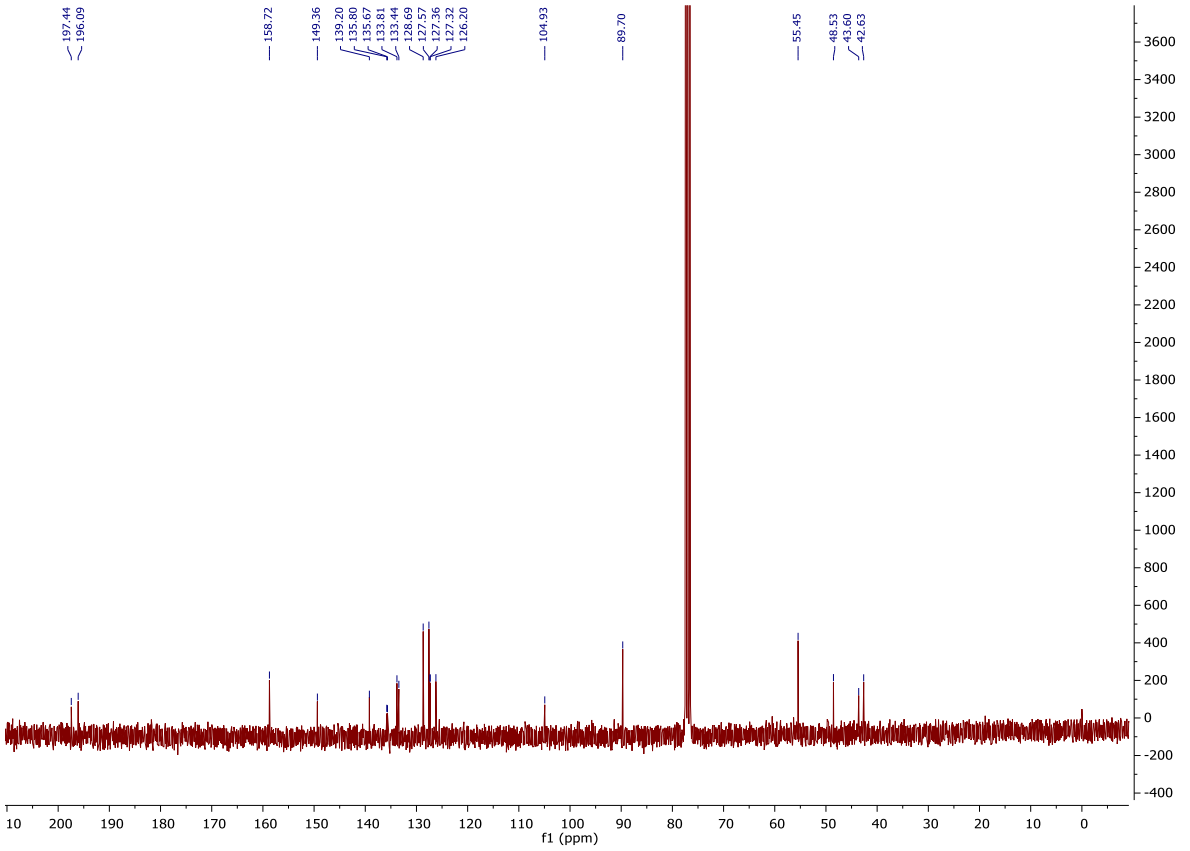

OMe
OH
MeO
N
Bn
Me
Me
3r
f1 (ppm)


f1 (ppm)


9.57
7.89
7.41
7.39
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.33
7.33
7.27
7.25
6.72
6.69
6.62
6.60
6.33
6.32
6.25
6.24
5.41
4.04
3.71
3.16
OMe
OH
MeO
N
Bn
OMe
OMe
3s
0.96
1.08
4.09
1.23
1.01
1.15
1.99
1.91
5.62
2.97
3.00
f1 (ppm)


160.1
156.3
150.7
149.5
148.7
147.2
140.2
130.3
128.3
126.2
126.2
123.2
116.2
114.5
107.6
105.9
103.4
103.2
91.4
88.1
77.4 CDCl3
77.0
76.6 CDCl3
56.8
55.6
55.4
55.0
54.7
f1 (ppm)


8.17
8.16
8.15
8.14
8.14
8.08
8.07
8.06
8.06
8.05
7.76
7.74
7.74
7.73
7.73
7.72
7.72
7.71
7.69
7.41
7.40
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.31
7.31
7.30
7.29
7.28
7.27
7.26
5.88
4.78
4.76
4.75
4.73
4.34
3.64
3.62
3.58
3.57
3.53
3.06
3.04
3.01
2.99
0.00
OMe
O
MeO
N
Bn
O
6
0.96
1.13
2.01
6.23
2.00
1.11
1.99
3.77
3.07
1.11
f1 (ppm)


197.44
196.09
158.72
149.36
139.20
135.80
135.67
133.81
133.44
128.69
127.57
127.36
127.32
126.20
104.93
89.70
55.45
48.53
43.60
42.63
f1 (ppm)