Supplementary Information

Rh(I)-Catalysed Imine-Directed C-H Functionalization by the Oxidative [3+2] Cycloaddition of Benzylamine Derivatives with Maleimides

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Table of Contents

1. General information

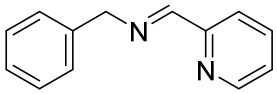
All chemicals were measured and added to a sealed tube under argon atmosphere. The reaction tube was then closed and kept in an oil bath. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), and ^{19}F NMR (376 Hz) spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. All ^{1}H NMR chemical shifts were recorded in ppm (δ) and referenced to tetramethylsilane. All ^{13}C{^{1}H} NMR chemical shifts are given in ppm (δ) relative to carbon resonances in $CDCl_3$ at δ 77.16. Infrared spectra (IR) were recorded on a JASCO FT/IR-4200 spectrometer using the ATR method. High resolution mass spectra (HRMS) were obtained using a JEOL JMS-700 spectrometer and recorded by EI using a double-focusing mass spectrometer. Melting points were determined using a Stanford Research Systems MPA100 apparatus equipped with a digital thermometer. Flash column chromatography was performed using SiO_2 F60 (0.040–0.0663 nm, 230-400 mesh). Some compounds were isolated by LC-908 HPLC (GPC) or HPLC (Phenomenex Luna 5u Silica (2) 100 × 21.20 mm column with hexane/EtOAc as an eluent).

2. Materials

$[Rh(OAc)(cod)]_2$ was prepared from $RhCl_3.H_2O$ by following the literature procedure.[1] $Rh_2(OAc)_4$ was purchased from Wako Pure Chemical Industries, Ltd. $[RhCl(cod)]_2$, $[RhCl(nbd)]_2$ and $[RhCl(PPh_3)_3]_2$ were purchased from Tokyo Chemical Industry Co., Ltd., $AgSbF_6$ and $Pd(OAc)_2$ were purchased from Wako Pure Chemical Industries, Ltd., $[Cp^*RhCl_2]_2$, AgOAc and $[IrCl(coe)]_2$ were purchased from Sigma-Aldrich accordingly. All the chemicals were used as received without further purification. Substrates **2a**-**2q**,[2] **2a'**[2] and **1c-D**[3] were prepared following literatures. Toluene and chloroform were purchased from Wako Pure Chemical Industries, Ltd. and Kanto Chemical Co., Inc. as dry solvents and used as received. Solvents for work up, column chromatography and general use (toluene, chloroform, hexane, EtOAc and $CDCl_3$) were used without further purification.

3. Preparation of substrates

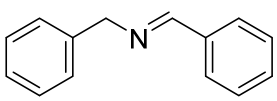
(*E*)-N-benzyl-1-(pyridin-2-yl)methanimine (2a)



2a was prepared following a literature procedure with minor modifications.[2] After placing MS 4A (5.0 g) In a 100 mL round bottom flask, it was acivated by heating. Anhydrous chloroform (20 mL, 0.50 M) was then added to the flask under an argon atmosphere with stirring. An equimolar amount of benzylamine (1.1 mL, 10 mmol) and 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol) were added sequentially to the solution which was then strirred at room temperature for 12 hours. After filtering the solution through a pad of celite and quenching the reaction by adding 20 mL of a 1 N aq. NaOH soultion. The organic phase was extracted with chloroform and washed repeatedly with brine, and the chloroform phase was then dried over Na_2SO_4. After removing the solvent under reduced pressure, 2 mL of toluene was added to the residue which was then evaporated to dryness and stored under a high vacuum for 1 hour to remove chloroform completely to give the corresponding product **2a** as a pale yellow oil (1.62 g, 83% yield), which was used without purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (ddd, J = 4.8, 1.6, 1.0 Hz, 1H), 8.53 – 8.47 (m, 1H), 8.07 (dt, J = 7.9, 1.0 Hz, 1H), 7.78 – 7.69 (m, 1H), 7.39 – 7.26 (m, 6H), 4.88 (d, J = 1.5 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.98, 154.69, 149.55, 138.83, 136.70, 128.71, 128.32, 127.31, 124.97, 121.50, 65.06. IR (neat, ν/cm^{-1}) 3029, 2882, 1647, 1586, 1567, 1468, 1453, 1436, 1362, 1336, 1222, 1147, 1043, 992, 863, 771, 738, 698. HRMS (EI$^+$) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{13}N_2$ 197.1073; found 197.1075.

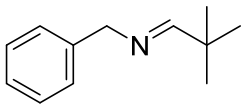
(*E*)-N-benzyl-1-phenylmethanimine (2b)



2b was prepared by the same procedure as was used for **2a** except that benzaldehyde was used instead of 2-pyridinecarboxaldehyde and the scale of the reaction was 5 mmol instead of 10 mmol to give **2b** as a yellow liquid (799 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (brs, 1H), 7.83 – 7.73 (m, 2H), 7.46 – 7.21 (m, 8H), 4.82 (d, *J* = 0.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.11, 139.40, 136.26, 130.88, 128.72, 128.61, 128.39, 128.09, 127.10, 65.16. IR (neat, ν/cm^{-1}) 3061, 3028, 2839, 1642, 1579, 1494, 1451, 1378, 1310, 1220, 1076, 1026, 910, 857, 803, 750, 692. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{14}H_{13}N$ 195.1048; found 195.1043.

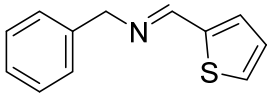
(*E*)-*N*-benzyl-2,2-dimethylpropan-1-imine (2c)



2c was prepared by the same procedure as was used for **2a** except that pivalaldehyde was used instead of 2-pyridinecarboxaldehyde and the scale of the reaction was 5 mmol instead of 10 mmol to give **2c** as a pale yellow liquid (693 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 1.3 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.22 (m, 3H), 4.58 (s, 2H), 1.11 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 173.58, 139.80, 128.47, 127.70, 126.86, 64.68, 36.42, 27.09. IR (neat, ν/cm^{-1}) 3029, 2959, 2867, 2816, 1666, 1496, 1453, 1364, 1206, 1050, 1030, 913, 732, 696. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{12}H_{17}N$ 175.1361; found 175.1365.

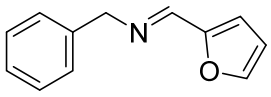
(*E*)-*N*-benzyl-1-(thiophen-2-yl)methanimine (2d)



2d was prepared by the same procedure as was used for **2a** except that thiophenecarboxaldehyde was used instead of 2-pyridinecarboxaldehyde and the scale of the reaction was 5 mmol instead of 10 mmol to give **2d** as a white sticky solid (921 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 1.0 Hz, 1H), 7.38 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.37 – 7.28 (m, 5H), 7.28 – 7.22 (m, 1H), 7.07 – 7.04 (m, 1H), 4.78 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 155.29, 142.54, 139.13, 130.75, 129.15, 128.59, 128.13, 127.46, 127.12, 64.54. IR (neat, ν/cm^{-1}) 3028, 2838, 1631, 1494, 1451, 1431, 1346, 1239, 1217, 1044, 908, 859, 835, 696. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{12}H_{11}NS$ 201.0612; found 201.0614.

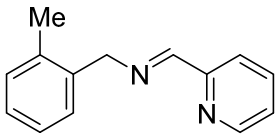
(*E*)-*N*-benzyl-1-(furan-2-yl)methanimine (2e)



2e was prepared by the same procedure as was used for **2a** except that thiophenecarboxaldehyde was used instead of 2-furancarboxaldehyde and the scale of the reaction was 5 mmol instead of 10 mmol to give **2d** as a deep red liquid (858 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, *J* = 1.3 Hz, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.37 – 7.22 (m, 5H), 6.78 (d, *J* = 3.4 Hz, 1H), 6.48 – 6.47 (m, 1H), 4.79 (d, *J* = 1.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.70, 150.52, 144.94, 138.88, 128.65, 128.36, 127.23, 114.30, 111.75, 65.24. IR (neat, ν/cm^{-1}) 3029, 2877, 1739, 1644, 1483, 1452, 1360, 1273, 1153, 1080, 1014, 928, 884, 822, 735, 697. HRMS (EI^{+}) *m/z*: [M]$^{+}$ Calcd for $C_{12}H_{11}NO$ 185.0841; found 185.0842.

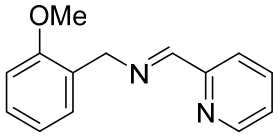
(*E*)-*N*-(2-methylbenzyl)-1-(pyridin-2-yl)methanimine (2f)



2f was prepared by the same procedure as was used for **2a** except that 2-methylbenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2f** as an orange liquid (1.01 g, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.8, 1.7, 1.0 Hz, 1H), 8.43 (dd, *J* = 1.5, 1.0 Hz, 1H), 8.07 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.74 (td, *J* = 7.9, 1.7 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.20 – 7.17 (m, 3H), 4.88 (d, *J* = 1.2 Hz, 2H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.80, 154.80, 149.51, 136.97, 136.69, 136.57, 130.41, 128.95, 127.51, 126.30, 124.92, 121.43, 62.69. IR (neat, ν/cm^{-1}) 3054, 2859, 1647, 1586, 1567, 1466, 1436, 1360, 1329, 1045, 991, 865, 777, 741. HRMS (EI^{+}) *m/z*: [M]$^{+}$ Calcd for $C_{14}H_{14}N_2$ 210.1157; found 210.1159.

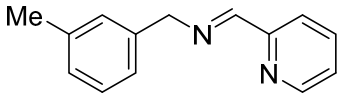
(*E*)-*N*-(2-methoxybenzyl)-1-(pyridin-2-yl)methanimine (2g)



2g was prepared by the same procedure as was used for **2a** except that 2-methoxybenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2g** as an orange liquid (761 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.8, 0.6 Hz, 1H), 8.45 (dd, *J* = 1.4, 1.0 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.33 – 7.23 (m, 3H), 6.96 – 6.87 (m, 2H), 4.89 (d, *J* = 1.3 Hz, 2H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.02, 157.41, 154.91, 149.42, 136.58, 129.76, 128.52, 127.02, 124.76, 121.39, 120.69, 110.45, 59.19, 55.45. IR (neat, ν/cm^{-1}) 3006, 2836, 1647, 1587, 1567, 1492, 1465, 1437, 1289, 1277, 1115, 1029, 992, 781. HRMS (EI^{+}) *m/z*: [M]$^{+}$ Calcd for $C_{14}H_{14}N_2O$ 226.1106; found 226.1105.

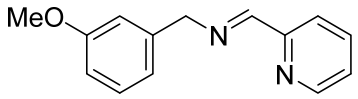
(*E*)-*N*-(3-methylbenzyl)-1-(pyridin-2-yl)methanimine (2h)



2h was prepared by the same procedure as was used for **2a** except that 3-methylbenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2h** as a yellow liquid (861 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 1H), 8.48 – 8.45 (m, 1H), 8.07 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.31 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.16 – 7.14 (m, 2H), 7.09 – 7.08 (m, 1H), 4.84 (d, *J* = 0.8 Hz, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.84, 154.68, 149.51, 138.63, 138.33, 136.66, 129.09, 128.60, 128.04, 125.38, 124.92, 121.49, 65.10, 21.53. IR (neat, ν/cm^{-1}) 3012, 2917, 1647, 1587, 1567, 1468, 1435, 1361, 1327, 1222, 1147, 1092, 1043, 991, 773, 744, 698. HRMS (EI^{+}) *m/z*: [M+H]$^{+}$ Calcd for $C_{14}H_{15}N_2$ 211.1230; found 211.1235.

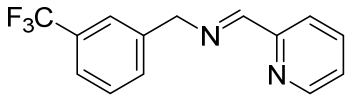
(*E*)-*N*-(3-methoxybenzyl)-1-(pyridin-2-yl)methanimine (2i)



2i was prepared by the same procedure as was used for **2a** except that 3-methoxybenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2i** as a yellow liquid (1.02 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.63 (m, 1H), 8.48 (brs, 1H), 8.06 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.31 – 7.24 (m, 2H), 6.94 – 6.91 (m, 2H), 6.81 (dd, *J* = 8.2, 2.6 Hz, 1H), 4.84 (s, 2H), 3.79 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.95, 159.88, 154.57, 149.45, 140.32, 136.60, 129.62, 124.89, 121.41, 120.54, 113.85, 112.69, 64.86, 55.25. IR (neat, ν/cm^{-1}) 3006, 2835, 1647, 1586, 1489, 1466, 1436, 1326, 1261, 1149, 1043, 992, 865, 781, 695. HRMS (EI^{+}) *m/z*: [M]$^{+}$ Calcd for $C_{14}H_{14}N_2O$ 226.1106; found 226.1108.

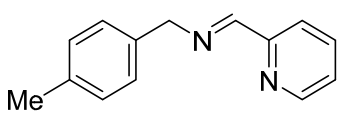
(*E*)-1-(pyridin-2-yl)-*N*-(3-(trifluoromethyl)benzyl)methanimine (2j)



2j was prepared by the same procedure as was used for **2a** except that 3-trifluoromethylbenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2j** as a yellow liquid (1.23 g, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.66 (m, 1H), 8.53 (s, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.64 (s, 1H), 7.56 – 7.53 (m, 2H), 7.48 – 7.44 (m, 1H), 7.35 – 7.32 (m, 1H), 4.92 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.61, 154.36, 149.61, 139.94, 136.76, 131.52, 130.97 (q, *J* = 32.4 Hz), 129.08, 125.15, 124.91 (q, *J* = 3.6 Hz), 124.28 (q, *J* = 273.4 Hz), 124.10 (q, *J* = 3.7 Hz), 121.56, 64.38. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.45. IR (neat, ν/cm^{-1}) 3057, 2884, 1649, 1588, 1569, 1437, 1325, 1163, 1120, 1073, 1045, 992, 796, 775, 702. HRMS (EI^{+}) *m/z*: [M]$^{+}$ Calcd for $C_{14}H_{11}F_3N_2$ 264.0874; found 264.0876.

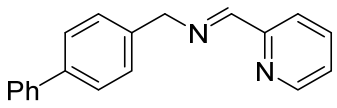
(*E*)-*N*-(4-methylbenzyl)-1-(pyridin-2-yl)methanimine (2k)



2k was prepared by the same procedure as was used for **2a** except that 4-methylbenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2k** as a yellow liquid (978 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 1H), 8.47 – 8.46 (m, 1H), 8.06 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.73 (td, *J* = 7.9, 1.7 Hz, 1H), 7.31 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.84 (s, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.70, 154.71, 149.49, 136.91, 136.64, 135.69, 129.37, 128.29, 124.89, 121.45, 64.81, 21.23. IR (neat, ν/cm^{-1}) 3008, 2920, 1647, 1586, 1567, 1514, 1468, 1435, 1361, 1222, 1043, 992, 801, 775. HRMS (EI^{+}) *m/z*: $[M+H]^{+}$ Calcd for $C_{14}H_{15}N_2$ 211.1230; found 211.1237.

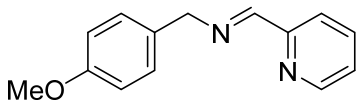
(*E*)-*N*-([1,1'-biphenyl]-4-ylmethyl)-1-(pyridin-2-yl)methanimine (2l)



2l was prepared by the same procedure as was used for **2a** except that 4-phenylbenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2l** as an off-white solid (1.28 g, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.8, 1.6, 1.0 Hz, 1H), 8.52 (brs, 1H), 8.07 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.58 – 7.56 (m, 5H), 7.43 – 7.39 (m, 3H), 7.34 – 7.27 (m, 2H), 4.90 (brs, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.98, 154.57, 149.48, 140.99, 140.20, 137.80, 136.63, 128.92, 128.82, 128.70, 128.49, 127.41, 127.28, 127.15, 124.92, 121.44, 64.67. IR (neat, ν/cm^{-1}) 3029, 2880, 1646, 1586, 1566, 1486, 1468, 1435, 1408, 1361, 1043, 1008, 992, 841, 761, 697. HRMS (EI^{+}) *m/z*: $[M]^{+}$ Calcd for $C_{19}H_{16}N_2$ 272.1313; found 272.1315. M.p = 61-63 °C.

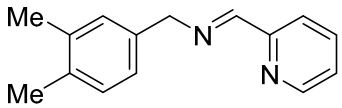
(*E*)-*N*-(4-methoxybenzyl)-1-(pyridin-2-yl)methanimine (2m)



2m was prepared by the same procedure as was used for **2a** except that 4-methoylbenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2m** as a yellow liquid (1.02 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.63 (m, 1H), 8.46 (brs, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.71 (ddd, *J* = 7.9, 1.6, 0.8 Hz, 1H), 7.31 – 7.24 (m, 3H), 6.90 – 6.87 (m, 2H), 4.81 (brs, 2H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.50, 158.90, 154.66, 149.45, 136.60, 130.81, 129.50, 124.84, 121.40, 114.08, 64.41, 55.35. IR (neat, ν/cm^{-1}) 3004, 2835, 1646, 1611, 1586, 1567, 1499, 1466, 1301, 1251, 1175, 1035, 992, 818, 777, 752. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{14}H_{14}N_2O$ 226.1106; found 226.1101.

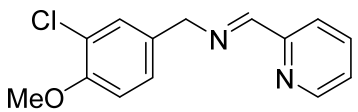
(*E*)-*N*-(3,4-dimethylbenzyl)-1-(pyridin-2-yl)methanimine (2n)



2n was prepared by the same procedure as was used for **2a** except that 3,4-dimethylbenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2n** as an off-white solid (1.03 g, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.8, 1.6, 1.0 Hz, 1H), 8.46 (brs, 1H), 8.05 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.31 – 7.28 (m, 1H), 7.12 – 7.06 (m, 3H), 4.81 (brs, 2H), 2.25 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.56, 154.70, 149.43, 136.83, 136.58, 136.02, 135.53, 129.90, 129.70, 125.80, 124.83, 121.42, 64.86, 19.85, 19.51. IR (neat, ν/cm^{-1}) 3007, 2919, 1647, 1586, 1567, 1503, 1468, 1436, 1359, 1324, 1044, 1024, 992, 881, 818, 777. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{15}H_{16}N_2$ 224.1313; found 224.1312. M.p = 47-49 °C.

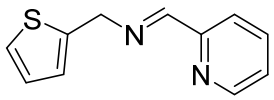
(*E*)-*N*-(3-chloro-4-methoxybenzyl)-1-(pyridin-2-yl)methanimine (2o)



2o was prepared by the same procedure as was used for **2a** except that 3-chloro-4-methoxybenzylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2o** as a yellow liquid (1.23 g, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.63 (m, 1H), 8.45 (brs, 1H), 8.04 – 8.02 (m, 1H), 7.72 – 7.68 (m, 1H), 7.36 – 7.17 (m, 3H), 6.88 – 6.86 (m, 1H), 4.76 (s, 2H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.74, 154.25, 154.01, 149.31, 136.44, 131.82, 129.88, 127.38, 124.80, 122.29, 121.26, 111.99, 63.59, 56.03. IR (neat, ν/cm^{-1}) 3007, 2838, 1647, 1604, 1586, 1567, 1501, 1467, 1437, 1256, 1147, 1064, 1023, 992, 877, 810, 777, 753, 691. HRMS (EI^{+}) *m/z*: [M]$^{+}$ Calcd for $C_{14}H_{13}ClN_2O$ 260.0716; found 260.0713. M.p = 46-48 ℃.

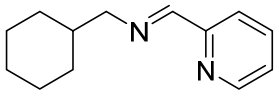
(*E*)-1-(pyridin-2-yl)-*N*-(thiophen-2-ylmethyl)methanimine (2p)



2p was prepared by the same procedure as was used for **2a** except that 2-thiopenemethylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2p** as a yellow liquid (961 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.54 (m, 1H), 8.45 (brs, 1H), 8.07 (dd, *J* = 8.8, 0.9 Hz, 1H), 7.74 (td, *J* = 7.8, 1.7 Hz, 1H), 7.32 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.01 – 6.98 (m, 2H), 5.04 – 5.04 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.35, 163.10, 154.52, 149.67, 149.46, 141.33, 136.71, 127.35, 126.84, 125.81, 125.44, 125.30, 125.21, 125.07, 124.74, 121.61, 59.07. IR (neat, ν/cm^{-1}) 3009, 2882, 1739, 1647, 1586, 1567, 1468, 1435, 1367, 1315, 1227, 1042, 1015, 991, 850, 828, 775, 741. HRMS (EI^{+}) *m/z*: [M]$^{+}$ Calcd for $C_{11}H_{10}N_2S$ 202.0565; found 202.0562.

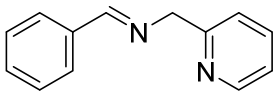
(*E*)-*N*-(cyclohexylmethyl)-1-(pyridin-2-yl)methanimine (2q)



2q was prepared by the same procedure as was used for **2a** except that cyclohexanemethylamine was used instead of benzylamine and the scale of the reaction was 5 mmol instead of 10 mmol to give **2q** as a pale yellow liquid (929 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 8.33 (brs, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.32 – 7.29 (m, 1H), 3.53 – 3.51 (m, 2H), 1.79 – 1.66 (m, 6H), 1.32 – 1.12 (m, 3H), 1.05 – 0.95 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.90, 154.73, 149.46, 136.61, 124.65, 121.26, 68.56, 38.88, 31.52, 26.63, 26.15. IR (neat, ν/cm^{-1}) 2921, 2850, 1649, 1587, 1567, 1468, 1449, 1437, 1331, 1146, 1028, 991, 770, 742, 666. HRMS (EI^{+}) *m/z*: $[M+H]^{+}$ Calcd for $C_{13}H_{19}N_2$ 203.1543; found 203.1552.

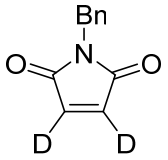
(*E*)-1-phenyl-*N*-(pyridin-2-ylmethyl)methanimine (2a')[2]



2a' was prepared by the same procedure as was used for **2a** except that 2-picolylamine was used instead of benzylamine and benzaldehyde instead of 2-pyridinecarboxaldehyde and the scale of the reaction was 5 mmol instead of 10 mmol to give **2a'** as a yellow liquid (856 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.55 (m, 1H), 8.46 – 8.45 (m, 1H), 7.82 – 7.79 (m, 2H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.42 – 7.37 (m, 4H), 7.15 – 7.12 (m, 1H), 4.95 (brs, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.06, 159.31, 149.24, 136.62, 136.10, 130.87, 128.60, 128.32, 122.25, 121.98, 66.78. IR (neat, ν/cm^{-1}) 3060, 2827, 1645, 1590, 1571, 1473, 1433, 1310, 1150, 1073, 1048, 1027, 995, 909, 755, 698. HRMS (EI^{+}) *m/z*: $[M+H]^{+}$ Calcd for $C_{13}H_{13}N_2$ 197.1073; found 197.1081.

1-benzyl-1*H*-pyrrole-2,5-dione-3,4-d_2 (1c-D)[3]



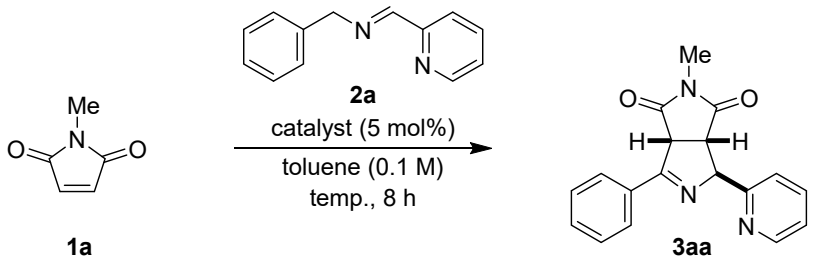
1c-D was prepared according to a previously reported procedure.[3] The isolated product had a deuterium content of 76%, as evidenced by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4.62H), 6.69 (s, 0.48H), 4.67 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.52, 136.30, 134.17, 128.80, 128.49, 127.97, 41.50.

4. Optimization of reaction condition with 1a and 2a (Table S1)

General procedure:

To a sealed tube equipped with a magnetic stirring bar was added the *N*-methylmaleimide (**1a**) (0.20 mmol or 0.40 mmol or 0.60 mmol), catalyst (0 mol% or 0.01 mmol, 5.0 mol%), additive (0 equiv or 0.02 mmol, 10 mol%) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2a** (0.2 mmol or 0.40 mmol or 0.60 mmol) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at a specified temperature for 8 hours. In all cases, the scale for the reaction was 0.2 mmol. The yield of the corresponding product was determined by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene as an internal standard.



Entry[a]	**1a**/**2a**	Catalyst	Temp.	Yield of 3aa (%)[b]
1	2/1	none	150 °C	n.d.
2	2/1	$[Rh(OAc)(cod)]_2$	150 °C	27
3	2/1	$[RhCl(cod)]_2$	150 °C	10
4	2/1	$[RhCl(cod)]_2$, AgOAc (10 mol%)	150 °C	12
5	2/1	[RhCl(cod)]2, AgSbF6 (10 mol%)	150 °C	n.d.
6	2/1	$[RhCl(nbd)]_2$	150 °C	18
7	2/1	$[RhCl(PPh_3)_3]_2$	150 °C	n.d.
8	2/1	$[Rh(OAc)]_2$	150 °C	9
9	2/1	$[Cp^*RhCl_2]_2$	150 °C	n.d.
10	2/1	$Pd(OAc)_2$	150 °C	n.d.
11	2/1	$[IrCl(coe)]_2$	150 °C	n.d.
12	2/1	$[Rh(OAc)(cod)]_2$	170 °C	32
13	3/1	$[Rh(OAc)(cod)]_2$	170 °C	16
14	1/1	$[Rh(OAc)(cod)]_2$	170 °C	41
15	1/2	$[Rh(OAc)(cod)]_2$	170 °C	72 (69)[c]
16	1/3	$[Rh(OAc)(cod)]_2$	170 °C	47

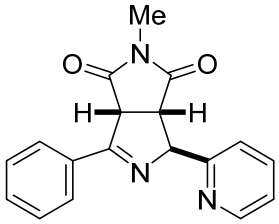
[a] Reaction conditions: **1a**, **2a**, catalyst (none or 5 mol%), additive (none or 10 mol%), toluene (2.0 mL) at specified temperature for 8 h. The scale of the reaction was 0.2 mmol in all cases. [b] Determined by ^{1}H NMR analysis of the crude mixture. [c] Isolated yield. n.d. = not detected.

Optimized reaction conditions (Table S1, entry 15):

To a sealed tube equipped with a magnetic stirring bar was added the *N*-methylmaleimide (**1a**) (22.2 mg, 0.20 mmol, 1.0 equiv), $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2a** (78.5 mg, 0.40 mmol, 2.0 equiv) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at 170 °C for 8 hours. The yield of the corresponding product was determined by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene as internal standard. After the reaction, the reaction mixture was allowed to cool to room temperature,

the solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography using *n*-hexane/EtOAc (4/1-1/1) as an eluent to afford the desired product **3aa**.

2-methyl-6-phenyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3aa)



3aa was prepared according to the procedure of entry 15, Table S1 (41.7 mg, 69%) to give the corresponding product as an off-white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.0 Hz, 1H), 8.22 – 8.19 (m, 2H), 7.70 (td, *J* = 7.6, 1.6 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.21 (dd, *J* = 6.8, 4.8 Hz, 1H), 5.78 – 5.76 (m, 1H), 4.86 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.27 (dd, *J* = 8.2, 2.8 Hz, 1H), 2.99 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.90, 173.61, 167.07, 159.07, 149.99, 137.06, 131.99, 131.71, 129.77, 128.53, 123.10, 123.01, 79.48, 57.09, 50.17, 25.38. IR (neat, ν/cm^{-1}) 3060, 2929, 1689, 1562, 1492, 1433, 1380, 1279, 1232, 1095, 911, 752, 692. HRMS (EI$^+$) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{16}N_3O_2$ 306.1237; found 306.1239. M.p = 120-122 °C.

5. Evaluation of directing groups (Table 1)

General procedure:

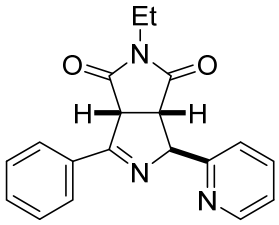
To a sealed tube equipped with a magnetic stirring bar was added the *N*-methylmaleimide (**1a**) (22.2 mg, 0.20 mmol, 1.0 equiv), $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2a** or **2b** or **2c** or **2d** or **2e** (0.40 mmol, 2.0 equiv) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at 170 °C for 8 hours. The yield of the corresponding product was determined by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene as an internal standard.

6. Substrate scope (Table 2)

General procedure:

To a sealed tube equipped with a magnetic stirring bar was added **1** (0.20 mmol, 1.0 equiv), catalyst $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2** (0.40 mmol, 2.0 equiv) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at 170 °C for 8 hours. After the reaction, the reaction mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography using *n*-hexane/EtOAc (4/1-1/2) as an eluent to afford the desired products.

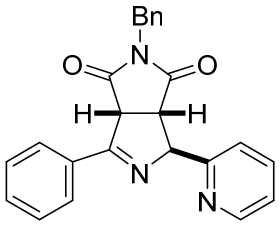
2-ethyl-6-phenyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ba)



3ba was prepared according to the general procedure to give the corresponding product as an off-white solid (45.4 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 8.22 – 8.19 (m, 2H), 7.70 (td, *J* = 7.6, 1.6 Hz, 1H), 7.54 – 7.43 (m, 4H), 7.21 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 5.76 – 5.75 (m, 1H), 4.84 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.26 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.62 – 3.50 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.64, 173.36, 167.18, 159.13, 149.96, 137.06, 132.01, 131.69, 129.77, 128.51, 123.07, 122.98, 79.51, 57.03, 50.13, 34.32, 13.09. IR (neat, ν/cm^{-1}) 3060, 2979, 1773, 1697, 1611, 1589, 1440, 1399, 1378, 1346, 1306, 1224, 1131, 1049, 997, 750, 691. HRMS (EI$^+$) *m/z*: $[M]^+$ Calcd for $C_{19}H_{17}N_3O_2$ 319.1321; found 319.1318. M.p = 129-131 °C.

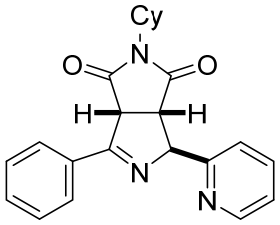
2-benzyl-6-phenyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ca)



3ca was prepared according to the general procedure to give the corresponding product as a yellow sticky solid (48.1 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.55 (m, 1H), 8.20 – 8.17 (m, 2H), 7.69 (td, *J* = 7.6, 1.8 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.34 – 7.25 (m, 5H), 7.21 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 5.76 – 5.75 (m, 1H), 4.86 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.71 – 4.56 (m, 2H), 4.28 (dd, *J* = 8.4, 3.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.44, 173.21, 167.14, 159.01, 149.90, 137.14, 135.55, 131.98, 131.72, 129.78, 128.84, 128.82, 128.53, 128.19, 123.11, 123.00, 79.54, 57.08, 50.16, 42.93. IR (neat, ν/cm^{-1}) 3062, 1775, 1702, 1610, 1588, 1494, 1433, 1392, 1342, 1169, 1049, 997, 909, 749, 693. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{24}H_{19}N_3O_2$ 381.1477; found 381.1472.

2-cyclohexyl-6-phenyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3da)

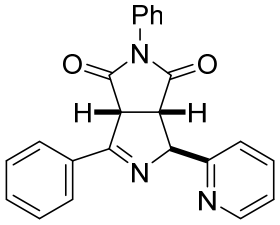


3da was prepared according to the general procedure to give the corresponding product as a yellow solid (40.3 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.55 (m, 1H), 8.21 – 8.18 (m, 2H), 7.69 (td, *J* = 7.6, 1.8 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.20 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 5.74 – 5.73 (m, 1H), 4.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.18 (dd, *J* = 8.4, 3.2 Hz, 1H), 3.94 (tt, *J* = 12.2, 3.8 Hz, 1H), 2.18 – 2.01 (m, 2H), 1.81 – 1.77 (m, 2H), 1.64 – 1.53 (m, 3H), 1.33 – 1.12 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.87, 173.63, 167.46, 159.22, 149.94, 137.05, 132.09, 131.64, 129.79, 128.49, 123.05, 122.99, 79.78, 56.69, 52.30, 49.86, 28.98, 28.80, 25.94, 25.90,

25.10. IR (neat, ν/cm^{-1}) 3060, 2932, 2857, 1772, 1696, 1610, 1589, 1370, 1344, 1258, 1189, 1145, 1049, 996, 910, 730, 691. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{23}H_{23}N_3O_2$ 373.1790; found 373.1788. M.p = 133-135 ℃.

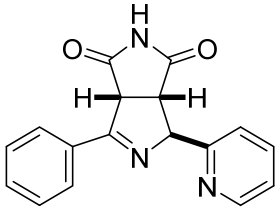
2,6-diphenyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ea)



3ea was prepared according to the general procedure to give the corresponding product as a yellow solid (30.9 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.57 (m, 1H), 8.25 – 8.22 (m, 2H), 7.73 (td, *J* = 7.8, 1.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.35 (m, 6H), 7.29 – 7.22 (m, 3H), 5.92 – 5.91 (m, 1H), 5.03 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.47 (dd, *J* = 8.4, 3.0 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 176.84, 172.47, 167.20, 158.80, 149.89, 137.31, 131.90, 131.81, 131.69, 129.89, 129.25, 128.86, 128.57, 126.57, 123.27, 79.98, 57.12, 50.17. IR (neat, ν/cm^{-1}) 3064, 1779, 1712, 1590, 1496, 1381, 1306, 1183, 1050, 998, 912, 744, 691. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{23}H_{17}N_3O_2$ 367.1321; found 367.1315. M.p = 156-158 ℃.

6-phenyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3fa)

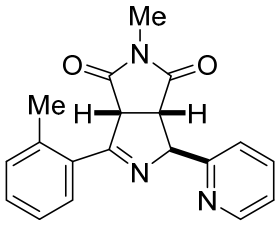


3fa was prepared according to the general procedure to give the corresponding product as a yellow solid (23.9 mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.56 (m, 1H), 8.18 – 8.13 (m, 3H), 7.70 (td, *J* = 7.6, 1.8 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.23 – 7.20 (m, 1H), 5.82 – 5.81 (m, 1H), 4.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.30 (dd, *J* = 8.4, 3.0 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.75, 173.25, 166.93, 158.95, 149.95, 137.17, 131.86, 131.77, 129.77, 128.58, 123.18, 122.93, 79.59, 58.18, 51.41. IR (neat, ν/cm^{-1}) 3061, 2757, 1774, 1713, 1611, 1474, 1437, 1338,

1250, 1180, 1050, 999, 913, 766, 691. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{17}H_{13}N_3O_2$ 291.1008; found 291.1010. M.p = 125-127 ℃.

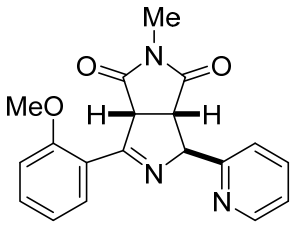
2-methyl-4-(pyridin-2-yl)-6-(o-tolyl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3af)



3af was prepared according to the general procedure to give the corresponding product as a yellow solid (46.0 mg, 72%).

^1H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.57 (m, 1H), 7.72 – 7.66 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.19 (m, 4H), 5.87 – 5.85 (m, 1H), 4.86 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.24 (dd, *J* = 8.2, 2.8 Hz, 1H), 2.99 (s, 3H), 2.49 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 178.20, 173.45, 168.82, 158.91, 149.93, 138.27, 137.01, 131.72, 131.58, 130.50, 130.28, 125.70, 123.08, 122.95, 80.08, 59.19, 49.39, 25.30, 22.08. IR (neat, ν/cm^{-1}) 2956, 1778, 1699, 1589, 1433, 1380, 1281, 1126, 1044, 994, 754. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{19}H_{17}N_3O_2$ 319.1321; found 319.1317. M.p = 96-98 ℃.

6-(2-methoxyphenyl)-2-methyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ag)

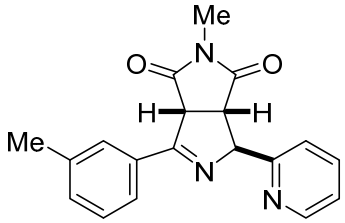


3ag was prepared according to the general procedure to give the corresponding product as a yellow sticky solid (36.2 mg, 54%).

^1H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.60 (m, 1H), 7.72 – 7.66 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.43 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.01 – 6.95 (m, 2H), 5.71 – 5.69 (m, 1H), 5.27 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.20 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.96 (s, 3H), 2.95 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 178.47, 173.62, 168.03, 159.20,

158.78, 149.96, 136.98, 132.64, 130.92, 122.97, 122.89, 121.86, 120.93, 111.84, 79.12, 58.65, 55.92, 49.72, 25.18. IR (neat, ν/cm^{-1}) 2944, 1695, 1566, 1490, 1466, 1433, 1379, 1278, 1247, 1125, 1090, 1023, 751. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{19}H_{17}N_3O_3$ 335.1270; found 335.1264.

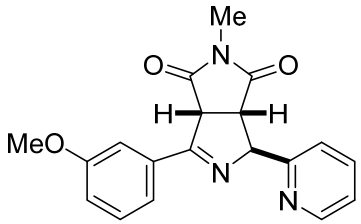
2-methyl-4-(pyridin-2-yl)-6-(m-tolyl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ah)



3ah was prepared according to the general procedure to give the corresponding product as an off-white solid (46.0 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.56 (m, 1H), 8.00 – 7.98 (m, 2H), 7.70 (td, *J* = 7.6, 1.4 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.23 – 7.20 (m, 1H), 5.77 – 5.75 (m, 1H), 4.86 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.24 (dd, *J* = 8.4, 3.0 Hz, 1H), 2.99 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.92, 173.60, 167.32, 159.08, 150.00, 138.25, 137.06, 132.55, 131.83, 129.99, 128.39, 127.17, 123.09, 122.96, 79.41, 57.05, 50.20, 25.35, 21.47. IR (neat, ν/cm^{-1}) 3018, 1688, 1561, 1486, 1432, 1379, 1279, 1228, 1098, 997, 911, 749, 694. HRMS (EI$^+$) *m/z*: [M+H]$^+$ Calcd for $C_{19}H_{18}N_3O_2$ 320.1394; found 320.1396. M.p = 118-120 ℃.

6-(3-methoxyphenyl)-2-methyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ai)

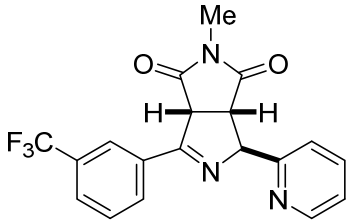


3ai was prepared according to the general procedure to give the corresponding product as a yellow sticky solid (44.9 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 4.8, 1.6, 1.0 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.70 (td, *J* = 7.8, 1.6 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.23 – 7.20 (m,

1H), 7.06 – 7.03 (m, 1H), 5.78 – 5.77 (m, 1H), 4.83 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.26 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.86 (s, 3H), 3.00 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 177.88, 173.58, 166.99, 159.69, 159.07, 150.01, 137.06, 133.28, 129.52, 123.11, 122.98, 122.59, 118.41, 113.99, 79.40, 57.16, 55.57, 50.24, 25.40. IR (neat, ν/cm^{-1}) 2933, 1178, 1700, 1585, 1433, 1381, 1284, 1173, 1126, 1045, 874, 771, 689. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{19}H_{17}N_3O_3$ 335.1270; found 335.1271.

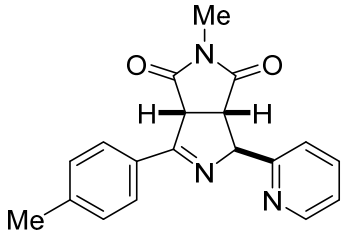
2-methyl-4-(pyridin-2-yl)-6-(3-(trifluoromethyl)phenyl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3aj)



3aj was prepared according to the general procedure to give the corresponding product as a yellow solid (53.0 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.56 (m, 1H), 8.50 (s, 1H), 8.40 (d, *J* = 7.8 Hz, 1H), 7.73 (td, *J* = 7.6, 1.6 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.25 – 7.22 (m, 1H), 5.80 – 5.78 (m, 1H), 4.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.31 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.01 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 177.65, 173.39, 165.84, 158.50, 150.07, 137.21, 133.14, 132.67, 131.10 (q, *J* = 32.8 Hz), 129.06, 128.10 (q, *J* = 3.7 Hz), 126.54 (q, *J* = 3.5 Hz), 123.94 (q, *J* = 271.7 Hz), 123.31, 123.17, 79.60, 57.14, 50.10, 25.44. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63. IR (neat, ν/cm^{-1}) 2925, 1776, 1698, 1624, 1571, 1435, 1382, 1324, 1278, 1167, 1125, 1073, 754, 695. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{19}H_{14}F_3N_3O_2$ 373.1038; found 373.1033. M.p = 152-154 ℃.

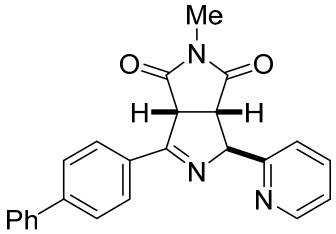
2-methyl-4-(pyridin-2-yl)-6-(p-tolyl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ak)



3ak was prepared according to the general procedure to give the corresponding product as an off-white solid (47.9 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.56 (m, 1H), 8.09 – 8.07 (m, 2H), 7.69 (td, *J* = 7.6, 1.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.22 – 7.19 (m, 1H), 5.76 – 5.74 (m, 1H), 4.84 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.24 (dd, *J* = 8.4, 3.0 Hz, 1H), 2.99 (s, 3H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.96, 173.69, 166.98, 159.21, 149.96, 142.23, 137.04, 129.72, 129.24, 123.04, 122.92, 79.36, 56.99, 50.19, 25.35, 21.67. IR (neat, ν/cm^{-1}) 3057, 2922, 1775, 1689, 1610, 1561, 1433, 1381, 1278, 1094, 997, 822, 750. HRMS (EI$^+$) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{18}N_3O_2$ 320.1394; found 320.1397. M.p = 110-112 ℃.

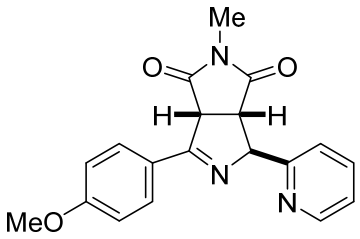
6-([1,1'-biphenyl]-4-yl)-2-methyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3al)



3al was prepared according to the general procedure to give the corresponding product as a yellow solid (62.6 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 8.29 – 8.26 (m, 2H), 7.73 – 7.67 (m, 3H), 7.64 – 7.61 (m, 2H), 7.55 – 7.53 (m, 1H), 7.48 – 7.43 (m, 2H), 7.40 – 7.35 (m, 1H), 7.23 – 7.20 (m, 1H), 5.80 – 5.79 (m, 1H), 4.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.28 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.01 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.92, 173.73, 166.75, 159.08, 150.00, 144.40, 140.31, 137.09, 130.83, 130.25, 129.01, 128.06, 127.32, 127.20, 123.12, 123.00, 79.50, 57.09, 50.20, 25.41. IR (neat, ν/cm^{-1}) 3057, 1776, 1701, 1605, 1433, 1379, 1282, 1126, 995, 910, 848, 761, 697. HRMS (EI$^+$) *m/z*: $[M]^+$ Calcd for $C_{24}H_{19}N_3O_2$ 381.1477; found 381.1481. M.p = 160-162 ℃.

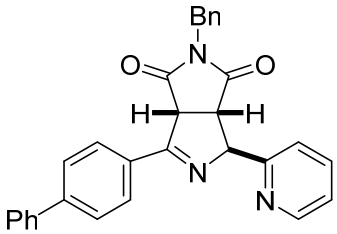
6-(4-methoxyphenyl)-2-methyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3am)



3am was prepared according to the general procedure to give the corresponding product as a yellow sticky solid (56.3 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 4.8, 1.6, 1.0 Hz, 1H), 8.18 – 8.15 (m, 2H), 7.70 (td, *J* = 7.8, 1.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.98 – 6.94 (m, 2H), 5.74 – 5.73 (m, 1H), 4.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.23 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.86 (s, 3H), 2.99 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.98, 173.86, 166.33, 162.47, 159.36, 149.99, 137.05, 131.62, 124.69, 123.04, 122.95, 113.89, 79.26, 56.98, 55.54, 50.28, 25.37. IR (neat, ν/cm^{-1}) 2934, 1776, 1701, 1572, 1513, 1434, 1381, 1283, 1252, 1177, 1126, 1030, 840, 752. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{19}H_{17}N_3O_3$ 335.1270; found 335.1265.

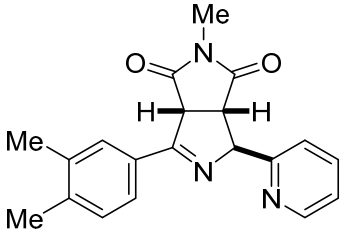
6-([1,1'-biphenyl]-4-yl)-2-benzyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3cl)



3cl was prepared according to the general procedure to give the corresponding product as a yellow solid (65.9 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.56 (m, 1H), 8.27 – 8.25 (m, 2H), 7.73 – 7.67 (m, 3H), 7.64 – 7.61 (m, 2H), 7.55 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 7.40 – 7.26 (m, 6H), 7.23 – 7.20 (m, 1H), 5.78 – 5.77 (m, 1H), 4.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.73 – 4.58 (m, 2H), 4.29 (dd, *J* = 8.4, 3.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.49, 173.36, 166.81, 159.04, 149.97, 144.43, 140.32, 137.16, 135.52, 130.81, 130.28, 129.03, 128.88, 128.23, 128.08, 127.34, 127.22, 123.15, 123.01, 79.57, 57.08, 50.21, 42.98. IR (neat, ν/cm^{-1}) 3031, 1698, 1568, 1487, 1432, 1394, 1340, 1172, 1131, 1083, 909, 846, 751, 698. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{30}H_{23}N_3O_2$ 457.1790; found 457.1785. M.p = 137-139 °C.

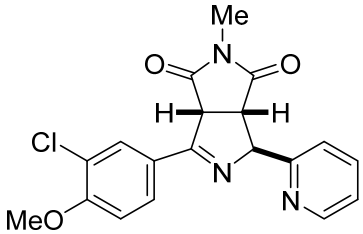
6-(3,4-dimethylphenyl)-2-methyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3an)



3an was prepared according to the general procedure to give the corresponding product as an orange solid (55.3 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.8, 1.6, 1.0 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.69 (td, *J* = 7.6, 1.8 Hz, 1H), 7.51 – 7.49 (m, 1H), 7.23 – 7.18 (m, 2H), 5.75 – 5.74 (m, 1H), 4.84 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.21 (dd, *J* = 8.4, 3.0 Hz, 1H), 2.98 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.97, 173.70, 167.24, 159.27, 149.98, 141.01, 137.02, 136.88, 130.44, 129.74, 129.56, 127.62, 123.03, 122.90, 79.35, 56.97, 50.23, 25.32, 20.01, 19.84. IR (neat, ν/cm^{-1}) 2945, 1776, 1701, 1605, 1433, 1380, 1280, 1126, 995, 911, 827, 733, 677. HRMS (EI$^+$) *m/z*: [M]$^+$ Calcd for $C_{20}H_{19}N_3O_2$ 333.1477; found 333.1474. M.p = 130-132 ℃.

6-(3-chloro-4-methoxyphenyl)-2-methyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ao)

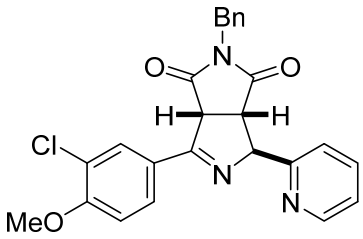


3ao was prepared according to the general procedure to give the corresponding product as an orange solid (51.0 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.56 (m, 1H), 8.25 (d, *J* = 2.2 Hz, 1H), 8.11 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.71 (td, *J* = 7.8, 1.8 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.24 – 7.20 (m, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 5.74 – 5.72 (m, 1H), 4.80 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.26 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.95 (s, 3H), 3.00 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.79, 173.66, 165.37, 158.98, 157.69, 149.98, 137.18, 131.33, 130.21, 125.49, 123.18, 123.06, 122.99, 111.33, 79.33, 57.02, 56.42, 50.25, 25.40. IR (neat, ν/cm^{-1}) 3015, 1774, 1696, 1599,

1571, 1501, 1465, 1434, 1381, 1276, 1102, 1064, 1019, 816, 750. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{19}H_{16}ClN_3O_3$ 369.0880; found 369.0875. M.p = 139-141 ℃.

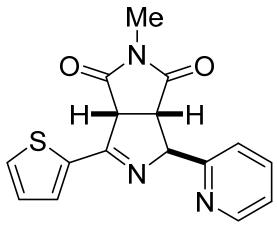
2-benzyl-6-(3-chloro-4-methoxyphenyl)-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3co)



3co was prepared according to the general procedure to give the corresponding product as a yellow sticky solid (56.2 mg, 63%).

^1H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.55 (m, 1H), 8.24 (d, *J* = 2.2 Hz, 1H), 8.09 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.70 (td, *J* = 7.8, 1.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.27 (m, 5H), 7.23 – 7.19 (m, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 5.72 – 5.71 (m, 1H), 4.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.71 – 4.56 (m, 2H), 4.26 (dd, *J* = 8.4, 3.2 Hz, 1H), 3.95 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 177.39, 173.29, 165.34, 158.97, 157.67, 150.01, 137.14, 135.47, 131.31, 130.21, 128.88, 128.83, 128.23, 125.44, 123.16, 122.99, 111.31, 79.43, 56.96, 56.42, 50.24, 42.96. IR (neat, ν/cm^{-1}) 3032, 1774, 1699, 1600, 1570, 1501, 1465, 1434, 1394, 1338, 1276, 1171, 1064, 1019, 817, 753, 700. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{25}H_{20}ClN_3O_3$ 445.1193; found 445.1194.

2-methyl-4-(pyridin-2-yl)-6-(thiophen-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3ap)

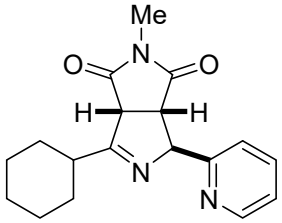


3ap was prepared according to the general procedure to give the corresponding product as an orange solid (26.8 mg, 43%).

^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.8, 1.8, 0.8 Hz, 1H), 8.08 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.70 (td, *J* = 7.6, 1.8 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.23 – 7.20 (m, 1H), 7.15 (dd, *J* = 5.0, 3.8 Hz, 1H), 5.75 – 5.74 (m, 1H), 4.72 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.26 (dd, *J* = 8.4,

2.8 Hz, 1H), 3.02 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 177.73, 173.46, 161.45, 158.96, 149.96, 137.09, 136.66, 133.98, 131.05, 128.16, 123.13, 122.99, 79.13, 57.64, 50.56, 25.46. IR (neat, ν/cm^{-1}) 3110, 1700, 1604, 1432, 1284, 1128, 993, 772. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{16}H_{13}N_3O_2S$ 311.0728; found 311.0732. M.p = 134-136 °C.

6-cyclohexyl-2-methyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3aq)



3aq was obtained as an orange solid (17.4 mg, 28%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.56 (m, 1H), 7.68 (td, *J* = 7.8, 1.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.19 (m, 1H), 5.59 (dd, *J* = 4.0, 2.2 Hz, 1H), 4.33 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.99 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.00 (s, 3H), 2.69 – 2.63 (m, 1H), 2.17 – 2.14 (m, 1H), 1.89 – 1.67 (m, 5H), 1.62 – 1.52 (m, 1H), 1.46 – 1.19 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 178.31, 175.86, 174.18, 159.30, 149.96, 136.91, 122.93, 122.56, 79.32, 57.74, 49.50, 40.01, 31.22, 29.65, 26.22, 26.06, 25.58, 25.24. IR (neat, ν/cm^{-1}) 2930, 2854, 1777, 1700, 1634, 1590, 1434, 1379, 1281, 1125, 984, 909, 753, 733. HRMS (EI^+) *m/z*: $[M]^+$ Calcd for $C_{18}H_{21}N_3O_2$ 311.1634; found 311.1639. M.p = 114-116 °C.

7. One-pot reaction between benzylamines and maleimides (Table 3)

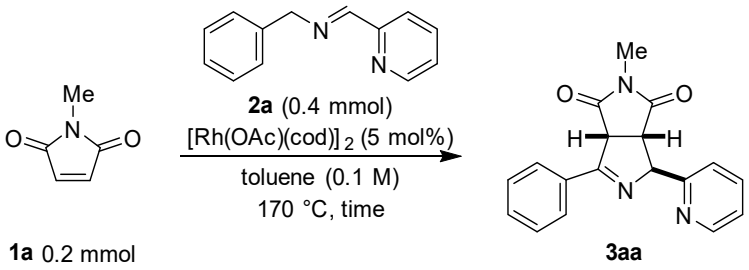
Procedure for synthesis of 3ba via one-pot methodology:

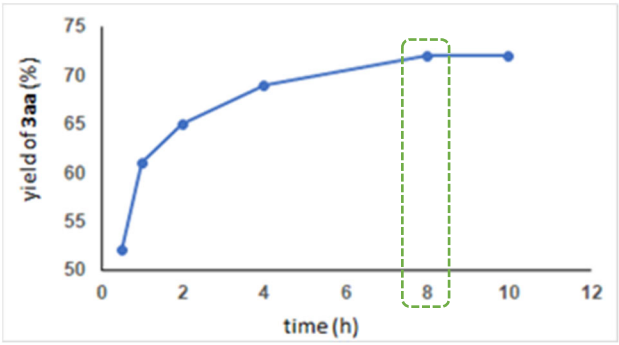
To a sealed tube equipped with a magnetic stirring bar was added the *N*-ethylmaleimide (**1b**) (25.0 mg, 0.20 mmol, 1.0 equiv), $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%) and dry toluene (2.0 mL) under an argon atmosphere. To this mixture, benzylamine (44 μL, 0.40 mmol, 2.0 equiv), 2-pyridinecarboxaldehyde (38 μL, 0.40 mmol, 2.0 equiv) were added and the resulting mixture was stirred at 170 °C for 8 hours. The yield of the corresponding product **3ba** was determined by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene as an internal standard.

8. Mechanistic studies (1) (Scheme S1)

a) Monitoring the reaction:

To a sealed tube equipped with a magnetic stirring bar were added the *N*-methylmaleimide (**1a**) (22.2 mg, 0.20 mmol, 1.0 equiv), $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%), internal standard 1,3,5-trimethoxybenzene (11.2 mg, 0.07 mmol, 0.33 equiv) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2a** (78.5 mg, 0.40 mmol, 2.0 equiv) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at 170 °C for specified hours. The yield of the corresponding product was determined by ^{1}H NMR analysis of the crude mixture at specified time intervals. Monitoring the progress of the reaction showed that it proceeds sufficiently rapidly to give **3aa** in 62% yield only after 1 hour (Scheme S1a). After 8 hours, the formation of **3aa** reached the saturation point with a yield of 72%.

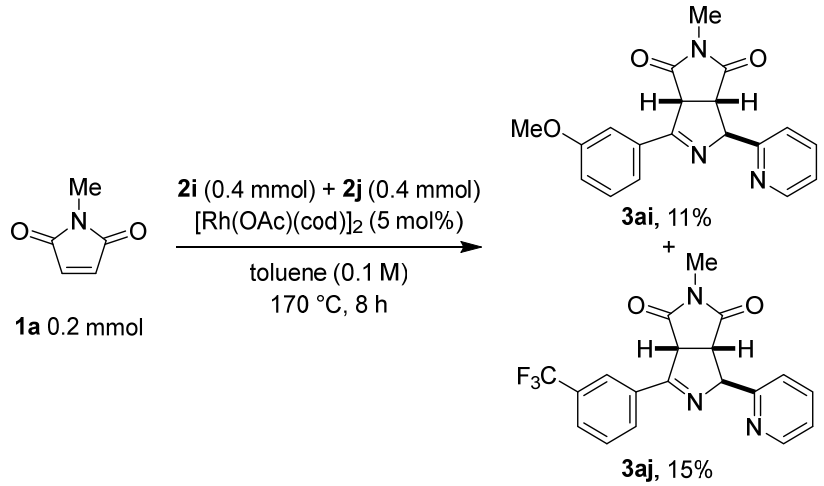




b) Control experiments between substrates with electron donating and electron withdrawing groups:

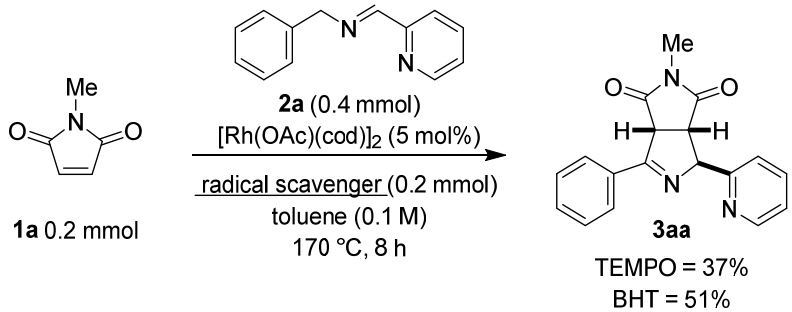
To a sealed tube equipped with a magnetic stirring bar were added the *N*-methylmaleimide (**1a**) (22.2 mg, 0.20 mmol, 1.0 equiv), $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2i** (90.5 mg, 0.40 mmol, 2.0 equiv) and **2j** (106 mg, 0.40 mmol, 2.0 equiv) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at 170 °C for 8 hours. The yields of the corresponding products were determined by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene as internal standard. The reaction produced the corresponding

products in comparable yields, indicating that electronic effects do not appear to have a significant effect on reactivity (Scheme S1b).



c) Radical trapping experiment using radical scavengers:

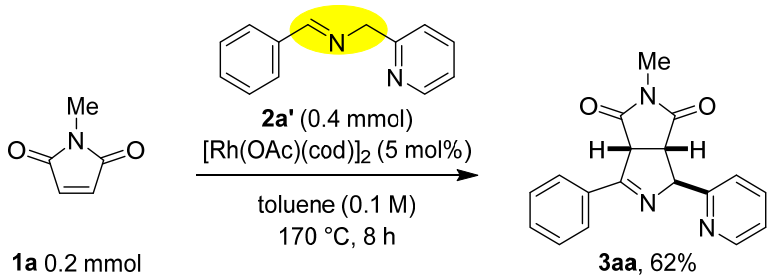
To a sealed tube equipped with a magnetic stirring bar were added the *N*-methylmaleimide (**1a**) (22.2 mg, 0.20 mmol, 1.0 equiv), $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%), a radical scavenger (TEMPO or BHT, 0.20 mmol, 1.0 equiv) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2a** (78.5 mg, 0.40 mmol, 2.0 equiv) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at 170 °C for 8 hours. The yields of the corresponding products were determined by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene as internal standard. A 37% yield of **3aa** was obtained in the presence of TEMPO (Scheme S1c). The addition of BHT had no effect on the reaction, with **3aa** being formed in 51% yield (Scheme S1c). These results overrule the possibility of the in-situ generation of a radical species during the progress of the reaction.



d) Catalytic reaction with imine derived from benzaldehyde and 2-picolylamine:

To a sealed tube equipped with a magnetic stirring bar were added the *N*-methylmaleimide (**1a**) (22.2 mg, 0.20 mmol, 1.0 equiv), $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%) and

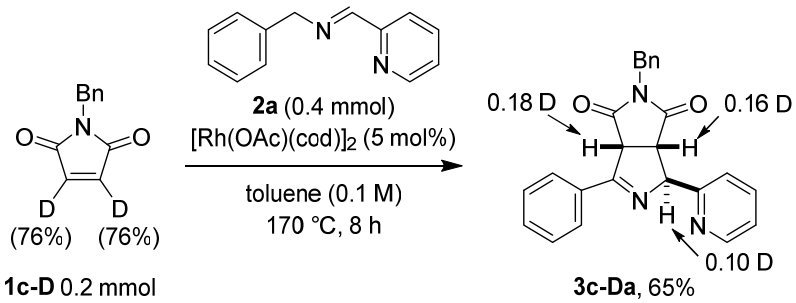
dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2a'** (78.5 mg, 0.40 mmol, 2.0 equiv) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at 170 °C for 8 hours. After the reaction, the reaction mixture was allowed cool to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography using *n*-hexane/EtOAc (4/1-1/1) as an eluent to afford the desired product **3aa** in 62% isolated yield (Scheme S1d).



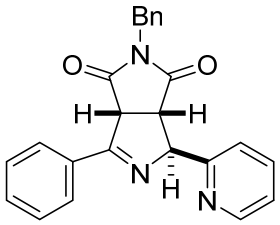
9. Mechanistic studies (2) (Scheme S2)

a) Deuterium labelling experiment of 2a with deuterated maleimide:

To a sealed tube equipped with a magnetic stirring bar were added the deuterated *N*-benzylmaleimide (**1c-D**) (37.8 mg, 0.20 mmol, 1.0 equiv), $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, a solution of **2a** (78.5 mg, 0.40 mmol, 2.0 equiv) in dry toluene (1.5 mL) was added and the resulting mixture was stirred at 170 °C for 8 hours. After the reaction, the reaction mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography using *n*-hexane/EtOAc (4/1-2/1) as an eluent to afford the desired product **3c-Da**. The deuterium content of the product was determined by ^{1}H NMR and ^{2}H NMR analysis of the isolated product.



2-benzyl-6-phenyl-4-(pyridin-2-yl)-4,6a-dihydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (3c-Da)

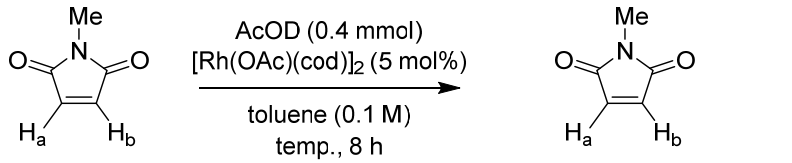


3c-Da was obtained as a yellow sticky solid (50.0 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.55 (m, 1H), 8.19 – 8.17 (m, 2H), 7.69 (td, *J* = 7.6, 1.8 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.34 – 7.26 (m, 5H), 7.22 – 7.19 (m, 1H), 5.76 – 5.75 (m, 0.82H), 4.86 (dd, *J* = 8.4, 2.4 Hz, 0.90H), 4.71 – 4.56 (m, 2H), 4.28 (dd, *J* = 8.4, 3.2 Hz, 0.84H).

b) H/D scrambling of maleimide in presence of deuterated acetic acid:

To a sealed tube equipped with a magnetic stirring bar were added the *N*-methylmaleimide (**1a**) (22.2 mg, 0.20 mmol, 1.0 equiv), catalyst $[Rh(OAc)(cod)]_2$ (5.4 mg, 0.01 mmol, 5 mol%) and dry toluene (0.50 mL) under an argon atmosphere. To this mixture, deuterated acetic acid AcOH-*d* (23 μL, 0.40 mmol, 2.0 equiv) was added and the resulting mixture was stirred at 50 °C for 8 hours. Two other reactions were carried out at two different temperatures, 100 °C and 170 °C for 8 hours. The extent of deuterium incorporation in the maleimide for three separate reactions depending on three different temperatures was determined by ^{1}H NMR analysis of the crude product.



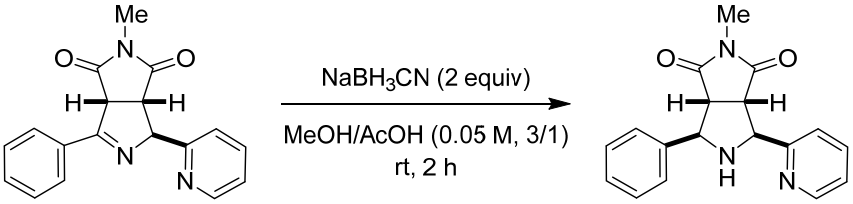
$H_a = H_b$ = 0.86 H (50 °C)
$H_a = H_b$ = 0.81 H (100 °C)
$H_a = H_b$ = 0.48 H (170 °C)

10. Reduction of pyrroline moiety of 3aa (Scheme S3)

General procedure:

4 was prepared from **3aa** following a literature procedure with minor modifications.[4] To a reaction vial equipped with a magnetic stirring bar were added the **3aa** (31 mg, 0.10 mmol,

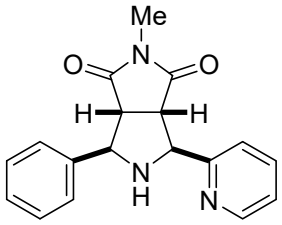
1.0 equiv) and MeOH/AcOH (0.05 M, 3/1). To this mixture, $NaBH_3CN$ (12 mg, 0.20 mmol, 2.0 equiv) was added in one portion and the reaction mixture was stirred at room temperature for 2 hours. After that the reaction mixture was quenched with 10% $NaHCO_3$ solution. The organic phase was extracted with EtOAc and washed repeatedly with brine, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography using *n*-hexane/EtOAc (1/1-1/2) with 1% Et_3N as an eluent to afford the desired product **4**.



3aa 0.1 mmol

4, 68%

2-methyl-4-phenyl-6-(pyridin-2-yl)tetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (4)[2]



4 was obtained as an off-white solid (20.9 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.59 (m, 1H), 7.73 (td, *J* = 7.6, 1.8 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.55 – 7.53 (m, 1H), 7.42 – 7.24 (m, 4H), 4.44 (dd, *J* = 7.2, 3.4 Hz, 2H), 3.69 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.55 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.05 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 177.17, 177.06, 158.30, 149.75, 140.10, 137.21, 128.87, 128.05, 127.01, 123.38, 123.15, 66.64, 66.11, 54.94, 54.24, 25.10. IR (neat, ν/cm^{-1}) 2924, 2359, 1774, 1699, 1593, 1433, 1381, 1281, 1128, 958, 756, 701. HRMS (EI^+) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{18}N_3O_2$ 308.1394; found 308.1397. M.p = 124-126 ℃.

11. X-ray structural data of 3ap and 3ea

Data for 3ap:

Compound **3ap** was crystallized from a solvent mixture of $CHCl_3$/hexane (2/3) and the structural and crystallographic information of this compound are given below.

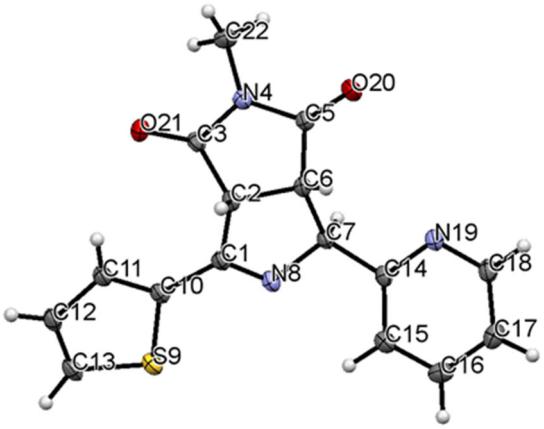


Figure S1. The structure of **3ap** was determined by single X-ray diffraction. Hydrogen atoms are not labelled for clarity. The crystallographic structure of **3ap** was presented using Mercury software.

CCDC 2117470 contains supplementary crystallographic data for compound **3ap**. Clear yellow prisms of C16 H13 N3 O2 S having approximate dimensions of 0.182 × 0.093 × 0.052 mm was mounted in a loop. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation. The data were collected at a temperature of 293 K.

The structure was solved by direct methods[5] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the CrystalStructure[6] crystallographic software package except for refinement, which was performed using OLEX2[7] or SHELXL97.[8]

Table S2. Crystal data and structure refinement for 3ap

Identification code	**3ap**
Empirical formula	$C_{16}H_{13}N_3O_2S$
Formula weight	311.35
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7589(2)
b/Å	7.74990(10)
c/Å	16.8477(3)

α/°	90
β/°	100.056(2)
γ/°	90
Volume/Å^3	1383.19(4)
Z	4
ρ_{calc}g/cm^3	1.495
μ/mm^{-1}	2.182
F(000)	648.0
Crystal size/mm^3	0.182 × 0.093 × 0.052
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.086 to 148.564
Index ranges	-13 ≤ h ≤ 13, -9 ≤ k ≤ 9, -21 ≤ l ≤ 19
Reflections collected	12816
Independent reflections	2804 [R_{int} = 0.0413, R_{sigma} = 0.0366]
Data/restraints/parameters	2804/0/200
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0358, wR_2 = 0.0954
Final R indexes [all data]	R_1 = 0.0381, wR_2 = 0.0976
Largest diff. peak/hole / e Å^{-3}	0.27/-0.33

Table S3. Bond Lengths for 3ap

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S9	C10	1.7317(14)	C7	C6	1.5596(18)
S9	C13	1.7203(14)	C1	C2	1.5251(18)
O21	C3	1.2109(17)	C1	C10	1.4559(18)
O20	C5	1.2033(17)	C3	C2	1.5239(19)
N8	C7	1.4695(17)	C2	C6	1.5374(17)
N8	C1	1.2806(18)	C5	C6	1.5198(19)
N4	C3	1.3843(17)	C15	C16	1.386(2)
N4	C5	1.3933(17)	C10	C11	1.379(2)
N4	C22	1.4545(18)	C18	C17	1.381(2)

N19	C14	1.3402(18)	C12	C11	1.4171(19)
N19	C18	1.3465(19)	C12	C13	1.362(2)
C14	C7	1.5195(18)	C17	C16	1.389(2)
C14	C15	1.387(2)			

Table S4. Bond Angles for 3ap

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	S9	C10	91.79(7)	C3	C2	C1	115.01(11)
C1	N8	C7	110.42(11)	C3	C2	C6	104.91(11)
C3	N4	C5	113.62(11)	O20	C5	N4	124.05(13)
C3	N4	C22	122.24(11)	O20	C5	C6	127.88(12)
C5	N4	C22	124.06(12)	N4	C5	C6	108.07(11)
C14	N19	C18	117.15(12)	C2	C6	C7	104.56(10)
N19	C14	C7	115.02(12)	C5	C6	C7	112.08(11)
N19	C14	C15	122.77(13)	C5	C6	C2	105.07(11)
C15	C14	C7	122.14(12)	C16	C15	C14	119.14(13)
N8	C7	C14	112.06(11)	C1	C10	S9	120.52(10)
N8	C7	C6	106.91(10)	C11	C10	S9	110.93(10)
C14	C7	C6	113.84(11)	C11	C10	C1	128.55(13)
N8	C1	C2	115.48(11)	N19	C18	C17	124.13(13)
N8	C1	C10	122.41(12)	C13	C12	C11	113.10(13)
C10	C1	C2	122.08(12)	C10	C11	C12	112.48(13)
O21	C3	N4	123.53(13)	C18	C17	C16	117.86(13)
O21	C3	C2	128.25(12)	C15	C16	C17	118.94(13)
N4	C3	C2	108.22(11)	C12	C13	S9	111.70(10)
C1	C2	C6	102.53(10)				

Data for 3ea:

Compound **3ea** was crystallized from a solvent mixture of $CHCl_3$/hexane (2/3) and the structural and crystallographic information of this compound are given below.

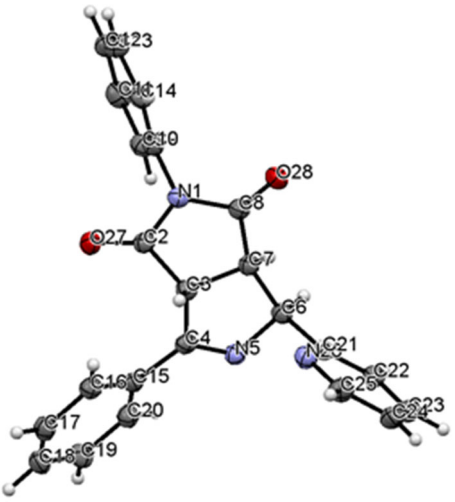


Figure S2. The structure of **3ea** was determined by single X-ray diffraction. Hydrogen atoms are not labelled for clarity. The crystallographic structure of **3ea** was presented using Mercury software.

CCDC 2117471 contains supplementary crystallographic data for compound **3ea**. Clear yellow prisms of C23 H17 N3 O2 having approximate dimensions of 0.179 × 0.121 × 0.045 mm was mounted in a loop. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation. The data were collected at a temperature of 123 K.

The structure was solved by direct methods[5] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the CrystalStructure[6] crystallographic software package except for refinement, which was performed using OLEX2[7] or SHELXL97.[8]

Table S5. Crystal data and structure refinement for 3ea

Identification code	**3ea**
Empirical formula	$C_{23}H_{17}N_3O_2$
Formula weight	367.39
Temperature/K	123
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.6645(3)

b/Å	6.15540(10)
c/Å	20.4618(5)
α/°	90
β/°	107.871(2)
γ/°	90
Volume/Å^3	1757.88(7)
Z	4
ρ_{calc}mg/mm^3	1.388
μ/mm^{-1}	0.729
F(000)	768.0
Crystal size/mm^3	0.179 × 0.121 × 0.045
2Θ range for data collection	6.562 to 148.292°
Index ranges	-18 ≤ h ≤ 18, -5 ≤ k ≤ 7, -25 ≤ l ≤ 25
Reflections collected	17488
Independent reflections	3572[R(int) = 0.0439]
Data/restraints/parameters	3572/0/253
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0370, wR_2 = 0.0966
Final R indexes [all data]	R_1 = 0.0413, wR_2 = 0.1002
Largest diff. peak/hole / e Å^{-3}	0.19/-0.19

Table S6. Bond Lengths for 3ea

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O27	C2	1.2068(15)	C16	C17	1.3917(17)
O28	C8	1.2080(15)	C8	C7	1.5150(16)
N5	C4	1.2836(15)	C20	C19	1.3861(17)
N5	C6	1.4814(15)	C3	C2	1.5228(16)
N1	C9	1.4402(15)	C3	C7	1.5322(16)
N1	C8	1.3953(15)	C3	C4	1.5310(16)
N1	C2	1.3960(15)	C7	C6	1.5440(16)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N26	C21	1.3431(16)	C14	C13	1.3887(18)
N26	C25	1.3386(17)	C22	C23	1.3920(18)
C9	C14	1.3886(17)	C18	C19	1.3887(19)
C9	C10	1.3825(17)	C18	C17	1.3871(19)
C15	C16	1.3957(17)	C10	C11	1.3902(19)
C15	C20	1.4026(17)	C13	C12	1.3872(19)
C15	C4	1.4802(16)	C23	C24	1.382(2)
C21	C6	1.5218(16)	C12	C11	1.388(2)
C21	C22	1.3894(17)	C25	C24	1.385(2)

Table S7. Bond Angles for 3ea

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	N5	C6	109.91(10)	O27	C2	C3	127.68(11)
C8	N1	C9	123.24(10)	N1	C2	C3	107.72(9)
C8	N1	C2	113.28(10)	C8	C7	C3	104.95(9)
C2	N1	C9	123.46(10)	C8	C7	C6	112.97(10)
C25	N26	C21	117.23(11)	C3	C7	C6	104.92(9)
C14	C9	N1	119.15(11)	N5	C4	C15	121.75(11)
C10	C9	N1	119.58(11)	N5	C4	C3	114.99(10)
C10	C9	C14	121.27(11)	C15	C4	C3	123.24(10)
C16	C15	C20	119.32(11)	N5	C6	C21	106.35(9)
C16	C15	C4	120.99(11)	N5	C6	C7	106.02(9)
C20	C15	C4	119.59(10)	C21	C6	C7	112.55(10)
N26	C21	C6	115.75(10)	C13	C14	C9	118.83(12)
N26	C21	C22	123.11(11)	C21	C22	C23	118.57(12)
C22	C21	C6	121.09(11)	C17	C18	C19	119.54(11)
C17	C16	C15	120.16(11)	C20	C19	C18	120.78(12)
O28	C8	N1	124.28(11)	C9	C10	C11	119.41(12)
O28	C8	C7	127.56(11)	C18	C17	C16	120.36(11)
N1	C8	C7	108.15(10)	C12	C13	C14	120.51(12)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C19	C20	C15	119.81(11)	C24	C23	C22	118.79(12)
C2	C3	C7	105.25(9)	C13	C12	C11	119.99(12)
C2	C3	C4	110.72(9)	N26	C25	C24	123.71(13)
C4	C3	C7	102.00(9)	C12	C11	C10	119.98(12)
O27	C2	N1	124.56(11)	C23	C24	C25	118.57(12)

12. References

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[7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

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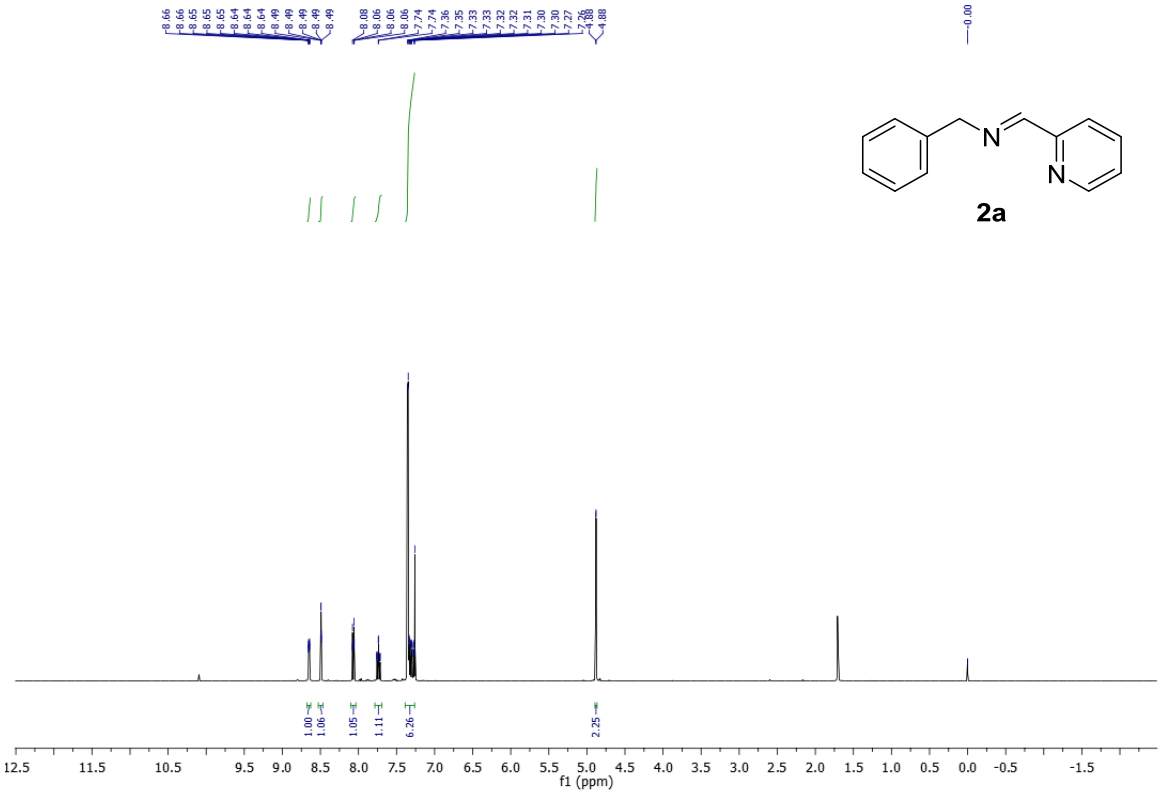
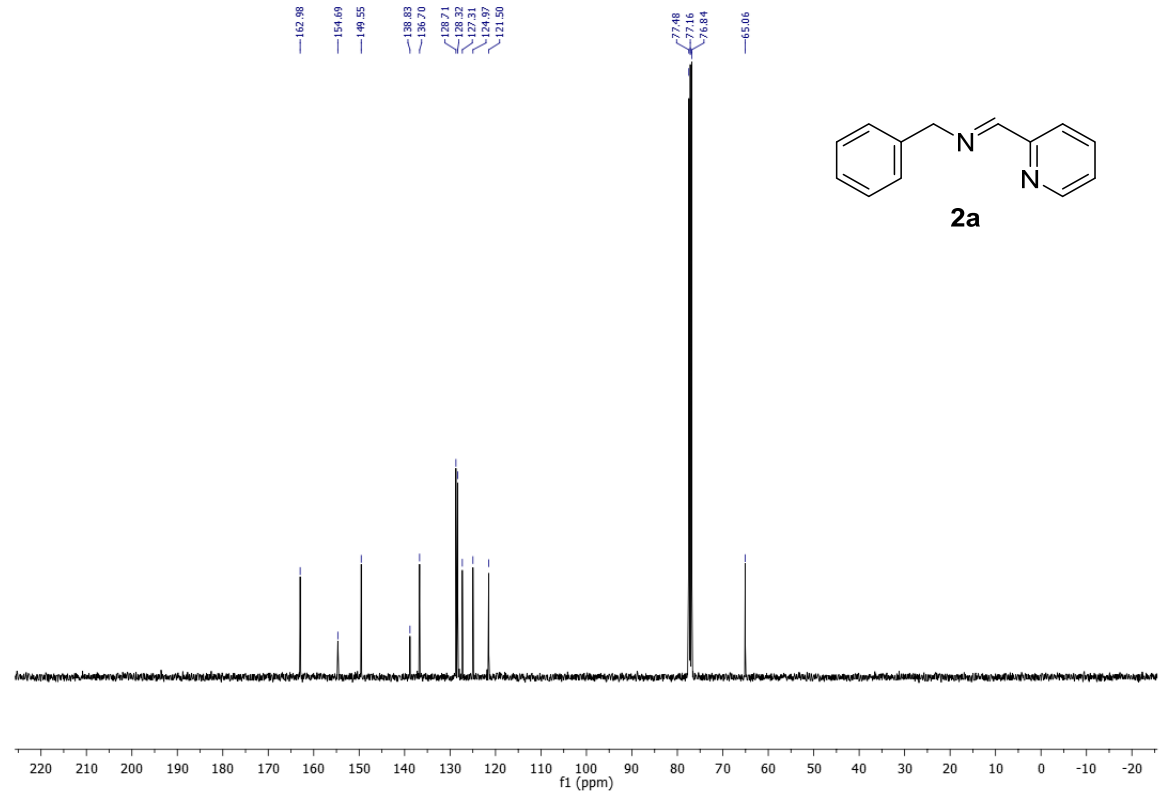
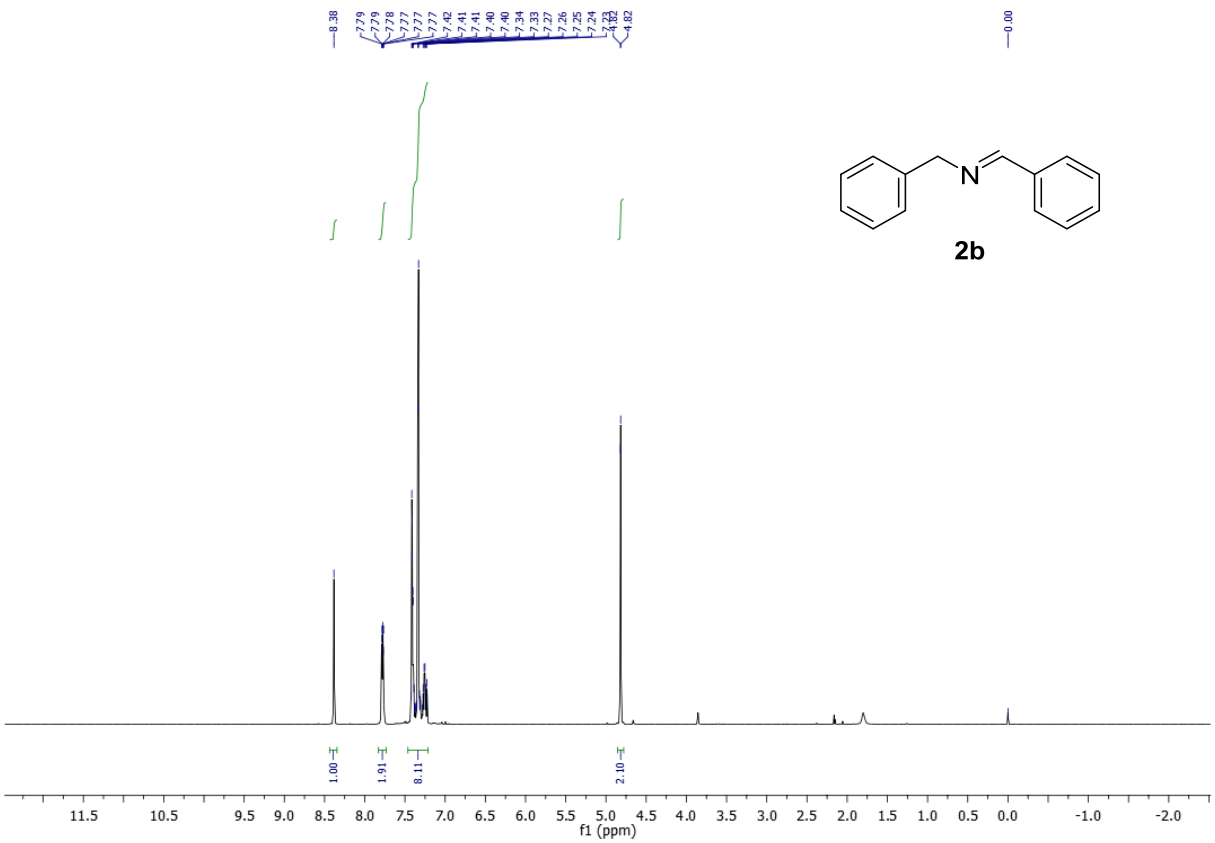
13. ^{1}H and ^{13}C NMR spectra of new compounds

NMR spectra of starting materials



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7.25
7.24
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0.00
1.00
1.91
8.11
2.10
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0
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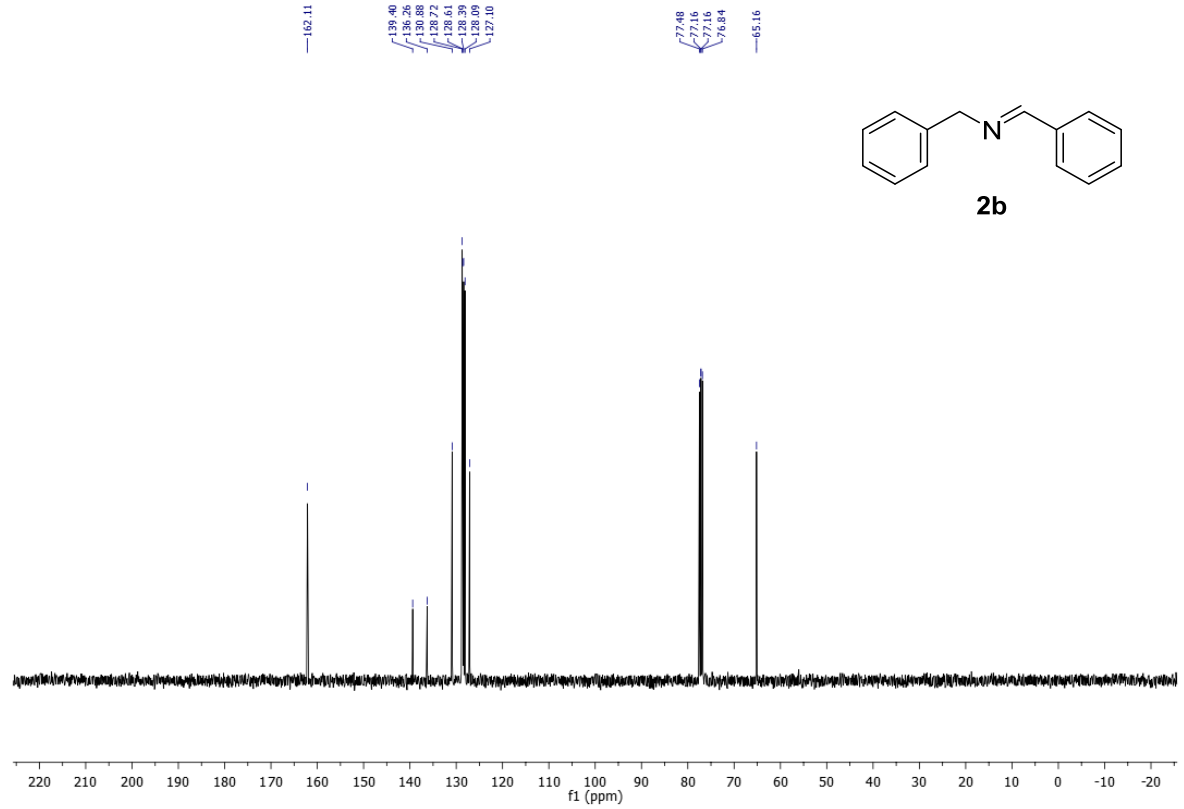
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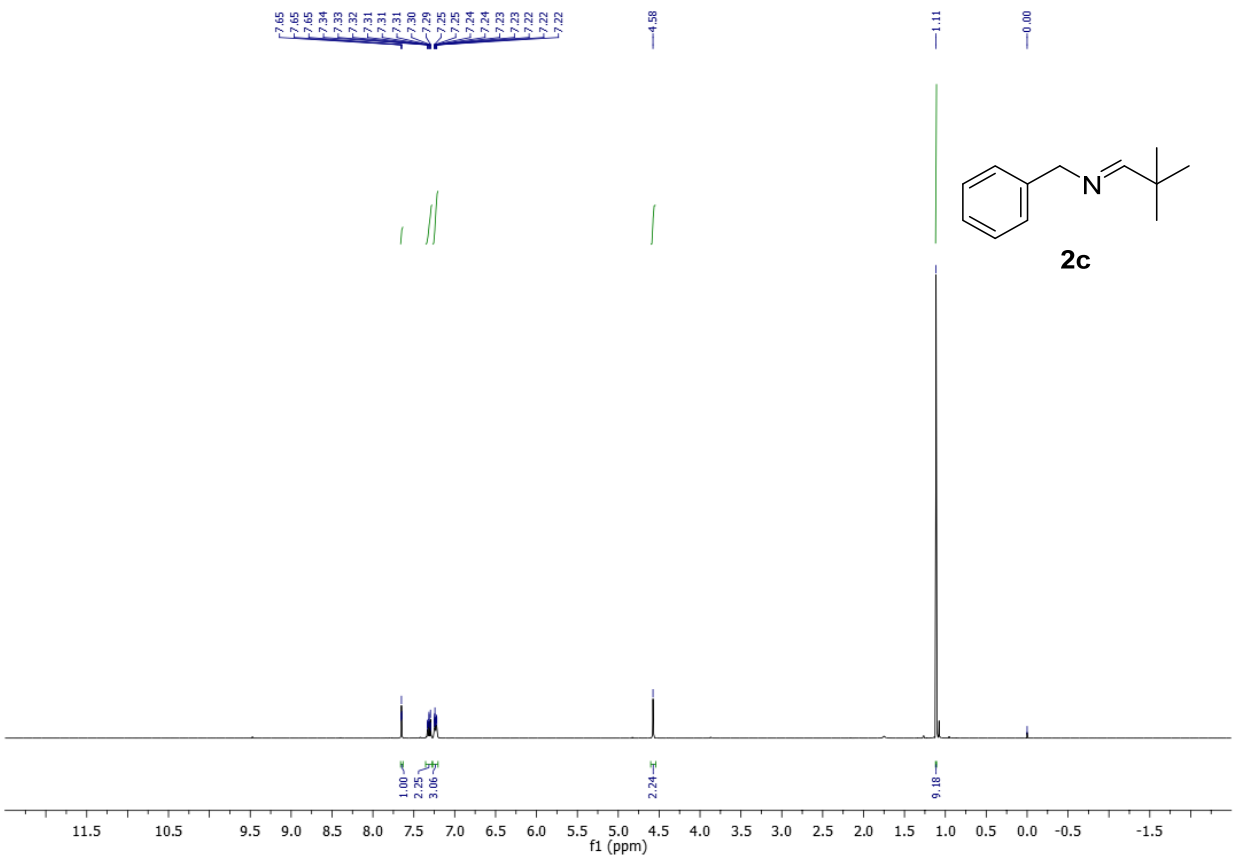
2b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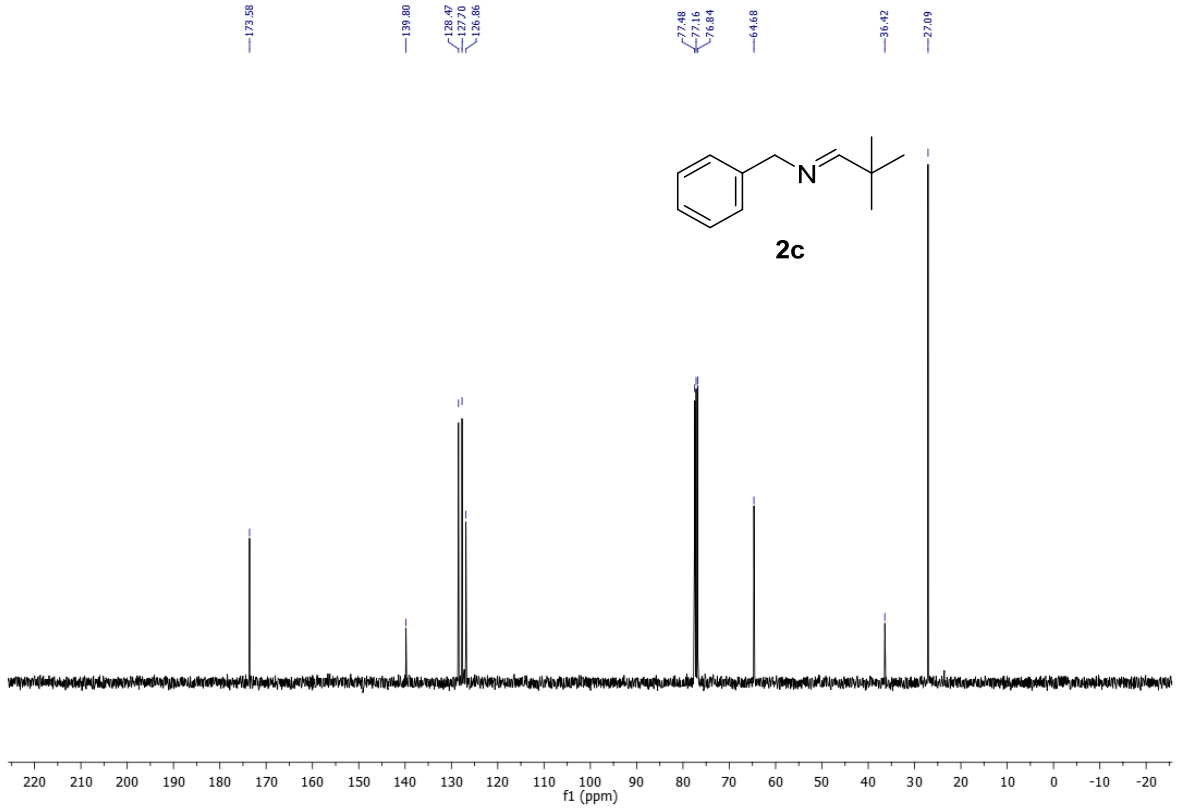
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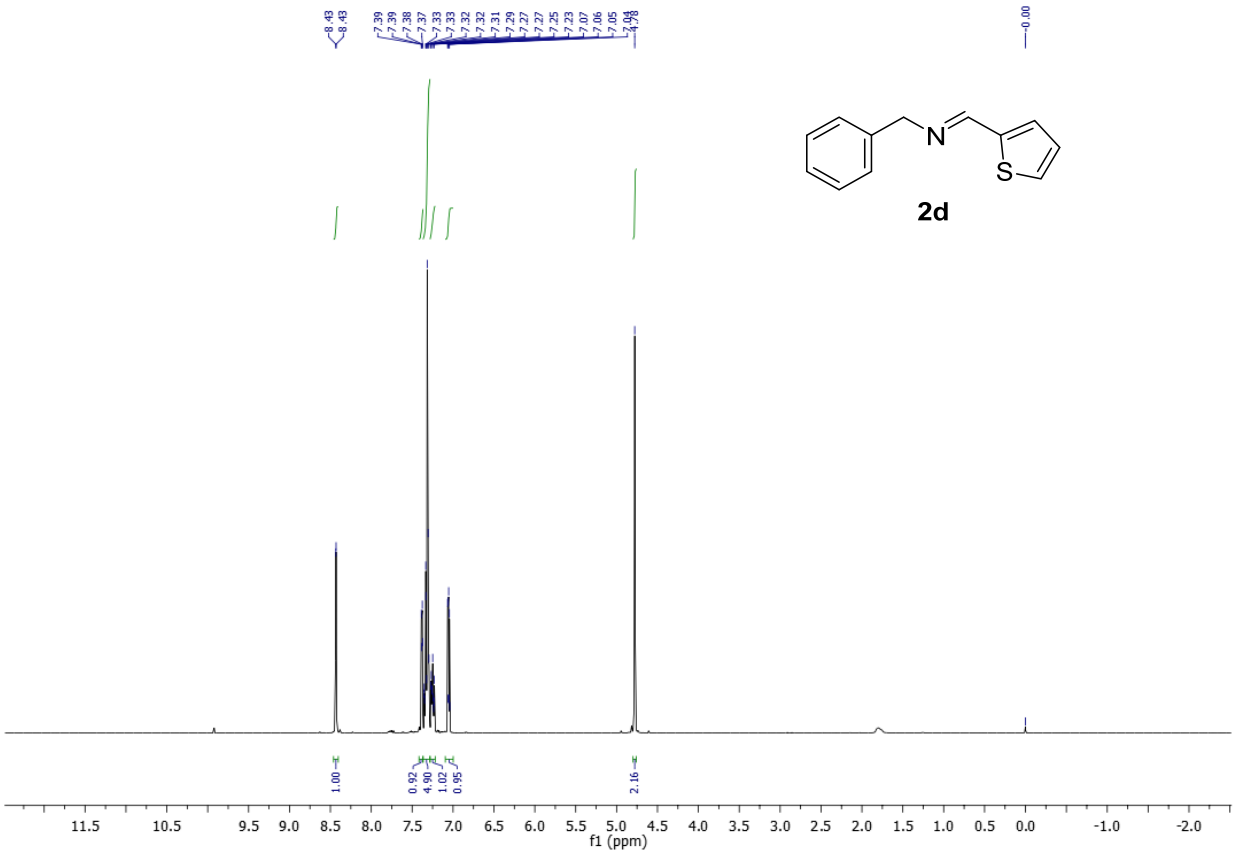
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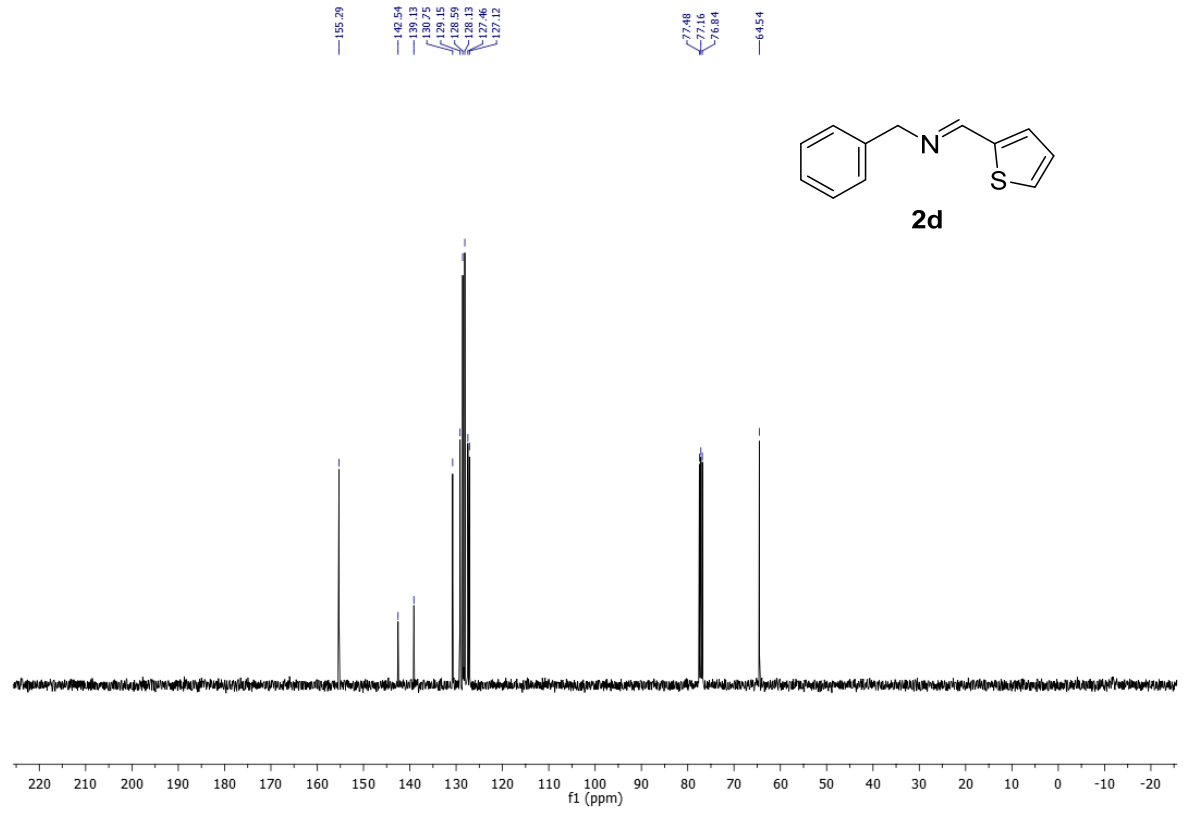
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S
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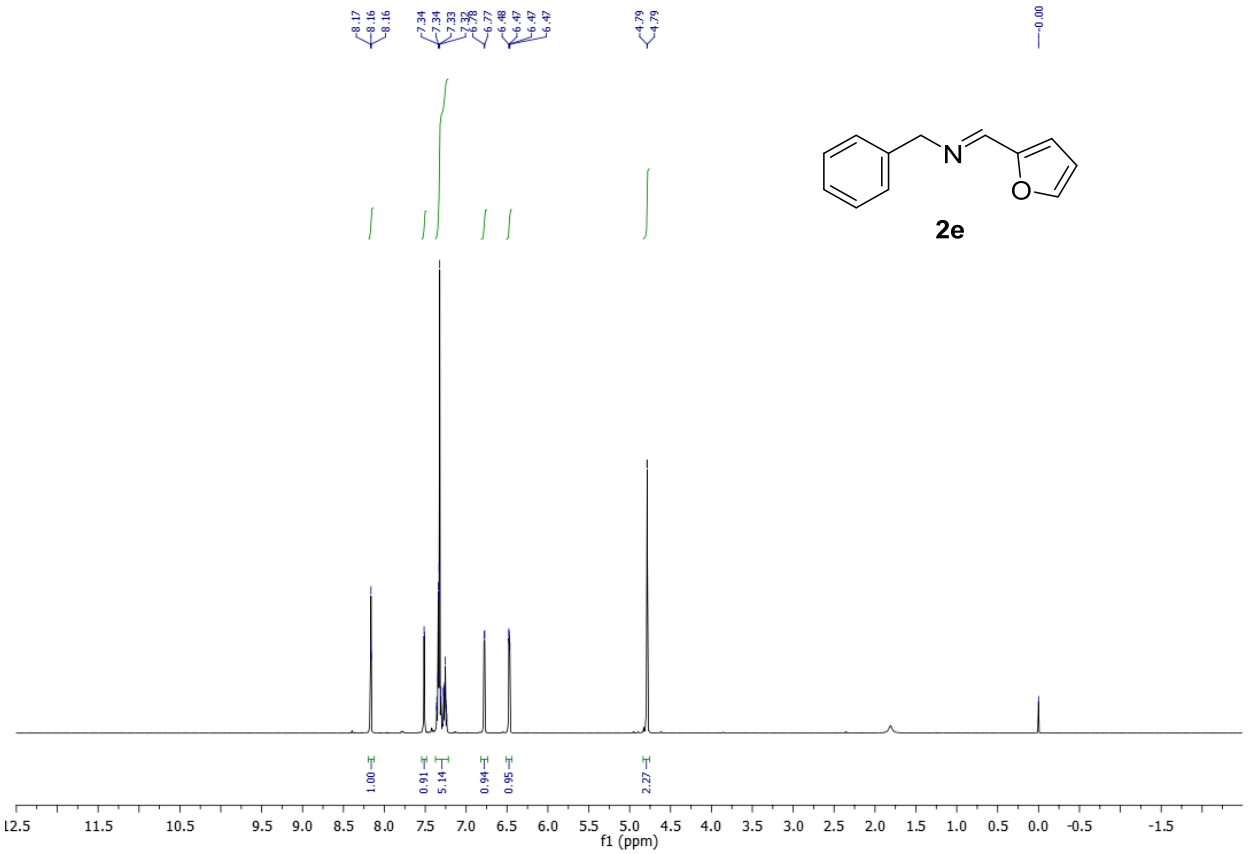
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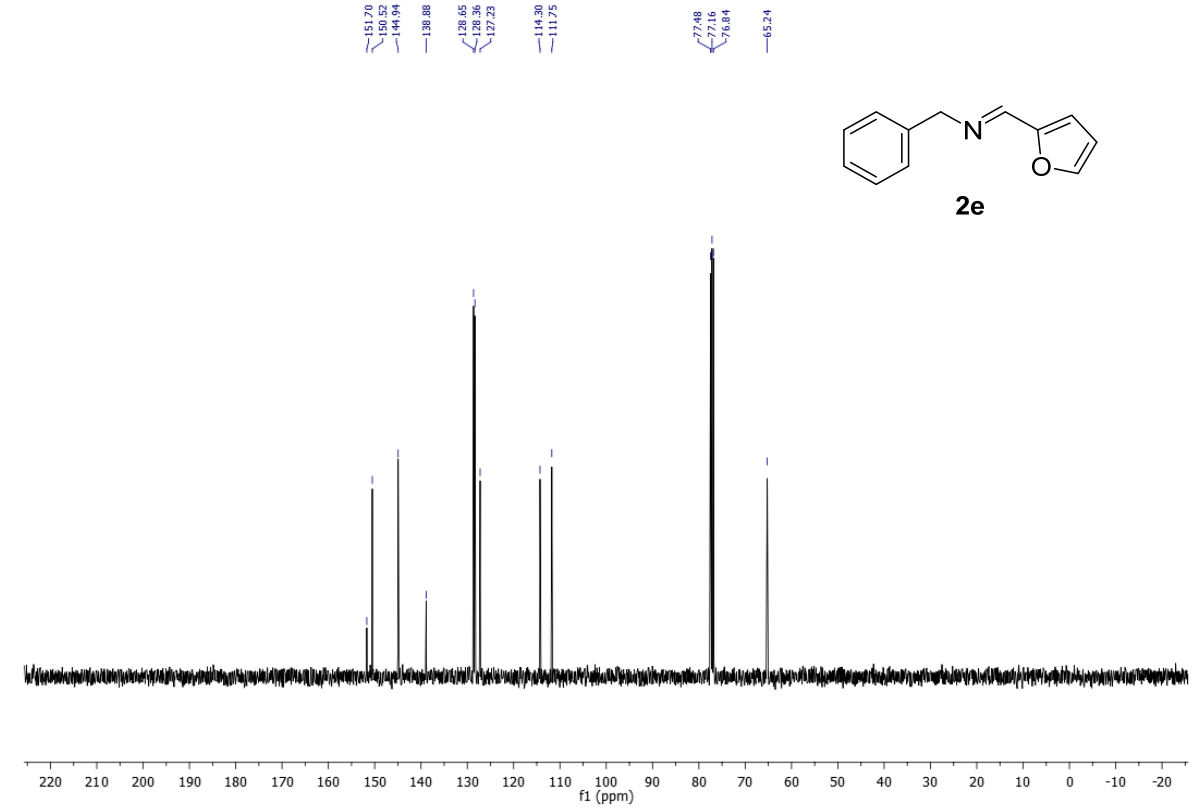
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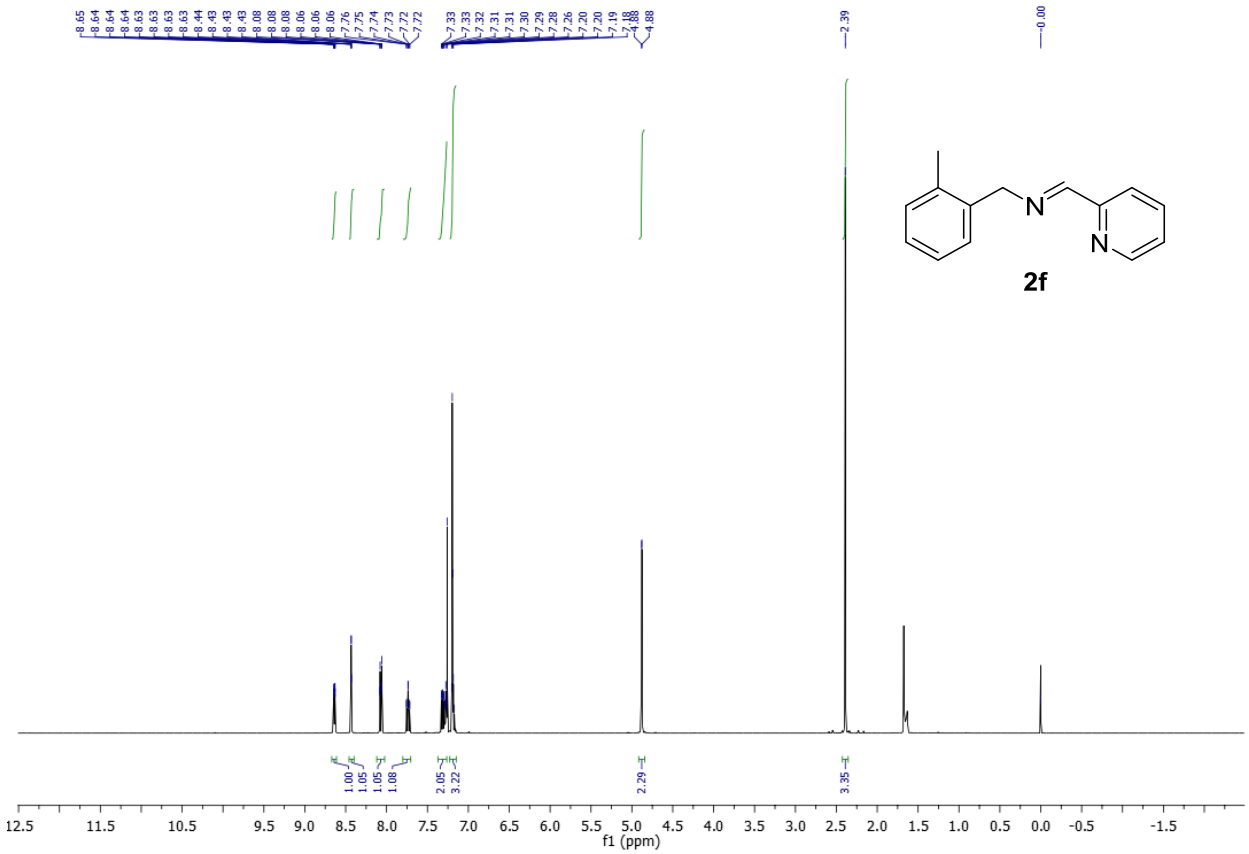
2e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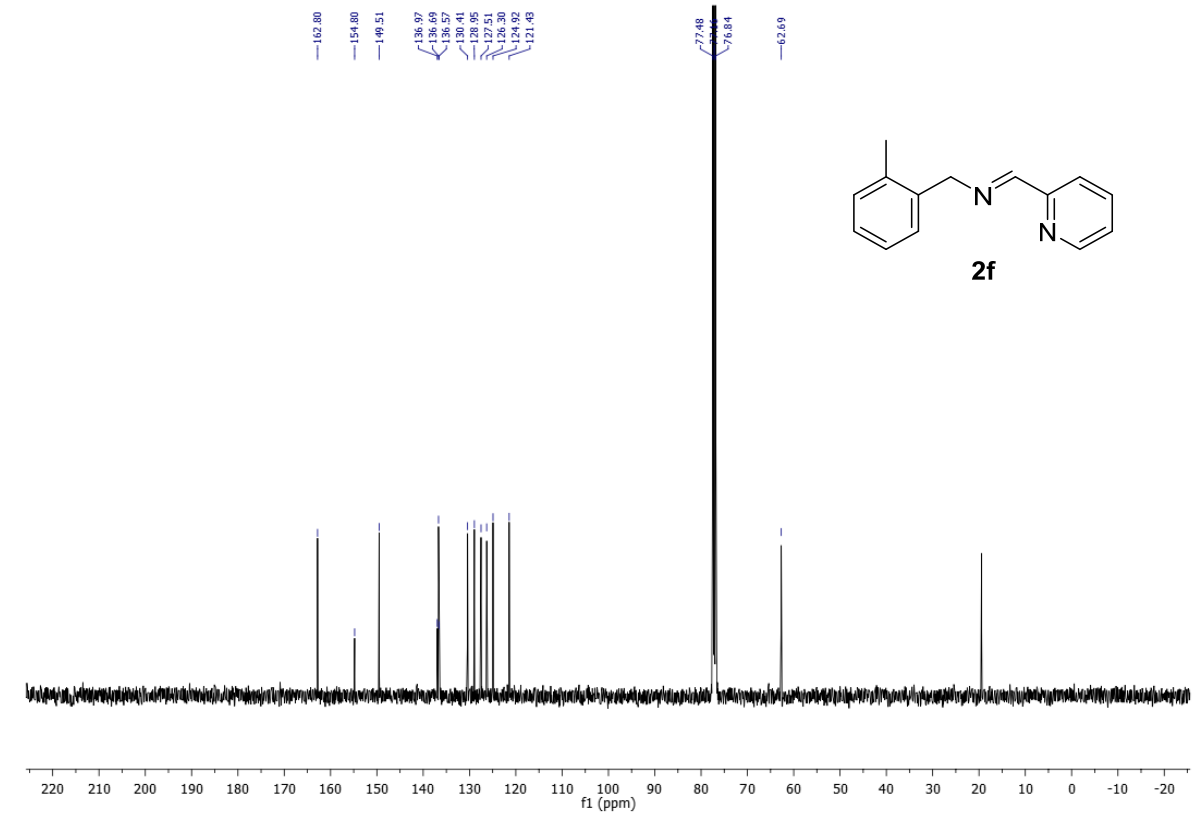
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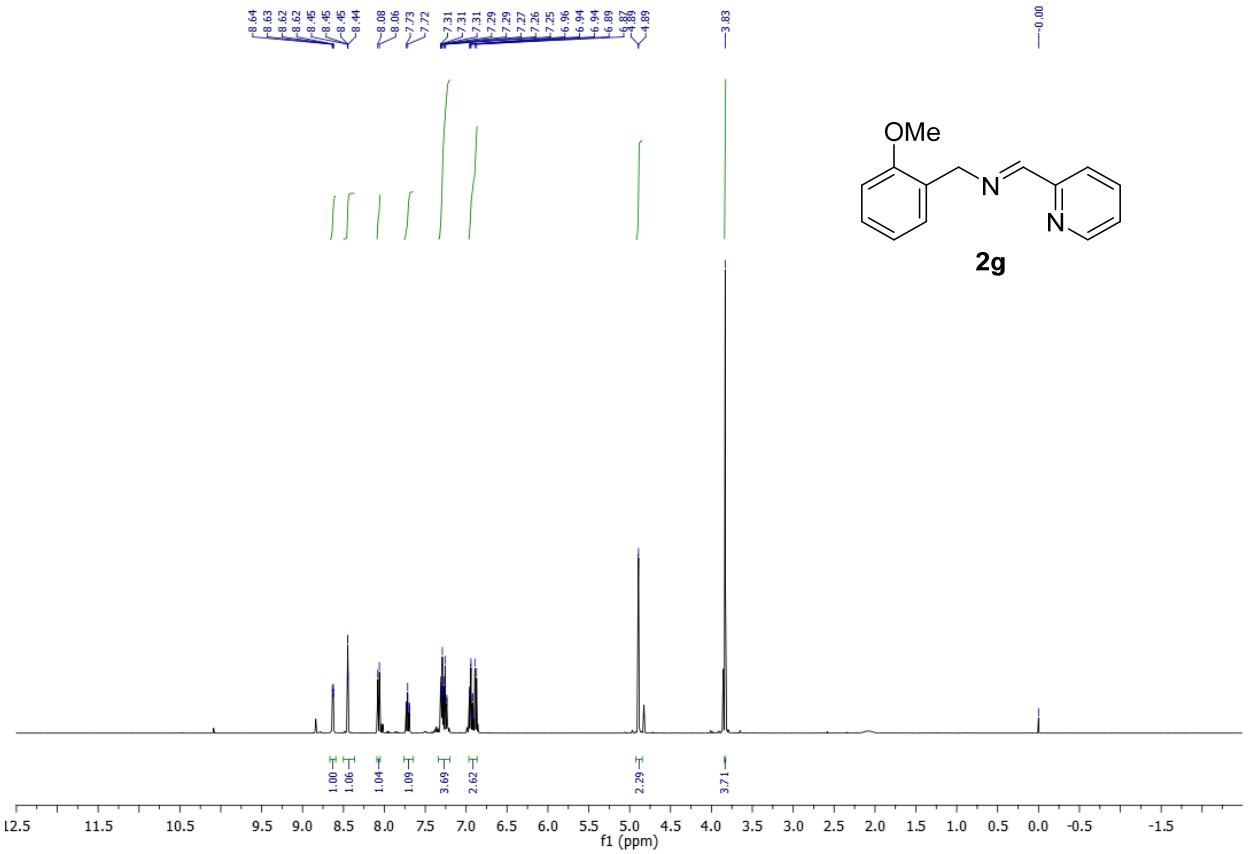
2f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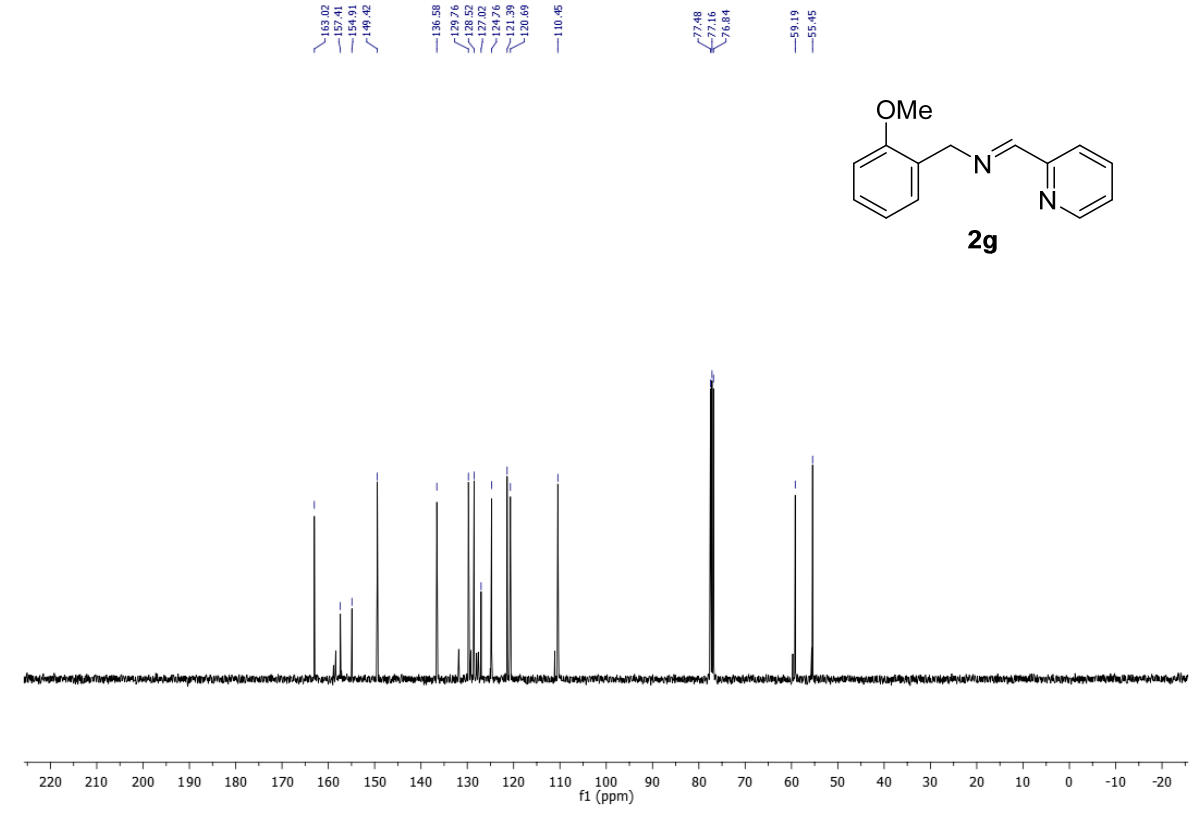
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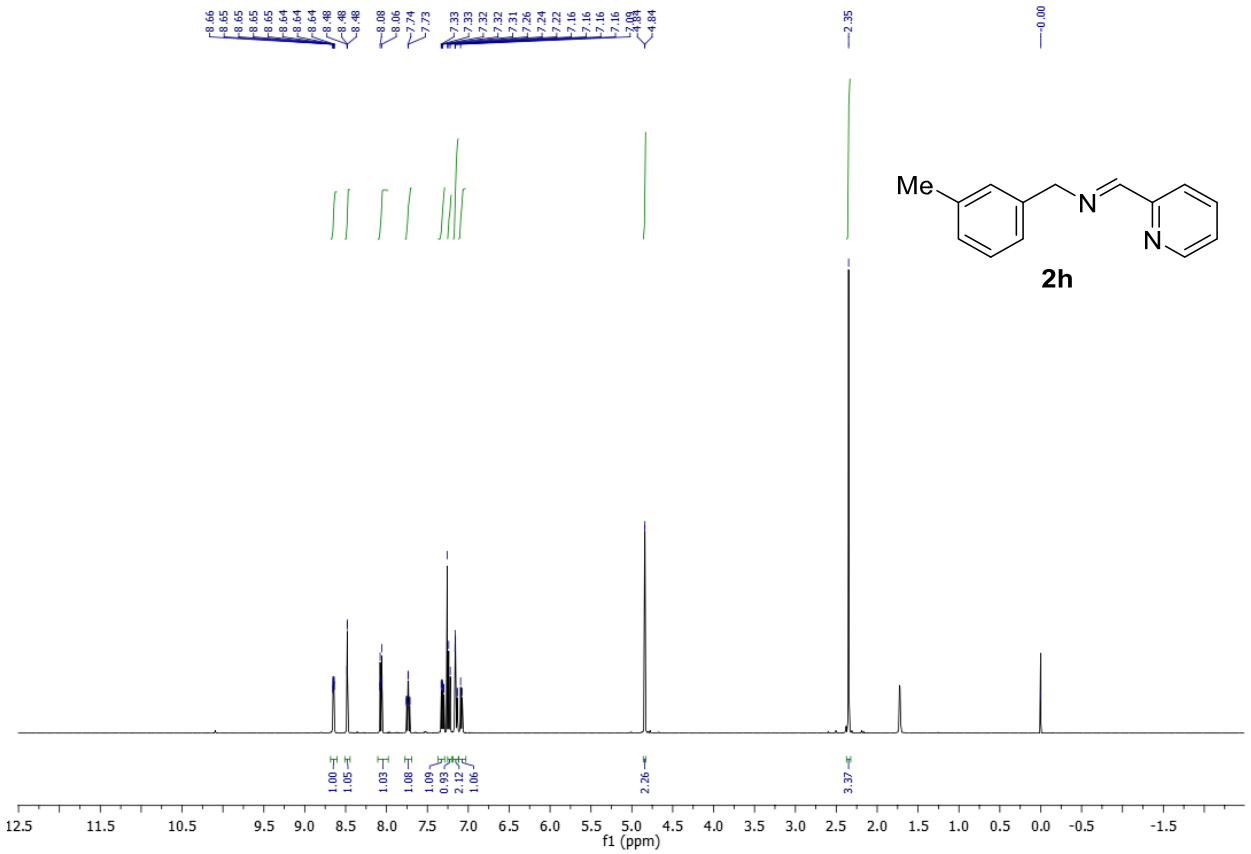
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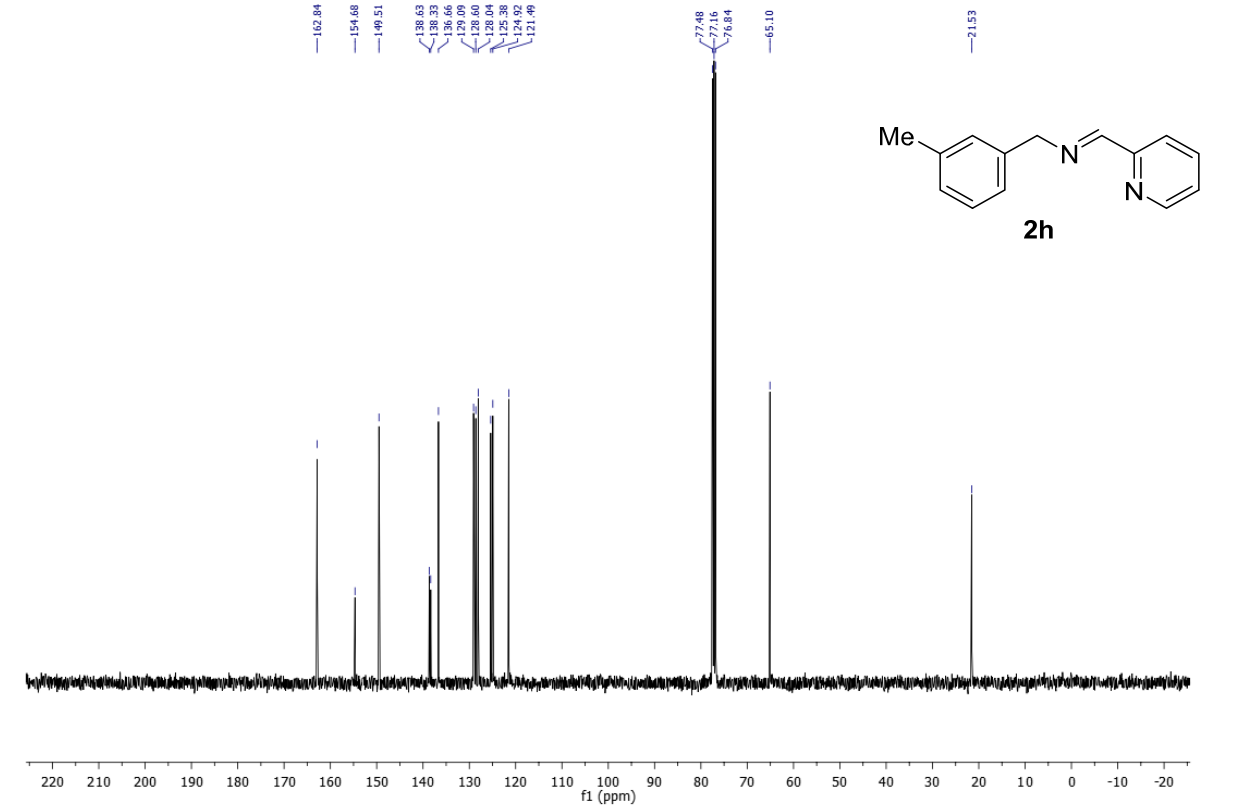
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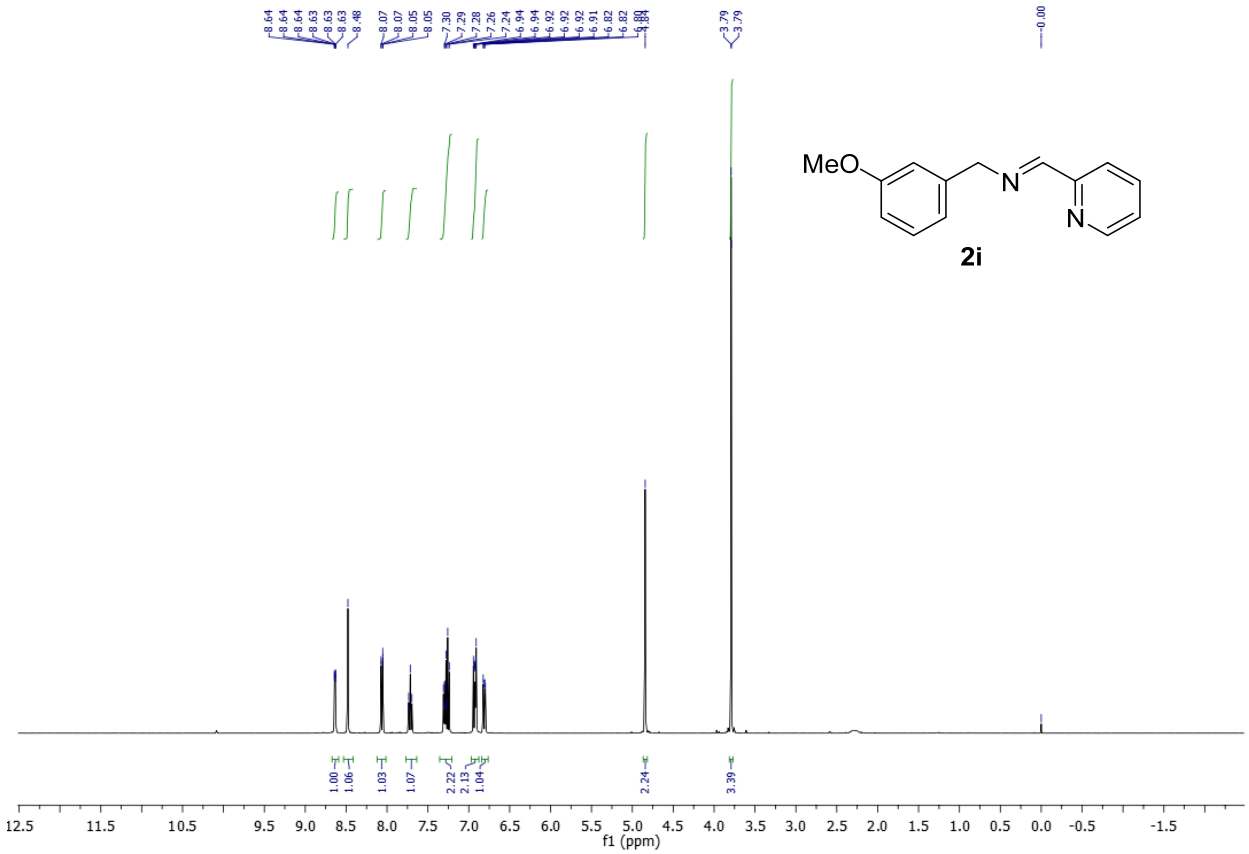
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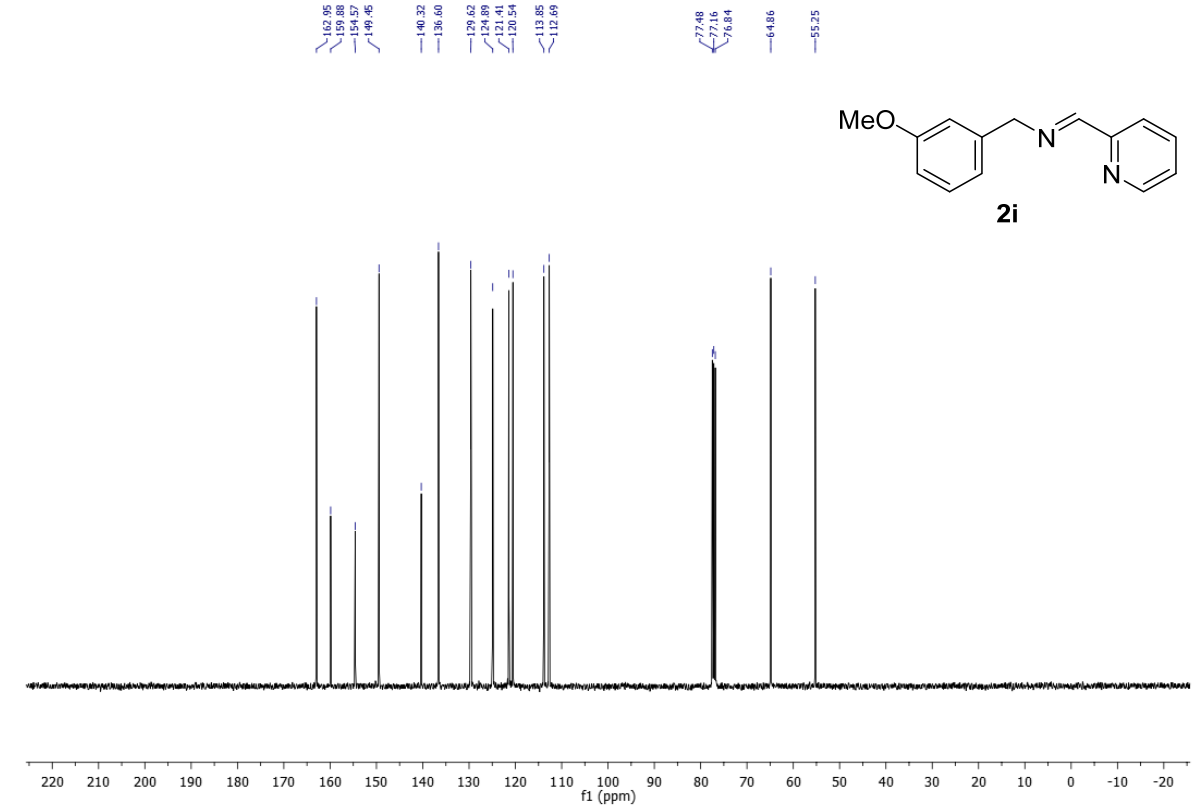
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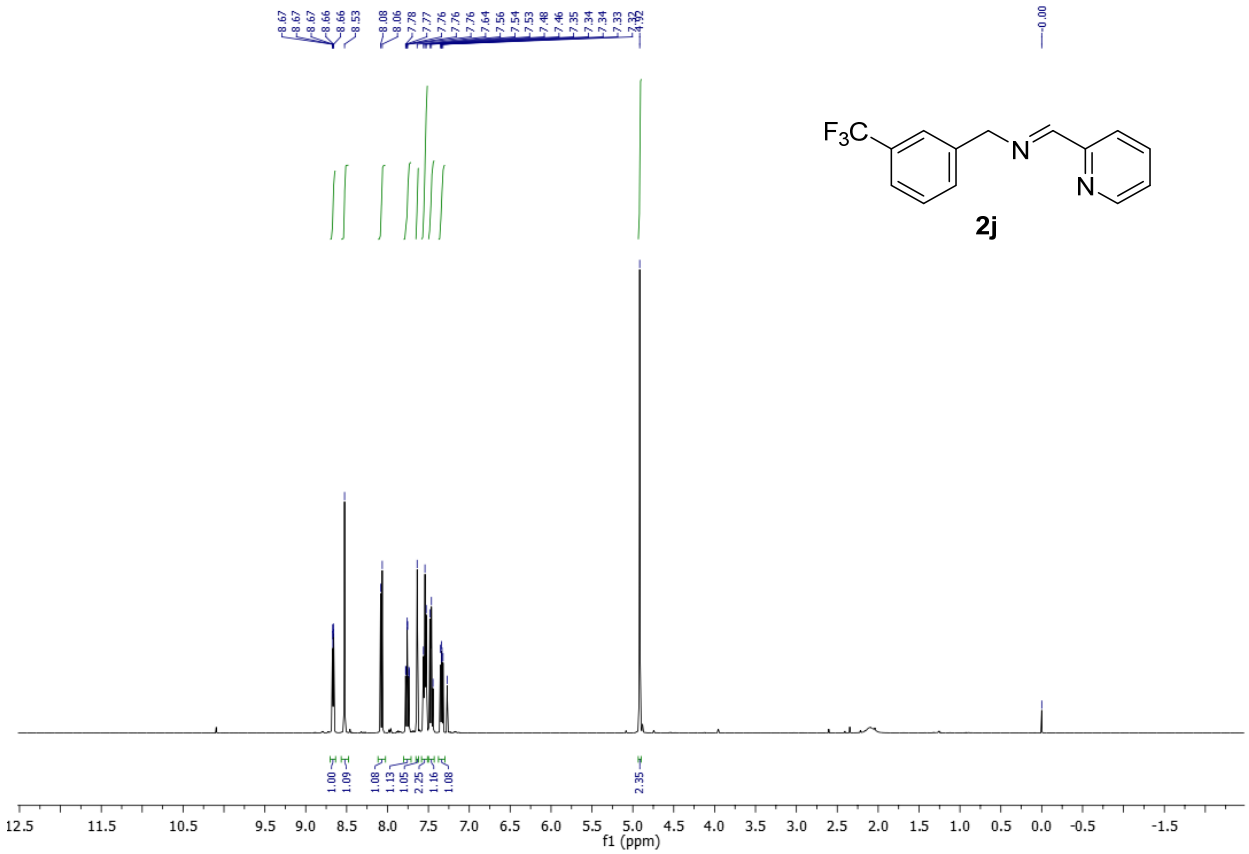
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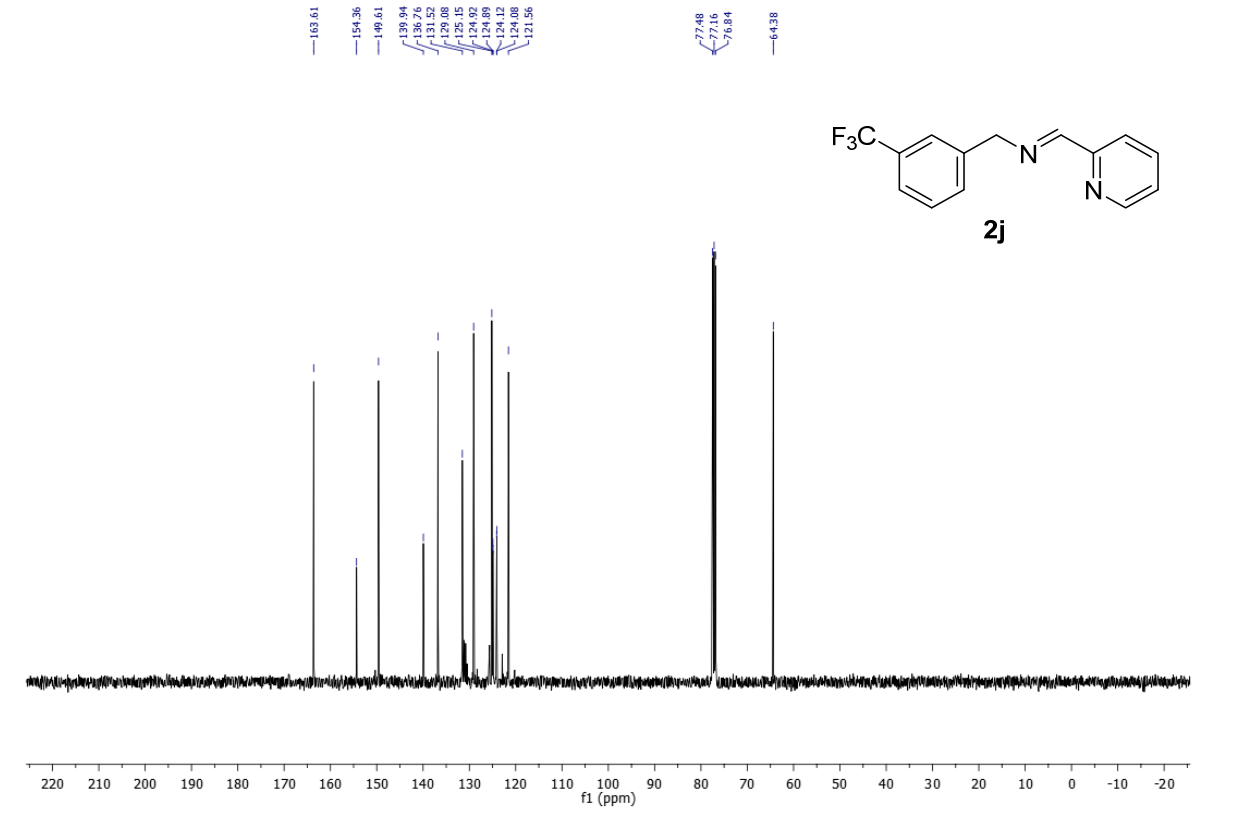
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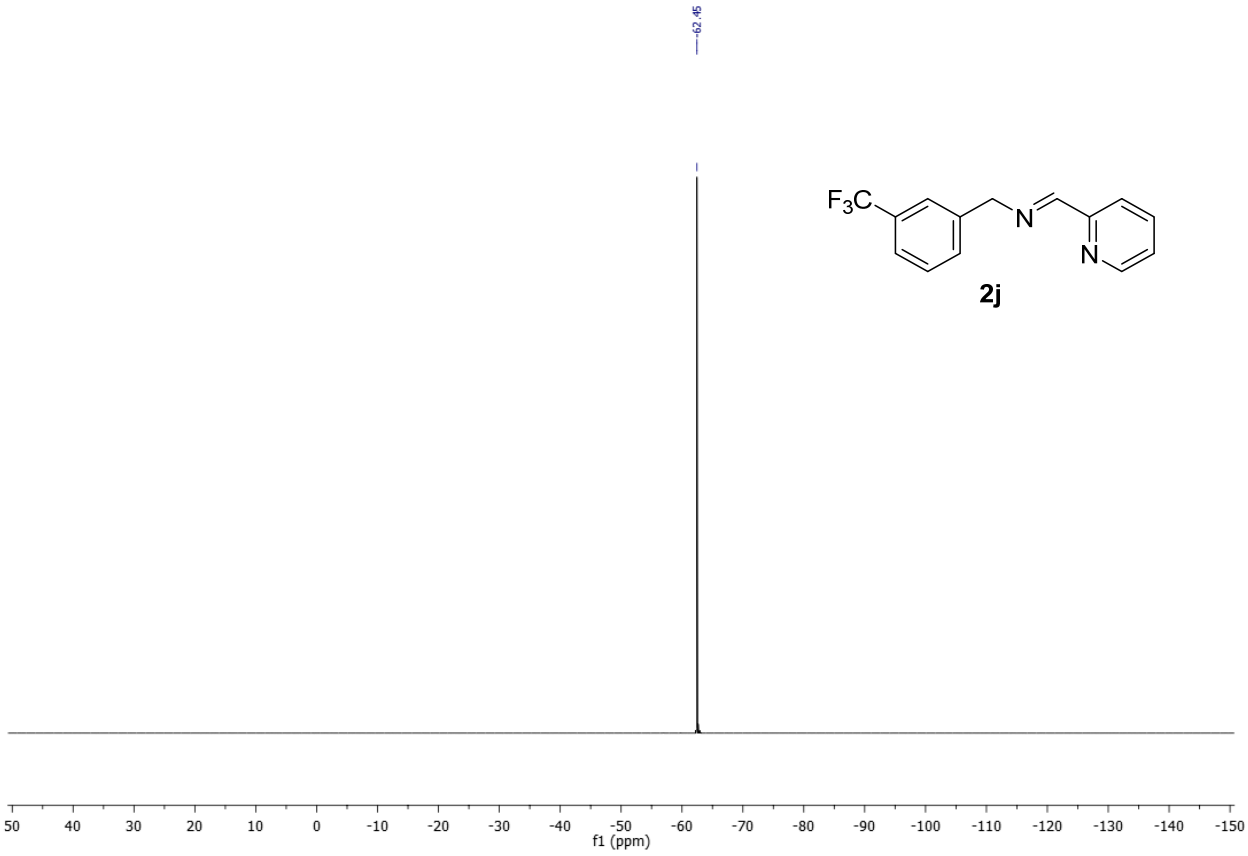
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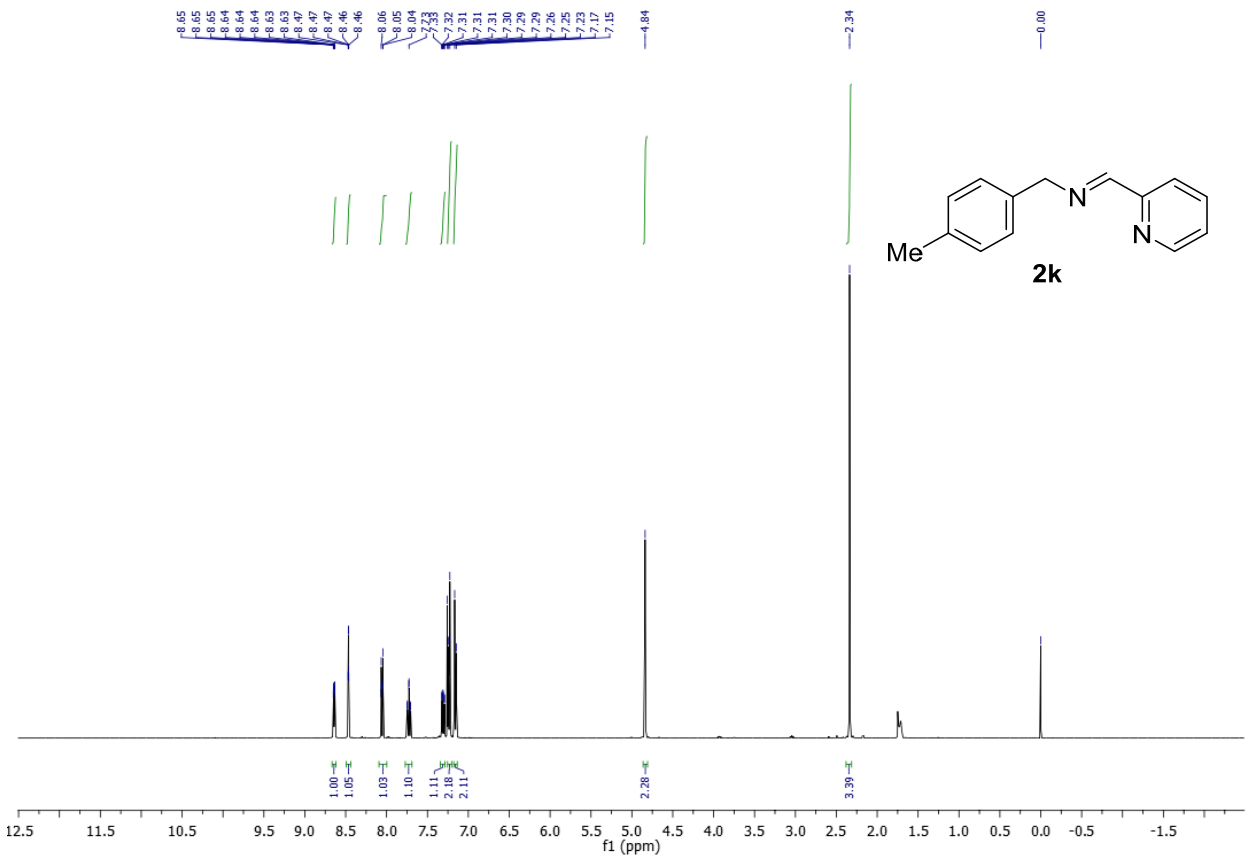
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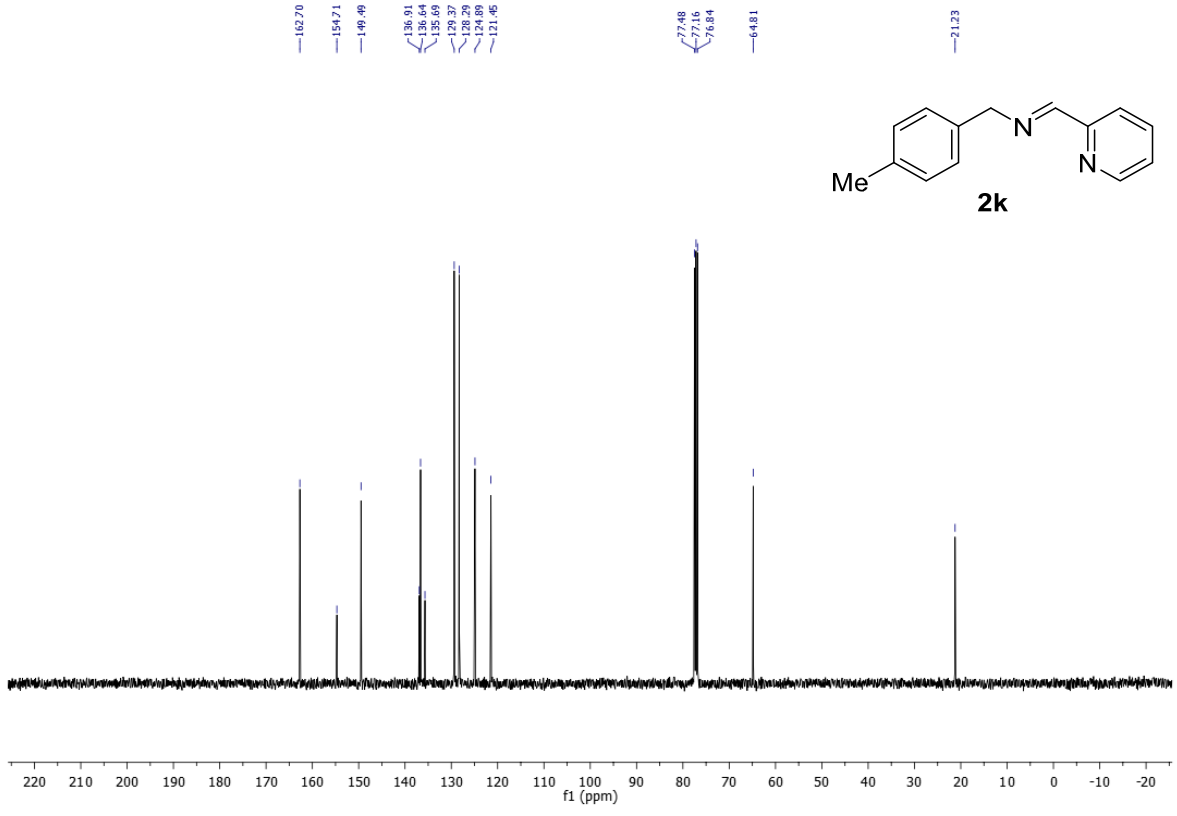
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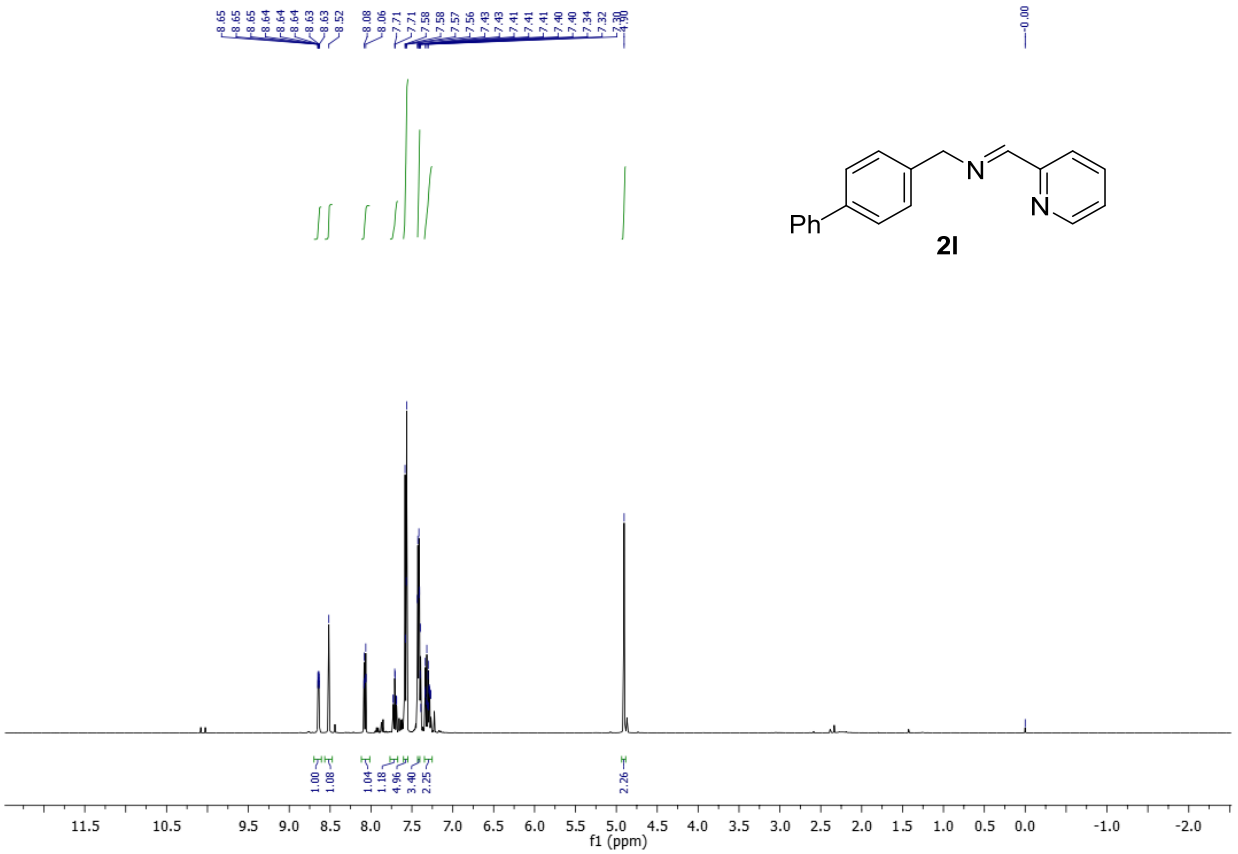
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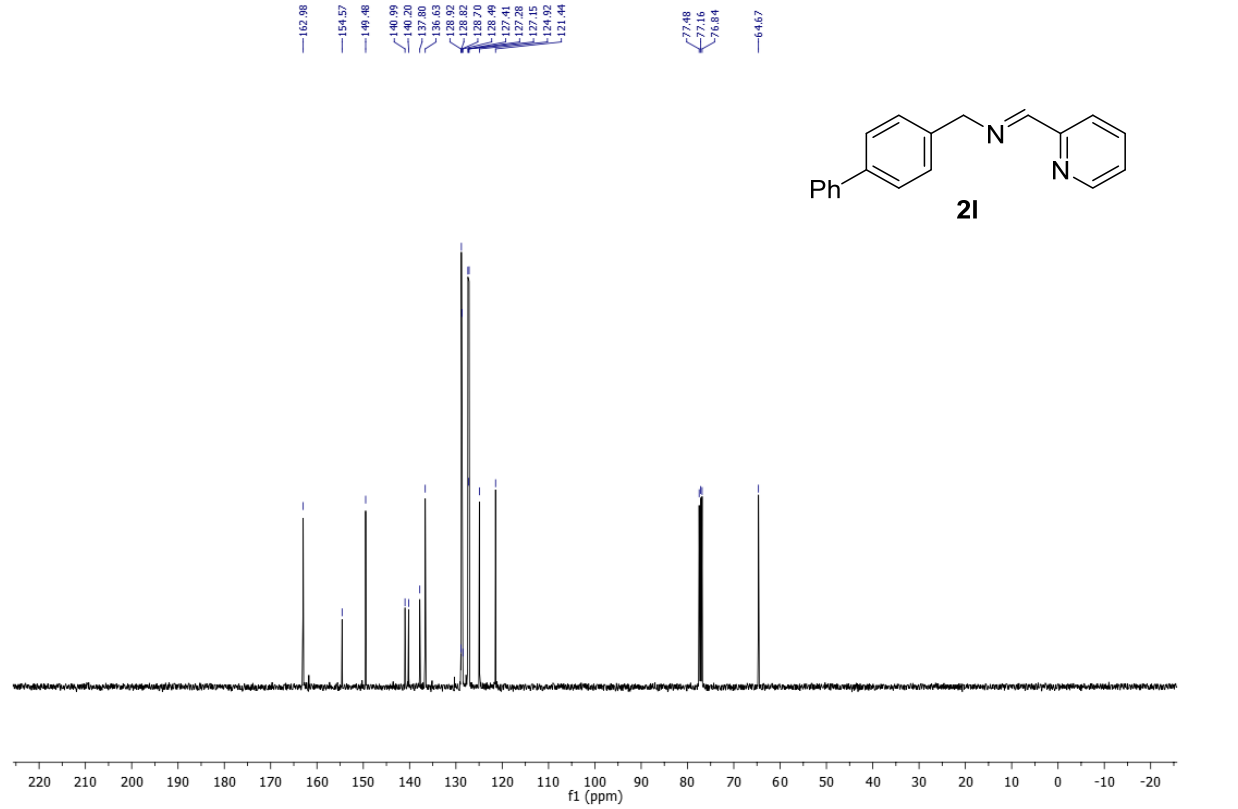
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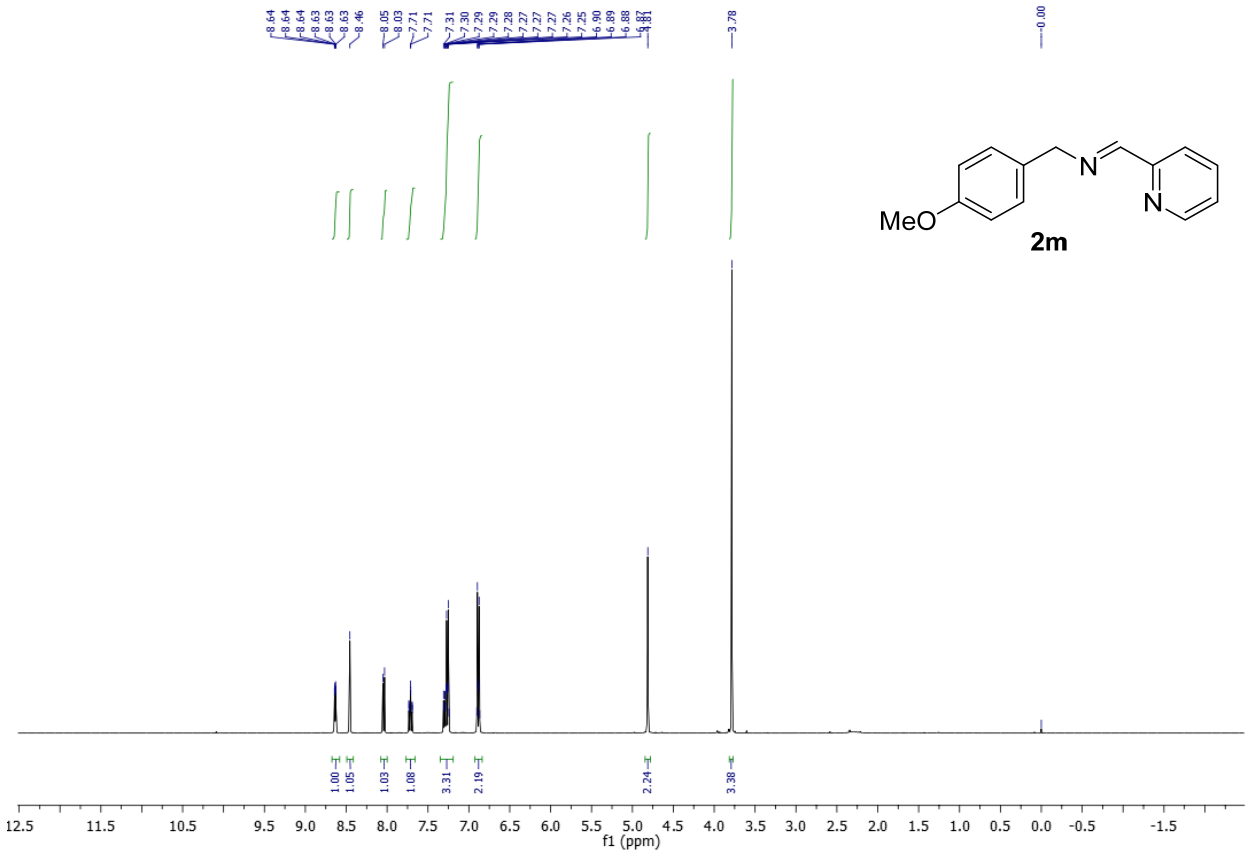
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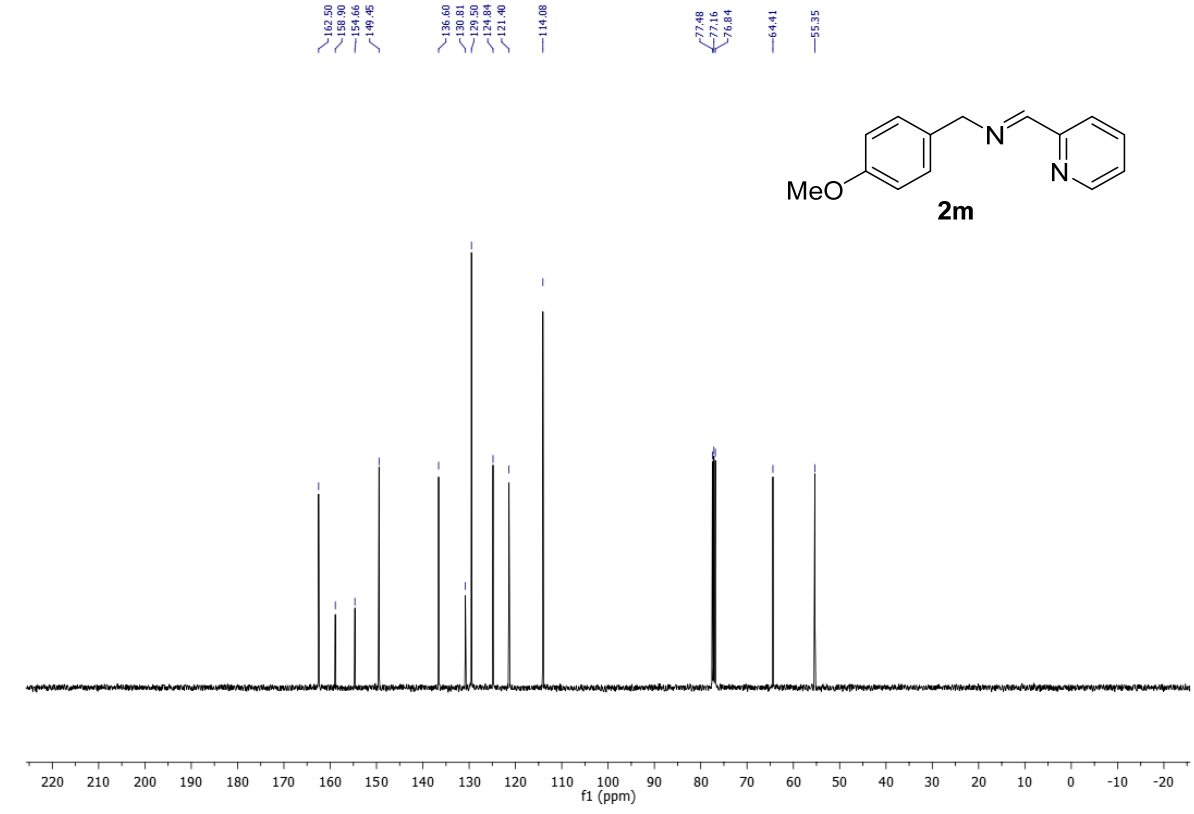
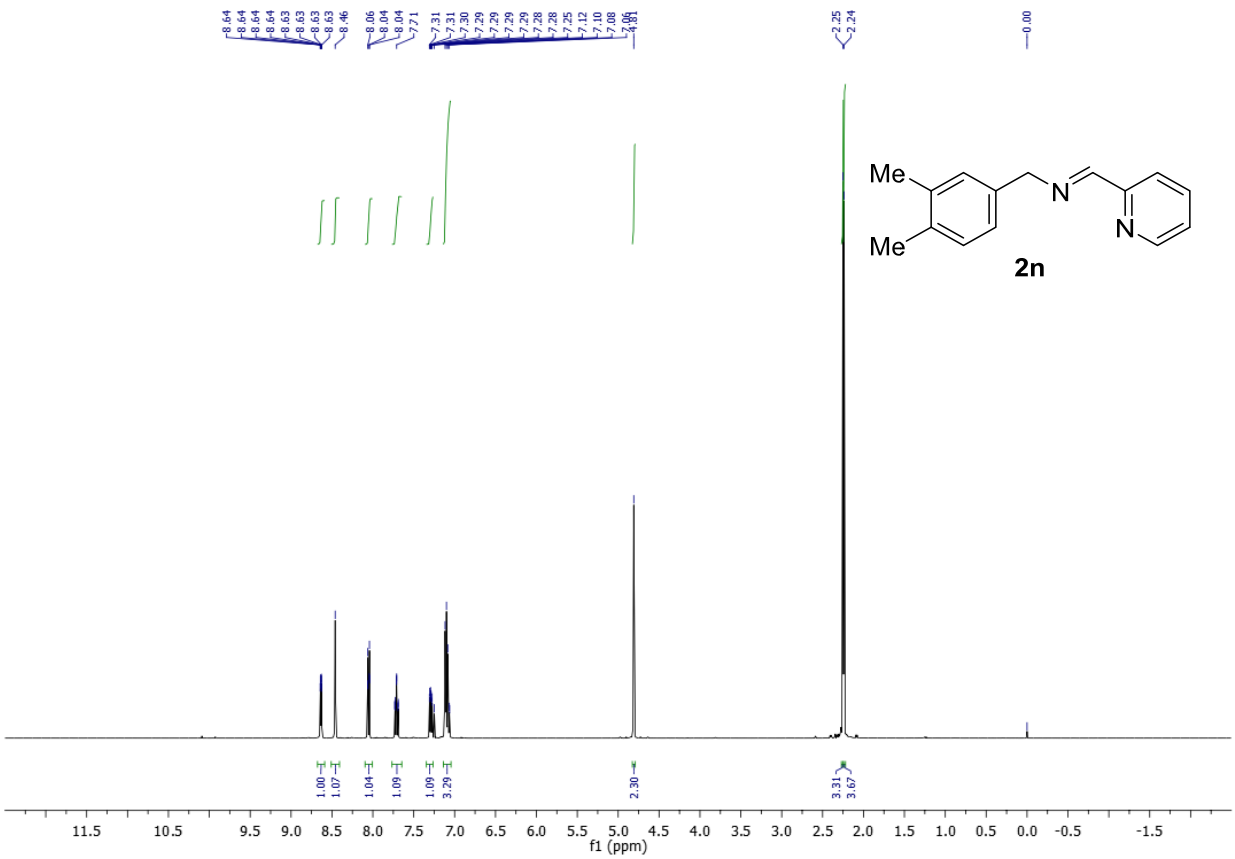
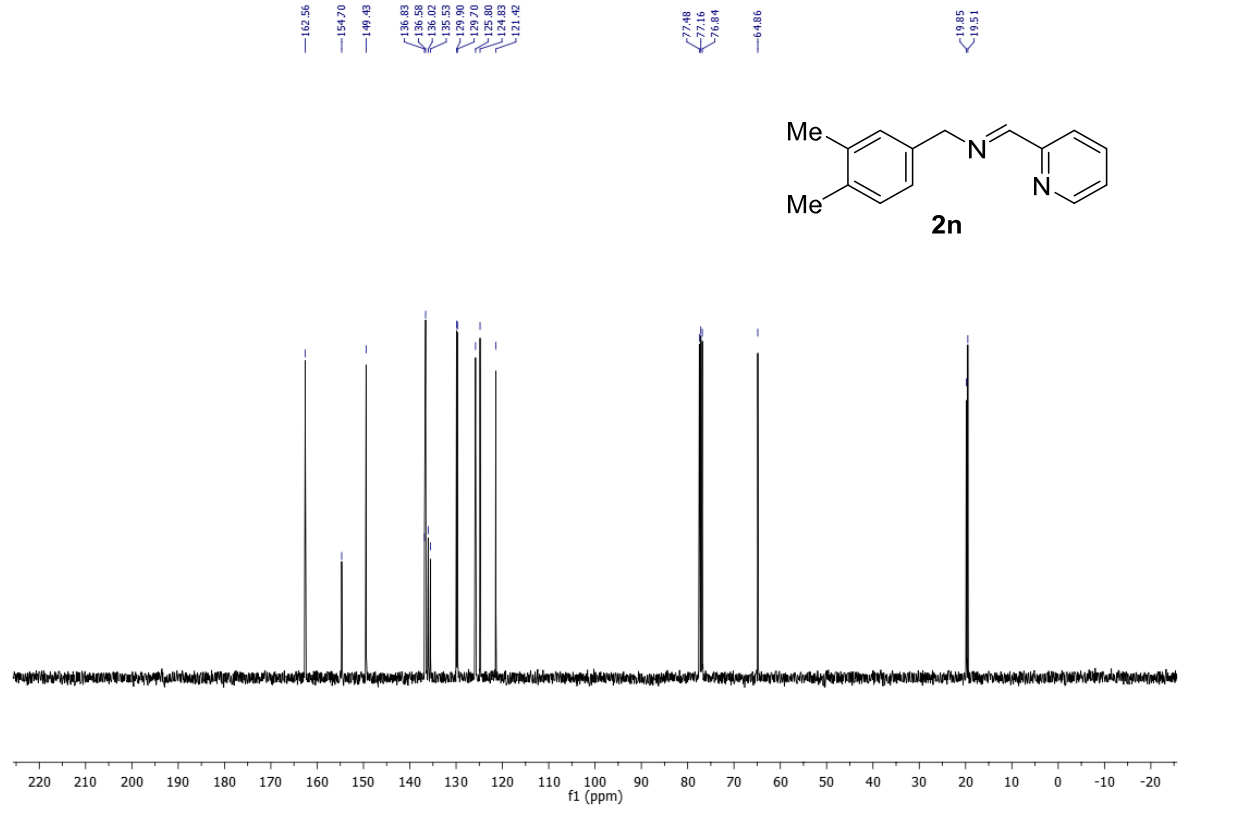
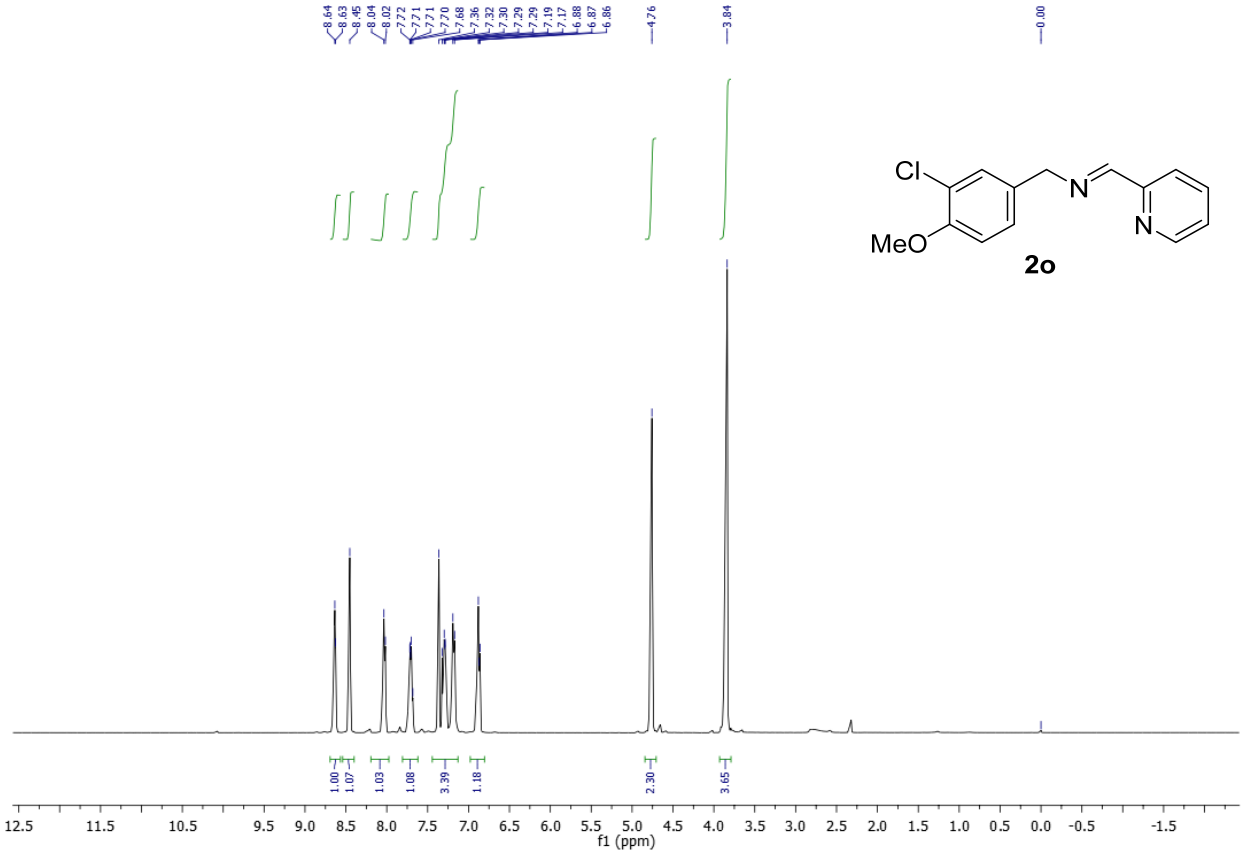
2m
f1 (ppm)


MeO
N
N
2m
f1 (ppm)


Me
Me
N
N
2n
f1 (ppm)


Me
Me
N
N
2n
f1 (ppm)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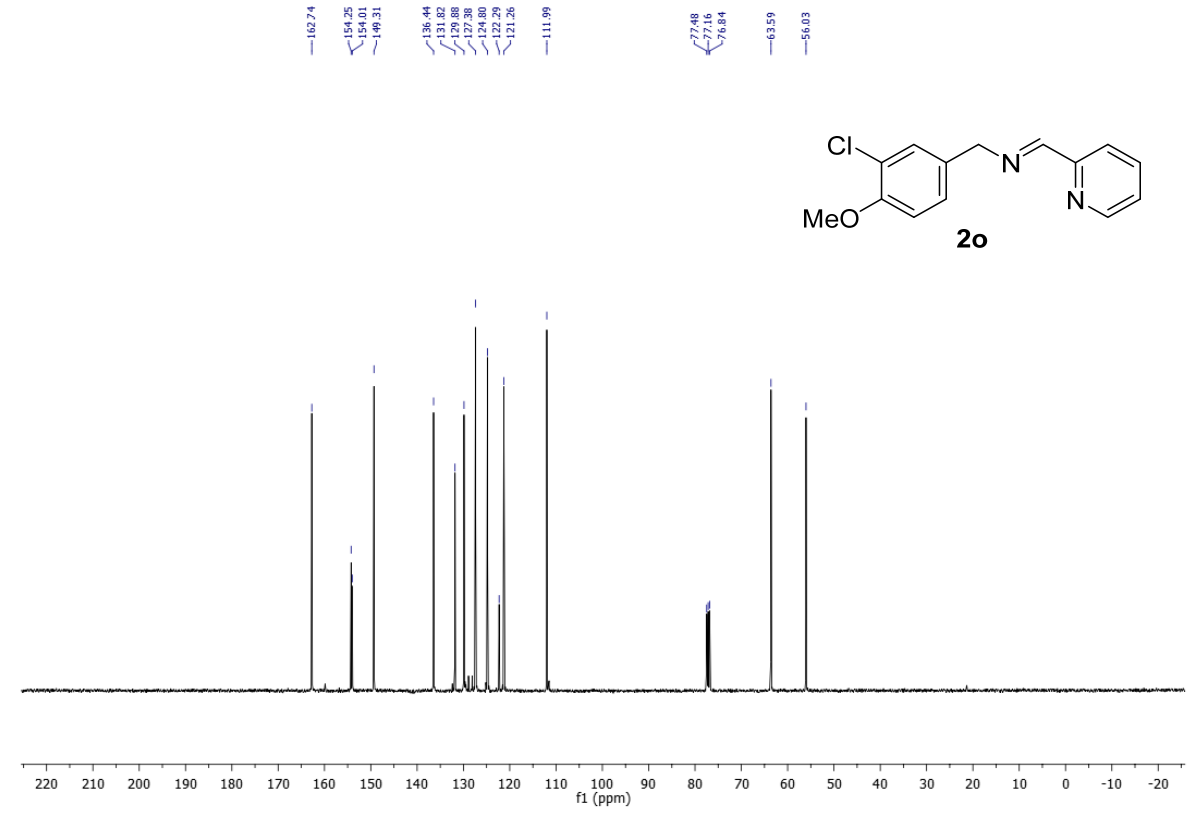
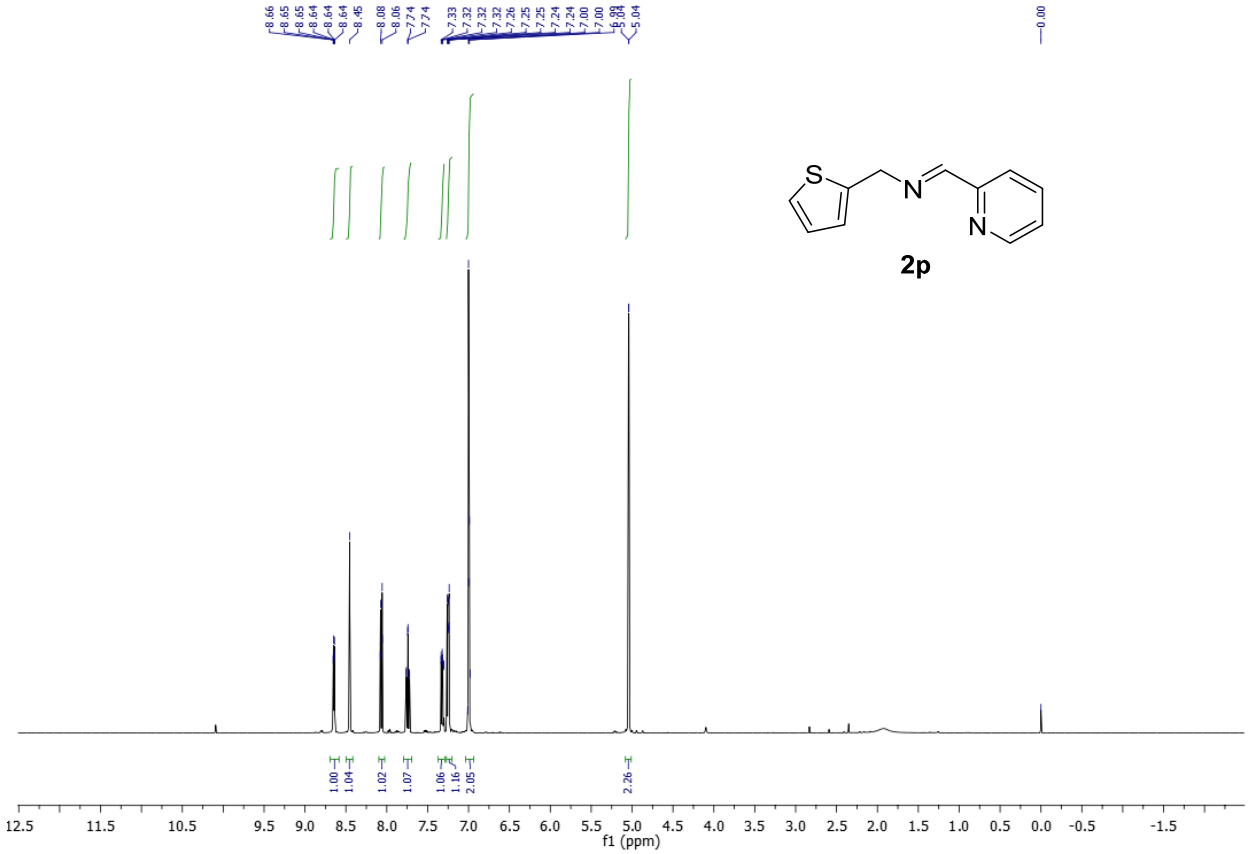
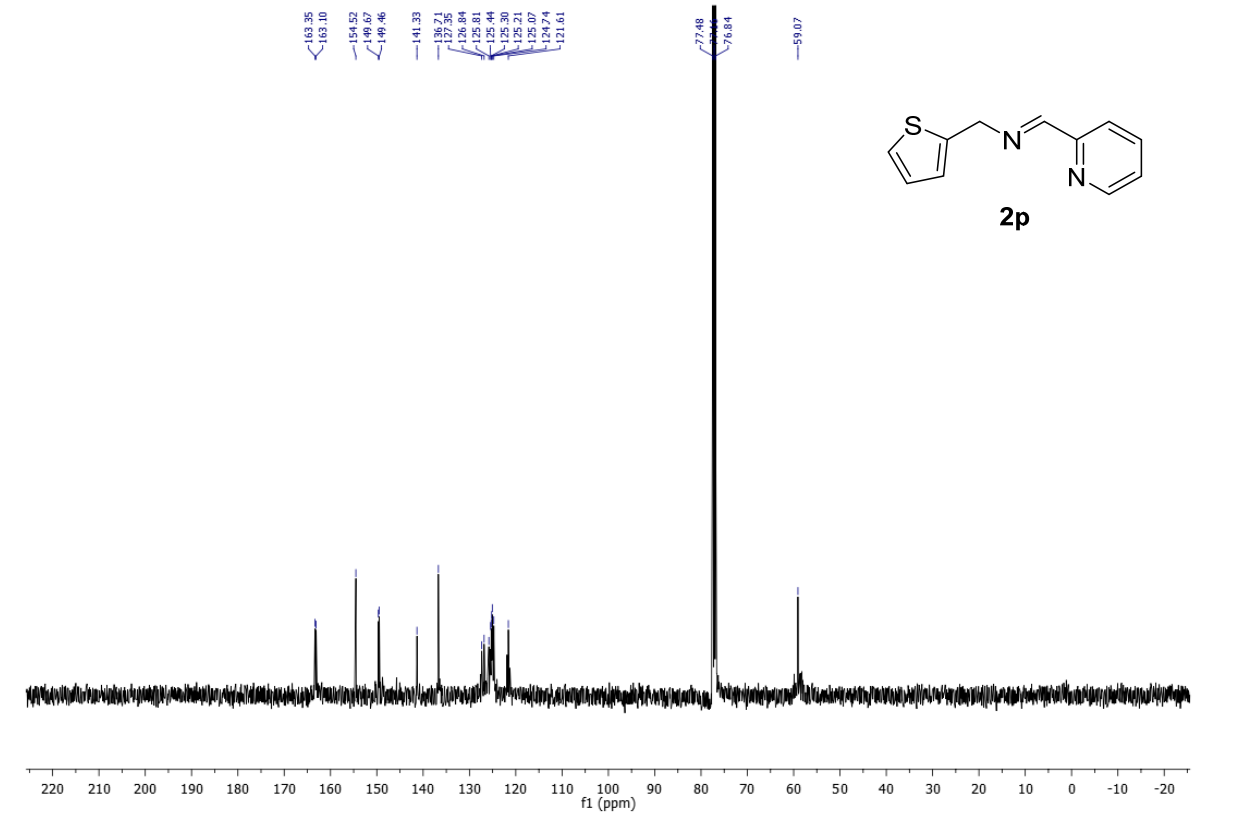
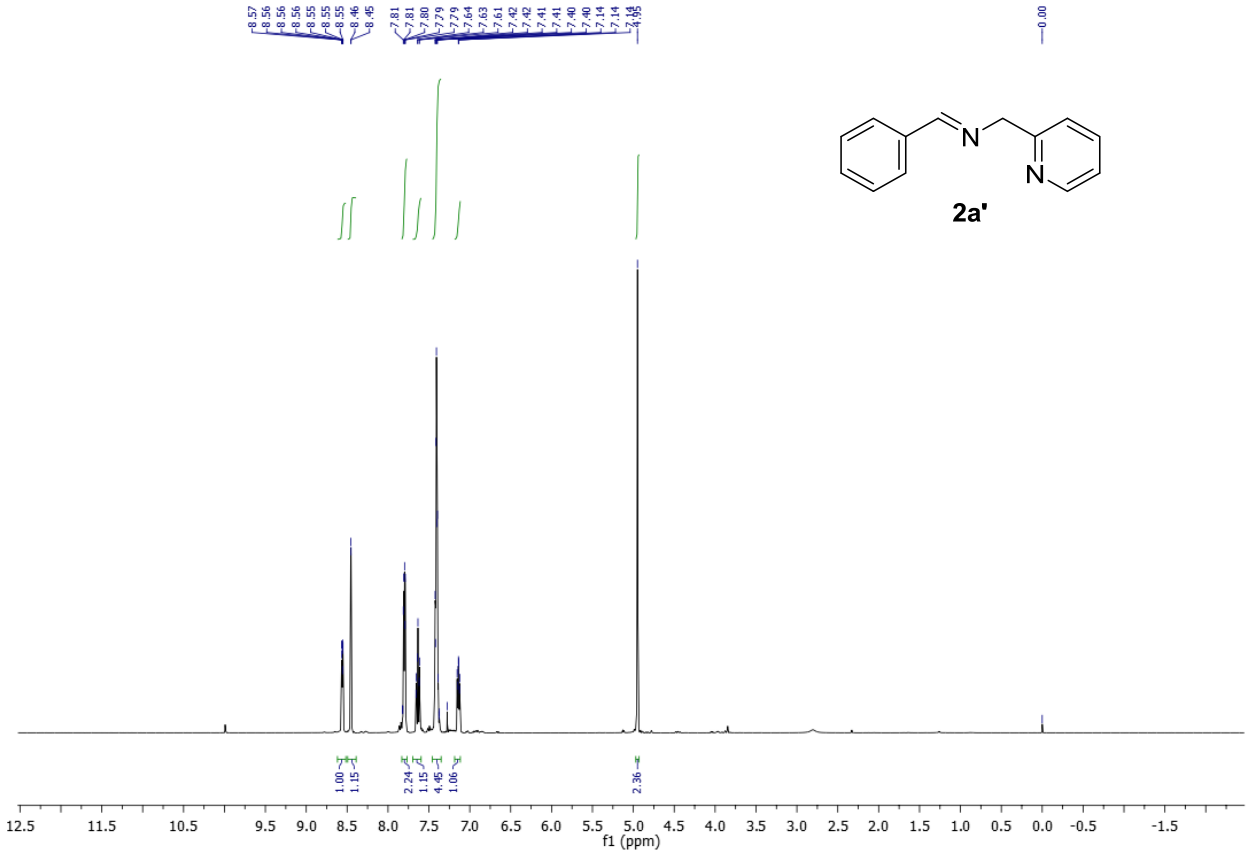
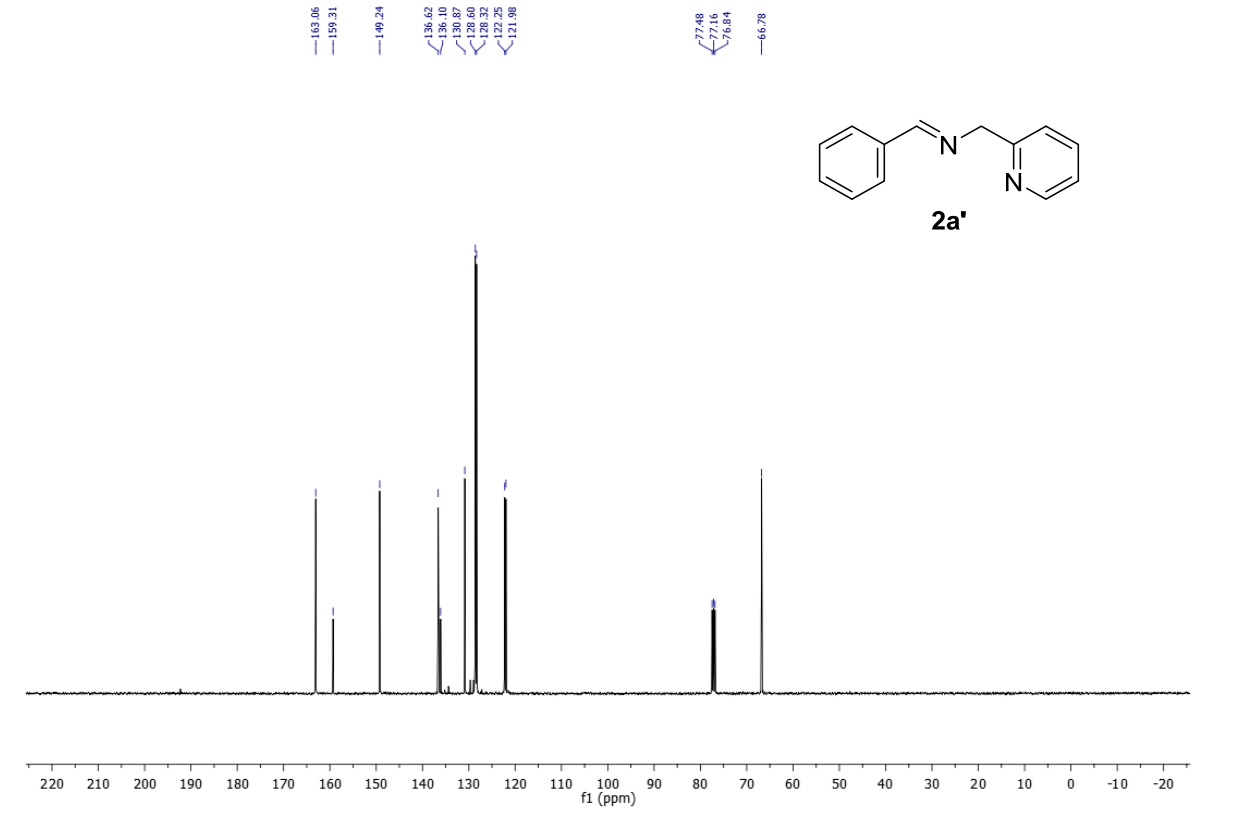
8.63
8.45
8.04
8.02
7.72
7.71
7.71
7.70
7.68
7.36
7.32
7.30
7.29
7.29
7.19
7.17
6.88
6.87
6.86
4.76
3.84
0.00
Cl
N
MeO
N
2o
1.00
1.07
1.03
1.08
3.39
1.18
2.30
3.65
f1 (ppm)

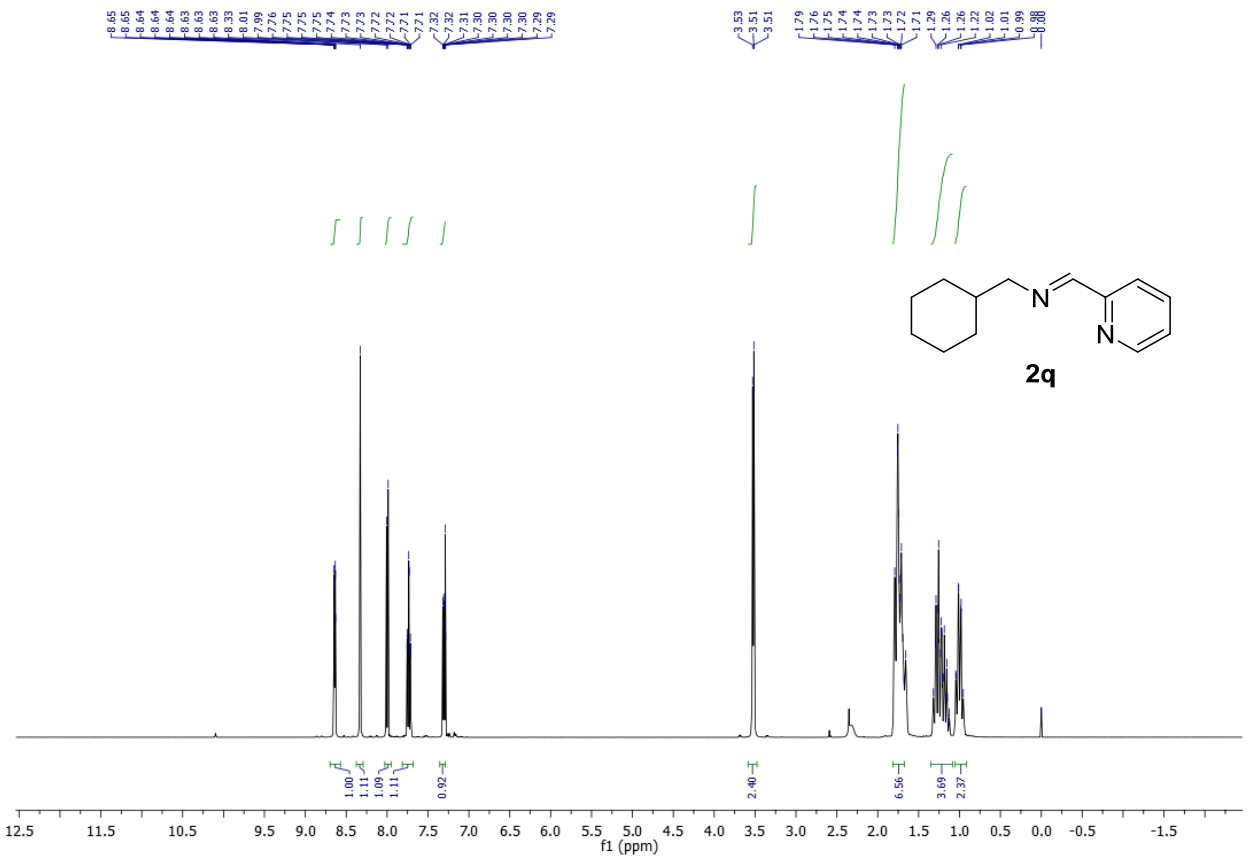

162.74
154.25
154.01
149.31
136.44
131.82
129.88
127.38
124.80
122.29
121.26
111.99
77.48
77.16
76.84
63.59
56.03
Cl
N
MeO
N
2o
f1 (ppm)

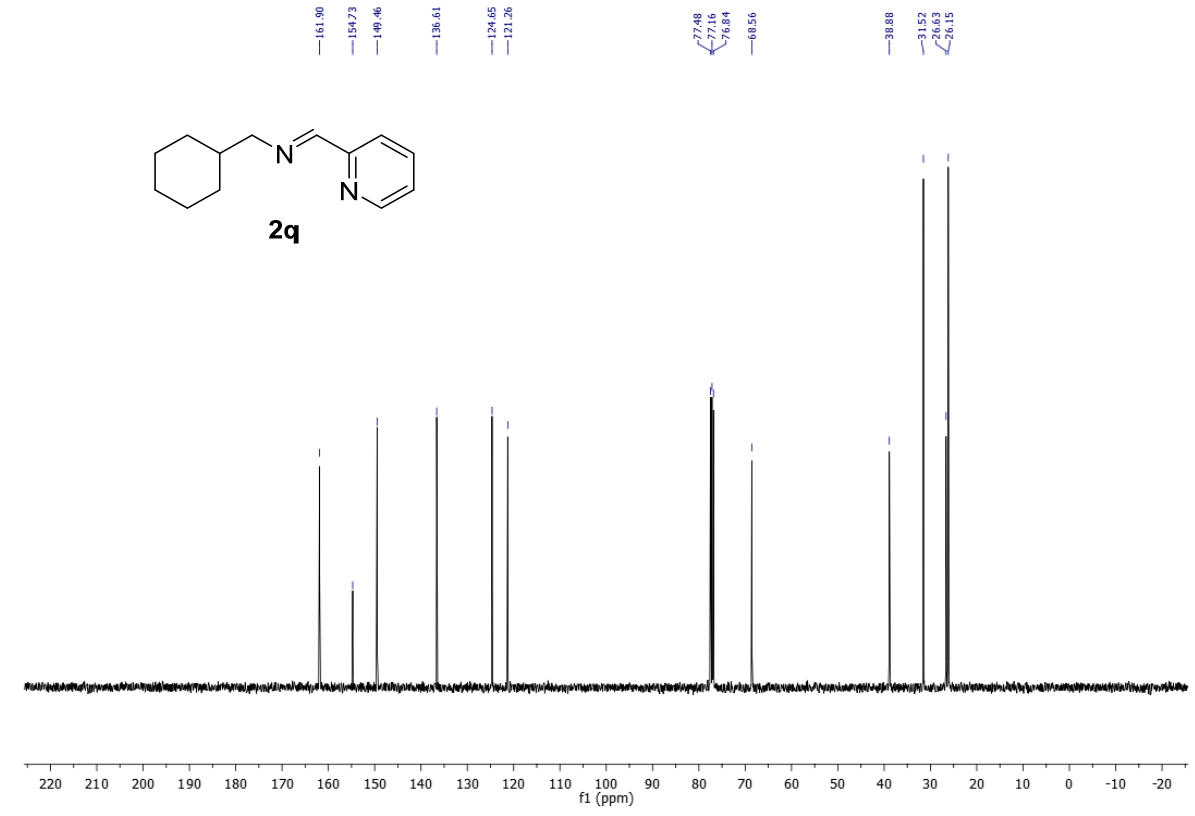

8.66
8.65
8.65
8.64
8.64
8.64
8.45
8.08
8.06
7.74
7.74
7.33
7.32
7.32
7.32
7.26
7.25
7.25
7.24
7.24
7.00
7.00
5.04
0.00
S
N
N
2p
1.00
1.04
1.02
1.07
1.06
1.16
2.05
2.26
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)

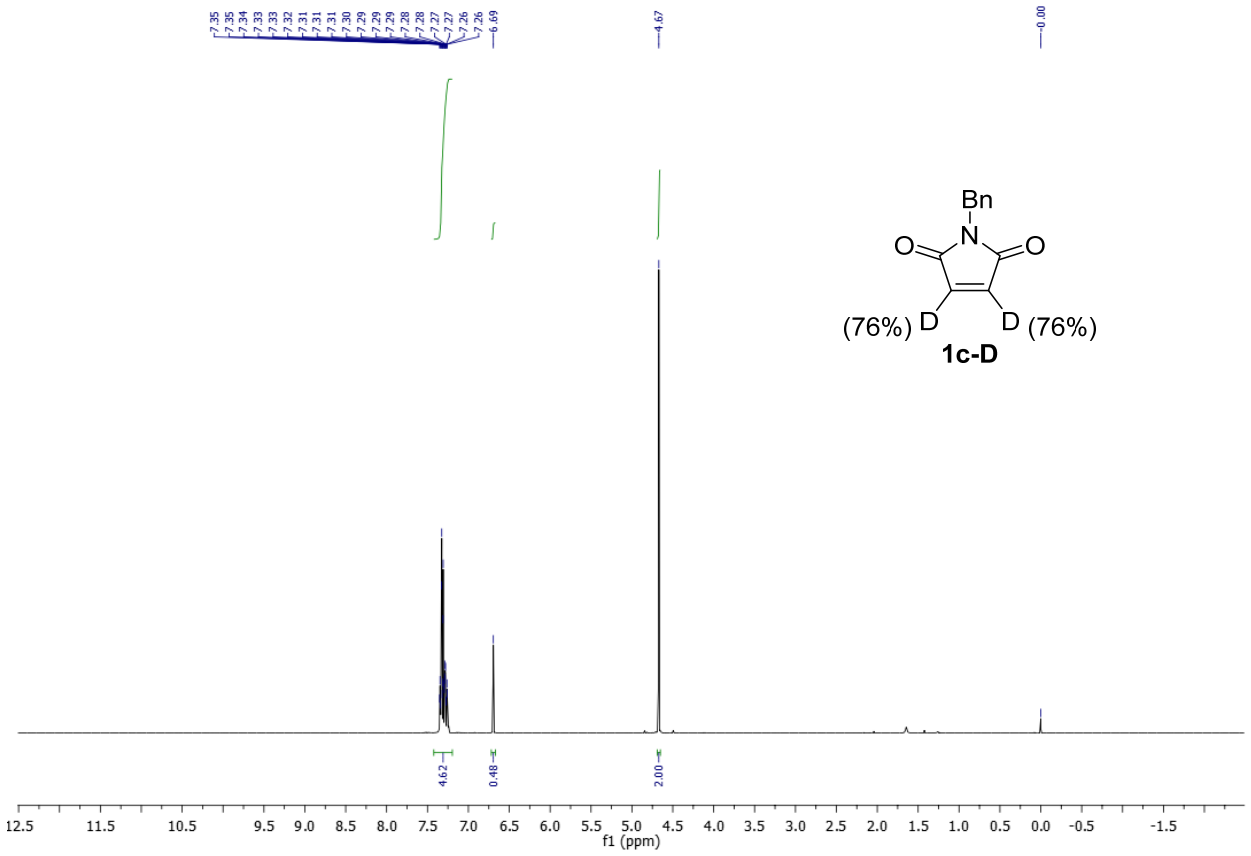

163.35
163.10
154.52
149.67
149.46
141.33
136.21
127.35
126.84
125.81
125.44
125.30
125.21
125.07
124.74
121.61
77.48
77.16
76.84
59.07
S
N
N
2p
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

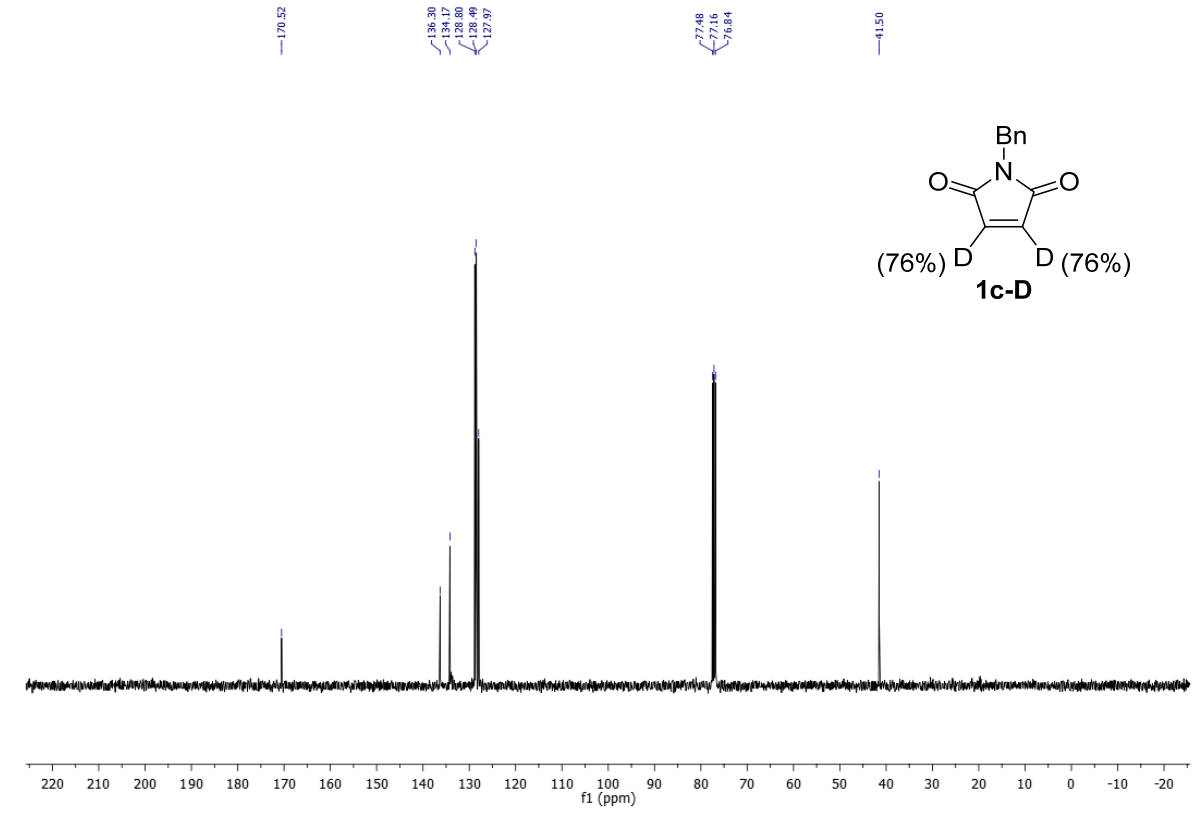

8.57
8.56
8.56
8.56
8.55
8.55
8.55
8.46
8.45
7.81
7.81
7.80
7.79
7.79
7.64
7.63
7.61
7.42
7.42
7.41
7.41
7.40
7.40
7.14
7.14
4.95
0.00
1.00
1.15
2.24
1.15
4.45
1.06
2.36
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)
N
N
2a'


163.06
159.31
149.24
136.62
136.10
130.87
128.60
128.32
122.25
121.98
77.48
77.16
76.84
66.78
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)
N
N
2a'

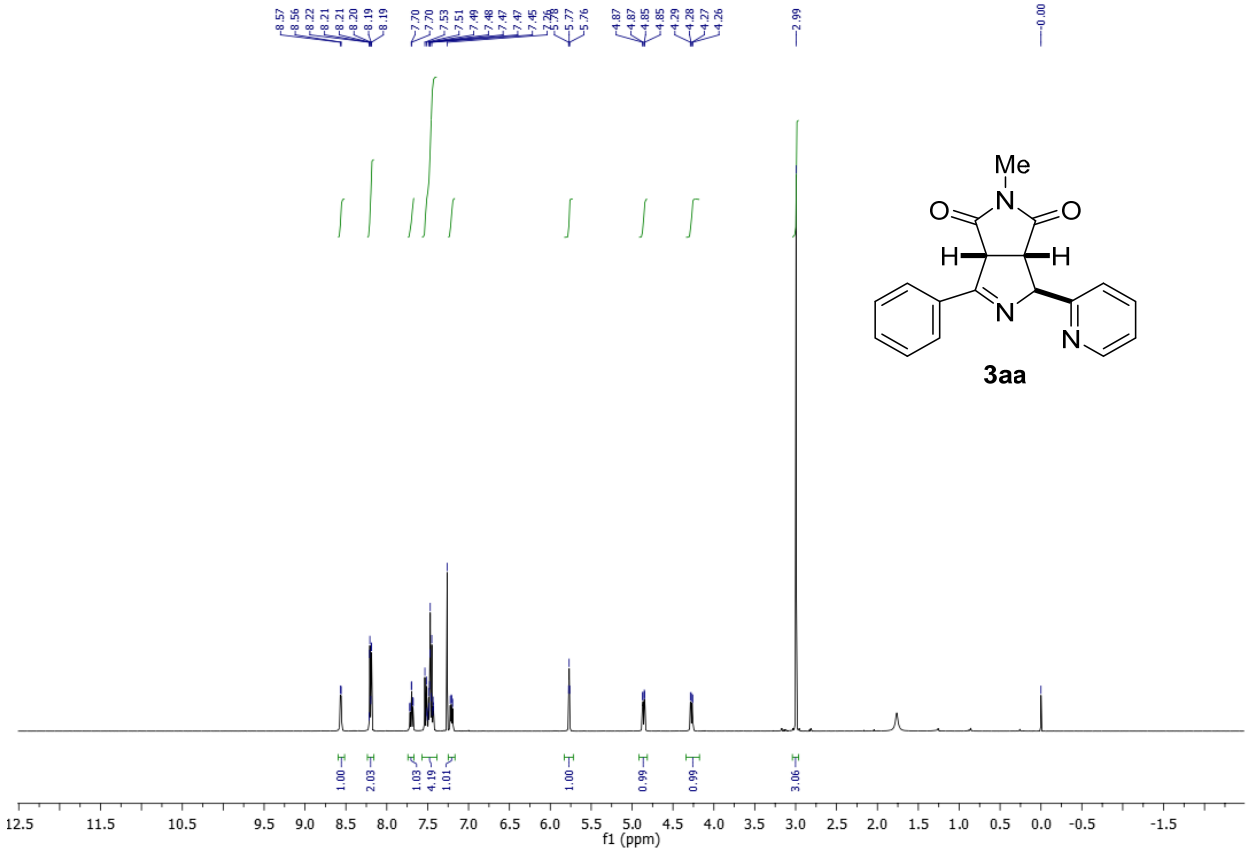

8.65
8.65
8.64
8.64
8.64
8.63
8.63
8.63
8.33
8.01
7.99
7.76
7.75
7.75
7.75
7.74
7.73
7.73
7.72
7.72
7.71
7.71
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.29
3.53
3.51
3.51
1.79
1.76
1.75
1.74
1.74
1.73
1.73
1.72
1.71
1.29
1.26
1.26
1.22
1.02
1.01
0.99
8.88
8.88
N
N
2q
1.00
1.11
1.09
1.11
0.92
2.40
6.56
3.69
2.37
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)

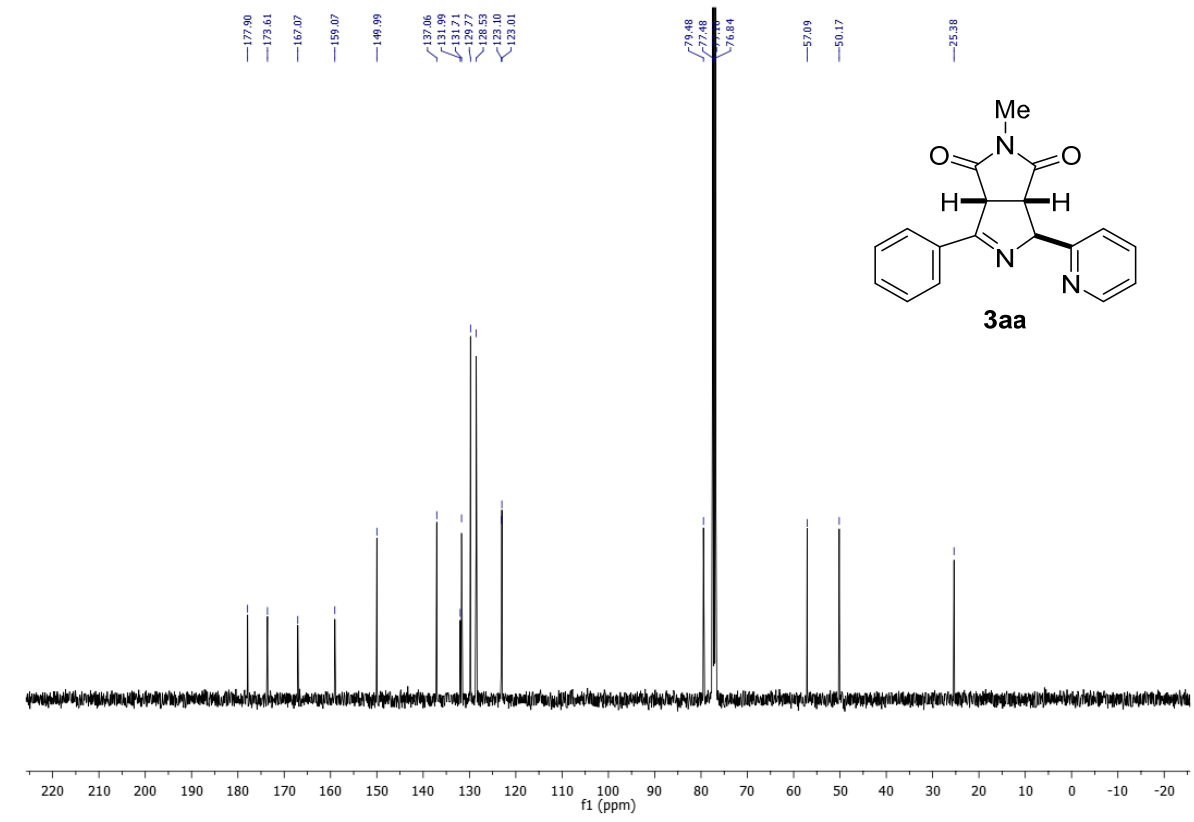

161.90
154.73
149.46
136.61
124.65
121.26
77.48
77.16
76.84
68.56
38.88
31.52
26.63
26.15
N
N
2q
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

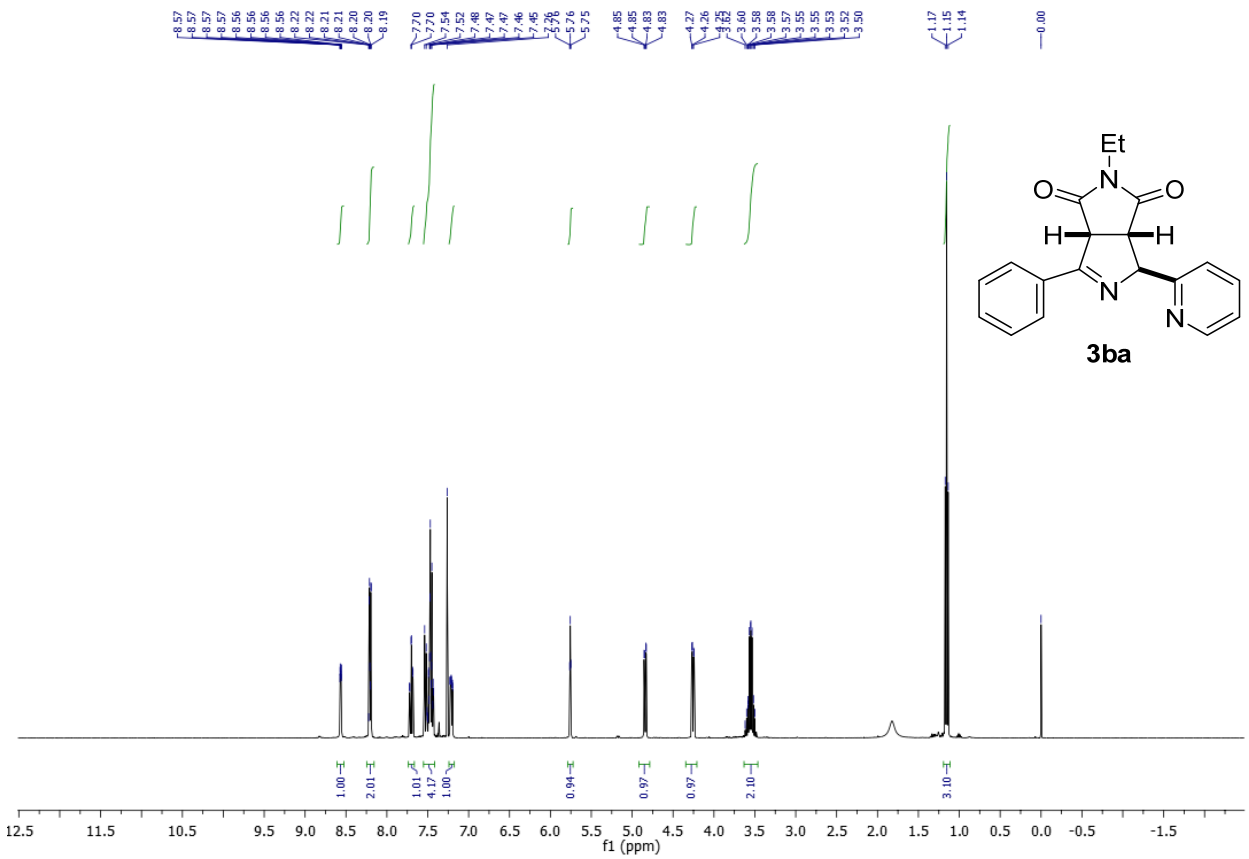

Bn
N
O
O
(76%) D
D (76%)
1c-D
f1 (ppm)

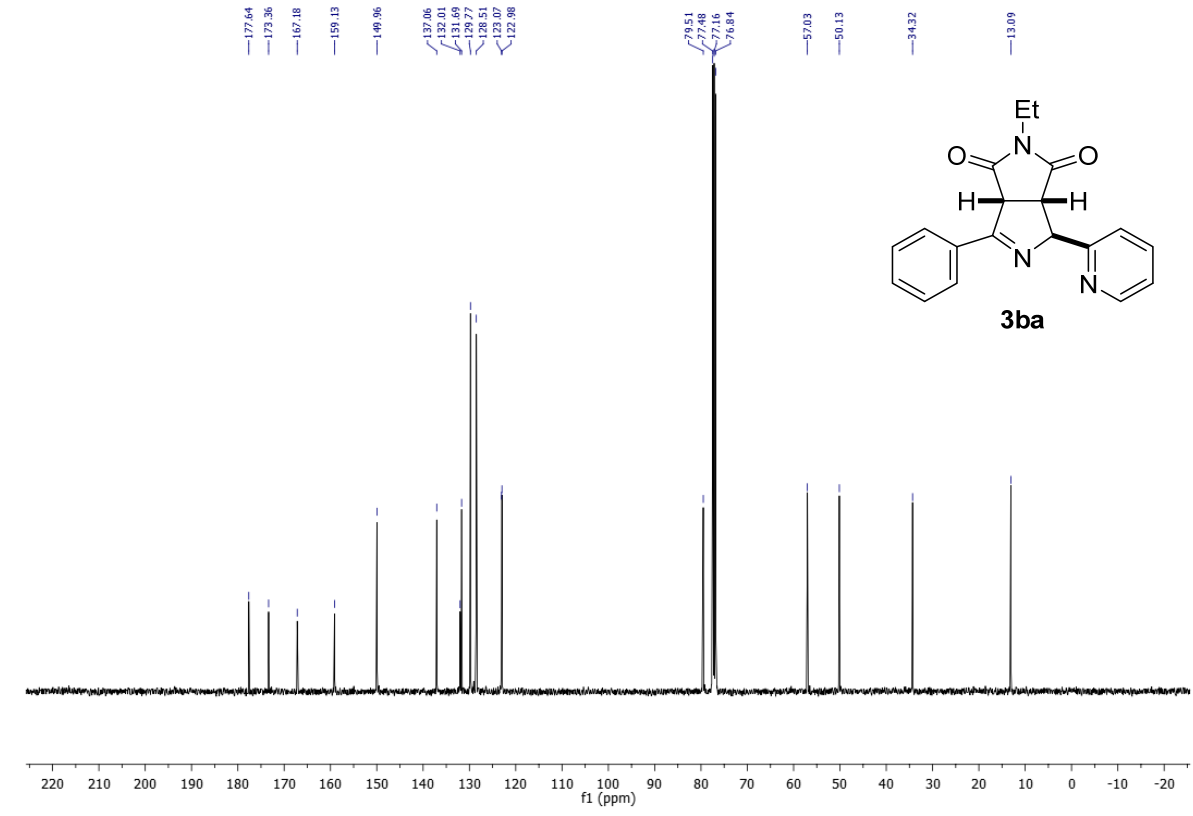

Bn
N
O
O
(76%) D
D (76%)
1c-D
f1 (ppm)

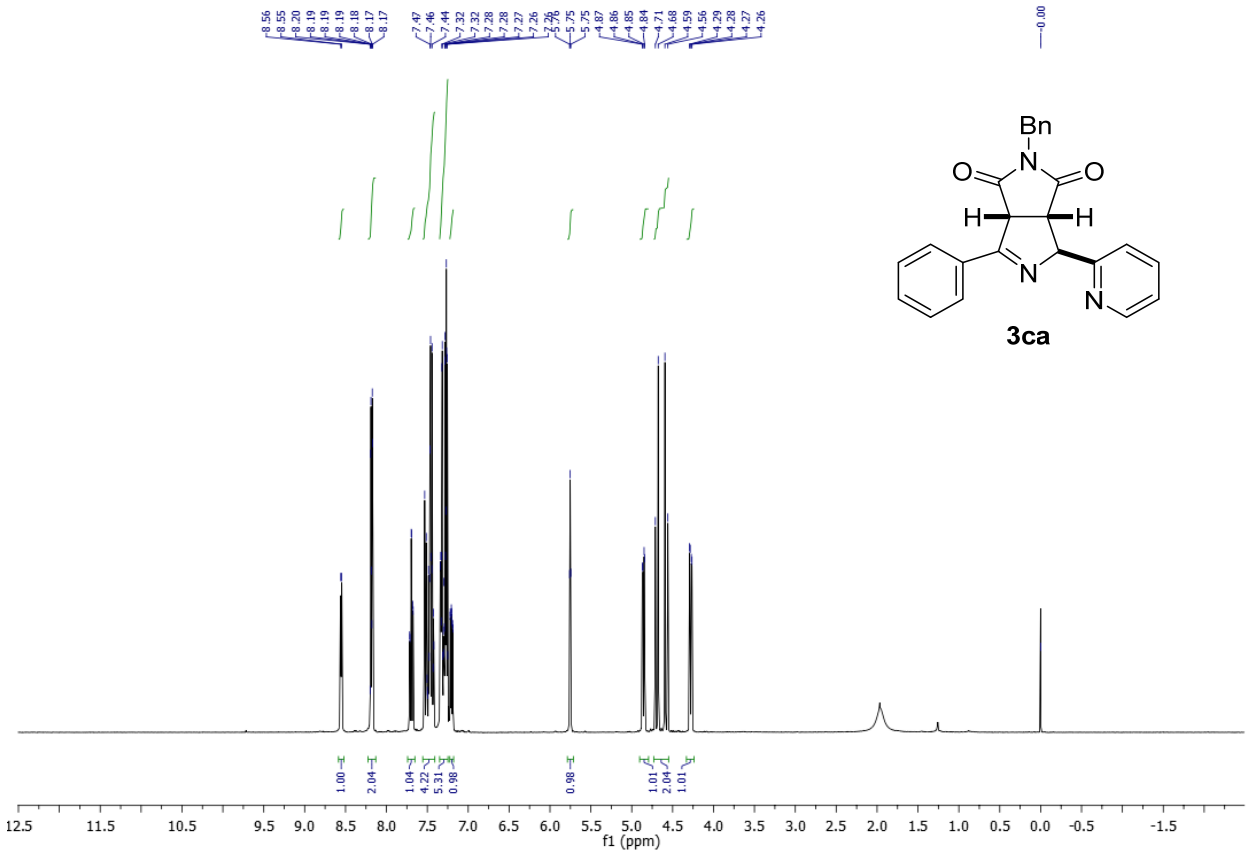
NMR spectra of products

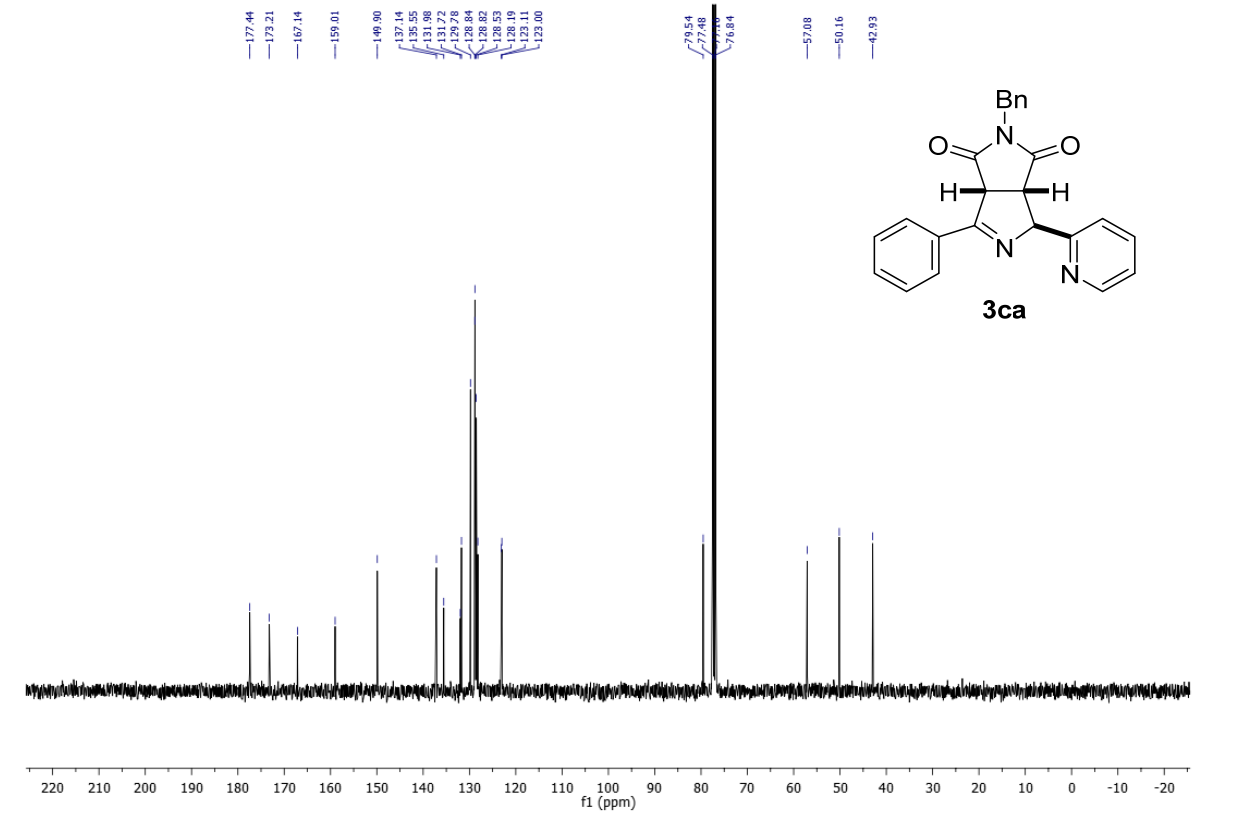


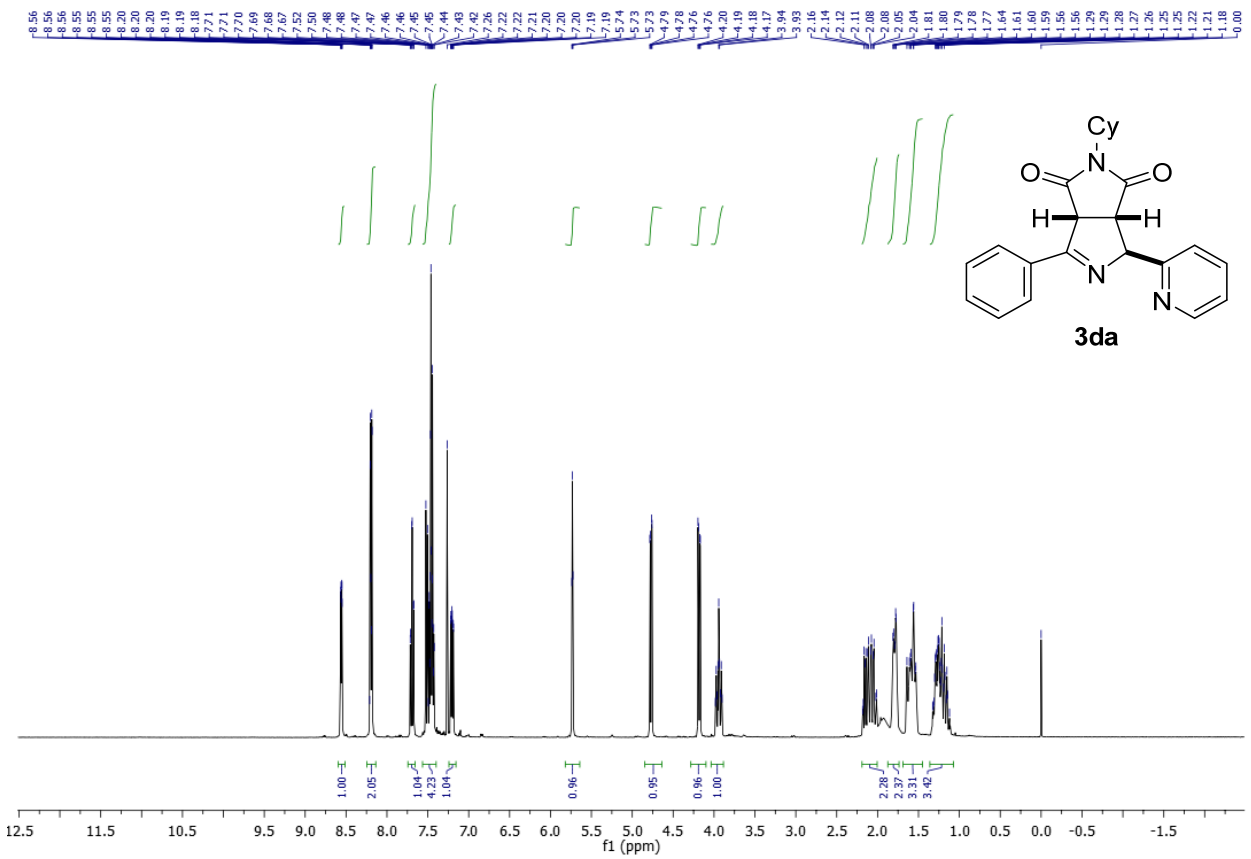


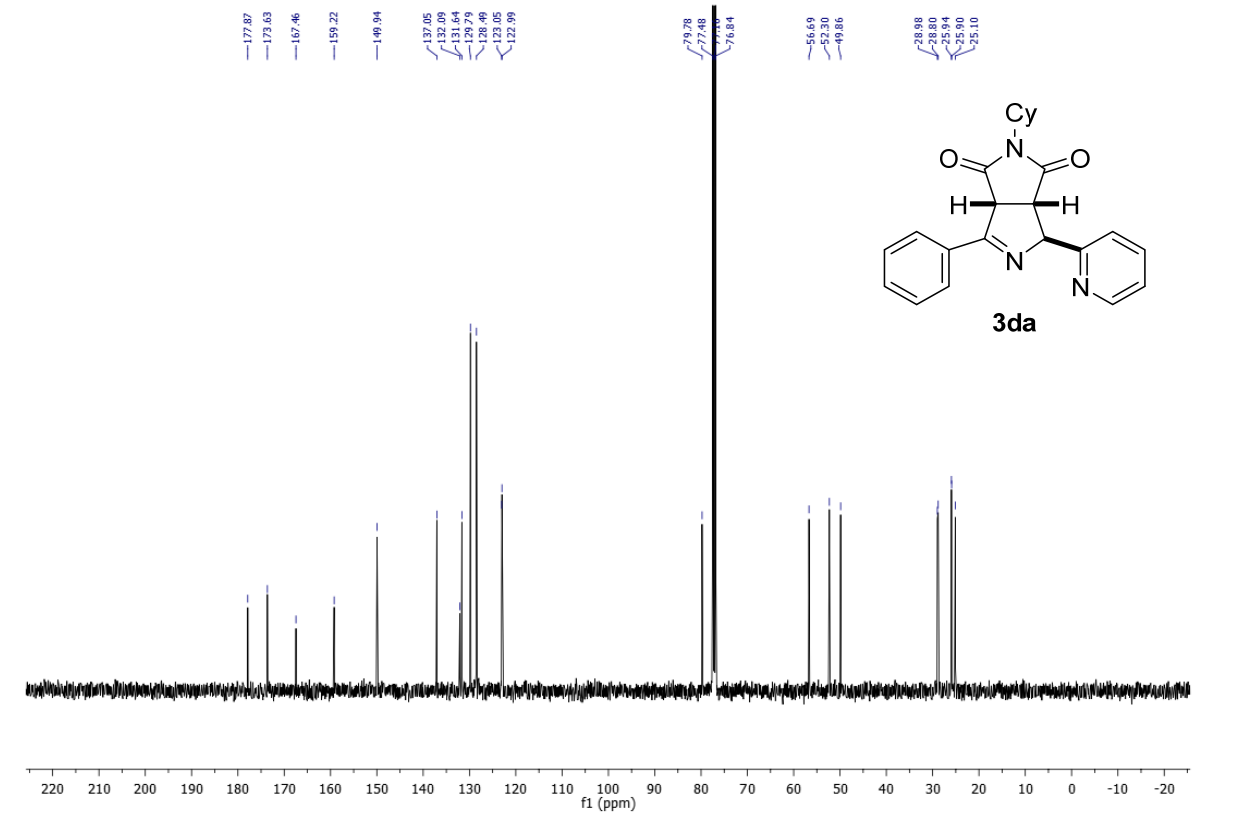

Et
N
O
O
H
H
N
N
3ba
f1 (ppm)

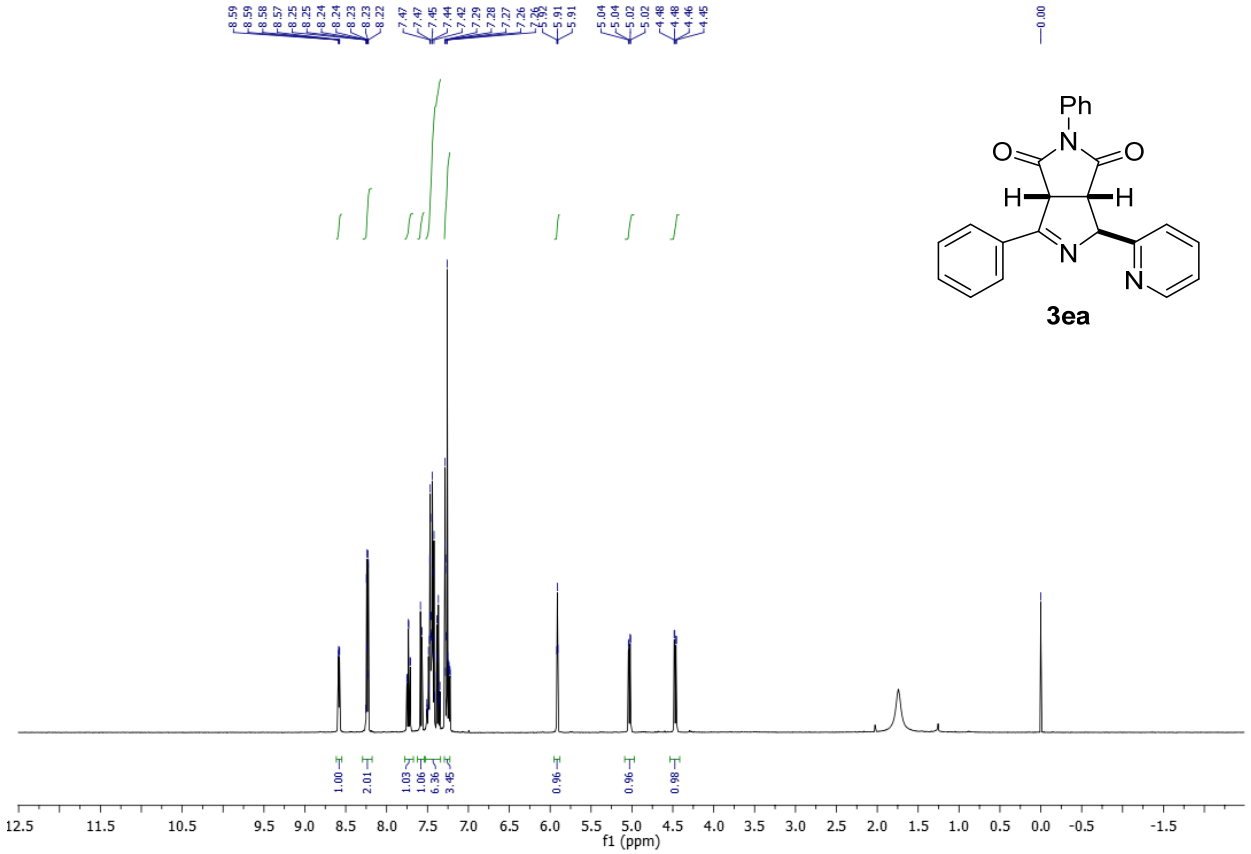

Et
N
O
O
H
H
N
N
3ba
f1 (ppm)

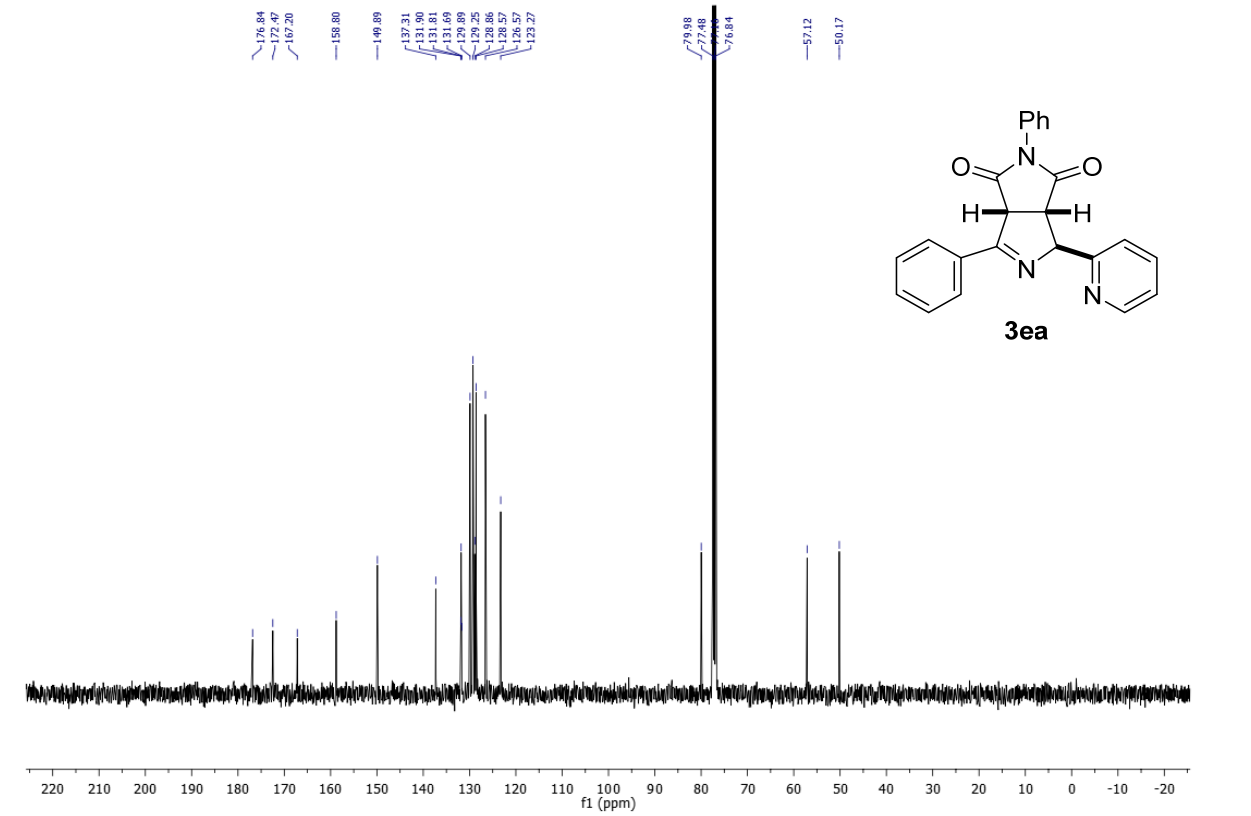

Bn
N
O
O
H
H
N
N
3ca
f1 (ppm)

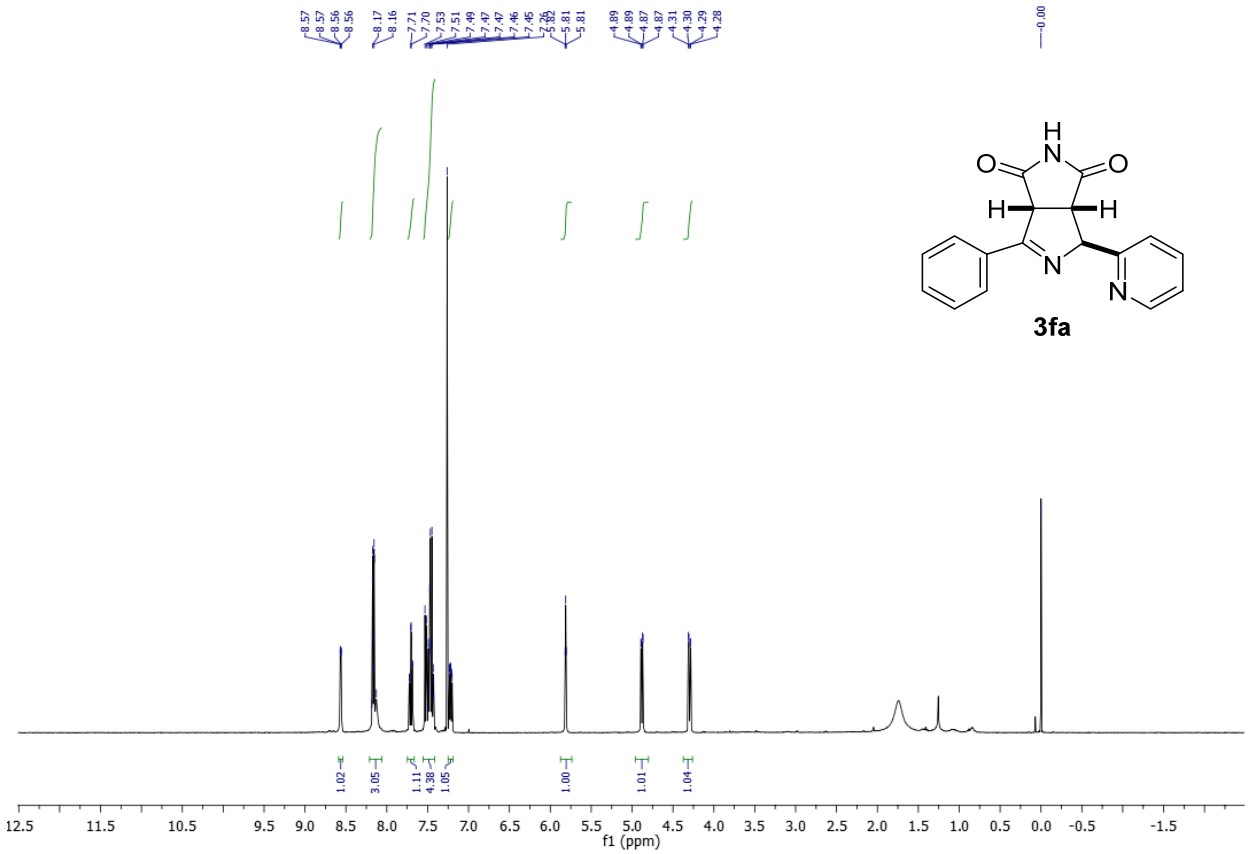

Bn
N
O
O
H
H
N
N
3ca
f1 (ppm)


Cy
O
N
O
H
H
N
N
3da
f1 (ppm)

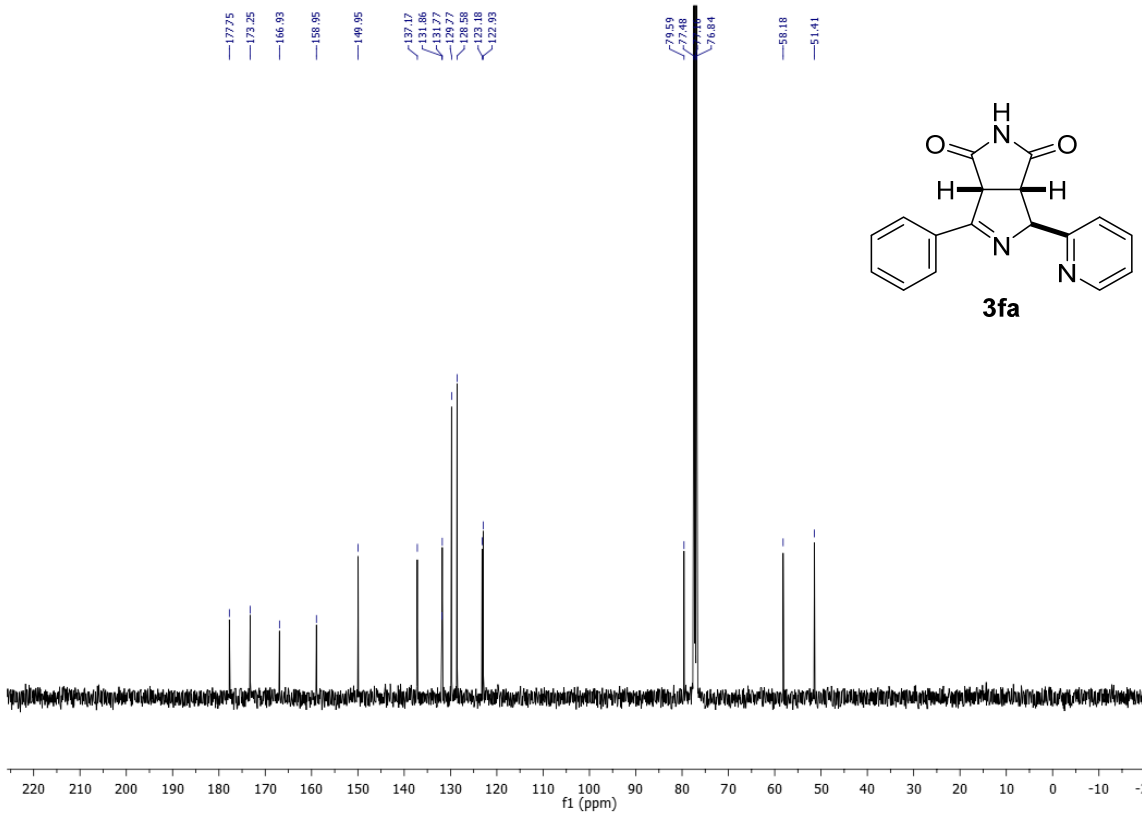

Cy
O
N
O
H
H
N
N
3da
f1 (ppm)


Ph
N
O
O
H
H
N
N
3ea
f1 (ppm)

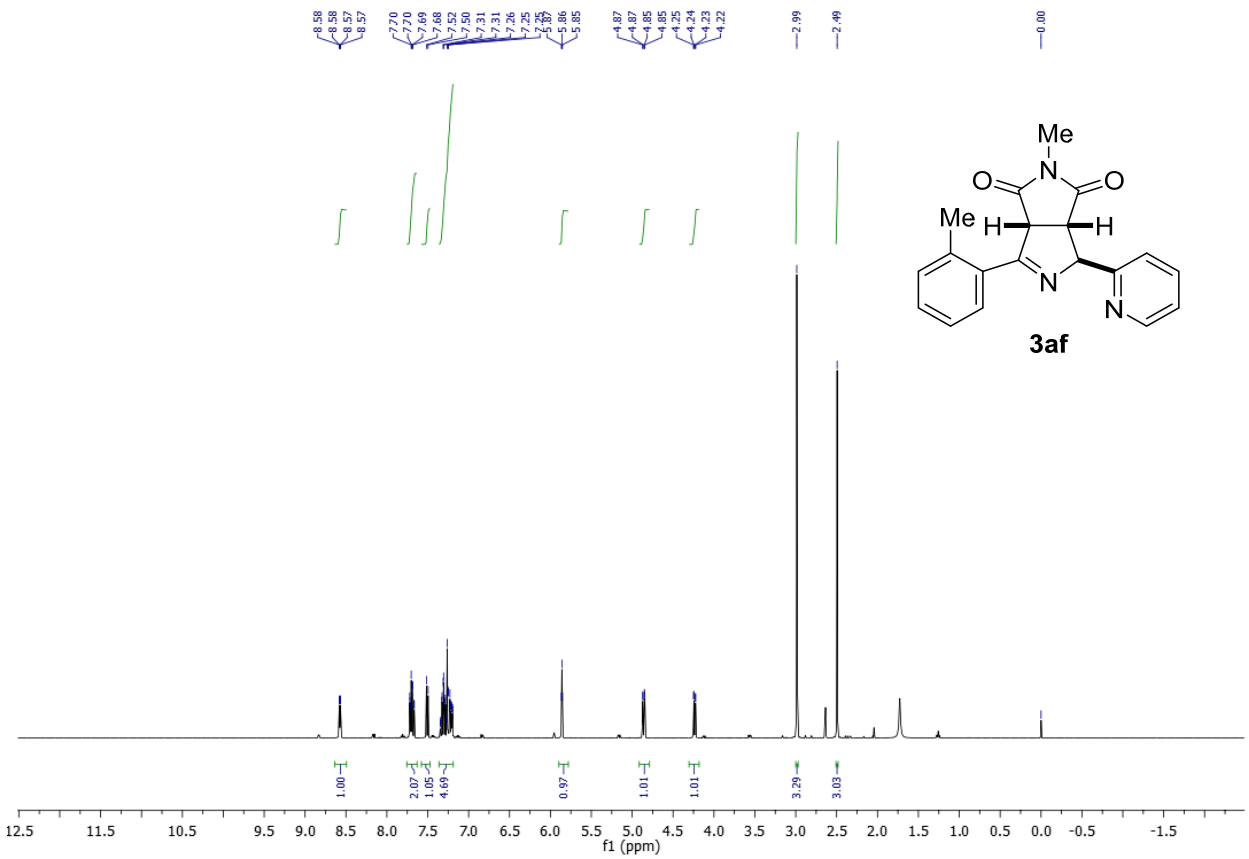

Ph
N
O
O
H
H
N
N
3ea
f1 (ppm)

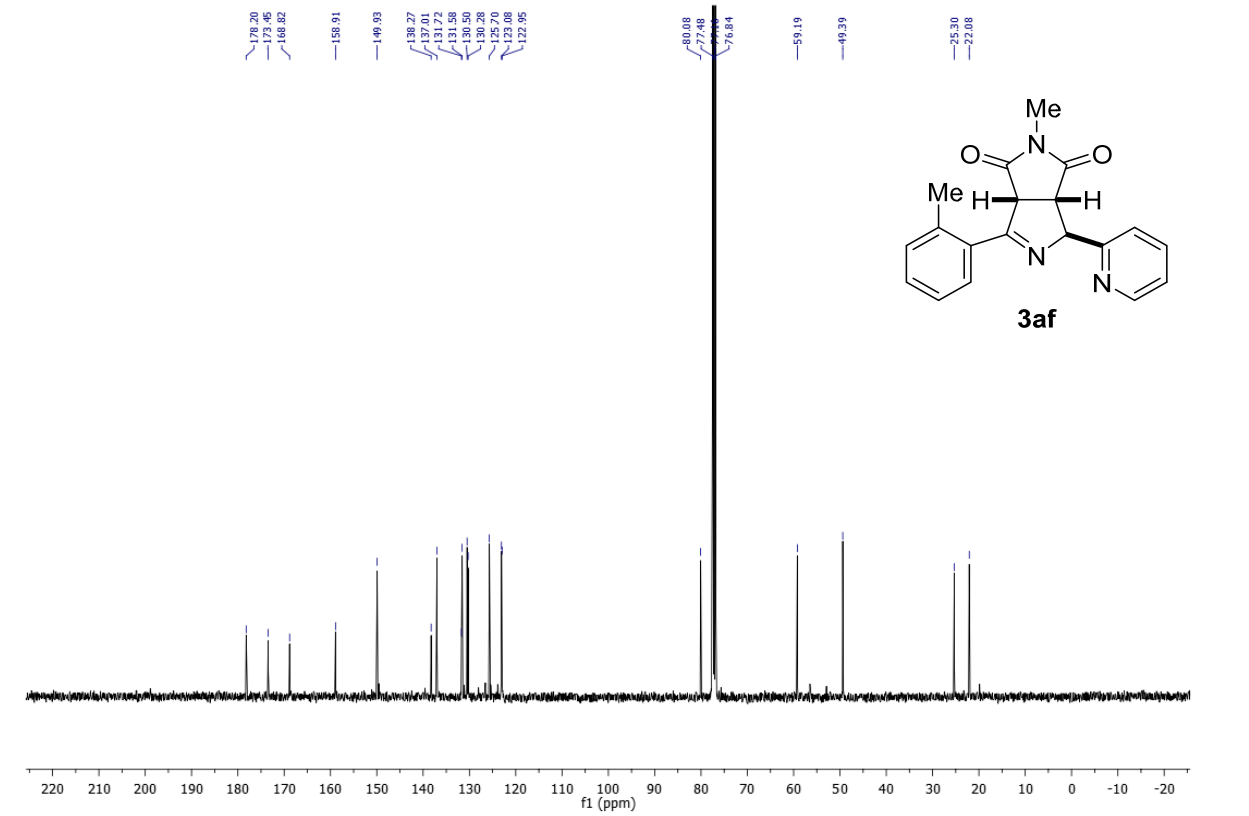


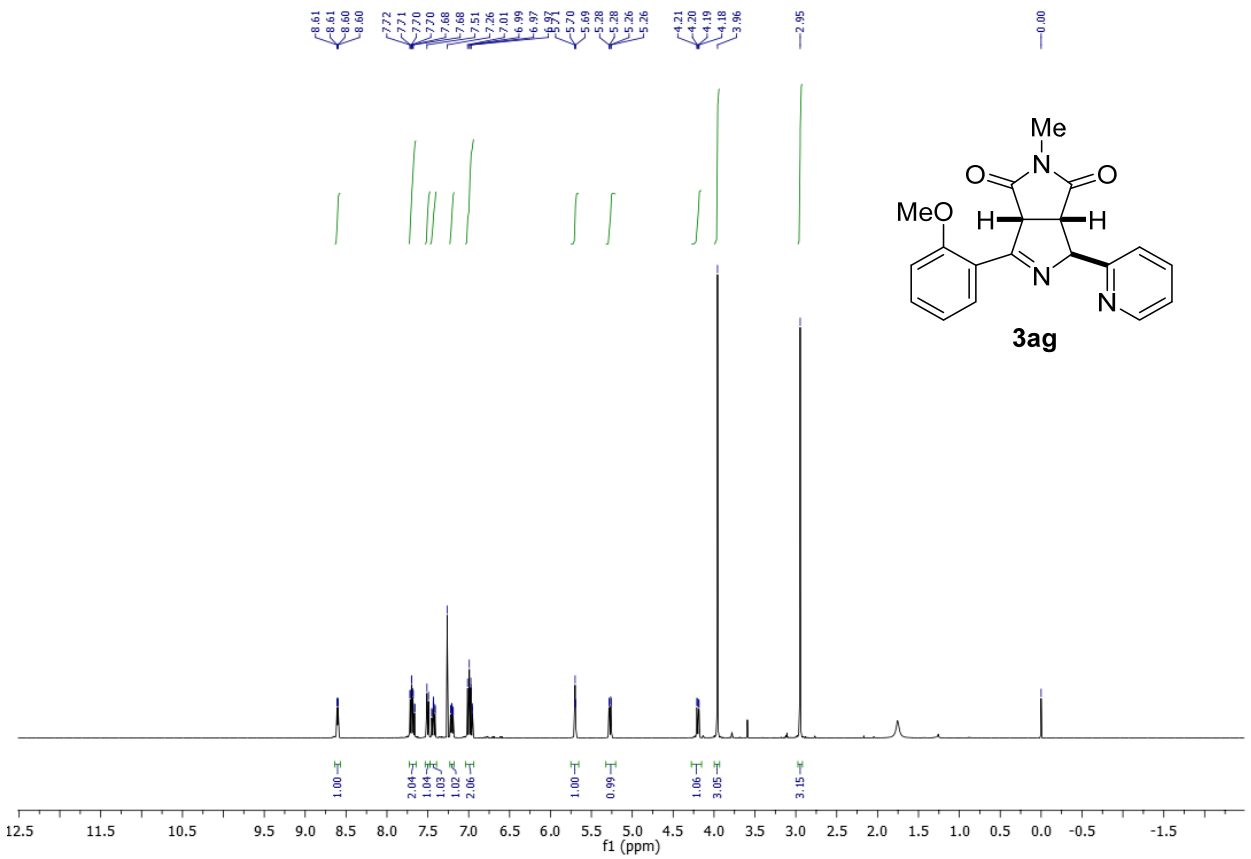
3fa

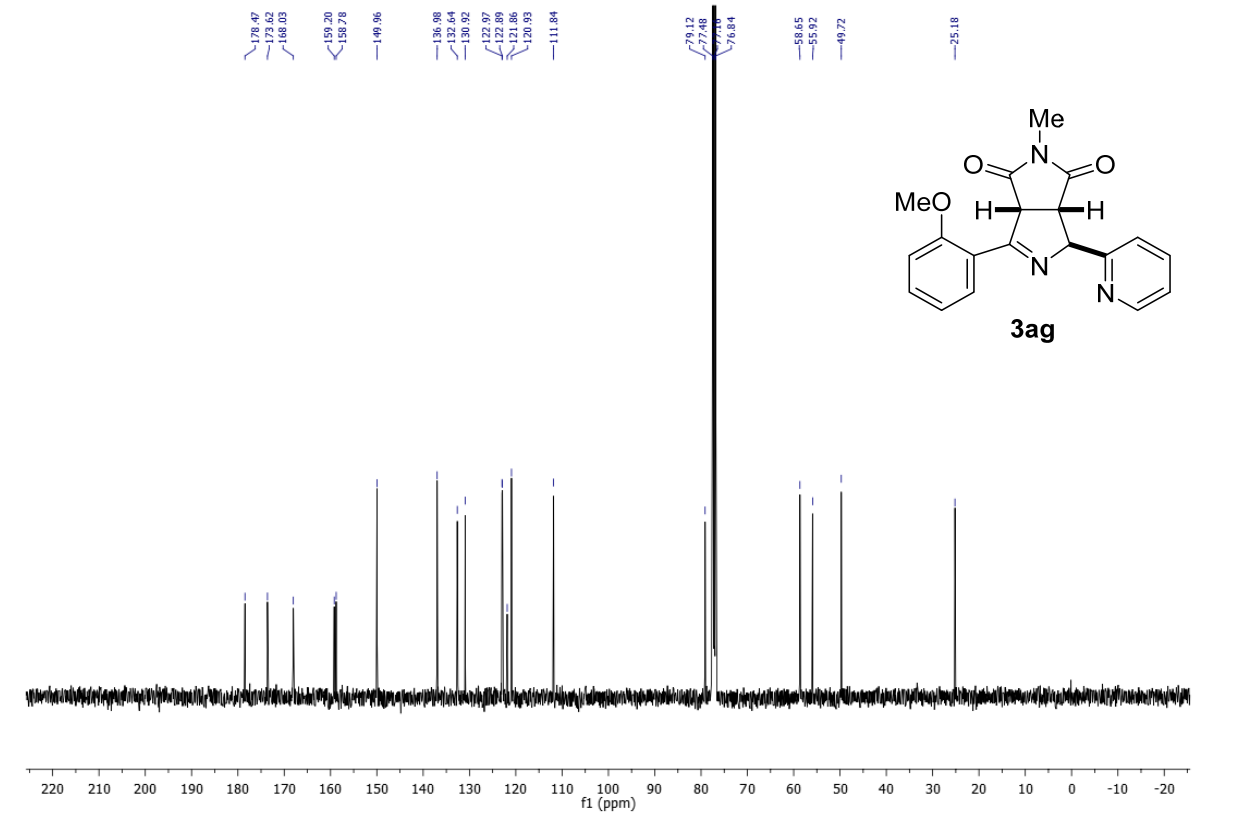


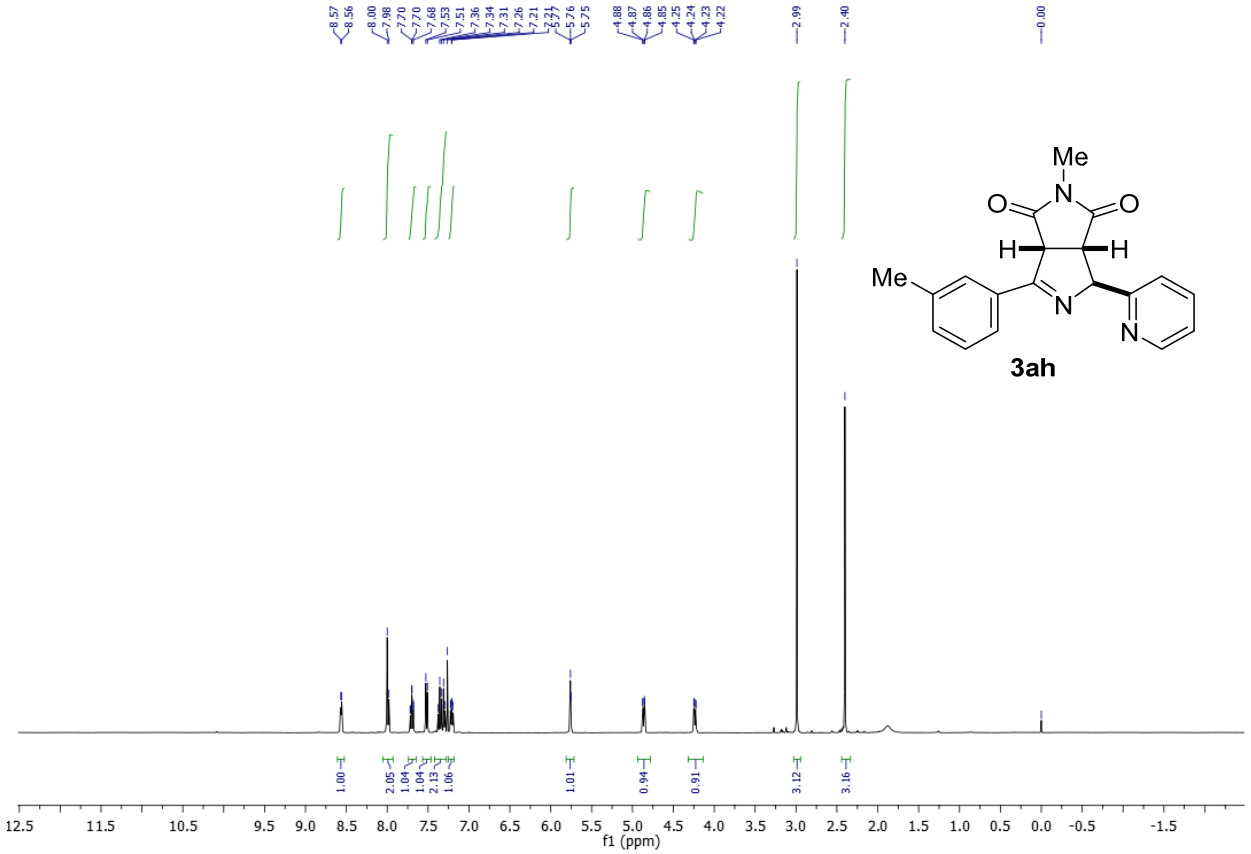
3fa


Me
O
N
O
Me
H
H
N
N
3af
f1 (ppm)


Me
O
N
O
Me
H
H
N
N
3af
f1 (ppm)


Me
N
O
O
MeO
H
H
N
N
3ag
f1 (ppm)


Me
N
O
O
MeO
H
H
N
N
3ag
f1 (ppm)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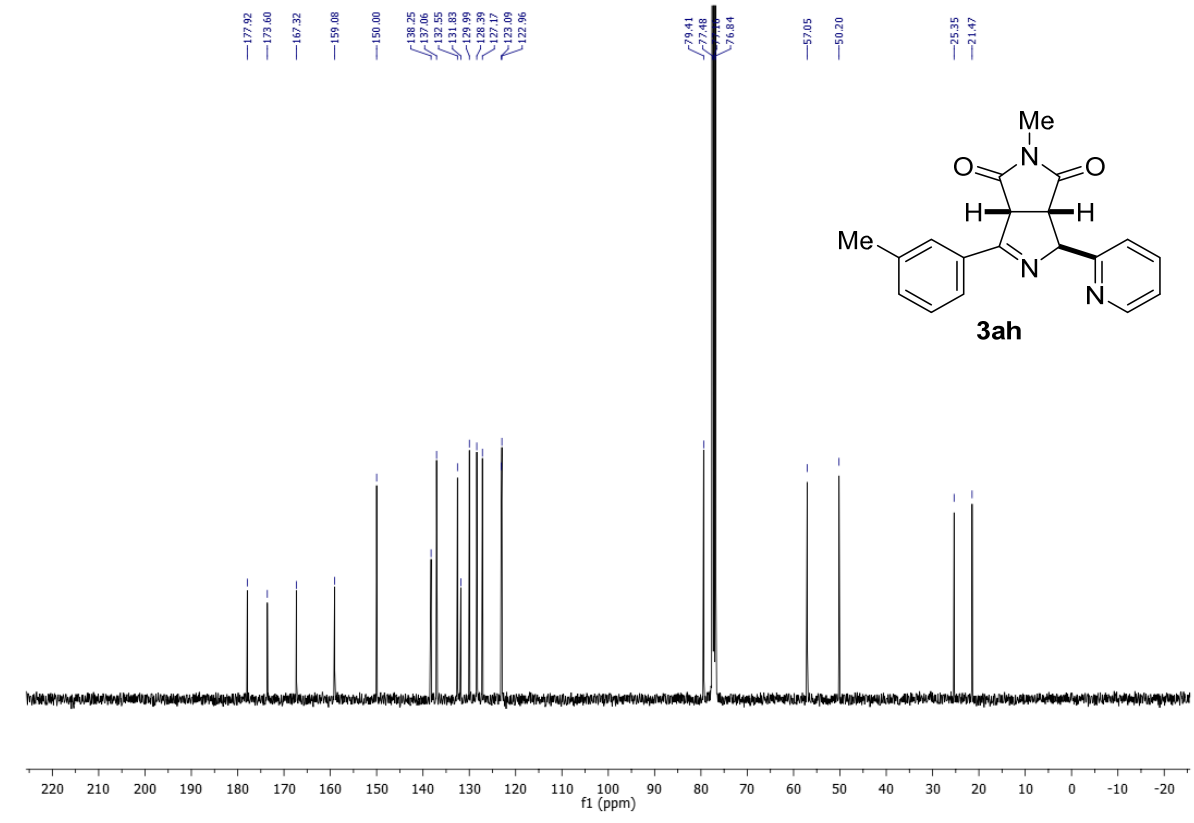
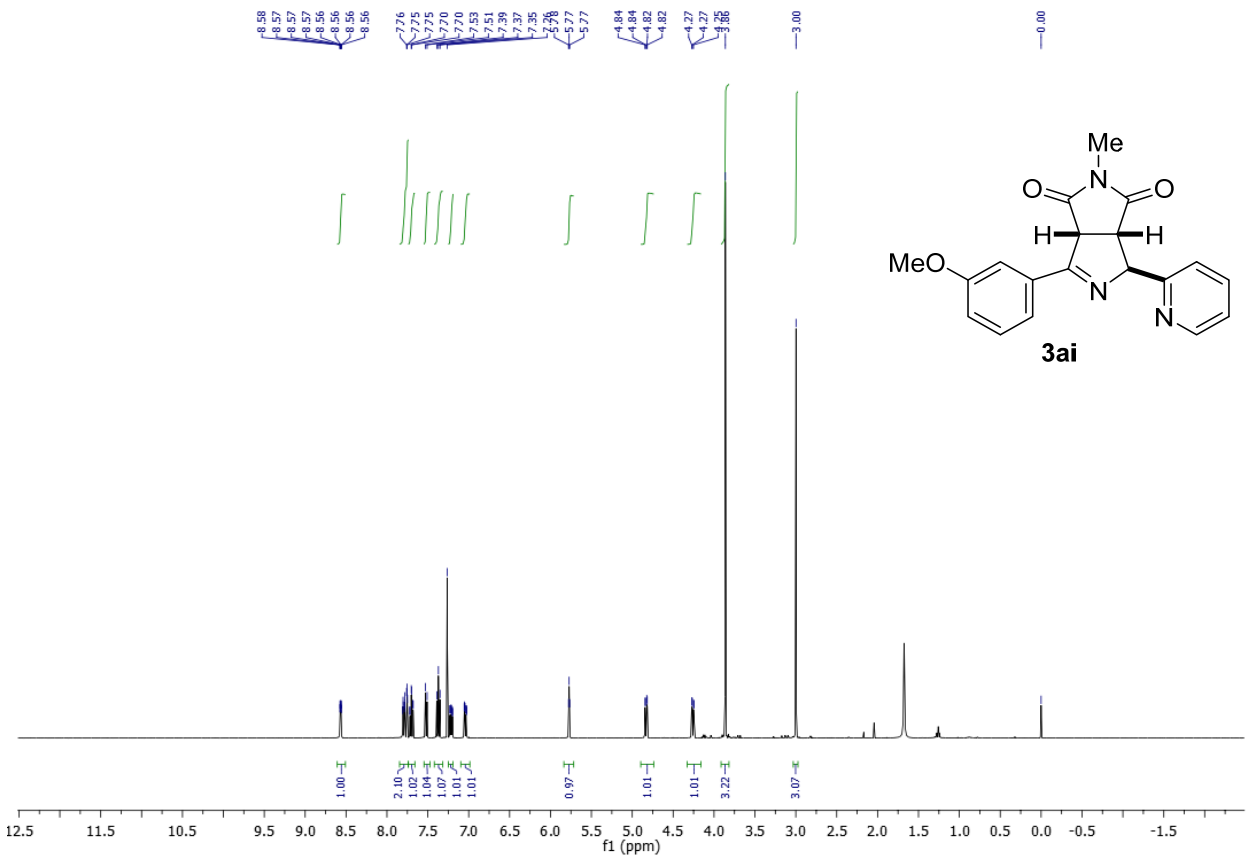
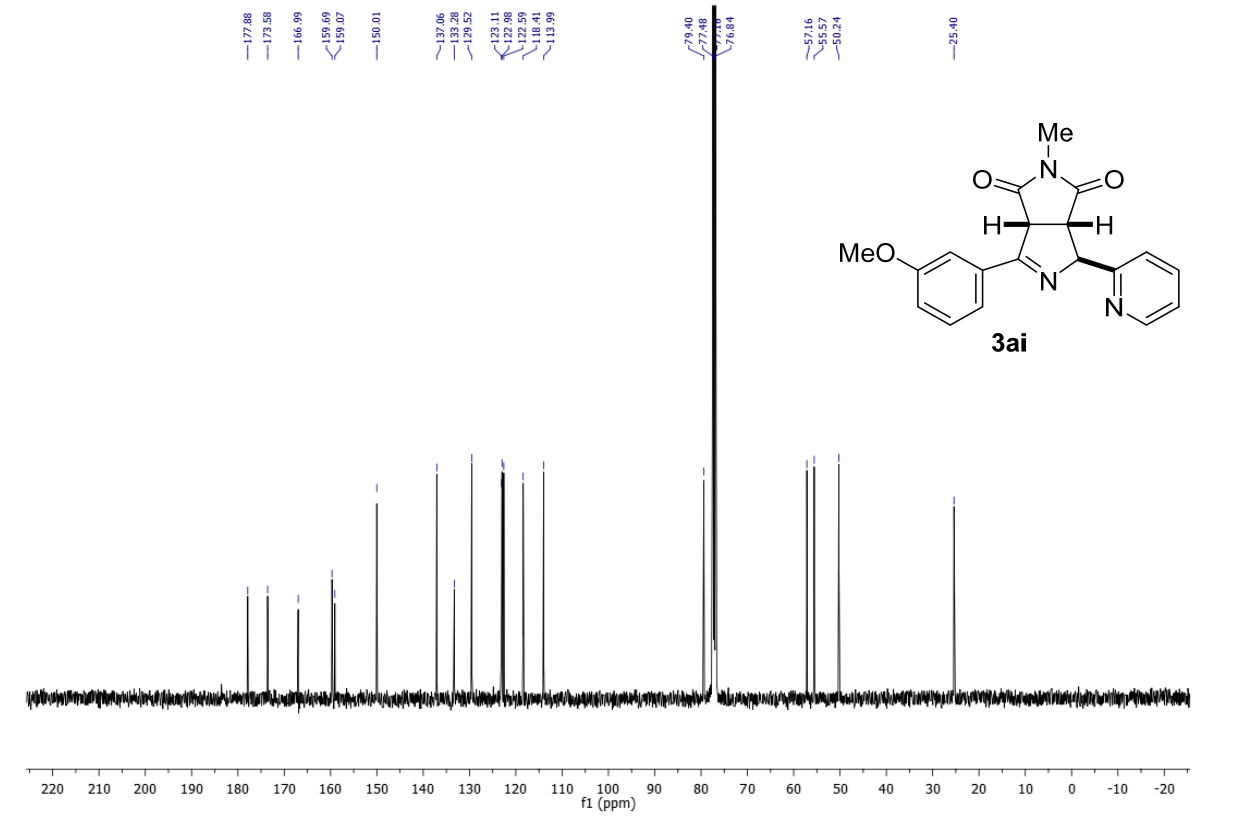
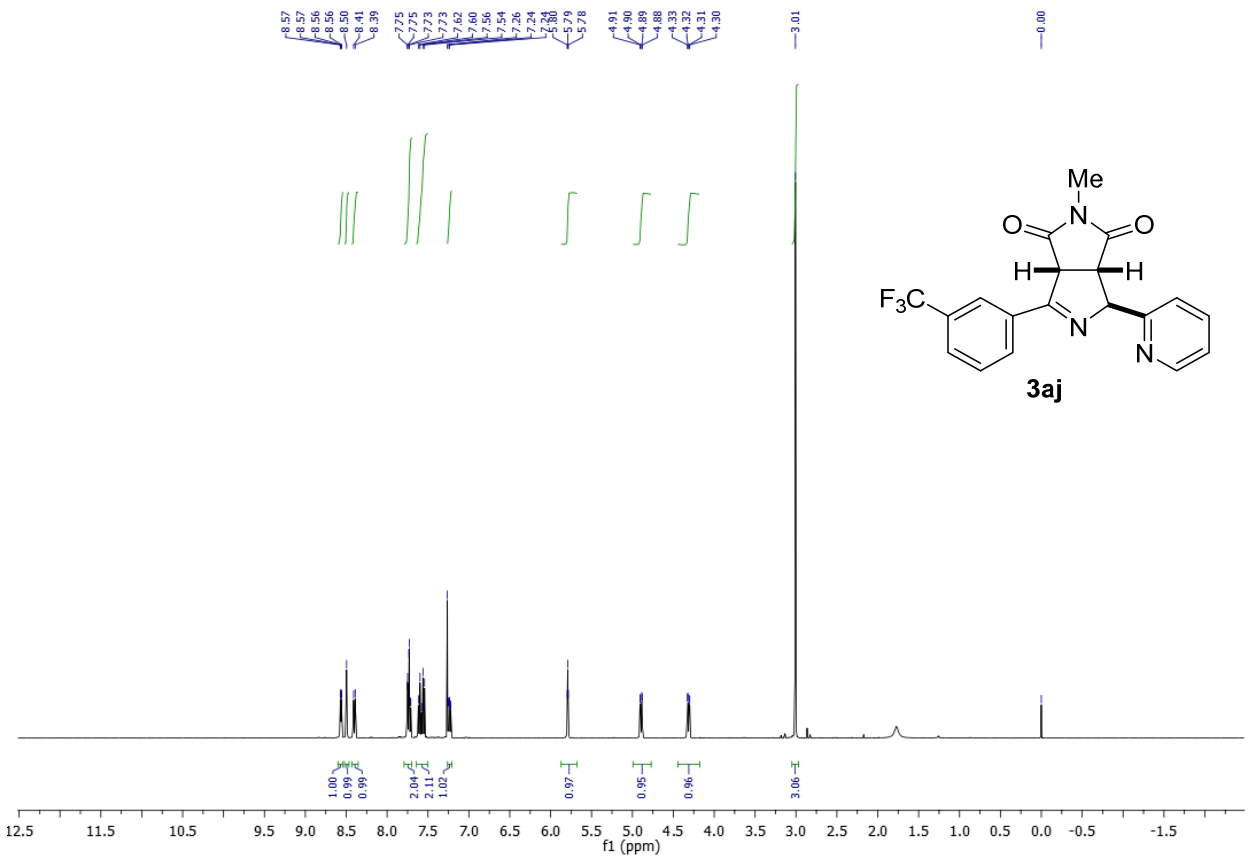
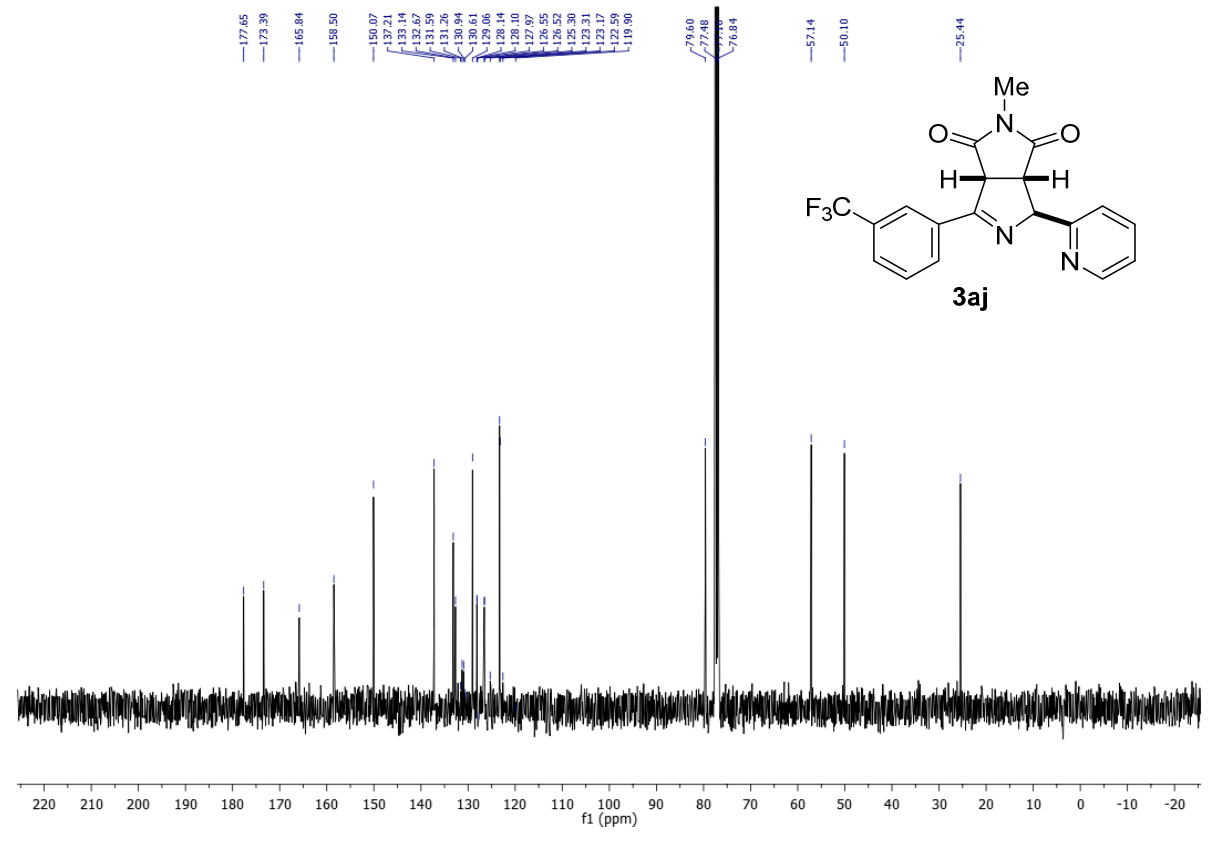
7.70
7.70
7.68
7.53
7.51
7.36
7.34
7.31
7.26
7.21
5.77
5.76
5.75
4.88
4.87
4.86
4.85
4.25
4.24
4.23
4.22
2.99
2.40
0.00
1.00
2.05
1.04
1.04
2.13
1.06
1.01
0.94
0.91
3.12
3.16
f1 (ppm)
Me
N
O
O
H
H
Me
N
N
3ah

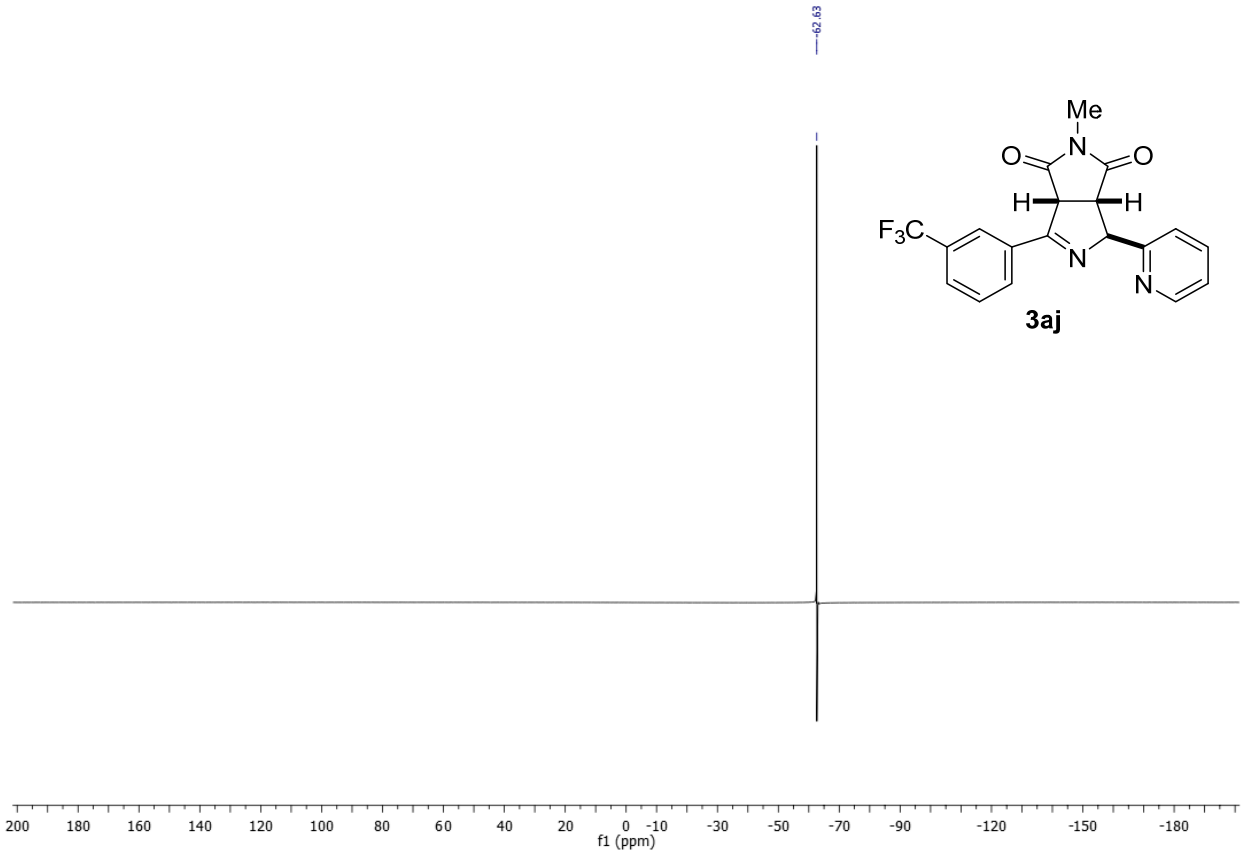

177.92
173.60
167.32
159.08
150.00
138.25
137.06
132.55
131.83
129.99
128.39
127.17
123.09
122.96
79.41
77.48
76.84
57.05
50.20
25.35
21.47
f1 (ppm)
Me
N
O
O
H
H
Me
N
N
3ah

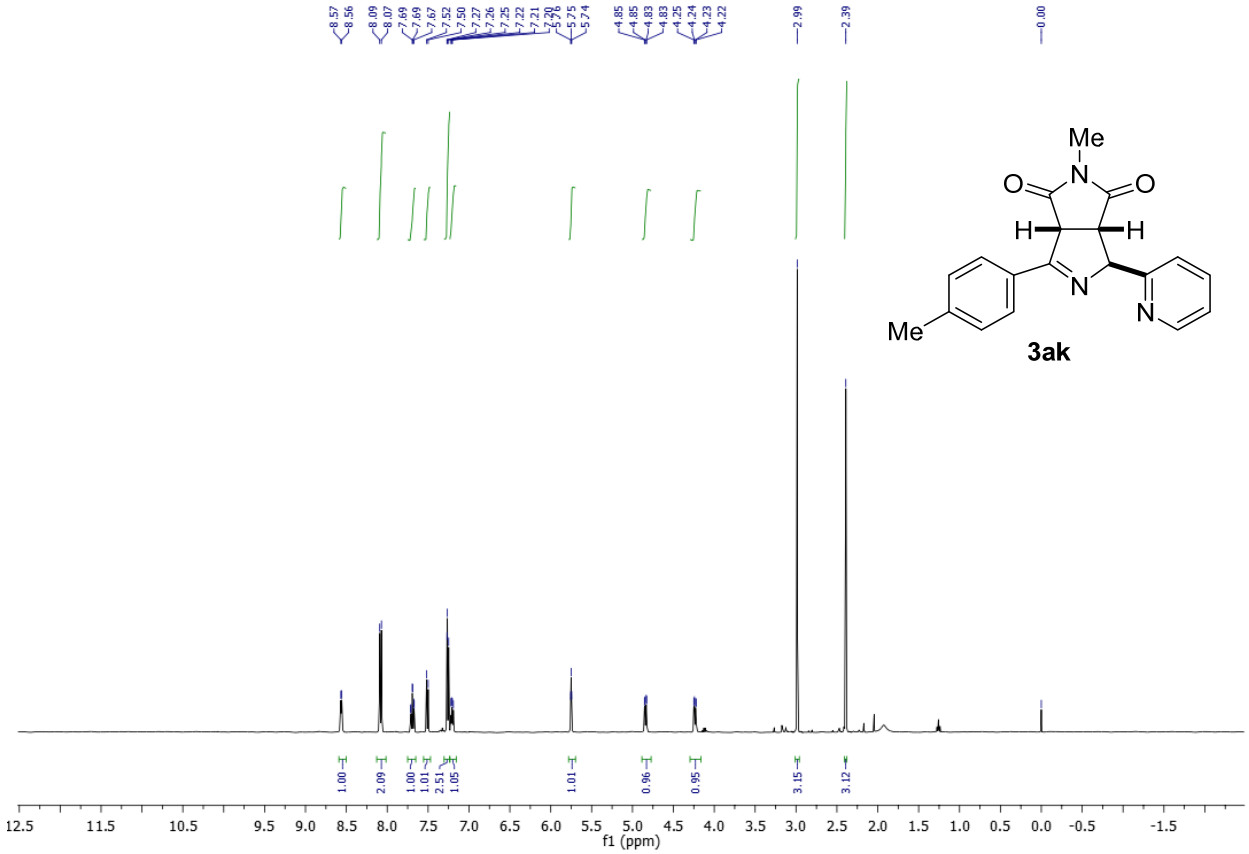

Me
O
N
O
H
H
MeO
N
N
3ai
f1 (ppm)

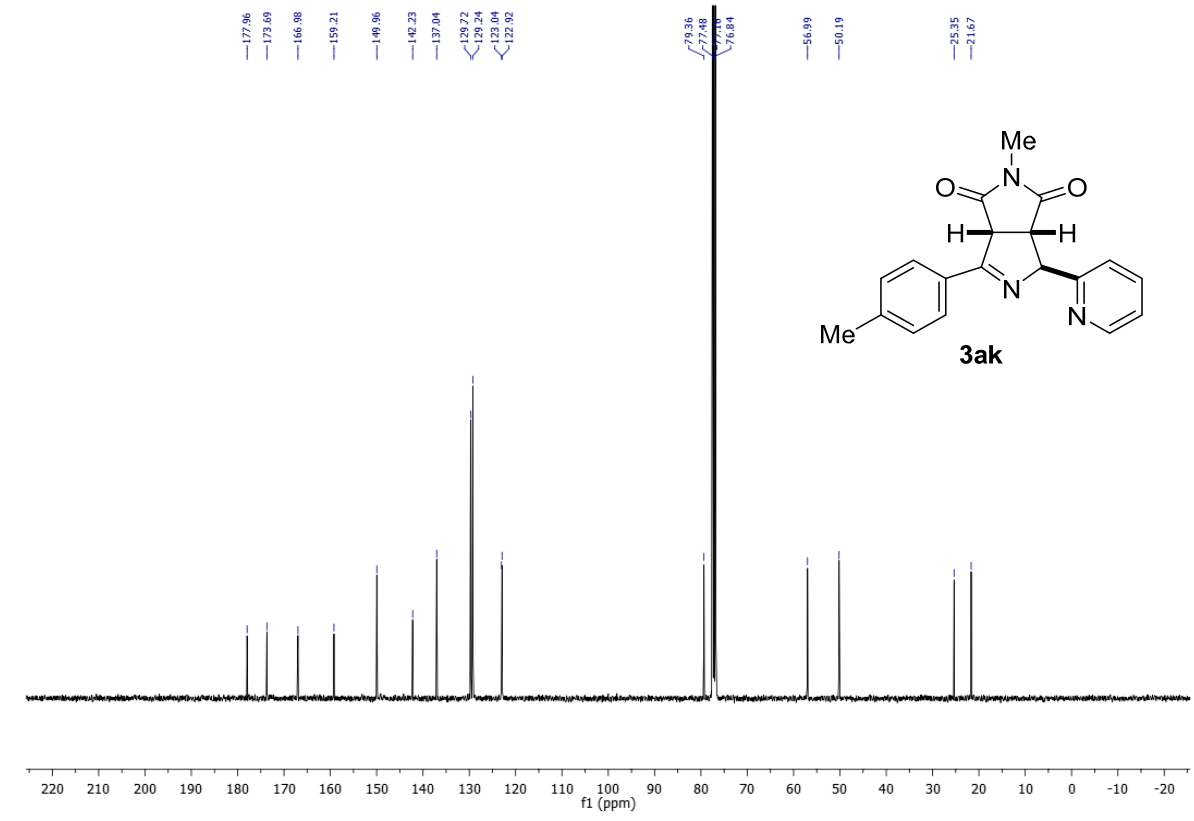

Me
O
N
O
H
H
MeO
N
N
3ai
f1 (ppm)

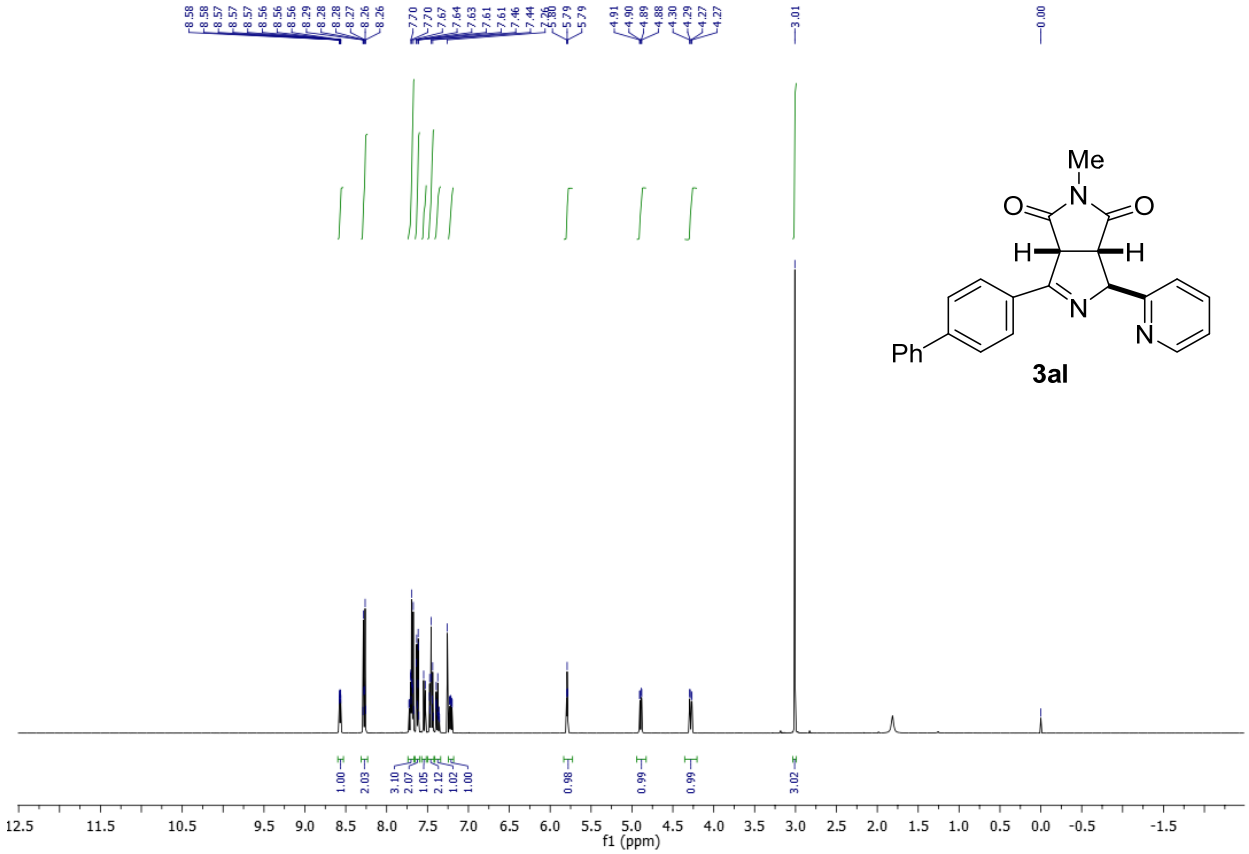

Me
N
O
O
H
H
F3C
N
N
3aj
f1 (ppm)

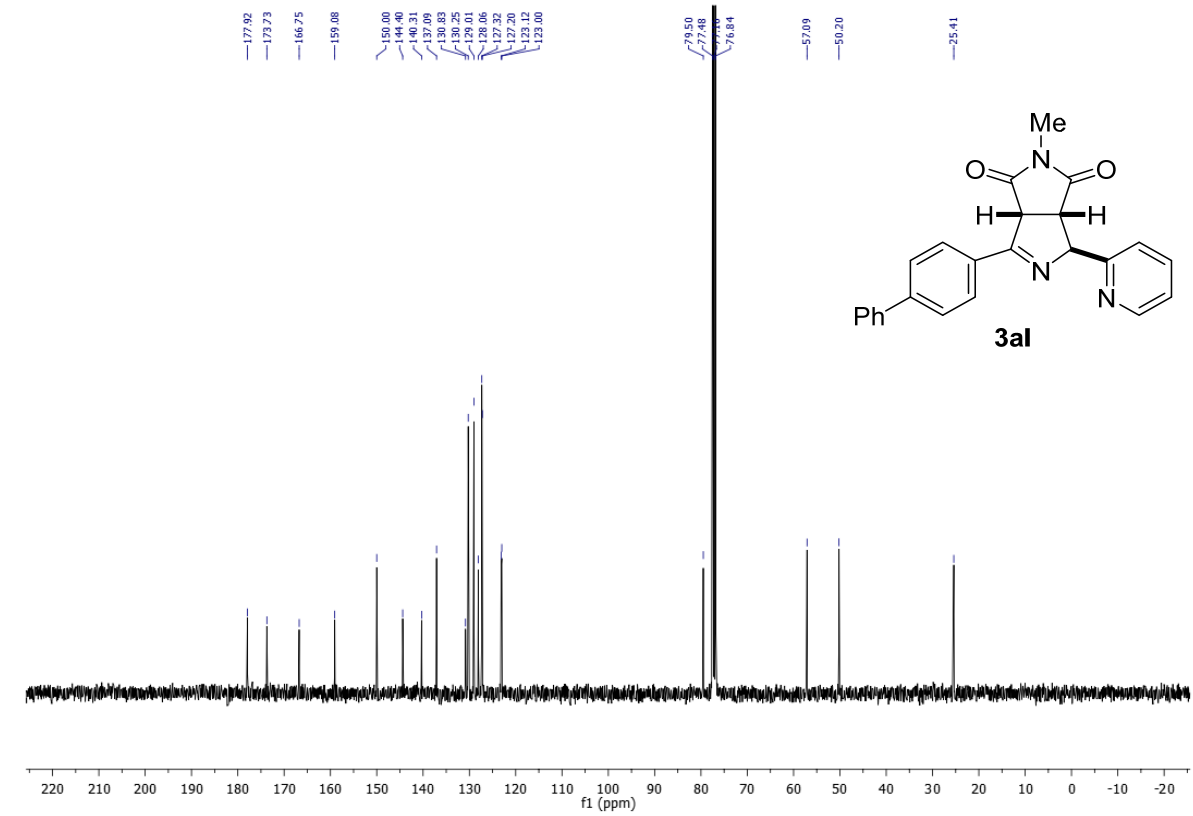

Me
N
O
O
H
H
F3C
N
N
3aj
f1 (ppm)

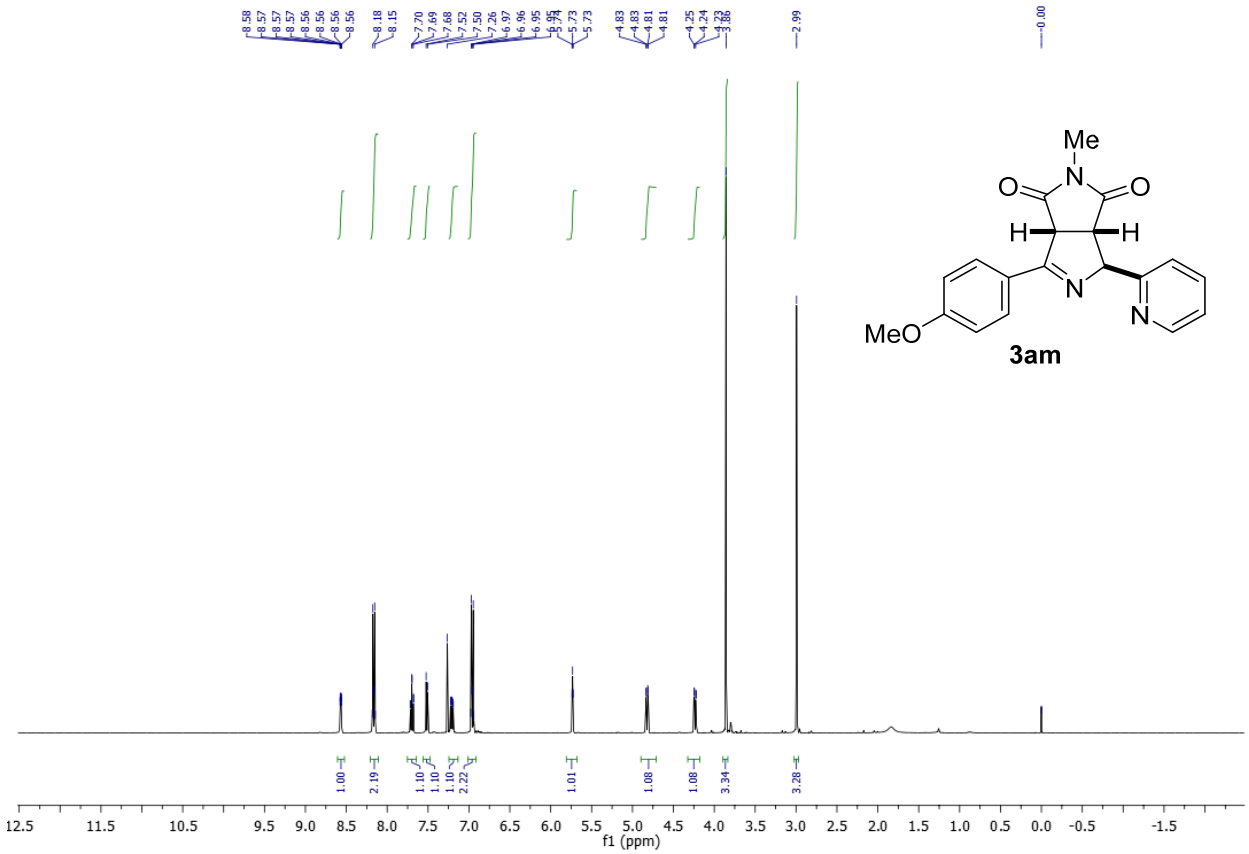

-62.63
Me
N
O
O
H
H
F3C
N
N
3aj
200
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180
f1 (ppm)

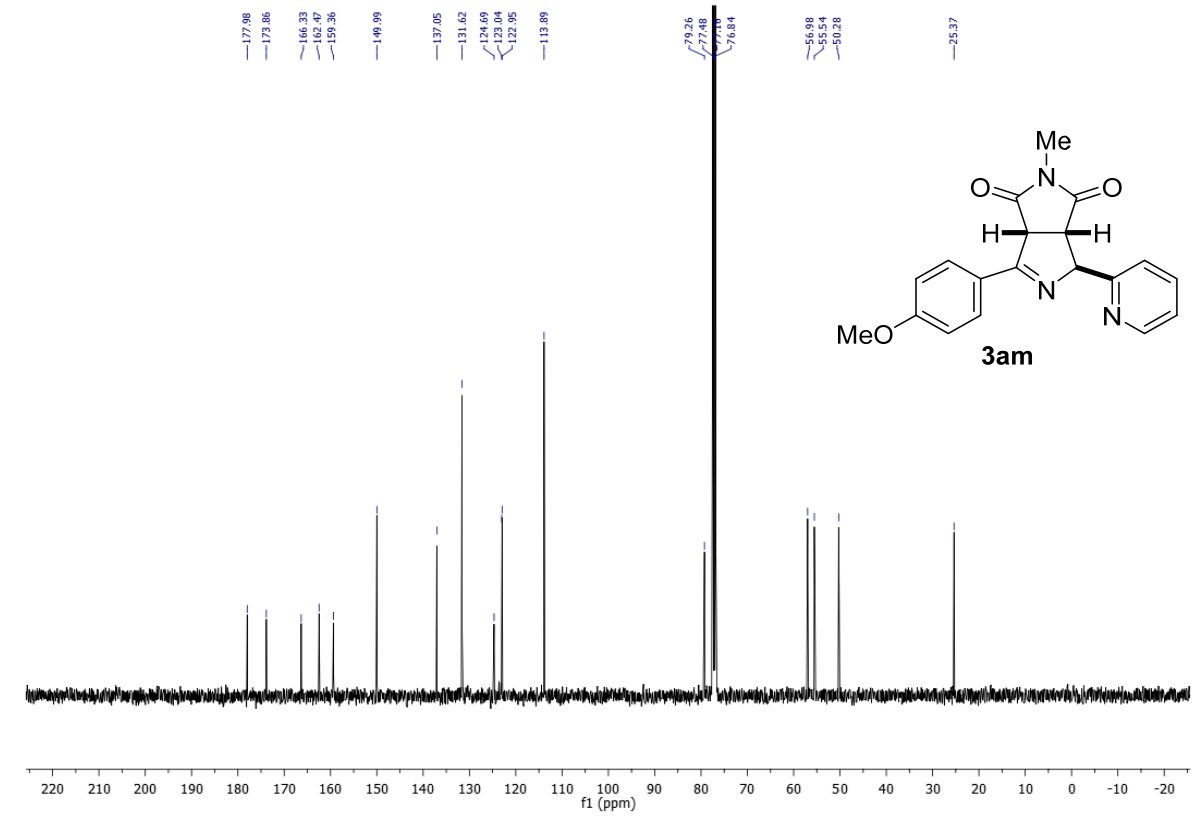

8.57
8.56
8.09
8.07
7.69
7.69
7.67
7.67
7.52
7.50
7.27
7.26
7.25
7.22
7.21
5.76
5.75
5.74
4.85
4.85
4.83
4.83
4.25
4.24
4.23
4.22
2.99
2.39
0.00
1.00
2.09
1.00
1.01
2.51
1.05
1.01
0.96
0.95
3.15
3.12
f1 (ppm)
Me
O
N
O
H
H
N
N
Me
3ak

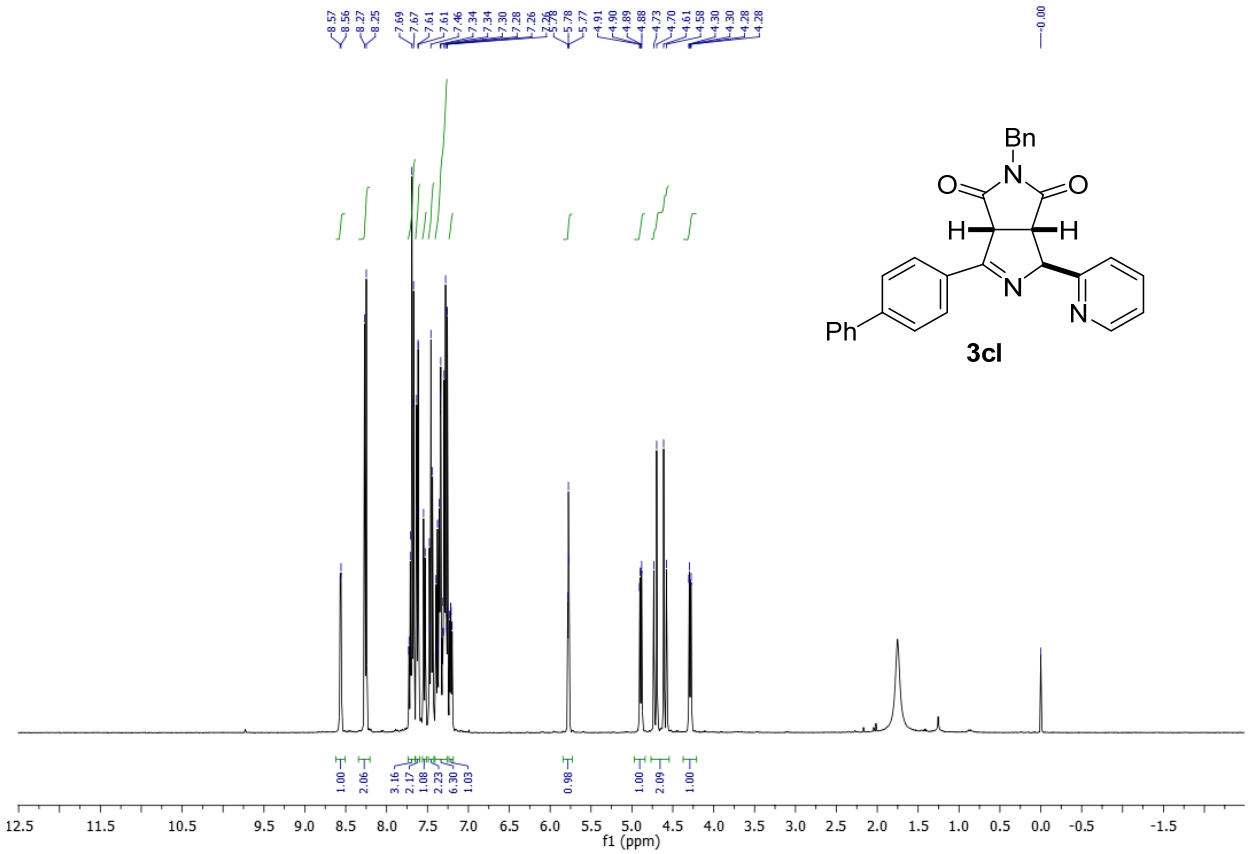

177.96
173.69
166.98
159.21
149.96
142.23
137.04
129.72
129.24
123.04
122.92
79.36
77.48
76.84
56.99
50.19
25.35
21.67
f1 (ppm)
Me
O
N
O
H
H
N
N
Me
3ak

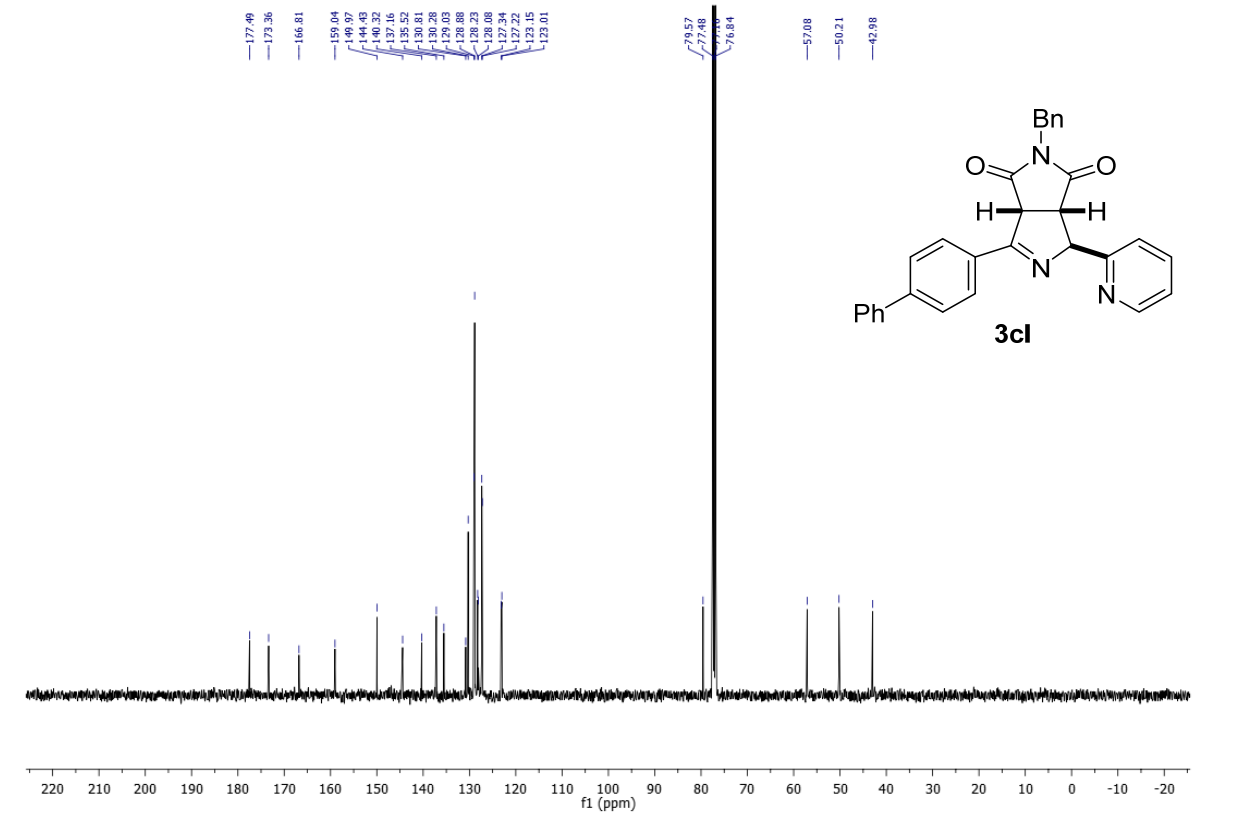

Me
N
O
O
H
H
N
N
Ph
3al
f1 (ppm)

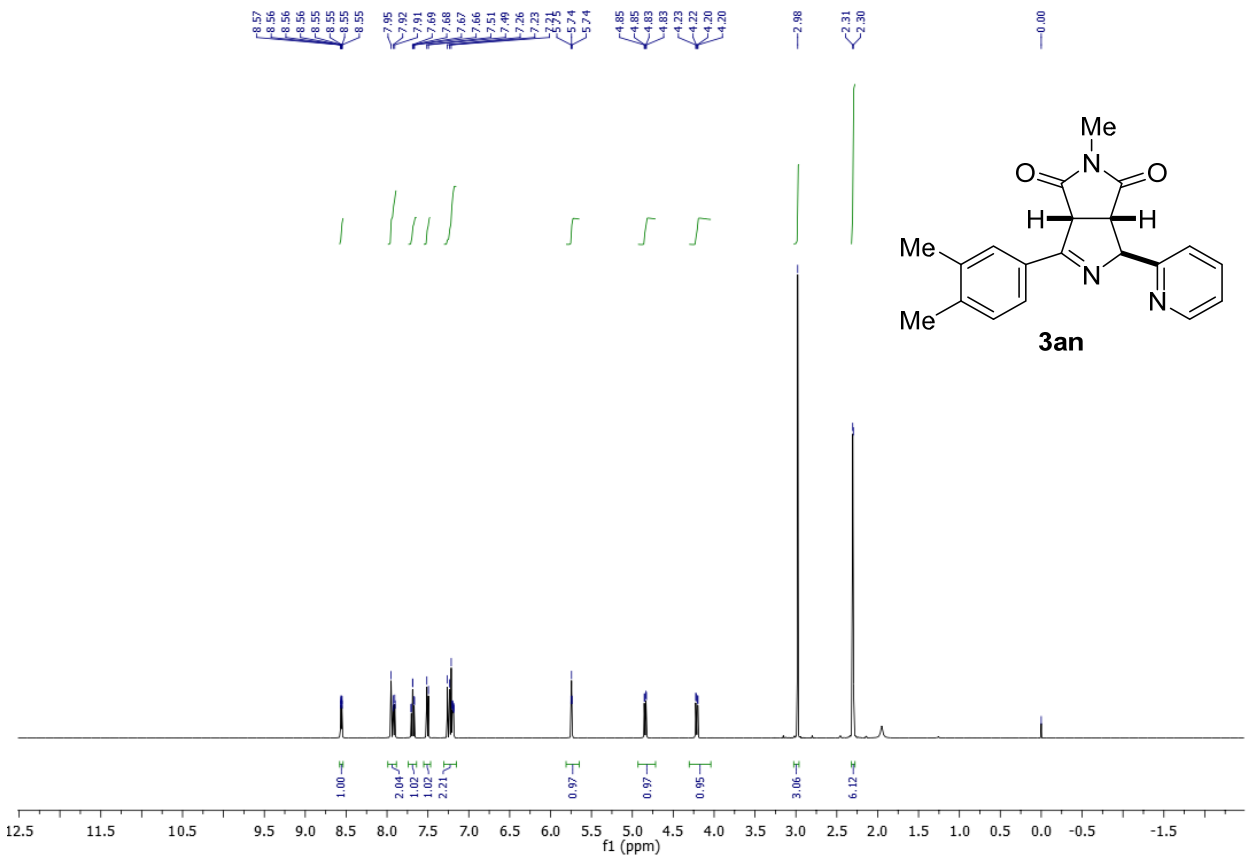

Me
N
O
O
H
H
N
N
Ph
3al
f1 (ppm)

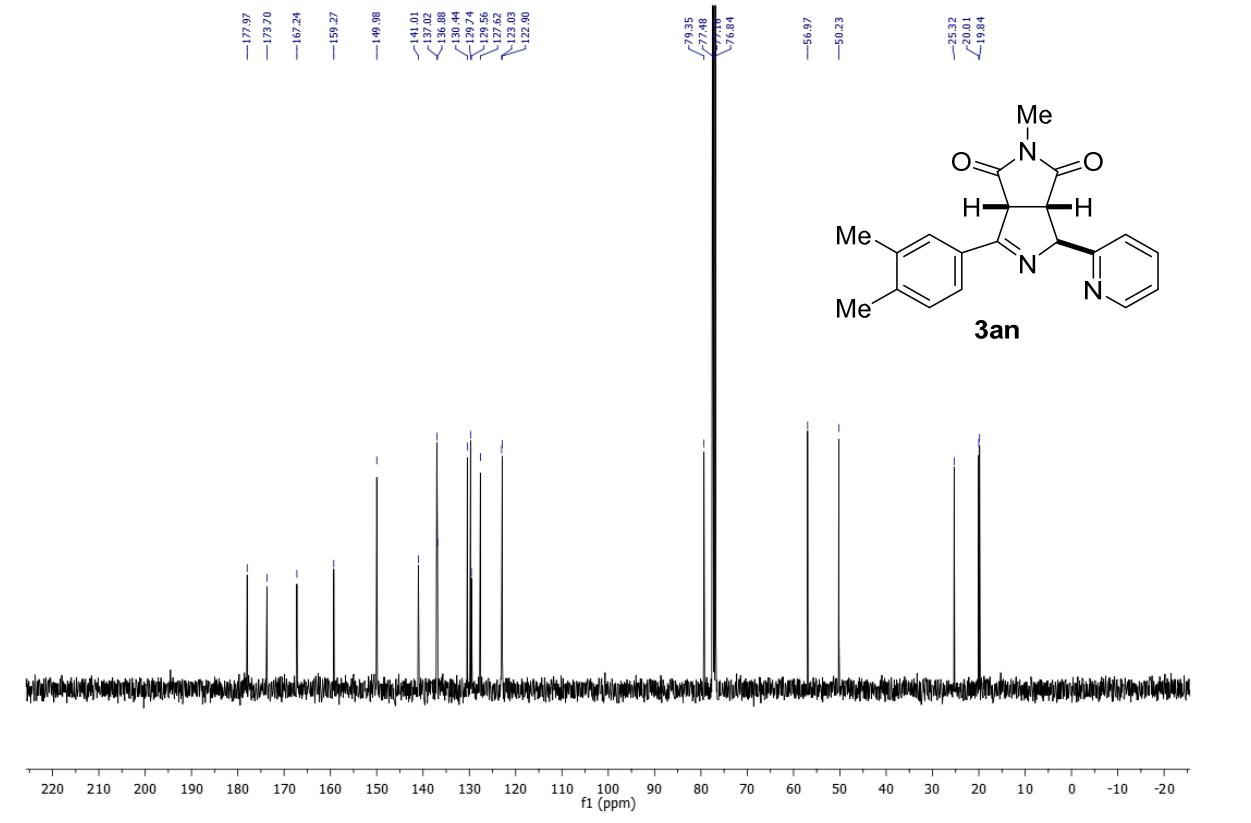

Me
N
O
O
H
H
N
N
MeO
3am
f1 (ppm)

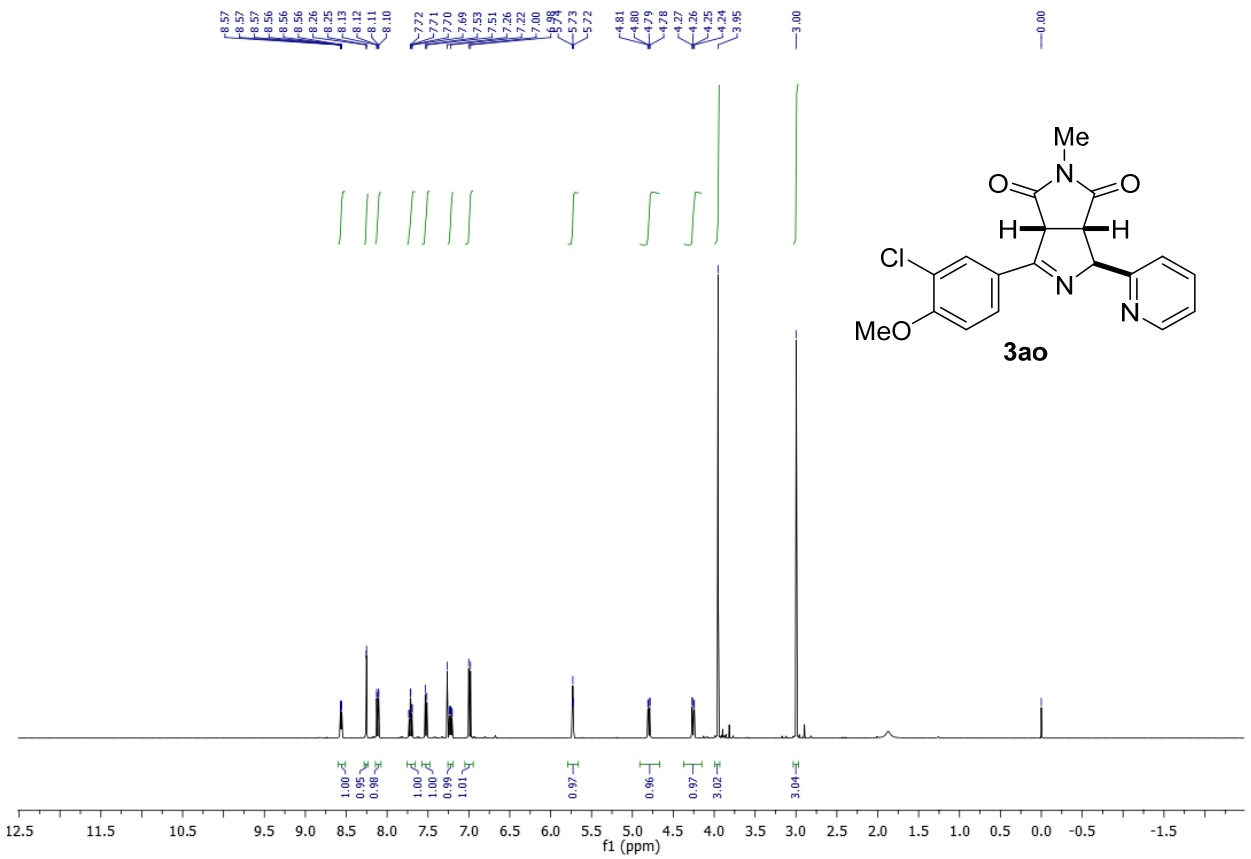

Me
N
O
O
H
H
N
N
MeO
3am
f1 (ppm)

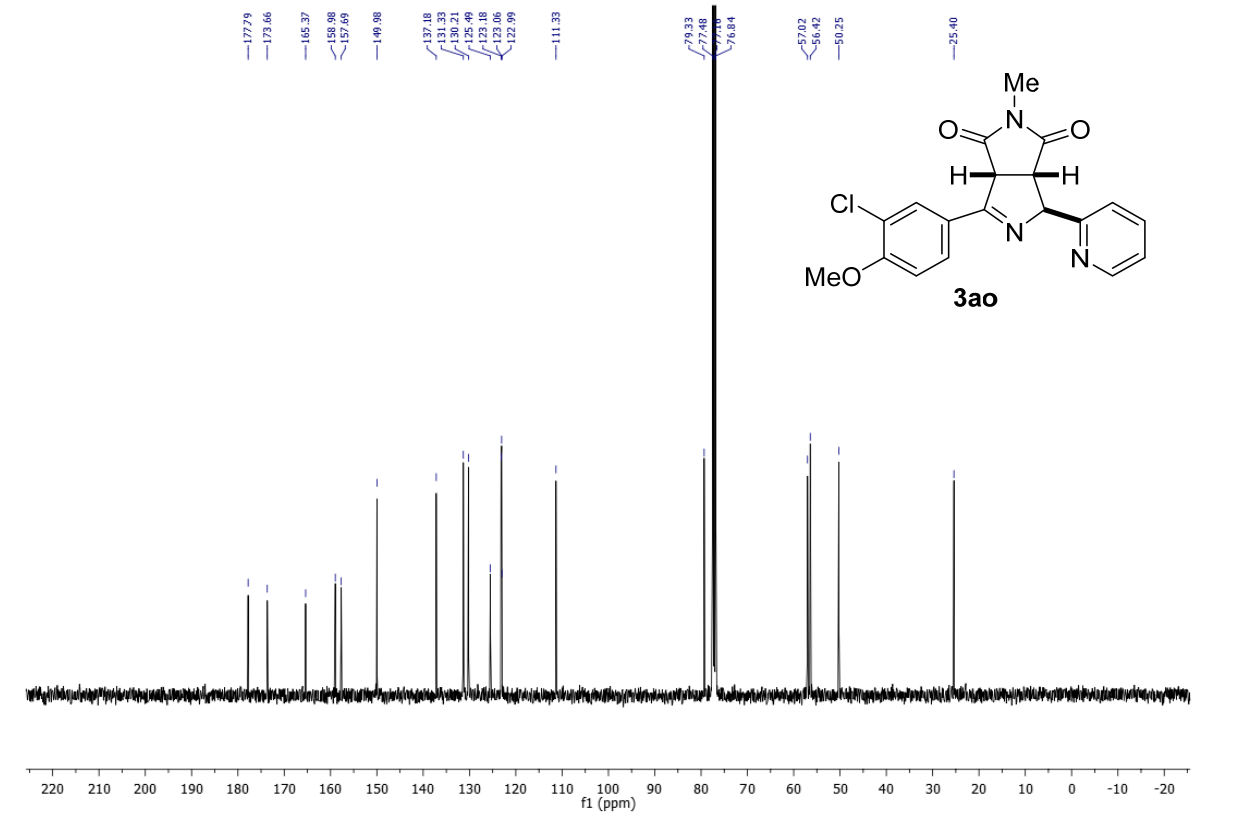

Bn
O
N
O
H
H
N
N
Ph
3cl
f1 (ppm)

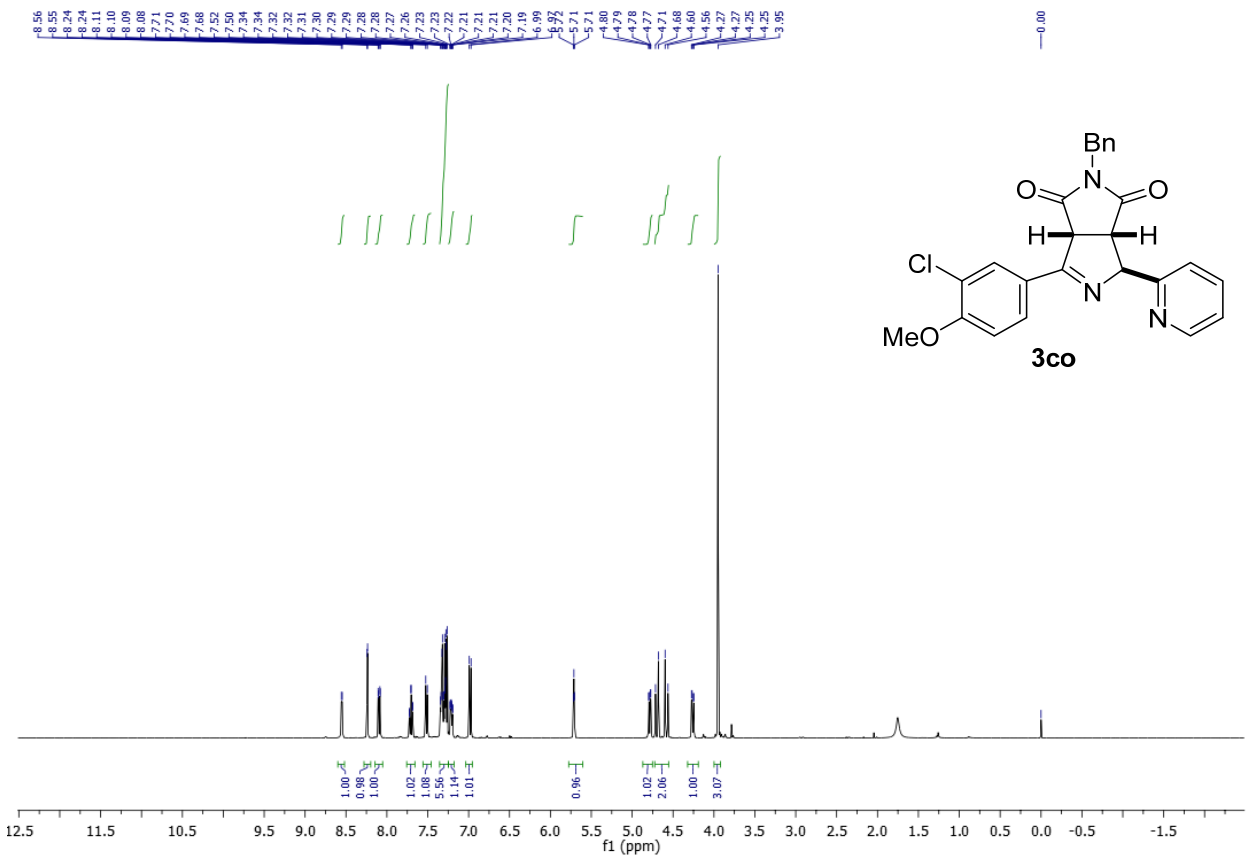

Bn
O
N
O
H
H
N
N
Ph
3cl
f1 (ppm)

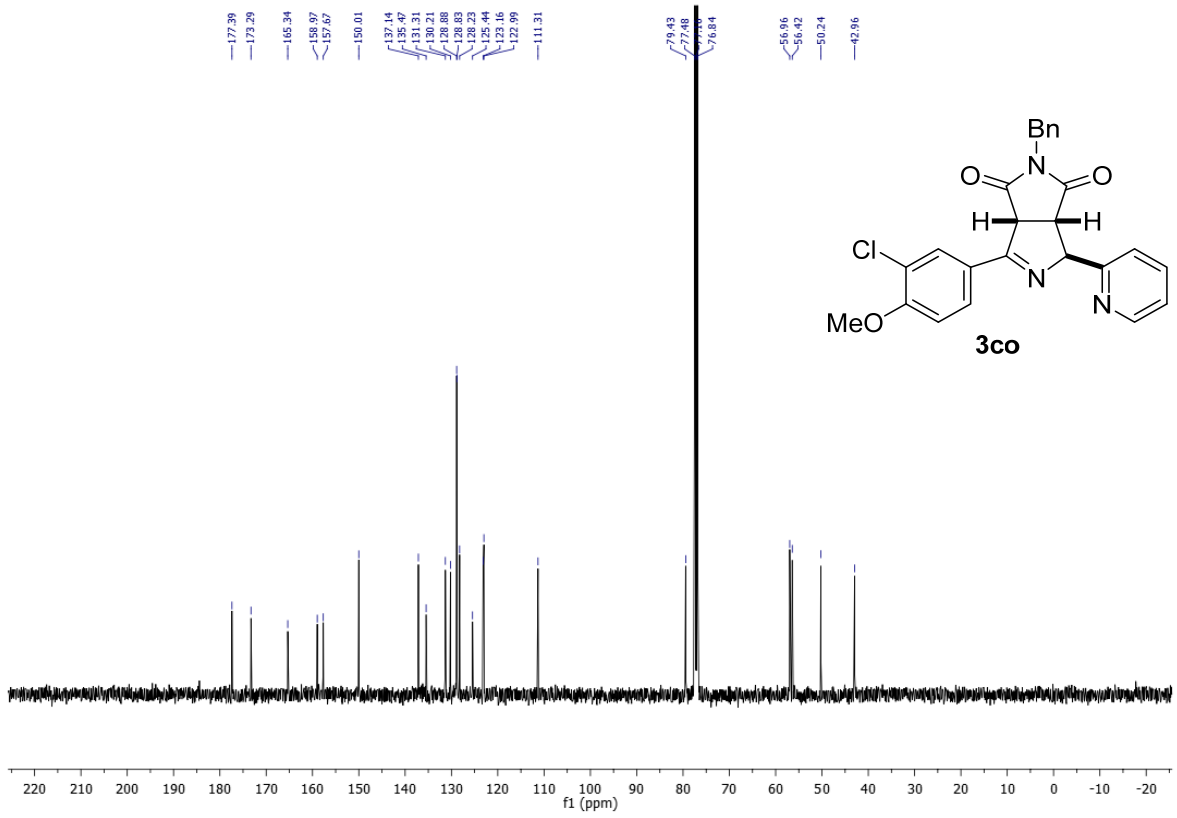

Me
N
O
O
H
H
Me
Me
N
N
3an
f1 (ppm)

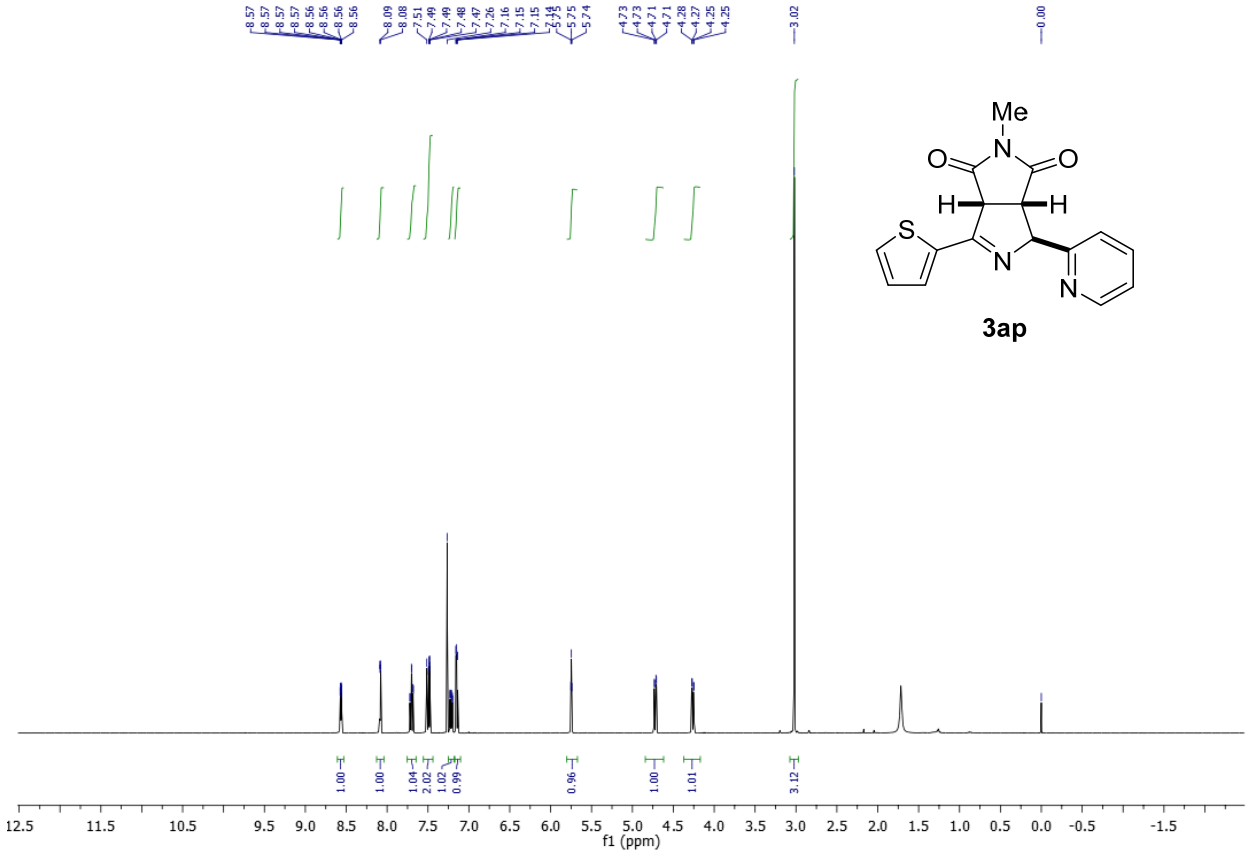

Me
N
O
O
H
H
Me
Me
N
N
3an
f1 (ppm)

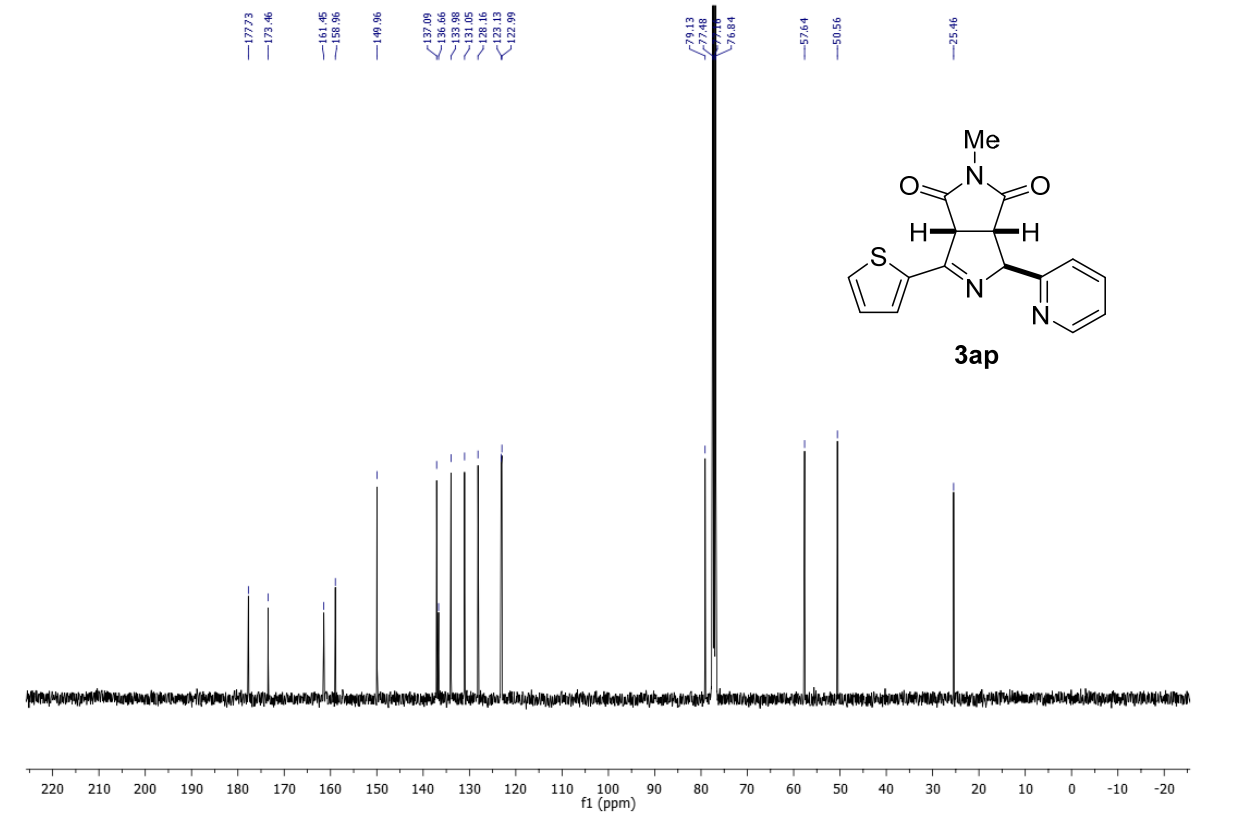

Me
N
O
O
H
H
Cl
N
N
MeO
3ao
f1 (ppm)

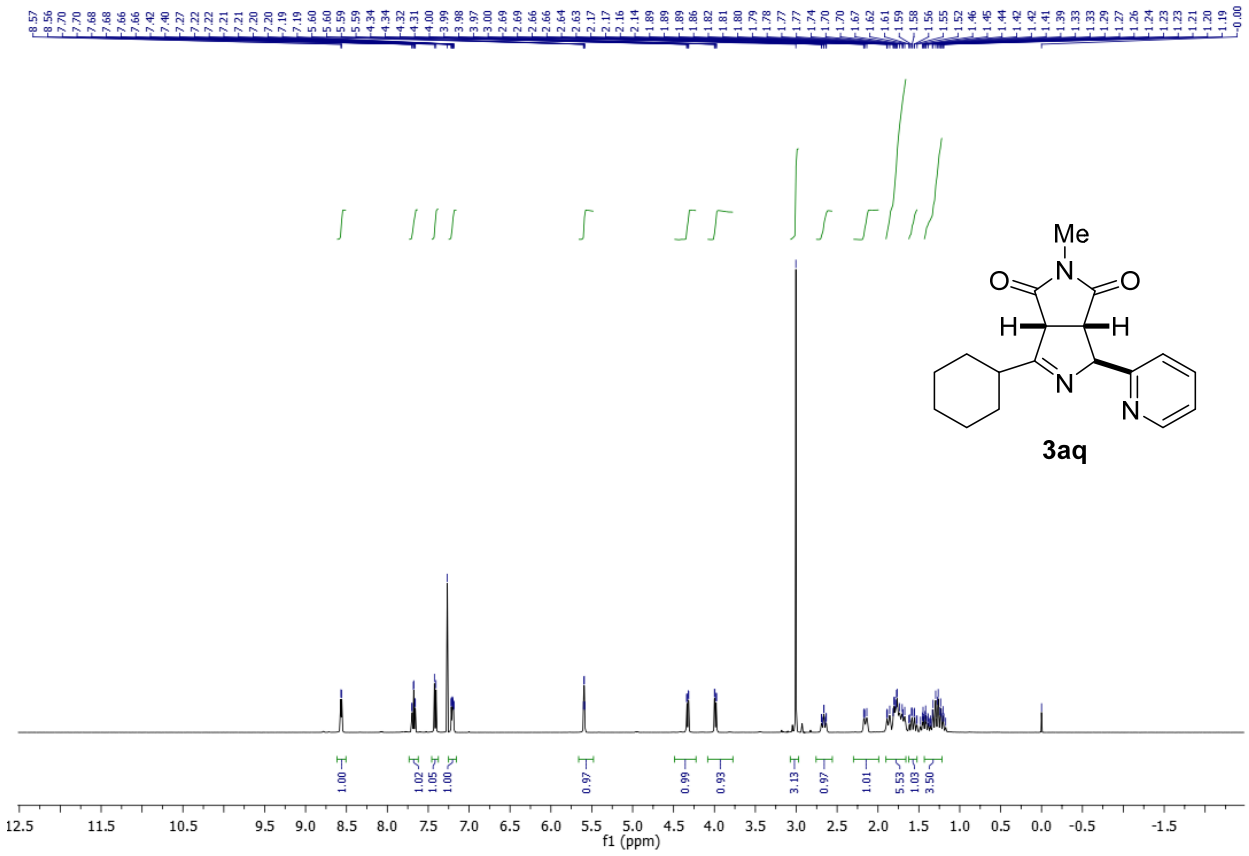

Me
N
O
O
H
H
Cl
N
N
MeO
3ao
f1 (ppm)

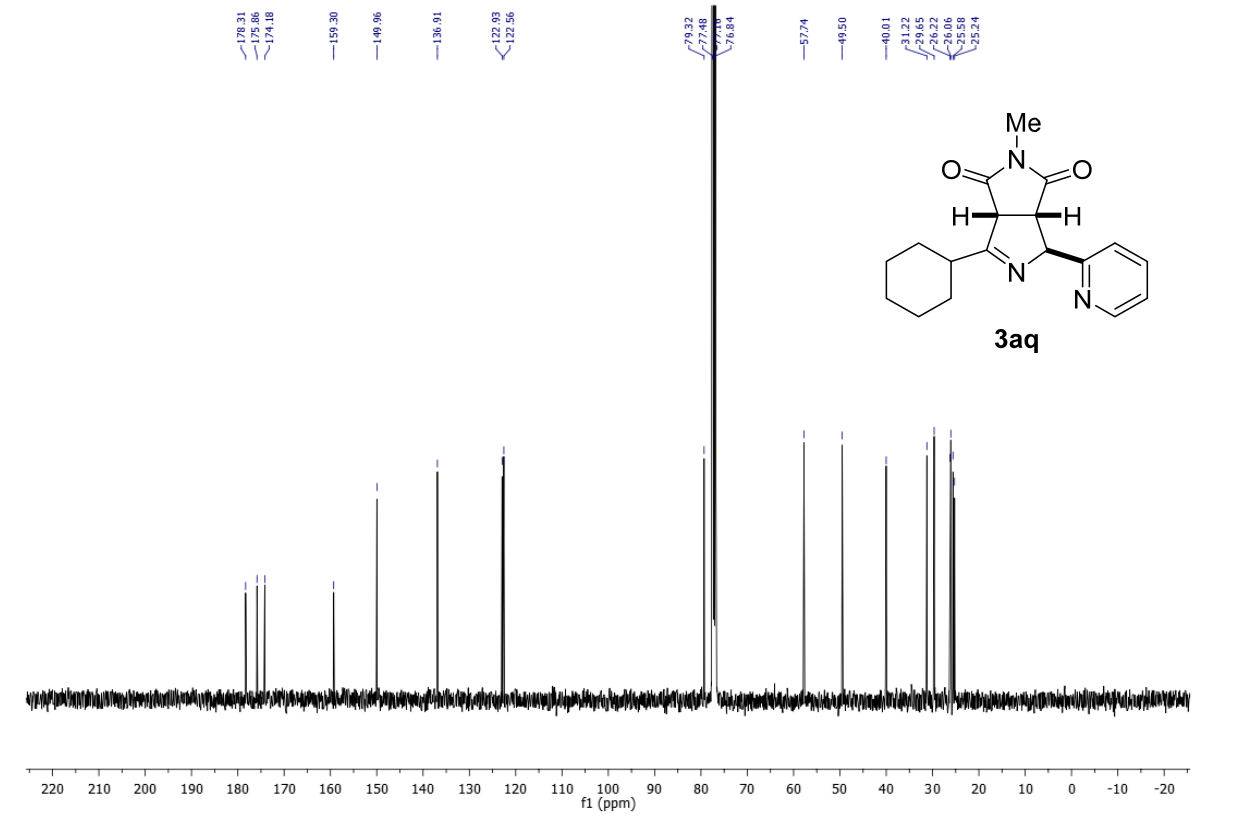

Bn
O
N
O
H
H
Cl
N
N
MeO
3co
f1 (ppm)

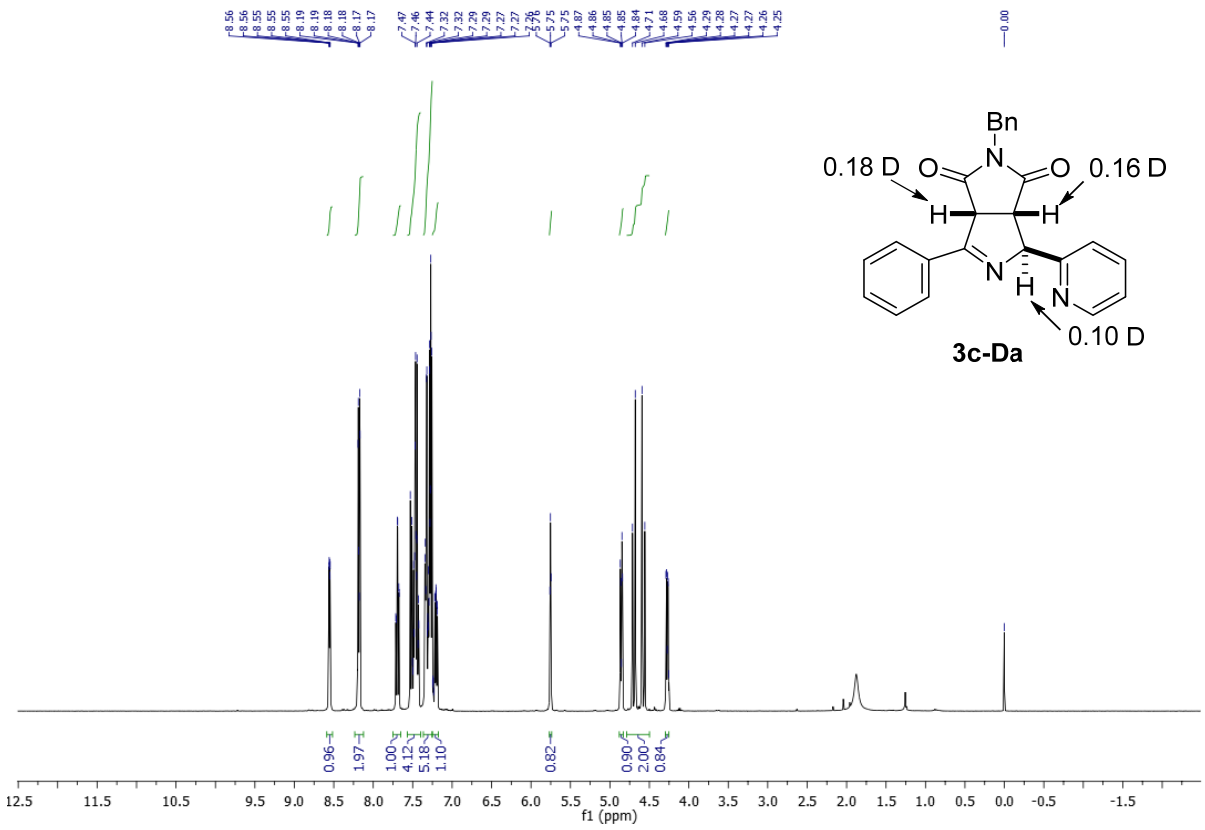

Bn
O
N
O
H
H
Cl
N
N
MeO
3co
f1 (ppm)

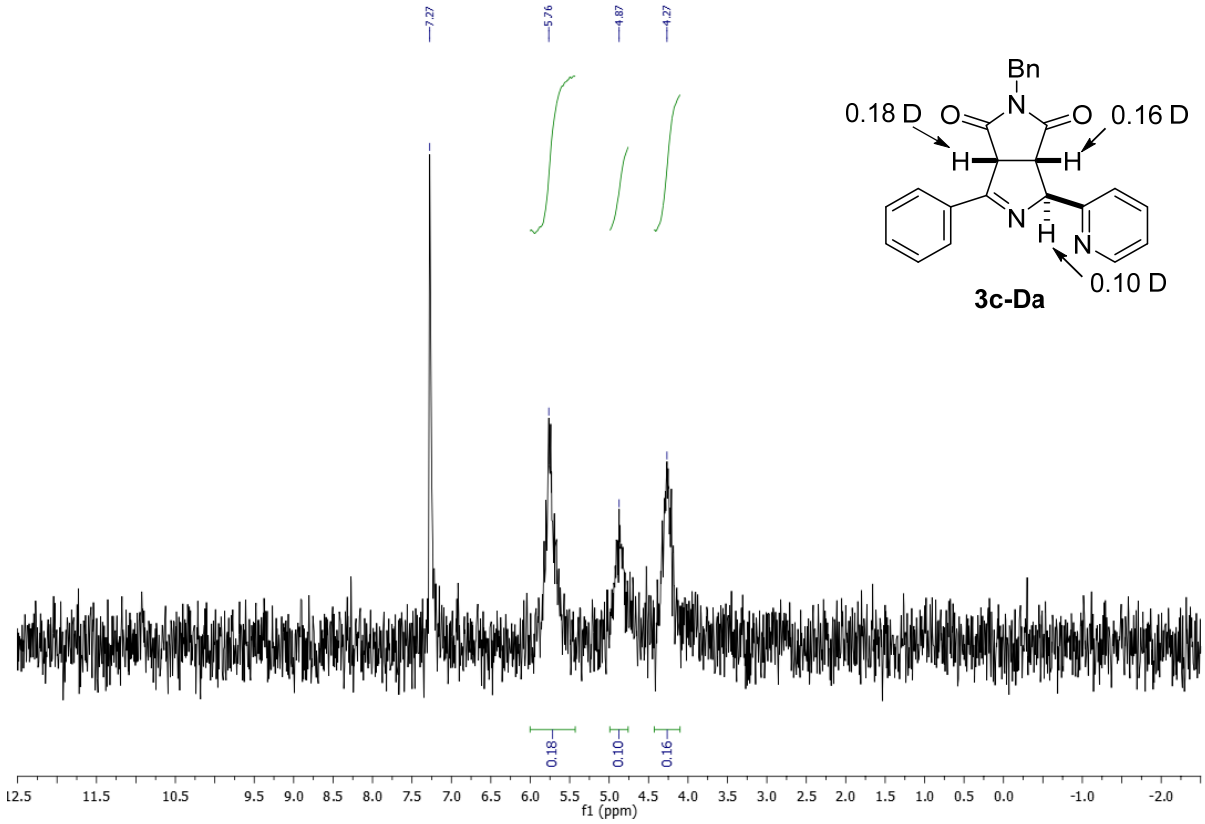

Me
N
O
O
H
H
S
N
N
3ap
f1 (ppm)

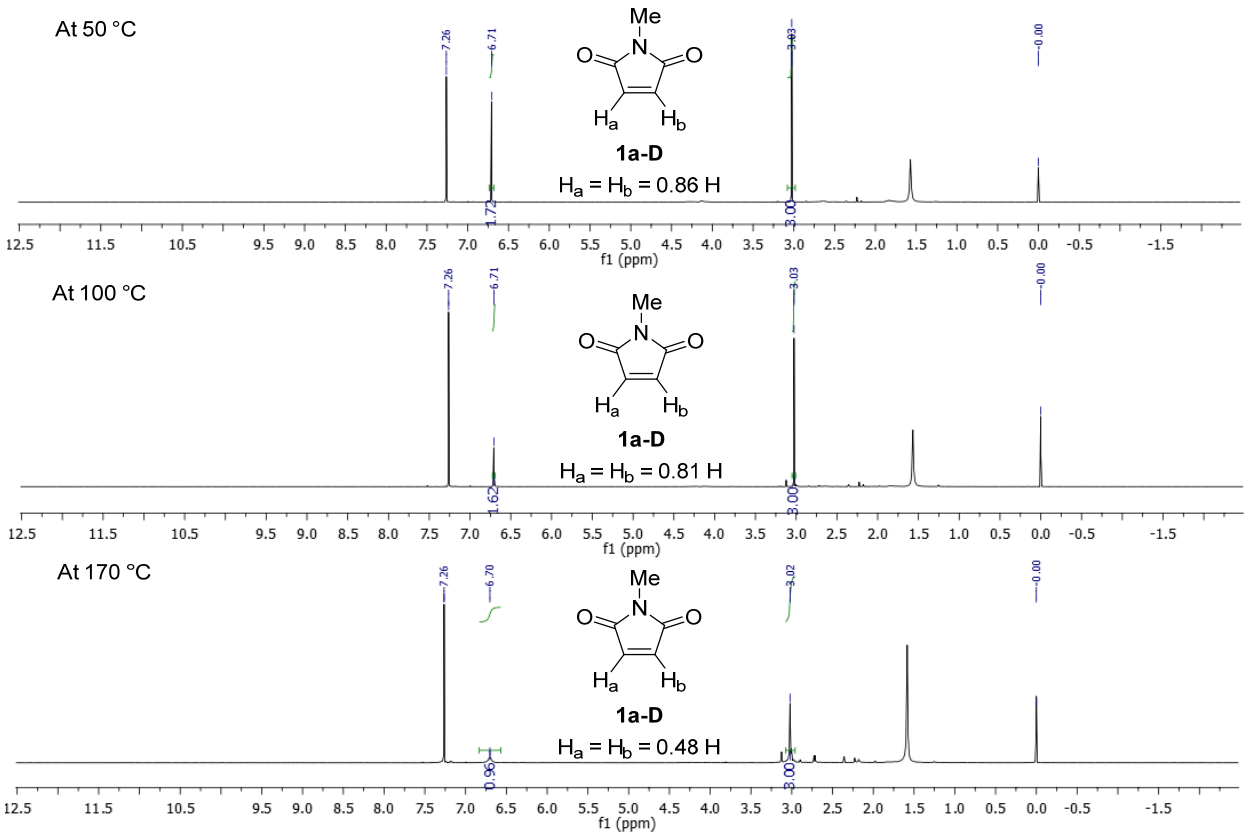

Me
N
O
O
H
H
S
N
N
3ap
f1 (ppm)

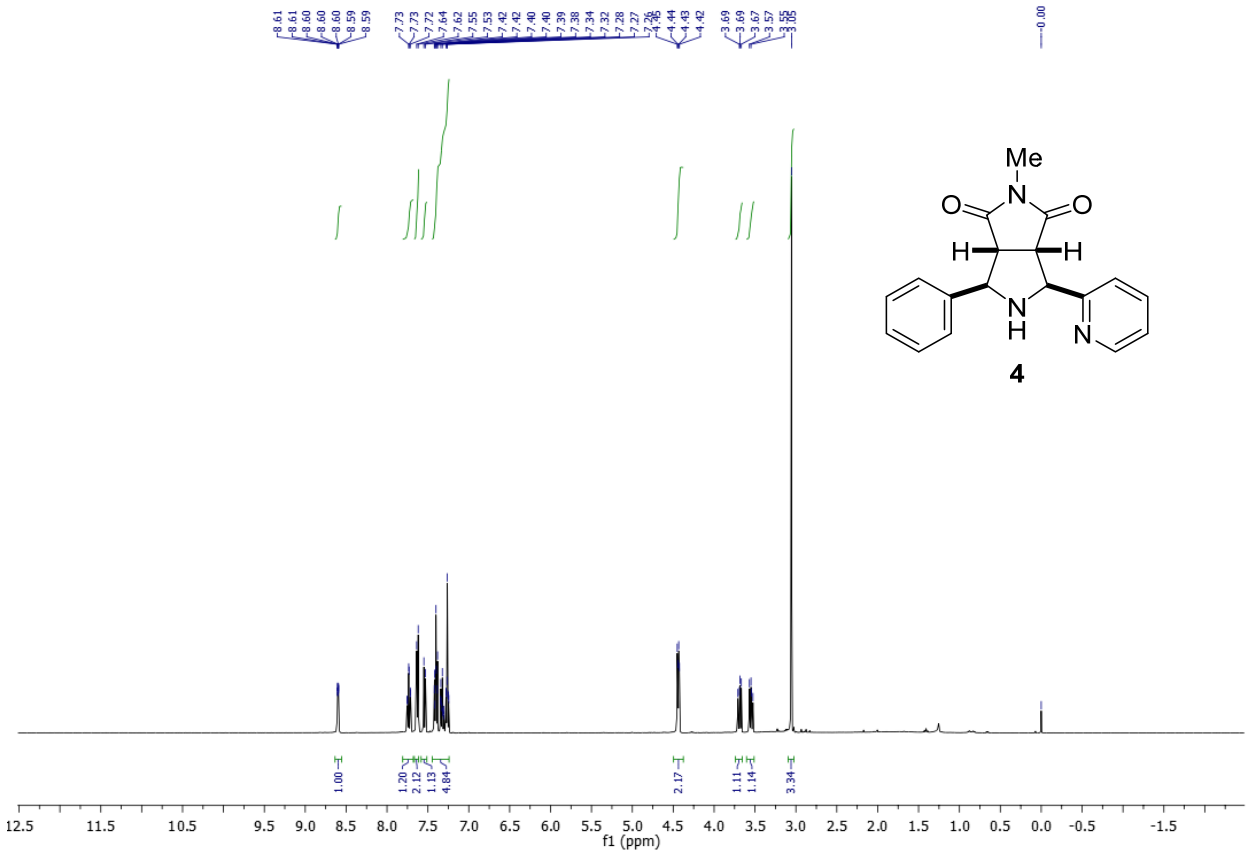

Me
N
O
O
H
H
N
N
3aq
f1 (ppm)

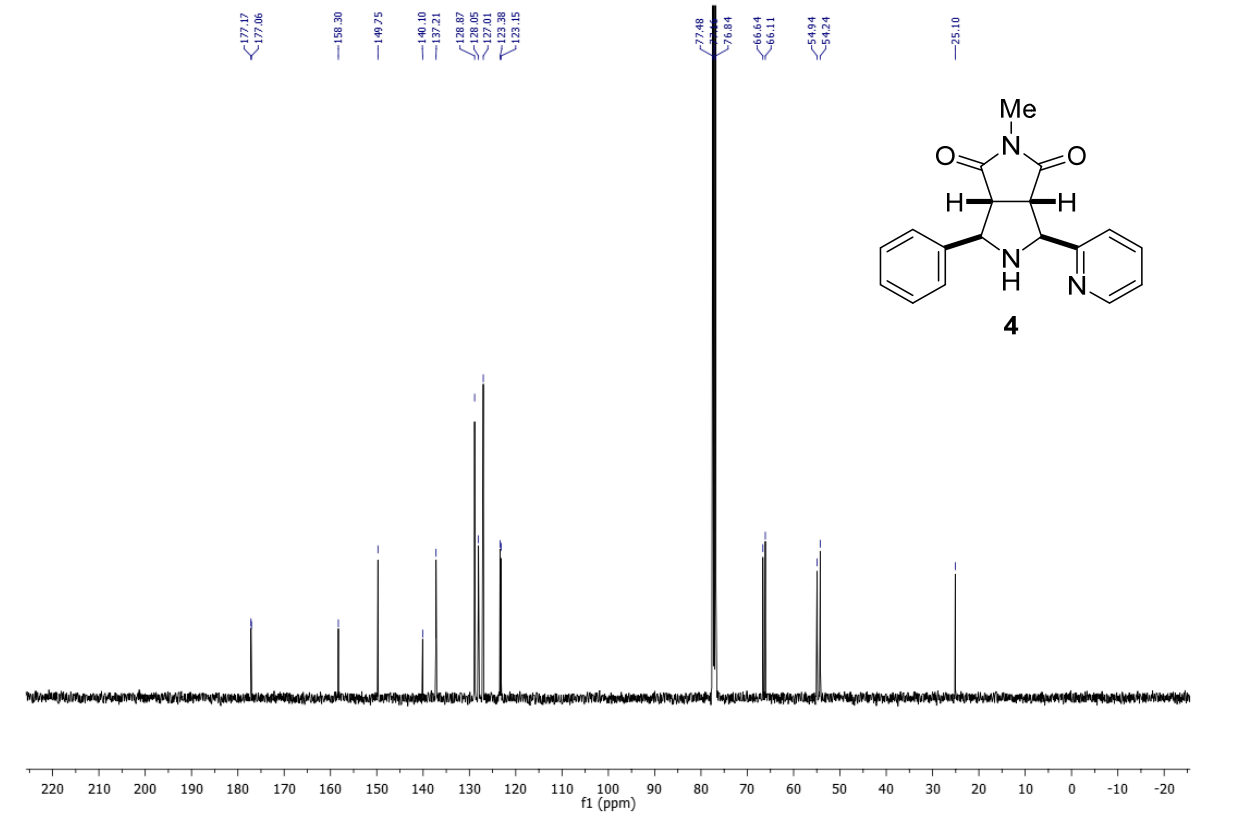

Me
N
O
O
H
H
N
N
3aq
f1 (ppm)


Bn
0.18 D
0.16 D
0.10 D
3c-Da
f1 (ppm)


Bn
0.18 D
0.16 D
0.10 D
3c-Da
f1 (ppm)


At 50 °C
Me
N
O
O
Ha
Hb
1a-D
Ha = Hb = 0.86 H
7.26
6.71
3.03
0.00
1.72
3.00
f1 (ppm)
At 100 °C
Me
N
O
O
Ha
Hb
1a-D
Ha = Hb = 0.81 H
7.26
6.71
3.03
0.00
1.62
3.00
f1 (ppm)
At 170 °C
Me
N
O
O
Ha
Hb
1a-D
Ha = Hb = 0.48 H
7.26
6.70
3.02
0.00
0.96
3.00
f1 (ppm)


Me
N
O
O
H
H
N
H
N
4
f1 (ppm)


Me
N
O
O
H
H
N
H
N
4
f1 (ppm)