Visible-light-mediated direct C3-arylation of 2*H*-indazoles enabled by an electron-donor-acceptor complex

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Supporting Information

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General information

Reactions were performed in a well-dried flask under an Ar atmosphere. Unless otherwise mentioned, all solvents and reagents were commercially available and utilized without further purification. Column chromatography was performed with silica gel 60 (70−230 mesh) using a mixture of EtOAc/hexane as an eluent.^{1}H and ^{13}C NMR spectra were, respectively, recorded on an Agilent 400 MHz (^{1}H NMR) and 101MHz (^{13}C NMR) spectrometer in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal reference. Data are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, coupling constant (Hz), and integration. High-resolution mass spectroscopy was performed using a magnetic sector analyzer. Spotlight-type LED bulbs purchased from CR Lighting Technology (model no.: CR-MR16 5 W Cool White LED Bulb, CR-MR16 4 W Green LED Bulb, and CR-MR16 4 W Blue LED Bulb), and OSRAM 20 W CFL (model no. Duluxstar compact 20 W/865) were used without using filters. Borosilicate glass irradiation vessels were used. When the reaction was carried out, the distance from the light source to the irradiation vessel was 5.0 cm.

1. Preparation of starting compounds

1.1 Synthesis of 2-aryl-2*H*-indazole[1]

A solution of aniline (6 mmol, 1 equiv.), and 2-nitrobenzaldehyde (6 mmol, 1 equiv.) in EtOH (0.5 M) was refluxed for 8 h. The resulting crystalline solid was collected by filtration, and dried under reduced pressure. The collected solid was refluxed for 12 h in triethyl phosphite (60 mmol, 10 equiv.). The resulting mixture was partitioned between CH_2Cl_2 and water. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography with EtOAc/hexane afforded the desired product (15–75 %). The analytical data were identical in all respects to those previously reported.[1]

1.2 Synthesis of 2-methyl-2*H*-indazole[2]

A well dried flask equipped with a magnetic stirring bar was charged with 1*H*-indazole (3 mmol, 1.0 equiv.). It was evacuated and was back filled with argon. Dry EtOAc (9.0 mL, 0.3 M), and trimethyloxonium tetrafluoroborate (3.9 mmol, 1.3 equiv.) were added. The mixture was stirred at room temperature for 5 h. The resulting mixture was partitioned between EtOAc and water. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography with EtOAc/hexane afforded the desired product (67%). The analytical data were identical in all respects to those previously reported.[2]

1.3 Synthesis of 5-fluoro-2-phenyl-*2H*-indazole[3]

A well dried flask equipped with a magnetic stirring bar was charged with a solution of 2-bromo-5-fluorobenzaldehyde (6.0 mmol, 1 equiv.), aniline (6.6 mmol, 1.1 equiv.), CuI (0.6 mmol, 0.1 equiv.), NaN_3 (12 mmol, 2.0 equiv.), and TMEDA (0.6 mmol, 0.1 equiv.) in DMSO (0.2 M). The reaction mixture was heated to 120 ^oC for 12 h. The resulting mixture was partitioned between CH_2Cl_2 and water. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography with EtOAc/hexane afforded the desired product (35%). The analytical data were identical in all respects to those previously reported.[3]

1.4 Synthesis of diazonium salts[4]

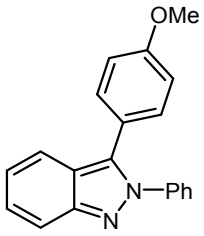
HBF_4 (48% in water, 5 mmol, 1.0 equiv.) was added to a solution of aniline (5 mmol, 1.0 equiv.) in ethanol (1.5 mL, 3.3 M), the reaction mixture was stirred for 2 min at room temperature. The mixture

was cooled to 0 °C and tert-butyl nitrite (5 mmol, 1.0 equiv.) was added dropwise. After addition, the mixture was stirred at 0 °C for 5 min and then was stirred at room temperature for 1 h. Diethyl ether (20 mL) was added to the reaction mixture and the resulting solids were filtered, washed with diethyl ether (3 x 20 mL) and dried under high vacuum (74–91%).

2. General procedure for the synthesis of 3-aryl-2*H*-indazole 3

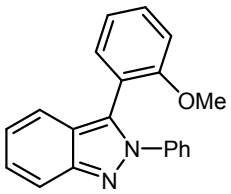
2*H*-indazole **1** (1.0 mmol, 2.0 equiv.), and aryl diazonium salt **2** (0.5 mmol, 1.0 equiv.) were added into a well dried 4 mL borosilcate vial (15 x 45 mm) with a magnetic stirring bar. It was evacuated and was back filled with argon. Dry DMSO (2.0 mL, 0.25 M), and pyridine (0.5 mmol, 1.0 equiv.) were added. The reaction mixture was stirred and irradiated by 4 W blue LEDs (455 nm) at room temperature for 15 h. The resulting mixture was partitioned between EtOAc and water. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography with diethyl ether/hexane afforded the desired product.

3. Physical data for the compounds



3aa

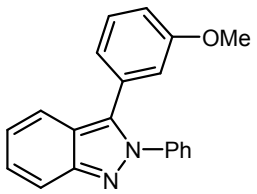
3-(4-Methoxyphenyl)-2-phenyl-2*H*-indazole (3aa)[5]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 110 mg (73% yield) of product as a light yellow solid. mp 103–106 °C (lit.[6] 103– 105 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.9 Hz, 2H), 7.40–7.31 (m, 4H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 149.0, 140.3, 135.4, 131.0, 129.0, 128.2, 127.0, 126.0, 122.2, 122.2, 121.6, 120.6, 117.7, 114.3, 55.3; IR 3057, 3001, 2925, 2838, 1601, 1498, 1457, 1358, 1285, 1249, 1174, 1068, 1024, 972, 923, 751 cm^{-1}; HRMS (EI); Mass calcd for $C_{20}H_{16}N_2O$ $[M]^+$: 300.1263; found 300.1261.



3ab

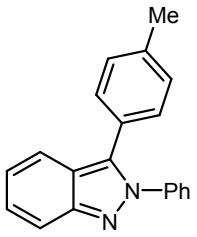
3-(2-Methoxyphenyl)-2-phenyl-2*H*-indazole (3ab)[7]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 2-methoxybenzenediazonium tetrafluoroborate **2ab**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 97 mg (65% yield) of product as a light yellow solid. mp 117–119 °C (lit.[7] 121–122 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.58 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.47–7.22 (m, 8H), 7.13–7.02 (m, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 3.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ156.7, 148.9, 141.4, 132.5, 131.6, 130.6, 128.6, 127.7, 126.7, 124.5, 122.6, 122.0, 120.9, 120.7, 119.1, 117.7, 111.5,

54.8; IR 2925, 2839, 1597, 1493, 1460, 1358, 1248, 1189, 1114, 1016, 974, 920, 828, 742, 689, 610, 557, 520, 437 cm^{-1}; LRMS (EI); Mass calcd for $C_{20}H_{16}N_2O$ $[M]^+$: 300; found 300.



3ac

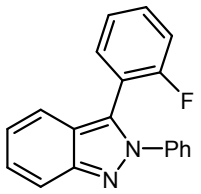
3-(3-Methoxyphenyl)-2-phenyl-2*H*-indazole (3ac)[8]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 3-methoxybenzenediazonium tetrafluoroborate **2ac**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 92 mg (61% yield) of product as a light yellow solid. mp 148–151 °C (lit.[8] 148–149 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dt, *J* = 8.8, 0.9 Hz, 1H), 7.74 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.47–7.33 (m, 6H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.14 (ddd, *J* = 8.5, 6.6, 0.8 Hz, 1H), 6.96–6.86 (m, 3H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 149.0, 140.3, 135.3, 131.0, 129.8, 129.0, 128.3, 127.0, 126.0, 122.6, 122.1, 121.7, 120.6, 117.8, 114.9, 114.2, 55.2.; IR 2924, 2847, 1571, 1495, 1436, 1357, 1287, 1235, 1163, 1048, 996, 916, 839, 743, 696, 560, 501, 459 cm^{-1}; LRMS (EI); Mass calcd for $C_{20}H_{16}N_2O$ $[M]^+$: 300; found 300.



3ad

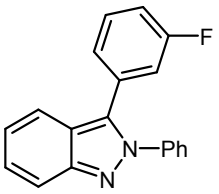
2-Phenyl-3-(*p*-tolyl)-2*H*-indazole (3ad)[5]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 4-methylbenzenediazonium tetrafluoroborate **2ad**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 100 mg (70% yield) of product as a light yellow solid. mp 109–111 °C (lit.[9] 108–110 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.43 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.39–7.30 (m, 4H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1H), 2.36 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.0, 140.3, 138.3, 135.6, 129.5, 129.0, 128.2, 127.0, 126.9, 126.0, 122.3, 121.7, 120.7, 117.7, 21.4.; IR 3059, 2917, 2857, 1590, 1546, 1499, 1450, 1358, 1286, 1218, 1176, 1072, 1026, 973, 913, 819, 740, 687, 607, 557, 505 cm^{-1}; LRMS (EI); Mass calcd for $C_{20}H_{16}N_2$ $[M]^+$: 284; found 284.



3ae

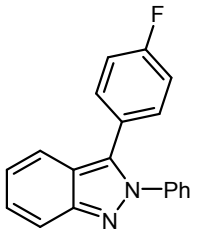
3-(2-Fluorophenyl)-2-phenyl-2*H*-indazole (3ae)[8]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 2-fluorobenzenediazonium tetrafluoroborate **2ae**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 95 mg (66% yield) of product as a light yellow solid. mp 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.8 Hz, 1H), 7.59 (dd, J = 8.5, 1.1 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.33 (m, 6H), 7.19 (td, J = 7.6, 1.1 Hz, 1H), 7.17 – 7.07 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): 159.6 (d, J_{cf} = 250.4 Hz), 149.0, 140.4, 131.9 (d, J_{cf} = 2.5 Hz), 130.9 (d, J_{cf} = 8.1 Hz), 129.6, 129.0, 128.3, 127.0, 125.1, 124.5 (d, J_{cf} = 3.7 Hz), 122.7 (d, J_{cf} = 3.7 Hz), 120.2 (d, J_{cf} = 1.7 Hz), 118.1 (d, J_{cf} = 15.3 Hz), 117.9, 116.4 (d, J_{cf} = 21.5 Hz); IR 3060, 2924, 1591, 1497, 1448, 1358, 1262, 1223, 1099, 1027, 974, 920, 814, 744, 688, 609, 536, 458 cm^{-1}; LRMS (EI); Mass calcd for $C_{19}H_{13}FN_2$ $[M]^+$: 288; found 288.



3af

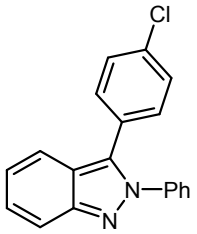
3-(3-Fluorophenyl)-2-phenyl-2*H*-indazole (3af)[10]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 2-fluorobenzenediazonium tetrafluoroborate **2af**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 117 mg (81% yield) of product as a light yellow solid. mp 112–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.8 Hz, 1H), 7.70 (dt, J = 8.5, 1.0 Hz, 1H), 7.47 – 7.28 (m, 7H), 7.15 (ddd, J = 8.5, 6.6, 0.8 Hz, 1H),

7.11 (dt, J = 7.7, 1.1 Hz, 1H), 7.09 – 7.02 (m, 2H).;^{13}C NMR (101 MHz, $CDCl_3$):δ 162.7 (d, J_{cf} = 247.2 Hz), 149.0, 140.0, 133.9 (d, J_{cf} = 2.5 Hz), 131.9 (d, J_{cf} = 8.3 Hz), 130.4 (d, J_{cf} = 8.6 Hz), 129.1, 128.6, 127.1, 126.0, 125.5 (d, J_{cf} = 3.0 Hz), 123.0, 121.8, 120.1, 117.9, 116.5 (d, J_{cf} = 22.6 Hz), 115.3 (d, J_{cf} = 21.0 Hz); IR 3055, 1584, 1498, 1457, 1359, 1292, 1223, 1151, 1076, 1013, 916, 858, 750, 697, 563, 501, 435 cm^{-1}; LRMS (EI); Mass calcd for $C_{19}H_{13}FN_2$ $[M]^+$: 288; found 288.



3ag

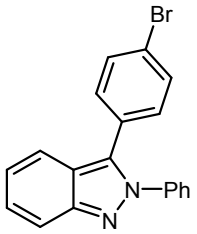
3-(4-Fluorophenyl)-2-phenyl-2*H*-indazole (3ag)[5]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 4-fluorobenzenediazonium tetrafluoroborate **2ag**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 63 mg (44% yield) of product as a white solid. mp 144–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.43 – 7.27 (m, 8H), 7.15 – 7.03 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.6 (d, J_{cf} = 249.4 Hz), 149.0, 140.0, 134.3, 131.5 (d, J_{cf} = 8.2 Hz), 129.1, 128.4, 127.1, 126.0, 125.9, 122.7, 121.7, 120.2, 117.9, 116.0 (d, J_{cf} = 21.8 Hz); IR 1595, 1499, 1456, 1360, 1289, 1217, 1157, 1104, 1072, 1021, 974, 915, 837, 749, 687 ,609, 517, 450 cm^{-1}; LRMS (EI); Mass calcd for $C_{19}H_{13}FN_2$ $[M]^+$: 288; found 288.



3ah

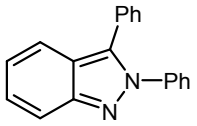
3-(4-Chlorophenyl)-2-phenyl-2*H*-indazole (3ah)[5]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 4-chlorobenzenediazonium tetrafluoroborate **2ah**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 94 mg (62% yield) of product as a white solid. mp 137–139 °C (lit.[9] 134–135 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.80 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.33 (m, 8H), 7.29 – 7.25 (m, 2H), 7.16 – 7.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.0, 140.0, 134.4, 134.1, 130.8, 129.2, 129.1, 128.5, 128.4, 127.1, 126.0, 122.9, 121.7, 120.1, 117.9; IR 3058, 2926, 1592, 1545, 1496, 1453, 1403, 1361, 1293, 1220, 1184, 1091, 1019, 972, 913, 835, 742, 691, 605, 486 cm^{-1}; LRMS (EI); Mass calcd for $C_{19}H_{13}ClN_2$ $[M]^+$: 304; found 304.



3ai

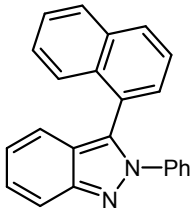
3-(4-Bromophenyl)-2-phenyl-2*H*-indazole (3ai) [5]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and 4-bromobenzenediazonium tetrafluoroborate **2ai**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 105 mg (60% yield) of product as a white solid. mp 112–115 °C (lit.[9] 109–110 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.44 – 7.34 (m, 6H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.17 – 7.12 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.0, 140.0, 134.1, 132.1, 131.1, 129.2, 128.8, 128.5, 127.1, 126.0, 122.9, 122.7, 121.7, 120.1, 117.9; IR 3046, 2935, 2858, 1590, 1496, 1451, 1396, 1360, 1292, 1218, 1182, 1071, 1007, 968, 911, 837, 747, 689, 609, 572, 501 cm^{-1}; LRMS (EI); Mass calcd for $C_{19}H_{13}BrN_2$ $[M]^+$: 348; found 348.



3aj

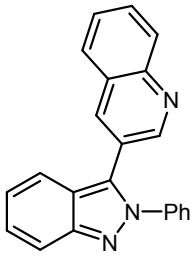
2,3-Diphenyl-2*H*-indazole (3aj)[5]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and benzenediazonium tetrafluoroborate **2aj**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 68 mg (50% yield) of product as a white solid. mp 100–102 °C (lit.[9] 102–103 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.32 (m, 11H), 7.12 (ddd, *J* = 8.5, 6.6, 0.8 Hz, 1H); ^{13}C NMR (101

MHz, $CDCl_3$): δ149.0, 140.2, 135.4, 129.9, 129.7, 129.0, 128.8, 128.4, 128.3, 128.3, 127.0, 126.0, 122.5, 121.8, 120.5, 117.8; IR 3051, 2926, 2852, 1592, 1499, 1452, 1358, 1273, 1226, 1069 972, 916, 828, 747, 692, 606, 565, 504, 438 cm^{-1}; LRMS (EI); Mass calcd for $C_{19}H_{14}N_2$ $[M]^+$: 270; found 270.



3ak

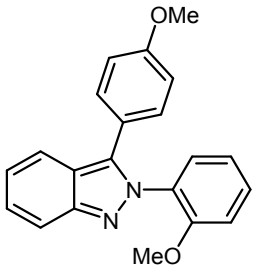
3-(Naphthalen-1-yl)-2-phenyl-2*H*-indazole (3ak)[5]: Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and naphthalene-1-diazonium tetrafluoroborate **2ak**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to 1afford 111 mg (69% yield) of product as a white solid. mp 150–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.87 (m, 3H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.33 (m, 8H), 7.24 – 7.18 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.9, 140.2, 134.0, 133.7, 132.0, 129.6, 129.5, 128.8, 128.5, 128.0, 127.6, 127.1, 126.8, 126.3, 125.6, 125.3, 125.0, 123.4, 122.3, 120.9, 117.8; IR 3044, 2923, 2854, 1592, 1497, 1359, 1286, 1217, 1167, 1109, 1071 ,1017, 914, 745, 689, 610, 530, 440 cm^{-1}; LRMS (EI); Mass calcd for $C_{23}H_{16}N_2$ $[M]^+$: 320; found 320.



3al

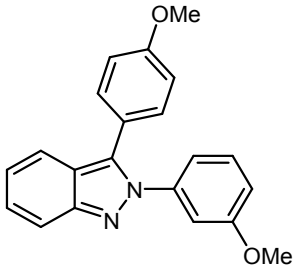
3-(2-Phenyl-2*H*-indazol-3-yl) quinoline (3al): Prepared according to the general procedure using 2-phenyl-2*H*-indazole **1aa**, and quinoline-3-diazonium tetrafluoroborate **2al**. The reaction mixture was purified by flash chromatography using 50% diethyl ether/hexane to afford 96 mg (60% yield) of product as a light yellow solid. mp 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 2.2 Hz, 1H), 8.20 (d, *J* = 1.7 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.59 – 7.54 (m, 1H), 7.47 – 7.42 (m, 2H), 7.41 – 7.35 (m, 4H), 7.21 – 7.16 (m, 1H); ^{13}C NMR (101

MHz, $CDCl_3$): δ 150.4, 149.2, 147.1, 139.8, 136.1, 132.0, 130.4, 129.4, 129.4, 128.8, 128.0, 127.5, 127.5, 127.3, 126.0, 123.4, 123.4, 122.3, 119.8, 118.1; IR 3060, 2951, 1710, 1600, 1498, 1374, 1319,1225, 1173, 1126, 1073, 1017, 914, 854, 749, 694, 607, 558, 479, 437 cm^{-1}; HRMS (EI); Mass calcd for $C_{22}H_{15}N_3$ $[M]^+$: 321.1266; found 321.1265.



3am

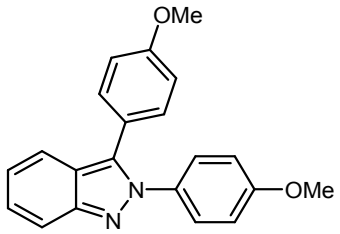
2-(2-Methoxyphenyl)-3-(4-methoxyphenyl)-2*H*-indazole (3am): Prepared according to the general procedure using 2-(2-methoxyphenyl)-2*H*-indazole **1am**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 50% diethyl ether/hexane to afford 68 mg (41% yield) of product as an orange solid. mp 120–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.46 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.13 – 7.08 (m, 1H), 7.03 (td, *J* = 7.6, 1.1 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 154.0, 149.0, 137.4, 130.5, 130.0, 129.4, 129.0, 126.6, 122.7, 121.9, 120.8, 120.6, 120.5, 117.7, 113.9, 112.2, 55.5, 55.2.; IR 3059, 2925, 2841, 1734, 1602, 1502, 1461, 1359, 1247, 1174, 1078, 1018, 838, 749, 663, 612, 578, 534, 437 cm^{-1}; HRMS (EI); Mass calcd for $C_{21}H_{18}N_2O_2$ $[M]^+$: 330.1368; found 330.1368.



3an

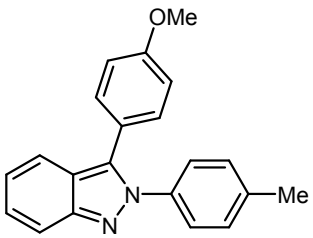
2-(3-Methoxyphenyl)-3-(4-methoxyphenyl)-2*H*-indazole (3an): Prepared according to the general procedure using 2-(3-methoxyphenyl)-2*H*-indazole **1an**, and 4-methoxybenzenediazonium

tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 50% diethyl ether/hexane to afford 132 mg (80% yield) of product as a brown solid. mp 121–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.23 (m, 4H), 7.13 – 7.04 (m, 2H), 6.98 – 6.87 (m, 4H), 3.81 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 159.6, 148.9, 141.3, 135.4, 130.9, 129.6, 127.0, 122.2, 122.2, 121.6, 120.6, 118.3, 117.7, 114.5, 114.3, 111.3, 55.4, 55.3; IR 3194, 3052, 2932, 2837, 2720, 2632, 2589, 2543, 1595, 1492, 1358, 1322, 1243, 1173, 1107, 1027, 981, 888, 825, 750 ,690, 570, 521, 467 cm^{-1}; HRMS (EI); Mass calcd for $C_{21}H_{18}N_2O_2$ $[M]^+$: 330.1368; found 330.1369.



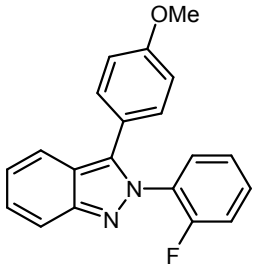
3ao

2-(4-Methoxyphenyl)-3-(4-methoxyphenyl)-2*H*-indazole (3ao): Prepared according to the general procedure using 2-(4-methoxyphenyl)-2*H*-indazole **1ao**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 50% diethyl ether/hexane to afford 134 mg (81% yield) of product as a light yellow solid. mp 102–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.23 (m, 5H), 7.14 – 7.06 (m, 1H), 6.94 – 6.84 (m, 4H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 159.2, 148.8, 135.2, 133.4, 130.9, 127.2, 126.8, 122.3, 122.0, 121.4, 120.6, 117.6, 114.3, 114.1, 55.5, 55.3; IR 2925, 2840, 1605, 1508, 1460, 1361, 1294, 1249, 1172, 1109, 1024, 974, 832, 749, 663, 602, 515 cm^{-1}; HRMS (EI); Mass calcd for $C_{21}H_{18}N_2O_2$ $[M]^+$: 330.1368; found 330.1370.



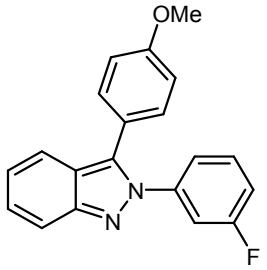
3ap

3-(4-Methoxyphenyl)-2-(*p*-tolyl)-2*H*-indazole (3ap): Prepared according to the general procedure using 2-(p-tolyl)-2*H*-indazole **1ap**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 118 mg (75% yield) of product as a white solid. mp 135–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.26 (d, J = 8.9 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.11 – 7.06 (m, 1H), 6.89 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 148.9, 138.1, 137.9, 135.2, 130.9, 129.6, 126.8, 125.8, 122.3, 122.1, 121.6, 120.6, 117.6, 114.3, 55.3, 21.2; IR 3059, 3001, 2926, 2839, 1605, 1509, 1458, 1359, 1286, 1245, 1173, 1115, 1023, 973, 819, 749, 655, 579, 502 cm^{-1}; HRMS (EI); Mass calcd for $C_{21}H_{18}N_2O$ $[M]^+$: 314.1419; found 314.1417.



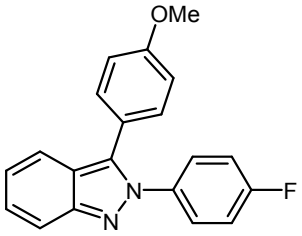
3aq

2-(2-Fluorophenyl)-3-(4-methoxyphenyl)-2*H*-indazole (3aq): Prepared according to the general procedure using 2-(2-fluorophenyl)-2*H*-indazole **1aq**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 70 mg (44% yield) of product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.56 (td, J = 7.7, 1.7 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.31 – 7.22 (m, 3H), 7.15 – 7.07 (m, 2H), 6.89 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 156.5 (d, J_{cf} = 253.8 Hz), 149.4, 137.6, 130.8 (d, J_{cf} = 7.7 Hz), 130.3, 129.3, 128.5 (d, J_{cf} = 12.0 Hz), 127.2, 124.7 (d, J_{cf} = 4.0 Hz), 122.3, 121.8 (d, J_{cf} = 1.1 Hz), 120.7, 120.7, 117.7, 116.7 (d, J_{cf} = 19.6 Hz), 114.3, 55.2; IR 1607, 1506 ,1460, 1362, 1246, 1175, 1116 ,1030, 975, 907, 833, 745, 663, 609, 572, 531, 438 cm^{-1}; HRMS (EI); Mass calcd for $C_{20}H_{15}FN_2O$ $[M]^+$: 318.1168; found 318.1168.



3ar

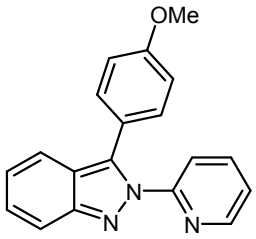
2-(3-Fluorophenyl)-3-(4-methoxyphenyl)-2*H*-indazole (3ar): Prepared according to the general procedure using 2-(3-fluorophenyl)-2*H*-indazole **1ar**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 116 mg (73% yield) of product as a yellow solid. mp 115–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.37 – 7.17 (m, 6H), 7.13 – 7.02 (m, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5 (d, J_{cf} = 247.8 Hz), 159.8, 149.1, 141.6 (d, J_{cf} = 10.0 Hz), 135.6, 130.9, 130.2 (d, J_{cf} = 9.0 Hz), 127.3, 122.5, 121.7 (d, J_{cf} = 3.7 Hz), 121.6 (d, J_{cf} = 3.2 Hz), 120.6, 117.7, 115.2 (d, J_{cf} = 21.1 Hz), 114.5, 113.7, 113.4, 55.3; IR 3029, 2928, 2839, 1603, 1488, 1359, 1292, 1249, 1173, 1033, 941, 868, 832, 792, 747, 661, 568, 522, 474, 430 cm^{-1}; HRMS (EI); Mass calcd for $C_{20}H_{15}FN_2O$ $[M]^+$: 318.1168; found 318.1169.



3as

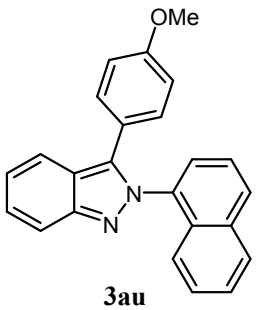
2-(4-Fluorophenyl)-3-(4-methoxyphenyl)-2*H*-indazole (3as): Prepared according to the general procedure using 2-(4-fluorophenyl)-2*H*-indazole **1as**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 103 mg (65% yield) of product as a white solid. mp 102–106 °C. ^{1}H NMR (400

MHz, $CDCl_3$): δ7.76 (d, J = 8.7 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.13 – 7.02 (m, 3H), 6.92 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.0 (d, J_{cf} = 248.5 Hz), 159.7, 148.9, 136.5, 136.4, 135.5, 130.9, 127.7 (d, J_{cf} = 8.6 Hz), 127.1, 122.3, 121.7 (d, J_{cf} = 32.0 Hz), 120.6, 117.6, 116.0 (d, J_{cf} = 23.0 Hz), 114.4, 55.3; IR 1607, 1508, 1465, 1362, 1288, 1247, 1171, 1086, 1023, 973, 913, 835, 750, 657, 578, 512, 427 cm^{-1}; HRMS (EI); Mass calcd for $C_{20}H_{15}FN_2O$ $[M]^+$: 318.1168; found 318.1168.



3at

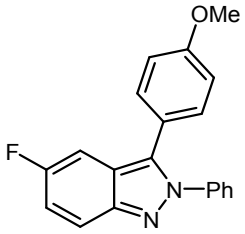
3-(4-Methoxyphenyl)-2-(pyridin-2-yl)-2*H*-indazole (3at): Prepared according to the general procedure using 2-(pyridin-2-yl)-2*H*-indazole **1at**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 50% diethyl ether/hexane to afford 96 mg (64% yield) of product as a brown solid. mp 131–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 3.7 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.68 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.37 – 7.27 (m, 4H), 7.14 – 7.06 (m, 1H), 6.92 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 152.8, 149.2, 148.9, 138.2, 135.9, 130.9, 127.4, 123.3, 122.6, 122.4, 121.8, 120.9, 120.4, 118.0, 114.2, 55.3; IR 3057, 3014, 2931, 2827, 1575, 1470, 1426 ,1357, 1243, 1174, 1018, 966, 881, 836, 778, 737, 607, 565, 519 cm^{-1}; HRMS (EI); Mass calcd for $C_{19}H_{15}N_3O$ $[M]^+$: 301.1215; found 301.1216.



3au

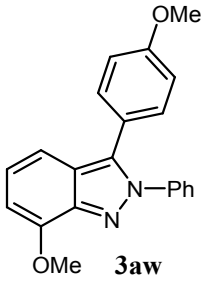
3-(4-Methoxyphenyl)-2-(naphthalen-1-yl)-2*H*-indazole (3au): Prepared according to the general

procedure using 2-(naphthalen-1-yl)-2*H*-indazole **1au**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 54 mg (31% yield) of product as a yellow solid. mp 144–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 10.9, 8.6 Hz, 2H), 7.81 (t, *J* = 8.7 Hz, 2H), 7.51 – 7.38 (m, 6H), 7.19 (d, *J* = 8.9 Hz, 3H), 6.73 (d, *J* = 8.9 Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 149.1, 137.8, 136.8, 134.1, 130.3, 130.3, 129.6, 128.1, 127.6, 127.0, 126.7, 125.8, 124.9, 123.2, 122.3, 121.9, 120.8, 120.6, 117.8, 114.1, 55.2; IR 2929, 2840, 1606, 1502, 1460, 1380, 1286, 1246, 1173, 1109, 1025, 966, 920, 831, 746, 670, 535 cm^{-1}; HRMS (EI); Mass calcd for $C_{24}H_{18}N_2O$ $[M]^+$: 350.1419; found 350.1419.



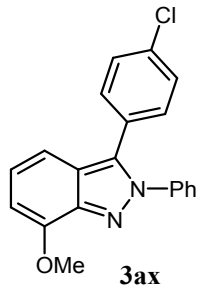
3av

5-Fluoro-3-(4-methoxyphenyl)-2-phenyl-2*H*-indazole (3av): Prepared according to the general procedure using 5-fluoro-2-phenyl-2*H*-indazole **1av**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 20% diethyl ether/hexane to afford 89 mg (56% yield) of product as a light yellow solid. mp 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (ddd, *J* = 9.3, 4.6, 0.6 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.28 – 7.20 (m, 3H), 7.15 (td, *J* = 9.2, 2.4 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 159.7, 157.6, 143.2 (d, J_{cf} = 620.2 Hz), 135.6 (d, J_{cf} = 8.6 Hz), 130.8, 129.0, 128.3, 125.9, 121.8, 120.9 (d, J_{cf} = 11.2 Hz), 119.8 (d, J_{cf} = 9.6 Hz), 118.5 (d, J_{cf} = 28.9 Hz), 114.4, 103.0 (d, J_{cf} = 24.4 Hz), 55.28; IR 3010, 2933, 2837, 1603, 1502, 1454, 1293, 1248, 1172, 1117, 1028, 970, 912, 837, 764, 692, 583, 524, 481 cm^{-1}; HRMS (EI); Mass calcd for $C_{20}H_{15}FN_2O$ $[M]^+$: 318.1168; found 318.1167.



3aw

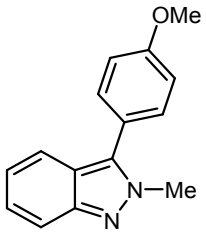
7-Methoxy-3-(4-methoxyphenyl)-2-phenyl-2*H*-indazole (3aw): Prepared according to the general procedure using 7-methoxy-2-phenyl-2*H*-indazole **1aw**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 50% diethyl ether/hexane to afford 112 mg (68% yield) of product as a brown solid. mp 143–146 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H), 7.38 – 7.31 (m, 3H), 7.28 – 7.23 (m, 3H), 7.03 (dd, *J* = 8.5, 7.3 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 7.1 Hz, 1H), 4.04 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 150.3, 142.5, 140.3, 135.5, 130.9, 128.8, 128.1, 126.2, 123.1, 122.8, 122.3, 114.2, 112.4, 103.2, 55.4, 55.3.; IR 2968, 2927, 2842, 1601, 1539, 1428, 1367, 1252, 1174, 1111, 1032, 966, 927, 833, 719, 614, 519, 453 cm^{-1}; HRMS (EI); Mass calcd for $C_{21}H_{18}N_2O_2$ $[M]^+$: 330.1368; found 330.1370.



3ax

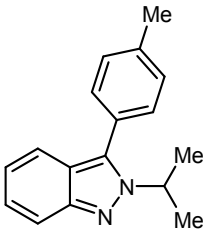
3-(4-Chlorophenyl)-7-methoxy-2-phenyl-2*H*-indazole (3ax)[9]: Prepared according to the general procedure using 7-methoxy-2-phenyl-2*H*-indazole **1aw**, and 4-chlorobenzenediazonium tetrafluoroborate **2ah**. The reaction mixture was purified by flash chromatography using 30% diethyl ether/hexane to afford 127 mg (76% yield) of product as an orange solid. mp 125–129 °C (lit.[9] 129 – 131 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.38 – 7.31 (m, 5H), 7.28 – 7.19 (m, 3H), 7.08 – 7.01 (m, 1H), 6.61 (d, *J* = 7.3 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4, 142.5, 139.9, 134.3, 134.2, 130.8, 129.0, 129.0, 128.4, 128.4, 126.2, 123.6, 123.2,

111.9, 103.4, 55.5; IR 3065, 2992, 2935, 2838, 2233, 1597, 1502, 1423, 1359, 1256, 1177, 1126, 1086, 997, 912, 833, 721, 613, 554, 501, 443 cm^{-1}; LRMS (EI); Mass calcd for $C_{20}H_{15}ClN_2O$ $[M]^+$: 334; found 334.



3ay

3-(4-Methoxyphenyl)-2-methyl-2*H*-indazole (3ay): Prepared according to the general procedure using 2-methyl-2*H*-indazole **1ay**, and 4-methoxybenzenediazonium tetrafluoroborate **2aa**. The reaction mixture was purified by flash chromatography using 50% diethyl ether/hexane to afford 57 mg (48% yield) of product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 2H), 7.28 (ddd, *J* = 8.7, 6.6, 1.1 Hz, 1H), 7.08 – 7.02 (m, 3H), 4.13 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 148.0, 136.0, 130.9, 126.2, 121.9, 121.5, 121.1, 120.2, 116.9, 114.5, 55.4, 38.4; IR 1608, 1501, 1360, 1245, 1173, 1112, 1005, 875, 833, 743, 657, 576, 517, 437 cm^{-1}; HRMS (EI); Mass calcd for $C_{15}H_{14}N_2O$ $[M]^+$: 238.1106; found 238.1104.



3az

2-Isopropyl-3-(*p*-tolyl)-2H-indazole (3az)[11]: Prepared according to the general procedure using 2-isopropyl-2*H*-indazole **1az**, and 4-methylbenzenediazonium tetrafluoroborate **2ad**. The reaction mixture was purified by flash chromatography using 10% diethyl ether/hexane to afford 29 mg (23% yield) of product as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J*

= 8.4 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 7.06 – 7.01 (m, 1H), 4.88 (hept, *J* = 6.6 Hz, 1H), 2.46 (s, 3H), 1.62 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 138.7, 135.0, 129.7, 129.7, 127.1, 125.9, 121.3, 121.0, 120.3, 117.3, 51.2, 23.3, 21.4; IR 3052, 2974, 2933, 2866, 2730, 1778, 1731, 1624, 1457, 1370, 1270, 1218, 1169, 1071, 1001, 893, 812, 742, 617, 571, 512 cm^{-1}; LRMS (EI); Mass calcd for $C_{17}H_{18}N_2$ $[M]^+$: 250; found 250.

4. Reaction profile

The reaction was monitored using different amounts of 2-phenyl-2*H*-indazole **1aa** (1.0 equiv. and 2.0 equiv. of **1aa** respectively). The isolated yield of the resulting product **3aa** was obtained over time (1, 3, 6, 9, 12, 15, 18 h, Fig. S1).

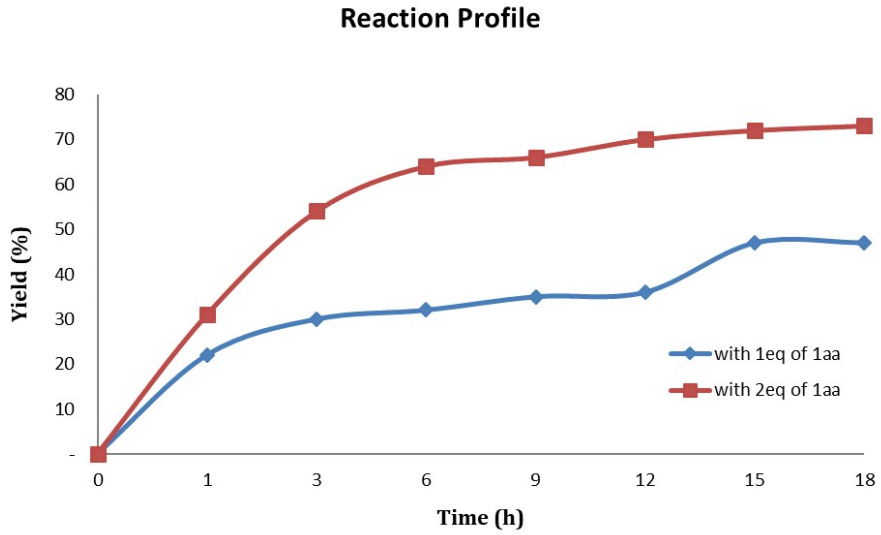


Figure S1. Reaction profile

In our optimization experiments, the addition of 2 equiv. of indazole **1aa** improved the reaction yield compared with only 1 equiv. of **1aa** (Table 1, entries 1 and 2, 47% vs 73% yield). Interestingly, only 1 equiv. of **1aa** reacted with aryl diazonium salt **2aa** to afford the desired product; 1 equiv. of starting indazole **1aa** was recovered after the reaction. It seems that the additional **1aa** might be helping to accelerate the reaction by controlling the overall reaction profile. In the presence of 2 equiv. of **1aa**, the yield increased smoothly over time. In contrast, in the presence of only 1 equiv. of **1aa**, the yield was around 30% after three hours, and then increased very slowly.

Mechanistic studies

1. UV-Vis absorption studies

1.1. Absorption spectra of individual components and the reaction mixture

Solutions of 2-phenyl-2*H*-indazole (**1aa**, 0.1 M in DMSO), 4-methoxybenzenediazonium tetrafluoroborate (**2aa**, 0.1 M in DMSO), pyridine (0.1 M in DMSO), a mixture of 2-phenyl-2*H*-indazole and 4-methoxybenzenediazonium tetrafluoroborate (1:1, 0.1 M in DMSO), a mixture of 2-phenyl-2*H*-indazole and pyridine (1:1, 0.1 M in DMSO), and a mixture of 2-phenyl-2*H*-indazole, 4-methoxybenzenediazonium tetrafluoroborate, and pyridine (1:1:1, 0.1 M in DMSO) were prepared individually. When a solution of **2aa** in DMSO was treated with **1aa**, the color of the mixture turned yellow, and a significant bathochromic shift was observed in the UV-vis spectrum, which is diagnostic of an EDA complex. A clear bathochromic shift was also observed with a mixture of **2aa** and pyridine in DMSO. Interestingly, a mixture of **1aa**, **2aa**, and pyridine showed a further bathochromic shift, thereby suggesting the formation of a ternary EDA complex.

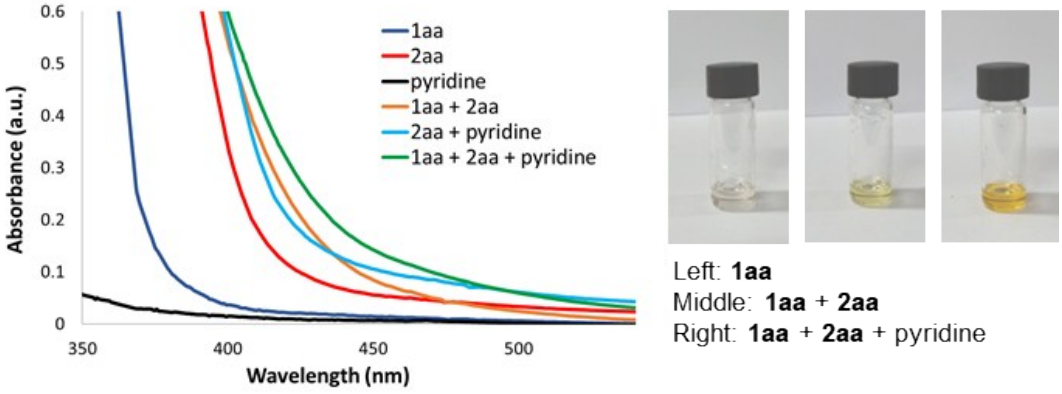


Figure S2. Absorption spectra of the individual reaction components and the reaction mixture.

1.2. Investigations into the role of pyridine.

To clarify the role of pyridine in forming the EDA complex, a 1:1 mixture of **1aa** and **2aa** in DMSO was treated with different amounts of pyridine (0–10 equiv.), and the absorption was analyzed by UV-vis spectroscopy. Solutions of 2-phenyl-2*H*-indazole and 4-methoxybenzenediazonium tetrafluoroborate (1:1, 0.2 M in DMSO) with varying amounts of pyridine (0, 0.5, 3.0, 5.0, 10.0 equiv.) were prepared separately. The intensity of the absorption increased upon increasing the pyridine concentration. These results suggest that pyridine would be involved in the formation of the EDA complex.

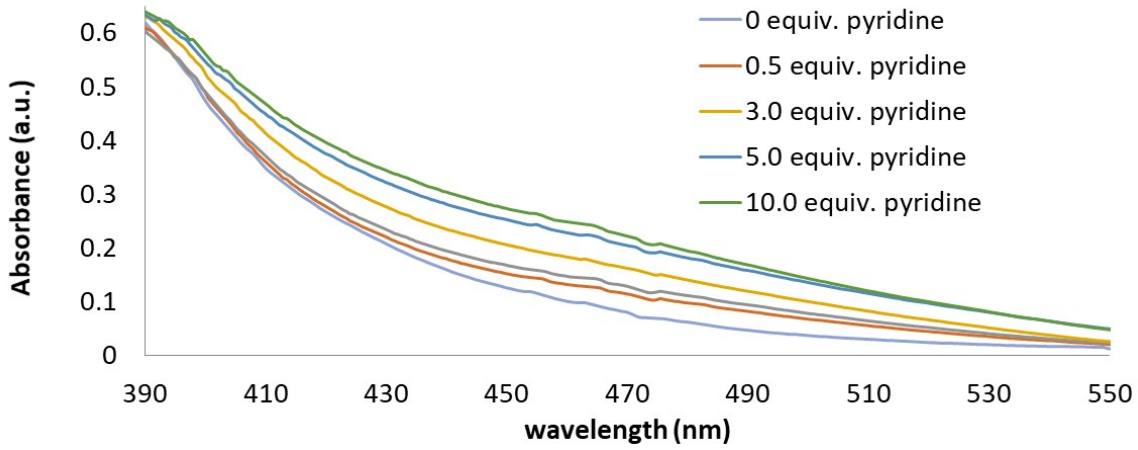


Figure S3. Absorption spectra of a 1:1 mixture of 1aa and 2aa with varying amounts of pyridine.

1.3. Monitoring of the ternary EDA complex formation.

Absorption spectra of 2-phenyl-2*H*-indazole **1aa**, 4-methoxybenzenediazonium tetrafluoroborate **2aa**, and pyridine (2:1:1, 0.1 M in DMSO) solution was recorded at different time with irradiation of 4 W blue LEDs (455nm).

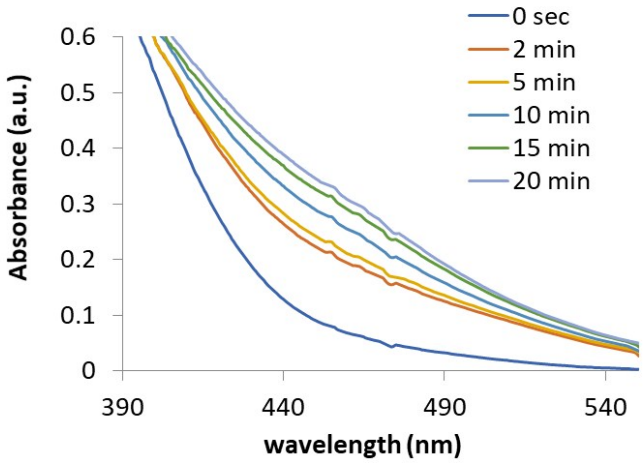


Figure S4. Monitoring of the absorption spectra the reaction mixture in different length of exposure to light.

1.4. Determination of the donor/acceptor ratio of EDA

The stoichiometry of the donor-acceptor complex was investigated by constructing a Job plot of the UV-Vis spectroscopy results. A solution of the donor (2-phenyl-2*H*-indazole **1aa**, 0.2 M in CH_3CN) and the acceptor (4-methoxybenzenediazonium tetrafluoroborate **2aa**, 0.2 M in CH_3CN) were prepared and then mixed with the ratio of donor/acceptor from 0% to 100%. All the absorption spectra were recorded in 1 cm path quartz cuvettes. Table S1 summarizes the observed absorption (Abs_{EDA}) associated to the variation of the donor/acceptor ratio at 425 nm of the EDA complex

Table S1: Values of Abs(EDA) for EDA in CH_3CN for different donor/acceptor ratios.

Ratio donor/acceptor	(% donor)	2-phenyl-2*H*-indazole (M)	4-methoxybenzene diazonium salt (M)	Abs_{EDA}
5/0	100	0.2	0.0	0.0208
4/1	80	0.16	0.04	0.1115
3/1	75	0.15	0.05	0.1079
2/1	67	0.1333	0.0667	0.1292
1/1	50	0.1	0.1	0.1353
1/2	33	0.0667	0.1333	0.1172
1/3	25	0.05	0.15	0.1091
1/4	20	0.04	0.16	0.0843
0/5	0	0.0	0.2	0.0210

From the above data, a symmetrical curve was obtained on plotting Abs_{EDA} vs. the donor/acceptor ratio (Fig. S5). The maximum absorption was obtained for a 1:1 mixture of **1aa**/**2aa**.

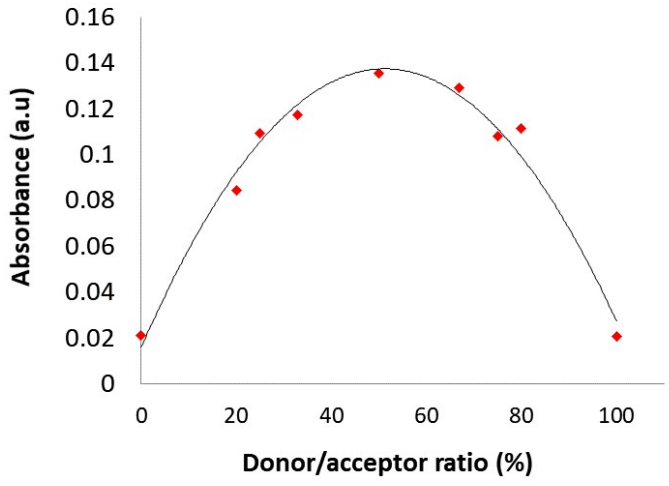


Figure S5. Job plot

2. NMR studies

^{1}H NMR spectra of 4-methoxybenzenediazonium tetrafluoroborate (**2aa**), and the reaction mixture in DMSO-d_6 were measured. The result showed that the aryl diazonium salt would act as an electron-acceptor in the EDA complex, a noticeable chemical shift of the methoxy group of **2aa** was observed in the presence of **1aa** and pyridine (Fig. S6).

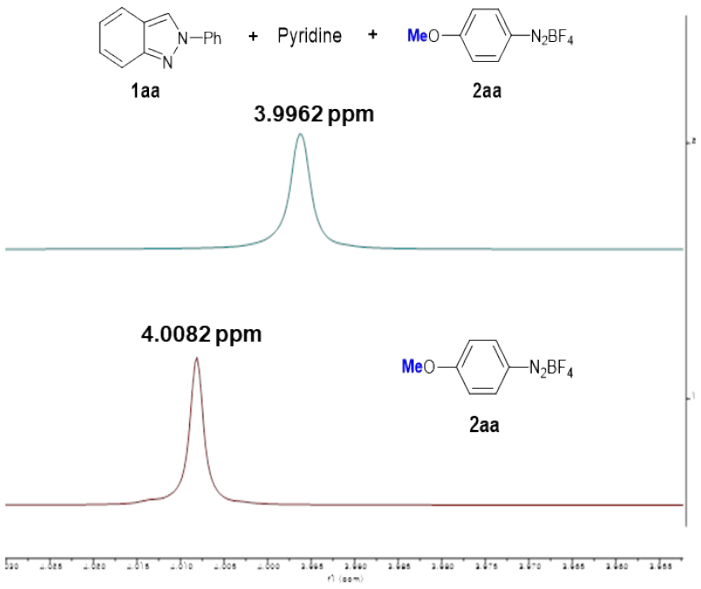


Figure S6: ^{1}H NMR spectra of 4-methoxybenzenediazonium tetrafluoroborate (2aa), and the reaction mixture in DMSO-d_6

In more detail, we could observe a noticeable chemical shift of the methoxy group of **2aa** in the presence of **1aa** in DMSO-d_6. A clear chemical shift is also observed in the presence of pyridine even though reduced differences in chemical shift were observed in this case (Fig. S7). The result supports that the aryl diazonium salt would act as an electron-acceptor in the EDA complex. In addition, other experimental results such as UV-Vis and Job plot experiments support the formation of a ternary EDA complex. Based on these results, we suggested that pyridine, aryl diazonium salts, and indazole would be involved in the formation of a ternary EDA complex (1:1:1 ratio).

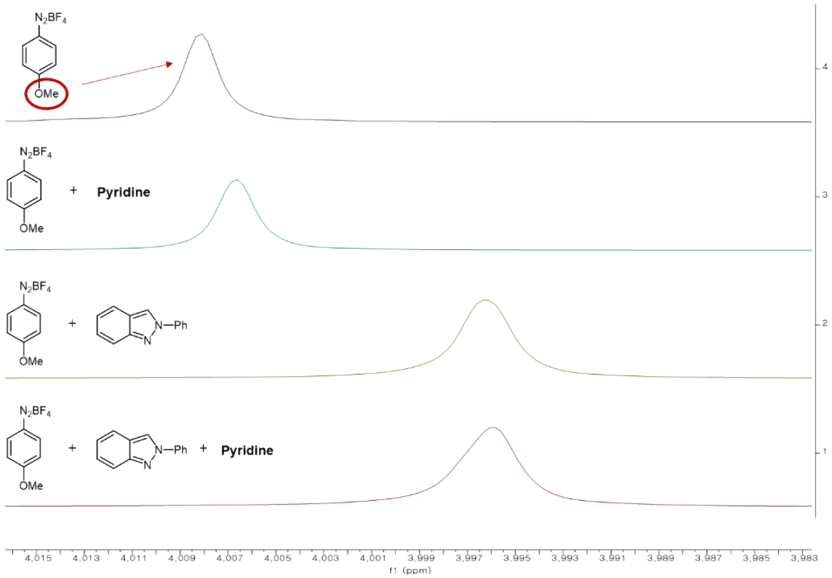
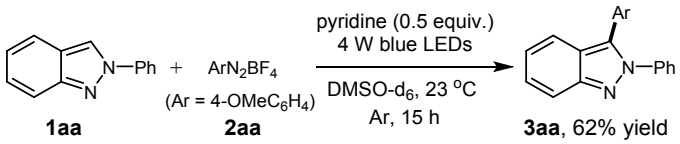
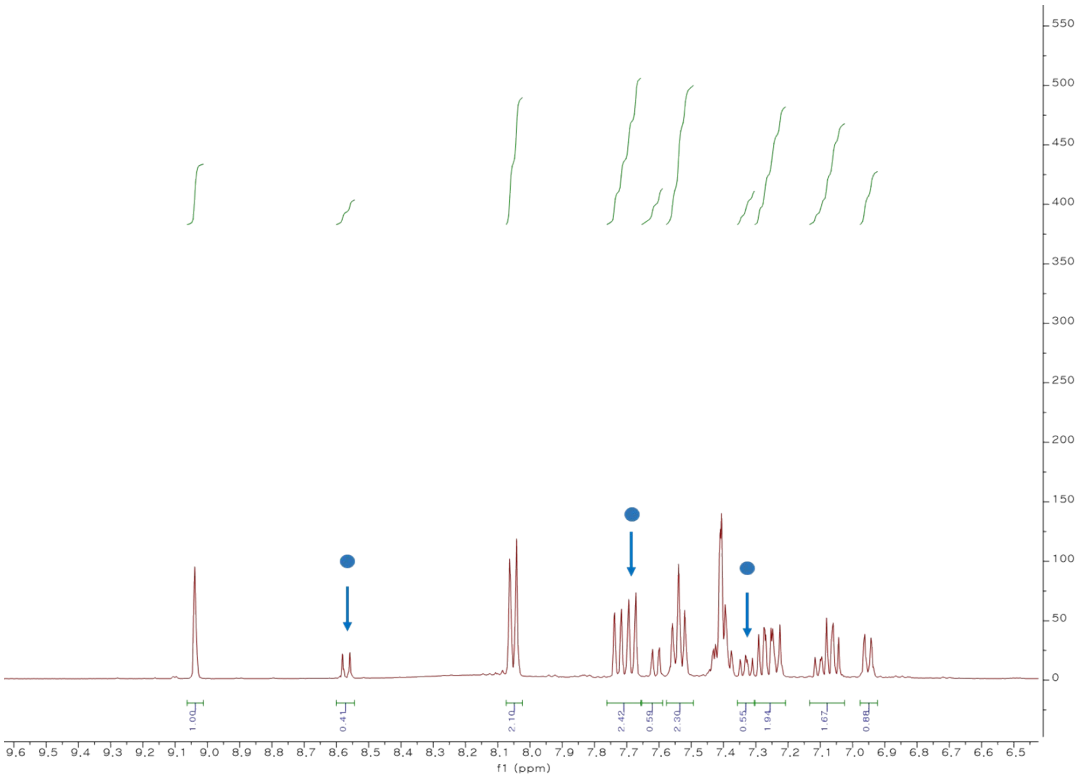


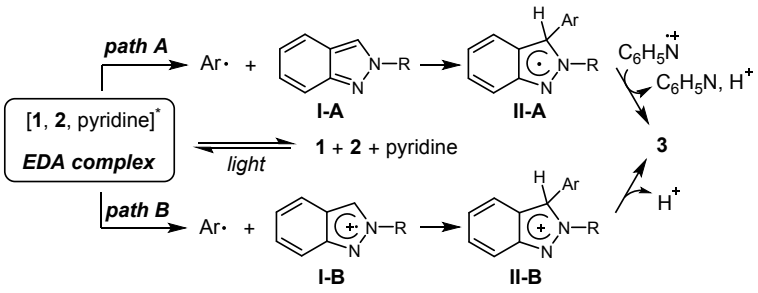
Figure S7: ^{1}H NMR spectra of 4-methoxybenzenediazonium tetrafluoroborate (2aa), and the reaction mixtures in DMSO-d_6

Next, to demonstrate the reaction mechanism in more detail, we have performed additional NMR studies. If the intermediate **II-A** would be oxidized by pyridinium radical cation, pyridine would be recovered. To check this, we carried out the reaction in the presence of 0.5 equiv. of pyridine in DMSO-d_6. After 15 h, the crude mixture was simply filtered using a syringe filter, and directly measured by ^{1}H NMR.





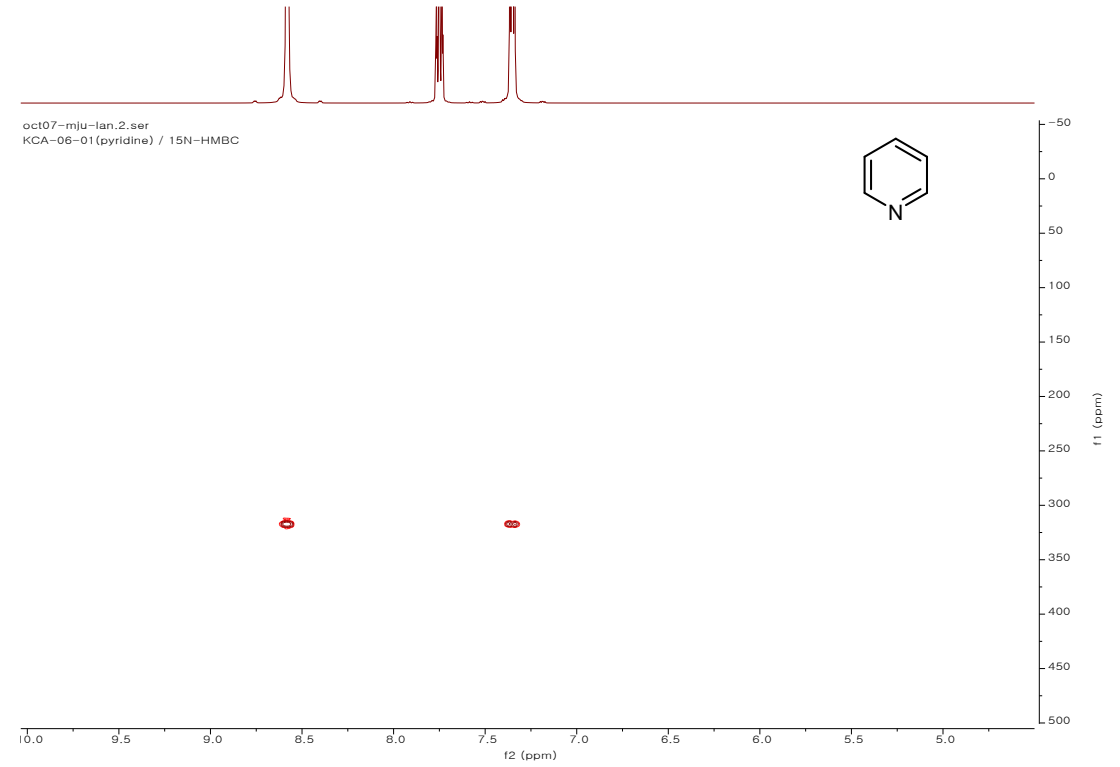
We could observe pyridine after the reaction in the crude sample (blue point parts). Based on these results, we have provided a proposed reaction mechanism in Scheme 3.

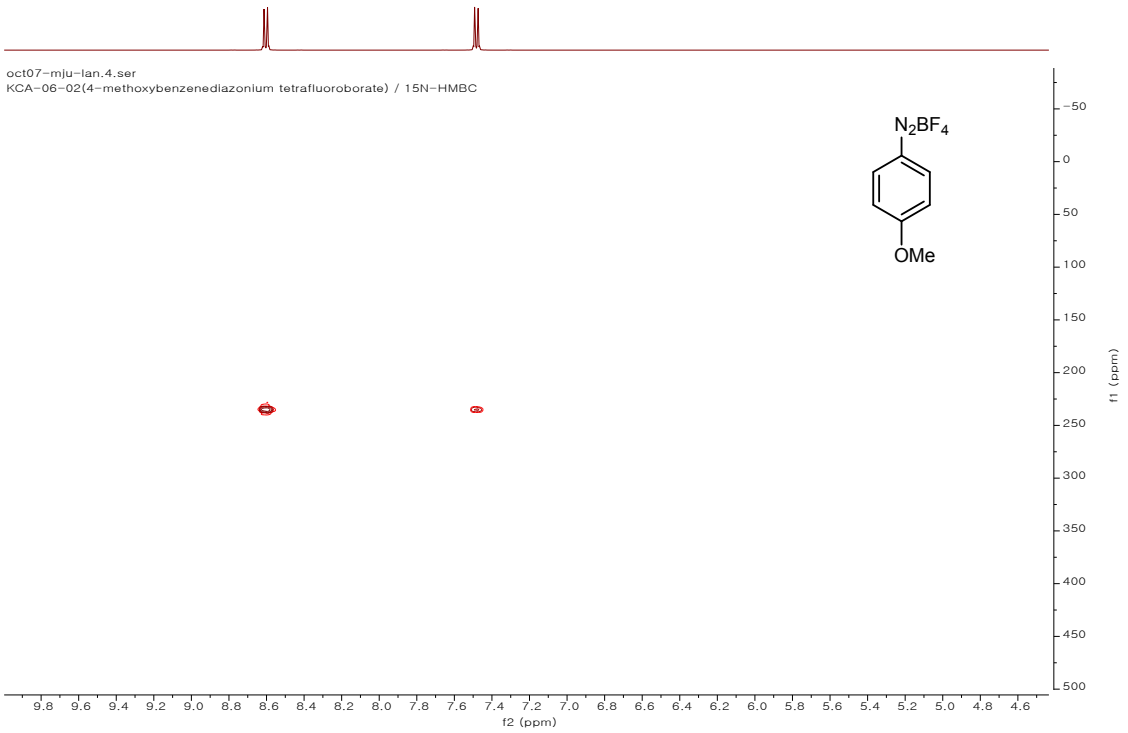


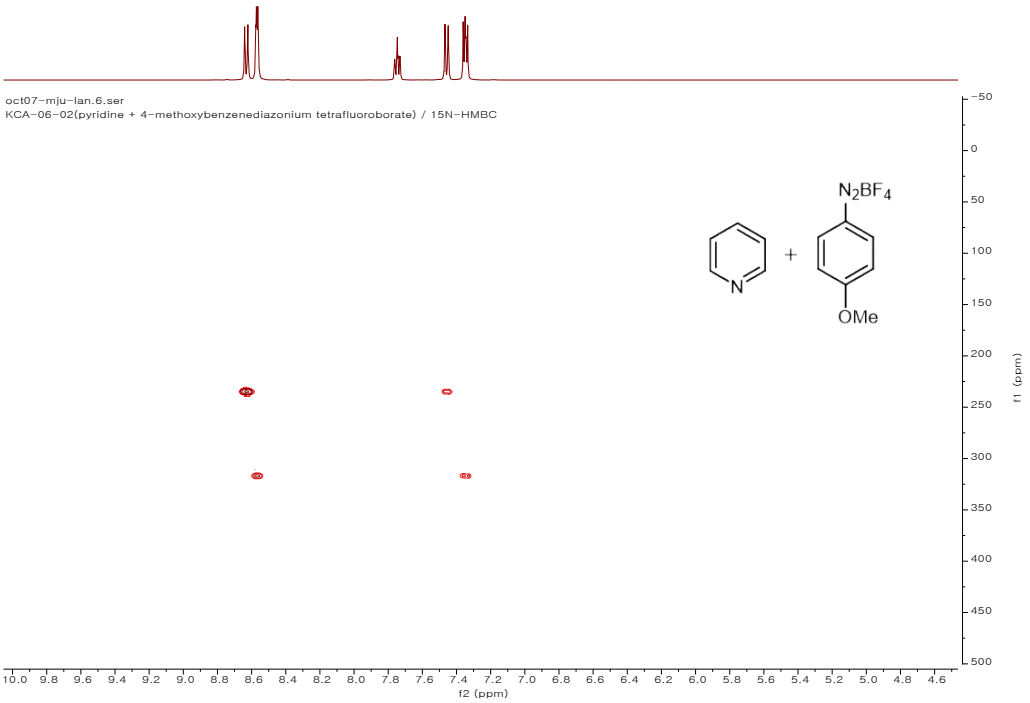
^{1}H-^{15}N HMBC Studies

It is known that diazopyridinium salts (which are not considered as EDA complexes) could be formed at low temperatures.[12] To prove the formation of the real photochemical intermediate of our study, we performed ^{1}H-^{15}N HMBC NMR studies.[13] We analyzed pyridine and **2aa** (aryl diazonium salt) individually and the mixtures of both in DMSO-d_6. Only ^{1}H-^{15}N correlations of individual pyridine

and **2aa** were observed in the mixture solution, and other possible active intermediates such as diazopyridinium salts were not detected.

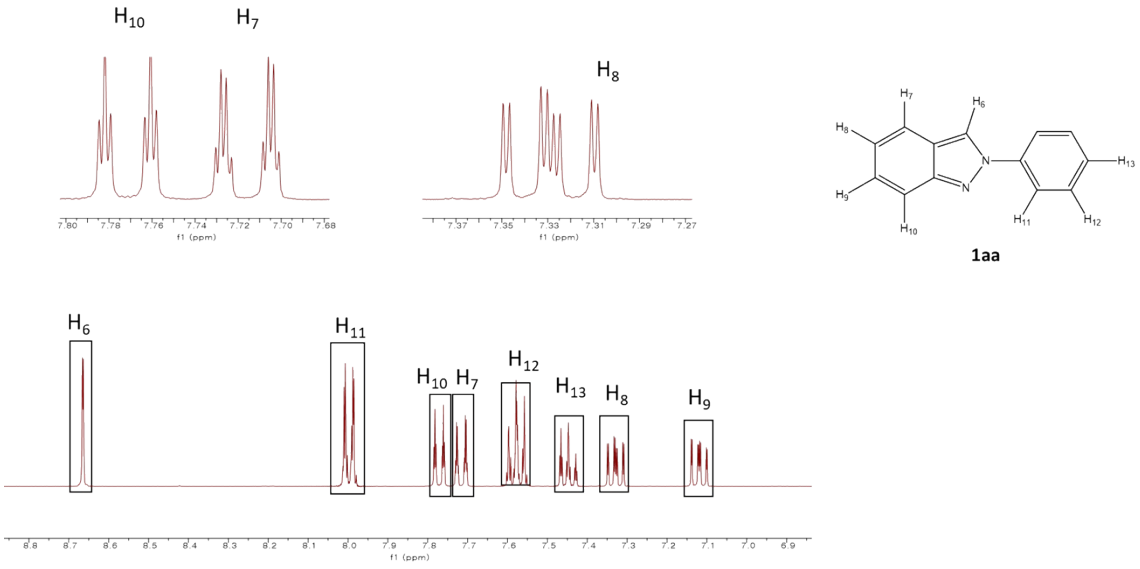




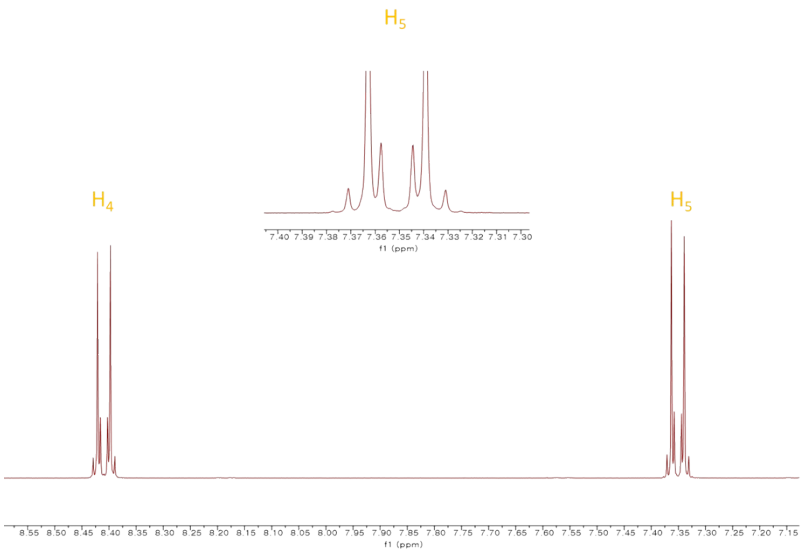


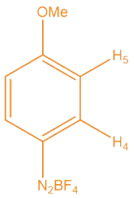
NOESY / DOSY Studies

In NOESY studies, we observed possible correlations between **1aa-2aa**, and **2aa-pyridine** in mixtures.

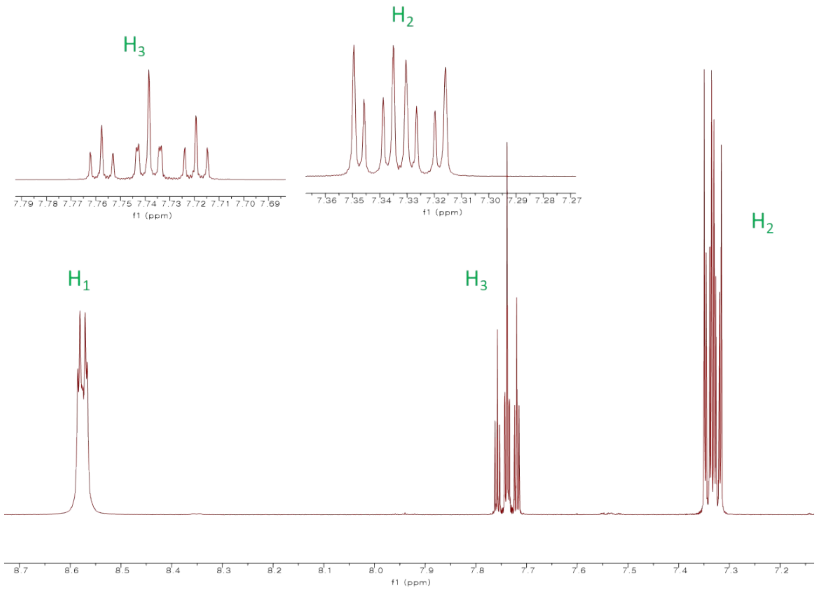


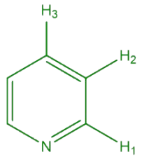
1aa



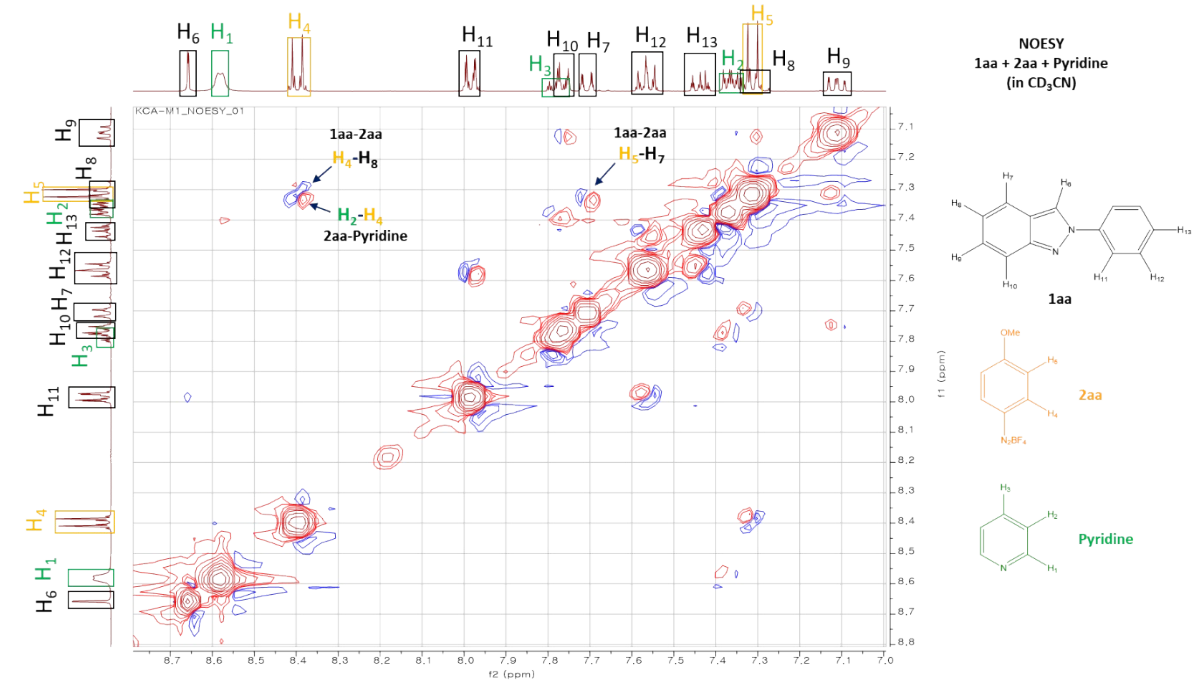


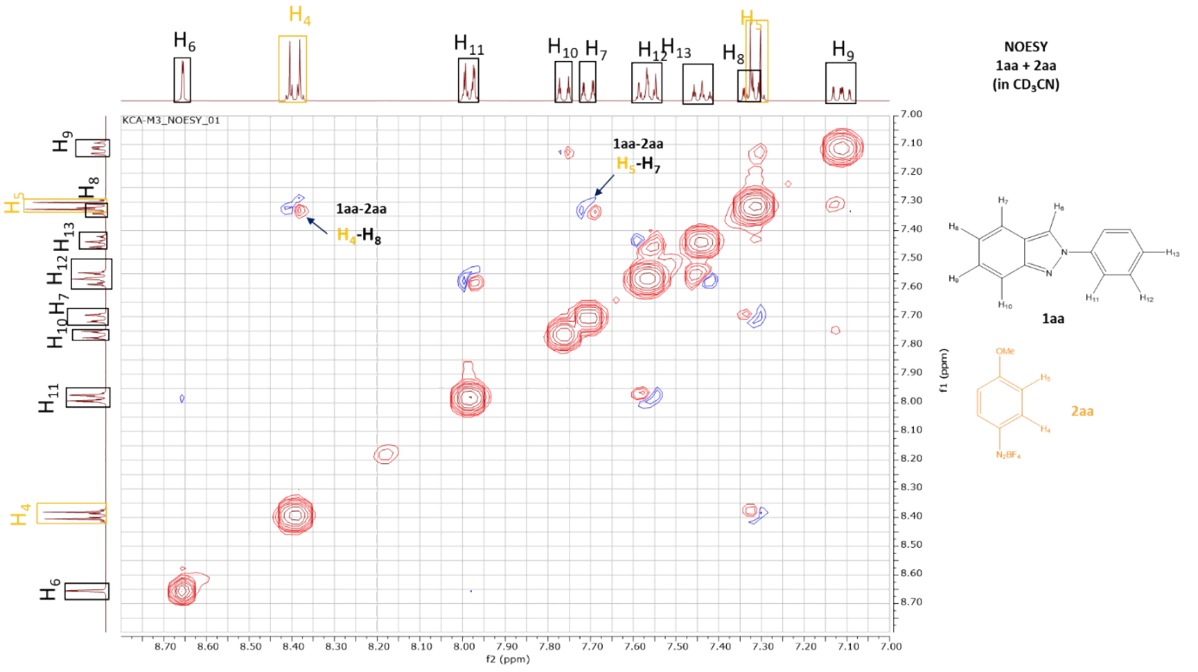
2aa

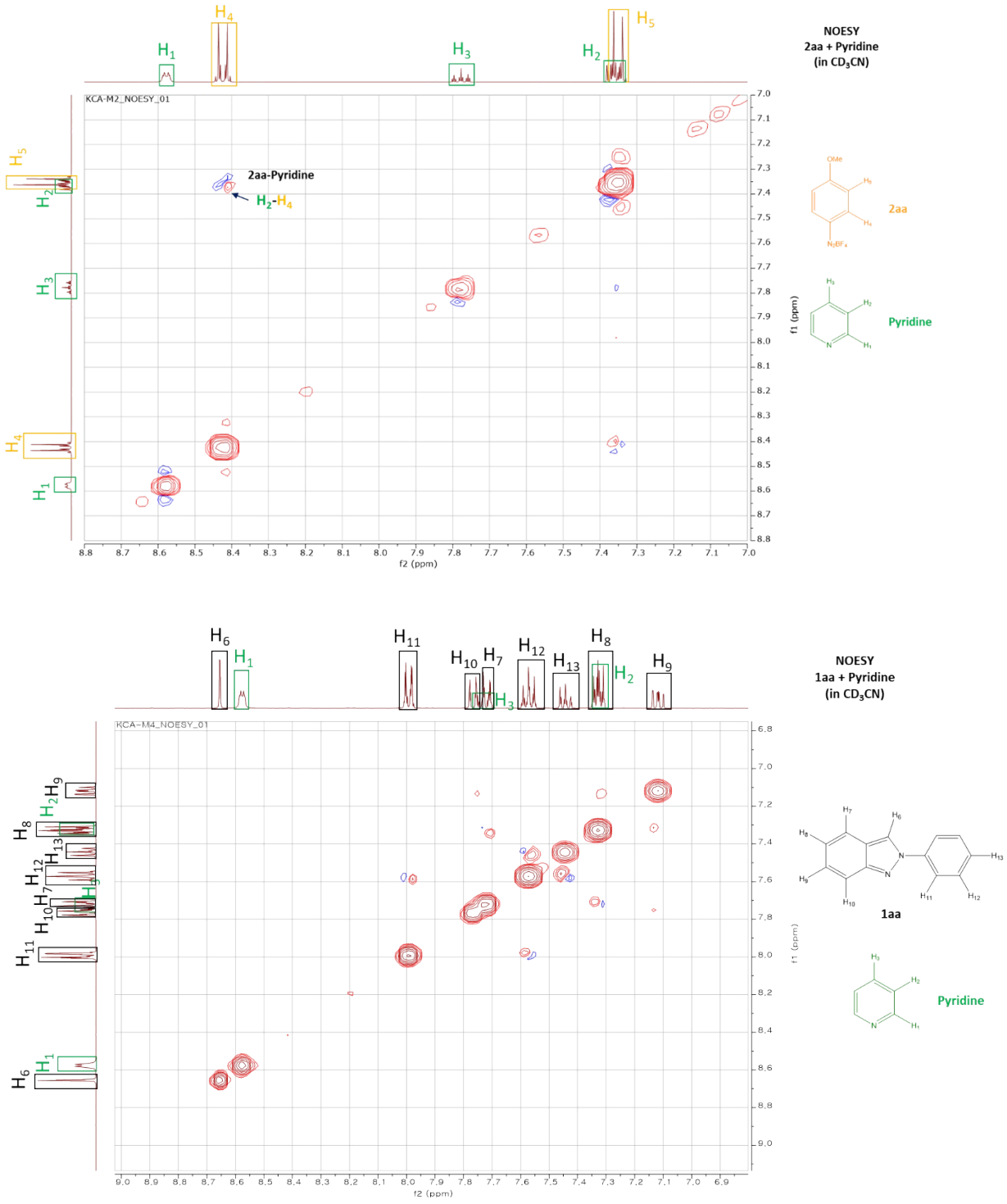




Pyridine


KCA-M1_NOESY_01
1aa-2aa
H4-H8
H2-H4
2aa-Pyridine
1aa-2aa
H5-H7
f2 (ppm)
f1 (ppm)
NOESY
1aa + 2aa + Pyridine
(in CD3CN)
1aa
2aa
Pyridine


KCA-M3_NOESY_01
1aa-2aa
H4-H8
1aa-2aa
H5-H7
f2 (ppm)
f1 (ppm)
NOESY
1aa + 2aa
(in CD3CN)
1aa
2aa

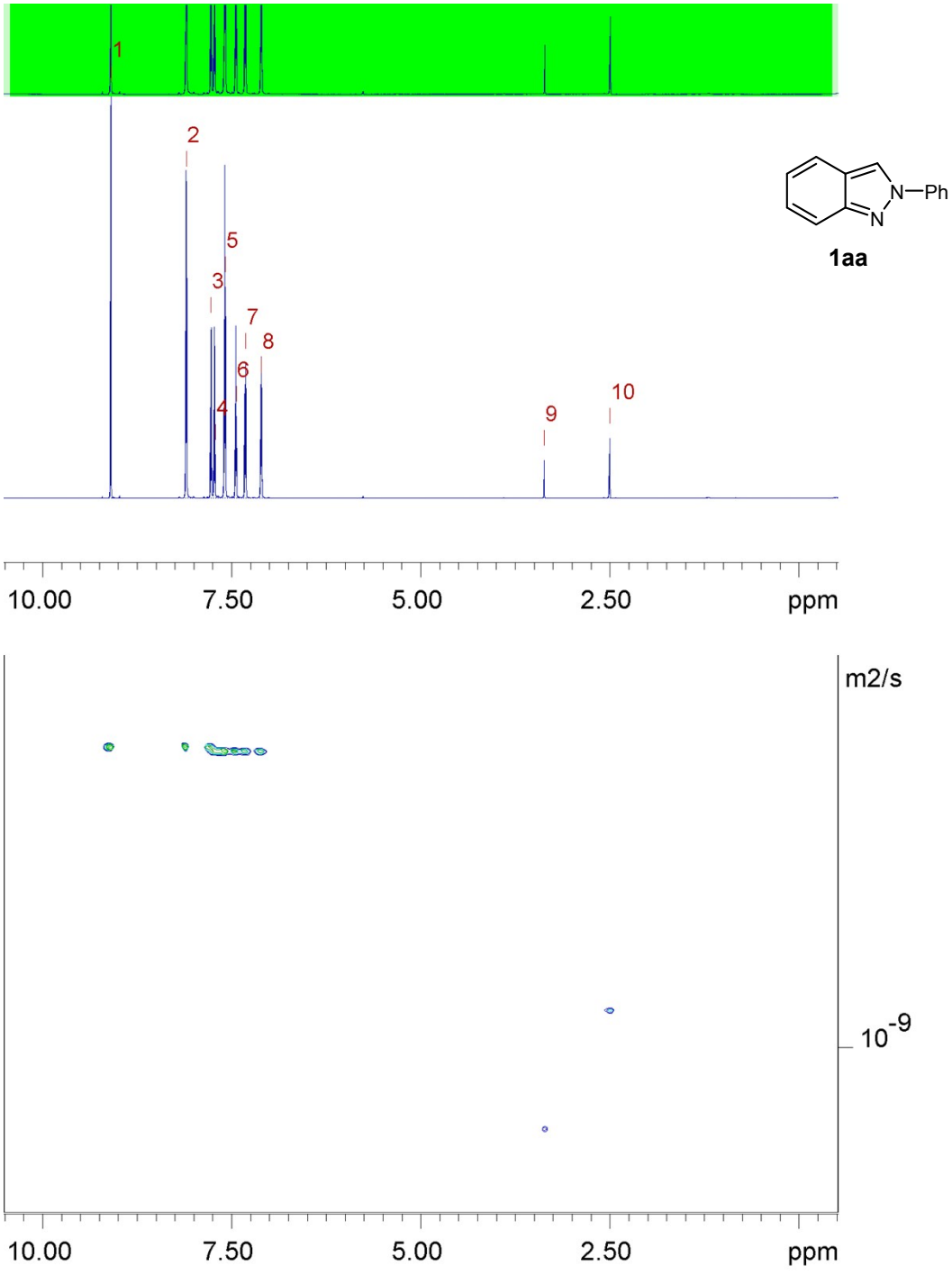


In DOSY studies, the D value (Diffusion coefficient) was decreased when we measured the mixture (**1aa**+**2aa**, **2aa**+pyridine, **1aa**+**2aa**+pyridine). On the other hand, in the mixture of **1aa** and pyridine, the D value was not decreased. Pyridine and **1aa** would act as an electron donor, therefore, they would not form an EDA complex. These results would support the formation of a ternary EDA complex even though the difference of the D value was not that big. The main reason for the small

difference in the D value would be because of the little difference in size of these compounds (**1aa**, **2aa**, and pyridine).

DOSY NMR (in DMSO-d_6)

1aa



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used big delta:	0.049900 s
used gradient strength:	variable
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Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
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Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

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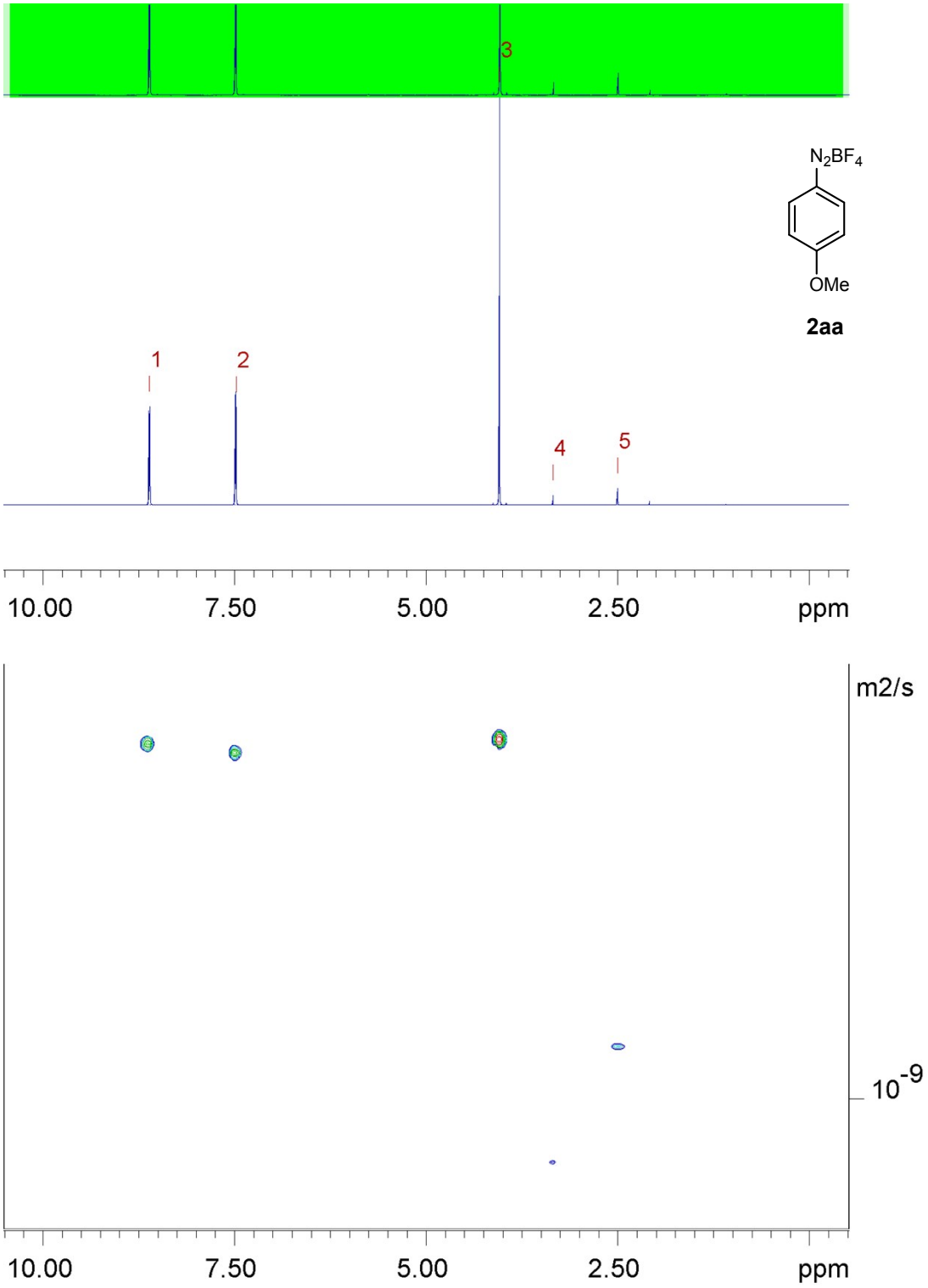
4	7.718	5.38e-10	1.630e-12
5	7.586	5.37e-10	9.202e-13
6	7.441	5.38e-10	9.970e-13
7	7.314	5.39e-10	1.100e-12
8	7.105	5.38e-10	1.784e-12
9	3.364	1.19e-09	1.002e-11
10	2.500	9.25e-10	2.058e-12

DOSY NMR (in DMSO-d_6)

2aa



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used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
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Used Gradient strength:	all values (including replicates) used

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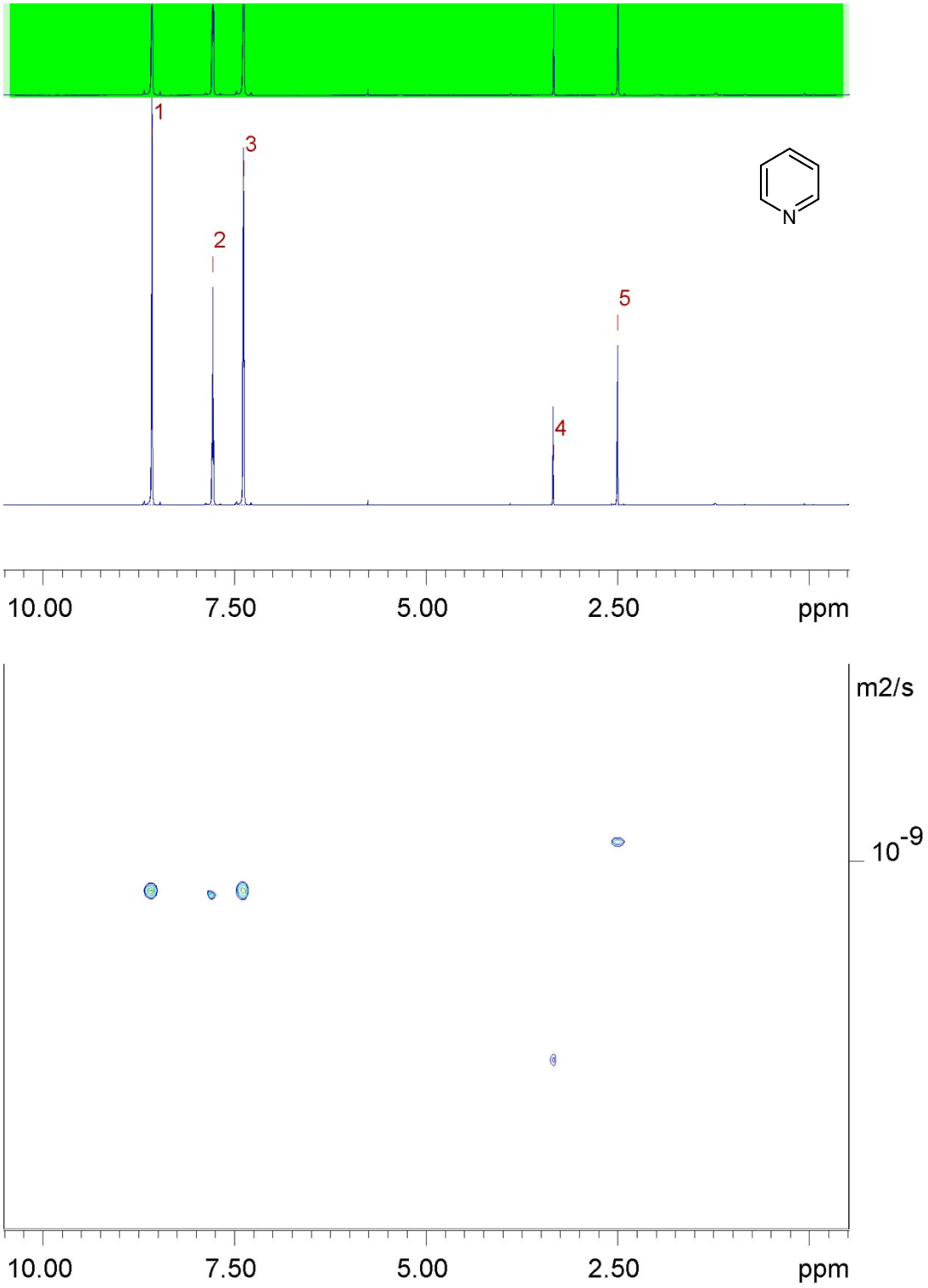
3	4.041	3.99e-10	4.540e-12
4	3.343	1.17e-09	4.163e-12
5	2.499	8.69e-10	2.580e-12

DOSY NMR (in DMSO-d_6)

Pyridine



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used little delta:	0.0020000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
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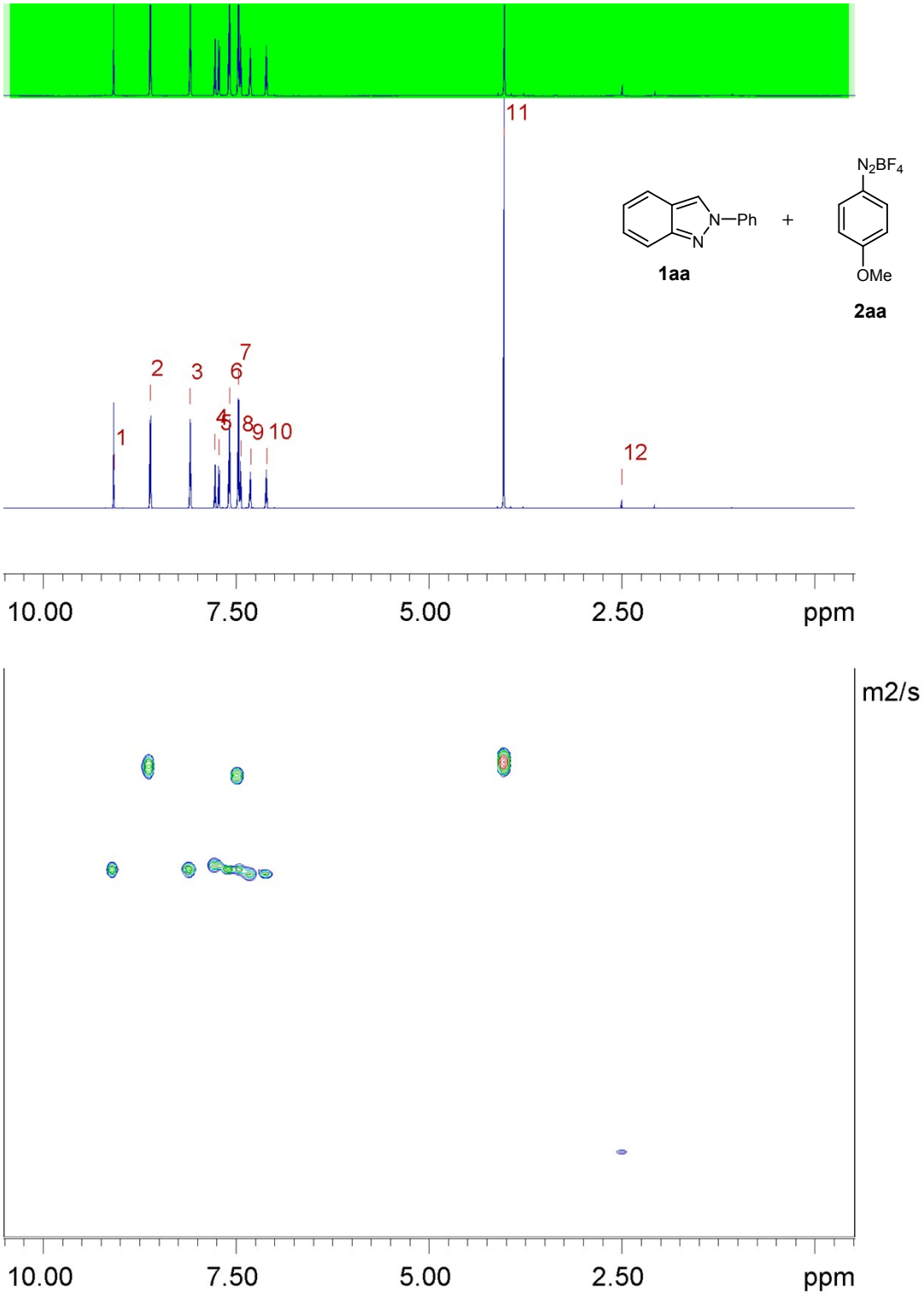
3	7.378	1.03e-09	7.044e-12
4	3.338	1.23e-09	9.923e-12
5	2.499	9.79e-10	4.356e-12

DOSY NMR (in DMSO-d_6)

1aa + **2aa**



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used little delta:	0.0020000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
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Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2	D [m2/s]	error
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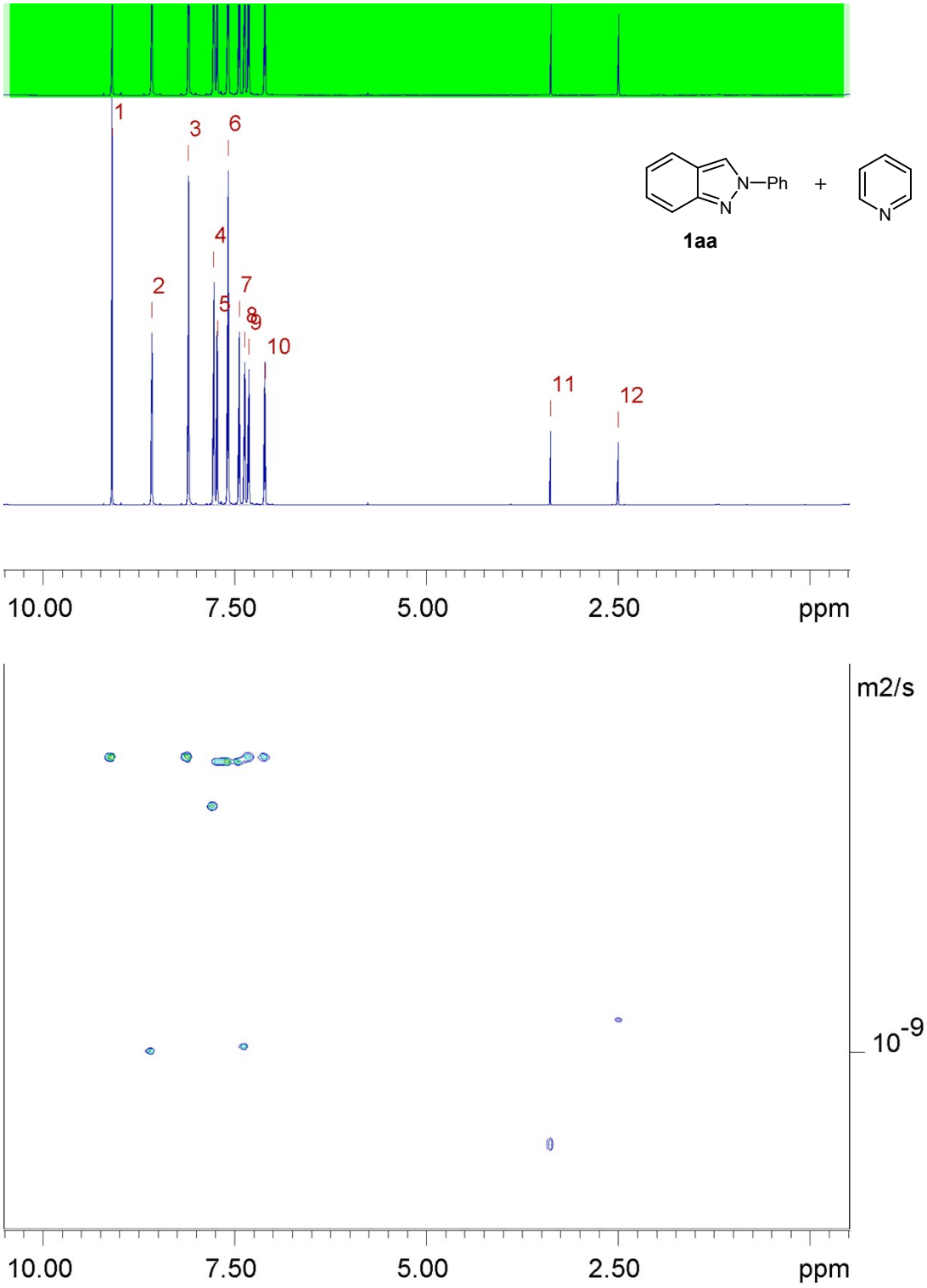
3	8.095	4.74e-10	3.355e-12
4	7.774	4.73e-10	3.602e-12
5	7.725	4.72e-10	2.979e-12
6	7.584	4.76e-10	2.086e-12
7	7.473	3.93e-10	3.491e-12
8	7.440	4.76e-10	3.044e-12
9	7.312	4.80e-10	3.685e-12
10	7.104	4.78e-10	2.788e-12
11	4.026	3.83e-10	5.125e-12
12	2.499	8.35e-10	3.278e-12

DOSY NMR (in DMSO-d_6)

1aa + **Pyridine**

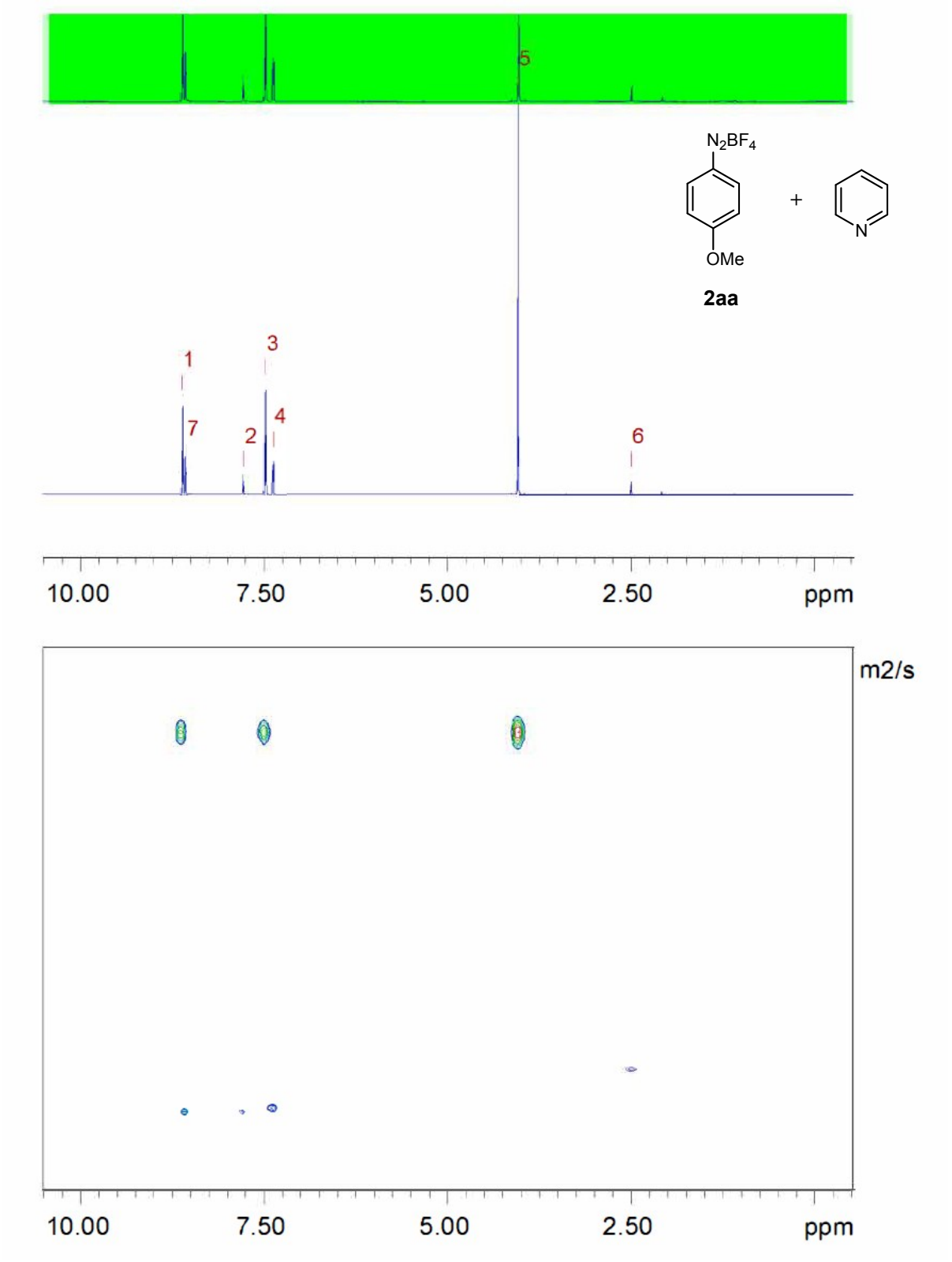


Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0020000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from E:/Data/nmrsu/oct24-mju-lan- DOSY/41/pdata/1/peaklist1D.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2	D [m2/s]	error
1	9.095	5.38e-10	3.153e-12
2	8.580	1.00e-09	3.100e-12
3	8.104	5.40e-10	3.453e-12
4	7.775	5.97e-10	4.075e-12
5	7.720	5.45e-10	3.238e-12
6	7.584	5.43e-10	2.278e-12
7	7.439	5.46e-10	2.305e-12
8	7.368	9.90e-10	3.953e-12
9	7.313	5.42e-10	4.441e-12
10	7.104	5.41e-10	3.849e-12
11	3.382	1.22e-09	1.948e-11
12	2.499	9.34e-10	3.212e-12

DOSY NMR (in DMSO-d_6)

2aa + **Pyridine**

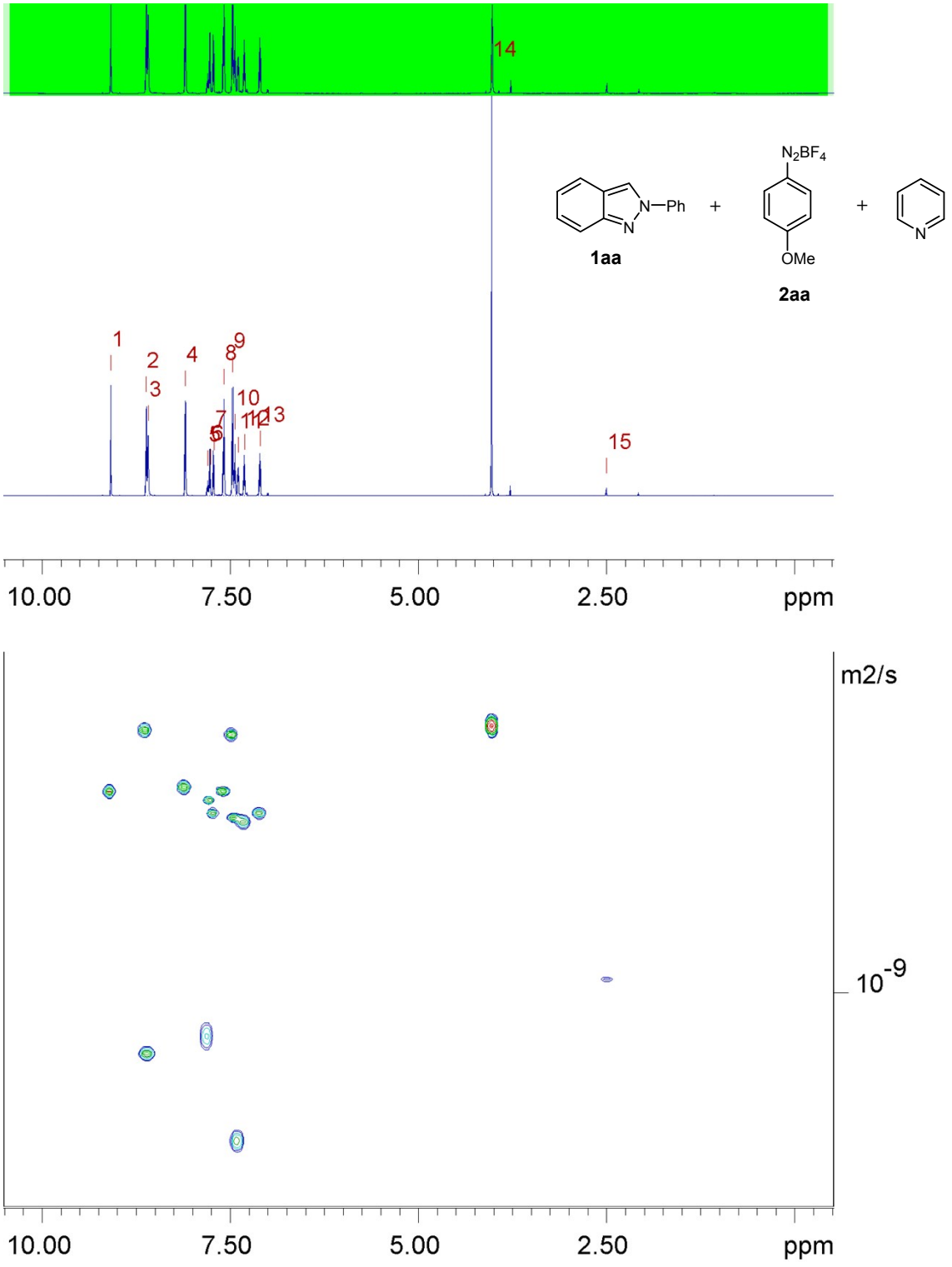


Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0020000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from E:/Data/nmrsu/oct24-mju-lan- DOSY/21/pdata/1/peaklist1D.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2	D [m2/s]	error
1	8.617	4.01e-10	7.003e-12
2	7.778	9.47e-10	5.806e-12
3	7.487	4.02e-10	6.953e-12
4	7.376	9.41e-10	6.511e-12
5	4.038	4.00e-10	7.533e-12
6	2.499	8.66e-10	6.099e-12
7	8.569	9.53e-10	4.262e-12

DOSY NMR (in DMSO-d_6)

1aa + **2aa** + **Pyridine**



Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0020000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from E:/Data/nmrsu/oct24-mju-lan-DOSY/11/pdata/1/peaklist1D.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	D [m2/s]	error
1	9.084	4.77e-10	4.765e-12
2	8.617	3.86e-10	4.613e-12
3	8.586	0.97e-09	1.101e-11
4	8.097	4.75e-10	5.036e-12
5	7.797	0.92e-09	3.422e-11
6	7.764	4.91e-10	4.284e-12
7	7.716	4.95e-10	4.966e-12
8	7.582	4.81e-10	3.863e-12
9	7.471	3.98e-10	3.766e-12
10	7.437	4.97e-10	4.553e-12
11	7.392	1.26e-09	2.867e-11
12	7.311	5.11e-10	6.637e-12
13	7.103	4.95e-10	5.426e-12
14	4.024	3.81e-10	6.796e-12
15	2.499	9.68e-10	7.808e-12

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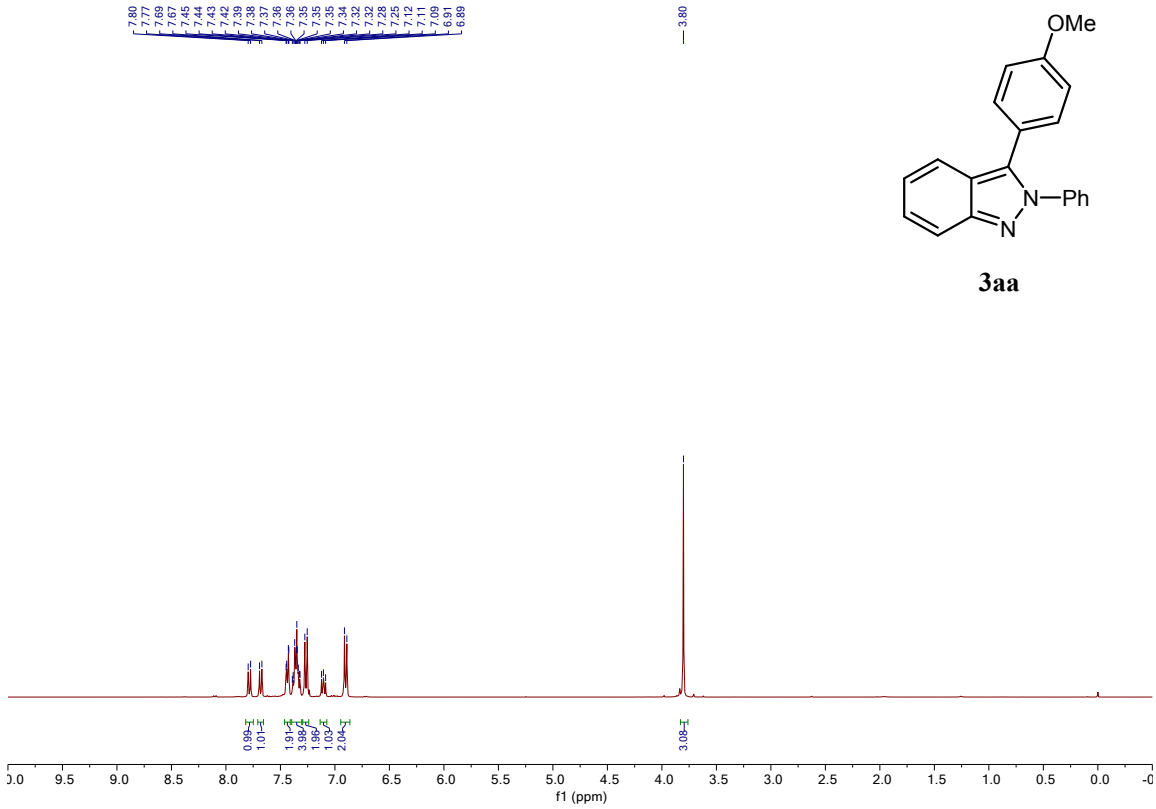
NMR spectra



3aa


7.82
7.82
7.81
7.80
7.79
7.79
7.59
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7.58
7.57
7.56
7.56
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.39
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7.33
7.32
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7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.24 cdcl3
7.11
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7.09
7.09
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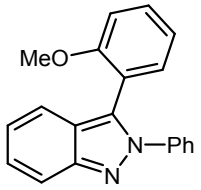
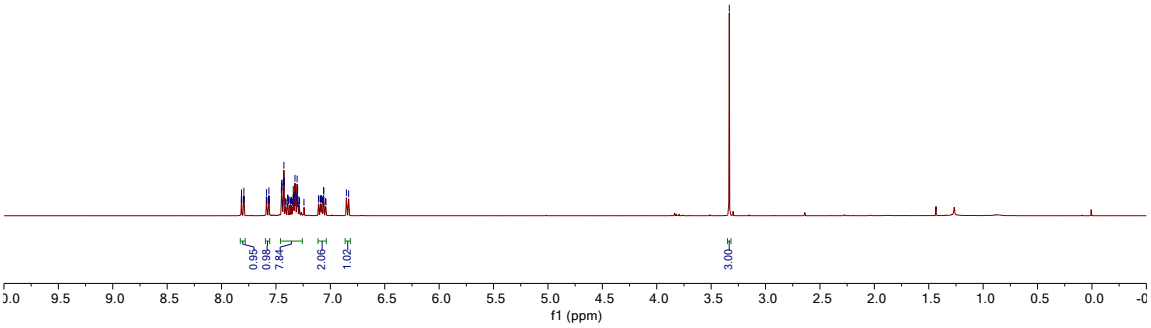
7.06
7.04
7.04
6.85
6.83
3.33


MeO
N—Ph
N

3ab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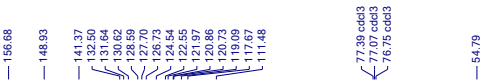
0.98
7.84
2.06
1.02
3.00
f1 (ppm)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148.93
141.37
132.50
131.64
130.62
128.59
127.70
126.73
124.54
122.55
121.97
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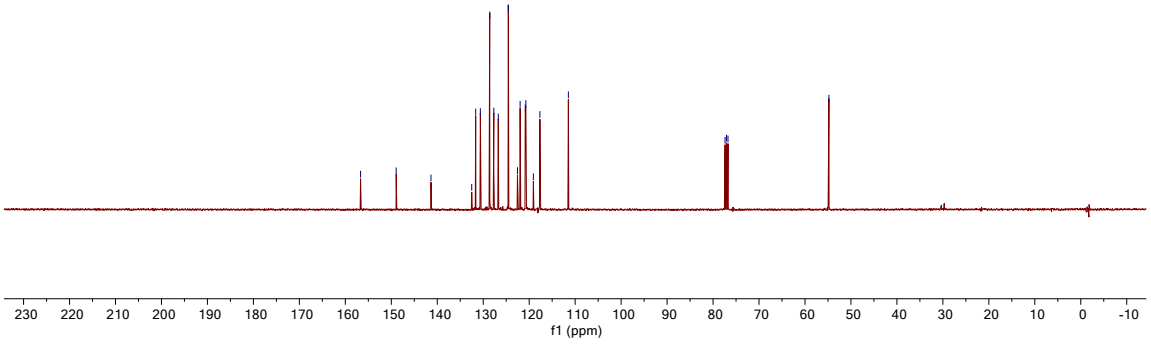
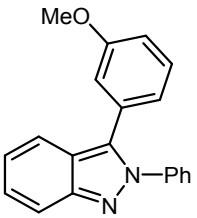
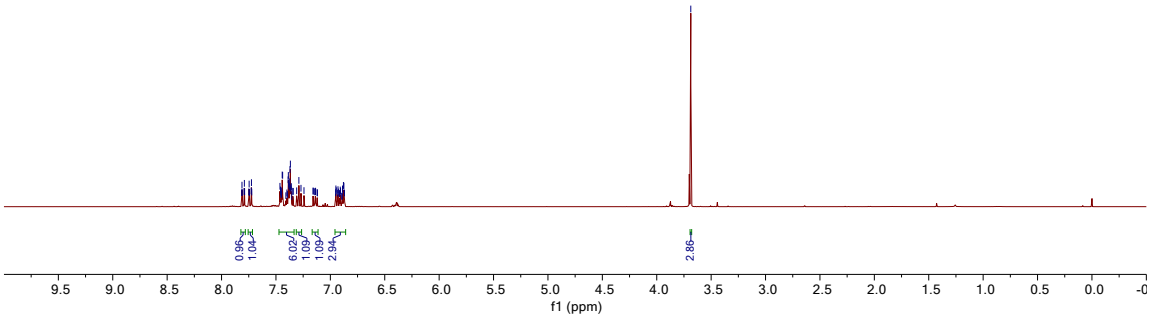
77.39 cdcl3
77.07 cdcl3
76.75 cdcl3
54.79


f1 (ppm)


7.81 7.81 7.81 7.79 7.79 7.79 7.75 7.75 7.74 7.73 7.73 7.72 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.31 7.29 7.27 7.24 cdcl3 7.16 7.16 7.14 7.14 7.14 7.12 7.12 6.95 6.95 6.95 6.93 6.93 6.93 6.92 6.91 6.91 6.91 6.89 6.89 6.89 6.89 6.88 6.88 6.88 6.87 3.69


MeO
N—Ph
N

3ac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1.09
1.09
2.94
2.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.64
148.95
140.25
135.25
131.04
129.83
129.00
128.30
127.01
126.02
122.55
122.10
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120.55
117.76
114.84
114.21
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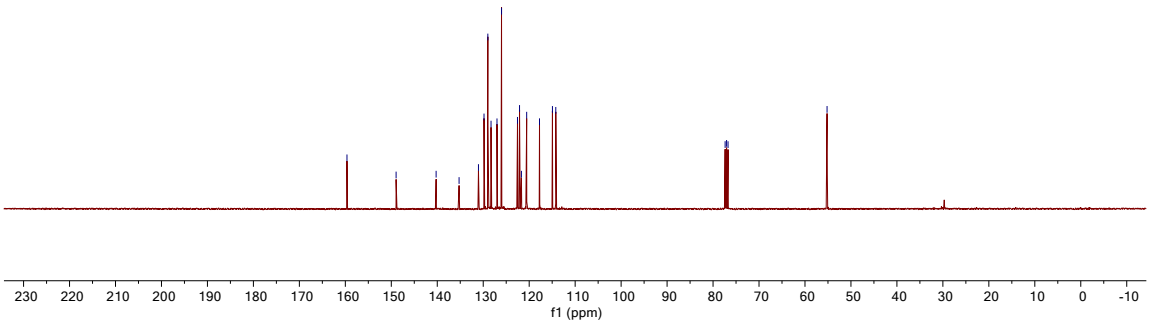
77.06 cdcl3
76.74 cdcl3
55.20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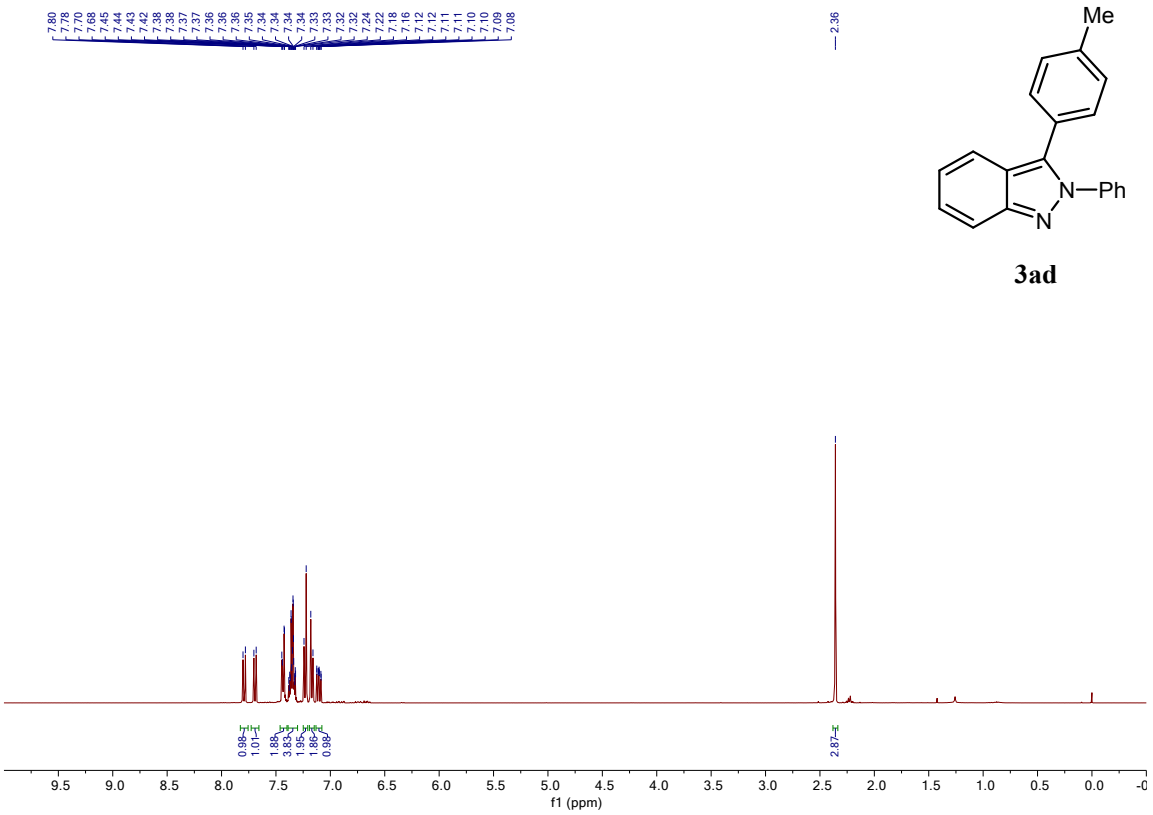
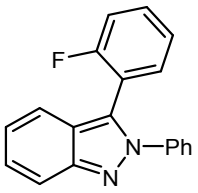
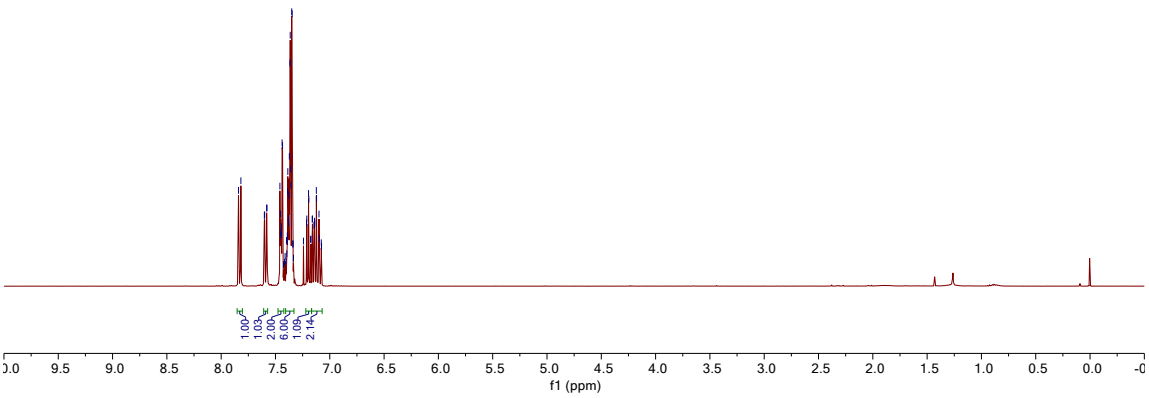
f1 (ppm)


Me
N—Ph
N
3ad
f1 (ppm)
f1 (ppm)


F
N—Ph
N

3ae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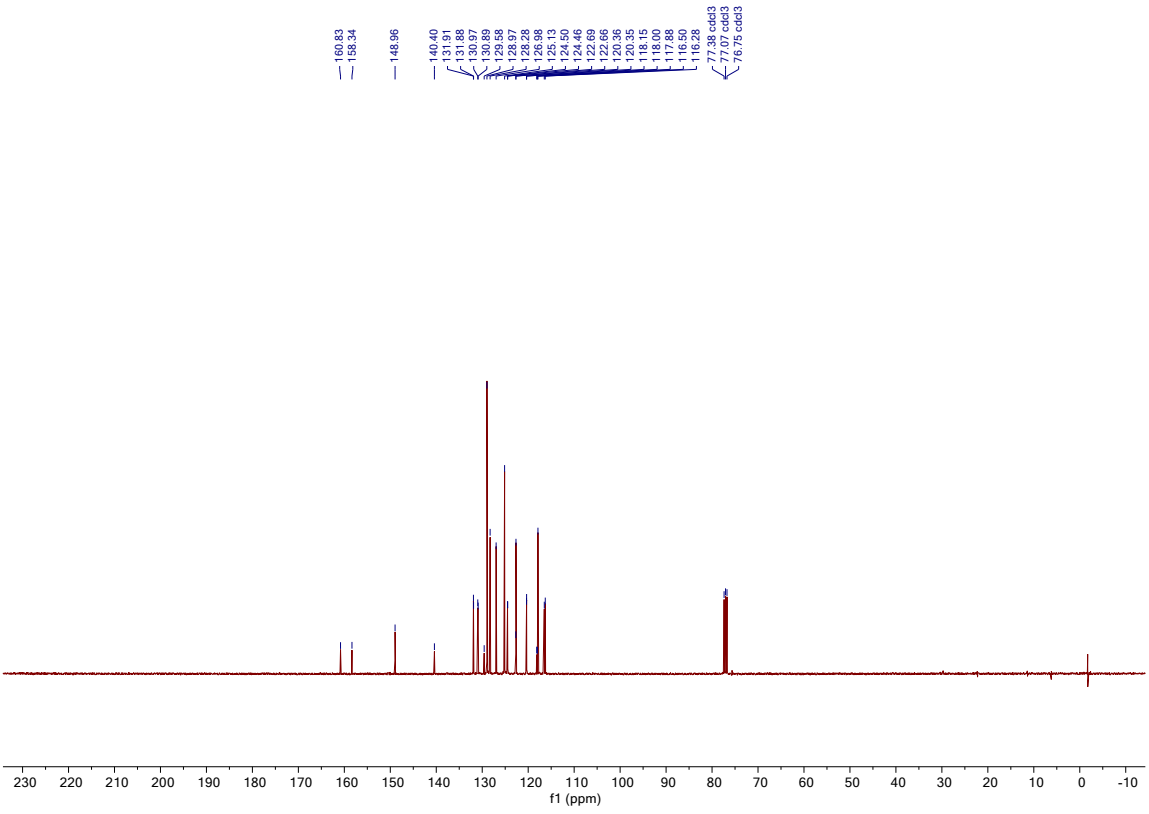
f1 (ppm)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158.34
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128.28
126.98
125.13
124.50
124.46
122.69
122.66
120.36
120.35
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117.88
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116.28
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77.07 cdcl3
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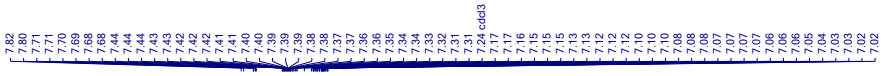
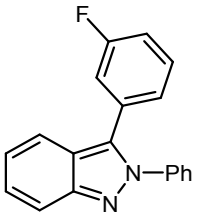
f1 (ppm)





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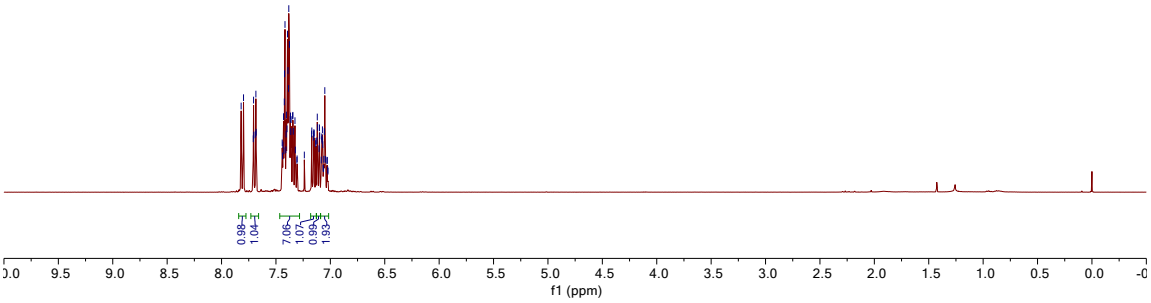

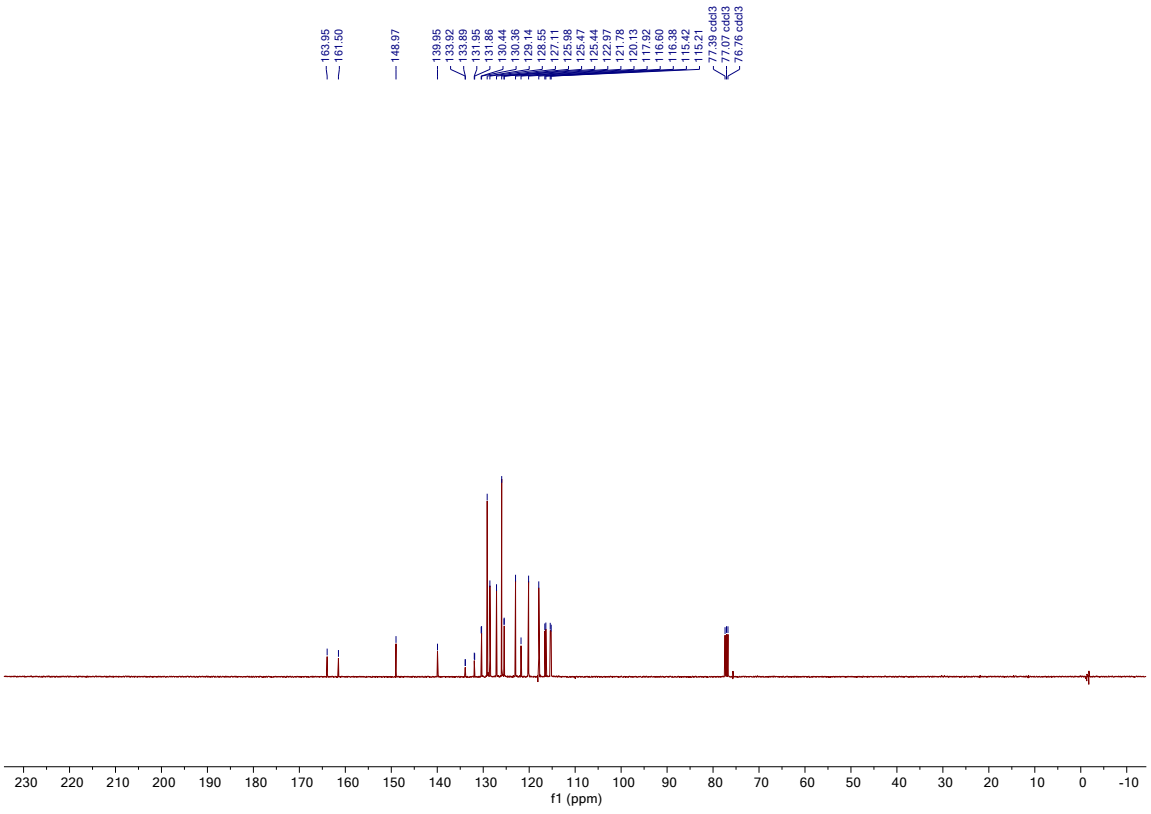


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7.66
7.63
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7.41
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7.39
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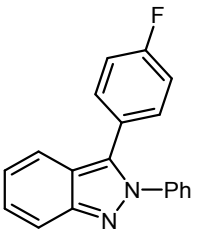
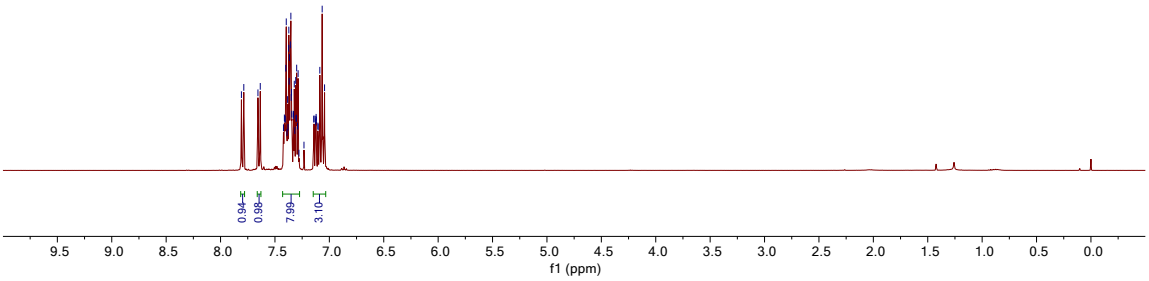
7.07
7.04


F
N—Ph
N

3ag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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.81
161.33
148.96
140.04
134.34
131.51
131.43
129.09
128.40
127.07
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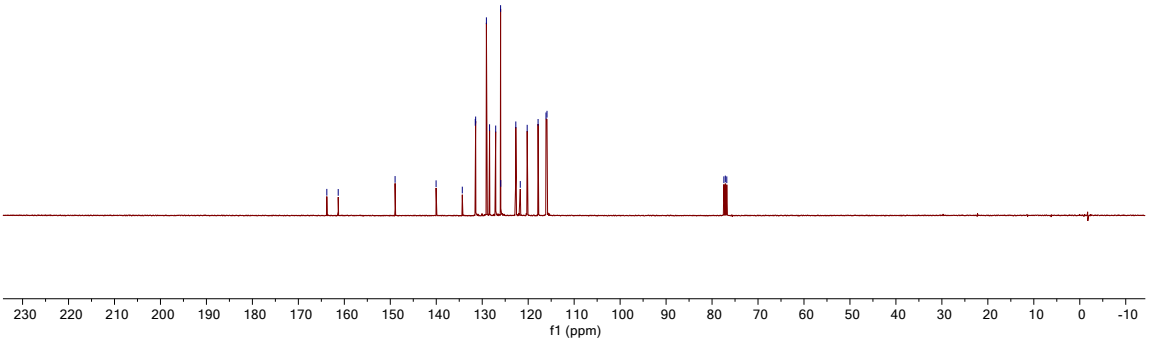
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80
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60
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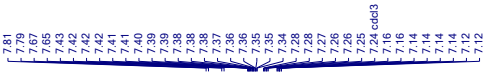
40
30
20
10
0
-10
f1 (ppm)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7.39
7.39
7.38
7.38
7.37
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7.36
7.35
7.35
7.34
7.28
7.28
7.27
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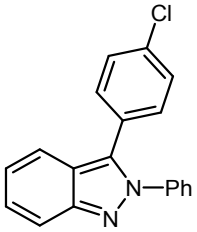
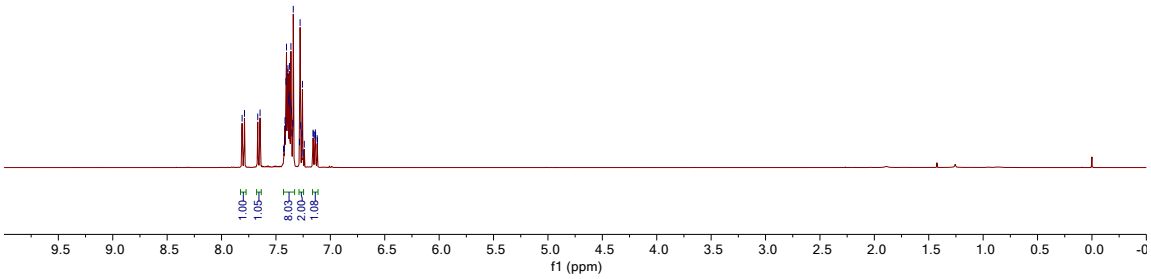
7.14
7.12
7.12


Cl
N—Ph
N

3ah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1.08
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.00
139.98
134.44
134.06
130.84
129.15
129.13
128.49
128.37
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126.01
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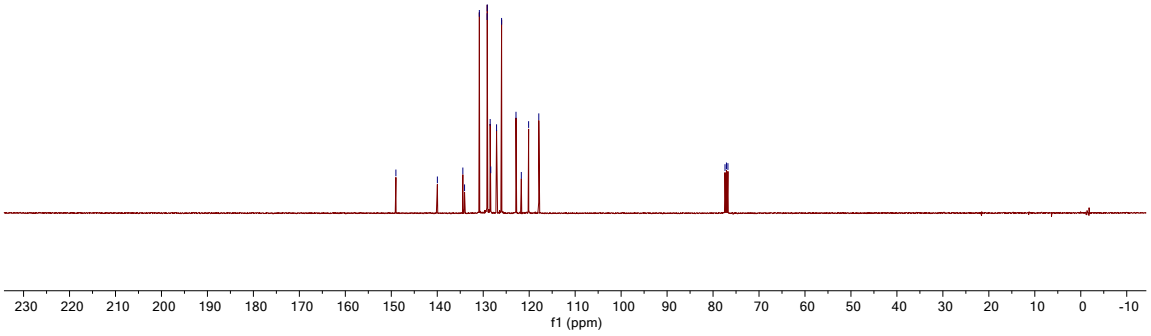
117.91
77.40 cdcl3
77.08 cdcl3
76.76 cdcl3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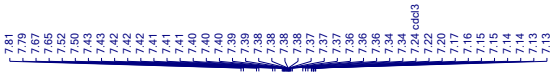
20
10
0
-10
f1 (ppm)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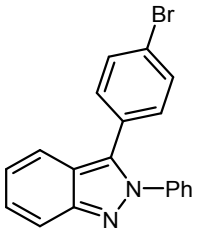
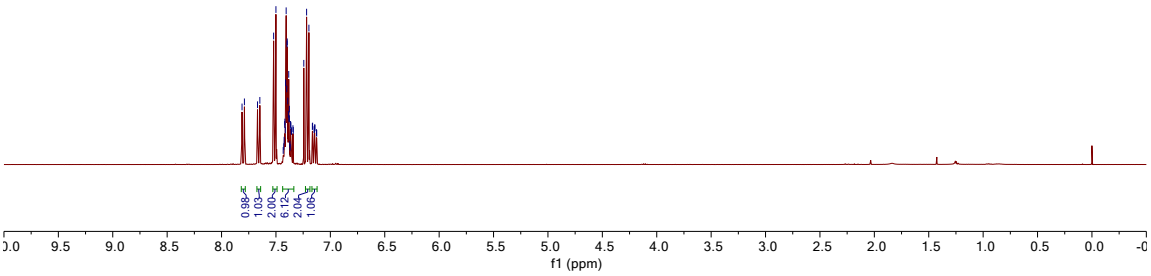
7.13


Br
N—Ph
N

3ai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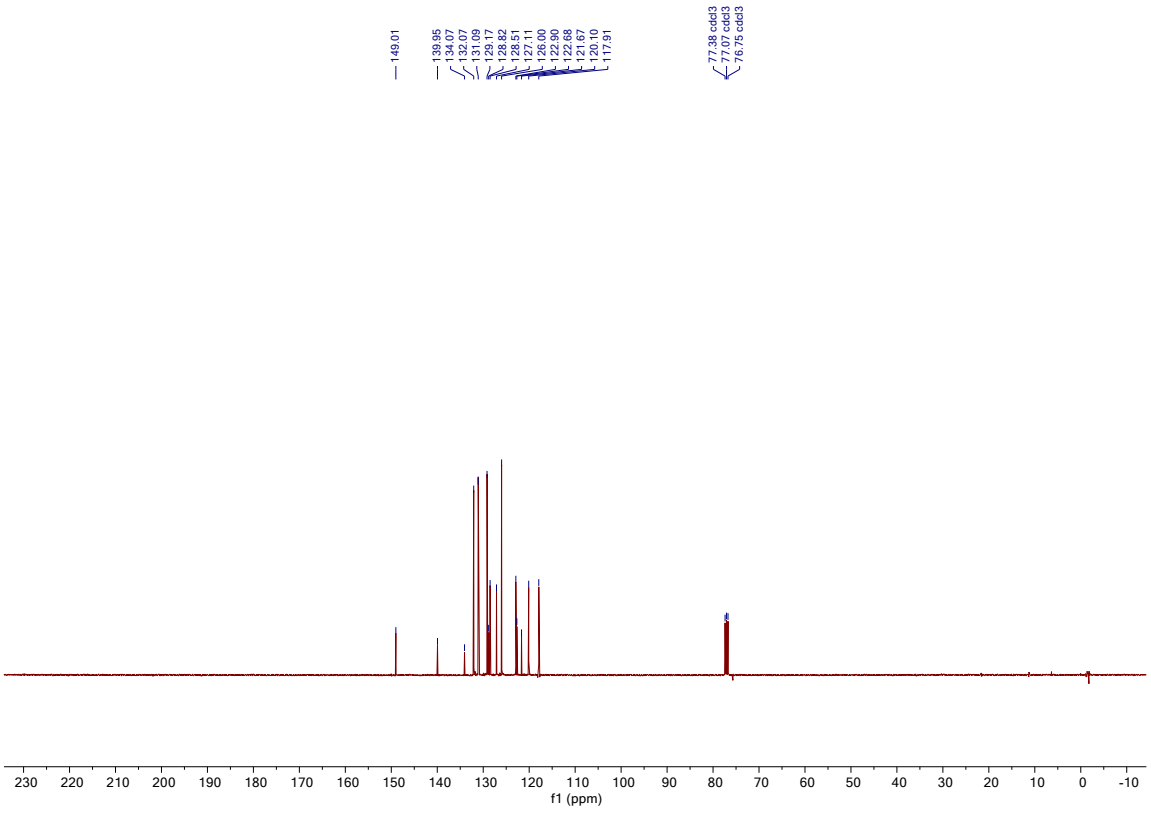
1
2.04
1.06
f1 (ppm)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139.95
134.07
132.07
131.09
129.17
128.82
128.51
127.11
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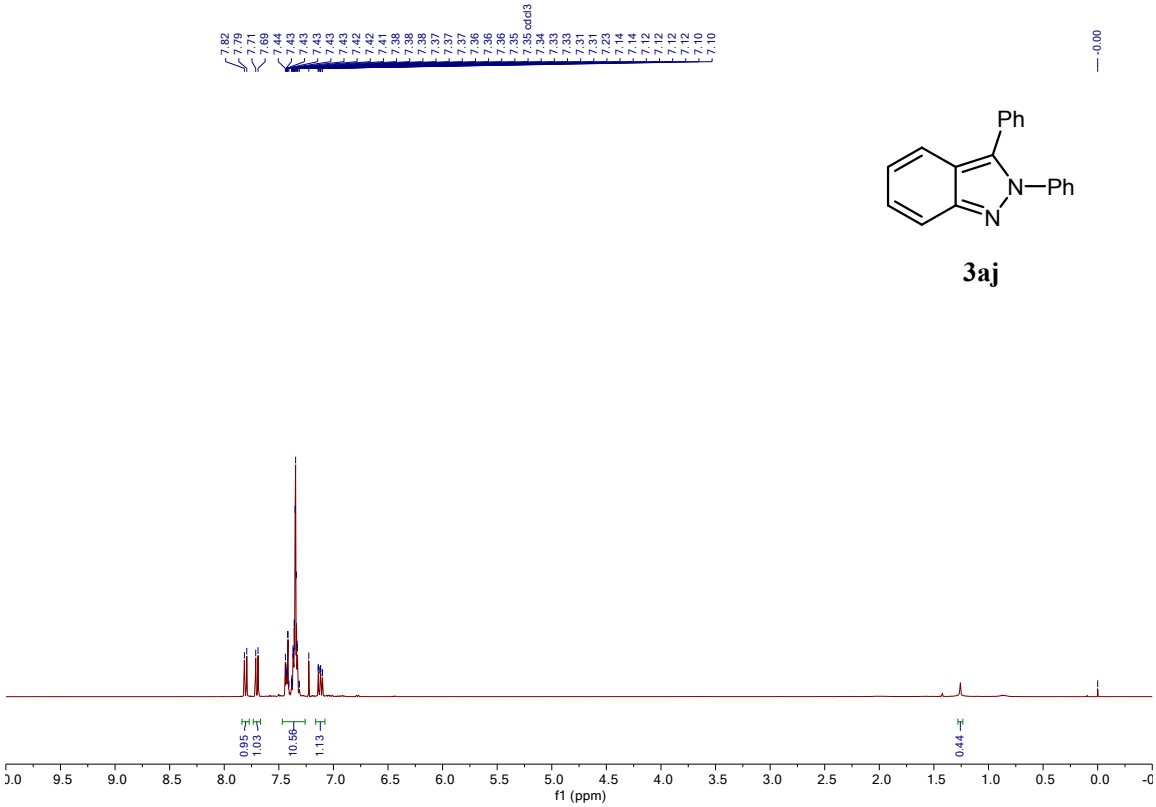
122.68
121.67
120.10
117.91
77.38 cdcl3
77.07 cdcl3
76.75 cdcl3
f1 (ppm)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7.42
7.41
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35 cdcl3
7.34
7.33
7.33
7.31
7.31
7.23
7.14
7.12
7.12
7.12
7.12
7.10
7.10
0.00
Ph
N
Ph
N
3aj
0.95
1.03
10.56
1.13
0.44
f1 (ppm)
149.01
140.24
135.41
129.90
129.69
129.00
128.78
128.39
128.33
128.27
127.03
126.03
122.54
121.77
120.54
117.77
77.43 cdcl3
77.11 cdcl3
76.79 cdcl3
f1 (ppm)


7.94
7.93
7.92
7.91
7.89
7.87
7.67
7.65
7.51
7.50
7.48
7.46
7.44
7.40
7.40
7.39
7.38
7.38
7.37
7.35
7.25 cdcl3
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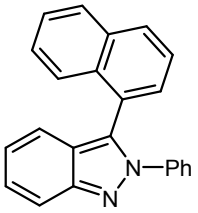
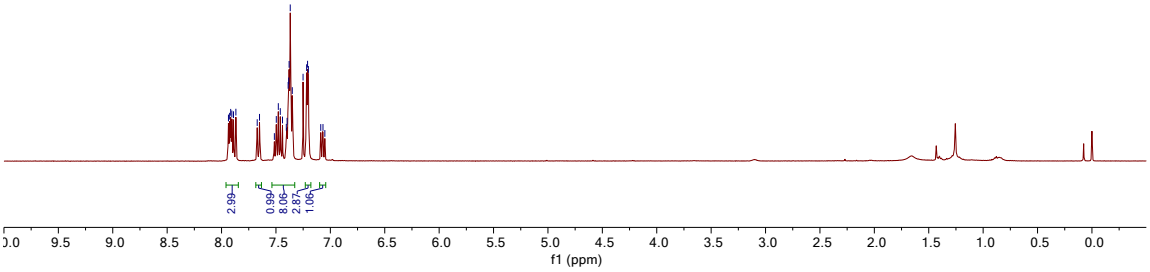
7.21
7.20
7.09
7.07
7.05


N—Ph
N

3ak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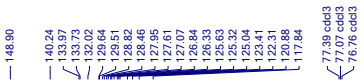
f1 (ppm)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140.24
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133.73
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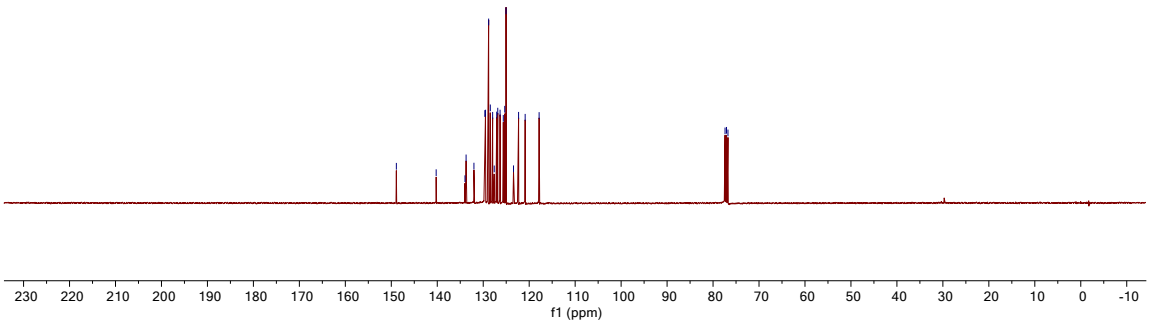
129.64
129.51
128.82
128.46
127.95
127.61
127.07
126.84
126.33
125.63
125.32
125.04
123.41
122.31
120.88
117.84
77.39 cdcl3
77.07 cdcl3
76.76 cdcl3


f1 (ppm)


8.78
8.78
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8.09
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7.83
7.79
7.79
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7.77
7.77
7.76
7.76
7.75
7.75
7.75
7.74
7.74
7.74
7.73
7.73
7.73
7.72
7.72
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7.58
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7.57
7.56
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7.46
7.45
7.45
7.45
7.44
7.44
7.44
7.41
7.41
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7.37
7.36
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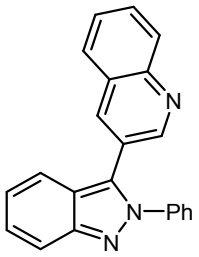
7.17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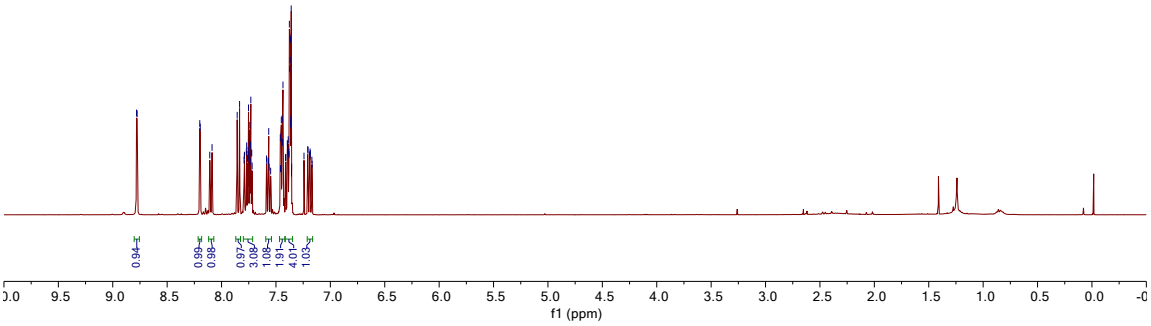
N

3al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0.99
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0.97
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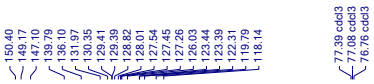
1.08
1.91
4.01
1.03
f1 (ppm)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147.10
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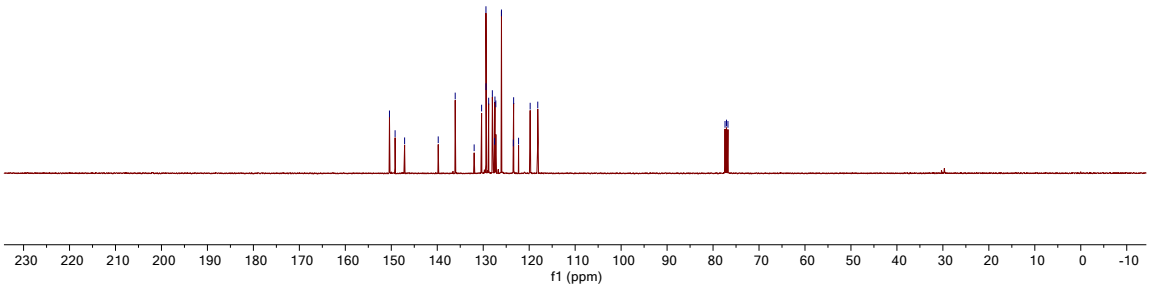
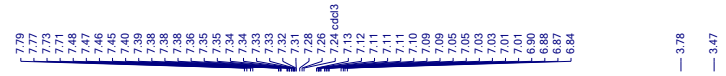
136.10
131.97
130.35
129.41
129.39
128.82
128.01
127.54
127.45
127.26
126.03
123.44
123.39
122.31
119.79
118.14
77.39 cdcl3
77.08 cdcl3
76.76 cdcl3


f1 (ppm)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7.46
7.45
7.40
7.39
7.38
7.38
7.38
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.28
7.26
7.24 cdcl3
7.13
7.12
7.11
7.11
7.10
7.09
7.09
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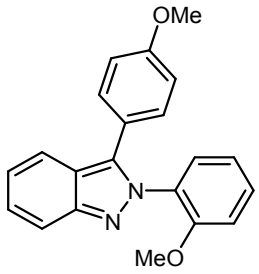
6.90
6.88
6.87
6.84
3.78
3.47


OMe
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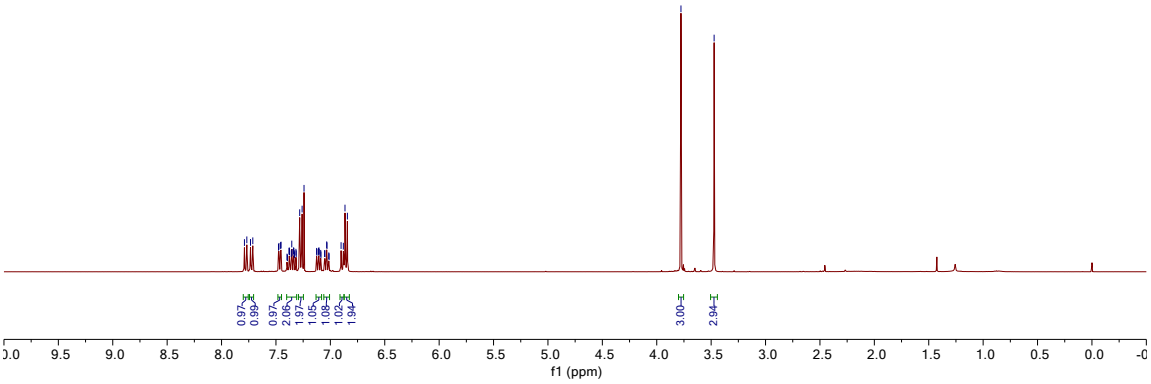
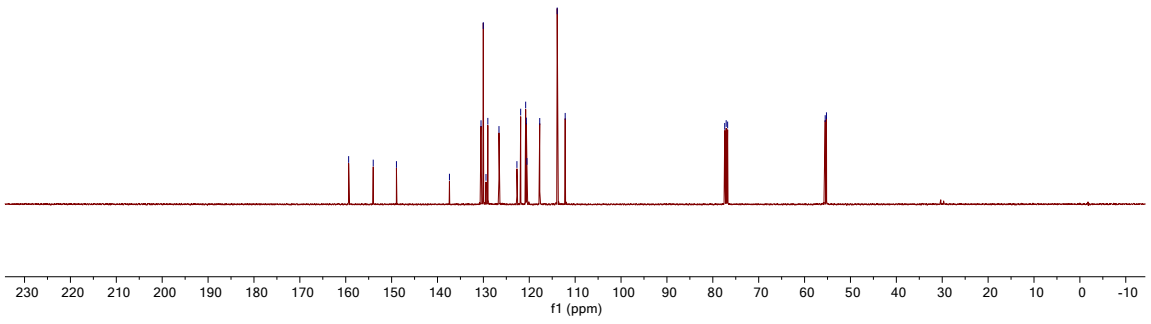
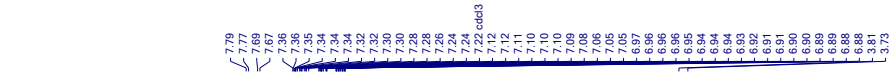
N
MeO

3am


0.97
0.99
0.97
2.06
1.97
1.95
1.08
1.02
1.94
3.00
2.94
f1 (ppm)


159.37
154.01
148.95
137.40
130.52
130.02
129.43
129.03
126.60
122.69
121.87
120.79
120.64
120.51
117.72
113.91
112.17
77.40 cdcl3
77.09 cdcl3
76.77 cdcl3
55.51
55.23


f1 (ppm)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7.32
7.32
7.30
7.30
7.28
7.28
7.26
7.24
7.24
cdcl3
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7.12
7.11
7.10
7.10
7.09
7.08
7.06
7.05
7.05
6.97
6.96
6.96
6.96
6.95
6.94
6.94
6.94
6.93
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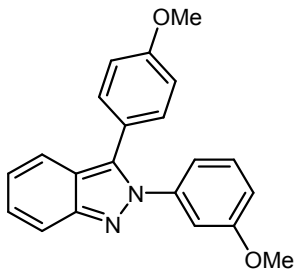
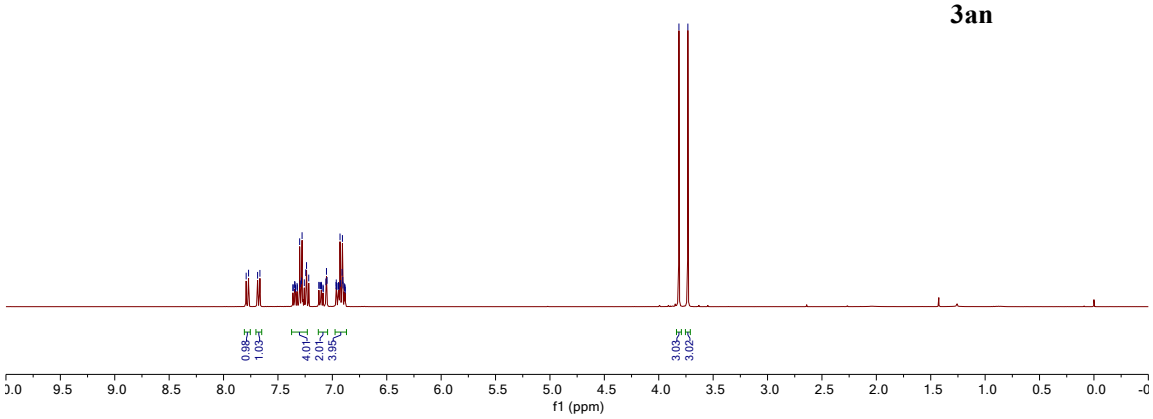
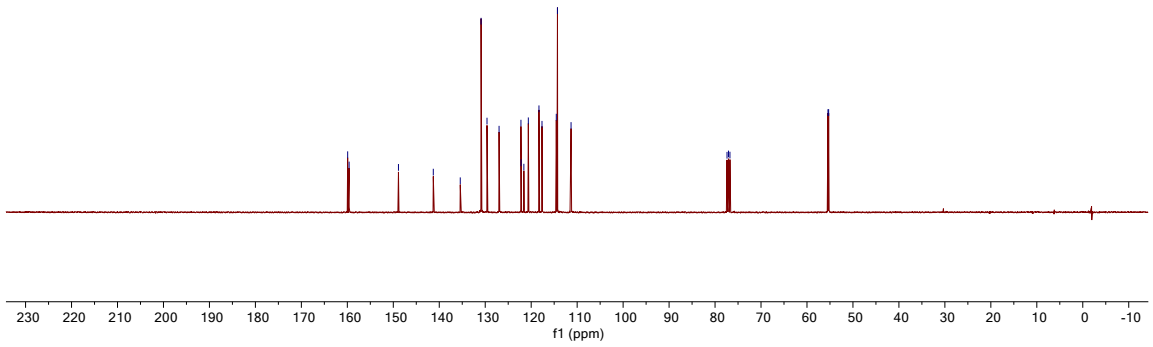
6.89
6.89
6.88
6.88
3.81
3.73


OMe
N
N
OMe

3an

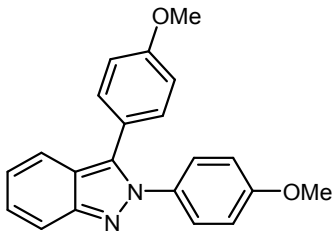

0.98
1.03
4.01
2.01
3.95
3.03
3.02
f1 (ppm)


159.93
159.61
148.88
141.30
135.43
130.90
129.61
126.99
122.23
121.19
121.19
120.62
118.31
117.65
114.54
114.28
111.33
77.40 cdcl3
77.08 cdcl3
76.76 cdcl3
55.43
55.29

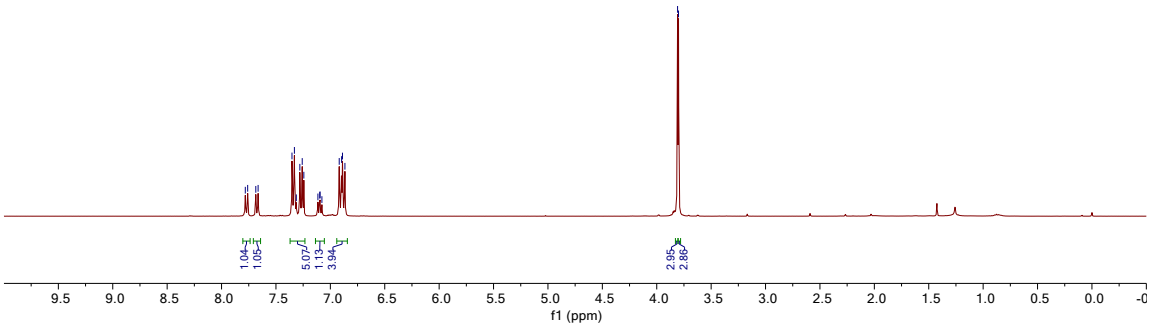

f1 (ppm)


7.78
7.76
7.69
7.66
7.35
7.33
7.31 cdcl3
7.28
7.26
7.24
7.11
7.10
7.09
7.08
6.92
6.90
6.89
6.87

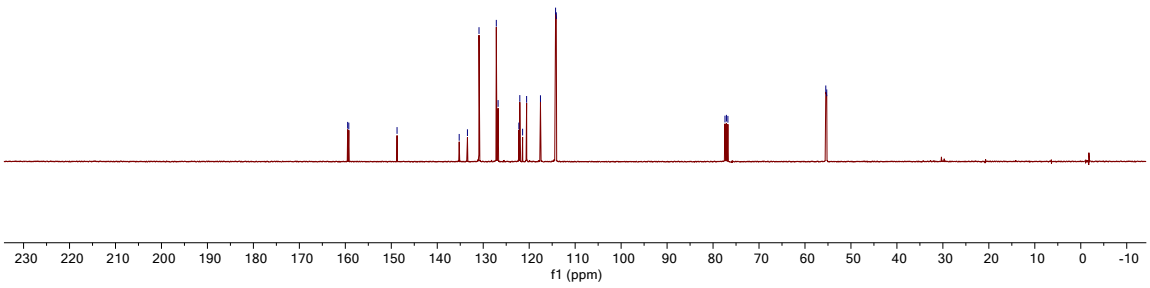

3.81
3.80

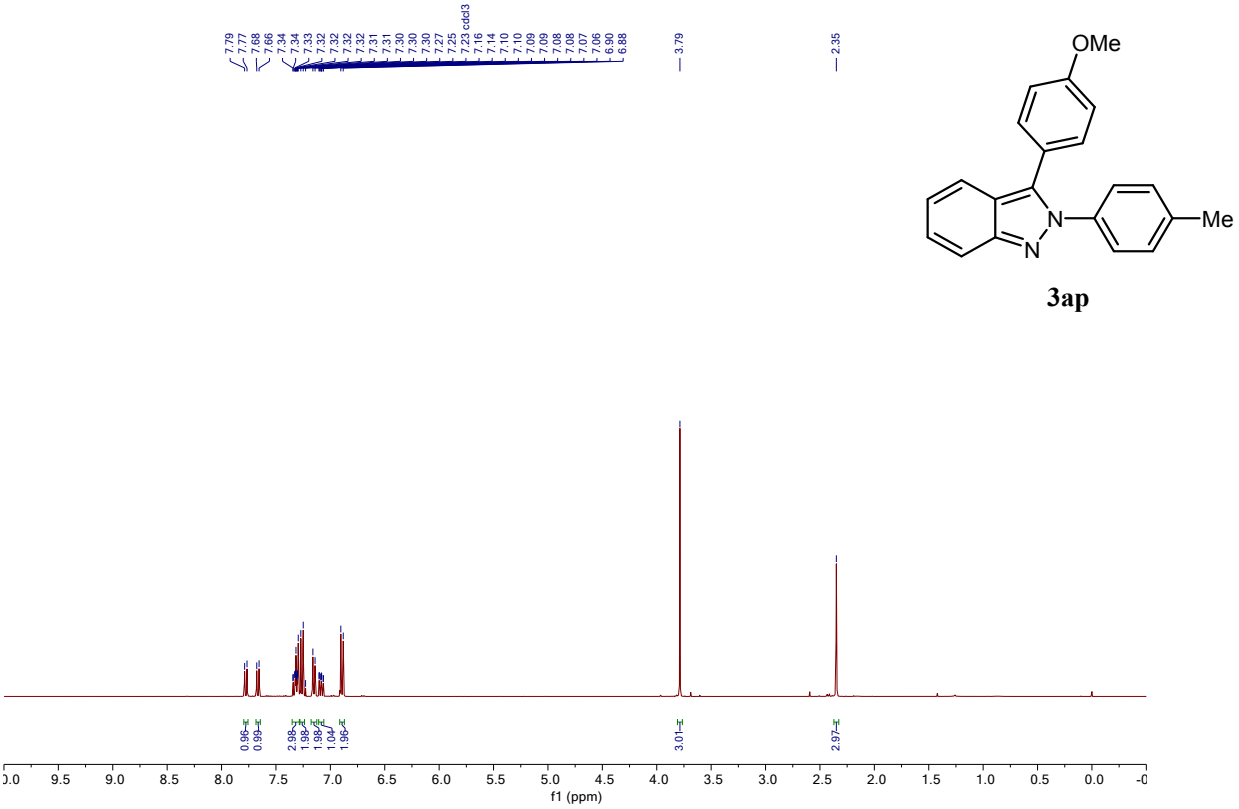

OMe
N
N
OMe

3ao


1.04
1.05
5.07
1.13
3.94
2.95
2.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.60
159.24
148.75
135.23
133.44
130.92
127.15
126.76
122.25
122.04
121.43
120.96
117.55
114.26
114.11
77.41 cdcl3
77.09 cdcl3
76.77 cdcl3
55.47
55.27


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.77
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7.66
7.34
7.33
7.32
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.27
7.25
7.23 cdcl3
7.16
7.14
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.06
6.90
6.88
3.79
2.35
0.96
0.99
2.98
1.98
1.98
1.04
1.96
3.01
2.97
f1 (ppm)
159.53
148.85
138.09
137.89
135.24
130.94
129.56
126.81
125.75
122.28
122.09
121.57
120.60
117.64
114.26
77.45 cdcl3
77.13 cdcl3
76.81 cdcl3
55.26
21.16
f1 (ppm)

OMe
N
N
Me

3ap


7.79
7.77
7.73
7.71
7.59
7.58
7.57
7.56
7.55
7.54
7.41
7.40
7.40
7.40
7.40
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7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.34
7.34
7.30
7.29
7.29
7.28
7.27
7.26
7.25
7.25 cdcl3
7.24
7.24
7.24
7.24
7.24
7.22
7.22
7.15
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7.13
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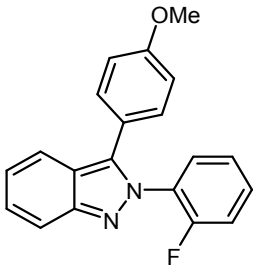
7.11
7.10
7.08
7.08
6.90
6.88
3.79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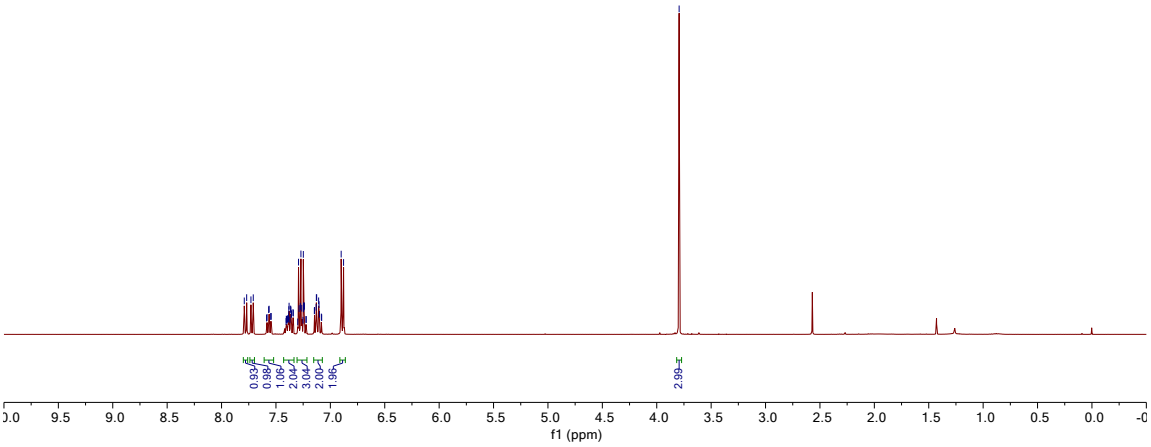
N
N
F

3aq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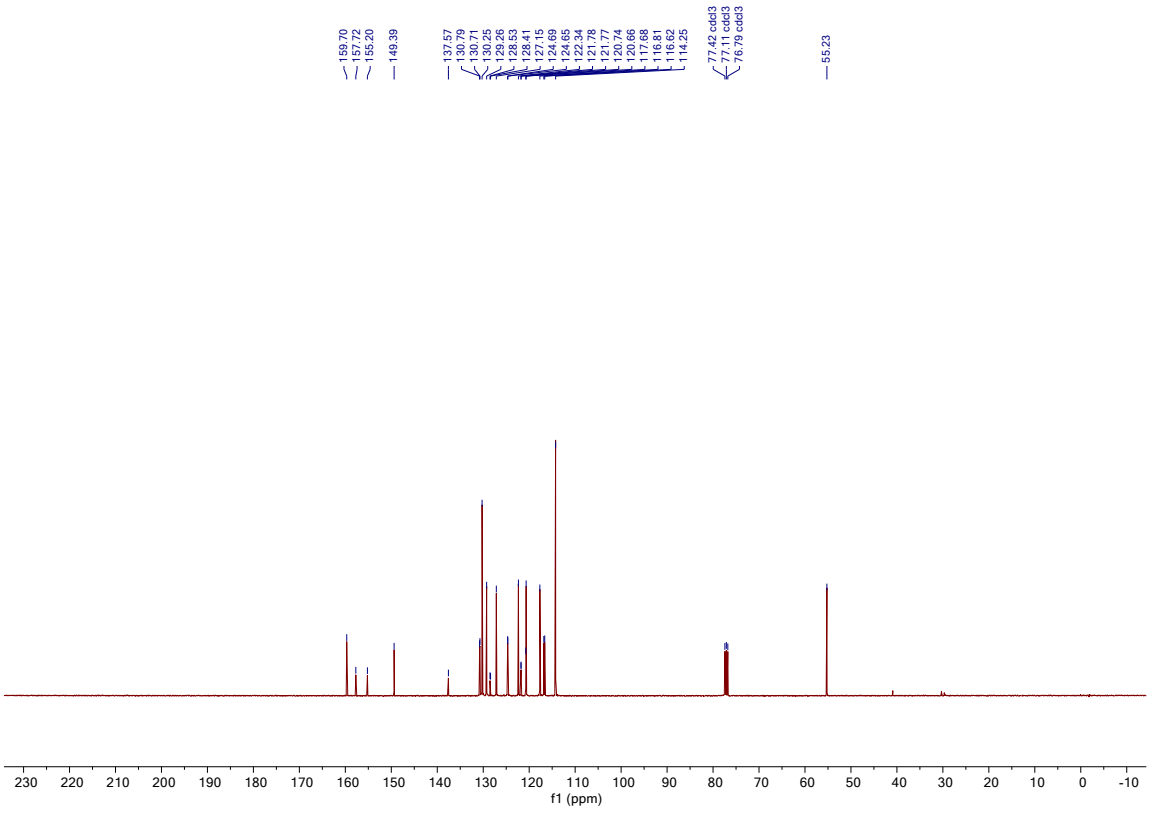
2.04
3.04
2.00
1.95
2.99
f1 (ppm)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157.72
155.20
149.39
137.57
130.79
130.71
130.25
129.26
128.53
128.41
127.15
124.69
124.65
123.34
121.78
121.77
120.74
120.66
117.68
116.81
116.62
114.25
77.42 cdcl3
77.11 cdcl3
76.79 cdcl3
55.23
f1 (ppm)


7.78
7.75
7.66
7.64
7.36
7.35
7.34
7.34
7.34
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7.30
7.29
7.28
7.27
7.26
7.26
7.25
7.24 cdcl3
7.23
7.23
7.20
7.20
7.20
7.18
7.18
7.18
7.18
7.12
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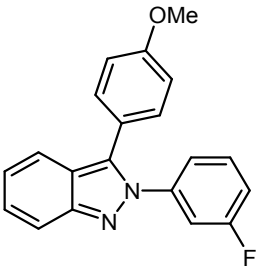
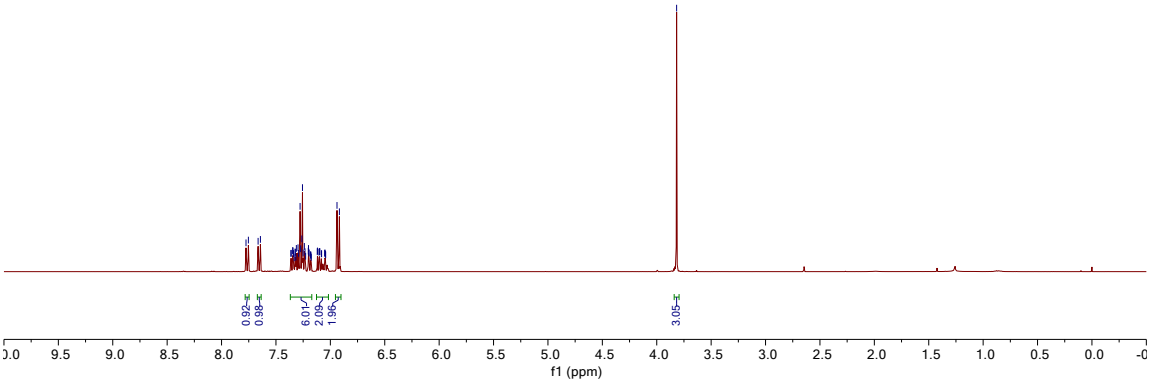
7.10
7.08
7.08
7.05
7.05
7.04
6.94
6.92
3.82


OMe
N
N
F

3ar


0.92
0.98
6.01
2.05
1.96
3.05
f1 (ppm)


163.71
161.25
159.81
149.07
141.66
141.56
135.57
130.92
130.19
130.10
127.29
122.48
121.76
121.72
121.65
121.62
120.63
117.77
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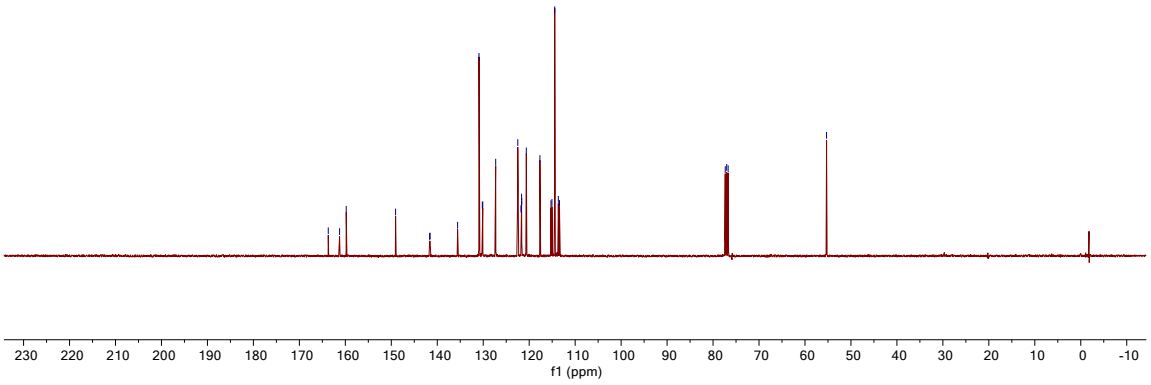
115.05
114.45
113.66
113.41
77.35 cdcl3
77.04 cdcl3
76.72 cdcl3
55.31


f1 (ppm)


7.77
7.75
7.68
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7.42
7.41
7.41
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7.39
7.39
7.36
7.36
7.35
7.34
7.34
7.34
7.32
7.26
7.24
7.12
7.11
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7.08
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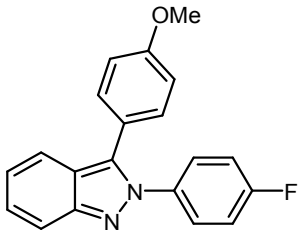
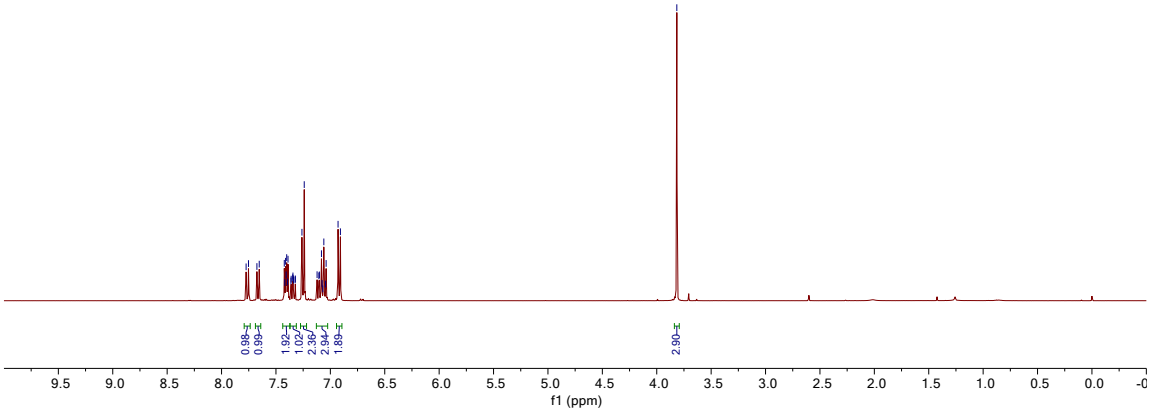
7.06
7.04
7.04
6.93
6.91

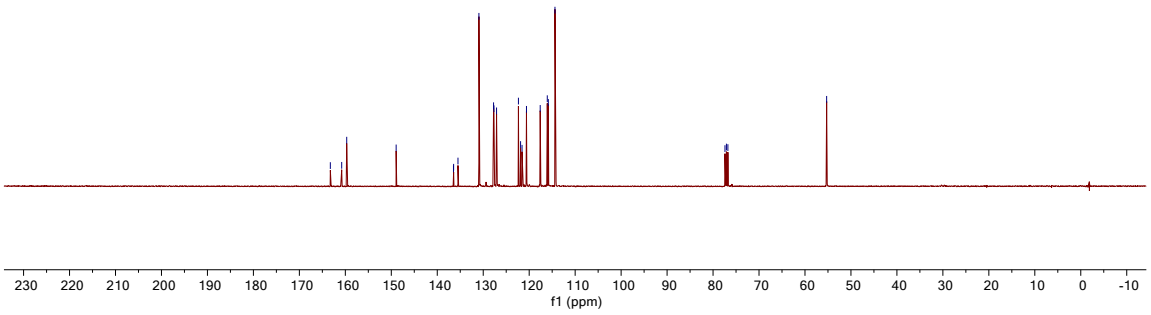
3.82


OMe
N
N
F

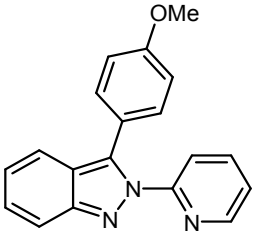
3as


0.98
0.99
1.92
1.97
2.36
2.94
1.89
2.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

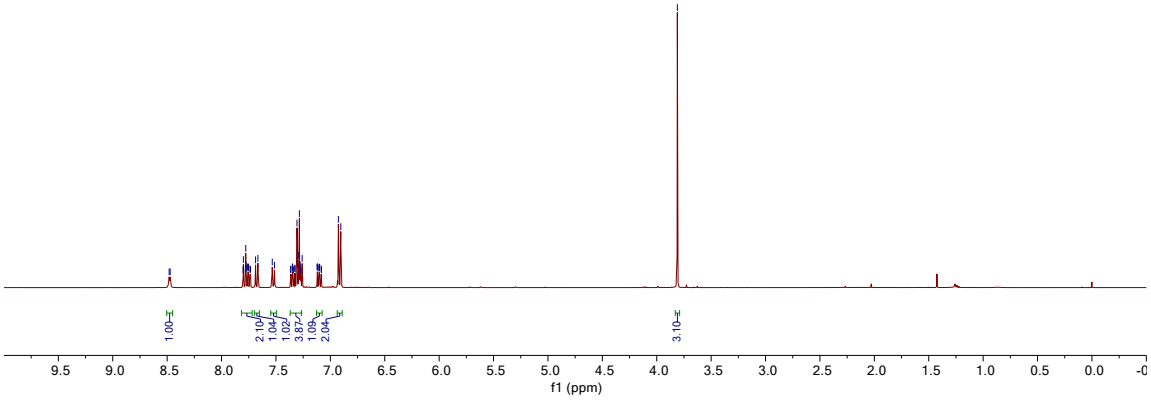

163.26
160.79
159.70
148.94
136.47
136.44
135.49
130.94
127.75
127.67
127.10
122.34
121.87
121.56
120.59
117.60
116.06
115.84
114.39
77.41 cdd3
77.09 cdd3
76.77 cdd3
55.29


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

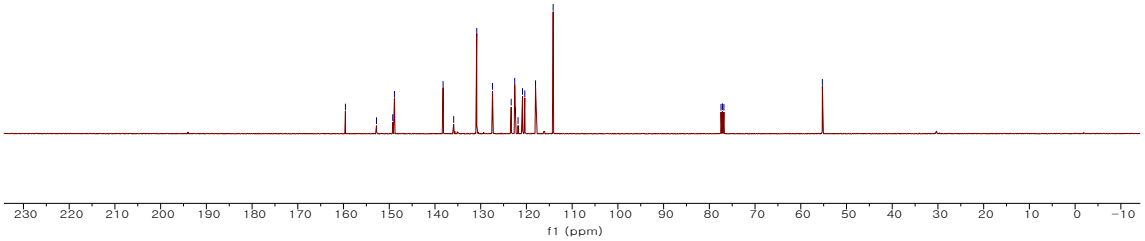

8.48
8.47
7.80
7.80
7.80
7.80
7.78
7.78
7.77
7.76
7.76
7.75
7.75
7.74
7.73
7.69
7.67
7.53
7.51
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.27
7.27
7.26 cdcl3
7.12
7.12
7.11
7.10
7.10
7.08
7.08
6.93
6.90
3.81


OMe
N
N
N

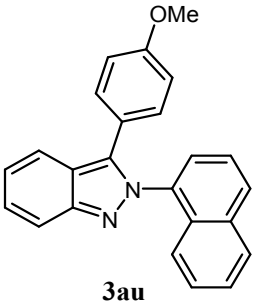
3at


1.00
2.10
1.04
1.02
3.07
1.06
2.04
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

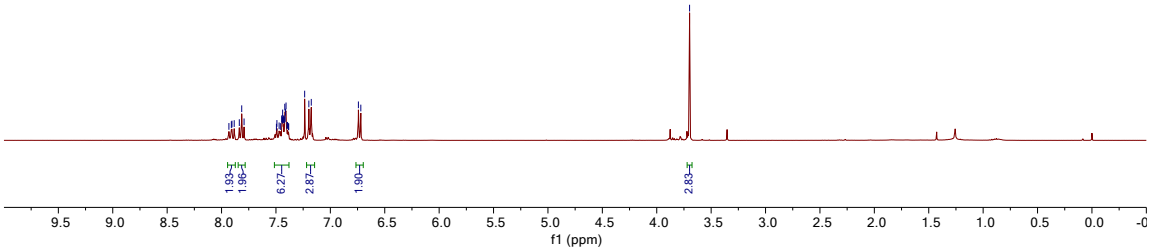

159.59
152.79
149.24
148.87
138.23
135.91
130.67
127.42
123.33
122.56
121.40
121.03
120.86
120.36
118.01
114.16
77.44 cdcl3
77.13 cdcl3
76.81 cdcl3
55.27

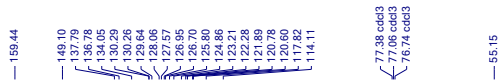

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

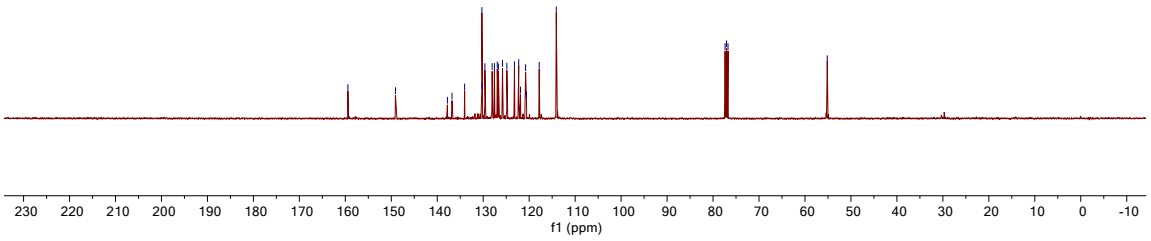

7.93
7.91
7.90
7.88
7.84
7.81
7.79
7.50
7.49
7.47
7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.24 cdcl3
7.20
7.18
6.74
6.72
3.70

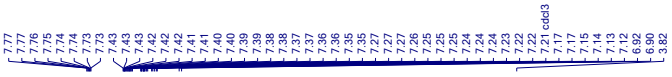

OMe
N
N

3au


1.93
1.96
6.27
2.87
1.90
2.83
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.44
149.10
137.79
136.78
134.05
130.29
130.26
129.64
128.06
127.57
126.95
126.70
125.80
124.86
123.71
122.28
121.89
120.78
120.60
117.82
114.11
77.38 cdcl3
77.06 cdcl3
76.74 cdcl3
55.15


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.77
7.77
7.76
7.75
7.74
7.74
7.73
7.73
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.27
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.23
7.22
7.22
7.21
cdcl3
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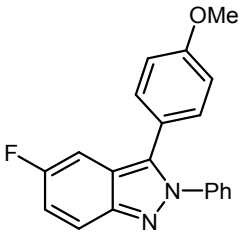
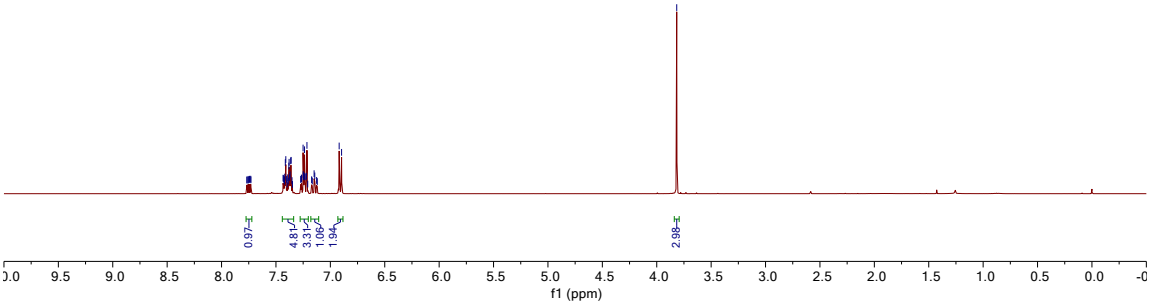
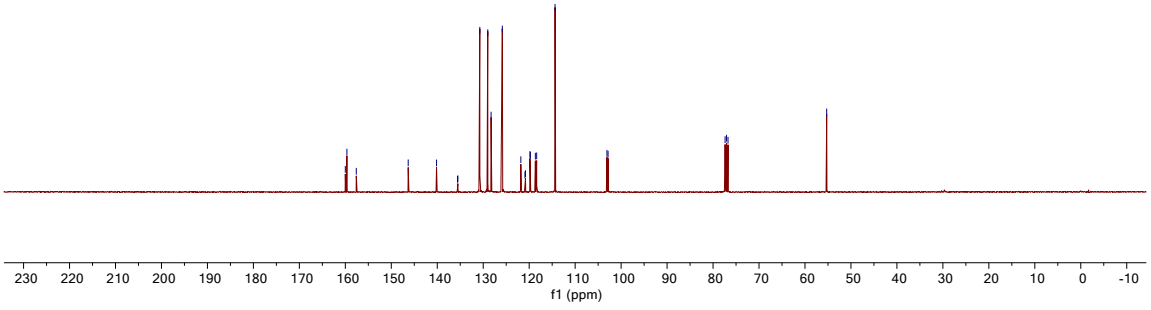
7.15
7.14
7.13
7.12
6.92
6.90
3.82

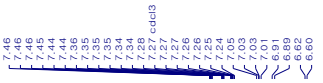

OMe
F
N—Ph
N

3av

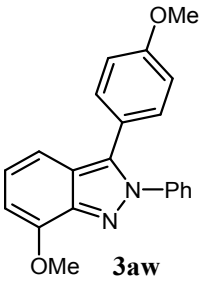

0.97
4.81
3.31
1.06
1.94
2.98
f1 (ppm)


160.01
159.66
157.62
146.32
140.16
135.60
135.51
130.75
129.01
128.29
125.85
121.82
120.92
120.81
119.84
119.74
118.66
118.37
114.37
103.08
102.84
77.38 cdcl3
77.06 cdcl3
76.75 cdcl3
55.28

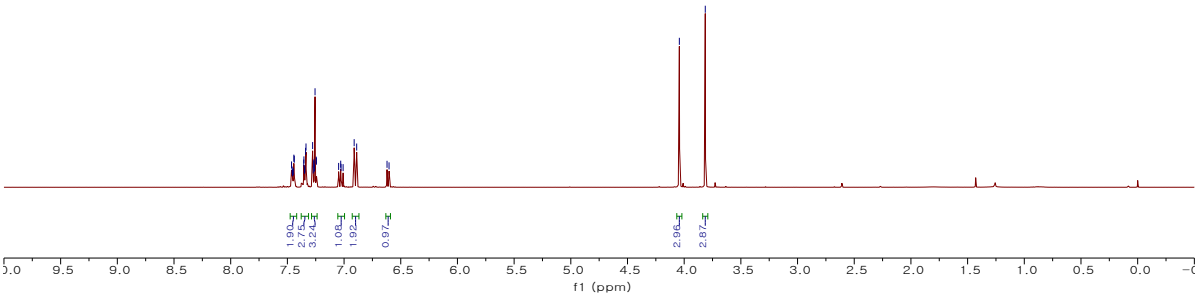

f1 (ppm)

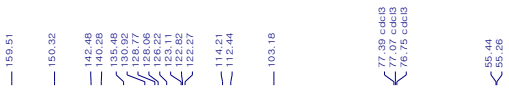

7.46
7.46
7.46
7.45
7.44
7.44
7.36
7.35
7.35
7.34
7.34
7.28
7.27 cdcl3
7.27
7.27
7.26
7.26
7.25
7.24
7.05
7.03
7.03
7.01
6.91
6.89
6.82
6.80

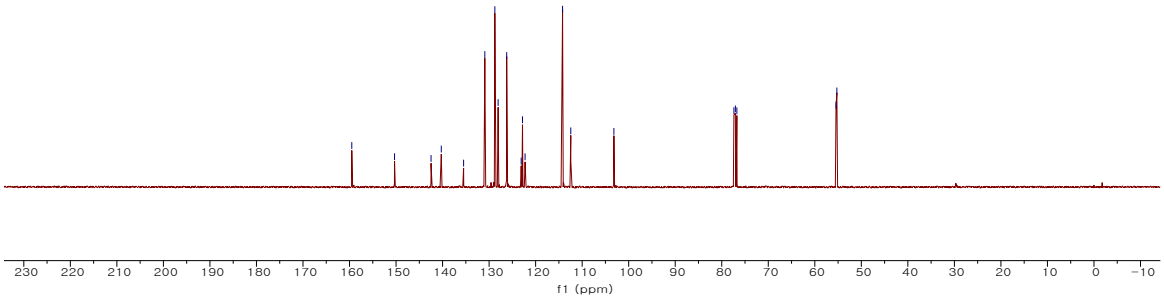

4.04
3.81

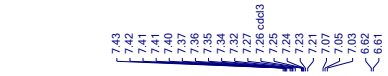

OMe
N—Ph
N
OMe

3aw

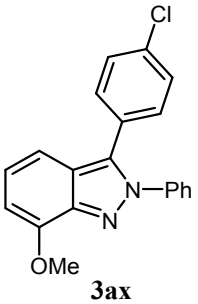

1.90
2.75
3.24
1.08
1.92
0.97
2.96
2.87
f1 (ppm)


159.51
150.32
142.48
140.28
135.48
130.92
128.77
128.66
126.22
123.11
122.82
122.27
114.21
112.44
103.18
77.39 cdcl3
77.07 cdcl3
76.75 cdcl3
55.44
55.26

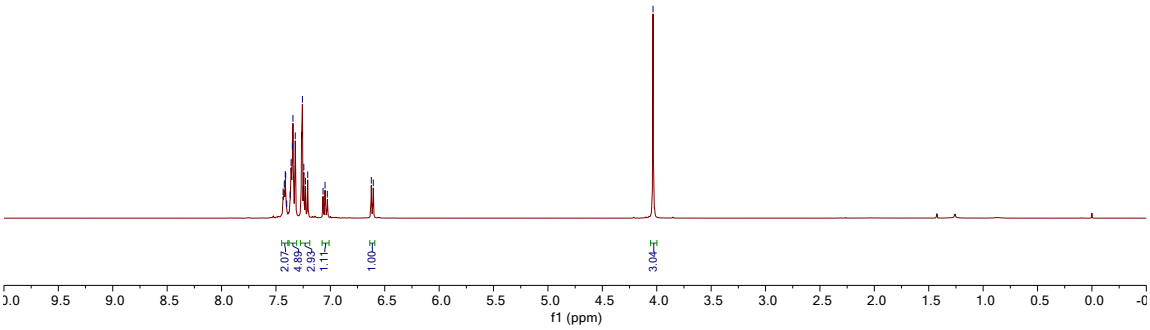

f1 (ppm)


7.43
7.42
7.41
7.40
7.37
7.36
7.35
7.34
7.32
7.27
7.26 cdcl3
7.25
7.24
7.23
7.21
7.07
7.05
7.03
6.62
6.61

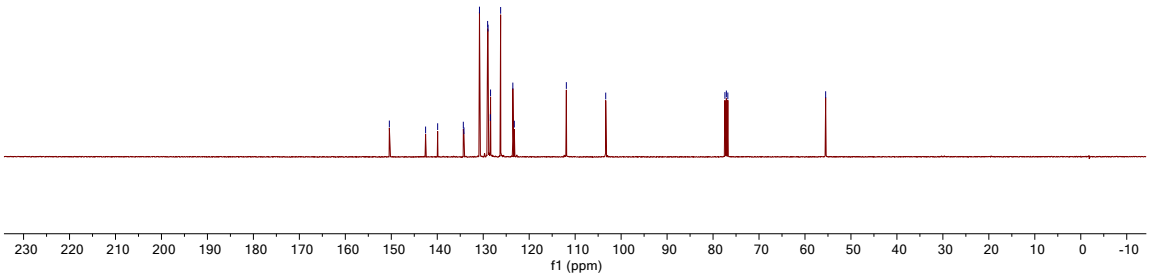
4.03

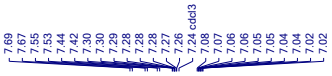

Cl
N—Ph
N
OMe

3ax


2.07
4.89
2.93
1.11
1.00
3.04
f1 (ppm)


150.42
142.54
139.91
134.33
134.19
130.82
129.04
128.95
128.44
128.41
126.21
123.56
123.24
111.92
103.35
77.42 cdcl3
77.10 cdcl3
76.78 cdcl3
55.50


f1 (ppm)


7.69
7.67
7.55
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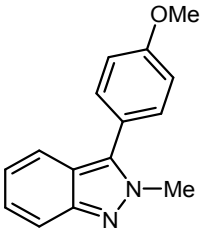
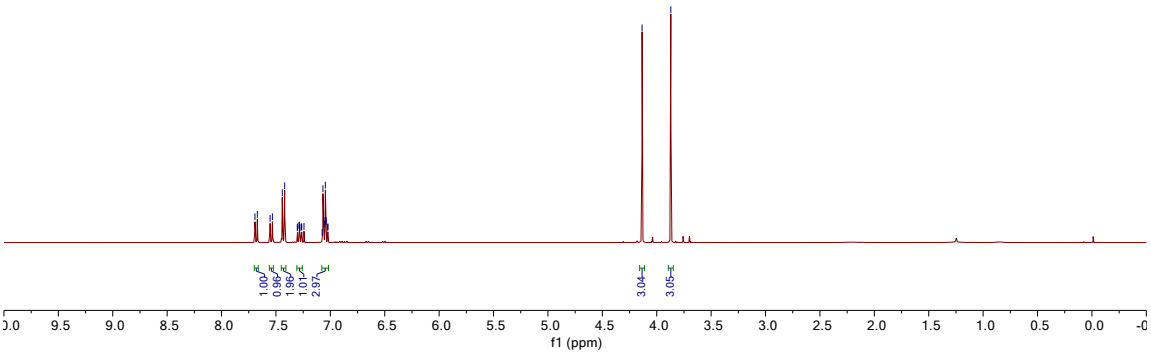
7.44
7.42
7.30
7.29
7.28
7.28
7.28
7.27
7.26
7.24 cdcl3
7.08
7.07
7.06
7.06
7.05
7.05
7.04
7.04
7.02
7.02

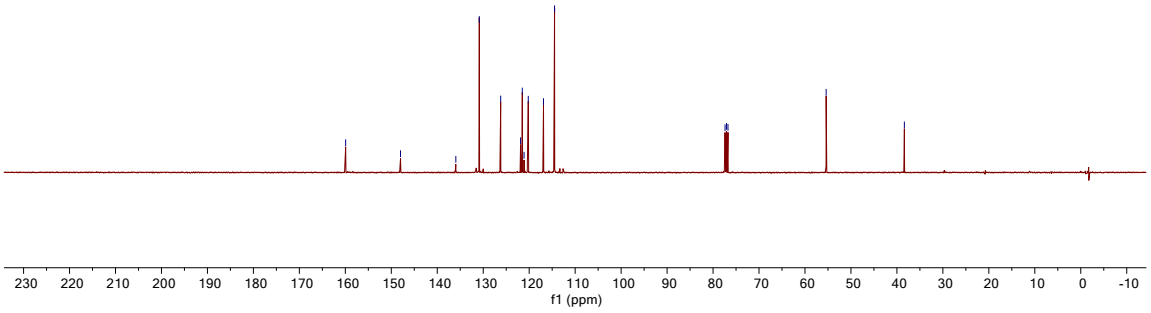
4.13
3.87


OMe
N—Me
N

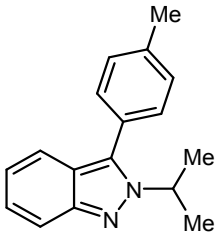
3ay


1.00
0.96
1.96
1.01
2.97
3.04
3.05
f1 (ppm)

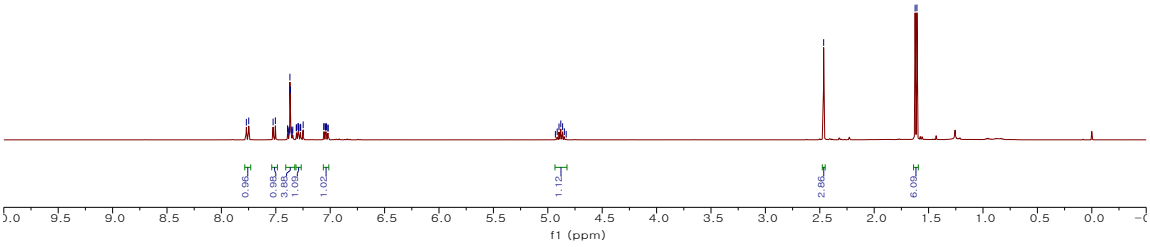

159.93
147.99
135.96
130.86
126.20
121.88
121.50
121.11
120.20
116.89
114.48
77.39 cdcl3
77.07 cdcl3
76.75 cdcl3
55.39
38.38


f1 (ppm)

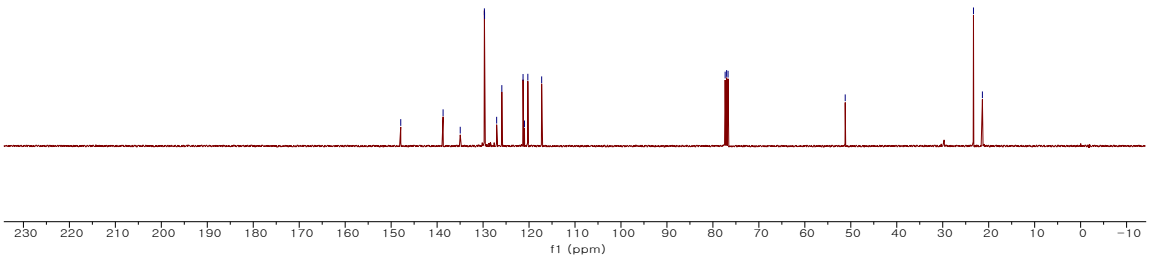

7.77
7.75
7.52
7.50
7.39
7.39
7.38
7.37
7.36
7.35
7.34
7.31
7.30
7.29
7.29
7.27
7.27
cdcl3
7.06
7.04
7.04
7.04
7.02
7.02
4.93
4.91
4.90
4.88
4.86
4.85
4.83
2.46
1.62
1.61


Me
Me
N
N
Me

3az


0.96
0.98
3.86
1.03
1.02
1.12
2.86
6.08
f1 (ppm)


147.91
138.70
134.97
129.71
129.68
127.05
125.92
121.30
121.00
120.26
111.28
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
51.22
23.31
21.37


f1 (ppm)