Rhodium(III) -catalyzed Indazole Synthesis by C-H Bond Functionalization and Cyclative Capture

Yajing Lian, Robert G. Bergman, Luke D. Lavis* and Jonathan A. Ellman*

Supporting Information

I. General Methods S-2

II. Preparation of Starting Materials S-3

III. Rh(III)-catalyzed Indazole Synthesis by Reaction with Phenyldiazene S-8

IV. Rh(III)-catalyzed Indazole Synthesis by Reaction with Phenyldiazenylphenol S-12

V. Oxidative Cleavage of Phenol S-18

VI. Normalized absorbance (abs), fluorescence excitation (ex), and fluorescence emission (em) spectra for selected fluorophores S-21

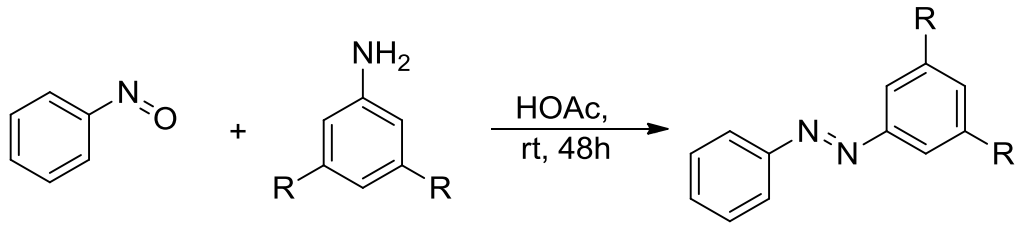
VII. References S-23

VIII. Spectral Data S-24

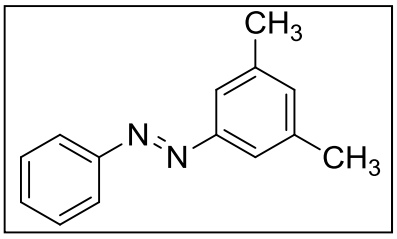
I. General Information

Unless noted, all catalytic reactions were set up inside an inert atmosphere (N_2) glovebox utilizing glassware that was oven-dried (150 ^oC) and evacuated while hot prior to use, whereas the work-up and isolation of the products from the catalytic reactions were conducted on the bench-top using standard techniques. Dioxane, THF and other solvents were passed through a column of activated alumina under nitrogen and were stored in a glovebox over activated 4 Å molecular sieves prior to use. Chloroform-d1 (Cambridge Isotopes) was used as received. All aldehydes were freshly distilled or purified by flash column chromatography before use. Unless otherwise noted, all other reagents and materials were obtained from commercial suppliers and used without further purification. $[Cp^*RhCl_2]_2$[1] and azobenzenes[2,3] were synthesized according to published procedures. Chromatography was performed on Merck 60 230-240 mesh silica gel. ^1H and $^{13}C\{1H\}$ NMR characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1 and 125.8 MHz (respectively) with chemical shifts reported in parts per million relative to $CHCl_3$ (^1H NMR; 7.26 ppm, $^{13}C\{1H\}$ NMR; 77.00 ppm). IR spectra were recorded on a Nicolet 6700 FTIR spectrometer and only partial data are provided. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Mass spectra (HRMS) were obtained by the Keck Center of Yale University using a Bruker 9.4 TAPEXQe FT-ICR mass spectrometer.

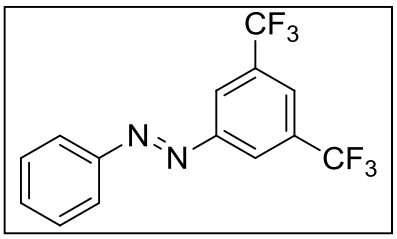
II. Preparation of Starting Materials



General Procedure for the Preparation of Azobenzenes (Method A): To a round bottom flask equipped with a stir bar was combined the indicated aniline (12.0 mmol, 1.2 equiv) and nitrosobenzene (1.07 g, 10.0 mmol, 1.0 equiv) in glacial acetic acid (100 mL) as solvent. The flask was covered with aluminum foil, and the reaction mixture was stirred at room temperature for 48 h. The reaction mixture was diluted with hexanes and was transferred to a separatory funnel with water (500 mL). The organic layer was collected and washed with water (300 mL). The organic layer was dried with $MgSO_4$, and concentrated. Purification by flash column chromatography with hexanes/ ethyl acetate (30:1) afforded the azobenzenes.

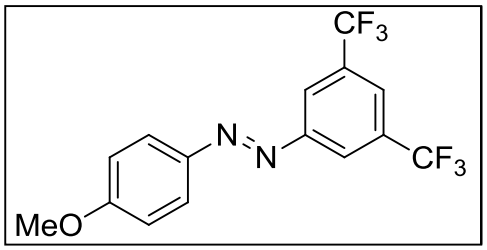


(*E*)-1-(3,5-Dimethylphenyl)-2-phenyldiazene (1e): From 3,5-dimethylaniline (1.45 g, 12.0 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (30/1) as eluent the product **1e** (1.48 g, 70% yield) was obtained as a red oil. IR (film): 1609, 1453, 1286, 1149, 1122, 1070, 852, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91-7.96 (m, 2H), 7.57 (s, 2H), 7.51-7.56 (m, 2H), 7.45-7.50 (m, 1H), 7.14 (s, 1H), 2.44 (s, 6H); ^{13}C {^1H} NMR ($CDCl_3$) δ 152.9, 152.7, 138.7, 132.7, 130.8, 129.0, 122.7, 120.6, 21.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{14}H_{15}N_2$: 211.1230. Found 211.1228.

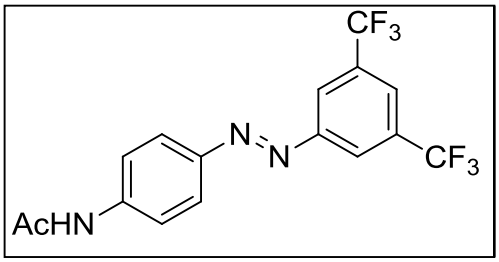


(*E*)-1-(3,5-Bis(trifluoromethyl)phenyl)-2-phenyldiazene (1f): From 3,5-bis(trifluoromethyl)aniline (2.75 g, 12.0 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (30/1) as eluent the product **1f** (1.87 g, 59% yield) was obtained as an orange

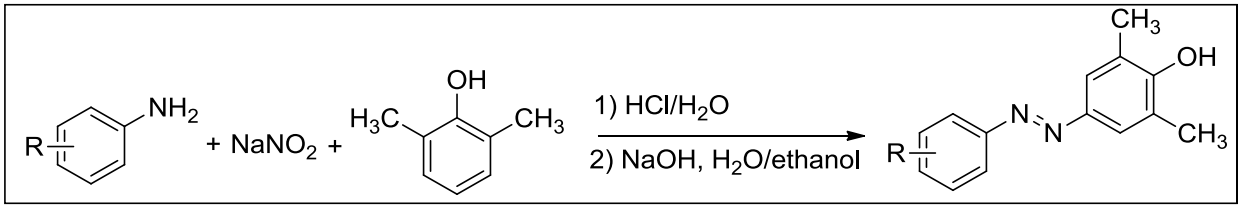
powder (mp: 60-61 °C). IR (film): 1367, 1274, 1164, 1119, 1104, 897, 842, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.38 (s, 2H), 7.95-8.02 (m, 3H), 7.53-7.60 (m, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 152.9, 152.0, 132.7 (q, *J* = 33.9 Hz), 132.5, 129.3, 123.8 (hept. *J* = 7.6 Hz), 123.4, 123.1 (q, *J* = 272.9 Hz), 123.0 (q, *J* = 3.3 Hz); GC-MS(M^{+}) calcd. for $C_{14}H_8F_6N_2$: 318. Found 318.



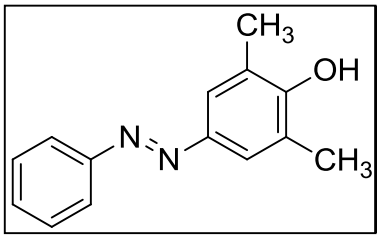
(*E*)-1-(3,5-Bis(trifluoromethyl)phenyl)-2-(4-methoxyphenyl)diazene (1h): From 1-nitroso-3,5-bis(trifluoromethyl)benzene (1.22 g, 5.0 mmol, 1.0 equiv) and *p*-anisidine (0.739 g, 6.0 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (20/1) as eluent the product **1h** (1.36 g, 78% yield) was obtained as an orange powder (mp: 73-74 °C). IR (film): 1603, 1584, 1503, 1371, 1277, 1250, 1164, 1122, 1027, 898, 834 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.32 (s, 2H), 7.95 – 8.02 (m, 2H), 7.93 (s, 1H), 7.02 – 7.08 (m, 2H), 3.92 (s, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 163.3, 153.1, 146.5, 132.6 (q, *J* = 33.7 Hz), 135.6, 123.2 (q, *J* = 272.9 Hz), 123.1 (hept. *J* = 7.6 Hz), 122.7 (q, *J* = 3.2 Hz), 114.5, 55.7; HRMS (ESI/$[M+H]^{+}$) calcd. for $C_{15}H_{11}F_6N_2O$: 349.0770. Found 349.0763.



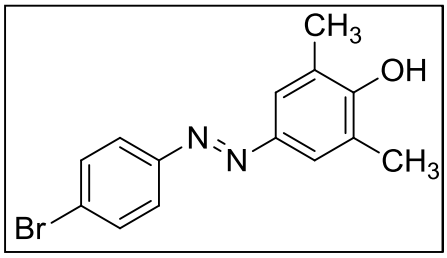
(*E*)-N-(4-((3,5-bis(trifluoromethyl)phenyl)diazenyl)phenyl)acetamide (1i): From 1-nitroso-3,5-bis(trifluoromethyl)benzene (1.22 g, 5.0 mmol, 1.0 equiv) and *N*-(4-aminophenyl)acetamide (0.901 g, 6.0 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (2/1) as eluent the product **1i** (1.29 g, 69% yield) was obtained as an orange powder (mp: 171-173 °C). IR (film): 3323, 1656, 1595, 1547, 1505, 1368, 1277, 1169, 1126, 902, 844, 698, 682 cm^{-1}; ^{1}H NMR (Acetone) δ 9.58 (s, 1H), 8.41 (s, 2H), 8.18 (s, 1H), 8.03 – 7.96 (m, 2H), 7.93 – 7.88 (m, 2H), 2.15 (s, 3H); ^{13}C {^{1}H} NMR (Acetone) δ 169.6, 154.3, 148.7, 145.0, 133.3 (q, *J* = 33.7 Hz), 125.6, 124.4 (hept. *J* = 7.6 Hz), 124.3 (q, *J* = 272.2 Hz), 123.6 (q, *J* = 3.2 Hz), 120.1, 24.6; HRMS (ESI/$[M+H]^{+}$) calcd. for $C_{16}H_{12}F_6N_3O$: 376.0879. Found 376.0881.



General Procedure for the Preparation of Azobenzenes (Method B): To a round bottom flask equipped with a stir bar was added the indicated aniline (10.0 mmol, 1.0 equiv) to an aqueous HCl solution (25 mL, 1M) at 0 ^{o}C. After 10 min, $NaNO_2$ (0.725 g, 10.5 mmol, 1.05 equiv) in water (35 mL) was added dropwise. The solution was stirred for additional 10 min and then was transferred into a round bottom flask containing 1,3-dimethylphenol (1.22 g, 10.0 mmol, 1.0 equiv), and NaOH (0.400 g, 10.0 1.0 equiv) in a mixture of water (100 mL) and ethanol (35 mL) at 0 ^{o}C was added via cannula. Red precipitate formed instantly, and the solution was stirred for 6 h at 0 ^{o}C. The mixture was filtered, and the red solid residue was purified by flash column chromatography with hexanes/ ethyl acetate (9:1) to afford the azobenzene as a red powder.

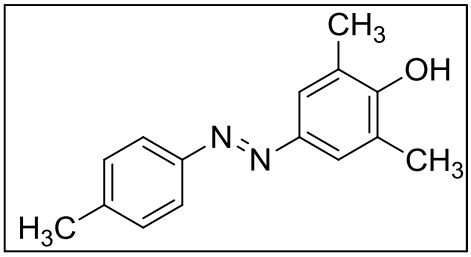


(*E*)-2,6-Dimethyl-4-(phenyldiazenyl)phenol (1g): From aniline (0.932 g, 10.0 mmol, 1.0 equiv) with purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent the product (1.80 g, 80% yield) was obtained as an orange powder **1g** (mp: 87-89 °C). IR (film): 3305(br), 1591, 1479, 1410, 1294, 1185, 1119, 1019, 894, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.84-7.89 (m, 2H), 7.64 (s, 2H), 7.47-7.53 (m, 2H), 7.41-7.46 (m, 1H), 4.98 (s, 1H), 2.34 (s, 6H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 155.0, 152.8, 146.4, 130.2, 129.0, 123.7, 123.5, 122.5, 16.0; HRMS (ESI/$[M+H]^+$) calcd. for $C_{14}H_{15}N_2O$: 227.1179. Found 227.1175.

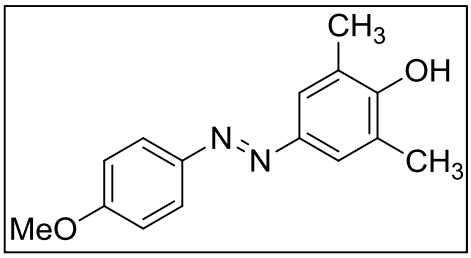


(*E*)-4-((4-Bromophenyl)diazenyl)-2,6-dimethylphenol (1j): From 4-bromoaniline (1.71 g, 10.0 mmol, 1.0 equiv) with purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent the product **1j** (2.09 g, 69% yield) was obtained as a red powder (mp: 126-128 °C). IR (film): 3351(br), 1591, 1475, 1418, 1268, 1190, 1114, 828 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.72-7.76 (m, 2H), 7.63 (s, 2H), 7.60-7.64 (m, 2H), 4.99 (s, 1H), 2.34 (s, 6H); ^{13}C {^{1}H} NMR

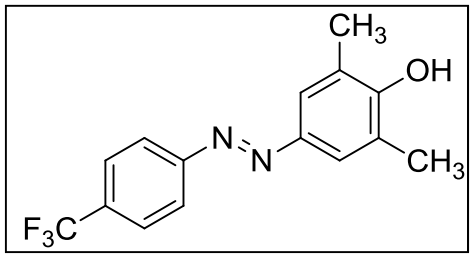
($CDCl_3$) δ 155.4, 151.5, 146.2, 132.2, 124.4, 124.0, 123.9, 123.6, 16.0; HRMS (ESI/$[M+H]_+$) calcd. for $C_{14}H_{14}BrN_2O$: 305.0284. Found 305.0281.



(*E*)-2,6-Dimethyl-4-(*p*-tolyldiazenyl)phenol (1k): From 4-methylaniline (1.08 g, 10.0 mmol, 1.0 equiv) with purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent the product **1k** (1.51 g, 63% yield) was obtained as a red powder (mp: 64-66 °C). IR (film): 3361(br), 1589, 1471, 1343, 1261, 1189, 1114, 817 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78 (dm, *J* = 8.0 Hz, 2H), 7.63 (s, 2H), 7.30 (dm, *J* = 8.0 Hz, 2H), 4.99 (br, 1H), 2.43 (s, 3H), 2.33 (s, 6H); ^{13}C {^1H} NMR ($CDCl_3$) δ 154.8, 150.9, 146.4, 140.6, 139.7, 123.6, 123.5, 122.4, 21.4, 16.0; HRMS (ESI/$[M+H]_+$) calcd. for $C_{15}H_{17}N_2O$: 241.1335. Found 241.1333.

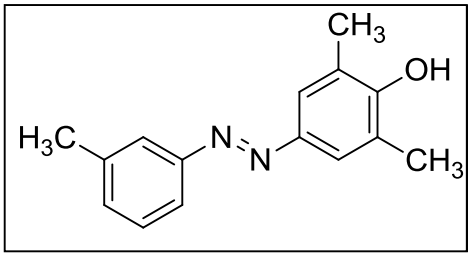


(*E*)-4-((4-Methoxyphenyl)diazenyl)-2,6-dimethylphenol (1l): From *p*-anisidine (1.23 g, 10.0 mmol, 1.0 equiv) with purification by silica gel column chromatography using hexane/EtOAc (4/1) as eluent the product **1l** (1.87 g, 73% yield) was obtained as a red powder (mp: 123-125 °C). IR (film): 3314 (br), 1604, 1501, 1320, 1243, 1184, 1149, 1027, 831 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85-7.89 (m, 2H), 7.60 (s, 2H), 6.98-7.02 (m, 2H), 4.94 (s, 1H), 3.88 (s, 3H), 2.33 (s, 6H); ^{13}C {^1H} NMR ($CDCl_3$) δ 161.4, 154.5, 147.1, 146.2, 124.2, 123.5, 123.3, 114.2, 55.5, 16.0; HRMS (ESI/$[M+H]_+$) calcd. for $C_{14}H_{15}N_2O_2$: 257.1285. Found 257.1282.

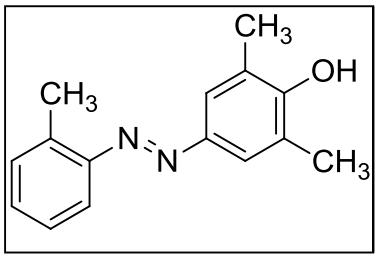


(*E*)-2,6-Dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)phenol (1m): From *p*-anisidine (1.61 g, 10.0 mmol, 1.0 equiv) with purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent the product **1m** (1.83 g, 62% yield) was obtained as a red powder (mp: 55-57 °C). IR (film): 3430 (br), 1612, 1591, 1473, 1315, 1173, 1116, 1099, 1063, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.67 (s, 2H), 5.08 (br, 1H), 2.34 (s, 6H); ^{13}C {^1H} NMR ($CDCl_3$) δ 156.0, 154.6,

146.2, 131.4 (q, *J* = 32.4 Hz), 126.2 (q, *J* = 3.8 Hz), 124.2, 124.0 (q, *J* = 272.2 Hz), 122.6, 15.9; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{14}F_3N_2O$: 295.1053. Found 295.1049.



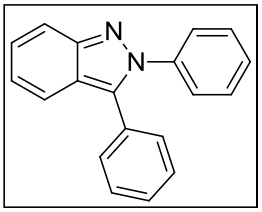
(*E*)-2,6-Dimethyl-4-(*m*-tolyldiazenyl)phenol (1n): From 3-methylaniline (1.08 g, 10.0 mmol, 1.0 equiv) with purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent the product **1n** (1.61 g, 67% yield) was obtained as a red powder (mp: 74-75 °C). IR (film): 3367(br), 1589, 1480, 1280, 1190, 1153, 118, 926, 772 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.66 – 7.71 (m, 2H), 7.64 (s, 2H), 7.36 – 7.42 (m, 1H), 7.30 – 7.23-7.27 (m, 1H), 4.98 (s, 1H), 2.46 (s, 3H), 2.34 (s, 6H); ^{13}C {^1H} NMR ($CDCl_3$) δ 155.1, 152.8, 146.3, 138.9, 131.0, 128.8, 123.7, 123.6, 122.5, 120.1, 21.4, 16.0; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{17}N_2O$: 241.1335. Found 241.1329.



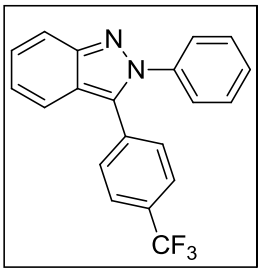
(*E*)-2,6-dimethyl-4-(*o*-tolyldiazenyl)phenol (1o): From 2-methylaniline (1.08 g, 10.0 mmol, 1.0 equiv) with purification by silica gel column chromatography using hexane/EtOAc (9/1) as eluent the product (1.93 g, 79% yield) was obtained as a red powder **1o** (mp: 84-86 °C). IR (film): 3384(br), 1592, 1473, 1334, 1256, 1187, 1100, 1022, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65 (s, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.32-7.35 (m, 2H), 7.24-7.30 (m, 1H), 4.97 (br, 1H), 2.73 (s, 3H), 2.36 (s, 6H); ^{13}C {^1H} NMR ($CDCl_3$) δ 154.9, 150.9, 146.8, 137.3, 131.1, 130.1, 126.4, 123.8, 123.4, 115.5, 17.5, 16.0; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{17}N_2O$: 241.1335. Found 241.1330.

III. Rh(III)-catalyzed Indazole Synthesis by Reaction with Phenyldiazene

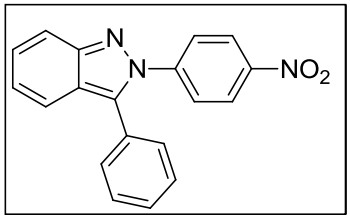
General Procedure: In a N_2-filled glovebox, $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.05 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.20 equiv), the indicated phenyldiazene (0.200 mmol, 1.0 equiv) and aldehyde (0.400 mmol, 2.0 equiv) were added to a screw-capped conical vial with a stir bar followed by addition of dioxane (1.0 mL, [*O*-methyl oxime] = 0.20 M). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath at 110 °C. After 24 h of stirring, the vial was removed from the oil bath and was cooled to ambient temperature. The mixture was filtered through a pad of celite, and the solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.



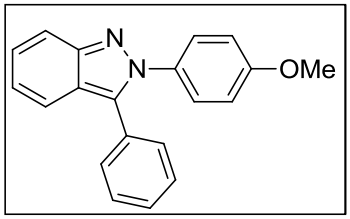
2,3-Diphenyl-*2H*-indazole (3a): Derived from azobenzene (**1a**) (36.5 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (9/1) as eluent afforded the product **3a** (41.1 mg, 76% yield) as a white powder. ^{1}H NMR ($CDCl_3$): δ 7.81 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.72 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.42-7.47 (m, 2H), 7.34-7.42 (m, 9H), 7.15 (ddd, , *J* = 8.6, 7.5, 0.9 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.0, 140.2, 135.4, 129.9, 129.7, 129.0, 128.8, 128.30, 128.25, 127.0, 126.0, 122.5, 121.7, 120.5, 117.8. The analytical data for this compound are consistent with previously reported data.[4]



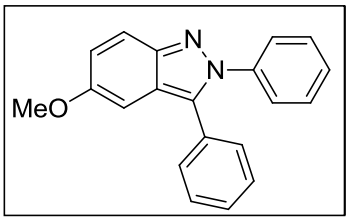
2-Phenyl-3-(4-(trifluoromethyl)phenyl)-*2H*-indazole (3h): Derived from azobenzene (**1a**) (36.5 mg) and 4-trifluoromethylbenzaldehyde (69.7 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (9/1) as eluent afforded the product **3h** (50.7 mg, 76% yield) as a white powder. The analytical data for this compound are consistent with previously reported data.[4]



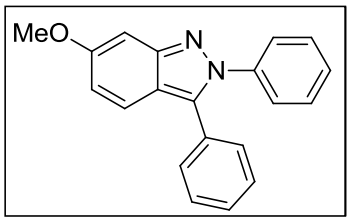
2-(4-Methoxyphenyl)-3-phenyl-*2H*-indazole (3b): Derived from (*E*)-1-(4-nitrophenyl)-2-phenyldiazene (**1b**) (45.5 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded the product **3b** (39.1 mg, 62% yield) as a yellow powder. The analytical data for this compound are consistent with previously reported data.[5]



2-(4-Methoxyphenyl)-3-phenyl-*2H*-indazole (3c): Derived from (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**1c**) (42.5 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (9/1) as eluent afforded the product **3c** (25.3 mg, 42% yield) and product **3c'** (14.4 mg, 24% yield) as a white powder. The analytical data for this compound are consistent with previously reported data.[5]

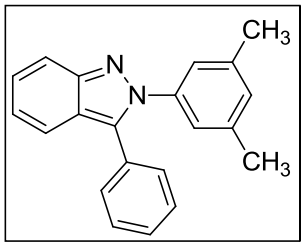


5-Methoxy-2,3-diphenyl-*2H*-indazole (3c'): (mp: 169-171 °C). IR (film): 3051, 2823, 1595, 1491, 1455, 1215, 1072, 1023, 969, 823, 764 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.71 (dd, *J* = 9.3, 0.6 Hz, 1H), 7.33-7.43 (m, 10H), 7.08 (dd, *J* = 9.3, 2.4 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 3.83 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 155.9, 145.9, 140.3, 134.2, 130.3, 129.6, 128.9, 128.8, 128.04, 127.97, 125.8, 122.1, 121.6, 119.2, 96.3, 55.4; HRMS (ESI/$[M+H]_+$) calcd. for $C_{20}H_{17}N_2O$: 301.1335. Found 301.1326.

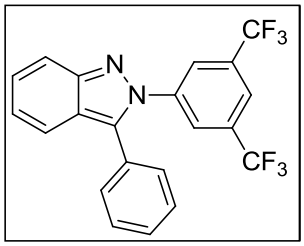


6-Methoxy-2,3-diphenyl-*2H*-indazole (3d): Derived from (*E*)-1-(3-methoxyphenyl)-2-phenyldiazene (**1d**) (42.5 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (9/1) as eluent afforded the product **3d** (36.6 mg, 61% yield) as a white powder (mp: 119-120 °C). IR (film): 3062, 2919, 1628, 1507, 1443, 1369, 1307, 1233, 1207, 1170, 1128, 1016, 916, 821, 764 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.57 (dd, *J* = 9.1, 0.8 Hz, 1H),

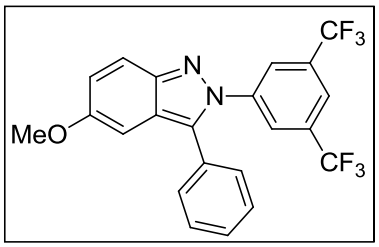
7.32-7.44 (m, 10H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.84 (dd, *J* = 9.1, 2.0 Hz, 1H), 3.91 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 159.5, 149.9, 140.2, 135.5, 129.9, 129.6, 128.9, 128.7, 128.3, 127.9, 125.8, 121.4, 117.7, 117.6, 94.4, 55.3; HRMS (ESI/$[M+H]_+$) calcd. for $C_{20}H_{17}N_2O$: 301.1335. Found 301.1326.



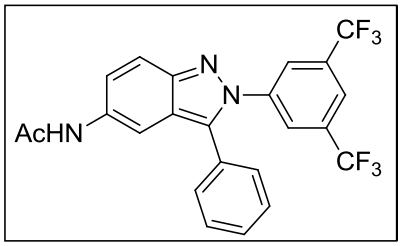
2-(3,5-Dimethylphenyl)-3-phenyl-*2H*-indazole (3e): Derived from (*E*)-1-(3,5-dimethylphenyl)-2-phenyldiazene (**1e**) (42.1 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (20/1) as eluent afforded the product **3e** (36.7 mg, 61% yield) as a white powder (mp: 102-103 °C). IR (film): 2917, 1610, 1596, 1497, 1446, 1361, 1184, 1012, 908, 852 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.82 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.33-7.43 (m, 6H), 7.14 (ddd, *J* = 8.6, 6.6, 0.7 Hz, 1H), 7.06 (s, 2H), 7.00 (s, 1H), 2.28 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.8, 140.0, 138.7, 135.2, 130.0, 129.9, 129.6, 128.6, 128.2, 126.8, 123.7, 122.3, 121.6, 120.5, 117.7, 21.1; HRMS (ESI/$[M+H]_+$) calcd. for $C_{21}H_{19}N_2$: 299.1543. Found 299.1533.



2-(3,5-Bis(trifluoromethyl)phenyl)-3-phenyl-*2H*-indazole (3f): Derived from (*E*)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenyldiazene (**1f**) (63.7 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv) in 0.4 mL of dioxane. Purification by silica gel column chromatography using hexane/ethyl acetate (20/1) as eluent afforded the product **3f** (43.1 mg, 53% yield) as a white powder (mp: 106-108 °C). IR (film): 3041, 1503, 1413, 1378, 1349, 1280, 1271, 1173, 1114, 900, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.95 (s, 2H), 7.85 (s, 1H), 7.80 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.68 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.45-7.51 (m, 3H), 7.41 (ddd, *J* = 8.6, 6.6, 0.9 Hz, 1H), 7.34-7.38 (m, 2H), 7.17 (ddd, *J* = 8.6, 6.6, 0.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 149.7, 141.4, 136.0, 132.5 (q, *J* = 34.1 Hz), 129.7, 129.29, 129.27, 129.0, 128.1, 125.7 (d, *J* = 3.3 Hz), 123.4, 122.6 (q, *J* = 273.1 Hz), 122.3, 121.3 (hept, *J* = 3.8 Hz), 120.5, 117.8; HRMS (ESI/$[M+H]_+$) calcd. for $C_{21}H_{13}F_6N_2$: 407.0977. Found 407.0972.



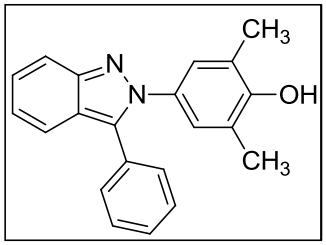
2-(3,5-Bis(trifluoromethyl)phenyl)-5-methoxy-3-phenyl-*2H*-indazole (3v): Derived from (*E*)-1-(3,5-bis(trifluoromethyl)phenyl)-2-(4-methoxyphenyl)diazene (**1h**) (69.6 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv) in 0.4 mL of dioxane. Purification by silica gel column chromatography using hexane/ethyl acetate (20/1) as eluent afforded the product **3v** (38.4 mg, 44% yield) as a white powder (mp: 123-125 °C). IR (film): 3071, 1505, 1370, 1279, 1174, 1129, 1102, 898, 811 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.89 (m, 2H), 7.81 (s, 1H), 7.69 (dd, *J* = 9.4, 0.6 Hz, 1H), 7.46 – 7.52 (m, 3H), 7.32 – 7.38 (m, 2H), 7.11 (dd, *J* = 9.4, 2.4 Hz, 1H), 6.82 (d, *J* = 2.1 Hz, 1H), 3.83 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 156.4, 146.7, 141.4, 134.6, 132.4 (q, *J* = 34.1 Hz), 129.6, 129.4, 129.3, 129.0, 125.3 (q, *J* = 3.3 Hz), 123.6, 122.6 (q, *J* = 273.0 Hz), 122.3, 120.9 (hept, *J* = 3.9 Hz), 119.2, 95.7, 55.4; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{15}F_6N_2O$: 437.1083. Found 437.1081



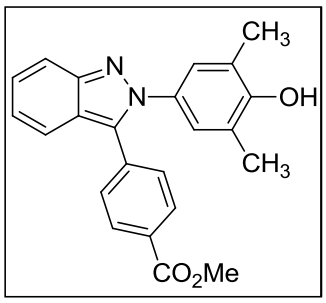
N-(2-(3,5-bis(trifluoromethyl)phenyl)-3-phenyl-*2H*-indazol-5-yl)acetamide (3w): Derived from (*E*)-N-(4-((3,5-bis(trifluoromethyl)phenyl)diazenyl)phenyl)acetamide (**1i**) (75.1 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv) in 0.4 mL of dioxane. Purification by silica gel column chromatography using hexane/ethyl acetate (1/1) as eluent afforded the product **3w** (38.9 mg, 42% yield) as a white powder (mp: 216-218 °C). IR (film): 3303, 1661, 1582, 1527, 1502, 1405, 1345, 1277, 1261, 1175, 1125, 1100, 892, 880, 809, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 7.90 (s, 2H), 7.84 (d, *J* = 13.6 Hz, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.40-7.58 (br, 1H), 7.37 – 7.47 (m, 3H), 7.36 – 7.27 (m, 2H), 7.23 (dd, *J* = 9.2, 1.9 Hz, 1H), 2.18 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 168.5, 147.4, 141.3, 136.0, 133.1, 132.4 (q, *J* = 34.2 Hz), 129.6, 129.3, 129.2, 128.8, 125.5 (q, *J* = 3.3 Hz), 123.9, 122.6 (q, *J* = 273.0 Hz), 122.1, 121.3 (hept, *J* = 3.9 Hz), 118.6, 109.4, 24.5; HRMS (ESI/$[M+H]^+$) calcd. for $C_{23}H_{16}F_6N_3O$: 464.1192. Found 464.1195.

III. Rh(III)-catalyzed Indazole Synthesis by Reaction with Phenyldiazenylphenol

General procedure: In a N_2-filled glovebox, $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.05 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.20 equiv), $MgSO_4$ (100 mg), the indicated phenyldiazenylphenol (0.200 mmol, 1.0 equiv) and aldehyde (0.400 mmol, 2.0 equiv) were added to a screw-capped conical vial with a stir bar followed by addition of THF (1.0 mL, [*O*-methyl oxime] = 0.20 M). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath at 110 °C. After stirring for 24 h, the vial was removed from the oil bath and was cooled to ambient temperature. The mixture was filtered through a pad of celite, and the solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.

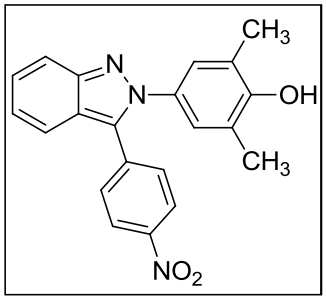


2,6-Dimethyl-4-(3-phenyl-*2H*-indazol-2-yl)phenol (3g): Derived from (*E*)-2,6-dimethyl-4-(phenyldiazenyl)phenol (**1g**) (45.3 mg) and benzaldehyde (**2a**) (42.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (10/1) as eluent afforded the product **3g** (42.8 mg, 68% yield) as a white powder (mp: 232-234 °C). IR (film): 3051 (br), 1500, 1487, 1203, 1017, 757 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.79 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.73 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.33-7.42 (m, 6H), 7.14 (ddd, *J* = 8.6, 6.6, 0.7 Hz, 1H), 6.99 (s, 2H), 5.52 (br, 1H), 2.17 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.3, 148.5, 135.3, 132.5, 129.9, 129.6, 128.6, 128.2, 126.8, 126.0, 124.4, 122.3, 121.4, 120.5, 117.48, 16.1; HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{19}N_2O$: 315.1492. Found 315.1479.

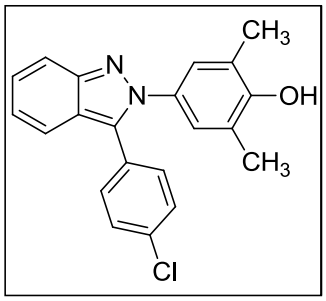


Methyl 4-(2-(4-hydroxy-3,5-dimethylphenyl)-*2H*-indazol-3-yl)benzoate (3i): Derived from (*E*)-2,6-dimethyl-4-(phenyldiazenyl)phenol (**1g**) (45.3 mg) and methyl 4-formylbenzoate (65.7 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (7/3) as eluent afforded the product **3i** (49.9 mg, 67% yield) as a white powder (mp: 241-242

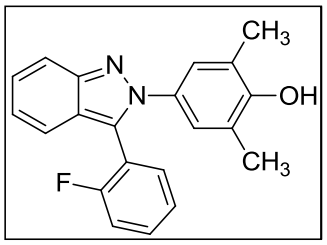
°C). IR (film): 3064 (br), 1709, 1493, 1380, 1310, 1280, 1234, 1194, 1101, 865, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.81 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.73 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.39 (ddd, *J* = 8.6, 6.6, 0.9 Hz, 1H), 7.18 (ddd, *J* = 8.7, 6.6, 1.0 Hz, 1H), 6.98 (s, 2H), 5.63 (br, 1H), 3.94 (s, 3H), 2.17 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 166.7, 152.6, 148.6, 134.4, 134.0, 132.2, 129.9, 129.4, 129.4, 127.0, 126.0, 124.6, 122.9, 121.5, 120.1, 117.7, 52.3, 16.1; HRMS (ESI/$[M+H]^+$) calcd. for $C_{23}H_{21}N_2O_3$: 373.1547. Found 373.1543.



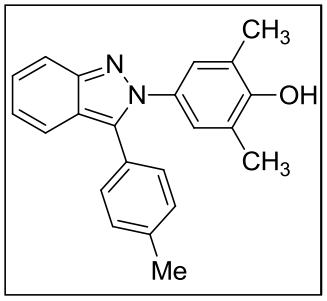
2,6-Dimethyl-4-(3-(4-nitrophenyl)-*2H*-indazol-2-yl)phenol (3j): Derived from (*E*)-2,6-dimethyl-4-(phenyldiazenyl)phenol (**1g**) (45.3 mg) and methyl 4-nitrobenzaldehyde (60.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded the product **3j** (52.5 mg, 73% yield) as a white powder (mp: 225-226 °C). IR (film): 3064 (br), 1598, 1513, 1489, 1343, 1235, 1193, 1100, 852, 724 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.25 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.42 (dd, *J* = 8.7, 8.6 Hz, 1H), 7.23 (ddd, *J* = 8.7, 8.6 Hz, 1H), 6.98 (s, 2H), 5.60 (br, 1H), 2.20 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 152.9, 148.6, 147.0, 136.4, 132.7, 131.9, 130.0, 127.2, 126.0, 124.8, 124.0, 123.7, 121.7, 119.6, 118.0, 16.1; HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{18}N_3O_3$: 360.1343. Found 360.1338.



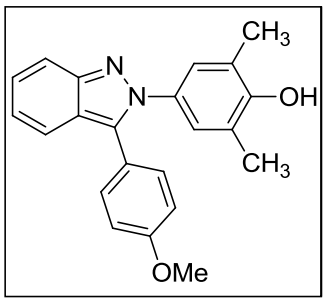
4-(3-(4-Chlorophenyl)-*2H*-indazol-2-yl)-2,6-dimethylphenol (3k): Derived from (*E*)-2,6-dimethyl-4-(phenyldiazenyl)phenol (**1g**) (45.3 mg) and 4-chlorobenzaldehyde (56.3 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded the product **3k** (55.8 mg, 80% yield) as a white powder (mp: 243-244 °C). IR (film): 3064 (br), 1500, 1371, 1222, 1093, 1011, 880, 840, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.80 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.68 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.35-7.40 (m, 3H), 7.29-7.33 (m, 2H), 7.16 (ddd, *J* = 8.4, 6.6, 0.9 Hz, 1H), 6.96 (s, 2H), 5.83 (br, 1H), 2.18 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 152.6, 148.4, 134.3, 134.1, 132.1, 130.7, 129.0, 128.4, 126.9, 126.0, 124.8, 122.6, 121.3, 120.1, 117.6, 16.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{18}ClN_2O$: 349.1102. Found 349.1101.



4-(3-(2-Fluorophenyl)-*2H*-indazol-2-yl)-2,6-dimethylphenol (3l): Derived from (*E*)-2,6-dimethyl-4-(phenyldiazenyl)phenol (**1g**) (45.3 mg) and *o*-fluorobenzaldehyde (49.7 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded product **3l** (53.9 mg, 81% yield) as a white powder (mp: 223-225 °C). IR (film): 3117 (br), 1498, 1449, 1368, 1254, 1221, 1182, 1103, 1014, 872, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.82 (dt, *J* = 8.8, 0.9 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.36-7.42 (m, 2H), 7.33 (td, *J* = 7.4, 1.7 Hz, 1H), 7.10-7.21 (m, 3H), 6.96 (s, 2H), 6.04 (s, 1H), 2.13 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 160.7, 158.7, 152.5, 148.3, 132.4, 132.0 (d, *J* = 2.5 Hz), 130.8 (d, *J* = 8.1 Hz), 129.7, 126.8, 125.3, 124.7, 122.34, 122.30, 120.4 (d, *J* = 1.8 Hz), 118.0 (d, *J* = 15.8 Hz), 117.5, 116.2 (d, *J* = 21.5 Hz), 16.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{18}FN_2O$: 333.1398. Found 333.1388.

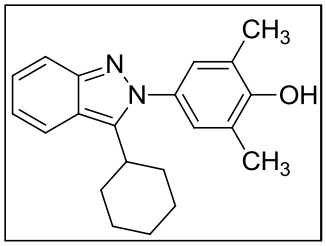


2,6-Dimethyl-4-(3-(p-tolyl)-2H-indazol-2-yl)phenol (3m): Derived from (*E*)-2,6-dimethyl-4-(phenyldiazenyl)phenol (**1g**) (45.3 mg) and *p*-tolualdehyde (48.1 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded product **3m** (44.0 mg, 67% yield) as a white powder (mp: 240-241 °C). IR (film): 3057 (br), 1492, 1369, 1220, 1183, 1101, 1014, 887, 820, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.79 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.72 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.36 (ddd, *J* = 8.4, 6.6, 0.9 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.18 (ddd, *J* = 8.4, 6.6, 0.9 Hz, 1H), 6.96 (s, 2H), 6.01 (br, 1H), 2.38 (s, 3H), 2.16 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 152.5, 148.4, 138.1, 135.6, 132.5, 129.4, 129.4, 126.9, 126.80, 126.0, 124.8, 122.1, 121.2, 120.7, 117.3, 21.3, 16.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{21}N_2O$: 329.1648. found 329.1637.

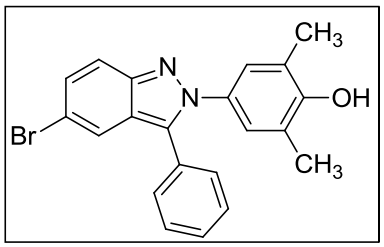


4-(3-(4-Methoxyphenyl)-*2H*-indazol-2-yl)-2,6-dimethylphenol (3n): Derived from (*E*)-2,6-dimethyl-4-(phenyldiazenyl)phenol (**1g**) (45.3 mg) and *p*-anisaldehyde (54.5 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded the product **3n** (43.4 mg, 63% yield)

as a white powder (mp: 244-246 °C). IR (film): 3059 (br), 2916, 2849, 1504, 1373, 1291, 1226, 1175, 1017, 880, 839, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.77 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.69 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.34 (ddd, *J* = 8.4, 6.6, 0.9 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.11 (ddd, *J* = 8.4, 6.6, 0.9 Hz, 1H), 7.05 (s, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H), 2.21 (s, 6H); $^{13}C\{^{1}H\}$ NMR (DMSO): δ 159.1, 153.2, 147.8, 134.5, 131.5, 130.6, 126.3, 125.7, 124.7, 121.8, 121.7, 120.7, 120.4, 117.2, 114.3, 55.2, 16.6; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{21}N_2O_2$: 345.1598. Found 345.1593.

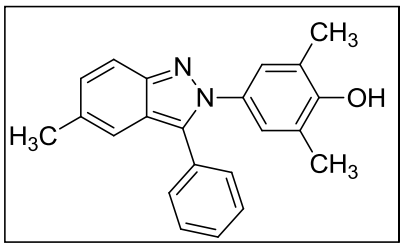


4-(3-Cyclohexyl-*2H*-indazol-2-yl)-2,6-dimethylphenol (3o): Derived from (*E*)-2,6-dimethyl-4-(phenyldiazenyl)phenol (**1g**) (45.3 mg) and cyclohexanecarboxaldehyde (44.9 mg, 0.400 mmol, 2.0 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded product **3o** (23.7 mg, 37% yield) as a white powder (mp: 268-270 °C). IR (film): 3060 (br), 2934, 2853, 1626, 1500, 1387, 1220, 1105, 988, 871, 743 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.38 (s, 1H), 7.32 (ddd, *J* = 8.7, 6.6, 1.0 Hz, 1H), 7.06 (ddd, *J* = 8.5, 6.6, 1.0 Hz, 1H), 6.89 (s, 2H), 2.91 (tt, *J* = 11.7, 4.2 Hz, 1H), 2.23 (s, 6H), 1.69-2.03 (m, 7H), 1.19-1.40 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 153.4, 147.9, 141.6, 131.6, 126.4, 126.1, 126.0, 121.2, 120.4, 119.0, 117.3, 37.1, 32.5, 26.5, 25.9, 16.6.; HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{25}N_2O$: 321.1961. Found 321.1959.

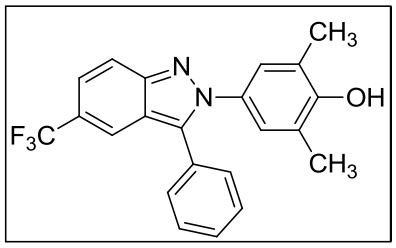


4-(5-Bromo-3-phenyl-*2H*-indazol-2-yl)-2,6-dimethylphenol (3p): Derived from (*E*)-4-((4-bromophenyl)diazenyl)-2,6-dimethylphenol (**1j**) (61.1 mg, 0.20 mmol, 1.0 equiv) and benzaldehyde (**2a**) (42.5 mg). Purification by silica gel column chromatography using hexane/ethyl acetate (10/1) as eluent afforded product **3p** (47.1 mg, 60% yield) as a white powder (mp: 209-211 °C). IR (film): 3233 (br), 1492, 1322, 1250, 1188, 1043, 1013, 950, 865, 802 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.87 (m, 1H), 7.66 (d, *J* = 9.1 Hz, 1H), 7.36-7.43 (m, 4H), 7.32-7.36 (m, 2H), 6.98 (s, 2H), 5.41 (br, 1H), 2.16 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 152.5, 146.9, 135.0, 132.2, 130.4, 129.5, 129.4, 128.8, 128.5,

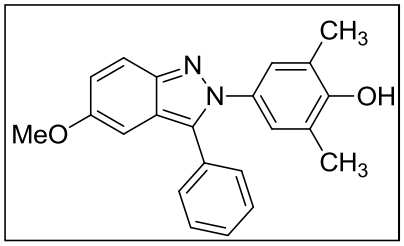
125.9, 124.3, 122.7, 122.6, 119.3, 115.7, 16.0; HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{18}BrN_2O$: 395.0579. Found 395.0568.



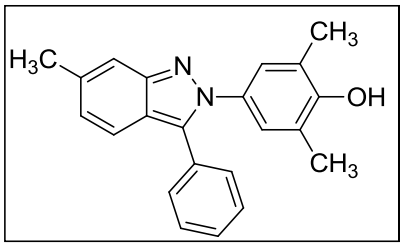
2,6-Dimethyl-4-(5-methyl-3-phenyl-*2H*-indazol-2-yl)phenol (3q): Derived from ((*E*)-2,6-dimethyl-4-(*p*-tolyldiazenyl)phenol (**1k**) (48.1 mg, 0.20 mmol, 1.0 equiv) and benzaldehyde (**2a**) (42.5 mg). Purification by silica gel column chromatography using hexane/ethyl acetate (10/1) as eluent afforded the product **3q** (40.7 mg, 62% yield) as a white powder (mp: 213-215 °C). IR (film): 3279 (br), 1504, 1491, 1189, 1101, 802 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.47 (m, 1H), 7.31-7.41 (m, 5H), 7.22 (dd, *J* = 8.8, 1.5 Hz, 1H), 6.93 (s, 2H), 6.19 (s, 1H), 2.44 (s, 3H), 2.14 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.4, 147.3, 134.6, 132.4, 131.7, 130.0, 129.8, 129.6, 128.6, 128.0, 125.9, 124.9, 121.5, 118.5, 117.1, 21.8, 16.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{21}N_2O$: 329.1648. Found 329.1636.



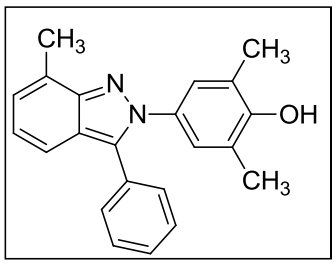
2,6-Dimethyl-4-(3-phenyl-5-(trifluoromethyl)-*2H*-indazol-2-yl)phenol (3r): Derived from ((*E*)-2,6-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)phenol (**1m**) (58.9 mg, 0.20 mmol, 1.0 equiv) and benzaldehyde (**2a**) (42.5 mg). Purification by silica gel column chromatography using hexane/ethyl acetate (10/1) as eluent afforded the product **3r** (35.2 mg, 46% yield) as a white powder (mp: 190-192 °C). IR (film): 3240 (br), 1639, 1491, 1423, 1323, 1264, 1189, 1115, 1048, 895, 814, 756, 693 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.03 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.52 (dd, *J* = 9.1, 0.9 Hz, 1H), 7.35-7.46 (m, 5H), 7.02 (s, 2H), 4.38-5.67 (br, 1H), 2.19 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.3, 148.8, 137.4, 132.0, 129.6, 129.0, 128.93, 128.86, 125.9, 124.7 (q, *J* = 271.5 Hz), 124.4 (q, *J* = 32.0 Hz), 124.1, 124.8 (q, *J* = 2.9 Hz), 120.2, 119.5 (q, *J* = 5.0 Hz), 118.6, 16.0; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{18}F_3N_2O$: 383.1366. Found 383.1360.



4-(5-Methoxy-3-phenyl-*2H*-indazol-2-yl)-2,6-dimethylphenol (3s): Derived from (*E*)-4-((4-methoxyphenyl)diazenyl)-2,6-dimethylphenol (**1l**) (51.3 mg, 0.20 mmol, 1.0 equiv) and benzaldehyde (**2a**) (42.5 mg). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded the product **3s** (42.7 mg, 62% yield) as a white powder (mp: 230-231 °C). IR (film): 3059 (br), 1503, 1326, 1205, 1106, 1016, 823, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.70 (dd, *J* = 9.1, 0.9 Hz, 1H), 7.31-7.42 (m, 5H), 7.08 (dd, *J* = 9.1, 2.4 Hz, 1H), 6.92 (m, 3H), 6.04 (s, 1H), 3.83 (s, 3H), 2.14 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 155.7, 152.3, 145.2, 134.4, 132.4, 130.3, 129.4, 128.6, 127.9, 125.9, 124.8, 121.7, 121.1, 118.8, 96.5, 55.4, 16.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{21}N_2O_2$: 345.1598. Found 345.1598.



2,6-Dimethyl-4-(6-methyl-3-phenyl-*2H*-indazol-2-yl)phenol (3t): Derived from ((*E*)-2,6-dimethyl-4-(*m*-tolyldiazenyl)phenol (**1n**) (48.1 mg, 0.20 mmol, 1.0 equiv) and benzaldehyde (**2a**) (42.5 mg). Purification by silica gel column chromatography using hexane/ethyl acetate (10/1) as eluent afforded the product **3t** (39.4 mg, 60% yield) as a white powder (mp: 212-214 °C). IR (film): 3555 (br), 1631, 1491, 1370, 1253, 1191, 1104, 1014, 882, 798 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.62 (d, *J* = 8.7 Hz, 1H), 7.55 (m, 1H), 7.31-7.41 (m, 5H), 6.99 (dd, *J* = 8.7, 1.2 Hz, 1H), 6.93 (s, 2H), 6.13 (s, 1H), 2.49 (s, 3H), 2.14 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 152.4, 148.9, 136.8, 135.3, 132.4, 129.9, 129.5, 128.6, 128.1, 126.0, 125.2, 124.9, 120.1, 119.7, 115.7, 22.2, 16.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{21}N_2O$: 329.1648. Found 329.1635.

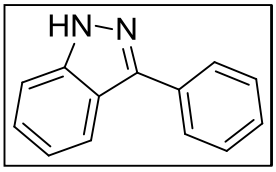


2,6-Dimethyl-4-(7-methyl-3-phenyl-*2H*-indazol-2-yl)phenol (3u): Derived from ((*E*)-2,6-dimethyl-4-(*o*-tolyldiazenyl)phenol (**1o**) (48.1 mg, 0.20 mmol, 1.0 equiv) and benzaldehyde (**2a**) (42.5 mg). Purification by silica gel column chromatography using hexane/ethyl acetate (10/1) as eluent afforded the product **3u** (49.9 mg, 76% yield) as a white powder (mp: 265-266 °C). IR (film): 3548 (br), 1506, 1492, 1368,

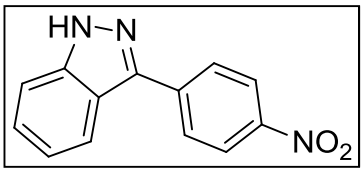
1338, 1215, 1190, 1078, 1012, 879, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.29-7.39 (m, 5H), 7.17 (dt, *J* = 6.7, 0.8 Hz, 1H), 7.08 (dd, *J* = 8.4, 6.7 Hz, 1H), 7.06 (br, 1H), 6.90 (s, 2H), 2.78 (s, 3H), 2.17 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 152.9, 148.4, 136.1, 132.2, 129.8, 129.5, 128.5, 128.1, 127.3, 126.2, 126.1, 126.0, 122.7, 120.8, 118.0, 17.2, 16.5; HRMS (ESI/$[M+H]^+$) calcd. for $C_{22}H_{21}N_2O$: 329.1648. Found 329.1643.

IV. Oxidative Cleavage of Phenol

General Procedure: To a round bottom flask equipped with a stir bar was added the indicated (2H-indazol-2-yl)phenol (0.1 mmol, 1.0 equiv) in MeOH (2 mL) at 0 ^{o}C. After 10 min, CAN (0.110g, 0.20 mmol, 2.0 equiv) in MeOH (2 mL) was added dropwise. The solution was stirred for additional 15 min and then was concentrated under reduced pressure. The solid residue was purified directly by flash column chromatography with pentane/ether (2:1) to afford the free indazole as a powder.

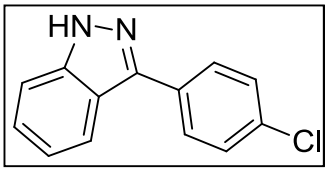


3-Phenyl-*1H*-indazole (7g): Derived from 2,6-dimethyl-4-(3-phenyl-2H-indazol-2-yl)phenol (**3g**) (31.5 mg, 0.10 mmol, 1.0 equiv). Purification by silica gel column chromatography using pentane/ether (2:1) as eluent afforded product **7g** (17.5 mg, 90% yield) as a white powder. The analytical data for this compound are consistent with previously reported data.[6]

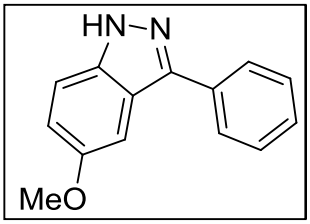


3-(4-Nitrophenyl)-*1H*-indazole (7j): Derived from 4-(3-(4-nitrophenyl)-2H-indazol-2-yl)-2,6-dimethylphenol (**3j**) (35.9 mg, 0.10 mmol, 1.0 equiv). Purification by silica gel column chromatography using pentane/ether (2:1) as eluent afforded the product **7j** (21.1 mg, 89% yield) as a yellow powder (mp: 180-182 °C). IR (film): 3047 (br), 1595, 1513, 1337, 1262, 1099, 987, 851, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.00-11.0 (br, 1H), 8.35-8.39 (m, 2H), 8.16-8.22 (m, 2H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.49 (td, *J* = 8.4, 0.9 Hz, 1H), 7.33 (td, *J* = 8.4, 0.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 147.3, 143.4, 141.7,

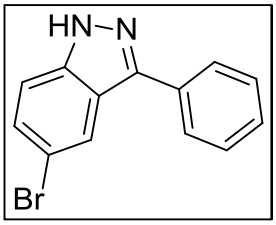
140.0, 127.8, 127.4, 124.2, 122.5, 120.9, 120.6, 110.4; HRMS (ESI/$[M+H]^+$) calcd. for $C_{13}H_{10}N_3O$: 240.0768. Found 240.0767.



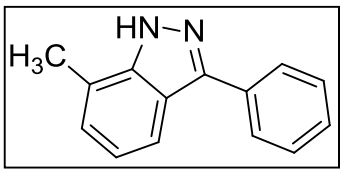
3-(4-Chlorophenyl)-*1H*-indazole (7k): Derived from 4-(3-(4-chlorophenyl)-2H-indazol-2-yl)-2,6-dimethylphenol (**3k**) (34.9 mg, 0.10 mmol, 1.0 equiv). Purification by silica gel column chromatography using pentane/ether (2:1) as eluent afforded the product **7k** (21.1 mg, 92% yield) as a white powder (mp: 129-131 °C). IR (film): 3110 (br), 1620, 1504, 1405, 1260, 1100, 1086, 992, 834 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.60-10.7 (br, 1H), 7.99 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.91-7.95 (m, 2H), 7.47-7.52 (m, 2H), 7.39-7.45 (m, 2H), 7.25 (ddd, *J* = 8.2, 5.5, 2.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.6, 141.6, 134.1, 131.9, 129.1, 128.8, 127.1, 121.7, 120.9, 120.8, 110.2; HRMS (ESI/$[M+H]^+$) calcd. for $C_{13}H_{10}ClN_2$: 229.0527. Found 229.0525.



5-Methoxy-3-phenyl-*1H*-indazole (7p): Derived from 4-(5-methoxy-3-phenyl-2H-indazol-2-yl)-2,6-dimethylphenol (**3p**) (34.4 mg, 0.10 mmol, 1.0 equiv). Purification by silica gel column chromatography using pentane/ether (2:1) as eluent afforded the product **7p** (19.5 mg, 87% yield) as a white powder. The analytical data for this compound are consistent with previously reported data.[7]



5-Bromo-3-phenyl-*1H*-indazole (7s): Derived from 4-(5-bromo-3-phenyl-2H-indazol-2-yl)-2,6-dimethylphenol (**3s**) (39.4 mg, 0.10 mmol, 1.0 equiv). Purification by silica gel column chromatography using pentane/ether (2:1) as eluent afforded the product **7s** (23.8 mg, 87% yield) as a white powder. The analytical data for this compound are consistent with previously reported data.[8]



7-Methyl-3-phenyl-*1H*-indazole (7u): Derived from 2,6-dimethyl-4-(7-methyl-3-phenyl-2H-indazol-2-yl)phenol (**3u**) (32.9 mg, 0.10 mmol, 1.0 equiv). Purification by silica gel column chromatography using pentane/ether (2:1) as eluent afforded the product **7t** (19.2 mg, 92% yield) as a white powder (mp: 152-154 °C). IR (film): 3045 (br), 1510, 1438, 1340, 1134, 1076, 985, 959, 790, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.00-10.50 (br, 1H), 7.94-7.99 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.14-7.23 (m, 2H), 2.58 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 146.1, 141.8, 133.4, 128.8, 128.2, 127.6, 127.0, 121.9, 120.6, 120.0, 118.7, 16.7; HRMS (ESI/$[M+H]^+$) calcd. for $C_{14}H_{13}N_2$: 209.1073. Found 209.1072.

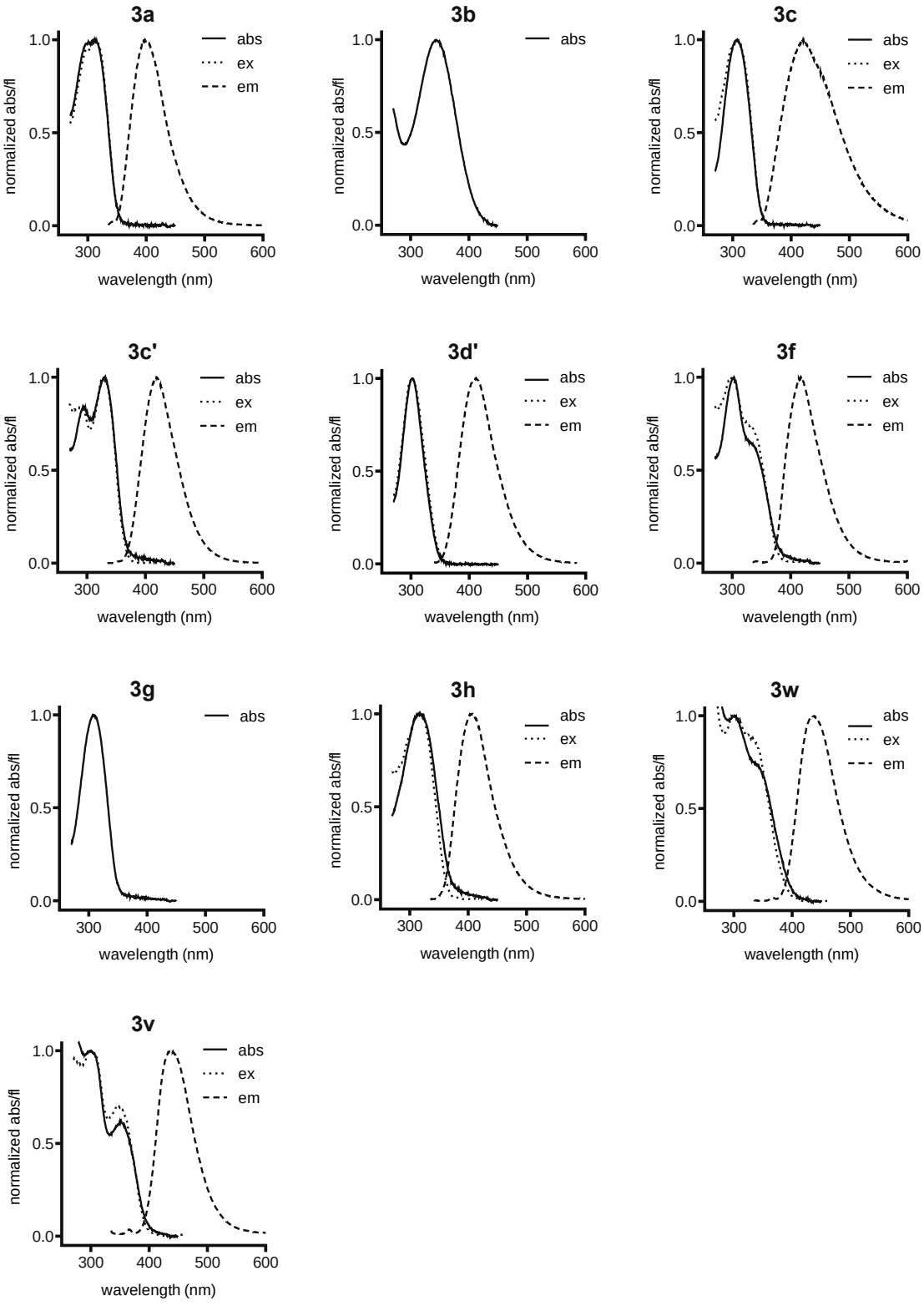


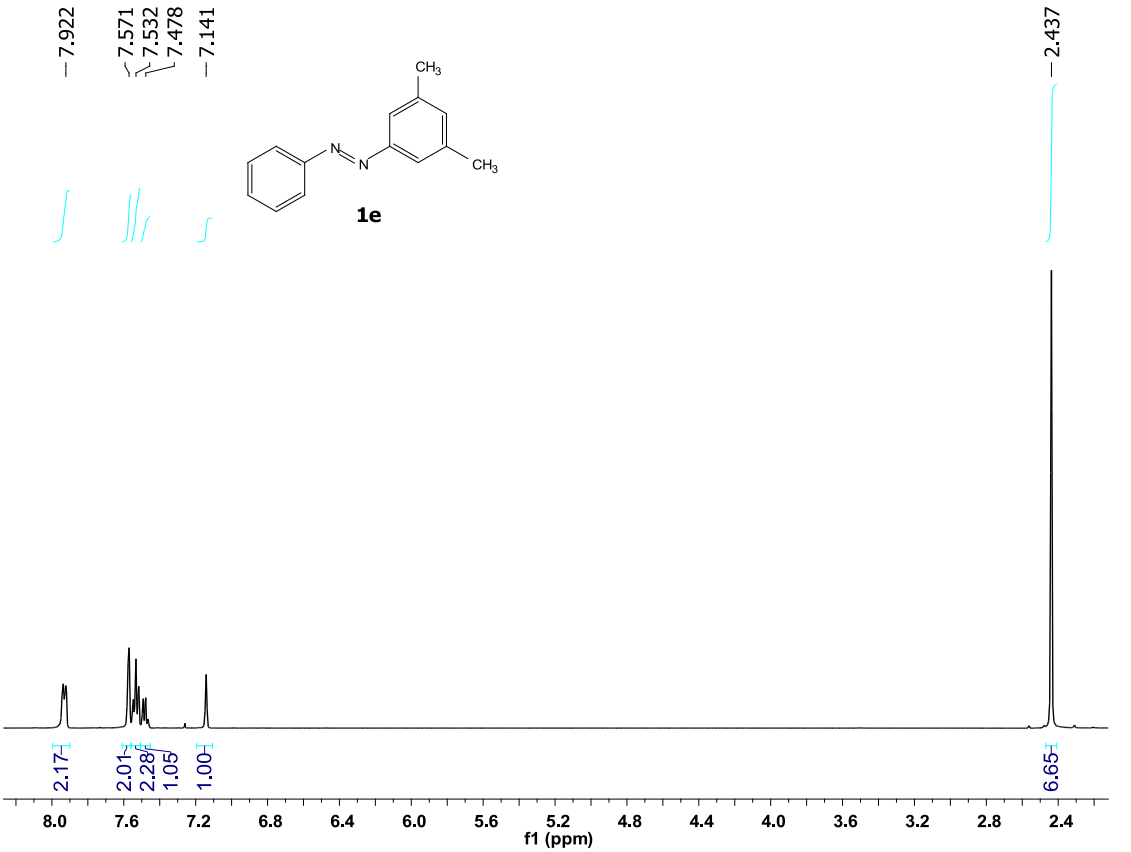
Figure S1: Normalized absorbance (abs), fluorescence excitation (ex), and fluorescence emission (em) spectra for selected fluorophores.

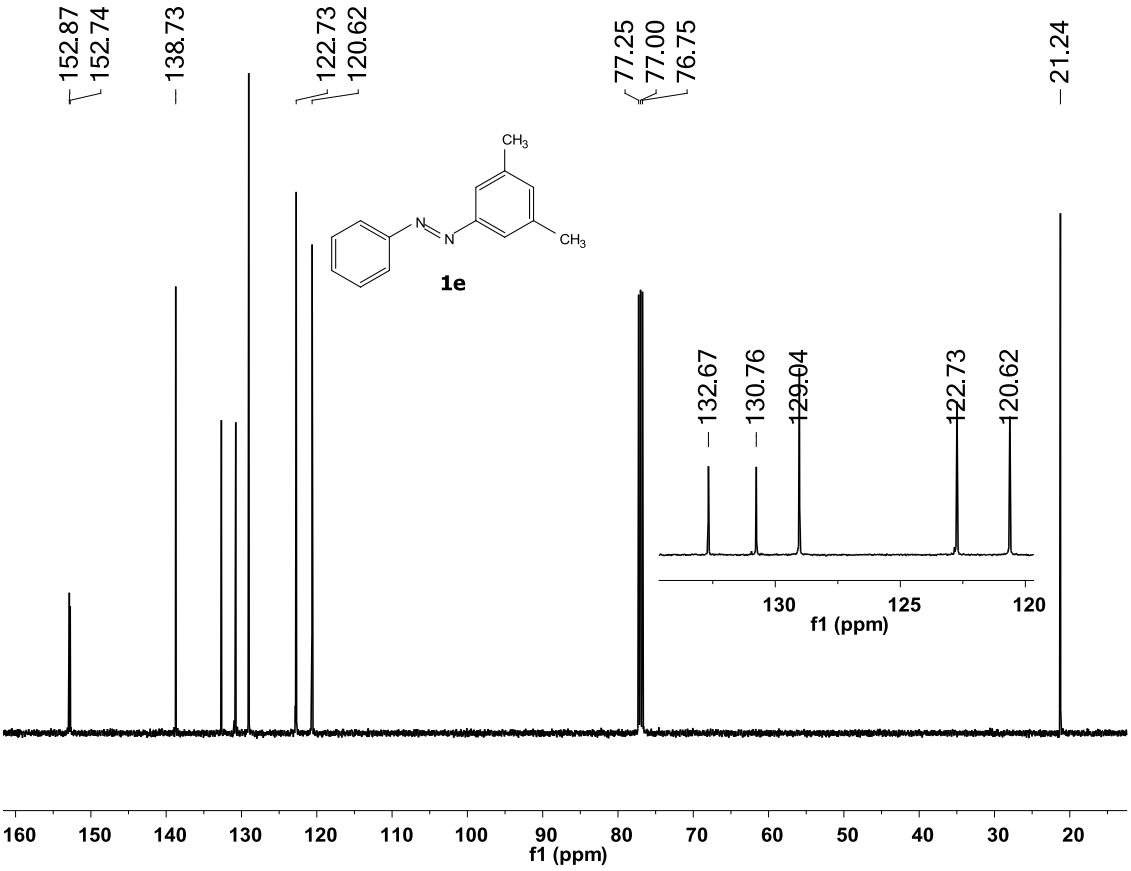
UV–vis and Fluorescence Spectroscopy. Fluorescent molecules were prepared as stock solutions in DMSO and diluted such that the DMSO concentration did not exceed 1% v/v. Spectroscopy was performed using 1-cm path length, 3.5-mL quartz cuvettes from Starna Cells. All measurements were taken at ambient temperature (22 ± 2 °C). Absorption spectra were recorded on a Cary Model 100 spectrometer (Varian). Maximum absorption wavelength (λ_{max}) and extinction coefficient (ε) were taken in 10 mM HEPES buffer, pH 7.3. Fluorescence spectra were recorded on a Cary Eclipse fluorometer (Varian).

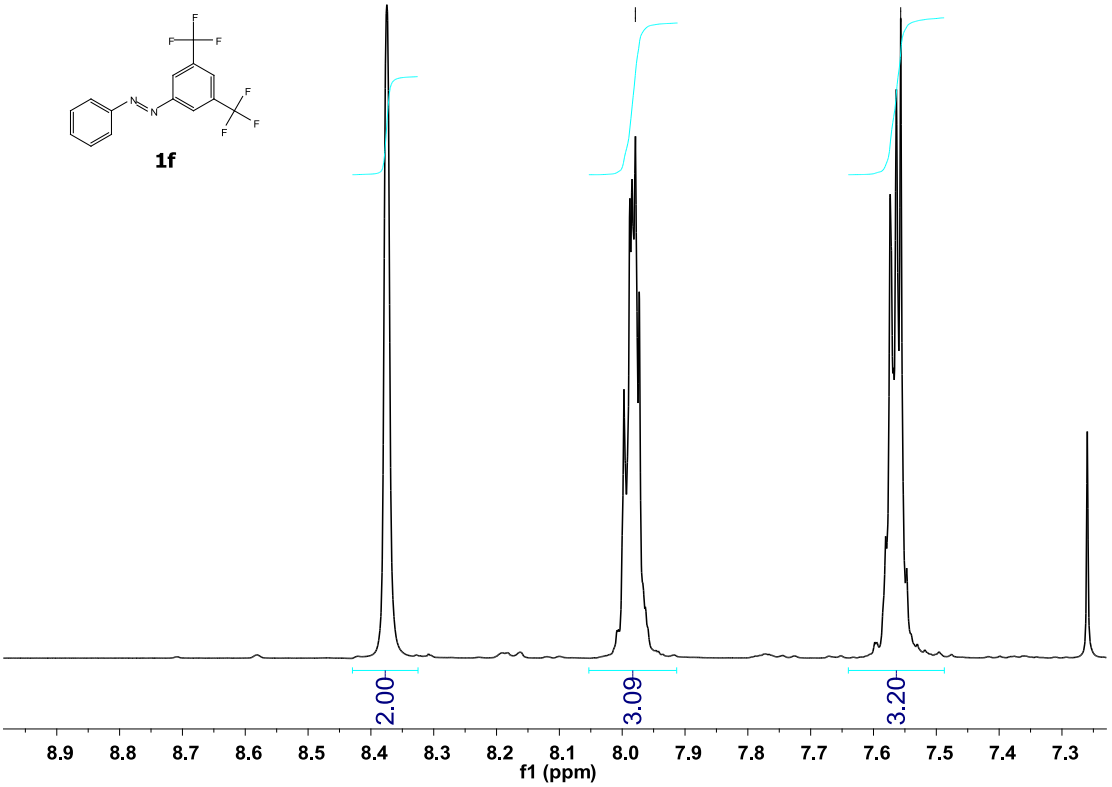
Quantum Yield Determination. Absolute quantum yields (Φ) were measured using a Quantaurus-QY spectrometer (model C11374) from Hamamatsu. This instrument uses an integrating sphere to determine photons absorbed and emitted by a sample. Measurements were carried out using dilute samples ($A < 0.1$) and self-absorption corrections were performed using the instrument software.[9]

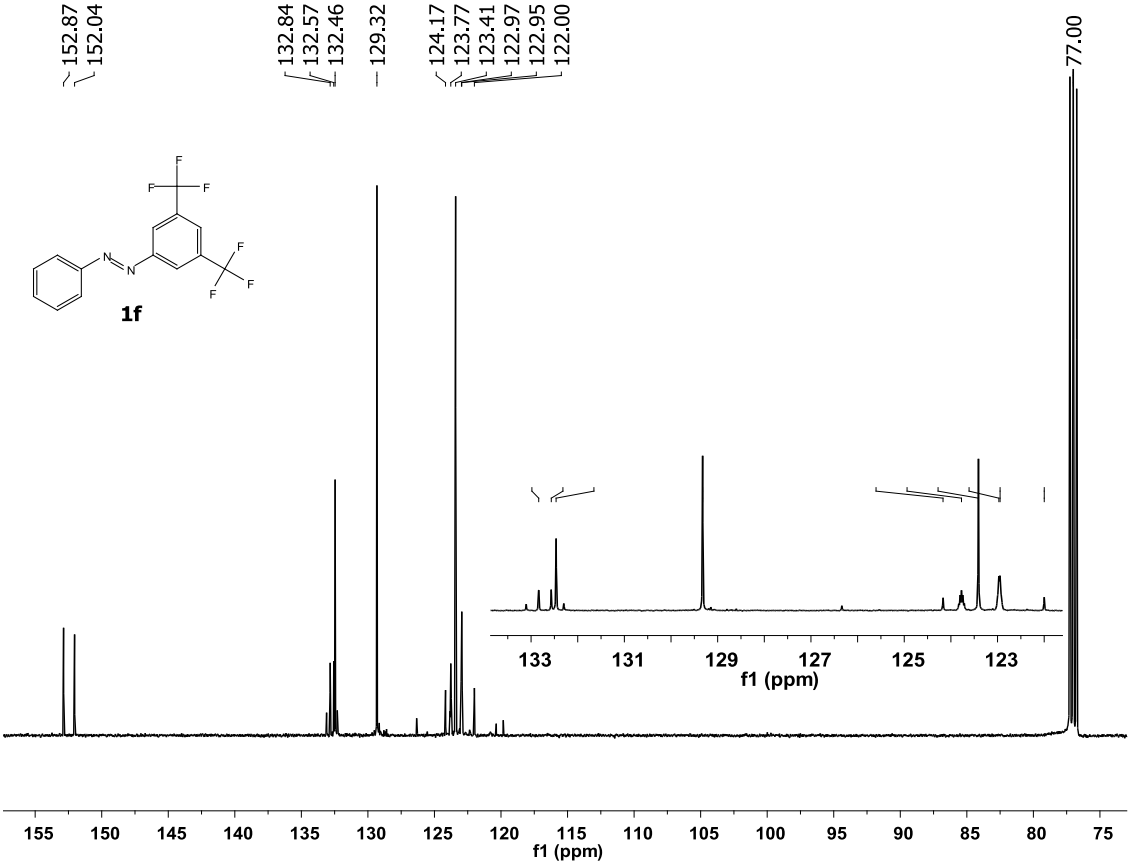
VI. Reference:

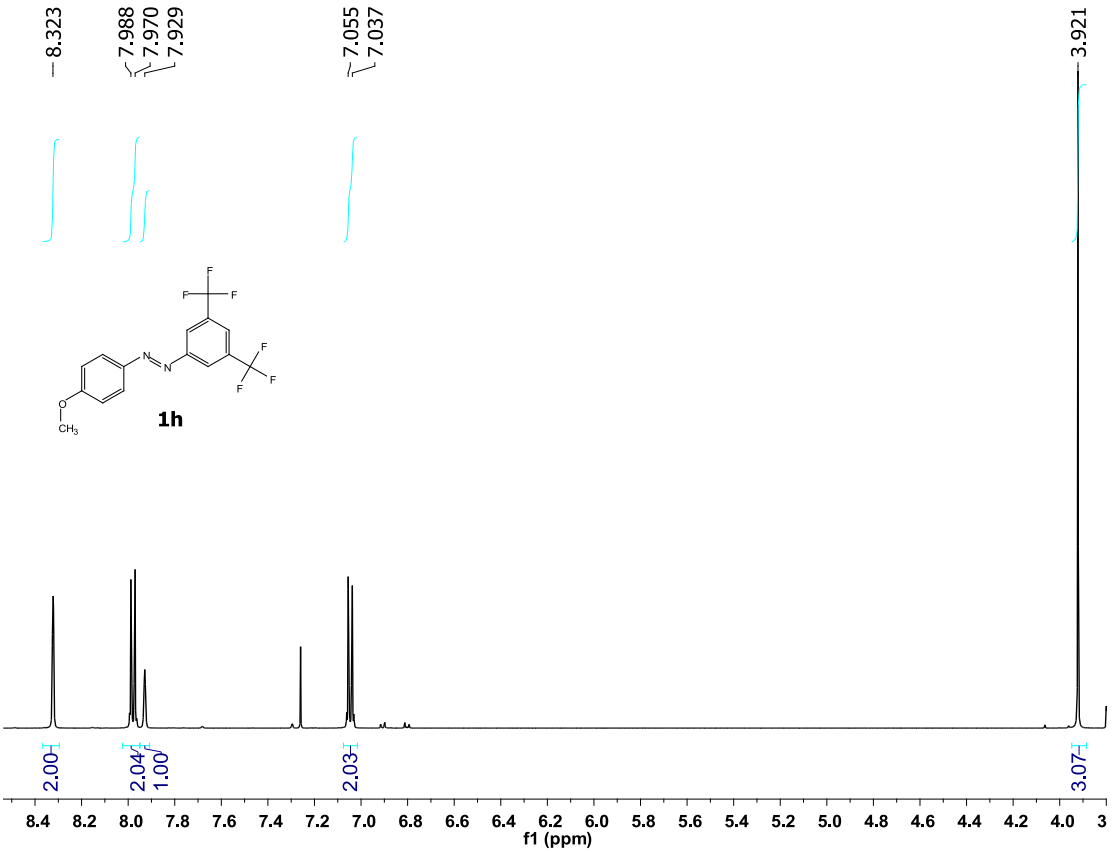
1. White, C.; Thompson S. J.; Maitlis P. M. *J. Chem. Soc., Dalton Trans.* **1977**, *17*, 1654.
2. Nojiri, A.; Kumagai, N.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2011**, *51*, 2137.
3. Mei, X.; Yang, S.; Chen, D.-Y.; Li, N.-J.; Li, H.; Xu, Q.-F.; Ge, J.-F.; Lu, J.-M. *Chem. Commun.* **2012**, *48*, 10010.
4. Hattori, K.; Yamaguchi, K.; Yamakuchi, J.; Itami, K. *Tetrahedron* **2012**, *68*, 7605.
5. Hu, J.-T.; Cheng, Y.-F., Yang, Y.-Q.; Rao, Y. *Chem. Commun.* **2011**, *47*, 10133.
6. Kovács, S.; Csincsi, Á. I.; Nagy, T. Z.; Boros, S.; Timári, G.; Novák, Z. *Org. Lett.* **2012**, *8*, 2022.
7. Salovich, J. M.; Lindsley, C. W.; Hopkins, C. R. *Tetrahedron Lett.* **2010**, *51*, 3796.
8. Zeng, Q.-P.; Bourbeau, M. P.; Wohlhieter, G. E.; Yao, G.-M.; Monenschein, H.; Rider, J. T.; Lee, M. R.; Zhang, S.-W.; Lofgren, J.; Freeman, D.; Li, C.; Tominey, E.; Huang, X.; Hoffman, D.; Yamane, H.; Tasker, A. S.; Dominguez, C.; Viswanadhan, V. N.; Hungate, R.; Zhang, X.-L. *Bioorg. Med. Chem. Lett.* **2012**, *20*, 1652.
9. Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850.

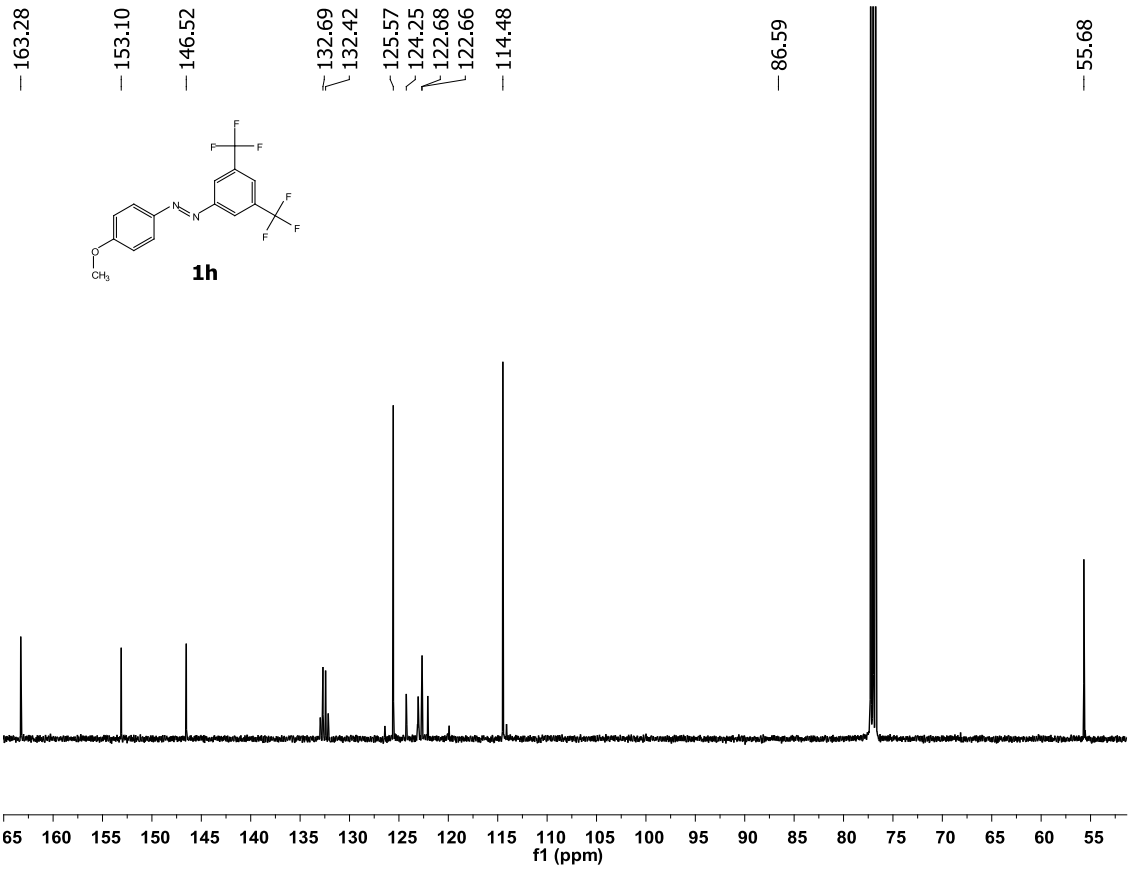

7.922
7.571
7.532
7.478
7.141
2.437
CH3
CH3
N
N
1e
2.17
2.01
2.28
1.05
1.00
6.65
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
f1 (ppm)

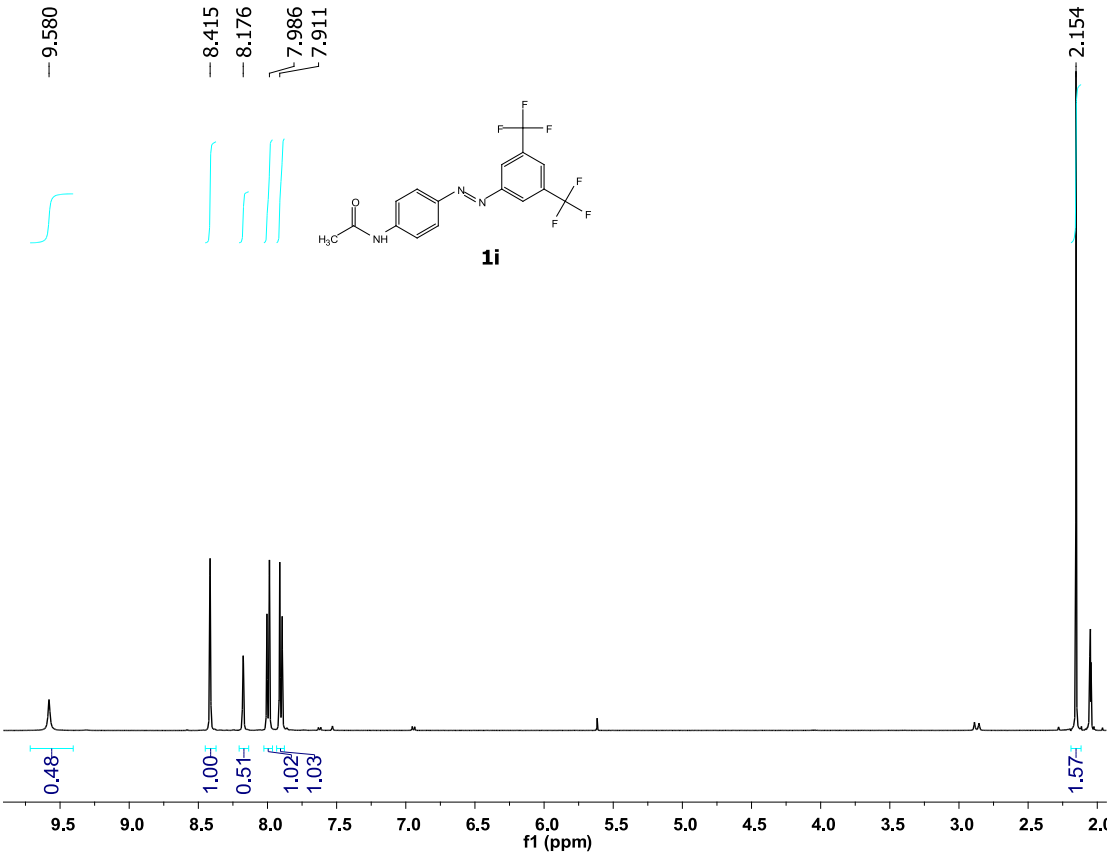

152.87
152.74
138.73
122.73
120.62
77.25
77.00
76.75
21.24
CH3
CH3
N
N
1e
132.67
130.76
129.04
122.73
120.62
130
125
120
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

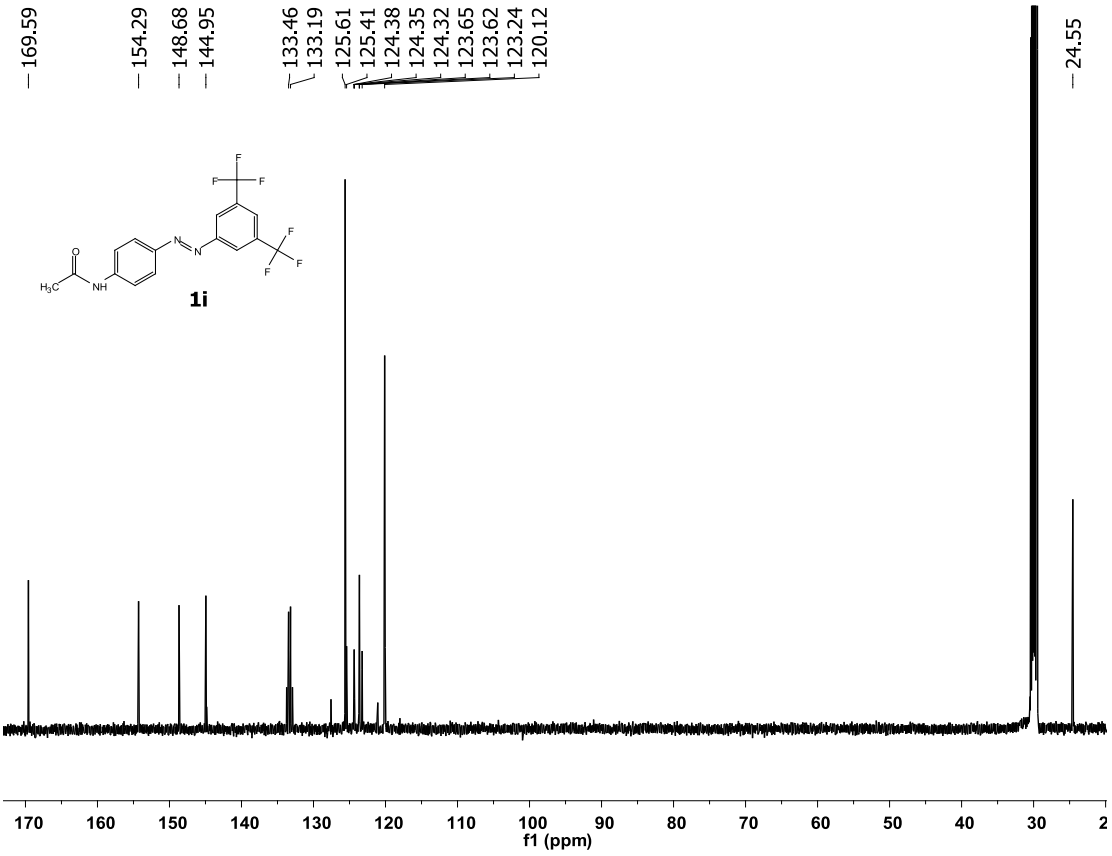

1f
2.00
3.09
3.20
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)

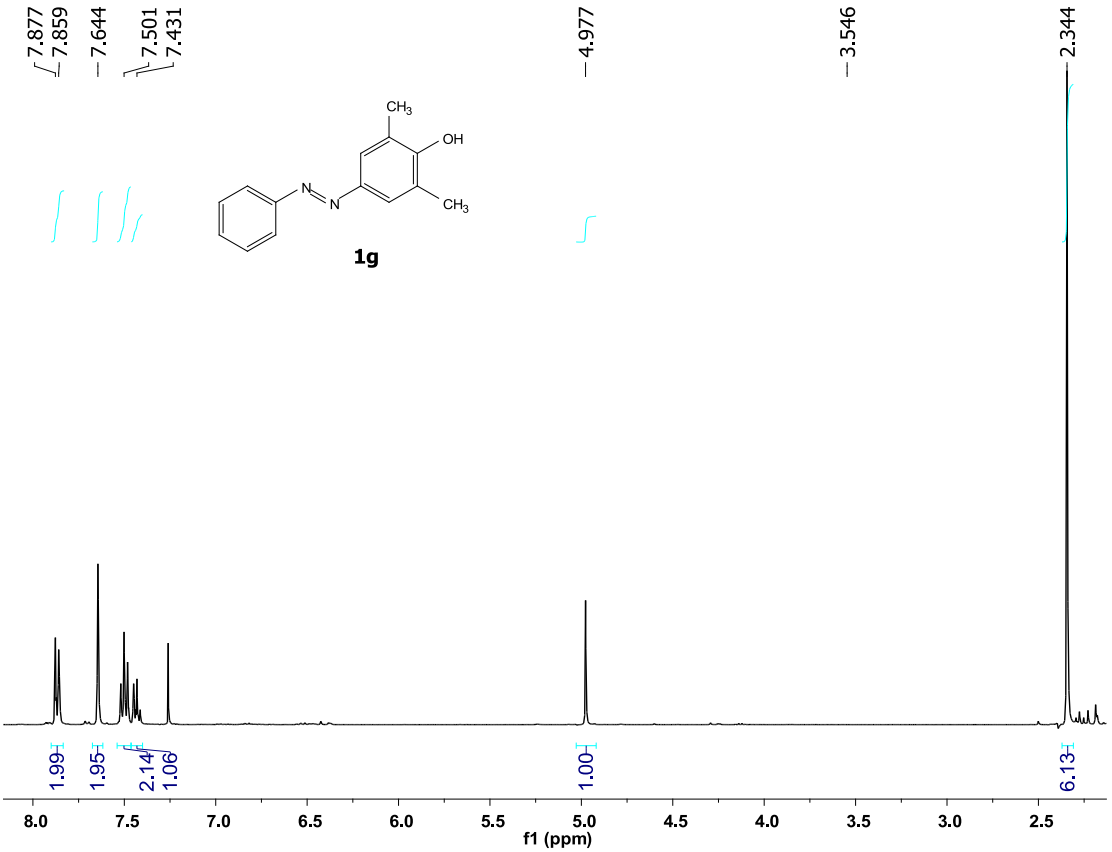

152.87
152.04
132.84
132.57
132.46
129.32
124.17
123.77
123.41
122.97
122.95
122.00
77.00
1f
133 131 129 127 125 123
f1 (ppm)
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75
f1 (ppm)

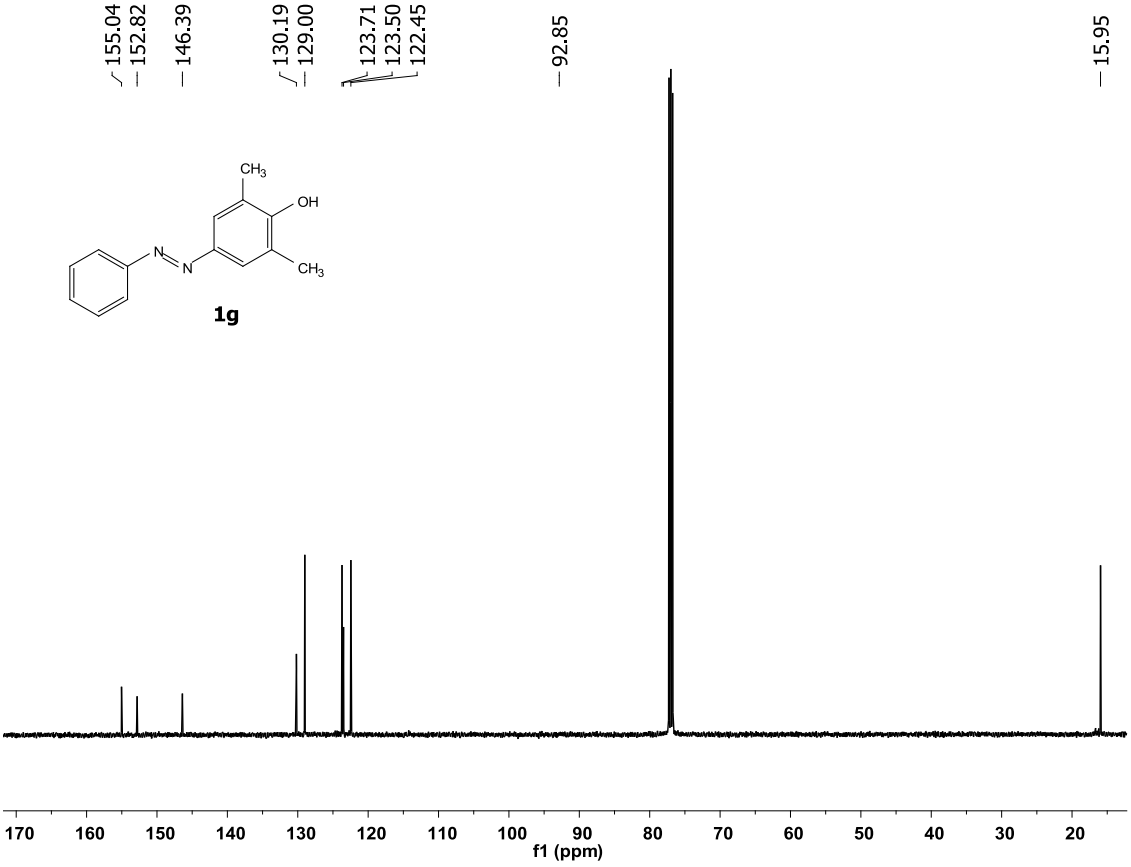

8.323
7.988
7.970
7.929
7.055
7.037
3.921
1h
2.00
2.04
1.00
2.03
3.07
f1 (ppm)

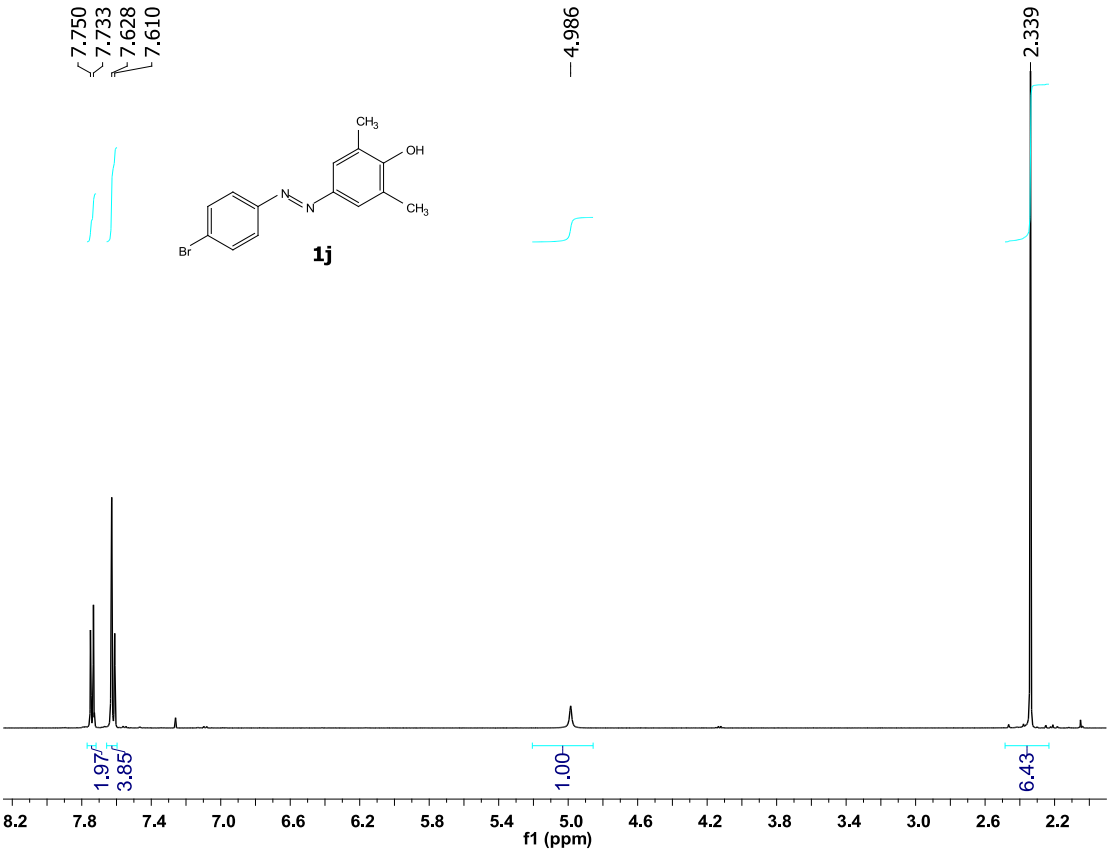

163.28
153.10
146.52
132.69
132.42
125.57
124.25
122.68
122.66
114.48
86.59
55.68
1h
f1 (ppm)

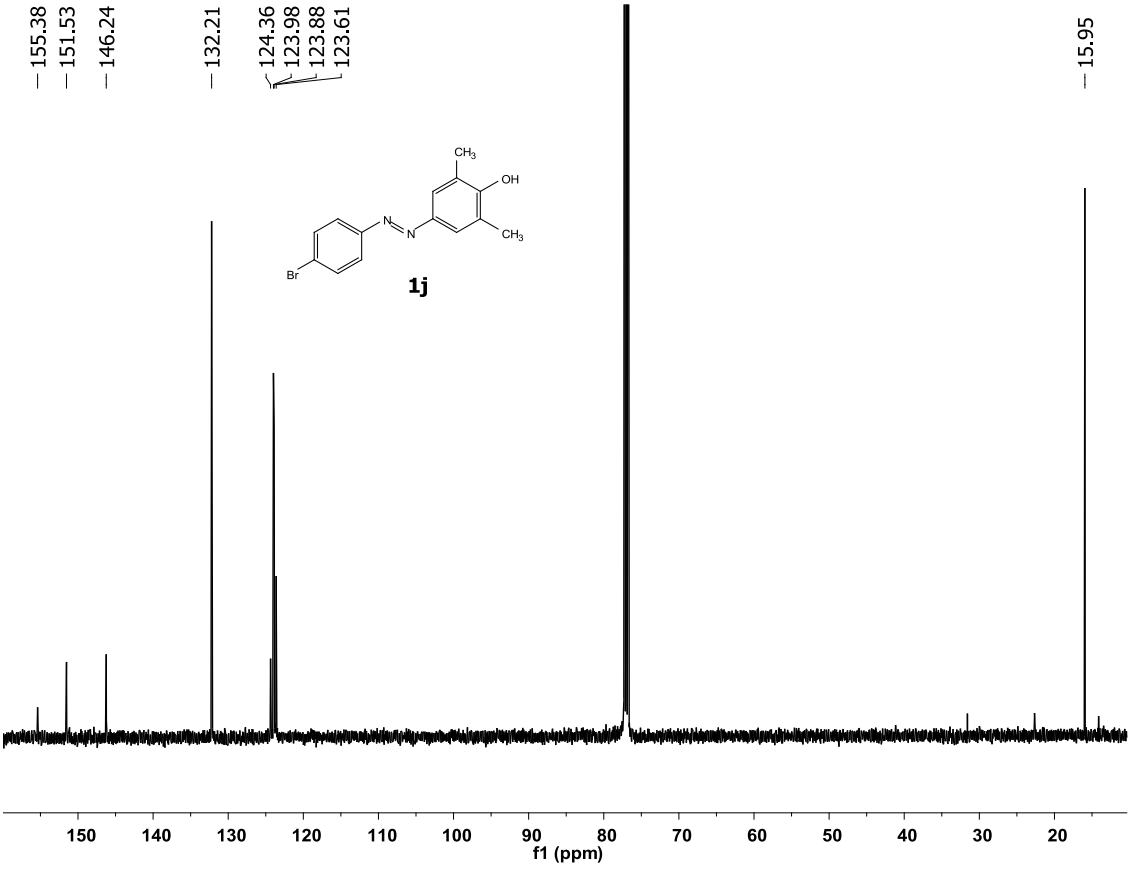

9.580
8.415
8.176
7.986
7.911
2.154
1i
0.48
1.00
0.51
1.02
1.03
1.57
f1 (ppm)

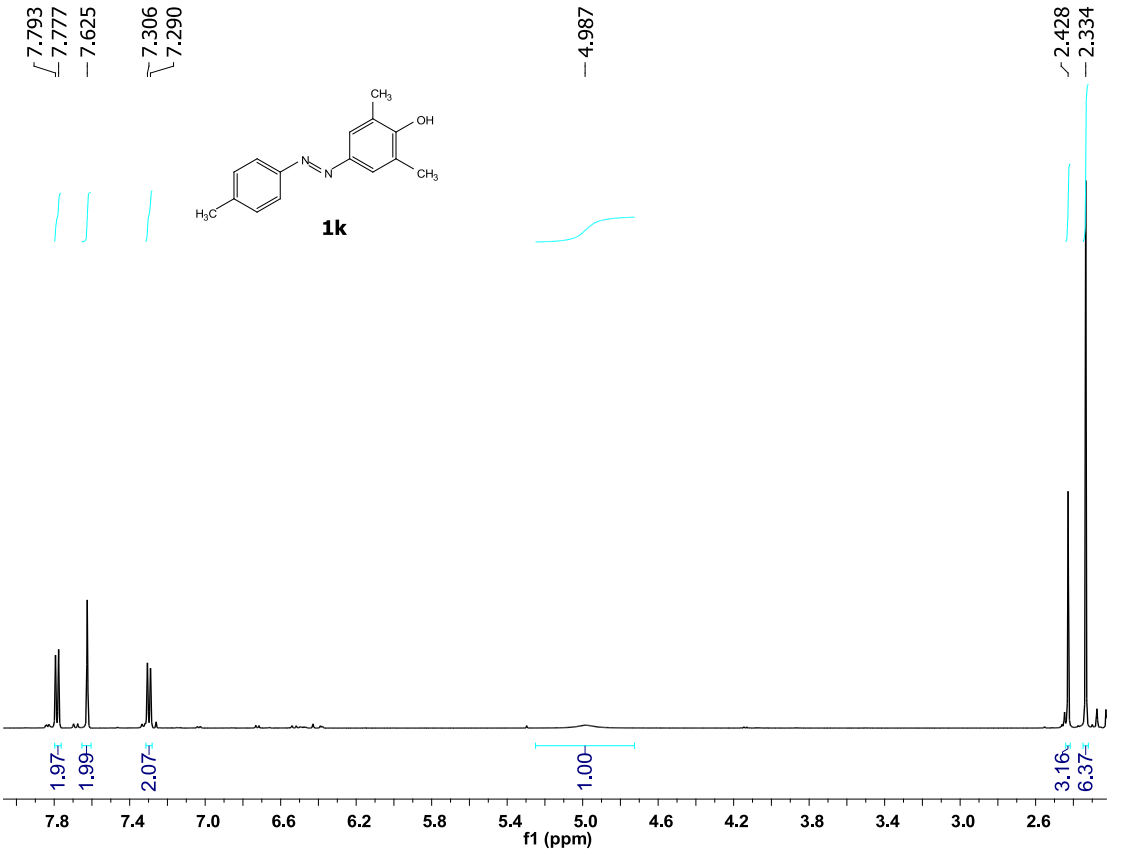

169.59
154.29
148.68
144.95
133.46
133.19
125.61
125.41
124.38
124.35
124.32
123.65
123.62
123.24
120.12
24.55
1i
f1 (ppm)

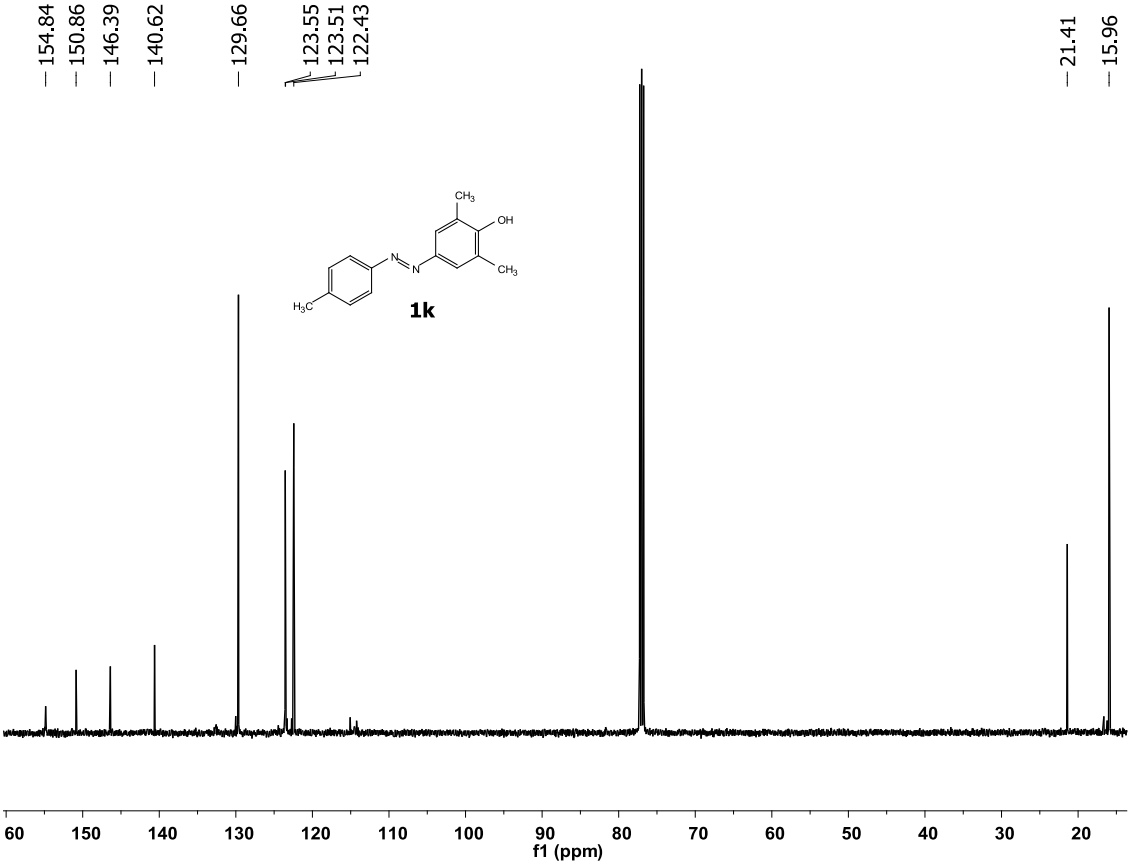

7.877
7.859
7.644
7.501
7.431
4.977
3.546
2.344
CH3
OH
CH3
N
N
1g
1.99
1.95
2.14
1.06
1.00
6.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

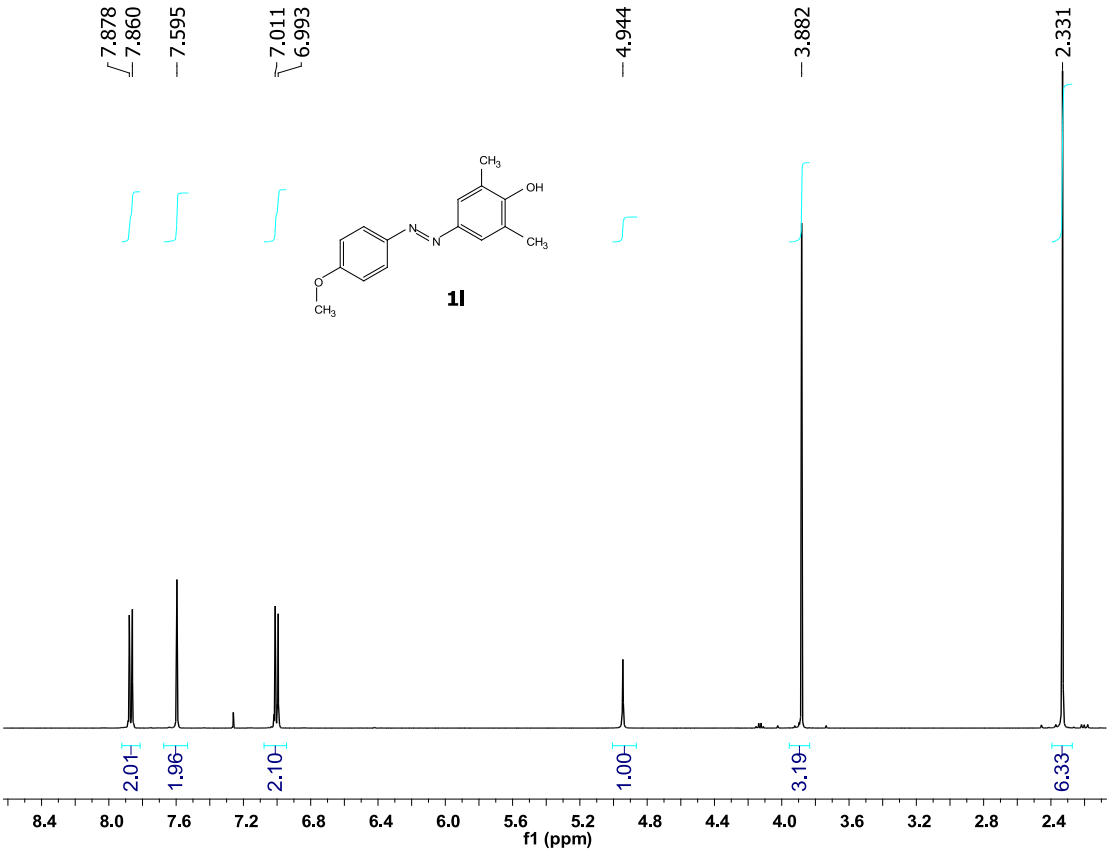

155.04
152.82
146.39
130.19
129.00
123.71
123.50
122.45
92.85
15.95
CH3
OH
CH3
N
N
1g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

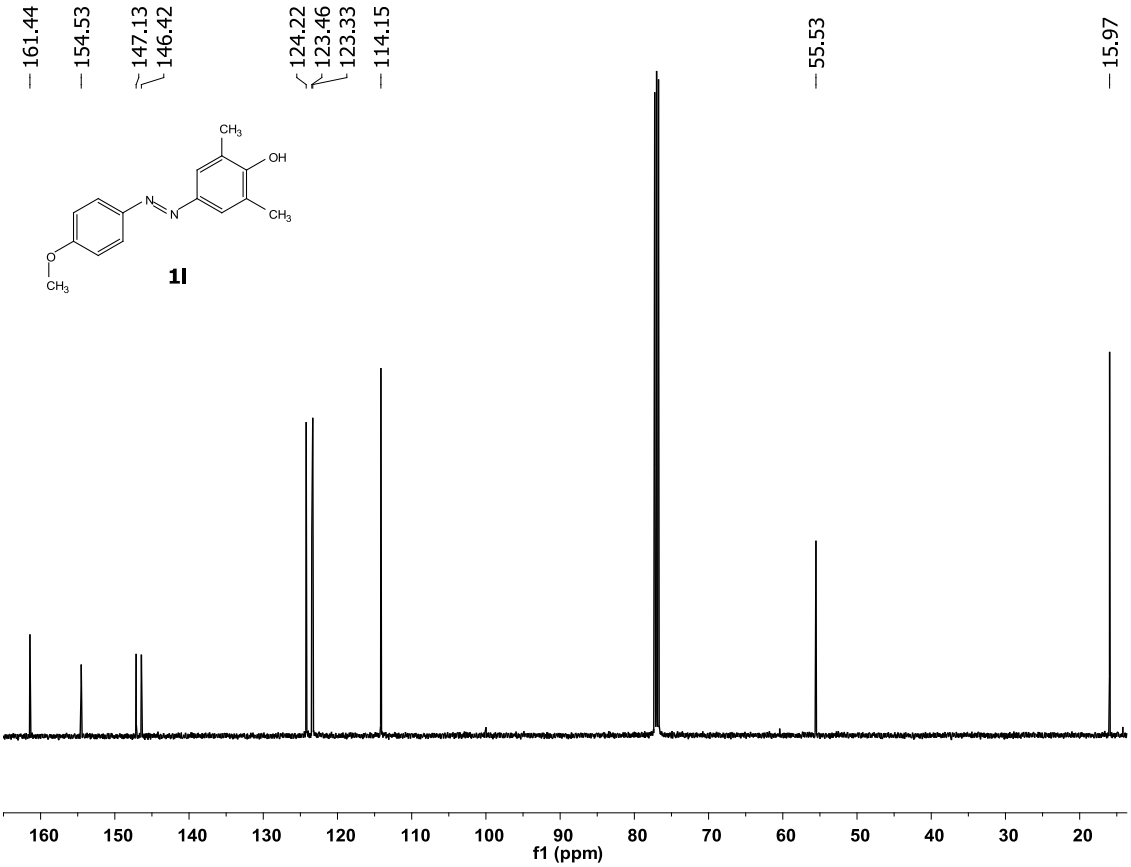

7.750
7.733
7.628
7.610
4.986
2.339
CH3
OH
CH3
N
N
Br
1j
1.97
3.85
1.00
6.43
8.2
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
f1 (ppm)

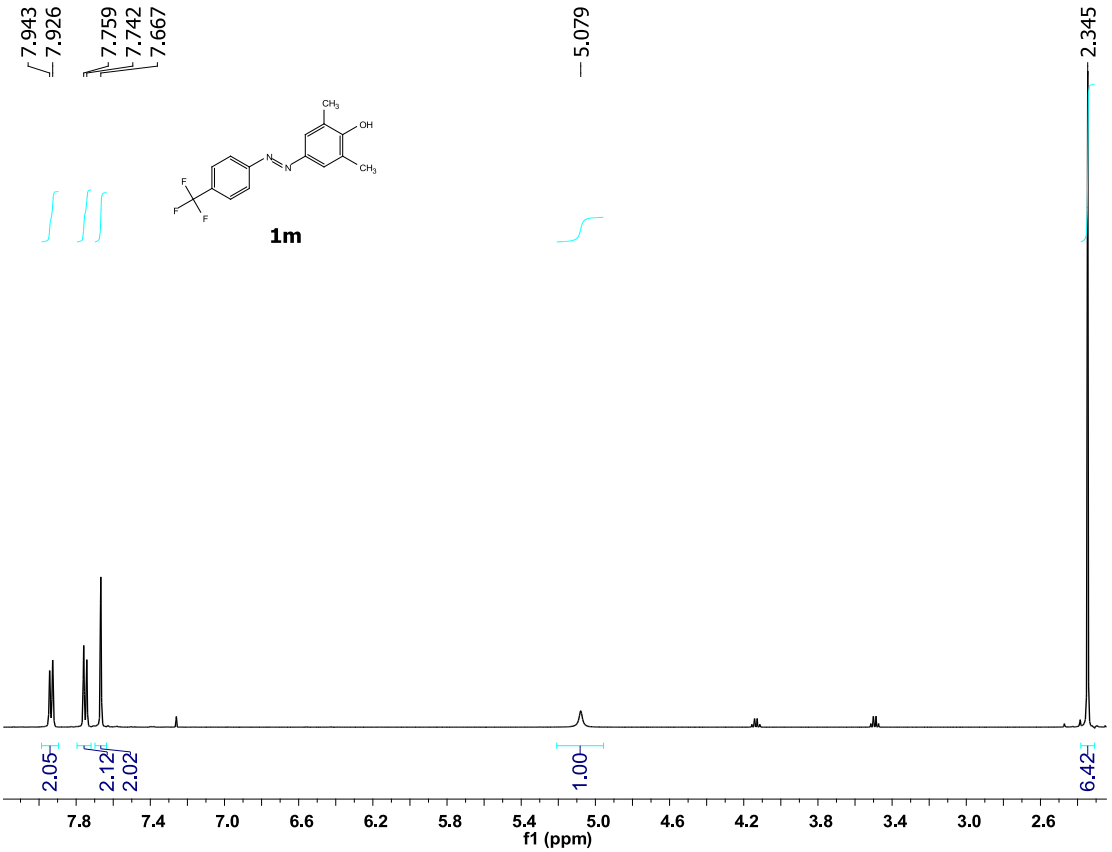

155.38
151.53
146.24
132.21
124.36
123.98
123.88
123.61
15.95
CH3
OH
CH3
N
N
Br
1j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

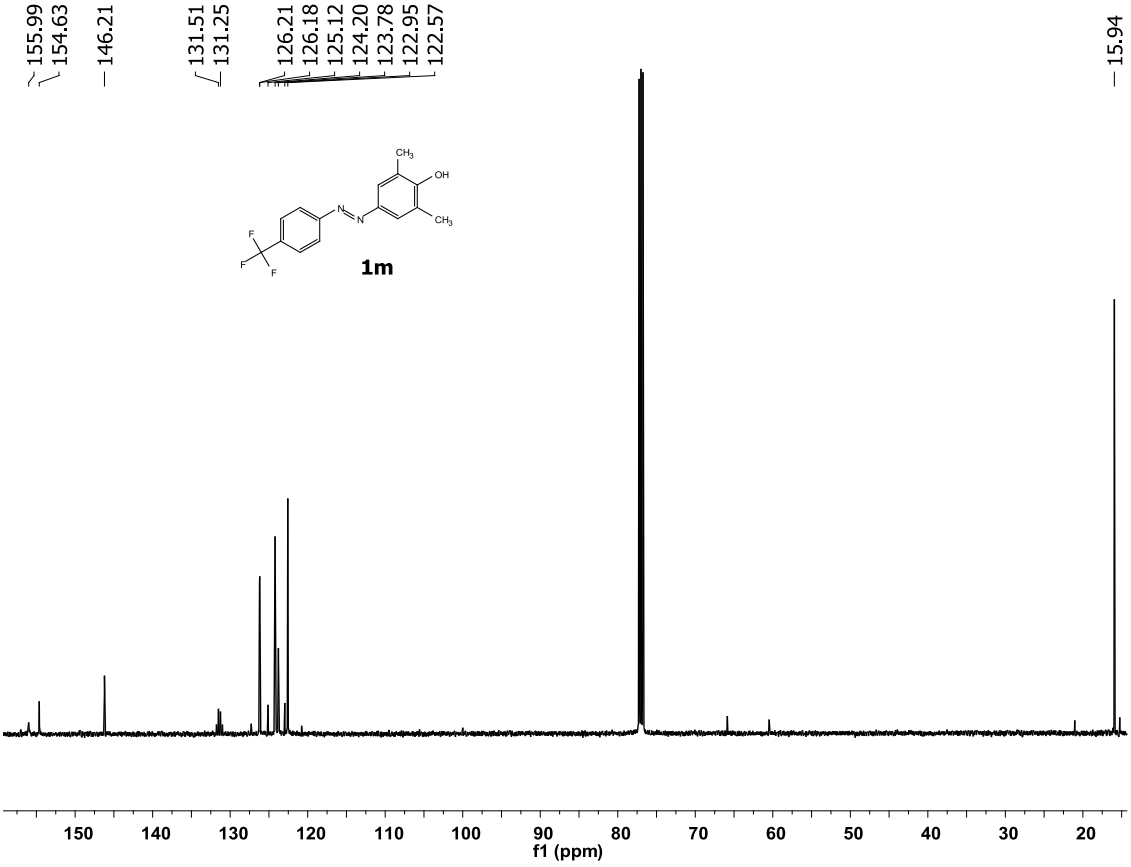

7.793
7.777
7.625
7.306
7.290
4.987
2.428
2.334
1k
1.97
1.99
2.07
1.00
3.16
6.37
f1 (ppm)

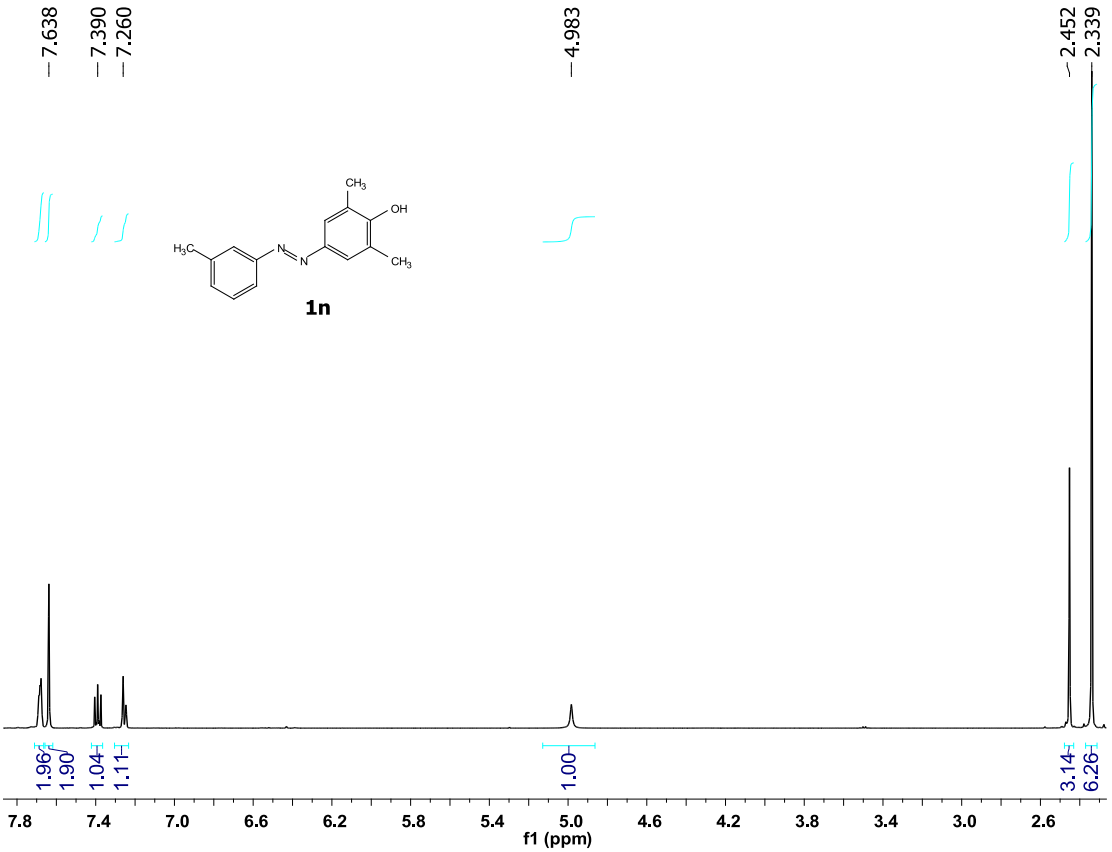

154.84
150.86
146.39
140.62
129.66
123.55
123.51
122.43
21.41
15.96
1k
f1 (ppm)

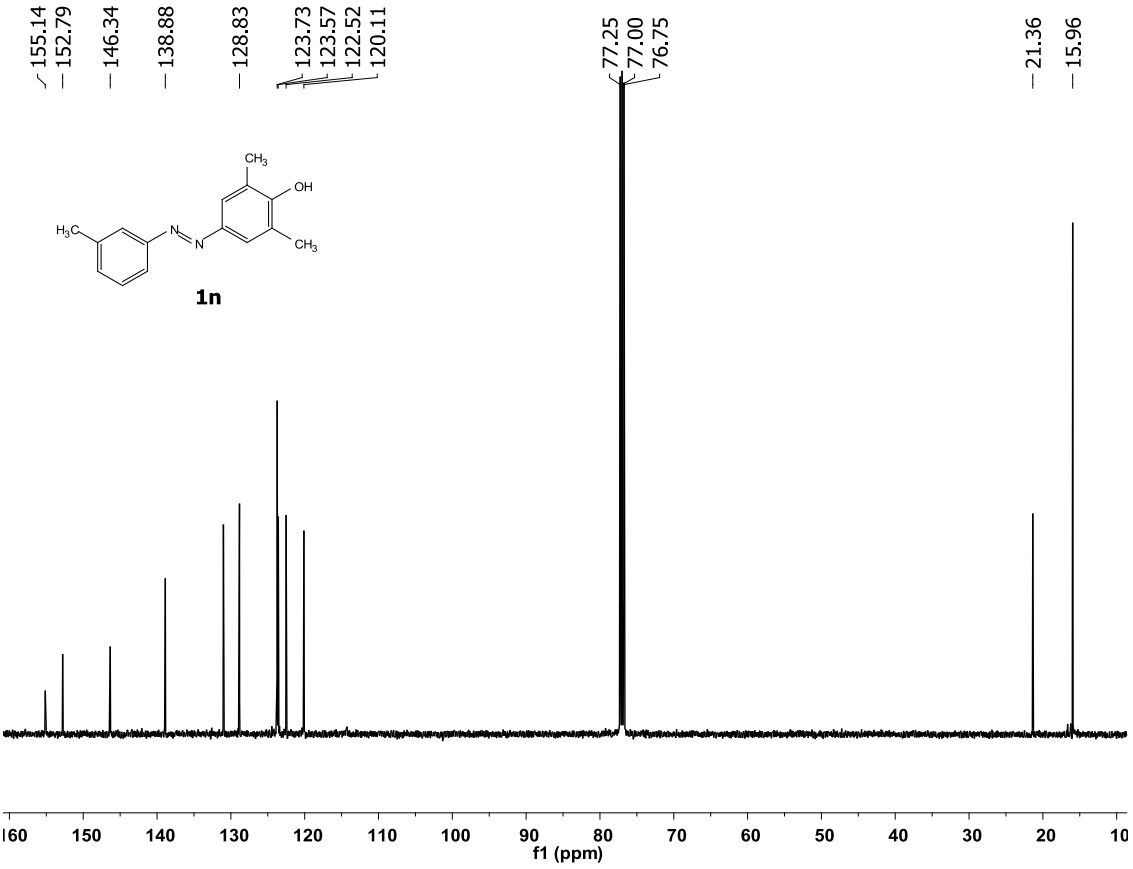

7.878
7.860
7.595
7.011
6.993
4.944
3.882
2.331
1l
2.01
1.96
2.10
1.00
3.19
6.33
f1 (ppm)

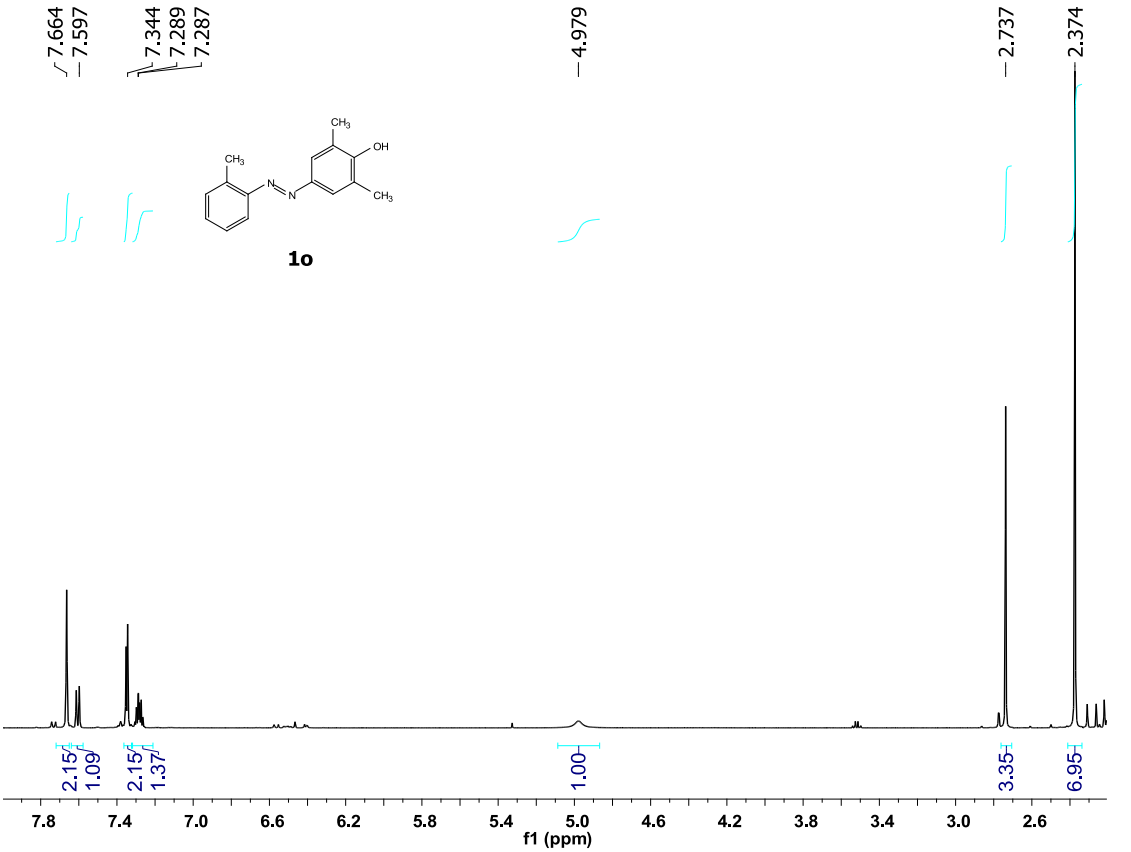

161.44
154.53
147.13
146.42
124.22
123.46
123.33
114.15
55.53
15.97
1l
f1 (ppm)

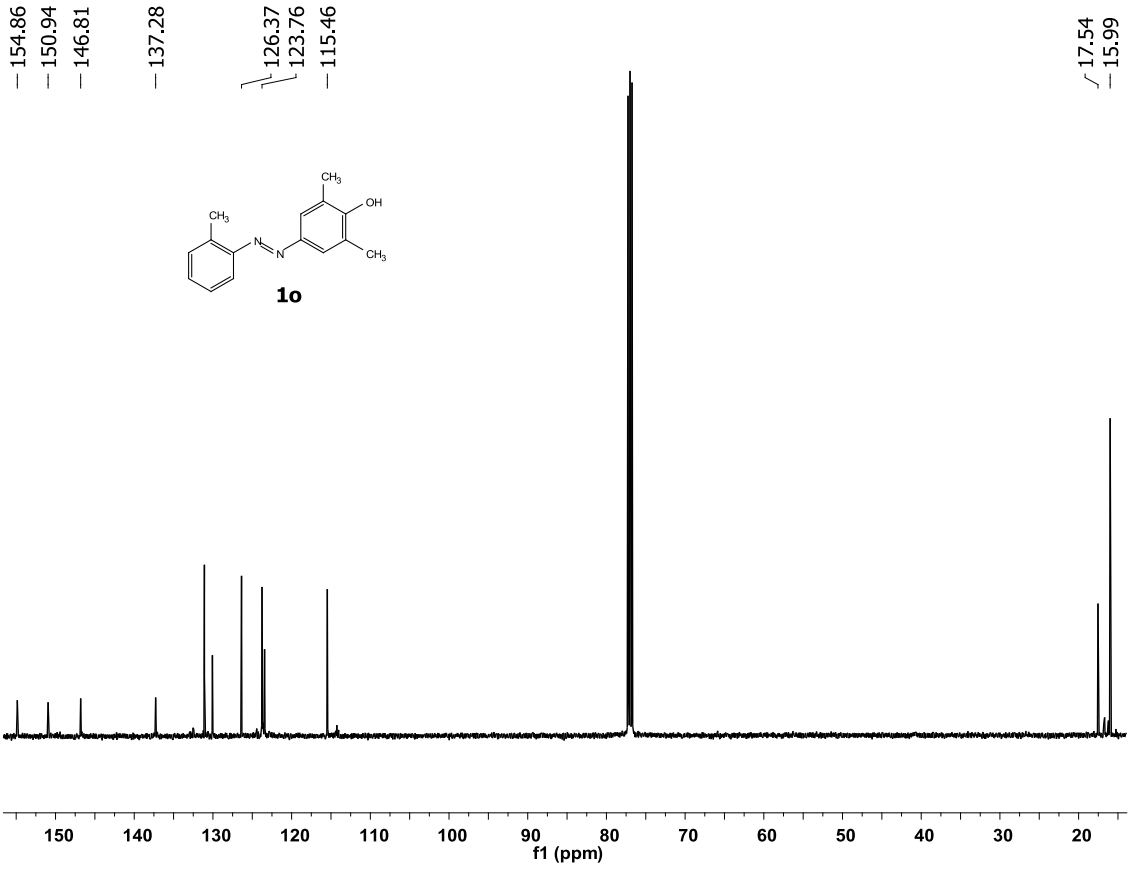

7.943
7.926
7.759
7.742
7.667
5.079
2.345
1m
2.05
2.12
2.02
1.00
6.42
f1 (ppm)

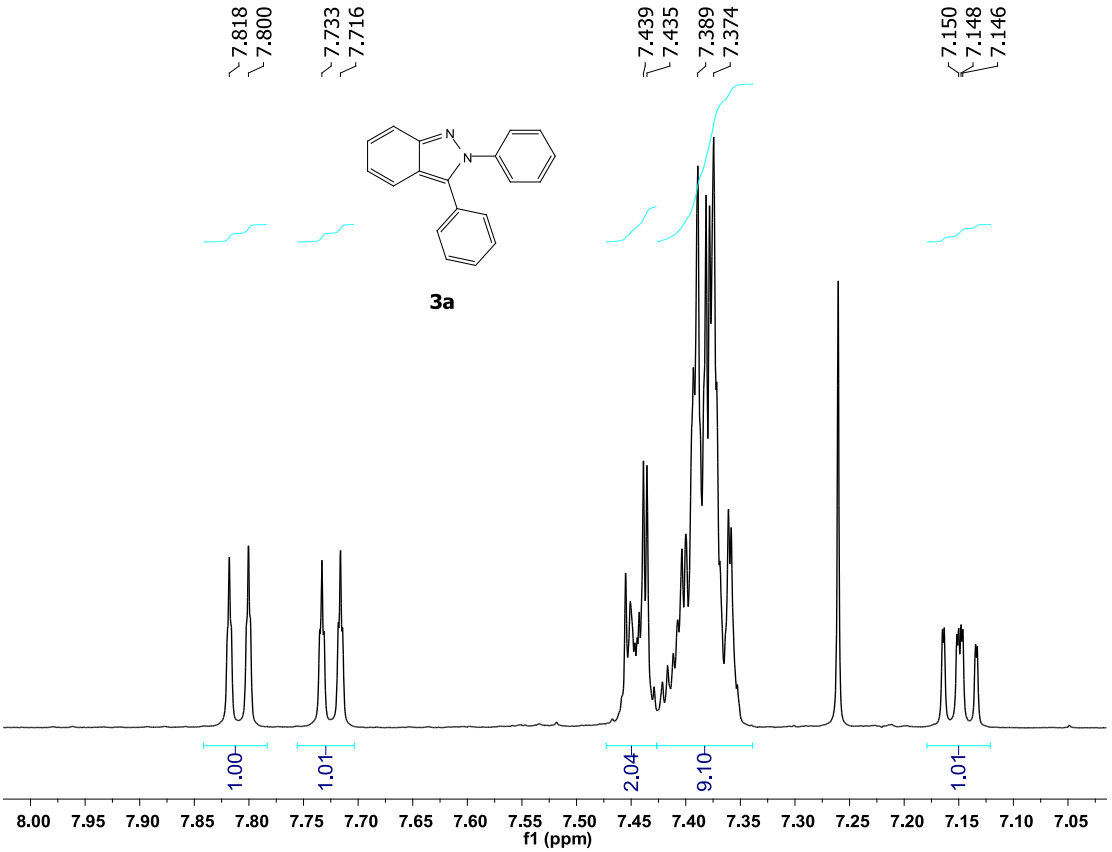

155.99
154.63
146.21
131.51
131.25
126.21
126.18
125.12
124.20
123.78
122.95
122.57
15.94
1m
f1 (ppm)

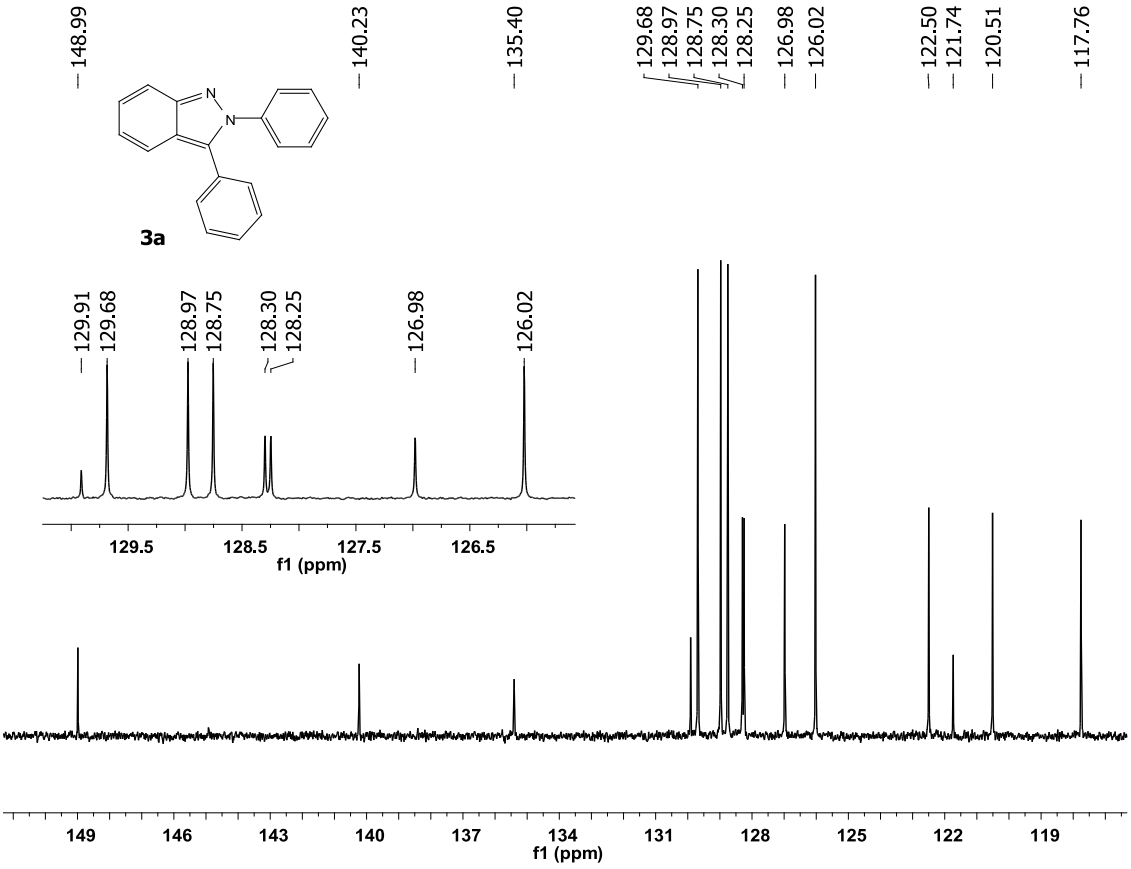

7.638
7.390
7.260
4.983
2.452
2.339
1n
1.96
1.90
1.04
1.11
1.00
3.14
6.26
f1 (ppm)

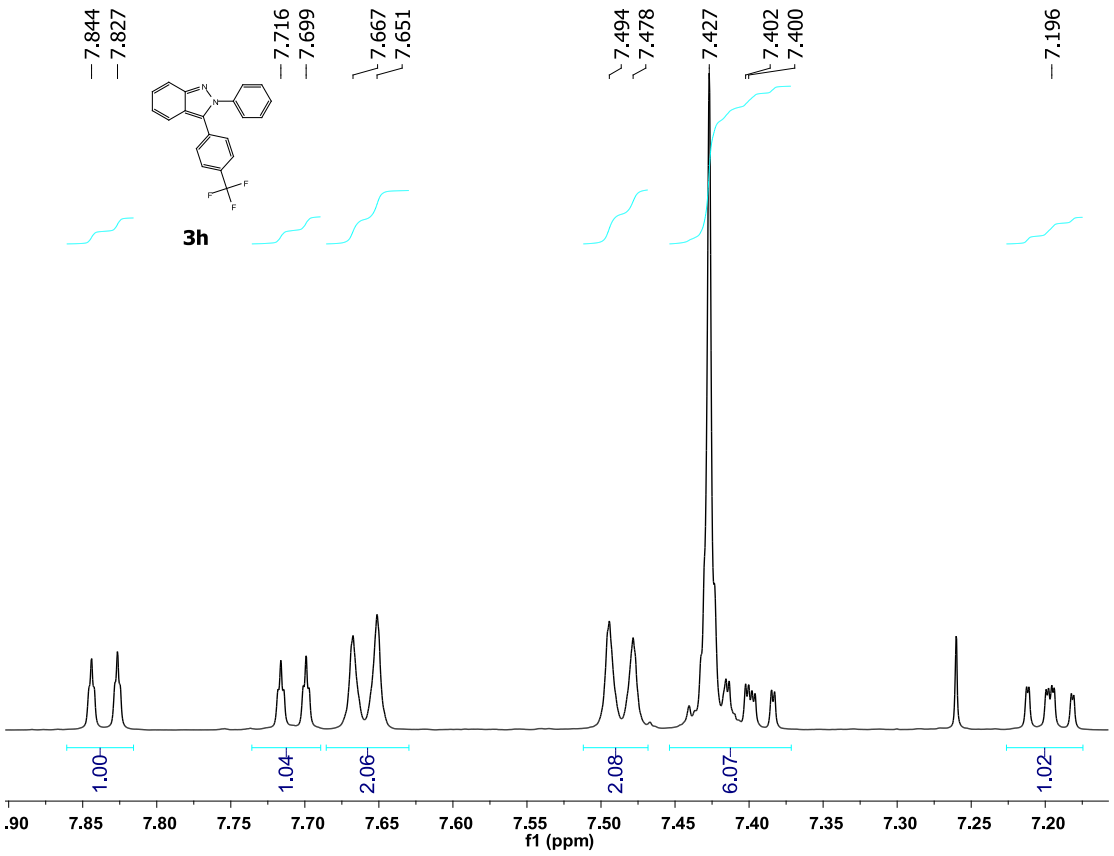

155.14
152.79
146.34
138.88
128.83
123.73
123.57
122.52
120.11
77.25
77.00
76.75
21.36
15.96
1n
f1 (ppm)

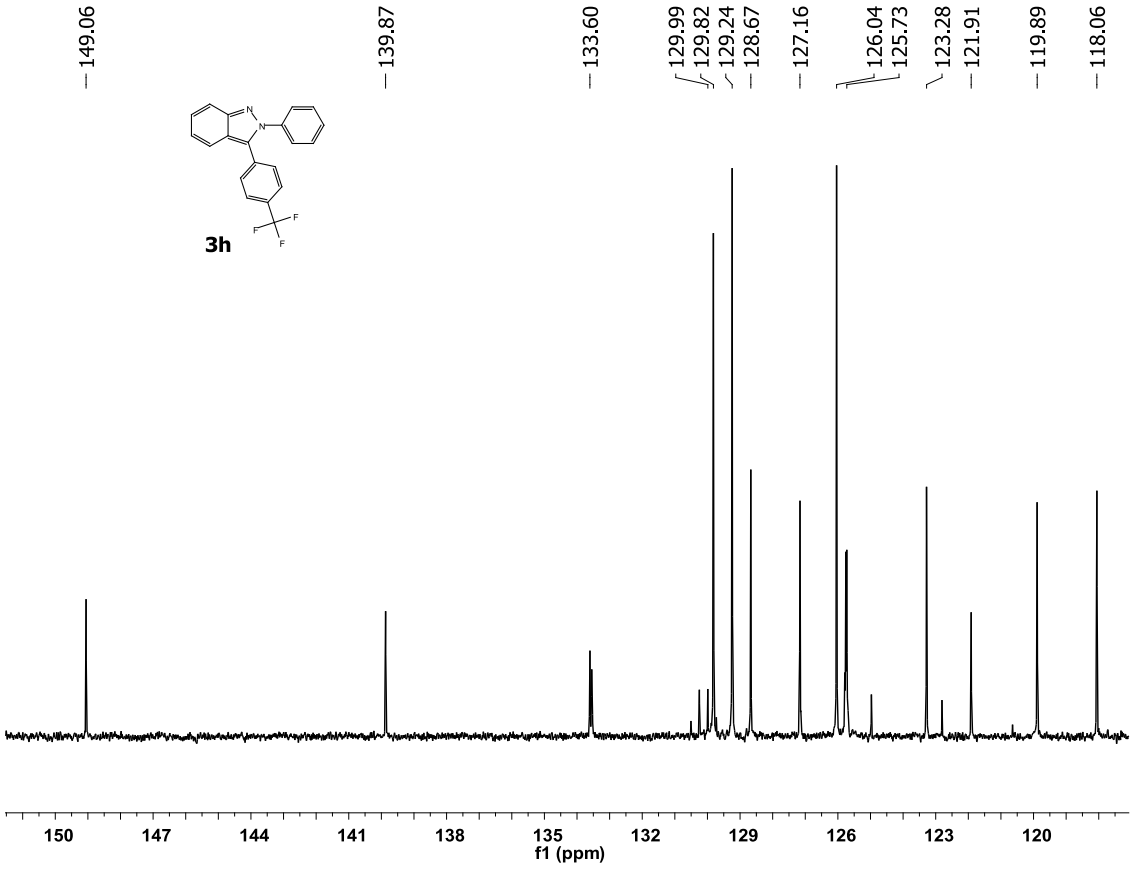

7.664
7.597
7.344
7.289
7.287
4.979
2.737
2.374
1o
2.15
1.09
2.15
1.37
1.00
3.35
6.95
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
f1 (ppm)

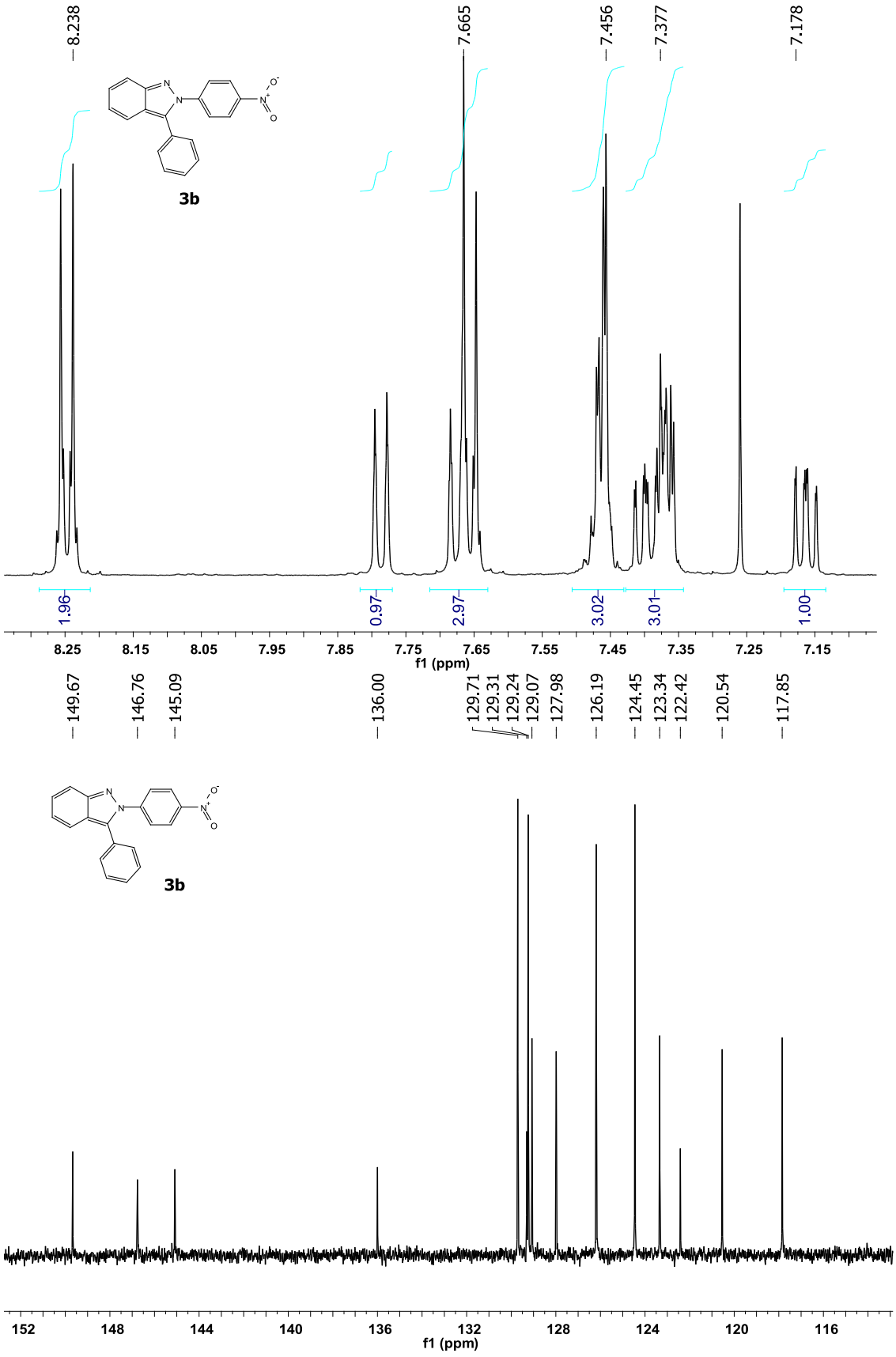

154.86
150.94
146.81
137.28
126.37
123.76
115.46
17.54
15.99
1o
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

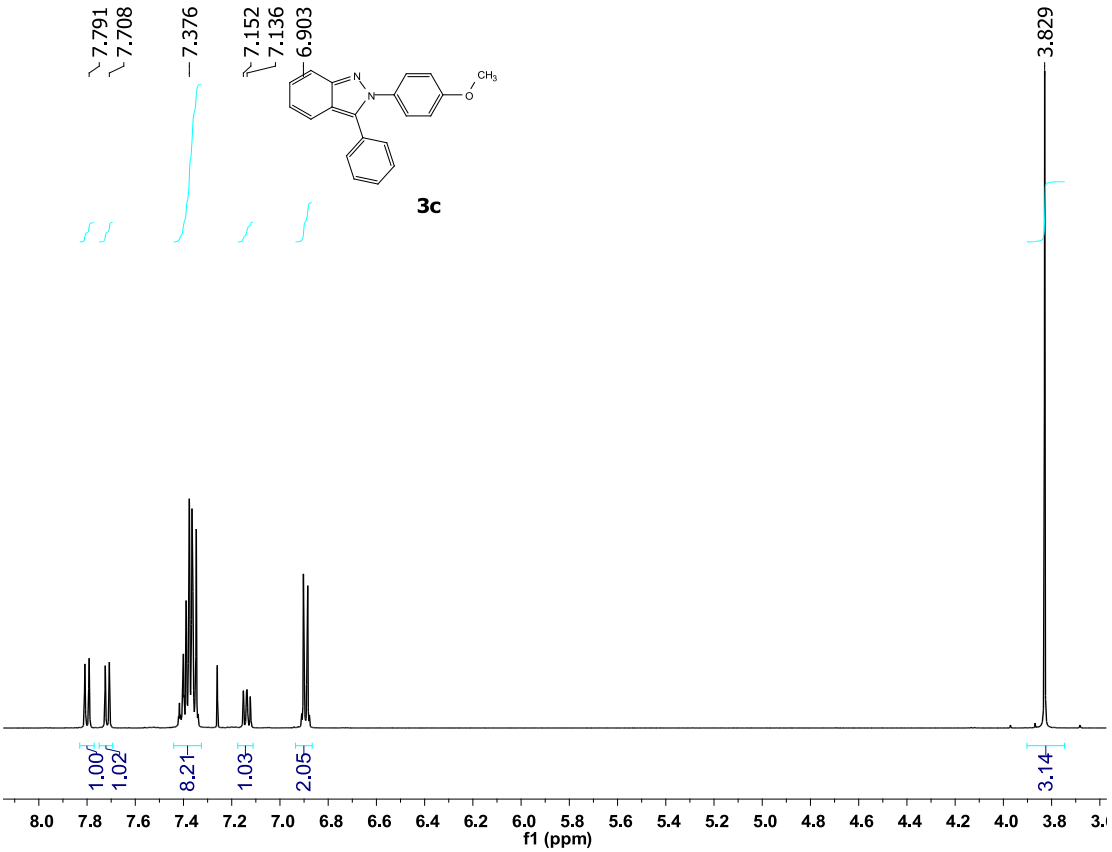

7.818
7.800
7.733
7.716
7.439
7.435
7.389
7.374
7.150
7.148
7.146
3a
1.00
1.01
2.04
9.10
1.01
8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)

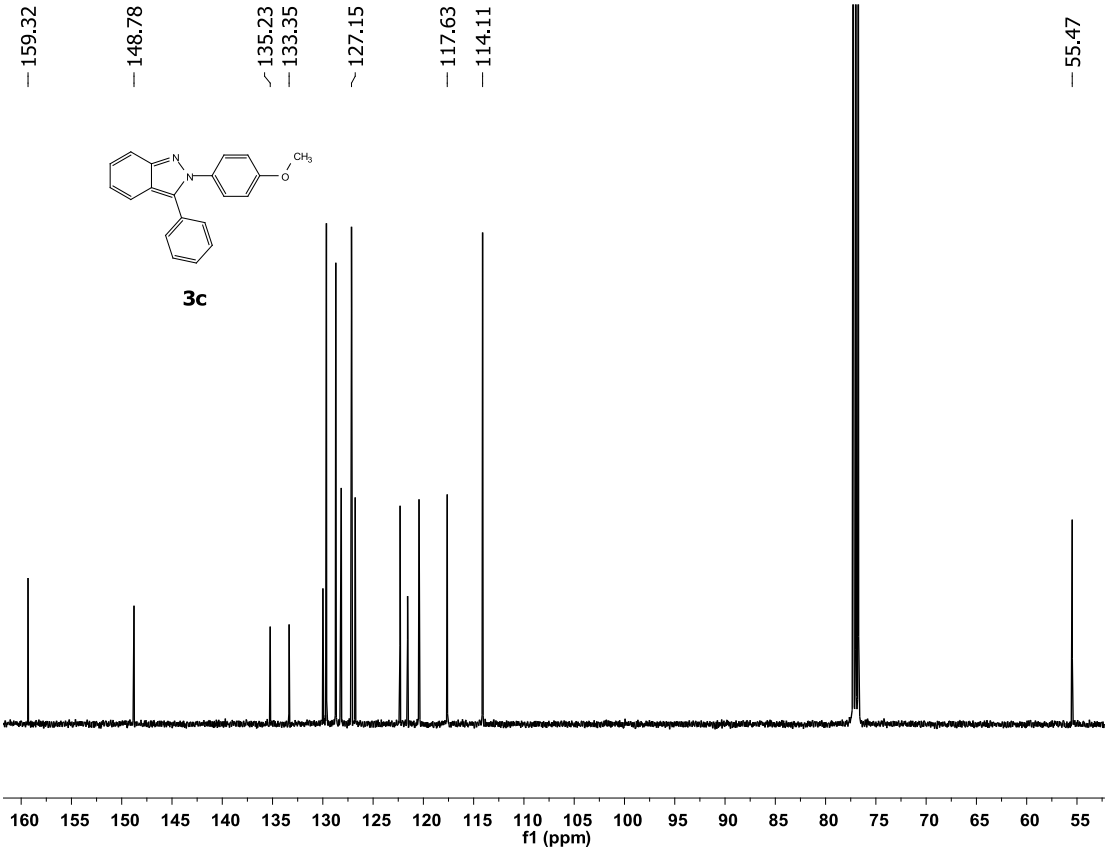

148.99
140.23
135.40
129.68
128.97
128.75
128.30
128.25
126.98
126.02
122.50
121.74
120.51
117.76
3a
129.91
129.68
128.97
128.75
128.30
128.25
126.98
126.02
129.5 128.5 127.5 126.5
f1 (ppm)
149 146 143 140 137 134 131 128 125 122 119
f1 (ppm)

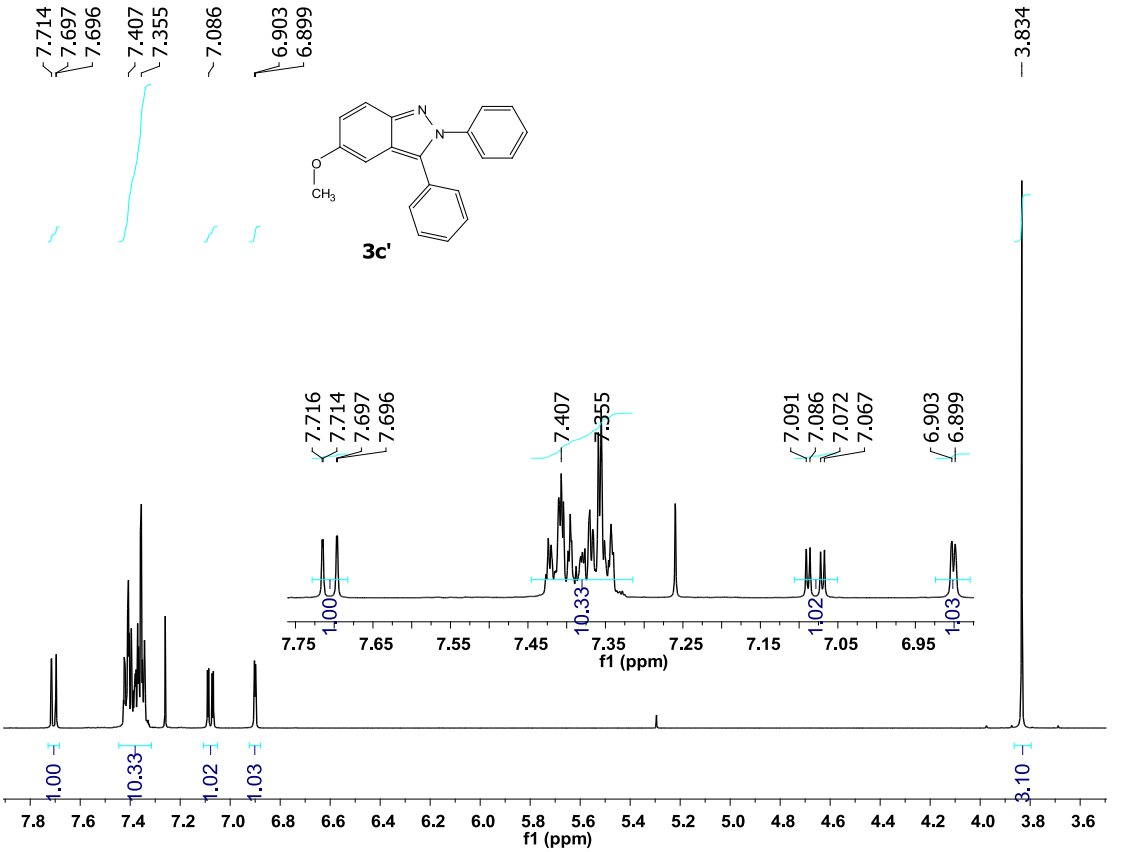

7.844
7.827
7.716
7.699
7.667
7.651
7.494
7.478
7.427
7.402
7.400
7.196
3h
1.00
1.04
2.06
2.08
6.07
1.02
f1 (ppm)

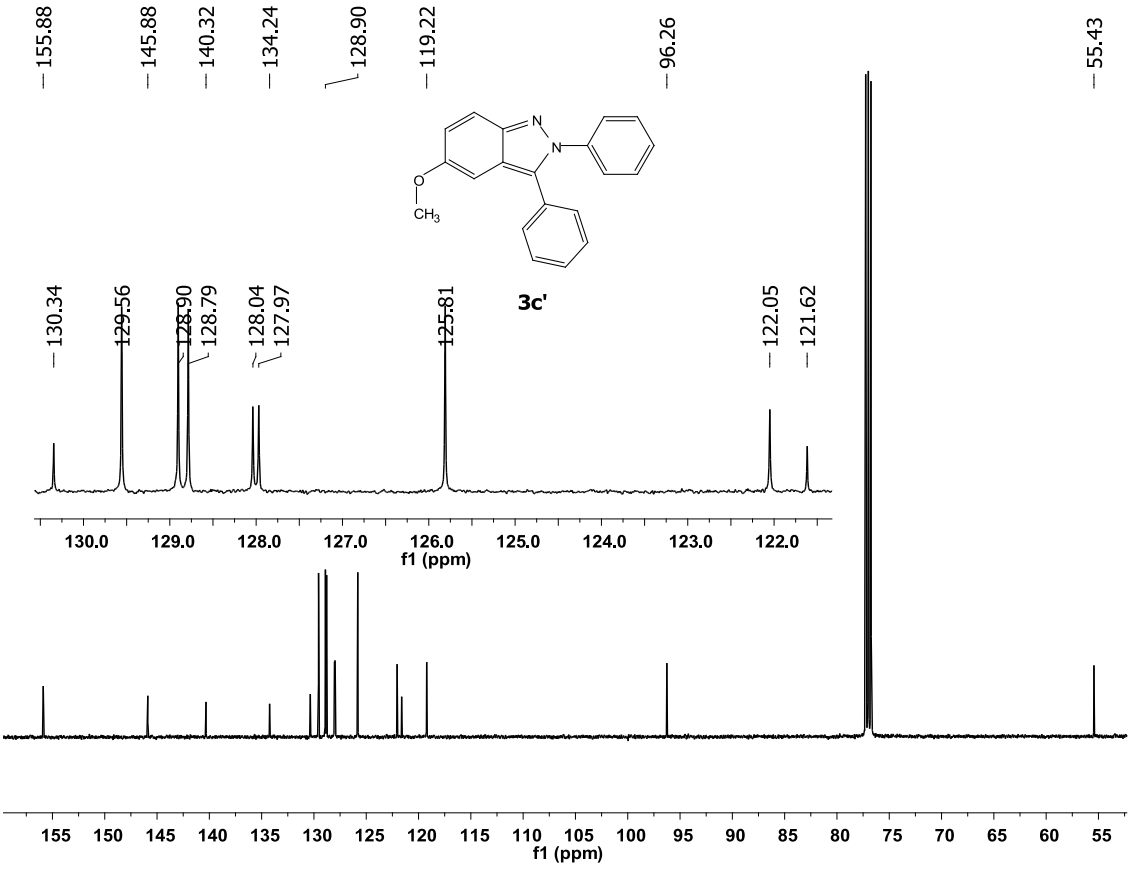

149.06
139.87
133.60
129.99
129.82
129.24
128.67
127.16
126.04
125.73
123.28
121.91
119.89
118.06
3h
f1 (ppm)

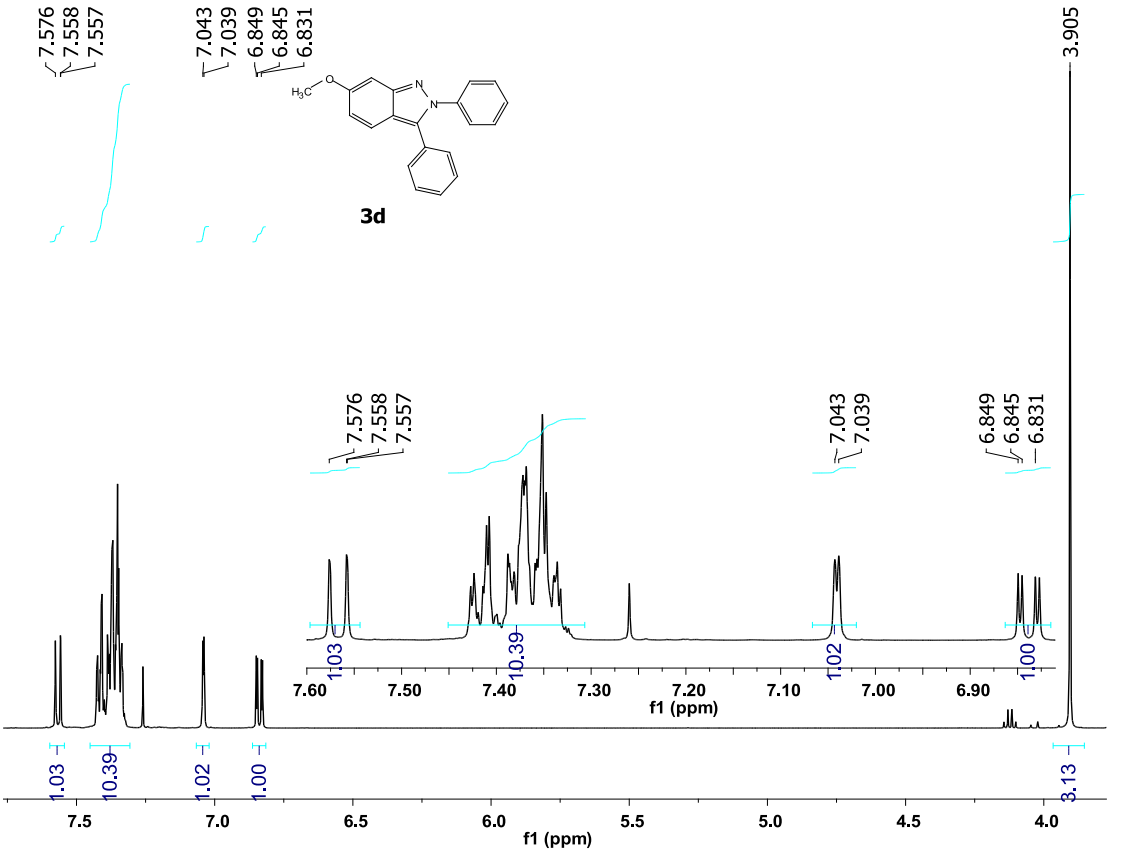

8.238
7.665
7.456
7.377
7.178
3b
1.96
0.97
2.97
3.02
3.01
1.00
8.25
8.15
8.05
7.95
7.85
7.75
7.65
7.55
7.45
7.35
7.25
7.15
f1 (ppm)
149.67
146.76
145.09
136.00
129.71
129.31
129.24
129.07
127.98
126.19
124.45
123.34
122.42
120.54
117.85
3b
152
148
144
140
136
132
128
124
120
116
f1 (ppm)

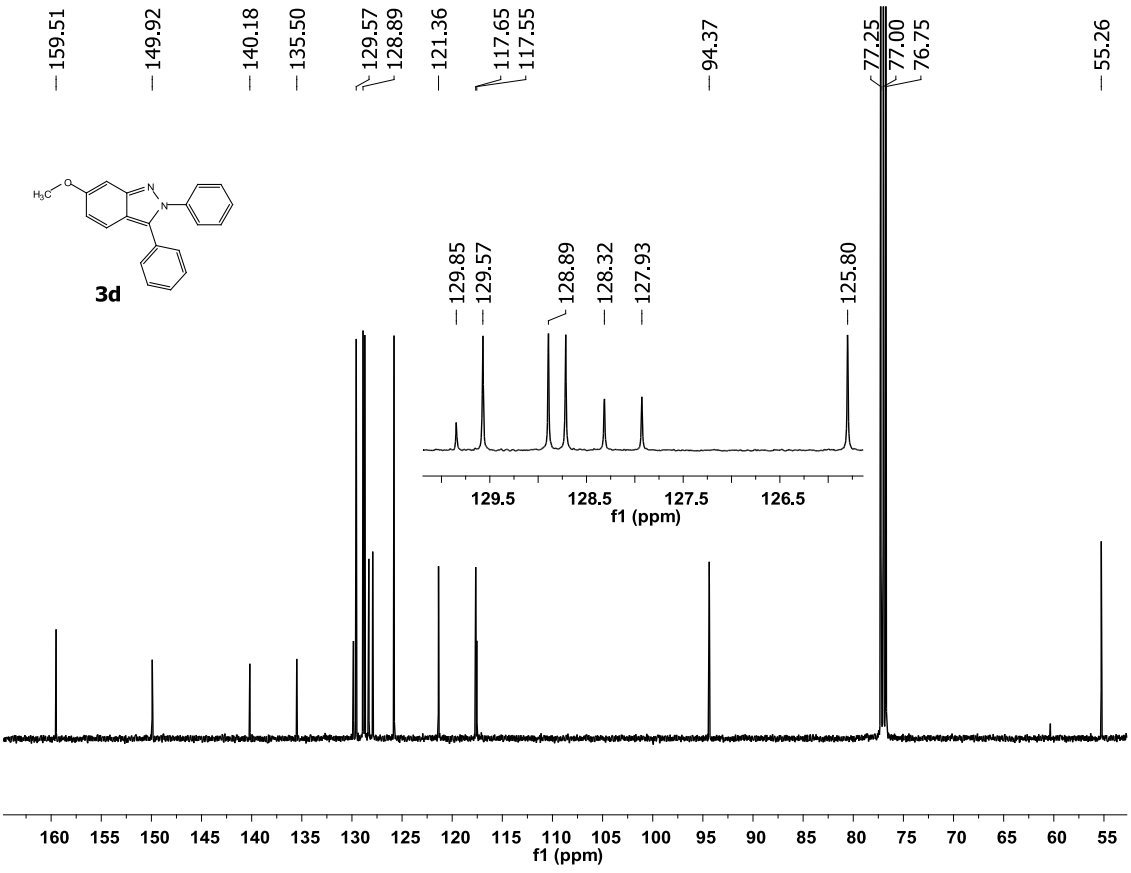

7.791
7.708
7.376
7.152
7.136
6.903
3.829
3c
1.00
1.02
8.21
1.03
2.05
3.14
f1 (ppm)

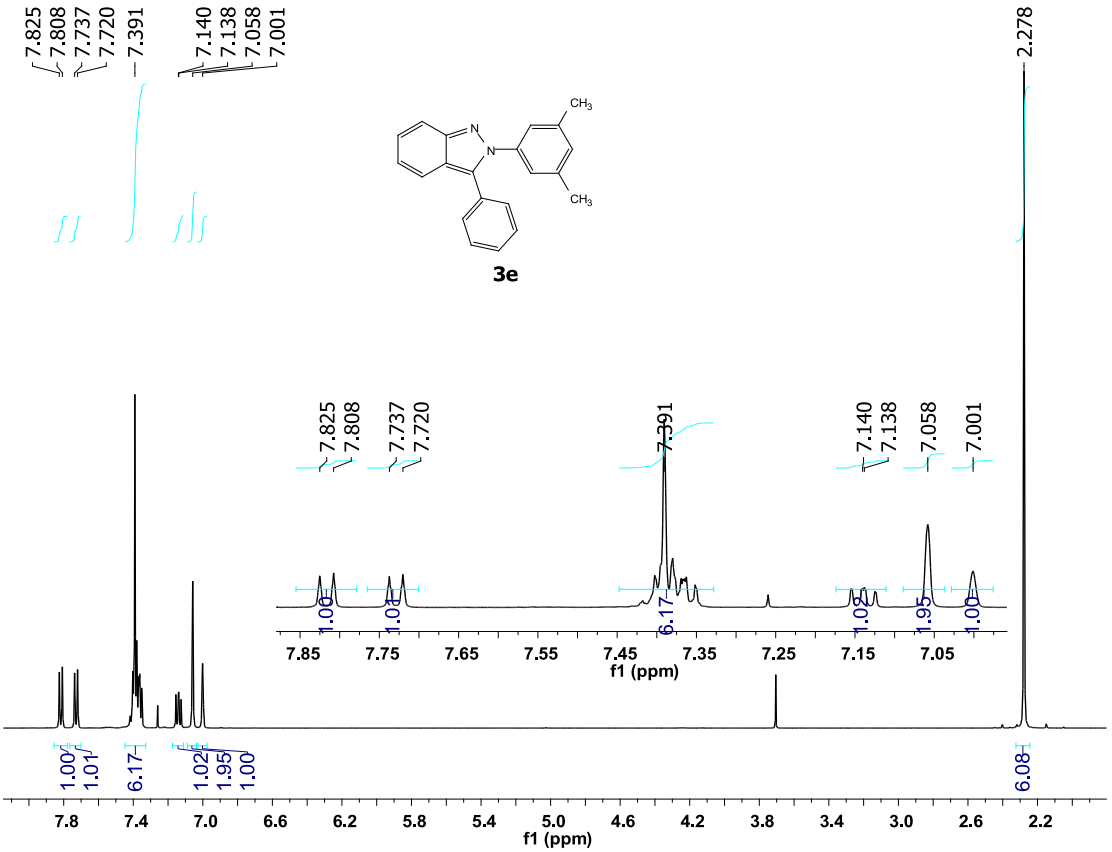

159.32
148.78
135.23
133.35
127.15
117.63
114.11
55.47
3c
f1 (ppm)

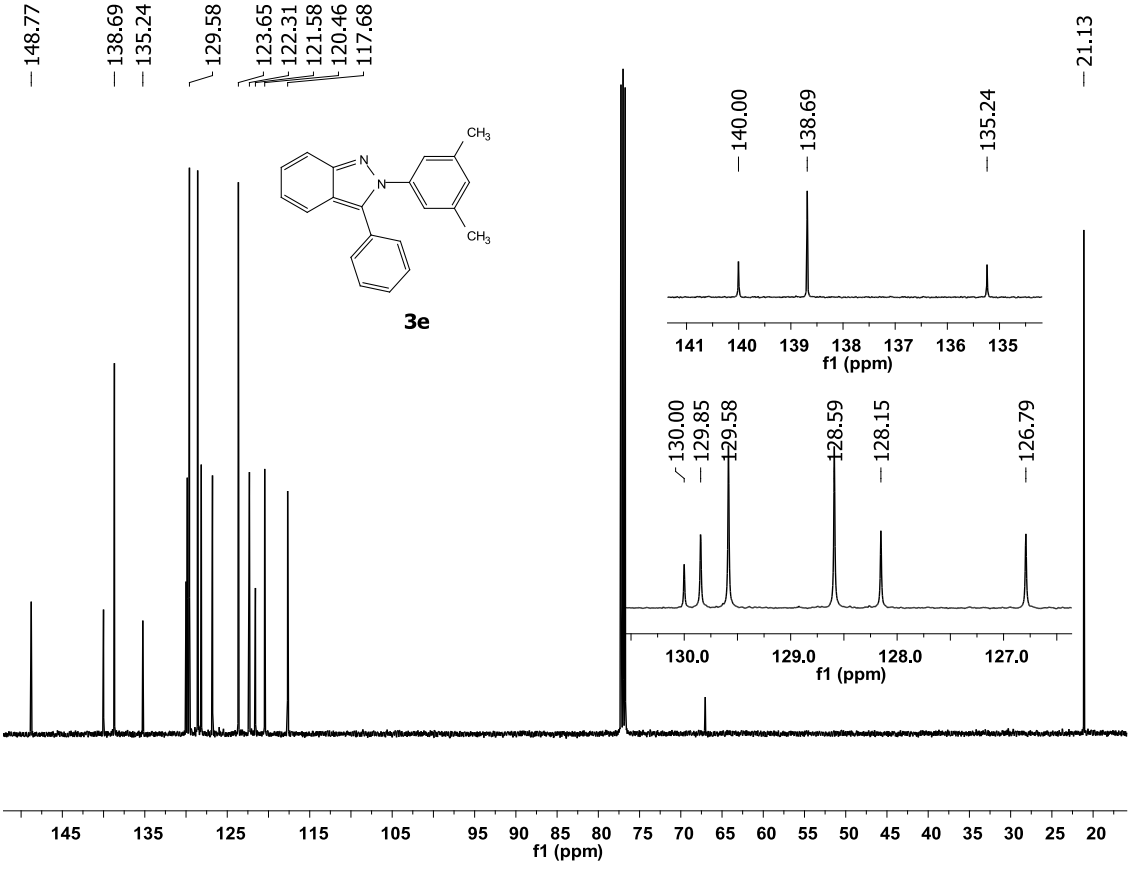

7.714
7.697
7.696
7.407
7.355
7.086
6.903
6.899
3.834
3c'
7.716
7.714
7.697
7.696
7.407
7.355
7.091
7.086
7.072
7.067
6.903
6.899
1.00
10.33
1.02
1.03
3.10
f1 (ppm)

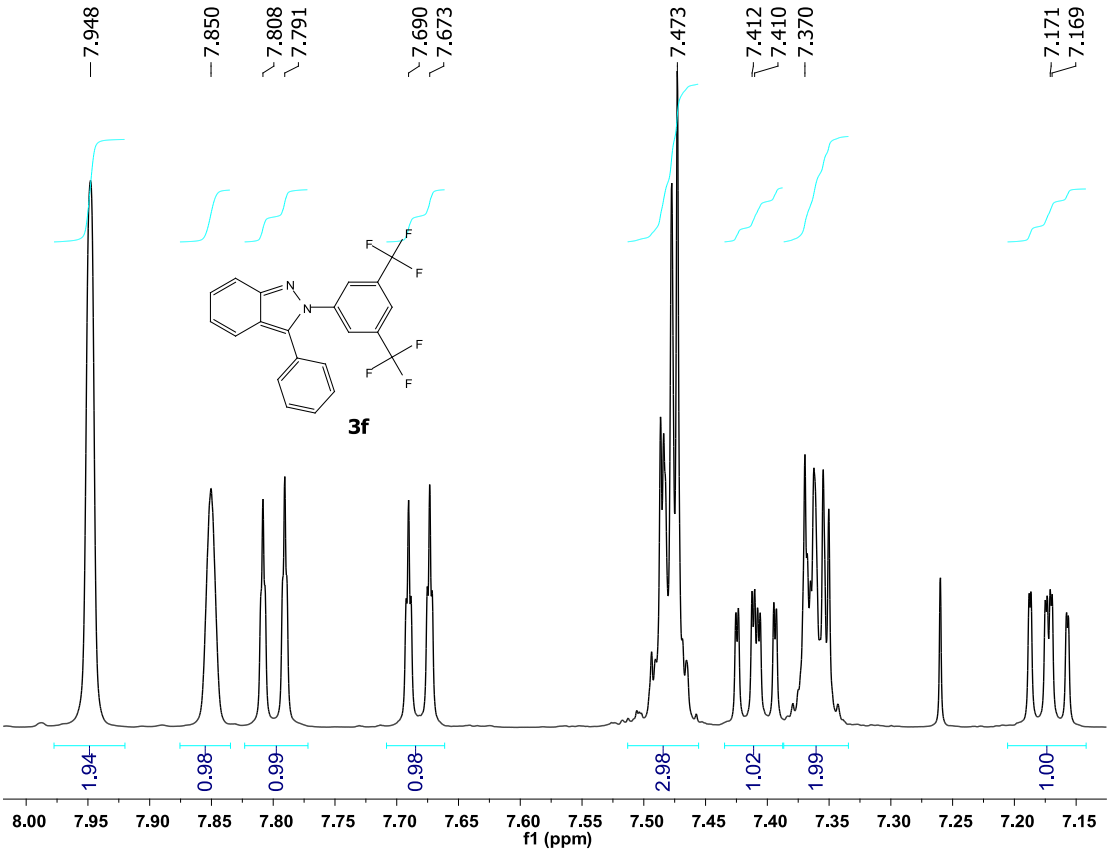

155.88
145.88
140.32
134.24
128.90
119.22
96.26
55.43
3c'
130.34
129.56
128.90
128.79
128.04
127.97
125.81
122.05
121.62
f1 (ppm)

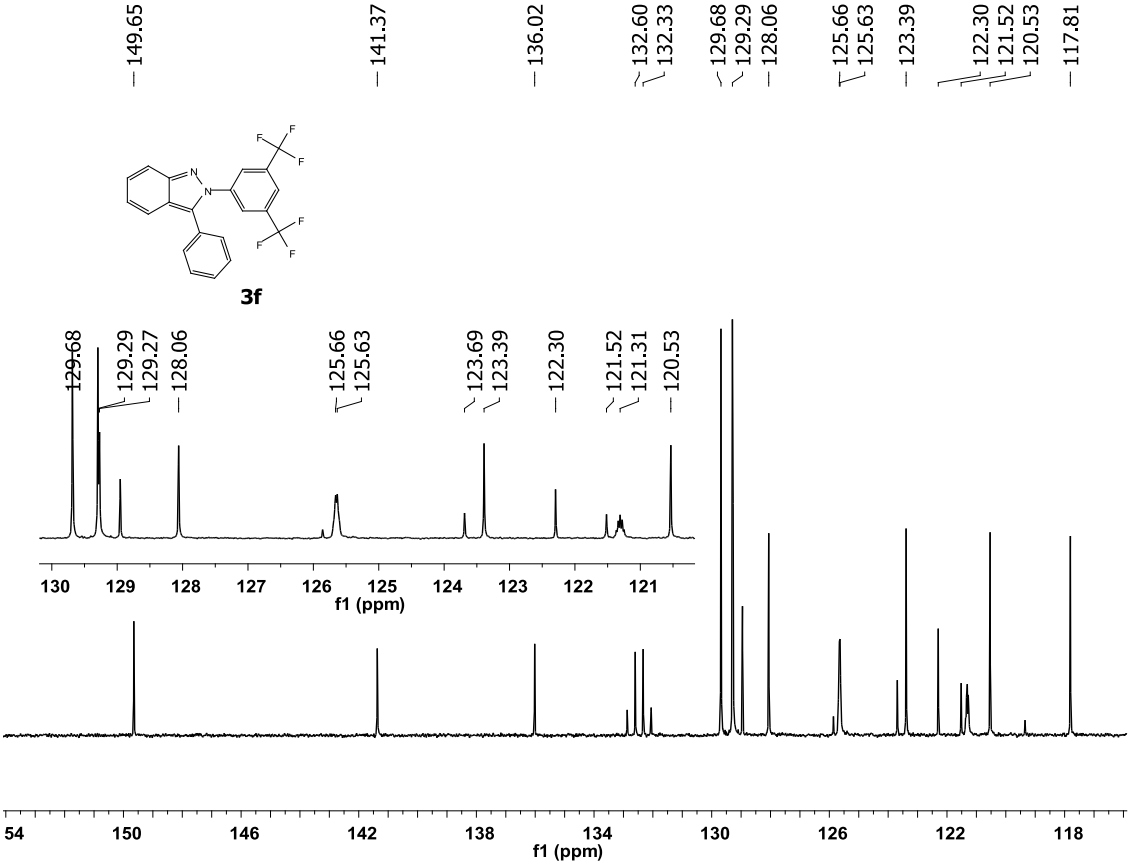

7.576
7.558
7.557
7.043
7.039
6.849
6.845
6.831
3.905
3d
1.03
10.39
1.02
1.00
3.13
f1 (ppm)

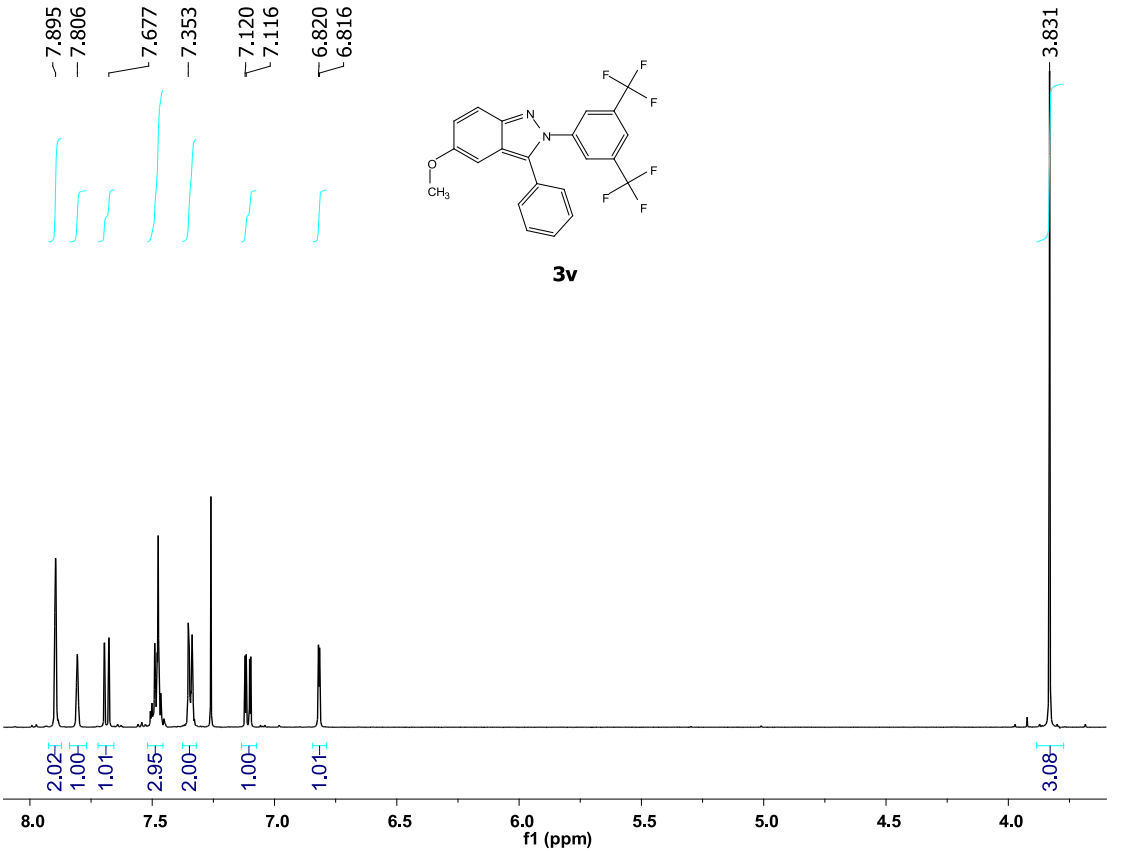

159.51
149.92
140.18
135.50
129.57
128.89
121.36
117.65
117.55
94.37
77.25
77.00
76.75
55.26
3d
129.85
129.57
128.89
128.32
127.93
125.80
f1 (ppm)

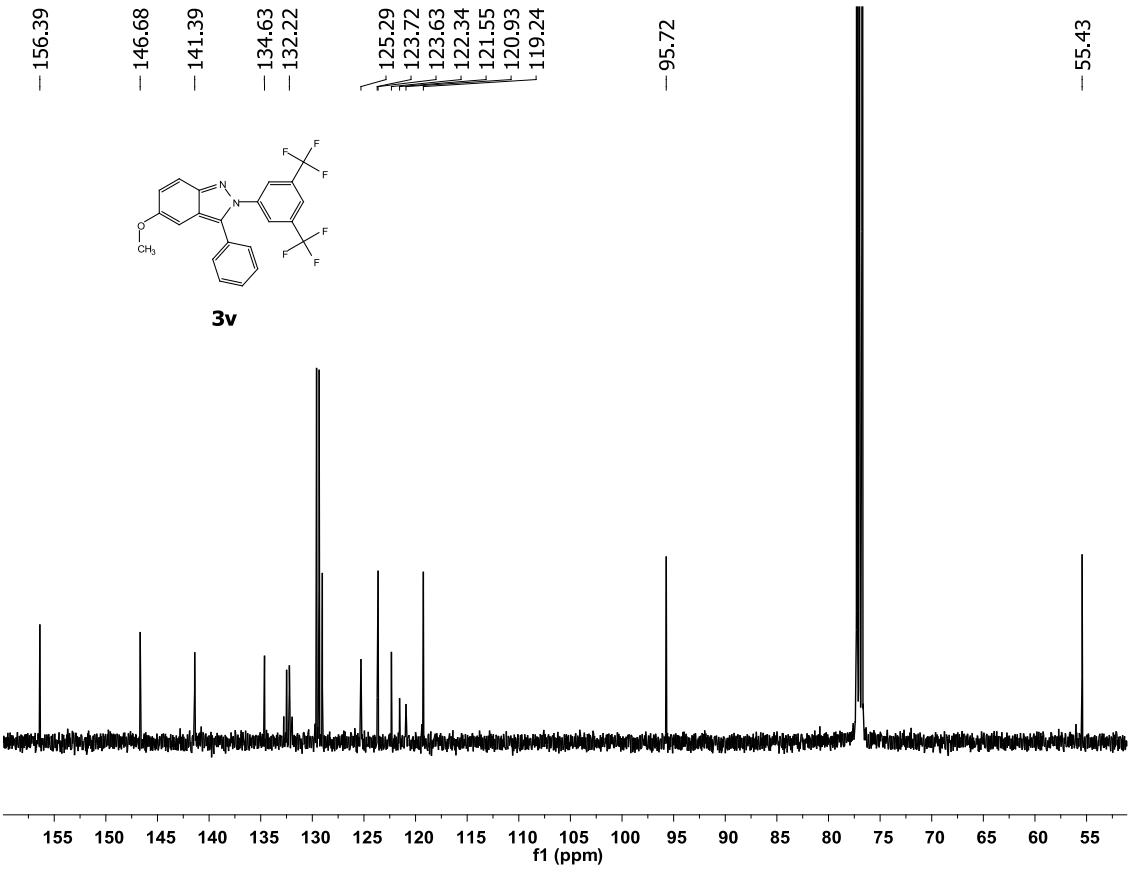

7.825
7.808
7.737
7.720
7.391
7.140
7.138
7.058
7.001
2.278
3e
1.00
1.01
6.17
1.02
1.95
1.00
6.08
f1 (ppm)

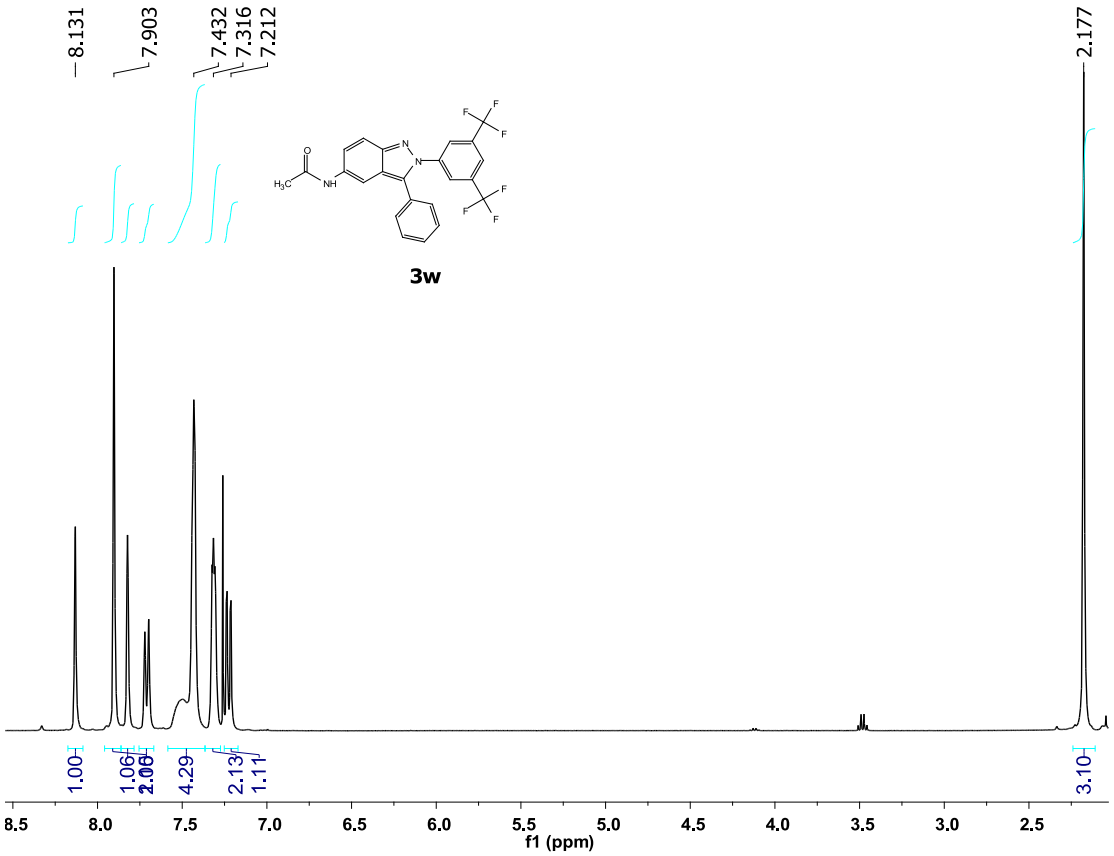

148.77
138.69
135.24
129.58
123.65
122.31
121.58
120.46
117.68
21.13
3e
140.00
138.69
135.24
130.00
129.85
129.58
128.59
128.15
126.79
f1 (ppm)

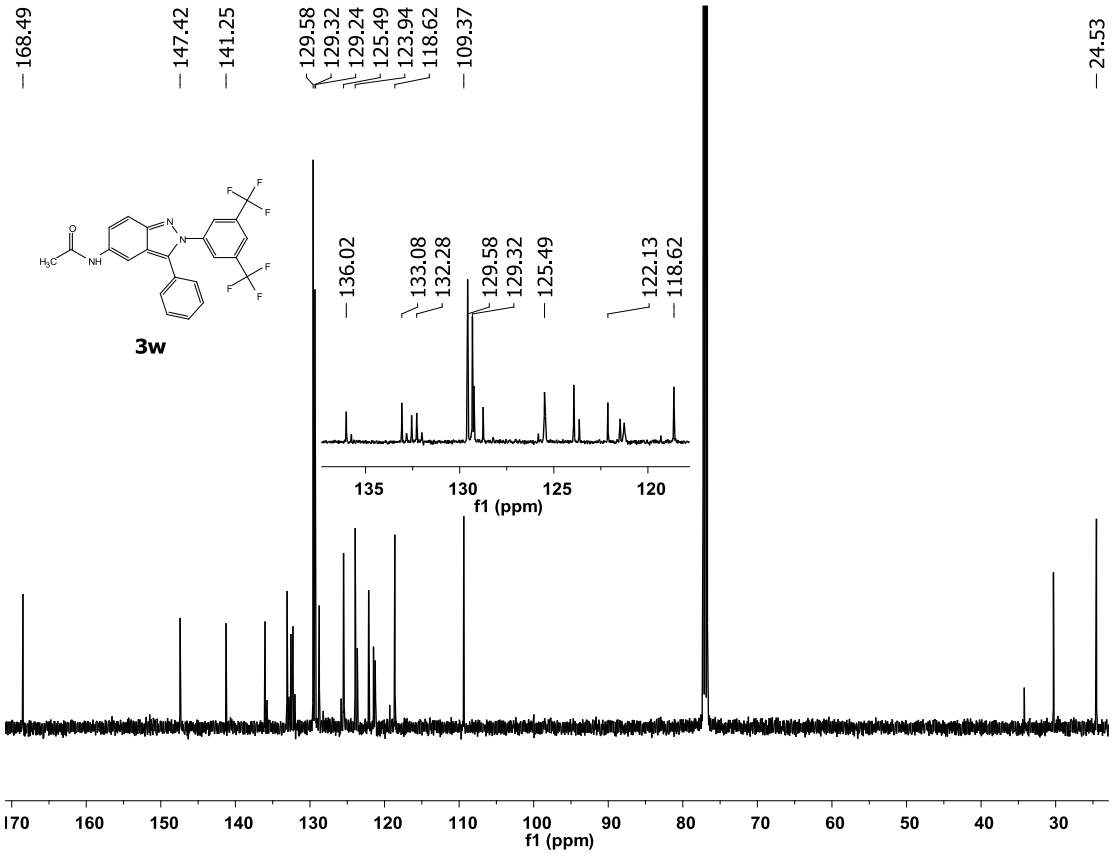

7.948
7.850
7.808
7.791
7.690
7.673
7.473
7.412
7.410
7.370
7.171
7.169
3f
1.94
0.98
0.99
0.98
2.98
1.02
1.99
1.00
f1 (ppm)

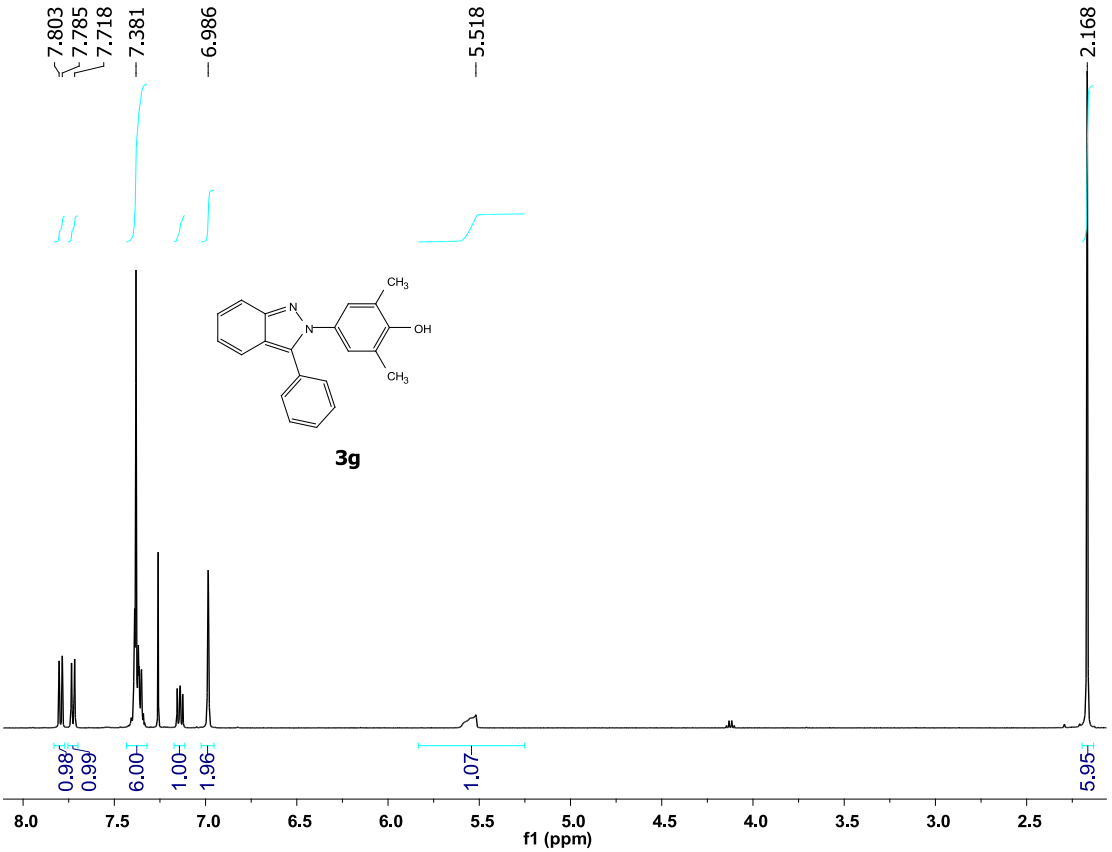

149.65
141.37
136.02
132.60
132.33
129.68
129.29
128.06
125.66
125.63
123.39
122.30
121.52
121.31
120.53
117.81
3f
129.68
129.29
129.27
128.06
125.66
125.63
123.69
123.39
122.30
121.52
121.31
120.53
f1 (ppm)
f1 (ppm)

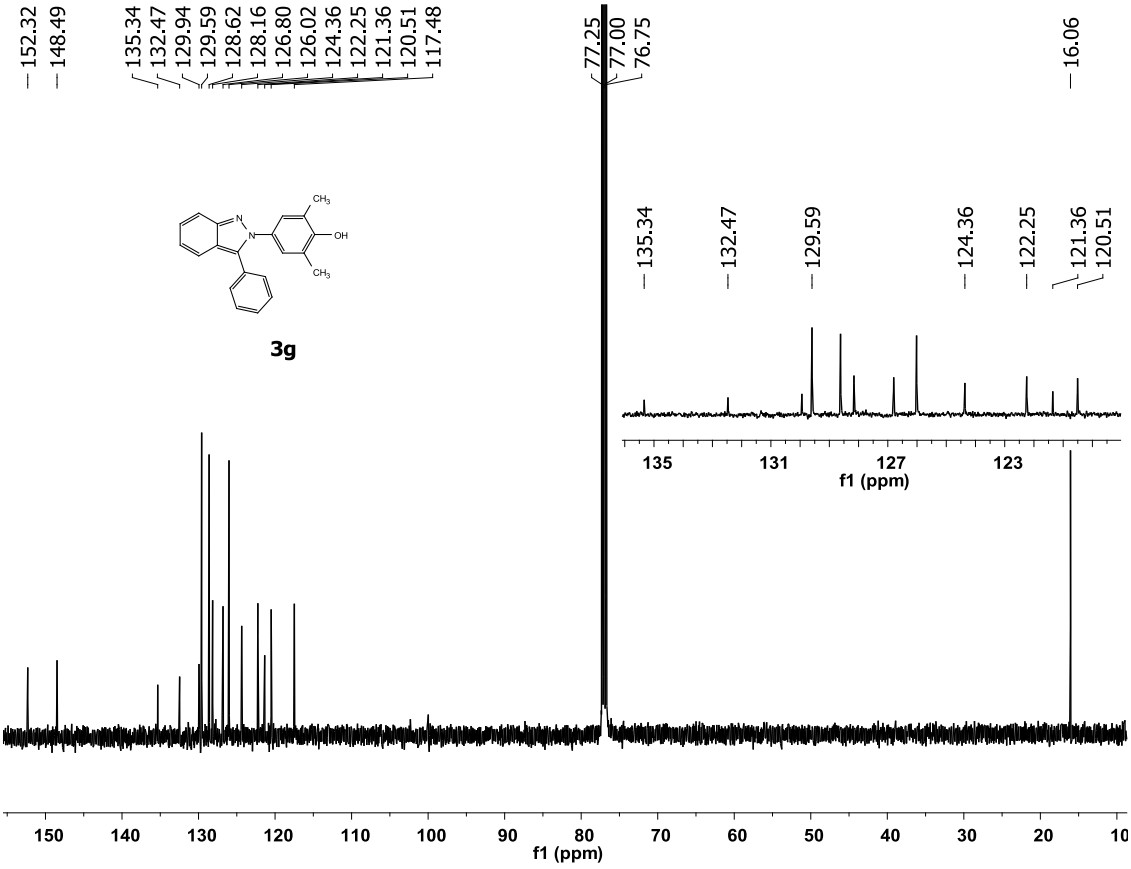

7.895
7.806
7.677
7.353
7.120
7.116
6.820
6.816
3.831
3v
2.02
1.00
1.01
2.95
2.00
1.00
1.01
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)

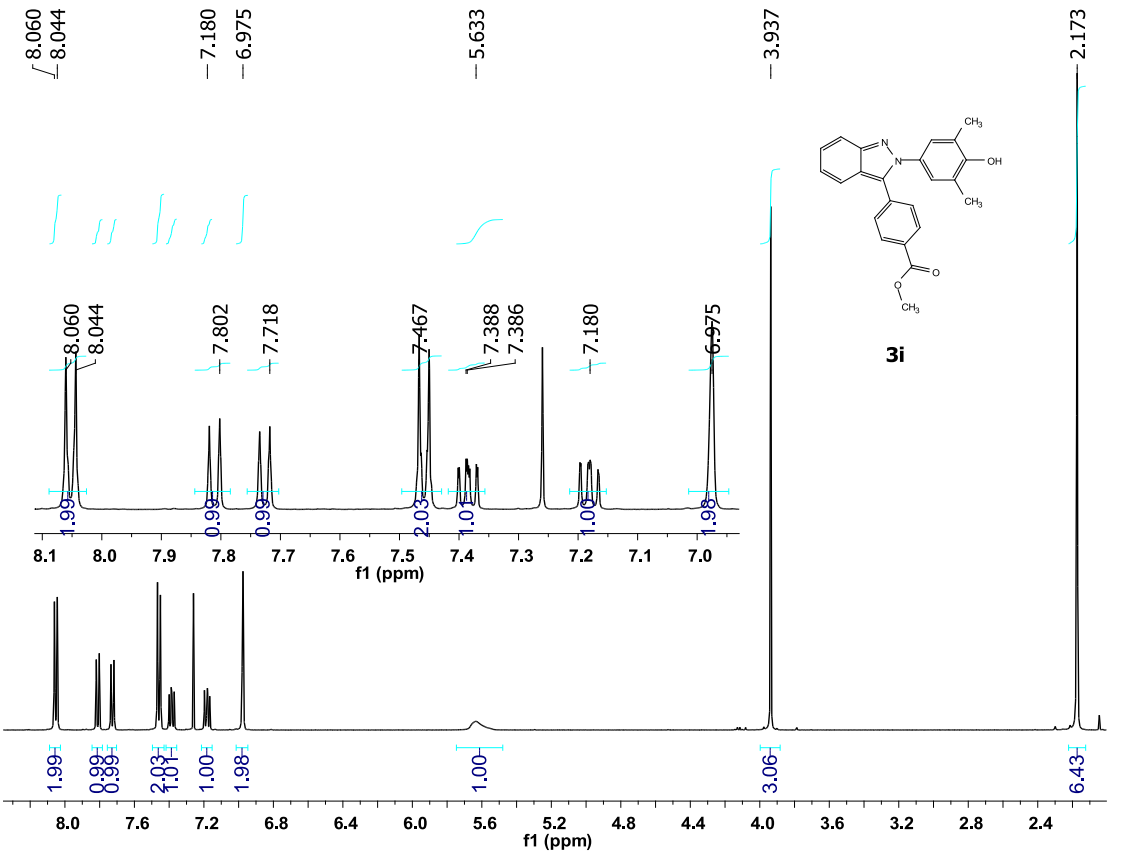

156.39
146.68
141.39
134.63
132.22
125.29
123.72
123.63
122.34
121.55
120.93
119.24
95.72
55.43
3v
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)

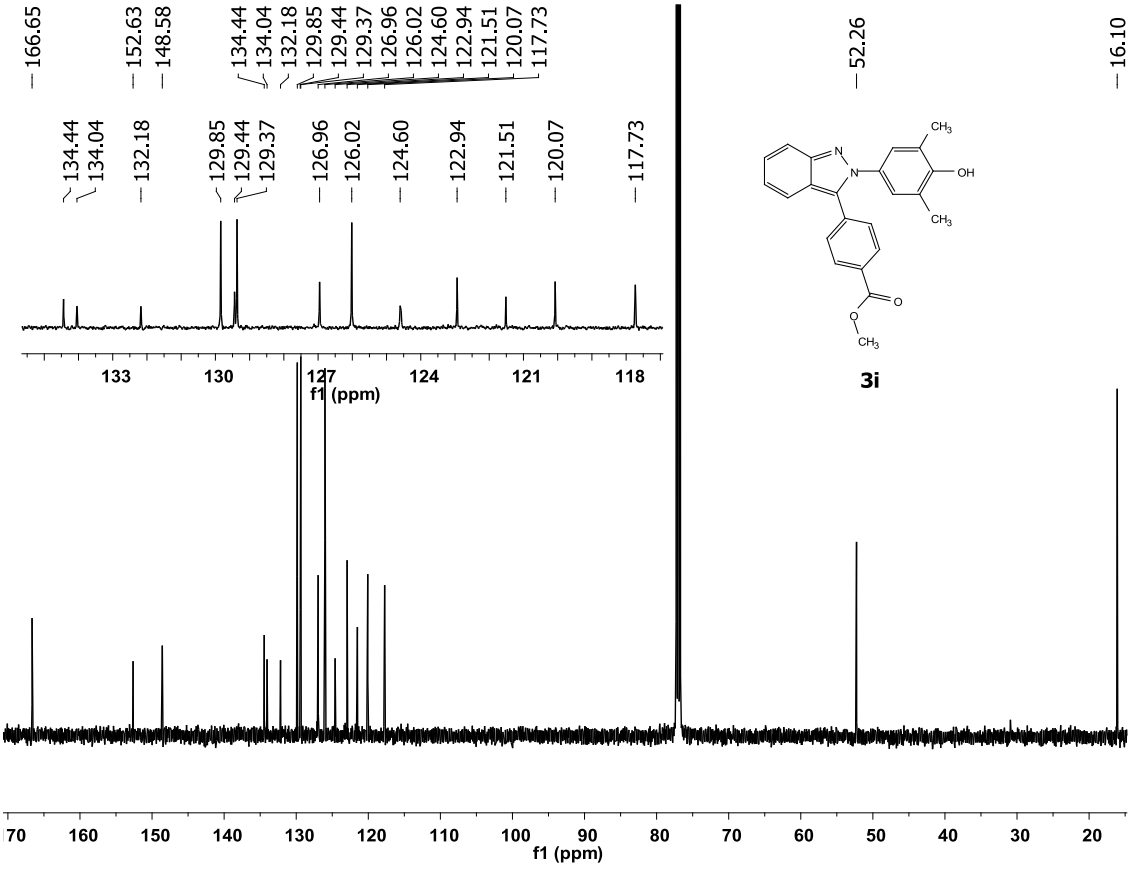

8.131
7.903
7.432
7.316
7.212
2.177
3w
1.00
1.06
2.00
4.29
2.13
1.11
3.10
f1 (ppm)

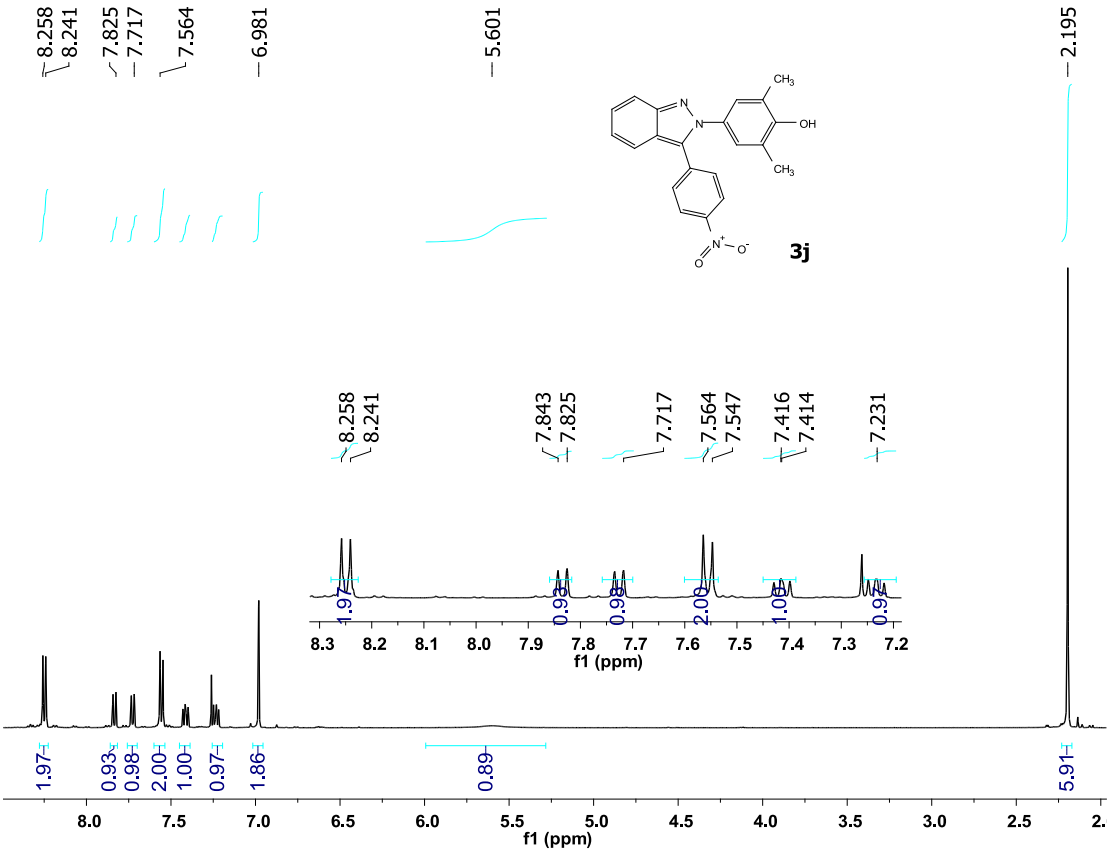

168.49
147.42
141.25
129.58
129.32
129.24
125.49
123.94
118.62
109.37
24.53
3w
136.02
133.08
132.28
129.58
129.32
125.49
122.13
118.62
f1 (ppm)
f1 (ppm)

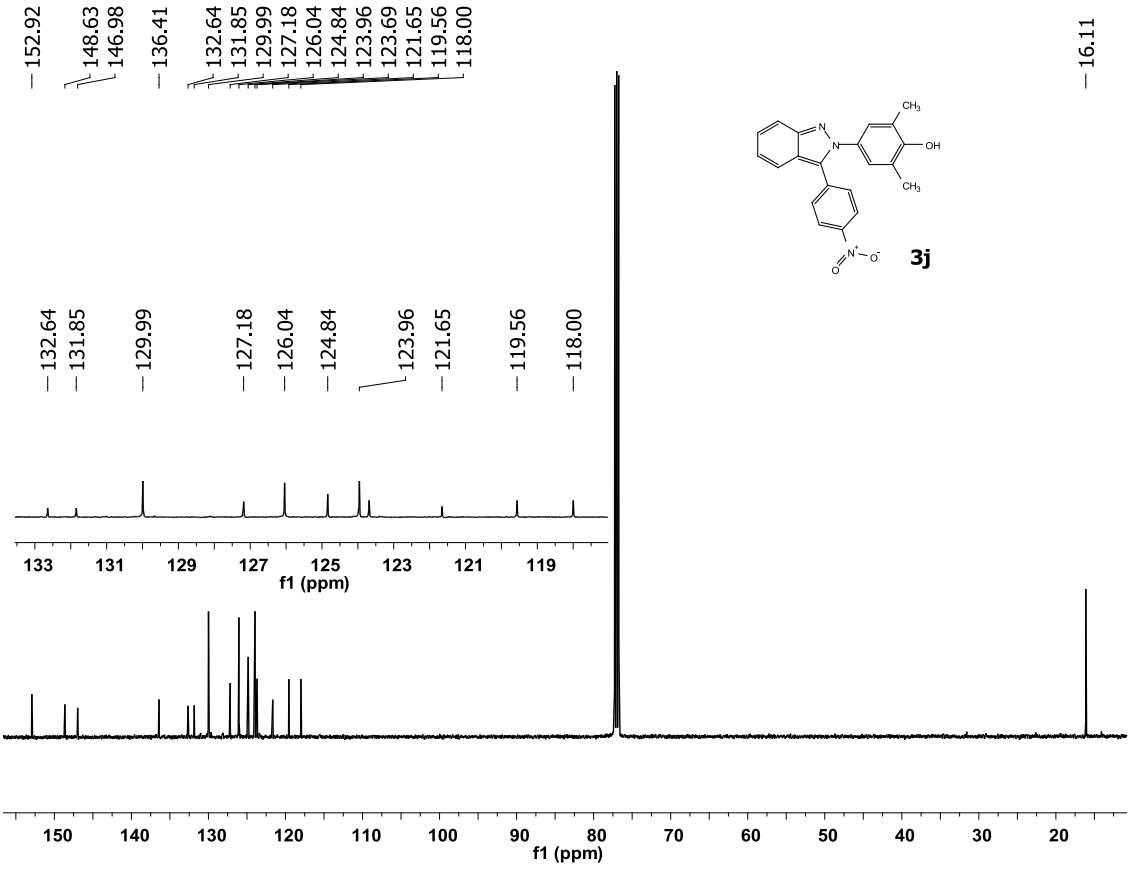

7.803
7.785
7.718
7.381
6.986
5.518
2.168
3g
0.98
0.99
6.00
1.00
1.96
1.07
5.95
f1 (ppm)

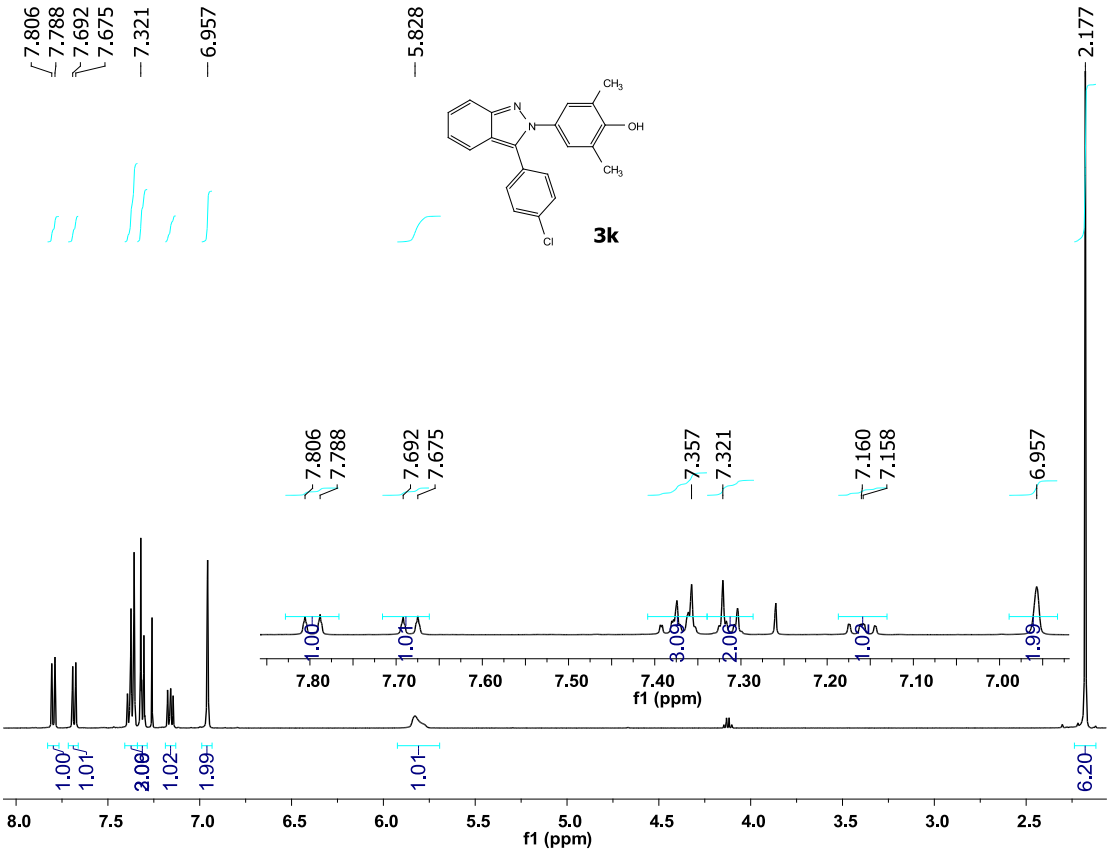

152.32
148.49
135.34
132.47
129.94
129.59
128.62
128.16
126.80
126.02
124.36
122.25
121.36
120.51
117.48
77.25
77.00
76.75
16.06
3g
f1 (ppm)

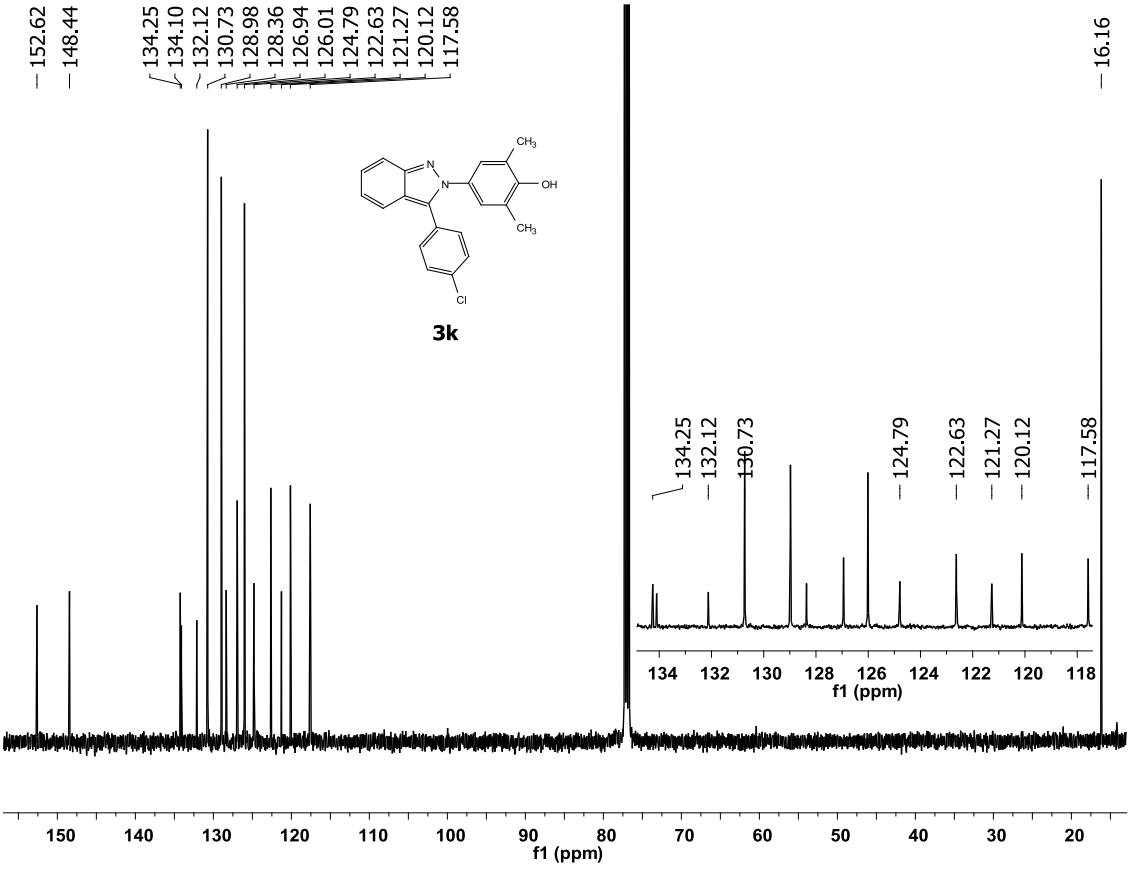

8.060
8.044
7.180
6.975
5.633
3.937
2.173
7.802
7.718
7.467
7.388
7.386
1.99
0.99
0.99
2.03
1.01
1.00
1.98
3.06
6.43
f1 (ppm)
3i

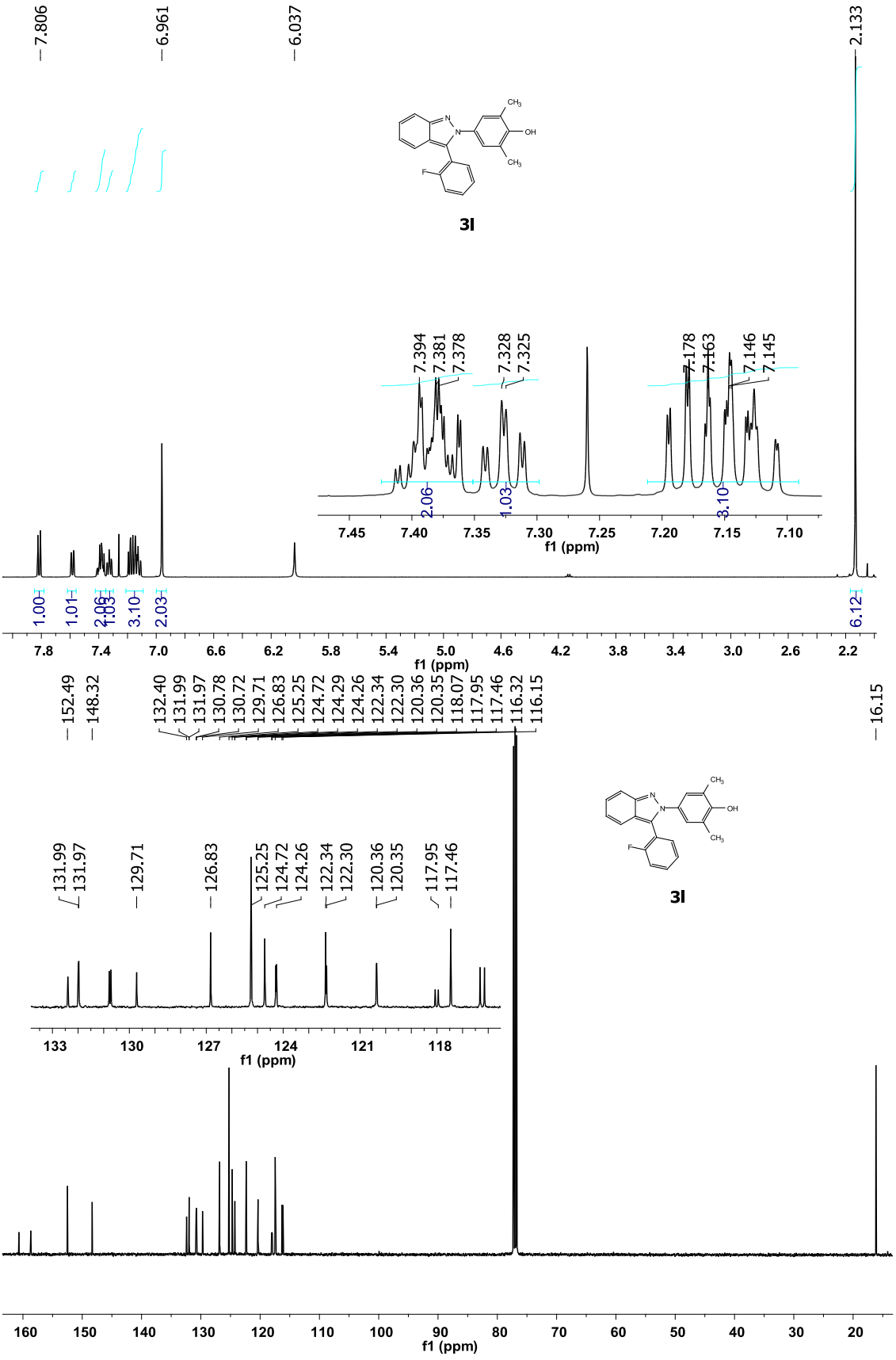

166.65
152.63
148.58
134.44
134.04
132.18
129.85
129.44
129.37
126.96
126.02
124.60
122.94
121.51
120.07
117.73
52.26
16.10
f1 (ppm)
3i

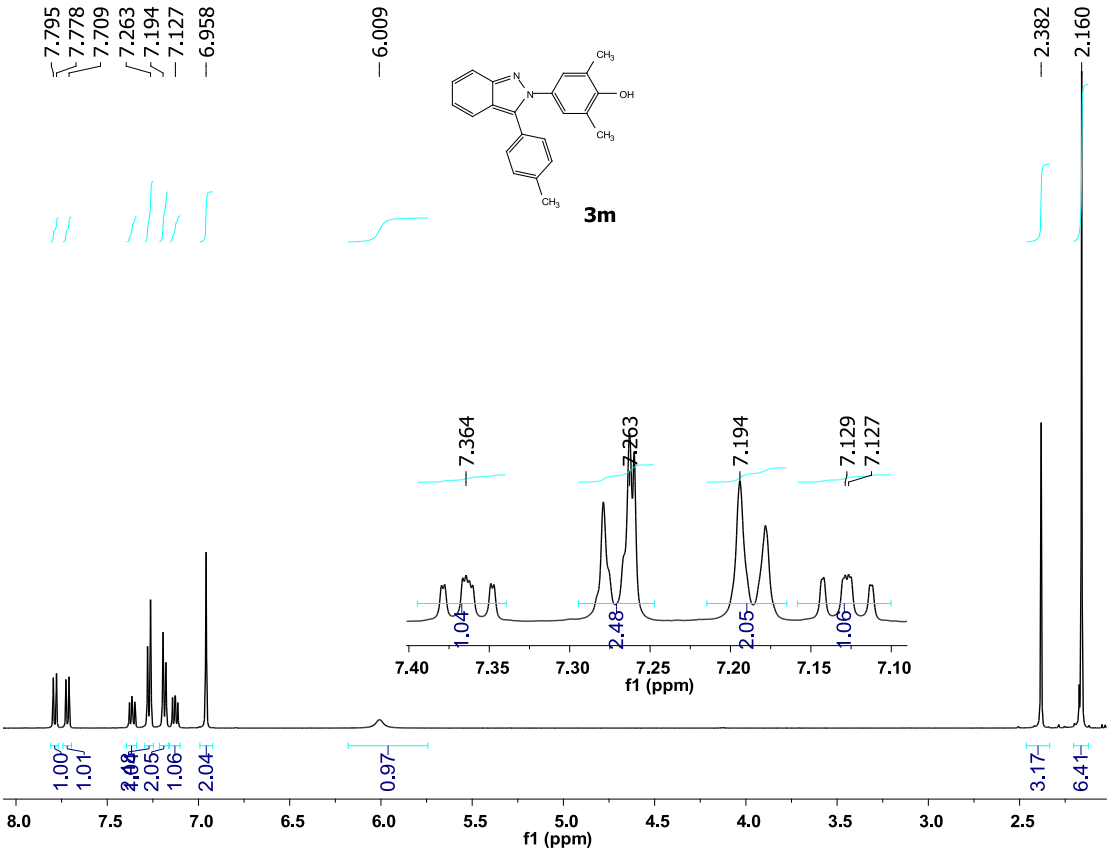

8.258
8.241
7.825
7.717
7.564
6.981
5.601
2.195
3j
7.843
7.825
7.717
7.564
7.547
7.416
7.414
7.231
1.97
0.93
0.98
2.00
1.00
0.97
1.86
0.89
5.91
f1 (ppm)

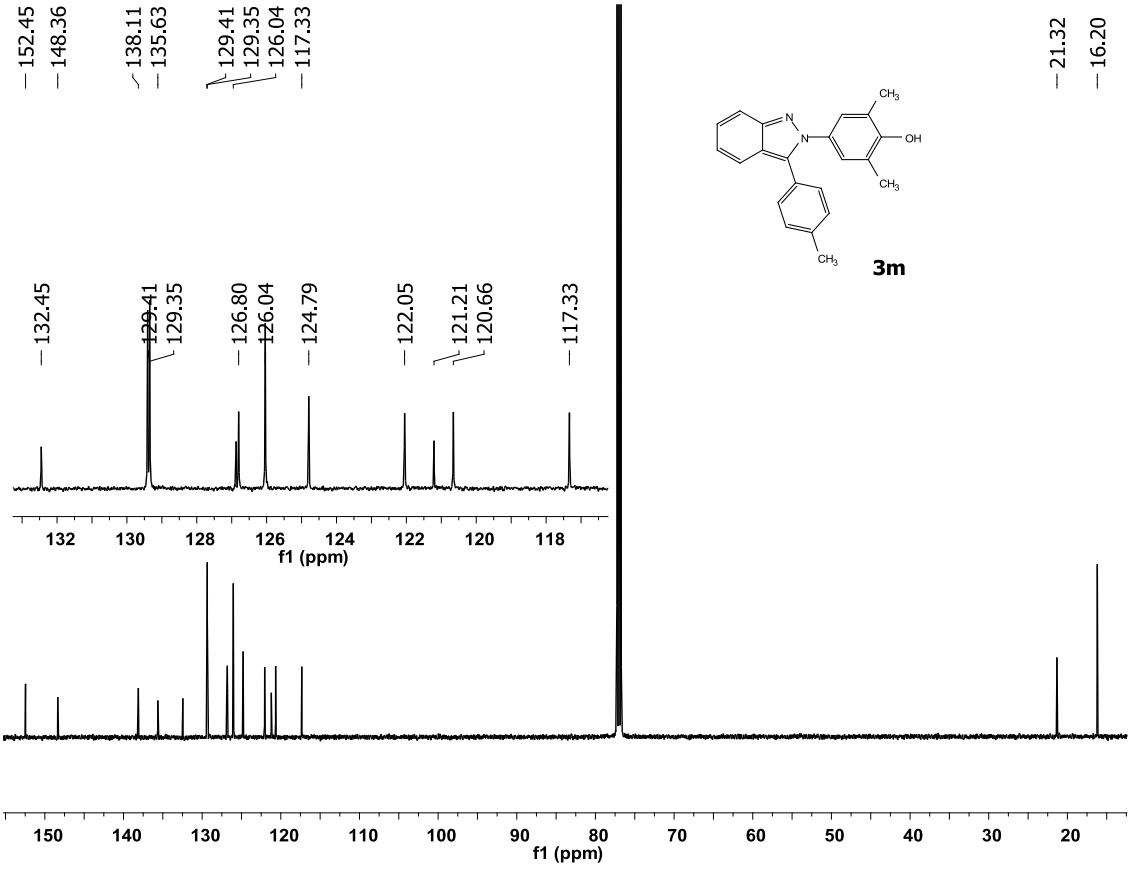

152.92
148.63
146.98
136.41
132.64
131.85
129.99
127.18
126.04
124.84
123.96
123.69
121.65
119.56
118.00
16.11
3j
f1 (ppm)

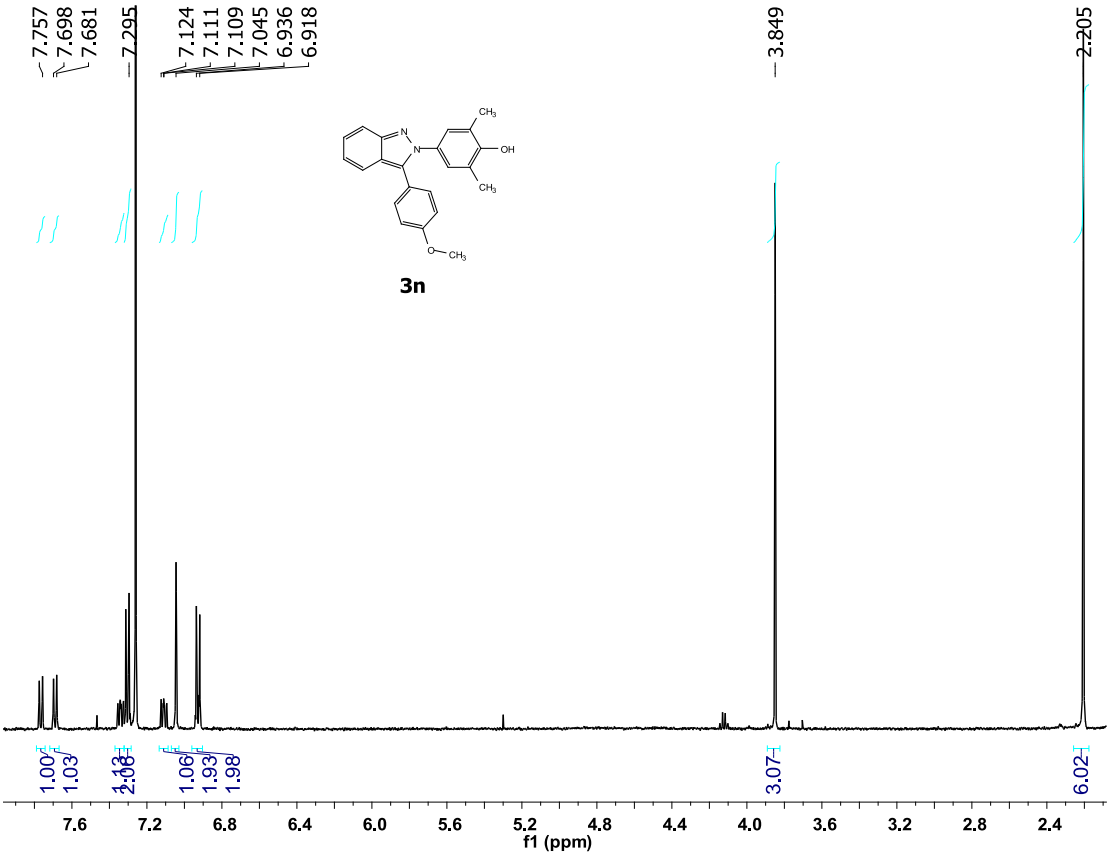

7.806
7.788
7.692
7.675
7.321
6.957
5.828
2.177
3k
7.806
7.788
7.692
7.675
7.357
7.321
7.160
7.158
6.957
1.00
1.01
1.01
3.09
2.06
1.02
1.99
f1 (ppm)
1.00
1.01
2.00
1.02
1.99
1.01
6.20
f1 (ppm)

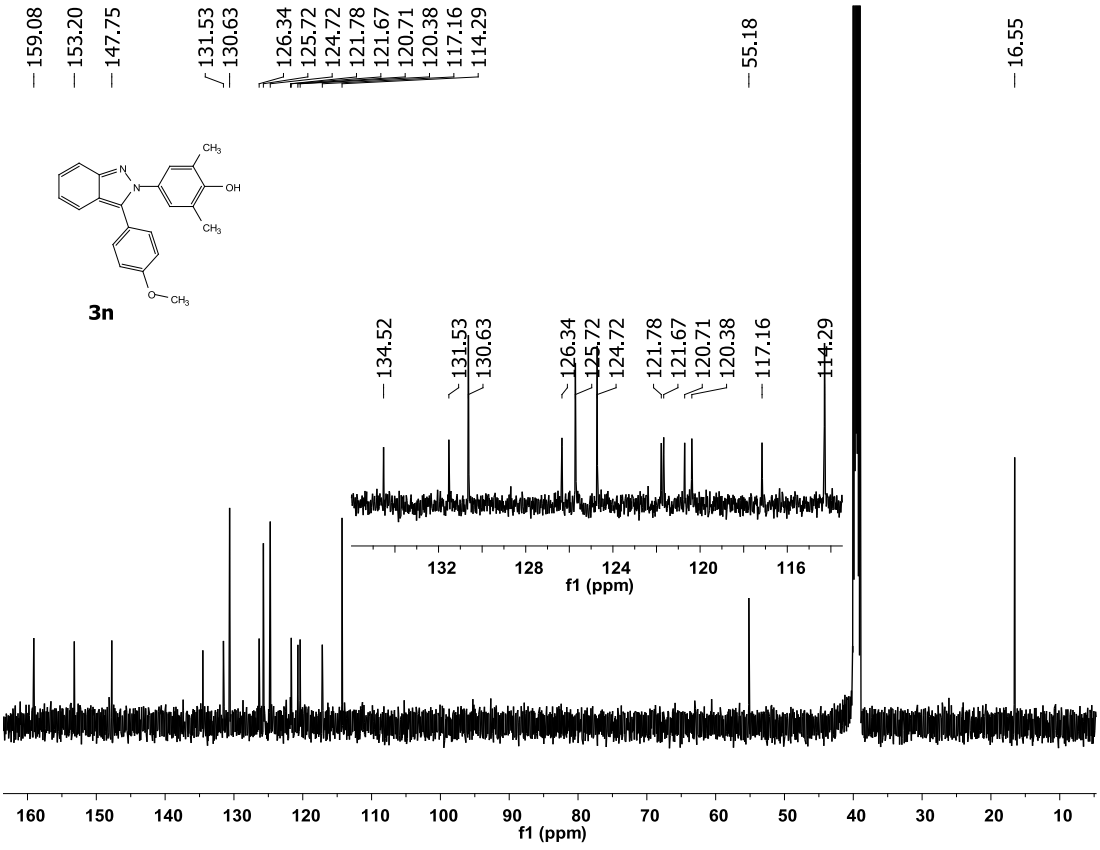

152.62
148.44
134.25
134.10
132.12
130.73
128.98
128.36
126.94
126.01
124.79
122.63
121.27
120.12
117.58
16.16
3k
134.25
132.12
130.73
124.79
122.63
121.27
120.12
117.58
f1 (ppm)
f1 (ppm)

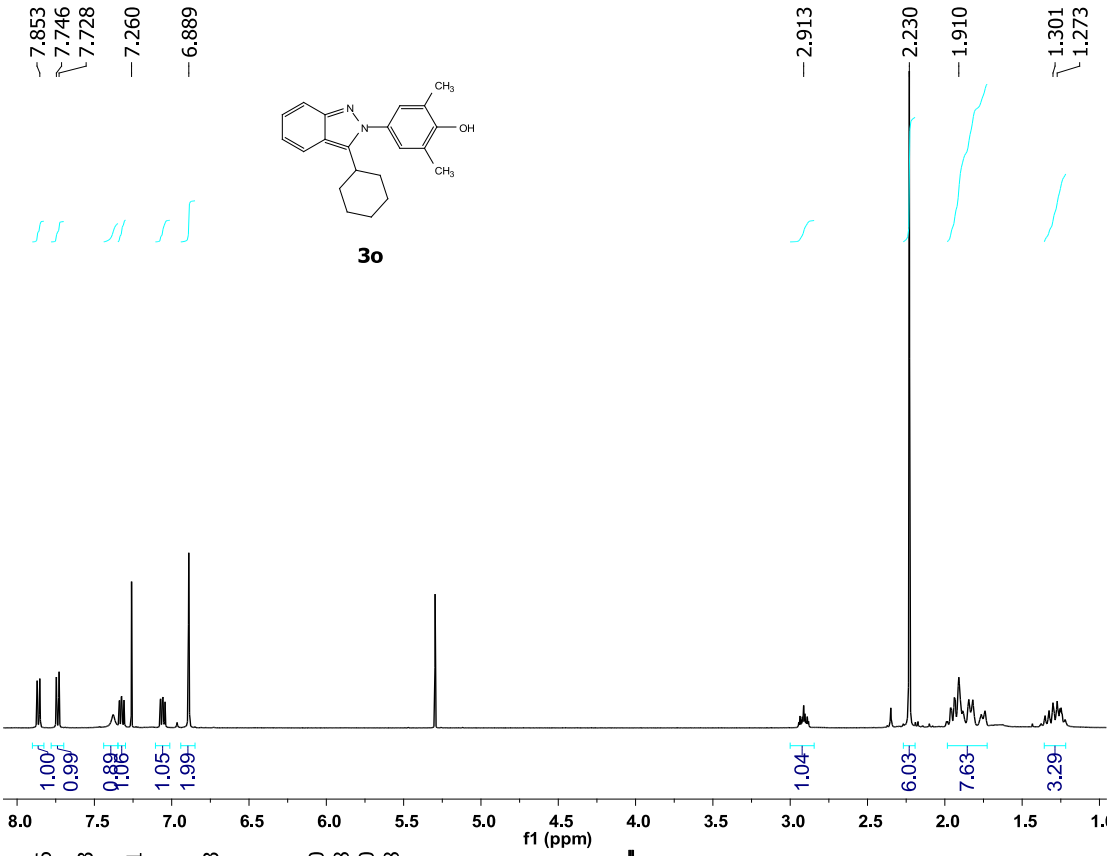

7.806
6.961
6.037
2.133
3l
7.394
7.381
7.378
7.328
7.325
7.178
7.163
7.146
7.145
2.06
1.03
3.10
f1 (ppm)
1.00
1.01
2.06
1.03
3.10
2.03
6.12
f1 (ppm)
152.49
148.32
132.40
131.99
131.97
130.78
130.72
129.71
126.83
125.25
124.72
124.29
124.26
122.34
122.30
120.36
120.35
118.07
117.95
117.46
116.32
116.15
16.15
3l
131.99
131.97
129.71
126.83
125.25
124.72
124.26
122.34
122.30
120.36
120.35
117.95
117.46
f1 (ppm)
f1 (ppm)

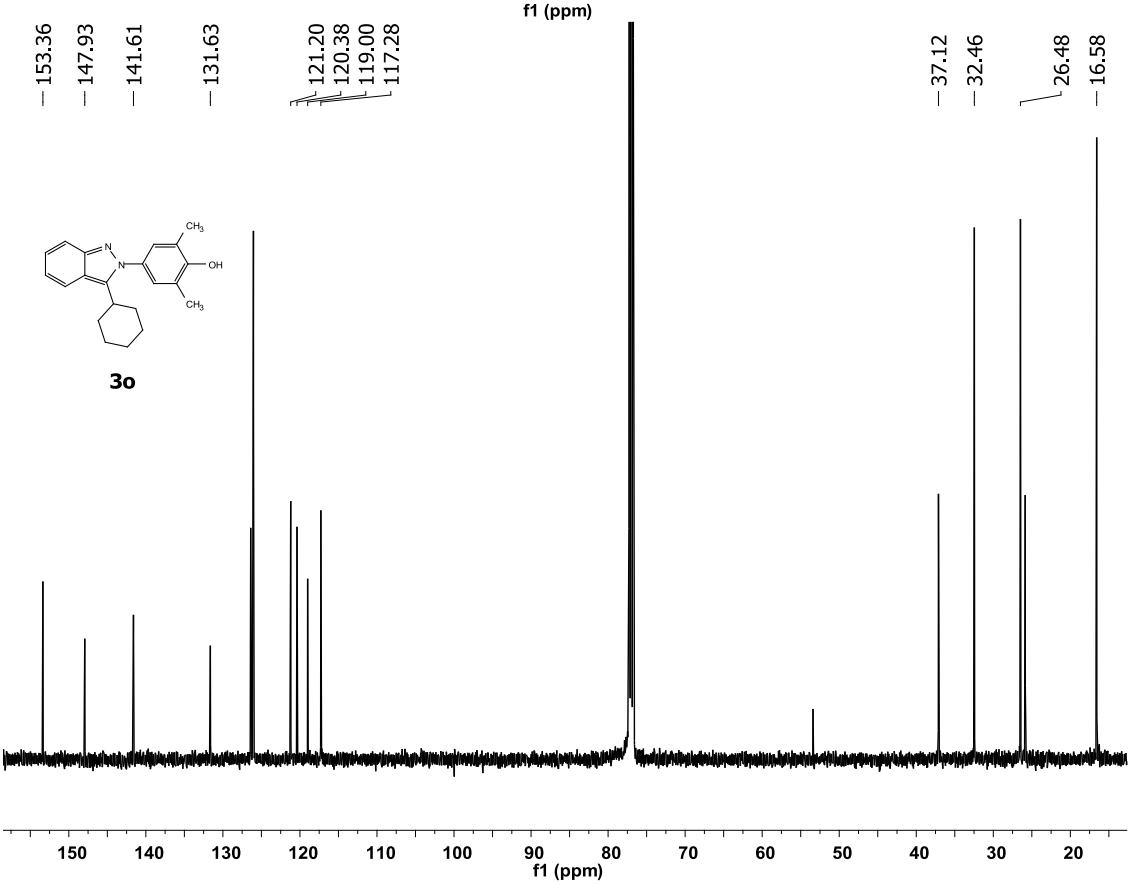

7.795
7.778
7.709
7.263
7.194
7.127
6.958
6.009
2.382
2.160
3m
7.364
7.263
7.194
7.129
7.127
1.04
2.48
2.05
1.06
7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
1.00
1.01
2.04
0.97
3.17
6.41
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
f1 (ppm)

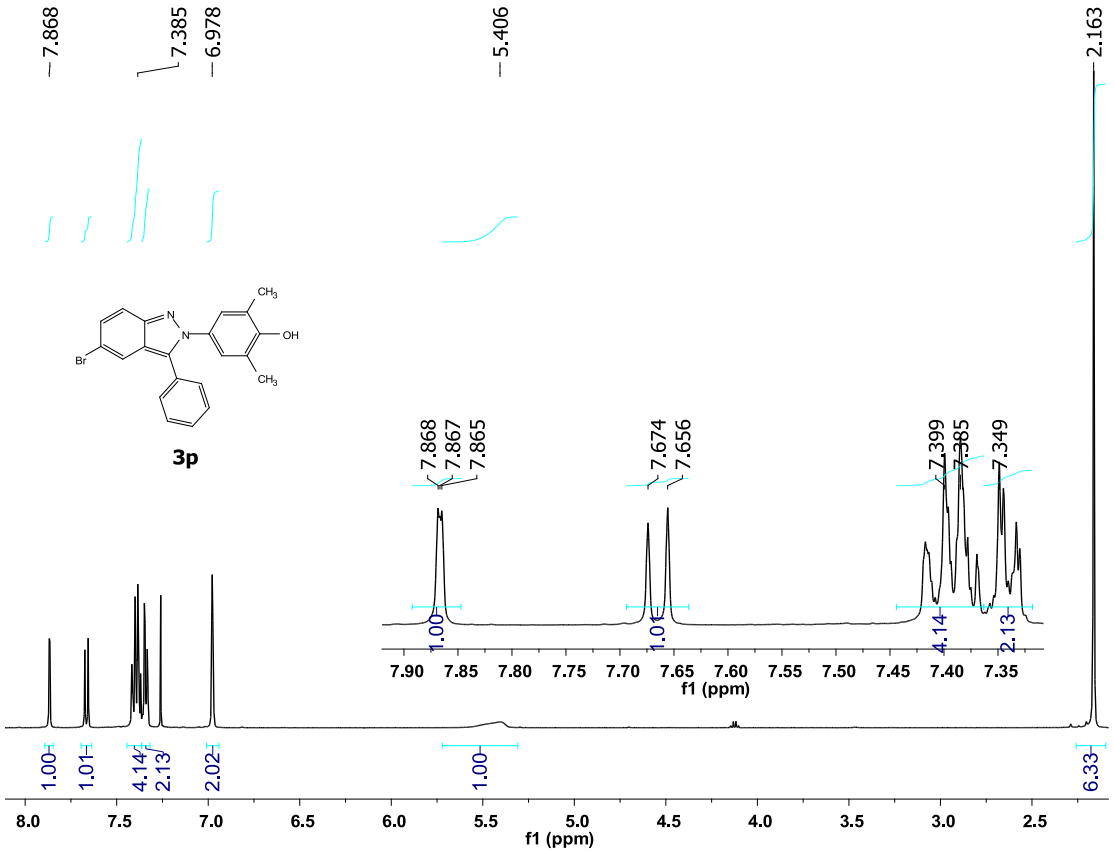

152.45
148.36
138.11
135.63
129.41
129.35
126.04
117.33
21.32
16.20
3m
132.45
129.41
129.35
126.80
126.04
124.79
122.05
121.21
120.66
117.33
132 130 128 126 124 122 120 118
f1 (ppm)
150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

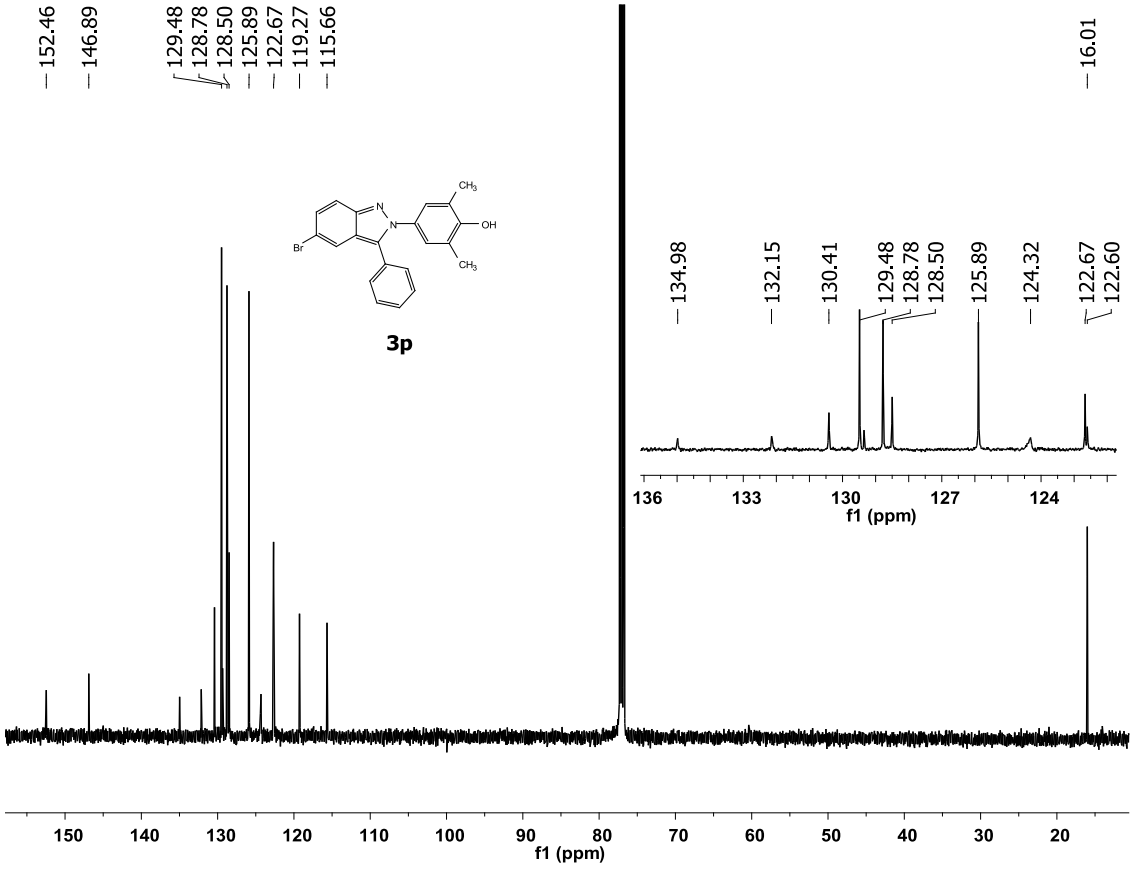

7.757
7.698
7.681
7.295
7.124
7.111
7.109
7.045
6.936
6.918
3.849
2.205
3n
1.00
1.03
2.13
2.08
1.06
1.93
1.98
3.07
6.02
f1 (ppm)

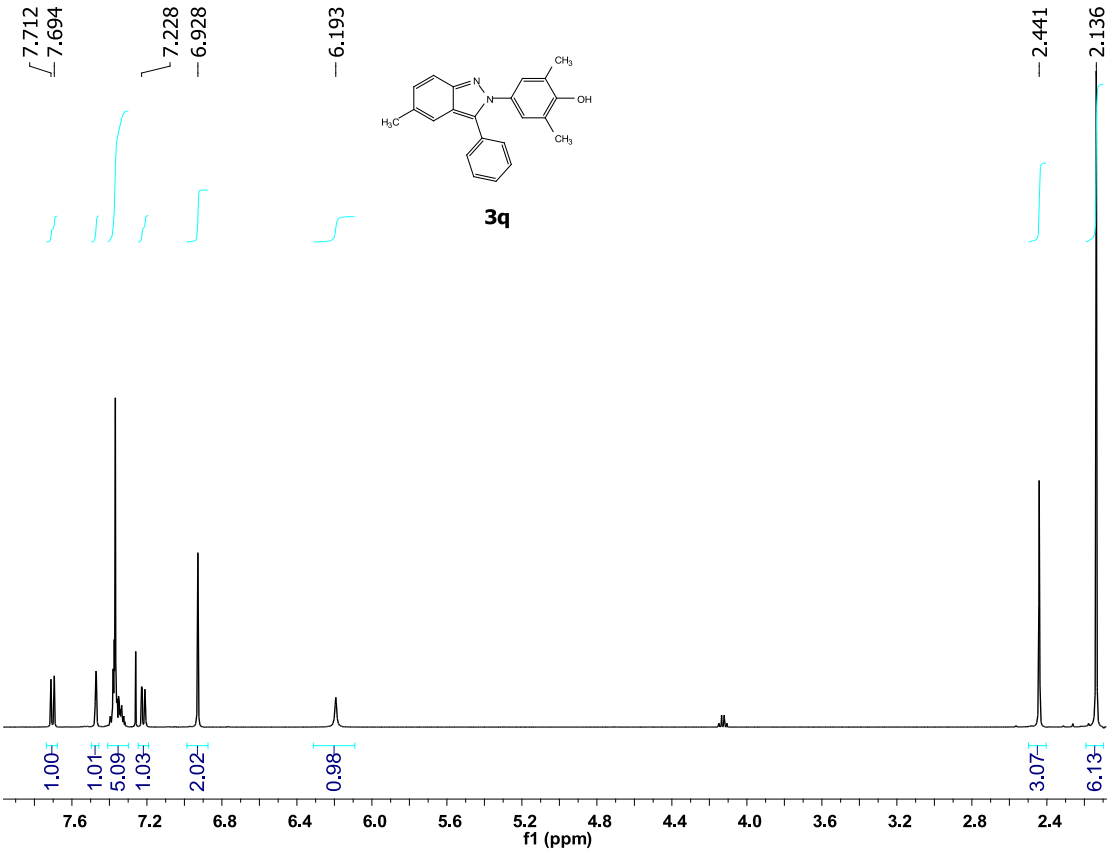

159.08
153.20
147.75
131.53
130.63
126.34
125.72
124.72
121.78
121.67
120.71
120.38
117.16
114.29
55.18
16.55
3n
134.52
131.53
130.63
126.34
125.72
124.72
121.78
121.67
120.71
120.38
117.16
114.29
132
128
124
120
116
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

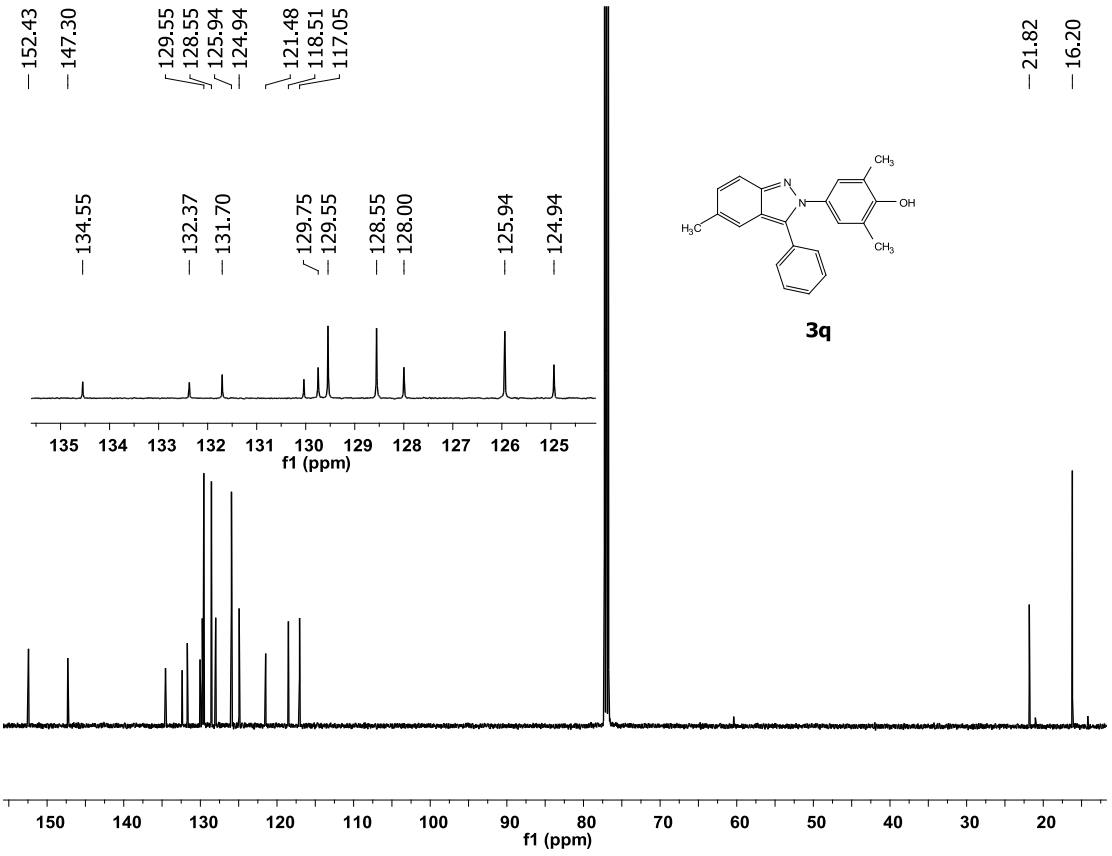

7.853
7.746
7.728
7.260
6.889
2.913
2.230
1.910
1.301
1.273
3o
1.00
0.99
0.89
1.06
1.05
1.99
1.04
6.03
7.63
3.29
f1 (ppm)

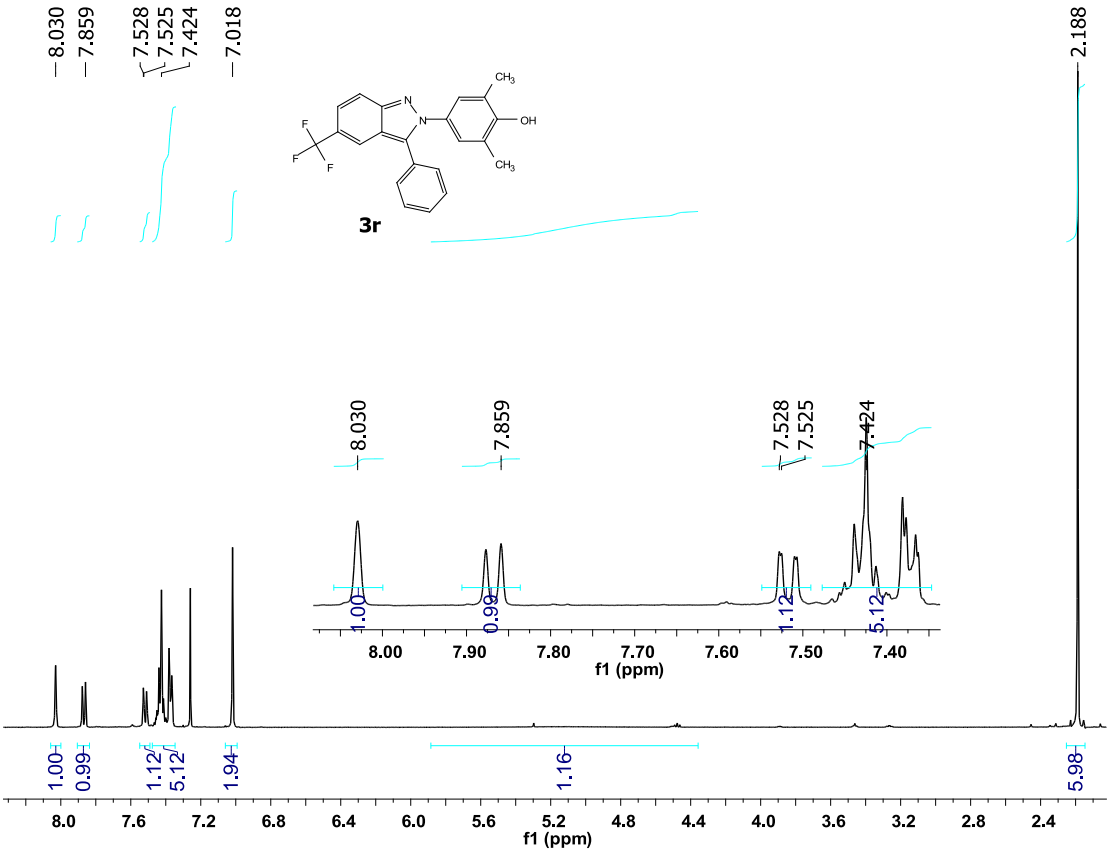

153.36
147.93
141.61
131.63
121.20
120.38
119.00
117.28
37.12
32.46
26.48
16.58
3o
f1 (ppm)

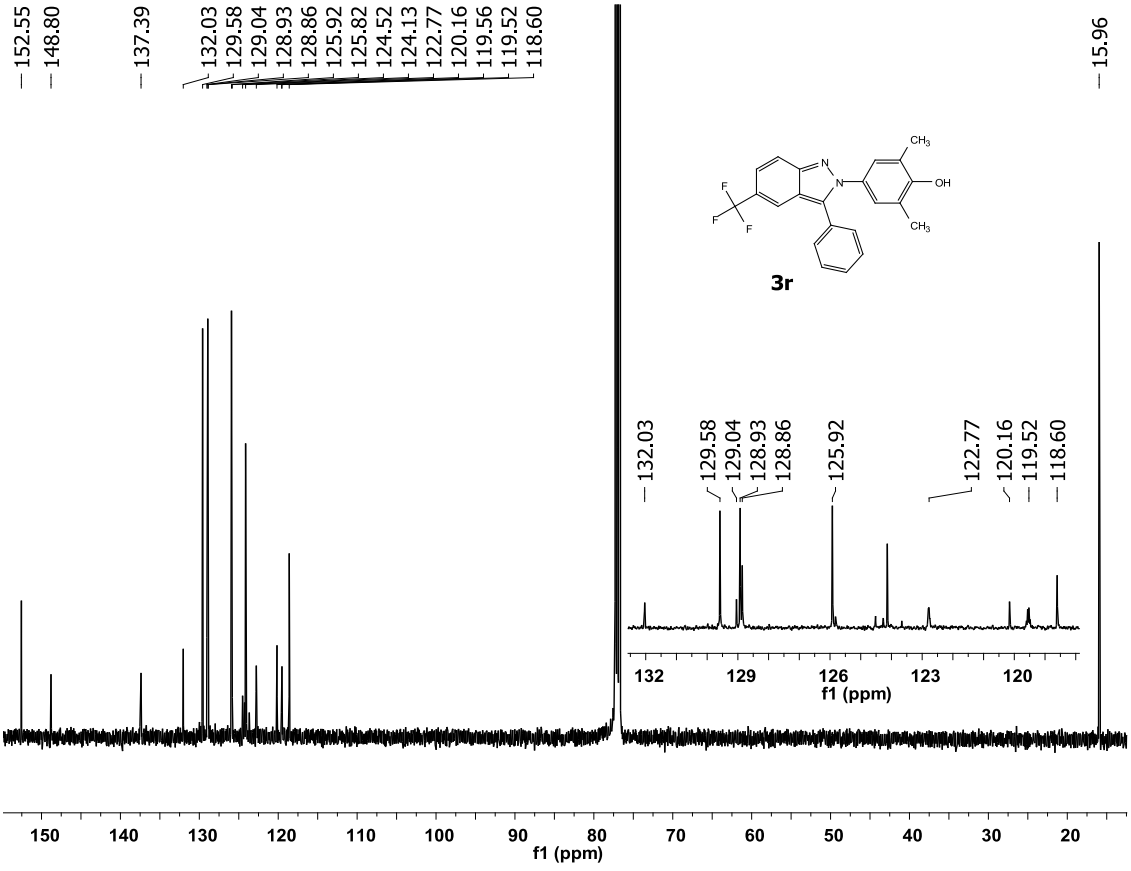

7.868
7.385
6.978
5.406
2.163
3p
7.868
7.867
7.865
7.674
7.656
7.399
7.385
7.349
1.00
1.01
4.14
2.13
2.02
1.00
6.33
f1 (ppm)

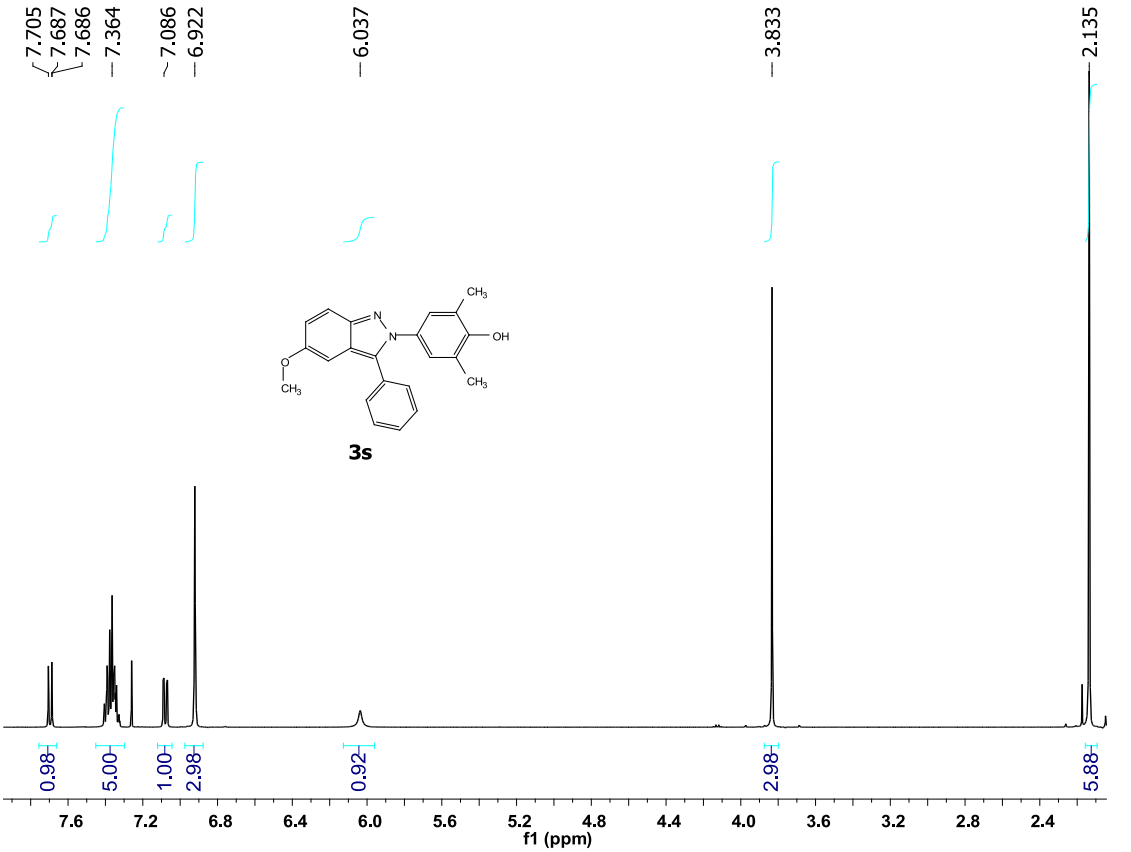

152.46
146.89
129.48
128.78
128.50
125.89
122.67
119.27
115.66
16.01
3p
134.98
132.15
130.41
129.48
128.78
128.50
125.89
124.32
122.67
122.60
f1 (ppm)

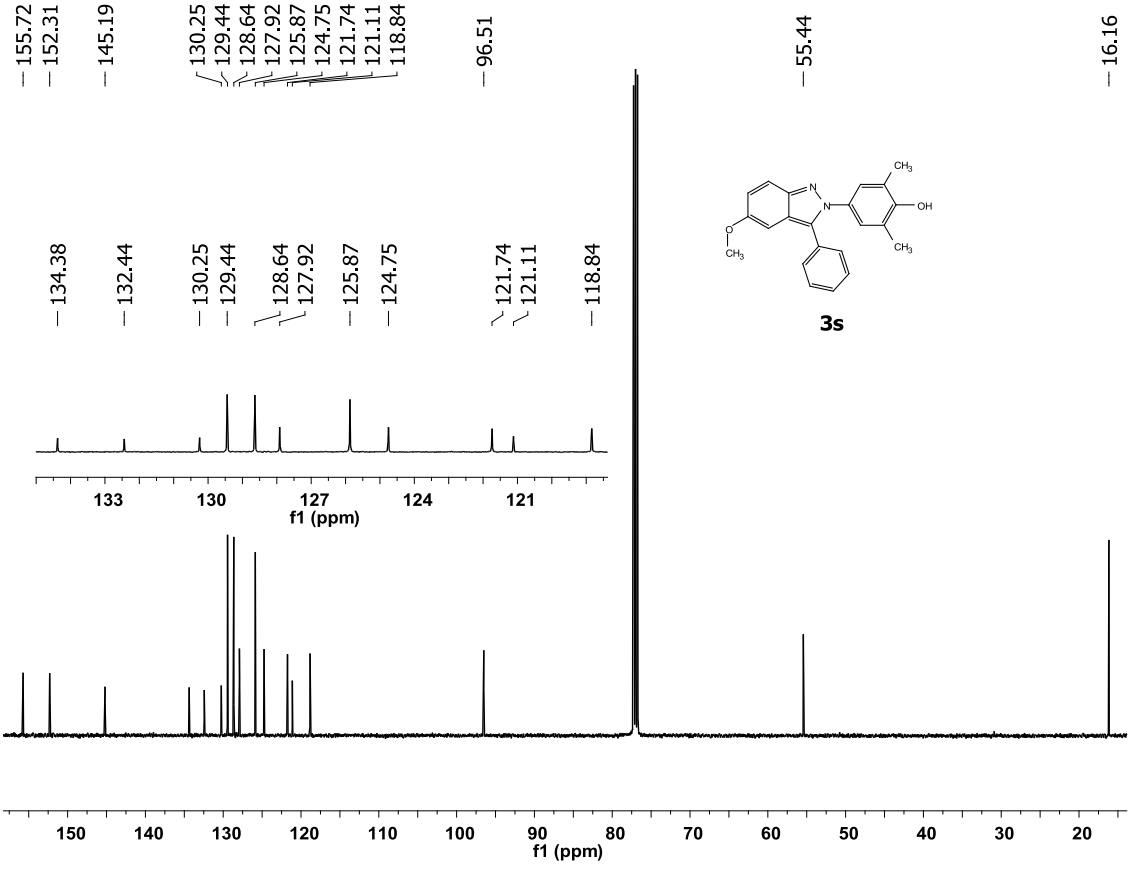

7.712
7.694
7.228
6.928
6.193
2.441
2.136
3q
1.00
1.01
5.09
1.03
2.02
0.98
3.07
6.13
f1 (ppm)

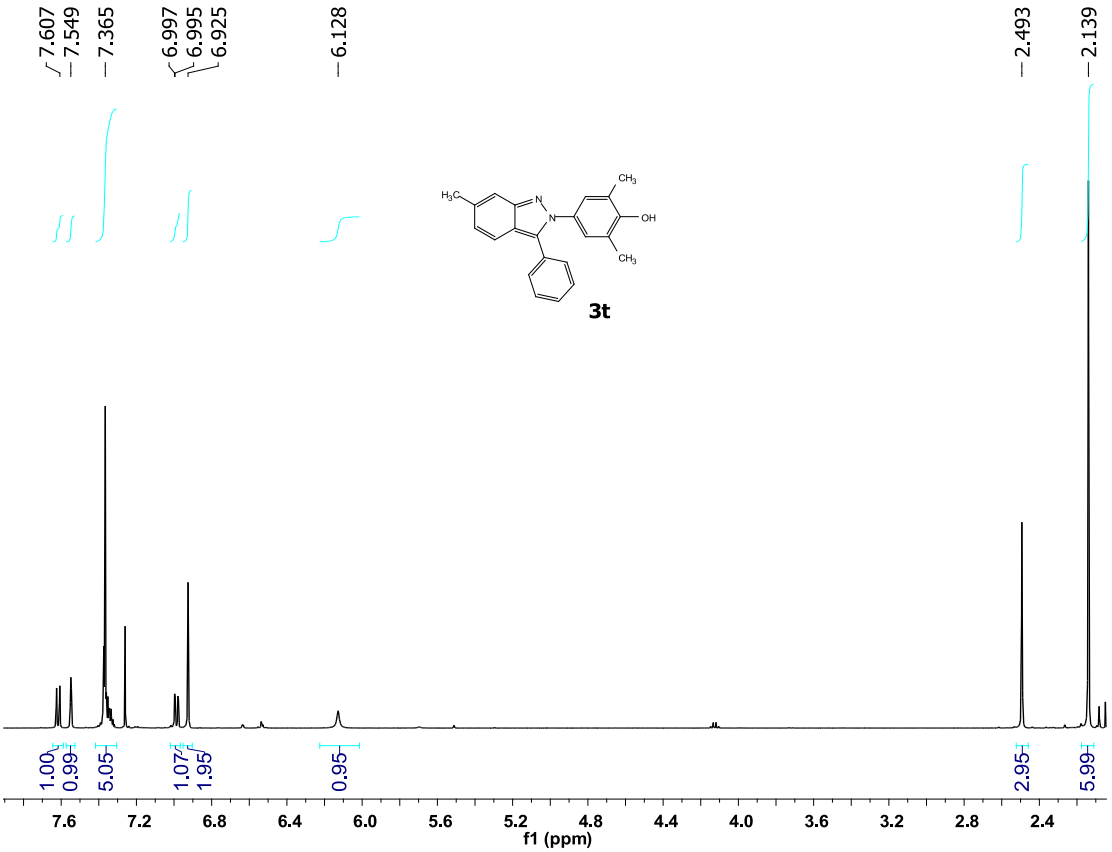

152.43
147.30
129.55
128.55
125.94
124.94
121.48
118.51
117.05
21.82
16.20
134.55
132.37
131.70
129.75
129.55
128.55
128.00
125.94
124.94
3q
f1 (ppm)

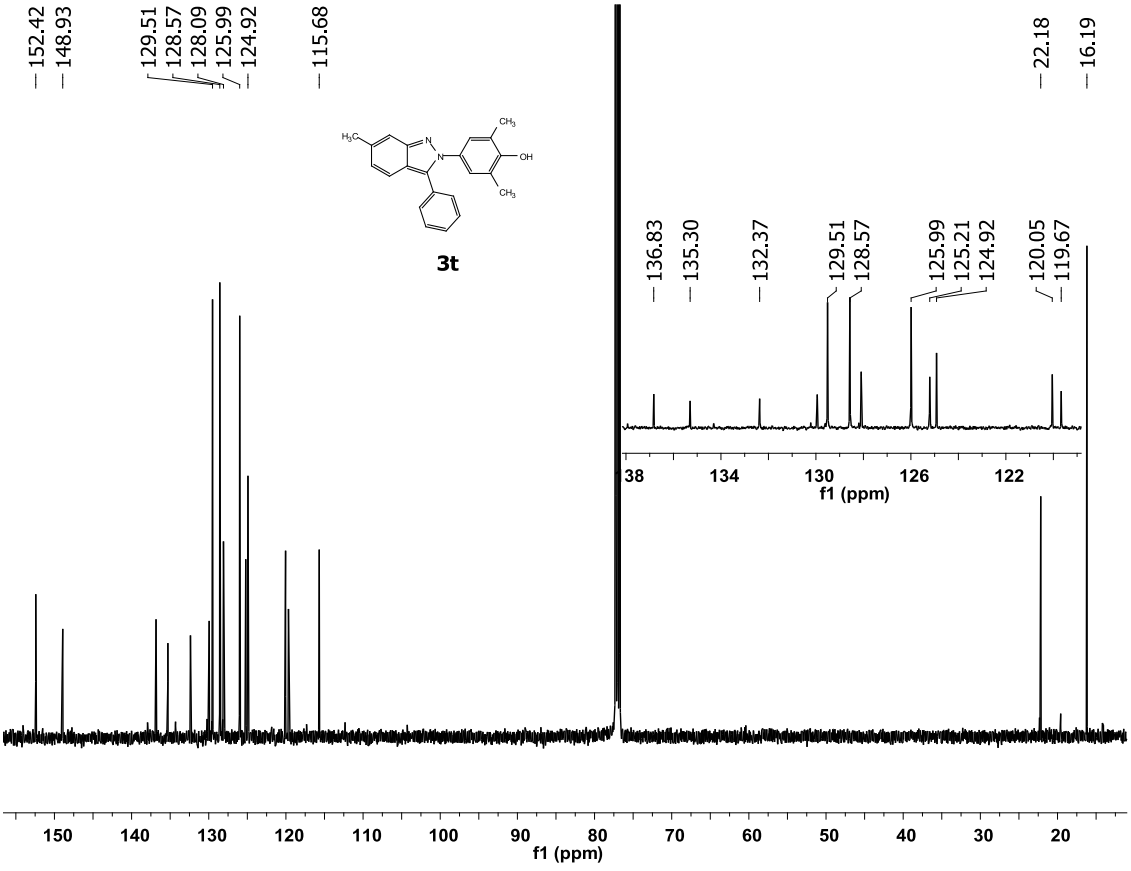

8.030
7.859
7.528
7.525
7.424
7.018
2.188
3r
1.00
0.99
1.12
5.12
1.94
1.16
5.98
f1 (ppm)

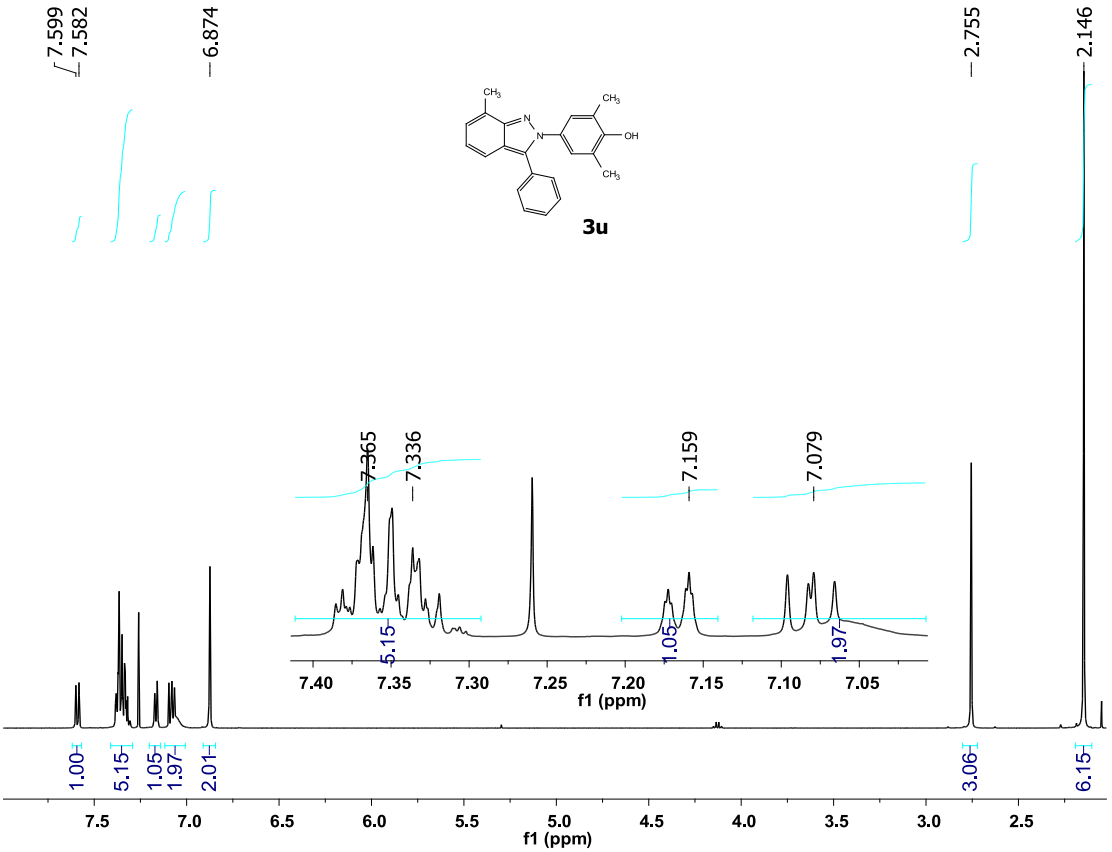

152.55
148.80
137.39
132.03
129.58
129.04
128.93
128.86
125.92
125.82
124.52
124.13
122.77
120.16
119.56
119.52
118.60
15.96
3r
f1 (ppm)

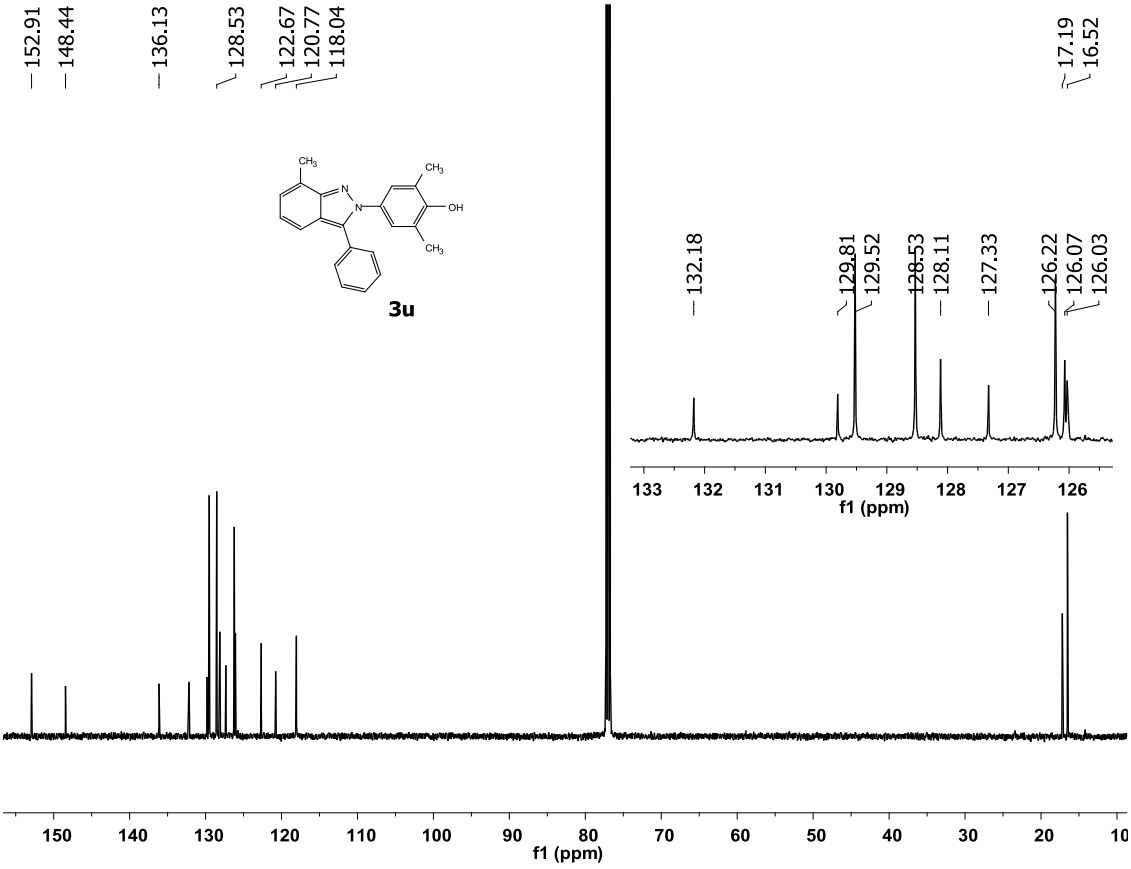

7.705
7.687
7.686
7.364
7.086
6.922
6.037
3.833
2.135
3s
0.98
5.00
1.00
2.98
0.92
2.98
5.88
f1 (ppm)

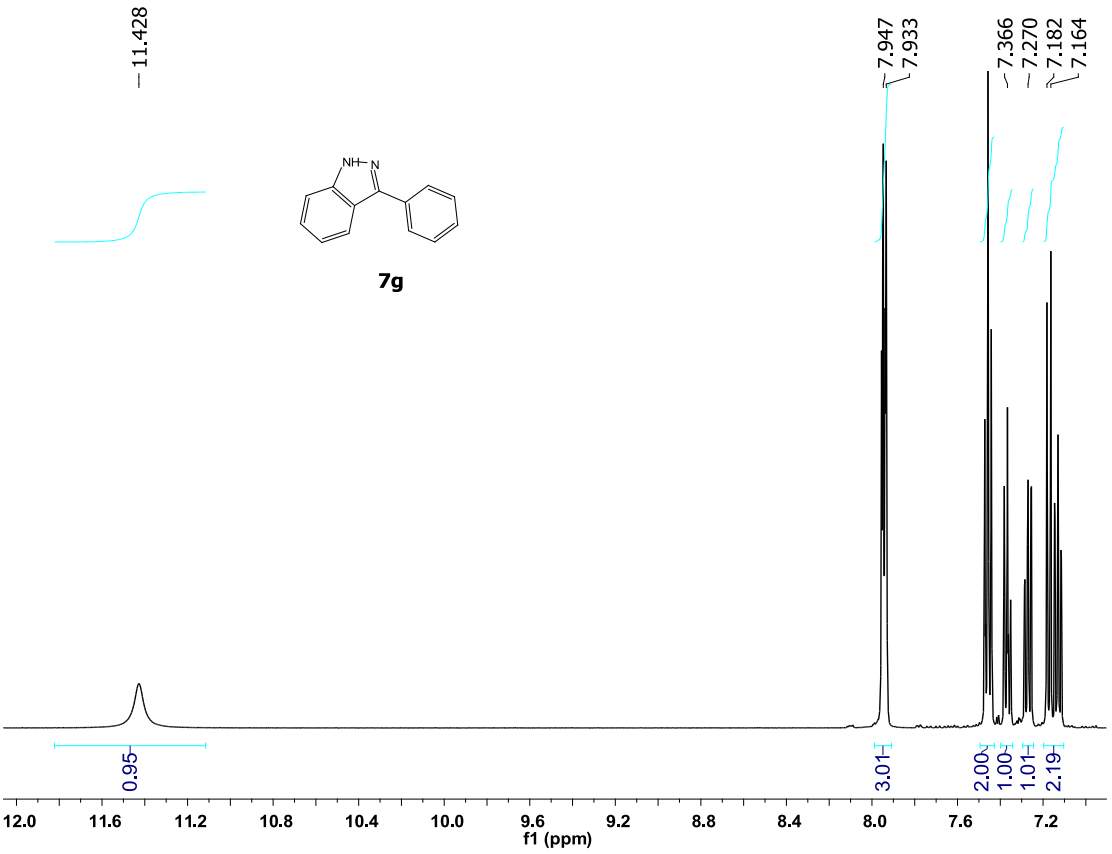

155.72
152.31
145.19
130.25
129.44
128.64
127.92
125.87
124.75
121.74
121.11
118.84
96.51
55.44
16.16
134.38
132.44
130.25
129.44
128.64
127.92
125.87
124.75
121.74
121.11
118.84
3s
f1 (ppm)

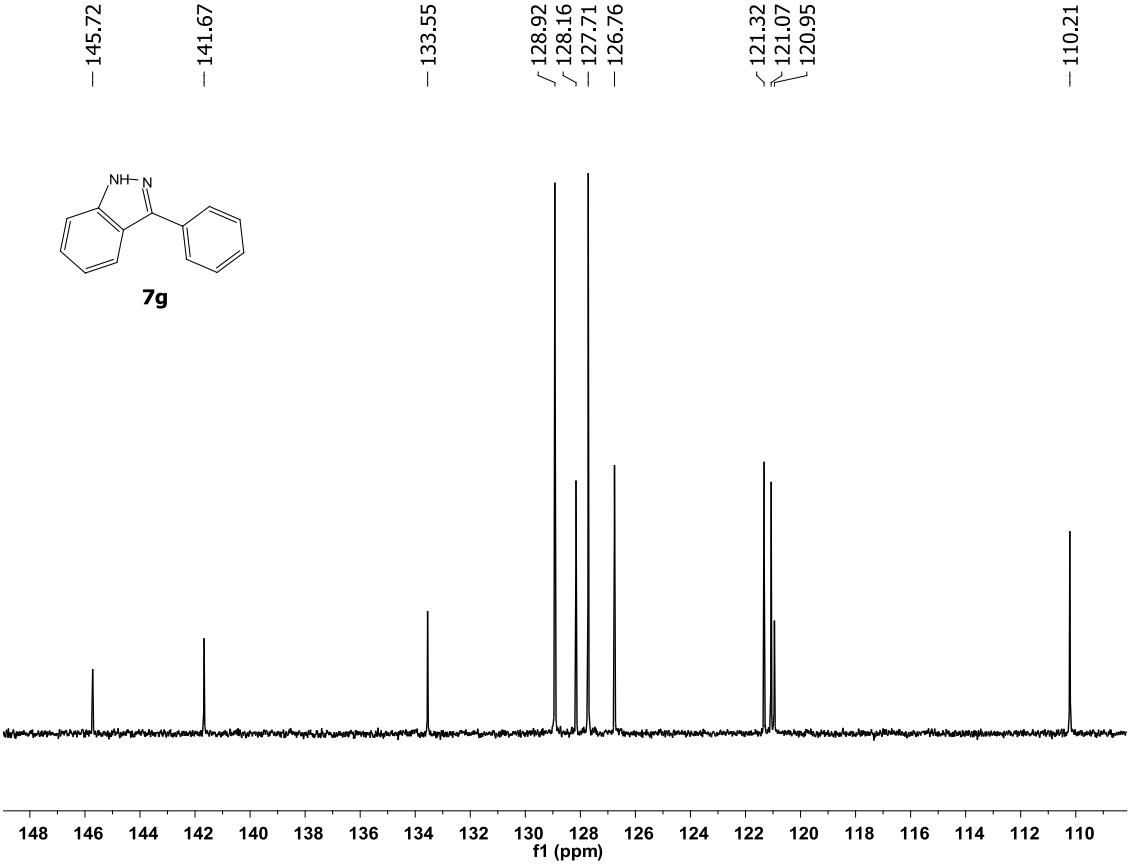

7.607
7.549
7.365
6.997
6.995
6.925
6.128
2.493
2.139
3t
1.00
0.99
5.05
1.07
1.95
0.95
2.95
5.99
f1 (ppm)

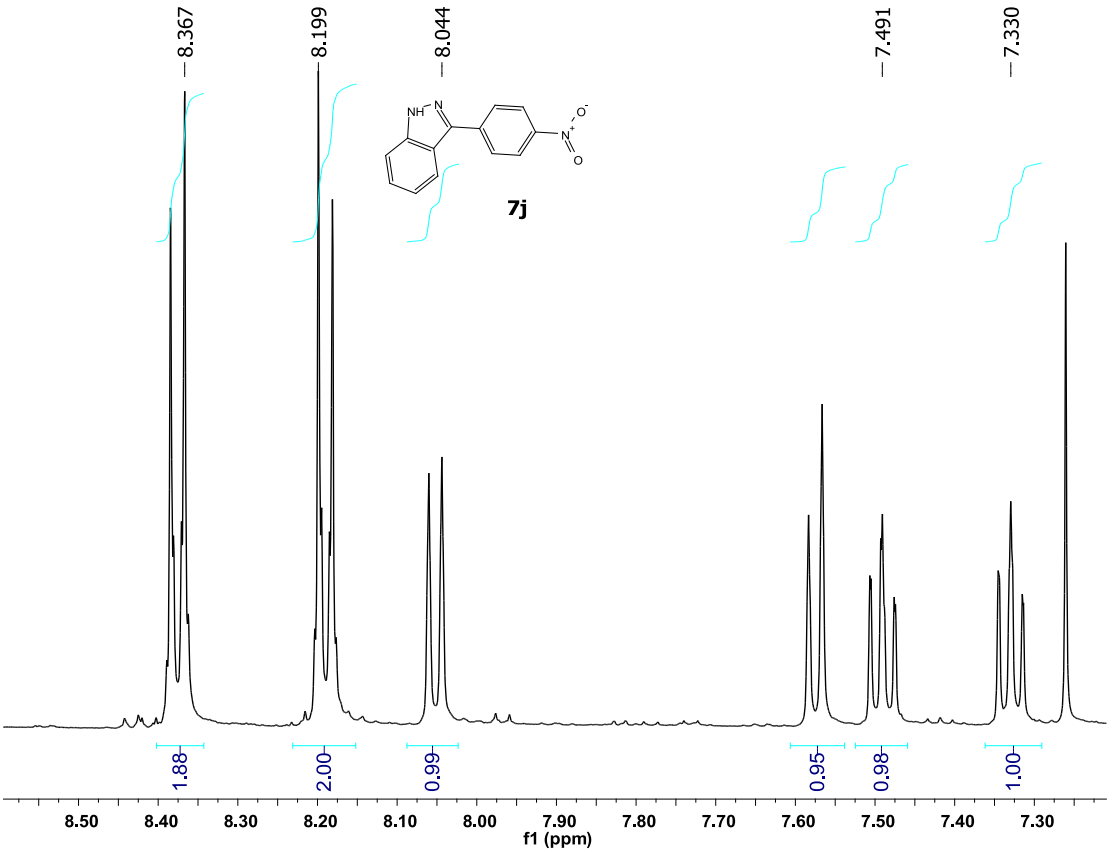

152.42
148.93
129.51
128.57
128.09
125.99
124.92
115.68
22.18
16.19
3t
136.83
135.30
132.37
129.51
128.57
125.99
125.21
124.92
120.05
119.67
f1 (ppm)
f1 (ppm)

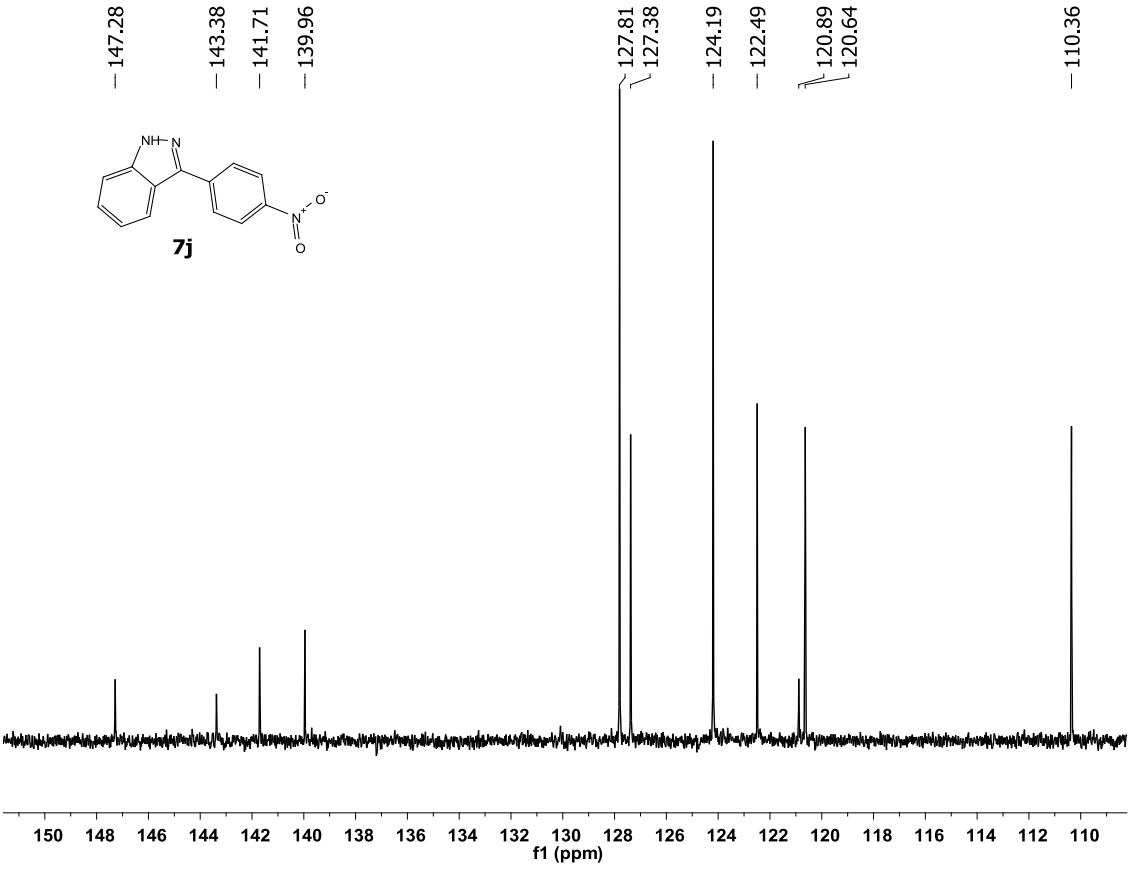

7.599
7.582
6.874
2.755
2.146
3u
7.365
7.336
7.159
7.079
5.15
1.05
1.97
1.00
5.15
1.05
1.97
2.01
3.06
6.15
f1 (ppm)

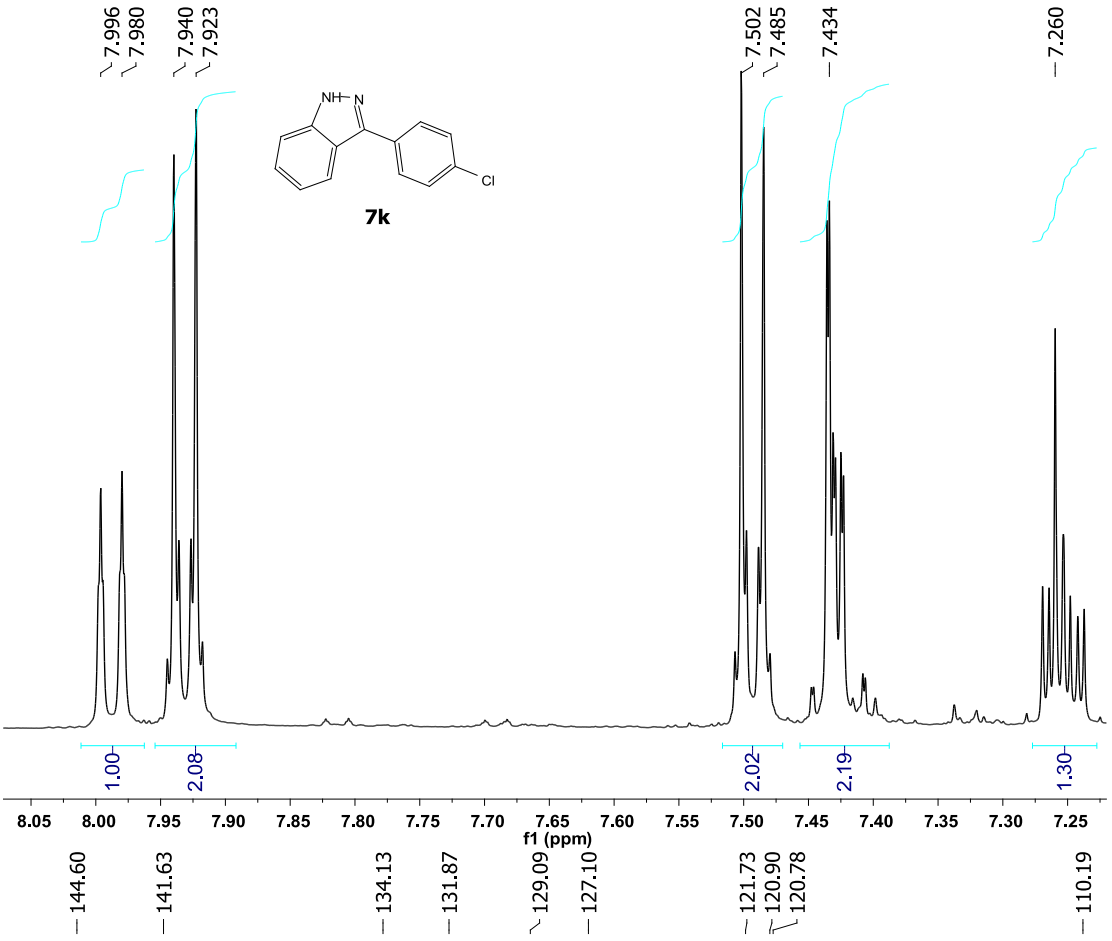

152.91
148.44
136.13
128.53
122.67
120.77
118.04
17.19
16.52
3u
132.18
129.81
129.52
128.53
128.11
127.33
126.22
126.07
126.03
f1 (ppm)

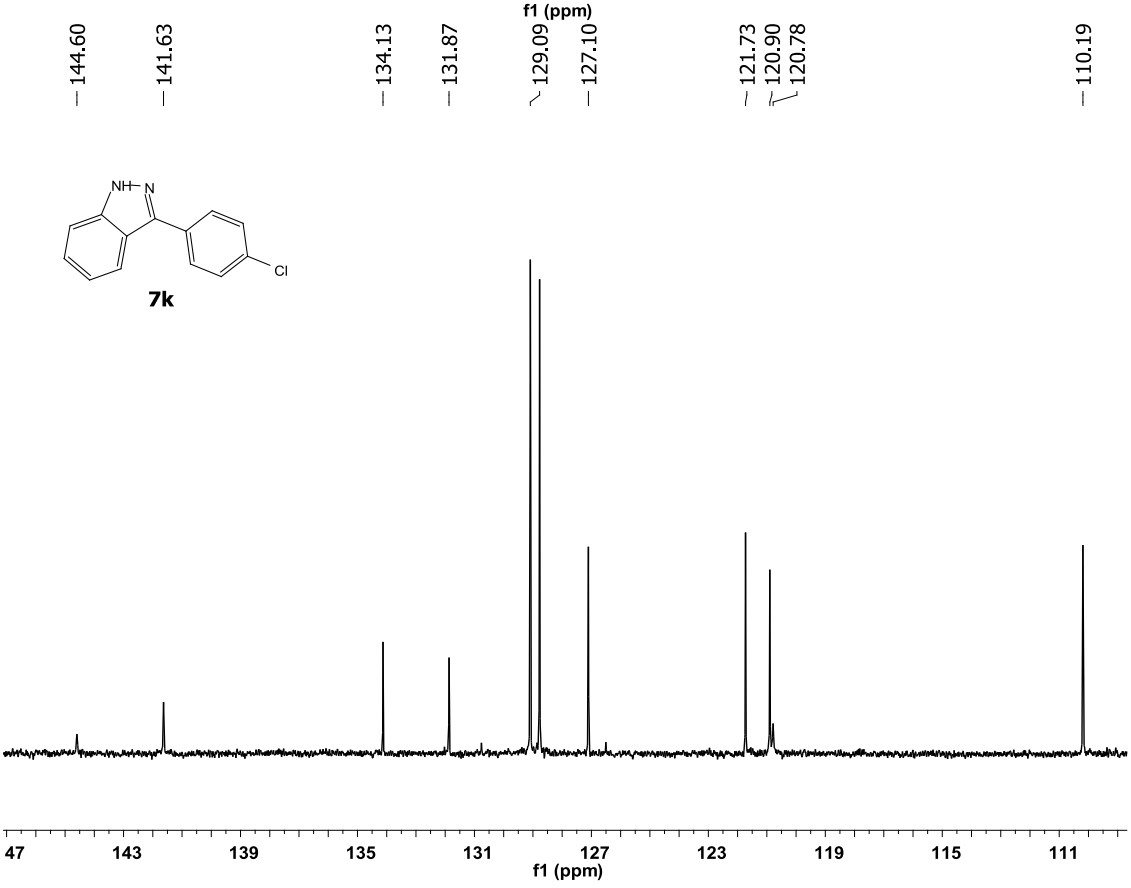

11.428
7.947
7.933
7.366
7.270
7.182
7.164
7g
0.95
3.01
2.00
1.00
1.01
2.19
12.0
11.6
11.2
10.8
10.4
10.0
9.6
9.2
8.8
8.4
8.0
7.6
7.2
f1 (ppm)

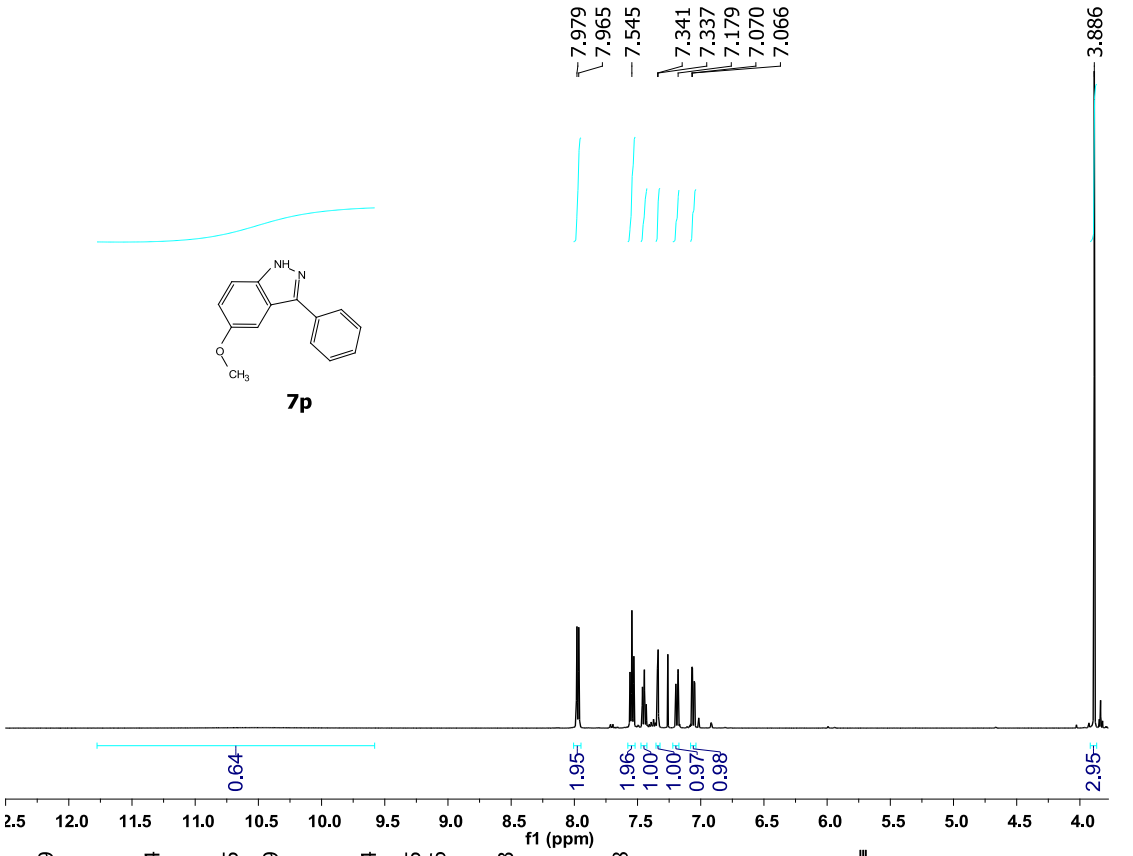

145.72
141.67
133.55
128.92
128.16
127.71
126.76
121.32
121.07
120.95
110.21
7g
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
110
f1 (ppm)

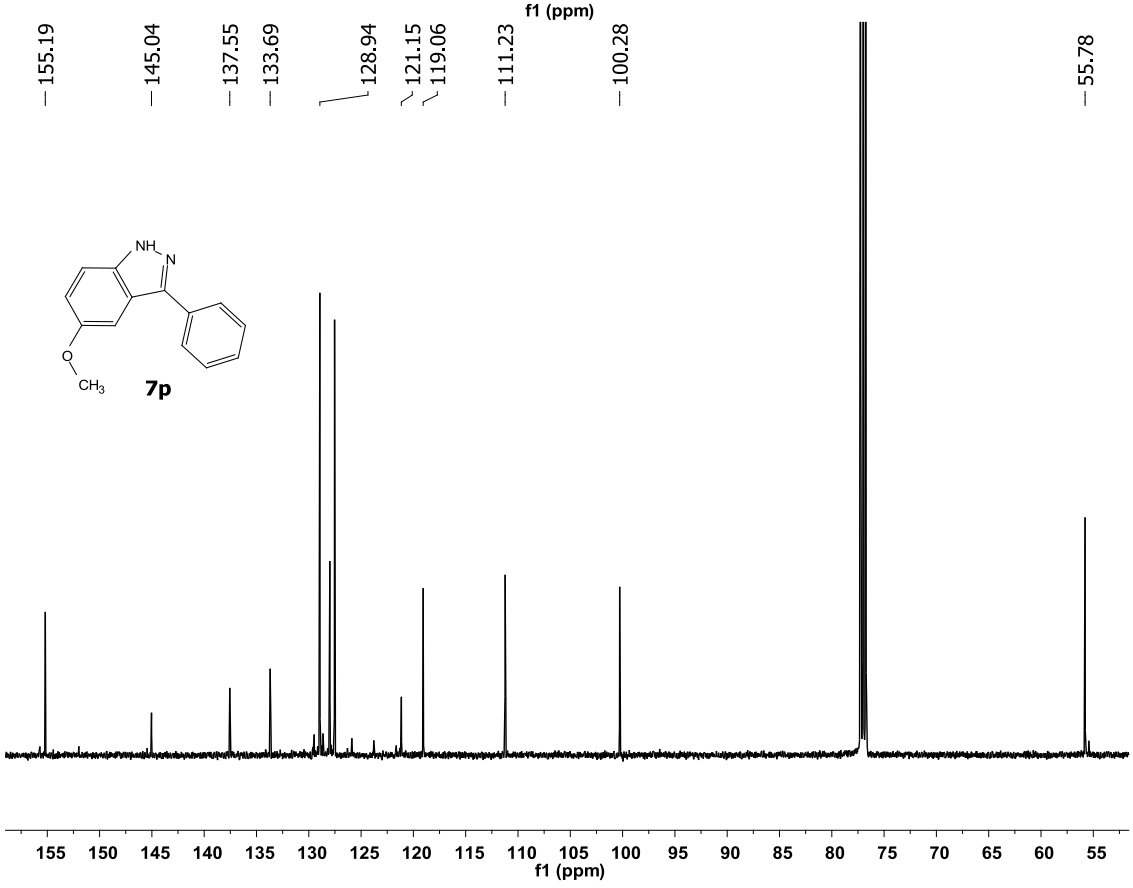

8.367
8.199
8.044
7.491
7.330
7j
1.88
2.00
0.99
0.95
0.98
1.00
8.50 8.40 8.30 8.20 8.10 8.00 7.90 7.80 7.70 7.60 7.50 7.40 7.30
f1 (ppm)

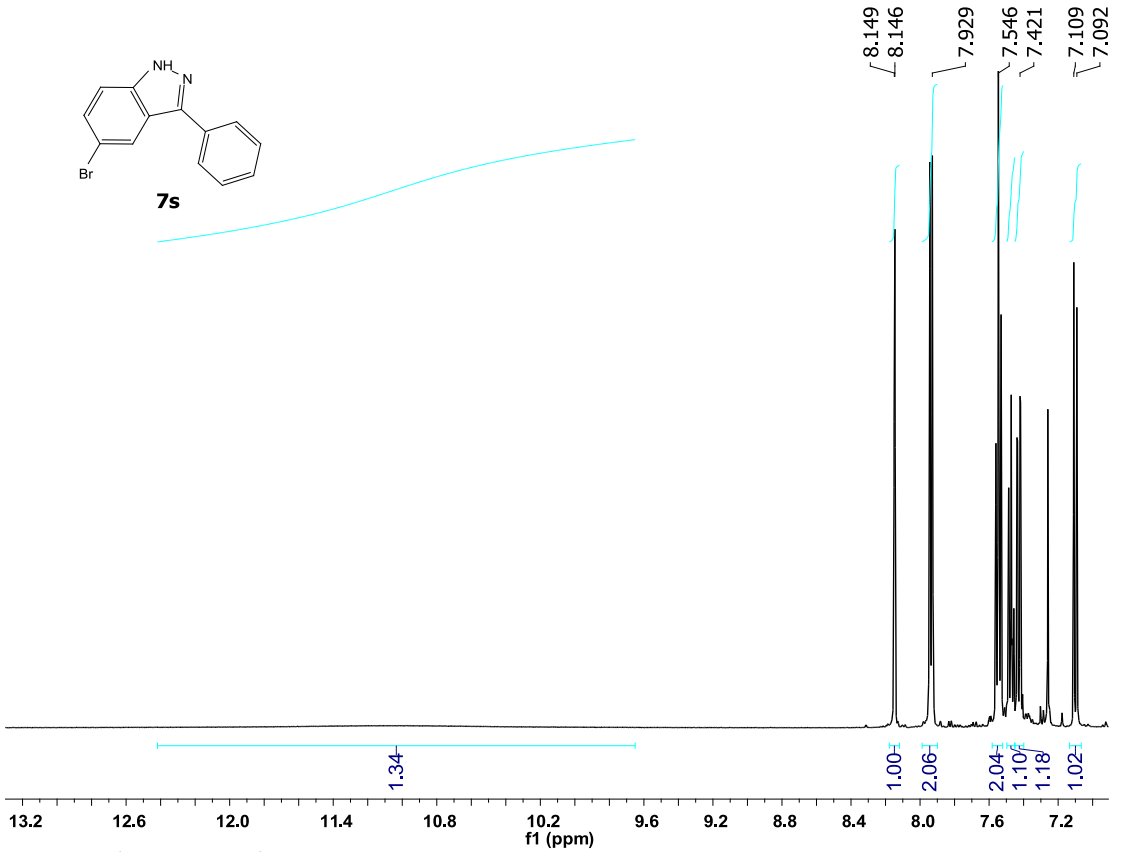

147.28
143.38
141.71
139.96
127.81
127.38
124.19
122.49
120.89
120.64
110.36
7j
150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110
f1 (ppm)

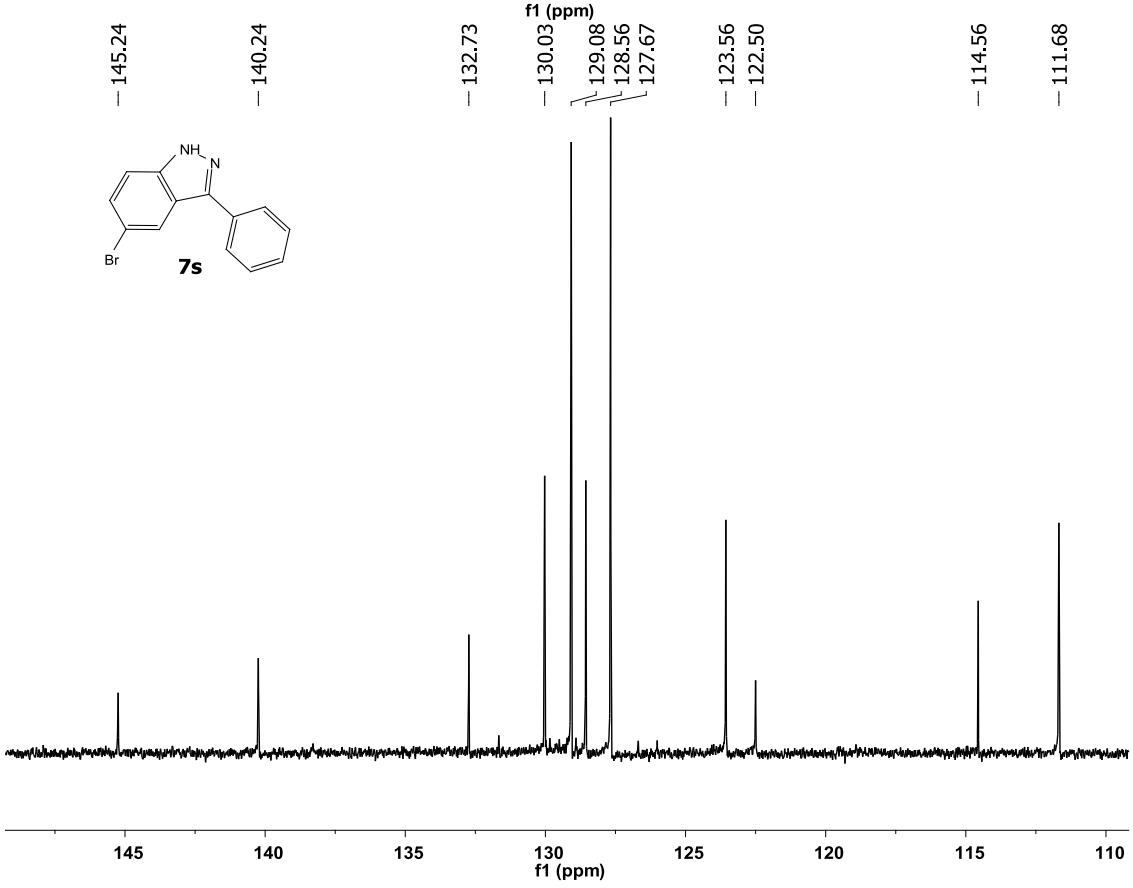

7.996
7.980
7.940
7.923
7.502
7.485
7.434
7.260
NH
N
Cl
7k
1.00
2.08
2.02
2.19
1.30
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
f1 (ppm)

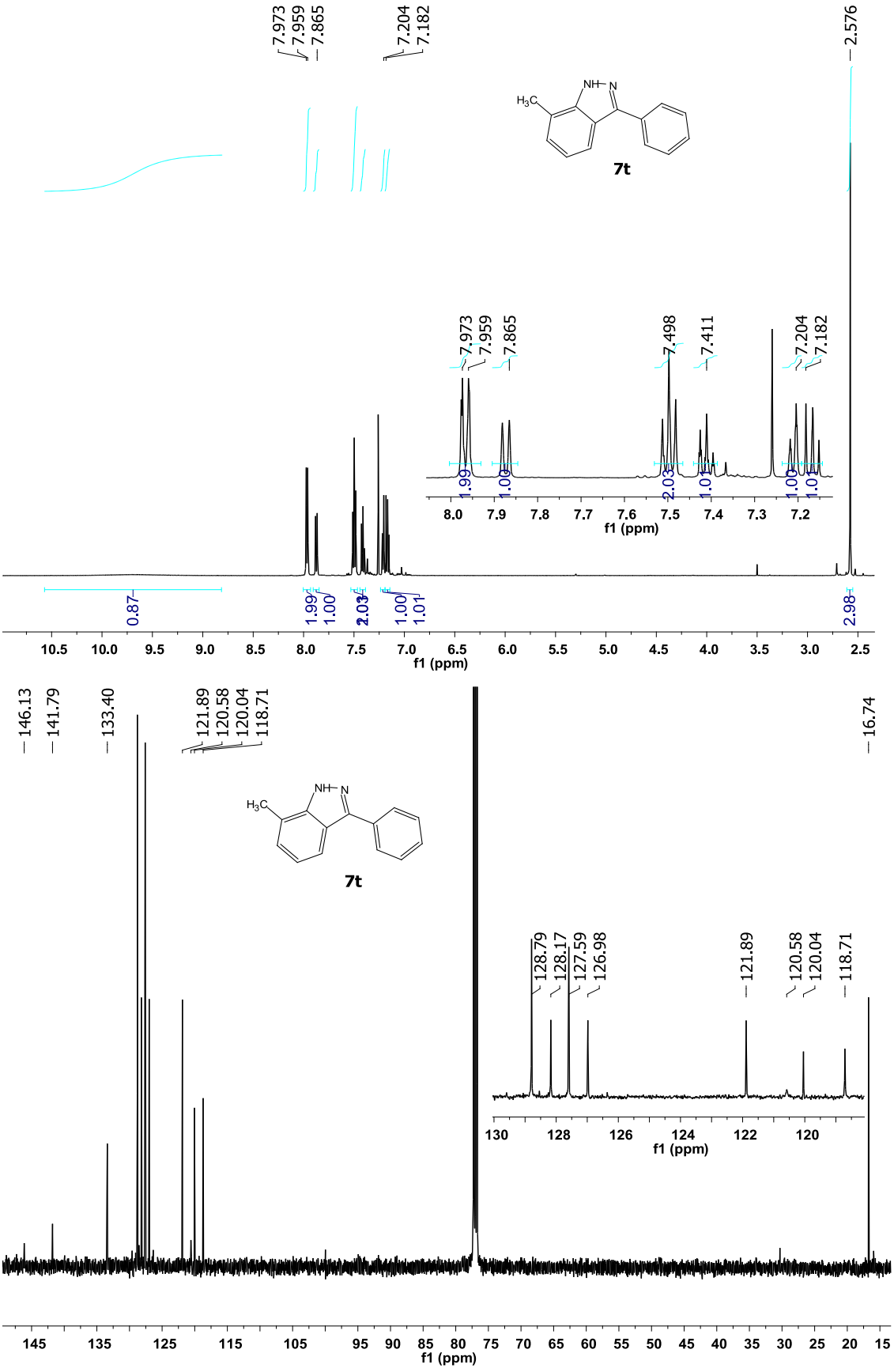

144.60
141.63
134.13
131.87
129.09
127.10
121.73
120.90
120.78
110.19
NH
N
Cl
7k
47
143
139
135
131
127
123
119
115
111
f1 (ppm)


7.979
7.965
7.545
7.341
7.337
7.179
7.070
7.066
3.886
NH
N
O
CH3
7p
0.64
1.95
1.96
1.00
1.00
0.97
0.98
2.95
f1 (ppm)


155.19
145.04
137.55
133.69
128.94
121.15
119.06
111.23
100.28
55.78
NH
N
O
CH3
7p
f1 (ppm)


8.149
8.146
7.929
7.546
7.421
7.109
7.092
NH
N
Br
7s
1.34
1.00
2.06
2.04
1.10
1.18
1.02
13.2
12.6
12.0
11.4
10.8
10.2
9.6
9.2
8.8
8.4
8.0
7.6
7.2
f1 (ppm)


145.24
140.24
132.73
130.03
129.08
128.56
127.67
123.56
122.50
114.56
111.68
NH
N
Br
7s
145
140
135
130
125
120
115
110
f1 (ppm)


7.973
7.959
7.865
7.204
7.182
2.576
7t
7.498
7.411
0.87
1.99
1.00
2.03
1.00
1.01
2.98
f1 (ppm)
146.13
141.79
133.40
121.89
120.58
120.04
118.71
16.74
128.79
128.17
127.59
126.98