Supporting Information

CuO nanoparticles catalysed synthesis of 2*H*-indazoles under a ligand free condition

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Experimental:

General information:

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60–120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H NMR (400 MHz) $CDCl_3$ solvent as the internal standard for ^{13}C NMR (100 MHz). Elemental analysis was performed with a Perkin Elmer 2400 elemental analyzer. IR spectra were recorded in KBr or neat on a Nicolet Impact 410 spectrophotometer. Commercially available CuO nano (<50 nm) were purchased from Sigma-Aldrich.

Crystallographic Analysis: Crystal data were collected with Bruker Smart Apex-II CCD diffractometer using graphite by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 298 K. Cell parameters were retrieved using SMART [1]USA, 1995 software and refined with SAINT[1] for all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentzian and polarization effects. Absorption corrections were applied with the SADABS program[2].The structures were solved by direct methods implemented in the SHELX-97[3] program and refined by full-matrix least-squares methods on F^2. All non-hydrogen atom positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. The crystals were isolated in rectangular shape from ethyl acetate and hexane mixture at room temperature.

References

1. SMART, SAINT and XPREP, Siemens Analytical X-ray Instruments Inc., Madison,Wisconsin.
2. G. M. Sheldrick, *SADABS: Empirical Absorption and Correction Software*, University of Gottingen, Institut fur Anorganische Chemieder Universitat, Tammanstrasse 4, D-3400 Gottingen, Germany, 1999–2003.
3. G. M. Sheldrick, SHELXS-97, University of Gottingen, Germany, 1997.

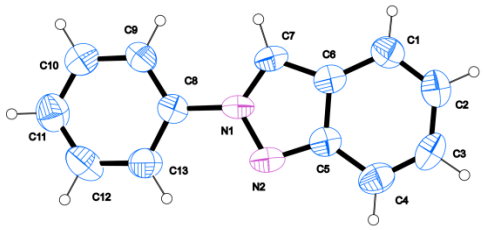
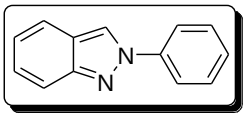


Figure 1. ORTEP views of 2-Phenyl-2H-indazole (**1a**)

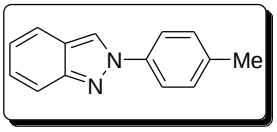
Crystallographic description of 2-Phenyl-2H-indazole (**1a**): $C_{13}H_{10}N_2$, crystal dimension 0.41 x 0.35 x 0.22 mm, M_r = 194.23, Monoclinic, Space group 'C c', a = 5.9752(9) Å, b = 25.124(4) Å, c = 13.8320(17) Å, α = 90.00, β = 97.080(9), γ = 90.00, V = 2060.6(5) Å^3, Z = 8, ρ_{calcd} = 1.252 mg/m^3, μ = 0.076 mm^{-1}, F(000) = 816.0, reflection collected / unique = 5146 / 2204, refinement method = full-matrix least-squares on F^2, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0681, wR_2 = 0.2066, R indices (all data): R_1(all) = 0.1370, wR_2(all) = 0.2543, goodness of fit = 1.009. CCDC-961653 (for 2-phenyl-2H-indazole **(1a)**) contains the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

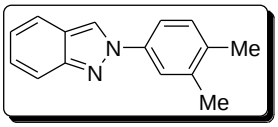
SPECTRAL DATA



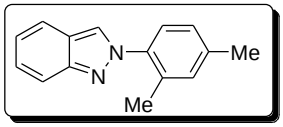
2-Phenyl-2H-indazole (**1a**): White solid; M.p. 81.5-83.5 ^{o}C (lit.[4] 80-82 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.11 (t, 1H, *J* = 7.6 Hz), 7.32 (t, 1H, *J* = 7.6 Hz), 7.39 (t, 1H, *J* = 7.2 Hz), 7.49-7.53 (m, 2H), 7.69 (d, 1H, *J* = 8.8 Hz), 7.79 (d, 1H, *J* = 8.8 Hz), 7.89 (d, 2H, *J* = 7.6 Hz), 8.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 118.1, 120.6, 121.2, 122.6, 122.9, 127.0, 128.1, 129.7, 140.7, 149.9; IR (KBr): 3126, 2923, 1624, 1593, 1517, 1493, 1378, 1311, 1198, 1072, 1044, 944, 753 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{10}N_2$ (194.2315): C 80.39, H 5.19, N 14.42; found C 80.47, H 5.12, N 14.35.



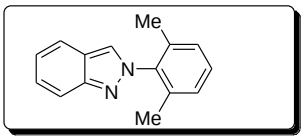
2-*p*-Tolyl-2H-indazole (**1b**): Yellow solid; M.p. 100-103 ^{o}C (lit.[5]101-103 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.41 (s, 3H), 7.09 (t, 1H, *J* = 7.6 Hz), 7.29-7.33 (m, 3H), 7.69 (d, 1H, *J* = 8.4 Hz), 7.76-7.80 (m, 3H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 21.2, 118.1, 120.5, 121.1, 122.5, 122.9, 126.8, 130.3, 138.1, 138.5, 149.9; IR (KBr): 3038, 2920, 2857, 1624, 1522, 1451, 1378, 1347, 1196, 1108, 1047, 822, 792, 757, 739 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{12}N_2$ (208.2580): C 80.74, H 5.81, N 13.45; found C 80.81, H 5.89, N 13.39.



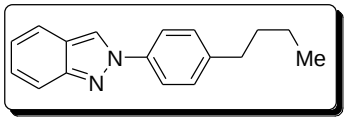
2-(3,4-Dimethylphenyl)-2H-indazole (**1c**): Brown solid; M.p. 117-119 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.33 (s, 3H), 2.37 (s, 3H), 7.11 (t, 1H, *J* = 8 Hz), 7.26 (s, 1H), 7.29-7.33 (m, 1H), 7.58 (d, 1H, *J* = 8 Hz), 7.70 (d, 2H, *J* = 8.4 Hz), 7.79 (d, 1H, *J* = 8.8 Hz), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 19.5, 20.0, 117.9, 118.2, 120.4, 122.2, 122.3, 122.8, 126.7, 130.6, 136.6, 138.2, 138.5, 149.7; IR (KBr): 2925, 2851, 1611, 1517, 1500, 1465, 1448, 1379, 1129, 1056, 882, 816, 776, 757 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{14}N_2$ (222.2845): C 81.05, H 6.35, N 12.60; found C 81.13, H 6.31, N 12.53.



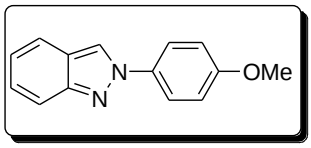
2-(2,4-Dimethylphenyl)-2H-indazole (**1d**): Liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.18 (s, 3H), 2.39 (s, 3H), 7.10-7.16 (m, 3H), 7.28-7.34 (m, 2H), 7.72 (d, 1H, *J* = 8.4 Hz), 7.78 (d, 1H, *J* = 8.8 Hz), 8.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 17.8, 21.2, 117.9, 120.4, 122.0, 122.1, 124.5, 126.3, 126.4, 127.2, 131.9, 133.5, 138.0, 139.1, 149.3; IR (KBr): 3059, 2922, 1627, 1520, 1505, 1386, 1349, 1198, 1146, 1129, 1042, 819, 784, 756 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{14}N_2$ (222.2845): C 81.05, H 6.35, N 12.60; found C 81.15, H 6.39, N 12.53.



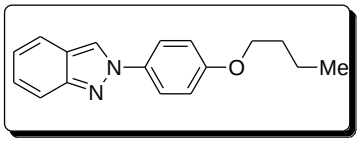
2-(2,6-Dimethylphenyl)-2H-indazole (**1e**): Semi-solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.99 (s, 6H), 7.13-7.19 (m, 3H), 7.30 (d, 1H, *J* = 8 Hz), 7.35 (t, 1H, *J* = 7.6 Hz), 7.76 (d, 1H, *J* = 8.8 Hz), 7.81 (d, 1H, *J* = 9.2 Hz), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 17.3, 118.2, 120.5, 121.9, 122.2, 124.6, 126.3, 128.3, 129.5, 135.7, 139.9, 149.3; IR (KBr): 2922, 2853, 1624, 1515, 1482, 1376, 1267, 1184, 1095, 1045, 954, 791, 763 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{14}N_2$ (222.2845): C 81.05, H 6.35, N 12.60; found C 81.11, H 6.38, N 12.54.



2-(4-Butylphenyl)-2H-indazole (**1f**): Yellow solid; M.p. 64-65 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.89-0.98 (m, 3H), 1.33-1.39 (m, 2H), 1.58-1.66 (m, 2H), 2.66 (t, 2H, *J* = 8.0 Hz), 7.09 (t, 1H, *J* = 8.0 Hz), 7.30 (d, 3H, *J* = 8.4 Hz), 7.68 (dd, 1H, J_1 = 1.2 Hz, J_2 = 8.4 Hz), 7.77 (d, 3H, *J* = 8.8 Hz), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 13.9, 22.3, 33.5, 35.1, 117.9, 120.3, 120.4, 120.8, 122.3, 122.8, 126.7, 129.4, 138.4, 142.9, 149.7; IR (KBr): 2955, 2925, 2854, 1626, 1520, 1466, 1430, 1383, 1349, 1208, 1121, 1047, 815, 780, 754 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{18}N_2$ (250.3375): C 81.56, H 7.25, N 11.19; found C 81.63, H 7.29, N 11.13.

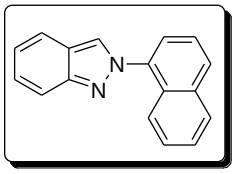


2-(4-Methoxyphenyl)-2H-indazole (**1g**): Brown solid; M.p. 130-132 ^{o}C (lit.[5] 130-132 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.84 (s, 3H), 6.99 (d, 2H, *J* = 8.8 Hz), 7.07-7.11 (m, 1H), 7.28-7.32 (m, 1H), 7.67 (d, 1H, *J* = 8.4 Hz), 7.77 (d, 3H, *J* = 8.8 Hz), 8.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 55.5, 114.6, 117.7, 120.3, 120.4, 122.19, 122.24, 122.7, 126.6, 134.0, 149.6, 159.2; IR (KBr): 3137, 2958, 2836, 1610, 1520, 1440, 1382, 1303, 1245, 1207, 1177, 1029, 837, 810, 754 cm^{-1}; Elemental analysis calcd (%) for $C_{14}H_{12}N_2O$ (224.2574): C 74.98, H 5.39, N 12.49; found C 75.05, H 5.33, N 12.43.

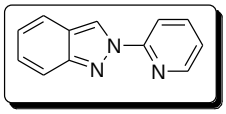


2-(4-Butoxyphenyl)-2H-indazole (**1h**): Yellow solid; M.p. 103-105 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.99 (t, 3H, *J* = 7.6 Hz), 1.52 (m, 2H), 1.80 (m, 2H), 4.02 (t, 2H, *J* = 6.8 Hz), 7.02 (d, 2H, *J* = 9.2 Hz), 7.11 (t, 1H, *J* = 7.6 Hz), 7.31 (t, 1H, *J* = 8.8 Hz), 7.70 (d, 1H, *J* = 8.4

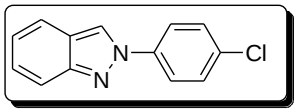
Hz), 7.78 (d, 3H, *J* = 9.2 Hz), 8.32 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 13.9, 19.3, 31.4, 68.2, 115.3, 117.8, 120.4, 122.3, 122.4, 122.8, 126.6, 133.9, 149.7, 158.9; IR (KBr): 2954, 2937, 2870, 1609, 1521, 1382, 1306, 1303, 1246, 1180, 1110, 1047, 1009, 837, 780, 753 cm^{-1}; Elemental analysis calcd (%) for $C_{17}H_{18}N_2O$ (266.3369): C 76.66, H 6.81, N 10.52; found C 76.74, H 6.78, N 10.45.



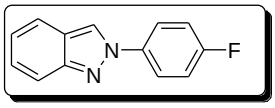
2-(Naphthalen-1-yl)-2H-indazole (**1i**): Liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.17 (t, 1H, *J* = 8.4 Hz), 7.37 (t, 1H, *J* = 8 Hz), 7.48 (t, 1H, *J* = 8.4 Hz), 7.55-7.59 (m, 2H), 7.65 (d, 1H, *J* = 7.2 Hz), 7.72 (d, 1H, *J* = 8.4 Hz), 7.78 (d, 1H, *J* = 8.6 Hz), 7.84 (d, 1H, *J* = 8.8 Hz), 7.94 (d, 1H, *J* = 8 Hz), 7.99 (d, 1H, *J* = 8.4 Hz), 8.29 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 118.2, 120.5, 122.2, 122.5, 123.2, 124.0, 125.1, 125.6, 126.8, 127.0, 127.8, 128.3, 129.2, 129.9, 134.3, 137.8, 149.8; IR (KBr): 3057, 2924, 2853, 1627, 1597, 1519, 1474, 1416, 1385, 1277, 1214, 1128, 1111, 1020, 939, 757, 733 cm^{-1}; Elemental analysis calcd (%) for $C_{17}H_{12}N_2$ (244.2901): C 83.58, H 4.95, N 11.47; found C 83.67, H 4.91, N 11.41.



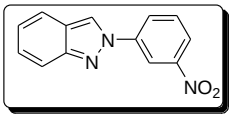
2-(Pyridin-2-yl)-2H-indazole (**1j**): Yellow solid; M.p. 106-108 ^{o}C (lit.[7]103-104 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.09 (t, 1H, *J* = 7.6 Hz), 7.28-7.34 (m, 2H), 7.74 (t, 2H, *J* = 8.8 Hz), 7.89 (t, 1H, *J* = 8.4 Hz), 8.29 (d, 1H, *J* = 8 Hz), 8.51 (d, 1H, *J* =4.8 Hz), 9.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 114.2, 118.2, 120.7, 121.3, 122.5, 122.8, 127.7, 138.9, 148.4, 150.4, 151.9; IR (KBr): 3148, 3059, 2924, 1590, 1573, 1518, 1476, 1434, 1376, 1250, 1198, 1139, 1053, 783, 761 cm^{-1}; Elemental analysis calcd (%) for $C_{12}H_9N_3$ (195.2196): C 73.83, H 4.65, N 21.52; found C 73.90, H 4.70, N 21.43.



2-(4-Chlorophenyl)-2H-indazole (**1k**): Yellowish-white solid; M.p. 137-139 ^{o}C (lit.[7] 138-140 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.10 (t, 1H, *J* = 7.2 Hz), 7.31 (t, 1H, *J* = 7.6 Hz), 7.47 (d, 2H, *J* = 8.8 Hz), 7.67 (d, 1H, *J* = 8.4 Hz), 7.75 (d, 1H, *J* = 8.8 Hz), 7.83 (d, 2H, *J* = 8.8 Hz), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 118.0, 120.4, 120.5, 122.0, 122.8, 123.0, 127.3, 129.8, 133.6, 139.1, 150.0; IR (KBr): 3131, 2962, 1628, 1518, 1495, 1423, 1382, 1204, 1093, 1046, 952, 825, 811, 778, 754, 727 cm^{-1}; Elemental analysis calcd (%) for $C_{13}H_9N_2Cl$ (228.6763): C 68.28, H 3.97, N 12.25; found C 68.37, H 3.92, N 12.17.

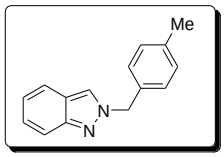


2-(4-Fluorophenyl)-2H-indazole (**1l**): Yellowish-white solid; M.p. 103-104 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.12 (t, 1H, *J* = 7.6 Hz), 7.21 (d, 1H, *J* = 8.4 Hz), 7.25 (d, 1H, *J* = 6.4 Hz), 7.33 (t, 1H, *J* = 7.6 Hz), 7.71 (d, 1H, *J* = 8.4 Hz), 7.78 (d, 1H, *J* = 8.8 Hz), 7.85-7.89 (m, 2H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 116.5 (d, $J_{C\text{-}F}$ = 22.1 Hz), 118.0, 120.6 (d, $J_{C\text{-}F}$ = 9.9 Hz), 122.7, 122.8, (d, $J_{C\text{-}F}$ = 8.4 Hz), 122.9, 127.1, 136.9, 149.9, 160.9, 163.4; IR (KBr): 3135, 2924, 1627, 1520, 1508, 1382, 1234, 1203, 1097, 1042, 951, 861, 839, 752, 779 cm^{-1}; Elemental analysis calcd (%) for $C_{13}H_9N_2F$ (212.2220): C 73.57, H 4.27, N 13.20; found C 73.66, H 4.33, N 13.12.

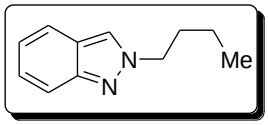


2-(3-Nitrophenyl)-2H-indazole (**1m**): Brown solid; M.p. 128-130 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.13 (t, 1H, *J* = 7.6 Hz), 7.34 (t, 1H, *J* = 8.8 Hz), 7.70 (d, 1H, *J* = 8 Hz), 7.75 (t, 2H, *J* = 8.8 Hz), 8.24 (d, 1H, *J* = 8 Hz), 8.32 (d, 1H, *J* = 8 Hz), 8.51 (s, 1H), 8.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 115.7, 118.3, 120.6, 120.7, 122.4, 123.4, 123.5, 126.4, 127.9, 130.8, 149.2, 150.5; IR (KBr): 2924, 2853, 1740, 1628, 1616, 1530, 1488, 1382, 1346, 1261,

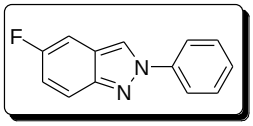
1099, 1045, 817, 802, 760, 734 cm^{-1}; Elemental analysis calcd (%) for $C_{13}H_9N_3O_2$ (239.2291): C 65.27, H 3.79, N 17.56; found C 65.33, H 3.82, N 17.49.



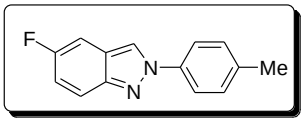
2-(4-Methylbenzyl)-2H-indazole (**1n**): Yellow solid; M.p. 80-82 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.33 (s, 3H), 5.54 (s, 2H), 7.06 (t, 1H, *J* = 7.2 Hz), 7.17 (q, 4H, *J* = 8 Hz), 7.25-7.28 (m, 1H), 7.60 (d, 1H, *J* = 8.4 Hz), 7.72 (d, 1H, *J* = 8.8 Hz), 7.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 21.3, 57.5, 117.7, 120.3, 121.8, 122.3, 122.8, 126.1, 128.3, 128.7, 129.8, 132.9, 138.4, 149.1; IR (KBr): 3119, 2921, 1623, 1512, 1465, 1440, 1421, 1385, 1350, 1136, 805, 791, 754, 729 cm^{-1}; Elemental analysis calcd (%) for $C_{15}H_{14}N_2$ (222.2845): C 81.05, H 6.35, N 12.60; found C 81.13, H 6.32, N 12.51.



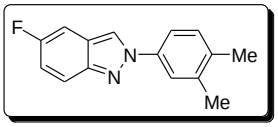
2-Butyl-2H-indazole (**1o**): Liquid; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.95 (t, 3H, *J* = 7.2 Hz), 1.35 (m, 2H), 1.99 (m, 2H), 4.41 (t, 2H, *J* = 7.2 Hz), 7.07 (t, 1H, *J* = 7.6 Hz), 7.25-7.29 (m, 1H), 7.64 (d, 1H, *J* = 7.6 Hz), 7.72 (d, 1H, *J* = 8.8 Hz), 7.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 13.7, 19.9, 32.7, 53.5, 117.4, 120.1, 121.6, 121.8, 122.7, 125.8, 148.8; IR (KBr): 3060, 2959, 2932, 2873, 1628, 1515, 1466, 1380, 1311, 1157, 1141, 1011, 907, 757 cm^{-1}; Elemental analysis calcd (%) for $C_{11}H_{14}N_2$ (174.2417): C 75.82, H 8.10, N 16.08; found C 75.88, H 8.08, N 15.98.



5-Fluoro-2-phenyl-2H-indazole (**2a**): Yellow solid; M.p. 135.5-137.5 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.12 (dt, 1H, J_1 = 2 Hz, J_2 = 8.0 Hz), 7.27 (d, 1H, J = 9.6 Hz), 7.41 (t, 1H, J = 7.6 Hz), 7.53 (t, 2H, J = 8.0 Hz), 7.75-7.81 (m, 1H), 7.88 (d, 2H, J = 8.4 Hz), 8.37 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 102.9 (d, J_{C-F} = 25.2 Hz), 118.6 (d, J_{C-F} = 29 Hz), 120.2 (d, J_{C-F} = 9.2 Hz), 120.6 (d, J_{C-F} = 9.2 Hz), 121.0, 122.2 (d, J_{C-F} = 12.2 Hz), 128.2, 129.8, 140.5, 147.4, 158.9 (d, J_{C-F} = 239.5 Hz); IR (KBr): 3129, 3035, 2924, 2853, 1683, 1595, 1523, 1504, 1460, 1408, 1329, 1228, 1215, 1147, 1123, 1073, 1053, 854 cm^{-1}; Elemental analysis calcd (%) for $C_{13}H_9N_2F$ (212.2220): C 73.57, H 4.27, N 13.20; found C 73.74, H 4.22, N 13.09.

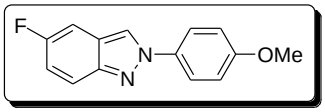


5-Fluoro-2-p-tolyl-2H-indazole (**2b**): Yellow solid; M.p. 139-141 ^{o}C (lit.[7] 140-142 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.43 (s, 3H), 7.12 (dt, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz), 7.26-7.29 (m, 1H), 7.32 (d, 2H, J = 8.0 Hz), 7.75 (d, 3H, J = 8.8 Hz), 8.33 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 21.1, 102.8 (d, J_{C-F} = 24.4 Hz), 118.4 (d, J_{C-F} = 29 Hz), 120.1 (d, J_{C-F} = 9.9 Hz), 120.5 (d, J_{C-F} = 7.7 Hz), 120.9, 122.1 (d, J_{C-F} = 12.2 Hz), 130.3, 138.2, 147.2, 158.8 (d, J_{C-F} = 239.5 Hz); IR (KBr): 3137, 3036, 2922, 1638, 1526, 1379, 1337, 1323, 1217, 1146, 1121, 1051, 830, 810, 762 cm^{-1}; Elemental analysis calcd (%) for $C_{14}H_{11}N_2F$ (226.2485): C 74.32, H 4.90, N 12.38; found C 74.42, H 4.95, N 12.30.

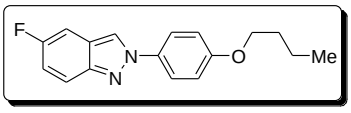


5-Fluoro-2-(3,4-dimethylphenyl)-2H-indazole (**2c**): Yellow solid; M.p. 105-106 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.32 (s, 3H), 2.36 (s, 3H), 7.11 (dt, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz), 7.25-7.28 (m, 2H), 7.54 (dd, 1H, J_1 = 2 Hz, J_2 = 8 Hz), 7.67 (s, 1H), 7.73-7.77 (m, 1H), 8.32 (s,

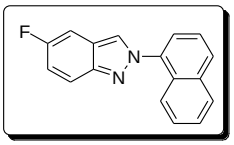
1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 19.4, 19.9, 102.8 (d, J_{C-F} = 24.4 Hz), 118.1, 118.4, 120.0 (d, J_{C-F} = 9.9 Hz), 120.5 (d, J_{C-F} = 8.4 Hz), 121.9, 122.1, 130.6, 136.8, 138.3, 138.4, 147.1, 158.7 (d, J_{C-F} = 238.7 Hz); IR (KBr): 3145, 2923, 1635, 1613, 1523, 1454, 1412, 1380, 1336, 1228, 1213, 1171, 1144, 1118, 1056, 850, 823, 805 cm^{-1}; Elemental analysis calcd (%) for $C_{15}H_{13}N_2F$ (240.2750): C 74.98, H 5.45, N 11.66; found C 75.06, H 5.49, N 11.57.



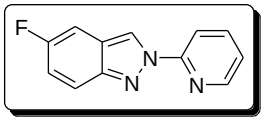
5-Fluoro-2-(4-methoxyphenyl)-2H-indazole (**2g**): Brown solid; M.p. 143-144 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.87 (s, 3H), 7.03 (d, 2H, J = 8.8 Hz), 7.11 (dt, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz), 7.25-7.28 (m, 1H), 7.70 (d, 3H, J = 8.8 Hz), 8.27 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 55.7, 102.8 (d, J_{C-F} = 24.4 Hz), 114.8, 118.2 (d, J_{C-F} = 29 Hz), 119.9 (d, J_{C-F} = 9.9 Hz), 120.5 (d, J_{C-F} = 8.4 Hz), 122.4, 134.1, 147.1, 158.7 (d, J_{C-F} = 238.7 Hz), 159.5; IR (KBr): 2960, 2932, 1609, 1522, 1511, 1450, 1435, 1337, 1298, 1249, 1219, 1145, 1027, 835, 814 cm^{-1}; Elemental analysis calcd (%) for $C_{14}H_{11}N_2OF$ (242.2479): C 69.41, H 4.58, N 11.56; found C 69.49, H 4.54, N 11.50.



2-(4-Butoxyphenyl)-5-fluoro-2H-indazole (**2h**): Yellow solid; M.p. 110-112 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.92 (t, 3H, J = 7.2 Hz), 1.44 (m, 2H), 1.73 (m, 2H), 3.94 (t, 2H, J = 6.8 Hz), 6.94 (d, 2H, J = 8.8 Hz), 7.04 (dt, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz), 7.18-7.20 (m, 1H), 7.68 (d, 3H, J = 8.8 Hz), 8.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 13.9, 19.3, 31.3, 68.1, 102.7 (d, J_{C-F} = 24.4 Hz), 115.1, 118.0 (d, J_{C-F} = 28.2 Hz), 119.8 (d, J_{C-F} = 9.9 Hz), 120.3 (d, J_{C-F} = 7.7 Hz), 122.1, 133.7, 146.9, 158.6 (d, J_{C-F} = 238.7 Hz), 158.9; IR (KBr): 3139, 2941, 2876, 1636, 1591, 1525, 1296, 1250, 1220, 1180, 1148, 1038, 1007, 836, 809, 768 cm^{-1}; Elemental analysis calcd (%) for $C_{17}H_{17}N_2OF$ (284.3274): C 71.81, H 6.03, N 9.85; found C 71.89, H 6.07, N 9.78.



5-Fluoro-2-(naphthalen-1-yl)-2H-indazole (**2i**): Yellowish-white solid; M.p. 120-122 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.19 (dt, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz), 7.34 (dd, 1H, J_1 = 2.0 Hz, J_2 = 7.2 Hz),7.48-7.59 (m, 3H), 7.63-7.65 (m, 1H), 7.71 (d, 1H, J = 8.4 Hz), 7.80-7.84 (m, 1H), 7.95 (d, 1H, J = 8.0 Hz), 7.99 (d, 1H, J = 8.4 Hz), 8.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 102.8 (d, J_{C-F} = 24.4 Hz), 118.4 (d, J_{C-F} = 29 Hz), 120.2 (d, J_{C-F} = 9.9 Hz), 121.4 (d, J_{C-F} = 11.4 Hz), 122.9, 123.9, 125.0, 125.7 (d, J_{C-F} = 8.4 Hz), 126.9, 127.8, 128.2, 128.9, 129.9, 134.2, 137.5, 147.1, 158.7 (d, J_{C-F} = 239.5 Hz); IR (KBr): 3058, 2924, 1634, 1595, 1522, 1420, 1387, 1227, 1175, 1147, 1120, 854, 798 cm^{-1}; Elemental analysis calcd (%) for $C_{17}H_{11}N_2F$ (262.2806): C 77.85, H 4.23, N 10.68; found C 77.93, H 4.29, N 10.60.



5-Fluoro-2-(pyridin-2-yl)-2H-indazole (**2j**): White solid; M.p. 133.5-135.5 (lit.[7] 129-130 ^{o}C) ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.11 (dt, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz), 7.26-7.30 (m, 2H), 7.69-7.73 (m, 1H), 7.88 (dt, 1H, J_1 = 2.0 Hz, J_2 = 8.4 Hz), 8.23 (d, 1H, J = 8.4 Hz), 8.49 (d, 1H, J = 4.8 Hz), 9.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 103.4 (d, J_{C-F} = 23.6 Hz), 114.1, 119.6 (d, J_{C-F} = 29 Hz), 120.4 (d, J_{C-F} = 9.1 Hz), 120.8 (d, J_{C-F} = 9.1 Hz), 121.8 (d, J_{C-F} = 12.2 Hz), 123.0, 139.0, 147.9, 148.5, 151.9, 158.9 (d, J_{C-F} = 241 Hz); IR (KBr): 3147, 2924, 1596, 1522, 1475, 1439, 1377, 1323, 1212, 1144, 1114, 1055, 863, 837, 808 cm^{-1}; Elemental analysis calcd (%) for $C_{12}H_8N_3F$ (213.2101): C 67.60, H 3.78, N 19.71; found C 67.68, H 3.82, N 19.62.

References

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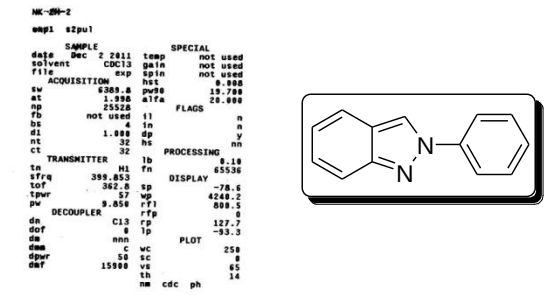
5. Y. Fang , C. Wu, R. C. Larock and Feng Shi, *J. Org. Chem.*, 2011, **76**, 8840.

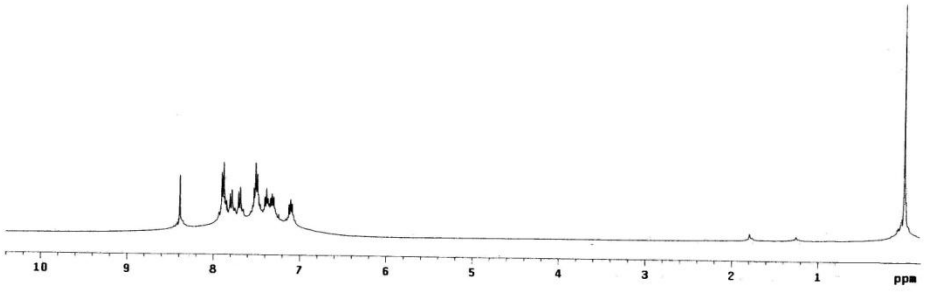
6. J. Hu, Y. Cheng, Y. Yang and Y. Rao, *Chem. Commun.*, 2011, **47**, 10133.

7. M. R. Kumar, A. Park, N. Park and S. Lee, *Org. Lett.*, **13**, 2542.

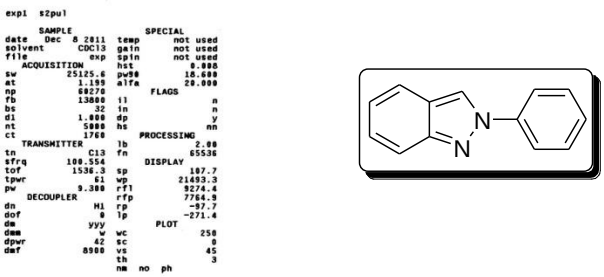
Spectra

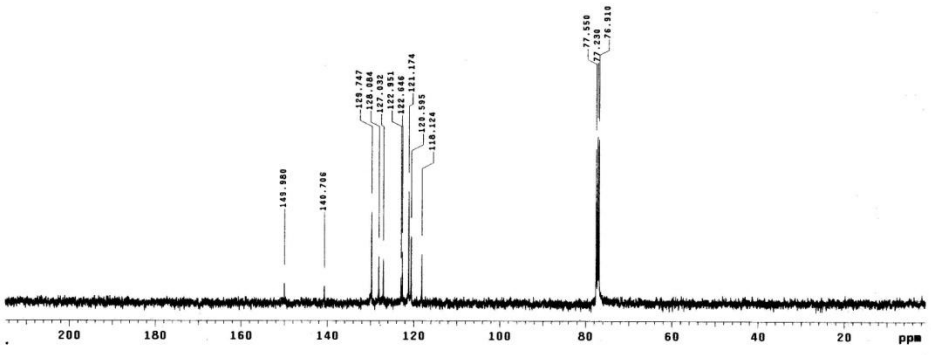
2-Phenyl-2H-indazole (1a): ^{1}H NMR (400 MHz, $CDCl_3$)



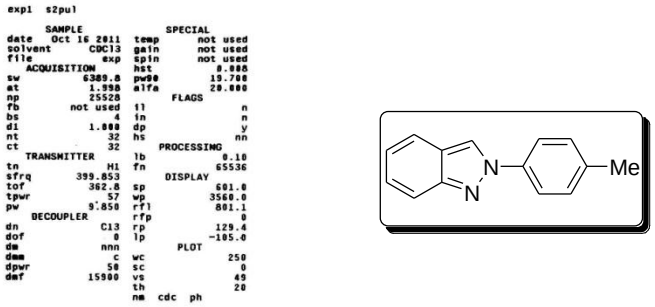


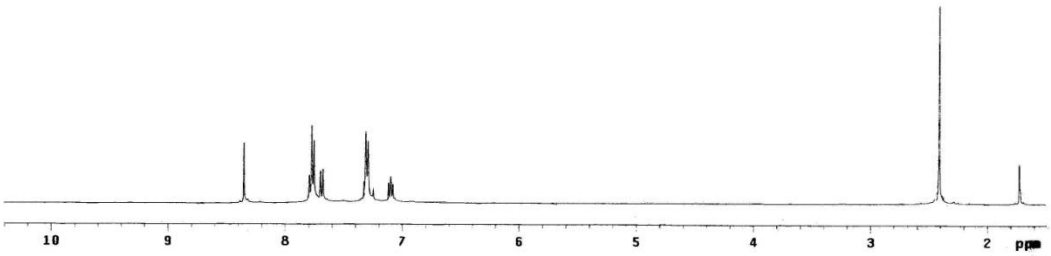
2-Phenyl-2H-indazole (1a): ^{13}C NMR (100 MHz, $CDCl_3$)



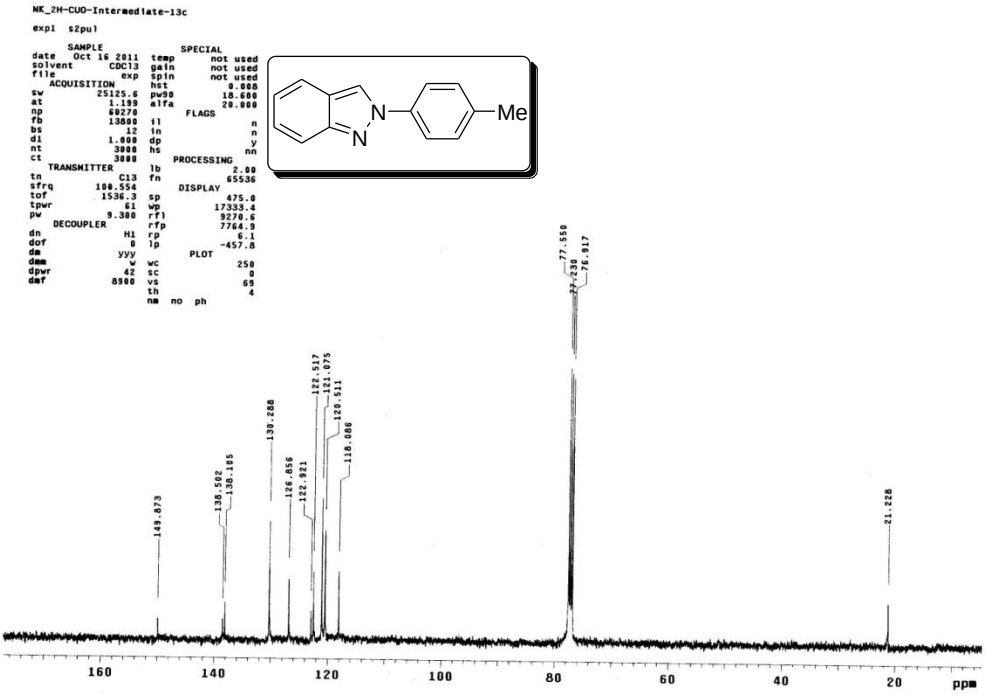


2-*p*-Tolyl-2H-indazole (1b): ^{1}H NMR (400 MHz, $CDCl_3$)

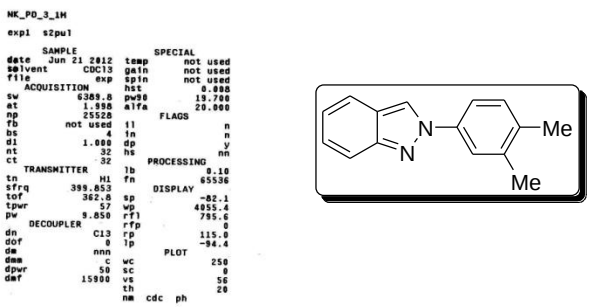


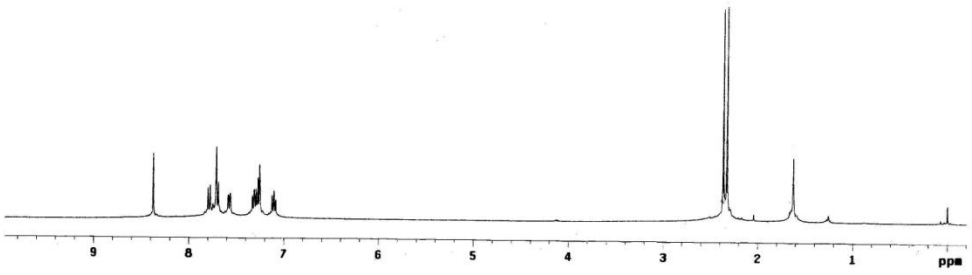


2-*p*-Tolyl-2H-indazole (1b): ^{13}C NMR (100 MHz, $CDCl_3$)

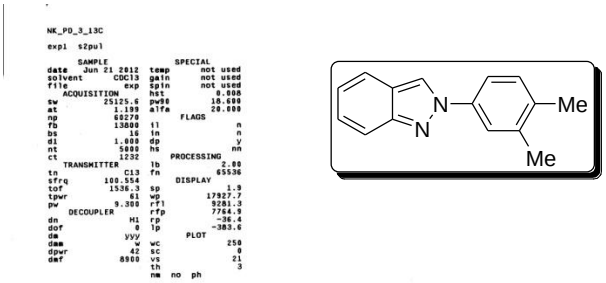


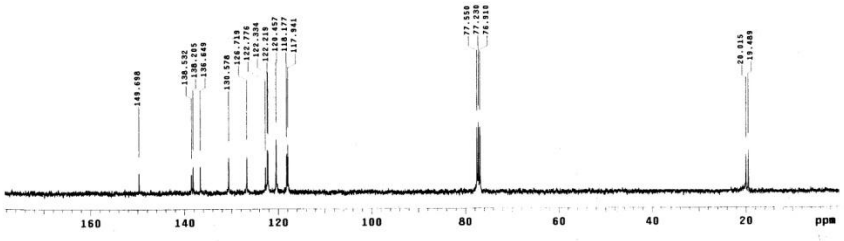
2-(3,4-Dimethylphenyl)-2H-indazole (1c): ^{1}H NMR (400 MHz, $CDCl_3$)



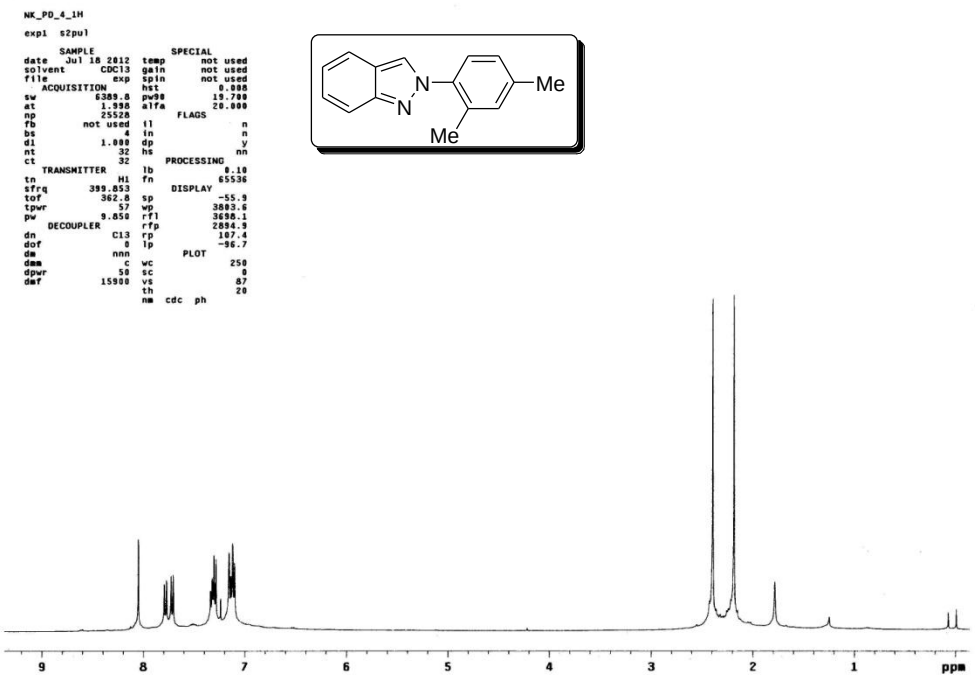


2-(3,4-Dimethylphenyl)-2H-indazole (1c): ^{13}C NMR (100 MHz, $CDCl_3$)

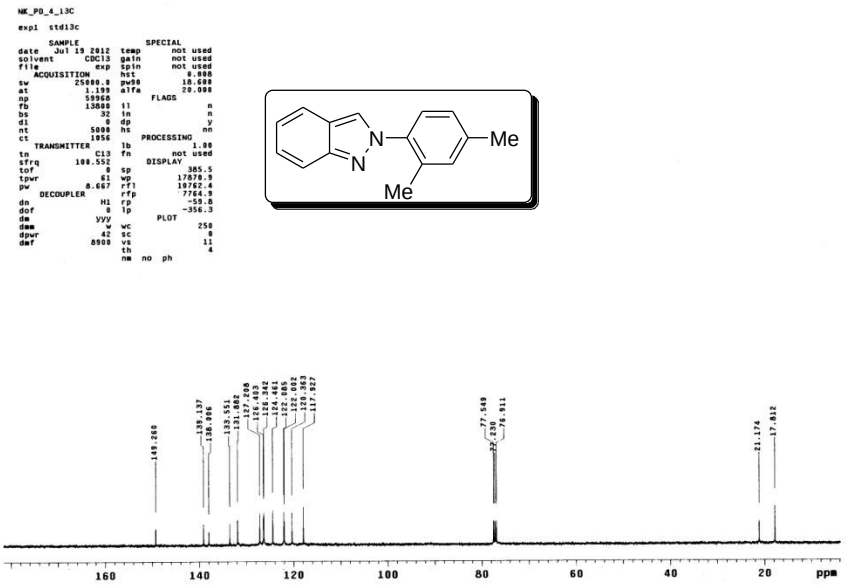




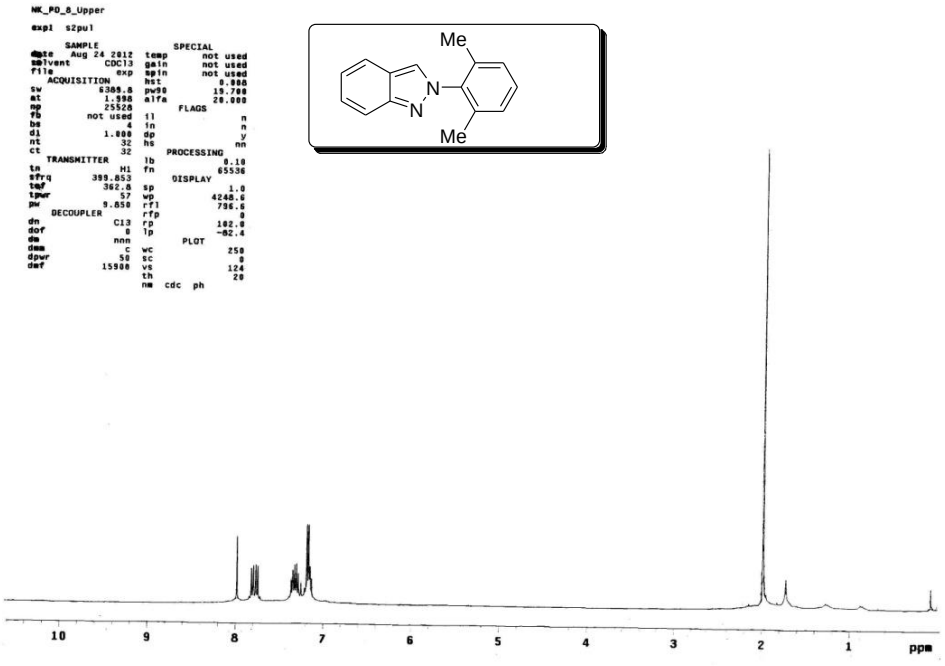
2-(2,4-Dimethylphenyl)-2H-indazole (1d): ^{1}H NMR (400 MHz, $CDCl_3$)



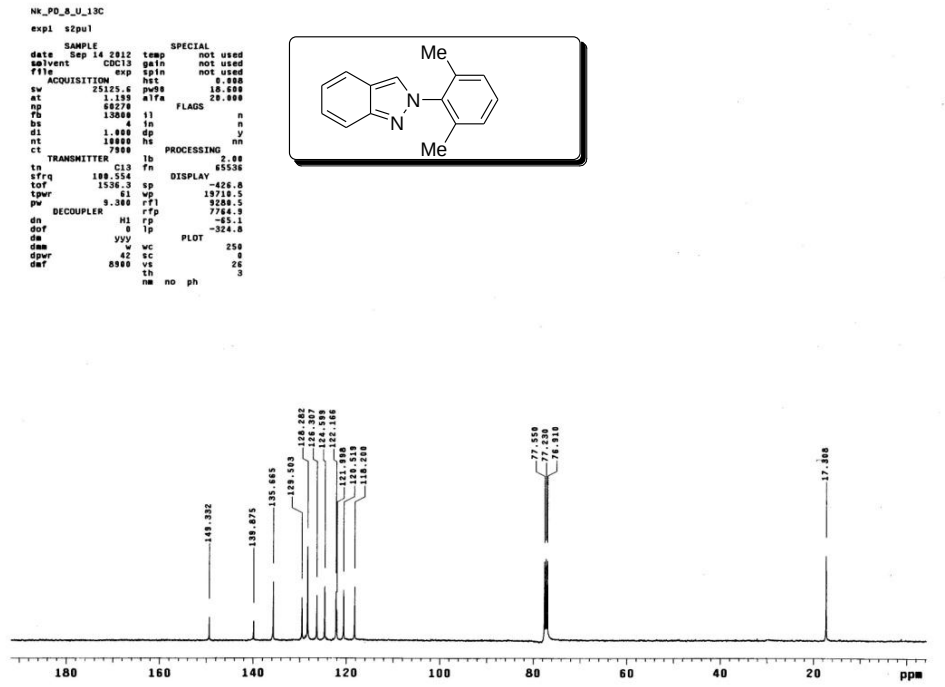
2-(2,4-Dimethylphenyl)-2H-indazole (1d): ^{13}C NMR (100 MHz, $CDCl_3$)



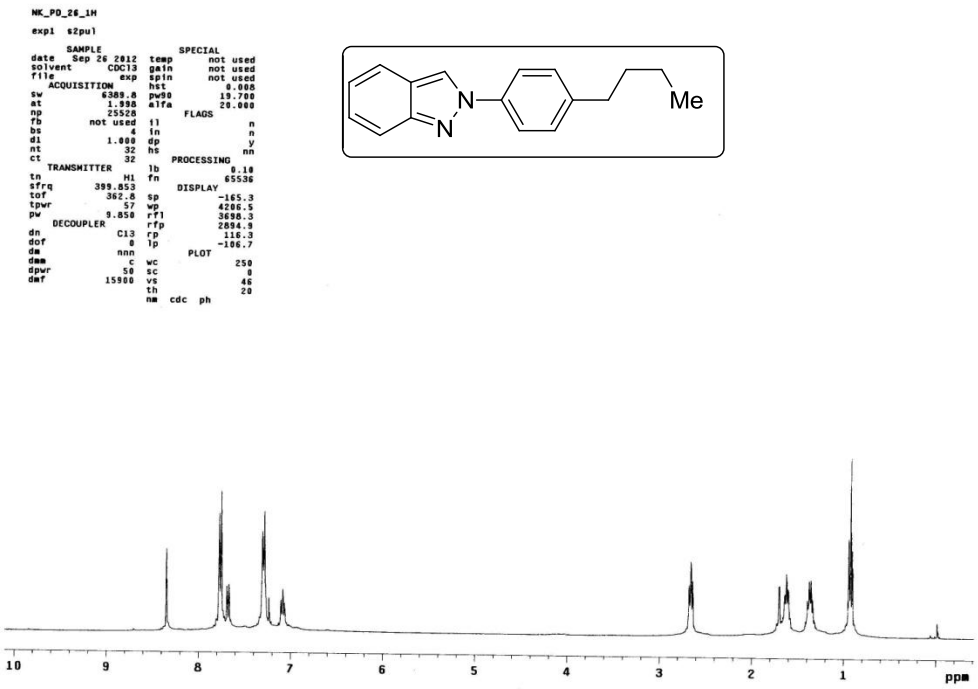
2-(2,6-Dimethylphenyl)-2H-indazole (1e): ^{1}H NMR (400 MHz, $CDCl_3$)



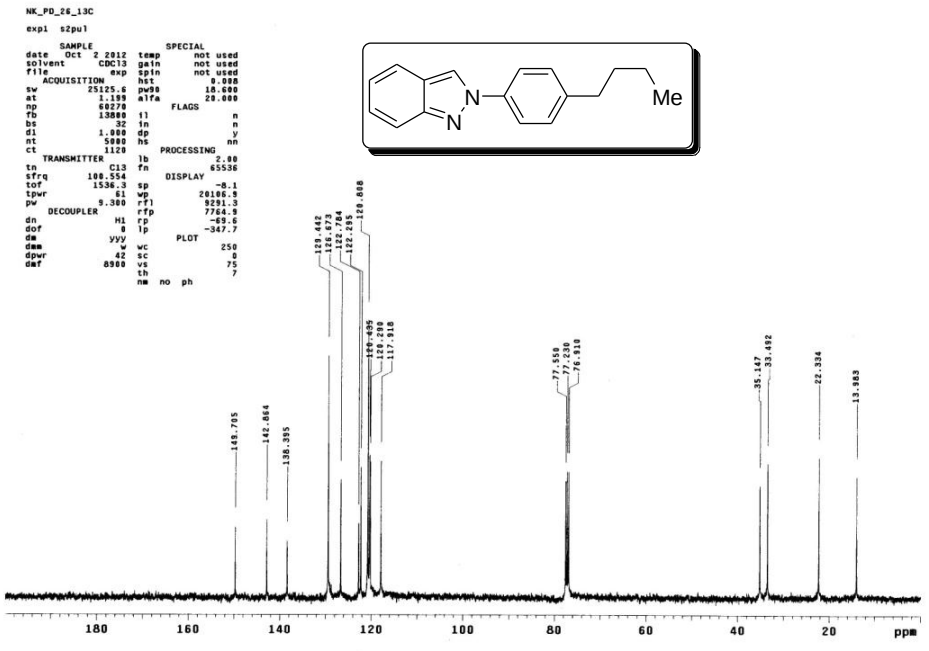
2-(2,6-Dimethylphenyl)-2H-indazole (1e): ^{13}C NMR (100 MHz, $CDCl_3$)



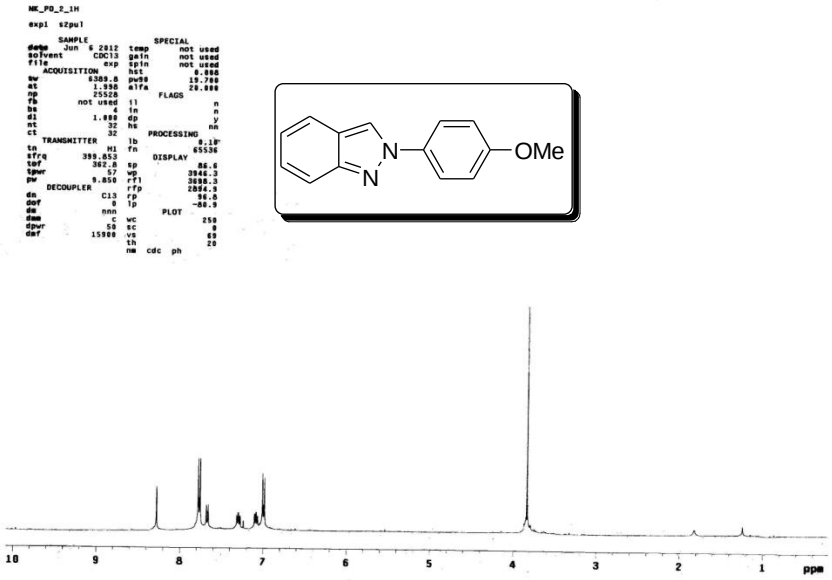
2-(4-Butylphenyl)-2H-indazole (1f): ^{1}H NMR (400 MHz, $CDCl_3$)



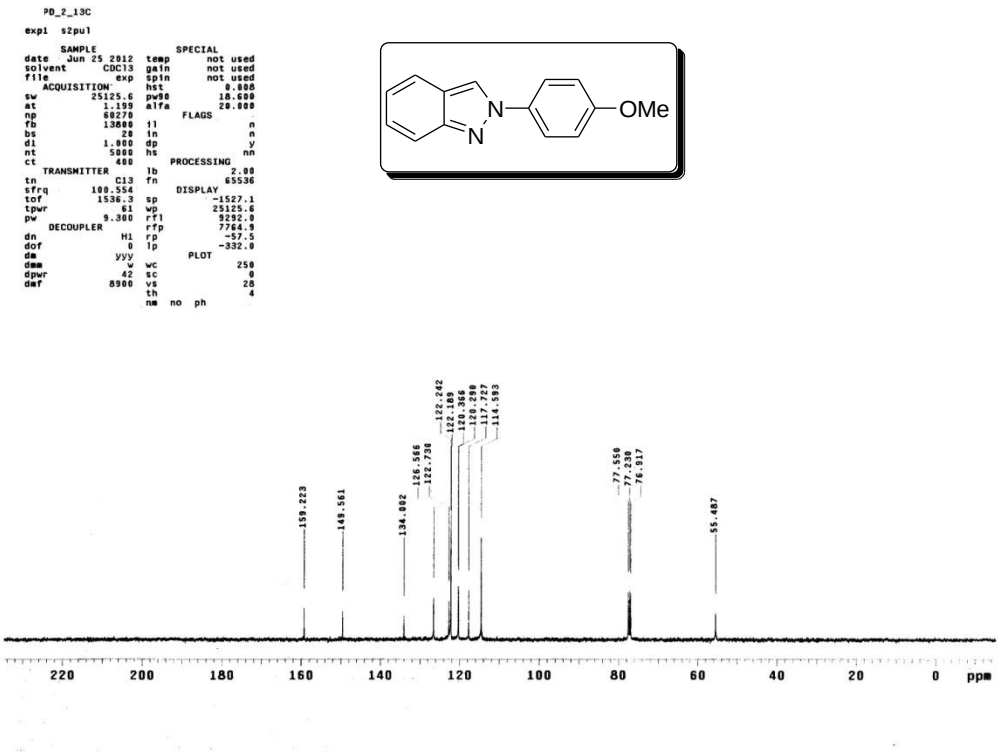
2-(4-Butylphenyl)-2H-indazole (1f): ^{13}C NMR (100 MHz, $CDCl_3$)



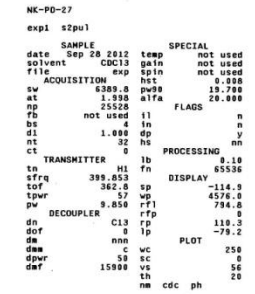
2-(4-Methoxyphenyl)-2H-indazole (1g): ^{1}H NMR (400 MHz, $CDCl_3$)

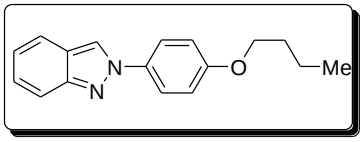


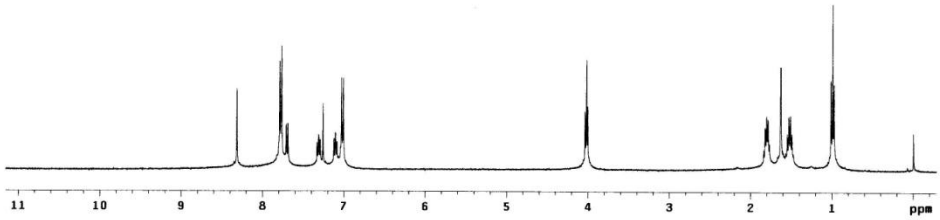
2-(4-Methoxyphenyl)-2H-indazole (1g): ^{13}C NMR (100 MHz, $CDCl_3$)



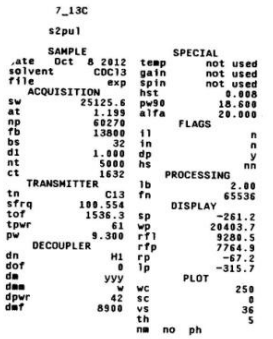
2-(4-Butoxyphenyl)-2H-indazole (1h): ^{1}H NMR (400 MHz, $CDCl_3$)

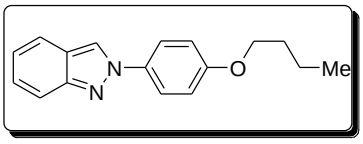


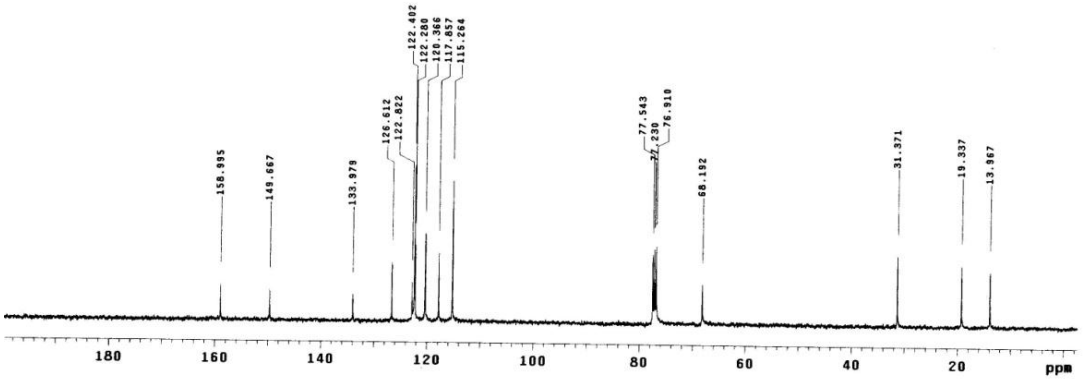




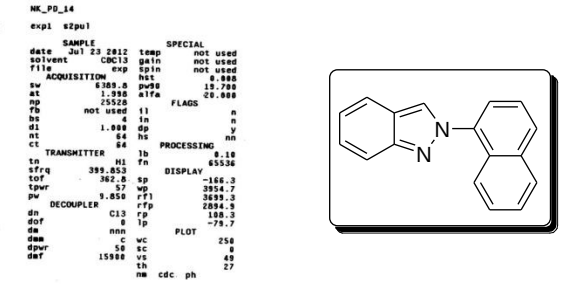
2-(4-Butoxyphenyl)-2H-indazole (1h): ^{13}C NMR (100 MHz, $CDCl_3$)

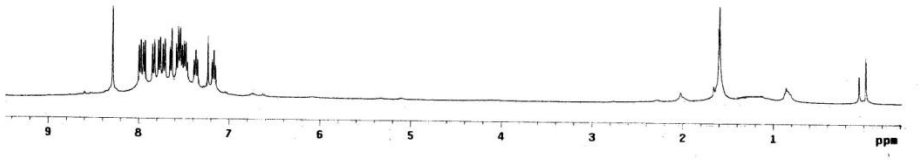




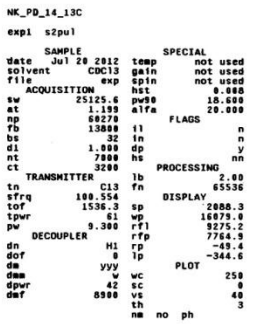


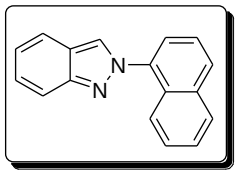
2-(Naphthalen-1-yl)-2H-indazole (1i): ^{1}H NMR (400 MHz, $CDCl_3$)

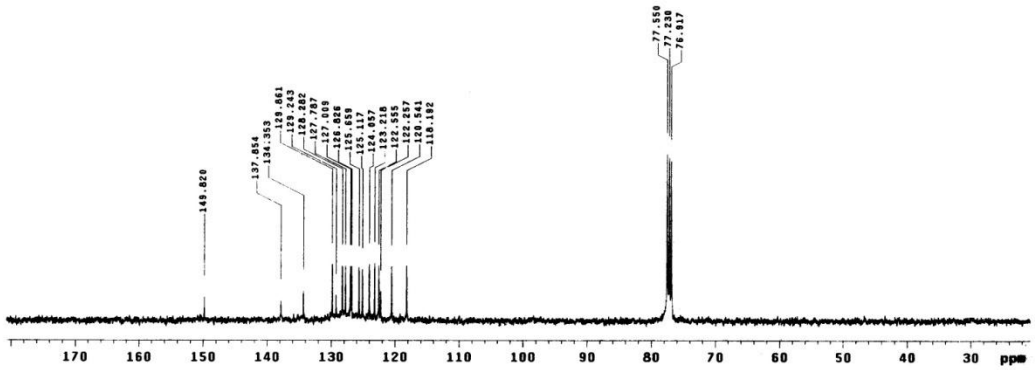




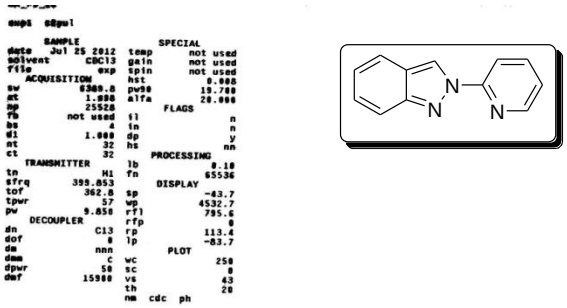
2-(Naphthalen-1-yl)-2H-indazole (1i): ^{13}C NMR (100 MHz, $CDCl_3$)

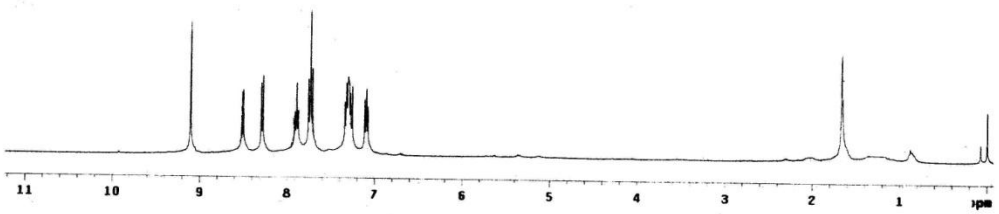




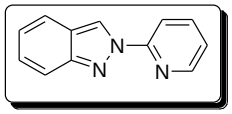


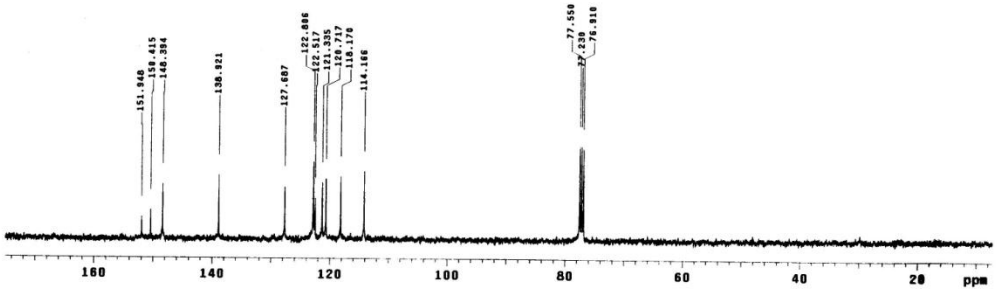
2-(Pyridin-2-yl)-2H-indazole (1j): ^{1}H NMR (400 MHz, $CDCl_3$)



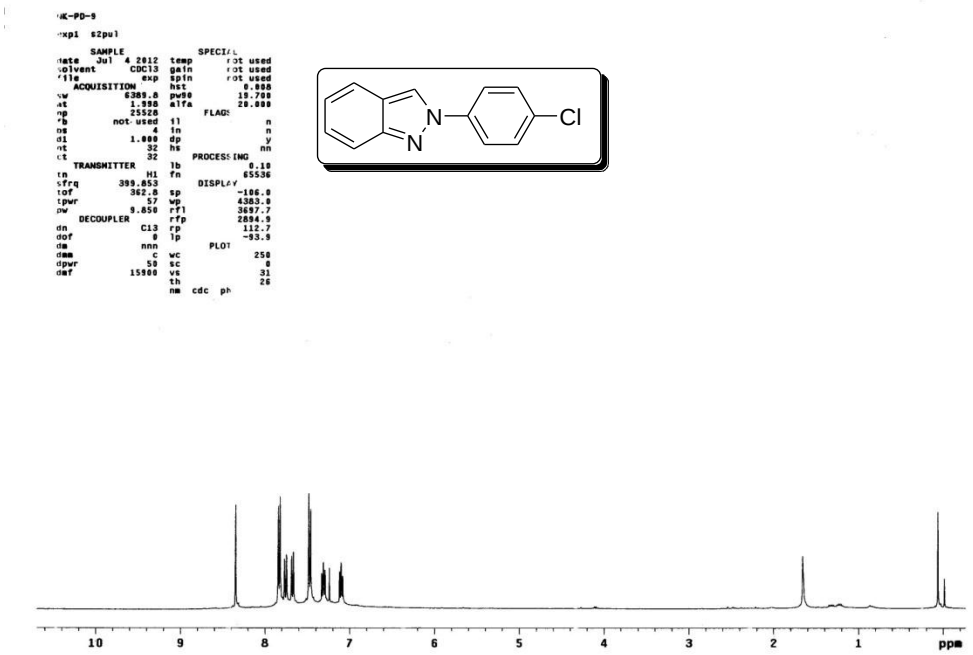


2-(Pyridin-2-yl)-2H-indazole (1j): ^{13}C NMR (100 MHz, $CDCl_3$)

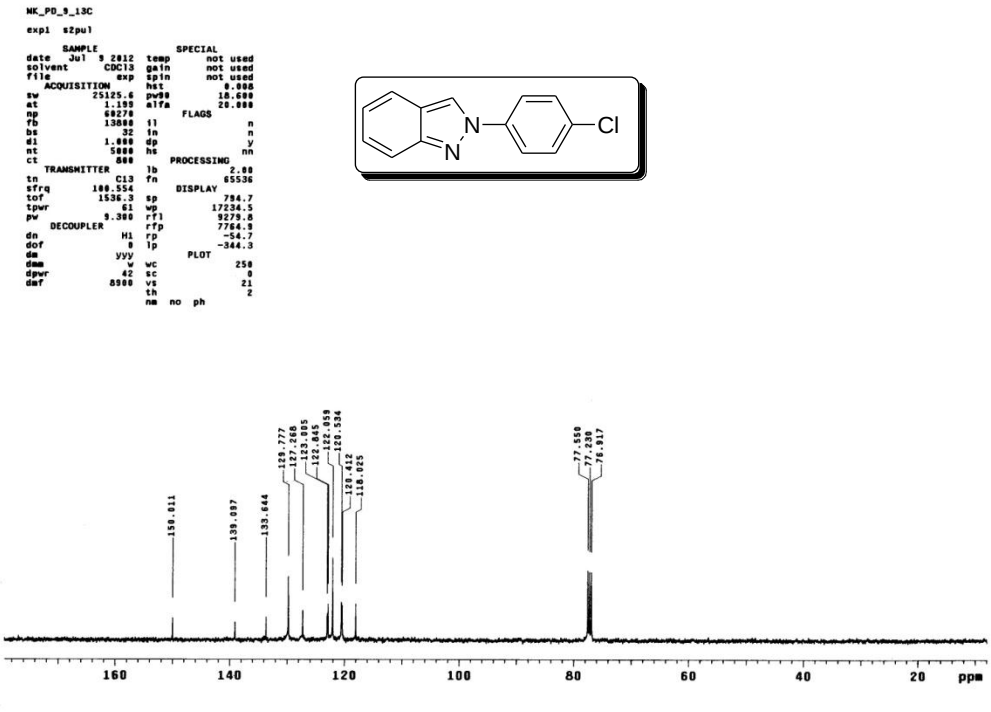




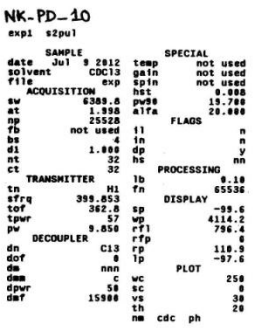
2-(4-Chlorophenyl)-2H-indazole (1k): ^{1}H NMR (400 MHz, $CDCl_3$)

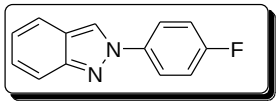


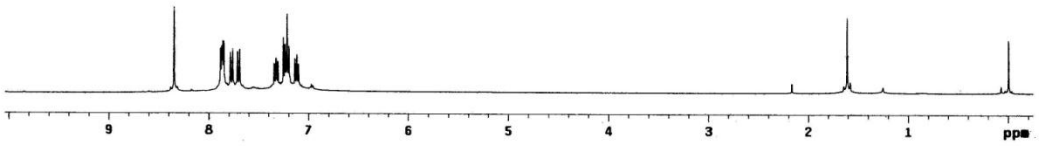
2-(4-Chlorophenyl)-2H-indazole (1k): ^{13}C NMR (100 MHz, $CDCl_3$)



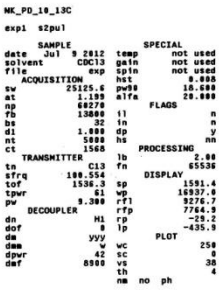
2-(4-Fluorophenyl)-2H-indazole (1l): ^{1}H NMR (400 MHz, $CDCl_3$)

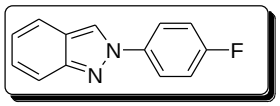


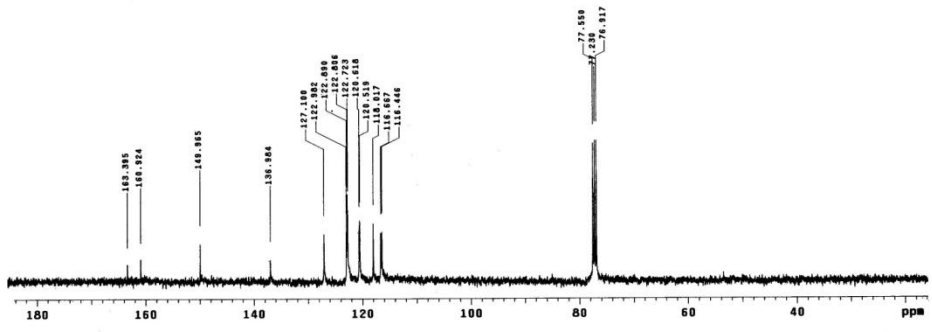




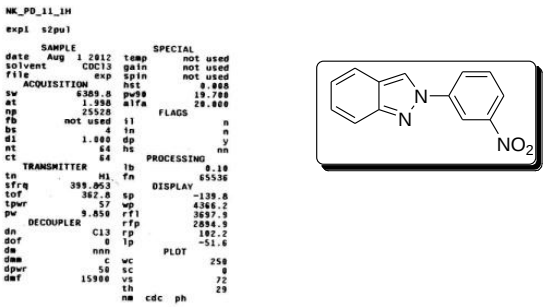
2-(4-Fluorophenyl)-2H-indazole (1l): ^{13}C NMR (100 MHz, $CDCl_3$)



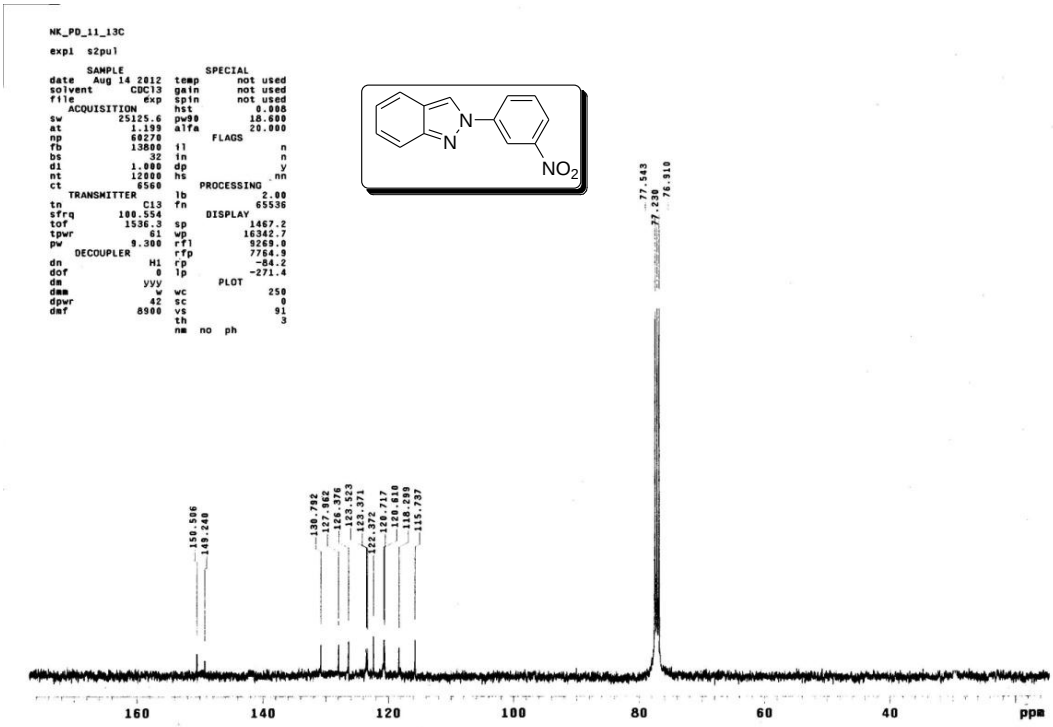




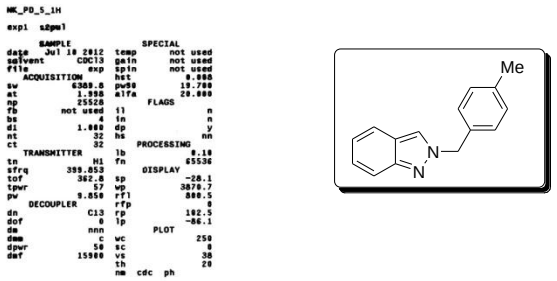
2-(3-Nitrophenyl)-2H-indazole (1m): ^{1}H NMR (400 MHz, $CDCl_3$)

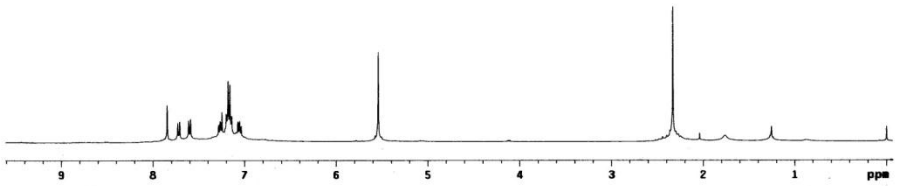


2-(3-Nitrophenyl)-2H-indazole (1m): ^{13}C NMR (100 MHz, $CDCl_3$)

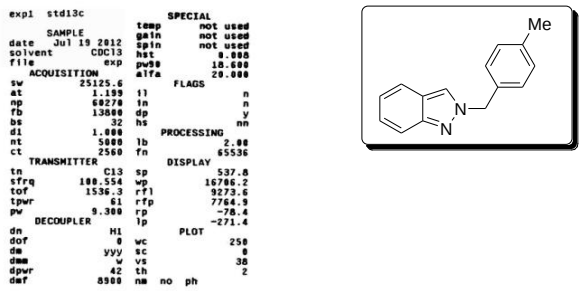


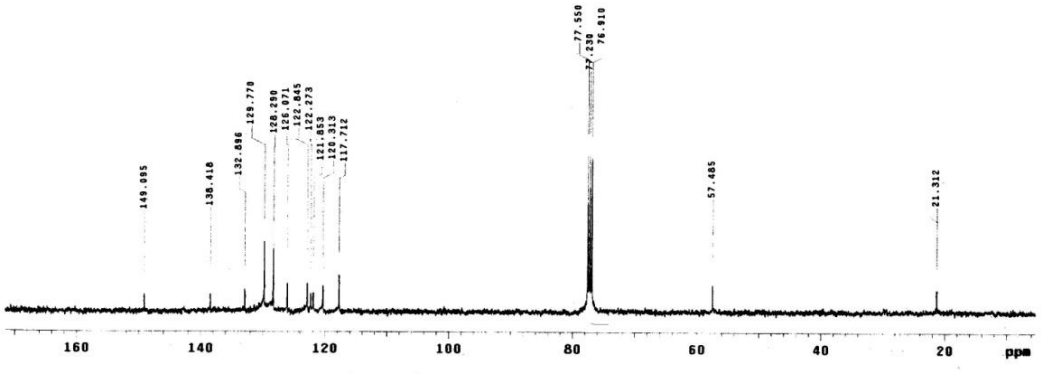
2-(4-Methylbenzyl)-2H-indazole (1n): ^{1}H NMR (400 MHz, $CDCl_3$)



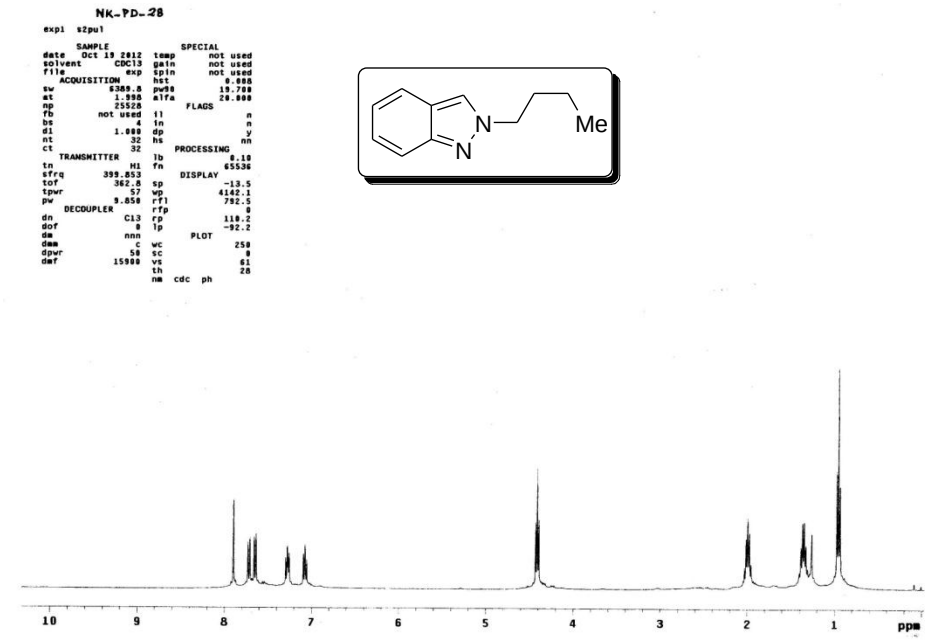


2-(4-Methylbenzyl)-2H-indazole (1n): ^{13}C NMR (100 MHz, $CDCl_3$)

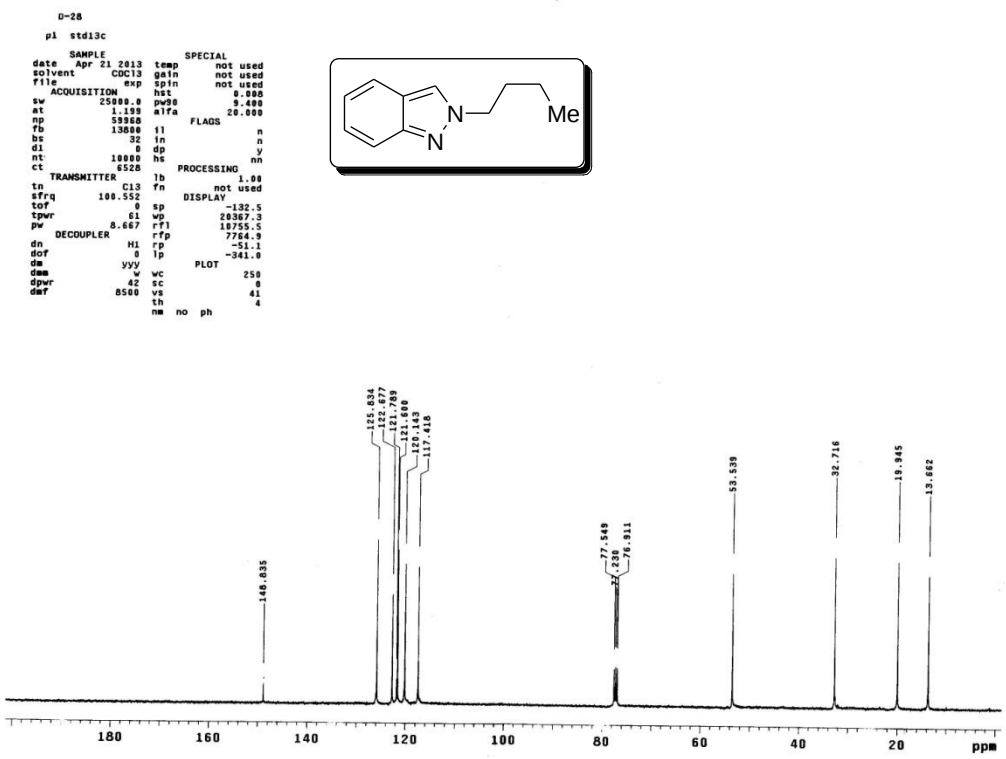




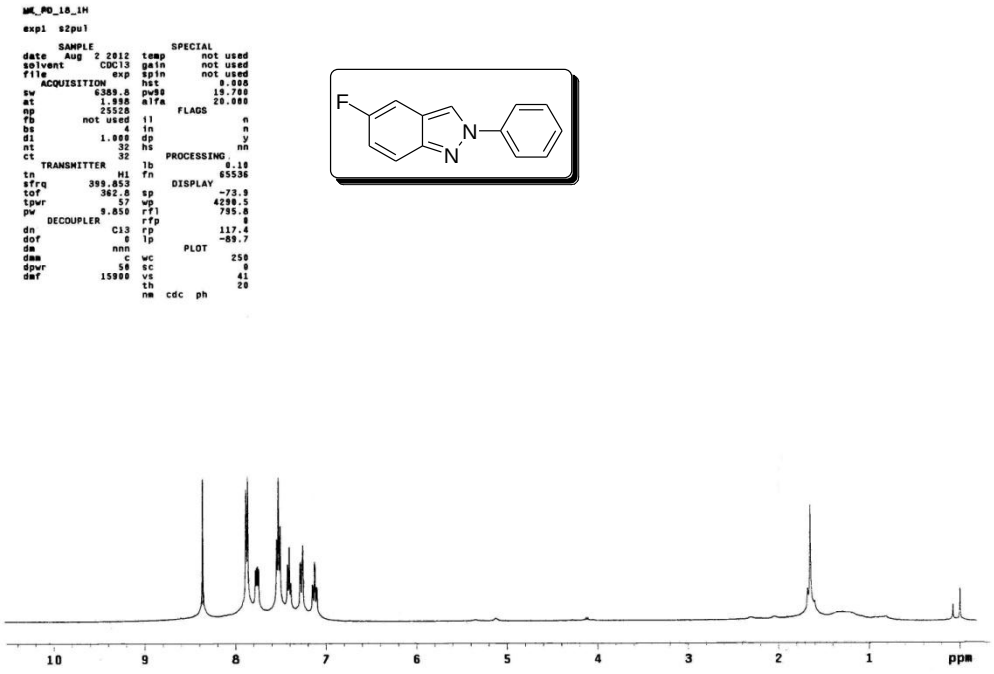
2-Butyl-2H-indazole (1o): ^{1}H NMR (400 MHz, $CDCl_3$)



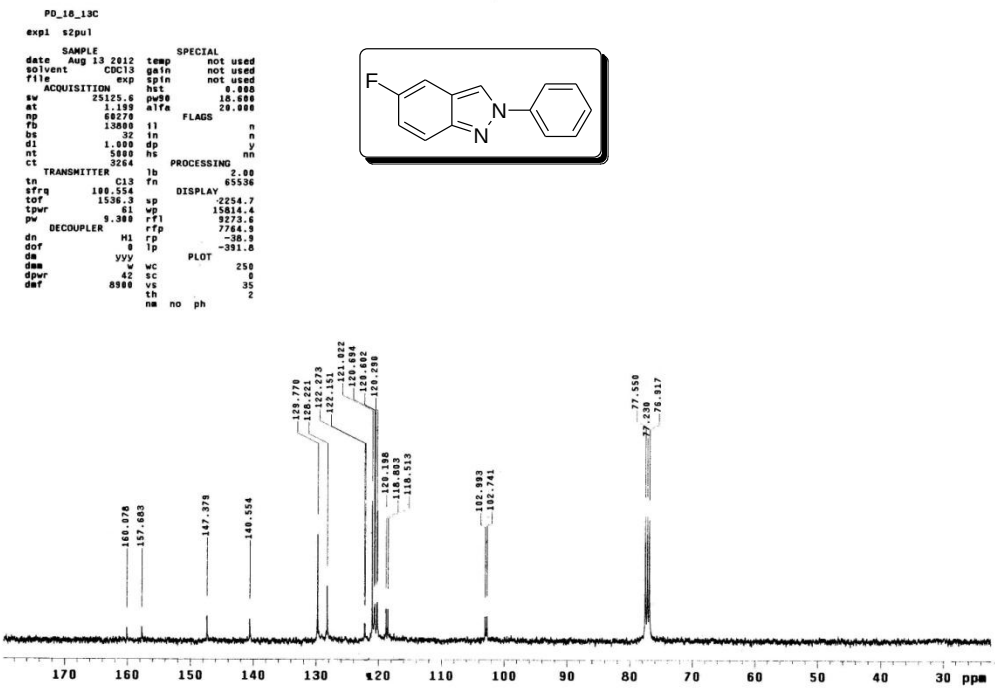
2-Butyl-2H-indazole (1o): ^{13}C NMR (100 MHz, $CDCl_3$)



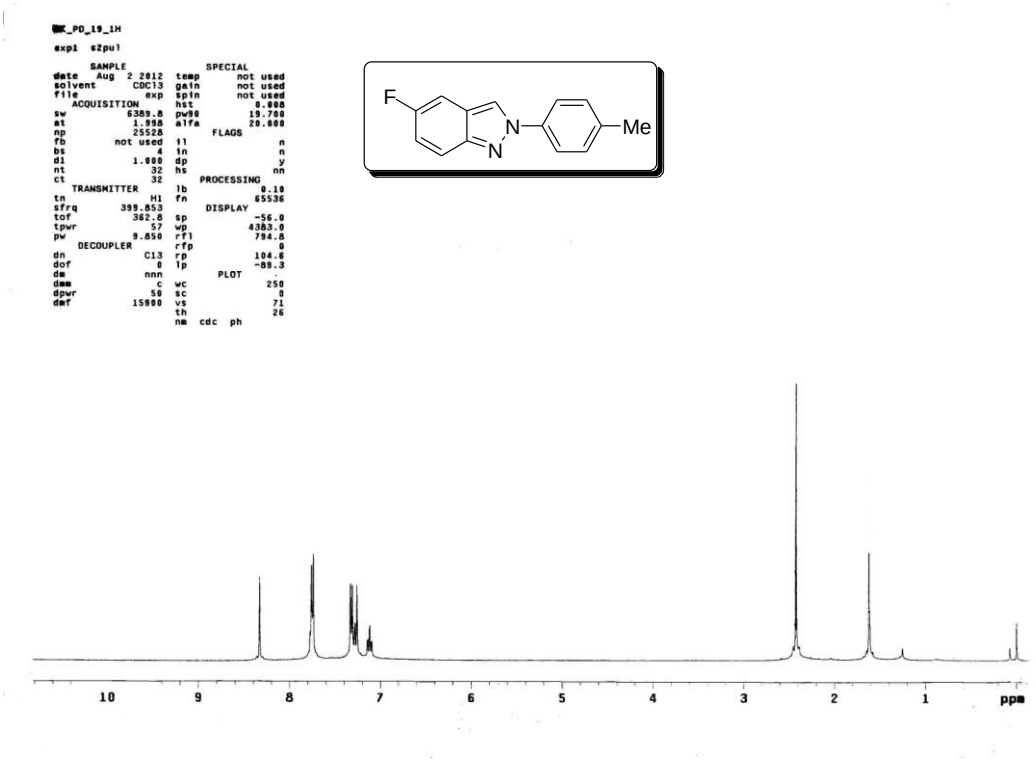
5-Fluoro-2-phenyl-2H-indazole (2a): ^{1}H NMR (400 MHz, $CDCl_3$)



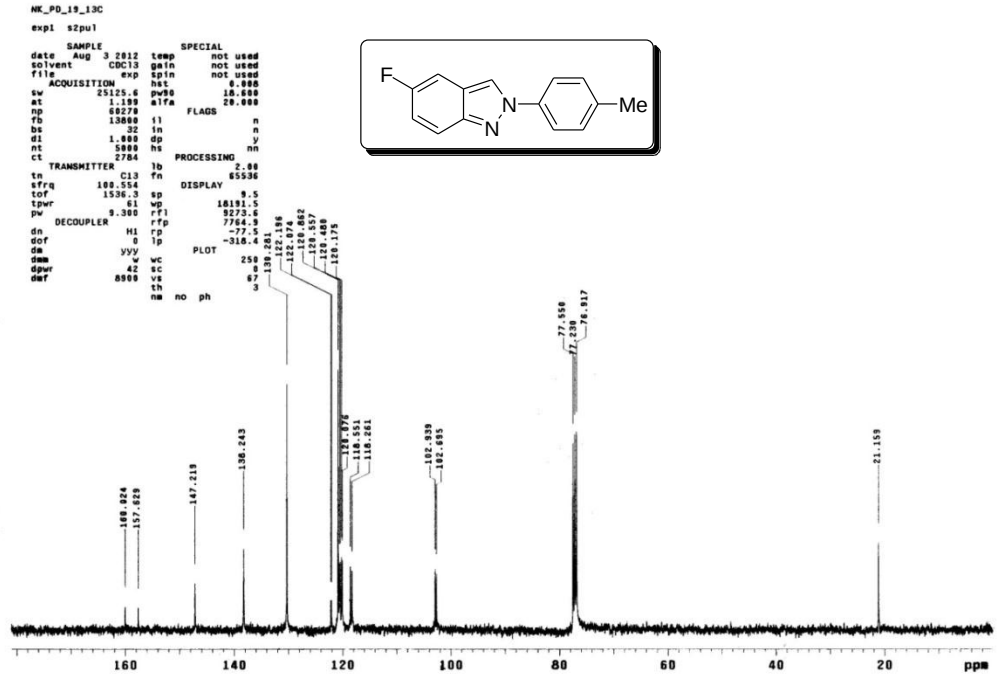
5-Fluoro-2-phenyl-2H-indazole (2a): ^{13}C NMR (100 MHz, $CDCl_3$)



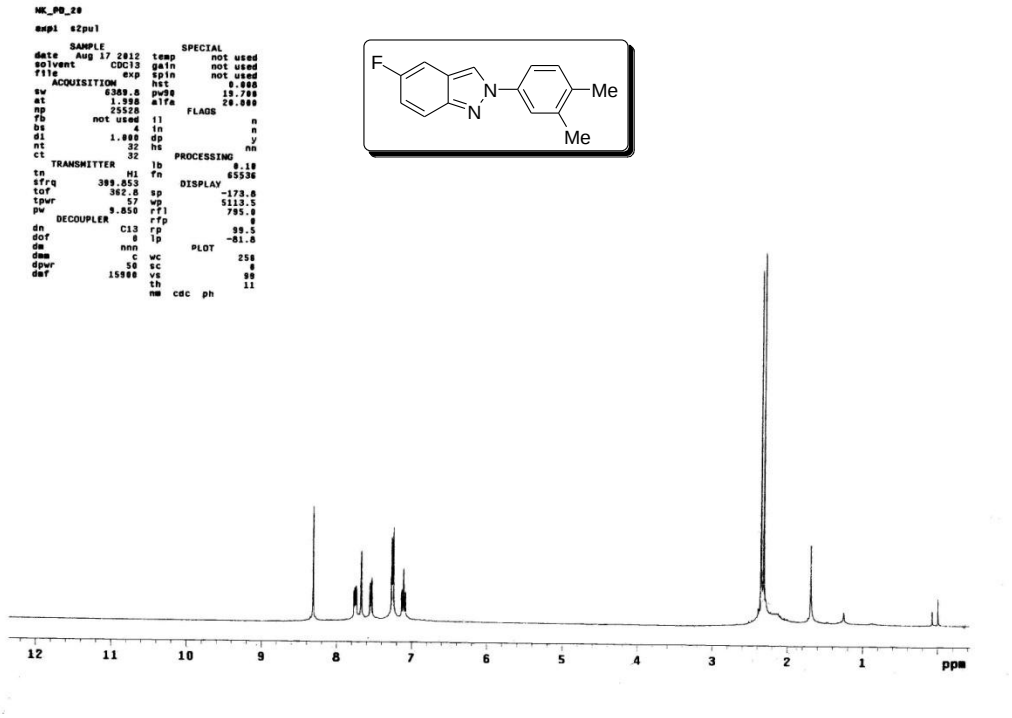
5-Fluoro-2-p-tolyl-2H-indazole (2b): ^{1}H NMR (400 MHz, $CDCl_3$)



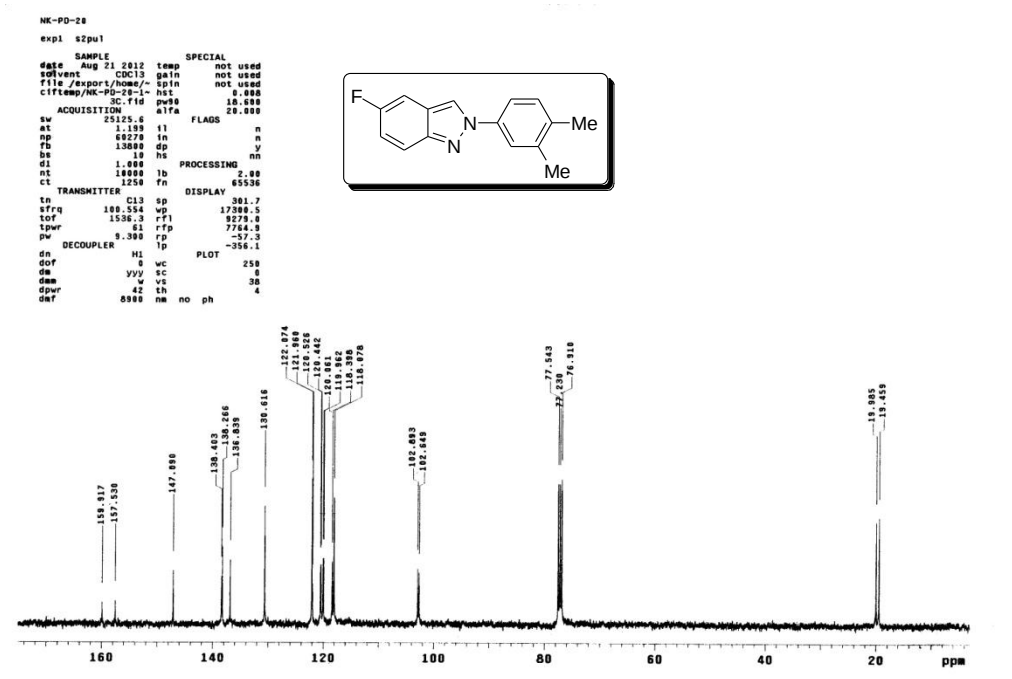
5-Fluoro-2-p-tolyl-2H-indazole (2b): ^{13}C NMR (100 MHz, $CDCl_3$)



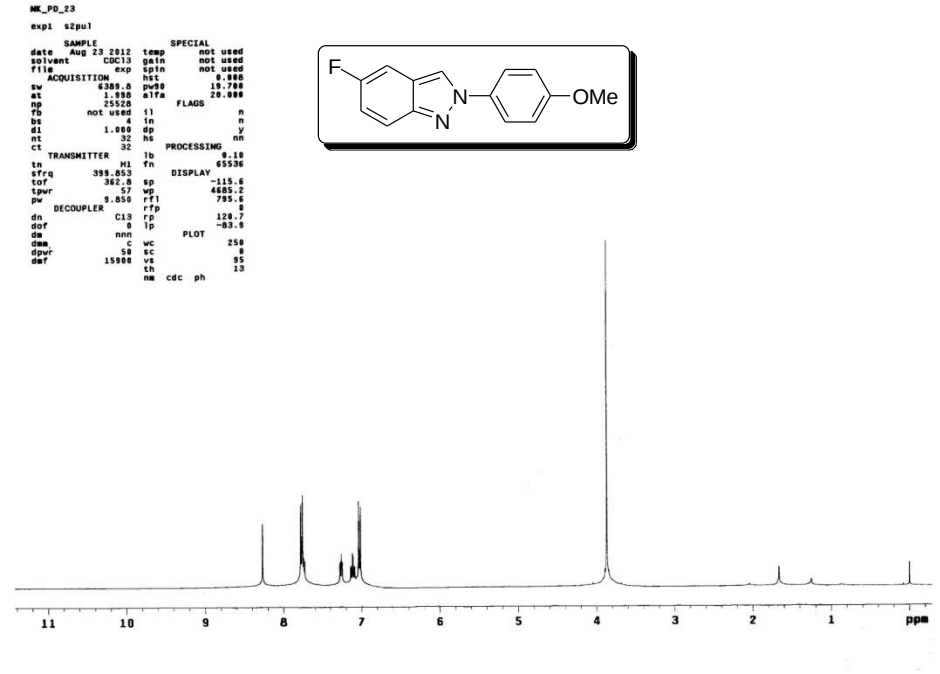
5-Fluoro-2-(3,4-dimethylphenyl)-2H-indazole (2c): ^{1}H NMR (400 MHz, $CDCl_3$)



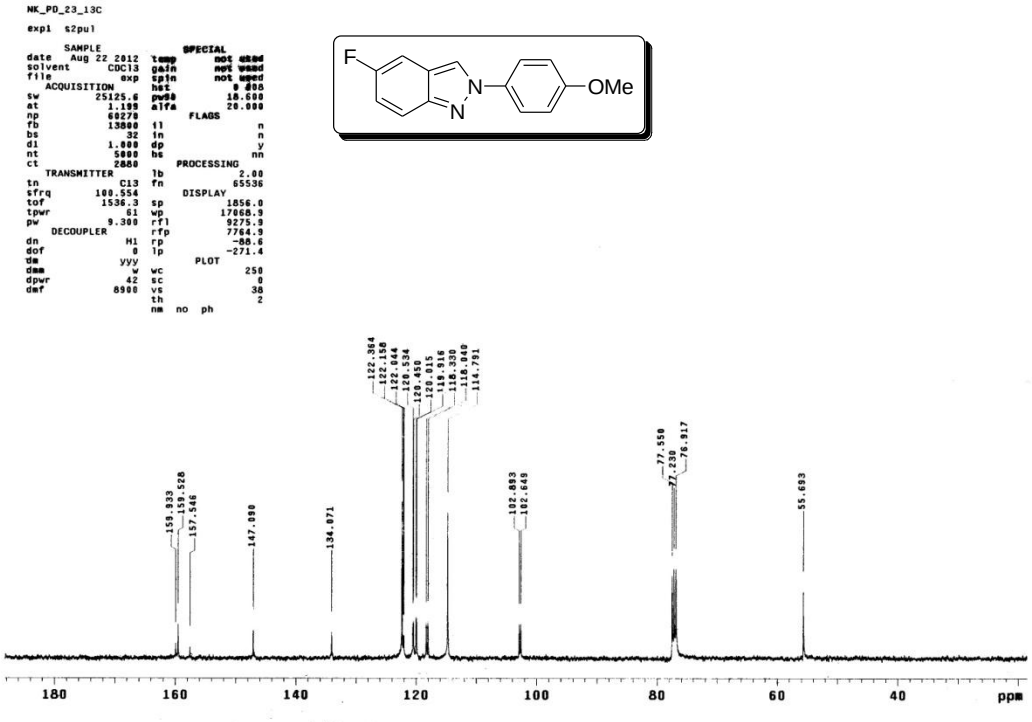
5-Fluoro-2-(3,4-dimethylphenyl)-2H-indazole (2c): ^{13}C NMR (100 MHz, $CDCl_3$)



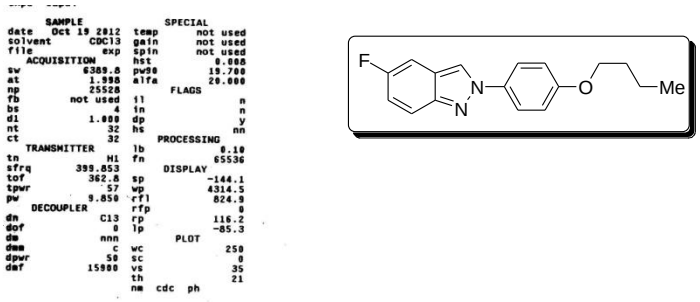
5-Fluoro-2-(4-methoxyphenyl)-2H-indazole (2g): ^{1}H NMR (400 MHz, $CDCl_3$)

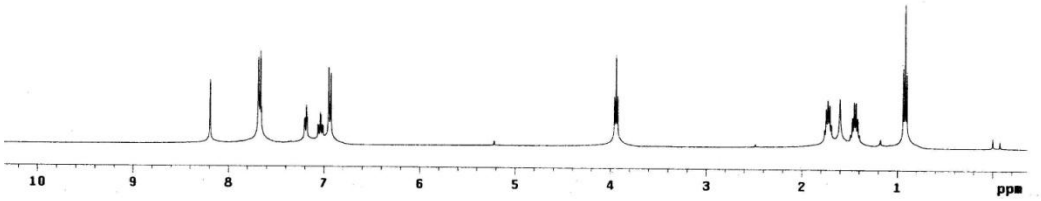


5-Fluoro-2-(4-methoxyphenyl)-2H-indazole (2g): ^{13}C NMR (100 MHz, $CDCl_3$)

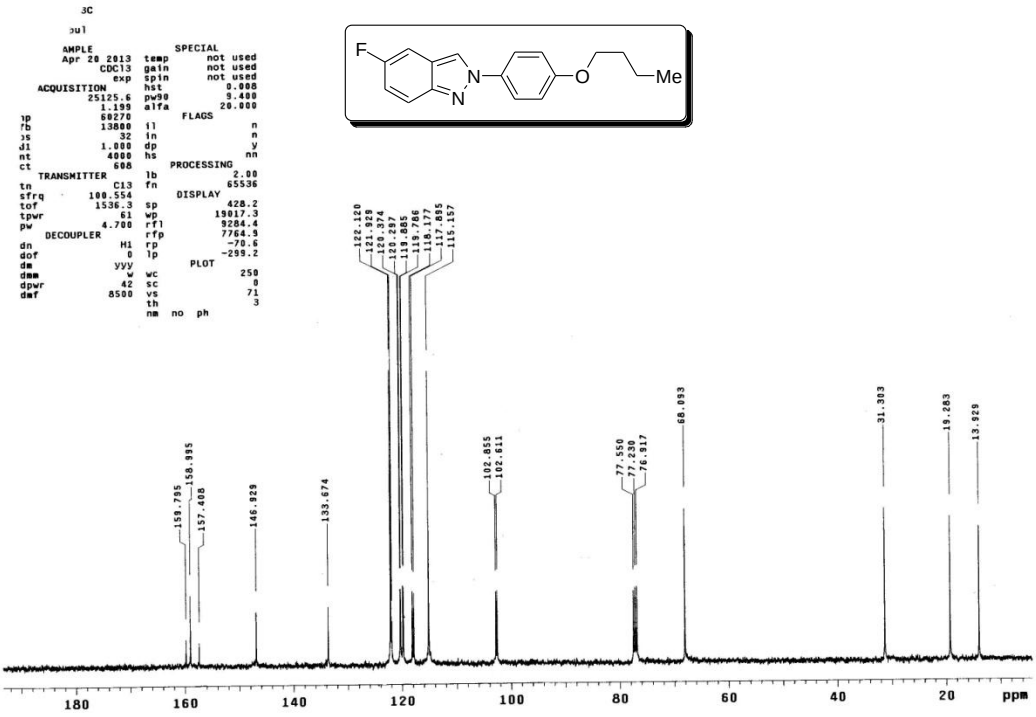


2-(4-Butoxyphenyl)-5-fluoro-2H-indazole (2h): ^{1}H NMR (400 MHz, $CDCl_3$)

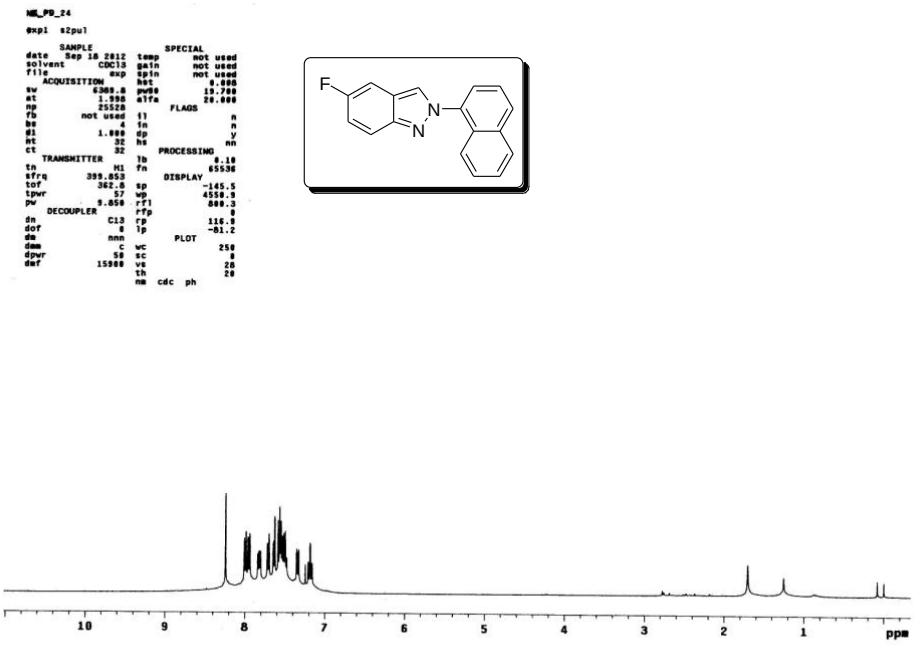




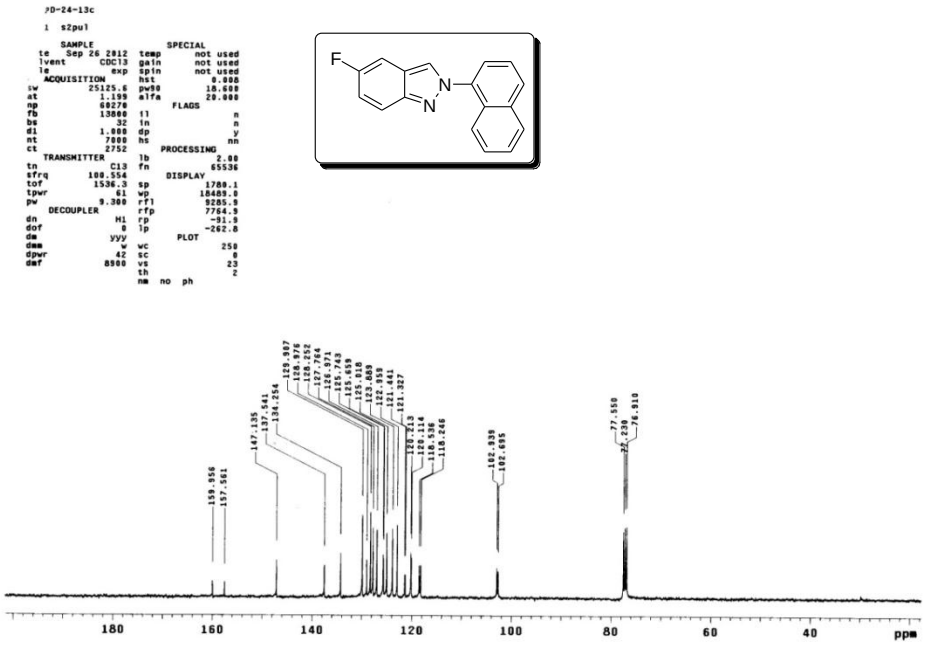
2-(4-Butoxyphenyl)-5-fluoro-2H-indazole (2h): ^{13}C NMR (100 MHz, $CDCl_3$)



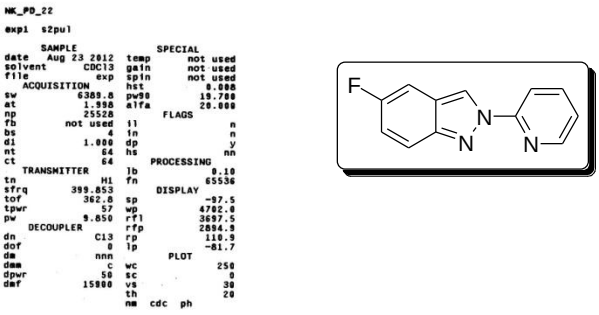
5-Fluoro-2-(naphthalen-1-yl)-2H-indazole (2i): ^{1}H NMR (400 MHz, $CDCl_3$)



5-Fluoro-2-(naphthalen-1-yl)-2H-indazole (2i): ^{13}C NMR (100 MHz, $CDCl_3$)



5-Fluoro-2-(pyridin-2-yl)-2H-indazole (2j): ^{1}H NMR (400 MHz, $CDCl_3$)



5-Fluoro-2-(pyridin-2-yl)-2H-indazole (2j): ^{13}C NMR (100 MHz, $CDCl_3$)