Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Cu^{II}–hydrotalcite catalyzed one–pot three component synthesis of 2*H*-indazoles by consecutive condensation, C–N and N–N bond formations

Avvari N. Prasad, Rapelli Srinivas and Benjaram M. Reddy*

Inorganic and Physical Chemistry Division, CSIR - Indian Institute of Chemical Technology,

Uppal Road, Hyderabad – 500 607, India

Supporting Information

List of Contents

1. Characterization techniques of Cu^{II}–hydrotalcite (Cu^{II}–HT) catalysts: The X-ray powder diffraction (XRD) patterns of the prepared catalysts were acquired with a Siemens D-5005 diffractometer using a Ni-filtered Cu-Kα radiation (0.15418 nm) source and a Scintillation counter detector. From XRD, we observed typical reflection peaks at 2Θ = 11.7, 23.6, 34.6, 35.6, 37.7, 40.4 and 53.31 which are almost identical to the characteristic peaks of the hydrotalcite phase (JCPDC # 460099). The FTIR spectra were recorded on a Nicolet 740 FT–IR spectrometer at ambient conditions, using KBr disks, with a nominal resolution of 4 cm^{-1} and an average of 100 spectra. From FTIR, we observed the intense absorption bands at around 1,350–1,410 and 800–890 cm^{-1} due to symmetric stretching (ν_3) and out-of-plane deformation vibrations (ν_2) of the interlayer carbonate anions, respectively, and broad band at ~3450 cm^{-1} is due to OH^- stretching vibration of *brucite-like* layers caused by the interlayer water molecules and the hydroxyl groups of the layers. The absorption band at around 445 cm^{-1} (δ O–M–O) is ascribed to the lattice vibrations of the octahedral sheets of the hydrotalcites.

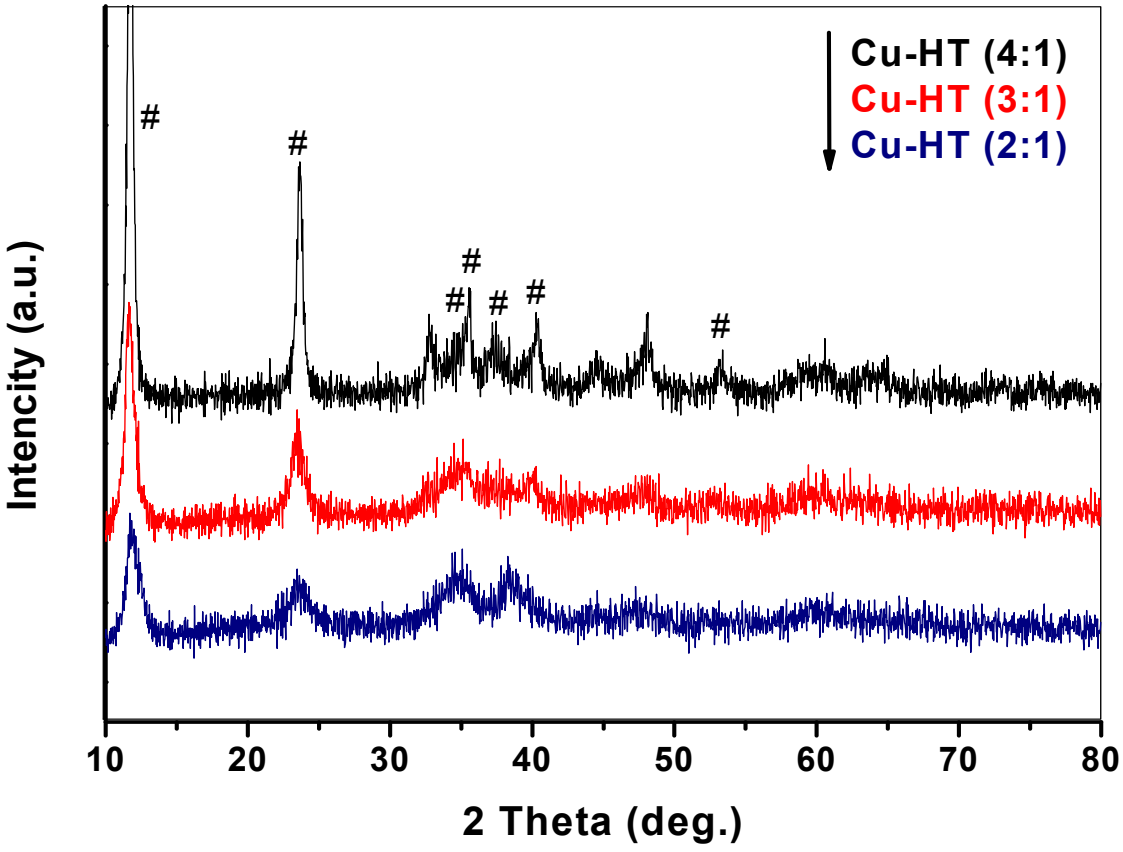


Figure 1. Powder X-ray diffraction patterns of the Cu^{II}–HT materials.

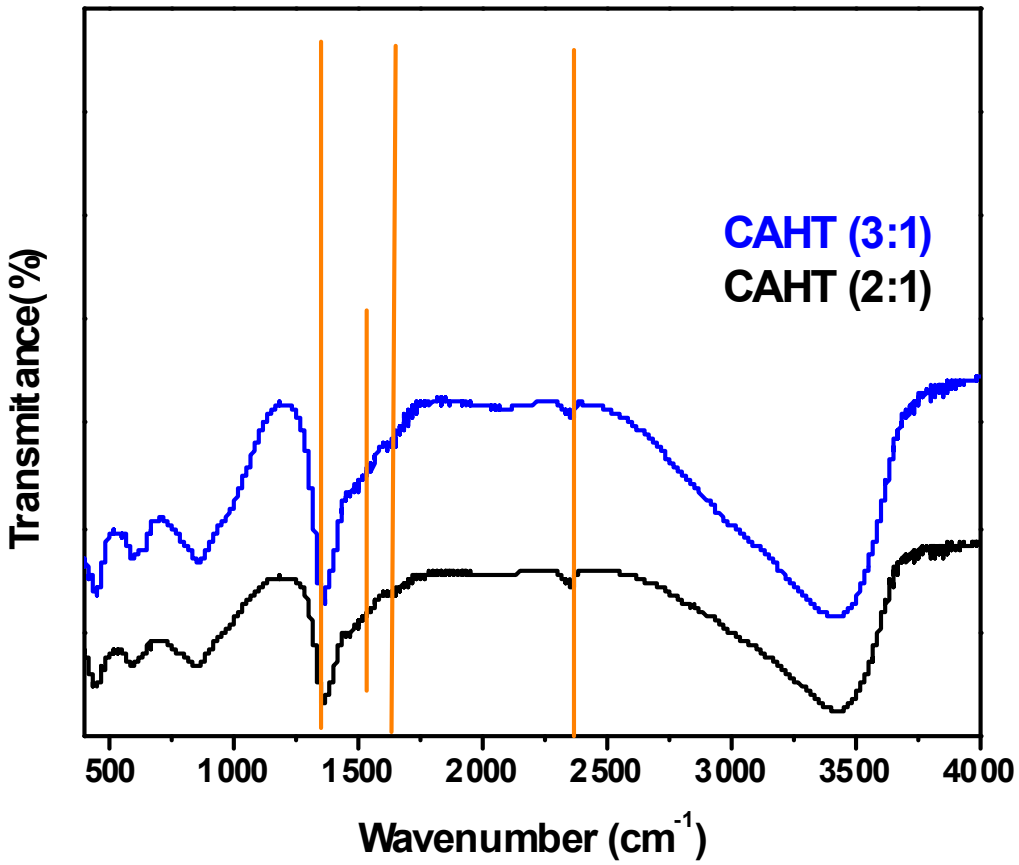


Figure 2. FT–IR spectra of Cu^{II}–HT materials.

2. Recyclability of the Cu^{II}–HT catalyst: We carried out catalyst-recycling experiments by using 2-bromobenzaldehyde, aniline and sodium azide as the model reaction. Remarkably, the used Cu^{II}–HT catalyst exhibited without any significant loss of activity and selectivity in terms of desired product (2*H*-indazole) up to three cycles.

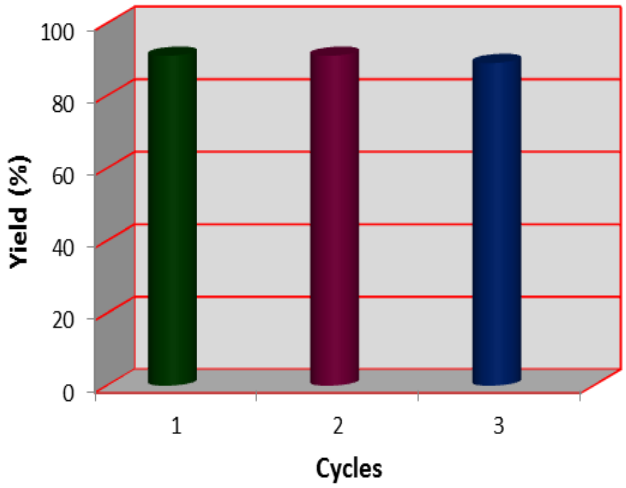
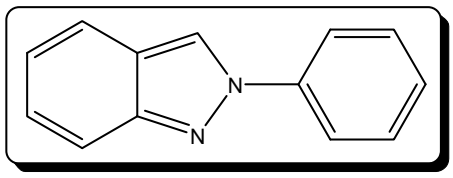


Figure 3. Recycling of Cu^{II}–HT catalyst for the reaction between 2-bromobenzaldehyde, aniline and sodium azide.

3. General information: ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-Unity 200 MHz, Bruker UXNMR/XWIN-NMR Avance-300 MHz, and GEMINI spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants (J) are reported in hertz (Hz). Splitting patterns of proton are described as s, d, dd, t, q, br s and m stand for the resonance multiplicities singlet, doublet, doublet of doublet, triplet, quartet, broad singlet and multiplet, respectively. Only the most important IR absorptions (cm^{-1}) and the molecular ions and/or base peaks in MS are given.

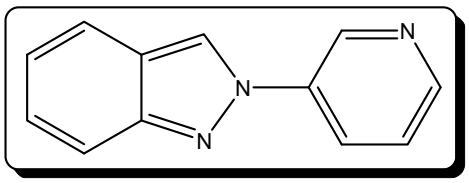
4. ^{1}H NMR, ^{13}C NMR, FTIR and MS data of isolated compounds:

Table 2, Entry 1: 2-Phenyl-2*H*-indazole:



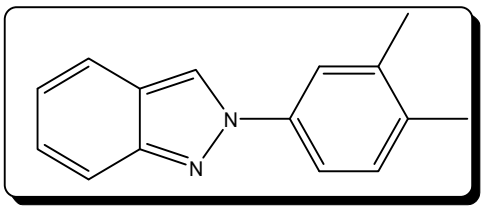
^{1}H NMR ($CDCl_3$): δ 8.38 (s, 1H), 7.92-7.88 (m, 3H), 7.77-7.73 (m,1H), 7.67-7.63 (m,1H), 7.53-7.48 (m, 2H), 7.40-7.30 (m,1H), 7.10-7.05 (m,1H); ^{13}C NMR ($CDCl_3$): δ 149.8, 140.5, 129.6, 127.9, 126.8, 122.4, 121.0, 120.5, 120.4, 117.9, 116.9; IR (KBr) ν 1628, 1518, 1497, 1385, 1317, 1204, 1046, 950, 908, 752, 686 cm^{-1}; MS (EI) *m*/*z*: 195 [M^{+}+1].

Table 2, Entry 2: 2-(Pyridine-3-yl)-2*H*-indazole:



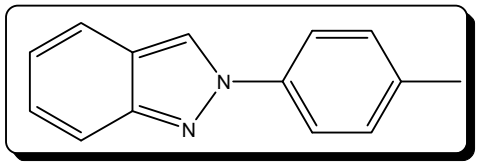
^{1}H NMR ($CDCl_3$): δ 9.11 (s, 1H), 8.56-8.48 (m, 1H), 8.33-8.25 (m,1H), 7.96-7.87 (m, 1H), 7.77-7.72 (m, 2H), 7.36-7.28 (m, 2H), 7.13-7.08 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 150.2, 148.2, 138.8, 127.5, 122.7, 122.6, 122.1, 120.5, 117.9, 114.0; IR (KBr) ν 1612, 1520, 1475, 1437, 1382, 1203, 1145, 1059, 909, 780, 731 cm^{-1}; MS (EI) *m*/*z*: 196 [M^{+}+1].

Table 2, Entry 3: 2-(3,4-Dimethylphenyl)-2*H*-indazole:



^{1}H NMR ($CDCl_3$): δ 8.37 (s, 1H), 7.79 (d, *J* = 8.68 Hz, 1H), 7.70 (d, *J* = 8.49 Hz, 2H), 7.59-7.56 (m, 1H), 7.34-7.27 (m, 2H), 7.13-7.08 (m, 1H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 149.5, 138.3, 138.0, 136.5, 130.4, 126.5, 122.1, 122.0, 120.2, 118.0, 117.7, 19.8, 19.3; IR (KBr) ν 2919, 2860, 1617, 1512, 1458, 1381, 1340, 1138, 1056, 967, 883, 811, 752, 562 cm^{-1}; MS (ESI) *m*/*z*: 223 [M^{+}+1].

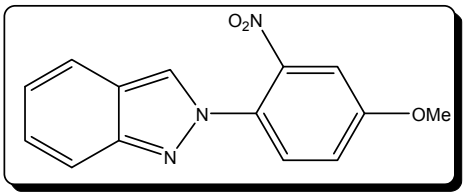
Table 2, Entry 4: 2-*p*-Tolyl-2*H*-indazole:



^{1}H NMR ($CDCl_3$): δ 8.37 (s, 1H), 7.79-7.69 (m, 4H), 7.33-7.26 (m, 3H), 7.13-7.08 (m, 1H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 149.5, 137.8, 130.0, 129.5,

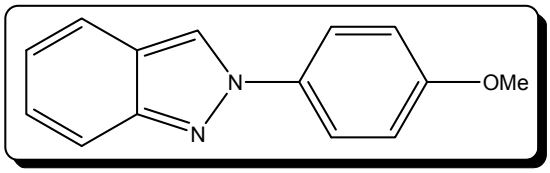
126.6, 122.6, 122.2, 120.7, 120.2, 119.7, 117.7, 20.9; IR (KBr) ν 2922, 2858, 1626, 1522, 1384, 1313, 1204, 1118, 1046, 908, 816, 782, 730, 508 cm^{-1}; MS (ESI) *m*/*z*: 209 [M^++1].

Table 2, Entry 5: 2-(4-Methoxy-2-nitrophenyl)-2*H*-indazole:



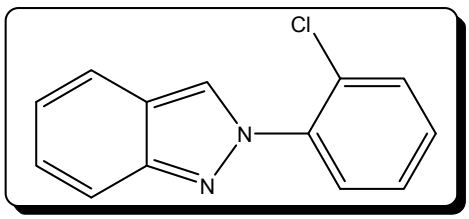
^{1}H NMR ($CDCl_3$): δ 8.91 (d, *J* = 9.82 Hz, 1H), 8.00-7.96 (m, 2H), 7.75-7.72 (m, 1H), 7.60-7.50 (m, 3H), 7.33-7.28 (m, 1H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 178.3, 165.9, 155.3, 132.5, 129.1, 129.0, 127.3, 125.5, 124.0, 123.7, 120.2, 108.9, 108.6, 55.9; IR (KBr) ν 2923, 2853, 1686, 1516, 1459, 1343, 1278, 1039, 757, 697 cm^{-1}; MS (ESI) *m*/*z*: 271 [M^++2].

Table 2, Entry 6: 2-(4-Methoxyphenyl)-2*H*-indazole:



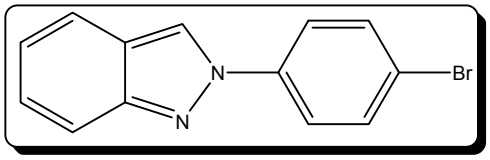
^{1}H NMR ($CDCl_3$): δ 8.37 (s, 1H), 7.84 (t, *J* = 9.00 Hz, 3H), 7.75 (d, *J* = 8.00 Hz, 1H), 7.36 (t, *J* = 9.00 Hz, 1H), 7.15 (t, *J* = 8.00 Hz, 1H), 7.08 (d, *J* = 9.00 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 159.2, 149.2, 134.0, 126.5, 122.6, 122.3,122.1, 120.2, 117.7, 114.5, 55.5; IR (KBr) ν 2924, 2854, 1597, 1500, 1462, 1252, 1148, 1024, 842, 740, 550 cm^{-1}; MS (ESI) *m*/*z*: 225 [M^++1].

Table 2, Entry 7: 2-(2-Chlorophenyl)-2*H*-indazole:



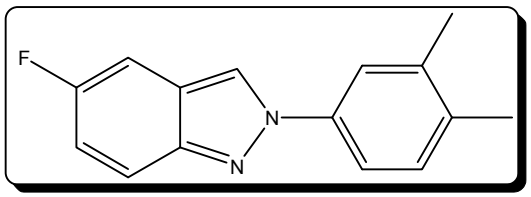
^{1}H NMR ($CDCl_3$): δ 8.34 (s, 1H), 7.80-7.76 (m, 1H), 7.71-7.67 (m, 1H), 7.60-7.57 (m, 1H), 7.50-7.42 m, 3H), 7.32-7.28 (m, 1H), 7.18-7.12 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 148.3, 146.0, 139.0, 135.1, 130.6, 129.9, 128.5, 127.7, 126.9, 125.2, 122.4, 120.5, 117.9; IR (KBr) ν 1628, 1518, 1484, 1385, 1193, 1060, 953, 757, 611, 537 cm^{-1}; MS (ESI) *m*/*z*: 229 [M^+].

Table 2, Entry 8: 2-(4-Bromophenyl)-2*H*-indazole:



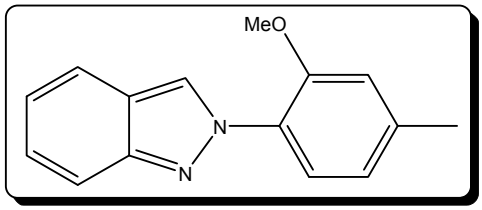
^{1}H NMR ($CDCl_3$): δ 8.37 (s, 1H), 7.81-7.77 (m, 4H), 7.74-7.62 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 149.8, 139.4, 132.6, 127.1, 122.8, 122.7, 122.2, 121.4, 120.3, 120.2, 117.8; IR (KBr) ν 2926, 2856, 1631, 1591, 1492, 1384, 1304, 1203, 1072, 1007, 952, 909, 817, 752 cm^{-1}; MS (ESI) *m*/*z*: 273 [M^++1].

Table 2, Entry 9: 5-Fluoro-2-(3,4-dimethylphenyl)-2*H*-indazole:



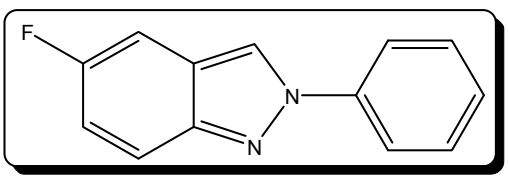
^{1}H NMR ($CDCl_3$): δ 8.32 (s, 1H), 7.77-7.74 (m, 1H), 7.70-7.67 (m, 1H), 7.57-7.52 (m, 2H), 7.27-7.24 (m, 2H), 7.13-7.09 (m, 1H), 2.36 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 160.1, 156.9, 138.1, 136.7, 130.4, 121.9, 120.4, 120.2, 119.8, 119.7, 118.3, 117.9, 19.8, 19.3; IR (KBr) ν 2924, 2855, 1640, 1522, 1457, 1382, 1230, 1171, 964, 806, 732 cm^{-1}; MS (ESI) *m*/*z*: 241 [M^++1].

Table 2, Entry 10: 2-(2-Methoxy-4-methylphenyl)-2*H*-indazole:



^{1}H NMR ($CDCl_3$): δ 8.52 (s, 1H), 7.79-7.70 (m, 2H), 7.39-7.28 (m, 1H), 7.22-7.17 (m, 1H), 7.13-7.06 (m, 1H), 7.03-6.98 (m, 1H), 3.87 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 156.8, 148.6, 135.6, 130.8, 129.5, 126.9, 126.8, 126.4, 125.5, 121.7, 120.4, 117.5, 112.3, 56.1, 20.3; IR (KBr) ν 2925, 2853, 1689, 1514, 1460, 1383, 1251, 1141, 1026, 911, 803, 735, 608 cm^{-1}; MS (ESI) *m*/*z*: 239 [M^++1].

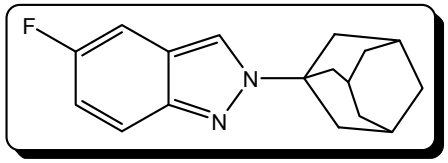
Table 2, Entry 11: 5-Fluoro-2-phenyl-2*H*-indazole:



^{1}H NMR ($CDCl_3$): δ 8.37 (s, 1H), 7.89-7.87 (d, *J* = 7.72 Hz, 2H), 7.78-7.75 (m, 1H), 7.53 (t, *J* = 7.72 Hz, 2H), 7.41 (t, *J* = 7.72 Hz, 1H), 7.29-7.26 (m, 1H), 7.15-7.11 (m, 1H); ^{13}C NMR ($CDCl_3$): δ

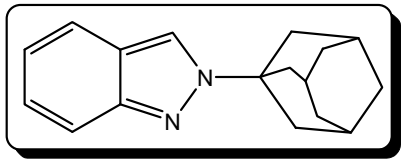
157.0, 147.1, 140.3, 129.5, 128.0, 120.8, 120.4, 120.0, 119.9, 118.6, 118.2, 102.7, 102.4; IR (KBr) ν 1682, 1526, 1374, 1214, 1149, 1079, 907, 732, 650 cm^{-1}; MS (ESI) *m*/*z*: 213 [M^{+}+1].

Table 2, Entry 12: 5-Fluoro2-adamantyl-2*H*-indazole:



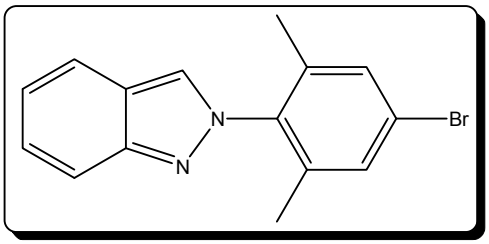
^{1}H NMR ($CDCl_3$): δ 7.99 (s, 1H), 7.71-7.68 (m, 1H), 7.24-7.21 (m, 1H), 7.07-7.03 (m, 1H), 2.32-2.27 (m, 9H), 1.82-1.80 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 145.4, 119.4, 119.3, 118.6, 118.5, 117.0, 116.6, 60.4, 43.1, 36.0, 29.5; IR (KBr) ν 2917, 2854, 1516, 1455, 1373, 1310, 1163, 857, 808, 766, 730 cm^{-1}; MS (ESI) *m*/*z*: 271 [M^{+}+1].

Table 2, Entry 13: 2-Adamantyl-2*H*-indazole:



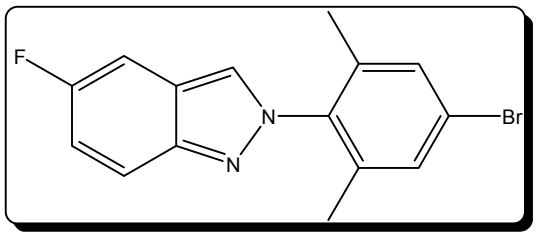
^{1}H NMR ($CDCl_3$): δ 8.05 (s, 1H), 7.75 (d, *J* = 8.39 Hz, 1H), 7.66 (d, *J* = 8.39 Hz, 1H), 7.26 (t, *J* = 8.39 Hz, 1H), 7.05 (t, *J* = 8.39 Hz, 1H), 2.34-2.28 (m, 9H), 1.83-1.80 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 148.0, 125.4, 121.0, 120.9, 120.1, 118.4, 117.4, 60.1, 43.1, 36.0, 29.5; IR (KBr) ν 2915, 2856, 1652, 1513, 1454, 1385, 1309, 1149, 1052, 908, 730, 647 cm^{-1}; MS (ESI) *m*/*z*: 253 [M^{+}+1].

Table 2, Entry 14: 2-(4-Bromo-2,6-dimethylphenyl)-2*H*-indazole:



^{1}H NMR ($CDCl_3$): δ 8.58 (s, 1H), 8.25-8.21(m, 1H), 7.64-7.60 (m, 1H), 7.46-7.32 (m, 2H), 7.24-7.20 (m, 2H), 2.13 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 162.6, 149.9, 134.3, 133.2, 132.6, 131.6, 130.6, 129.2, 128.6, 127.7, 125.8, 116.6, 18.1; IR (KBr) ν 2924, 2855, 1726, 1463, 1279, 1186, 1079, 967, 746, 606, 543 cm^{-1}; MS (ESI) *m*/*z*: 301 [M^{+}+1].

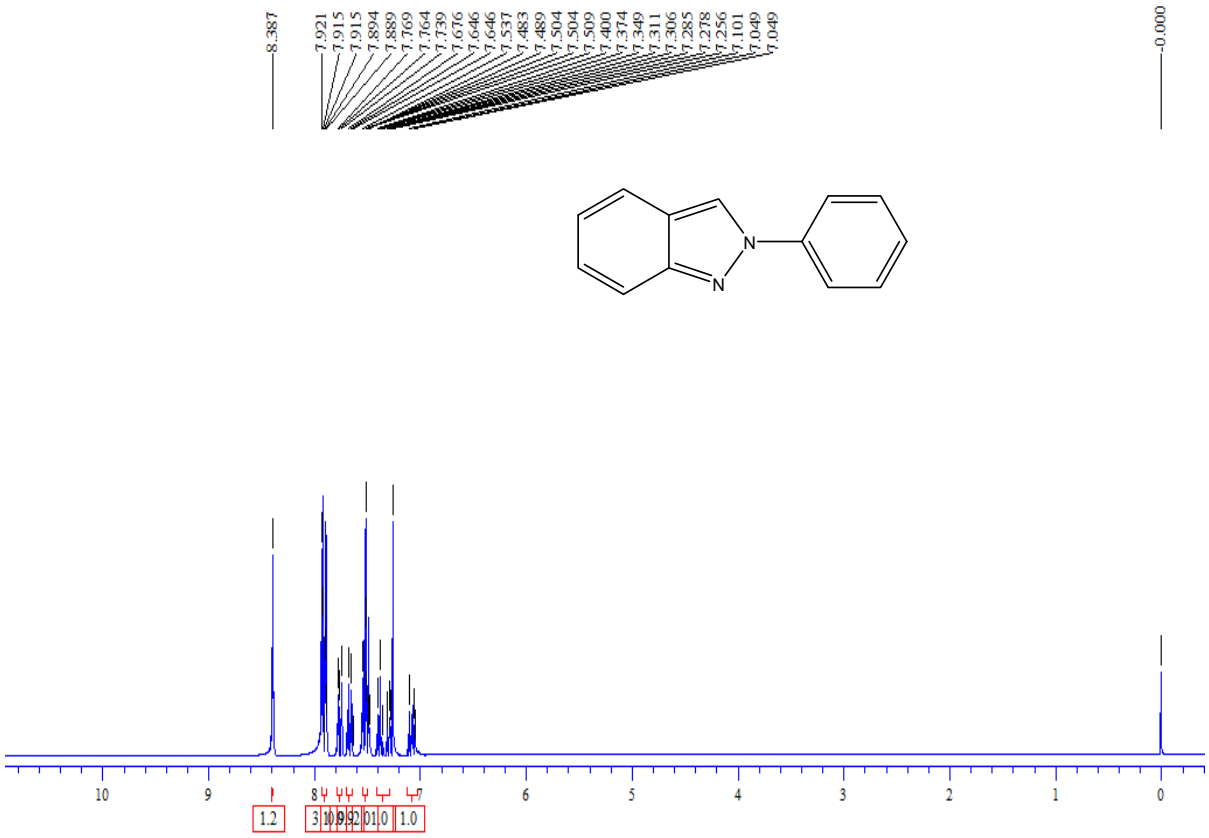
Table 2, Entry 15: 2-(4-Bromo-2,6-dimethylphenyl)-5-fluoro-2*H*-indazole:



^{1}H NMR ($CDCl_3$): δ 8.52 (d, J = 2.26 Hz, 1H), 7.98-7.94 (m, 1H), 7.64-7.57 (m, 2H), 7.24-7.21 (m, 2H), 2.13 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 161.5, 149.4, 138.8, 134.6, 134.5, 131.4, 130.7, 129.2, 120.2, 119.9, 116.9, 115.4, 115.1, 18.2; IR (KBr) ν 2923, 2855, 1522, 1459, 1375, 1244, 910, 724, 628, 520 cm^{-1}; MS (ESI) *m*/*z*: 319 [M^{+}+1].

5. ^{1}H NMR and ^{13}C NMR spectra of isolated compounds

Table 2, Entry 1: 2-Phenyl-2*H*-indazole:



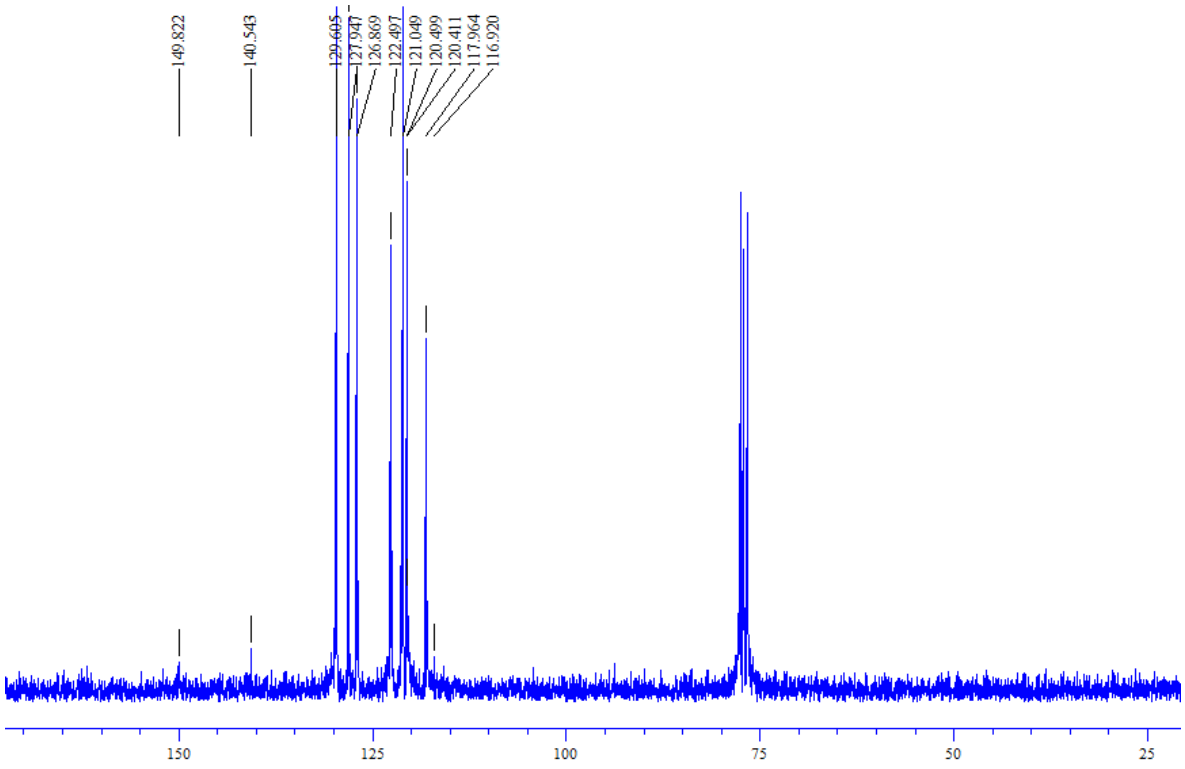
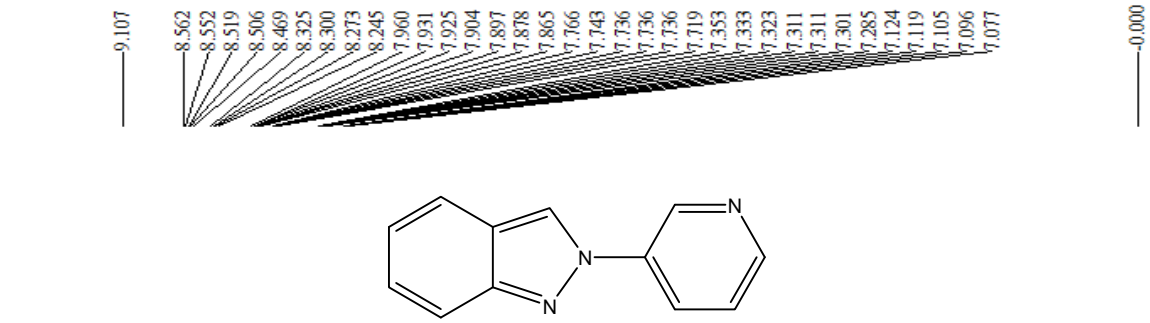
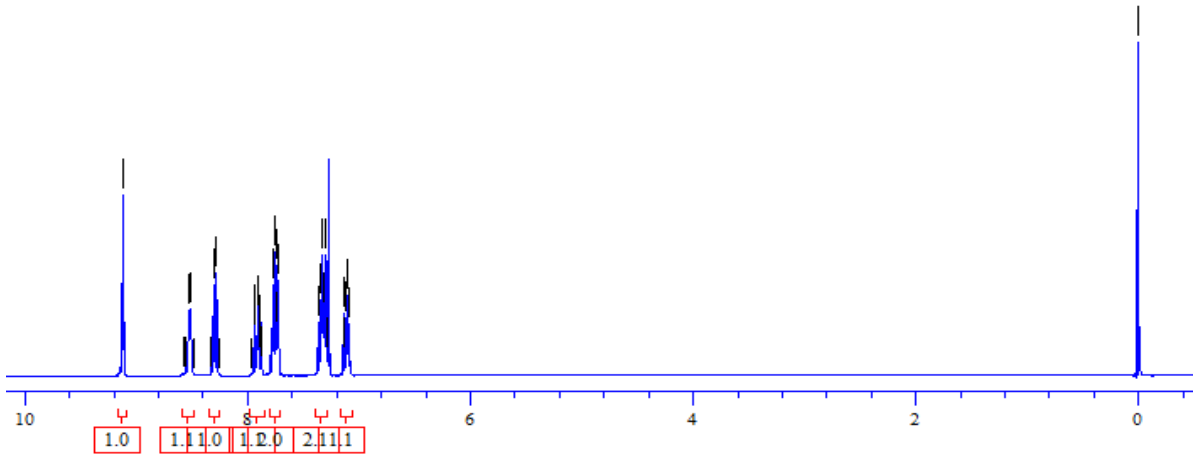


Table 2, Entry 2: 2-(Pyridine-3-yl)-2*H*-indazole:





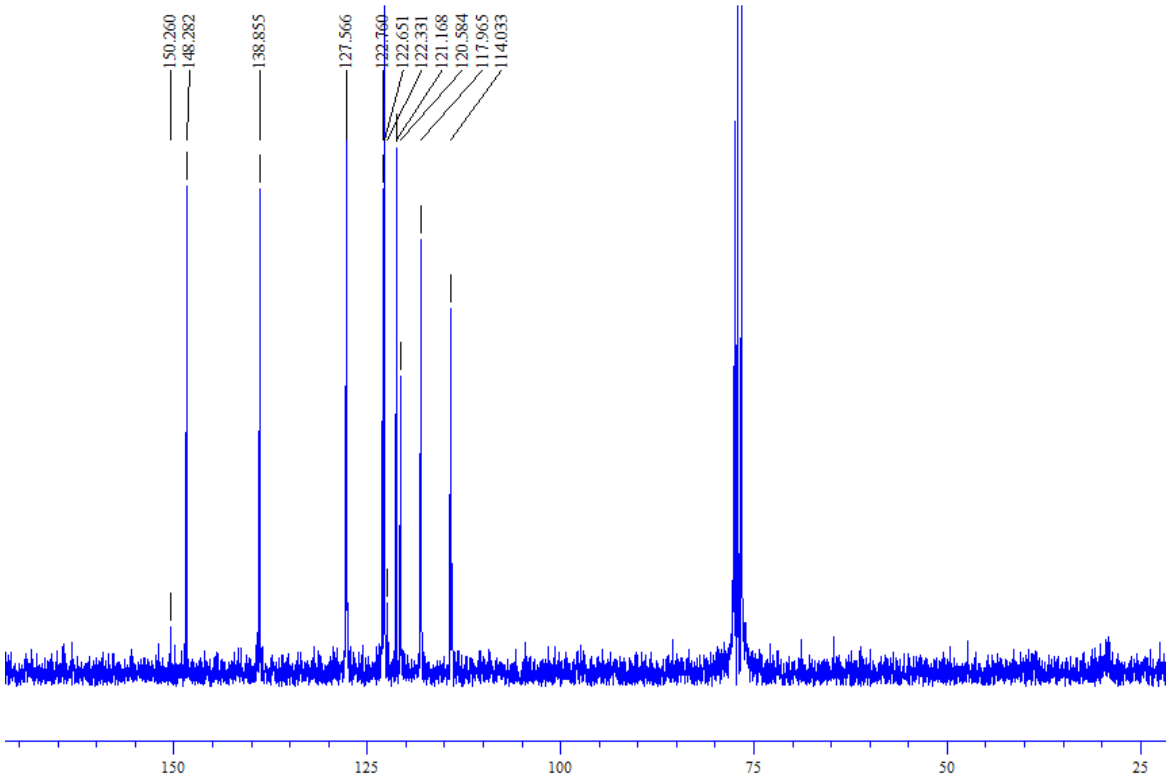
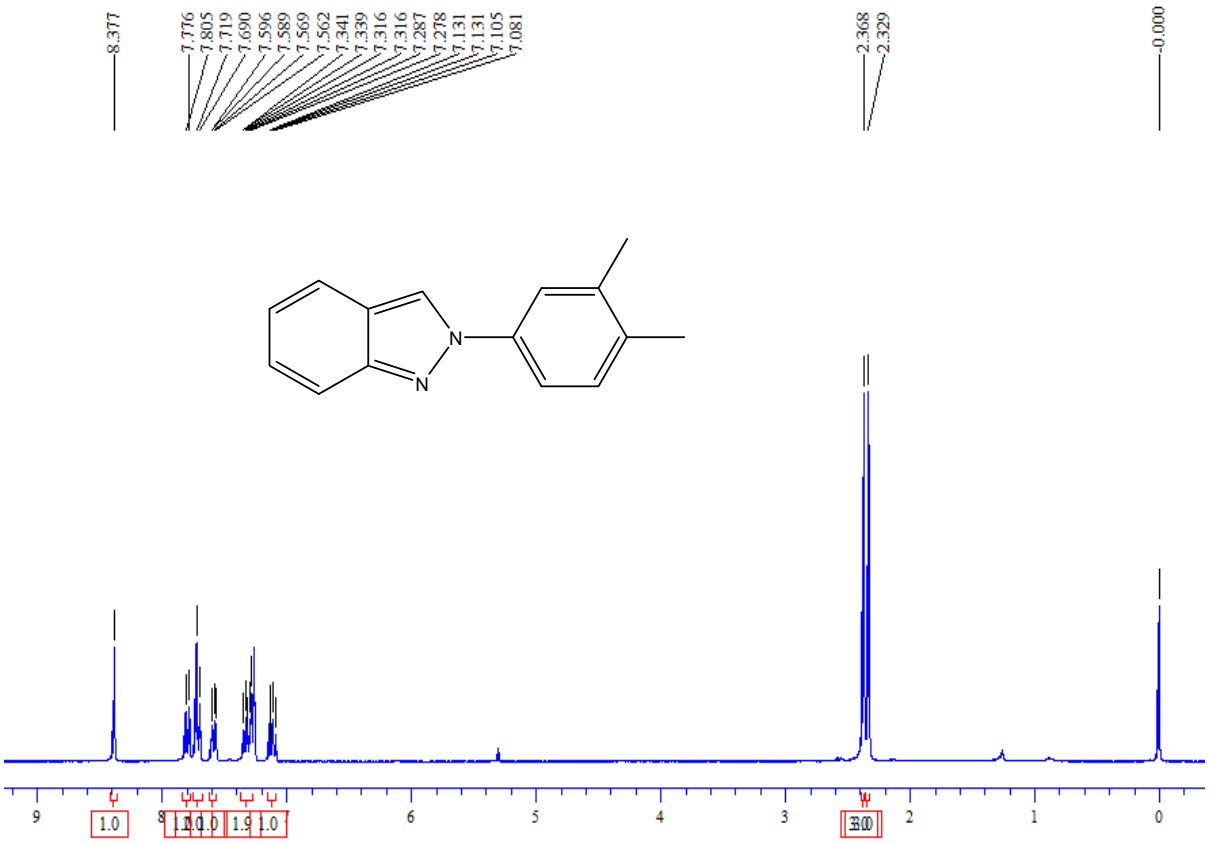


Table 2, Entry 3: 2-(3,4-Dimethylphenyl)-2*H*-indazole:



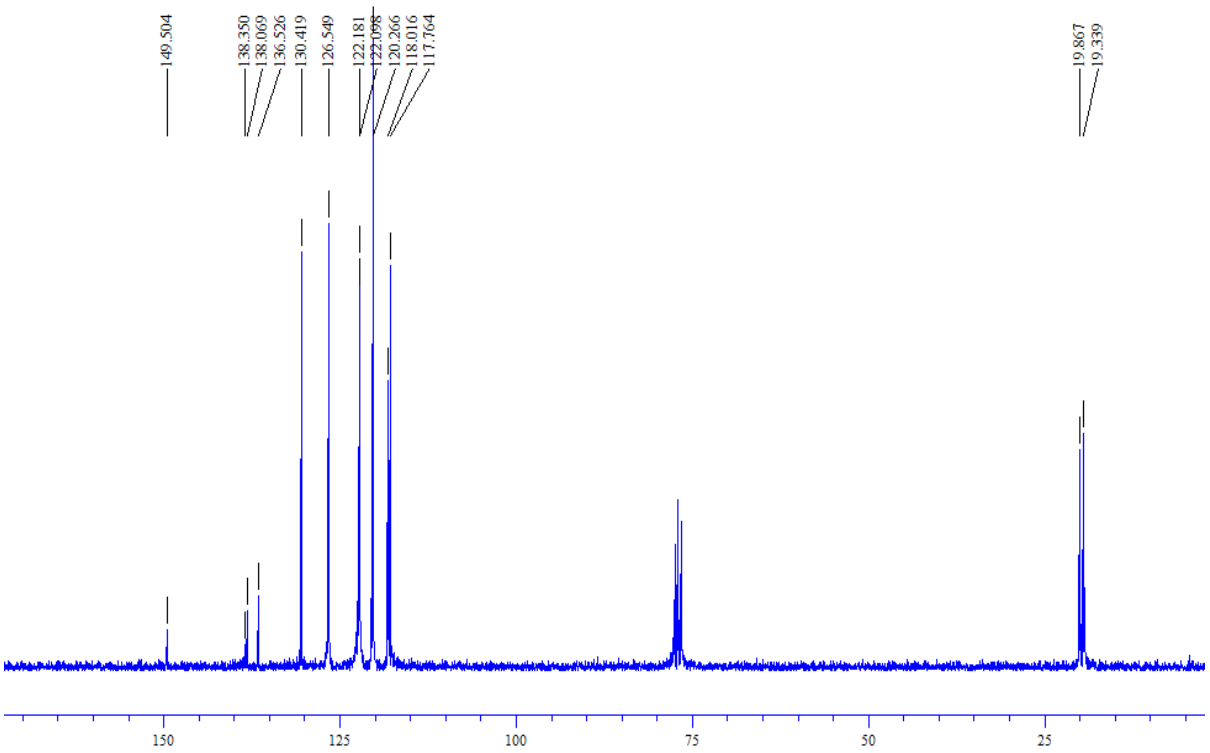
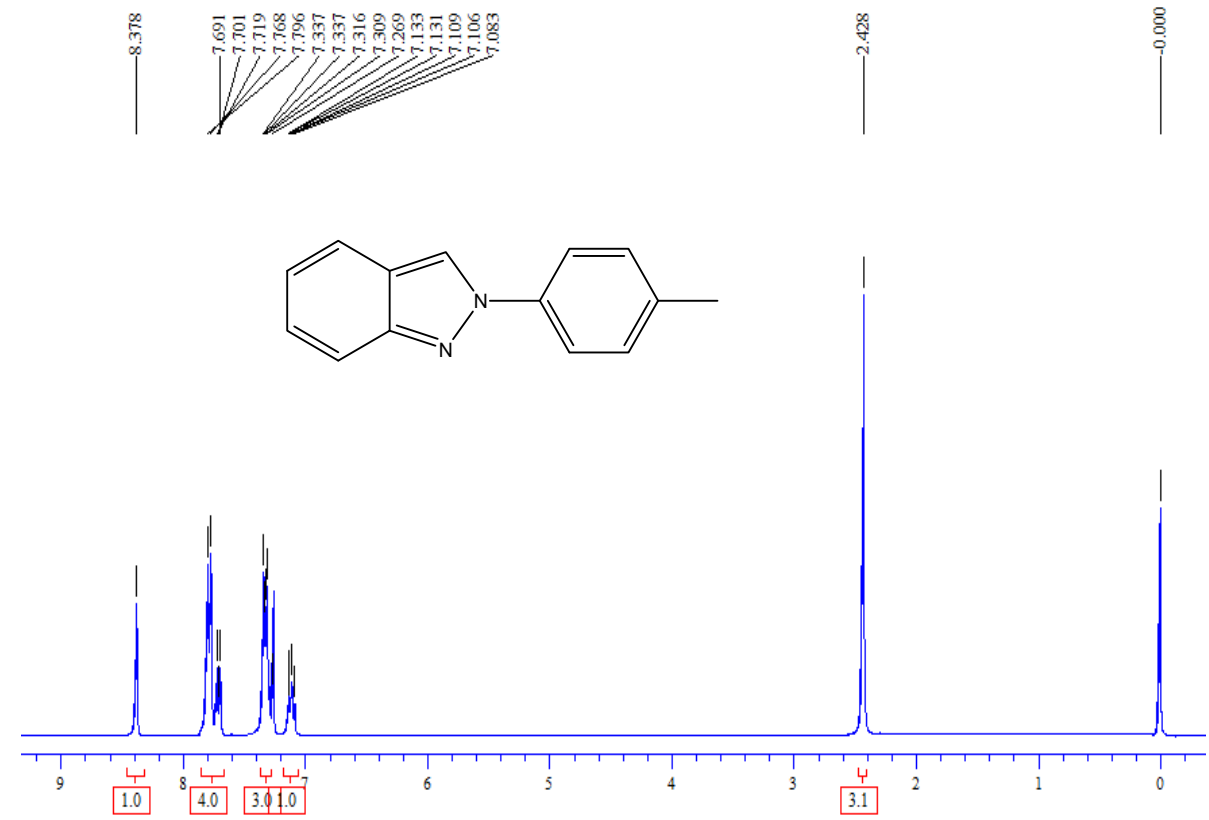


Table 2, Entry 4: 2-*p*-Tolyl-2*H*-indazole:



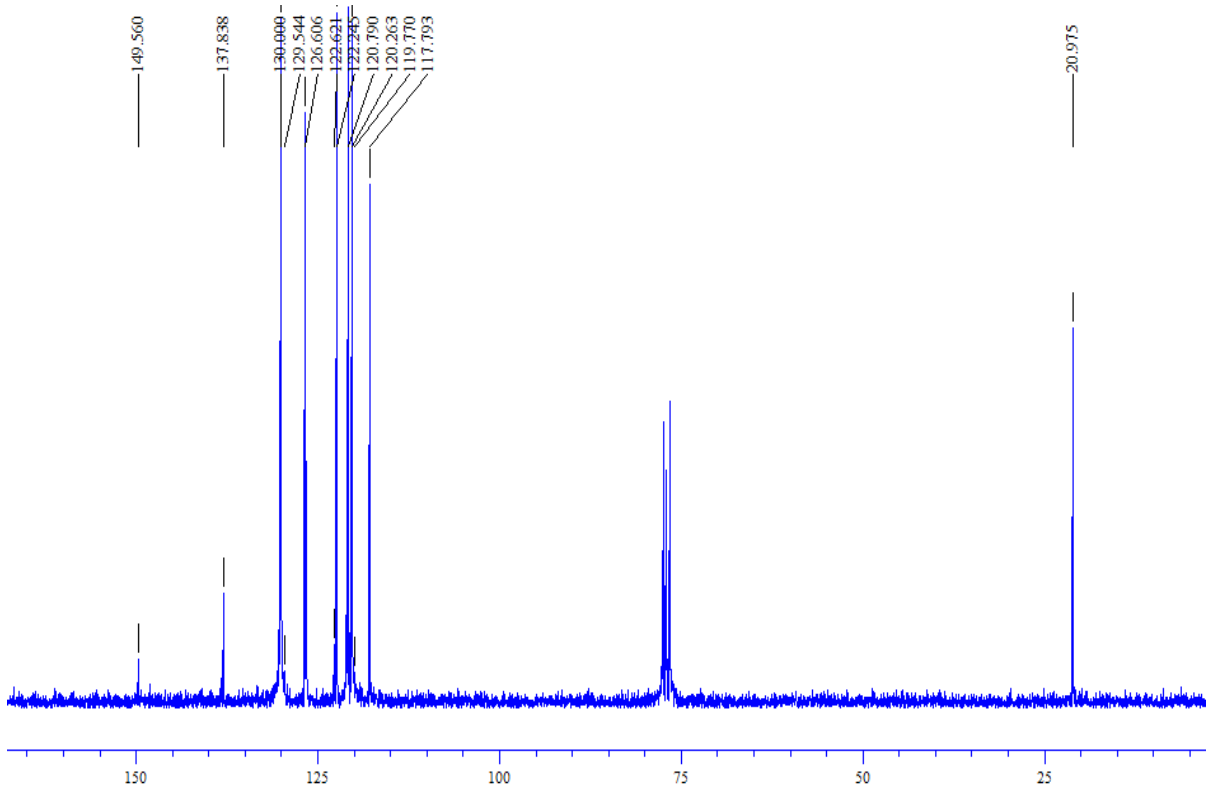
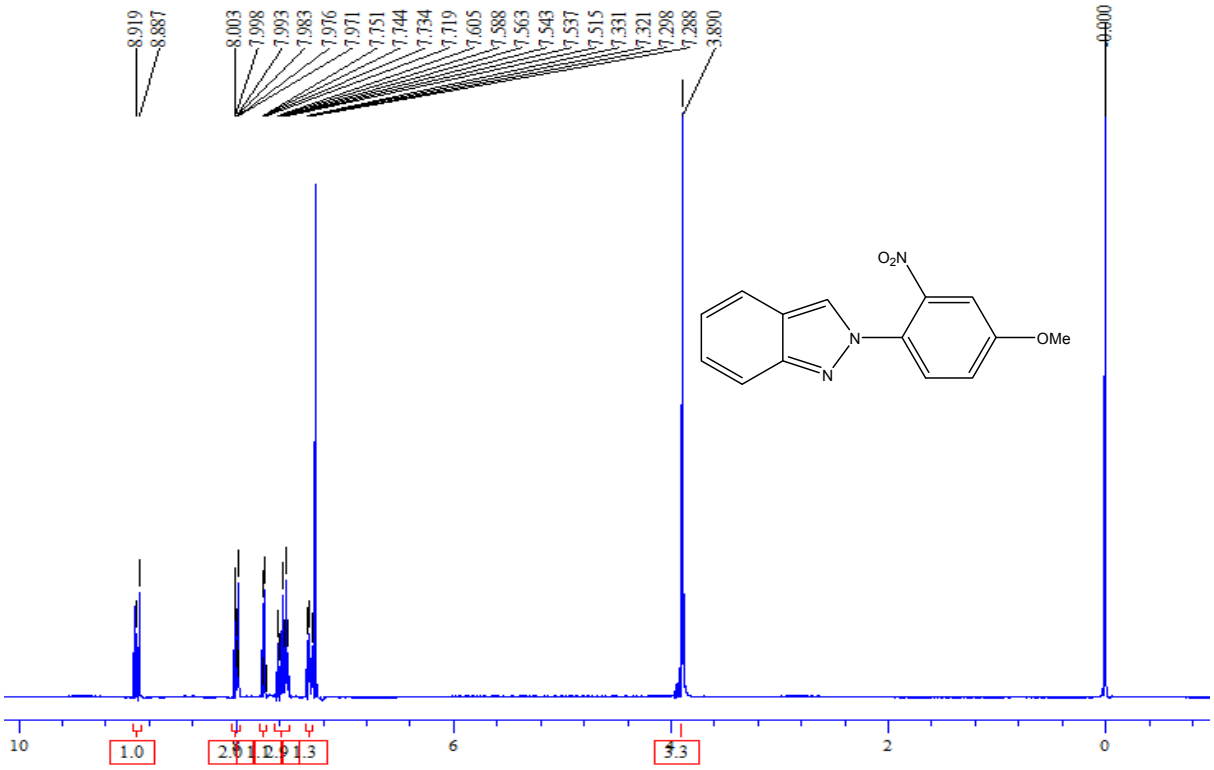


Table 2, Entry 5: 2-(4-Methoxy-2-nitrophenyl)-2*H*-indazole:



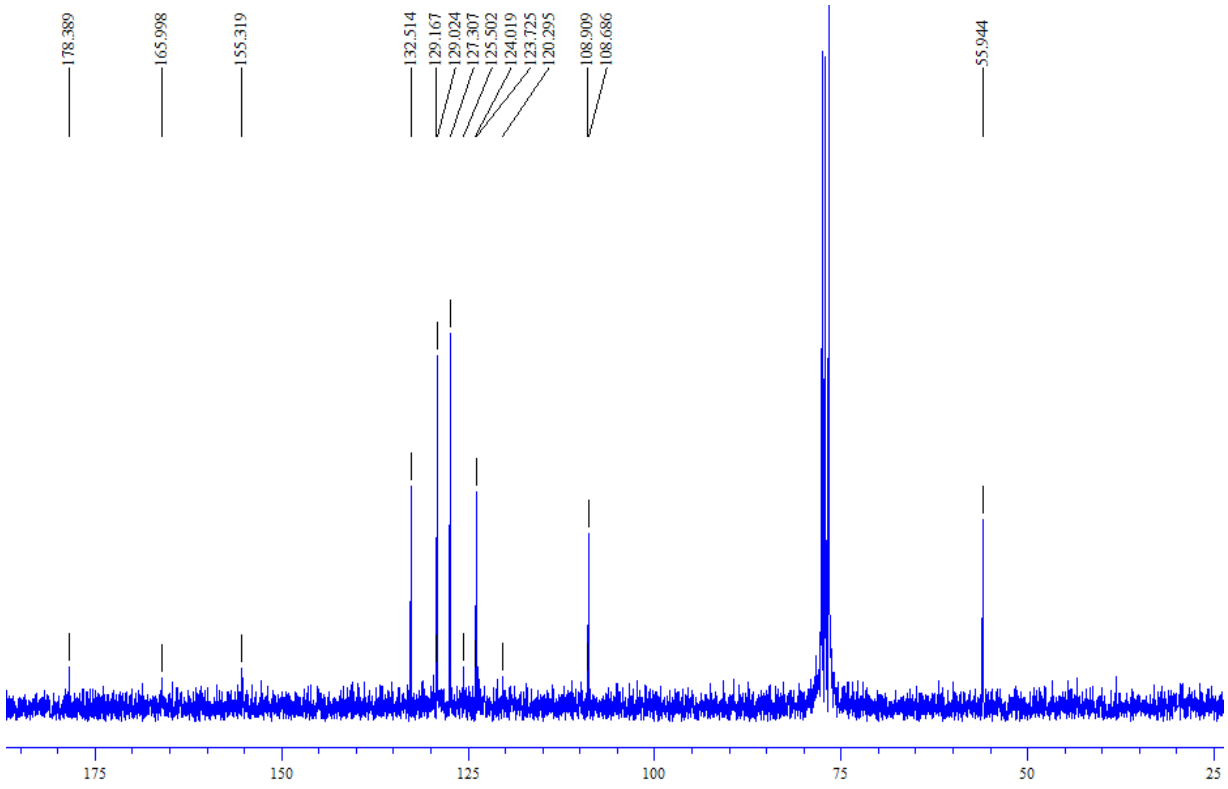


Table 2, Entry 6: 2-(4-Methoxyphenyl)-2*H*-indazole:

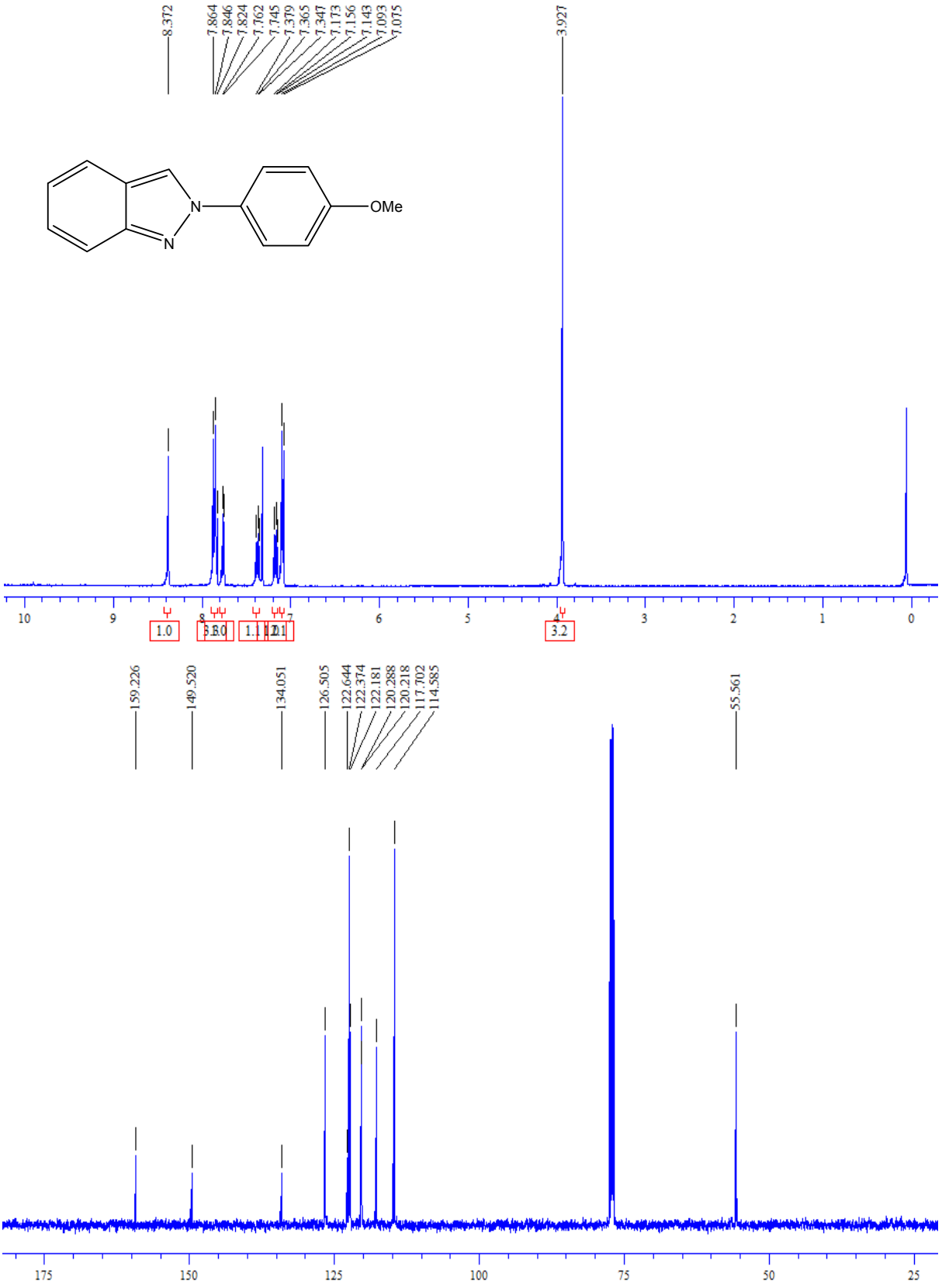
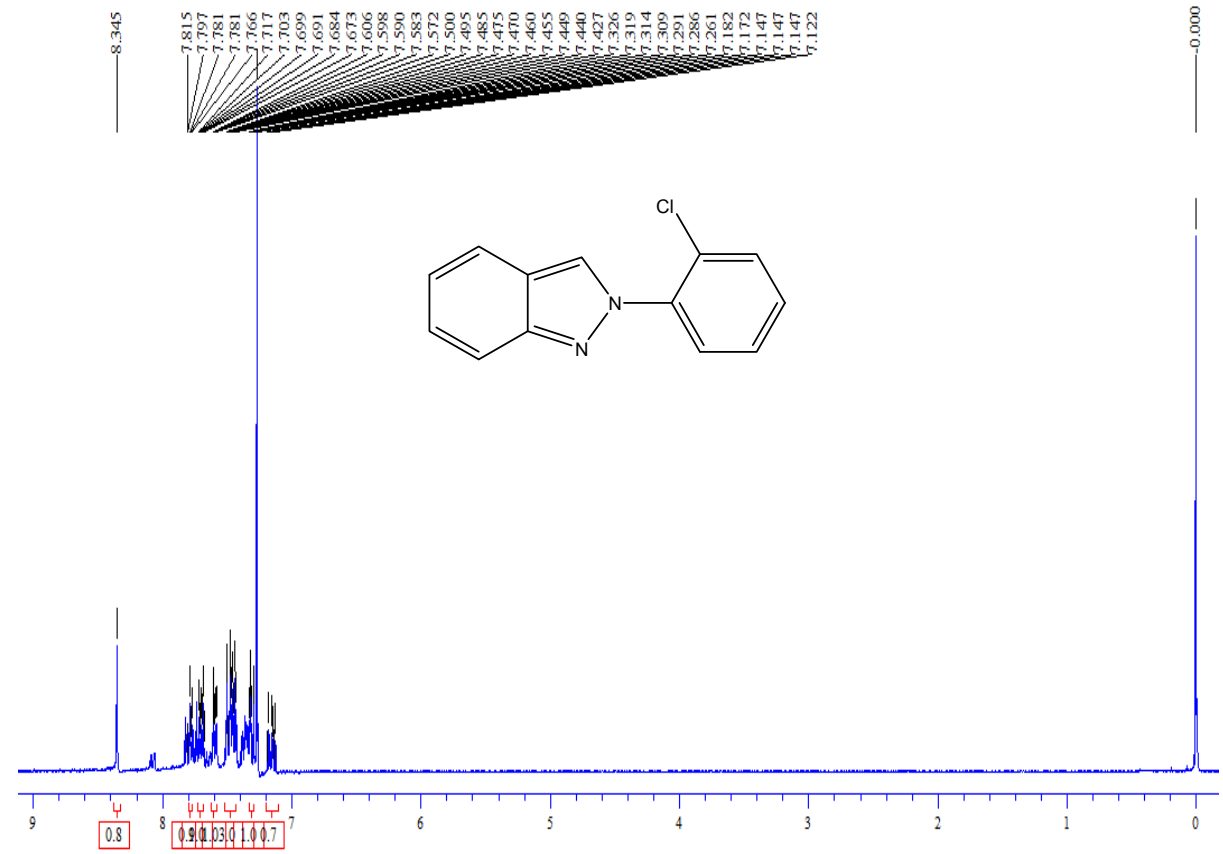


Table 2, Entry 7: 2-(2-Chlorophenyl)-2*H*-indazole:



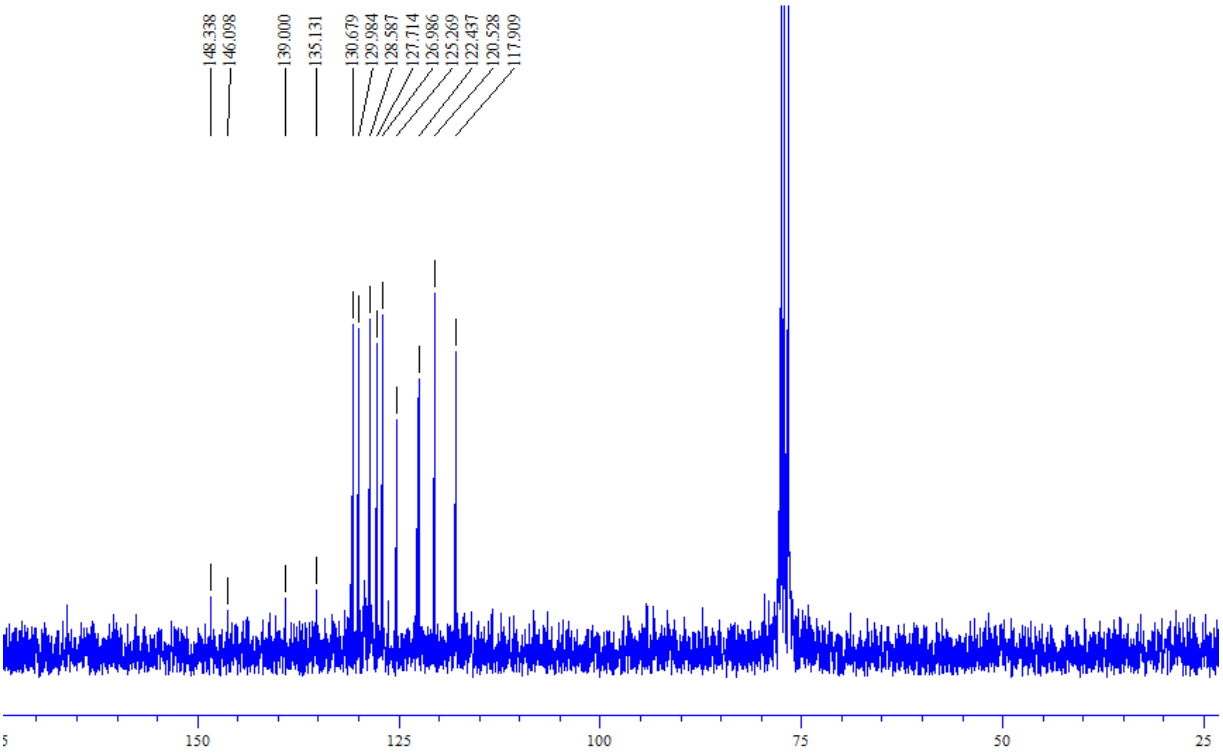
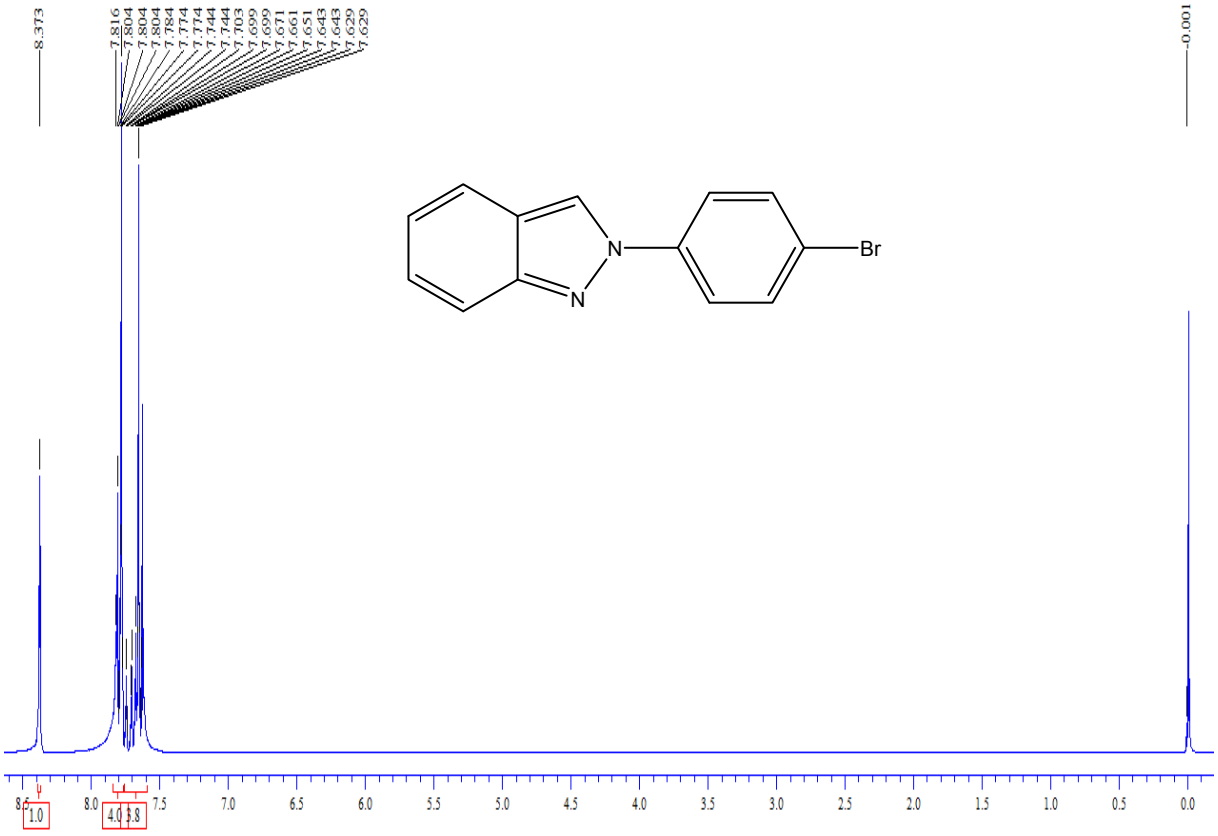


Table 2, Entry 8: 2-(4-Bromophenyl)-2*H*-indazole:



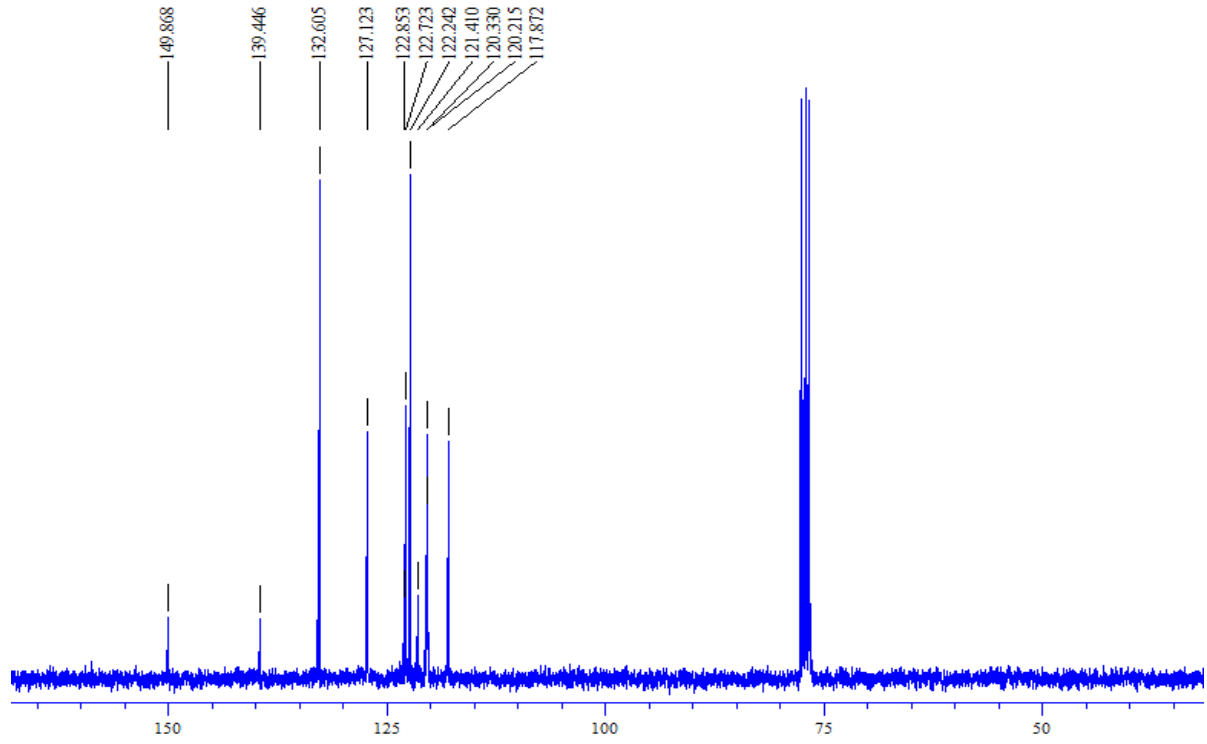


Table 2, Entry 9: 5-Fluoro-2-(3,4-dimethylphenyl)-2*H*-indazole:

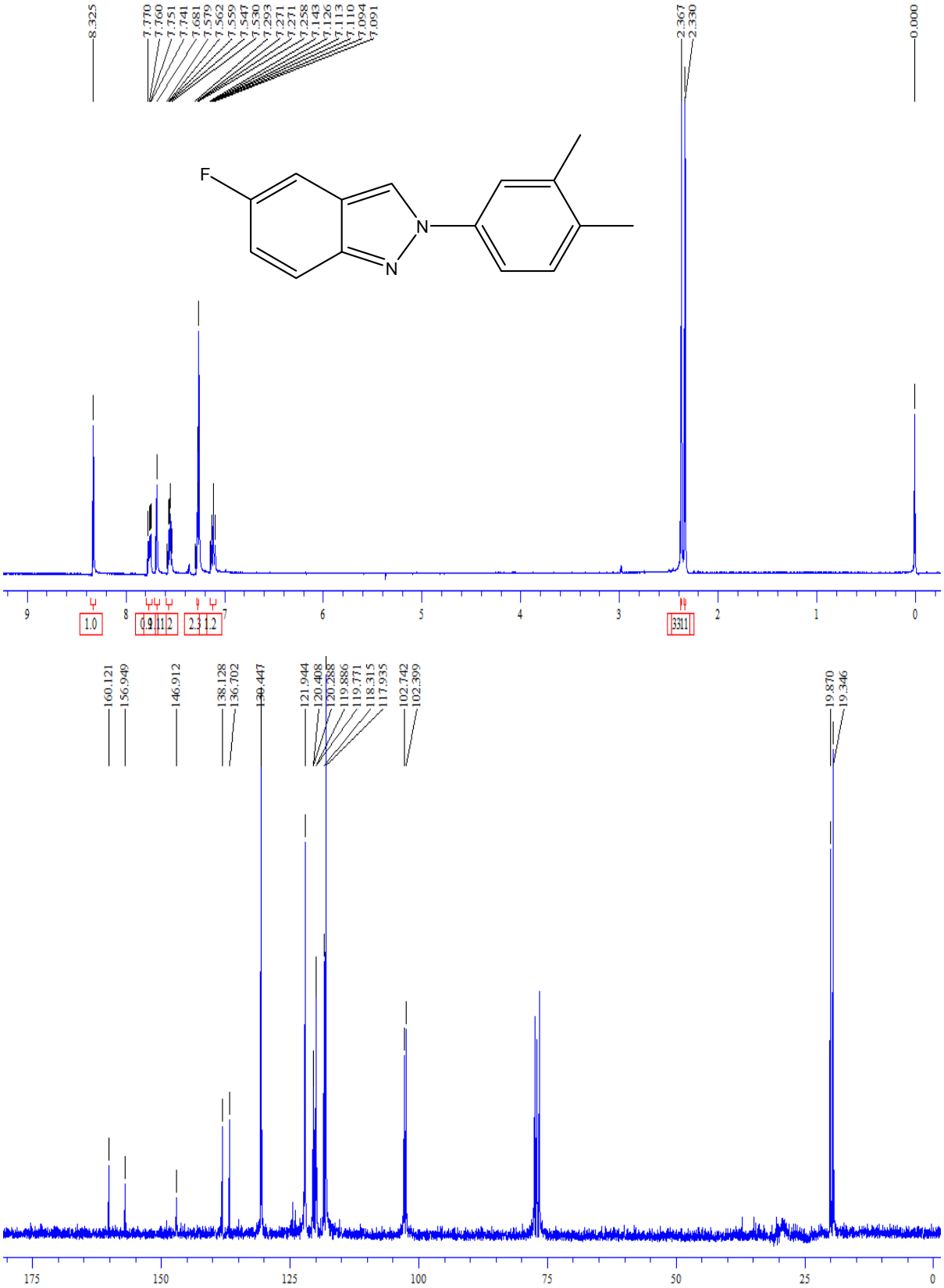
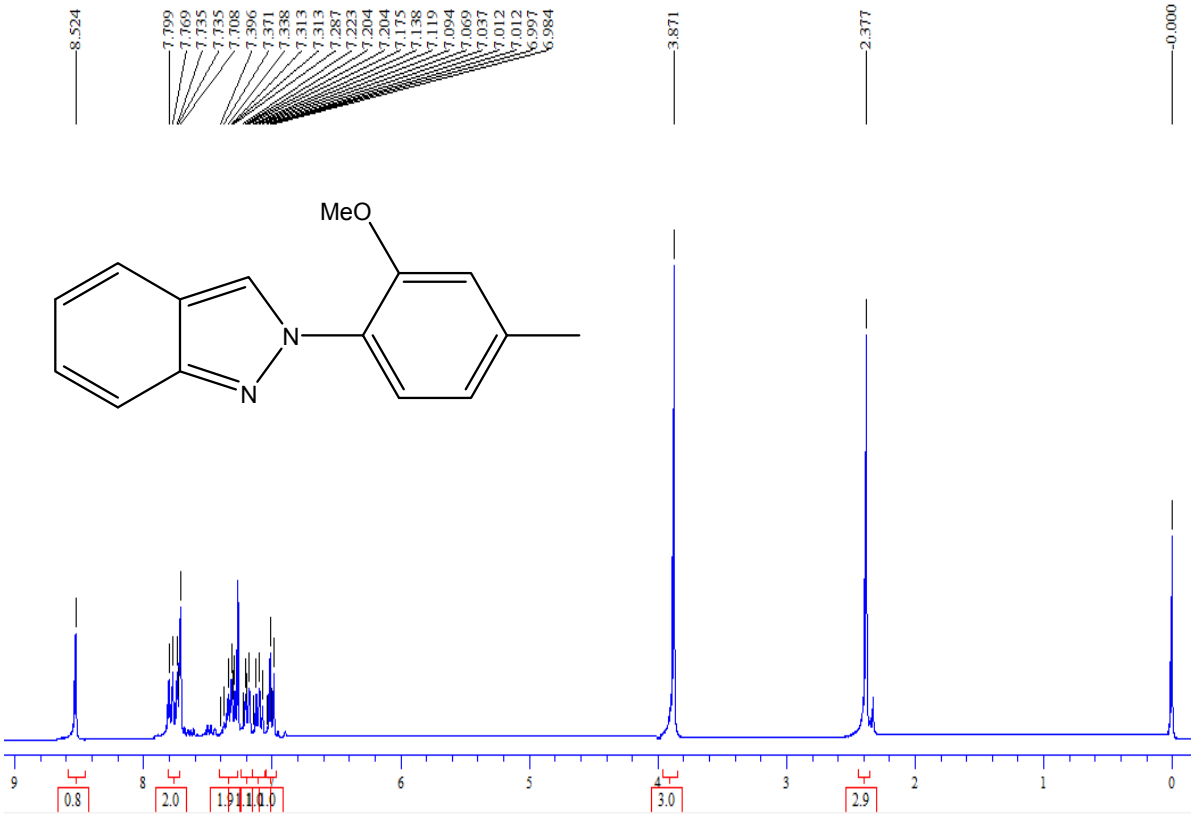


Table 2, Entry 10: 2-(2-Methoxy-4-methylphenyl)-2*H*-indazole:



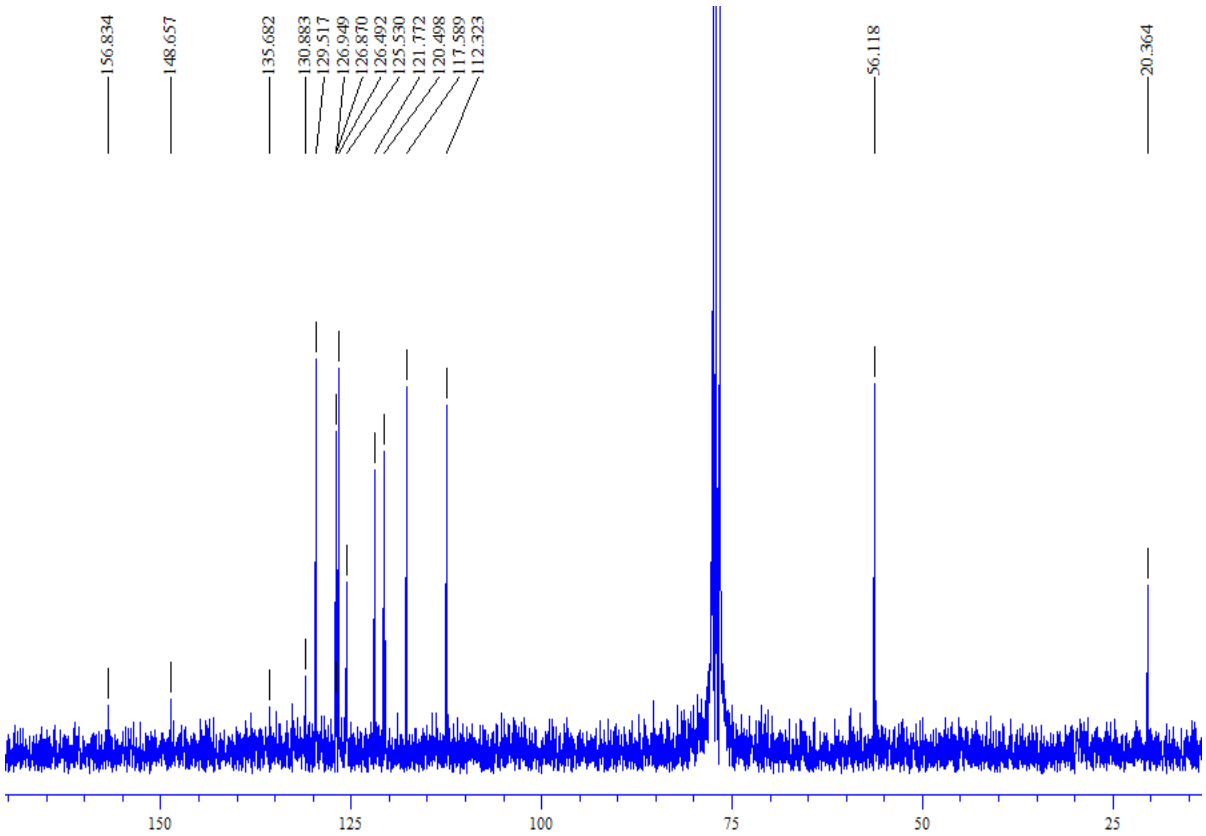


Table 2, Entry 11: 5-Fluoro-2-phenyl-2*H*-indazole:

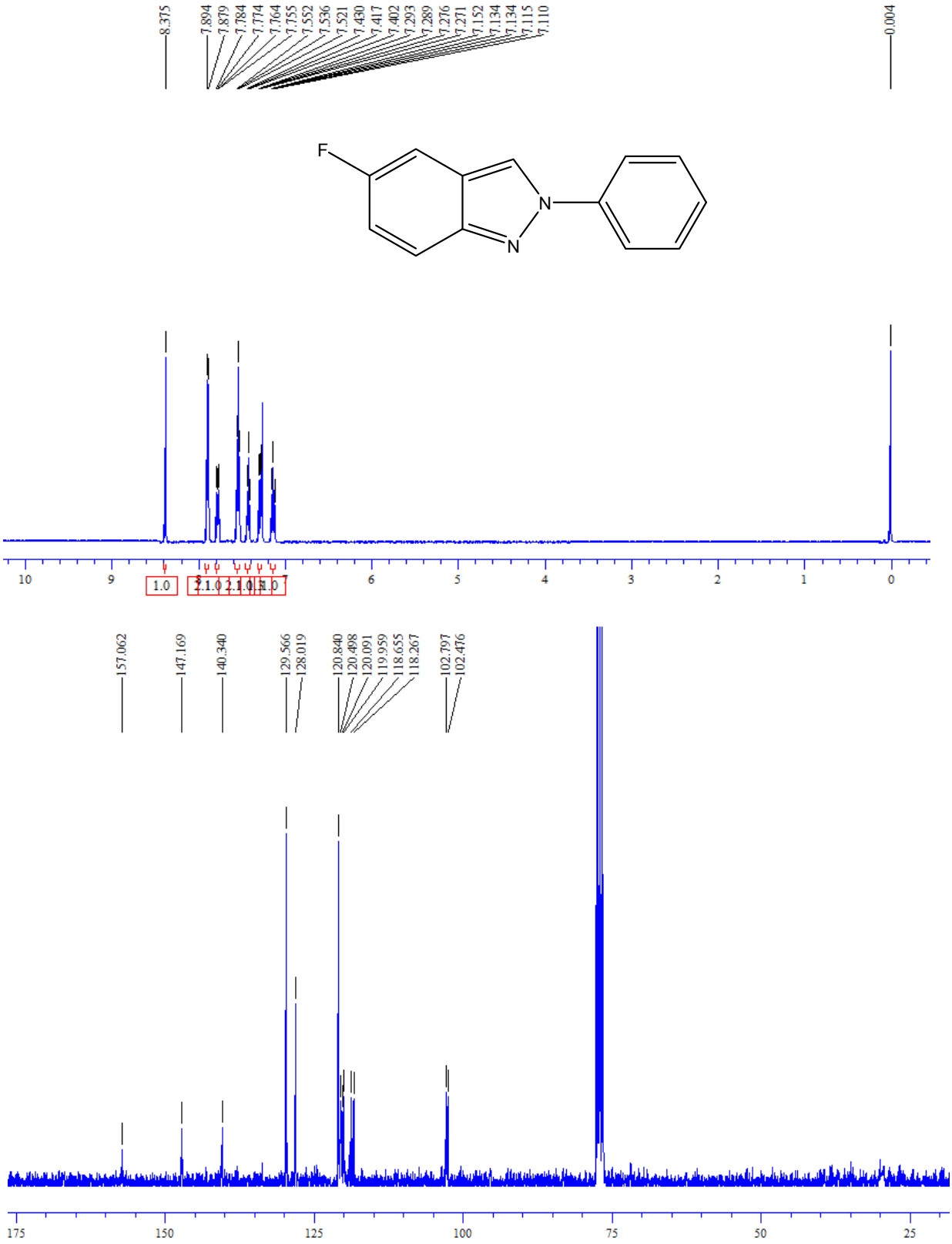
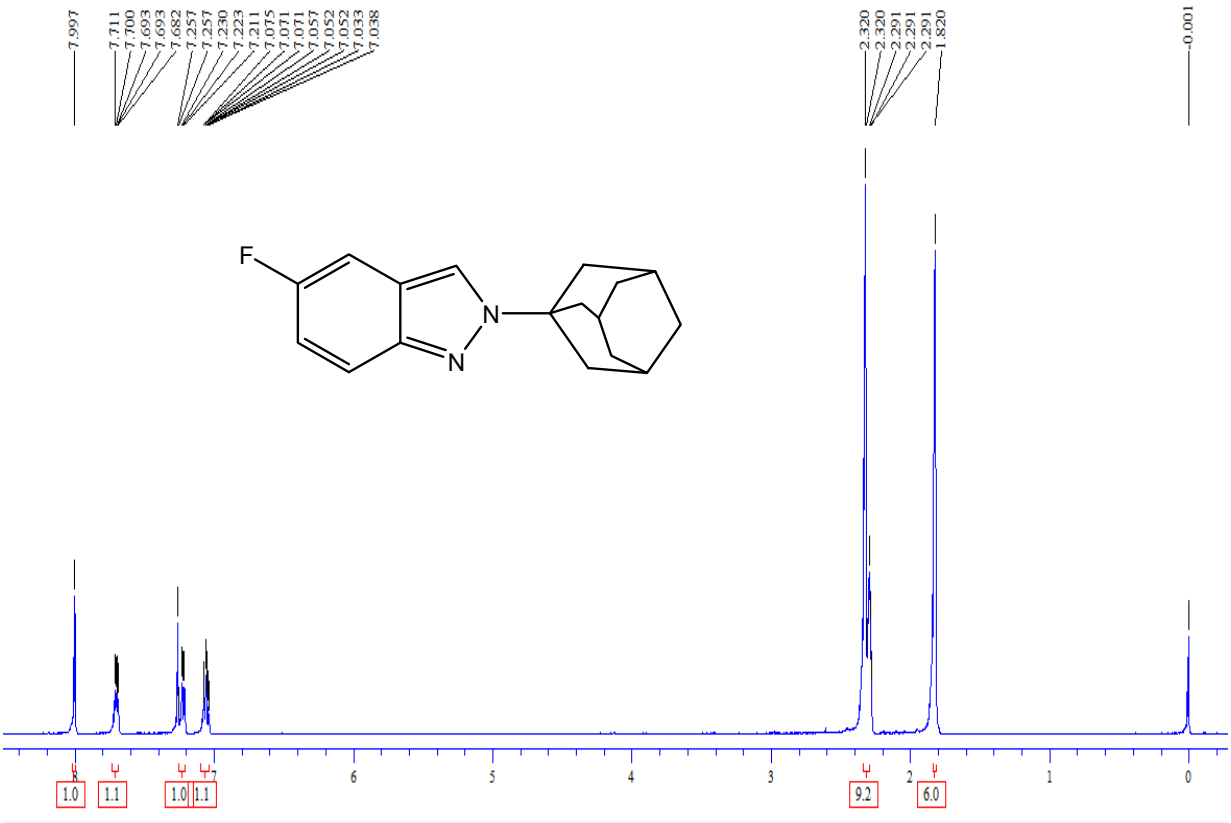


Table 2, Entry 12: 5-Fluoro2-adamantyl-2*H*-indazole:



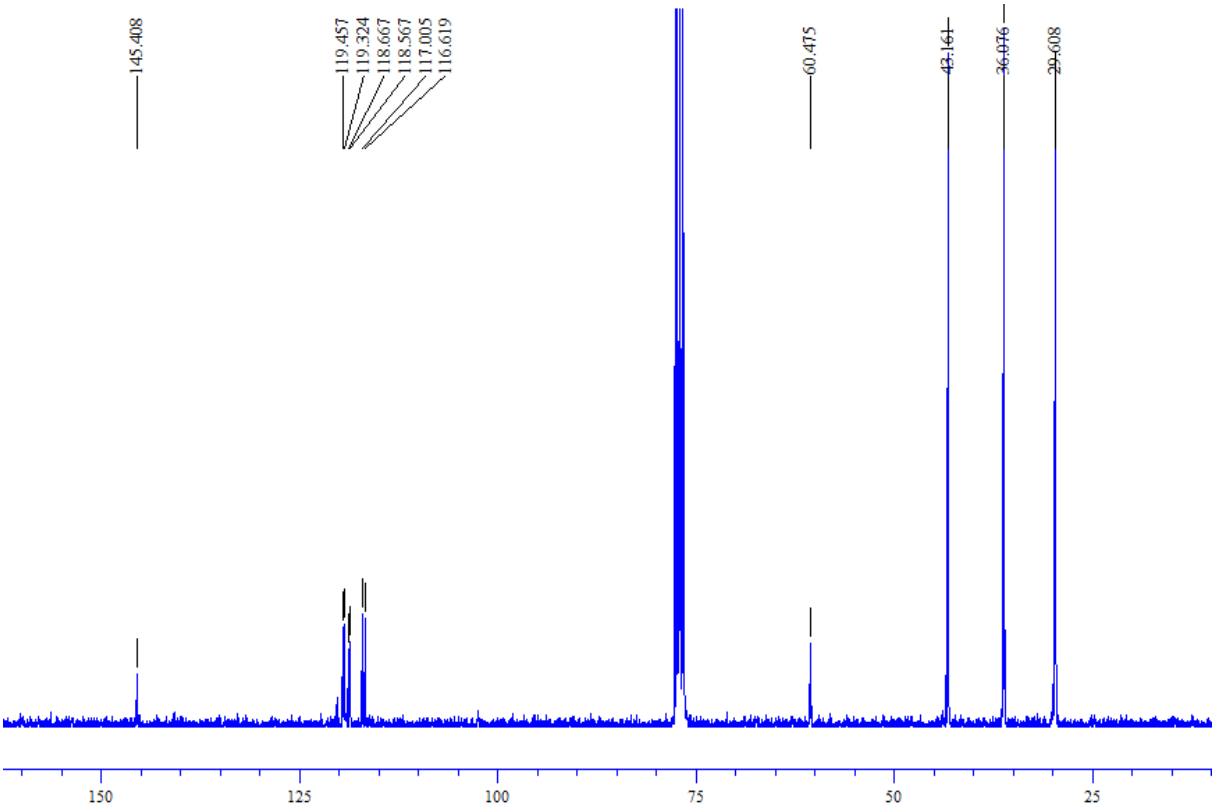
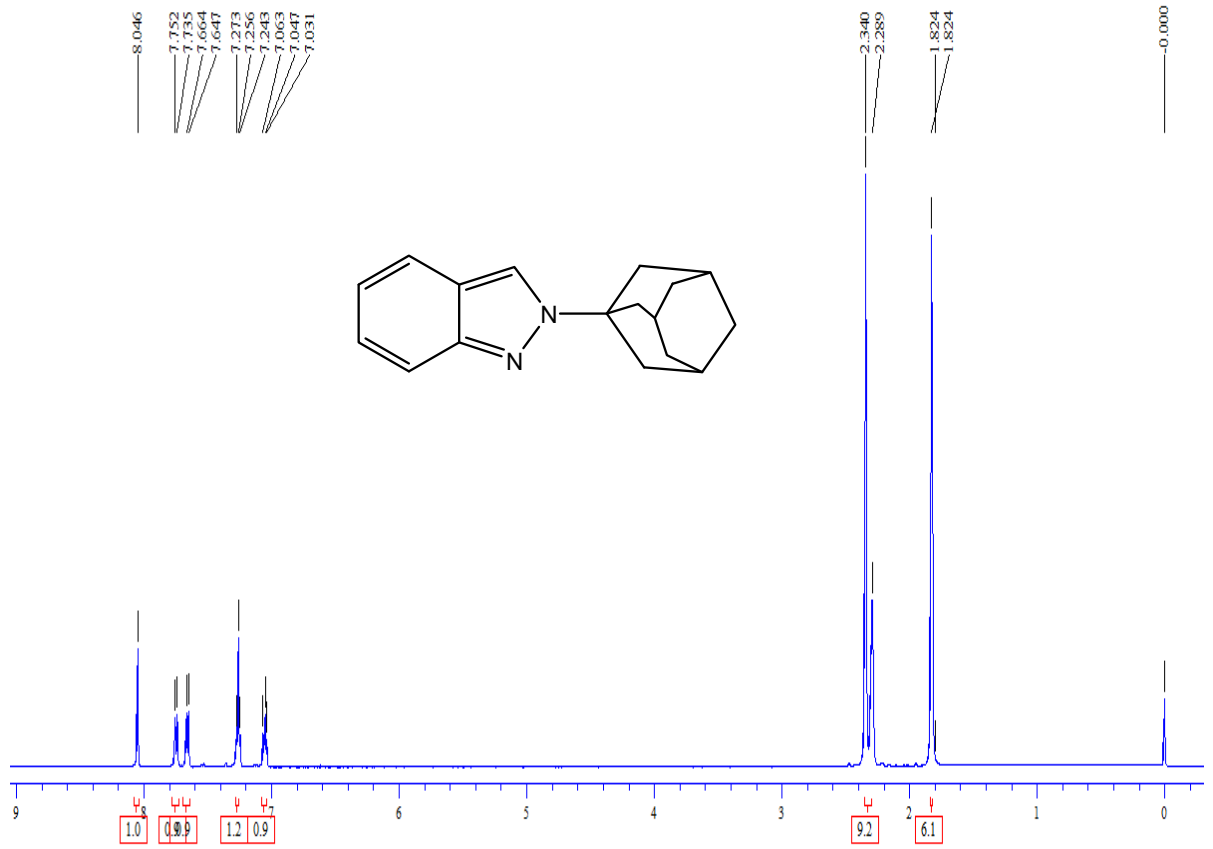


Table 2, Entry 13: 2-Adamantyl-2*H*-indazole:



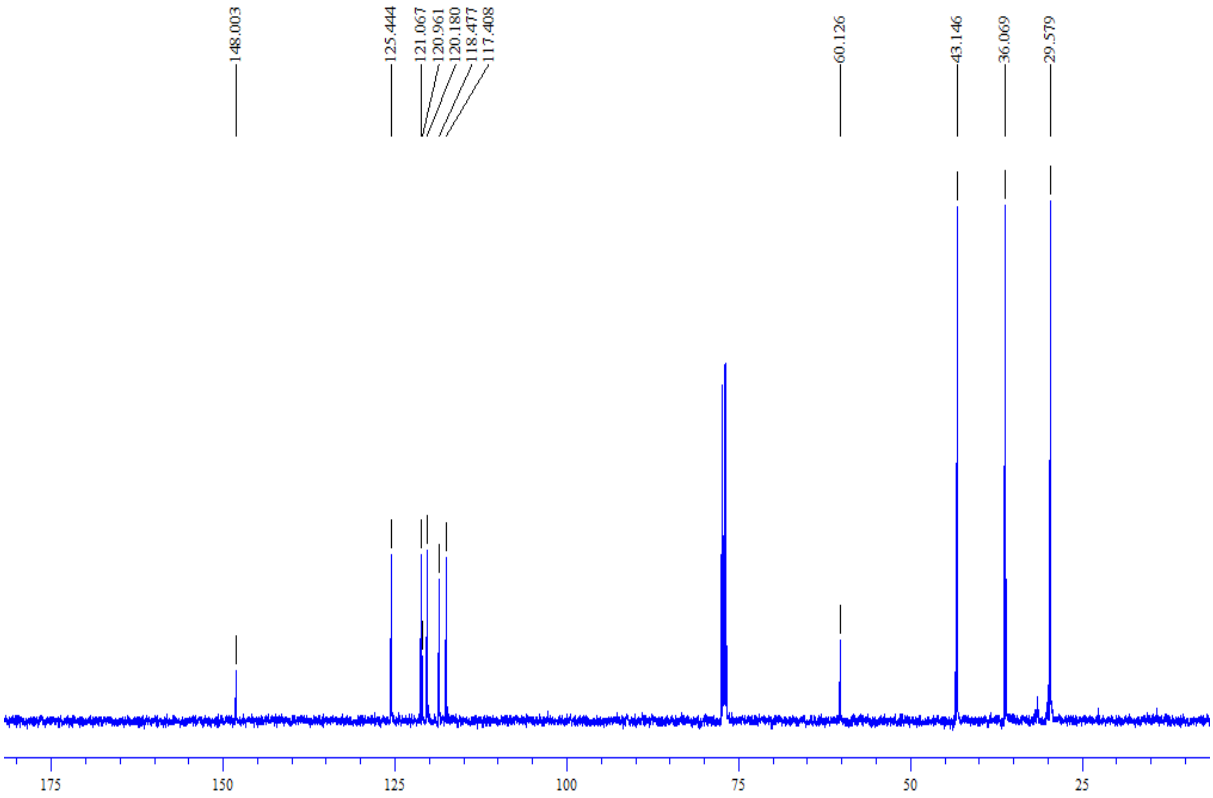
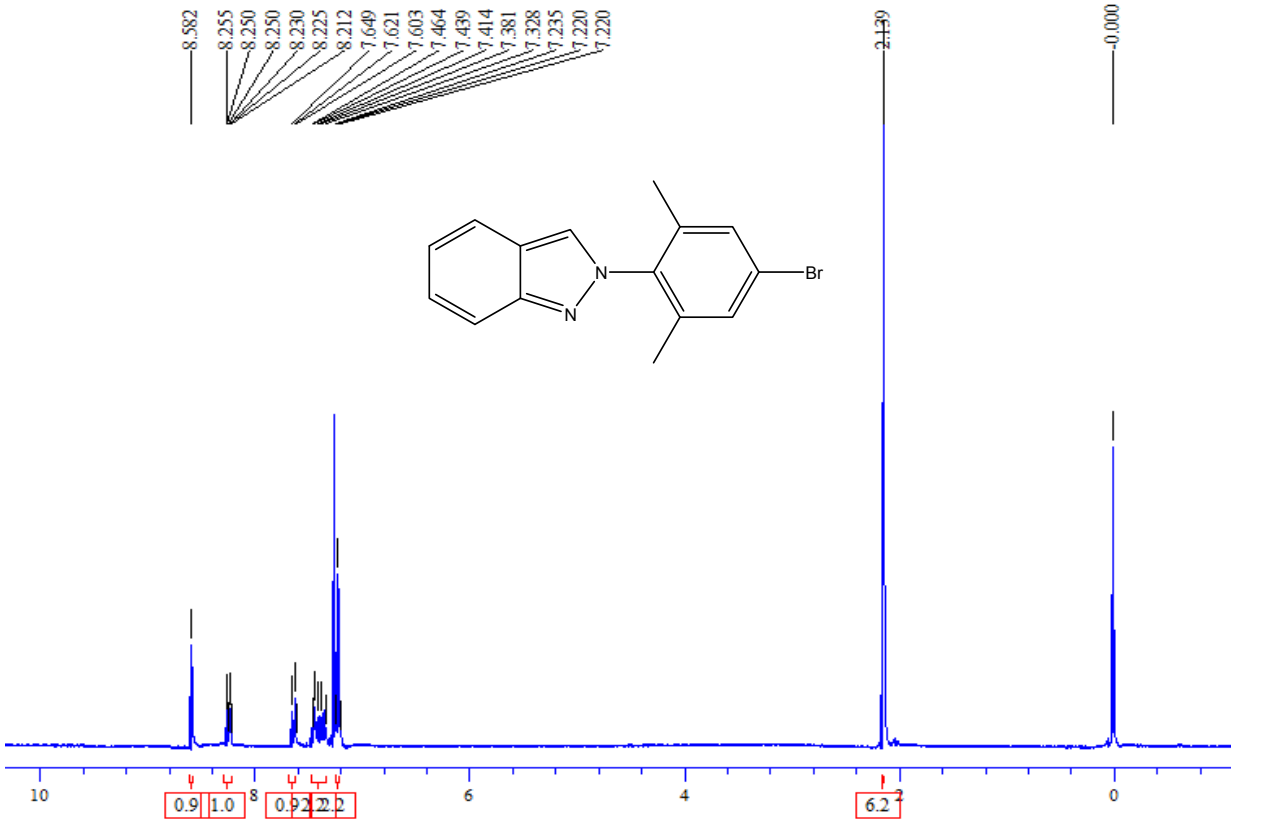


Table 2, Entry 14: 2-(4-Bromo-2,6-dimethylphenyl)-2*H*-indazole:



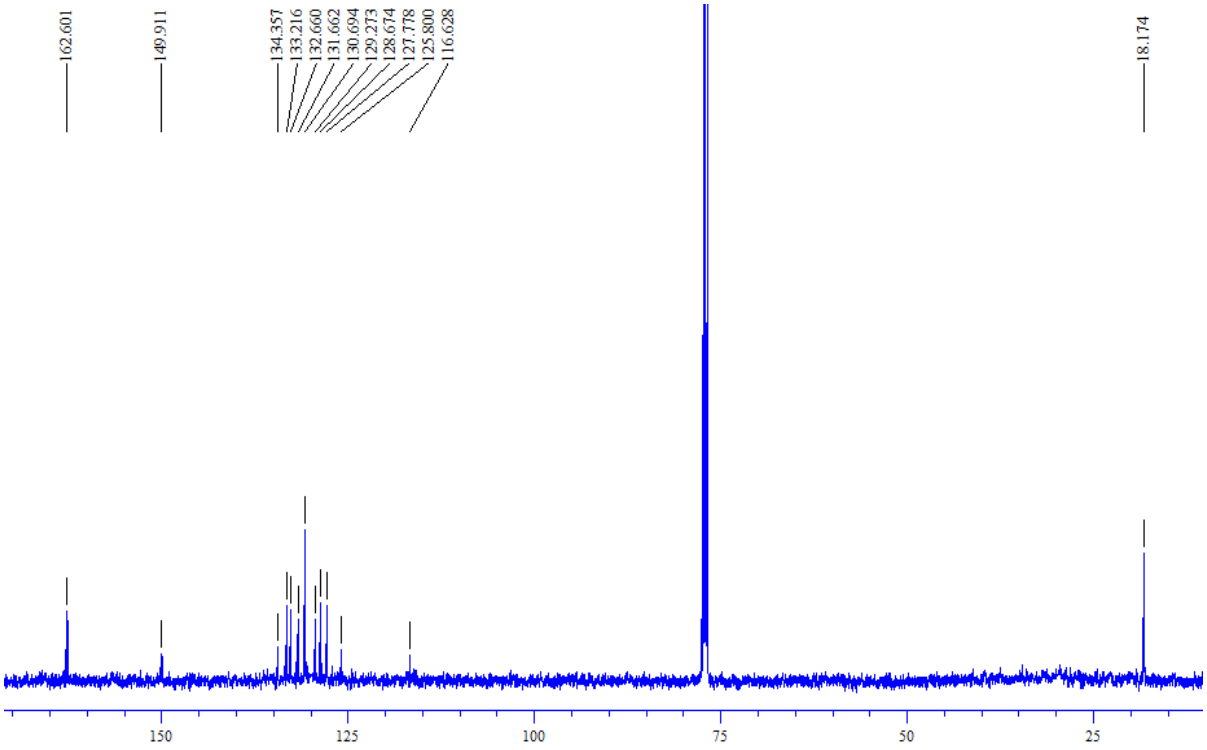


Table 2, Entry 15: 2-(4-Bromo-2,6-dimethylphenyl)-5-fluoro-2*H*-indazole: