Rh^{III}/Cu^{II}-Cocatalyzed Synthesis of 1*H*-indazoles through C–H Amidation and N–N Bond Formation

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Supporting Information

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1 General Considerations

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame dried glassware. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. The solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: CH_2Cl_2 (CaH_2) and toluene (CaH_2). Anhydrous DCE, 1,4-dioxane, *t*-amyl alcohol, DMSO and DMF were purchased from Acros Organics and stored over molecular sieves under argon.

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with UV light and vanillin, ninhydrine and/or $KMnO_4$ staining solutions followed by heating.

Flash chromatography was either performed on Merck silica gel (40-63 mesh) by standard technique or using a Biotage Isolera Flash Purification System eluting with gradients of solvents as stated for the R_f values.

^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicated. Chemical shifts (δ) for ^1H and ^{13}C NMR spectra are given in ppm relative to TMS, for ^{19}F NMR spectra relative to $\delta(CCl_3F) = 0$ ppm. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm; d_6-DMSO: δH = 2.50 ppm, δC = 39.52 ppm; d_6-CD_3OD: δH = 3.31 ppm, δC = 49.00 ppm). ^{19}F NMR spectra are not calibrated by any internal reference.

GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, Film: 0.25 μm). The major signals are quoted in *m*/*z* with the relative intensity in parentheses. The methods used start with the injection tempereature T0;

after holding this temperature for 3 min, the column is heated to temperature T1 (ramp) and this temperature is held for an additional time t:

Method **50_20**: T0 = 50 °C, T1 = 280 °C, ramp = 20 °C/min, t = 3 min;

Method **50_40**: T0 = 50 °C, T1 = 290 °C, ramp = 40 °C/min, t = 4 min;

Method **50_20_320**: T0 = 50 °C, T1 = 320 °C, ramp = 20 °C/min, t = 3 min.

Exact ESI mass spectra were recorded on a Bruker Daltonics MicroTof. Mass Calibration was carried out directly before the measurement of the sample using clusters of sodium formate.

2 Synthesis of Substrates

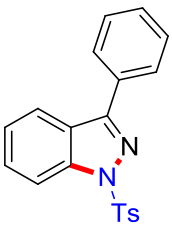
The benzimidates[1] and organo azides[2] were prepared according to the methods given in the cited references without any optimization of the reaction conditions.

3 Synthesis and Characterization of Products

General Procedure for the synthesis of indazoles:

GP1: In a flame dried red-cap tube, weighed molecular sieves (4Å MS) was activated under vacuum. In the glovebox, $[RhCp^*Cl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) and $Cu(OAc)_2$ (25 mol%) were weighed into the tube. Under Argon, the benzimidate substrate (0.2-0.25 mmol, 1 eq.) was added, followed by the sequential addition of *p*-toluenesulfonyl azide (2.5 eq.) and DCE (0.2 M) into the tube. The tube was degassed and refilled with molecular oxygen (1 atm). The tube was closed and stirred at 110 °C for 24 h. The reaction mixture was then cooled to room temperature and monitored over GC-MS and TLC. The reaction mixture was diluted with EtOAc and filtered over a short pad of celite pre-packed with EtOAc. The volatiles were removed and the analytically pure product was obtained by flash chromatography (silica; gradient of n-pentane/EtOAc).

GP2: Same procedure as mentioned in **GP1** except $Cu(OAc)_2$ was added in 2.1 eq. instead of 25 mol% and the reaction was carried out under an atmosphere of Argon.



3-Phenyl-1-tosyl-1*H*-indazole (3a)

Slightly yellowish solid;

GP2 (without 4Å MS): 29.3 mg, 0.08 mmol, 42%;

R_f (pentane/EtOAc 90:10): 0.39;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (dt, *J* = 8.6, 0.9 Hz, 1H, H_{arom}), 7.99 – 7.84 (m, 5H, H_{arom}), 7.58 (m, 1H, H_{arom}), 7.55 – 7.45 (m, 3H, H_{arom}), 7.37 (m, 1H, H_{arom}), 7.25 – 7.17 (m, 2H, H_{arom}), 2.34 (s, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.83 (C_{arom}), 145.37 (C_{arom}), 141.97 (C_{arom}), 134.76 (C_{arom}), 131.53 (C_{arom}), 129.92 (CH_{arom}), 129.68 (CH_{arom}), 129.19 (CH_{arom}), 128.95 (CH_{arom}), 128.39 (CH_{arom}), 127.72 (CH_{arom}), 124.56 (CH_{arom}), 124.44 (C_{arom}), 121.79 (CH_{arom}), 113.72 (CH_{arom}), 21.74 (CH_3);

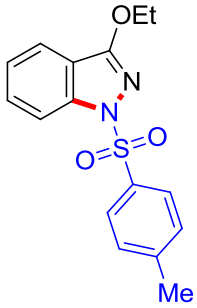
GC MS: t_R (50_40) = 12.1 min;

EI MS: *m/z* (%) = 65(15), 91(35), 139(17), 163(26), 164(28), 165(91), 166(14), 193(100), 194(18), 284(44), 285(10), 348(73);

Exact Mass ESI-MS: calculated m/z for $[C_{20}H_{16}N_2O_2SNa]^+$: 371.0825, found: 371.0826; for $[(C_{20}H_{16}N_2O_2S)_2Na]^+$: 719.1757, found: 719.1756;

ATR-FTIR (cm^{-1}): 3009, 2015, 1594, 1488, 1368, 1259, 1176, 1089, 1050, 1025, 730, 670, 564;

3-Ethoxy-1-tosyl-1*H*-indazole (3aa)



Slightly yellowish solid;

GP1: 45.4 mg, 0.15 mmol, 75%;

R_f (pentane/EtOAc 90:10): 0.39;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (dt, *J* = 8.6, 0.9 Hz, 1H, H_{arom}), 7.79 – 7.67 (m, 2H, H_{arom}), 7.61 – 7.48 (m, 2H, H_{arom}), 7.21 – 7.10 (m, 2H, H_{arom}), 4.47 (q, *J* = 7.1 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.42 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.68 (C_{arom}), 144.91 (C_{arom}), 143.20 (C_{arom}), 133.84 (C_{arom}), 130.16 (CH_{arom}), 129.58 (CH_{arom}), 127.63 (CH_{arom}), 124.26 (CH_{arom}), 120.34 (CH_{arom}), 118.41 (C_{arom}), 114.39 (CH_{arom}), 65.73 (CH_2), 21.71 (CH_3), 14.52 (CH_3);

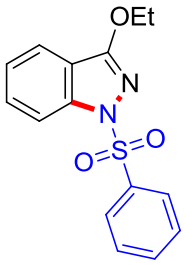
GC MS: t_R (50_40) = 10.6 min;

EI MS: *m/z* (%) = 65(17), 76(28), 77(30), 91(40), 104(24), 105(37), 133(100), 134(11), 155(13), 161(50), 316(59);

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{16}N_2O_3SNa]^+$: 339.0774, found: 339.0771;

ATR-FTIR (cm^{-1}): 2985, 2129, 1594, 1490, 1471, 1371, 1350, 1242, 1173, 1121, 1051, 817, 753, 675, 594;

3-Ethoxy-1-(phenylsulfonyl)-1*H*-indazole (3ab)



White solid;

GP1: 40.9 mg, 0.135 mmol, 68%;

Rf (pentane/EtOAc=20:1): 0.35;

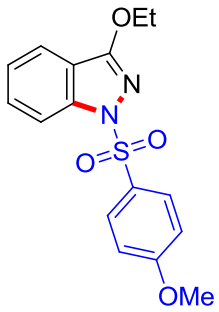
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.51 – 7.41 (m, 3H), 7.33-7.29 (m, 2H), 7.22 – 7.18 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.75, 143.17, 136.76, 133.84, 130.23, 128.94, 127.57, 124.36, 120.38, 118.42, 114.34, 65.76, 14.49;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{14}N_2O_3SNa]^+$: 325.0623, found: 325.0618;

ATR-FTIR (cm^{-1}): 3101, 2987, 1543, 1443, 1373, 1178, 753, 570;

3-Ethoxy-1-((4-methoxyphenyl)sulfonyl)-1*H*-indazole (3ac)



White solid;

GP1: 50.1 mg, 0.151 mmol, 76%;

R_f (pentane/EtOAc=20:1): 0.15;

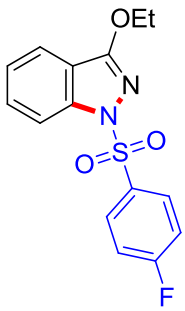
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.50 – 7.43 (m, 2H), 7.21 – 7.17 (m, 1H), 6.77 – 6.73 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.82, 161.65, 143.21, 130.10, 129.83, 128.29, 124.20, 120.31, 118.39, 114.38, 114.11, 65.69, 55.69, 14.52;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{16}N_2O_4SNa]^+$: 355.0728, found: 355.0727;

ATR-FTIR (cm^{-1}): 2992, 1594, 1541, 1496, 1371, 1354, 1264, 1245, 1164, 1019, 754, 677;

3-Ethoxy-1-((4-fluorophenyl)sulfonyl)-1*H*-indazole (3ad)



White solid;

GP1: 40.9 mg, 0.128 mmol, 64%;

R_f (pentane/EtOAc=20:1): 0.40;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.53 – 7.45 (m, 2H), 7.25 – 7.19 (m, 1H), 7.02 – 6.95 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H);

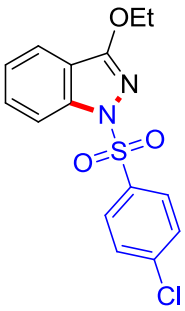
^{13}C NMR (75 MHz, $CDCl_3$) δ 165.65 (d, *J* = 256.6 Hz), 161.80, 142.97, 132.52 (d, *J* = 3.3 Hz), 130.30 (d, *J* = 9.7 Hz), 130.21, 124.38, 120.34, 118.36, 116.17 (d, *J* = 22.7 Hz), 114.16, 65.67, 14.35;

^{19}F NMR (282 MHz, $CDCl_3$) δ = -102.98.

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{13}FN_2O_3SNa]^+$: 343.0529, found: 343.0527;

ATR-FTIR (cm^{-1}): 3107, 2986, 1589, 1544, 1373, 1353, 1239, 1180, 755, 678;

1-((4-Chlorophenyl)sulfonyl)-3-ethoxy-1*H*-indazole (3ae)



White solid;

GP1: 41.8mg, 0.124 mmol, 62%;

R_f (pentane/EtOAc=20:1): 0.45;

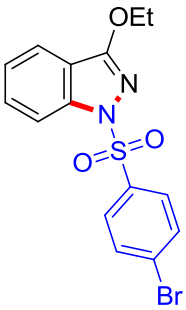
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.52 – 7.45 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24-7.20 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.02, 143.09, 140.54, 135.08, 130.41, 129.31, 129.02, 124.61, 120.54, 118.55, 114.30, 65.86, 14.51;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{13}ClN_2O_3SNa]^+$: 359.0233, found: 359.0238;

ATR-FTIR (cm^{-1}): 3097, 2984, 1591, 1541, 1377, 1345, 1179, 1089, 1011, 755, 655, 620;

1-((4-Bromophenyl)sulfonyl)-3-ethoxy-1*H*-indazole (3af)



White solid;

GP1: 45.7 mg, 0.120 mmol, 60%;

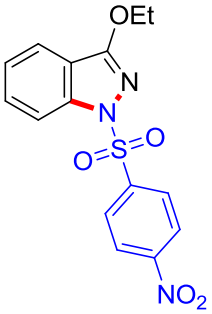
R_f (pentane/EtOAc=20:1): 0.45;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.52 – 7.43 (m, 4H), 7.24 – 7.22 (m, 1H), 4.39 (q, *J* = 7.0 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.03, 143.07, 135.60, 132.29, 130.41, 129.16, 129.06, 124.61, 120.55, 118.55, 114.29, 65.87, 14.52;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{13}BrN_2O_3SNa]^+$: 402.9728, found: 402.9721;

ATR-FTIR (cm^{-1}): 3093, 2977, 1543, 1379, 1350, 1248, 1170, 1014, 739, 654, 617;



3-Ethoxy-1-((4-nitrophenyl)sulfonyl)-1*H*-indazole (3ag)

Yellowish solid;

GP1: 32.0 mg, 0.092 mmol, 46%;

R_f (pentane/EtOAc=20:1): 0.20;

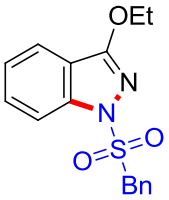
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 – 8.14 (m, 2H), 8.04 – 7.95 (m, 3H), 7.54 – 7.48 (m, 2H), 7.28 – 7.23 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.44, 150.72, 142.92, 141.94, 130.77, 128.95, 125.05, 124.21, 120.77, 118.70, 114.22, 66.05, 14.49;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{13}N_3O_5SNa]^+$: 370.0474, found: 370.0470;

ATR-FTIR (cm^{-1}): 3113, 1599, 1528, 1374, 1352, 1245, 1183, 739, 656, 615;

1-(Benzylsulfonyl)-3-ethoxy-1*H*-indazole (3ah)



White solid;

GP1: 31.2 mg, 0.099 mmol, 49%;

R_f (pentane/EtOAc=20:1): 0.20;

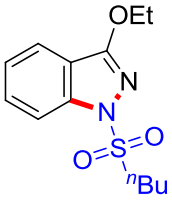
^{1}H NMR (300 MHz, $CDCl_3$) δ7.54 – 7.45 (m, 2H), 7.24 – 7.18 (m, 1H), 7.14 – 6.99 (m, 4H), 6.94 – 6.91 (m, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.42 (s, 2H), 1.46 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.10, 143.87, 130.67, 129.91, 129.10, 128.57, 126.86, 123.69, 119.98, 116.81, 113.37, 65.85, 58.74, 14.72;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{16}N_2O_3SNa]^+$: 339.0779, found: 339.0778;

ATR-FTIR (cm^{-1}): 2980, 1538, 1362, 1252, 1165, 742, 700;

1-(Butylsulfonyl)-3-ethoxy-1*H*-indazole (3ai)



Colorless oil

GP1: 28.6 mg, 0.101 mmol, 51%;

R_f (pentane/EtOAc=20:1): 0.35;

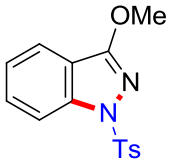
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.62 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.45 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H), 7.24 (ddd, *J* = 7.9, 7.1, 0.9 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.46 – 2.93 (m, 2H), 1.57 (ddt, *J* = 9.8, 5.0, 3.6 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.28 (h, *J* = 7.4 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.96, 143.12, 130.24, 123.95, 120.43, 117.24, 113.76, 65.79, 52.44, 24.86, 21.41, 14.68, 13.50;

Exact Mass ESI-MS: calculated m/z for $[C_{13}H_{18}N_2O_3SNa]^+$: 305.0936, found: 305.0937;

ATR-FTIR (cm^{-1}): 2990, 1543, 1371, 1354, 1256, 1166, 1019, 751, 654, 608;

3-Methoxy-1-tosyl-1*H*-indazole (3ba)



Slightly yellowish solid;

GP1: 49.9 mg, 0.17 mmol, 66%;

R_f (pentane/EtOAc 90:10): 0.35;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 – 8.06 (m, 1H, H_{arom}), 7.82 – 7.69 (m, 2H, H_{arom}), 7.54 (m, 2H, H_{arom}), 7.32 – 7.23 (m, 1H, H_{arom}), 7.17 (dd, *J* = 8.2, 1.0 Hz, 2H, H_{arom}), 4.09 (s, 3H, CH_3), 2.33 (s, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.27 (C_{arom}), 144.97 (C_{arom}), 143.30 (C_{arom}), 133.81 (C_{arom}), 130.24 (CH_{arom}), 129.61 (CH_{arom}), 127.62 (CH_{arom}), 124.32 (CH_{arom}), 120.27 (CH_{arom}), 118.06 (C_{arom}), 114.39 (CH_{arom}), 56.97 (CH_3), 21.71 (CH_3);

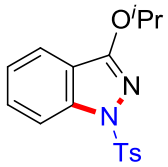
GC MS: t_R (50_40) = 10.5 min;

EI MS: *m/z* (%) = 65(18), 76(30), 91(30), 104(22), 119(44), 147(100), 148(11), 302(61);

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{14}N_2O_3SNa]^+$: 325.0617, found: 325.0618;

ATR-FTIR (cm^{-1}): 3033, 2921, 2851, 1597, 1548, 1490, 1449, 1386, 1367, 1242, 1170, 1119, 1050, 994, 954, 810, 752, 673, 752, 656, 596;

3-Isopropoxy-1-tosyl-1*H*-indazole (3ca)



White solid;

GP1: 56.7 mg, 0.17 mmol, 69%;

R_f (pentane/EtOAc 90:10): 0.38;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (dt, *J* = 8.4, 0.9 Hz, 1H, H_{arom}), 7.69 – 7.59 (m, 2H, H_{arom}), 7.45 (m, 2H, H_{arom}), 7.23 – 7.13 (m, 1H, H_{arom}), 7.12 – 7.01 (m, 2H, H_{arom}), 5.16 (hept, *J* = 6.2 Hz, 1H, CH), 2.24 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.28 (s, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = δ 161.04 (C_{arom}), 144.88 (C_{arom}), 143.18 (C_{arom}), 133.81 (C_{arom}), 130.08 (CH_{arom}), 129.51 (CH_{arom}), 127.64 (CH_{arom}), 124.20 (CH_{arom}), 120.41 (CH_{arom}), 119.02 (C_{arom}), 114.39 (CH_{arom}), 73.03 (CH), 21.82 (CH_3), 21.67 (CH_3);

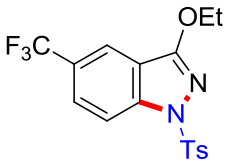
GC MS: t_R (50_40) = 10.6 min;

EI MS: *m/z* (%) = 76(16), 77(17), 91(28), 104(21), 105(14), 133(100), 134(11), 155(15), 288(17), 330(17);

Exact Mass ESI-MS: calculated m/z $[C_{17}H_{18}N_2O_3SNa]^+$: 353.0930, found: 353.0928;

ATR-FTIR (cm^{-1}): 2981, 2127, 1595, 1539, 1488, 1469, 1439, 1370, 1335, 1246, 1176, 1110, 1048, 989, 918, 752, 673, 594;

3-Ethoxy-1-tosyl-5-(trifluoromethyl)-1*H*-indazole (3da)



White solid;

GP1: 76.9 mg, 0.20 mmol, 80%;

R_f (pentane/EtOAc 90:10): 0.49;

^{1}H NMR (400 MHz, $CDCl_3$): 8.26 – 8.18 (m, 1H, H_{arom}), 7.89 (dq, *J* = 1.8, 0.9 Hz, 1H, H_{arom}), 7.80 – 7.72 (m, 3H, H_{arom}), 7.22 (dt, *J* = 7.4, 0.9 Hz, 2H, H_{arom}), 4.48 (q, *J* = 7.1 Hz, 2H, CH_2), 2.35 (s, 3H, CH_3), 1.44 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.05 (C_{arom}), 145.49 (C_{arom}), 144.13 (C_{arom}), 133.83 (C_{arom}), 130.42 (C_{arom}), 129.83 (CH_{arom}), 127.66 (CH_{arom}), 126.84 (q, $^3J_{CF3}$ = 3.0 Hz, CH_{arom}), 126.64(q, $^2J_{CF3}$ = 32.0 Hz, C_{arom}), 124.09 (q, $^1J_{CF3}$ = 272.4 Hz, CF_3), 118.53 (q, $^3J_{CF3}$ = 4.2 Hz, CH_{arom}), 114.76 (CH_{arom}), 66.16 (CH_2), 21.76 (CH_3), 14.47 (CH_3);

^{19}F NMR (282 MHz, $CDCl_3$) δ = -61.52 (s, CF_3);

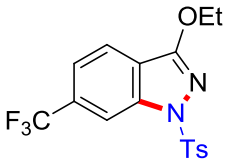
GC MS: t_R (50_40) = 10.1 min;

EI MS: *m/z* (%) = 65(27), 91(100), 92(15), 125(11), 144(28), 145(32), 155(95), 156(12), 172(19), 173(45), 201(62), 229(28), 384(62);

Exact Mass ESI-MS: calculated m/z $[C_{17}H_{15}F_3N_2O_3SNa]^+$: 407.0648, found: 407.0642;

ATR-FTIR (cm^{-1}): 3059, 2987, 2129, 1629, 1548, 1373, 1319, 1279, 1123, 1055, 1020, 906, 827, 810, 679, 665, 595;

3-Ethoxy-1-tosyl-6-(trifluoromethyl)-1*H*-indazole (3ea)



White solid;

GP1: 58.0 mg, 0.151 mmol, 76%;

R_f (pentane/EtOAc=20:1): 0.35;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H);

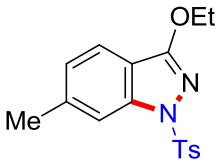
^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.76, 145.47, 142.14, 133.71, 132.19 (q, *J* = 32.6 Hz), 129.83, 127.70, 123.25 (q, *J* = 268.0 Hz), 121.33, 120.88 (q, *J* = 3.4 Hz), 120.21 (d, *J* = 1.4 Hz), 111.77 (q, *J* = 4.4 Hz), 66.15, 21.75, 14.46;

^{19}F NMR (282 MHz, $CDCl_3$) δ = -61.79;

Exact Mass ESI-MS: calculated m/z for $[C_{17}H_{15}F_3N_2O_3SNa]^+$: 407.0653, found: 407.0652;

ATR-FTIR (cm^{-1}): 2995, 1546, 1376, 1325, 1165, 1121, 1054, 665;

3-Ethoxy-6-methyl-1-tosyl-1*H*-indazole (3fa)



White solid;

GP1: 53.7 mg, 0.16 mmol, 65%;

R_f (pentane/EtOAc 90:10): 0.39;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (q, *J* = 1.0 Hz, 1H, H_{arom}), 7.76 – 7.67 (m, 2H, H_{arom}), 7.43 (dd, *J* = 8.0, 0.7 Hz, 1H, H_{arom}), 7.23 – 7.15 (m, 2H, H_{arom}), 7.09 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H, H_{arom}), 4.44 (q, *J* = 7.1 Hz, 2H, CH_2), 2.52 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 1.41 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.66 (C_{arom}), 144.80 (C_{arom}), 143.81 (C_{arom}), 141.04 (C_{arom}), 134.00 (C_{arom}), 129.56 (CH_{arom}), 127.64 (CH_{arom}), 126.07 (CH_{arom}), 119.81 (CH_{arom}), 116.36 (C_{arom}), 114.24 (CH_{arom}), 65.61 (CH_2), 22.31 (CH_3), 21.72 (CH_3), 14.54 (CH_3);

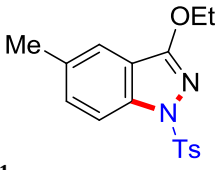
GC MS: t_R (50_40) = 10.4 min;

EI MS: *m/z* (%) = 65(29), 89(27), 90(24), 91(60), 118(23), 119(43), 147(100), 148(14), 175(92), 176(12), 330(66);

Exact Mass ESI-MS: calculated m/z $[C_{17}H_{18}N_2O_3SNa]^+$: 353.0930, found: 353.0925;

ATR-FTIR (cm^{-1}): 2986, 2882, 1595, 1540, 1433, 1370, 1304, 1261, 1173, 1091, 1043, 996, 814, 704, 668, 622, 577;

3-Ethoxy-5-methyl-1-tosyl-1*H*-indazole (3ga)



White solid;

GP1: 43.0 mg, 0.130 mmol, 65%;

R_f (pentane/EtOAc=20:1): 0.35;

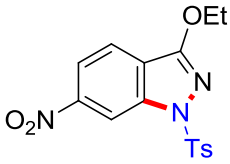
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.2 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 2.24 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.64, 144.76, 141.75, 134.30, 133.70, 131.79, 129.50, 127.60, 119.74, 118.79, 114.14, 65.64, 21.69, 21.23, 14.52;

Exact Mass ESI-MS: calculated m/z for $[C_{17}H_{18}N_2O_3SNa]^+$: 353.0936, found: 353.0930;

ATR-FTIR (cm^{-1}): 2993, 1590, 1543, 1366, 1247, 1178, 1065, 1020, 805, 668;

3-Ethoxy-6-nitro-1-tosyl-1*H*-indazole (3ha)



Yellow solid;

GP1: 56.8 mg, 0.158 mmol, 79%;

R_f (pentane/EtOAc=20:1): 0.15;

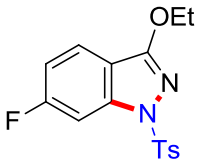
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 1.9, 0.7 Hz, 1H), 8.06 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 0.9 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.31, 149.17, 145.79, 141.83, 133.59, 129.97, 127.80, 121.44, 121.39, 118.98, 110.23, 66.44, 21.79, 14.45;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{15}N_3O_5SNa]^+$: 384.0630, found: 384.0629;

ATR-FTIR (cm^{-1}): 2991, 1595, 1548, 1526, 1474, 1375, 1344, 1172, 1129, 1068, 1015, 815, 667, 604;

3-Ethoxy-6-fluoro-1-tosyl-1*H*-indazole (3ia)



White solid;

GP1: 56.2 mg, 0.17 mmol, 65%;

R_f (pentane/EtOAc 90:10): 0.41;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.5 Hz, 1H, H_{arom}), 7.80 – 7.70 (m, 2H, H_{arom}), 7.46 (m, 1H, H_{arom}), 7.24 – 7.16 (m, 2H, H_{arom}), 6.90 (m, 1H, H_{arom}), 4.47 (q, *J* = 7.1 Hz, 2H, CH_2), 2.35 (s, 3H, CH_3), 1.44 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.28 (d, $^1J_{CF}$ = 252.1 Hz, C_{arom}), 154.47 (C_{arom}), 145.37 (C_{arom}), 145.30 (C_{arom}), 133.70 (C_{arom}), 131.52 (d, $^3J_{CF}$ = 7.7 Hz, C_{arom}), 129.73 (CH_{arom}), 127.69 (CH_{arom}), 110.31 (d, $^3J_{CF}$ = 4.6 Hz, CH_{arom}), 109.80 (d, $^2J_{CF}$ = 18.2 Hz, CH_{arom}), 107.74 (d, $^2J_{CF}$ = 19.7 Hz, CH_{arom}), 66.24 (CH_2), 21.76 (CH_3), 14.47 (CH_3);

^{19}F NMR (282 MHz, $CDCl_3$) δ = -117.77 (s, CF_{arom});

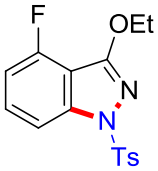
GC MS: t_R (50_40) = 10.5 min;

EI MS: *m/z* (%) = 65(19), 75(16), 91(50), 92(10), 94(30), 95(26), 122(19), 123(34), 151(100), 152(11), 155(31), 179(44), 334(47);

Exact Mass ESI-MS: calculated m/z $[C_{16}H_{15}FN_2O_3SNa]^+$: 357.0680, found: 357.0678;

ATR-FTIR (cm^{-1}): 2987, 1629, 1595, 1542, 1371, 1352, 1186, 1162, 1102, 1015, 920, 817, 782, 704, 670, 595;

3-Ethoxy-4-fluoro-1-tosyl-1*H*-indazole (3ja)



Slightly yellow solid;

GP1: 43.5 mg, 0.13 mmol, 52%; **GP2**: 55.2 mg, 0.17 mmol, 64%;

R_f (pentane/EtOAc 90:10): 0.39;

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 8.5, 0.6 Hz, 1H, H_{arom}), 7.79 – 7.69 (m, 2H, H_{arom}), 7.45 (m, 1H, H_{arom}), 7.22 – 7.16 (m, 2H, H_{arom}), 6.90 (m, 1H, H_{arom}), 4.47 (q, *J* = 7.1 Hz, 2H, CH_2), 2.35 (s, 3H, CH_3), 1.43 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.51 (d, $^3J_{CF}$ = 3.0 Hz, C_{arom}), 155.74 (d, $^1J_{CF}$ = 256.7 Hz, C_{arom}), 145.34 (d, $^3J_{CF}$ = 6.3 Hz, C_{arom}), 145.28 (C_{arom}), 133.75 (C_{arom}), 131.49 (d, $^3J_{CF}$ = 7.7 Hz, CH_{arom}), 129.71 (CH_{arom}), 127.67 (CH_{arom}), 110.29 (d, $^4J_{CF}$ = 4.5 Hz, CH_{arom}), 109.77 (d, $^2J_{CF}$ = 18.2 Hz, CH_{arom}), 107.72 (d, $^2J_{CF}$ = 19.8 Hz, C_{arom}), 66.22 (CH_2), 21.73 (CH_3), 14.46 (CH_3);

^{19}F NMR (564 MHz, $CDCl_3$) δ = -117.78 (s, CF_{arom});

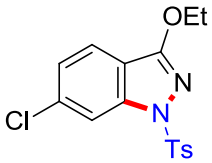
GC MS: t_R (50_40) = 10.5 min;

EI MS: *m/z* (%) = 65(20), 75(15), 91(52), 94(32), 95(27), 122(25), 123(35), 151(100), 152(14), 155(29), 179(47), 334(67);

Exact Mass ESI-MS: calculated m/z $[C_{16}H_{15}FN_2O_3SNa]^+$: 357.0680, found: 357.0683;

ATR-FTIR (cm^{-1}): 3725, 2990, 2931, 2361, 2341, 1931, 1629, 1598, 1541, 1419, 1371, 1352, 1283, 1184, 1161, 1101, 1049, 1017, 920, 877, 817, 781, 746, 704, 671, 646, 605;

6-Chloro-3-ethoxy-1-tosyl-1*H*-indazole (3ka)



White solid;

GP1: 48.1 mg, 0.137 mmol, 69%;

R_f (pentane/EtOAc=20:1): 0.40;

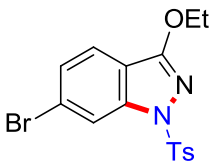
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 1.7, 0.6 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.41 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.19– 7.13 (m, 3H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.97, 145.26, 143.36, 136.68, 133.72, 129.74, 127.68, 125.13, 121.20, 116.74, 114.29, 65.94, 21.74, 14.47;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{15}ClN_2O_3SNa]^+$: 373.0390, found: 373.0385;

ATR-FTIR (cm^{-1}): 2992, 1584, 1540, 1425, 1375, 1172, 1065, 1019, 666;

6-Bromo-3-ethoxy-1-tosyl-1*H*-indazole (3la)



White solid;

GP1: 54.6 mg, 0.138 mmol, 69%;

R_f (pentane/EtOAc=20:1): 0.40;

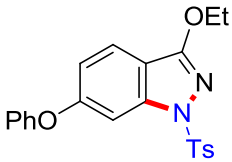
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.38–7.30 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.04, 145.27, 143.56, 133.72, 129.75, 127.78, 127.68, 124.81, 121.41, 117.24, 117.08, 65.94, 21.74, 14.46;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{15}BrN_2O_3SNa]^+$: 416.9884, found: 416.9866;

ATR-FTIR (cm^{-1}): 3087, 2992, 1583, 1540, 1375, 1172, 1018, 817, 698, 663;

3-Ethoxy-6-phenoxy-1-tosyl-1*H*-indazole (3ma)



White solid;

GP1: 59.2 mg, 0.145 mmol, 73%;

R_f (pentane/EtOAc=20:1): 0.30;

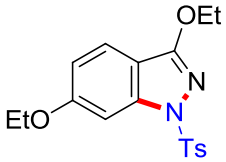
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 3H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.14 – 7.08 (m, 3H), 6.99 – 6.95 (m, 2H), 6.88 (dd, *J* = 8.7, 2.0 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.36, 159.79, 156.63, 145.01, 144.39, 133.79, 130.15, 129.62, 127.72, 124.33, 121.41, 119.44, 116.61, 114.01, 103.65, 65.76, 21.76, 14.55;

Exact Mass ESI-MS: calculated m/z for $[C_{22}H_{20}N_2O_4SNa]^+$: 431.1041, found: 431.1036;

ATR-FTIR (cm^{-1}): 2990, 2913, 1619, 1590, 1539, 1432, 1368, 1216, 1168, 668;

3,6-Diethoxy-1-tosyl-1*H*-indazole (3na)



White solid;

GP1: 53.2 mg, 0.15 mmol, 62%;

R_f (pentane/EtOAc 90:10): 0.29;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 – 7.66 (m, 2H, H_{arom}), 7.53 (d, *J* = 2.1 Hz, 1H, H_{arom}), 7.39 (d, *J* = 8.7 Hz, 1H, H_{arom}), 7.17 (d, *J* = 8.2 Hz, 2H, H_{arom}), 6.85 (dd, *J* = 8.7, 2.1 Hz, 1H, H_{arom}), 4.42 (q, *J* = 7.1 Hz, 2H, CH_2), 4.14 (q, *J* = 7.0 Hz, 2H, CH_2), 2.33 (s, 3H, CH_3), 1.47 (t, *J* = 7.0 Hz, 3H, CH_3), 1.39 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.52 (C_{arom}), 161.29 (C_{arom}), 144.94 (C_{arom}), 144.74 (C_{arom}), 133.72 (C_{arom}), 129.44 (CH_{arom}), 127.49 (CH_{arom}), 120.78 (CH_{arom}), 115.06 (CH_{arom}), 111.92 (C_{arom}), 97.34 (CH_{arom}), 65.43 (CH_2), 64.16 (CH_2), 21.59 (CH_3), 14.66 (CH_3), 14.41 (CH_3);

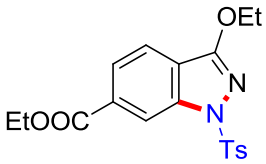
GC MS: t_R (50_40) = 11.8 min;

EI MS: *m/z* (%) = 63(10), 65(19), 91(27), 92(22), 120(13), 121(43), 148(10), 177(69), 205(100), 206(13), 360(50);

Exact Mass ESI-MS: calculated m/z $[C_{18}H_{20}N_2O_4SNa]^+$: 383.1036, found: 383.1035;

ATR-FTIR (cm^{-1}): 2983, 1614, 1598, 1539, 1436, 1366, 1352, 1280, 1175, 1122, 1021, 895, 811, 706, 674, 602;

Ethyl 3-ethoxy-1-tosyl-1*H*-indazole-6-carboxylate (3oa)



White solid;

GP1: 43.5 mg, 0.13 mmol, 78%;

R_f (pentane/EtOAc 90:10): 0.29;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (dd, *J* = 1.3, 0.8 Hz, 1H, H_{arom}), 7.96 (dd, *J* = 8.3, 1.3 Hz, 1H, H_{arom}), 7.80 – 7.69 (m, 2H, H_{arom}), 7.61 (dd, *J* = 8.3, 0.8 Hz, 1H, H_{arom}), 7.22 – 7.07 (m, 2H, H_{arom}), 4.47 (q, *J* = 7.0 Hz, 2H, CH_2), 4.45 (q, *J* = 7.0 Hz, 2H, CH_2), 2.33 (s, 3H, CH_3), 1.45 (t, *J* = 7.2 Hz, 3H, CH_3), 1.43 (t, *J* = 7.2 Hz, 3H, CH_3);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.15 (CO), 161.05 (C_{arom}), 145.21 (C_{arom}), 142.71 (C_{arom}), 133.79 (C_{arom}), 132.32 (C_{arom}), 129.72 (CH_{arom}), 127.72 (CH_{arom}), 125.13 (CH_{arom}), 120.97 (C_{arom}), 120.27 (CH_{arom}), 115.83 (CH_{arom}), 66.02 (CH_2), 61.78 (CH_2), 21.74 (CH_3), 14.49 (CH_3), 14.49 (CH_3);

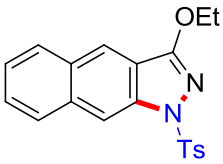
GC MS: t_R (50_40) = 13.0 min;

EI MS: *m/z* (%) = 43(14), 65(18), 75(13), 76(10), 89(11), 91(57), 103(38), 119(14), 120(13), 132(11), 149(29), 155(24), 176(16), 177(11), 191(11), 205(100), 206(13), 207(19), 233(46), 267(10), 281(10), 327(10), 343(14), 388(48);

Exact Mass ESI-MS: calculated m/z $[C_{19}H_{20}N_2O_5SNa]^+$: 411.0985, found: 411.0983;

ATR-FTIR (cm^{-1}): 3099, 2987, 2913, 2361, 2341, 1713, 1592, 1540, 1473, 1448, 1371, 1351, 1293, 1220, 1186, 1173, 1088, 1021, 996, 903, 811, 747, 666, 604;

3-ethoxy-1-tosyl-1*H*-benzo[f]indazole (3pa)



Yellowish solid;

GP1: 44.3 mg, 0.121 mmol, 61%;

R_f (pentane/EtOAc=20:1): 0.30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.00 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.49 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.39 (ddd, *J* =

8.1, 6.7, 1.2 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.19 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.23, 144.80, 140.30, 134.43, 133.32, 130.63, 129.50, 129.11, 128.63, 127.70, 127.59, 125.53, 119.91, 119.34, 111.48, 66.01, 21.65, 14.53;

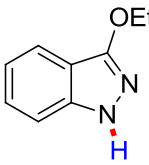
Exact Mass ESI-MS: calculated m/z for $[C_{20}H_{18}N_2O_3SNa]^+$: 389.0936, found: 389.0930;

ATR-FTIR (cm^{-1}): 2991, 1557, 1473, 1352, 1169, 1015, 869, 814, 747, 668;

4 Post-synthetic Modifications and Characterization of Products:

Detosylation of 3-ethoxy-1-tosyl-1*H*-indazole 3aa (GP3): The detosylation of indazole product **3aa** to **4aa** was carried out according to the procedure mentioned in the cited references except TBAB (5 mol%) was used as the phase transfer catalyst and the reaction was carried out for 24 h.[3]

3-Ethoxy-1*H*-indazole (4aa)[4]



White solid;

GP3: 21.1 mg, 0.13 mmol, 66%;

R_f (pentane/EtOAc 80:20): 0.29;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.07 (brs, 1H, NH), 7.62 (m, 1H, H_{arom}), 7.28 (m, 1H, H_{arom}), 7.19 (m, 1H, H_{arom}), 7.00 (m, 1H, H_{arom}), 4.39 (q, *J* = 7.1 Hz, 2H, CH_2), 1.42 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.73 (C_{arom}), 142.72 (C_{arom}), 127.85 (CH_{arom}), 120.07 (CH_{arom}), 119.86 (CH_{arom}), 112.99 (C_{arom}), 109.74 (CH_{arom}), 64.84 (CH_2), 14.98 (CH_3);

GC MS: t_R (50_40) = 7.9 min;

EI MS: *m/z* (%) = 76(12), 77(24), 105(33), 134(100), 162(57);

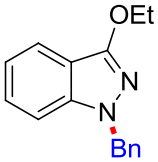
Exact Mass ESI-MS: calculated m/z $[C_9H_{10}N_2ONa]^+$: 185.0685, found: 185.0682;

ATR-FTIR (cm^{-1}): 3155, 3052, 2938, 2764, 2348, 1621, 1591, 1524, 1438, 1339, 1252, 1161, 1111, 1027, 906, 796, 743, 674;

Benzylation of 3-ethoxy-1-tosyl-1*H*-indazole 3aa to 4ab via in situ detosylation (GP4): Into an over-dried screw-capped vial (approx. 3 mL) fitted with a magnetic stirrer, indazole product **3aa** (1.0 eq., 0.25 mmol) and TBAB (2.0 eq.) were weighed in air. To this, o-dichlorobenzene (0.66 M), benzyl bromide (1.5 eq.) and potassium hydroxide (5.0 eq.) were added sequentially. The vial was closed tightly and kept stirring at 120 °C for

20 h. The reaction mixture was then cooled to room temperature and monitored over GC-MS and TLC. The reaction mixture was diluted with EtOAc and filtered over a short pad of celite pre-packed with EtOAc. The volatiles were removed and the analytically pure product was obtained by flash chromatography (silica; gradient of n-pentane/EtOAc).

1-Benzyl-3-ethoxy-1*H*-indazole (4ab)



Slightly yellow oil;

GP4: 39.7 mg, 0.16 mmol, 63%;

R_f (pentane/EtOAc 97:3): 0.29;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (m, 1H, H_{arom}), 7.26 – 7.13 (m, 4H), 7.13 – 7.03 (m, 3H, H_{arom}), 6.94 (m, 1H, H_{arom}), 5.31 (s, 2H), 4.37 (q, *J* = 7.1 Hz, 2H, CH_2), 1.40 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.13 (C_{arom}), 141.67 (C_{arom}), 137.65 (C_{arom}), 128.68 (CH_{arom}), 127.56 (CH_{arom}), 127.43 (CH_{arom}), 127.09 (CH_{arom}), 120.23 (CH_{arom}), 119.17 (CH_{arom}), 113.33 (C_{arom}), 108.93 (CH_{arom}), 64.88 (CH_2), 52.42 (CH_2), 15.01 (CH_3);

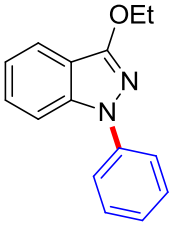
GC MS: t_R (50_40) = 9.3 min;

EI MS: *m/z* (%) = 65(10), 76(9), 77(6), 91(100), 92(9), 104(5), 223(7), 252(38);

Exact Mass ESI-MS: calculated m/z $[C_{16}H_{16}N_2ONa]^+$: 275.1155, found: 275.1159;

ATR-FTIR (cm^{-1}): 3062, 2980, 2934, 2362, 2339, 1617, 1529, 1495, 1442, 1376, 1348, 1254, 1188, 1144, 1101, 1044, 1006, 959, 892, 833, 740, 699, 654, 613;

Arylation of 3-Ethoxy-1-tosyl-1*H*-indazole 3aa via in situ detosylation (GP5): Into an oven-dried screw-capped vial (approx. 3 mL) fitted with a magnetic stirrer, CuI (10 mol%), indazole product **3aa** (1.0 eq., 0.25 mmol) and TBAB (2.0 eq.) were weighed in air. (Note: CuI and TBAB were previously stored in glovebox). To this, DMSO (1 M), aryl iodide (1.5 eq.) and potassium hydroxide (5.0 eq.) were added sequentially. The vial was closed tightly and kept stirring at 120 °C for 20 h. The reaction mixture was then cooled to room temperature and monitored over GC-MS and TLC. The reaction mixture was diluted with EtOAc and filtered over a short pad of celite pre-packed with EtOAc. The volatiles were removed and the analytically pure product was obtained by flash chromatography (silica; gradient of n-pentane/EtOAc).



3-Ethoxy-1-phenyl-1*H*-indazole (4ac)

White solid;

GP5: 43.5 mg, 0.18 mmol, 73%;

R_f (pentane/EtOAc 95:5): 0.29;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 – 7.64 (m, 4H, H_{arom}), 7.54 – 7.45 (m, 2H, H_{arom}), 7.41 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H, H_{arom}), 7.31 – 7.20 (m, 1H, H_{arom}). 7.14 (ddd, *J* = 7.9, 7.0, 0.8 Hz, 1H, H_{arom}), 4.55 (q, *J* = 7.1 Hz, 2H, CH_2), 1.54 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.76 (C_{arom}), 140.81 (C_{arom}), 140.22 (C_{arom}), 129.46 (CH_{arom}), 128.24 (CH_{arom}), 125.26 (CH_{arom}), 121.69 (CH_{arom}), 120.46 (CH_{arom}), 120.36 (CH_{arom}), 115.02 (C_{arom}), 110.19 (CH_{arom}), 65.01 (CH_2), 14.99 (CH_3);

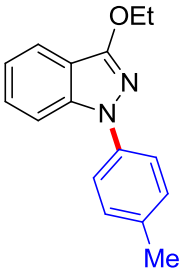
GC MS: t_R (50_40) = 9.3 min;

EI MS: *m/z* (%) = 51(11), 76(14), 77(44), 104(12), 105(11), 152(25), 181(24), 209(29), 210(100), 211(15), 238(97);

Exact Mass ESI-MS: calculated m/z $[C_{15}H_{14}N_2ONa]^+$: 261.0998, found: 261.0983;

ATR-FTIR (cm^{-1}): 2979, 2360, 1597, 1532, 1499, 1440, 1375, 1348, 1227, 1153, 1102, 1026, 953, 891, 768, 745, 697, 683, 651;

3-Ethoxy-1-(*p*-tolyl)-1*H*-indazole (4ad)



White solid;

GP5: 49.8 mg, 0.20 mmol, 79%;

R_f (pentane/EtOAc 97:3): 0.25;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (m, 1H, H_{arom}), 7.68 – 7.52 (m, 3H, H_{arom}), 7.39 (m, 1H, H_{arom}), 7.33 – 7.26 (m, 2H, H_{arom}), 7.12 (m, 1H, H_{arom}), 4.54 (q, *J* = 7.1 Hz, 2H, CH_2), 2.41 (s, 3H, CH^3), 1.53 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.76 (C_{arom}), 140.81 (C_{arom}), 140.22 (C_{arom}), 129.46 (CH_{arom}), 128.24 (CH_{arom}), 125.26 (CH_{arom}), 121.69 (CH_{arom}), 120.46 (CH_{arom}), 120.36 (CH_{arom}), 115.02 (C_{arom}), 110.19 (CH_{arom}), 65.01 (CH_2), 14.99 (CH_3);

^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.53 (C_{arom}), 140.28 (C_{arom}), 138.34 (C_{arom}), 135.10 (C_{arom}), 129.99 (CH_{arom}), 128.07 (CH_{arom}), 121.85 (CH_{arom}), 120.39 (CH_{arom}), 120.13 (CH_{arom}), 114.74 (C_{arom}), 110.13 (CH_{arom}), 64.98 (CH_2), 21.13 (CH_3), 15.00 (CH_3);

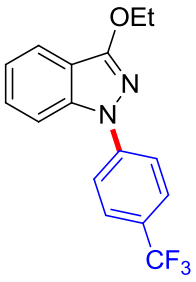
GC MS: t_R (50_40) = 9.6 min;

EI MS: *m/z* (%) = 65(17), 76(16), 77(12), 91(51), 104(15), 152(20), 165(17), 180(10), 181(14), 195(10), 223(45), 224(94), 225(15), 252(100);

Exact Mass ESI-MS: calculated m/z $[C_{16}H_{16}N_2ONa]^+$: 275.1155, found: 275.1157;

ATR-FTIR (cm^{-1}): 3034, 2984, 2900, 1611, 1534, 1513, 1440, 1346, 1221, 1155, 1106, 1029, 952, 891, 819, 741, 652, 601;

3-Ethoxy-1-(4-(trifluoromethyl)phenyl)-1*H*-indazole (4ae)



White solid;

GP5: 57.4 mg, 0.19 mmol, 75%;

R_f (pentane/EtOAc 97:3): 0.39;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 – 7.80 (m, 2H, H_{arom}), 7.80 – 7.66 (m, 4H, H_{arom}), 7.47 (m, 1H, H_{arom}), 7.20 (m, 1H, H_{arom}), 4.55 (q, *J* = 7.1 Hz, 2H, CH_2), 1.54 (t, *J* = 7.1 Hz, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.44 (C_{arom}), 143.76 (C_{arom}), 140.10 (C_{arom}), 128.85 (CH_{arom}), 126.67 (q, $^2J_{CF3}$ = 3.8 Hz, CH_{arom}), 126.38 (q, $^3J_{CF3}$ = 32.5 Hz, C_{arom}), 124.32 (q, $^1J_{CF3}$ = 272.2 Hz, CF_3), 121.17 (CH_{arom}), 120.78 (CH_{arom}), 120.48 (CH_{arom}), 116.00 (C_{arom}), 110.32 (CH_{arom}), 65.16 (CH_2), 14.91 (CH_3);

^{19}F NMR (282 MHz, $CDCl_3$) δ = -62.03 (s, CF_3);

GC MS: t_R (50_40) = 9.2 min;

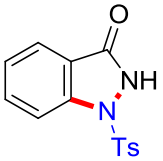
EI MS: *m/z* (%) = 76(13), 145(30), 181(11), 201(10), 277(17), 278(100), 279(16), 306(75);

Exact Mass ESI-MS: calculated m/z $[C_{16}H_{13}F_3N_2ONa]^+$: 329.0872, found: 329.0871;

ATR-FTIR (cm^{-1}): 3626, 2984, 2938, 2361, 1613, 1541, 1444, 1380, 1320, 1223, 1163, 1116, 1065, 1025, 953, 841, 742, 654, 632, 600;

sp^3 C–O cleavage of 3-ethoxy-1-tosyl-1*H*-indazole 3aa (GP6)[5]**:** A mixture of **3aa** (0.30 mmol, 94.8 mg) and 48% HBr (1.19 mmol, 200 µL) in AcOH (0.5 mL) in a sealed tube was heated at 50 °C for 2 h. The reaction mixture was cooled to room temperature and poured into a mixture of ice and saturated aq. $NaHCO_3$ solution. The reaction mixture was extracted with EtOAc three times. The extract was washed with brine, dried over $MgSO_4$ and concentrated to provided analytical pure 1-tosyl-1*H*-indazol-3(2*H*)-one **4b** (78.3 mg, 91% yield) as a yellow solid.

1-Tosyl-1*H*-indazol-3(2*H*)-one (4b)



Yellow solid;

GP6: 78.3 mg, 0.272 mmol, 91%;

R_f (EtOAc/MeOH/Et_3N=4:1:1): 0.25;

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.24 (s, 3H);

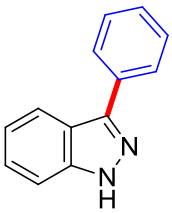
^{13}C NMR (75 MHz, CD_3OD) δ = 147.38, 145.69, 133.65, 133.58, 131.26, 130.51, 129.54, 126.97, 126.94, 123.71, 117.20, 21.48;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_{12}N_2O_3SNa]^+$: 311.0466, found: 311.0464;

ATR-FTIR (cm^{-1}): 3030, 2800, 1693, 1596, 1459, 1366, 1170, 1084, 917, 802, 762, 670;

sp^2 C–O cleavage and in situ detosylation of 3-ethoxy-1-tosyl-1*H*-indazole 3aa (GP7): Into a flame dried red-cap tube the **3aa** (0.15 mmol, 47.4 mg) was added under Argon, followed by the sequential addition of Grignard reagent at room temperature. In case, the Grignard reagent was prepared in the solution of ether, toluene (1.5 mL) was directly injected. In the case, the Grignard reagent was prepared in the solution of THF, clean removal of THF was required. (Most of the THF was firstly removed under vacuum. Then toluene (1 mL) was added and the solution was kept stirring for 5 minutes. Then the solvent was removed under vacuum. This procedure was repeated with toluene and ether each for two times). The tube was closed and stirred at 120 °C for 8-18 h. The reaction mixture was then cooled to room temperature and was diluted with EtOH. The volatiles were removed and the analytically pure product was obtained by flash chromatography (silica; gradient of n-pentane/EtOAc).

3-Phenyl-1*H*-indazole (4ca) [6]



White solid;

GP7: 12 h, 25.2 mg, 0.130 mmol, 87%;

R_f (pentane/EtOAc=6:1): 0.30;

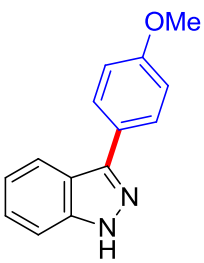
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.96 – 7.93 (m, 3H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.11 (m, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.79, 141.81, 133.67, 129.12, 128.33, 127.92, 127.86, 126.91, 121.45, 121.17, 110.48;

Exact Mass ESI-MS: calculated m/z for $[C_{13}H_{11}N_2]^+$: 195.0922, found: 195.0917;

ATR-FTIR (cm^{-1}): 3155, 3119, 2934, 1622, 1480, 1343, 1256, 1106, 905, 776, 734, 693;

3-(4-Methoxyphenyl)-1*H*-indazole (4cb) [7]



Yellowish oil.

GP7: 18 h, 24.2 mg, 0.108mmol, 72%;

R_f (pentane/EtOAc=6:1): 0.10;

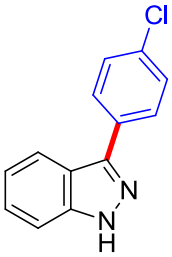
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.20 (m, 2H), 7.12 (ddd, *J* = 7.9, 6.5, 1.2 Hz, 1H), 6.99 (d,

J = 8.7 Hz, 2H), 3.81 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.81, 145.63, 141.78, 129.04, 126.88, 126.28, 121.28, 121.27, 121.00, 114.52, 110.33, 55.52;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_{13}N_2O]^+$: 225.1028, found: 225.1025;

ATR-FTIR (cm^{-1}): 3156, 3117, 2938, 1615, 1529, 1340, 1295, 1245, 1173, 1101, 1033, 906, 834, 732;



3-(4-Chlorophenyl)-1*H*-indazole (4cc)

White solid;

GP7: 12 h, 32.1 mg, 0.141 mmol, 94%;

R_f (pentane/EtOAc=6:1): 0.35;

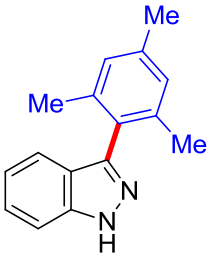
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.21 – 7.15 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.70, 141.77, 134.22, 132.11, 129.28, 128.97, 127.14, 121.77, 120.95, 120.89, 110.39;

Exact Mass ESI-MS: calculated m/z for $[C_{13}H_{10}ClN_2]^+$: 229.0533, found: 229.0537;

ATR-FTIR (cm^{-1}): 3144, 2936, 1619, 1506, 1476, 1403, 1336, 1258, 1088, 1009, 832, 743;

3-Mesityl-1*H*-indazole (4cd) [8]



Yellowish oil.

GP7: 12 h, 33.5 mg, 0.142 mmol, 95%;

R_f (pentane/EtOAc=6:1): 0.35;

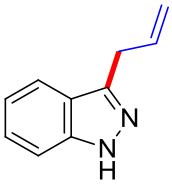
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.03 – 6.98 (m, 3H), 6.76 (d, *J* = 8.5 Hz, 1H), 2.36 (s, 3H), 1.99 (s, 6H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.16, 141.04, 138.71, 138.29, 129.18, 128.43, 126.61, 122.49, 120.83, 120.69, 110.46, 21.38, 20.51;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{17}N_2]^+$: 237.1392, found: 237.1392;

ATR-FTIR (cm^{-1}): 3151, 3118, 2922, 1618, 1454, 1337, 1095, 1004, 906, 852, 731 ;

3-Allyl-1*H*-indazole (4ce)



Yellowish oil.

GP7: 8 h, 14.8 mg, 0.094 mmol, 62%;

R_f (pentane/EtOAc=6:1): 0.25;

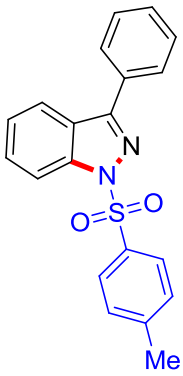
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.07 (ddd, *J* = 8.0, 6.7, 1.1 Hz, 1H), 6.06 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 5.26 – 5.00 (m, 2H), 3.72 (dt, *J* = 6.6, 1.5 Hz, 2H);

^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.32, 141.41, 135.14, 126.99, 122.35, 120.62, 120.55, 116.76, 109.90, 32.03;

Exact Mass ESI-MS: calculated m/z for $[C_{10}H_{11}N_2]^+$: 159.0922, found: 159.0913;

ATR-FTIR (cm^{-1}): 3181, 3080, 2922, 1622, 1499, 1428, 1347, 1254, 1067, 996, 915, 742, 631;

3-Phenyl-1-tosyl-1*H*-indazole (91)



Slightly yellowish solid;

GP1: 125.4 mg, 0.36 mmol, 72%;

R_f (pentane/EtOAc 90:10): 0.39;

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (dt, *J* = 8.6, 0.9 Hz, 1H, H_{arom}), 7.99 – 7.84 (m, 5H, H_{arom}), 7.58 (m, 1H, H_{arom}), 7.55 – 7.45 (m, 3H, H_{arom}), 7.37 (m, 1H, H_{arom}), 7.25 – 7.17 (m, 2H, H_{arom}), 2.34 (s, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.83 (C_{arom}), 145.37 (C_{arom}), 141.97 (C_{arom}), 134.76 (C_{arom}), 131.53 (C_{arom}), 129.92 (CH_{arom}), 129.68 (CH_{arom}), 129.19 (CH_{arom}), 128.95 (CH_{arom}), 128.39 (CH_{arom}), 127.72 (CH_{arom}), 124.56 (CH_{arom}), 124.44 (C_{arom}), 121.79 (CH_{arom}), 113.72 (CH_{arom}), 21.74 (CH_3);

GC MS: t_R (50_40) = 12.1 min;

EI MS: *m/z* (%) = 65(15), 91(35), 139(17), 163(26), 164(28), 165(91), 166(14), 193(100), 194(18), 284(44), 285(10), 348(73);

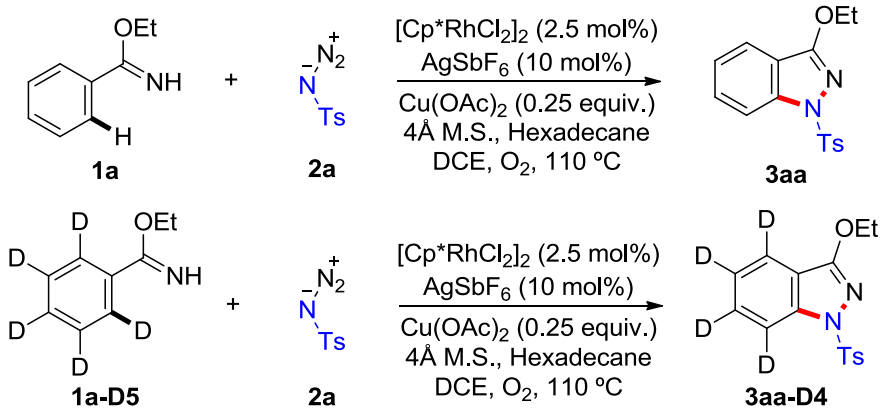
Exact Mass ESI-MS: calculated m/z for $[C_{20}H_{16}N_2O_2SNa]^+$: 371.0825, found: 371.0826; for $[(C_{20}H_{16}N_2O_2S)_2Na]^+$: 719.1757, found: 719.1756;

ATR-FTIR (cm^{-1}): 3009, 2015, 1594, 1488, 1368, 1259, 1176, 1089, 1050, 1025, 730, 670, 564.

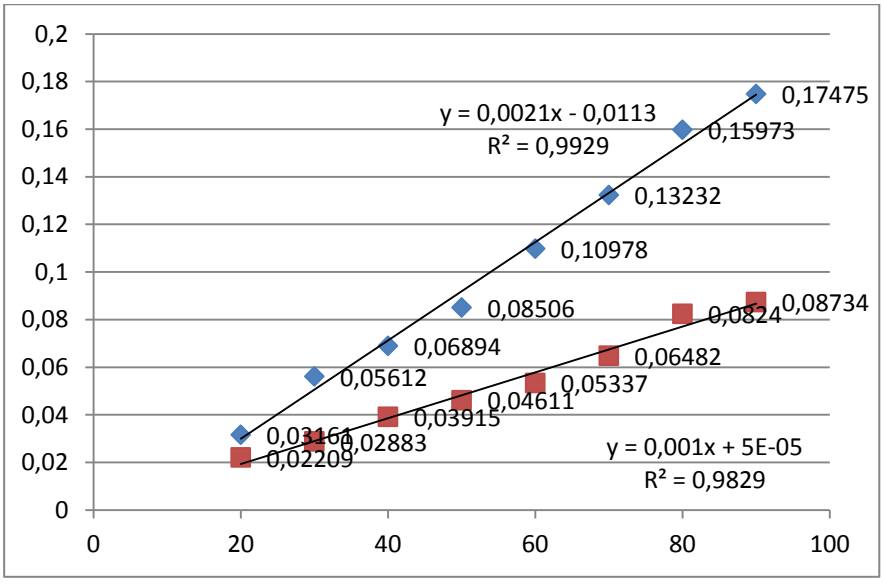
5 Mechanistic Insight

(1) KIE test.

In a flame dried red-cap tube, weighed molecular sieves (4Å MS) was activated under vacuum. In the glovebox, $[RhCp^*Cl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) and $Cu(OAc)_2$ (25 mol%) were weighed into the tube. Under Argon, the benzimidate **3aa** or **3aa-D5** (0.2 mmol, 1 eq.) was added, followed by the sequential addition of *p*-toluenesulfonyl azide (2.5 eq.), 20 μL of hexadecane and DCE (0.2 M) into the tube. The tube was degassed and refilled with molecular oxygen (1 atm). The tube was closed and stirred at 110 °C. An aliquot of each reaction mixture was taken at the time of 20 min, 30 min, 40 min, 50 min, 60 min, 70 min, 80 min, and 90 min (GC-yield is 35%). The corresponding yield of each product was determined



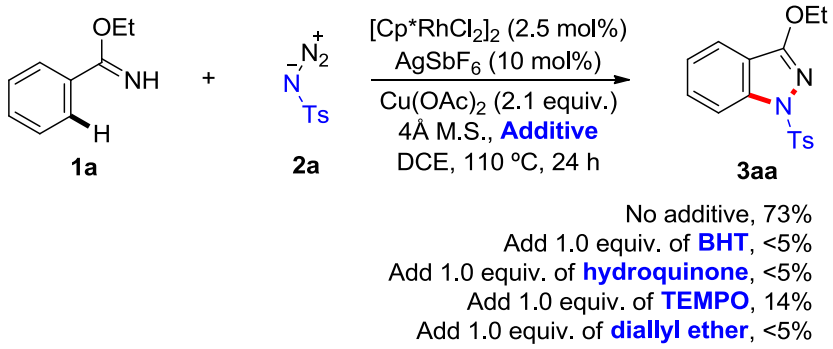
by GC (hexadecane as standard). A kinetic isotope effect value K_H/K_D = 2.1 was observed.



Scheme S1: The KIE test.

(2) The formation of the intermediate **V** was not detected (Table 1, entry 15). However, its derivatives, including *N*-(2-cyanophenyl)-4-methylbenzenesulfonamide and 2-

(4-methylphenylsulfonamido)benzamide, were detected, which indicated that this intermediate **V** was formed but not very stable in the reaction condition. Indeed, the imidate **1a** is also not very stable and prone to decompose to benzonitrile in the basic reaction condition, as demonstrated by the detection of much benzonitrile in the presence of 0.25 equiv. of CsOPiv (Table 1, entry 9).



Scheme S2: The effect of radical scavengers and clock on the reaction.

6 References

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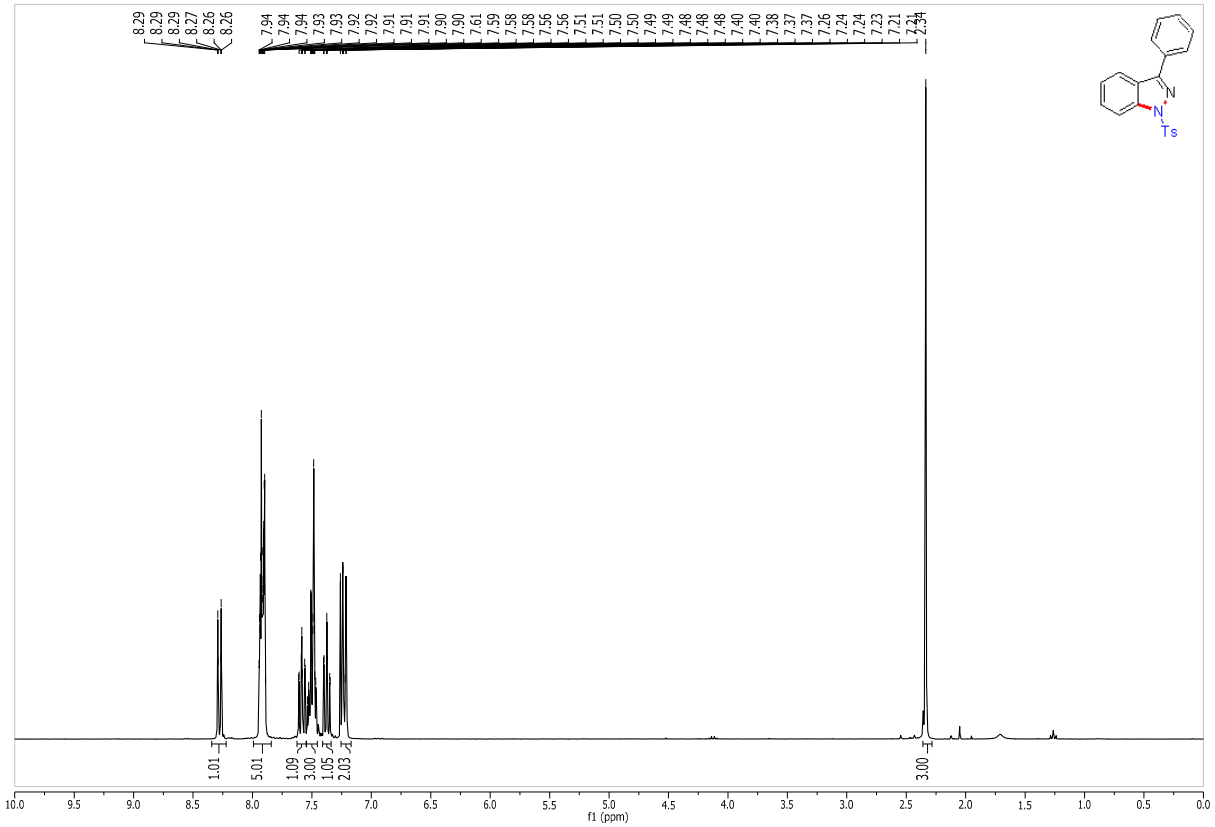
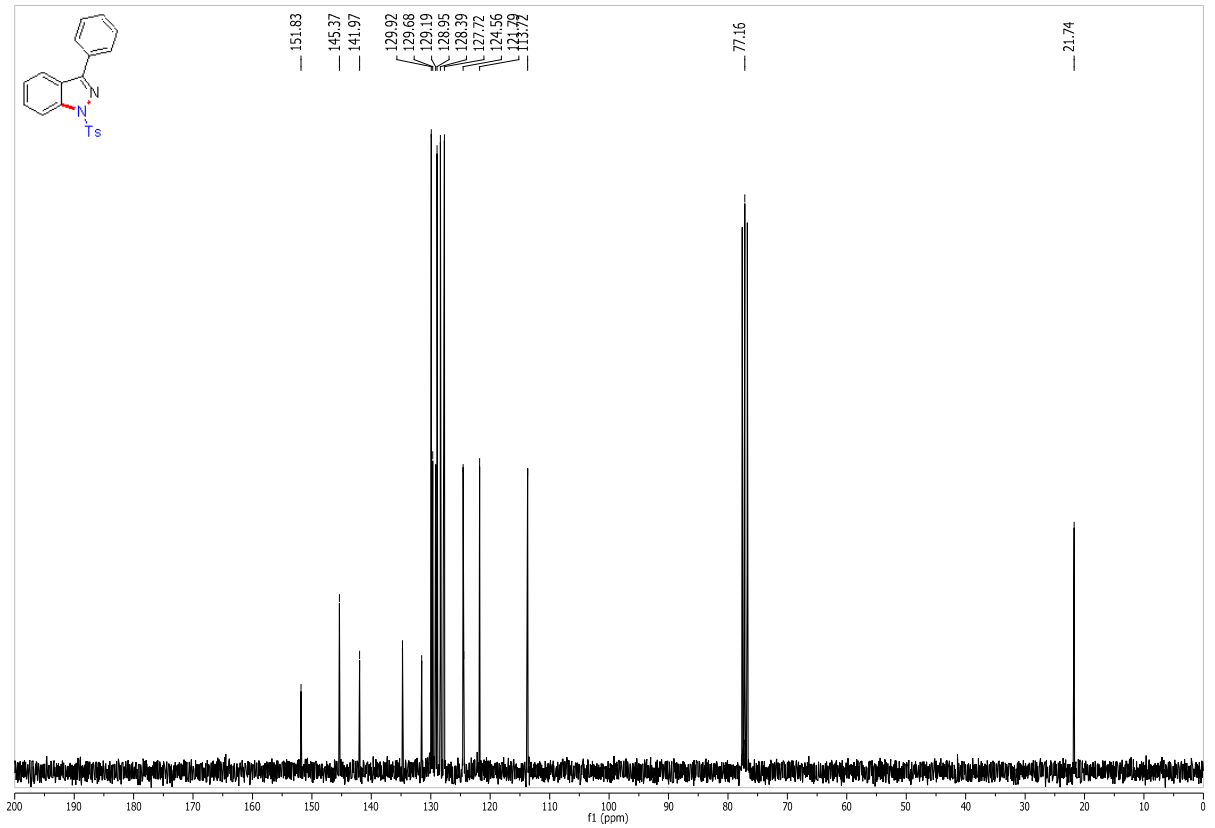
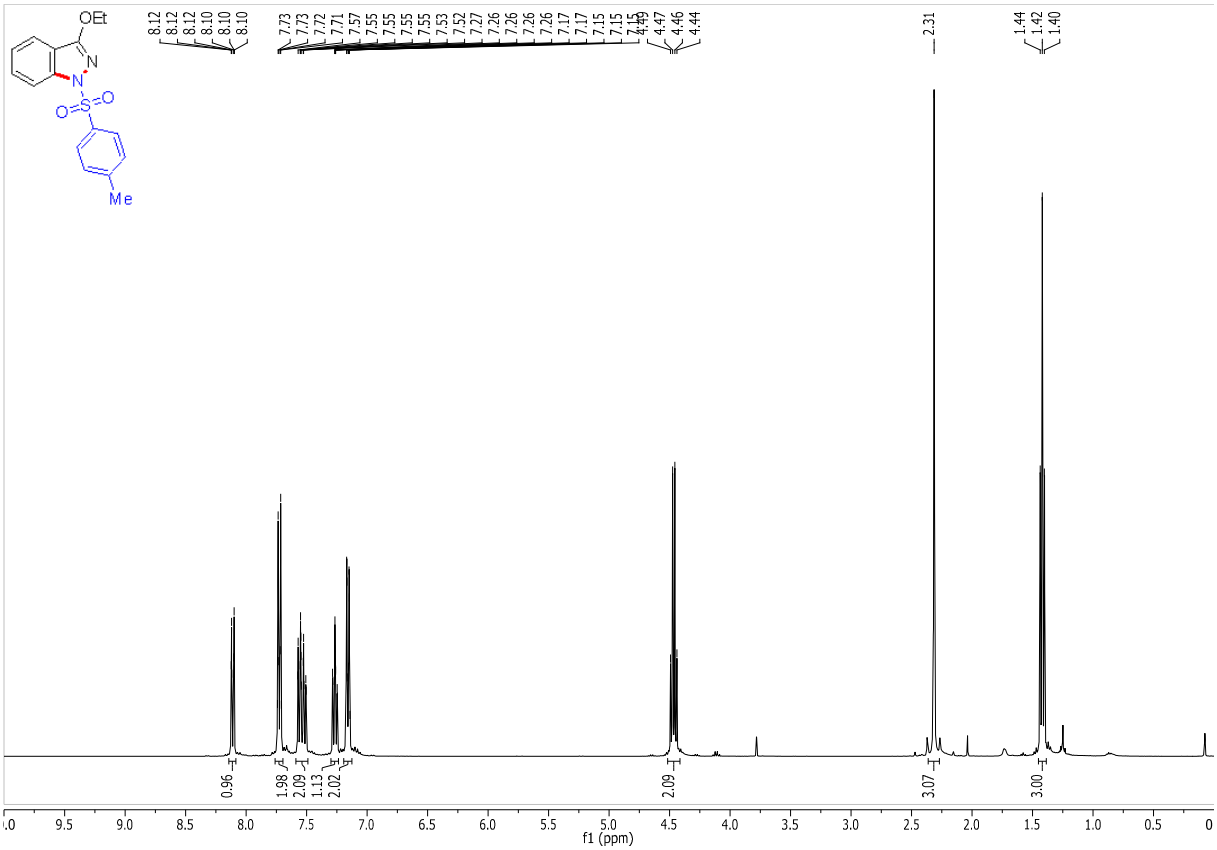
7 NMR Spectra of Products

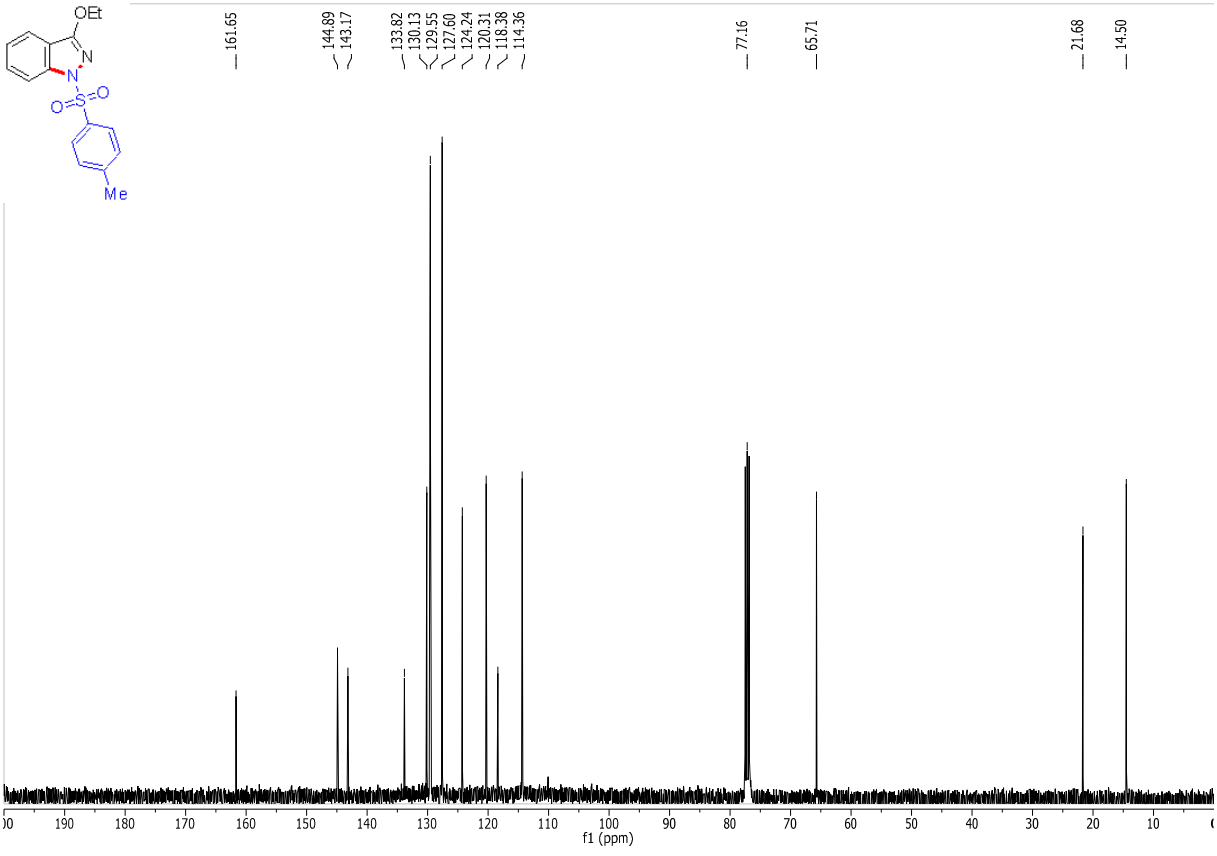
3-Phenyl-1-tosyl-1*H*-indazole (3a)



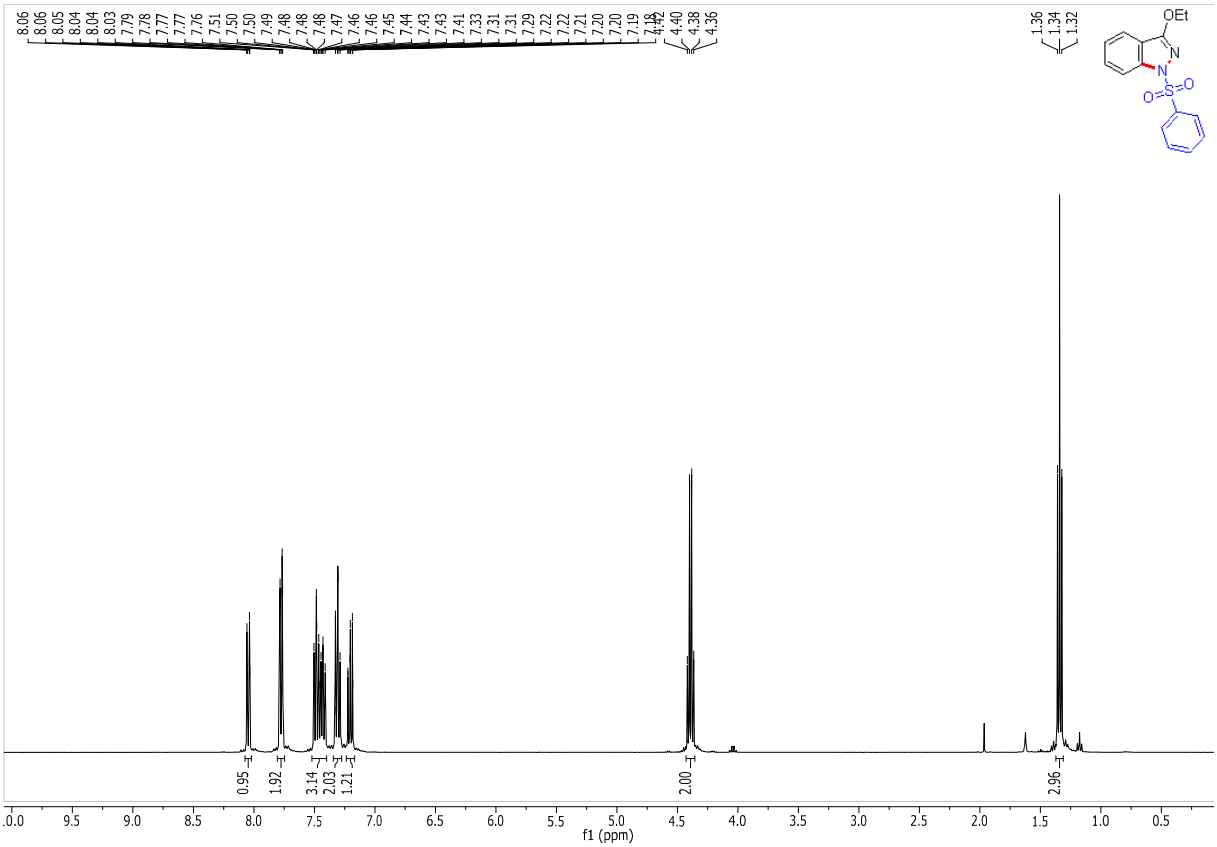


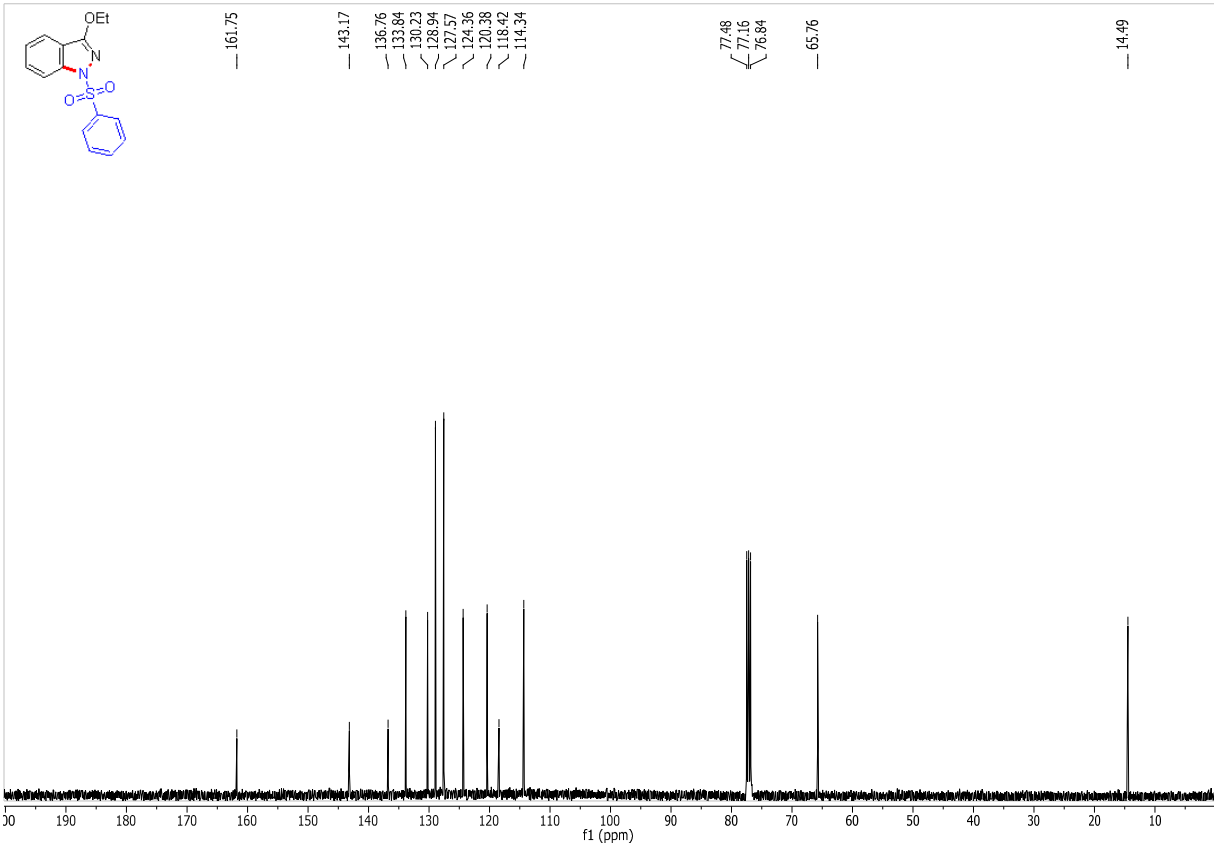
3-Ethoxy-1-tosyl-1*H*-indazole (3aa)



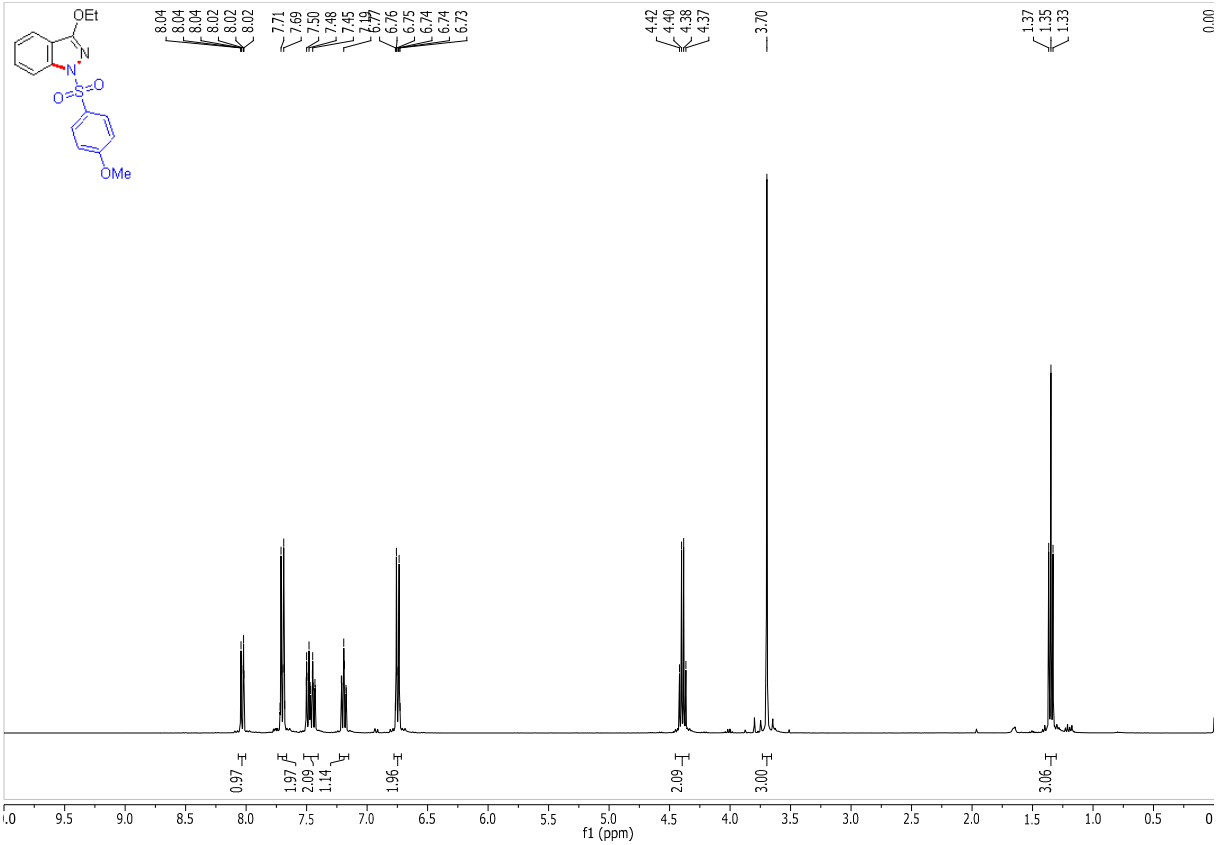


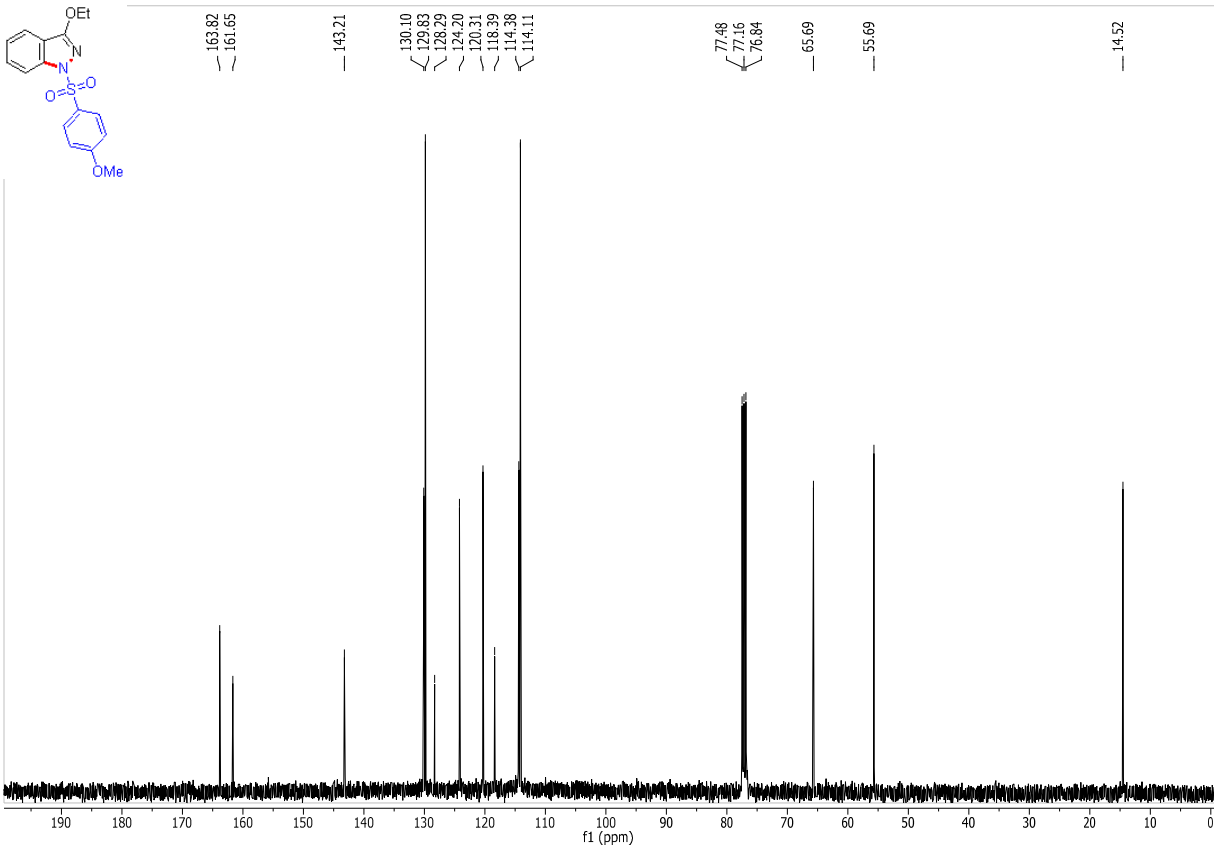
3-Ethoxy-1-(phenylsulfonyl)-1*H*-indazole (3ab)



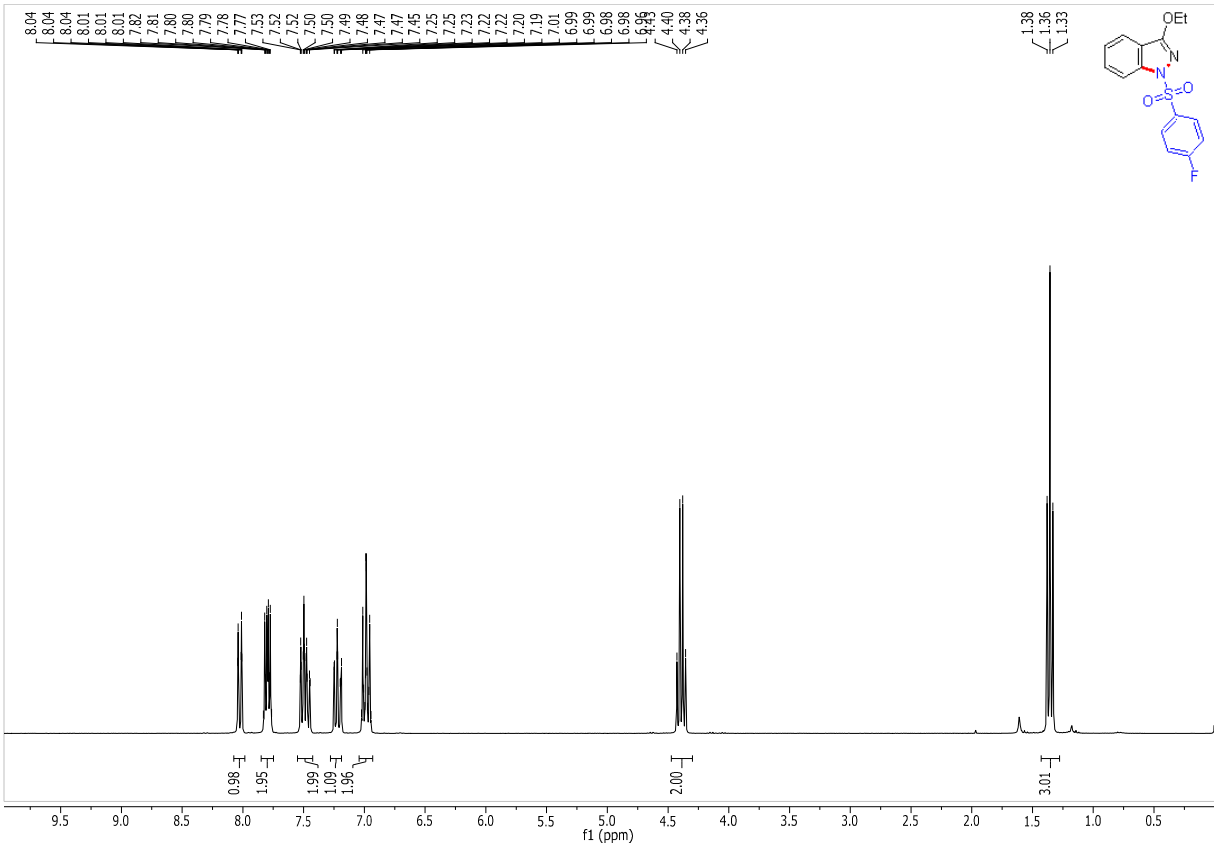


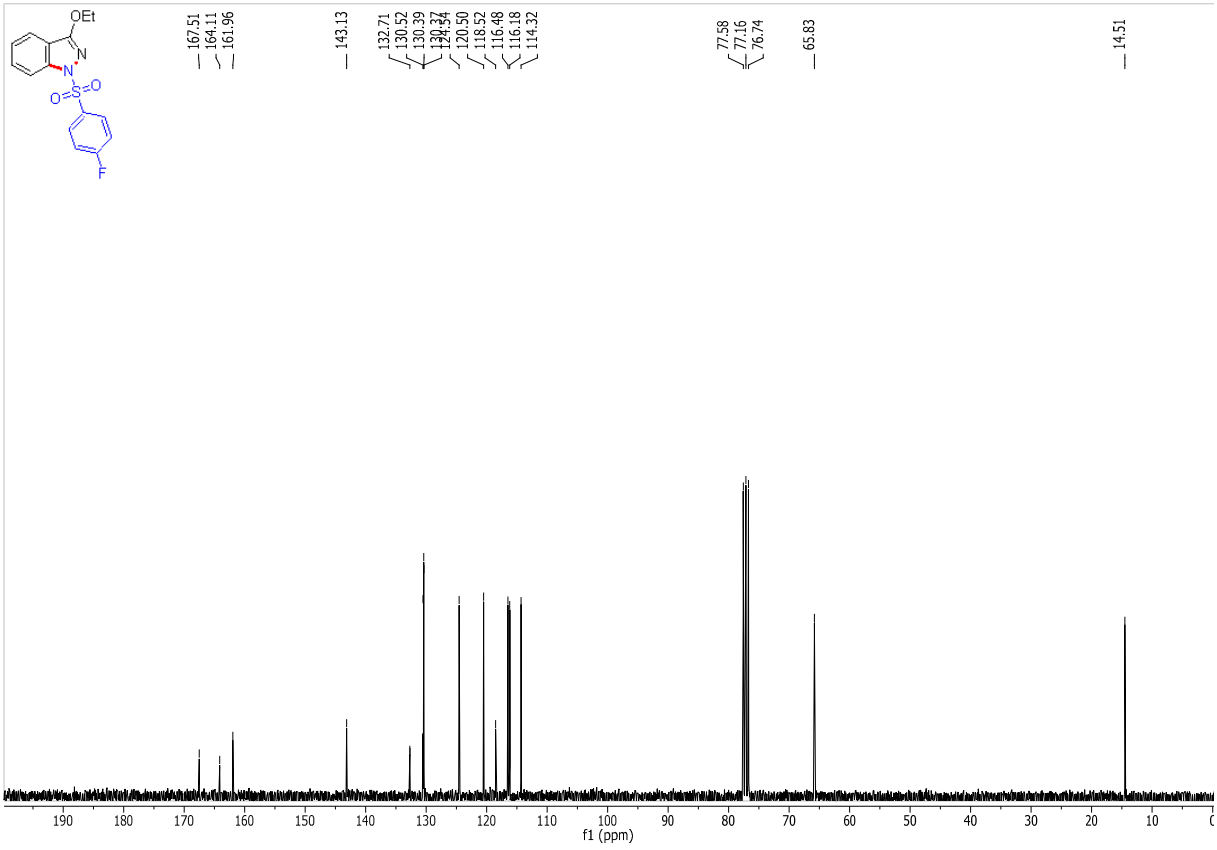
3-Ethoxy-1-((4-methoxyphenyl)sulfonyl)-1*H*-indazole (3ac)

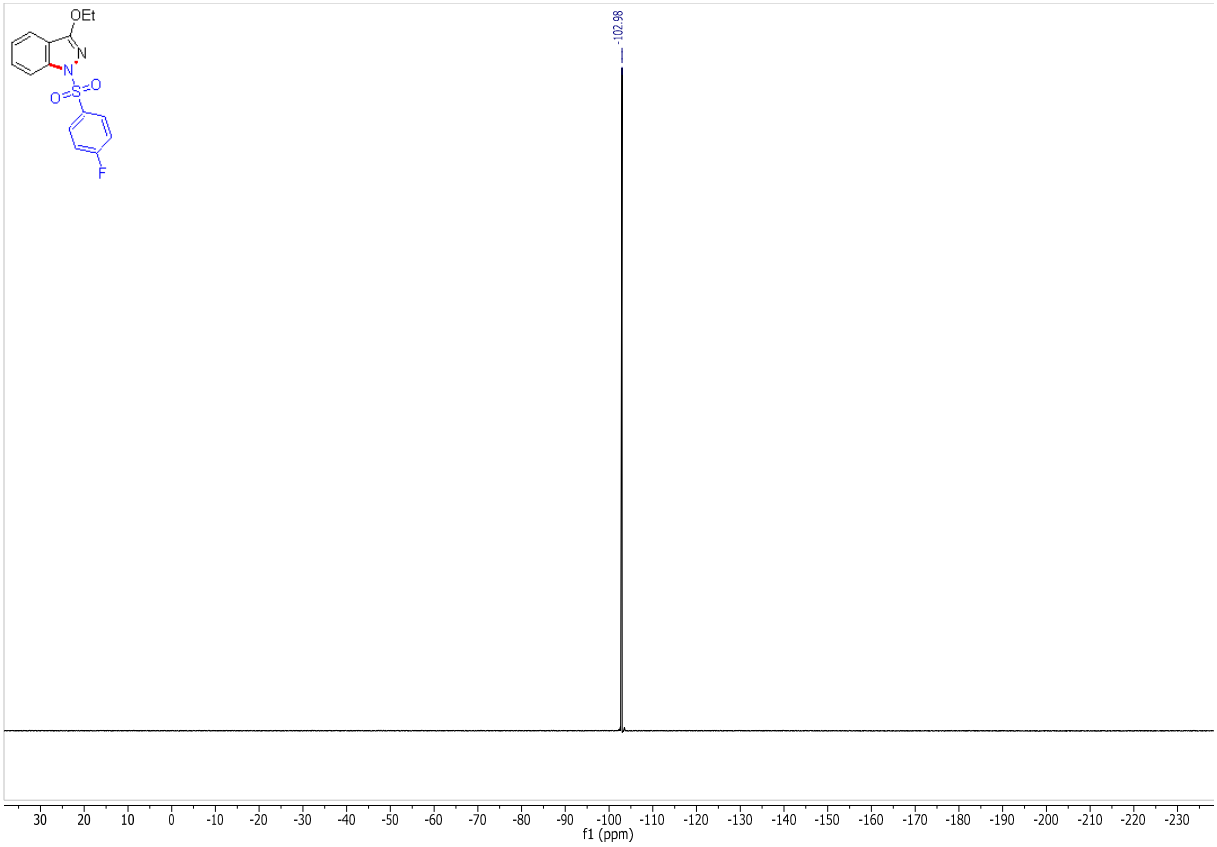




3-Ethoxy-1-((4-fluorophenyl)sulfonyl)-1*H*-indazole (3ad)



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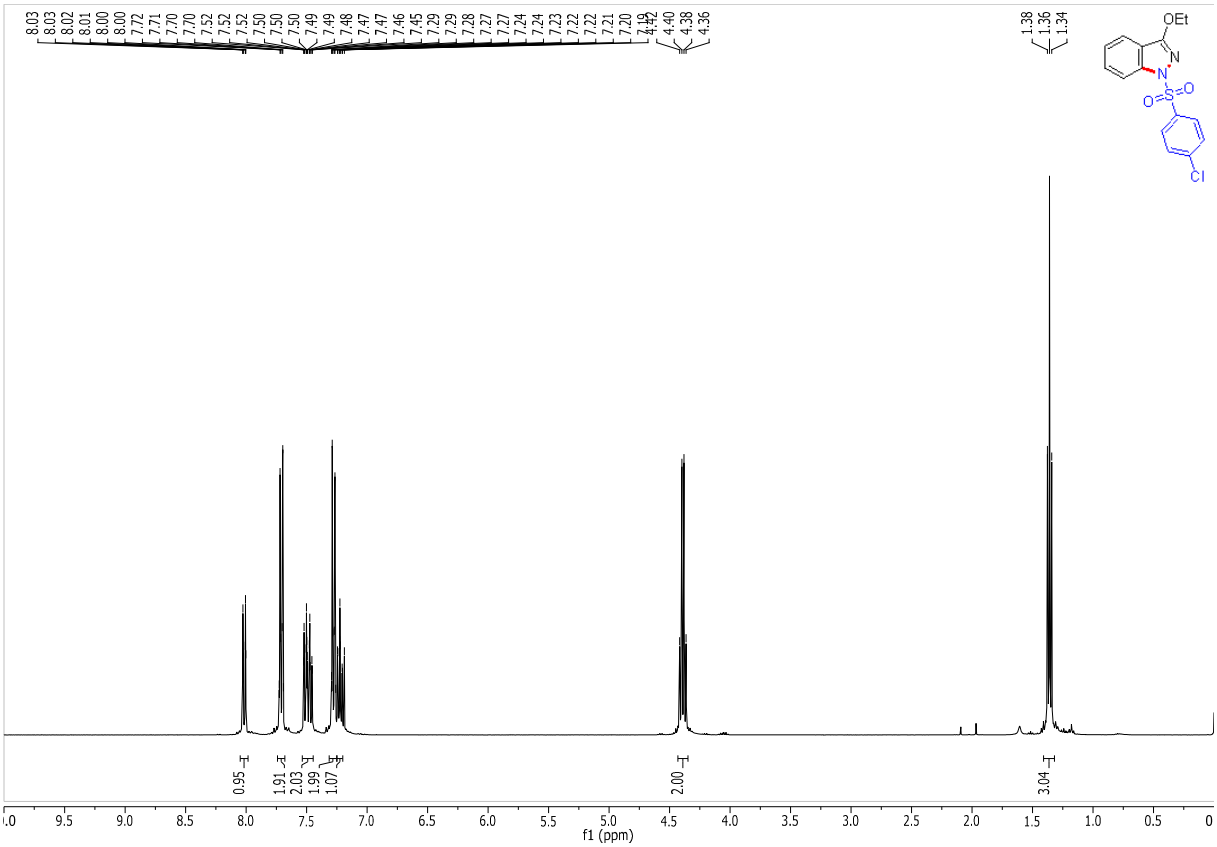
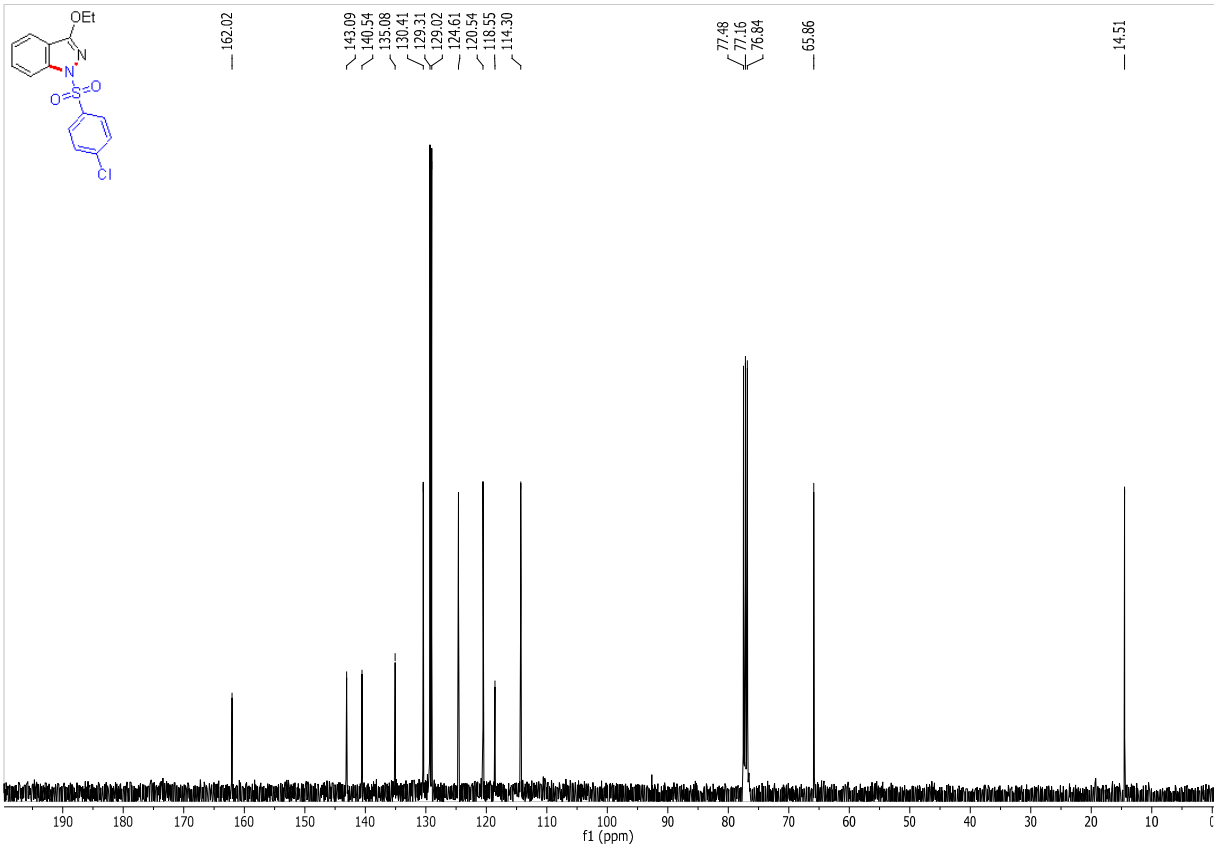
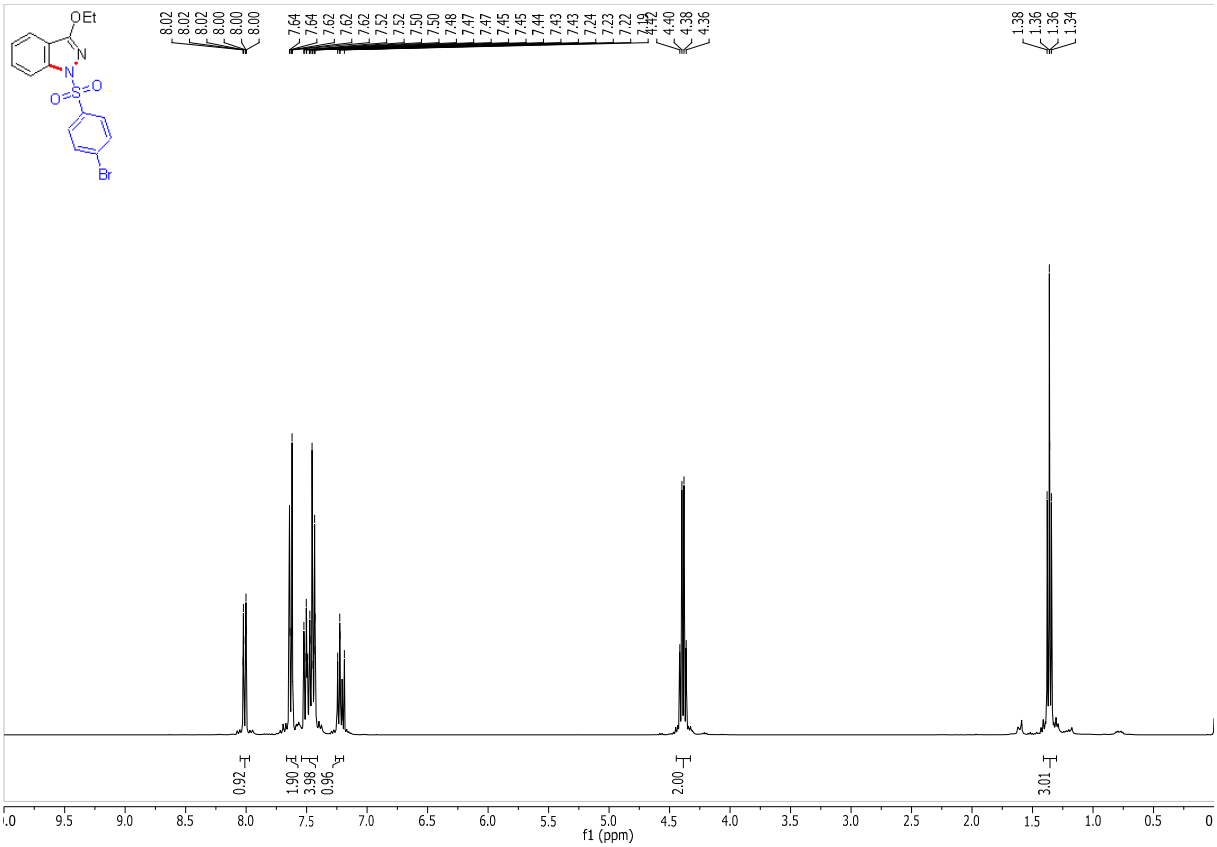
N
O=S=O
F
-102.98
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

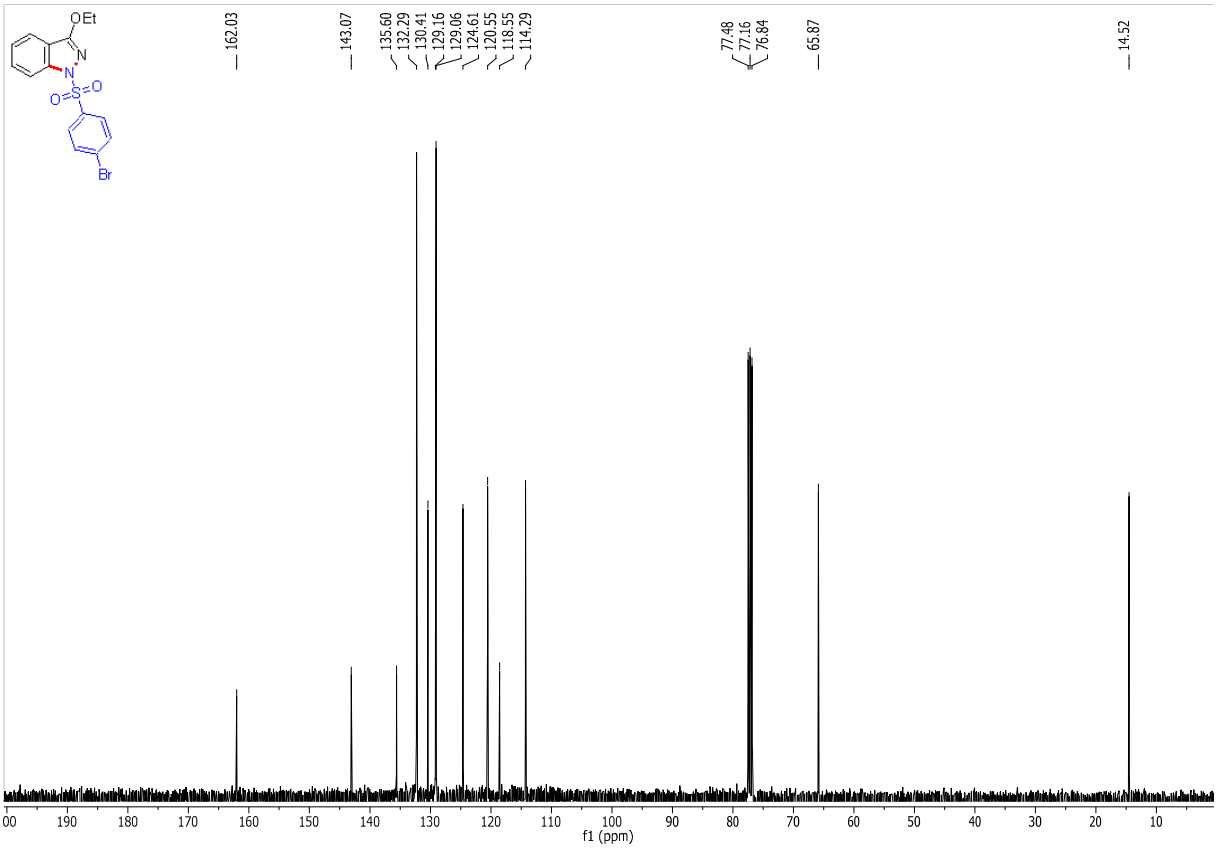
1-((4-Chlorophenyl)sulfonyl)-3-ethoxy-1*H*-indazole (3ae)



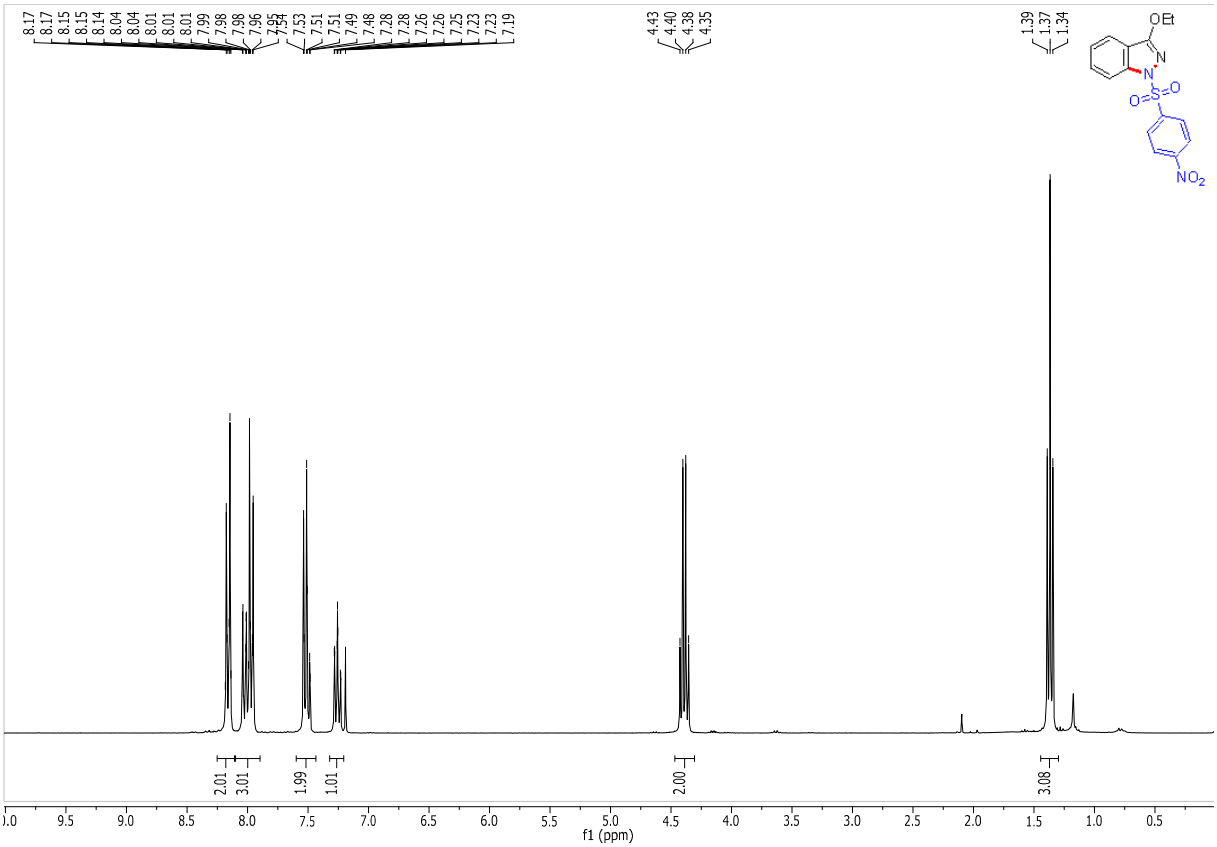


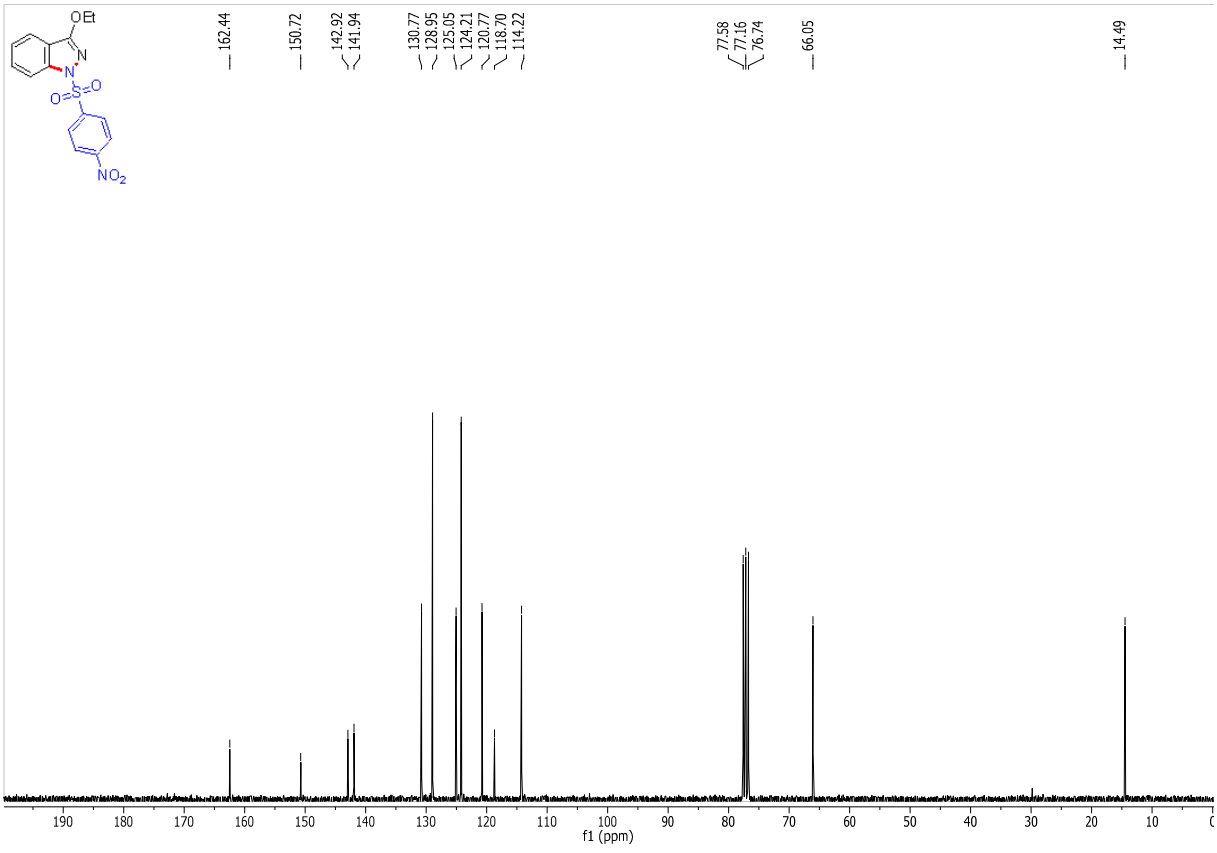
1-((4-Bromophenyl)sulfonyl)-3-ethoxy-1*H*-indazole (3af)



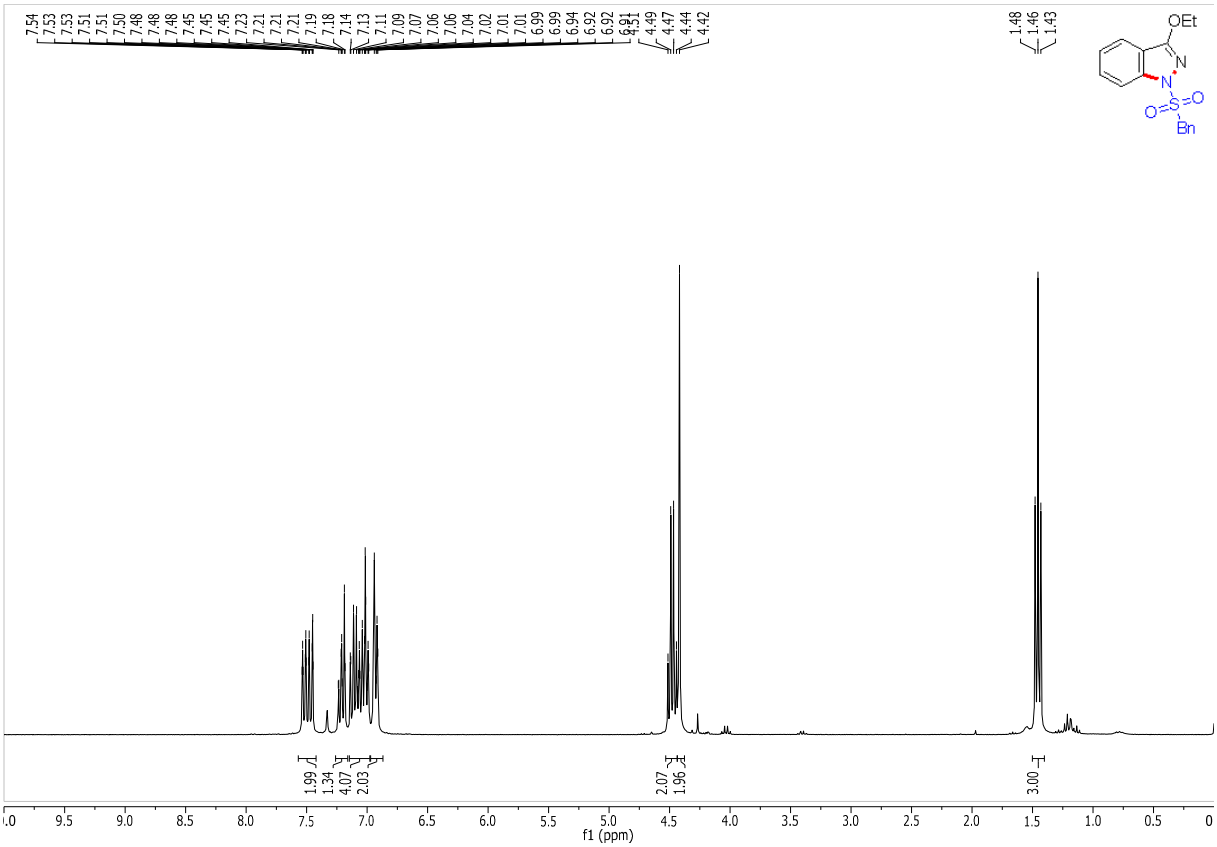


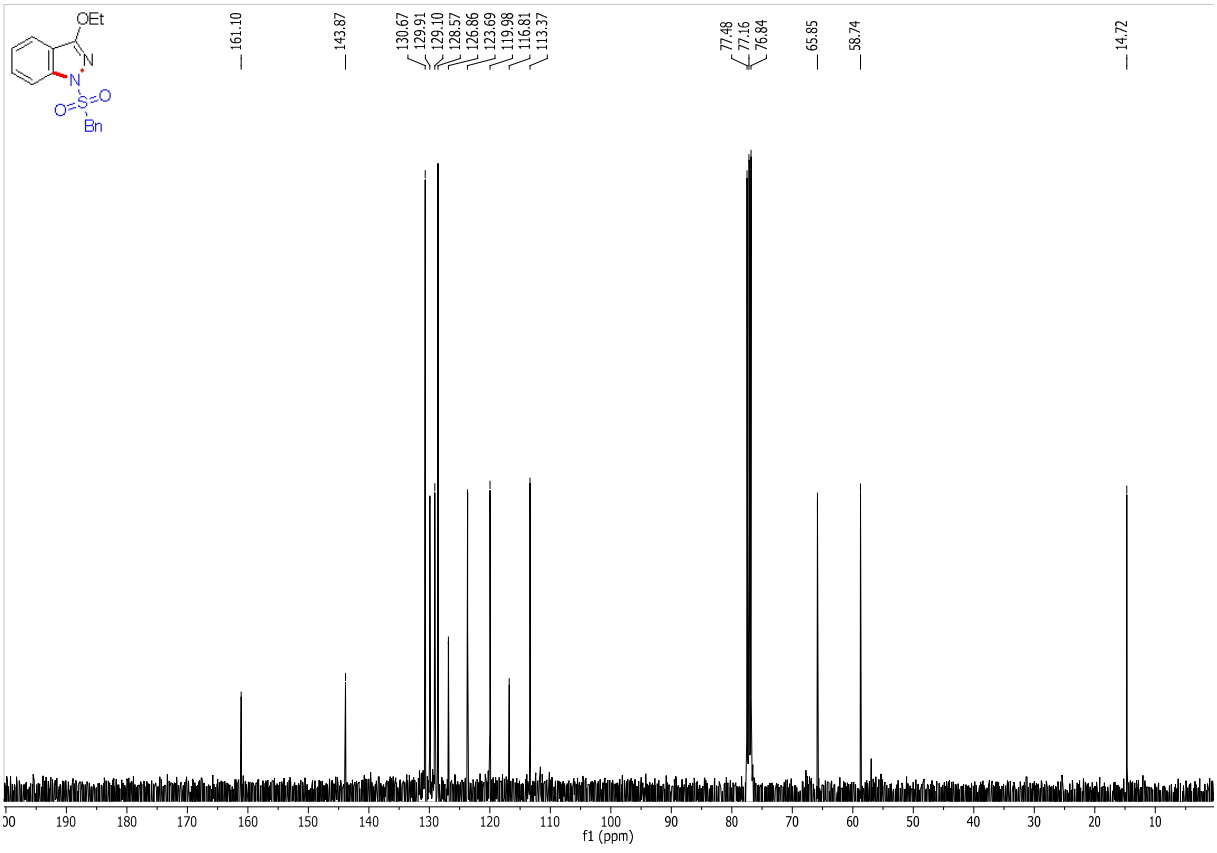
3-Ethoxy-1-((4-nitrophenyl)sulfonyl)-1*H*-indazole (3ag)



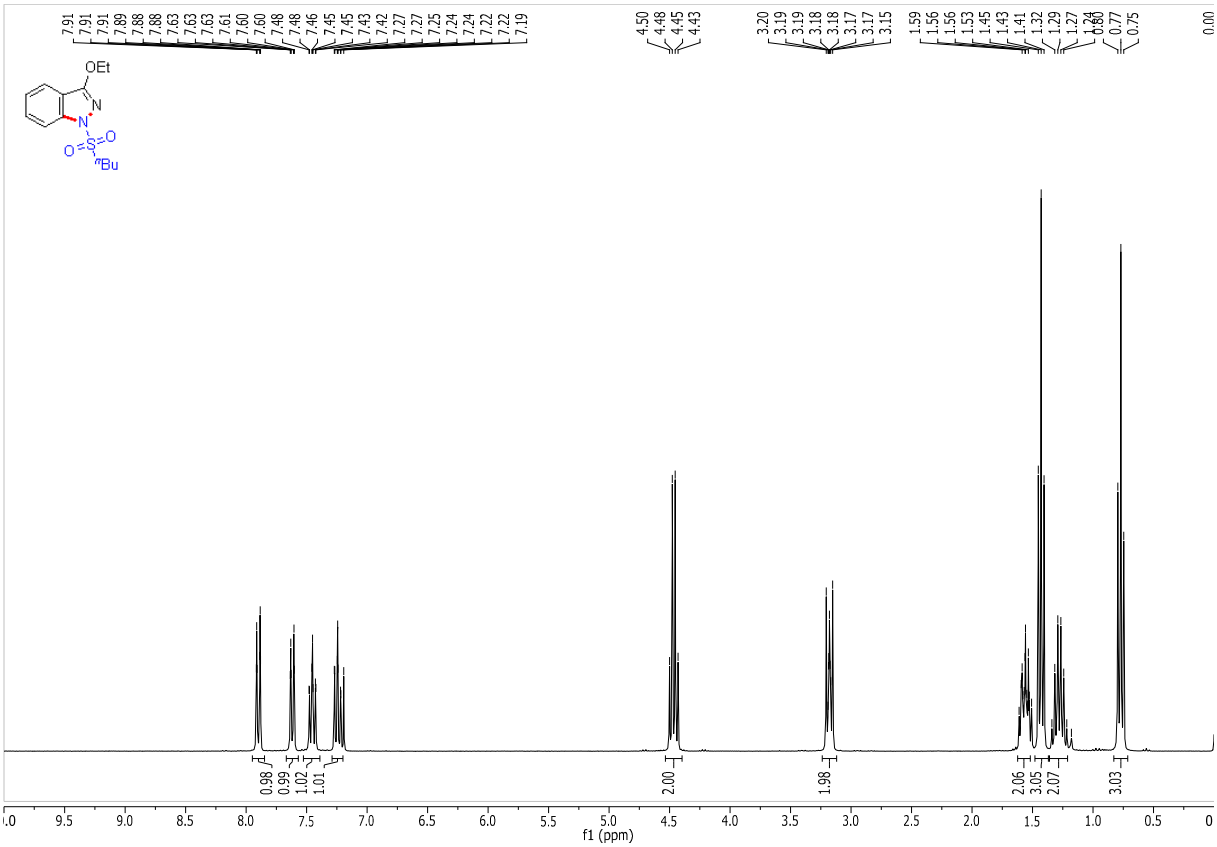


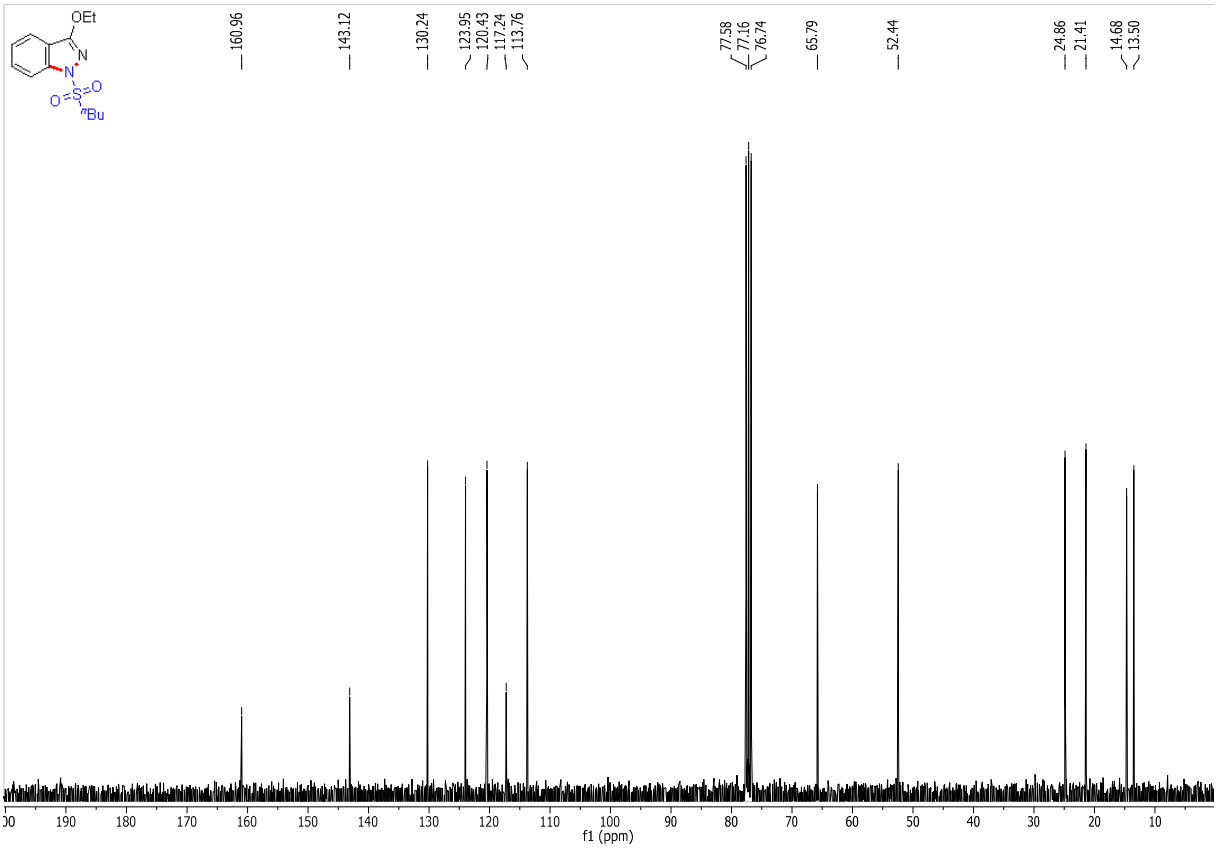
1-(Benzylsulfonyl)-3-ethoxy-1*H*-indazole (3ah)



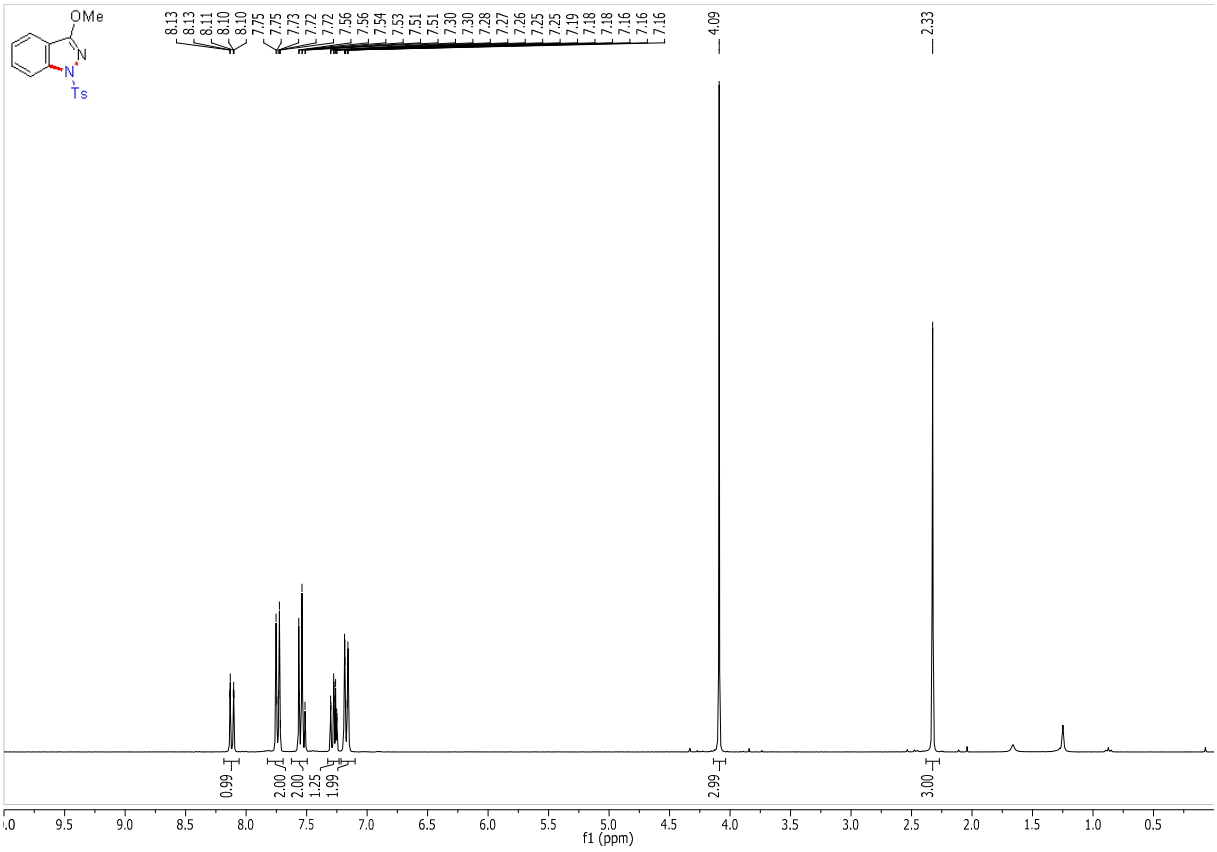


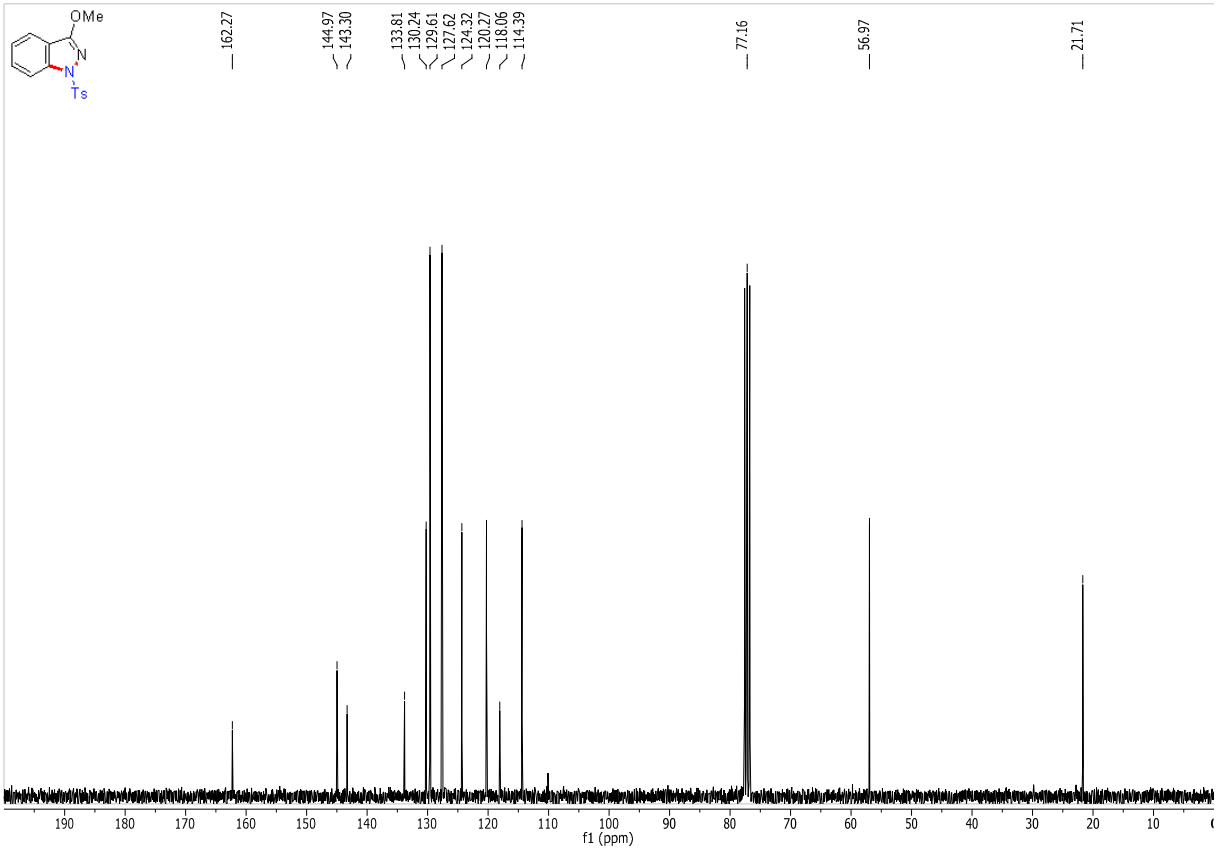
1-(Butylsulfonyl)-3-ethoxy-1*H*-indazole (3ai)



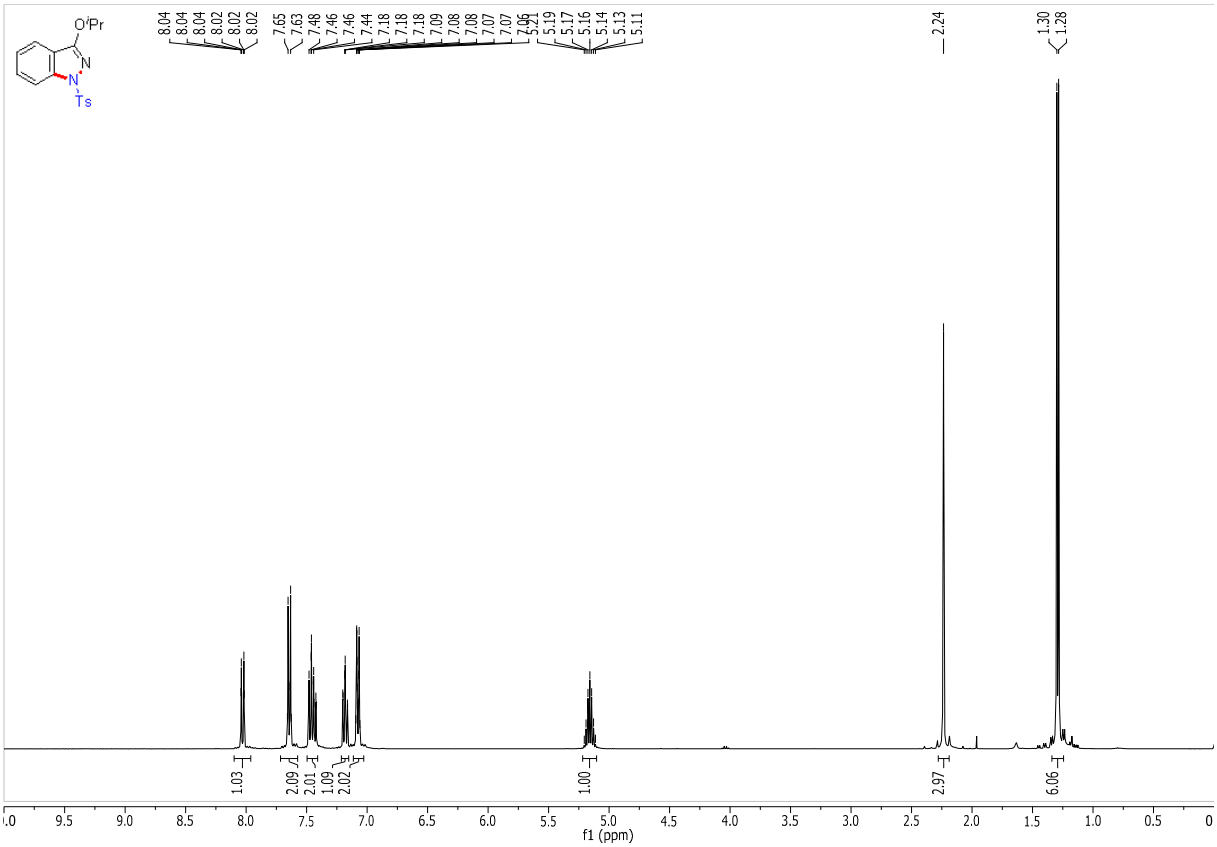


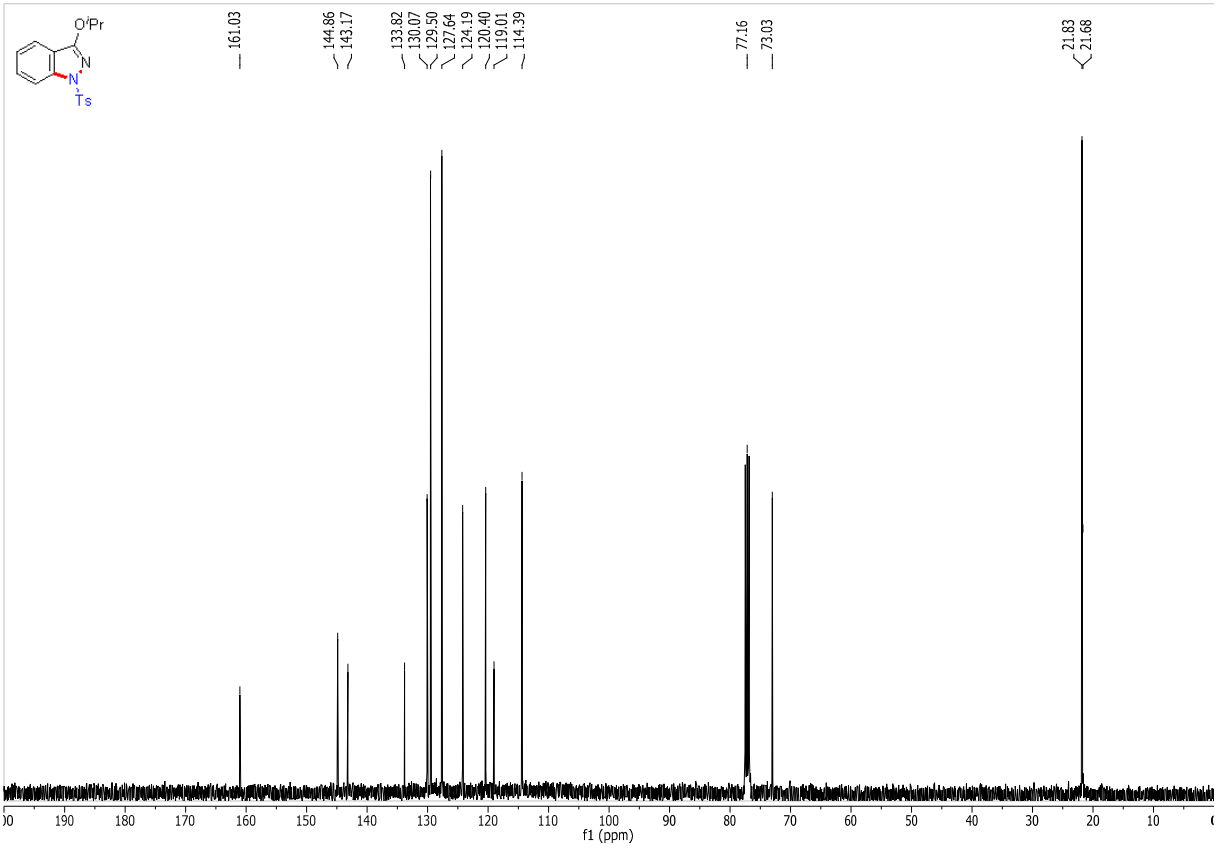
3-Methoxy-1-tosyl-1*H*-indazole (3ba)



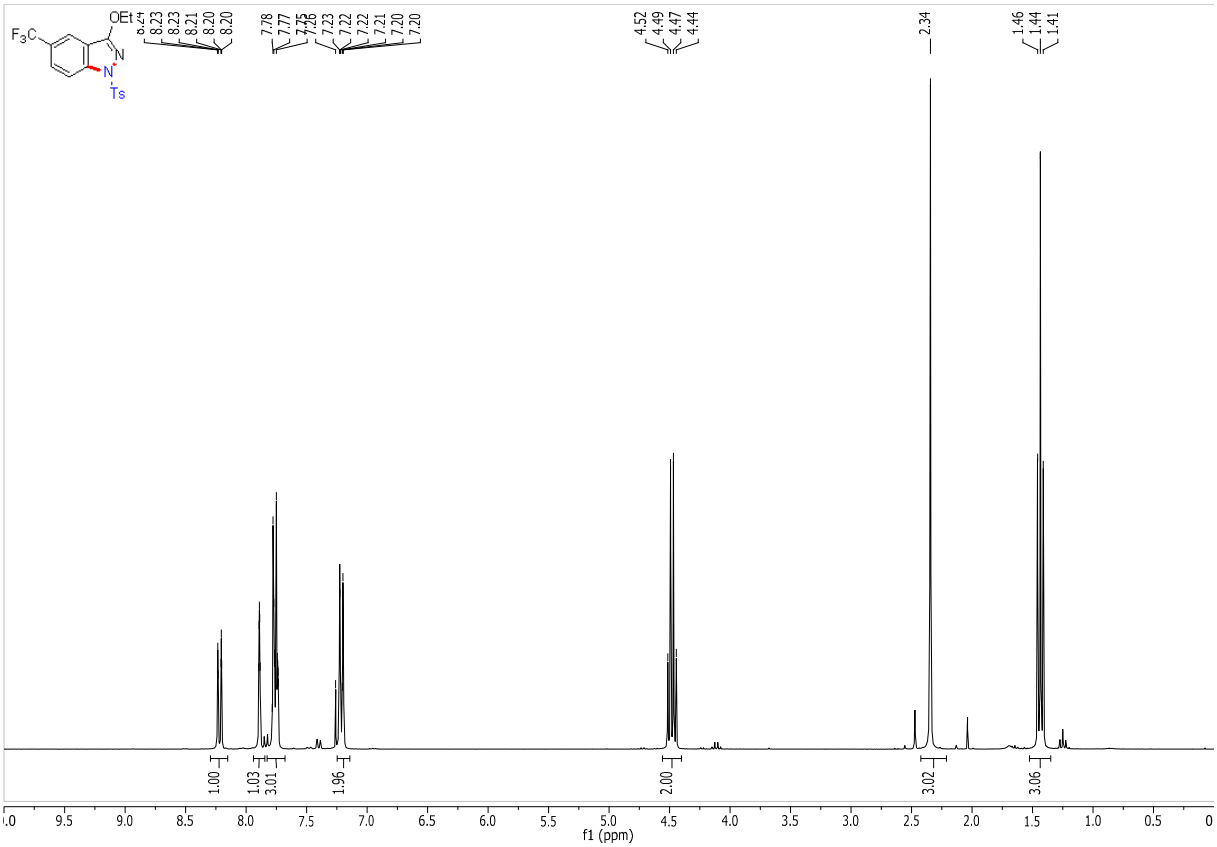


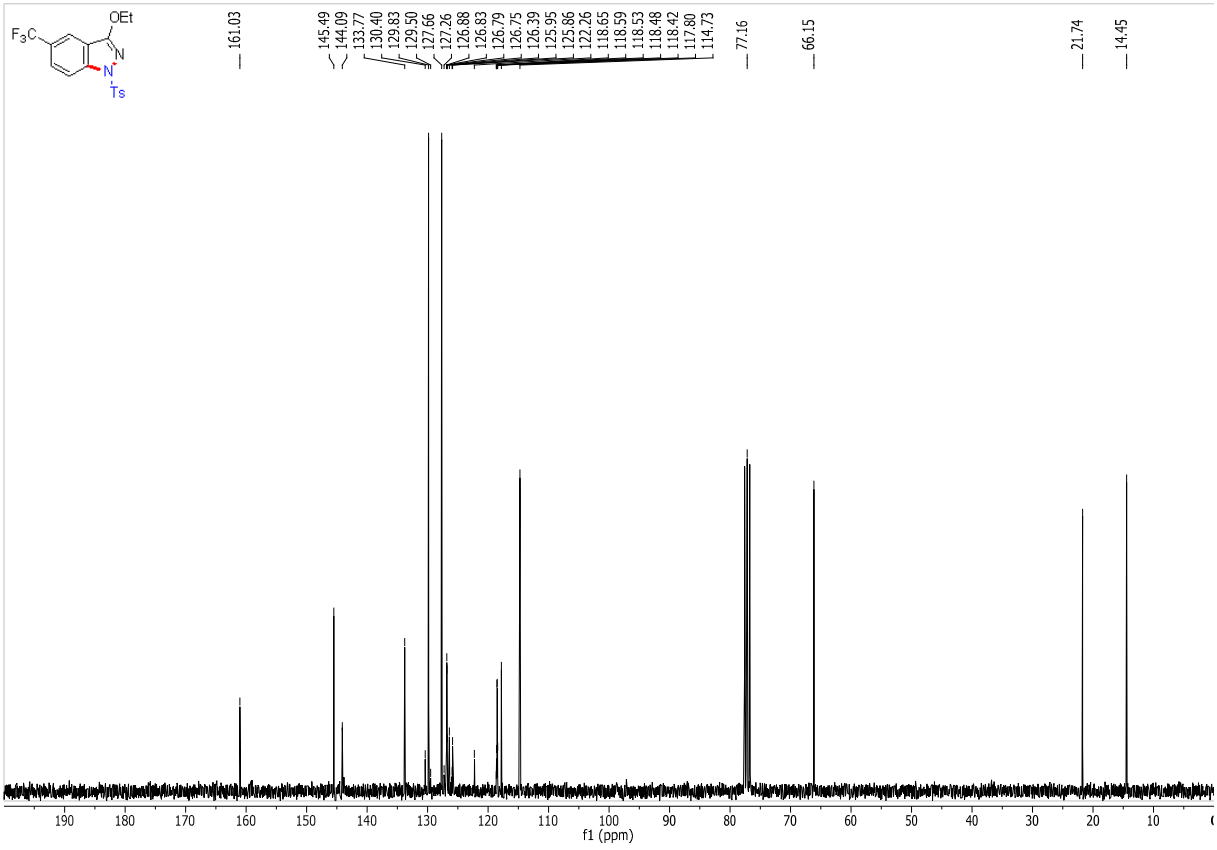
3-Isopropoxy-1-tosyl-1*H*-indazole (3ca)

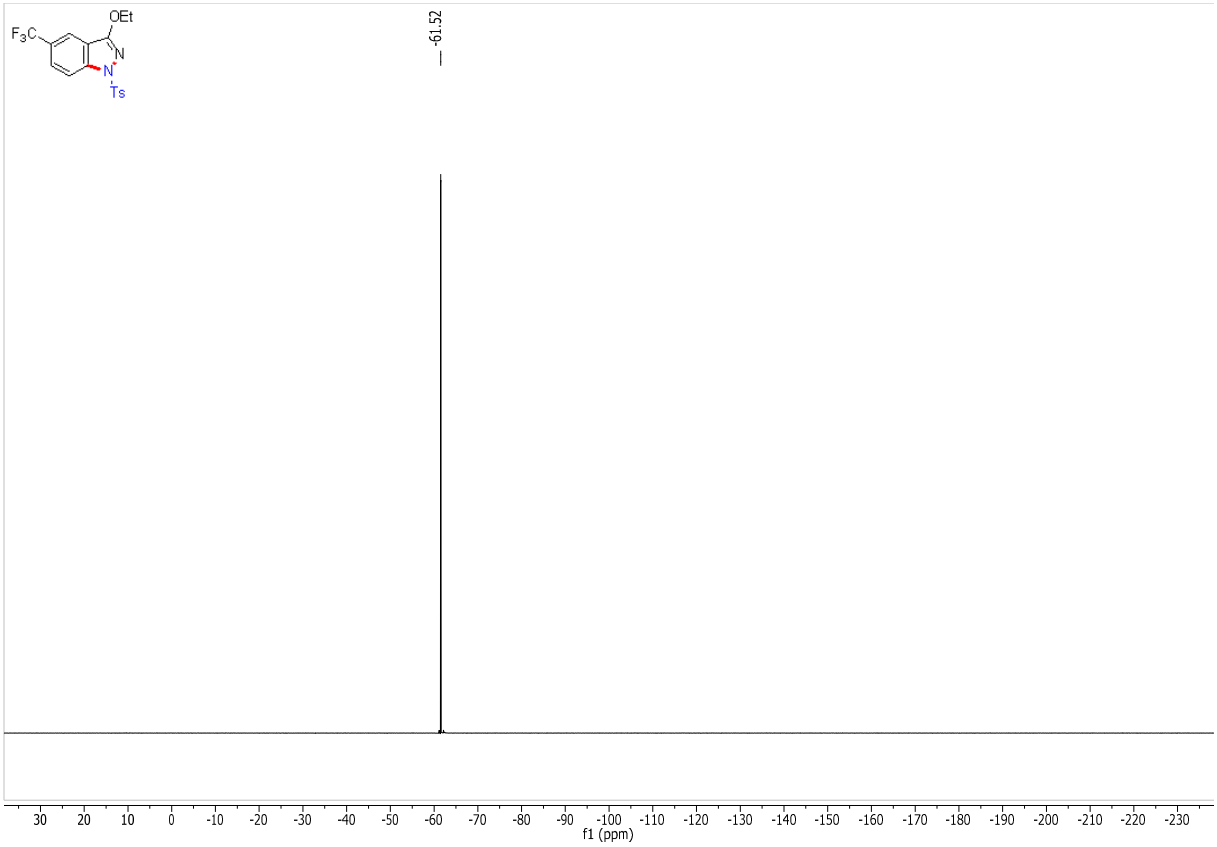




3-Ethoxy-1-tosyl-5-(trifluoromethyl)-1*H*-indazole (3da)



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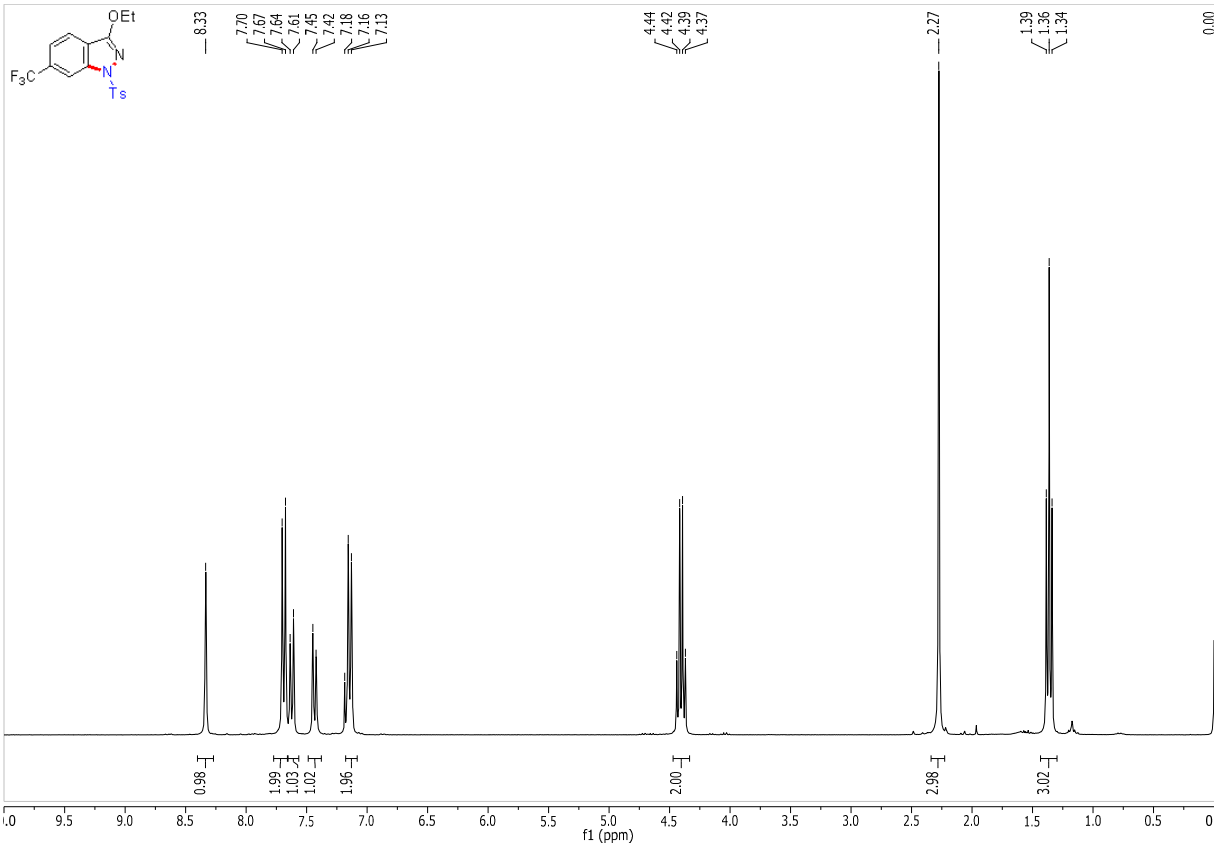
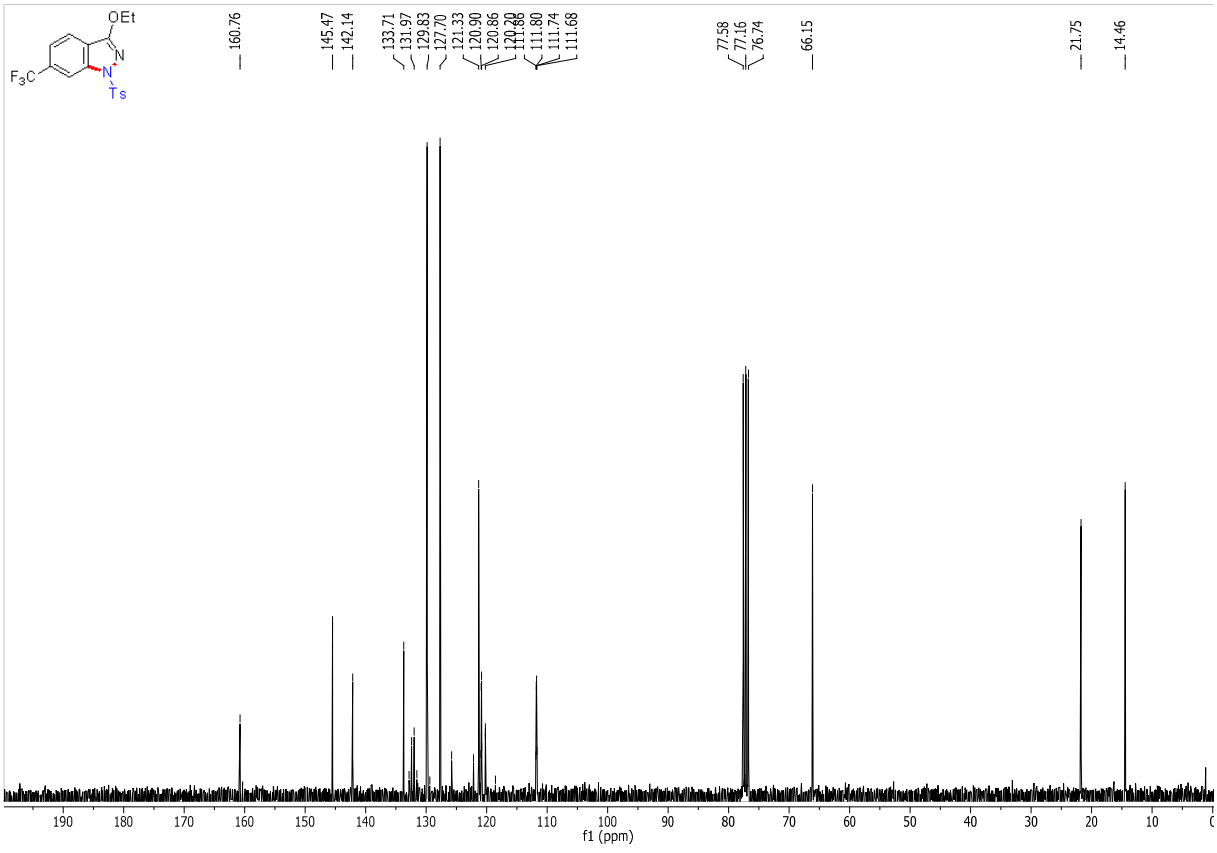
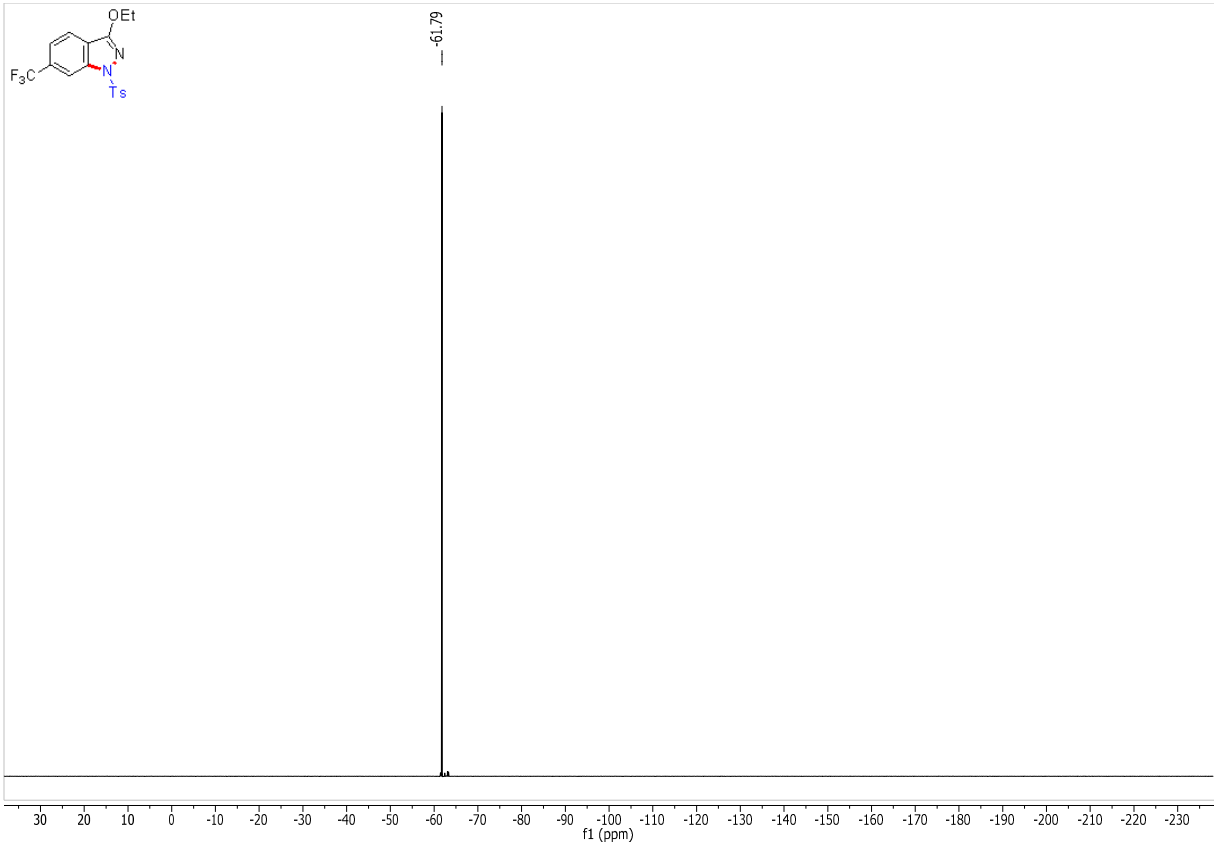
f1 (ppm)

3-Ethoxy-1-tosyl-6-(trifluoromethyl)-1*H*-indazole (3ea)



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Ts
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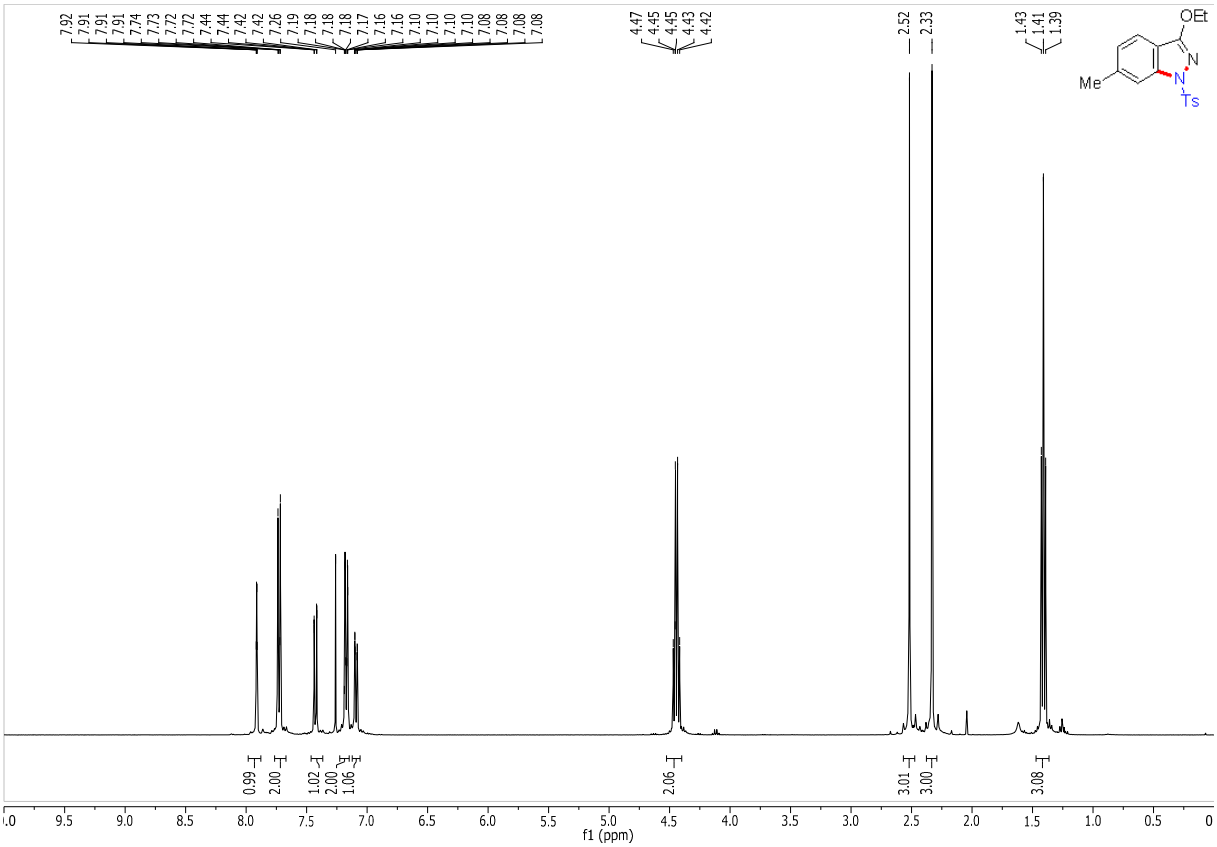
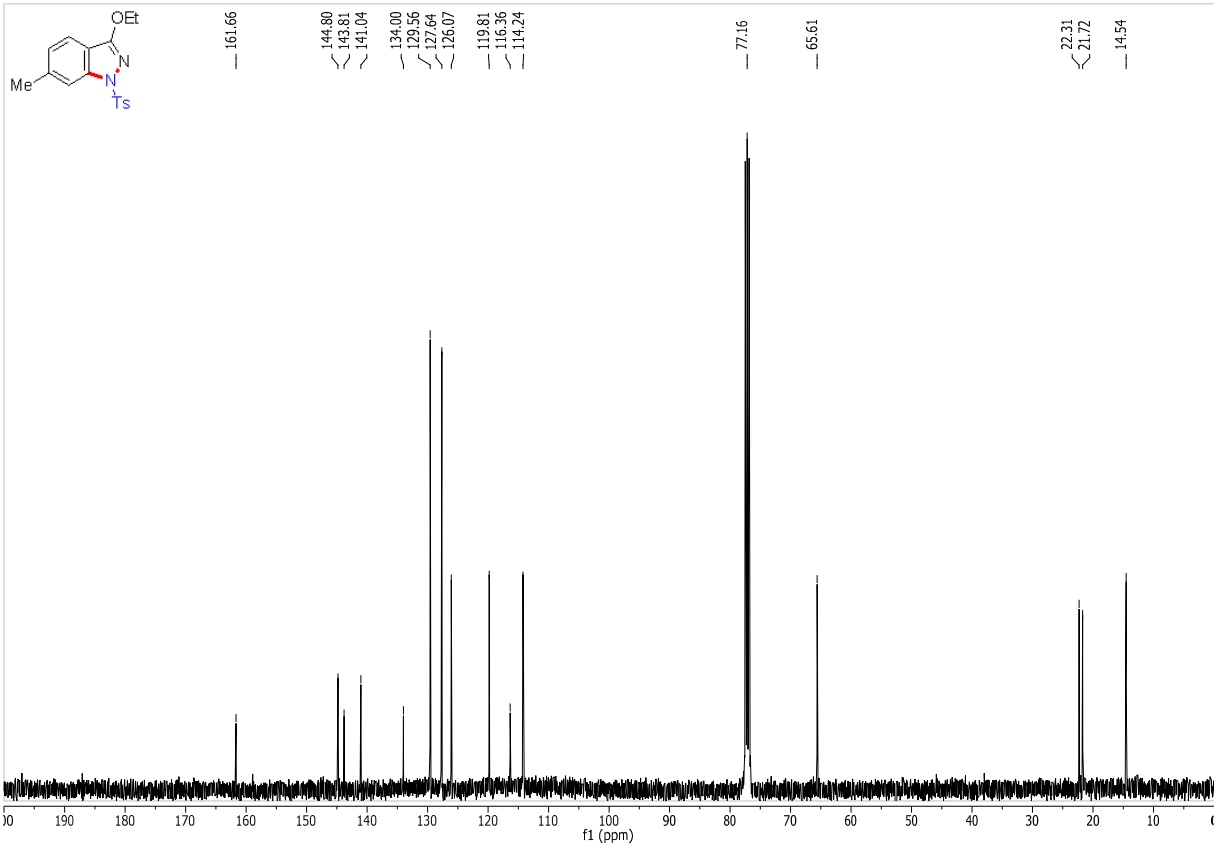
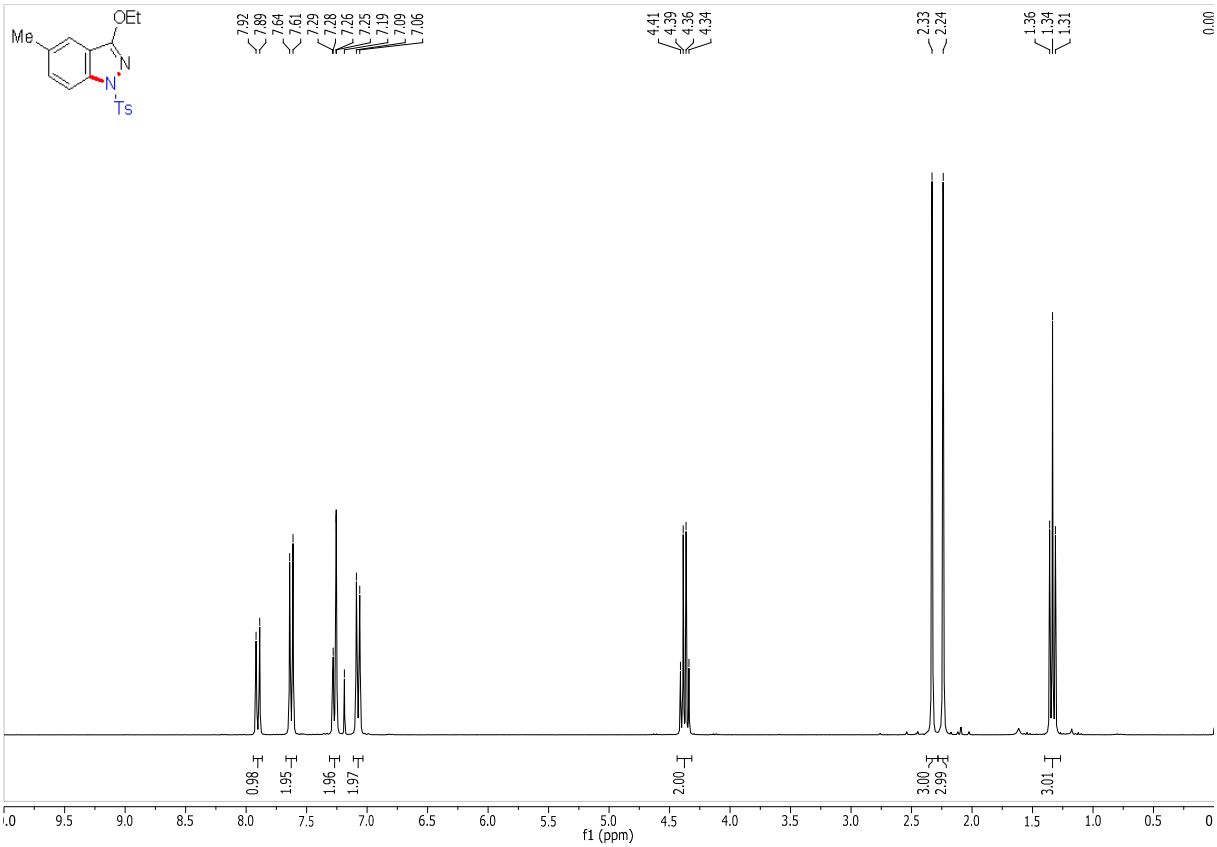
f1 (ppm)

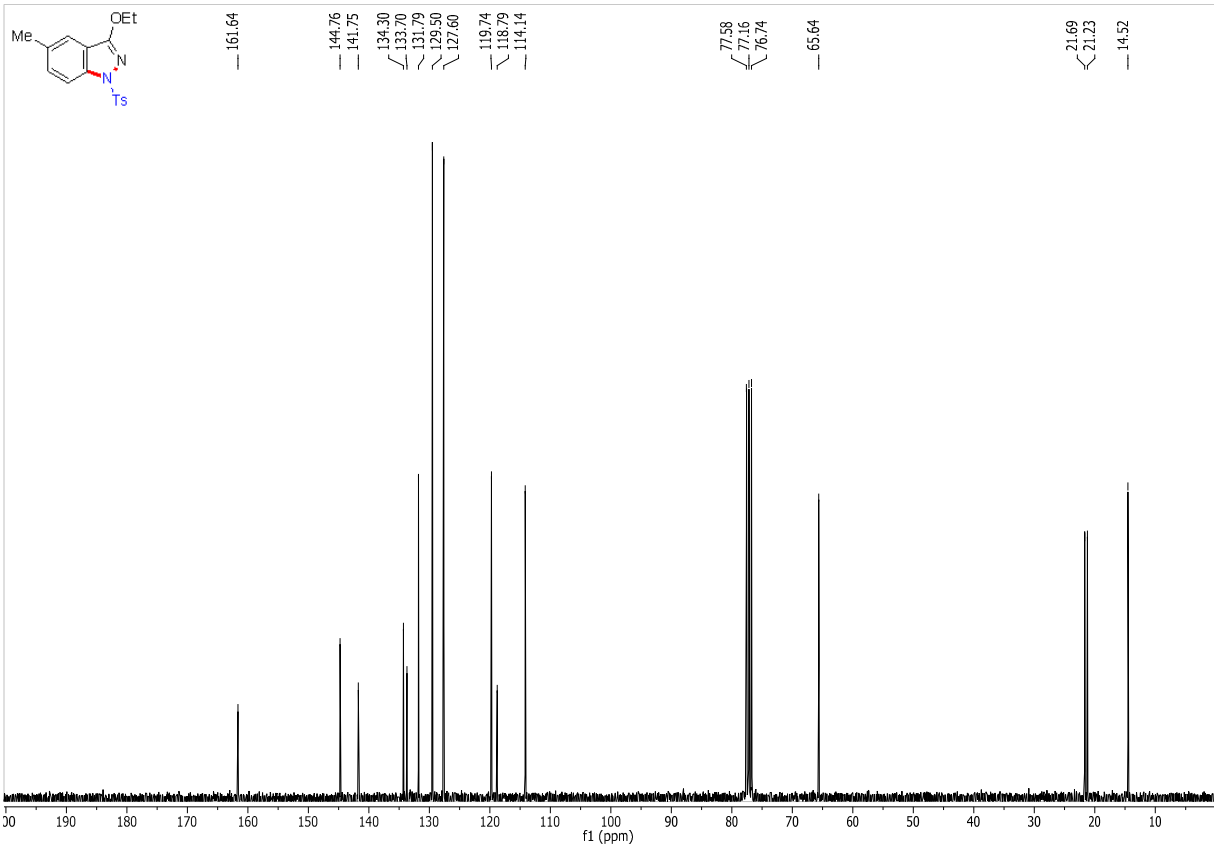
3-Ethoxy-6-methyl-1-tosyl-1*H*-indazole (3fa)



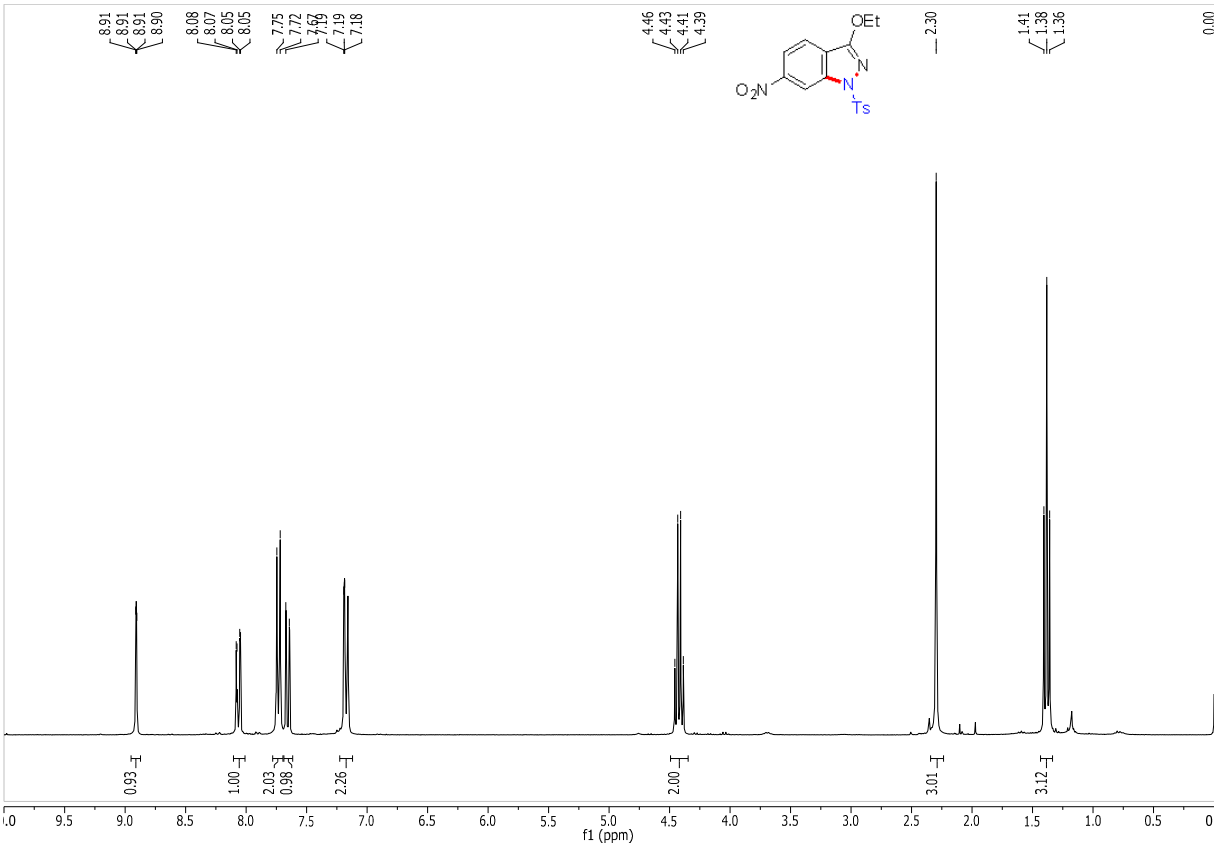


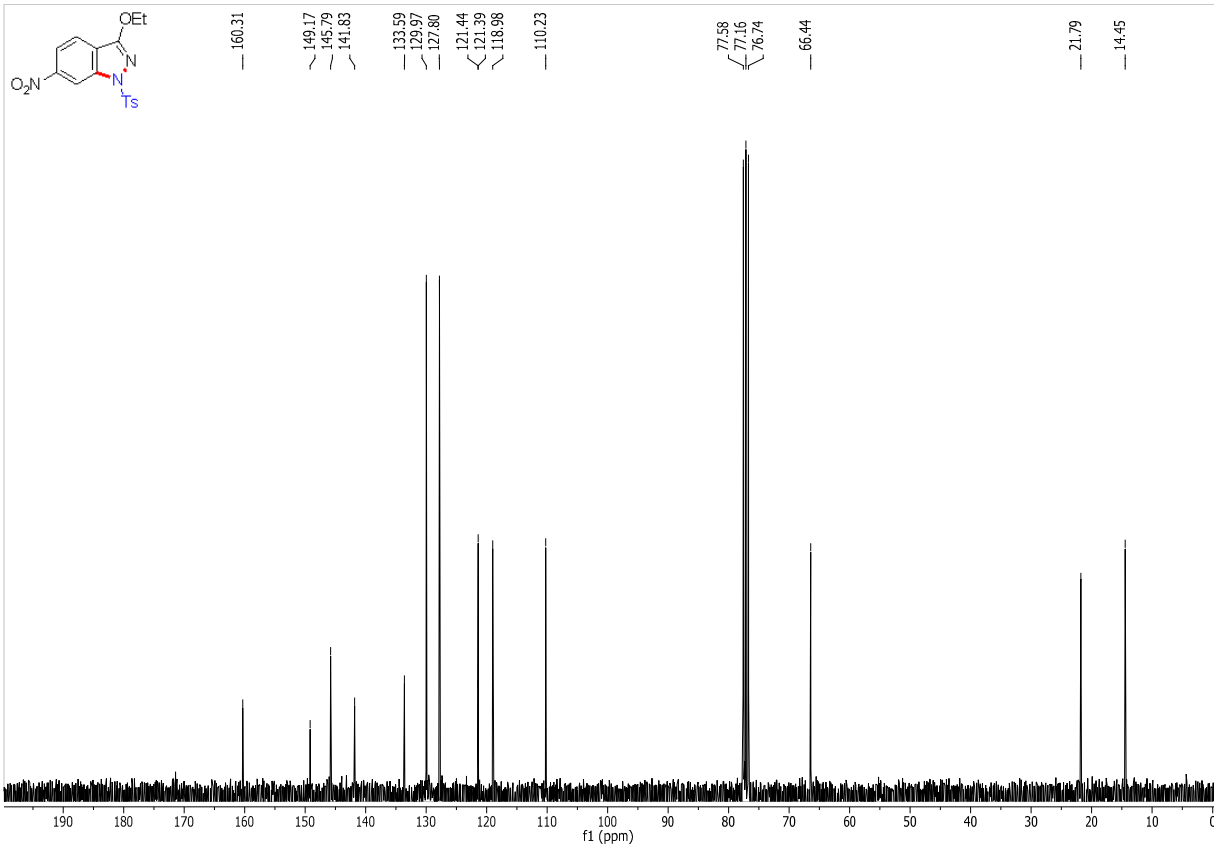
3-Ethoxy-5-methyl-1-tosyl-1*H*-indazole (3ga)



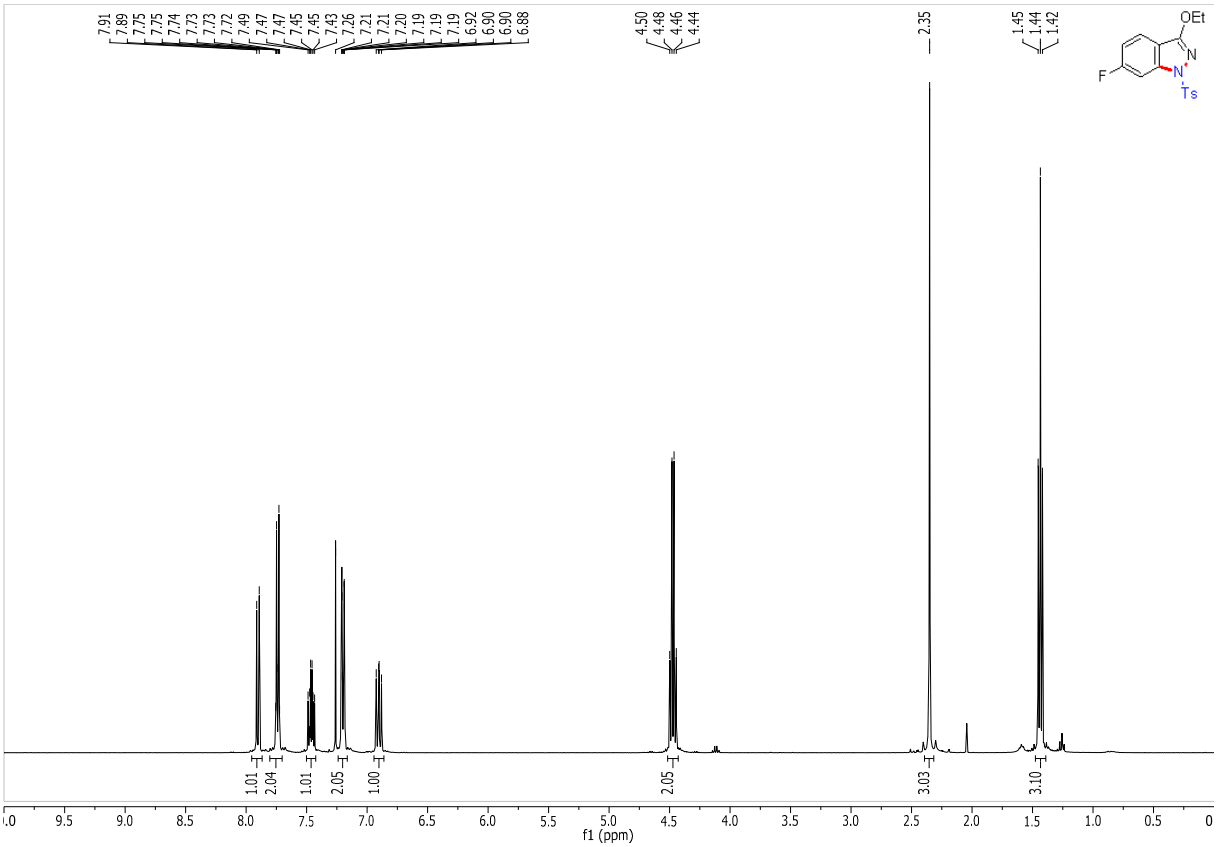


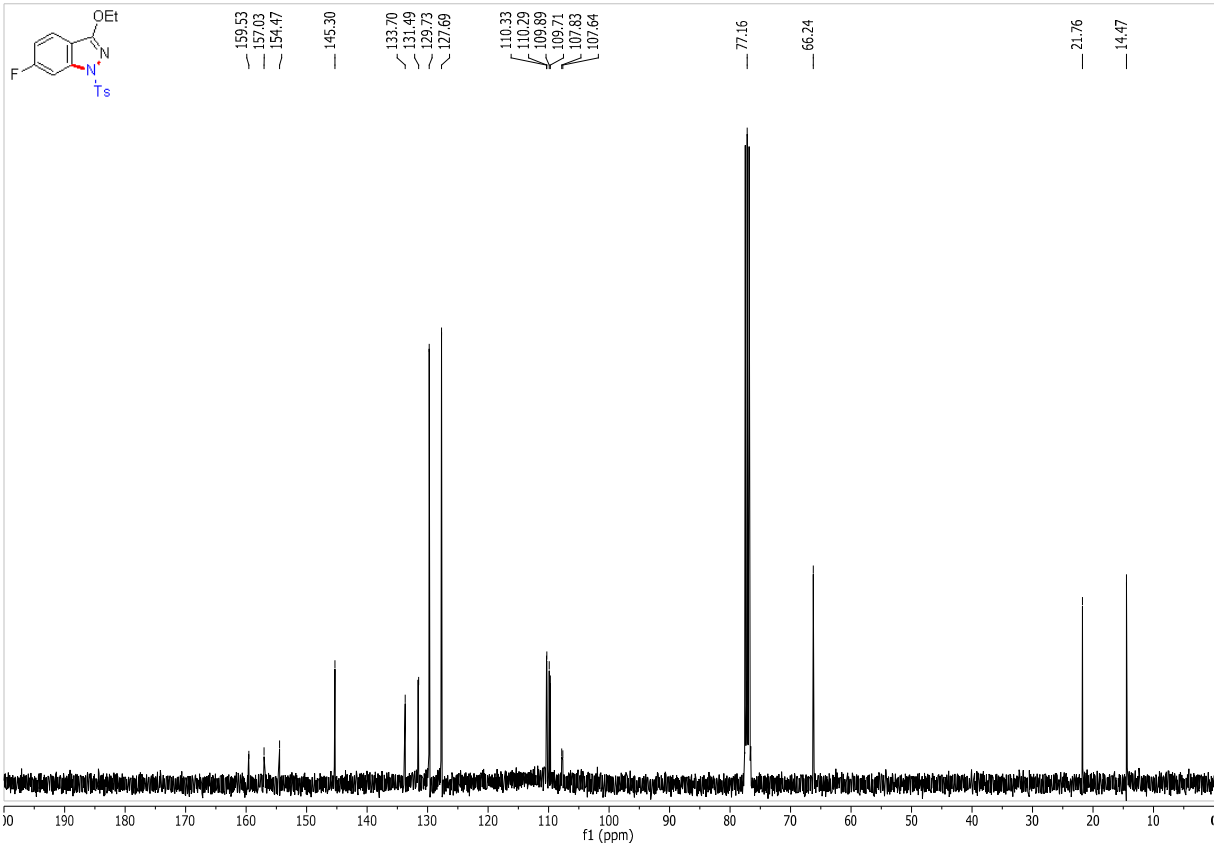
3-Ethoxy-6-nitro-1-tosyl-1*H*-indazole (3ha)

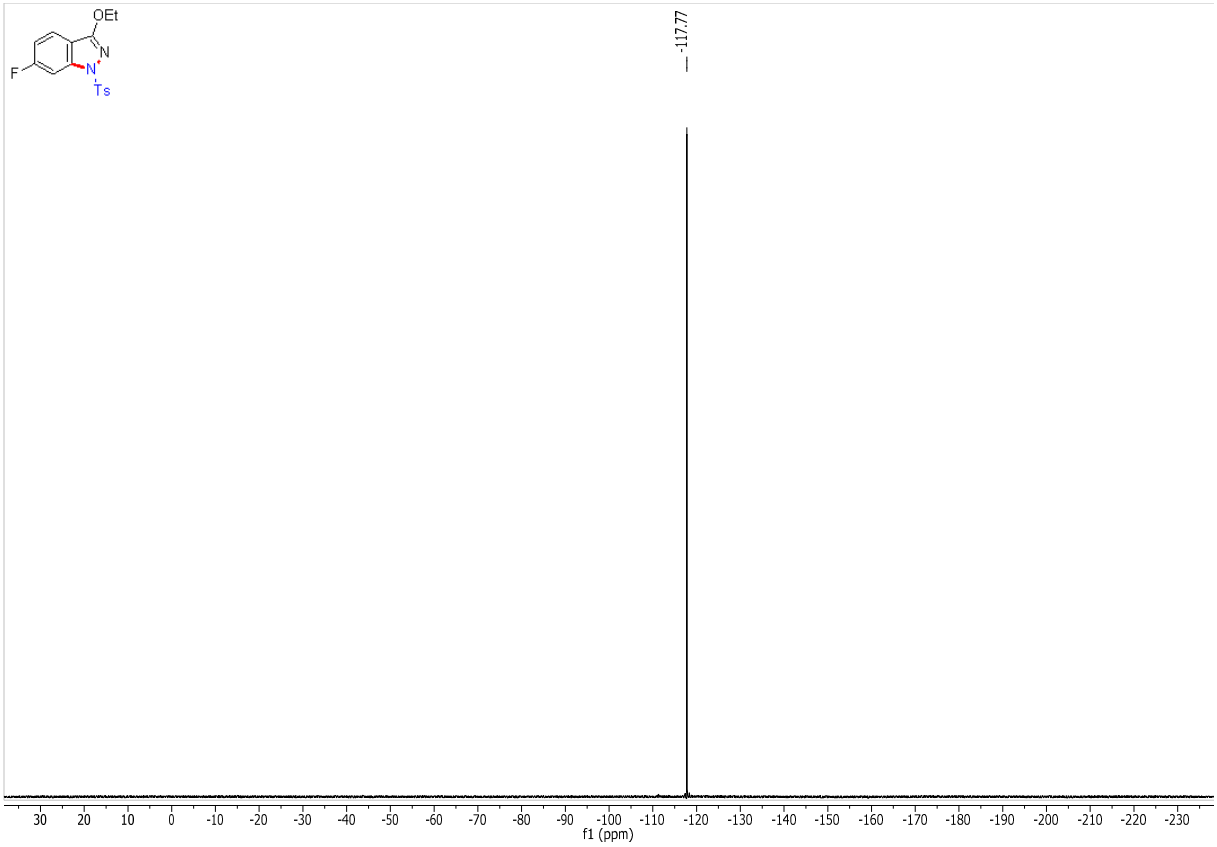




3-Ethoxy-6-fluoro-1-tosyl-1*H*-indazole (3ia)



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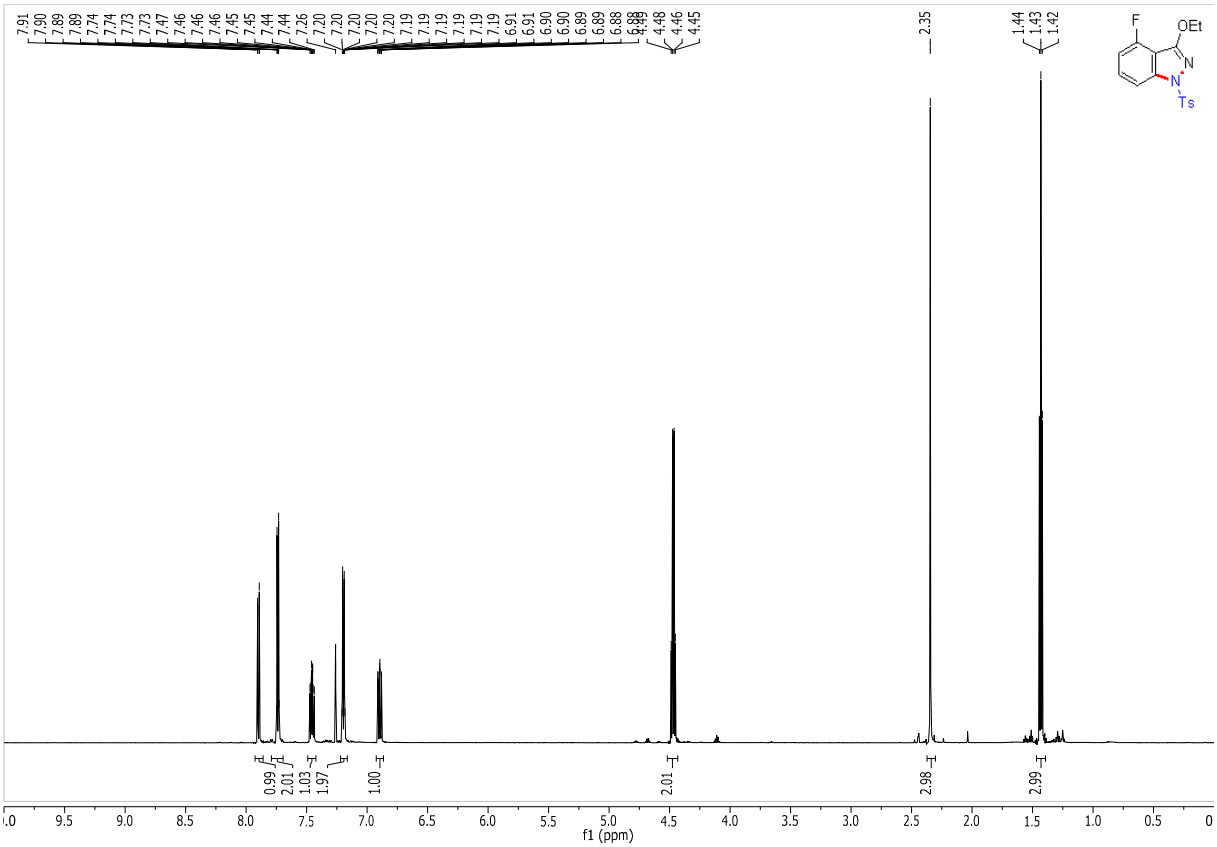
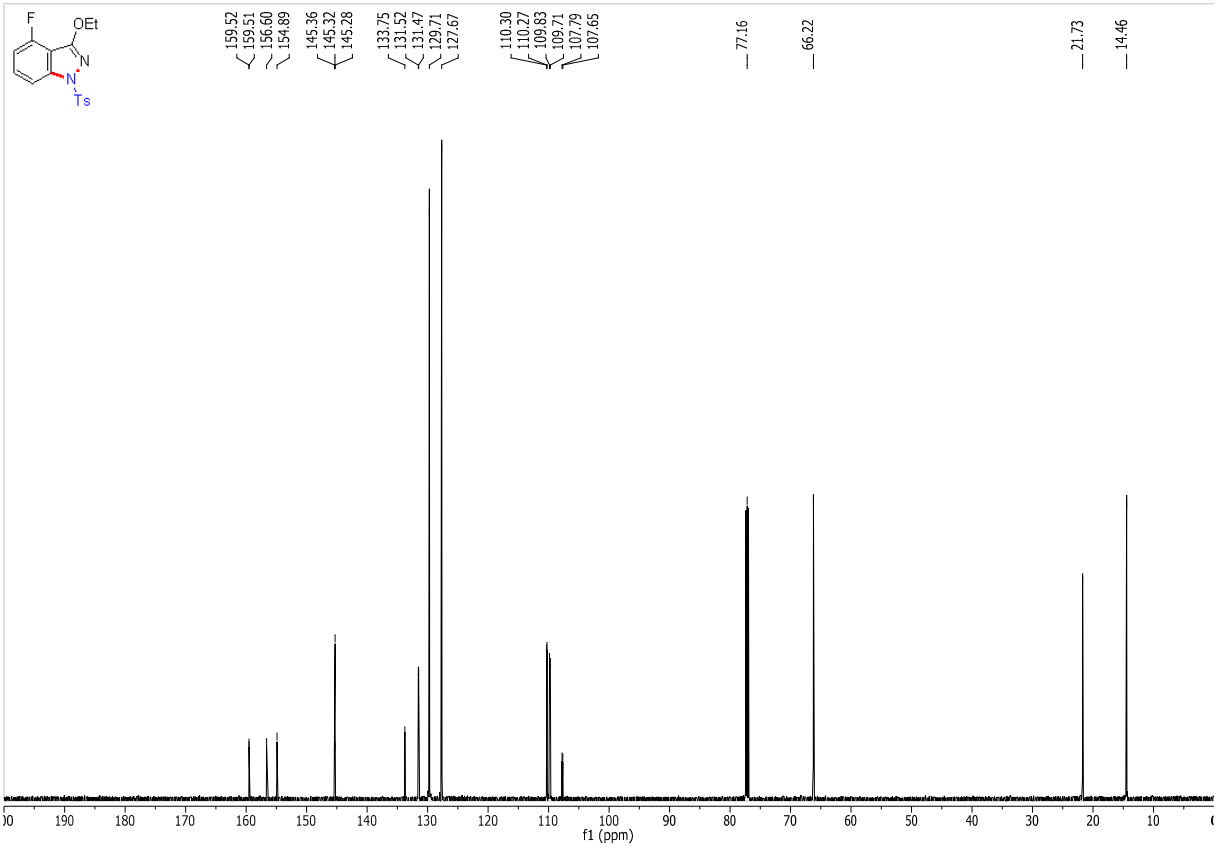
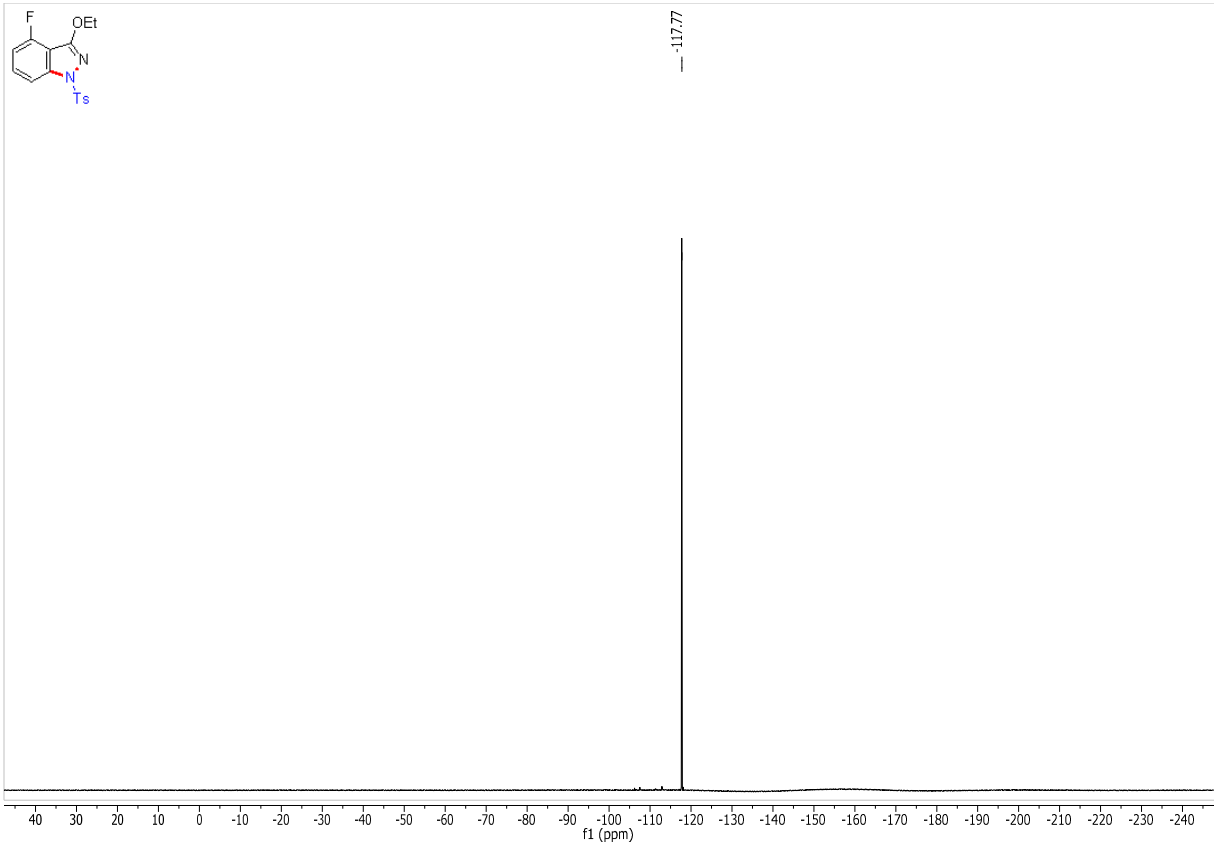
F
N
Ts
-117.77
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

3-Ethoxy-4-fluoro-1-tosyl-1*H*-indazole (3ja)



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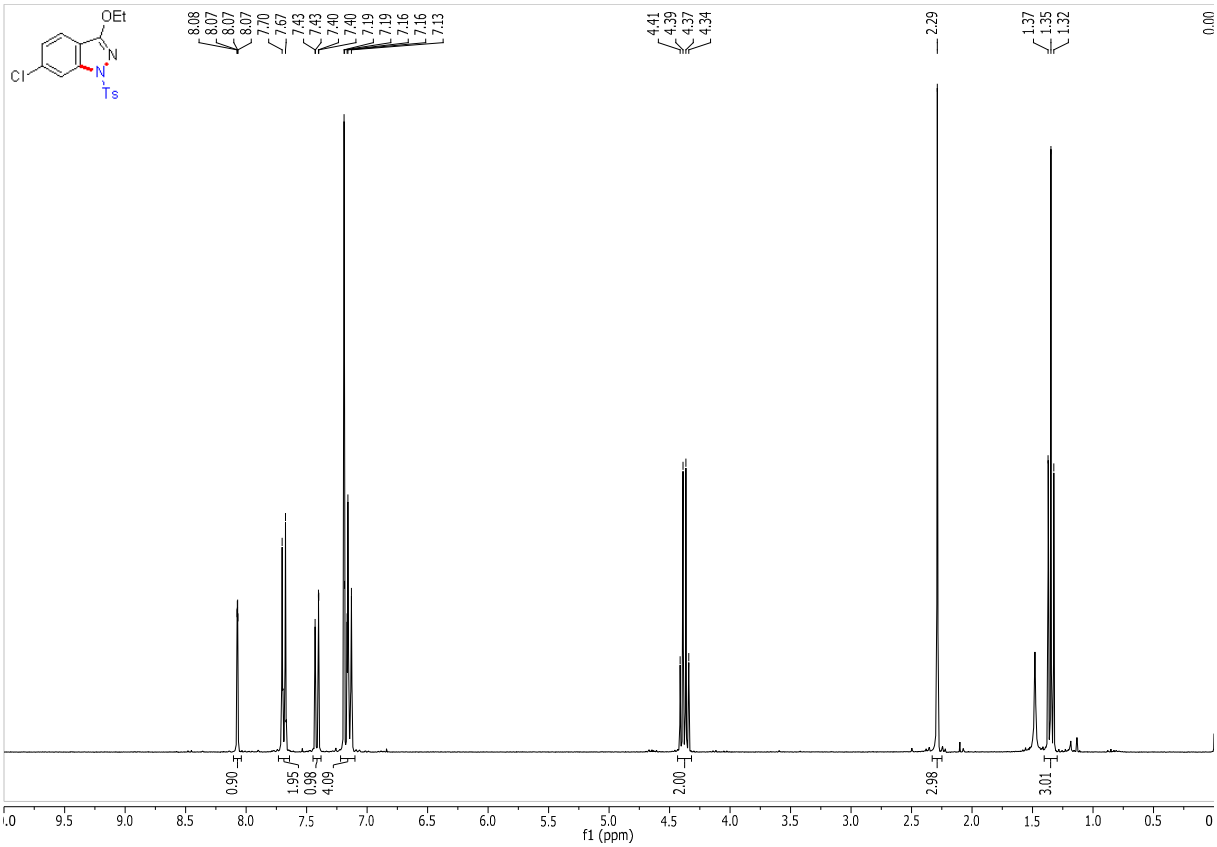
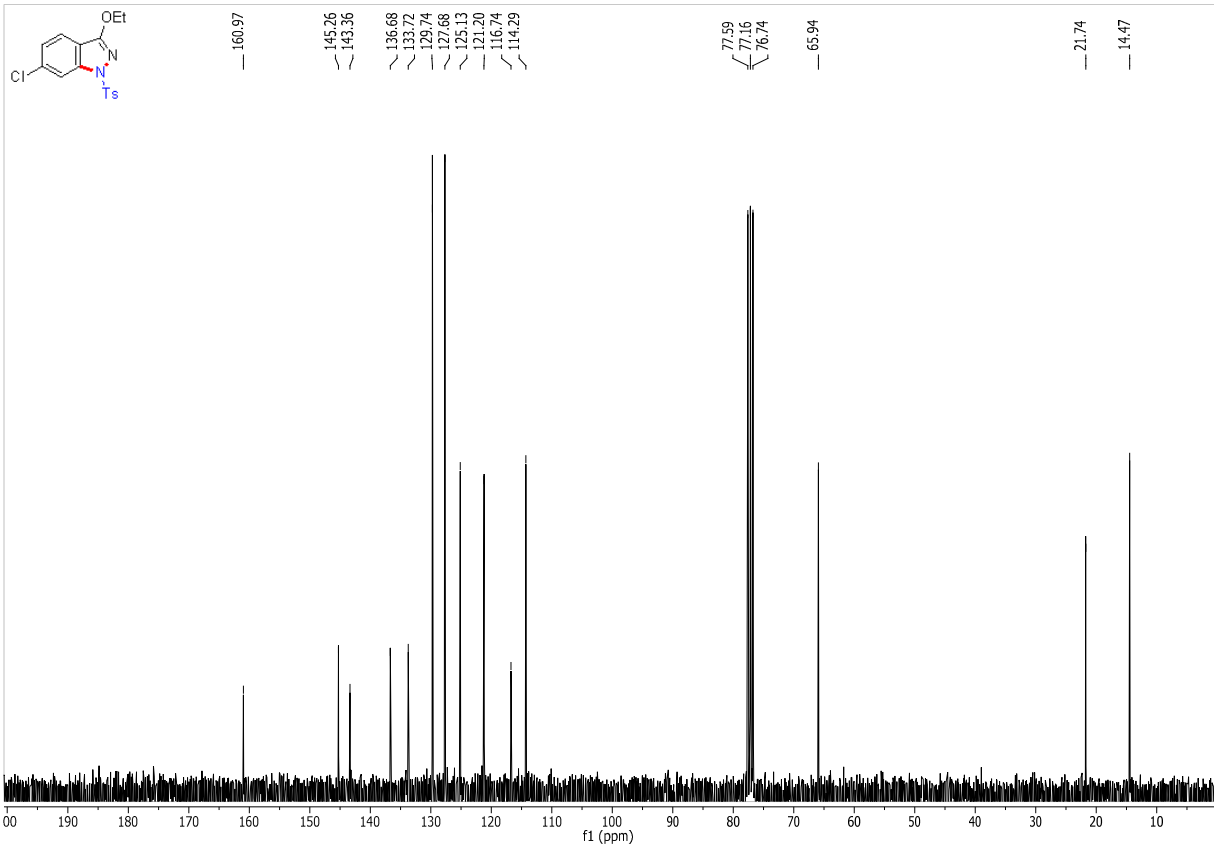
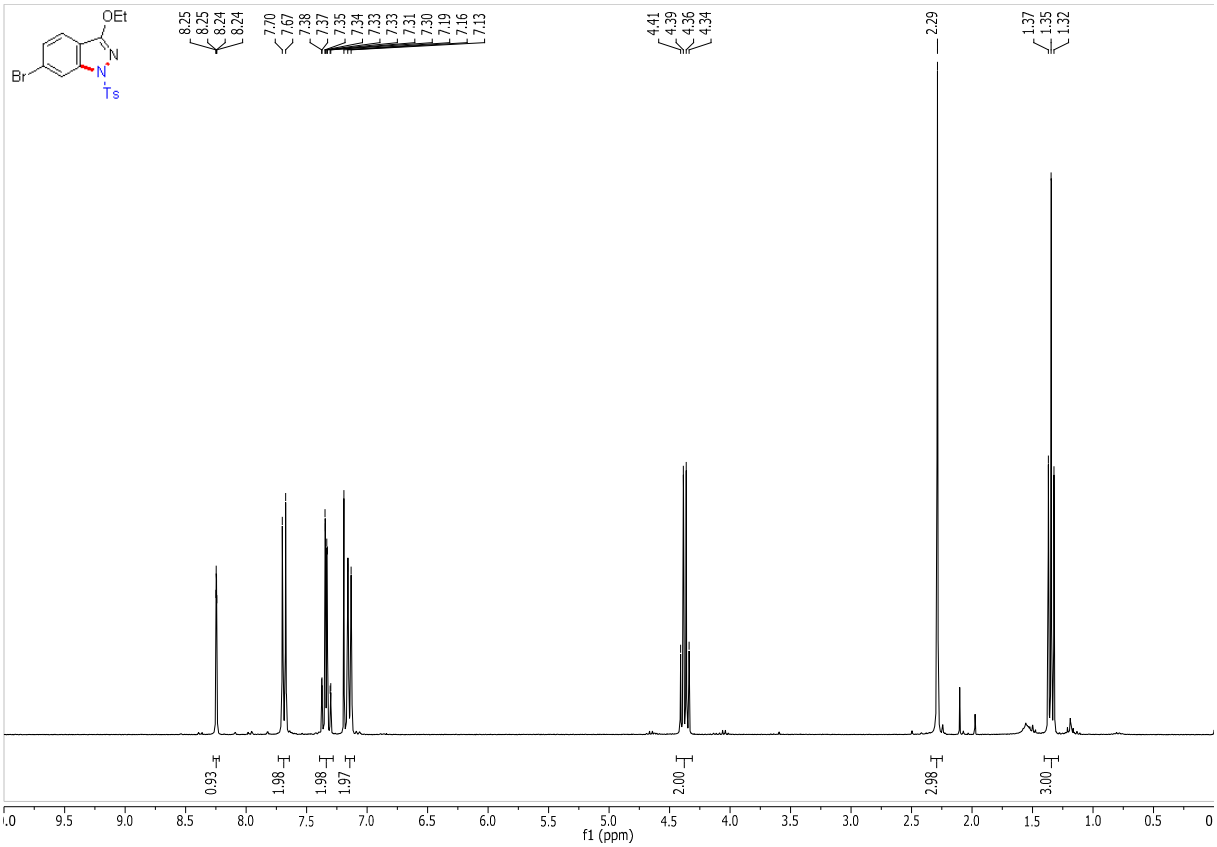
OEt
N
N
Ts
-117.77
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

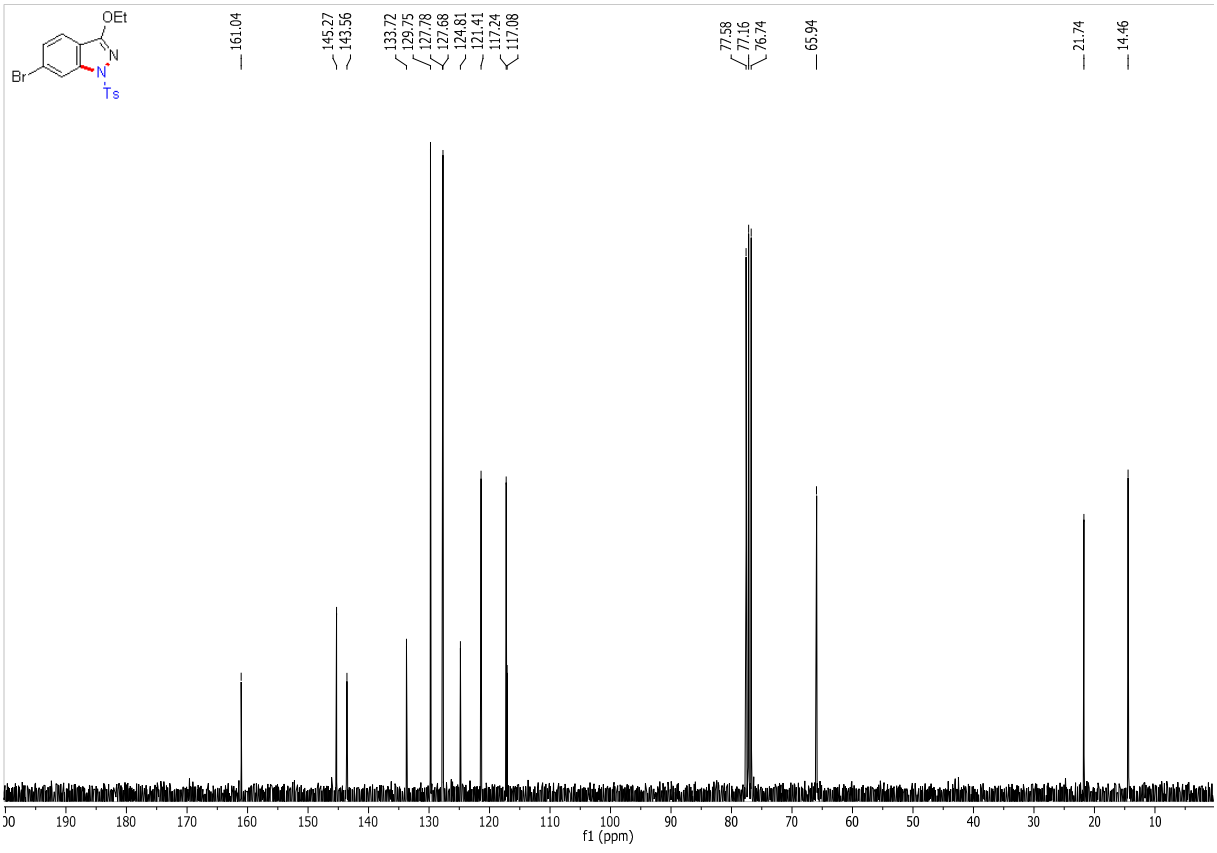
6-Chloro-3-ethoxy-1-tosyl-1*H*-indazole (3ka)



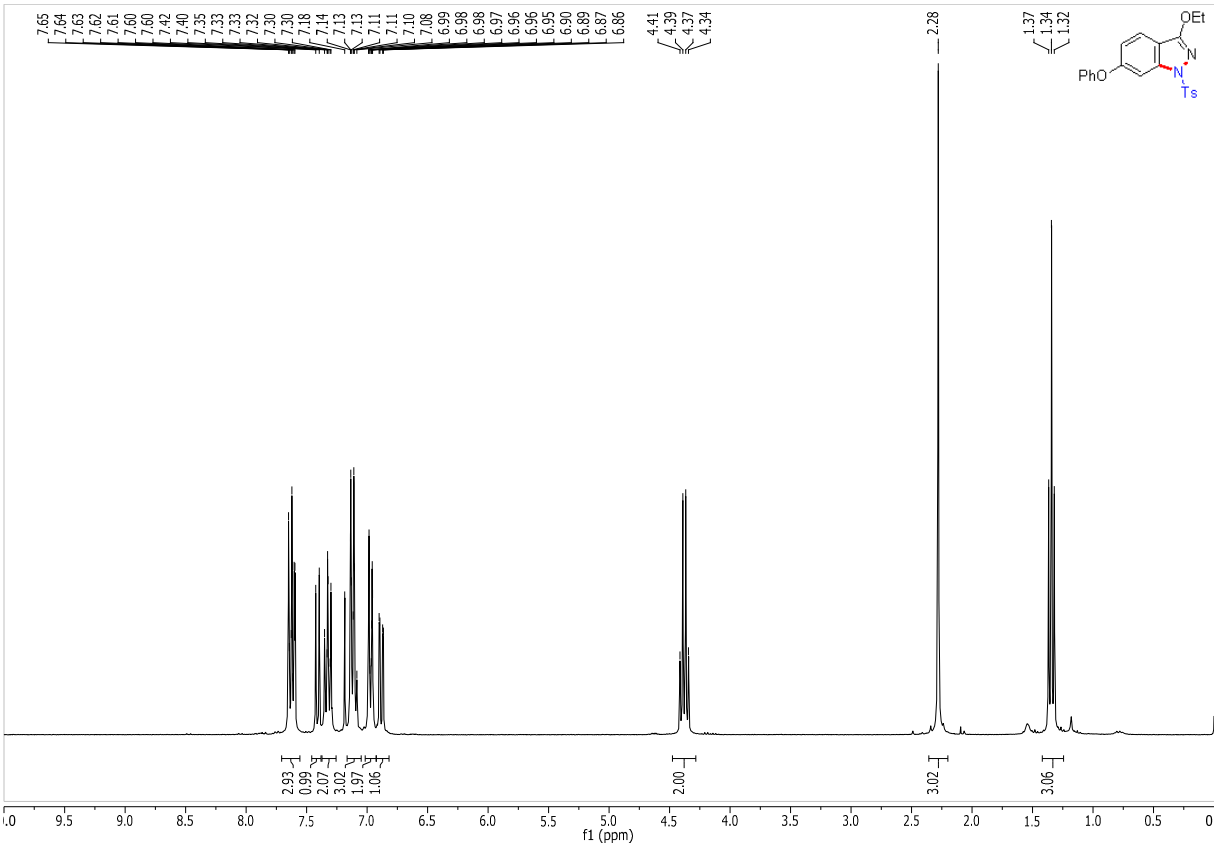


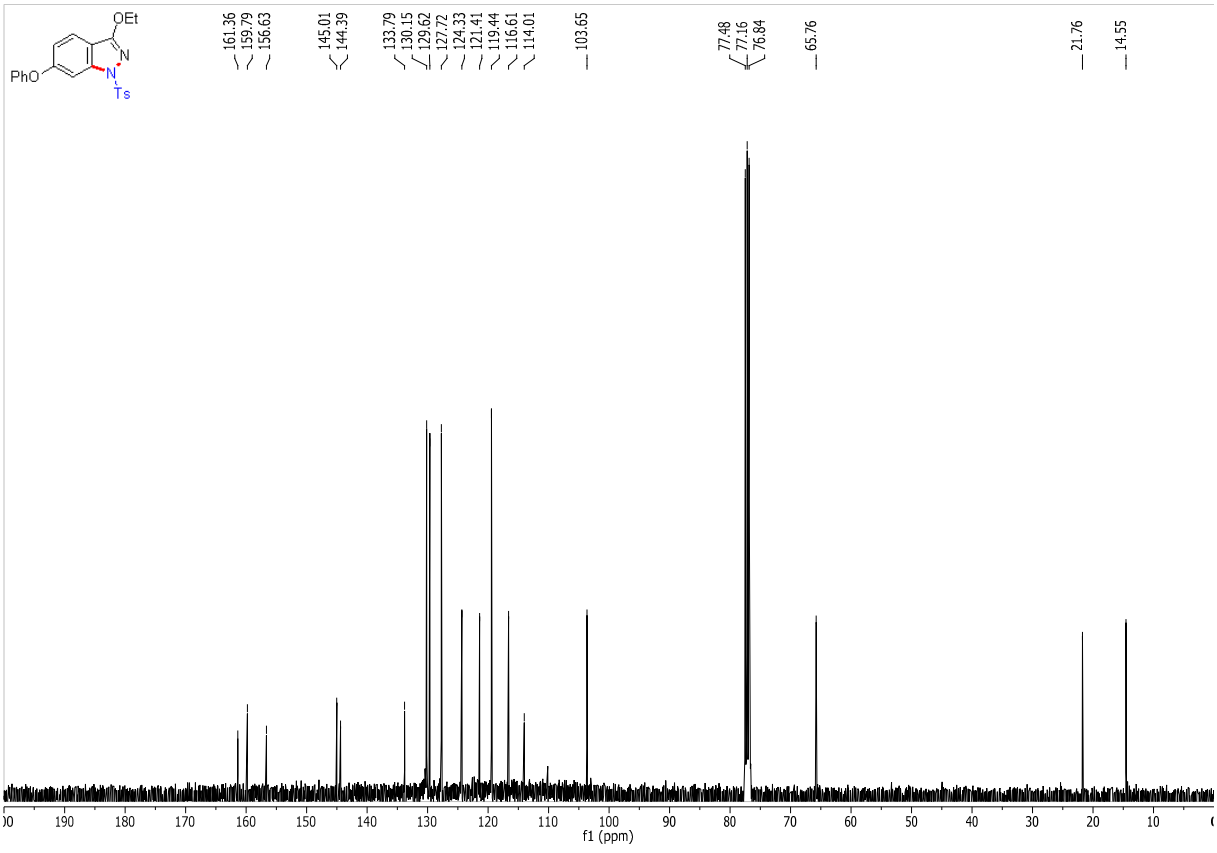
6-Bromo-3-ethoxy-1-tosyl-1*H*-indazole (3la)



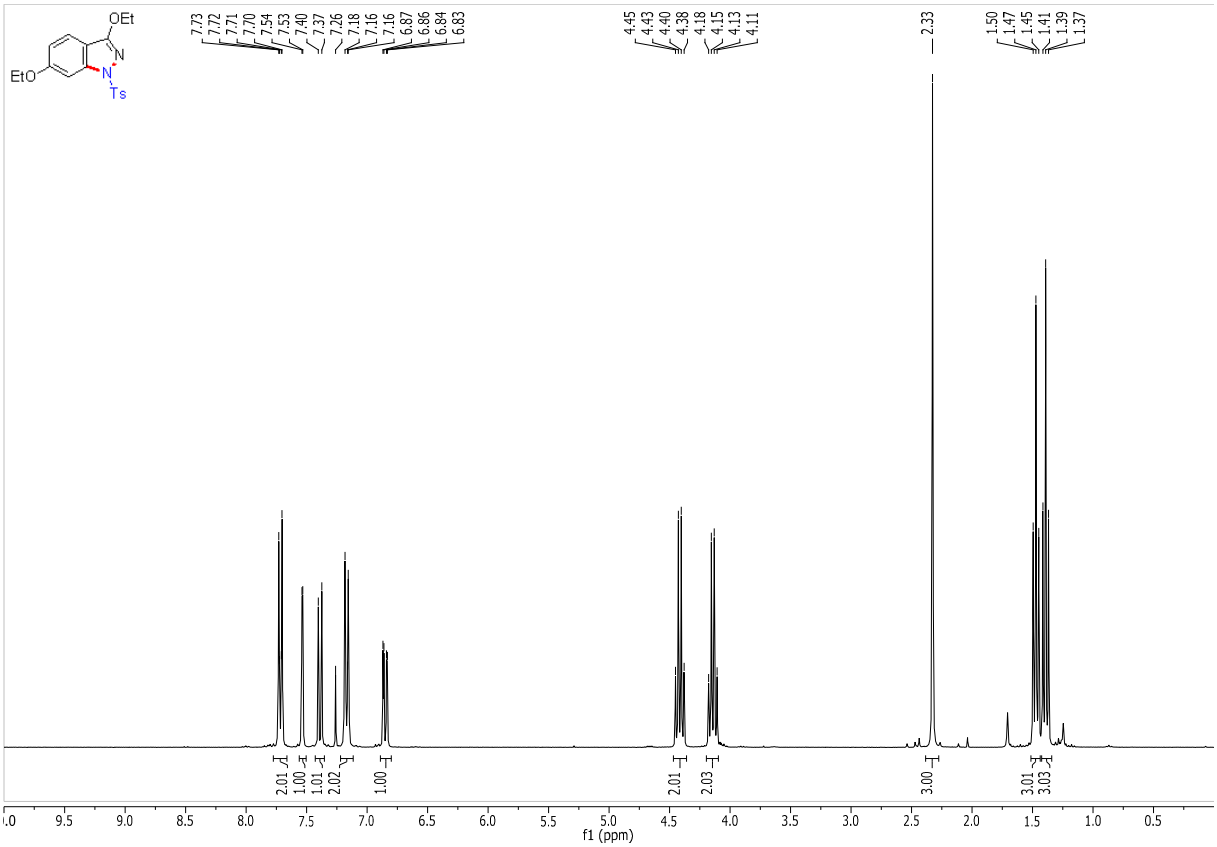


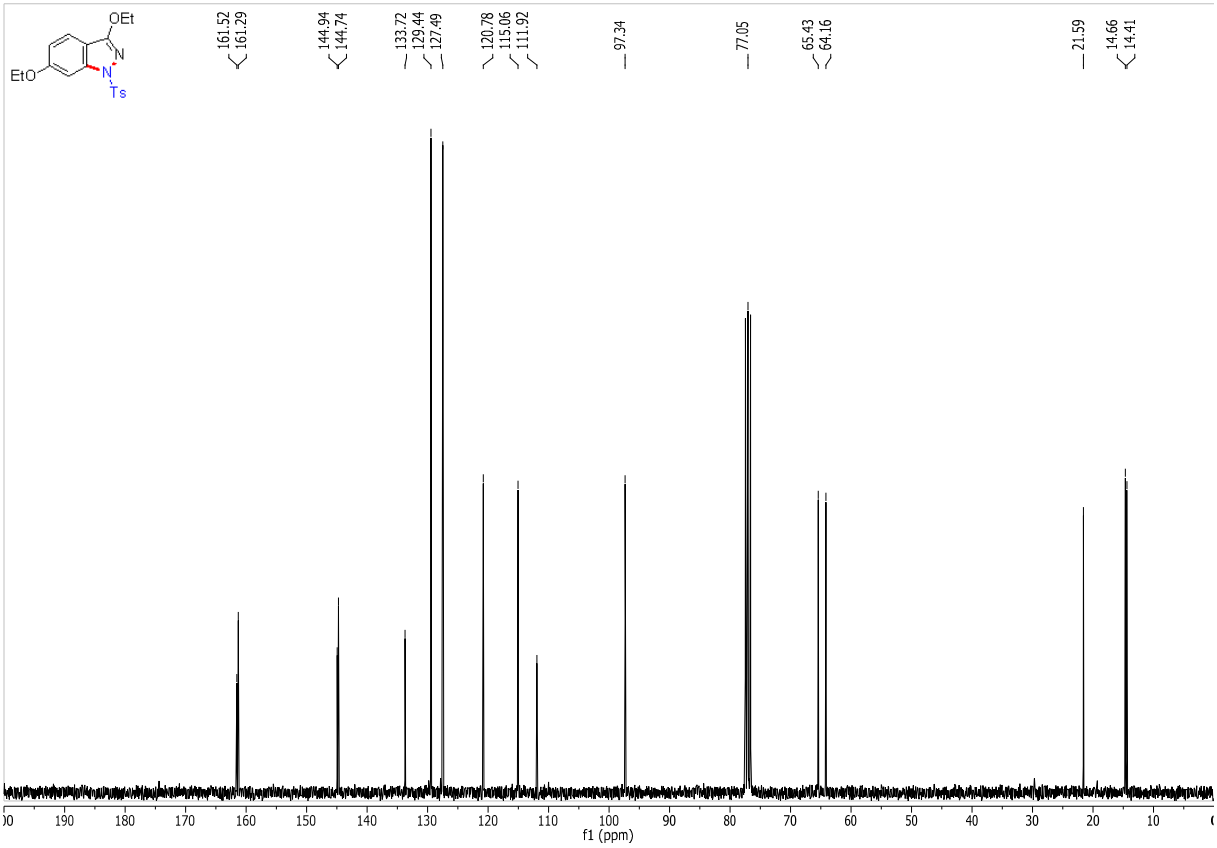
3-Ethoxy-6-phenoxy-1-tosyl-1*H*-indazole (3ma)



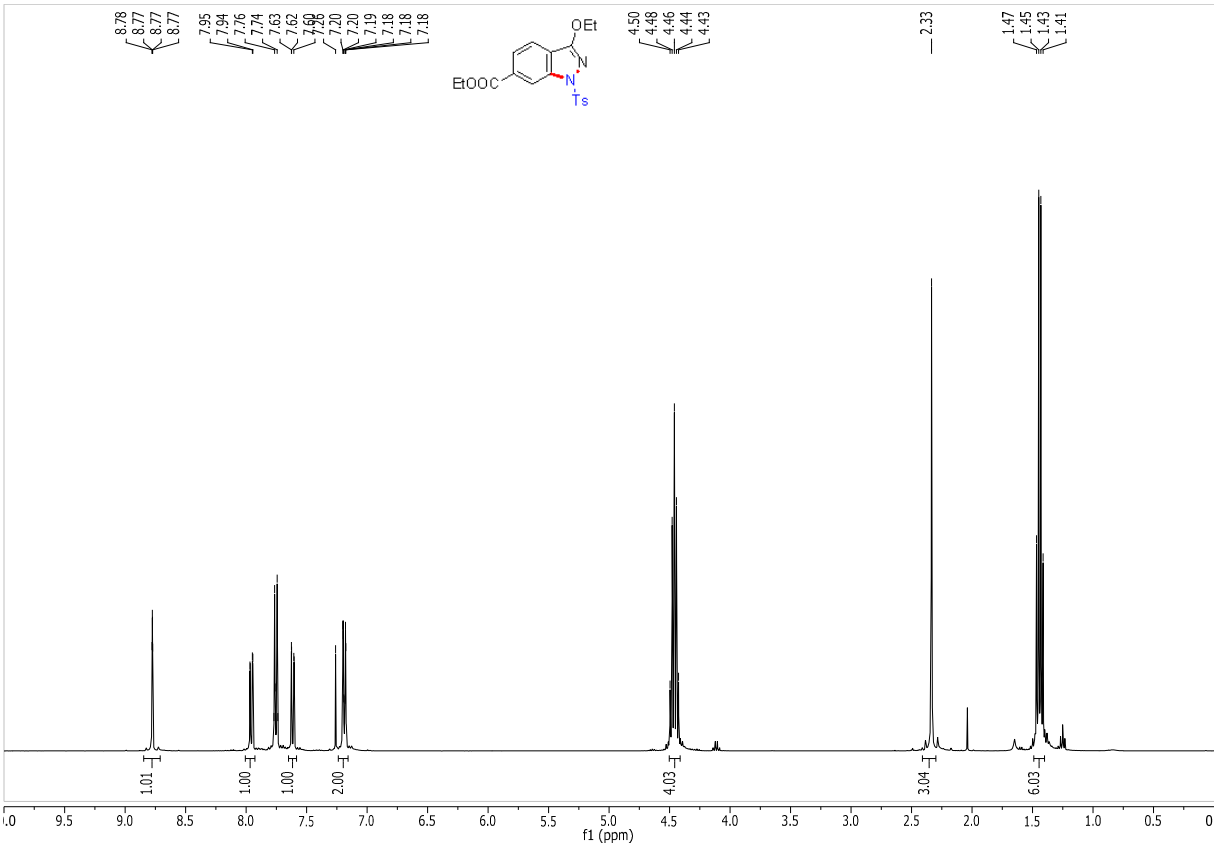


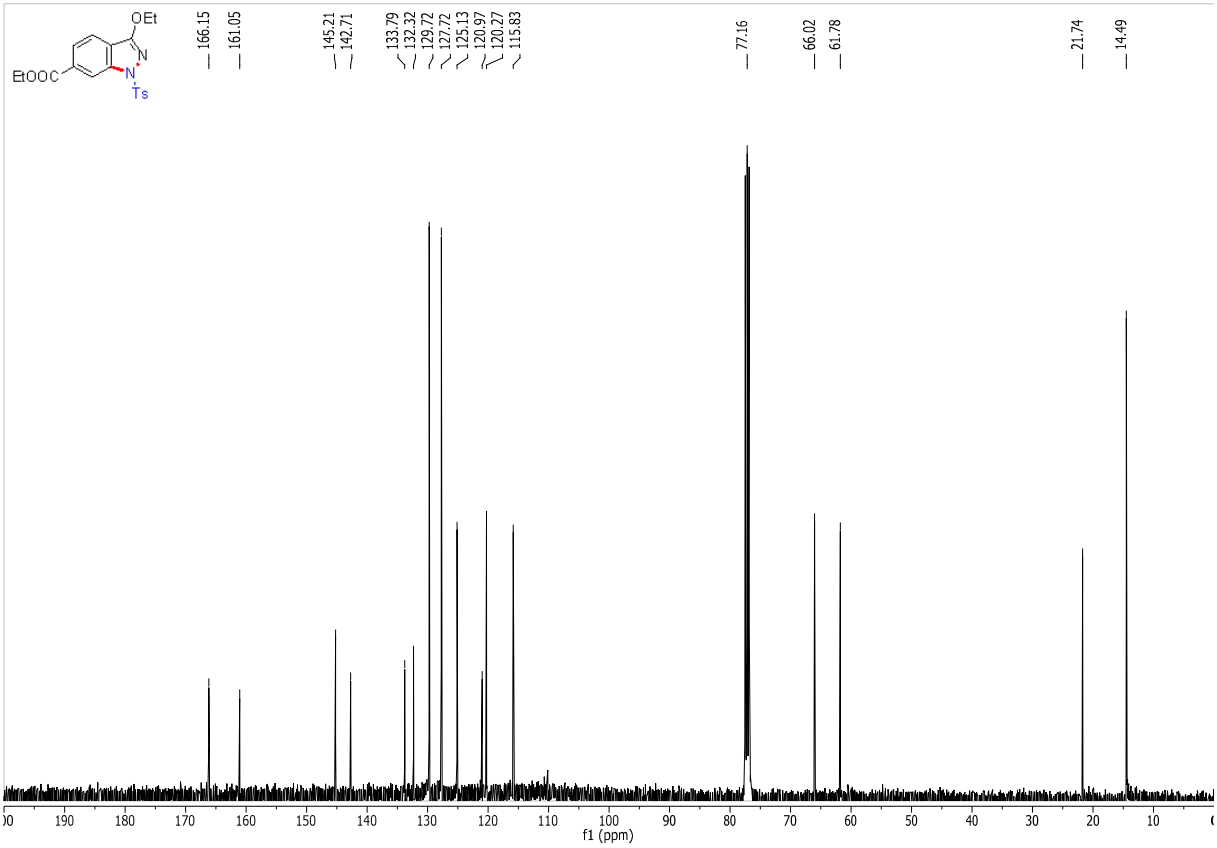
3,6-Diethoxy-1-tosyl-1*H*-indazole (3na)



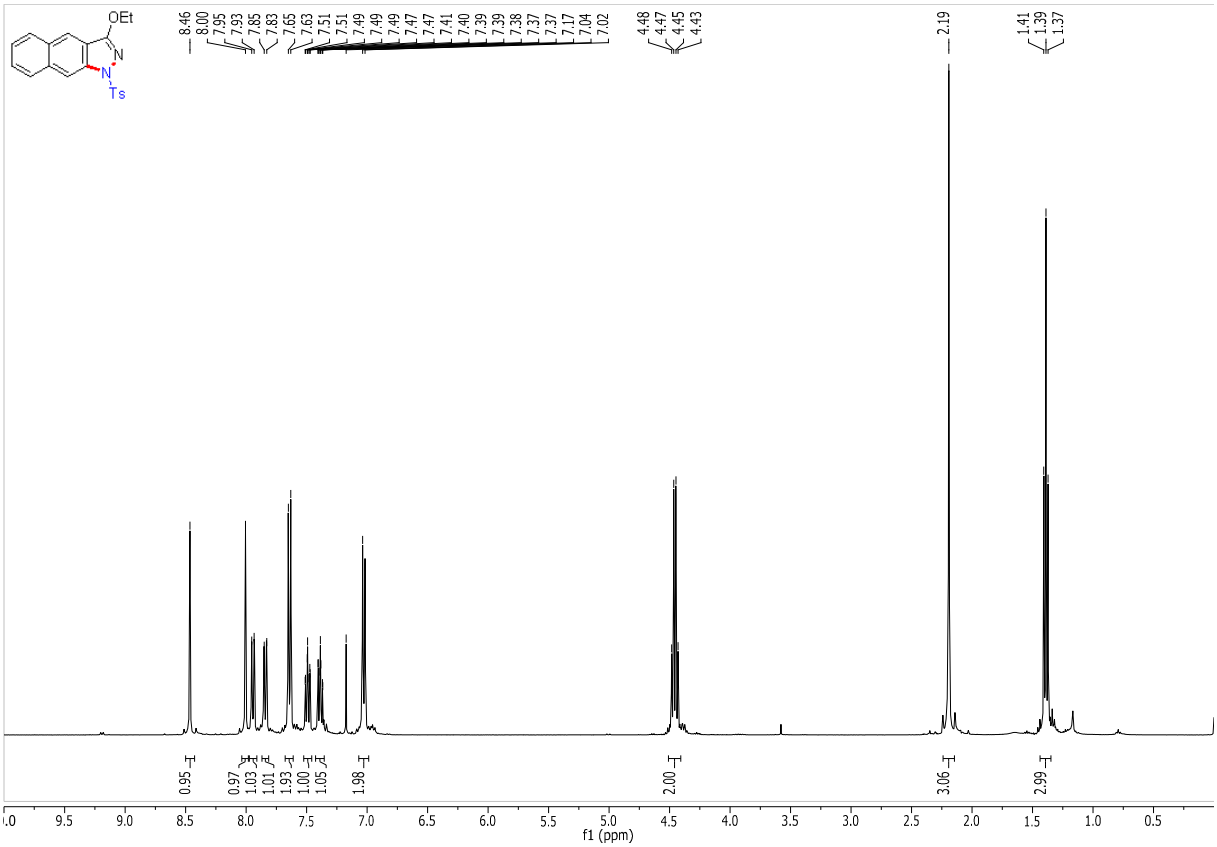


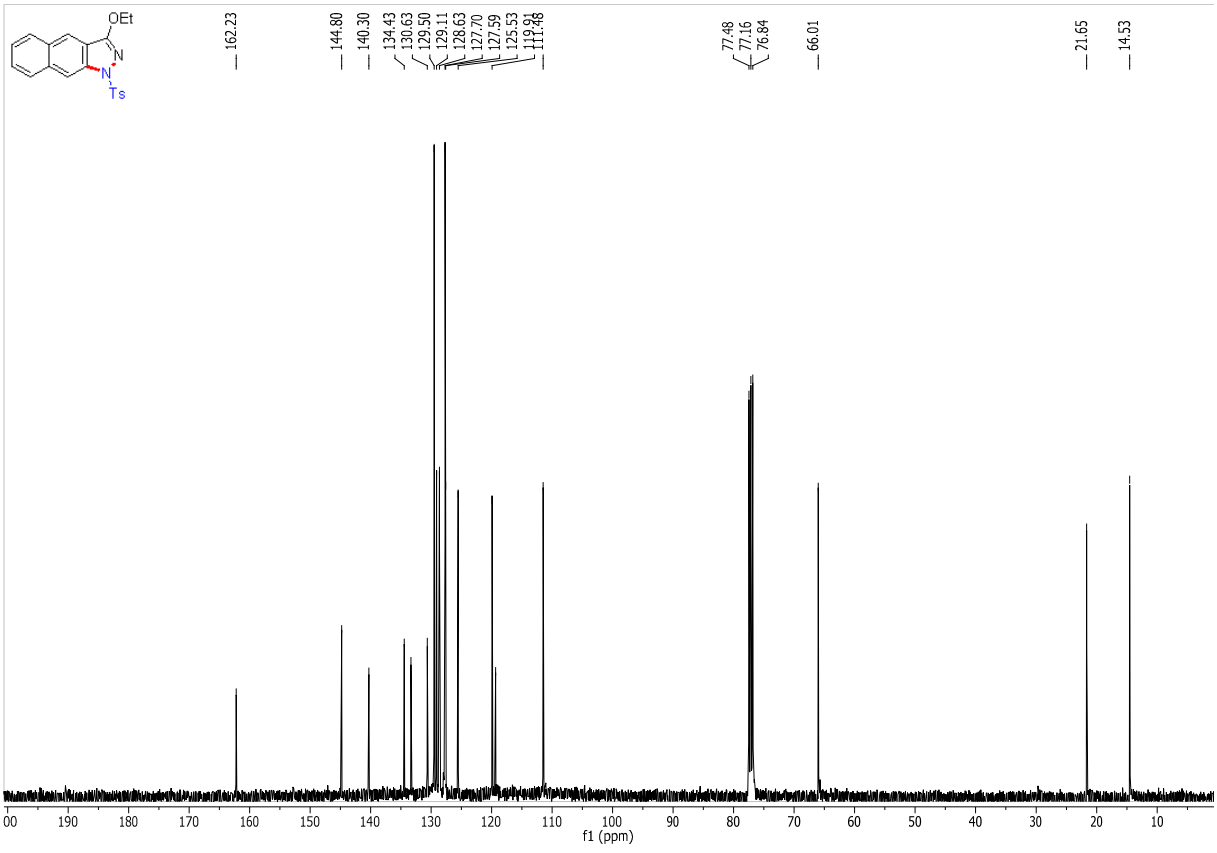
Ethyl 3-ethoxy-1-tosyl-1*H*-indazole-6-carboxylate (3oa)



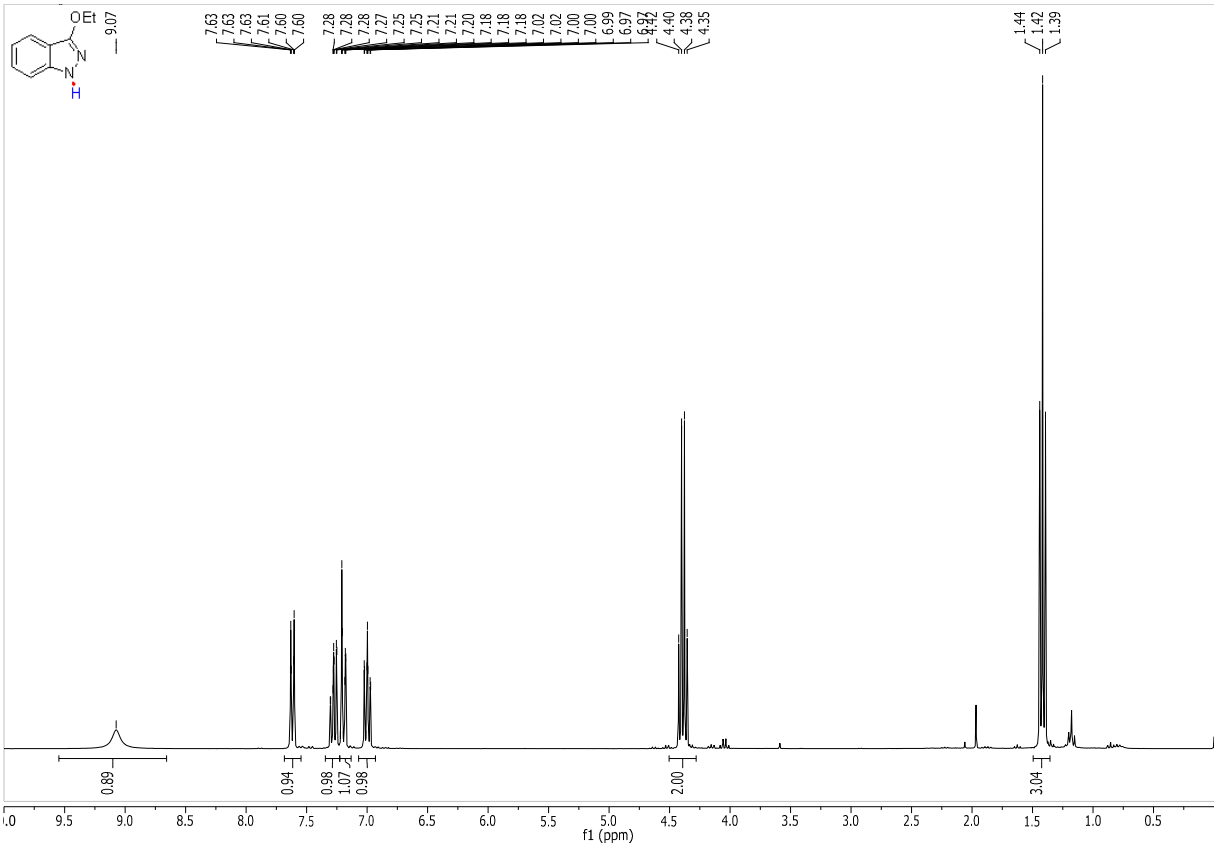


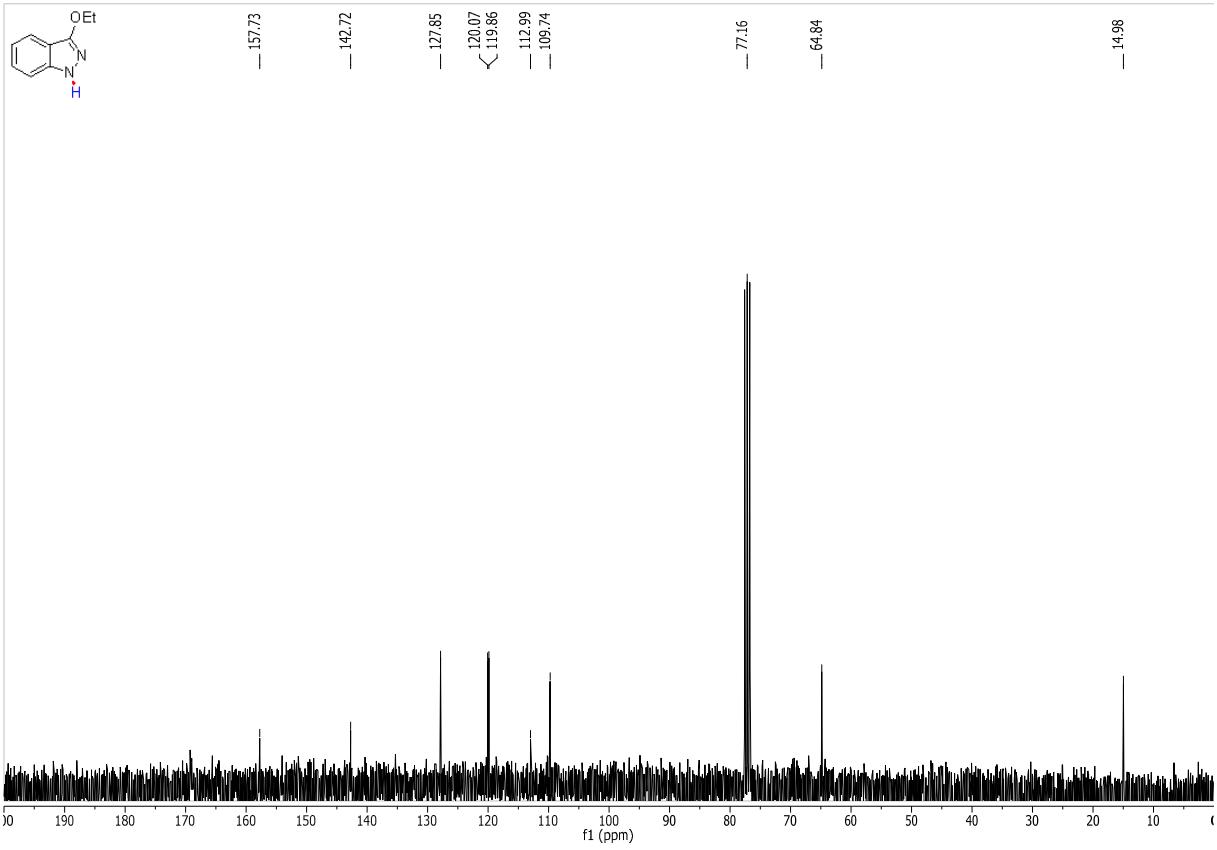
3-Ethoxy-1-tosyl-1*H*-benzo[f]indazole (3pa)



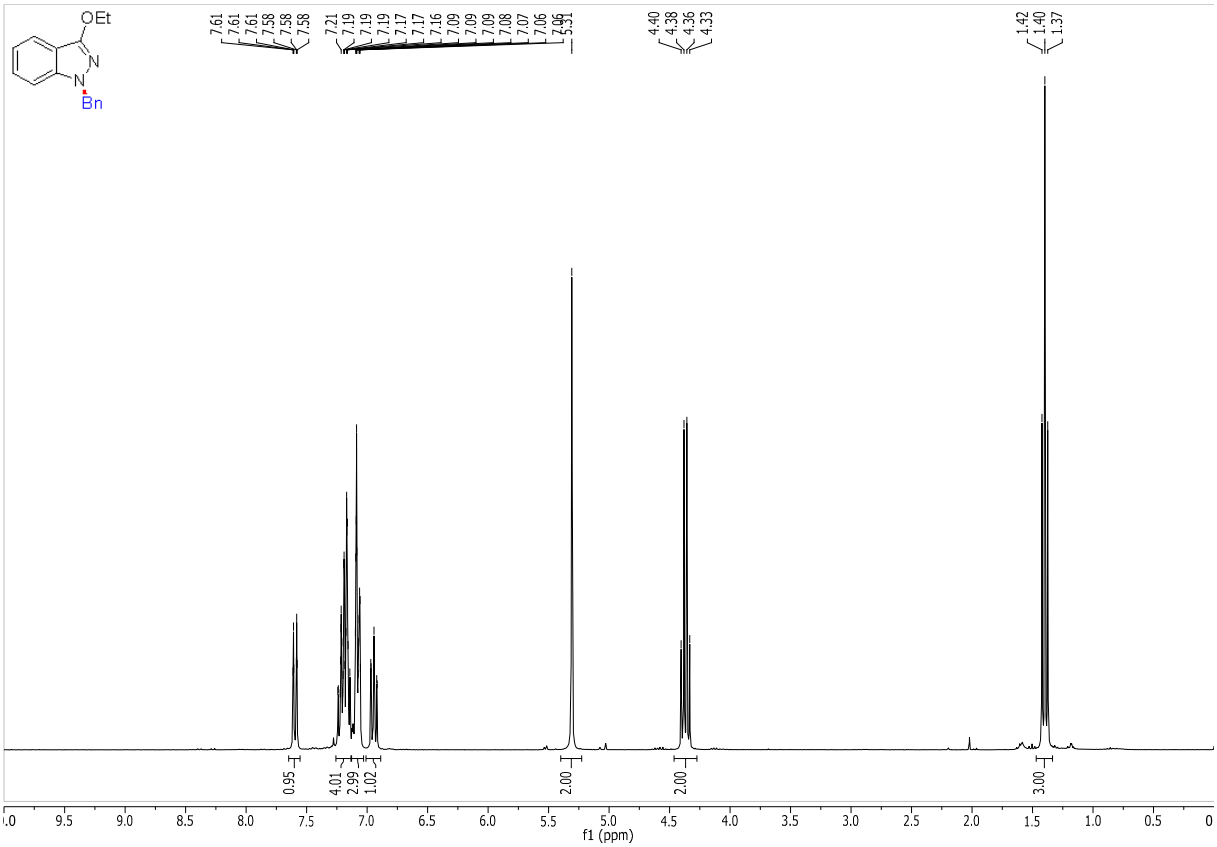


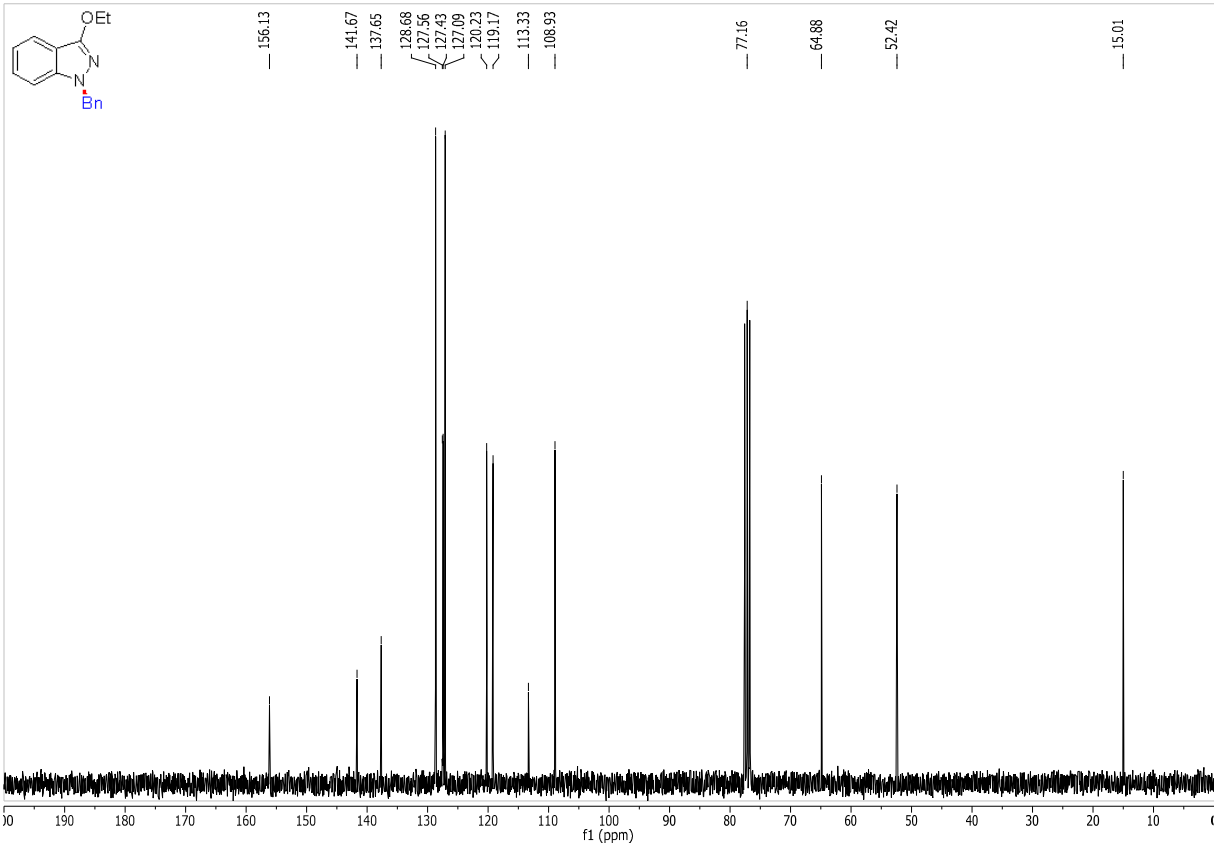
3-Ethoxy-1*H*-indazole (4aa)



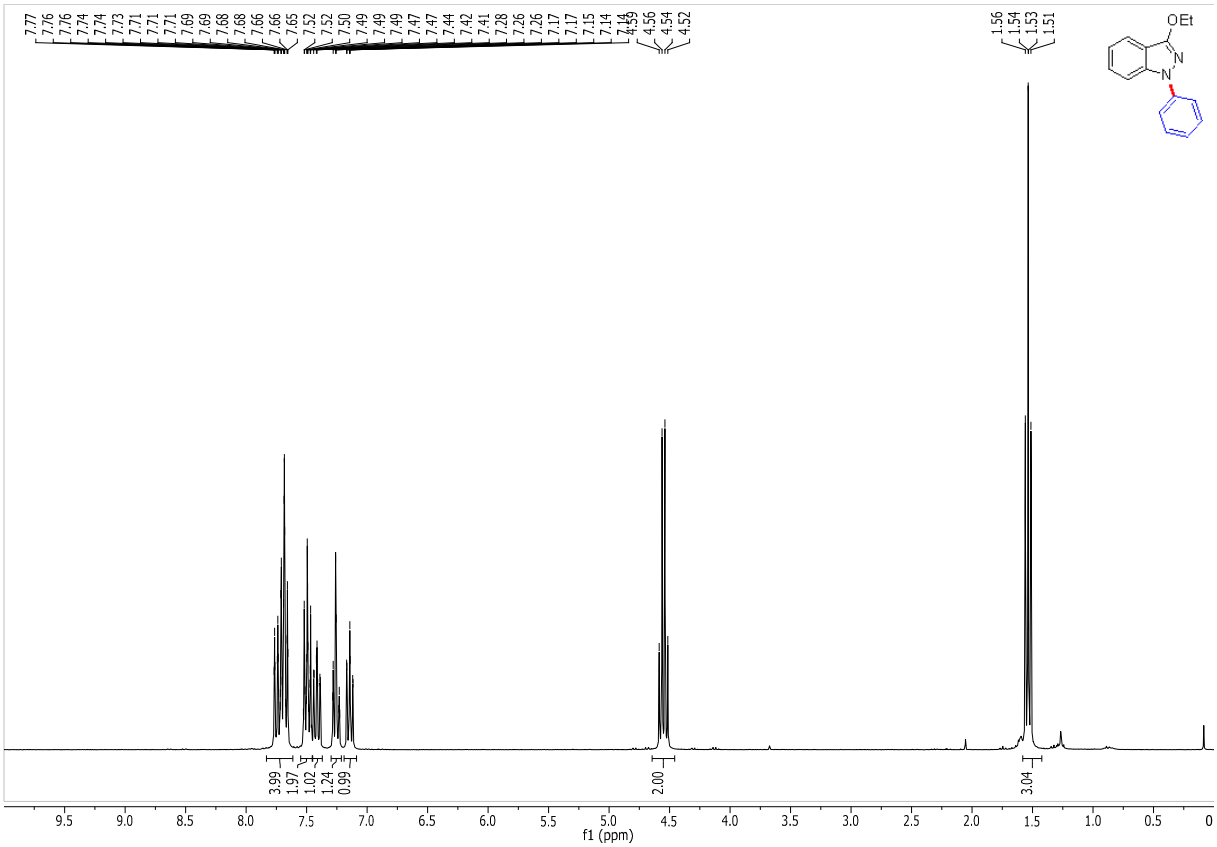


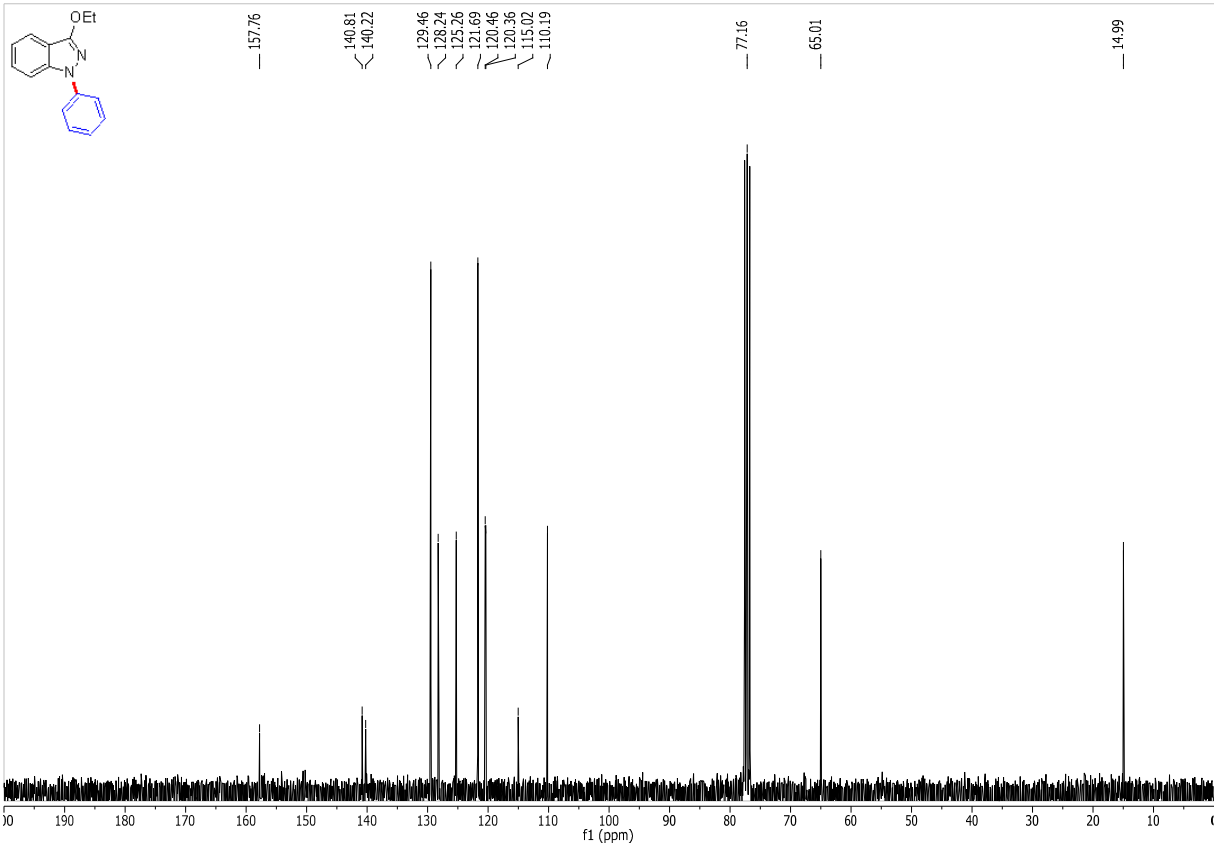
1-Benzyl-3-ethoxy-1*H*-indazole (4ab)



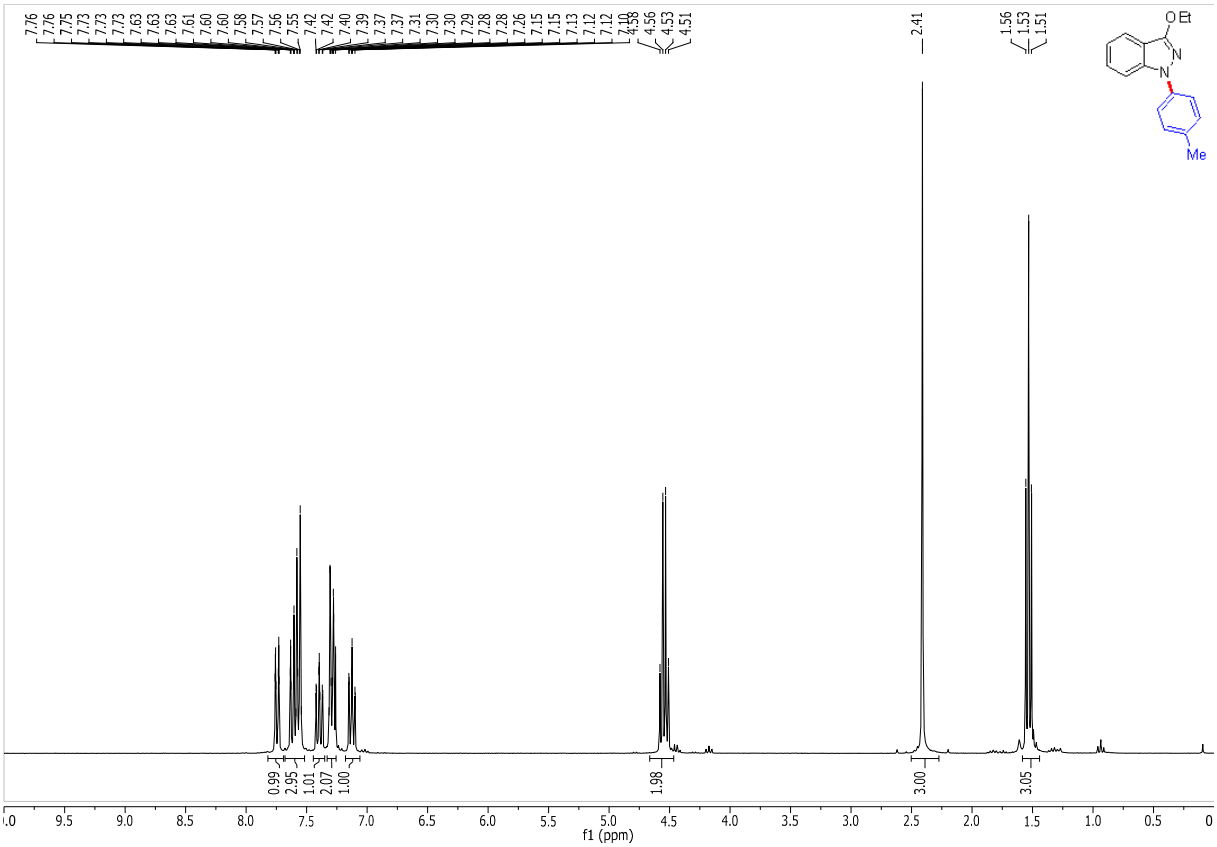


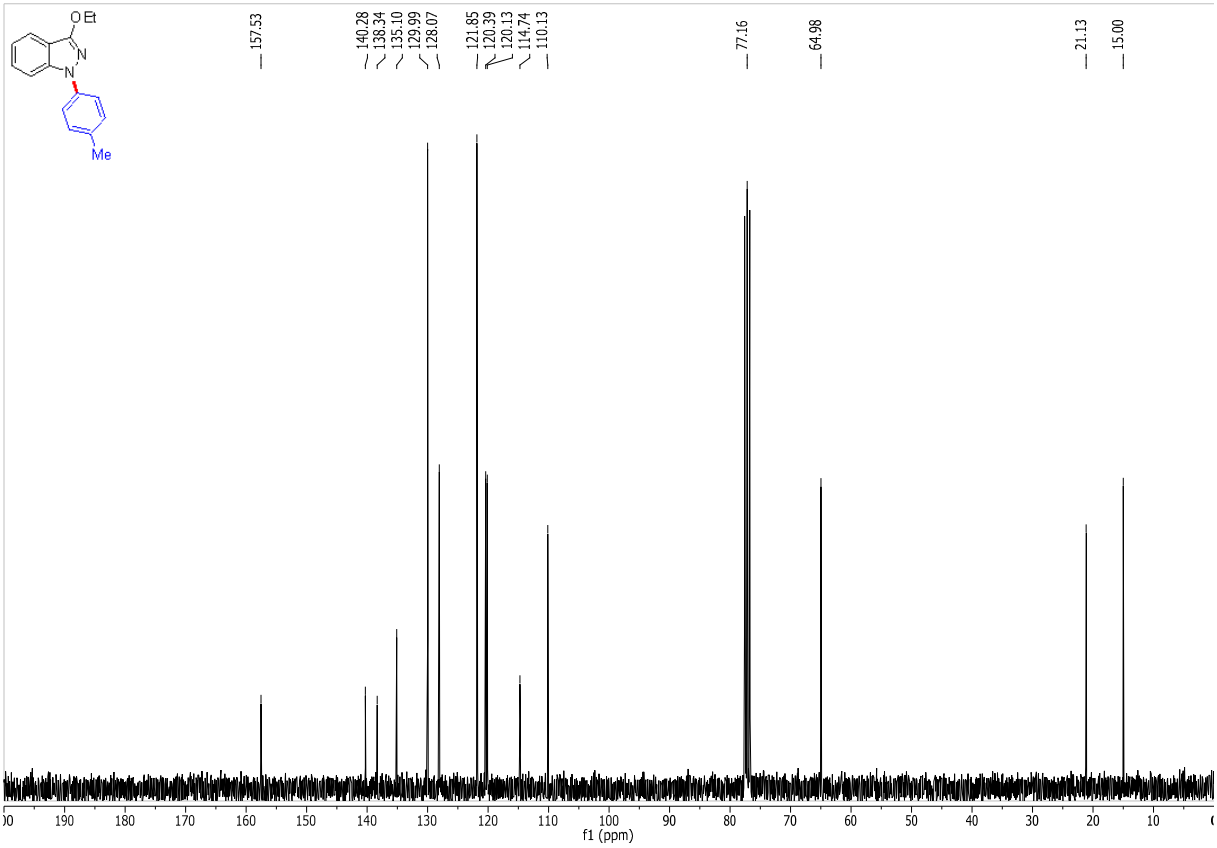
3-Ethoxy-1-phenyl-1*H*-indazole (4ac)



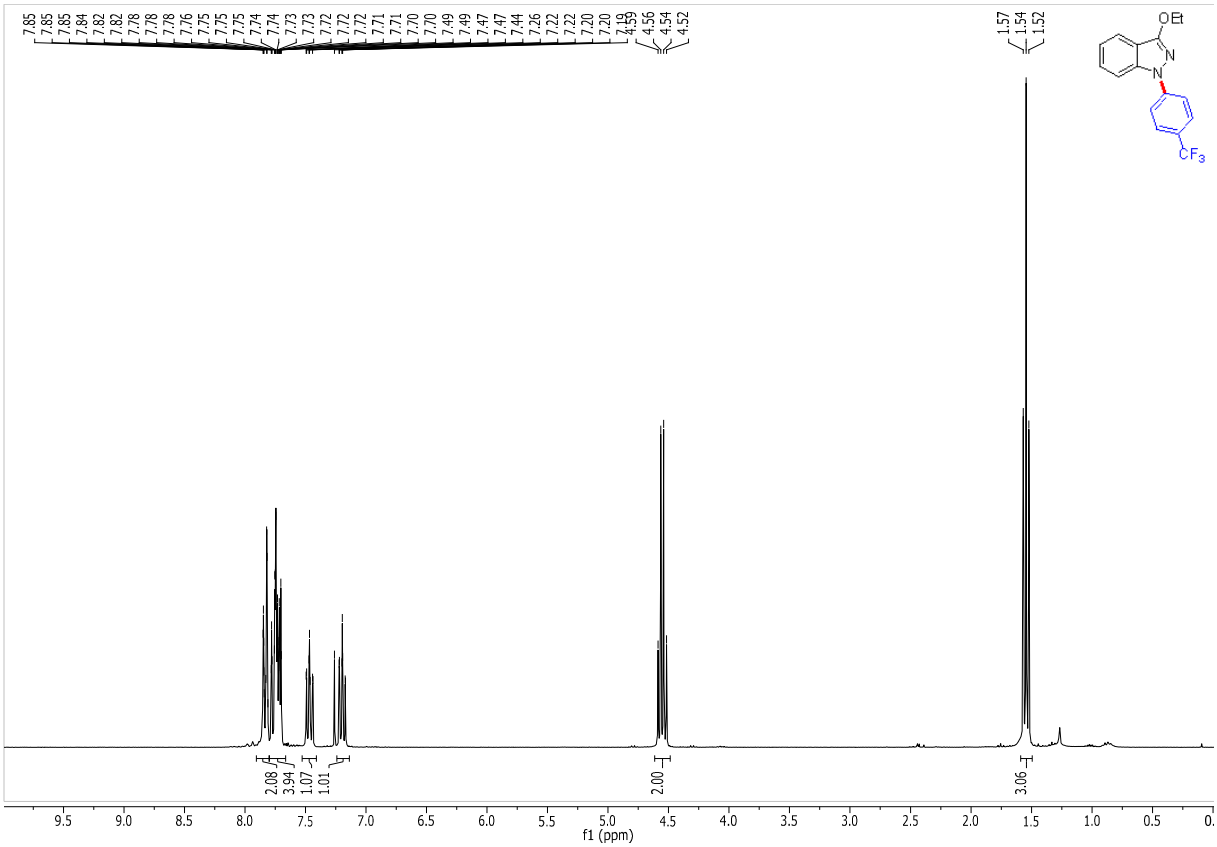


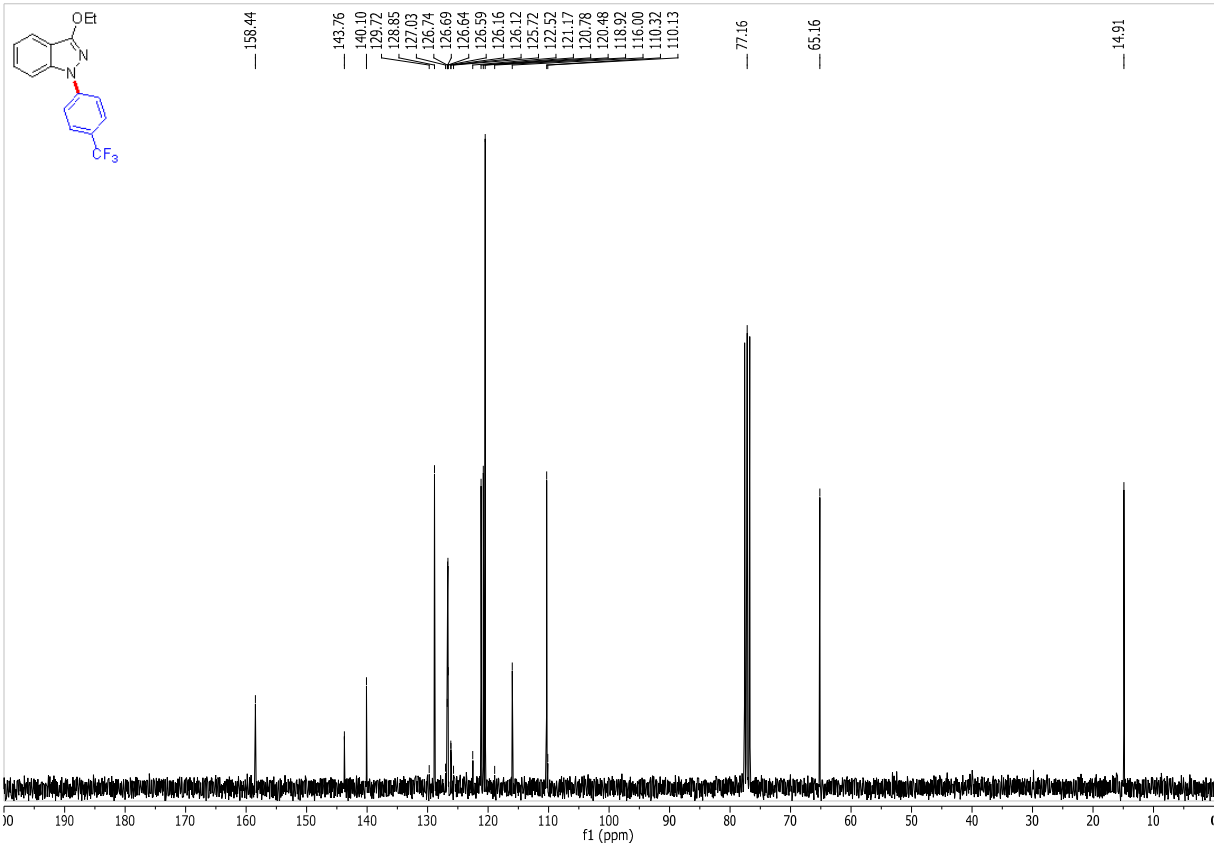
3-Ethoxy-1-(*p*-tolyl)-1*H*-indazole (4ad)

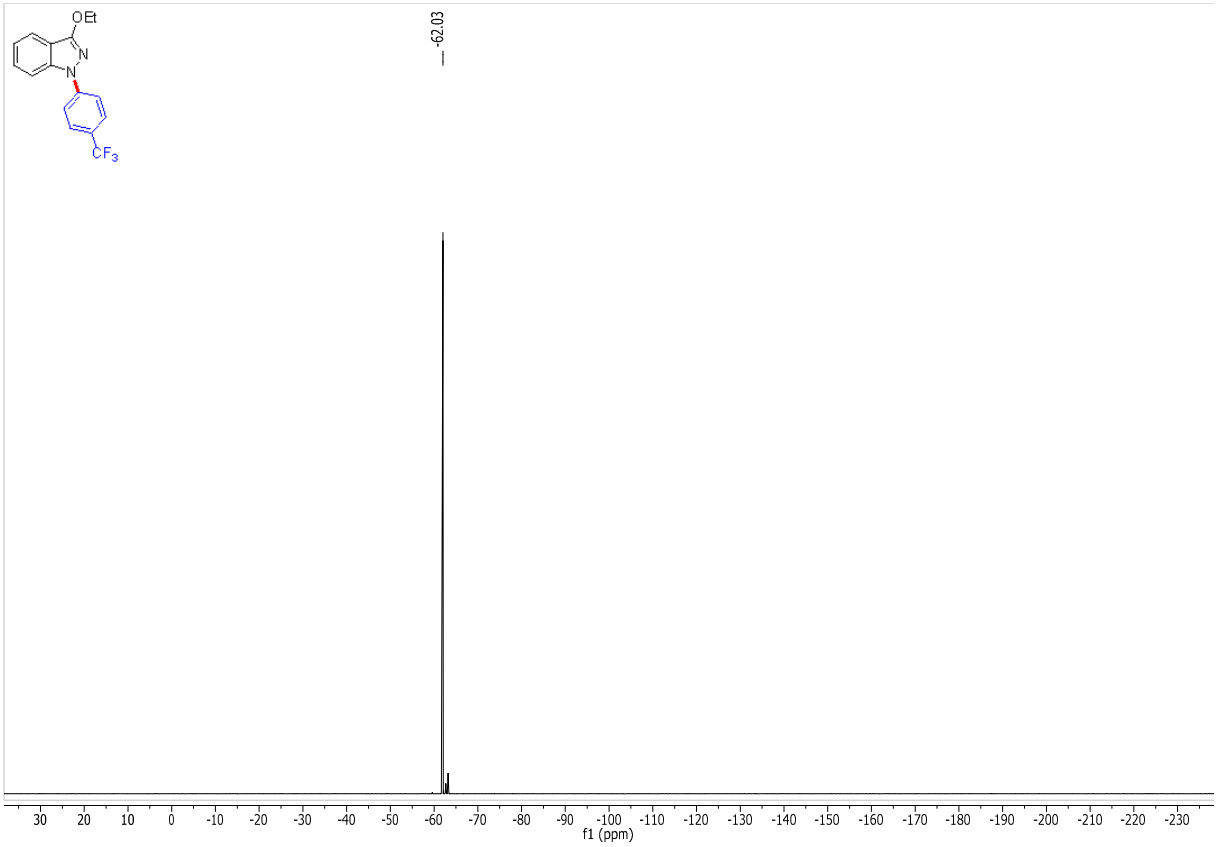




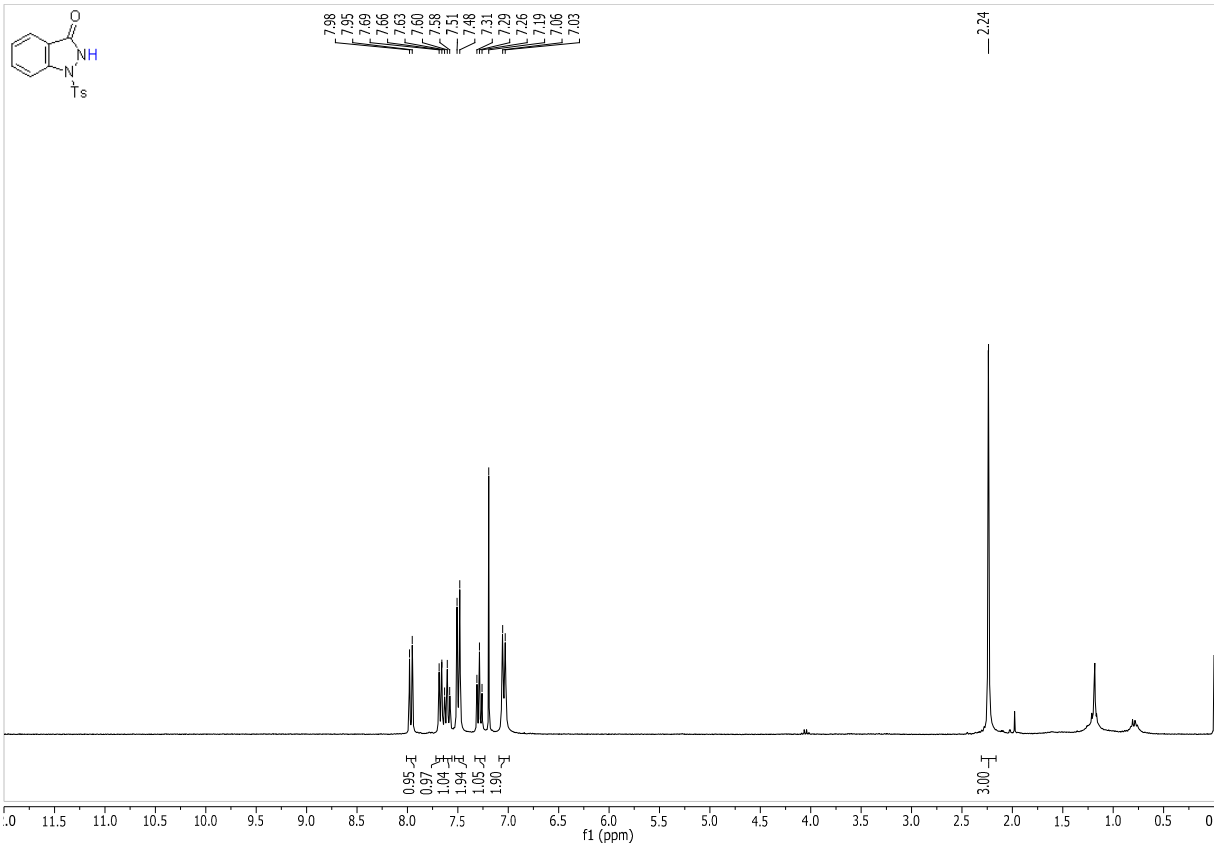
3-Ethoxy-1-(4-(trifluoromethyl)phenyl)-1*H*-indazole (4ae)

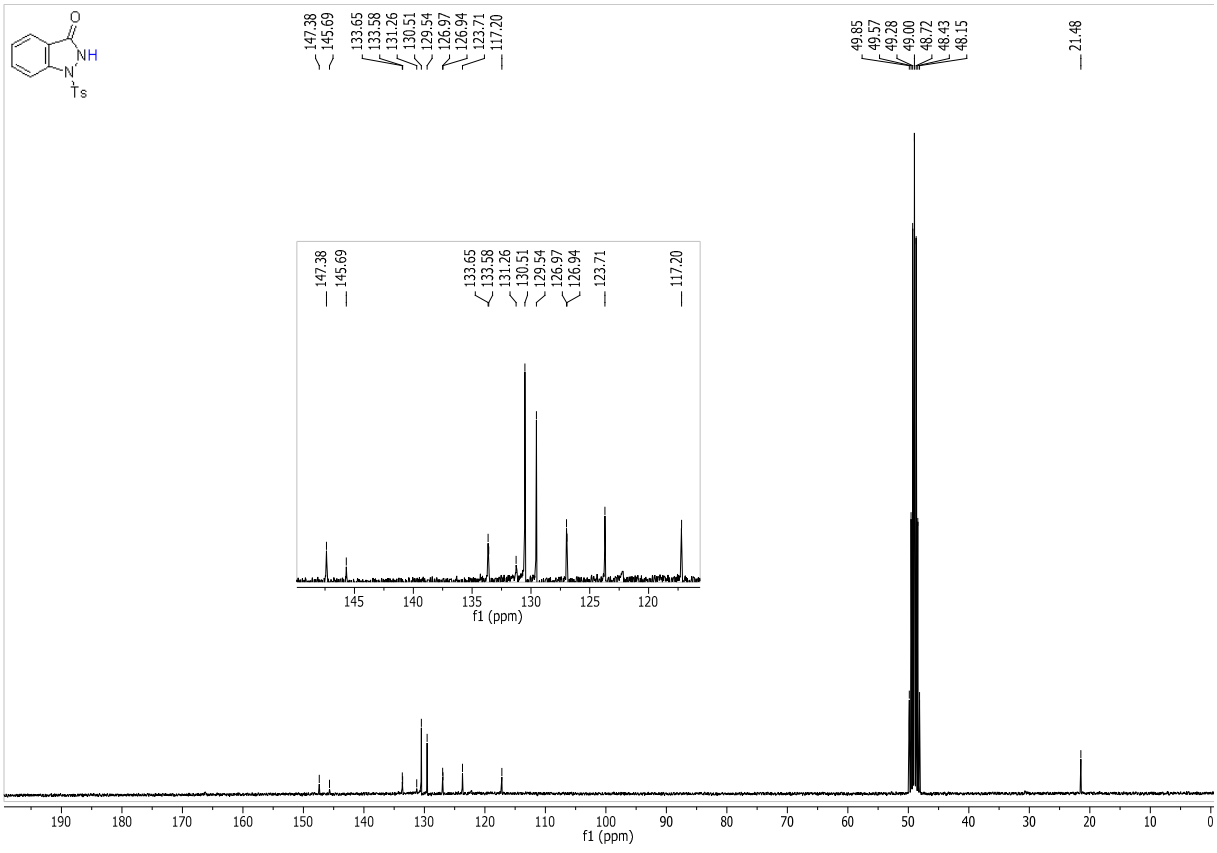




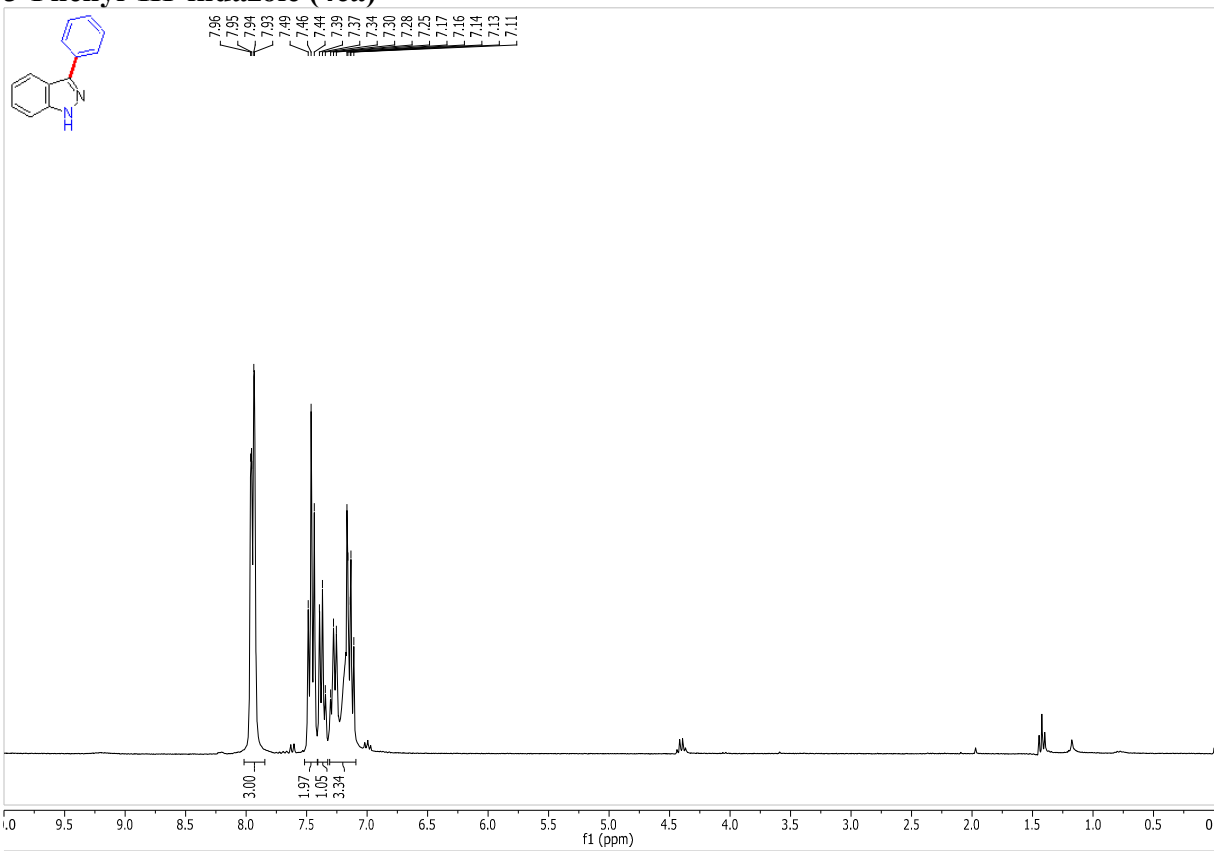

OEt
N
N
CF3
-62.03
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

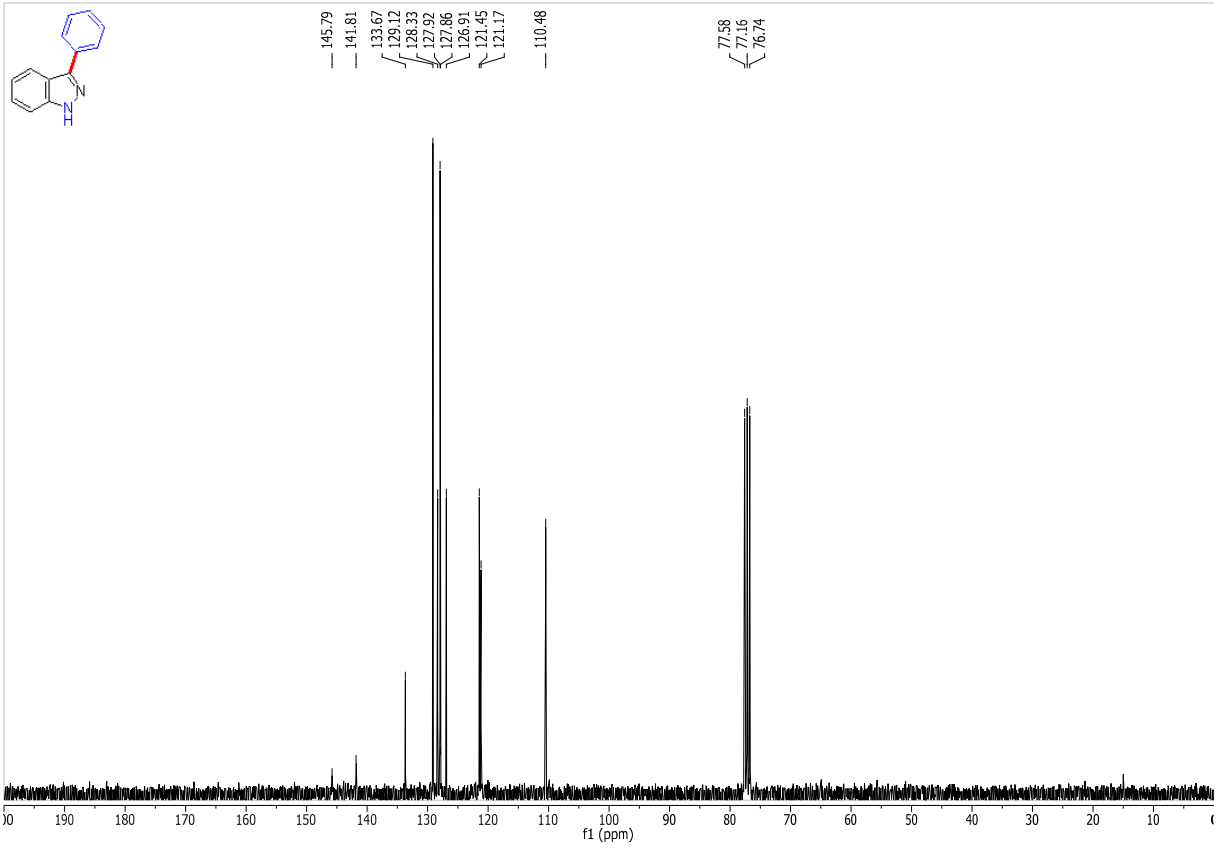
1-Tosyl-1*H*-indazol-3(2*H*)-one (4b)



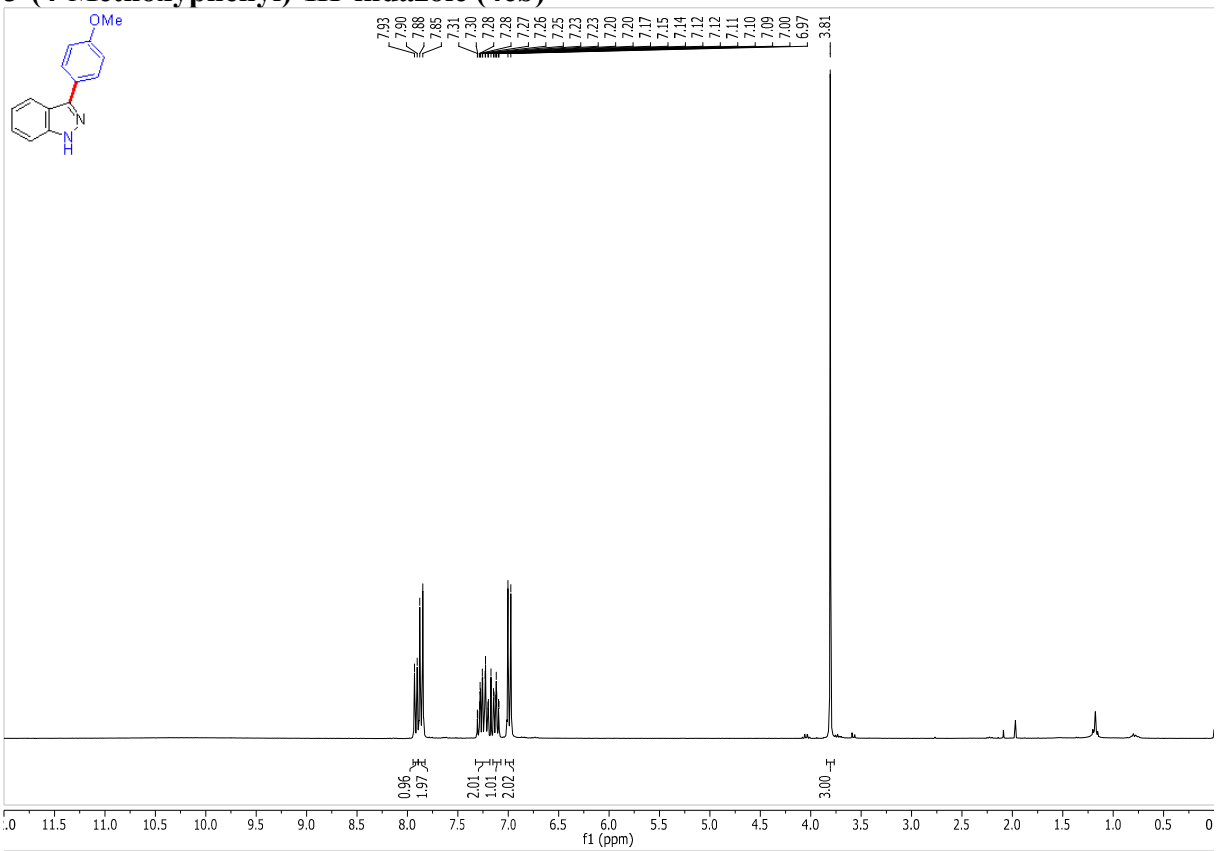


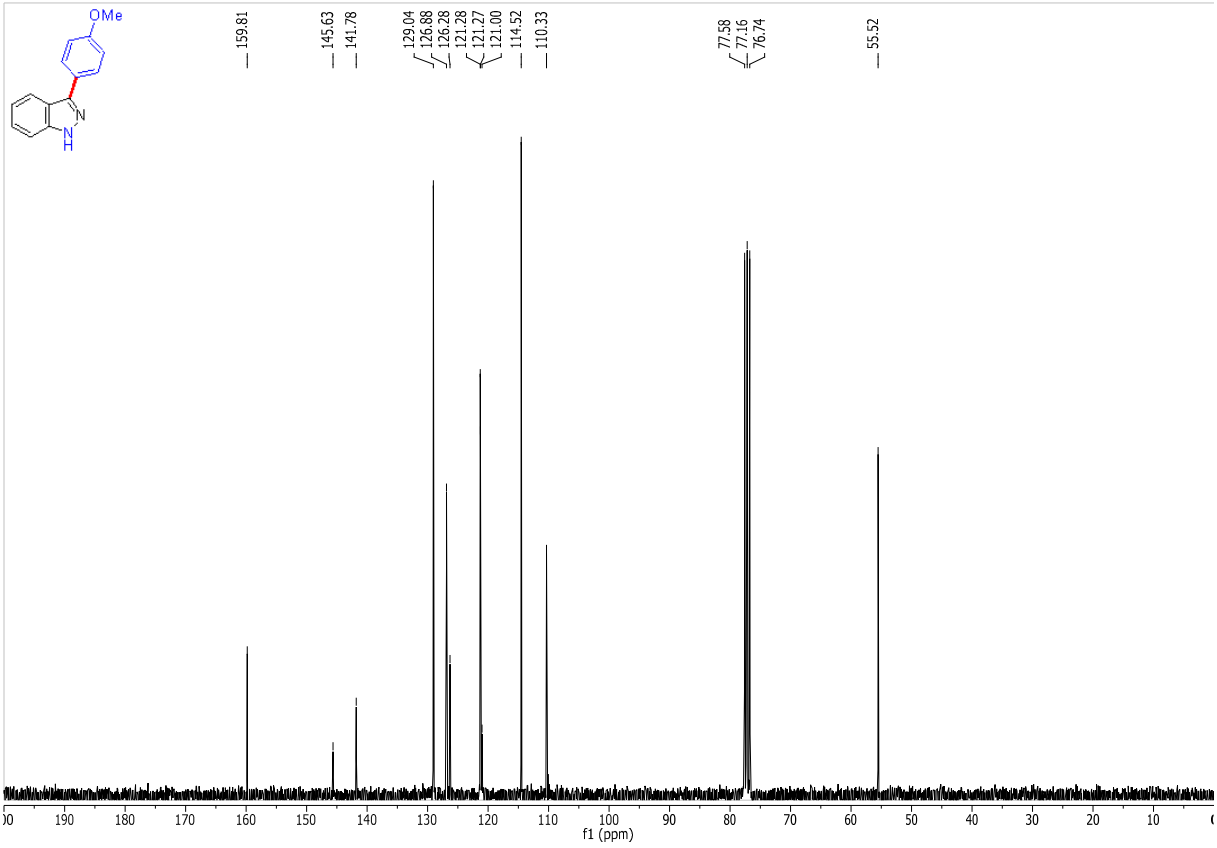
3-Phenyl-1*H*-indazole (4ca)



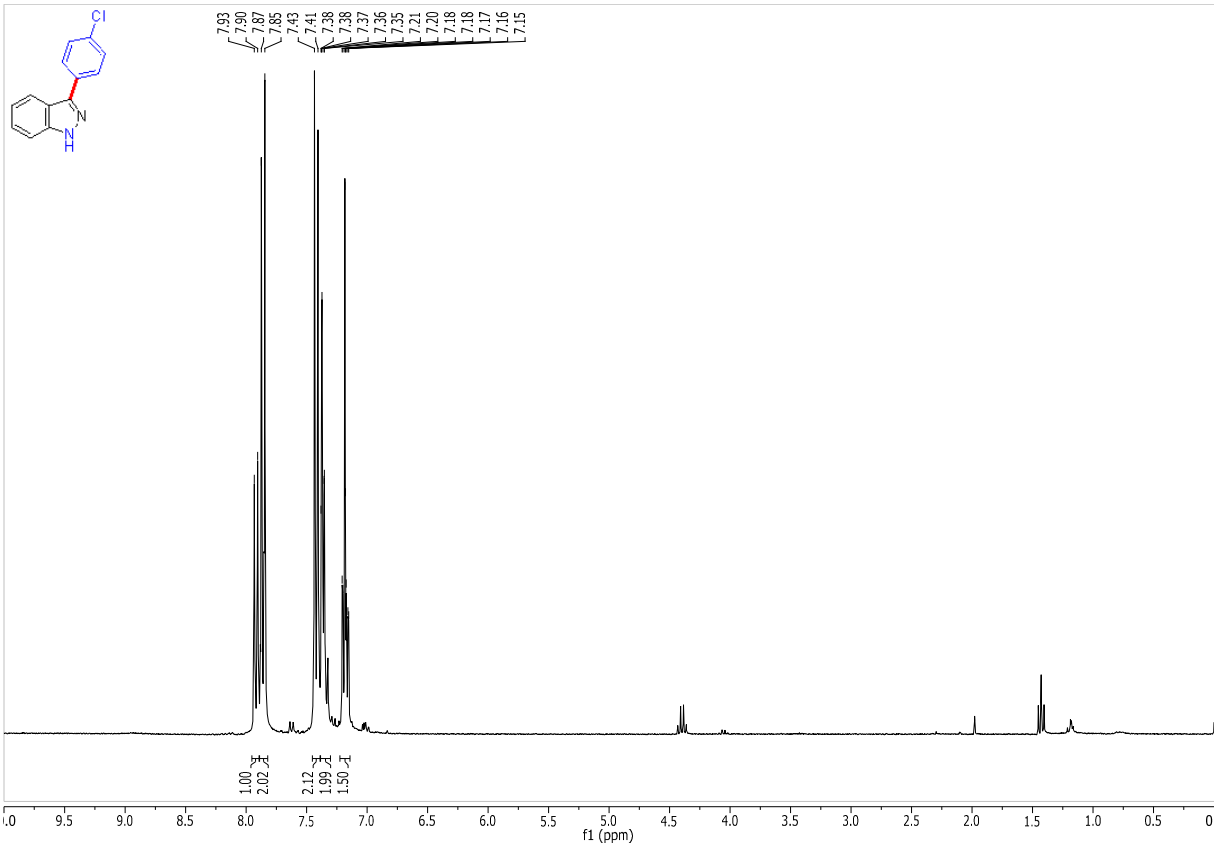


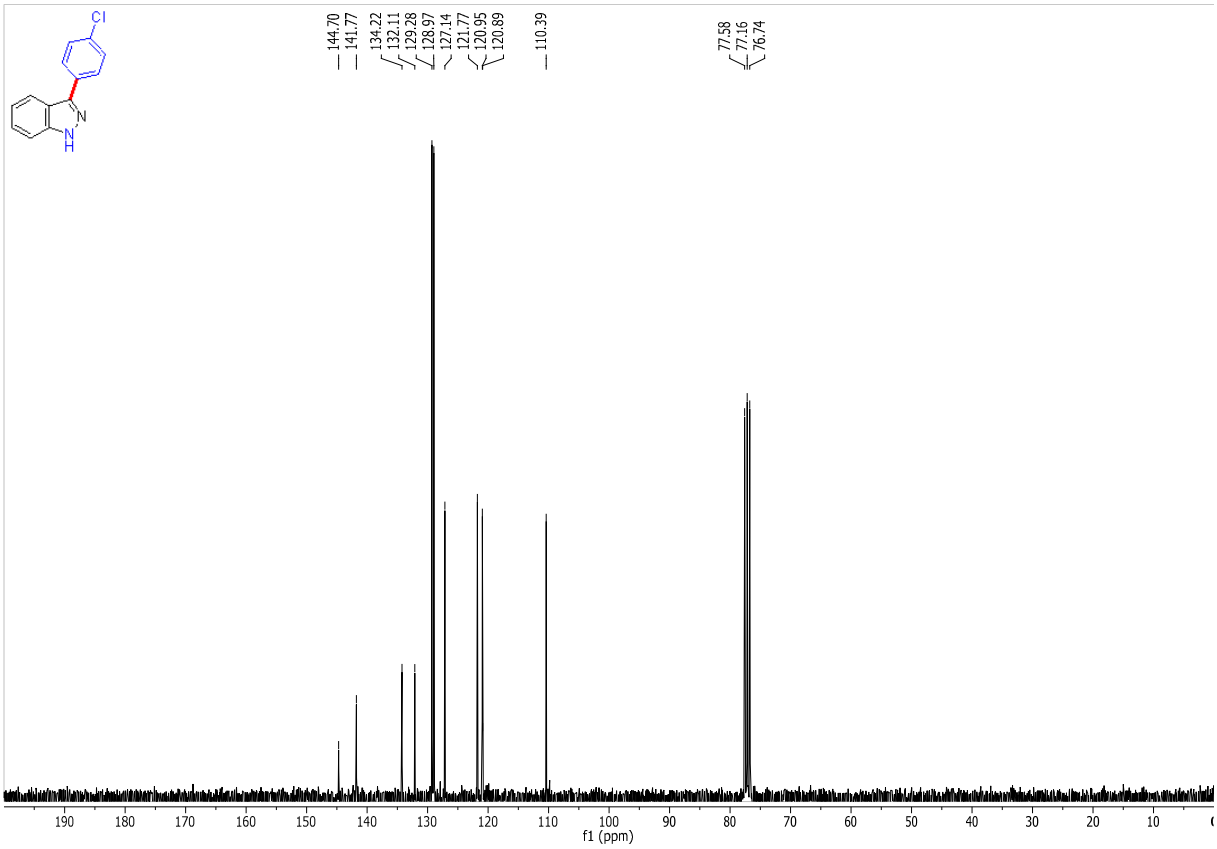
3-(4-Methoxyphenyl)-1*H*-indazole (4cb)



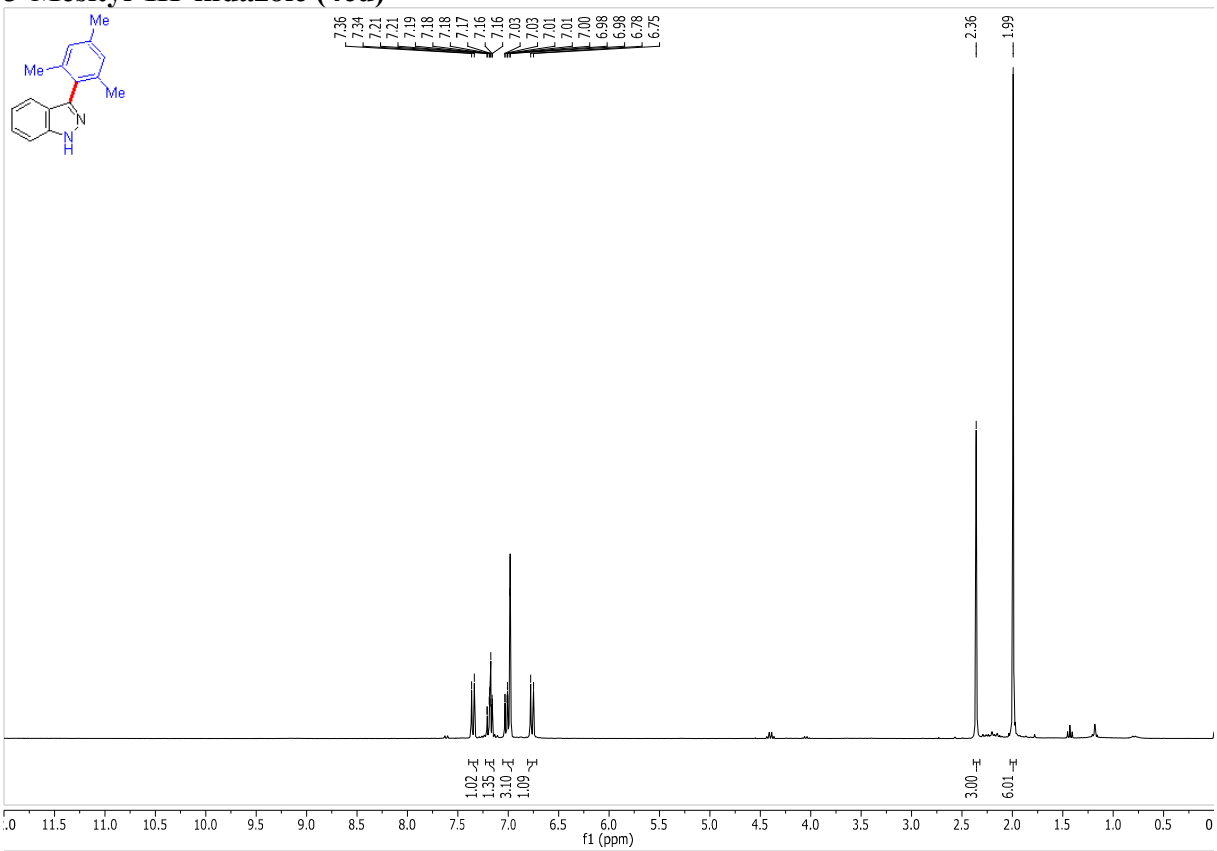


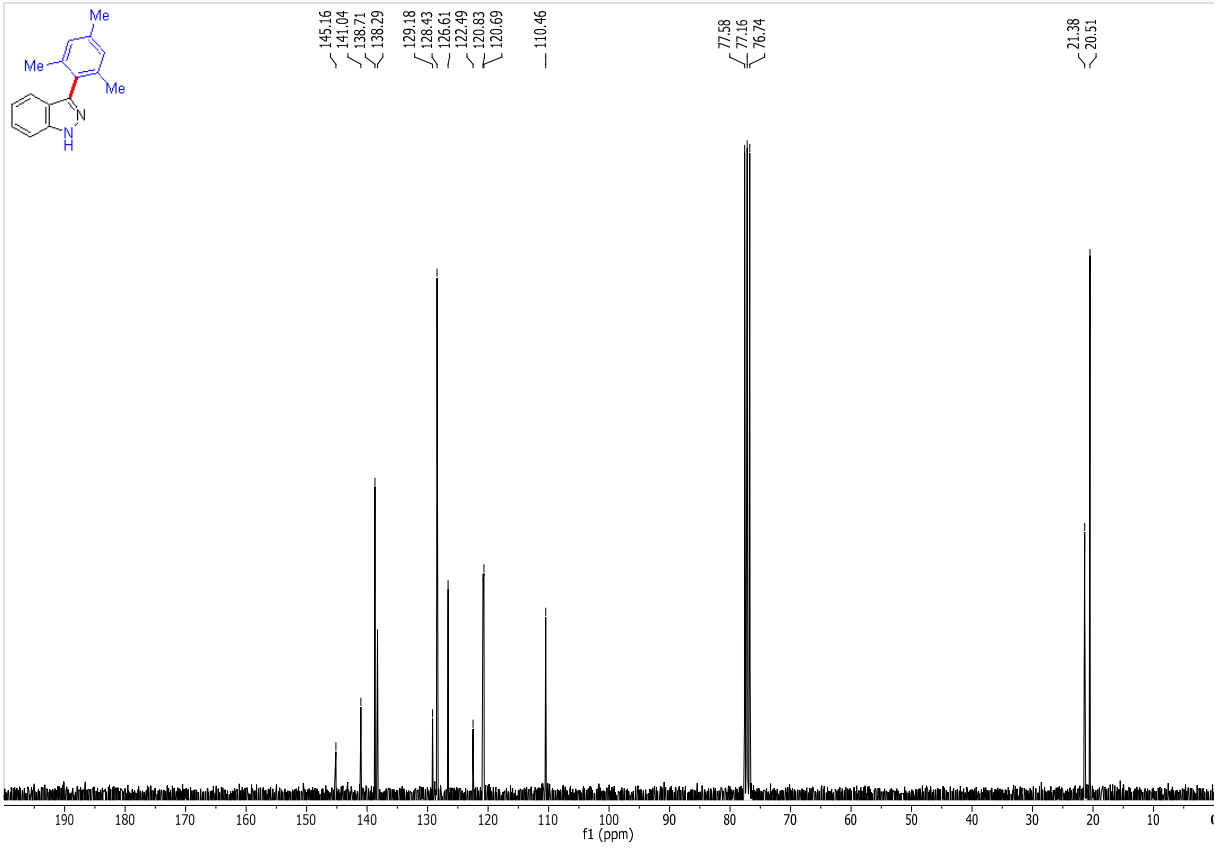
3-(4-Chlorophenyl)-1*H*-indazole (4cc)





3-Mesityl-1*H*-indazole (4cd)





3-Allyl-1*H*-indazole (4ce)