Supporting Information

Synthesis of 2-Aminoindoles through Gold-Catalyzed C–H Annulations of Sulfilimines with *N*-Arylynamides

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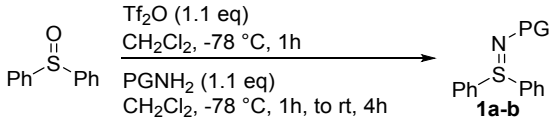
1. General Methods

Chemicals were purchased from commercial suppliers and used as delivered. The reagents **1**,[1] **2**[2] have been prepared according to the literature. Dry solvents were dispensed from the solvent purification system MB SPS-800. Deuterated solvents were bought from Euriso-Top. NMR spectra were, if not mentioned otherwise, recorded at room temperature on the following spectrometers: Bruker Avance-III-300, Bruker Avance III 400, and Bruker Avance-III-500. Chemical shifts are given in ppm and coupling constants in Hz. The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet) and m (multiplet) as well as combinations of them. When combinations of multiplicities are given the first character noted refers to the biggest coupling constant. All ^{13}C NMR spectra were measured with ^{1}H-decoupling. The multiplicities mentioned in these spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH_2-group), q (quartet, CH_3-group)] were determined by DEPT135 spectra. Mass spectra (MS and HRMS) were determined at the chemistry department of the University of Heidelberg under the direction of Dr. J. Gross. EI^+-spectra were measured on a JOEL JMS-700 spectrometer. For ESI^+-spectra a Bruker ApexQu FT-ICR-MS spectrometer was applied. Infrared Spectroscopy (IR) was processed on an FT-IR Bruker (IF528), IR Perkin Elmer (283) or FT-IR Bruker Vector 22. The solvent or matrix is denoted in brackets. For the most significant bands the wave number ν (cm^{-1}) is given. X-ray crystal structure analyses were measured at the chemistry department of the University of Heidelberg under the direction of Dr. F. Rominger on a Bruker Smart CCD or Bruker APEX-II CCD instrument using Mo-Kα-radiation. Diffraction intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS based on the Laue symmetry of reciprocal space. Heavy atom diffractions were solved by direct methods and refined against F2 with full matrix least square algorithm. Hydrogen atoms were either isotropically refined or calculated. The structures were solved and refined by Dr. F. Rominger using the SHELXTL software package. Gas Chromatography / Mass Spectrometry (GC/MS) spectra were measured on two different hardware systems: 1. HP 5972 Mass Selective Detector, coupled with a HP 5890 SERIES II plus gas chromatograph. 2. Agilent 5975C Mass Selective Detector, coupled with an Agilent 7890A gas chromatograph. In both cases, as a capillary column, an OPTIMA 5 cross-linked Methyl Silicone column (30 m x 0.32 mm, 0.25 µm) was employed and helium was used as the carrier gas. Gas Chromatography (GC) was carried out on a HP 5890 SERIES II plus gas chromatograph. As a capillary column, an OPTIMA 5 cross-linked Methyl Silicone column was employed and nitrogen was used as the carrier gas. Melting Points were measured in open glass capillaries in a Büchi melting point apparatus (according to Dr. Tottoli) and were not corrected. Flash Column Chromatography was accomplished using Silica gel 60 (0.04 - 0.063 mm / 230 - 400 mesh ASTM) purchased from Macherey-Nagel or Aluminium oxide (neutral or basic) purchased from Macherey-Nagel. As eluents, mixtures of petroleum ether (PE), ethyl acetate (EA) were used. Analytical Thin Layer Chromatography (TLC) was carried out on precoated Macherey-Nagel POLYGRAM® SIL G/UV254 or POLYGRAM® ALOX N/UV254 plastic sheets. Detection was accomplished using UV-light (254 nm), $KMnO_4$ (in 1.5 M Na_2CO_3 (aq.)), molybdatophosphoric acid (5 % in ethanol), vanillin/H_2SO_4 (in ethanol) or anisaldehyde/HOAc (in ethanol). IUPAC names of the compounds described in the experimental section were determined with the program ACDLabs 12.0®.

2. Experiment Procedures

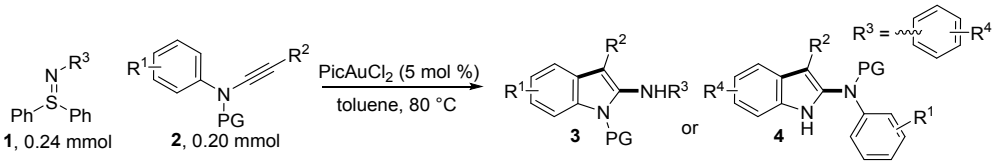
Substrates **1c-d** were prepared and characterized in our previous work.[3]

Procedure A: **Synthesis of *S*,*S*-diphenyl-*N*-sulfonylsulfilimines 1a-b from diphenyl sulfoxide and sulfonamides[1b]**



Under N_2, to a solution of diphenylsulfoxide (2.0 g, 10.0 mmol) in anhydrous CH_2Cl_2 (40 mL) was added trifluoromethanesulfonic anhydride (1.85 mL, 11.0 mmol) dropwise at −78 °C. After being stirred at −78 °C for 1 h, the reaction mixture was slowly treated with sulfonamide (11.0 mmol). The resulting solution was stirred for 1 h at −78 °C, and then for 4 h at room temperature. The mixture was washed with saturated $NaHCO_3$ aqueous solution, dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography using EtOAc and petroleum ether as eluent to give *S*,*S*-diphenyl-*N*-sulfonylsulfilimine **1a-b** in 86-88% yield.

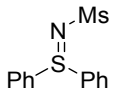
Procedure B: Synthesis of 2-aminoindoles 3 or 4 from sulfilimines 1 and *N*-phenylynamides 2



A mixture of sulfilimine **1** (0.3 mmol) and ynamide **2** (0.2 mmol) in 2 mL anhydrous toluene was treated with $PicAuCl_2$ (3.8 mg, 5 mol%) and then heated to 80 °C. After the total consumption of **2**, the solvent was reduced in vacuo, and the residue was purified through column chromatography using EtOAc and petroleum ether as eluent to give the corresponding 2-aminoindole **3** or **4**.

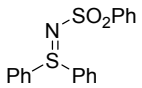
3. Characterization Data

***N*-(diphenyl-λ⁴-sulfanylidene)methanesulfonamide (1a)**



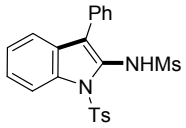
Yield: 2.40 g, 86%; white solid, mp 90-91 °C; R_f = 0.14 (EA/PE = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.64 (m, 4H), 7.52-7.42 (m, 6H), 2.89 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2 (s, 2C), 132.4 (d, 2C), 130.1 (d, 4C), 127.1 (d, 4C), 43.1 (q) ppm; IR (reflection) $\tilde{v}$ = 3063, 3004, 2924, 1750, 1580, 1475, 1443, 1331, 1268, 1179, 1120, 1082, 1022, 1000, 964, 919, 844, 793, 748, 721, 685 cm^{-1}; HRMS (ESI) (M+H) (*m/z*) $C_{13}H_{14}NO_2S_2$ calcd for 280.0460, found 280.0456.

***N*-(diphenyl-λ⁴-sulfanylidene)benzenesulfonamide (1b)[4]**



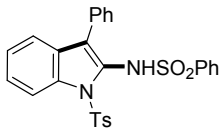
Yield: 3.00 g, 88%; white solid, mp 127-128 °C; R_f = 0.33 (EA/PE = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.3 Hz, 2H), 7.72-7.55 (m, 4H), 7.53-7.26 (m, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2 (s), 136.3 (d), 132.4 (d, 2C), 131.3 (s, 2C), 129.9 (d, 4C), 128.6 (d, 2C), 127.2 (d, 4C), 126.2 (d, 2C) ppm; IR (reflection) $\tilde{v}$ = 3059, 1738, 1475, 1445, 1316, 1283, 1141, 1086, 1022, 999, 953, 784, 746, 707, 689 cm^{-1}; HRMS (ESI) (M+H) (*m/z*) $C_{18}H_{16}NO_2S_2$ calcd for 342.0617, found 342.0605.

***N*-(3-phenyl-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3aa)**



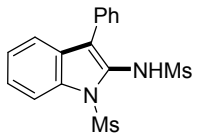
Yield: 72 mg, 82%; white solid, mp 195-196 °C; R_f = 0.18 (EA/PE = 1/5); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.18 (d, J = 20.0 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.96-7.90 (m, 2H), 7.62-7.56 (m, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.49 (d, J = 7.5 Hz, 1H), 7.47-7.41 (m, 2H), 7.35 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 2.54 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 145.7 (s), 134.6 (s), 134.5 (s), 131.3 (s), 130.3 (d, 2C), 130.1 (d, 2C), 129.3 (d, 2C), 128.7 (d), 127.9 (s), 127.7 (s), 127.5 (d, 2C), 126.5 (d), 124.8 (d), 123.7 (s), 120.5 (d), 115.5 (d), 42.6 (q), 21.5 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3303, 3071, 3013, 2932, 1597, 1495, 1447, 1432, 1408, 1356, 1346, 1326, 1154, 1117, 1088, 1041, 1012, 974, 956, 935, 877, 811, 785, 767, 752, 724, 701, 664, 636, 616 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{22}H_{21}N_2O_4S_2$ calcd for 441.0937, found 441.0937.

***N*-(3-phenyl-1-tosyl-1*H*-indol-2-yl)benzenesulfonamide (3ba)**



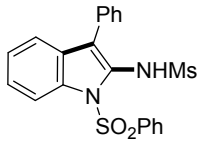
Yield: 50 mg, 50%; white solid, mp 59-60 °C; R_f = 0.25 (EA/PE = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.5 Hz, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.62 (s, 1H), 7.42-7.36 (m, 3H), 7.36-7.32 (m, 1H), 7.28-7.23 (m, 3H), 7.18 (s, 1H), 7.17-7.15 (m, 3H), 7.14-7.11 (m, 4H), 2.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5 (s), 139.9 (s), 134.6 (s), 134.5 (s), 132.7 (s), 131.2 (s), 129.9 (d, 2C), 129.6 (d, 2C), 128.6 (d, 2C), 128.48 (d, 2C), 128.46 (d), 127.8 (d), 127.2 (d, 2C), 127.0 (d, 2C), 126.7 (s), 125.7 (d), 124.1 (d), 121.4 (s), 120.4 (d), 114.7 (d), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3293, 3062, 2930, 2858, 1597, 1497, 1449, 1379, 1358, 1332, 1244, 1168, 1123, 1089, 1057, 1025, 959, 939, 910, 852, 813, 747, 728, 701, 685, 664 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{27}H_{23}N_2O_4S_2$ calcd for 503.1094, found 503.1072.

***N*-(1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (3ab)**



Yield: 60 mg, 82%; white solid, mp 183-184 °C; R_f = 0.36 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.5 Hz, 1H), 7.56-7.51 (m, 3H), 7.46 (d, J = 8.0 Hz, 2H), 7.39-7.34 (m, 2H), 7.28-7.23 (m, 1H), 7.01 (s, 1H), 3.40 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.1 (s), 131.3 (s), 129.9 (d, 2C), 129.2 (d, 2C), 128.5 (d), 127.3 (s), 126.4 (s), 126.2 (d), 124.1 (d), 120.5 (d), 120.4 (s), 113.9 (d), 42.4 (q), 42.2 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3307, 3020, 2934, 1739, 1622, 1596, 1498, 1451, 1398, 1368, 1329, 1320, 1247, 1227, 1203, 1171, 1150, 1124, 1064, 1020, 964, 912, 857, 788, 757, 742, 726, 698, 643 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{16}H_{17}N_2O_4S_2$ calcd for 365.0624, found 365.0622.

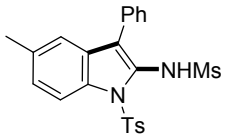
***N*-(3-phenyl-1-(phenylsulfonyl)-1*H*-indol-2-yl)methanesulfonamide (3ac)**



Yield: 66 mg, 78%; white solid, mp 164-166 °C; R_f = 0.31 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 7.5 Hz, 1H), 7.45 (d, J

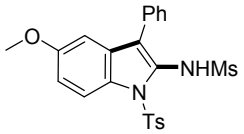
= 8.0 Hz, 2H), 7.42-7.37 (m, 5H), 7.34-7.28 (m, 3H), 7.18 (t, J = 8.0 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8 (s), 134.42 (s), 134.37 (d), 131.4 (s), 130.1 (d, 2C), 129.3 (d, 2C), 129.0 (d, 2C), 128.4 (d), 128.2 (s), 127.3 (d, 2C), 126.8 (s), 125.9 (d), 124.2 (d), 121.2 (s), 120.3 (d), 114.6 (d), 42.5 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3261, 2930, 1730, 1598, 1496, 1447, 1369, 1322, 1246, 1227, 1208, 1177, 1144, 1086, 1060, 1025, 999, 970, 915, 866, 781, 751, 720, 684, 646, 628 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{21}H_{19}N_2O_4S_2$ calcd for 427.0781, found 427.0778.

***N*-(5-methyl-3-phenyl-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3ad)**



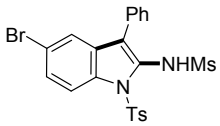
Yield: 75 mg, 82%; white solid, mp 149-151 °C; R_f = 0.36 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.46-7.38 (m, 4H), 7.32 (t, J = 7.5 Hz, 1H), 7.26 (s, 1H), 7.19 (s, 1H), 7.17 (d,J = 7.0 Hz, 2H), 7.12 (d,J = 8.5 Hz, 1H), 2.40 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5 (s), 134.8 (s), 133.9 (s), 132.5 (s), 131.7 (s), 130.1 (d, 2C), 129.9 (d, 2C), 128.9 (d, 2C), 128.5 (s), 128.3 (d), 127.3 (d, 2C), 127.2 (d), 126.9 (s), 120.9 (s), 120.1 (d), 114.4 (d), 42.3 (q), 21.7 (q), 21.3 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3354, 1596, 1413, 1373, 1351, 1334, 1321, 1233, 1201, 1186, 1151, 1085, 1062, 1030, 966, 869, 810, 785, 758, 702, 664 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{23}H_{23}N_2O_4S_2$ calcd for 455.1094, found 455.1082.

***N*-(5-methoxy-3-phenyl-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3ae)**



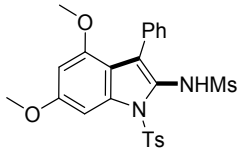
Yield: 81 mg, 86%; white solid, mp 205-207 °C; R_f = 0.31 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.5 Hz, 2H), 7.46-7.38 (m, 4H), 7.33 (t, J = 7.5 Hz, 1H), 7.26 (s, 1H), 7.17 (d,J = 7.5 Hz, 2H), 6.91 (dd,J = 9.0, 2.0 Hz, 1H),6.80 (d,J = 2.0 Hz, 1H), 3.68 (s, 3H), 2.43 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0 (s), 145.5 (s), 134.6 (s), 131.6 (s), 130.0 (d, 2C), 129.9 (d, 2C), 129.5 (s), 129.0 (d, 2C), 128.8 (s), 128.3 (d), 127.4 (s), 127.2 (d, 2C), 121.4 (s), 115.8 (d), 114.7 (d), 102.7 (d), 55.7 (q), 42.3 (q), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3225, 2839, 1739, 1613, 1596, 1475, 1453, 1441, 1361, 1326, 1283, 1223, 1188, 1160, 1122, 1087, 1055, 1024, 972, 948, 919, 869, 846, 812, 780, 728, 702, 664, 646, 607 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{23}H_{23}N_2O_5S_2$ calcd for 471.1043, found 471.1037.

***N*-(5-bromo-3-phenyl-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3af)**



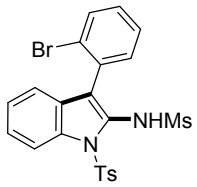
Yield: 57 mg, 55%; white solid, mp 106-108 °C; R_f = 0.18 (EA/PE = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 9.0 Hz, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 1.5 Hz, 1H), 7.45-7.38 (m, 5H), 7.37-7.32 (m, 2H), 7.22 (d, J = 8.5 Hz, 2H), 2.34 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0 (s), 134.6 (s), 132.8 (s), 130.9 (s), 130.10 (d, 2C), 130.06 (d, 2C), 129.98 (s), 129.1 (d, 2C), 128.62 (d), 128.56 (d), 128.0 (s), 127.4 (d, 2C), 122.8 (d), 119.3 (s), 117.6 (s), 116.0 (d), 42.7 (d), 21.7 (d) ppm; IR (reflection) $\tilde{\nu}$ = 3297, 2953, 2924, 2854, 1738, 1596, 1496, 1449, 1379, 1357, 1336, 1174, 1091, 1062, 1027, 973, 910, 874, 815, 784, 733, 705, 665 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{22}H_{20}{}^{79}BrN_2O_4S_2$ calcd for 519.0042, found 519.0031.

***N*-(4,6-dimethoxy-3-phenyl-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3ah)**



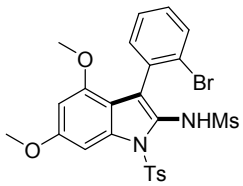
Yield: 87 mg, 87%; white solid, mp 195-196 °C; R_f = 0.29 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.27-7.22 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 1.5 Hz, 1H), 6.99 (s, 1H), 6.22 (d, *J* = 1.5 Hz, 1H), 3.81 (s, 3H), 3.52 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6 (s), 154.8 (s), 145.5 (s), 136.3 (s), 134.9 (s), 132.7 (s), 131.1 (d, 2C), 129.9 (d, 2C), 127.7 (d), 127.6 (d, 2C), 127.3 (d, 2C), 124.6 (s), 121.6 (s), 111.5 (s), 95.6 (d), 91.0 (d), 55.9 (q), 55.3 (q), 42.1 (q), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3218, 3066, 2970, 2937, 2834, 1739, 1611, 1599, 1577, 1500, 1452, 1433, 1414, 1352, 1316, 1261, 1224, 1202, 1168, 1151, 1133, 1089, 1070, 1017, 983, 960, 921, 871, 818, 774, 754, 703, 666 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{24}H_{25}N_2O_6S_2$ calcd for 501.1149, found 501.1137.

***N*-(3-(2-bromophenyl)-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3ai)**



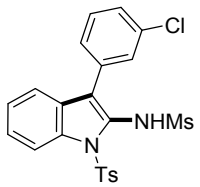
Yield: 93 mg, 89%; white solid, mp 196-198 °C; R_f = 0.36 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.63 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.39 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.35 (dt, *J* = 1.0, 7.5 Hz, 1H), 7.33-7.29 (m, 1H), 7.25-7.19 (m, 2H), 7.18-7.13 (m, 4H), 2.54 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7 (s), 134.7 (s), 134.3 (s), 133.23 (d), 133.15 (d), 132.3 (s), 130.2 (d), 130.0 (d, 2C), 128.3 (s), 127.62 (d), 127.55 (s), 127.3 (d, 2C), 125.8 (d), 124.4 (s), 124.3 (d), 120.3 (d), 120.0 (s), 114.9 (d), 42.1 (q), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3278, 1738, 1624, 1596, 1482, 1468, 1449, 1354, 1330, 1220, 1190, 1148, 1125, 1087, 1072, 1022, 972, 856, 813, 784, 746, 720, 700, 683, 661, 641 cm^{-1}; HRMS (ESI) (*m/z*) $C_{22}H_{20}{}^{79}BrN_2O_4S_2$ calcd for 519.0042, found 519.0035.

***N*-(3-(2-bromophenyl)-4,6-dimethoxy-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3aj)**



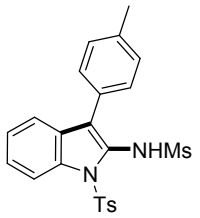
Yield: 57 mg, 49%; white solid, mp 199-200 °C; R_f = 0.35 (EA/PE = 1/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 6.3 Hz, 1H), 7.31-7.17 (m, 4H), 7.15-7.09 (m, 1H), 6.79 (s, 1H), 6.22 (s, 1H), 3.81 (s, 3H), 3.47 (s, 3H), 2.52 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7 (s), 153.6 (s), 144.5 (s), 135.4 (s), 133.8 (s), 132.7 (s), 132.4 (d), 131.0 (d), 128.9 (d, 2C), 128.4 (d), 126.2 (d, 2C), 125.5 (d), 123.7 (s), 120.2 (s), 110.7 (s), 94.9 (d), 90.3 (d), 54.8 (q), 54.4 (q), 40.9 (q), 20.6 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3247, 3135, 3069, 3031, 3001, 2970, 2939, 2831, 1738, 1612, 1591, 1497, 1462, 1416, 1376, 1358, 1328, 1310, 1263, 1202, 1168, 1154, 1128, 1088, 1073, 1055, 1024, 978, 963, 946, 932, 872, 814, 754, 715, 705, 666, 649, 608 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{24}H_{24}{}^{79}BrN_2O_6S_2$ calcd for 579.0254, found 579.0242.

***N*-(3-(3-chlorophenyl)-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3ak)**



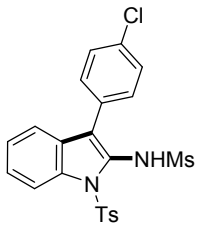
Yield: 83 mg, 88%; white solid, mp 204-205 °C; R_f = 0.20 (EA/PE = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.40-7.29 (m, 6H), 7.22-7.17 (m,3H), 2.53 (s, 3H), 2.23 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8 (s), 134.8 (s), 134.6 (s), 134.3 (s), 133.4 (s), 130.2 (d), 130.00 (d), 129.99 (d, 2C), 128.4 (d), 128.3 (d), 127.9 (s), 127.3 (d, 2C), 127.1 (s), 126.1 (d), 124.4 (d), 120.0 (d), 119.8 (s), 114.7 (d), 42.5 (q), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3250, 1739, 1595, 1563, 1482, 1448, 1432, 1372, 1355, 1330, 1233, 1216, 1190, 1154, 1118, 1087, 1043, 1021, 978, 936, 884, 852, 815, 786, 749, 730, 694, 659, 629 cm^{-1}; HRMS (ESI) (*m/z*) $C_{22}H_{20}{}^{35}ClN_2O_4S_2$ calcd for 475.0548, found 475.0543.

***N*-(3-(*p*-tolyl)-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3al)**



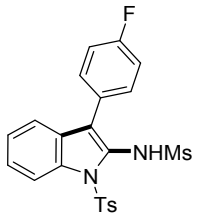
Yield: 76 mg, 83%; white solid, mp 209-210 °C; R_f = 0.40 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32-7.27 (m, 2H), 7.23-7.18 (m, 3H), 7.18-7.14 (m, 2H), 2.42 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6 (s), 138.2 (s), 134.8 (s), 134.4 (s), 129.93 (d, 2C), 129.89 (d, 2C), 129.7 (d, 2C), 128.5 (s), 128.4 (s), 127.3 (d, 2C), 126.7 (s), 125.8 (d), 124.1 (d), 121.1 (s), 120.3 (d), 114.6 (d), 42.5 (q), 21.7 (q), 21.4 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3339, 3052, 3036, 1618, 1596, 1513, 1494, 1453, 1415, 1377, 1358, 1333, 1321, 1246, 1226, 1197, 1182, 1169, 1152, 1120, 1087, 1060, 1027, 964, 852, 823, 809, 773, 739, 710, 662, 640 cm^{-1}; HRMS (ESI) (*m/z*) $C_{23}H_{23}N_2O_4S_2$ calcd for 455.1094, found 455.1092.

***N*-(3-(4-chlorophenyl)-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3am)**



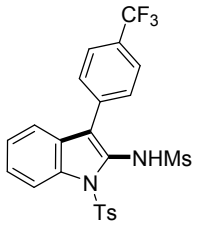
Yield: 62 mg, 65%; white solid, mp 176-178 °C; R_f = 0.46 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.40 (s, 4H), 7.37-7.31 (m, 2H), 7.29 (s, 1H), 7.22-7.19 (m, 3H), 2.54 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8 (s), 134.5 (s), 134.4 (s), 133.3 (s), 131.4 (d, 2C), 130.02 (s), 129.97 (d, 2C), 129.2 (d, 2C), 128.1, 127.3 (d, 2C), 126.9 (s), 126.0 (d), 124.3 (d), 120.2 (s), 120.0 (d), 114.8 (d), 42.4 (q), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3293, 2931, 2854, 1731, 1654, 1597, 1494, 1452, 1380, 1360, 1335, 1246, 1173, 1124, 1091, 1055, 1015, 971, 836, 776, 751, 730, 703, 669 cm^{-1}; HRMS (ESI) (*m/z*) $C_{22}H_{20}{}^{35}ClN_2O_4S_2$ calcd for 475.0548, found 475.0539.

***N*-(3-(4-fluorophenyl)-1-tosyl-1*H*-indol-2-yl)methanesulfonamide (3an)**



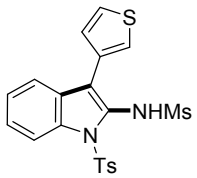
Yield: 58 mg, 63%; white solid, mp 223-224 °C; R_f = 0.38 (EA/PE = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.46-7.40 (m, 2H), 7.36-7.29 (m, 3H), 7.20-7.16 (m, 3H), 7.13-7.08 (m, 2H), 2.51 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (d, J_{C-F} =247.0 Hz), 145.7 (s), 134.6 (s), 134.4 (s), 131.8 (d, J_{C-F} =8.0 Hz, 2C), 130.0 (d, 2C), 128.3 (s), 127.5 (d, J_{C-F} =3.4 Hz), 127.3 (d, 2C), 126.9 (s), 126.0 (d), 124.3 (d), 120.4 (s), 120.1 (d), 116.1 (d, J_{C-F} =21.4 Hz, 2C), 114.8 (d), 42.4 (q), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3319, 3012, 1595, 1509, 1432, 1407, 1344, 1327, 1298, 1229, 1202, 1153, 1116, 1097, 1087, 1033, 1012, 972, 935, 845, 812, 776, 757, 719, 702, 684, 666, 646, 630 cm^{-1}; HRMS (ESI) (*m/z*) $C_{22}H_{20}FN_2O_4S_2$ calcd for 459.0843, found 459.0831.

_N_-(1-tosyl-3-(4-(trifluoromethyl)phenyl)-1_H_-indol-2-yl)methanesulfonamide (3ao)



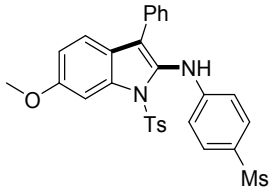
Yield: 87 mg, 85%; white solid, mp 200-201 °C; R_f = 0.28 (EA/PE = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.39-7.32 (m, 3H), 7.21-7.17 (m, 3H), 2.56 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9 (s), 135.5 (s), 134.42 (s),134.39 (s), 130.4 (d, 2C), 130.3 (q, J_{C-F} =32.4 Hz), 130.0 (d, 2C), 127.9 (s), 127.24 (d, 2C),127.19 (s), 126.2 (d), 125.8 (q, J_{C-F} =3.8 Hz, 2C), 124.5 (d),124.0 (q, J_{C-F} =270.8 Hz), 120.3 (s), 120.0 (d), 114.9 (d), 42.3 (q), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3259, 1621, 1597, 1449, 1409, 1386, 1370, 1322, 1245, 1225, 1204, 1189, 1177, 1158, 1144, 1117, 1088, 1067, 1028, 1016, 981, 853, 815, 787, 772, 752, 703, 683, 664, 645 cm^{-1}; HRMS (ESI) (*m/z*) $C_{23}H_{20}F_3N_2O_4S_2$ calcd for 509.0811, found 509.0810.

_N_-(3-(thiophen-3-yl)-1-tosyl-1_H_-indol-2-yl)methanesulfonamide (3ap)



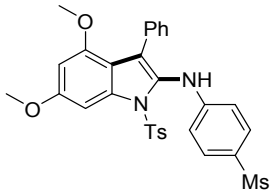
Yield: 78 mg, 88%; white solid, mp 251-252 °C; R_f = 0.42 (EA/PE = 1/3); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.15 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.90 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.75 (dd, *J* = 6.0, 3.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.46-7.42 (m, 1H), 7.35-7.29 (m, 3H), 2.71 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 145.7 (s), 134.6 (s), 134.5 (s), 131.1 (s), 130.3 (d, 2C), 128.8 (d), 127.8 (s), 127.44 (s), 127.41 (d, 2C), 127.3 (d), 126.5 (d), 125.6 (d), 124.8 (d), 120.8 (d), 119.2 (s), 115.6 (d), 42.4 (q), 21.5 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3292, 3105, 3011, 1738, 1596, 1432, 1406, 1361, 1329, 1319, 1207, 1193, 1169, 1156, 1137, 1117, 1089, 1042, 974, 938, 861, 813, 796, 754, 732, 702, 658, 632, 612 cm^{-1}; HRMS (ESI) (*m/z*) $C_{20}H_{19}F_3N_2O_4S_3$ calcd for 447.0501, found 447.0497.

6-methoxy-_N_-(4-(methylsulfonyl)phenyl)-3-phenyl-1-tosyl-1_H_-indol-2-amine (3cr)



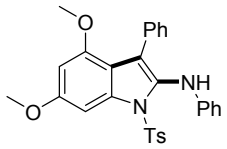
Yield: 95 mg, 87%; white solid, mp 209-211 °C; R_f = 0.21 (EA/PE = 1/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 4H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 3H), 6.52 (s, 1H), 6.34 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H), 2.84 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4 (s), 148.1 (s), 145.4 (s), 135.3 (s), 135.2 (s), 131.7 (s), 130.4 (s), 129.7 (d, 2C), 128.8 (d, 2C), 128.7 (d, 2C), 128.6 (s), 128.4 (d, 2C), 127.5 (d), 126.6 (d, 2C), 121.5 (s), 120.4 (d), 116.4 (s), 113.9 (d, 2C), 113.0 (d), 99.3 (d), 55.9 (q), 44.8 (q), 21.5 (q) ppm; IR (reflection) $\tilde{\nu}$ =3348, 2924, 1744, 1591, 1505, 1435, 1407, 1363, 1294, 1195, 1172, 1140, 1090, 1055, 1033, 990, 955, 833, 811, 764, 699, 665, 626 cm^{-1}; HRMS (ESI) (*m/z*) $C_{29}H_{27}N_2O_5S_2$ calcd for 547.1356, found 547.1360.

4,6-dimethoxy-*N*-(4-(methylsulfonyl)phenyl)-3-phenyl-1-tosyl-1*H*-indol-2-amine (3ch)



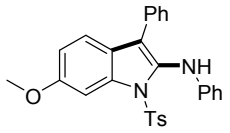
Yield: 101 mg, 88%; white solid, mp 191-192 °C; R_f = 0.21 (EA/PE = 1/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.26-7.22 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.08-7.03 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 2.0 Hz, 1H), 6.27 (d, *J* = 8.5 Hz, 2H), 6.21 (s, 1H), 3.86 (s, 3H), 3.59 (s, 3H), 2.84 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3 (s), 154.5 (s), 148.9 (s), 145.3 (s), 136.2 (s), 135.4 (s), 132.3 (s), 130.1 (d, 2C), 130.0 (s), 129.6 (d, 2C), 128.5 (d, 2C), 127.6 (s), 127.4 (d, 2C), 127.0 (d), 126.6 (d, 2C), 118.2 (s), 113.6 (d, 2C), 111.1 (s), 95.7 (d), 90.8 (d), 55.9 (q), 55.3 (q), 44.8 (q), 21.5 (q) ppm; IR (reflection) $\tilde{\nu}$ =3298, 3011, 2929, 1620, 1605, 1592, 1562, 1493, 1471, 1454, 1431, 1380, 1347, 1323, 1291, 1195, 1155, 1140, 1121, 1068, 1053, 1027, 976, 956, 944, 914, 810, 770, 748, 727, 707, 695, 649, 620 cm^{-1}; HRMS (ESI) (*m/z*) $C_{30}H_{29}N_2O_6S_2$ calcd for 577.1462, found 577.1465.

4,6-dimethoxy-*N*,3-diphenyl-1-tosyl-1*H*-indol-2-amine (3dh)



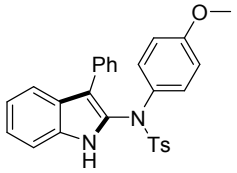
Yield: 75 mg, 75%; yellow solid, mp 148-150 °C; R_f = 0.38 (EA/PE = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.28-7.24 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 2H), 7.05-7.00 (m, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.79 (t, *J* = 8.5 Hz, 2H), 6.54 (t, *J* = 7.5 Hz, 1H), 6.30 (d, *J* = 2.0 Hz, 1H), 6.26 (d, *J* = 7.5 Hz, 2H), 5.89 (s,1H), 3.86 (s, 3H), 3.57 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6 (s), 154.2 (s), 144.6 (s), 144.2 (s), 135.8 (s), 135.5 (s), 132.9 (s), 130.5 (s), 130.3 (d, 2C), 129.5 (d, 2C), 128.5 (d, 2C), 127.1 (d, 2C), 126.9 (d, 2C), 126.6 (d), 119.3 (d), 116.0 (s), 114.4 (d, 2C), 111.7 (s), 95.6 (d), 91.3 (d), 55.9 (q), 55.3 (q), 21.5 (q) ppm; IR (reflection) $\tilde{\nu}$ =3393, 1602, 1577, 1495, 1456, 1434, 1418, 1376, 1358, 1318, 1257, 1217, 1200, 1189, 1166, 1122, 1088, 1056, 1026, 955, 926, 820, 768, 748, 704, 692, 666 cm^{-1}; HRMS (ESI) (*m/z*) $C_{29}H_{27}N_2O_4S$ calcd for 499.1686, found 499.1683.

6-methoxy-*N*,3-diphenyl-1-tosyl-1*H*-indol-2-amine (3dr)



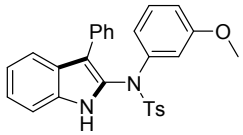
Yield: 23 mg, 25%; white solid, mp 138-140 °C; R_f = 0.43 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 3H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.22-7.16 (m, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.94-6.76 (m, 5H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.33 (s,1H), 6.32 (d, *J* = 7.5 Hz, 2H), 3.86 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7 (s), 144.7 (s), 142.9 (s), 135.2 (s), 134.8 (s), 132.4 (s), 131.5 (s), 129.5 (d, 2C), 128.6 (d, 2C), 128.42 (d, 2C), 128.40 (d, 2C), 126.9 (d, 3C), 122.5 (s), 119.7 (d, 2C), 114.8 (d, 2C), 113.2 (s), 112.5 (d), 99.7 (d), 55.9 (q), 21.5 (q) ppm; IR (reflection) $\tilde{\nu}$ =3395, 2922, 1720, 1596, 1510, 1489, 1436, 1386, 1366, 1306, 1284, 1247, 1199, 1173, 1147, 1116, 1086, 1049, 1033, 987, 910, 846, 812, 741, 700, 688, 667 cm^{-1}; HRMS (ESI) (*m/z*) $C_{28}H_{25}N_2O_5S$ calcd for 469.1580, found 469.1583.

_N_-(4-methoxyphenyl)-4-methyl-_N_-(3-phenyl-1_H_-indol-2-yl)benzenesulfonamide (4de)[3]



Yield: 93 mg, 99%; white solid, mp 80-82 °C; R_f = 0.19 (EA/PE = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.19-7.15 (m, 1H), 7.15-7.12 (m, 2H), 7.13-7.08 (m, 3H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 4H), 6.60-6.55 (m, 2H), 3.62 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6 (s), 144.3 (s), 136.0 (s), 133.6 (s), 133.4 (s), 132.9 (s), 129.7 (d, 2C), 129.6 (d, 2C), 129.58 (s), 128.8 (d, 2C), 128.0 (d, 2C), 127.9 (d, 2C), 126.7 (d), 126.6 (s), 123.5 (d), 120.4 (d), 120.0 (d), 114.9 (s), 114.1 (d, 2C), 111.3 (d), 55.4 (q), 21.7 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3353, 2902, 1603, 1507, 1453, 1335, 1250, 1159, 1090, 1029, 832, 809, 776, 749, 719, 690, 666, 624 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{28}H_{25}N_2O_3S$ calcd for 469.1580, found 469.1578.

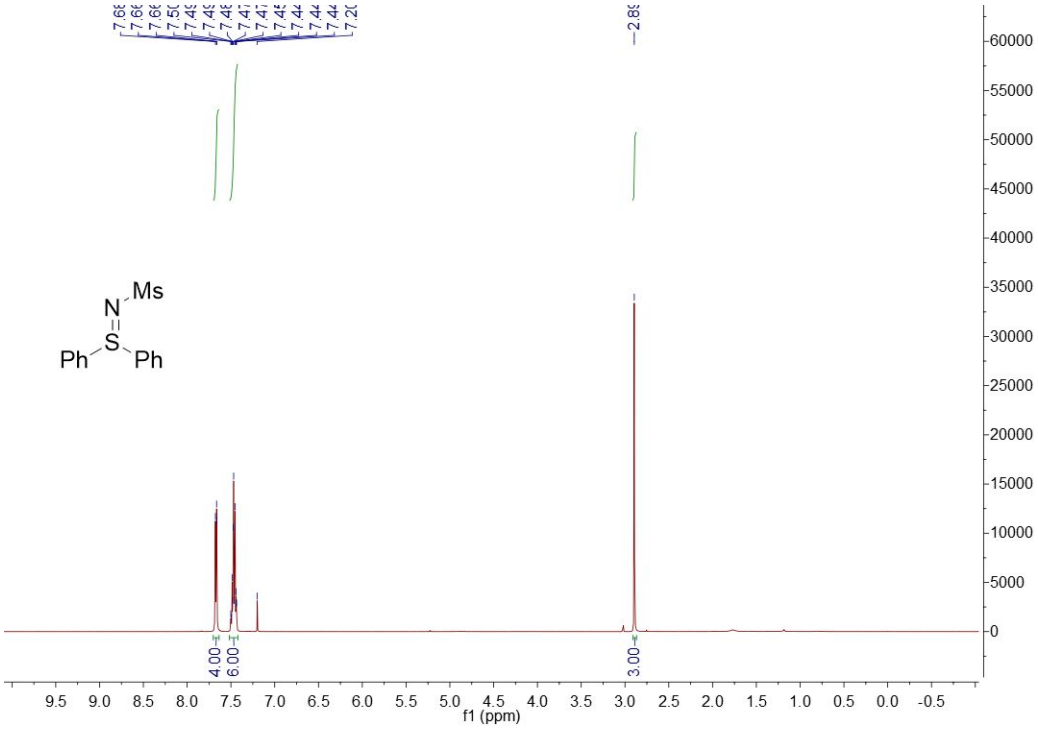
_N_-(3-methoxyphenyl)-4-methyl-_N_-(3-phenyl-1_H_-indol-2-yl)benzenesulfonamide (4dr)



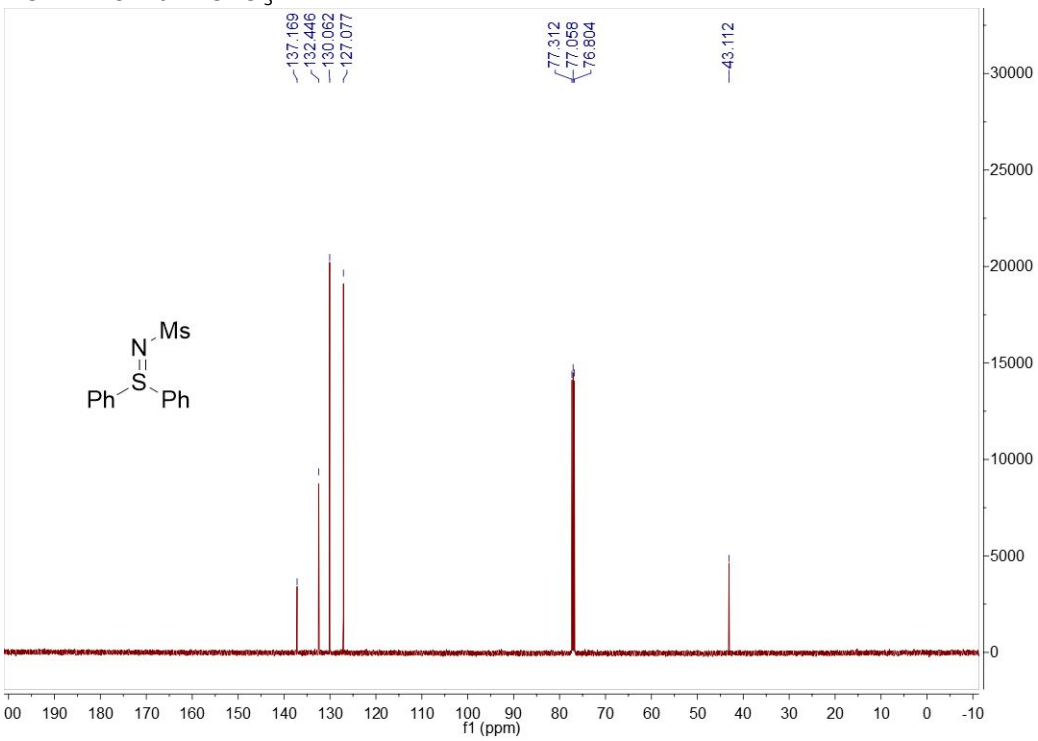
Yield: 68 mg, 73%; white solid, mp 171-174 °C; R_f = 0.26 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.22-7.06 (m, 6H), 7.04-6.95 (m, 2H), 6.95-6.86 (m, 2H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.63-6.52 (m, 2H), 3.53 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8 (s), 144.4 (s), 142.1 (s), 136.1 (s), 133.8 (s), 132.8 (s), 129.7 (d, 2C), 129.52 (d), 129.50 (d, 2C), 129.0 (s), 128.0 (d, 2C), 127.8 (d, 2C), 126.7 (d), 126.5 (s), 123.6 (d), 120.5 (d), 120.1 (d), 118.7 (d), 115.3 (s), 112.9 (d), 112.1 (d), 111.4 (d), 55.3 (q), 21.6 (q) ppm; IR (reflection) $\tilde{\nu}$ =3385, 2835, 1597, 1489, 1447, 1422, 1359, 1311, 1281, 1260, 1221, 1189, 1165, 1092, 1078, 1027, 984, 858, 834, 816, 778, 753, 701, 671, 643, 624 cm^{-1}; HRMS (ESI) (*m/z*) $[M+H]^+$ $C_{28}H_{25}N_2O_3S$ calcd for 469.1580, found 469.1578.

4. NMR spectra

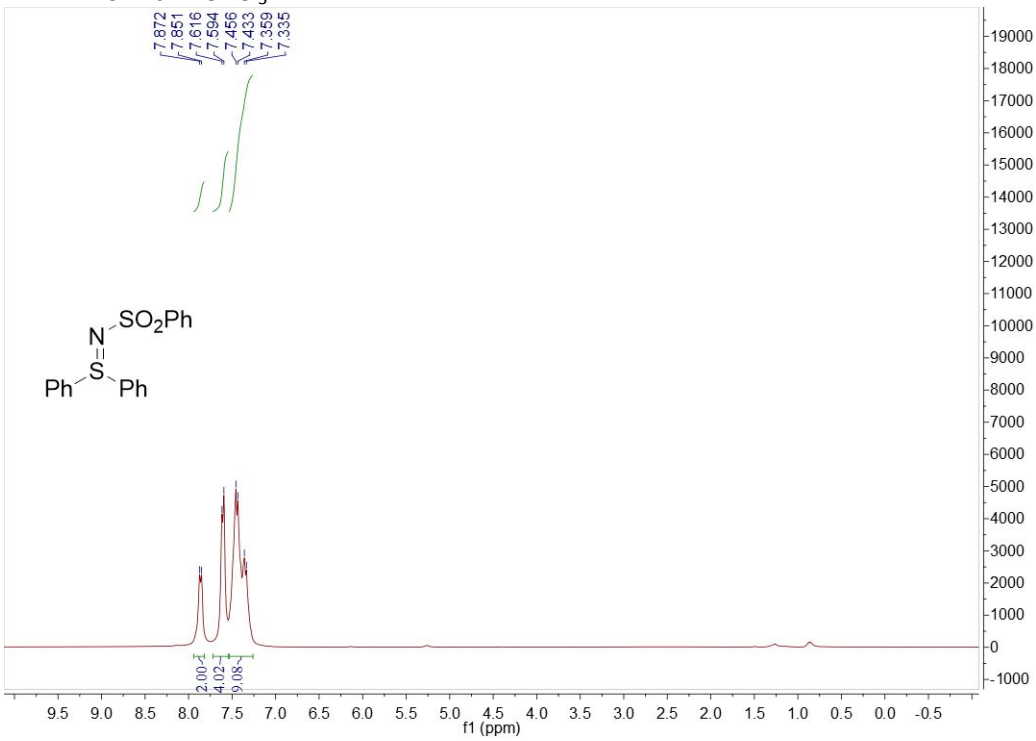
^{1}H NMR of **1a** in $CDCl_3$:



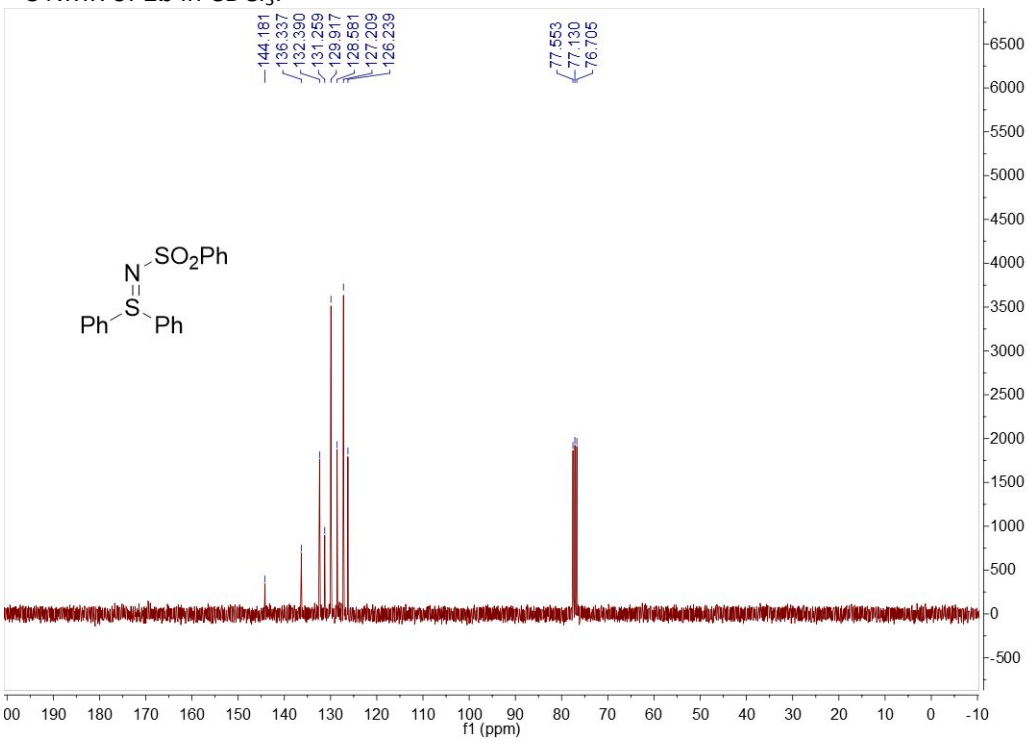
^{13}C NMR of **1a** in $CDCl_3$:



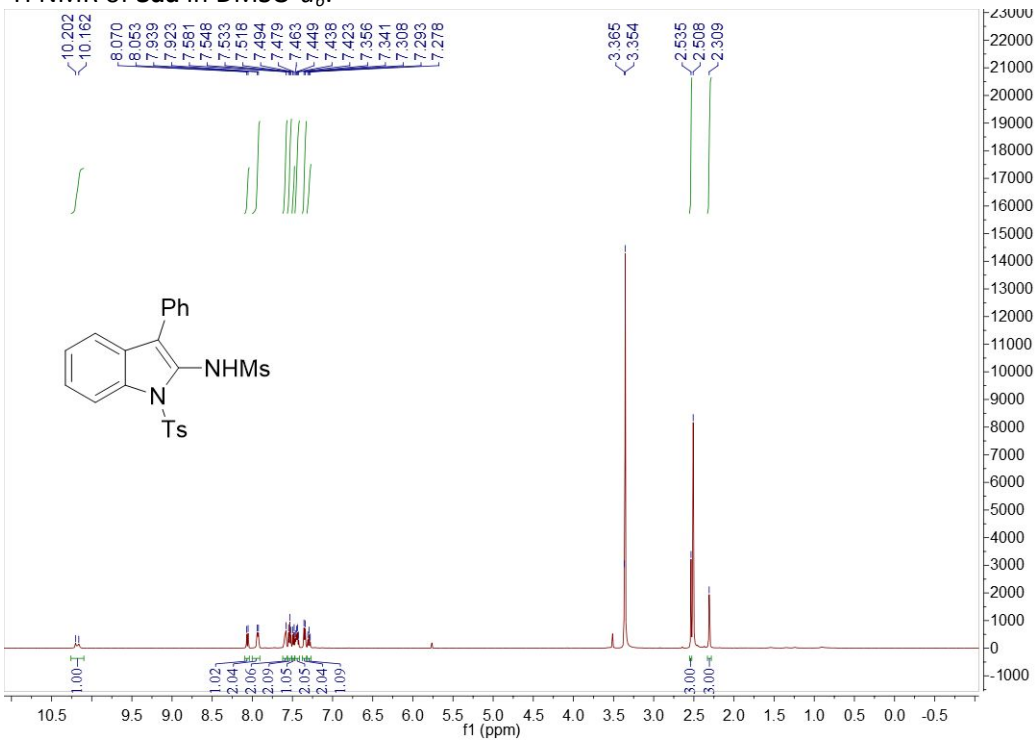
^{1}H NMR of **1b** in $CDCl_3$:



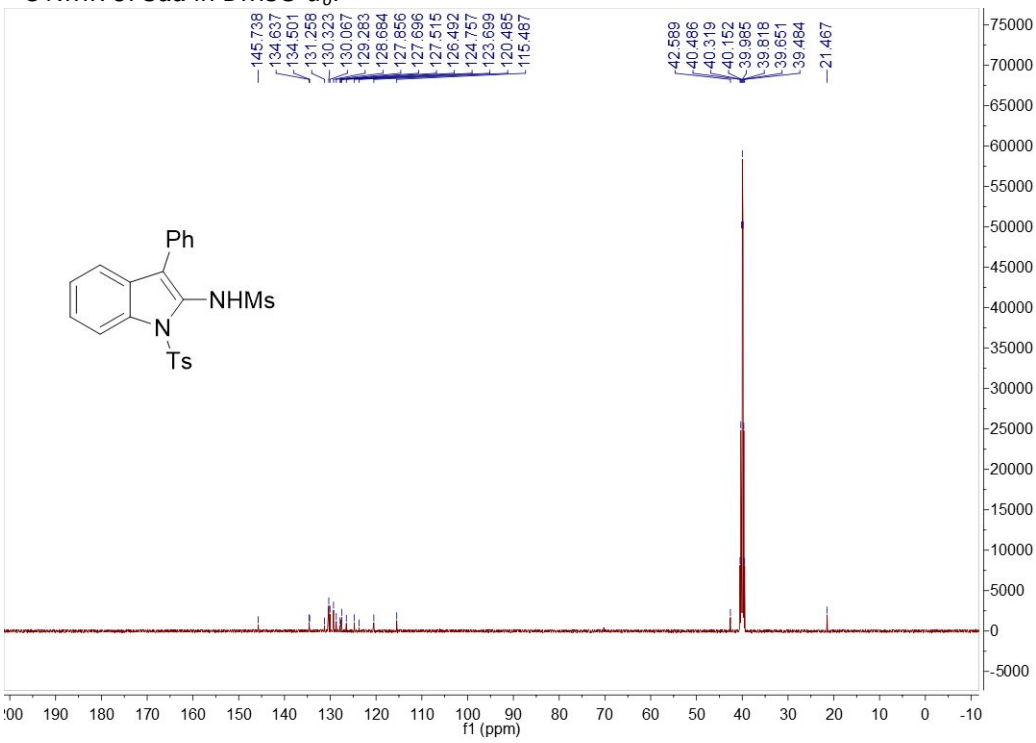
^{13}C NMR of **1b** in $CDCl_3$:



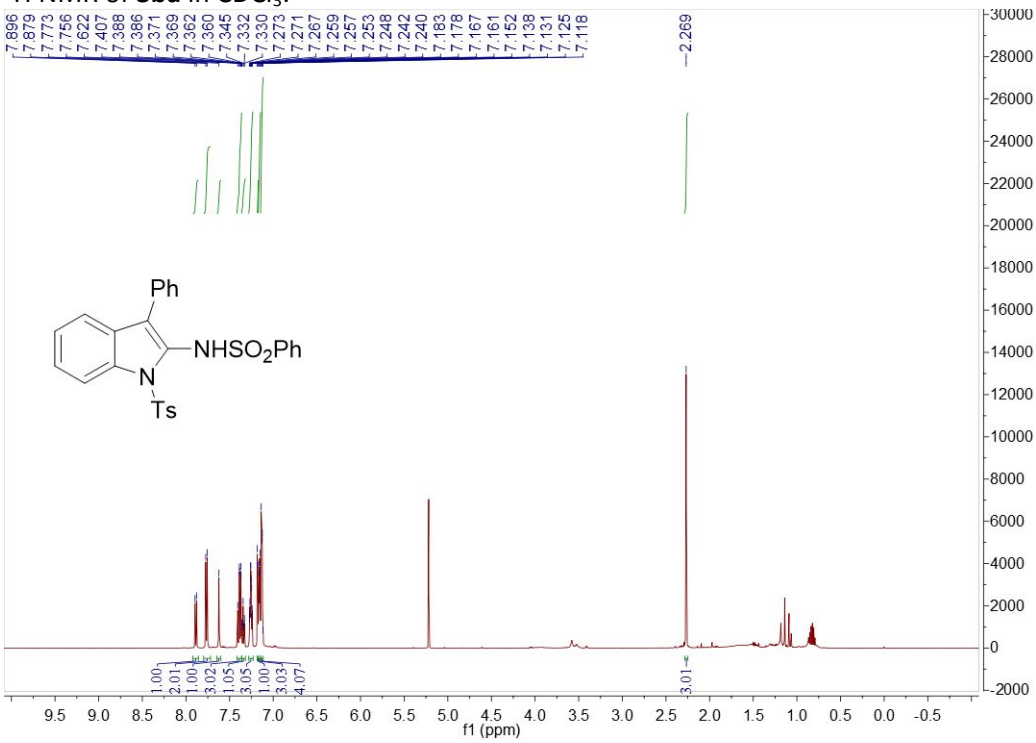
^{1}H NMR of **3aa** in DMSO-d_6:



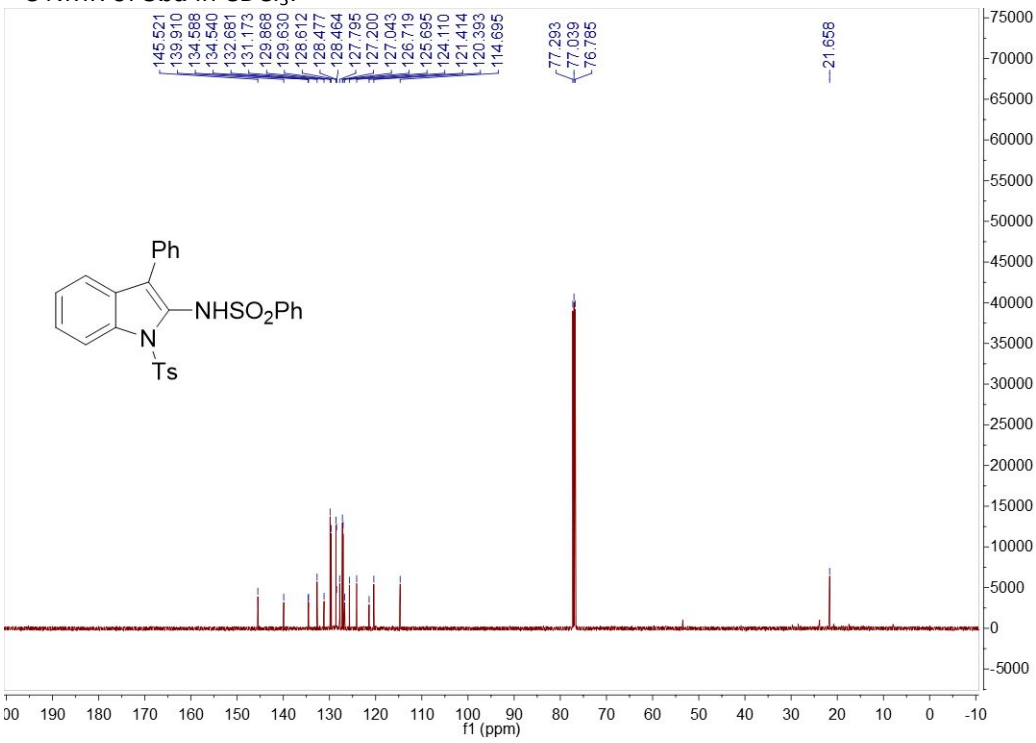
^{13}C NMR of **3aa** in DMSO-d_6:



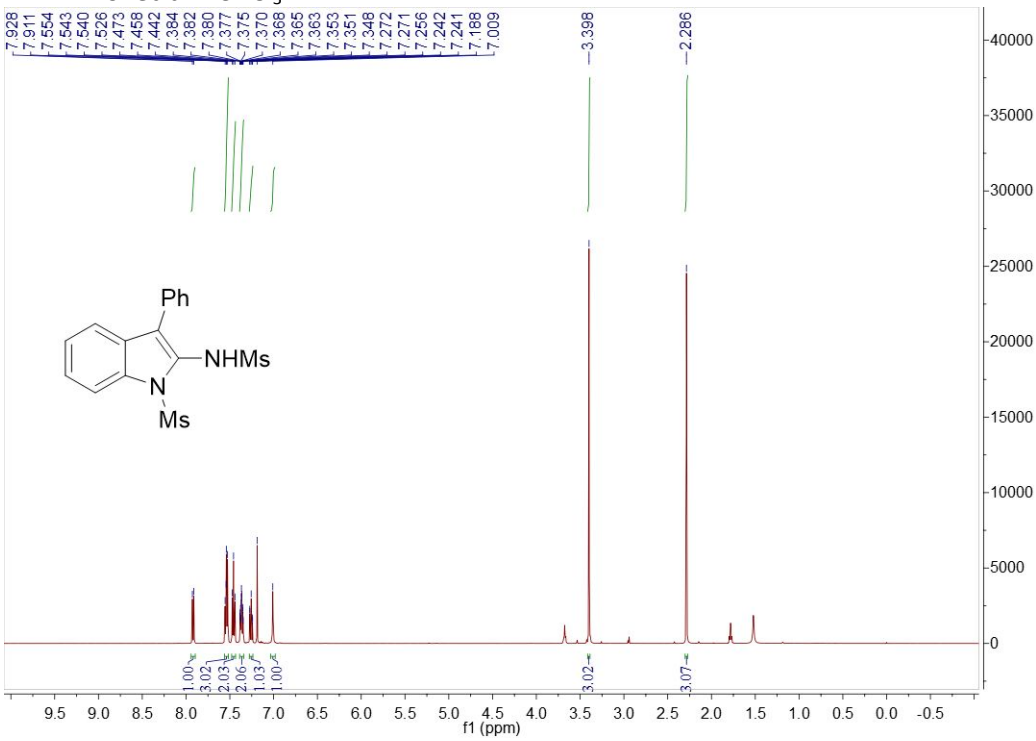
^{1}H NMR of **3ba** in $CDCl_3$:



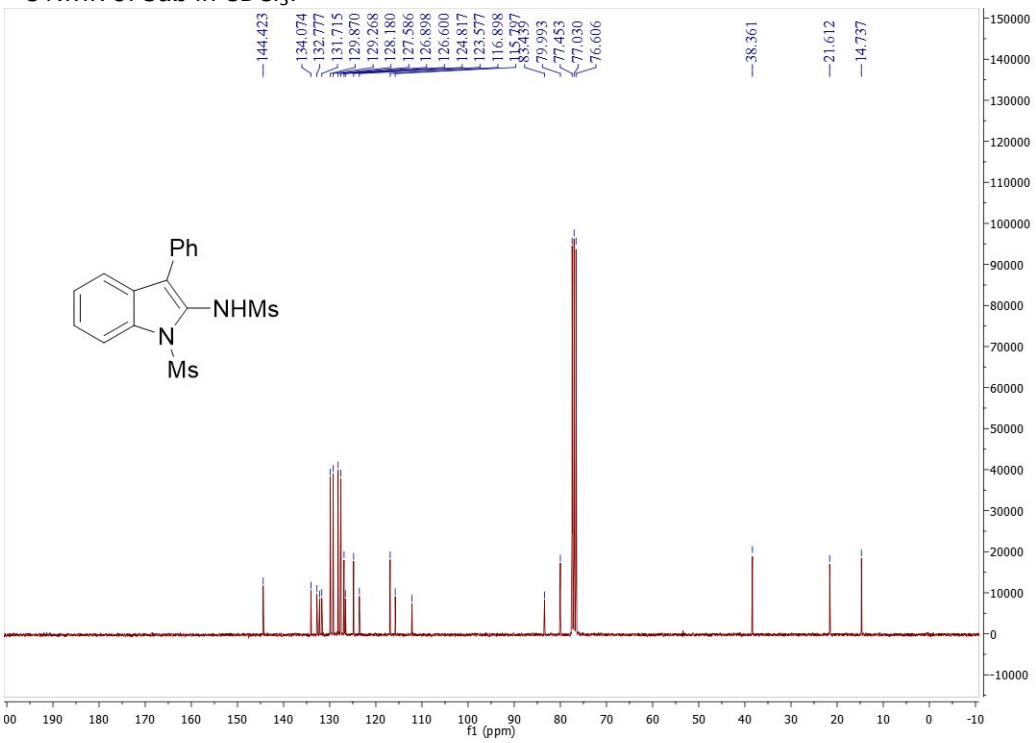
^{13}C NMR of **3ba** in $CDCl_3$:



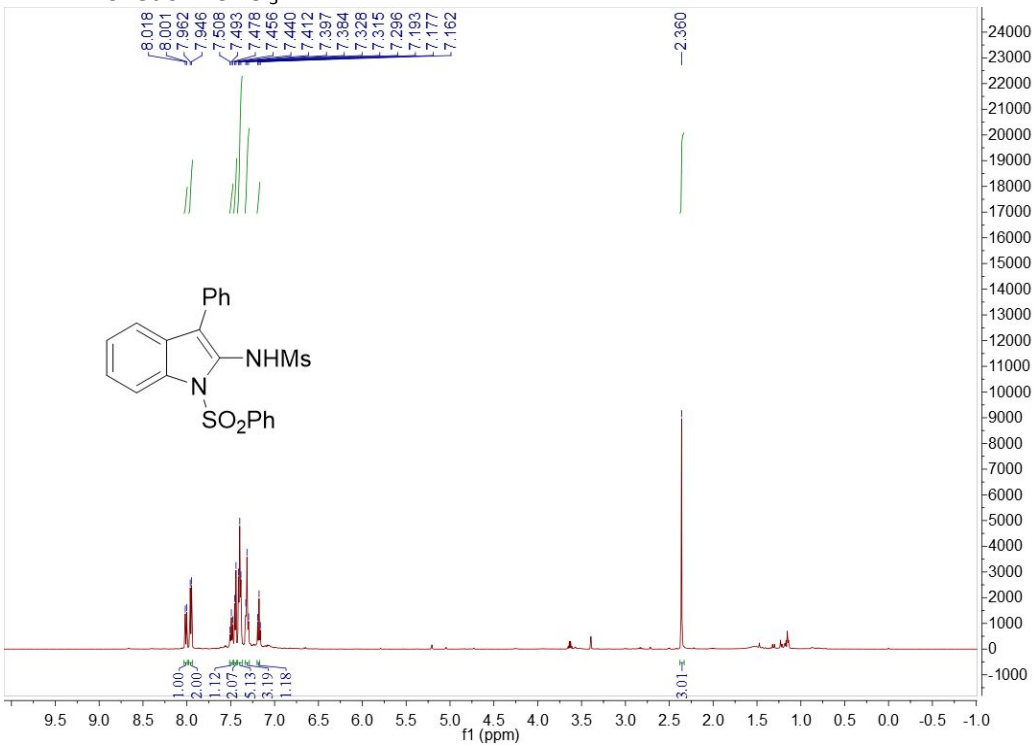
^{1}H NMR of **3ab** in $CDCl_3$:



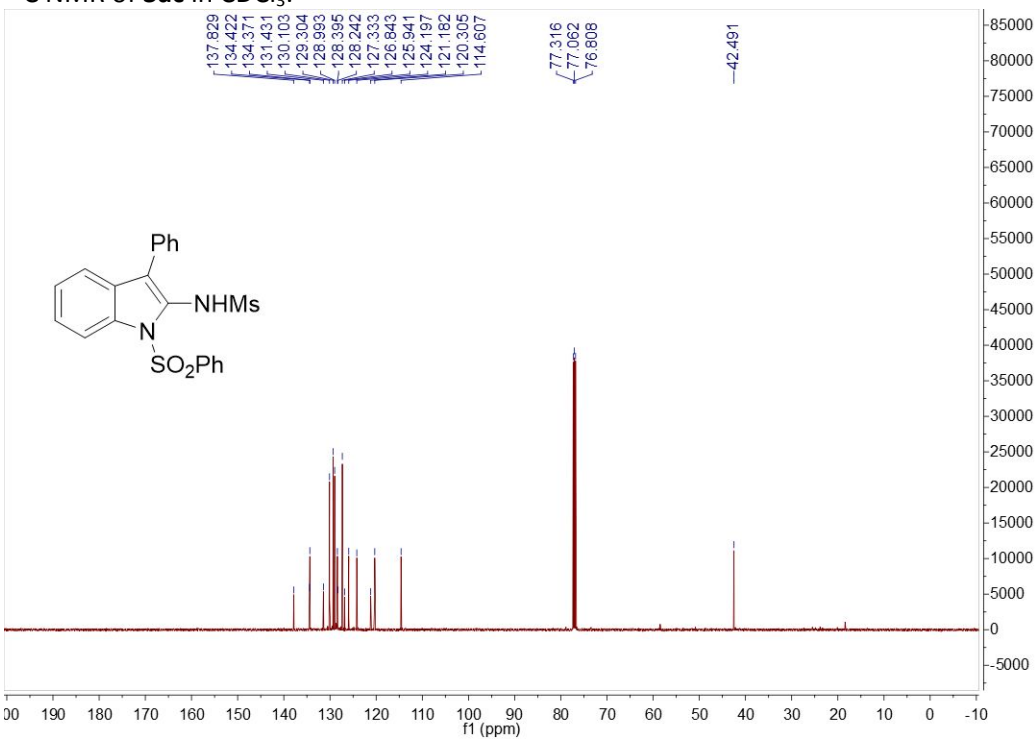
^{13}C NMR of **3ab** in $CDCl_3$:



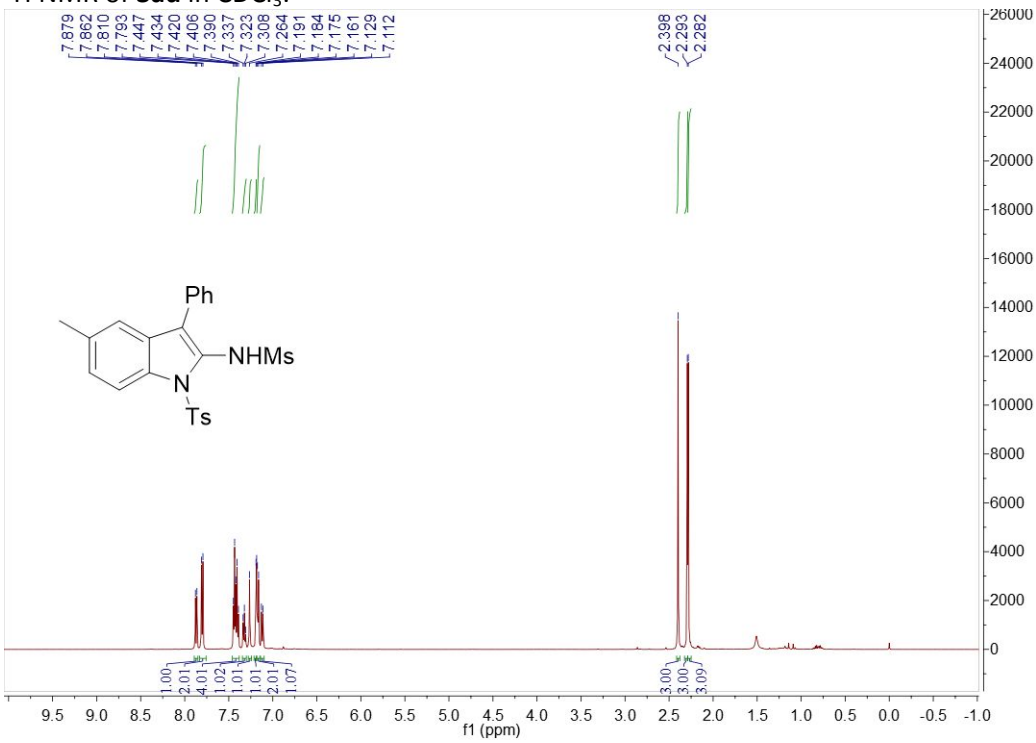
^{1}H NMR of **3ac** in $CDCl_3$:



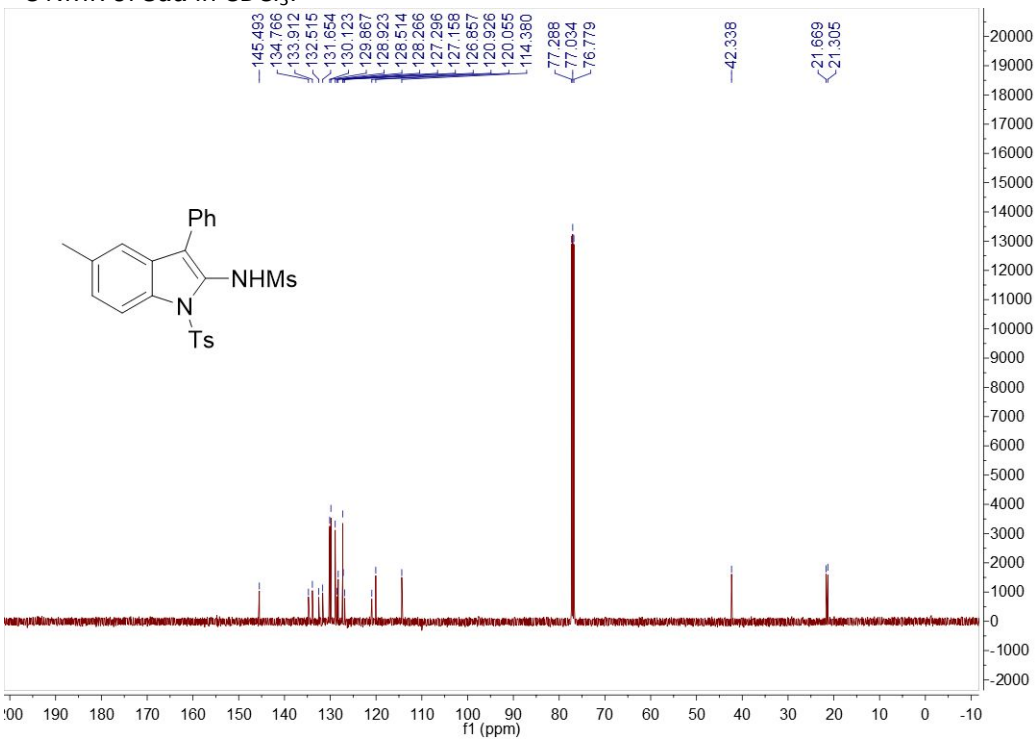
^{13}C NMR of **3ac** in $CDCl_3$:



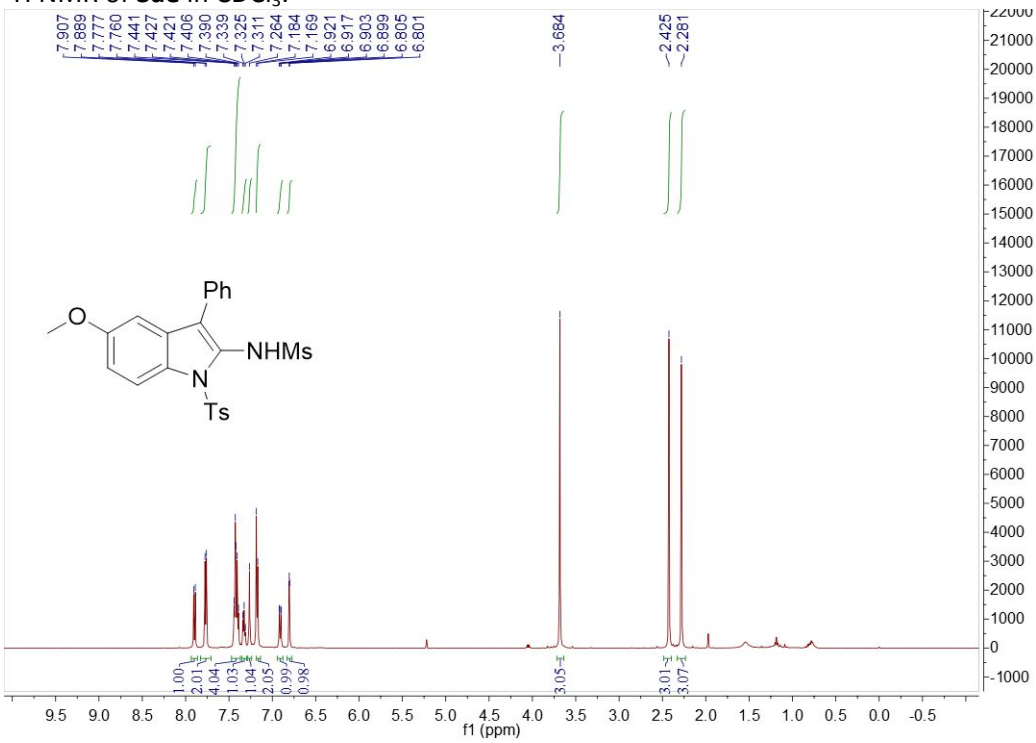
^{1}H NMR of **3ad** in $CDCl_3$:



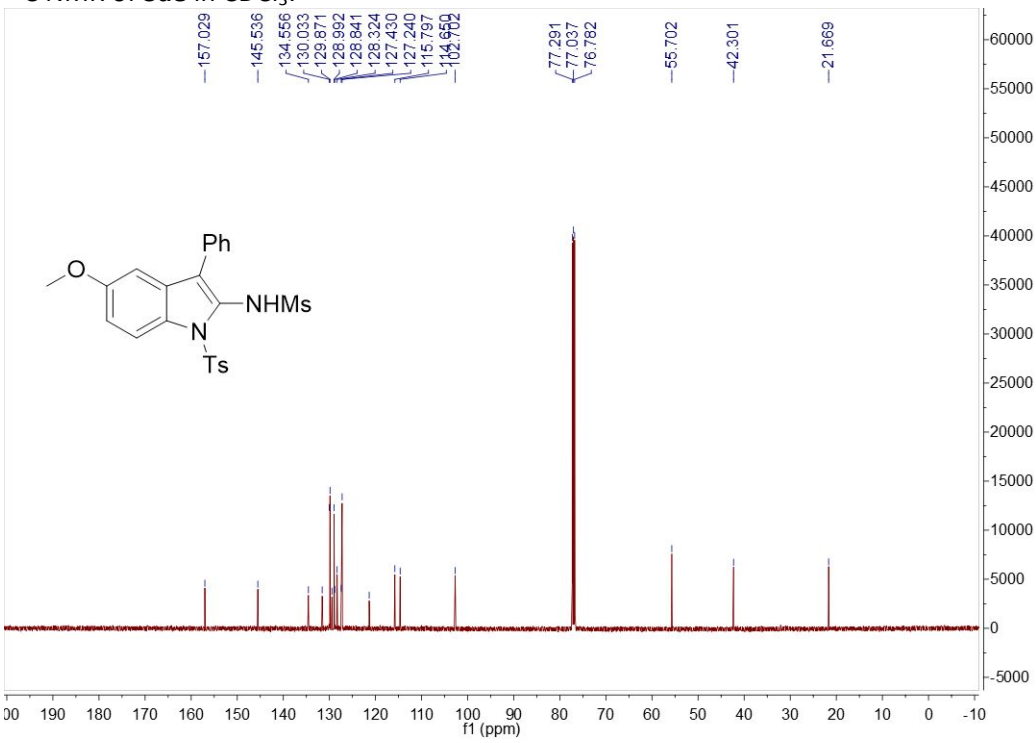
^{13}C NMR of **3ad** in $CDCl_3$:



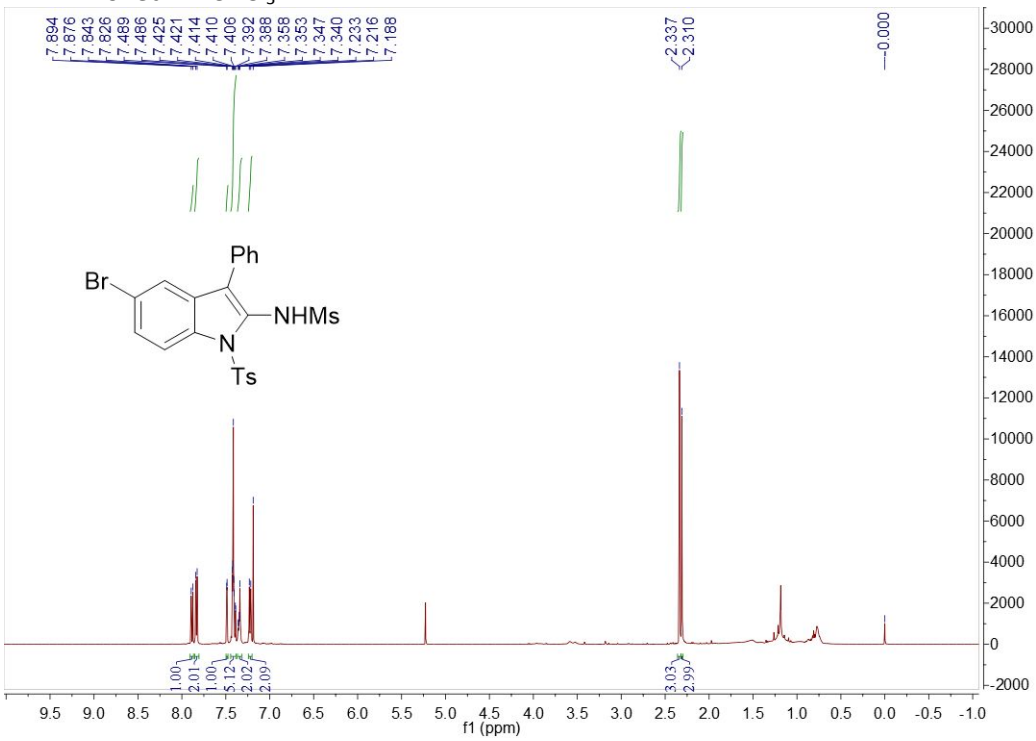
^{1}H NMR of **3ae** in $CDCl_3$:



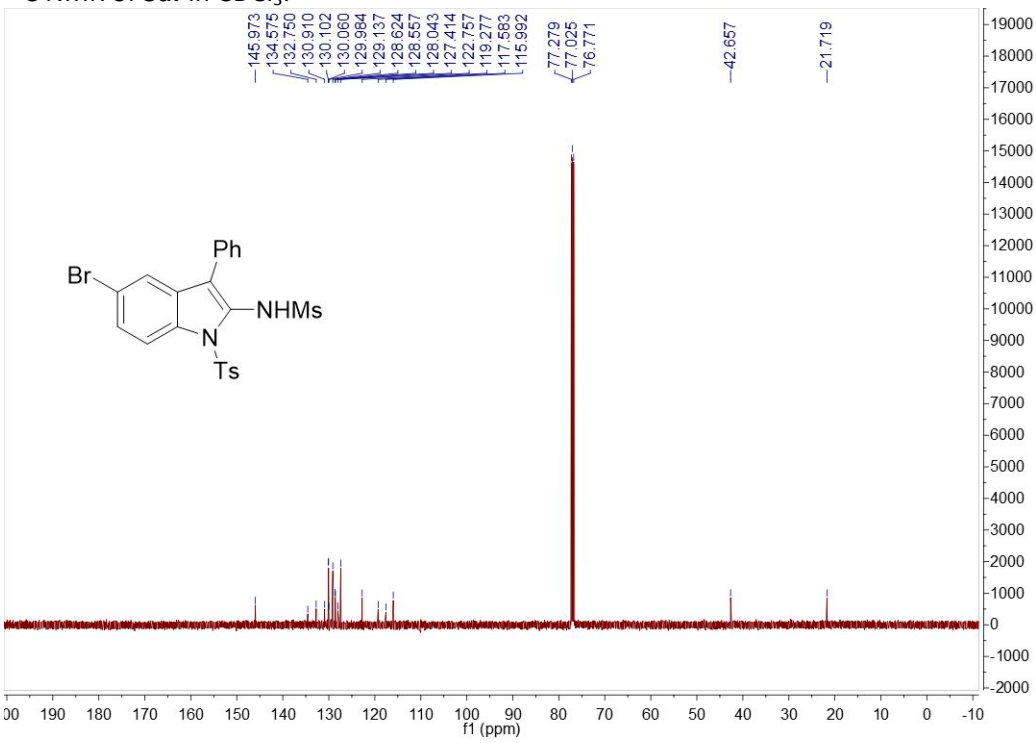
^{13}C NMR of **3ae** in $CDCl_3$:



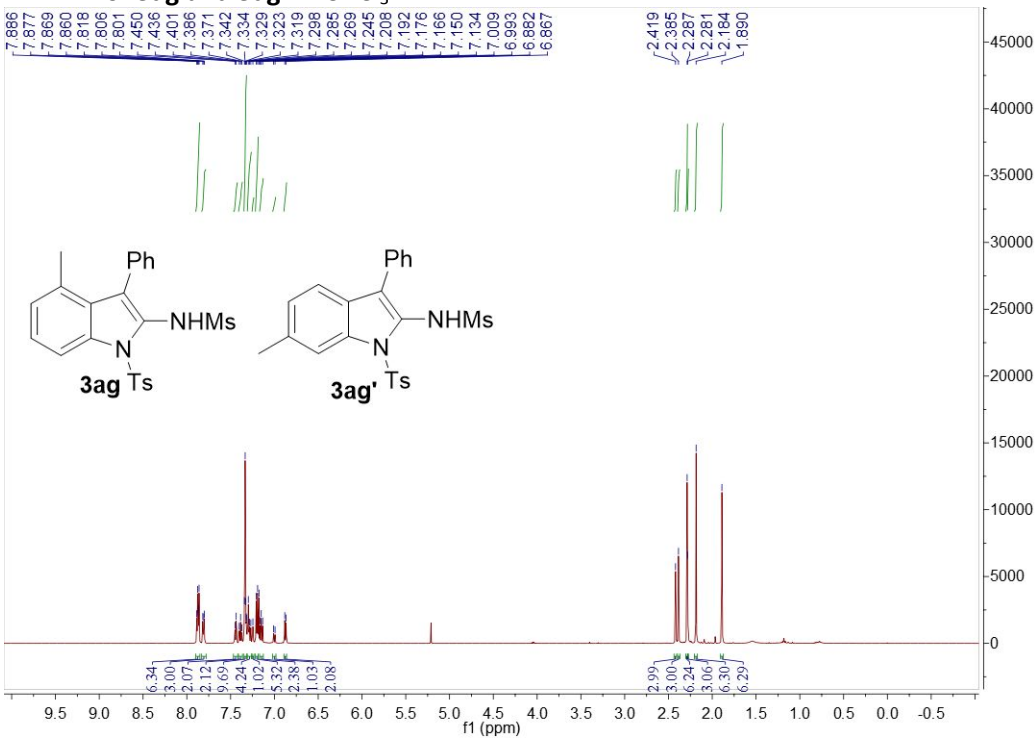
^{1}H NMR of **3af** in $CDCl_3$:



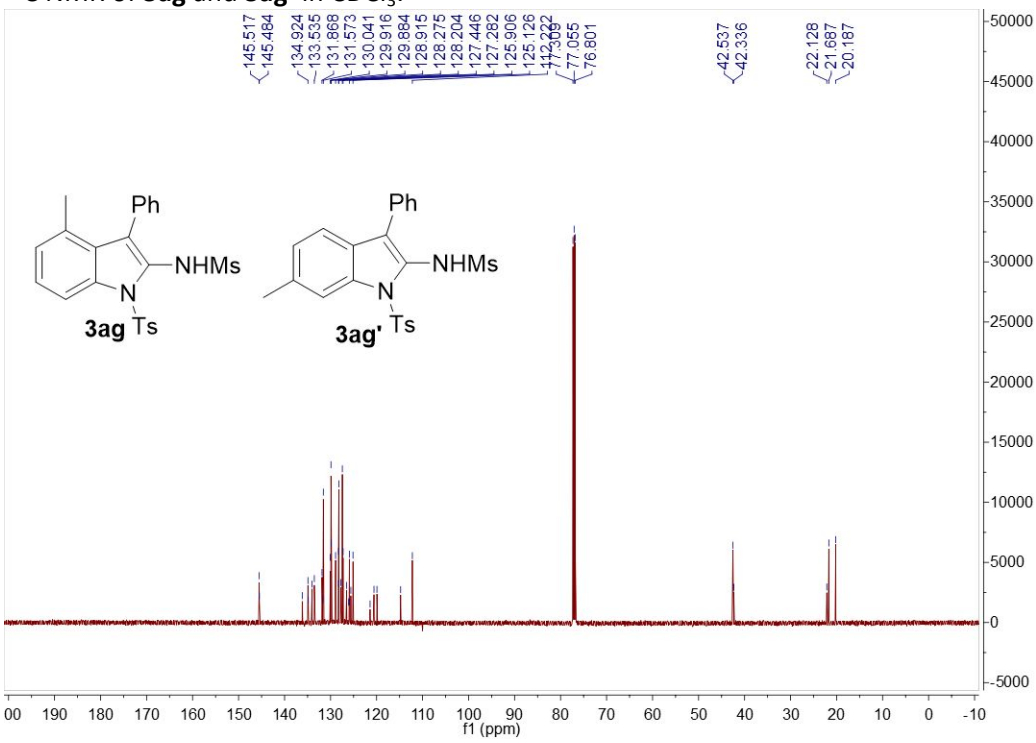
^{13}C NMR of **3af** in $CDCl_3$:



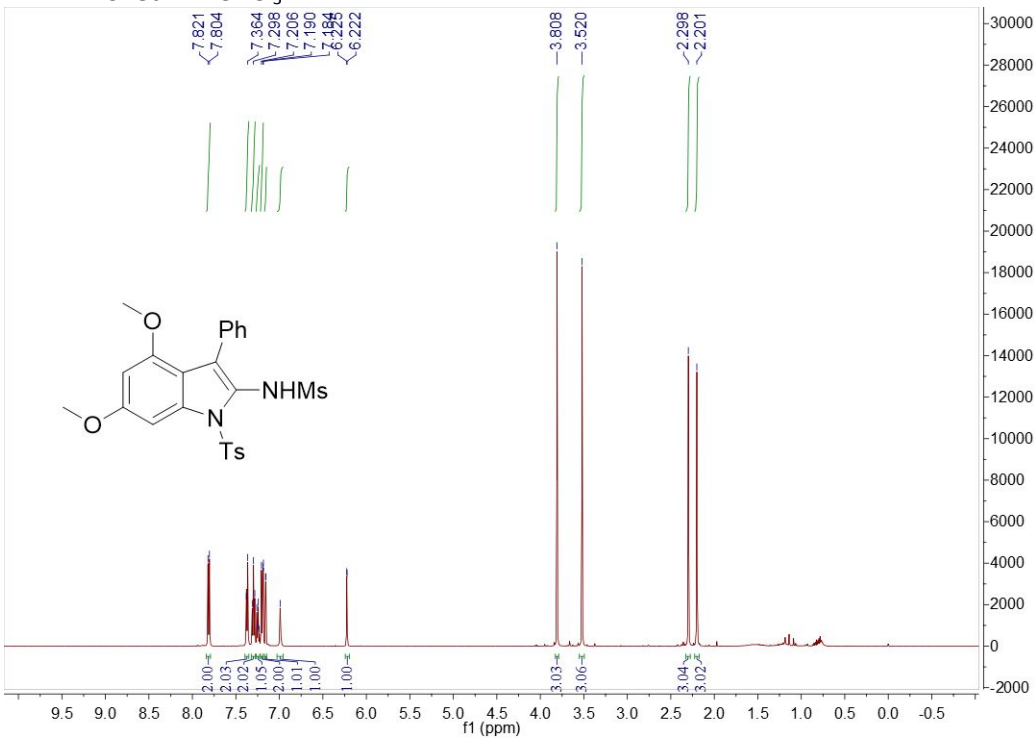
^{1}H NMR of **3ag** and **3ag'** in $CDCl_3$:



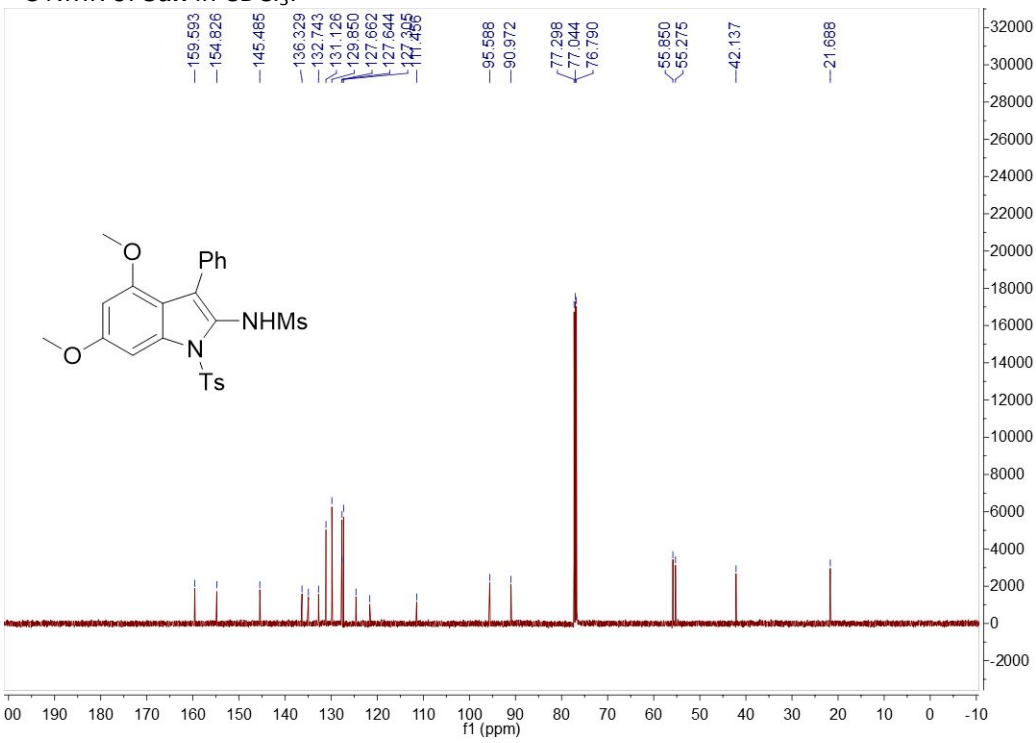
^{13}C NMR of **3ag** and **3ag'** in $CDCl_3$:



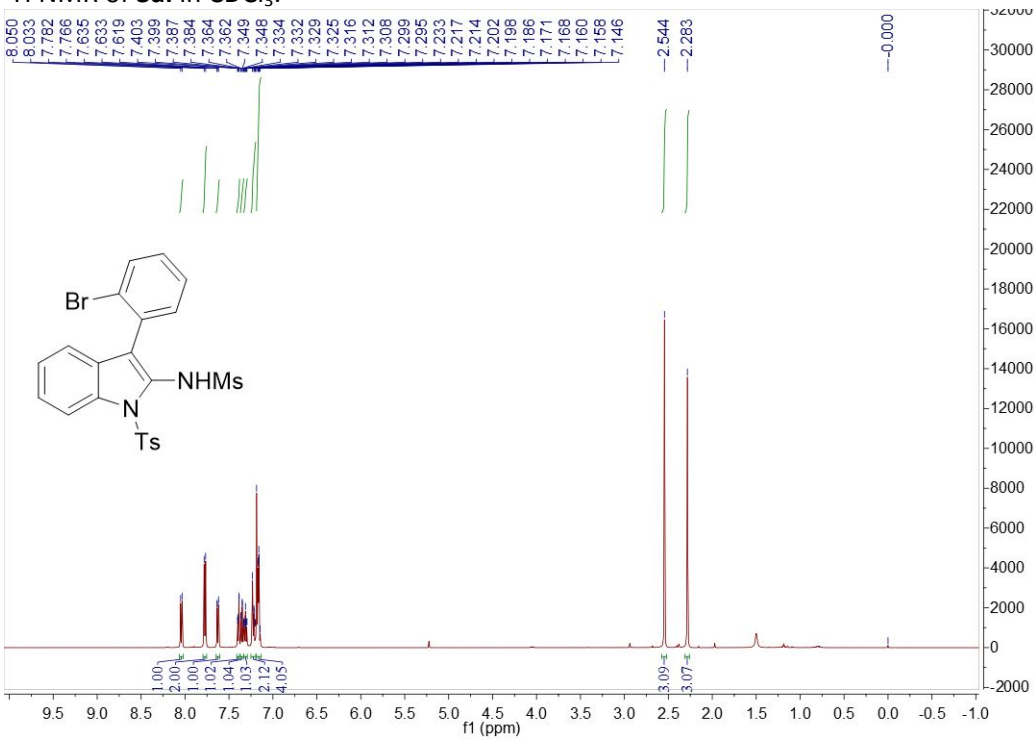
^{1}H NMR of **3ah** in $CDCl_3$:



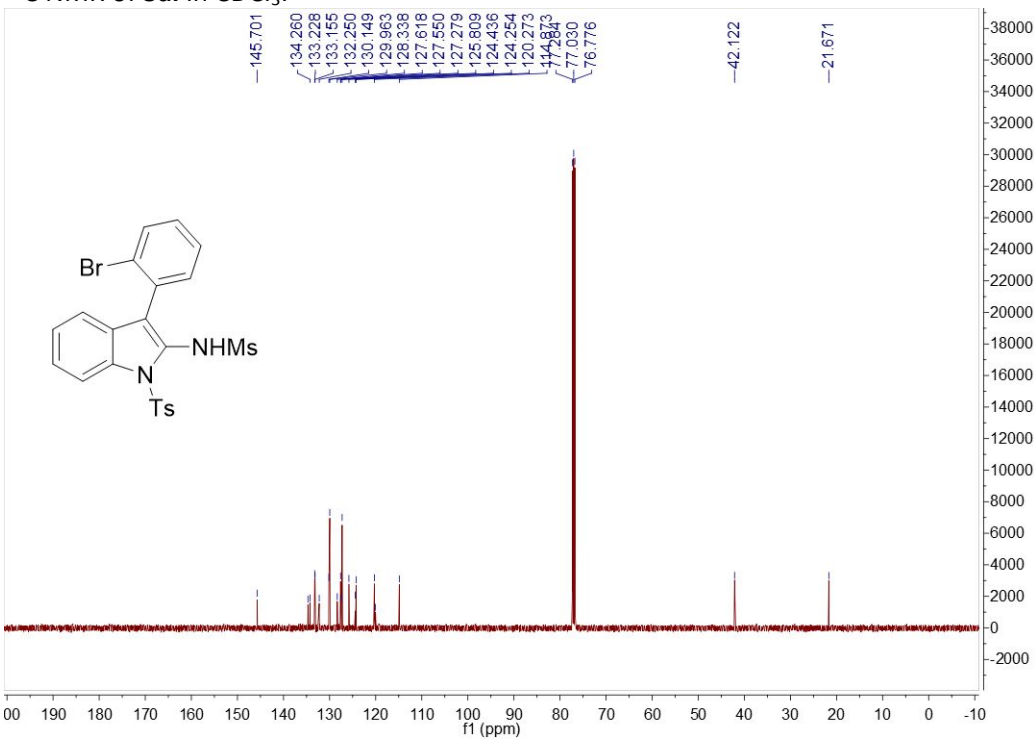
^{13}C NMR of **3ah** in $CDCl_3$:



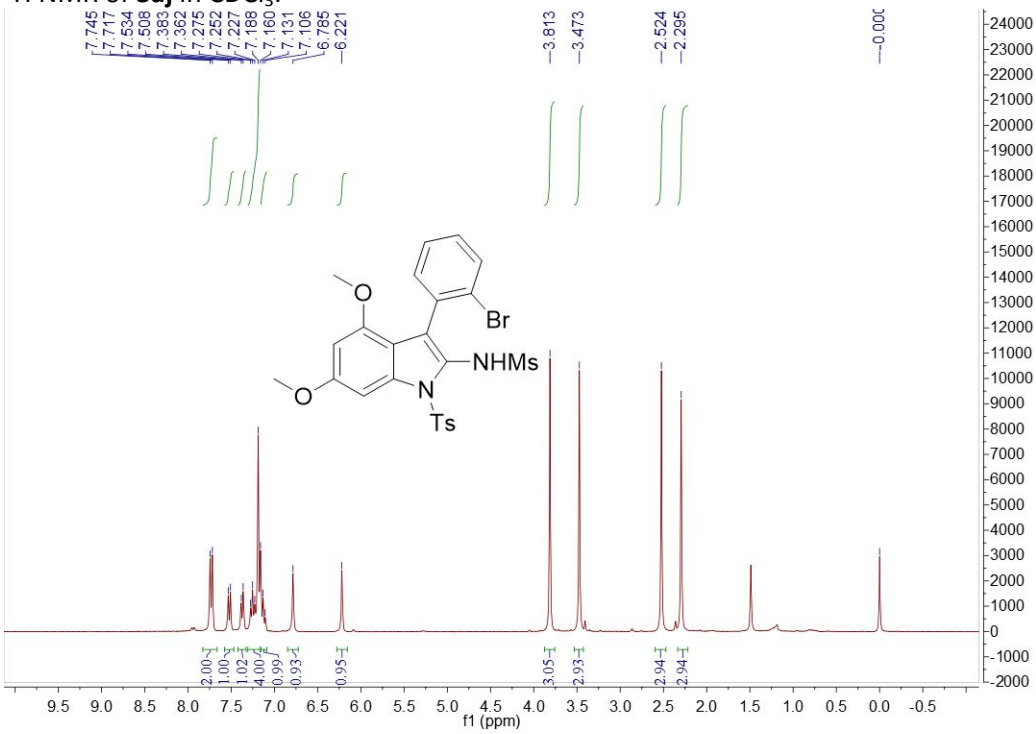
^{1}H NMR of **3ai** in $CDCl_3$:



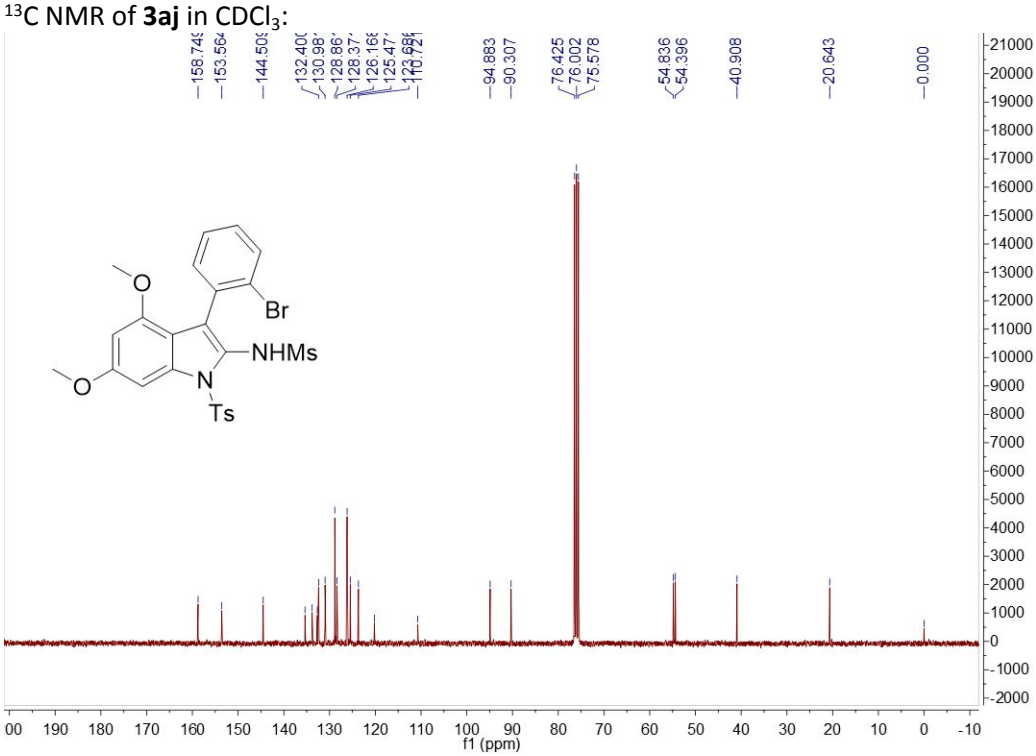
^{13}C NMR of **3ai** in $CDCl_3$:



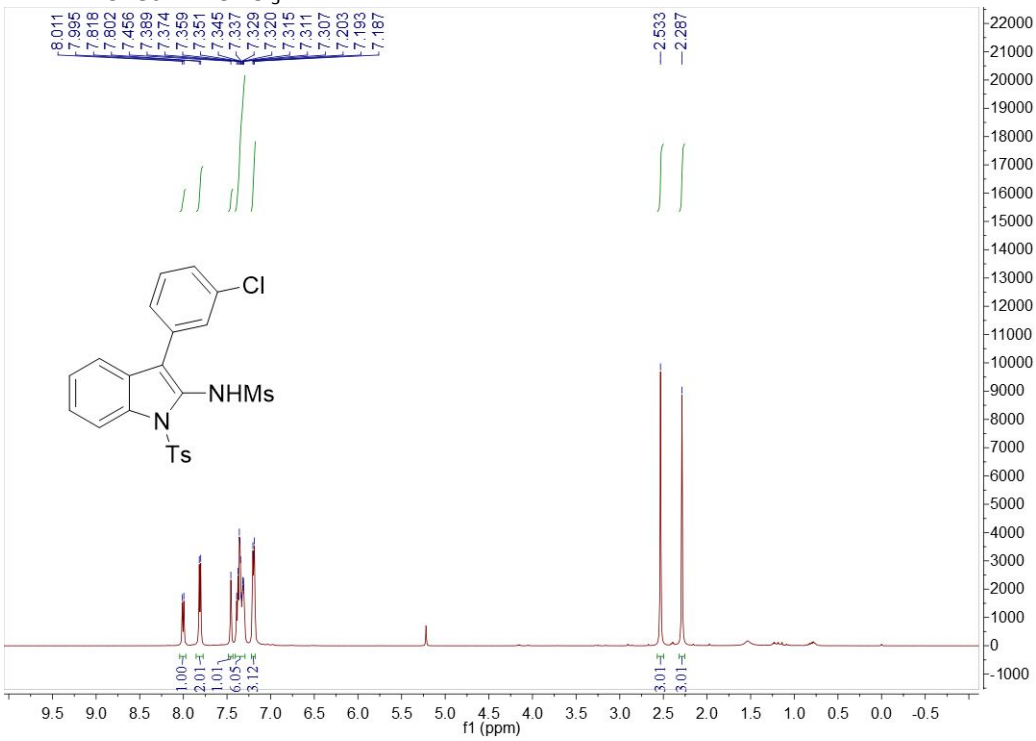
^{1}H NMR of **3aj** in $CDCl_3$:



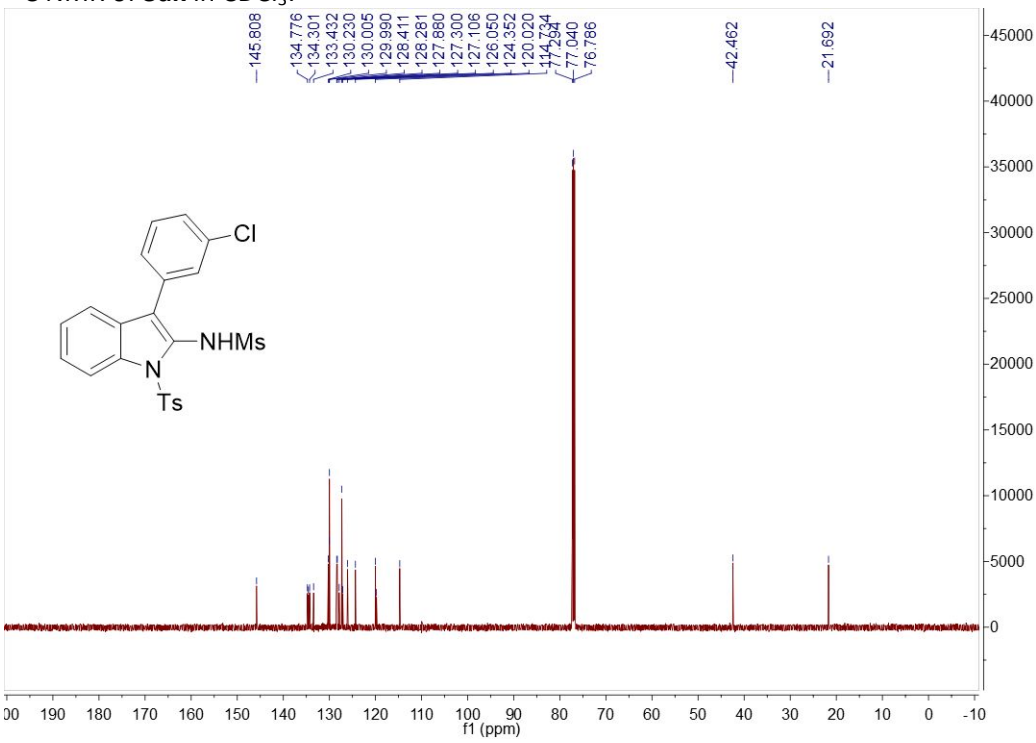
^{13}C NMR of **3aj** in $CDCl_3$:



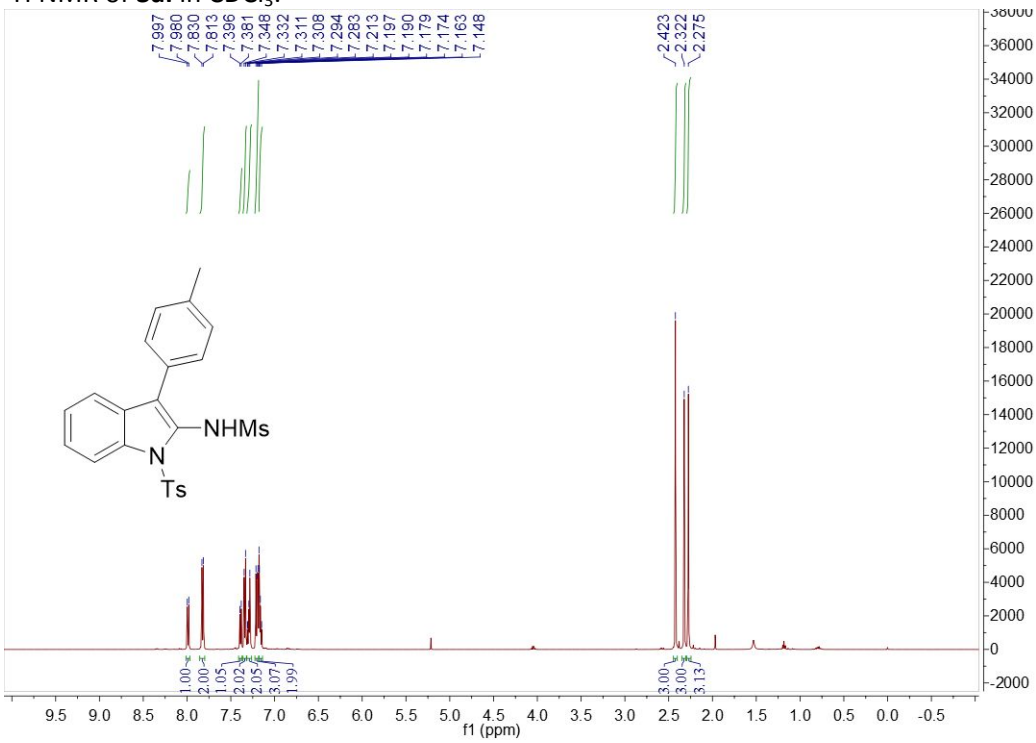
^{1}H NMR of **3ak** in $CDCl_3$:



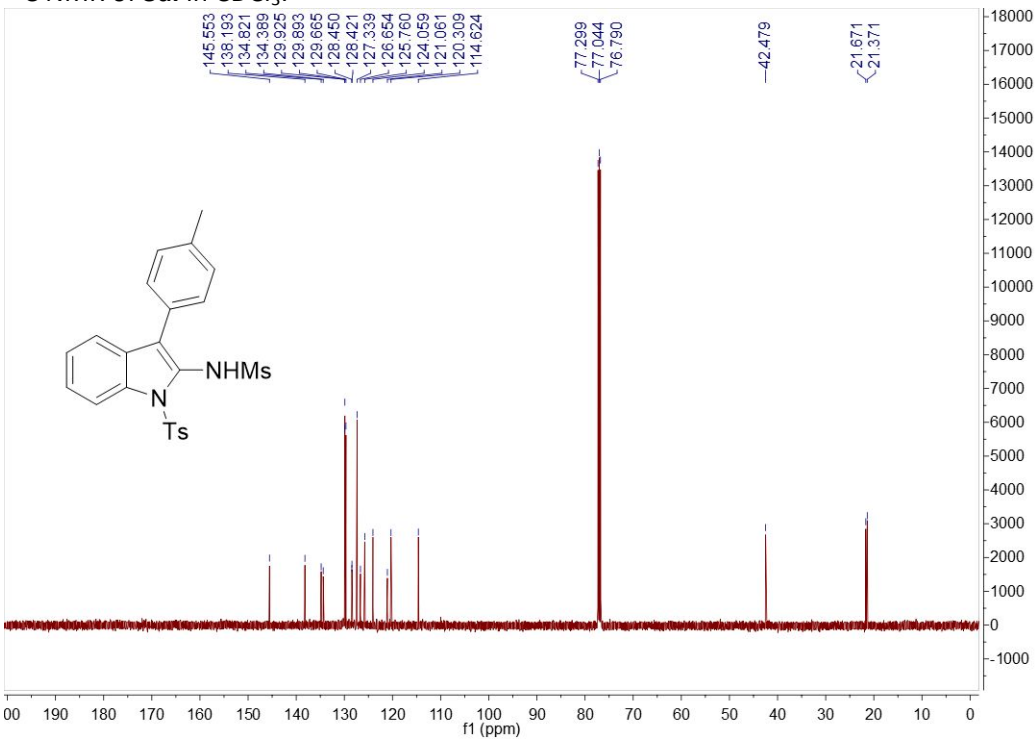
^{13}C NMR of **3ak** in $CDCl_3$:



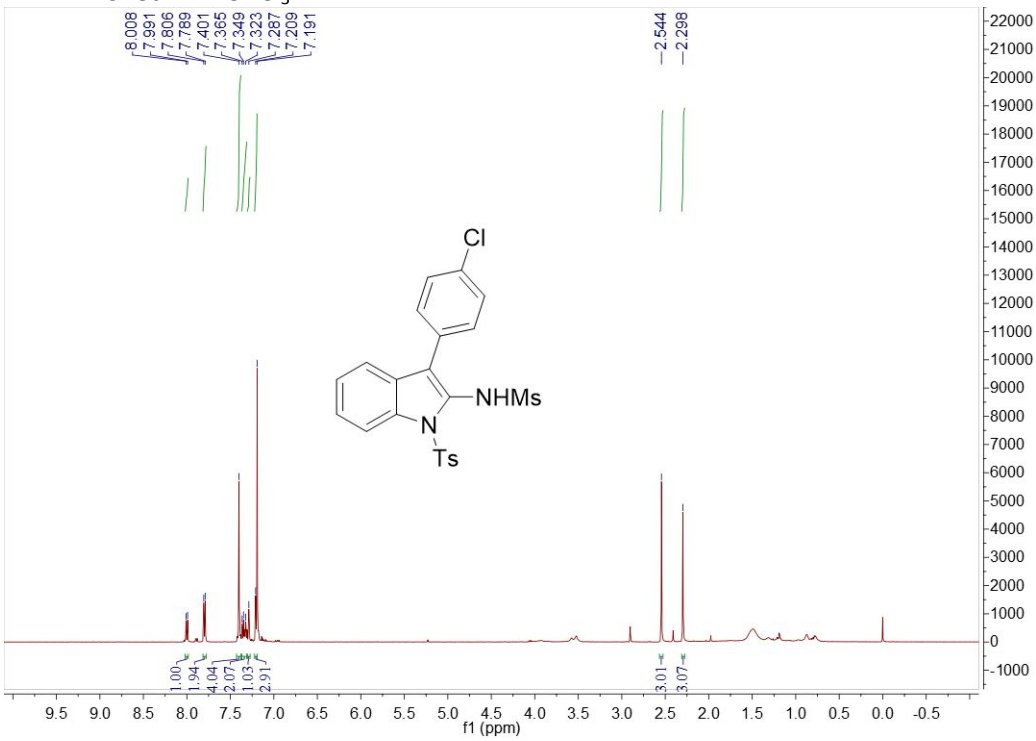
^{1}H NMR of **3al** in $CDCl_3$:



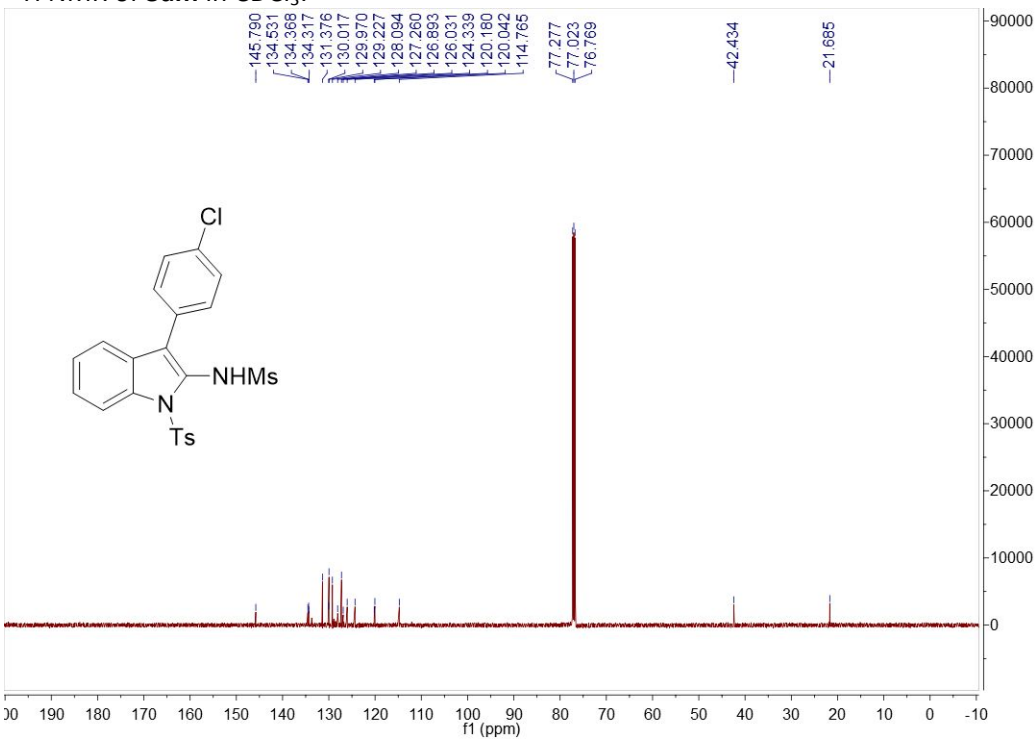
^{13}C NMR of **3al** in $CDCl_3$:



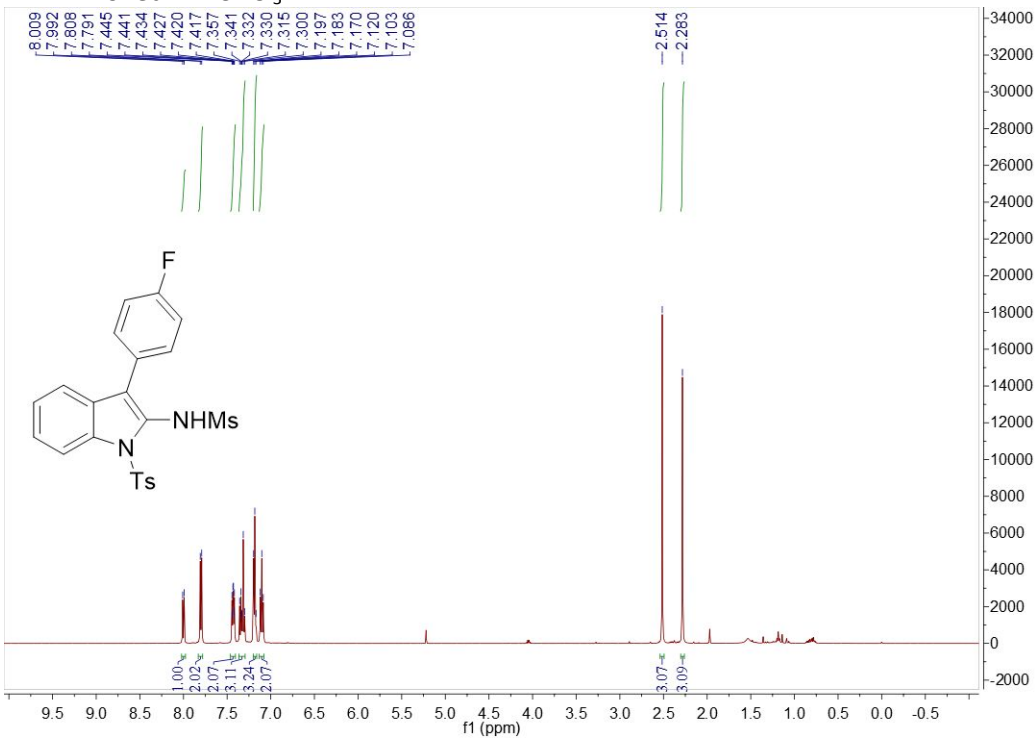
^{1}H NMR of **3am** in $CDCl_3$:



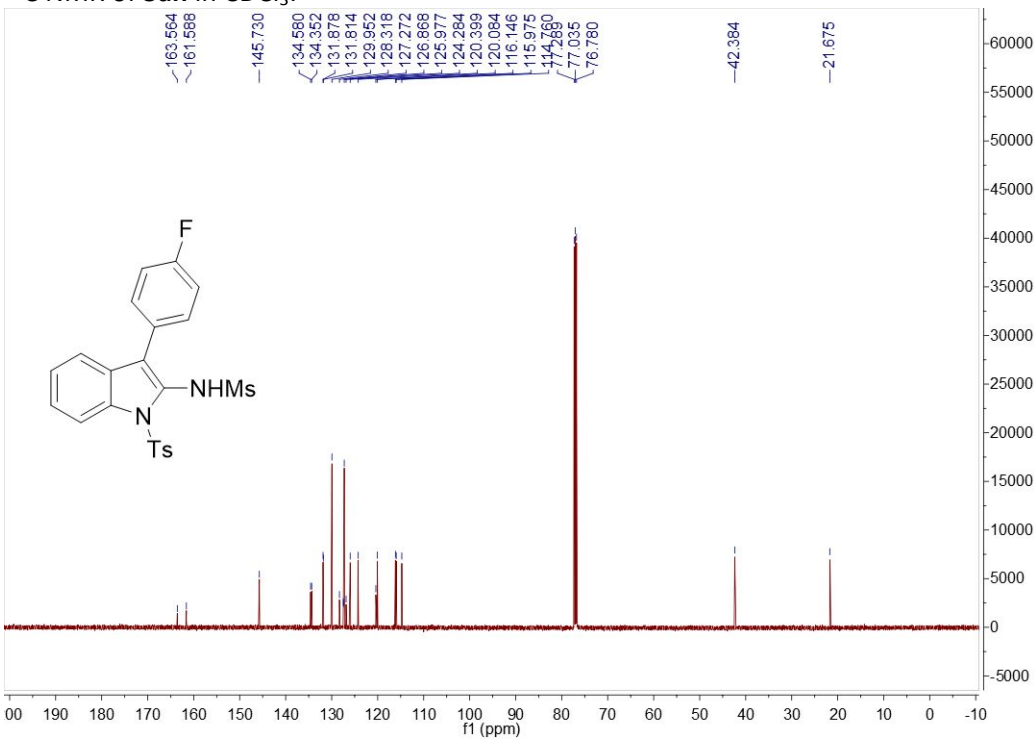
^{13}H NMR of **3am** in $CDCl_3$:



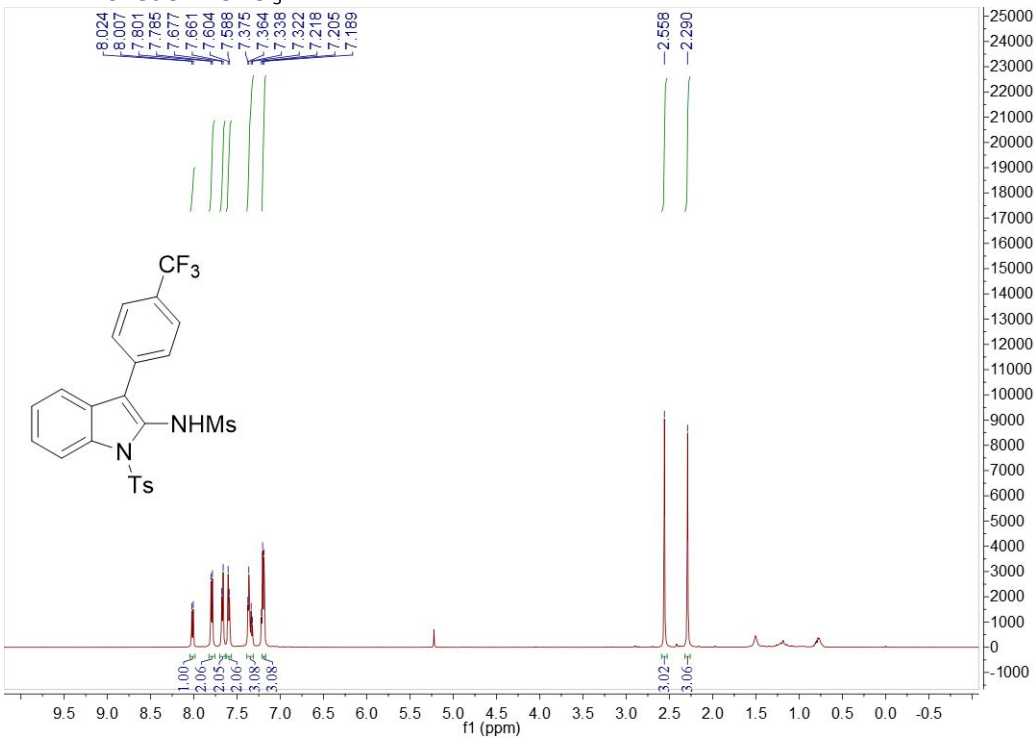
^{1}H NMR of **3an** in $CDCl_3$:



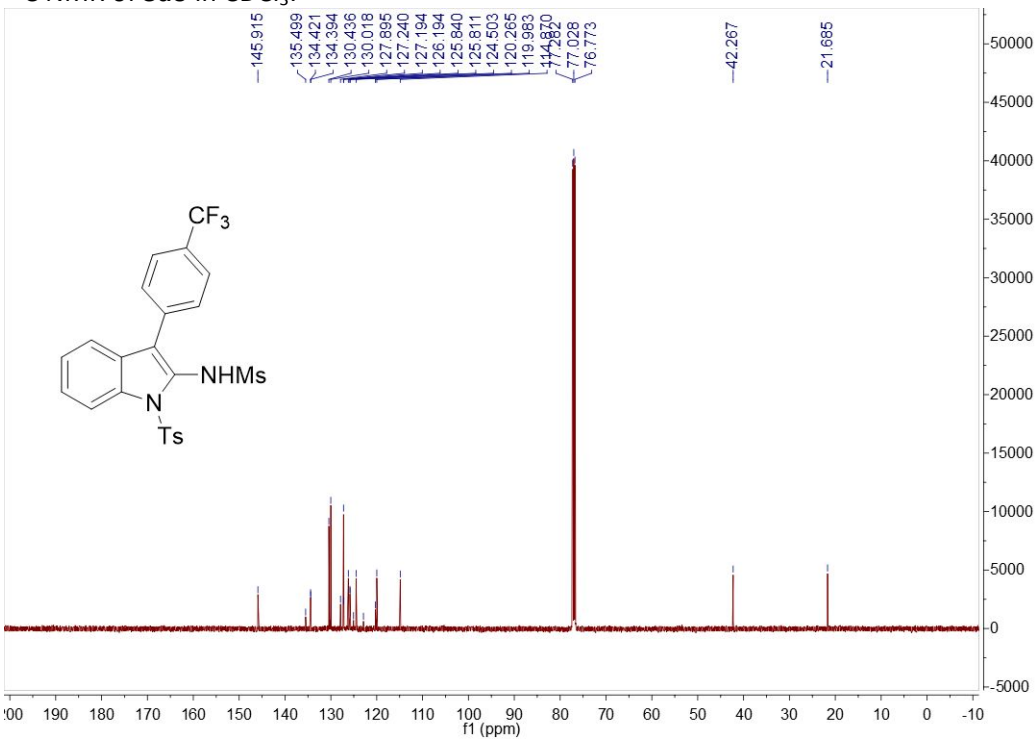
^{13}C NMR of **3an** in $CDCl_3$:



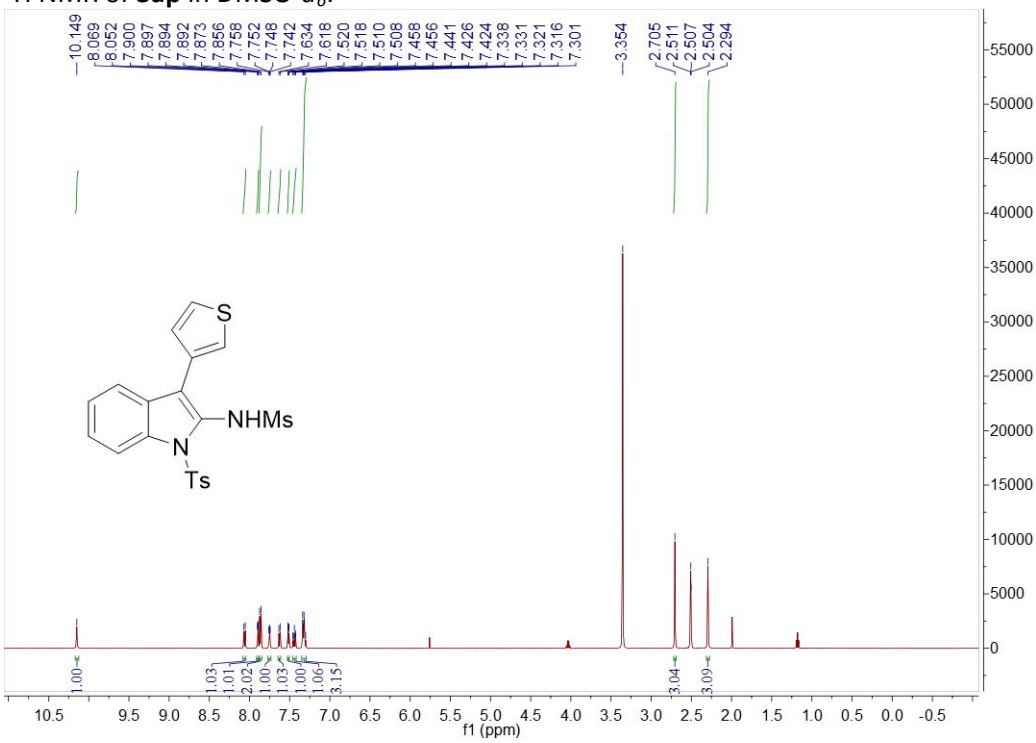
^{1}H NMR of **3ao** in $CDCl_3$:



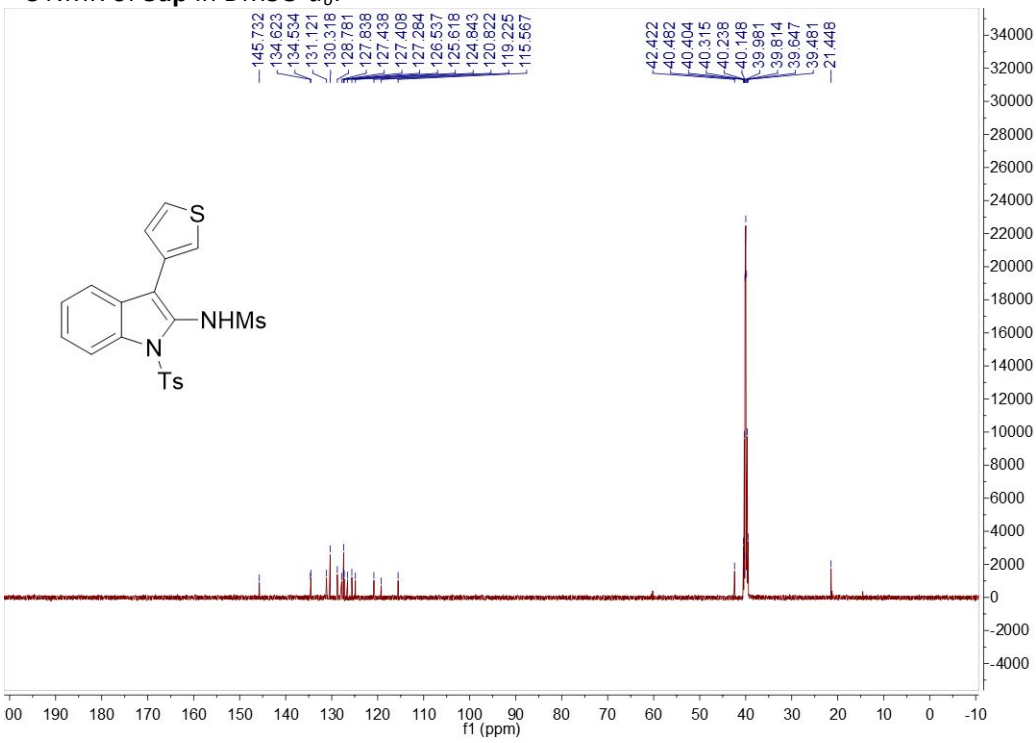
^{13}C NMR of **3ao** in $CDCl_3$:



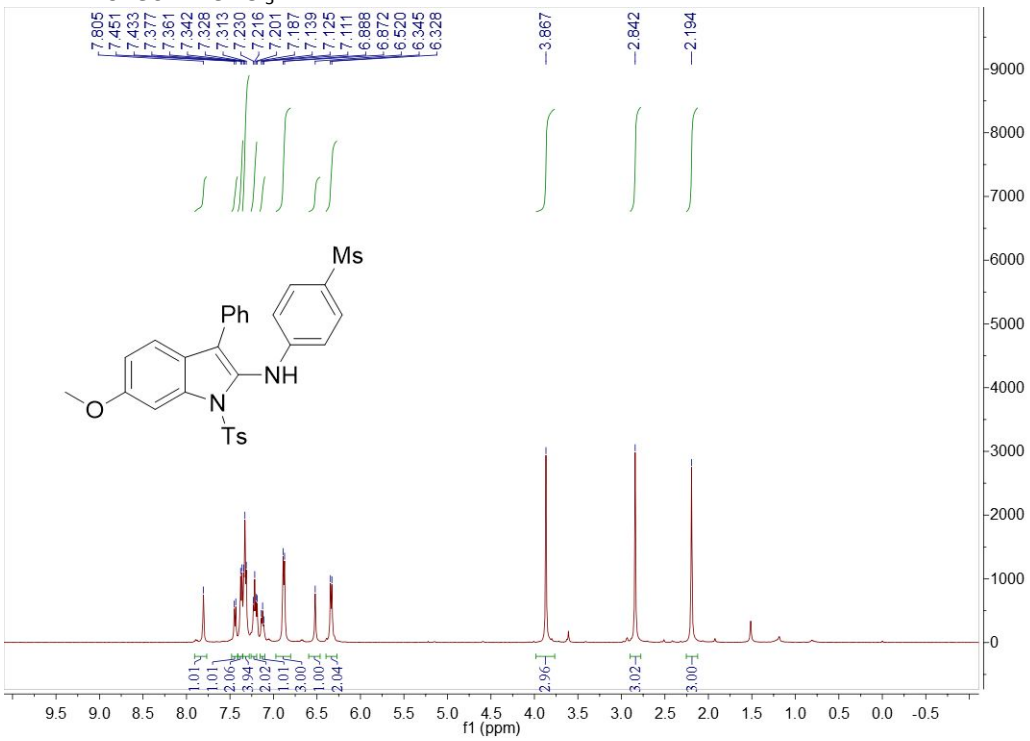
^{1}H NMR of **3ap** in DMSO-d_6:



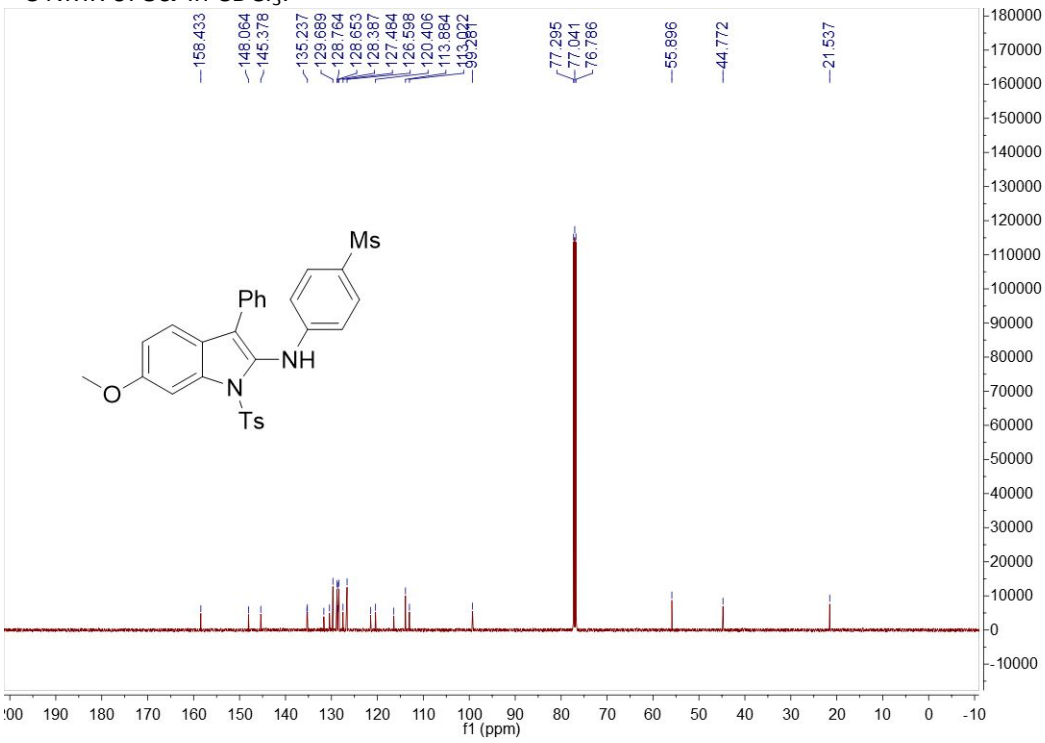
^{13}C NMR of **3ap** in DMSO-d_6:



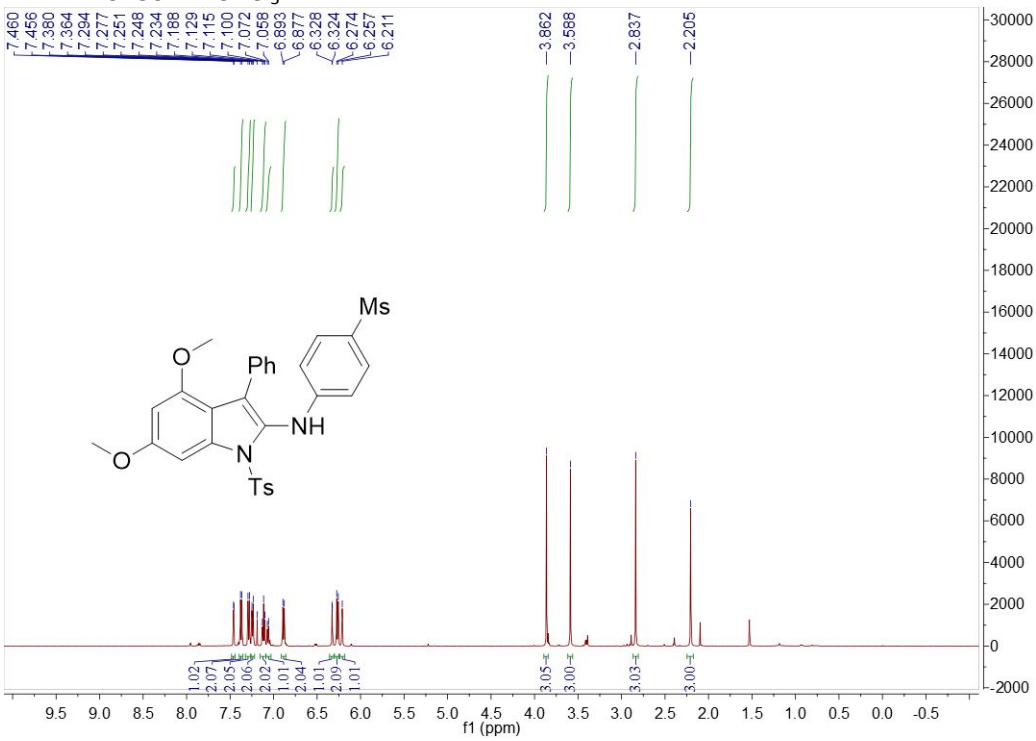
^{1}H NMR of **3cr** in $CDCl_3$:



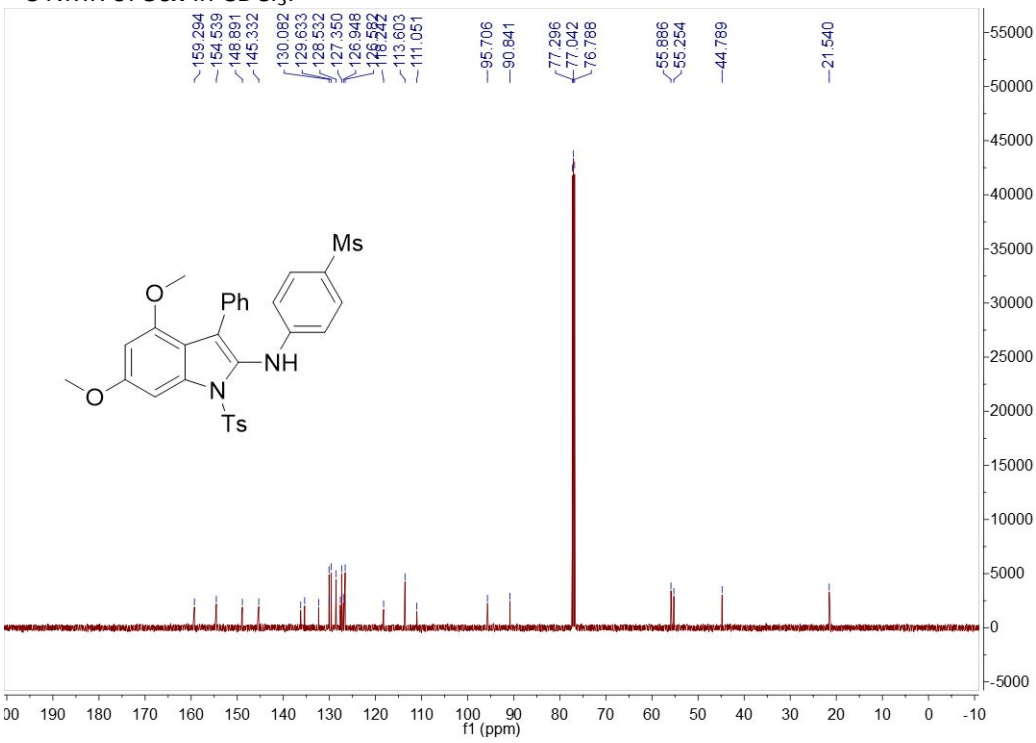
^{13}C NMR of **3cr** in $CDCl_3$:



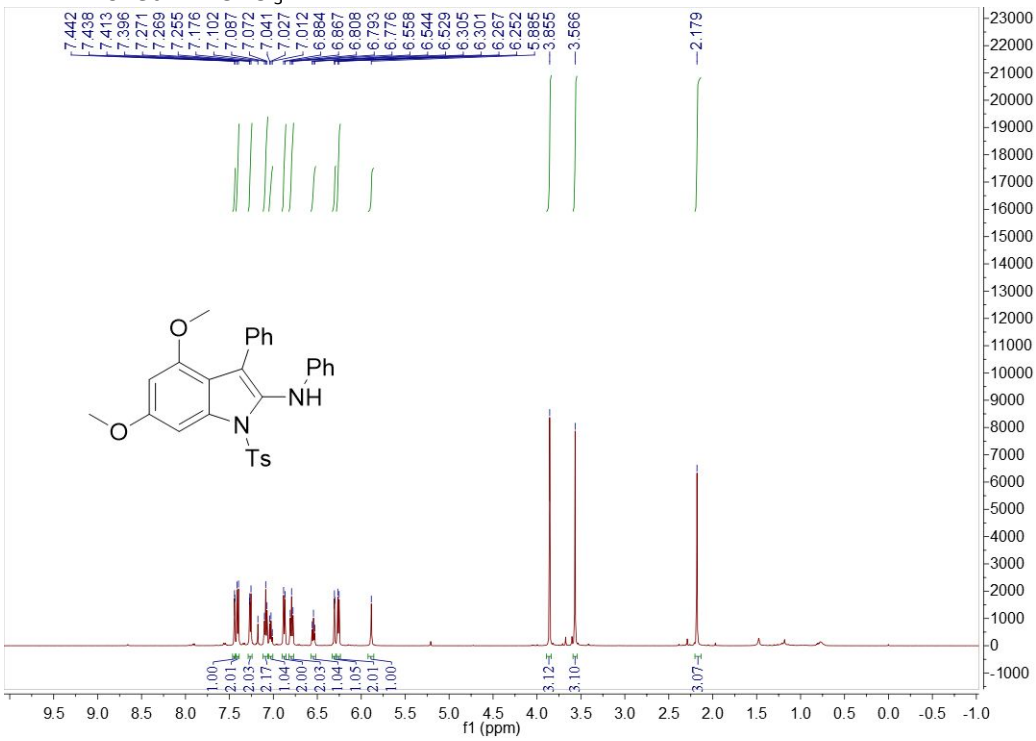
^{1}H NMR of **3ch** in $CDCl_3$:



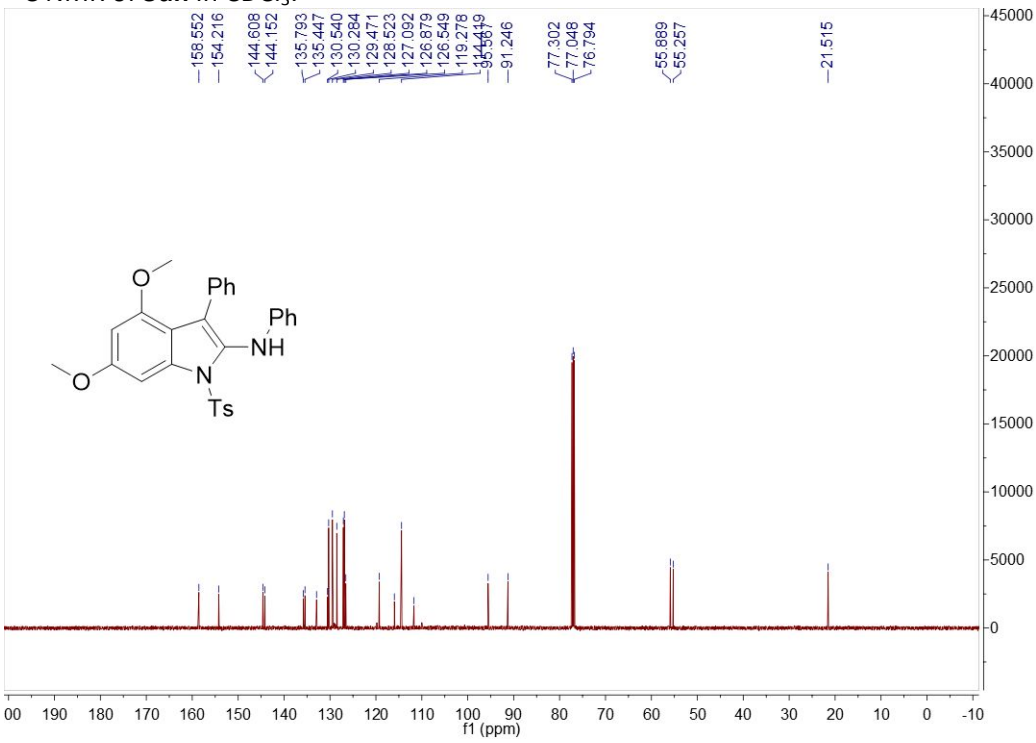
^{13}C NMR of **3ch** in $CDCl_3$:



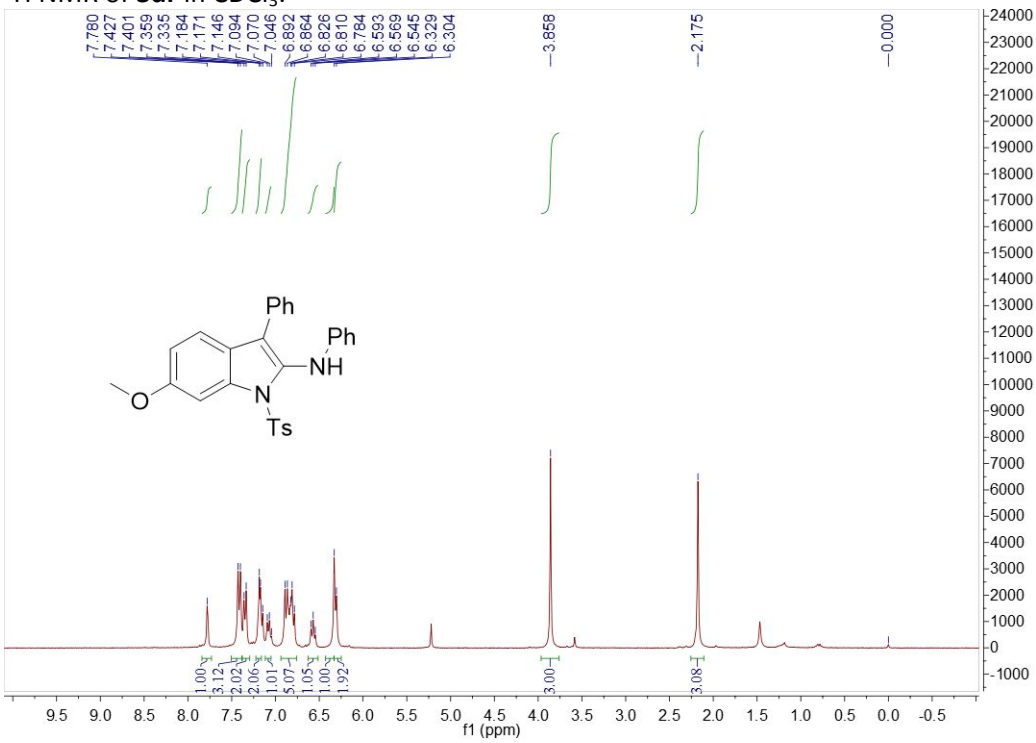
^{1}H NMR of **3dh** in $CDCl_3$:



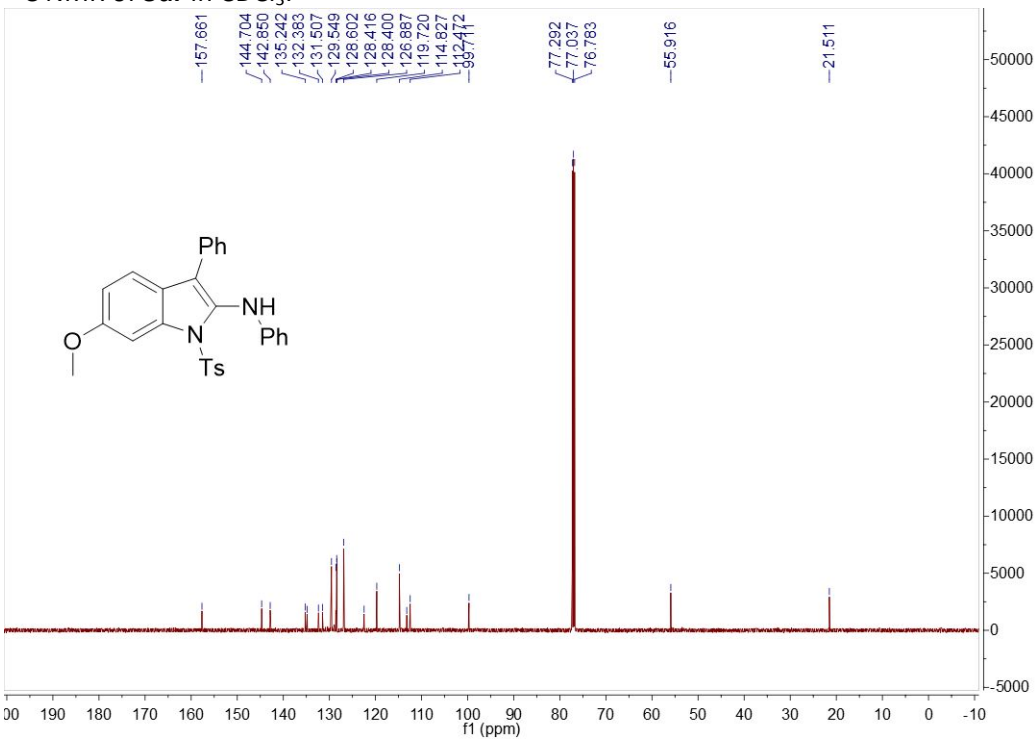
^{13}C NMR of **3dh** in $CDCl_3$:



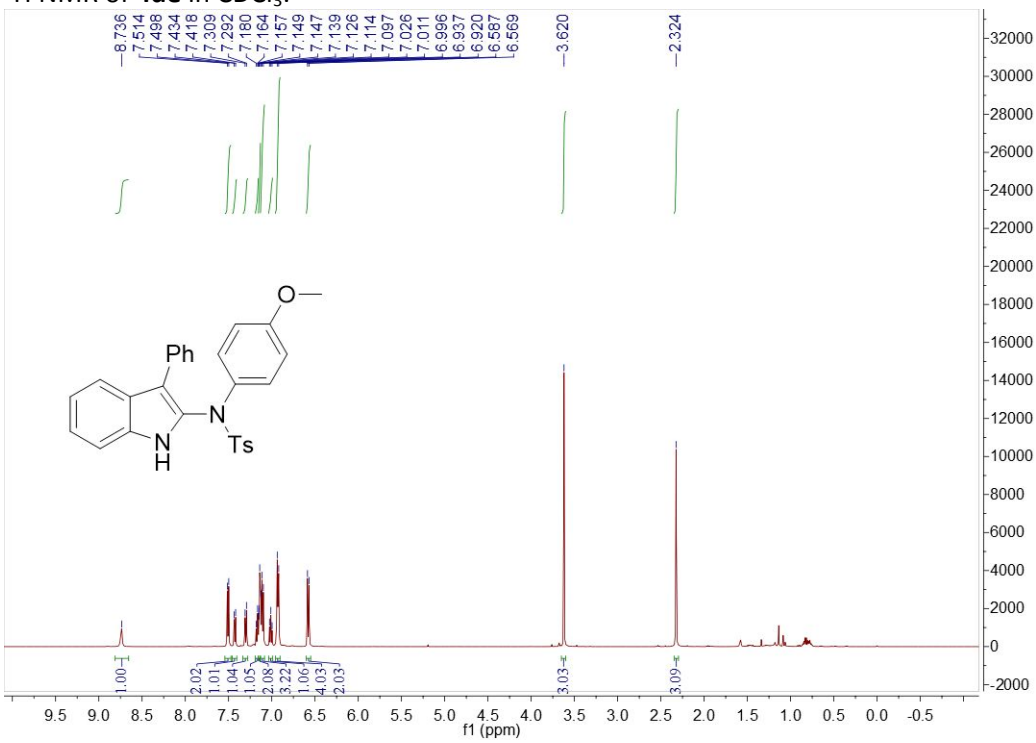
^{1}H NMR of **3dr** in $CDCl_3$:



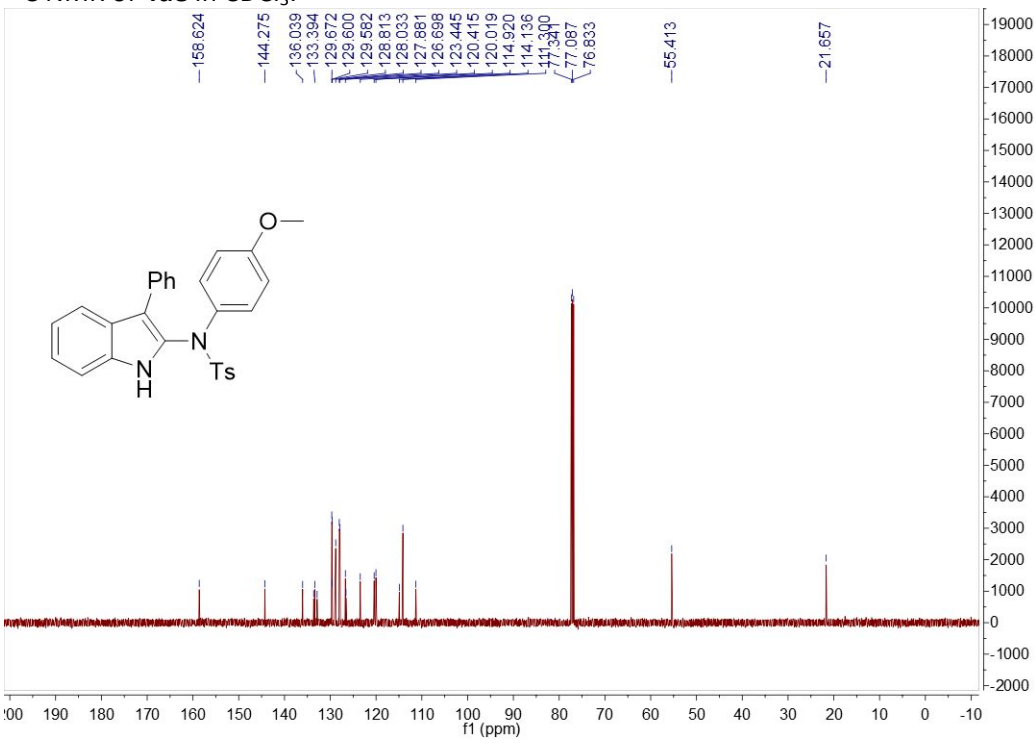
^{13}C NMR of **3dr** in $CDCl_3$:



^{1}H NMR of **4de** in $CDCl_3$:



^{13}C NMR of **4de** in $CDCl_3$:



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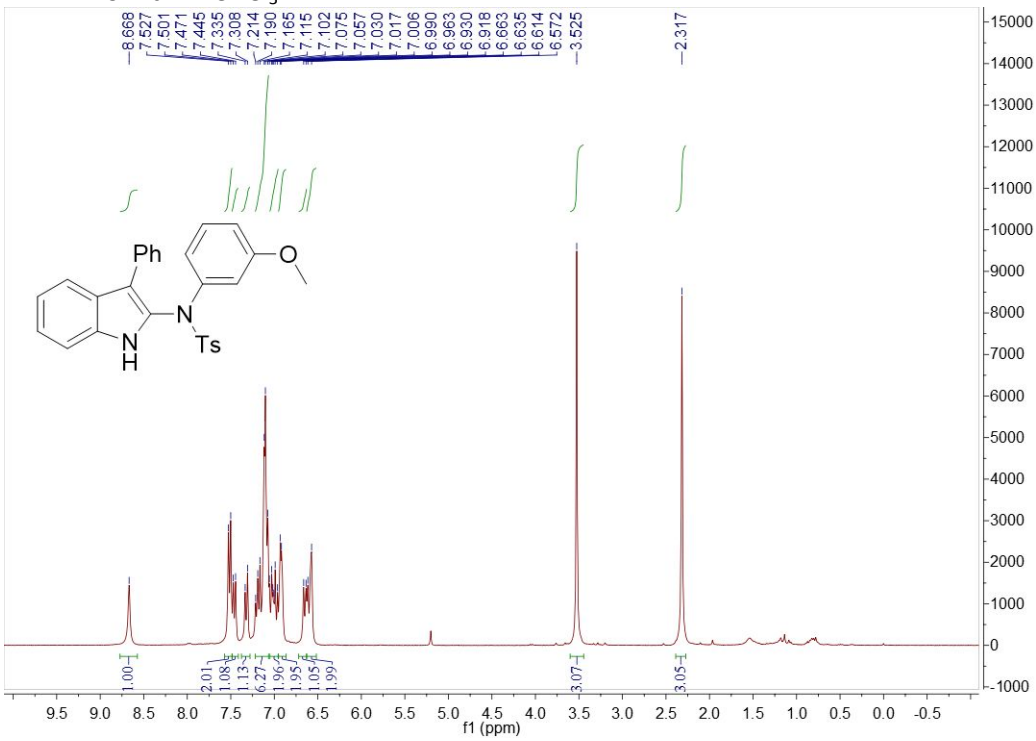
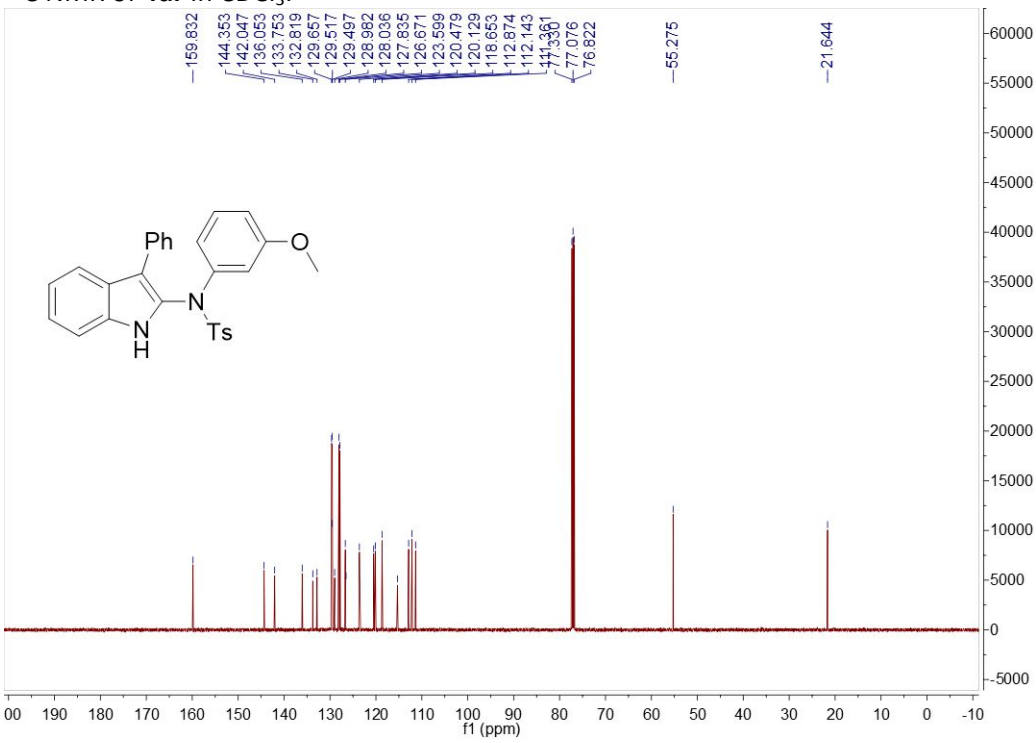
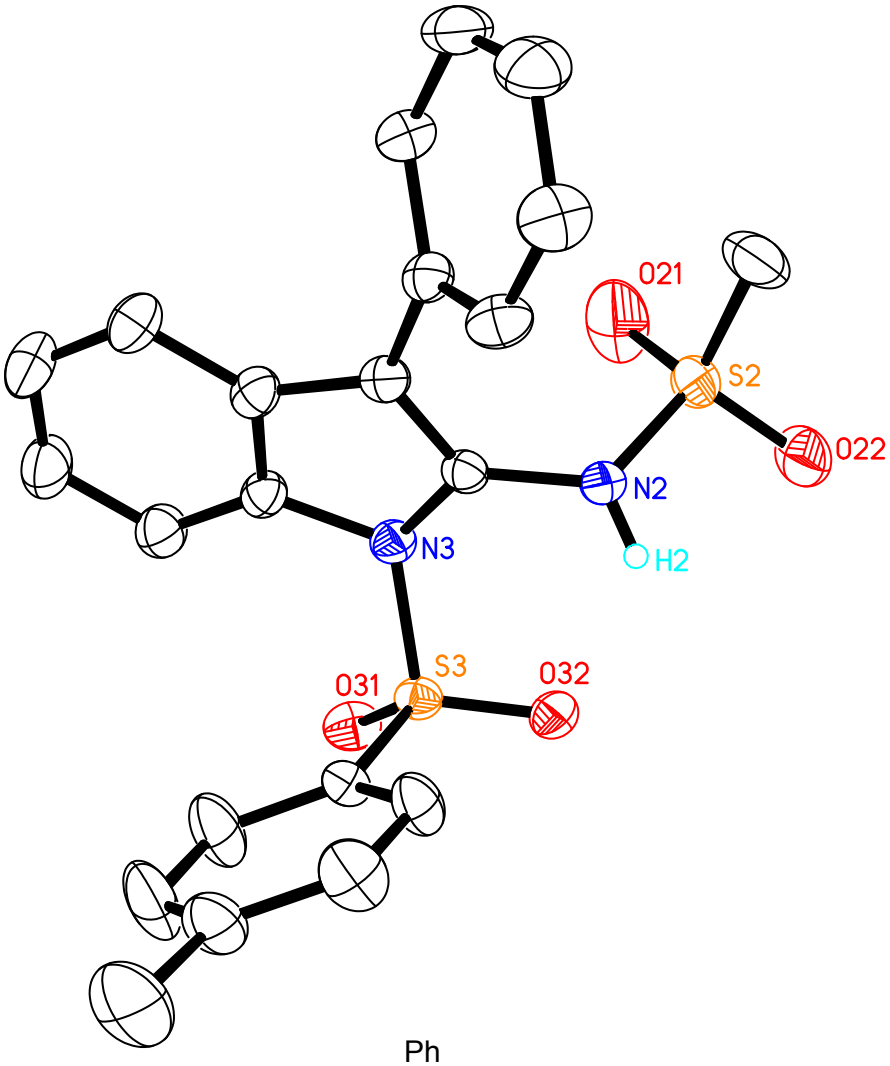
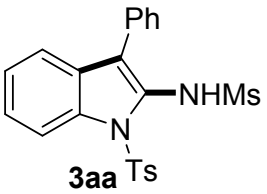


^{13}C NMR of **4dr** in $CDCl_3$:



5. Solid state molecular structure of 3aa





3aa

6. References

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