Supporting information

Synthesis of indole-3-carbinols (I3C) and their Application to Access unsymmetrical bis(3-indolyl)methanes (BIMs) bearing quaternary sp^3-carbon

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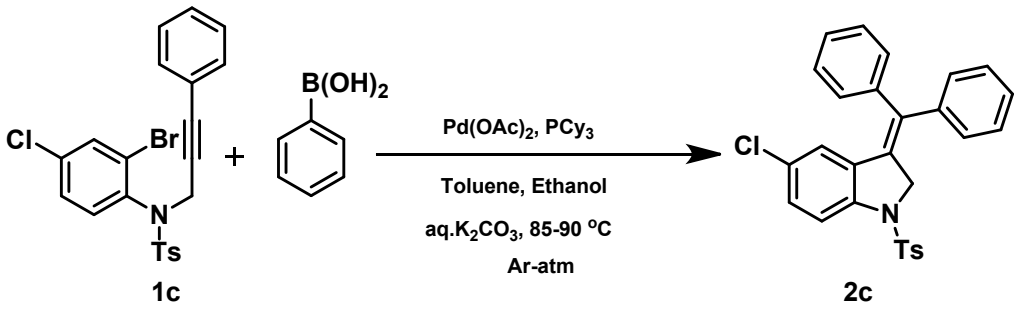
A. EXPERIMENTAL SECTION

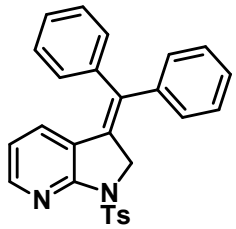
General: ^{1}H NMR spectra were recorded with a Bruker (300, 400, 500 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 7.26 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals includes: s = singlet, brs = broad singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet and dt = doublet of triplet. ^{13}C NMR spectra were recorded with a Bruker 300 (75 MHz), 400 (100 MHz), 500 (125 MHz) spectrometer as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 77.0 ppm) as an internal standard. The routine monitoring of reaction was performed with silica gel coated glass slides (Merck, silica gel G for TLC), which were analyzed with iodine. Solvents, reagents and chemicals were purchased from Aldrich, Merck, SRL, Spectrochem and Avra Chemicals. Nitromethane was dried from CaH_2 and toluene was dried by metallic sodium prior to use. All reactions involving moisture-sensitive reactants were executed with oven-dried glassware.

Representative experimental procedure for the synthesis of 5-chloro-3-(diphenylmethylene)-1-tosylindoline (2c):



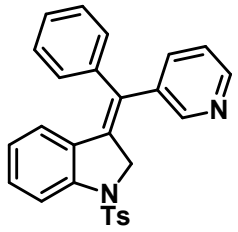
To a solution of *N*-(2-bromo-4-chlorophenyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide **1c** (237 mg, 0.5 mmol) in toluene (2 mL) and ethanol (2 mL), phenyl boronic acid (92 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), PCy_3 (14 mg, 0.05 mmol) and $Pd(OAc)_2$ (6 mg, 0.025 mmol) were added successively. The resulting solution was stirred at 85-90 °C under argon atmosphere for 3 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product **2c** as a yellow solid (167 mg, 0.36 mmol, 71%), m.p. 186 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.42 (s, 3H), 4.66 (s, 2H), 6.13 (s, 1H), 6.98-7.00 (m, 2H), 7.08 (d, *J*=8.1 Hz, 3H), 7.25-7.35 (m, 8H), 7.57-7.61 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) : δ 21.6, 59.2, 116.6, 124.7, 127.4, 127.9, 128.0, 128.6, 128.9, 129.0, 129.1, 129.8, 132.1, 133.5, 137.1, 140.2, 141.3, 143.4, 144.5 ppm. HRMS: cacld for $C_{28}H_{22}ClNNaO_2S$ $[M+Na]^+$ 494.0957; found 494.0959.

3-(diphenylmethylene)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine (2h) :



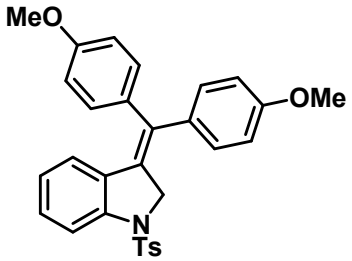
To a solution of *N*-(3-bromopyridin-2-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (220 mg, 0.5 mmol) in toluene (2 mL) and ethanol (2 mL), phenyl boronic acid (92 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), PCy_3 (14 mg, 0.05 mmol) and $Pd(OAc)_2$ (6 mg, 0.025 mmol) were added successively and treated as described for the synthesis of **2c** for 3.5 h to afford **2h** as a white solid (149 mg, 0.34 mmol, 68%), m.p. 159 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.40 (s, 3H), 4.81 (s, 2H), 6.41 (d, *J*=7.8 Hz, 1H), 6.52 (dd, *J*=2.7, 4.8 Hz, 1H), 7.16-7.19 (m, 3H), 7.25-7.38 (m, 9H), 8.02 (dd, *J*=4.8, 8.1 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) : δ 21.6, 54.0, 117.7, 122.9, 126.9, 127.9, 128.0, 128.2, 128.3, 128.7, 128.8, 129.3, 129.4, 132.1, 135.3, 138.1, 140.6, 140.8, 144.2, 147.8, 157.5 ppm. HRMS: cacld for $C_{27}H_{23}N_2O_2S$ $[M+H]^+$ 439.1480; found 439.1486.

(*Z*)-3-(phenyl(pyridin-3-yl)methylene)-1-tosylindoline (2i) :



To a solution of *N*-(2-bromophenyl)-4-methyl-*N*-(3-(pyridin-3-yl)prop-2-yn-1-yl)benzenesulfonamide (220 mg, 0.5 mmol) in toluene (2 mL) and ethanol (2 mL), phenyl boronic acid (92 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), PCy_3 (14 mg, 0.05 mmol) and $Pd(OAc)_2$ (6 mg, 0.025 mmol) were added successively and treated as described for the synthesis of **2c** for 3.5 h to afford **2i** as a white solid (145 mg, 0.33 mmol, 66%), m.p. 166 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.39 (s, 3H), 4.62 (s, 2H), 6.30 (d, *J*=7.8 Hz, 1H), 6.68 (t, *J*=7.8 Hz, 1H), 7.05 (t, *J*=3.6 Hz, 2H), 7.16 (t, *J*=8.1 Hz, 1H), 7.23-7.41 (m, 7H), 7.62 (d, *J*=8.1 Hz, 2H), 7.70 (d, *J*=8.1 Hz, 1H), 8.42 (s, 1H), 8.51 (d, *J*=3.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) : δ 21.5, 55.6, 115.5, 123.4, 123.6, 124.9, 127.4, 128.1, 129.2, 129.5, 129.8, 131.5, 132.1, 133.5, 135.7, 137.7, 139.9, 144.4, 145.2, 148.4, 148.9 ppm. HRMS: cacld for $C_{27}H_{23}N_2O_2S$ $[M+H]^+$ 439.1480; found 439.1479.

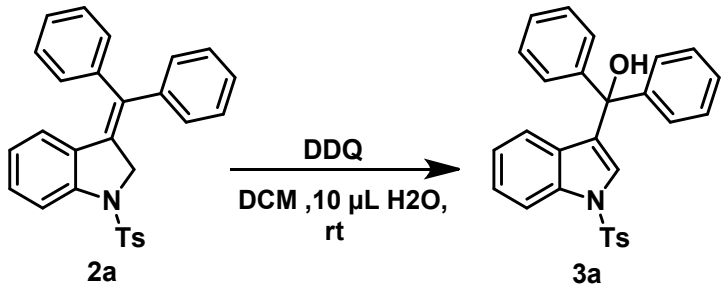
3-(bis(4-methoxyphenyl)methylene)-1-tosylindoline (2j) :



To a solution of *N*-(2-bromophenyl)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (235 mg, 0.5 mmol) in toluene (2 mL) and ethanol (2 mL), (4-methoxyphenyl)boronic acid (114 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), PCy_3 (14 mg, 0.05 mmol) and $Pd(OAc)_2$ (6 mg, 0.025 mmol) were added successively and treated as described for the synthesis of **2c** for 2 h to afford **2j** as a white solid (194 mg, 0.39 mmol, 78%), m.p. 187 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.39 (s, 3H), 3.81 (s, 3H), 3.83 (s, 3H), 4.66 (s, 2H), 6.36 (d, *J*=7.6 Hz, 1H), 6.70 (t, *J*=7.6 Hz, 1H), 6.81-6.90 (m, 6H), 6.99 (d, *J*=8.4 Hz, 2H), 7.11 (t, *J*=8.0 Hz, 1H), 7.23 (t, *J*=8.0 Hz, 2H), 7.60 (d, *J*=8.0 Hz, 2H), 7.66 (d, *J*=8.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 21.6, 55.3, 55.4, 56.4, 114.0, 114.3, 116.0, 123.6, 124.7, 127.6, 128.8, 129.1, 129.7, 130.7, 131.1, 133.5, 134.0, 134.7, 135.2, 144.2, 144.8, 159.0, 159.2 ppm. HRMS: cacld for $C_{30}H_{28}NO_4S$ $[M+H]^+$ 498.1739; found 498.1737.

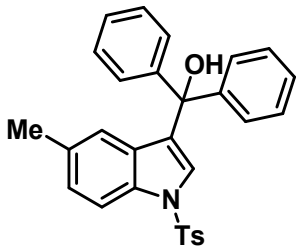
Compounds **2a**, **2b**, **2d**, **2e**, **2f**, **2g** were reported earlier and synthesised by the above similar procedure.

diphenyl(1-tosyl-1H-indol-3-yl)methanol (3a):



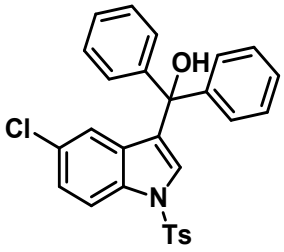
To a solution of **2a** (96 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) was added DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone) (50 mg, 0.22 mmol). The reaction mixture was stirred at room temperature for 3 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with dichloromethane. The organic extract was washed with sodium bicarbonate solution, dried over anhydrous Na_2SO_4 and concentrated. The product was purified by column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product **3a** as a white solid (99 mg, 0.22 mmol, 99%), m.p. 151 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.92 (s, 1H), 7.04 (d, *J* = 1.0 Hz, 1H), 7.06 – 7.12 (m, 1H), 7.24 – 7.29 (m, 4H), 7.32 – 7.35 (m, 10H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.97 – 8.02 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) : *δ* 21.7, 75.2, 116.5, 121.3, 121.5, 124.3, 126.1, 126.4, 127.2, 128.4, 128.6, 129.0, 129.1, 129.3, 129.8, 129.9, 132.8, 133.5, 137.4, 141.9, 142.5, 144.8, 148.0, 150.6 ppm. HRMS: cacld for $C_{28}H_{24}NO_3S$ $[M+H]^+$ 454.1477; found 454.1478.

(5-methyl-1-tosyl-1H-indol-3-yl)diphenylmethanol (3b) :



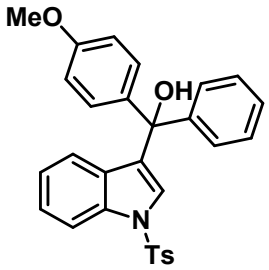
Compound **2b** (100 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) was treated DDQ (50 mg, 0.22 mmol) as described for the synthesis of **3a** for 3 h to afford **3b** as a white solid (101 mg, 0.21 mmol, 98%), m.p. 148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 2.24 (s, 3H), 2.36 (s, 3H), 6.92 (s, 1H), 7.04 (s, 1H), 7.09 (d, *J*=9 Hz, 1H), 7.21-7.30 (m, 12H), 7.67 (d, *J*=8.4 Hz, 2H), 7.85 (d, *J*=8.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) : *δ* 21.3, 21.5, 78.5, 113.5, 122.2, 126.3, 127.1, 127.6, 128.1, 129.0, 129.3, 129.8, 133.0, 134.3, 135.0, 144.9, 145.2, 162.3 ppm. HRMS: cacld for $C_{29}H_{26}NO_3S$ $[M+Na]^+$ 468.1633; found 468.1634.

(5-chloro-1-tosyl-1H-indol-3-yl)diphenylmethanol (3c) :



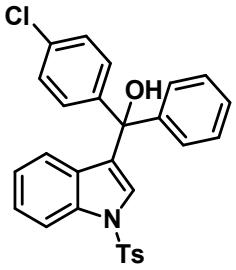
To a solution of compound **2c** (104 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) DDQ (50 mg, 0.22 mmol) was added as described for the synthesis of **3a** for 3 h to afford **3c** as a white solid (103 mg, 0.21 mmol, 96%), m.p. 167 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.38 (s, 3H), 7.00 (s, 1H), 7.20-7.34 (m, 14H), 7.66 (d, *J*=8.4 Hz, 2H), 7.88 (d, *J*=8.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 21.7, 78.6, 114.9, 122.3, 125.3, 126.9, 127.2, 127.4, 127.9, 128.4, 128.9, 129.4, 130.1, 130.6, 134.5, 135.0, 145.0, 145.4 ppm. HRMS: cacld for $C_{28}H_{22}ClNNaO_3S$ $[M+Na]^+$ 510.0907; found 510.0905.

(4-methoxyphenyl)(phenyl)(1-tosyl-1H-indol-3-yl)methanol (3d) :



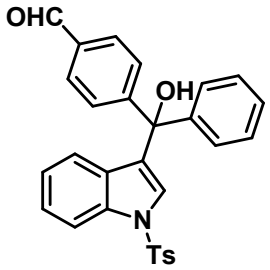
To a solution of compound **2d** (103 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) DDQ (50 mg, 0.22 mmol) was added as described for the synthesis of **3a** for 3 h to afford **3d** as a white solid (106 mg, 99%), m.p. 171 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 3H), 3.80 (s, 3H), 6.81-6.84 (m, 2H), 7.02-7.09 (m, 2H), 7.19 (s, 1H), 7.22-7.46 (m, 10H), 7.70 (d, *J*=8.4 Hz, 2H), 7.96 (d, *J*=8.4 Hz, 1H)ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 55.2, 78.1, 113.4, 113.7, 122.5, 123.2, 124.7, 126.0, 126.8, 127.0, 127.5, 128.1, 128.4, 128.7, 129.1, 129.5, 135.0, 136.0, 137.4, 145.0, 145.3, 158.9 ppm. HRMS: cacld for $C_{29}H_{26}NO_4S$ $[M+H]^+$ 484.1583; found 484.1588.

(4-chlorophenyl)(phenyl)(1-tosyl-1H-indol-3-yl)methanol (3e) :



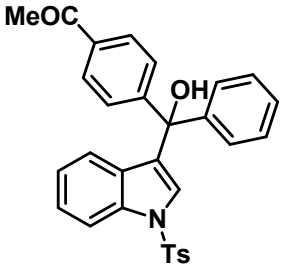
To a solution of compound **2e** (104 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) DDQ (50 mg, 0.22 mmol) was added as described for the synthesis of **3a** for 3 h to afford **3e** as a white solid (94 mg, 0.20 mmol, 88%), m.p. 165 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.37 (s, 3H), 7.00 (s, 1H), 7.08 (d, *J*=7.2 Hz, 1H), 7.18-7.42 (m, 12H), 7.67 (dd, *J*=8.4 Hz, 10.8 Hz, 3H), 7.96 (d, *J*=8.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 78.0, 113.8, 122.3, 123.3, 124.9, 126.0, 126.8, 126.9, 127.3, 127.8, 128.3, 128.6, 129.6, 129.9, 132.6, 133.4, 135.0, 135.9, 143.6, 144.7, 145.1 ppm. HRMS: cacld for $C_{28}H_{22}ClNO_3S$ $[M+H]^+$ 487.1009; found 487.1006.

4-(hydroxy(phenyl)(1-tosyl-1H-indol-3-yl)methyl)benzaldehyde (3f) :



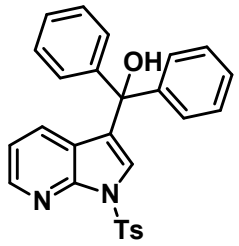
To as solution of compound **2f** (102 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) DDQ (50 mg, 0.22 mmol) was added as described for the synthesis of **3a** for 3.5 h to afford **3f** as a white solid (81 mg, 0.17 mmol, 76%), m.p. 159 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.37 (s, 3H), 7.02-7.11 (m, 2H), 7.18 (d, *J*=7.5 Hz, 1H), 7.23-7.32 (m, 8H), 7.53 (d, *J*=8.1 Hz, 2H), 7.70 (d, *J*=8.1 Hz, 2H), 7.80 (d, *J*=8.1 Hz, 2H), 7.97 (d, *J*=8.1 Hz, 1H), 9.96 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 78.2, 113.8, 122.2, 123.4, 125.0, 126.1, 126.8, 126.9, 127.7, 128.0, 128.2, 128.4, 128.7, 129.5, 129.9, 134.9, 135.4, 135.9, 144.3, 145.2, 151.6, 191.9 ppm. HRMS: cacld for $C_{29}H_{24}NO_4S$ $[M+H]^+$ 482.1426; found 482.1429.

1-(4-(hydroxy(phenyl)(1-tosyl-1H-indol-3-yl)methyl)phenyl)ethanone (3g) :



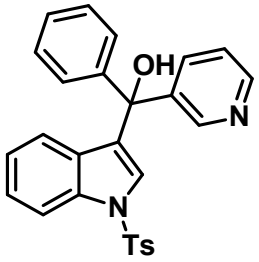
To a solution of compound **2g** (105 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) DDQ (50 mg, 0.22 mmol) was added as described for the synthesis of **3a** for 3.5 h to afford **3g** as a white solid (89 mg, 0.18 mmol, 80%), m.p. 171 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.37 (s, 3H), 2.58 (s, 3H), 7.01 (s, 1H), 7.06 (t, *J*=7.8 Hz, 2H), 7.17 (d, *J*=8.1 Hz, 1H), 7.23-7.31 (m, 6H), 7.45 (d, *J*=8.4 Hz, 3H), 7.70 (d, *J*=8.1 Hz, 2H), 7.88 (d, *J*=8.4 Hz, 2H), 7.96 (d, *J*=8.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.7, 26.7, 78.4, 114.0, 122.4, 123.5, 125.1, 126.3, 127.0, 127.1, 127.5, 128.1, 128.3, 128.5, 128.6, 128.9, 130.1, 135.3, 136.2, 136.5, 144.7, 145.3, 150.2, 197.7 ppm. HRMS: cacld for $C_{30}H_{26}NO_4S$ $[M+H]^+$ 496.1583; found 496.1589.

diphenyl(1-tosyl-1H-pyrrolo[2,3-b]pyridin-3-yl)methanol (3h) :



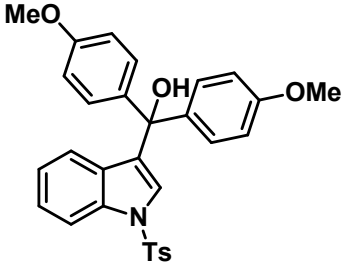
To a solution of compound **2h** (96 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) DDQ (50 mg, 0.22 mmol) was added as described for the synthesis of **3a** for 4 h to afford **3h** as a white solid (82 mg, 0.18 mmol, 82%), m.p. 173 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 2.39 (s, 3H), 7.00-7.04 (m, 1H), 7.22 (s, 1H), 7.26 (s, 1H), 7.30-7.33 (m, 11H), 7.54 (d, *J*=6.3 Hz, 1H), 8.04 (d, *J*=8.4 Hz, 2H), 8.38 (d, *J*=6.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 21.8, 78.7, 118.9, 121.8, 125.5, 125.6, 127.1, 127.9, 128.3, 128.4, 129.8, 131.0, 135.5, 144.9, 145.9, 145.2, 145.3 ppm. HRMS: cacld for $C_{27}H_{23}N_2O_3S$ $[M+H]^+$ 455.1429; found 455.1421.

phenyl(pyridin-3-yl)(1-tosyl-1H-indol-3-yl)methanol (3i) :



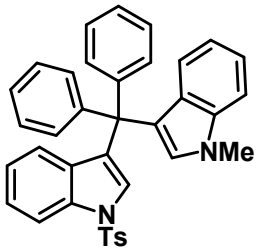
To a solution of compound **2i** (96 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) DDQ (50 mg, 0.22 mmol) was added as described for the synthesis of **3a** for 3.5 h to afford **3i** as a white solid (77 mg, 0.17 mmol, 72%), m.p. 163 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ* 2.28 (s, 3H), 6.93 (s, 1H), 6.98 (t, *J*=7.5 Hz, 2H), 7.09-7.27 (m, 9H), 7.57-7.59 (m, 1H), 7.62 (d, *J*=8.5 Hz, 2H), 7.89 (d, *J*=8.5 Hz, 1H), 8.38 (s, 1H), 8.49 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 21.7, 77.4, 113.9, 122.3, 123.1, 123.5, 125.1, 126.1, 126.9, 127.0, 128.1, 128.4, 128.5, 128.7, 130.1, 135.1, 136.1, 141.0, 144.4, 145.3, 148.4, 148.5 ppm. HRMS: cacld for $C_{27}H_{23}N_2O_3S$ $[M+H]^+$ 455.1429; found 455.1427.

bis(4-methoxyphenyl)(1-tosyl-1H-indol-3-yl)methanol (3j) :



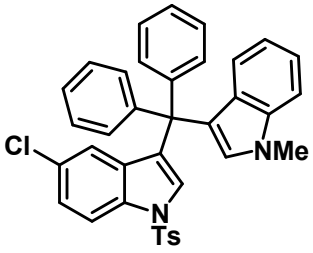
To a solution of compound **2j** (109 mg, 0.22 mmol) in mixture of DCM (2 mL) and water (2 equiv., 10 µL) DDQ (50 mg, 0.22 mmol) was added as described for the synthesis of **3a** for 3 h to afford **3j** as a white solid (104 mg, 0.20 mmol, 92%), m.p. 181 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 2.35 (s, 3H), 3.78 (s, 6H), 6.80 (d, *J*=8.8 Hz, 4H), 6.99 (s, 1H), 7.05 (t, *J*=8.0 Hz, 1H), 7.16-7.23 (m, 8H), 7.68 (d, *J*=8.4 Hz, 2H), 7.94 (d, *J*=8.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): *δ* 21.7, 55.3, 78.0, 113.5, 113.8, 122.6, 123.3, 124.8, 126.0, 126.9, 128.5, 129.3, 129.9, 130.0, 135.2, 136.1, 137.7, 145.1, 158.9 ppm. HRMS: cacld for $C_{30}H_{28}NO_5S$ $[M+H]^+$ 514.1688; found 514.1692.

3-(diphenyl(1-tosyl-1H-indol-3-yl)methyl)-1-methyl-1H-indole (4a) :



To a solution of **3a** (82 mg, 0.18 mmol) in dry nitromethane (2 mL) *N*-methylindole (24 mg, 0.18 mmol) and anhydrous $FeCl_3$ (3 mg, 0.018 mmol) were added successively. The reaction mixture was stirred at room temperature under an argon atmosphere for overnight. After the completion of the reaction (monitored by TLC), the solvent was evaporated and the product was purified by column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 97:3 (v/v) to afford the product **4a** as a white solid (72 mg, 0.13 mmol, 71%), m.p. 192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.60 (s, 3H), 6.13 (s, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 6.49 (s, 1H), 6.73 – 6.82 (m, 4H), 7.01 (dd, *J* = 7.9, 6.1 Hz, 3H), 7.06 – 7.13 (m, 2H), 7.17 (ddd, *J* = 10.7, 6.3, 3.1 Hz, 4H), 7.26 (d, *J* = 2.8 Hz, 6H), 7.30 – 7.34 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.44, 32.59, 64.16, 108.99, 114.11, 118.33, 119.47, 120.38, 121.57, 124.20, 124.62, 125.86, 127.12, 127.29, 127.52, 127.94, 128.20, 128.67, 128.76, 129.12, 131.94, 135.06, 135.37, 137.08, 137.31, 141.11, 141.65, 143.41, 143.75 ppm. HRMS: cacld for $C_{37}H_{31}N_2O_2S$ $[M+H]^+$ 567.2106; found 567.2109.

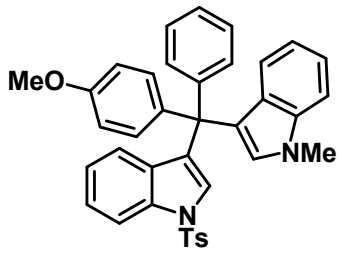
5-chloro-3-((1-methyl-1H-indol-3-yl)diphenylmethyl)-1-tosyl-1H-indole (4b) :



Compound **3c** (88 mg, 0.18 mmol) was treated with *N*-methylindole (24 mg, 0.18 mmol) and anhydrous $FeCl_3$ (3 mg, 0.018 mmol) under argon atmosphere at room temperature as

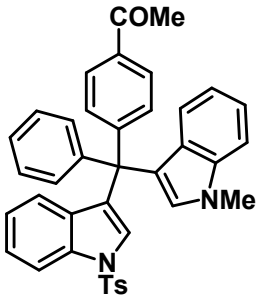
described for the synthesis of **4a** for overnight to afford **4b** as an white solid (72 mg, 0.12 mmol, 67%), m.p. 183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.62 (s, 3H), 6.15 (s, 1H), 6.23 (d, *J* = 2.2 Hz, 1H), 6.52 (s, 1H), 6.76 – 6.80 (m, 2H), 7.03 – 7.07 (m, 3H), 7.08 – 7.15 (m, 3H), 7.16 – 7.27 (m, 4H), 7.28 – 7.35 (m, 5H), 7.51 (dd, *J* = 10.0, 8.2 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.57, 32.72, 64.66, 109.22, 113.90, 119.35, 119.76, 120.40, 121.87, 124.76, 125.90, 127.40, 127.53, 128.07, 128.14, 128.23, 128.80, 128.93, 129.08, 129.38, 129.71, 133.77, 134.15, 135.32, 137.27, 139.06, 140.59, 141.32, 142.41, 143.79 ppm. HRMS: cacld for $C_{37}H_{30}ClN_2O_2S$ $[M+H]^+$ 601.1717; found 601.1714.

3-((4-methoxyphenyl)(1-methyl-1H-indol-3-yl)(phenyl)methyl)-1-tosyl-1H-indole (4c) :



Compound **3d** (87 mg, 0.18 mmol) was treated with *N*-methylindole (24 mg, 0.18 mmol) and anhydrous $FeCl_3$ (3 mg, 0.018 mmol) under argon atmosphere at room temperature as described for the synthesis of **4a** for overnight to afford **4c** as an off white solid (82 mg, 0.14 mmol, 76%), m.p. 198 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 2.39 (s, 3H), 3.68 (s, 3H), 3.77 (s, 3H), 6.59 (s, 1H), 6.60-6.75 (m, 5H), 6.86 (t, *J*=7.2 Hz, 1H), 7.10-7.26 (m, 13H), 7.66 (d, *J*=8.1 Hz, 2H), 7.97 (d, *J*=8.1 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 21.5, 32.6, 64.3, 78.6, 109.1, 114.3, 118.3, 119.6, 120.5, 121.7, 124.2, 124.7, 126.0, 127.2, 127.4, 127.6, 128.0, 128.3, 128.8, 128.9, 129.2, 131.9, 135.3, 135.7, 137.2, 137.4, 141.3, 141.8, 143.5, 144.0 ppm. HRMS: cacld for $C_{38}H_{33}N_2O_3S$ $[M+H]^+$ 597.2212; found 597.2214.

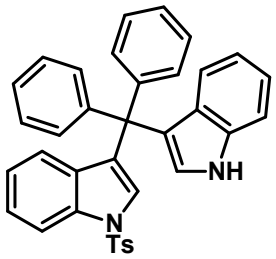
1-(4-((1-methyl-1H-indol-3-yl)(phenyl)(1-tosyl-1H-indol-3-yl)methyl)phenyl)ethanone (4d) :



Compound **3g** (89 mg, 0.18 mmol) was treated with *N*-methylindole (24 mg, 0.18 mmol) and anhydrous $FeCl_3$ (3 mg, 0.018 mmol) under argon atmosphere at room temperature as described for the synthesis of **4a** for overnight to afford **4d** as an white solid (81 mg, 0.13 mmol, 74%), as a mixture of non-separable isomers (*E*:*Z*=1:1), m.p. 147 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 2.35 (s, 6H), 2.57 (s, 3H), 2.62 (s, 3H), 3.62 (s, 6H), 6.14 (d, *J*=12 Hz, 2H), 6.40 (t, *J*=9.6 Hz, 2H), 6.49 (s, 1H), 6.54 (s, 1H), 6.74 (d, *J*=7.6 Hz, 2H), 6.81 (t, *J*=7.6 Hz, 3H), 6.88 (d,

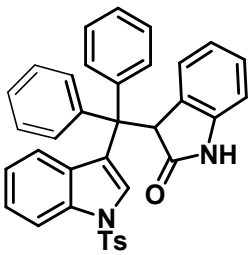
J=8.0 Hz, 3H), 7.03 (d, *J*=8.0 Hz, 7H), 7.12 (t, *J*=7.6 Hz, 3H), 7.18-7.23 (m, 9H), 7.28-7.34 (m, 5H), 7.39 (d, *J*=8.0 Hz, 1H), 7.48 (d, *J*=7.6 Hz, 1H), 7.61-7.64 (m, 2H), 7.70 (d, *J*=8.0 Hz, 2H), 7.87 (d, *J*=8.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 21.5, 26.7, 32.6, 32.7, 64.0, 64.3, 109.1, 109.2, 113.8, 113.9, 118.2, 119.6, 119.7, 120.3, 121.3, 121.7, 124.3, 124.6, 124.9, 125.9, 127.3, 127.5, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.8, 128.9, 129.1, 129.2, 129.6, 129.7, 131.1, 131.4, 135.5, 135.6, 135.7, 136.0, 136.2, 136.3, 136.6, 137.2, 140.5, 141.2, 143.5, 143.6, 144.2, 146.4, 146.6, 197.5 ppm. HRMS: cacld for $C_{39}H_{33}N_2O_3S$ $[M+H]^+$ 609.2212; found 609.2212.

3-((1H-indol-3-yl)diphenylmethyl)-1-tosyl-1H-indole (4e) :



Compound **3a** (96 mg, 0.22 mmol) was treated with indole (22 mg, 0.22 mmol) and anhydrous $FeCl_3$ (3 mg, 0.022 mmol) under argon atmosphere at room temperature as described for the synthesis of **4a** for overnight to afford **4f** as an yellow solid (76 mg, 0.13 mmol, 62%), m.p. 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 6.17 (s, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 6.74 – 6.82 (m, 3H), 7.00 (dd, *J* = 16.4, 7.9 Hz, 3H), 7.05 – 7.22 (m, 5H), 7.24 – 7.37 (m, 7H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.44, 64.15, 110.91, 115.75, 118.24, 119.97, 120.31, 122.06, 124.15, 124.21, 124.58, 125.36, 127.21, 127.25, 127.54, 128.02, 128.15, 128.79, 129.06, 129.16, 131.89, 134.86, 135.34, 136.27, 137.48, 141.13, 141.59, 143.44, 143.77 ppm. HRMS: cacld for $C_{36}H_{29}N_2O_3S$ $[M+H]^+$ 55261847; found 552.6851.

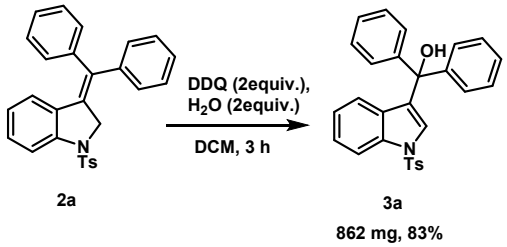
3-(diphenyl(1-tosyl-1H-indol-3-yl)methyl)indolin-2-one (4f) :



Compound **3a** (82 mg, 0.18 mmol) was treated with indoline-2-one (24 mg, 0.18 mmol) and anhydrous $FeCl_3$ (3 mg, 0.018 mmol) under argon atmosphere at room temperature as described for the synthesis of **4a** for overnight to afford **4e** as an yellow solid (88 mg, 0.15 mmol, 77%), m.p. 162 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 2.40 (s, 3H), 2.61 (d, *J*=22.8 Hz, 1H), 3.19 (d, *J*=21.9 Hz, 1H), 6.36 (d, *J*=7.5 Hz, 1H), 6.69-6.77 (m, 4H), 6.99 (t, *J*=7.5 Hz, 2H), 7.09-7.17 (m, 6H), 7.21-7.29 (m, 7H), 7.89 (t, *J*=9.0 Hz, 3H), ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 21.6, 34.7, 69.7, 110.8, 114.7, 122.3, 123.4, 124.1, 124.4, 124.6, 127.0, 127.4, 127.9, 128.5, 129.2,

129.8, 129.9, 133.6, 139.8, 140.7, 141.0, 141.3, 143.6, 144.5, 173.0 ppm. HRMS: cacld for $C_{36}H_{29}N_2O_3S$ $[M+H]^+$ 569.1899; found 569.1898.

Gram-scale synthesis of diphenyl(1-tosyl-1H-indol-3-yl)methanol (3a):

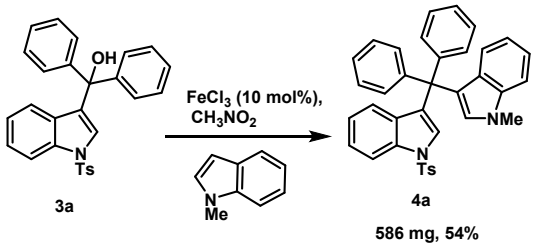


2a **3a**

862 mg, 83%

To a solution of **2a** (1.00 gm, 2.28mmol) in mixture of DCM (5 mL) and water (2 equiv.) DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone) (517 mg, 2.28 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with dichloromethane. The organic extract was washed with sodium bicarbonate solution, dried over anhydrous Na_2SO_4 and concentrated. The product was purified by column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product **3a** as a white solid (862 mg, 83%), m.p. 151 °C.

3-(diphenyl(1-tosyl-1H-indol-3-yl)methyl)-1-methyl-1H-indole (4a) :

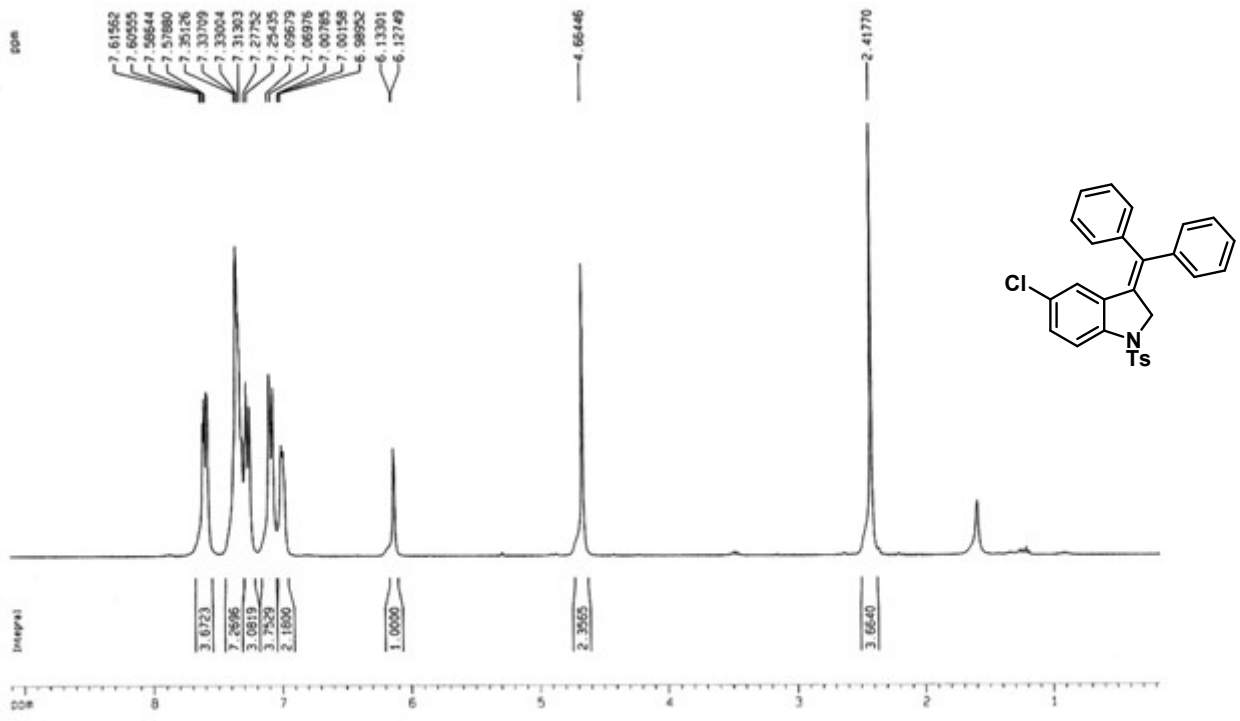


3a **4a**

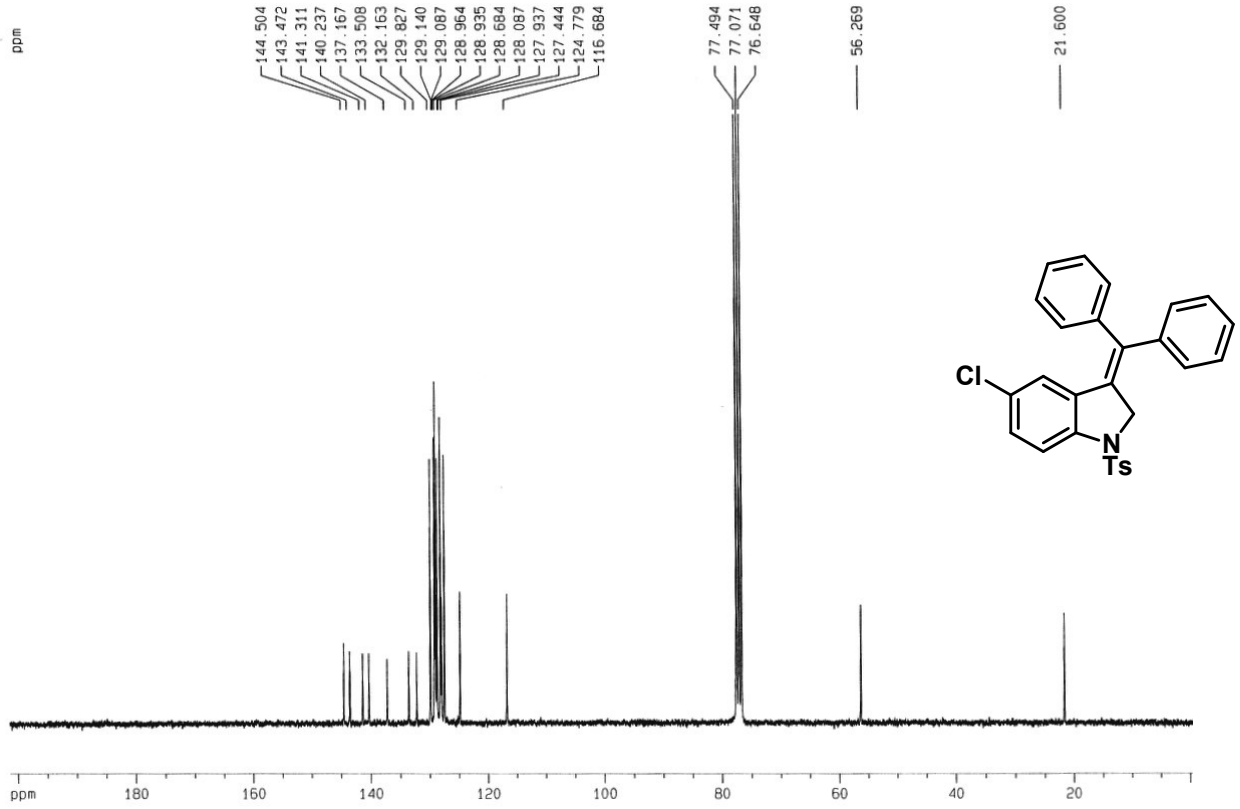
586 mg, 54%

To a solution of **3a** (862 mg, 1.9 mmol) in dry nitromethane (5 mL) *N*-methylindole (431 mg, 1.9 mmol) and anhydrous $FeCl_3$ (3 mg, 0.19 mmol) were added successively. The reaction mixture was stirred at room temperature under an argon atmosphere for overnight. After the completion of the reaction (monitored by TLC), the solvent was evaporated and the product was purified by column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 97:3 (v/v) to afford the product **4a** as a white solid (586 mg, 54%), m.p. 192 °C.

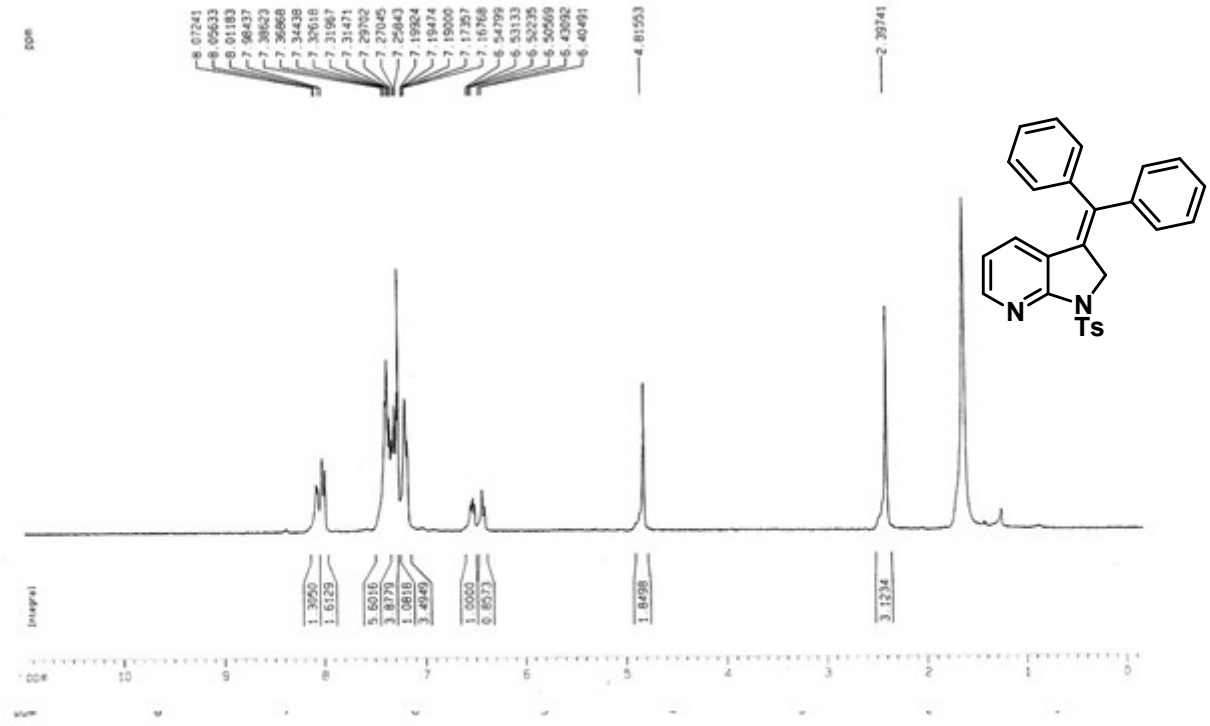
^{1}H NMR of 2c, $CDCl_3$, 300 MHz



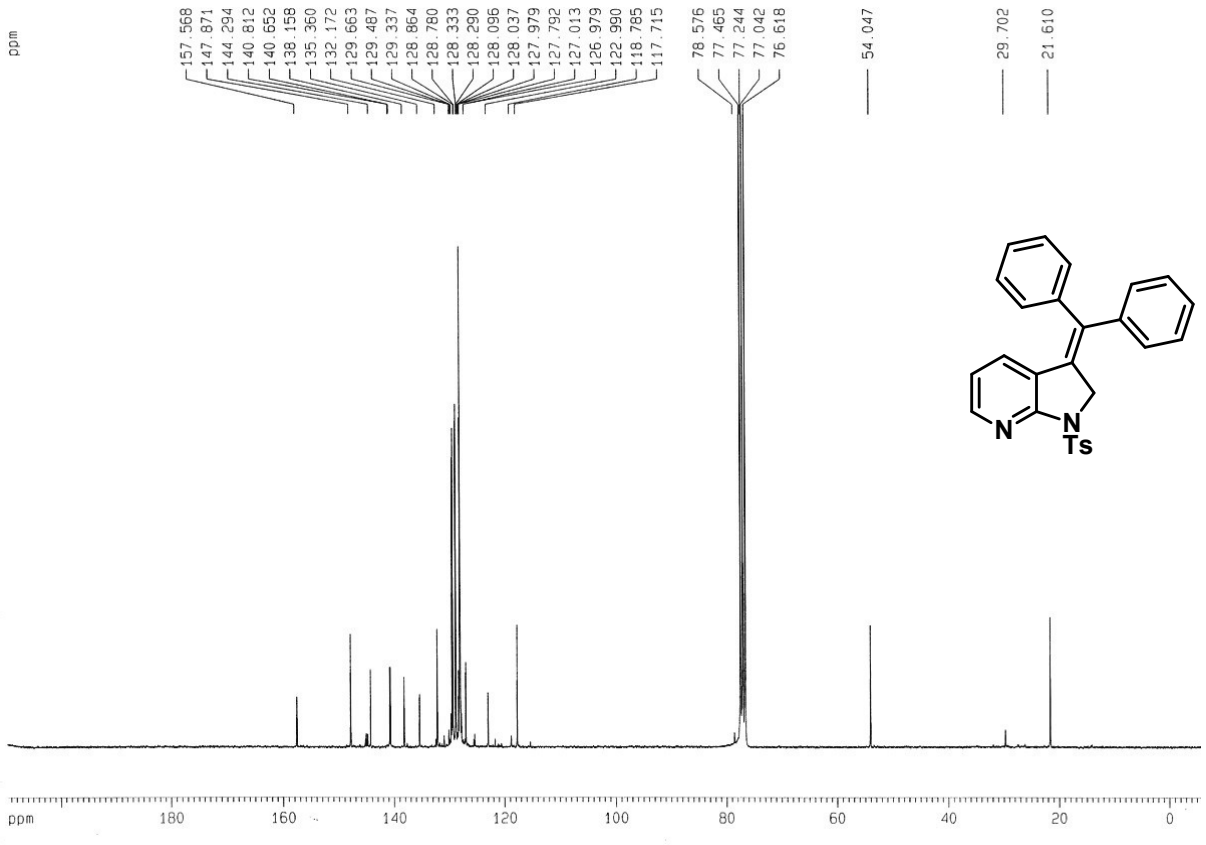
^{13}C NMR of 2c, $CDCl_3$, 75 MHz



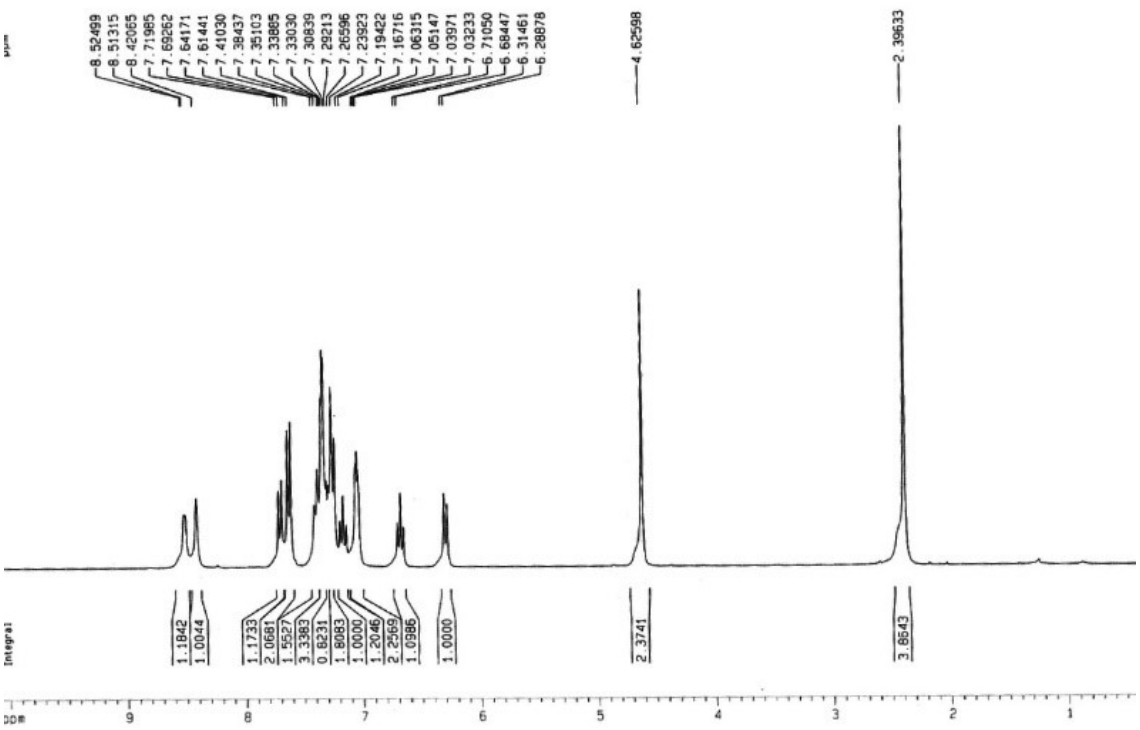
^{1}H NMR of 2h, $CDCl_3$, 300 MHz

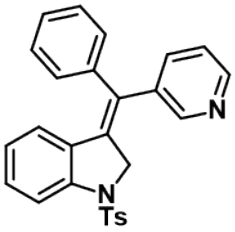


^{13}C NMR of 2h, $CDCl_3$, 75 MHz

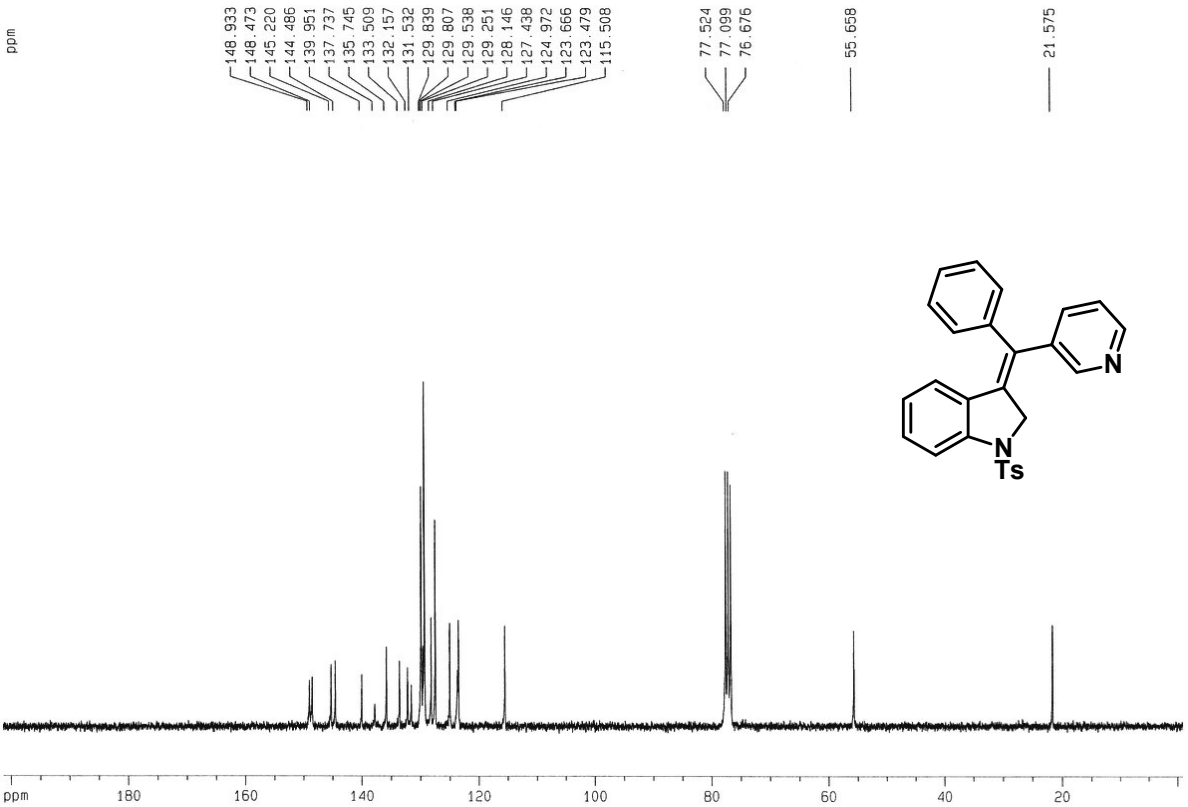


^{1}H NMR of 2i, $CDCl_3$, 300 MHz

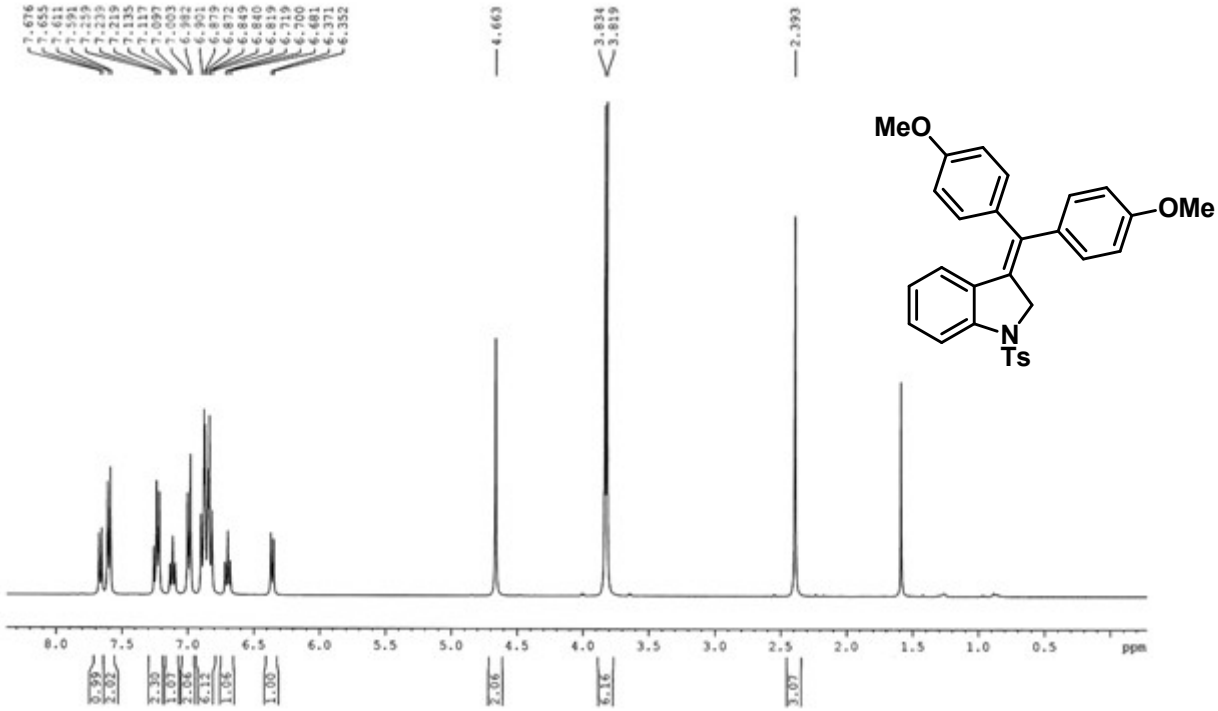




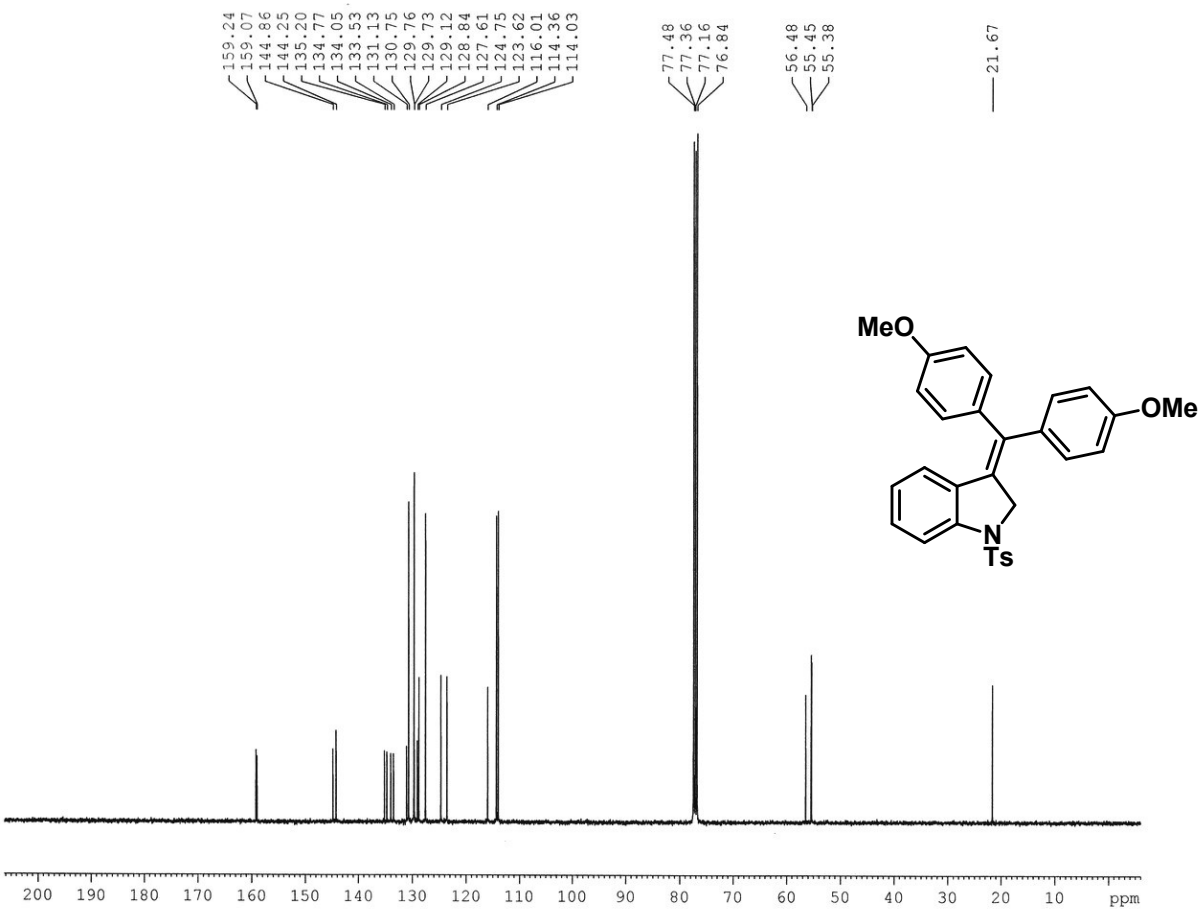
^{13}NMR of 2i, $CDCl_3$, 75 MHz



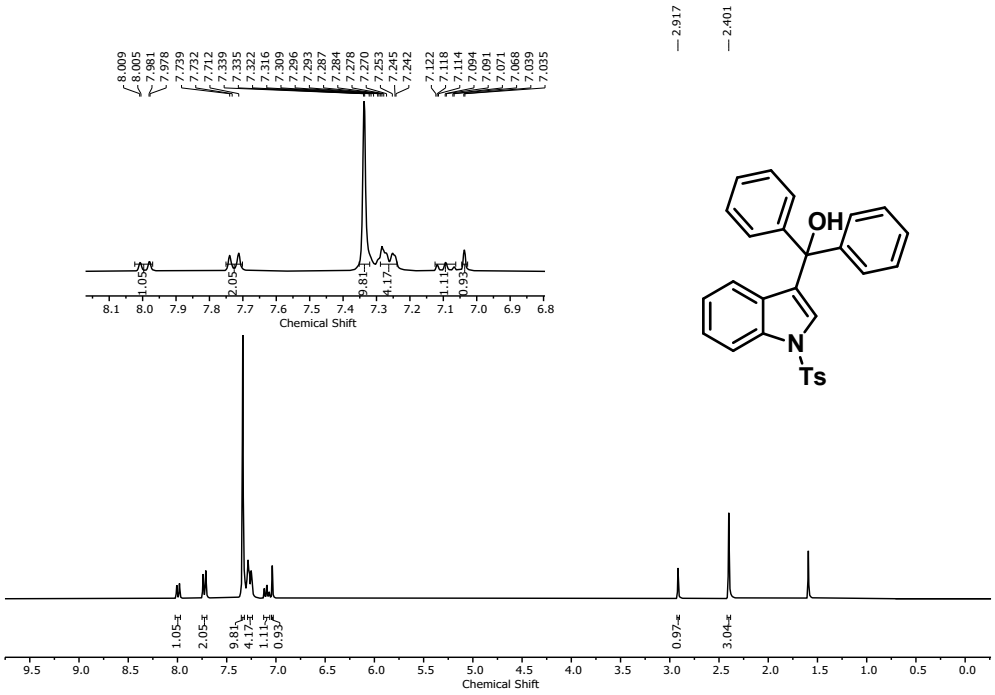
^{1}H NMR of 2j, $CDCl_3$, 400 MHz



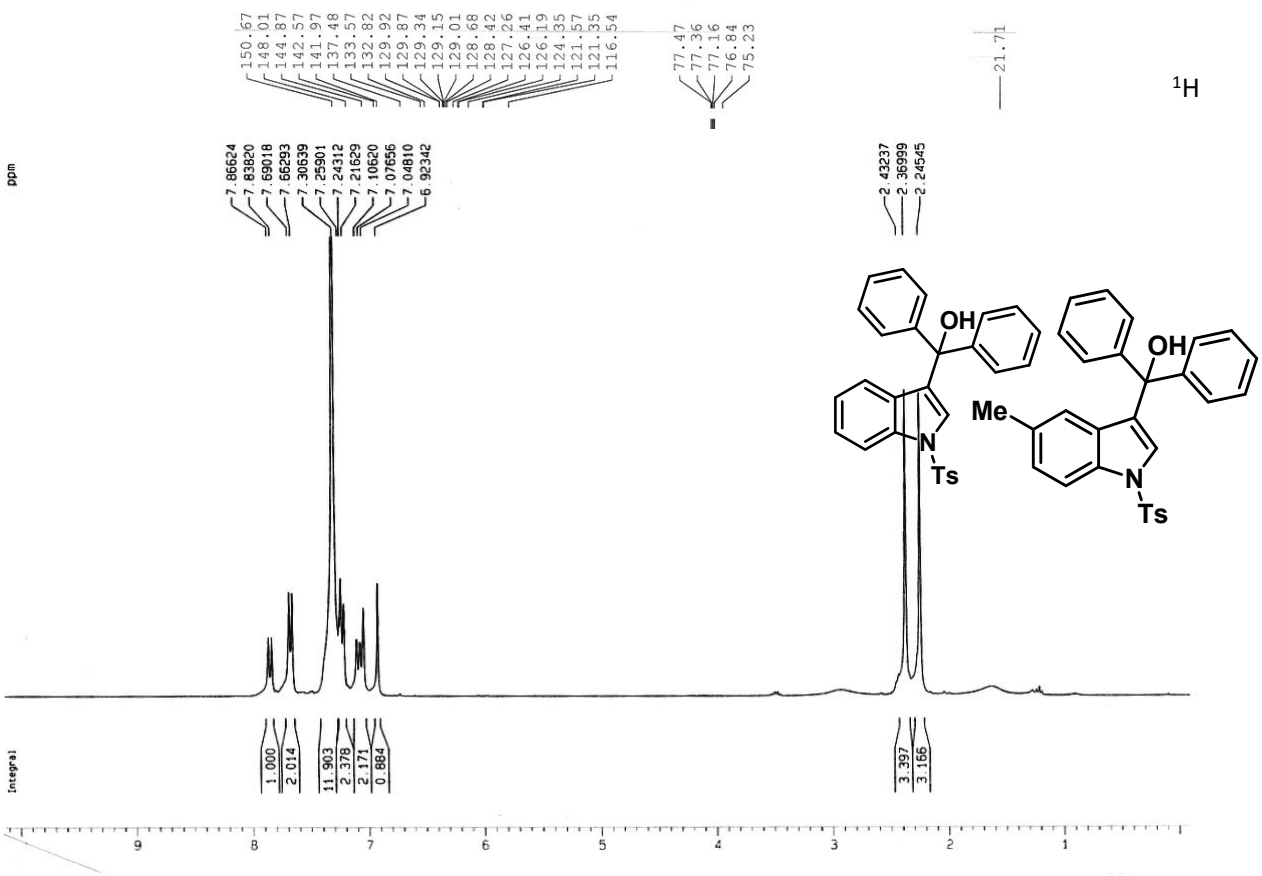
^{13}NMR of 2j, $CDCl_3$, 100 MHz



^{1}H NMR of 3a, $CDCl_3$, 300 MHz



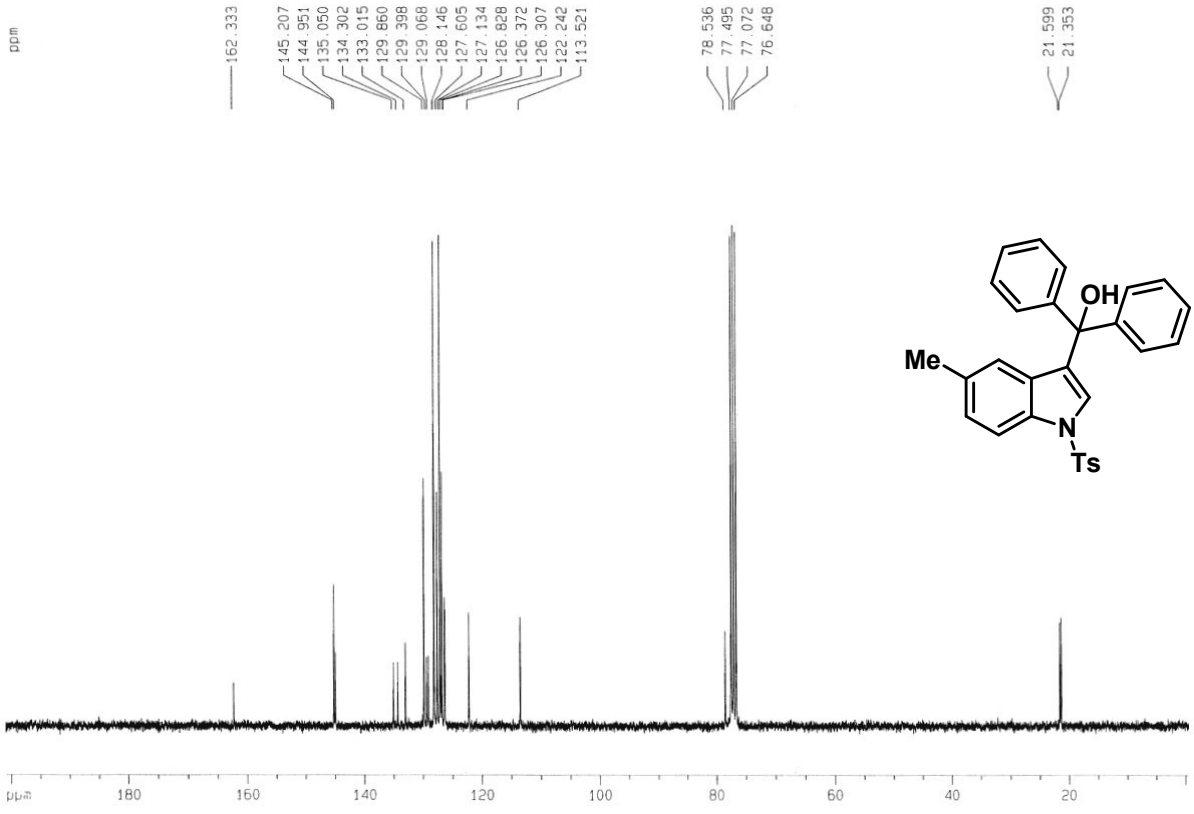
^{13}C NMR of 3a, $CDCl_3$, 100 MHz



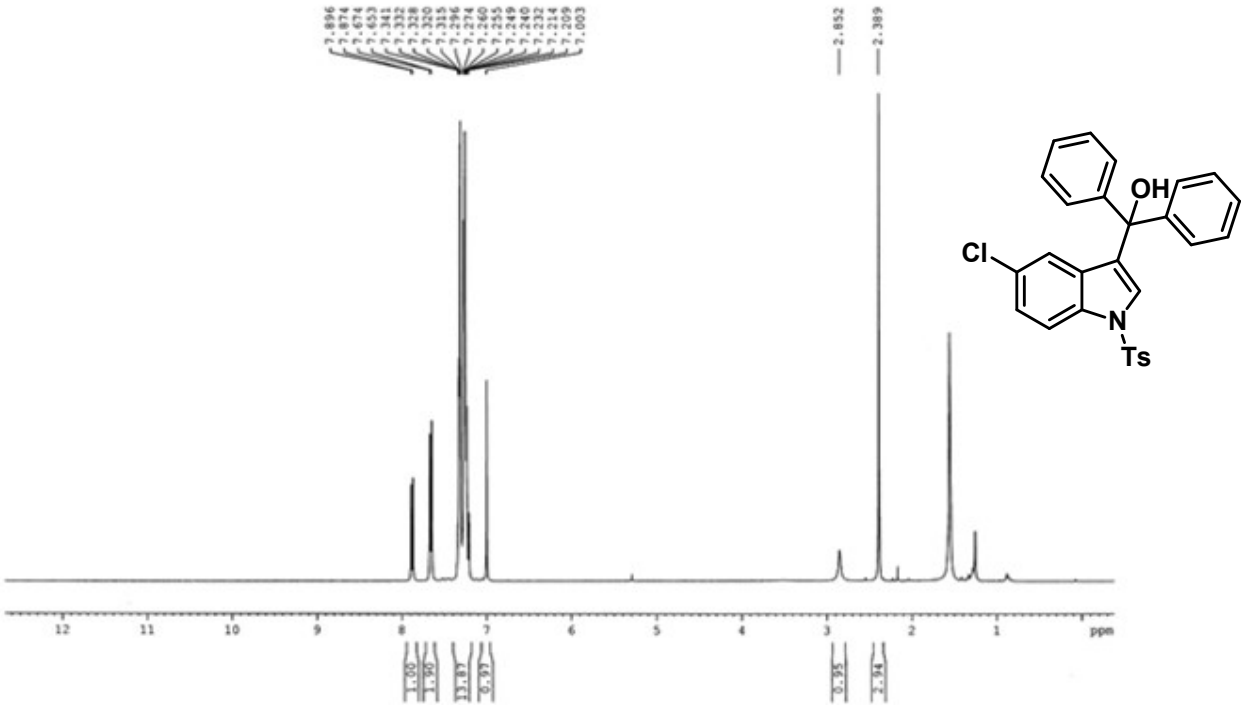
^{1}H

NMR of 3b, $CDCl_3$, 300 MHz

^{13}C NMR of 3b, $CDCl_3$, 75 MHz

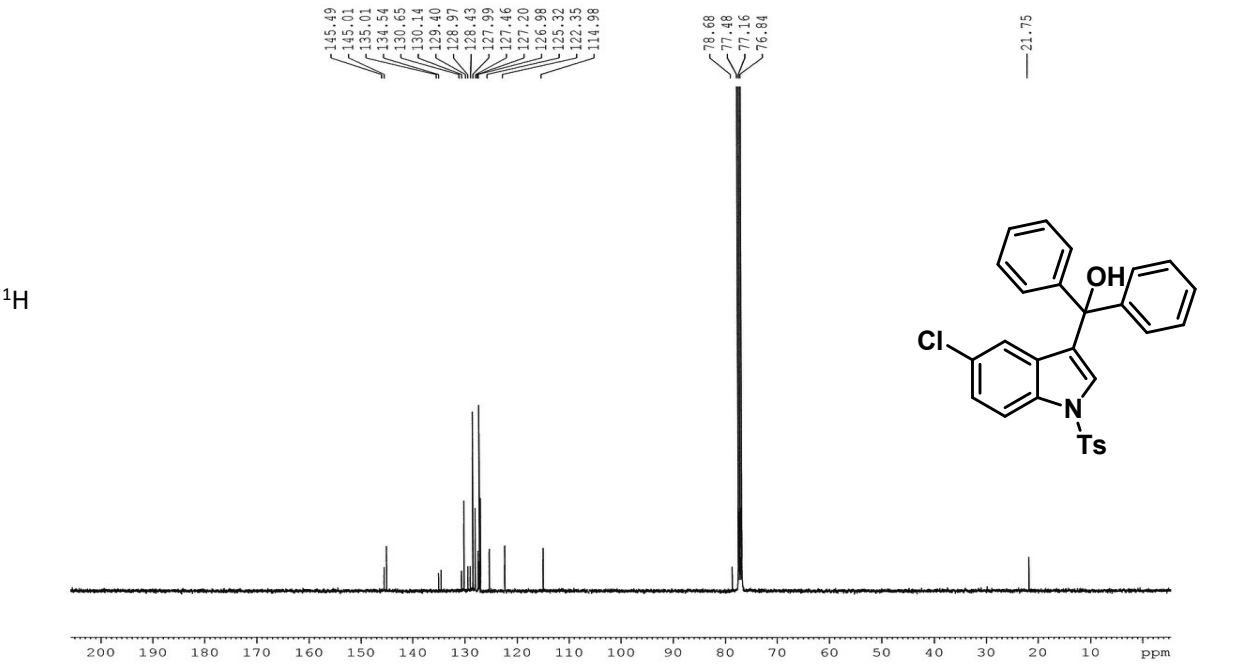


^{1}H NMR of 3c, $CDCl_3$, 400 MHz

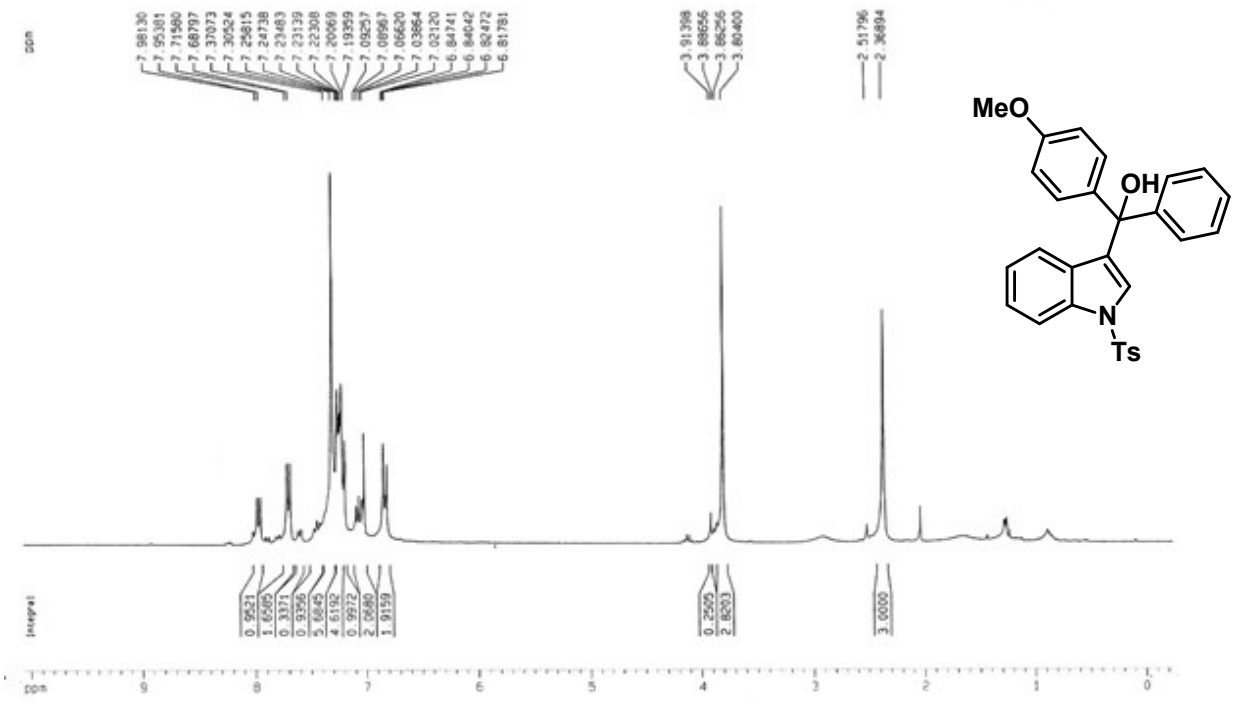


^{13}C NMR of 3c, $CDCl_3$, 100 MHz

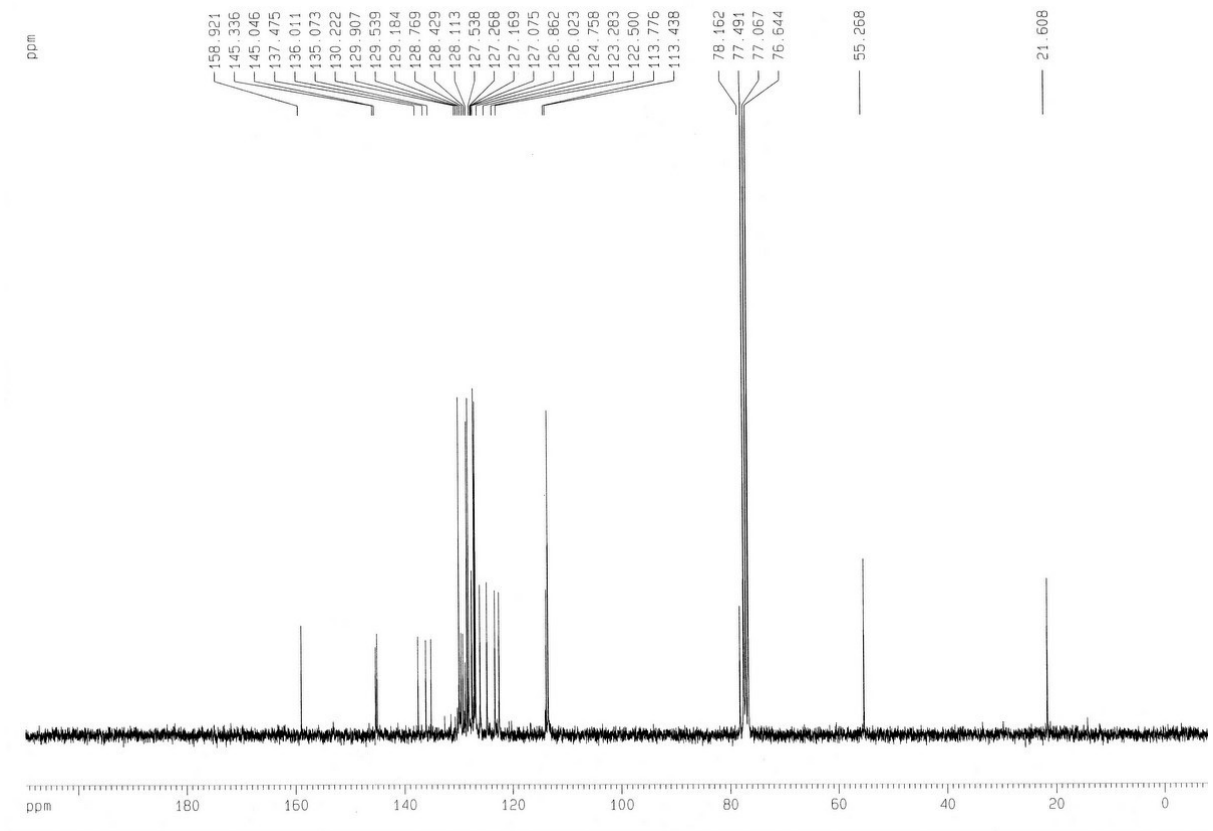
^{1}H



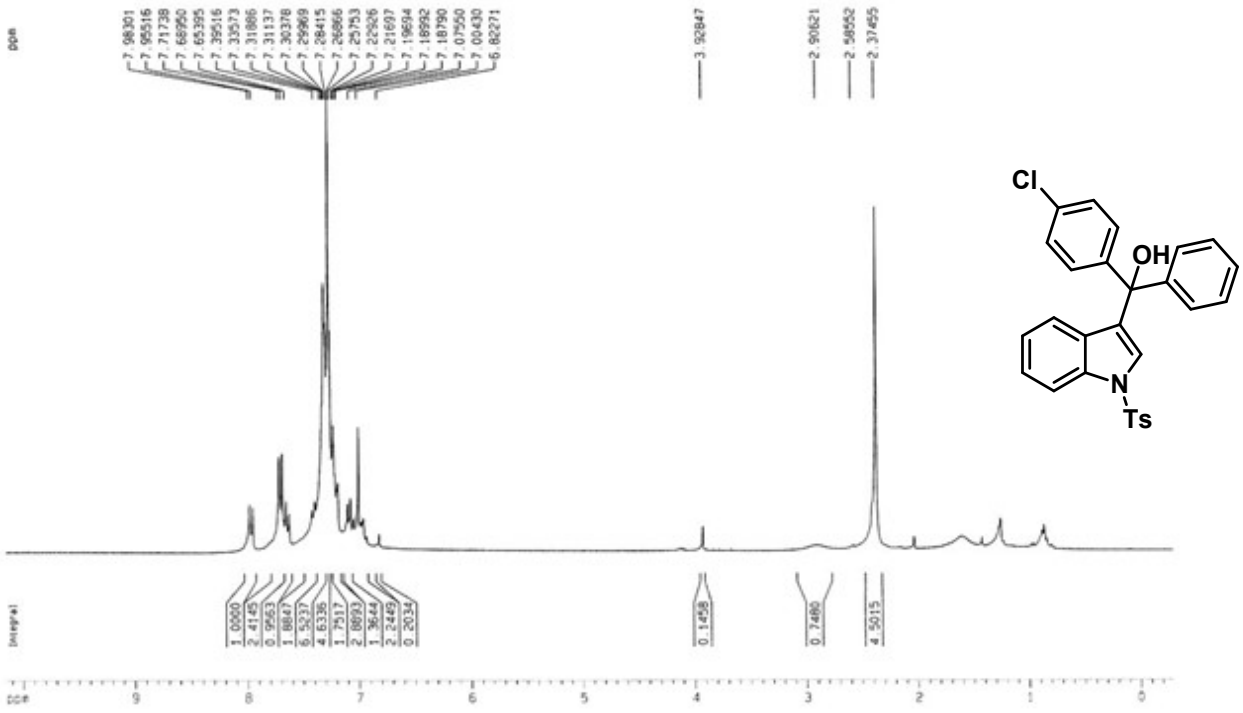
NMR of 3d, $CDCl_3$, 300 MHz



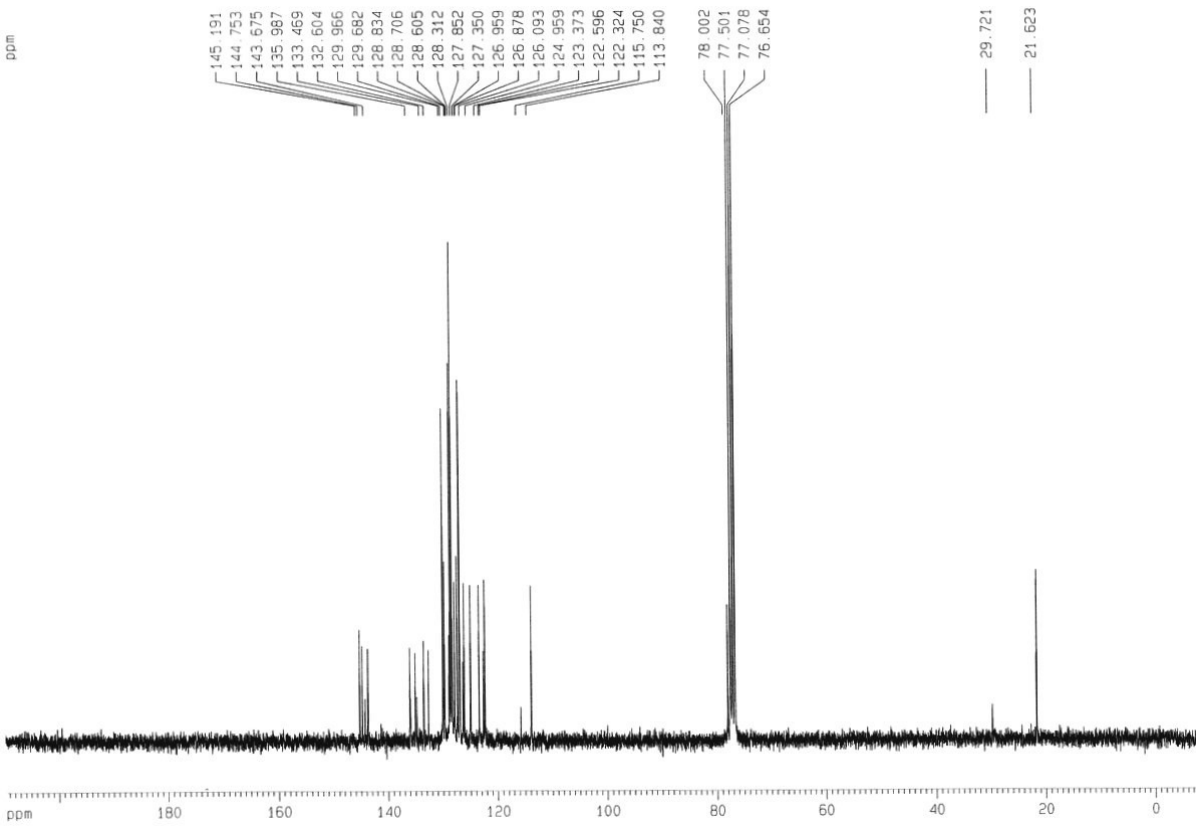
^{13}C NMR of 3d, $CDCl_3$, 75 MHz



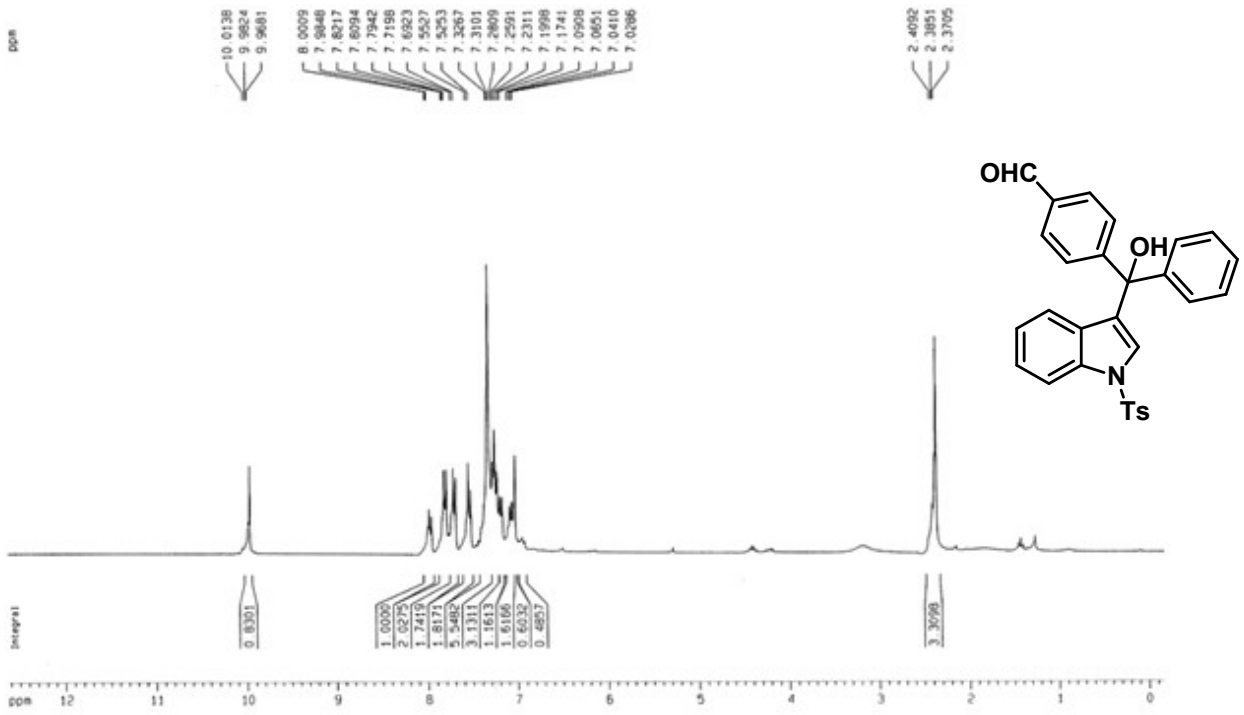
^{1}H NMR of 3e, $CDCl_3$, 300 MHz



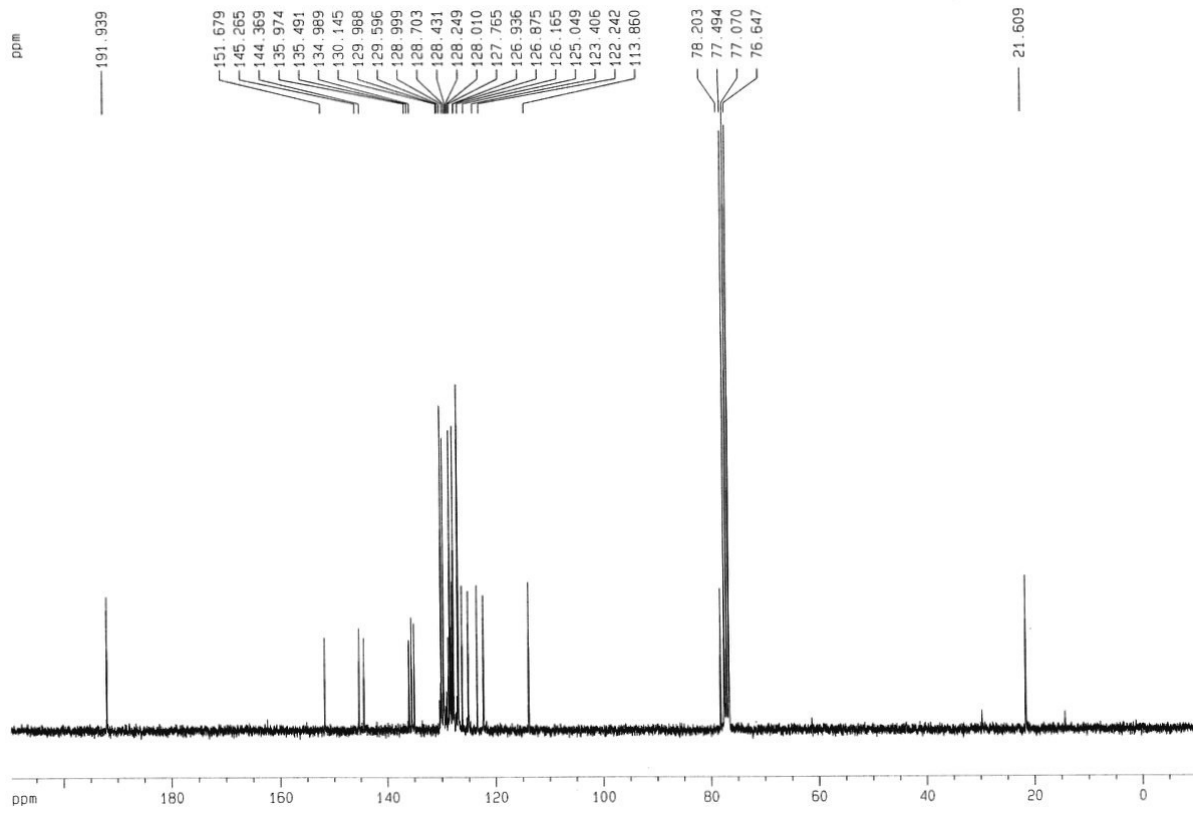
^{13}C NMR of 3e, $CDCl_3$, 75 MHz



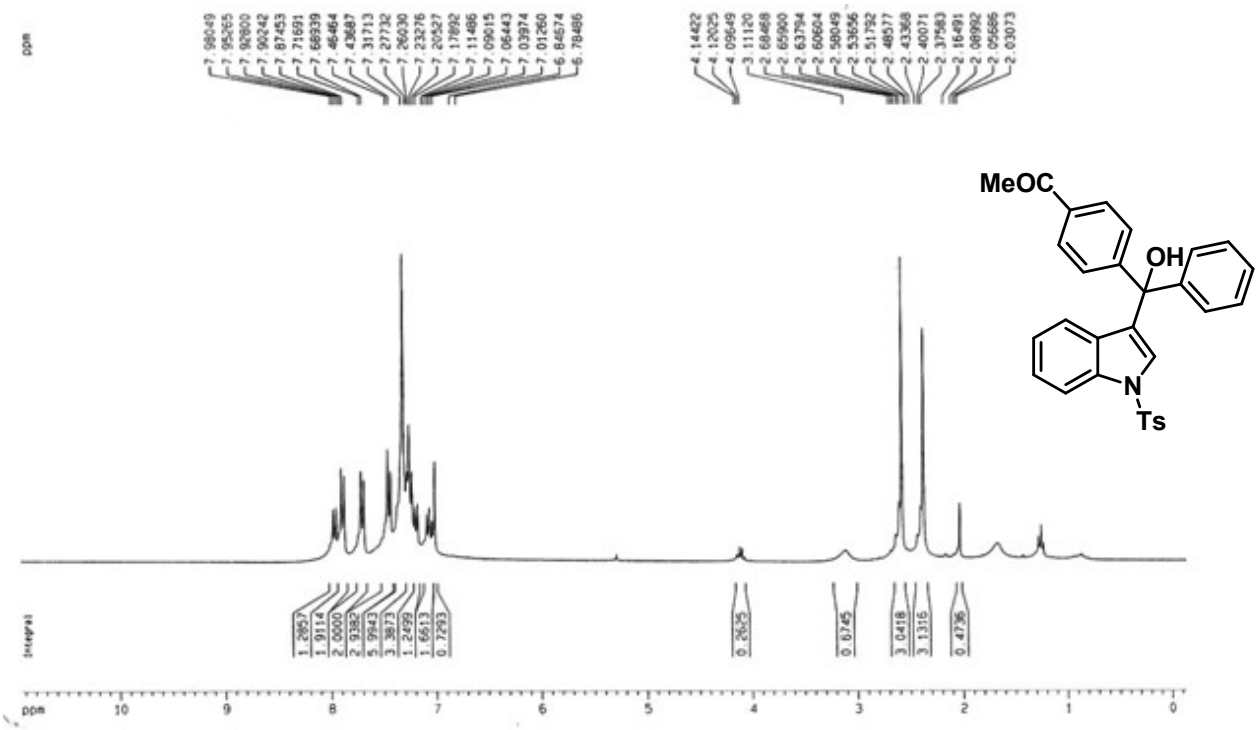
^{1}H NMR of 3f, $CDCl_3$, 300 MHz



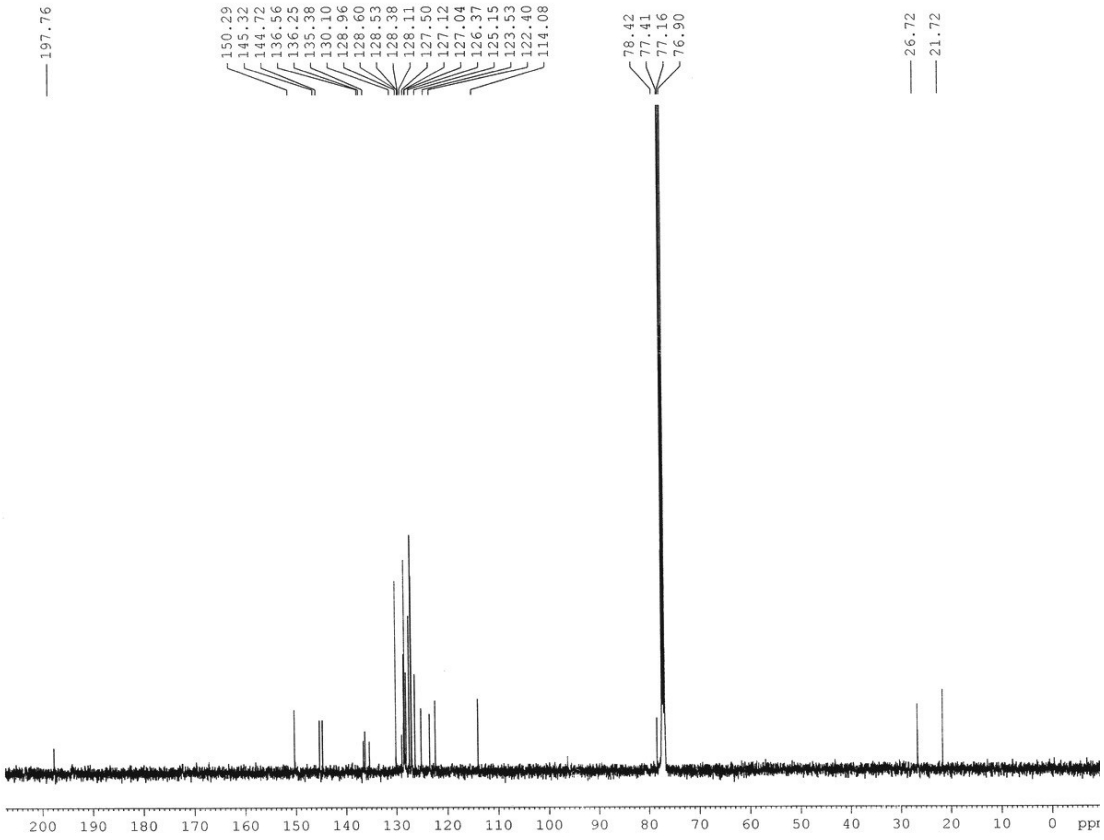
^{13}C NMR of 3f, $CDCl_3$, 75 MHz



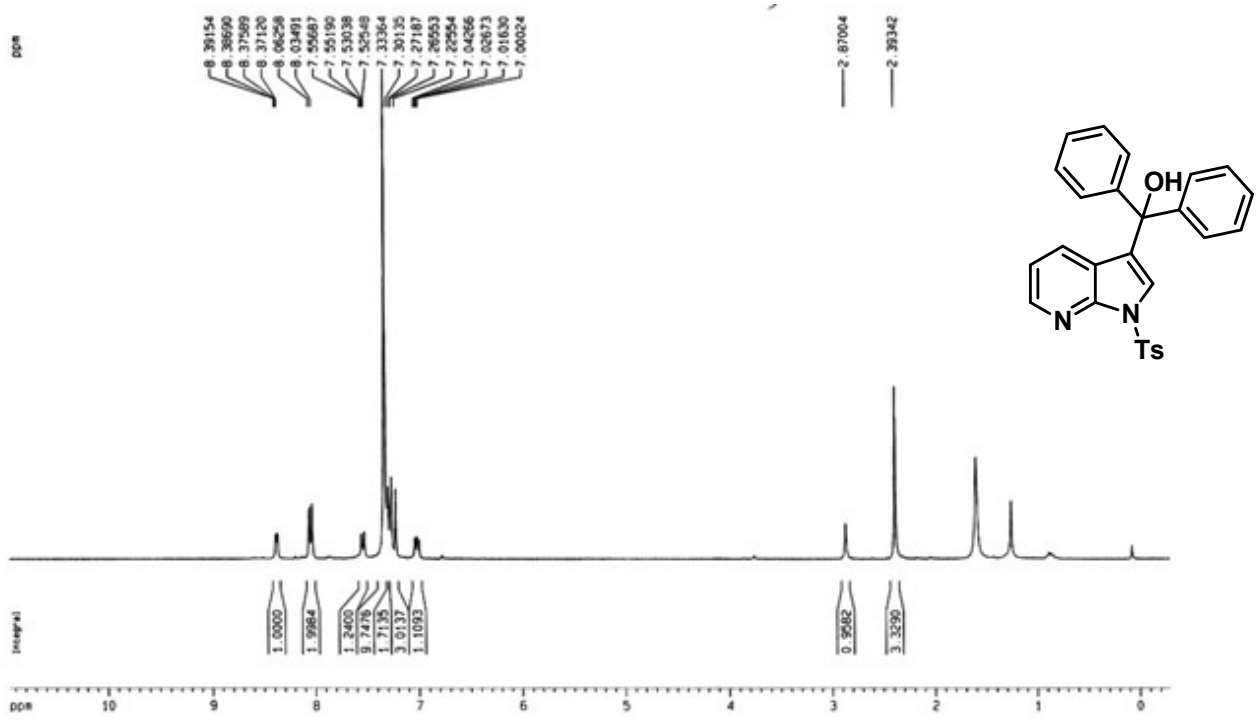
^{1}H NMR of 3g, $CDCl_3$, 300 MHz



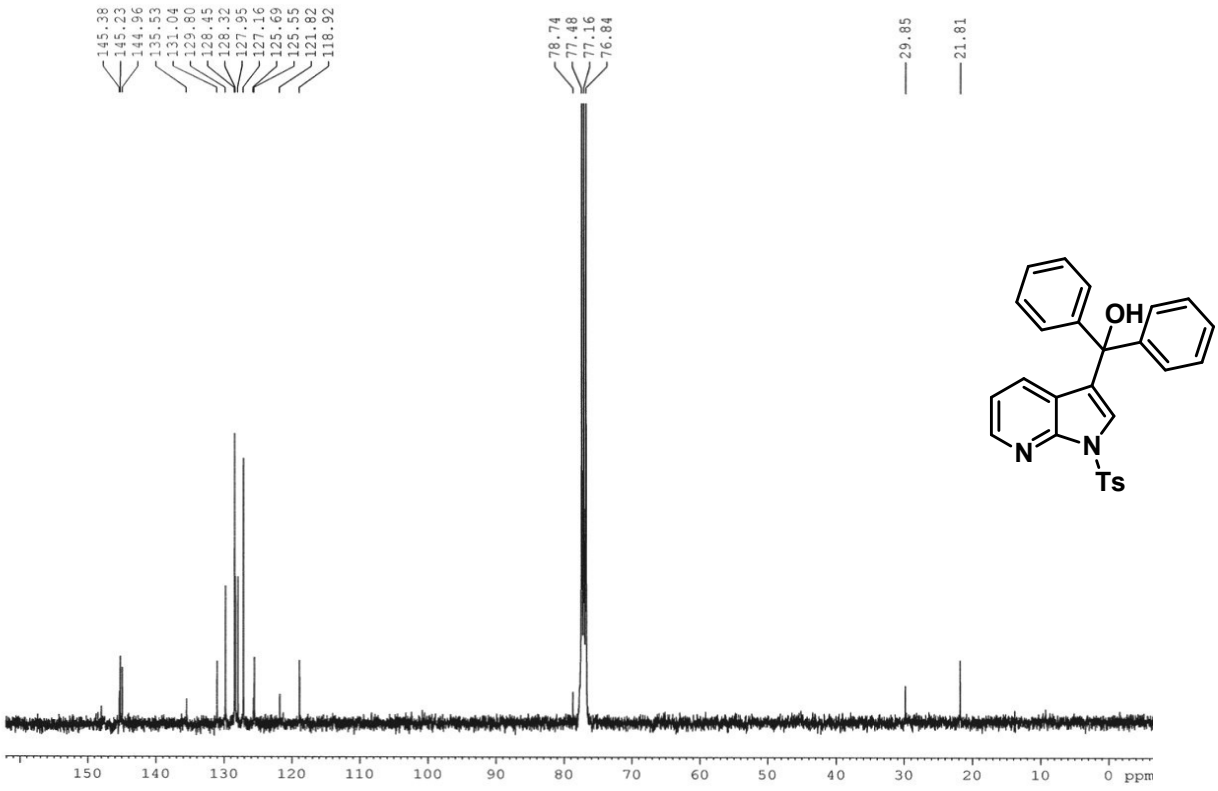
^{13}C NMR of 3g, $CDCl_3$, 125 MHz



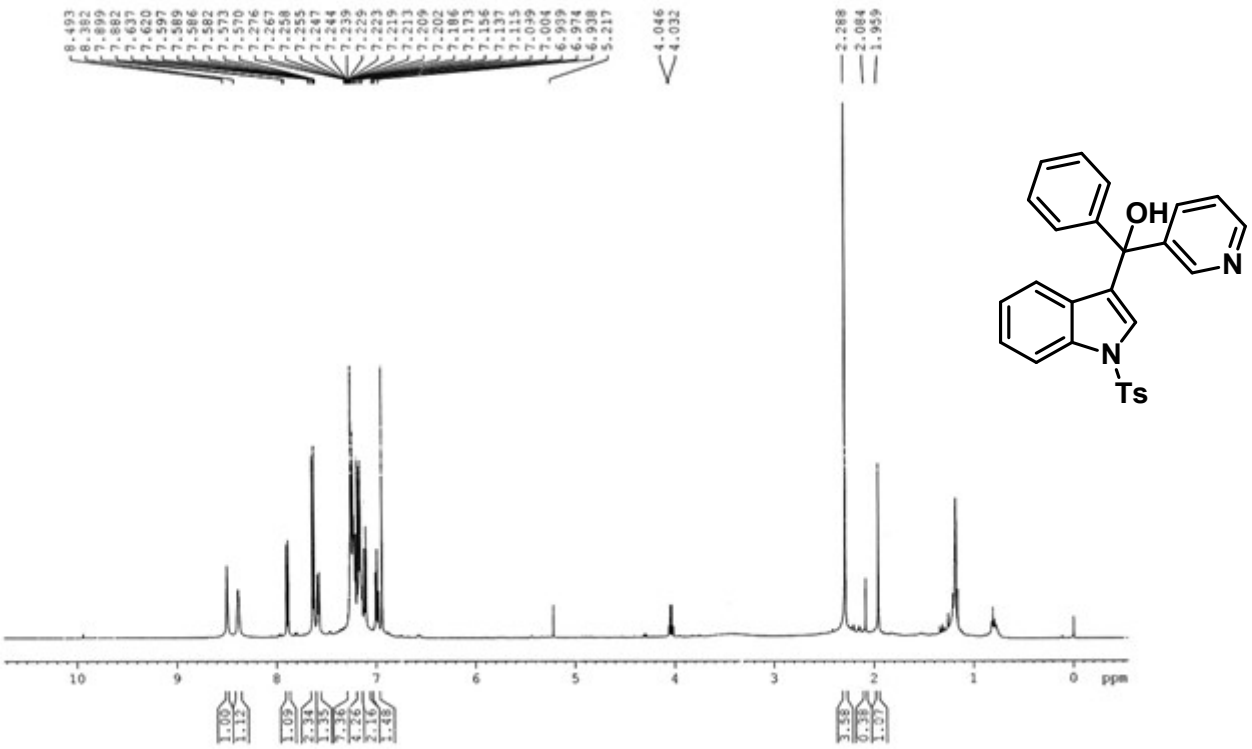
^{1}H NMR of 3h, $CDCl_3$, 300 MHz



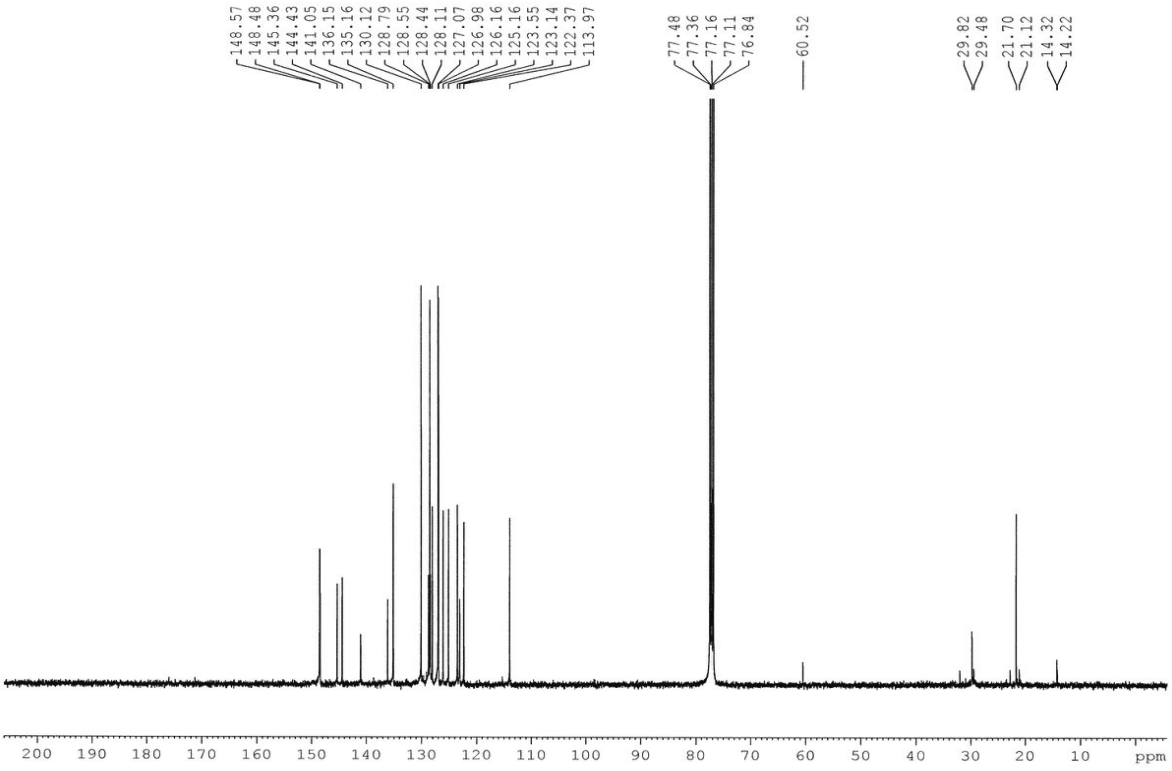
^{13}C NMR of 3h, $CDCl_3$, 100 MHz



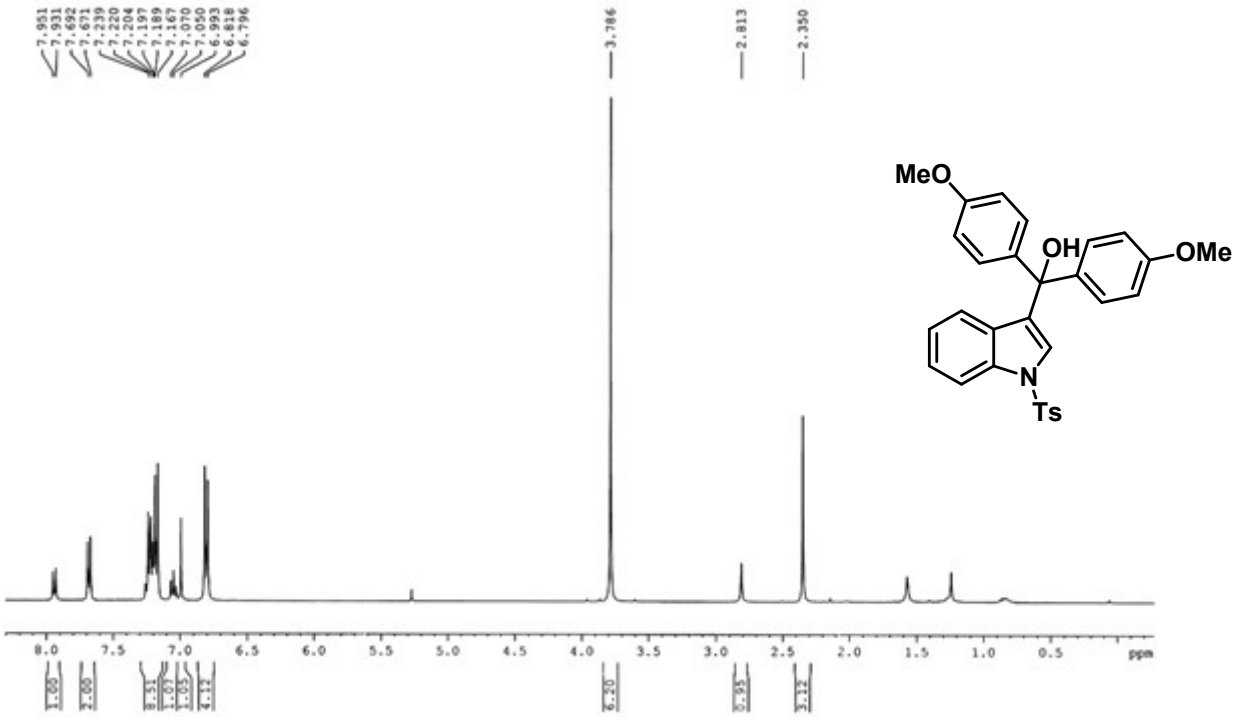
^{1}H NMR of 3i, $CDCl_3$, 500 MHz



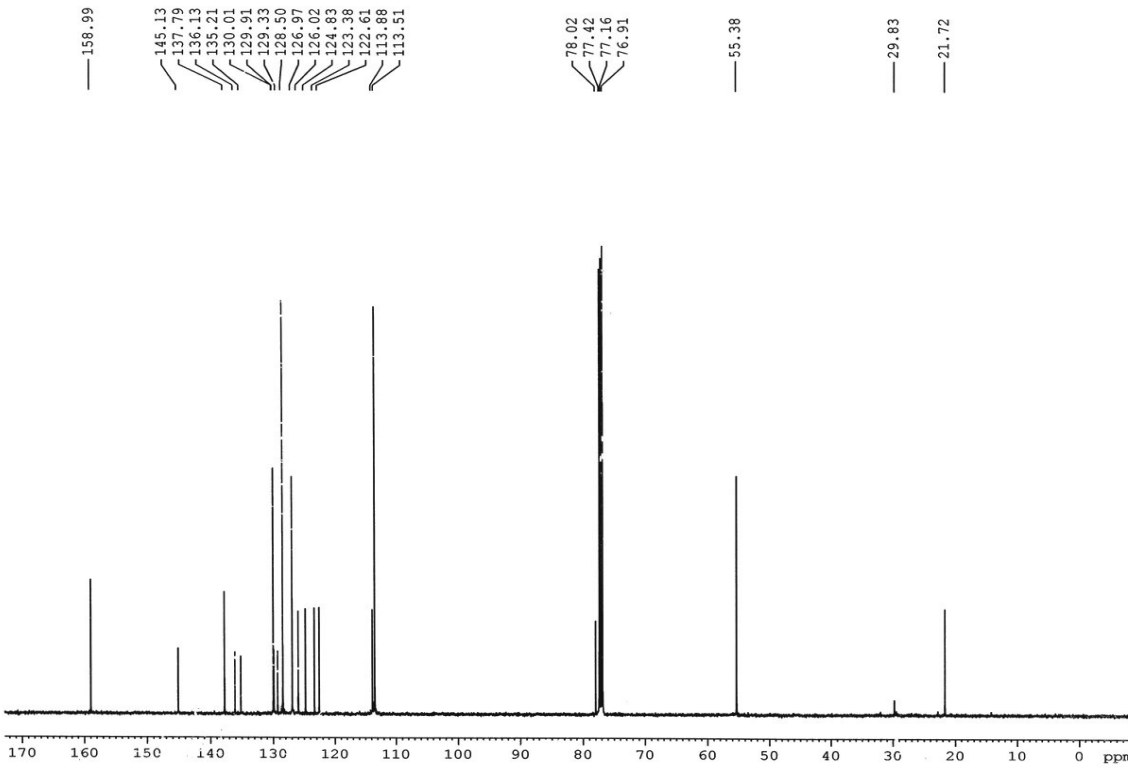
^{13}NMR of 3i, $CDCl_3$, 100 MHz



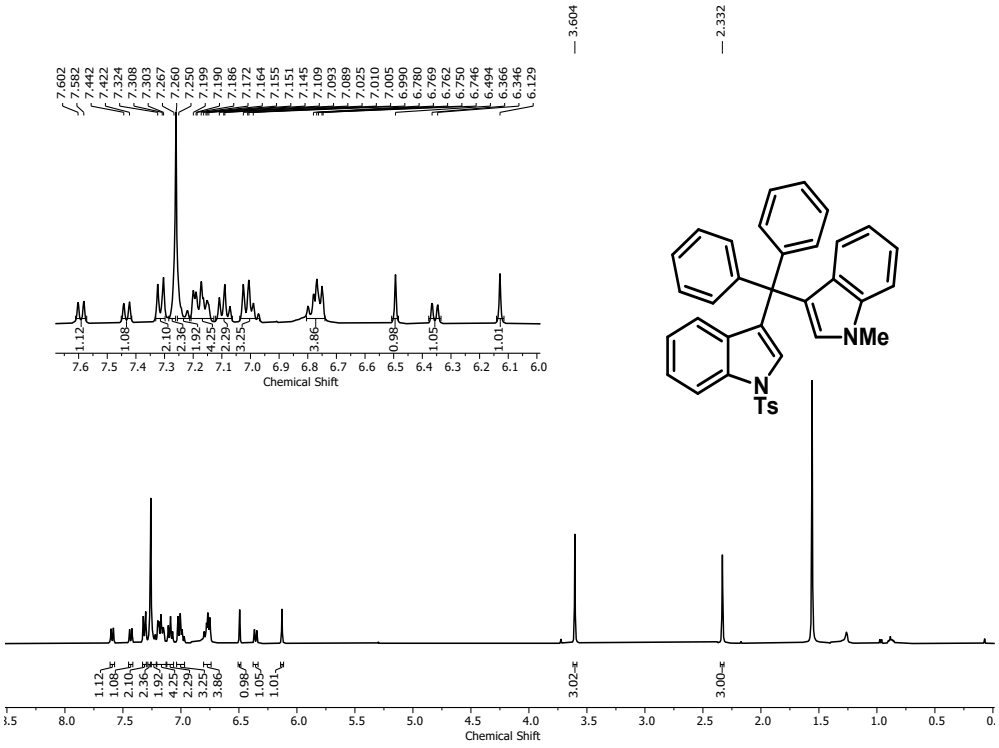
^{1}H NMR of 3j, $CDCl_3$, 400 MHz



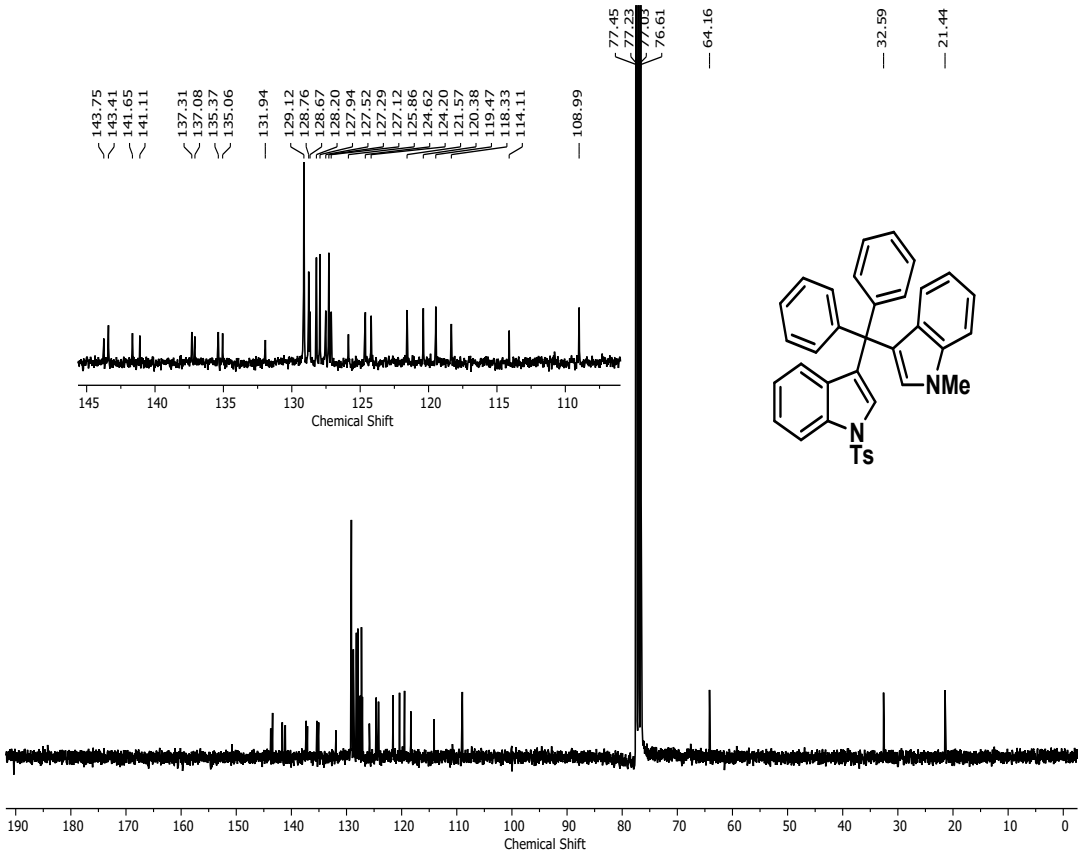
^{13}C NMR of 3j, $CDCl_3$, 125 MHz



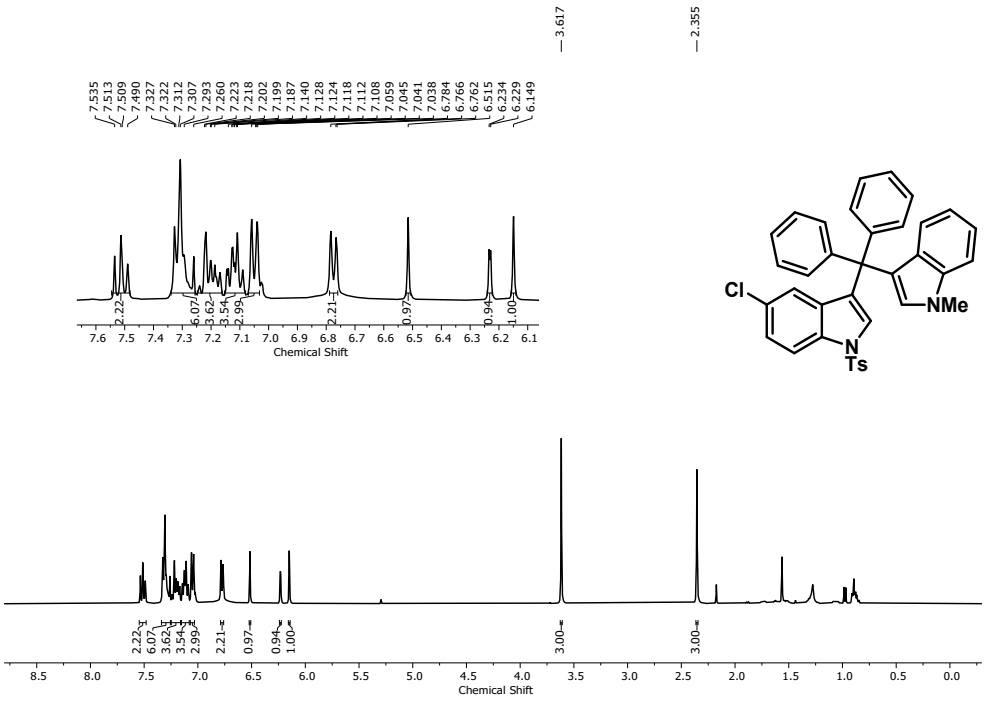
^{1}H NMR of 4a, $CDCl_3$, 400 MHz



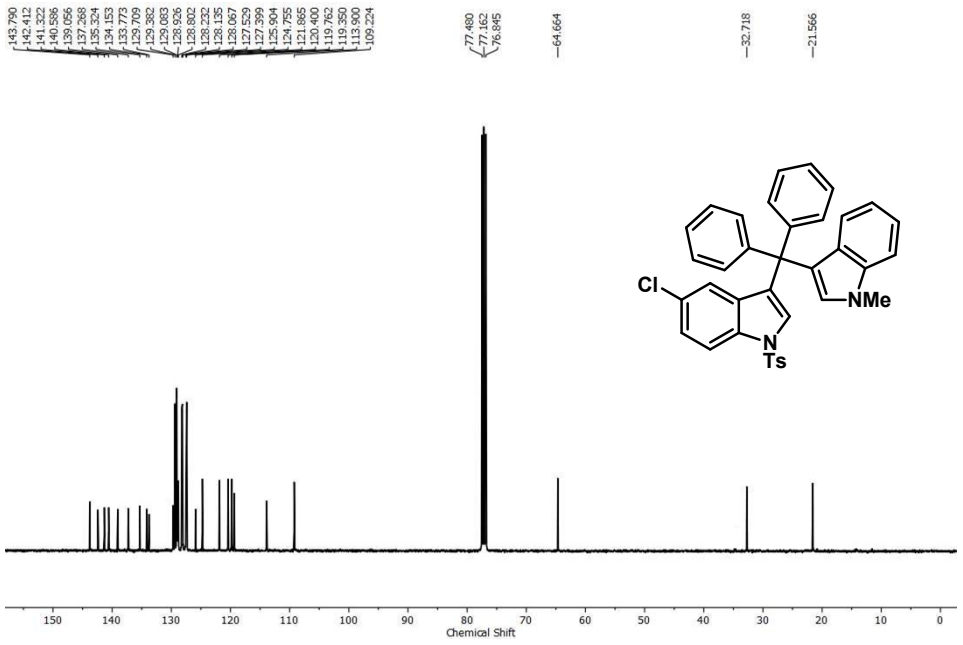
^{13}C NMR of 4a, $CDCl_3$, 100 MHz



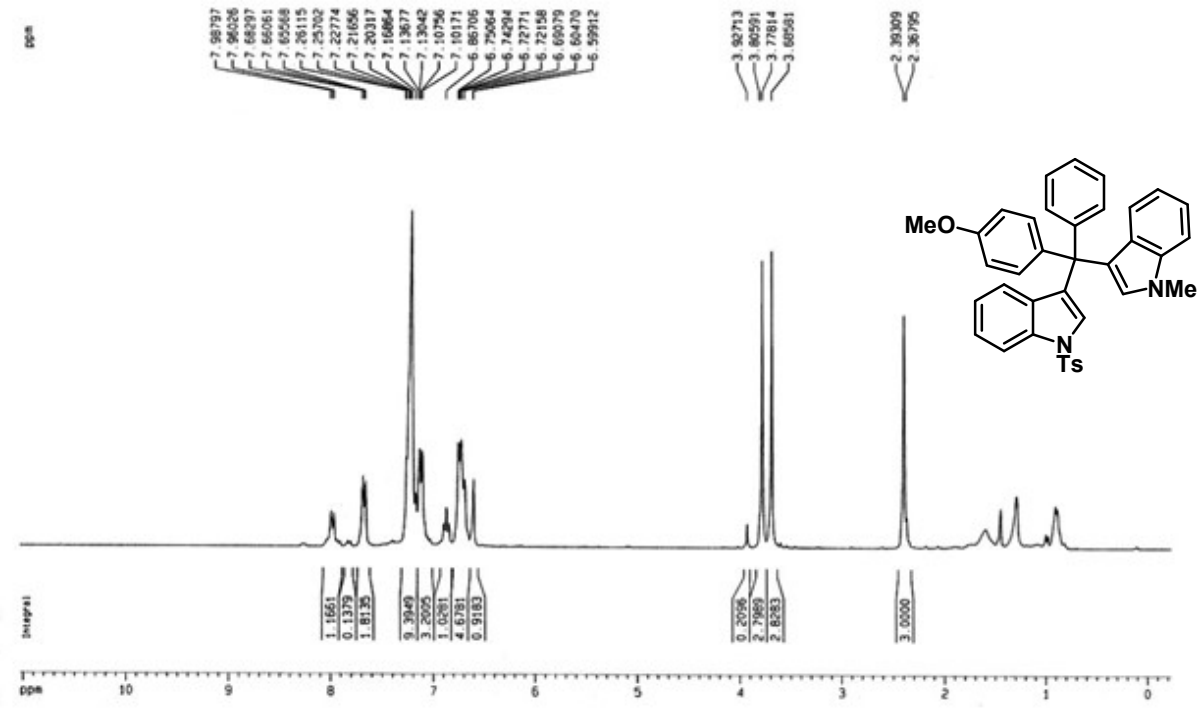
^{1}H NMR of 4b, $CDCl_3$, 400 MHz



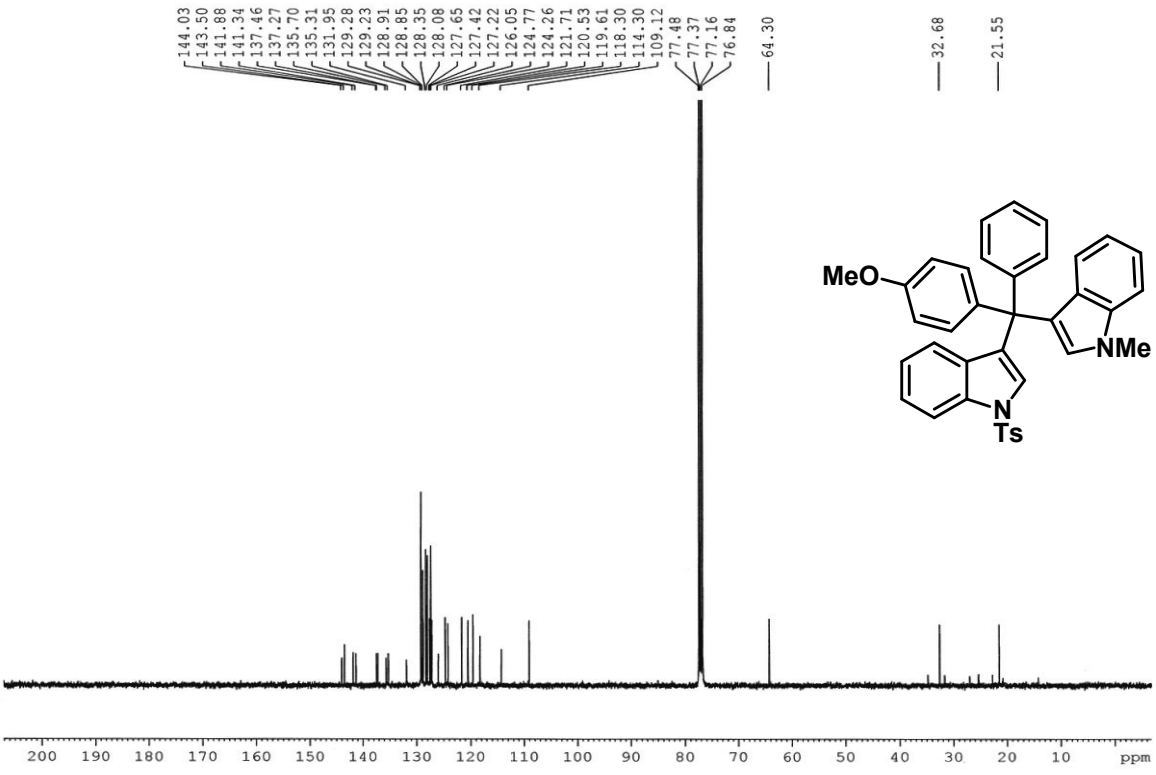
^{13}C NMR of 4b, $CDCl_3$, 100 MHz



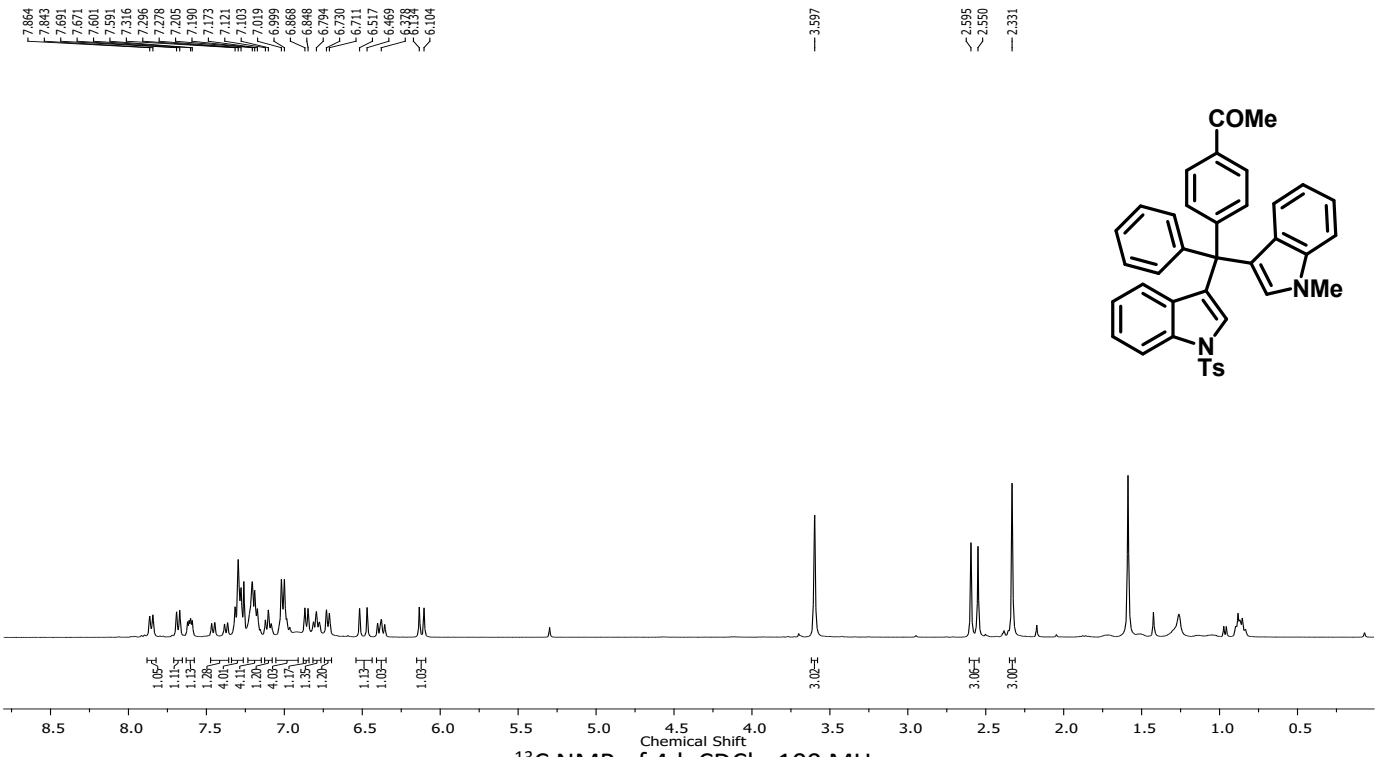
^{1}H NMR of 4c, $CDCl_3$, 300 MHz



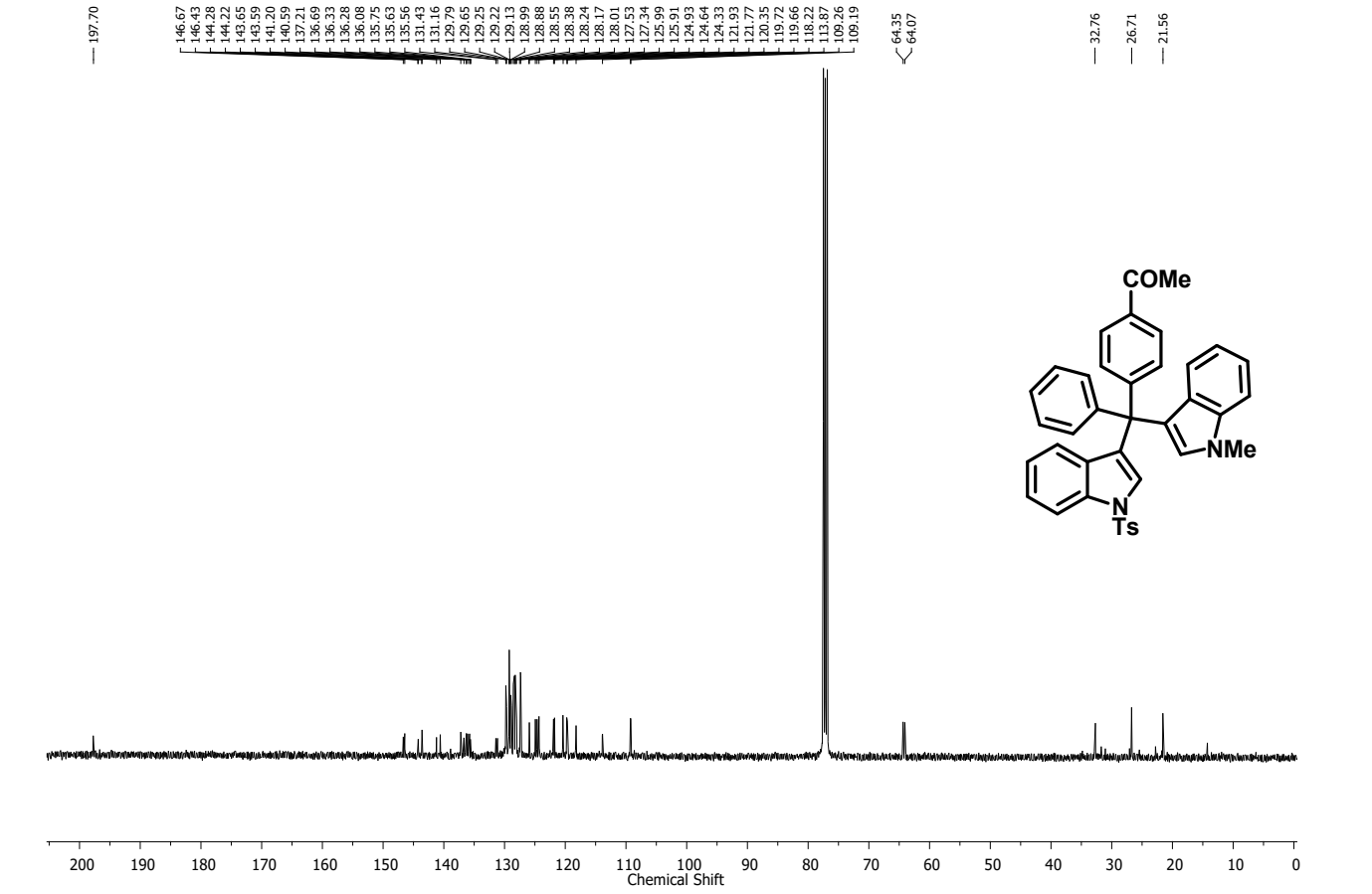
^{13}C NMR of 4c, $CDCl_3$, 100 MHz



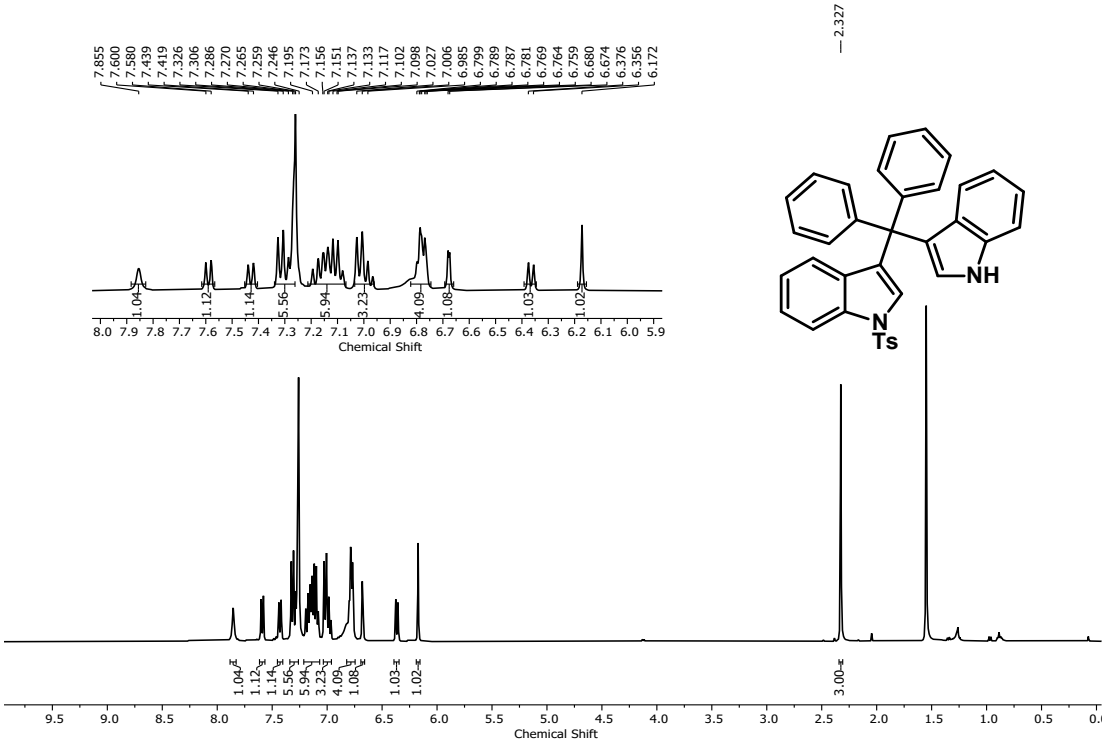
^{1}H NMR of 4d, $CDCl_3$, 400 MHz



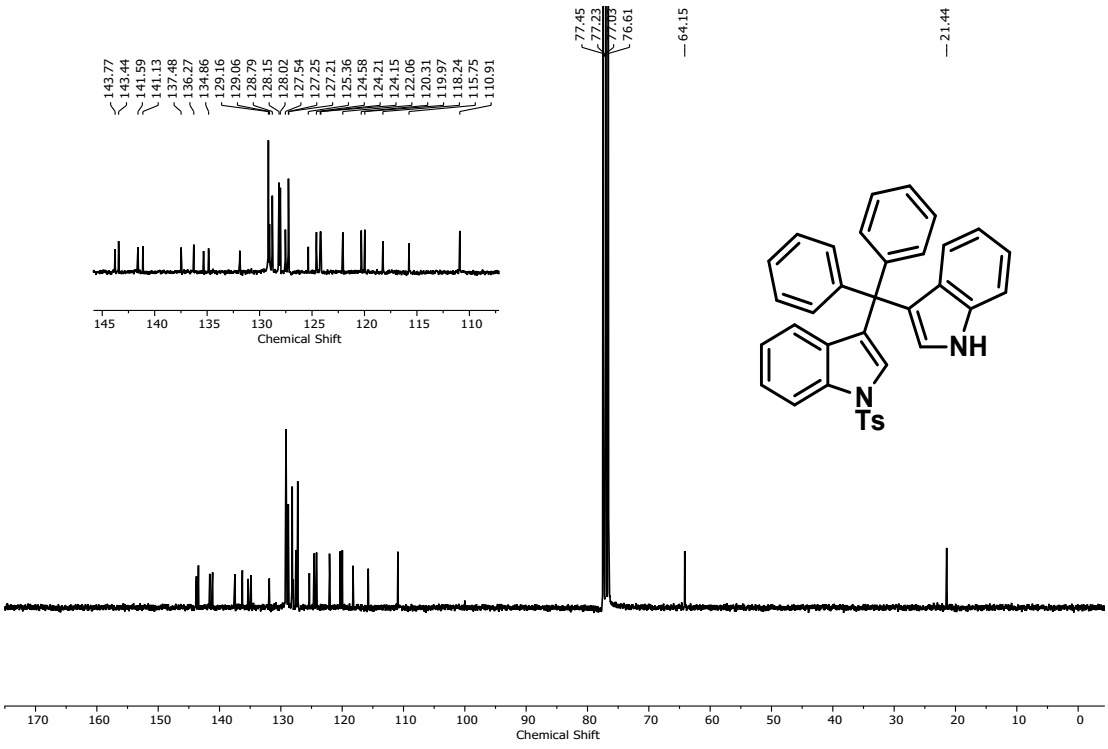
^{13}C NMR of 4d, $CDCl_3$, 100 MHz



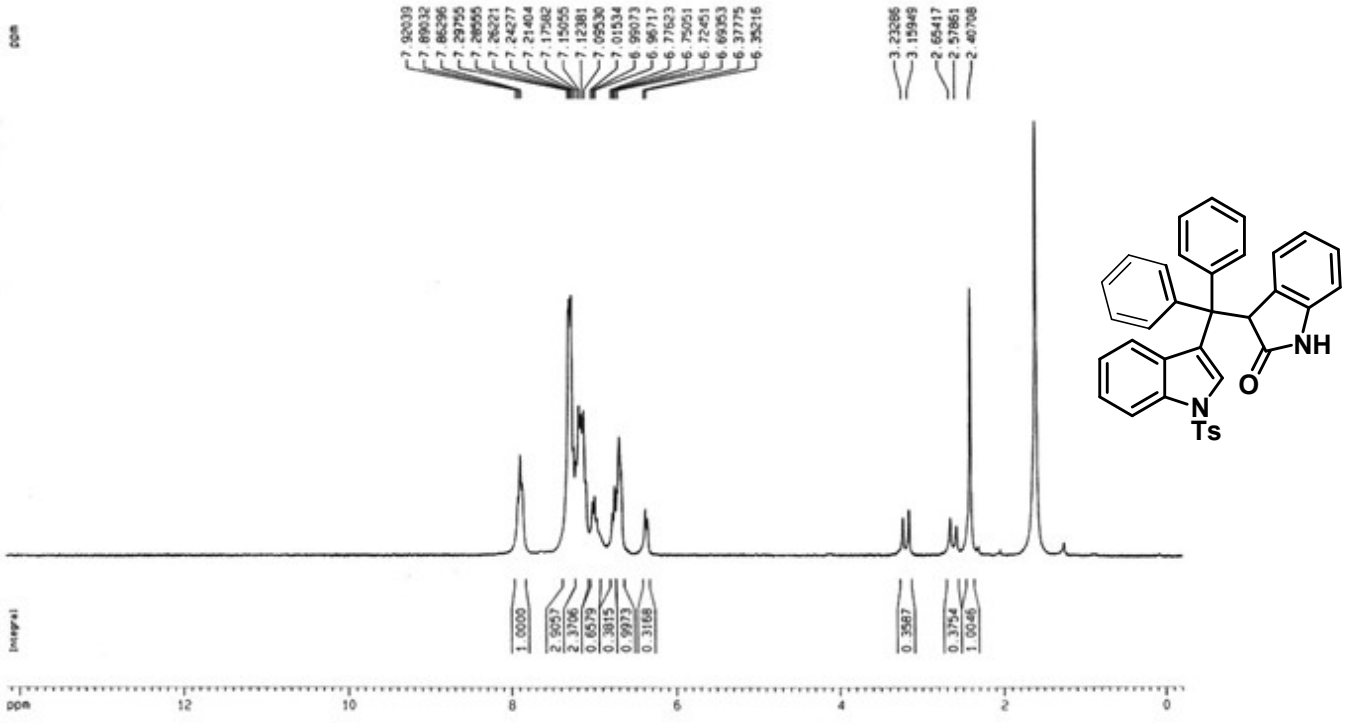
^{1}H NMR of 4f, $CDCl_3$, 400 MHz



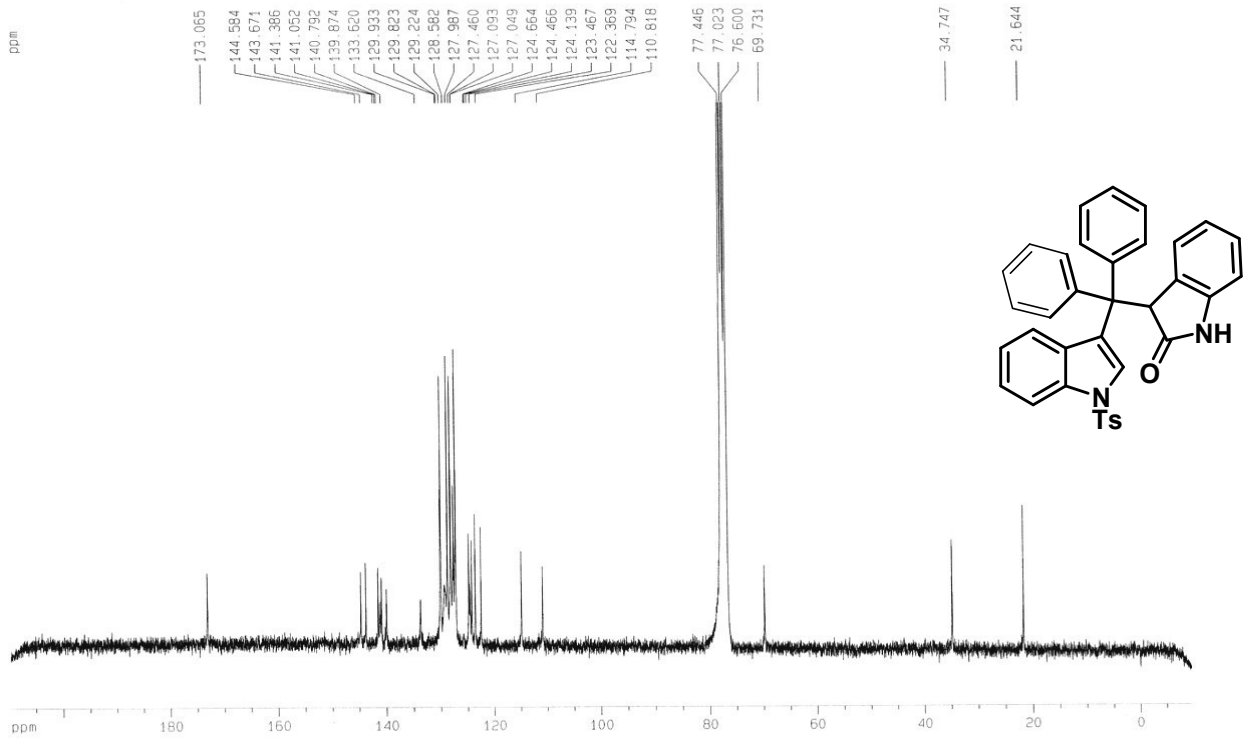
^{13}C NMR of 4f, $CDCl_3$, 75 MHz



^{1}H NMR of 4e, $CDCl_3$, 300 MHz



^{13}C NMR of 4e, $CDCl_3$, 75 MHz



Crystallographic data of 3h:

	3h
Formula	$C_{27}H_{22}N_2O_4S$
M_r	470.53
Crystal system	Triclinic
Space group	P -1
a / Å	8.6868(10)
b / Å	11.8781(14)
c / Å	13.2771(15)
α /°	104.028(3)
β /°	95.447(3)
γ /°	108.651(3)
V /Å^3	1237.0(2)
Z	2
D_{calcd} /mg m^{-3}	1.263
μ /mm^{-1}	0.166
θ /°	1.890 – 24.999
T /K	273

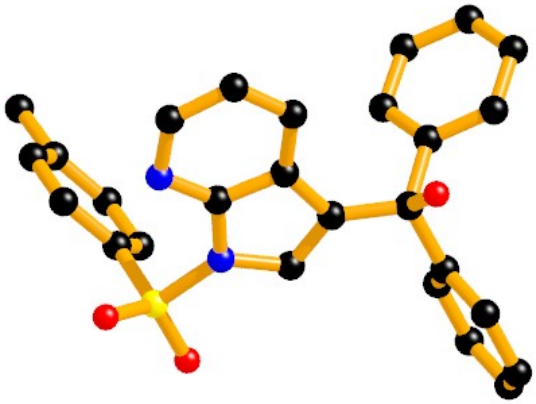


Fig. 1: Crystal structure of **3h**.