Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of *N*-alkyl-3-sulfonylindoles and *N*-alkyl-3-sulfanylindoles by cascade annulation of 2-alkynyl-*N*,*N*-dialkylanilines

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Contents

Experimental section

General information:

^{1}H NMR spectra were recorded with a Bruker AVANCE 400 spectrometer (400 MHz) in $CDCl_3$ by using tetramethylsilane (δ = 0 ppm) as an internal standard and acetone-*d6* as solvents. ^{13}C NMR spectra were recorded with a Bruker AVANCE 400 (100 MHz) spectrometer by using residual non-deuterated solvent peak ($CHCl_3$, δ = 77.00 ppm) as an internal standard. Infrared spectra were recorded with a Bruker ALPHA FT-IR spectrometer and only partial data were listed. High-resolution mass spectra (HRMS) were recorded with a Bruker micro TOF spectrometer in the ESI mode. Melting points were recorded with a Sanyo Gallenkamp apparatus. Reactions were monitored by thin-layer chromatography and visualized by UV and a solution of $KMnO_4$. *N,N*-Dialkyl-2-(1-alkynyl)anilines were synthesized according to literature procedures.[23] The structures of known compounds were corroborated by comparing their ^{1}H NMR and ^{13}C NMR data with those in the literature.

All reagents and solvents were obtained from commercial sources and used without further purification. Column chromatography was performed by using Merck silica gel 60 (Art 7734).

General procedure for the synthesis of *N,N*-dialkyl-2-(1-alkynyl)anilines[23]

To an oven-dried reaction flask was added *N,N*-dialkyl-2-iodoaniline (5.0 mmol), $PdCl_2(PPh_3)_2$ (45.6 mg, 0.065 mmol), CuI (9.5 mg, 0.05 mmol), and Et_3N (10 mL). The reaction flask was flushed with Ar. Terminal alkyne was added to the reaction mixture and the reaction mixture was stirred at room temperature for overnight. After completion, the reaction was quenched with saturated NH_4Cl solution (5 mL) followed by extraction with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to provide the corresponding *N,N*-dialkyl-2-(1-alkynyl)aniline product.

General procedure for the synthesis *N*-alkyl-3-sulfonylindoles

To a solution of *N,N*-dialkyl-2-(1-ethynyl)aniline **1** (0.25 mmol), arenesulfonyl hydrazide **2** (1.25 mmol, and 70% aqueous TBHP (1.5 mmol) in EtOAc (2 mL) was added iodine (0.3 mmol). The reaction was stirred at 80 ^{o}C for 2–6 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (2 mL) followed by extraction with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and filtered. The solvent was removed (aspirator) and the crude residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to afford the corresponding 3-sulfonylindole product.

General procedure for the synthesis *N*-alkyl-3-sulfanylindoles

To a solution of *N,N*-dialkyl-2-(1-ethynyl)aniline **1** (0.25 mmol) and arenesulfonyl hydrazide **2** (0.75 mmol) in EtOAc (2 mL) was added iodine (0.275 mmol). The reaction was stirred at 80 ^{o}C for 2 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (2 mL) followed by extraction with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and filtered. The solvent was removed (aspirator) and the crude residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to afford the corresponding 3-sulfanylindole product.

1-Methyl-2-(*p*-tolyl)-3-tosyl-1H-indole (3aa). white solid (81.7 mg, 87%); mp = 153–155 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.33–8.30 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.35–7.34 (m, 3H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 3.48 (s, 3H), 2.48 (s, 3H), 2.31 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.5, 142.7, 141.4, 139.7, 136.1, 130.7, 129.1, 128.8, 126.5, 126.1, 125.0, 123.4, 122.5, 120.7, 109.9, 30.9, 21.5, 21.4 ppm.; IR (neat) *v* 1310, 1143, 1083 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{23}H_{21}NO_2SNa$ 398.1191, found 398.1192.

1-Methyl-3-(phenylsulfonyl)-2-(*p*-tolyl)-1H-indole (3ab). pale yellow solid (47.9 mg, 53%); mp = 183–185 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.35–8.32 (m, 1H), 7.65–7.63 (m, 2H), 7.42–7.28 (m, 8H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.49 (s, 3H), 2.48 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.7, 144.1, 139.8, 136.1, 132.0, 130.6, 129.1, 128.8, 128.5, 126.4, 125.9, 125.0, 123.4, 122.6, 120.6, 113.0, 110.0, 30.9, 21.5 ppm.; IR (neat) *v* 1296, 1138, 1080 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{19}NO_2SNa$ 384.1034, found 384.1036.

3-((4-Chlorophenyl)sulfonyl)-1-methyl-2-(*p*-tolyl)-1H-indole (3ac). yellow solid (85.1 mg, 86%); mp = 190–192 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.30–8.29 (m, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.37–7.36 (m, 3H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.27–7.24 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 3.50 (s, 3H), 2.48 (s, 3 H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.8, 142.7, 140.0, 138.4, 136.1, 130.6, 128.9, 128.7, 127.9, 125.8, 124.9, 123.6, 122.8, 120.5, 112.7, 110.1, 31.0, 21.5 ppm.; IR (neat) *v* 1296, 1138, 1080 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{18}ClNO_2SNa$ 418.0644, found 418.0646.

3-((4-Bromophenyl)sulfonyl)-1-methyl-2-(*p*-tolyl)-1H-indole (3ad). pale yellow solid (106.8 mg, 97%); mp = 220–223 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.32–8.29 (m, 1H), 7.48–7.41 (m, 4H), 7.37–7.35 (m, 3H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 3.50 (s, 3H), 2.48 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.8, 143.2, 140.0, 136.1, 131.7, 130.6, 128.9, 128.0, 126.9, 125.8, 124.9, 123.6, 122.8, 120.5, 112.6, 110.1, 31.0, 21.5 ppm.; IR (neat) *v* 1322, 1147, 1080 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{18}BrNO_2SNa$ 462.0139, found 462.0124.

1-Methyl-3-((4-nitrophenyl)sulfonyl)-2-(*p*-tolyl)-1H-indole (3ae). yellow solid (75.2 mg, 74%); mp = 192–194 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.33–8.30 (m, 1H), 8.12 (d, *J* = 8.9 Hz, 2H), 7.74 (d, *J* = 8.9 Hz, 2H), 7.40–7.39 (m, 3H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 3.52 (s, 3H), 2.50 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 149.6, 145.6, 140.4, 136.2, 130.6, 129.0, 127.6, 125.4, 124.9, 123.9, 123.8, 123.2, 120.4, 111.5, 110.3, 31.1, 21.5 ppm.; IR (neat) *v* 1294, 1146, 1079 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{18}N_2O_4SNa$ 429.0885, found 429.0886.

3-((3-Fluorophenyl)sulfonyl)-1-methyl-2-(*p*-tolyl)-1H-indole (3af). colourless solid (74.9 mg, 79%); mp = 153–155 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.32–8.30 (m, 1H), 7.44–7.41 (m, 1H), 7.38–7.36 (m, 3H), 7.32–7.23 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.11–7.06 (m, 1H), 3.50 (s, 3H), 2.48 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 163.0 (d, $J_{C,F}$ = 251 Hz), 146.1 (d, $J_{C,F}$ = 6 Hz), 145.0, 140.1, 136.1, 130.6, 130.3, 128.9, 125.7, 125.0, 123.6, 122.8, 122.2 (d, $J_{C,F}$ = 3 Hz), 120.5, 119.3 (d, $J_{C,F}$ = 21 Hz), 113.8 (d, $J_{C,F}$ = 24 Hz), 112.4, 110.1, 31.0, 21.5 ppm.; IR (neat) *v* 1295, 1133, 1078 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{18}FNO_2SNa$ 402.0940, found 402.0943.

3-((2,4-Dimethylphenyl)sulfonyl)-1-methyl-2-(*p*-tolyl)-1H-indole (3ag). white solid (10.7 mg, 11%); mp = 187–189 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.37–8.35 (m, 1H), 7.38–7.32 (m, 3H), 7.17 (s, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 3.49 (s, 3H), 2.41 (s, 3H), 2.24 (s, 3H), 2.10 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.1, 140.7, 139.4, 135.6, 134.9, 134.4, 132.6, 131.6, 130.8, 130.4, 129.3, 128.6, 125.7, 125.5, 123.2, 122.4, 121.0, 109.9, 30.8, 21.4, 20.5, 19.5 ppm.; IR (neat) *v* 1281, 1129, 1059 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{24}H_{23}NO_2SNa$ 412.1347, found 412.1345.

5-Bromo-1-methyl-2-(*p*-tolyl)-3-tosyl-1H-indole (3ba). white solid (44.3 mg, 39%); mp = 179–181 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.48 (d, *J* = 1.8 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.42 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.22–7.16 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.45 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.3, 143.0, 141.1, 140.0, 134.8, 131.5, 130.6, 130.4, 129.2, 128.9, 126.5, 126.4, 125.6, 123.2, 116.1, 111.4, 31.0, 21.5, 21.4 ppm.; IR (neat) *v* 1313, 1145, 1082 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{20}BrNO_2SNa$ 476.0296, found 476.0294.

5-Chloro-1-methyl-2-(*p*-tolyl)-3-tosyl-1H-indole (3ca). white solid (44.1 mg, 43%); mp = 173–175 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.33–8.32 (m, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.31–7.24 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 6.8 Hz, 2H), 3.46 (s, 3H), 2.48 (s, 3H), 2.33 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.5, 143.0, 141.1, 140.0, 134.5, 130.6, 130.4, 129.2, 128.9, 128.5, 126.5, 126.0, 125.6, 123.9, 120.2, 111.0, 31.1, 21.5, 21.4 ppm.; IR (neat) *v* 1313, 1147, 1083 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{20}ClNO_2SNa$ 432.0801, found 432.0807.

6-Chloro-1-methyl-2-(*p*-tolyl)-3-tosyl-1H-indole (3da). white solid (73.8 mg, 72%); mp = 182–84 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.23 (d, *J* = 8.9 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.35–7.29 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.44 (s, 3H), 2.47 (s, 3H), 2.32 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.0, 143.0, 141.0, 140.0, 136.5, 130.6, 129.4, 129.2, 128.8, 126.5, 125.6, 123.5, 123.2, 121.7, 113.8, 110.1, 31.0, 21.5, 21.4 ppm.; IR (neat) *v* 1313, 1148, 1084 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{23}H_{21}ClNO_2S$ 410.0982, found 410.0988.

5-Fluoro-1-methyl-2-(*p*-tolyl)-3-tosyl-1H-indole (3ea). white solid (35.4 mg, 36%); mp = 170–173 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.00 (dd, *J* = 9.7, 2.4 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.31–7.25 (m, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.12–7.10 (m, 3H), 3.47 (s, 3H), 2.47 (s, 3H), 2.32 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 159.3 (d, $J_{C,F}$ = 238 Hz), 145.6, 142.9, 141.2, 139.9, 132.6, 130.6, 129.2, 128.8, 126.5, 125.8, 125.6 (d, $J_{C,F}$ = 11 Hz), 113.6, 111.9 (d, $J_{C,F}$ = 26 Hz), 110.8 (d, $J_{C,F}$ = 10 Hz), 106.1 (d, $J_{C,F}$ = 26 Hz), 31.1, 21.5, 21.4 ppm.; IR (neat) *v* 1312, 1168, 1082 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{23}H_{21}FNO_2S$ 394.1277, found 394.1280.

1,5-Dimethyl-2-(*p*-tolyl)-3-tosyl-1H-indole (3fa). white solid (68.2 mg, 70%); mp = 169–170 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.10 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.29–7.14 (m, 6H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.44 (s, 3H), 2.52 (s, 3H), 2.46 (s, 3H), 2.31 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.3, 142.6, 141.5, 139.6, 134.5, 132.1, 130.7, 129.1, 128.7, 126.4, 126.2, 125.2, 124.9, 120.2, 112.7, 109.6, 30.9,21.6, 21.5, 21.4 ppm.; IR (neat) *v* 1313, 1142, 1081 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{24}H_{24}NO_2S$ 390.1528, found 390.1522.

1-Methyl-2-phenyl-3-tosyl-1H-indole (3ga). pale yellow solid (43.4 mg, 48%); mp = 131–133 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.35–8.33 (m, 1H), 7.54–7.47 (m, 5H), 7.37–7.26 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.48 (s, 3H), 2.31 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.1, 142.7, 141.3, 136.1, 130.8, 129.6, 129.6, 129.1, 128.0, 126.5, 125.0, 123.5, 122.6, 120.7, 113.6, 110.0, 30.9, 21.4 ppm.; IR (neat) *v* 1313, 1145, 1082 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{19}NO_2SNa$ 384.1034, found 384.1037.

2-(4-Fluorophenyl)-1-methyl-3-tosyl-1H-indole (3ha). white solid (52.2 mg, 55%); mp = 159–162 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.34–8.31 (m, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.37–7.34 (m, 3H), 7.32–7.29 (m, 2H), 7.21–7.18 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.49 (s, 3H), 2.32 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 163.5 (d, $J_{C,F}$ = 250 Hz), 142.9, 141.2, 136.1, 132.8 (d, $J_{C,F}$ = 8 Hz), 129.2, 126.4, 125.0 (d, $J_{C,F}$ = 3 Hz), 124.9, 123.6,

122.7, 120.7, 115.3 (d, $J_{C,F}$ = 22 Hz), 113.9, 110.0, 30.9, 21.4 ppm.; IR (neat) *v* 1317, 1143, 1082 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{19}FNO_2SNa$ 402.0940, found 402.0937.

2-(3-Fluorophenyl)-1-methyl-3-tosyl-1H-indole (3ia). white solid (47.4 mg, 50%); mp = 144–147 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 8.33–8.31 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.50–7.45 (m, 1H), 7.38–7.36 (m, 3H), 7.27–7.24 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 3H), 7.00–6.97 (m, 1H), 3.49 (s, 3H), 2.33 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 162.1 (d, $J_{C,F}$ = 248 Hz), 143.0, 142.4, 141.1, 136.1, 131.1 (d, $J_{C,F}$ = 8 Hz), 129.8 (d, $J_{C,F}$ = 8 Hz), 129.2, 126.8, 126.5, 124.8, 123.8, 122.8, 120.8, 117.9 (d, $J_{C,F}$ = 22 Hz), 116.8 (d, $J_{C,F}$ = 21 Hz), 114.0, 110.0, 31.0, 21.4 ppm.; IR (neat) *v* 1295, 1133, 1078 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{18}FNO_2SNa$ 402.0940, found 402.0935.

2-(3-Bromophenyl)-1-methyl-3-tosyl-1H-indole (3ja). yellow solid (58.3 mg, 53%); mp = 115–117 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 8.35–8.33 (m, 1H), 7.68–7.66 (m, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.41–7.28 (m, 6H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.50 (s, 3H), 2.34 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 143.1, 142.0, 141.0, 136.1, 133.3, 132.8, 131.2, 129.7, 129.6, 129.3, 126.6, 124.8, 123.8, 122.8, 122.0, 120.9, 110.0, 31.0, 21.5 ppm.; IR (neat) *v* 1312, 1144, 1083 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{22}H_{19}BrNO_2S$ 440.0320, found 440.0316.

2-(4-Bromophenyl)-1-methyl-3-tosyl-1H-indole (3ka). pale yellow solid (89.2 mg, 81%); mp = 185–187 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 8.33–8.30 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.37–7.35 (m, 3H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 3.49 (s, 3H), 2.33 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 143.0, 142.6, 141.2, 136.2, 132.5, 131.4, 129.3, 128.5, 128.0, 126.4, 124.9, 124.4, 123.8, 122.8, 120.8, 110.0, 31.0, 21.4 ppm.; IR (neat) *v* 1299, 1144, 1083 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{22}H_{19}BrNO_2S$ 440.0320, found 440.0317.

1-Methyl-2-(4-nitrophenyl)-3-tosyl-1H-indole (3la). yellow solid (53.9 mg, 53%); mp = 208–210 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 8.37 (d, *J* = 8.8 Hz, 2H), 8.31–8.29 (m, 1H), 7.58–7.52 (m, 4H), 7.41–7.38 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.51 (s, 3H), 2.33 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.6, 143.4, 140.9, 136.5, 135.9, 132.2, 130.2, 130.1, 129.4, 126.3, 124.7, 124.3, 123.2, 123.1, 120.9, 110.1, 31.2, 21.5 ppm.; IR (neat) *v* 1302, 1147, 1082 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{18}N_2O_4SNa$ 429.0885, found 429.0880.

1-Methyl-3-tosyl-2-(4-(trifluoromethyl)phenyl)-1H-indole (3ma). white solid (39.7 mg, 37%); mp = 198–200 °C (from CH_2Cl_2/hexanes) ; ^1H NMR (400 MHz; $CDCl_3$) δ 8.34 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.52–7.46 (m, 4H), 7.40–7.37 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.49 (s, 3H), 2.32 (s, 3H) ppm.; ^{13}C NMR (125 MHz; $CDCl_3$) δ 143.1, 142.0, 141.1, 136.3, 133.0, 131.8 (q, $J_{C,F}$ = 33 Hz), 131.4, 129.8, 126.5, 125.0 (q, $J_{C,F}$ = 4 Hz), 124.9, 124.0, 123.9 (q, $J_{C,F}$ = 273 Hz), 122.9, 120.9, 114.5, 110.1, 31.1, 21.4 ppm.; IR (neat) *v* 1321, 1146, 1083 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{23}H_{18}F_3NO_2SNa$ 452.0908, found 452.0915.

2-(4-Methoxyphenyl)-1-methyl-3-tosyl-1H-indole (3na). pale yellow solid (51.9 mg, 53%); mp = 165–167 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 8.34–8.31 (m, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.35–7.32 (m, 3H), 7.26–7.23 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 3.49 (s, 3H), 2.31 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.6, 144.3, 142.7, 141.4, 136.1, 132.3, 130.1, 129.1, 126.5, 125.1, 123.4, 122.5, 121.0, 120.7, 113.5, 109.9, 55.4, 30.9, 21.4 ppm.; IR (neat) *v* 1289, 1144, 1082 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{21}NO_3SNa$ 414.1140, found 414.1145.

2-(2-Bromophenyl)-1-methyl-3-tosyl-1H-indole (3oa). colourless solid (12.1 mg, 11%); mp = 182–184 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 8.31–8.29 (m, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H),

7.50–7.48 (m, 2H), 7.44–7.35 (m, 4H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.48 (s, 3H), 2.33 (s, 3H) ppm.; ^{13}C NMR (125 MHz; $CDCl_3$) δ 143.0, 142.2, 140.7, 136.0, 133.9, 132.3, 131.4, 130.6, 129.2, 127.0, 126.8, 124.7, 124.6, 123.5, 122.6, 120.7, 113.7, 110.1, 30.6, 21.5 ppm.; IR (neat) *v* 1299, 1146, 1081 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{18}BrNO_2SNa$ 462.0139, found 462.0134.

1-Methyl-2-(naphthalen-2-yl)-3-tosyl-1H-indole (3qa). brown solid (75.1 mg, 73%); mp = 170–172 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.40–8.37 (m, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.77 (s, 1H), 7.64–7.58 (m, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.40–7.37 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 2H), 3.51 (s, 3H), 2.30 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.1, 142.9, 141.3, 136.2, 133.6, 132.5, 130.9, 129.1, 128.4, 127.9, 127.8, 127.6, 127.3, 126.7, 126.6, 125.1, 123.6, 122.7, 120.8, 114.0, 110.0, 31.1, 21.4 ppm.; IR (neat) *v* 1298, 1144, 1082 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{26}H_{21}NO_2SNa$ 434.1191, found 434.1197.

2-Hexyl-1-methyl-3-tosyl-1H-indole (3ra). colourless solid (54.5 mg, 59%); mp = 100–103 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.14–8.12 (m, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.28–7.20 (m, 5H), 3.68 (s, 3H), 3.16–3.12 (m, 2H), 2.34 (s, 3H), 1.57–1.51 (m, 4H), 1.47–1.43 (m, 4H), 1.33–1.29 (m, 4H), 0.92–0.88 (m, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 146.3, 142.9, 141.8, 136.3, 129.7, 129.4, 126.1, 125.1, 122.8, 122.2, 120.0, 109.5, 31.5, 29.9, 29.6, 29.5, 25.0, 22.5, 21.4, 14.1 ppm.; IR (neat) *v* 1298, 1141, 1083 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{22}H_{28}NO_2S$ 370.1841, found 370.1839.

1-Ethyl-2-(p-tolyl)-3-tosyl-1H-indole (3sa). pale solid (35.1 mg, 36%); mp = 145–147 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.32–8.30 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.39–7.28 (m, 5H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 3.93 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 2.32 (s, 3H), 1.21 (t, *J* = 8.3 Hz, 2H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.0, 142.7, 141.4, 139.6, 134.9, 130.5, 129.1, 128.8, 126.6, 126.3, 125.2, 123.3, 122.4, 120.8, 113.6, 110.1, 39.0, 21.5, 21.4, 15.1 ppm.; IR (neat) *v* 1284, 1135, 1083 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{23}NO_2SNa$ 412.1347, found 412.1341.

1-(4-Iodobutyl)-2-(p-tolyl)-3-tosyl-1H-indole (3ta). white solid (34.0 mg, 25%); mp = 135–137 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.33–8.31 (m, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.38–7.26 (m, 5H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.91 (t, *J* = 7.3 Hz, 2H), 2.98 (t, *J* = 6.7 Hz, 2H), 2.48 (s, 3H), 2.32 (s, 3H), 1.76–1.70 (m, 2H), 1.65–1.60 (m, 2H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.0, 142.3, 141.2, 139.8, 135.1, 130.7, 129.2, 128.9, 126.6, 126.0, 125.1, 123.5, 122.5, 120.9, 110.2, 42.9, 30.4, 30.3, 21.6, 21.4, 5.2 ppm.; IR (neat) *v* 1297, 1138, 1085 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{26}H_{26}INO_2SNa$ 566.0627, found 566.0630.

1-Methyl-2-(p-tolyl)-3-(p-tolylthio)-1H-indole (4aa). pale yellow solid (80.7 mg, 94%); mp = 113–115 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.33–7.24 (m, 5H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.95 (s, 4H), 3.73 (s, 3H), 2.40 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.9, 138.6, 137.5, 136.4, 134.0, 130.4, 129.8, 129.4, 129.0, 127.5, 125.6, 122.6, 120.8, 119.7, 90.7, 31.6, 21.4, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{21}NSNa$ 366.1292, found 366.1292.

1-Methyl-3-(phenylthio)-2-(p-tolyl)-1H-indole (4ab).[23c] pale yellow solid (76.6 mg, 93%); mp = 114–116 °C (from CH_2Cl_2/hexanes) (lit.[23c] mp 112.6–113.8 °C); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.33–7.23 (m, 5H), 7.20–7.11 (m, 3H), 7.05–6.99 (m, 3H), 3.73 (s, 3H), 2.40 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 146.1, 140.1, 138.7, 137.5, 130.4, 129.7, 129.0, 128.6, 127.4, 125.4, 124.3, 122.6, 120.8, 119.7, 109.8, 99.2, 31.6, 21.4 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{22}H_{20}NS$ 330.1316, found 330.1318.

3-((4-Chlorophenyl)thio)-1-methyl-2-(p-tolyl)-1H-indole (4ac). colourless solid (88.2 mg, 97%); mp = 135–137 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.25–7.09 (m, 6H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.63 (s, 3H), 2.32 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ

146.2, 138.9, 138.7, 137.5, 130.3, 130.0, 129.5, 129.0, 128.6, 127.3, 126.6, 122.8, 121.0, 119.5, 109.9, 98.8, 31.6, 21.4 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{22}H_{19}ClNS$ 364.0927, found 364.0930.

3-((4-Bromophenyl)thio)-1-methyl-2-(p-tolyl)-1H-indole (4ad). colourless solid (97.0 mg, 95%); mp = 133–135 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.33–7.17 (m, 8H), 6.89 (d, *J* = 8.3 Hz, 2H), 3.72 (s, 3H), 2.40 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 146.2, 139.4, 138.9, 137.5, 131.5, 130.3, 129.4, 129.1, 127.2, 126.9, 122.8, 121.0, 119.5, 117.8, 109.9, 98.6, 31.7, 21.4 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{22}H_{19}BrNS$ 408.0422, found 408.0425.

1-Methyl-3-((4-nitrophenyl)thio)-2-(*p*-tolyl)-1H-indole (4ae). yellow solid (87.1 mg, 93%); mp = 128–130 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.26–7.20 (m, 5H), 7.09 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 2.40 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 150.5, 146.6, 144.7, 139.2, 137.6, 130.2, 129.2, 129.0, 126.9, 124.8, 123.8, 123.1, 121.3, 119.1, 110.1, 96.7, 31.7, 21.4 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{18}N_2O_2SNa$ 397.0987, found 397.0988.

3-((3-Fluorophenyl)thio)-1-methyl-2-(*p*-tolyl)-1H-indole (4af). pale yellow solid (82.5 mg, 95%); mp = 88–90 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.34–7.18 (m, 6H), 7.11–7.06 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.71–6.68 (m, 2H), 3.73 (s, 3H), 2.40 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 163.1 (d, $J_{C,F}$ = 245 Hz), 146.3, 142.9 (d, $J_{C,F}$ = 2 Hz), 138.9, 137.6, 130.3, 129 (d, $J_{C,F}$ = 8 Hz), 129.5, 129.1, 127.3, 122.8, 121.0, 120.9 (d, $J_{C,F}$ = 2 Hz), 119.5, 112.2 (d, $J_{C,F}$ = 24 Hz), 111.2 (d, $J_{C,F}$ = 22 Hz), 109.9, 98.4, 31.7, 21.4 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{22}H_{19}FNS$ 348.1222, found 348.1220.

3-((2,4-Dimethylphenyl)thio)-1-methyl-2-(*p*-tolyl)-1H-indole (4ag). pale yellow solid (85.8 mg, 96%); mp = 85–87 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.32–7.29 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H). 6.97 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.4 Hz, 1H), 6.57 (s, 1H), 3.75 (s, 3H), 2.39 (s, 3H), 2.34 (s, 3H), 2.05 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.9, 138.5, 138.4, 137.7, 135.6, 131.3, 130.4, 129.9, 129.6, 129.0, 127.5, 125.7, 125.0, 122.5, 120.7, 119.8, 109.7, 99.1, 31.7, 21.4, 21.1, 19.4 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{24}H_{24}NS$ 358.1629, found 358.1622

3-((4-Methoxyphenyl)thio)-1-methyl-2-(*p*-tolyl)-1H-indole (4ah). pale yellow solid (74.6 mg, 83%); mp = 97–99 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.31–7.23 (m, 5H), 7.20–7.17 (m, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 3.70 (s, 6H), 2.41 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 157.4, 145.6, 138.6, 137.5, 132,6, 130.5, 129.8, 129.0, 127.8, 127.6, 122.5, 120.7, 119.7, 114.6, 114.4, 109.7, 55.2, 31.6, 21.4 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{23}H_{22}NOS$ 360.1422, found 360.1429

1-Methyl-3-(methylthio)-2-(*p*-tolyl)-1H-indole (4ai). oil (38.8 mg, 58%); ^1H NMR (400 MHz; $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.38–7.23 (m, 7H), 3.63 (s, 3H), 2.45 (s, 3H), 2.20 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.2, 138.4, 137.2, 130.6, 129.5, 129.0, 128.0, 122.3, 120.3, 119.3, 109.7, 104.6, 31.3, 21.4, 20.2 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{17}H_{18}NS$ 268.1160, found 268.1151

5-Bromo-1-methyl-2-(*p*-tolyl)-3-(*p*-tolylthio)-1H-indole (4ba). pale yellow solid (102.4 mg, 97%); mp = 200–202 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.76 (d, *J* = 1.8 Hz, 1H), 7.37 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.29–7.24 (m, 5H), 6.97–6.90 (m, 4H), 3.70 (s, 3H), 2.40 (s, 3H), 2.25 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 147.1, 139.0, 136.2, 135.9, 134.3, 131.6, 130.4, 129.5, 129.1, 127.1, 125.7, 125.5, 122.2, 114.3, 111.3, 31.8, 21.4, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{20}BrNSNa$ 446.0377, found 446.0383.

5-Chloro-1-methyl-2-(*p*-tolyl)-3-(*p*-tolylthio)-1H-indole (4ca). pale yellow solid (87.9 mg, 93%); mp = 181–183 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.60 (d, *J* = 1.3 Hz, 1H), 7.32–7.22 (m, 6H), 6.97–6.90 (m, 4H), 3.70 (s, 3H), 2.40 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 147.2, 139.0, 135.9, 134.3, 131.0, 130.3, 129.5, 129.1, 127.1, 126.7, 125.7, 122.9, 119.1, 110.8, 99.6, 31.8, 21.4, 20.8 ppm.; HRMS (ESI-TOF) *m/z* [M]$^+$ calcd for $C_{23}H_{20}ClNS$ 377.1005, found 377.1006.

6-Chloro-1-methyl-2-(*p*-tolyl)-3-(*p*-tolylthio)-1H-indole (4da). amorphous solid (92.6 mg, 98%); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 1H), 7.39 (s, 1H), 7.26 (dd, *J* = 14.1, 8.2 Hz, 4H), 7.12 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.93 (dd, *J* = 15.0, 8.2 Hz, 4H), 3.67 (s, 3H), 2.40 (s, 3H), 2.23 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 146.5, 138.9, 137.9, 135.9, 134.3, 130.4, 129.4, 129.1, 128.4, 128.3, 127.1, 125.7, 121.4, 120.6, 109.9, 100.3, 31.7, 21.4, 20.8 ppm.; HRMS (ESI-TOF) *m/z* [M]$^+$ calcd for $C_{23}H_{20}ClNS$ 377.1005, found 377.1006.

5-Fluoro-1-methyl-2-(*p*-tolyl)-3-(*p*-tolylthio)-1H-indole (4ea). pale yellow solid (81.3 mg, 90%); mp = 129–131 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.33–7.24 (m, 6H), 7.02 (td, *J* = 9.0, 2.5 Hz, 1H), 6.97–6.91 (m, 4H), 3.71 (s, 3H), 2.40 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 158.7 (d, $J_{C,F}$ = 236 Hz), 147.4, 138.9, 135.9, 134.3, 134.0, 130.6 (d, $J_{C,F}$ = 10 Hz), 130.4, 129.5, 129.0, 127.3, 125.7, 110.9 (d, $J_{C,F}$ = 26 Hz), 110.5 (d, $J_{C,F}$ = 10 Hz), 99.9, 31.8, 21.4, 20.8 ppm.; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{23}H_{21}FNS$ 362.1379, found 362.1377.

1,5-Dimethyl-2-(*p*-tolyl)-3-(*p*-tolylthio)-1H-indole (4fa). pale yellow solid (86.7 mg, 97%); mp = 144–146 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.43 (s, 1H), 7.31–7.27 (m, 3H), 7.24–7.22 (m, 2H), 7.12 (dd, *J* = 1.2, 8.3 Hz, 1H), 6.95 (s, 4H), 3.69 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 146.0, 138.5, 136.7, 135.9, 133.8, 130.4, 130.2, 130.1, 129.4, 128.9, 127.6, 125.4, 124.2, 119.2, 109.4, 98.7, 31.7, 21.4, 21.3, 20.8 ppm.; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{24}H_{24}NS$ 358.1629, found 358.1623.

1-Methyl-2-phenyl-3-(*p*-tolylthio)-1H-indole (4ga).[23c] colourless solid (78.2 mg, 95%); mp = 111–113 °C (from CH_2Cl_2/hexanes) (lit.[23c] mp 106.1–106.8 °C); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.45–7.39 (m, 6H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.22–7.17 (m, 1H), 6.94 (s, 4H), 3.72 (s, 3H), 2.23 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.7, 137.5, 136.3, 134.1, 130.6, 130.5, 129.7, 129.4, 128.7, 128.2, 125.7, 122.7, 120.8, 119.8, 109.8, 100.0, 31.7, 20.8 ppm.; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{22}H_{20}NS$ 330.1316, found 330.1311.

2-(4-Fluorophenyl)-1-methyl-3-(*p*-tolylthio)-1H-indole (4ha). pale yellow solid (82.5 mg, 95%); mp = 86–88 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.42–7.30 (m, 4H), 7.23–7.11 (m, 3H), 6.93 (s, 4H), 3.71 (s, 3H), 2.23 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 162.9 (d, $J_{C,F}$ = 249 Hz), 144.6, 137.5, 136.1, 134.2, 132.4 (d, $J_{C,F}$ = 8 Hz), 129.7, 129.5, 126.5, 125.7, 122.9, 121.0, 119.8, 115.4 (d, $J_{C,F}$ = 22 Hz), 109.8, 100.4, 31.6, 20.8 ppm.; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{22}H_{19}FNS$ 348.1222, found 348.1228.

2-(3-Fluorophenyl)-1-methyl-3-(*p*-tolylthio)-1H-indole (4ia). pale yellow solid (83.4 mg, 96%); mp = 77–79 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.43–7.37 (m, 2H), 7.35–7.30 (m, 1H), 7.23–7.13 (m, 2H), 7.12–7.09 (m, 2H), 6.94 (s, 4H), 3.72 (s, 3H), 2.23 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 162.3 (d, $J_{C,F}$ = 247 Hz), 144.1, 137.6, 135.9, 134.3, 132.6 (d, $J_{C,F}$ = 8 Hz), 129.8 (d, $J_{C,F}$ = 8 Hz), 129.7, 129.5, 126.4 (d, $J_{C,F}$ = 3 Hz), 125.8, 123.0, 121.0, 120.0, 117.6 (d, $J_{C,F}$ = 22 Hz), 115.6 (d, $J_{C,F}$ = 21 Hz), 109.8, 100.9, 31.7, 20.8 ppm.; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{22}H_{19}FNS$ 348.1222, found 348.1232.

2-(3-Bromophenyl)-1-methyl-3-(*p*-tolylthio)-1H-indole (4ja). amorphous solid (98.0 mg, 96%); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.56–7.54 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.35–7.28 (m, 3H), 7.24–7.18 (m, 1H), 6.94 (s, 4H), 3.72 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 143.8, 137.6, 135.8, 134.4, 133.4, 132.6, 131.7, 129.7, 129.6, 129.5, 129.3, 126.0, 123.1, 122.2, 121.0, 120.0, 109.8, 101.2, 31.7, 20.8 ppm.; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{22}H_{19}BrNS$ 410.0401, found 410.0408.

2-(3-Bromophenyl)-1-methyl-3-(*p*-tolylthio)-1H-indole (4ka). colourless solid (100.0 mg, 98%); mp = 133–134 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 6.6 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.35–7.25 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.96–6.91 (m, 4H), 3.72 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.3, 137.6, 136.0, 134.3, 132.1, 131.5, 129.7, 129.5, 129.4, 125.7, 123.2, 123.0, 121.0, 119.9, 109.8, 100.6, 31.7, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{18}BrNSNa$ 432.0221, found 432.0233.

1-Methyl-2-(4-nitrophenyl)-3-(*p*-tolylthio)-1H-indole (4la). yellow solid (40.3 mg, 43%); mp = 187–189 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 6.97–6.91 (m, 4H) , 3.77 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 147.6, 142.7, 138.0, 137.1, 135.4, 134.7, 131.5, 129.7, 129.6, 125.8, 123.7, 123.4, 121.4, 120.2, 110.0, 102.3, 32.0, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{18}N_2O_2SNa$ 397.0987, found 397.0988.

1-Methyl-3-(*p*-tolylthio)-2-(4-(trifluoromethyl)phenyl)-1H-indole (4ma). orange solid (99.4 mg, 81%); mp = 101–103 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.67 (dd, *J* = 8.6, 8.2 Hz, 3H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.36–7.31 (m, 1H), 7.22–7.18 (m, 1H), 6.94 (s, 4H), 3.72 (s, 3H), 2.23 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 143.8, 137.8, 135.7, 134.4, 134.2, 131.0, 130.5 (q, $J_{C,F}$ = 33 Hz), 129.7, 129.5, 125.8, 125.2 (q, $J_{C,F}$ = 4 Hz), 124.0 (q, $J_{C,F}$ = 272 Hz), 123.3, 121.2, 120.0, 109.9, 101.3, 31.8, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M]^+$ calcd for $C_{23}H_{18}F_3NS$ 397.1112, found 397.1116.

2-(4-Methoxyphenyl)-1-methyl-3-(*p*-tolylthio)-1H-indole (4na).[23b] pale yellow solid (78.2 mg, 87%); mp = 153–155 °C (from CH_2Cl_2/hexanes) (lit.[23b] mp 153–155 °C); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.34–7.28 (m, 3H), 7.19–7.16 (m, 1H), 6.98–6.95 (m, 6H), 3.84 (s, 3H), 3.72 (s, 3H), 2.23 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 159.9, 145.7, 137.5, 136.4, 134.0, 131.8, 129.8, 129.4, 125.6, 122.7, 122.5, 120.8, 119.6, 113.7, 109.7, 99.6, 55.3, 31.6, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{23}H_{22}NOS$ 360.1422, found 360.1428.

2-(2-Bromophenyl)-1-methyl-3-(*p*-tolylthio)-1H-indole (4oa). pale yellow solid (101.1 mg, 99%); mp = 108–110 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.41–7.31 (m, 4H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.96 (dd, *J* = 20.0, 8.3 Hz, 4H), 3.64 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.4, 137.2, 135.5, 134.2, 133.2, 132.7, 132.4, 130.7, 129.3, 127.2, 126.2, 125.3, 122.8, 120.8, 120.0, 109.8, 101.1, 31.2, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{22}H_{19}BrNS$ 410.0401, found 410.0404.

2-Mesityl-1-methyl-3-(*p*-tolylthio)-1H-indole (4pa). colourless solid (92.0 mg, 99%); mp = 152–153 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.32–7.28 (m, 1H), 7.22–7.16 (m, 1H), 6.97–6.89 (m, 6H), 3.47 (s, 3H), 2.33 (s, 3H), 2.21 (s, 3H), 1.92 (s, 6H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.3, 138.8, 138.5, 137.3, 135.2, 134.1, 129.7, 129.2, 128.9, 128.1, 127.2, 126.4, 122.0, 120.5, 119.7, 109.7, 100.2, 30.3, 21.2, 20.8, 20.1 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{25}H_{25}NSNa$ 394.1605, found 394.1607.

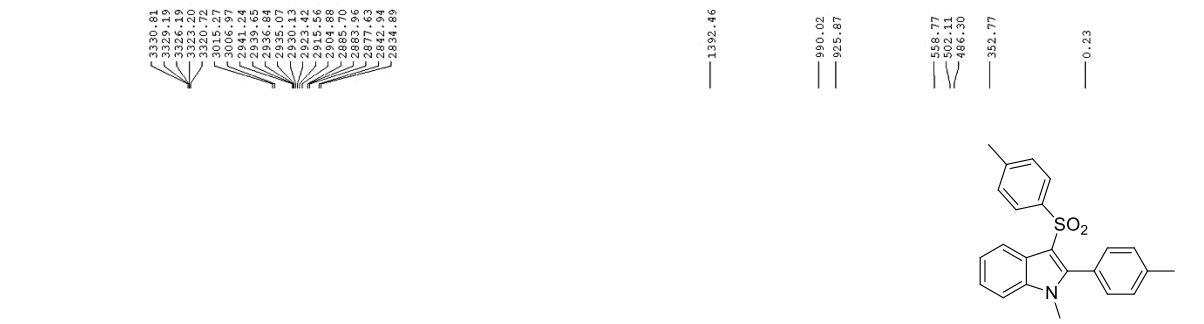
1-Methyl-2-(naphthalen-2-yl)-3-(*p*-tolylthio)-1H-indole (4qa). pale yellow solid (87.3 mg, 92%); mp = 148–150 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.91–7.87 (m, 3H), 7.83–7.81 (m, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.53–7.50 (m, 3H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.36–7.32 (m, 1H), 7.24–7.19 (m, 1H), 6.99–6.94 (m, 4H), 3.77 (s, 3H), 2.24 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.6, 137.7, 136.3, 134.2, 133.1, 132.9, 130.3, 129.9, 129.4, 128.3, 128.0, 127.9, 127.8, 127.7, 126.7, 126.4, 126.0, 122.8, 120.9, 119.9, 109.8, 100.7, 31.8, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{26}H_{21}NSNa$ 402.1292, found 402.1294.

2-Hexyl-1-methyl-3-(*p*-tolylthio)-1H-indole (4ra). oil (38.8 mg, 46%); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.47–7.21 (m, 1H), 7.14–7.10 (m, 1H), 6.94 (s, 4H), 3.76 (s, 3H), 2.94–2.91 (m, 2H), 2.23 (s, 3H), 1.57–1.50 (m, 2H), 1.33–1.22 (m, 6H), 0.85–0.82 (m, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 146.8, 137.2, 136.3, 134.0, 129.8, 129.3, 125.6, 121.6, 120.4, 119.0, 109.1, 98.3, 31.5, 30.3, 29.7, 29.1, 25.0, 22.5, 20.8, 14.0 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{27}NSNa$ 360.1762, found 360.1755.

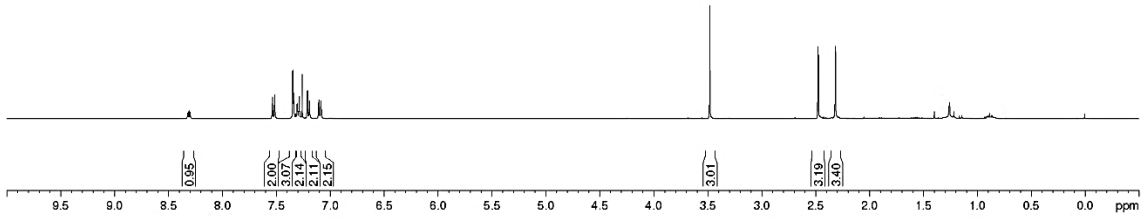
1-Ethyl-2-(*p*-tolyl)-3-(*p*-tolylthio)-1H-indole (4sa). pale yellow solid (85.8 mg, 96%); mp = 128–130 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.31–7.23 (m, 5H), 7.18–7.14 (m, 1H), 6.94 (s, 4H), 4.17 (q, *J* =7.2 Hz, 2H), 2.40 (s, 3H), 2.23 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.6, 138.6, 136.4, 136.3, 134.0, 130.2, 130.0, 129.3, 129.0, 127.9, 125.7, 122.4, 120.7, 119.9, 110.0, 100.1, 39.4, 21.4, 20.8, 15.4 ppm.; HRMS (ESI-TOF) *m/z* $[M]^+$ calcd for $C_{24}H_{23}NS$ 357.1551, found 357.1565.

1-(4-Iodobutyl)-2-(*p*-tolyl)-3-(*p*-tolylthio)-1H-indole (4ta). white solid (89.5 mg, 70%); mp = 142–140 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.31–7.24 (m, 5H), 7.19–7.15 (m, 1H), 6.96–6.91 (m, 4H), 4.17 (t, *J* = 7.2 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 2.23 (s, 3H), 1.83–1.77 (m, 2H), 1.66–1.60 (m, 2H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.7, 138.8, 136.5, 136.2, 134.0, 130.3, 129.9, 129.4, 129.2, 127.7, 125.7, 122.6, 120.8, 119.9, 110.1, 100.7, 43.3, 30.6, 30.5, 21.4, 20.8, 5.5 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{26}H_{26}INSNa$ 534.0728, found 534.0731.

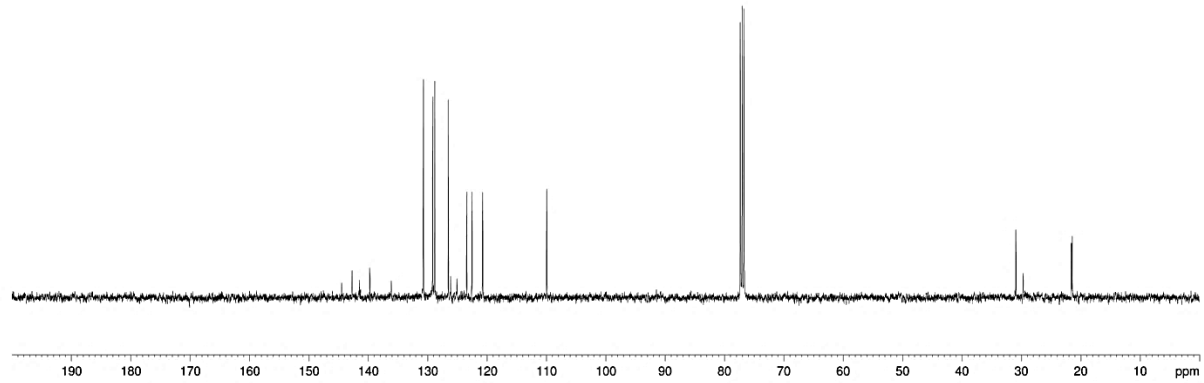
2-(2,3-Dimethoxyphenyl)-1-methyl-3-(*p*-tolylthio)-1H-indole (4ua). white solid (81.8 mg, 84%); mp = 114–116 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.34–7.29 (m, 1H), 7.20–7.19 (m, 1H), 7.11–7.07 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.96–6.91 (m, 4H), 6.58 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 3.63 (s, 3H), 3.47 (s, 3H), 2.22 (s, 3H) ppm.; ^{13}C NMR (100 MHz; $CDCl_3$) δ 152.7, 147.7, 142.7, 137.4, 136.1, 134.0, 129.6, 129.3, 125.7, 125.1, 124.6, 123.8, 122.4, 120.5, 119.7, 113.3, 109.7, 99.8, 60.7, 55.8, 31.3, 20.8 ppm.; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{23}NO_2SNa$ 412.1347, found 412.1351.

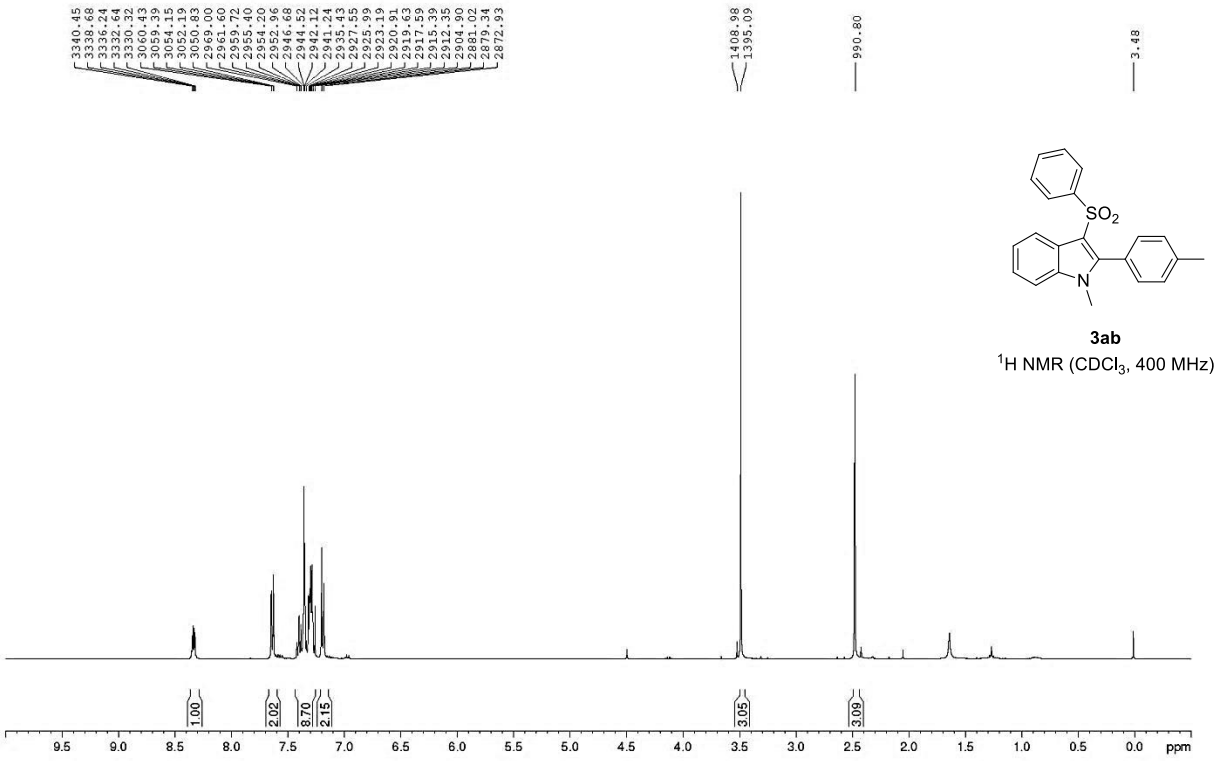


3aa
^{1}H NMR ($CDCl_3$, 400 MHz)
(from substrate **1a)**



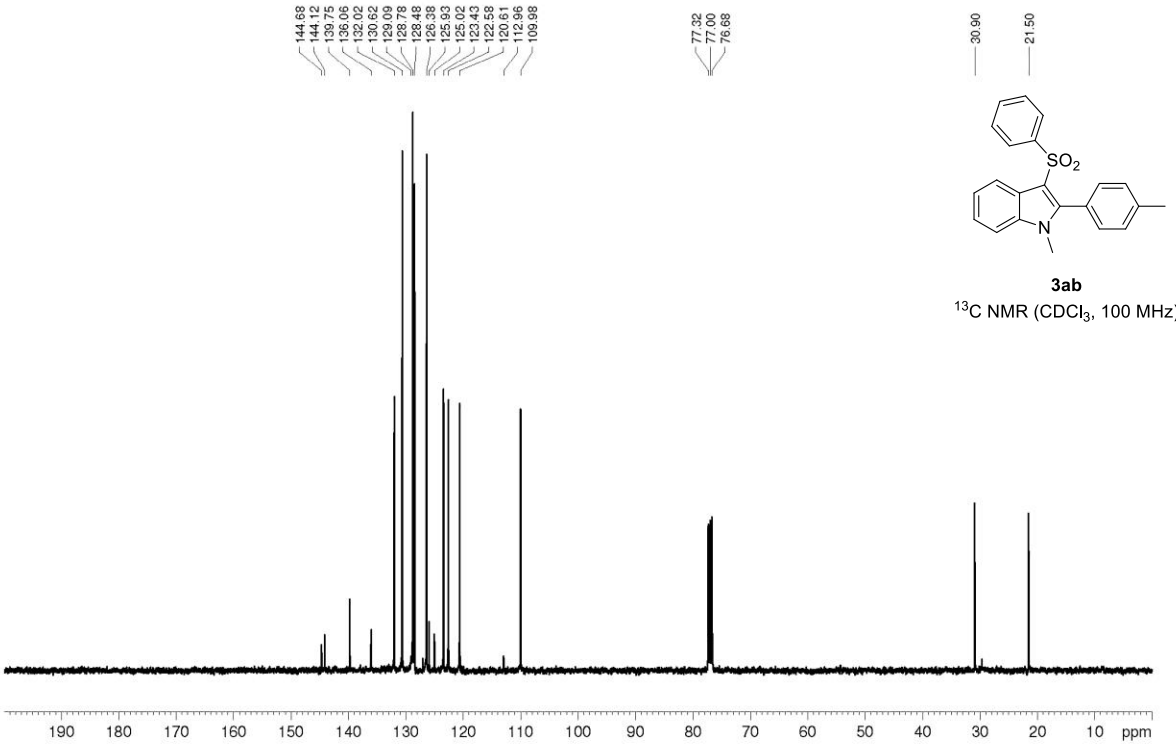
3aa
^{13}C NMR ($CDCl_3$, 100 MHz)
(from substrate **1a)**





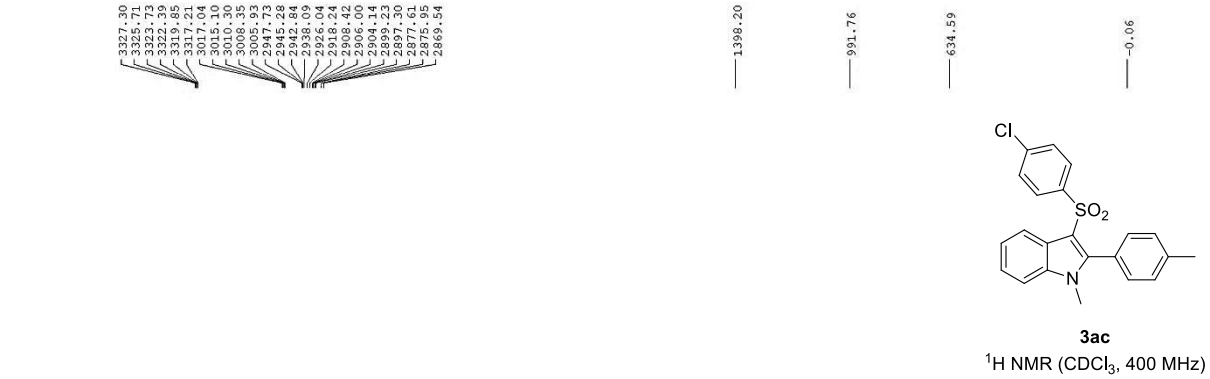
3ab

^{1}H NMR ($CDCl_3$, 400 MHz)



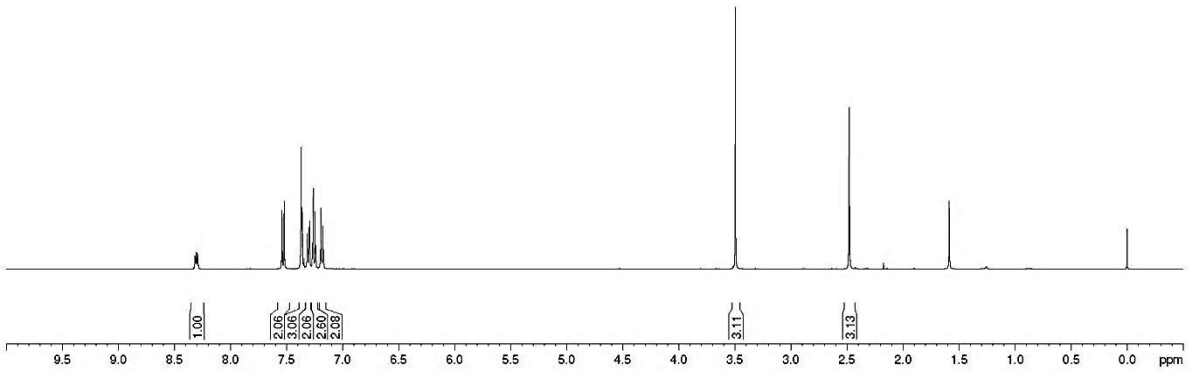
3ab

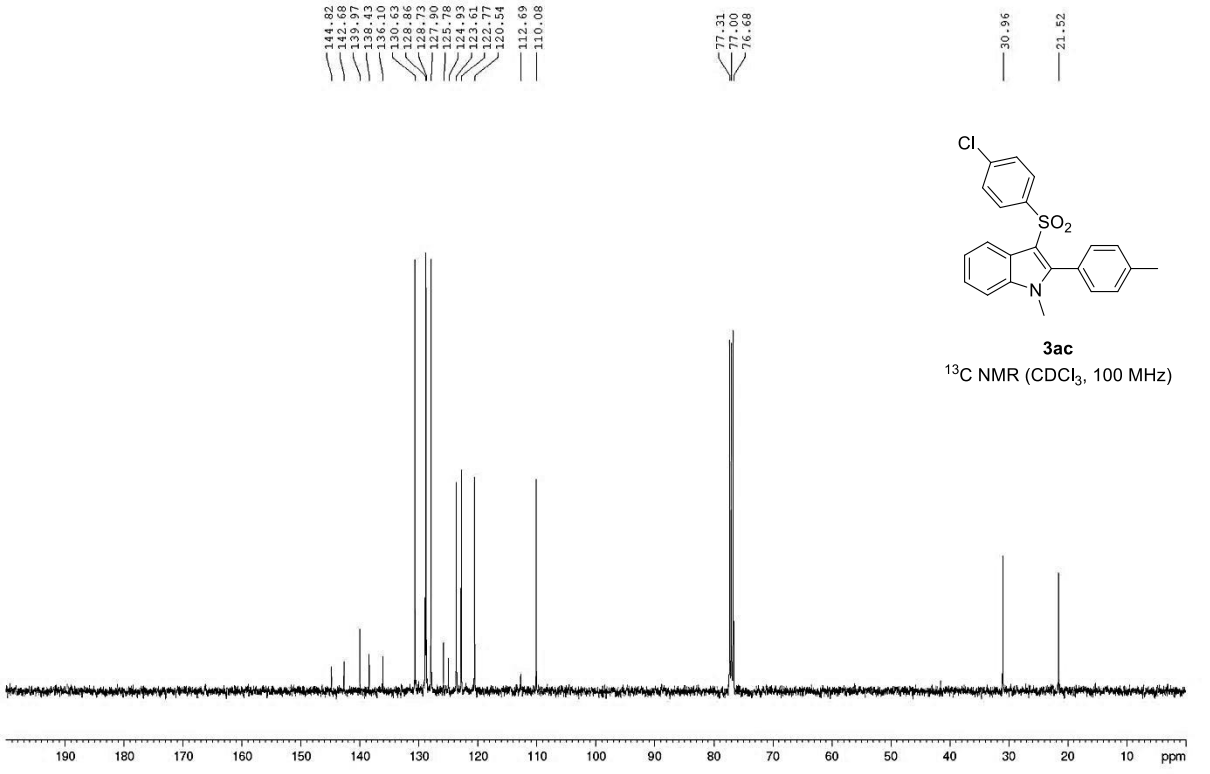
^{13}C NMR ($CDCl_3$, 100 MHz)



3ac

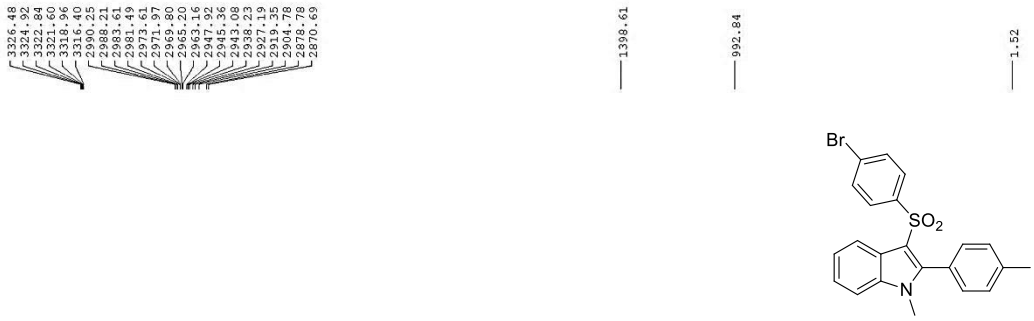
^{1}H NMR ($CDCl_3$, 400 MHz)





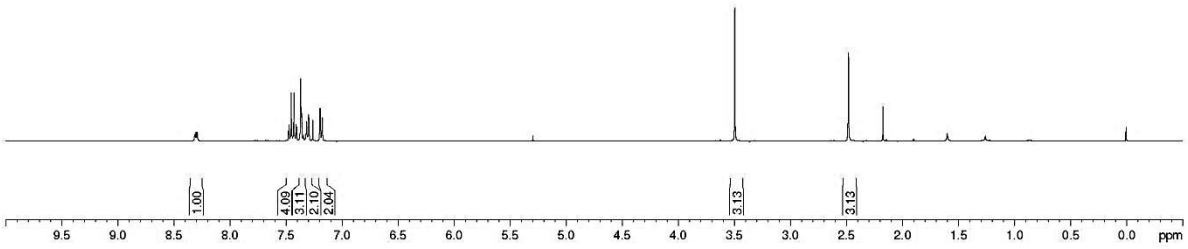
3ac

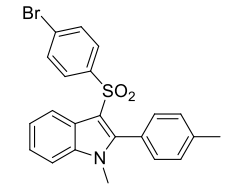
^{13}C NMR ($CDCl_3$, 100 MHz)



3ad

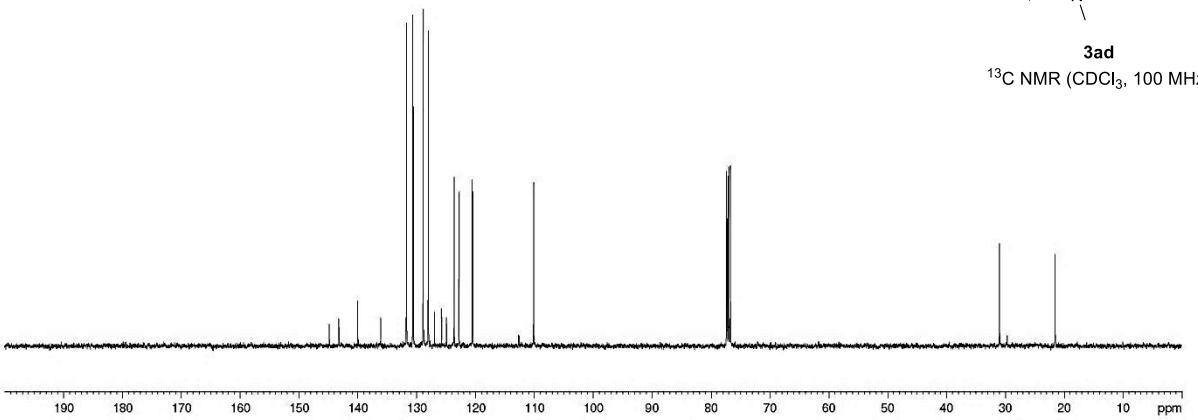
^{1}H NMR ($CDCl_3$, 400 MHz)

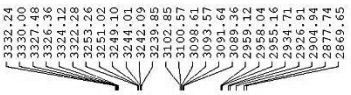


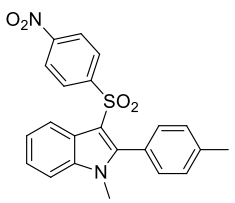


3ad

^{13}C NMR ($CDCl_3$, 100 MHz)

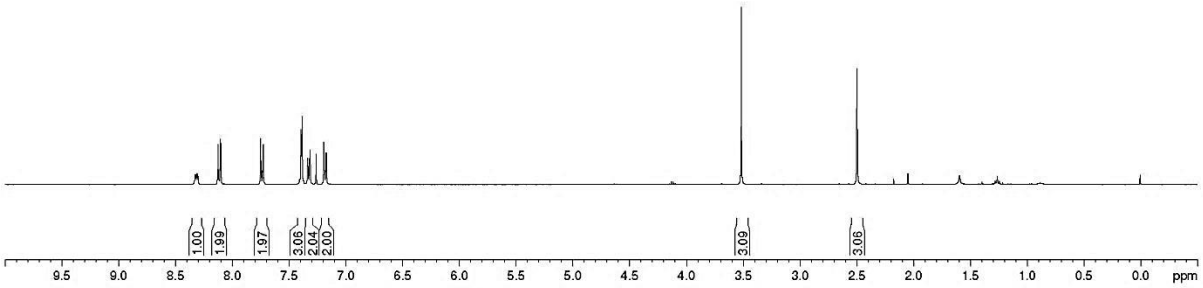


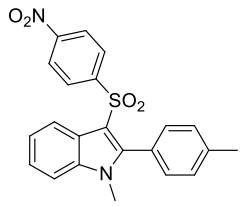




3ae

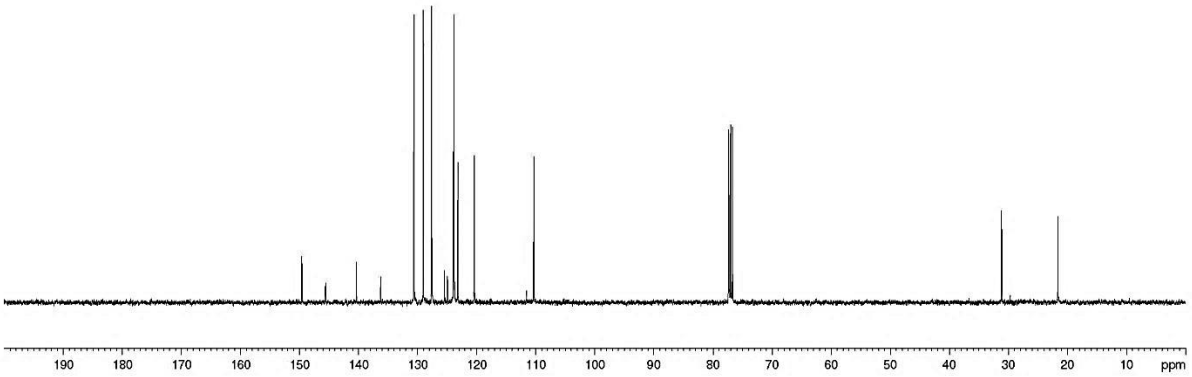
^{1}H NMR ($CDCl_3$, 400 MHz)

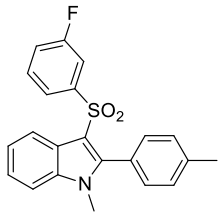




3ae

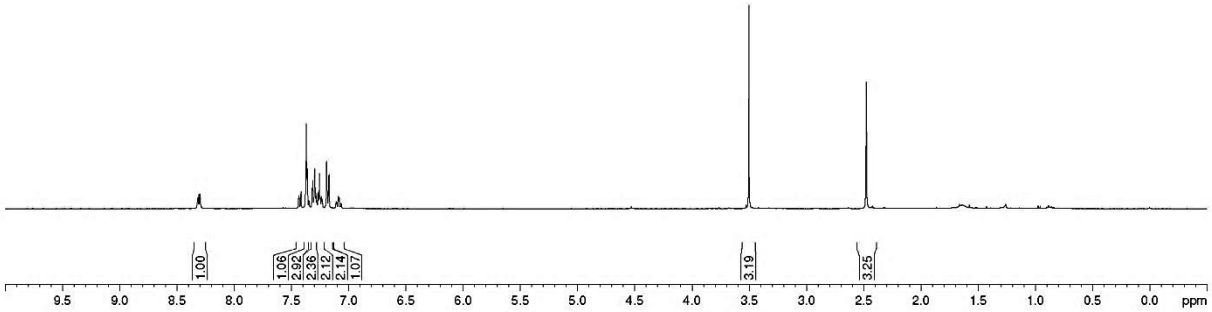
^{13}C NMR ($CDCl_3$, 100 MHz)

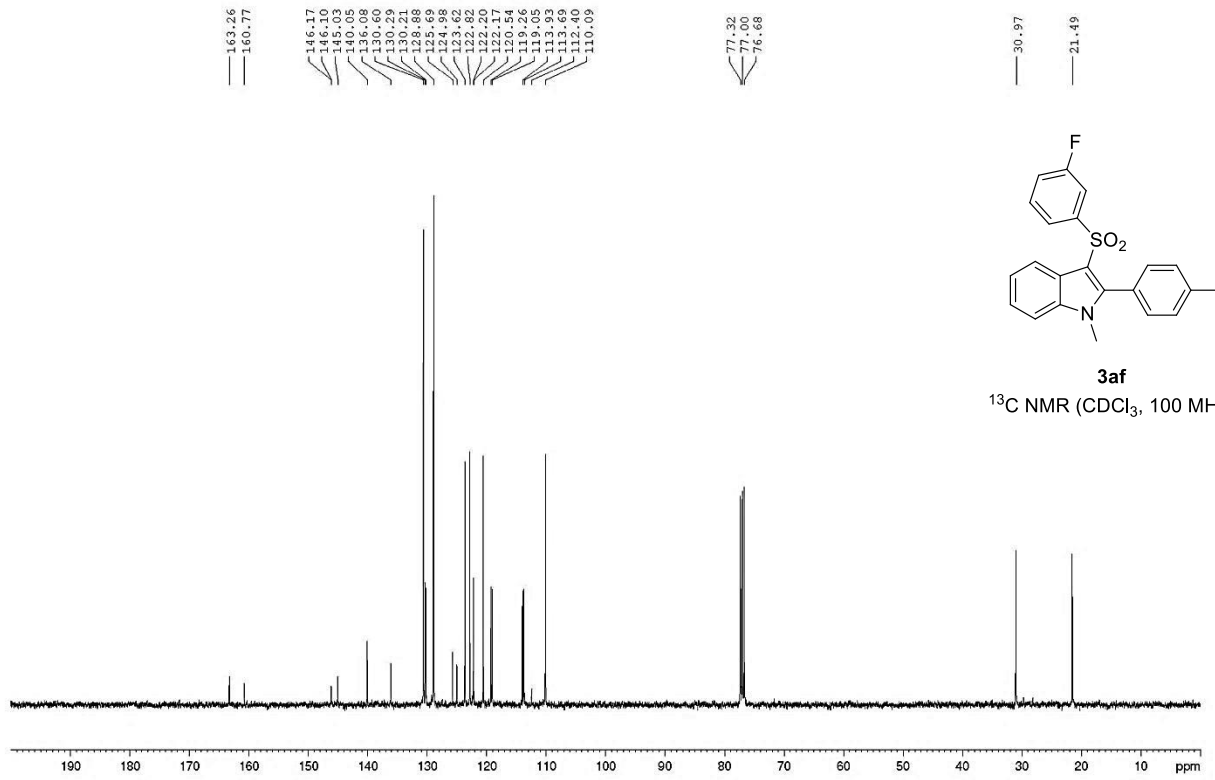




3af

^{1}H NMR ($CDCl_3$, 400 MHz)



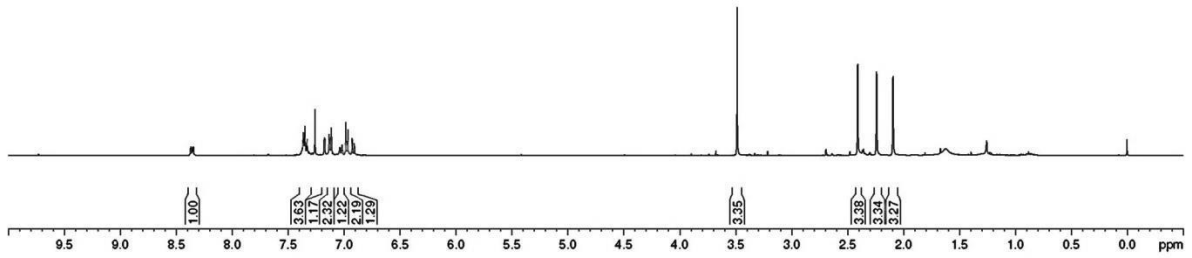


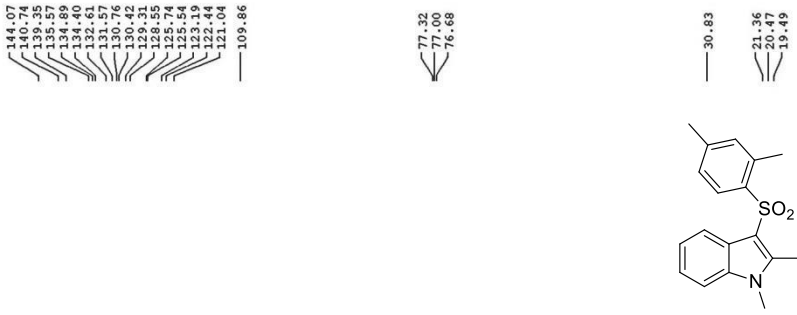
3af

^{13}C NMR ($CDCl_3$, 100 MHz)

3ag

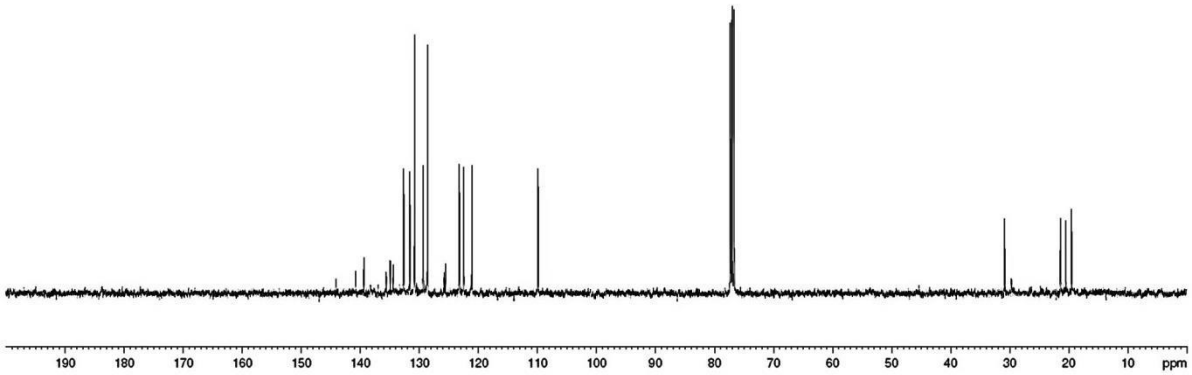
^{1}H NMR ($CDCl_3$, 400 MHz)

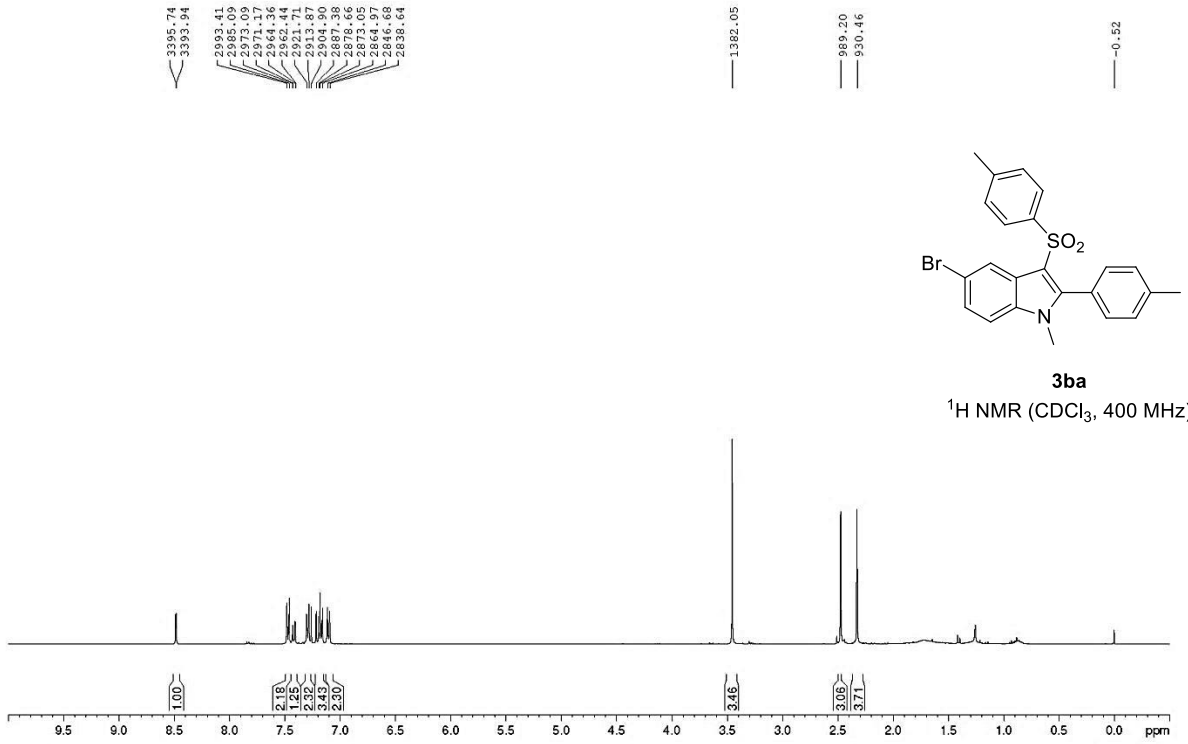




3ag

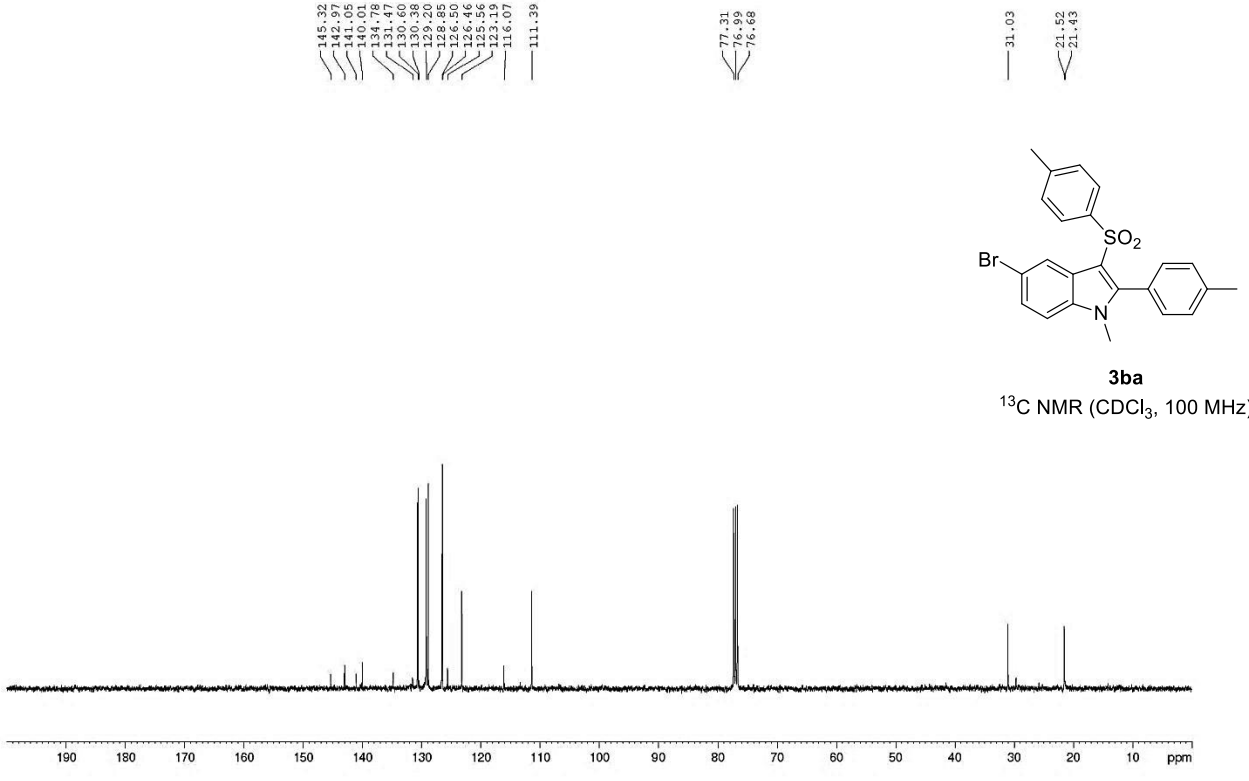
^{13}C NMR ($CDCl_3$, 100 MHz)





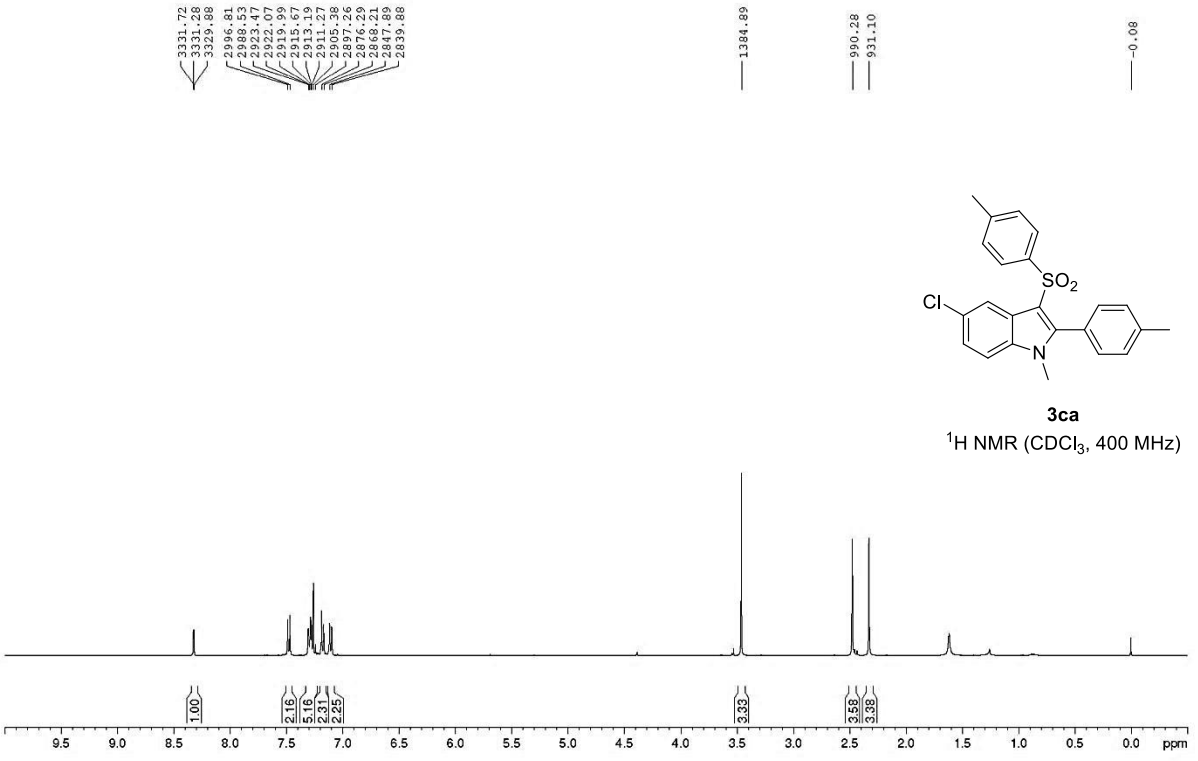
3ba

^{1}H NMR ($CDCl_3$, 400 MHz)



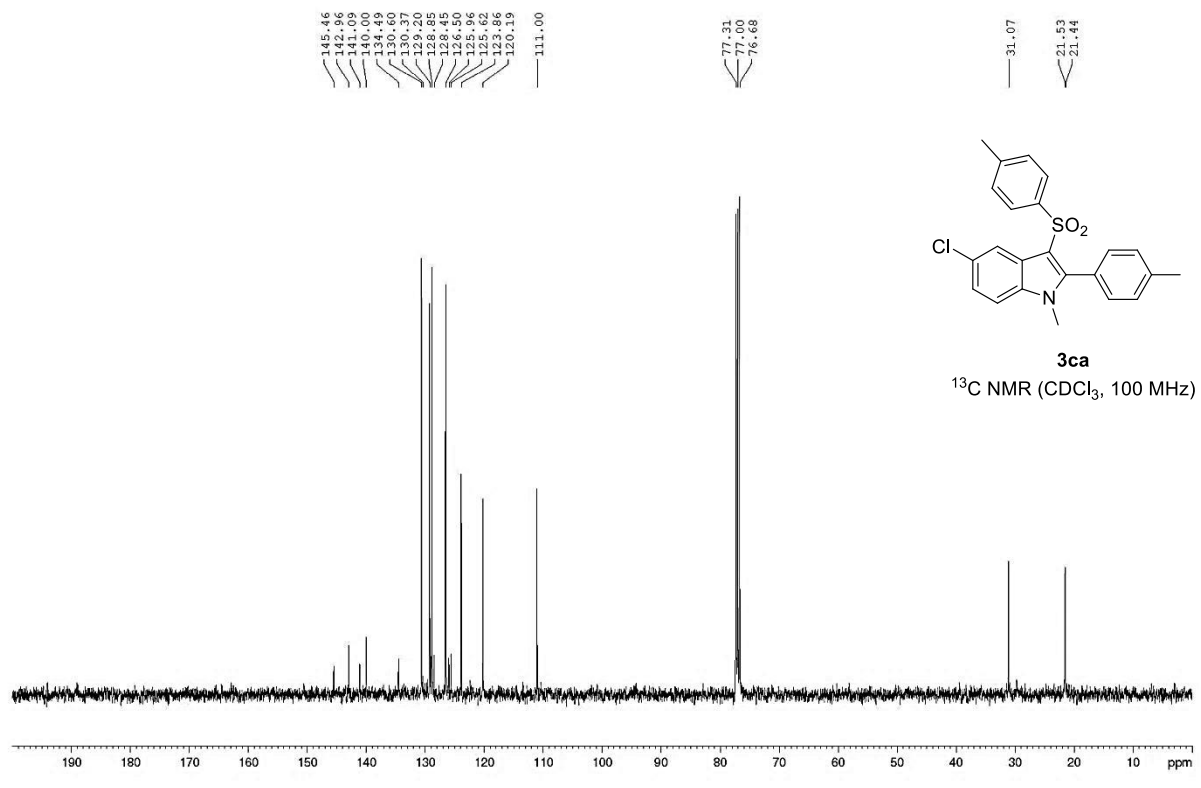
3ba

^{13}C NMR ($CDCl_3$, 100 MHz)



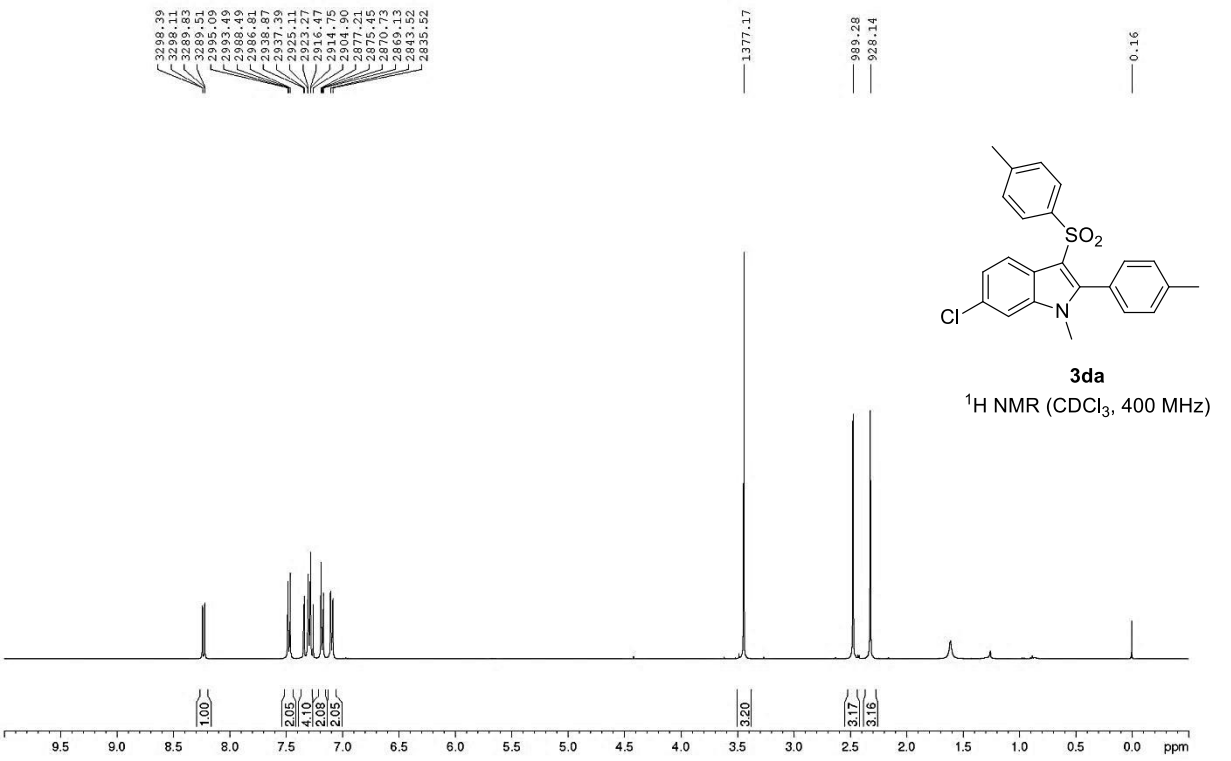
3ca

^{1}H NMR ($CDCl_3$, 400 MHz)



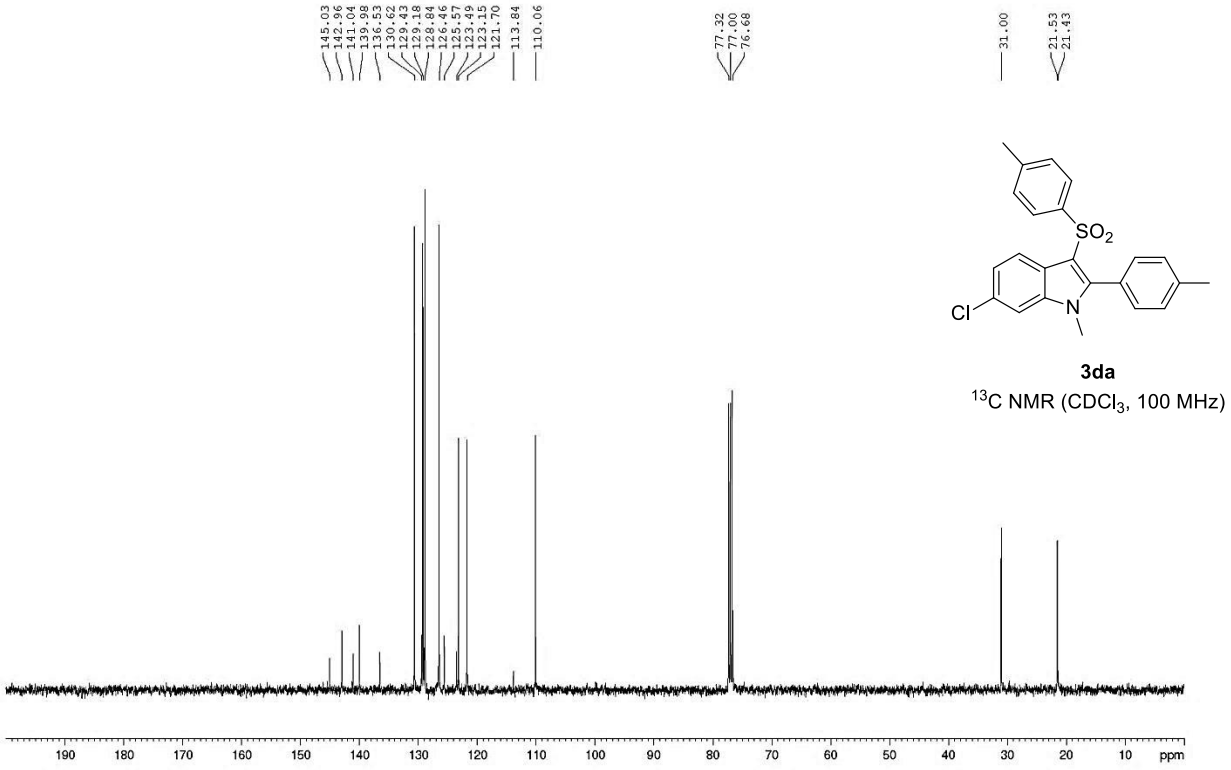
3ca

^{13}C NMR ($CDCl_3$, 100 MHz)



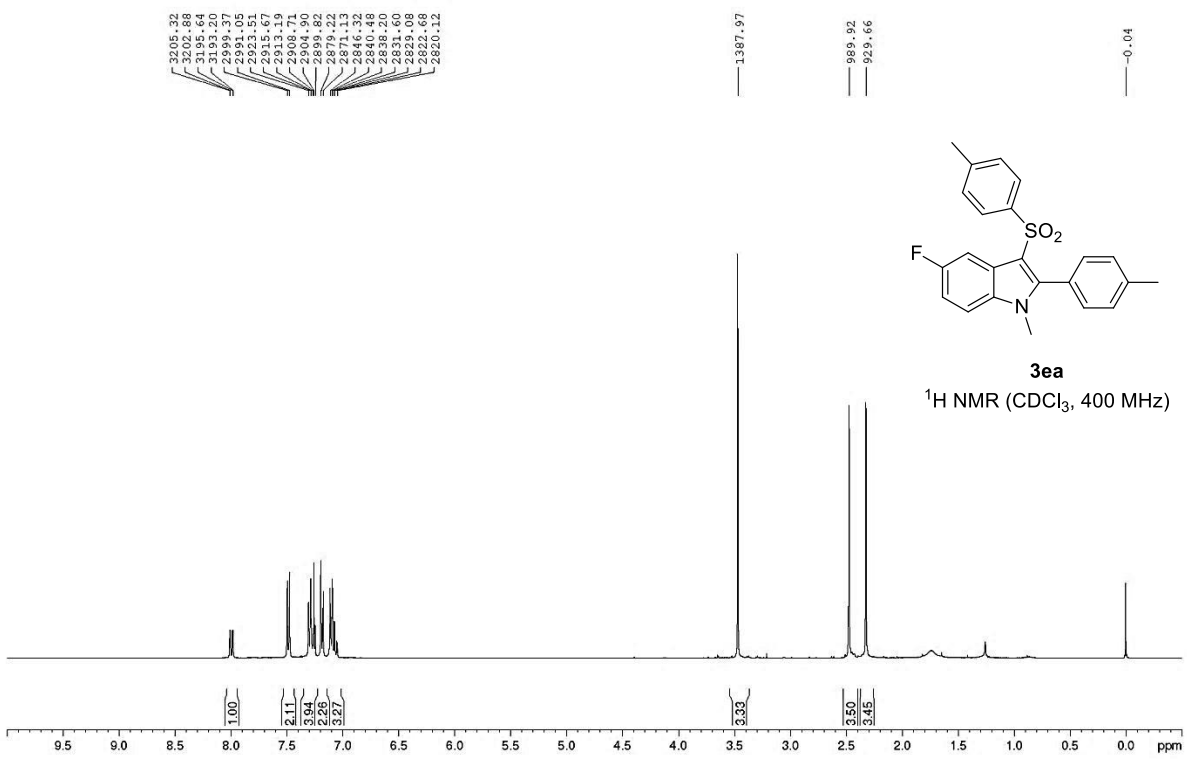
3da

^{1}H NMR ($CDCl_3$, 400 MHz)



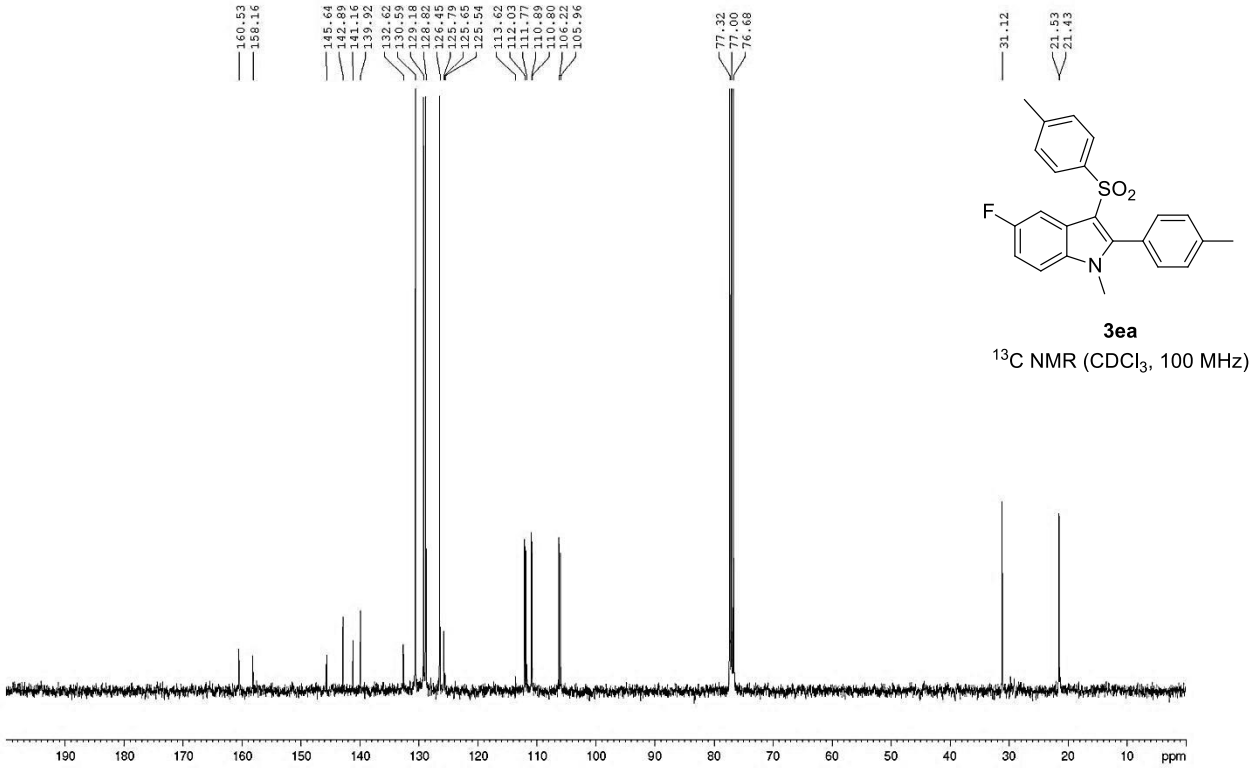
3da

^{13}C NMR ($CDCl_3$, 100 MHz)



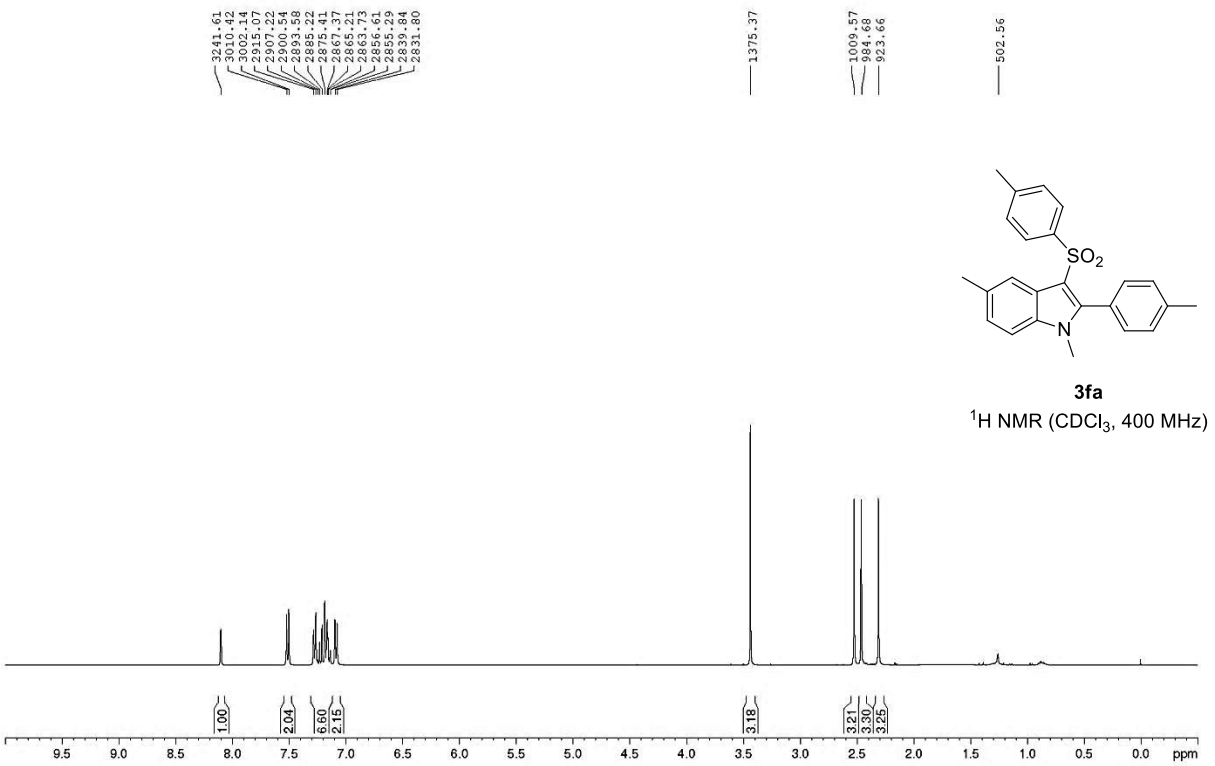
3ea

^{1}H NMR ($CDCl_3$, 400 MHz)



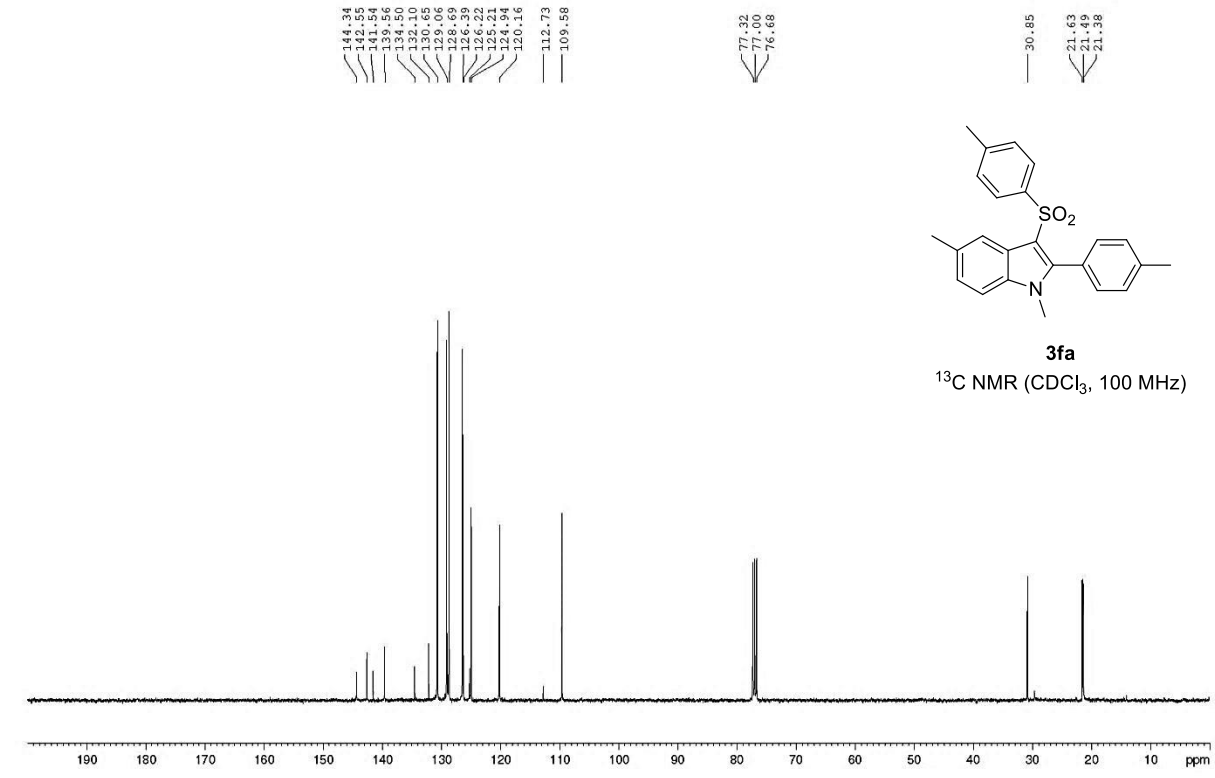
3ea

^{13}C NMR ($CDCl_3$, 100 MHz)



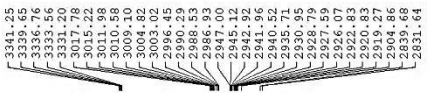
3fa

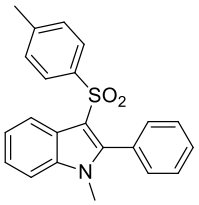
^{1}H NMR ($CDCl_3$, 400 MHz)



3fa

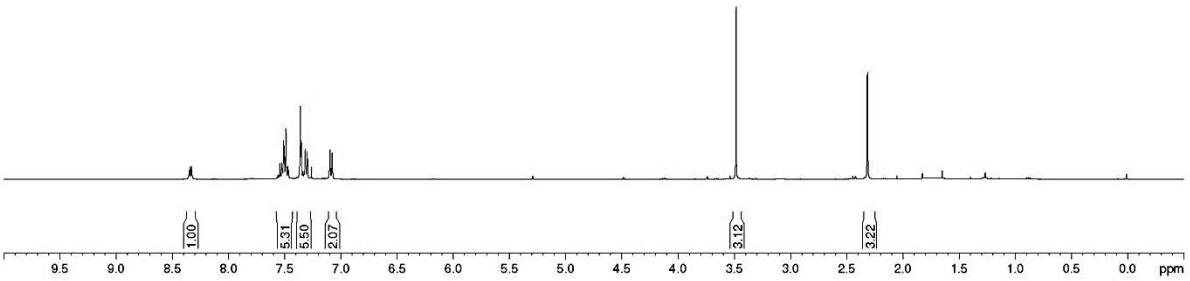
^{13}C NMR ($CDCl_3$, 100 MHz)

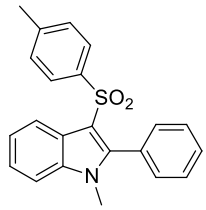




3ga

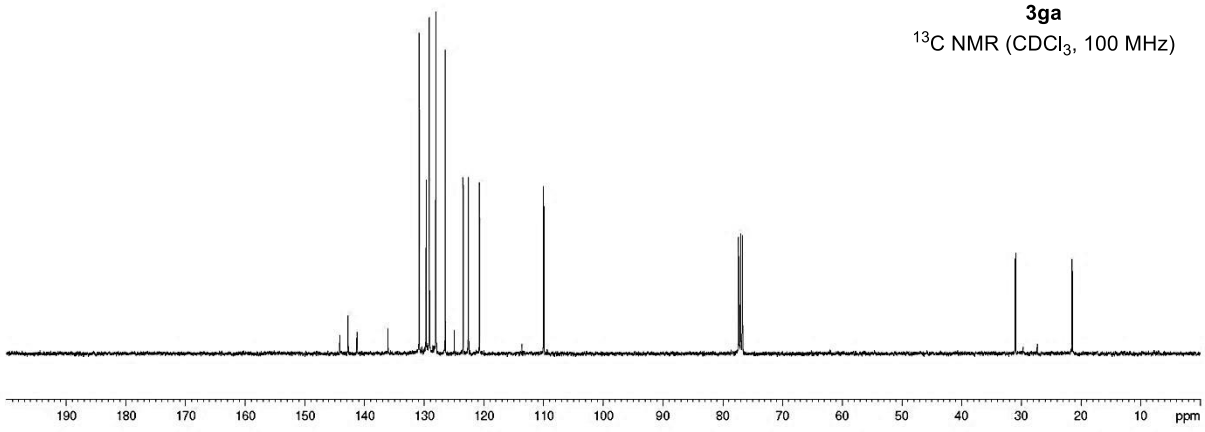
^{1}H NMR ($CDCl_3$, 400 MHz)

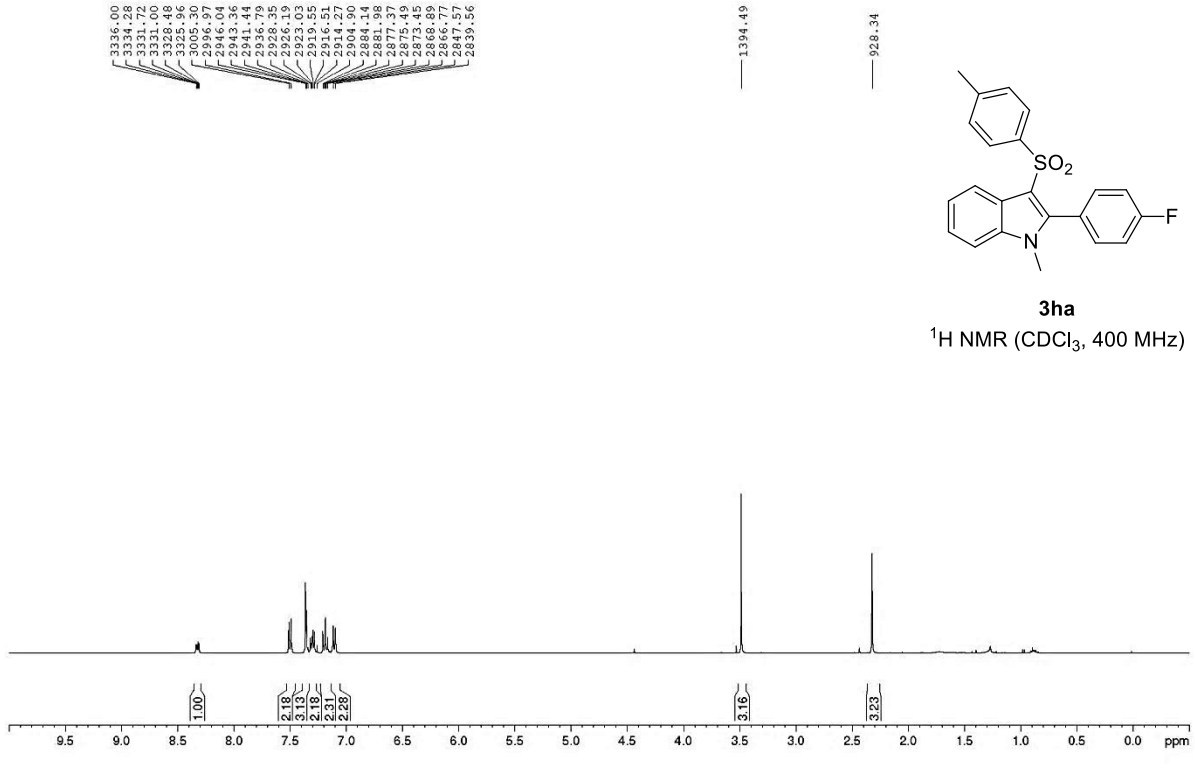




3ga

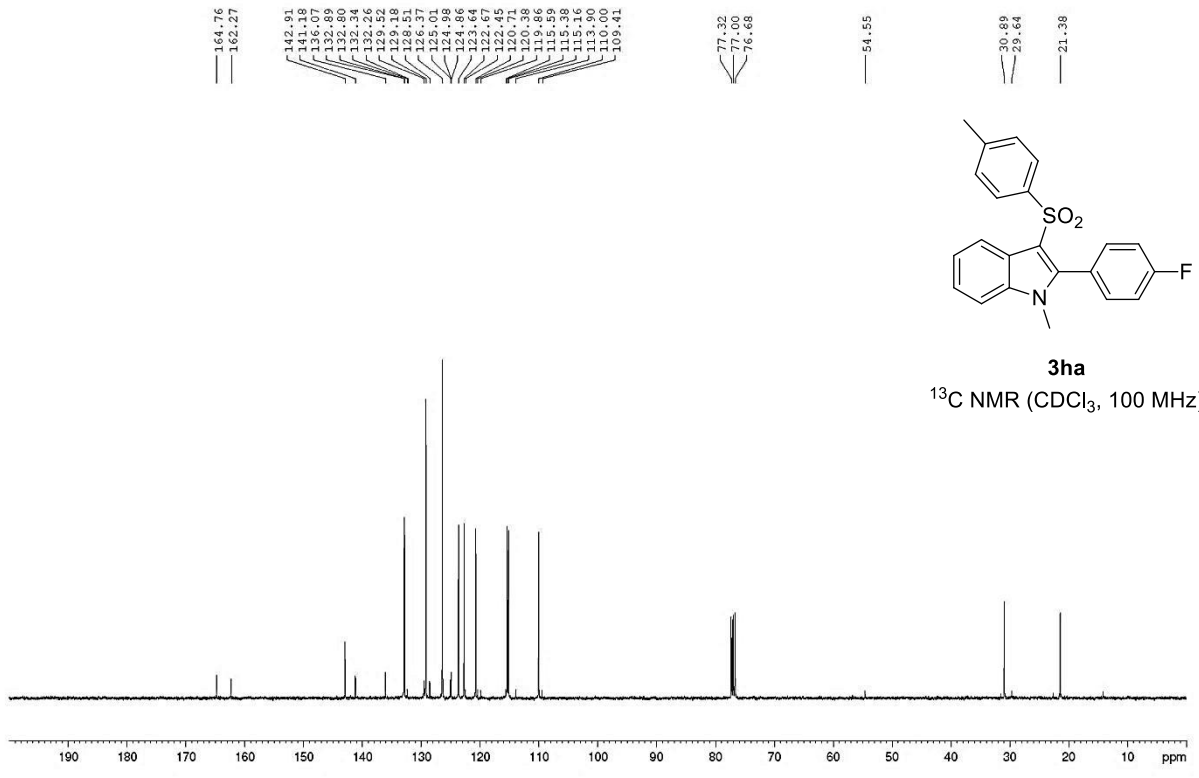
^{13}C NMR ($CDCl_3$, 100 MHz)





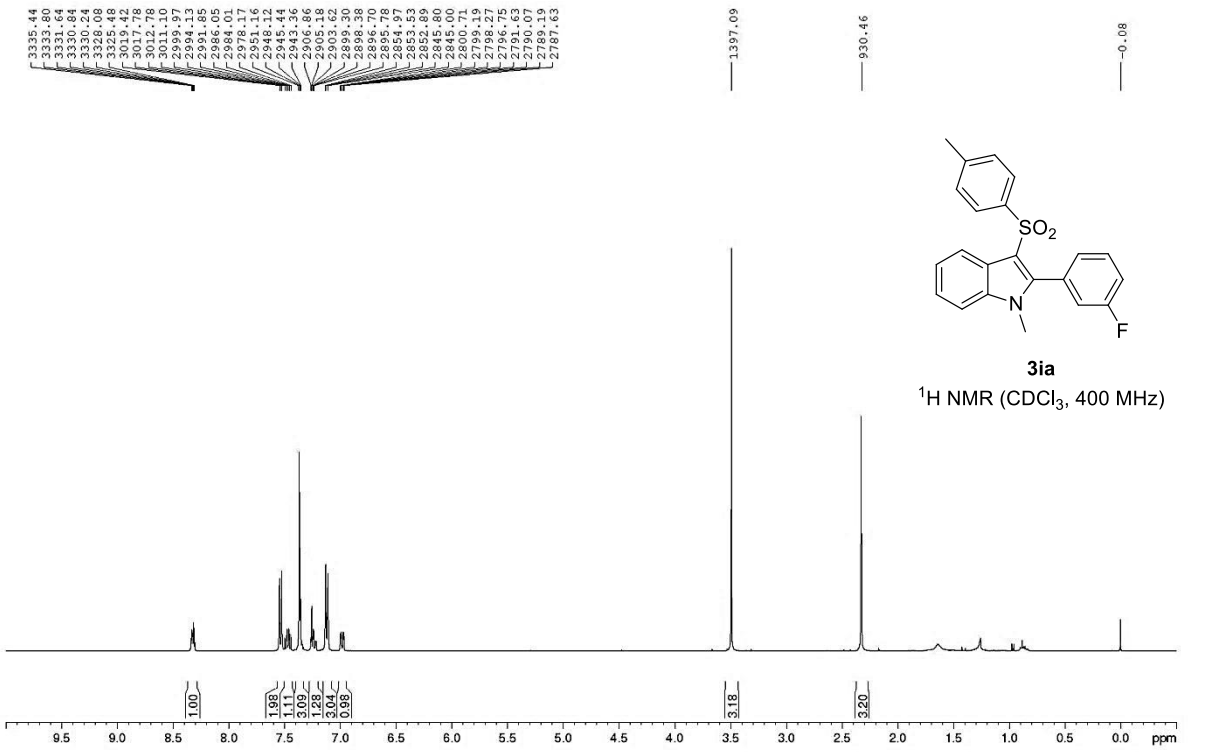
3ha

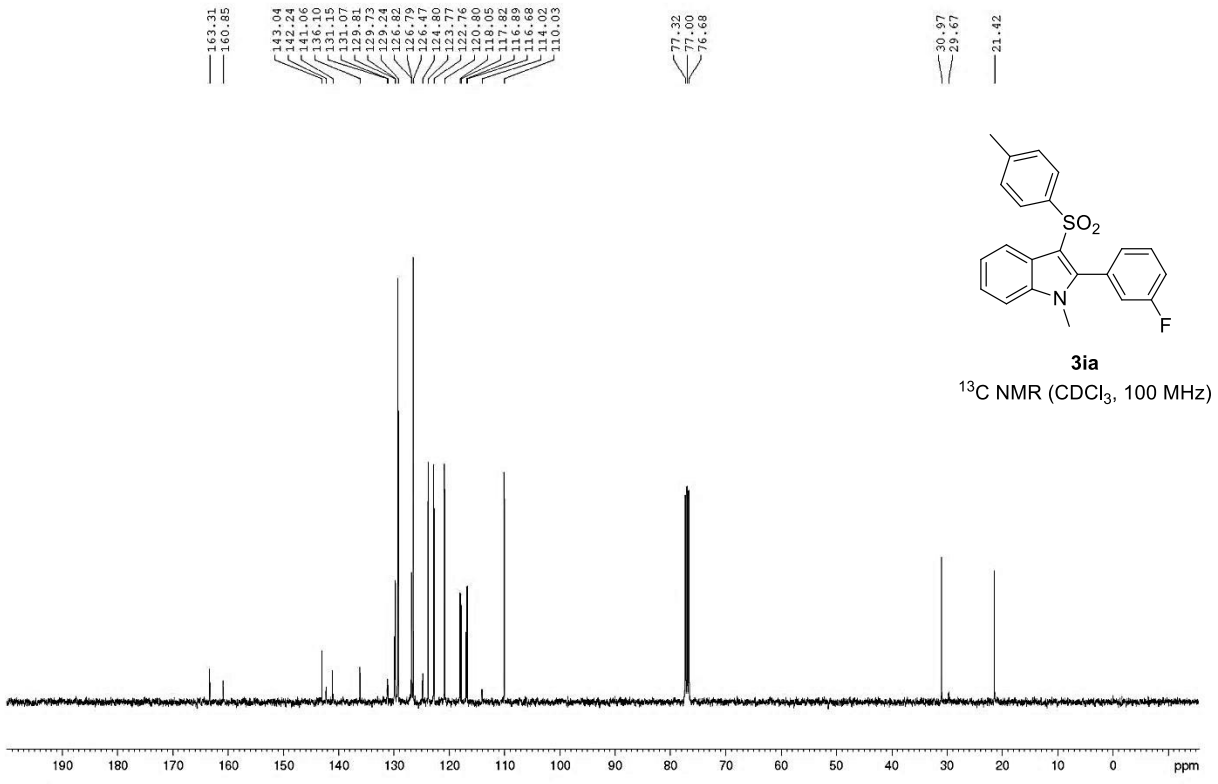
^{1}H NMR ($CDCl_3$, 400 MHz)

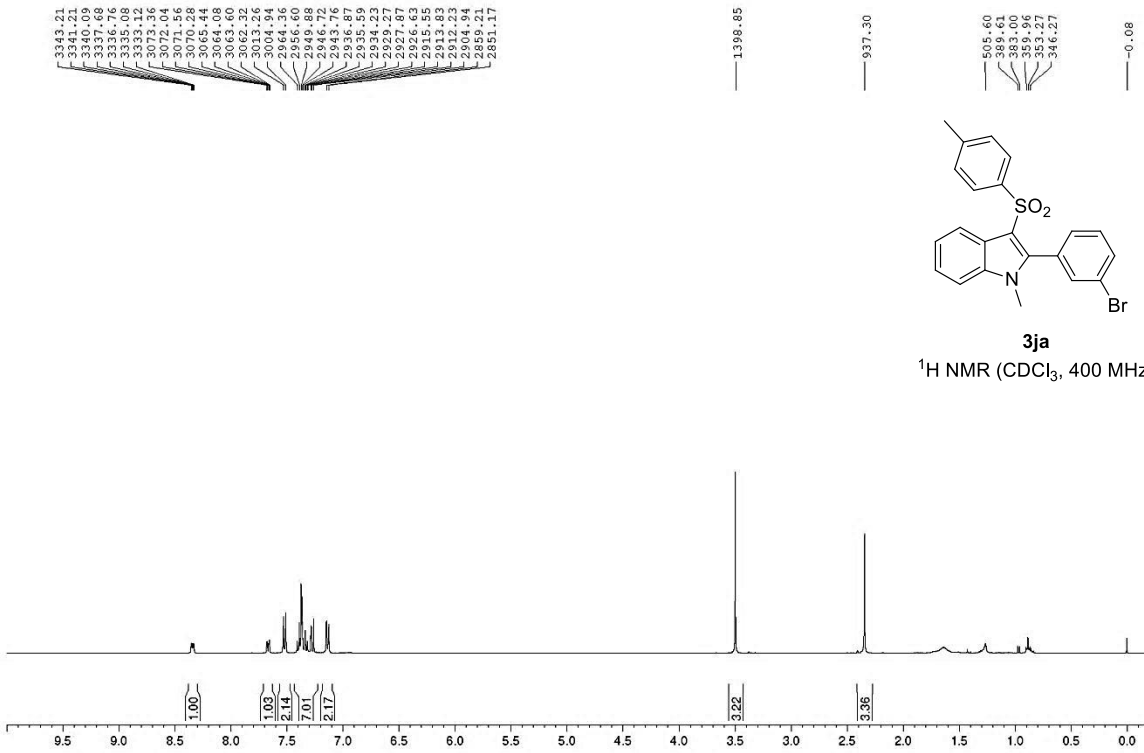


3ha

^{13}C NMR ($CDCl_3$, 100 MHz)

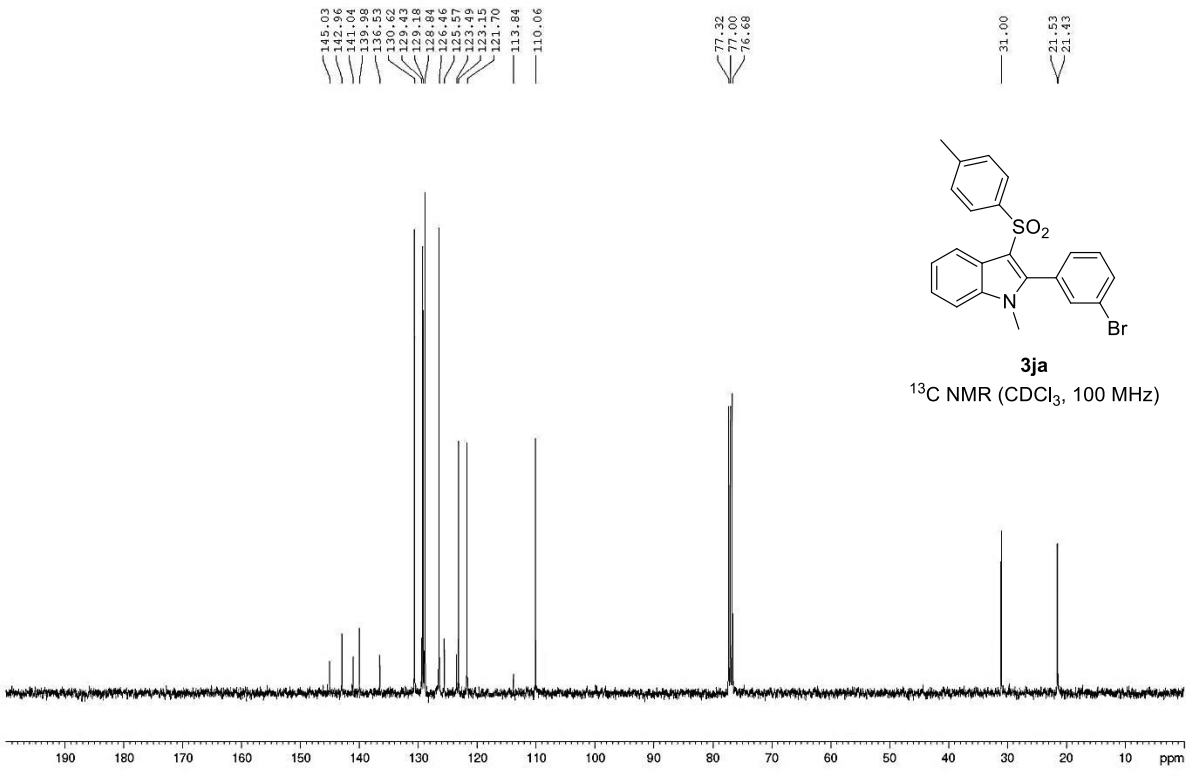

3335.44
3333.80
3331.64
3330.84
3330.24
3328.08
3325.48
3019.42
3017.78
3012.78
3011.10
2999.97
2994.13
2991.85
2986.05
2984.01
2978.17
2951.16
2948.12
2945.44
2943.36
2906.86
2905.18
2903.62
2899.38
2896.70
2895.78
2854.97
2853.53
2852.89
2845.80
2845.00
2800.71
2799.19
2798.27
2796.75
2791.63
2790.07
2789.19
2787.63
1397.09
930.46
0.08
SO2
N
F
3ia
1H NMR (CDCl3, 400 MHz)
1.00
1.98
1.11
3.09
1.28
3.04
0.98
3.18
3.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


163.31
160.85
143.04
142.24
141.06
136.10
131.15
131.07
129.81
129.73
129.24
126.82
126.79
126.47
124.80
123.77
122.76
120.80
118.05
117.82
116.89
116.68
114.02
110.03
77.32
77.00
76.68
30.97
29.67
21.42
SO2
N
F
3ia
13C NMR (CDCl3, 100 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



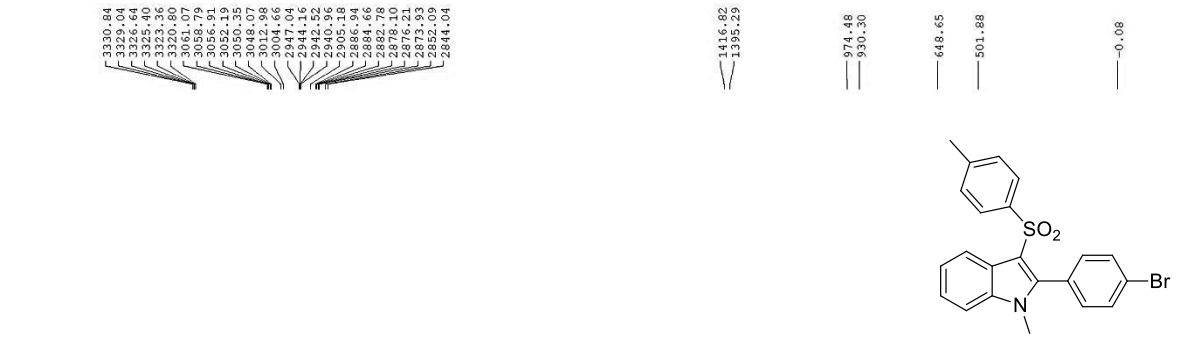
3ja

^{1}H NMR ($CDCl_3$, 400 MHz)



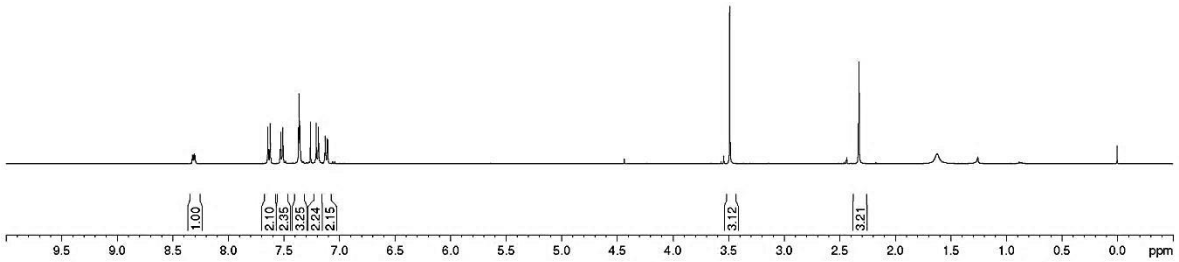
3ja

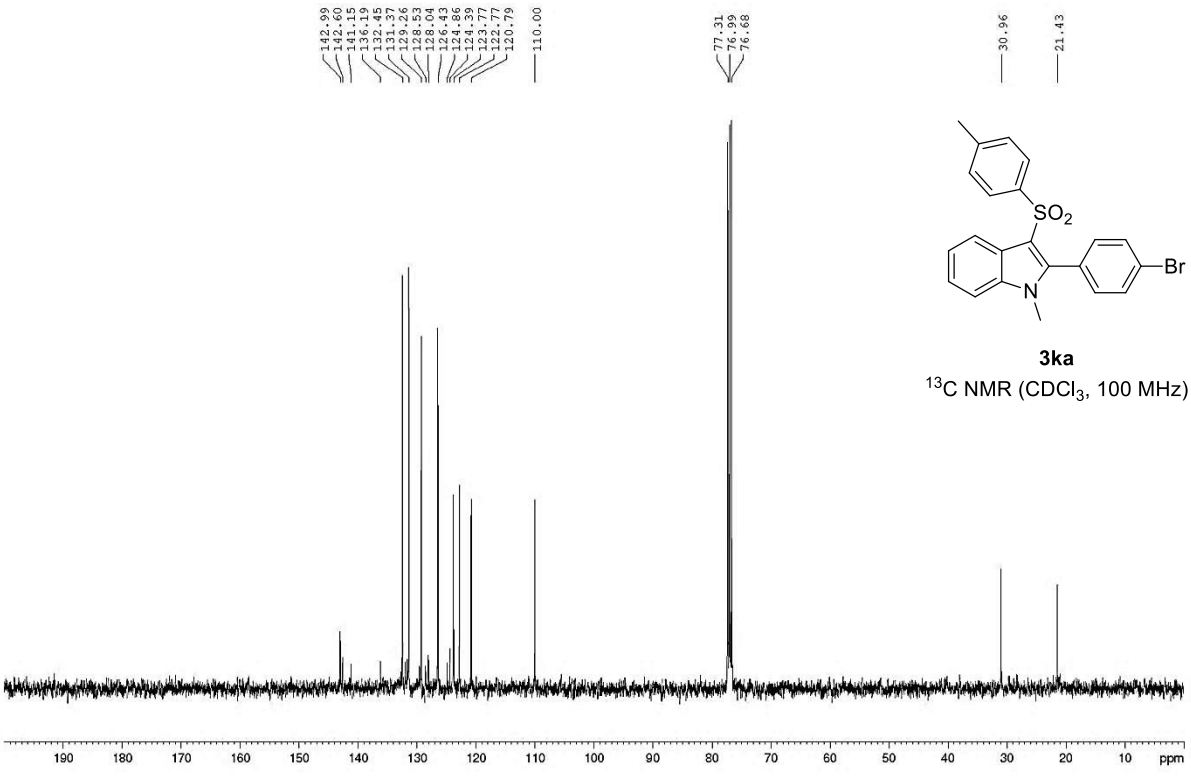
^{13}C NMR ($CDCl_3$, 100 MHz)



3ka

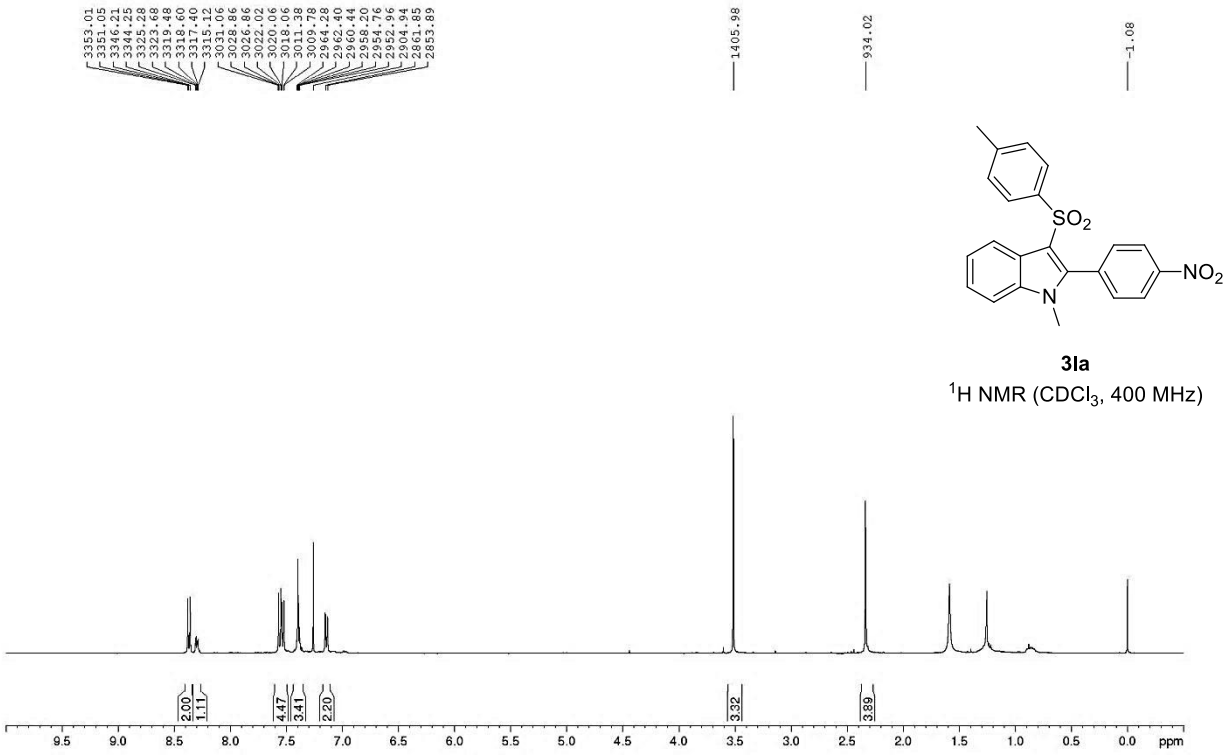
^{1}H NMR ($CDCl_3$, 400 MHz)





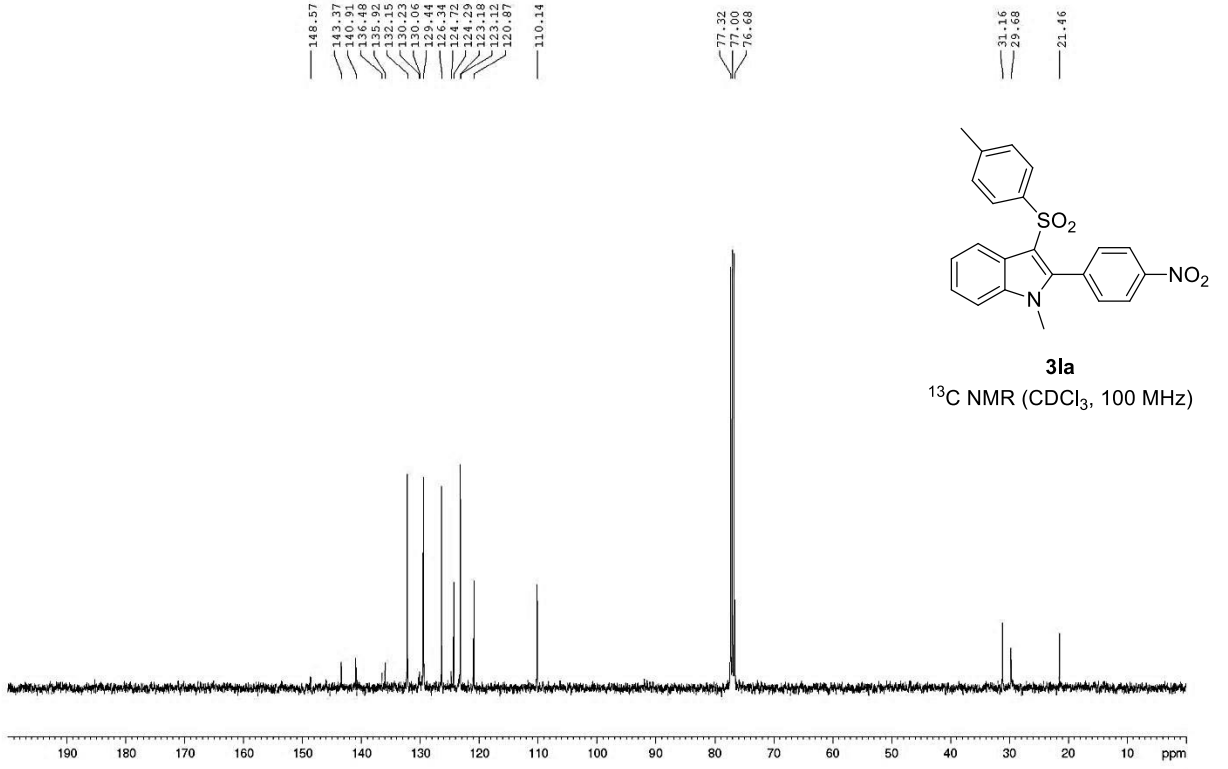
3ka

^{13}C NMR ($CDCl_3$, 100 MHz)



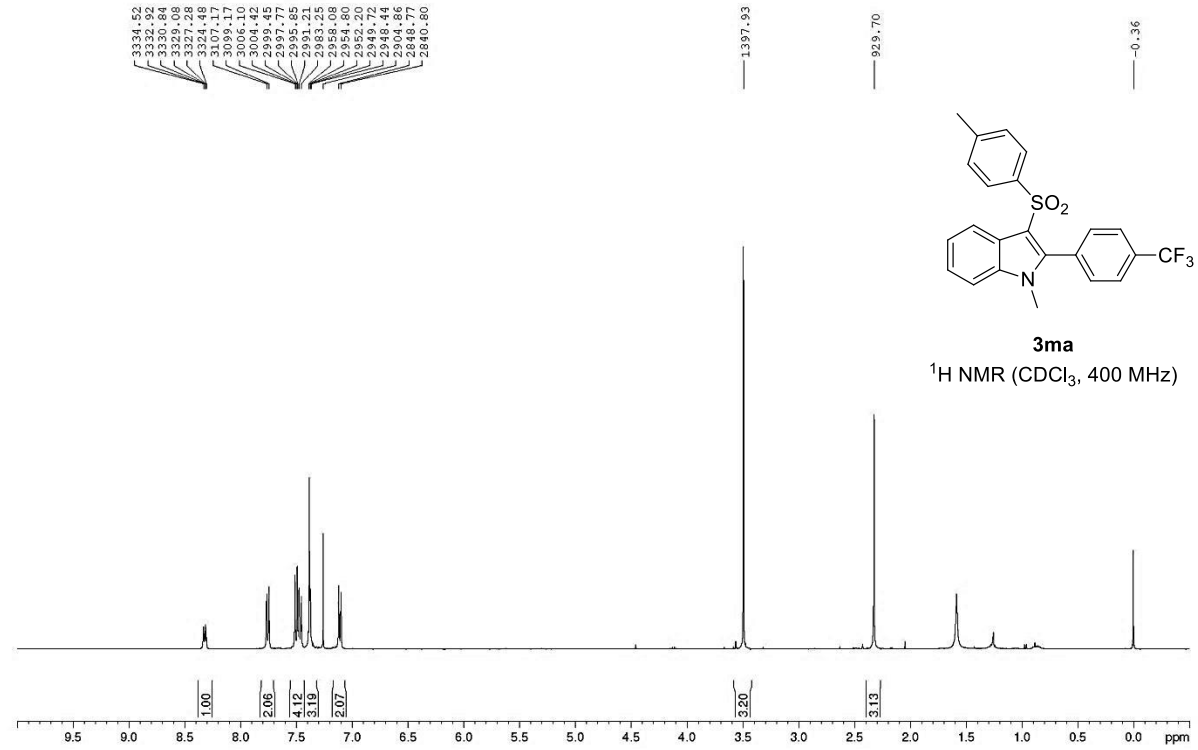
3la

^{1}H NMR ($CDCl_3$, 400 MHz)



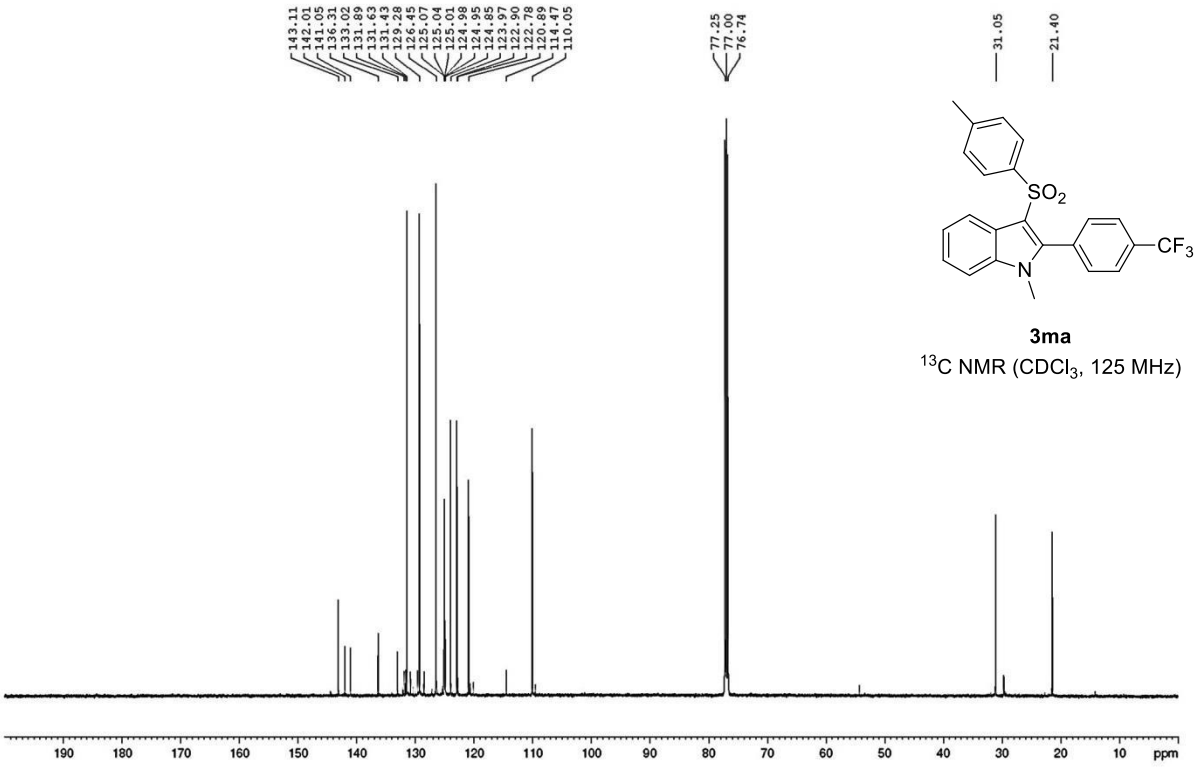
3la

^{13}C NMR ($CDCl_3$, 100 MHz)



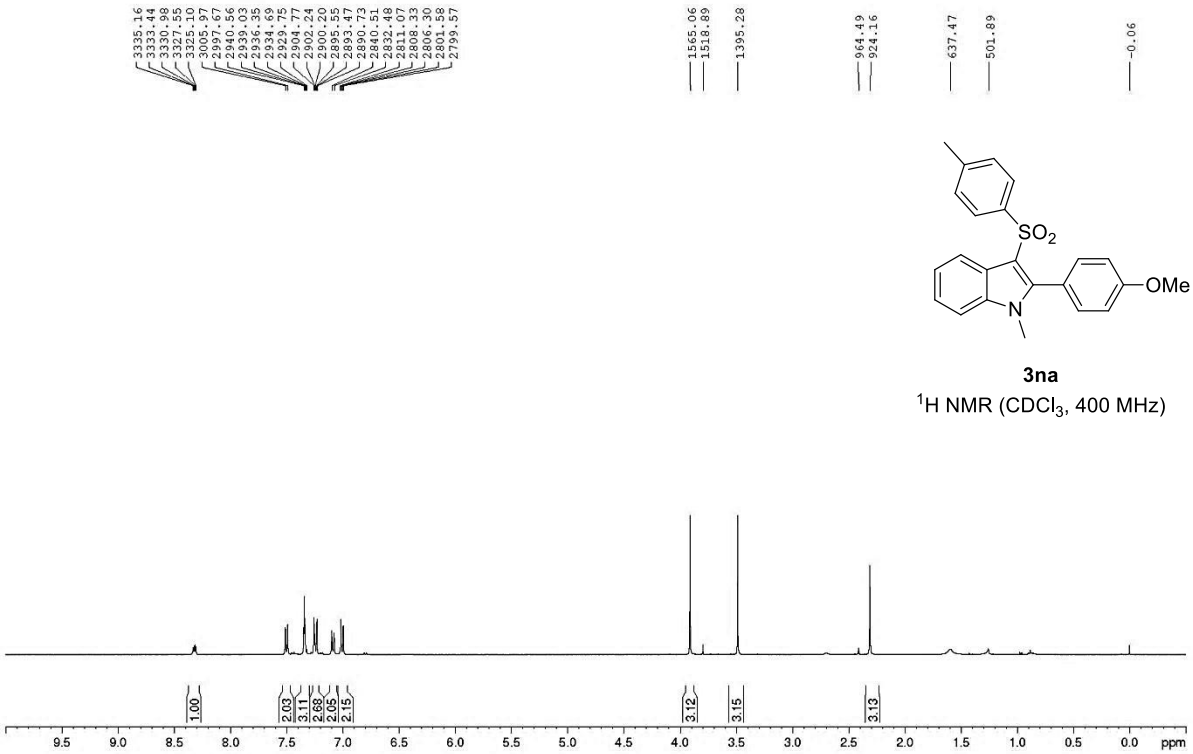
3ma

^{1}H NMR ($CDCl_3$, 400 MHz)



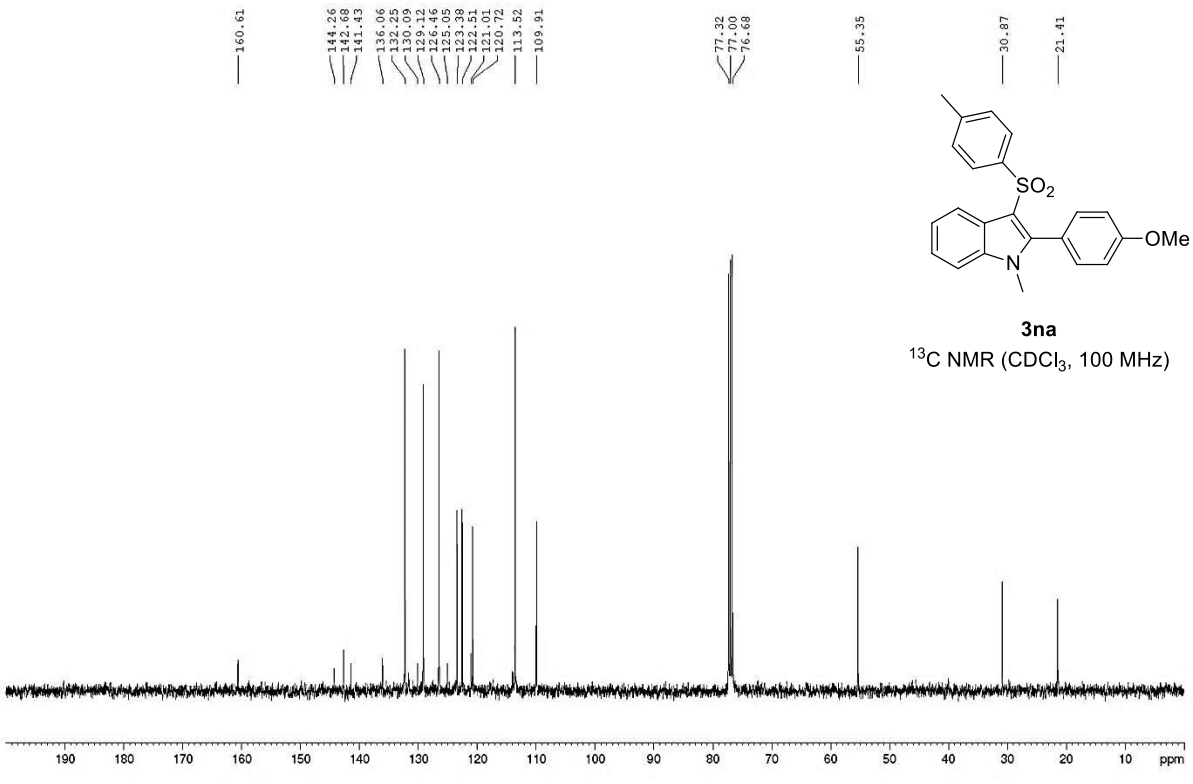
3ma

^{13}C NMR ($CDCl_3$, 125 MHz)



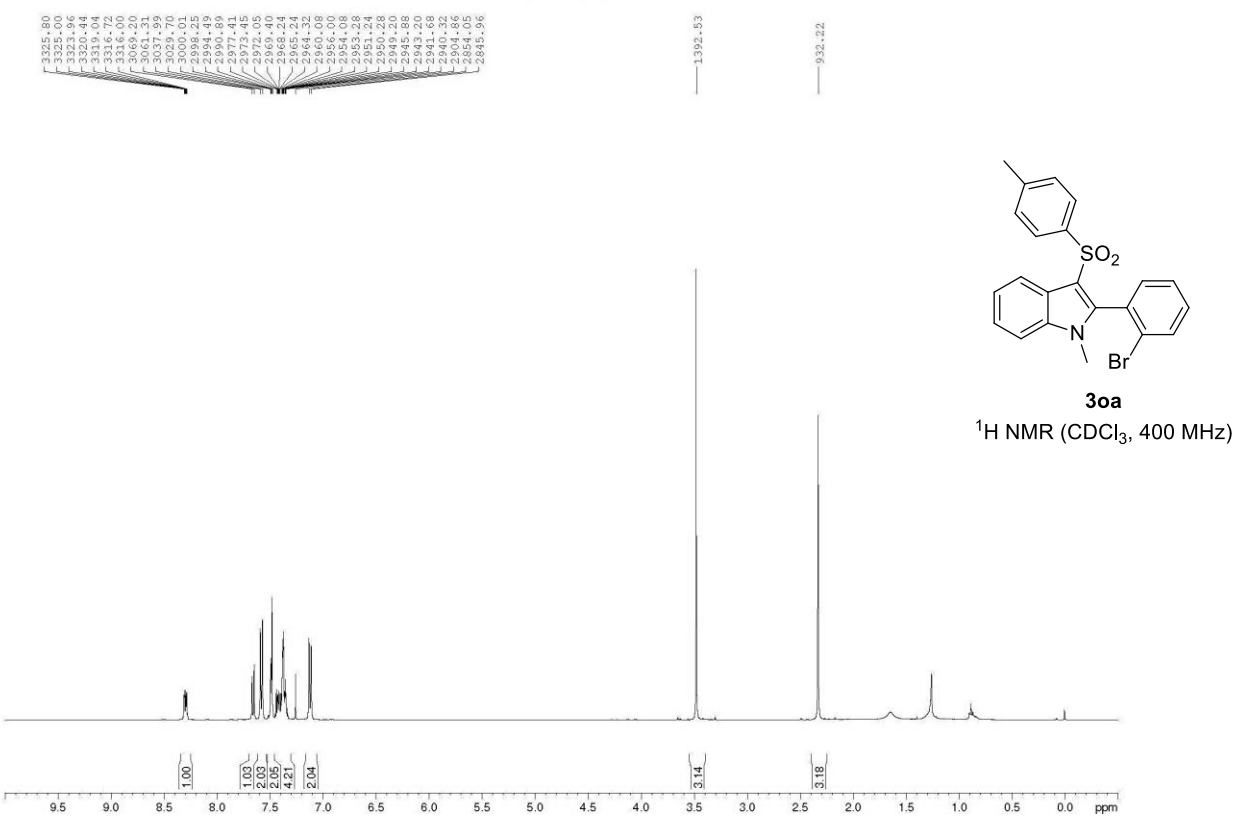
3na

^{1}H NMR ($CDCl_3$, 400 MHz)



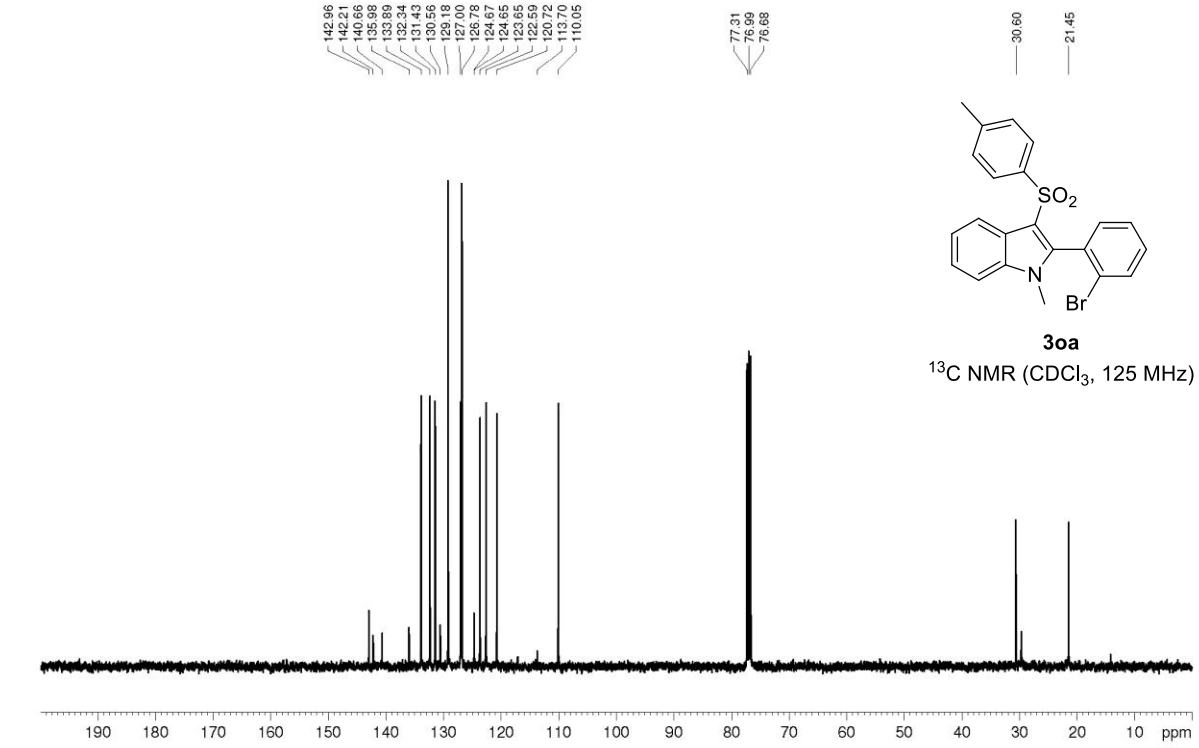
3na

^{13}C NMR ($CDCl_3$, 100 MHz)



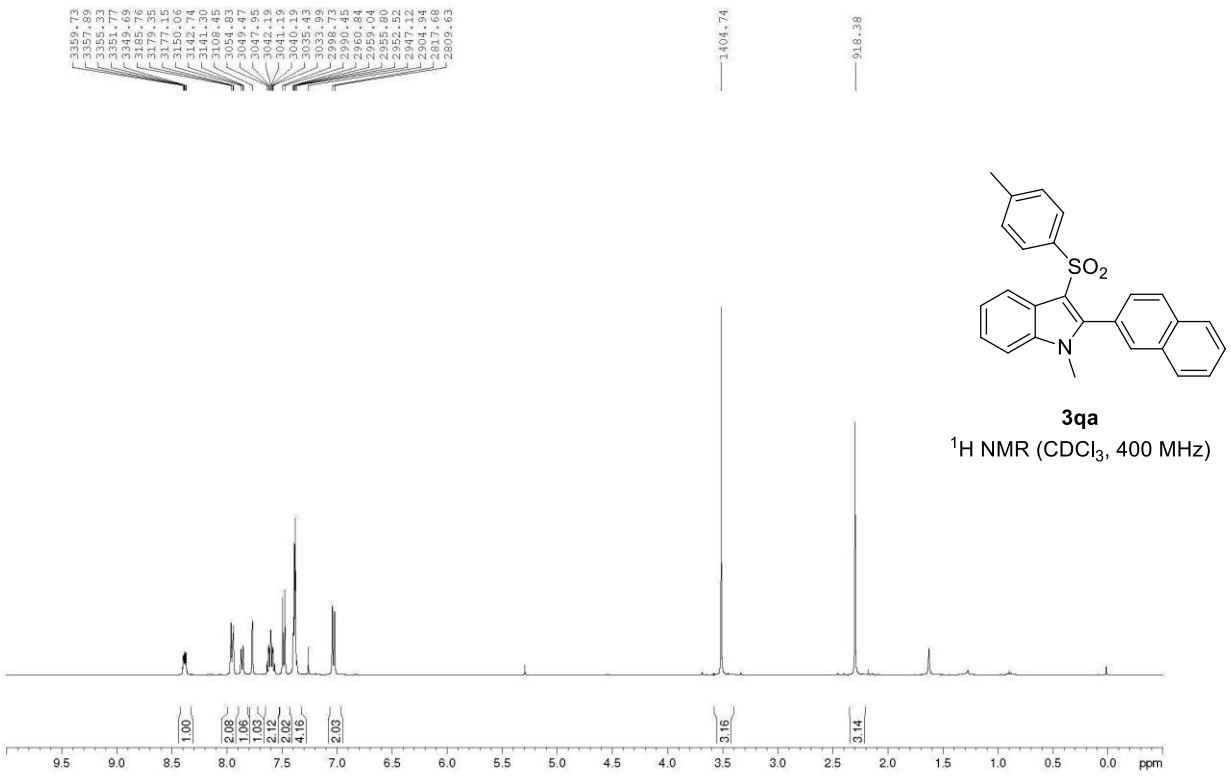
3oa

^{1}H NMR ($CDCl_3$, 400 MHz)



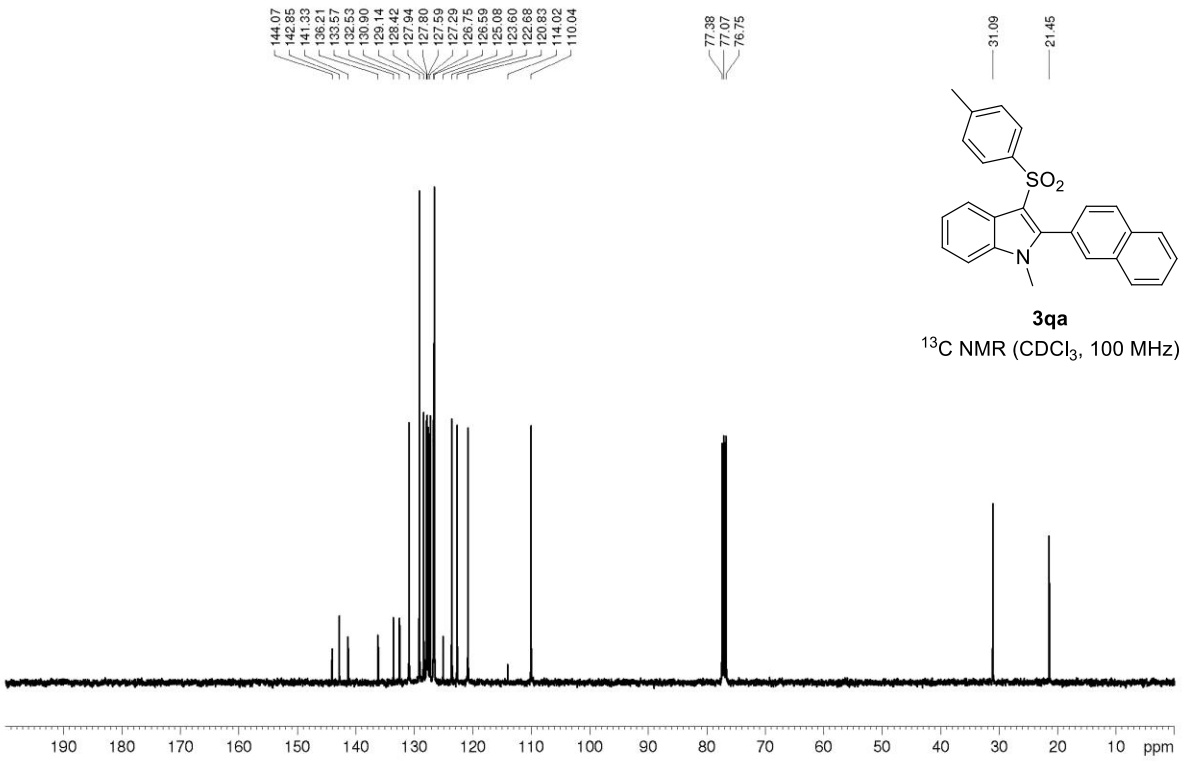
3oa

^{13}C NMR ($CDCl_3$, 125 MHz)



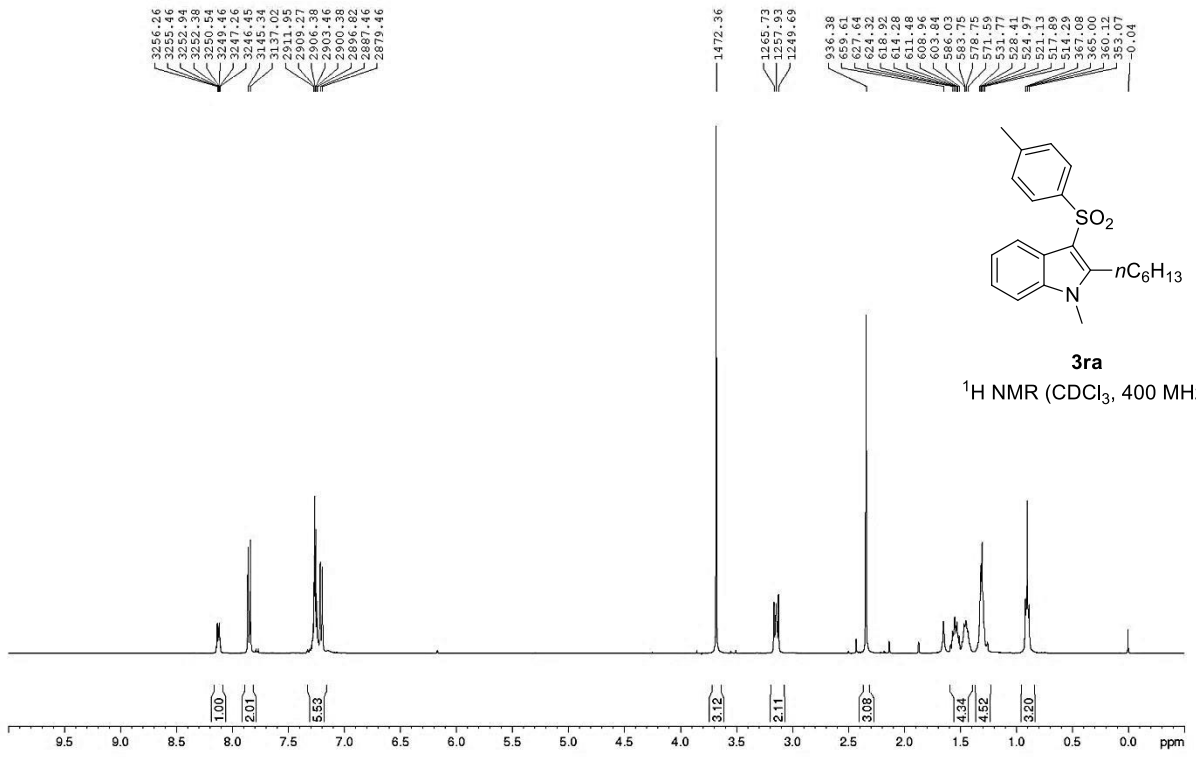
3qa

^{1}H NMR ($CDCl_3$, 400 MHz)



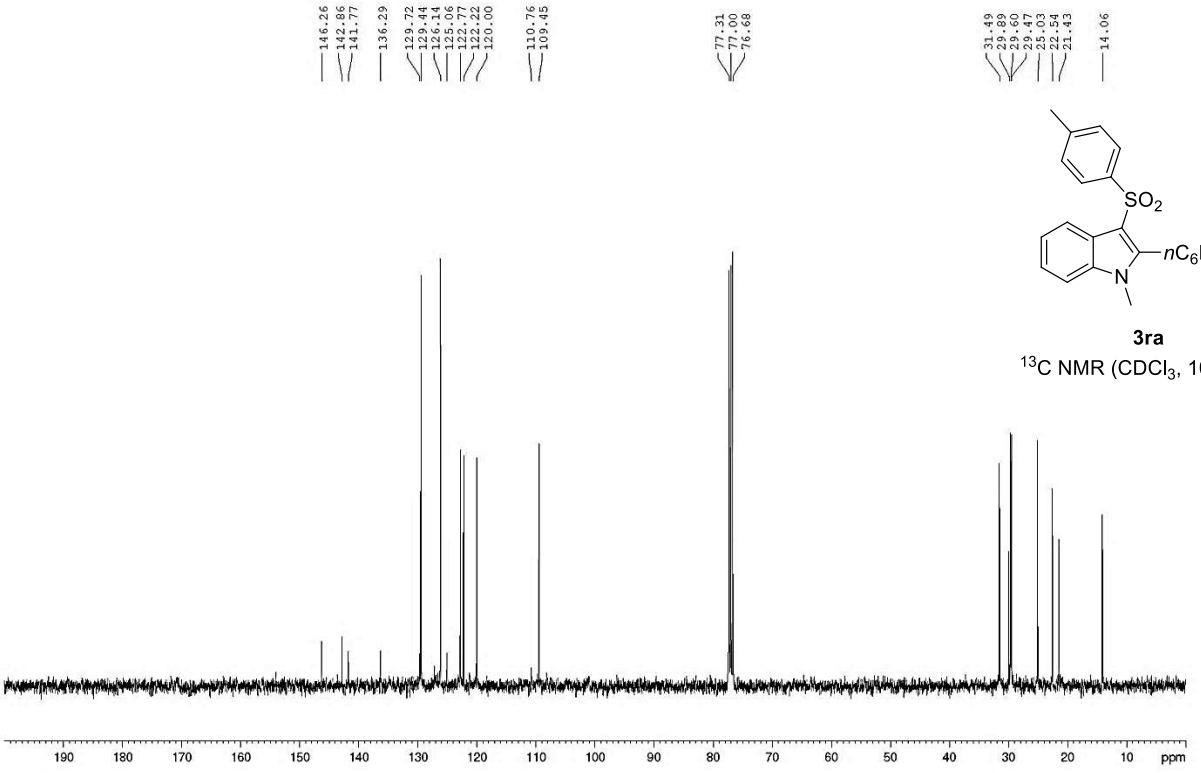
3qa

^{13}C NMR ($CDCl_3$, 100 MHz)



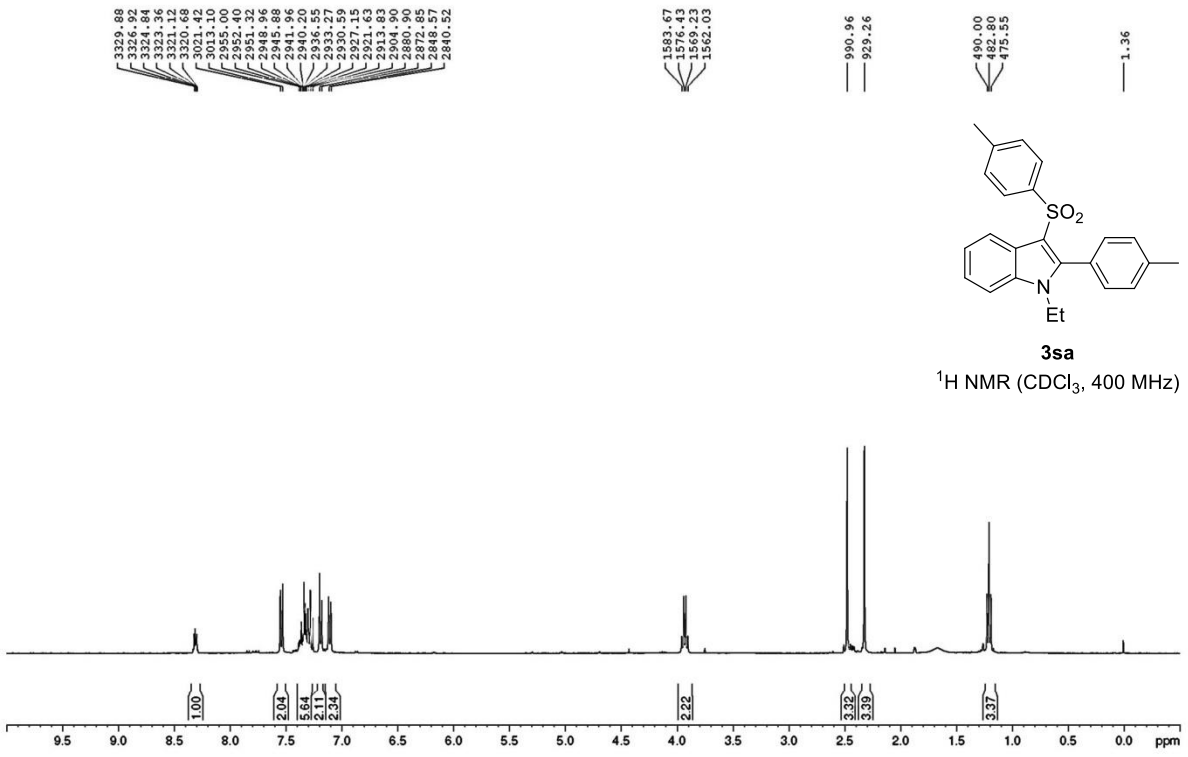
3ra

^{1}H NMR ($CDCl_3$, 400 MHz)



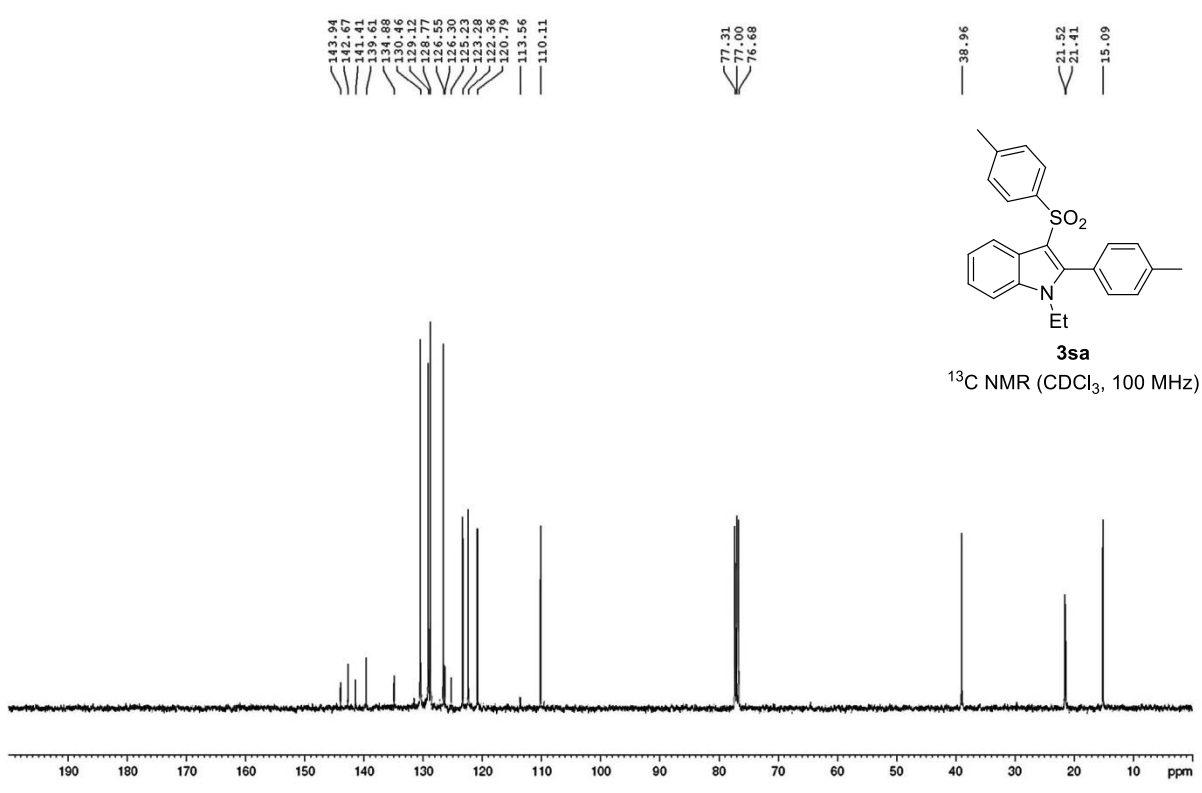
3ra

^{13}C NMR ($CDCl_3$, 100 MHz)



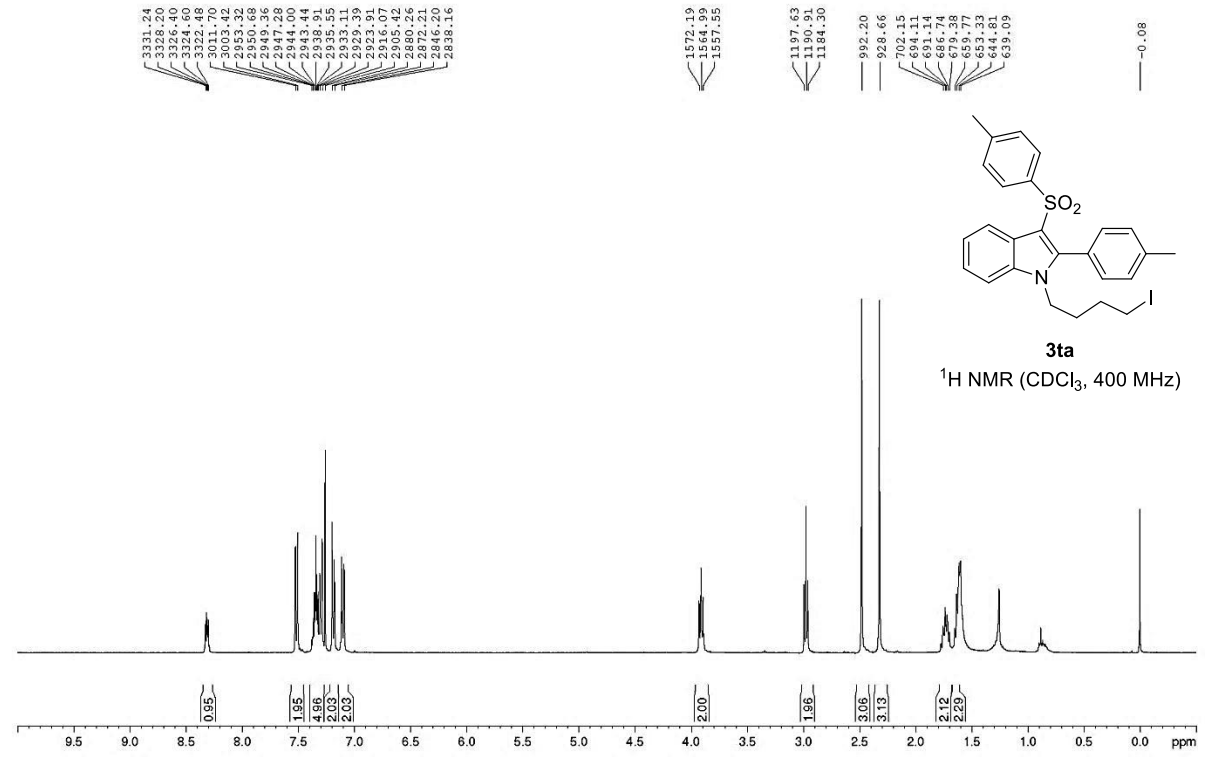
3sa

^{1}H NMR ($CDCl_3$, 400 MHz)



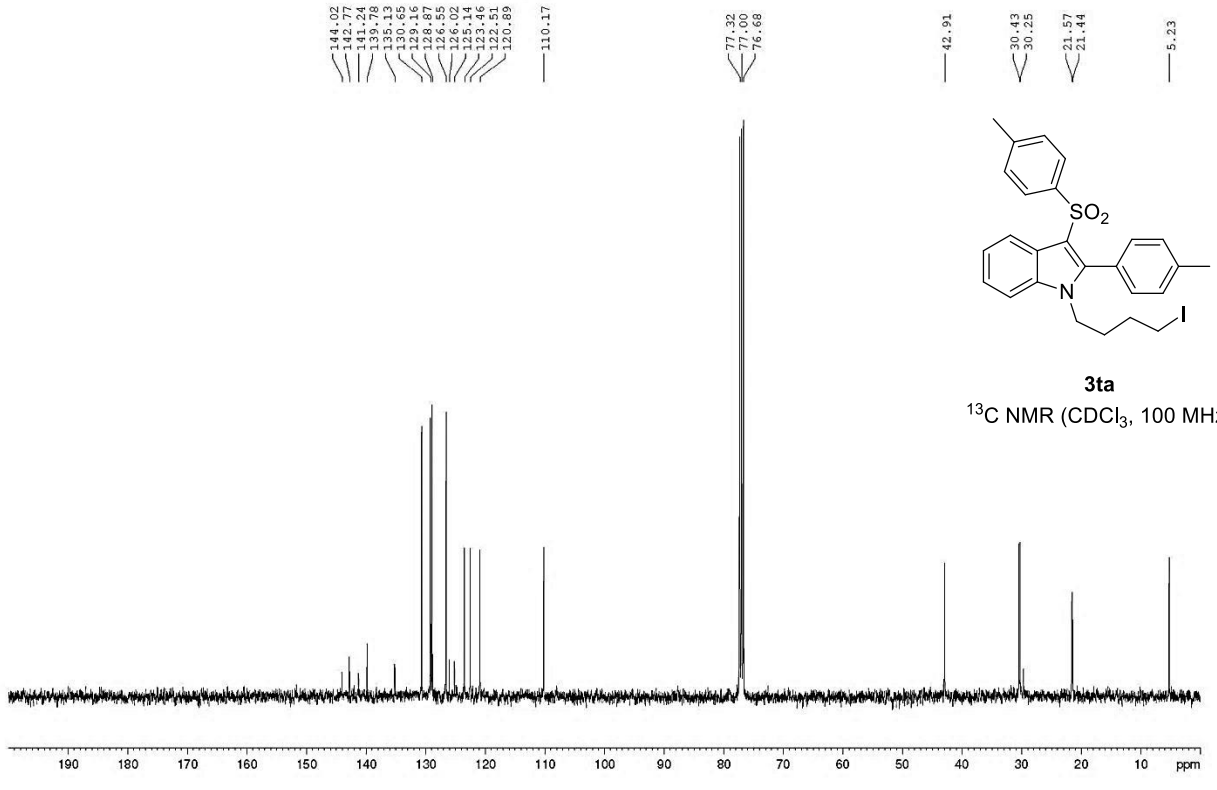
3sa

^{13}C NMR ($CDCl_3$, 100 MHz)



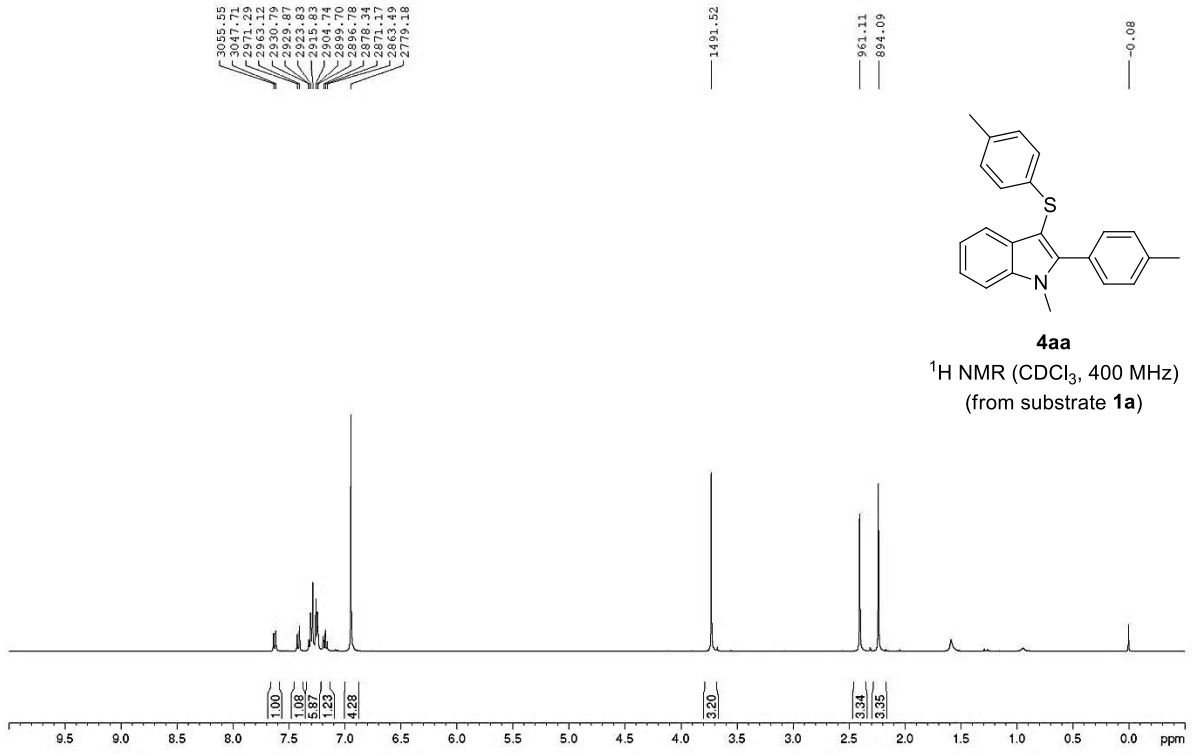
3ta

^{1}H NMR ($CDCl_3$, 400 MHz)



3ta

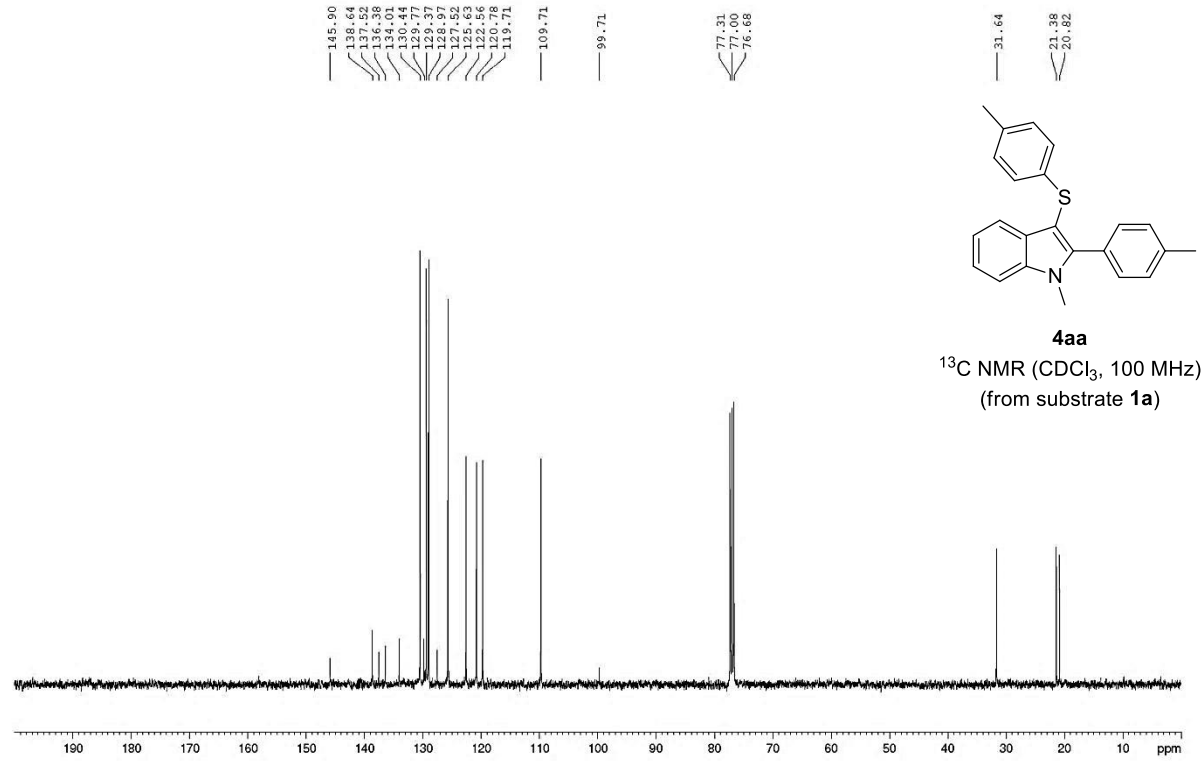
^{13}C NMR ($CDCl_3$, 100 MHz)



4aa

^{1}H NMR ($CDCl_3$, 400 MHz)

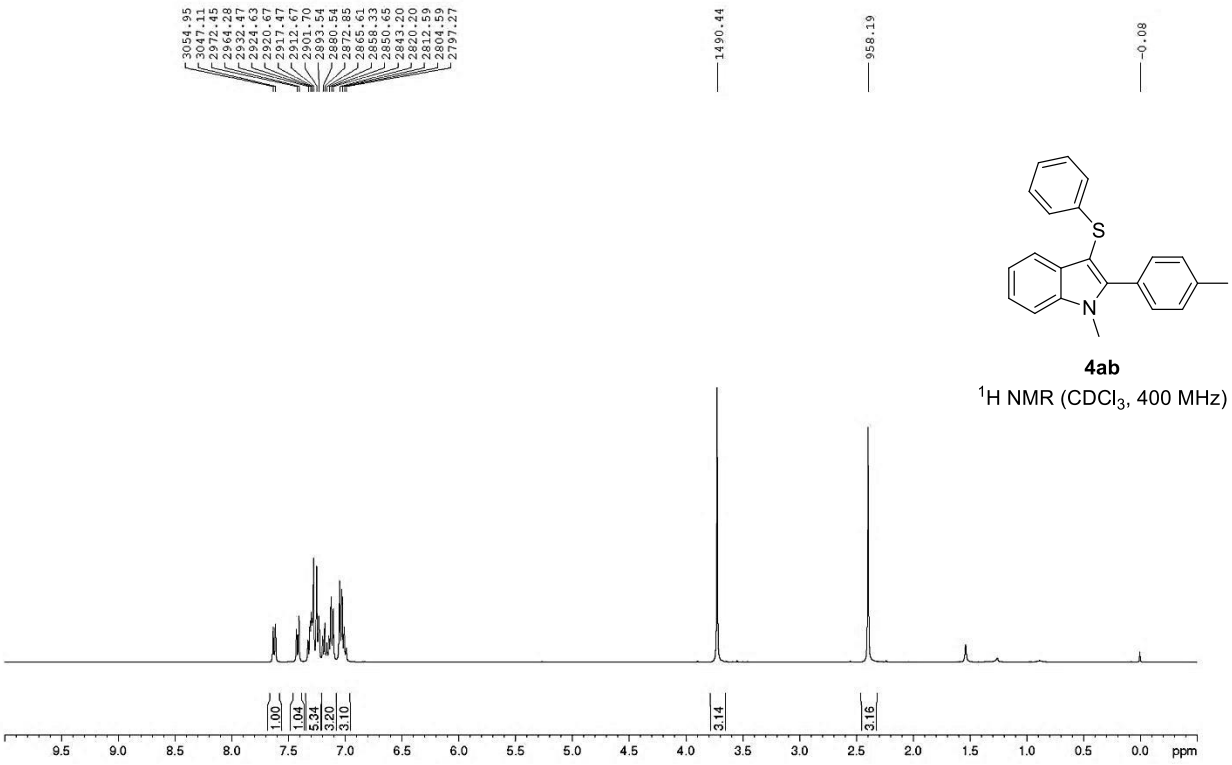
(from substrate **1a**)



4aa

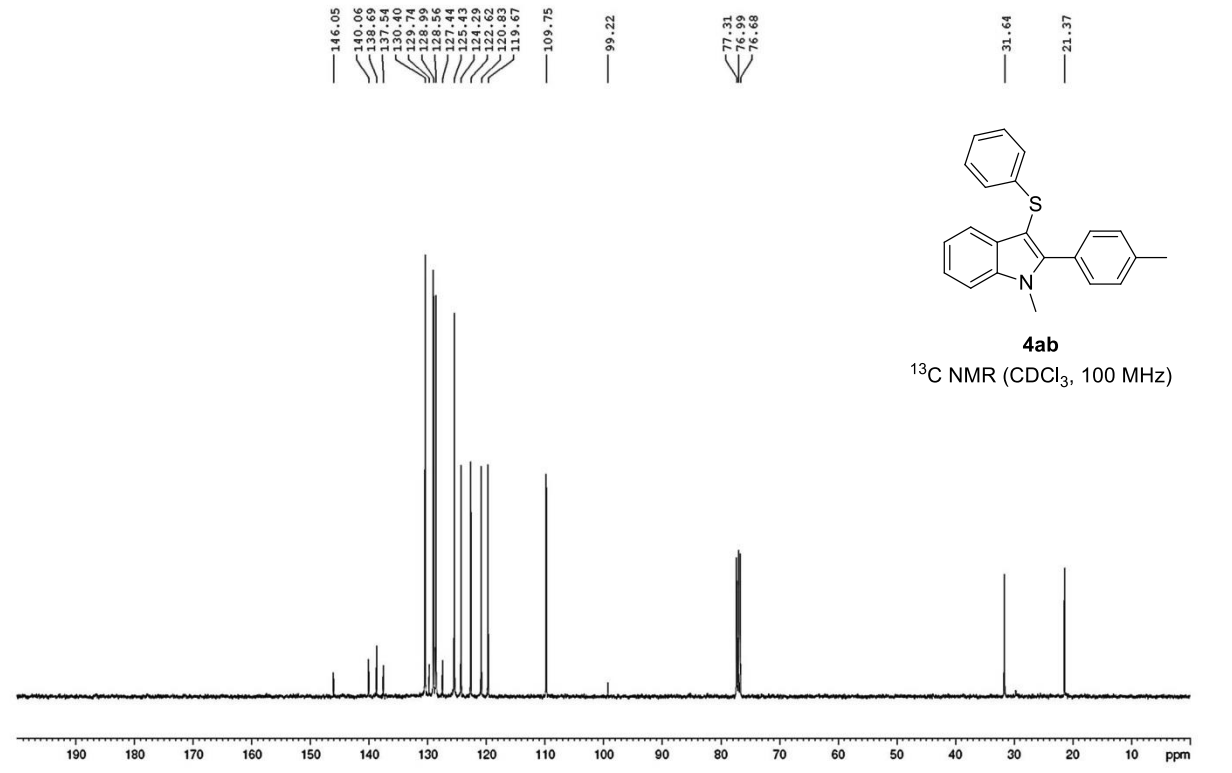
^{13}C NMR ($CDCl_3$, 100 MHz)

(from substrate **1a**)



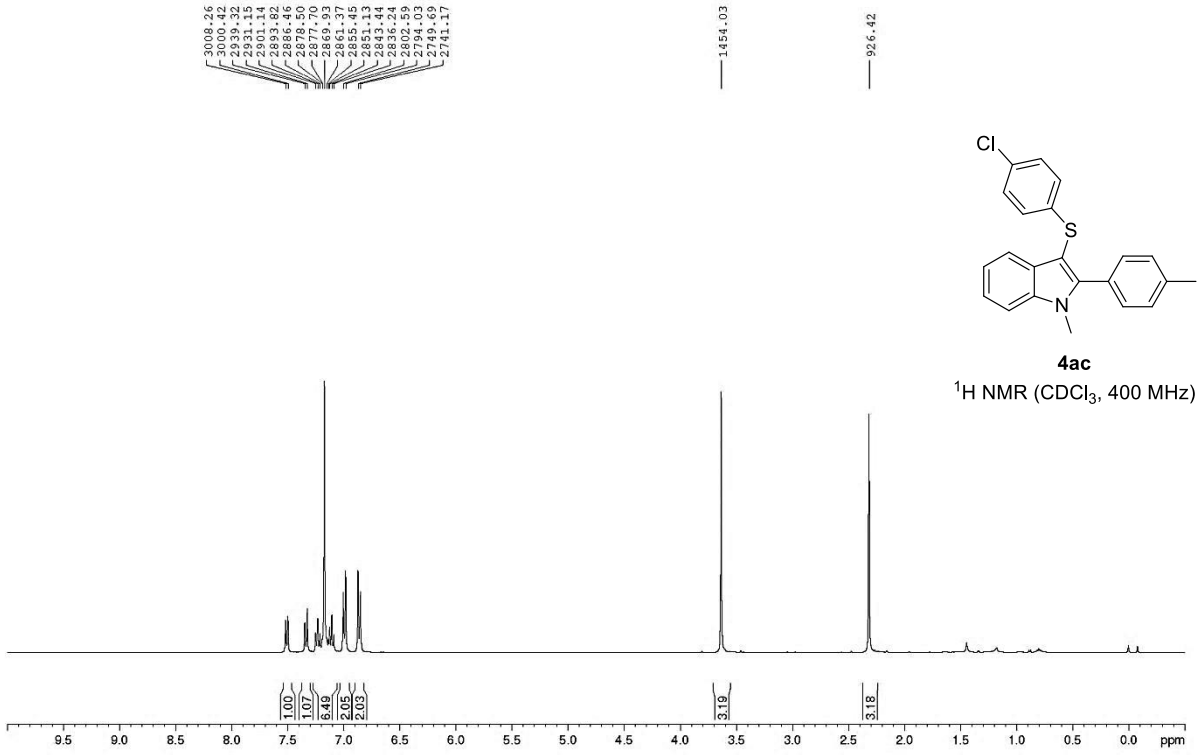
4ab

^{1}H NMR ($CDCl_3$, 400 MHz)



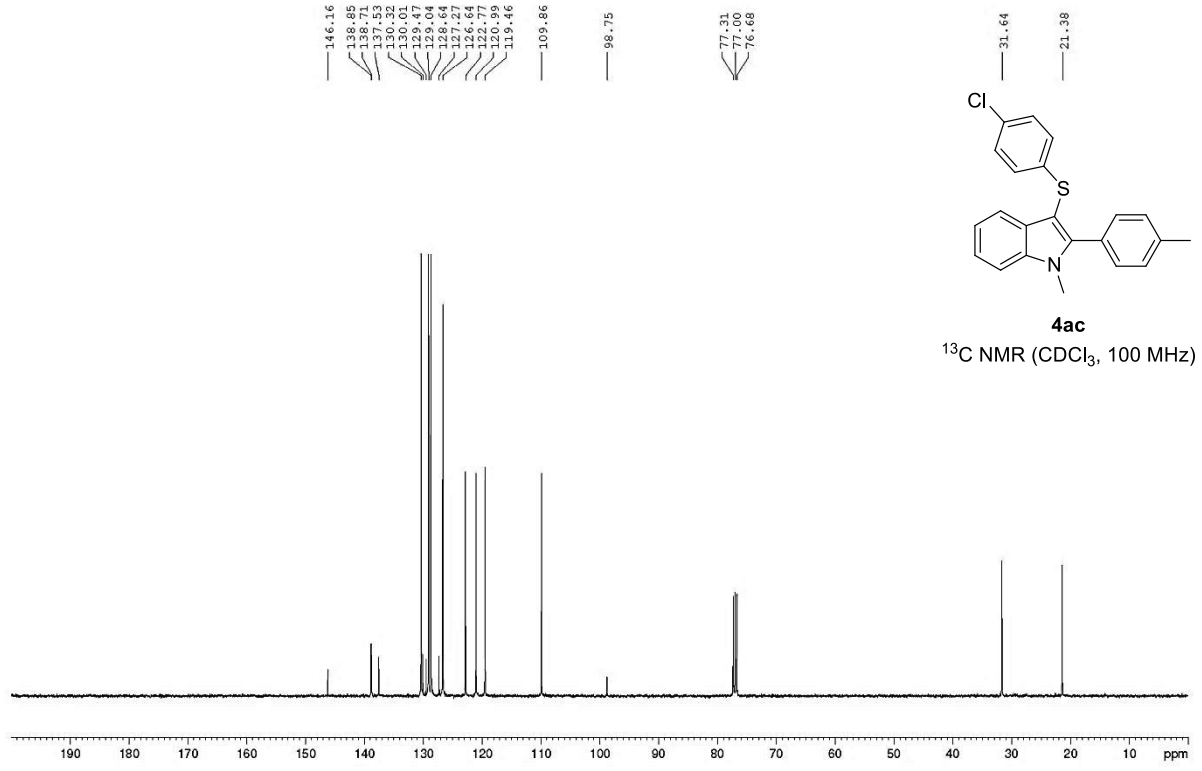
4ab

^{13}C NMR ($CDCl_3$, 100 MHz)



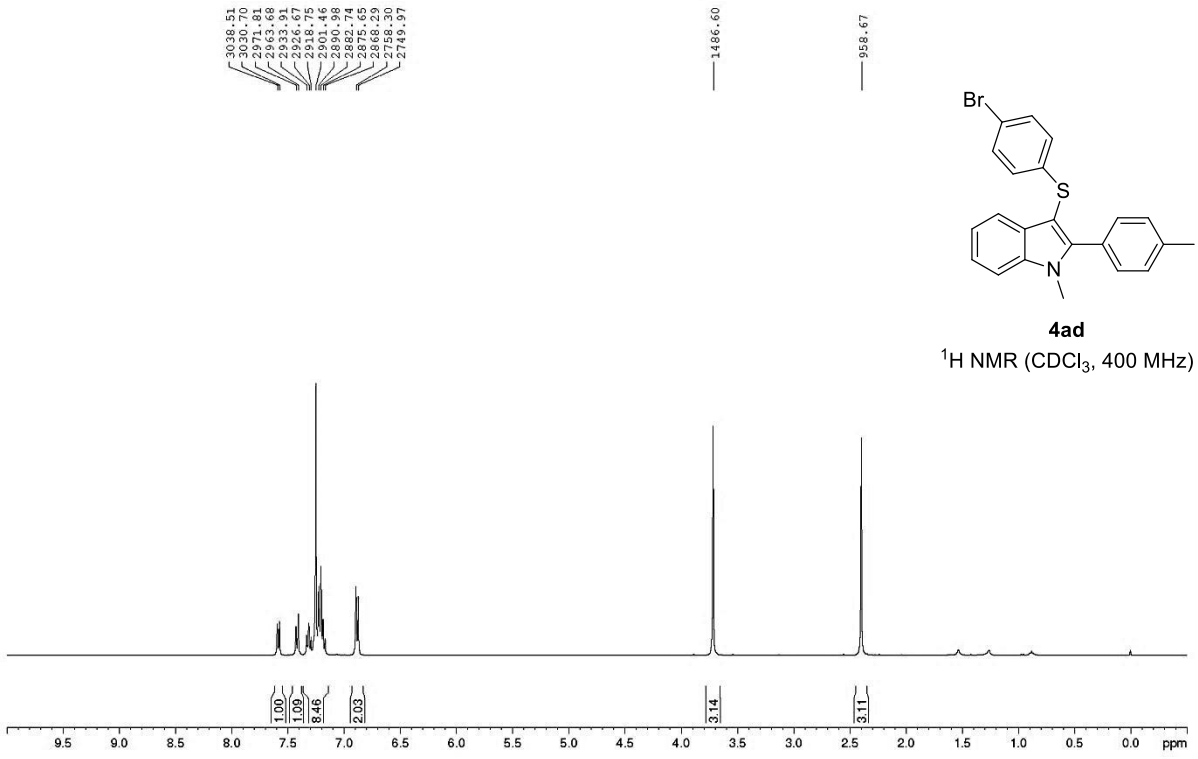
4ac

^{1}H NMR ($CDCl_3$, 400 MHz)



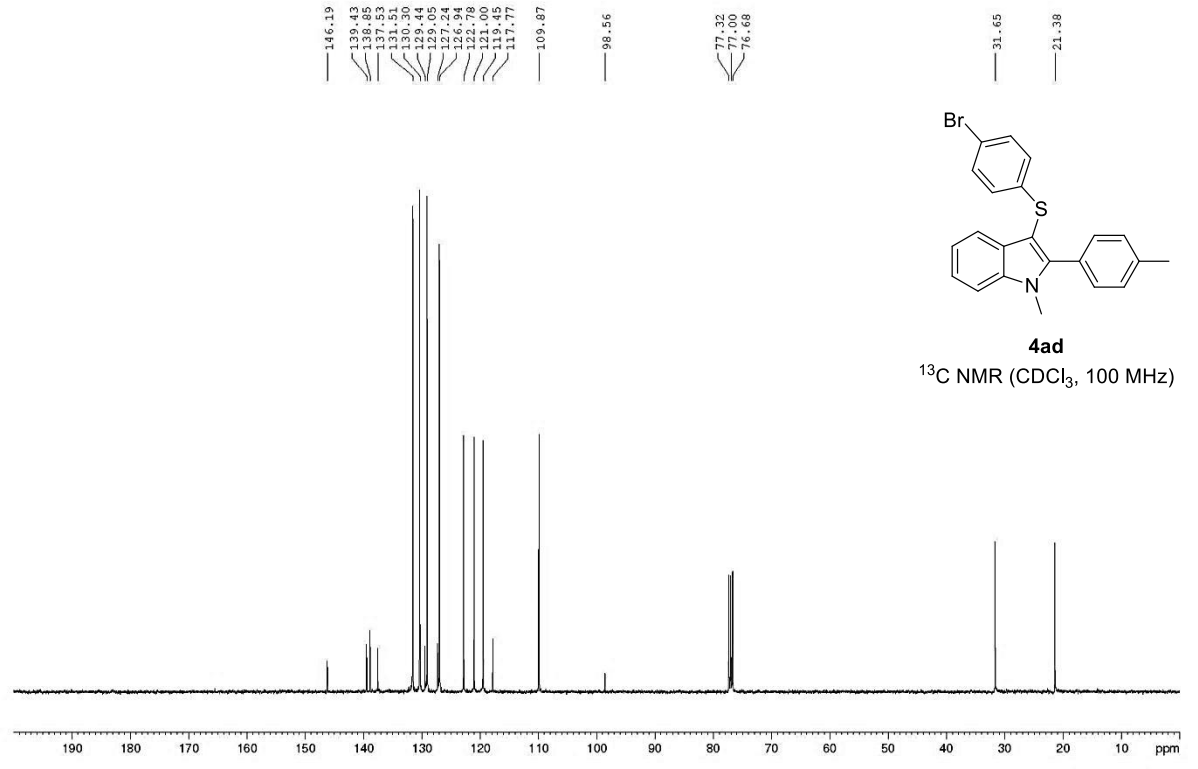
4ac

^{13}C NMR ($CDCl_3$, 100 MHz)



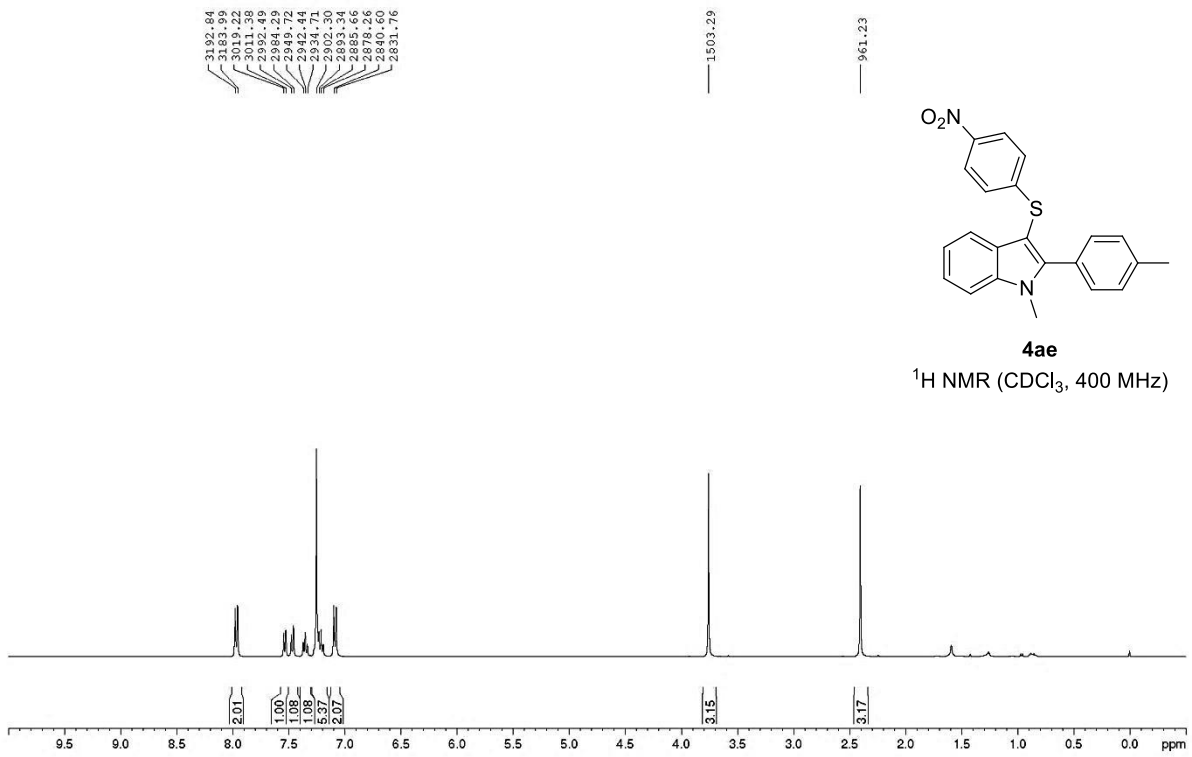
4ad

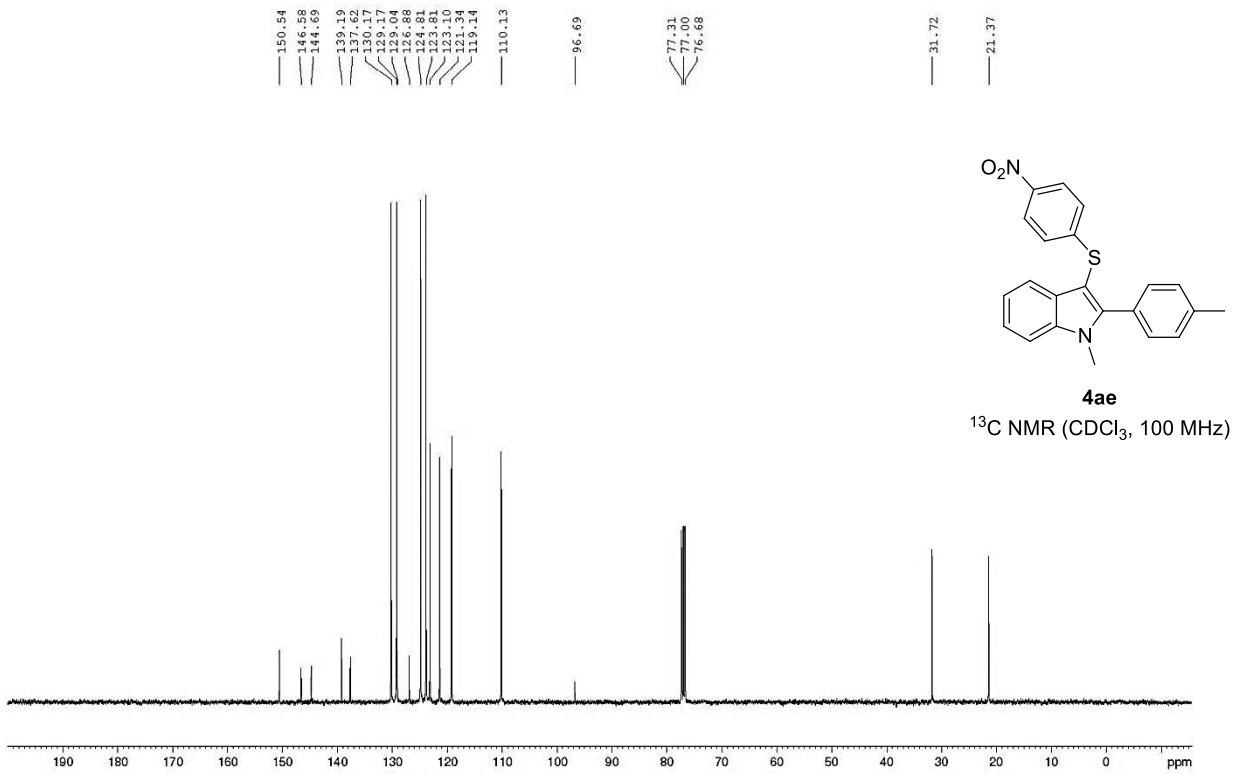
^{1}H NMR ($CDCl_3$, 400 MHz)

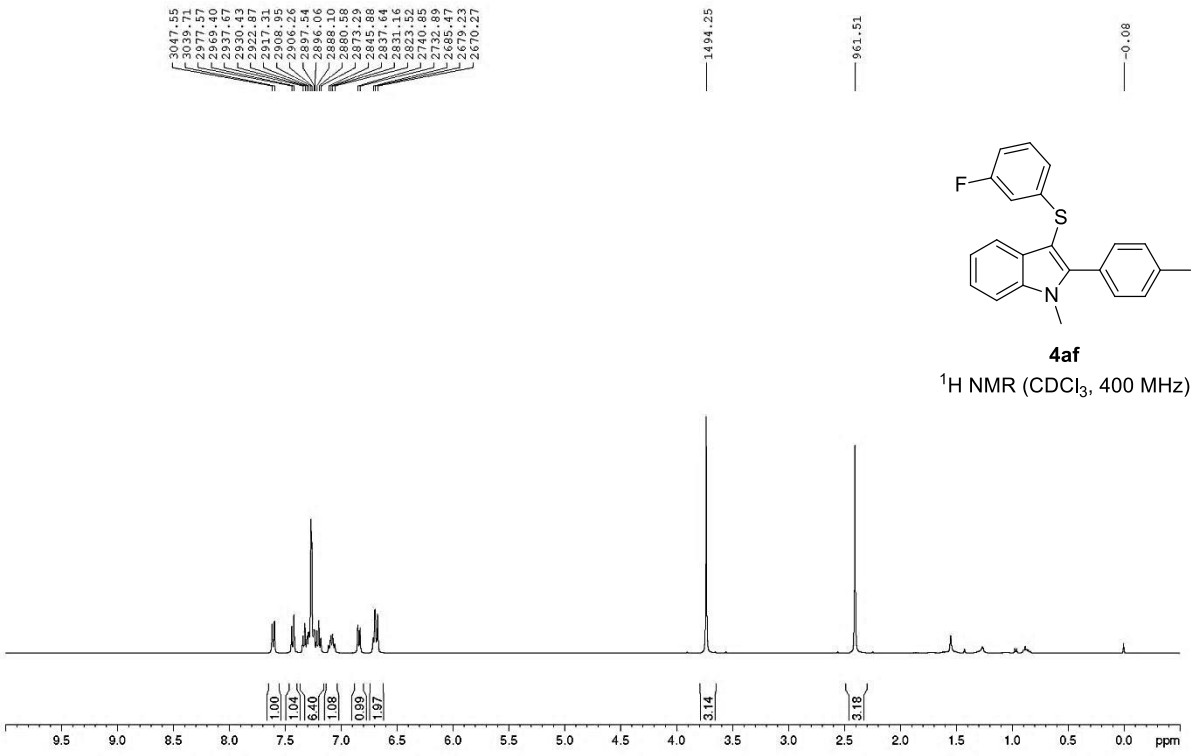


4ad

^{13}C NMR ($CDCl_3$, 100 MHz)

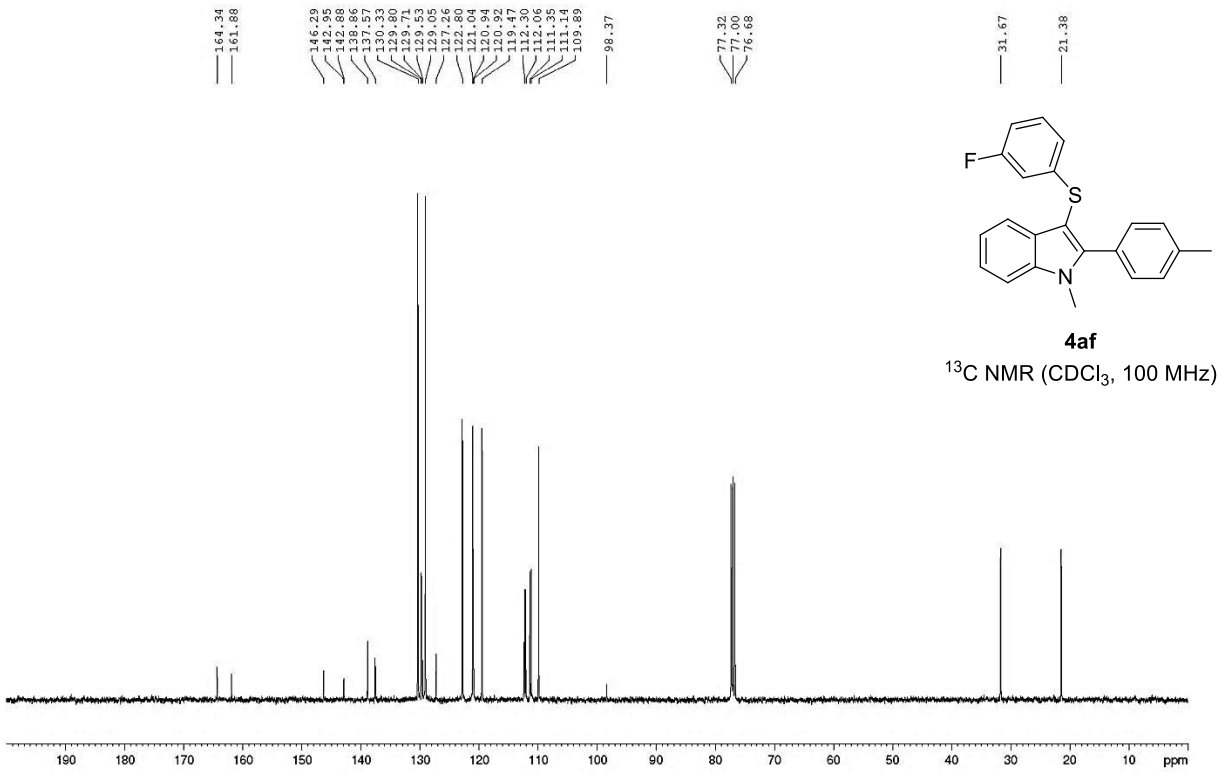

3192.84
3183.99
3019.22
3011.38
2992.49
2984.29
2949.72
2942.44
2934.71
2902.30
2893.34
2879.66
2871.26
2840.60
2831.76
1503.29
961.23
O2N
S
N
4ae
1H NMR (CDCl3, 400 MHz)
2.01
1.00
1.08
1.08
5.37
2.07
3.15
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


150.54
146.58
144.69
139.19
137.62
130.17
129.17
129.04
126.88
124.81
123.81
123.10
121.34
119.14
110.13
96.69
77.31
77.00
76.68
31.72
21.37
O2N
S
N
4ae
13C NMR (CDCl3, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



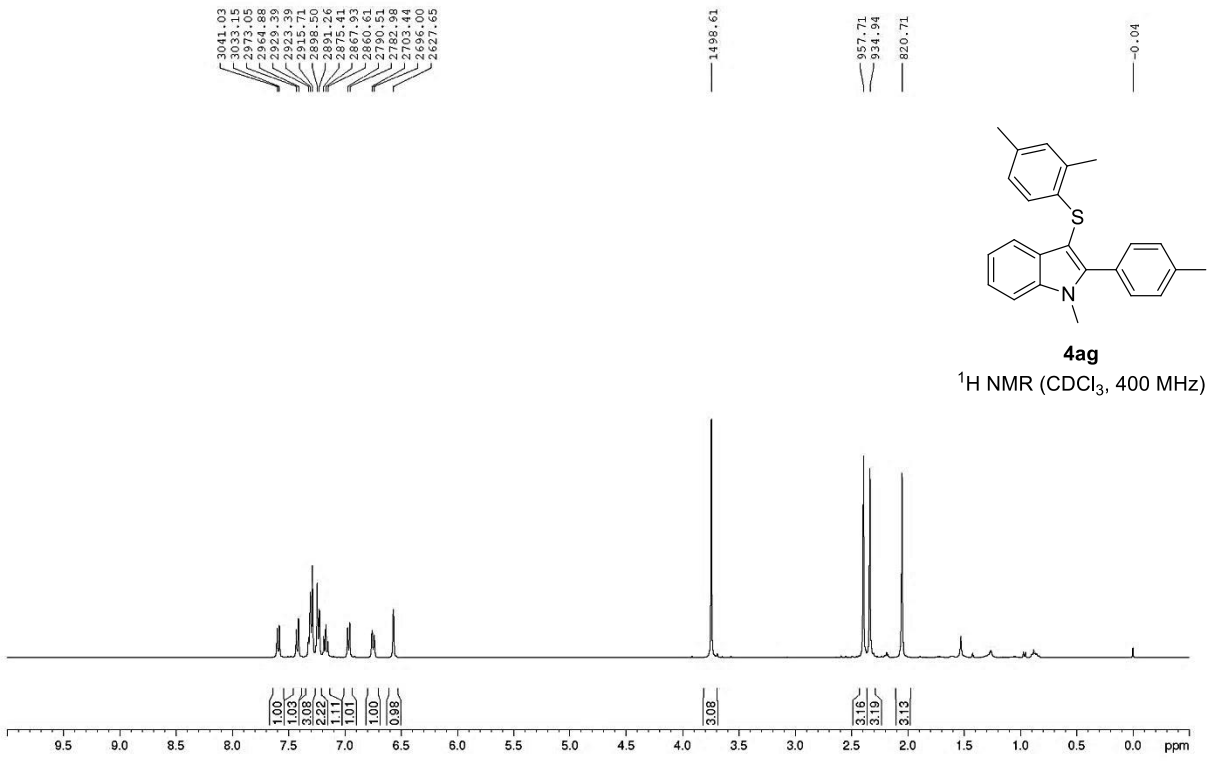
4af

^{1}H NMR ($CDCl_3$, 400 MHz)



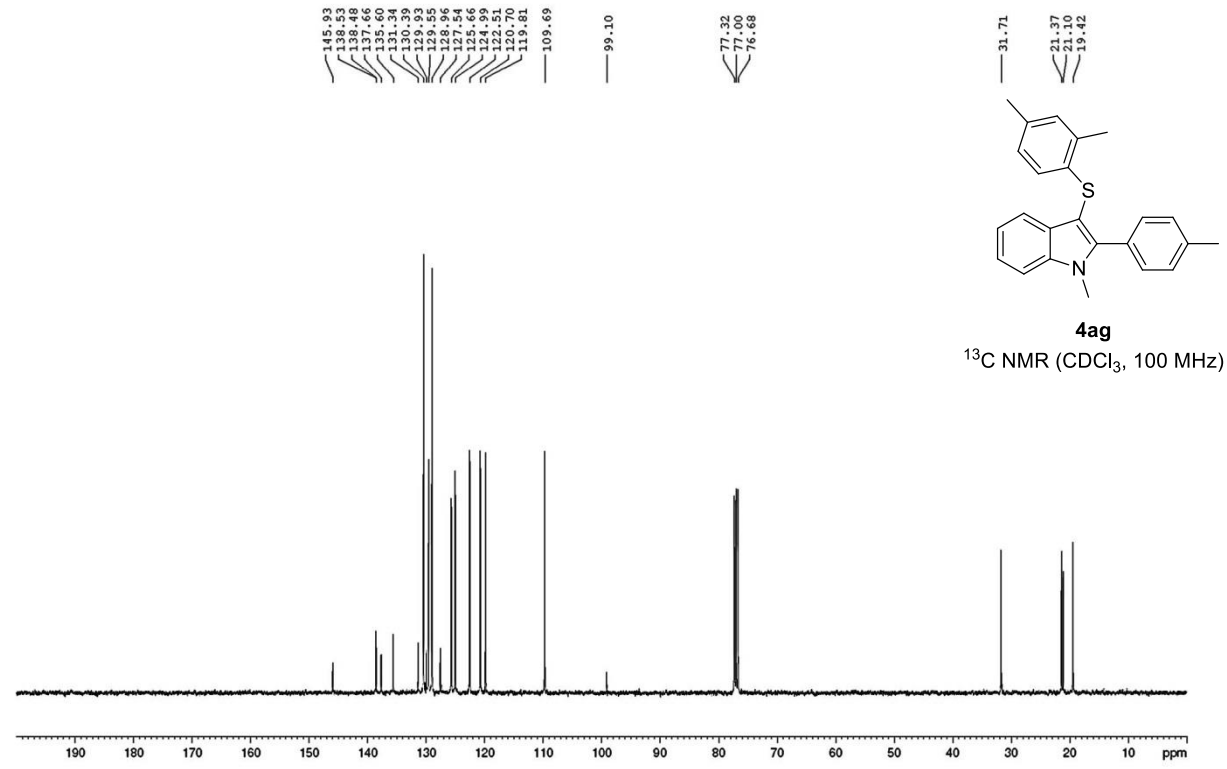
4af

^{13}C NMR ($CDCl_3$, 100 MHz)



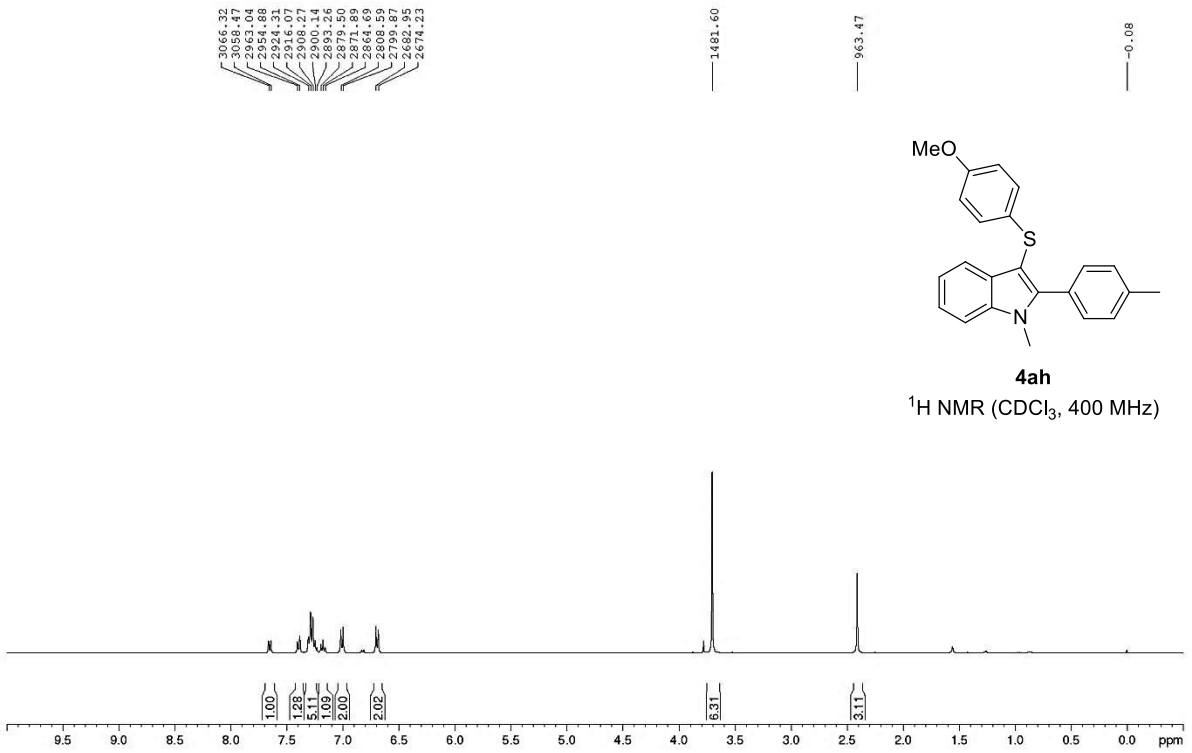
4ag

^{1}H NMR ($CDCl_3$, 400 MHz)



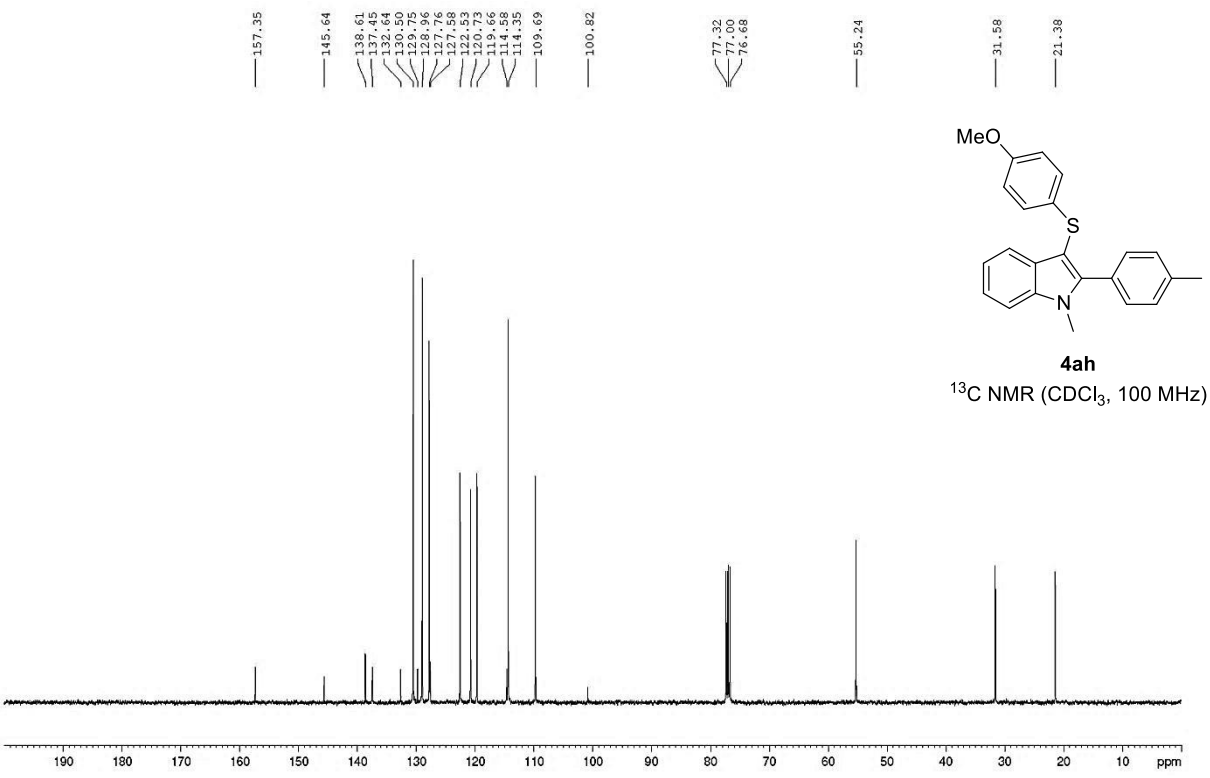
4ag

^{13}C NMR ($CDCl_3$, 100 MHz)



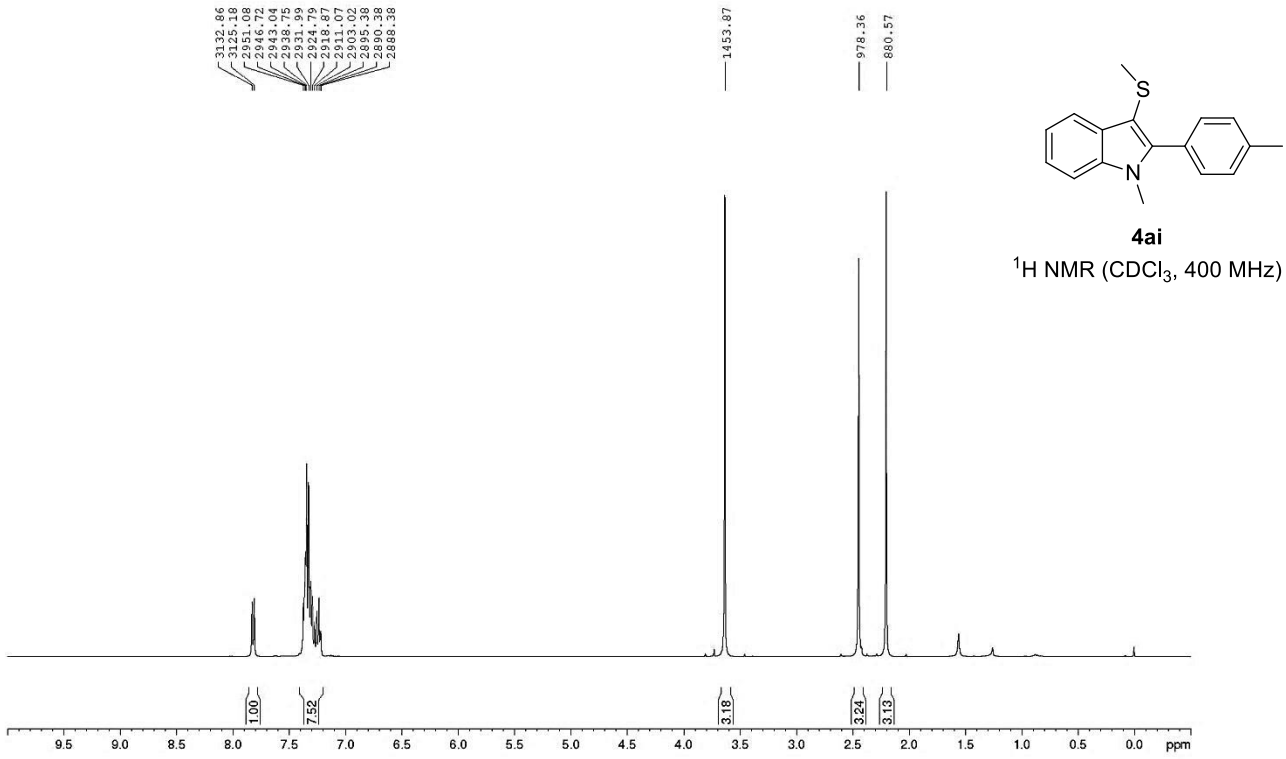
4ah

^{1}H NMR ($CDCl_3$, 400 MHz)



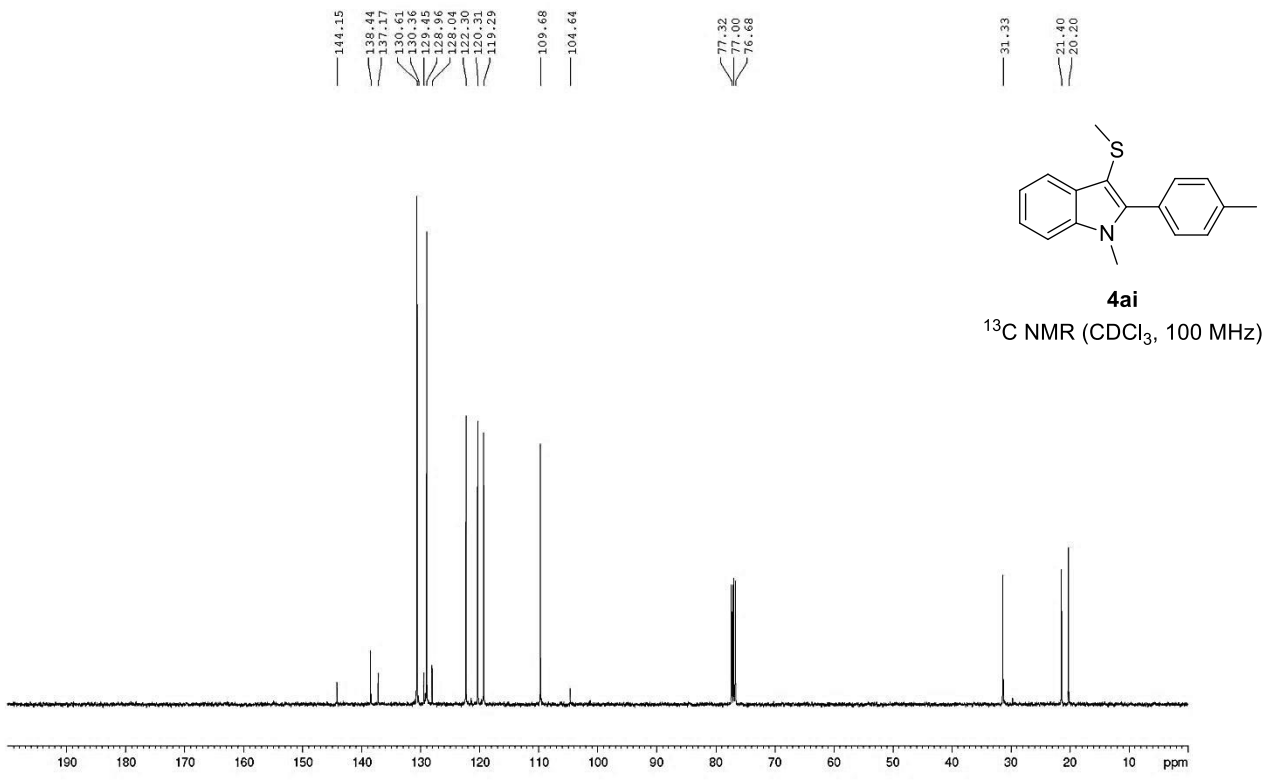
4ah

^{13}C NMR ($CDCl_3$, 100 MHz)



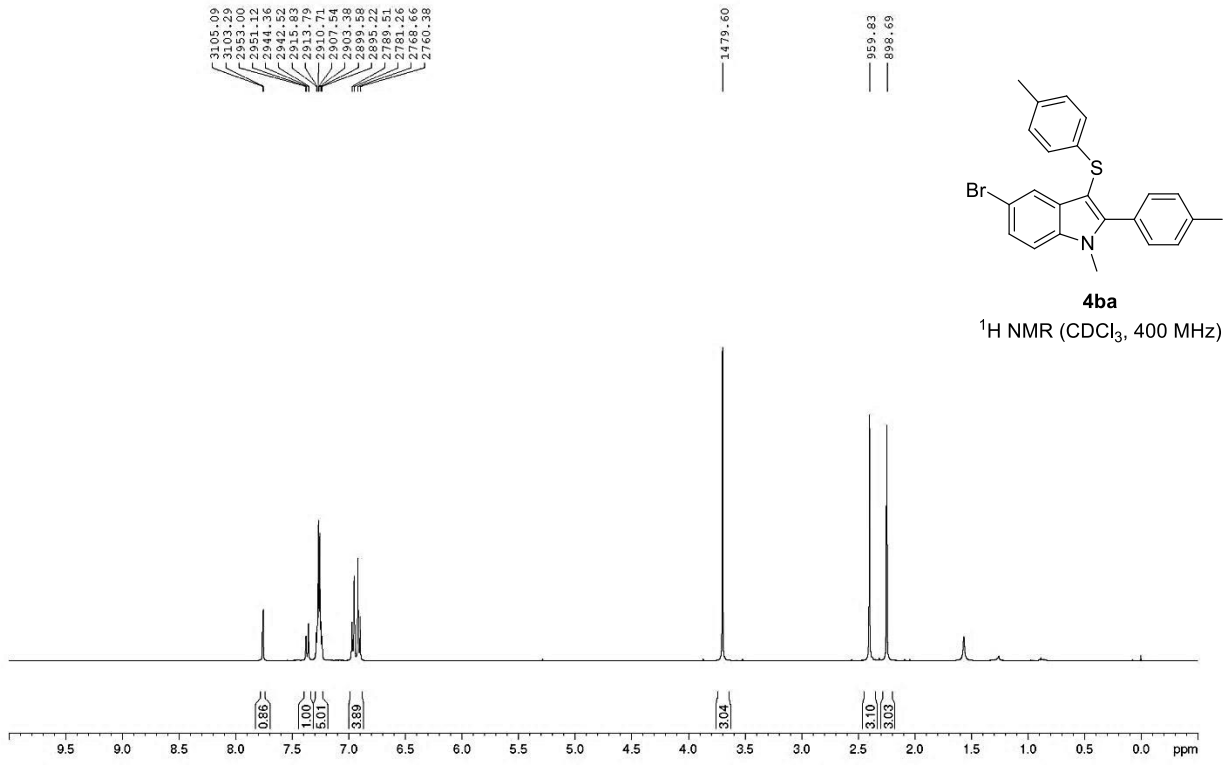
4ai

^{1}H NMR ($CDCl_3$, 400 MHz)



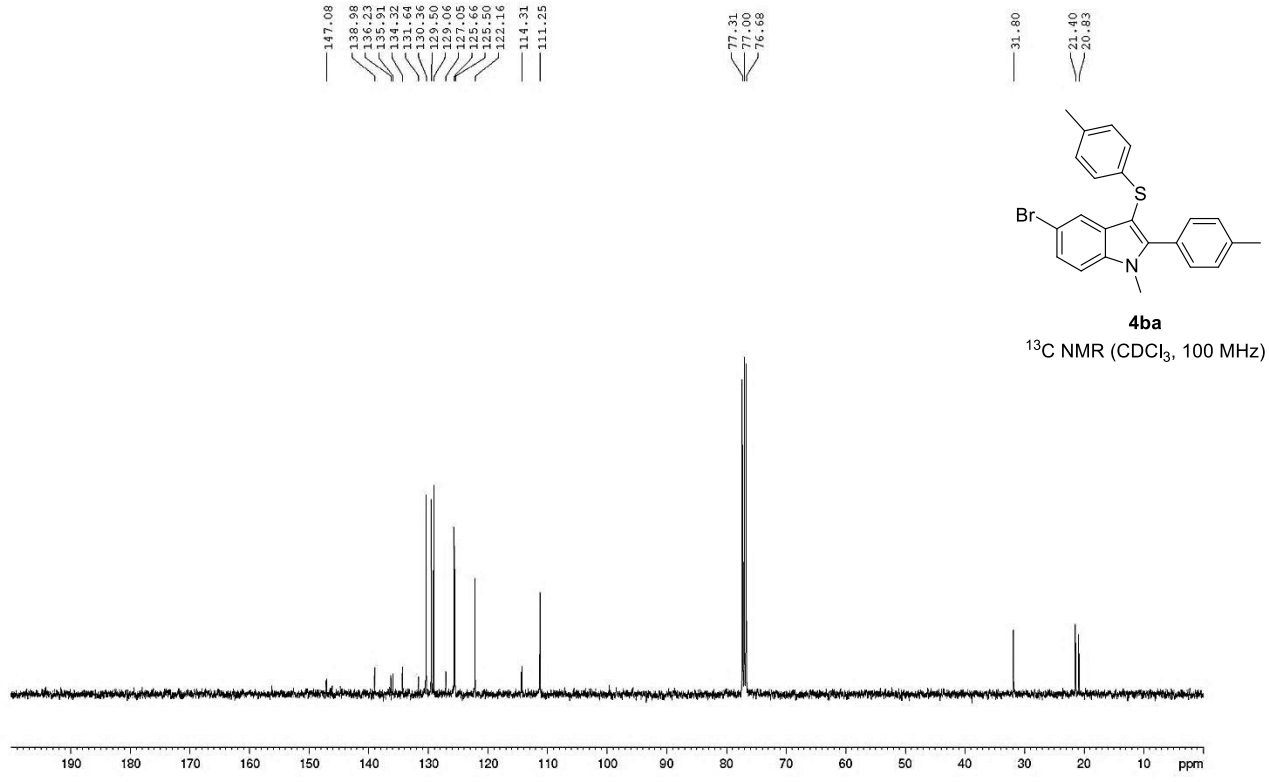
4ai

^{13}C NMR ($CDCl_3$, 100 MHz)



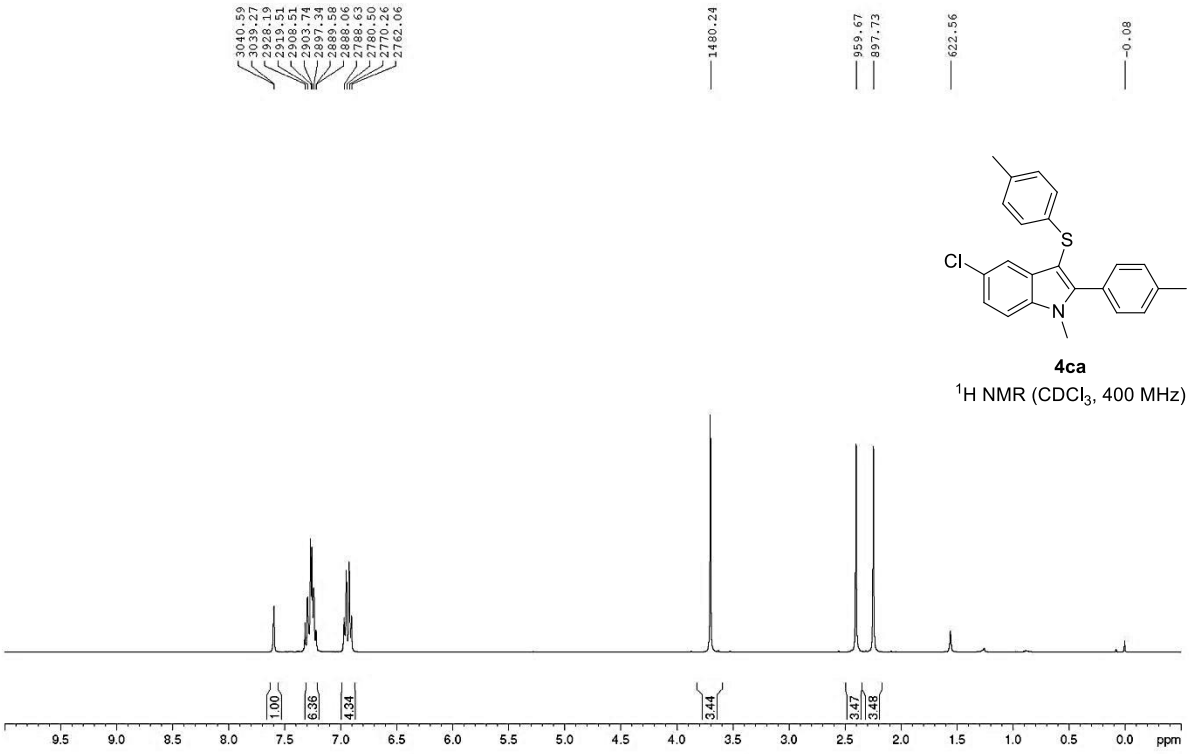
4ba

^{1}H NMR ($CDCl_3$, 400 MHz)



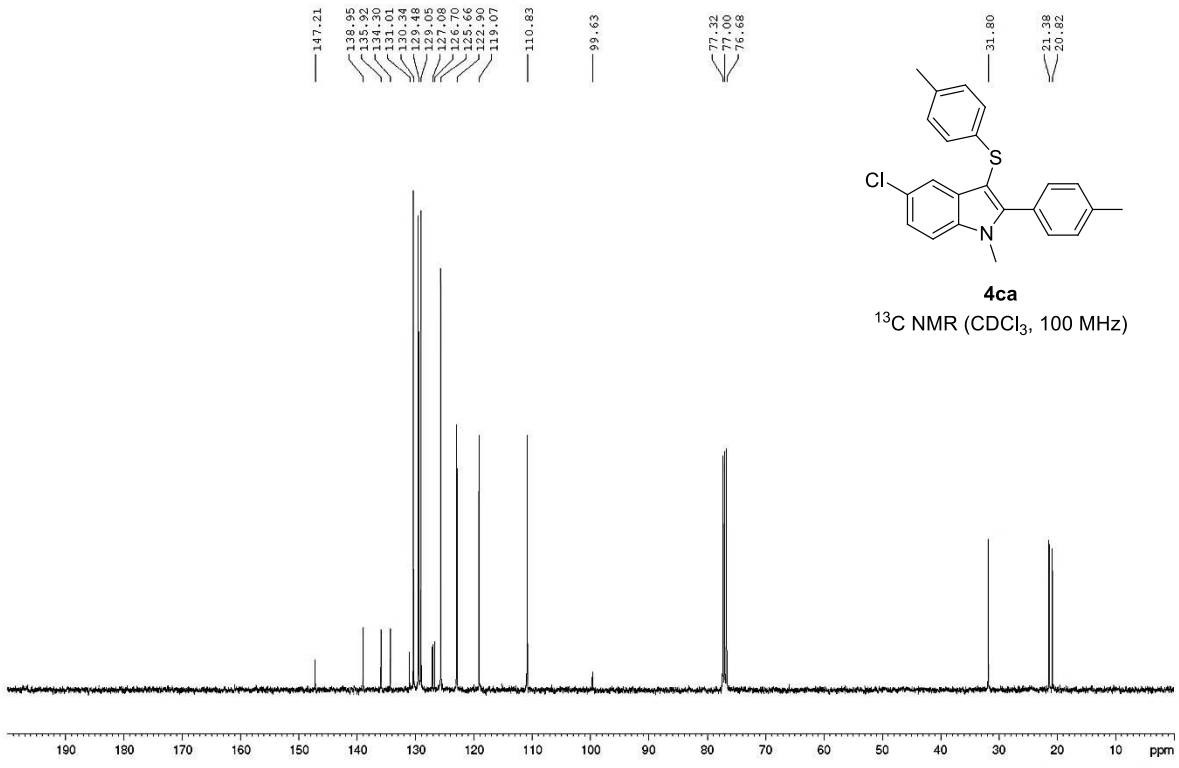
4ba

^{13}C NMR ($CDCl_3$, 100 MHz)



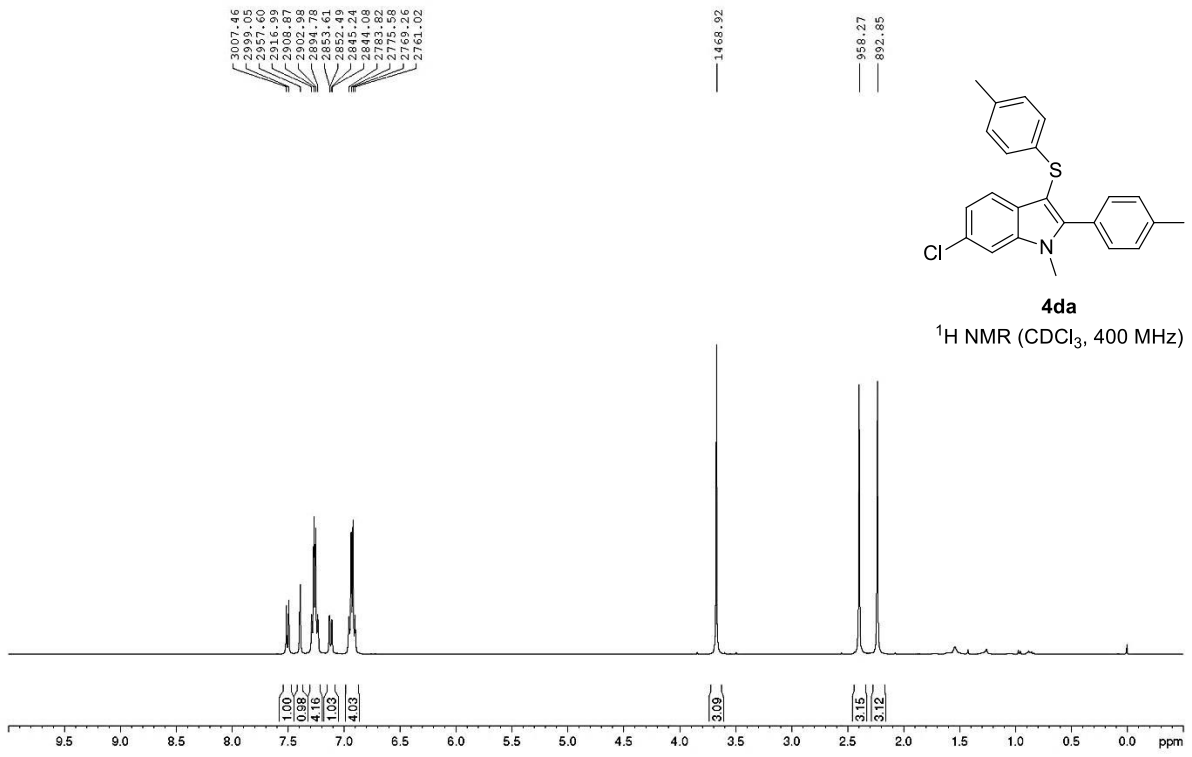
4ca

^{1}H NMR ($CDCl_3$, 400 MHz)



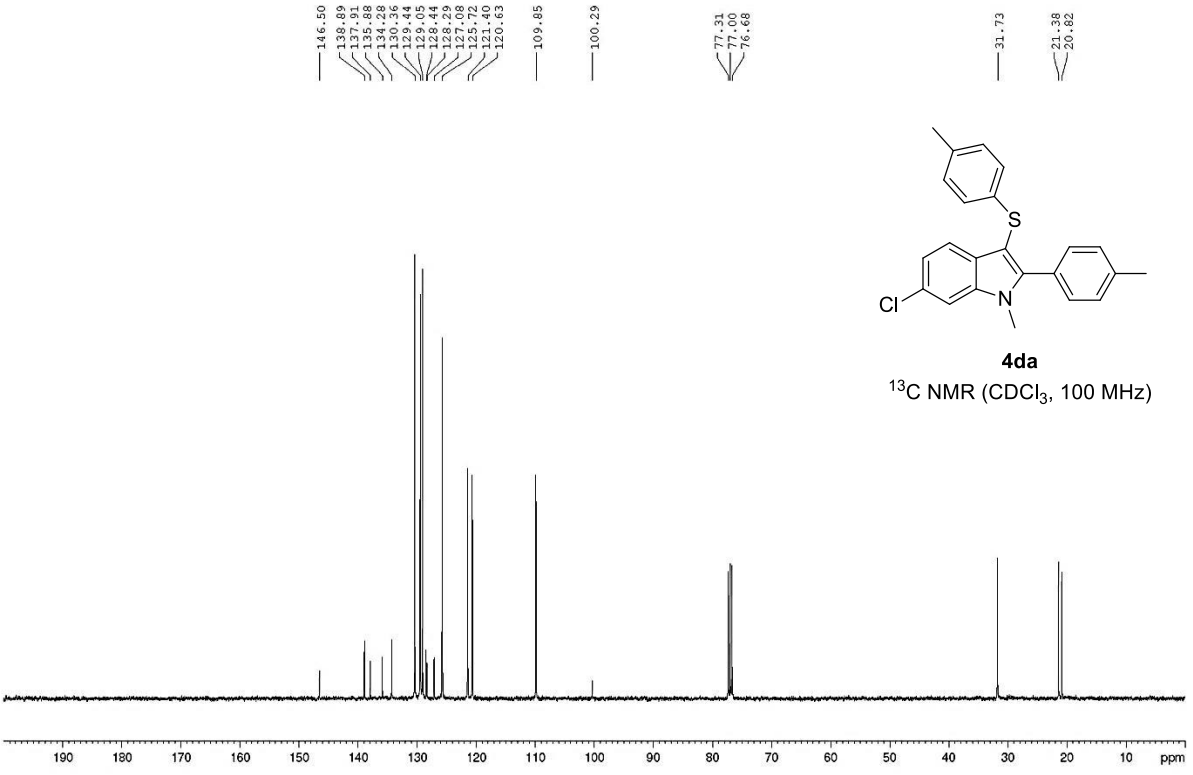
4ca

^{13}C NMR ($CDCl_3$, 100 MHz)



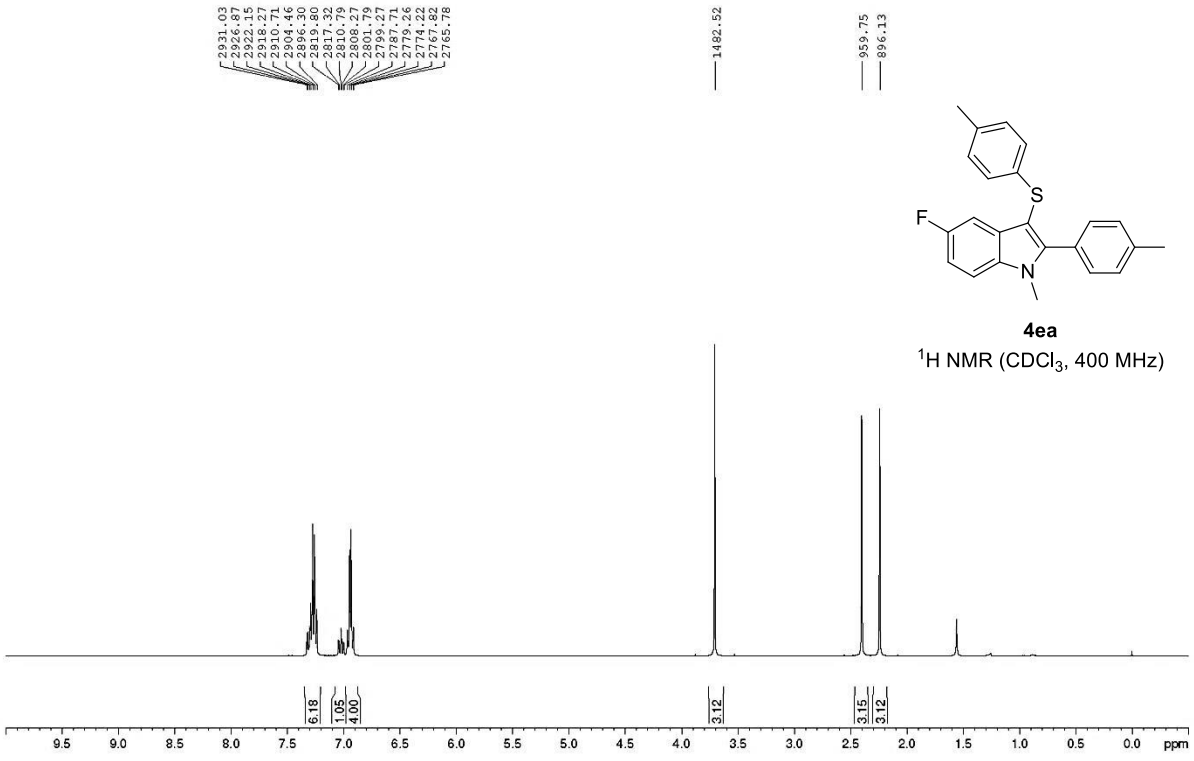
4da

^{1}H NMR ($CDCl_3$, 400 MHz)



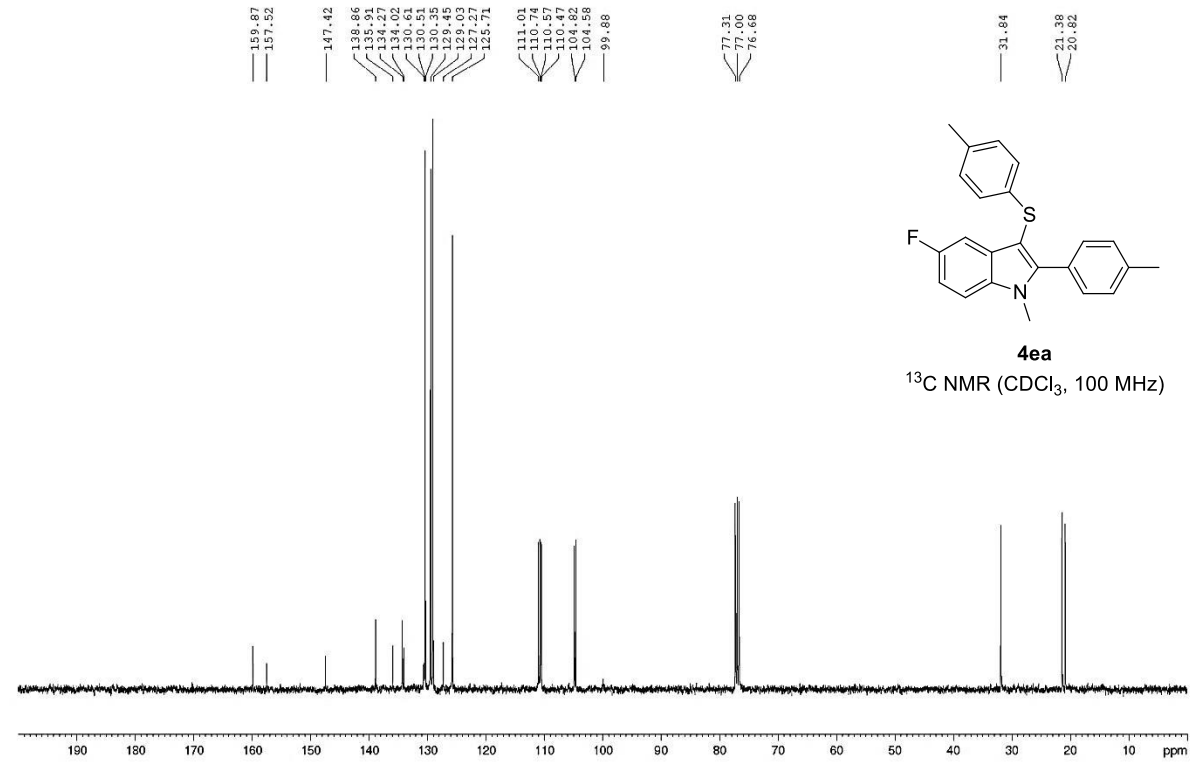
4da

^{13}C NMR ($CDCl_3$, 100 MHz)



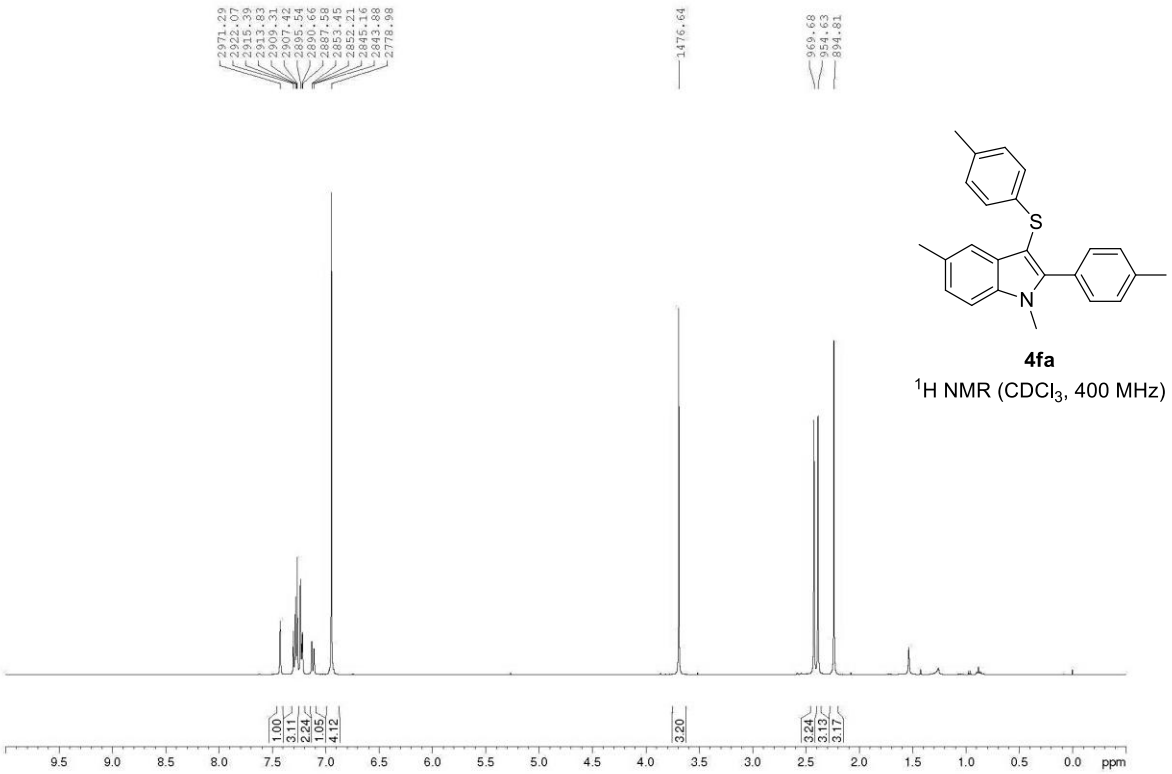
4ea

^{1}H NMR ($CDCl_3$, 400 MHz)



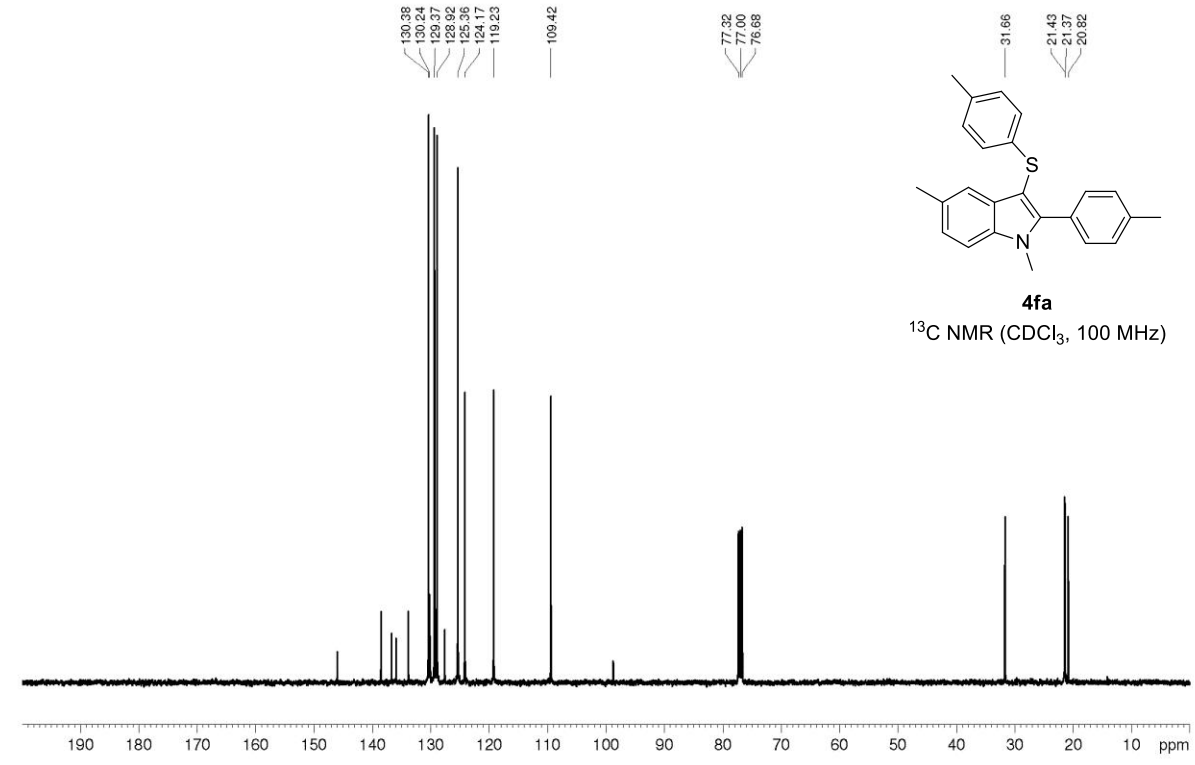
4ea

^{13}C NMR ($CDCl_3$, 100 MHz)



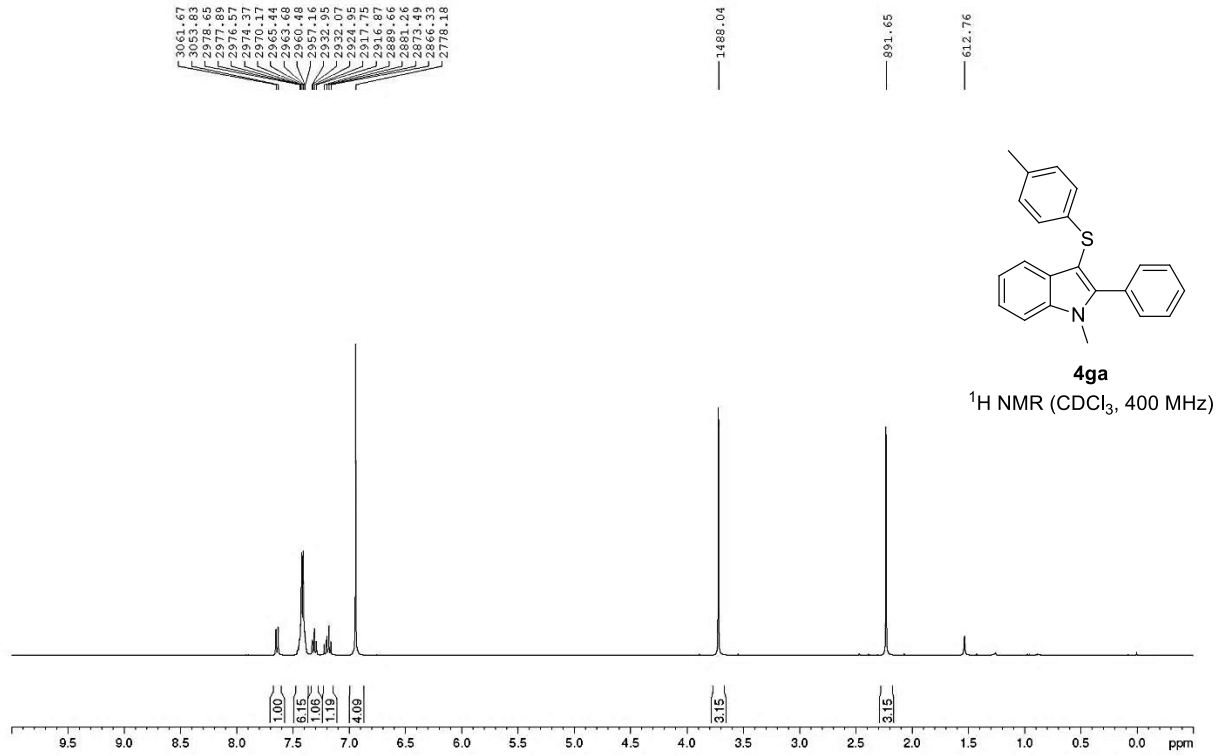
4fa

^{1}H NMR ($CDCl_3$, 400 MHz)



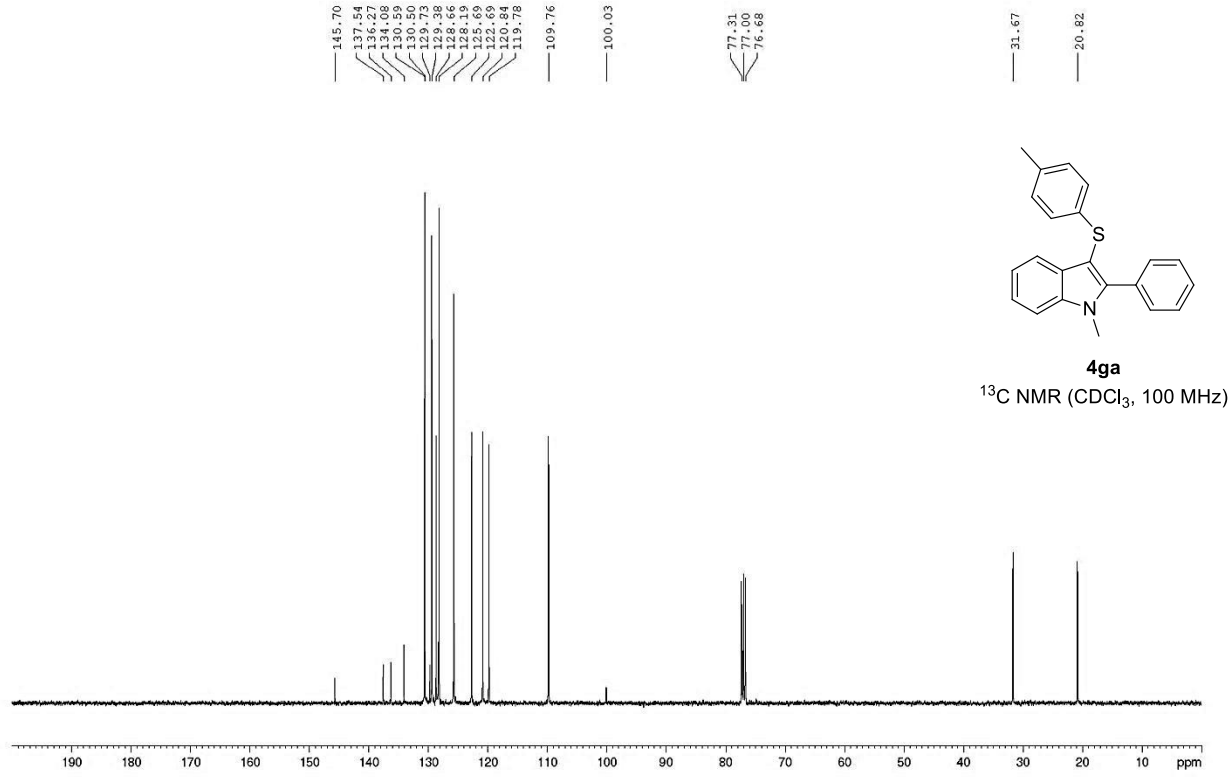
4fa

^{13}C NMR ($CDCl_3$, 100 MHz)



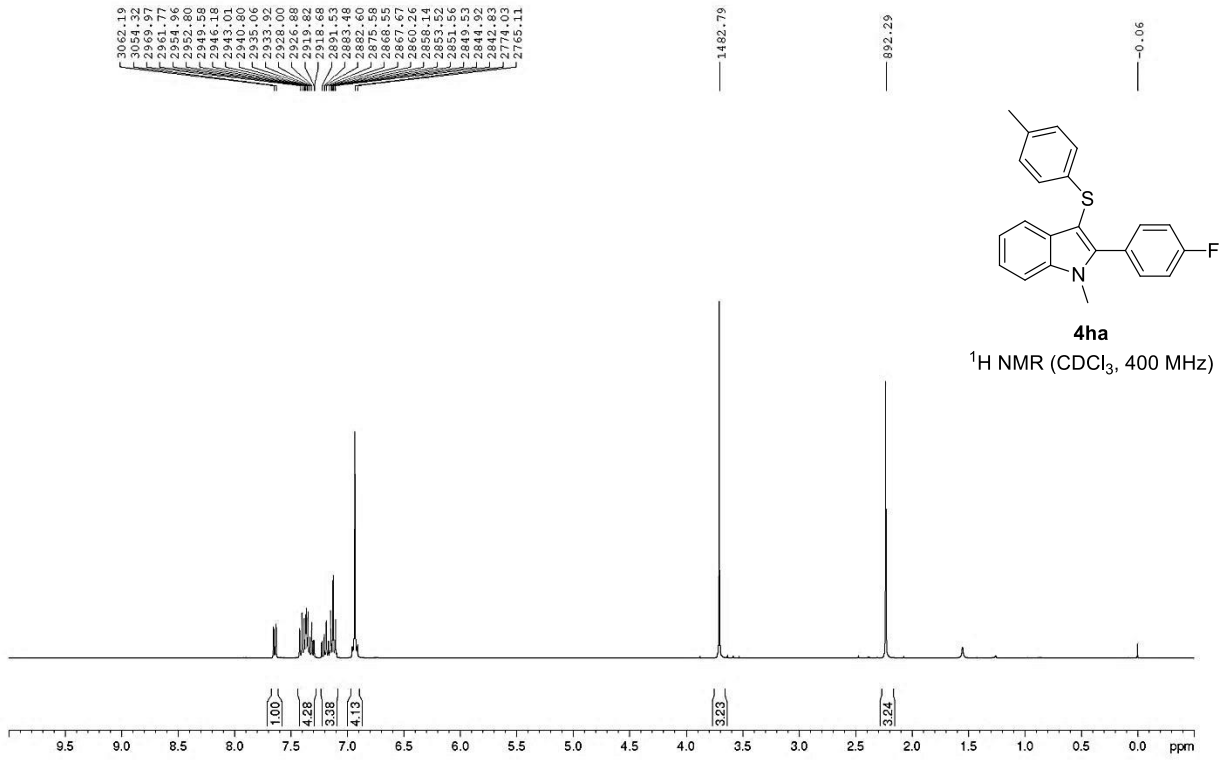
4ga

^{1}H NMR ($CDCl_3$, 400 MHz)



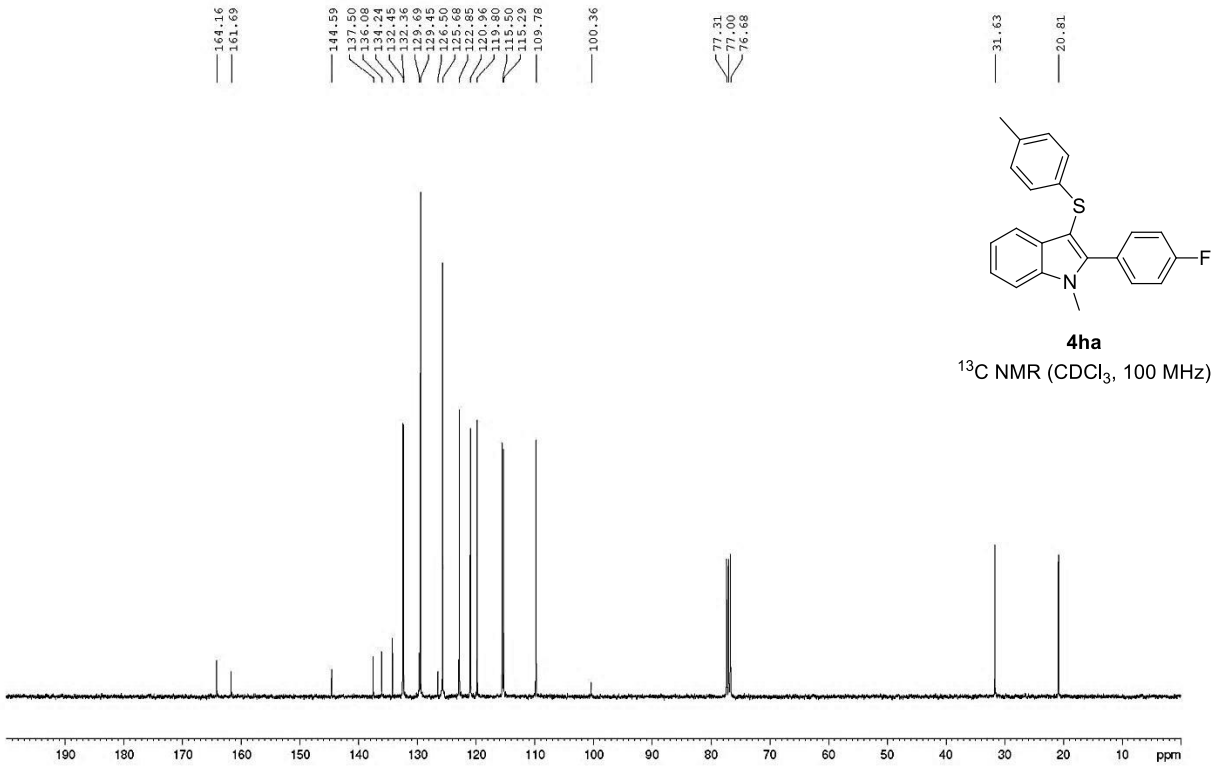
4ga

^{13}C NMR ($CDCl_3$, 100 MHz)



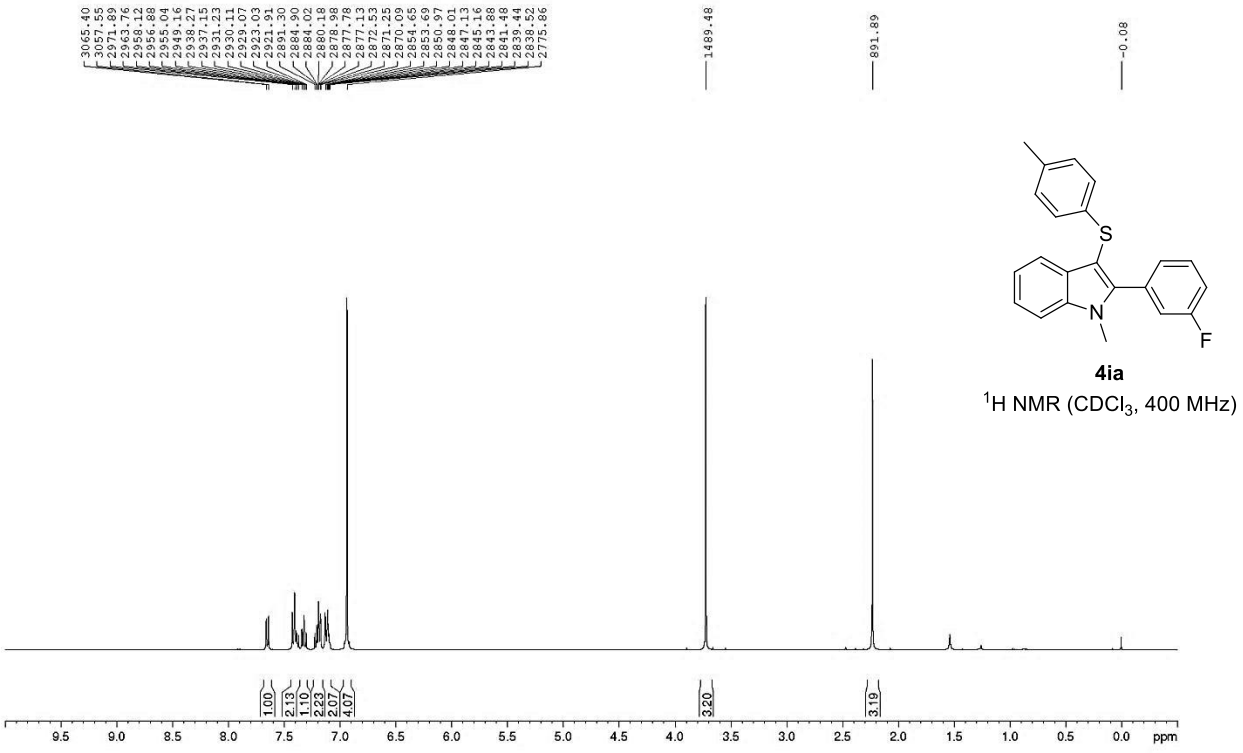
4ha

^{1}H NMR ($CDCl_3$, 400 MHz)



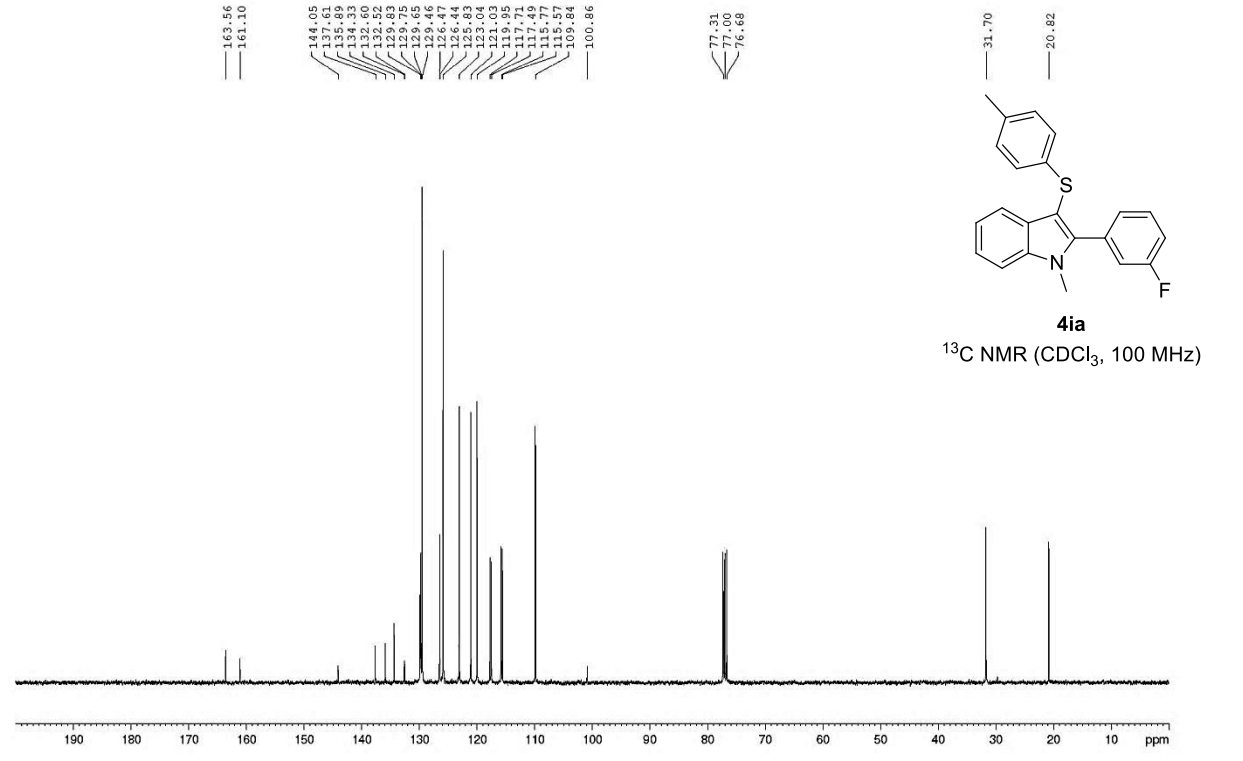
4ha

^{13}C NMR ($CDCl_3$, 100 MHz)



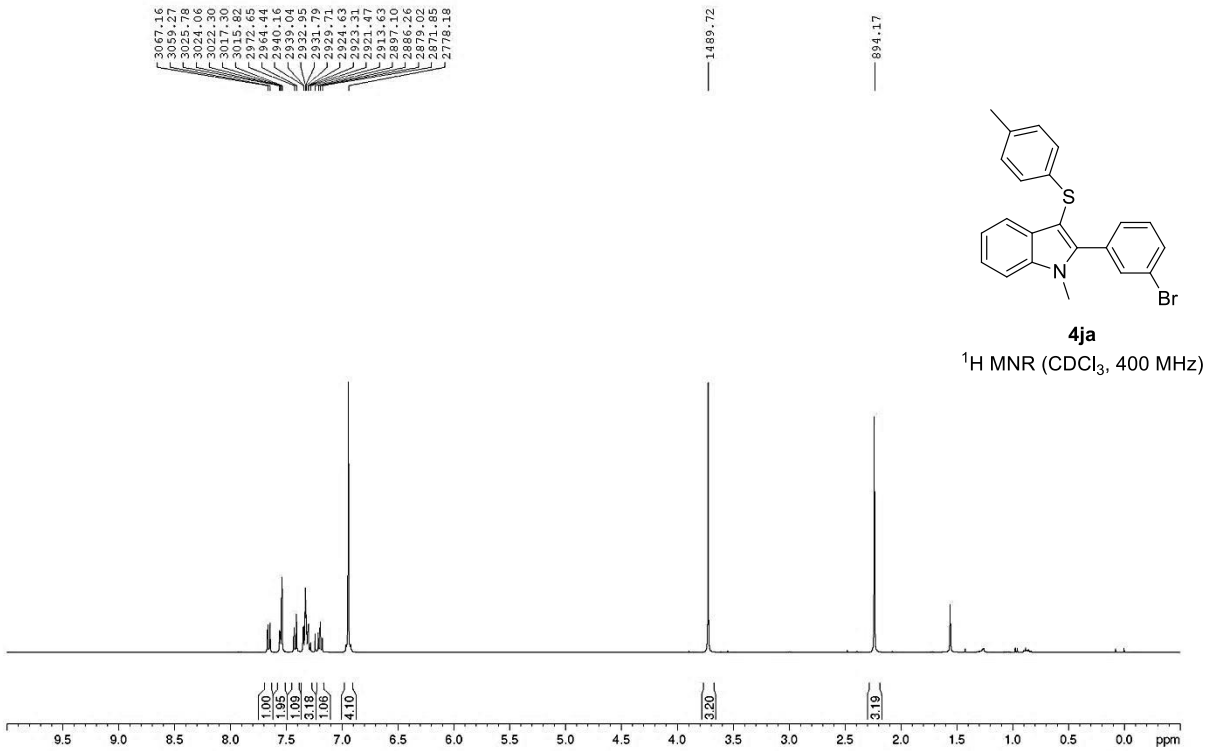
4ia

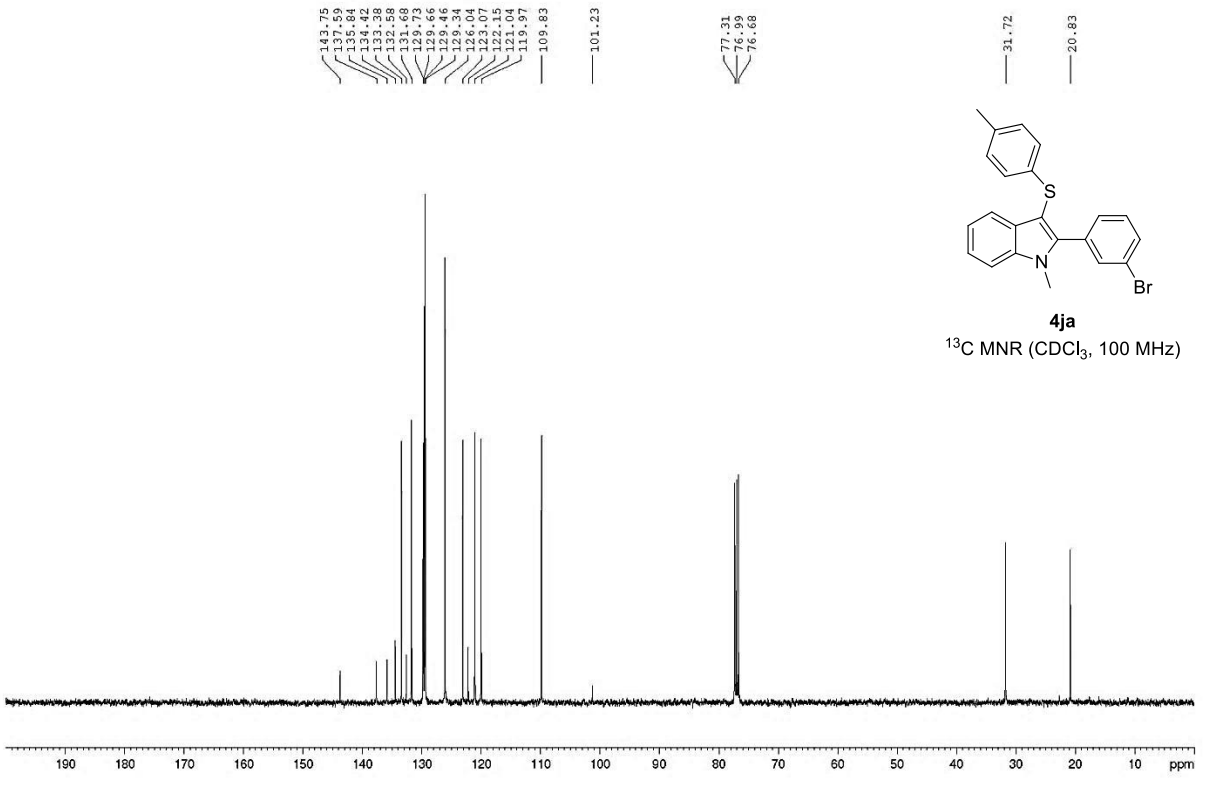
^{1}H NMR ($CDCl_3$, 400 MHz)

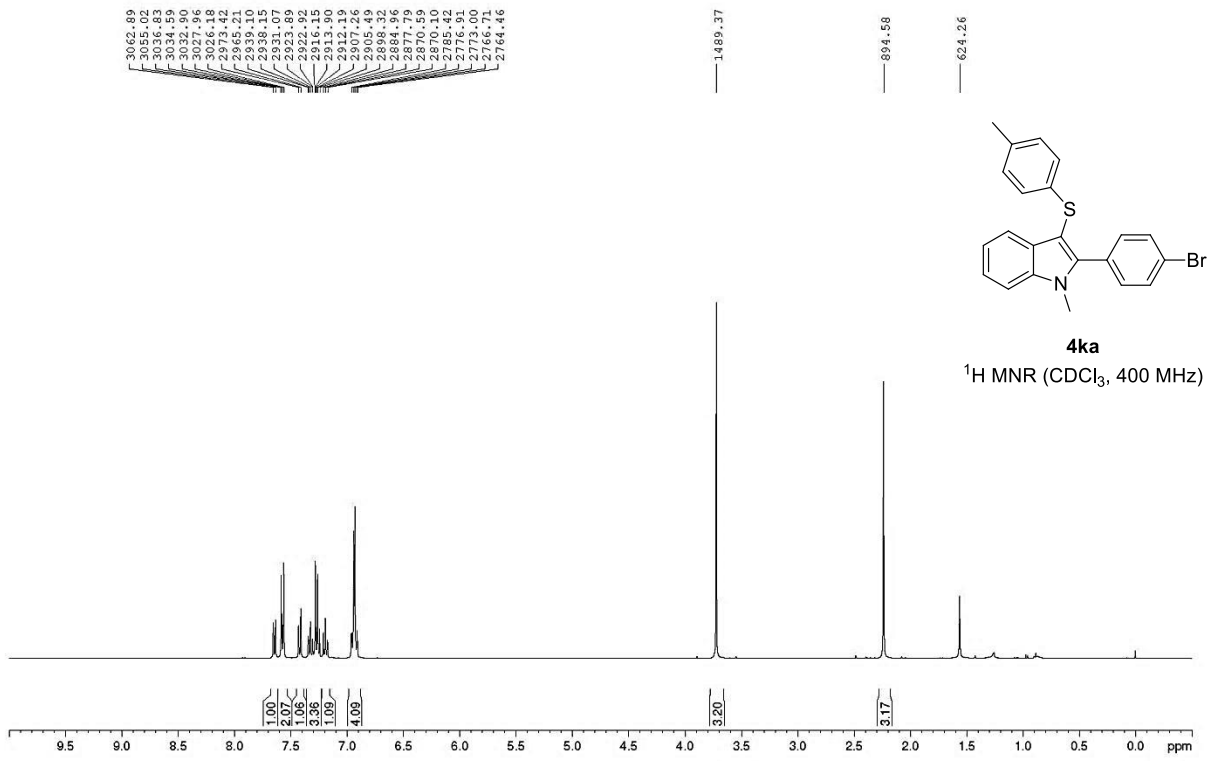


4ia

^{13}C NMR ($CDCl_3$, 100 MHz)

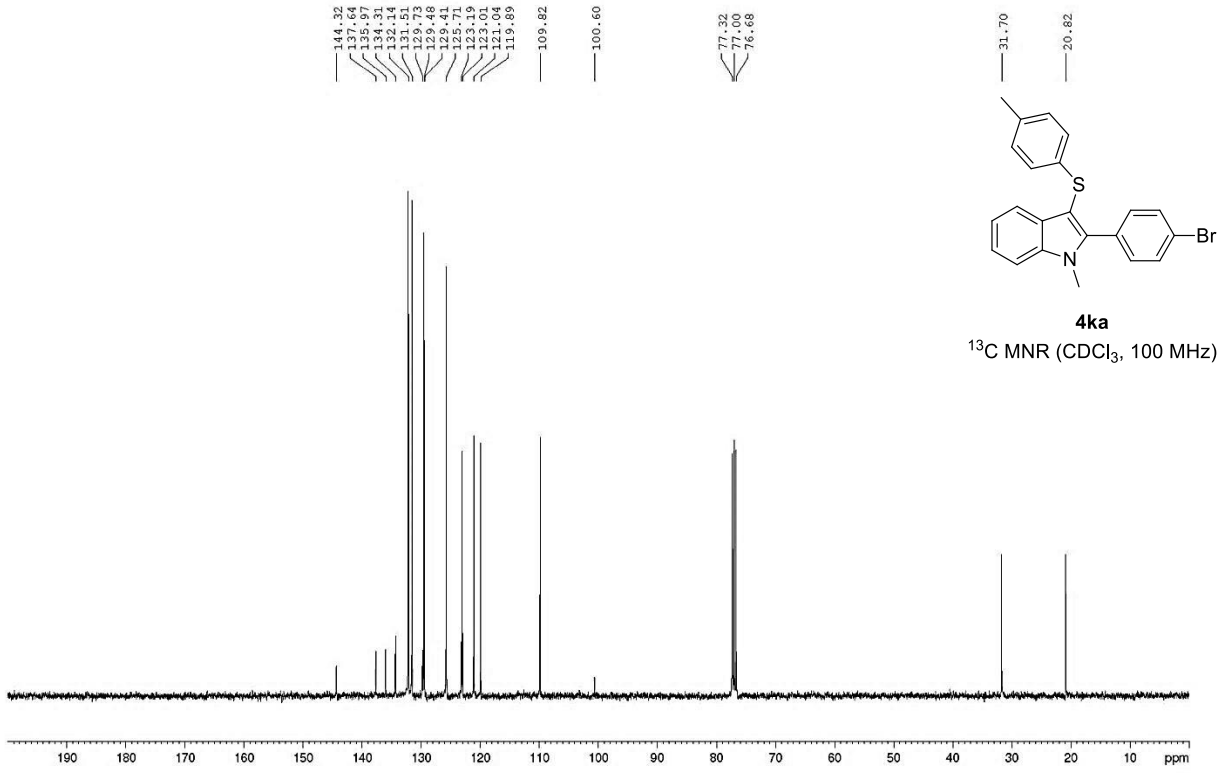

3067.16
3059.27
3025.78
3024.06
3022.30
3017.30
3015.82
2972.65
2964.44
2940.16
2939.04
2932.95
2931.79
2930.71
2924.63
2923.31
2921.47
2913.63
2897.10
2886.26
2879.02
2871.85
2778.18
1489.72
894.17
S
N
Br
4ja
1H MNR (CDCl3, 400 MHz)
1.00
1.95
1.09
3.18
1.06
4.10
3.20
3.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


143.75
137.59
135.84
134.42
133.38
132.58
131.68
129.73
129.66
129.46
129.34
126.04
123.07
122.15
121.04
119.97
109.83
101.23
77.31
76.99
76.68
31.72
20.83
S
N
Br
4ja
13C MNR (CDCl3, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



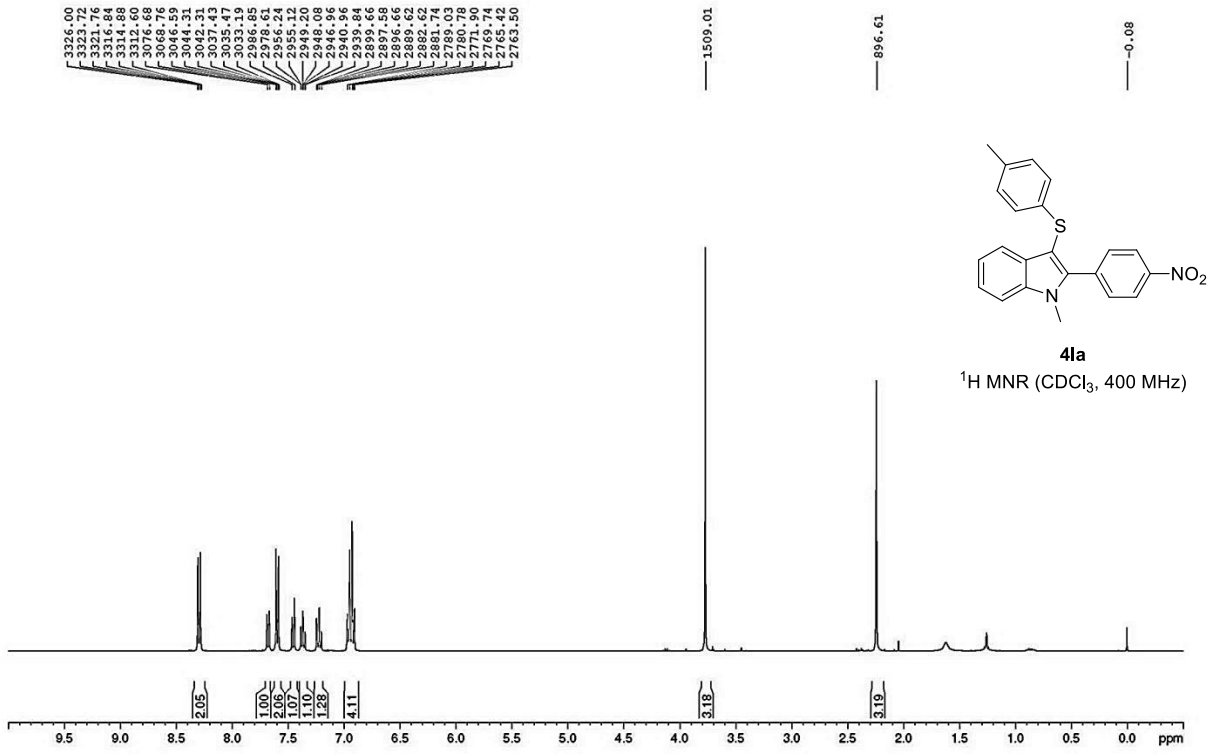
4ka

^{1}H MNR ($CDCl_3$, 400 MHz)



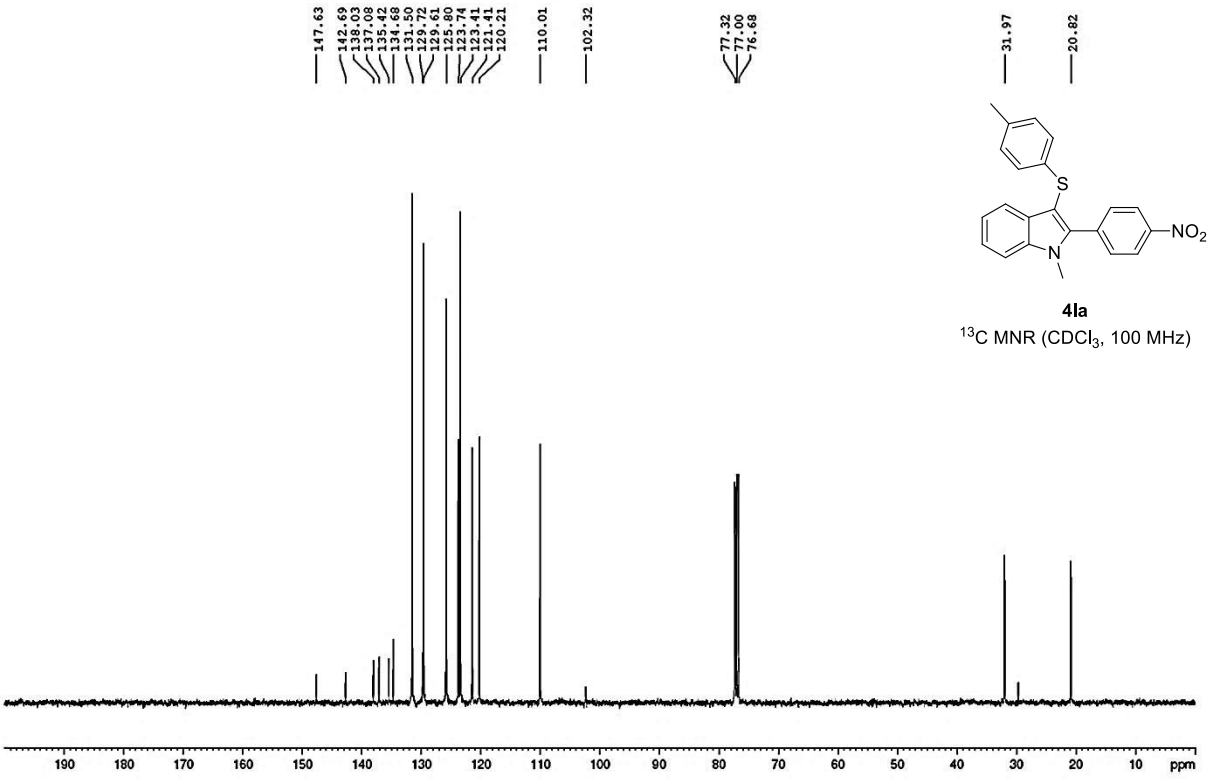
4ka

^{13}C MNR ($CDCl_3$, 100 MHz)



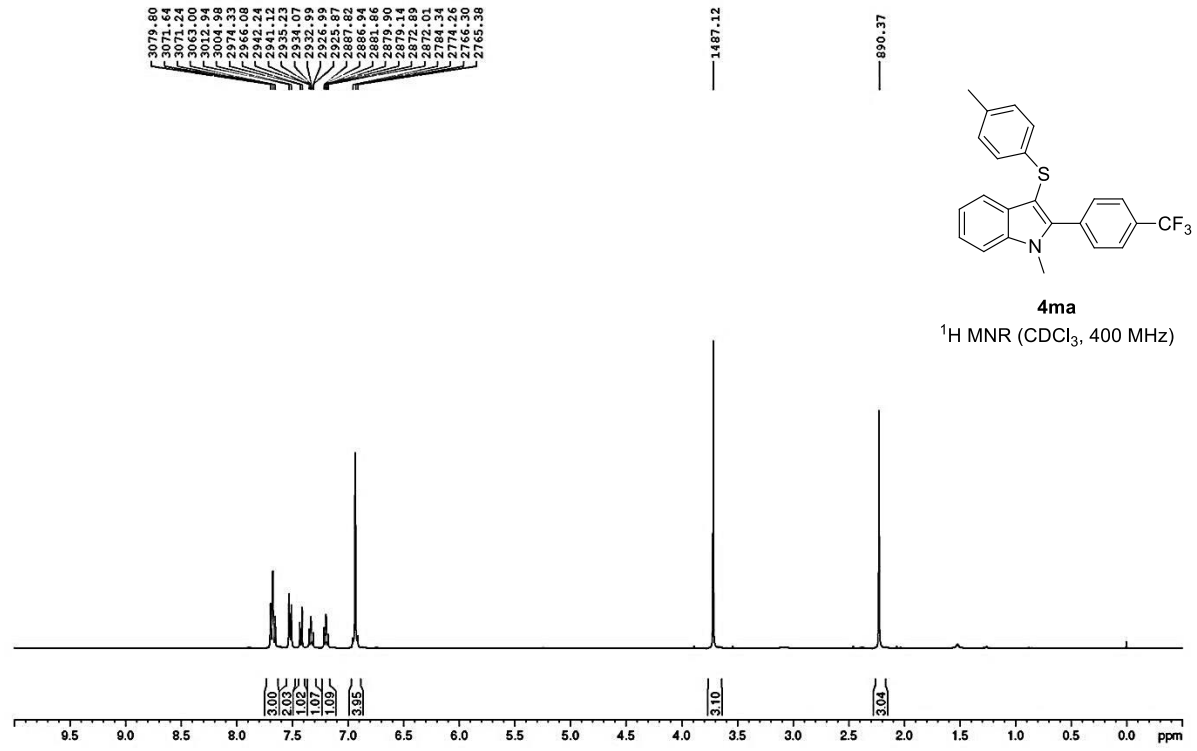
4la

^{1}H MNR ($CDCl_3$, 400 MHz)



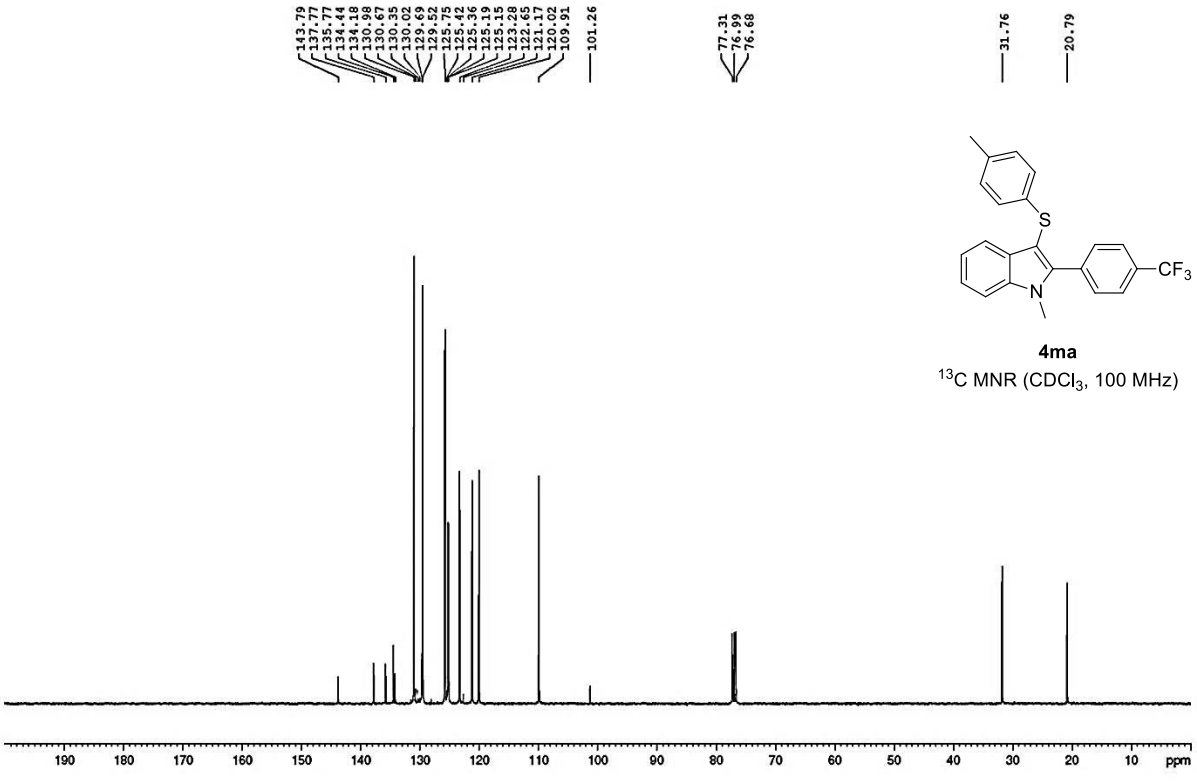
4la

^{13}C MNR ($CDCl_3$, 100 MHz)



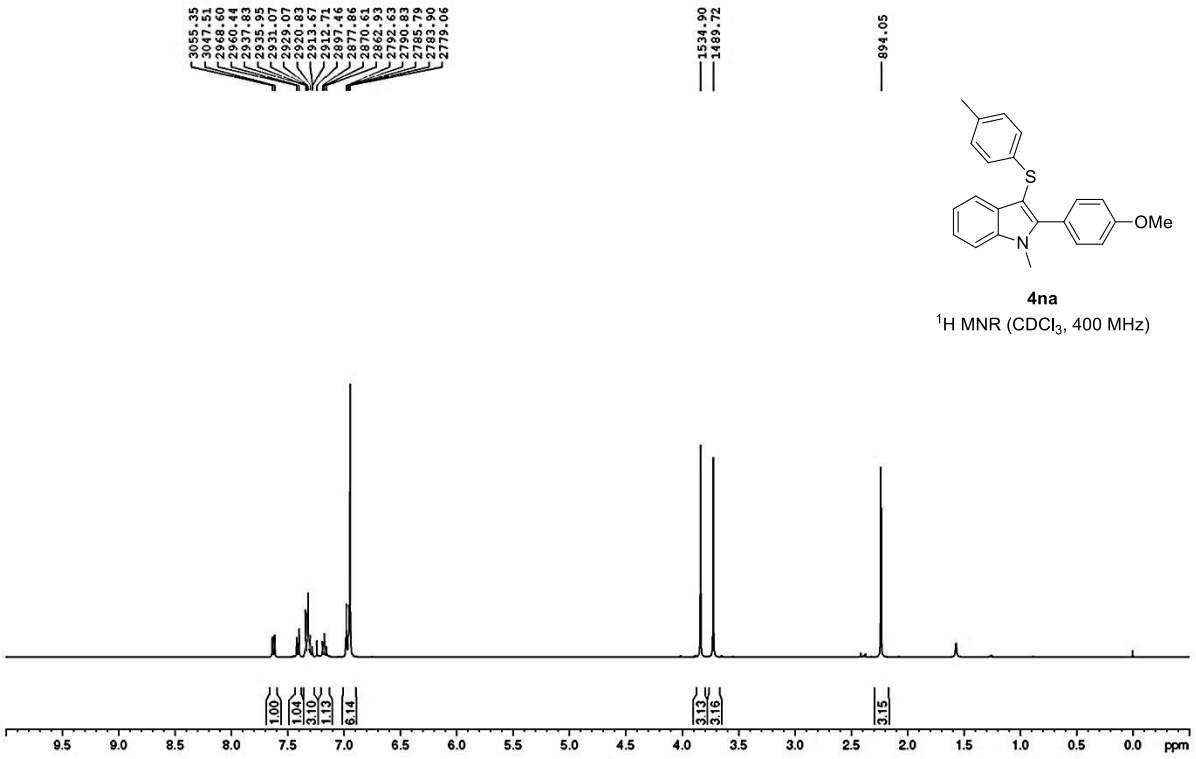
4ma

^{1}H MNR ($CDCl_3$, 400 MHz)



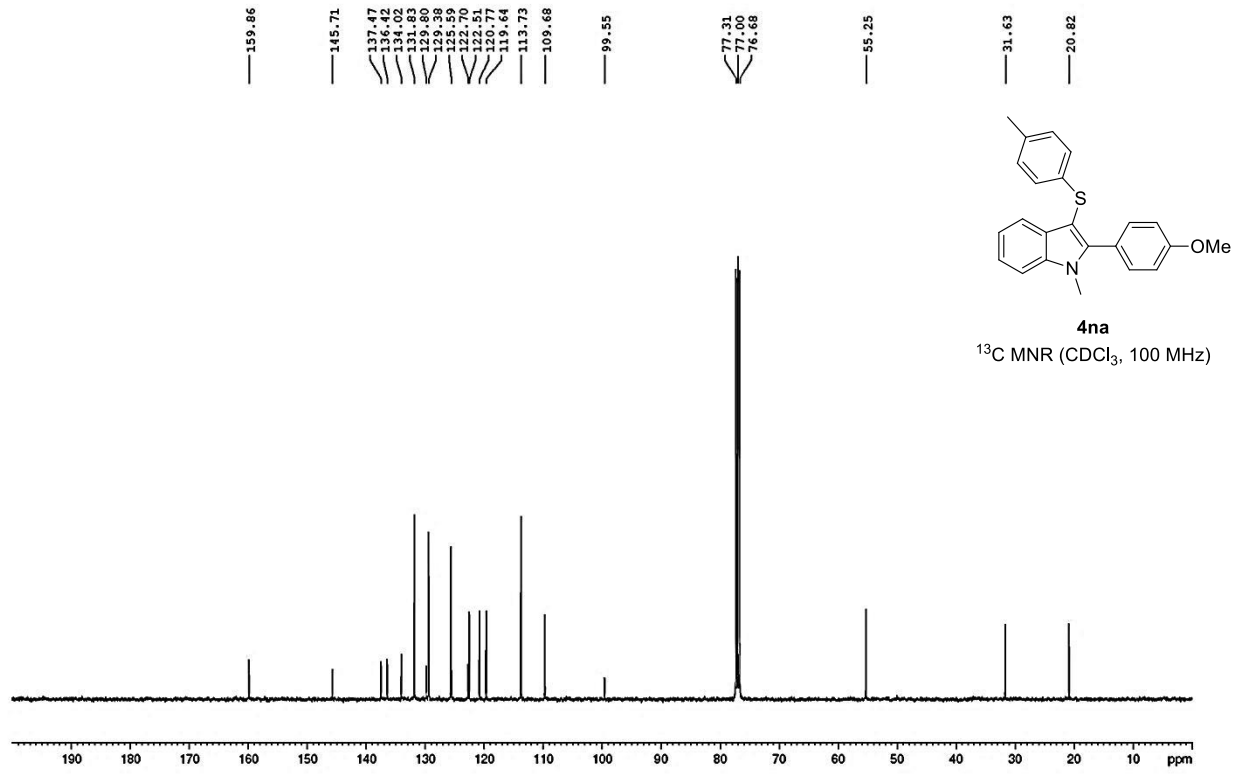
4ma

^{13}C MNR ($CDCl_3$, 100 MHz)



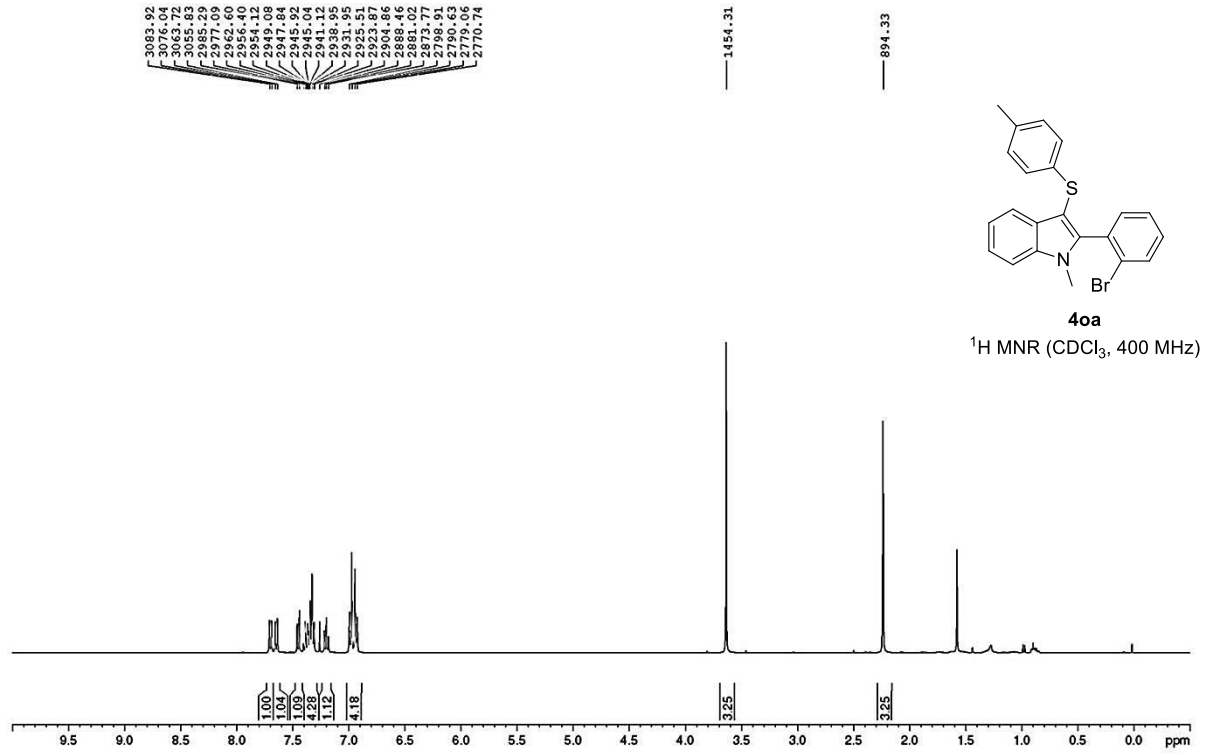
4na

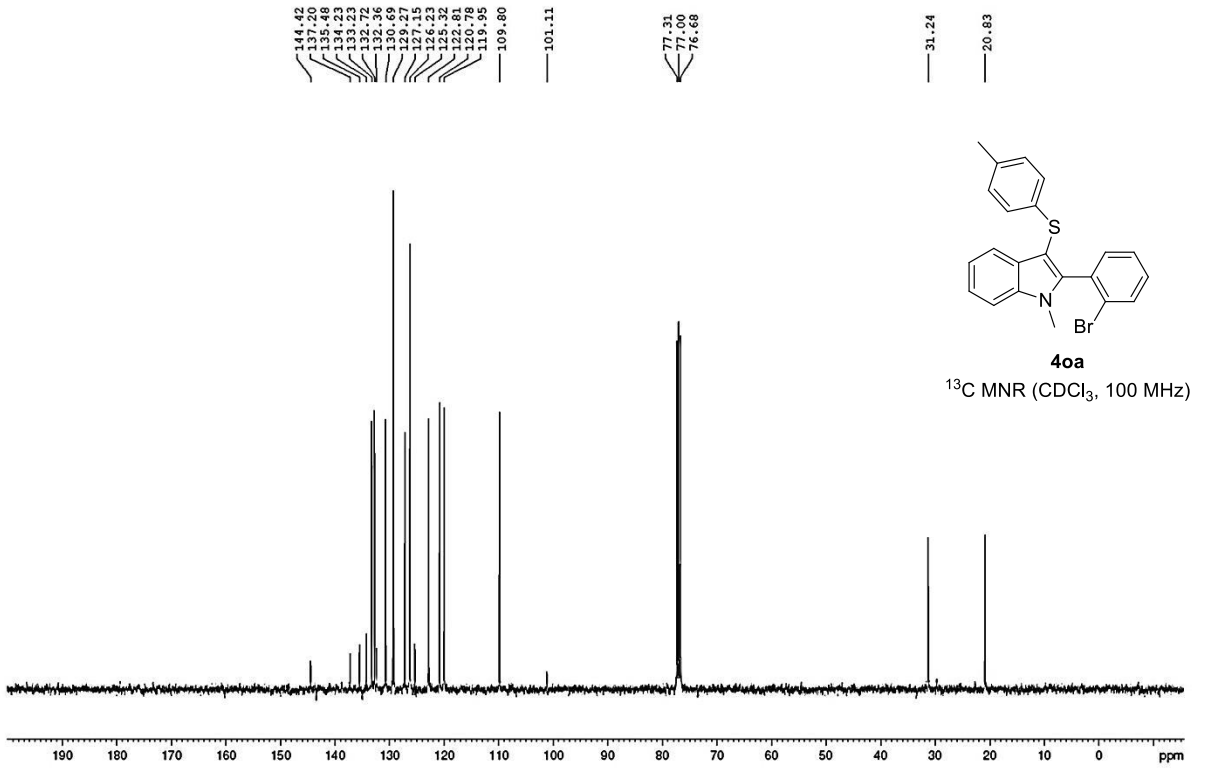
^{1}H MNR ($CDCl_3$, 400 MHz)

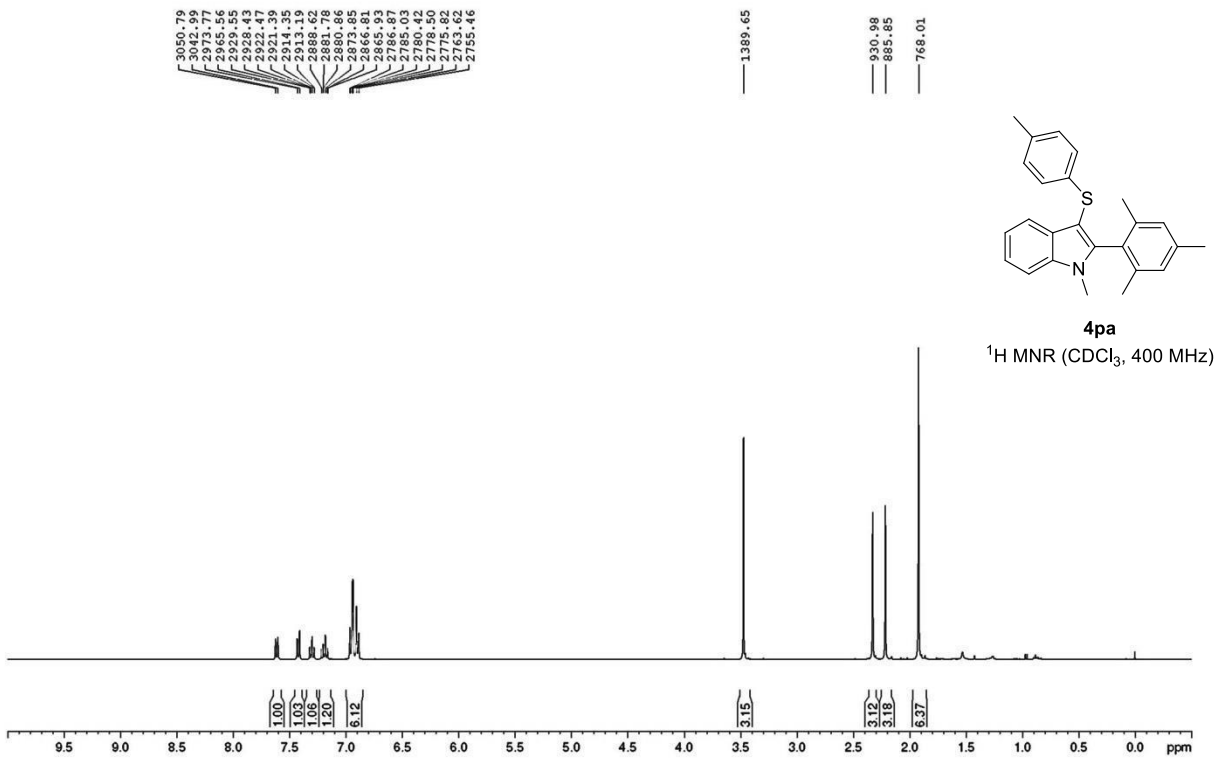


4na

^{13}C MNR ($CDCl_3$, 100 MHz)

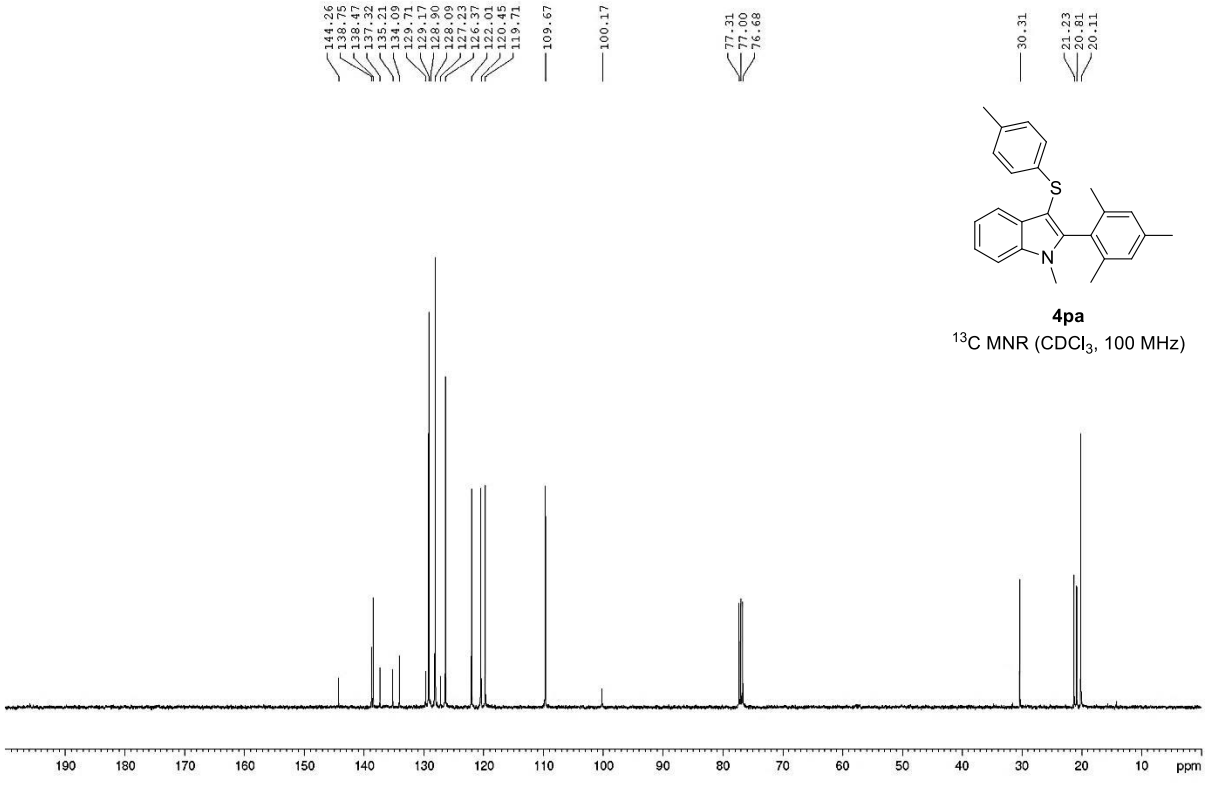

3083.92
3076.04
3063.72
3055.83
2985.29
2977.09
2962.60
2956.40
2954.12
2949.08
2947.84
2945.92
2945.04
2941.12
2938.95
2931.95
2925.51
2923.87
2904.86
2888.46
2881.02
2873.77
2798.91
2790.63
2779.06
2770.74
1454.31
894.33
S
N
Br
4oa
1H MNR (CDCl3, 400 MHz)
1.00
1.04
1.09
4.28
1.12
4.18
3.25
3.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


144.42
137.20
135.48
134.23
133.23
132.72
132.36
130.69
129.27
127.15
126.23
125.32
121.81
120.78
119.95
109.80
101.11
77.31
77.00
76.68
31.24
20.83
S
N
Br
4oa
13C MNR (CDCl3, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



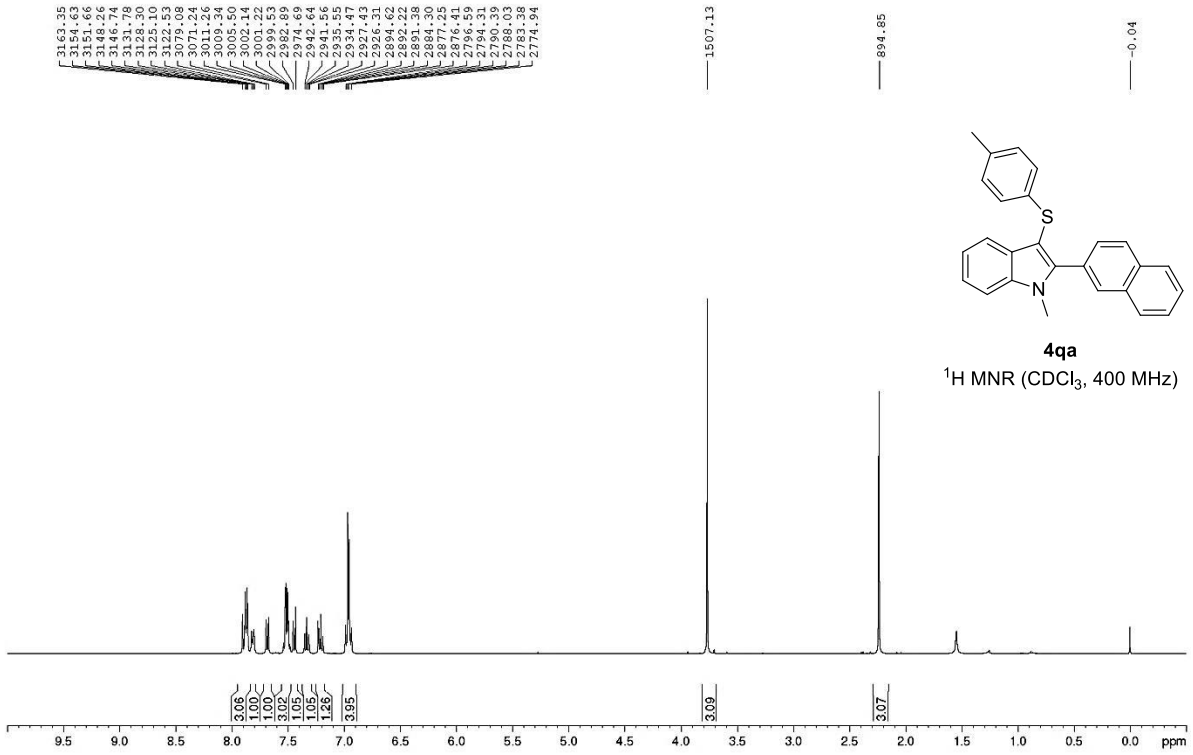
4pa

^{1}H MNR ($CDCl_3$, 400 MHz)



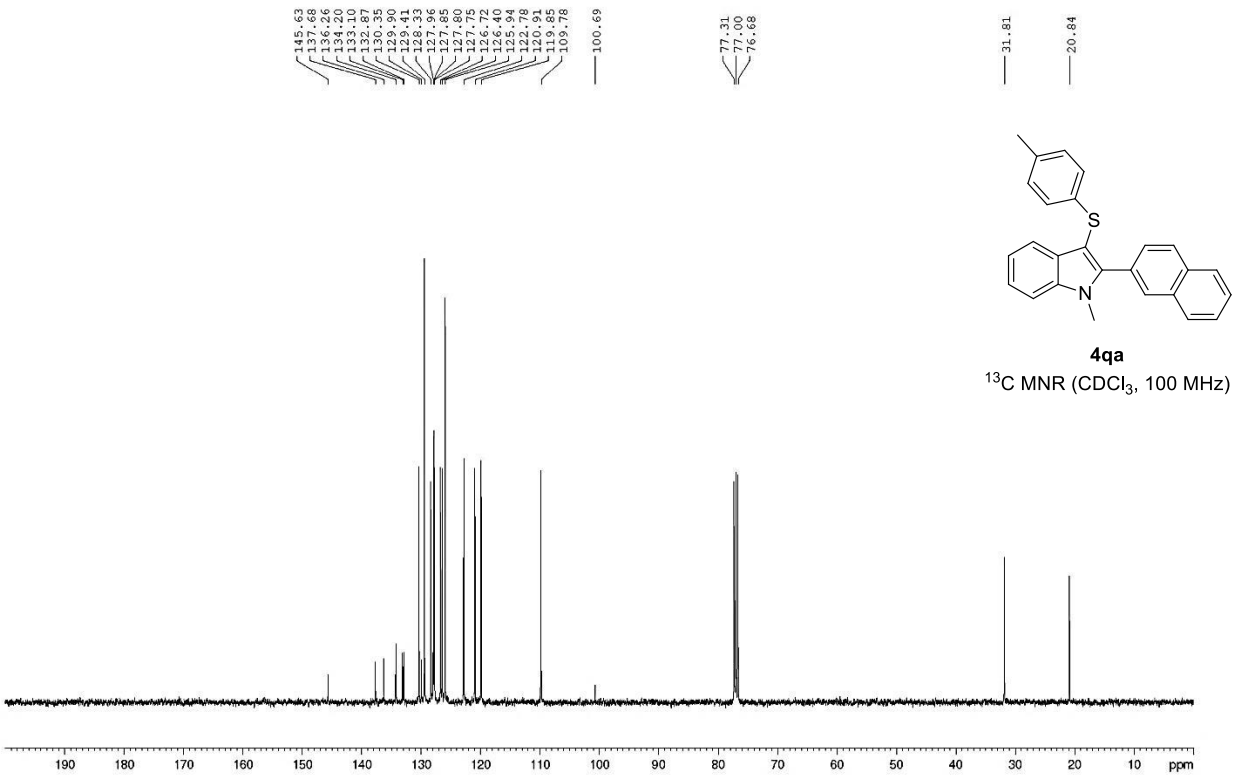
4pa

^{13}C MNR ($CDCl_3$, 100 MHz)



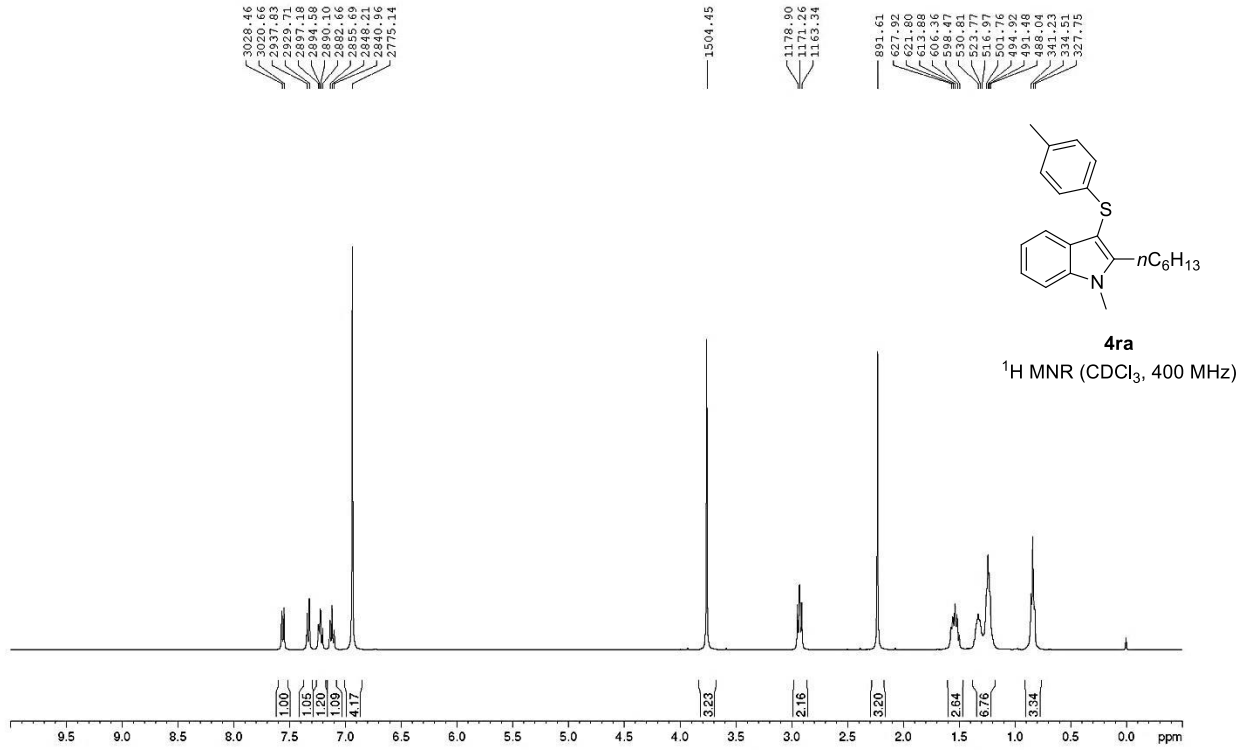
4qa

^{1}H MNR ($CDCl_3$, 400 MHz)



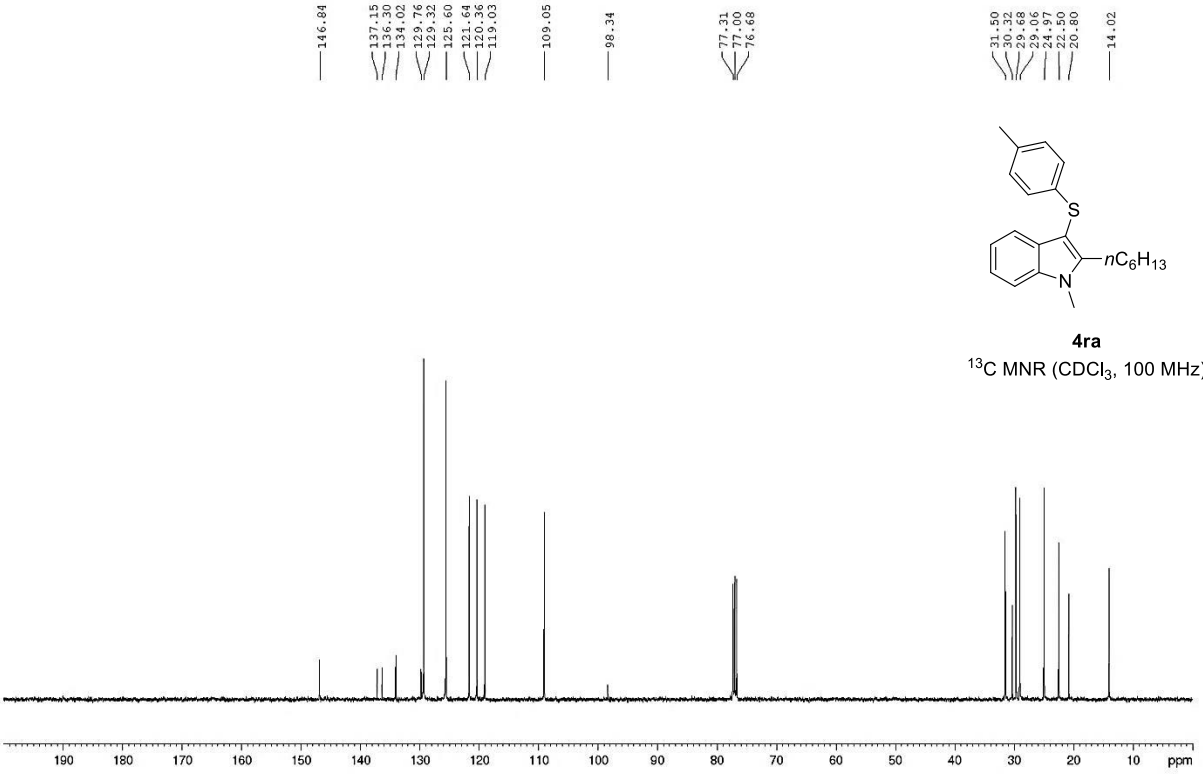
4qa

^{13}C MNR ($CDCl_3$, 100 MHz)



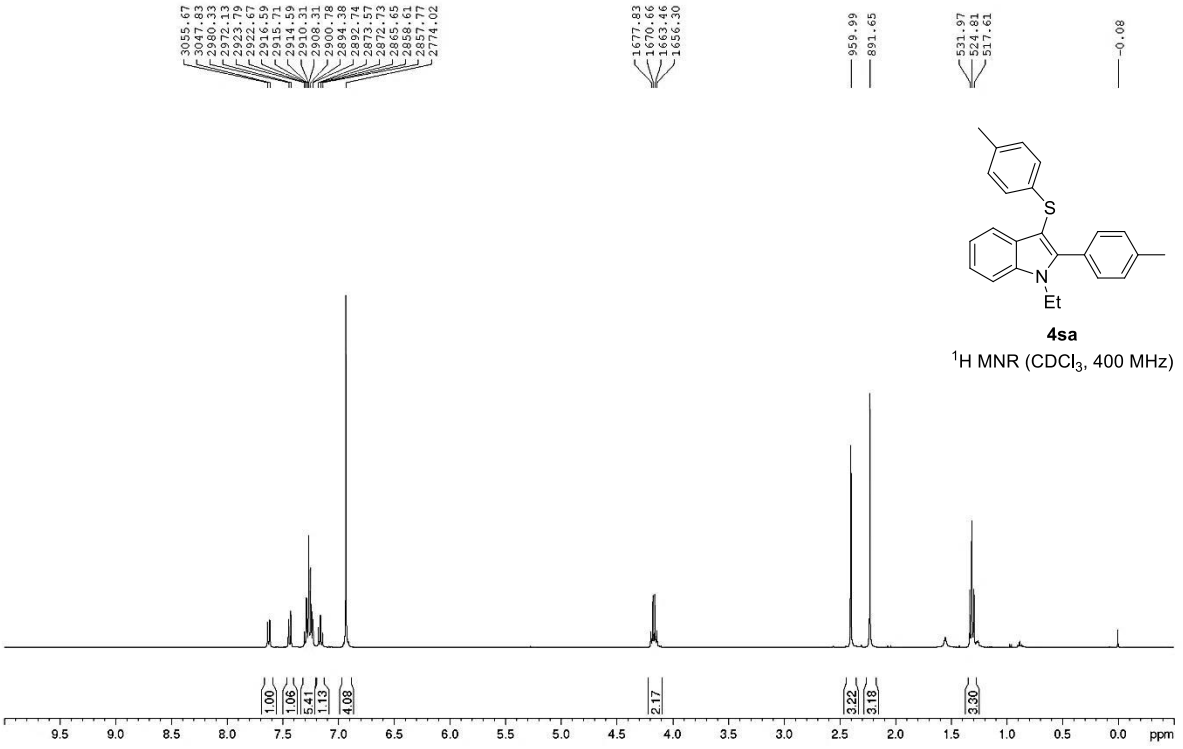
4ra

^{1}H MNR ($CDCl_3$, 400 MHz)



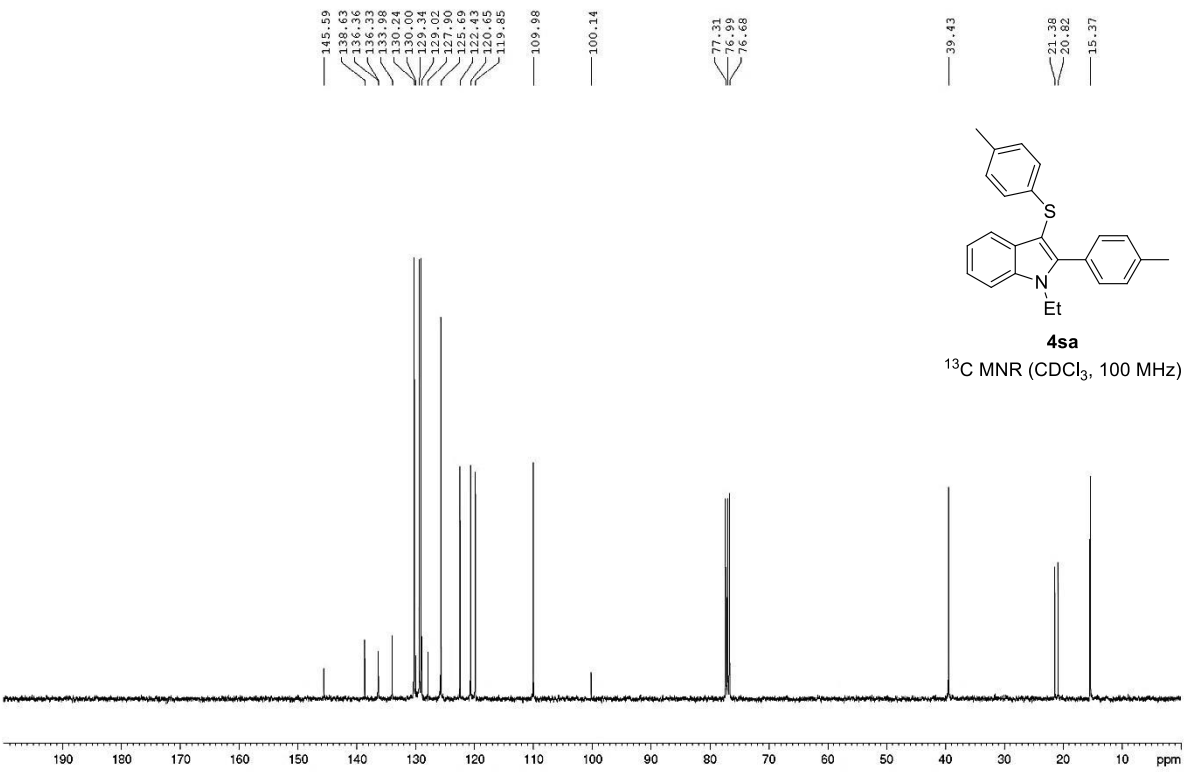
4ra

^{13}C MNR ($CDCl_3$, 100 MHz)



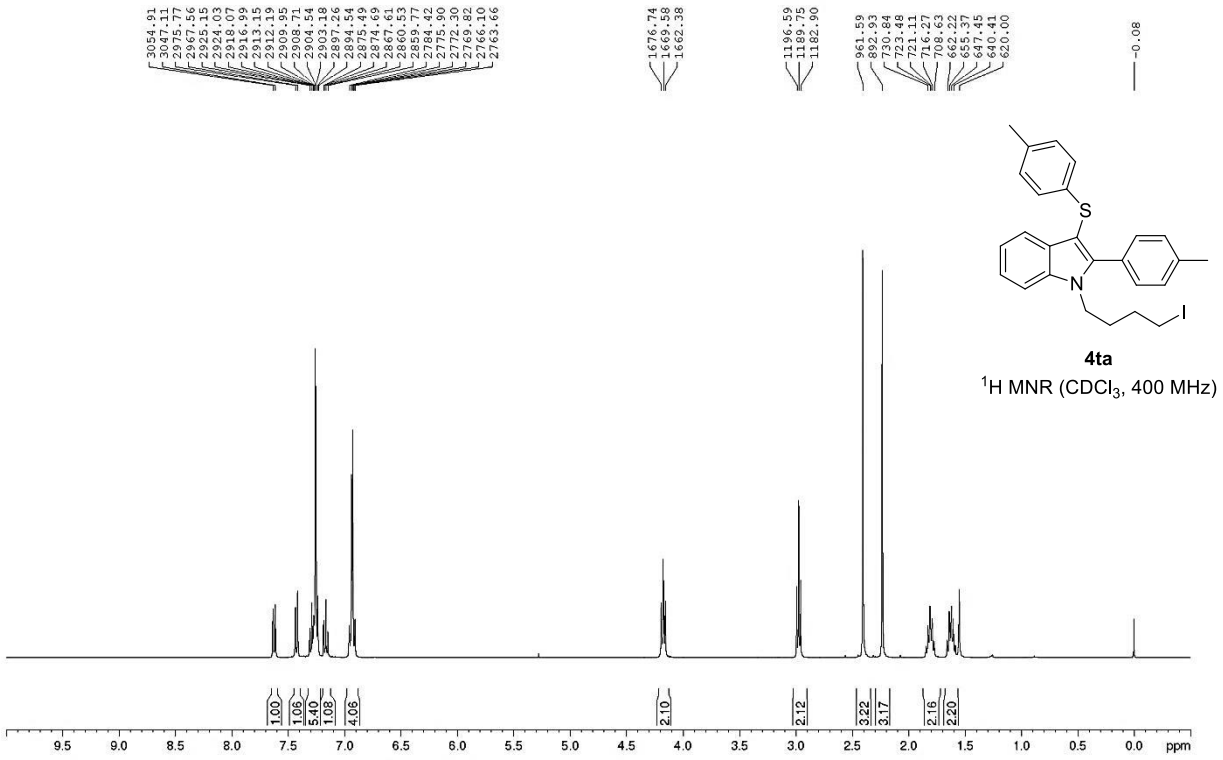
4sa

^{1}H MNR ($CDCl_3$, 400 MHz)



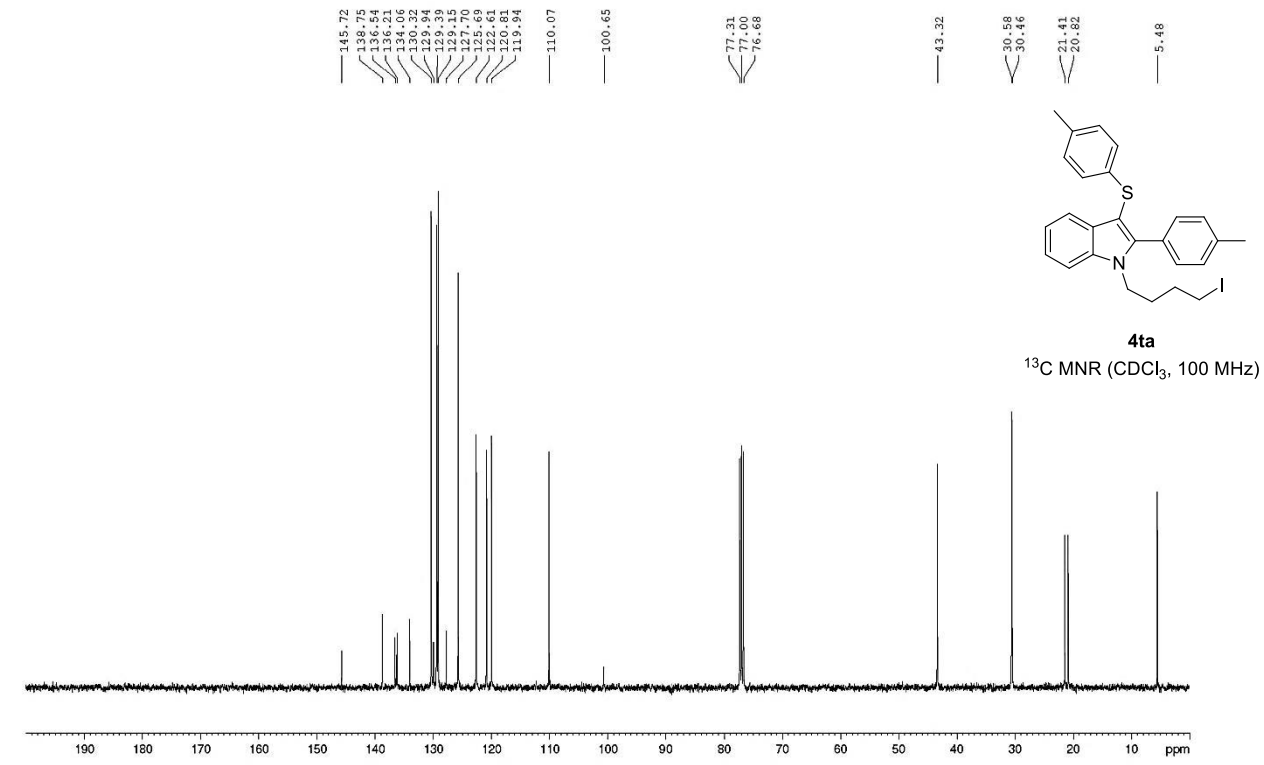
4sa

^{13}C MNR ($CDCl_3$, 100 MHz)



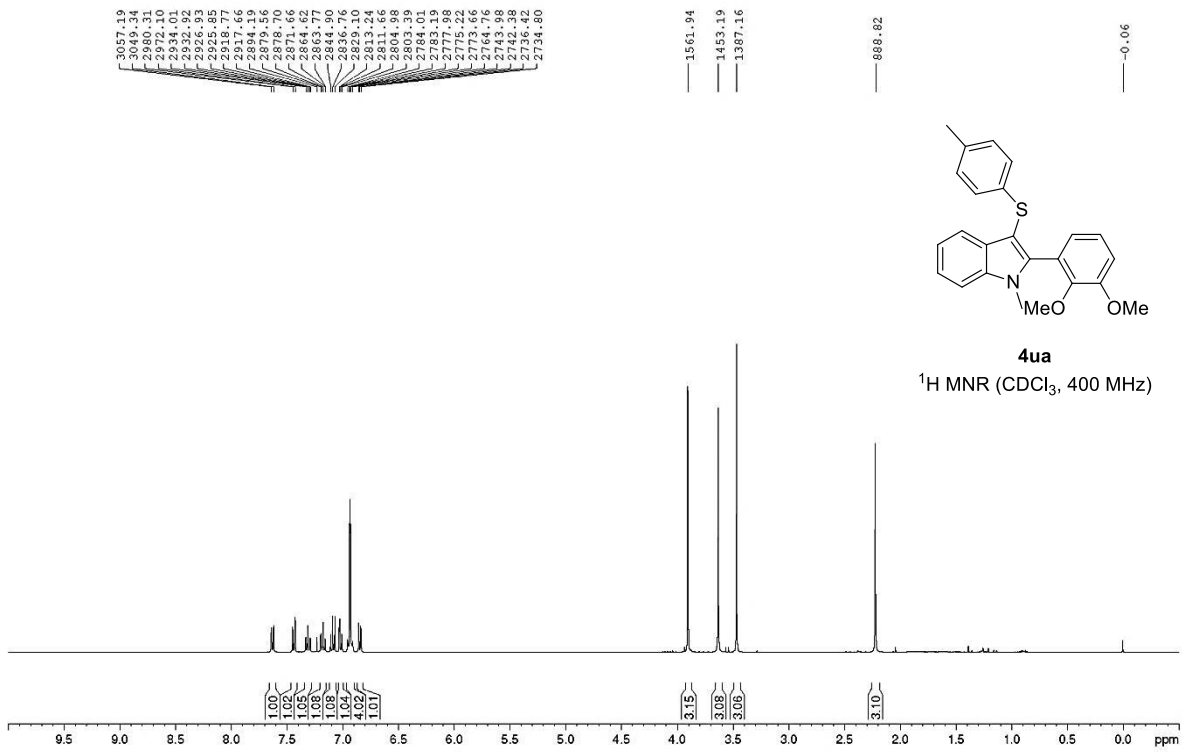
4ta

^{1}H MNR ($CDCl_3$, 400 MHz)



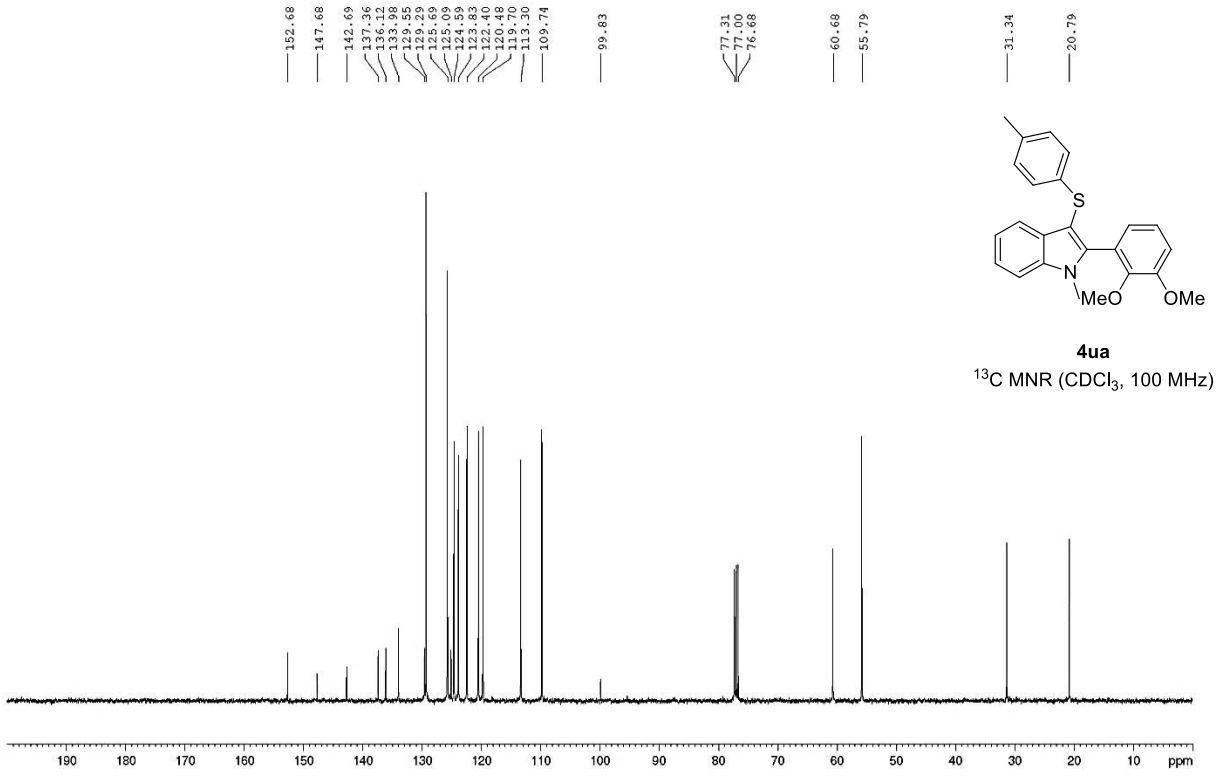
4ta

^{13}C MNR ($CDCl_3$, 100 MHz)



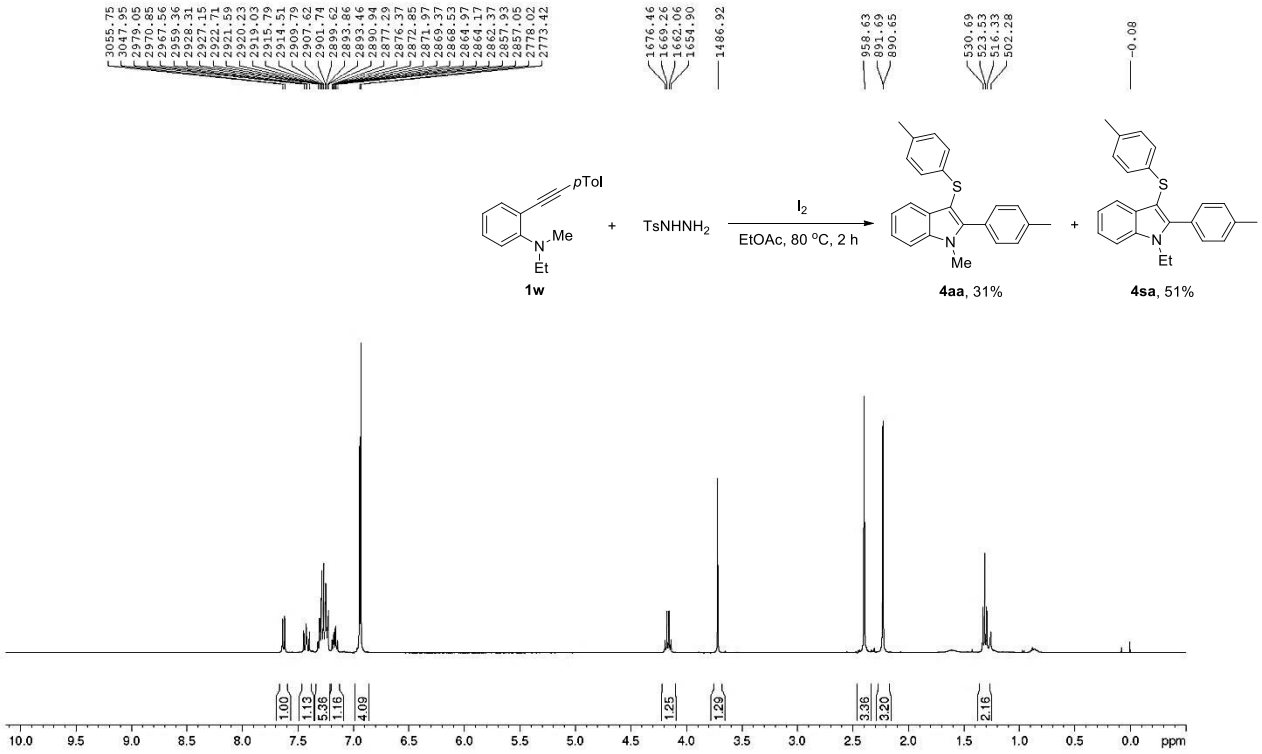
4ua

^{1}H MNR ($CDCl_3$, 400 MHz)



4ua

^{13}C MNR ($CDCl_3$, 100 MHz)


3055.75
3047.95
2979.05
2970.85
2967.56
2959.36
2928.31
2927.15
2922.71
2921.59
2920.23
2919.03
2915.79
2914.51
2909.79
2907.62
2901.74
2899.62
2893.86
2893.46
2890.94
2877.29
2876.37
2872.85
2871.97
2869.37
2868.53
2864.97
2864.17
2862.37
2857.93
2857.05
2778.02
2773.42
1676.46
1669.26
1662.06
1654.90
1486.92
958.63
891.69
890.65
530.69
523.53
516.33
502.28
-0.08
pTol
N
Me
Et
1w
+
TsNHNH2
I2
EtOAc, 80 °C, 2 h
S
N
Me
4aa, 31%
+
S
N
Et
4sa, 51%
1.00
1.13
5.36
1.16
4.09
1.25
1.29
3.36
3.20
2.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm