Synthesis of 3-sulfenylated indoles by simple NaOH promoted sulfenylation reaction

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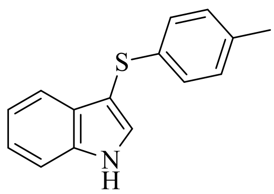
General experimental information

All chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. ^{1}H and ^{13}C NMR were recorded in 400 MHz apparatus. The frequency for ^{1}H NMR and ^{13}C NMR test are 400 MHz and 100 MHz, respectively. The chemical shifts were reported in ppm using TMS as internal standard. Melting points were tested in X-4A instrument without correcting temperature. HRMS were tested under EI model.

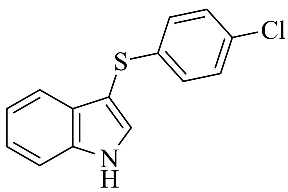
General procedure for the synthesis of sulfenylated indoles 3. In a 25 mL round bottom flask, indole **1** (0.25 mmol), thiol **2** (0.5 mmol), NaOH (0.5 mmol) and DMSO (2.0 mL) were employed. The mixture was stirred for 6 h at 70 ^{o}C (TLC) and open air atmosphere. Upon completion, the reaction was allowed to cool down to room temperature, and 10 mL water was added. The heterogeneous mixture was the extracted with ethyl acetate (3 ×10 mL). The combined organic phase was dried overnight with anhydrous Na_2SO_4. After filtering, the filtrate was collected and the solvent was removed at reduced pressure. The residue was subjected to silica gel column chromatography to give pure products using mixed petroleum ether and ethyl acetate (V_{PET}: V_{EA} = 10:1).

Procedure for scale up experiment. Indole **1a** (5 mmol), *p*-chlorothiophenol **2b** (10 mmol) were employed with NaOH (10 mmol) in DMSO (20.0 mL). The resulting mixed was heated at 70 ^{o}C for 6 h with stirring (open air atmosphere). After cooling down to room temperature, water (50 mL) was added and the resulting mixture was extracted with ethyl acetate (3 ×15 mL). The organic phase was combined and dried with anhydrous Na_2SO_4. The solid was then filtered away and the solution was subjected to evaporation under reduce pressure. The residure was then purfied by silica gel column chromatography to give product **3b** using mixed petroleum ether and ethyl acetate (V_{PET}: V_{EA} = 10:1).

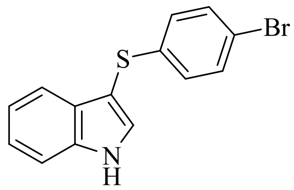
Characterization data



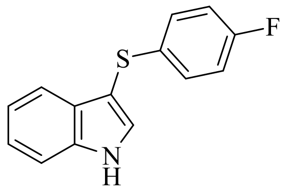
3-(*p*-Tolylthio)-1*H*-indole (3a).[1] White solid, m.p. 125-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1 H), 7.61 (d, 1 H, *J* = 8.0 Hz), 7.44 (d, 1 H, *J* = 2.0 Hz), 7.40 (d, 1 H, *J* = 8.0 Hz), 7.24 (d, 1 H, *J* = 8.0 Hz), 7.15 (t, 1 H, *J* = 8.0 Hz), 7.02 (d, 2 H, *J* = 8.0 Hz), 6.96 (d, 2 H, *J* = 8.0 Hz), 2.24 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.5, 135.5, 134.7, 130.5, 129.5, 129.1, 126.3, 123.0, 120.8, 119.7, 111.6, 103.4, 20.9.



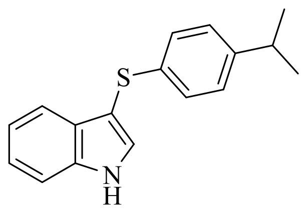
3-(4-Chlorophenylthio)-1*H*-indole (3b).[1] White solid, m.p. 130-132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1 H), 7.55 (d, 1 H, *J* = 8.0 Hz), 7.41-7.37 (m, 2 H), 7.25 (t, 1 H, J = 8.0 Hz), 7.15 (t, 1 H, J = 8.0 Hz), 7.08 (d, 2 H, J = 8.0 Hz), 6.98 (d, 2 H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 136.6, 131.0, 130.9, 130.6, 128.9, 127.2, 123.3, 121.1, 119.6, 111.9, 102.2.



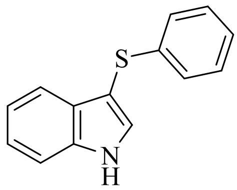
3-(4-Bromophenylthio)-1*H*-indole (3c).[1] White solid, m.p. 142-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1 H), 7.56 (d, 1 H, J = 8.0 Hz), 7.46 (d, 1 H, J = 4.0 Hz), 7.43 (d, 1 H, J = 8.0 Hz), 7.26-7.24 (m, 3 H) 7.16 (t, 1 H, J = 4.0 Hz), 6.94 (d, 2 H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6, 136.5, 131.7, 130.8, 128.8, 127.4, 123.2, 121.1, 119.6, 118.3, 111.7, 102.2.



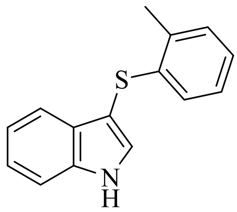
3-(4-Fluorophenylthio)-1*H*-indole (3d).[1] White solid, m.p. 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1 H), 7.59 (d, 1 H, J = 8.0 Hz), 7.45-7.39 (m, 2 H), 7.26 (t, 1 H, J = 8.0 Hz), 7.16 (t, 1 H, J = 8.0 Hz), 7.10-7.06 (m, 2 H), 6.85 (t, 2 H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 136.6, 134.1, 130.6, 128.9, 127.9, 123.2, 121.0, 119.6, 115.9, 111.7, 103.4.



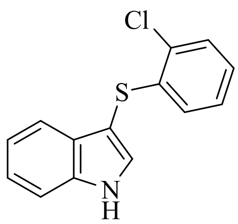
3-(4-Isopropylphenylthio)-1*H*-indole (3e). White solid, m.p. 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H), 7.63 (d, 1 H, J = 4.0 Hz), 7.39 (s, 2 H), 7.24 (s, 1 H), 7.15 (s, 1 H), 7.03 (s, 4 H), 2.79 (brs, 1 H), 1.16 (d, 6 H, J = 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8, 136.5, 136.0, 130.7, 129.3, 126.9, 126.2, 123.0, 120.9, 119.8, 111.6, 103.3, 33.6, 24.0, 24.0. EI-HRMS Calcd for $C_{17}H_{17}NS$ $[M]^+$: 267.1076; Found: 267.1081.



3-(Phenylthio)-1*H*-indole (3f).[1] White solid, m.p. 150-152 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1 H), 7.61 (d, 1 H, *J* = 8.0 Hz), 7.44-7.40 (m, 2 H), 7.25 (t, 1 H, *J* = 8.0 Hz), 7.17-7.09 (m, 5 H), 7.05 (d, 1 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 136.5, 130.8, 130.6, 129.1, 128.7, 125.8, 124.8, 123.1, 120.9, 119.6, 111.6.

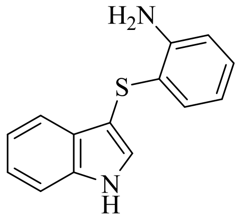


3-(*o*-Tolylthio)-1*H*-indole (3g).[2] White solid, m.p. 115-119 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 7.57 (d, 1 H, *J* = 8.0 Hz), 7.39-7.37 (m, 2 H), 7.25 (t, 1 H, *J* = 8.0 Hz), 7.16-7.11 (m, 2 H), 6.96 (t, 1 H, *J* = 8.0 Hz), 6.87 (t, 1 H, *J* = 8.0 Hz), 6.69 (d, 1 H, *J* = 8.0 Hz), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 136.6, 134.4, 130.9, 129.9, 129.3, 126.3, 125.3, 124.5, 123.1, 120.9, 119.8, 111.7, 102.3, 20.0.

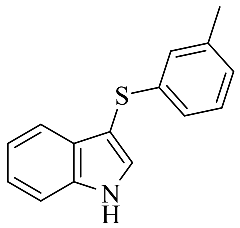


3-(2-Chlorophenylthio)-1*H*-indole (3h).[3] White solid, m.p. 138-140 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 7.55 (d, 1 H, *J* = 8.0 Hz), 7.44-7.40 (m, 2 H), 7.27 (t, 2 H, *J* = 8.0 Hz), 7.14 (t, 1 H, *J* = 8.0 Hz), 6.94 (t, 1 H, *J* = 8.0 Hz), 6.87 (t, 1

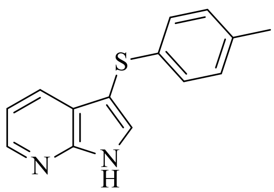
H, J = 8.0 Hz), 6.60 (d, 1 H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5, 136.6, 131.6, 130.0, 129.4, 129.0, 127.0, 126.3, 125.5, 123.3, 121.2, 119.6, 111.9, 101.0.



3-(2-Aminophenylthio)-1*H*-indole (3i).[4] Yellow solid, m.p. 88-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 1 H), 7.63 (d, 1 H, J = 8.0 Hz), 7.24-7.20 (m, 2 H), 7.16 (d, 2 H, J = 8.0 Hz), 7.11 (t, 1 H, J = 8.0 Hz), 6.98 (t, 1 H, J = 8.0 Hz), 6.64 (d, 1 H, J = 8.0 Hz), 6.59 (t, 1 H, J = 8.0 Hz), 4.11 (brs, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 136.4, 131.9, 129.4, 128.7, 128.1, 122.9, 121.0, 120.7, 119.4, 119.1, 115.5, 111.7, 103.8.

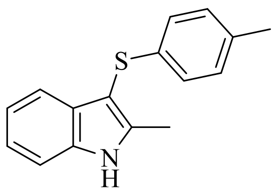


3-(*m*-Tolylthio)-1*H*-indole (3j).[2] White solid, m.p. 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H), 7.65 (d, 1 H, J = 8.0 Hz), 7.44-7.41 (m, 2 H), 7.28 (t, 1 H, J = 8.0 Hz), 7.18 (t, 1 H, J = 8.0 Hz), 7.06 (t, 1 H, J = 8.0 Hz), 7.01 (s, 1 H), 6.90 (d, 2 H, J = 8.0 Hz), 2.24 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 138.6, 136.5, 130.9, 130.8, 129.2, 128.7, 126.5, 125.9, 123.1, 120.9, 119.7, 111.7, 102.8, 21.4.

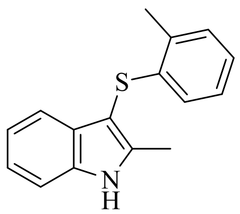


3-(*p*-Tolylthio)-1*H*-pyrrolo[2,3-b]pyridine (3k). Yellow solid, m.p. 162-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.88 (s, 1 H), 8.38 (d, 1 H, J = 4.0 Hz), 7.94 (d, 1 H, J

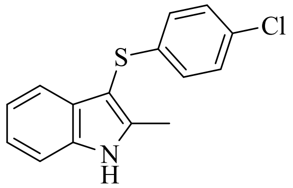
= 8.0 Hz), 7.68 (s, 1 H), 7.13-7.09 (m, 1 H), 7.03 (d, 2 H, J = 8.0 Hz), 6.97 (d, 2 H, J = 8.0 Hz), 2.23 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 142.9, 135.0, 132.0, 130.0, 129.7, 128.6, 126.5, 122.3, 116.7, 101.7, 20.8; EI-HRMS Calcd for $C_{14}H_{12}N_2S$ $[M]^+$: 240.0716; Found: 240.0712.



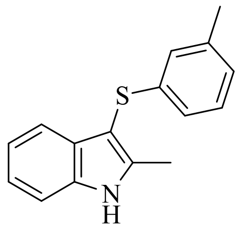
2-Methyl-3-(*p*-tolylthio)-1*H*-indole (3l).[5] Yellow solid, m.p. 97-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.59 (d, 1 H, J = 8.0 Hz), 7.30 (d, 1 H, J = 8.0 Hz), 7.21 (t, 1 H, J = 8.0 Hz), 7.15 (t, 1 H, J = 8.0 Hz), 6.99 (brs, 4 H), 2.47 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 135.8, 135.5, 134.4, 130.4, 129.7, 125.9, 122.3, 120.7, 119.1, 110.8, 99.6, 20.8, 12.1.



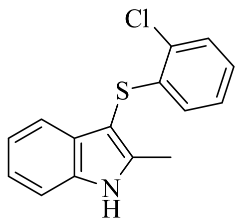
2-Nethyl-3-(o-tolylthio)-1*H*-indole (3m). Yellow solid, m.p. 112-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.49 (d, 1 H, J = 8.0 Hz), 7.25 (d, 1 H, J = 8.0 Hz), 7.16 (t, 1 H, J = 8.0 Hz), 7.11-7.07 (m, 2 H), 6.93 (t, 1 H, J = 8.0 Hz), 6.84 (t, 1 H, J = 8.0 Hz), 6.57 (d, 1 H, J = 8.0 Hz), 2.49 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4, 138.3, 135.6, 134.3, 130.4, 130.0, 126.3, 124.7, 124.3, 122.2, 120.8, 119.0, 110.9, 98.6, 20.0, 12.2; EI-HRMS Calcd for $C_{16}H_{15}NS$ $[M]^+$: 253.0920; Found: 253.0924.



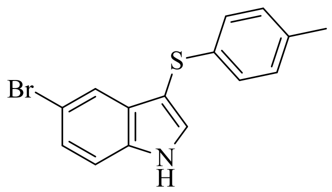
3-(4-Chlorophenylthio)-2-methyl-1*H*-indole (3n).[5] Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.32 (s, 1 H), 7.50 (d, 1 H, J = 8.0 Hz), 7.33 (d, 1 H, J = 8.0 Hz), 7.19 (t, 1 H, J = 8.0 Hz), 7.13 (d, 1 H, J = 8.0 Hz), 7.09 (d, 2 H, J = 8.0 Hz), 6.94 (d, 2 H, J = 8.0 Hz), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 141.4, 138.2, 135.5, 130.2, 130.0, 128.9, 126.7, 122.5, 121.0, 118.9, 110.8, 98.9, 12.2.



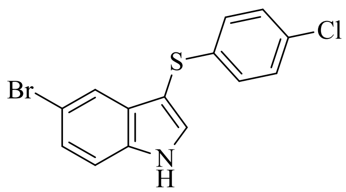
2-Methyl-3-(*m*-tolylthio)-1*H*-indole (3o). Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.04 (s, 1 H), 7.54 (d, 1 H, J = 8.0 Hz), 7.25 (d, 1 H, J = 8.0 Hz), 7.16 (t, 1 H, J = 8.0 Hz), 7.10 (t, 1 H, J = 8.0 Hz), 7.00 (t, 1 H, J = 8.0 Hz), 6.91 (s, 1 H), 6.83 (d, 1 H, J = 8.0 Hz), 6.78 (d, 1 H, J = 8.0 Hz), 2.41 (s, 3 H), 2.19 (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 141.2, 139.2, 138.5, 135.5, 130.4, 128.7, 126.1, 125.6, 122.6, 122.2, 120.7, 119.1, 110.8, 99.3, 21.5, 12.2; EI-HRMS Calcd for $C_{16}H_{15}NS$ $[M]^+$: 253.0920; Found: 253.0925.



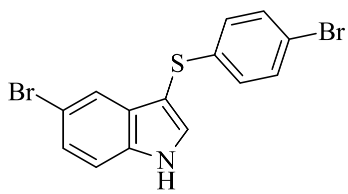
3-(2-Chlorophenylthio)-2-methyl-1*H*-indole (3p).[3] Yellow solid, m.p. 128-130 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.24 (s, 1 H), 7.49 (d, 1 H, J = 8.0 Hz), 7.32-7.30 (m, 2 H), 7.19 (t, 1 H, J = 8.0 Hz), 7.11 (t, 1 H, J = 8.0 Hz), 6.94 (t, 1 H, J = 8.0 Hz), 6.88 (t, 1 H, J = 8.0 Hz), 6.52 (d, 1 H, J = 8.0 Hz), 2.44 (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 141.9, 138.4, 135.6, 130.1, 130.1, 129.4, 126.9, 125.93, 125.3, 122.4, 120.9, 119.0, 110.9, 97.7, 12.1.



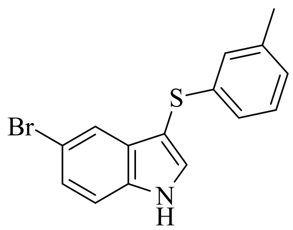
5-Bromo-3-(p-tolylthio)-1*H*-indole (3q).[4] Pale yellow solid, m.p. 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 7.75 (s, 1 H), 7.43 (d, 1 H, *J* = 2.0 Hz), 7.32 (d, 1 H, *J* = 8.0 Hz), 7.26 (d, 1 H, *J* = 8.0 Hz), 6.99 (brs, 4 H), 2.25 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.1, 135.0, 131.7, 131.6, 131.0, 129.6, 126.3, 126.0, 122.3, 114.4, 113.1, 103.5, 20.9.



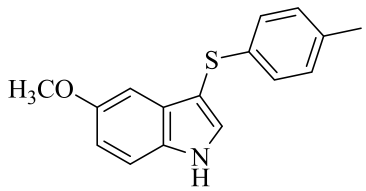
5-Bromo-3-(4-chlorophenylthio)-1*H*-indole (3r).[6] Pale yellow solid, m.p. 141-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 7.70 (d, 1 H, *J* = 2.0 Hz), 7.46 (d, 1 H, *J* = 2.0 Hz), 7.35-7.33 (m, 1 H), 7.29 (d, 1 H, *J* = 8.0 Hz), 7.12 (d, 2 H, *J* = 8.0 Hz), 6.98 (d, 2 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3, 135.1, 132.1, 131.9, 130.8, 128.9, 127.1, 126.3, 122.1, 114.6, 113.3, 102.3.



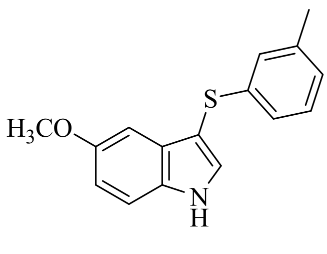
5-Bromo-3-(4-bromophenylthio)-1*H*-indole (3s). Pale yellow solid, m.p. 155-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 7.70 (s, 1 H), 7.47 (d, 1 H, *J* = 2.0 Hz), 7.36-7.31 (m, 2 H), 7.29-7.25 (m, 2 H), 6.92 (d, 2 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 135.1, 132.1, 131.9, 130.7, 127.4, 126.3, 122.1, 118.6, 114.7, 113.3, 102.1; EI-HRMS Calcd for $C_{14}H_9Br_2NS$ $[M]^+$: 380.8817; Found: 380.8811.



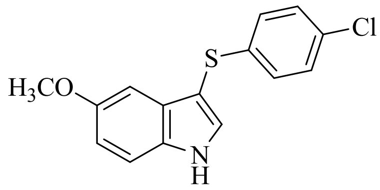
5-Bromo-3-(*m*-tolylthio)-1*H*-indole (3t). Pale yellow solid, m.p. 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1 H), 7.75 (s, 1 H), 7.38 (d, 1 H, *J* = 4.0 Hz), 7.31-7.29 (m, 1 H), 7.22 (d, 1 H, *J* = 8.0 Hz), 7.03 (t, 1 H, *J* = 8.0 Hz), 6.93 (s, 1 H), 6.88-6.83 (m, 2 H), 2.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 138.0, 134.6, 131.6, 131.4, 130.6, 128.4, 125.7, 122.6, 121.7, 114.0, 112.8, 112.6, 102.2, 21.0; EI-HRMS Calcd for $C_{15}H_{12}BrNS$ $[M]^+$: 316.9868; Found: 316.9871



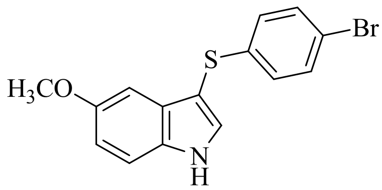
5-Methoxy-3-(p-tolylthio)-1*H*-indole (3u).[4] Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 7.38 (d, 1 H, *J* = 4.0 Hz), 7.27 (d, 1 H, *J* = 8.0 Hz), 7.04 (s, 1 H), 6.99 (q, 4 H, *J* = 8.0 Hz), 6.89 (dd, 1 H, *J1* = 8.0 Hz, *J2* = 2.4 Hz), 3.77 (s, 3 H), 2.24 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 135.7, 134.6, 131.4, 131.2, 130.0, 129.6, 126.1, 113.5, 112.5, 102.7, 100.9, 55.8, 20.9.



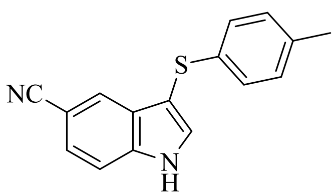
5-Methoxy-3-(m-tolylthio)-1*H*-indole (3v). Pale yellow solid, m.p. 75-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 7.38 (d, 1 H, *J* = 4.0 Hz), 7.27 (d, 1 H, *J* = 8.0 Hz), 7.05-7.02 (m, 2 H, *J* = 8.0 Hz), 6.96 (s, 1 H), 6.90 (dd, 1 H, *J1* = 8.0 Hz, *J2* = 2.0 Hz), 6.86 (d, 2 H, *J* = 8.0 Hz), 3.77 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 139.2, 138.5, 131.5, 131.4, 130.1, 128.7, 126.3, 125.7, 122.8, 113.6, 112.5, 102.2, 100.9, 55.8, 21.4; EI-HRMS Calcd for $C_{16}H_{15}NOS$ $[M]^+$: 269.0869; Found: 269.0875.



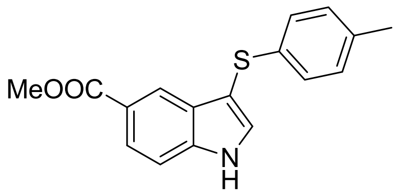
3-(4-Chlorophenylthio)-5-methoxy-1*H*-indole (3w).[7] Brown solid, m.p. 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H), 7.40 (d, 1 H, *J* = 2.0 Hz), 7.29 (d, 1 H, *J* = 8.0 Hz), 7.10 (d, 2 H, *J* = 8.0 Hz), 6.99 (d, 3 H, *J* = 8.0 Hz), 6.91 (dd, 1 H, *J1* = 8.0 Hz, *J2* = 2.0 Hz), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 138.0, 131.4, 130.4, 129.7, 128.9, 128.7, 127.0, 113.8, 112.7, 101.6, 100.7, 55.8.



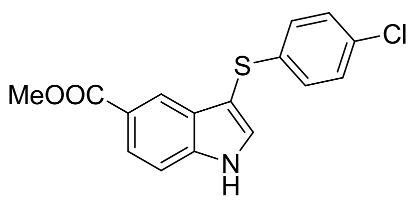
3-(4-Bromophenylthio)-5-methoxy-1H-indole (3x). Brown solid, m.p. 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1 H), 7.41 (d, 1 H, *J* = 2.0 Hz), 7.30 (d, 1 H, *J* = 8.0 Hz), 7.25 (d, 2 H, *J* = 8.0 Hz), 6.99 (d, 1 H, *J* = 2.0 Hz), 6.94-6.90 (m, 3 H), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 138.7, 131.7, 131.6, 131.4, 129.7, 127.2, 118.3, 113.7, 112.7, 101.5, 100.7, 55.8; EI-HRMS Calcd for $C_{15}H_{12}BrNOS$ $[M]^+$: 332.9817; Found: 332.9820.



3-(*p*-Tolylthio)-1H-indole-5-carbonitrile (3y). Pale yellow solid, m.p. 201-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (s, 1 H), 7.96 (s, 1 H), 7.63 (s, 1 H), 7.51 (s, 2 H), 7.28 (s, 1 H), 7.04 (brs, 3 H), 2.29 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.5, 134.9, 134.7, 134.4, 129.8, 128.5, 126.4, 124.9, 123.6, 120.2, 113.8, 102.2, 101.8, 20.4; EI-HRMS Calcd for $C_{16}H_{12}N_2S$ $[M]^+$: 264.0716; Found: 264.0716.



Methyl 3-(*p*-tolylthio)-1H-indole-5-carboxylate (**3z**). White solid, m.p. 181-183 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.77 (brs, 1 H), 8.42 (s, 1 H), 7.98 (d, 1 H, J = 6.0 Hz), 7.55 (s, 1 H), 7.46 (d, 1 H, J = 12 Hz), 7.05 (d, 2 H, J = 6.0 Hz), 7.00 (d, 2 H, J = 6.0 Hz); 3.92 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 167.9, 139.2, 135.1, 134.9, 131.8, 129.9, 129.5, 128.9, 126.4, 124.3, 123.1, 122.4, 111.3, 51.7, 20.8; ESI-HRMS Calcd for $C_{17}H_{16}NO_2S$ $[M+H]^+$: 298.0896; Found: 298.0893.



Methyl 3-((4-chlorophenyl)thio)-1H-indole-5-carboxylate (**3aa**). White solid, m.p. 206-207 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.71 (brs, 1 H), 8.36 (s, 1 H), 8.01 (d, 1 H, J = 6.0 Hz), 7.59 (s, 1 H), 7.49 (d, 1 H, J = 12.0 Hz), 7.15 (d, 2 H, J = 6.0 Hz), 7.03, (d, 2 H, J = 6.0 Hz), 3.93 (s, 3 H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 167.7, 139.0, 137.4, 132.0, 130.8, 128.8, 128.4, 127.2, 124.6, 123.4, 122.2, 111.5, 104.4, 52.1; ESI-HRMS Calcd for $C_{16}H_{13}ClNO_2S$ $[M+H]^+$: 318.0350; Found: 318.0342.

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(3) Regina, G. L.; Gatti, V.; Famiglini, V.; Piscitelli, F.; Silvestri, R. *ACS Comb. Sci.* **2012**, *14*, 258-262.129.4,

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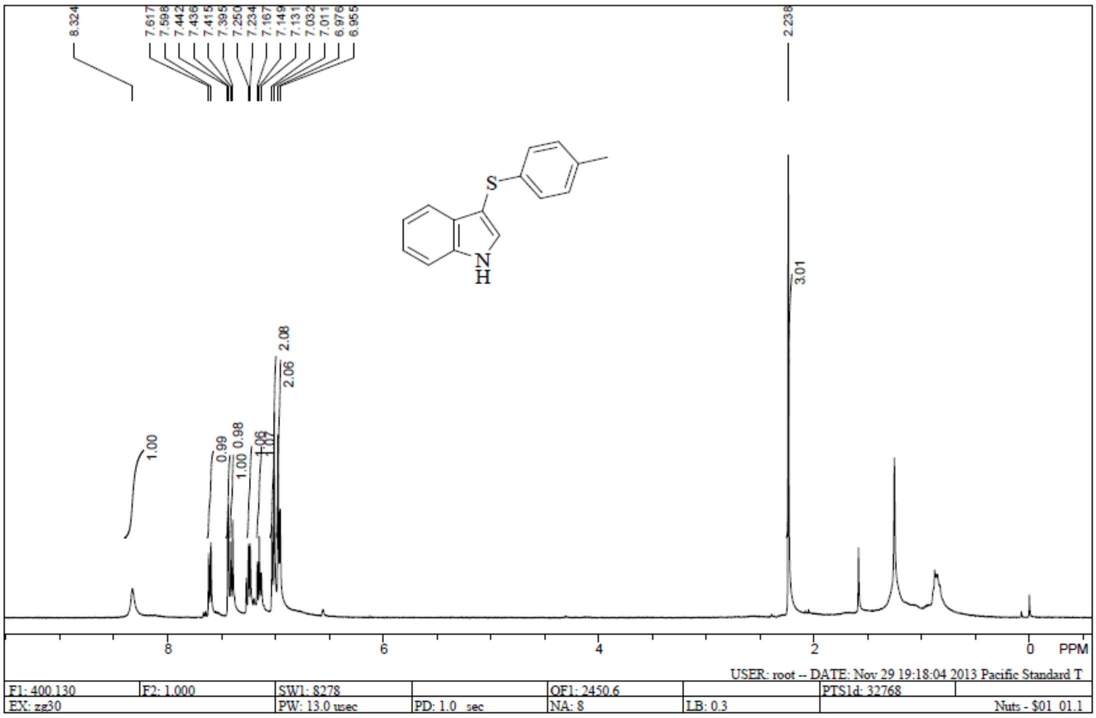
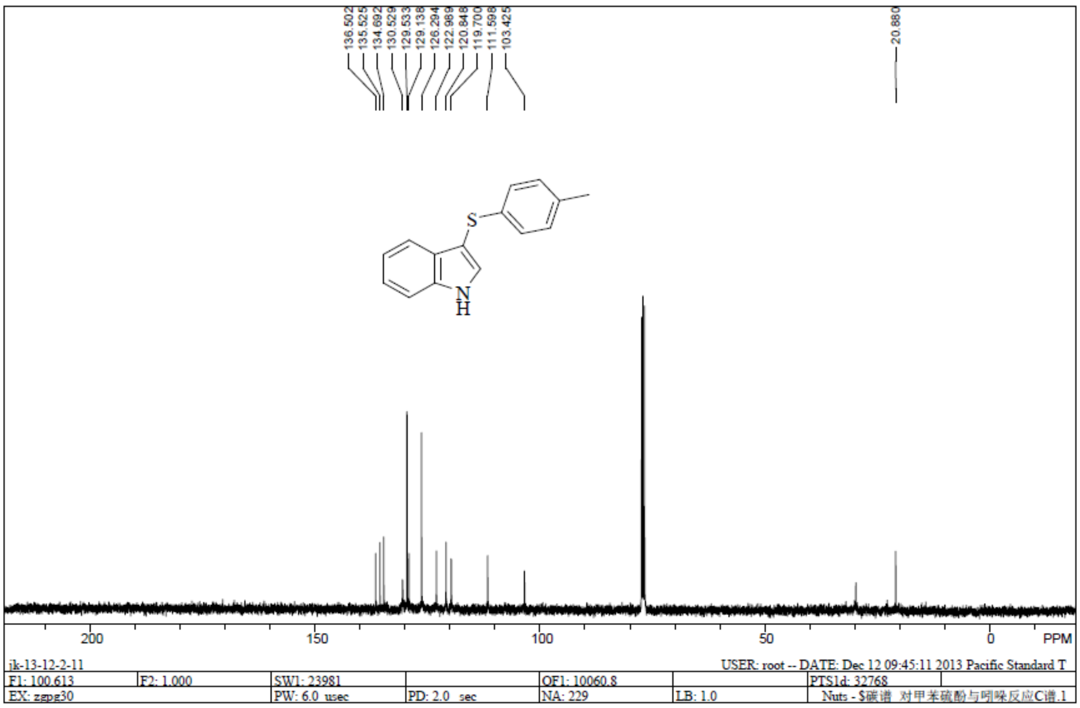
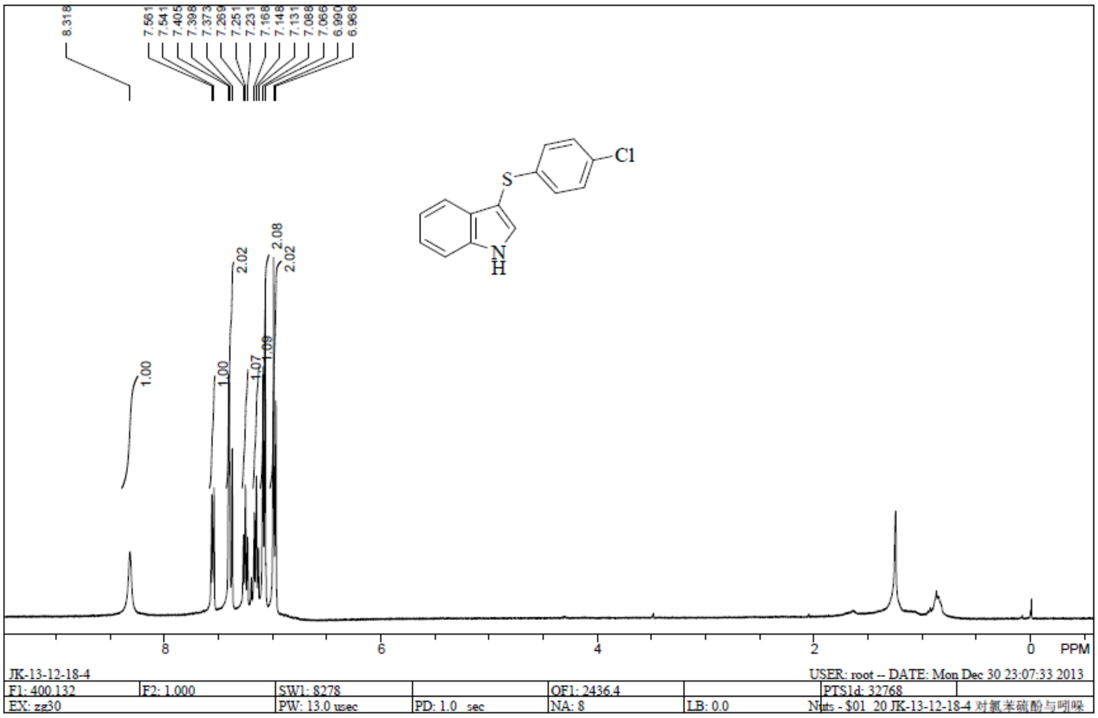
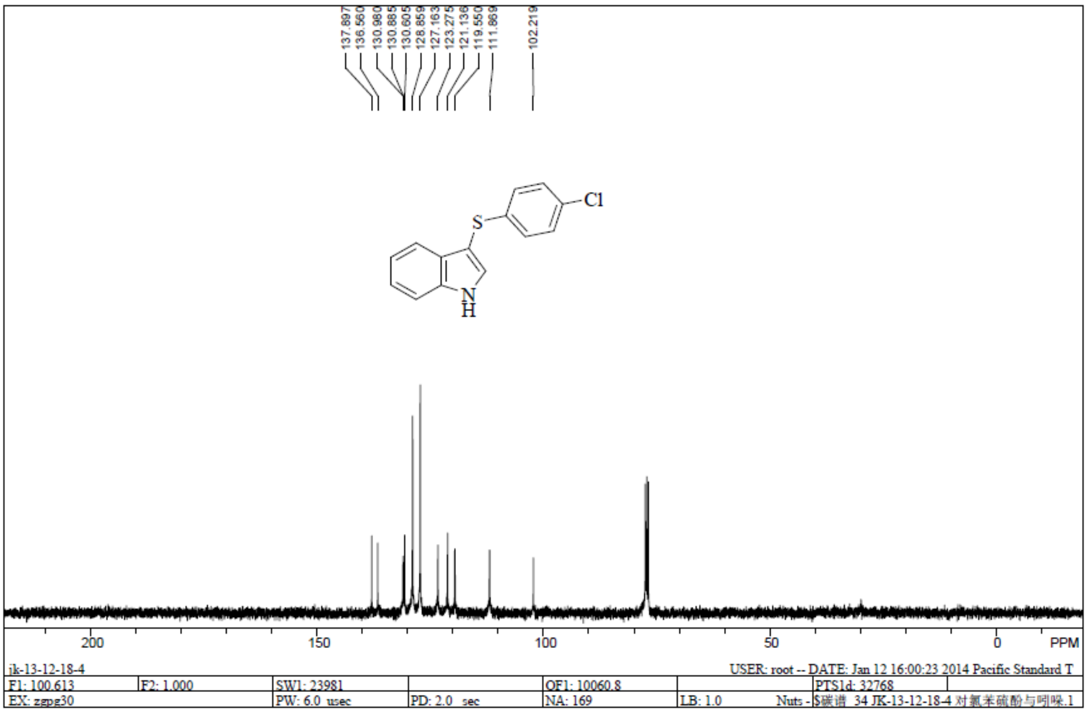
^{1}H and ^{13}C NMR spectra of **3a**



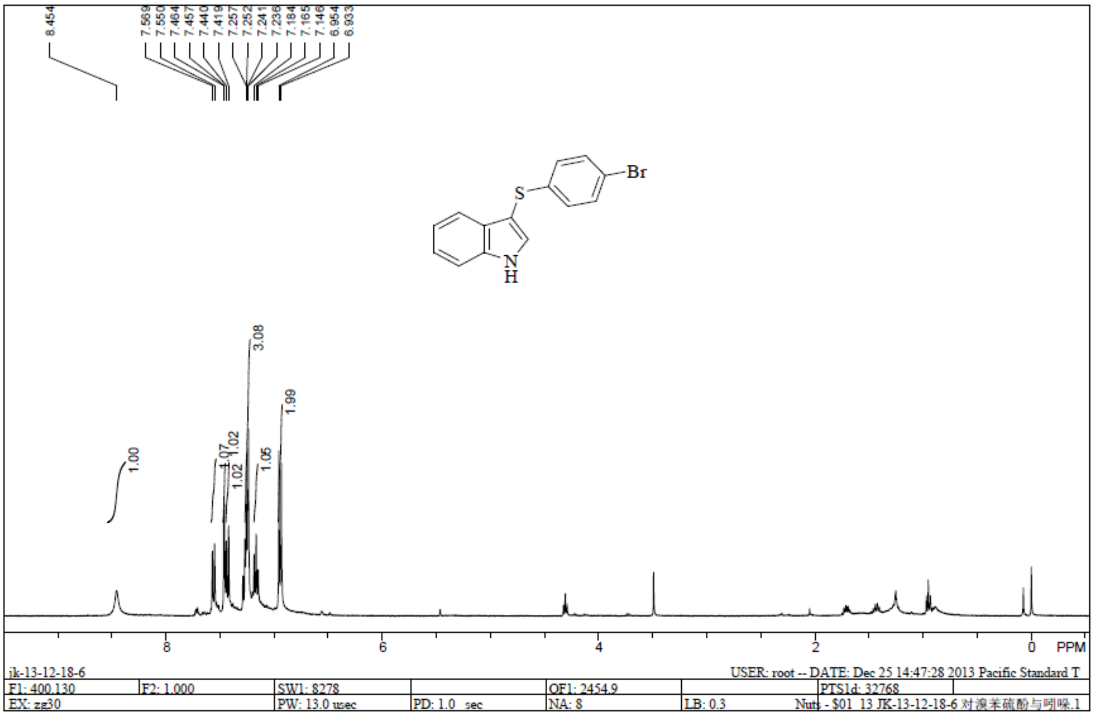


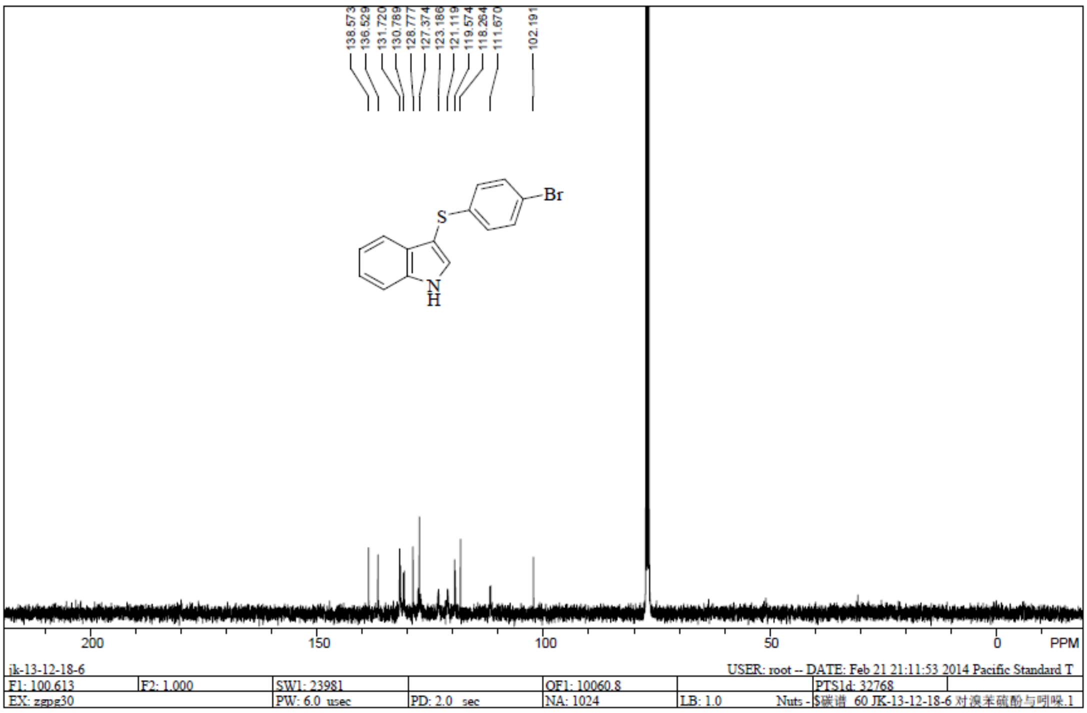
[1]H and [13]C NMR spectra of **3b**



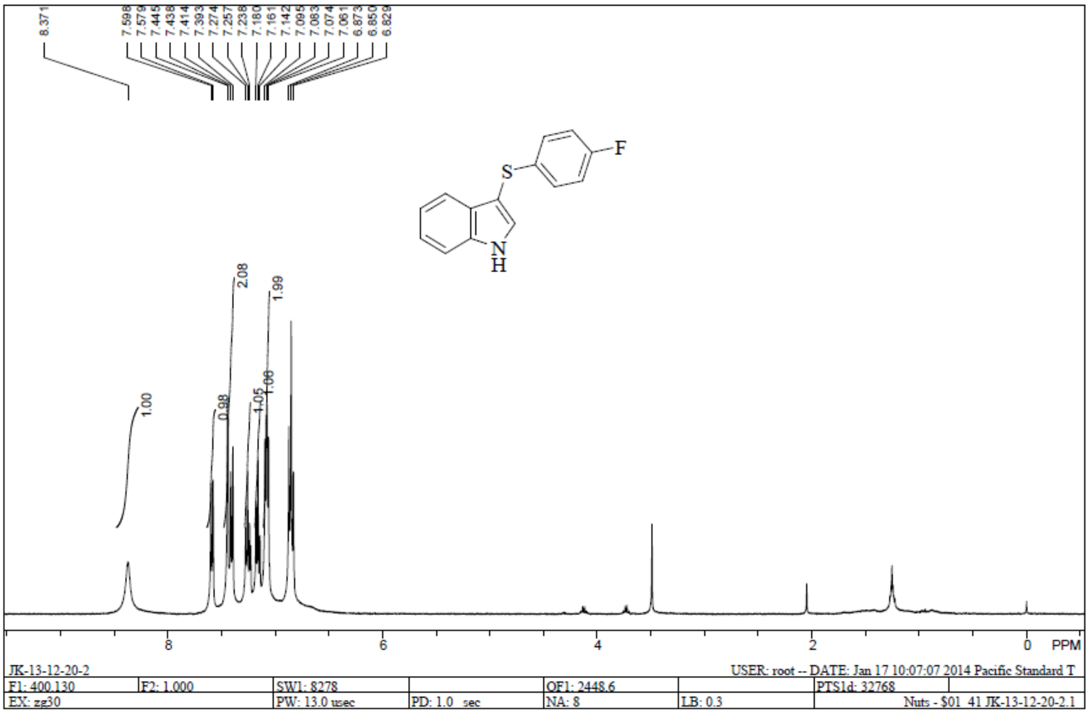


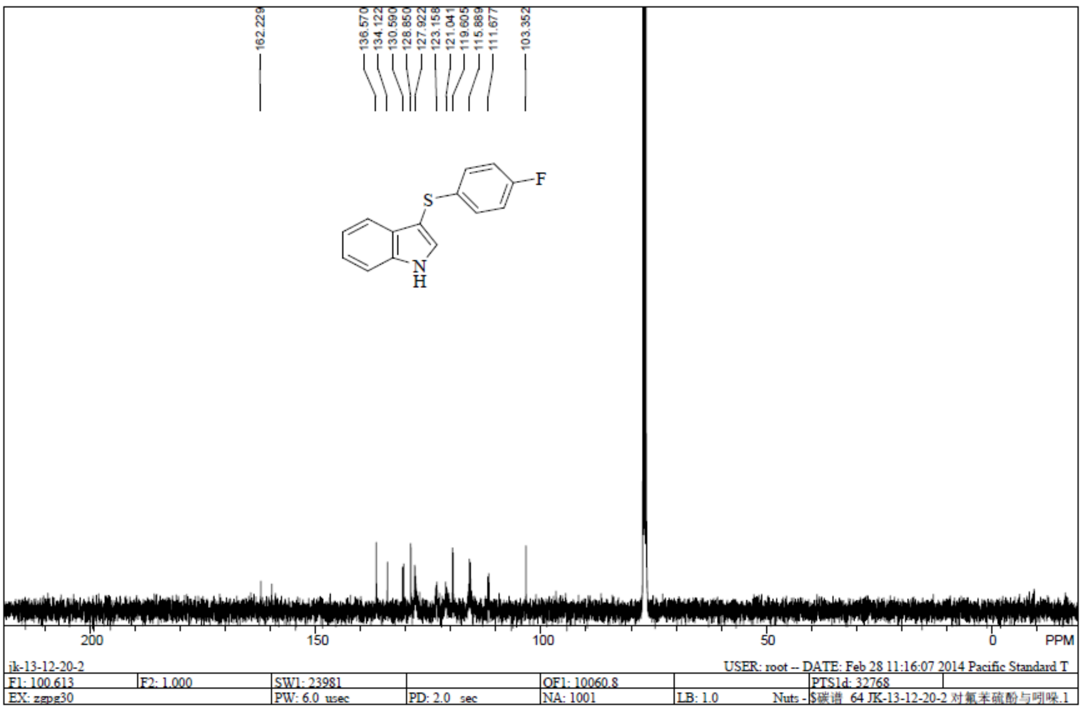
[1]H and [13]C NMR spectra of **3c**



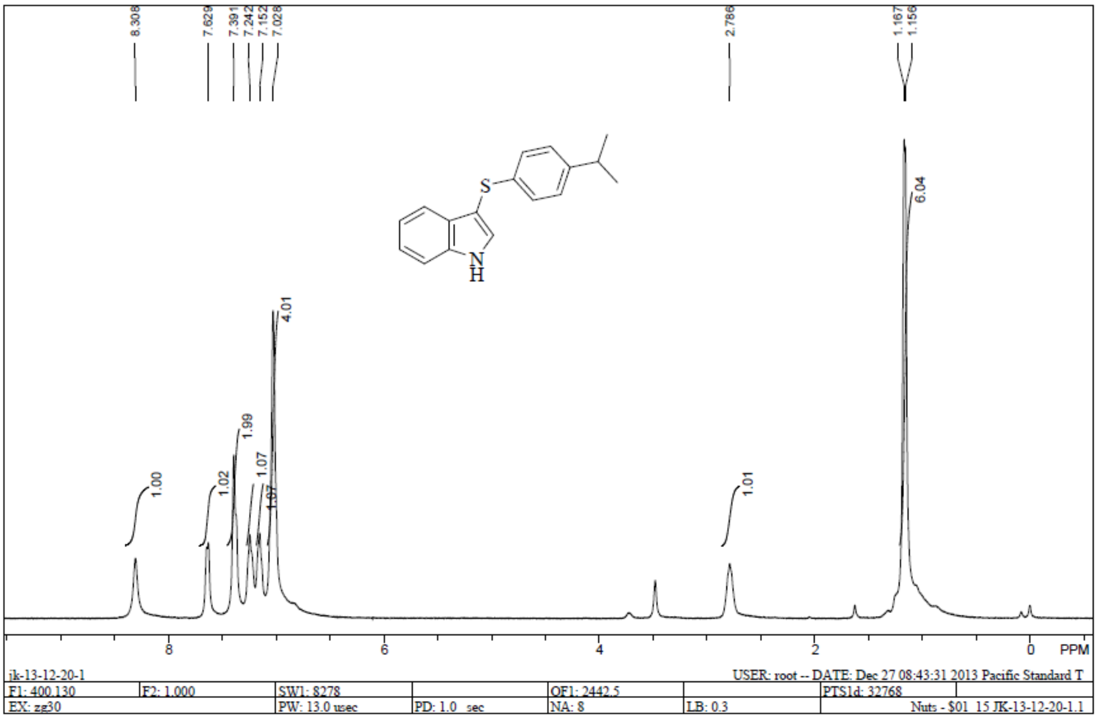


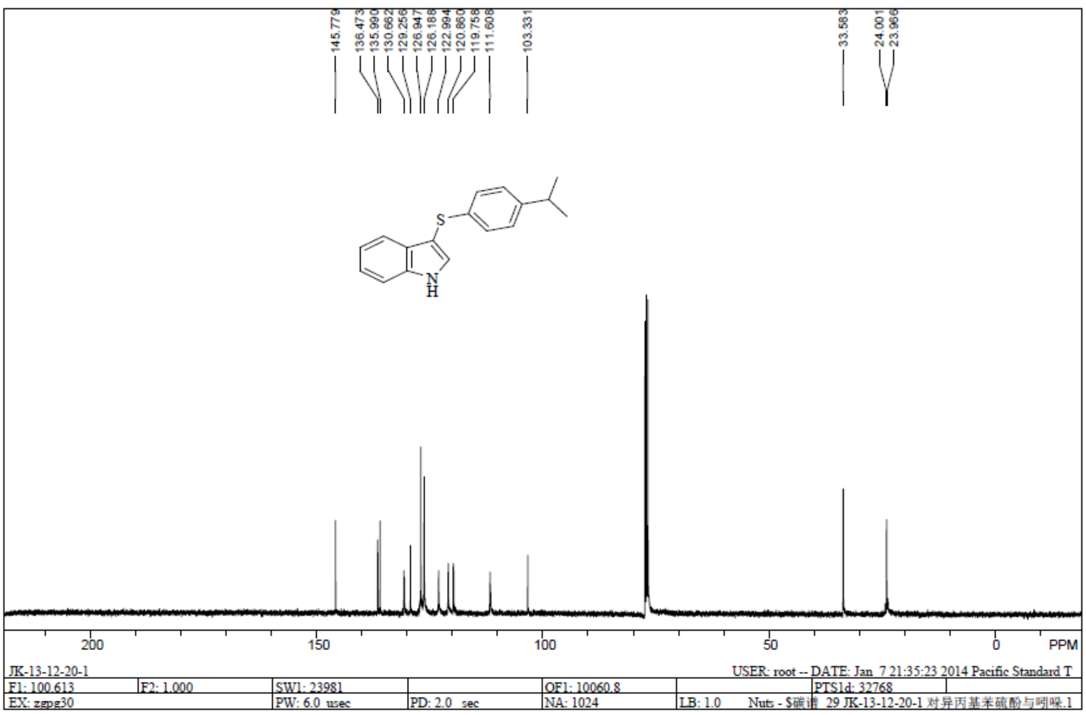
[1]H and [13]C NMR spectra of **3d**



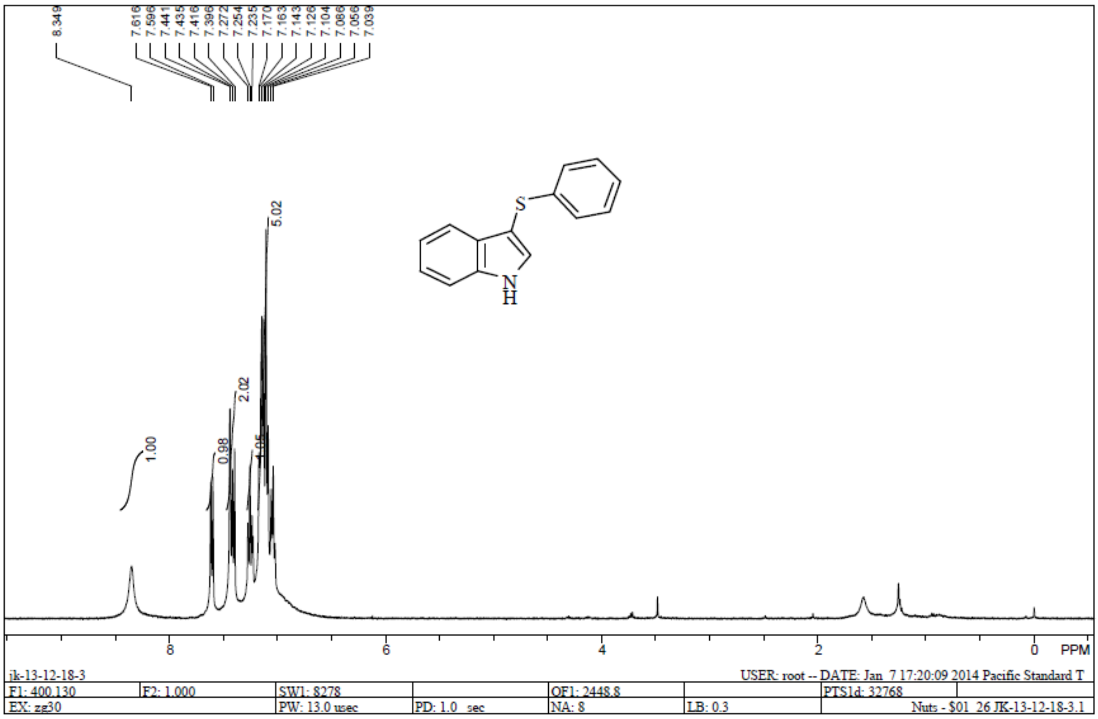


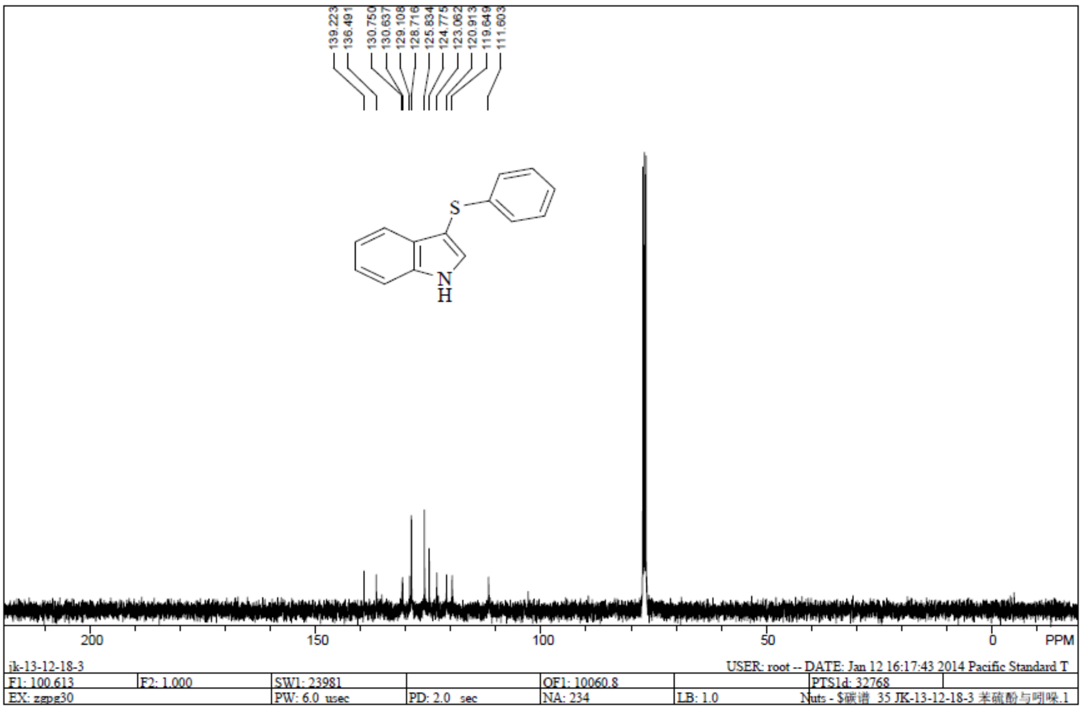
^{1}H and ^{13}C NMR spectra of **3e**



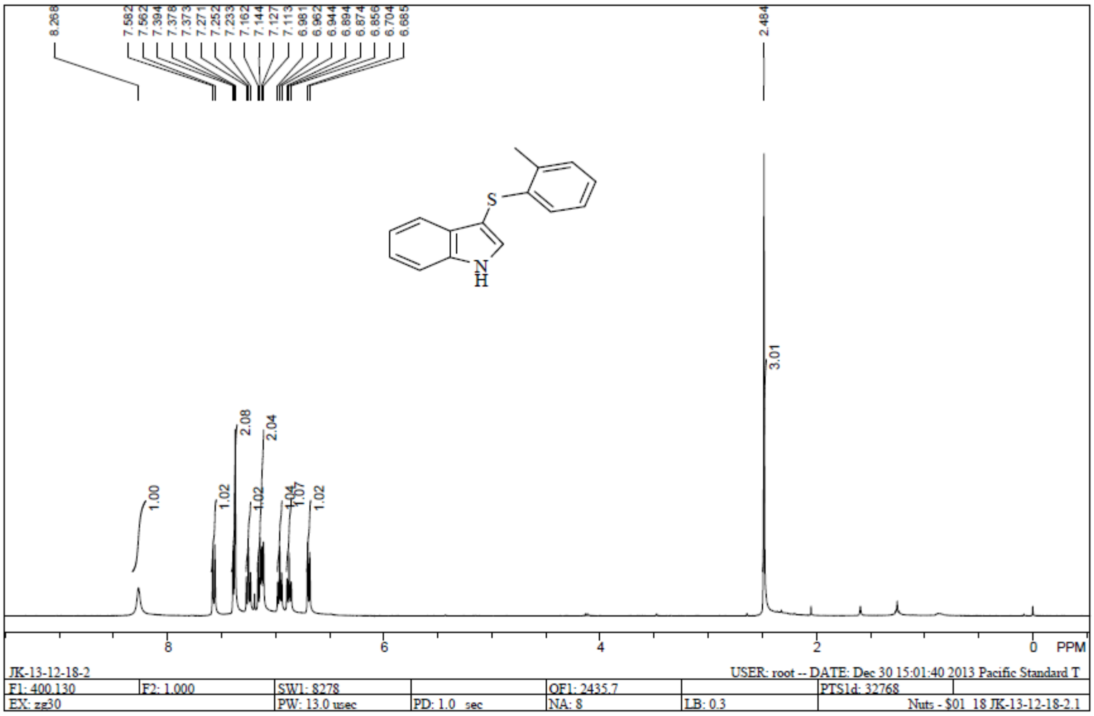


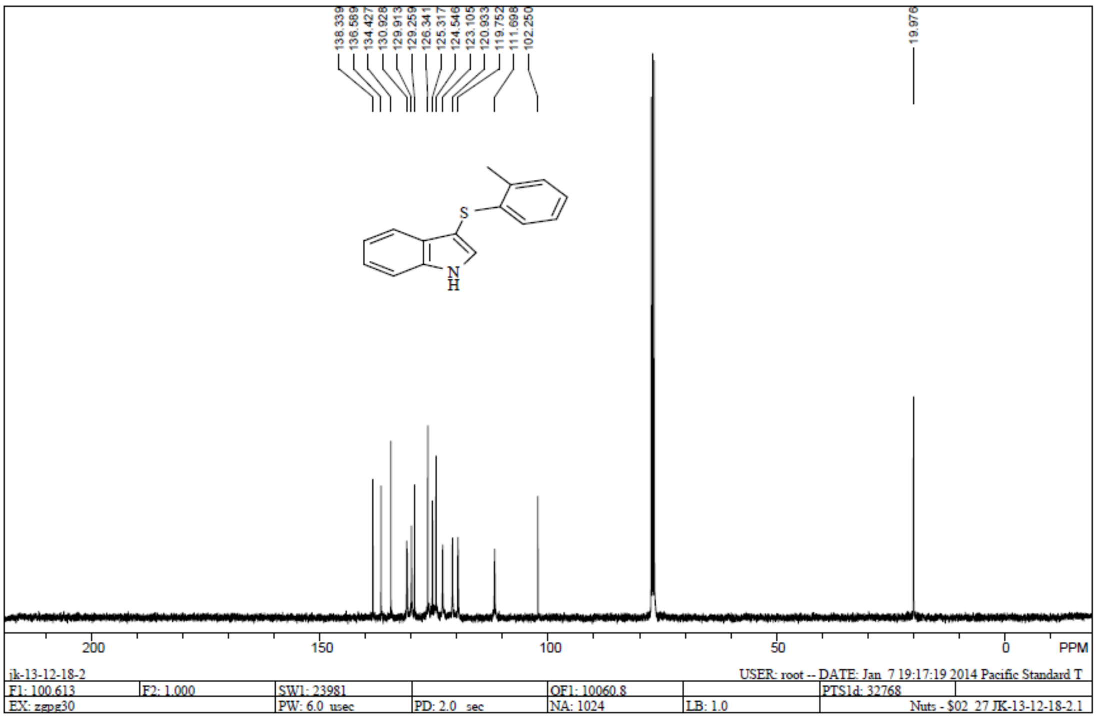
[1]H and [13]C NMR spectra of **3f**



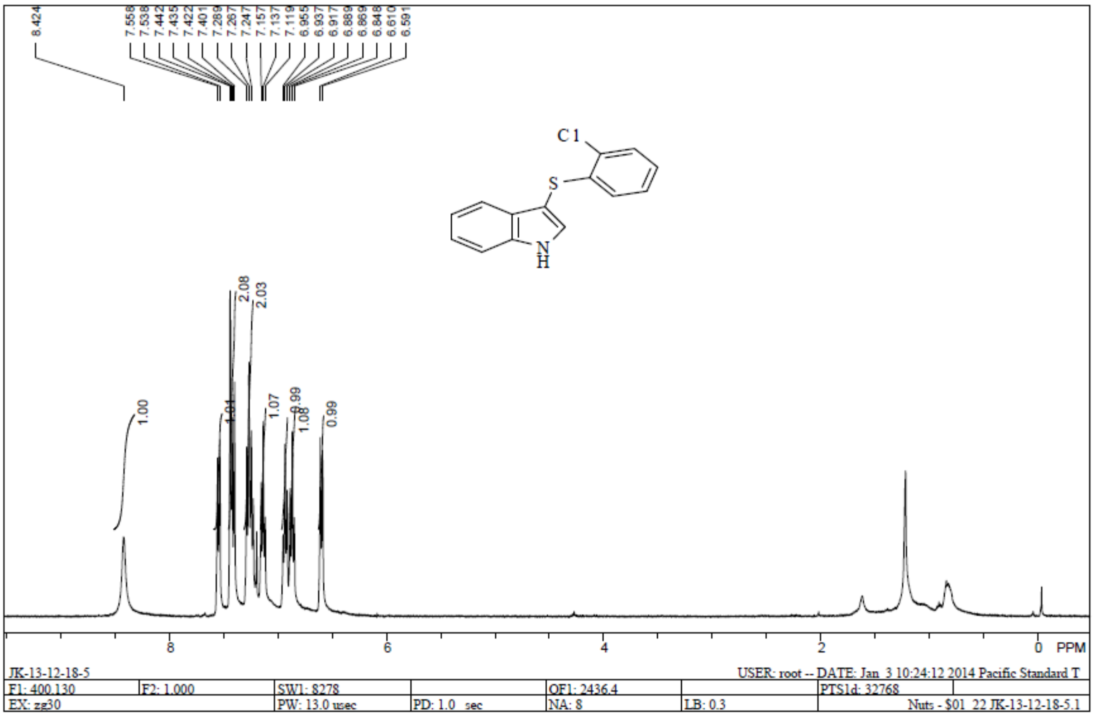


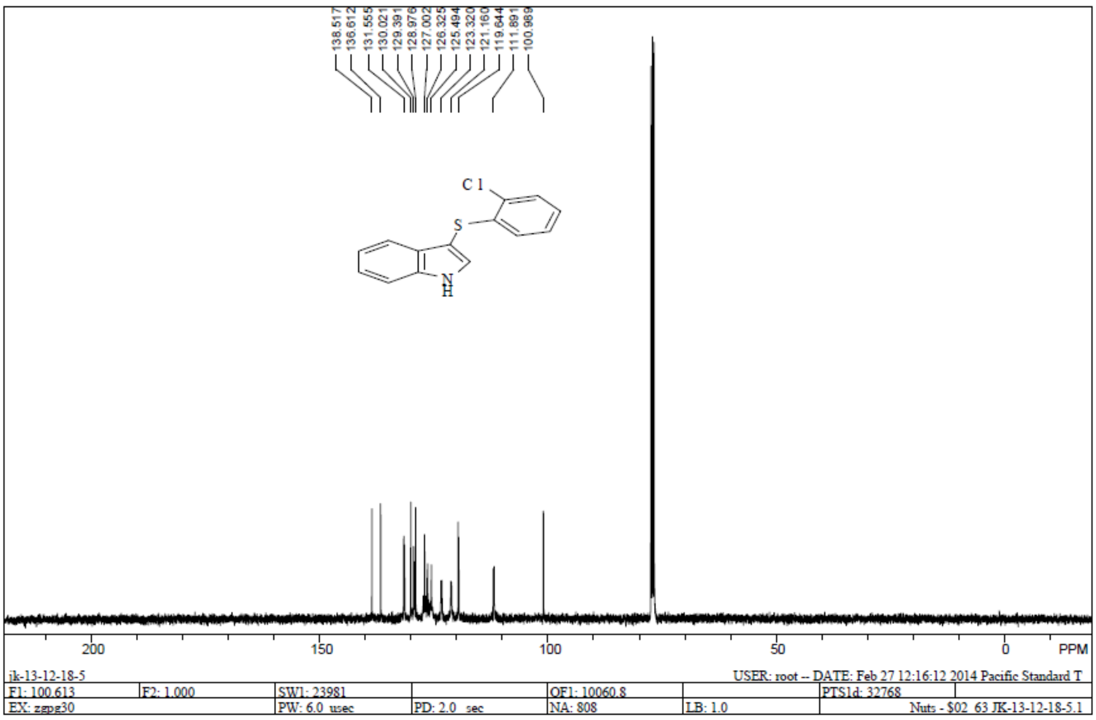
[1]H and [13]C NMR spectra of **3g**



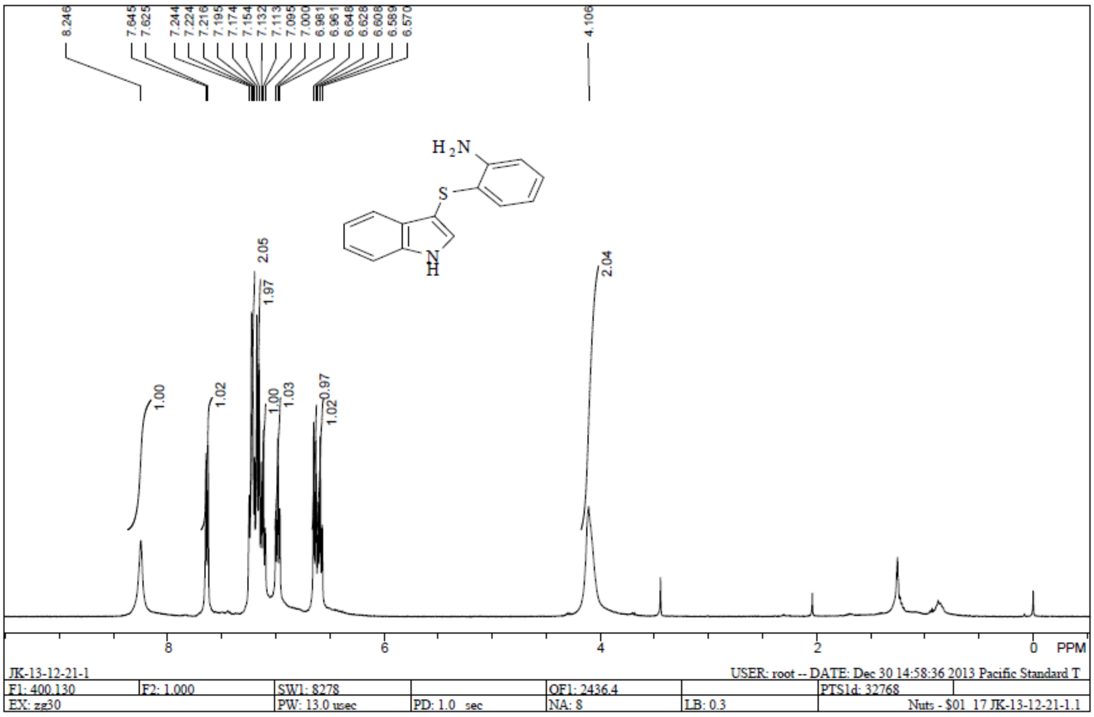


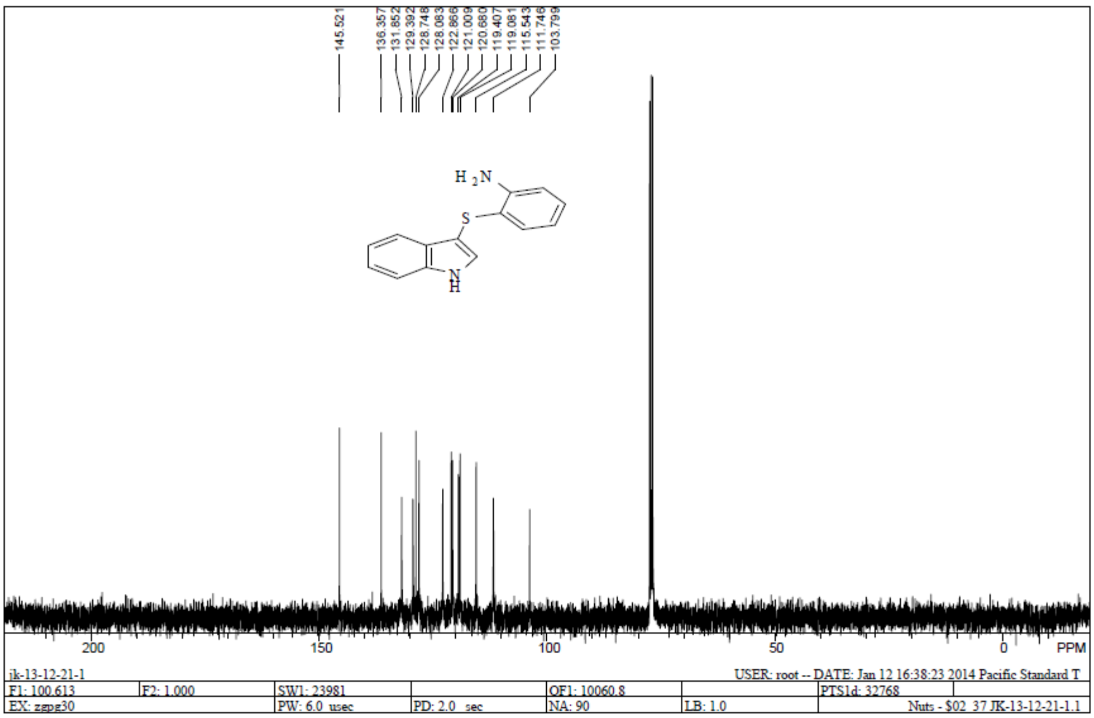
^{1}H and ^{13}C NMR spectra of **3h**



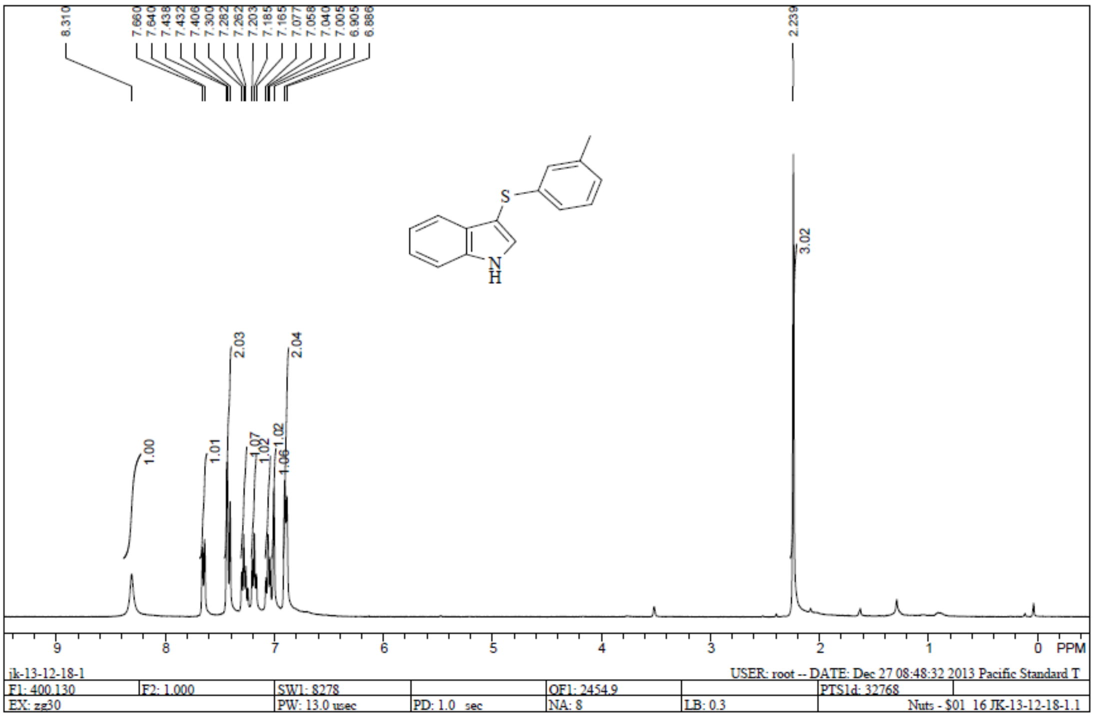


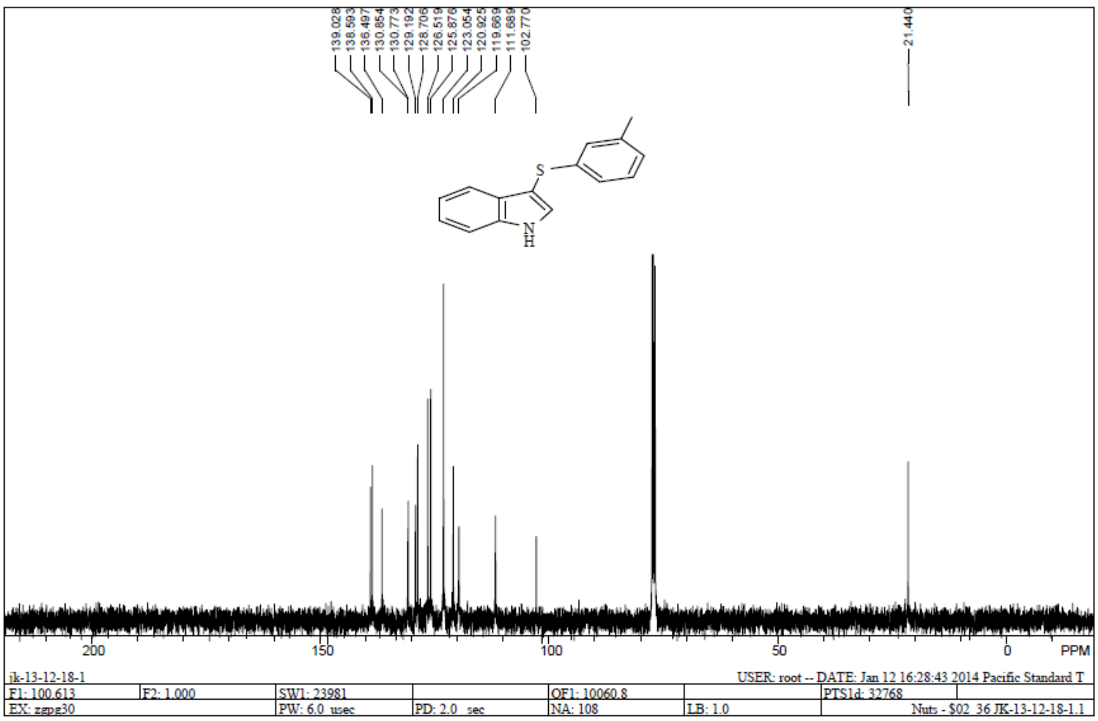
^{1}H and ^{13}C NMR spectra of **3i**



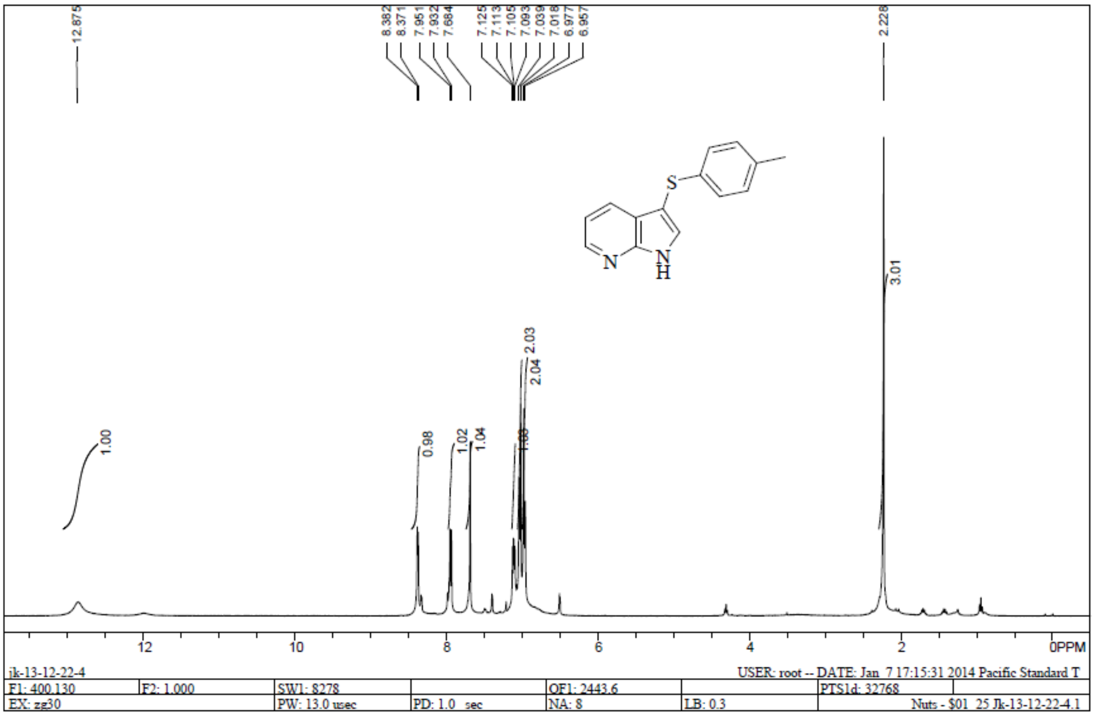


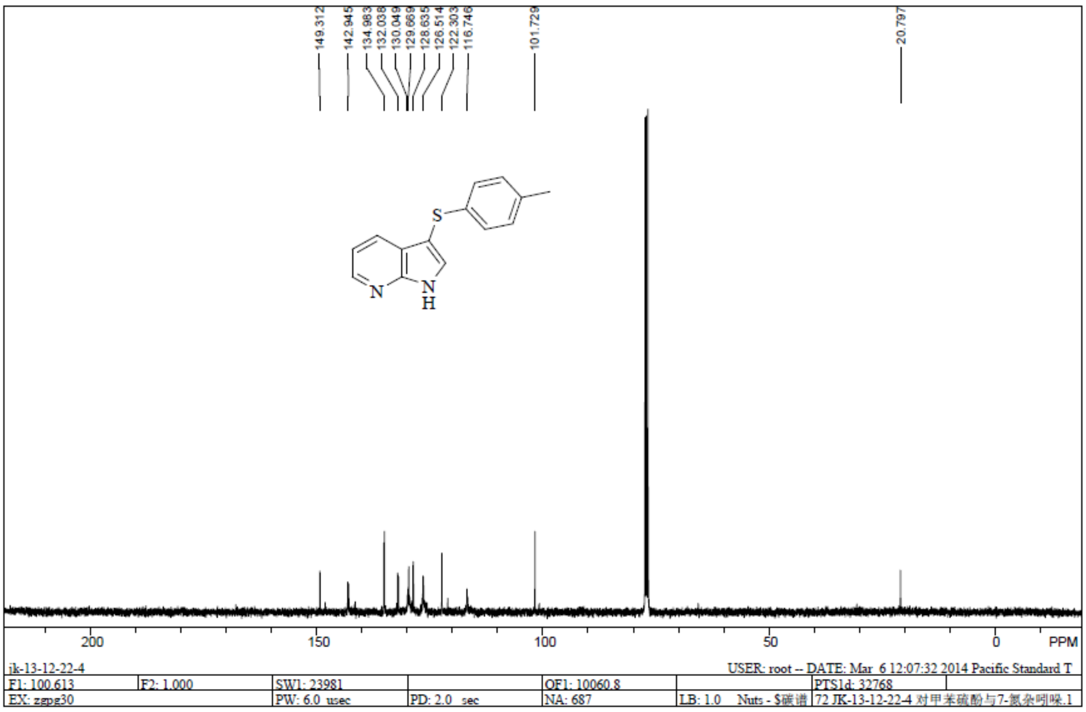
^{1}H and ^{13}C NMR spectra of **3j**



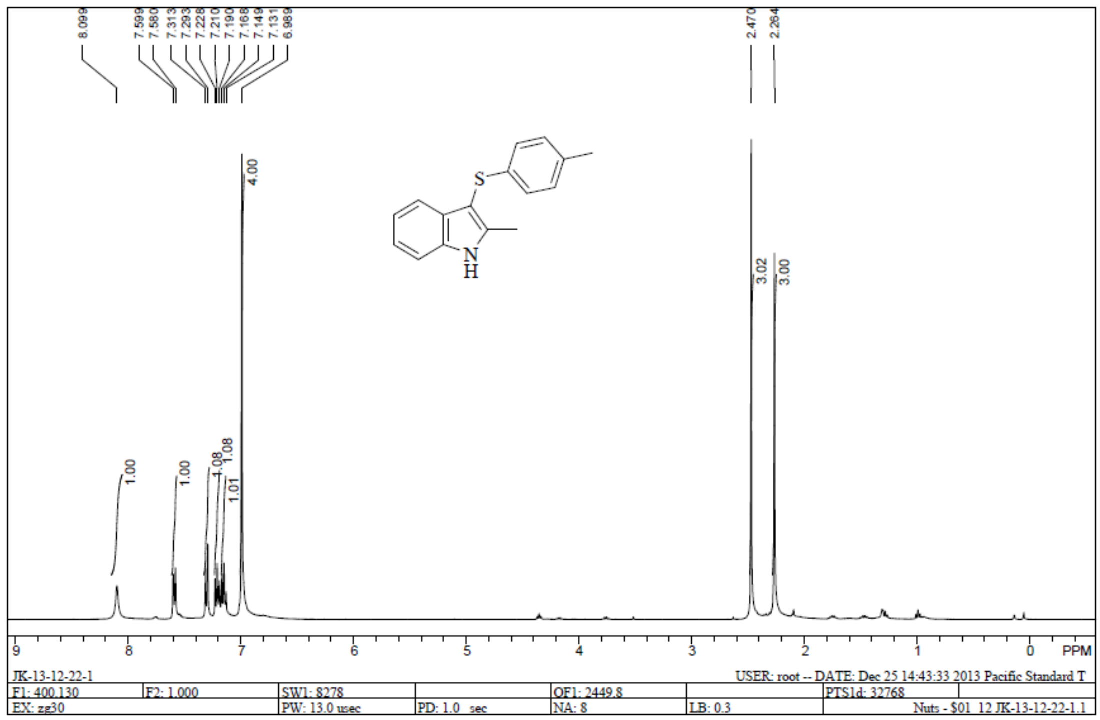


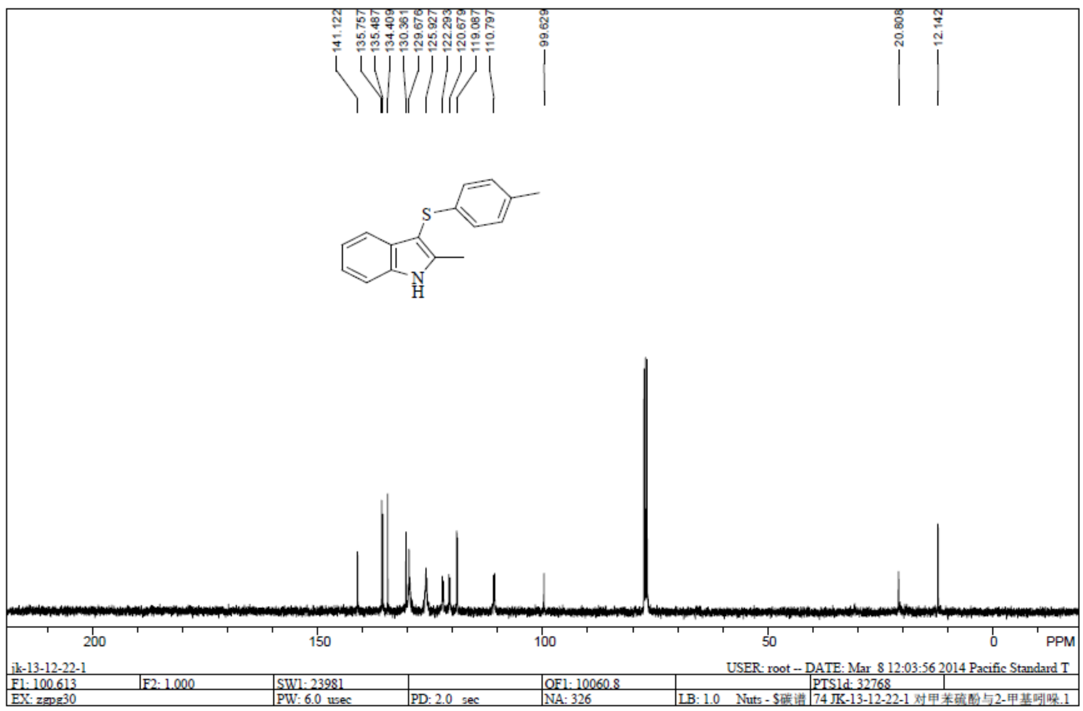
^{1}H and ^{13}C NMR spectra of **3k**



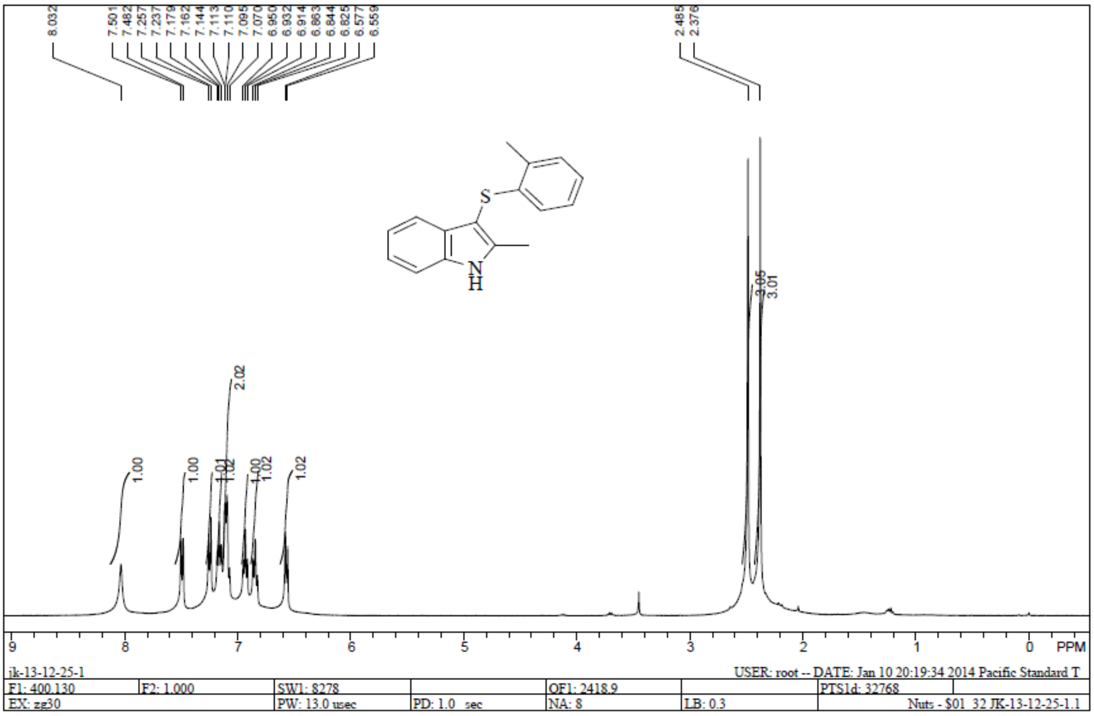


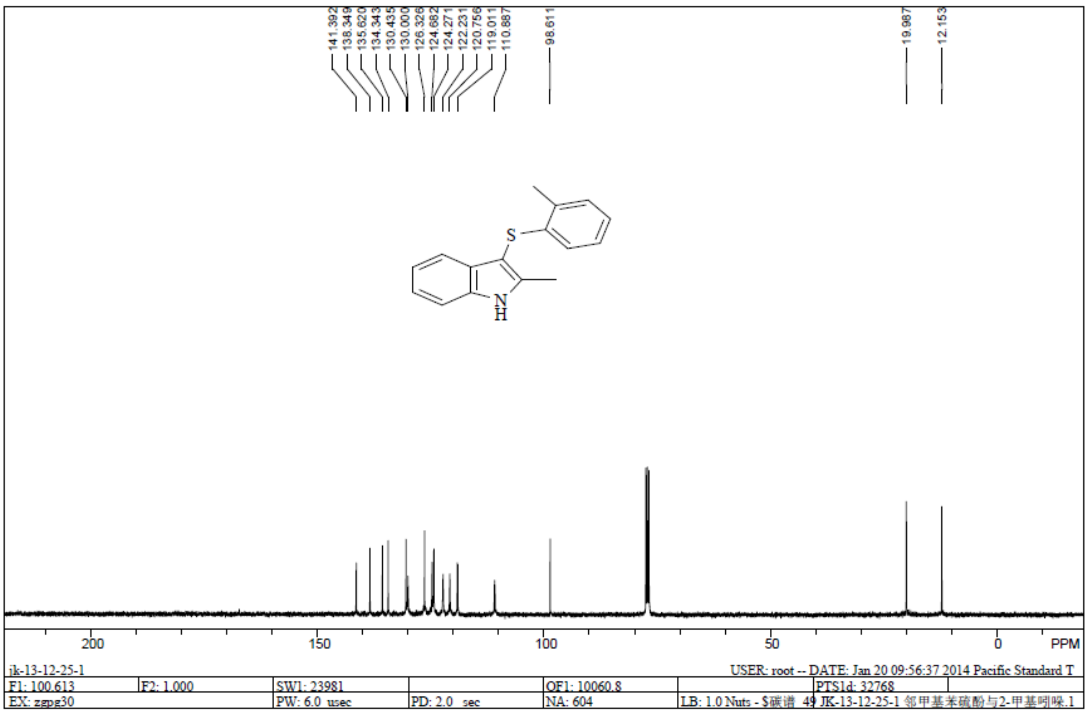
[1]H and [13]C NMR spectra of **3l**



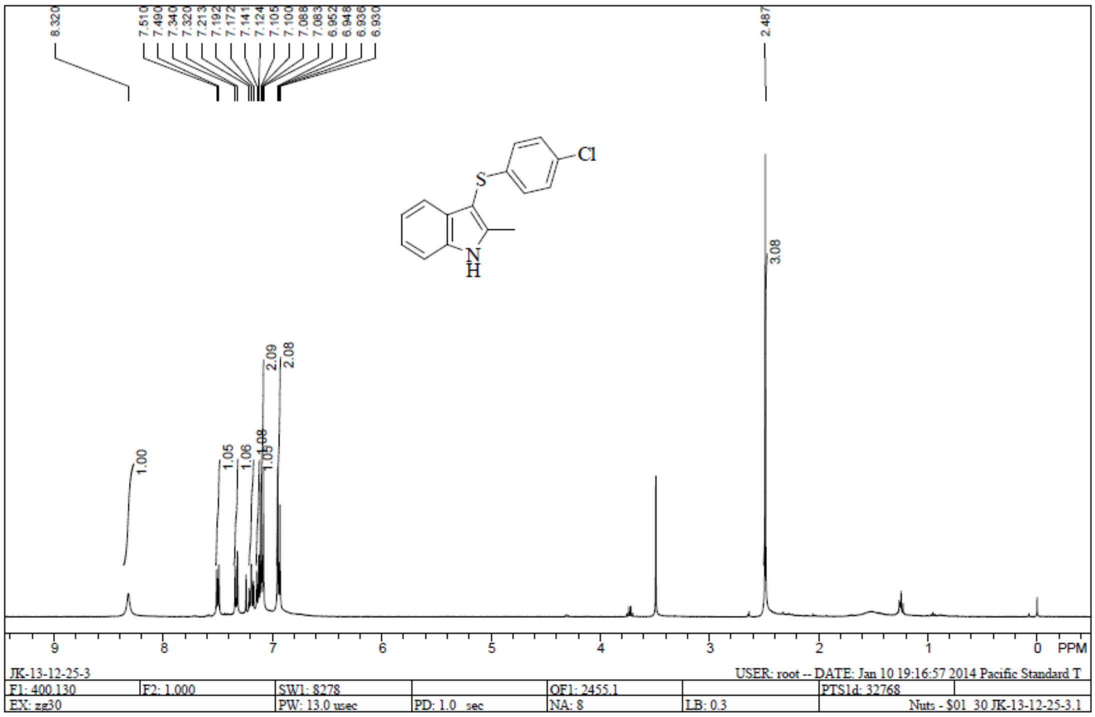


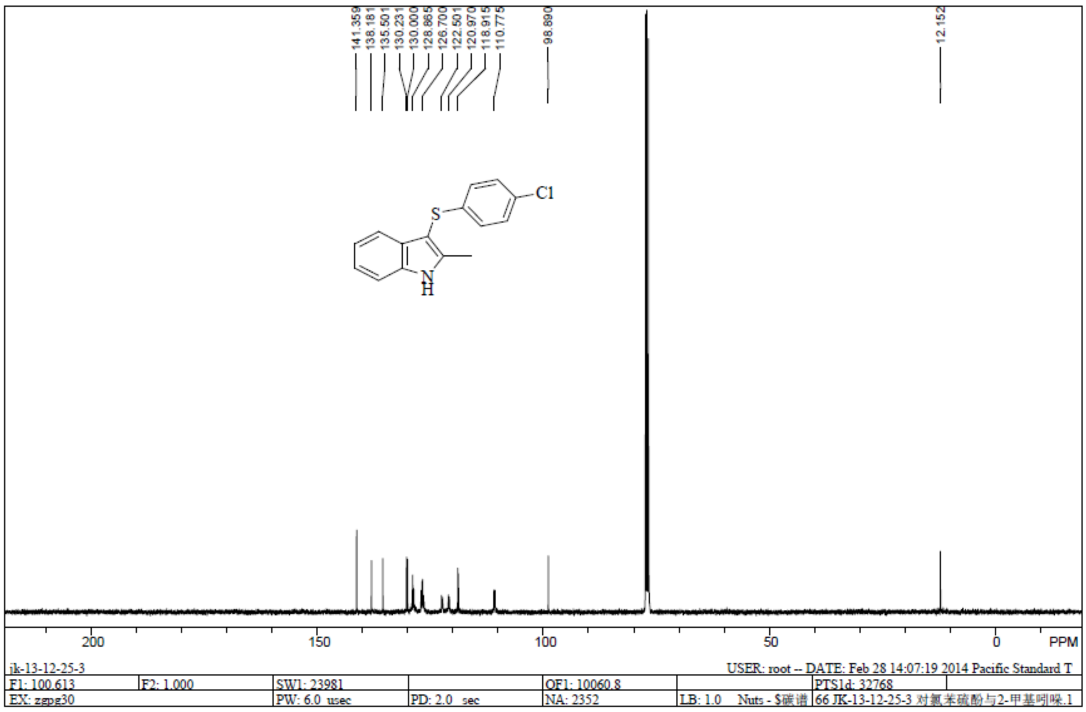
[1]H and [13]C NMR spectra of **3m**



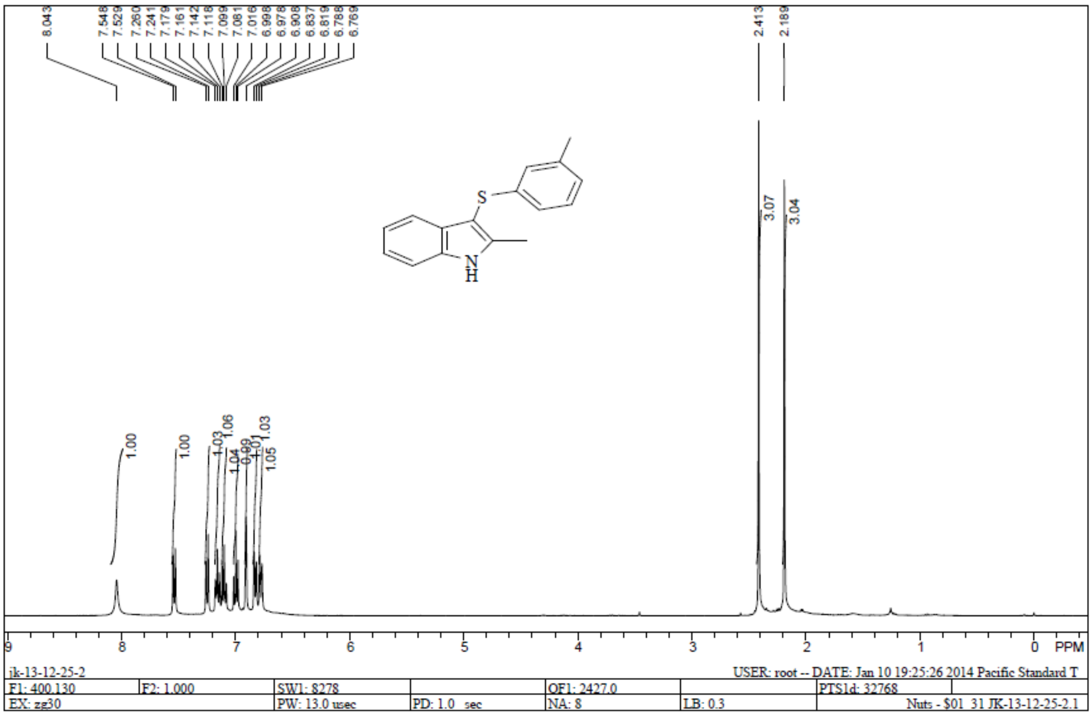


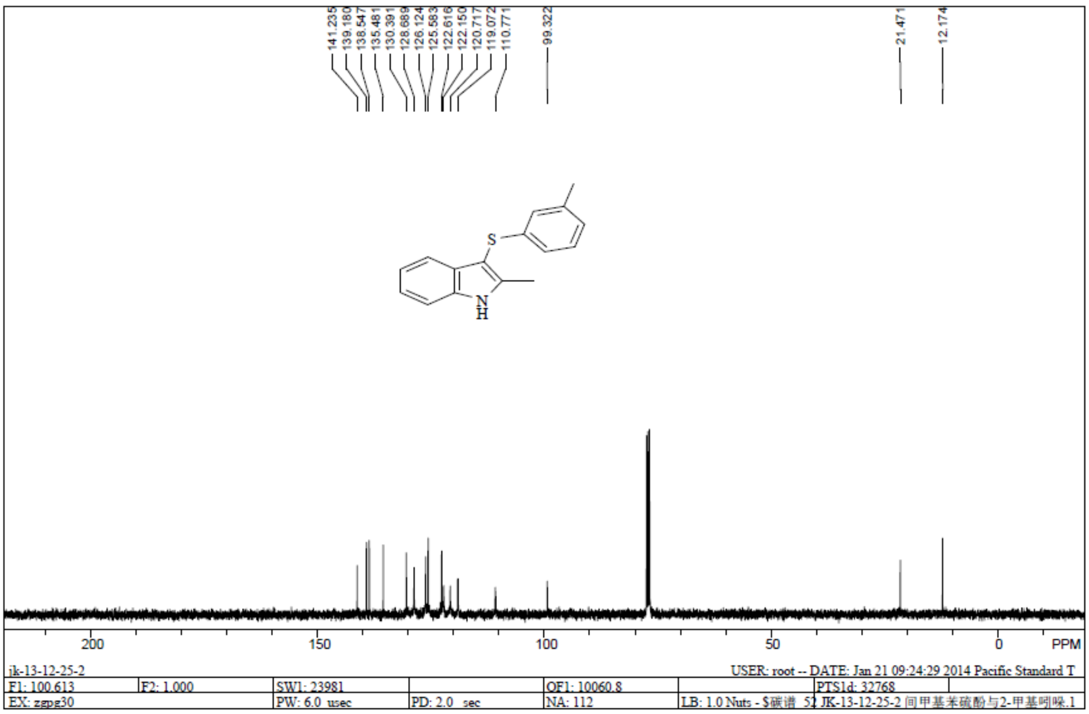
^{1}H and ^{13}C NMR spectra of **3n**



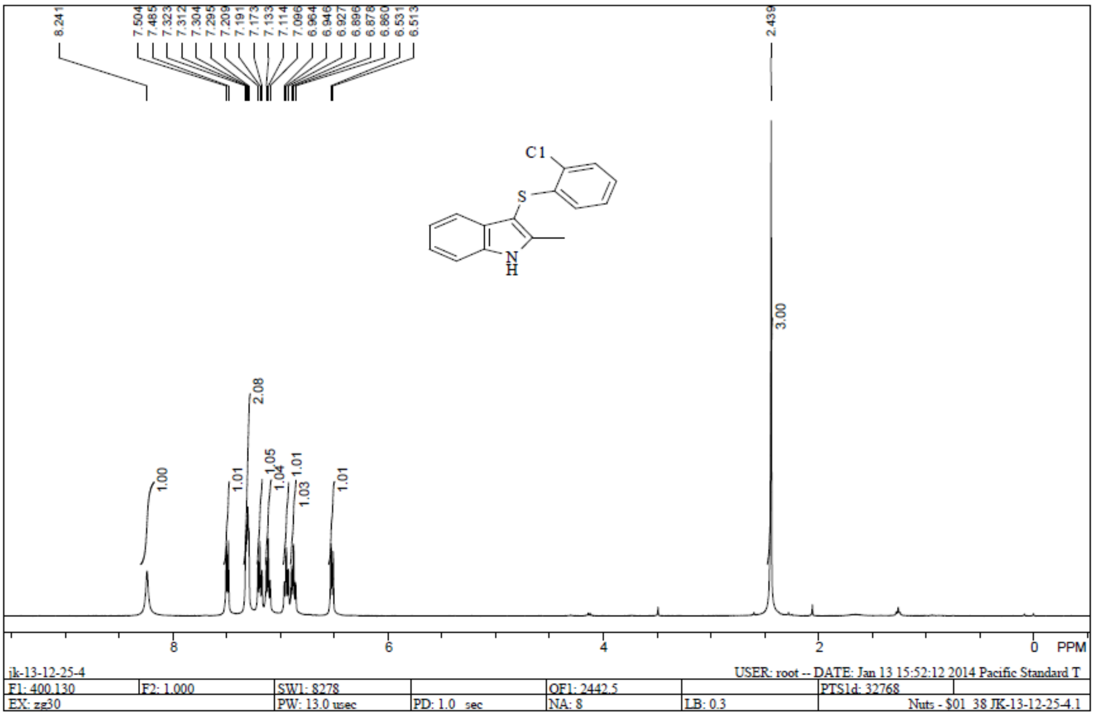


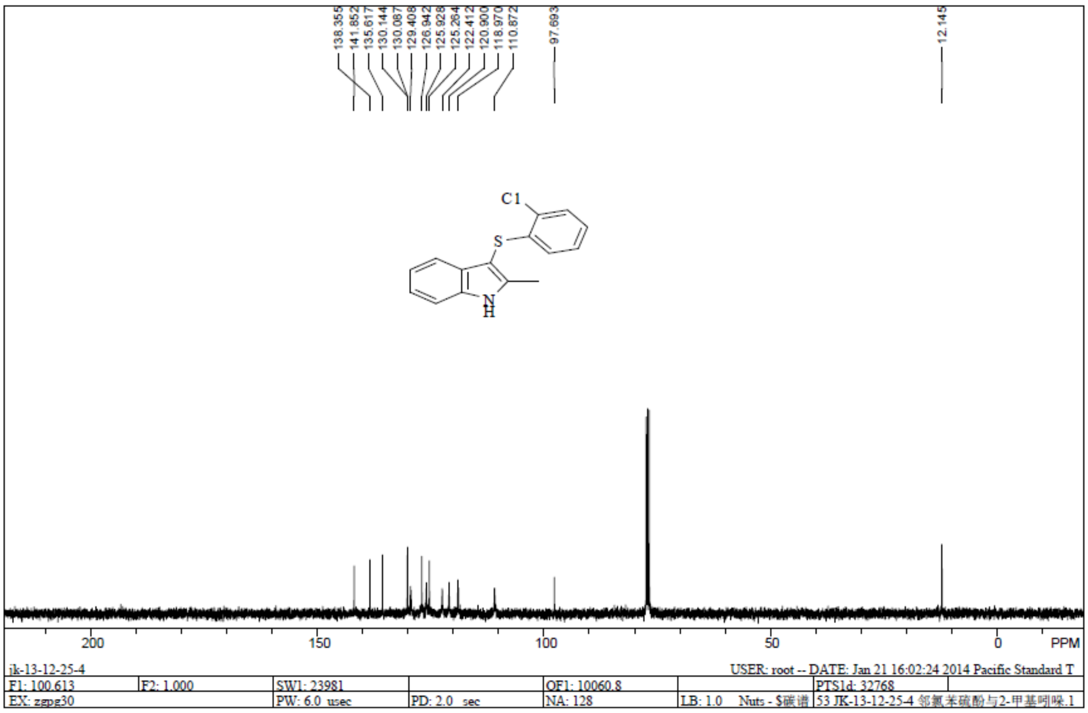
^1H and ^{13}C NMR spectra of **3o**



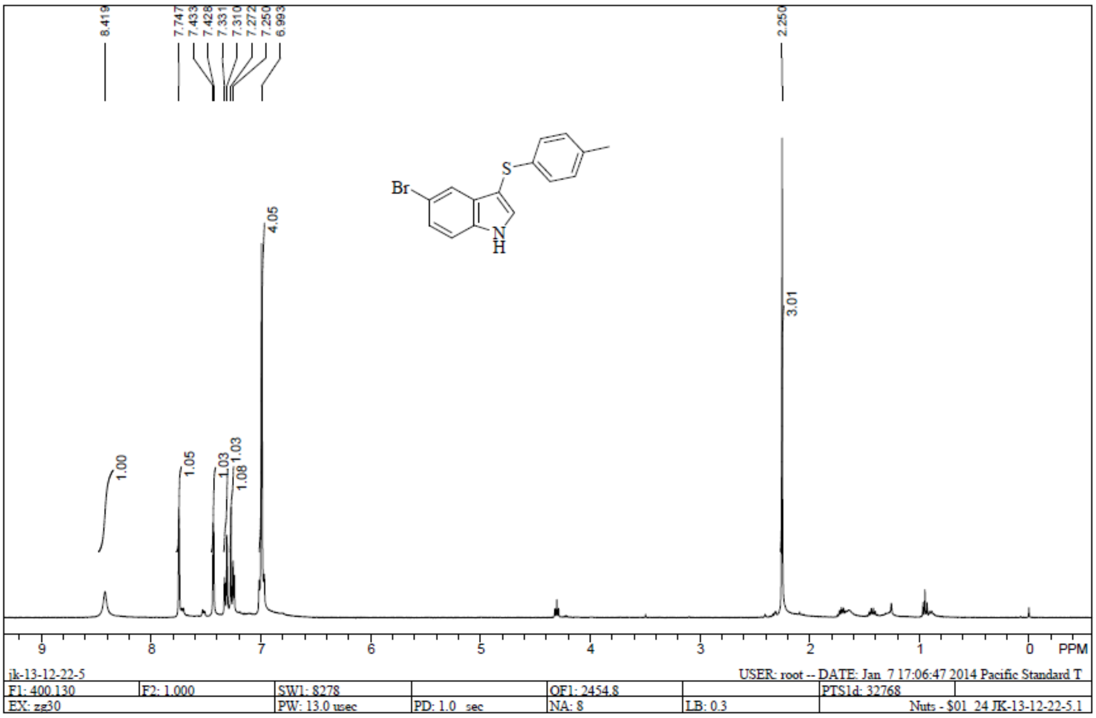


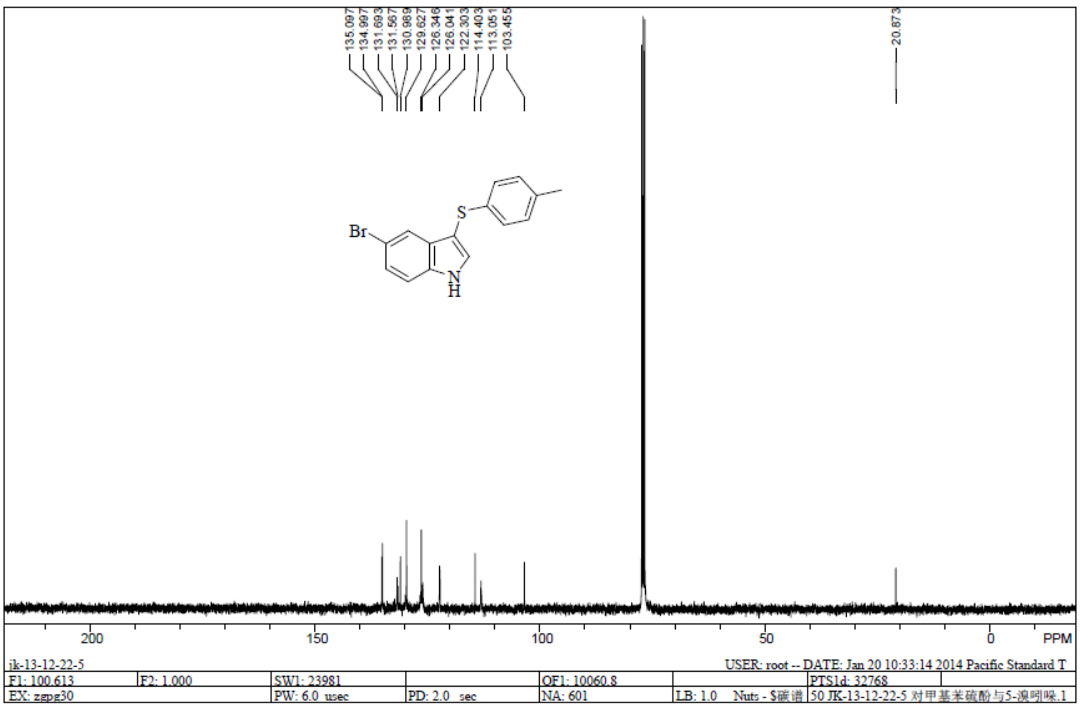
^1H and ^{13}C NMR spectra of **3p**



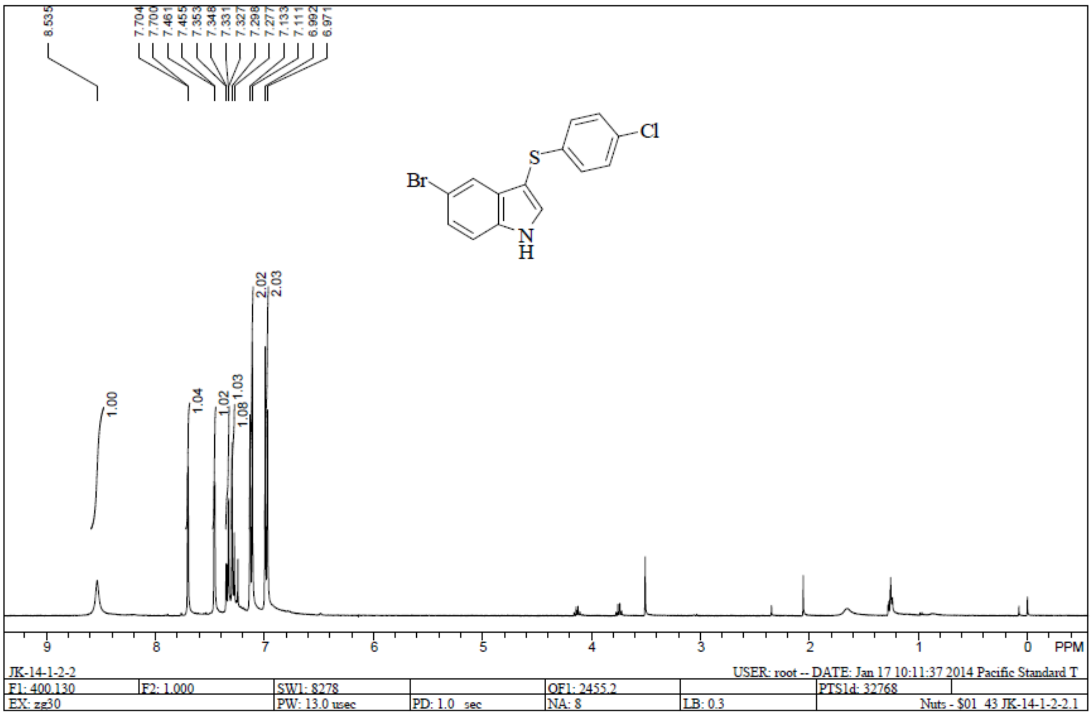


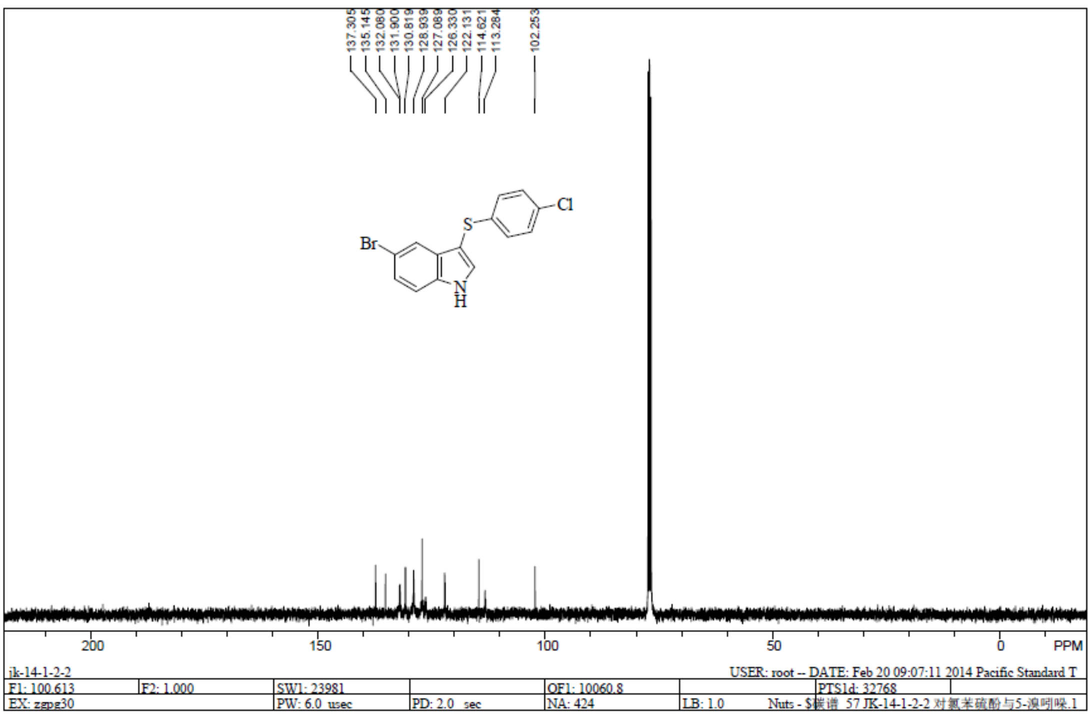
[1]H and [13]C NMR spectra of **3q**



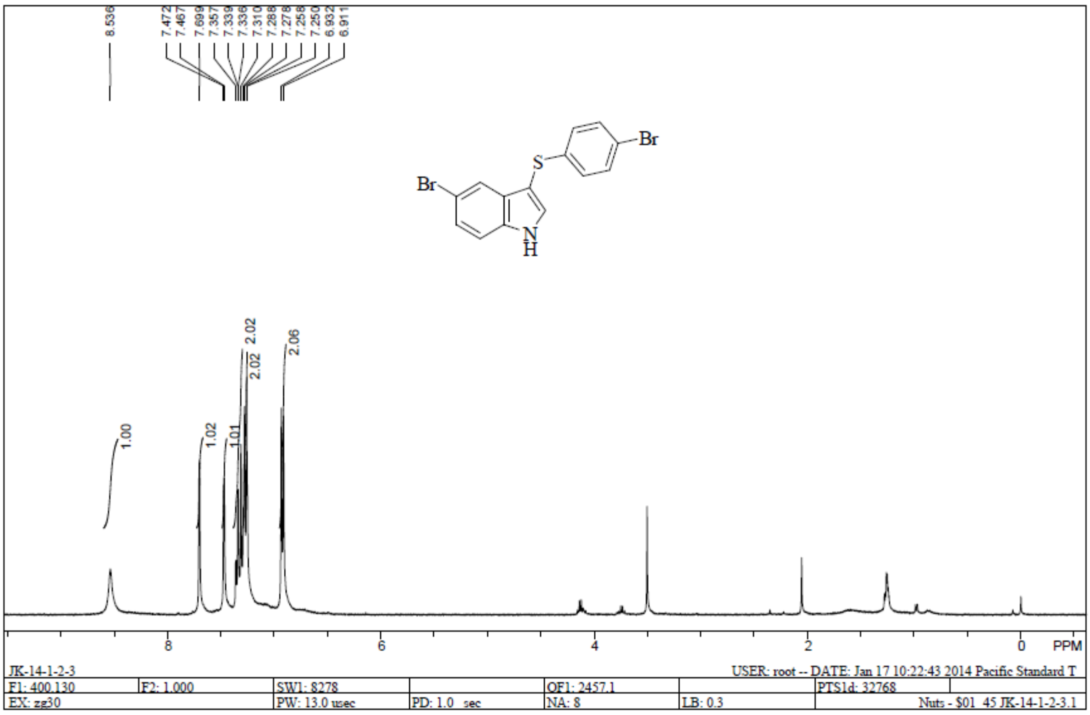


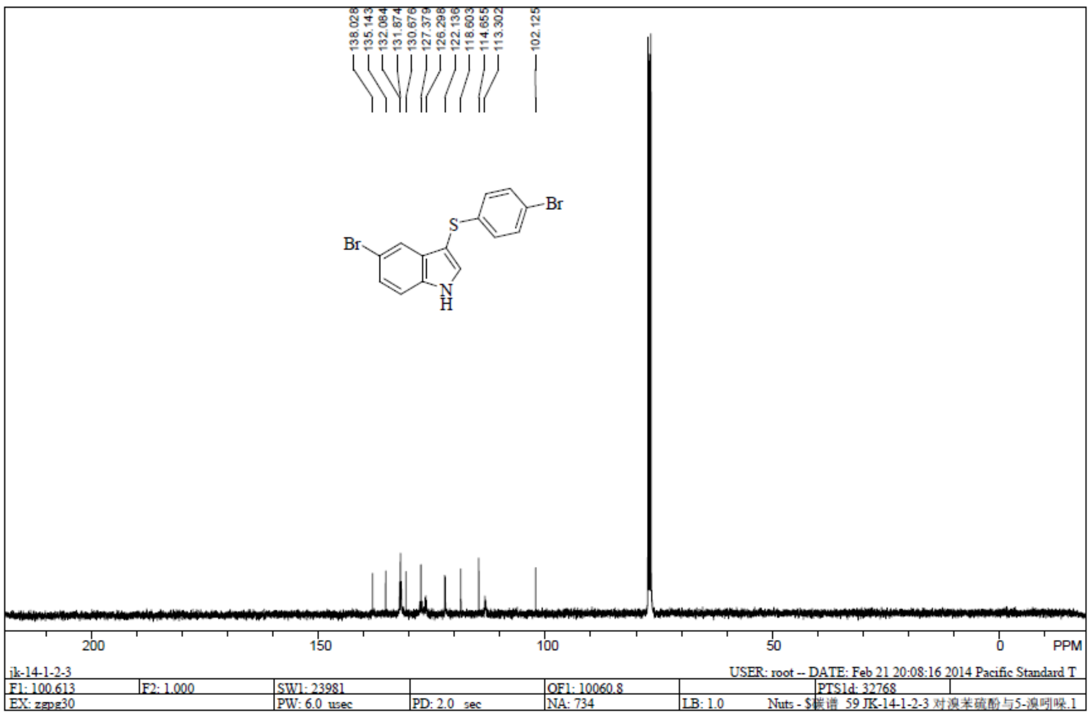
[1]H and [13]C NMR spectra of **3r**



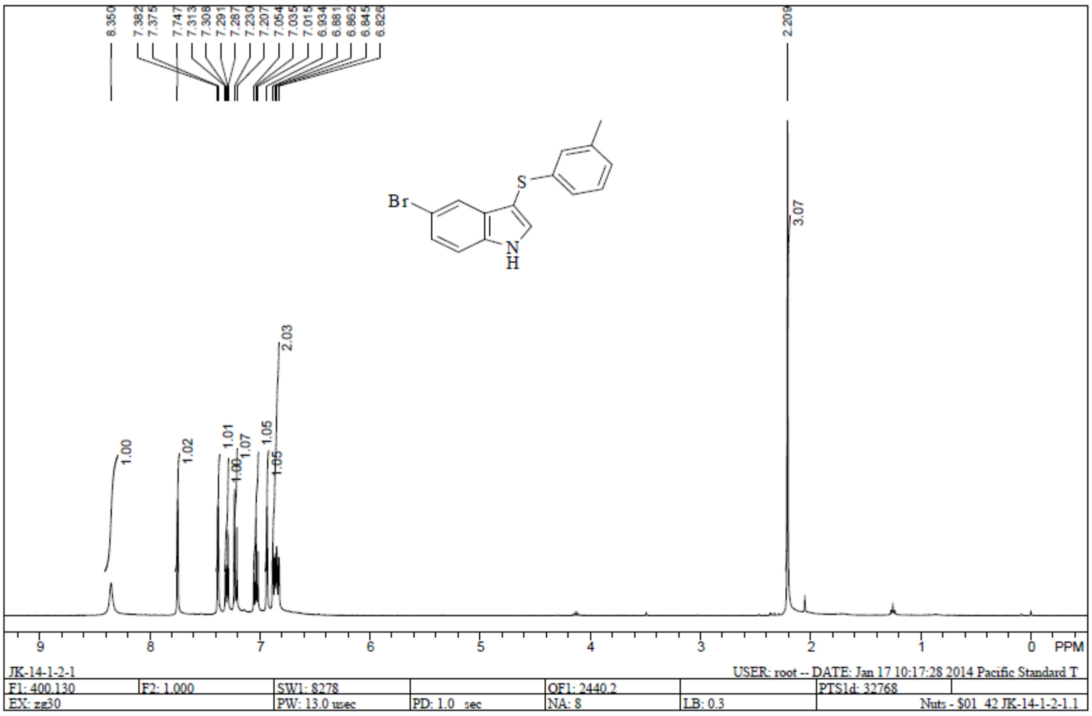


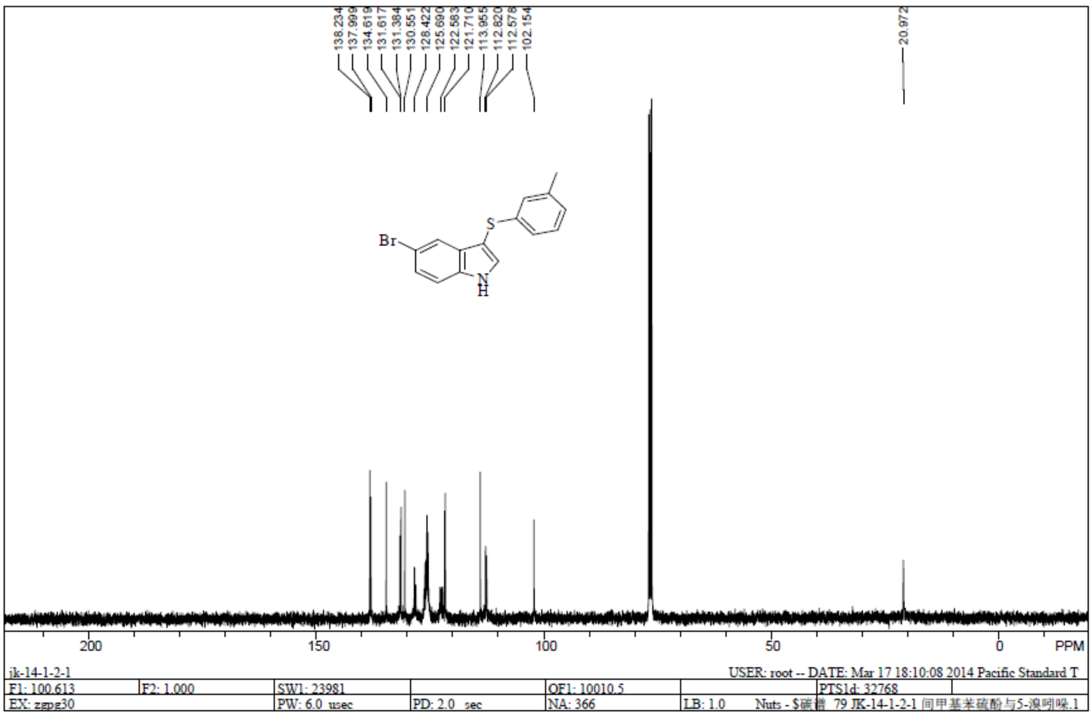
[1]H and [13]C NMR spectra of **3s**



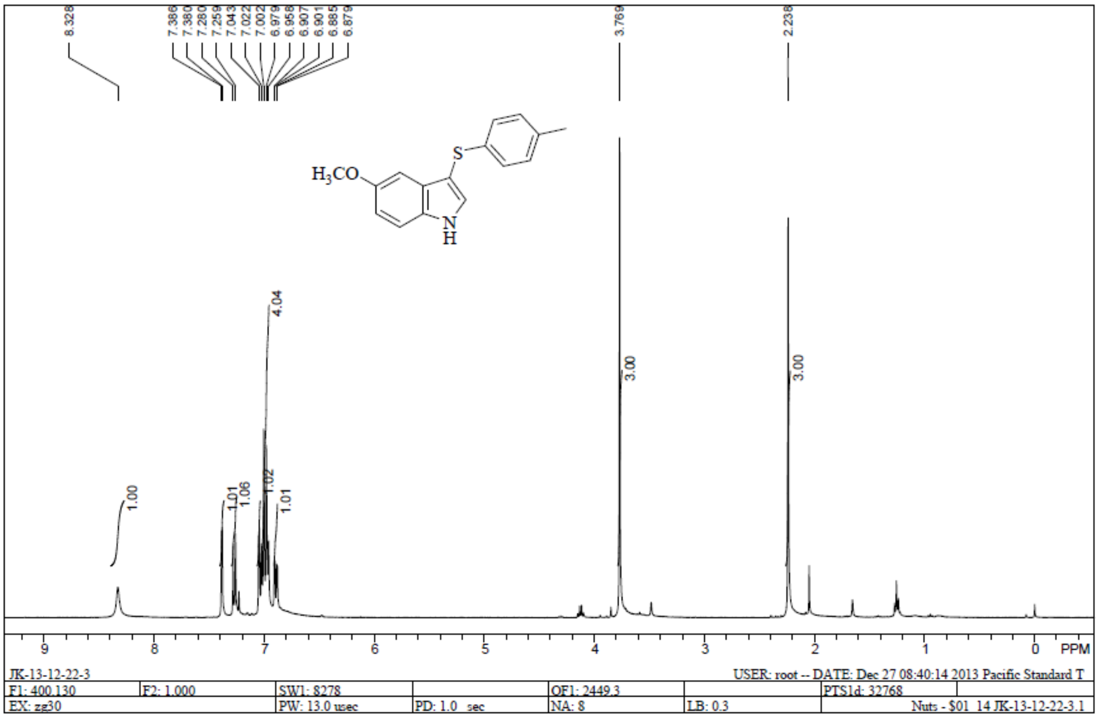


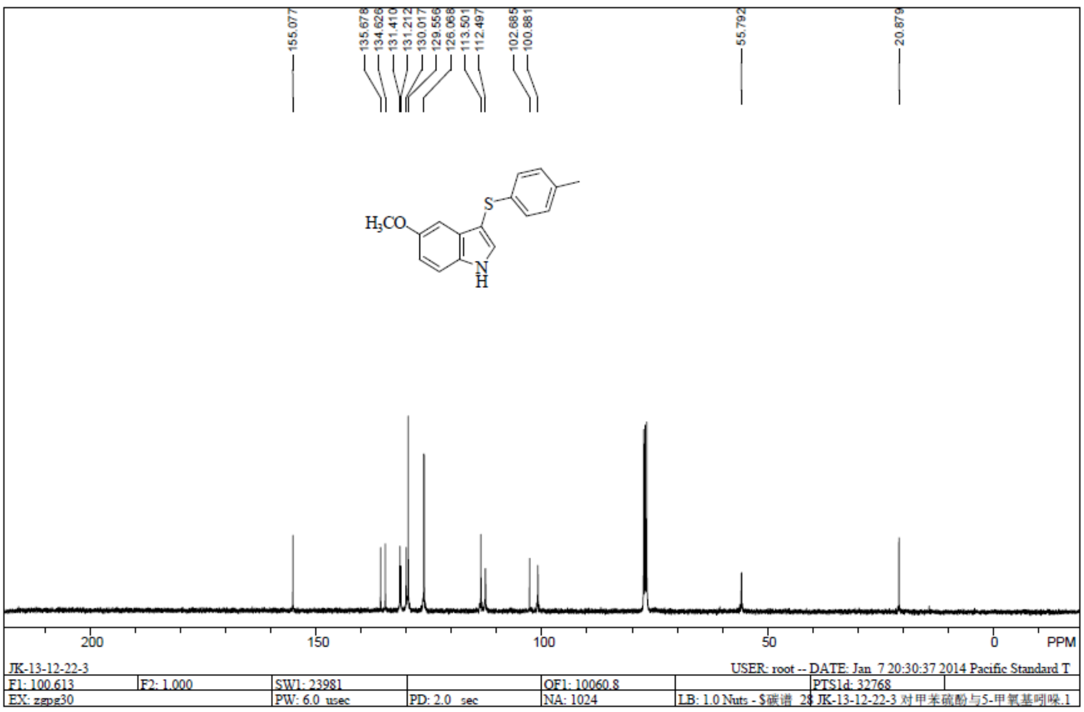
[1]H and [13]C NMR spectra of **3t**



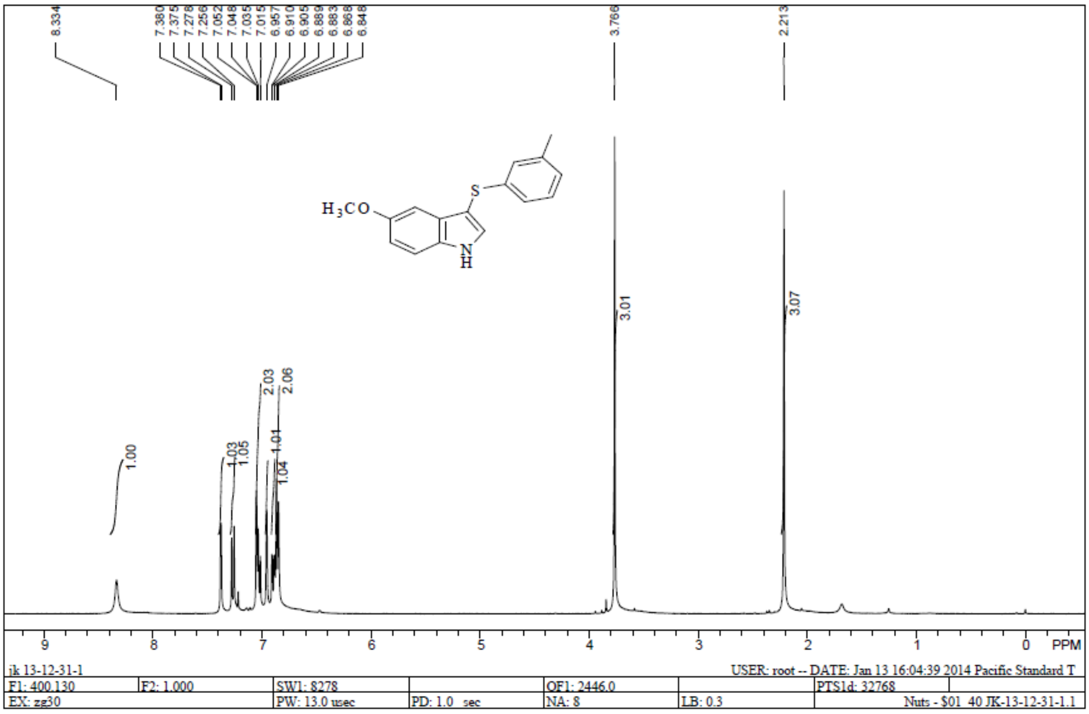


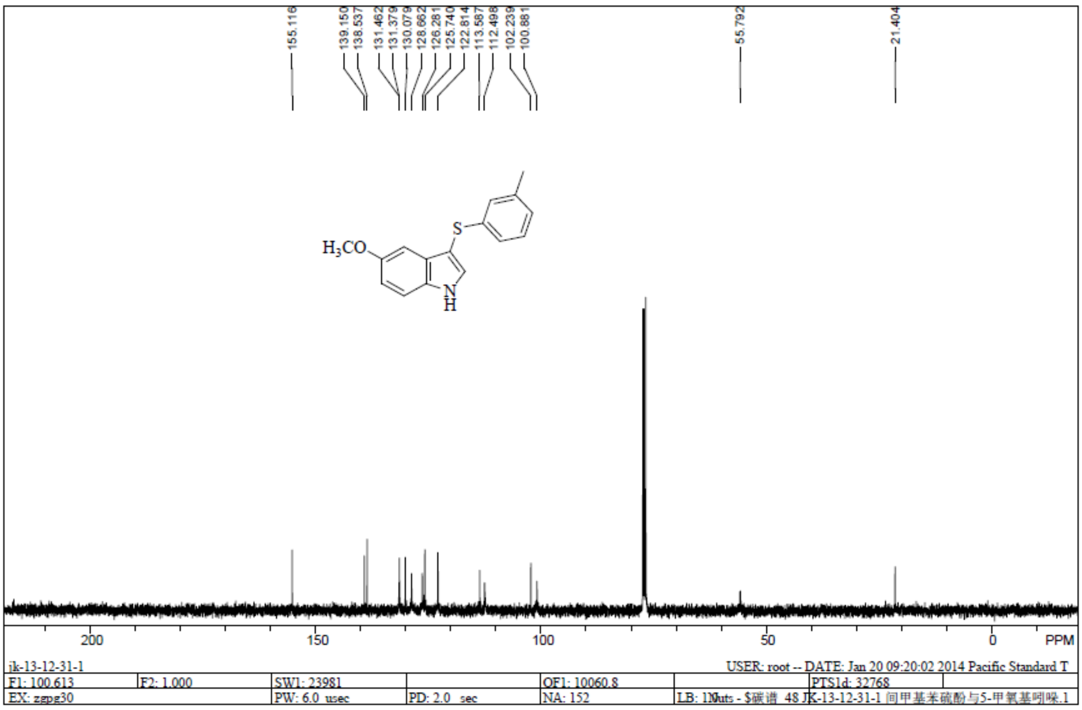
^{1}H and ^{13}C NMR spectra of **3u**



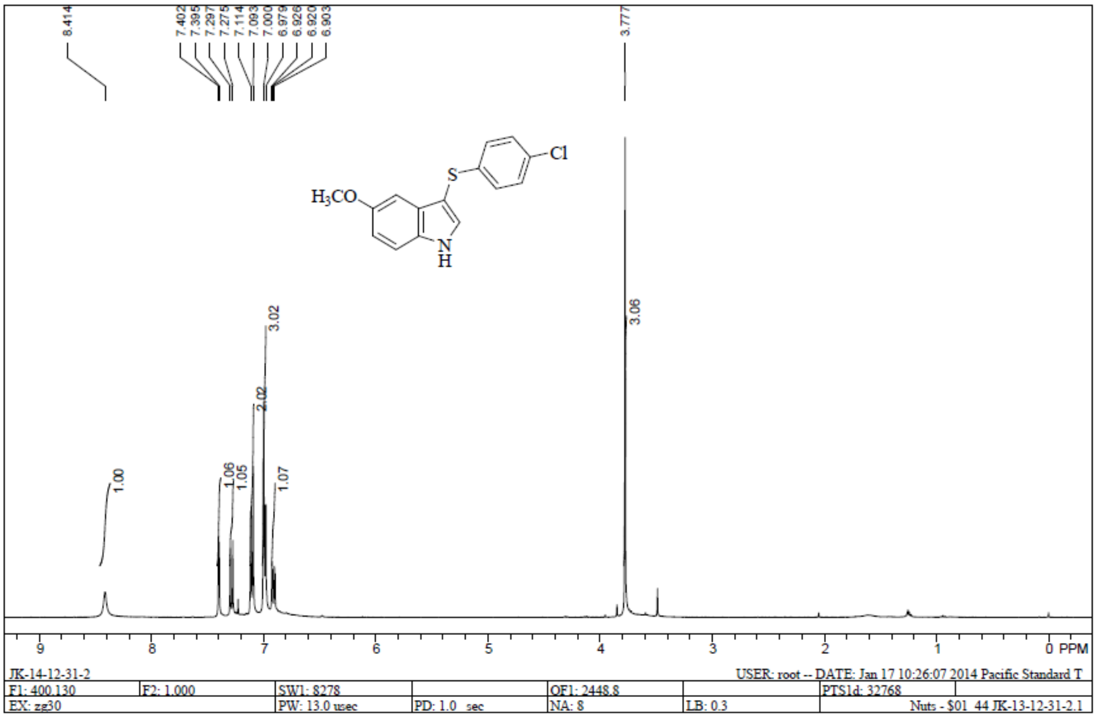


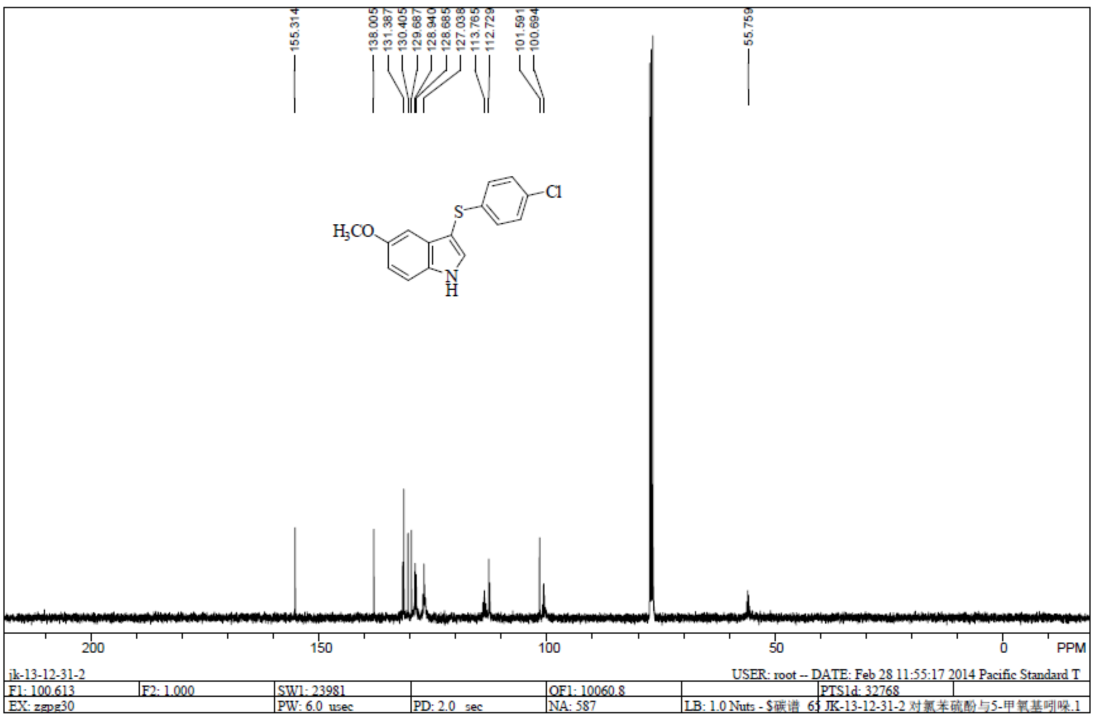
[1]H and [13]C NMR spectra of **3v**



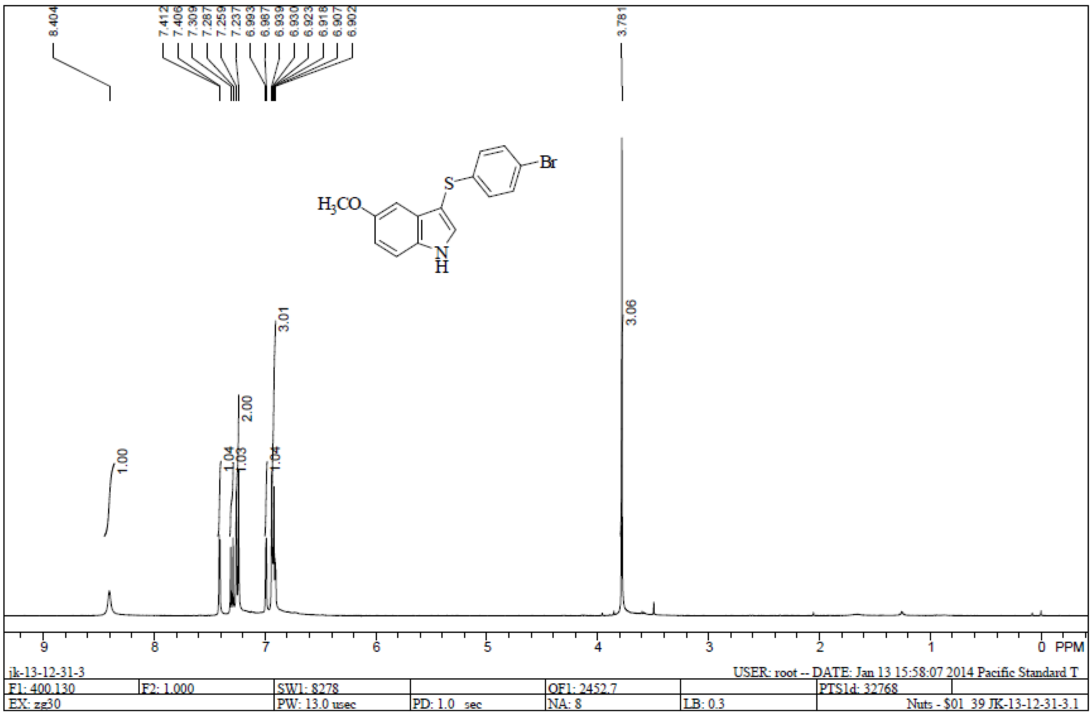


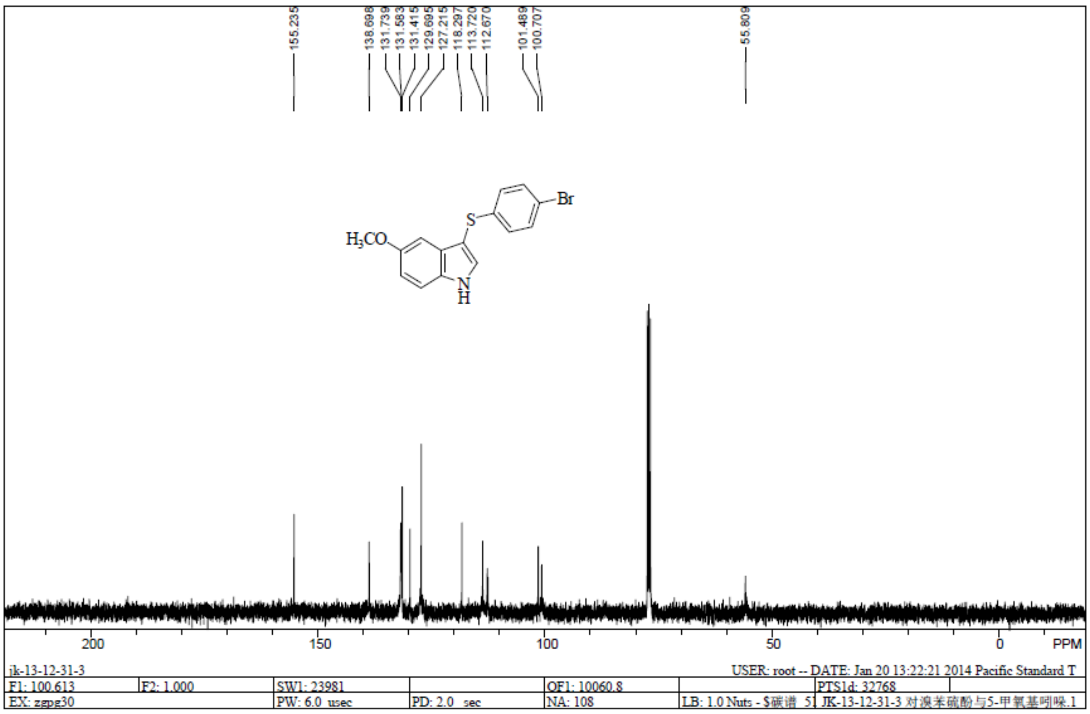
^{1}H and ^{13}C NMR spectra of **3w**



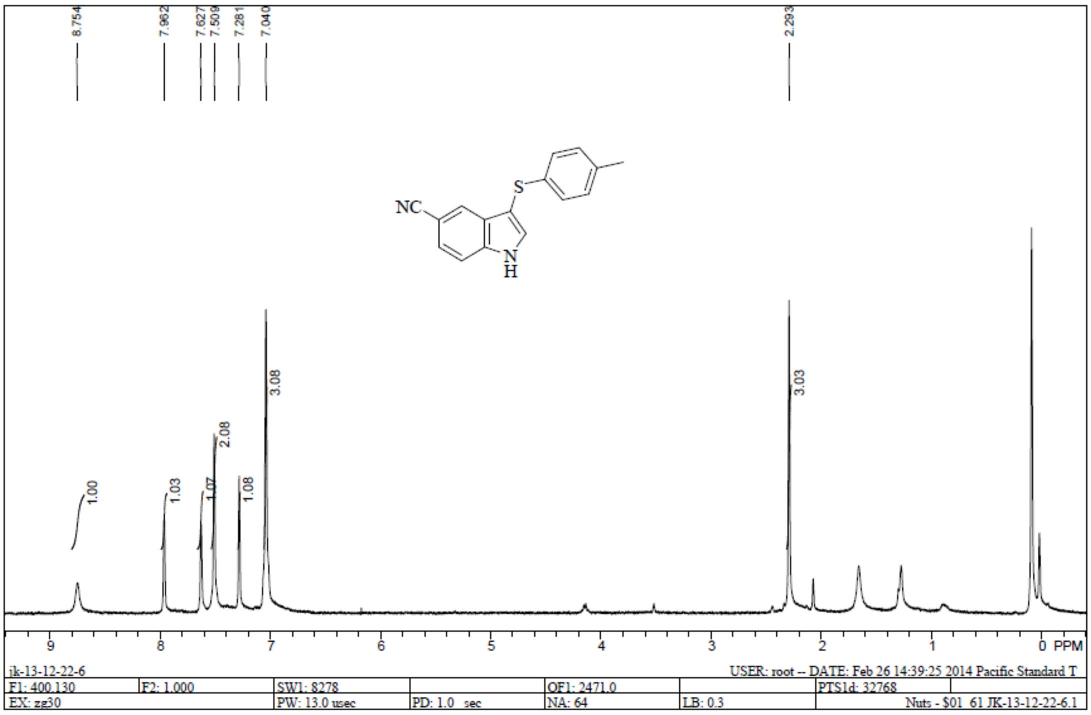


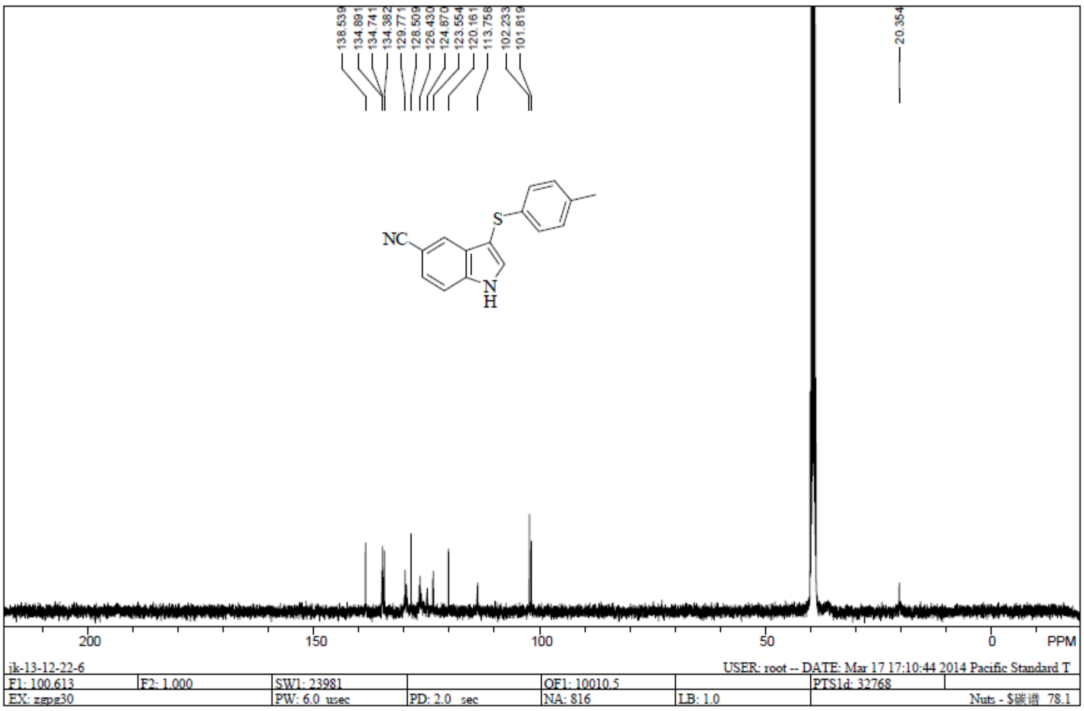
[1]H and [13]C NMR spectra of **3x**



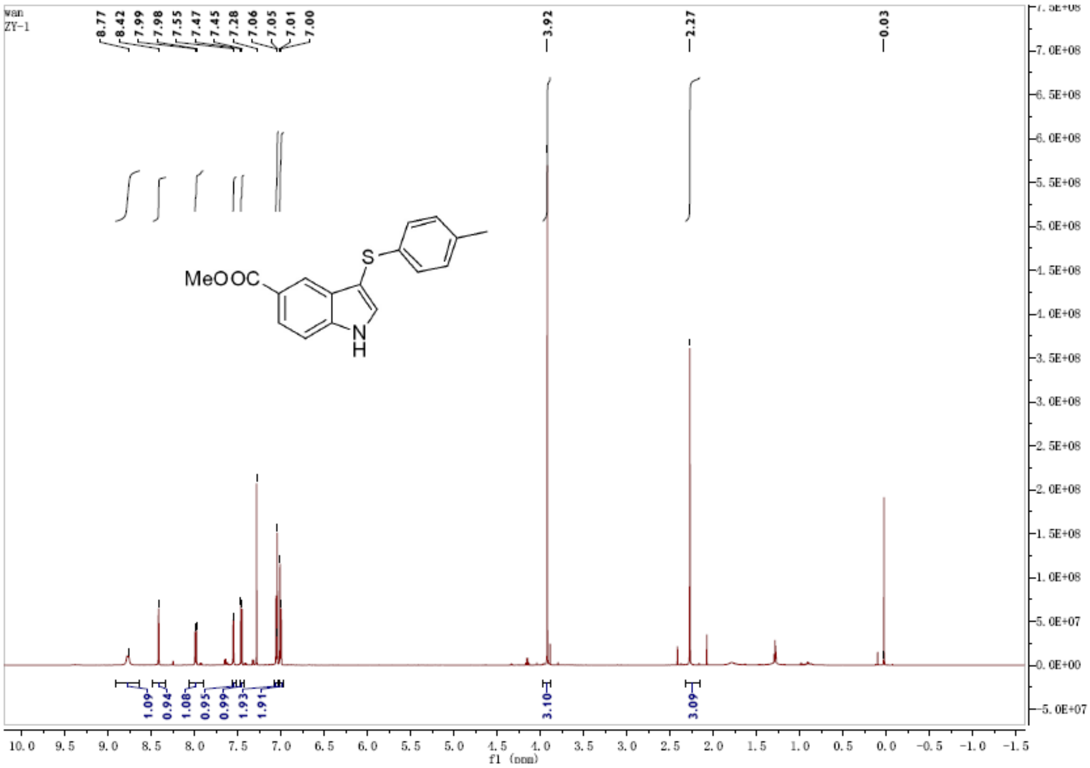


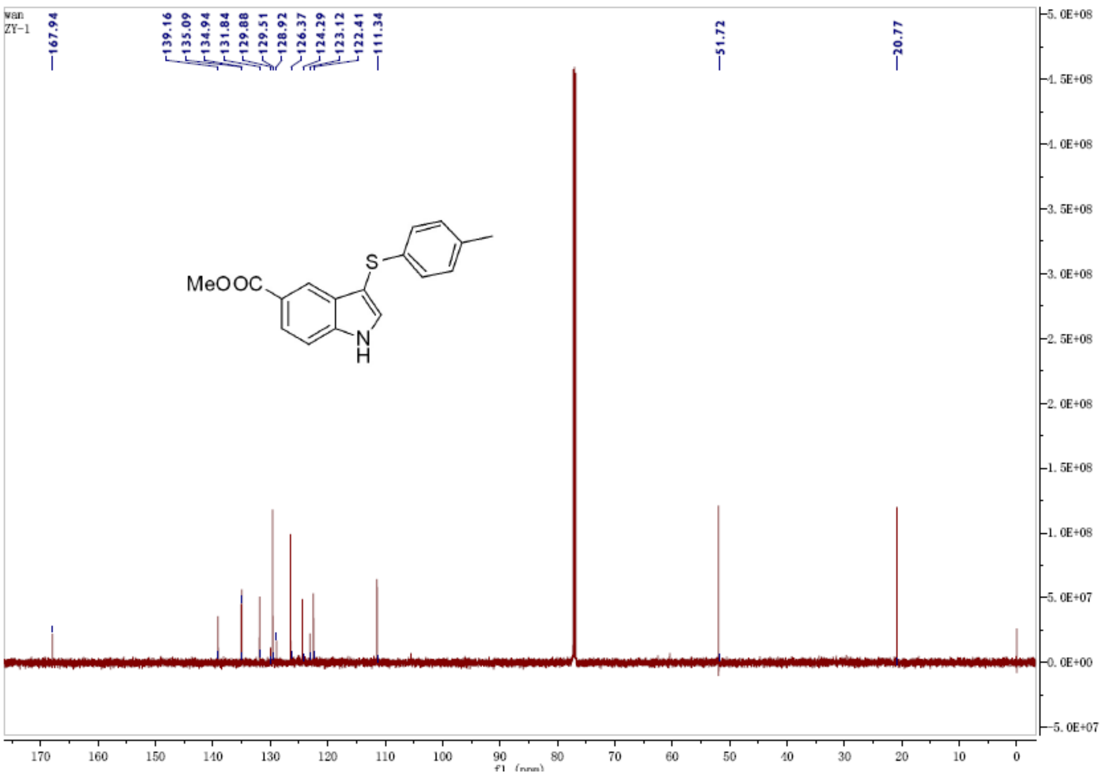
[1]H and [13]C NMR spectra of **3y**





[1]H and [13]C NMR spectra of **3z**





[1]H and [13]C NMR spectra of **3aa**