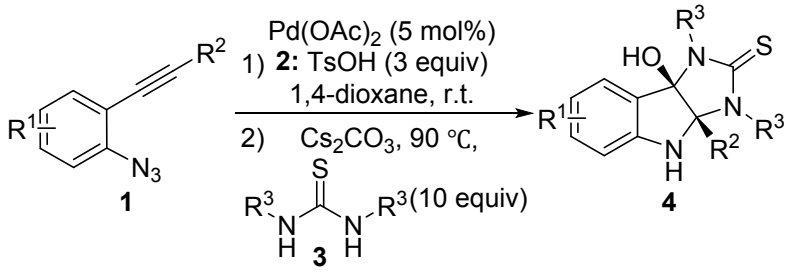
Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

General Considerations

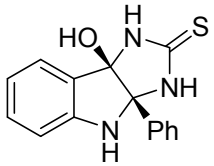
Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (Ethyl acetate: Petrol ether as eluant). ^{1}H and ^{13}C NMR spectra were measured on 400 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet). The number of protons (n) for a given resonance is indicated by nH and coupling constants are reported as a J value in Hz. High resolution mass spectra (HRMS) were obtained on a LTQ Orbitrap LC/HRMS mass spectrometer. All the starting materials **1** (2-alkynyl arylazides) were prepared by our reported methods.[1]

General experimental procedure for the synthesis of 4.



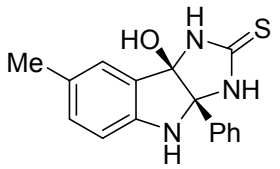
To a 5 ml of test tube was added 2-alkynyl arylazides **1** (0.1 mmol, 1 equiv), TsOH **2** (0.3 mmol, 3 equiv), $Pd(OAc)_2$ (5 mol%), and 1,4-dioxane (1 mL). The reaction mixture was stirred at room temperature. After the 2-alkynyl arylazides **1** disappeared monitored by TLC, Cs_2CO_3 (0.35 mmol, 3.5 equiv) and **3** (1 mmol, 10 equiv) were added to the reaction solution, which was then stirred at 90 ℃ and monitored by TLC analysis. On completion, the reaction mixture was directly subjected to purification by flash column chromatography on silica gel to give the desired **4**. (eluent: petrol ether: ethyl acetate = 10:1 to 2:1).

***cis*-8b-Hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4aa)**



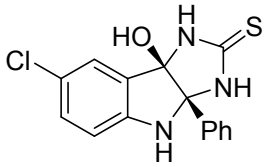
Isolated yield = 93%; yellow solid; m.p. 102.1-103.6 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.25 (s, 1 H), 6.64-6.67 (m, 2 H), 6.93 (s, 1 H), 7.09-7.13 (m, 1 H), 7.16 (d, J = 7.6 Hz, 1 H), 7.32-7.38 (m, 5 H), 9.24 (s, 1 H), 9.34 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 90.6, 98.8, 108.9, 117.8, 124.6, 128.0, 128.1, 128.2, 128.5, 130.2, 137.9, 150.1, 181.8; HRMS (ESI) calcd for $C_{15}H_{14}N_3OS$ $[M+H]^+$ 284.0858, found 284.0862.

***cis*-8b-Hydroxy-7-methyl-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ab)**



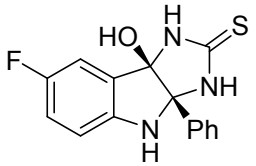
Isolated yield = 87%; yellow solid; m.p. 121.5-122.8 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.21 (s, 3 H), 6.19 (s, 1 H), 6.56 (d, J = 8.0 Hz, 1 H), 6.69 (s, 1 H), 6.93 (d, J = 8.0 Hz, 1 H), 6.99 (s, 1 H), 7.30-7.37 (m, 5 H), 9.19 (s, 1 H), 9.28 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 20.9, 90.9, 98.8, 108.9, 125.0, 126.4, 128.0, 128.1, 128.4, 130.5, 138.1, 147.9, 181.8; HRMS (ESI) calcd for $C_{16}H_{16}N_3OS$ $[M+H]^+$ 298.1014, found 298.1022.

***cis*-7-Chloro-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ac)**



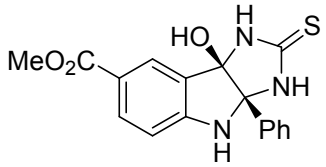
Isolated yield = 93%; yellow solid; m.p. 85.8-86.9 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.44 (s, 1 H), 6.65 (d, J = 8.0 Hz, 1 H), 7.13-7.16 (m, 3 H), 7.37 (s, 5 H), 9.36 (s, 2 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 91.1, 98.2, 110.2, 120.8, 124.5, 128.0, 128.1, 128.7, 129.9, 130.1, 137.4, 148.9, 182.0; HRMS (ESI) calcd for $C_{15}H_{13}ClN_3OS$ $[M+H]^+$ 318.0468, found 318.0474.

cis-7-Fluoro-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ad)



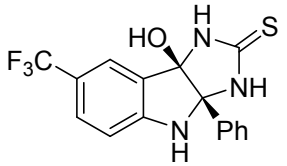
Isolated yield = 80%; yellow solid; m.p. 150.8-152.2 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.40 (s, 1 H), 6.62-6.65 (m, 1 H), 6.85 (s, 1 H), 6.92-6.99 (m, 2 H), 7.32-7.38 (m, 5 H), 9.31 (s, 1 H), 9.35 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 91.4, 98.4, 109.5 (d, J = 7.4 Hz), 111.5 (d, J = 24.2 Hz), 116.5 (d, J = 22.8 Hz), 128.0, 128.1, 128.6, 129.5 (d, J = 7.6 Hz), 137.7, 146.4, 155.8 (d, J = 230.7 Hz), 182.1; HRMS (ESI) calcd for $C_{15}H_{13}FN_3OS$ $[M+H]^+$ 302.0763, found 302.07701.

cis-Methyl 8b-hydroxy-3a-phenyl-2-thioxo-1,2,3,3a,4,8b-hexahydroimidazo[4,5-*b*] indole-7-carboxylate (4ae)



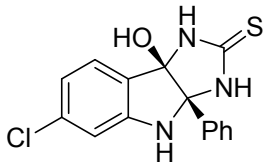
Isolated yield = 97%; white solid; m.p. 155.3-156.4 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 3.78 (s, 3 H), 6.49 (s, 1 H), 6.69 (d, J = 8.0 Hz, 1 H), 7.34-7.41 (m, 5 H), 7.78-7.81 (m, 2 H), 7.87 (s, 1 H), 9.42 (s, 1 H), 9.47 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 51.9, 90.9, 97.9, 107.8, 118.4, 126.5, 127.9, 128.2, 128.3, 128.8, 132.9, 137.0, 154.3, 166.6, 181.9; HRMS (ESI) calcd for $C_{17}H_{16}N_3O_3S$ $[M+H]^+$ 342.0912, found 342.0924.

***cis*-8b-Hydroxy-3a-phenyl-7-(trifluoromethyl)-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4af)**



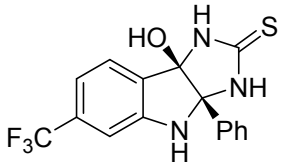
Isolated yield = 90%; yellow solid; m.p. 123.8-125.5 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.54 (s, 1 H), 6.76 (d, J = 8.4 Hz, 1 H), 7.35-7.46 (m, 7 H), 7.72 (s, 1 H), 9.44 (s, 1 H), 9.45 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 90.9, 97.8, 108.3, 117.6 (d, J = 31.8 Hz), 121.9 (d, J = 3.3 Hz), 125.6 (d, J = 269.0 Hz), 125.7, 128.0, 128.2, 128.5, 128.8, 137.0, 153.1, 182.1; HRMS (ESI) calcd for $C_{16}H_{13}F_3N_3OS$ $[M+H]^+$ 352.0731, found 352.0740.

***cis*-6-Chloro-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ag)**



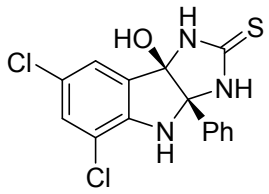
Isolated yield = 95%; yellow solid; m.p. 150.4-151.9 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.38 (s, 1 H), 6.63 (s, 1 H), 6.66-6.68 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz,, 1 H), 7.11 (d, J = 8.0 Hz, 1 H), 7.26 (s, 1 H), 7.32-7.40 (m, 5 H), 9.34 (s, 1 H), 9.42 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 90.9, 97.9, 108.3, 117.2, 125.9, 127.2, 128.0, 128.2, 128.7, 134.6, 137.4, 151.5, 181.9; HRMS (ESI) calcd for $C_{15}H_{13}ClN_3OS$ $[M+H]^+$ 318.0468, found 318.0453.

***cis*-8b-Hydroxy-3a-phenyl-6-(trifluoromethyl)-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ah)**



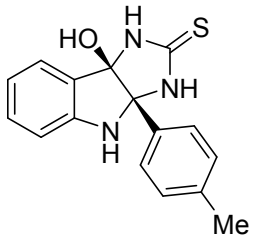
Isolated yield = 88%; yellow solid; m.p. 85.5-86.9 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.54 (s, 1 H), 6.76 (d, J = 8.4 Hz, 1 H), 7.35-7.46 (m, 7 H), 7.72 (s, 1 H), 9.44 (s, 1 H), 9.45 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 90.9, 97.9, 104.5 (d, J = 3.7 Hz), 114.4 (d, J = 4.0 Hz), 123.5 (d, J = 270.6 Hz), 125.3, 128.0, 128.2, 128.7, 130.7 (d, J = 30.9 Hz), 132.2, 137.2, 150.5, 182.2; HRMS (ESI) calcd for $C_{16}H_{13}F_3N_3OS$ $[M+H]^+$ 352.0731, found 352.0743.

cis-5,7-Dichloro-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-_b_]indole-2(1_H_)-thione (4ai)



Isolated yield = 97%; yellow solid; m.p. 185.5-187.3 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.64 (s, 1 H), 7.11 (s, 1 H), 7.34-7.41 (m, 6 H), 7.46 (s, 1 H), 9.38 (s, 1 H), 9.45 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 90.8, 98.4, 113.2, 121.2, 123.4, 128.1, 128.2, 128.8, 129.1, 131.6, 136.7, 145.6, 182.3; HRMS (ESI) calcd for $C_{15}H_{12}Cl_2N_3OS$ $[M+H]^+$ 352.0078, found 352.0063.

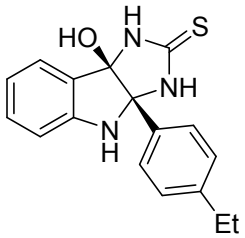
cis-8b-Hydroxy-3a-(_p_-tolyl)-3,3a,4,8b-tetrahydroimidazo[4,5-_b_]indole-2(1_H_)-thione (4aj)



Isolated yield = 85%; brown solid; m.p. 130.8-132.5 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.31 (s, 3 H), 6.18 (s, 1 H), 6.63-6.65 (m, 2 H), 6.86 (s, 1 H), 7.08-7.18 (m, 4 H), 7.25 (d, J = 8.0 Hz, 2 H), 9.19 (s, 1 H), 9.30 (s, 1 H); ^{13}C NMR (DMSO-d_6,100 MHz): δ = 21.2, 90.6, 98.6, 108.8, 117.7, 124.6, 128.0, 128.2, 128.6, 130.1, 134.9, 137.7, 150.1, 181.8; HRMS (ESI) calcd for $C_{16}H_{16}N_3OS$ $[M+H]^+$ 298.1014, found

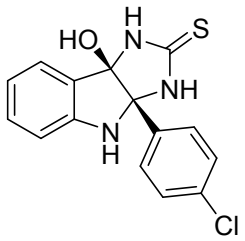
298.1022.

cis-3a-(4-Ethylphenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ak)



Isolated yield = 84%; brown solid; m.p. 116.7-118.0 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.19 (t, J = 7.6 Hz, 3 H), 2.58-2.64 (q, 2 H), 6.21 (s, 1 H), 6.63-6.66 (m, 2 H), 6.87 (s, 1 H), 7.08-7.12 (m, 1 H), 7.15 (d, J = 7.6 Hz, 1 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.4 Hz, 2 H), 9.19 (s, 1 H), 9.31 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 16.1, 28.3, 90.6, 98.6, 108.8, 117.7, 124.6, 127.5, 128.1, 128.2, 130.1, 135.2, 144.0, 150.1, 181.8; HRMS (ESI) calcd for $C_{17}H_{18}N_3OS$ $[M+H]^+$ 312.1171, found 312.1182.

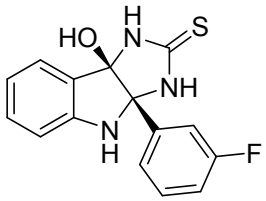
cis-3a-(4-Chlorophenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4al)



Isolated yield = 85%; yellow solid; m.p. 93.8-95.2 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.32 (s, 1 H), 6.64-6.68 (m, 2 H), 6.99 (s, 1 H), 7.09-7.13 (m, 1 H), 7.16 (d, J = 7.2 Hz, 1 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.8 Hz, 2 H), 9.29 (s, 1 H), 9.41 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 90.1, 98.8, 108.9, 117.9, 124.6, 128.0, 130.0, 130.3, 133.3, 137.1, 149.9, 181.9; HRMS (ESI) calcd for $C_{15}H_{13}ClN_3OS$ $[M+H]^+$ 318.0468, found 318.0472.

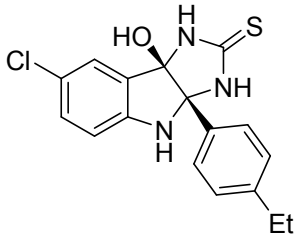
cis-3a-(3-Fluorophenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-

2(1*H*)-thione (4am)



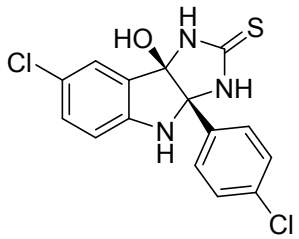
Isolated yield = 86%; yellow solid; m.p. 104.7-106.0 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.36 (s, 1 H), 6.65-6.69 (m, 2 H), 7.02 (s, 1 H), 7.10-7.21 (m, 5 H), 7.39-7.45 (m, 1 H), 9.30 (s, 1 H), 9.43 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 90.1, 98.9, 109.0, 114.9, 115.3 (d, J = 21.8 Hz), 118.0, 124.2 (d, J = 2.2 Hz), 124.6, 127.9, 130.0 (d, J = 8.1 Hz), 130.3, 141.1 (d, J = 6.9 Hz), 149.9, 162.2 (d, J = 240.7 Hz), 181.9; HRMS (ESI) calcd for $C_{15}H_{13}FN_3OS$ $[M+H]^+$ 302.0763, found 302.0772.

***cis*-7-Chloro-3a-(4-ethylphenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4an)**



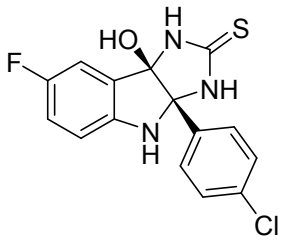
Isolated yield = 81%; yellow solid; m.p. 93.8-95.5 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.18 (t, J = 7.6 Hz, 3 H), 2.58-2.64 (q, 2 H), 6.40 (s, 1 H), 6.64 (d, J = 8.0 Hz, 1 H), 7.09-7.14 (m, 3 H), 7.19-7.27 (m, 4 H), 9.30 (s, 1 H), 9.32 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 16.1, 28.3, 91.1, 98.0, 110.1, 120.7, 124.5, 127.5, 128.0, 129.8, 130.2, 134.7, 144.2, 148.9, 181.9; HRMS (ESI) calcd for $C_{17}H_{17}ClN_3OS$ $[M+H]^+$ 346.0781, found 346.0773.

***cis*-7-Chloro-3a-(4-chlorophenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ao)**



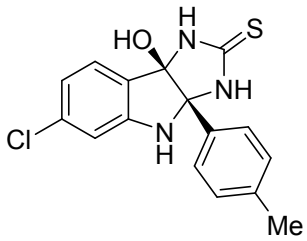
Isolated yield = 92%; brown solid; m.p. 141.1-143.6 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.51 (s, 1 H), 6.65 (d, J = 8.0 Hz, 1 H), 7.13-7.16 (m, 2 H), 7.22 (s, 1 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.46 (d, J = 8.4 Hz, 2 H), 9.41 (s, 1 H), 9.42 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 90.5, 98.3, 110.3, 120.9, 124.5, 128.1, 129.9, 133.5, 136.5, 148.7, 182.1; HRMS (ESI) calcd for $C_{15}H_{12}Cl_2N_3OS$ $[M+H]^+$ 352.0078, found 352.0085.

cis-3a-(4-Chlorophenyl)-7-fluoro-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-_b_]indole-2(1_H_)-thione (4ap)



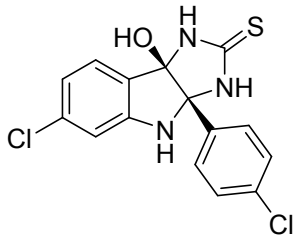
Isolated yield = 77%; yellow solid; m.p. 125.3-127.1 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.47 (s, 1 H), 6.62 (d, J = 4.0 Hz, 1 H), 6.91-6.98 (m, 3 H), 7.35 (d, J = 8.4 Hz, 2 H), 7.45 (d, J = 8.4 Hz, 2 H), 9.36 (s, 1 H), 9.41 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 90.8, 98.4, 109.7 (d, J = 7.8 Hz), 111.5 (d, J = 24.2 Hz), 116.6 (d, J = 23.4 Hz), 128.1, 129.4, 130.0, 133.4, 136.8, 146.2, 155.8 (d, J = 231.3 Hz), 182.1; HRMS (ESI) calcd for $C_{15}H_{12}ClFN_3OS$ $[M+H]^+$ 336.0374, found 336.0381.

cis-6-Chloro-8b-hydroxy-3a-(_p_-tolyl)-3,3a,4,8b-tetrahydroimidazo[4,5-_b_]indole-2(1_H_)-thione (4aq)



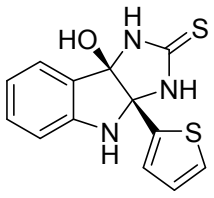
Isolated yield = 87%; yellow solid; m.p. 133.2-135.6 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.31 (s, 3 H), 6.31 (s, 1 H), 6.62 (d, J = 1.2 Hz, 1 H), 6.64-6.67 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 1 H), 7.10 (d, J = 8.0 Hz, 1 H), 7.17-7.24 (m, 5 H), 9.29 (s, 1 H), 9.37 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 21.1, 90.9, 97.8, 108.3, 117.2, 125.9, 127.3, 127.9, 128.7, 134.4, 134.5, 137.9, 151.5, 181.9; HRMS (ESI) calcd for $C_{16}H_{15}ClN_3OS$ $[M+H]^+$ 332.0624, found 332.0633.

cis-6-Chloro-3a-(4-chlorophenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ar)



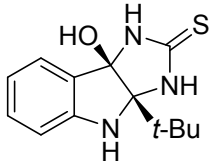
Isolated yield = 93%; yellow solid; m.p. 139.3-140.6 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.46 (s, 1 H), 6.64 (s, 1 H), 6.68 (d, J = 8.0 Hz, 1 H), 7.13 (d, J = 8.0 Hz, 1 H), 7.33-7.36 (m, 3 H), 7.46 (d, J = 8.4 Hz, 2 H), 9.39 (s, 1 H), 9.49 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 90.4, 98.1, 108.4, 117.5, 125.9, 127.0, 128.2, 129.9, 133.5, 134.7, 136.5, 151.3, 182.0; HRMS (ESI) calcd for $C_{15}H_{12}Cl_2N_3OS$ $[M+H]^+$ 352.0078, found 352.0085.

cis-8b-Hydroxy-3a-(thiophen-2-yl)-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4as)



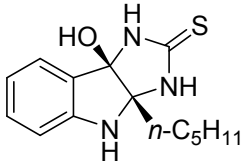
Isolated yield = 56%; brown solid; m.p. 117.6-118.9 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.38 (s, 1 H), 6.58-6.67 (m, 2 H), 6.91 (s, 1 H), 6.95 (d, J = 5.2 Hz, 1 H), 7.07-7.11 (m, 1 H), 7.17 (d, J = 7.2 Hz, 1 H), 7.39-7.40 (m, 1 H), 7.46-7.48 (m, 1 H), 9.27 (s, 1 H), 9.36 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 88.7, 98.2, 109.1, 117.8, 124.2, 124.5, 125.9, 128.1, 128.2, 130.1, 140.1, 149.7, 181.5; HRMS (ESI) calcd for $C_{13}H_{12}N_3OS_2$ $[M+H]^+$ 290.0422, found 290.0431.

cis-3a-(_tert_-Butyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-_b_]indole-2(1_H_)-thione (4at)



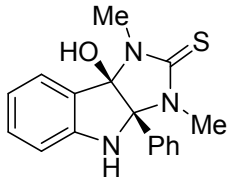
Isolated yield = 85%; brown solid; m.p. 174.9-176.5 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.09 (s, 9 H), 6.43 (s, 1 H), 6.45 (s, 1 H), 6.53-6.59 (m, 2 H), 7.00-7.04 (m, 1 H), 7.16 (d, J = 7.2 Hz, 1 H), 8.66 (s, 1 H), 9.08 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 25.6, 37.9, 91.5, 98.8, 108.8, 117.0, 123.8, 129.9, 130.2, 149.6, 180.9; HRMS (ESI) calcd for $C_{13}H_{18}N_3OS$ $[M+H]^+$ 264.1171, found 264.1183.

cis-8b-hydroxy-3a-pentyl-3,3a,4,8b-tetrahydroimidazo[4,5-_b_]indole-2(1_H_)-thione (4au)



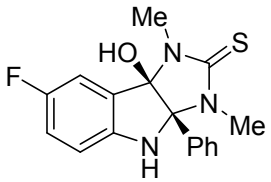
Isolated yield = 66%; brown solid; m.p. 74.4-75.6 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 0.86 (t, J = 6.8 Hz, 3 H), 1.21-1.48 (m, 6 H), 1.65-1.74 (m, 2 H), 6.41 (s, 1 H), 6.48 (d, J = 7.6 Hz, 1 H), 6.54 (s, 1 H), 6.57-6.61 (m, 1 H), 7.00-7.04 (m, 1 H), 7.15 (d, J = 7.2 Hz, 1 H), 8.82 (s, 1 H), 9.16 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 14.4, 22.5, 22.7, 32.3, 34.3, 88.2, 97.4, 109.1, 117.4, 124.1, 129.2, 129.9, 149.6, 180.5; HRMS (ESI) calcd for $C_{14}H_{20}N_3OS$ $[M+H]^+$ 278.1327, found 278.1332.

***cis*-8b-Hydroxy-1,3-dimethyl-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ba)**



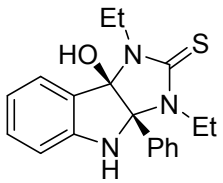
Isolated yield = 95%; brown solid; m.p. 202.8-204.0 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.93 (s, 3 H), 3.09 (s, 3 H), 6.56 (s, 1 H), 6.69-6.75 (m, 2 H), 7.18-7.21 (m, 1 H), 7.26-7.29 (m, 3 H), 7.36-7.45 (m, 3 H), 7.54 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 29.5, 31.6, 92.3, 98.8, 108.9, 118.1, 125.0, 125.7, 128.4, 128.7,128.9, 130.9, 135.4, 149.7, 182.2; HRMS (ESI) calcd for $C_{17}H_{18}N_3OS$ $[M+H]^+$ 312.1171, found 312.1184.

***cis*-7-Fluoro-8b-hydroxy-1,3-dimethyl-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4bb)**



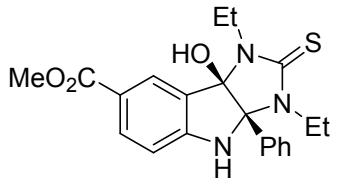
Isolated yield = 91%; yellow solid; m.p. 241.9-243.3 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.91 (s, 3 H), 3.08 (s, 3 H), 6.69-6.72 (m, 2 H), 7.01-7.07 (m, 1 H), 7.11-7.14 (m, 1 H), 7.26 (d, J = 7.6 Hz, 2 H), 7.36-7.45 (m, 4 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 29.5, 31.6, 93.0, 98.5, 109.6 (d, J = 7.8 Hz), 112.1 (d, J = 24.1 Hz), 117.2 (d, J = 23.1 Hz), 126.9 (d, J = 7.4 Hz), 128.3, 128.7, 129.0, 135.2, 146.0, 155.8 (d, J = 231.4 Hz), 182.4; HRMS (ESI) calcd for $C_{17}H_{17}FN_3OS$ $[M+H]^+$ 330.1076, found 330.1083.

***cis*-1,3-Diethyl-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4bc)**



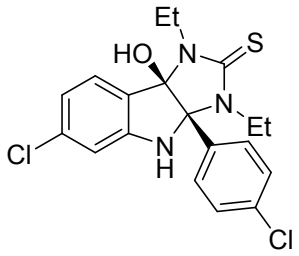
Isolated yield = 96%; yellow solid; m.p. 189.8-190.2 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.07 (t, J = 6.4 Hz, 3 H), 1.12 (t, J = 6.0 Hz, 3 H), 3.14-3.19 (m, 1 H), 3.61-3.74 (m, 3 H), 6.49 (s, 1 H), 6.66-6.74 (m, 2 H), 7.15-7.19 (m, 1 H), 7.26 (d, J = 7.2 Hz, 1 H), 7.32 (d, J = 7.2 Hz, 2 H), 7.37 (d, J = 6.8 Hz, 1 H), 7.40-7.44 (m, 2 H), 7.48 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 14.4, 14.7, 37.9, 39.9, 93.1, 98.9, 108.8, 117.9, 124.8, 126.0, 128.4, 128.8, 128.9, 130.8, 135.7, 149.8, 181.3; HRMS (ESI) calcd for $C_{19}H_{22}N_3OS$ $[M+H]^+$ 340.1484, found 340.1493.

cis-Methyl 1,3-diethyl-8b-hydroxy-3a-phenyl-2-thioxo-1,2,3,3a,4,8b-hexahydro -imidazo[4,5-_b_]indole-7-carboxylate (4bd)



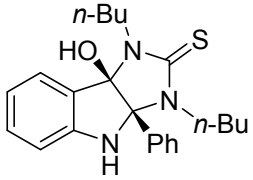
Isolated yield = 97%; yellow solid; m.p. 87.9-89.2 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.07 (t, J = 7.2 Hz, 3 H), 1.12 (t, J = 6.8 Hz, 3 H), 3.12-3.20 (m, 1 H), 3.58-3.74 (m, 3 H), 6.76-6.78 (m, 2 H), 7.29 (d, J = 7.6 Hz, 2 H), 7.37-7.46 (m, 3 H), 7.83-7.85 (m, 2 H), 8.33 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 14.3, 14.6, 37.9, 52.0, 93.4, 98.2, 108.1, 118.7, 126.2, 126.3, 128.6, 128.7, 129.2, 133.4, 134.8, 153.9, 166.4, 181.4; HRMS (ESI) calcd for $C_{21}H_{24}N_3O_3S$ $[M+H]^+$ 398.1538, found 398.1546.

cis-6-chloro-3a-(4-chlorophenyl)-1,3-diethyl-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-b]indole-2(1H)-thione (4be)



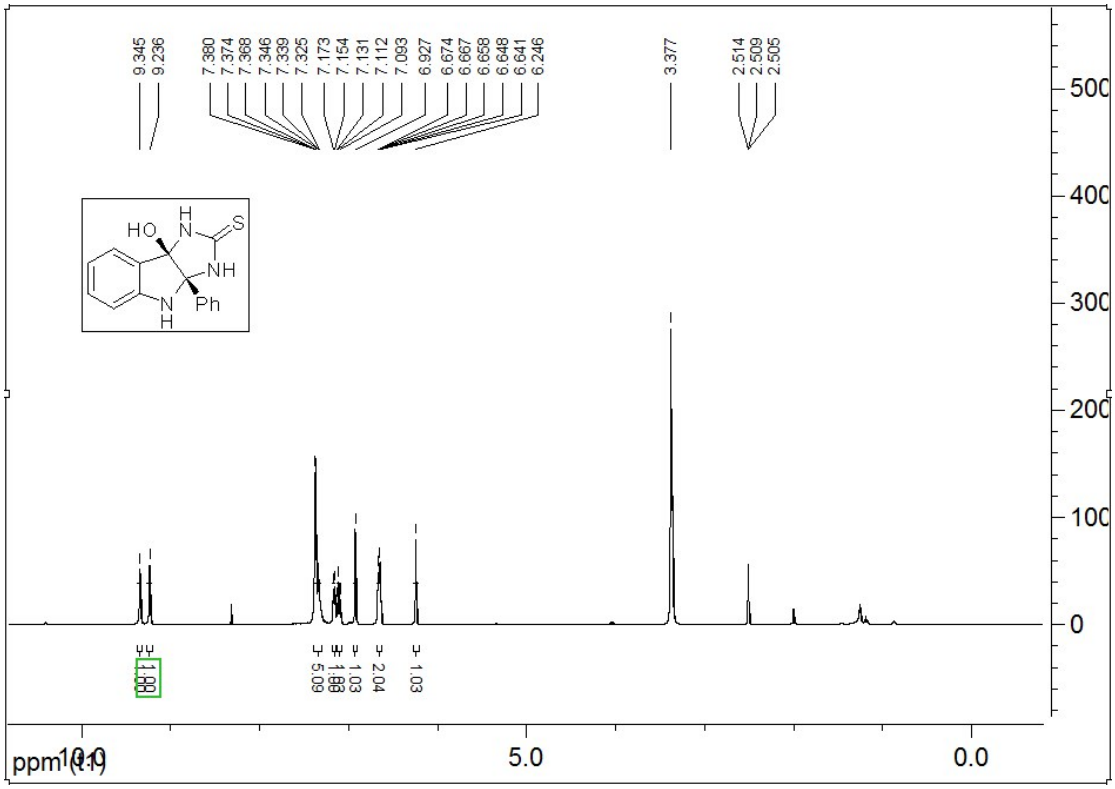
Isolated yield = 97%; white solid; m.p. 180.7-182.3 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.05 (t, J = 6.8 Hz, 3 H), 1.11 (t, J = 6.8 Hz, 3 H), 3.11-3.19 (m, 1 H), 3.58-3.73 (m, 3 H), 6.68 (s, 1 H), 6.69-6.71 (m, 2 H), 7.25-7.30 (m, 3 H), 7.51 (d, J = 8.4 Hz, 2 H), 7.83 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 14.3, 14.6, 37.9, 92.9, 98.3, 108.5, 117.7, 124.9, 126.2, 128.6, 130.7, 133.9, 134.3, 135.3, 150.9, 181.5; HRMS (ESI) calcd for $C_{19}H_{20}Cl_2N_3OS$ $[M+H]^+$ 408.0704, found 408.0712.

cis-1,3-Dibutyl-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4bf)



Isolated yield = 86%; yellow solid; m.p. 118.7-120.4 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 0.80 (t, J = 7.6 Hz, 3 H), 0.84 (t, J = 7.2 Hz, 3 H), 1.12-1.27 (m, 4 H), 1.32-1.41 (m, 1 H), 1.50-1.68 (m, 3 H), 2.98-3.05 (m, 1 H), 3.49-3.68 (m, 3 H), 6.50 (s, 1 H), 6.65-6.69 (m, 1 H), 6.72 (d, J = 8.0 Hz, 1 H), 7.14-7.18 (m, 1 H), 7.24 (d, J = 7.6 Hz, 1 H), 7.31 (d, J = 7.2 Hz, 2 H), 7.34-7.43 (m, 3 H), 7.45 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 14.1, 14.2, 20.2, 20.3, 30.5, 30.9, 43.1, 45.2, 93.0, 98.9, 108.9, 117.8, 124.8, 126.1, 128.4, 128.8, 128.9, 130.8, 135.6, 149.7, 181.8; HRMS (ESI) calcd for $C_{23}H_{30}N_3OS$ $[M+H]^+$ 396.2110, found 396.2122.

Figure 1. ^{1}H and ^{13}C NMR Spectra of ***cis*-8b-Hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4aa)**



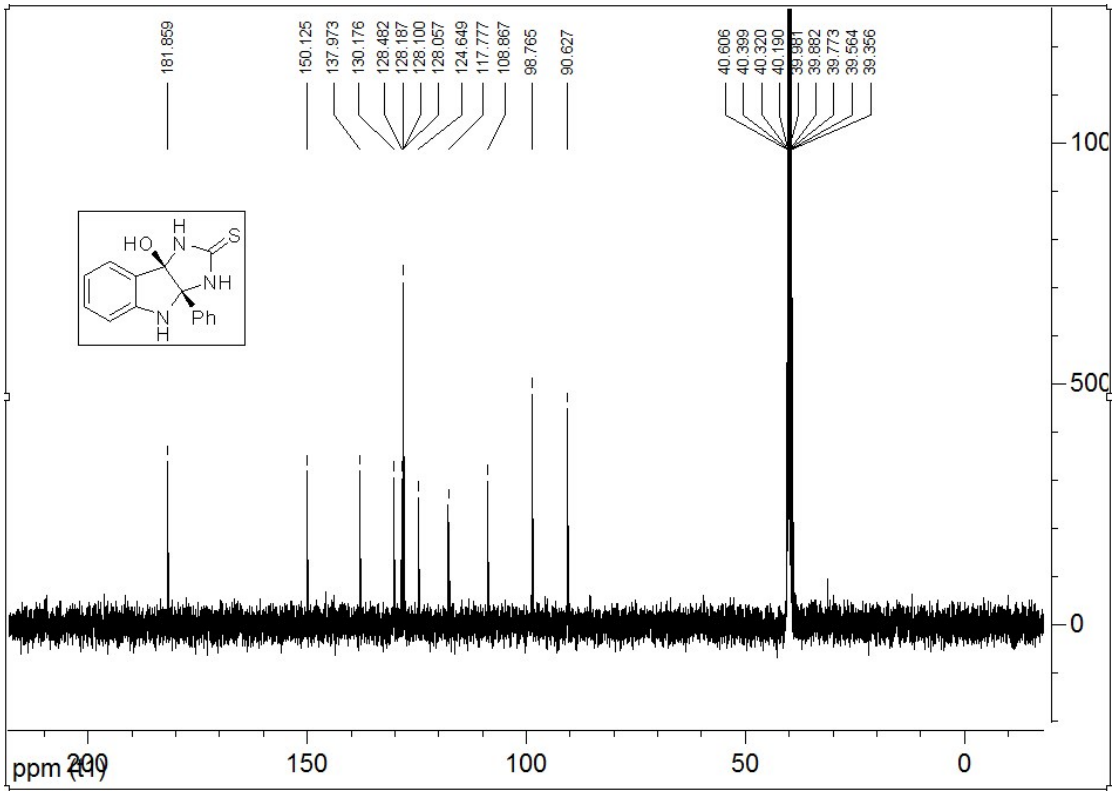
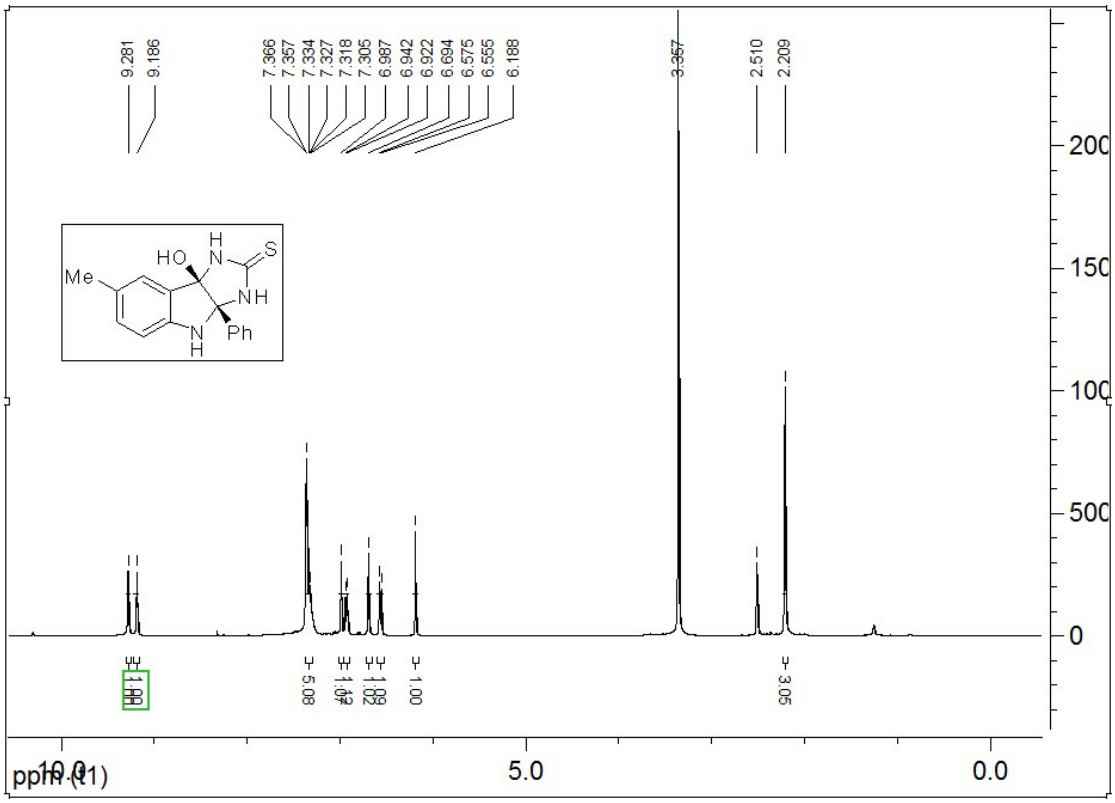


Figure 2. ^{1}H and ^{13}C NMR Spectra of ***cis*-8b-Hydroxy-7-methyl-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ab)**



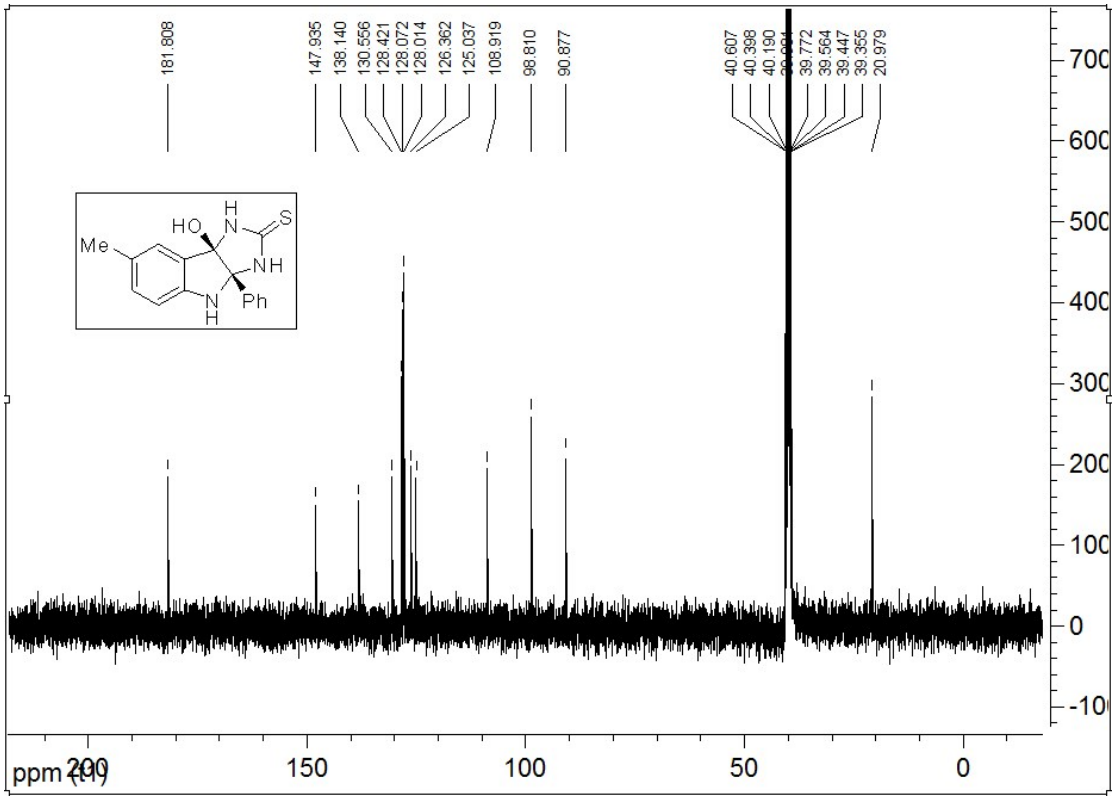
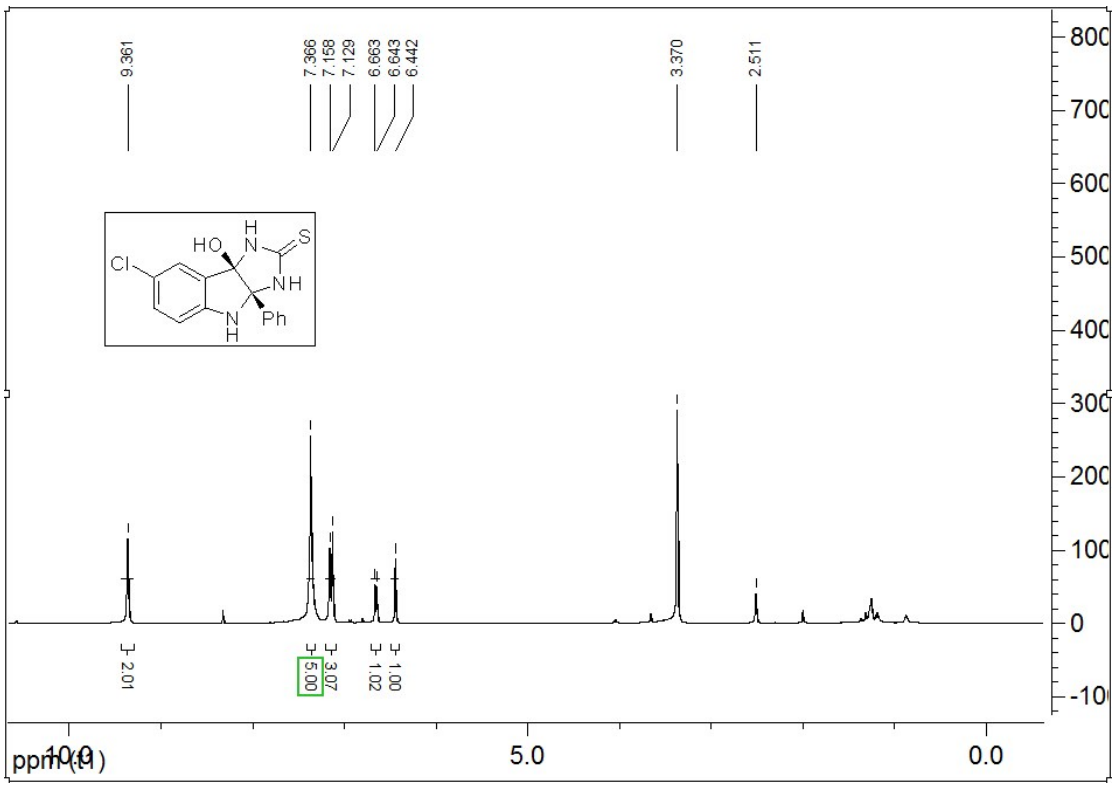


Figure 3. ^{1}H and ^{13}C NMR Spectra of ***cis*-7-Chloro-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ac)**



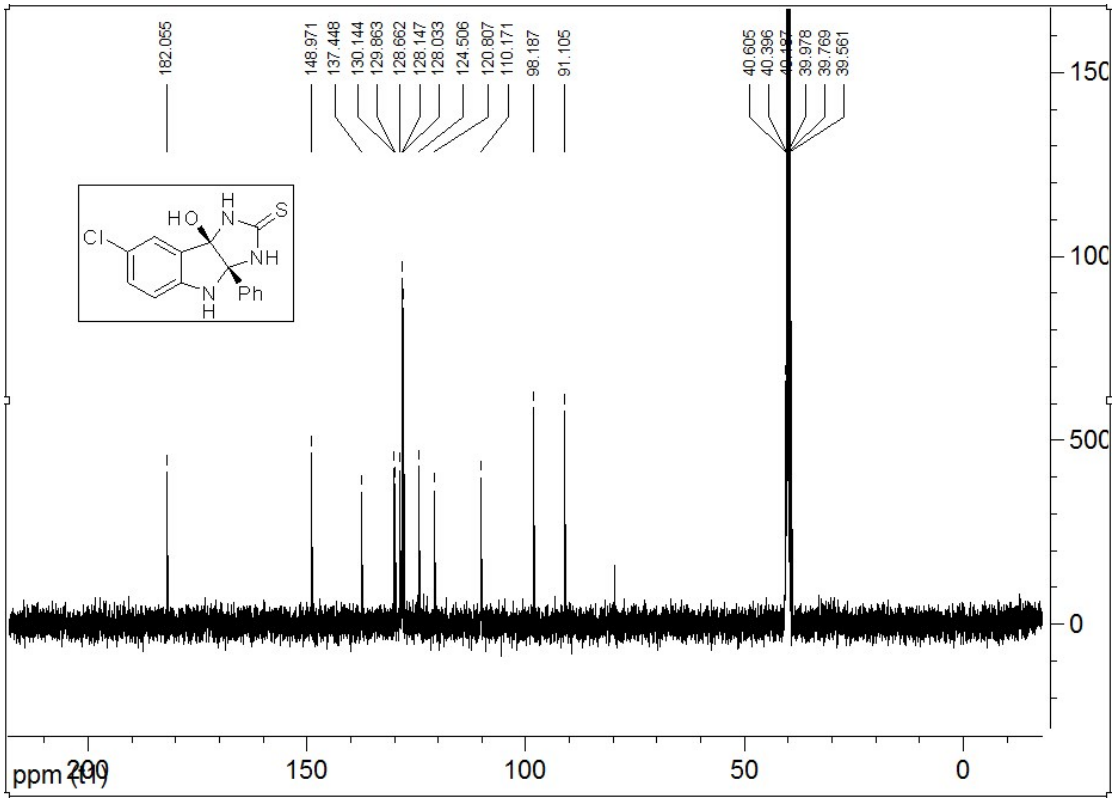
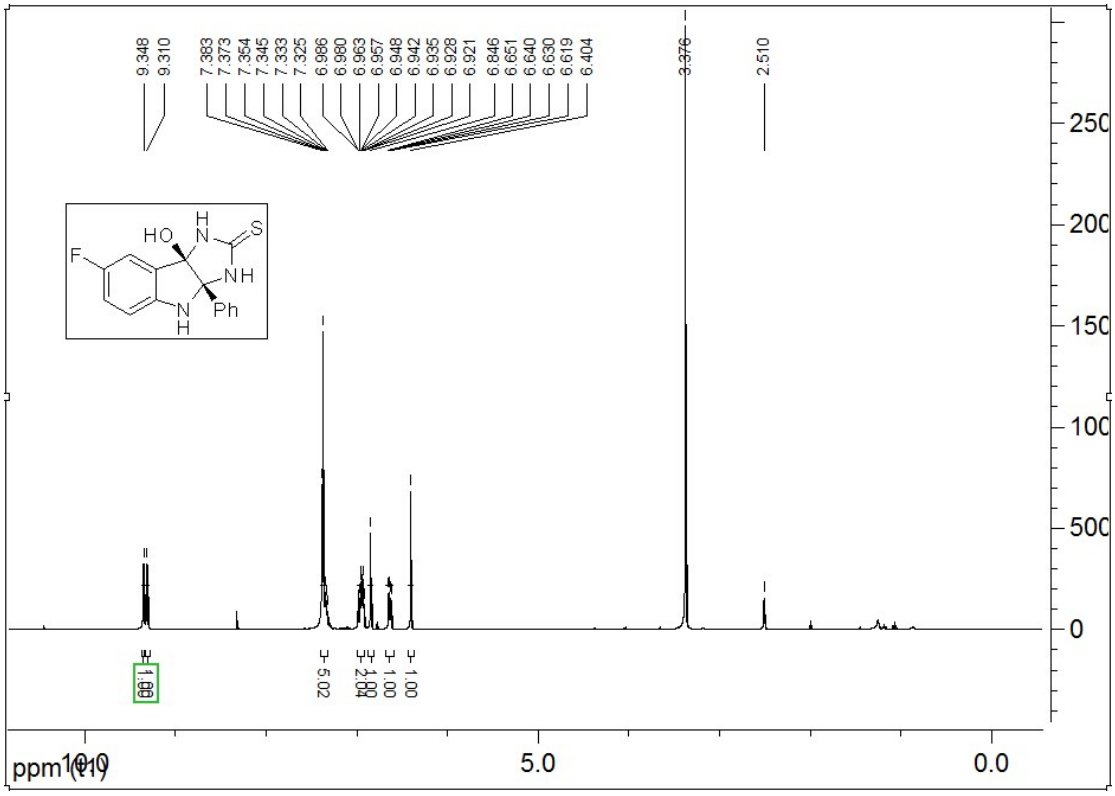


Figure 4. ^{1}H and ^{13}C NMR Spectra of ***cis*-7-Fluoro-8b-hydroxy-3a-phenyl-3,3a, 4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ad)**



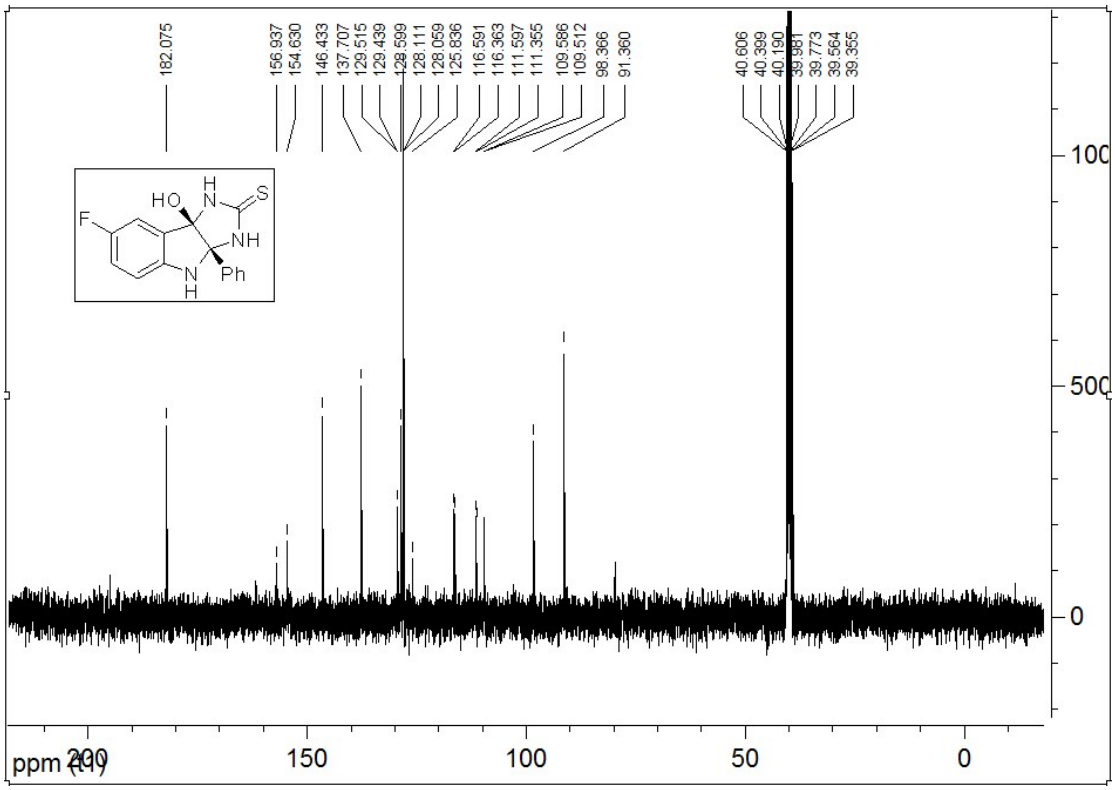
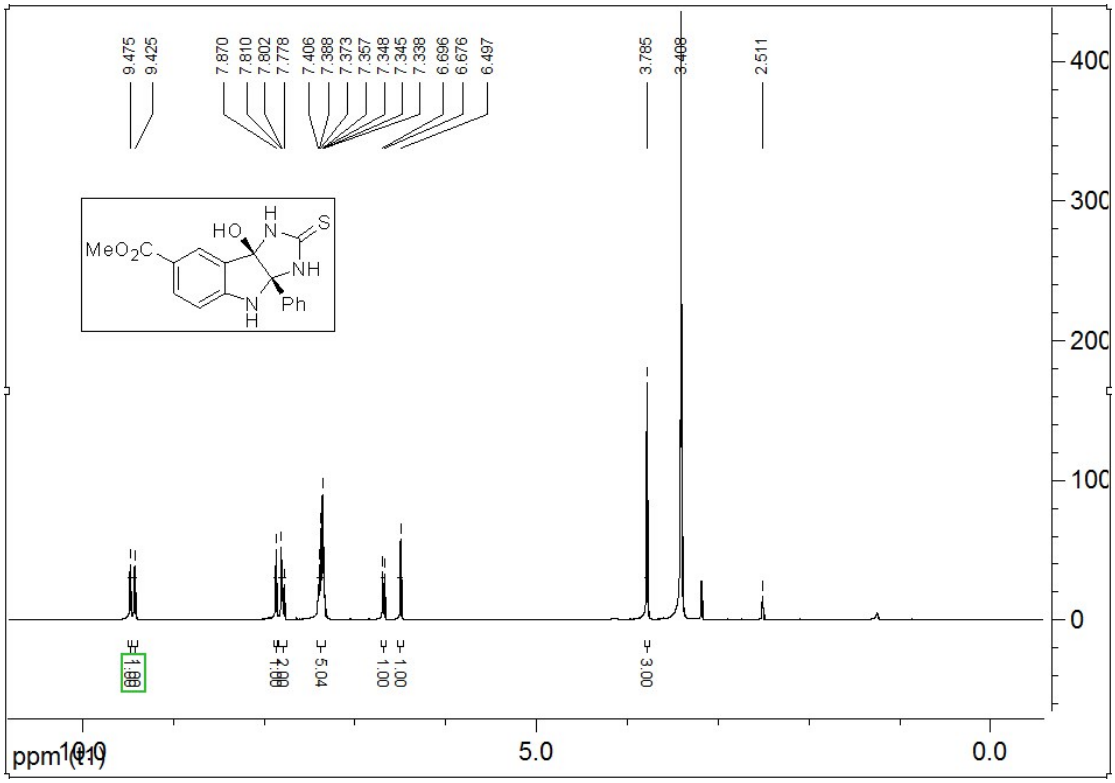


Figure 5. ^{1}H and ^{13}C NMR Spectra of ***cis*-Methyl 8b-hydroxy-3a-phenyl-2-thioxo-1,2,3,3a,4,8b-hexahydroimidazo[4,5-*b*]indole-7-carboxylate (4ae)**



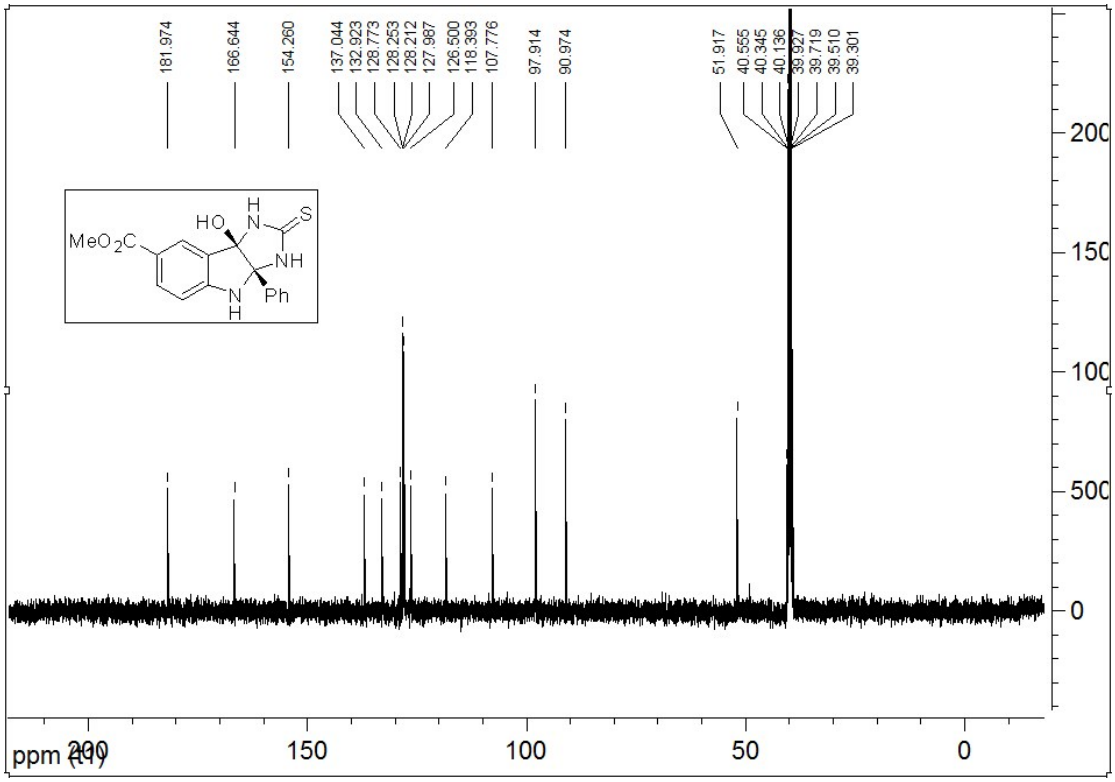
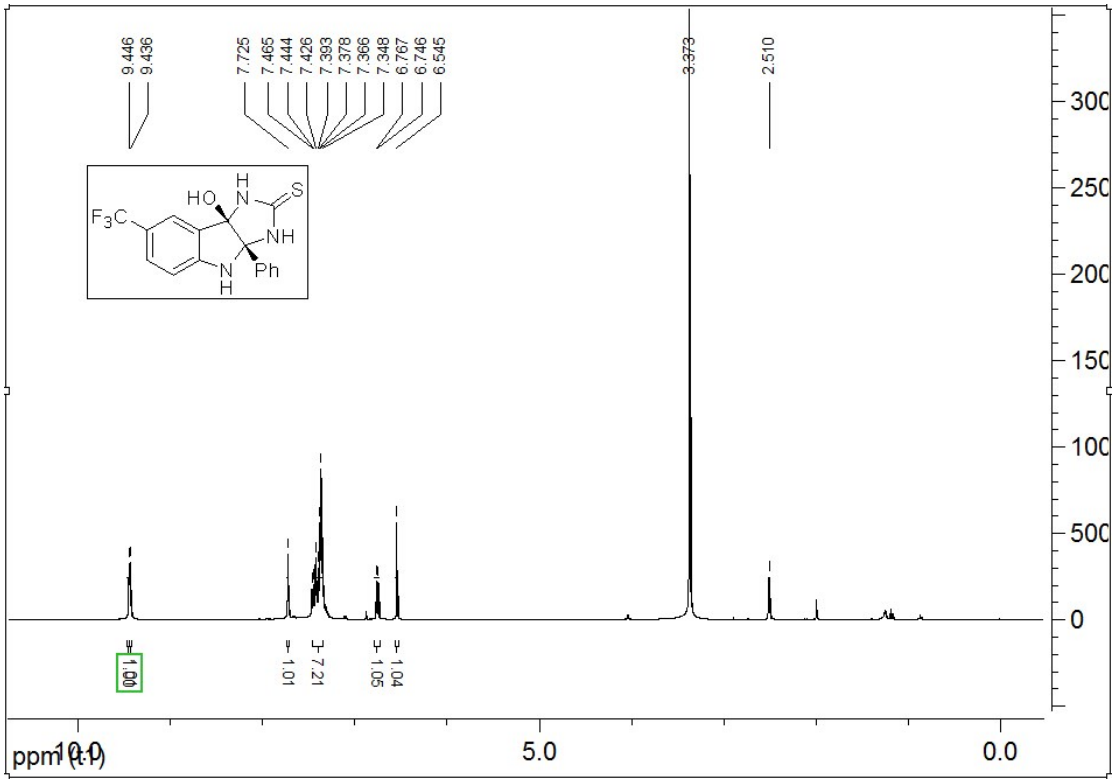


Figure 6. ^{1}H and ^{13}C NMR Spectra of ***cis*-8b-Hydroxy-3a-phenyl-7-(trifluoro -methyl)-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4af)**



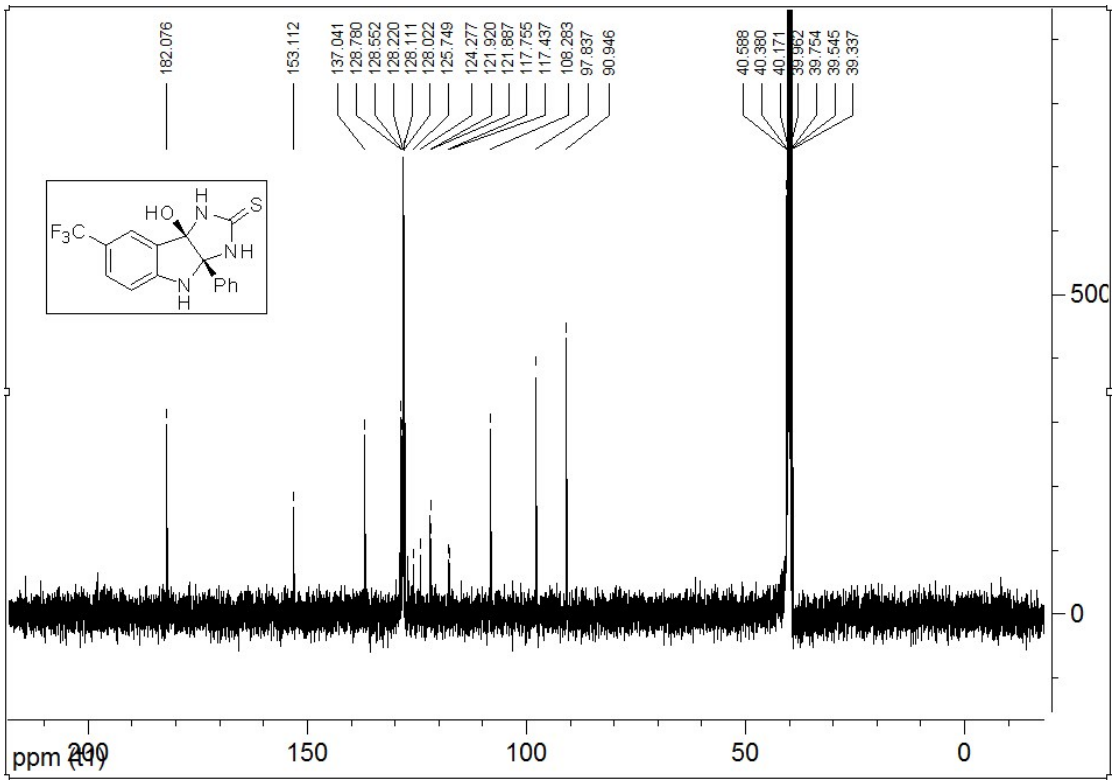
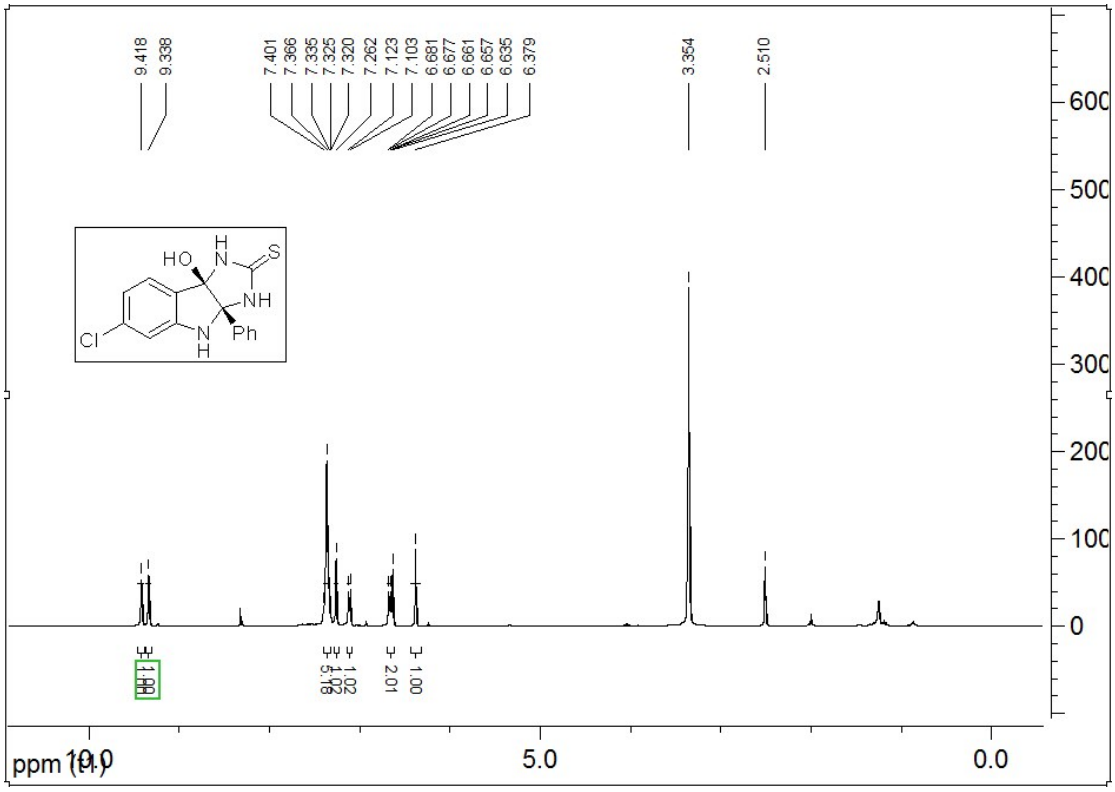


Figure 7. ^{1}H and ^{13}C NMR Spectra of ***cis*-6-Chloro-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ag)**



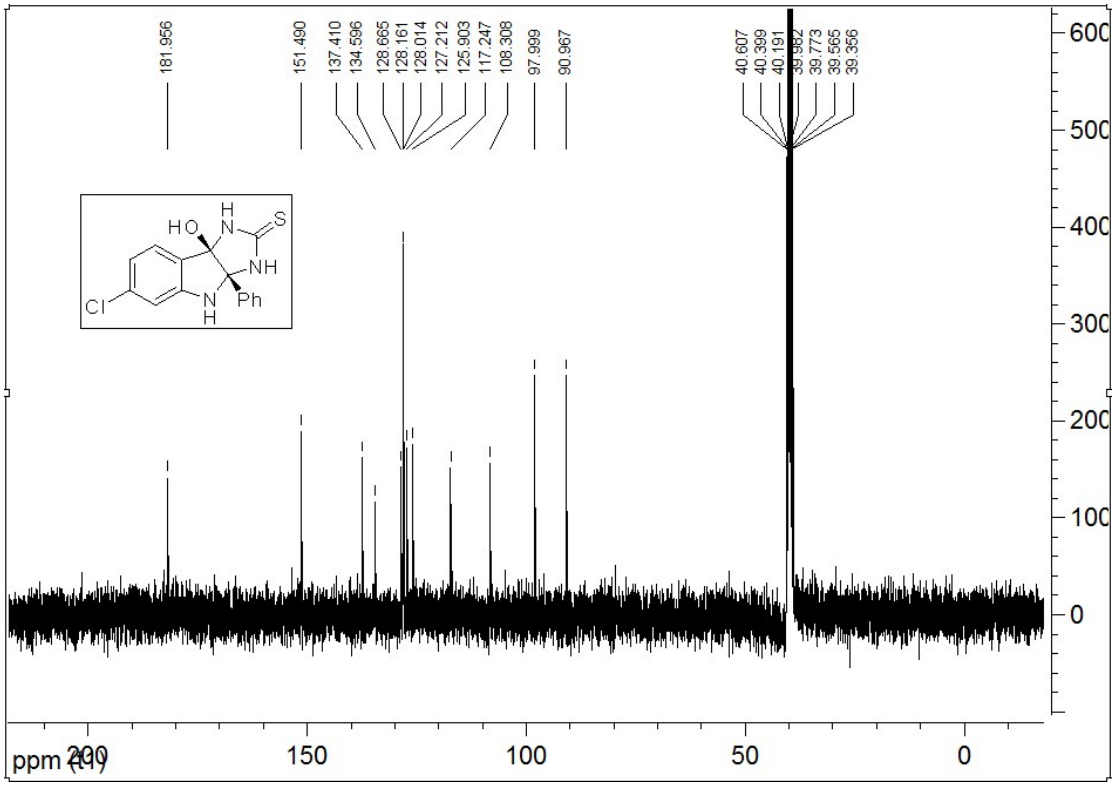
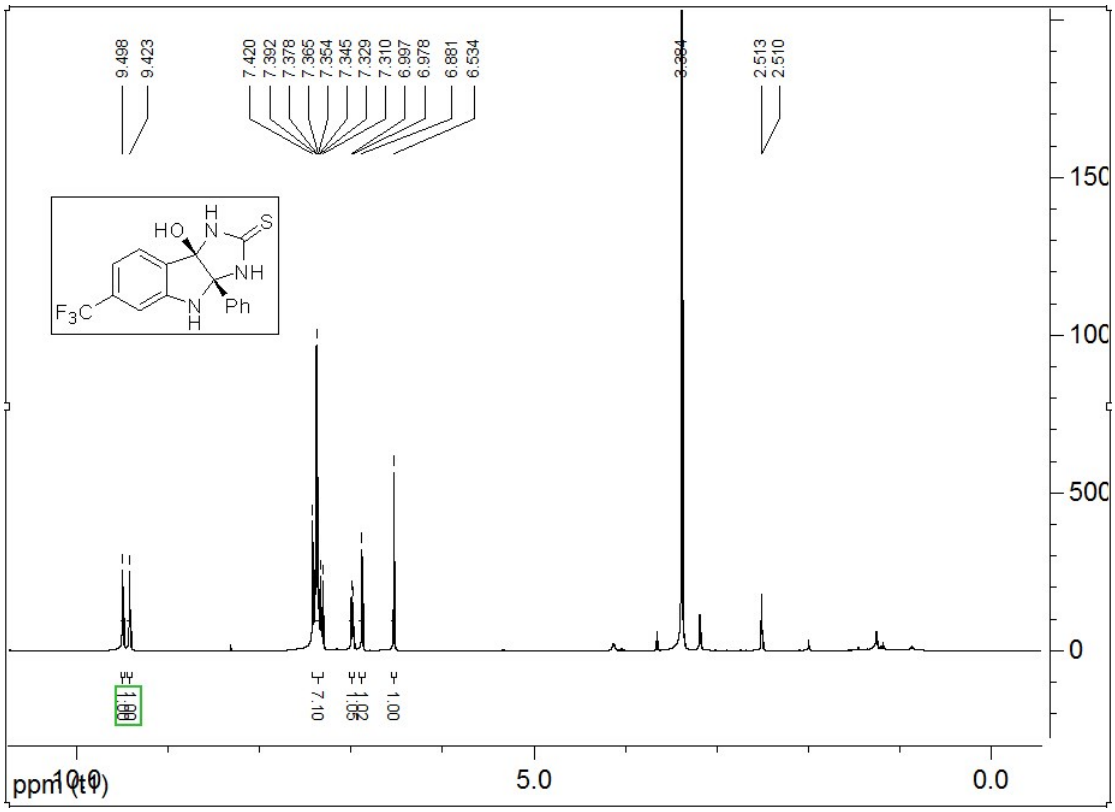


Figure 8. ^{1}H and ^{13}C NMR Spectra of ***cis*-8b-Hydroxy-3a-phenyl-6-(trifluoro -methyl)-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ah)**



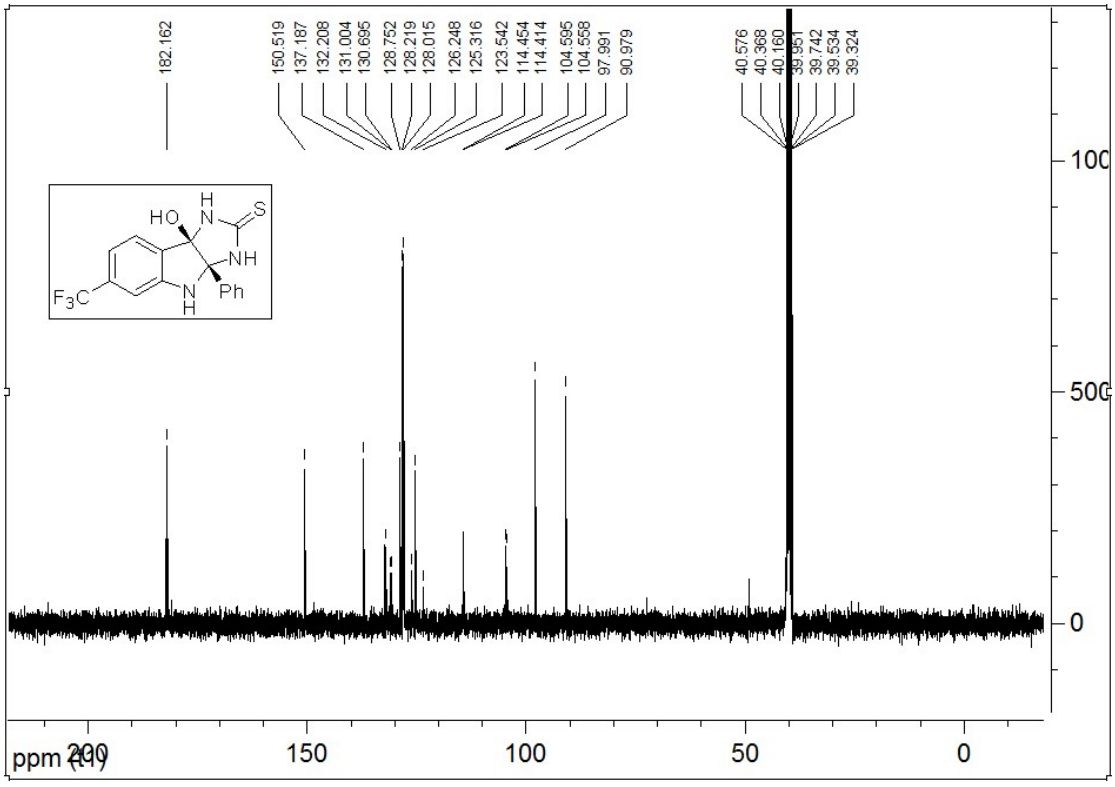
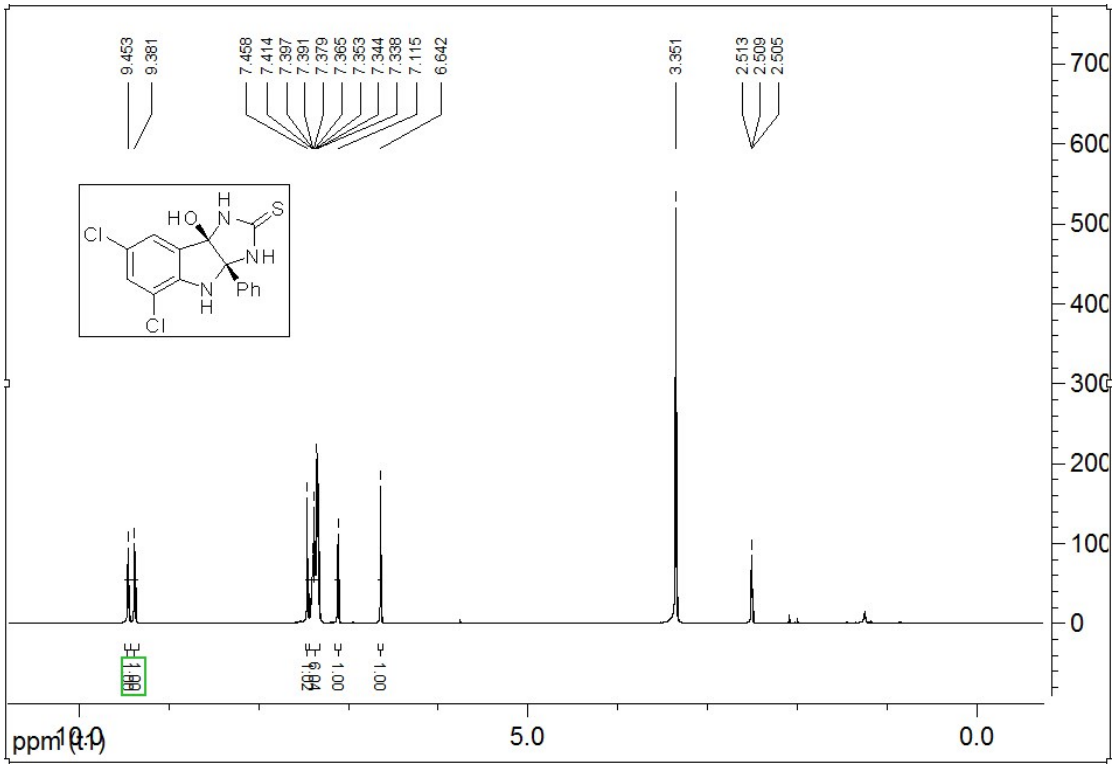


Figure 9. ^{1}H and ^{13}C NMR Spectra of ***cis*-5,7-Dichloro-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ai)**



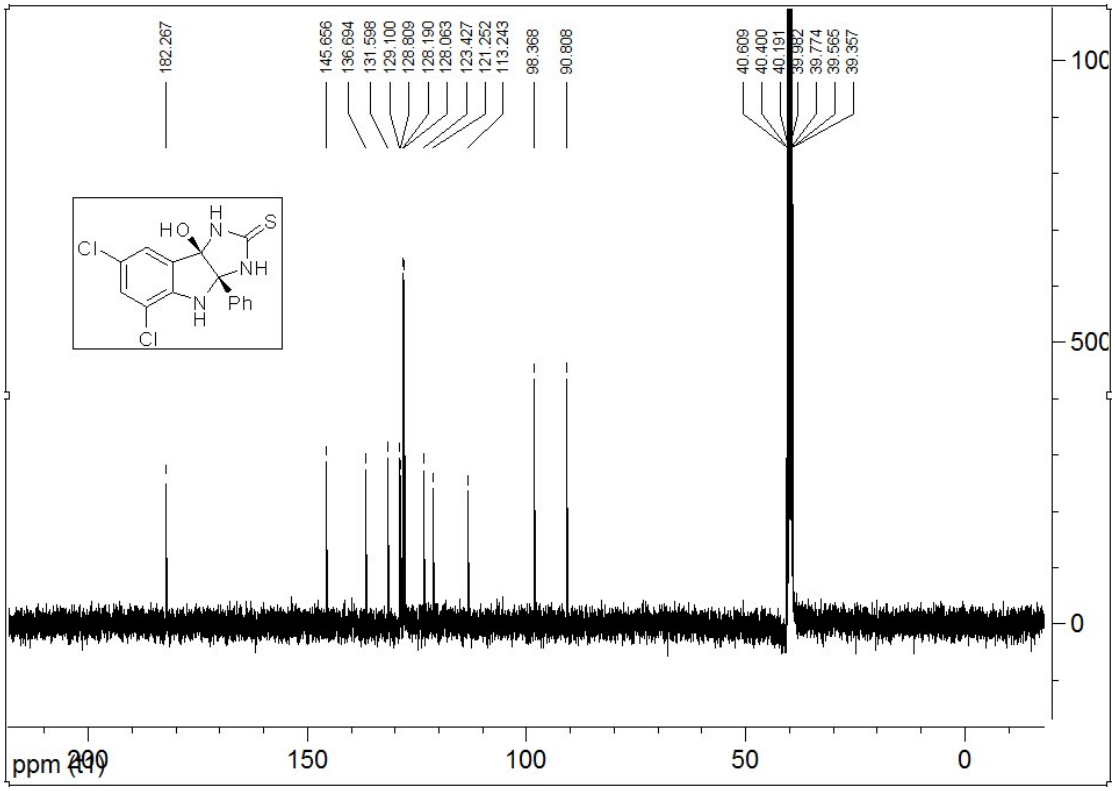
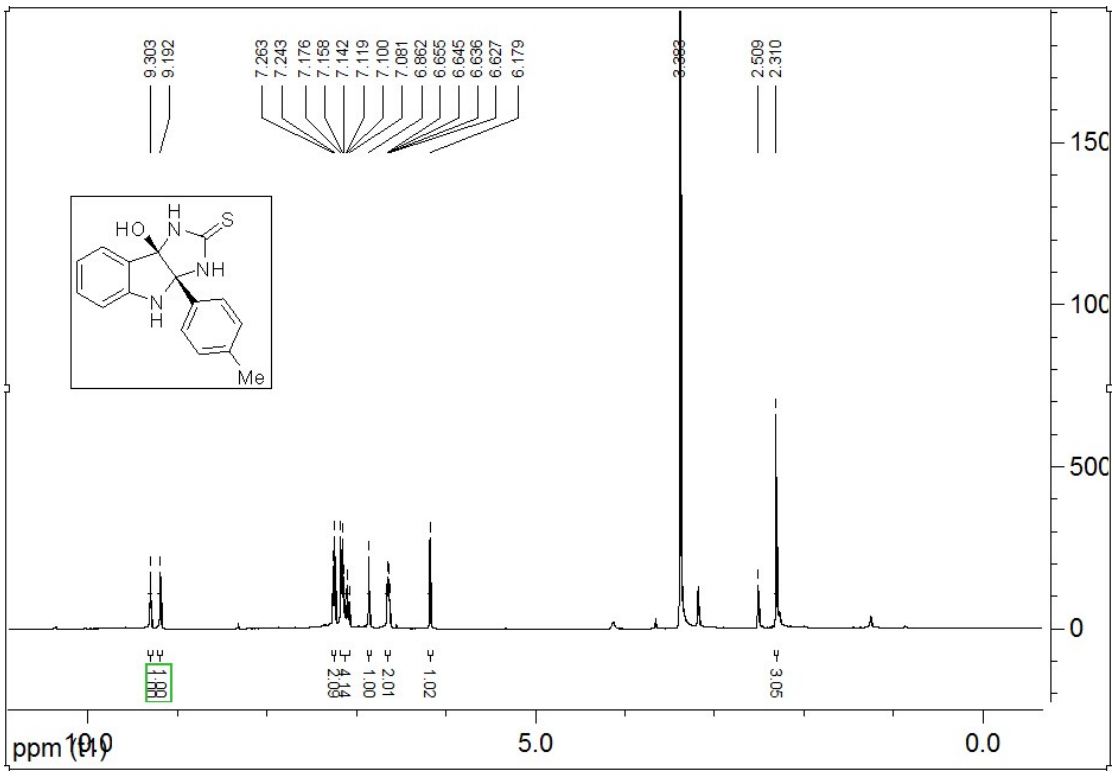


Figure 10. ^{1}H and ^{13}C NMR Spectra of ***cis*-8b-Hydroxy-3a-(*p*-tolyl)-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4aj)**



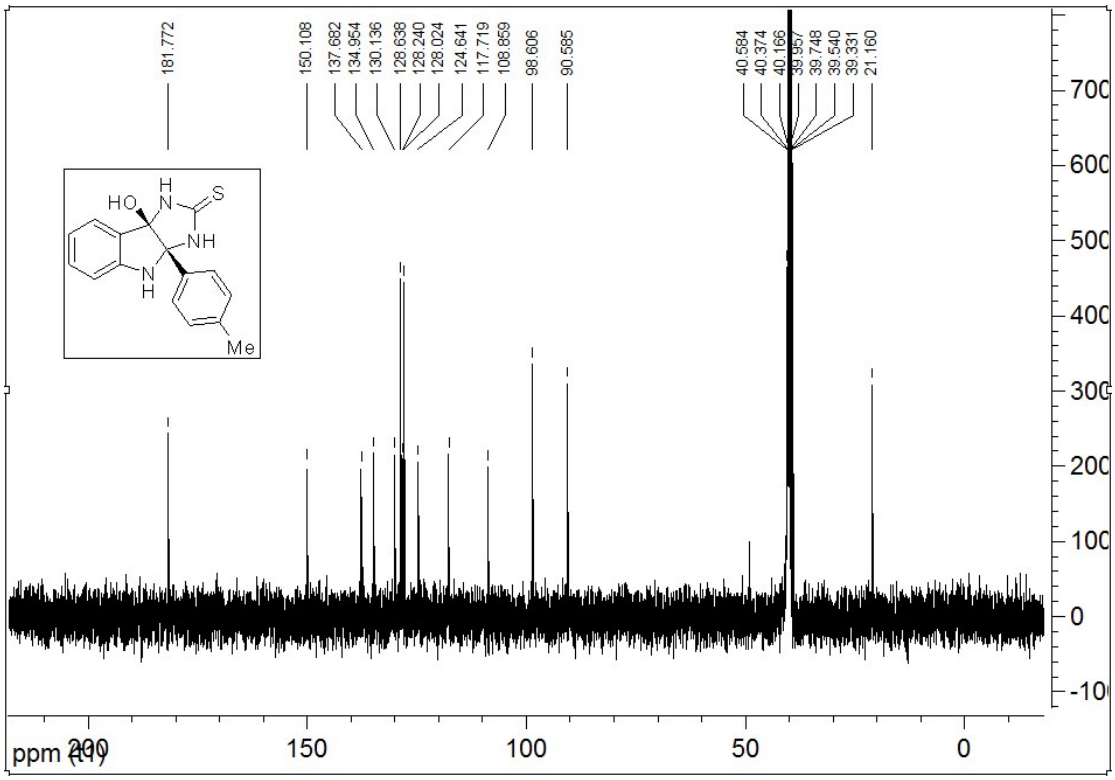
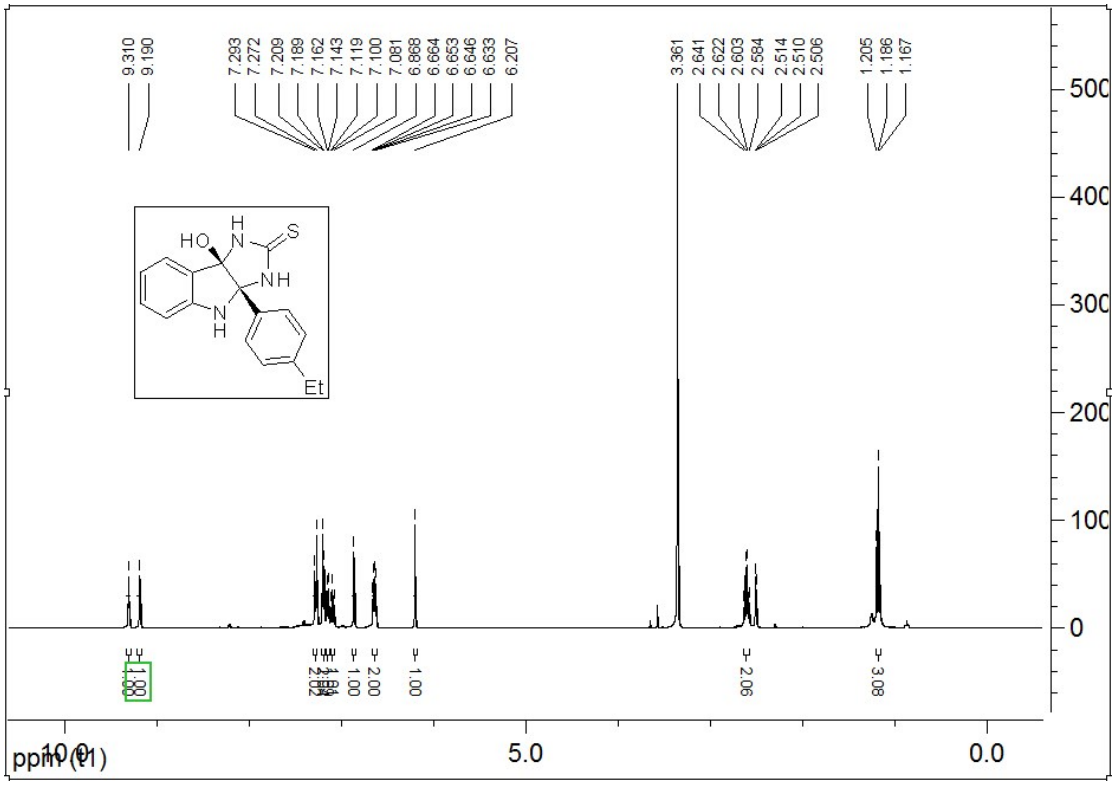


Figure 11. ^{1}H and ^{13}C NMR Spectra of ***cis*-3a-(4-Ethylphenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ak)**



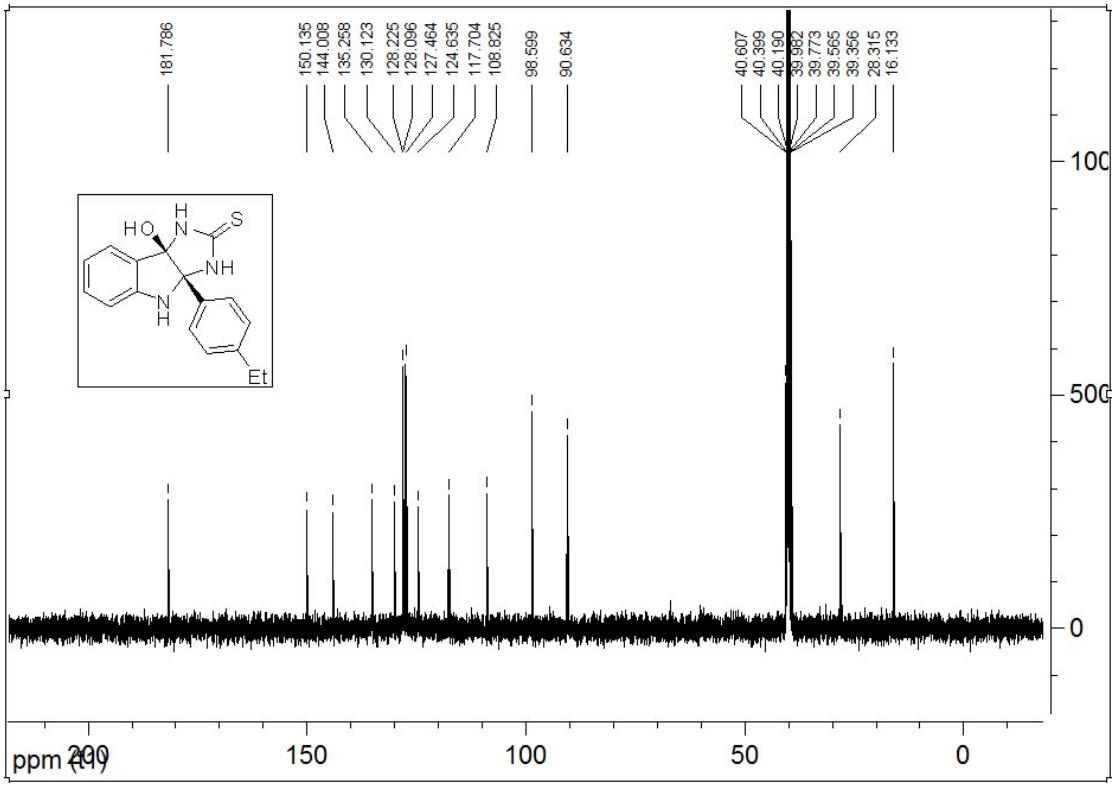
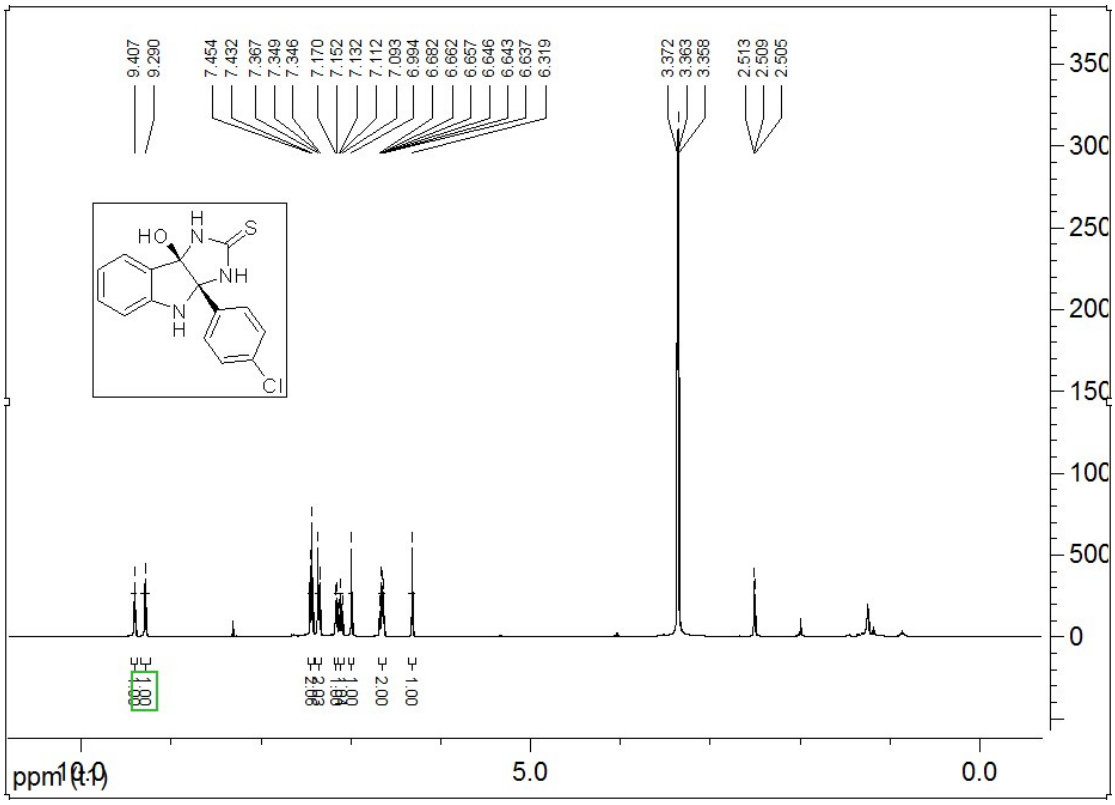


Figure 12. ^{1}H and ^{13}C NMR Spectra of ***cis*-3a-(4-Chlorophenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4al)**



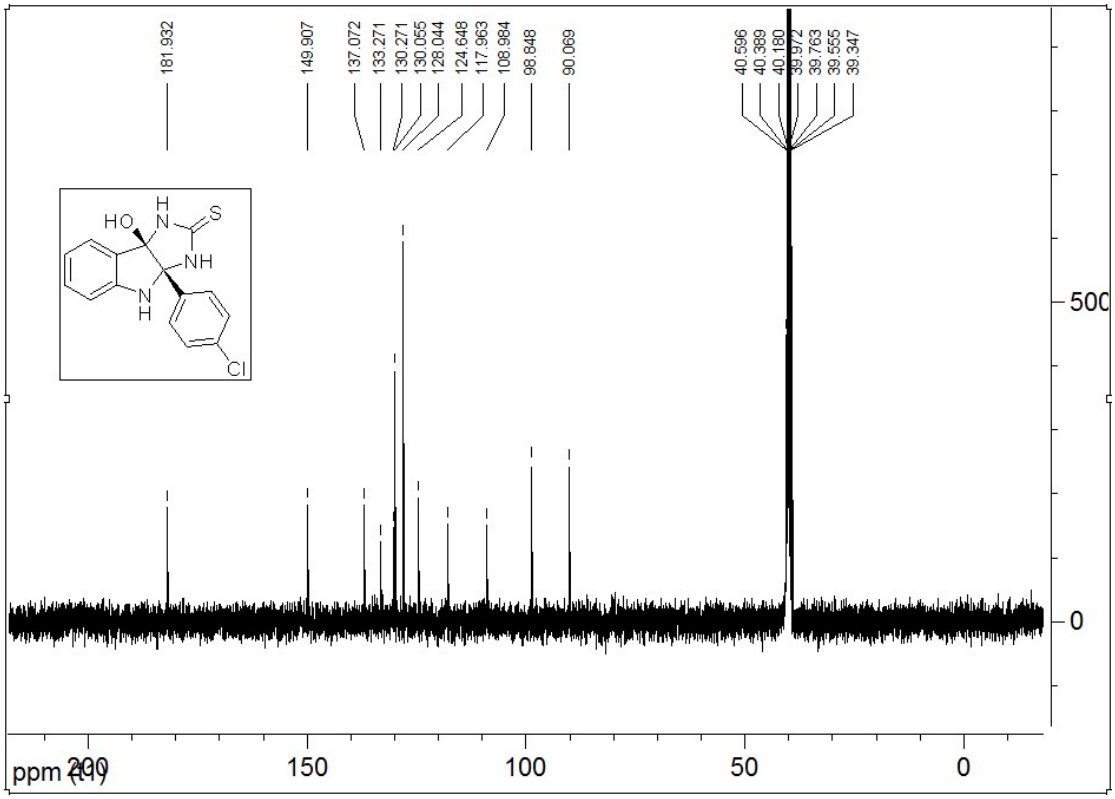
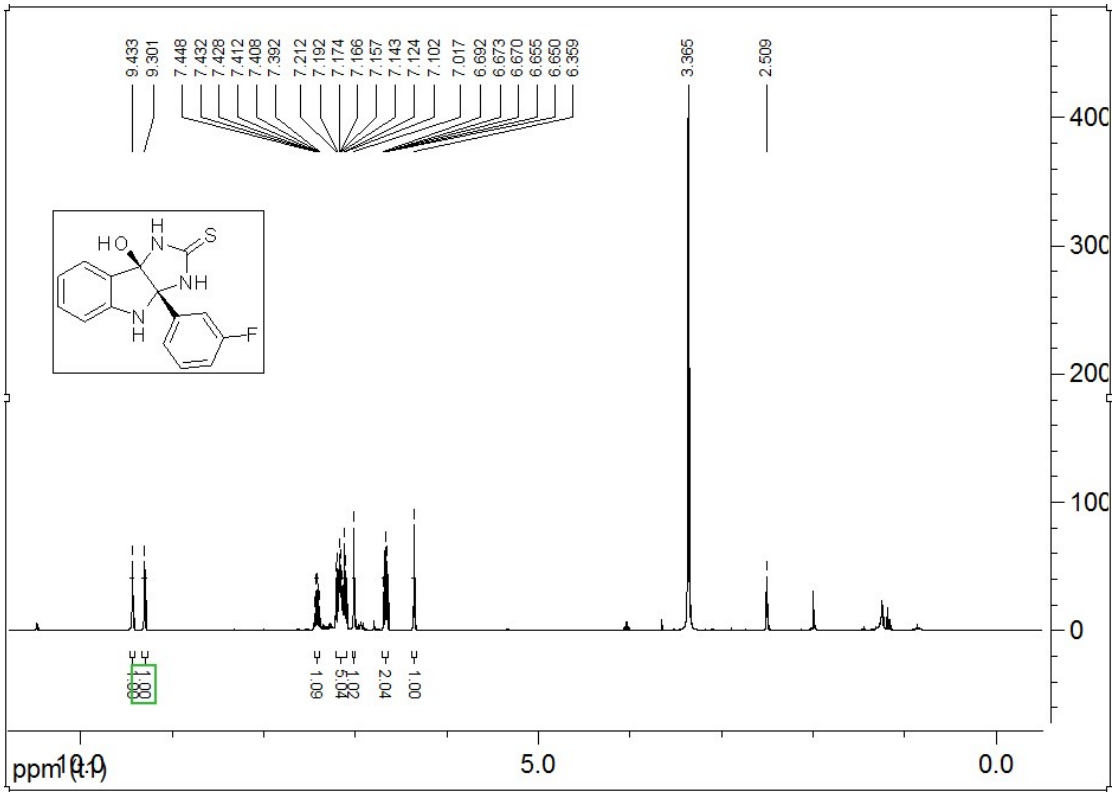


Figure 13. ^{1}H and ^{13}C NMR Spectra of ***cis*-3a-(3-Fluorophenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4am)**



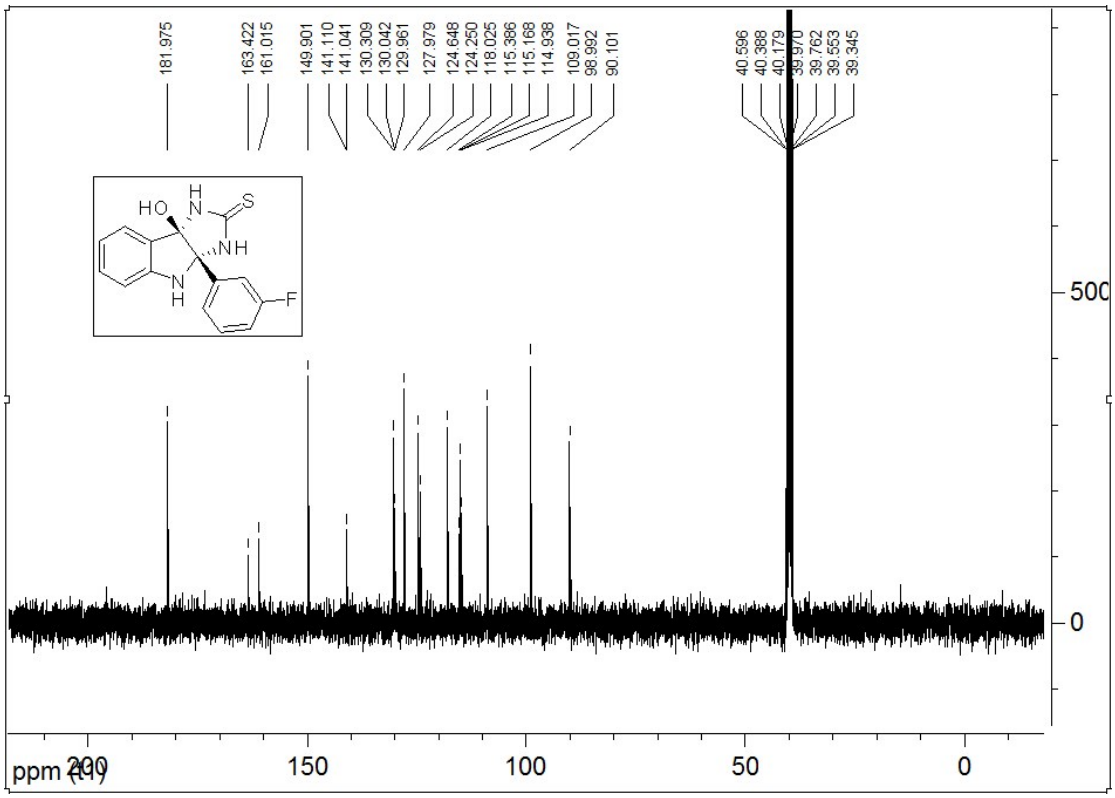
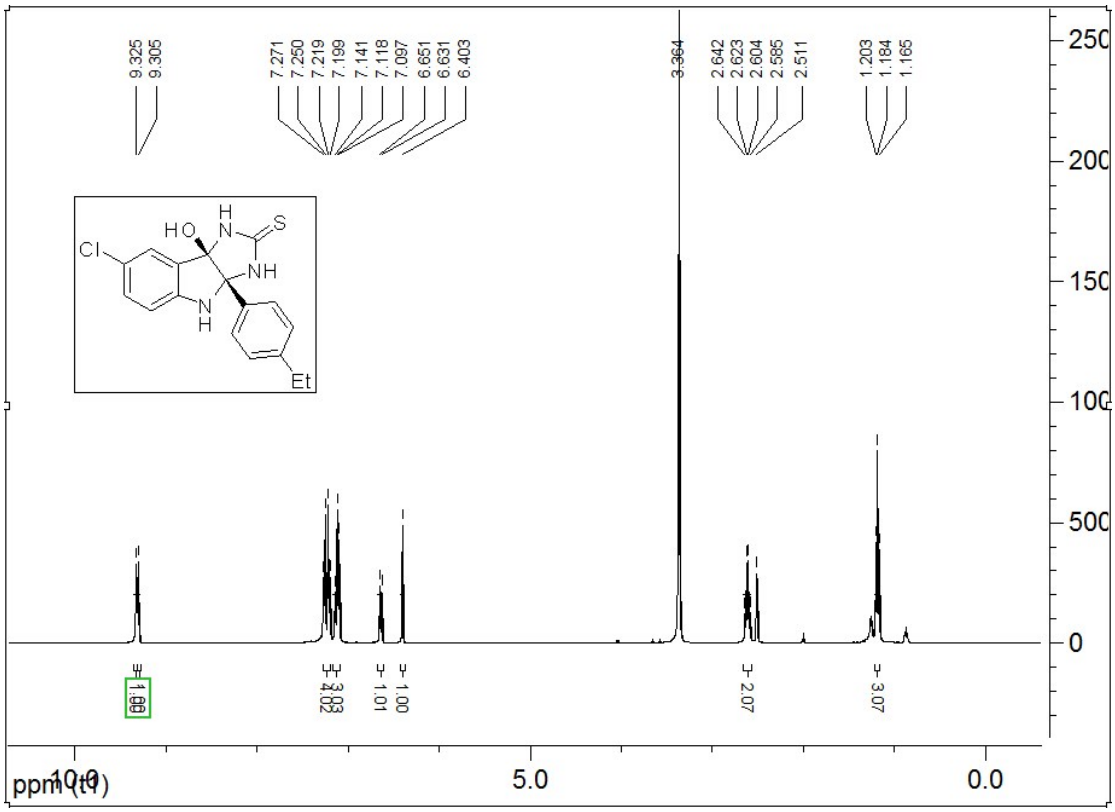


Figure 14. ^{1}H and ^{13}C NMR Spectra of ***cis*-7-Chloro-3a-(4-ethylphenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4an)**



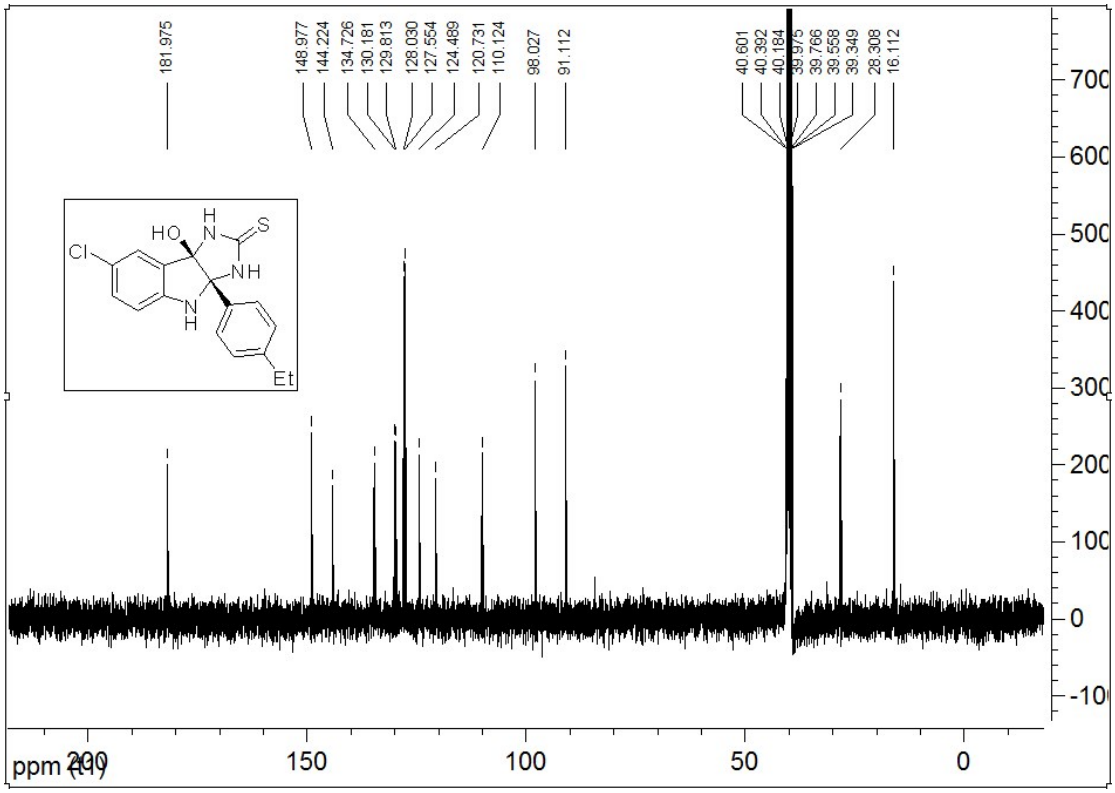
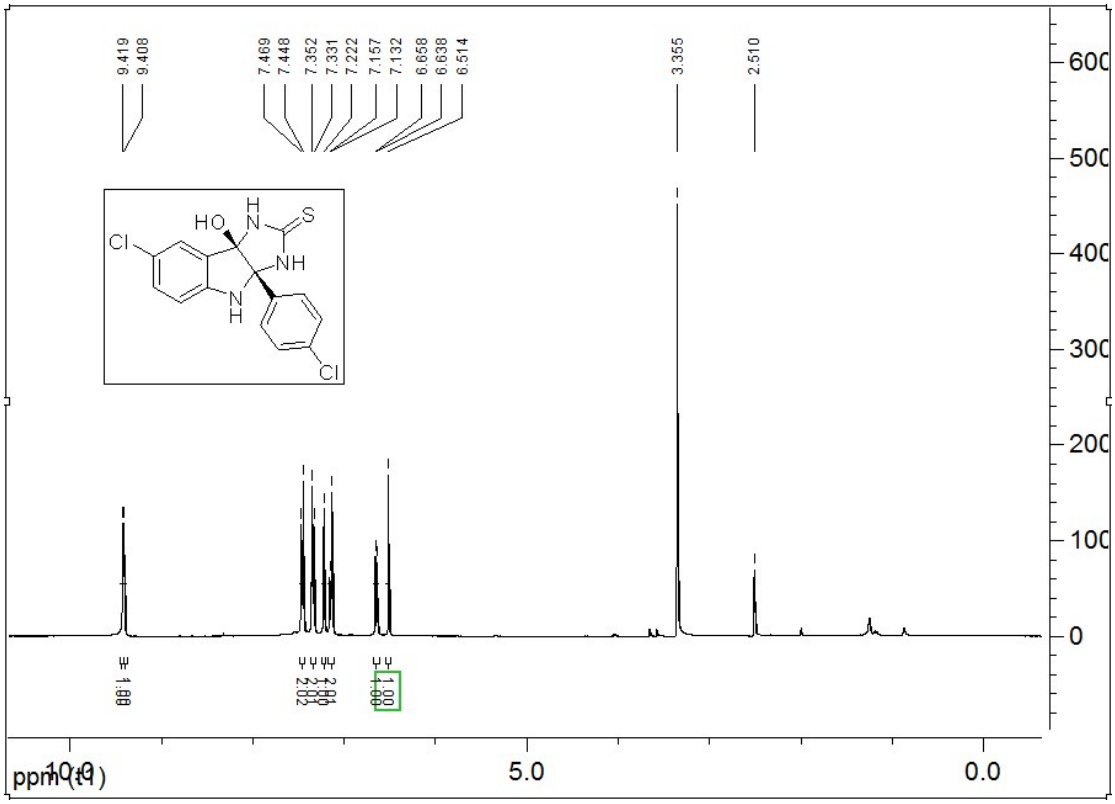


Figure 15. ^{1}H and ^{13}C NMR Spectra of ***cis*-7-Chloro-3a-(4-chlorophenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ao)**



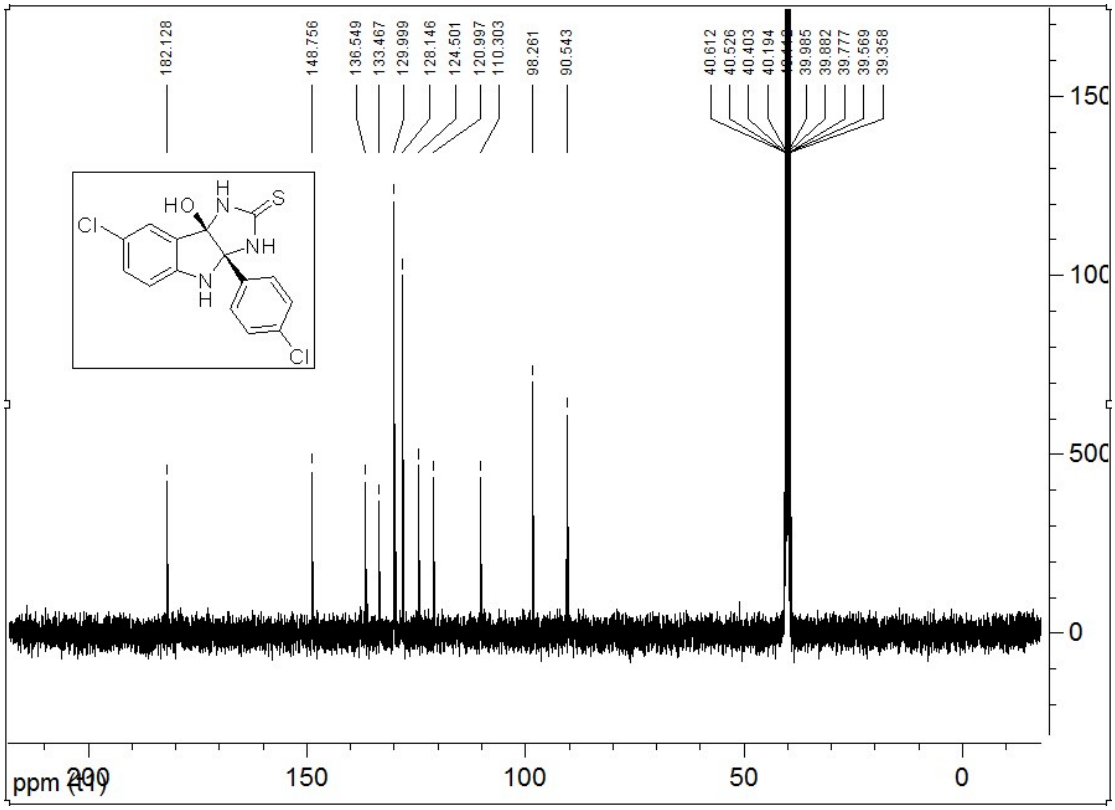
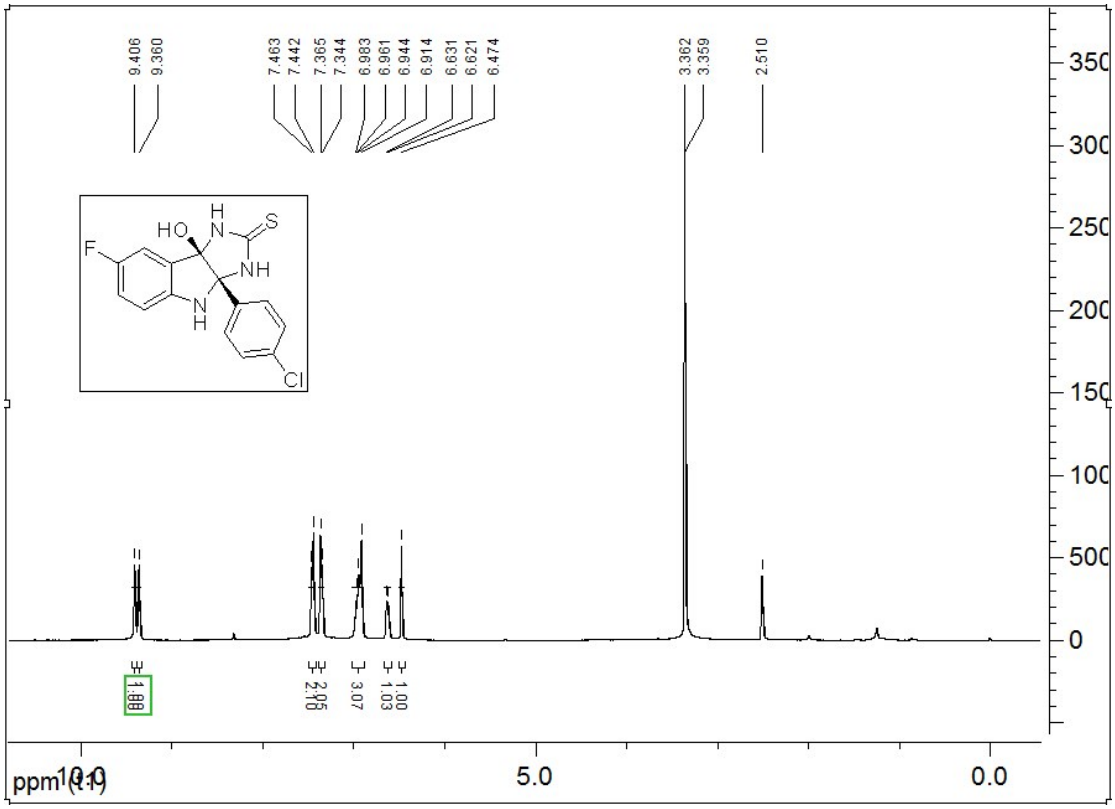


Figure 16. ^{1}H and ^{13}C NMR Spectra of ***cis*-3a-(4-Chlorophenyl)-7-fluoro-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ap)**



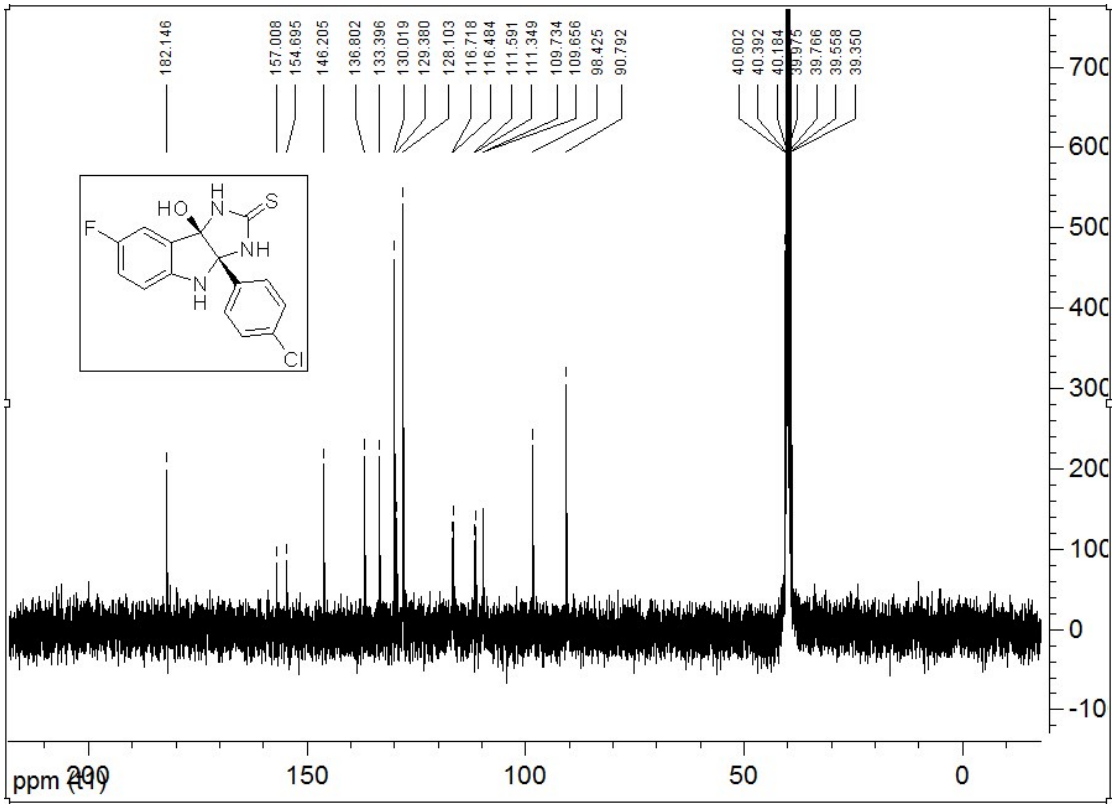
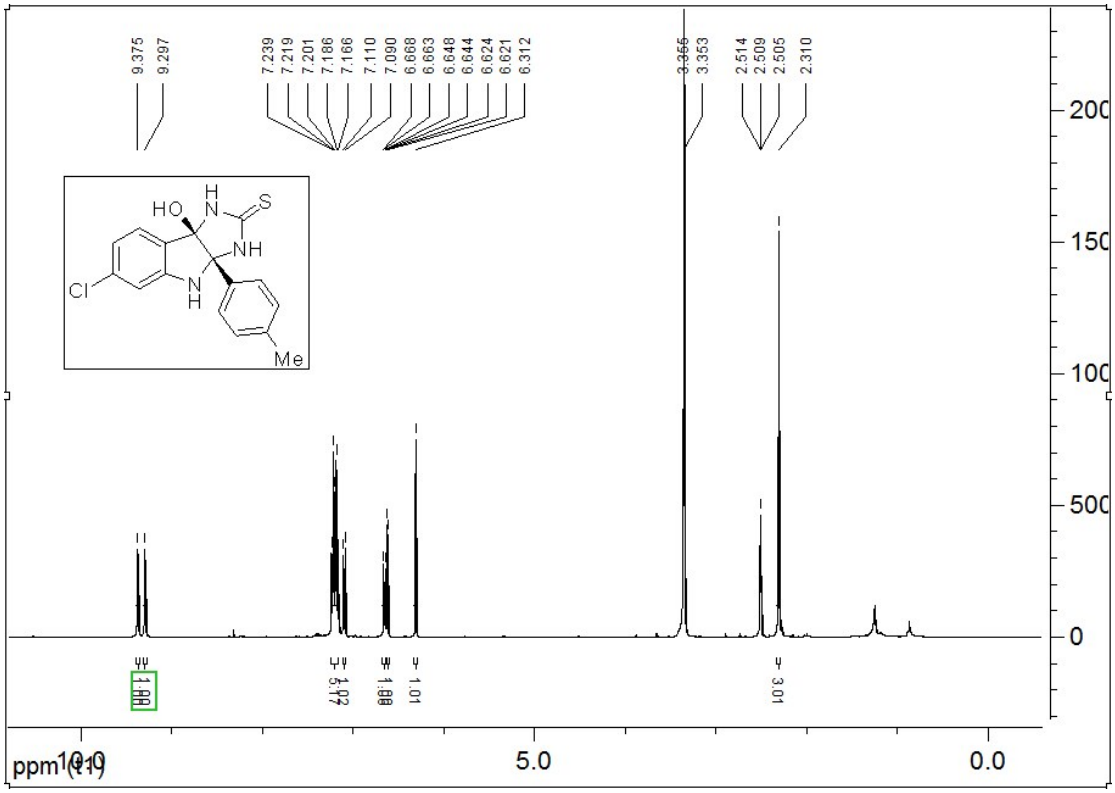


Figure 17. ^{1}H and ^{13}C NMR Spectra of ***cis*-6-Chloro-8b-hydroxy-3a-(*p*-tolyl)-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4aq)**



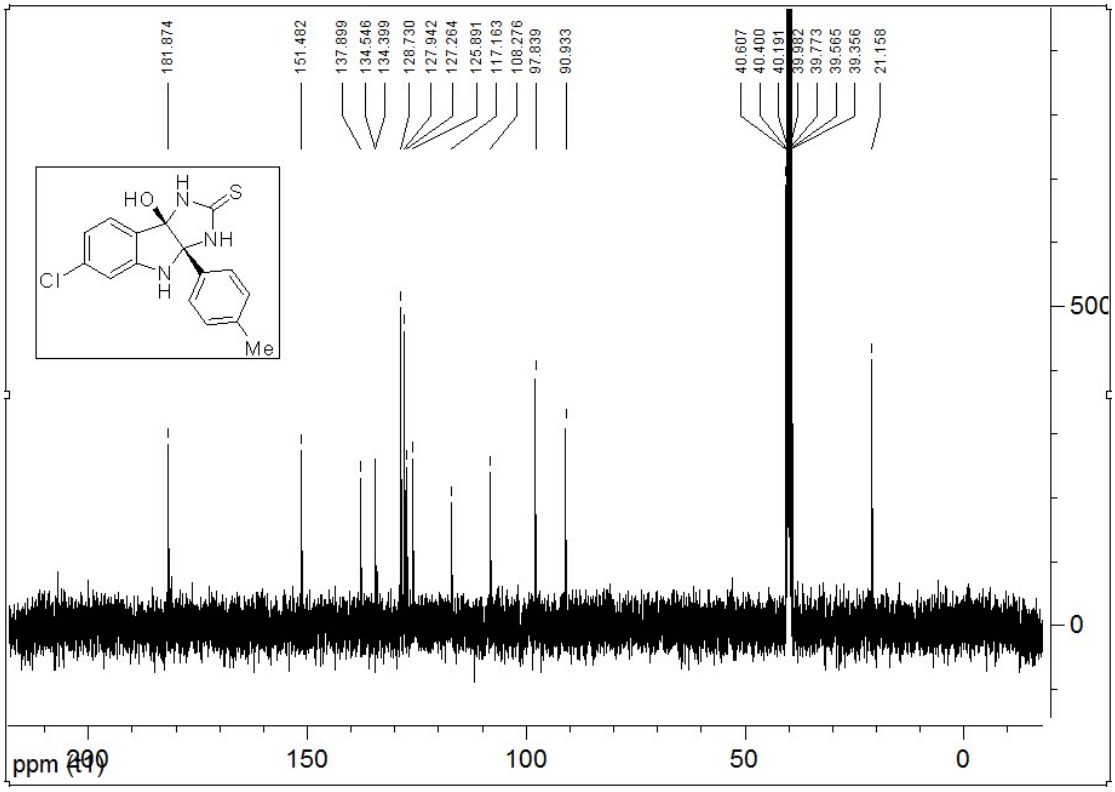
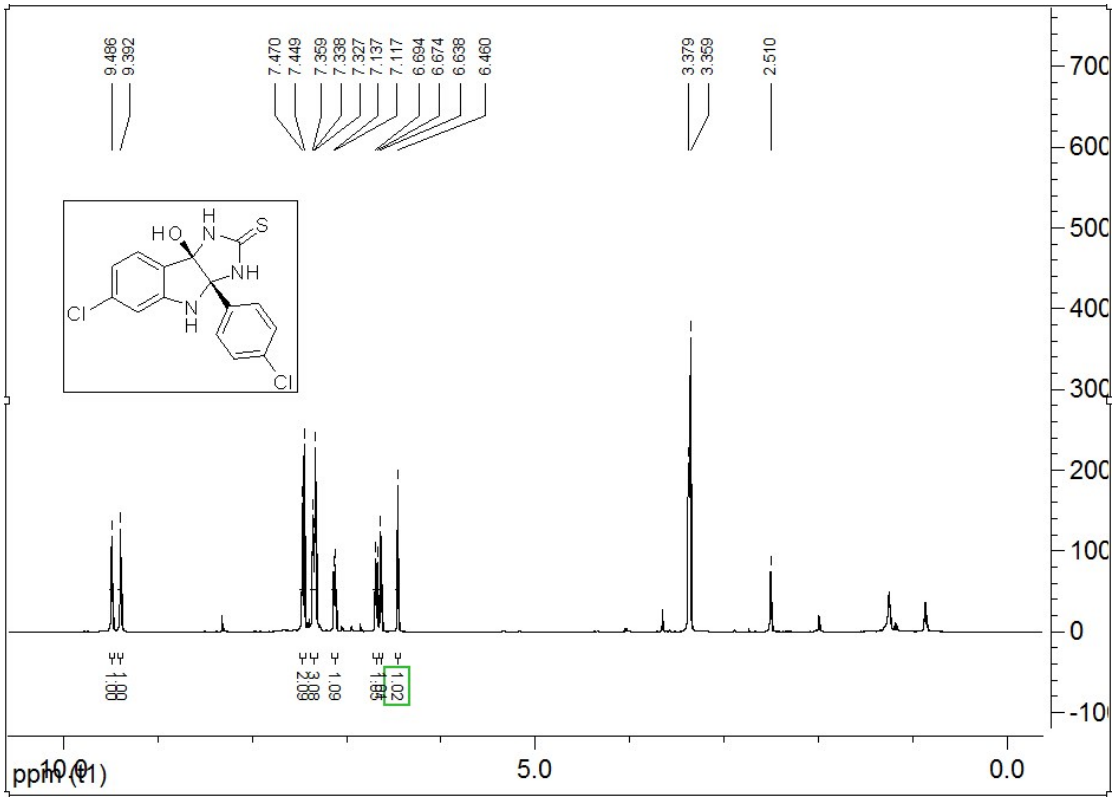


Figure 18. ^{1}H and ^{13}C NMR Spectra of ***cis*-6-Chloro-3a-(4-chlorophenyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ar)**



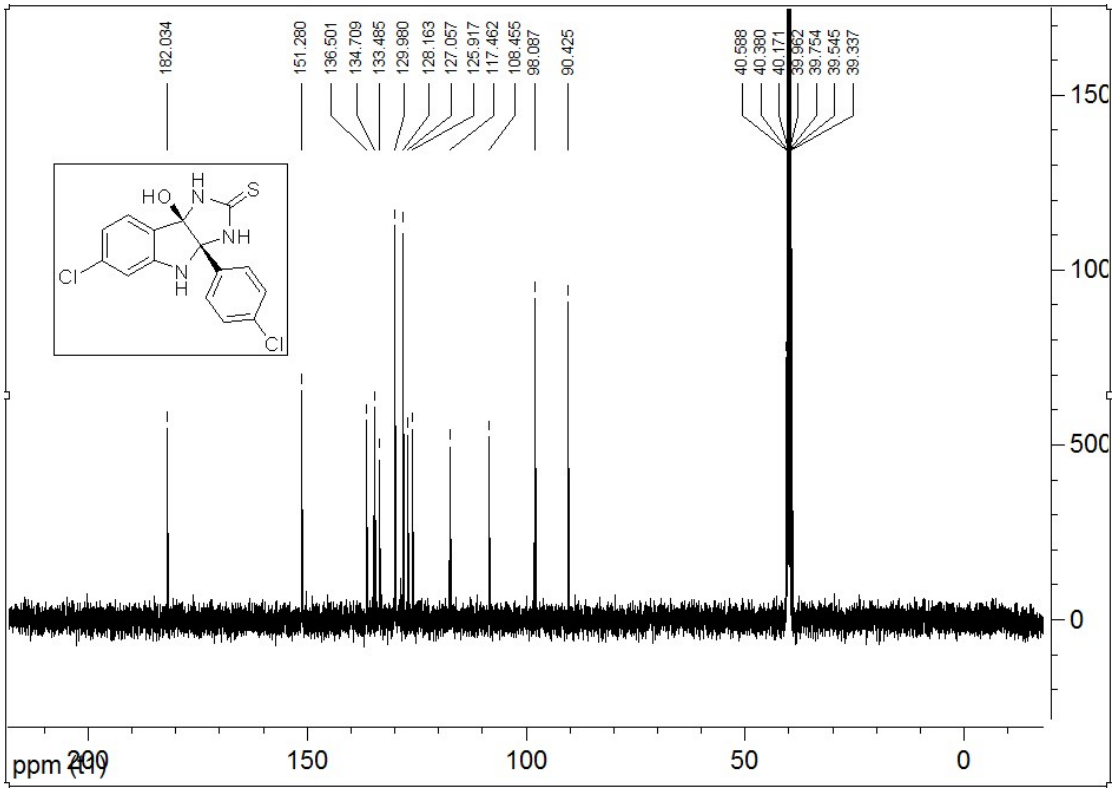
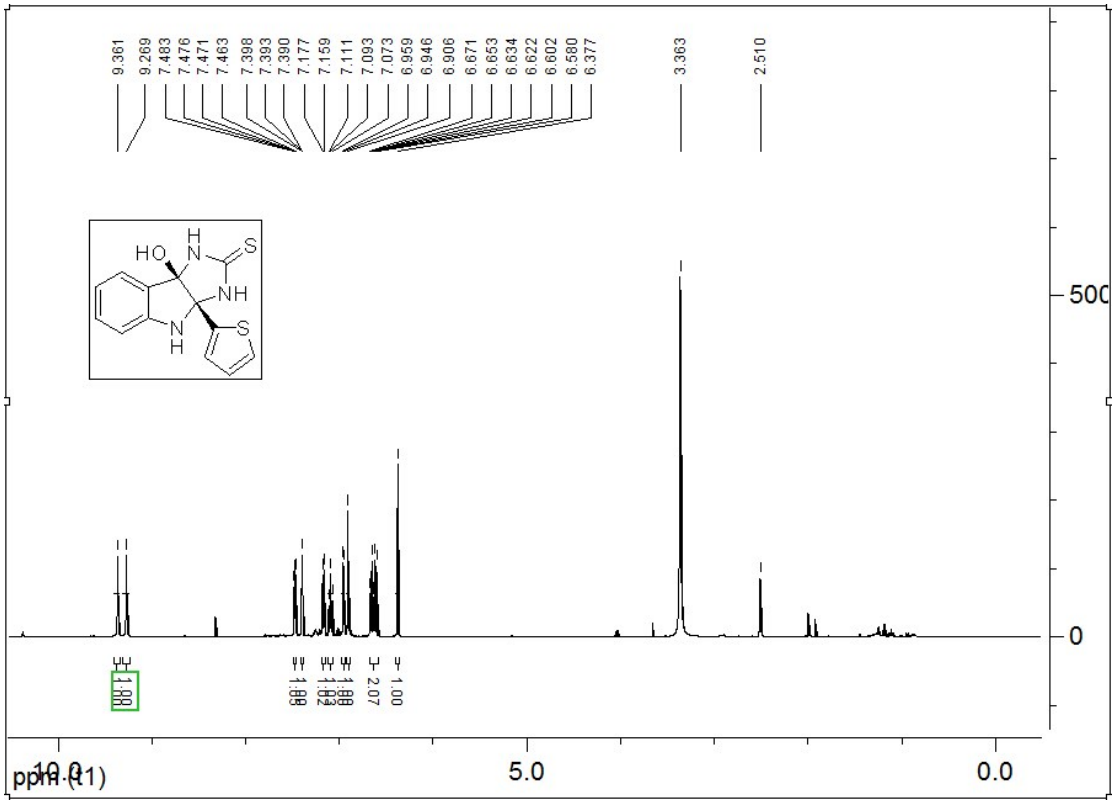


Figure 19. ^{1}H and ^{13}C NMR Spectra of ***cis*-8b-Hydroxy-3a-(thiophen-2-yl)-3,3a, 4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4as)**



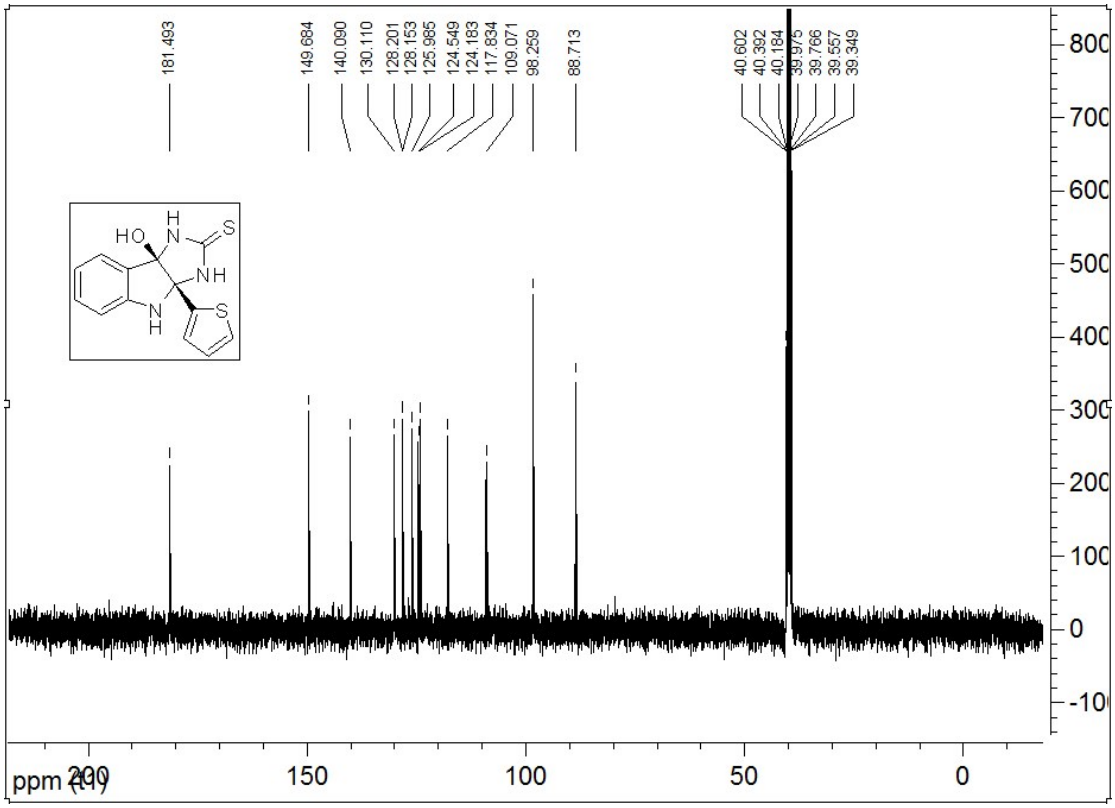
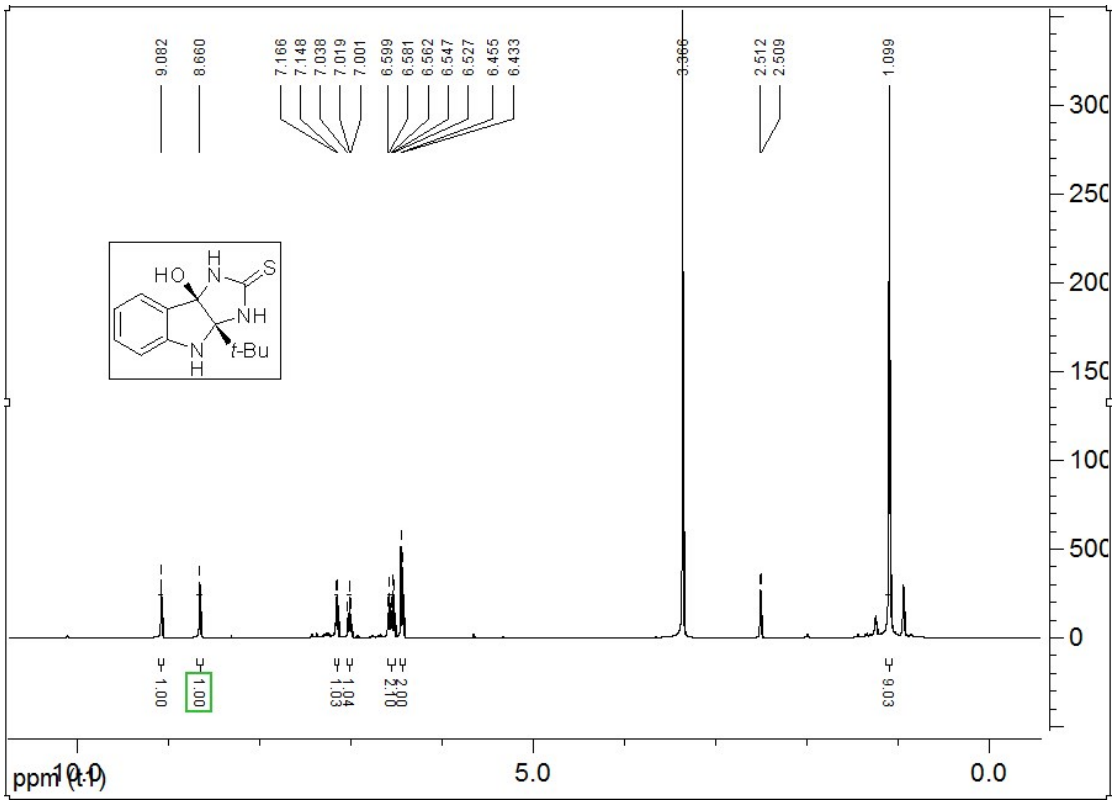


Figure 20. ^{1}H and ^{13}C NMR Spectra of ***cis*-3a-(*tert*-Butyl)-8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4at)**



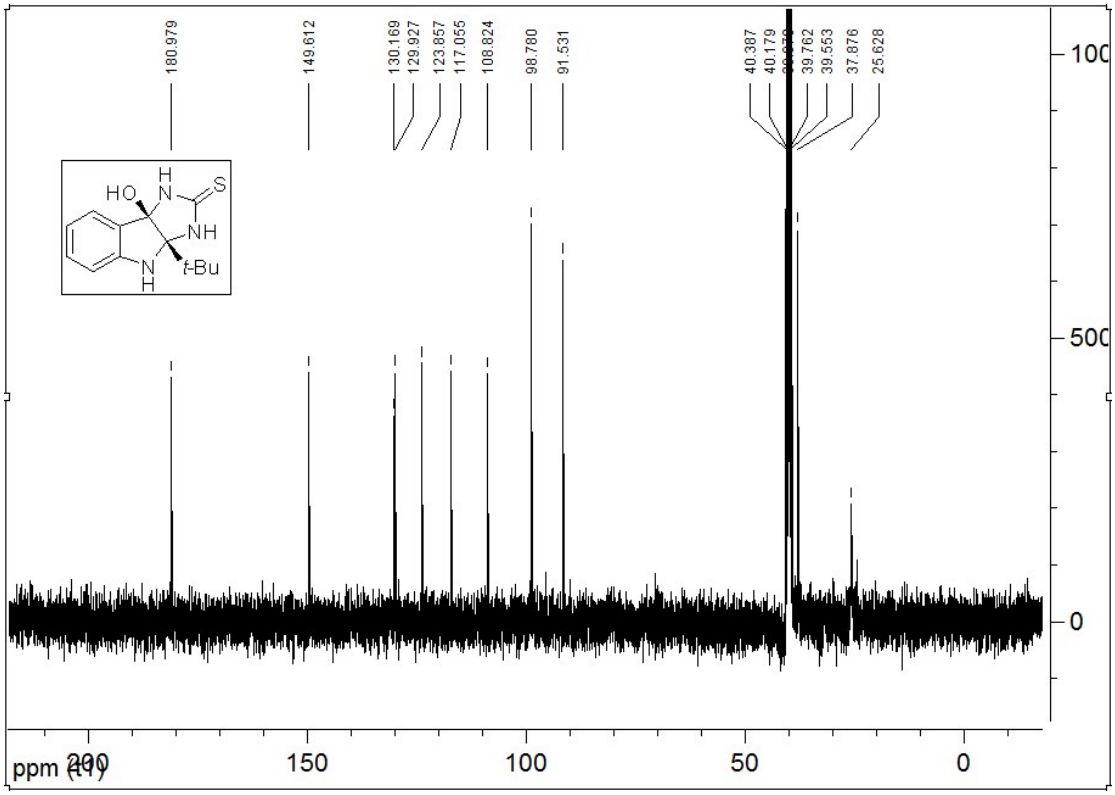
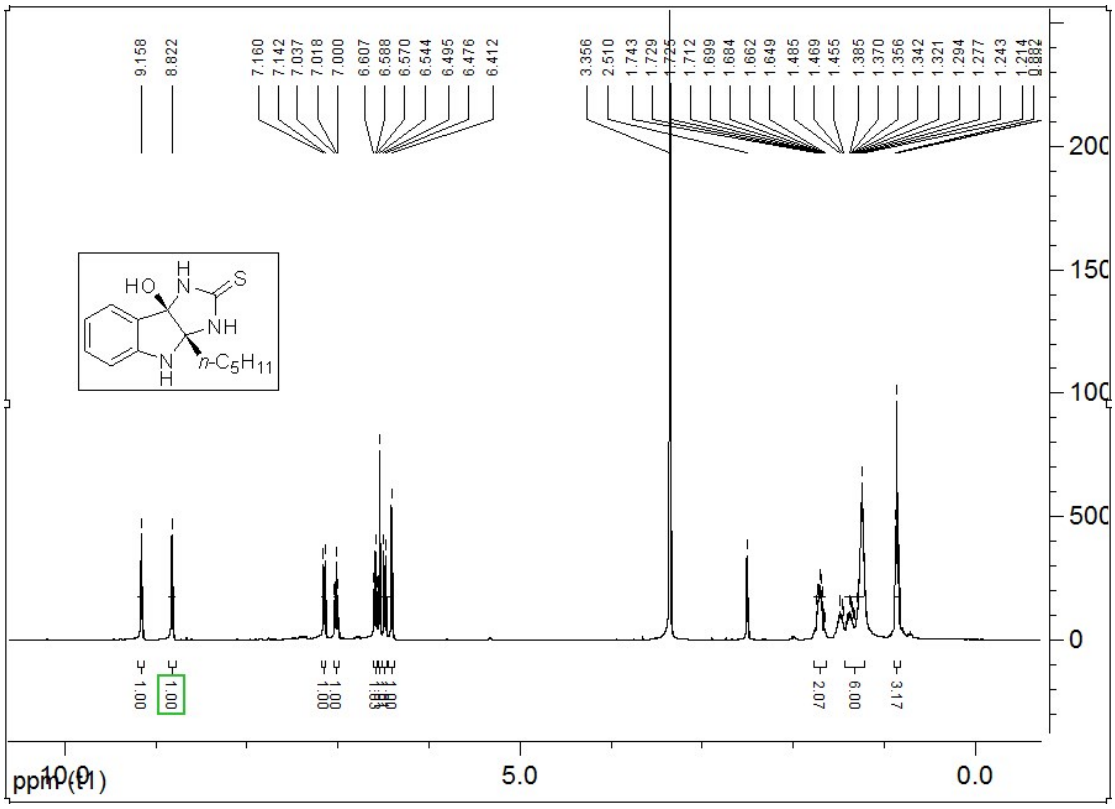


Figure 21. ^{1}H and ^{13}C NMR Spectra of ***cis*-8b-hydroxy-3a-pentyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4au)**



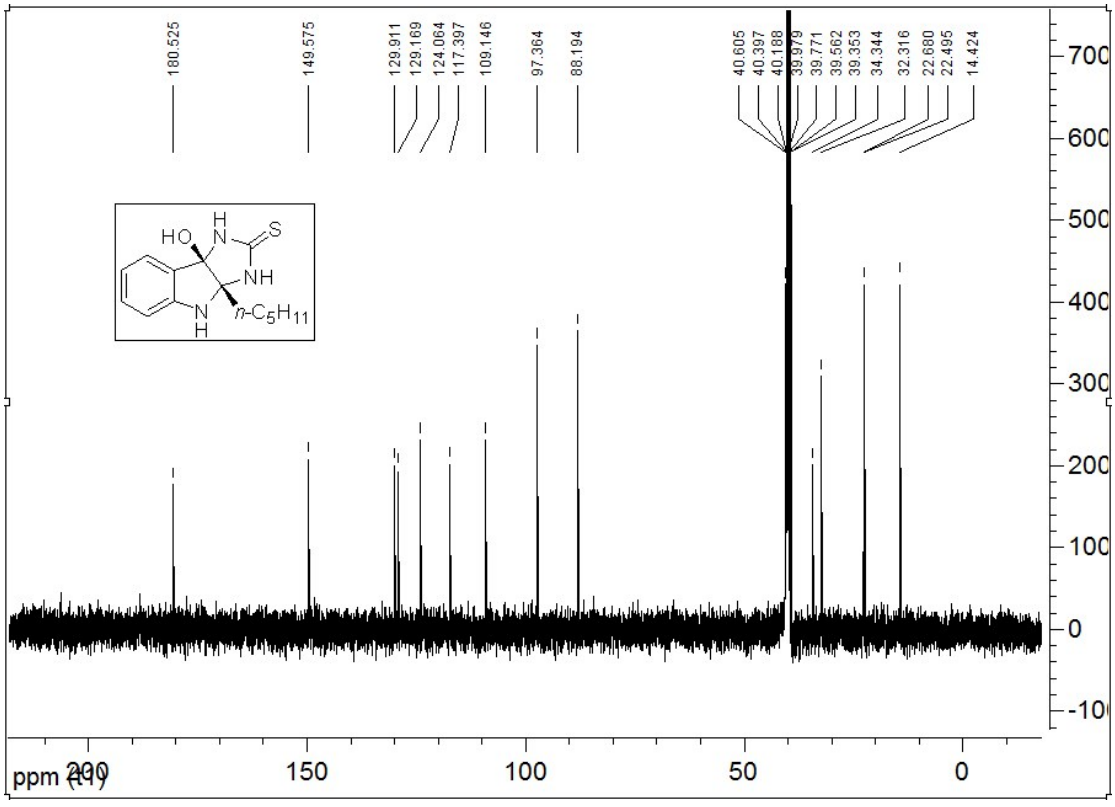
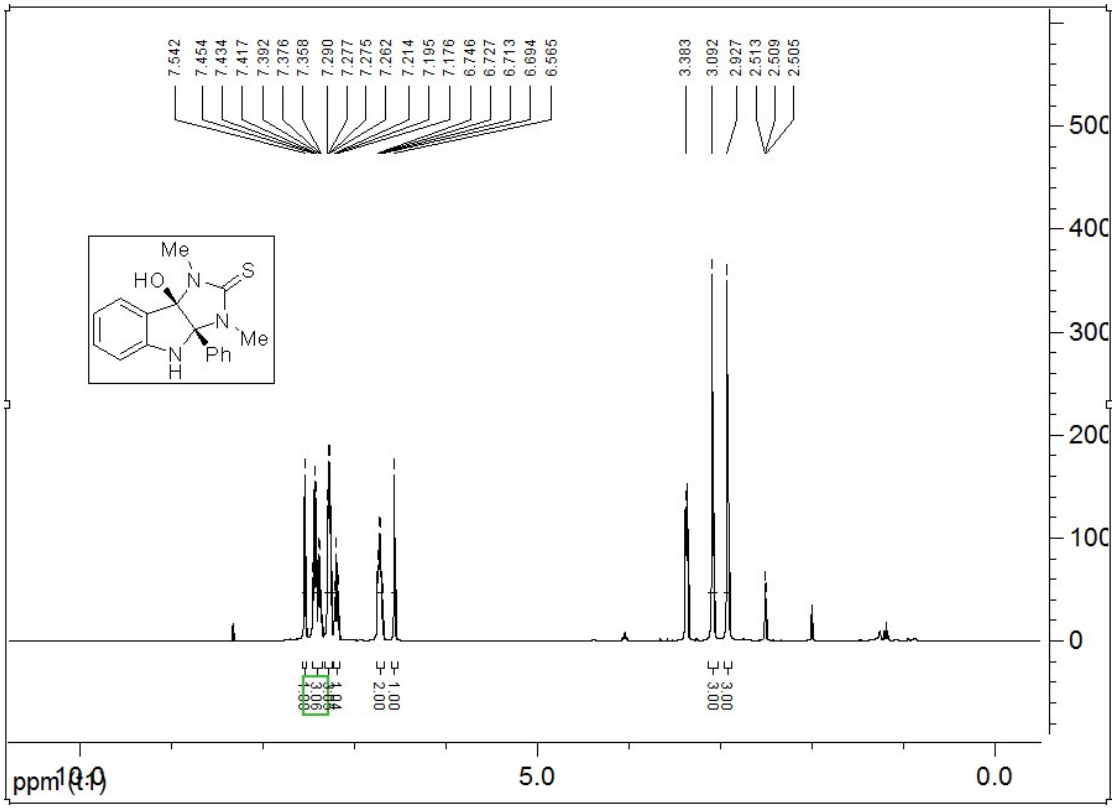


Figure 22. ^{1}H and ^{13}C NMR Spectra of ***cis*-8b-Hydroxy-1,3-dimethyl-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ba)**



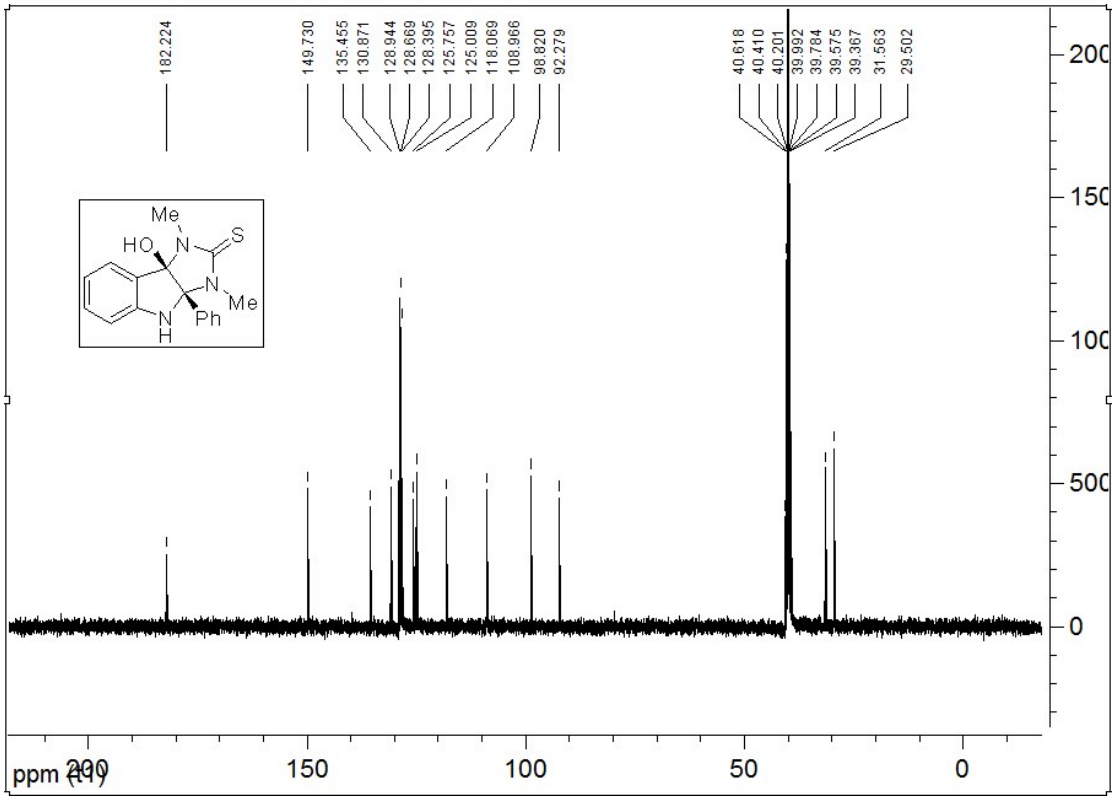
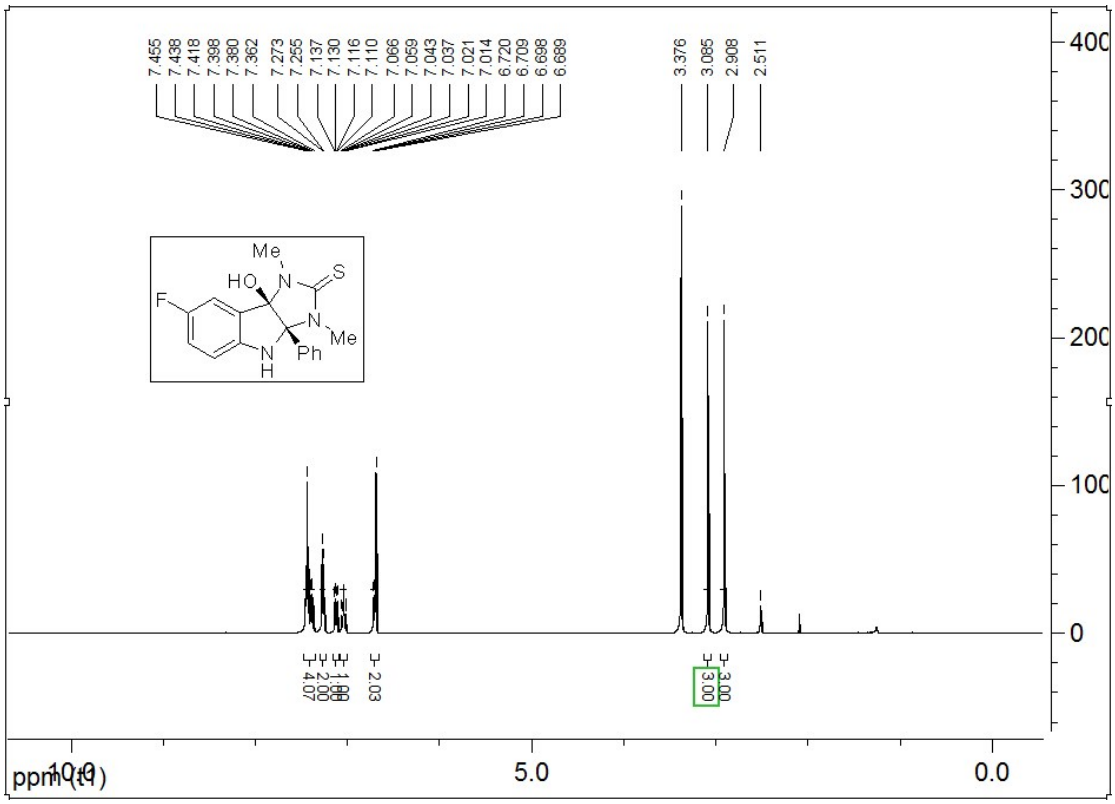


Figure 23. ^{1}H and ^{13}C NMR Spectra of ***cis*-7-Fluoro-8b-hydroxy-1,3-dimethyl-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4bb)**



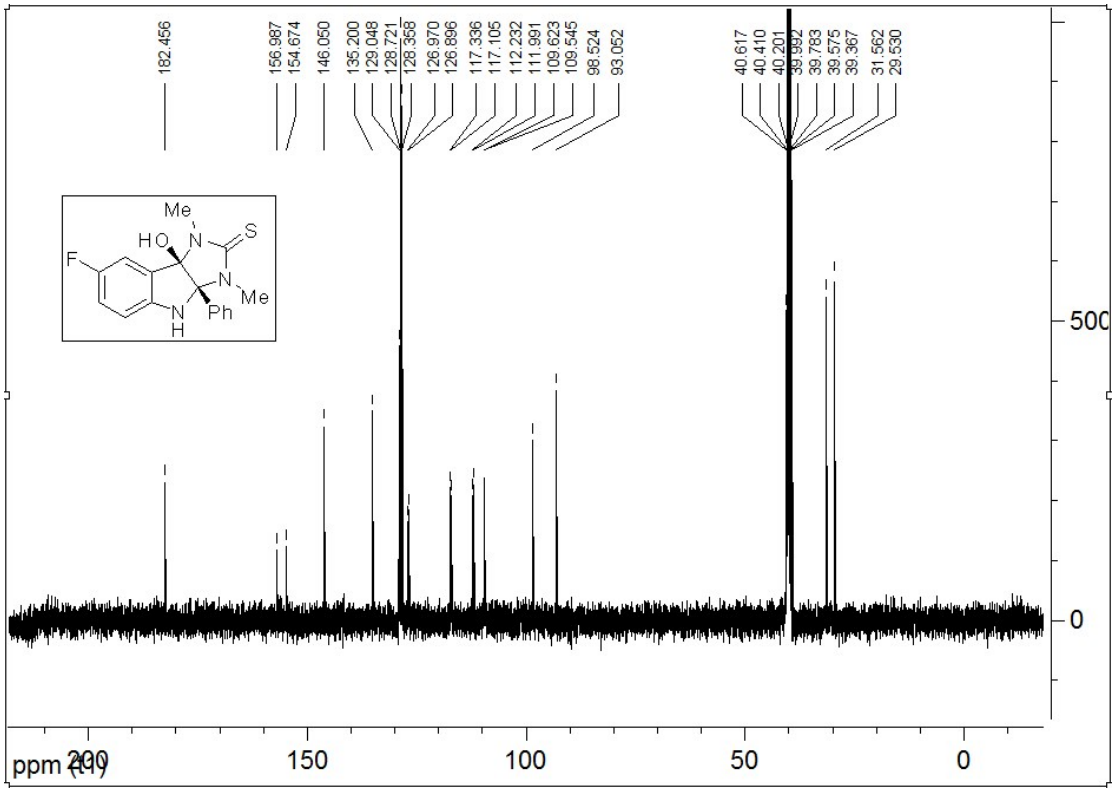
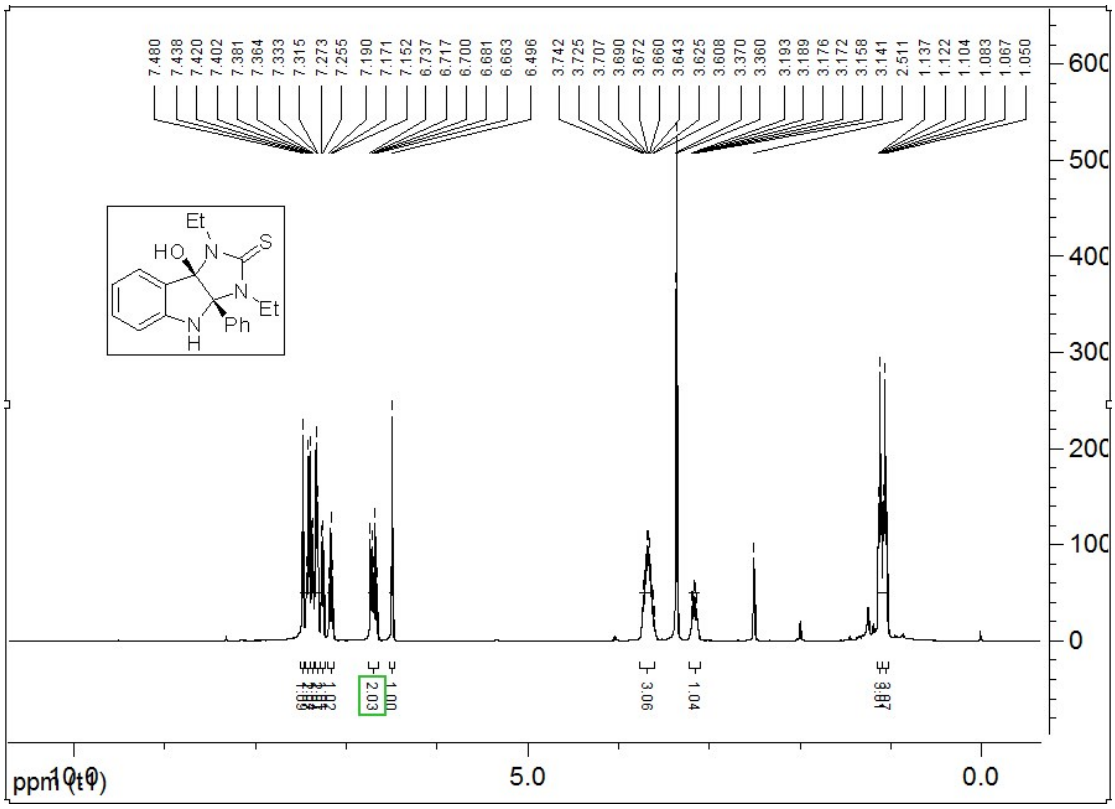


Figure 24. ^{1}H and ^{13}C NMR Spectra of ***cis*-1,3-Diethyl-8b-hydroxy-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4bc)**



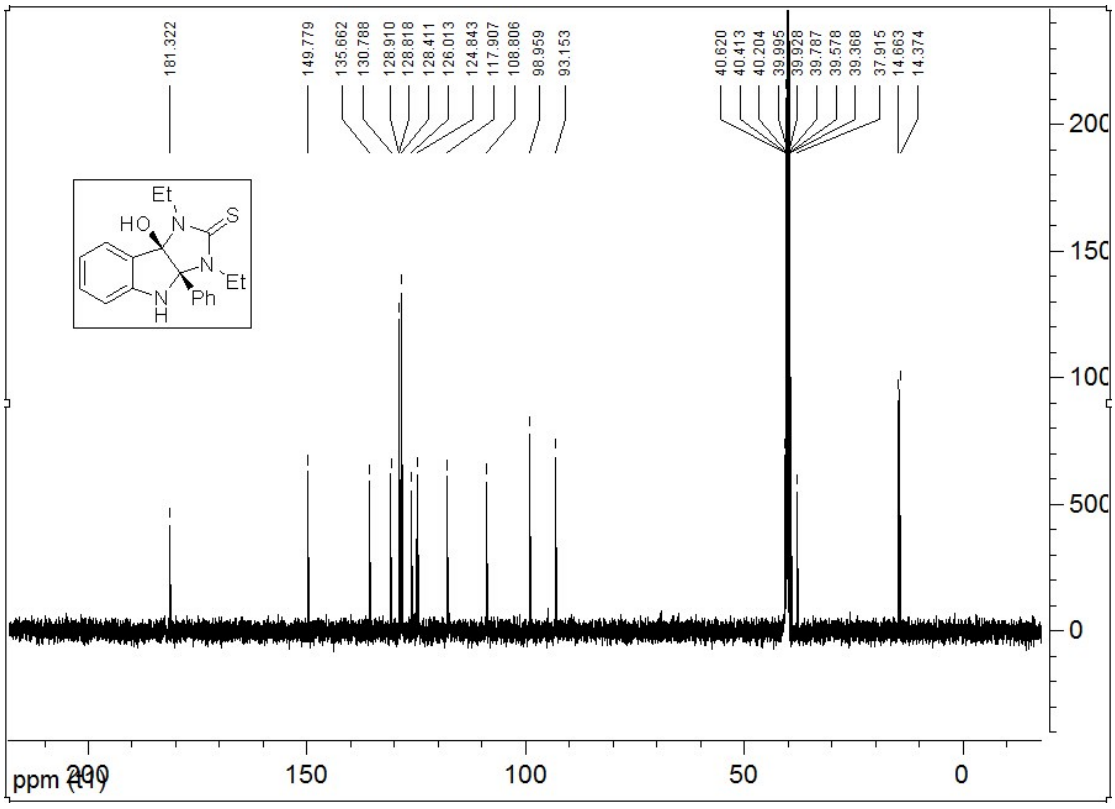
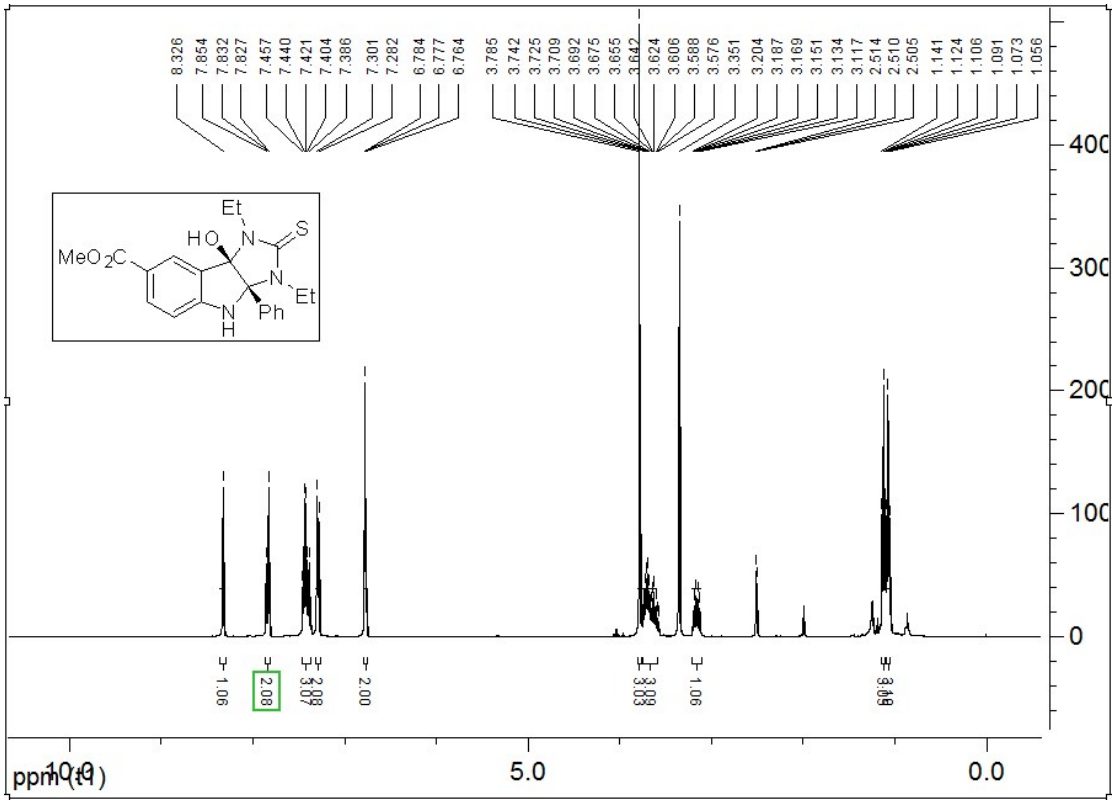


Figure 25. ^{1}H and ^{13}C NMR Spectra of ***cis*-Methyl 1,3-diethyl-8b-hydroxy-3a -phenyl-2-thioxo-1,2,3,3a,4,8b-hexahydro-imidazo[4,5-*b*]indole-7-carboxylate (4bd)**



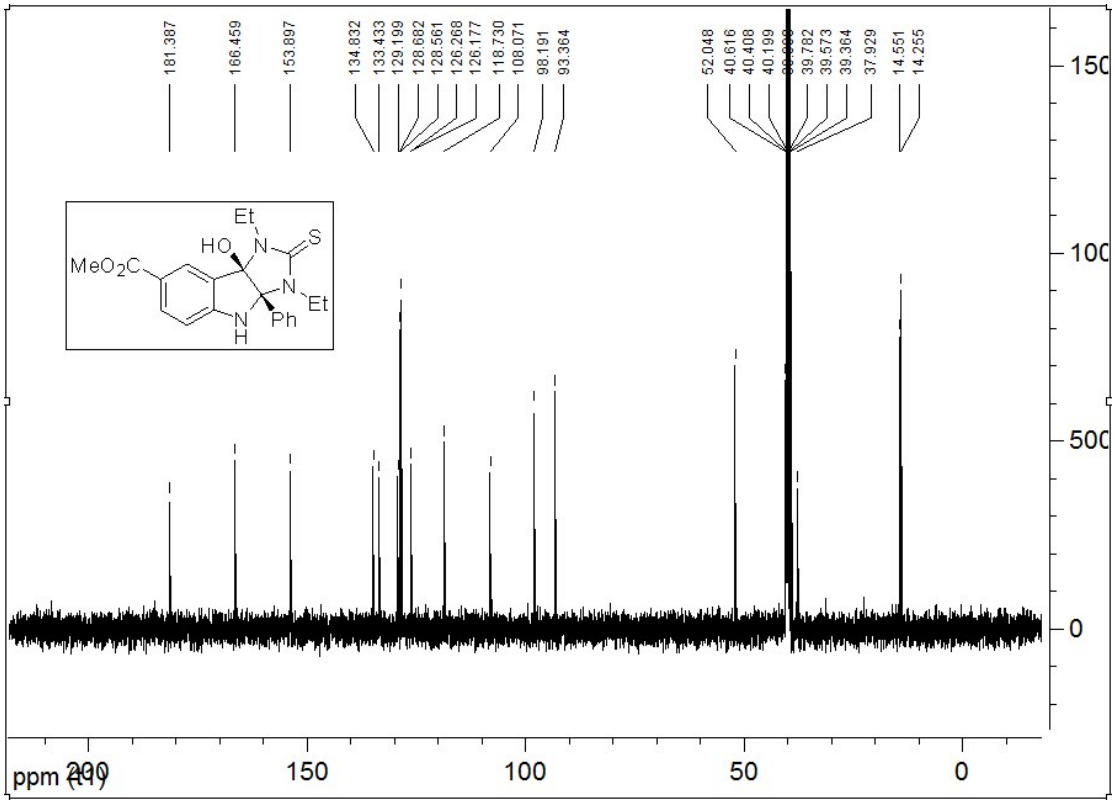
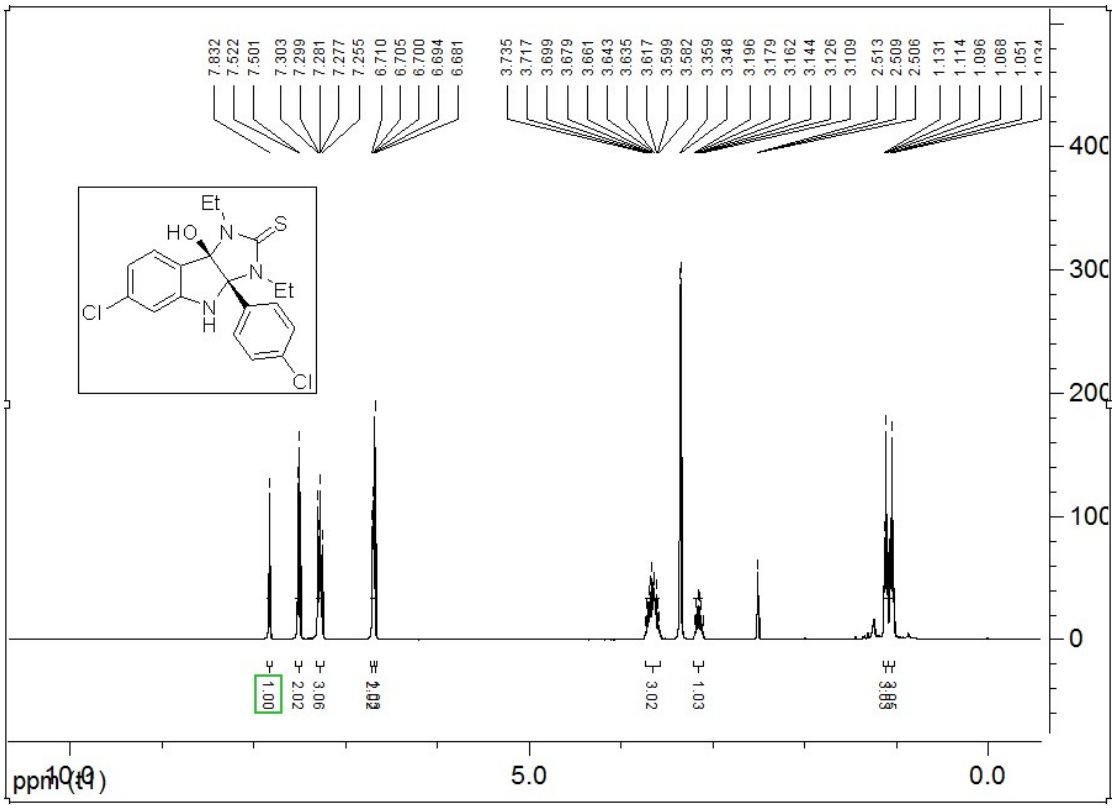


Figure 26. ^{1}H and ^{13}C NMR Spectra of ***cis*-6-chloro-3a-(4-chlorophenyl)-1,3-diethyl -8b-hydroxy-3,3a,4,8b-tetrahydroimidazo[4,5-b]indole-2(1H)-thione (4be)**



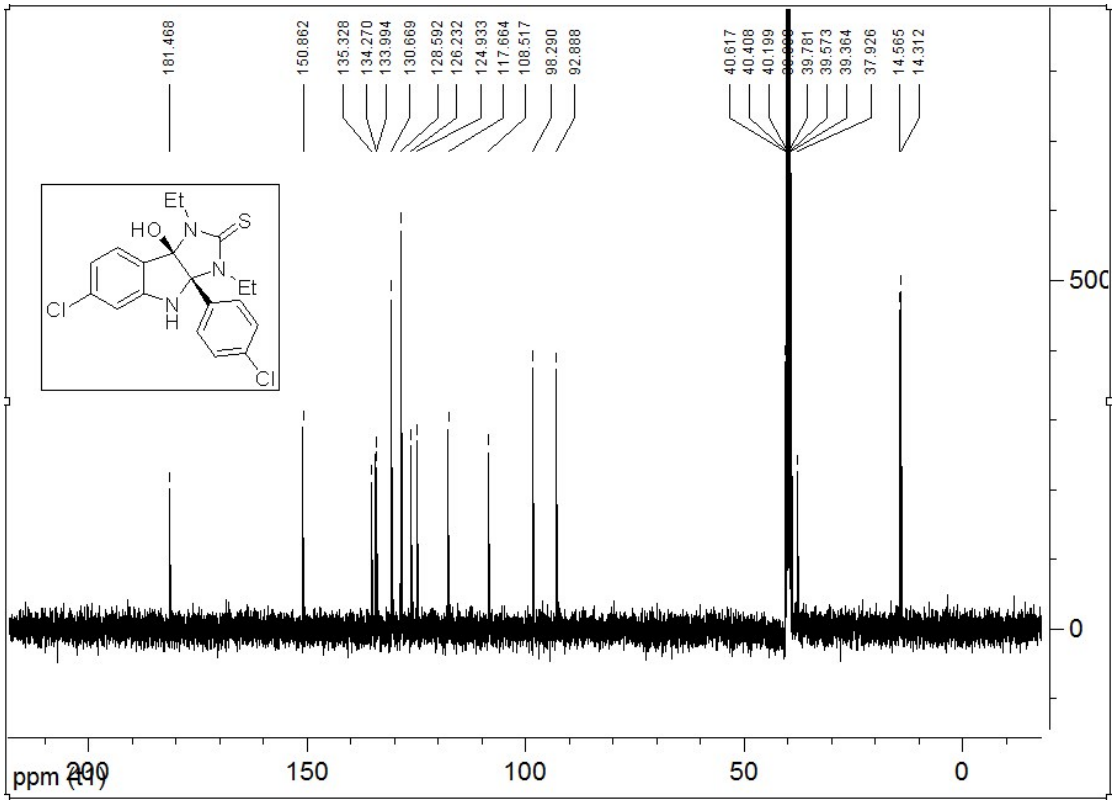
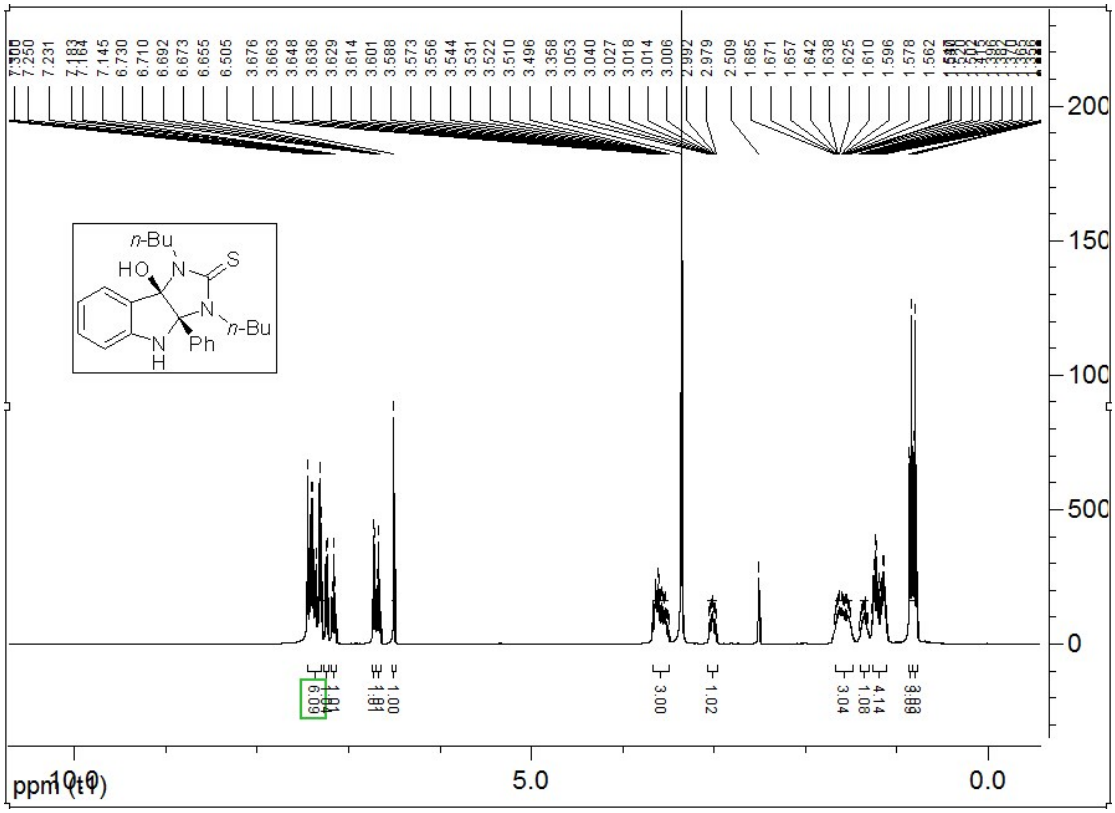


Figure 27. ^{1}H and ^{13}C NMR Spectra of ***cis*-1,3-Dibutyl-8b-hydroxy-3a-phenyl -3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4bf)**



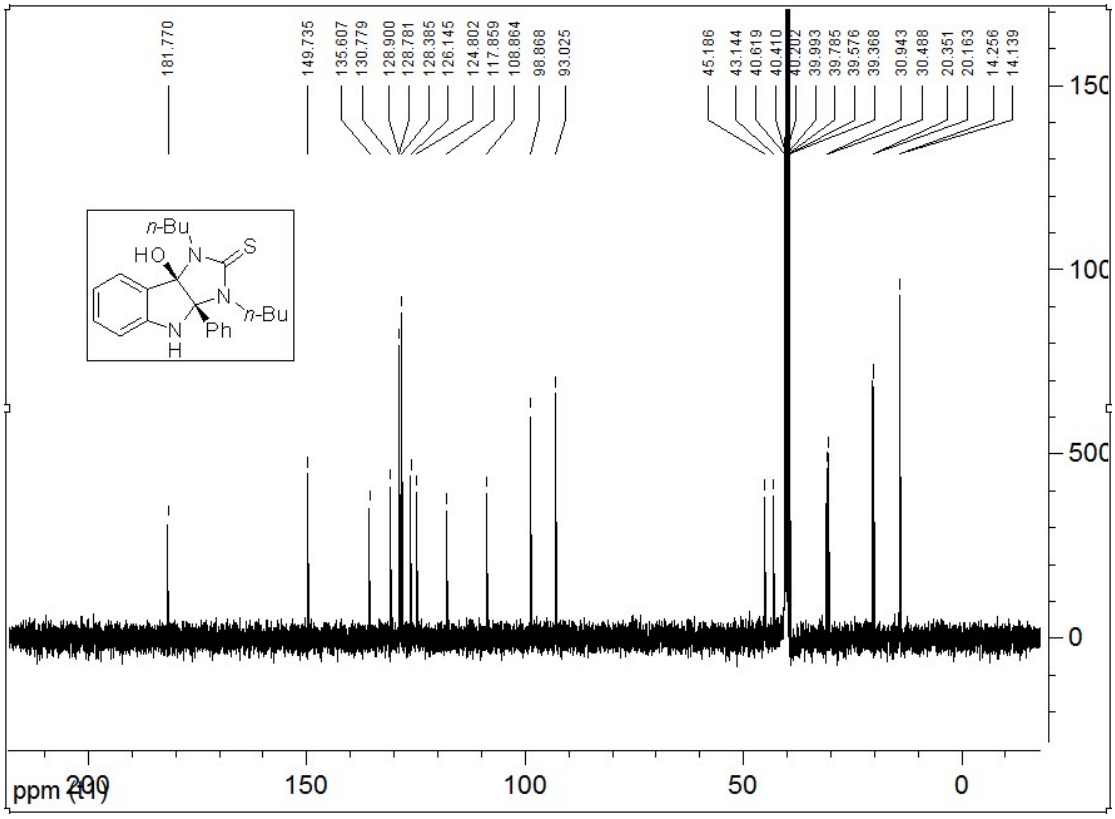
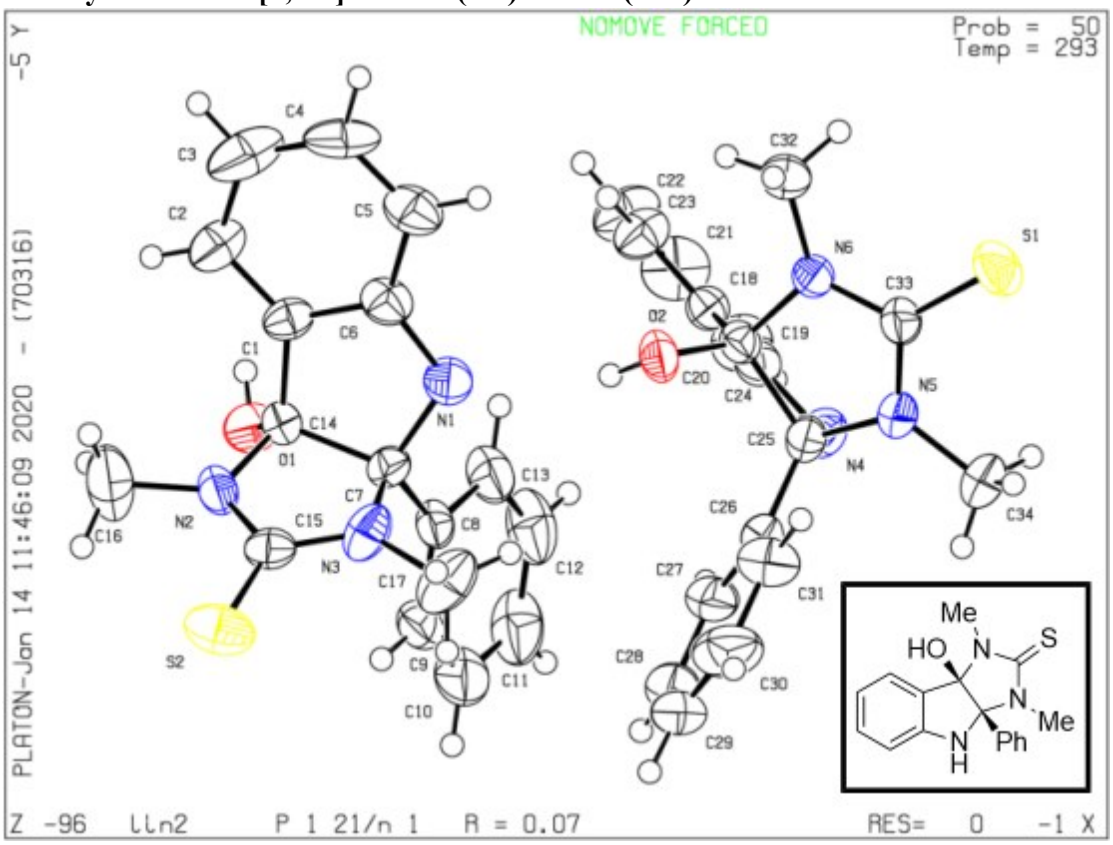


Figure 28. ORTEP Drawing of *cis*-**8b-hydroxy-1,3-dimethyl-3a-phenyl-3,3a,4,8b-tetrahydroimidazo[4,5-*b*]indole-2(1*H*)-thione (4ba)**



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alpha=90 beta=101.546(11) gamma=90
Temperature: 293 K

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Hall group	-P 2yn	-P 2yn
Moiety formula	C17 H16 N3 O S	C17 H16 N3 O S
Sum formula	C17 H16 N3 O S	C17 H16 N3 O S
Mr	310.39	310.39
Dx,g cm-3	1.304	1.304
Z	8	8
Mu (mm-1)	0.210	0.210
F000	1304.0	1304.0
F000'	1305.43	
h,k,lmax	11,25,17	11,25,17
Nref	5556	5554
Tmin,Tmax	0.971,0.977	0.715,1.000
Tmin'	0.971	

Correction method= # Reported T Limits: Tmin=0.715 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 24.999

R(reflections)= 0.0722(2915) wR2(reflections)= 0.1823(5554)

S = 1.059 Npar= 403