Supporting Information

Photocatalytical Aerobic α-Thiolation/Annulation of Carbonyls with Mercaptobenzimidazoles

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1. **General Information**

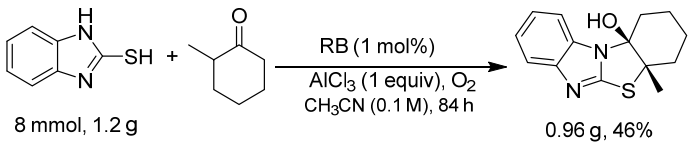
All reactions were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200 – 300 mesh). ^{1}H NMR, ^{13}C NMR spectra were recorded on Bruker-AV instrument (400 and 100 MHz, respectively), and chloroform and dimethyl sulfoxide are the solvent with TMS as the internal standard, with the chemical shifts referenced to signals at 7.26 and 77.16 ppm, 2.50 and 39.52 ppm, respectively. High-resolution mass spectra were recorded on thermo scientific LTQ orbitrap XL instrument. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. All reagents obtained from commercial suppliers were used without further purification.

2. Experimental procedure

General experimental procedure: 2-Mercaptobenzimidazole **1** (0.3 mmol, 1.0 equiv), carbonyl **2** (0.3 mmol, 1.0 equiv), $AlCl_3$ (0.3 mmol, 1 equiv) and Rose Bengal (1 mol%), and acetonitrile (3.0 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at room temperature under the irradiation by a 7 W blue LED with an oxygen balloon for 48 h. The reaction was monitored by TLC. After completion, 15 mL water was added, and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried with anhydrous Mg_2SO_4. After filtering, the solvent was evaporated under vacuum, and the crude product was purified by preparative TLC or column chromatography (silica gel, petroleum ether/ethyl acetate) to obtain the pure product.

Gram-scale synthesis of compound 3g

2-Mercaptobenzimidazole **1** (1.2 g, 8 mmol), Cyclohexanone **2** (0.78 g, 8 mmol), $AlCl_3$ (1.07 g, 8 mmol) and Rose Bengal (0.08 g, 1 mol%), and acetonitrile (80 mL) were added into a 100 mL Round-bottomed flask successively. The reaction mixture was stirred at room temperature under the irradiation by two 7 W blue LEDs with an oxygen balloon for 84 h. The reaction was monitored by TLC. After completion, 50 mL water was added, and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried with anhydrous Mg_2SO_4. After filtering, the solvent was evaporated under vacuum, and the crude product was purified by preparative TLC or column chromatography (silica gel, petroleum ether/ethyl acetate) to obtain the pure product.

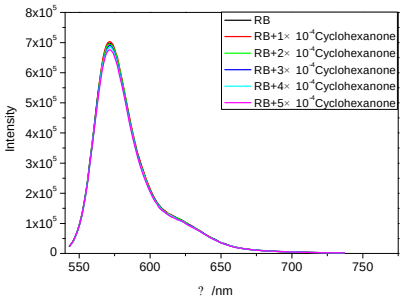


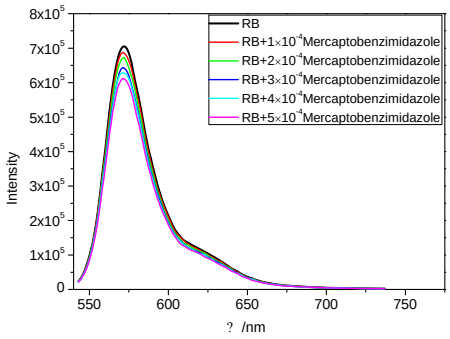
8 mmol, 1.2 g

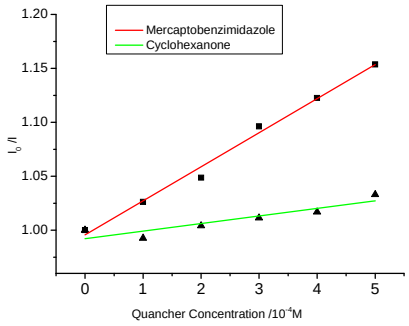
0.96 g, 46%

3. Luminescence quenching studies

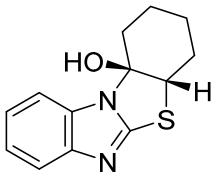
Emission intensities were recorded using a fluorescence spectrophotometer and collected at 571 nm (with a 5 nm slit width). In a typical experiment, to a 6*10 $^{-8}$ M solution of Rose Bengal in MeCN was added the appropriate amount of quencher in a quartz cuvette. The fluorescence quenching data were measured in the presence of five concentrations.[1]





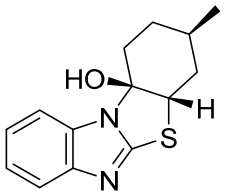


4. Characterization data of products



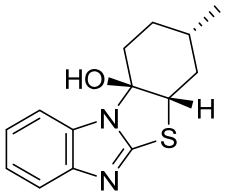
2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3a)[2]

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3a** (39 mg, 53%) as a white solid. mp: 161 – 164 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 – 7.58 (m, 1H), 7.48 – 7.46 (m, 1H), 7.17 – 7.12 (m, 3H), 4.26 (t, J = 5.2 Hz, 1H), 2.25 – 2.06 (m, 3H), 1.77 – 1.70 (m, 1H), 1.62 – 1.51 (m, 3H), 1.43 – 1.36 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ 155.2, 148.6, 132.6, 121.6, 121.4, 117.9, 109.8, 90.2, 57.6, 32.9, 28.8, 21.9, 21.0. HRMS (ESI) m/z calcd for $C_{13}H_{15}N_2OS^+$ $(M+H)^+$ 247.0900, found 247.0903.



(3R,4aS,11aS)-3-methyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3b (cis))

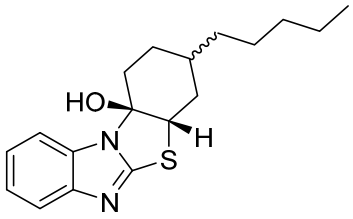
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) yielded **3b (cis)** (27 mg, 35%) as a white solid. mp: 158 – 160 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 – 7.57 (m, 1H), 7.48 – 7.46 (m, 1H), 7.34 (s, 1H), 7.14 – 7.12 (m, 2H), 4.50 – 4.49 (m, 1H), 2.18 (d, J = 12.6 Hz, 1H), 1.97 (d, J = 14.1 Hz, 1H), 1.82 – 1.52 (m, 4H), 1.27 – 1.17 (m, 1H), 0.95 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.5, 148.2, 132.6, 121.7, 121.4, 118.0, 109.7, 90.4, 56.3, 32.7, 32.0, 28.9, 26.6, 21.2. HRMS (ESI) m/z calcd for $C_{14}H_{17}N_2OS^+$ $(M+H)^+$ 261.1056, found 261.1059.



(3S,4aS,11aS)-3-methyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3b (trans))

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) yielded **3b (trans)** (15 mg, 19%) as a white solid. mp: 158 – 160 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ

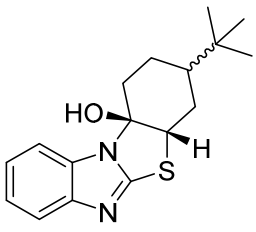
7.59 – 7.57 (m, 1H), 7.48 – 7.46 (m, 1H), 7.15 – 7.12 (m, 2H), 6.77 (s, 1H), 3.96 (dd, *J* = 11.6, 5.6 Hz, 1H), 3.09 (d, *J* = 14.8 Hz, 1H), 2.31 (d, 12.4 Hz, 1H), 2.05 (td, *J* = 13.2, 3.2 Hz, 1H), 1.74 (d, *J* = 13.6 Hz, 1H), 1.25 – 1.23 (m, 1H), 1.13 – 1.07 (m, 1H), 0.97 – 0.93 (m, 1H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.5, 149.2, 132.9, 122.2, 122.0, 118.2, 110.1, 89.8, 60.1, 43.9, 33.9, 31.5, 30.4, 21.5.



(dr = 2.3:1)

3-pentyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3c)

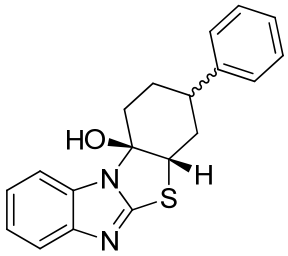
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3c** (54.8 mg, 58%) as a white solid. mp: 163 – 167 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 – 7.56 (m, 1H), 7.47 – 7.44 (m, 1H), 7.31 (s, 0.7H), 7.15 – 7.10 (m, 2H), 6.79 (s, 0.3H), 4.49 (s, 0.7H), 3.96 (dd, *J* = 11.6, 5.6 Hz, 0.3H), 2.39 – 2.33 (m, 0.3H), 2.19 (d, *J* = 13.6 Hz, 0.7H), 2.00 – 1.97 (m, 1H), 1.77 – 1.57 (m, 3H), 1.31 – 1.18 (m, 9.1H), 0.88 – 0.81 (m, 3.9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.0, 152.7, 149.2, 149.0, 148.2, 132.7, 132.6, 121.7, 121.5, 118.0, 109.8, 109.7, 90.6, 89.7, 59.9, 56.4, 55.3, 41.7, 40.5, 36.1, 36.0, 35.4, 35.2, 34.9, 33.6, 32.9, 31.9, 31.6, 31.5, 31.4, 31.1, 28.1, 26.8, 26.3, 26.0, 22.2, 22.1, 14.0, 14.0. HRMS (ESI) m/z calcd for $C_{18}H_{25}N_2OS^+$ $(M+H)^+$ 317.1682, found 317.1682.



(dr = 4:1)

3-(tert-butyl)-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3d)

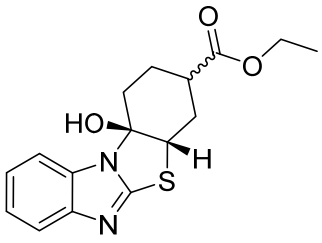
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3d** (49.7 mg, 55%) as a white solid. mp: 193 – 197 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 – 7.57 (m, 1H), 7.48 – 7.46 (m, 1H), 7.35 (s, 0.2H), 7.17 – 7.13 (m, 2H), 6.80 (s, 0.8H), 3.98 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.11 (dt, *J* = 14.8, 3.6 Hz, 1H), 2.41 – 2.36 (m, 1H), 2.08 – 2.00 (m, 1H), 1.85 – 1.81 (m, 1H), 1.34 – 1.28 (m, 1H), 1.19 – 1.10 (m, 1H), 0.96 – 0.91 (m, 1H), 0.87 (s, 1.8H), 0.78 (s, 7.2H). ^{13}C NMR (100 MHz, DMSO) δ 159.1, 152.5, 149.2, 149.1, 148.2, 132.7, 132.6, 121.8, 121.8, 121.5, 121.4, 121.3, 118.0, 109.9, 109.7, 90.3, 89.5, 60.7, 57.2, 55.6, 46.3, 46.2, 41.1, 40.6, 40.2, 40.0, 36.7, 36.6, 34.0, 32.5, 32.3, 32.2, 32.0, 27.9, 27.6, 27.5, 27.3, 27.3, 25.7, 23.0, 21.5. HRMS (ESI) m/z calcd for $C_{17}H_{23}N_2OS^+$ $(M+H)^+$ 303.1526, found 303.1527.



(dr = 1.5:1)

3-phenyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3e)

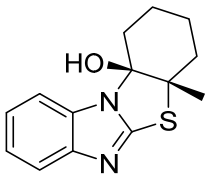
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3e** (40.6 mg, 42%) as a white solid. mp: 164 – 166 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 – 7.61 (m, 1H), 7.51 – 7.49 (m, 1H), 7.35 – 7.32 (m, 4H), 7.24 – 7.21 (m, 1H), 7.17 – 7.14 (m, 2H), 4.66 – 4.64 (m, 1H), 3.04 – 2.98 (m, 1H), 2.33 – 2.23 (m, 2H), 2.16 (d, *J* = 15.2 Hz, 1H), 1.85 – 1.72 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.3, 148.2, 145.0, 132.6, 128.6, 127.0, 126.5, 121.8, 121.5, 118.1, 109.7, 90.2, 56.5, 37.6, 32.5, 31.6, 28.3. HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2OS^+$ $(M+H)^+$ 323.1213, found 323.1216.



(dr = 1.5:1)

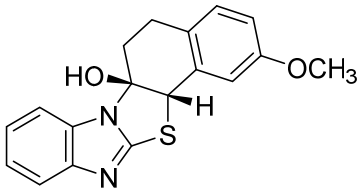
Ethyl-11a-hydroxy-1,2,3,4,4a,11a-hexahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazole-3-carboxylate (3f)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3f** (46.6 mg, 49%) as a white solid. mp: 166 – 171 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 – 7.57 (m, 1H), 7.51 – 7.46 (m, 1H), 7.41 (s, 0.6H), 7.17 – 7.13 (m, 2H), 7.00 (s, 0.4H), 4.49 (t, J = 4.4 Hz, 0.6H), 4.13 – 4.09 (m, 1.2H), 4.09 – 4.07 (m, 0.4H), 4.02 – 3.99 (m, 0.8H), 2.97 (dt, J = 15.2, 4.0 Hz, 0.4H). 2.70 – 2.67 (m, 0.6H), 2.27 – 1.89 (m, 4H), 1.78 – 1.67 (m, 1H), 1.62 – 1.53 (m, 0.6H), 1.38 – 1.35 (m, 0.4H), 1.20 (t, J = 7.2 Hz, 1.8H), 1.14 (t, J = 7.2 Hz, 1.2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.0, 173.4, 158.0, 153.4, 149.0, 148.4, 132.6, 132.6, 121.9, 121.7, 121.6, 118.1, 109.9, 109.8, 89.9, 89.3, 60.4, 60.3, 58.5, 55.8, 40.2, 40.0, 39.8, 37.4, 35.7, 32.1, 31.1, 28.2, 24.2, 23.5, 14.2, 14.1. HRMS (ESI) m/z calcd for $C_{16}H_{19}N_2O_3S^+$ $(M+H)^+$ 319.1111, found 319.1117.



4a-methyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3g)

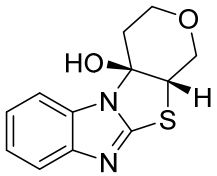
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3g** (40.6 mg, 52%) as a white solid. mp: 187 – 192 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 – 7.59 (m, 1H), 7.48 – 7.46 (m, 1H), 7.15 – 7.12 (m, 2H), 6.91 (s, 1H), 2.73 (dt, J = 14.8, 4.2 Hz, 1H), 2.16 (dt, J = 14.0, 4.4 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.78 – 1.68 (m, 2H), 1.60 (s, 3H), 1.54 – 1.49 (m, 2H), 1.27 – 1.20 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.5, 148.4, 133.0, 121.7, 121.4, 117.9, 109.9, 91.3, 67.1, 40.4, 31.7, 22.6, 22.0, 19.9. HRMS (ESI) m/z calcd for $C_{14}H_{17}N_2OS^+$ $(M+H)^+$ 261.1056, found 261.1055.



2-methoxy-5,13a-dihydrobenzo[4,5]imidazo[2,1-b]naphtho[2,1-d]thiazol-6a(6H)-ol (3h)

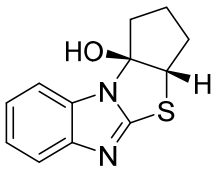
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3h** (47.9 mg, 49%) as a white solid. mp: 150 – 152 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 –

7.65 (m, 1H), 7.55 (s, 1H), 7.51 – 7.48 (m, 1H), 7.19 – 7.16 (m, 2H), 7.11 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 6.84 (dd, J = 8.4, 2.4 Hz, 1H), 5.53 (s, 1H), 3.75 (s, 3H), 2.87 (ddd, J = 16.0, 8.4, 4.8 Hz, 1H), 2.65 – 2.54 (m, 2H), 2.29 (ddd, J = 12.4, 7.2, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.1, 154.2, 148.9, 134.5, 132.2, 129.7, 127.6, 121.9, 121.6, 118.1, 114.4, 114.2, 109.8, 90.1, 59.6, 55.3, 30.9, 25.0. HRMS (ESI) m/z calcd for $C_{18}H_{17}N_2O_2S^+$ $(M+H)^+$ 325.1005, found 325.1010.



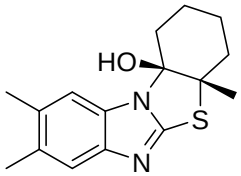
1,3,4,11a-tetrahydro-4aH-benzo[4,5]imidazo[2,1-b]pyrano[4,4,3-d]thiazol-4a-ol (3i)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3i** (30 mg, 40%) as a white solid. mp: 184 – 188 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 – 7.59 (m, 1H), 7.51 – 7.48 (m, 1H), 7.23 (s, 1H), 7.19 – 7.12 (m, 2H), 4.18 (dd, J = 12, 5.2 Hz, 1H), 4.10 (dd, J = 8.4, 5.6 Hz, 1H), 3.87 (dt, J = 12, 4.4 Hz, 1H), 3.34 – 3.29 (m, 2H), 2.81 (ddd, J = 14.4, 4.4, 2.8 Hz, 1H), 2.26 – 2.20 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.9, 149.1, 132.5, 122.0, 121.7, 118.2, 110.1, 87.6, 69.0, 63.9, 56.4, 34.0. HRMS (ESI) m/z calcd for $C_{12}H_{13}N_2O_2S^+$ $(M+H)^+$ 249.0692, found 249.0693.



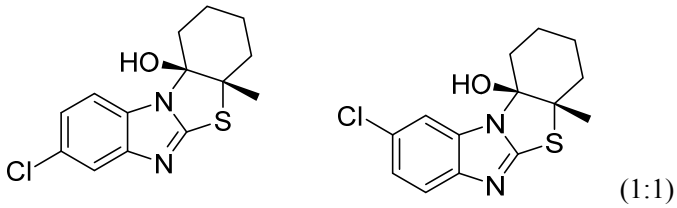
1,2,3,3a-tetrahydro-10aH-benzo[4,5]imidazo[2,1-b]cyclopenta[d]thiazol-10a-ol (3j)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3j** (31.5 mg, 45%) as a white solid. mp: 157 – 161 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 – 7.45 (m, 2H), 7.35 (s, 1H), 7.16 – 7.13 (m, 2H), 4.38 (dd, J = 8.0, 4.4 Hz, 1H), 2.47 – 2.38 (m, 2H), 2.29 – 2.22 (m, 1H), 1.89 – 1.79 (m, 2H), 1.67 – 1.58 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.4, 149.7, 131.7, 121.7, 121.2, 117.9, 109.5, 98.2, 62.0, 38.2, 35.9, 24.2.



4a,8,9-trimethyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3k)

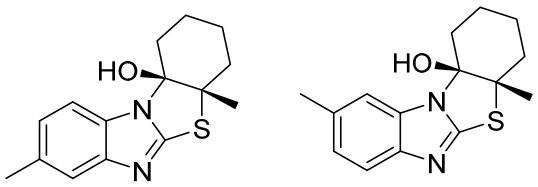
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3k** (34.6 mg, 40%) as a white solid. mp: 217 – 221 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (s, 1H), 7.24 (s, 1H), 6.72 (s, 1H), 2.72 (d, J = 15.2 Hz, 1H), 2.27 (d, J = 13.2 Hz, 6H), 2.15 (d, J = 14.4 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.76 – 1.68 (m, 2H), 1.58 (s, 3H), 1.52 – 1.47 (m, 2H), 1.22 – 1.17 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.7, 147.0, 131.5, 130.0, 129.9, 118.3, 110.3, 91.2, 67.1, 40.9, 31.7, 22.7, 22.3, 20.1, 19.9, 19.7. HRMS (ESI) m/z calcd for $C_{16}H_{21}N_2OS^+$ $(M+H)^+$ 289.1369, found 289.1371.



(1:1)

8-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol and 9-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (3l and **3l')**

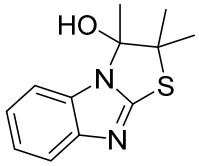
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3l** and **3l'** (51.7 mg, 59%) as a white solid. mp: 215 – 217 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (s, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.54 (s, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.20 – 7.16 (m, 2H), 6.96 – 6.94 (m, 2H), 2.71 – 2.67 (m, 2H), 2.19 – 2.14 (m, 2H), 2.01 (t, J = 12.8 Hz, 2H), 1.80 – 1.68 (m, 4H), 1.60 (s, 6H), 1.52 (s, 4H), 1.23 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.5, 157.7, 149.3, 147.1, 133.4, 131.7, 126.2, 125.9, 121.9, 121.3 118.9, 117.4, 110.8, 109.7, 91.5, 91.5, 67.3, 67.1, 40.3, 31.6, 31.5, 22.5, 22.4, 21.9, 20.0, 19.7. HRMS (ESI) m/z calcd for $C_{14}H_{16}ClN_2OS^+$ $(M+H)^+$ 295.0666, found 295.0670.



(1:1)

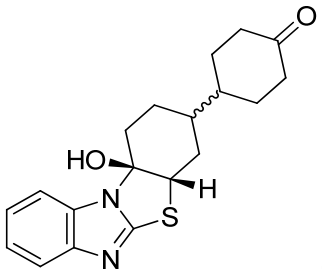
4a,8-dimethyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol) and 4a,9-dimethyl-2,3,4,4a-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-11a(1H)-ol (1:1) (3m and **3m')**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3m** and **3m'** (45.7 mg, 56%) as a white solid. mp: 196 – 201 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 1.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 1.6 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.80 (s, 2H), 2.73 – 2.68 (m, 2H), 2.39 (s, 3H), 2.36 (s, 3H), 2.18 – 2.14 (m, 2H), 2.03 – 1.94 (m, 2H), 1.77 – 1.68 (m, 4H), 1.58 (s, 6H), 1.52 – 1.46 (m, 4H), 1.24 – 1.17 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.7, 156.1, 148.8, 146.5, 133.3, 131.1, 130.9, 130.9, 123.1, 122.7, 118.0, 117.6, 110.0, 109.4, 91.3, 91.3, 67.2, 67.1, 40.78, 40.7, 31.7, 31.7, 22.7, 22.7, 22.2, 21.5, 21.2, 19.8, 19.7. HRMS (ESI) m/z calcd for $C_{15}H_{19}N_2OS^+$ $(M+H)^+$ 275.1213, found 275.1214.



2,2,3-trimethyl-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (3n)

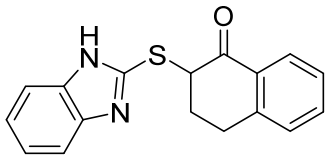
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1) yielded **3n** (20 mg, 29%) as a white solid. mp: 176 – 178 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 – 7.59 (m, 1H), 7.47 – 7.44 (m, 1H), 7.14 – 7.12 (m, 2H), 6.94 (s, 1H), 1.83 (s, 3H), 1.58 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.5, 133.0, 121.7, 121.2, 117.9, 110.1, 92.0, 66.5, 27.1, 25.0, 23.1, 20.6. HRMS (ESI) m/z calcd for $C_{12}H_{15}N_2OS^+$ $(M+H)^+$ 235.0900, found 235.0902.



(dr = 1:1)

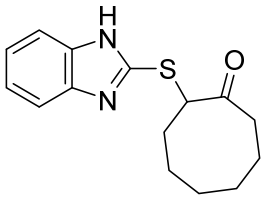
11a-hydroxy-1,2,3,4,4a,11a-hexahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazol-3-yl)cyclohexan-1-one (3o)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3o** (35 mg, 34%) as a white solid. mp: 190 – 196 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 – 7.57 (m, 1H), 7.48 – 7.46 (m, 1H), 7.33 (s, 0.5H), 7.16 – 7.11 (m, 2H), 6.80 (s, 0.5H), 4.55 (s, 0.5H), 4.01 – 3.97 (m, 0.5H), 3.14 – 3.09 (d, *J* = 14.8 Hz, 0.5H), 2.41 – 2.34 (m, 1.5H), 2.30 – 2.09 (m, 4H), 2.06 – 2.00 (m, 1H), 1.98 – 1.80 (m, 3H), 1.74 – 1.62 (m, 2H), 1.59 – 1.52 (m, 1H), 1.48 – 1.29 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 211.0, 211.0, 158.9, 152.7, 149.2, 148.2, 132.7, 132.5, 121.7, 121.5, 121.4, 118.0, 109.8, 109.7, 90.4, 89.5, 60.1, 56.7, 40.4, 40.2, 40.0, 39.9, 39.0, 35.4, 33.6, 32.1, 29.2, 29.0, 28.9, 28.4, 25.2, 23.9, 20.8, 14.1. HRMS (ESI) m/z calcd for $C_{19}H_{23}N_2O_2S^+$ $(M+H)^+$ 343.1475, found 343.1478.



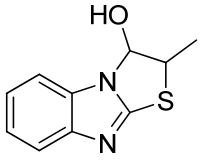
2-((1H-benzo[d]imidazol-2-yl)thio)-3,4-dihydronaphthalen-1(2H)-one (3p)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3p** (41.2 mg, 47%) as a white solid. mp: 180 – 181 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.67 (s, 1H), 7.90 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.61 (td, *J* = 7.6, 1.6 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.16 – 7.11 (m, 2H), 5.05 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.23 – 3.15 (m, 1H), 3.08 (dt, *J* = 17.2, 4.8 Hz, 1H), 2.70 – 2.63 (m, 1H), 2.43 – 2.33 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.0, 148.0, 143.9, 134.1, 131.3, 129.1, 127.1, 126.9, 121.6, 52.9, 30.4, 28.0. HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2OS^+$ $(M+H)^+$ 295.0900, found 295.0903.



2-((1H-benzo[d]imidazol-2-yl)thio)cyclooctan-1-one (3q)

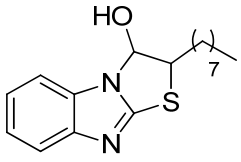
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **3q** (39.6 mg, 48%) as a white solid. mp: 124 – 125 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.58 (s, 1H), 7.51 – 7.49 (m, 1H), 7.37 – 7.35 (m , 1H), 7.13 – 7.10 (m, 2H), 4.91 (dd, *J* = 10.0, 3.6 Hz, 1H), 2.85 (ddd, *J* = 11.6, 8.4, 3.2 Hz, 1H), 2.41 – 2.30 (m, 2H), 2.07 – 1.87 (m, 2H), 1.79 – 1.68 (m, 2H), 1.60 – 1.47 (m, 4H), 1.11 – 1.01 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 212.4, 148.6, 132.3, 122.3, 121.6, 109.5, 54.4, 40.6, 31.1, 26.5, 25.5, 24.4, 24.0. HRMS (ESI) m/z calcd for $C_{15}H_{19}N_2OS^+$ $(M+H)^+$ 275.1213, found 275.1217.



(dr = 1.5:1)

2-methyl-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (5a)[3]

Purification by TLC (petroleum ether/ethyl acetate = 3/1) yielded **5a** (30.6 mg, 50%) as a white solid. mp: 188 – 195 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 – 7.44 (m, 2H), 7.30 (d, *J* = 6.4 Hz, 0.6H), 7.18 – 7.12 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 0.4H), 6.05 (dd, *J* = 6.0, 4.8 Hz, 0.4H), 5.89 (dd, *J* = 6.4, 2 Hz, 0.6H), 4.73 – 4.67(m, 0.4H), 4.20 (qd, *J* = 7.2, 2.4 Hz, 0.6H), 1.52 (m, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.3, 156.8, 149.0, 148.5, 133.0, 132.9, 121.9, 121.8, 121.5, 121.5, 117.8, 117.8, 110.2, 110.2, 84.4, 79.2, 55.8, 52.7, 20.7, 14.1.

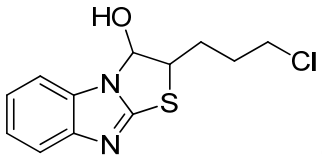


(dr = 1.2:1)

2-octyl-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (5b)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **5b** (30 mg, 45%) as a white solid. mp: 118 – 123 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 – 7.44 (m, 2H), 7.32 (d, *J* = 6.8, 0.45H), 7.18 – 7.12 (m, 2H), 7.06 (d, *J* = 6.8 Hz, 0.55H), 6.10 (dd, *J* = 7.2, 5.2 Hz, 0.55H), 5.97 (dd, *J* = 8.5, 2.4 Hz, 0.45H), 4.63 (ddd, *J* = 8.8, 6.4, 4.9 Hz, 0.55H),

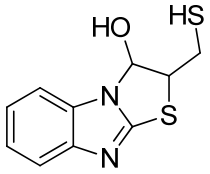
4.17 – 4.12 (m, 0.45H), 2.02 – 1.66 (m, 2H), 1.49 – 1.24 (m, 12H), 0.88 – 0.83 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.9, 156.5, 149.0, 148.5, 133.0, 132.8, 121.8, 121.5, 121.4, 117.8, 117.8, 110.2, 110.1, 83.2, 78.5, 61.4, 58.5, 34.3, 31.4, 31.3, 29.0, 28.9, 28.9, 28.7, 27.9, 26.8, 22.2, 22.2, 14.1, 14.0. HRMS (ESI) m/z calcd for $C_{17}H_{25}N_2OS^+$ $(M+H)^+$ 305.1682, found 305.1686.



(dr = 1.5:1)

2-(3-chloropropyl)-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (5c)

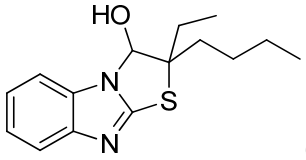
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **5c** (32.7 mg, 41%) as a white solid. mp: 187 – 188 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 – 7.45 (m, 2H), 7.33 (d, J = 6.4 Hz, 0.6H), 7.18 – 7.12 (m, 2.4H), 6.14 (dd, J = 6.8, 4.8Hz, 0.4H), 6.02 (dd, J = 6.8, 2.4 Hz, 0.6H), 4.68 (td, J = 6.8, 4.4Hz, 0.4H), 4.24 – 4.20 (m, 0.6H), 3.75 (t, J = 6.0 Hz, 0.8H), 3.70 (t, J = 6.4 Hz, 1.2H), 2.16 – 1.82 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.7, 156.5, 149.0, 148.5, 132.9, 139.8, 121.9, 121.8, 121.5, 121.4, 117.9, 117.8, 110.2, 110.2, 82.9, 78.3, 60.7, 57.5, 45.0, 44.9, 31.8, 30.7, 29.7, 26.5. HRMS (ESI) m/z calcd for $C_{12}H_{14}ClN_2OS^+$ $(M+H)^+$ 269.0510, found 269.0515.



(dr > 20:1)

2-(mercaptomethyl)-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (5d)

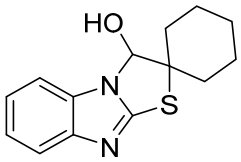
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) yielded **5d** (50 mg, 70%) as a white solid. mp: 223 – 233 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 – 7.52 (m, 1H), 7.46 – 7.42 (m, 1H), 7.18 – 7.13 (m, 2H), 6.96 (d, J = 6.4 Hz, 1H), 6.08 – 6.05 (m, 1H), 3.52 (td, J = 12.4, 2.4 Hz, 1H), 3.12 (ddd, J = 12.8, 5.2, 3.2 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.27 – 2.18 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.5, 142.5, 134.8, 122.1, 121.0, 117.1, 109.8, 73.2, 30.7, 20.0.



(dr = 1:1)

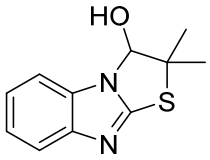
2-butyl-2-ethyl-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (5e)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **5e** (37.5 mg, 45%) as **c**olorless liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 – 7.44 (m, 2H), 7.18 – 7.11 (m, 3H), 5.85–5.77 (m, 1H), 2.12 – 1.88 (m, 3H), 1.80 – 1.65 (m, 1H), 1.33 – 1.23 (m, 4H), 1.02 – 0.82 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.4, 156.3, 148.4, 133.0, 133.0, 121.7, 121.4, 117.7, 110.2, 110.2, 82.9, 82.6, 73.5, 73.4, 37.1, 32.2, 30.8, 27.0, 26.31, 25.9, 22.8, 22.4, 13.9, 13.8, 9.7, 9.0. HRMS (ESI) m/z calcd for $C_{15}H_{21}N_2OS^+$ $(M+H)^+$ 277.1369, found 277.1370.



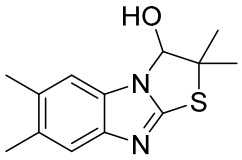
3H-spiro[benzo[4,5]imidazo[2,1-b]thiazole-2,1'-cyclohexan]-3-ol (5f)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **5f** (40.6 mg, 52%) as a white solid. mp: 210 – 218 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 – 7.45 (m, 2H), 7.18 – 7.11 (m, 3H), 5.81 (d, J = 5.6 Hz, 1H), 2.15 – 2.11 (m, 1H), 1.93 – 1.86 (m, 1H), 1.84 – 1.70 (m, 4H), 1.68 – 1.62 (m, 2H), 1.39 – 1.27 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.4, 148.5, 133.3, 121.8, 121.4, 117.8, 110.3, 83.9, 71.6, 37.5, 32.1, 24.8, 24.0, 23.2. HRMS (ESI) m/z calcd for $C_{14}H_{17}N_2OS^+$ $(M+H)^+$ 261.1056, found 261.1056.



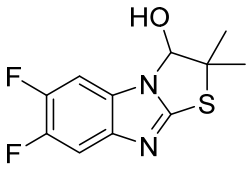
2,2-dimethyl-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (5g)

Purification by TLC (petroleum ether/ethyl acetate = 3/1) yielded **5g** (30 mg, 47%) as a white solid. mp: 238 – 239 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 – 7.45 (m, 2H), 7.28 (d, J = 6.4 Hz, 1H), 7.18 – 7.12 (m, 2H), 5.70 (d, J = 6.4 Hz, 1H), 1.59 (d, J = 3.6 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.9, 148.4, 133.4, 122.1, 121.7, 117.9, 110.4, 85.1, 65.0, 30.0, 23.1. HRMS (ESI) m/z calcd for $C_{11}H_{13}N_2OS^+$ $(M+H)^+$ 221.0743, found 221.0747.



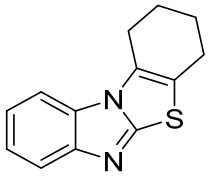
2,2,6,7-tetramethyl-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (5h)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **5h** (31.8 mg, 43%) as a white solid. mp: 238 – 248 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.25 – 7.23 (m, 2H), 7.13 (dd, J = 6.8, 1.6 Hz, 1H), 5.62 (dd, J = 7.2, 2.4 Hz, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.57 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 155.4, 146.9, 131.7, 129.8, 129.7, 118.2, 110.6, 84.7, 64.7, 29.9, 23.0, 20.0, 19.9. HRMS (ESI) m/z calcd for $C_{13}H_{17}N_2OS^+$ $(M+H)^+$ 249.1056, found 249.1052.



6,7-difluoro-2,2-dimethyl-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol (5i)

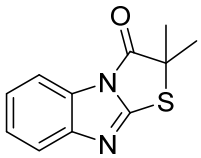
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) yielded **5i** (31.4 mg, 41%) as a white solid. mp: 240 – 245 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 – 7.54 (m, 2H), 7.39 (s, 1H), 5.73 (d, J = 4.0 Hz, 1H), 1.60 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.3, 146.3 (dd, J = 235, 12 Hz), 145.8 (dd, J = 236, 15 Hz), 143.7 (d, J = 10 Hz), 128.8 (d, J = 8 Hz), 105.5 (d, J = 20 Hz), 99.2 (d, J = 23 Hz), 85.1 (d, J = 4 Hz), 64.8 (d, J = 5 Hz), 29.7, 22.9. HRMS (ESI) m/z calcd for $C_{11}H_{11}F_2N_2OS^+$ $(M+H)^+$ 257.0555, found 257.0556.



1,2,3,4-tetrahydrobenzo[d]benzo[4,5]imidazo[2,1-b]thiazole (6a) [4]

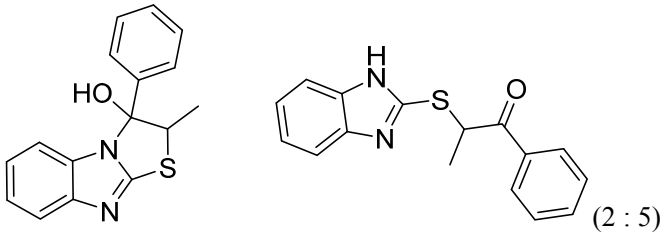
A solution of 100 mg (0.4 mmol) of **3a** in 1.5 mL of concentrated hydrochloric with water and neutralised with sodium bicarbonate. Extraction with $CHCl_3$ and removal of the solvent gave 94 mg of the product (90 mg, 99%) as white solid. mp: 150 – 153 °C. ^{1}H NMR (400 MHz,

Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.21 – 7.16 (m, 1H), 3.05 – 3.02 (m, 2H), 2.72 – 2.68 (m, 2H), 2.06 – 2.00 (m, 2H), 1.98 – 1.92 (m, 2H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.7, 147.8, 130.1, 127.3, 122.8, 120.5, 119.2, 119.0, 110.5, 24.4, 23.3, 22.7, 21.8.



2,2-dimethylbenzo[4,5]imidazo[2,1-b]thiazol-3(2H)-one (6b)[4]

To a solution of compound **5b** (33 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was added PCC (65 mg, 0.75 mmol).Then, the reaction mixture was stirred for 24 h at room temperature. Purification by TLC (petroleum ether/ethyl acetate = 5/1) yielded **1** (20 mg, 60%) as as colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 1H), 7.62 (dt, *J* = 8, 0.8 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 1.87 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 155.8, 149.9, 130.2, 126.1, 124.0, 119.2, 112.8, 61.4, 28.2. HRMS (ESI) m/z calcd for $C_{11}H_{11}N_2OS^+$ $(M+H)^+$ 219.0587, found 219.0585.


(2 : 5)

2-((1H-benzo[d]imidazol-2-yl)thio)-1-phenylpropan-1-one and

2-methyl-3-phenyl-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazol-3-ol

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) yielded 28 mg (33%) as a white solid. mp: 114 – 118 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.66 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.46 (m, 6H), 7.39 – 7.37 (m, 0.8H), 7.15 – 7.13 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 0.4H), 6.90 (t, *J* = 7.6 Hz, 0.4H), 6.32 (d, *J* = 8.0 Hz, 0.4H), 5.77 (dd, *J* = 14.0, 6.8 Hz, 1H), 4.68 – 4.62 (m, 0.4H), 1.63 (d, *J* = 7.2 Hz, 3H), 1.37 (d, *J* = 6.8 Hz, 1.2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.0, 147.8, 134.6, 133.7, 129.0, 128.9, 128.6, 126.5, 126.2, 121.7, 121.0, 118.0, 110.0, 90.6, 59.8, 59.1, 45.5, 20.8, 18.4, 14.1, 12.3. HRMS (ESI) m/z calcd for $C_{16}H_{15}N_2OS^+$ $(M+H)^+$ 283.0900, found 283.0903.

5. References

[1]. R. Mao, A. Frey, J. Balon, X. Hu, *Nat. Cat.* **2018**, *1*, 120–126.

[2]. D. Martin, F. Tittelbach, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 0, 1007-1013.

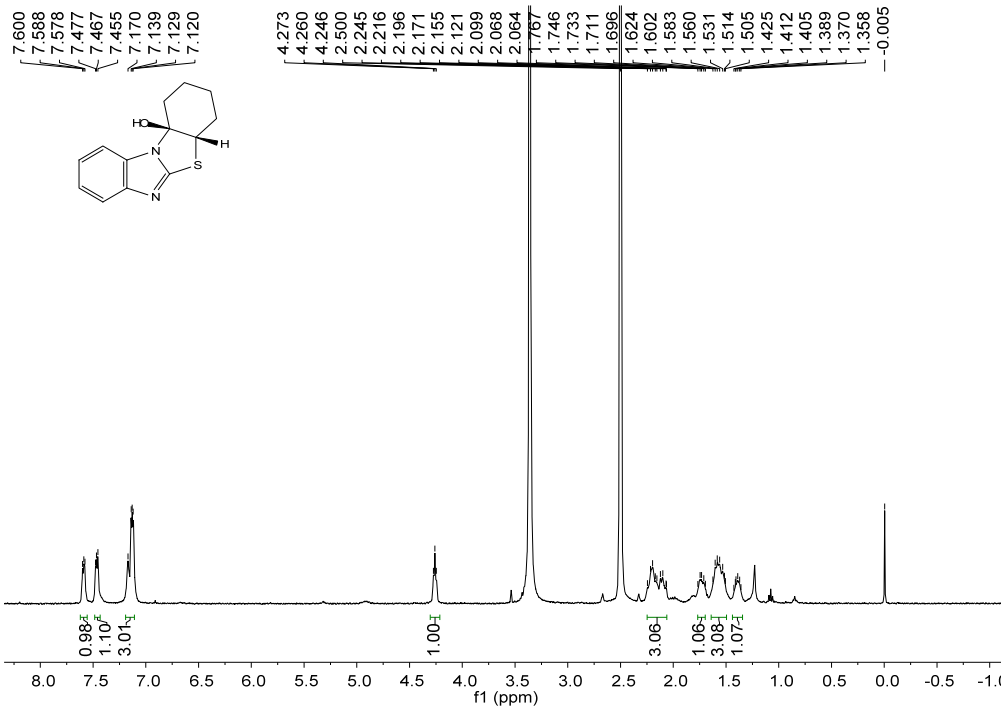
[3] Anne E. Alper, A. Taurins, *Canadian J. Chem.* **1967**, 45, 2903-2912.

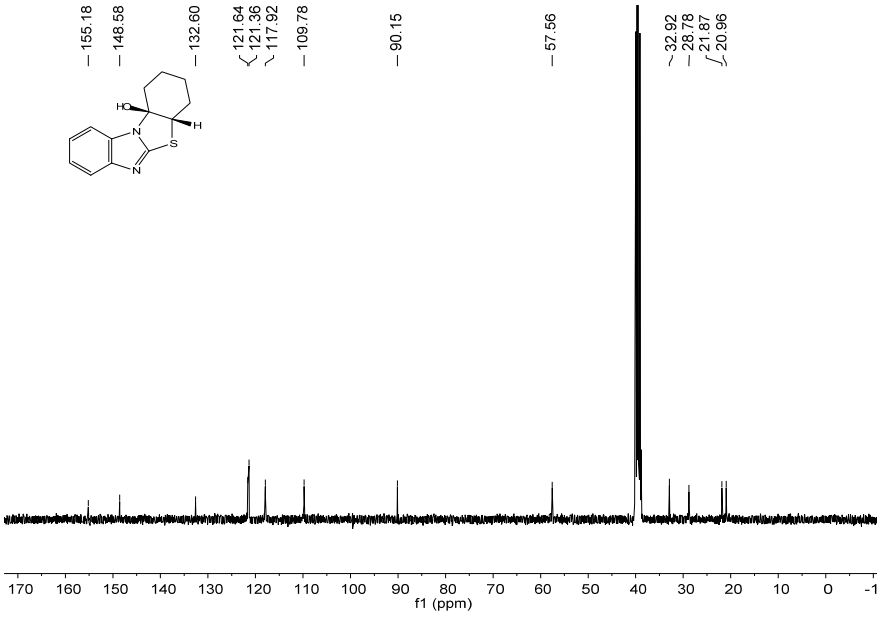
[4]. F. Tittelbach, S. Vieth, M. Schneider, *Eur. J. Org.Chem.* **1998**, *3*, 515–520.

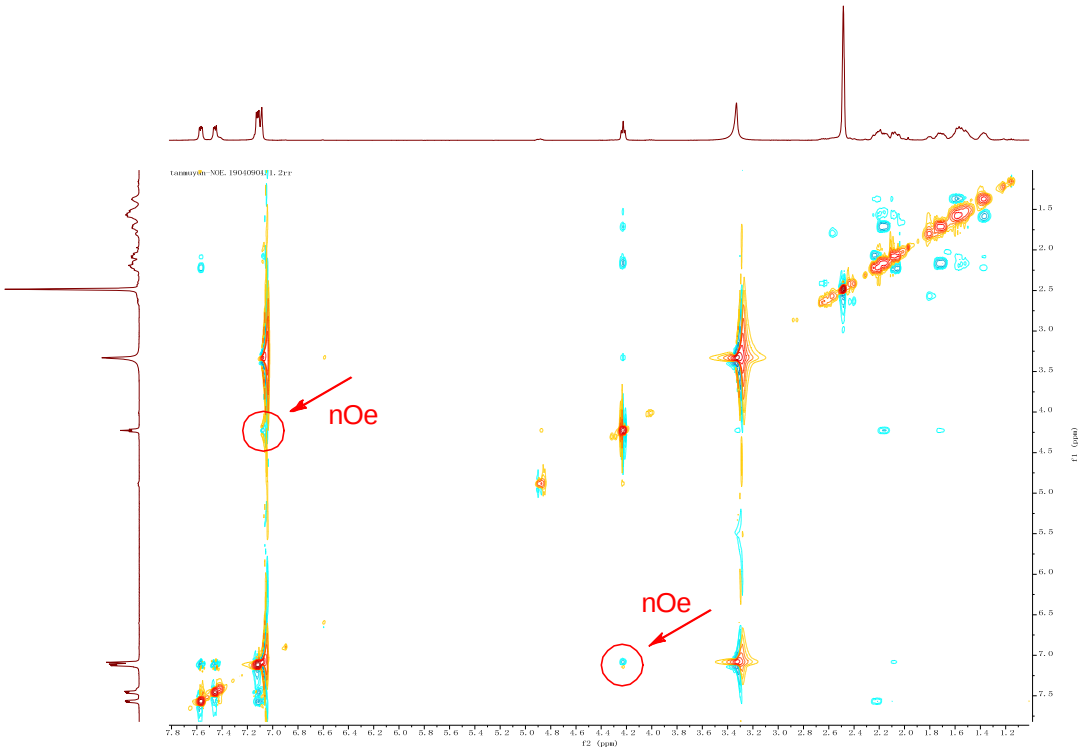
[5]. Y. Lee, S.-G. Kim, *J. Org. Chem.* **2014**, *79*, 8234−8243.

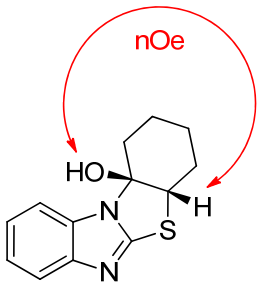
6. Copies of 1H and 13C NMR spectra

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



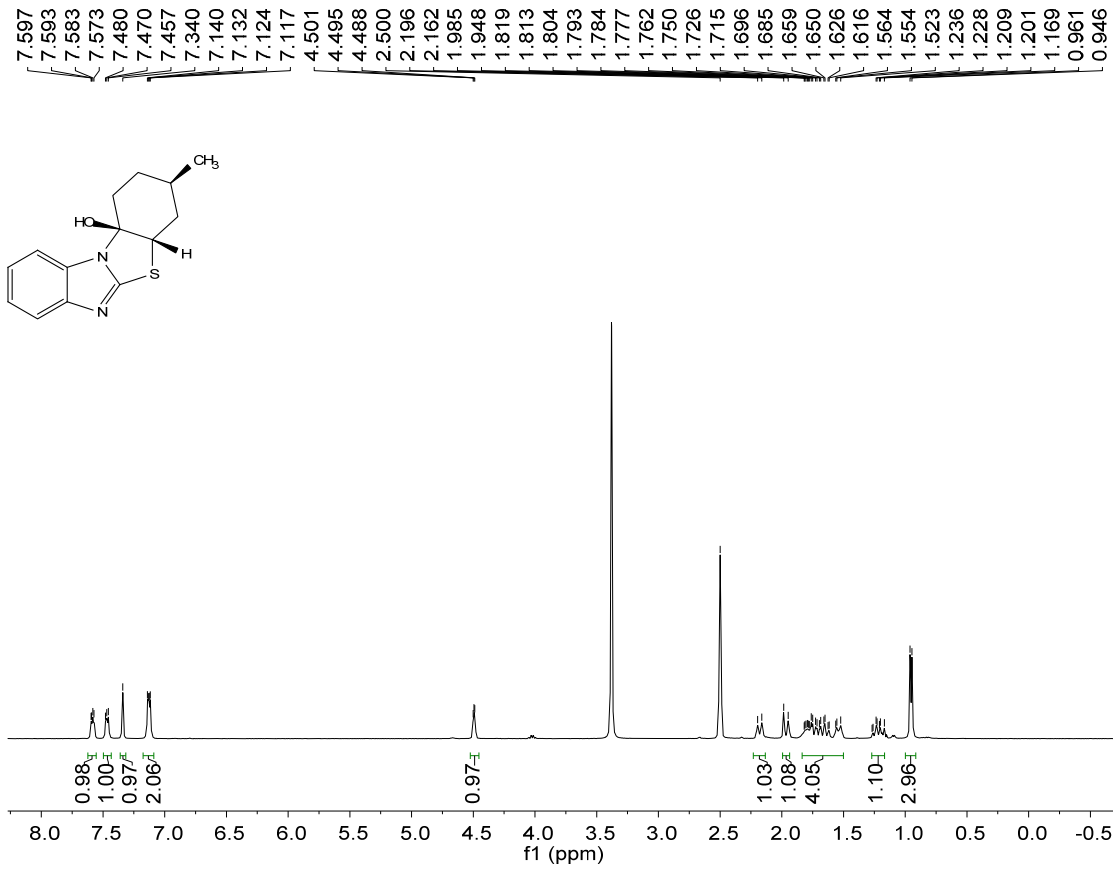


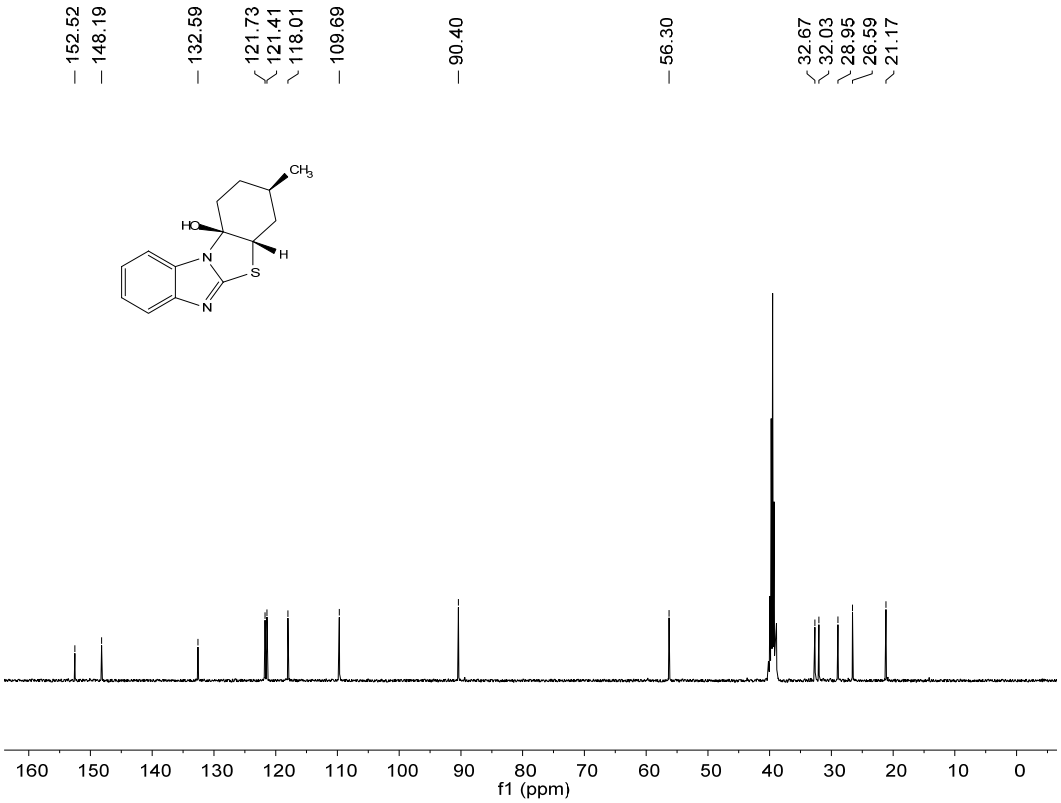


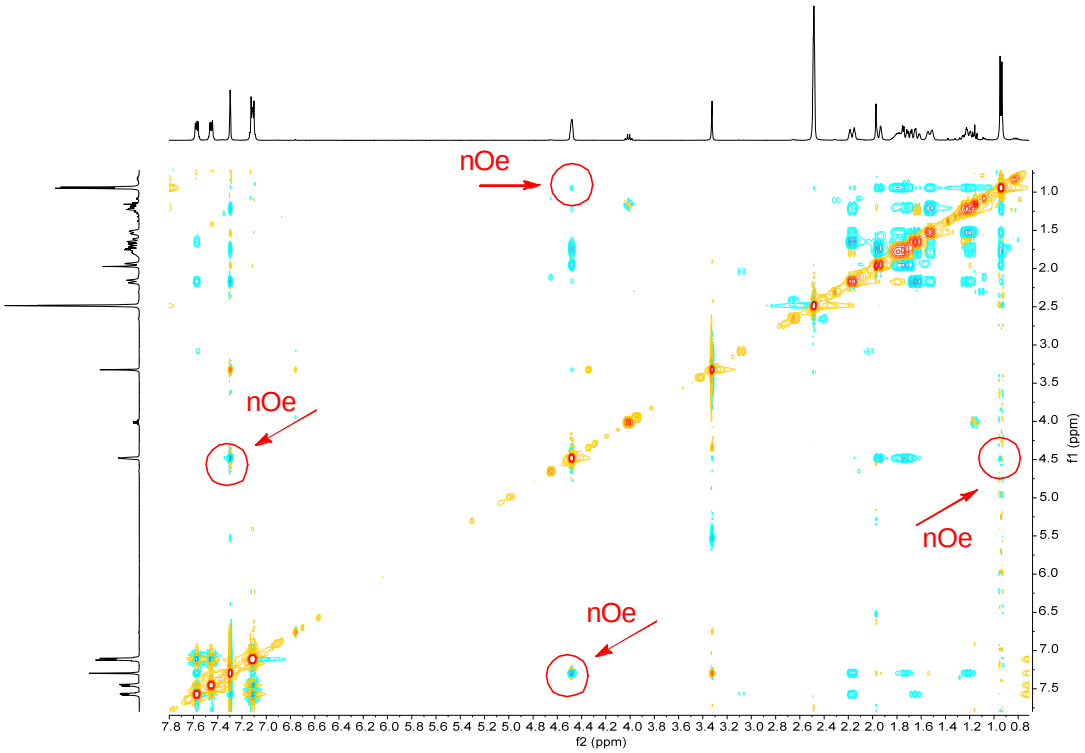


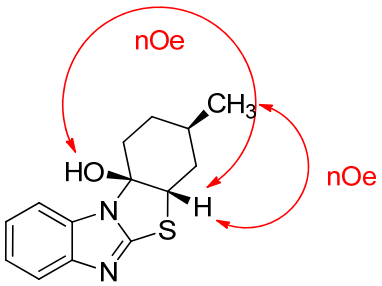
3a

^{1}H and ^{13}C NMR spectra of **3b (cis)**

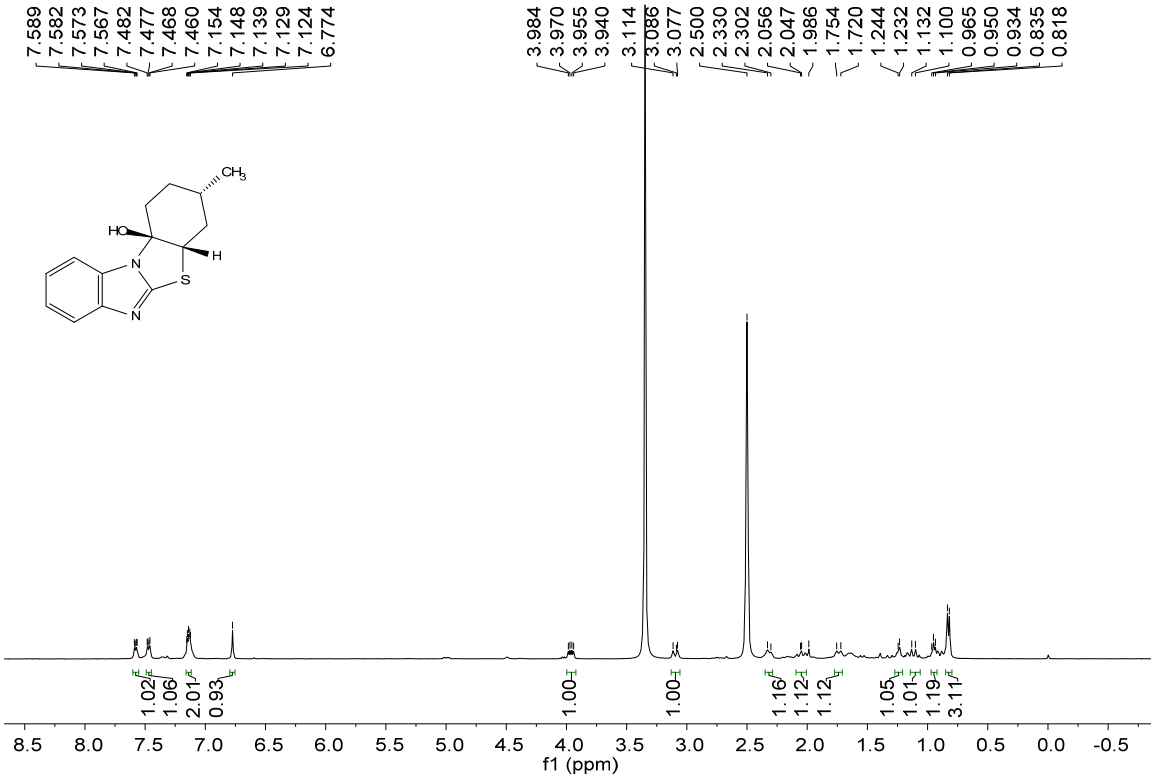


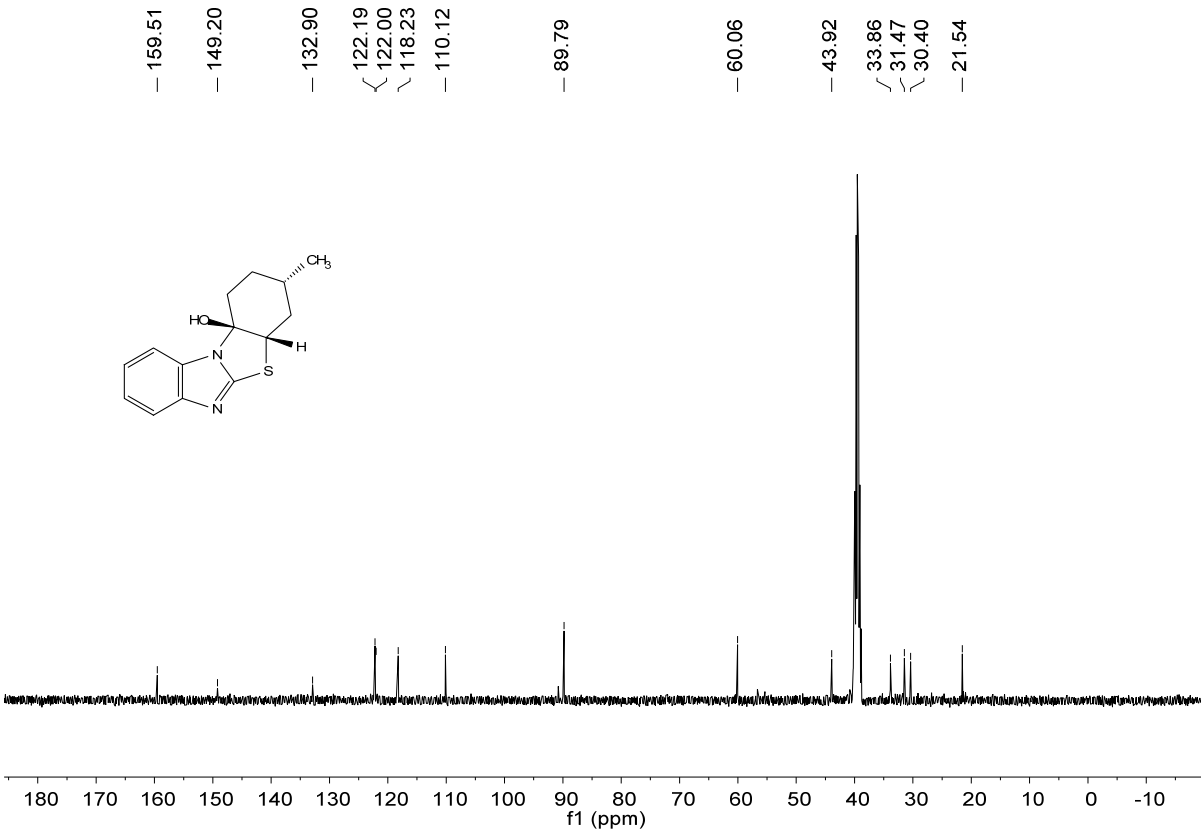



nOe
nOe
nOe
nOe
f2 (ppm)
f1 (ppm)

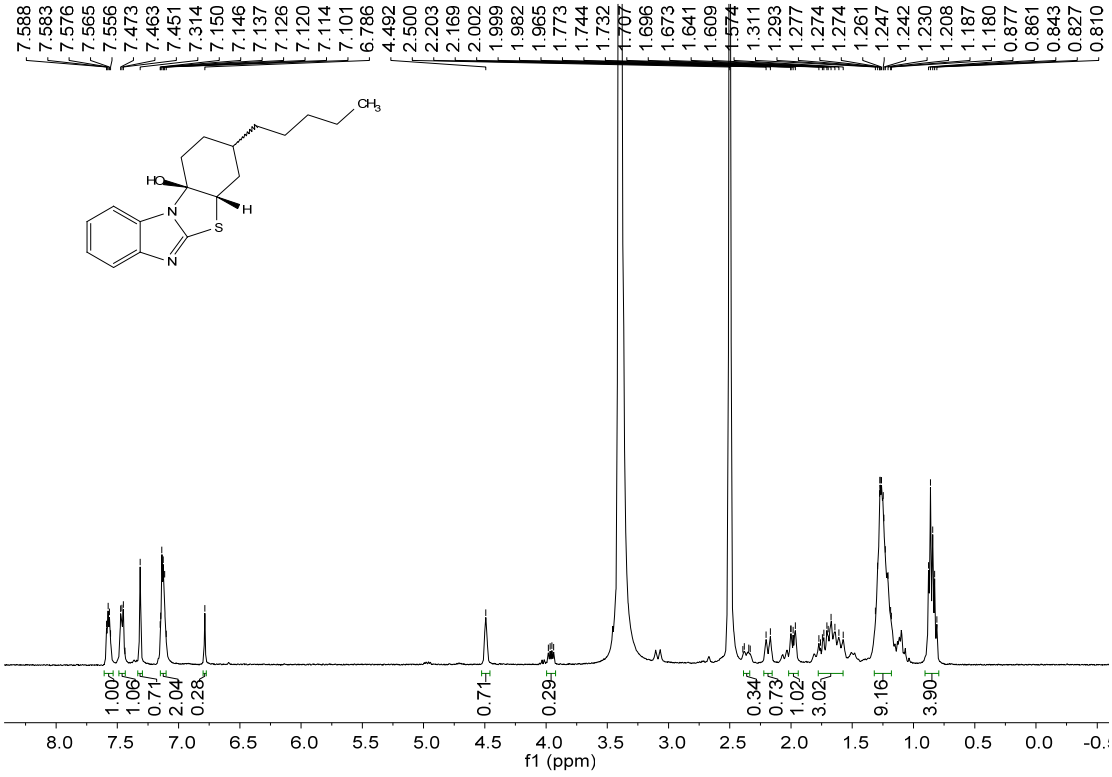

nOe
nOe
CH3
HO
N
S
H
N

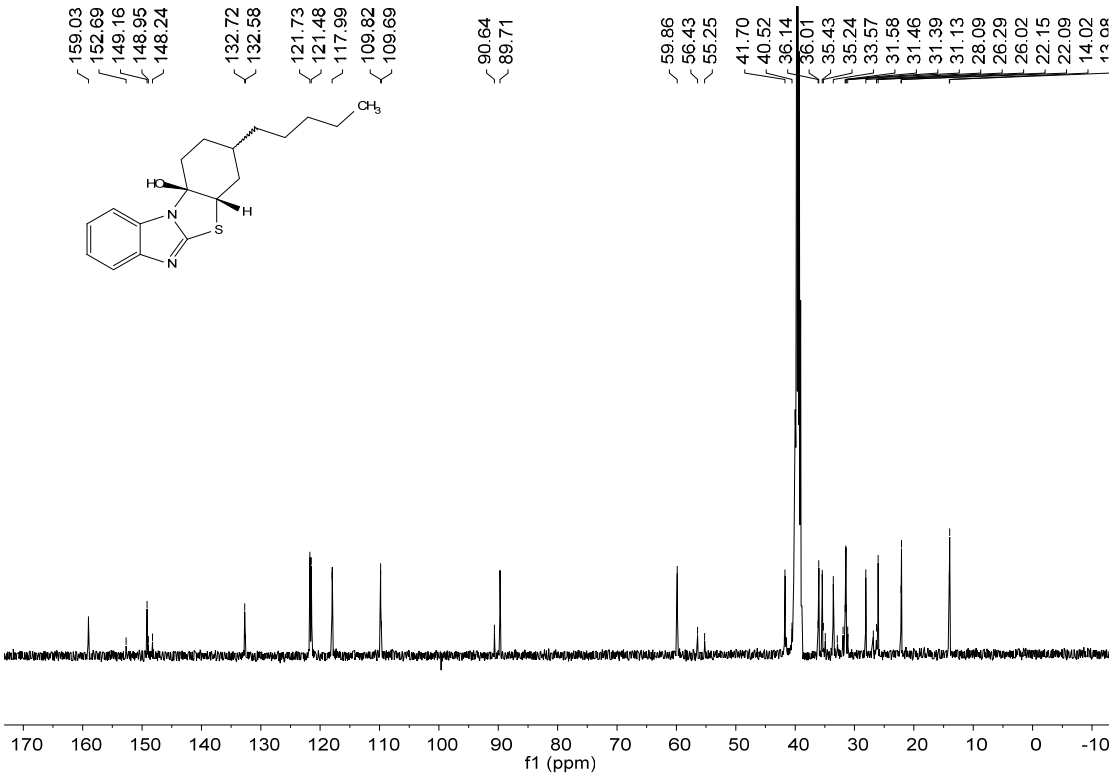
^{1}H and ^{13}C NMR spectra of **3b (trans)**



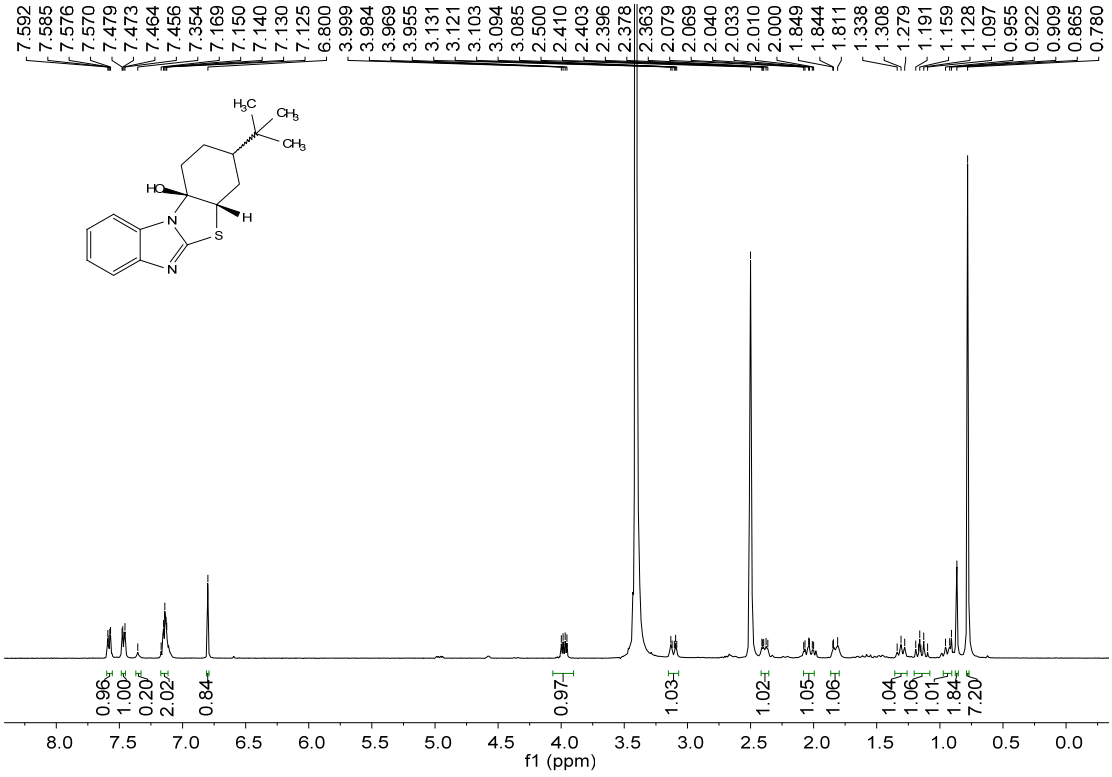


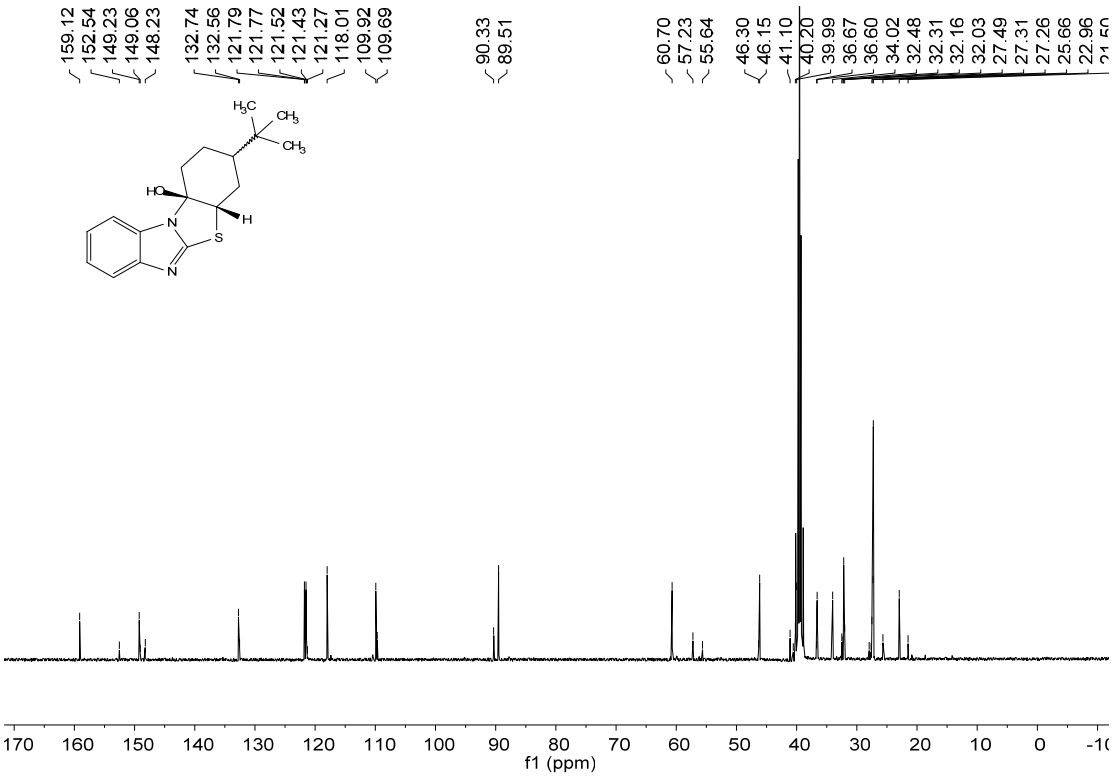
^{1}H and ^{13}C NMR spectra of **3c**



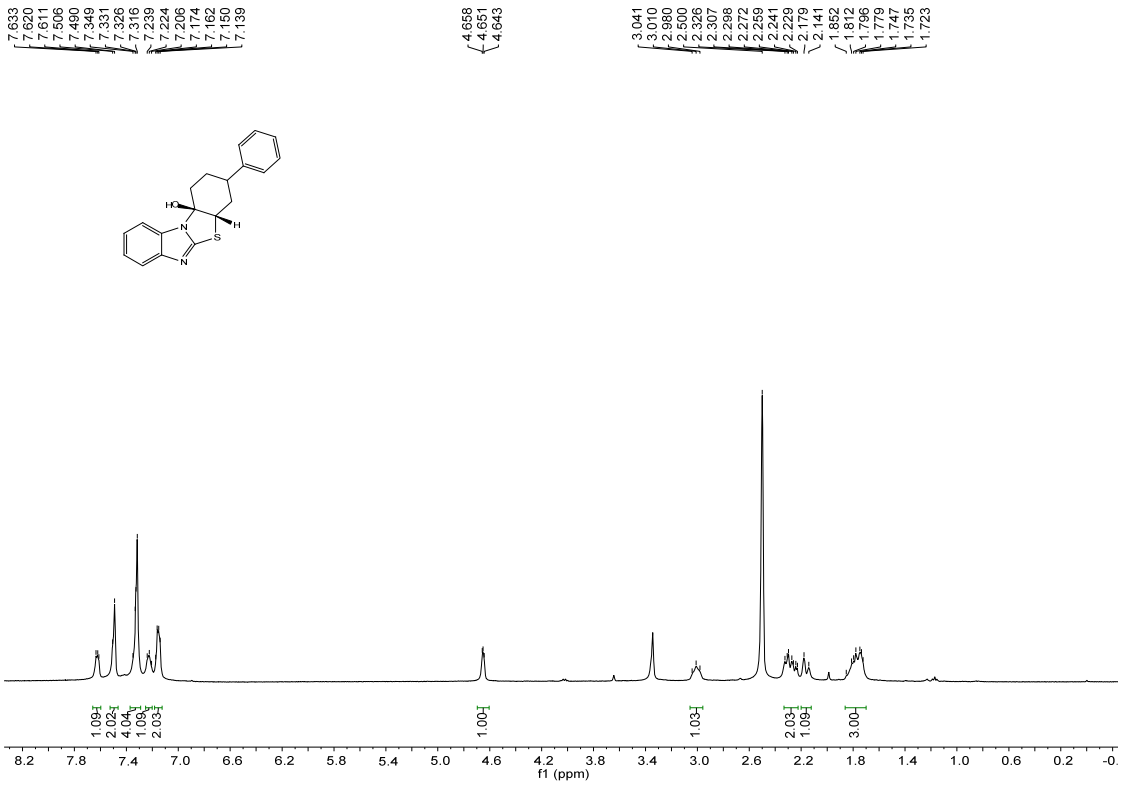


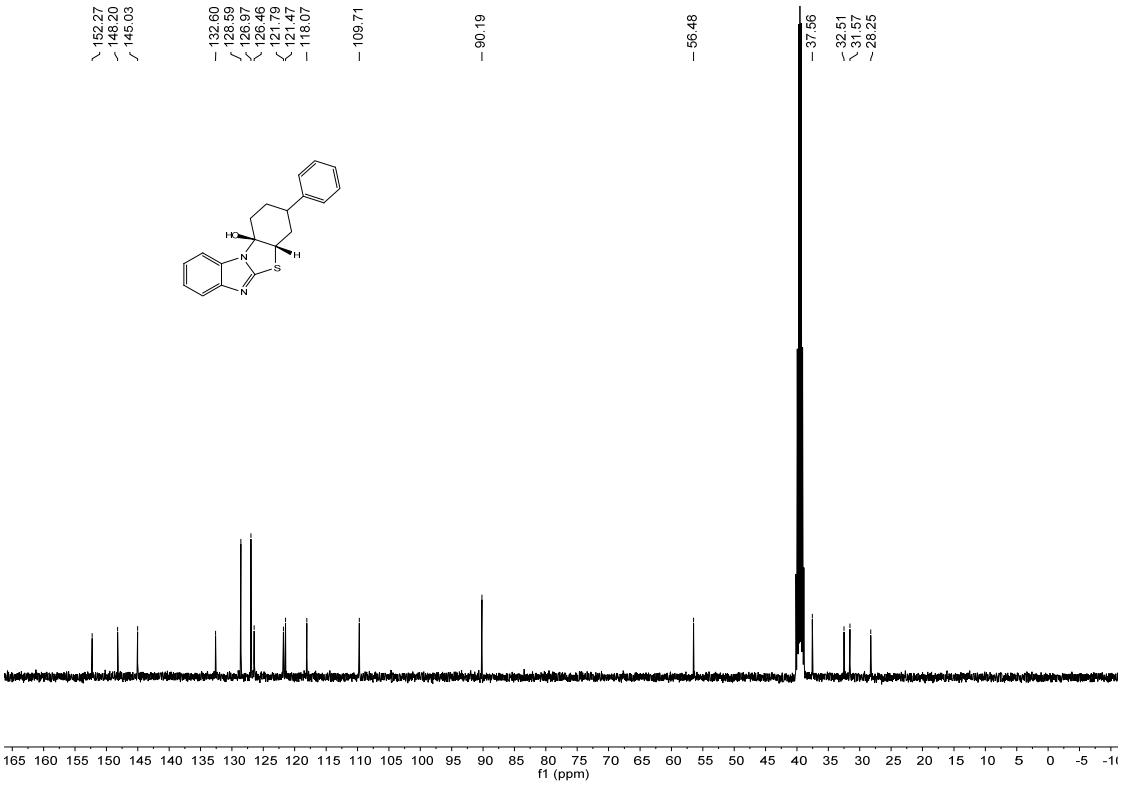
^{1}H and ^{13}C NMR spectra of **3d**



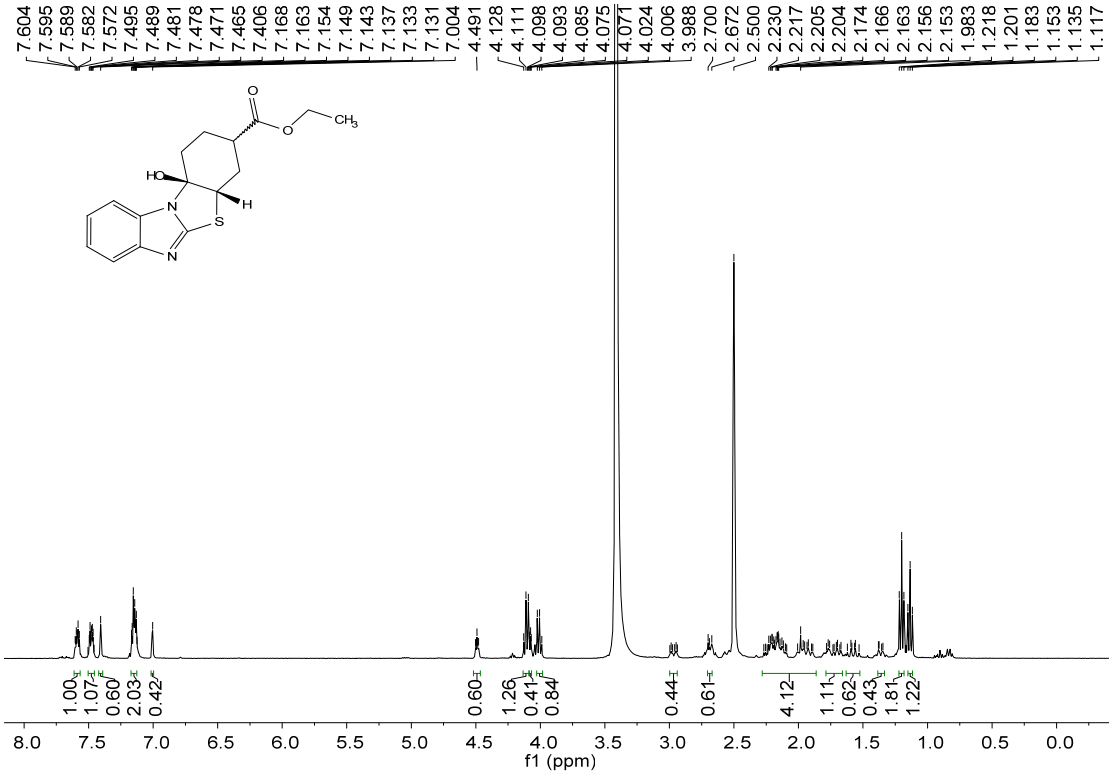


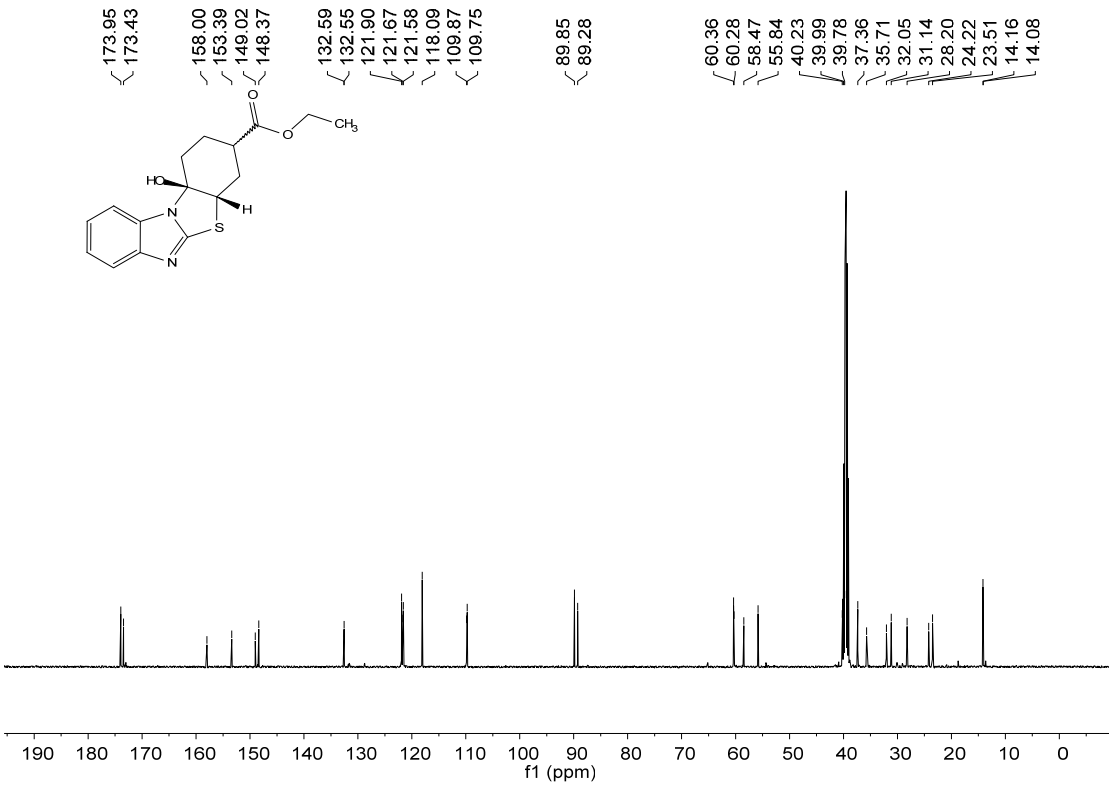
^{1}H and ^{13}C NMR spectra of **3e**



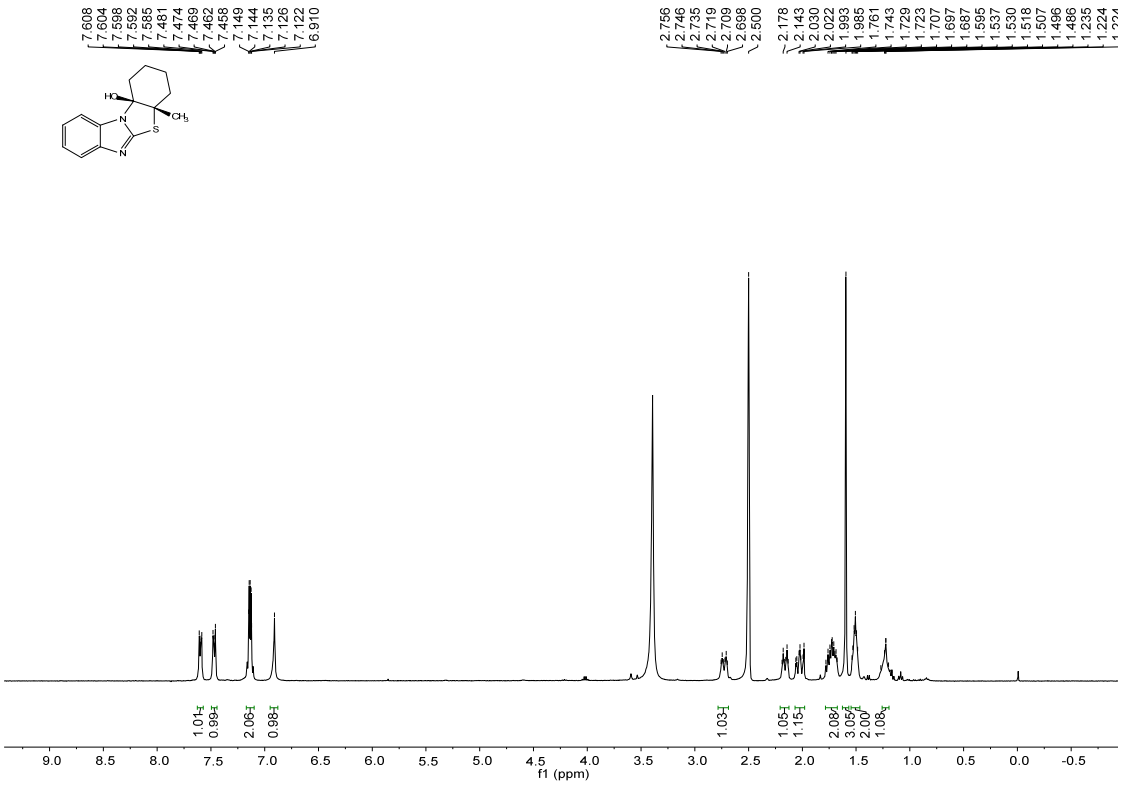


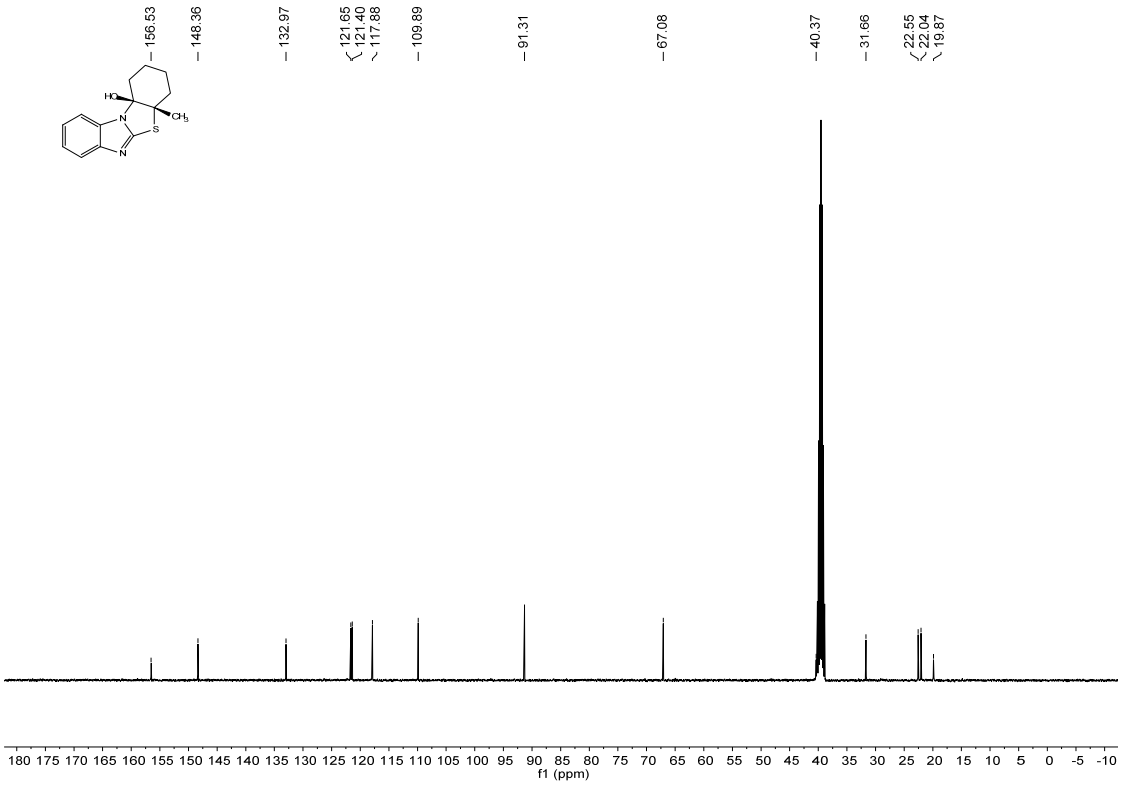
^{1}H and ^{13}C NMR spectra of **3f**

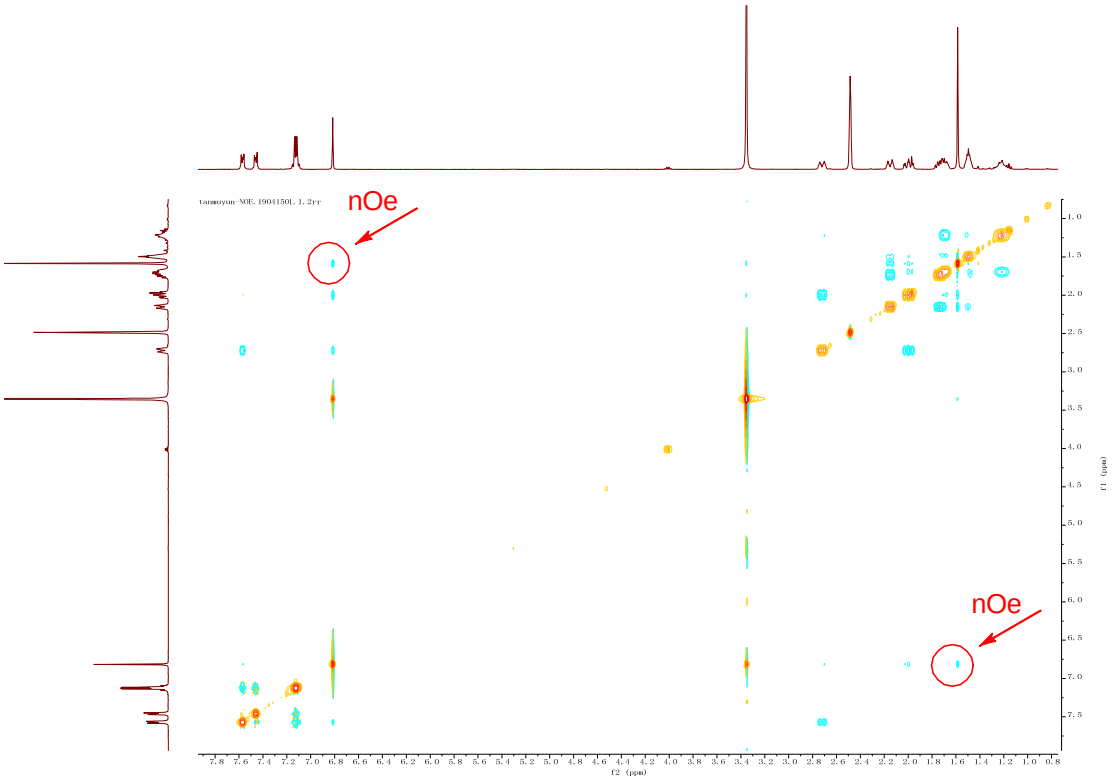


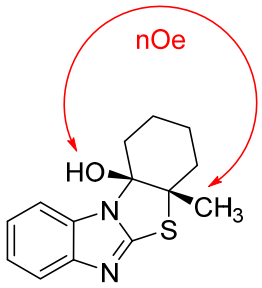


^{1}H and ^{13}C NMR spectra of **3g**



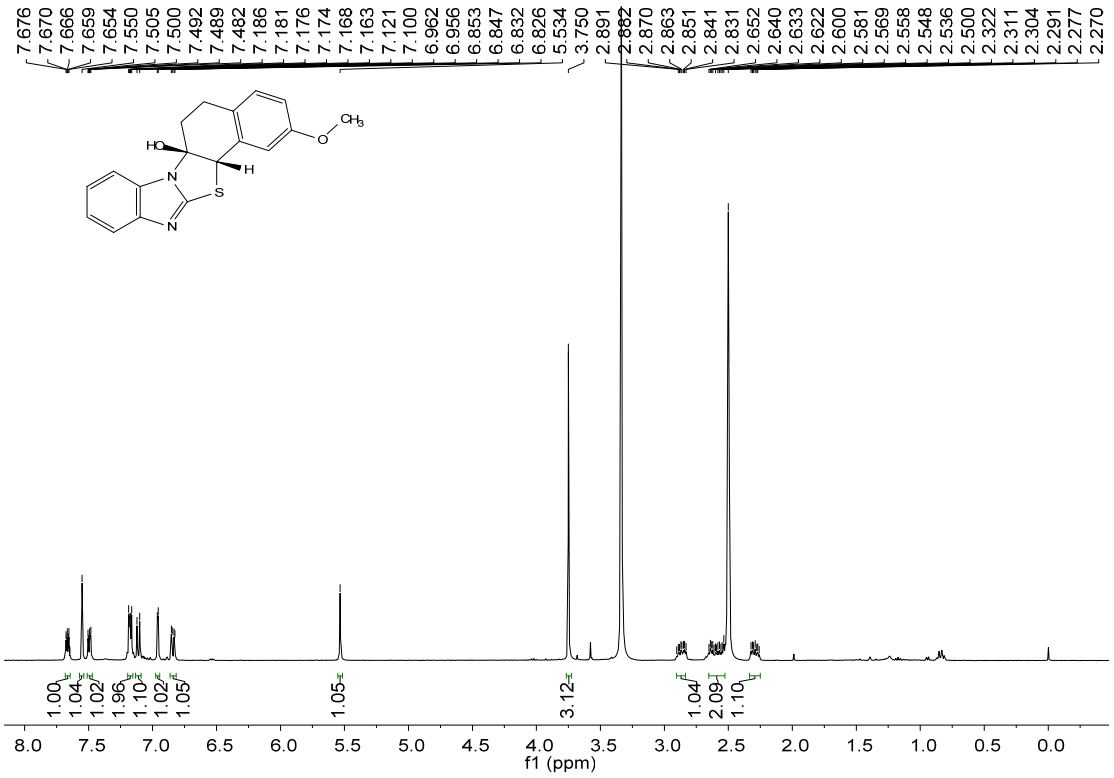


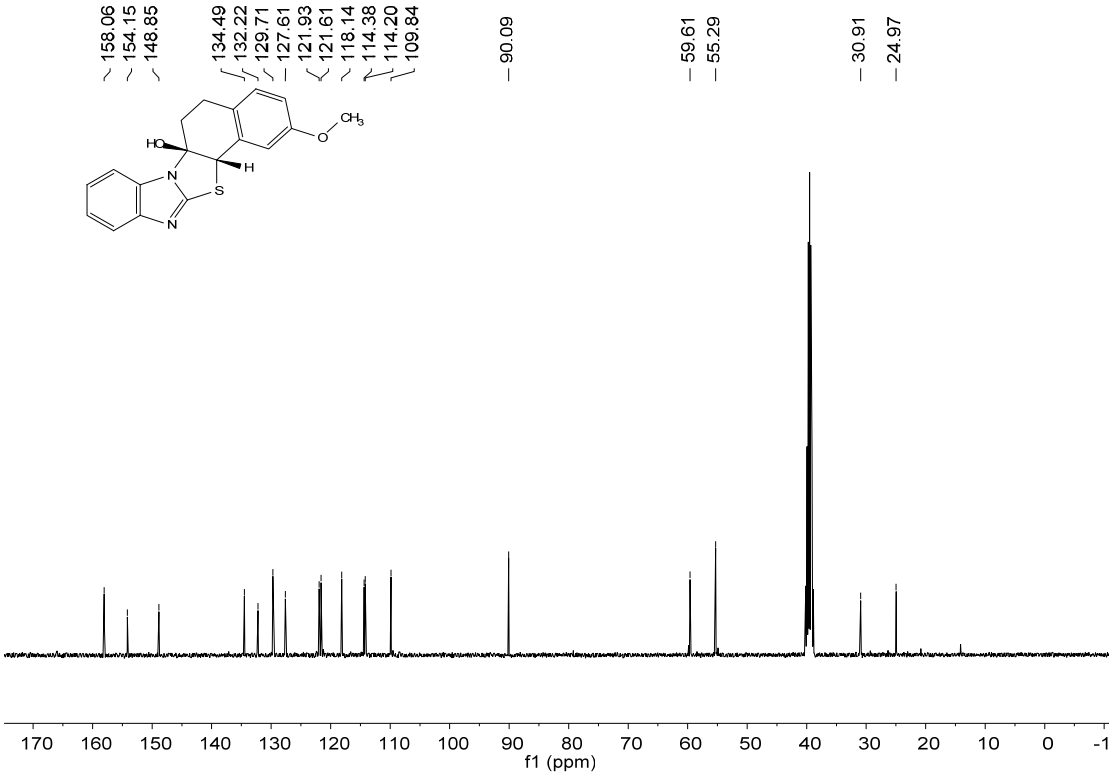




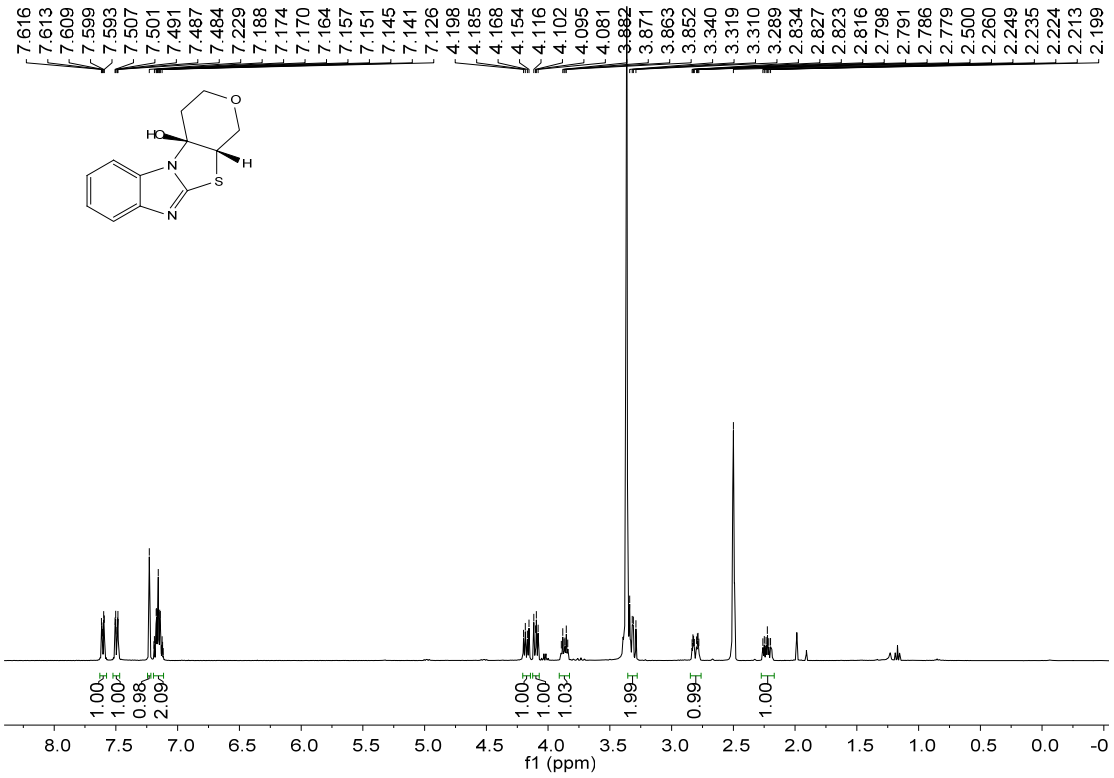
3g

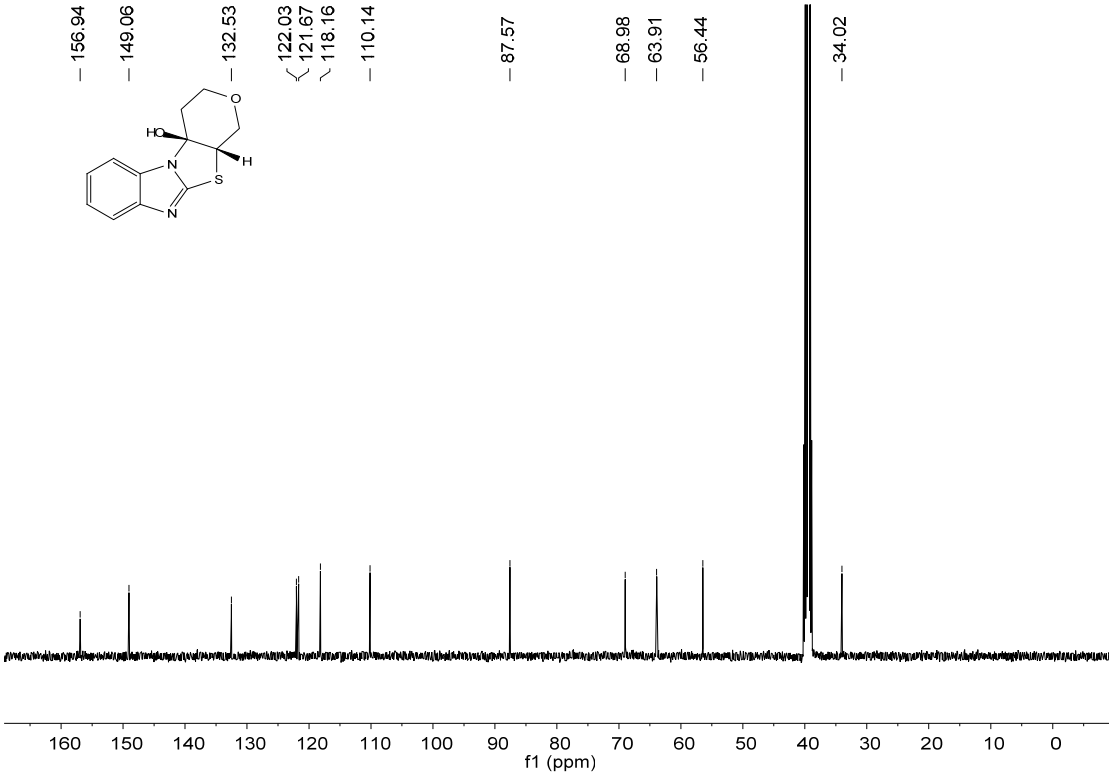
^{1}H and ^{13}C NMR spectra of **3h**



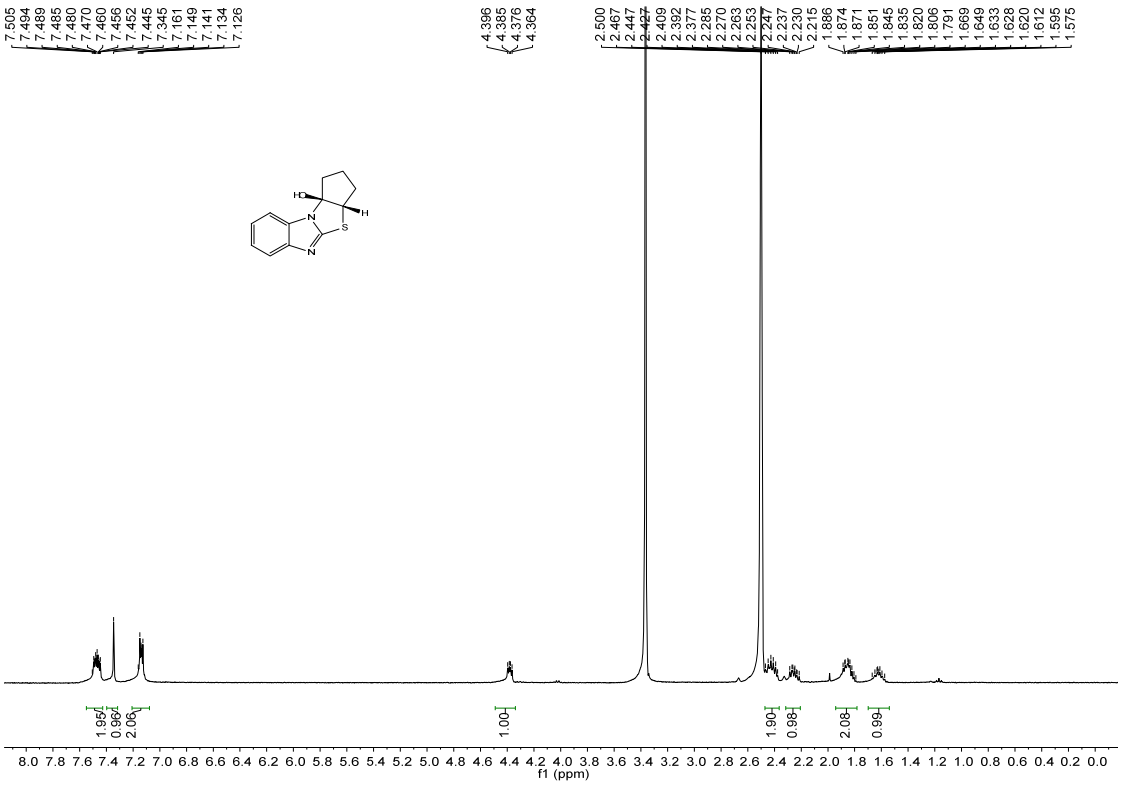


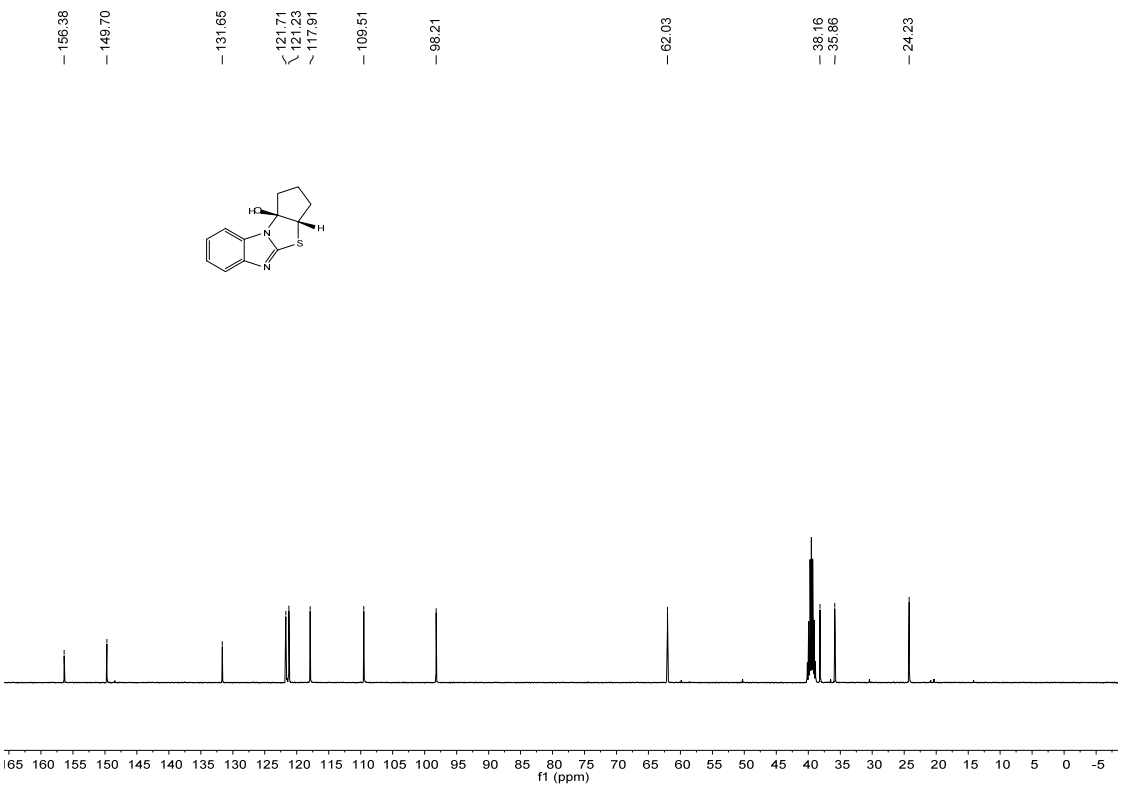
^{1}H and ^{13}C NMR spectra of **3i**



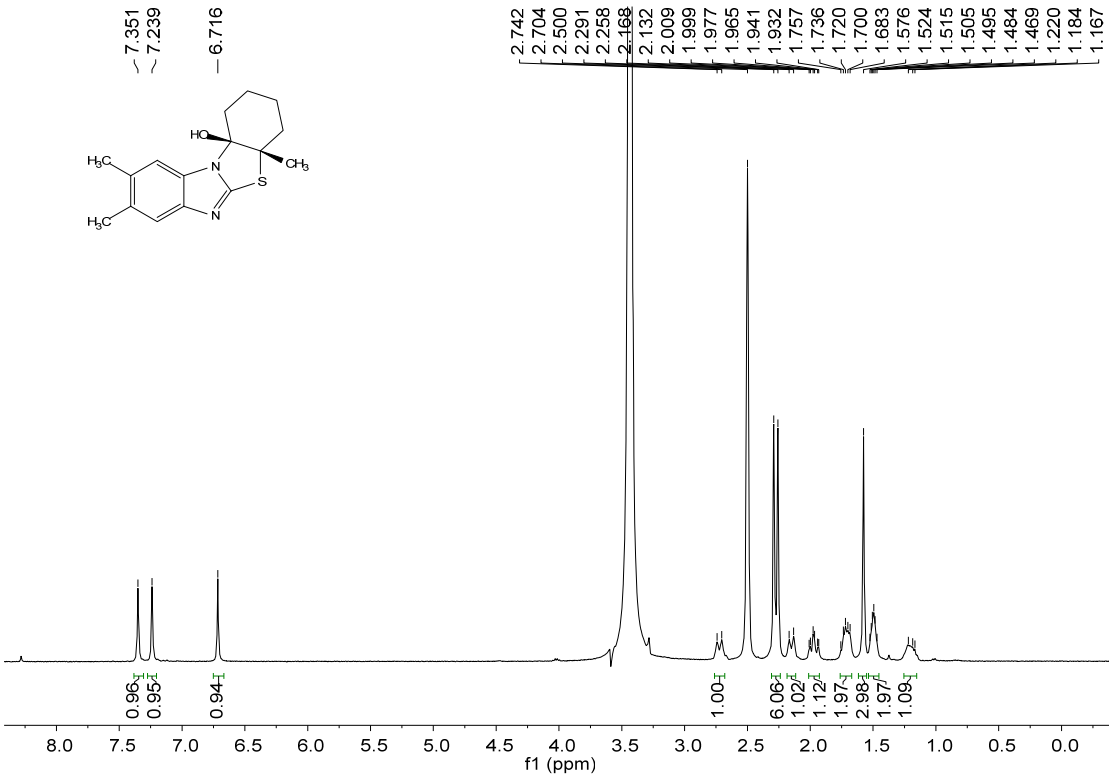


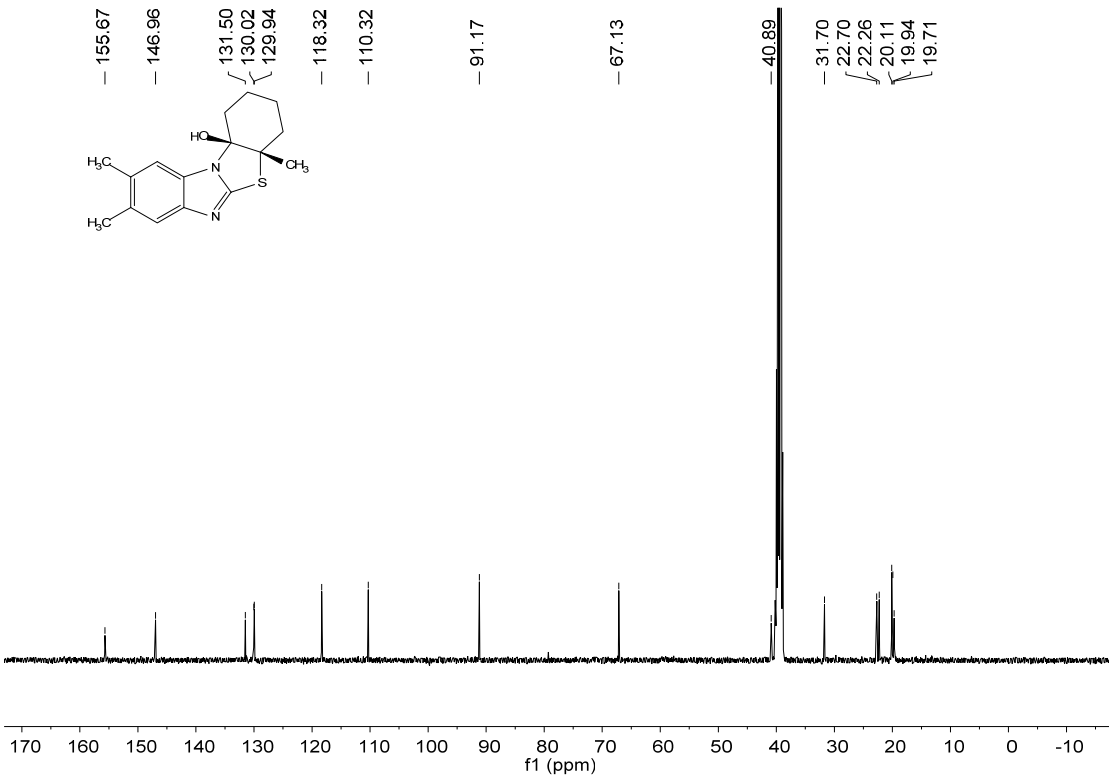
^{1}H and ^{13}C NMR spectra of **3j**



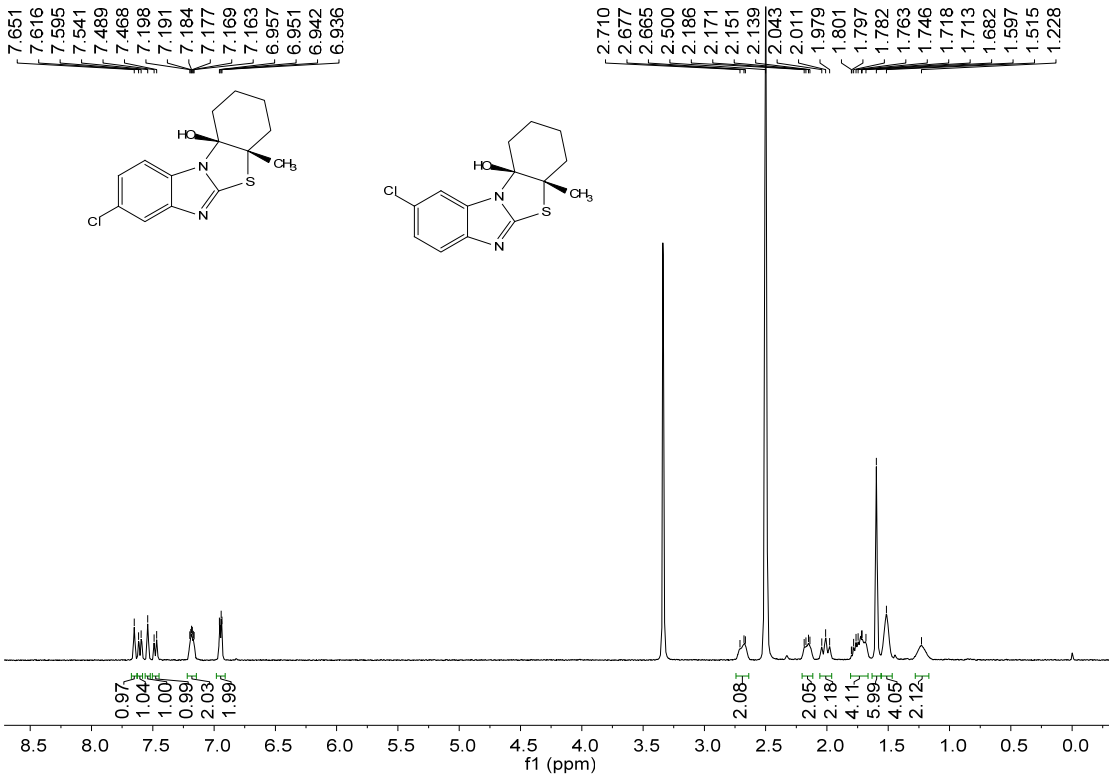


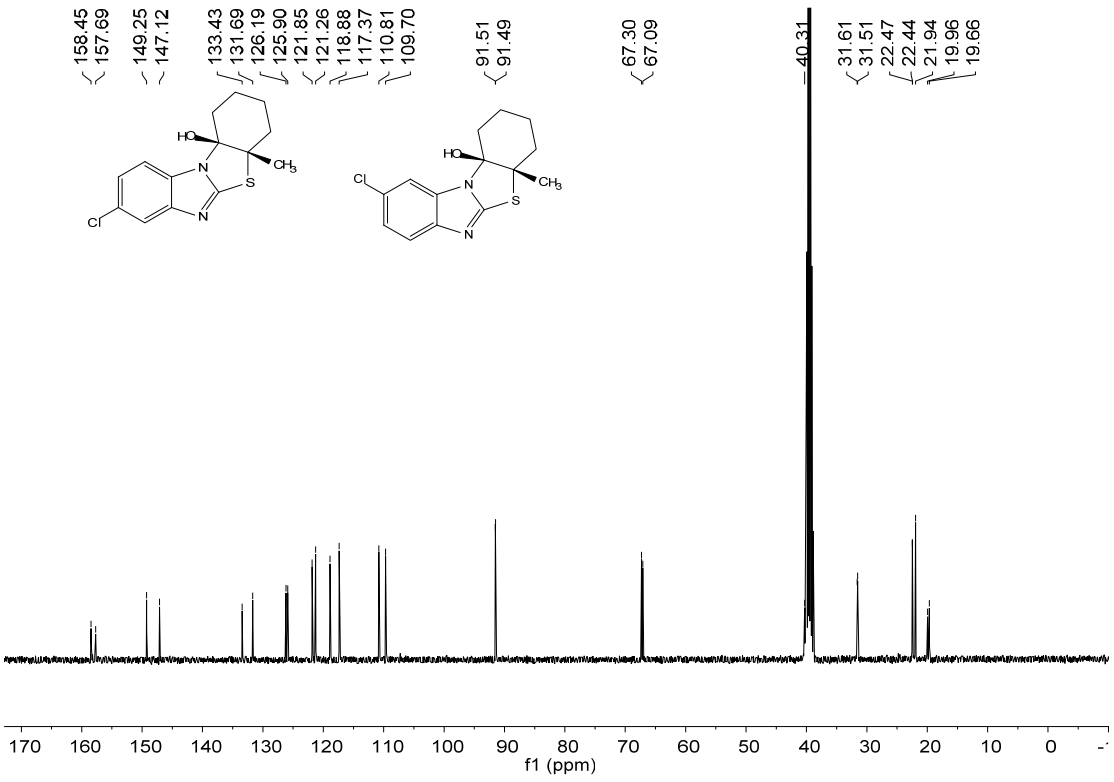
^{1}H and ^{13}C NMR spectra of **3k**



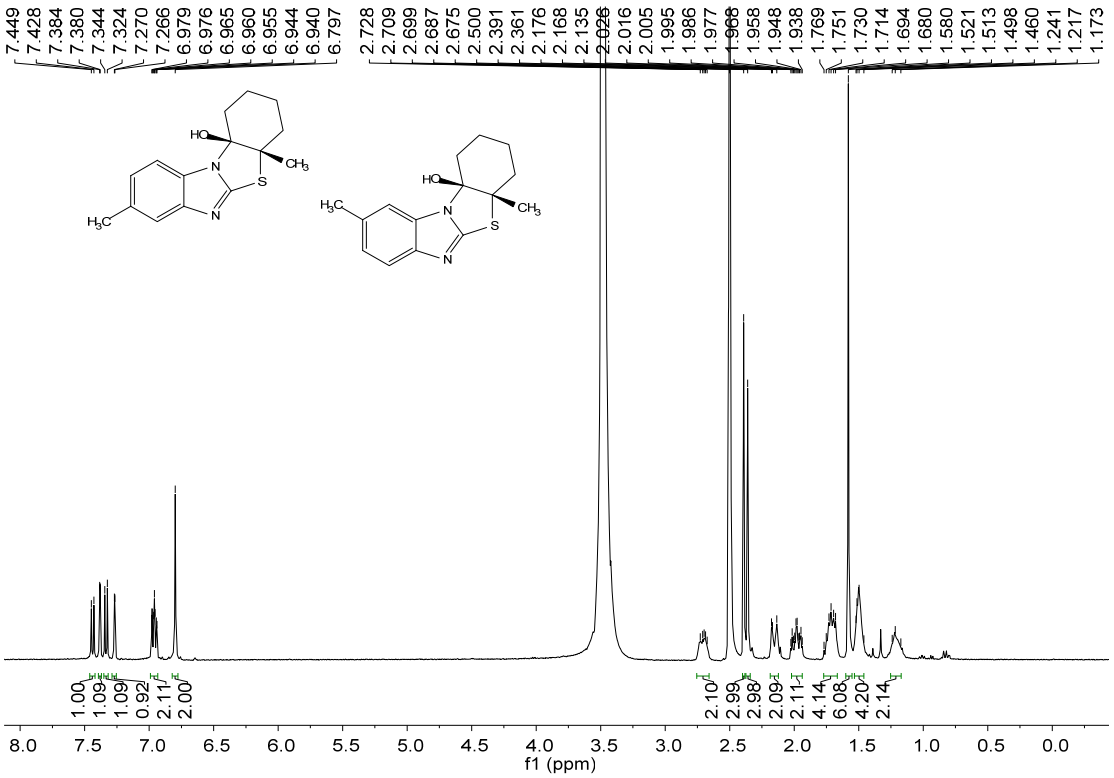


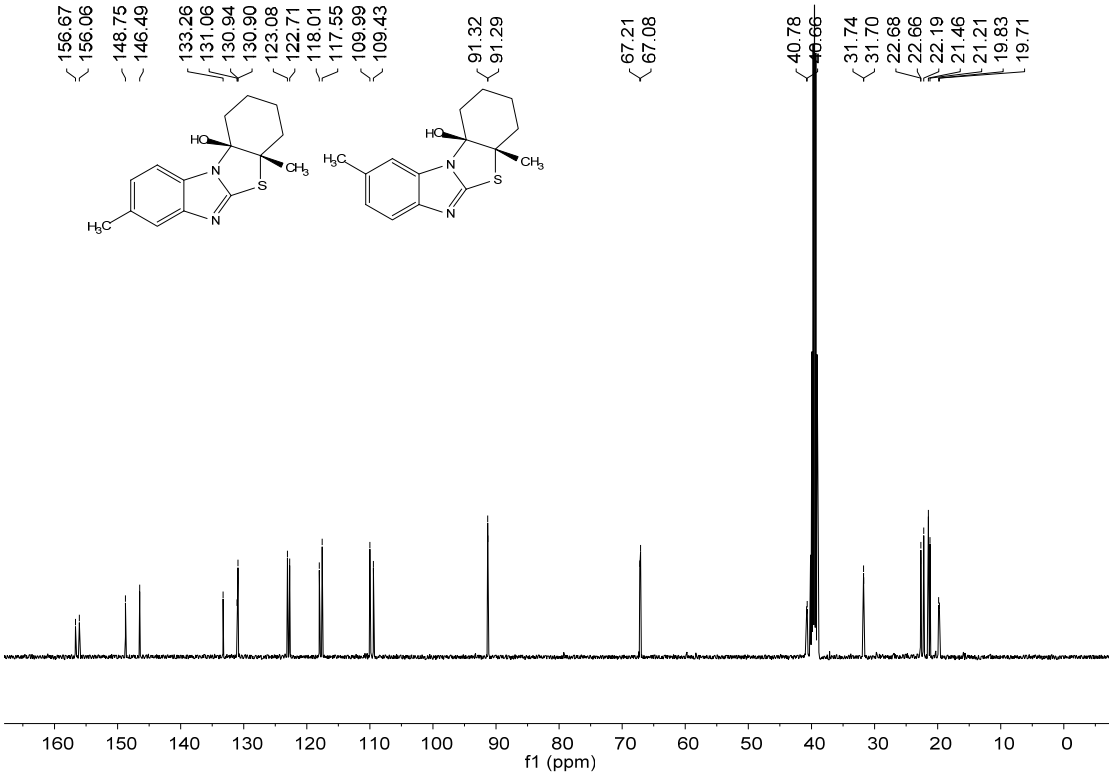
^{1}H and ^{13}C NMR spectra of **3l and 3l'**



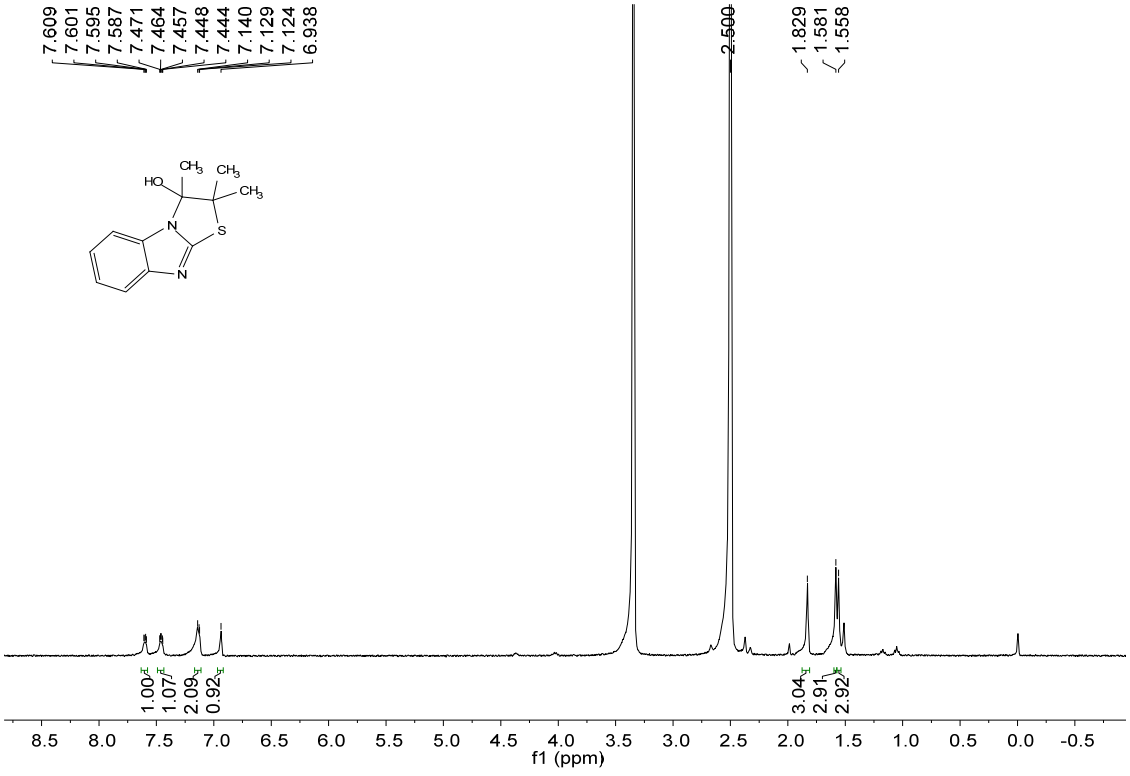


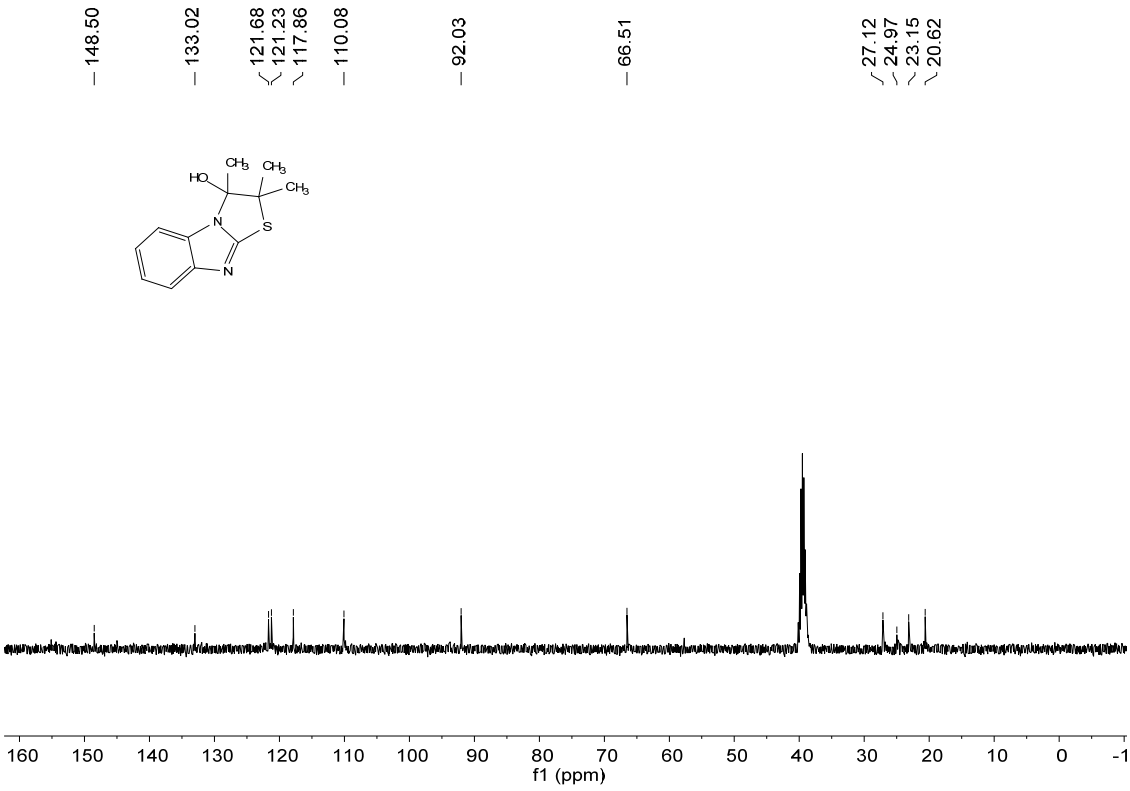
^{1}H and ^{13}C NMR spectra of **3m and 3m'**



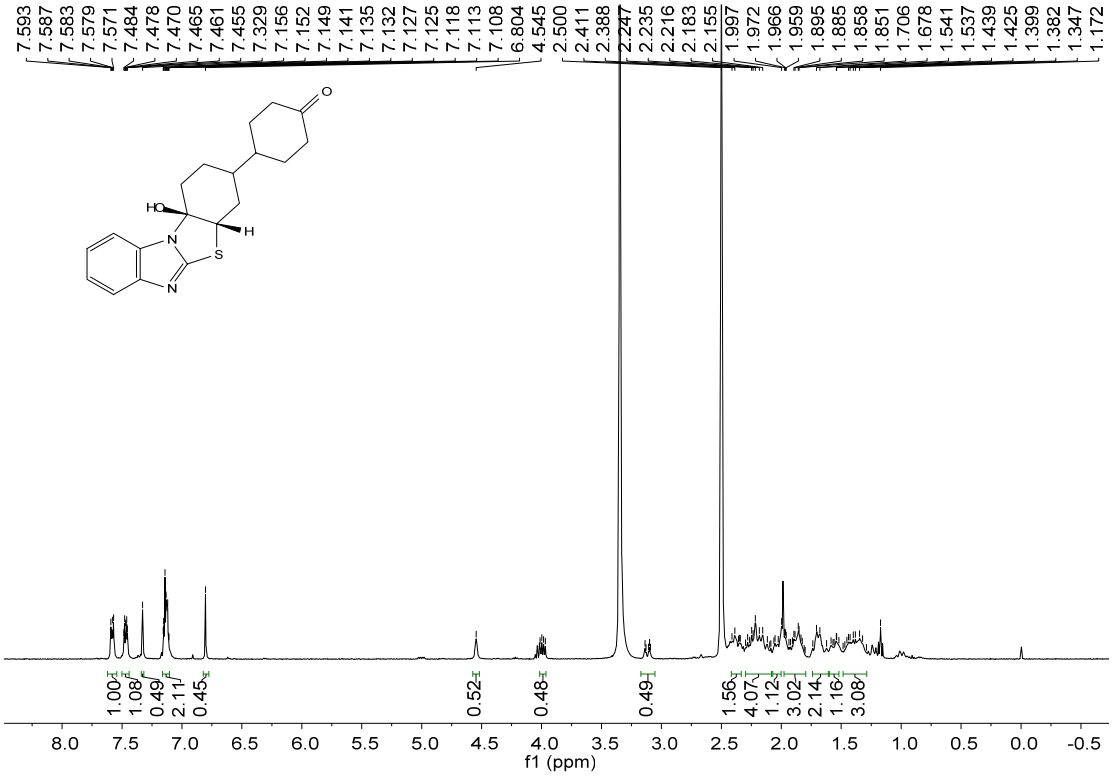


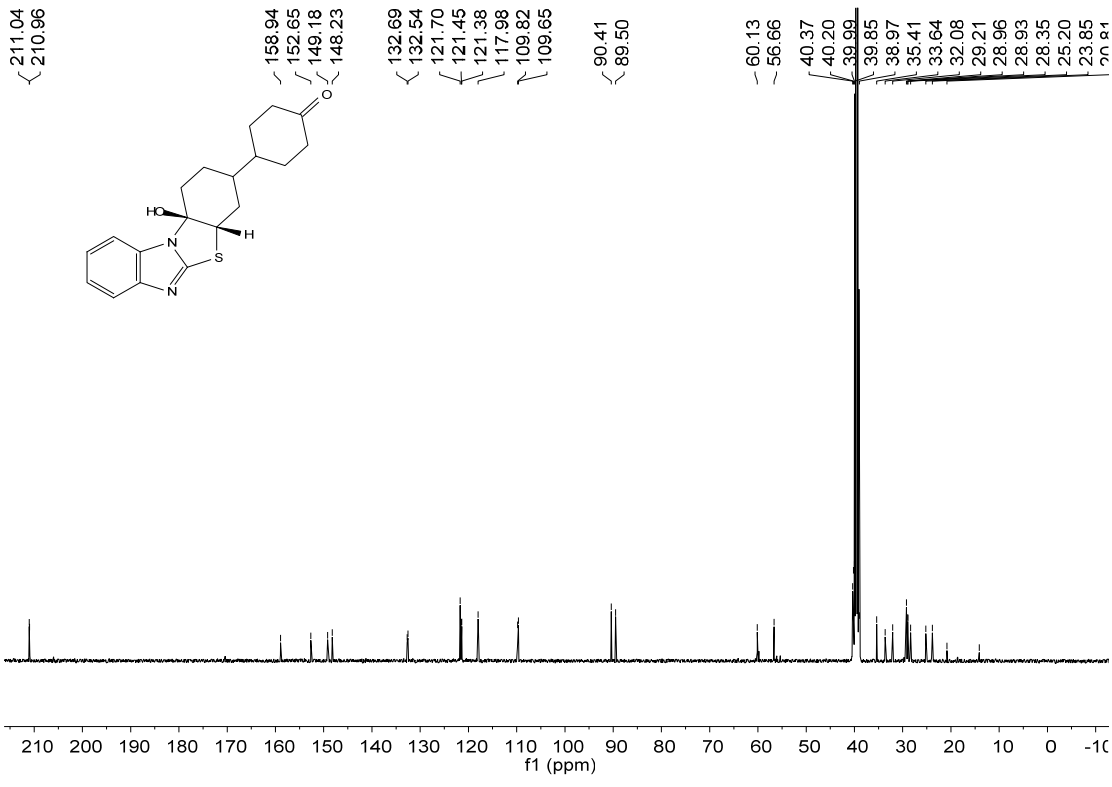
^{1}H and ^{13}C NMR spectra of **3n**



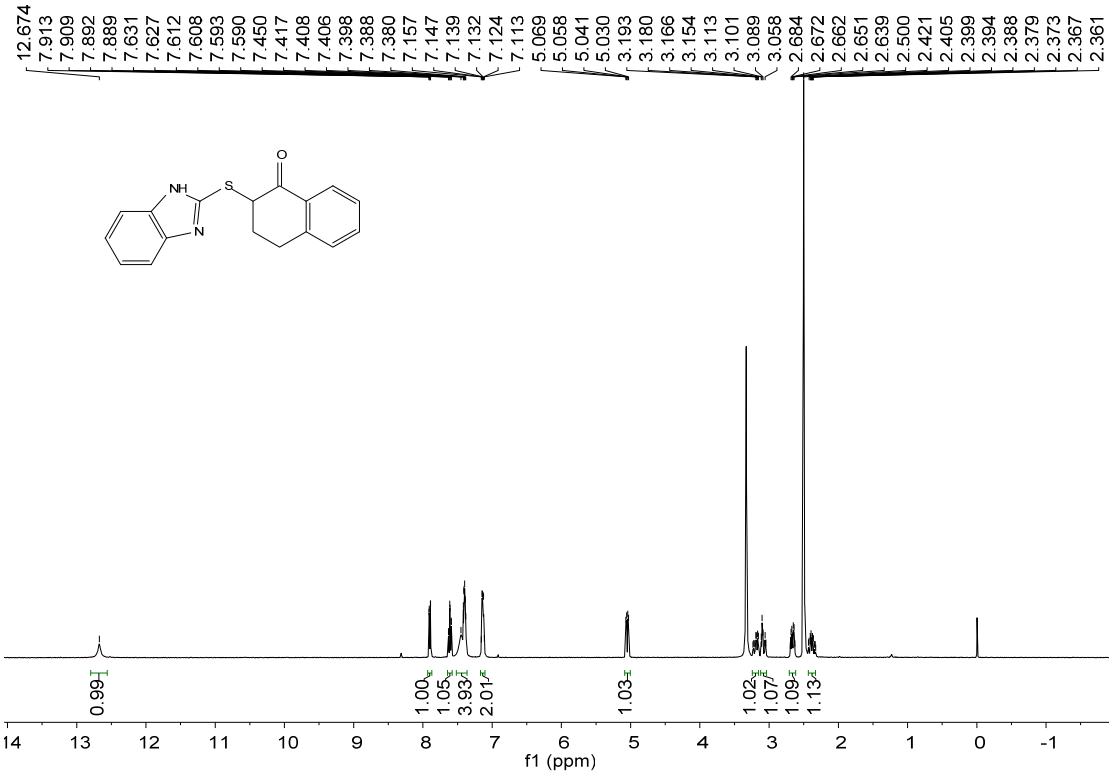


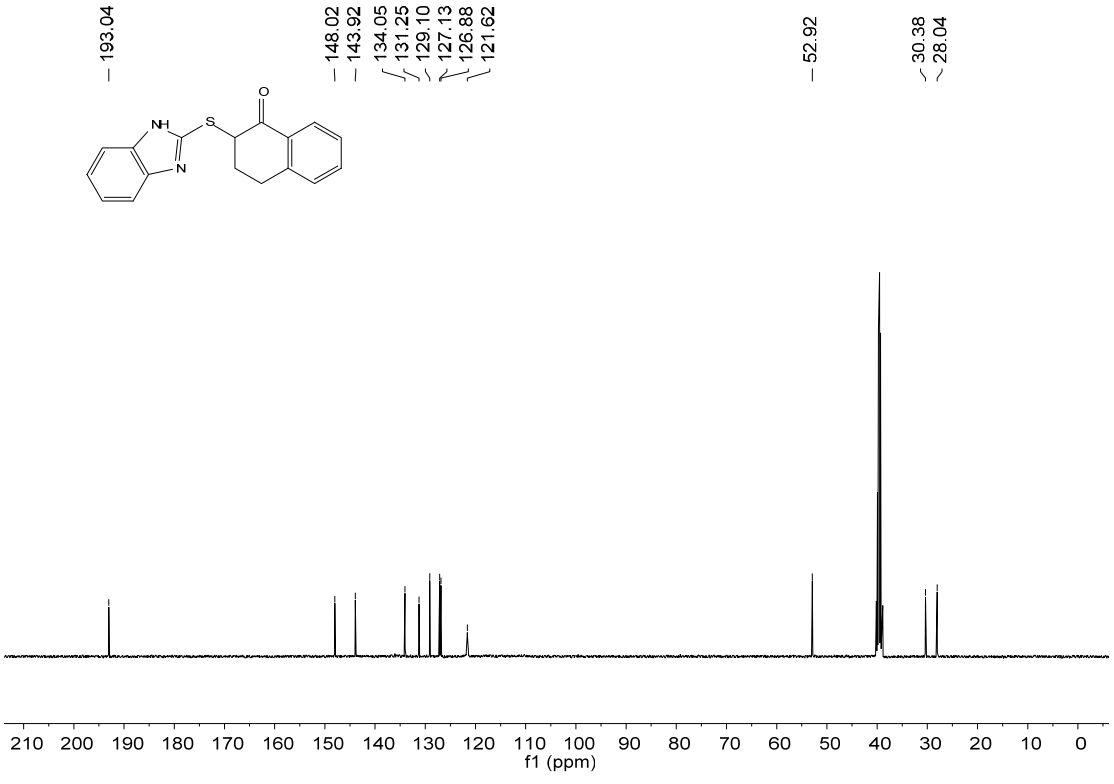
^{1}H and ^{13}C NMR spectra of **3o**



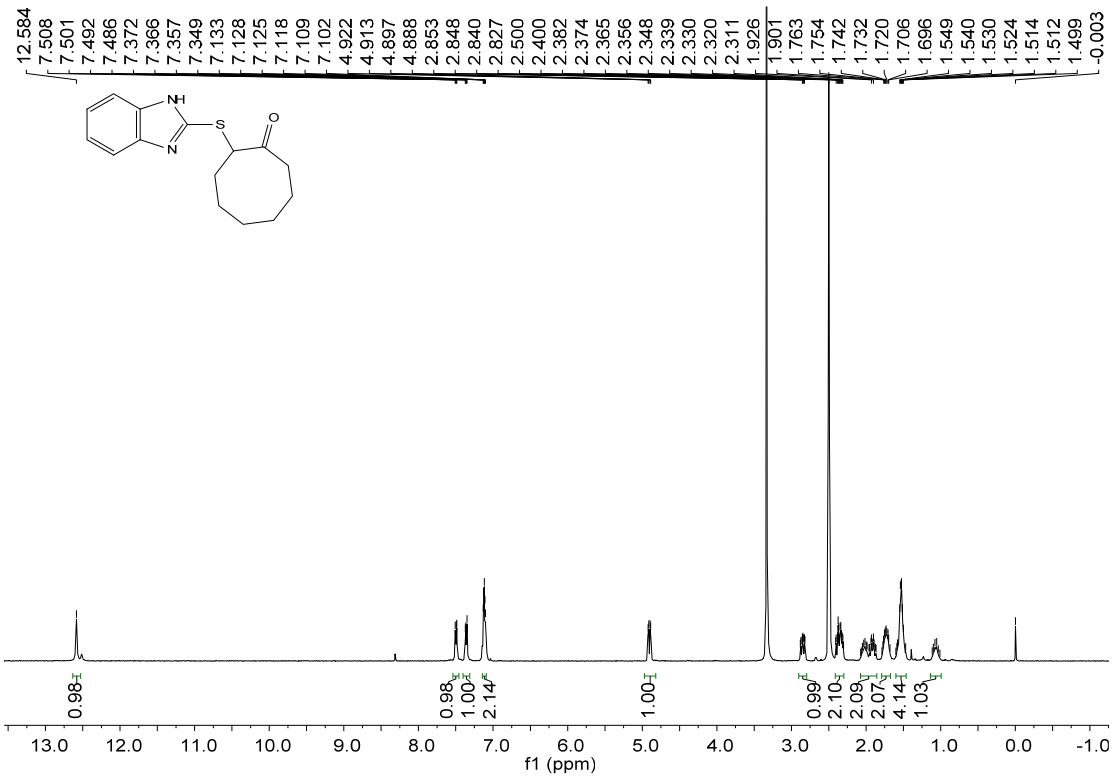


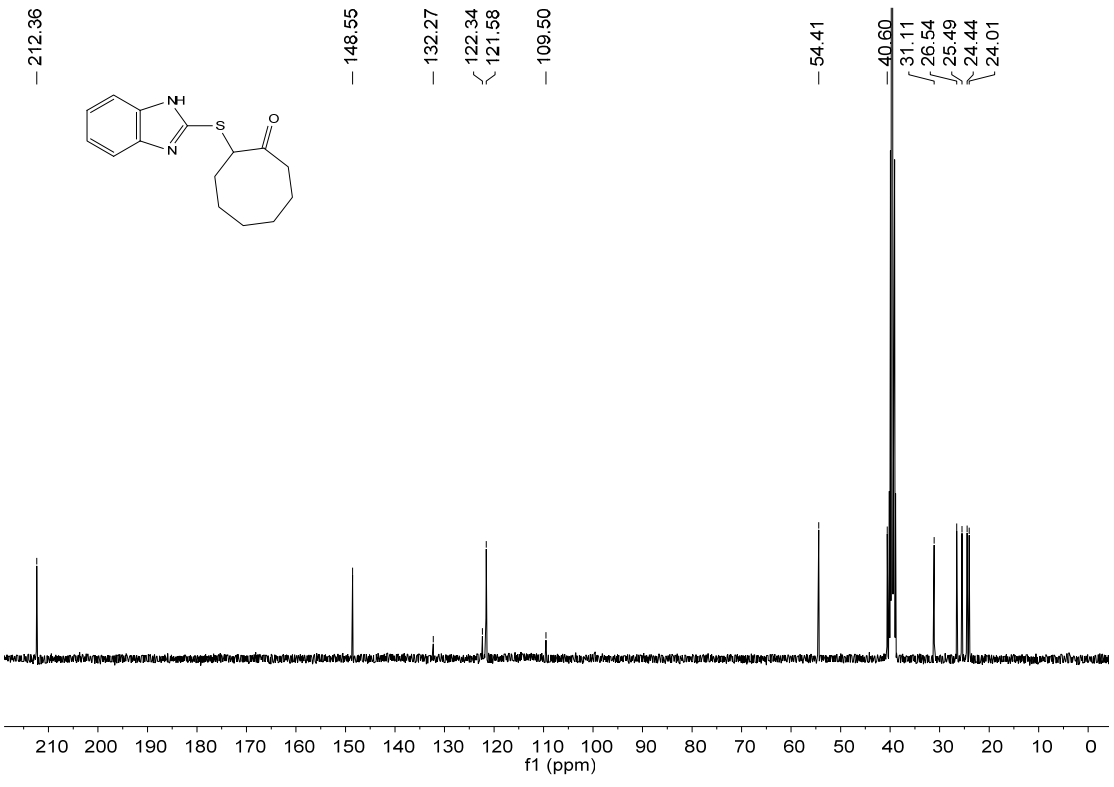
^{1}H and ^{13}C NMR spectra of **3p**



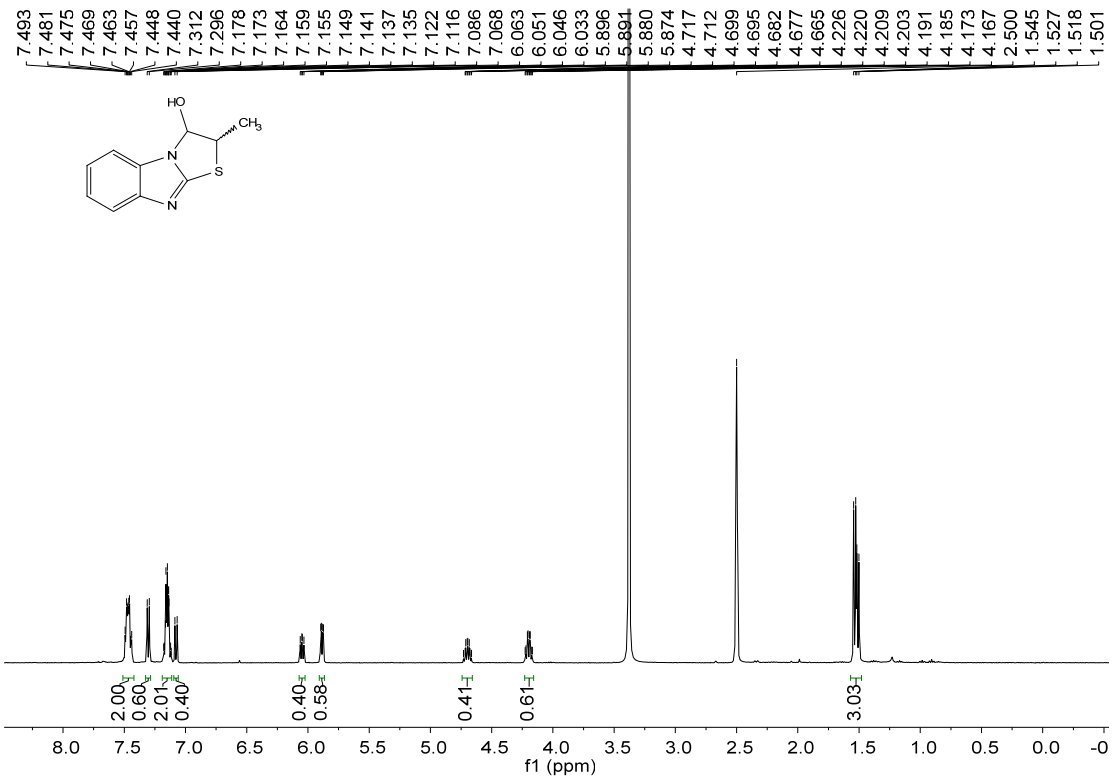


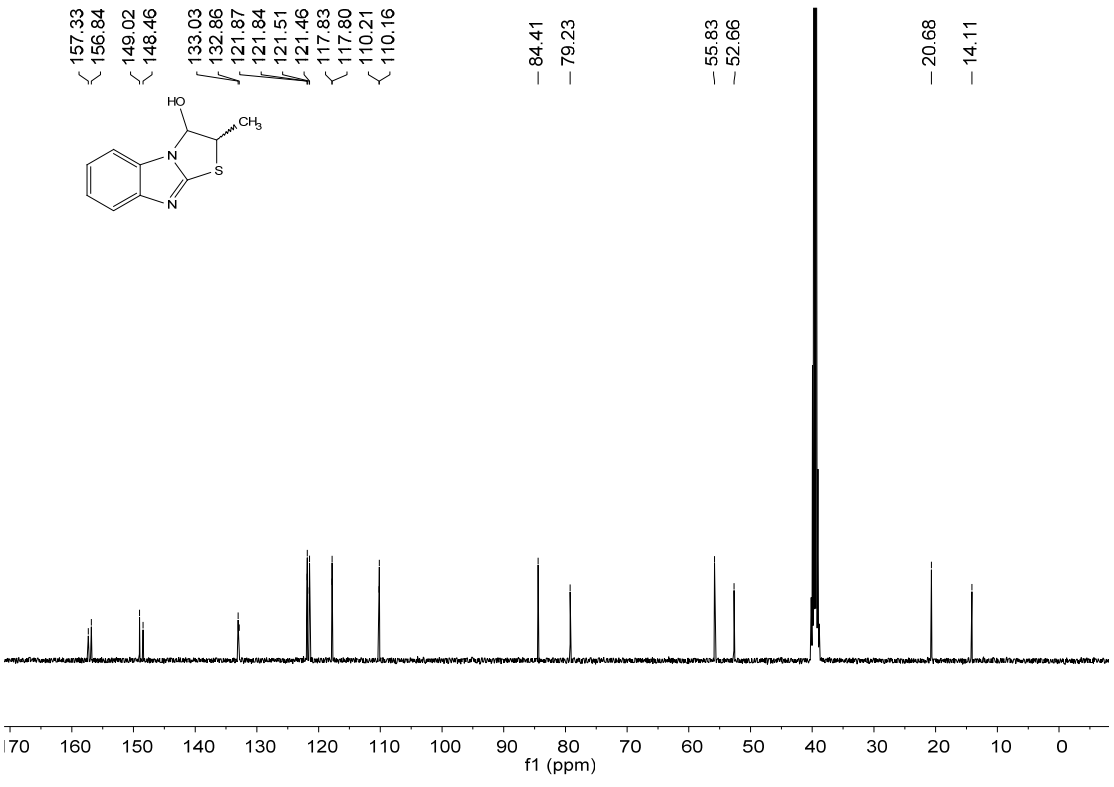
^{1}H and ^{13}C NMR spectra of **3q**



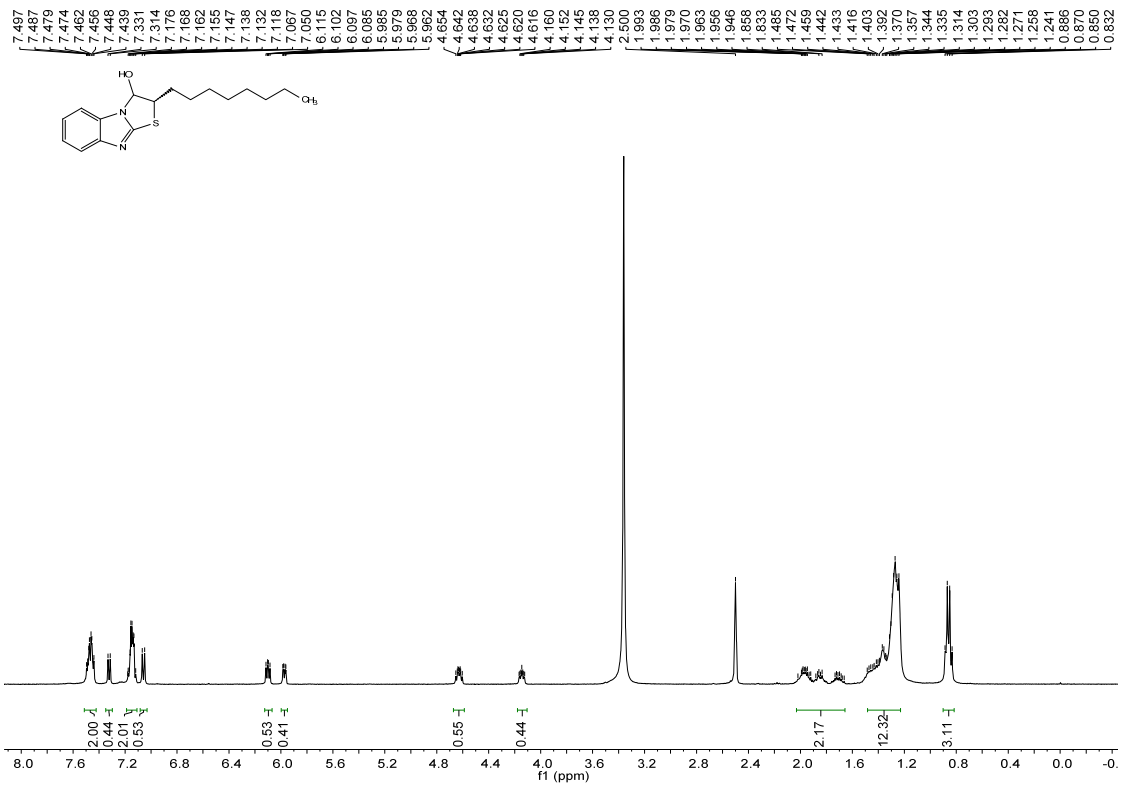


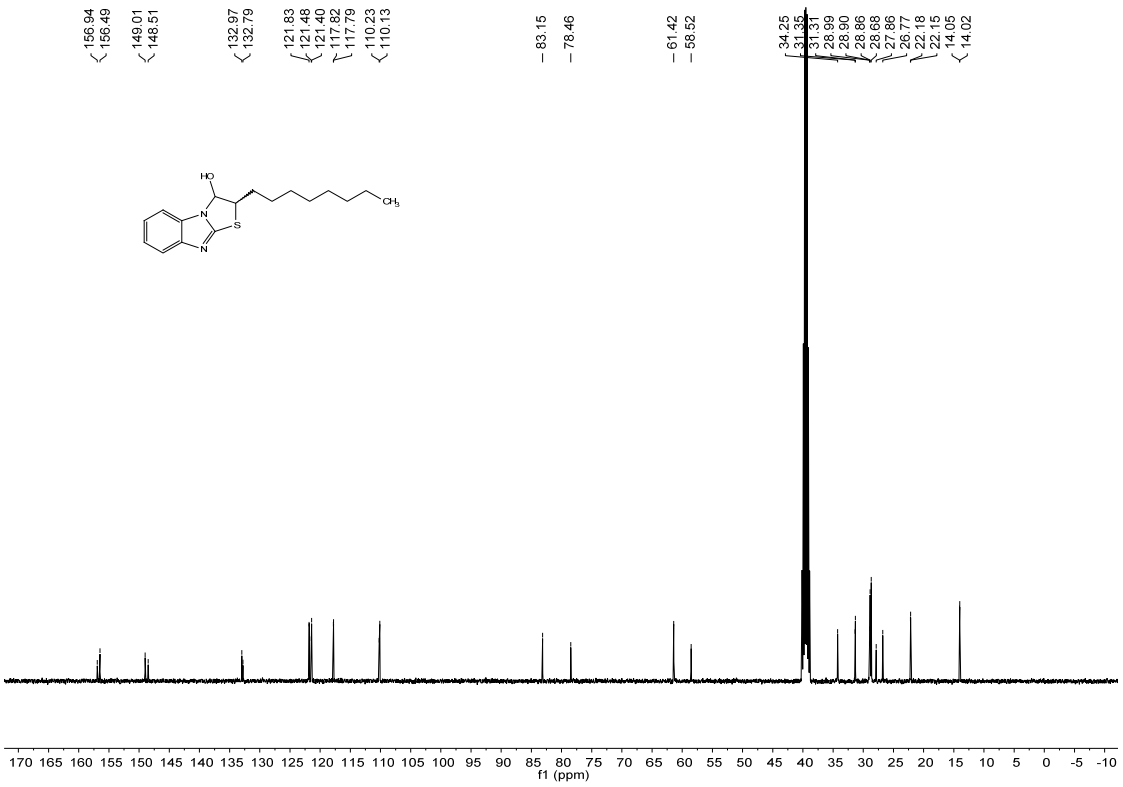
^{1}H and ^{13}C NMR spectra of **5a**



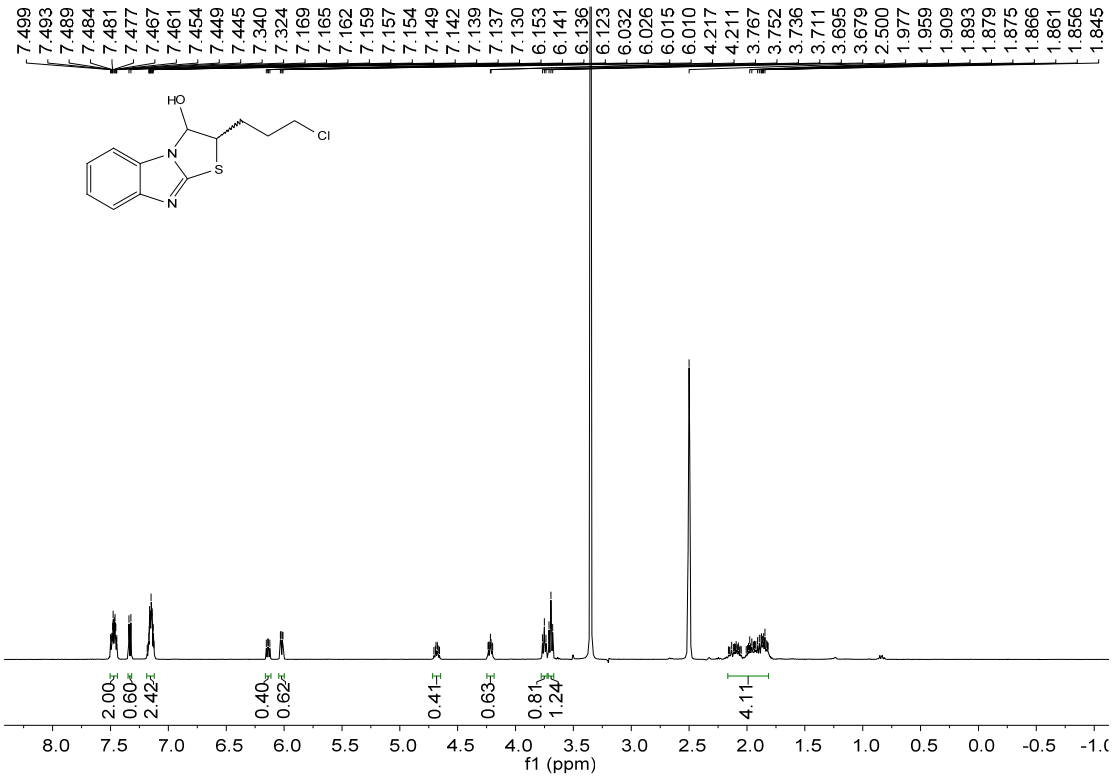


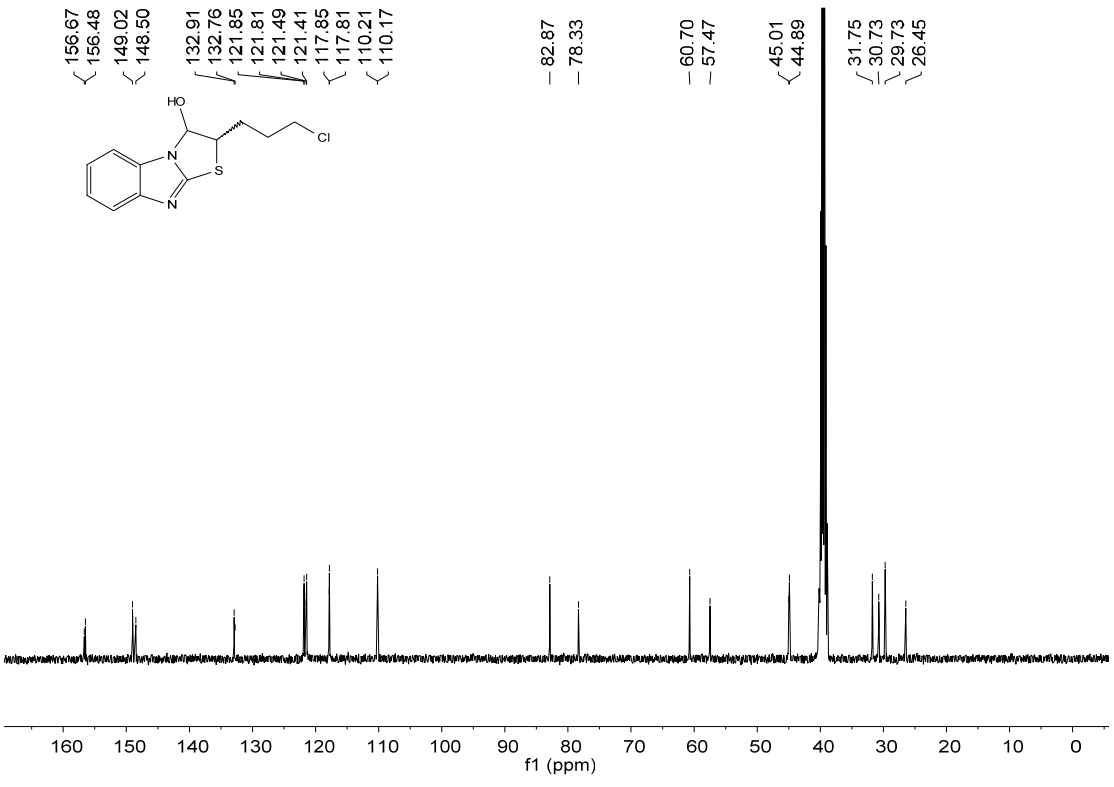
^{1}H and ^{13}C NMR spectra of **5b**



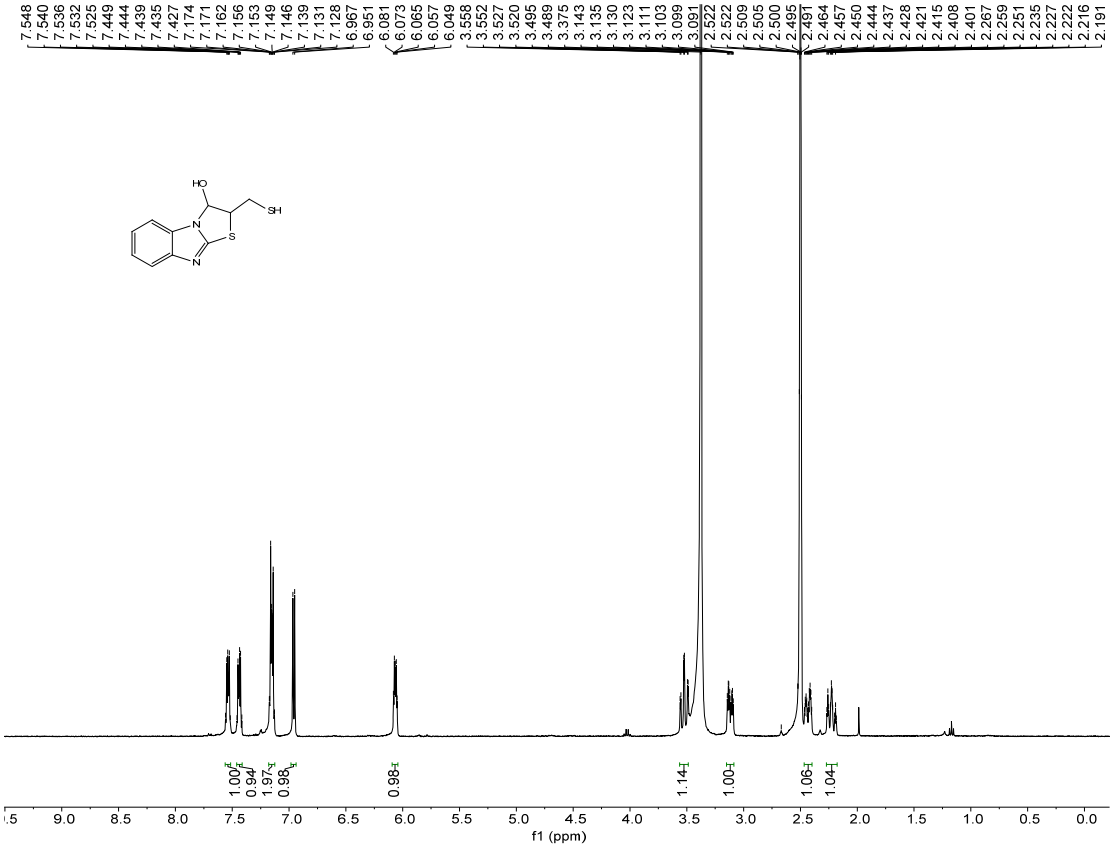


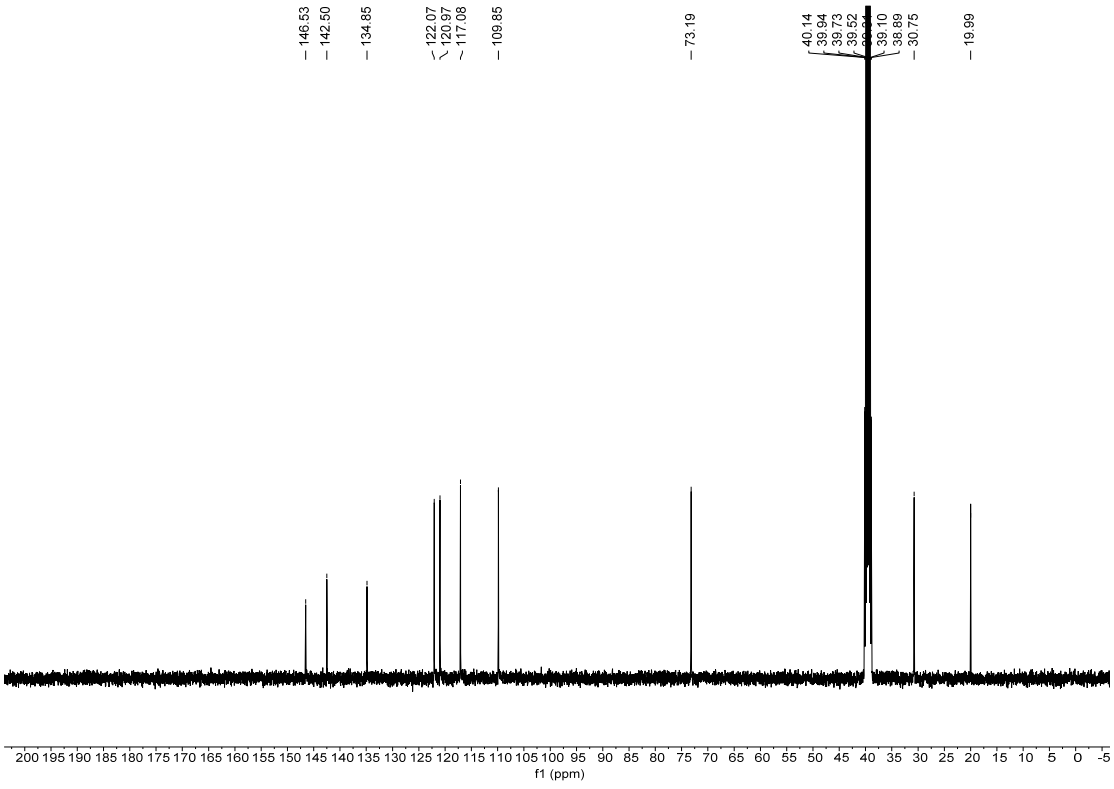
^{1}H and ^{13}C NMR spectra of **5c**



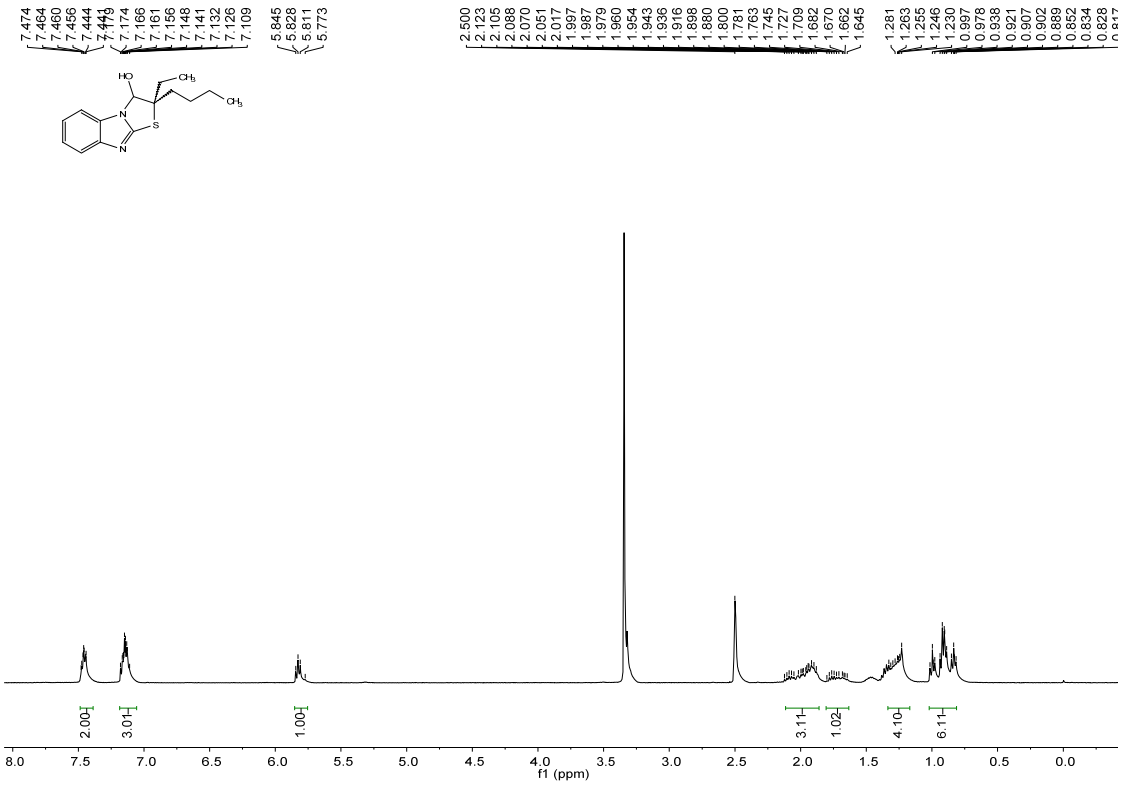


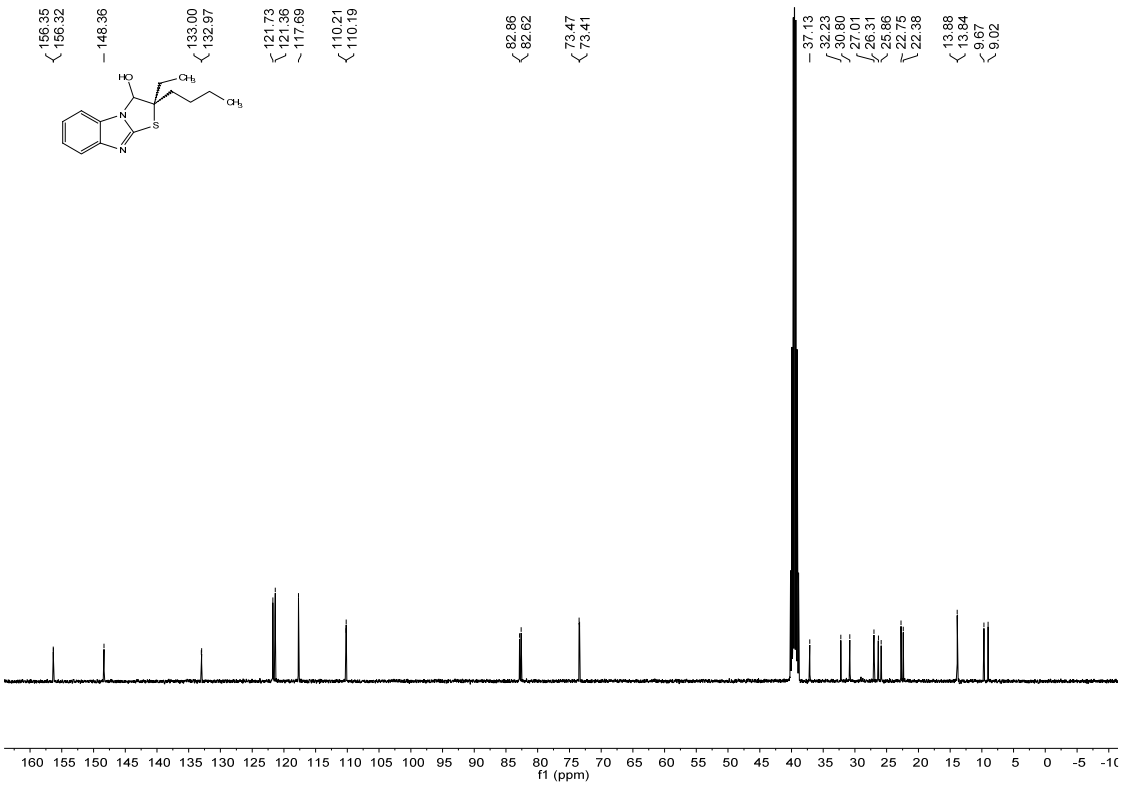
^{1}H and ^{13}C NMR spectra of **5d**



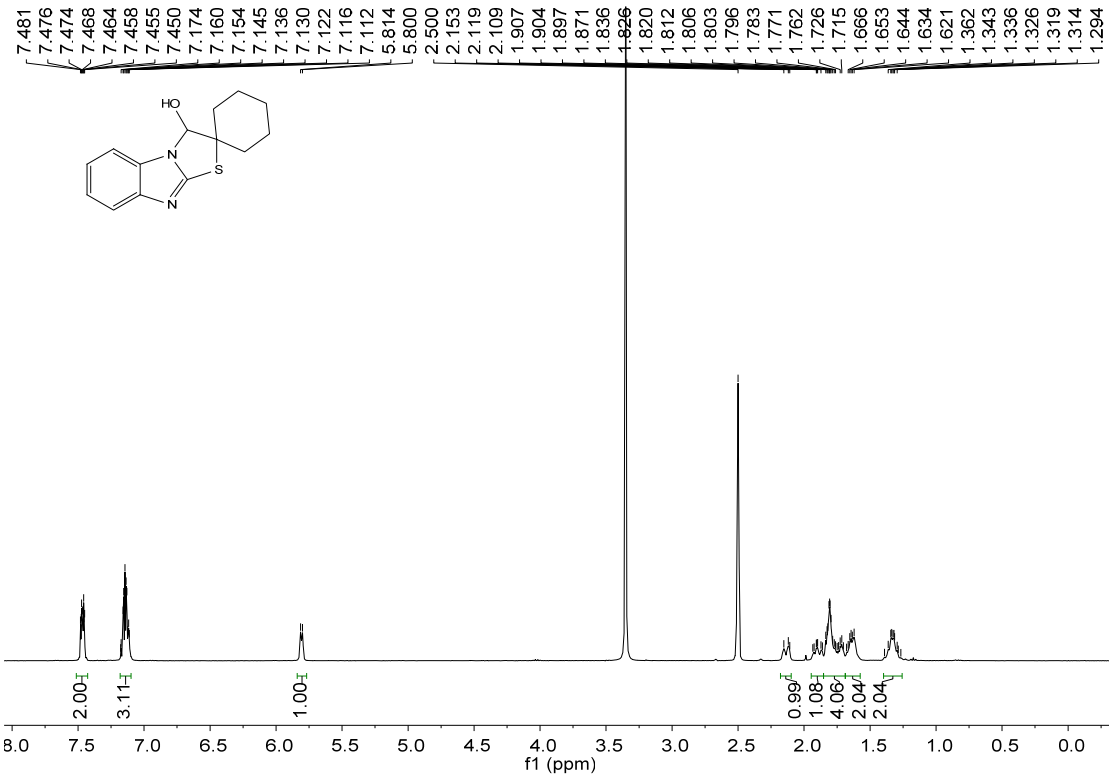


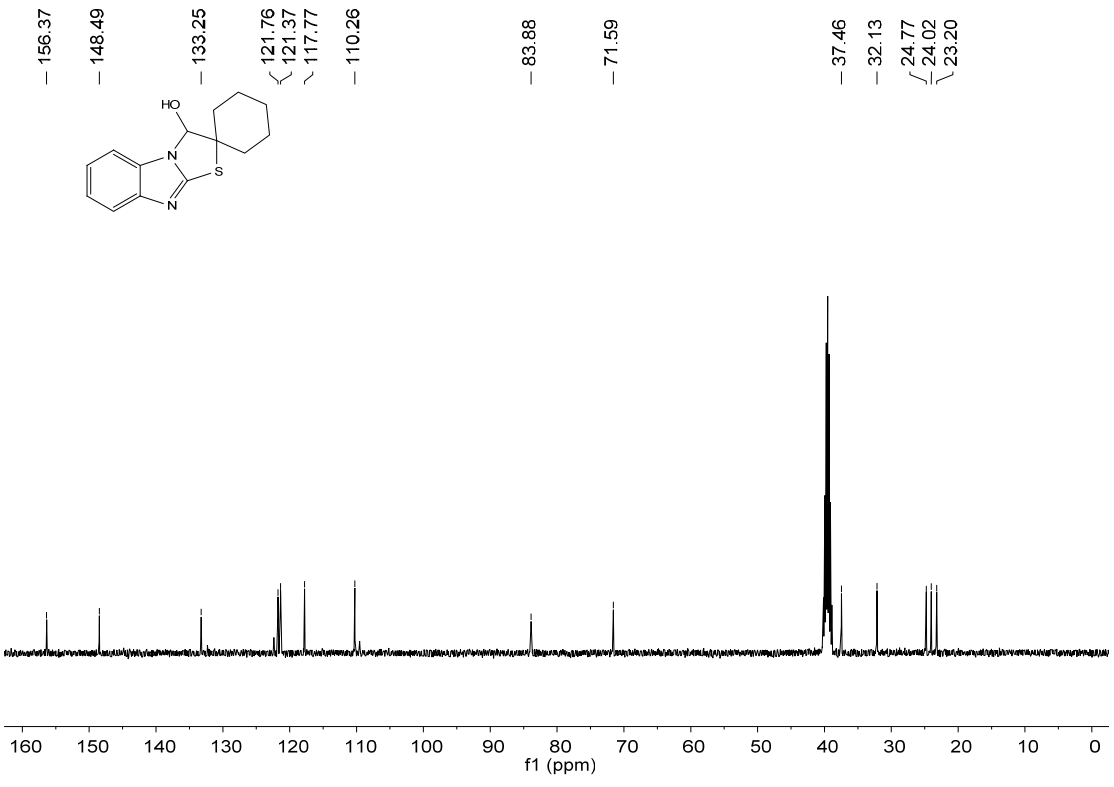
^{1}H and ^{13}C NMR spectra of **5e**



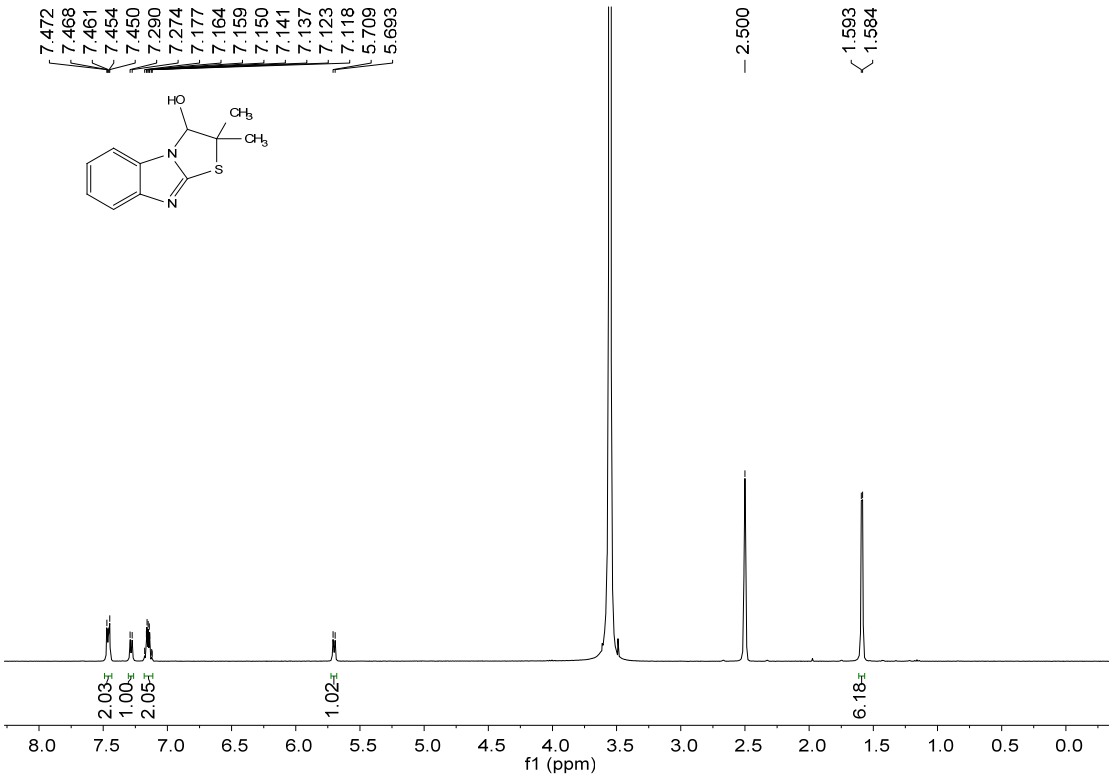


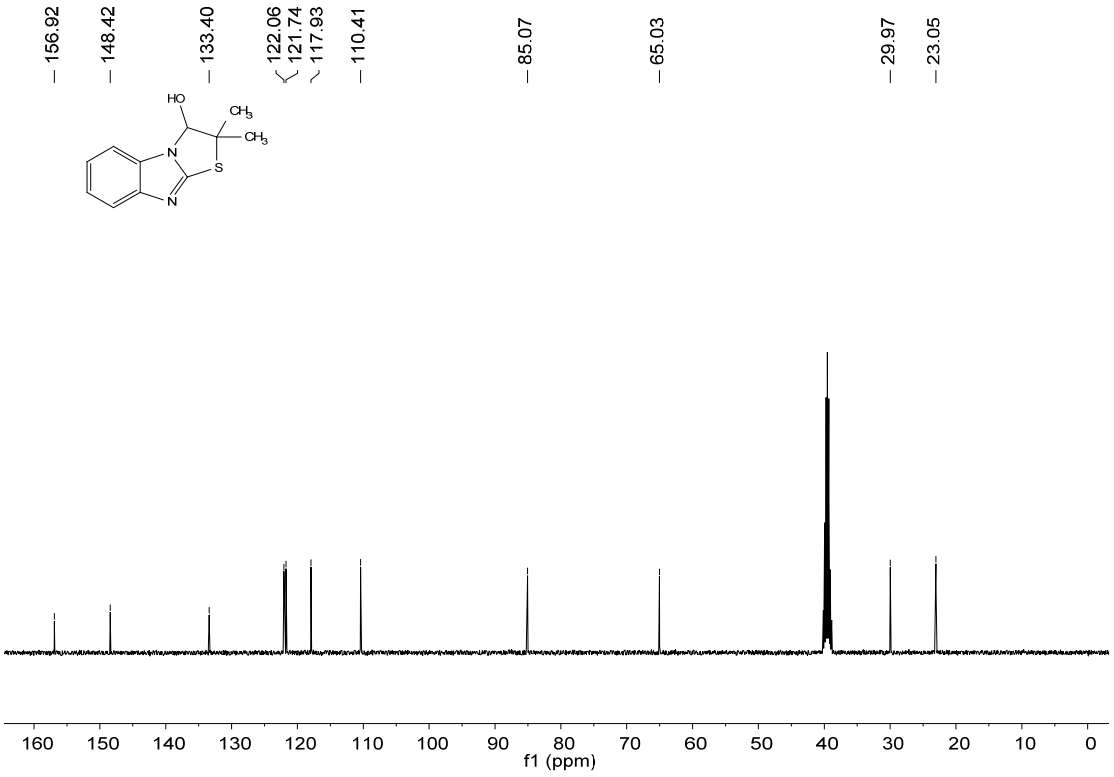
^{1}H and ^{13}C NMR spectra of **5f**



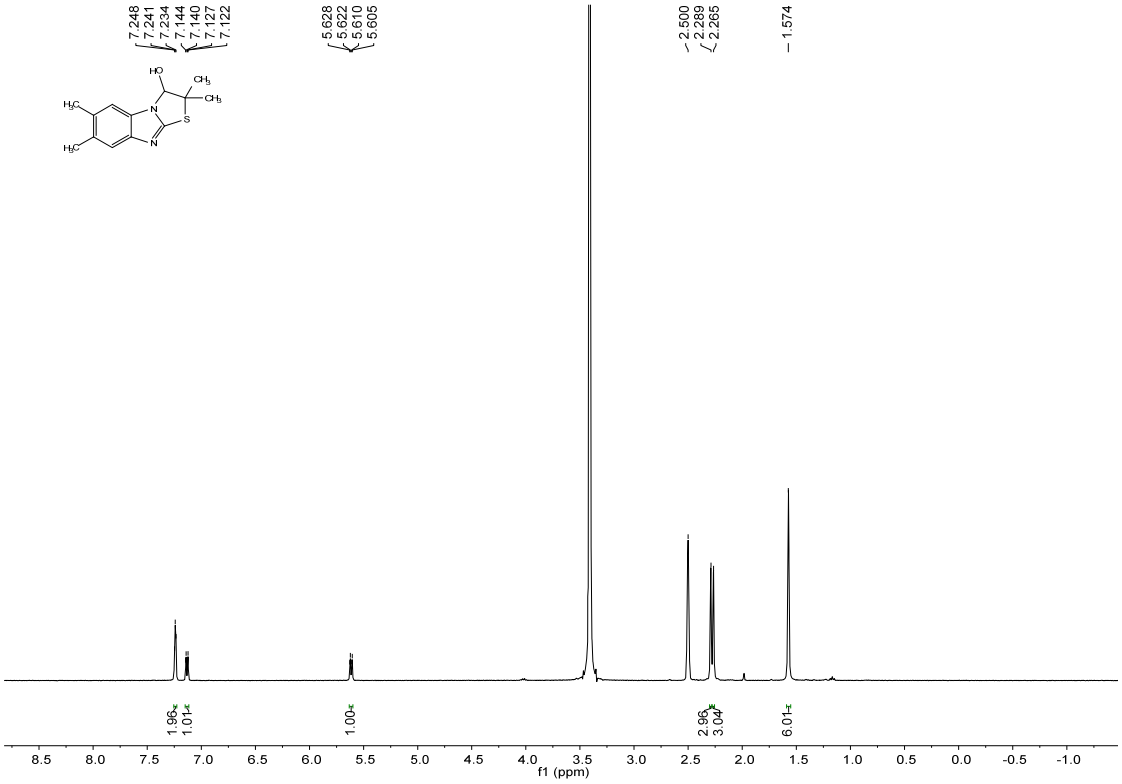


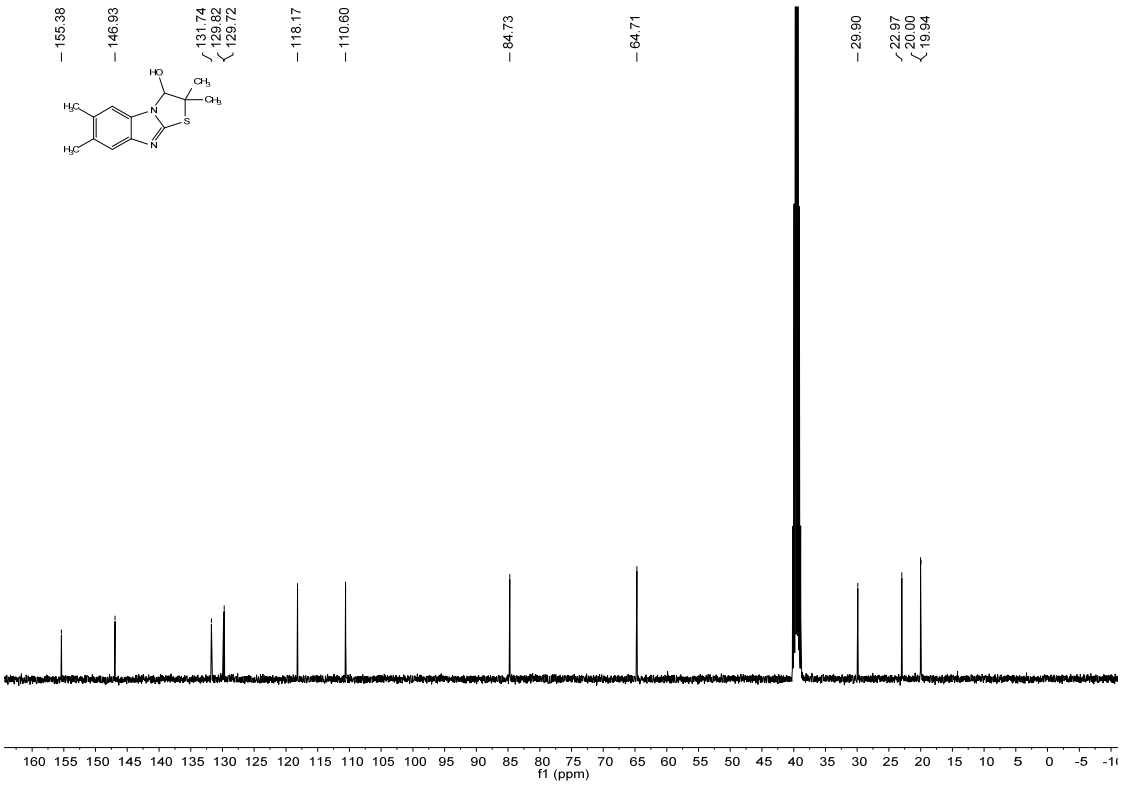
^{1}H and ^{13}C NMR spectra of **5g**



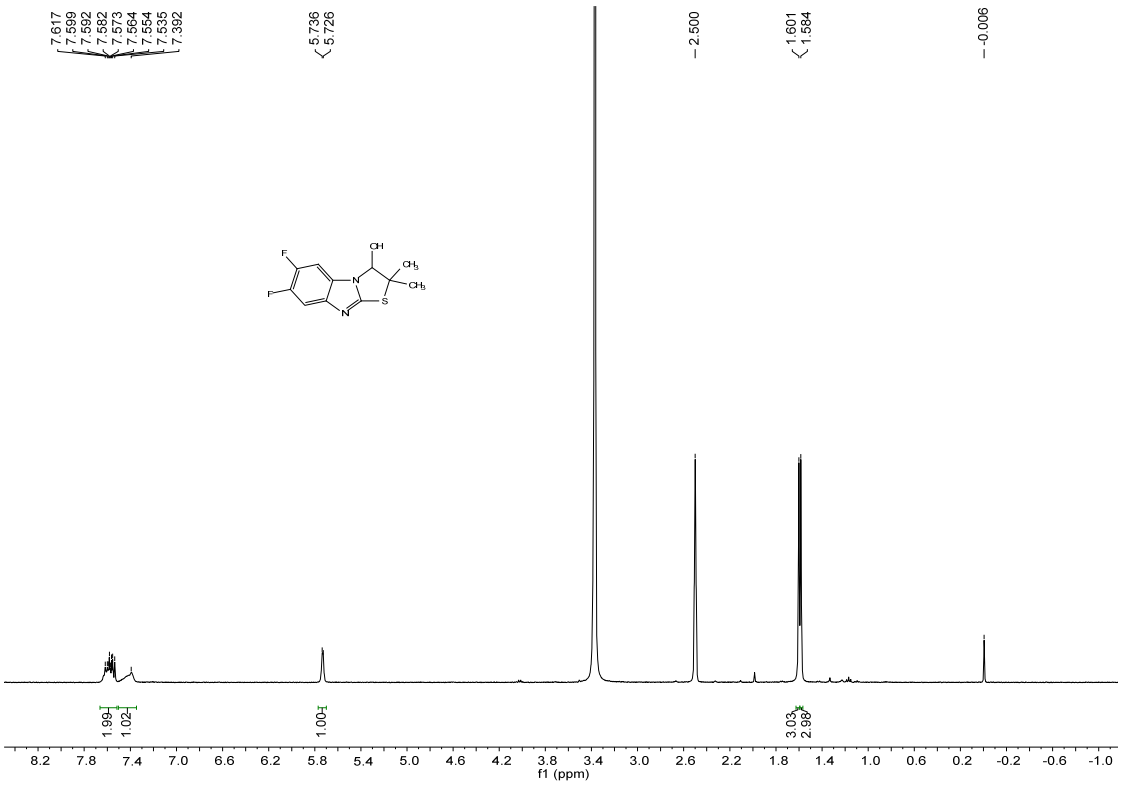


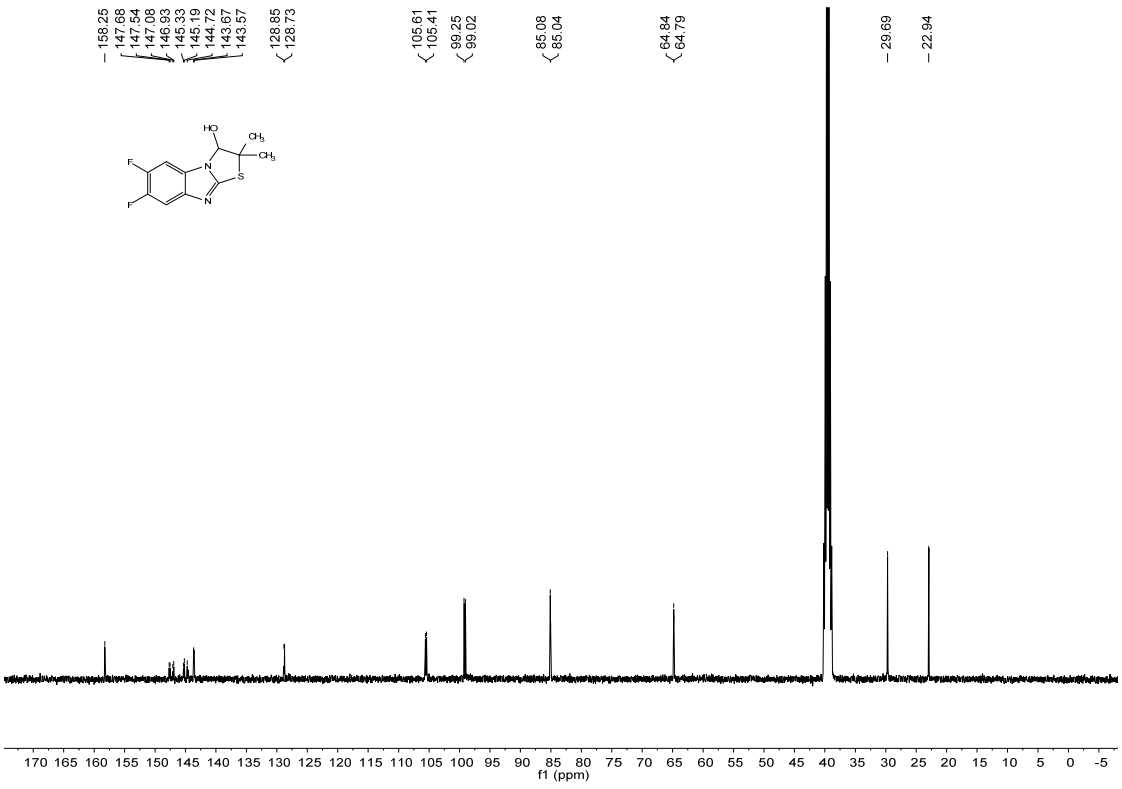
^{1}H and ^{13}C NMR spectra of **5h**



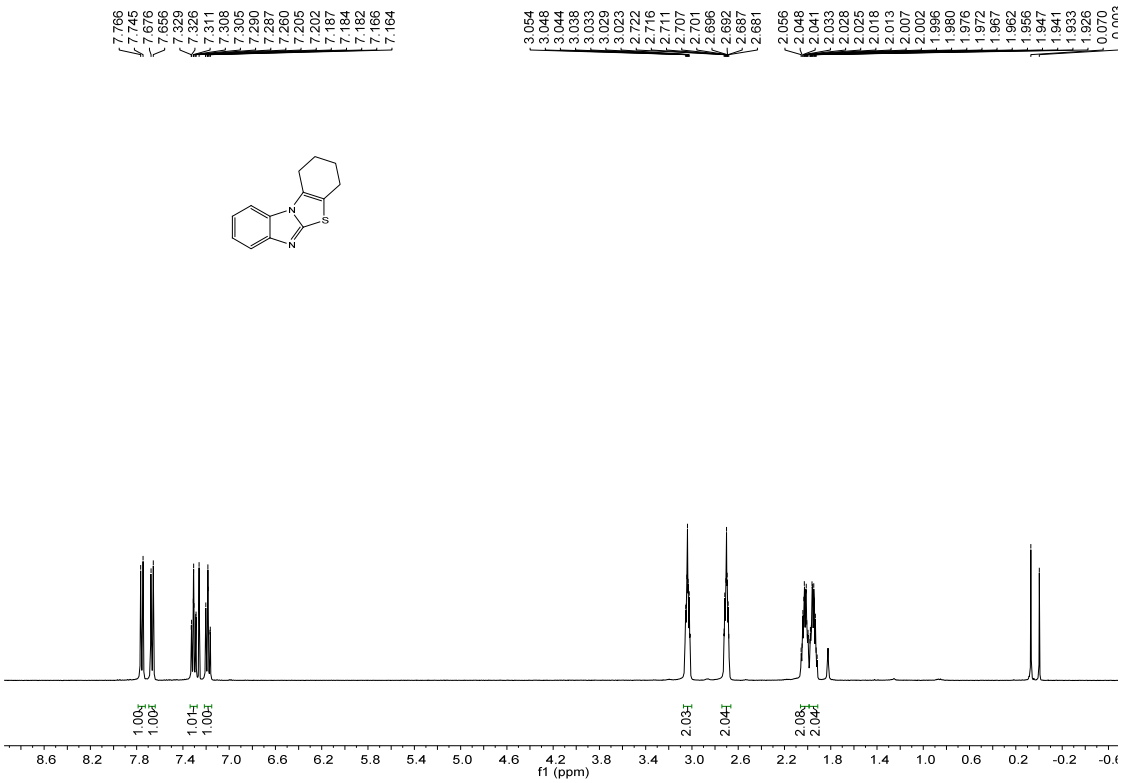


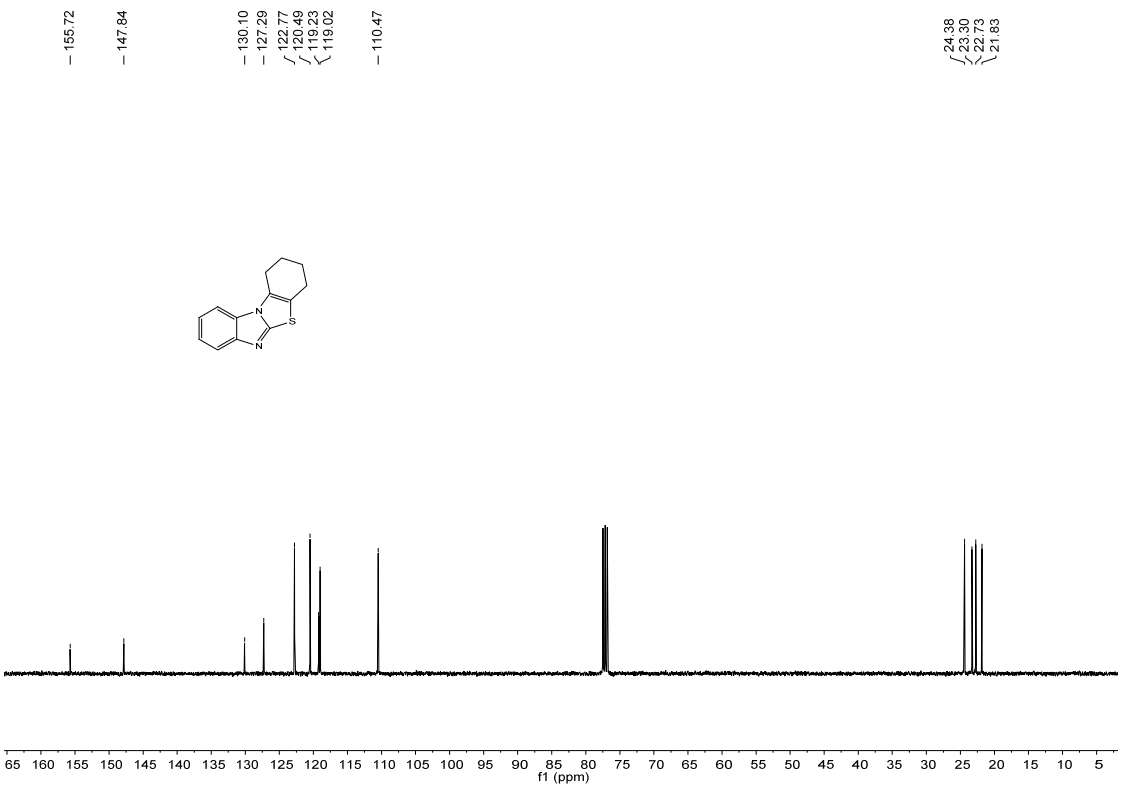
^{1}H and ^{13}C NMR spectra of **5i**



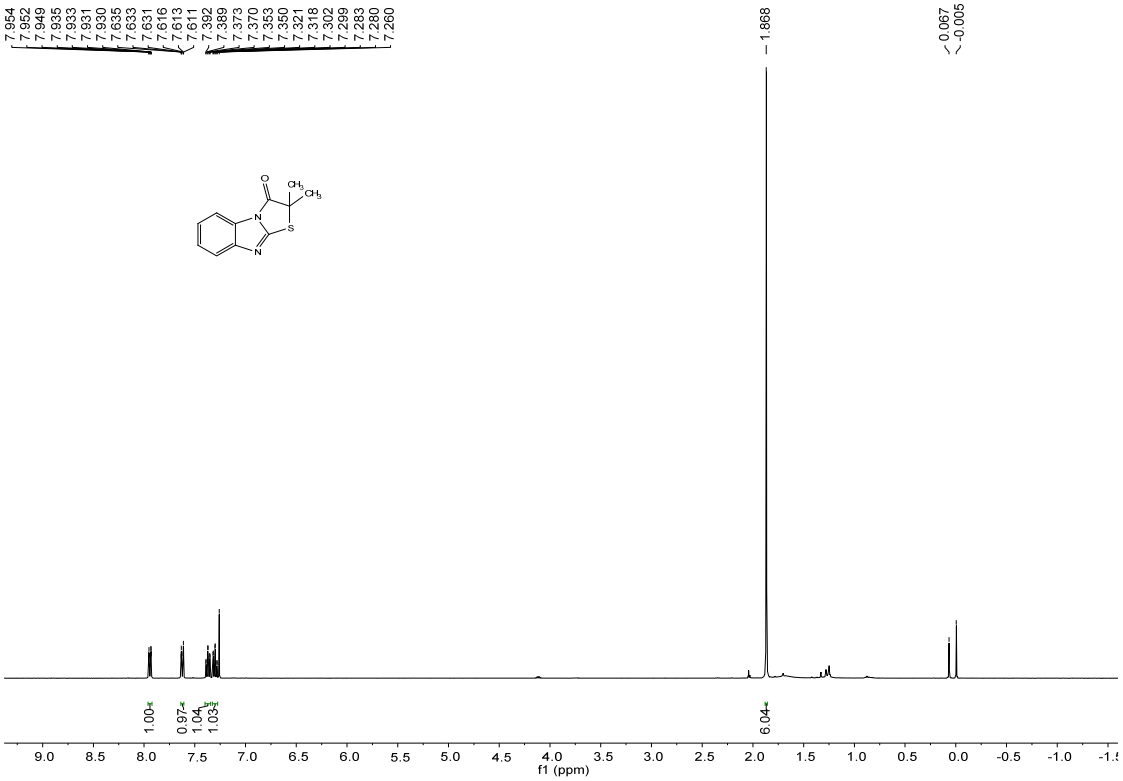


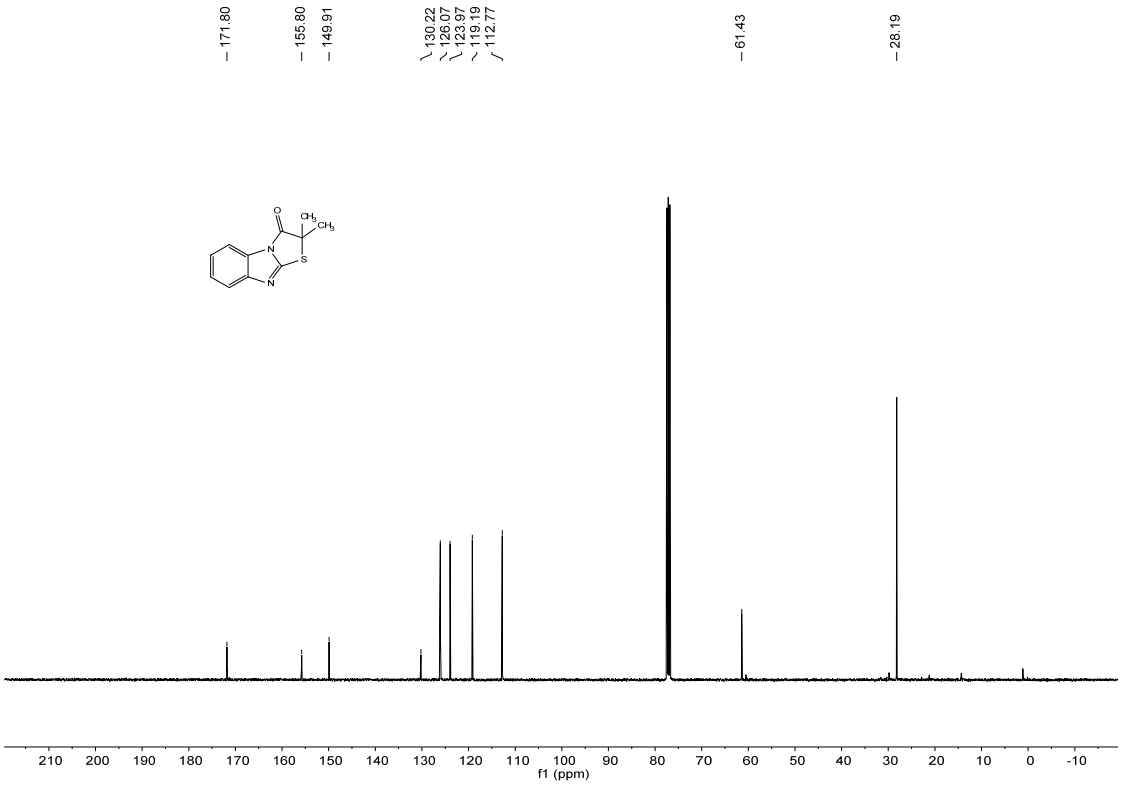
^{1}H and ^{13}C NMR spectra of **6a**





^{1}H and ^{13}C NMR spectra of **6b**





^{1}H and ^{13}C NMR spectra