Distinct Reactivity of Aromatic and Aliphatic Thiols for the Efficient Synthesis of Chromeno[2,3-*d*]pyrimidine and Chromeno[4,3-*b*]chromene Derivatives: Mechanistic Investigations and Reaction Scope

Suman Sourabh[1], Yogesh Bhaskar Singh Tanwer[1], Raj Rani[1], Sabyasachi Bhunia*[1], Sanchari Pal[2], Debjit Das*[2]

[1]*Department of Chemistry, Central University of Jharkhand, Ranchi, Jharkhand, India*
E-mail: sabyasachi.bhunia@cuj.ac.in

[2]*Department of Chemistry, Triveni Devi Bhalotia College, Raniganj, India*
E-mail: debjitofchem@gmail.com

Table of Contents:

S-1. General methods

Commercial reagents and solvents were employed as received without additional purification. ^{1}H and ^{13}C NMR spectra were acquired on Bruker 400, 500, 700 instruments and were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents respectively δ H 7.26, δ C 77.00 for chloroform ($CDCl_3$) or δ H 2.50, δ C 39.52 for Dimethyl Sulfoxide (DMSO) or tetramethylsilane signal. Chemical shifts were reported in δ units (ppm) relative to the TMS signal as an internal reference in $CDCl_3$ and DMSO. Coupling constants, *J* were reported in Hz. Signal multiplicity was reported as follows: s (singlet), d (doublet), t (triplet), m (multiplet, for complex multiplicity). High-resolution mass spectrometry (HRMS) data were obtained via XEVO-G2XSQTOF mass spectrometer. Melting points were measured on a MAC apparatus. TLC monitoring was done by TLC on a silica gel 60 F254 plate.

S-2. Experimental procedures

(a) General procedure for the preparation of chromeno[4,3-*b*]chromene/ chromeno[2,3-*d*]pyrimidine derivatives (4a-4n/5a-5q)

Salicylaldehyde (0.25 mmol), aromatic thiol (0.25 mmol), and 1,3-dimethylbarbituric acid/4-hydroxycoumarin (0.25 mmol) were dissolved in EtOH (2.0 mL), followed by addition of *p*-TSA (10 mol%). The reaction mixture was stirred at 80 ^{o}C for 12 h, with progress monitored by TLC. Upon completion, the reaction mixture was treated with brine, cooled to precipitate the product, which was isolated by filtration, washed with water and ice-cold EtOH, and purified by recrystallization.

(b) Preparation of intermediate B

Salicylaldehyde (0.25 mmol), and 1,3-dimethylbarbituric acid (0.25 mmol) were dissolved in EtOH (2.0 mL), followed by addition of *p*-TSA (10 mol%). The reaction mixture was stirred at 80 ^{o}C for 1 h and monitored by TLC. The mixture was quenched with brine, cooled, and extracted three times by DCM. The combine organic layer was evaporated under reduce pressure. The crude intermediate **B** was then purified under silica column to get the analytically pure sample with 30% yield.

(c) Preparation of compounds 6a

Salicylaldehyde (0.25 mmol), 2-mercaptoethanol (0.3 mmol), and 1,3-dimethylbarbituric acid (0.25 mmol) were dissolved in EtOH (2.0 mL), followed by addition of *p*-TSA (10 mol%). The reaction mixture was stirred at 80 ^{o}C for 12 h, with progress monitored by TLC. Upon completion, the reaction mixture was treated with brine, cooled to precipitate the product **6a**, which was isolated by filtration, washed with water and ice-cold EtOH, and purified by recrystallization.

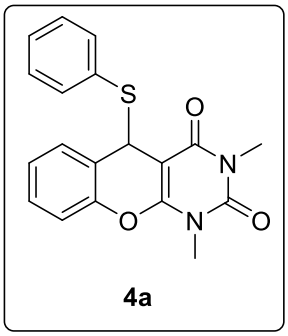
(d) Preparation of compounds 7a

Salicylaldehyde (0.25 mmol), propanethiol (0.3 mmol), and 4-hydroxycoumarin (0.25 mmol) were dissolved in EtOH (2.0 mL), followed by addition of *p*-TSA (10 mol%). The reaction mixture was stirred at 80 ^{o}C for 12 h, with progress monitored by TLC. Upon completion, the reaction mixture was treated with brine, cooled to precipitate the product **7a**, which was isolated by filtration, washed with water and ice-cold EtOH, and purified by recrystallization.

(e) Large scale synthesis of 4a

Following the general procedure [S-2(a)], a mixture of salicylaldehyde (10 mmol), thiophenol (10 mmol), 1,3 dimethyl barbituric acid (10 mmol) and *p*-TSA (10 mol%) in ethanol (80 mL) was stirred at 80 ºC for 12 h to obtain chromeno[4,3-*b*]chromene derivative **4a** with 89% yield.

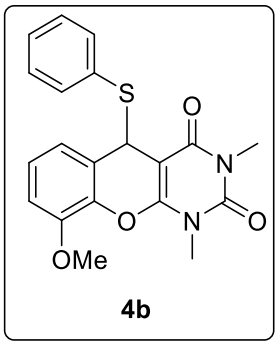
1. Spectral data



4a

1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4a)

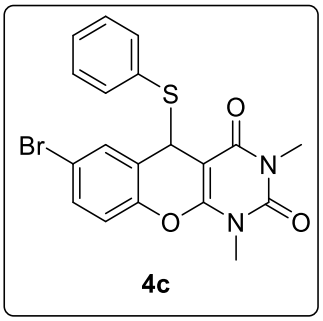
White solid, mp 128 °C; R_f = 0.5 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (s, 3H), 3.44 (s, 3H), 5.41 (s, 1H), 6.82 - 6.84 (m, 1H), 6.95 - 6.97 (m, 2H), 7.12 (t, 2H, *J* = 7.6 Hz), 7.20 - 7.22 (m, 2H), 7.27 - 7.31 (m, 1H), 7.35 - 7.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 28.6, 42.5, 87.0, 115.7, 122.2, 126.0, 128.3, 128.4, 129.1, 129.4, 130.9, 136.8, 149.6, 150.4, 153.9, 161.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{16}N_2O_3SNa$ $[M + Na]^+$ 375.0779; found: 375.0779.



4b

9-methoxy-1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4b)

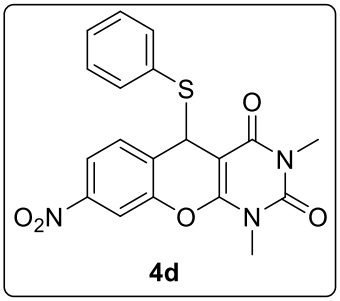
White solid, mp 145 °C; R_f = 0.54 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.33 (s, 3H), 3.44 (s, 3H), 3.80 (s, 3H), 5.39 (s, 1H), 6.79 (d, 1H, *J* = 8.0 Hz), 6.90 (d, 1H, *J* = 7.5 Hz), 7.01 (d, 2H, *J* = 7.0 Hz), 7.11 - 7.15 (m, 3H), 7.28 - 7.32 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2, 28.7, 42.7, 56.2, 86.7, 110.8, 120.4, 123.2, 125.6, 128.3, 129.1, 131.1, 136.6, 139.5, 147.4, 150.5, 153.9, 161.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{18}N_2O_4SNa$ $[M + Na]^+$ 405.0885; found: 405.0885.



4c

7-bromo-1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4c)

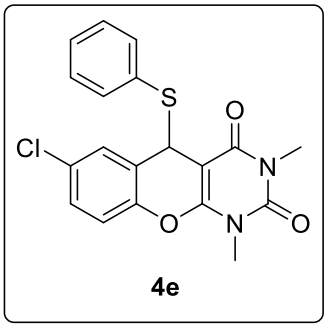
White solid, mp 230 °C; R_f = 0.49 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (s, 3H), 3.44 (s, 3H), 5.33 (s, 1H), 6.73 (d, 1H, *J* = 8.8 Hz), 7.01 (d, 2H, *J* = 7.6 Hz), 7.16 (t, 2H, *J* = 7.6 Hz), 7.30 - 7.33 (m, 2H), 7.44 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.3, 28.7, 42.1, 86.5, 117.5, 118.3, 124.3, 128.5, 129.4, 130.5, 131.4, 132.0, 136.9, 148.6, 150.3, 153.6, 160.7. Anal. Calcd for $C_{19}H_{15}BrN_2O_3S$: C, 52.91; H, 3.51; N, 6.50. Found: C, 52.73; H, 3.54; N, 6.44.



4d

1,3-dimethyl-8-nitro-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4d)

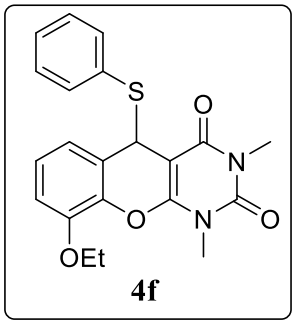
White solid, mp 180 °C; R_f = 0.46 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.34 (s, 3H), 3.46 (s, 3H), 5.43 (s, 1H), 7.00 (d, 2H, *J* = 7.5 Hz), 7.18 (t, 2H, *J* = 7.5 Hz), 7.35 (t, 1H, *J* = 7.5 Hz), 7.50 (d, 1H, *J* = 8.5 Hz), 7.75 (s, 1H), 8.07 (d, 1H, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 28.8, 41.9, 86.2, 111.7, 120.7, 128.7, 129.5, 129.7, 130.1, 130.3, 136.6, 147.2, 149.2, 150.1, 153.6, 160.6. Anal. Calcd for $C_{19}H_{15}N_3O_5S$: C, 57.42; H, 3.80; N, 10.57. Found: C, 57.54; H, 3.85; N, 10.64.



4e

7-chloro-1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4e)

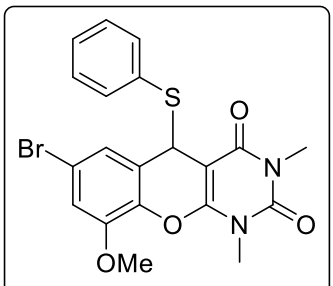
White solid, mp 185 °C; R_f = 0.44 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (s, 3H), 3.44 (s, 3H), 5.33 (s, 1H), 6.78 (d, 1H, *J* = 8.8 Hz), 6.99 - 7.01 (m, 2H), 7.14 - 7.19 (m, 3H), 7.29 - 7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 28.7, 42.2, 86.5, 117.1, 123.9, 128.4, 128.50, 128.55, 129.0, 129.4, 130.6, 130.9, 136.9, 148.0, 153.7, 160.8. Anal. Calcd for $C_{19}H_{15}ClN_2O_3S$: C, 58.99; H, 3.91; N, 7.24. Found: C, 60.18; H, 4.10; N, 7.31.



4f

9-ethoxy-1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4f)

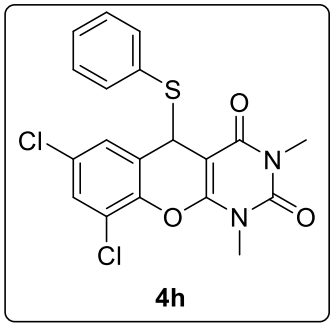
White solid, mp 160 °C; R_f = 0.52 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (t, 3H, *J* = 6.50 Hz), 3.32 (s, 3H), 3.43 (s, 3H), 3.94 - 4.05 (m, 2H), 5.37 (s, 1H), 6.77 (d, 1H, *J* = 8.5 Hz), 6.86 (d, 1H, *J* = 8.0 Hz), 7.02 (d, 2H, *J* = 7.5 Hz), 7.08 (t, 1H, *J* = 8.0 Hz), 7.13 (t, 2H, *J* = 8.0 Hz), 7.28 (t, 1H, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 28.2, 28.6, 42.8, 64.8, 86.7, 112.3, 120.4, 123.2, 125.5, 128.2, 129.0, 131.3, 136.5, 139.8, 146.7, 150.5, 153.9, 161.0. Anal. Calcd for $C_{21}H_{20}N_2O_4S$: C, 63.62; H, 5.08; N, 7.07. Found: C, 62.49; H, 5.15; N, 7.12.



4g

7-bromo-9-methoxy-1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4g)

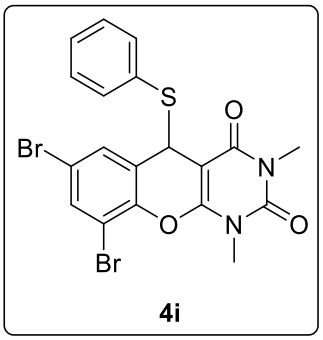
White solid, mp 190 °C; R_f = 0.48 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (s, 3H), 3.43 (s, 3H), 3.79 (s, 3H), 5.28 (s, 1H), 6.89 (d, 1H, *J* = 2.0 Hz), 7.00 - 7.04 (m, 3H), 7.16 (t, 2H, *J* = 7.5 Hz), 7.32 (t, 1H, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.3, 28.7, 42.3, 56.4, 86.4, 114.1, 117.8, 122.9, 124.6, 128.4, 129.4, 130.7, 136.7, 138.6, 148.0, 150.3, 153.6, 160.8. Anal. Calcd for $C_{20}H_{17}BrN_2O_4S$: C, 52.07; H, 3.71; N, 6.07;. Found: C, 52.22; H, 3.75; N, 6.01.



4h

7,9-dichloro-1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4h)

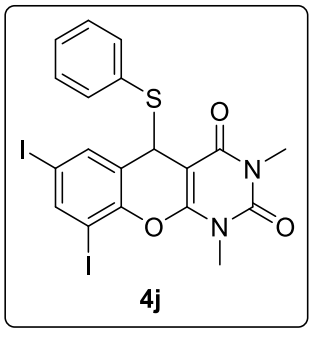
White solid, mp 175 °C; R_f = 0.42 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.33 (s, 3H), 3.44 (s, 3H), 5.32 (s, 1H), 7.00 (d, 2H, *J* = 7.5 Hz), 7.18 - 7.21 (m, 3H), 7.28 (d, 1H, *J* = 2.5 Hz), 7.36 (t, 1H, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 28.8, 42.4, 86.5, 122.2, 125.3, 127.3, 128.62, 128.69, 129.7, 130.2, 130.7, 136.8, 144.3, 150.1, 153.4, 160.6. Anal. Calcd for $C_{19}H_{14}Cl_2N_2O_3S$: C, 54.17; H, 3.35; N, 6.65. Found: C, 53.97; H, 3.26; N, 6.76.



4i

7,9-dibromo-1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4i)

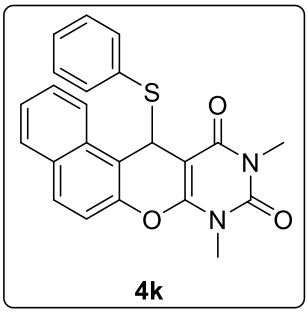
White solid, mp 185 °C; R_f = 0.42 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, DMSO) δ 3.17 (s, 3H), 3.27 (s, 3H), 5.58 (s, 1H), 6.87 (d, 2H, *J* = 7.5 Hz), 7.22 (t, 2H, *J* = 7.5 Hz), 7.41 (t, 1H, *J* = 7.5 Hz), 7.78 (s, 1H), 7.84 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 29.0, 42.5, 86.6, 110.8, 118.2, 125.6, 128.6, 129.7, 130.2, 130.9, 134.1, 136.8, 145.7, 150.1, 153.5, 160.5. Anal. Calcd for $C_{19}H_{14}Br_2N_2O_3S$: C, 44.73; H, 2.77; N, 5.49. Found: C, 44.89; H, 2.73; N, 5.41.



4j

7,9-diiodo-1,3-dimethyl-5-(phenylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4j)

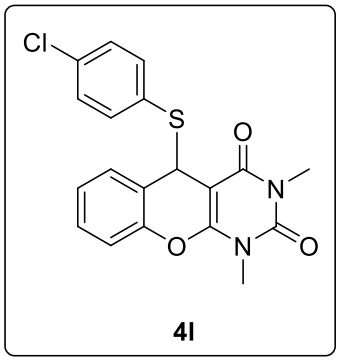
White solid, mp 160 °C; R_f = 0.42 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37 (s, 3H), 3.44 (s, 3H), 5.30 (s, 1H), 6.96 (d, 2H, *J* = 7.5 Hz), 7.20 (t, 2H, *J* = 7.5 Hz), 7.37 (t, 1H, *J* = 7.5 Hz), 7.54 (d, 1H, *J* = 1.5 Hz), 7.95 (d, 1H, *J* = 1.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 29.5, 42.5, 84.2, 86.8, 89.3, 125.3, 128.5, 129.7, 130.2, 136.9, 137.9, 145.3, 148.9, 150.1, 153.7, 160.4. Anal. Calcd for $C_{19}H_{14}I_2N_2O_3S$: C, 37.77; H, 2.34; N, 4.64. Found: C, 37.68; H, 2.39; N, 4.59.



4k

8,10-dimethyl-12-(phenylthio)-8,12-dihydro-9*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*)-dione (4k)

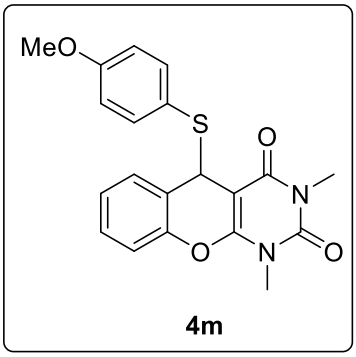
White solid, mp 170 °C; R_f = 0.51 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.29 (s, 3H), 3.50 (s, 3H), 6.04 (s, 1H), 6.70 (d, 2H, *J* = 7.05 Hz), 6.91 (d, 1H, *J* = 9.0 Hz), 7.04 (t, 2H, *J* = 7.5 Hz), 7.26 - 7.29 (m, 1H), 7.56 (t, 1H, *J* = 7.5 Hz), 7.67 (t, 1H, *J* = 7.5 Hz), 7.73 (d, 1H, *J* = 9.0 Hz), 7.87 (d, 1H, *J* = 8.5 Hz), 8.27 (d, 1H, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 28.5, 39.9, 87.1, 114.2, 115.5, 124.0, 125.8, 127.5, 128.0, 128.6, 129.2, 129.6, 129.8, 130.7, 131.6, 137.3, 147.7, 150.4, 153.6, 161.0. Anal. Calcd for $C_{23}H_{18}N_2O_3S$: C, 68.64; H, 4.51; N, 6.96. Found: C, 68.51; H, 4.59; N, 6.88.



4l

5-((4-chlorophenyl)thio)-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4l)

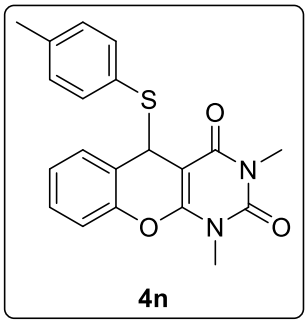
White solid, mp 180 °C; R_f = 0.49 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (s, 3H), 3.45 (s, 3H), 5.41 (s, 1H), 6.88 - 6.92 (m, 3H), 7.12 (d, 2H, *J* = 8.4 Hz), 7.23 (t, 2H, *J* = 3.6 Hz), 7.34 - 7.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 28.8, 42.8, 86.8, 115.9, 121.9, 126.1, 128.5, 128.6, 129.4, 129.7, 135.7, 137.9, 149.6, 150.4, 153.9, 160.9. Anal. Calcd for $C_{19}H_{15}ClN_2O_3S$: C, 58.99; H, 3.91; N, 7.24. Found: C, 59.17; H, 3.85; N, 7.33.



4m

5-((4-methoxyphenyl)thio)-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4m)

White solid, mp 145 °C; R_f = 0.55 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.31 (s, 3H), 3.44 (s, 3H), 3.75 (s, 3H), 5.31 (s, 1H), 6.63 - 6.66 (m, 2H), 6.81 - 6.85 (m, 3H), 7.20 - 7.22 (m, 2H), 7.36 - 7.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 28.7, 42.4, 55.3, 87.0, 113.8, 115.7, 121.5, 122.3, 125.9, 128.3, 129.5, 138.4, 149.6, 150.5, 153.8, 160.7, 161.0. Anal. Calcd for $C_{20}H_{18}N_2O_4S$: C, 62.81; H, 4.74; N, 7.33. Found: C, 63.05; H, 4.65; N, 7.41.

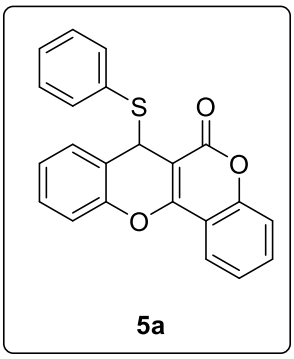


4n

1,3-dimethyl-5-(*p*-tolylthio)-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (4n)

White solid, mp 125 °C; R_f = 0.51 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.31 (s, 3H), 3.44 (s, 3H), 5.35 (s, 1H), 6.83 - 6.86 (m, 3H), 6.93 (d, 2H, *J* = 7.5 Hz), 7.20 - 7.22 (m, 2H), 7.34 - 7.35 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 28.3,

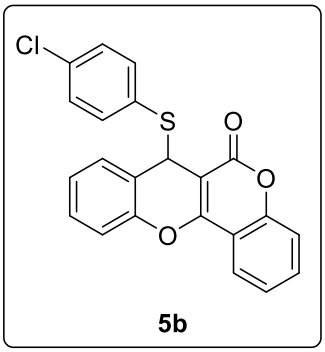
28.6, 42.4, 87.0, 115.7, 122.4, 125.9, 127.4, 128.3, 129.1, 129.4, 136.7, 139.3, 149.6, 150.4, 153.8, 161.0. Anal. Calcd for $C_{20}H_{18}N_2O_3S$: C, 65.55; H, 4.95; N, 7.64. Found: C, 65.72; H, 4.86; N, 7.69.



5a

7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5a)[1]

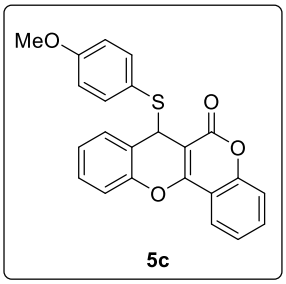
White solid, mp 180 °C; R_f = 0.5 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, DMSO) δ 5.56 (s, 1H), 6.76 - 6.78 (m, 2H), 7.01 - 7.07 (m, 3H), 7.25 - 7.28 (m, 1H), 7.31 - 7.34 (m, 2H), 7.38 - 7.42 (m, 1H), 7.49 - 7.51 (m, 1H), 7.60 - 7.62 (m, 1H), 7.67 - 7.71 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 41.7, 100.1, 113.2, 116.0, 116.6, 120.8, 122.3, 124.6, 125.8, 128.4, 128.9, 129.3, 129.6, 129.9, 132.8, 136.2, 149.6, 151.8, 156.0, 159.5. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{22}H_{14}NaO_3S$ $[M + Na]^+$ 381.0561; found: 381.0561.



5b

7-((4-chlorophenyl)thio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5b)[1]

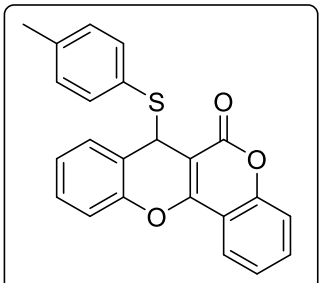
White solid, mp 170 °C; R_f = 0.49 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (s,1H), 6.84 (d, 2H, *J* = 8.0 Hz), 6.98 - 7.00 (m, 3H), 7.24 - 7.27 (m, 2H), 7.33 (t, 1H, *J* = 7.2 Hz), 7.40 (d, 1H, *J* = 8.4 Hz), 7.43 - 7.45 (m, 1H), 7.57 - 7.61 (m,1H), 7.75 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.7, 100.6, 113.8, 116.3, 116.9, 121.1, 122.6, 124.3, 125.9, 128.5, 128.8, 129.1, 129.6, 132.4, 135.8, 138.0, 150.0, 152.4, 156.8, 160.6.



5c

7-((4-methoxyphenyl)thio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5c)[1]

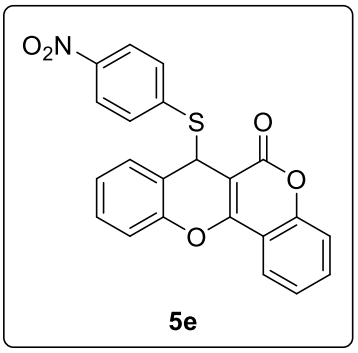
White solid, mp 150 °C; R_f = 0.55 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 5.36 (s, 1H), 6.51 (d, 2H, *J* = 8.4 Hz), 6.77 (d, 2H, *J* = 8.4 Hz), 6.91 - 6.93 (m, 1H), 7.22 - 7.25 (m,2H), 7.30 (t, 1H, *J* = 7.6 Hz), 7.39 (d, 1H, *J* = 8.4 Hz), 7.43 - 7.46 (m, 1H), 7.57 (t, 1H, *J* = 7.6 Hz), 7.70 (d, 1H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.4, 55.2, 100.76, 113.8, 113.9, 116.1, 116.8, 121.0, 121.4, 122.5, 124.1, 125.7, 128.5, 129.7, 132.1, 138.4, 150.0, 152.4, 156.6, 160.76, 160.79.



5d

7-(*p*-tolylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5d)[1]

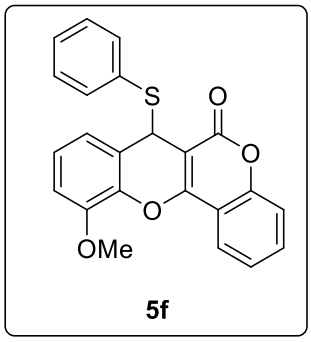
White solid, mp 175 °C; R_f = 0.52 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23 (s, 3H), 5.39 (s, 1H), 6.80 (s, 4H), 6.93 - 6.95 (m, 1H), 7.22 - 7.24 (m, 2H), 7.28 - 7.32 (m, 1H), 7.38 - 7.43 (m, 2H), 7.55 - 7.59 (m, 1H), 7.71 (dd, 1H, *J* = 8.0 Hz, 1.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 42.4, 100.8, 113.9, 116.1, 116.8, 121.5, 122.5, 124.1, 125.7, 126.9, 128.5, 129.1, 129.6, 132.1, 136.7, 139.3, 149.9, 152.4, 156.7, 160.7.



5e

7-((4-nitrophenyl)thio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5e)[1]

White solid, mp 190 °C; R_f = 0.49 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, DMSO) δ 5.89 (s, 1H), 7.22 - 7.24 (m, 1H), 7.30 - 7.34 (m, 3H), 7.38 - 7.41 (m, 1H), 7.44 - 7.47 (m, 1H), 7.53 (d, 1H, *J* = 8.5 Hz), 7.60 (dd, 1H, *J* = 10 Hz , 1.6 Hz), 7.72 - 7.76 (m, 1H), 7.86 (dd, 1H, *J* = 8.0 Hz, 1.5 Hz), 7.96 - 7.98 (m, 2H,). ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.2, 100.5, 113.7, 116.6, 117.1, 120.8, 122.7, 123.3, 124.5, 126.3, 129.4, 129.6, 132.9, 136.3, 140.4, 148.0, 150.0, 152.6, 157.1, 160.7.

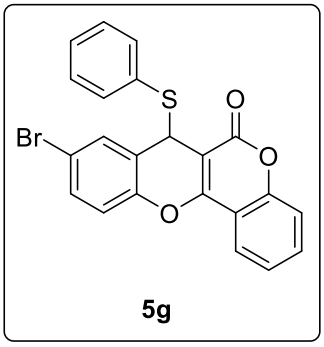


5f

11-methoxy-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5f)

White solid, mp 155 °C; R_f = 0.54 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 5.41 (s, 1H), 6.81 (d, 1H, *J* = 8.0 Hz), 6.95 - 7.03 (m, 5H), 7.14 (t, 1H, *J* = 8.0 Hz), 7.23 (t, 1H, *J* = 7.5 Hz), 7.29 (t, 1H, *J* = 7.5 Hz), 7.37 (d, 1H, *J* = 8.5 Hz), 7.55 (t, 1H, *J* = 8.5 Hz), 7.76 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.5, 56.3, 100.4, 111.2, 114.0, 116.6, 120.8, 122.3, 122.8, 124.2, 125.4, 128.3, 129.1, 130.6, 132.1, 136.6, 140.0, 147.7, 152.3,

156.6, 160.8. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{23}H_{16}O_4SNa$ $[M + Na]^+$ 411.0667; found: 411.0667.

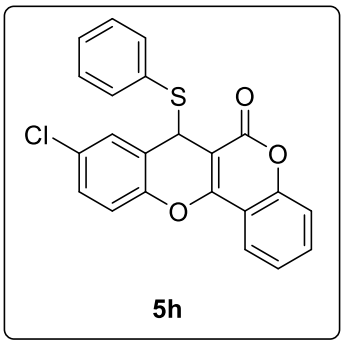


5g

9-bromo-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5g)

White solid, mp 180 °C; R_f = 0.49 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, DMSO) δ 5.61 (s, 1H), 6.79 (d, 2H, *J* = 7.6 Hz), 7.06 (t, 3H, *J* = 7.4 Hz), 7.28 (t, 1H, *J* = 7.4 Hz), 7.40 (t, 1H, *J* = 7.5 Hz), 7.51 (d, 2H, *J* = 8.5 Hz), 7.67 – 7.72 (m, 2H), 7.84 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 41.12, 99.9, 113.0, 116.6, 117.1, 118.3, 122.3, 123.4, 124.6, 128.5, 129.2, 129.6, 131.6, 132.2, 132.9, 136.4, 148.8, 151.8, 155.9, 159.3.

Anal. Calcd for $C_{22}H_{13}BrO_3S$: C, 60.42; H, 3.00; Found: C, 60.64; H, 3.09.

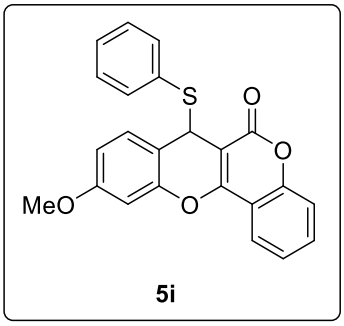


5h

9-chloro-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5h)

White solid, mp 160 °C; R_f = 0.44 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (s, 1H), 6.90 (d, 1H, *J* = 9.0 Hz), 6.97 (d, 2H, *J* = 7.0 Hz), 7.06 (t, 2H, *J* = 8.0 Hz), 7.22 (dd, 1H, *J* = 9.0 Hz, 2.0 Hz), 7.27 - 7.28 (m, 1H), 7.33 (t, 1H, *J* = 7.5 Hz), 7.41 - 7.43 (m, 2H), 7.59 - 7.63 (m, 1H), 7.69 (dd, 1H, *J* = 7.5 Hz, 1.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.1, 100.32, 113.6, 116.9, 117.5, 122.4, 123.1, 124.3, 128.5, 128.7, 129.2, 129.4, 130.0, 130.6, 132.4,

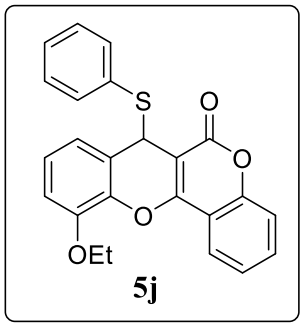
136.9, 148.4, 152.4, 156.5, 160.5. Anal. Calcd for $C_{22}H_{13}ClO_3S$: C, 67.26; H, 3.34; Found: C, 67.49; H, 3.29.



5i

10-methoxy-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5i)

White solid, mp 190 °C; R_f = 0.51 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 5.40 (s, 1H), 6.45 (d, 1H, *J* = 2.5 Hz), 6.81 (dd, 1H, *J* = 8.5 Hz, 3.0 Hz), 6.92 - 6.93 (m, 2H), 7.01 (t, 2H, *J* = 8.0 Hz), 7.22 (t, 1H, *J* = 7.5 Hz), 7.27 - 7.30 (m, 1H), 7.33 (d, 1H, *J* = 8.5 Hz), 7.38 (d, 1H, *J* = 8.0 Hz), 7.54 - 7.58 (m, 1H), 7.67 (dd, 1H, *J* = 8.0 Hz, 1.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.3, 55.5, 100.8, 101.1, 112.8, 113.3, 113.8, 116.8, 122.4, 124.1, 128.2, 129.0, 130.3, 130.6, 132.1, 136.8, 150.7, 152.3, 156.5, 159.7, 160.7. $C_{23}H_{16}O_4S$: C, 71.12; H, 4.15; Found: C, 70.89; H, 4.07.

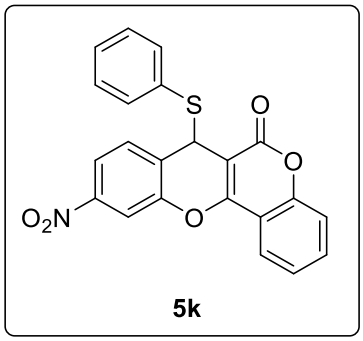


5j

11-ethoxy-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5j)

White solid, mp 165 °C; R_f = 0.52 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (t, 3H, *J* = 7.0 Hz), 3.98 - 4.10 (m, 2H), 5.42 (s, 1H), 6.81 (d, 1H, *J* = 8.0 Hz), 6.96 - 6.99 (m, 3H), 7.03 (t, 2H, *J* = 7.5 Hz), 7.11 (t, 1H, *J* = 8.0 Hz), 7.22 (t, 1H, *J* = 7.0 Hz), 7.30 (t, 1H, *J* = 8.0 Hz), 7.38 (d, 1H, *J* = 8.5 Hz), 7.56 (t, 1H, *J* = 8.5 Hz), 7.74 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.8, 42.6, 65.1, 100.4, 113.0, 114.1, 116.7, 120.9, 122.4, 122.8, 124.2,

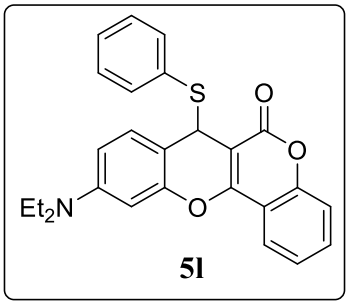
125.3, 128.3, 129.0, 130.7, 132.1, 136.6, 140.4, 147.0, 152.4, 156.6, 160.8. $C_{24}H_{18}O_4S$: C, 71.62; H, 4.51; Found: C, 71.53; H, 4.44.



5k

10-nitro-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5k)

White solid, mp 200 °C; R_f = 0.49 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (s, 1H), 6.95 (d, 2H, *J* = 8.0 Hz), 7.05 (t, 2H, *J* = 7.5 Hz), 7.28 (t, 1H, *J* = 7.35 Hz), 7.36 (t, 1H, *J* = 7.5 Hz), 7.43 (d, 1H, *J* = 8.5 Hz), 7.59 (d, 1H, *J* = 8.5 Hz), 7.63 (t, 1H, *J* = 8.0 Hz), 7.71 (d, 1H, *J* = 7.8 Hz), 7.83 (s, 1H), 8.09 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.8, 100.3, 112.0, 113.2, 117.0, 120.3, 122.4, 124.6, 128.8, 129.6, 129.8, 130.6, 132.9, 136.7, 147.4, 149.7, 152.5, 156.5, 160.2. $C_{23}H_{13}NO_5S$: C, 65.50; H, 3.25; N, 3.47; Found: C, 65.35; H, 3.34; N, 3.42.

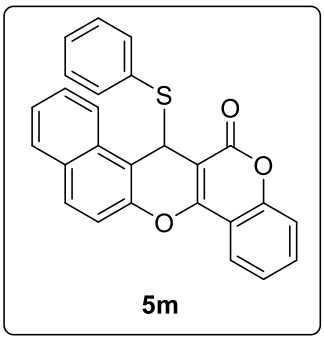


5l

10-(diethylamino)-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5l)

White solid, mp 165 °C; R_f = 0.50 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (700 MHz, $CDCl_3$) δ 1.18 (t, 6H, *J* = 7.0 Hz), 3.30 - 3.40 (m, 4H), 5.41 (s, 1H), 6.147 - 6.149 (m, 1H), 6.56 - 6.58 (m, 1H), 6.96 - 7.01 (m, 4H), 7.20 - 7.24 (m, 2H), 7.27 (t, 1H, *J* = 7.7 Hz), 7.37 (d, 1H, *J* = 8.4 Hz), 7.55 (t, 1H, *J* = 7.7 Hz), 7.72 (dd, 1H, *J* = 8.4 Hz, 1.4 Hz). ^{13}C NMR (176 MHz, $CDCl_3$) δ 12.3, 43.0, 44.5, 97.9, 101.3, 107.2, 110.1, 114.1, 116.7, 122.5, 124.0, 128.0, 128.7, 129.0, 130.1,

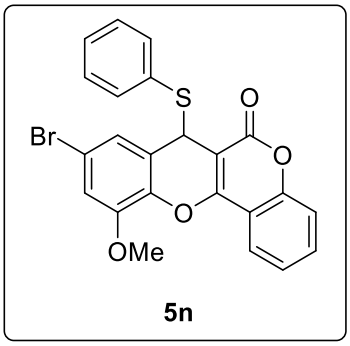
131.1, 131.9, 136.9, 148.1, 151.3, 152.3, 156.7, 161.0. $C_{26}H_{23}NO_3S$: C, 72.70; H, 5.40; N, 3.26; Found: C, 72.85; H, 5.49; N, 3.30.



5m

7-(phenylthio)-6*H*,7*H*-benzo[*f*]chromeno[4,3-*b*]chromen-6-one (5m)

White solid, mp 135 °C; R_f = 0.51 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 (s, 1H), 6.63 (d, 2H, *J* = 7.5 Hz), 6.87 (t, 2H, *J* = 7.5 Hz), 7.01 (d, 1H, *J* = 9.0 Hz), 7.17 (t, 1H, *J* = 7.5 Hz), 7.31 (t, 1H, *J* = 8.0 Hz), 7.41 (d, 1H, *J* = 8.5 Hz), 7.52 - 7.60 (m, 2H), 7.66 - 7.67 (m, 2H), 7.74 (d, 1H, *J* = 9.0 Hz), 7.86 (d, 1H, *J* = 8.0 Hz), 8.29 (d, 1H, *J* = 8.35 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.8, 100.7, 113.0, 113.7, 116.1, 116.8, 122.3,123.6, 124.2, 125.6, 127.4, 128.0, 128.6, 129.2, 129.7, 130.0, 130.2, 131.5, 132.1, 137.2, 148.2, 152.3, 156.1, 160.9. $C_{26}H_{16}O_4S$: C, 76.45; H, 3.95; Found: C, 76.37; H, 3.88.

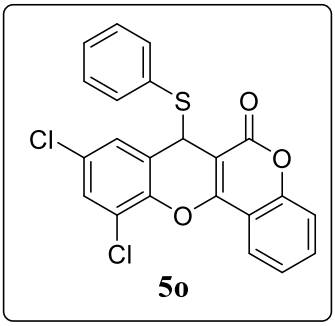


5n

9-bromo-11-methoxy-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5n)

White solid, mp 215 °C; R_f = 0.48 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, DMSO) δ 3.84 (s, 3H), 5.56 (s, 1H), 6.79 (d, 2H, *J* = 7.2 Hz), 7.06 (t, 2H, *J* = 7.6 Hz), 7.21 - 7.22 (m, 1H), 7.30 (t, 1H, *J* = 7.6 Hz), 7.38 - 7.42 (m, 2H), 7.50 (d, 1H, *J* = 8.4 Hz), 7.56 (d, 1H, *J* = 7.2 Hz), 7.70 (t, 1H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, DMSO) δ 41.2, 56.7, 99.8, 113.1, 114.6,

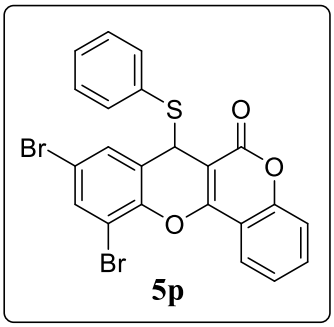
116.6, 116.9, 122.0, 123.0, 123.5, 124.7, 128.5, 129.3, 129.6, 132.9, 136.3, 138.8, 148.1, 151.7, 155.6, 159.3. $C_{23}H_{15}BrO_4S$: C, 59.11; H, 3.24; Found: C, 58.98; H, 3.34.



5o

9,11-dichloro-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5o)

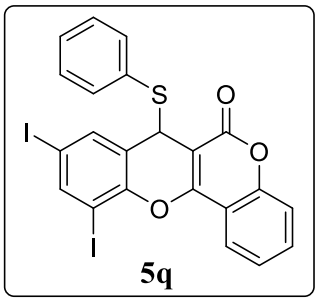
White solid, mp 145 °C; R_f = 0.44 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (s, 1H), 6.95 (d, 2H, *J* = 7.0 Hz), 7.07 (t, 2H, *J* = 7.5 Hz), 7.28 - 7.34 (m, 4H), 7.40 (d, 1H, *J* = 8.5 Hz), 7.59 - 7.62 (m, 1H), 7.72 (dd, 1H, *J* = 8.0 Hz, 1.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.2, 100.4, 113.4, 116.8, 122.6, 122.7, 124.4, 124.5, 127.5, 128.6, 128.9, 129.70, 129.79, 130.3, 132.7, 136.8, 144.6, 152.4, 156.2, 160.2. $C_{22}H_{12}Cl_2O_3S$: C, 61.84; H, 2.83; Found: C, 61.98; H, 2.77.



5p

9,11-dibromo-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5p)

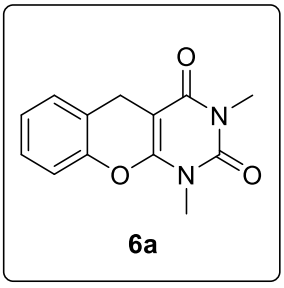
White solid, mp 180 °C; R_f = 0.42 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (s, 1H), 6.92 (d, 2H, *J* = 7.5 Hz), 7.06 (t, 2H, *J* = 7.5 Hz), 7.28 - 7.34 (m, 2H), 7.39 (d, 1H, *J* = 8.5 Hz), 7.44 - 7.45 (m, 1H), 7.59 - 7.61 (m, 2H), 7.72 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.3, 100.5, 111.4, 113.4, 116.8, 117.8, 122.7, 124.5, 124.7, 128.5, 129.6, 129.8, 131.2, 132.7, 134.4, 136.8, 146.0, 152.4, 156.3, 160.1. $C_{22}H_{12}Br_2O_3S$: C, 51.19; H, 2.34; Found: C, 51.37; H, 2.38.



5q

9,11-diiodo-7-(phenylthio)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (5q)

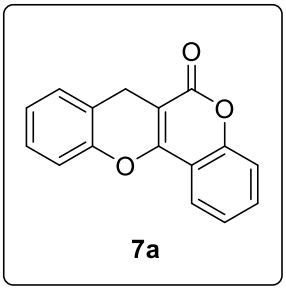
White solid, mp 205 °C; R_f = 0.42 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (s, 1H), 6.90 (d, 2H, *J* = 7.0 Hz), 7.07 (t, 2H, *J* = 8.0 Hz), 7.29 - 7.35 (m, 2H), 7.39 (d, 1H, *J* = 8.5 Hz), 7.58 - 7.62 (m, 2H), 7.76 (dd, 1H, *J* = 8.0 Hz, 1.5 Hz), 7.96 (d, 1H, *J* = 1.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.3, 84.1, 87.8, 99.8, 112.3, 115.8, 122.0, 123.3, 123.5, 127.5, 128.6, 128.8, 131.6, 135.9, 137.2, 144.5, 147.9, 151.3, 155.6, 159.0. $C_{22}H_{12}I_2O_3S$: C, 43.30; H, 1.98; Found: C, 43.09; H, 2.03.



6a

1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione (6a)

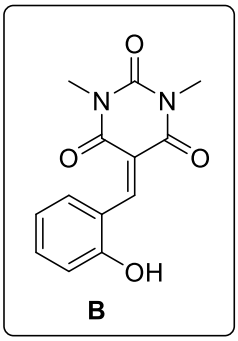
White solid, mp 128 °C; R_f = 0.4 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.50 (s, 3H), 3.71 (s, 2H), 7.05 (d, 1H, *J* = 8.0 Hz), 7.12 - 7.15 (m, 1H), 7.21 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 28.0, 28.9, 85.3, 116.4, 119.8, 125.5, 127.9, 129.6, 149.1, 150.7, 152.6, 162.6. $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47; Found: C, 63.76; H, 5.04; N, 11.40.



7a

6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (7a)

White solid, mp 128 °C; R_f = 0.4 (petroleum ether : ethyl acetate = 7 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 2H), 7.14 - 7.19 (m, 2H), 7.24 - 7.29 (m, 2H), 7.34 - 7.38 (m, 2H), 7.57 (t, 1H, *J* = 7.6 Hz), 7.96 (d, 1H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 99.9, 114.4, 116.7, 116.8, 119.3, 122.5, 124.1, 125.3, 128.2, 129.7, 131.9, 149.2, 152.4, 156.3, 162.4. $C_{16}H_{10}O_3$: C, 76.79; H, 4.03; Found: C, 76.93; H, 4.10.



B

5-(2-hydroxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(*1H,3H,5H*)- trione (B)[2]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.42 (s, 3H), 3.44 (s, 3H), 7.01-7.07 (m, 2H), 7.47 (t, 1H, *J* = 8.0 Hz), 7.63 (d, 1H, *J* = 8.0 Hz), 8.76 (s, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ (ppm) 28.8, 29.2, 115.9, 120.1, 120.9, 122.8, 135.4, 135.7, 150.6, 157.0, 158.8, 162.1, 163.7.

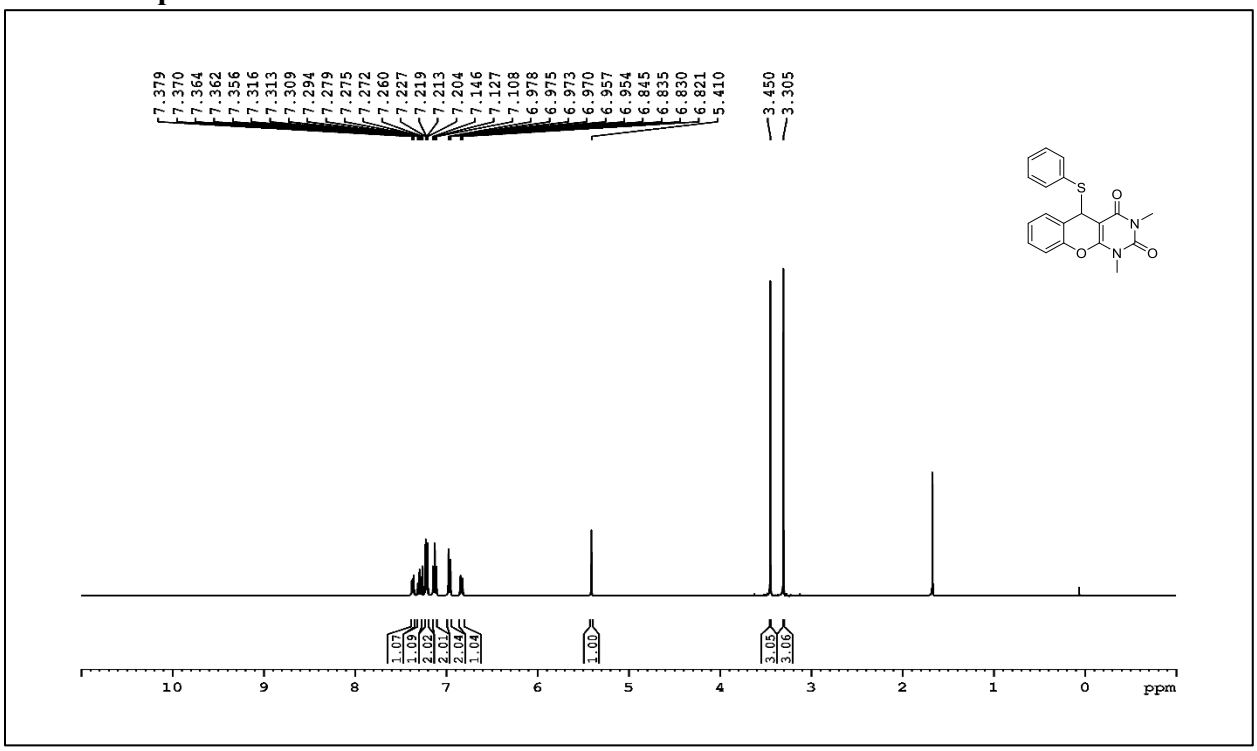
4. References

1. M. F. C. Cardoso, L. S. M. Forezi, V. G. S. Cavalcante, C. S. R. Juliani, J. A. L. C. Resende, David R. da Rocha, F. C. da Silvaa and V. F. Ferreira, *J. Braz. Chem. Soc.*, 2017, **28**, 1926.

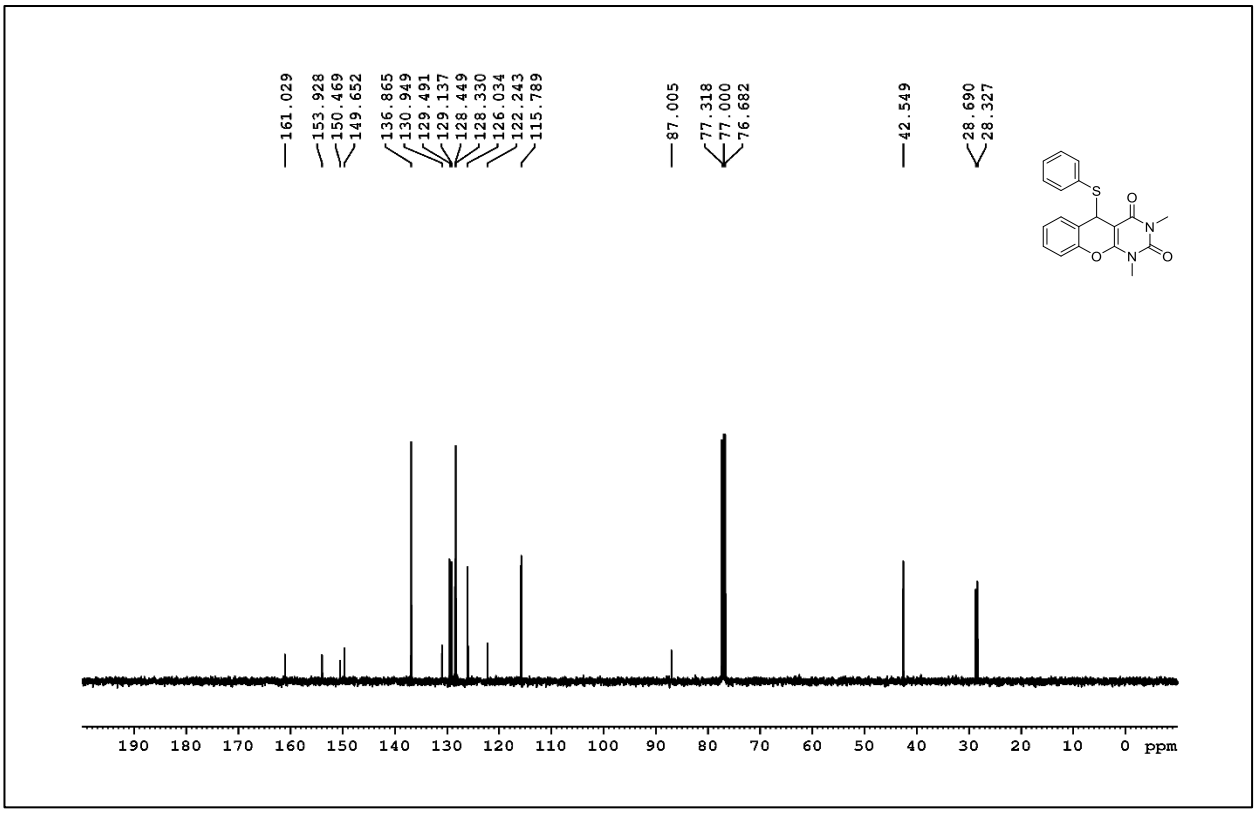
2. Y. B. S. Tanwer, S. W. Sangma, S. R. Patra, K. Swain, S. Bhunia, S. Pal and D. Das, *ACS Sustainable Resour. Manage*., 2025, **2**, 492.

5. Spectra of products

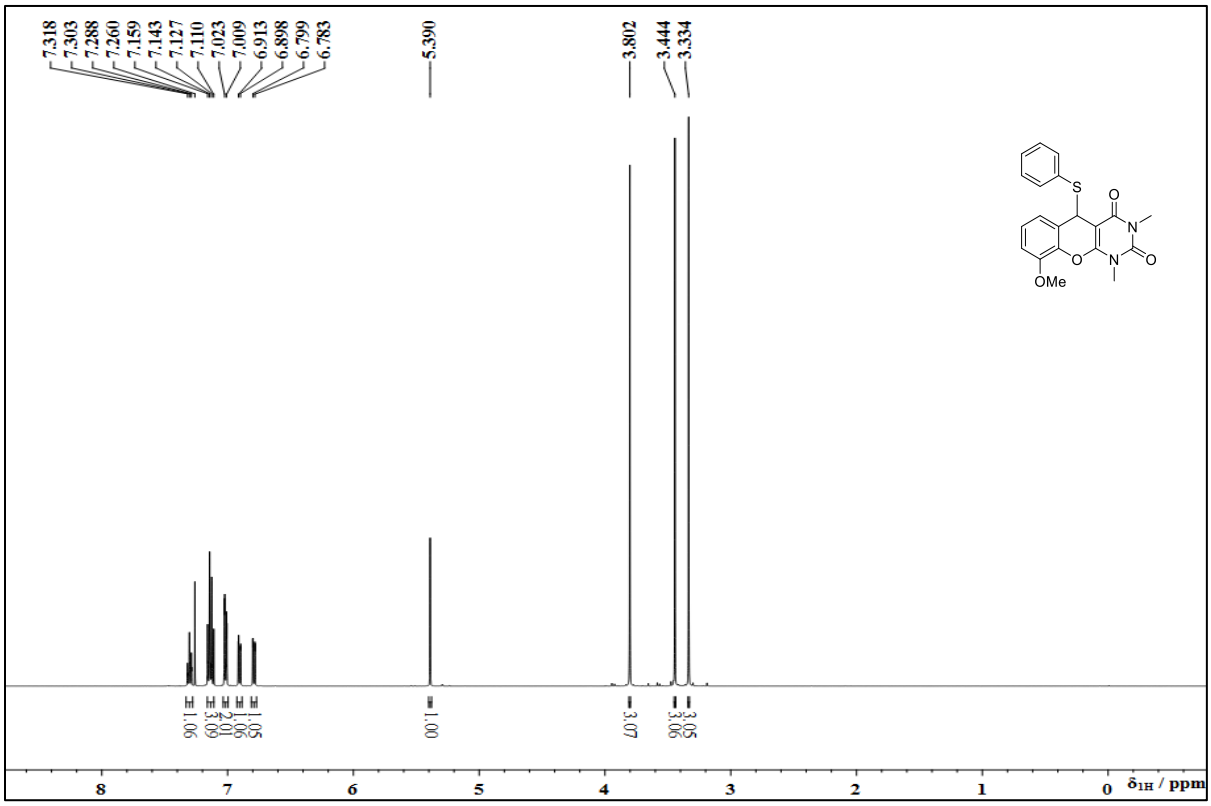
^{1}H NMR Spectra of 4a



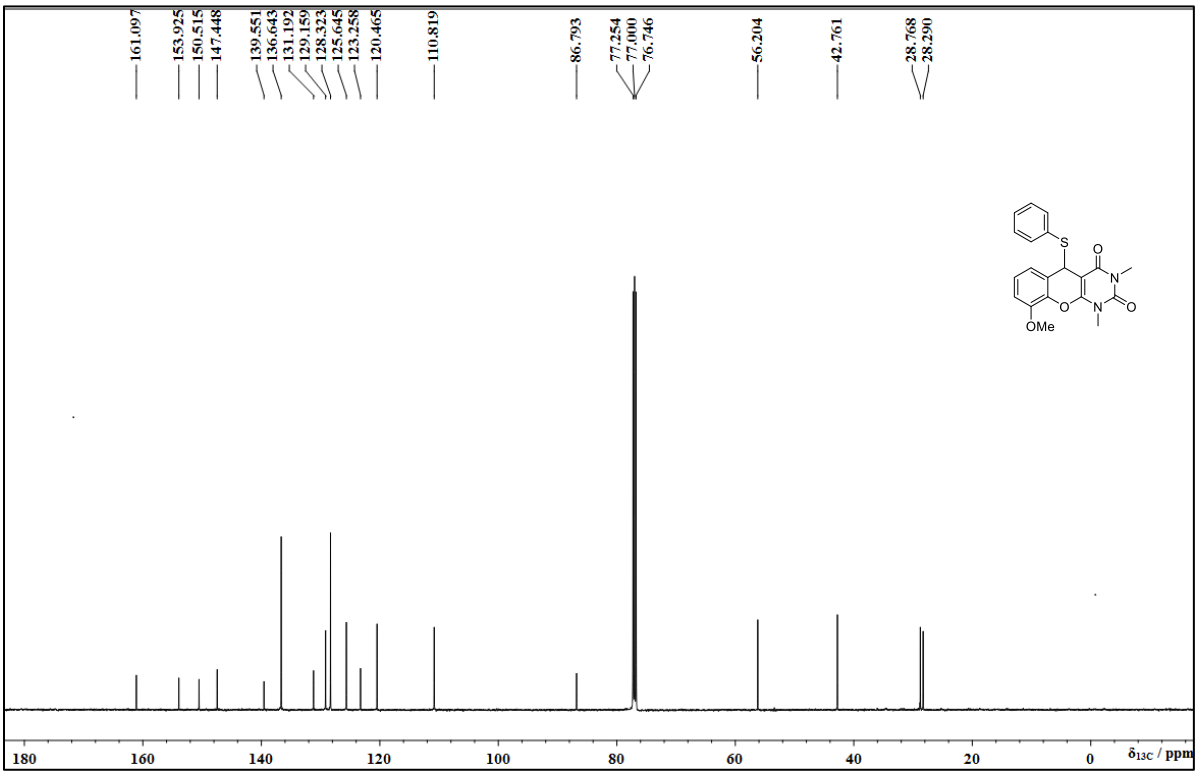
^{13}C NMR Spectra of 4a



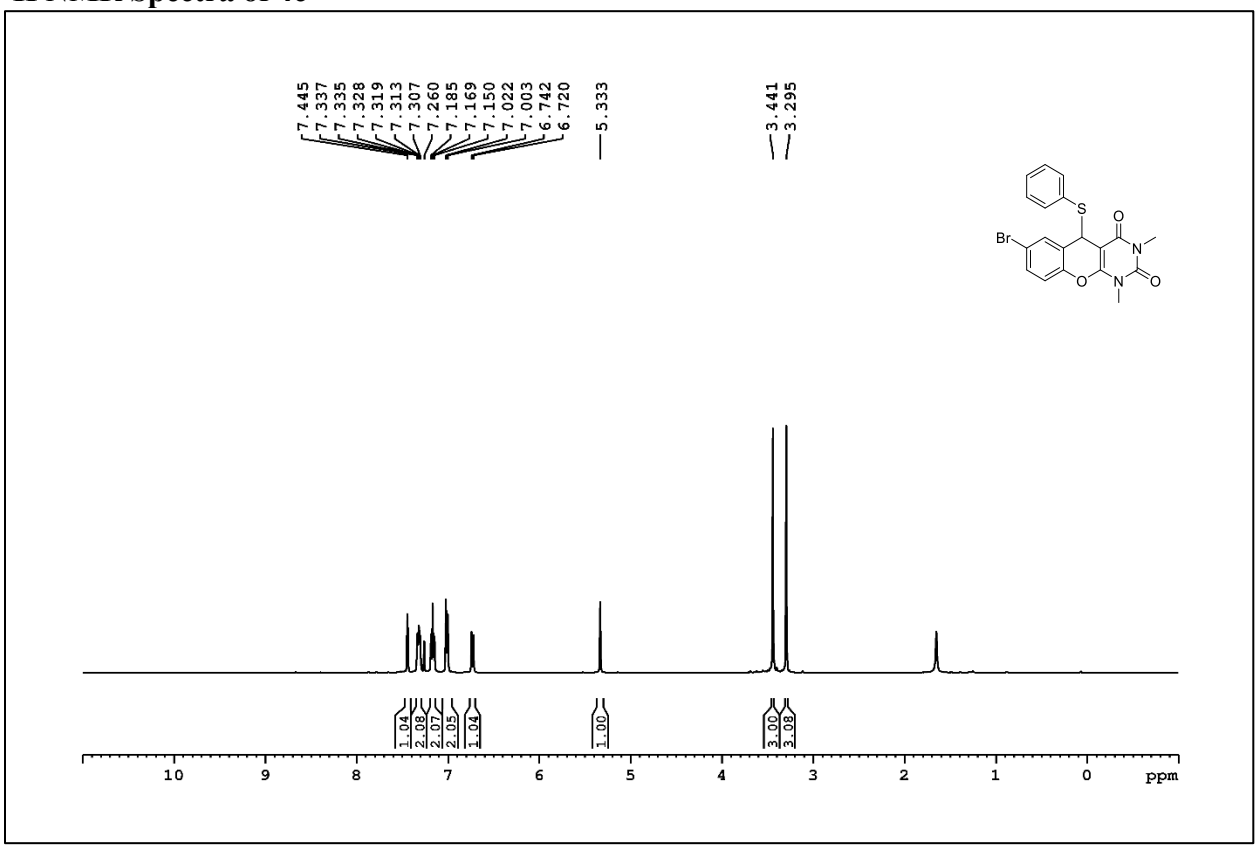
^{1}H NMR Spectra of 4b



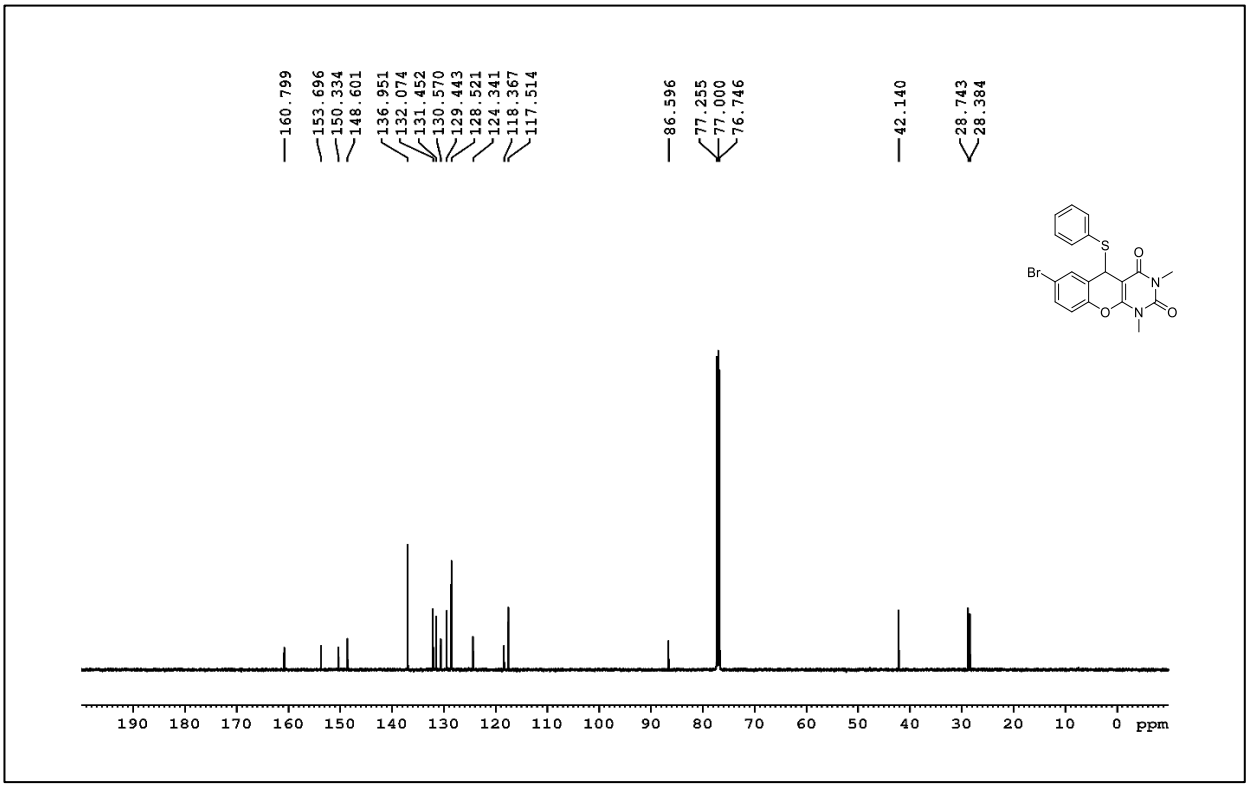
^{13}C NMR Spectra of 4b



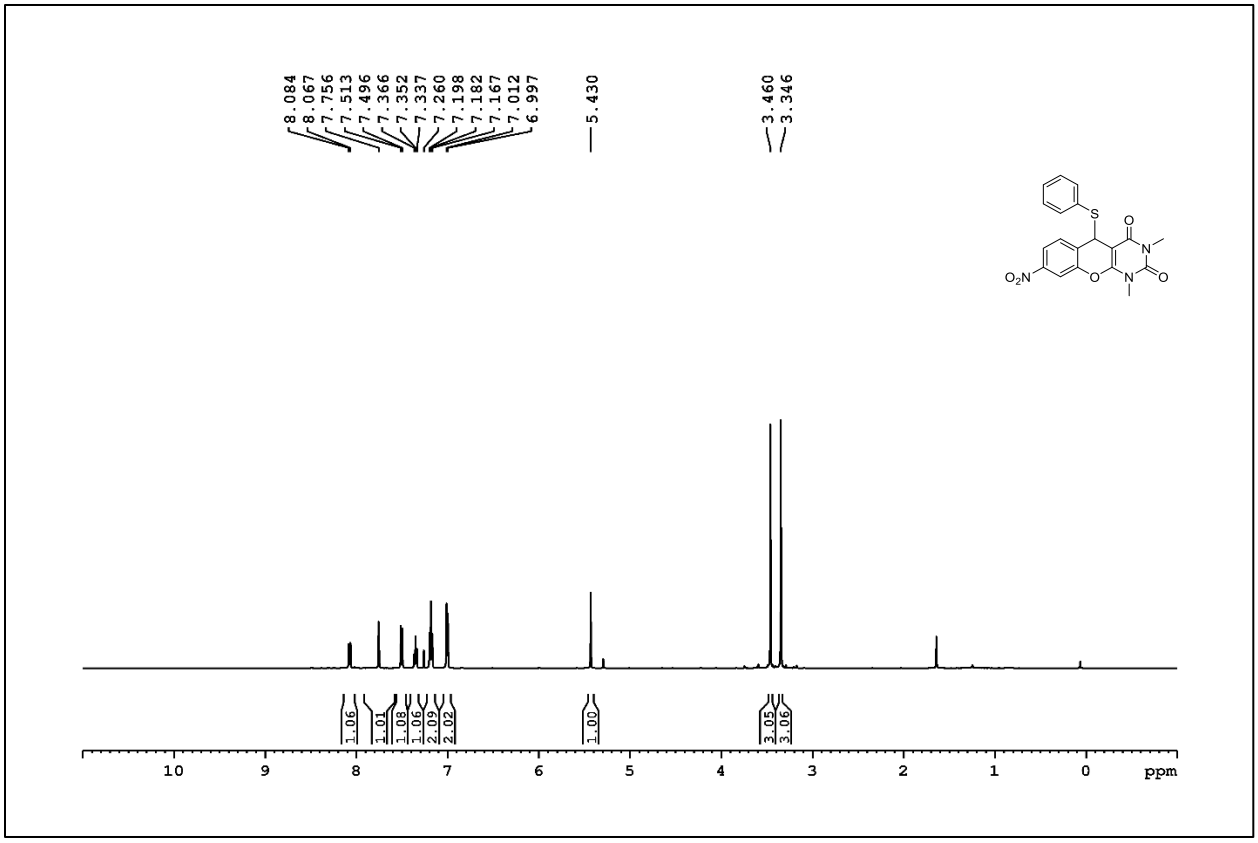
^{1}H NMR Spectra of 4c



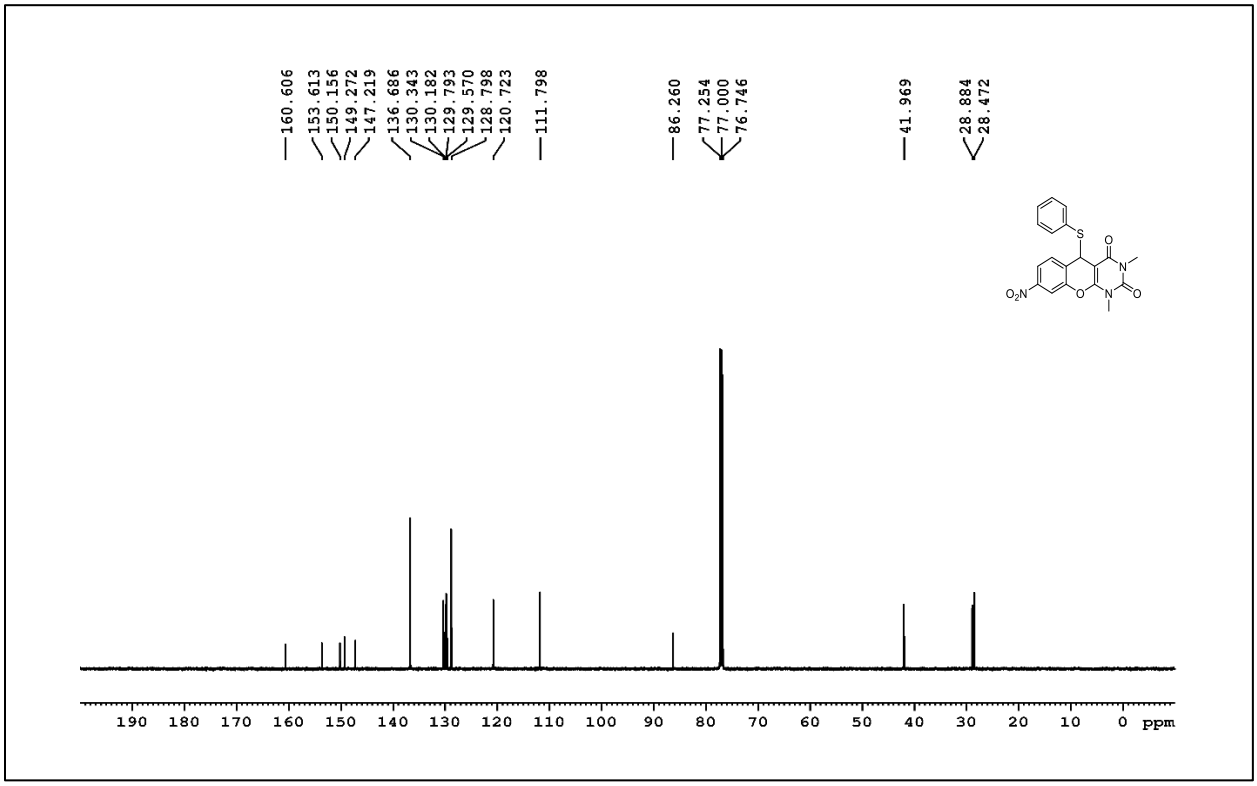
^{13}C NMR Spectra of 4c



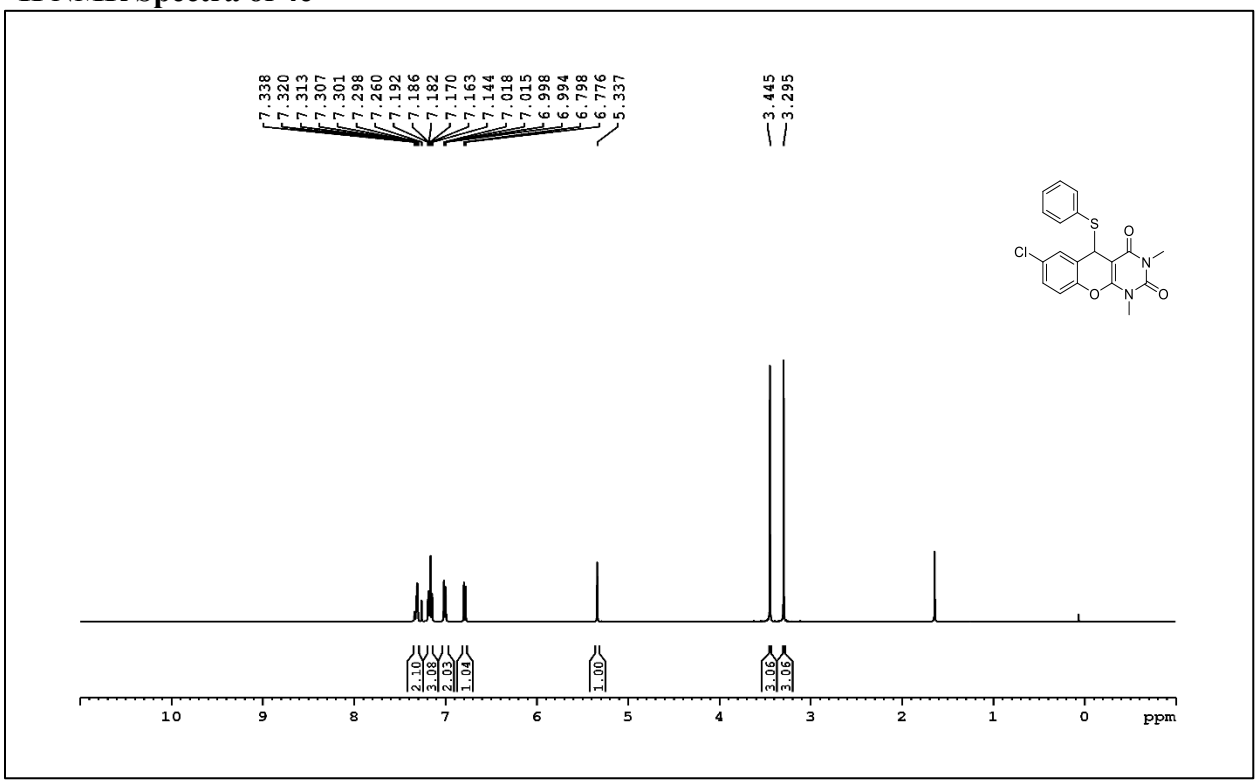
^{1}H NMR Spectra of 4d



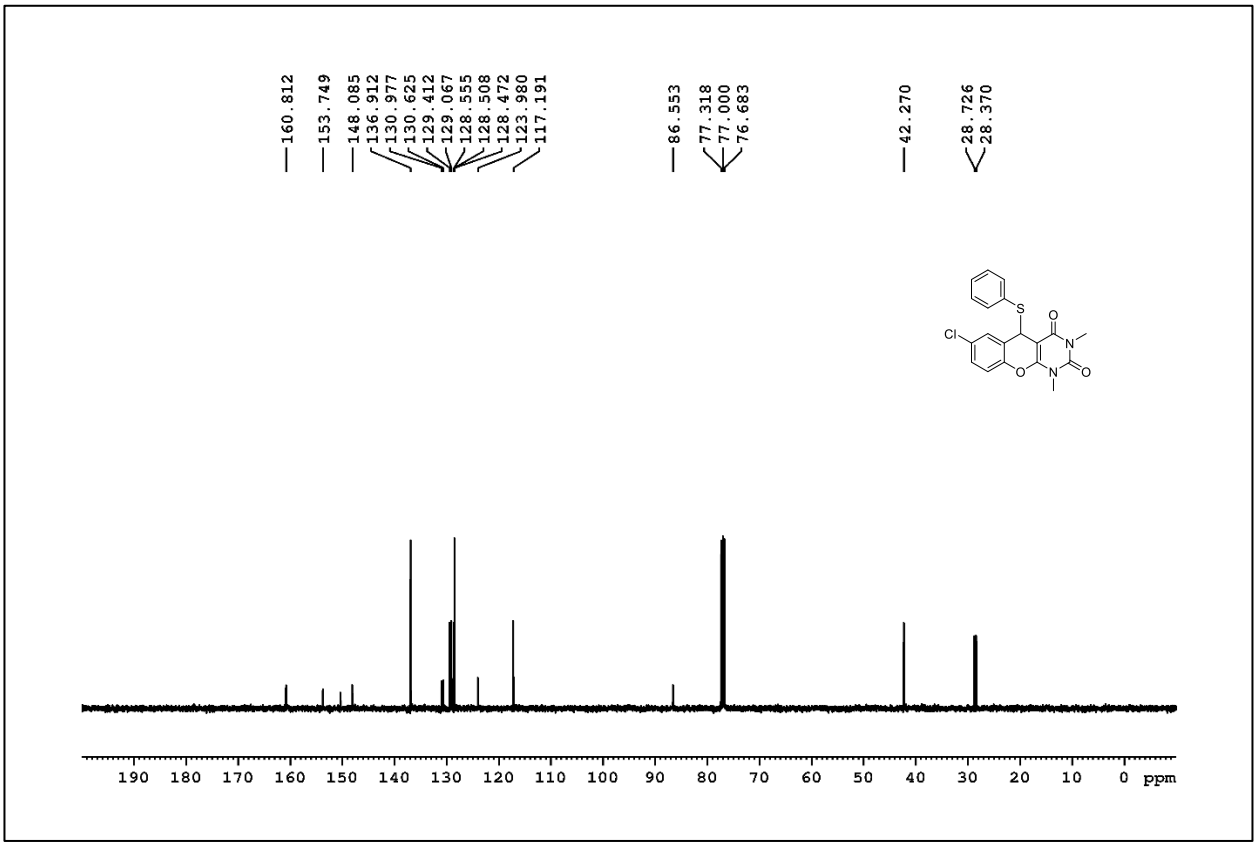
^{13}C NMR Spectra of 4d



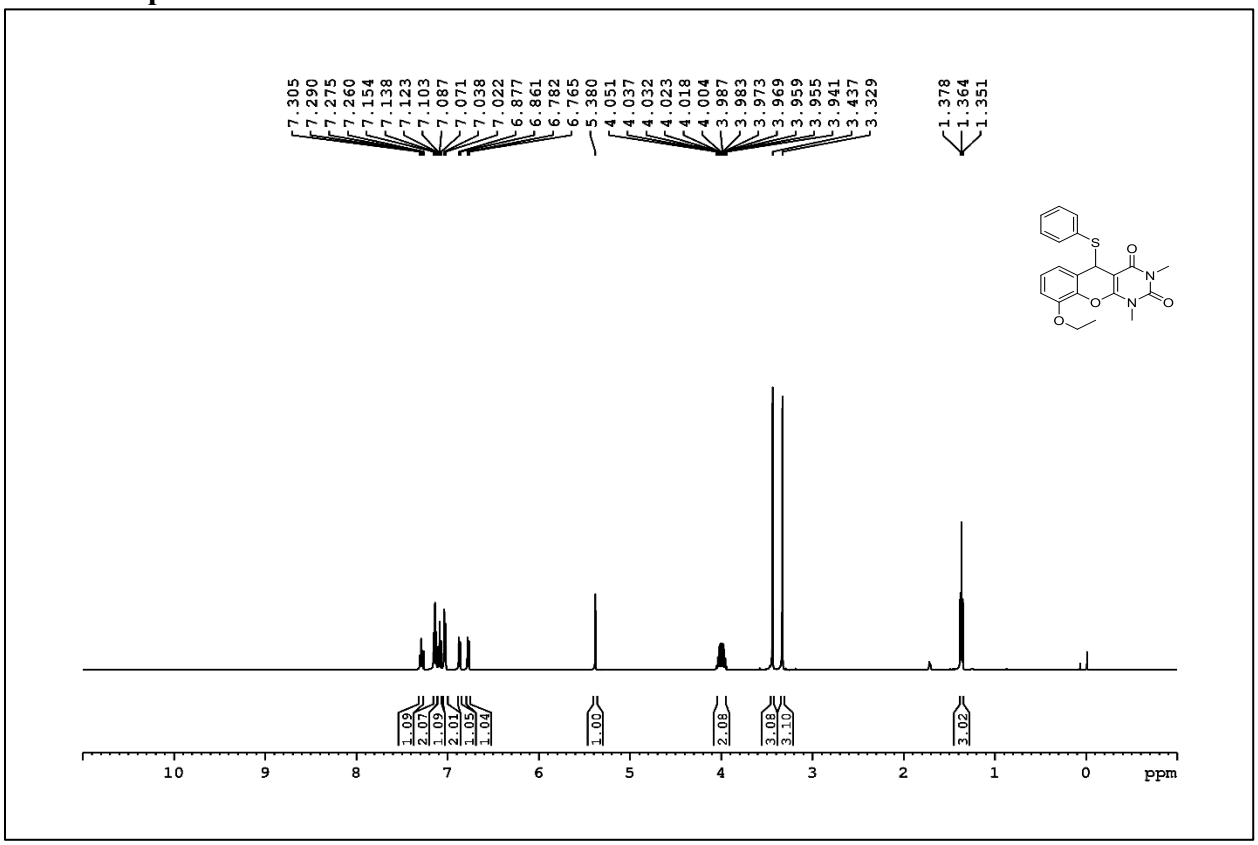
^{1}H NMR Spectra of 4e



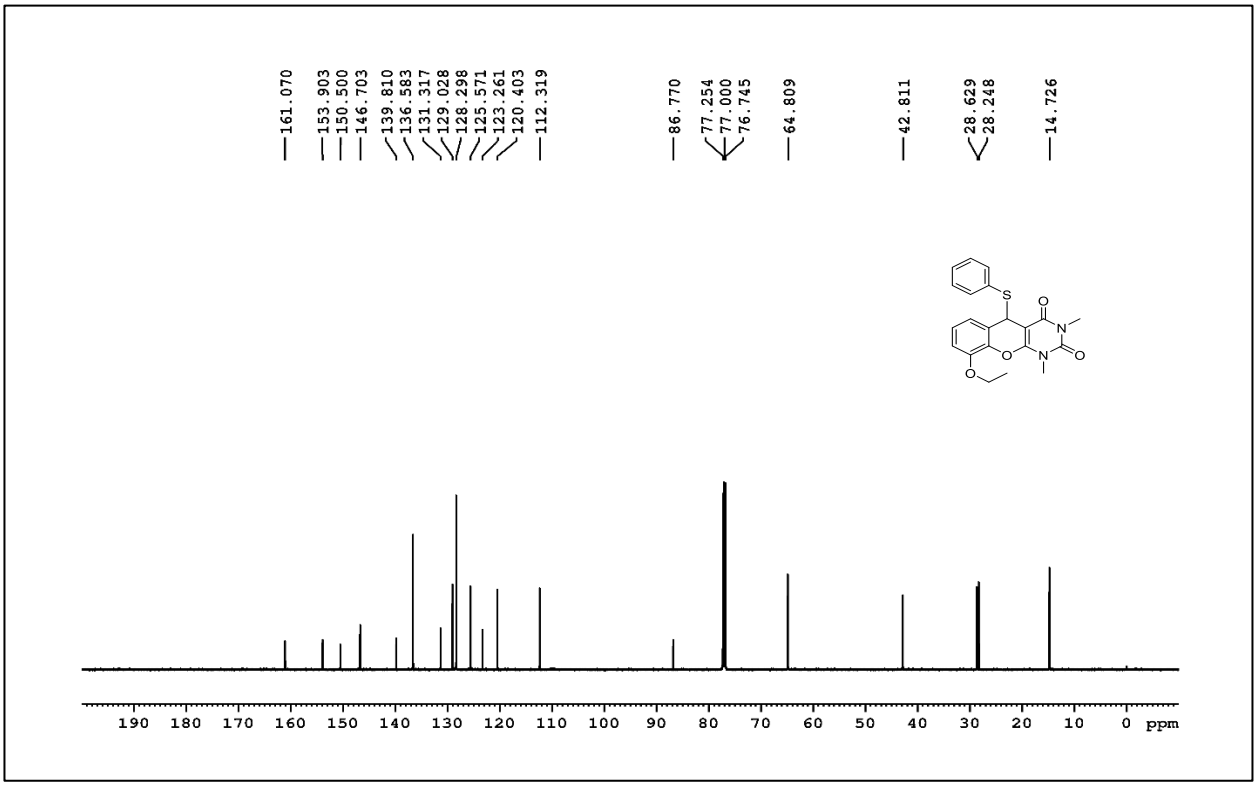
^{13}C NMR Spectra of 4e



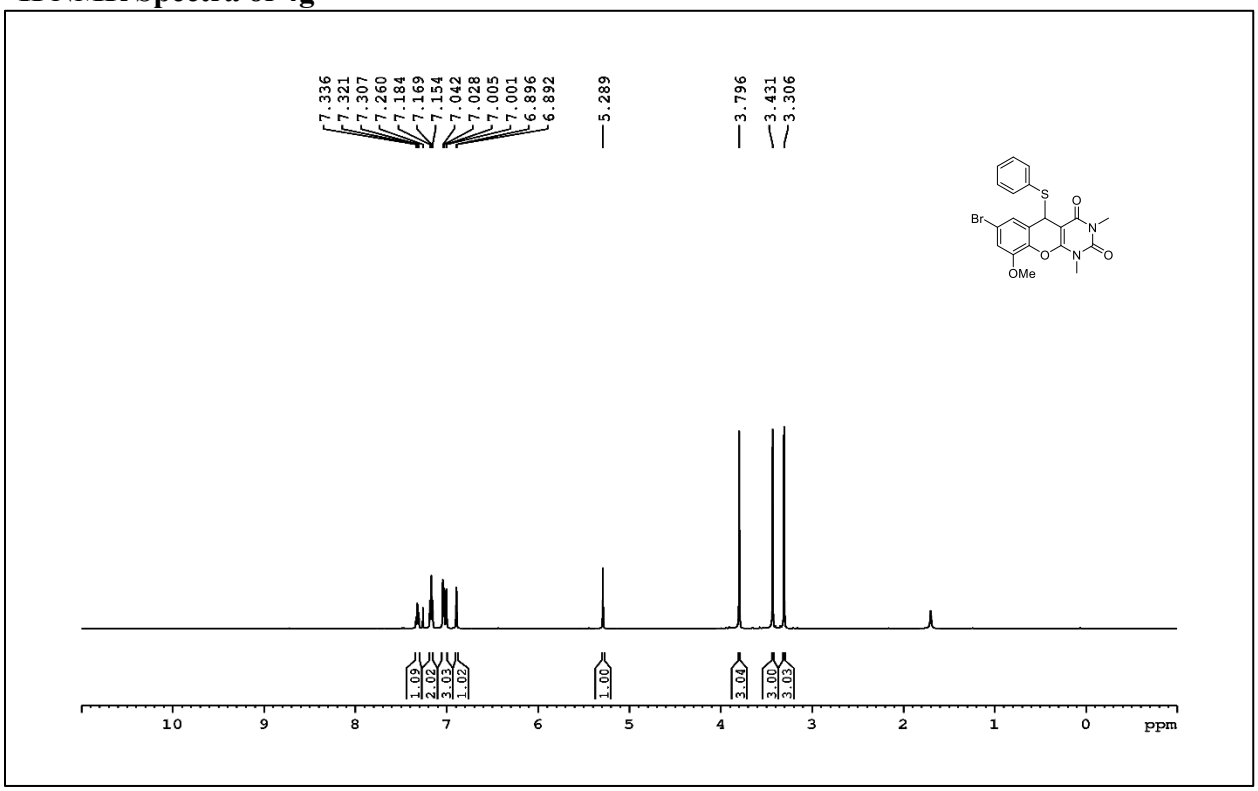
^{1}H NMR Spectra of 4f



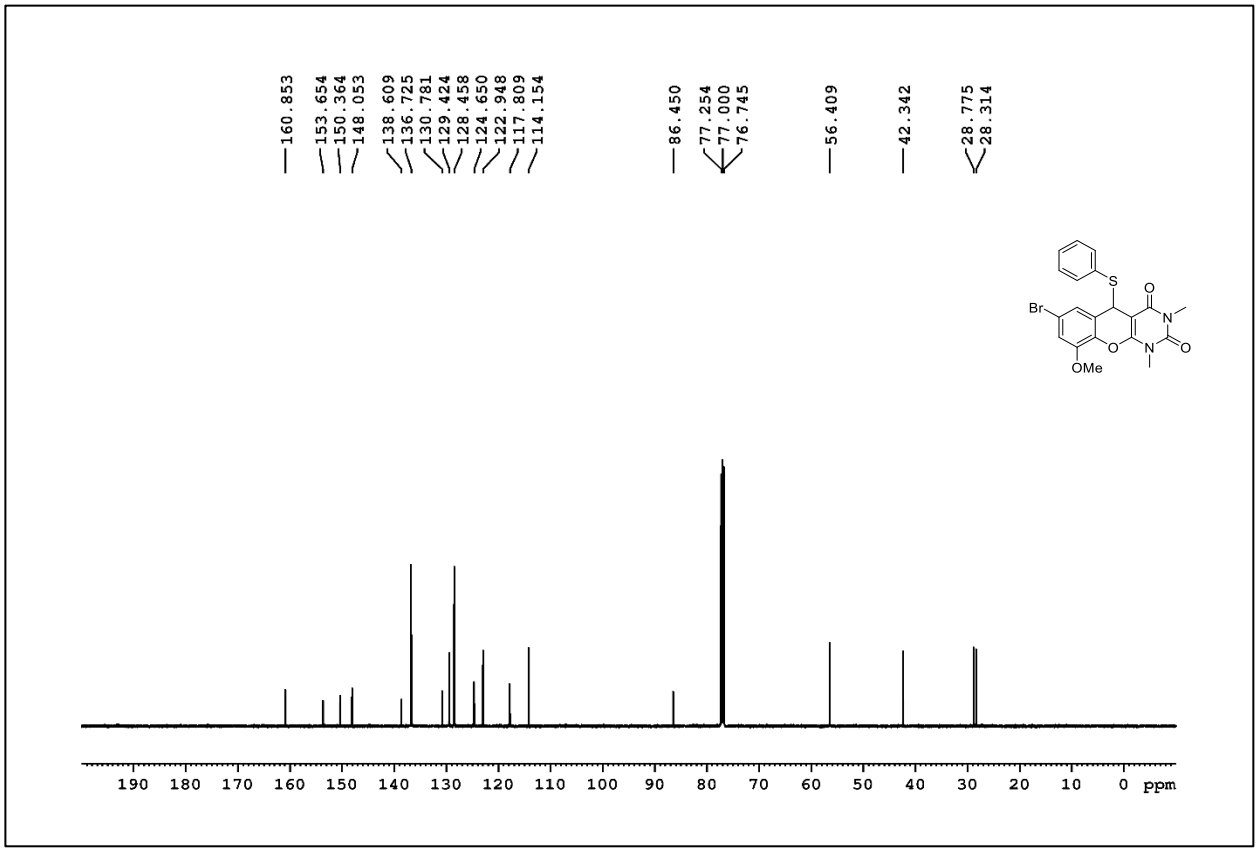
^{13}C NMR Spectra of 4f



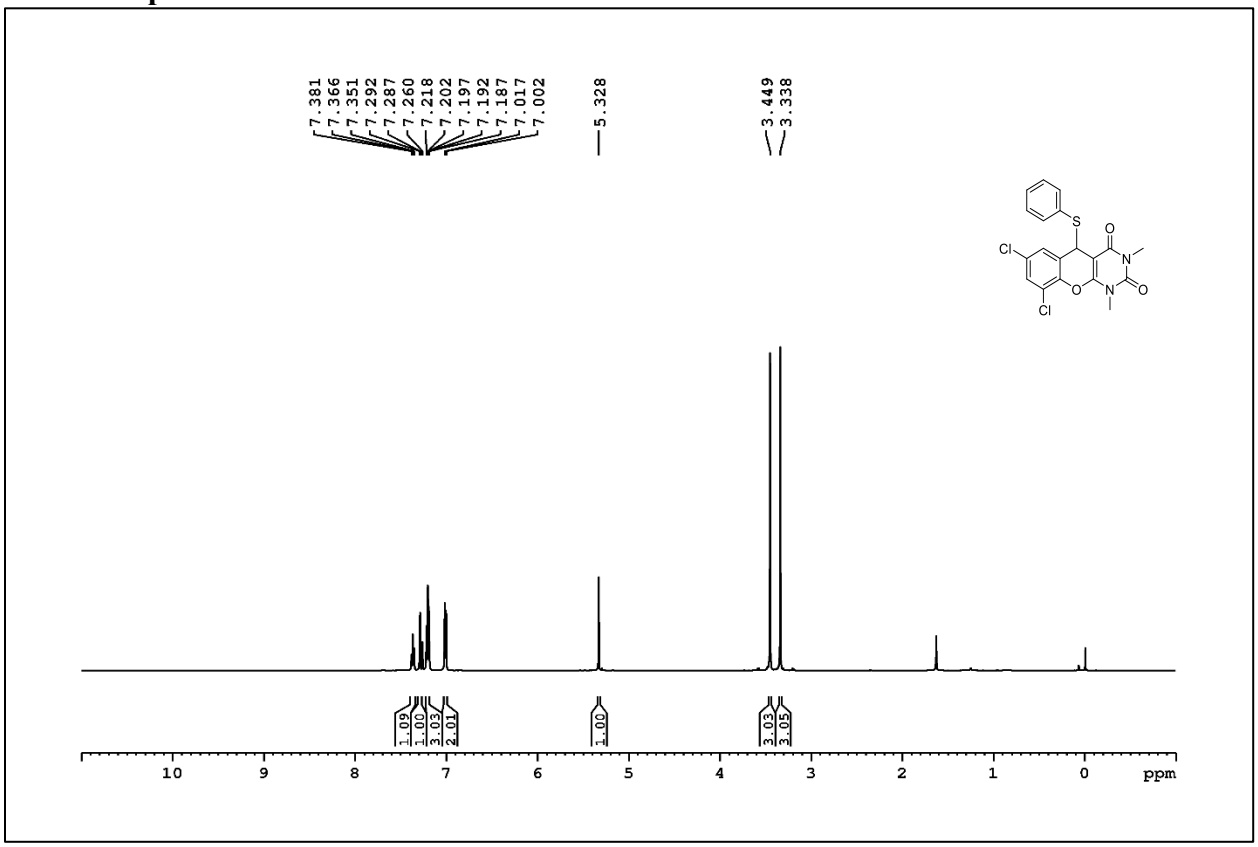
^{1}H NMR Spectra of 4g



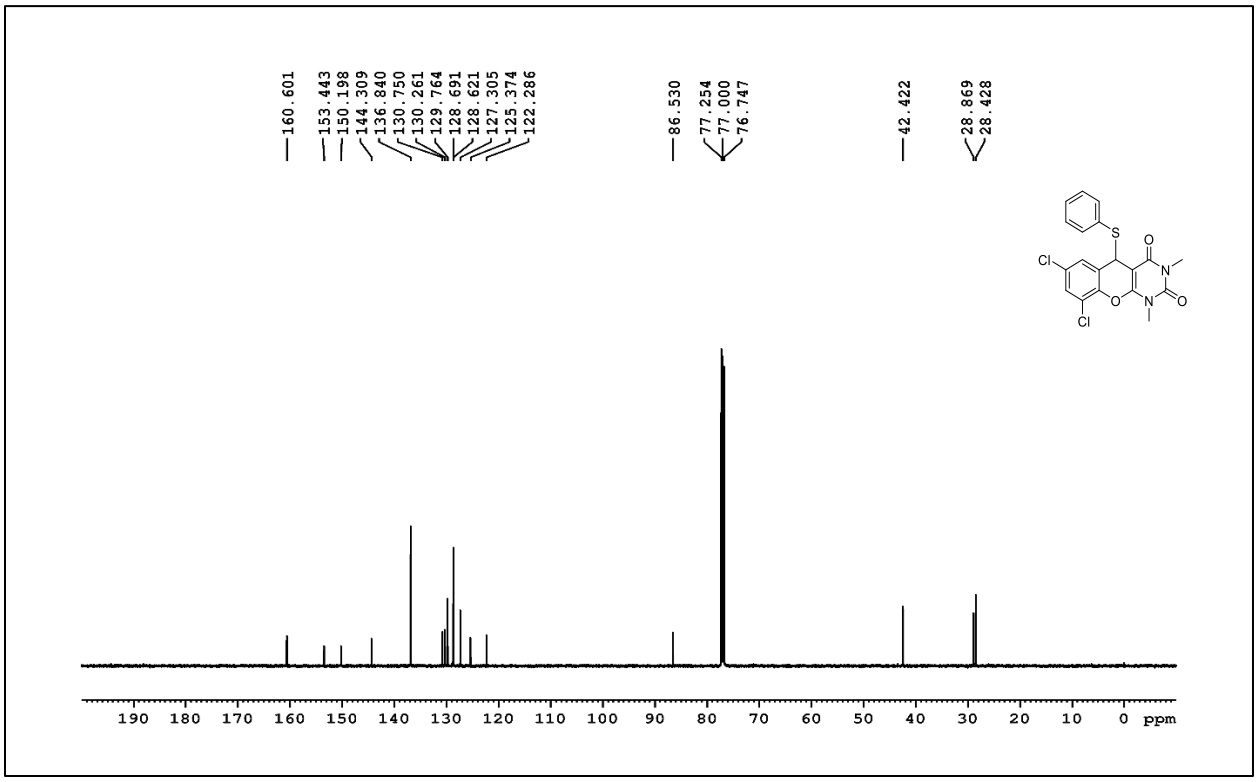
^{13}C NMR Spectra of 4g



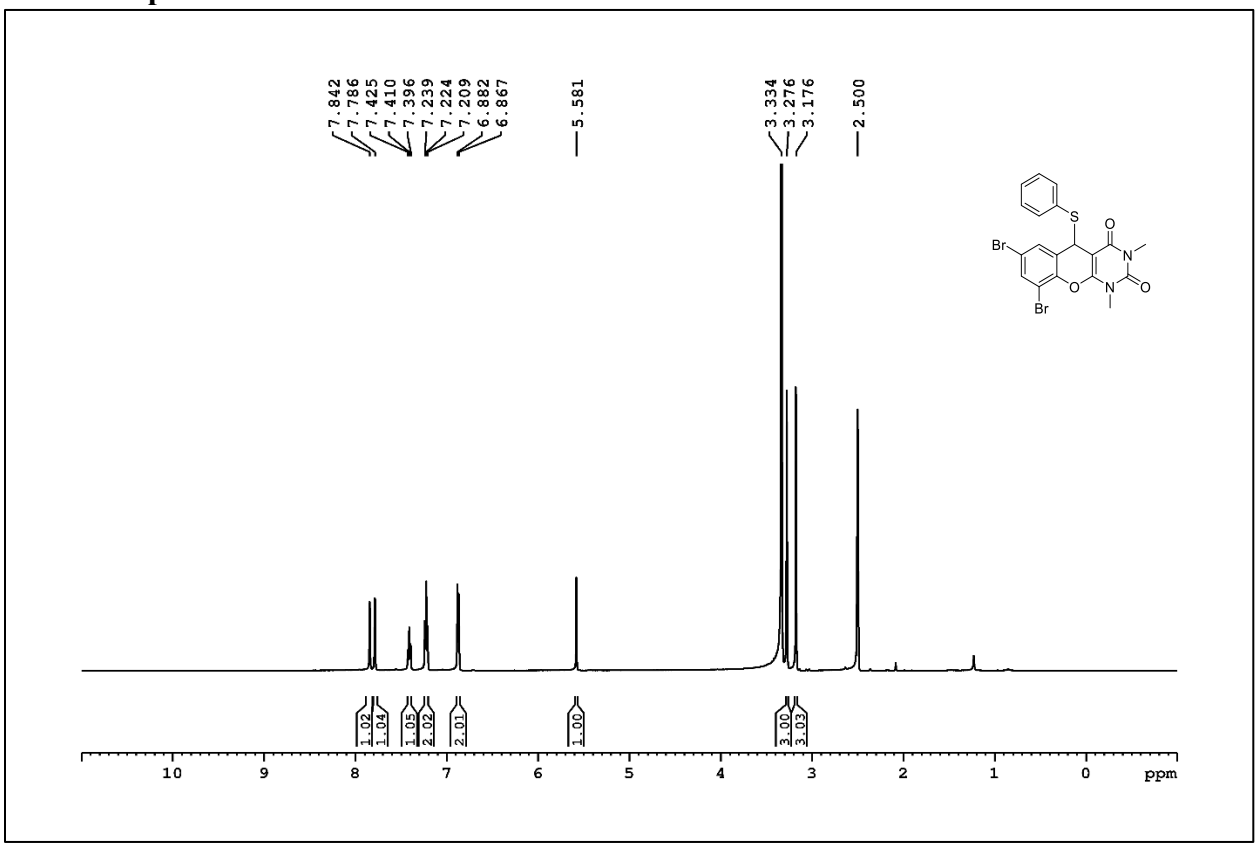
^{1}H NMR Spectra of 4h



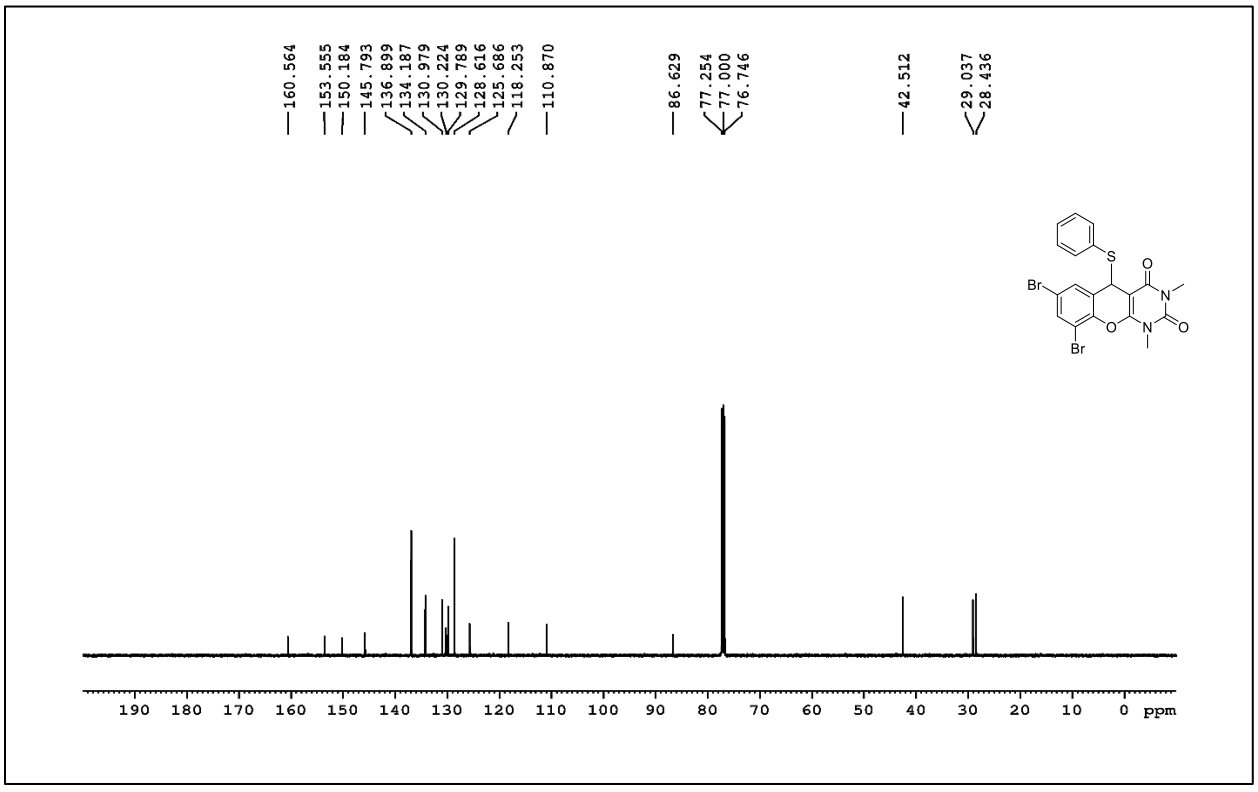
^{13}C NMR Spectra of 4h



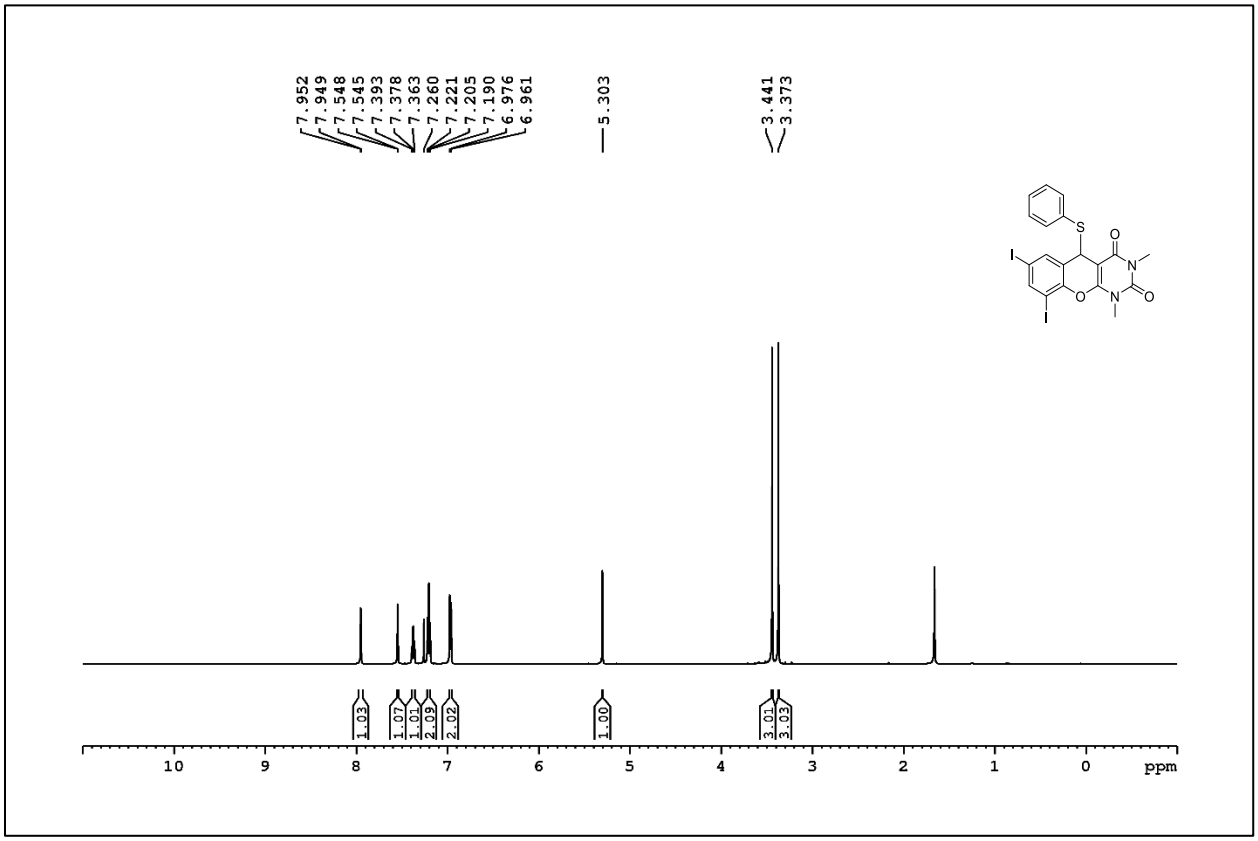
^{1}H NMR Spectra of 4i



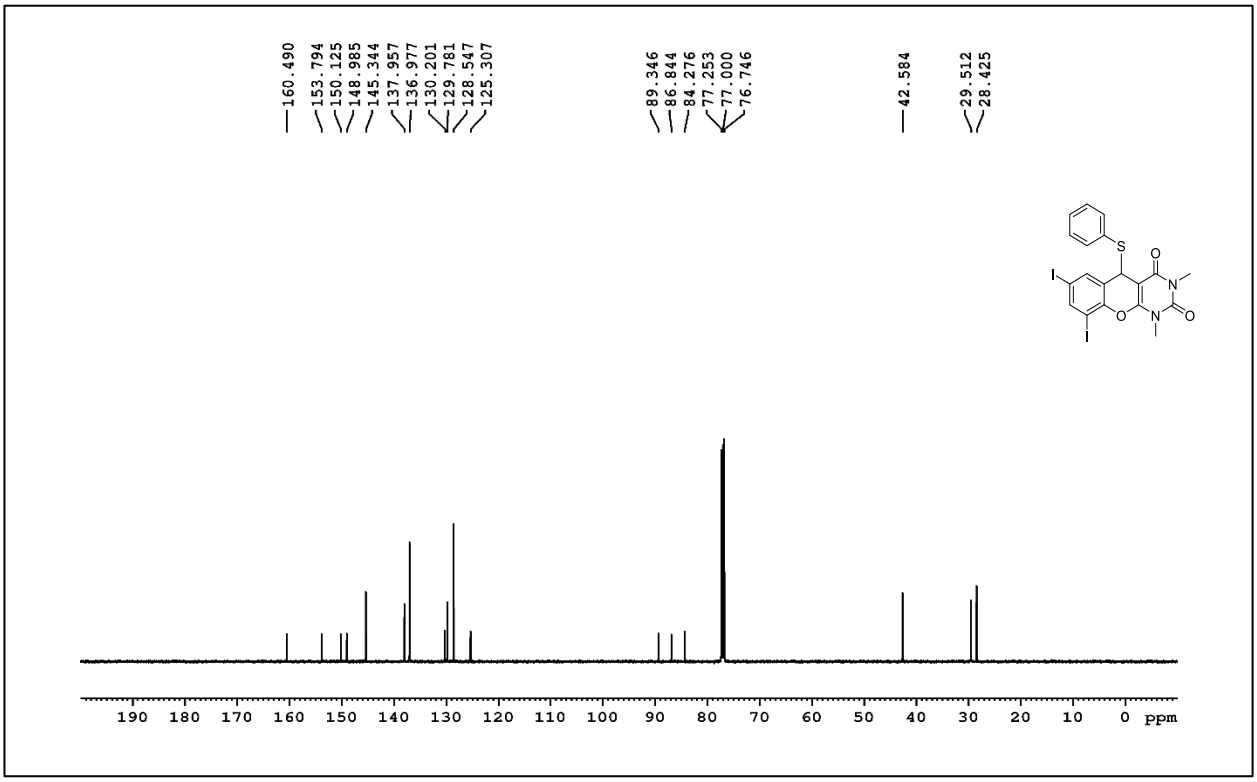
^{13}C NMR Spectra of 4i



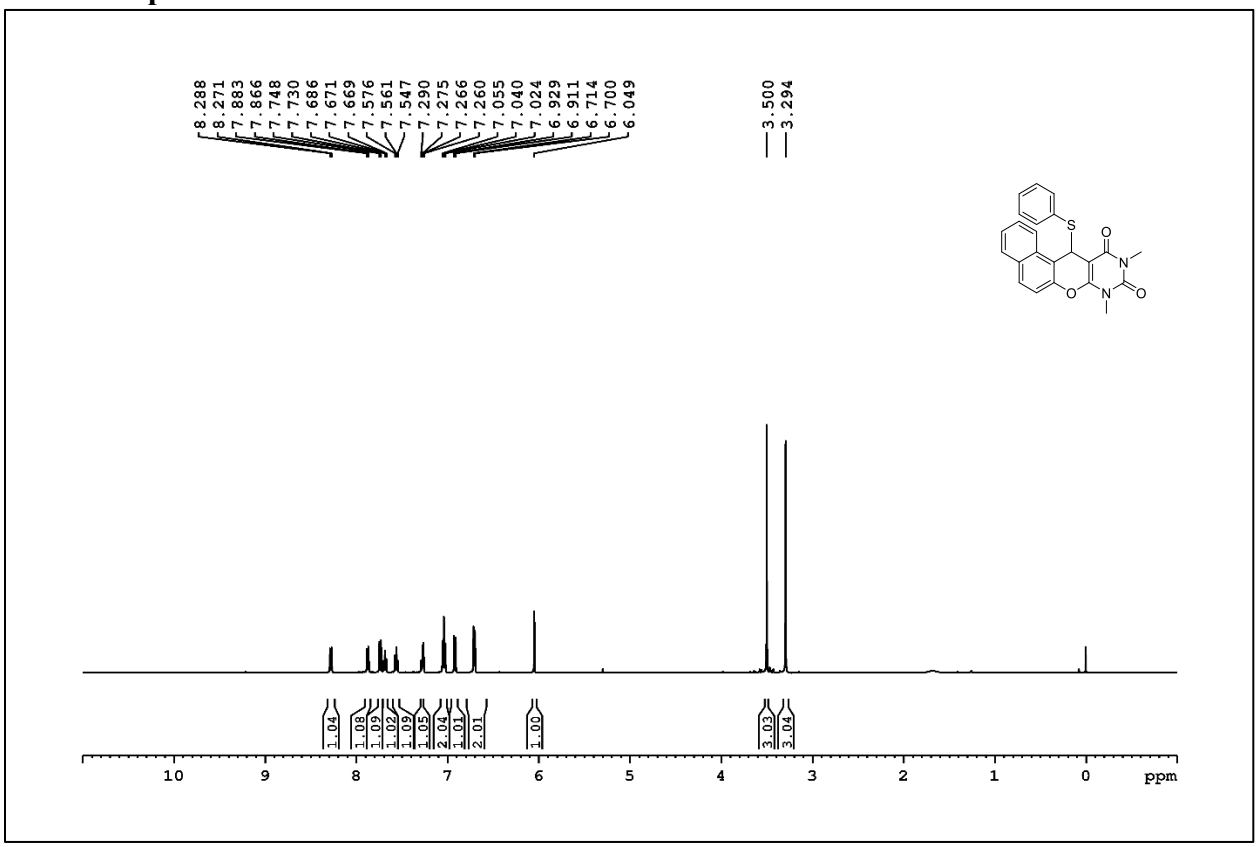
^{1}H NMR Spectra of 4j



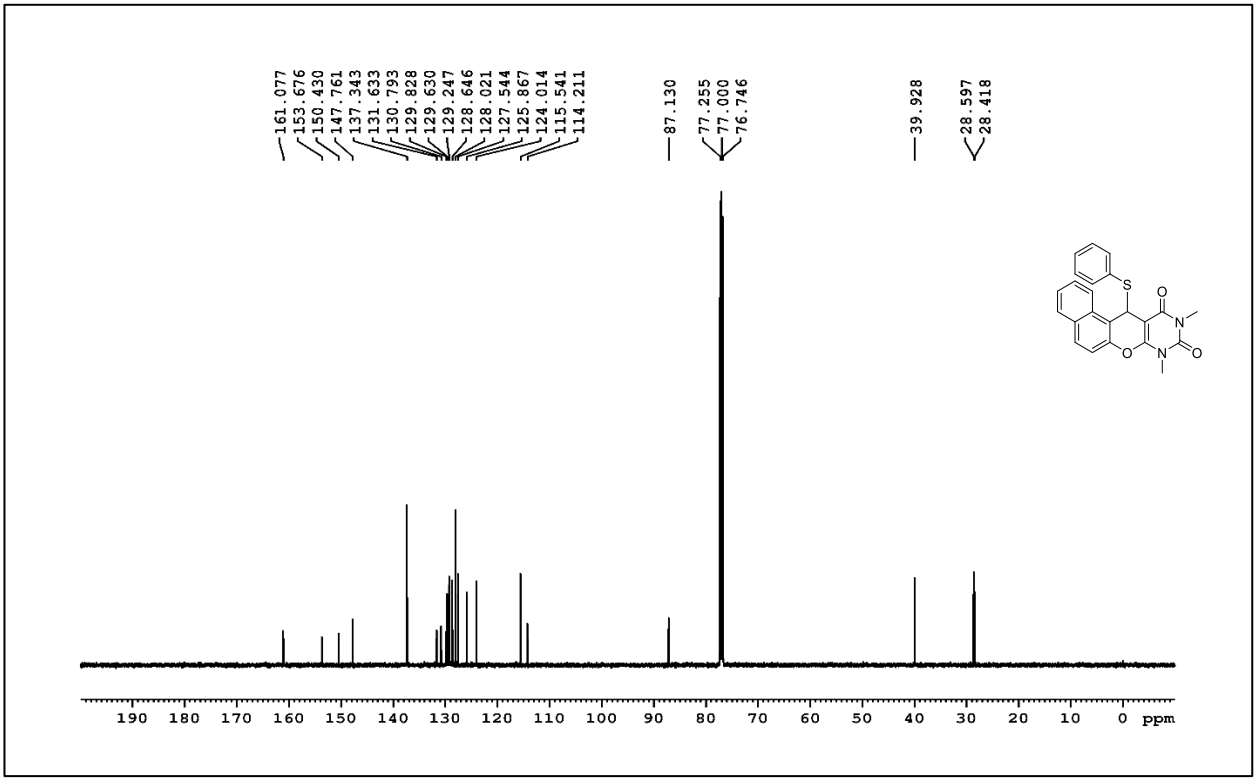
^{13}C NMR Spectra of 4j



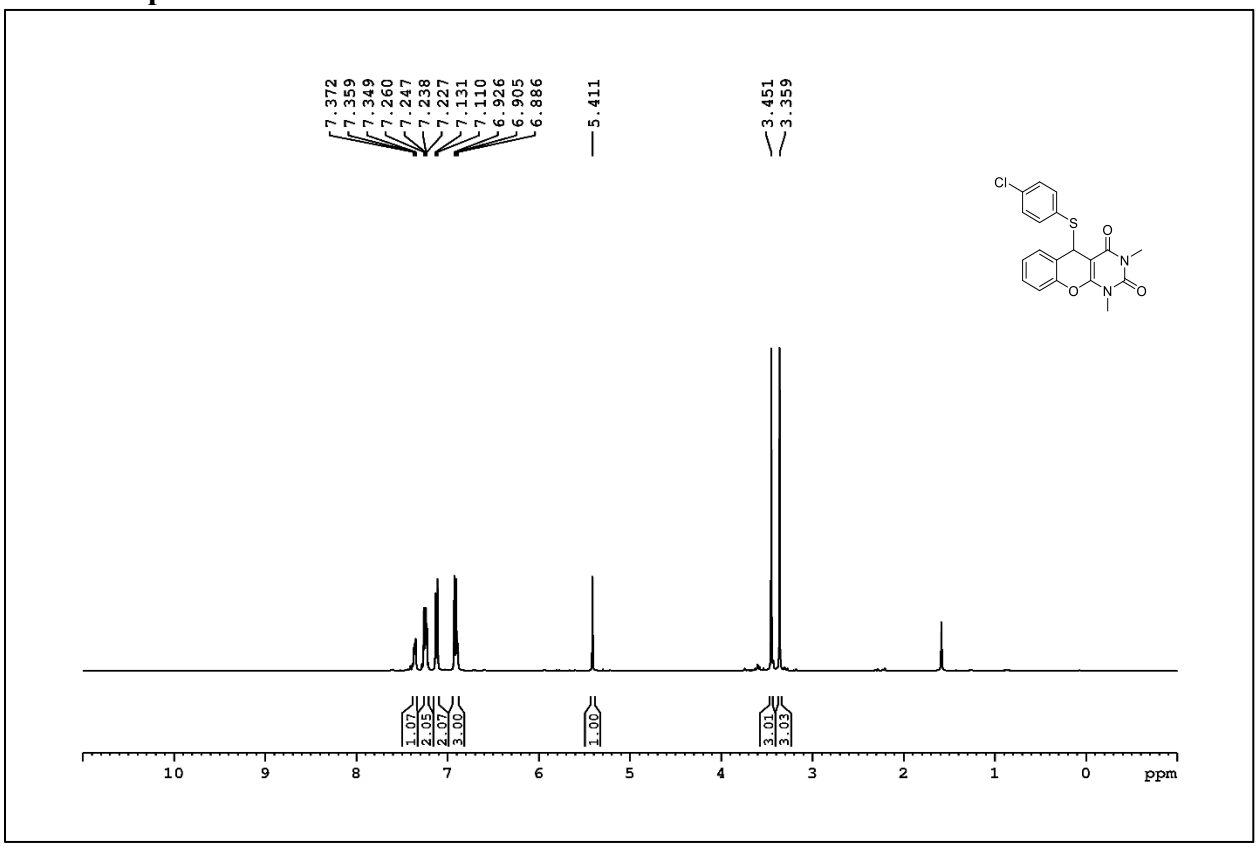
^{1}H NMR Spectra of 4k



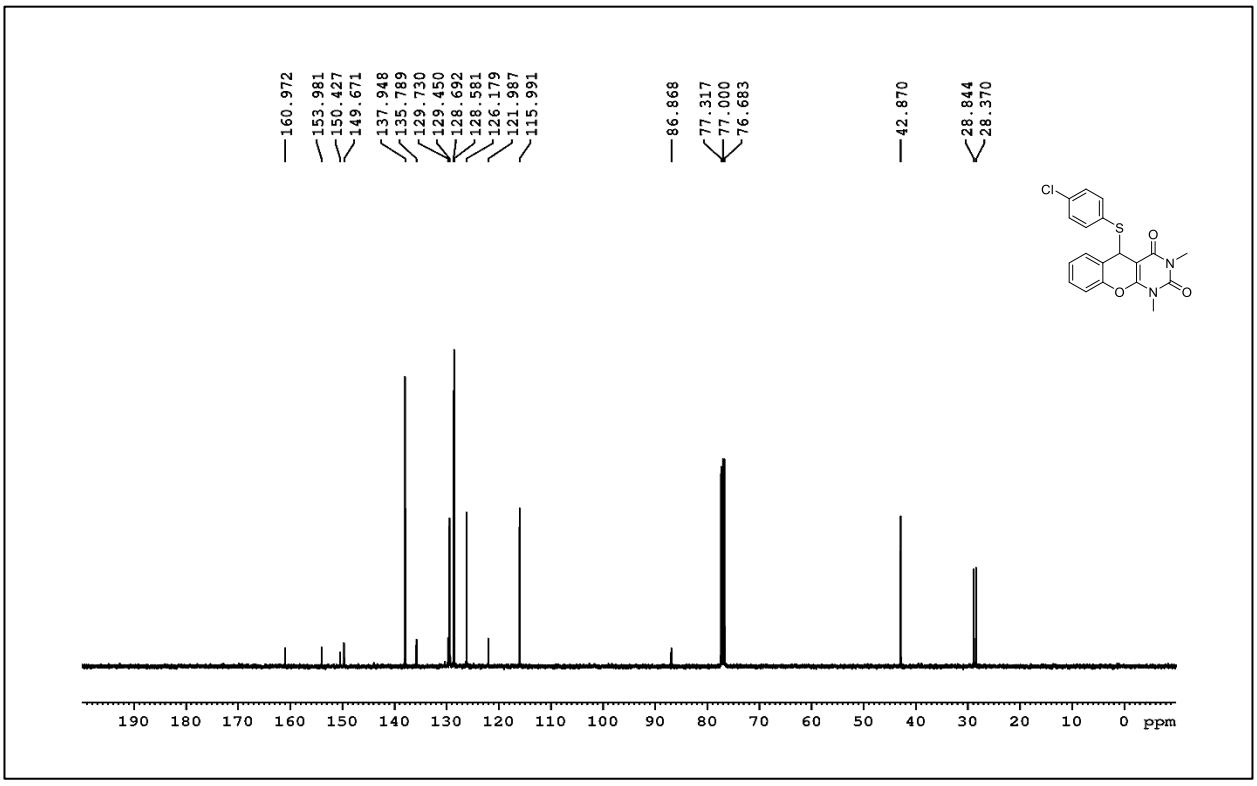
^{13}C NMR Spectra of 4k



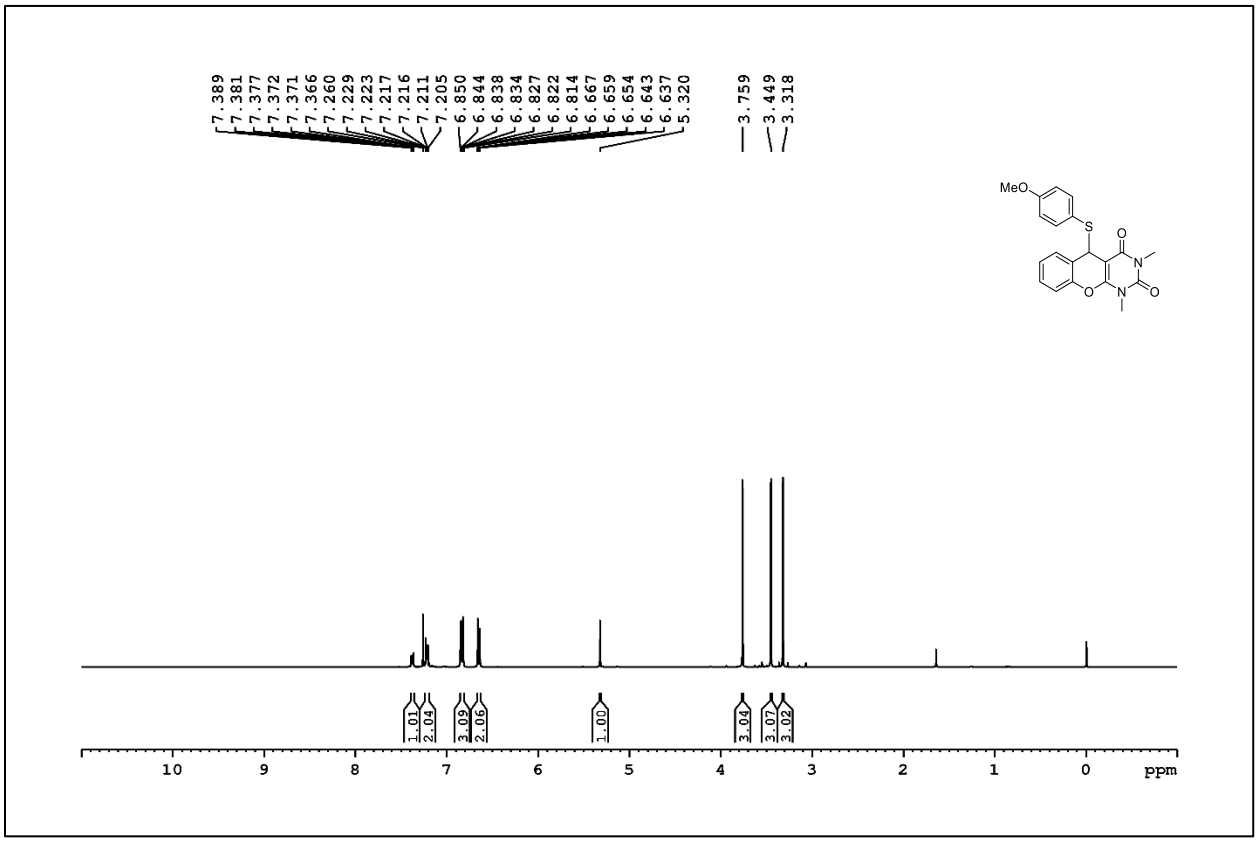
^{1}H NMR Spectra of 4l



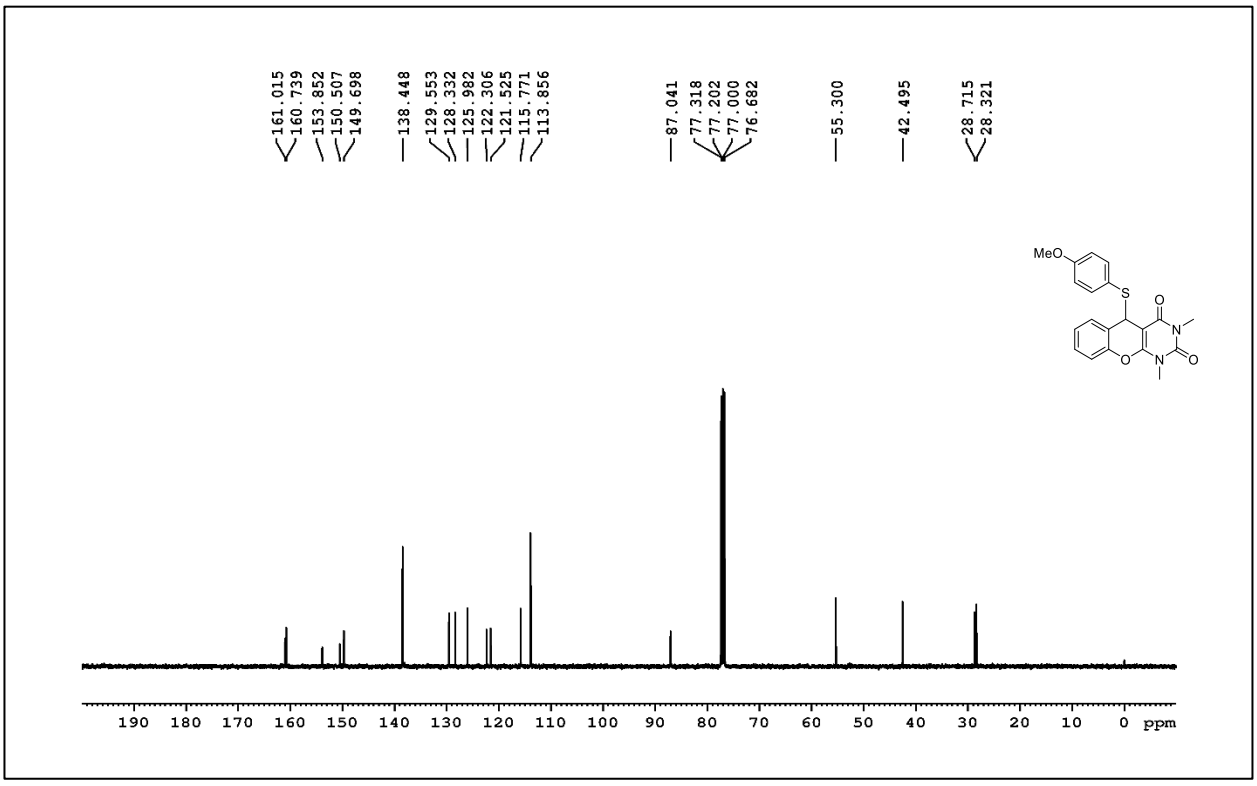
^{13}C NMR Spectra of 4l



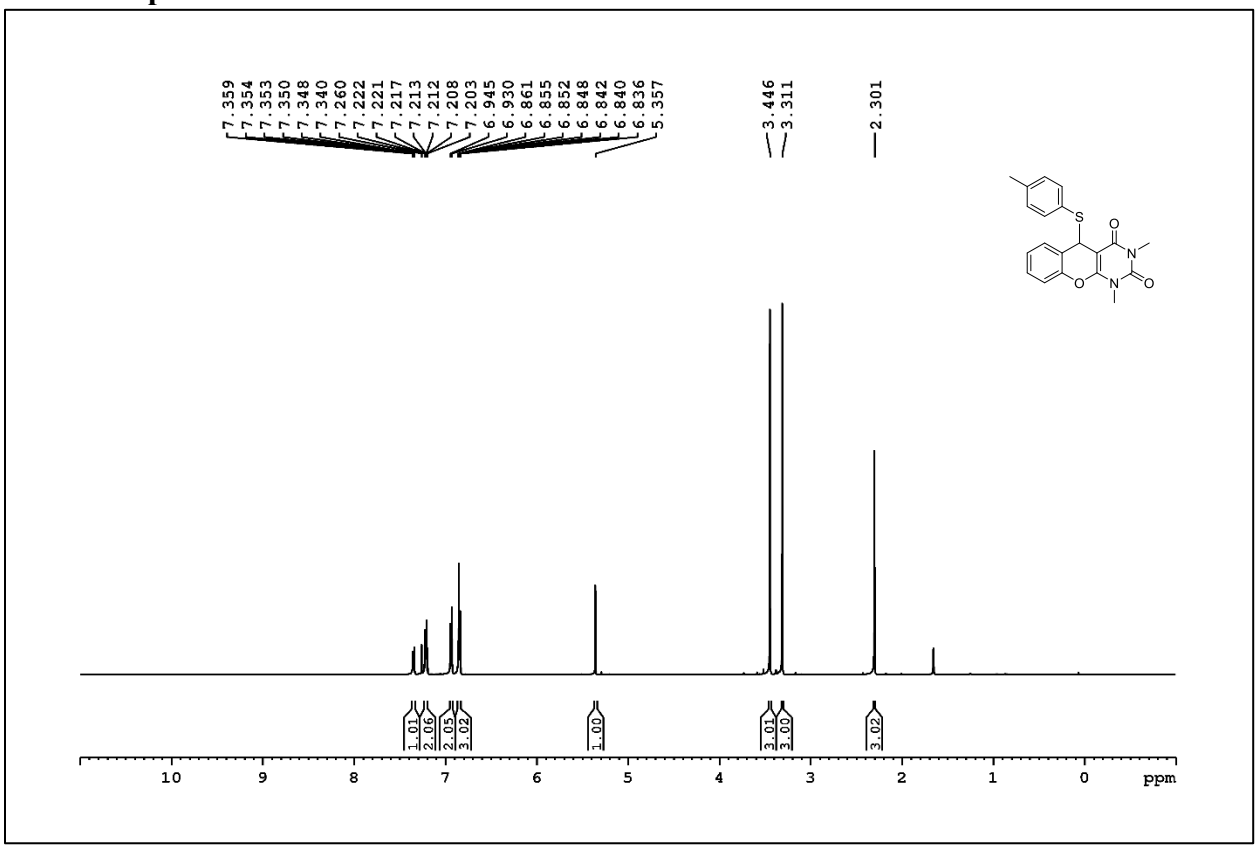
^{1}H NMR Spectra of 4m



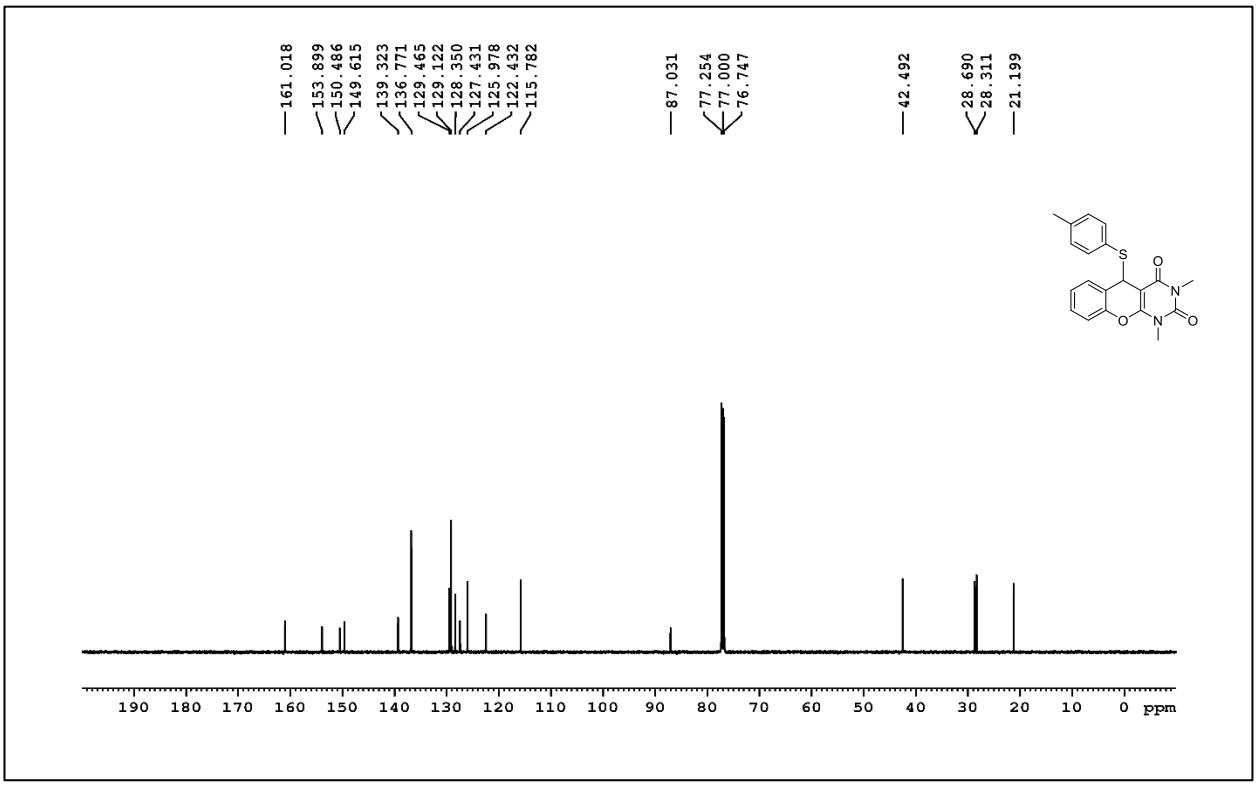
^{13}C NMR Spectra of 4m



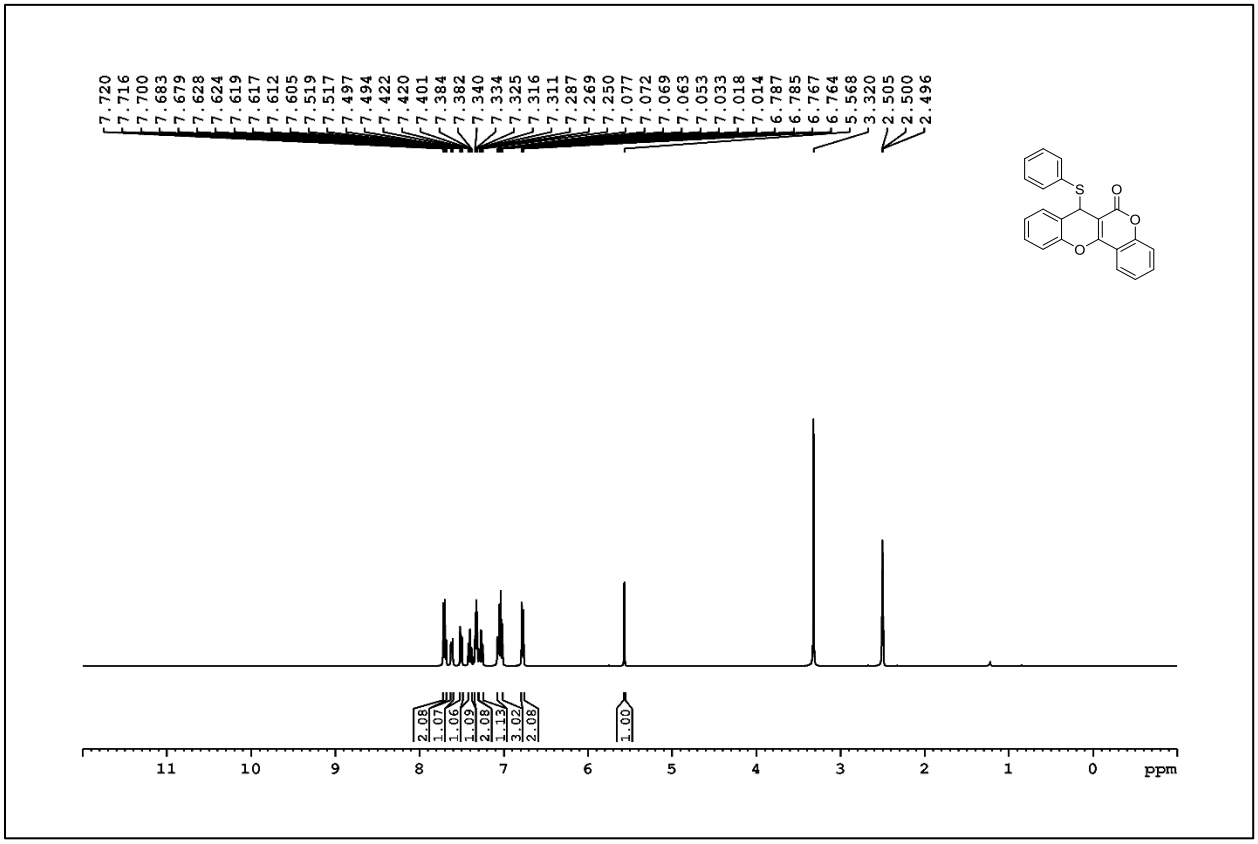
^{1}H NMR Spectra of 4n



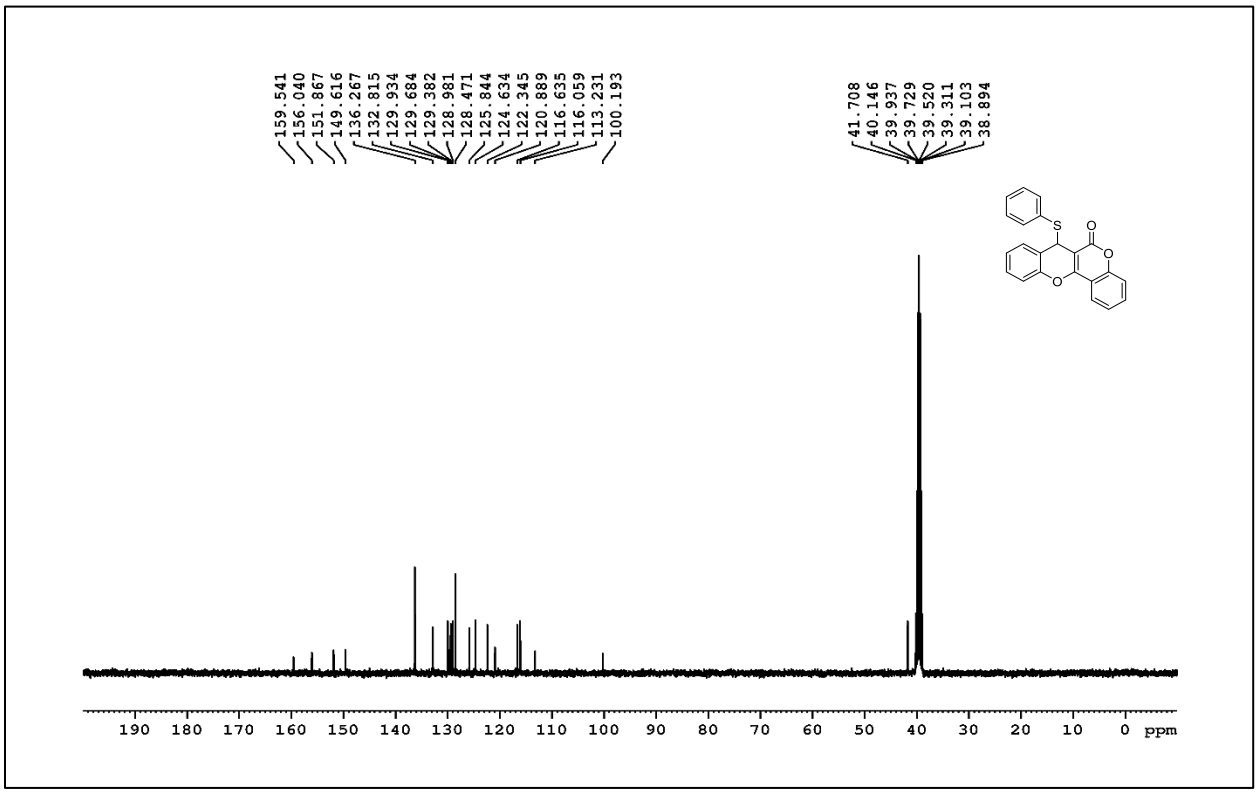
^{13}C NMR Spectra of 4n



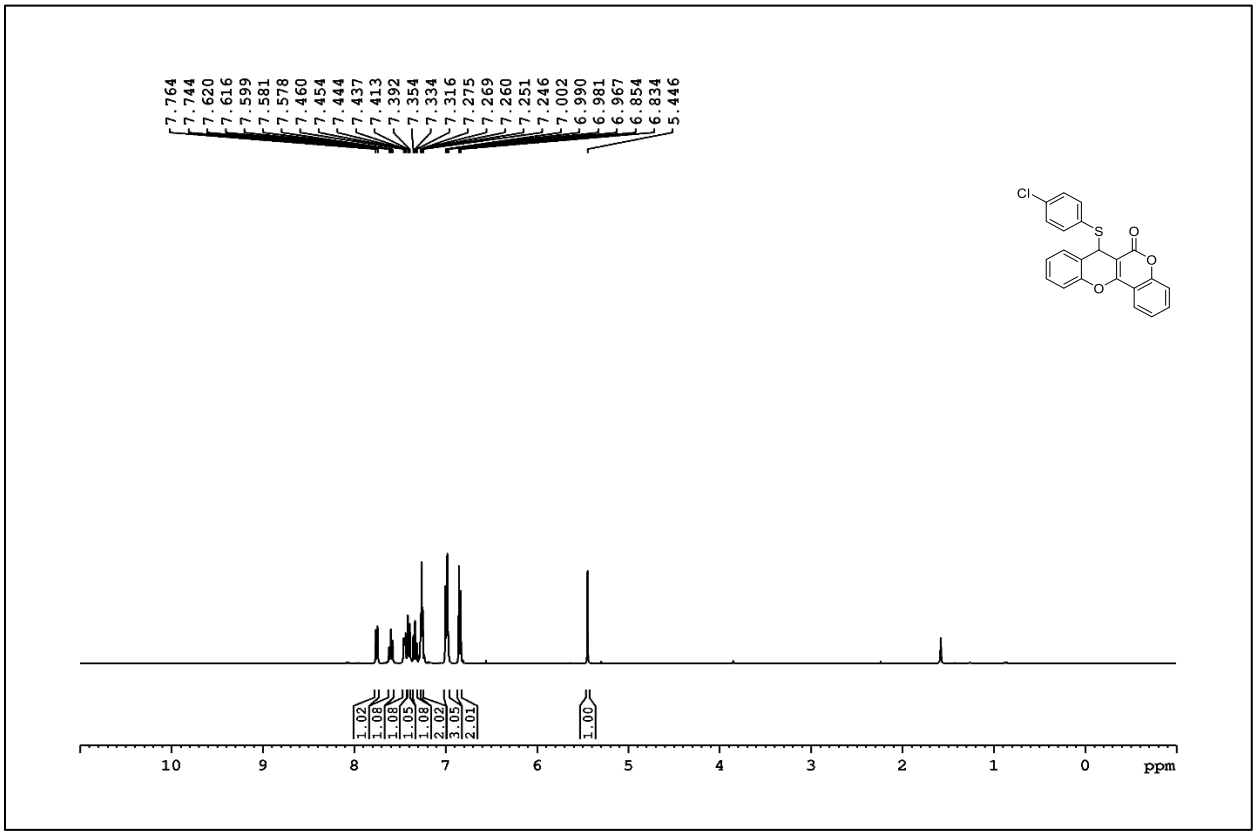
^{1}H NMR Spectra of 5a



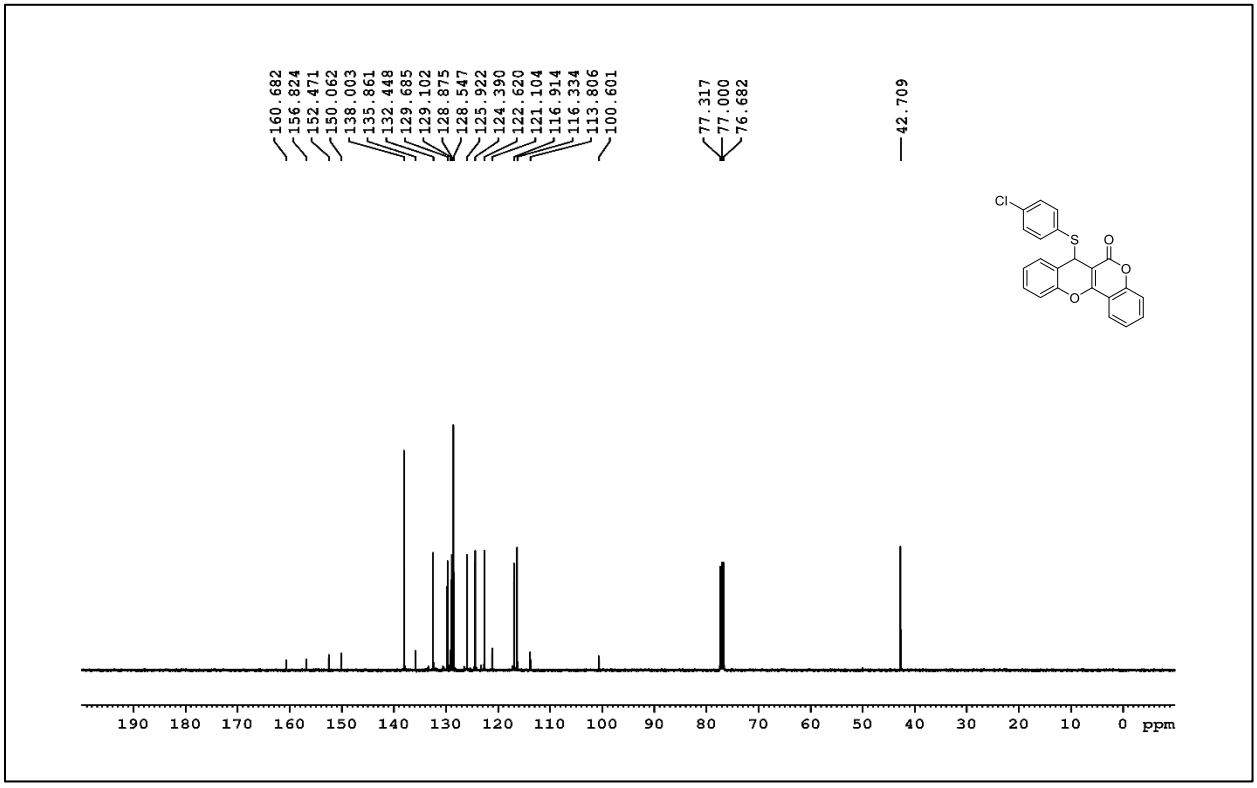
^{13}C NMR Spectra of 5a



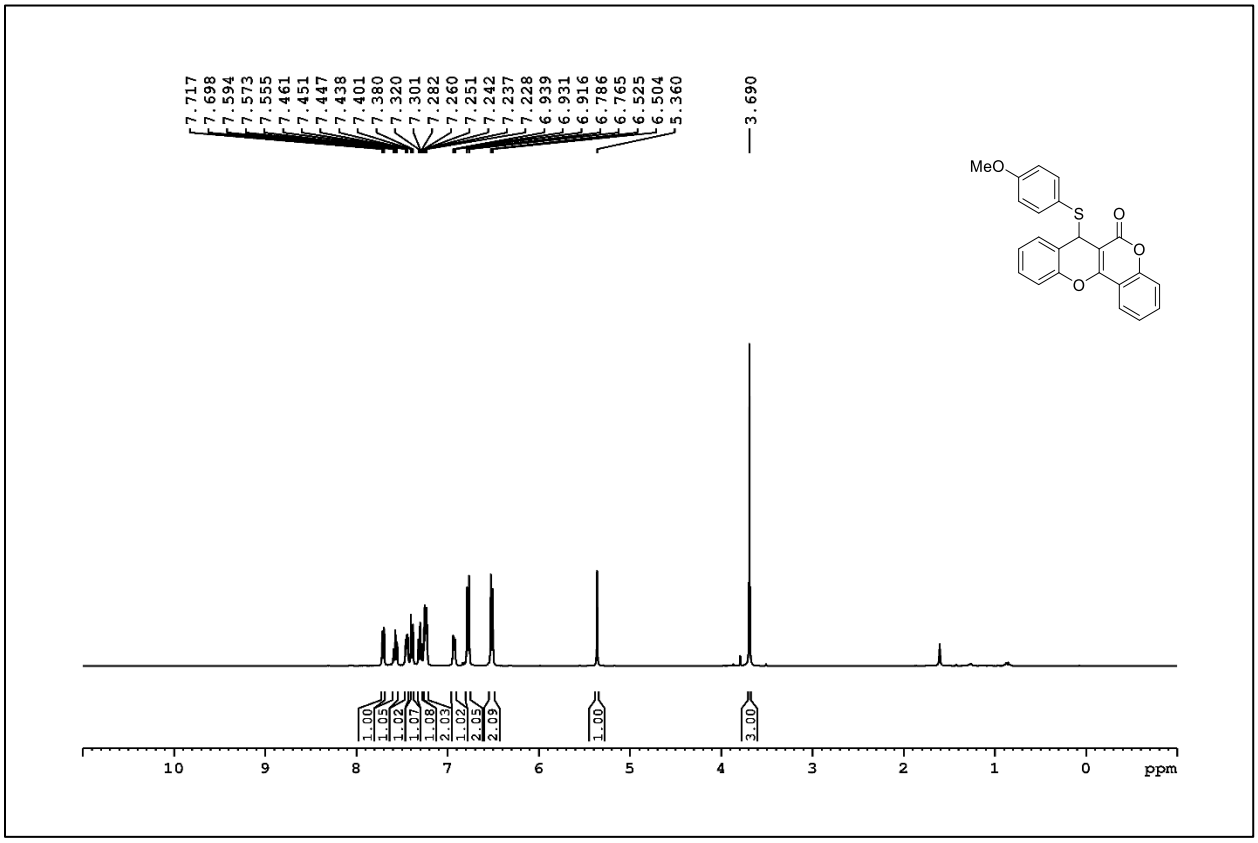
^{1}H NMR Spectra of 5b



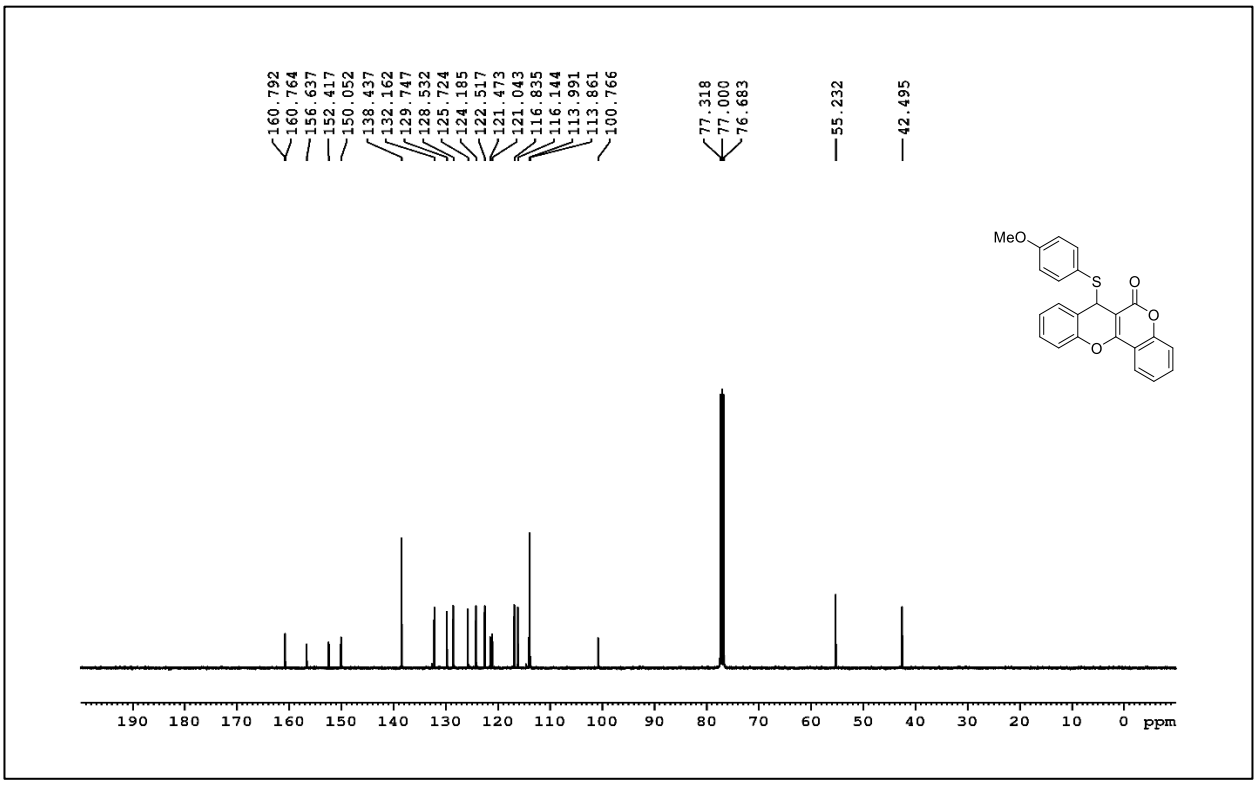
^{13}C NMR Spectra of 5b



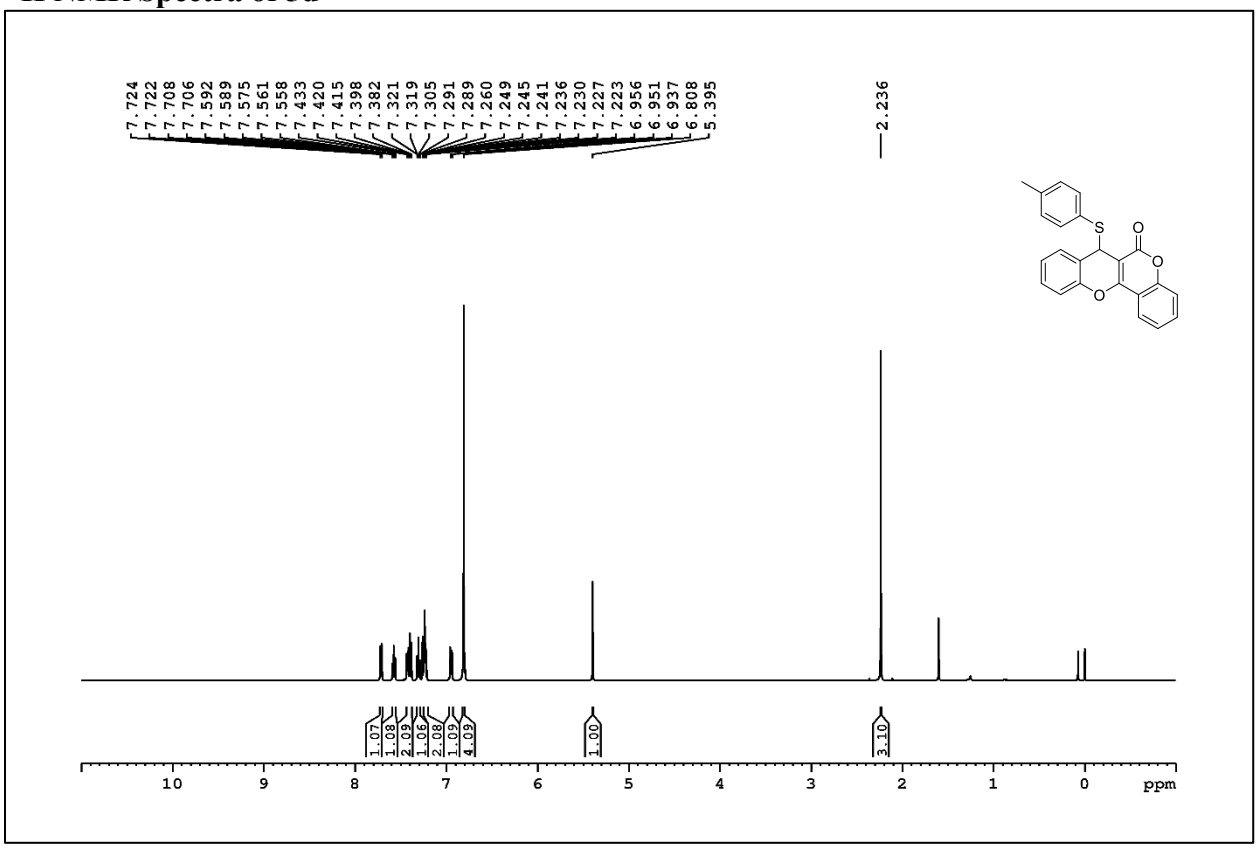
^{1}H NMR Spectra of 5c



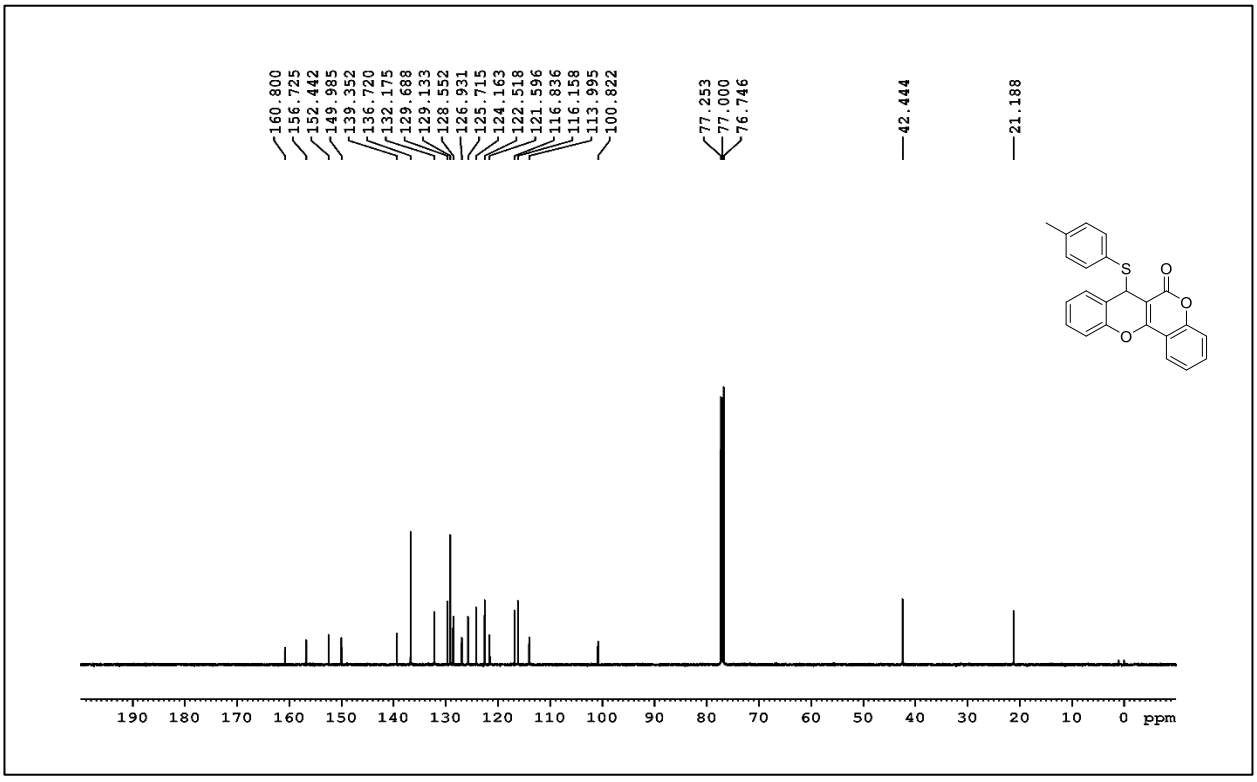
^{13}C NMR Spectra of 5c



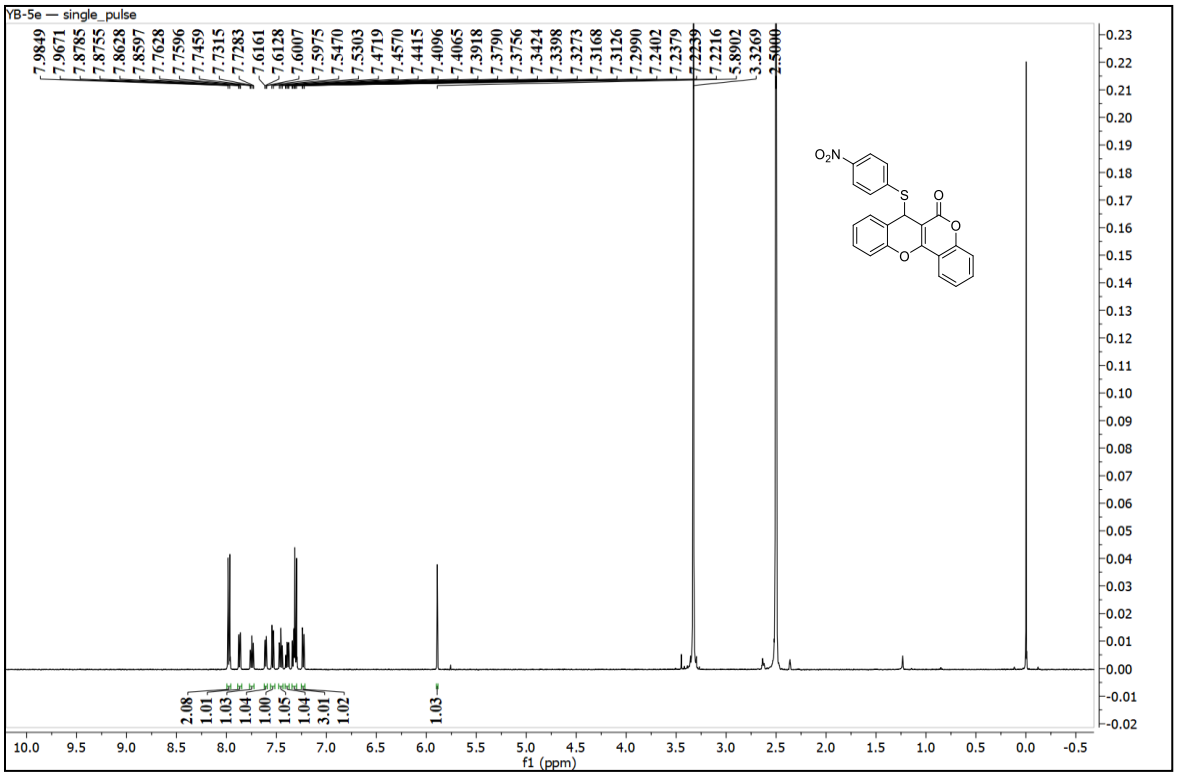
^{1}H NMR Spectra of 5d



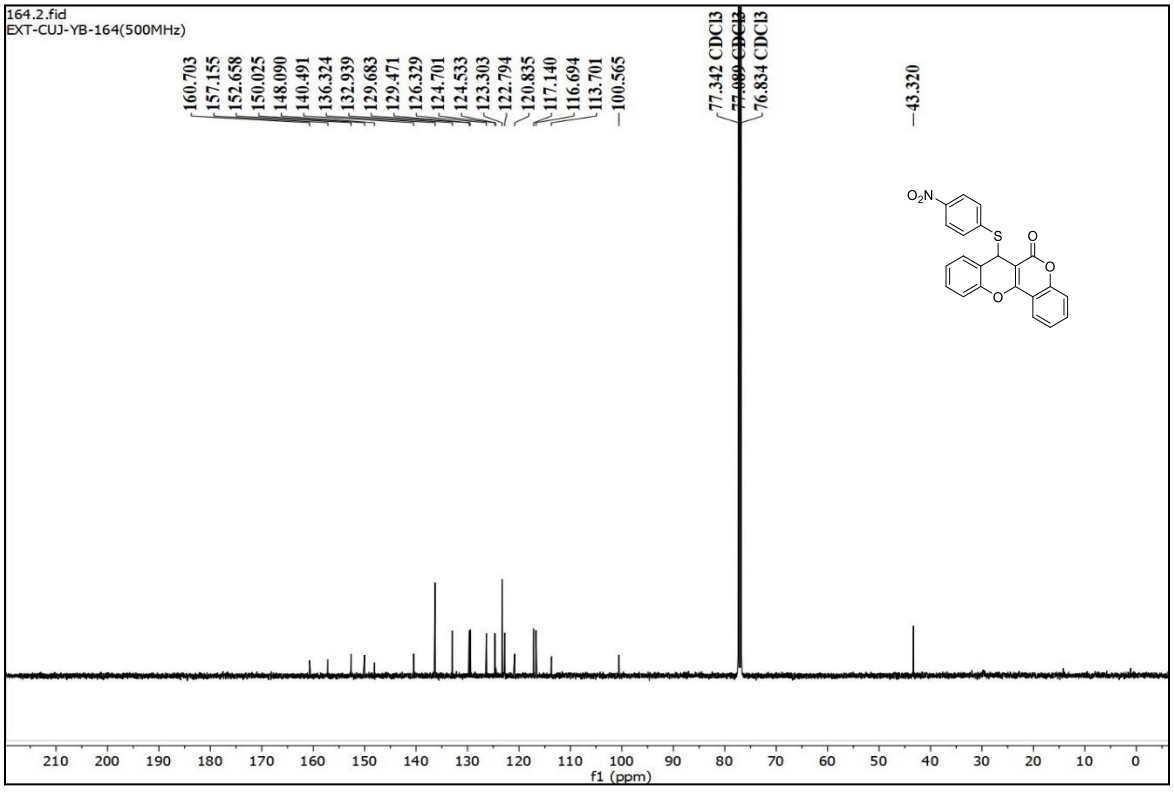
^{13}C NMR Spectra of 5d



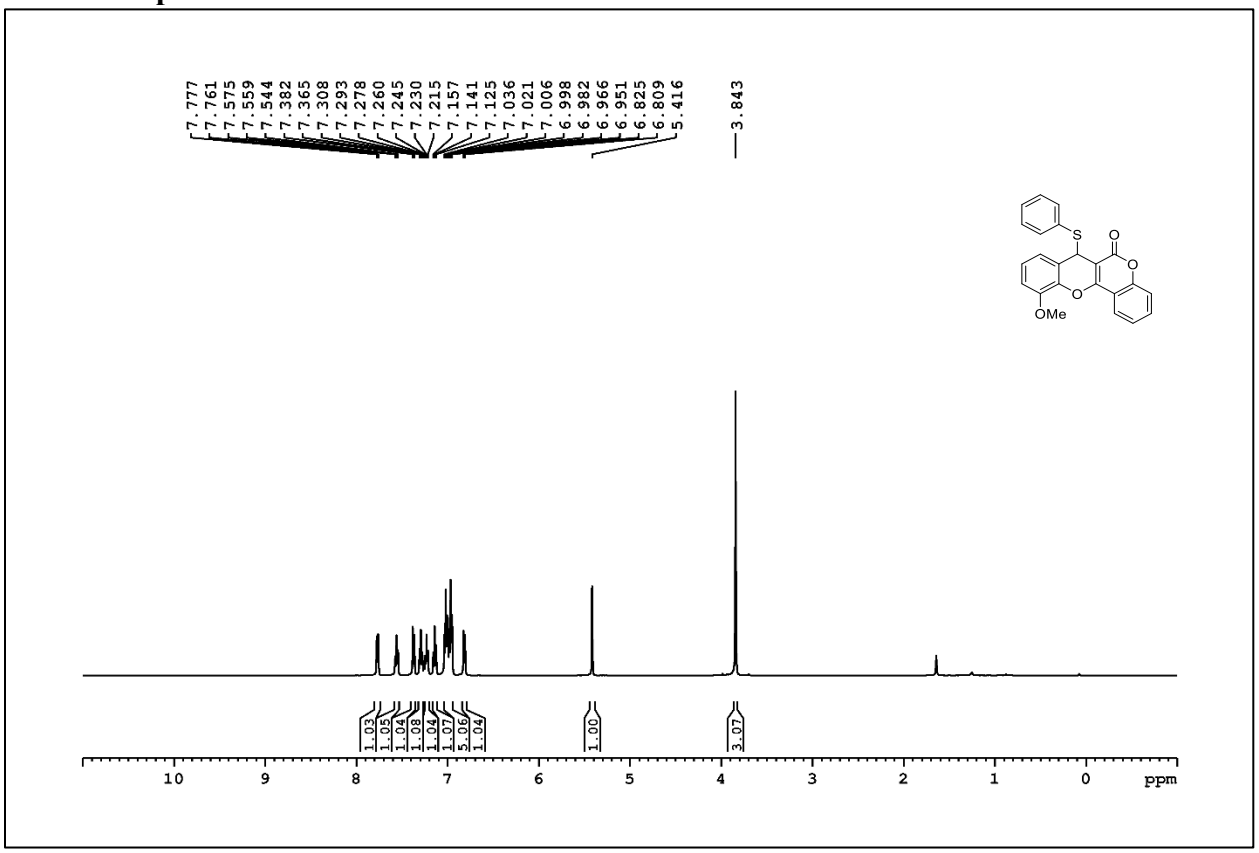
^{1}H NMR Spectra of 5e



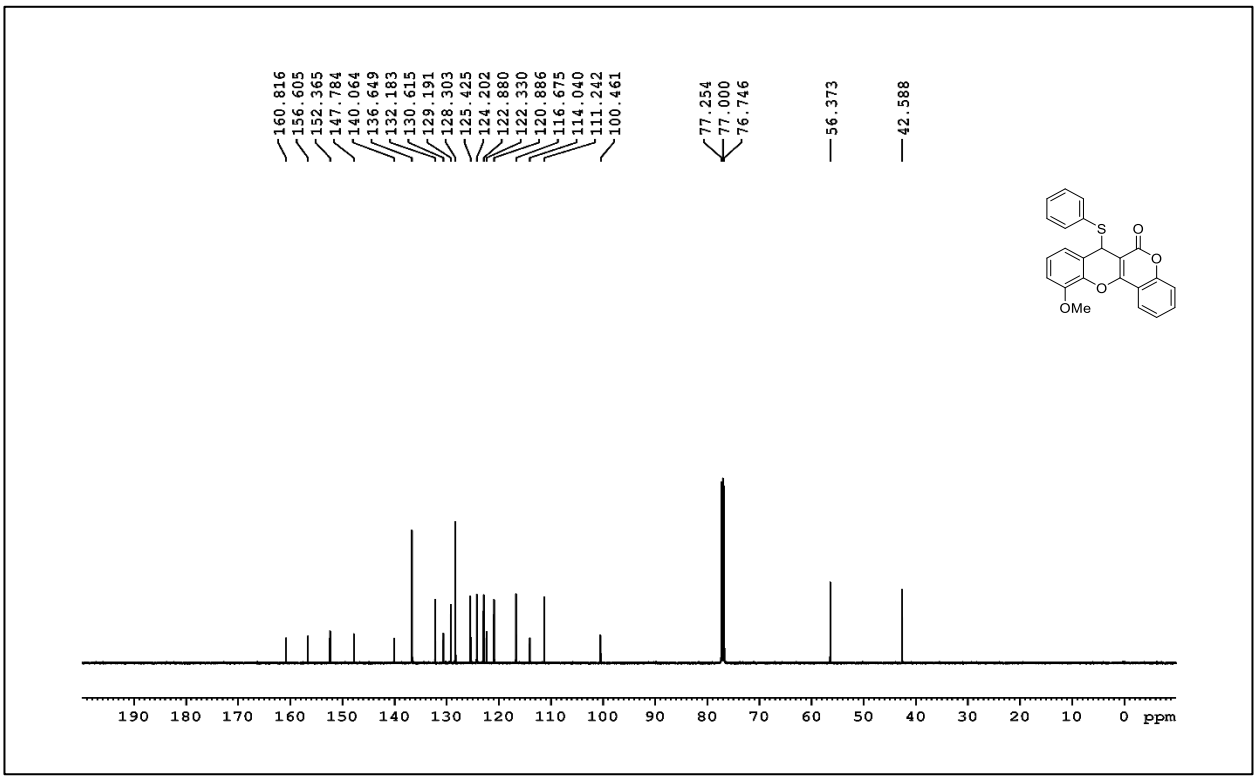
^{13}C NMR Spectra of 5e



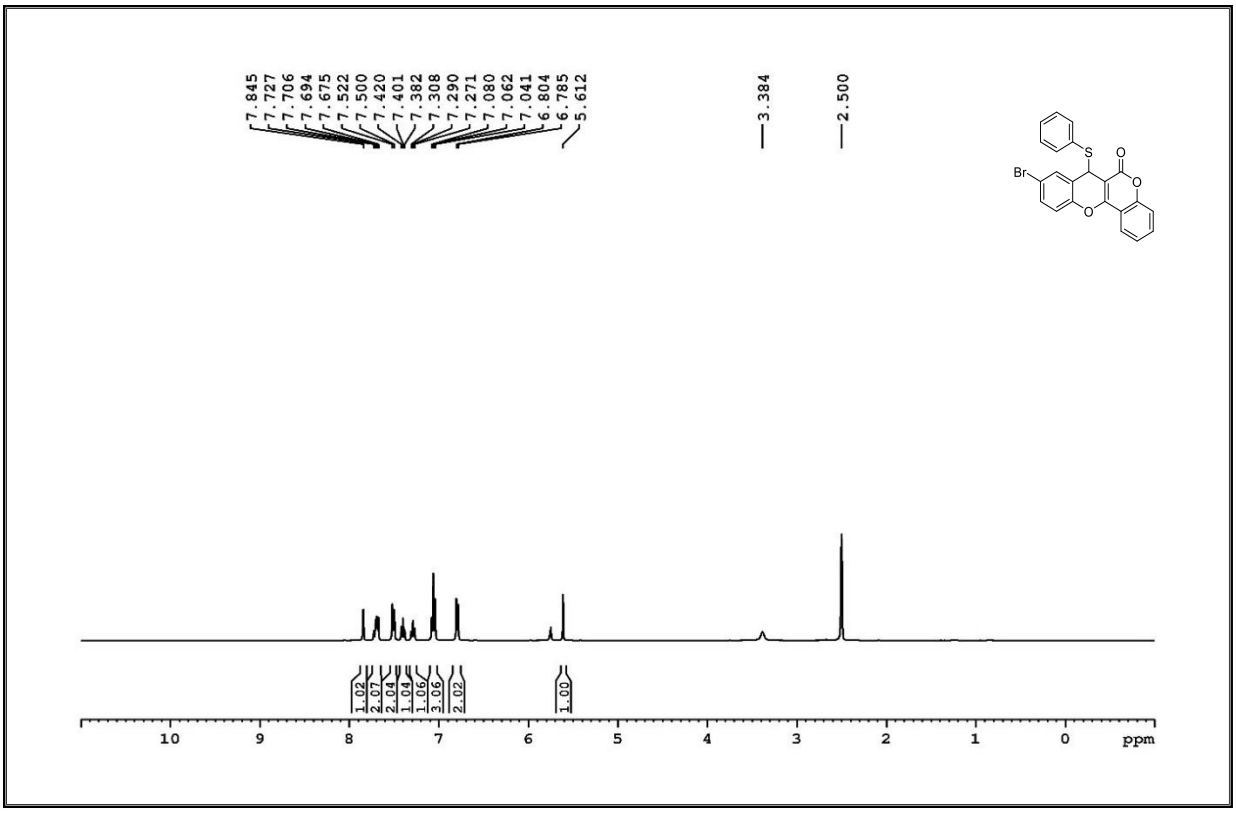
^{1}H NMR Spectra of 5f



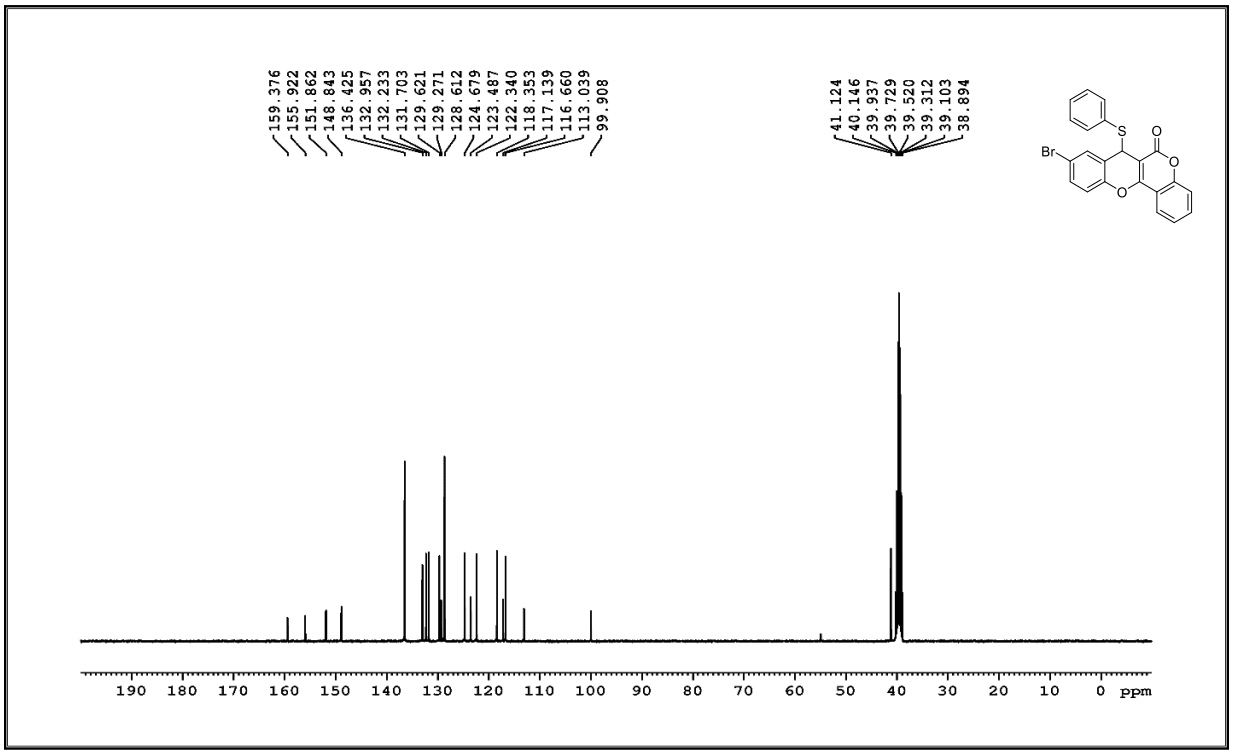
^{13}C NMR Spectra of 5f



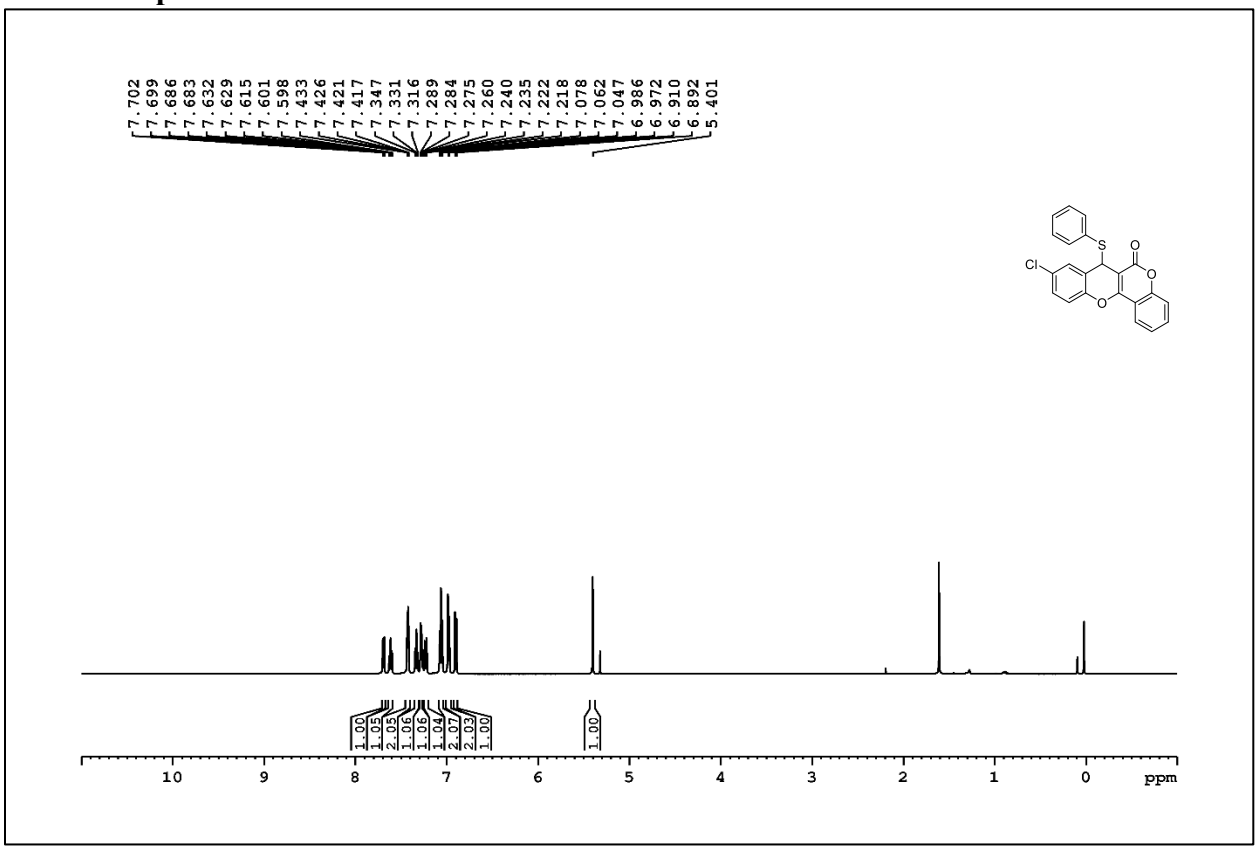
[1]H NMR Spectra of 5g



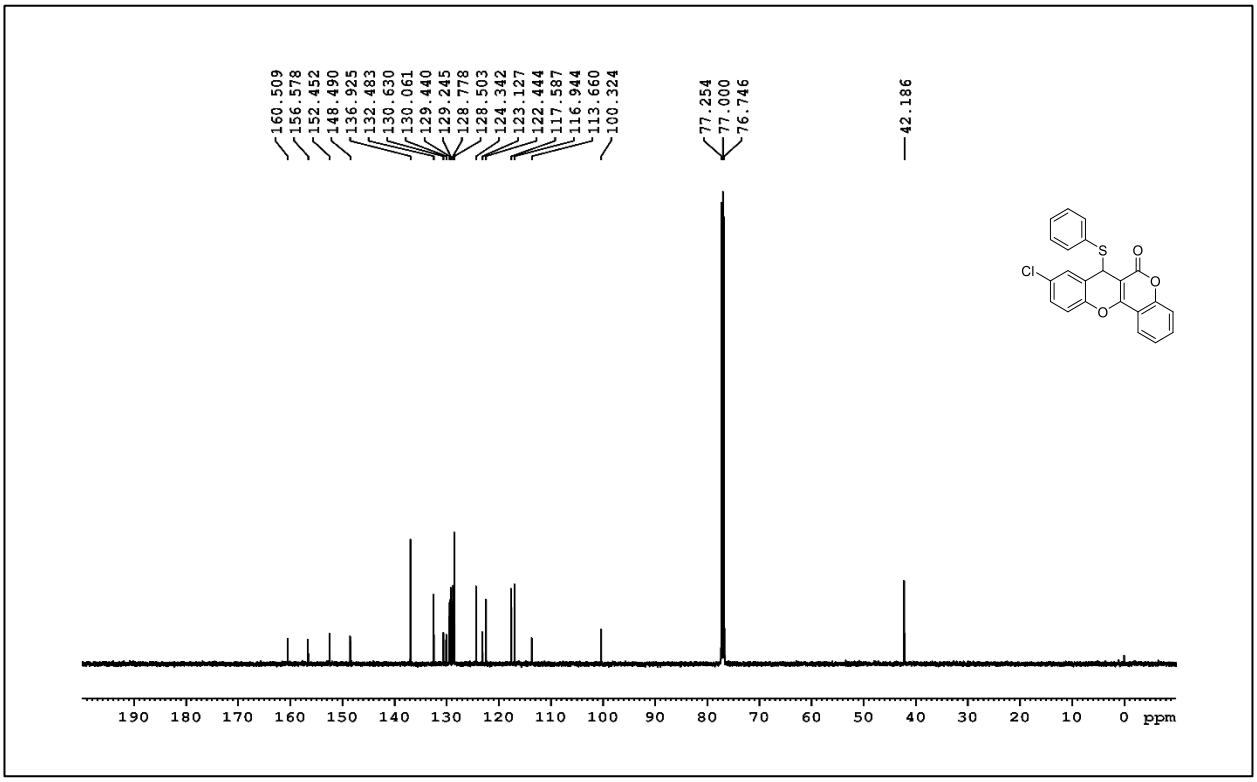
[13]C NMR Spectra of 5g



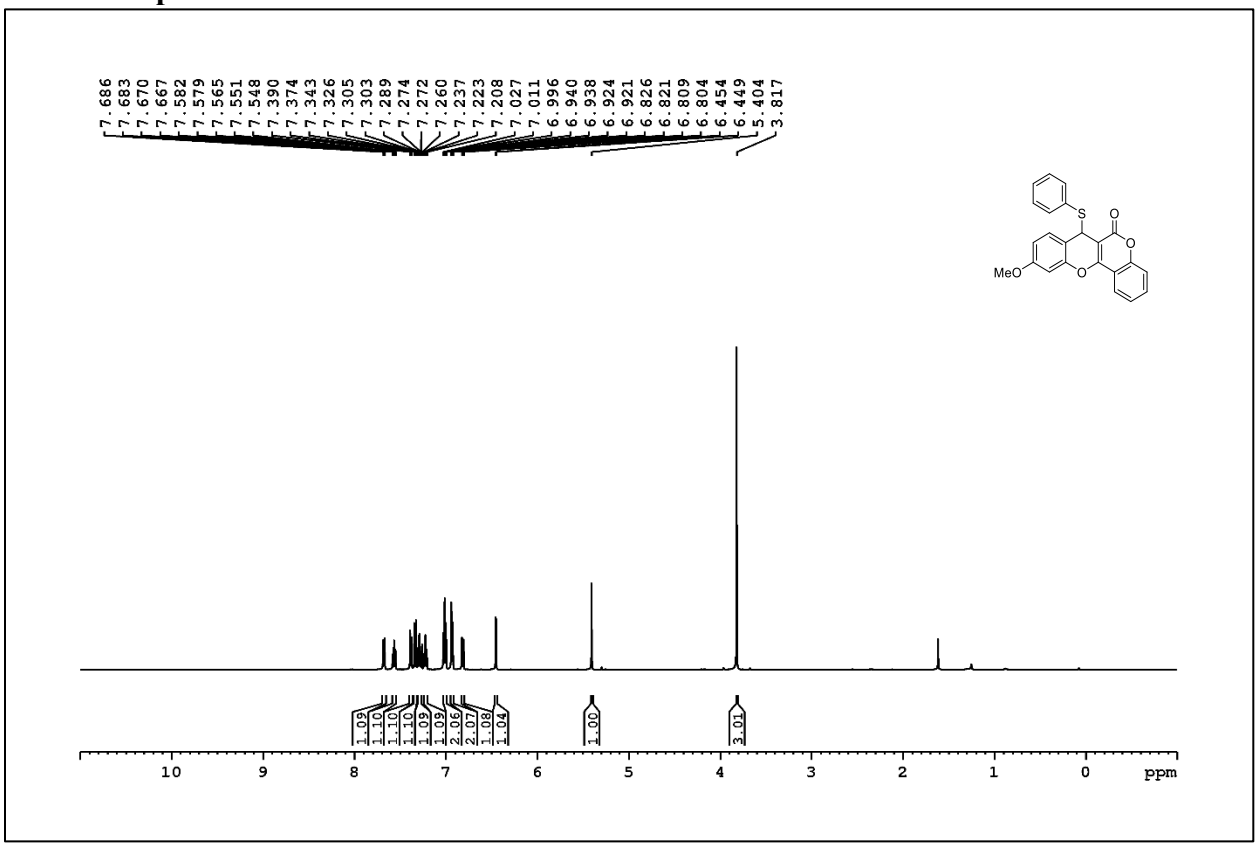
^{1}H NMR Spectra of 5h



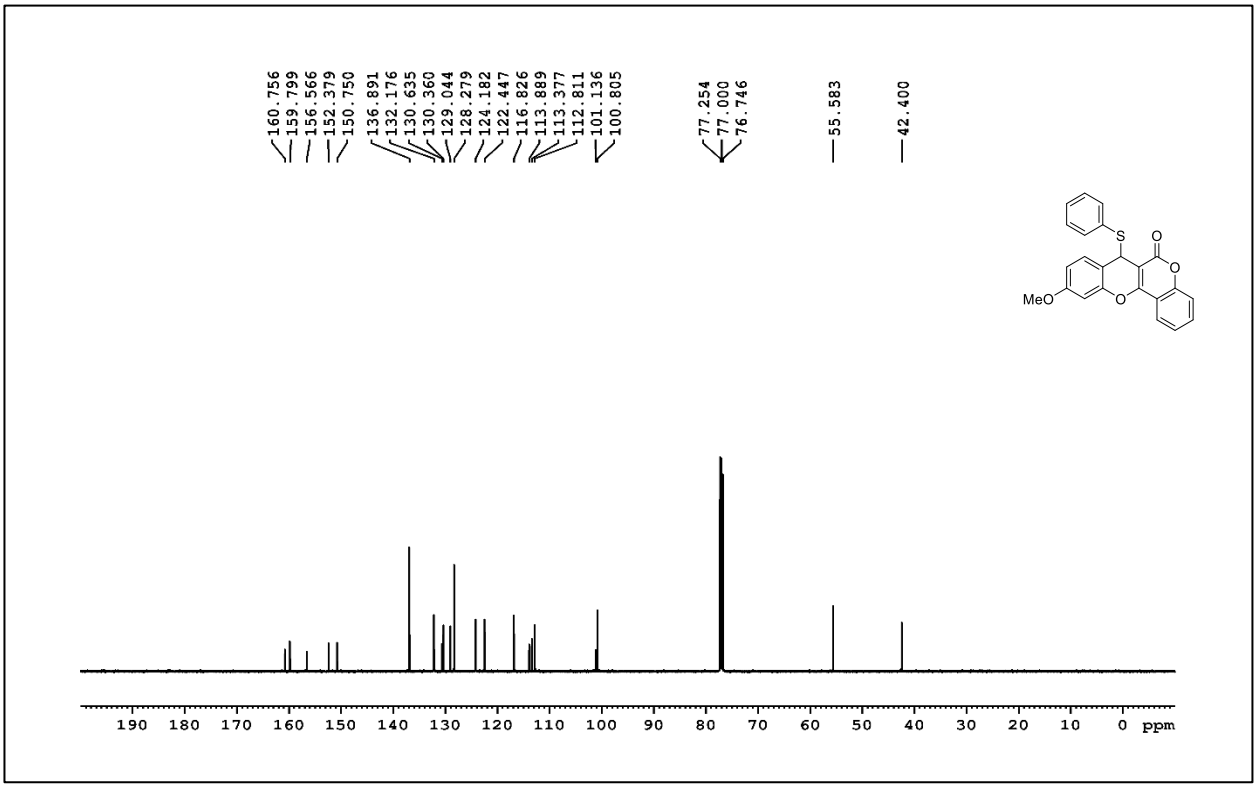
^{13}C NMR Spectra of 5h



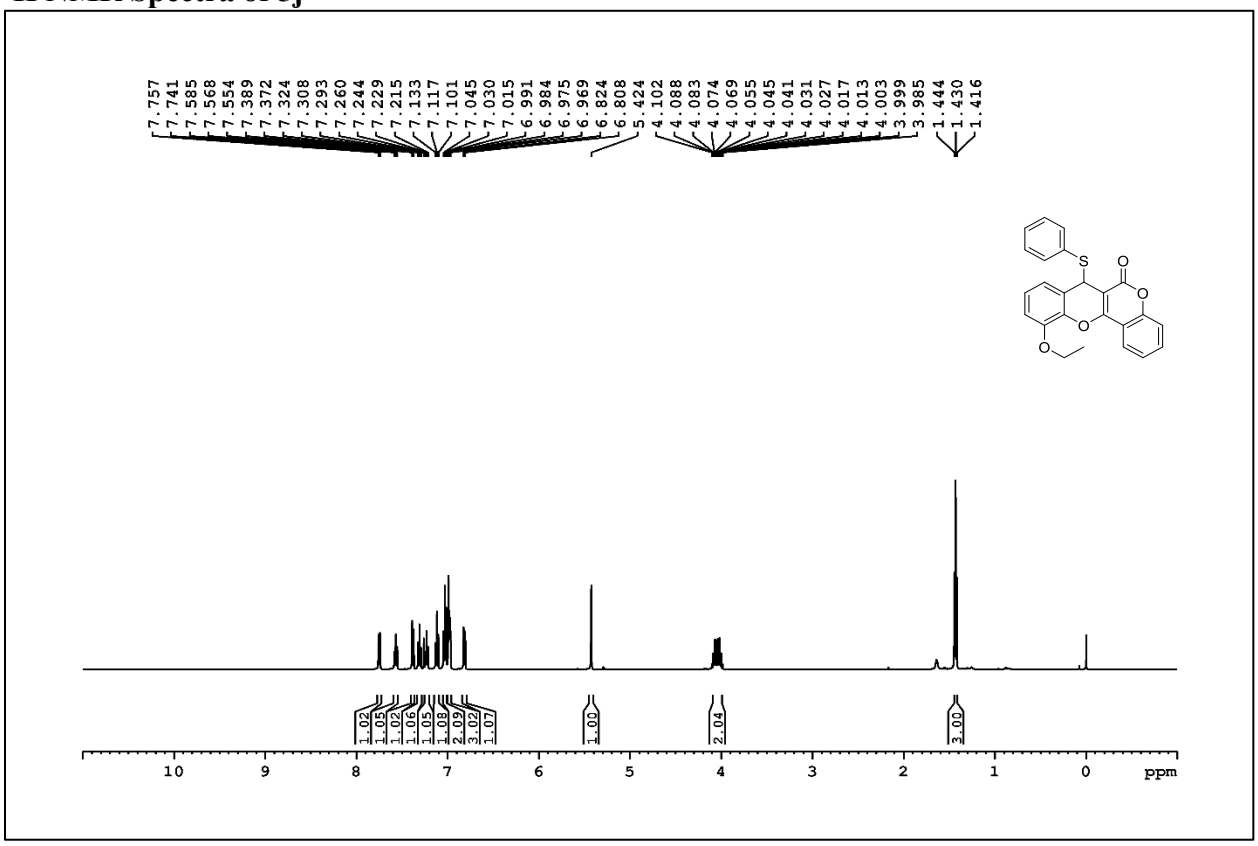
^{1}H NMR Spectra of 5i



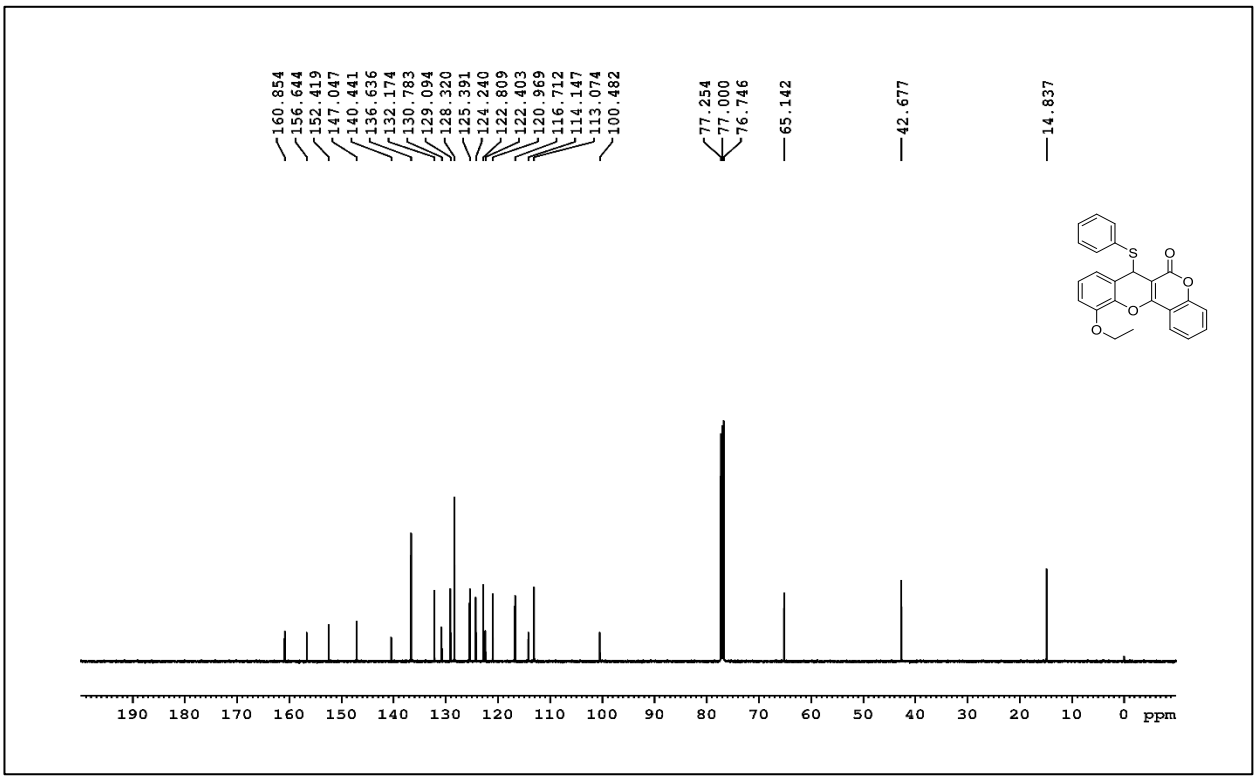
^{13}C NMR Spectra of 5i



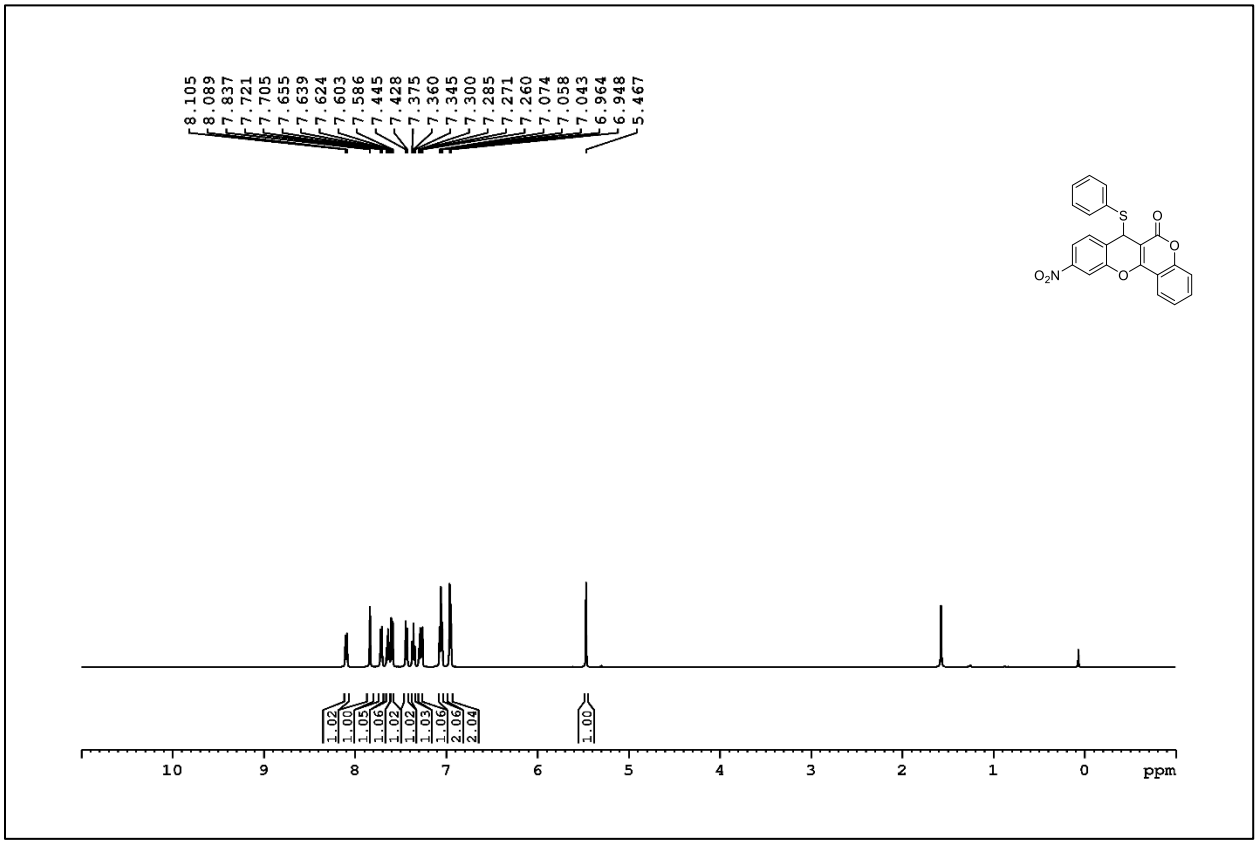
^{1}H NMR Spectra of 5j



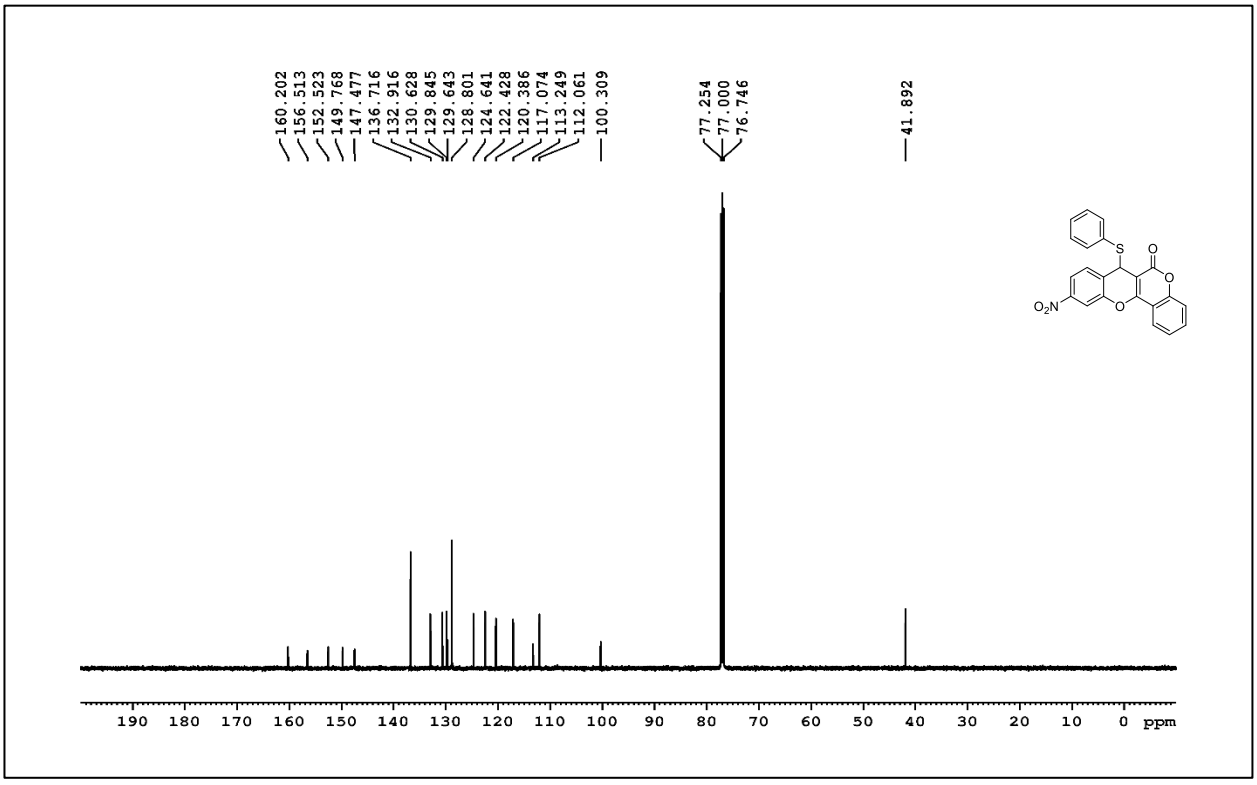
^{13}C NMR Spectra of 5j



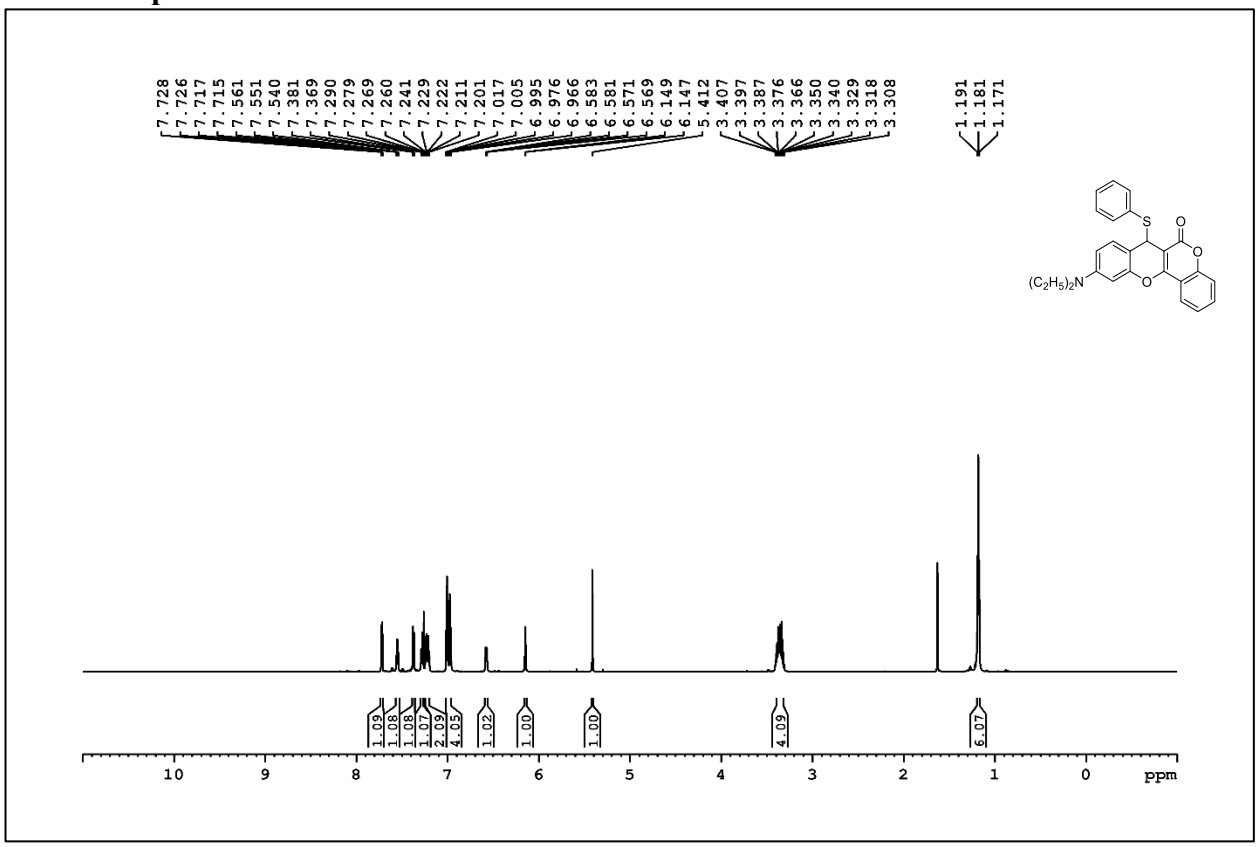
^{1}H NMR Spectra of 5k



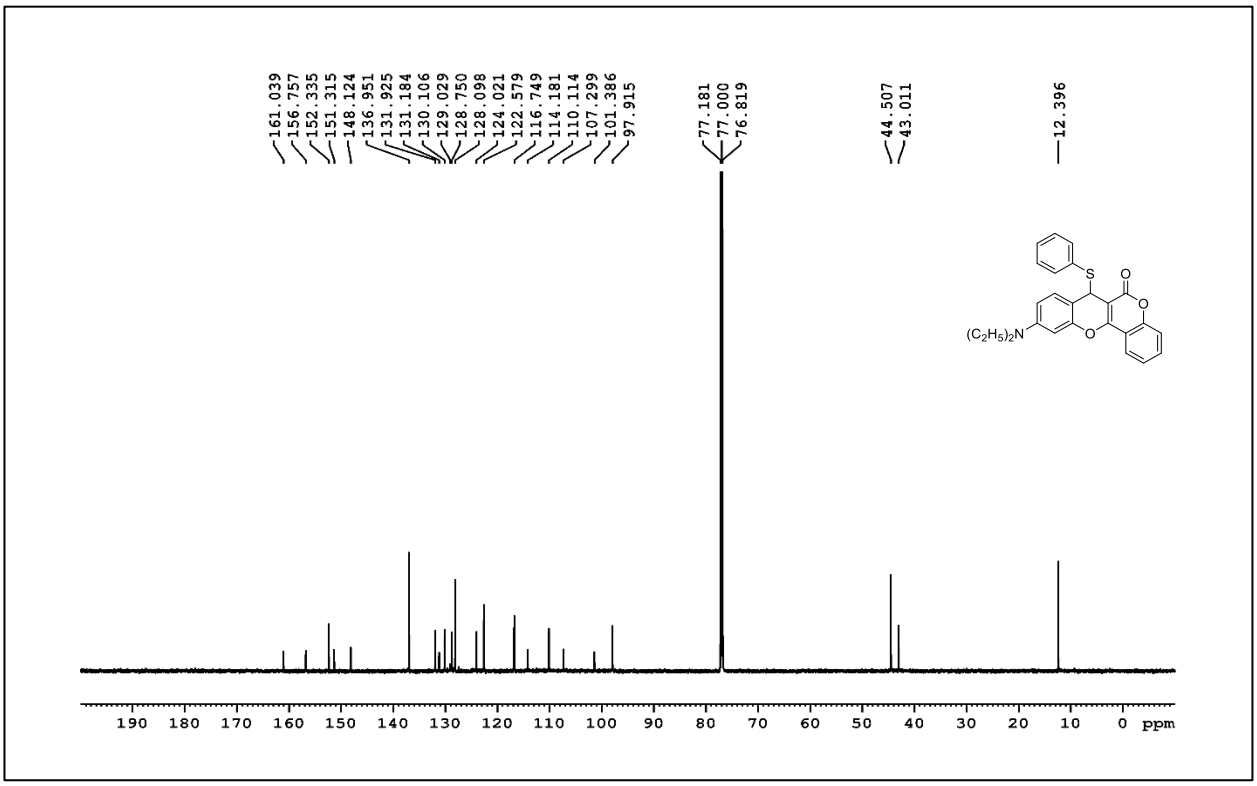
^{13}C NMR Spectra of 5k



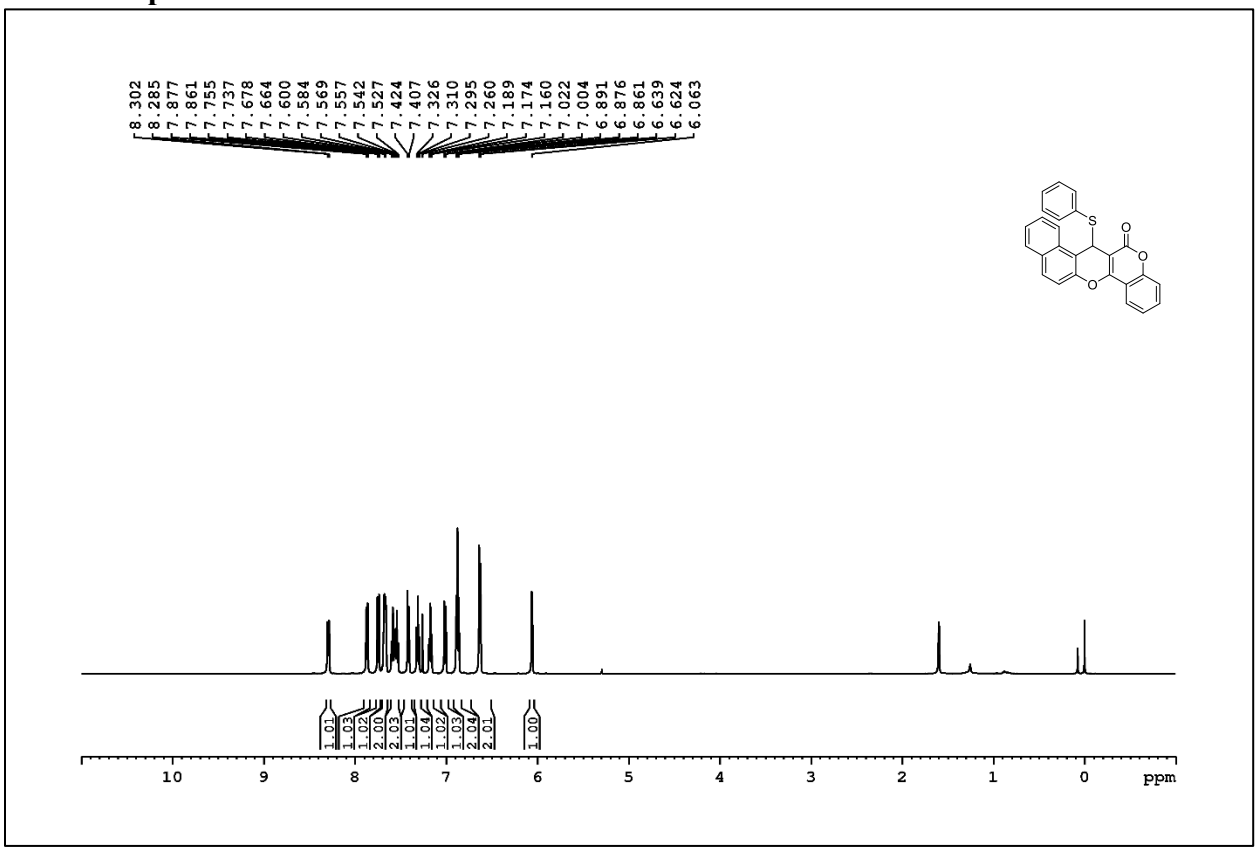
^{1}H NMR Spectra of 5l



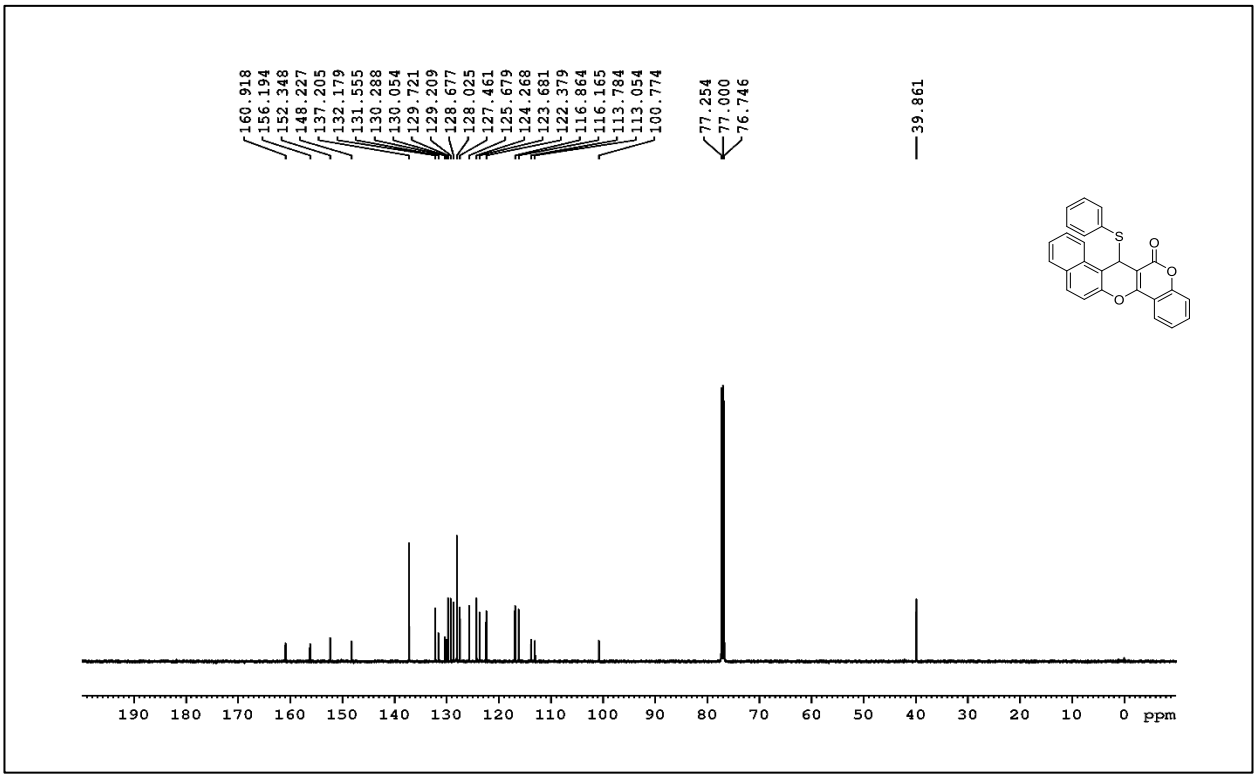
^{13}C NMR Spectra of 5l



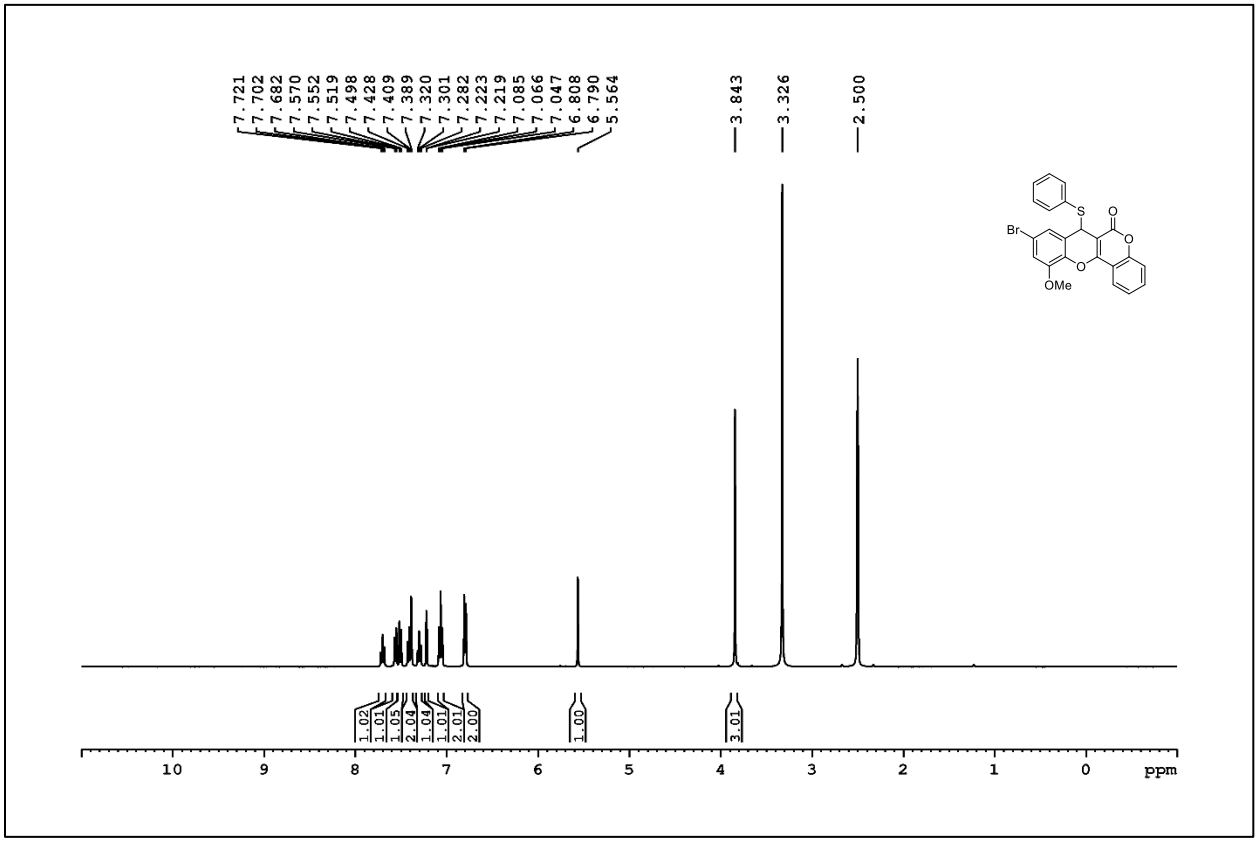
^{1}H NMR Spectra of 5m



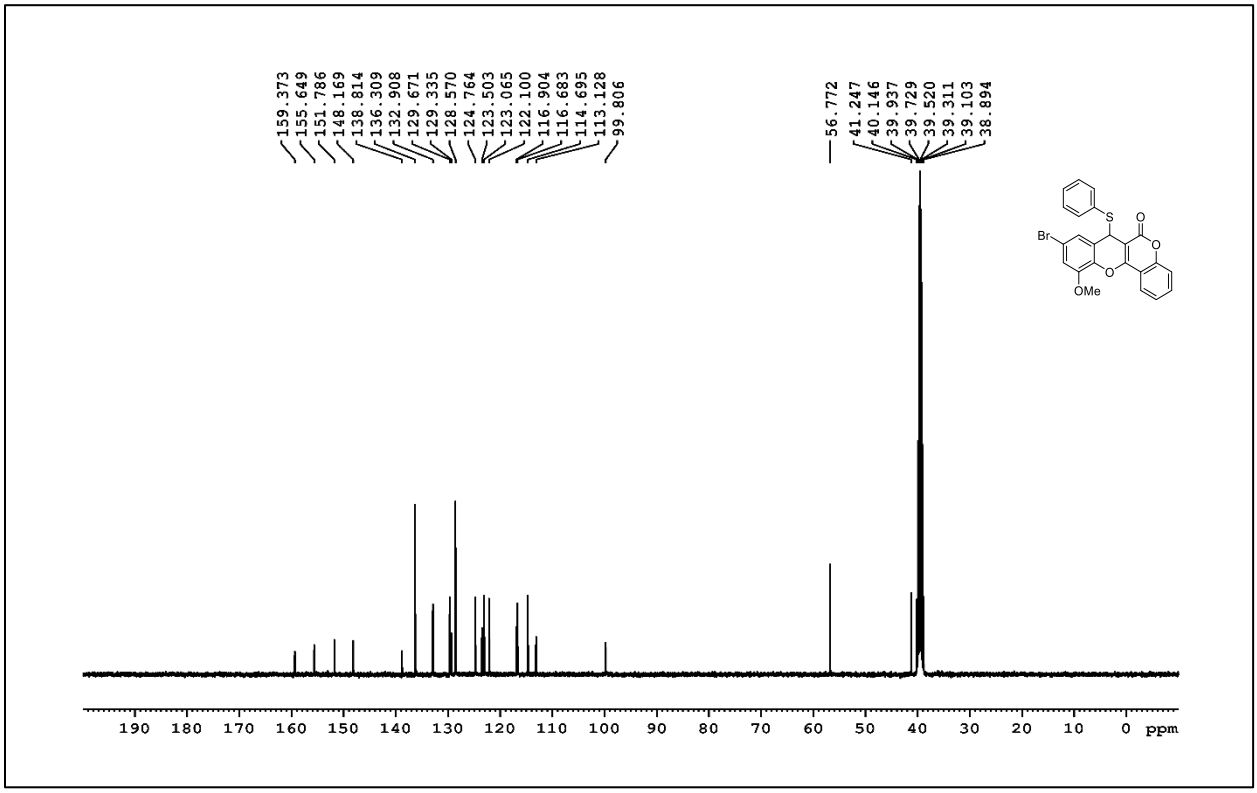
^{13}C NMR Spectra of 5m



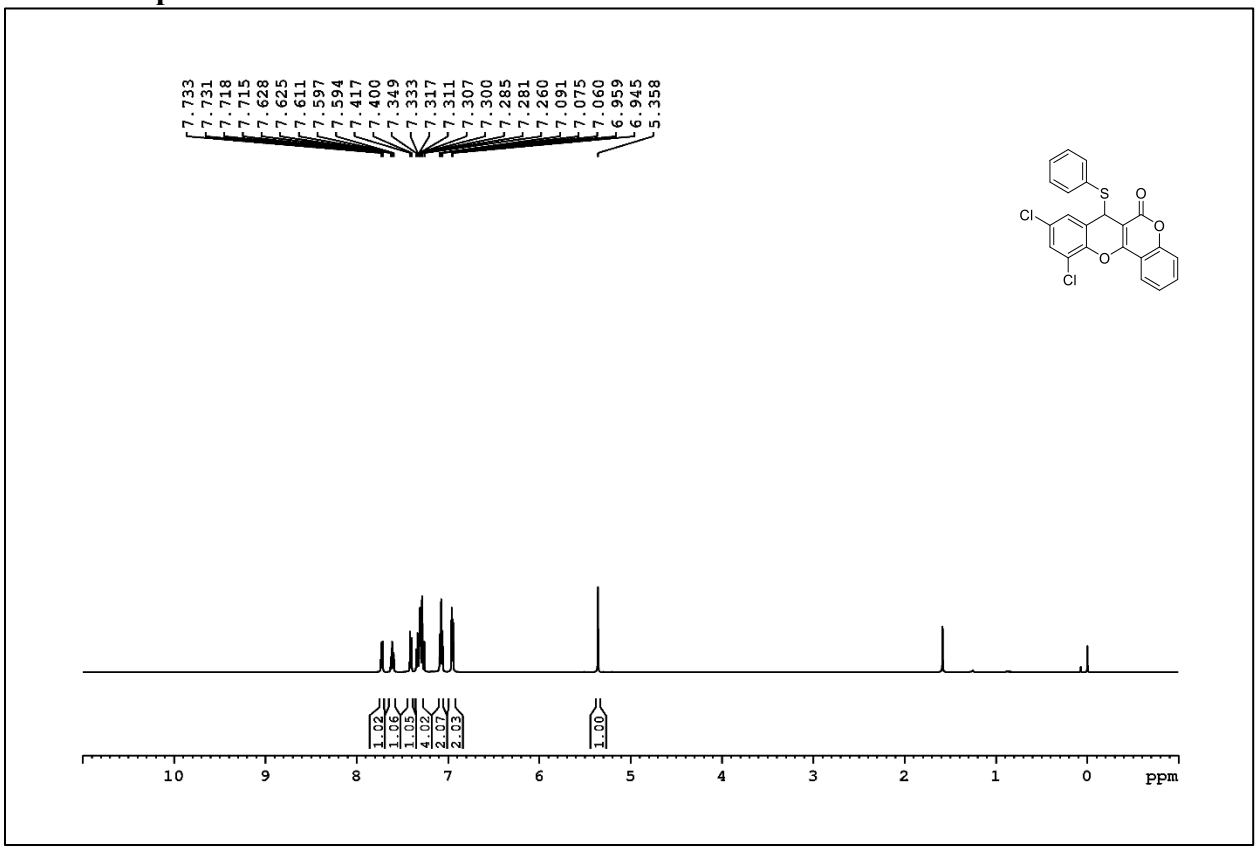
^{1}H NMR Spectra of 5n



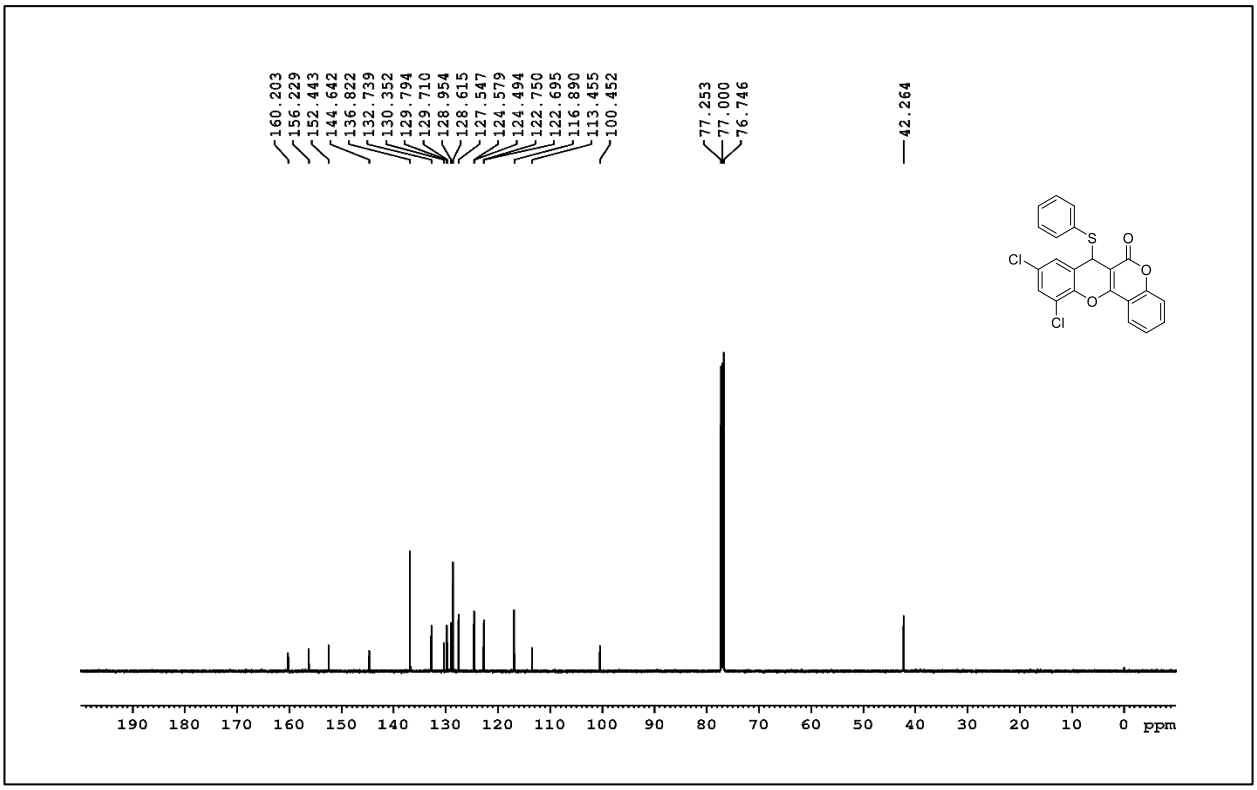
^{13}C NMR Spectra of 5n



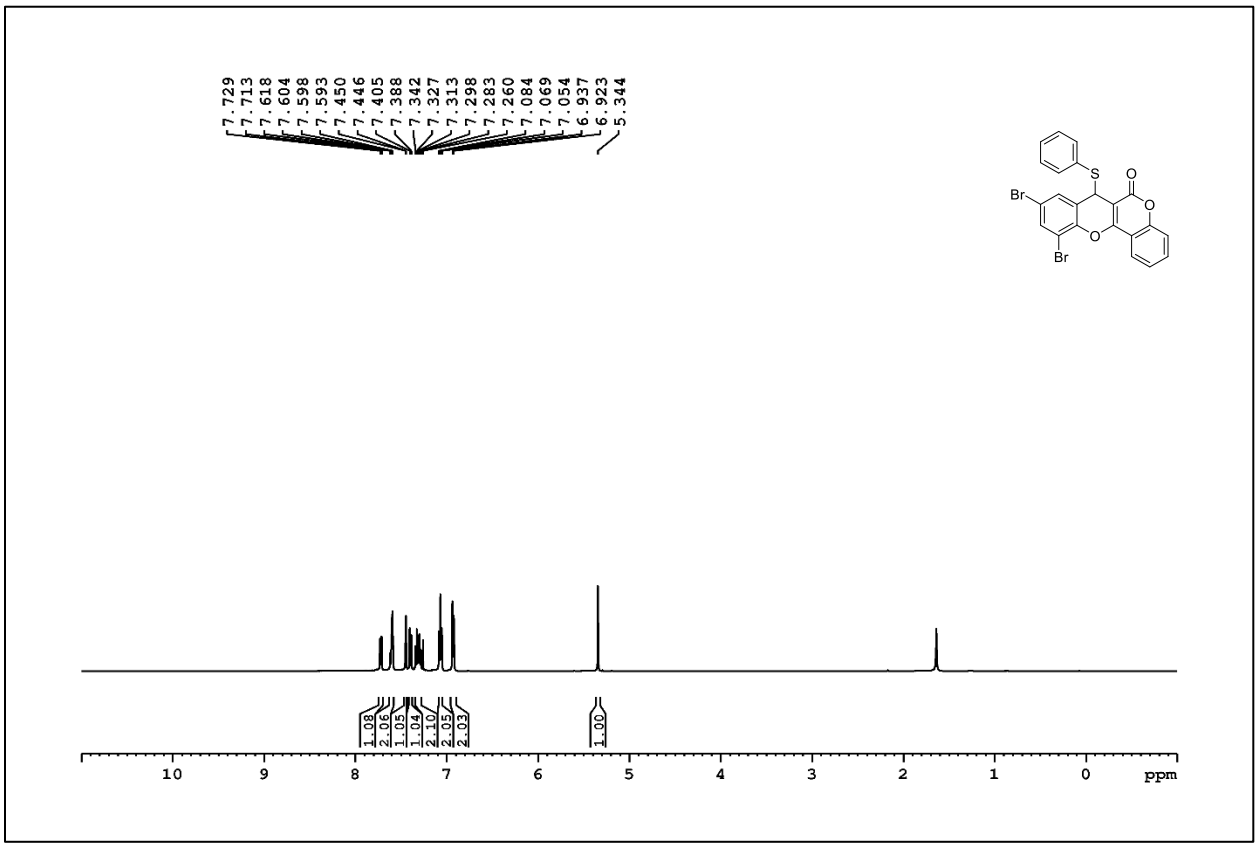
^{1}H NMR Spectra of 5o



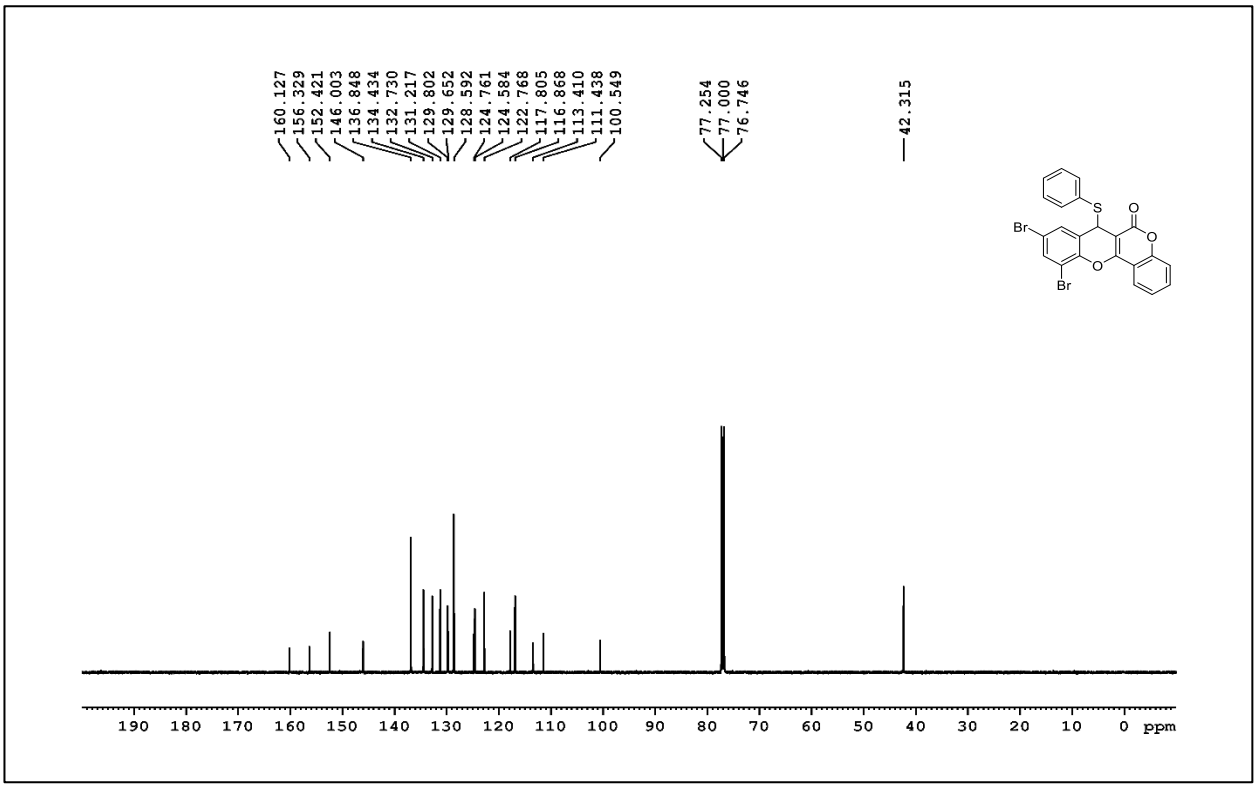
^{13}C NMR Spectra of 5o



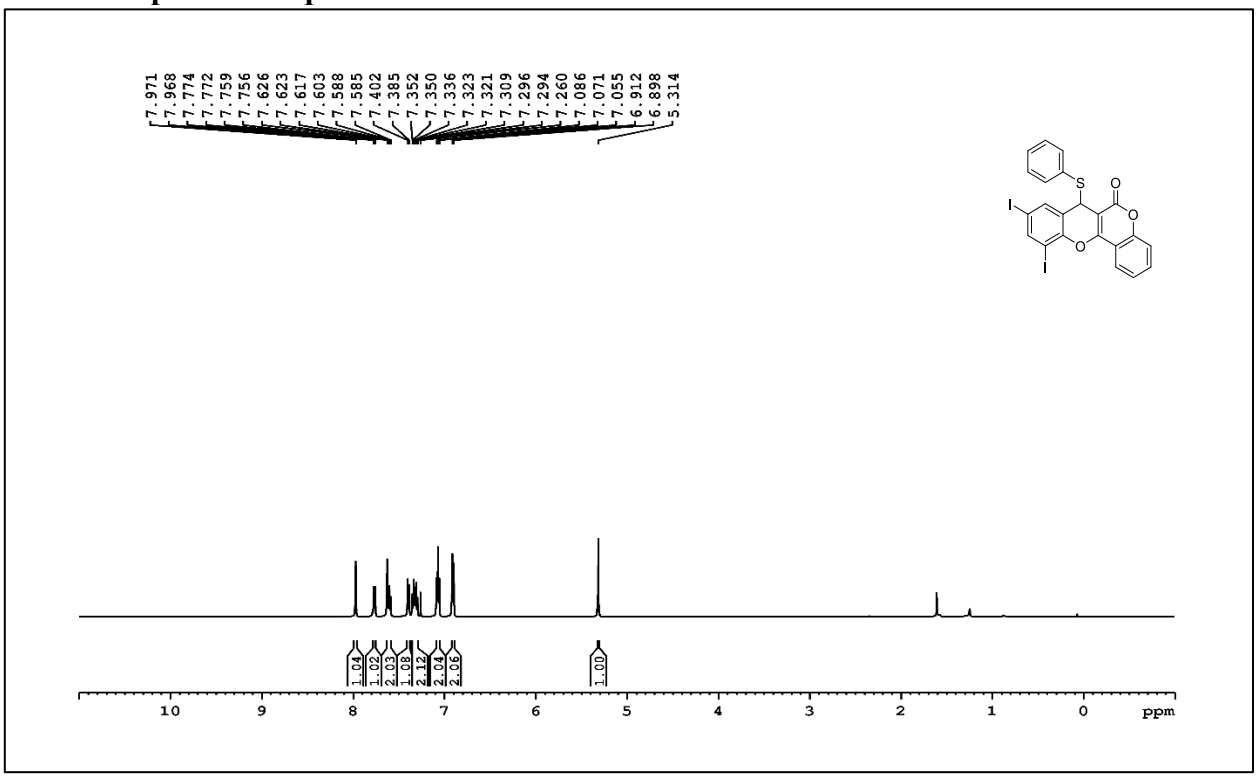
^{1}H NMR Spectra of 5p



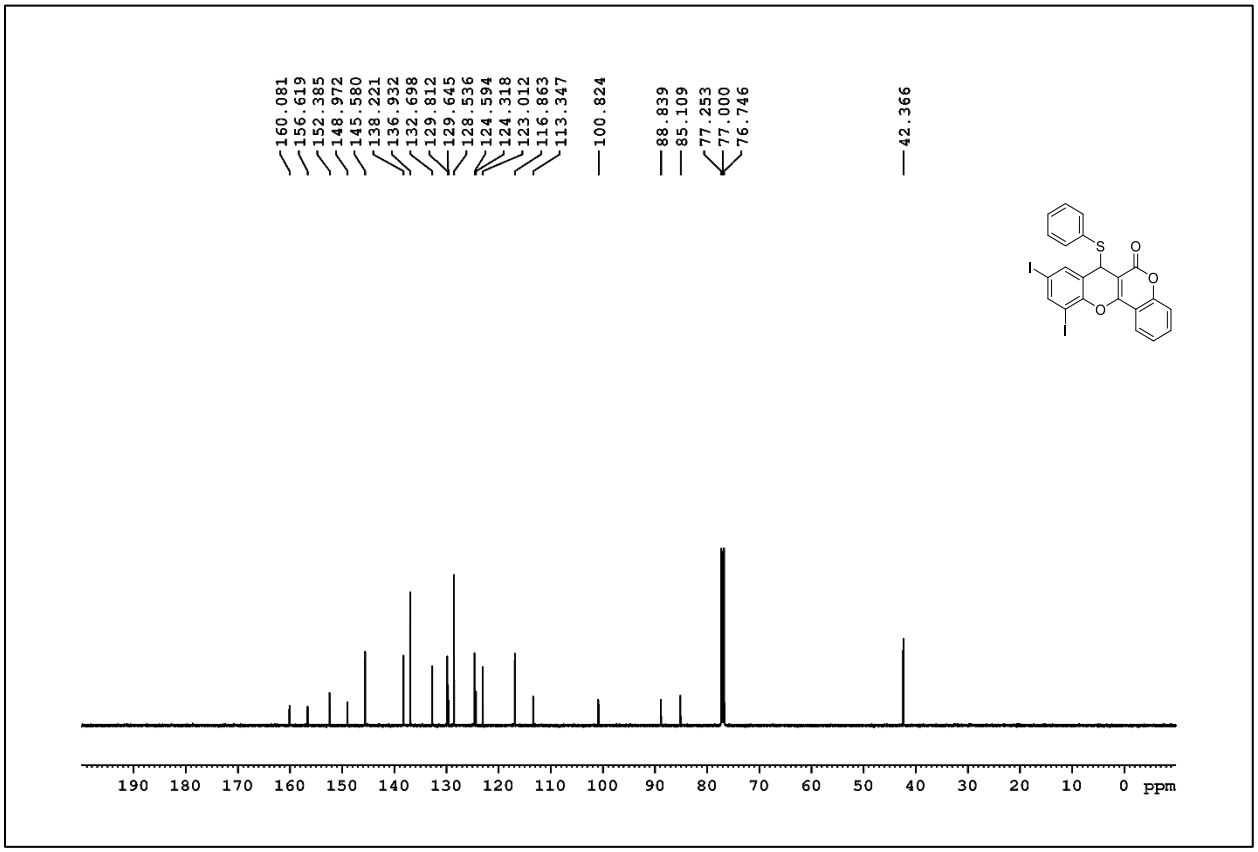
^{13}C NMR Spectra of 5p



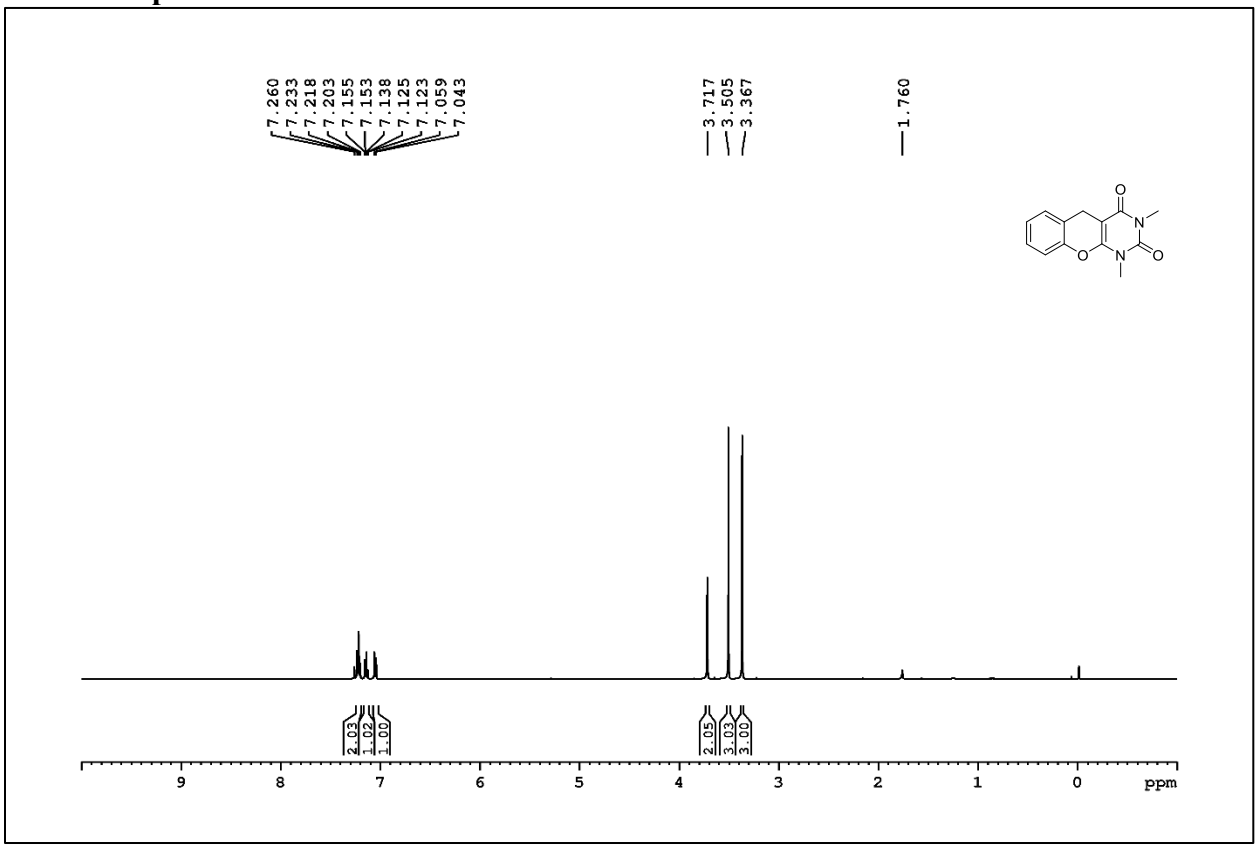
^{1}H NMR Spectra of 5q



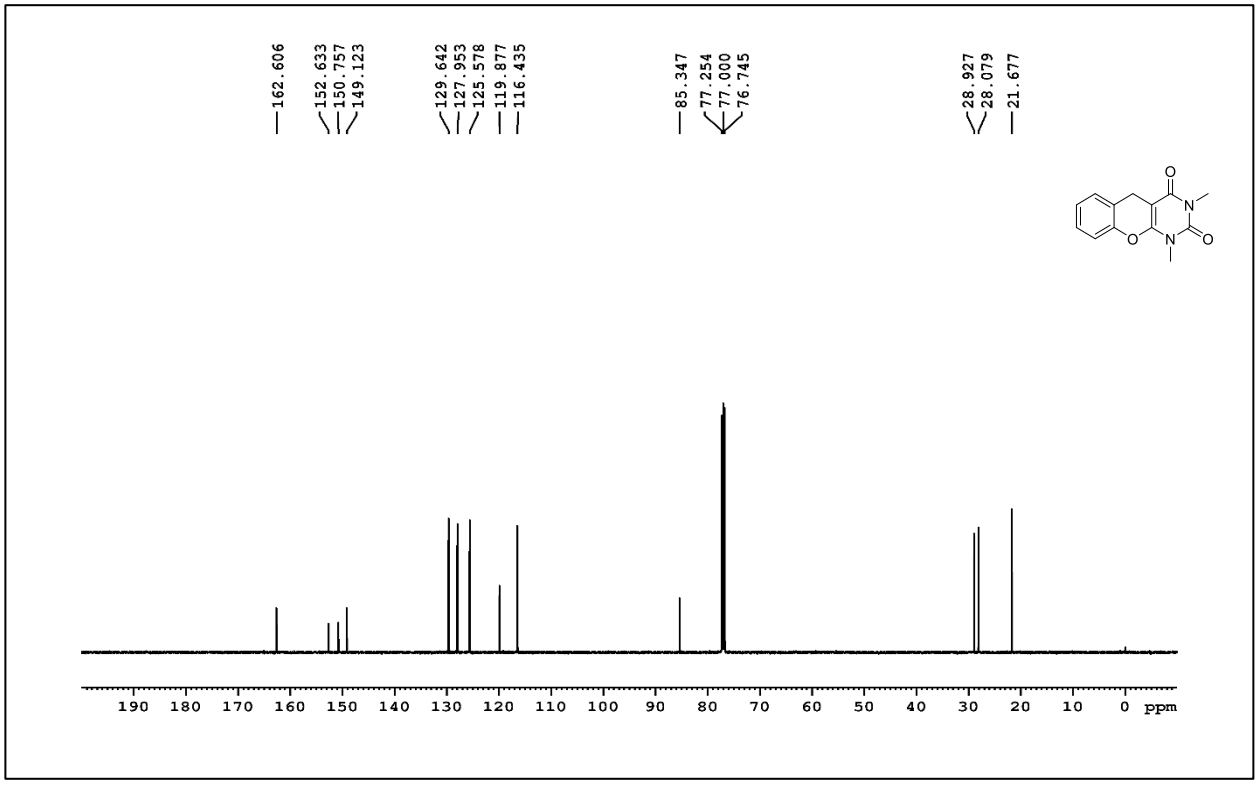
^{13}C NMR Spectra of 5q



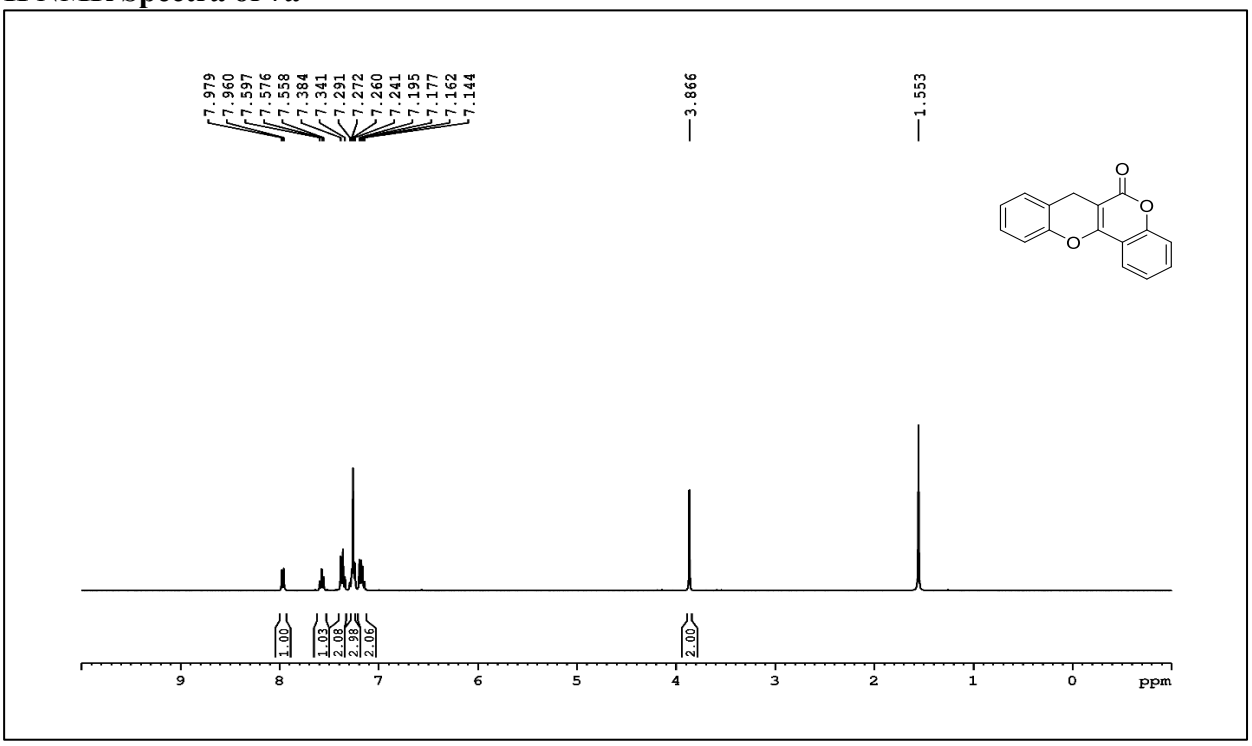
^{1}H NMR Spectra of 6a



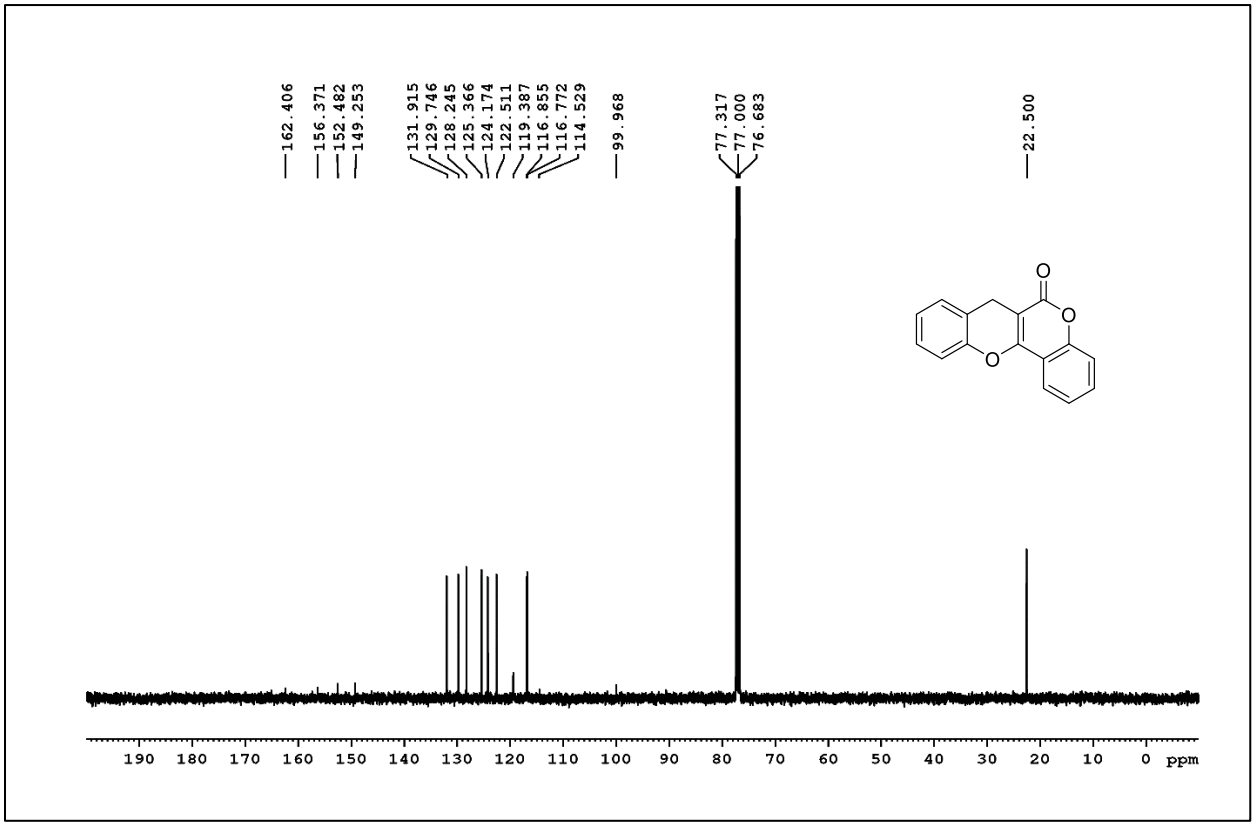
^{13}C NMR Spectra of 6a



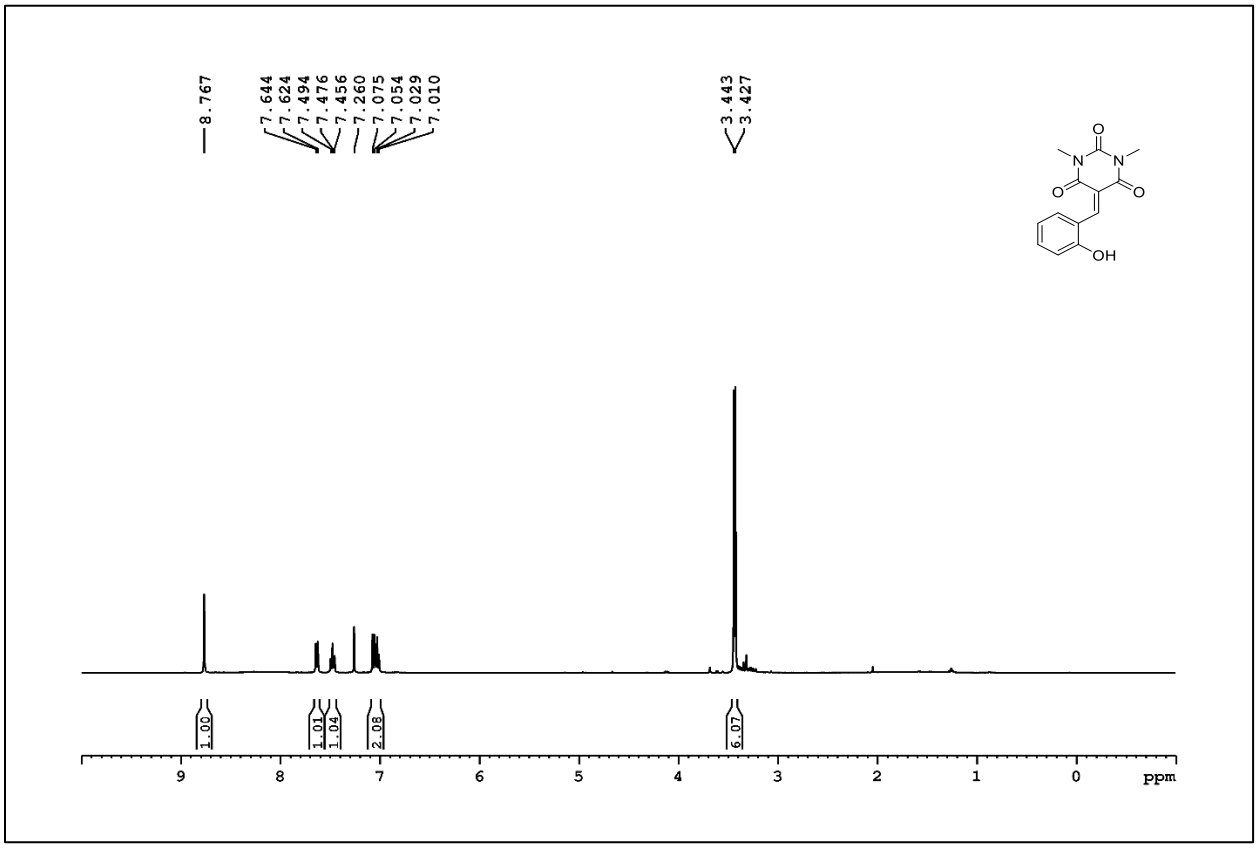
^{1}H NMR Spectra of 7a



^{13}C NMR Spectra of 7a



^{1}H NMR Spectra of B



^{13}C NMR Spectra of B