Electronic Supplementary Material (ESI) for Green Chemistry.

Photoinduced radical cascade reactions for the thioalkylation of quinoxalin-2(1*H*)-one: An access to β-heteroaryl thioethers under metal and catalyst free condition

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1. General information

Commercial grade reagents, solvents, and starting materials were purchased of pure analytical grades and used as purchased without further purification unless otherwise stated. Commercially available 7 mL screw cap vials fitted with PTFE/silicone septa were purchased from Sigma-Aldrich for performing the reaction. Chromatographic purification of products was undertaken on silica gel (230-400 mesh) using a proper eluent system. For thin-layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used and visualized with UV light and developed using an ethanol solution of phosphomolybdic acid or basic aqueous potassium permanganate ($KMnO_4$) stain solutions. Organic solutions were concentrated under vacuum pressure using a rotary evaporator. The ^{1}H (400 MHz and 500 MHz) and ^{13}C (101 MHz and 126 MHz) nuclear magnetic resonance spectra were recorded on 400 MHz and 500 MHz spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C are reported in parts per million (ppm) relative to internal standard tetramethylsilane (tetramethylsilane @ 0 ppm) and residual solvent peak in the NMR solvent (for ^{1}H NMR (DMSO @ 2.50 ppm and $CHCl_3$ @ 7.26 ppm), for ^{13}C NMR (DMSO @ 39.52 ppm and $CHCl_3$ @ 77.16 ppm). Coupling constants are given in Hertz (Hz). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; p, pentet; sept, septet; m, multiplet; br, broad signal. During the optimization yields were determined by Agilent, 1260 Infinity II high performance liquid chromatography (HPLC) instrument. Ultraviolet-visible experiments were recorded on a SHIMADZU-UV-1900i instrument using HPLC grade ethyl acetate (EtOAc). The fluorescence emission spectra were carried out on a model FLS920 (Edinburgh Instruments) spectrofluorometer using HPLC grade EtOAc. High-resolution mass spectra (HRMS) were recorded on a Mass Spectrometry Unit using electrospray ionization-time of flight (ESI-TOF) reflectron experiments.

2. General procedures for the synthesis of starting Materials

2.1. General procedure for the synthesis of quinoxalin-2(1*H*)-one derivatives

The quinoxalin-2(*1H*)-ones were synthesized according to previously reported literature.[1] A solution of 1,2-phenylenediamine derivatives (12 mmol, 1.0 equiv.) and ethyl glyoxalate (~50% in toluene, 28.8 mmol, 2.4 equiv.) in ethanol (40 mL) in a 100 mL round bottom flask with a magnetic stirring bead was stirred at 55 °C until the starting material was consumed. Then, the mixture was filtered and washed thrice with distilled water. After that, the solid product was dried under reduced pressure to obtain the quinoxalin-2(1*H*)-one derivative. For the alkylation of quinoxalin-2(1*H*)-ones, a solution of quinoxalin-2(1*H*)-ones (1.0 mmol, 1.0 equiv.) and potassium carbonate (1.2 equiv.) in DMSO (0.25 M) was added to a 50 mL round-bottomed flask followed by the addition of the corresponding alkyl halides (1.6 equiv.). The resultant solution was stirred overnight at room temperature. After completion, the reaction mixture was extracted with saturated brine solution and EtOAc (three times). Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The purification of resultant residues was achieved by column chromatography to get the desired *N*-alkylation of quinoxalin-2(1*H*)-ones.

2.2. General procedure for the synthesis of 2-(2-oxo-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-1(2*H*)-yl)ethyl (*S*)-2-(4-isobutylphenyl)propanoate

First, 1-(2-hydroxyethyl)quinoxalin-2(1*H*)-one was synthesized according to the procedures mentioned above. In a 100 mL round bottom flask, a solution of 1-(2-hydroxyethyl)quinoxalin-2(1*H*)-one (1.0 equiv.), (*S*)-Ibuprofen (1.1 equiv.), and DMAP (10 mol%) in dry DCM (0.33 M) was cooled to 0 °C. Subsequently, DCC (1.5 equiv.) was mixed with the cooled reaction mixture. After that, ice bath was removed and allowed for stirring overnight. The reaction mixture was quenched with HCl (1M). Then, the reaction mixture was washed with $NaHCO_3$ and extracted with EtOAc three times. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The purification of resultant residues was achieved by column chromatography to get the desired *N*-alkylated quinoxalin-2(1*H*)-ones.

2.3. General procedure for the synthesis of aryl disufides derivatives

The aryl disulfides were synthesized according to previously reported literature.[2] A solution of aryl thiols (10 mmol) and potassium carbonate (0.25 mmol) in acetonitrile (25 mL) in a 50 mL round bottom flask with a magnetic stirring bead was stirred at room temperature until the starting material was consumed. After completion, the reaction mixture was extracted with saturated brine

solution and EtOAc three times. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The purification of resultant residues was achieved by column chromatography to get the desired aryl disulfides.

2.3. General procedure for the synthesis of 1,2-di(pyridin-2-yl)disulfane derivatives

The 1,2-di(pyridin-2-yl)disulfane were synthesized according to previously reported literature.[3] In a solution of aryl thiols (4.5 mmol) in dichloromethane (10 mL) in a 50 mL round bottom flask with a magnetic stirring bead added potassium permanganate (14 mmol) slowly and then stirred at room temperature until the starting material was consumed. After completion, the reaction mixture was extracted with saturated brine solution and EtOAc three times. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The purification of resultant residues was achieved by column chromatography to get the desired aryl disulfide.

3. Reaction Set-up:

The light setup for the photochemical reaction is shown in Figure S-01. The photochemical reactions were carried out under blue light irradiation using a light set-up (Kessil® PR160-456 nm lamp with a fan kit) with 100% intensity connected with a compact fan for maintaining ambient temperature. The approximate distance between the glass vial and the Kessel LED was measured to be 4 cm.

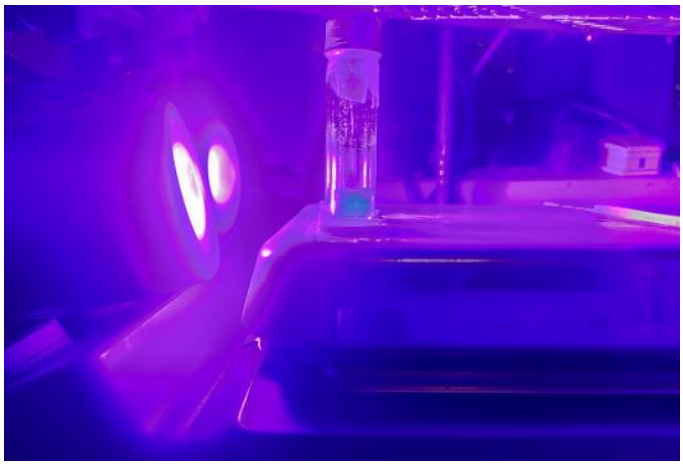
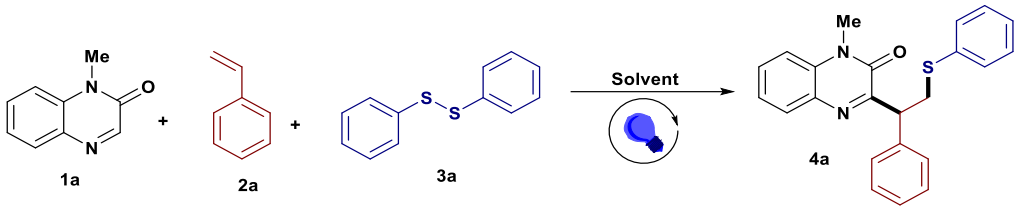


Figure S-01: Kessel light set-up.

4. General procedure for photochemical thioalkylation:

In a 7 mL glass vial having a septum cap with a magnetic stirring bead, quinoxalin-2(*1H*)-one (0.2 mmol), aryl disulfide (0.4 mmol), and styrene derivatives (0.24 mmol) were added and, then 0.8 mL of ethyl acetate solvent was added. The reaction mixtures were irradiated with a Kessil® PR160-456 nm lamp with a cooling fan at a distance of 4 cm and stirred for 24 hours under an argon atmosphere. After the completion, the reaction mixture was quenched and extracted with EtOAc. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The resultant residue was purified by column chromatography using hexane/EtOAc to achieve the desired thioalkylated quinoxalin-2(*1H*)-ones.

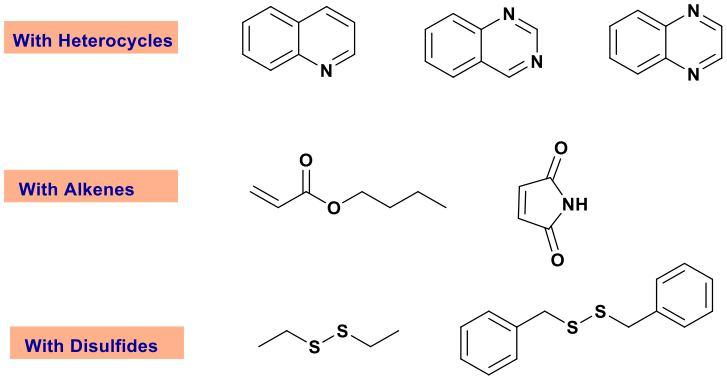
5. Optimization studies for the photochemical thioalkylation:



Entry	Solvent	equiv. (**1a**:**2a**:**3a**)	Yield (%)[b]
1	MeCN	1:2:4	42
2	EtOAc	1:2:4	60
3	THF	1:2:4	63
4	Isopropanol	1:2:4	34
5	DCE	1:2:4	17
6	1,4-Dioxane	1:2:4	42
7	DMSO	1:2:4	n.r.
8	EtOAc	1:2:2	65
9[a]	**EtOAc**	**1:1.2:2**	**76**
10[c]	EtOAc	1:1.2:2	n.r.
11[d]	EtOAc	1:1.2:2	trace
12	EtOAc	1:1.2:1.5	63
13[e]	EtOAc	1:1.2:2	71
14[f]	EtOAc	1:1.2:2	54
15[g]	EtOAc	1:1.2:2	n.r.

[a]Reaction conditions: Unless otherwise specified, quinoxaline-2(1*H*)-one (**1a**) (0.2 mmol), **2a** (0.24 mmol), **3a** (0.4 mmol) in 0.8 mL solvent irradiated with blue LED (456 nm) for 24 h under argon atmosphere. [b]yields determined by HPLC. [c]Under dark conditions. [d]Under aerobic conditions. [e]Irradiation with 440 nm LED. [f]Irradiation with 440 nm LED. [g]Irradiation with 526 nm.

6. Unsuccessful Reactions:



7. Reaction setup and procedure for scale-up reaction:

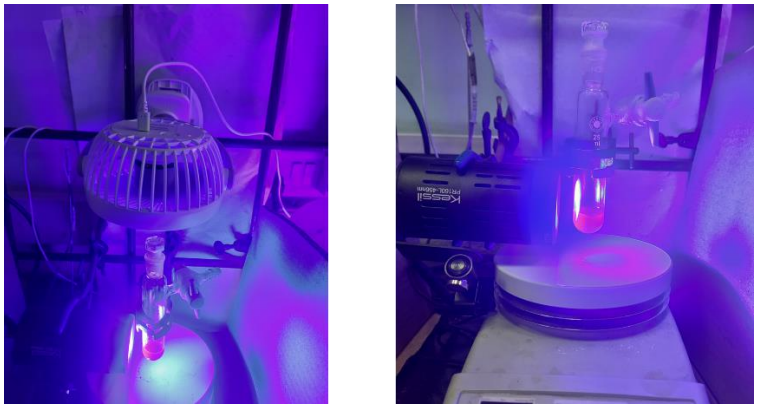


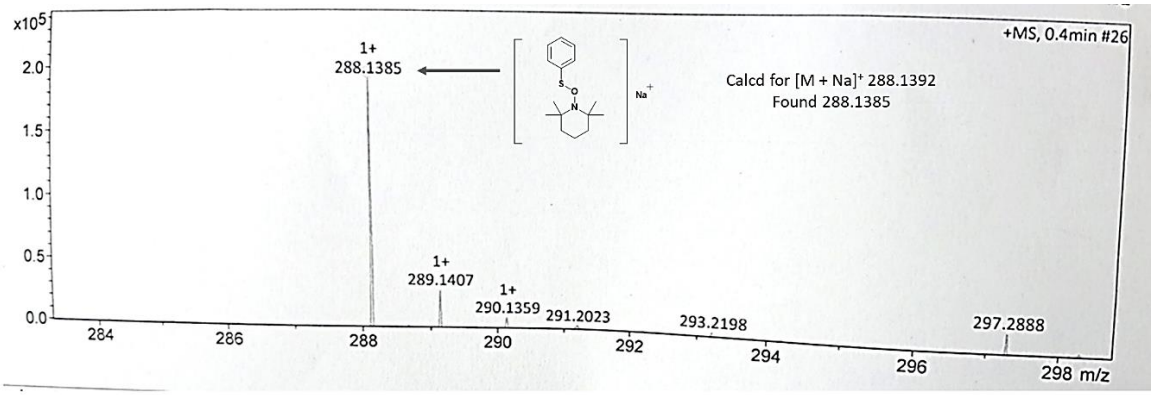
Figure S-02: Kessil lamp setup with equipped fan for scale-up reaction.

7.1. Scaled up synthesis for 4a

In a 25 mL Schlenk tube having a glass cap with a magnetic stirring bead, quinoxalin-2(*1H*)-one (2 mmol), aryl disulfide (4 mmol), and styrene derivatives (2.4 mmol) were added and, then 6 mL of ethyl acetate solvent was added. The reaction mixtures were irradiated with a Kessil® PR160-456 nm lamp (Figure S-02) with a cooling fan at a distance of 2 cm and stirred for 36 hours under an argon atmosphere. After the completion, the reaction mixture was quenched and extracted with EtOAc. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The resultant residue was purified by column chromatography using hexane/EtOAc to achieve the desired thioalkylated quinoxalin-2(*1H*)-ones (67% yield, 0.49g).

8. Radical inhibition experiments

In a 7 mL glass vial having a septum cap with a magnetic stirring bead, quinoxalin-2(*1H*)-one (0.2 mmol), aryl disulfide (0.4 mmol), styrene derivatives (0.24 mmol), and TEMPO (0.4 mmol) were added and, then 0.8 mL of ethyl acetate solvent was added. The reaction mixtures were irradiated with a Kessil® PR160-456 nm lamp with a cooling fan at a distance of 4 cm and stirred for 24 hours under an argon atmosphere. After completion of the reaction, an aliquot portion of the reaction mixture was subjected to HRMS (Figure S-03). We were able to detect thiyl adduct with TEMPO. The HRMS data of TEMPO-adduct of phenyl disulfide was given below (Figure S-03).



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
288.138507	1	C15H23NNaOS	288.139256	2.6	1758.7	4.5	ok	even	14.9	38.2	n.a.	n.a.	n.a.	n.a.

Figure S-03: HRMS data of TEMPO adduct of thiyl radical

9. Cross-over experiments

In a 7 mL glass vial having a septum cap with a magnetic stirring bead, *p*-methoxy phenyl disulfide (0.2 mmol) and phenyl disulphide (0.2 mmol) were added and, then 0.4 mL of ethyl acetate solvent was added. The reaction mixtures were irradiated with a Kessil® PR160-456 nm lamp with a cooling fan at a distance of 4 cm and stirred for 24 hours under an argon atmosphere. After that, an aliquot portion (10 µL) was taken from the reaction mixture and diluted up to 1 mL with EtOAc.

From this solution, 1 µL was injected and analysed in GC-MS. The corresponding data is shown in Figure S04. It was observed that 3a:3s:3l was obtained in the ratio of 1:1.7:2.

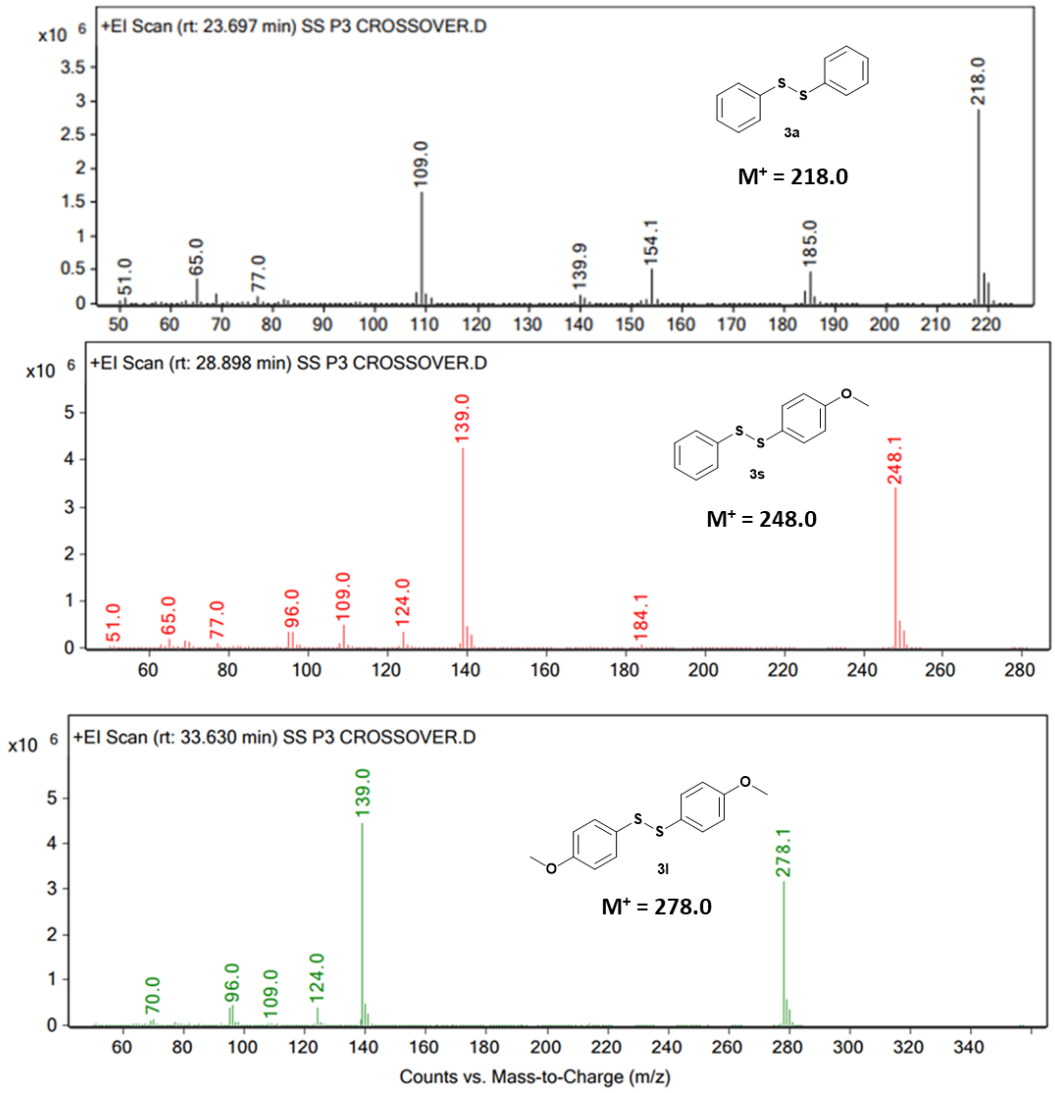


Figure S-04: GCMS data of cross-over experiment

10. Switch on/off experiment

In six 7 mL glass vial having a septum cap with a magnetic stirring bead, quinoxalin-2(*1H*)-one (0.2 mmol), aryl disulfide (0.4 mmol), and styrene derivatives (0.24 mmol) were added and, then 0.8 mL of ethyl acetate solvent was added. The reaction mixtures were irradiated with a Kessil® PR160-456 nm lamp with a cooling fan at a distance of 4 cm and stirred for 4 hours under an argon atmosphere. After the completion, the reaction mixture was quenched and extracted with EtOAc. Then, the crude ^{1}H NMR of resultant residue was taken using the trichloroethylene as an internal

standard to obtain the yield of thioalkylated product. Thereafter, for a fresh batch of reaction at first light was irradiated for 4 hours and then the light source was switched off with continuous stirring for next 4 hours. After that, the crude ^{1}H NMR of resultant residue was taken using the trichloroethylene as an internal standard to obtain the yield of thioalkylated product. This cycle was repeated three times and the yield of **4a** with respect to time was plotted as shown in the adjoining figure (Figure S-05).

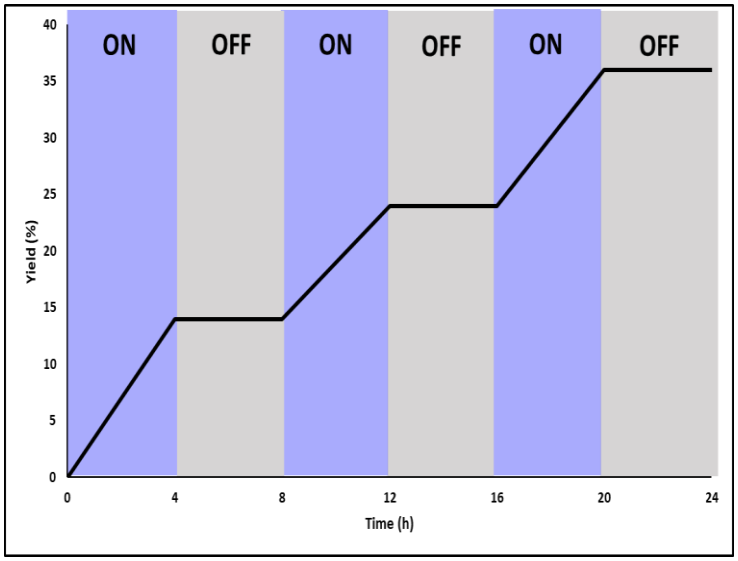


Figure S-05: Switch on/off experiment

11. UV-Vis absorption studies

The UV-Vis measurements were performed using a UV-Vis spectrophotometer (SHIMADZU-UV-1900i) using a quartz cuvette equipped with a Teflon® septum (1 cm path length). The UV-Vis spectra were collected in the 300-500 nm range. The absorption spectra of N-methyl quinoxalin-2(1*H*)-one (3.3 mM), phenyl disulfide (3.3 mM), and styrene (3.3 mM) were recorded in EtOAc as shown in figure S-06. The absorption spectra of N-methyl quinoxalin-2(1*H*)-one (3.3 mM), quinoline (3.3 mM), and quinazoline (3.3 mM) were also collected in EtOAc, as shown in figure S-07. *Dotted blue trace represent the emission window of the used high power LED light*.

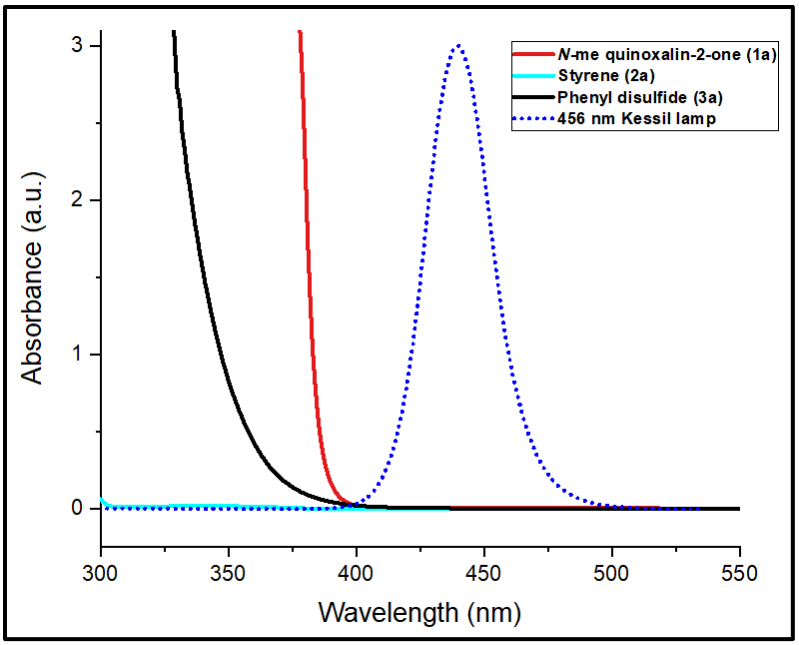


Figure S-06: UV-Vis spectra of solution of *N*-methyl quinoxalin-2(1*H*)-one (3.3 mM), phenyl disulfide (3.3 mM), and styrene (3.3 mM)

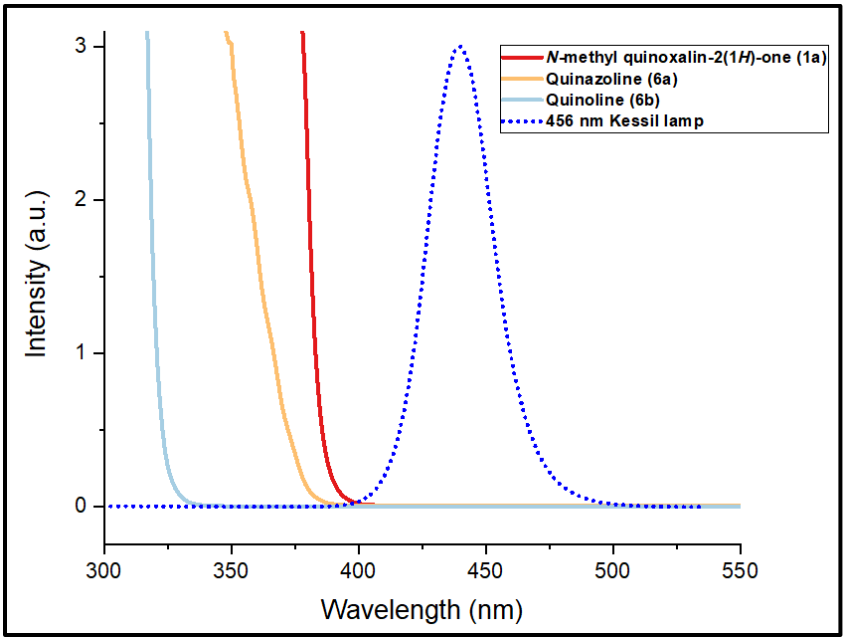
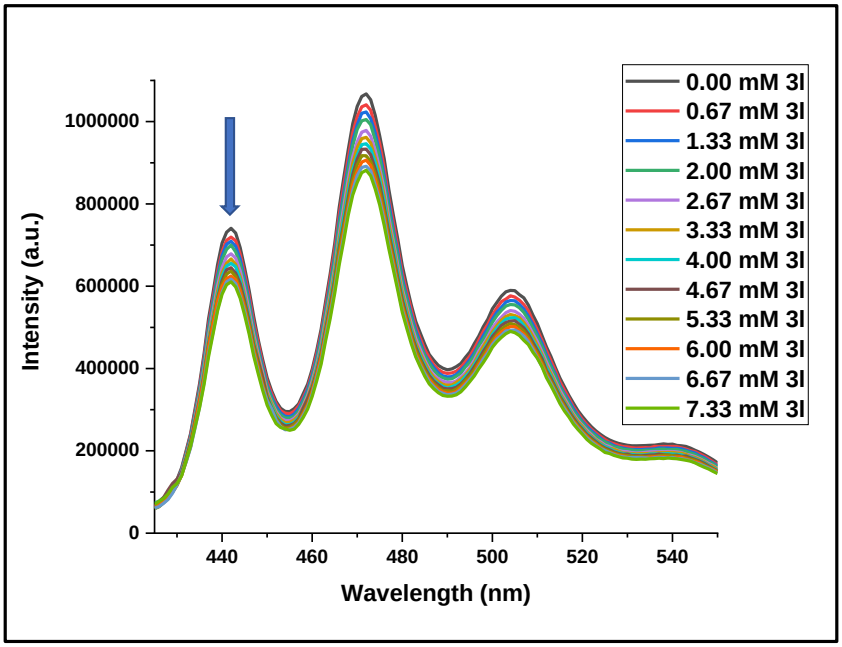


Figure S-07: UV-Vis spectra of solution of *N*-methyl quinoxalin-2(1*H*)-one (3.3 mM), quinazoline (3.3 mM), and quinoline (3.3 mM).

12. Fluorescence Quenching Experiment and Stern-Volmer Studies:

Fluorescence quenching experiment were carried out on a model FLS920 (Edinburgh Instruments) spectrofluorometer using a quartz cuvette with 1 cm path length equipped with a Teflon® septum. A 0.02 M solution of *N*-methyl quinoxalin-2(1*H*)-one in EtOAc was prepared and taken in a 3 mL fluorescence cuvette. For collection of data, the excitation and emission slit widths were fixed at 3 and 6 nm, respectively. Fluorescence emission spectra of *N*-methyl quinoxalin-2(1*H*)-one were recorded from 425 nm to 550 nm with an excitation wavelength of 415 nm. λ_{max}(emission) of *N*-methyl quinoxalin-2(1*H*)-one was observed at 442 nm. For each fluorescence quenching experiment, a 10 µL of 0.2 M solution of the *p*-methoxy phenyl disulphide and styrene (prepared in EtOAc) was added individually to *N*-methyl quinoxalin-2(1*H*)-one solution (0.02 M) taken in a fluorescence cuvette, and emission spectra were recorded after each sequential addition. Figure S08a shows a decrease in emission intensity after each addition of *p*-methoxy phenyl disulphide (0.2 M) and respective Stern-Volmer plot are shown in Figure S08b.



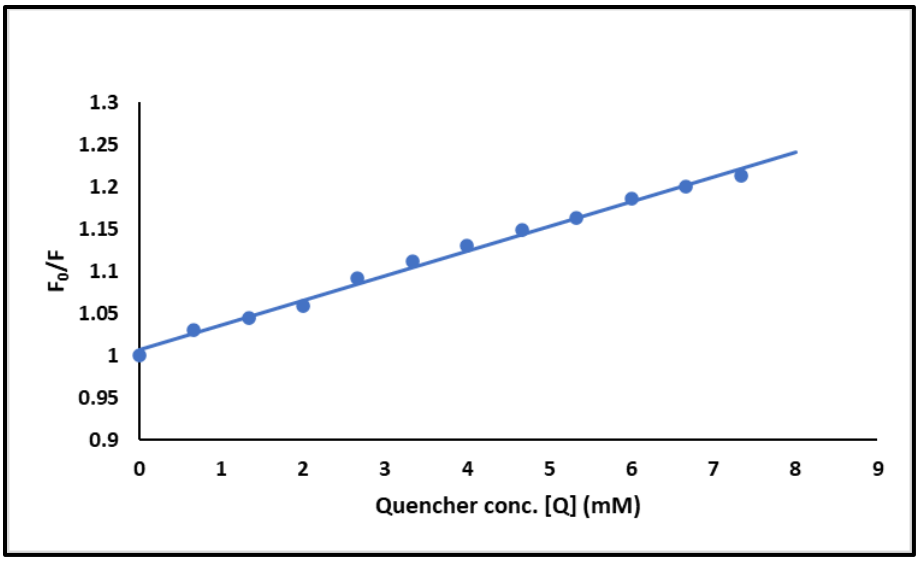
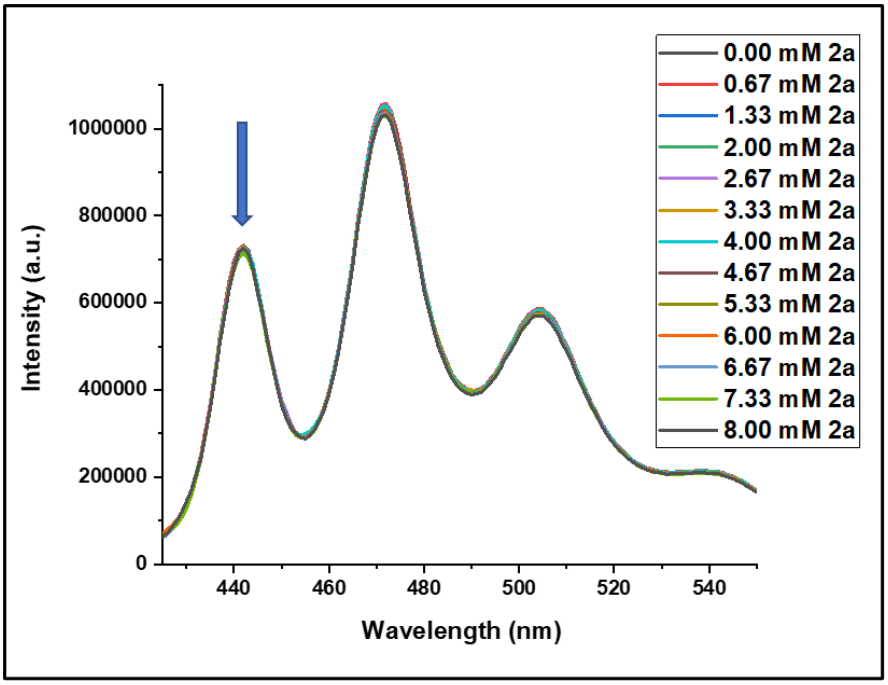


Figure S-08: (a) Fluorescence quenching spectra **(b)** Stern-Volmer plot of solution of *N*-methyl quinoxalin-2(1*H*)-one (0.02 M) in EtOAc with *p*-methoxy phenyl disulphide (0.2 M) as the quencher.

In a similar fashion fluorescence quenching experiment of *N*-methyl quinoxalin-2(1*H*)-one solution (0.02 M) was performed with styrene (0.2 M). The collective emission spectra and the Stern Volmer plot shown in Figure S09a-b.



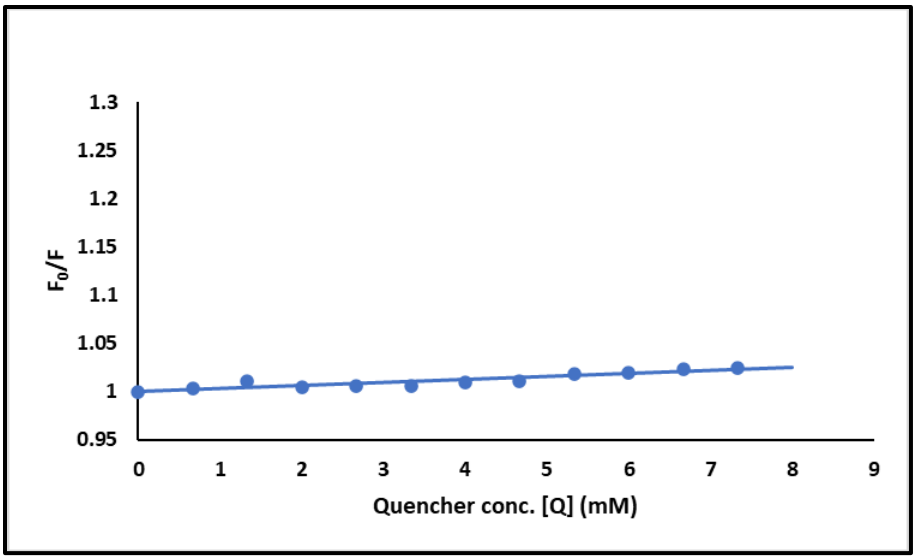


Figure S-09: (a) Fluorescence quenching spectra **(b)** Stern-Volmer plot of solution of *N*-methyl quinoxalin-2(1*H*)-one (0.02 M) in EtOAc with styrene (0.2 M) as the quencher.

Combined Stern-Volmer plot of solution of *N*-methyl quinoxalin-2(1*H*)-one (0.02 M) in EtOAc with phenyl disulfide (Blue line) and styrene (Orange line) suggest

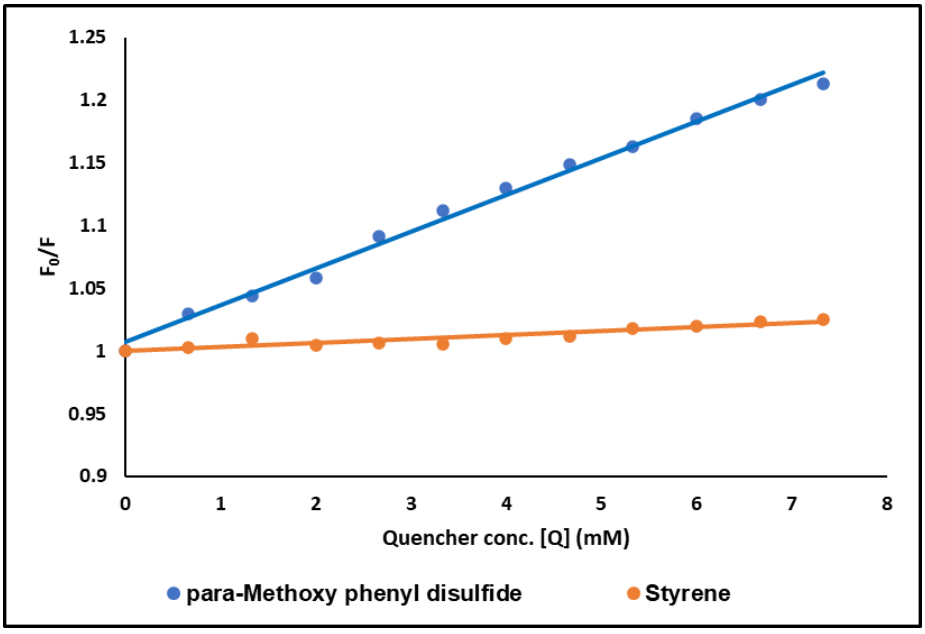


Figure S-10: Combined Stern-Volmer plot of solution of *N*-methyl quinoxalin-2(1*H*)-one (0.02 M) in EtOAc with phenyl disulfide (Blue line) and styrene (Orange line) as the quencher.

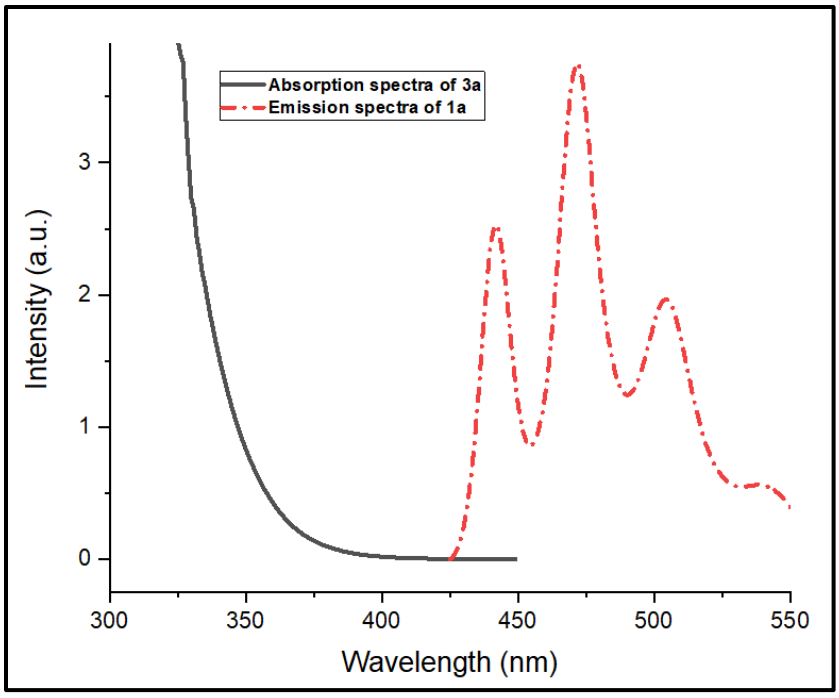


Figure S-11: Absorption plot of phenyl disulfide (Black line) and emission plot of *N*-methyl quinoxalin-2(1*H*)-one (Red dash dot line).

We thank Prof. Pramit K Chowdhury, IIT Delhi, for providing access to Fluorimeter to perform the fluorescence quenching experiments.

13. Characterization data of the synthesized compounds:

1-Methyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (4a): yield 76% (56.6 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54-7.50 (m, 1H), 7.42 (d, J = 7.4 Hz, 2H), 7.37-7.34 (m, 3H), 7.29-7.19 (m, 6H), 7.16-7.13 (m, 1H), 4.97 (dd, *J* = 9.3, 5.9 Hz, 1H), 4.05 (dd, *J* = 13.2, 9.3 Hz, 1H), 3.59 (s, 3H), 3.49 (dd, *J* = 13.2, 5.9 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.4, 154.4, 140.0, 135.1, 133.2, 132.6, 132.3, 131.5, 130.3, 130.3, 129.1, 128.7, 128.6, 127.4, 123.7, 113.7, 47.8, 38.2, 29.25. **HRMS-ESI:** calcd for $C_{23}H_{20}N_2NaOS$ $[M+Na]^+$ 395.1189, found 395.1182. **m.p:** 142 °C

1-Methyl-3-(2-(phenylthio)-1-(m-tolyl)ethyl)quinoxalin-2(1*H*)-one (4b): yield 64% (49.5 mg); Yellow liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.36-7.33 (m, 3H), 7.25-7.22 (m, 5H), 7.18-7.12 (m, 2H), 7.01 (d, J = 7.4 Hz, 1H), 4.94 (dd, *J* = 9.3, 5.8 Hz, 1H), 4.04 (dd, J = 13.1, 9.4 Hz, 1H), 3.58 (s, 3H), 3.47 (dd, *J* = 13.2, 5.7 Hz, 1H), 2.29 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 154.4, 140.1, 138.2, 136.7, 133.2, 132.7, 130.4, 130.1, 129.8, 129.2, 128.9, 128.5, 128.2, 126.1, 125.6, 123.6, 113.6, 47.7, 37.9, 29.2, 21.6. **HRMS-ESI:** calcd for $C_{24}H_{22}N_2NaOS$ $[M+Na]^+$ 409.1345, found 409.1351.

3-(1-(4-Methoxyphenyl)-2-(phenylthio)ethyl)-1-methylquinoxalin-2(1*H*)-one (4c): yield 72% (57.9 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.36-7.34 (m, 5H), 7.25-7.23 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.91 (dd, *J* = 8.9, 6.3 Hz, 1H), 4.01 (dd, *J* = 13.1, 9.1 Hz, 1H), 3.74 (s, 3H), 3.60 (s, 3H), 3.48 (dd, *J* = 13.1, 6.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 158.9, 154.4, 136.7, 133.2, 132.7, 132.2, 130.3, 130.1, 129.8, 129.6, 129.0, 126.1, 123.6, 114.1, 113.7, 55.3, 46.8, 37.9, 29.2. **HRMS-ESI:** calcd for $C_{24}H_{22}N_2NaO_2S$ $[M+Na]^+$ 425.1294, found 425.1287. **m.p:** 148 °C

3-(1-(4-Fluorophenyl)-2-(phenylthio)ethyl)-1-methylquinoxalin-2(1*H*)-one (4d): yield 58% (45.3 mg); Yellow liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56-7.52 (m, 1H), 7.40-7.34 (m, 5H), 7.27-7.23 (m, 3H), 7.17-7.14 (m, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 4.94 (dd, *J* = 8.7, 6.5 Hz, 1H), 4.00 (dd, *J* = 13.2, 8.8 Hz, 1H), 3.61 (s, 3H), 3.48 (dd, *J* = 13.2, 6.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2, 159.5, 154.4, 136.4, 135.9 (d, *J* = 3.1 Hz), 133.3, 132.7, 130.4, 130.2, 130.2 (d, *J* = 15.3 Hz), 130.1, 129.0, 126.3, 123.8,

115.4, 114.7 (d, *J* = 234.4 Hz), 47.0, 38.1, 29.3. **HRMS-ESI:** calcd for $C_{23}H_{19}FN_2NaOS$ $[M+Na]^+$ 413.1094, found 413.1093.

3-(1-(2-Chlorophenyl)-2-(phenylthio)ethyl)-1-methylquinoxalin-2(1*H*)-one (4e): yield 46% (37.4 mg); Yellow liquid, Hexane/EtOAc = 97/3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.58-7.55 (m, 1H), 7.42-7.37 (m, 4H), 7.32-7.29 (m, 1H), 7.26-7.22 (m, 3H), 7.17-7.08 (m, 3H), 5.56 – 5.48 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.94 (dd, *J* = 13.3, 9.6 Hz, 1H), 3.63 (s, 3H), 3.39 (dd, *J* = 13.3, 5.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0, 154.4, 138.0, 136.7, 134.9, 133.4, 132.6, 130.5, 130.4, 130.2, 129.7, 128.9, 128.6, 128.4, 126.9, 126.3, 123.8, 113.8, 44.3, 37.7, 29.3. **HRMS-ESI:** calcd for $C_{23}H_{19}ClN_2NaOS$ $[M+Na]^+$ 429.0799, found 429.0799.

3-(1-(3-Chlorophenyl)-2-(phenylthio)ethyl)-1-methylquinoxalin-2(1*H*)-one (4f): yield 56% (45.6 mg); Yellow liquid, Hexane/EtOAc = 97/3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.56-7.53 (m, 1H), 7.38-7.31 (m, 5H), 7.27-7.14 (m, 6H), 4.93 (dd, *J* = 9.0, 6.2 Hz, 1H), 3.99 (dd, *J* = 13.1, 9.0 Hz, 1H), 3.61 (s, 3H), 3.47 (dd, *J* = 13.2, 6.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0, 154.4, 142.2, 136.3, 134.4, 133.3, 132.6, 130.5, 130.4, 130.2, 129.9, 129.0, 128.5, 127.6, 127.2, 126.4, 123.8, 113.7, 47.4, 38.0, 29.3. **HRMS-ESI:** calcd for $C_{23}H_{19}ClN_2NaOS$ $[M+Na]^+$ 429.0788, found 429.0799.

3-(1-(4-Chlorophenyl)-2-(phenylthio)ethyl)-1-methylquinoxalin-2(1*H*)-one (4g): yield 65% (52.9 mg); Yellow solid, Hexane/EtOAc = 97/3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.56-7.52 (m, 1H), 7.38-7.33 (m, 5H), 7.27-7.22 (m, 5H), 7.17-7.15 (m, 1H), 4.92 (dd, *J* = 8.6, 6.6 Hz, 1H), 3.99 (dd, *J* = 13.3, 8.7 Hz, 1H), 3.60 (s, 3H), 3.47 (dd, *J* = 13.3, 6.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.2, 154.4, 138.6, 136.3, 133.2, 133.2, 132.6, 130.4, 130.4, 130.1, 130.0, 129.0, 128.8, 126.4, 123.8, 113.7, 47.1, 37.9, 29.3. **HRMS-ESI:** calcd for $C_{23}H_{19}ClN_2NaOS$ $[M+Na]^+$ 429.0798, found 429.0799. **m.p:** 128 °C

3-(1-(4-Bromophenyl)-2-(phenylthio)ethyl)-1-methylquinoxalin-2(1*H*)-one (4h): yield 63% (56.9 mg); Yellow solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.39-7.37 (m, 3H), 7.35-7.33 (m, 2H), 7.30-7.23 (m, 5H), 7.17-7.14 (m, 1H), 4.90 (dd, *J* = 8.2, 6.9 Hz, 1H), 3.98 (dd, *J* = 13.2, 8.7 Hz, 1H), 3.60 (s, 3H), 3.47 (dd, *J* = 13.3, 6.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.1, 154.4, 139.1, 136.3, 133.2, 132.6, 131.8, 130.4, 130.4, 130.1, 129.0, 126.4, 123.8, 121.4, 113.8, 47.2, 37.8, 29.3. **HRMS-ESI:** calcd for $C_{23}H_{19}BrN_2NaOS$ $[M+Na]^+$ 473.0294, found 473.0271. **m.p:** 120 °C

4-(1-(4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-(phenylthio)ethyl)phenyl acetate (4i): yield 65% (56.0 mg); Colourless liquid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56-7.52 (m, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.36 (dd, *J* = 9.2, 7.8 Hz, 3H), 7.28-7.22 (m, 3H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 4.99 (dd, *J* = 9.4, 5.8 Hz, 1H), 4.04 (dd, *J* = 13.2, 9.4 Hz, 1H), 3.61 (s, 3H), 3.48 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 159.4, 154.5, 149.9, 137.7, 136.5, 133.3, 132.7, 130.4, 130.3, 130.1, 129.7, 129.0, 126.3, 123.7, 121.7, 113.7, 47.1, 37.9, 29.3, 21.3. **HRMS-ESI:** calcd for $C_{25}H_{22}N_2NaO_3S$ $[M+Na]^+$ 453.1243, found 453.1249.

3-(1-(4-Methoxyphenyl)-2-(p-tolylthio)ethyl)-1-methylquinoxalin-2(1*H*)-one (4j): yield 72% (60.0 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91-7.89 (m, 1H), 7.52 (dd, *J* = 11.3, 4.3 Hz, 1H), 7.37-7.32 (m, 3H), 7.25 (t, *J* = 9.4 Hz, 3H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.81 (dd, *J* = 8.6, 4.4 Hz, 2H), 4.90 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.98 (dd, *J* = 13.1, 9.1 Hz, 1H), 3.74 (d, *J* = 2.1 Hz, 3H), 3.60 (s, 3H), 3.42 (dd, *J* = 13.2, 6.1 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 158.8, 154.5, 136.4, 133.3, 132.8, 130.9, 130.3, 130.0, 129.8, 129.7, 126.5, 126.0, 123.6, 114.1, 113.6, 55.3, 47.0, 38.8, 29.2, 21.1. **HRMS-ESI:** calcd for $C_{25}H_{24}N_2NaO_2S$ $[M+Na]^+$ 439.1451, found 439.1444. **m.p:** 145 °C

1-Methyl-3-(1-phenyl-2-(p-tolylthio)ethyl)quinoxalin-2(1*H*)-one (4k): yield 78% (60.3 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.44-7.40 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.28-7.22 (m, 5H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 4.95 (dd, *J* = 9.2, 5.9 Hz, 1H), 4.02 (dd, *J* = 13.1, 9.3 Hz, 1H), 3.60 (s, 3H), 3.43 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 154.5, 140.3, 136.5, 133.3, 132.7, 131.0, 130.4, 130.2, 130.1, 129.8, 128.7, 128.6, 127.3, 123.6, 113.6, 47.8, 38.8, 29.2, 21.1. **HRMS-ESI:** calcd for $C_{24}H_{22}N_2NaOS$ $[M+Na]^+$ 409.1345, found 409.1356. **m.p:** 136 °C

3-(2-((4-Methoxyphenyl)thio)-1-phenylethyl)-1-methylquinoxalin-2(1*H*)-one (4l): yield 80% (64.4 mg); Yellow solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.53-7.50 (m, 1H), 7.41-7.38 (m, 2H), 7.36-7.33 (m, 2H), 7.27-7.23 (m, 3H), 7.20-7.17 (m, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.94 (dd, *J* = 9.4, 5.7 Hz, 1H), 3.99 (dd, *J* = 13.2, 9.4 Hz, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 3.35 (dd, *J* = 13.2, 5.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 159.1, 154.5, 140.4, 134.1, 133.2, 132.7, 130.3, 130.1, 128.6, 128.6, 127.2, 126.5, 123.6,

114.6, 113.6, 55.4, 47.9, 40.2, 29.2. **HRMS-ESI:** calcd for $C_{24}H_{22}N_2NaO_2S$ $[M+Na]^+$ 425.1294, found 425.1279. **m.p:** 140 °C

1-Methyl-3-(1-phenyl-2-(o-tolylthio)ethyl)quinoxalin-2(1*H*)-one (4m): yield 63% (48.7 mg); Yellow liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 17.1, 7.9 Hz, 2H), 7.29-7.24 (m, 3H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.09 (ddd, *J* = 23.8, 14.7, 7.3 Hz, 3H), 4.98 (dd, *J* = 9.2, 5.8 Hz, 1H), 4.06 (dd, *J* = 12.9, 9.3 Hz, 1H), 3.60 (s, 3H), 3.43 (dd, *J* = 12.9, 5.7 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 154.5, 140.3, 138.4, 135.8, 133.3, 132.7, 130.4, 130.2, 130.1, 129.4, 128.7, 128.6, 127.3, 126.5, 126.1, 123.6, 113.7, 47.8, 37.3, 29.2, 20.6. **HRMS-ESI:** calcd for $C_{24}H_{22}N_2NaOS$ $[M+Na]^+$ 409.1345, found 409.1350.

3-(2-((3-Methoxyphenyl)thio)-1-phenylethyl)-1-methylquinoxalin-2(1*H*)-one (4n): yield 62% (49.9 mg); Yellow liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 13.1, 5.1 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.89 (s, 1H), 6.68 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.98 (dd, *J* = 9.2, 5.9 Hz, 1H), 4.06 (dd, *J* = 13.1, 9.3 Hz, 1H), 3.76 (s, 3H), 3.61 (d, *J* = 9.4 Hz, 3H), 3.49 (dd, *J* = 13.2, 5.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 159.6, 154.5, 140.2, 138.0, 133.3, 132.7, 130.4, 130.2, 129.8, 128.7, 128.6, 127.4, 123.7, 122.0, 115.1, 113.7, 112.1, 55.4, 47.8, 37.8, 29.2. **HRMS-ESI:** calcd for $C_{24}H_{22}N_2NaO_2S$ $[M+Na]^+$ 425.1294, found 425.1310.

3-(2-((4-Chlorophenyl)thio)-1-(4-methoxyphenyl)ethyl)-1-methylquinoxalin-2(1*H*)-one (4o): yield 48% (41.9 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 17.3, 8.0 Hz, 3H), 7.26 (d, *J* = 7.8 Hz, 3H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.89 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.99 (dd, *J* = 13.0, 9.2 Hz, 1H), 3.74 (s, 3H), 3.60 (s, 3H), 3.45 (dd, *J* = 13.2, 6.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 158.9, 154.4, 135.2, 133.2, 132.6, 132.2, 131.9, 131.4, 130.3, 130.2, 129.6, 129.0, 123.7, 114.1, 113.7, 55.3, 46.9, 38.3, 29.2. **HRMS-ESI:** calcd for $C_{24}H_{21}ClN_2NaO_2S$ $[M+Na]^+$ 459.0904, found 459.0904. **m.p:** 124 °C

1-Methyl-3-(2-(naphthalen-2-ylthio)-1-phenylethyl)quinoxalin-2(1*H*)-one (4p): yield 52% (43.9 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.77 (s, 1H), 7.73-7.64 (m, 3H), 7.52-7.39 (m, 6H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (dd, *J* = 17.8, 7.8 Hz, 2H), 5.03 (dd, *J* = 9.3, 5.6 Hz, 1H), 4.19 (dd, *J* = 13.2, 9.5

Hz, 1H), 3.57 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.52 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.4, 140.3, 134.0, 133.8, 133.2, 131.9, 130.3, 130.2, 128.7, 128.6, 128.4, 128.3, 128.1, 127.8, 127.4, 127.3, 126.5, 125.8, 123.6, 116.9, 113.6, 48.1, 37.9, 29.2. **HRMS-ESI:** calcd for $C_{27}H_{23}N_2OS$ $[M+H]^+$ 423.1526, found 423.1531. **m.p:** 148 °C

1-Methyl-3-(1-phenyl-2-(pyridin-2-ylthio)ethyl)quinoxalin-2(1*H*)-one (4q): yield 61% (45.6 mg); Yellow liquid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 12.1, 4.0 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.60 (dd, *J* = 18.1, 7.6 Hz, 1H), 7.54 – 7.44 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.24 (ddd, *J* = 22.2, 14.5, 7.1 Hz, 4H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.97 – 6.90 (m, 1H), 5.08 (dd, *J* = 8.8, 6.2 Hz, 1H), 4.10 (dd, *J* = 13.0, 9.5 Hz, 1H), 3.95 (dd, *J* = 13.2, 5.9 Hz, 1H), 3.58 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 159.0, 149.6, 140.5, 137.5, 135.8, 132.7, 130.4, 130.1, 128.7, 128.6, 127.2, 123.6, 122.4, 121.2, 119.8, 119.4, 113.6, 47.8, 33.5, 29.2. **HRMS-ESI:** calcd for $C_{22}H_{19}N_3NaOS$ $[M+Na]^+$ 396.1141, found 396.1147.

1-(Cyclopropylmethyl)-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5a): yield 62% (51.2 mg); Yellow liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.39-7.32 (m, 4H), 7.30-7.18 (m, 5H), 7.14 (t, *J* = 7.3 Hz, 1H), 5.00-4.96 (m, 1H), 4.14-4.02 (m, 3H), 3.52-3.48 (m, 1H), 1.29-1.28 (m, 1H), 0.54-0.40 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 154.5, 140.3, 136.7, 132.9, 132.7, 130.6, 130.0, 130.0, 129.0, 128.6, 128.6, 127.3, 126.2, 123.4, 113.9, 47.6, 46.4, 38.2, 9.7, 4.4, 4.1. **HRMS-ESI:** calcd for $C_{26}H_{24}N_2NaOS$ $[M+Na]^+$ 435.1502, found 435.1495.

1-Benzyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5b): yield 61% (54.73 mg); Yellow liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.46-7.44 (m, 2H), 7.40-7.36 (m, 3H), 7.31-7.27 (m, 3H), 7.25-7.21 (m, 5H), 7.21-7.17 (m, 2H), 7.15-7.12 (m, 3H), 5.47 (d, *J* = 15.7 Hz, 1H), 5.29 (d, *J* = 15.7 Hz, 1H), 5.04 (dd, *J* = 9.2, 6.0 Hz, 1H), 4.07 (dd, *J* = 13.1, 9.2 Hz, 1H), 3.53 (dd, *J* = 13.1, 6.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 154.6, 140.2, 136.6, 135.3, 132.9, 132.6, 130.5, 130.1, 130.0, 129.0, 128.8, 128.7, 128.6, 127.7, 127.4, 126.9, 126.2, 123.7, 114.5, 47.8, 46.1, 38.2. **HRMS-ESI:** calcd for $C_{29}H_{24}N_2NaOS$ $[M+Na]^+$ 471.1502, found 471.1491.

Ethyl 2-(2-oxo-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-1(2*H*)-yl)acetate (5c): yield 64% (56.9 mg); Yellow liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.52-7.46 (m, 1H), 7.41-7.35 (m, 5H), 7.29-7.19 (m, 5H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 5.06-4.82 (m, 3H), 4.18 (tt, *J* = 7.1, 3.5 Hz, 2H), 4.02 (dd, *J* = 13.2, 8.9 Hz,

1H), 3.52 (dd, *J* = 13.2, 6.3 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 159.5, 154.0, 140.0, 136.6, 132.8, 132.4, 130.7, 130.3, 130.0, 129.0, 128.7, 128.6, 127.4, 126.3, 124.0, 113.2, 62.1, 47.7, 43.8, 38.1, 14.2. **HRMS-ESI:** calcd for $C_{26}H_{24}N_2NaO_3S$ $[M+Na]^+$ 467.1400, found 467.1401.

Ethyl 2-(3-(1-(4-methoxyphenyl)-2-(phenylthio)ethyl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (5d): yield 70% (66.4 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.51-7.48 (m, 1H), 7.37-7.30 (m, 5H), 7.26-7.22 (m, 3H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.02-4.83 (m, 3H), 4.19 (qd, *J* = 7.1, 1.8 Hz, 2H), 3.98 (dd, *J* = 13.2, 8.7 Hz, 1H), 3.75 (s, 3H), 3.50 (dd, *J* = 13.2, 6.6 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 159.7, 158.9, 154.0, 136.7, 132.8, 132.4, 132.0, 130.7, 130.2, 130.0, 129.7, 129.0, 126.2, 124.0, 114.1, 113.2, 62.1, 55.3, 46.9, 43.8, 38.2, 14.2. **HRMS-ESI:** calcd for $C_{27}H_{26}N_2NaO_4S$ $[M+Na]^+$ 497.1505, found 497.1511. **m.p:** 128 °C

1-Allyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5e): yield 57% (45.4 mg); Yellow liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.50-7.47 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.36-7.32 (m, 3H), 7.29-7.19 (m, 6H), 7.15-7.12 (m, 1H), 5.85 (ddd, *J* = 22.4, 10.4, 5.2 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 5.12 (d, *J* = 17.3 Hz, 1H), 4.98 (dd, *J* = 9.1, 6.1 Hz, 1H), 4.87 (dd, *J* = 16.1, 5.3 Hz, 1H), 4.73 (dd, *J* = 16.1, 5.1 Hz, 1H), 4.04 (dd, *J* = 13.1, 9.2 Hz, 1H), 3.50 (dd, *J* = 13.1, 6.0 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 154.0, 140.2, 136.7, 132.9, 132.5, 130.8, 130.5, 130.1, 130.0, 129.0, 128.7, 128.6, 127.3, 126.2, 123.6, 118.3, 114.2, 47.7, 44.8, 38.2. **HRMS-ESI:** calcd for $C_{25}H_{22}N_2NaOS$ $[M+Na]^+$ 421.1345, found 421.1339.

6-Fluoro-1-methyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5f): yield 72% (56.2 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.7, 2.8 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.30-7.20 (m, 7H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.97 (dd, *J* = 9.4, 5.7 Hz, 1H), 4.03 (dd, *J* = 13.2, 9.5 Hz, 1H), 3.60 (s, 3H), 3.47 (dd, *J* = 13.2, 5.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2, 159.8, 154.1, 139.9, 136.5, 135.5, 133.2 (d, *J* = 10.8 Hz), 130.0, 129.2, 129.0, 128.7 (d, *J* = 17.2 Hz), 127.5, 126.3, 117.9 (d, *J* = 24.0 Hz), 115.8 (d, *J* = 22.6 Hz), 114.7 (d, *J* = 8.7 Hz), 47.9, 37.9, 29.5. **HRMS-ESI:** calcd for $C_{23}H_{19}FN_2NaOS$ $[M+Na]^+$ 413.1094, found 413.1109. **m.p:** 137 °C

7-Fluoro-1-methyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5g): yield 72% (56.2 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.8,

6.0 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.29-7.19 (m, 5H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.05 (td, *J* = 8.5, 2.5 Hz, 1H), 6.92 (dd, *J* = 10.0, 2.5 Hz, 1H), 4.93 (dd, *J* = 9.4, 5.8 Hz, 1H), 4.03 (dd, *J* = 13.2, 9.5 Hz, 1H), 3.53 (s, 3H), 3.47 (dd, *J* = 13.2, 5.8 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.3 (d, *J* = 250.6 Hz), 158.4, 154.3, 140.1, 136.5, 134.7 (d, *J* = 11.7 Hz), 132.2 (d, *J* = 10.2 Hz), 129.9, 129.4 (d, *J* = 2.3 Hz), 129.0, 128.7, 128.6, 127.4, 126.2, 111.4 (d, *J* = 23.4 Hz), 100.6 (d, *J* = 27.7 Hz), 47.6, 37.9, 29.5. **HRMS-ESI:** calcd for $C_{23}H_{19}FN_2NaOS$ $[M+Na]^+$ 413.1094, found 413.1109. **m.p:** 139 °C

6-bromo-1,8-dimethyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5h): yield 55% (51.2 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.34-7.32 (m, 3H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.25-7.19 (m, 4H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.95 (dd, *J* = 9.5, 5.6 Hz, 1H), 4.02 (dd, *J* = 13.2, 9.6 Hz, 1H), 3.54 (s, 3H), 3.46 (dd, *J* = 13.2, 5.6 Hz, 1H), 2.71 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.9, 154.1, 140.7, 140.0, 136.5, 134.2, 129.9, 129.0, 128.7, 128.5, 128.0, 127.4, 126.3, 123.9, 114.6, 47.8, 38.1, 29.5, 17.6. **HRMS-ESI:** calcd for $C_{24}H_{21}BrN_2NaOS$ $[M+Na]^+$ 487.0450, found 487.0451. **m.p:** 114 °C

2-(2-oxo-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-1(2*H*)-yl)ethyl (*S*)-2-(4-isobutylphenyl) propanoate (5i): yield 52% (61.4 mg); Pale yellow solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 18.7, 6.3 Hz, 3H), 7.35-7.12 (m, 9H), 7.14 (d, *J* = 6.7 Hz, 1H), 7.08-7.03 (m, 4H), 4.94 (ddd, *J* = 9.0, 6.0, 3.1 Hz, 1H), 4.46-4.23 (m, 4H), 4.03 (dd, *J* = 12.6, 9.7 Hz, 1H), 3.52-3.42 (m, 2H), 2.42 (dd, *J* = 7.0, 4.9 Hz, 2H), 1.82 (td, *J* = 13.3, 6.7 Hz, 1H), 1.36 (dd, *J* = 7.1, 4.4 Hz, 3H), 0.88 (d, *J* = 6.5, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.8, 159.4, 154.3, 140.8, 140.2, 137.4, 136.6, 132.8, 132.7, 132.6, 130.6, 130.6, 130.2, 130.0, 129.9, 129.5, 129.5, 129.0, 128.7, 128.6, 128.6, 127.4, 127.2, 127.2, 126.2, 123.7, 113.8, 113.8, 61.0, 60.9, 47.6, 45.2, 45.0, 45.0, 41.0, 38.0, 30.3, 22.5, 18.4. **HRMS-ESI:** calcd for $C_{37}H_{38}N_2NaO_3S$ $[M+Na]^+$ 613.2495, found 613.2501. **m.p:** 156 °C

3-(1-phenyl-2-(phenylthio)ethyl)-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (5j): yield 54% (55.7 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.45-7.40 (m, 3H), 7.38-7.34 (m, 2H), 7.33-7.29 (m, 3H), 7.29-7.22 (m, 5H), 7.18-7.14 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 5.50 (d, *J* = 16.1 Hz, 1H), 5.37 (d, *J* = 16.0 Hz, 1H), 5.02 (dd, *J* = 9.4, 5.9 Hz, 1H), 4.08 (dd, *J* = 13.1, 9.4 Hz, 1H), 3.53 (dd, *J* = 13.1, 5.9 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 154.5, 140.1, 139.4, 136.6, 132.9, 132.3, 130.7, 130.3, 130.0, 129.0, 128.8, 128.6, 127.5, 127.3, 126.3, 126.1 (q, *J* = 4.0 Hz), 124.0,

114.1, 47.8, 45.7, 38.1. **HRMS-ESI:** calcd for $C_{30}H_{23}F_3N_2NaOS$ $[M+Na]^+$ 539.1375, found 539.1371. **m.p:** 141 °C

4-methyl-3-oxo-2-(1-phenyl-2-(phenylthio)ethyl)-3,4-dihydroquinoxaline-6-carbonitrile (5k): yield 52% (41.3 mg); Yellow solid, Hexane/EtOAc = 92/8, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.59 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.53 (d, *J* = 1.2 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.26 (dt, *J* = 22.5, 7.6 Hz, 6H), 7.16 (d, *J* = 7.4 Hz, 1H), 4.99 (dd, *J* = 9.6, 5.5 Hz, 1H), 4.03 (dd, *J* = 13.3, 9.7 Hz, 1H), 3.59 (s, 3H), 3.46 (dd, *J* = 13.3, 5.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ δ 163.2, 153.9, 139.3, 136.2, 133.7, 131.2, 130.2, 129.0, 128.9, 128.6, 127.7, 126.6, 126.5, 118.3, 117.8, 113.2, 48.2, 37.8, 29.5. **HRMS-ESI:** calcd for $C_{24}H_{19}N_3NaOS$ $[M+Na]^+$ 420.4852, found 420.4850. **m.p:** 126 °C

7-chloro-1-methyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5l): yield 83% (67.6 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.4 Hz, 1H), 7.48 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.35-7.34 (m, 2H), 7.27 (dd, *J* = 12.4, 4.5 Hz, 3H), 7.23 (dd, *J* = 9.2, 7.7 Hz, 2H), 7.16 (dd, *J* = 11.2, 5.4 Hz, 2H), 4.97 (dd, *J* = 9.5, 5.7 Hz, 1H), 4.02 (dd, *J* = 13.2, 9.5 Hz, 1H), 3.58 (s, 3H), 3.46 (dd, *J* = 13.3, 5.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 154.2, 139.8, 136.5, 133.2, 131.9, 130.1, 130.0 129.7, 129.0, 128.8, 128.6, 128.2, 127.5, 126.3, 114.8, 47.9, 37.9, 29.4. **HRMS-ESI:** calcd for $C_{23}H_{19}ClN_2NaOS$ $[M+Na]^+$ 429.0799, found 429.0798. **m.p:** 132 °C

1,6-dimethyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5ma) and 1,7-dimethyl-3-(1-phenyl-2-(phenylthio)ethyl)quinoxalin-2(1*H*)-one (5mb): yield 61% (47.2 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.74 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.28-7.19 (m, 5H), 7.18-7.03 (m, 3H), 4.98-4.93 (m, 1H), 4.06-4.01 (m, 1H), 3.57 (s, 3H), 3.57-3.46 (m, 1H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.5, 158.3, 154.6, 154.4, 140.9, 140.4, 140.3, 136.8, 136.7, 133.5, 133.2, 132.6, 131.3, 131.1, 130.9, 130.2, 130.1, 129.8, 128.9, 128.7, 128.6, 128.6, 127.3, 127.3, 126.1, 124.9, 113.8, 113.4, 47.7, 47.6, 37.9, 29.8, 29.2, 29.2, 22.2, 20.7 **HRMS-ESI:** calcd for $C_{24}H_{22}N_2NaOS$ $[M+Na]^+$ 409.1345, found 409.1344. **m.p:** 128 °C.

1-methyl-3-(1-phenyl-2-(phenylthio)vinyl)quinoxalin-2(1*H*)-one (7): yield 60% (44.5 mg); Yellow solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.60 (td, *J* = 8.5, 1.3 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.36-7.32 (m,

7H), 7.30-7.24 (m, 2H), 7.11 (s, 1H), 3.68 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.6, 154.0, 139.2, 137.0, 136.5, 133.8, 132.8, 132.5, 130.9, 130.6, 130.5, 129.3, 128.6, 127.6, 127.5, 126.5, 123.9, 113.9, 29.4. **HRMS-ESI:** calcd for $C_{23}H_{18}N_2NaOS$ $[M+Na]^+$ 393.1032, found 393.1032. **m.p:** 95 °C

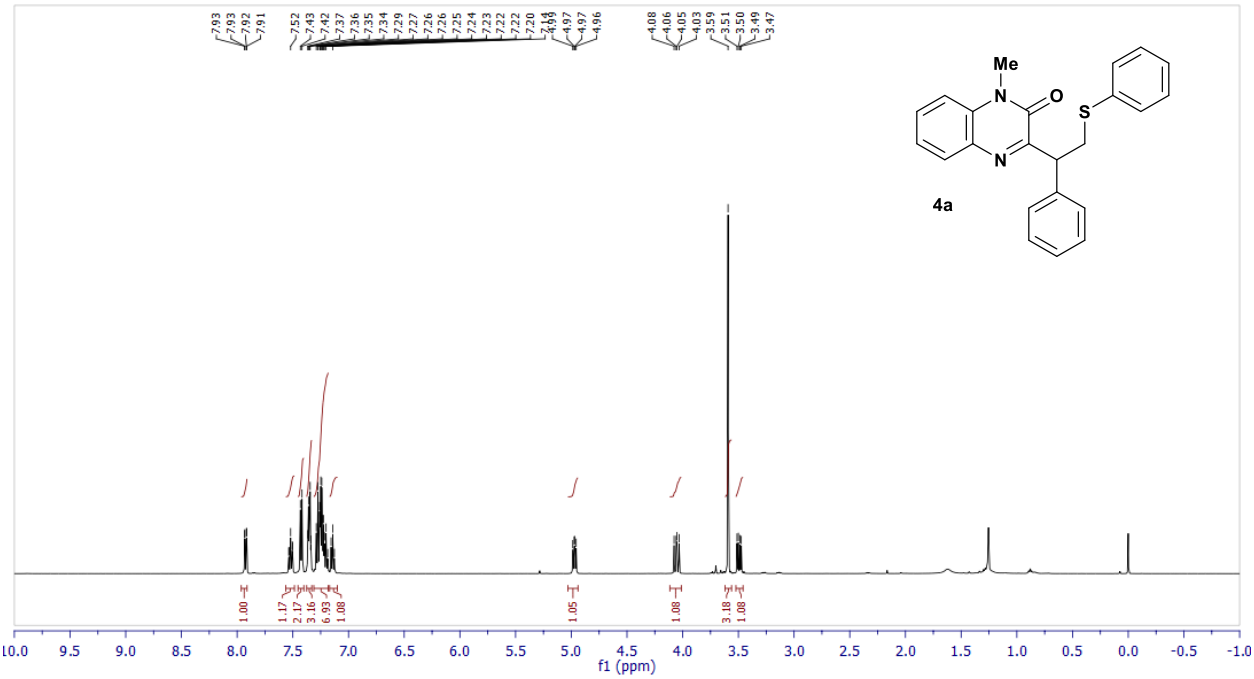
3-(benzylthio)-1-methylquinoxalin-2(1*H*)-one (11): yield 92% (52.0 mg); Colourless liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.46 (dd, *J* = 11.0, 4.3 Hz, 3H), 7.35-7.21 (m, 5H), 4.42 (s, 2H), 3.69 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.5, 153.4, 137.5, 133.5, 131.7, 129.4, 128.6, 128.5, 128.4, 127.3, 124.0, 113.9, 34.2, 29.4.

14. References

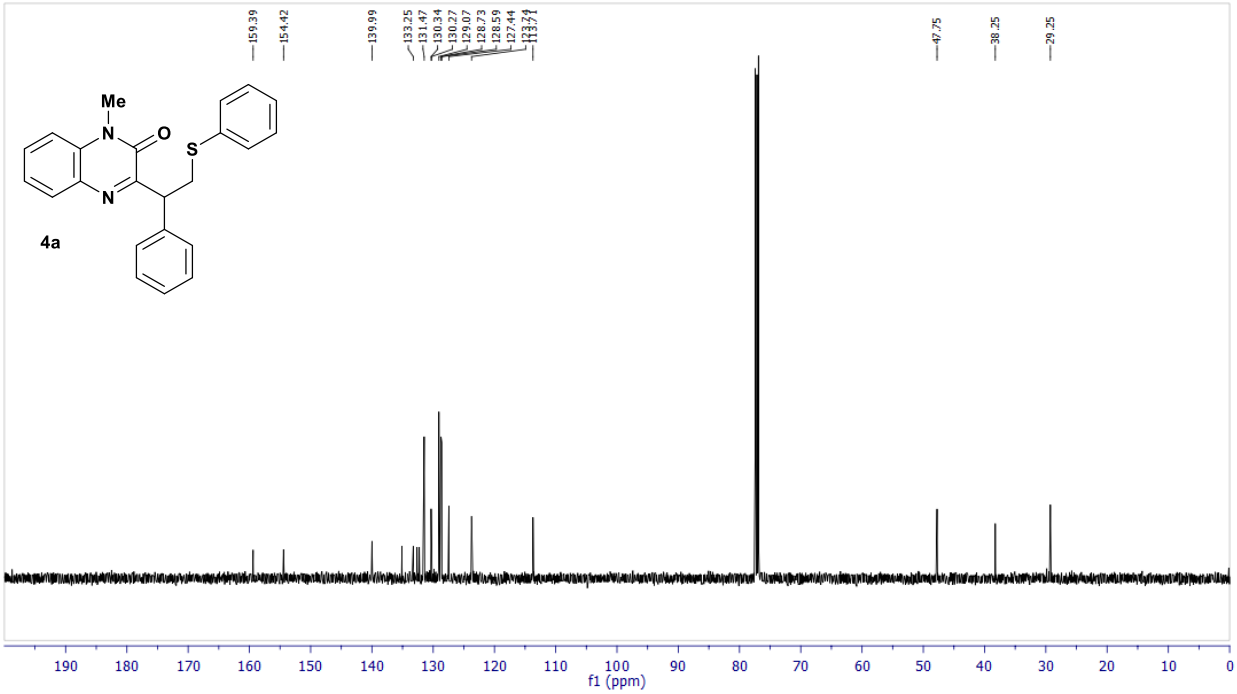
1. S. Singh, N. Dagar and S. Raha Roy, *Org. Biomol. Chem.*, 2021, **19**, 5383–5394.
2. W.-L. Dong, G.-Y. Huang, Z.-M. Li and W.-G. Zhao, *Phosphorus. Sulfur. Silicon Relat. Elem.*, 2009, **184**, 2058–2065.
3. J. Men, X. Yang, H. Zhang and J. Zhou, *Dye. Pigment.*, 2018, **153**, 206–212.

15. ^{1}H and ^{13}C NMR Spectra:

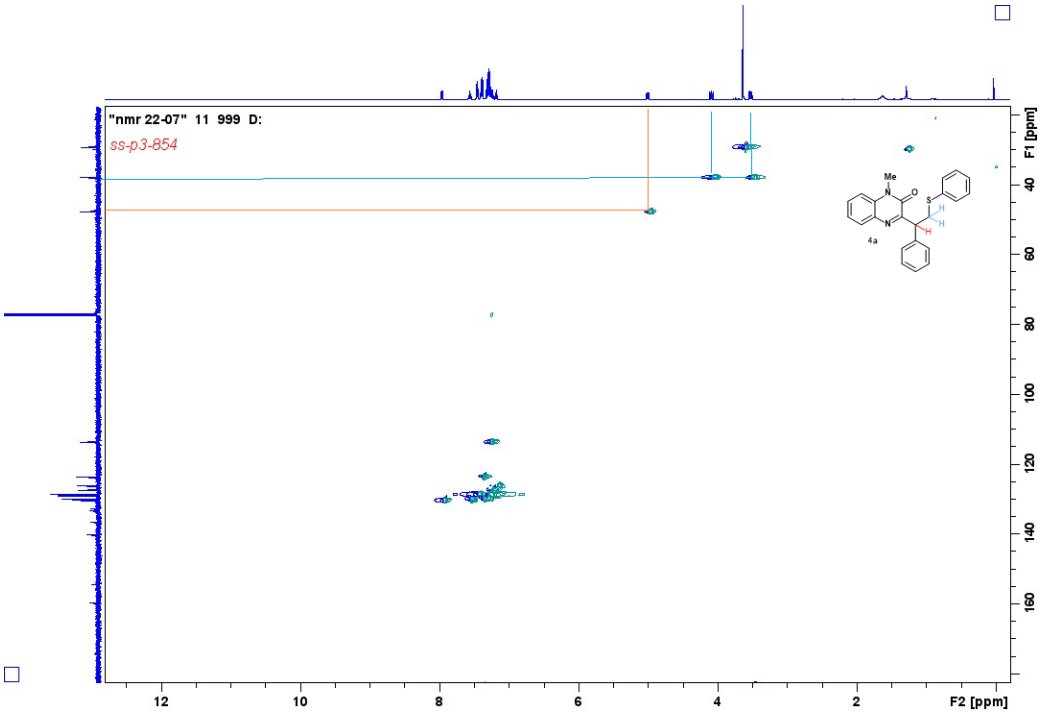
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4a**



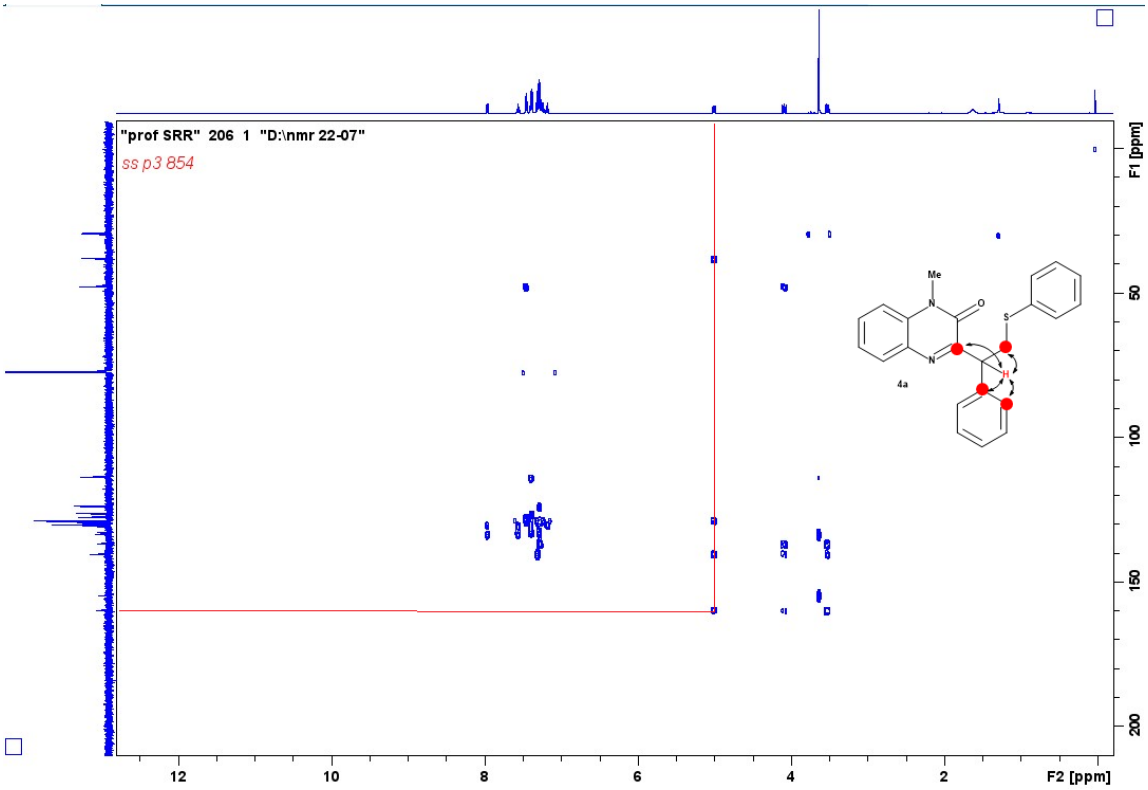
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4a**



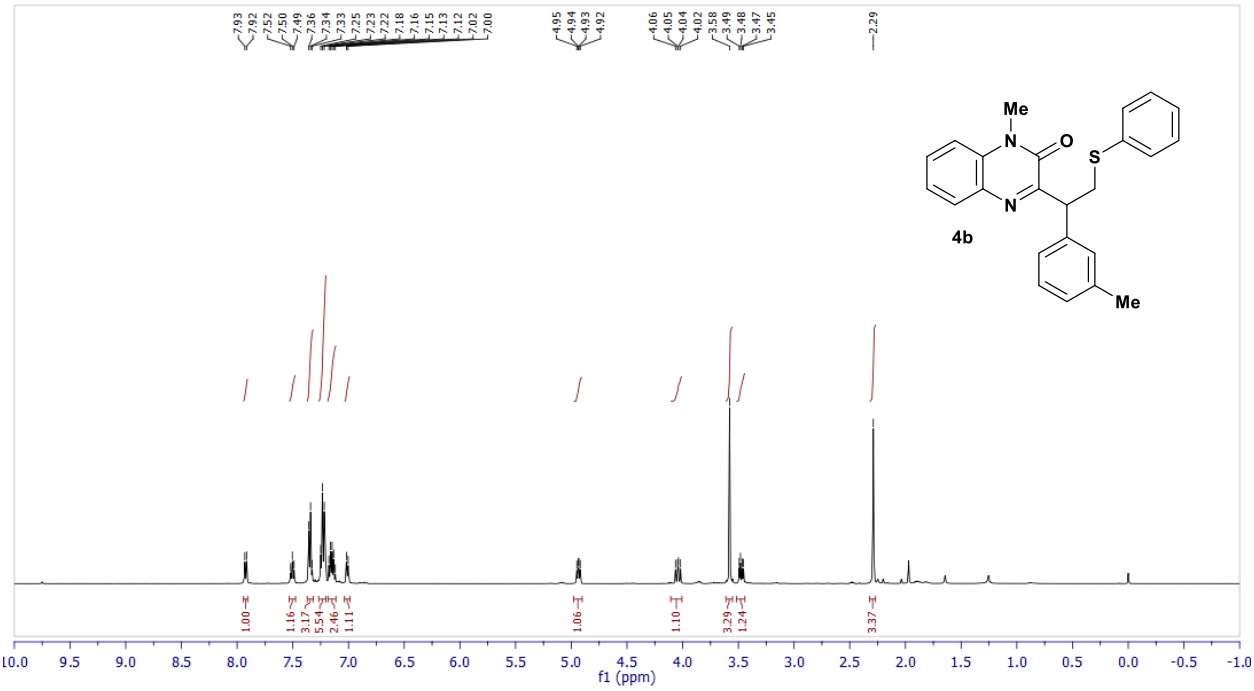
HSQC NMR ($CDCl_3$) of compound **4a**



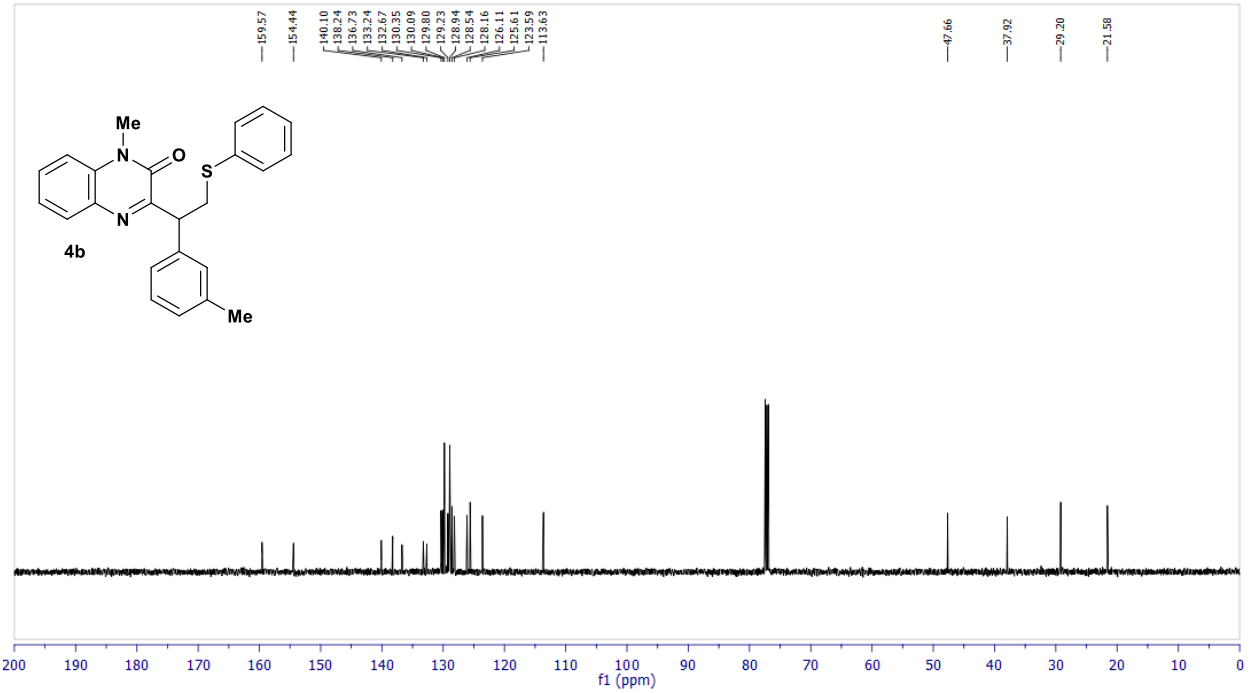
HMBC NMR ($CDCl_3$) of compound **4a**



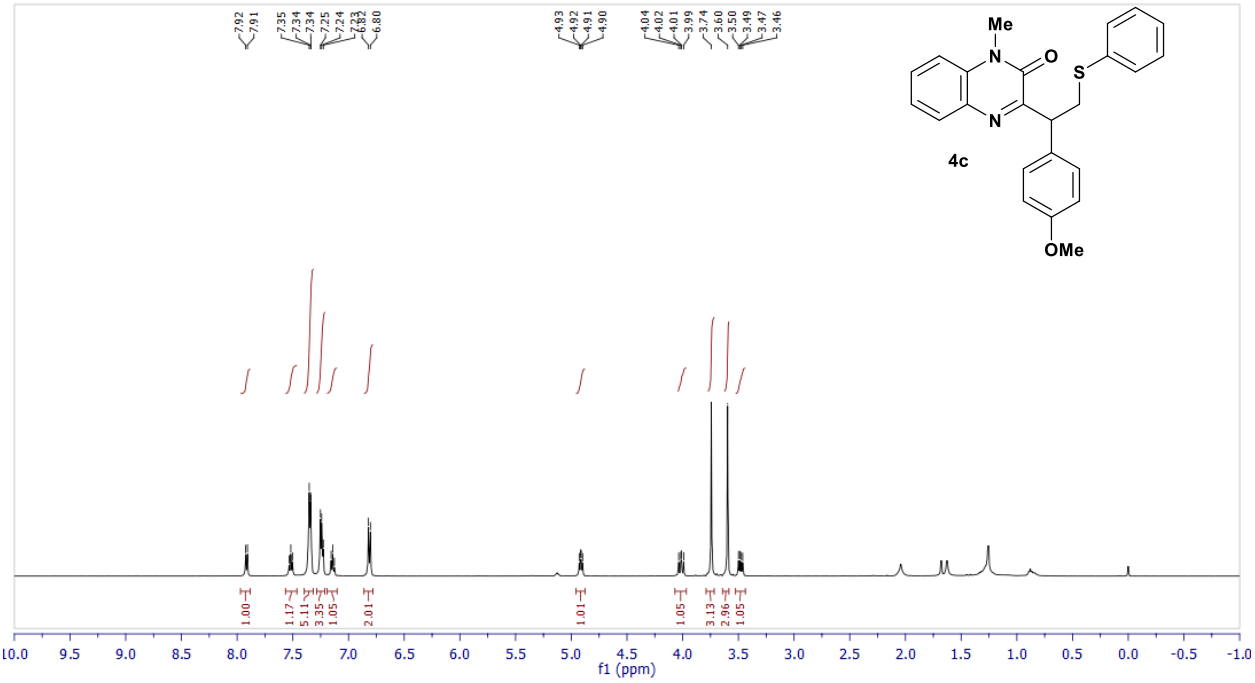
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b**



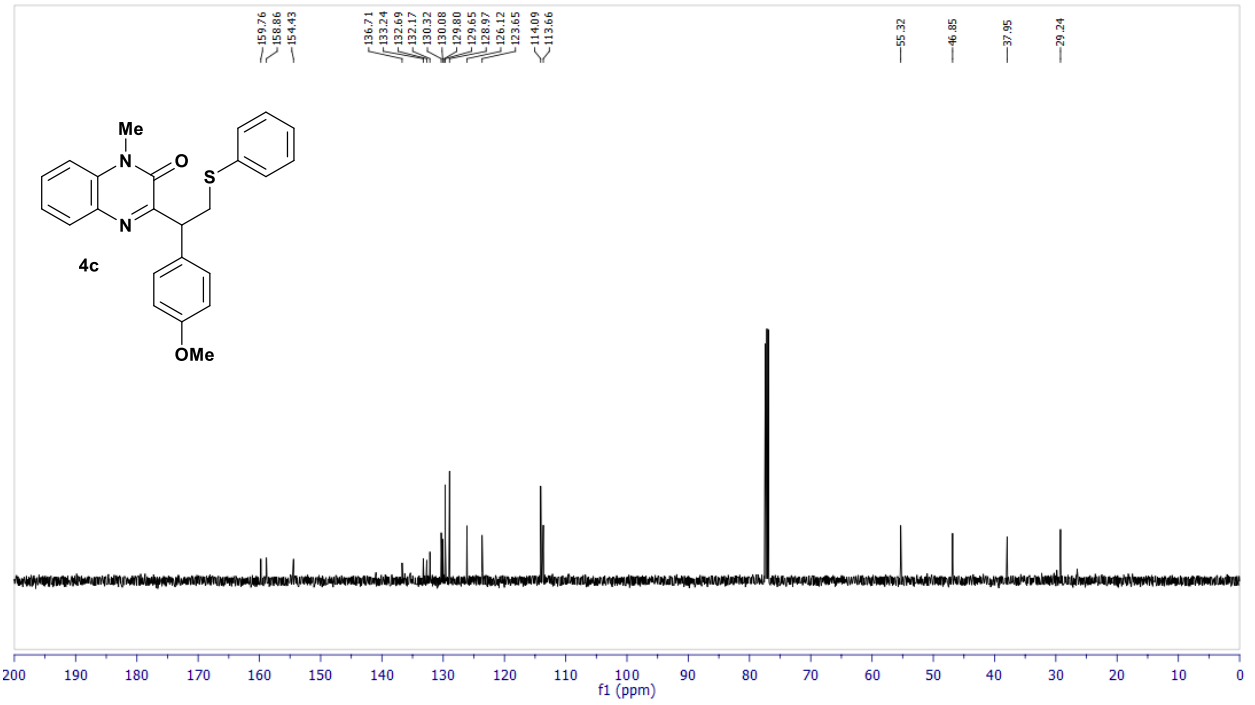
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4b**



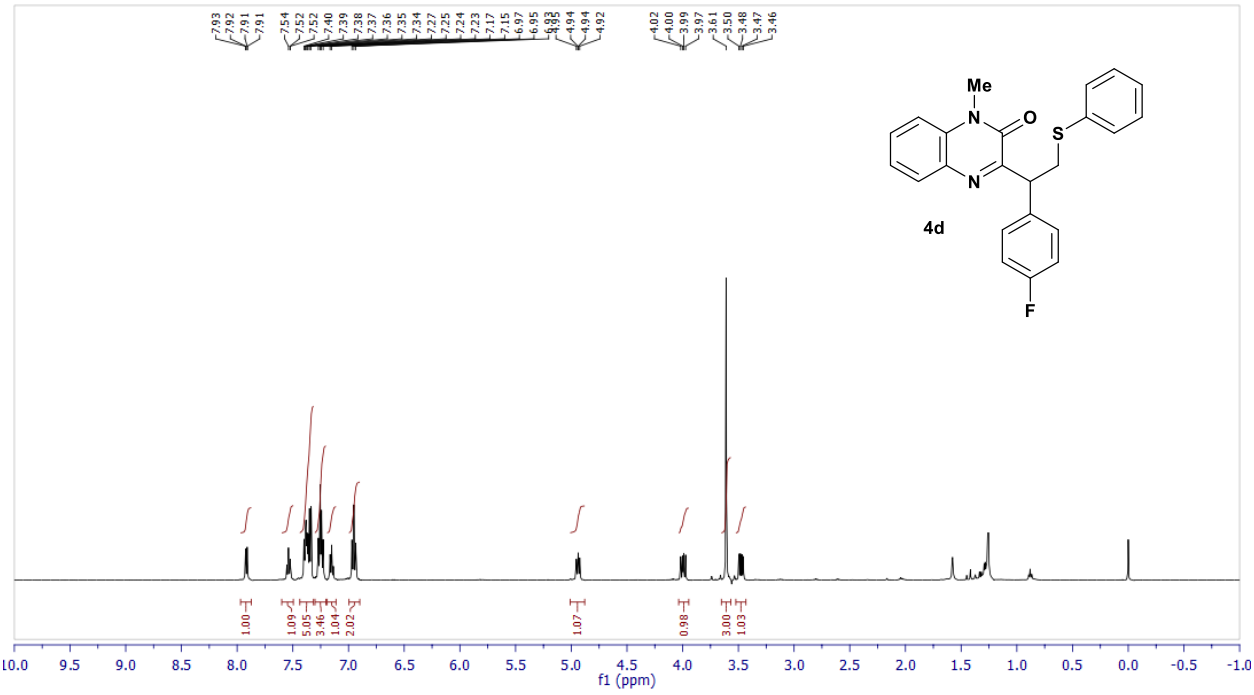
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4c**



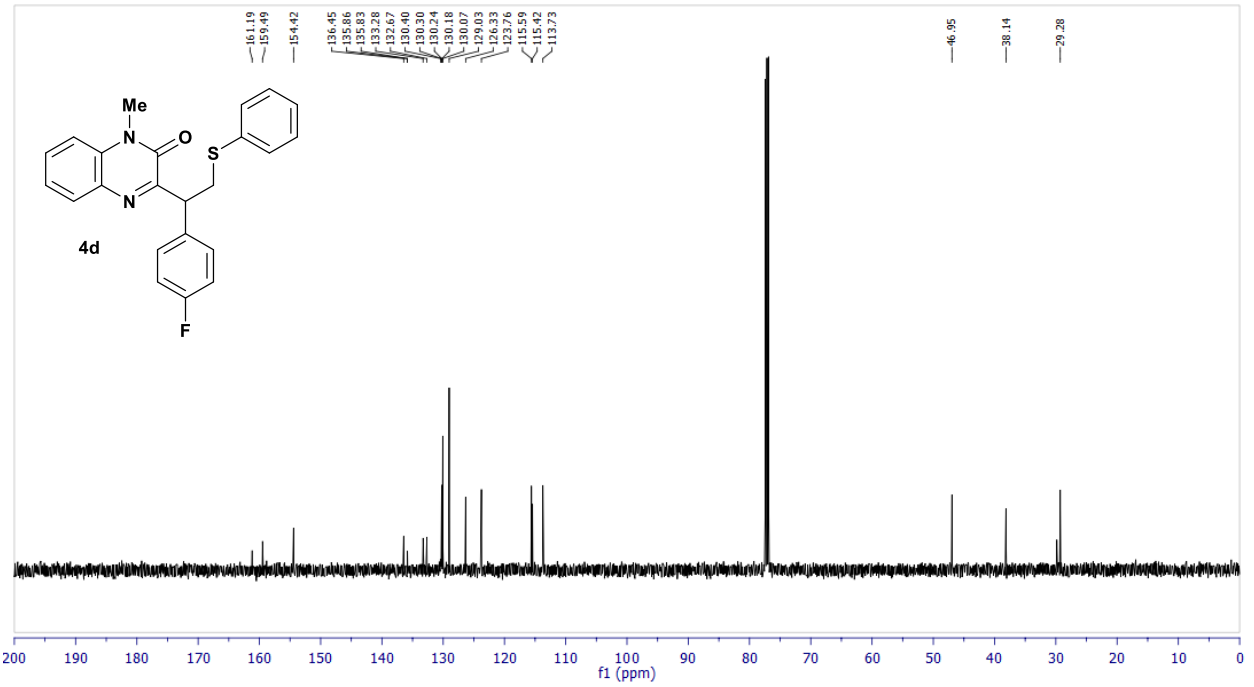
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4c**



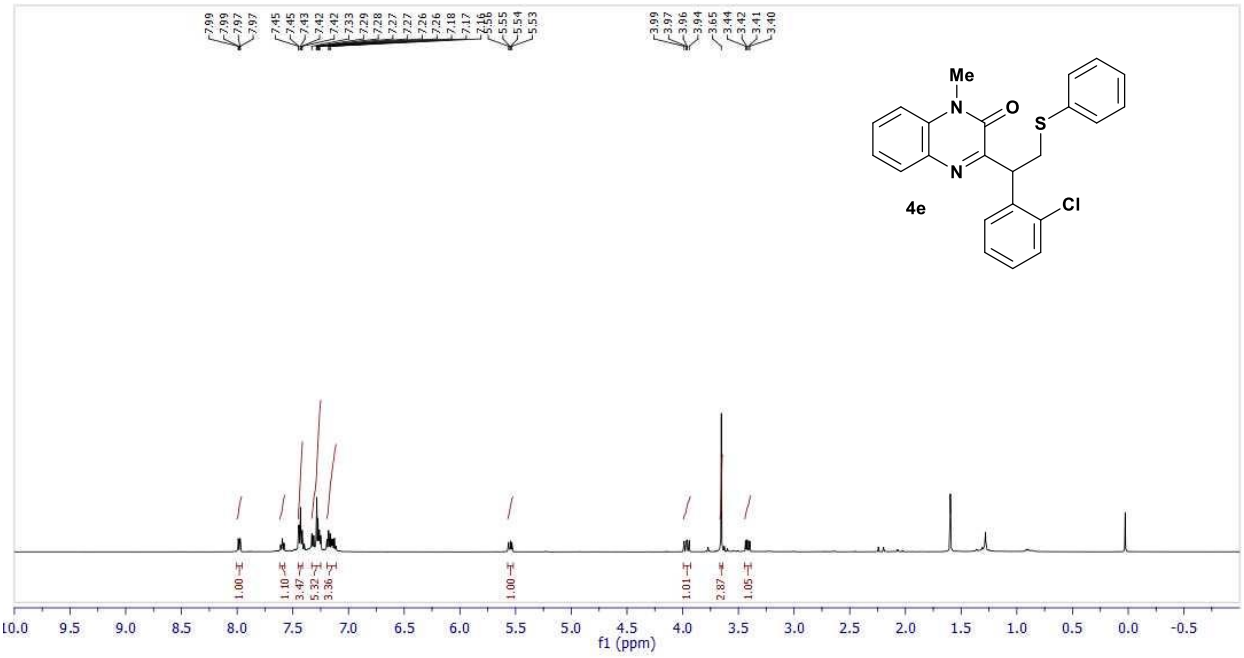
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4d**



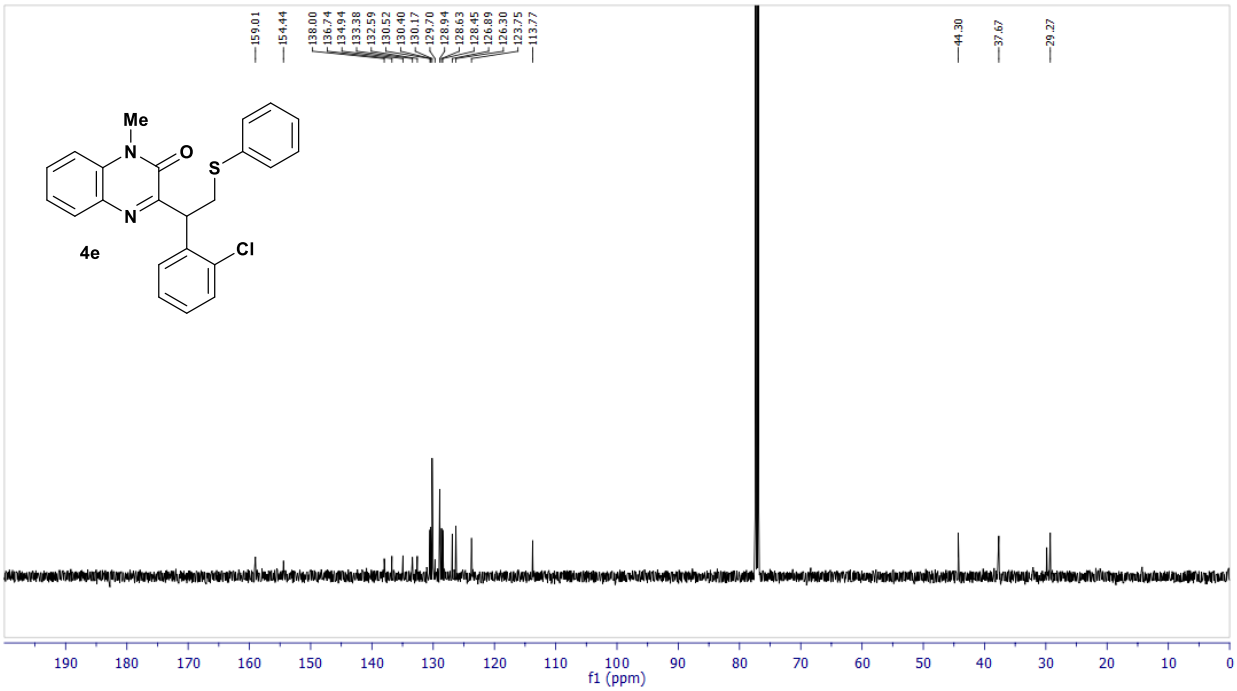
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4d**



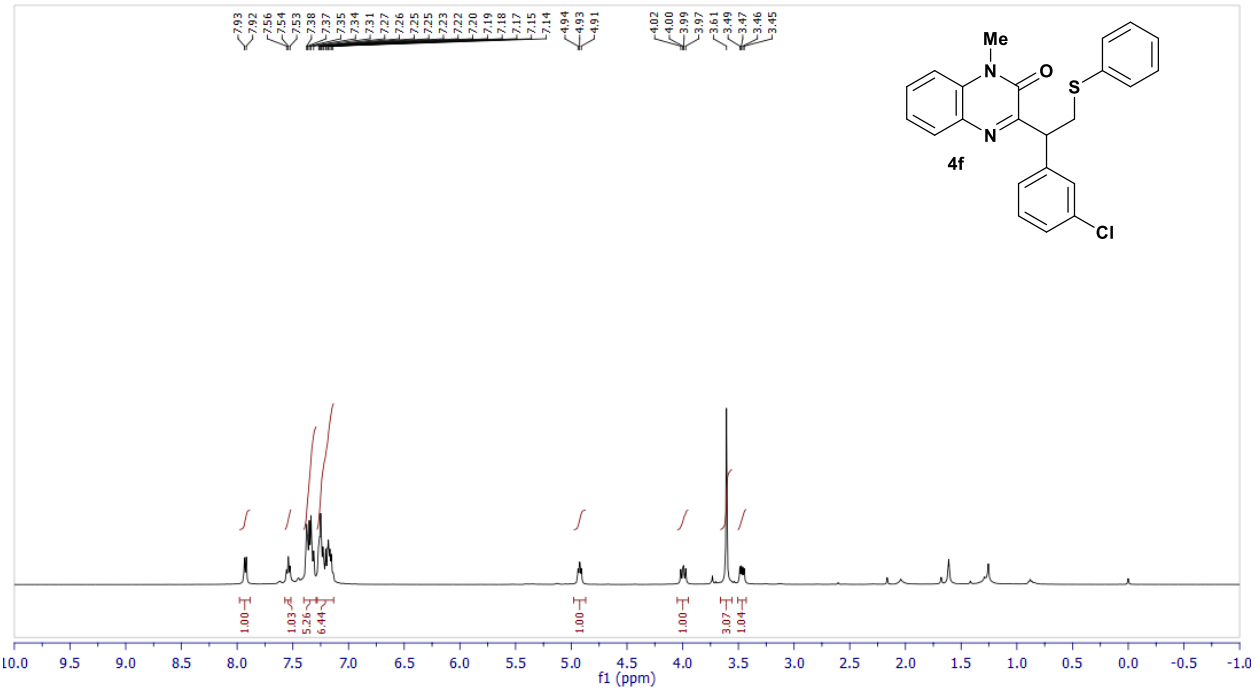
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4e**



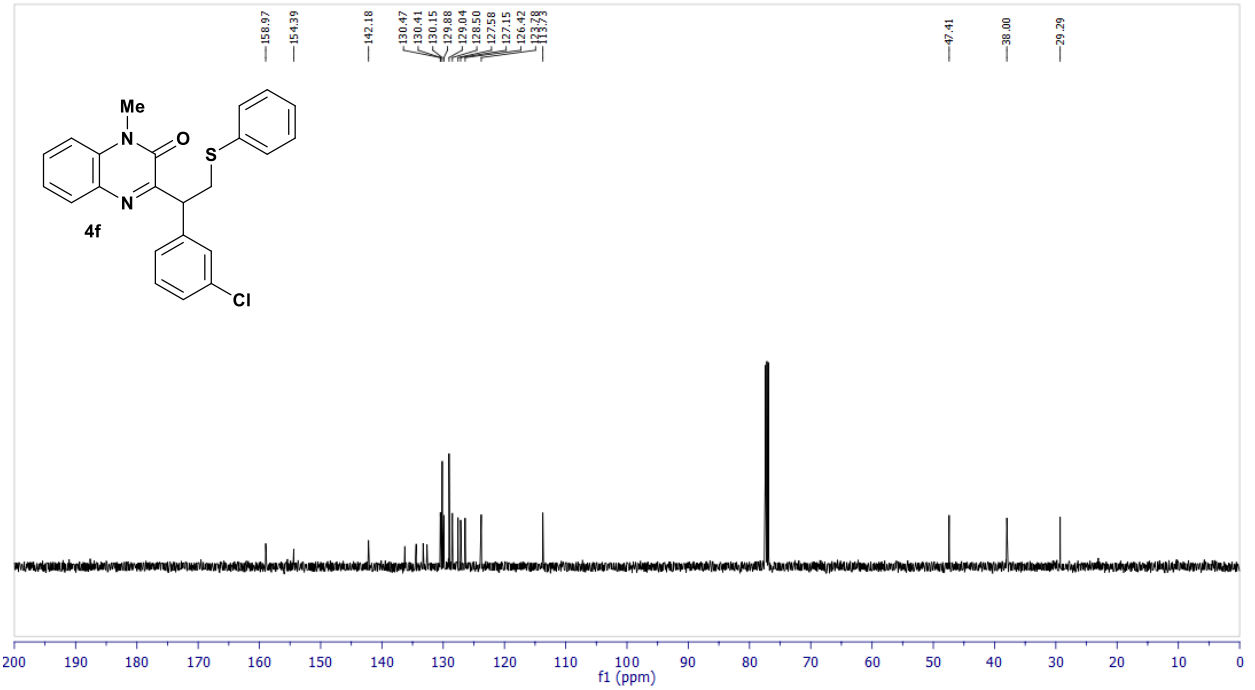
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4e**



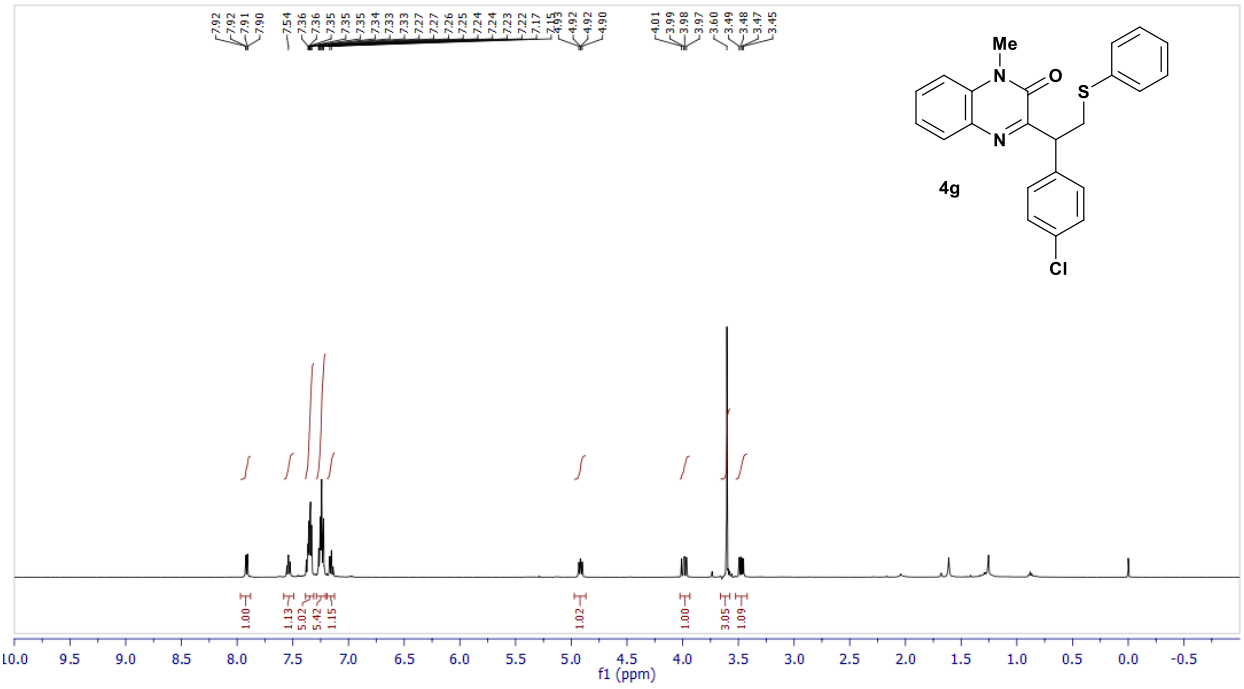
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4f**



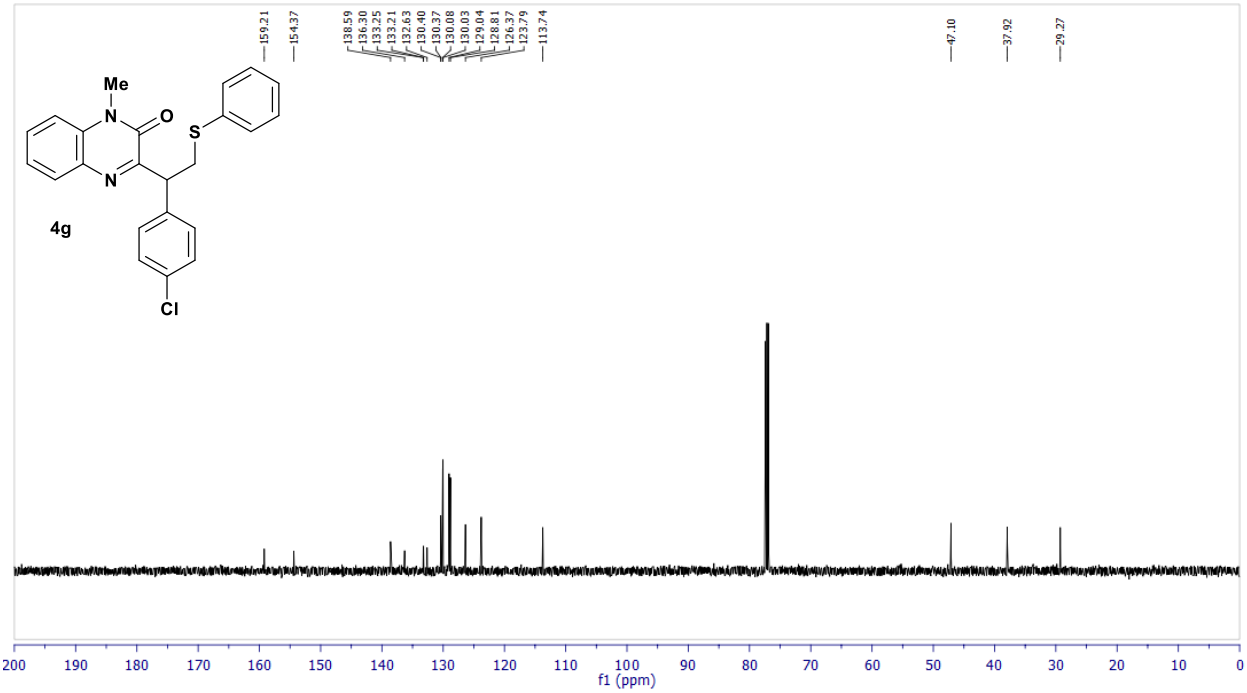
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4f**



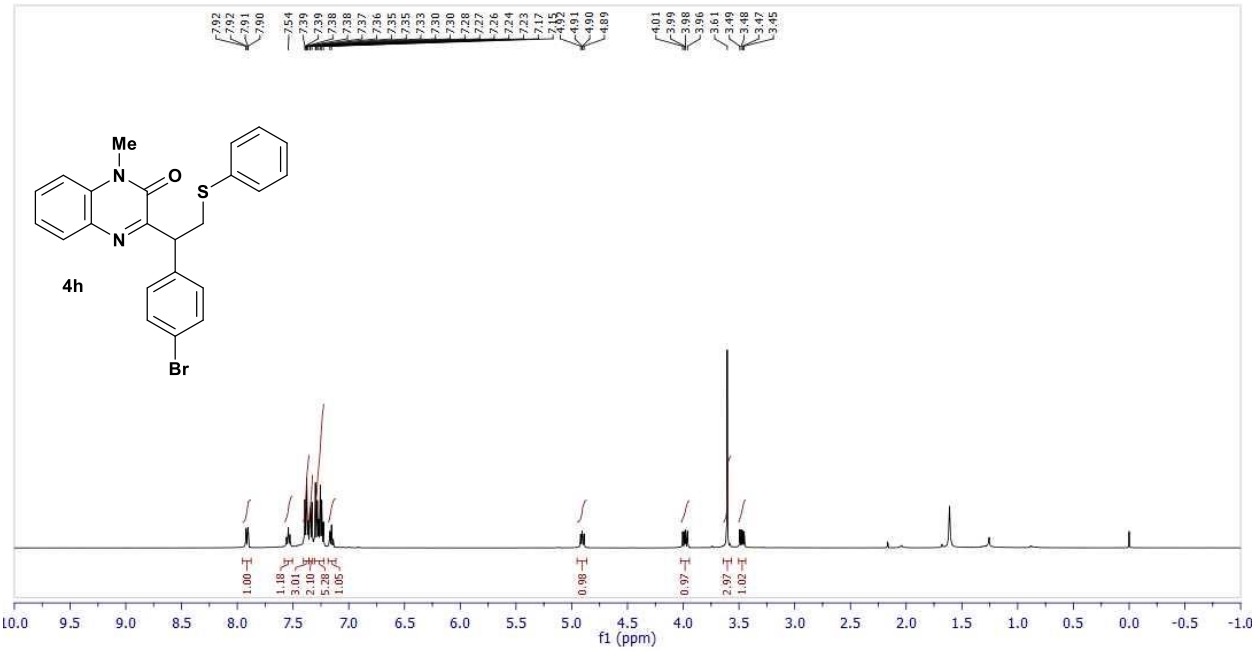
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4g**



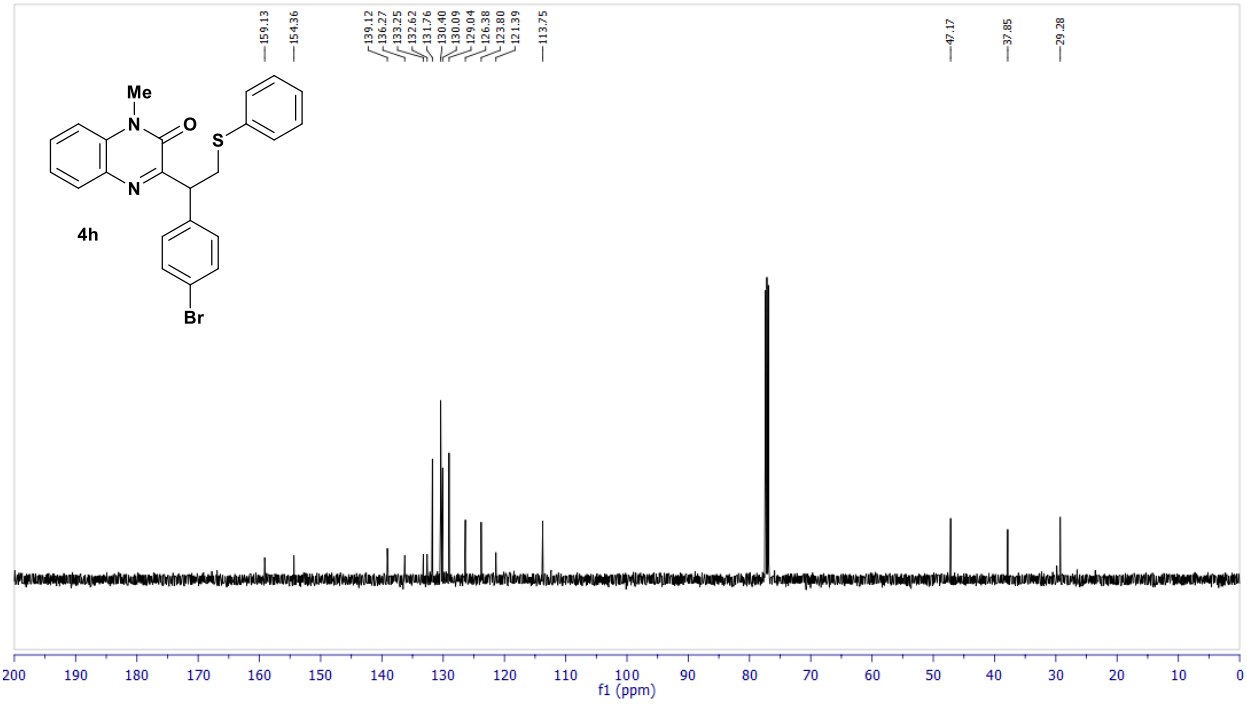
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4g**



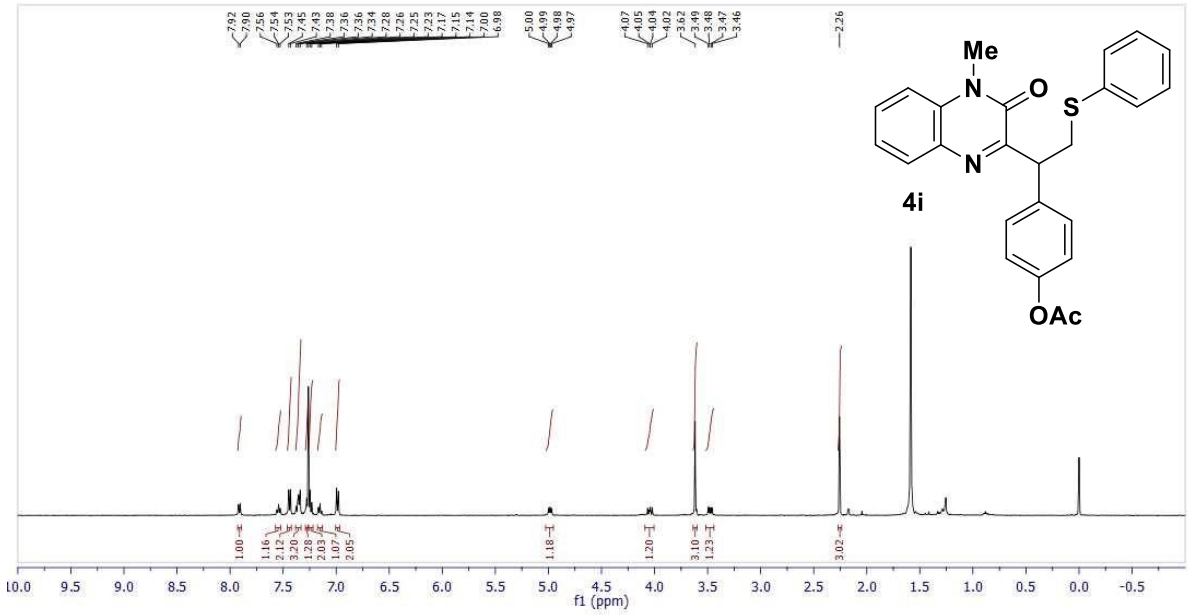
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4h**



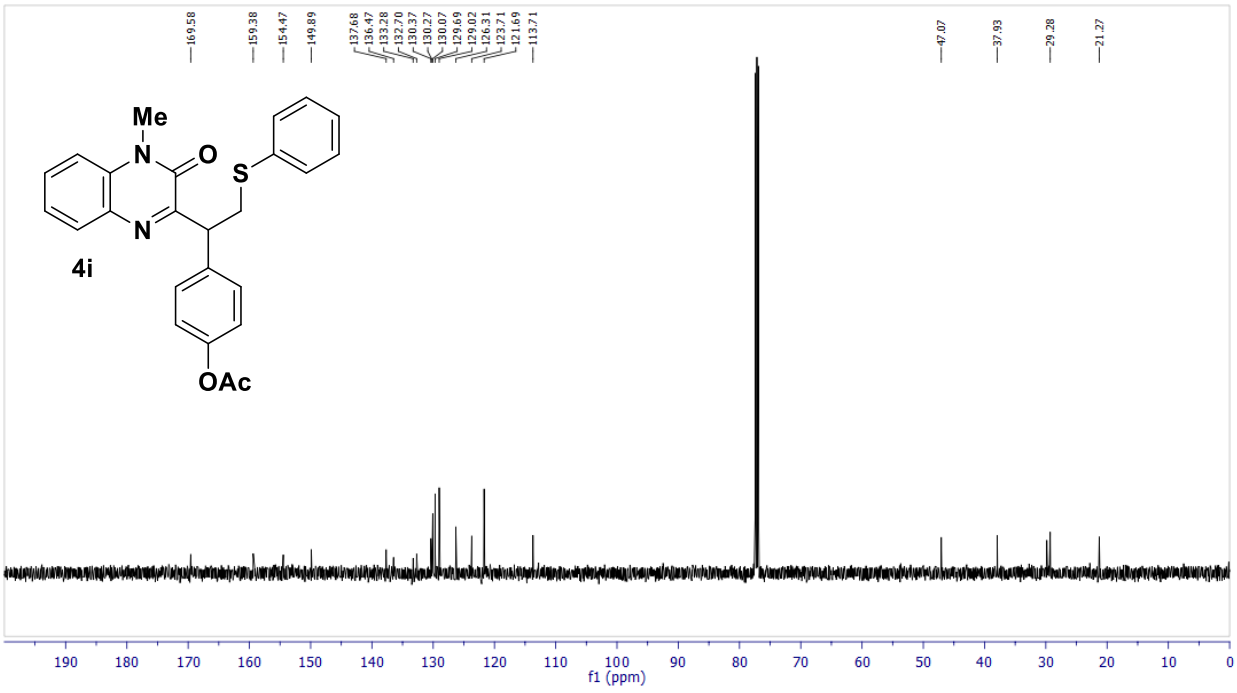
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4h**



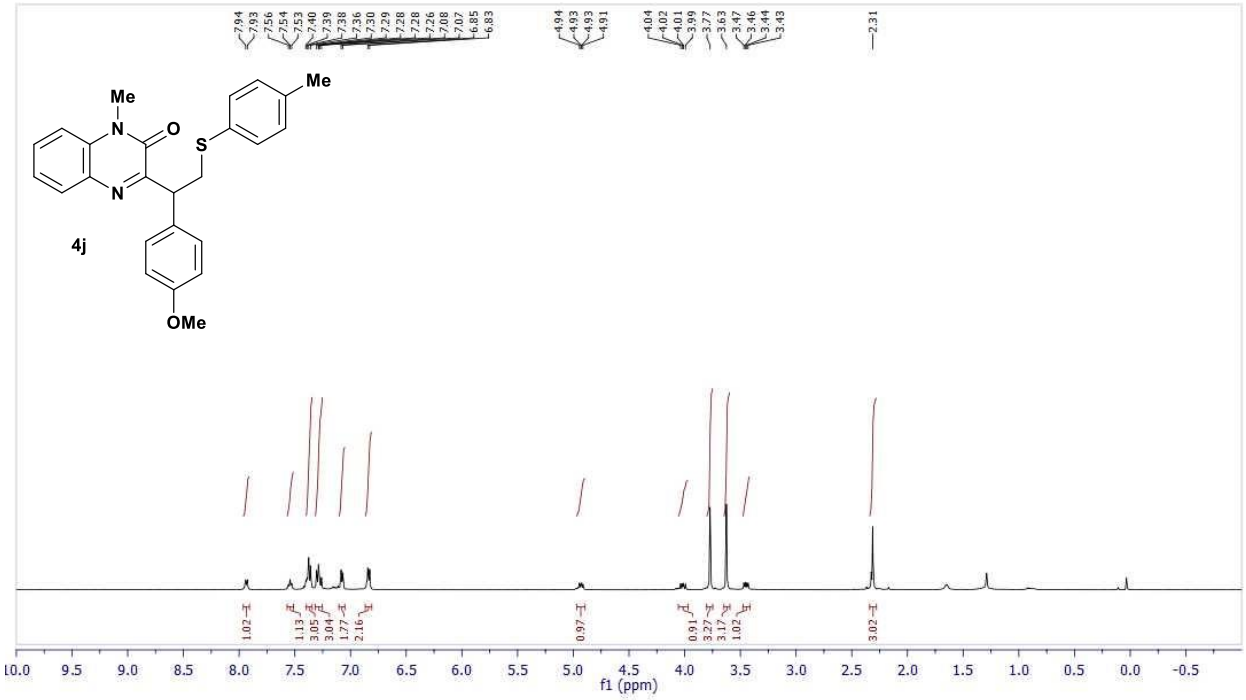
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4i**



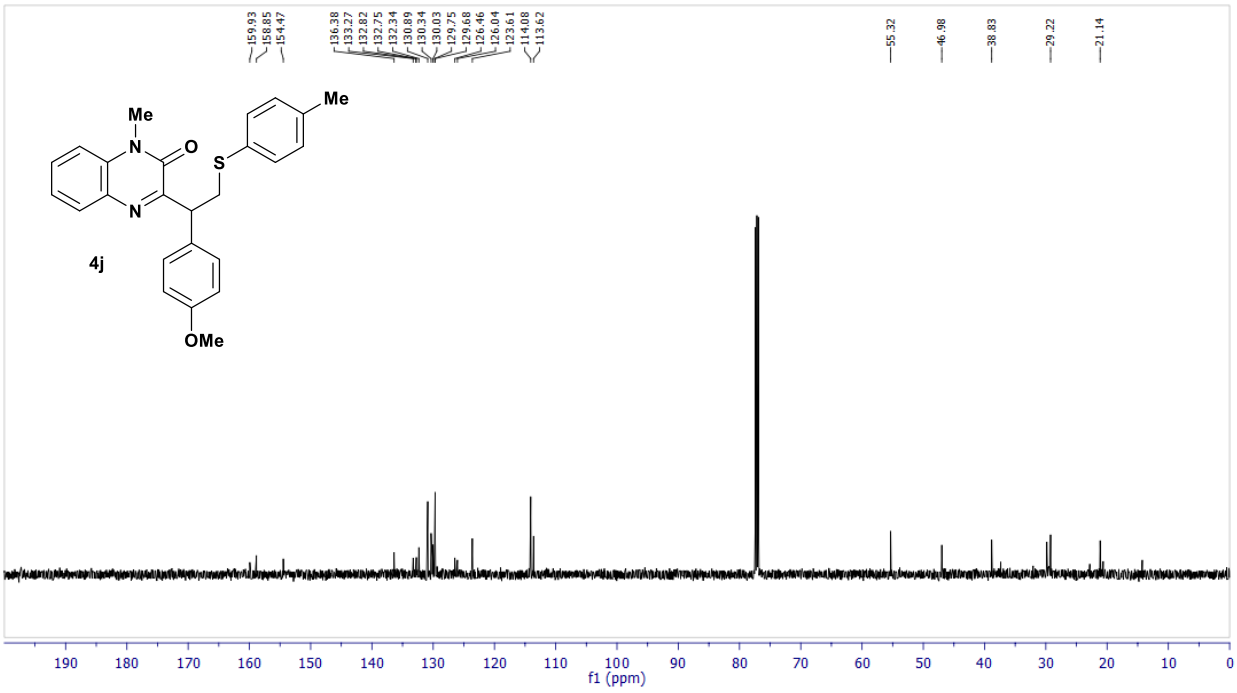
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4i**



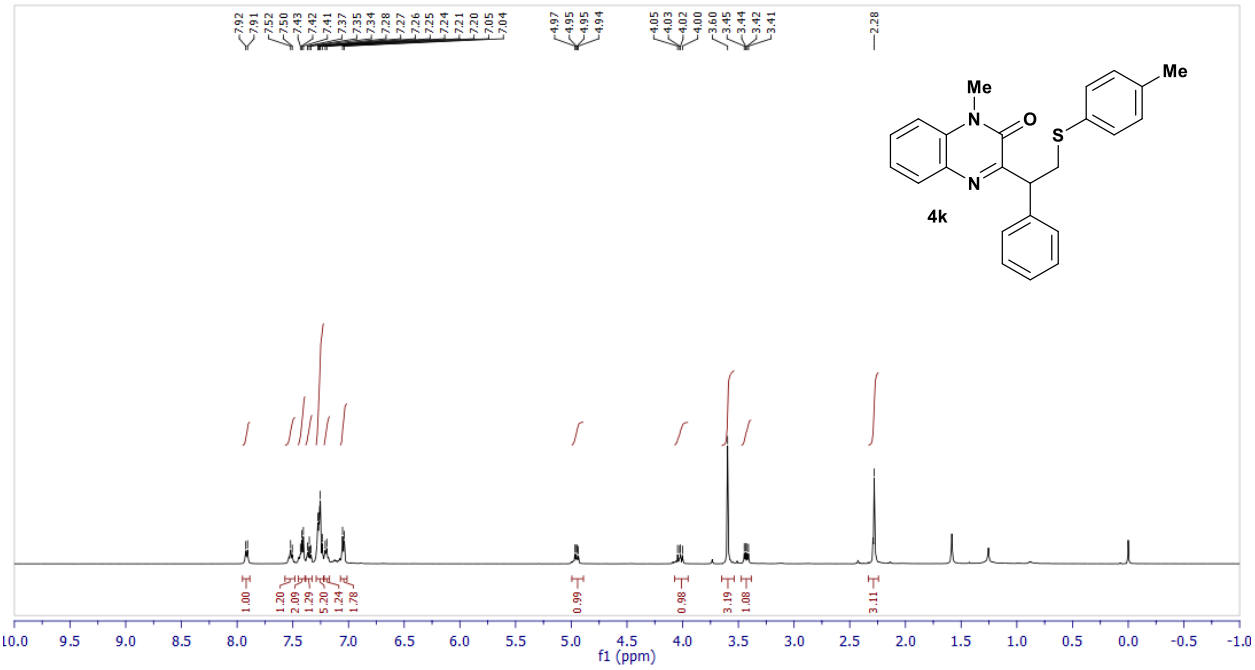
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4j**



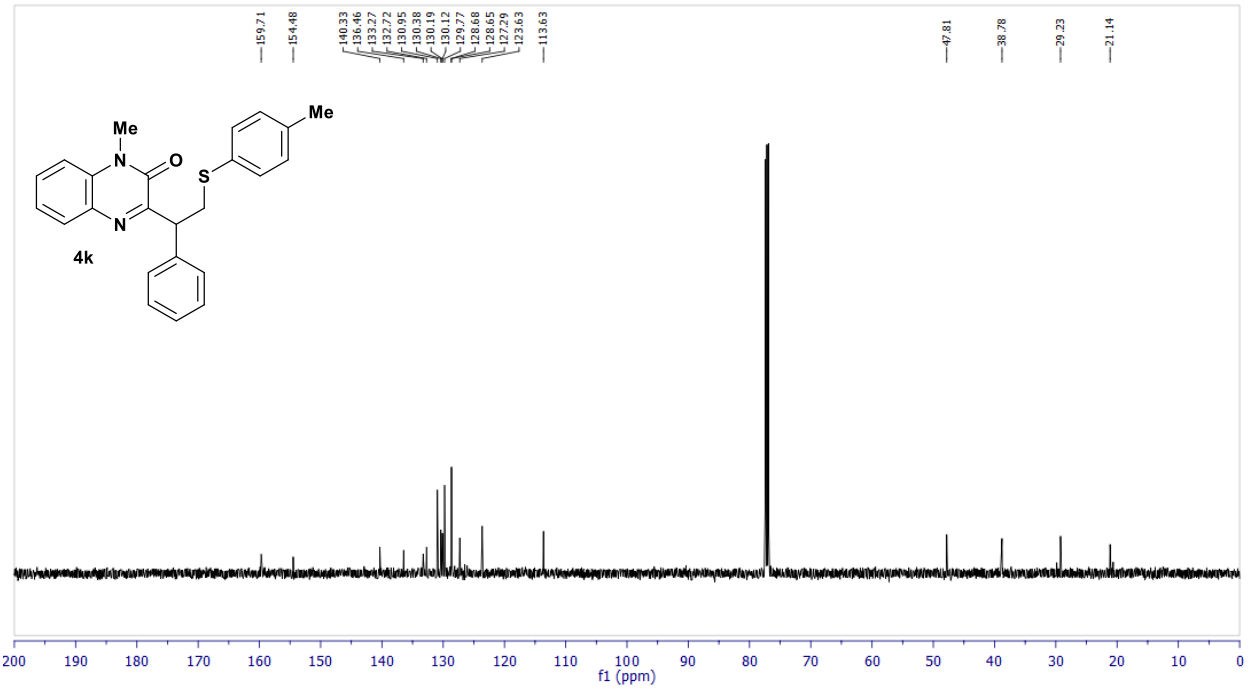
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4j**



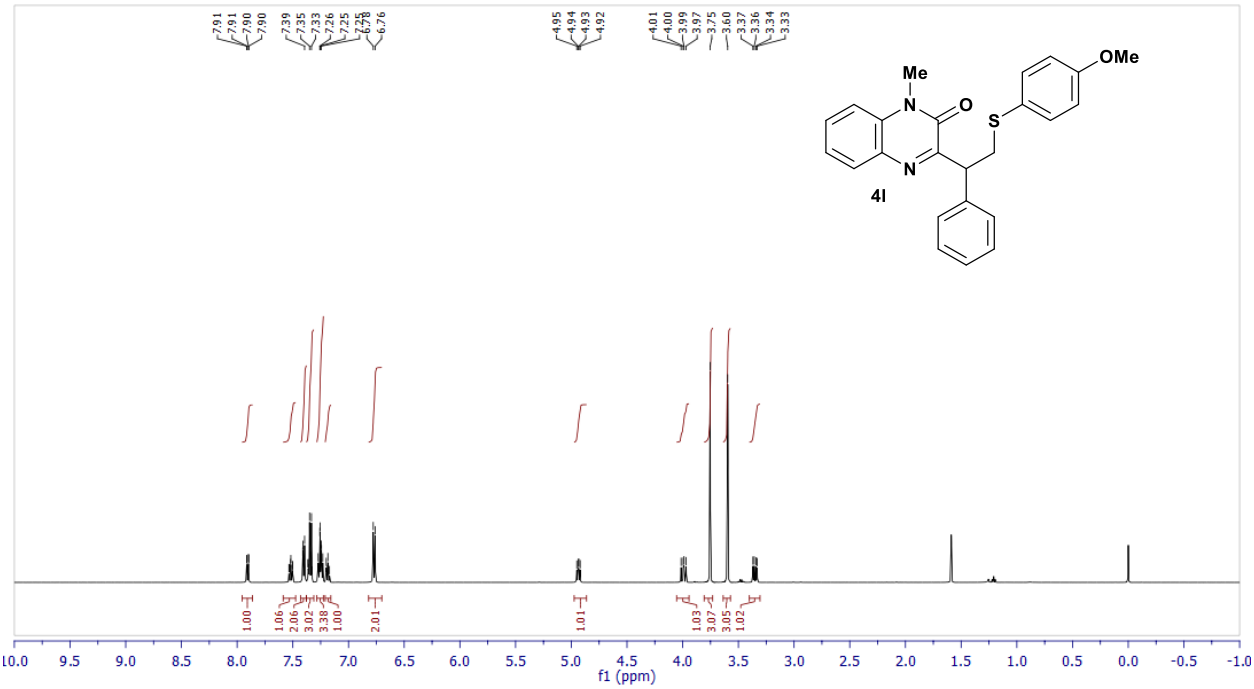
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4k**



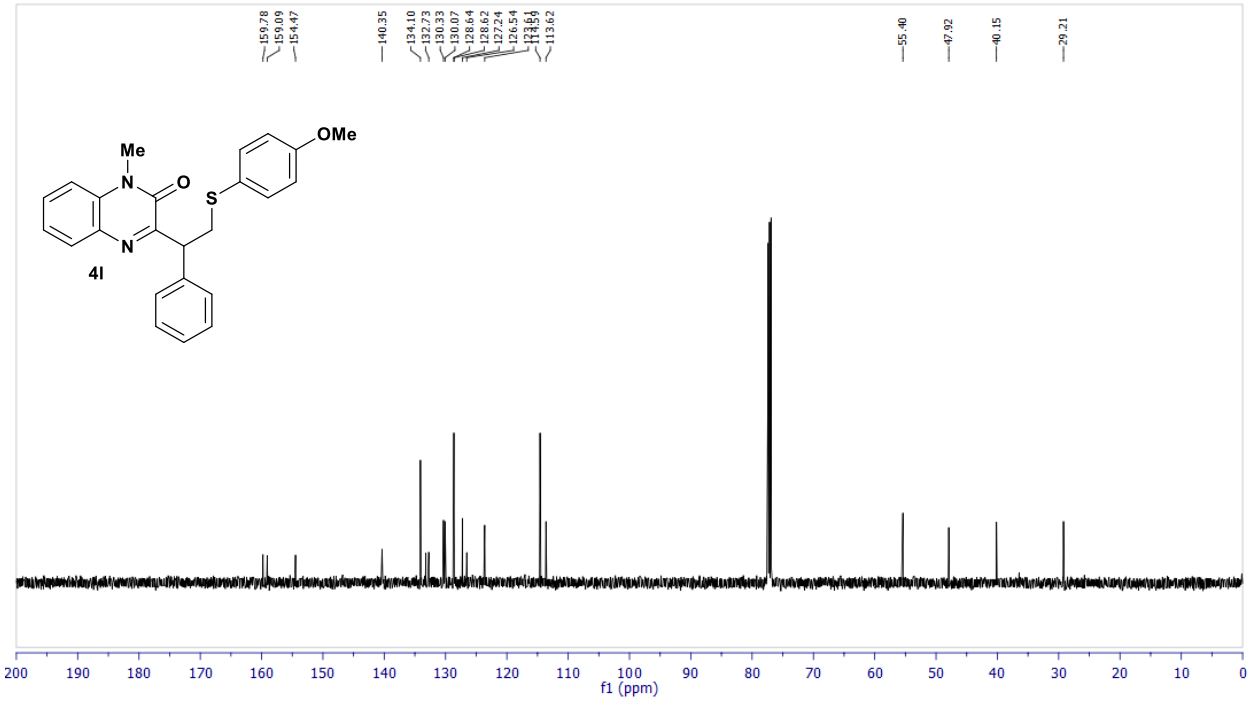
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4k**



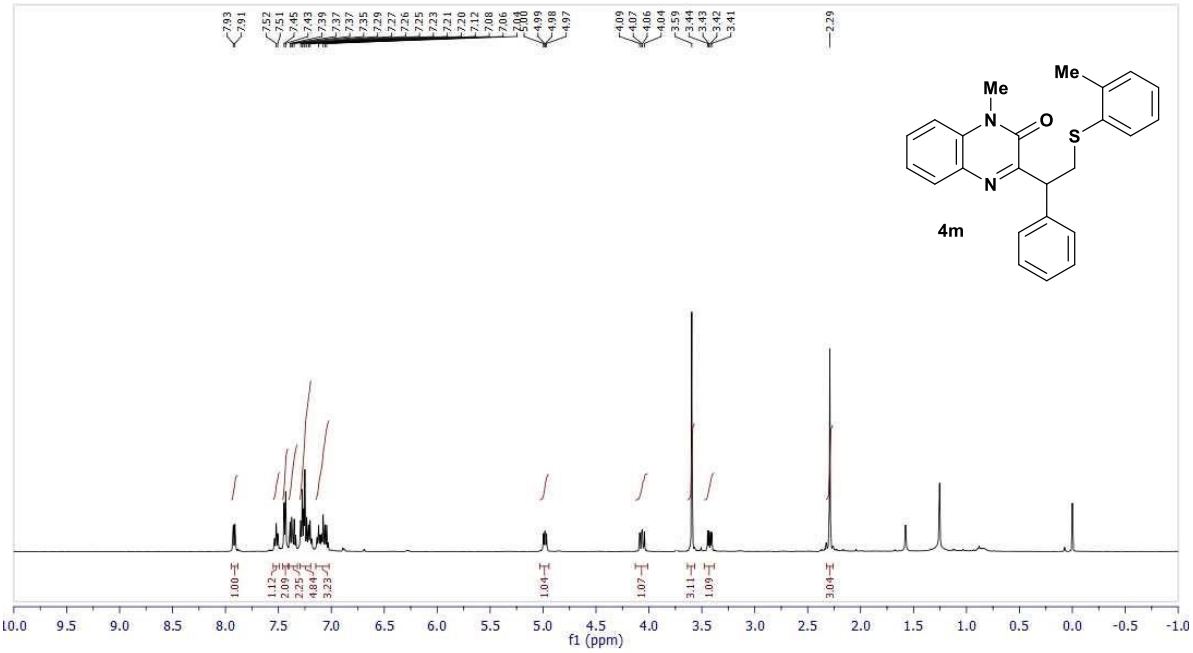
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4l**



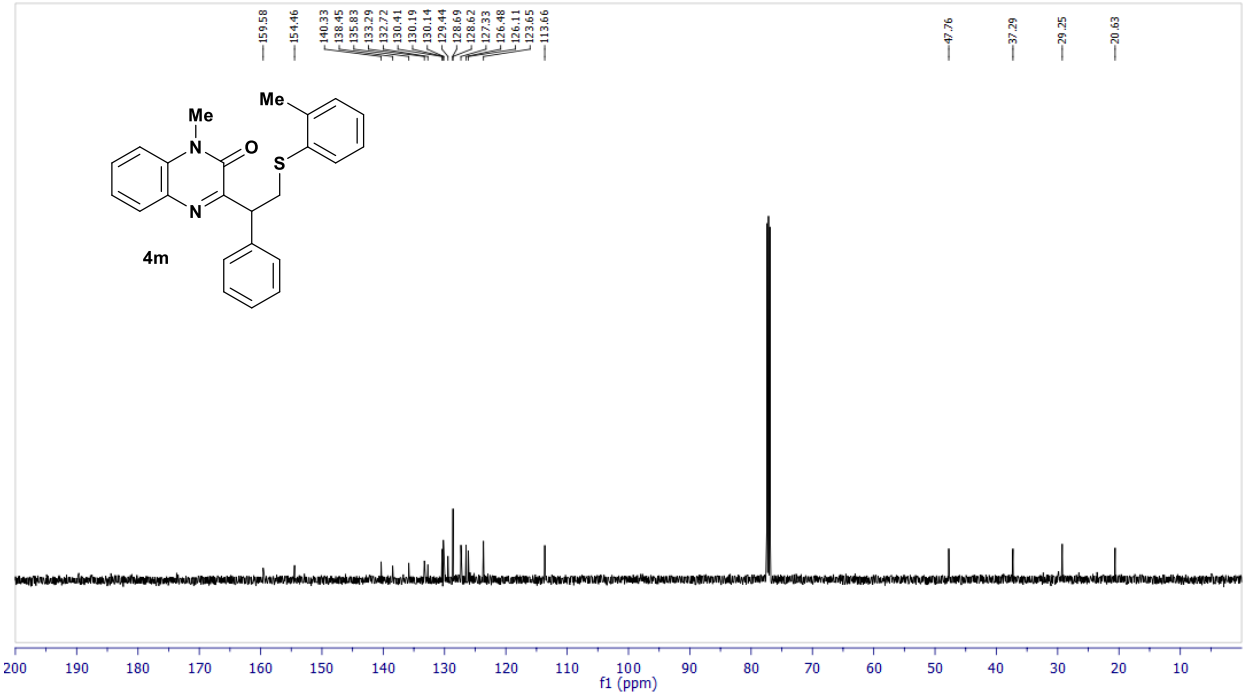
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4l**



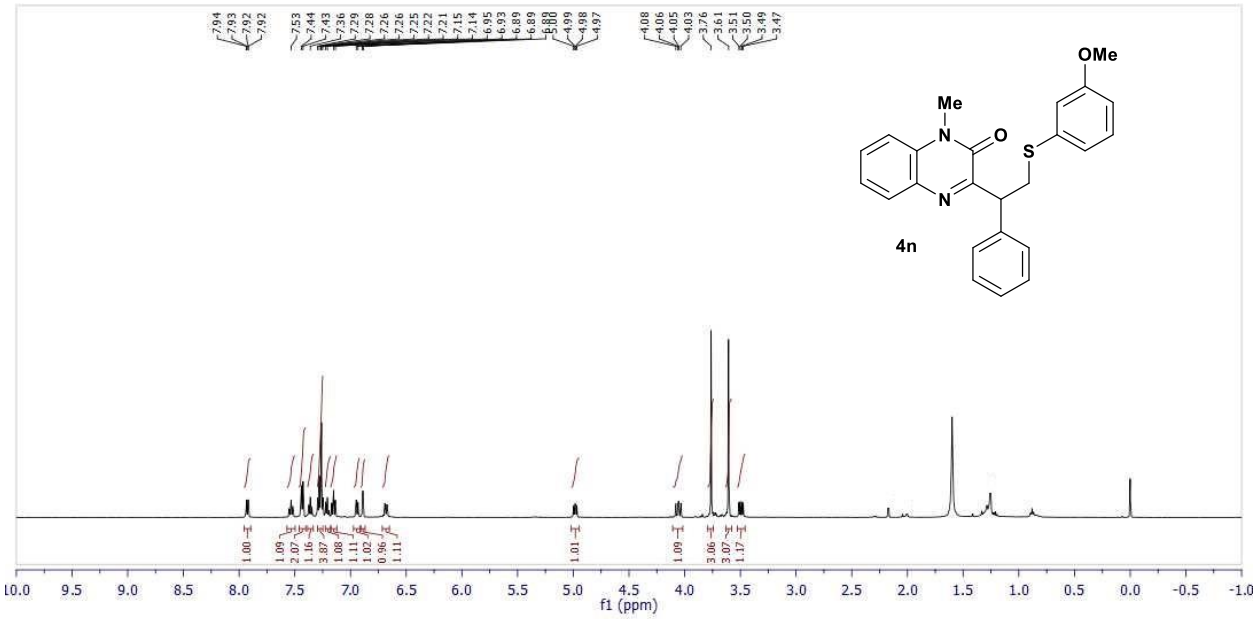
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4m**



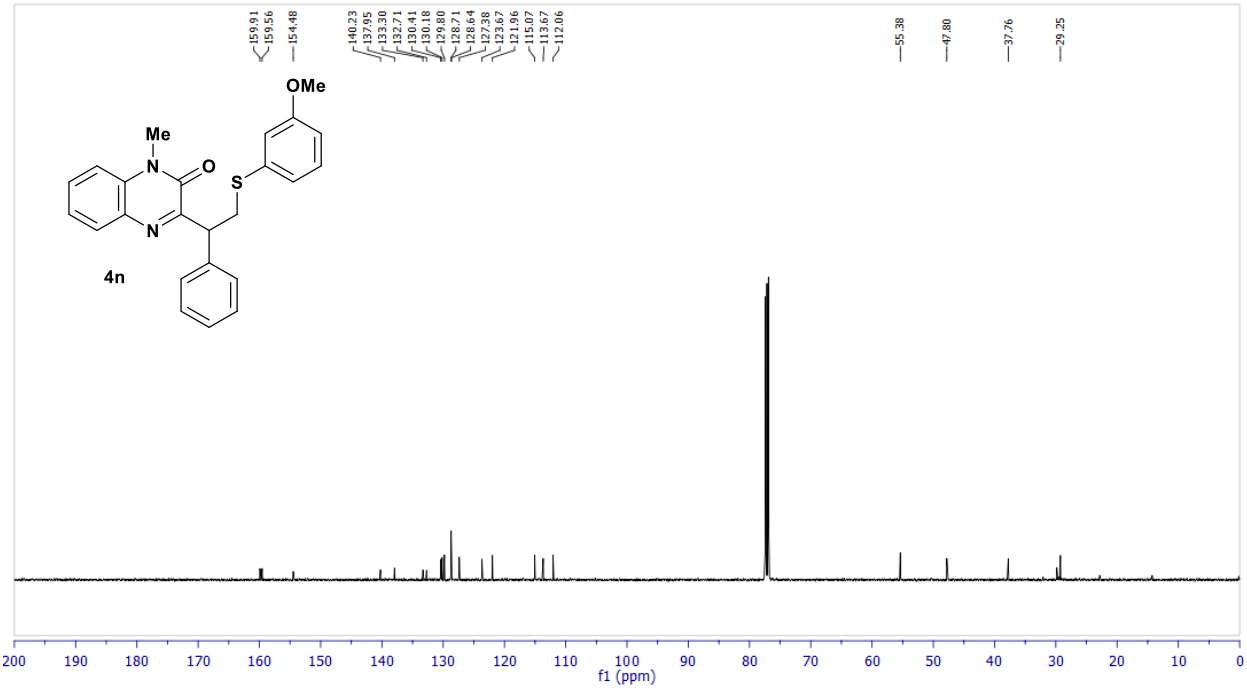
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4m**



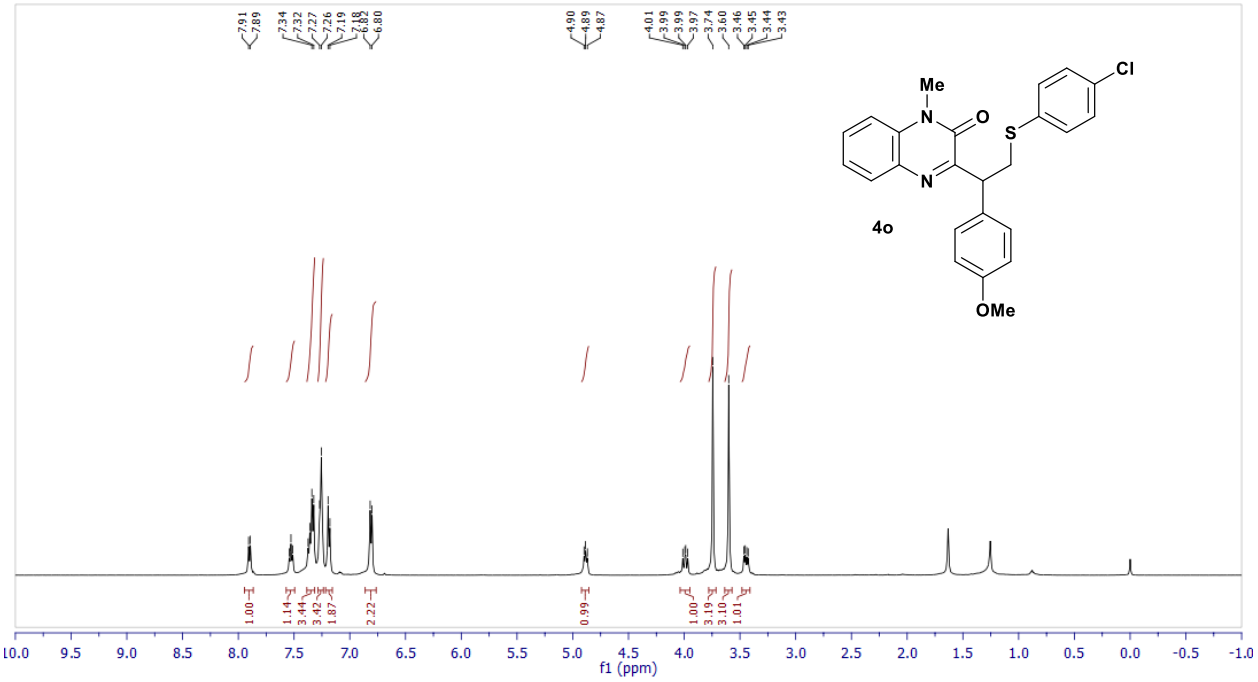
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4n**



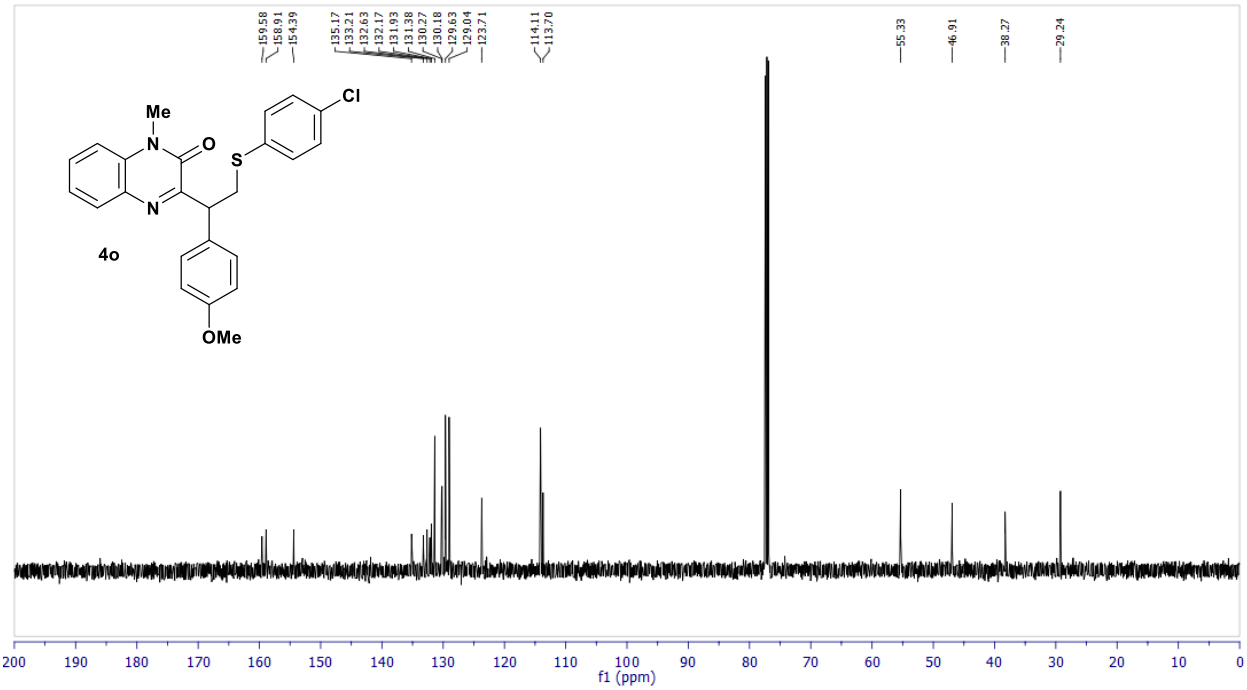
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4n**



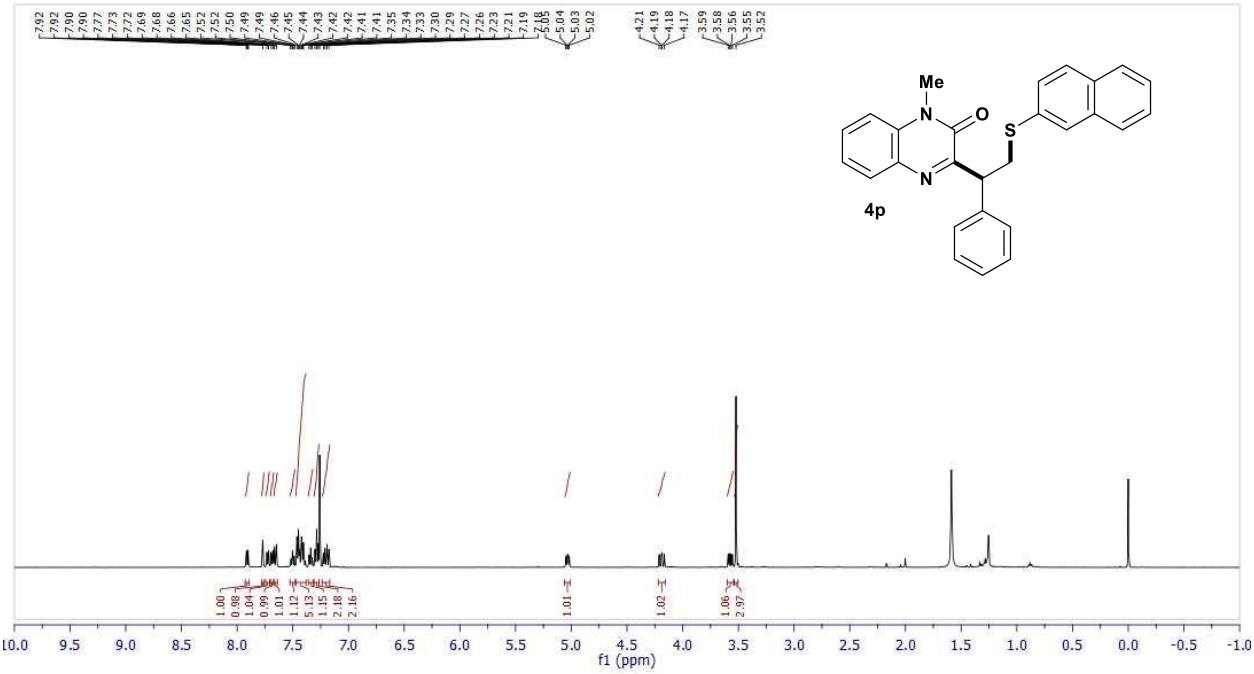
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4o**



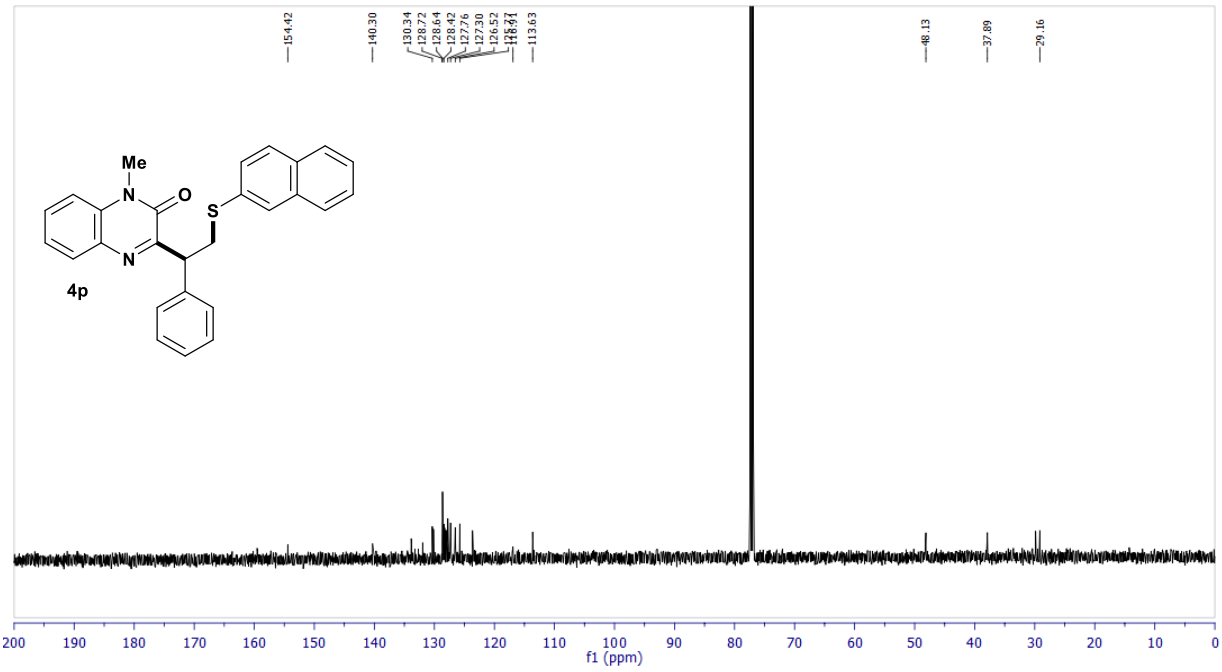
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4o**



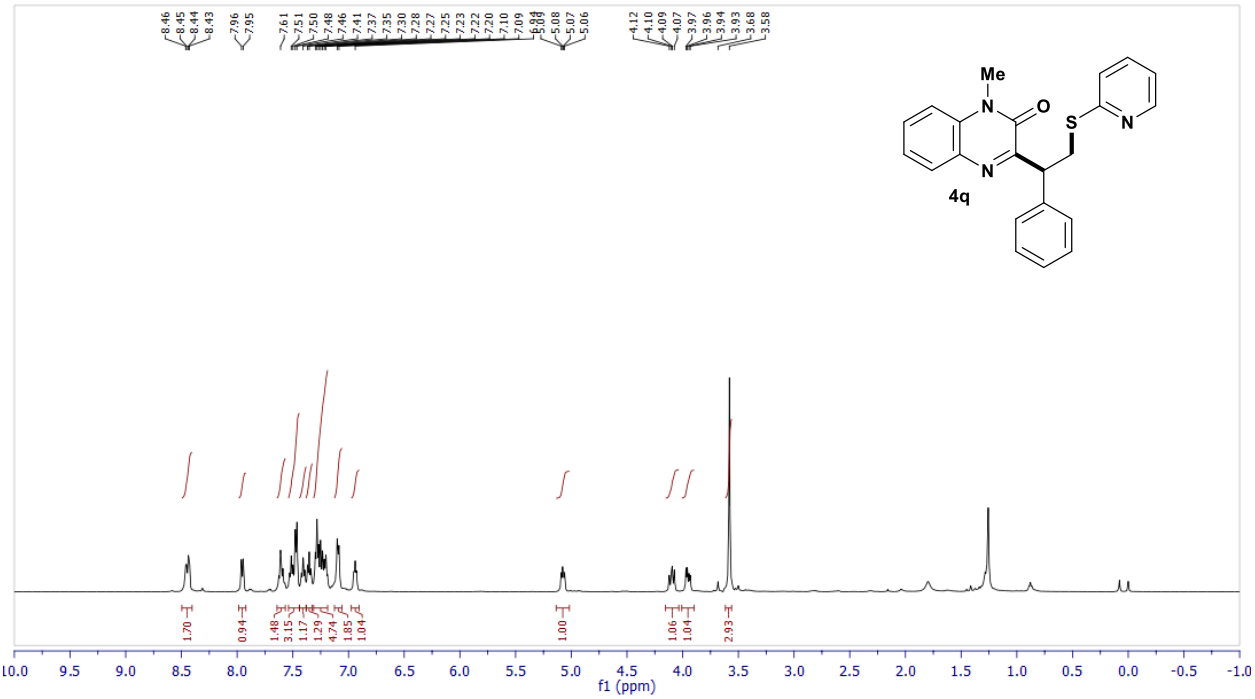
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4p**



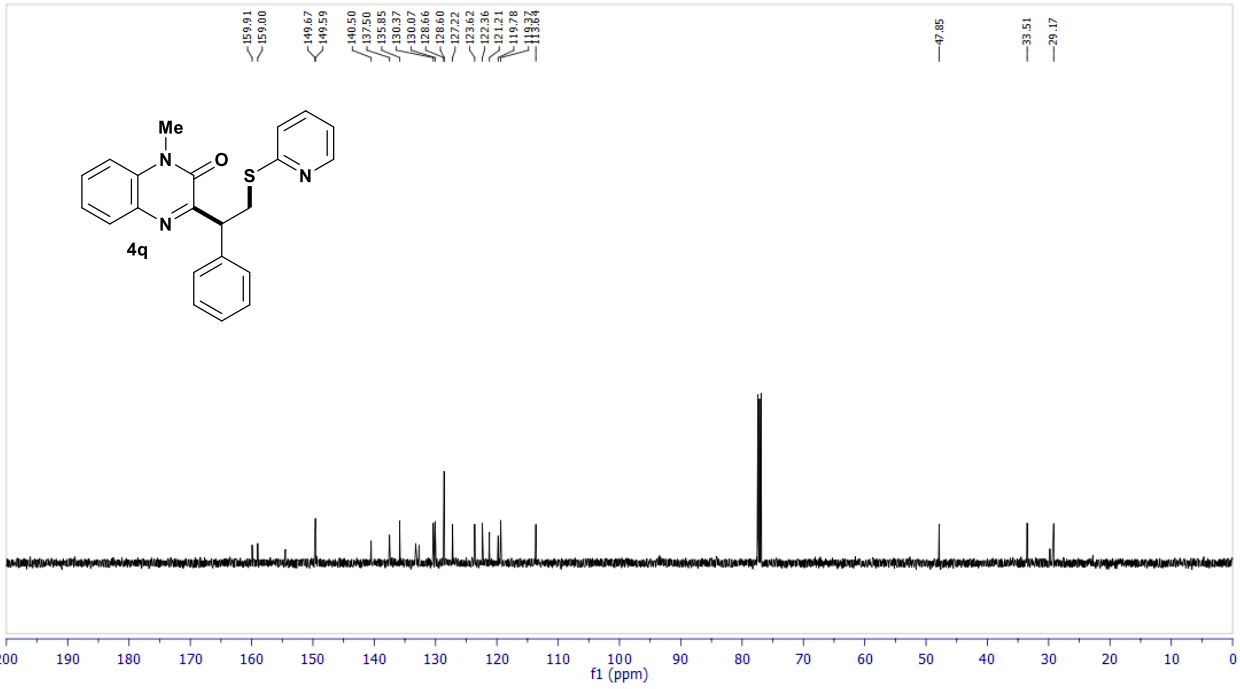
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4p**



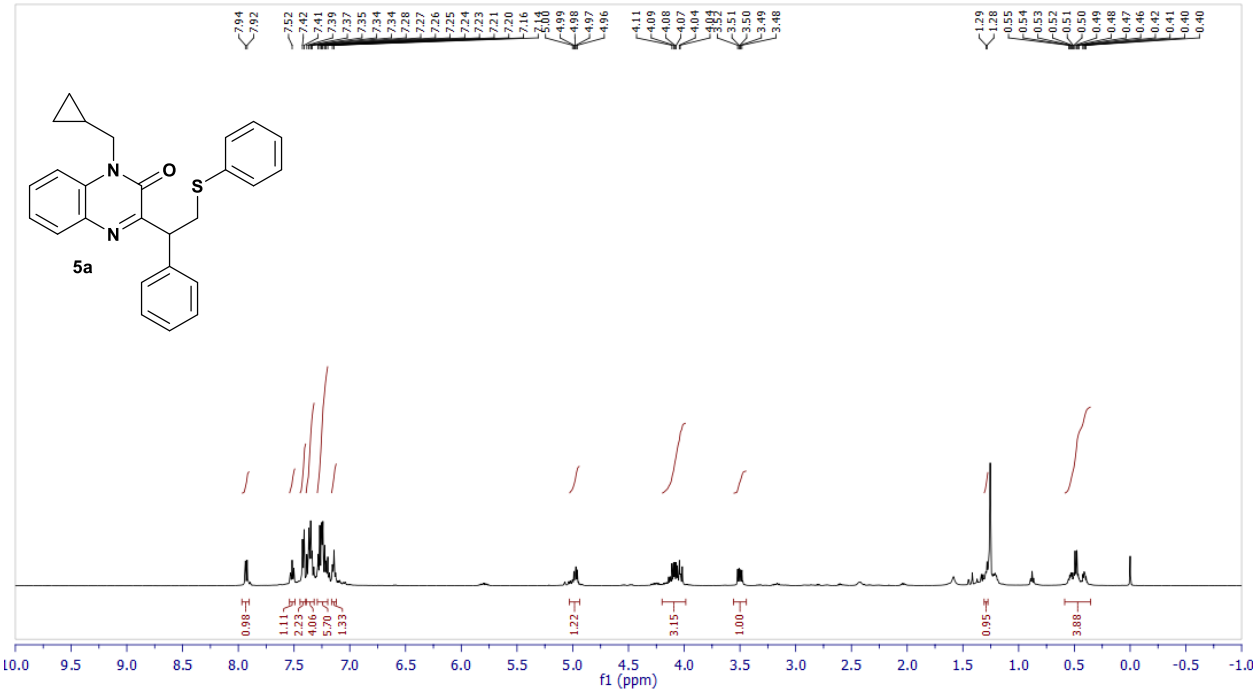
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4q**



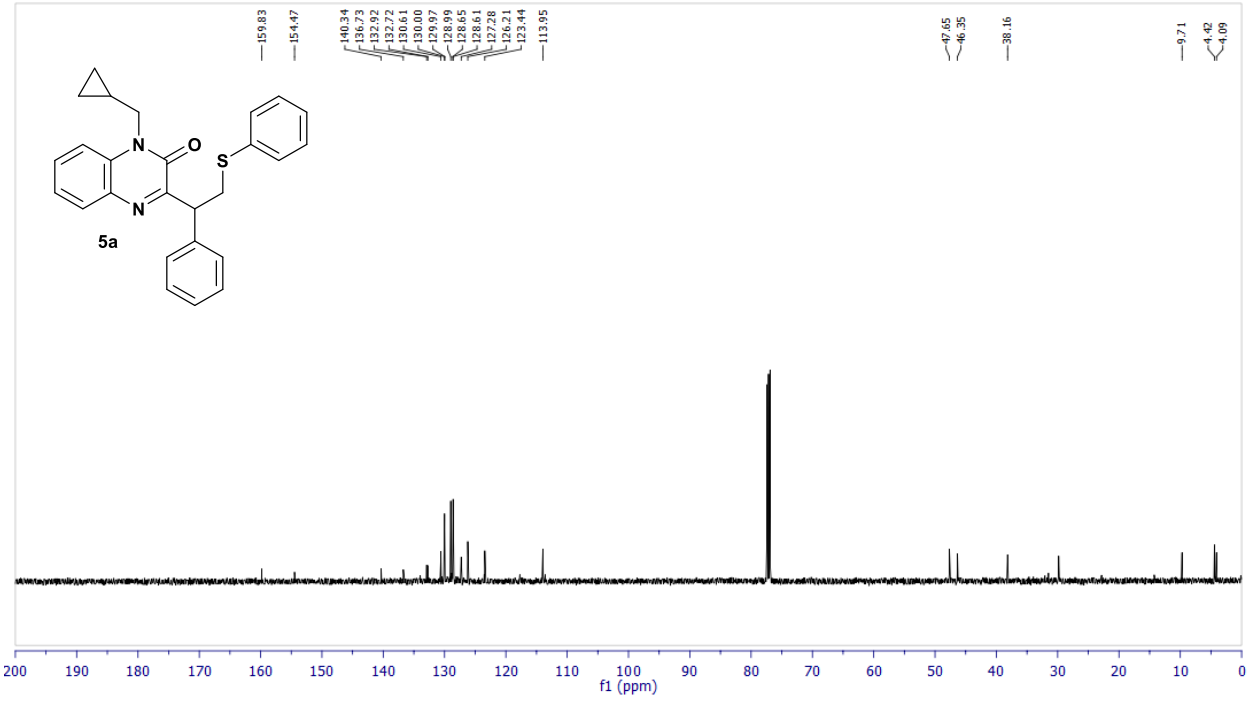
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4q**



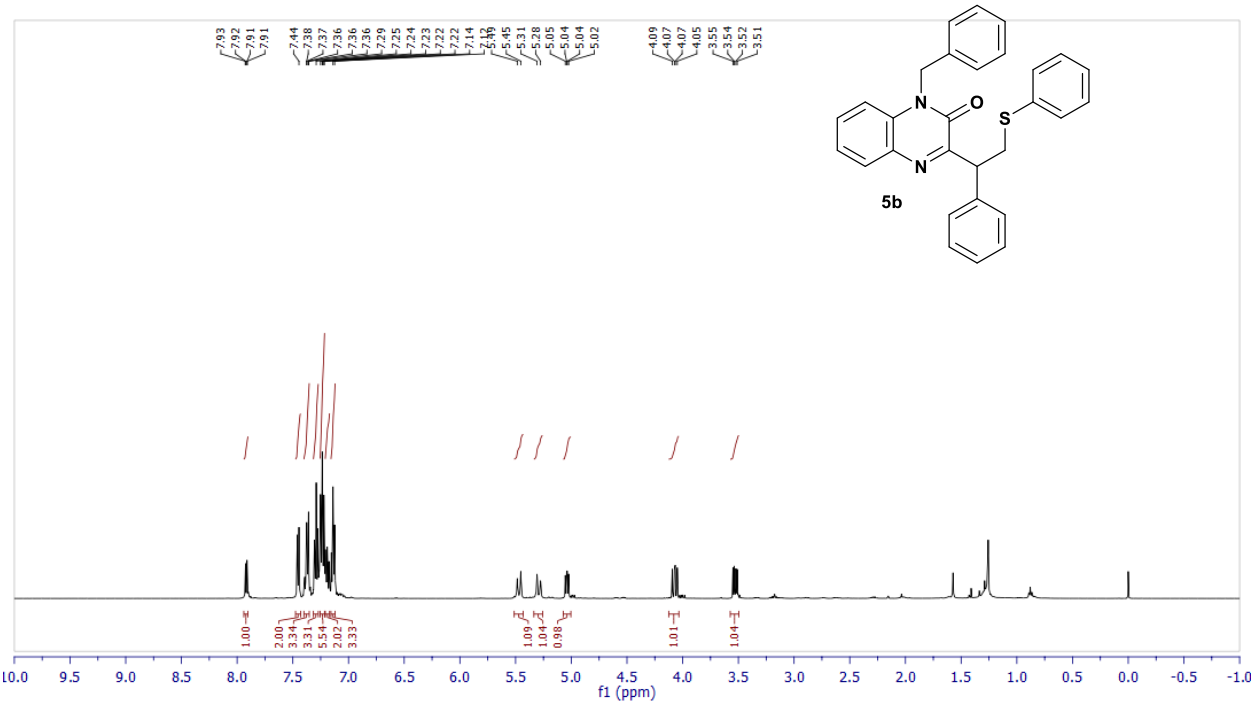
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5a**



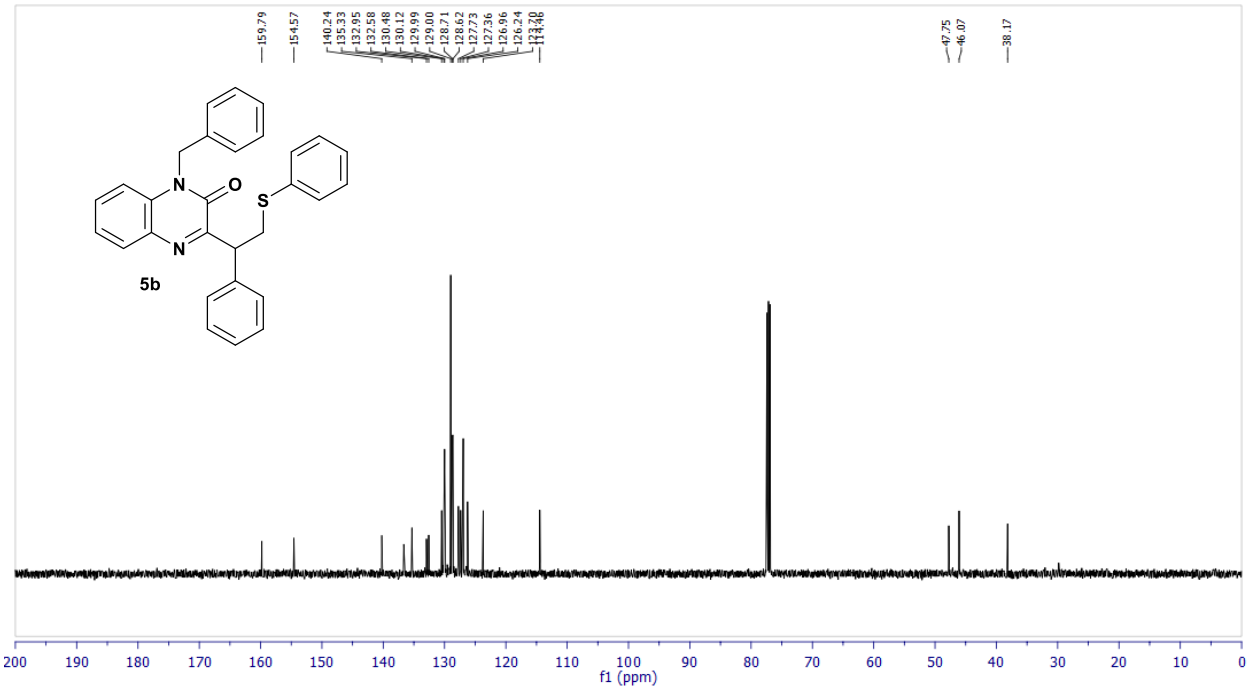
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5a**



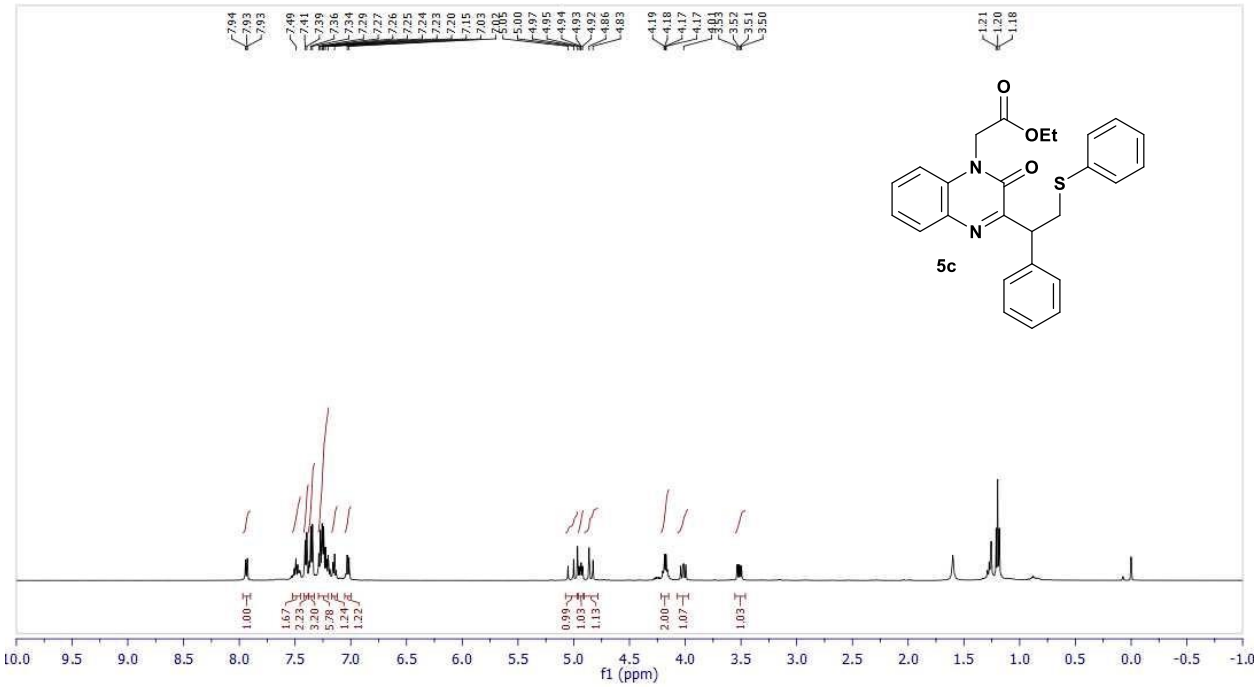
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5b**



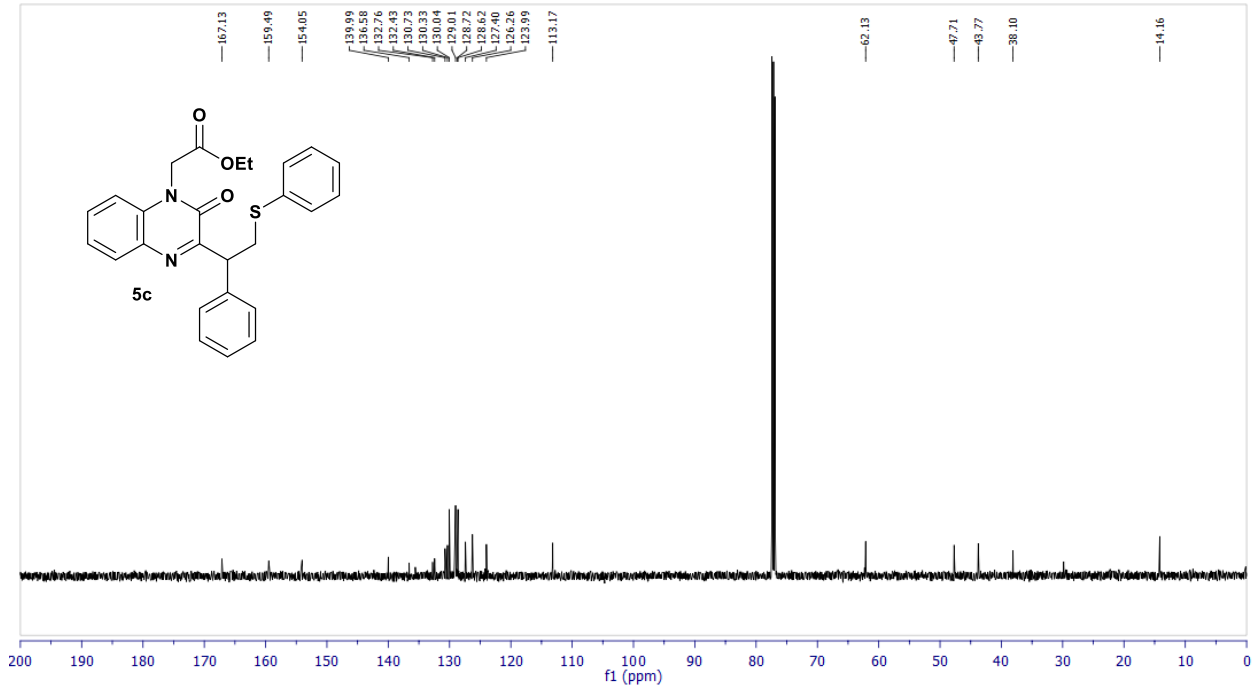
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5b**



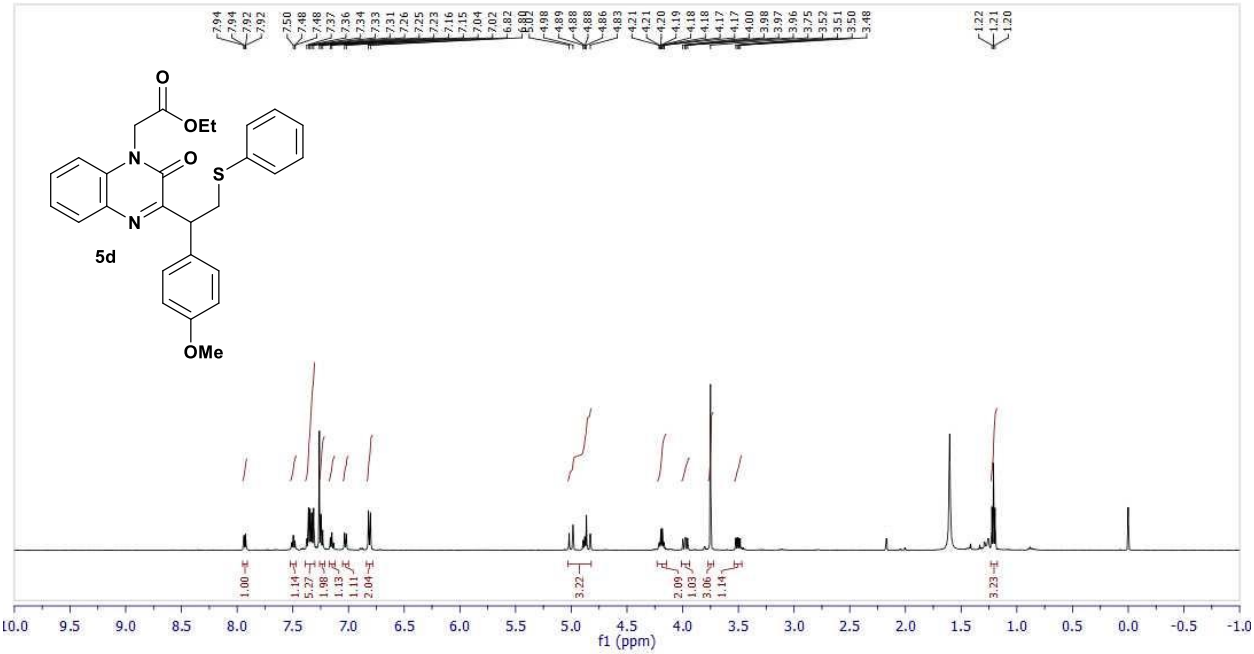
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5c**



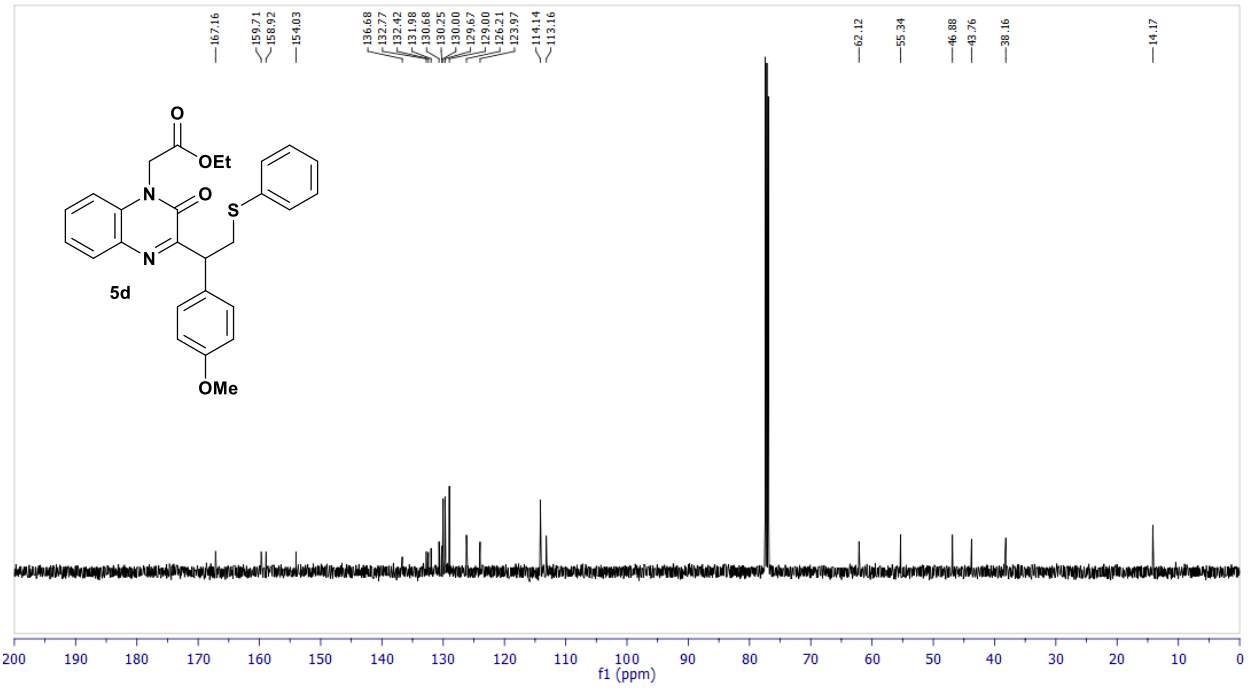
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5c**



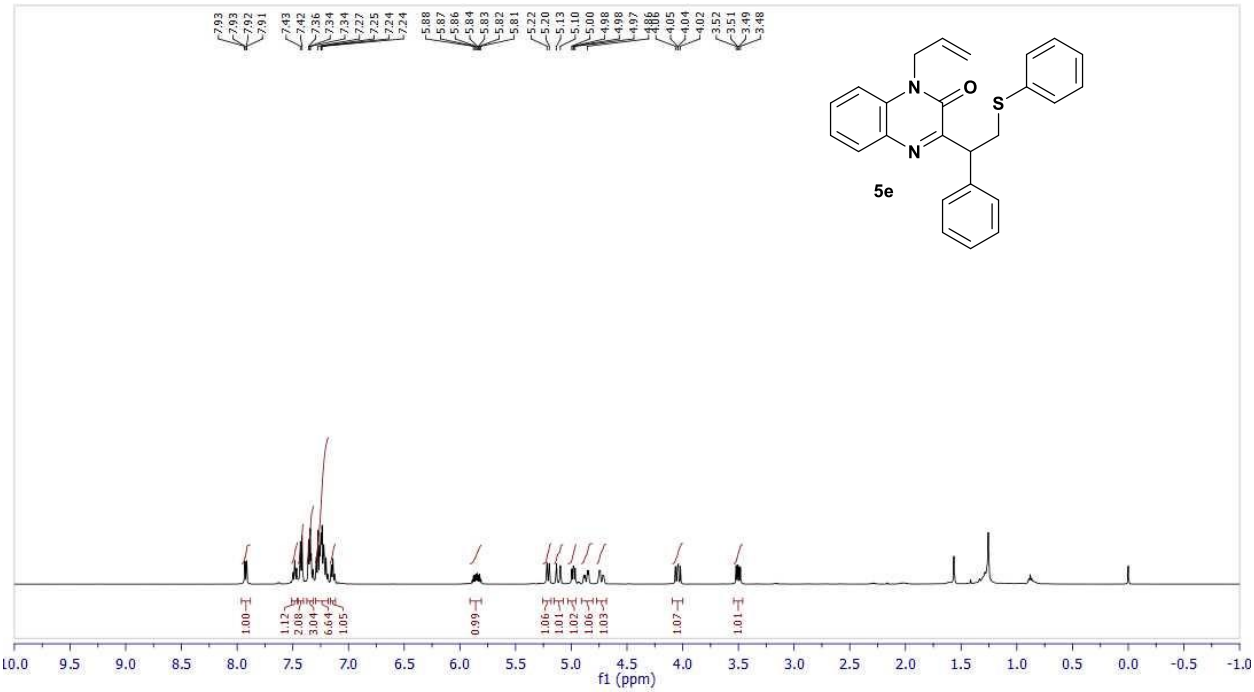
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5d**



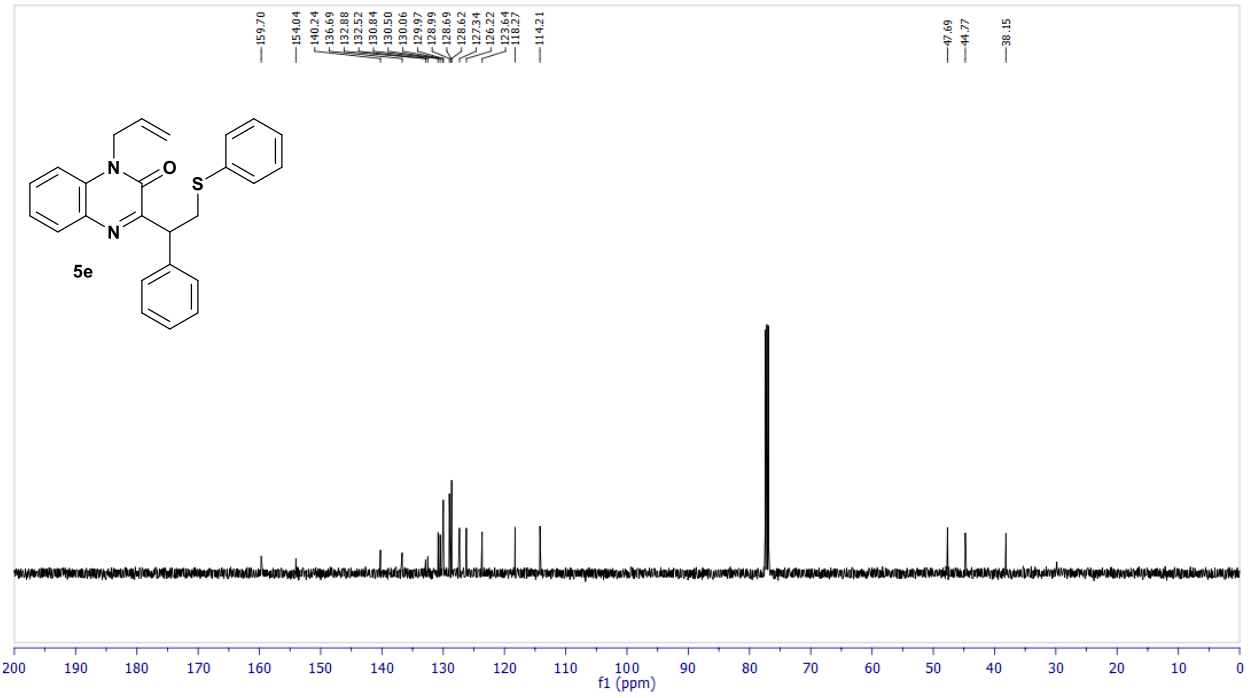
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5d**



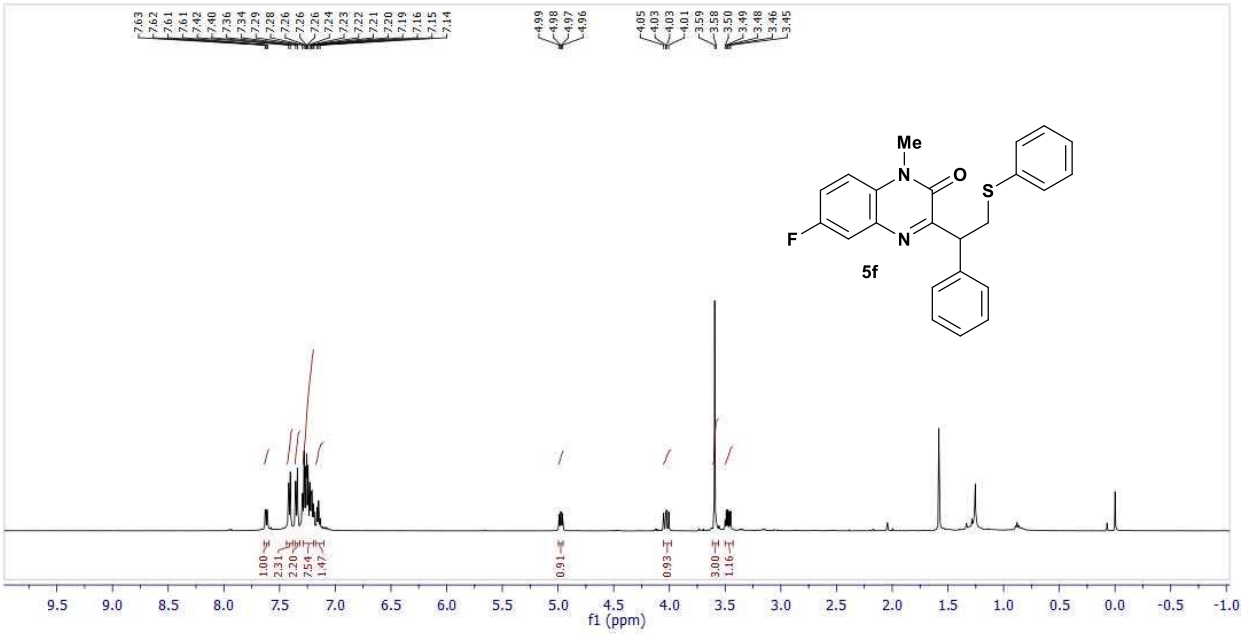
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5e**



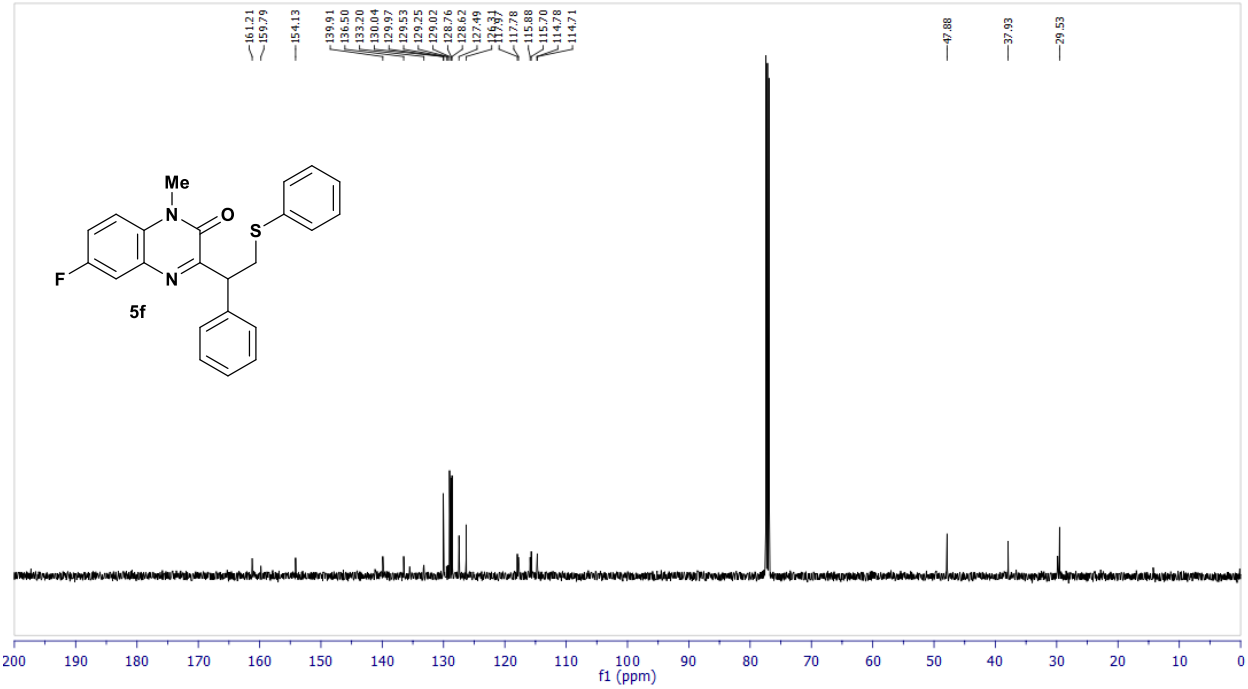
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5e**



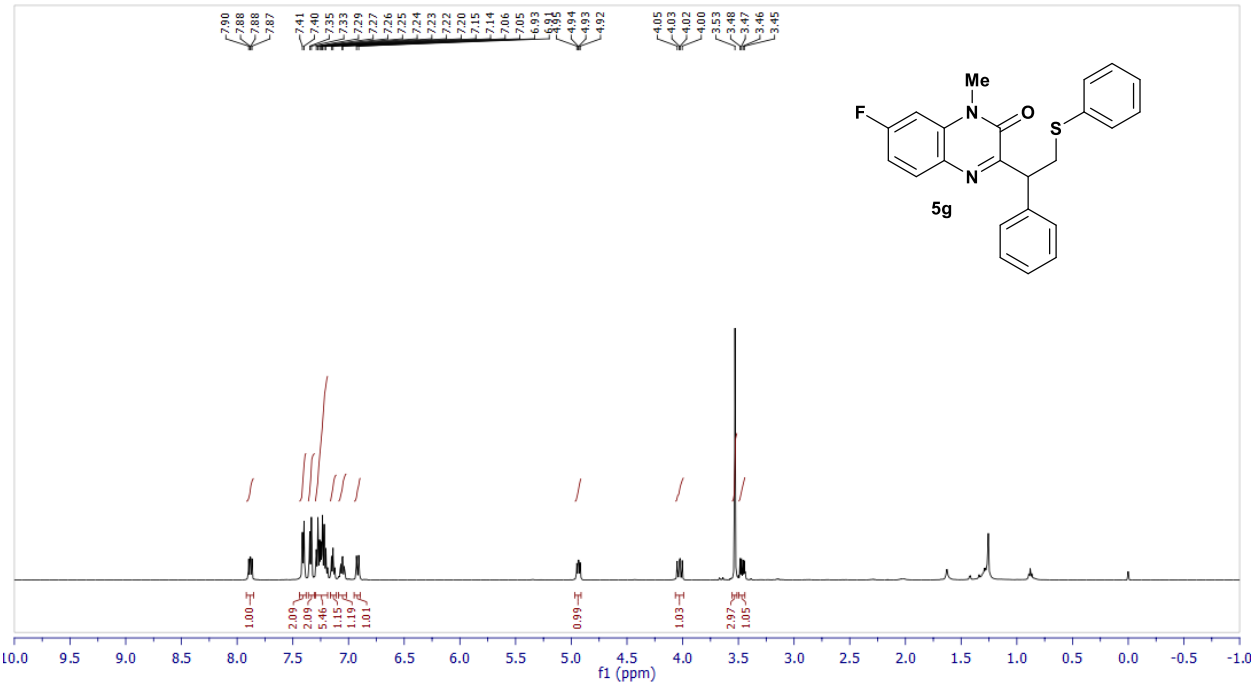
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5f**



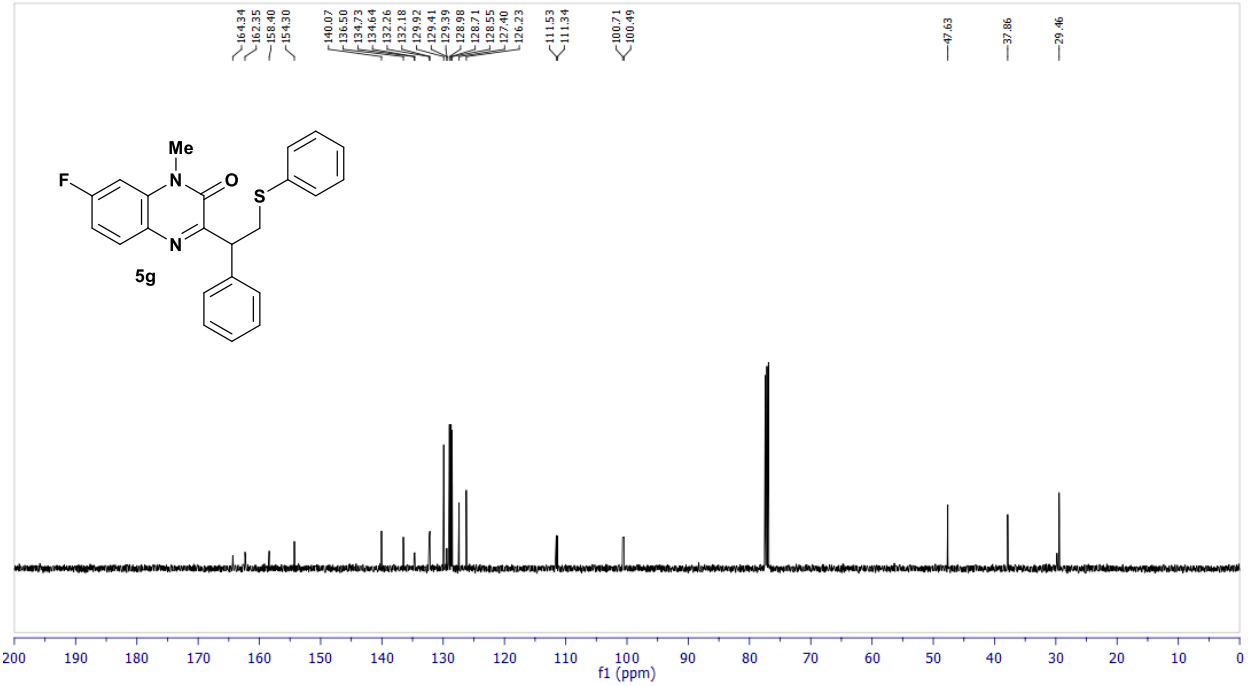
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5f**



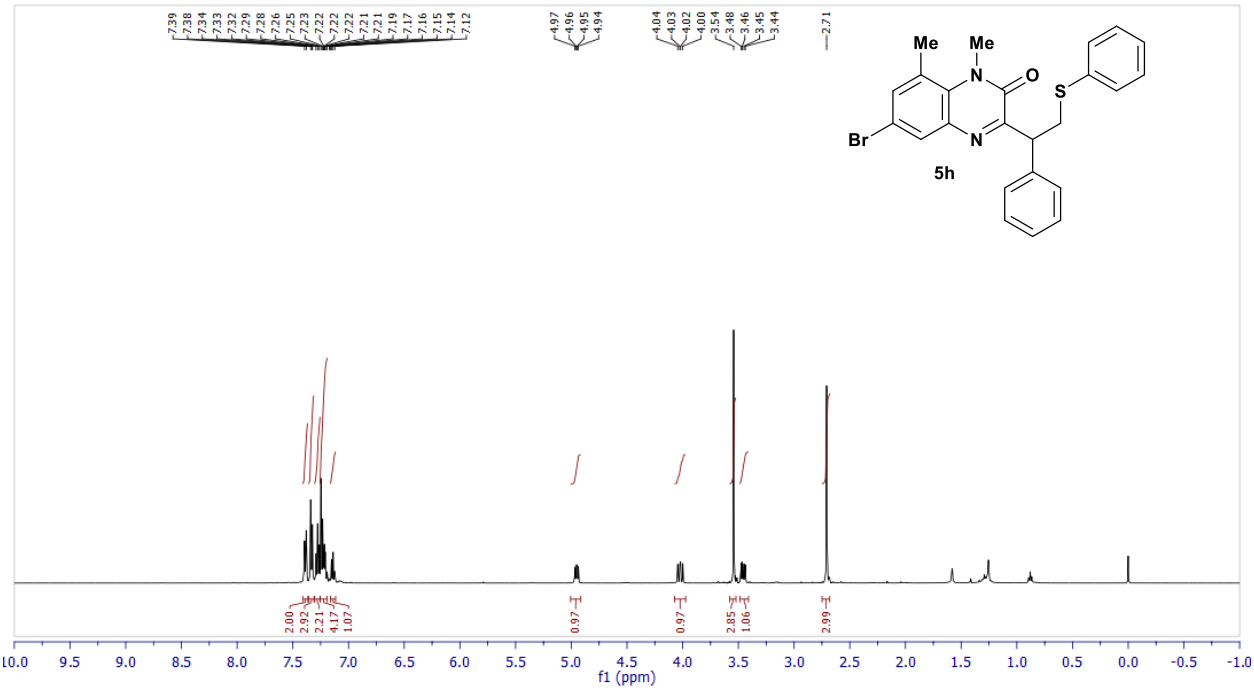
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5g**



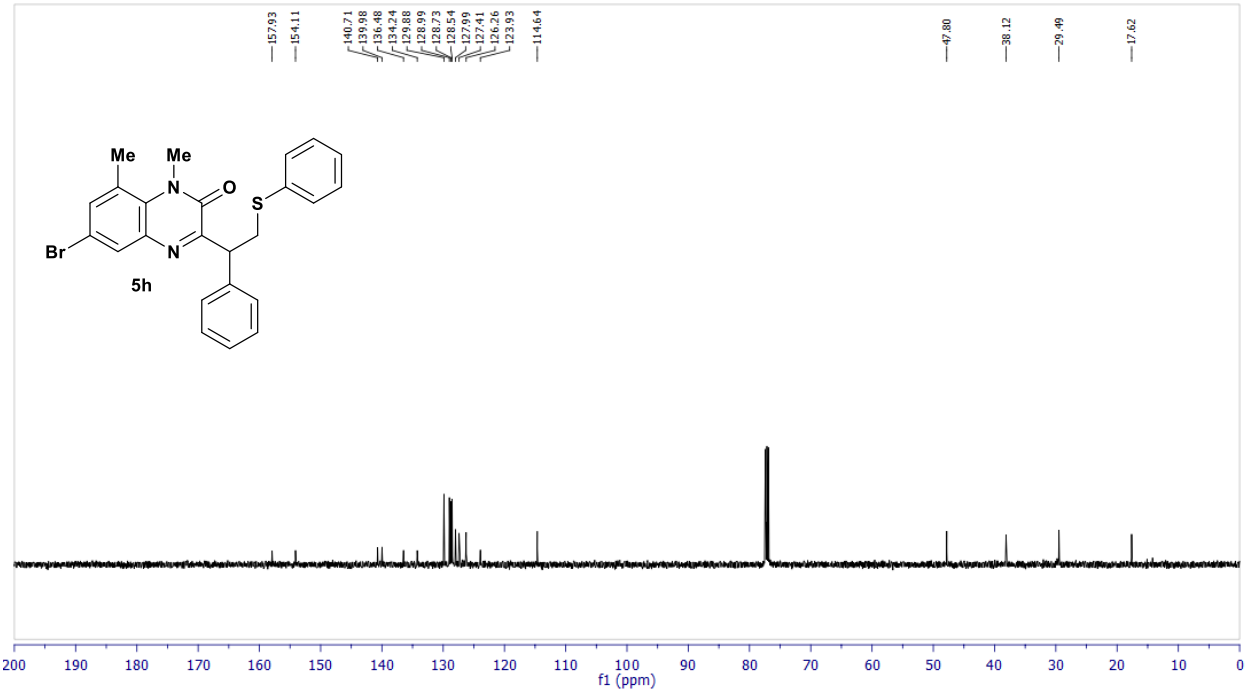
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5g**



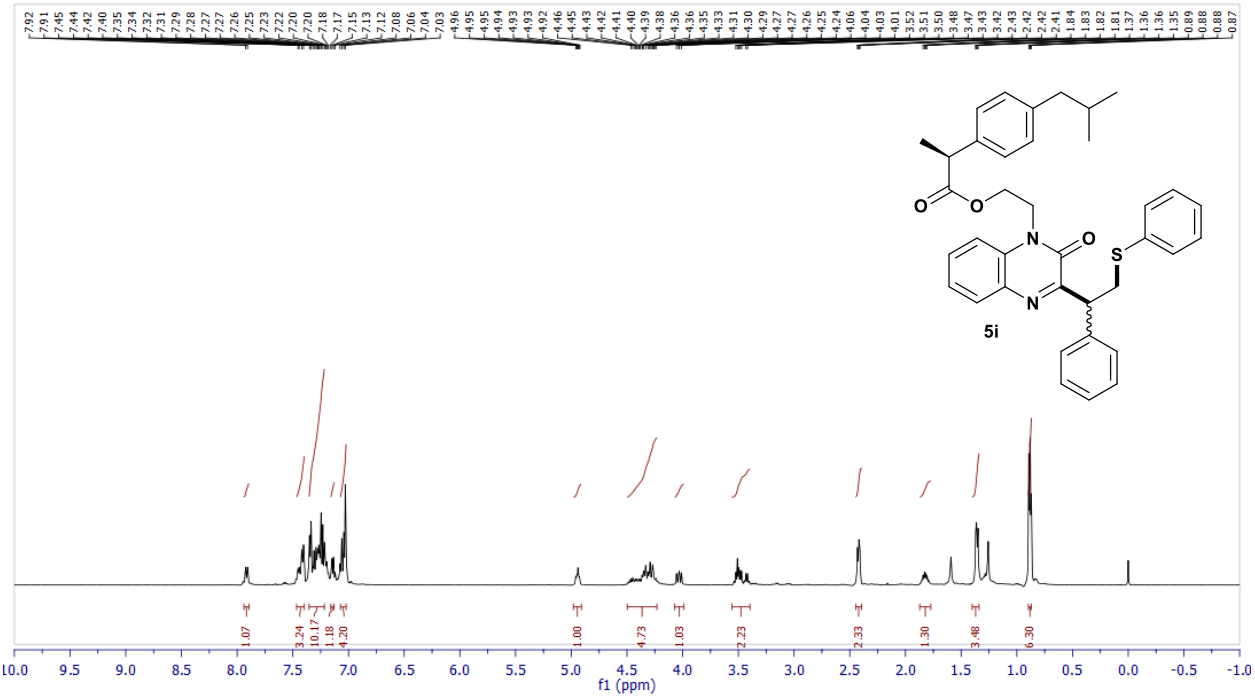
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5h**



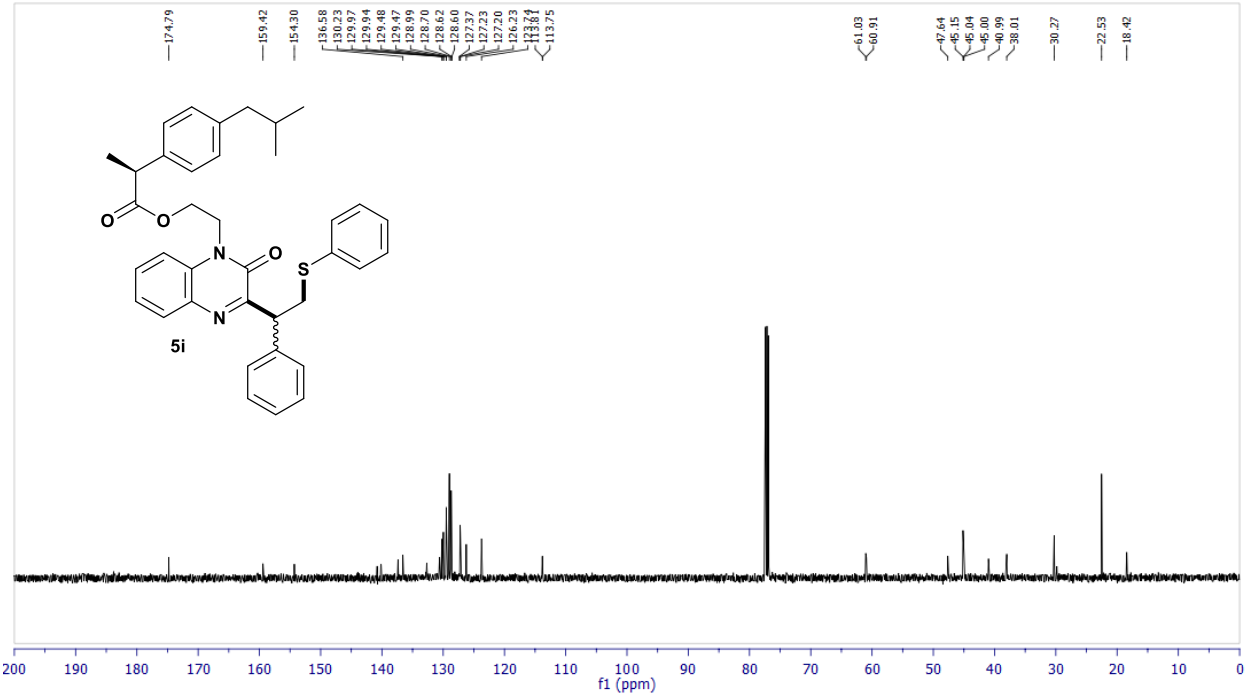
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5h**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5i**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **5i**



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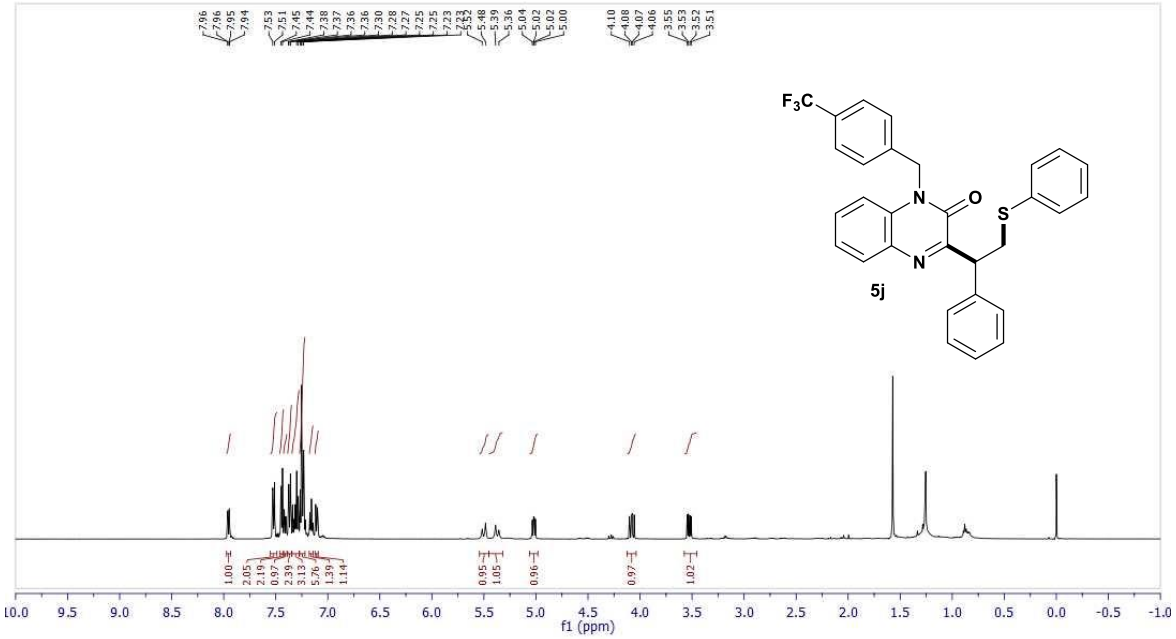
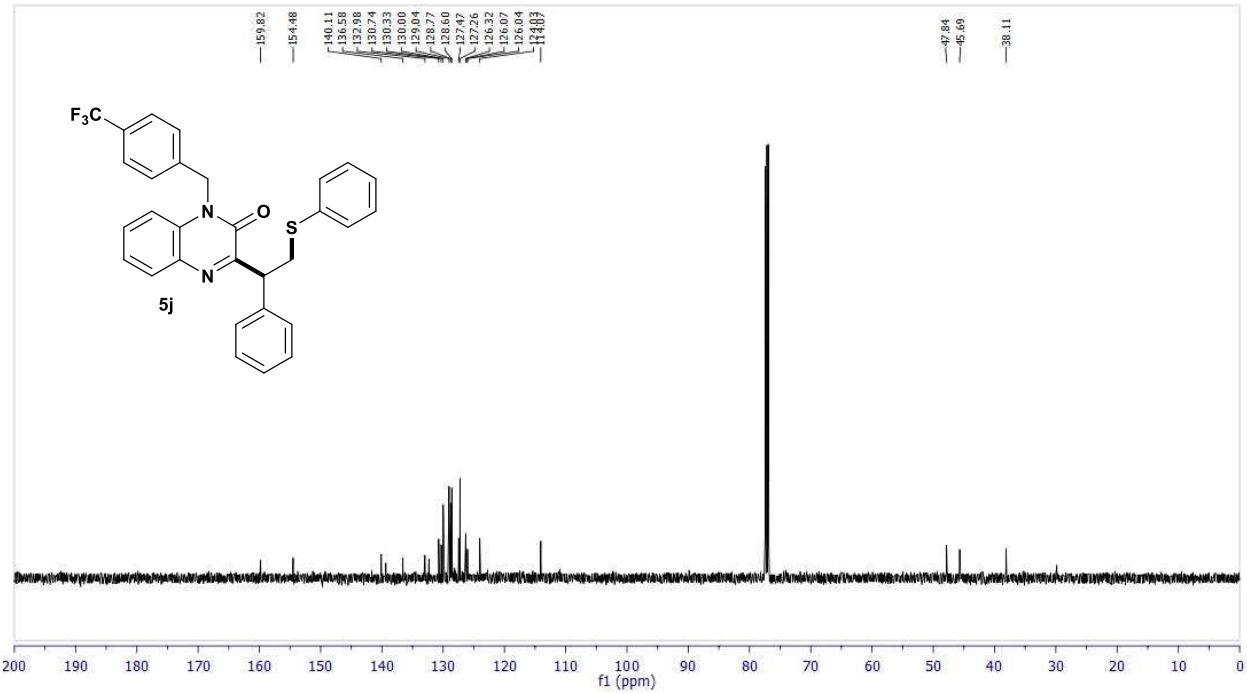
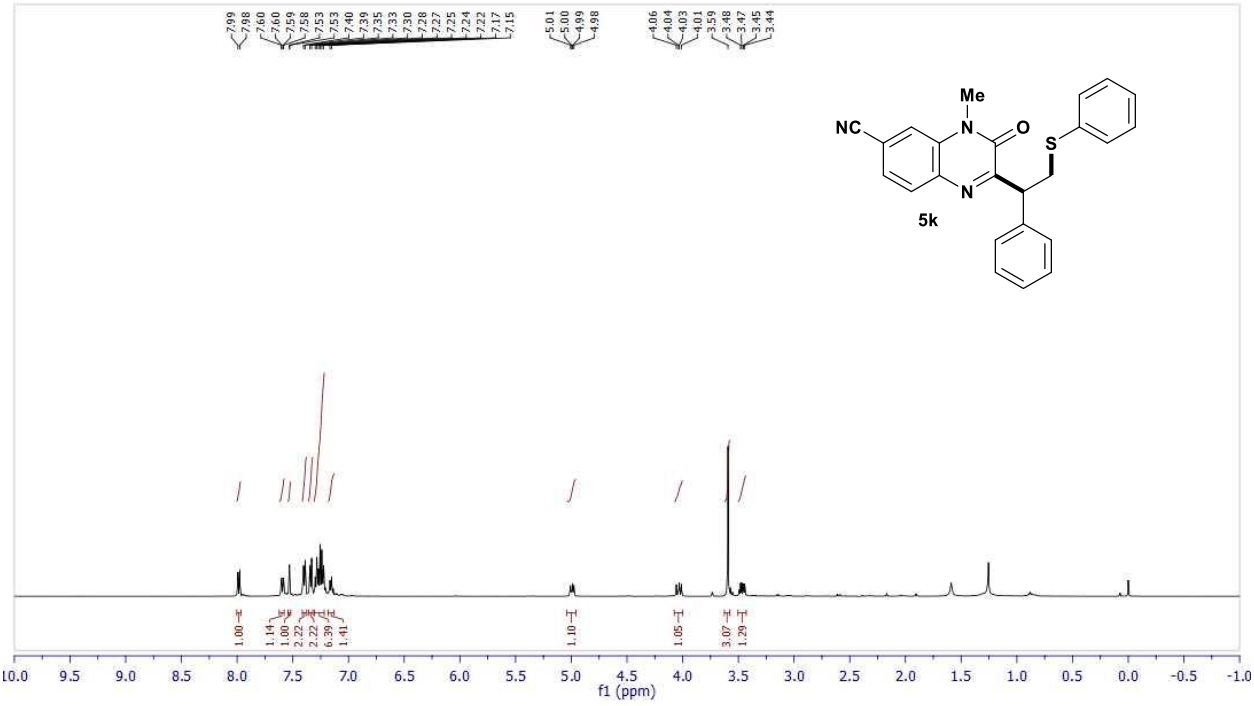


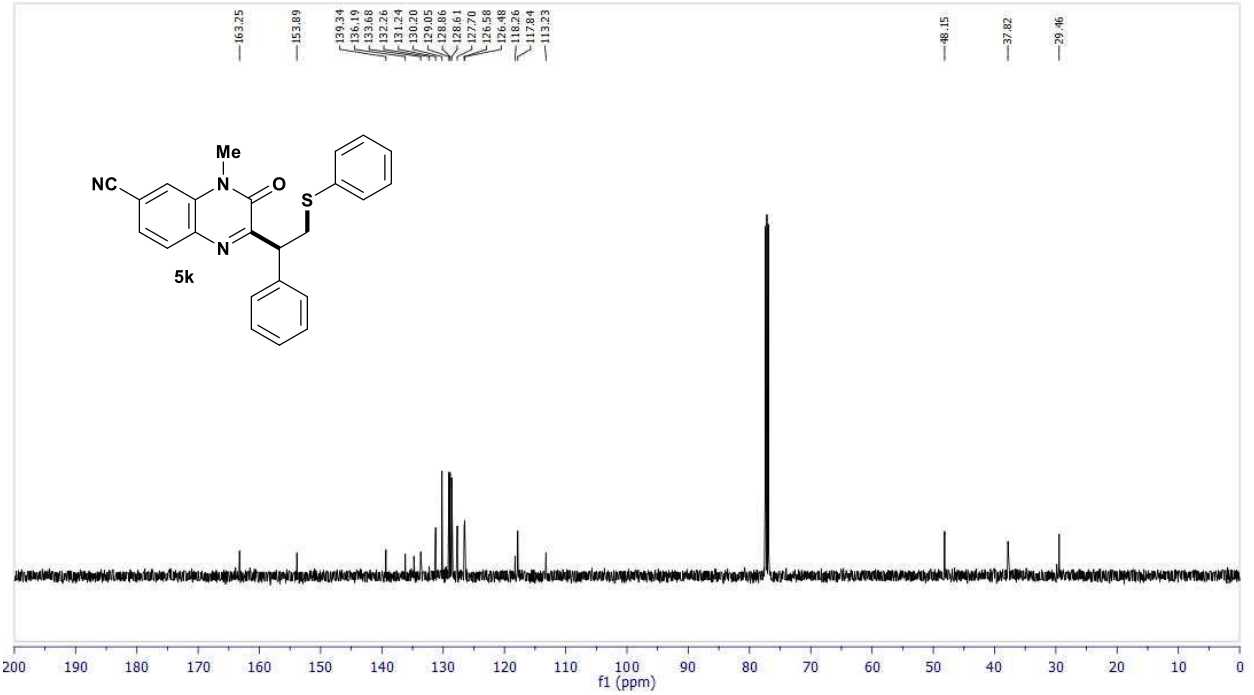
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5j**



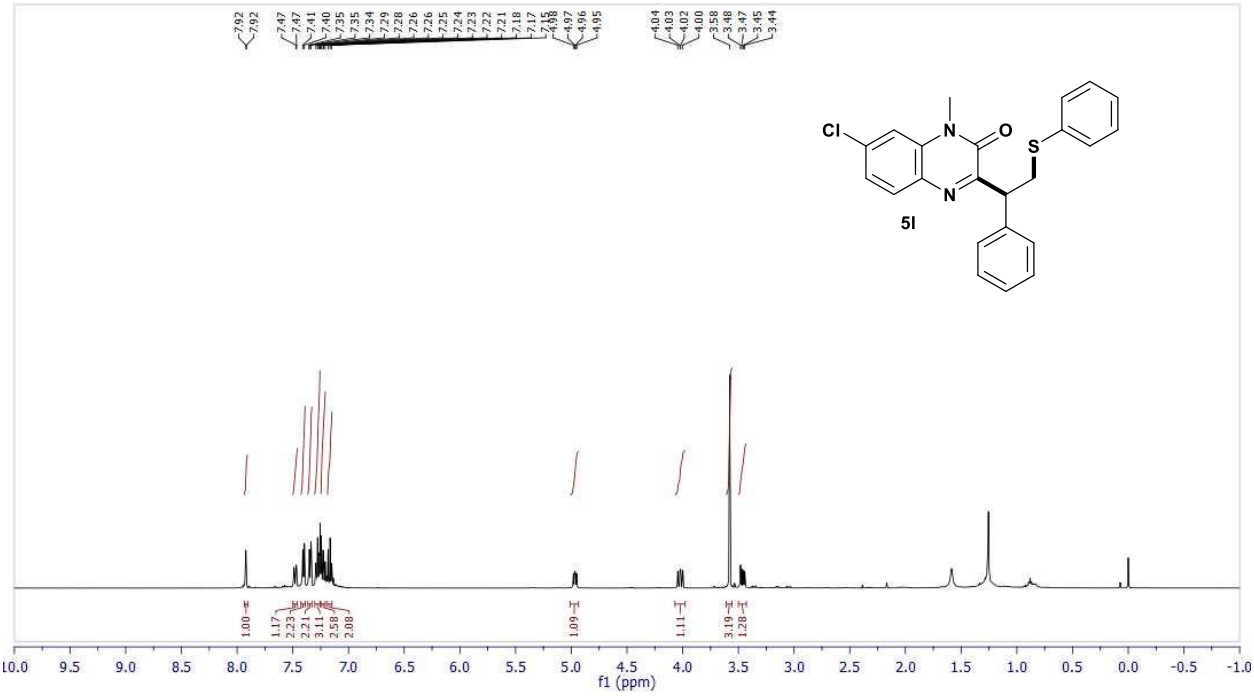
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5k**



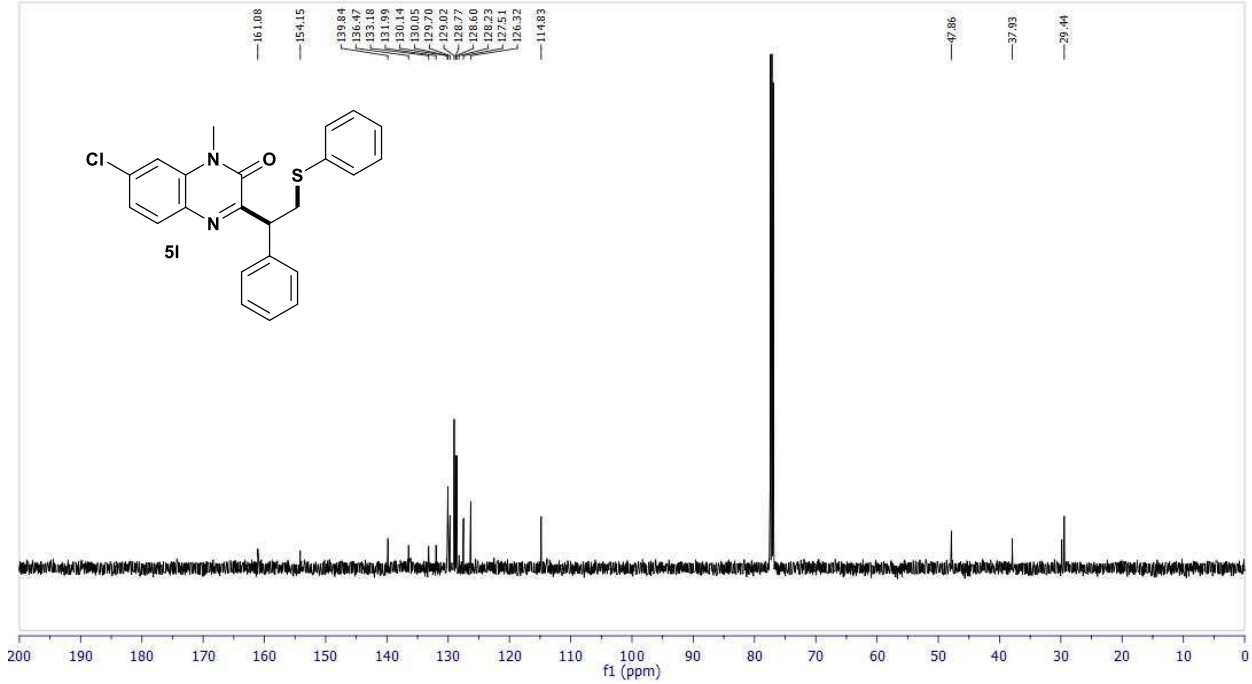
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5k**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5l**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **5l**



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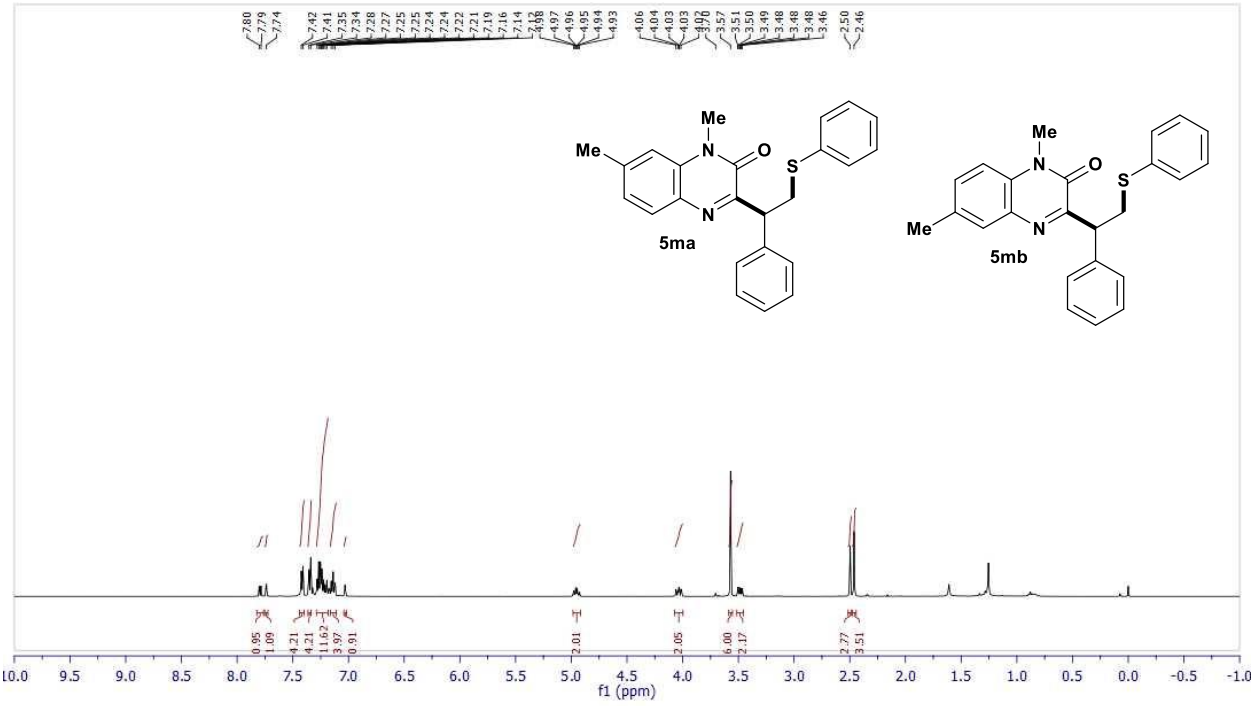
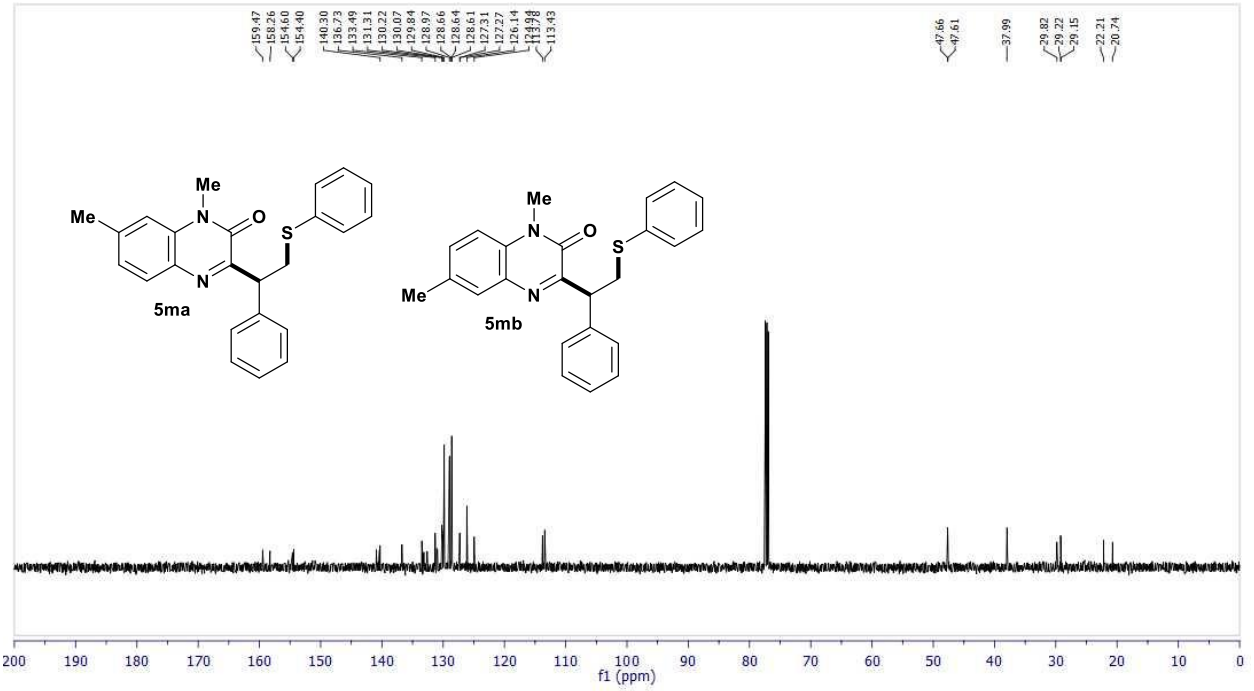
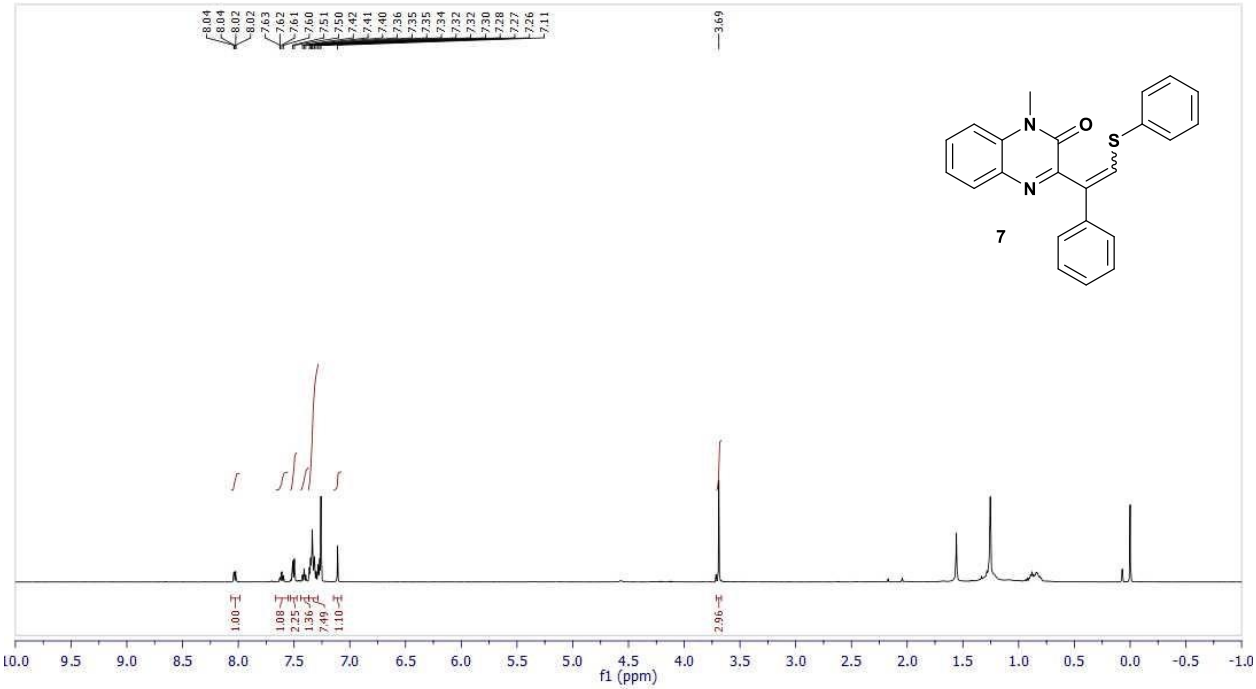


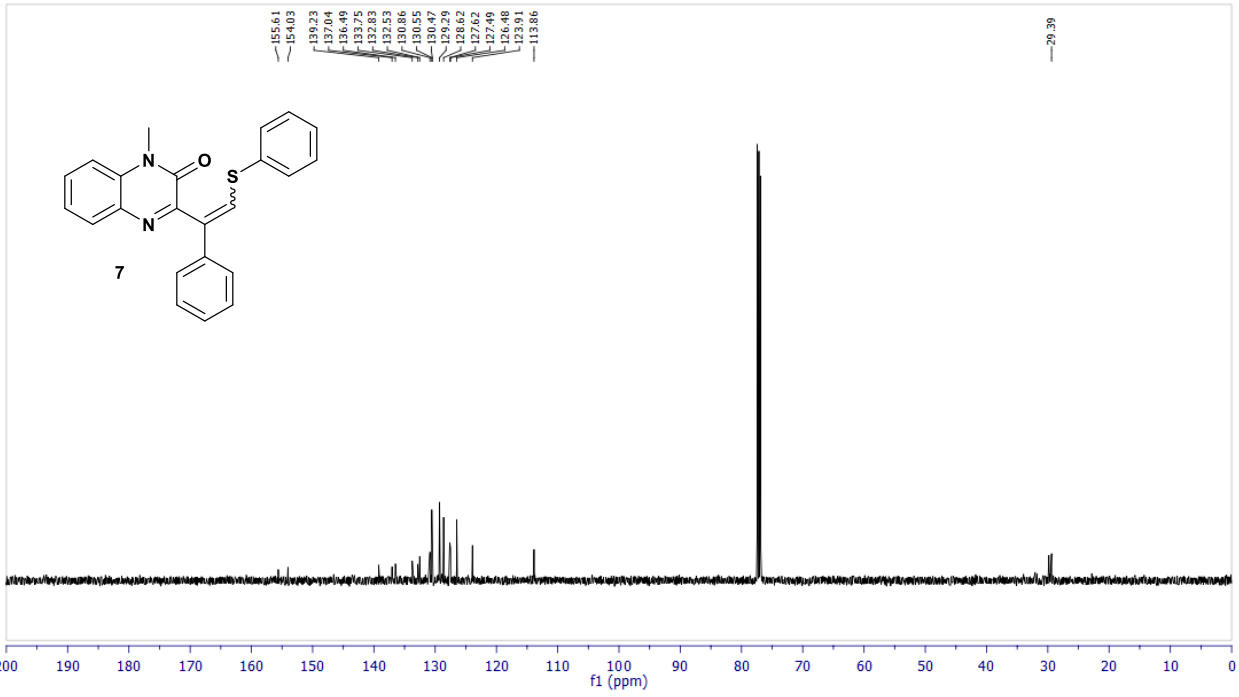
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5m**



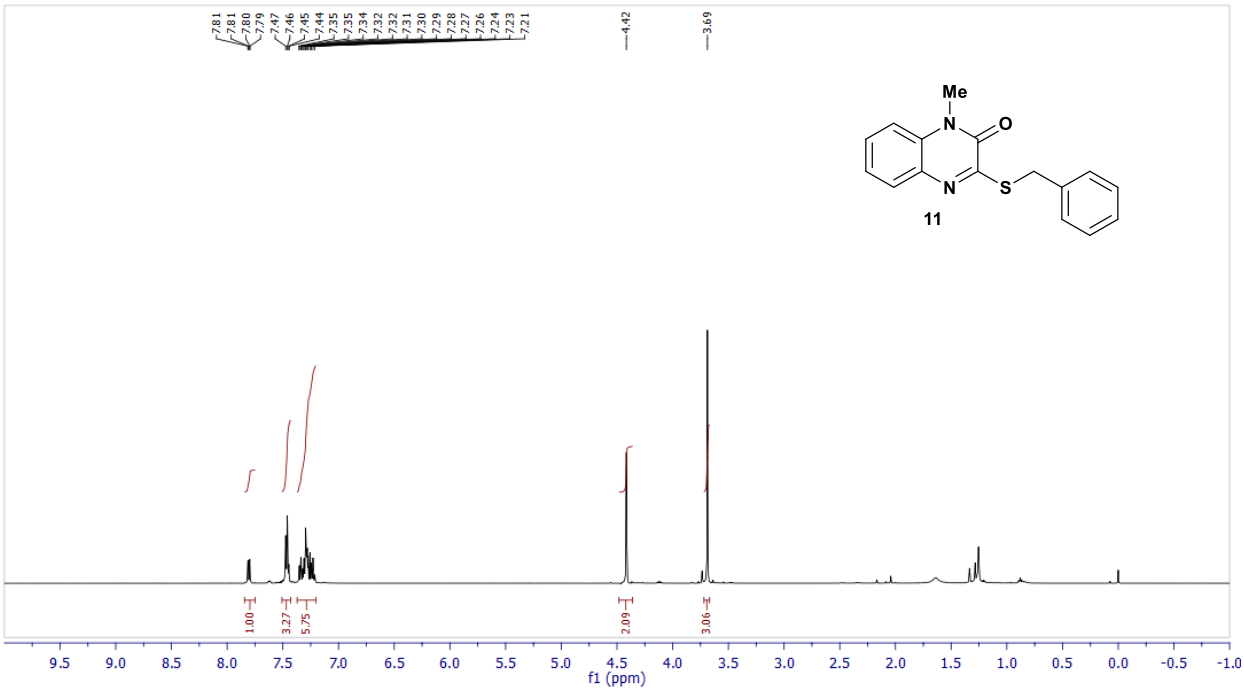
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **7**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **11**