Electrochemical cascade sequences for the remote C7–H bond thiocyanation of quinoxalin-2(1*H*)-ones with ammonium thiocyanate

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Table of Contents

General Information.

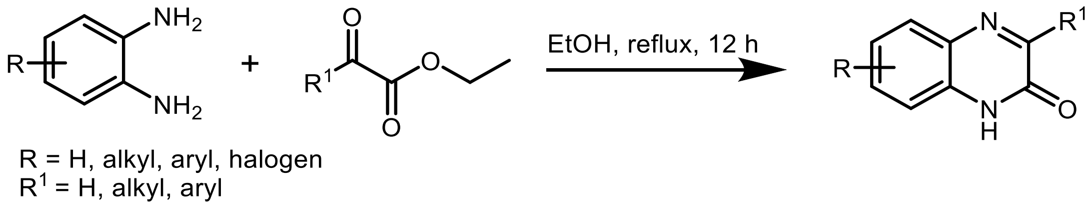
All reactions were carried out in oven-dried glassware. Reagents were purchased at the highest commercial quality and used as received, unless otherwise specified. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel plates (Merck silica gel 60, f$_{254}$); the spots were visualized with UV light (254 and 365 nm) and a solution of 5% H_2SO_4-MeOH or vanillin charring solution as developing agents. Flash column chromatography was performed using 230−400 mesh silica gel. Yields refer to isolated yields after chromatographic purification. ^{1}H NMR (600 MHz and 400 MHz) and ^{13}C NMR (151 MHz and 101 MHz) spectra were recorded in DMSO-d_6, $CDCl_3$, and Acetone-d_6 solvents and are reported relative to the residual solvent signal. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (J in Hz), and integration. The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS, *m/z*) were recorded using ESI (Q-TOF and Orbitrap, positive ion) mode. Infrared (IR) spectra were recorded on Fourier transform infrared spectroscopy; only intense peaks were reported in terms of frequency of absorption (cm^{-1}). Single-crystal X-ray data were recorded in a diffractometer with Mo Kα radiation. Melting points were determined in open-end capillary tubes and are uncorrected. Depending upon the availability of solvents in our laboratory, we used different deuterated solvents for recording ^{1}H and ^{13}C NMR spectra for the products.

Electrolysis general information

Electrochemical reactions were performed with ElectraSyn2.0 package (IKA) using the constant current or constant voltage modes. The reactions were conducted in a 10 mL vial for 5.0 mL of solvent with a stir bar and a carbon graphite-SK-50 (5.0 cm × 0.8 cm × 0.2 cm) working electrode (anode and cathode) with a distance of 0.6 cm between the two electrodes. The immersion depth of the electrode is about 1.5 cm.

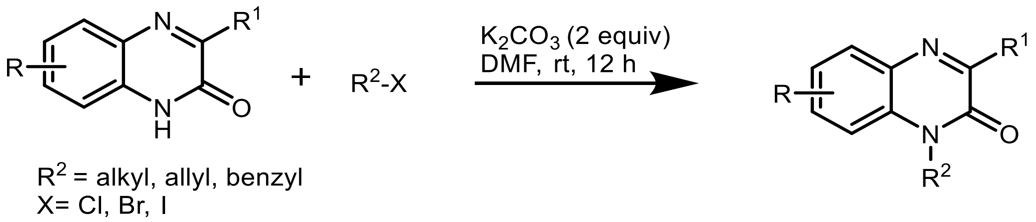
SI-1: General procedures for the synthesis of starting materials

SI-1-1: Preparation of quinoxalin-2 (1*H*)-one derivatives[1]



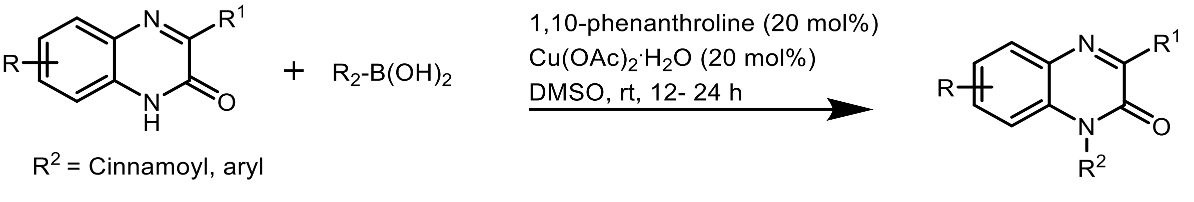
To a 100 mL round-bottomed flask with a stir bar was added 1,2-diaminobenzene (1.0 equiv), EtOH as a solvent, ethyl-2-oxoacetate (1.3 equiv), and then the mixture was refluxed at 80 °C for 12 h. The resulting precipitate was filtered, thoroughly washed with water, and dried under vacuum to afford quinoxalin-2 (1*H*) -ones.

SI-1-2: Preparation of *N–alkyl, –allyl, –benzyl* quinoxalin-2(1*H*)-one derivatives[2]



To a 100 mL round-bottomed flask with a stir bar was added quinoxalin-2(1*H*)-one (1.0 equiv), DMF solvent, K_2CO_3 (2.0 equiv) and stirred the mixture for 1 h and then R_2-X (1.5 equiv) was added dropwise. The reaction mixture was then stirred for 12 h at room temperature, brine solution was added and extracted with EtOAc. The combined extracts were dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography (*n*-hexane/EtOAc) to afford the desired products.

SI-1-3: Preparation of *N–cinnamoyl, –aryl* derivatives of quinoxalin-2(1*H*)-one[3]



To a 100 mL round-bottomed flask with a stir bar was added quinoxalin-2(1*H*)-one (1.0 equiv), aryl boronic acid (1.5 equiv), $Cu(OAc)_2{\cdot}H_2O$ (20 mol%), 1,10-phenanthroline (20 mol%) in DMSO, and the mixture was stirred at room temperature for 12-24 hours. After

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[1] M. Gao, Y. Li, L. Xie, R. Chauvin and X. Cui, *Chem. Commun.,* 2016, **52**, 2846-2849;

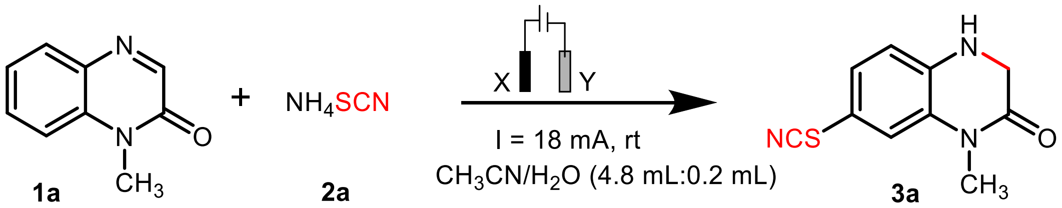
[2] H. Ni, X. Shi, Y. Li, X. Zhang, J. Zhao and F. Zhao, *Org. Biomol. Chem.,* 2020, **18**, 6558-6563;

[3] K. A. Kumar, P. Kannaboina, C. K. Jaladanki. P. V. Bharatam and P. Das, *ChemistrySelect,* 2016, **1**, 601–607;

completion of the reaction (monitored by TLC), brine solution was added and extracted with EtOAc. The combined extracts were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc) to afford the desired products.

SI-2: Optimization of reaction conditions

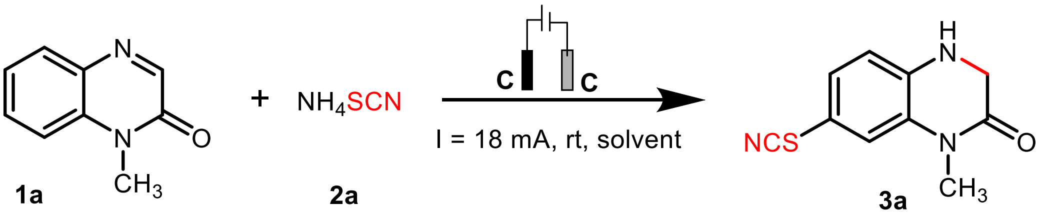
SI-2-1: Screening for the suitable electrodes (cathode and anode)



Entry	Anode (X)	Cathode (Y)	Time (h)	Yield **3a** (%)[a,b]
1	C	Pt	3.5	78
2	C	Ni	3.5	75
3	C	Ni foam	3.2	41
4	C	Sn	3.4	75
5	C	Mg	3.5	76
6	C	C	3.0	88
7	C	Glossy Carbon	3.0	78
8	Pt	Pt	3.2	41
9	Ni	C	3.5	n.r.
10	C	RVC	3.8	72

[a] Reaction conditions: Graphite plate anode (5.0 cm x 0.8 cm x 0.2 cm), Graphite plate cathode (5.0 cm x 0.8 cm x 0.2 cm), substrate **1a** (0.4 mmol), NH_4SCN **2a** (2.0 mmol), premixed solvent (CH_3CN/H_2O = 4.8:0.2, *v*/*v*, 5.0 mL), constant current (18 mA), under N_2, room temperature. [b] Isolated yield after column chromatography.

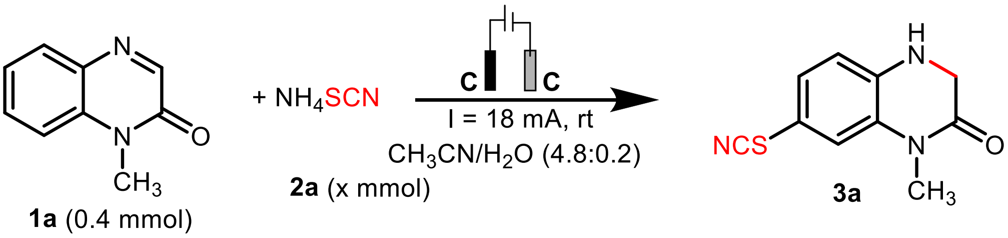
SI-2-2: Screening for the stoichiometry of water required



Entry	Solvent (mL)	Time (h)	Yield **3a** (%)[a,b]
1	dry CH_3CN (5)	6.0	16[c]
2	bottle grade CH_3CN (5)	3.3	66
3	$CH_3CN:H_2O$ (4.9:1)	3.3	73
4	$CH_3CN:H_2O$ (4.8:0.2)	3.0	88
5	$CH_3CN:H_2O$ (4.6:0.4)	3.4	42
6	$CH_3CN:H_2O$ (4:1)	3.4	40[c]
7	$CH_3CN:H_2O$ (3:2)	3.4	41[c]
8	$CH_3CN:H_2O$ (2.5:2.5)	4.3	21[c]
9	H_2O (5 mL)	5.0	n.r.

[a] Reaction conditions: Graphite plate anode (5.0 cm x 0.8 cm x 0.2 cm), Graphite plate cathode (5.0 cm x 0.8 cm x 0.2 cm), substrate **1a** (0.4 mmol), NH_4SCN **2a** (2.0 mmol), solvent (CH_3CN) or mixture of solvents (CH_3CN/H_2O, *v*/*v*, 5.0 mL), constant current (18 mA), under N_2, room temperature. [b] Isolated yield after column chromatography. [c] Starting decomposes.

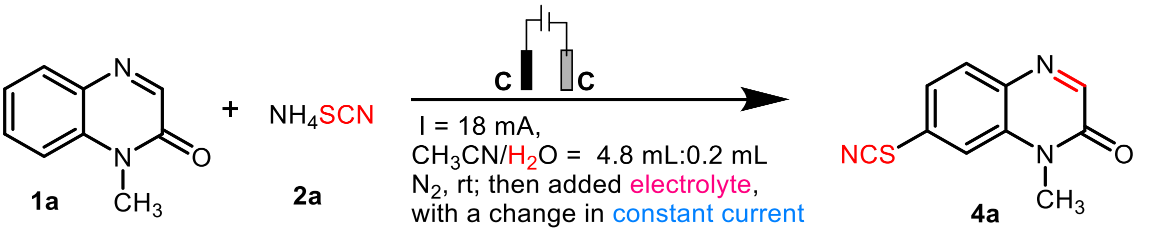
SI-2-3: Screening for the NH_4SCN (mmol) required



Entry	NH_4SCN (x mmol)	Time (h)	Yield **3a** (%)[a,b]
1	0.8	3.3	46[c]
2	1.2	3.3	53[c]
3	2	3.0	88
4	2.8	3.0	88

[a] Reaction conditions: Graphite plate anode (5.0 cm x 0.8 cm x 0.2 cm), Graphite plate cathode (5.0 cm x 0.8 cm x 0.2 cm), substrate **1a** (0.4 mmol), NH_4SCN **2a** (x mmol), premixed solvent (CH_3CN/H_2O = 4.8 mL:0.2 mL, *v*/*v*, 5.0 mL), constant current (18 mA), under N_2, room temperature. [b] Isolated yield after column chromatography. [c] Starting left.

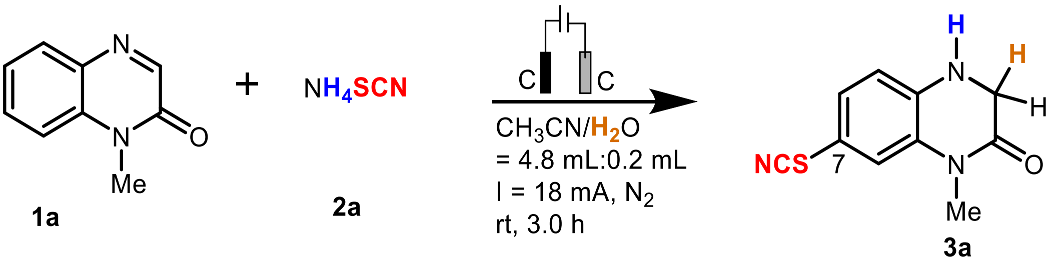
SI-2-4: Screening of electrolytes and applied constant current for the synthesis of 4a



Entry	Supporting electrolyte (equiv)	Constant current (mA)	Time (h)	Yield **4a** (%)[a,b]
1	$^{n}Bu_4NBF_4$ (1.5)	18	5.0	24[c]
2	$^{n}Bu_4NBF_4$ (1.5)	10	8.0	39[c]
3	$^{n}Bu_4NBF_4$ (1.5)	5	6.0	80
4	$^{n}Bu_4NBF_4$ (1.5)	2	7.5	77
5	$^{n}Bu_4NBF_4$ (1.0)	5	6.5	76
6	$^{n}Bu_4NBr$ (1.5)	5	6.5	68
7	$^{n}Bu_4NPF_6$ (1.5)	5	6.5	75
8	$LiClO_4$ (1.5)	5	6.5	60[c]
9	$^{n}Bu_4NClO_4$ (1.5)	5	6.5	70

[a] Reaction conditions: Graphite plate anode (5.0 cm x 0.8 cm x 0.2 cm), Graphite plate cathode (5.0 cm x 0.8 cm x 0.2 cm), substrate **1a** (0.4 mmol), NH_4SCN (2.0 mmol), premixed solvent (CH_3CN/H_2O = 4.8:0.2, v/v, 5.0 mL), constant current (18 mA), under N_2, room temperature; then added electrolyte with a constant current (5 mA). [b] Isolated yield after column chromatography. [c] Decomposition of **3a** with time.

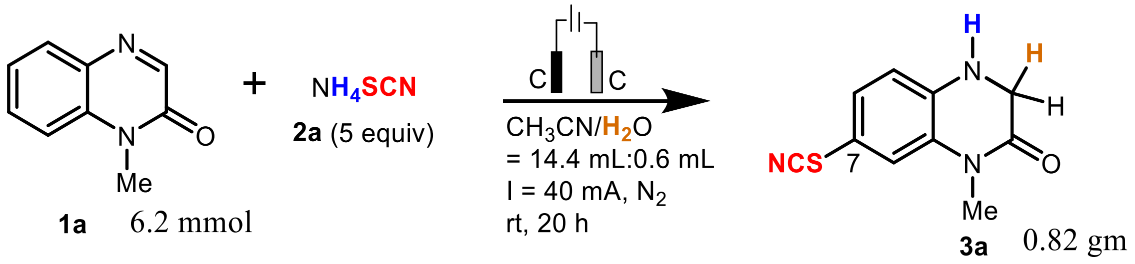
SI-3: General Procedure for the Synthesis of 3a from 1a



In an electrasyn undivided glass vial (10 mL) equipped with a stir bar, 1-methylquinoxalin-2(1*H*)-one **1a** (64 mg, 0.4 mmol), ammonium thiocyanate **2a** (152 mg, 2.0 mmol), and CH_3CN/H_2O (5.0 mL = 4.8:0.2) was added. The vial was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature for 3.0 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with DCM and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to afford the desired product **3a**.

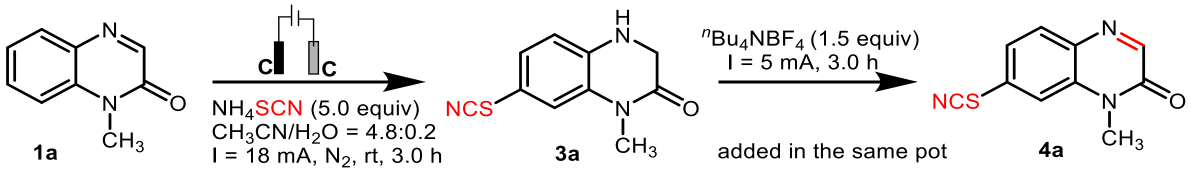
Following the same experimental protocol as mentioned, all the products **3** were prepared from **1** on a 0.4 mmol batch size.

SI-3-1: Procedure for gram scale Synthesis of 3a



In an electrasyn undivided glass vial (20 mL) equipped with a stir bar, 1-methylquinoxalin-2(1*H*)-one **1a** (1 gm, 6.2 mmol), ammonium thiocyanate **2a** (2.3 gm, 31 mmol), and CH_3CN/H_2O (15 mL = 14.4:0.6) was added. The vial was equipped with graphite plate as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 40 mA under N_2 atmosphere at room temperature for 20 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with DCM and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to afford 60% of the desired product **3a.**

SI-4: General Procedure for the Synthesis of 4a from 1a

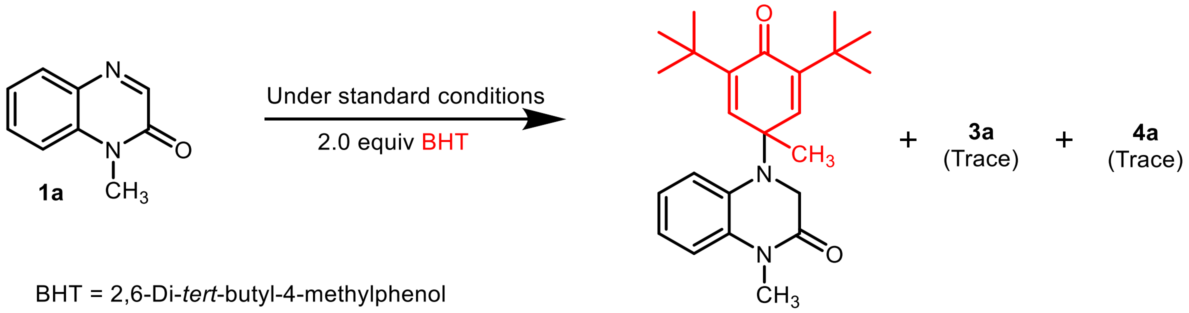


In an electrasyn undivided glass vial (10 mL) equipped with a stir bar, 1-methylquinoxalin-2(1*H*)-one **1a** (64 mg, 0.4 mmol), ammonium thiocyanate **2a** (152 mg, 2.0 mmol), CH_3CN/H_2O (5.0 mL = 4.8 mL:0.2 mL) was added. The vial was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature until complete consumption of **1a**. Therefore, supporting electrolyte $^{n}Bu_4NBF_4$ (197 mg, 1.5 equiv) was added into the same reaction pot and electrolyzed at a constant current of 5 mA under N_2 atmosphere at room temperature for 3.0 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with DCM and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to afford the desired product **4a**.

Following the same experimental protocol as mentioned, all the products **4** were prepared from **1** on a 0.4 mmol batch size via the intermediate **3**.

SI-5: Control experiment

SI-5-1: Radical trapping experiment with BHT (2,6-Di-*tert*-butyl-4-methylphenol)



BHT = 2,6-Di-*tert*-butyl-4-methylphenol

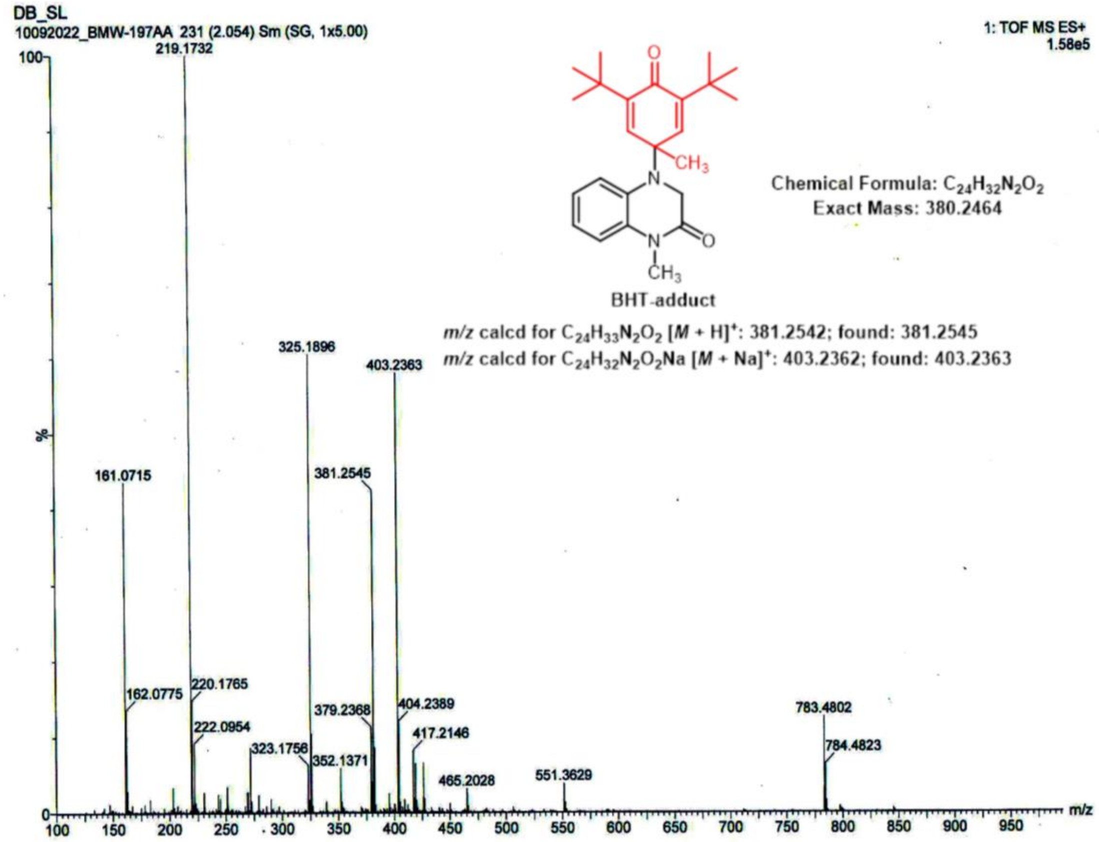
BHT-adduct (**5a**)
(detected by **^{1}H NMR spectroscopy** and **ESI-QTOF-HRMS** studies)

In an oven-dried undivided glass bottle (10 mL) equipped with a stir bar, **1a** (64 mg, 0.4 mmol, 1.0 equiv), ammonium thiocyanate **2a** (152 mg, 2.0 mmol), 2,6-di-*tert*-butyl-4-methylphenol BHT (176 mg, 2.0 equiv), CH_3CN/H_2O (4.8 mL:0.2 mL) were sequentially added. The bottle was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature for 30 minutes, then a small aliquot was taken for the ESI-QTOF-HRMS studies. The formation of a BHT-adduct **5a** (ESI-QTOF-HRMS: *m/z* calcd for $C_{24}H_{33}N_2O_2$ $[M + H]^+$: 381.2542; found: 381.2545 and *m/z* calcd for $C_{24}H_{32}N_2O_2Na$ $[M + Na]^+$: 403.2362; found: 403.2363) suggested that the reaction proceeds through the radical pathway. This further confirmed that the reaction initially underwent electrochemical reduction at the C=N double bond followed by the electrochemical thiocyanation at the C7-position to generate the desired product.

To isolate the corresponding **5a**, the crude mixture was purified by silica gel column chromatography. However, it remained inseparable with other unidentified product mixtures. We were able to collect the ^{1}H NMR of the mixture, where **5a** was the major product.

^{1}H NMR of the mixture **5a** (major product in the BHT-adduct)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1 H), 7.07 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.96-7.01 (m, 2 H), 6.43 (s, 2H), 3.66 (s, 2 H), 3.34 (s, 3 H), 1.42 (s, 3 H), 1.17 ppm (s, 18 H). HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{33}N_2O_2$ $[M + H]^+$: 381.2542; found: 381.2545 and *m/z* calcd for $C_{24}H_{32}N_2O_2Na$ $[M + Na]^+$: 403.2362; found: 403.2363

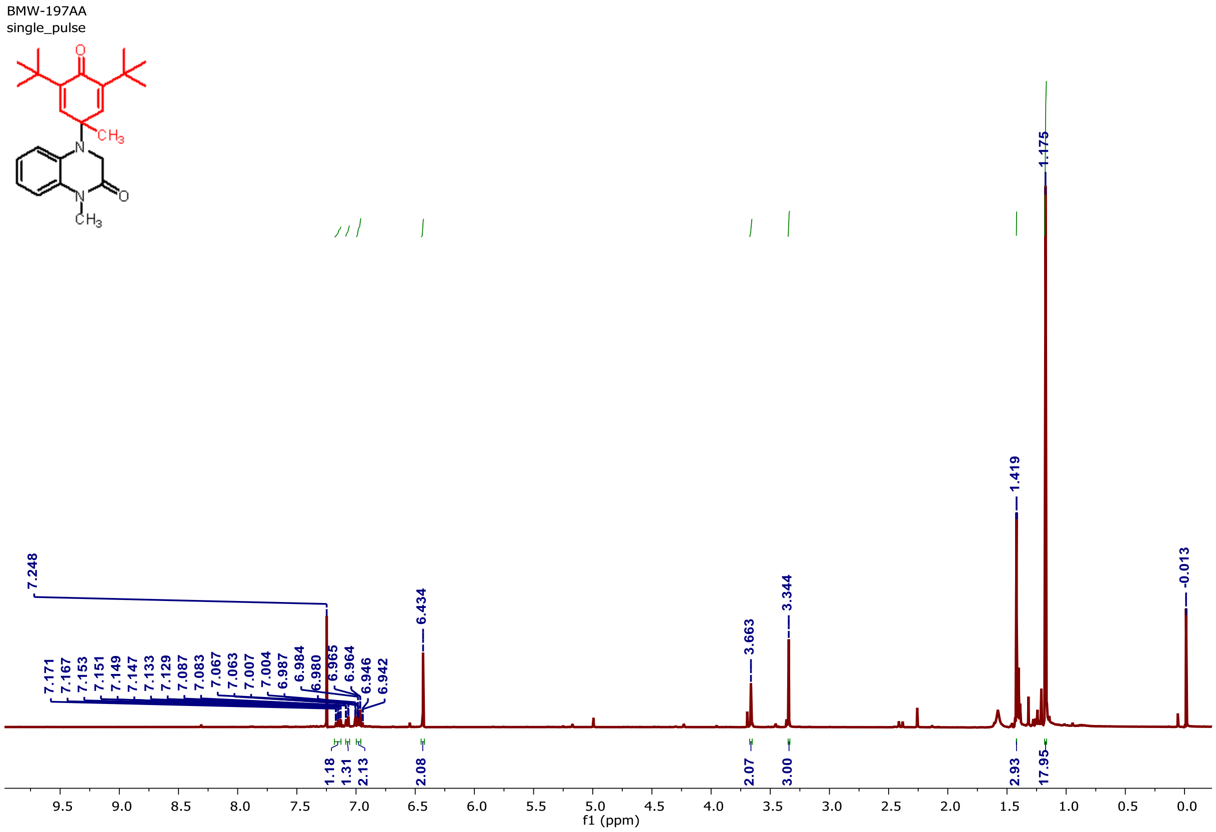
ESI-QTOF-HRMS spectra of **5a**:



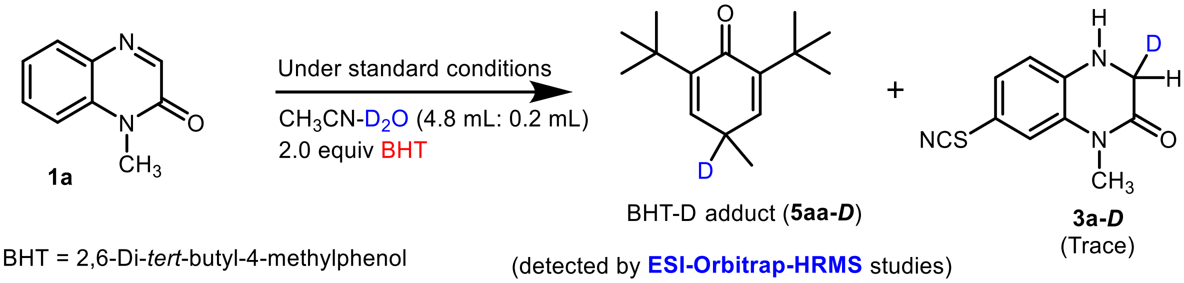
Chemical Formula: $C_{24}H_{32}N_2O_2$
Exact Mass: 380.2464

m/z calcd for $C_{24}H_{33}N_2O_2$ [*M* + H]$^+$: 381.2542; found: 381.2545
m/z calcd for $C_{24}H_{32}N_2O_2Na$ [*M* + Na]$^+$: 403.2362; found: 403.2363

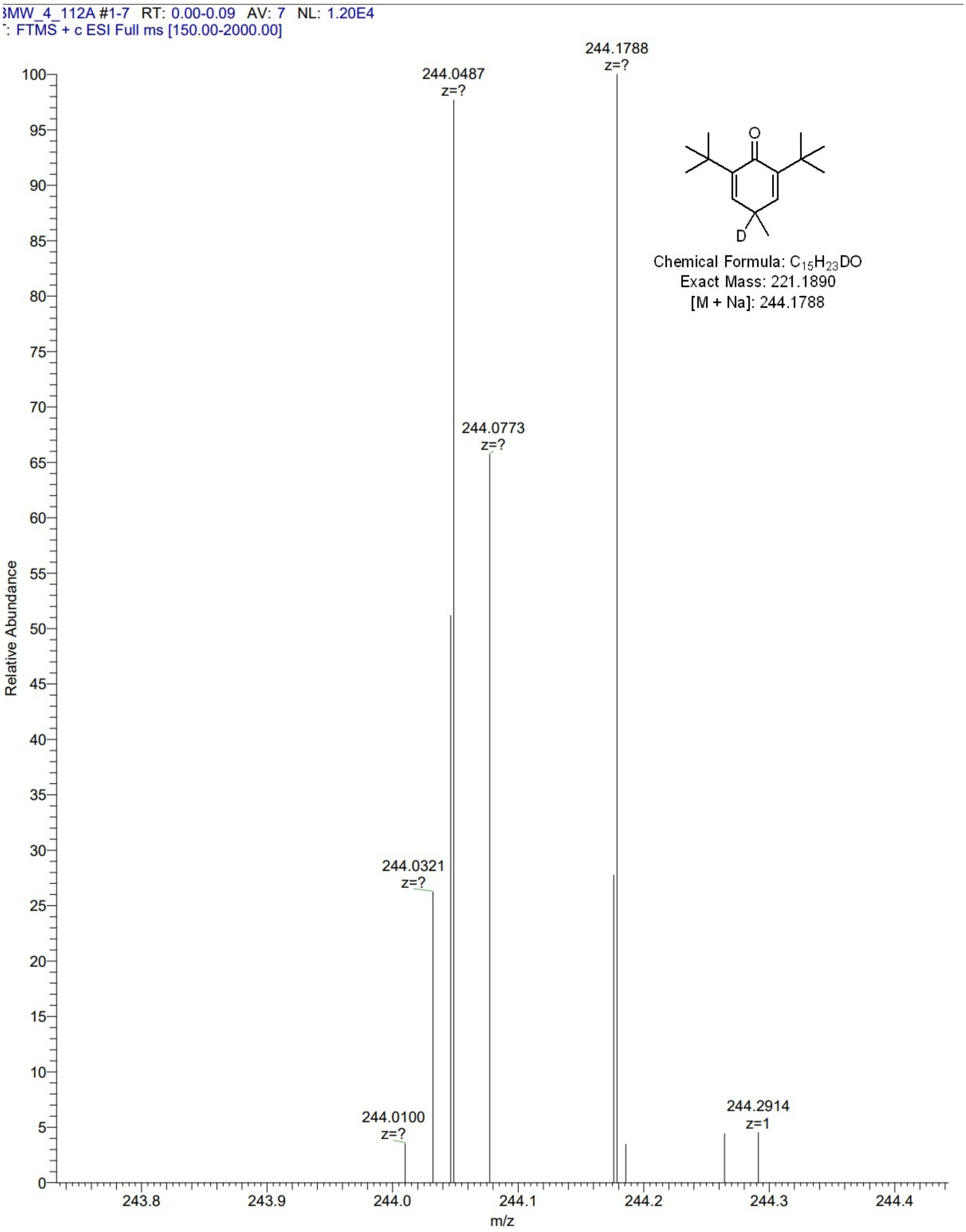
^{1}H (400 MHz, $CDCl_3$) NMR spectra of **5a**, contaminated with inseparable mixtures:



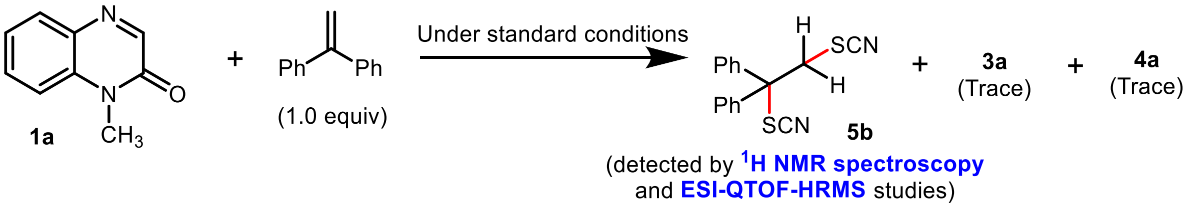
SI-5-1a: Deuterium radical trapping experiment with BHT.



In an oven-dried undivided glass bottle (10 mL) equipped with a stir bar, **1a** (64 mg, 0.4 mmol), ammonium thiocyanate **2a** (152 mg, 2.0 mmol), 2,6-di-*tert*-butyl-4-methylphenol BHT (176 mg, 2.0 equiv), dry CH_3CN/D_2O (4.8 mL:0.2 mL) were sequentially added. The bottle was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature for 30 minutes, then a small aliquot was taken for the ESI-Orbitrap-HRMS studies. The formation of a BHT-D adduct **5aa-*D*** (ESI-Orbitrap-HRMS: *m/z* calcd for *m/z* calcd for $C_{15}H_{23}DONa$ $[M + Na]^+$: 244.1788; found: 244.1788 suggested that the deuterium radical formed during cathodic reduction of D_2O. The cathodic reduction of D_2O may generate deuterium radical which can combine with C-3 carbon radical center of **1a** to form intermediate **II** (Proposed mechanism in Scheme 3 of the manuscript).


3MW_4_112A #1-7 RT: 0.00-0.09 AV: 7 NL: 1.20E4
: FTMS + c ESI Full ms [150.00-2000.00]
244.1788
z=?
244.0487
z=?
244.0773
z=?
244.0321
z=?
244.0100
z=?
244.2914
z=1
O
D
Chemical Formula: C15H23DO
Exact Mass: 221.1890
[M + Na]: 244.1788
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
243.8
243.9
244.0
244.1
244.2
244.3
244.4
m/z

SI-5-2: Trapping of the in-situ generated thiocyanogen (SCN)$_2$ intermediate

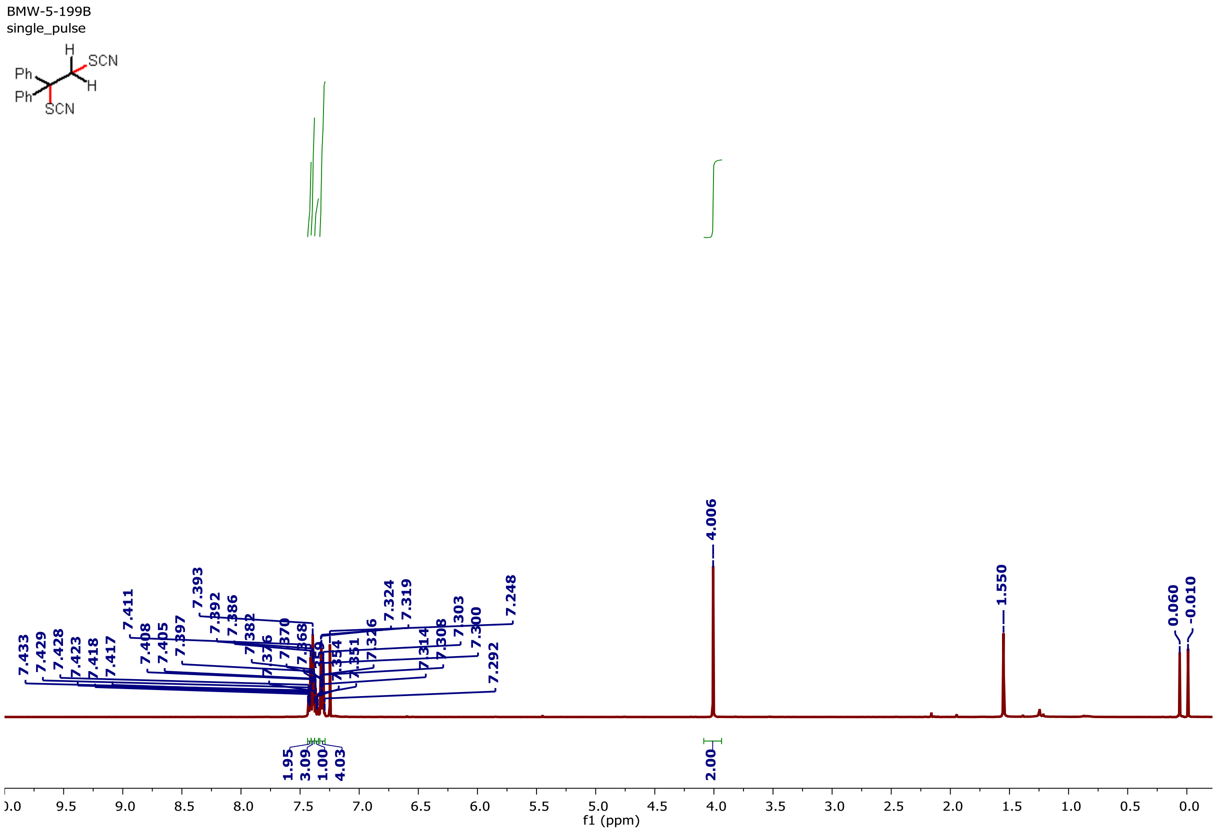


In an oven-dried undivided glass bottle (10 mL) equipped with a stir bar, **1a** (64 mg, 0.4 mmol), ammonium thiocyanate **2a** (152 mg, 2.0 mmol), 1,1-diphenylethylene (137 µL, 2.0 equiv), and CH_3CN/H_2O (5.0 mL = 4.8:0.2) were added. The bottle was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature for 30 minutes, then a small aliquot was taken for ESI-QTOF studies, which had supported the formation of an adduct via the addition of thiocyanogen (SCN)$_2$ to 1,1-diphenylethylene. The formation of the addition product (1,2-dithiocyanatoethane-1,1-diyl)dibenzene (**5b**) suggested that thiocyanogen was initially generated via the anodic oxidation of thiocyanate, which was utilized further for the thiocyanation to deliver the desired product.

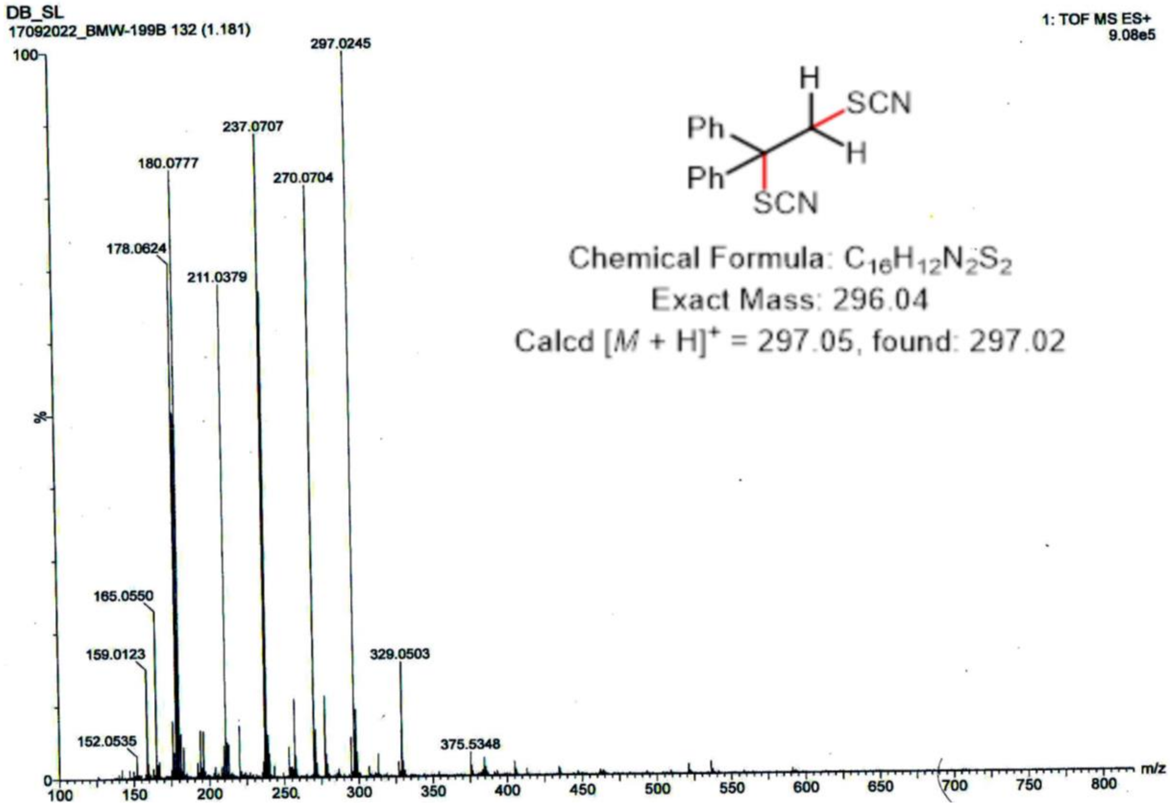
We were able to isolate the pure 1,2-dithiocyanatoethane-1,1-diyl)dibenzene (**5b**) after column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.44 (m, 2 H), 7.38-7.41 (m, 3 H), 7.35-7.38 (m, 1 H), 7.29-7.33 (m, 4 H), 4.01 ppm (s, 2 H).

^{1}H (400 MHz, $CDCl_3$) NMR spectra of 1,2-dithiocyanatoethane-1,1-diyl) dibenzene (**5b**)



ESI-QTOF spectra of 1,2-dithiocyanatoethane-1,1-diyl) dibenzene (**5b**)

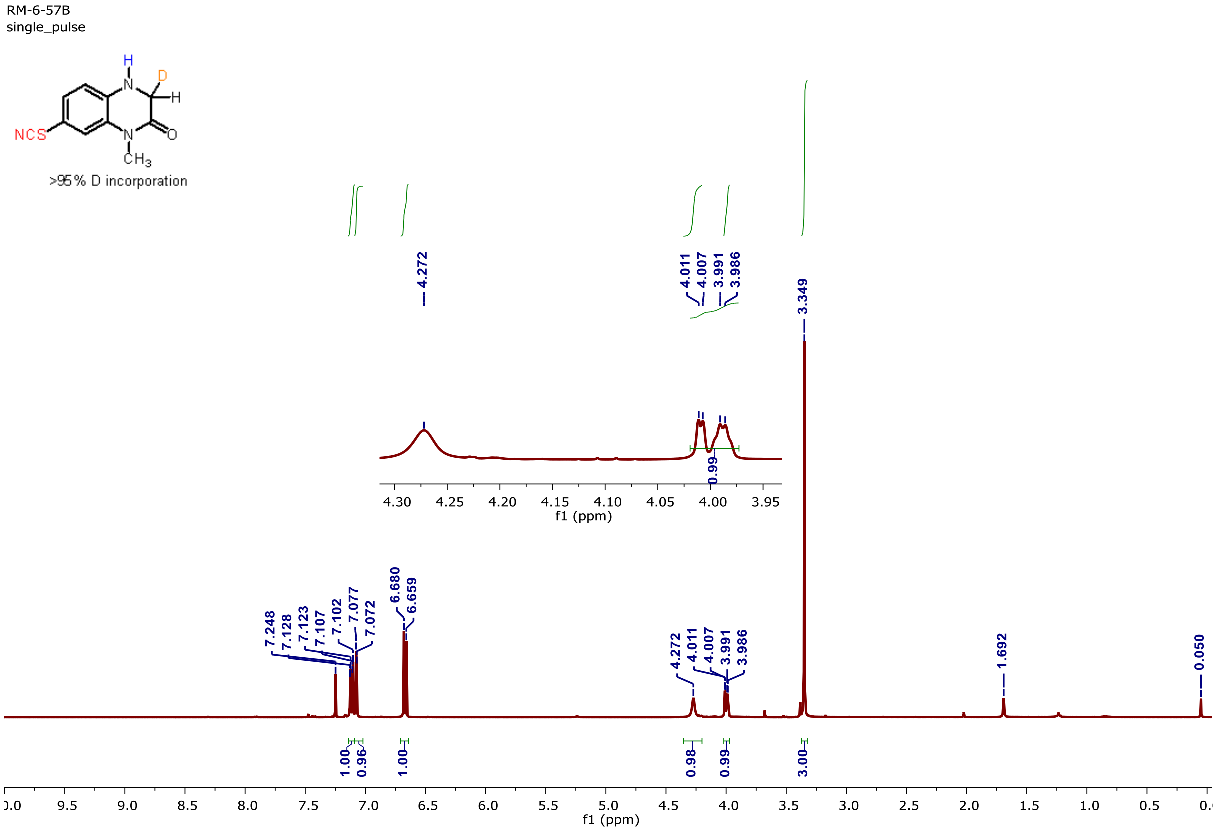


SI-6: Role of water during C=N reduction: Deuterium incorporation experiment

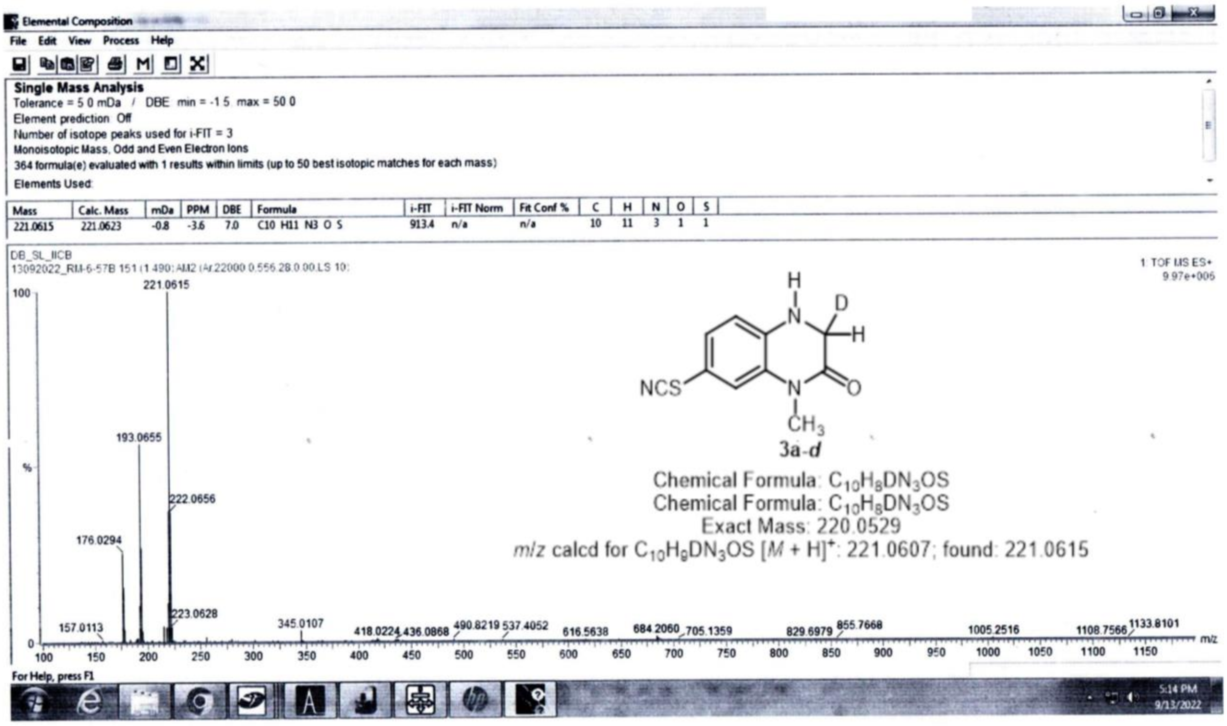
In an oven-dried undivided glass bottle (10 mL) equipped with a stir bar, **1a** (64 mg, 0.4 mmol), ammonium thiocyanate **2a** (152 mg, 2.0 mmol) and 5.0 mL of dry CH_3CN/D_2O (4.8 mL:0.2 mL) was added. The bottle was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature for 30 minutes, then a small aliquot was taken and analyzed by ESI-QTOF-HRMS studies. Isolation and detection of deuterium incorporated product **3a-*D*** (>95% D incorporation) suggested that during electrochemical reduction of **1a**, protonation at C-3 takes place from D_2O.

Analytical and spectral data of **3a-*D***: R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.12 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.07 (d, *J* = 2.0 Hz, 1 H), 6.67 (d, *J* = 8.4 Hz, 1 H), 4.27 (s, 1 H), 4.00 (m, 1 H), 3.35 ppm (s, 3 H); HRMS (ESI-QTOF): *m*/*z* calcd for $C_{10}H_9DN_3OS$ $[M + H]^+$: 221.0607; found: 221.0615.

^{1}H (400 MHz, CDCl$_3$) NMR spectra of **3a-*D***:



ESI-QTOF-HRMS spectra of **3a-*D***:

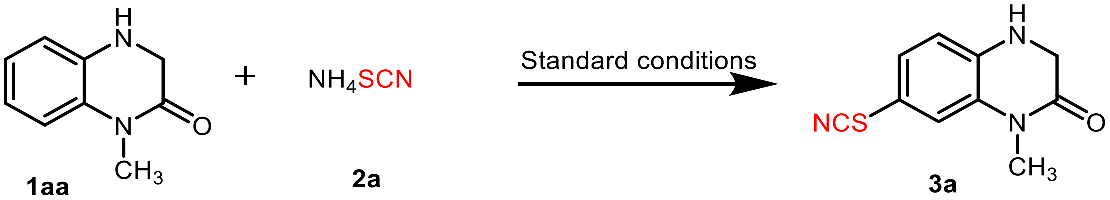


Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
364 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	S
221.0615	221.0623	-0.8	-3.6	7.0	C10 H11 N3 O S	913.4	n/a	n/a	10	11	3	1	1

Chemical Formula: $C_{10}H_8DN_3OS$
Chemical Formula: $C_{10}H_8DN_3OS$
Exact Mass: 220.0529
m/z calcd for $C_{10}H_8DN_3OS$ [*M* + H]$^+$: 221.0607; found: 221.0615

SI-7: Electrochemical thiocyanation of 1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (1aa)

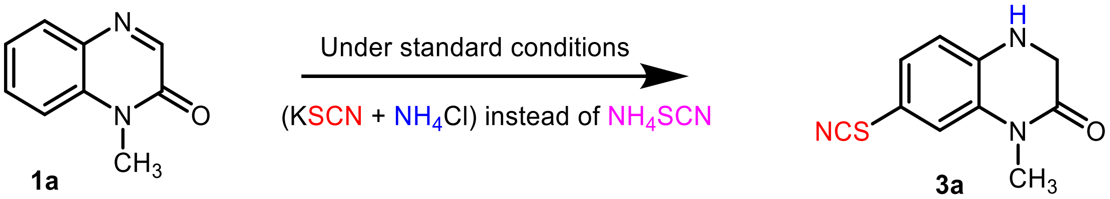


1aa **2a** **3a**

In an oven-dried undivided glass bottle (10 mL) equipped with a stir bar, 1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one **1aa** (64 mg, 0.39 mmol, 1.0 equiv), ammonium thiocyanate **2a** (148 mg, 5.0 equiv), and 5.0 mL of CH_3CN/H_2O (4.8 mL:0.2 mL) was added. The bottle was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature for 2 h. After completion of the reaction and usual work-up and purification procedure, the desired product (**3a**) was isolated in 49% yield, thereby suggesting that the reaction proceeded through **1aa** intermediate. The spectroscopic data of **3a** was exactly matched with that obtained from the original method.

SI-8: Role of NH_4^+ ion in electrochemical reduction

SI-8-1: Use of (KSCN + NH_4Cl) instead of NH_4SCN

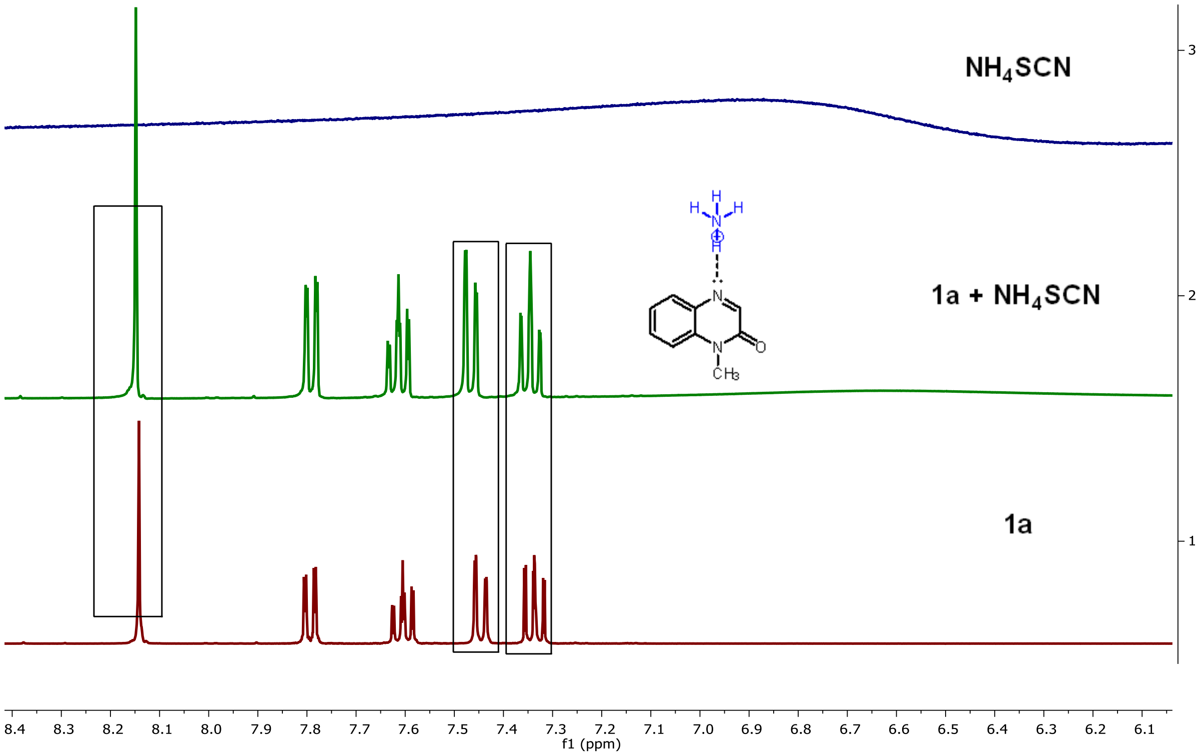


1a **3a**

In an oven-dried undivided glass bottle (10 mL) equipped with a stir bar, **1a** (64 mg, 0.4 mmol, 1.0 equiv), KSCN (116 mg, 3.0 equiv), NH_4Cl (63 mg, 3.0 equiv), and 5.0 mL of CH_3CN/H_2O (4.8:0.2) was added. The bottle was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature for 2 h. After usual work-up and purification, the desired product **3a** was isolated, albeit in low yield (26 mg, 29%). In contrast, when the reaction was conducted in the presence of KSCN instead of NH_4SCN, **3a** was not formed and the unreacted starting material was isolated. These control experiments suggested that ammonium ions had a definite role during the electrochemical reduction of the C=N bond at the cathode.

SI-8-2: Proof for the interaction of NH_4^+ ion (NH_4SCN) with the lone pair on nitrogen of 1a

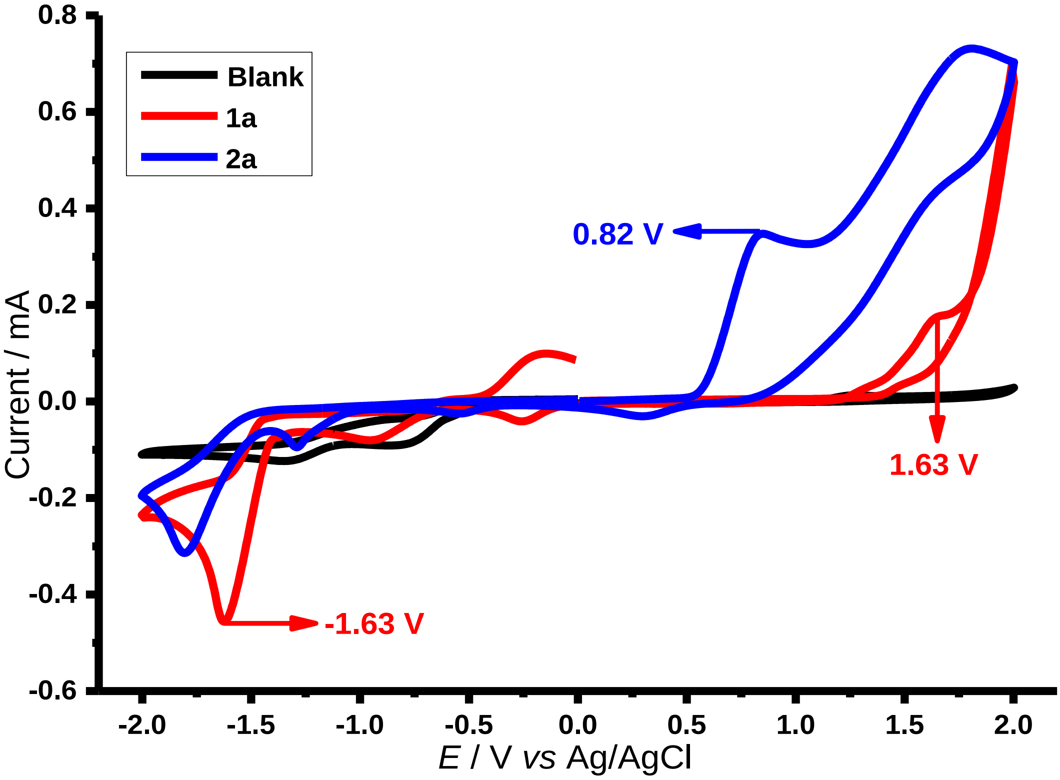
All the ^1H NMR (400 MHz) data was collected in a mixture of 5 mL CD_3CN/D_2O solvents (4.8 mL:0.2 mL). The chemical shift value of **1a** was found to be slightly down-fielded after addition of NH_4SCN, thereby suggesting the interaction of ammonium cation with lone pair on nitrogen of **1a**.



SI-9: Cyclic Voltammetry studies

All cyclic voltammetry studies were measured using Potentiostat-Galvanostat (Autolab PGSTAT204) at room temperature in acetonitrile and water solvent mixture (4.8:0.2, mL). Before collecting CV data, solution was degassed with argon gas to overcome one extra reduction potential peak coming for oxygen present in solution. $^nBu_4NPF_6$ (0.1 M) was used as the supporting electrolyte, and a glassy carbon electrode was used as the working electrode while the counter electrode was a platinum plate. The reference was an Ag/AgCl electrode submerged in a saturated aqueous KCl solution. The scan rate was 100 mV/s ranging from -2.0 V to +2.0 V.

SI-9-1: cyclic voltammetry of 1a and 2a



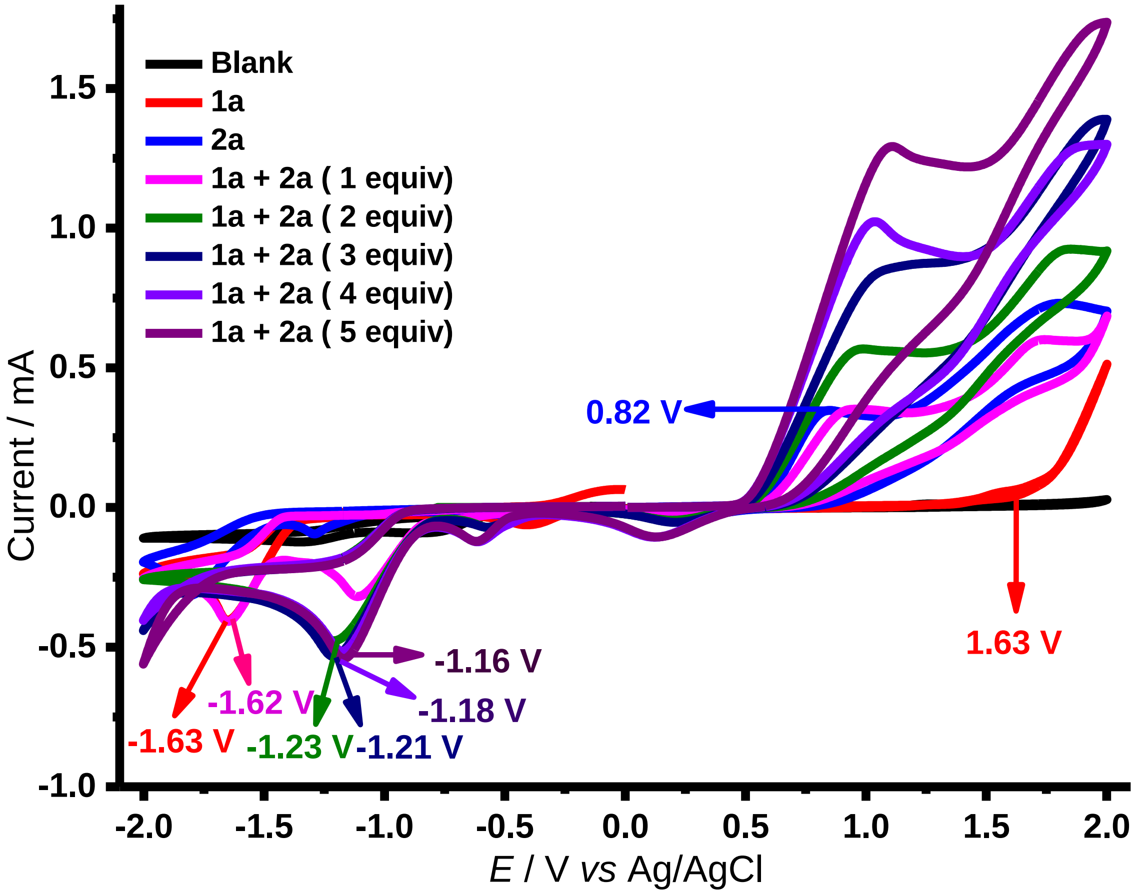
5.0 mL of CH_3CN/H_2O (4.8 mL:0.2 mL) solvent mixtures (i) containing 0.1 M of $^{n}Bu_4NPF_6$ (**black line**); (ii) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **1a** (**red line**); (iii) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **2a** (**blue line**).

Discussion: The CV of **1a** (0.015 M) showed a one-electron reduction peak in the potential at -1.63 V and an oxidation potential peak at +1.63 V was observed, whereas NH_4SCN (0.015 M) had oxidation potential 0.82 V. So, in this reaction NH_4SCN preferentially undergo anodic oxidation to form $SCN^{\bullet}$ and $(SCN)_2$ to initiate the reaction, subsequently, **1a** underdoes cathodic reduction on the graphite electrode surface.

SI-9-2: Role of NH_4^+ ions towards reduction potential of 1a

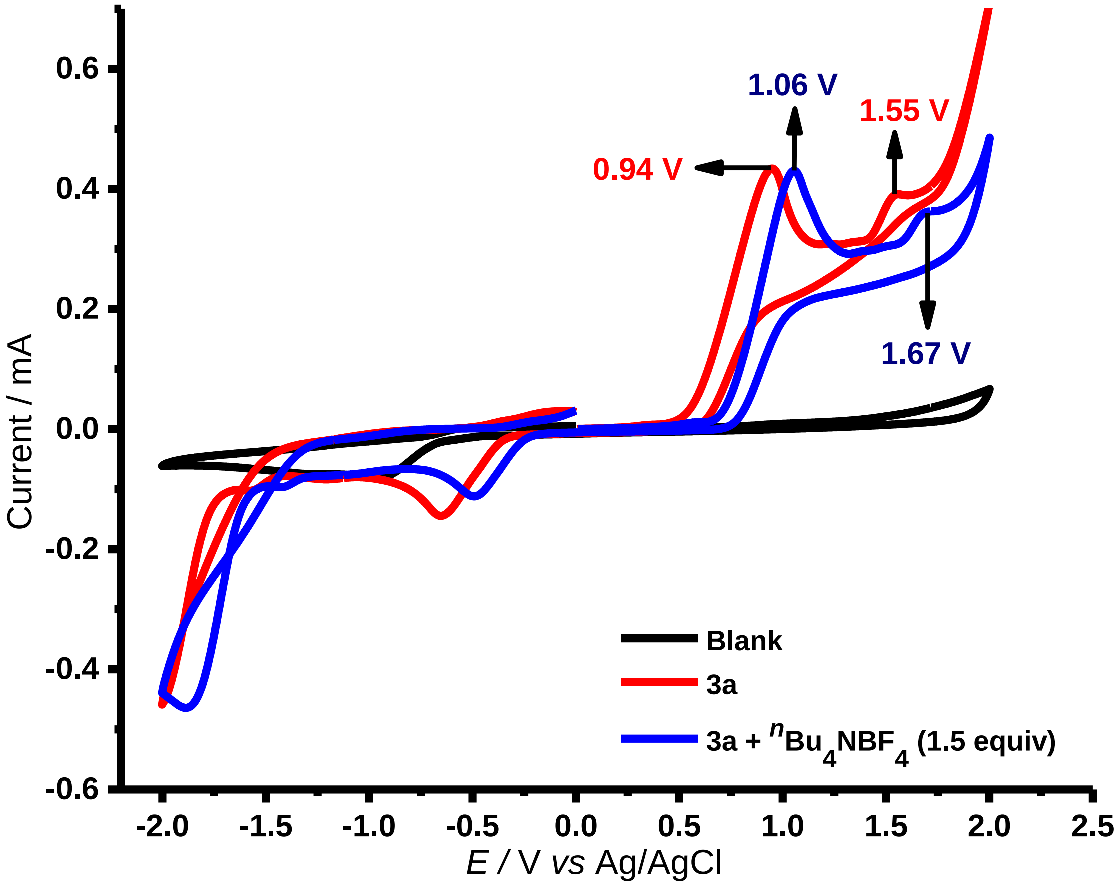
During cyclic voltammetry studies, we observed certain changes on reduction potential value of **1a** when NH_4SCN **2a** was added into the solution of **1a** (same concentration 0.015 M). In presence of NH_4SCN (1:2 equivalent), a decrease in reduction potential of **1a** was observed from -1.63 V to -1.23 V, which indicated NH_4^+ might co-ordinate or protonate with *N*-4 of **1a** and subsequently reduced the reduction potential value. This phenomenon was clearly noticed when the concentration of NH_4SCN was increased by 2 to 3, 4, 5 times; only one reduction peak was observed at -1.21 V, -1.18 V and -1.16 V which was lower than the initial reduction potential value of **1a**. This result indicated that with increasing concentration of NH_4SCN in the reaction mixture, **1a** undergoes protonation as a result reduction potential of protonated **1a** appear at more positive potential (-1.16 V *vs* Ag/AgCl) than **1a** (-1.63 V *vs*

Ag/AgCl) which facilitated the reduction of **1a** with ensuing thiocyanation, which ultimately improved the overall yield of the reaction.



5.0 mL of CH_3CN/H_2O (4.8 mL:0.2 mL) solvent mixtures (i) containing 0.1 M of $^{n}Bu_4NPF_6$ (**black line**); (ii) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **1a** (**red line**); (iii) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **2a** (**blue line**); (iv) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **1a** and 0.015 M of **2a** (**pink line**); (v) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **1a** and 0.030 M of **2a** (**green line**); (vi) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **1a** and 0.045 M of **2a** (**dark blue**); (vii) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **1a** and 0.060 M of **2a** (**violet**); (viii) containing 0.1 M of $^{n}Bu_4NPF_6$ with 0.015 M of **1a** and 0.075 M of **2a** (**purple**). The CV was measured after degassing each solution with argon gas

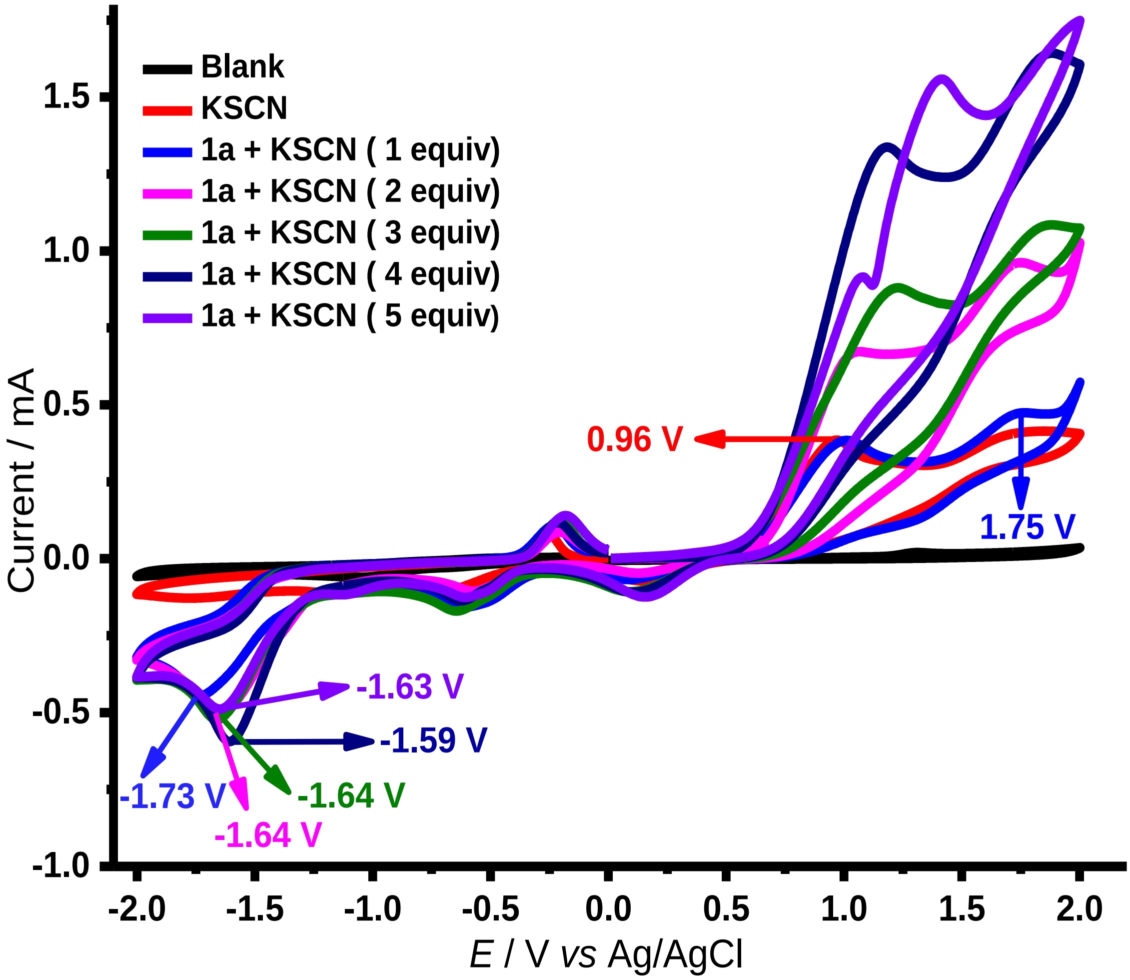
SI-9-3: CV plot of compound 3a in a mixture of CH_3CN/H_2O solvents



5.0 mL of CH_3CN/H_2O (4.8 mL:0.2 mL) solvent mixtures (i) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ (**black line**); (ii) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ with 0.015 M of Compound **3a** (**red line**); (iii) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ with 0.015 M of compound **3a** and 1.5 equivalent of ^{n}Bu$_4$NBF$_4$ (**blue line**).

Discussion: cyclic voltammetry measurement of **3a** shows two oxidation potential peaks at 0.94 V and 1.55 V (*vs* AgCl/Ag) but has no significant reduction potential peak, suggesting oxidation of **3a** at the anodic surface. Thus, after complete reduction and thiocyanation of **1a** to form **3a**, it underwent oxidation to furnish product **4a** when the current supply is reduced to 5 mA from 18 mA and ^{n}Bu$_4$NBF$_4$ was used as a supporting electrolyte.

SI-9-4: CV plot of 1a and KSCN at different concentration in CH_3CN/H_2O solvent mixtures



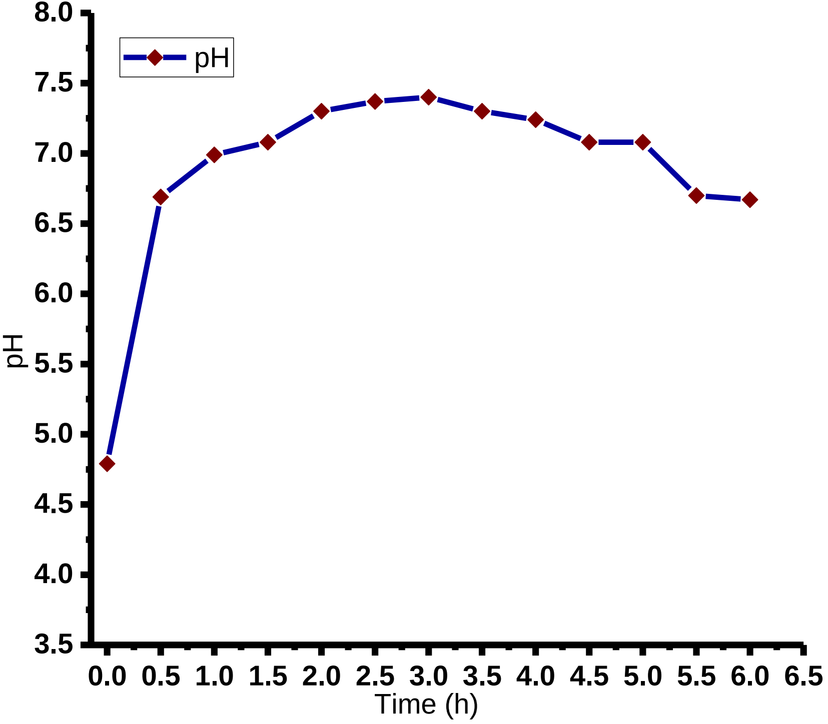
5.0 mL of CH_3CN/H_2O (4.8 mL:0.2 mL) solvent mixtures (i) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ (**black line**); (ii) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ with 0.015 M of KSCN (**red line**); (iii) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ with 0.015 M of compound **1a** and 0.015 M KSCN (**blue line**); (iv) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ with 0.015 M of compound **1a** and 0.030 M KSCN (**pink line**); (v) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ with 0.015 M of compound **1a** and 0.045 M KSCN (**green line**); (vi) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ with 0.015 M of compound **1a** and 0.060 M KSCN (**dark blue line**); (vii) containing 0.1 M of ^{n}Bu$_4$NPF$_6$ with 0.015 M of compound **1a** and 0.075 M KSCN (**violet line**). The CV was measured after degassing each solution with argon gas.

Discussion: Cyclic voltammetry measurement of **1a** shows a reduction potential peak at -1.63 V (*vs* AgCl/Ag). The addition of KSCN (instead of NH_4SCN) to the solution of **1a** did not affect the reduction potential of **1a**, might be due to the absence of any interaction of KSCN with *N*-4 of **1a**. Thus, reduction of **1a** in the presence of KSCN may not be possible under the standard reaction conditions.

SI-10: Change of pH of the reaction medium during electrolysis

We measured pH of the reaction mixture (before electrolysis and during electrolysis for synthesis of **3a** and **4a** starting from **1a**) using METTLER TOLEDO (FiveEasy Plus FP20) at 25 ˚C.

Electrolysis time (h)	Change of pH of the reaction medium
0	4.79
0.5	6.69
1.0	6.99
1.5	7.08
2.0	7.30
2.5	7.37
3.0	7.40
3.5	7.30
4.0	7.24
4.5	7.08
5.0	7.08
5.5	6.70
6.0	6.67



Discussion: We measured pH of the reaction mixture of **1a** before electrolysis (pH = 4.79) and during electrolysis for the synthesis of **3a** followed by 4a. We showed that pH of the reaction medium increases from (pH = 4.79) acidic to basic (pH = 7.40) during the synthesis of 3a. This might be due to protonation of 1a followed by cathodic reduction (PCET) decreases the ammonium cation (acidic) concentration and release ammonia (basic) in the reaction medium. Again, when we measured the pH for the 2nd step, we showed that pH of the reaction medium decreases from 7.40 to 6.67. Thus, reaction medium changes from basic to slightly acidic may be due to release of proton during anodic oxidation of 3a for synthesis of 4a, combine with ammonia(basic) to form ammonium cation (acidic).

SI-11: Calculation of Faraday Efficiency

The Faraday Efficiency (F.E.) is the percentage value that specifies the ratio of charged consumed by the system to charge given to the system. It is calculated for all hydrogenation followed by thiocyanation reaction and subsequent dehydrogenation reaction by using the following formula (0.4 mmol of **1**):

$$\mathrm{F.E.} = \frac{\mathrm{z} * \mathrm{Np} * \mathrm{F}}{\mathrm{I} * \mathrm{t}} \text{ x } 100\%$$

z: The number of electrons involves in the product formation; Np: Number of moles of product formed (mol); F: Faraday constant (96485 s. A. mol $^{-1}$); I: the current (A); t: the time (s).

For the product **3a** in **Table 2** (main manuscript), we calculated F.E. by considering cathodic reduction

$$\mathrm{F.E.\ of\ } \mathbf{3a} = \frac{2 * \ 0.352 * \ 10^{-3}\,\mathrm{mol} * \ 96485\,\mathrm{s.A.mol^{-1}}}{18 * \ 10^{-3}\ \mathrm{A} * \ 10800\,\mathrm{s}} \text{ x } 100\% = 35\%$$

For all other derivatives, F.E. was calculated by using the above formula, only replacing the mmol of different products and reaction time.

Product ID	Yield of product (%)	Time of reaction (h)	Faradaic Efficiency (%)
3a	88	3.0	35.0
3b	79	3.2	29.4
3c	83	3.3	30.0
3d	64	3.3	32.2
3e	90	3.1	34.6
3f	36	3.1	13.8
3g	52	3.3	18.8
3h	80	3.4	28.0
3i	78	3.5	26.6
3j	60	3.3	21.6
3k	79	3.0	31.4
3l	55	2.5	26.2
3m	79	3.3	28.6
3n	88	3.2	32.8
3o	86	3.5	29.2
3p	68	3.25	25.0
3q	81	3.3	29.2
3r	41	3.1	15.8
3s	85	3.3	30.6
3t	67	3.0	26.6
3u	70	3.2	26.0
3v	83	3.5	28.2

3w	60	2.5	28.6
3x	72	2.5	34.2

For calculation of F.E. for one pot two step electrochemical process (1st step hydrogenation followed by thiocyanation to yield **3** and subsequent anodic dehydrogenation in the 2nd step to form product **4**), we consider four electron process (two electrons for cathodic reduction and two electrons for anodic oxidation). For the synthesis of **4a** in **Table 3**, F.E. was calculated by using the following formula:

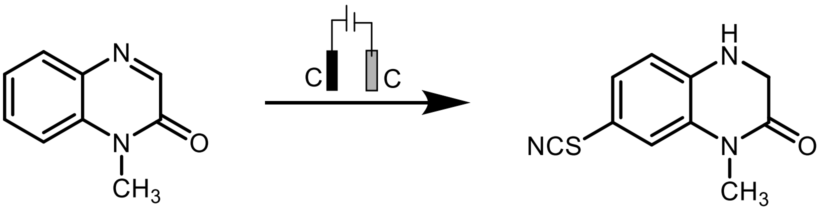
$$\mathrm{F.E.\ of\ }\mathbf{4a} = \frac{4\ *\ 0.32 *\ 10^{-3}\ \mathrm{mol}\ *\ 96485\ \mathrm{s.A.mol^{-1}}}{(18\ *\ 10^{-3}\ \mathrm{A} * 10800\ \mathrm{s}) + (5\ *\ 10^{-3}\ \mathrm{A}\ * 1\,0800\ \mathrm{s})}\ \mathrm{x}\ 100\% = 50\%$$

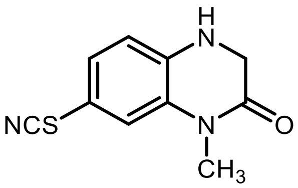
F.E. of all other derivatives of **4** was calculated by using the above formula by replacing mmol of product and corresponding reaction time.

Product ID	Yield of product (%)	Time of reaction (h)	Faradaic Efficiency (%)
4a	80	6.0	50.0
4b	86	6.3	49.6
4c	70	6.3	40.3
4d	52	6.3	30.0
4e	58	6.3	33.4
4f	70	6.1	42.4
4g	89	6.3	51.3
4h	70	6.2	41.3
4i	40	6.3	23.0
4j	70	6.5	38.5
4k	67	6.3	39.0
4l	78	6.5	43.0
4m	75	6.2	44.3

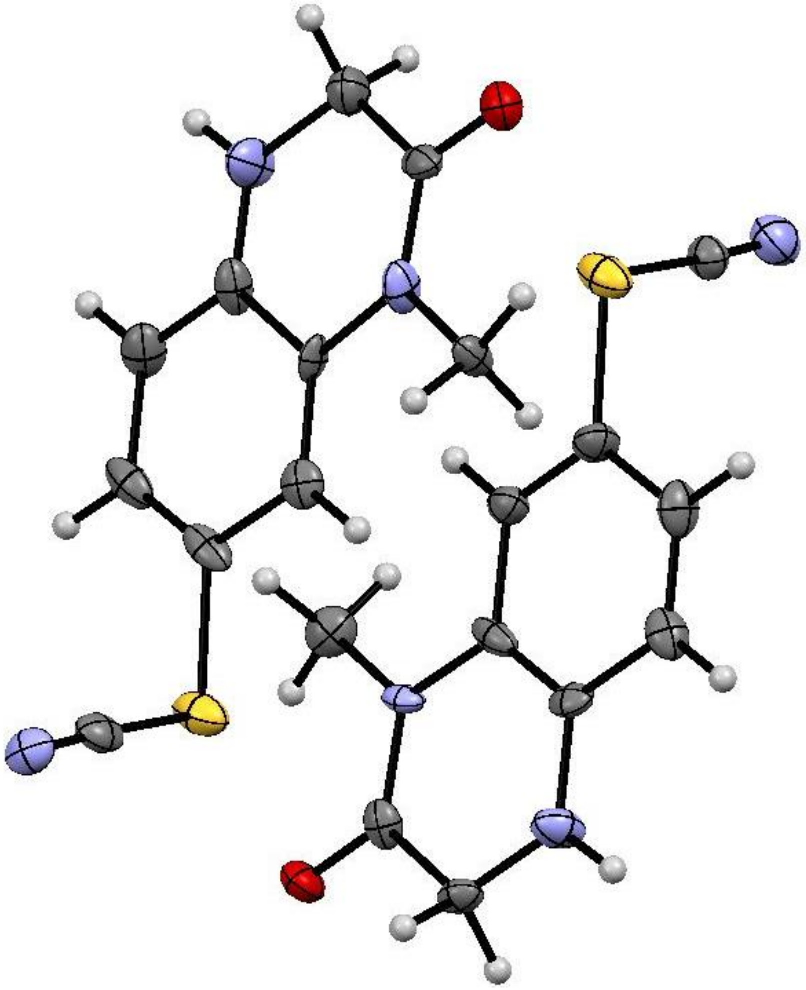
SI-12: Analytical and Spectral Data

SI-12-1: Analytical and Spectral data of **3a**





1-Methyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3a: Prepared according to the general procedure discussed above: reaction time = 3.0 h; $R_f = 0.3$; eluent, EtOAc/*n*-hexane (30%); white solid (77 mg, 88%); mp 158–160 ˚C; solvent of crystallization, DCM/MeOH (1.5 mL:0.5 mL, *v*/*v*) at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.13$ (dd, $J = 8.4, 2.0$ Hz, 1 H), 7.08 (d, $J = 2.0$ Hz, 1 H), 6.67 (d, $J = 8.4$ Hz, 1 H), 4.20 (s, 1 H), 4.02 (d, $J = 1.6$ Hz, 2 H), 3.36 ppm (s, 3 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 164.7$, 137.7, 130.0, 128.6, 119.0, 114.9, 111.9, 111.3, 47.0, 28.9 ppm; HRMS (ESI-QTOF): m/z calcd for $C_{10}H_{10}N_3OS$ $[M + H]^+$: 220.0544; found: 220.0545.



X-ray determined molecular structure of **3a** (**CCDC 2266370**). The thermal ellipsoids are shown in 50% probability level. Solvent of crystallization, DCM/MeOH (1.5 mL:0.5 mL, *v*/*v*) at room temperature 25–30 °C.

Datablock 3a

Bond precision: C-C = 0.0086 A Wavelength=1.54178

Cell:	a=8.2596(7)	b=11.1219(9)	c=11.4922(9)
	alpha=90	beta=110.896(3)	gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	986.27(14)	986.27(14)
Space group	P c	P 1 c 1
Hall group	P -2yc	P -2yc
Moiety formula	C10 H9 N3 O S	C10 H9 N3 O S
Sum formula	C10 H9 N3 O S	C10 H9 N3 O S
Mr	219.26	219.26
Dx,g cm-3	1.477	1.477
Z	4	4
Mu (mm-1)	2.716	2.716
F000	456.0	456.0
F000'	458.53	
h,k,lmax	9,13,13	9,13,13
Nref	3625[1819]	3260
Tmin,Tmax	0.710,0.742	0.501,0.753
Tmin'	0.553	

Correction method= # Reported T Limits: Tmin=0.501 Tmax=0.753
AbsCorr = MULTI-SCAN

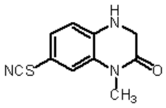
Data completeness= 1.79/0.90 Theta(max)= 68.513

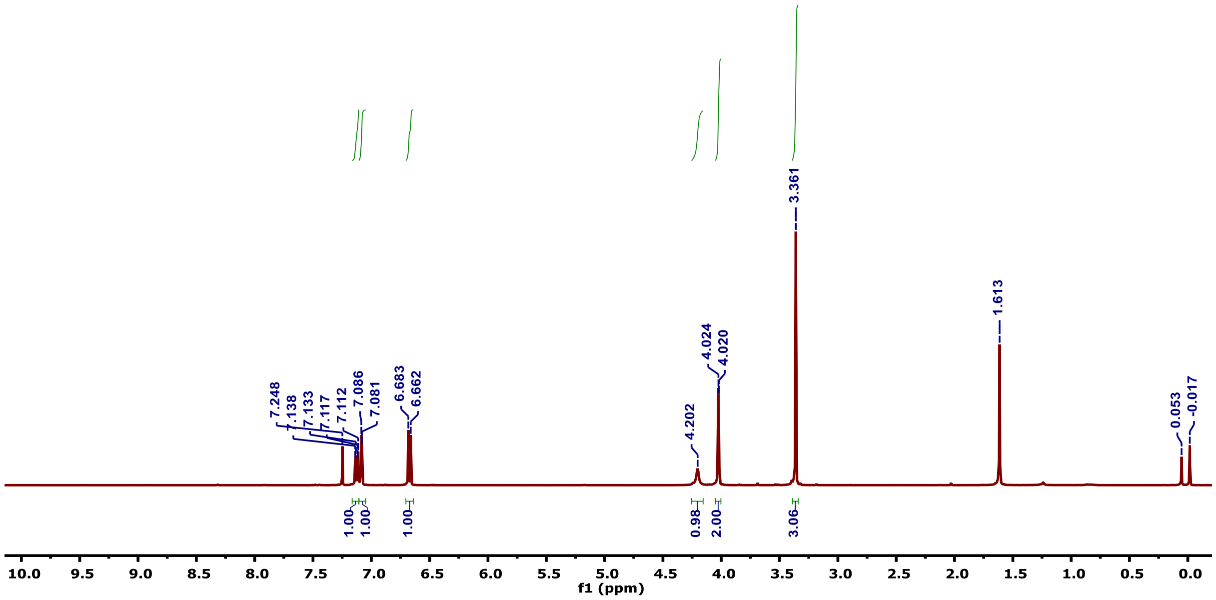
R(reflections)= 0.0408 (3084) wR2(reflections)= 0.1073 (3260)

S = 1.074 Npar= 273

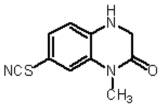
^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **3a:**

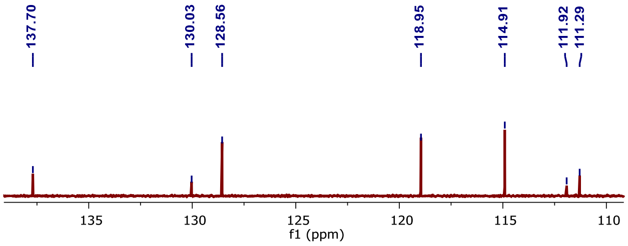
BMW-4-57C1
single_pulse

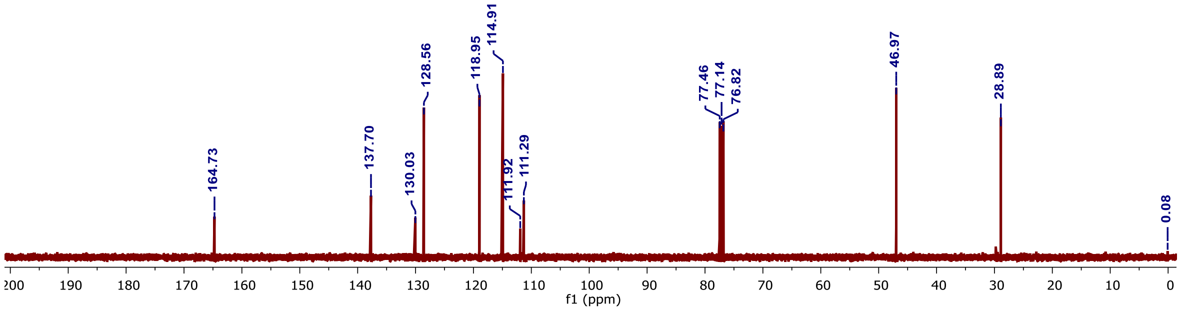




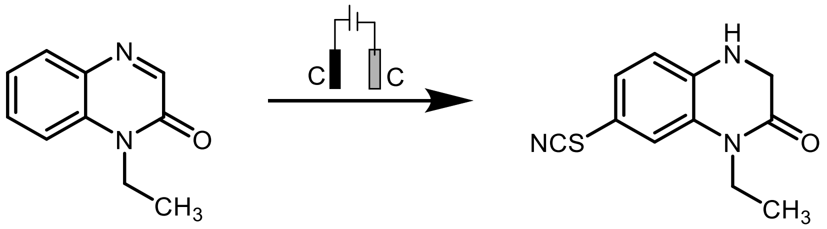
RM-5-147AB
single pulse decoupled gated NOE

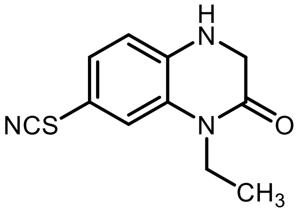






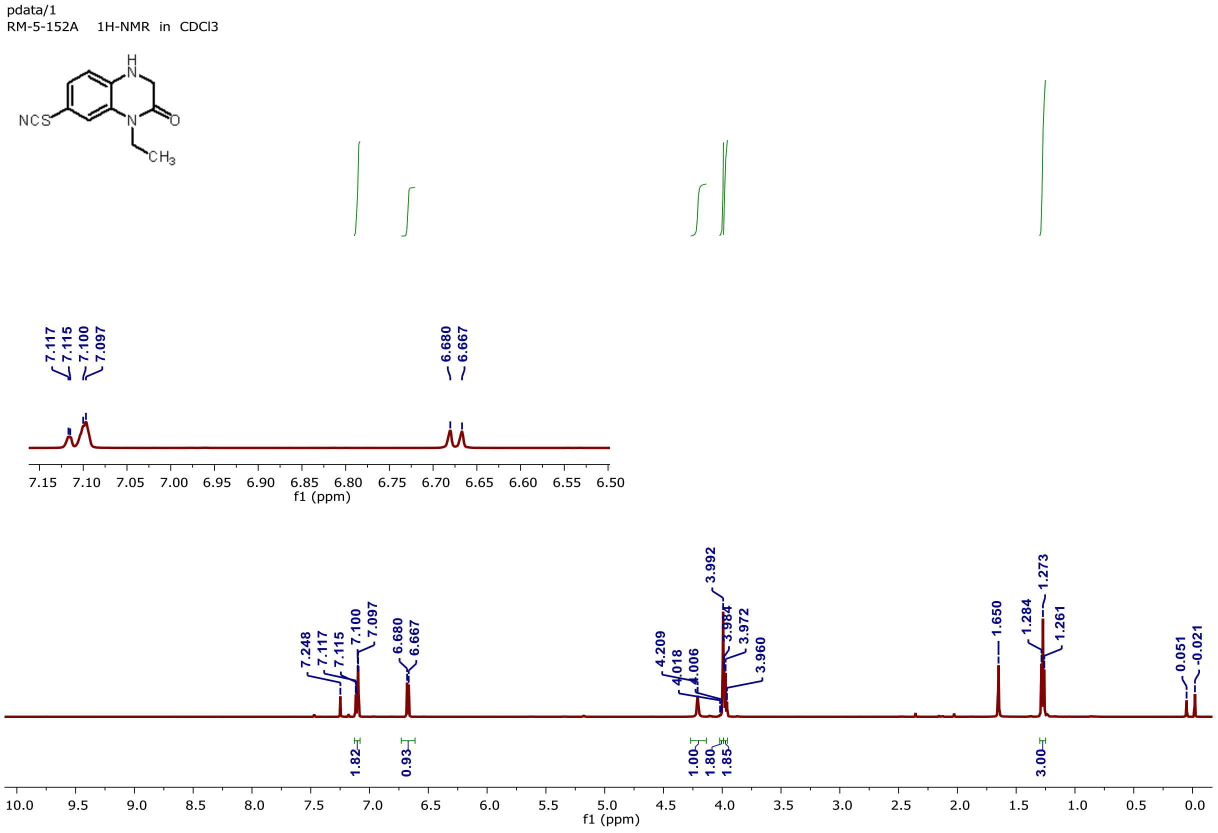
SI-12-2: Analytical and Spectral data of **3b**

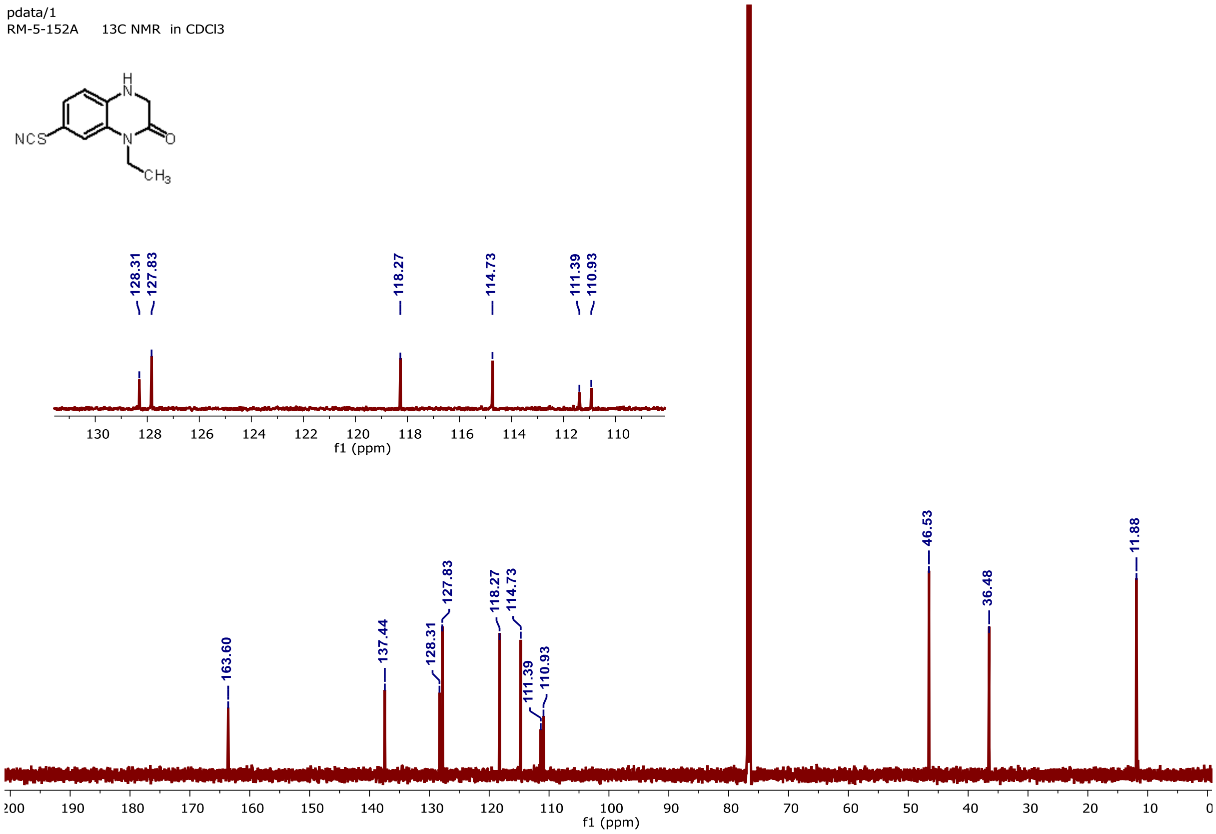


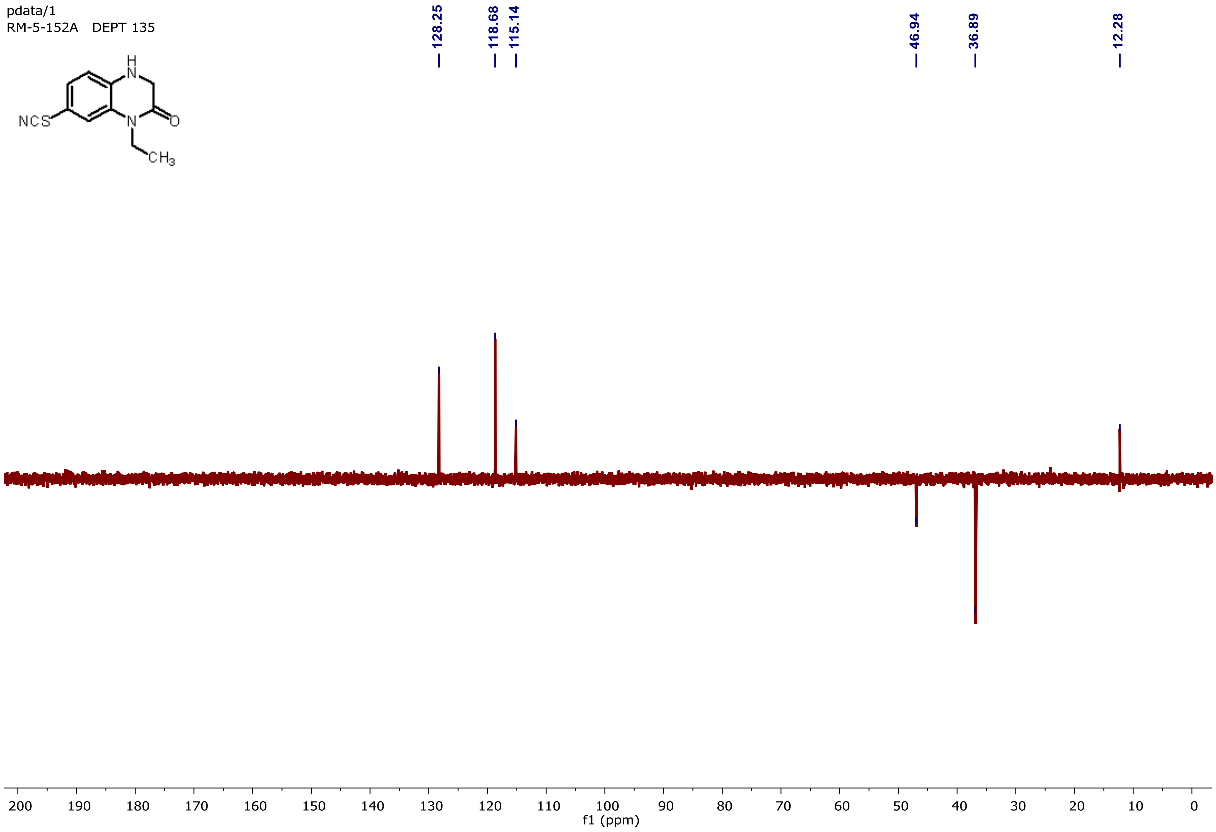


1-Benzyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3b: Prepared according to the general procedure discussed above: reaction time = 3.2 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (74 mg, 79%); mp 177–180 ˚C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.10-7.12 (m, 2 H), 6.67 (d, *J* = 7.8 Hz, 1 H), 4.21 (s, 1 H), 3.99-4.02 (m, 2 H), 3.97 (q, *J* = 7.2 Hz, 2 H), 1.27 ppm (t, *J* = 7.2 Hz, 3 H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 163.6, 137.4, 128.3, 127.8, 118.3, 114.7, 111.4, 110.9, 46.5 (CH_2), 36.5 (CH_2), 11.9 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{11}H_{12}N_3OS$ $[M + H]^+$: 234.0701; found: 234.0693.

^{1}H (600 MHz, $CDCl_3$), ^{13}C{^{1}H} (151 MHz, $CDCl_3$), and DEPT-135 (151 MHz, $CDCl_3$) NMR spectra of **3b**:




pdata/1
RM-5-152A 13C NMR in CDCl3
NCS
H
N
N
O
CH3
128.31
127.83
118.27
114.73
111.39
110.93
130
128
126
124
122
120
118
116
114
112
110
f1 (ppm)
163.60
137.44
128.31
127.83
118.27
114.73
111.39
110.93
46.53
36.48
11.88
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


pdata/1
RM-5-152A DEPT 135
NCS
H
N
N
O
CH3
128.25
118.68
115.14
46.94
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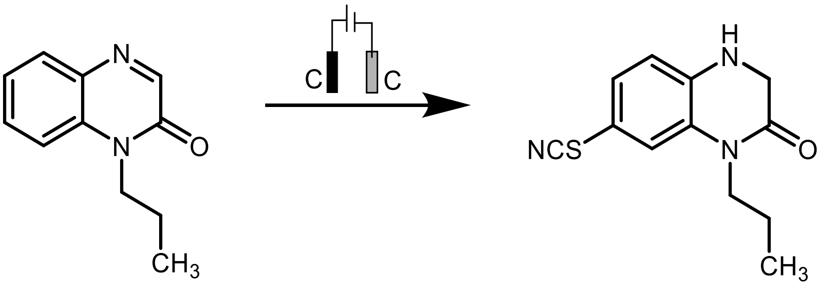
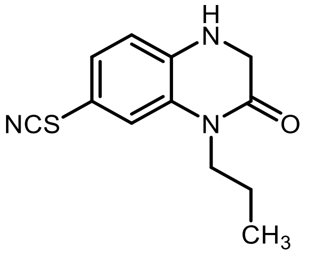
12.28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

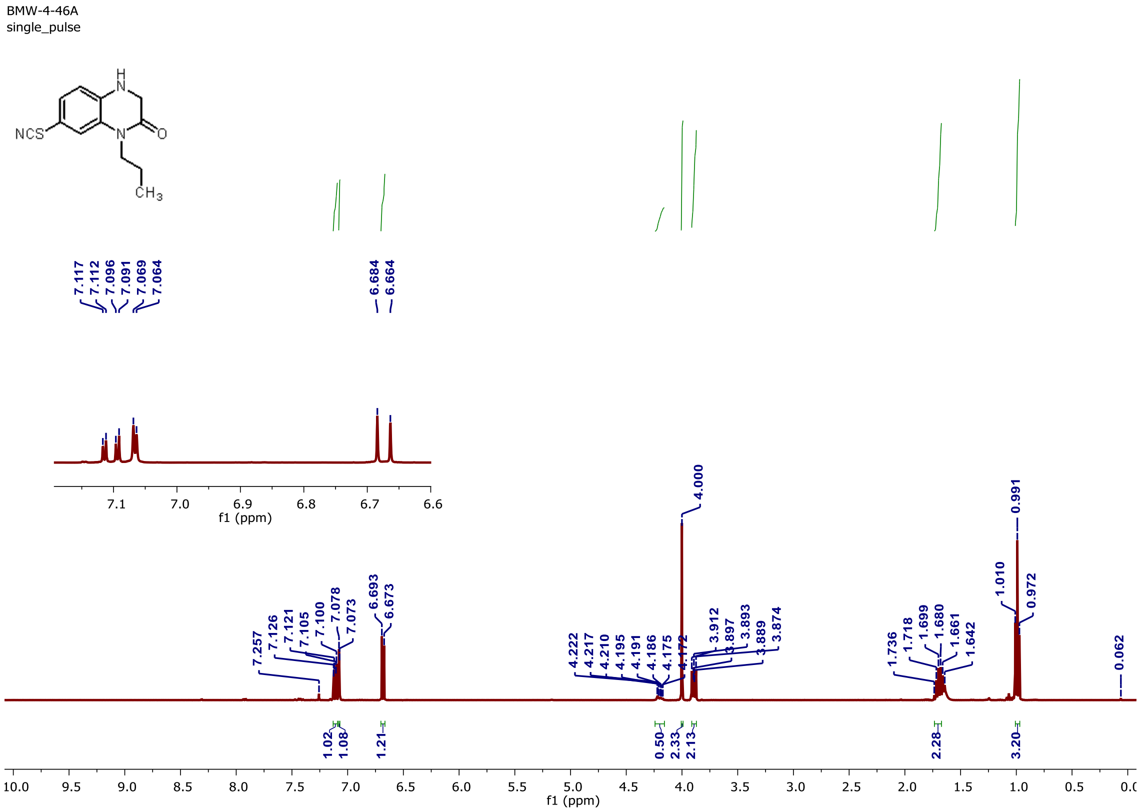
SI-12-3: Analytical and Spectral data of **3c**

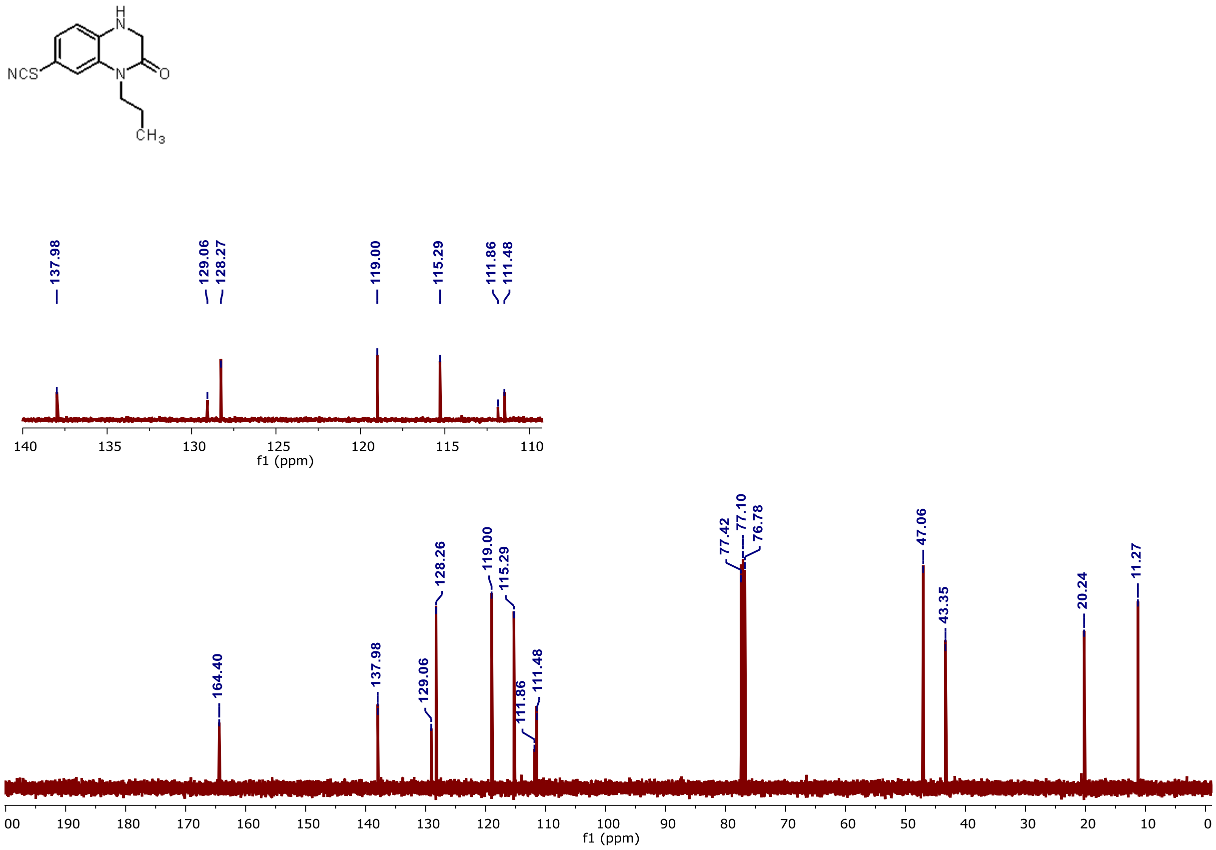


1-Propyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3c: Prepared according to the general procedure discussed above: reaction time = 3.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (82 mg, 83%); mp 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (dd, J = 8.4, 2.0 Hz, 1 H), 7.08 (d, J = 2.0 Hz, 1 H), 6.68 (d, J = 8.0 Hz, 1 H), 4.17-4.22 (m, 1 H), 4.00 (s, 2 H), 3.87-3.91 (m, 2 H), 1.64-1.74 (m, 2 H), 0.98 ppm (d, J = 7.6 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.4, 138.0, 129.1, 128.3, 119.0, 115.3, 111.9, 111.5, 47.1 (CH_2), 43.4 (CH_2), 20.2 (CH_2), 11.3 ppm; HRMS (ESI-QTOF): m/z calcd for $C_{12}H_{14}N_3OS$ $[M + H]^+$: 248.0858; found: 248.0852.

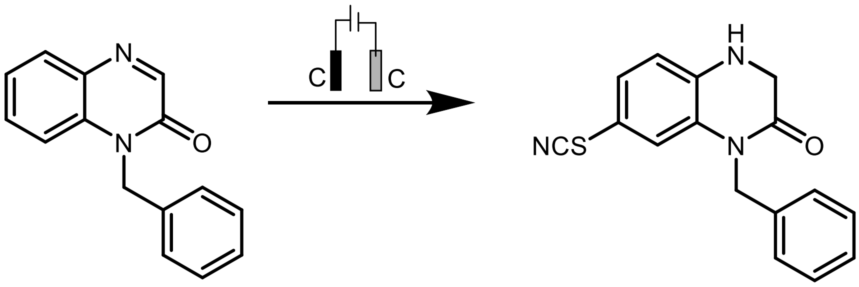


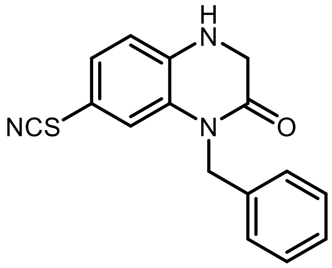
^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **3c:**





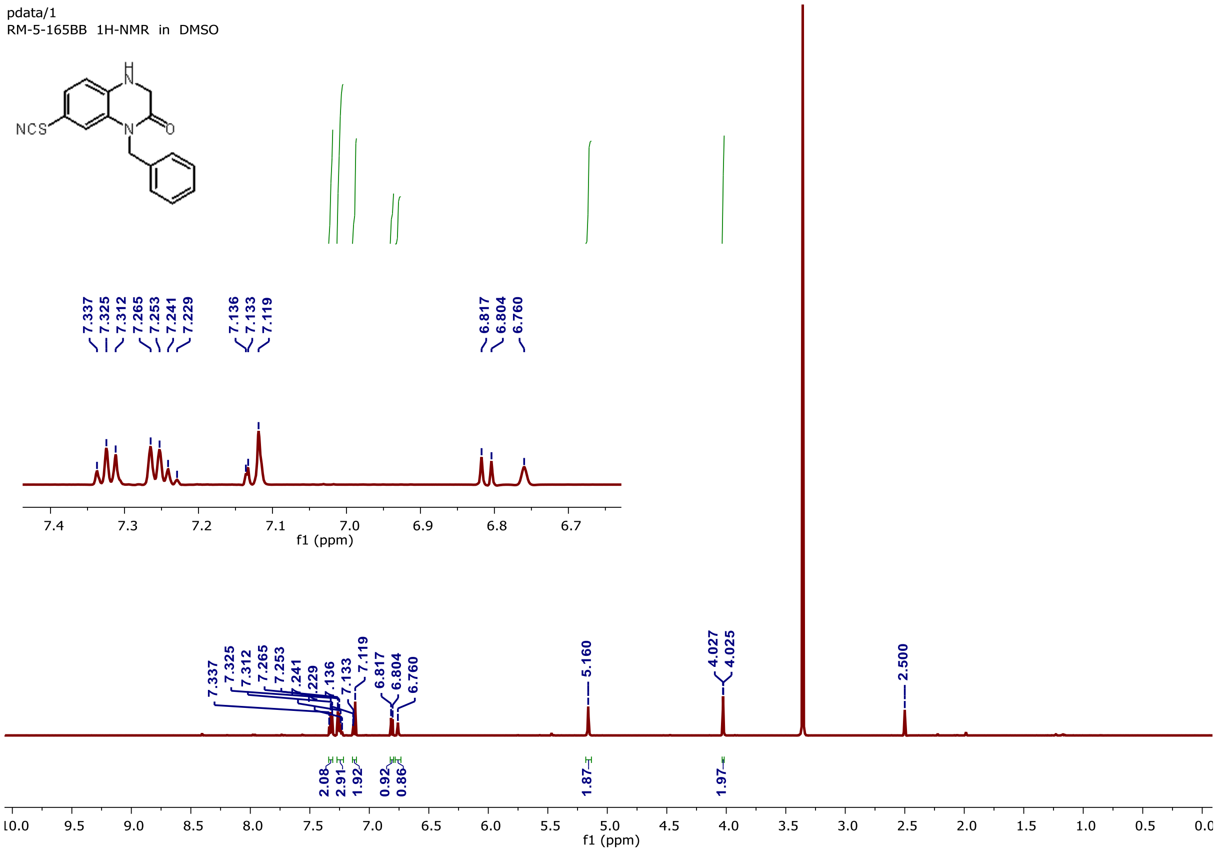
SI-12-4: Analytical and Spectral data of **3d**

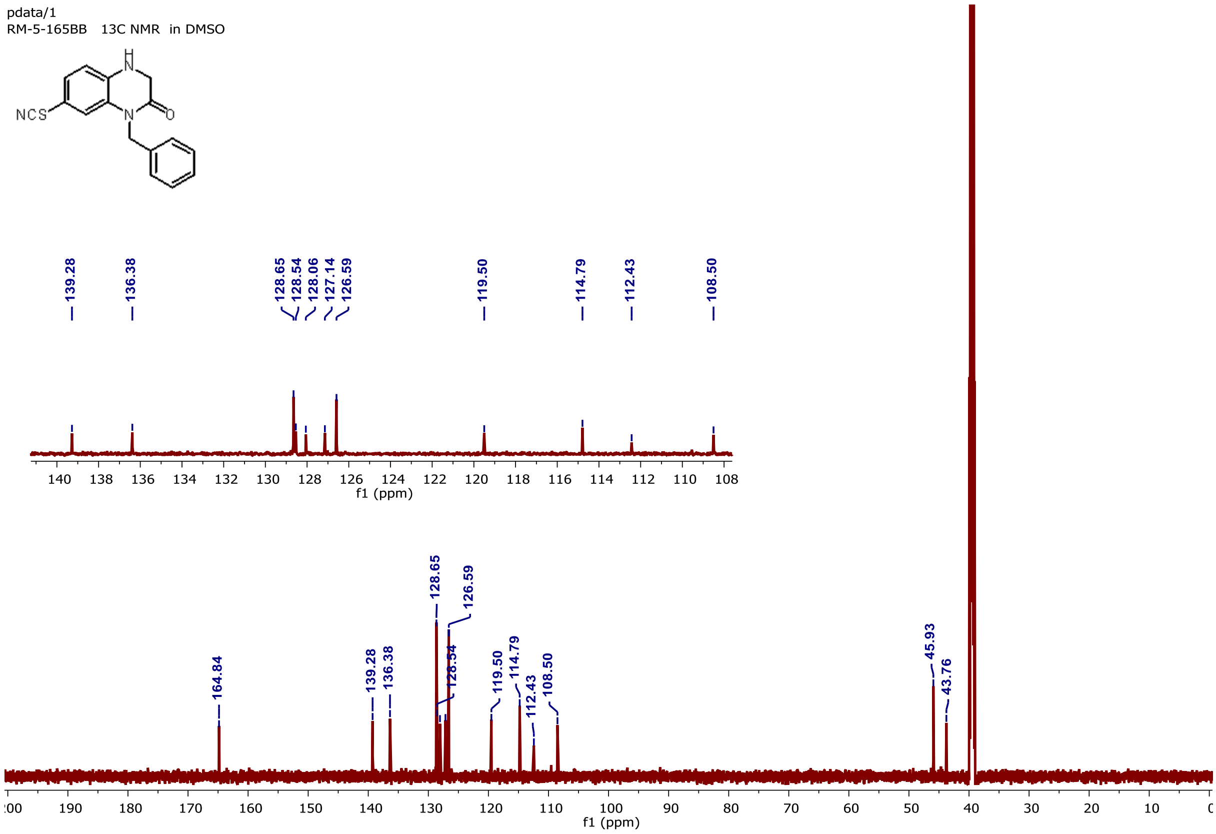




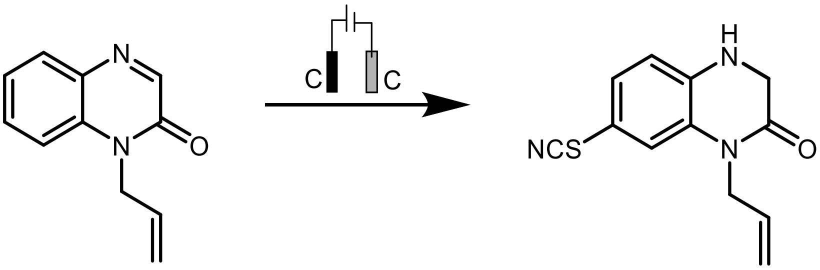
1-Benzyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3d: Prepared according to the general procedure discussed above: reaction time = 3.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (76 mg, 64%); mp 110 –112 ˚C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.32 (t, J = 7.2 Hz, 2 H), 7.23-7.27 (m, 3 H), 7.12-7.14 (m, 2 H), 6.81 (d, J = 7.8 Hz, 1 H), 6.76 (s, 1 H), 5.16 (s, 2 H), 4.03 ppm (d, J = 1.2 Hz, 2 H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ = 164.8, 139.3, 136.4, 128.6 (2 CH), 128.5, 128.1, 127.1, 126.6 (2 CH), 119.5, 114.8, 112.4, 108.5, 45.9 (CH_2), 43.8 (CH_2) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{14}N_3OS$ [M + H]$^+$: 296.0858; found: 296.0847.

^{1}H (600 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) spectra of **3d:**

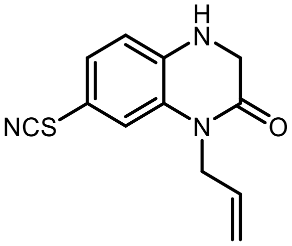




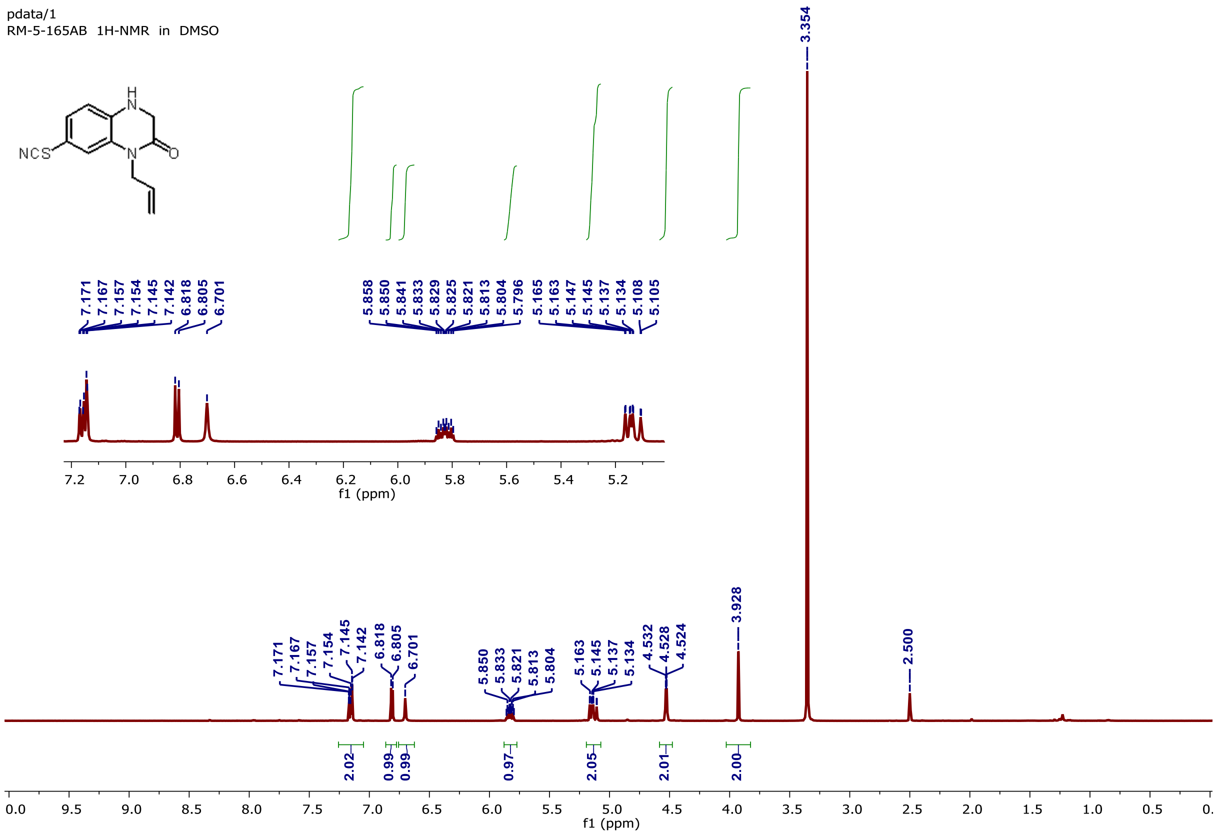
SI-12-5: Analytical and Spectral data of **3e**

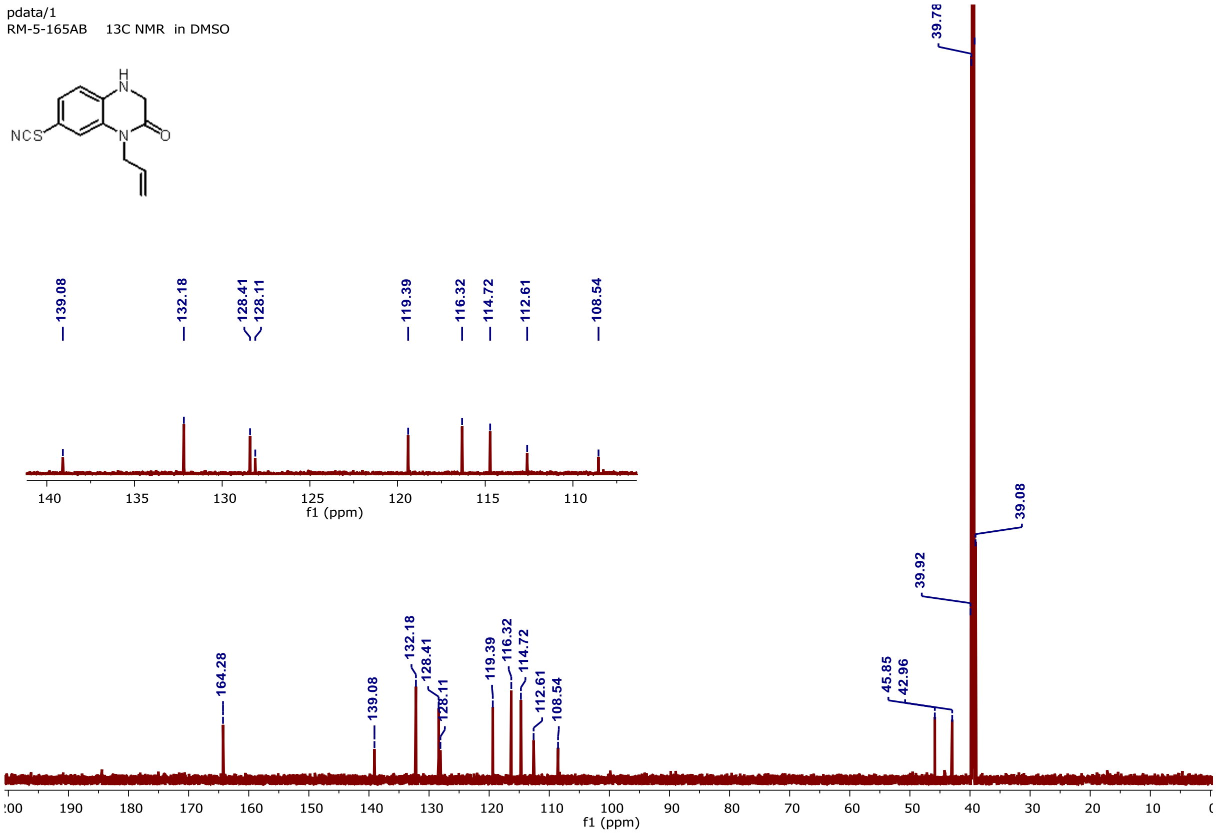


1-Allyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3e: Prepared according to the general procedure discussed above: reaction time = 3.1 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); yellow solid (89 mg, 90%); mp 135–138 ˚C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.14-7.17 (m, 2 H), 6.81 (d, J = 7.8 Hz, 1 H), 6.70 (s, 1 H), 5.83 (ddt, J = 17.4, 10.2, 4.8 Hz, 1 H), 5.10-5.17 (m, 2 H), 4.52-4.53 (m, 2 H), 3.93 ppm (s, 2 H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ = 164.3, 139.1, 132.2, 128.4, 128.1, 119.4, 116.3, 114.7, 112.6, 108.5, 45.9 (CH_2), 43.0 (CH_2) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{12}H_{12}N_3OS$ [*M* + H]$^+$: 246.0701; found: 246.0700.

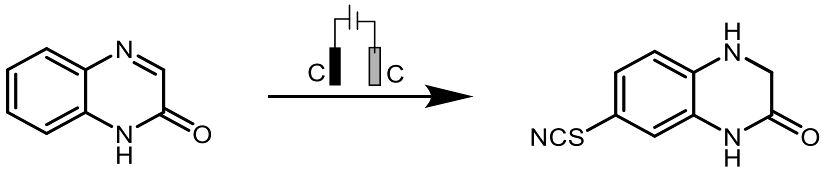


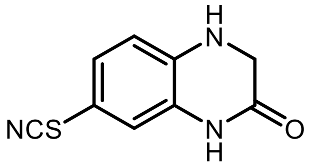
^{1}H (600 MHz, DMSO-*d*$_6$) and ^{13}C{^{1}H} (151 MHz, DMSO-*d*$_6$) NMR spectra of **3e:**





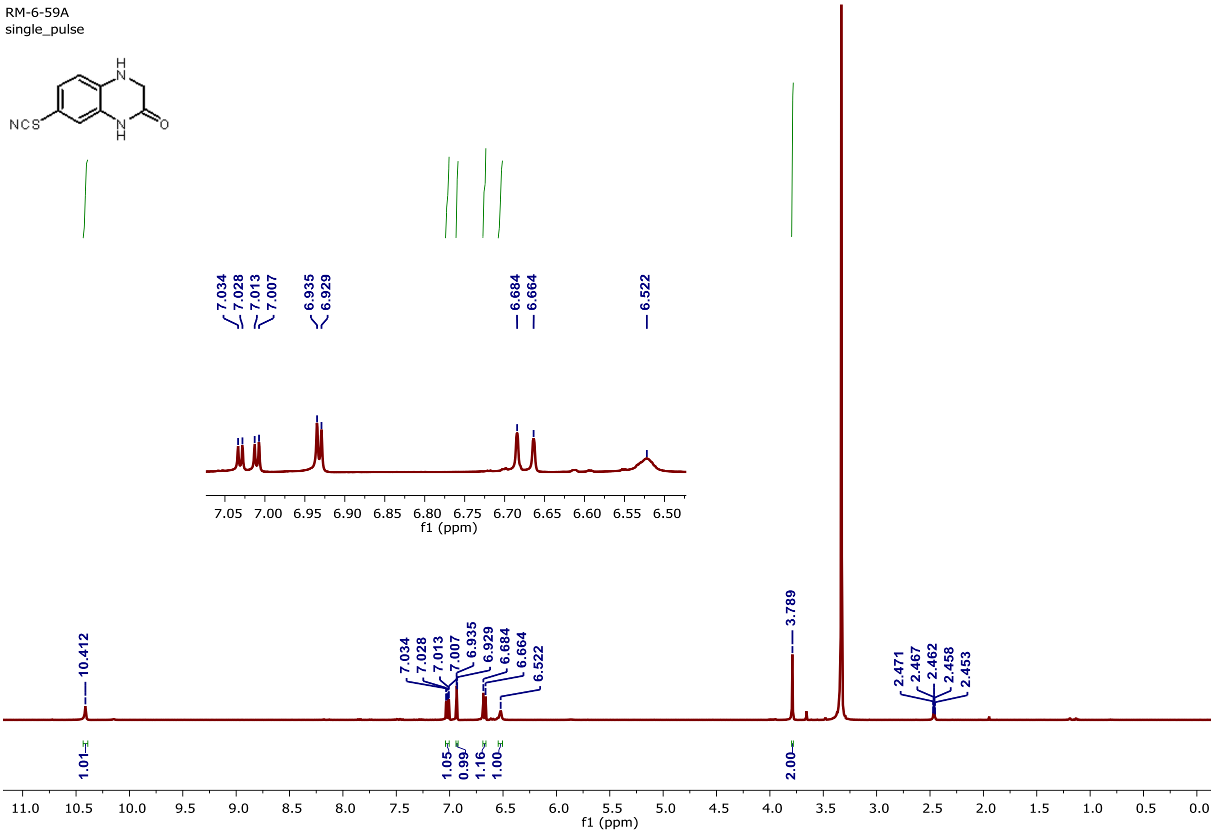
SI-12-6: Analytical and Spectral data of **3f**

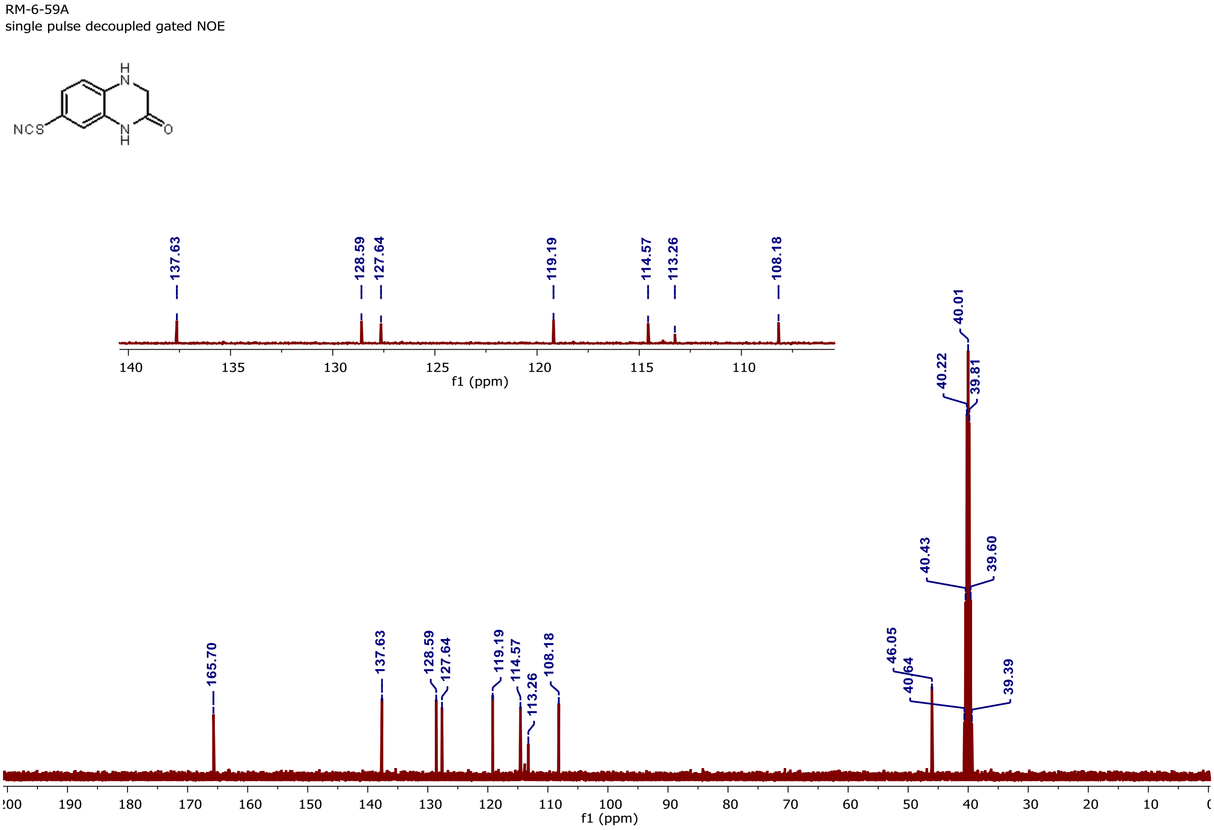




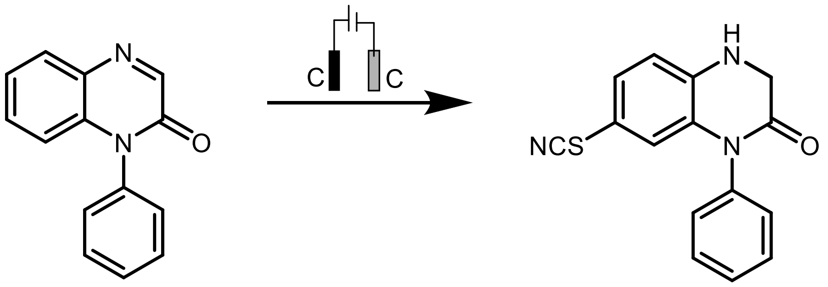
7-Thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3f: Prepared according to the general procedure discussed above: reaction time = 3.1 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (40%); white solid (30 mg, 36%); mp 204–206 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.41 (s, 1 H), 7.02 (dd, J = 8.4, 2.4 Hz, 1 H), 6.93 (d, J = 2.4 Hz, 1 H), 6.67 (d, J = 8.0 Hz, 1 H), 6.52 (s, 1 H), 3.79 ppm (s, 2 H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 165.7, 137.6, 128.6, 127.6, 119.2, 114.6, 113.3, 108.2, 46.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_9H_8N_3OS$ [M + H]$^+$: 206.0388; found: 206.0380.

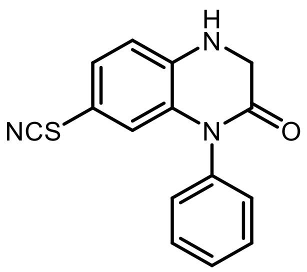
^{1}H (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} (101 MHz, DMSO-d_6) NMR spectra of **3f:**





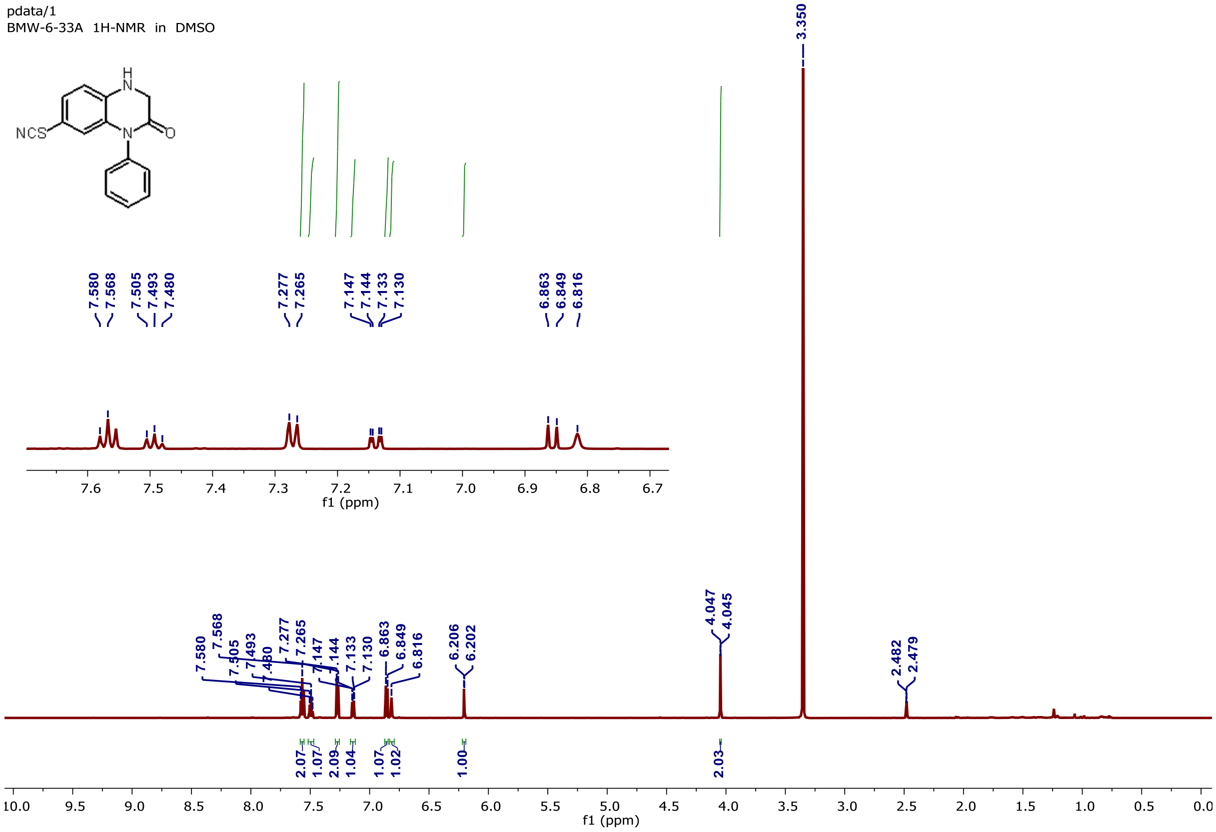
SI-12-7: Analytical and Spectral data of **3g**

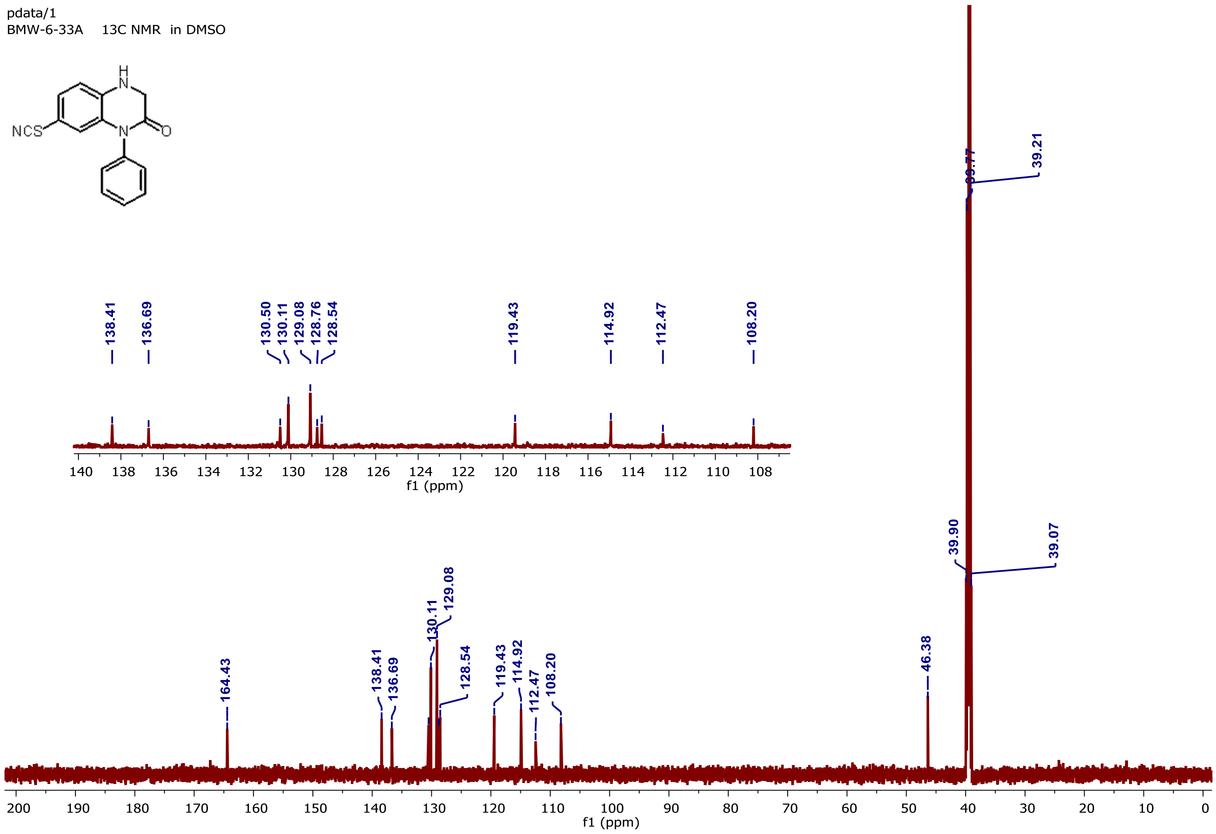




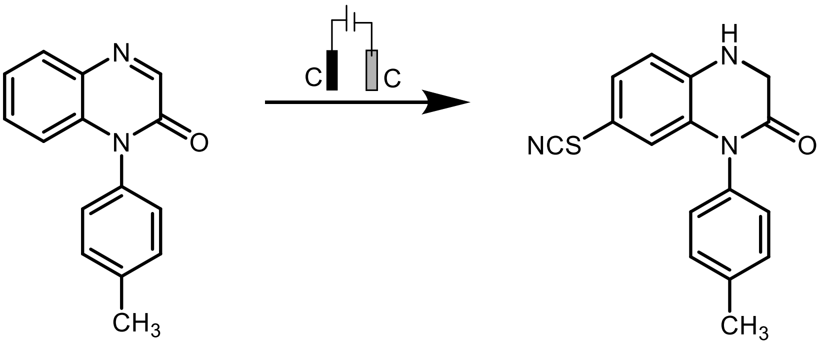
1-Phenyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3g: Prepared according to the general procedure discussed above: reaction time = 3.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (60 mg, 52%); mp 177–179 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.57 (t, J = 7.2 Hz, 2 H), 7.49 (t, J = 7.2 Hz, 1 H), 7.27 (d, J = 7.2 Hz, 2 H), 7.14 (dd, J = 8.4, 1.8 Hz, 1 H), 6.86 (d, J = 8.4 Hz, 1 H), 6.82 (s, 1 H), 6.20 (d, J = 2.4 Hz, 1 H), 4.05 ppm (d, J = 1.2 Hz, 2 H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ = 164.4, 138.4, 136.7, 130.5, 130.1 (2 CH), 129.1 (2 CH), 128.8, 128.5, 119.4, 114.9, 112.5, 108.2, 46.4 (CH_2) ppm. HRMS (ESI-QTOF): *m/z* calcd for $C_{15}H_{12}N_3OS$ $[M + H]^+$: 282.0701; found: 282.0703.

^{1}H (600 MHz, DMSO-d_6) and ^{13}C{^{1}H} (151 MHz, DMSO-d_6) NMR spectra of **3g**:

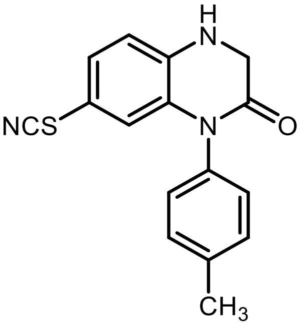




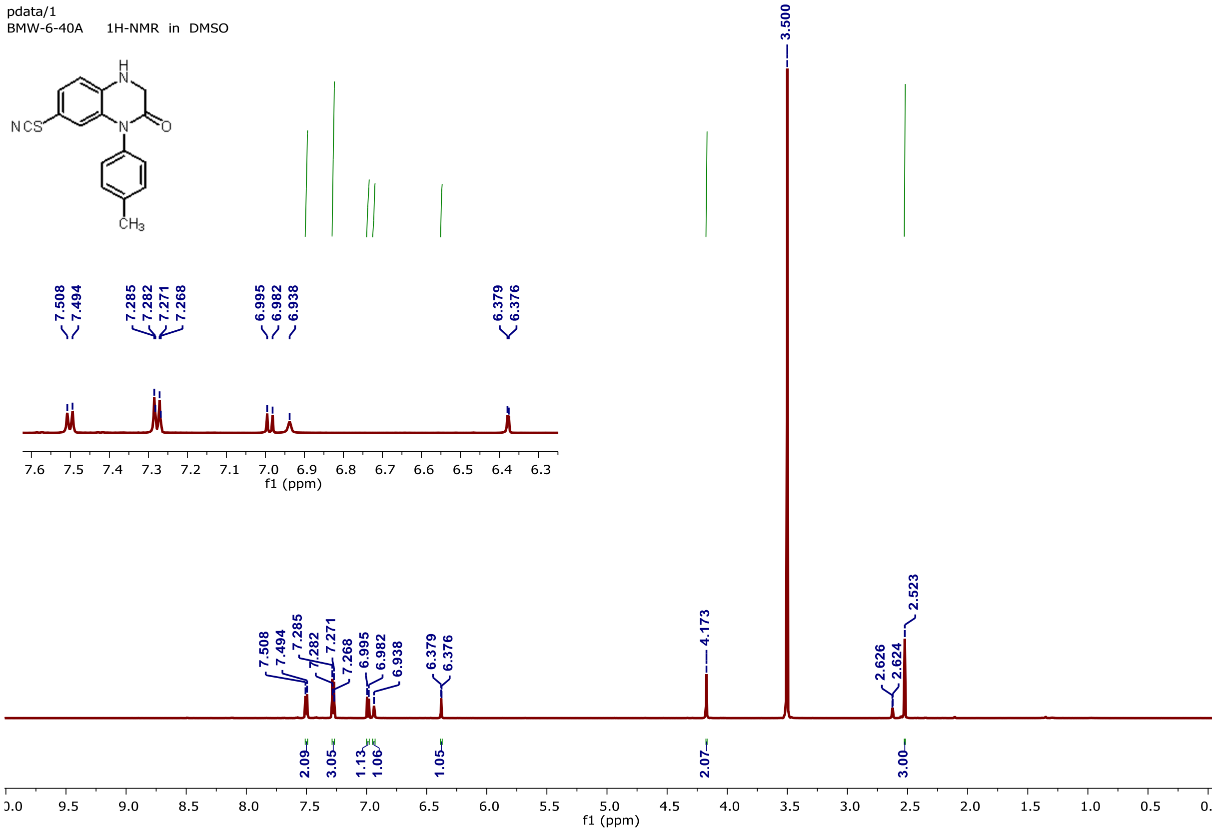
SI-12-8: Analytical and Spectral data of **3h**

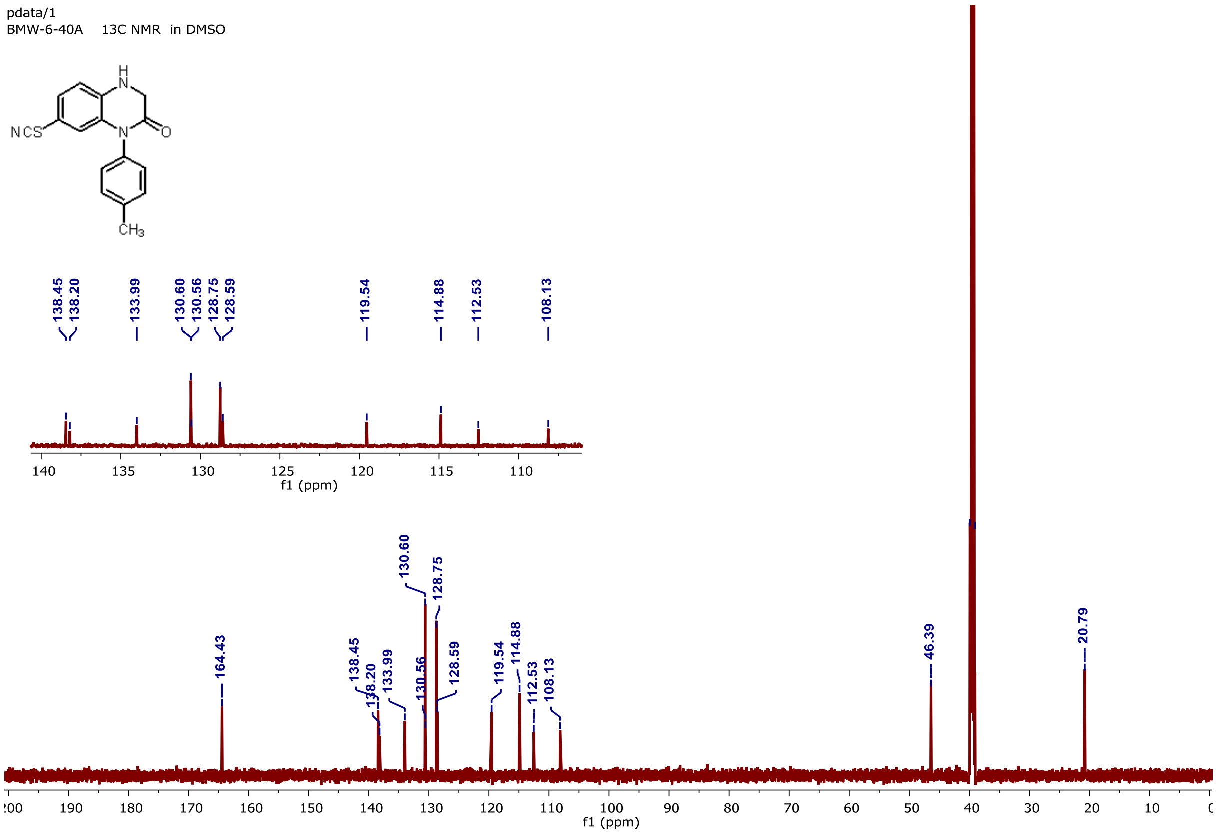


7-Thiocyanato-1-(*p*-tolyl)-3,4-dihydroquinoxalin-2(1*H*)-one 3h: Prepared according to the general procedure discussed above: reaction time = 3.4 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (96 mg, 80%); mp 194–196 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.50 (d, J = 8.4 Hz, 2 H), 7.28 (dd, J = 8.4, 1.8 Hz, 3 H), 6.99 (d, J = 7.8 Hz, 1 H), 6.94 (s, 1 H), 6.38 (d, J = 1.8 Hz, 1 H), 4.17 (s, 2 H), 2.52 ppm (s, 3 H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ = 164.4, 138.4, 138.2, 134.0, 130.6 (2 CH), 130.6, 128.8 (2 CH), 128.6, 119.5, 114.9, 112.5, 108.1, 46.4 (CH$_2$), 20.8 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{14}N_3OS$ [M + H]$^+$: 296.0858; found: 296.0856.

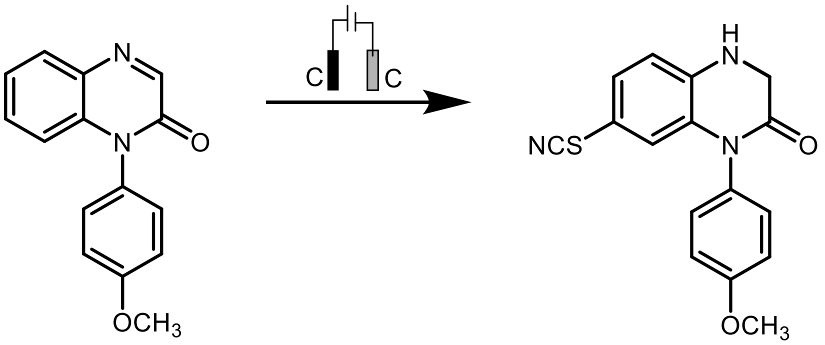


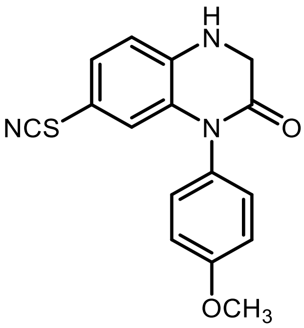
^1H (600 MHz, DMSO-d_6) and $^{13}C\{^1H\}$ (151 MHz, DMSO-d_6) NMR spectra of **3h:**





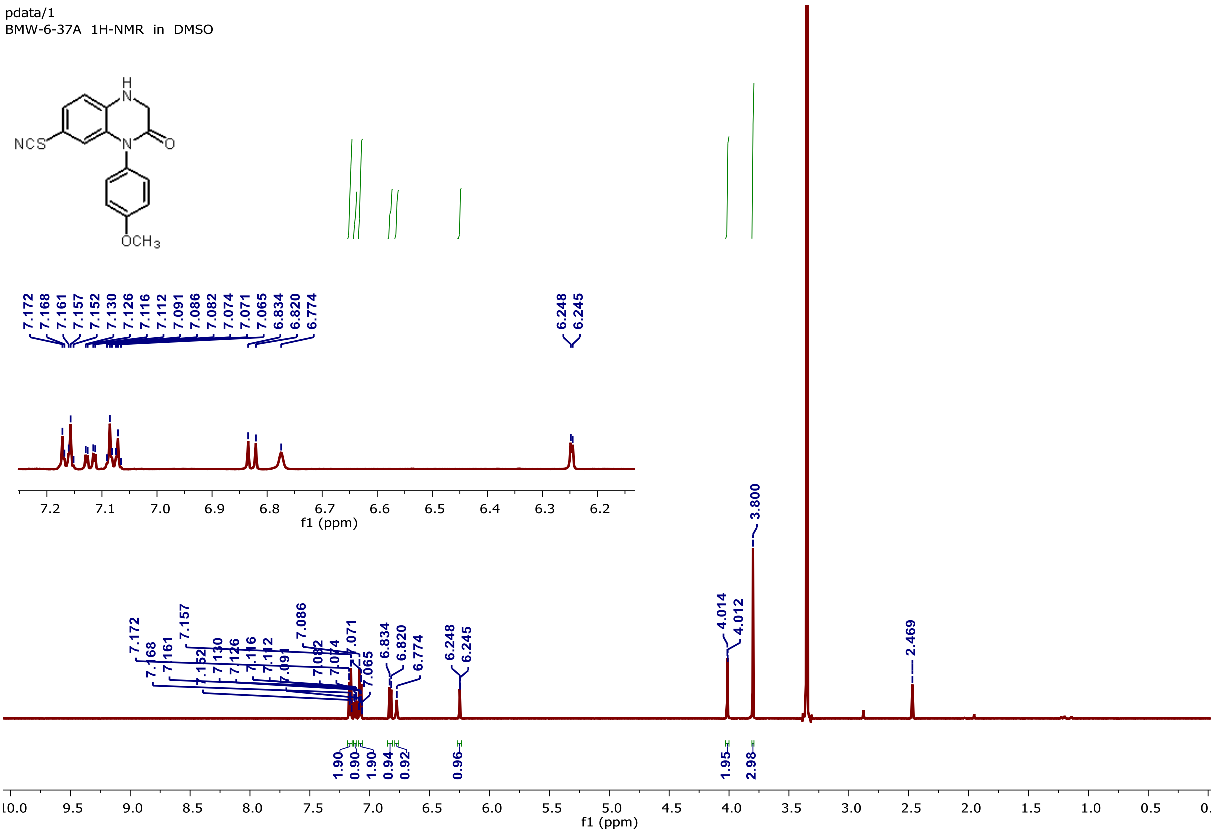
SI-12-9: Analytical and Spectral data of **3i**

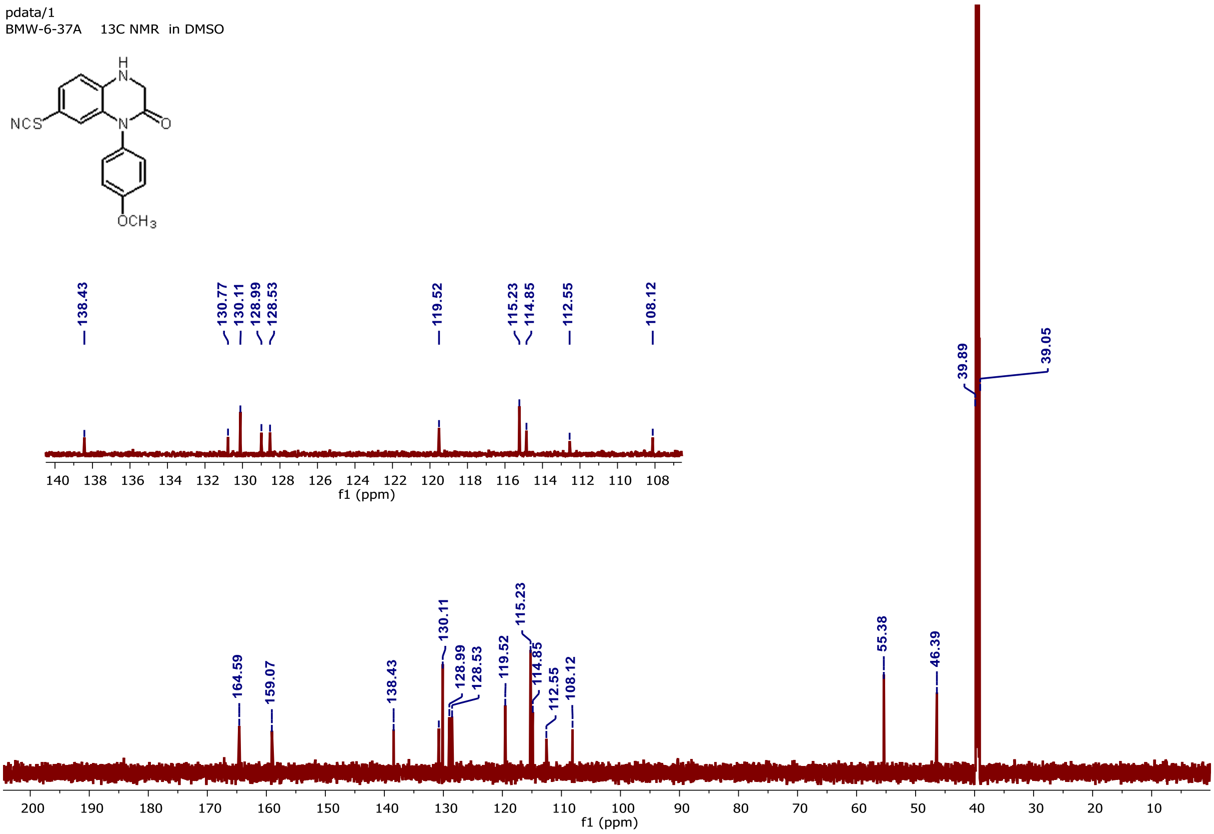




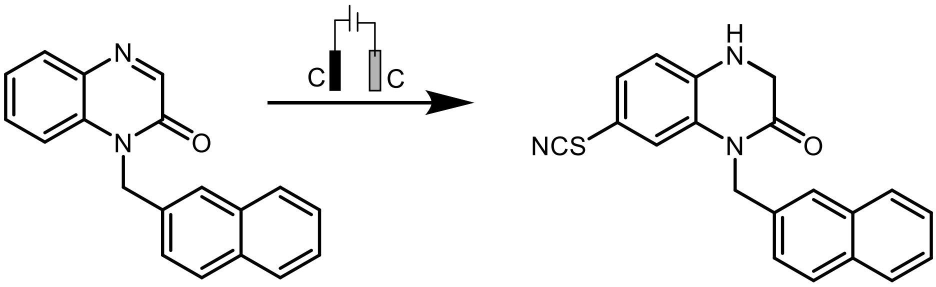
1-(4-Methoxyphenyl)-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3i: Prepared according to the general procedure discussed above: reaction time = 3.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (98 mg, 78%); mp 180–182 ˚C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.15-7.17 (m, 2 H), 7.12 (dd, J = 8.4, 2.4 Hz, 1 H), 7.06-7.10 (m, 2 H), 6.83 (d, J = 8.4 Hz, 1 H), 6.77 (s, 1 H), 6.25 (d, J = 1.8 Hz, 1 H), 4.01 (d, J = 1.2 Hz, 2 H), 3.80 ppm (s, 3 H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ = 164.6, 159.1, 138.4, 130.8, 130.1 (2 CH), 129.0, 128.5, 119.5, 115.2 (2 CH), 114.9, 112.6, 108.1, 55.4, 46.4 (CH$_2$) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{14}N_3O_2S$ [*M* + H]$^+$: 312.0806; found: 312.0802.

^{1}H (600 MHz, DMSO-*d*$_6$) and ^{13}C{^{1}H} (151 MHz, DMSO-*d*$_6$) NMR spectra of **3i:**

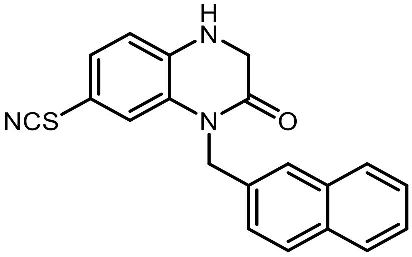




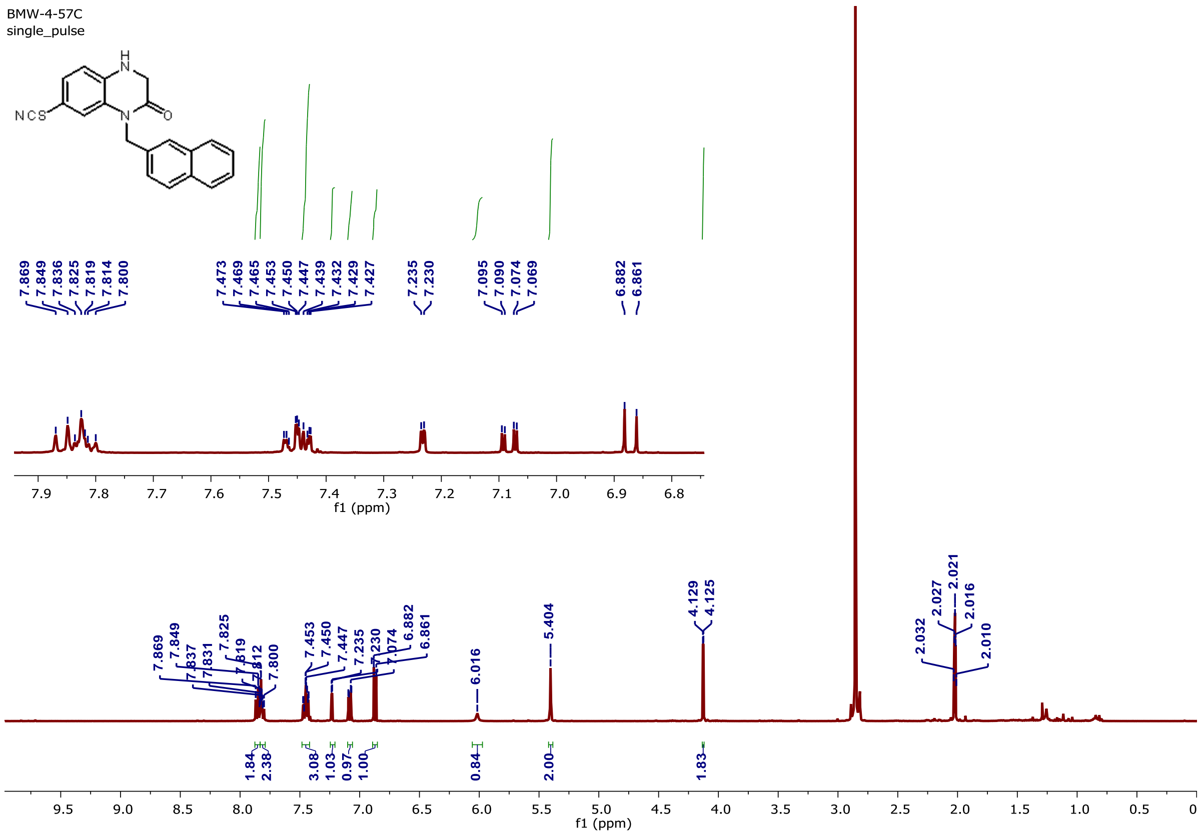
SI-12-10: Analytical and Spectral data of **3j**

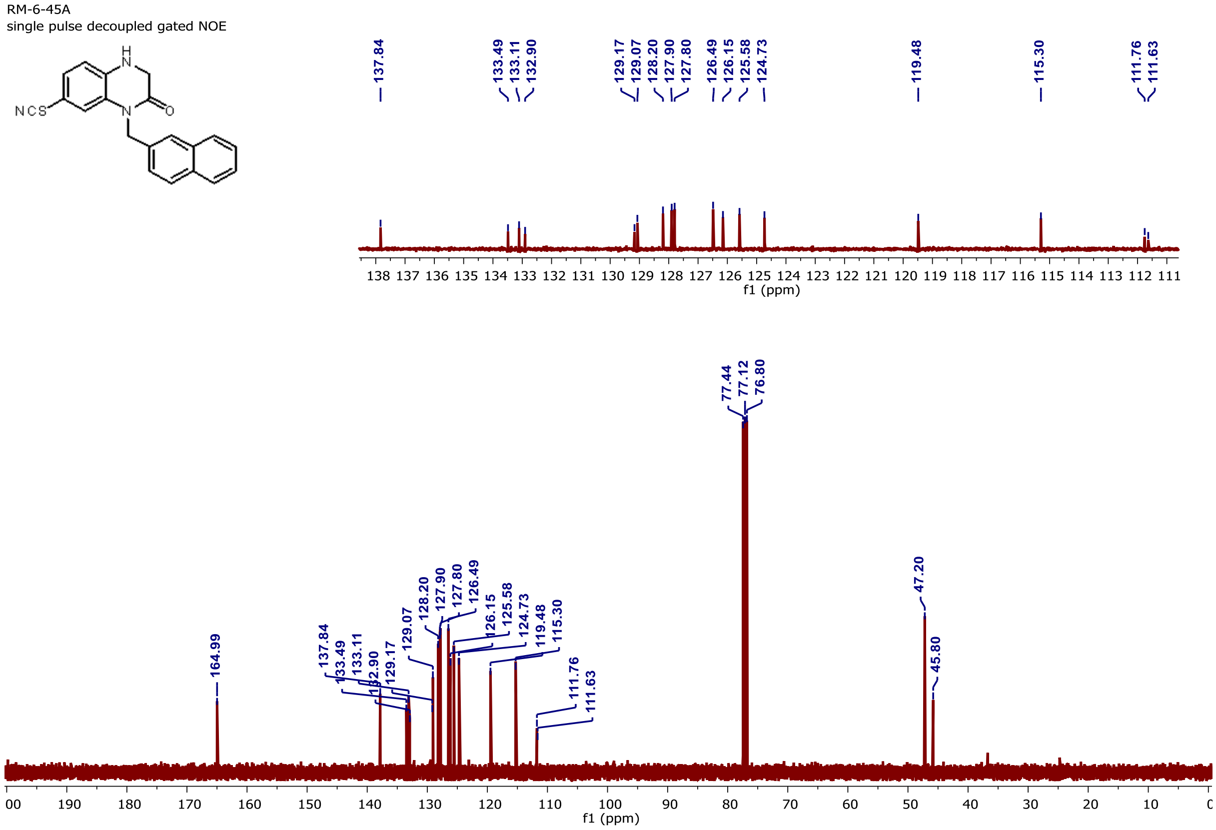


1-(Naphthalen-2-ylmethyl)-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3j: Prepared according to the general procedure discussed above: reaction time = 3.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); colorless gum (84 mg, 60%). ^{1}H NMR (400 MHz, Acetone-d_6): δ = 7.84-7.87 (m, 2 H), 7.80-7.83 (m, 2 H), 7.43-7.47 (m, 3 H), 7.23 (d, J = 2.0 Hz, 1 H), 7.08 (dd, J = 8.4, 2.0 Hz, 1 H), 6.87 (d, J = 8.4 Hz, 1 H), 6.02 (s, 1 H), 5.40 (s, 2 H), 4.13 (d, J = 1.6 Hz, 2 H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 165.0, 137.8, 133.5, 133.1, 132.9, 129.2, 129.1, 128.2, 127.9, 127.8, 126.5, 126.1, 125.6, 124.7, 119.5, 115.3, 111.8, 111.6, 47.2 (CH$_2$), 45.8 (CH$_2$) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{16}N_3OS$ [*M* + H]$^+$: 346.1014; found: 346.1010.

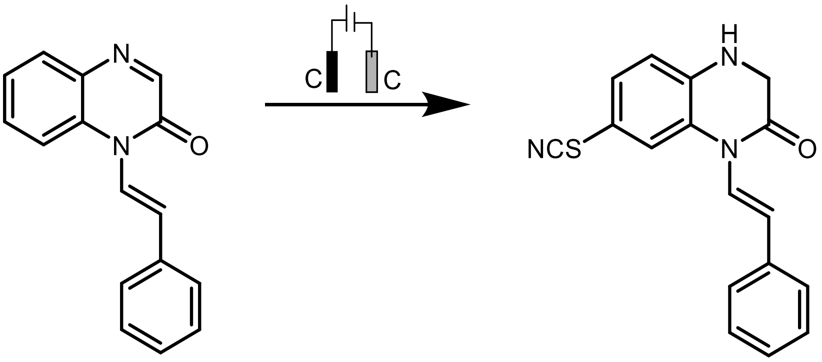


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of **3j:**

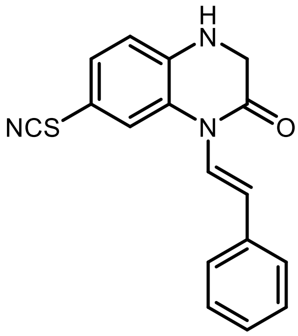




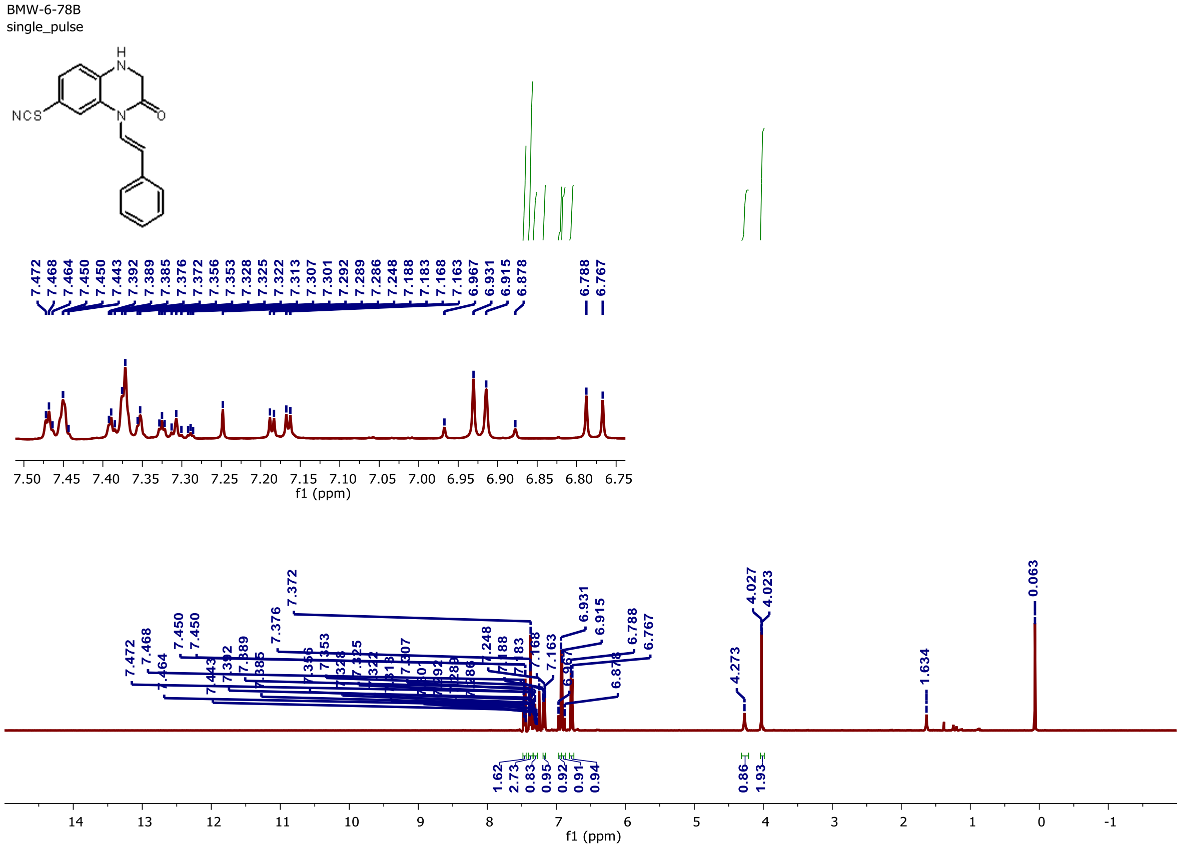
SI-12-11: Analytical and Spectral data of **3k**

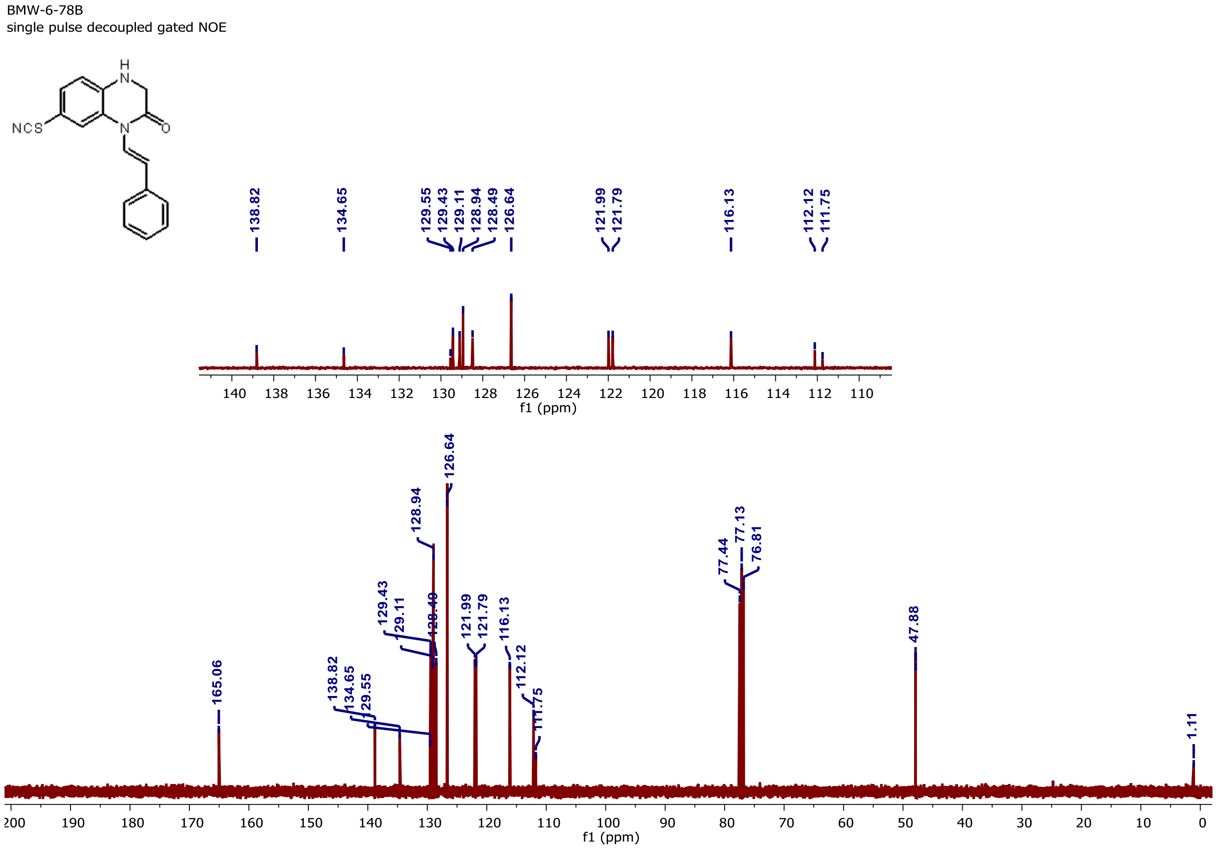


(*E*)-1-styryl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3k: Prepared according to the general procedure discussed above: reaction time = 3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); Colorless gum (97 mg, 79%). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.44-7.47 (m, 2 H), 7.35-7.39 (m, 3 H), 7.29-7.33 (m, 1 H), 7.18 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.95 (d, *J* = 14.4 Hz, 1 H), 6.90 (d, *J* = 14.8 Hz, 1 H), 6.78 (d, *J* = 8.4 Hz, 1 H), 4.27 (s, 1 H), 4.02 ppm (d, *J* = 1.6 Hz, 2 H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ = 165.1, 138.8, 134.6, 129.5, 129.4, 129.1, 128.9 (2 CH), 128.5, 126.6 (2 CH), 122.0, 121.8, 116.1, 112.1, 111.8, 47.9 (CH$_2$) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{14}N_3OS$ [*M* + H]$^+$: 308.0857; found: 308.0859.

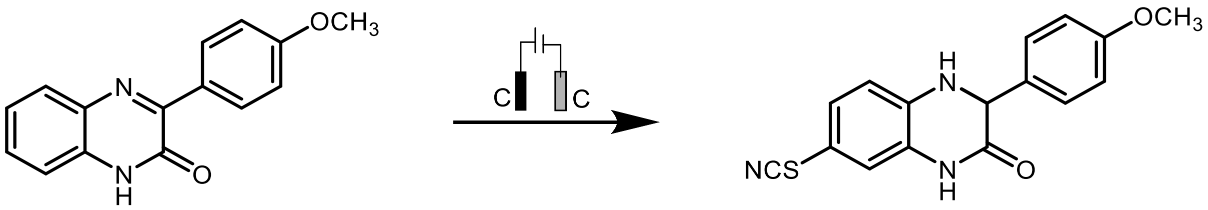


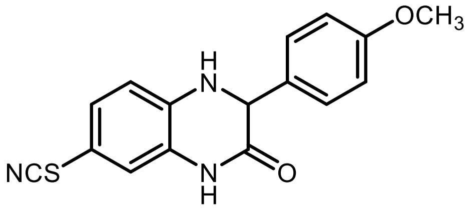
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3k:**





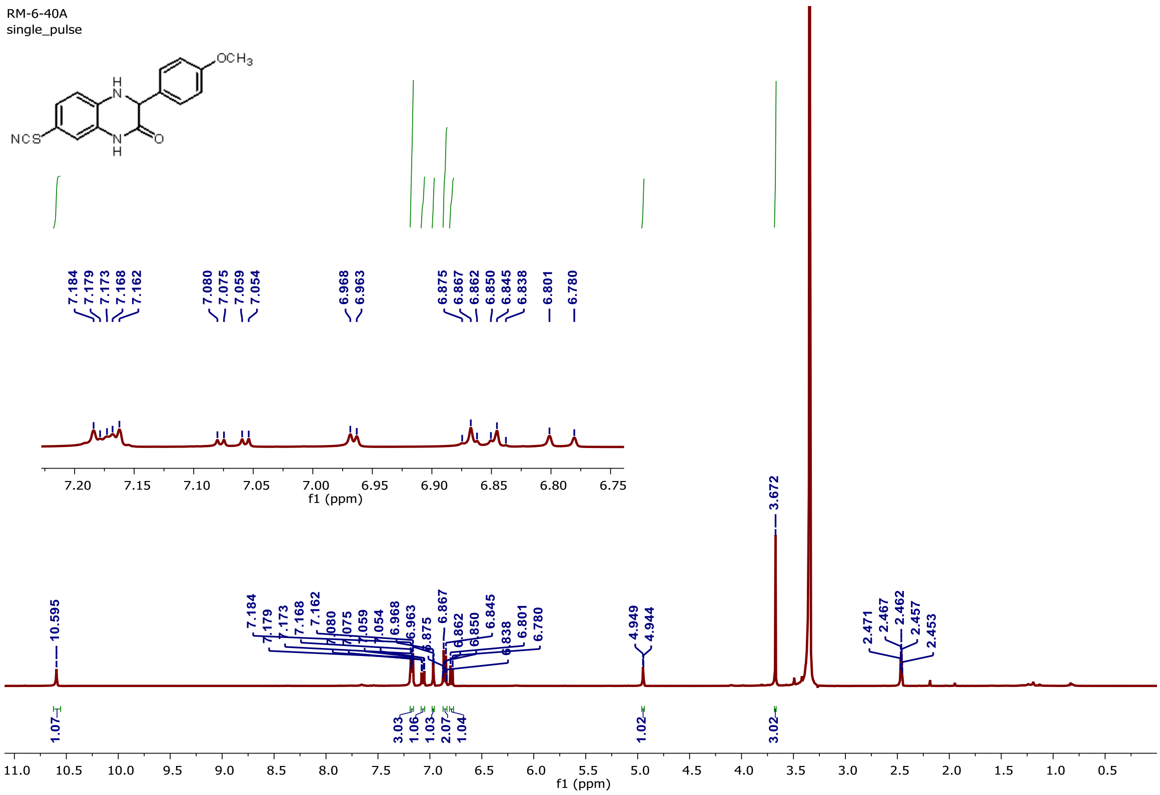
SI-12-12: Analytical and Spectral data of **3l**

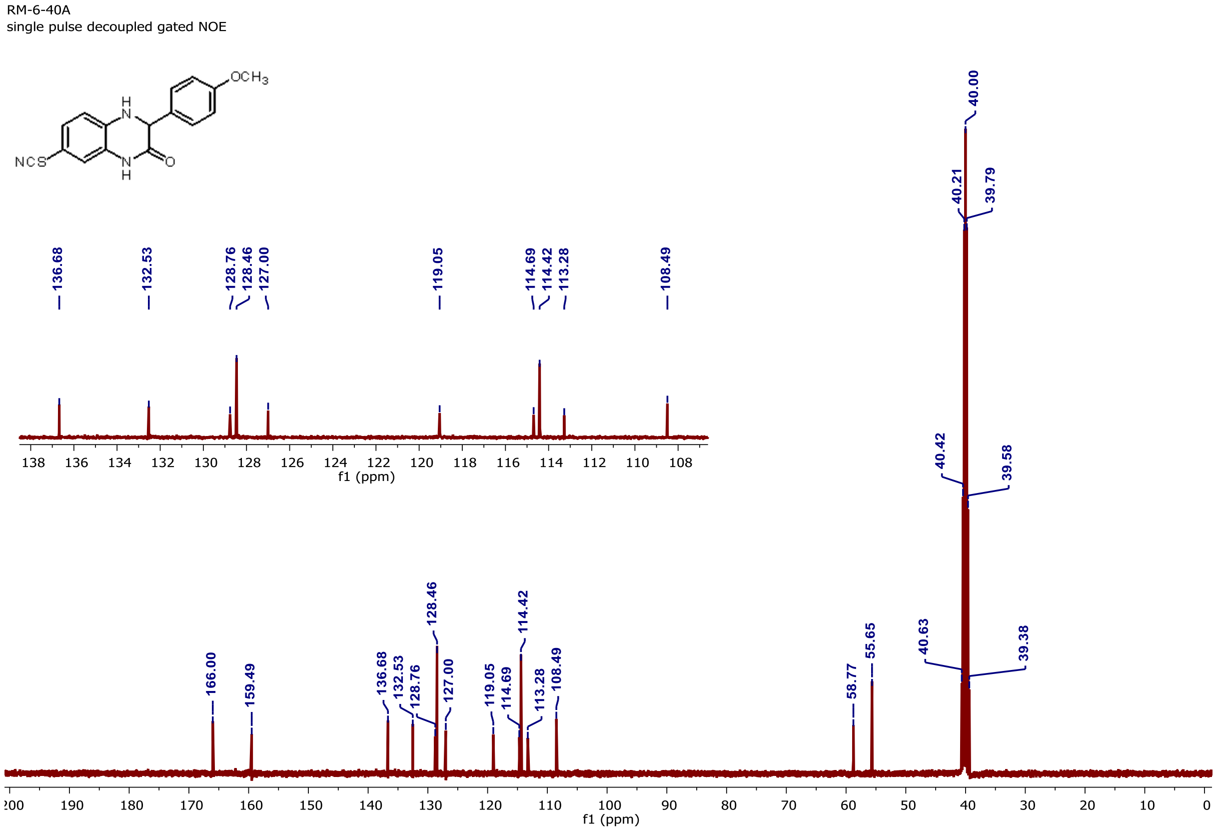




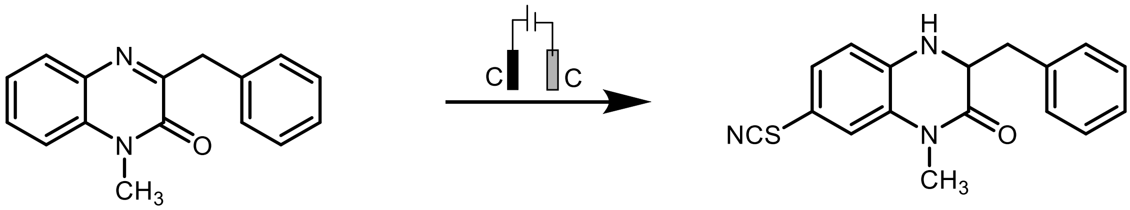
3-(4-Methoxyphenyl)-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3l: Prepared according to the general procedure discussed above: reaction time = 2.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (68 mg, 55%); mp 154–156 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.59 (s, 1 H), 7.16-7.18 (m, 3 H), 7.07 (dd, J = 8.4, 2.0 Hz, 1 H), 6.97 (d, J = 2.0 Hz, 1 H), 6.84-6.87 (m, 2 H), 6.79 (d, J = 8.4 Hz, 1 H), 4.95 (d, J = 2.0 Hz, 1 H), 3.67 ppm (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 166.0, 159.5, 136.7, 132.5, 128.8, 128.5 (2 CH), 127.0, 119.0, 114.7, 114.4 (2 CH), 113.3, 108.5, 58.8, 55.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{14}N_3O_2S$ [*M* + H]$^+$: 312.0806; found: 312.0800.

^{1}H (400 MHz, DMSO-d_6) and $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6) NMR spectra of **3l:**

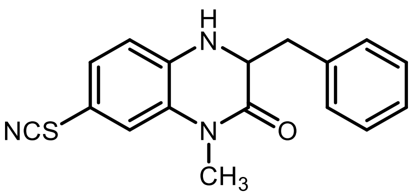




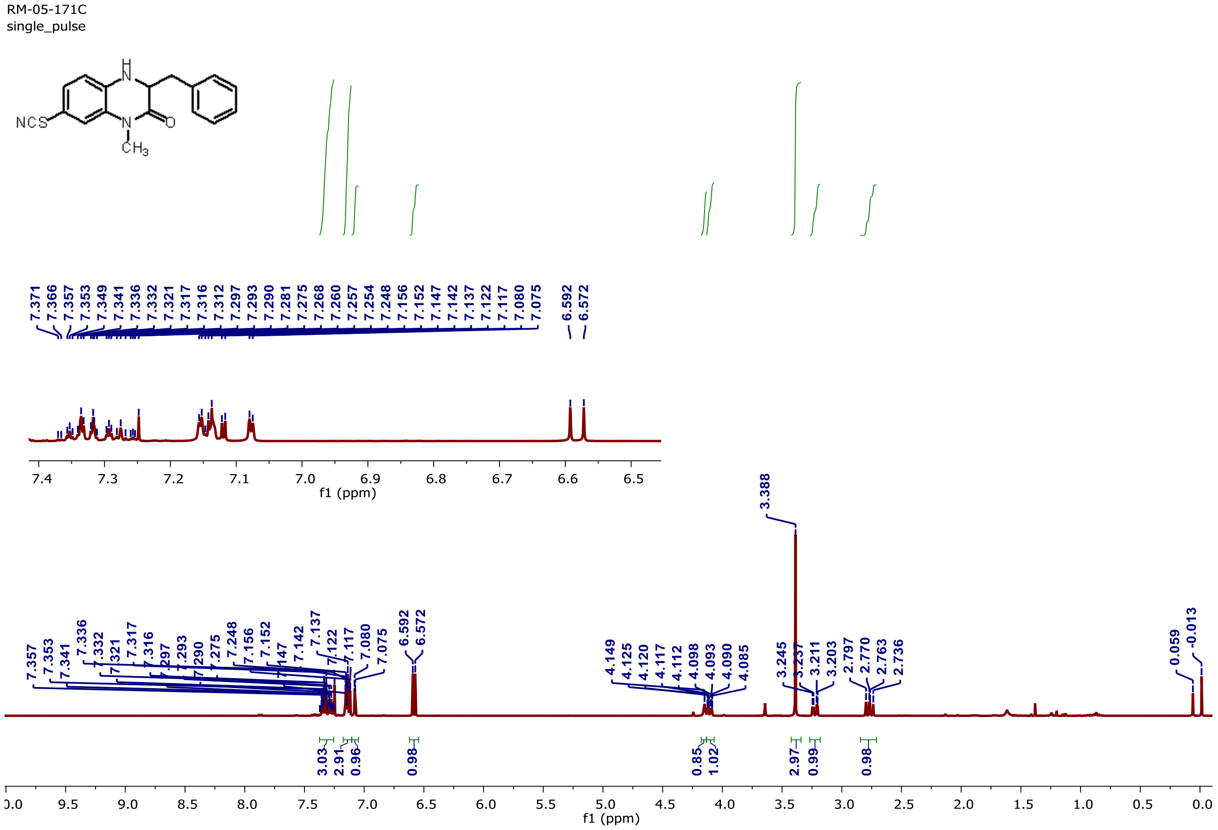
SI-12-13: Analytical and Spectral data of **3m**

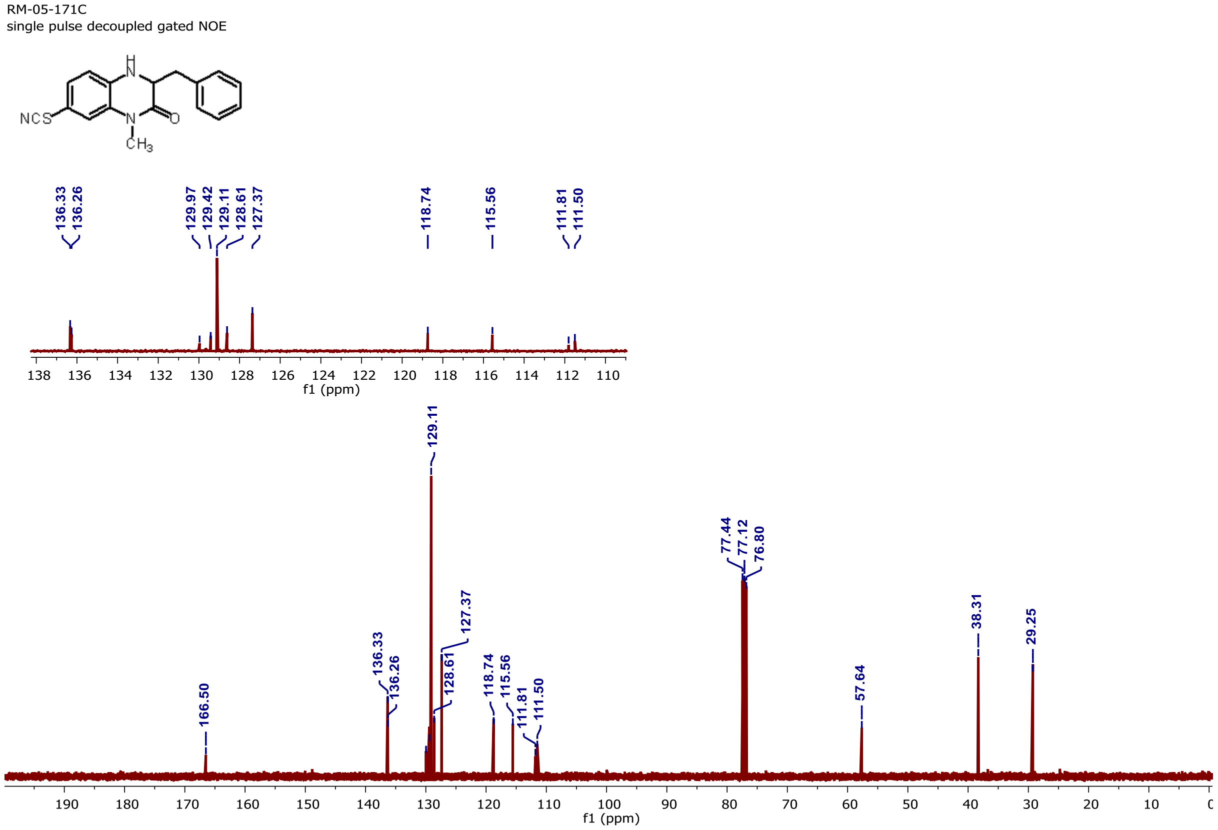


3-Benzyl-1-methyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one **3m**: Prepared according to the general procedure discussed above: reaction time = 3.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (98 mg, 79%); mp 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.37 (m, 3 H), 7.12-7.16 (m, 3 H), 7.08 (d, *J* = 2.0 Hz, 1 H), 6.58 (d, *J* = 8.0 Hz, 1 H), 4.15 (s, 1 H), 4.10 (ddd, *J* = 2.0, 3.2, 10.8 Hz, 1 H), 3.39 (s, 3 H), 3.22 (dd, *J* = 13.6, 3.2 Hz, 1 H), 2.77 ppm (dd, *J* = 13.6, 10.8 Hz, 1 H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 166.5, 136.3, 136.3, 130.0, 129.4, 129.1 (2 CH), 128.6, 127.4 (2 CH), 118.7, 115.6, 111.8, 111.5, 57.6, 38.3, 29.2 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{16}N_3OS$ [*M* + H]$^+$: 310.1014; found: 310.1011.

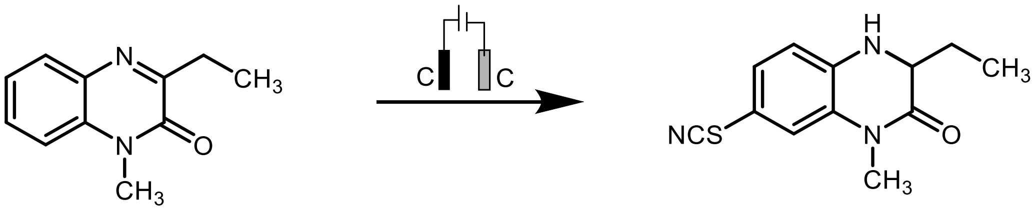


^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **3m:**

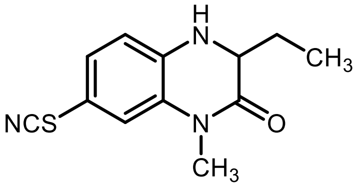




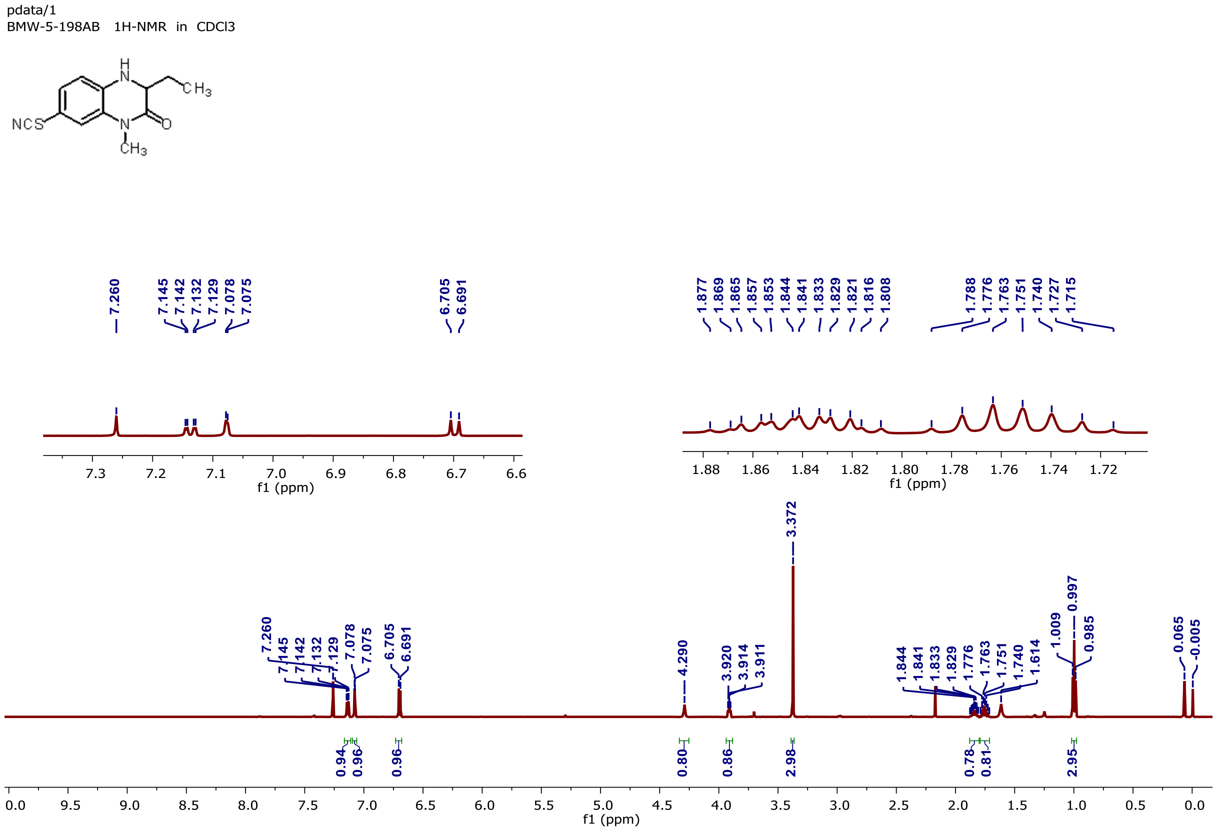
SI-12-14: Analytical and Spectral data of **3n**

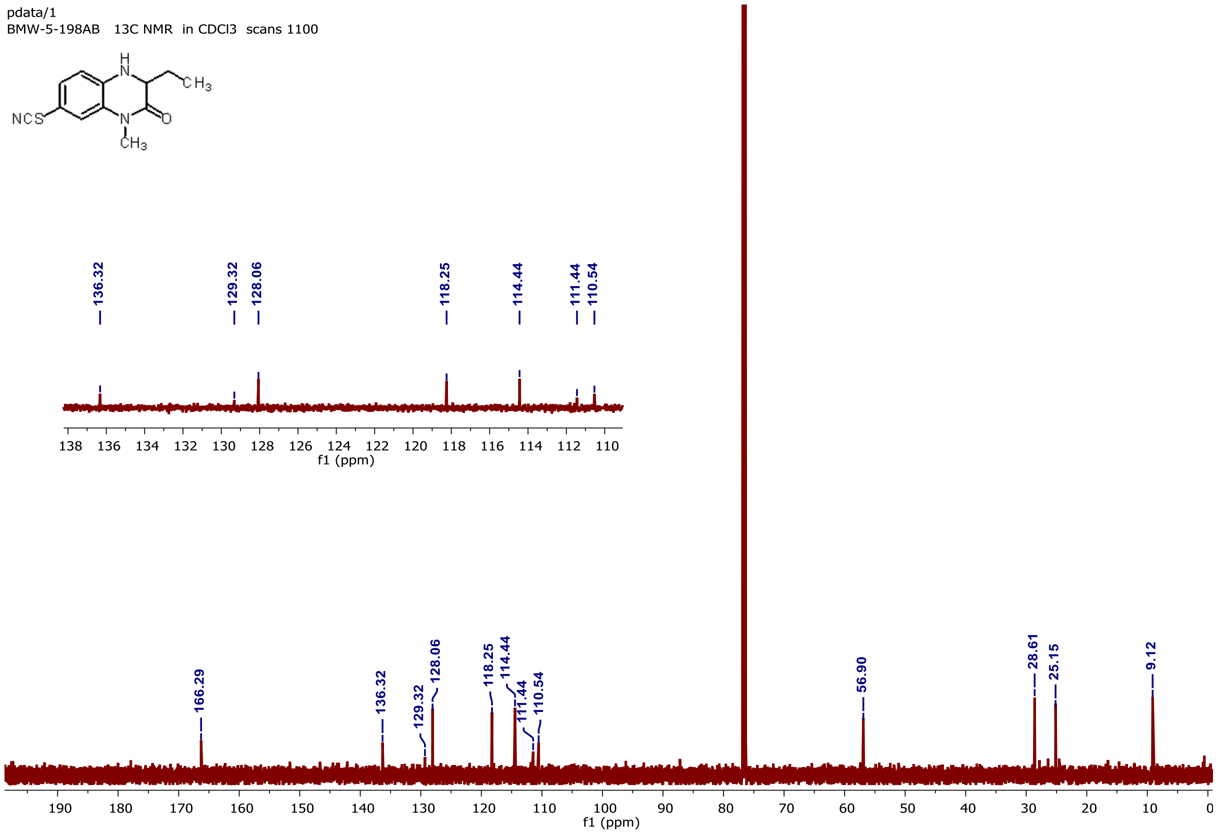


3-Ethyl-1-methyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3n: Prepared according to the general procedure discussed above: reaction time = 3.2 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (87 mg, 88%); mp 101–103 ˚C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.14 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.08 (d, *J* = 1.8 Hz, 1 H), 6.70 (d, *J* = 8.4 Hz, 1 H), 4.29 (s, 1 H), 3.90-3.92 (m, 1 H), 3.37 (s, 3 H), 1.84 (dtd, *J* = 15.0, 7.2, 4.8 Hz, 1 H), 1.75 (dp, *J* = 15.0, 7.2 Hz, 1 H), 1.00 ppm (t, *J* = 7.2 Hz, 3 H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 166.3, 136.3, 129.3, 128.1, 118.2, 114.4, 111.4, 110.5, 56.9, 28.6, 25.2, 9.1 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{12}H_{14}N_3OS$ [M + H]$^+$: 248.0857; found: 248.0864.

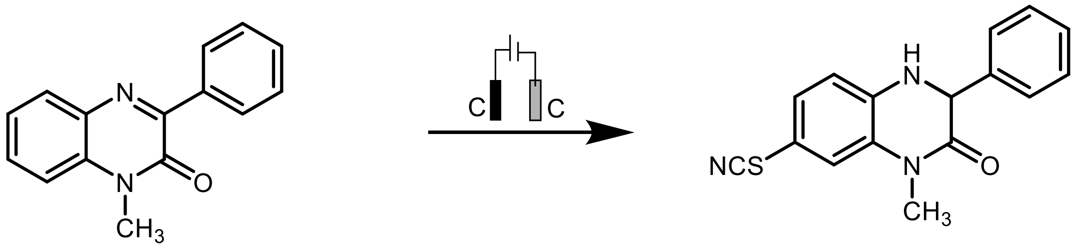


^{1}H (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} (151 MHz, CDCl$_3$) NMR spectra of **3n:**

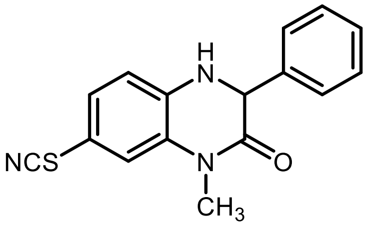




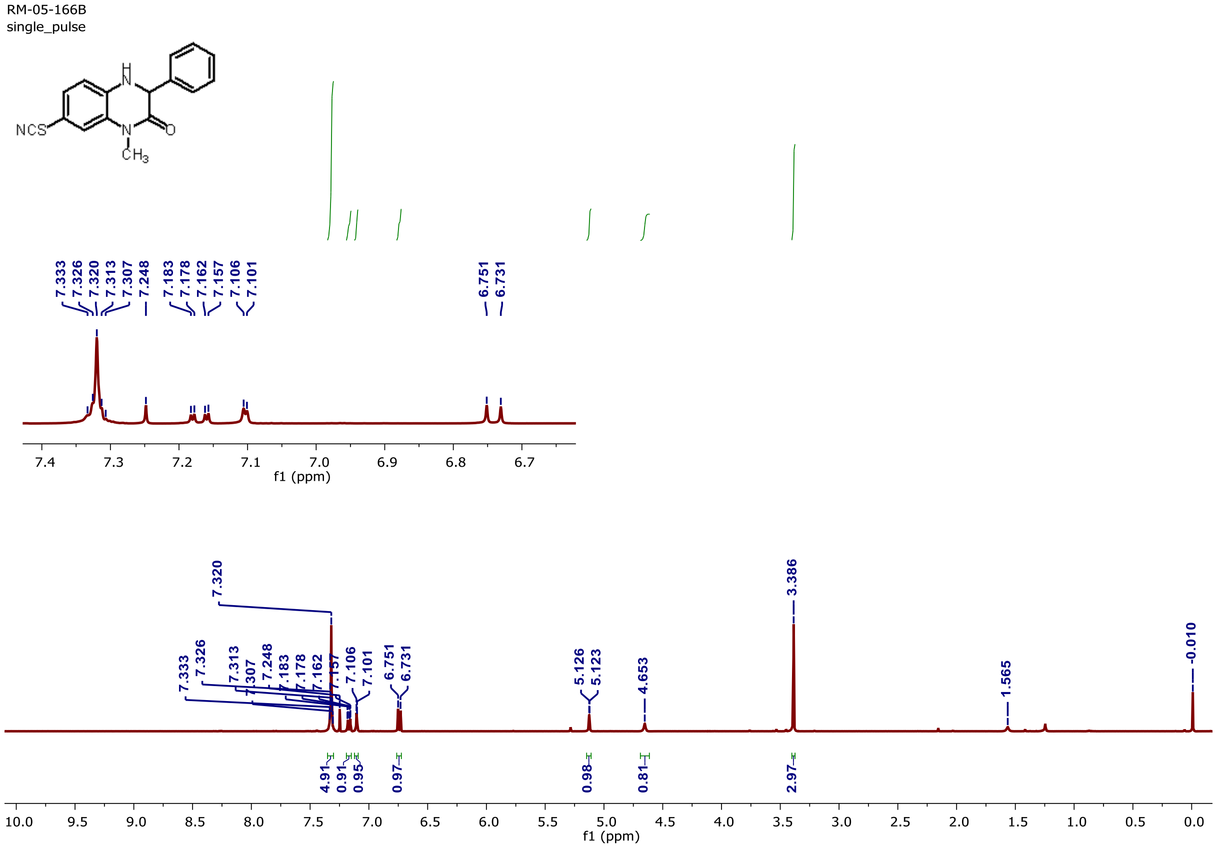
SI-12-15: Analytical and Spectral data of **3o**

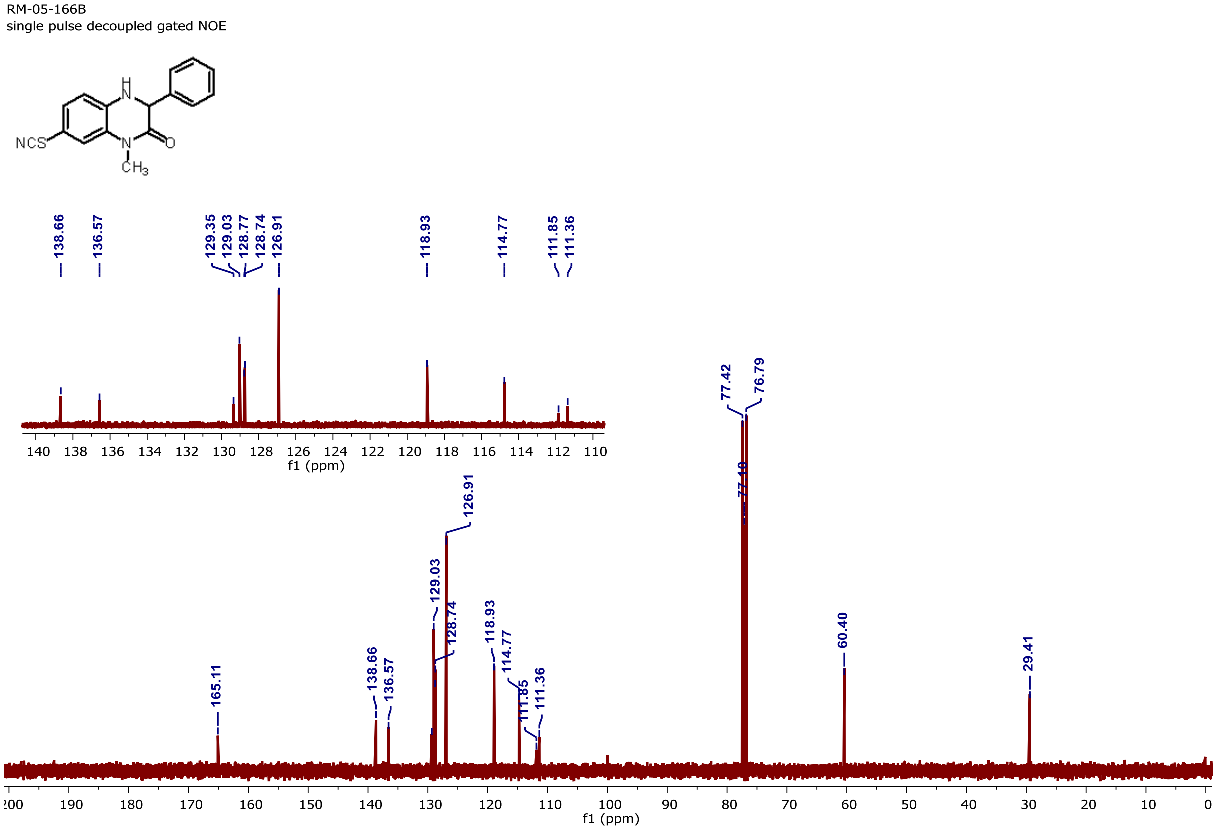


1-Methyl-3-phenyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3o: Prepared according to the general procedure discussed above: reaction time = 3.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (103 mg, 86%); mp 192–194 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.31-7.33 (m, 5 H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.10 (d, *J* = 2.0 Hz, 1 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 5.12 (d, *J* = 1.2 Hz, 1 H), 4.65 (s, 1 H), 3.39 ppm (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ* = 165.1, 138.7, 136.6, 129.4, 129.0 (2 CH), 128.8, 128.7, 126.9 (2 CH), 118.9, 114.8, 111.9, 111.4, 60.4, 29.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{14}N_3OS$ [*M* + H]$^+$: 296.0857; found: 296.0845.

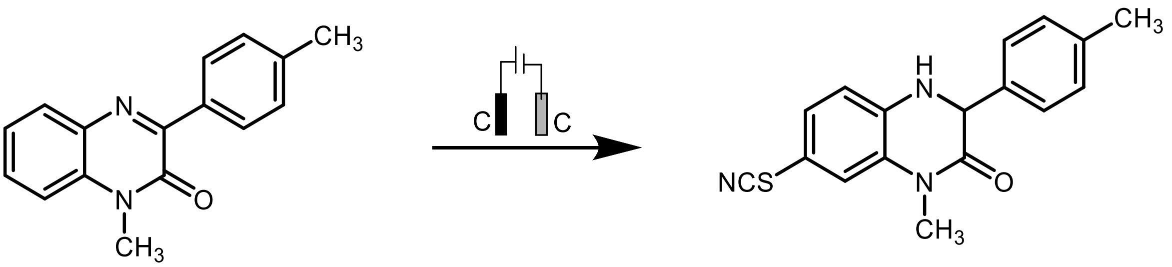


^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **3o:**

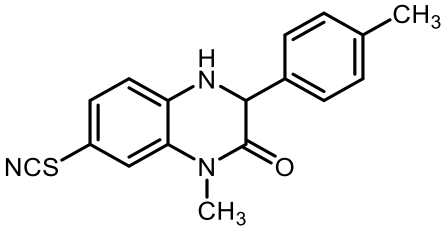




SI-12-16: Analytical and Spectral data of **3p**

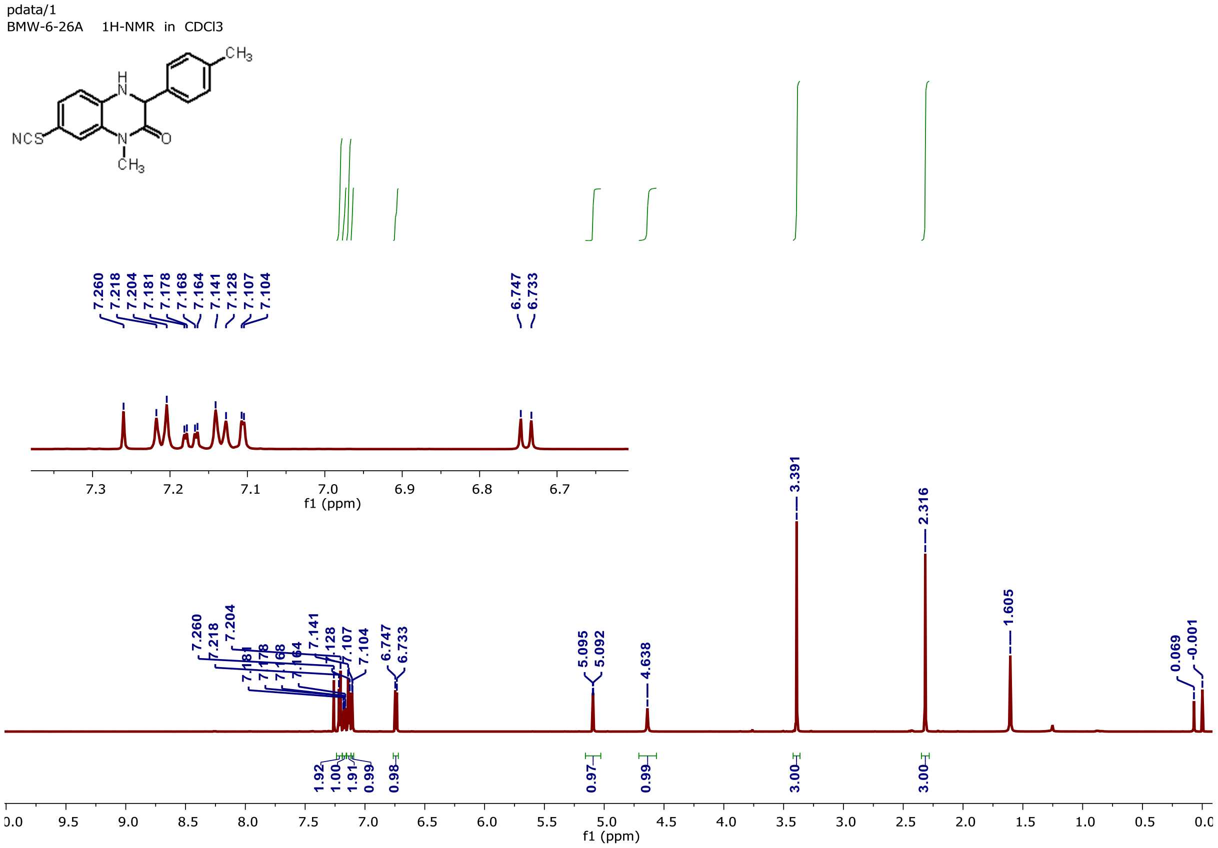


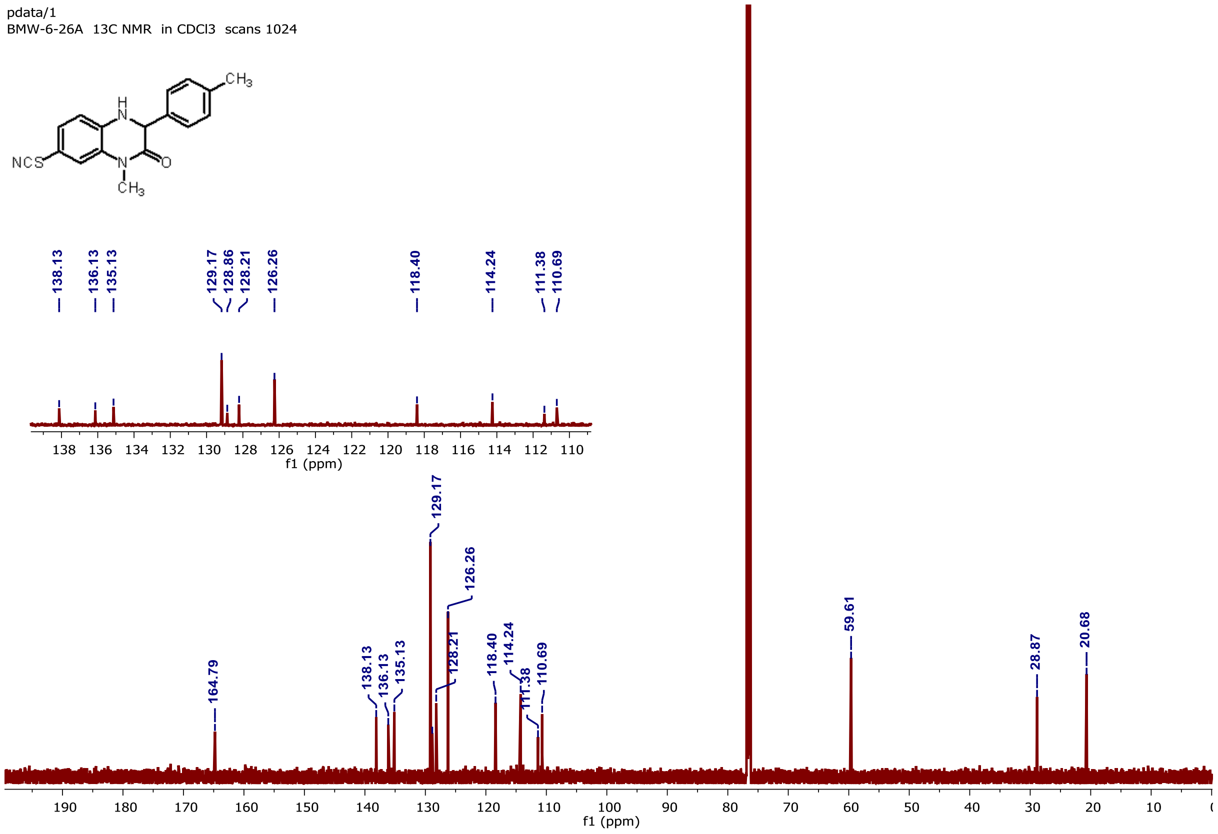
1-Methyl-7-thiocyanato-3-(*p*-tolyl)-3,4-dihydroquinoxalin-2(1*H*)-one 3p:



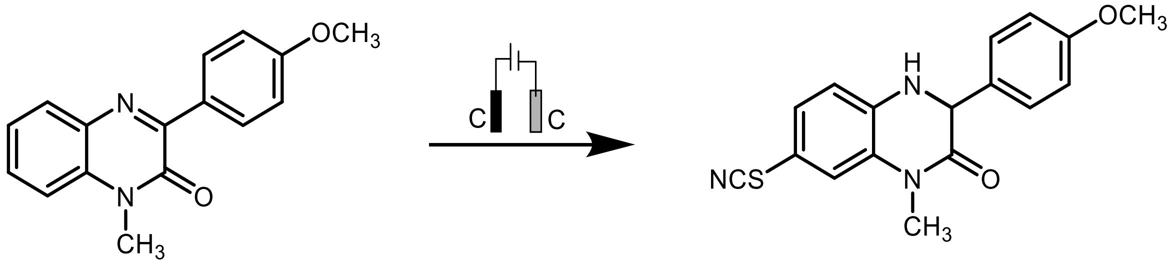
Prepared according to the general procedure discussed above: reaction time = 3.25 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (85 mg, 68%); mp 156–158 ˚C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.21 (d, J = 8.4 Hz, 2 H), 7.17 (dd, J = 7.8, 1.8 Hz, 1 H), 7.13 (d, J = 7.8 Hz, 2 H), 7.11 (d, J = 1.8 Hz, 1 H), 6.74 (d, J = 8.4 Hz, 1 H), 5.09 (s, 1 H), 4.64 (s, 1 H), 3.39 (s, 3 H), 2.32 ppm (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 164.8, 138.1, 136.1, 135.1, 129.2 (2 CH), 128.9, 128.2, 126.3 (2 CH), 118.4, 114.2, 111.4, 110.7, 59.6, 28.9, 20.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{16}N_3OS$ $[M + H]^+$: 310.1014; found: 310.1010.

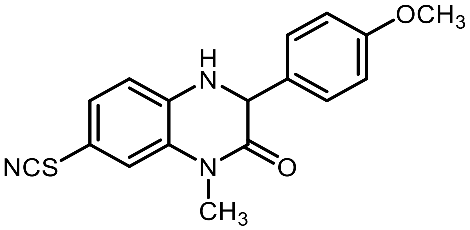
^1H (600 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ (151 MHz, $CDCl_3$) NMR spectra of **3p:**





SI-12-17: Analytical and Spectral data of **3q**

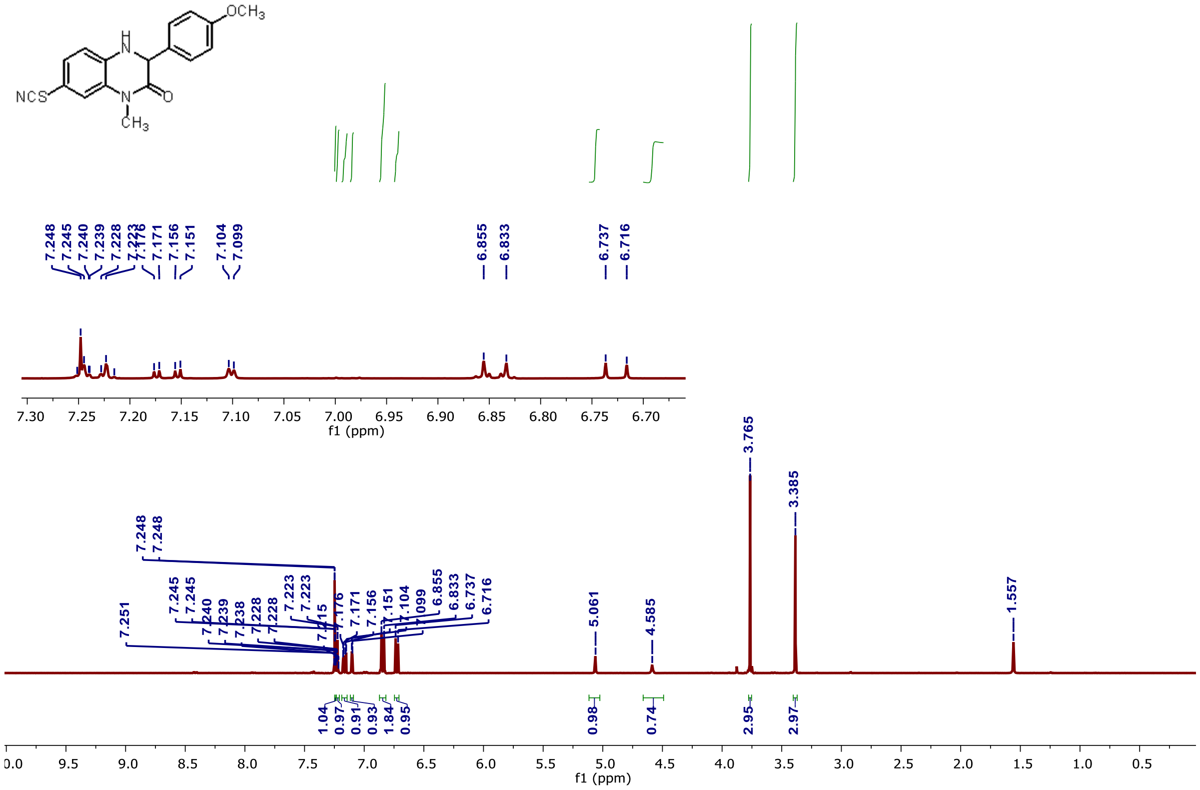




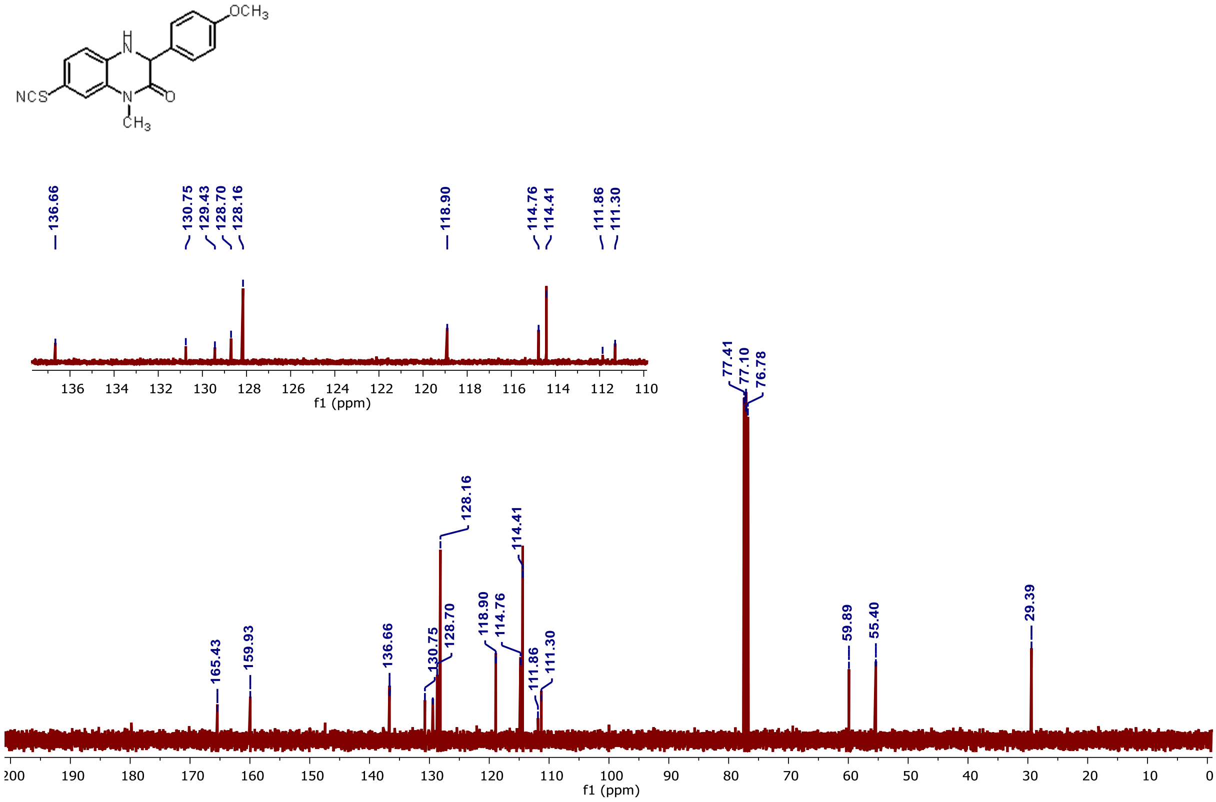
3-(4-Methoxyphenyl)-1-methyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3q: Prepared according to the general procedure discussed above: reaction time = 3.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); yellow solid (107 mg, 81%); mp 154–156 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.25 (m, 1 H), 7.21-7.23 (m, 1 H), 7.16 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.10 (d, *J* = 2.0 Hz, 1 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.73 (d, *J* = 8.4 Hz, 1 H), 5.06 (s, 1 H), 4.59 (s, 1 H), 3.76 (s, 3 H), 3.39 ppm (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.4, 159.9, 136.7, 130.8, 129.4, 128.7, 128.2 (2 CH), 118.9, 114.8, 114.4 (2 CH), 111.9, 111.3, 59.9, 55.4, 29.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{16}N_3O_2S$ [*M* + H]$^+$: 326.0963; found: 326.0955.

^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **3q:**

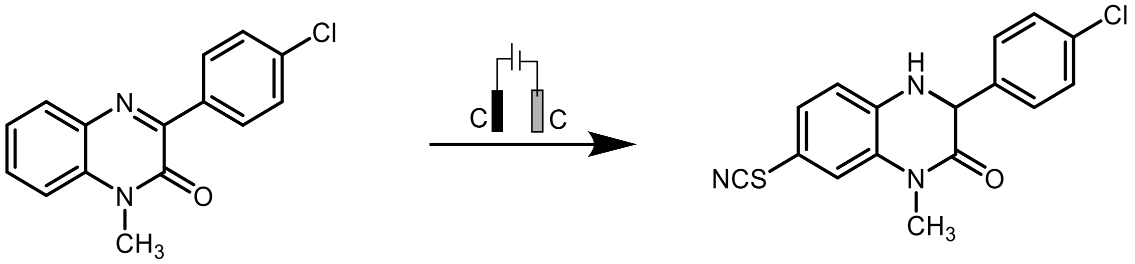
RM-6-53A
single_pulse

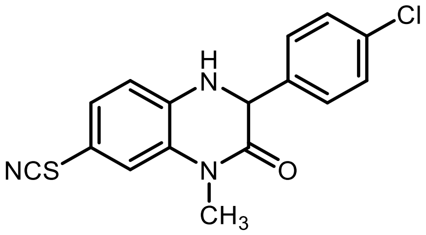


RM-6-53A
single pulse decoupled gated NOE



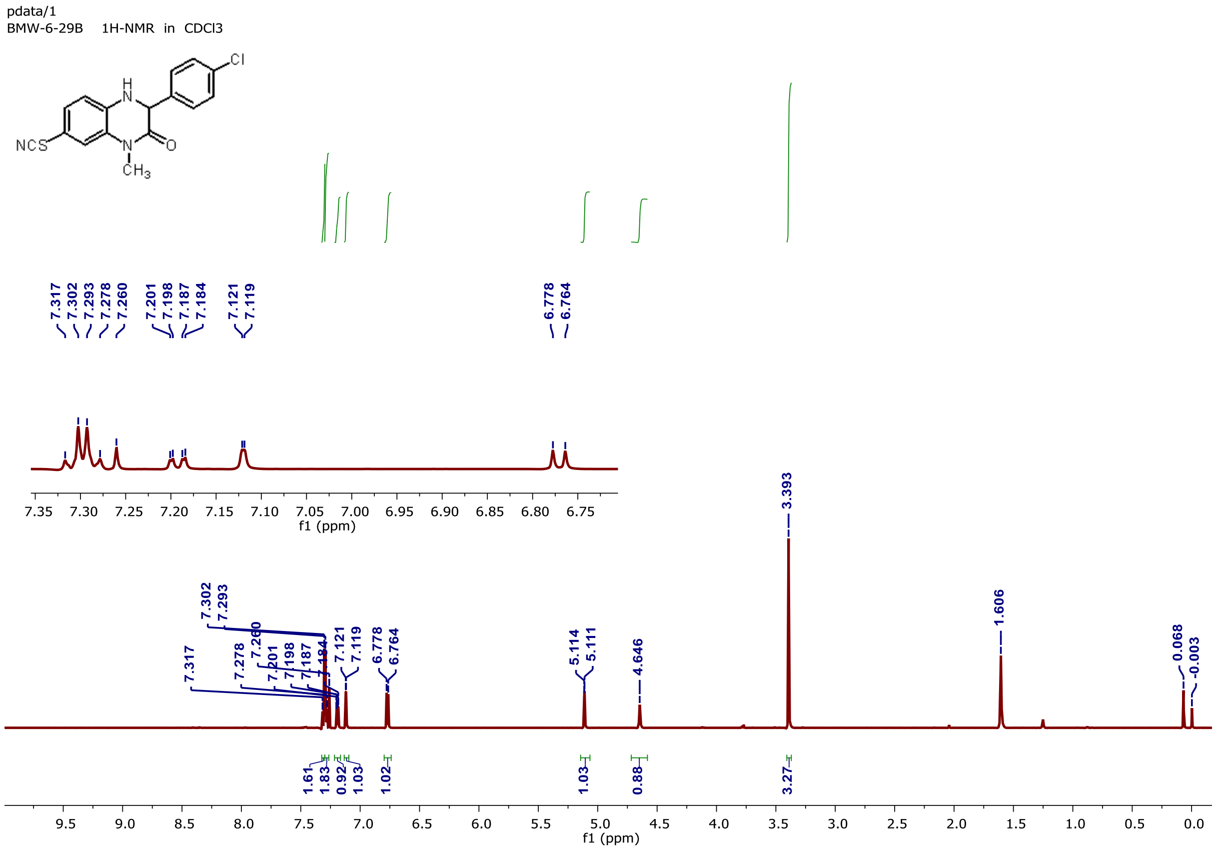
SI-12-18: Analytical and Spectral data of **3r**

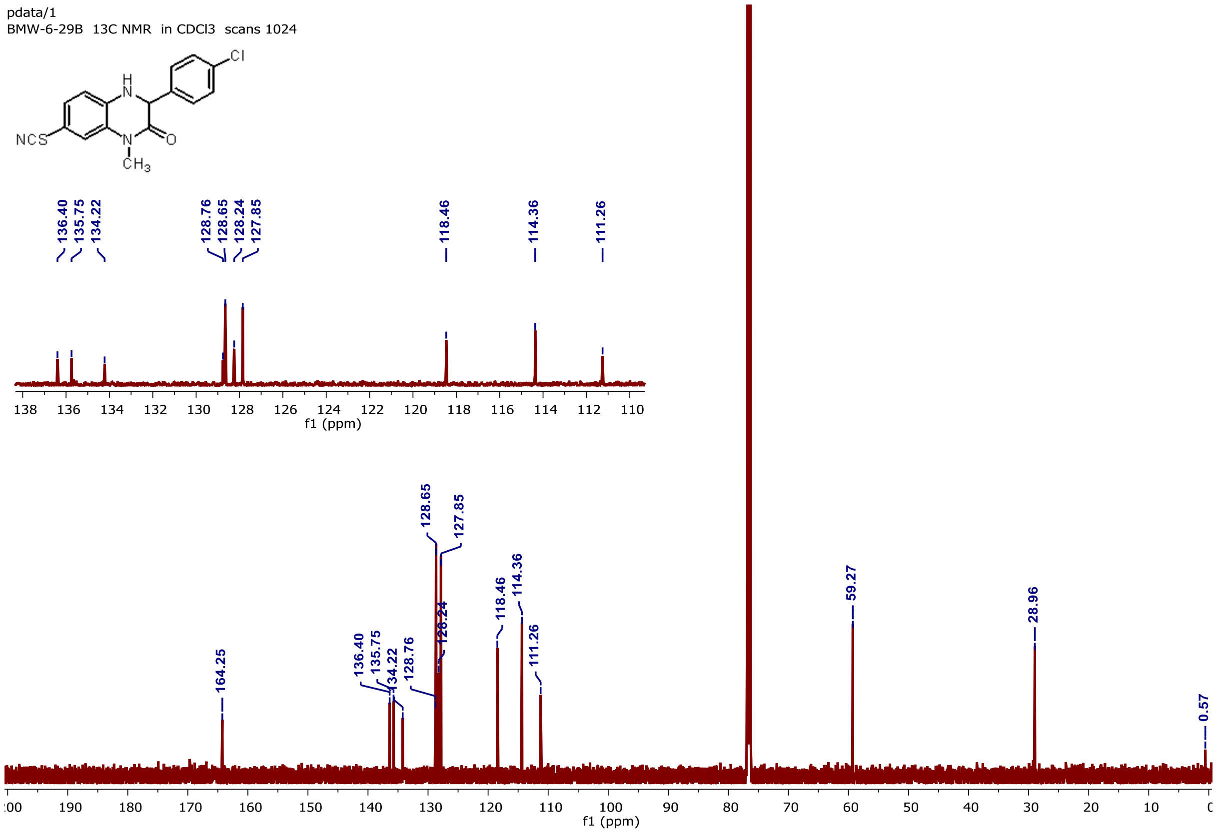




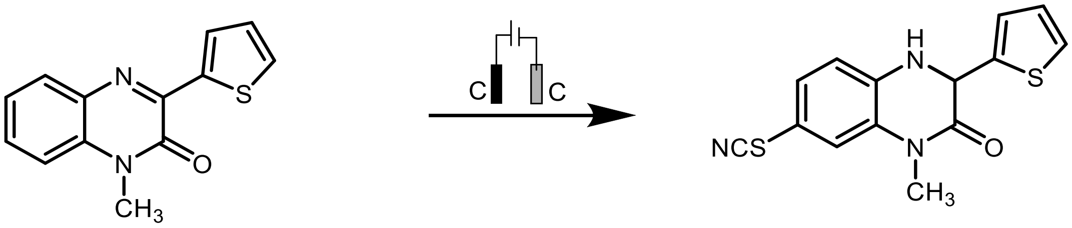
3-(4-Chlorophenyl)-1-methyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3r: Prepared according to the general procedure discussed above: reaction time = 3.1 h; *R*f = 0.3; eluent, EtOAc/*n*-hexane (30%); colorless gum (54 mg, 41%). ^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.31 (d, *J* = 9.0 Hz, 2 H), 7.29 (d, *J* = 9.0 Hz, 2 H), 7.19 (dd, *J* = 8.4, 1.8 Hz, 1 H), 7.12 (d, *J* = 1.2 Hz, 1 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 5.11 (s, 1 H), 4.65 (s, 1 H), 3.39 ppm (s, 3 H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): *δ* = 164.3, 136.4, 135.7, 134.2, 128.8, 128.7 (2 CH), 128.2, 127.9 (2 CH), 118.5, 114.4, 111.3, 59.3, 29.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{13}ClN_3OS$ [*M* + H]$^+$: 330.0468; found: 330.0455.

^{1}H (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} (151 MHz, CDCl$_3$) NMR spectra of **3r:**

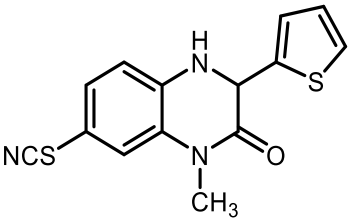




SI-12-19: Analytical and Spectral data of **3s**

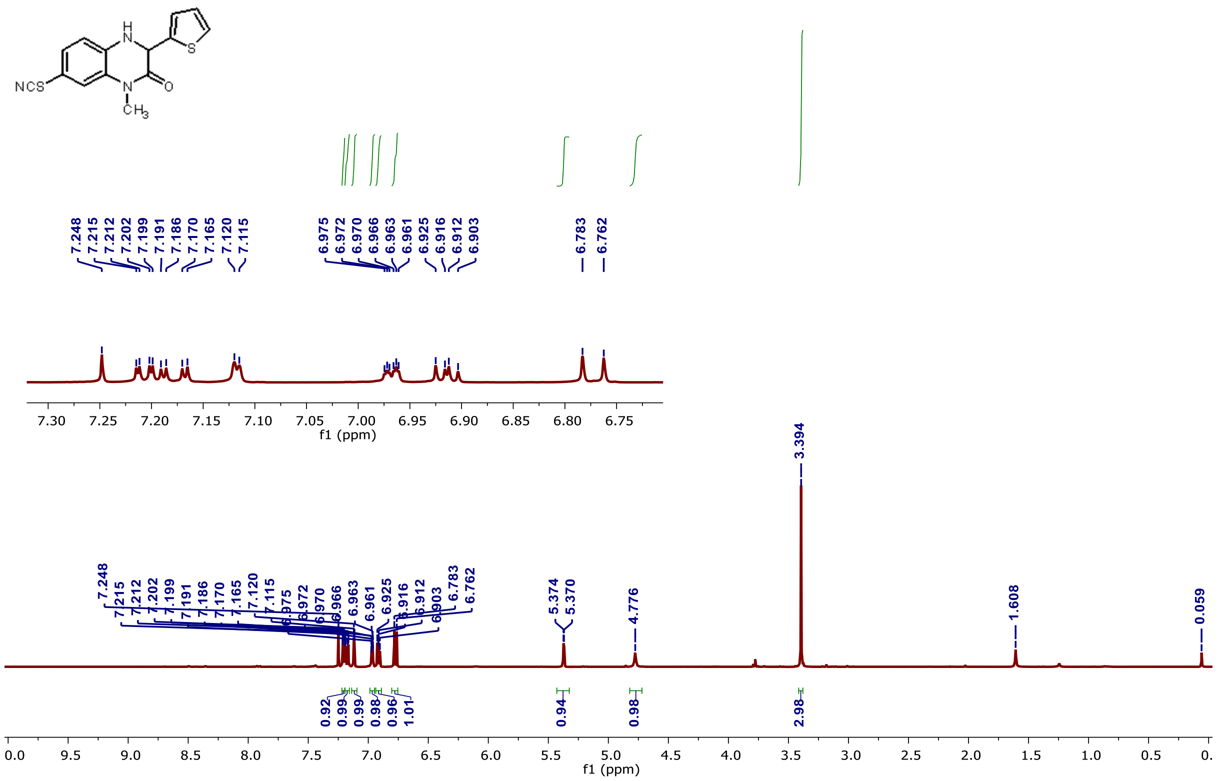


1-Methyl-7-thiocyanato-3-(thiophen-2-yl)-3,4-dihydroquinoxalin-2(1*H*)-one 3s: Prepared according to the general procedure discussed above: reaction time = 3.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); yellow solid (103 mg, 85%); mp 172–175 ˚C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.21 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.18 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.12 (d, *J* = 2.0 Hz, 1 H), 6.97 (dt, *J* = 3.6, 1.2 Hz, 1 H), 6.91 (dd, *J* = 5.2, 3.6 Hz, 1 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 5.37 (d, *J* = 1.6 Hz, 1 H), 4.78 (s, 1 H), 3.39 ppm (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 164.3, 141.0, 135.8, 129.5, 128.6, 127.1, 126.1, 125.8, 118.8, 115.6, 112.3, 111.7, 56.6, 29.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{14}H_{12}N_3OS_2$ [*M* + H]$^+$: 302.0422; found: 302.0410.

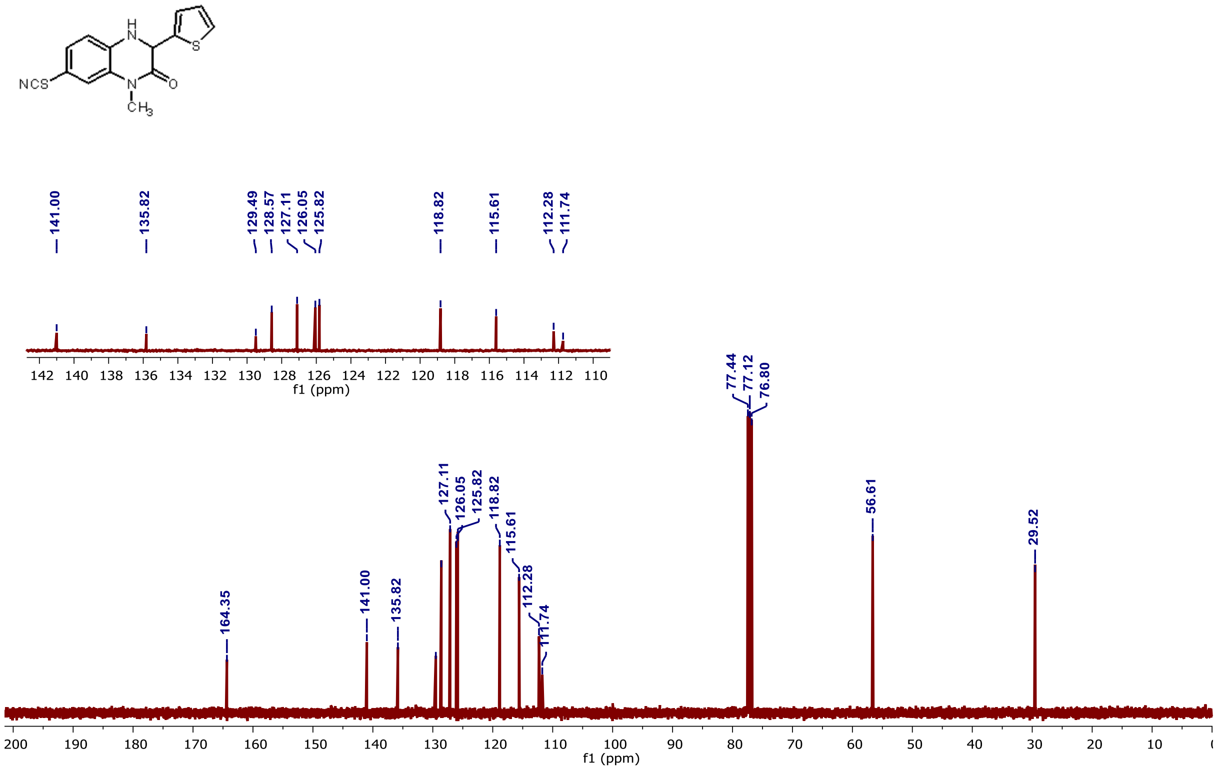


^1H (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3s:**

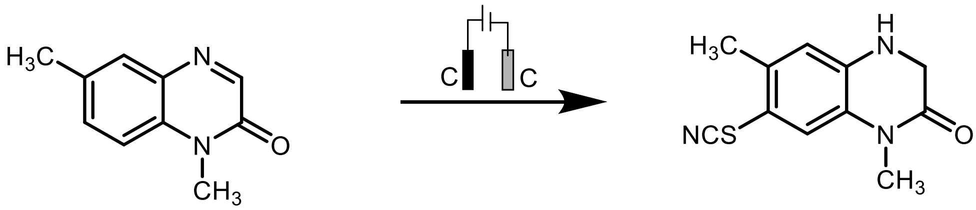
RM-6-48C
single_pulse



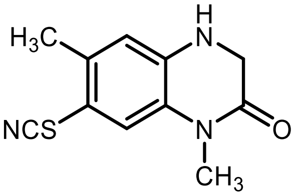
RM-6-48C
single pulse decoupled gated NOE



SI-12-20: Analytical and Spectral data of **3t**

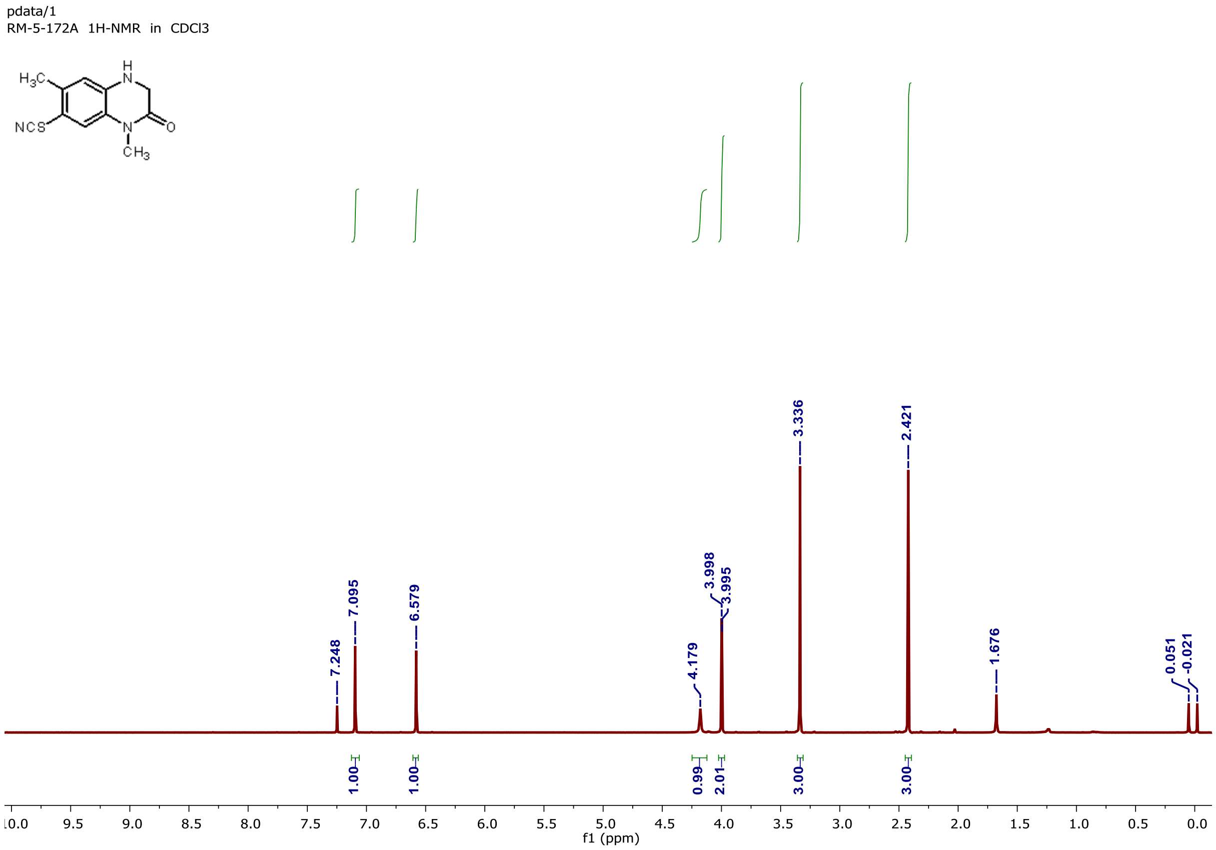


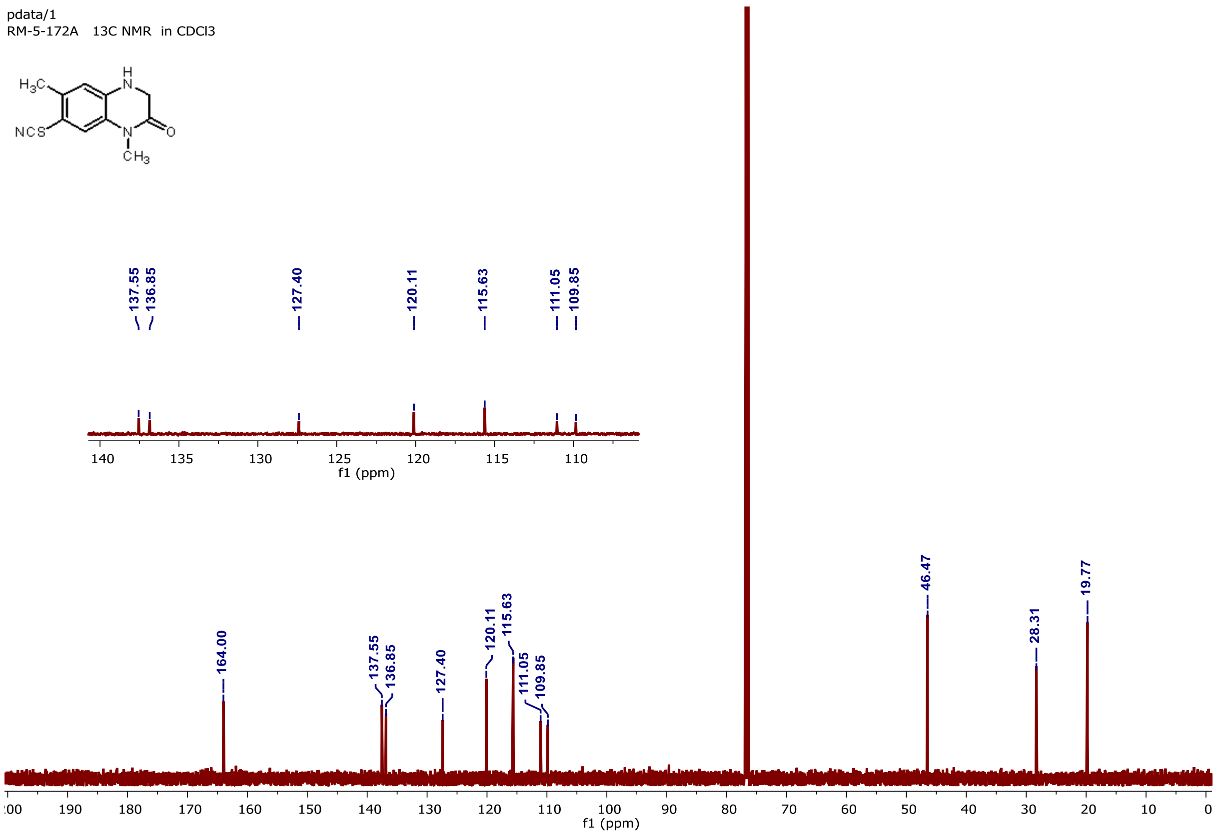
1,6-Dimethyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3t: Prepared according to



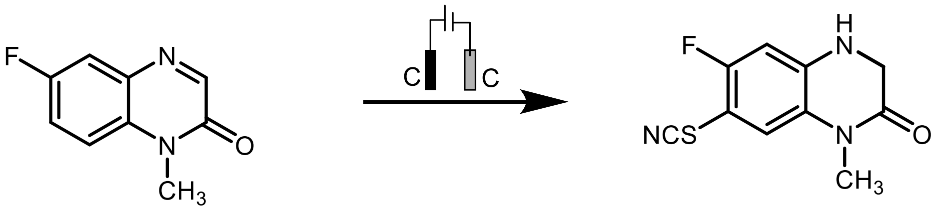
the general procedure discussed above: reaction time = 3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (63 mg, 67%); mp 184–186 ˚C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.10 (s, 1 H), 6.58 (s, 1 H), 4.18 (s, 1 H), 4.00 (d, J = 1.8 Hz, 2 H), 3.34 (s, 3 H), 2.42 ppm (s, 3 H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 164.0, 137.6, 136.9, 127.4, 120.1, 115.6, 111.1, 109.8, 46.5 (CH_2), 28.3, 19.8 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{11}H_{12}N_3OS$ [*M* + H]$^+$: 234.0701; found: 234.0704.

^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) spectra of **3t:**

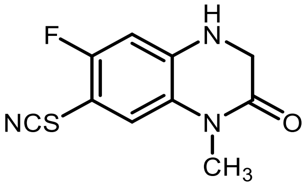




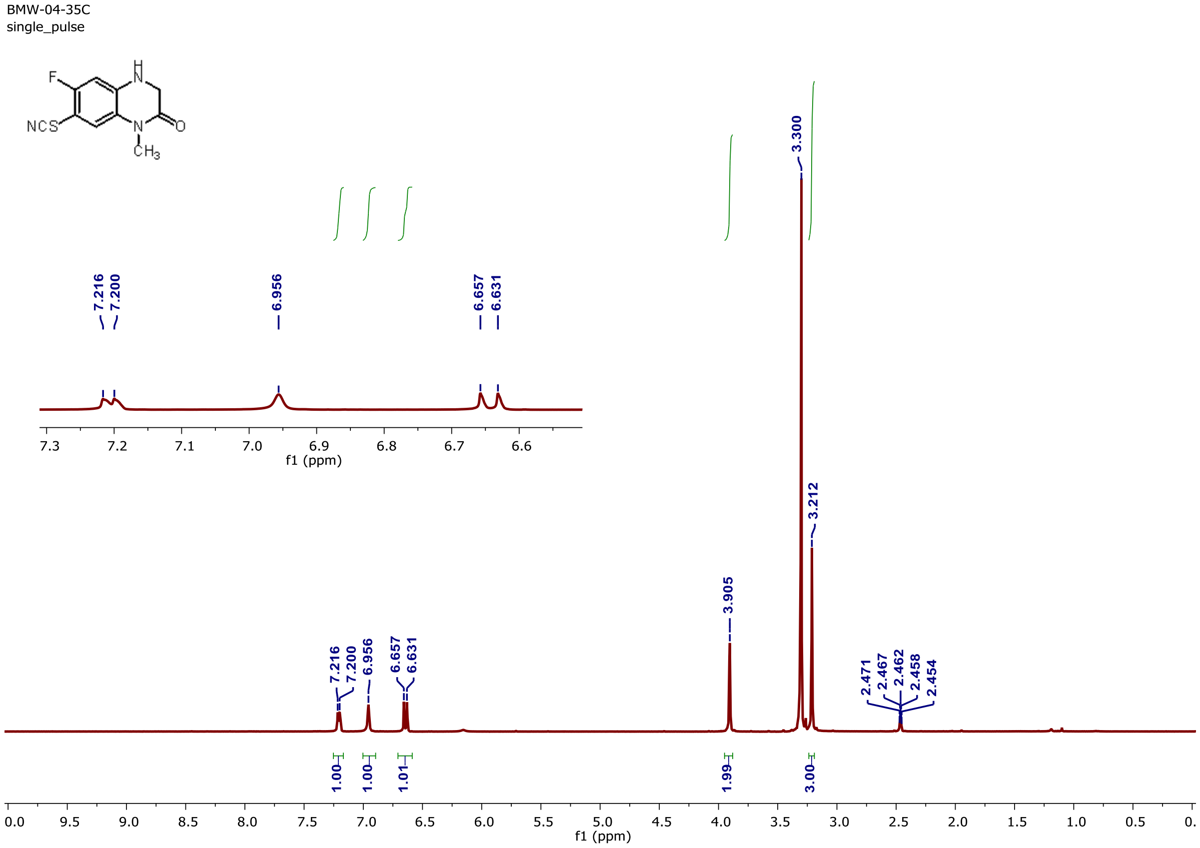
SI-12-21: Analytical and Spectral data of **3u**

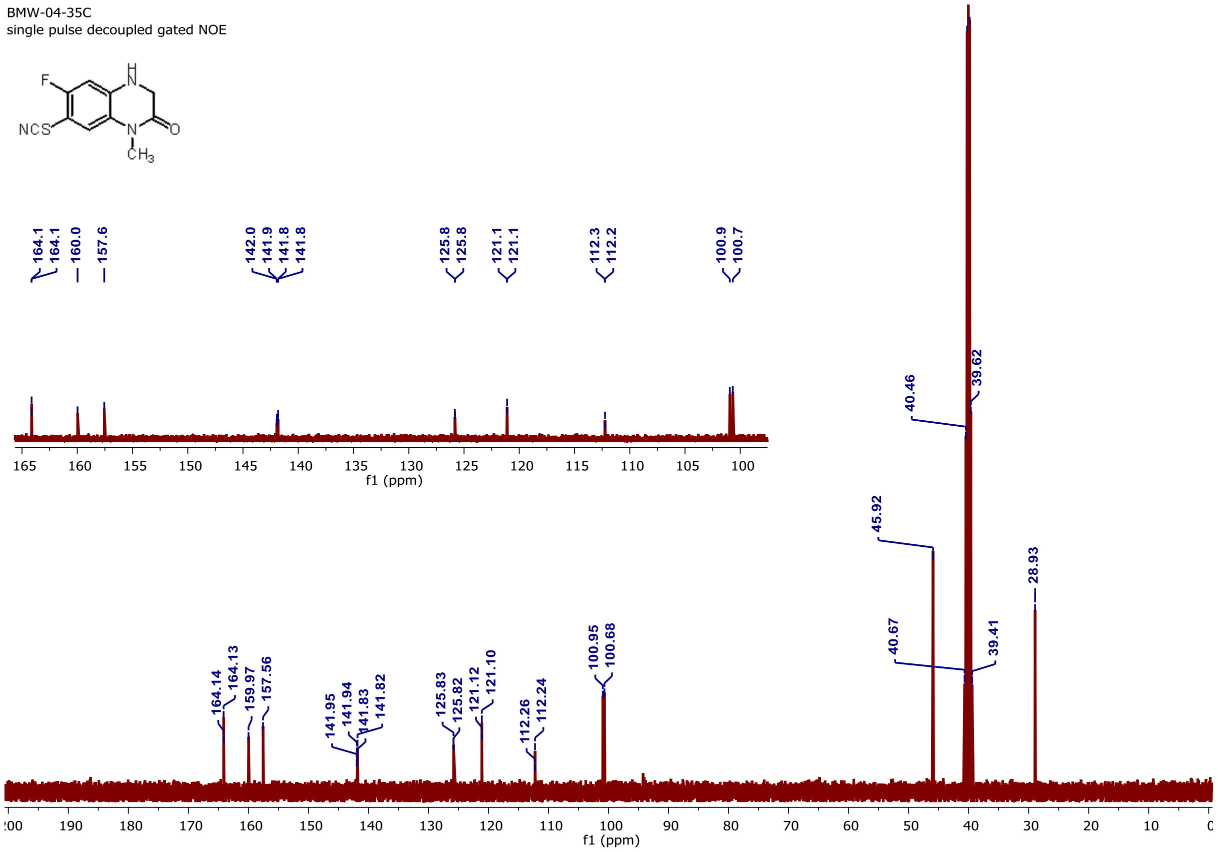


6-Fluoro-1-methyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3u: Prepared according to the general procedure discussed above: reaction time = 3.2 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (67 mg, 70%); mp 187–189 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.21 (d, J = 6.4 Hz, 1 H), 6.96 (s, 1 H), 6.64 (m, 1 H), 3.90 (s, 2 H), 3.21 ppm (s, 3 H); ^{13}C NMR (101 MHz, DMSO-d_6): δ = 164.1 (d, $J_{C\text{-}F}$ = 1.0 Hz, 1 C), 158.8 (d, $J_{C\text{-}F}$ = 242.4 Hz, 1 C), 141.9 (d, $J_{C\text{-}F}$ = 1.0 Hz, 1 C), 141.8 (d, $J_{C\text{-}F}$ = 1.0 Hz, 1 C), 125.8 (d, $J_{C\text{-}F}$ = 1.0 Hz, 1 C), 121.1 (d, $J_{C\text{-}F}$ = 1.0 Hz, 1 C), 112.2 (d, $J_{C\text{-}F}$ = 2.0 Hz, 1 C), 100.8 (d, $J_{C\text{-}F}$ = 27.3 Hz, 1 C), 45.9 (CH_2), 28.9 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{10}H_9FN_3OS$ [*M* + H]$^+$: 238.0450; found: 238.0441.

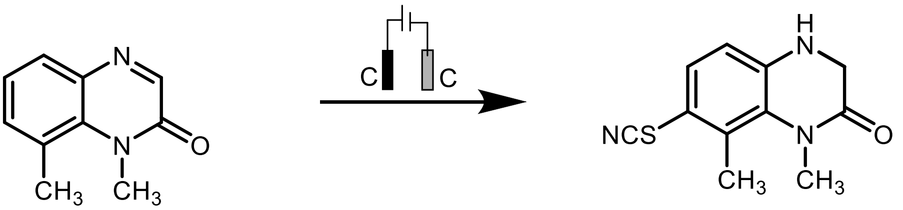


^{1}H (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} (101 MHz, DMSO-d_6) NMR spectra of **3u:**

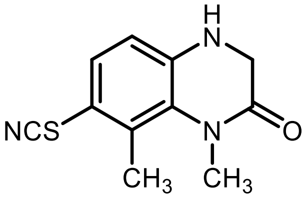




SI-12-22: Analytical and Spectral data of **3v**

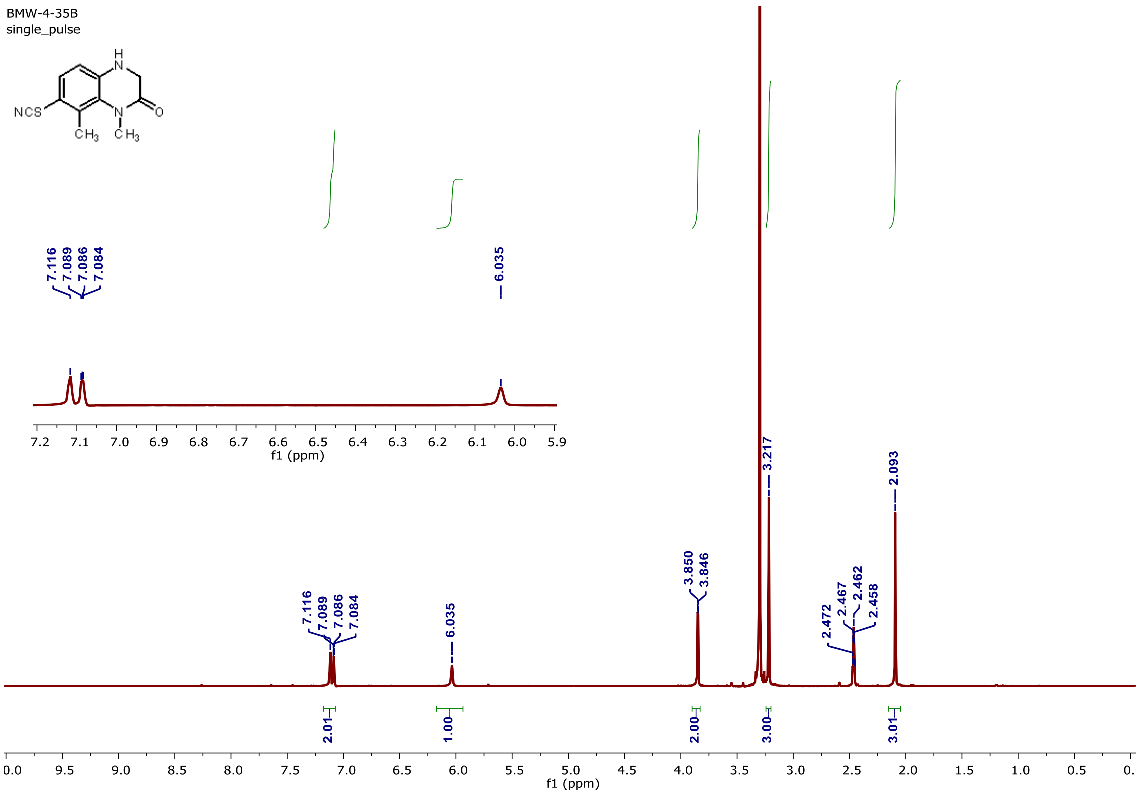


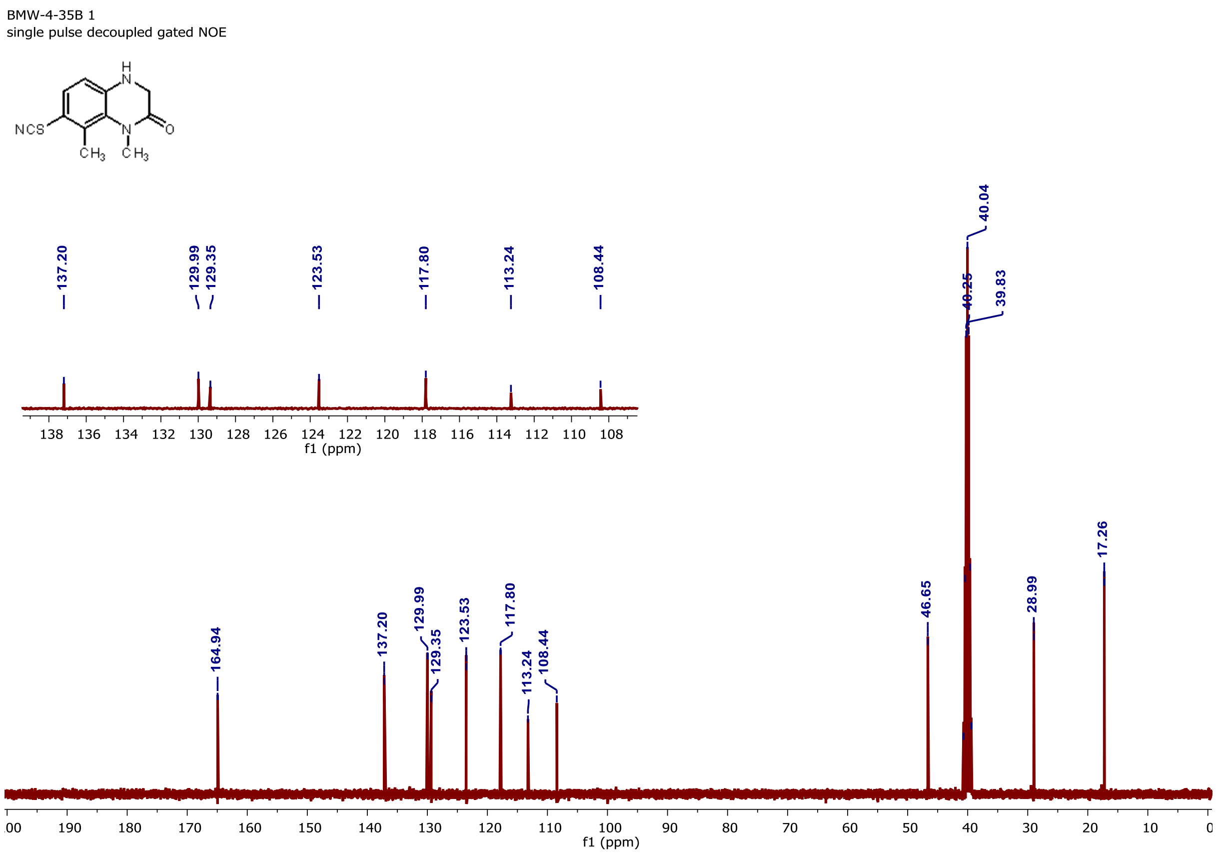
1,8-Dimethyl-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 3v: Prepared according to



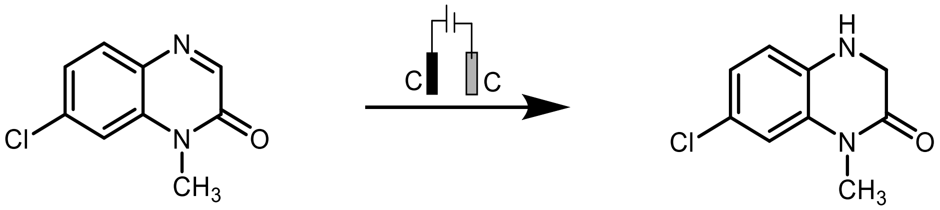
the general procedure discussed above: reaction time = 3.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (78 mg, 83%); mp 164–166 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.08-7.12 (m, 2 H), 6.04 (s, 1 H), 3.85 (d, *J* = 1.6 Hz, 2 H), 3.22 (s, 3 H), 2.09 ppm (s, 3 H); ^{13}C NMR (101 MHz, DMSO-d_6): δ = 164.9, 137.2, 130.0, 129.3, 123.5, 117.8, 113.2, 108.4, 46.6 (CH_2), 29.0, 17.3 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{11}H_{12}N_3OS$ [*M* + H]$^+$: 234.0701; found: 234.0700.

^{1}H (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} (101 MHz, DMSO-d_6) NMR spectra of **3v:**

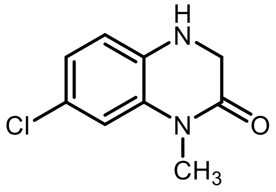




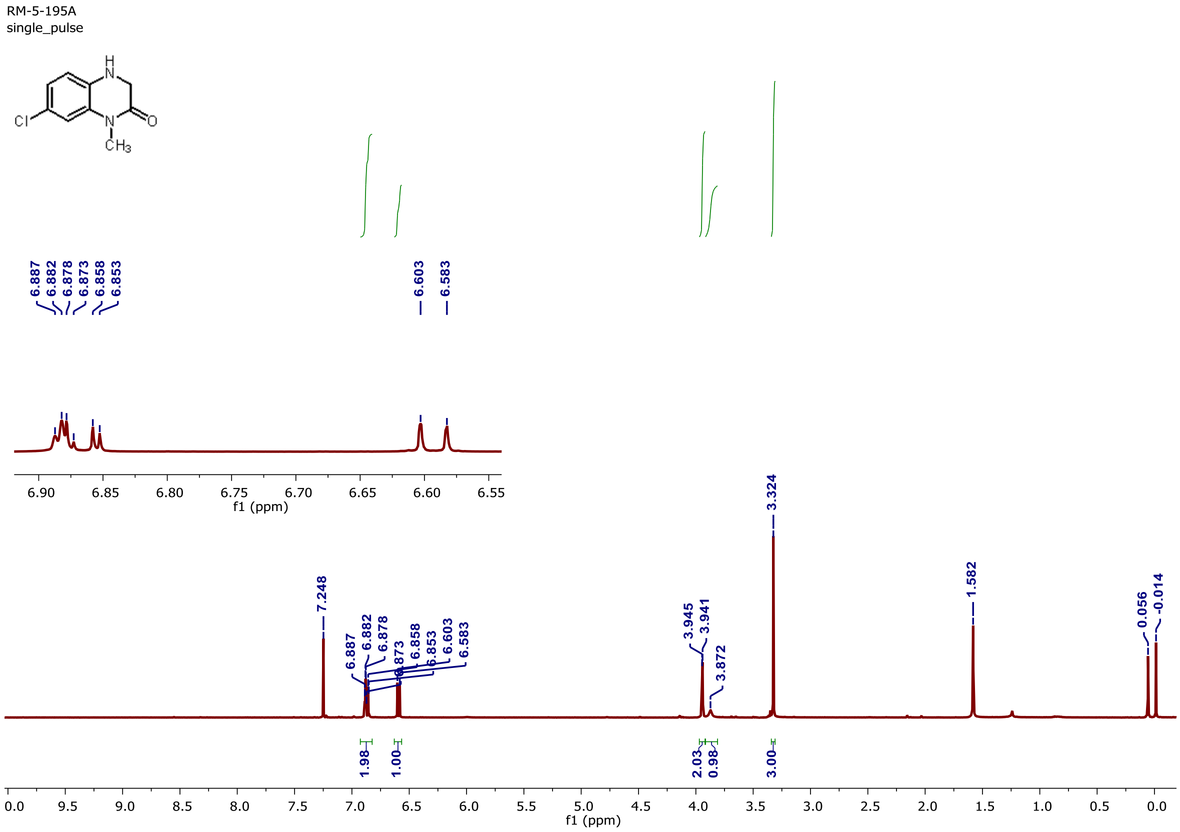
SI-12-23: Analytical and Spectral data of **3w**

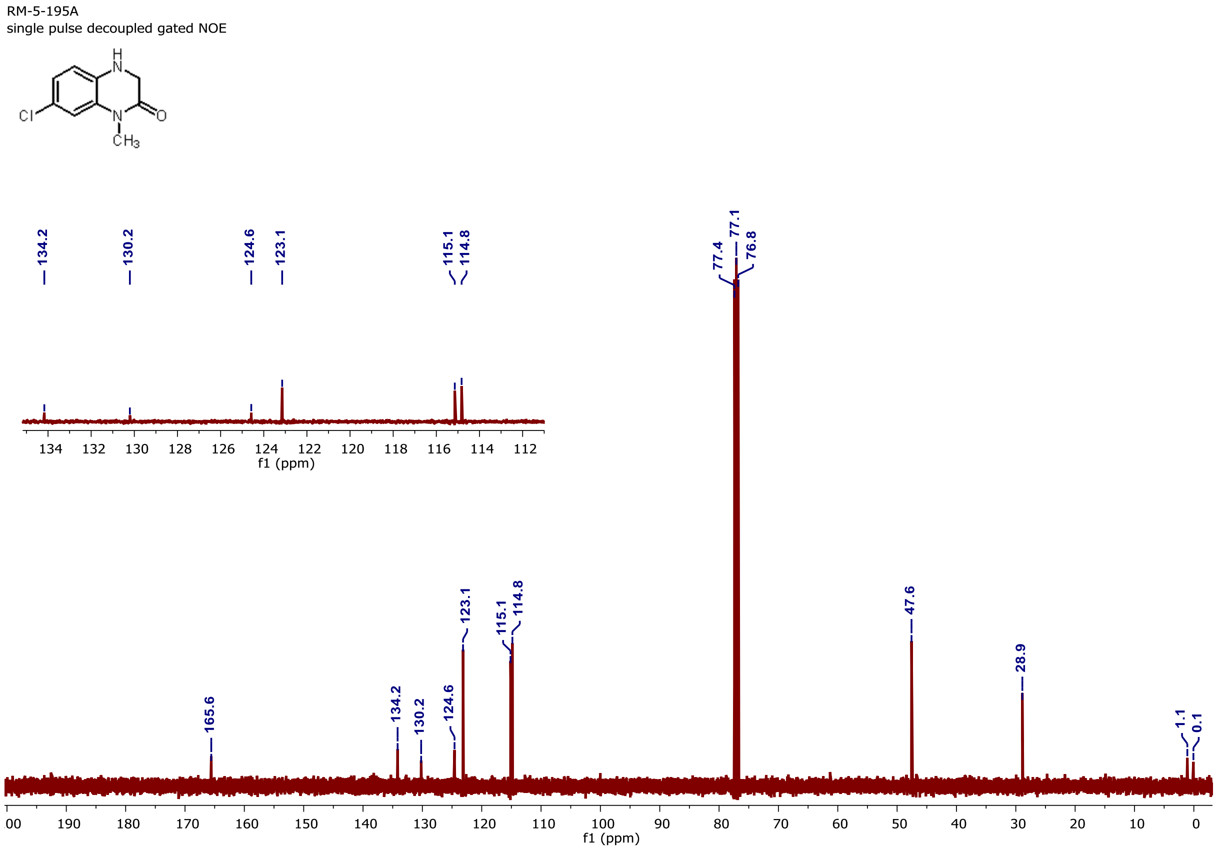


7-Chloro-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one 3w: Prepared according to the general procedure discussed above: reaction time = 2.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (47 mg, 60%); mp 165–167 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85-6.89 (m, 2 H), 6.59 (d, J = 8.0 Hz, 1 H), 3.94 (d, J = 1.6 Hz, 2 H), 3.87 (s, 1 H), 3.32 ppm (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.6, 134.2, 130.2, 124.6, 123.1, 115.1, 114.8, 47.6 (CH_2), 28.9 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_9H_{10}ClN_2O$ [*M* + H]$^+$: 197.0481; found: 197.0482.

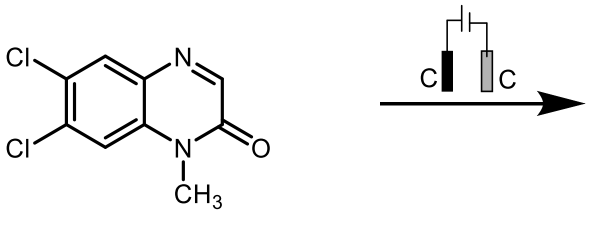


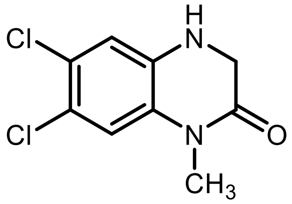
^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **3w:**





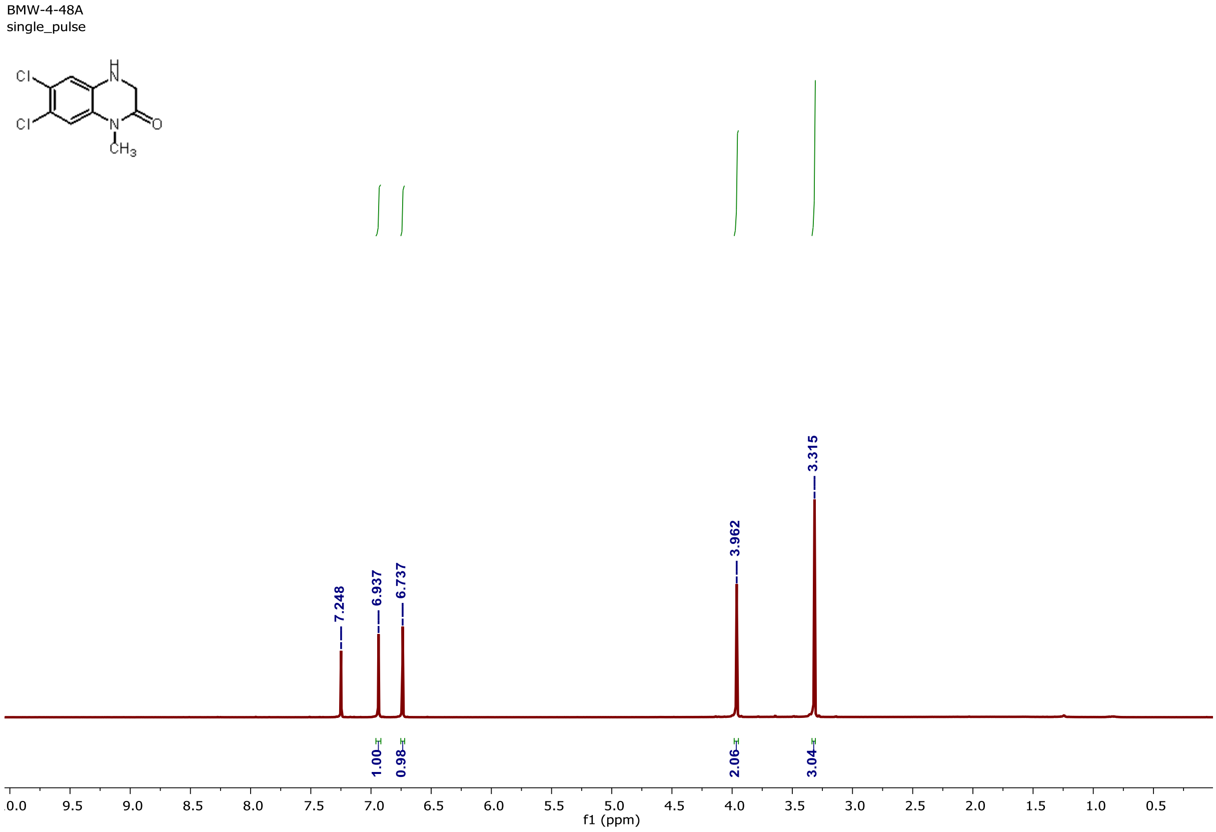
SI-12-24: Analytical and Spectral data of **3x**

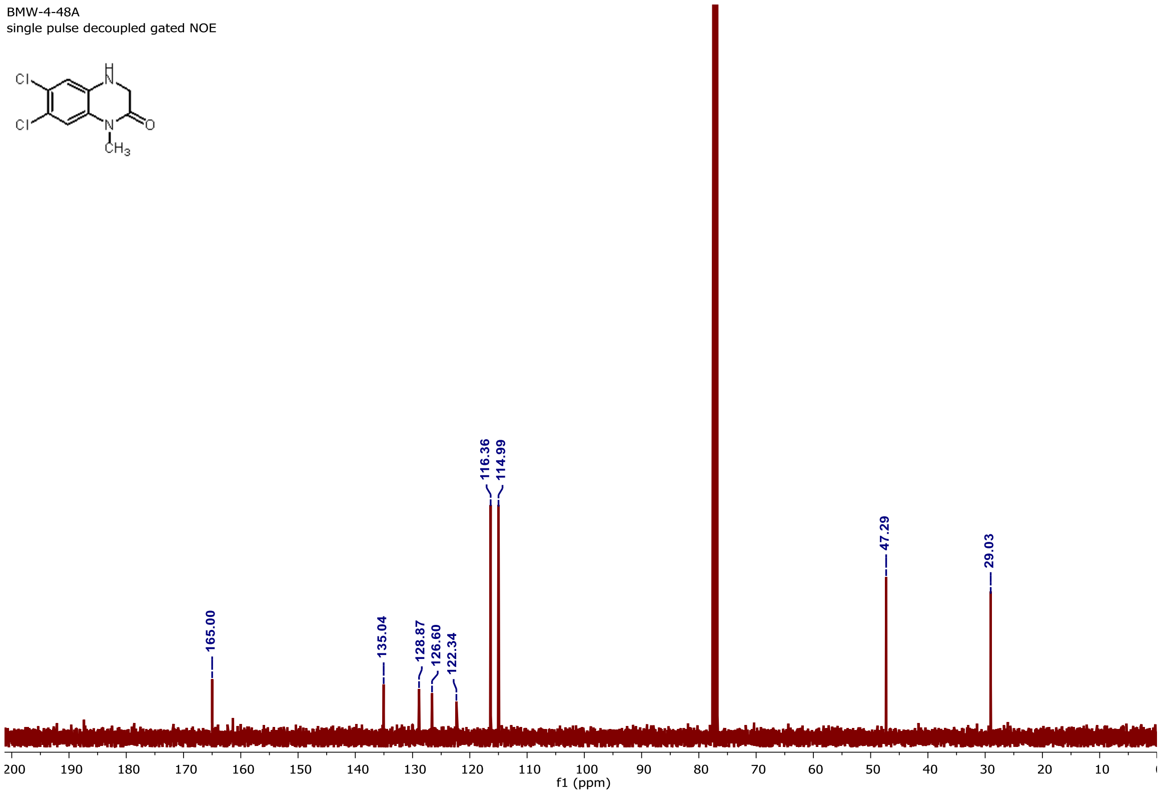




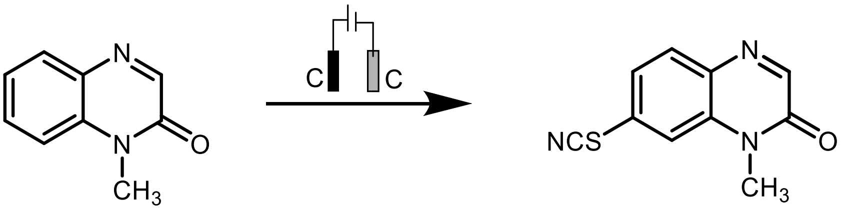
6,7-Dichloro-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one 3x: Prepared according to the general procedure discussed above: reaction time = 2.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); white solid (67 mg, 72%); mp 187–189 ˚C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.94 (s, 1 H), 6.74 (s, 1 H), 3.96 (s, 2 H), 3.32 ppm (s, 3 H), –NH peak absent; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 165.0, 135.0, 128.9, 126.6, 122.3, 116.4, 115.0, 47.3, 29.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_9H_9Cl_2N_2O$ [M + H]$^+$: 231.0092; found: 231.0100.

^1H (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3x:**

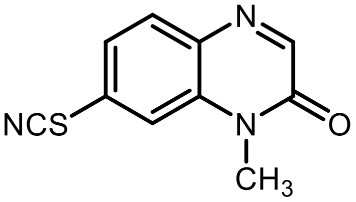




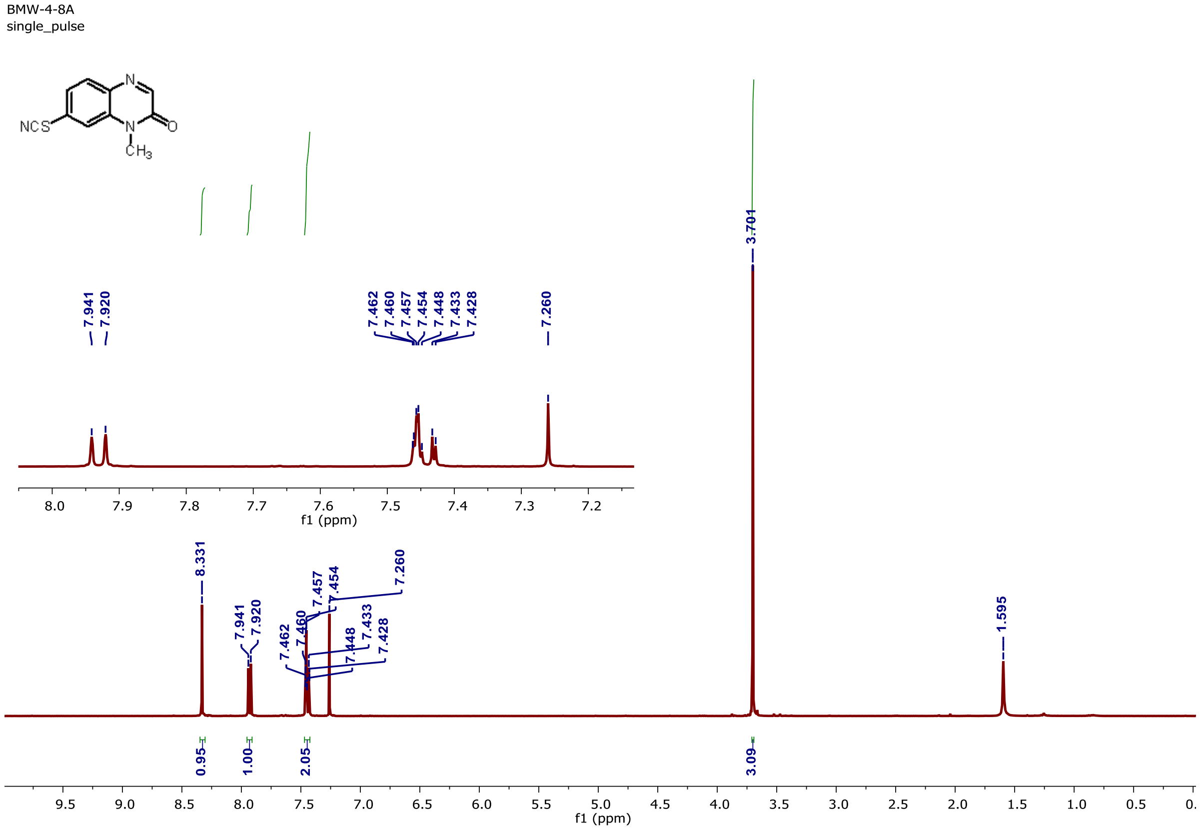
SI-12-25: Analytical and Spectral data of **4a**

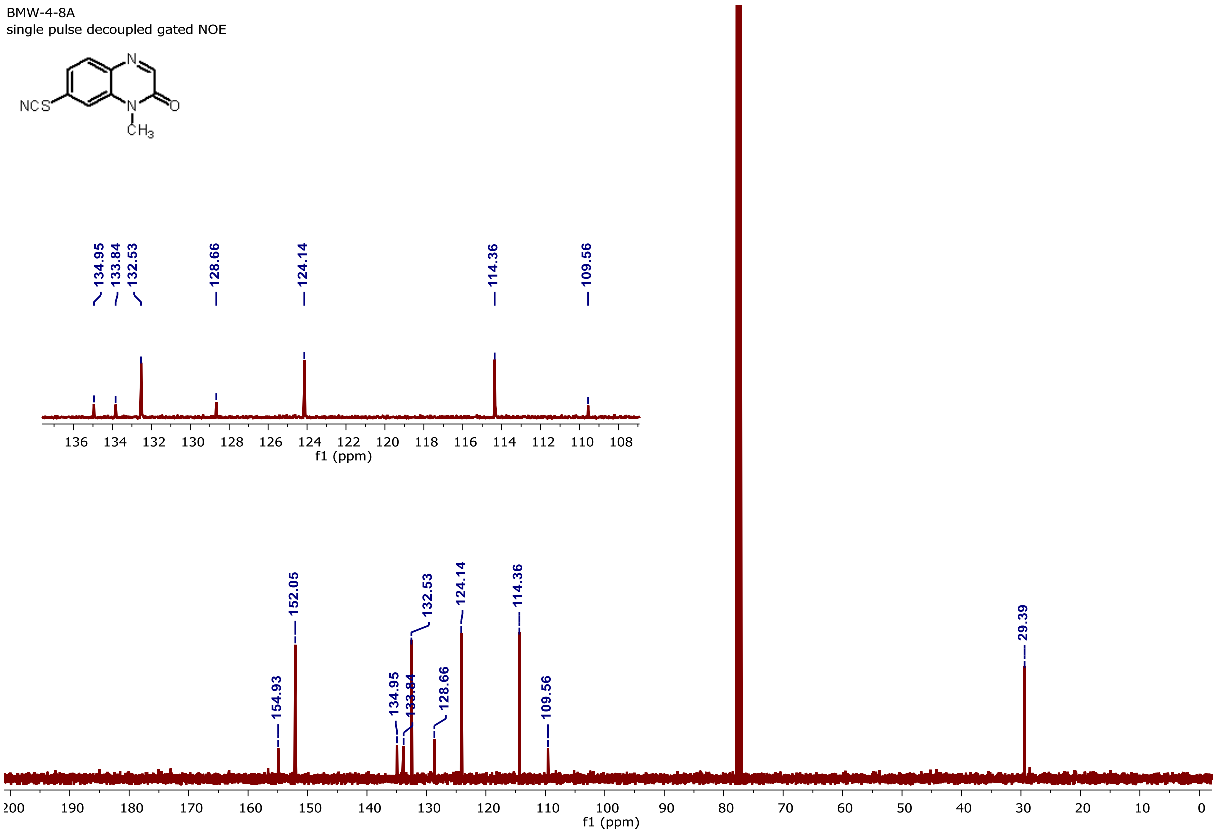


1-Methyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4a: Prepared according to the general procedure discussed above: reaction time = 6.0 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (70 mg, 80%); mp 133–135 ˚C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.33 (s, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.43-7.46 (m, 2 H), 3.70 ppm (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 154.9, 152.0, 135.0, 133.8, 132.5, 128.7, 124.1, 114.4, 109.6, 29.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{10}H_8N_3OS$ [*M* + H]$^+$: 218.0388; found: 218.0389.

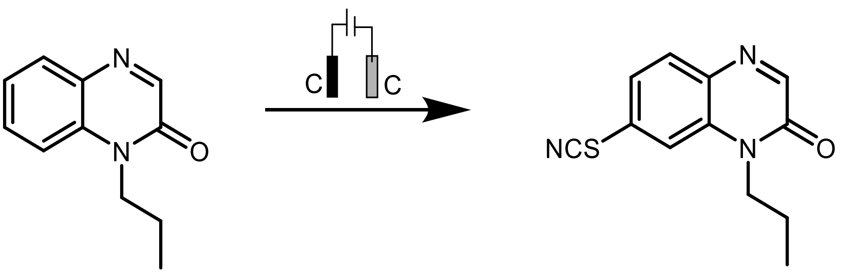


^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4a:**

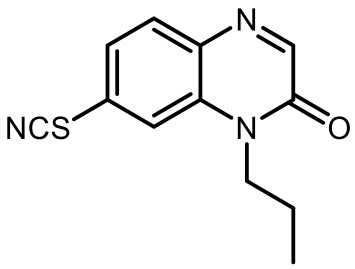




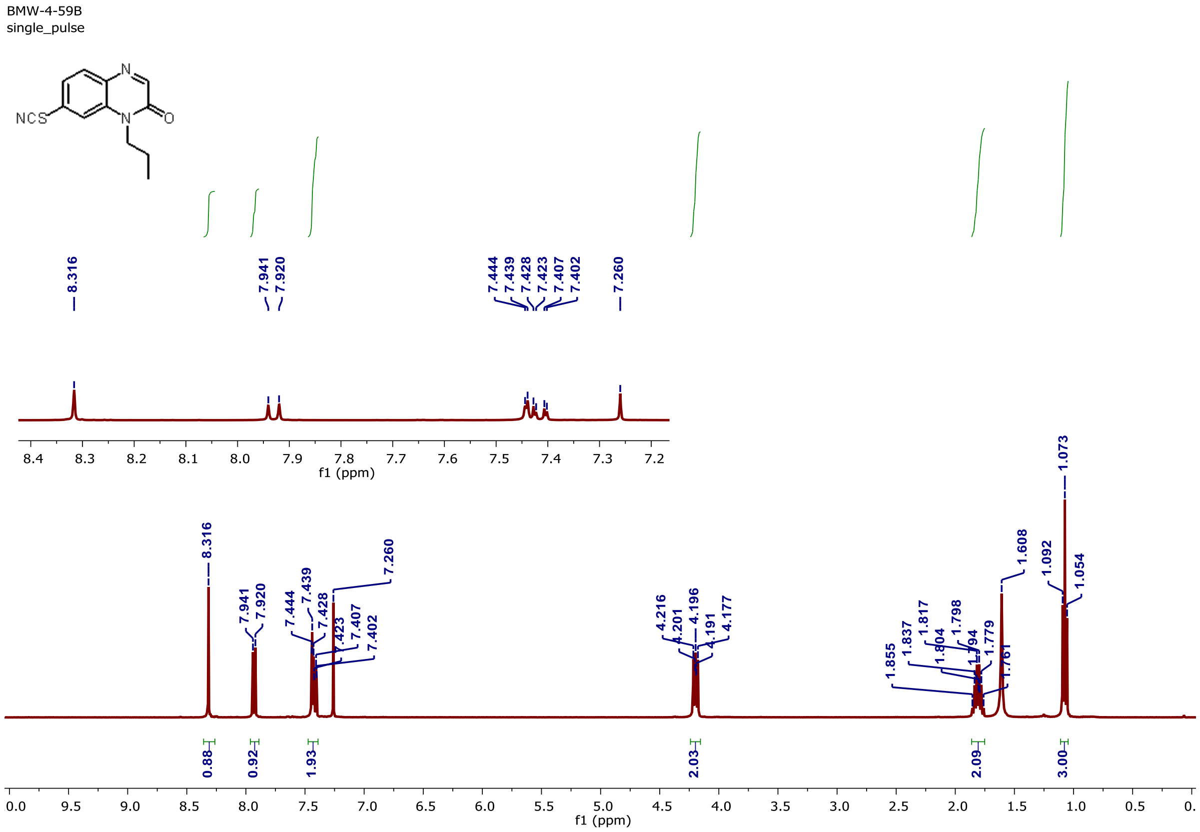
SI-12-26: Analytical and Spectral data of **4b**

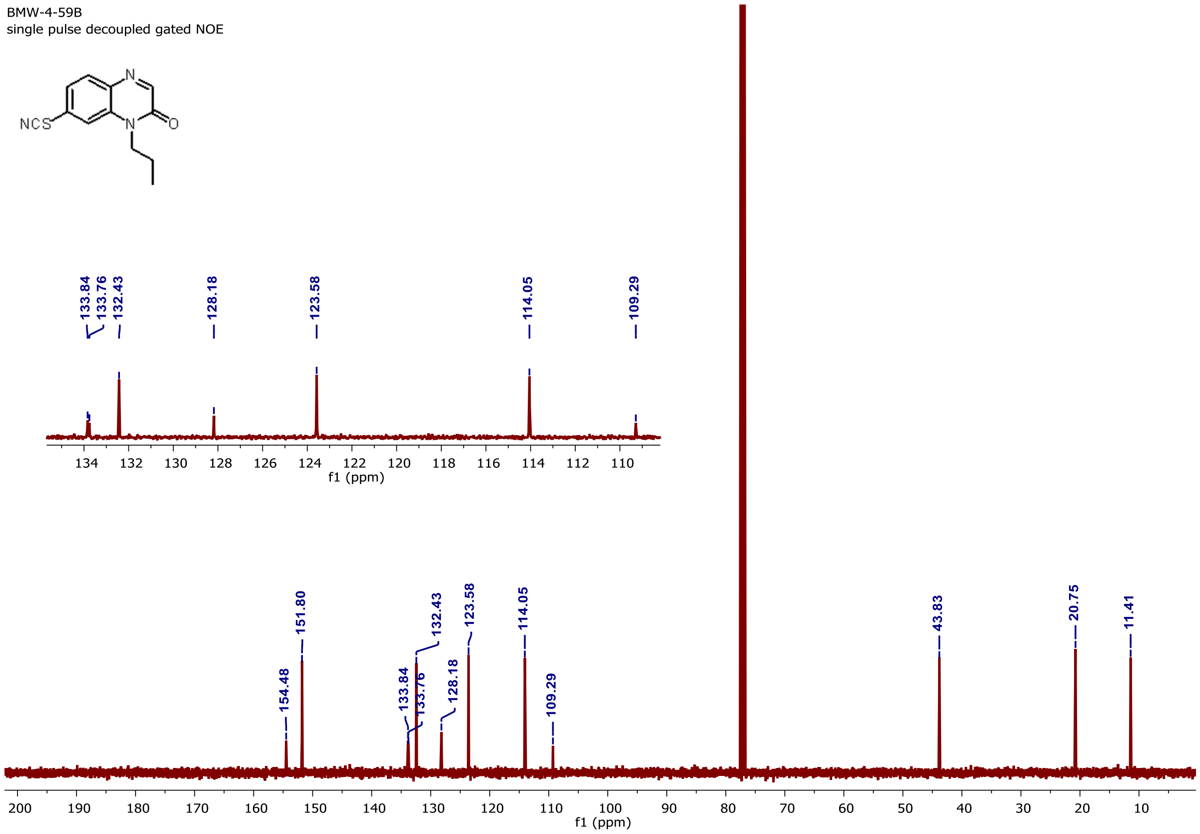


1-Propyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4b: Prepared according to the general procedure discussed above: reaction time = 6.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (86 mg, 86%); mp 150–152 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.32 (s, 1 H), 7.93 (d, J = 8.4 Hz, 1 H), 7.40-7.44 (m, 2 H), 4.18-4.22 (m, 2 H), 1.76-1.86 (m, 2 H), 1.07 ppm (t, J = 7.6 Hz, 3 H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 154.5, 151.8, 133.8, 133.8, 132.4, 128.2, 123.6, 114.1, 109.3, 43.8 (CH$_2$), 20.8 (CH$_2$), 11.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{12}H_{12}N_3OS$ [*M* + H]$^+$: 246.0701; found: 246.0690.

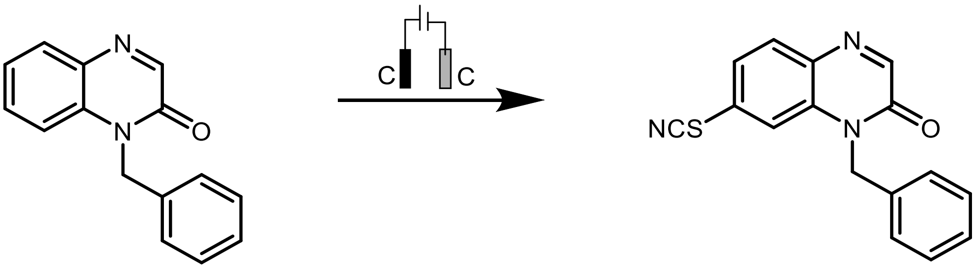


^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4b:**

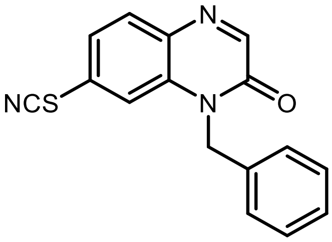




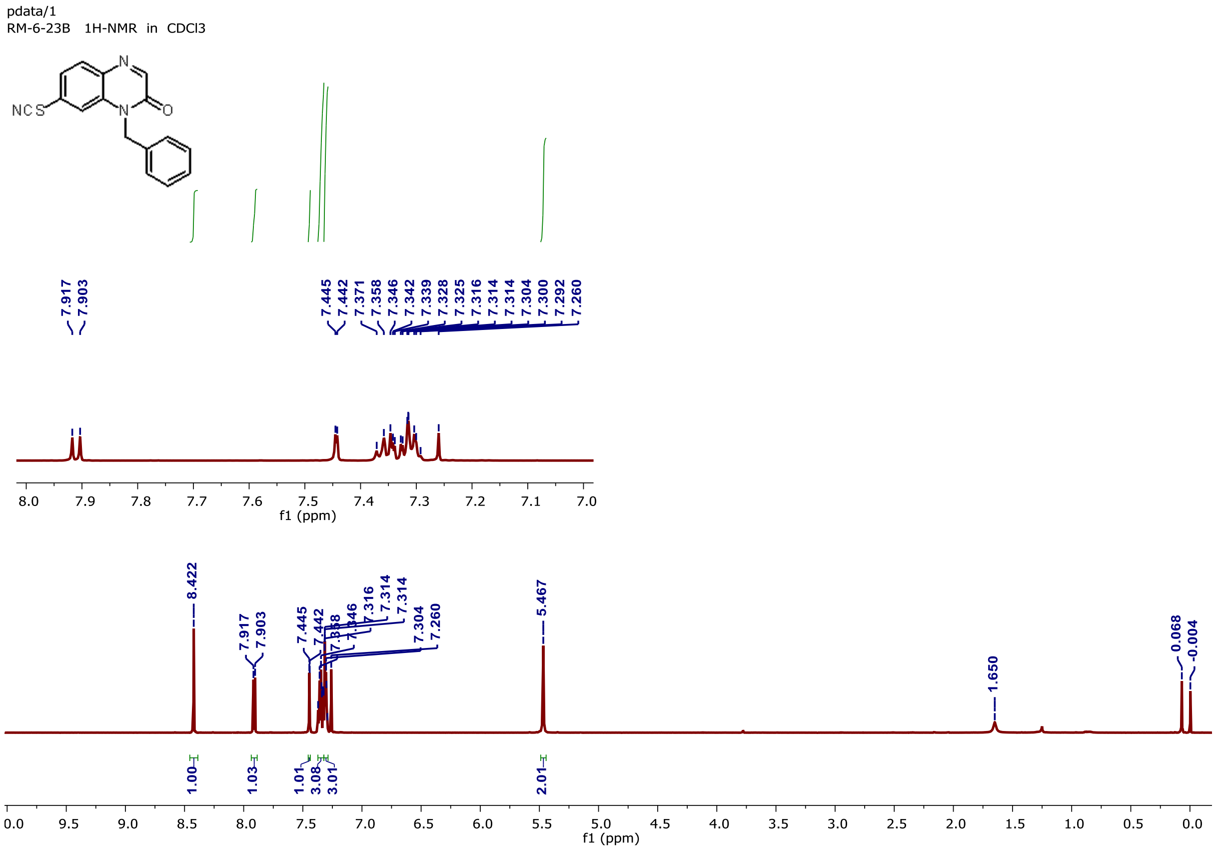
SI-12-27: Analytical and Spectral data of **4c**

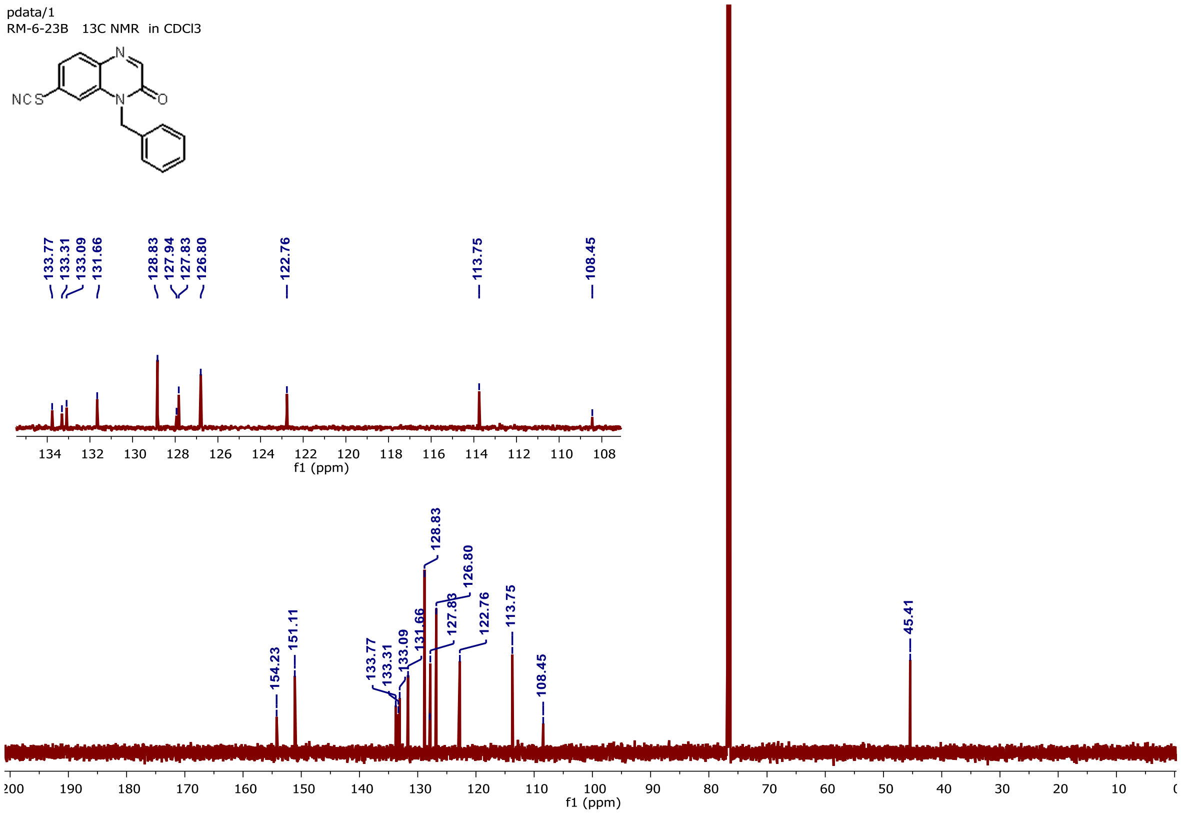


1-Benzyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4c: Prepared according to the general procedure discussed above: reaction time = 6.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (83 mg, 70%); mp 161–163 ˚C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.42 (s, 1 H), 7.91 (d, J = 8.4 Hz, 1 H), 7.44 (d, J = 1.8 Hz, 1 H), 7.32-7.37 (m, 3 H), 7.29-7.32 (m, 3 H), 5.47 ppm (s, 2 H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 154.2, 151.1, 133.8, 133.3, 133.1, 131.7, 128.8 (2 CH), 127.9, 127.8, 126.8 (2 CH), 122.8, 113.7, 108.4, 45.4 (CH$_2$) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{12}N_3OS$ [*M* + H]$^+$: 294.0701; found: 294.0702.

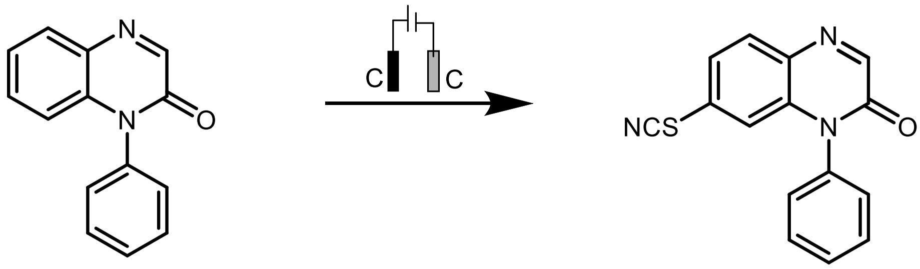


^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4c:**

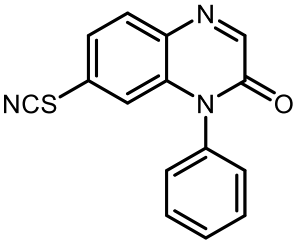




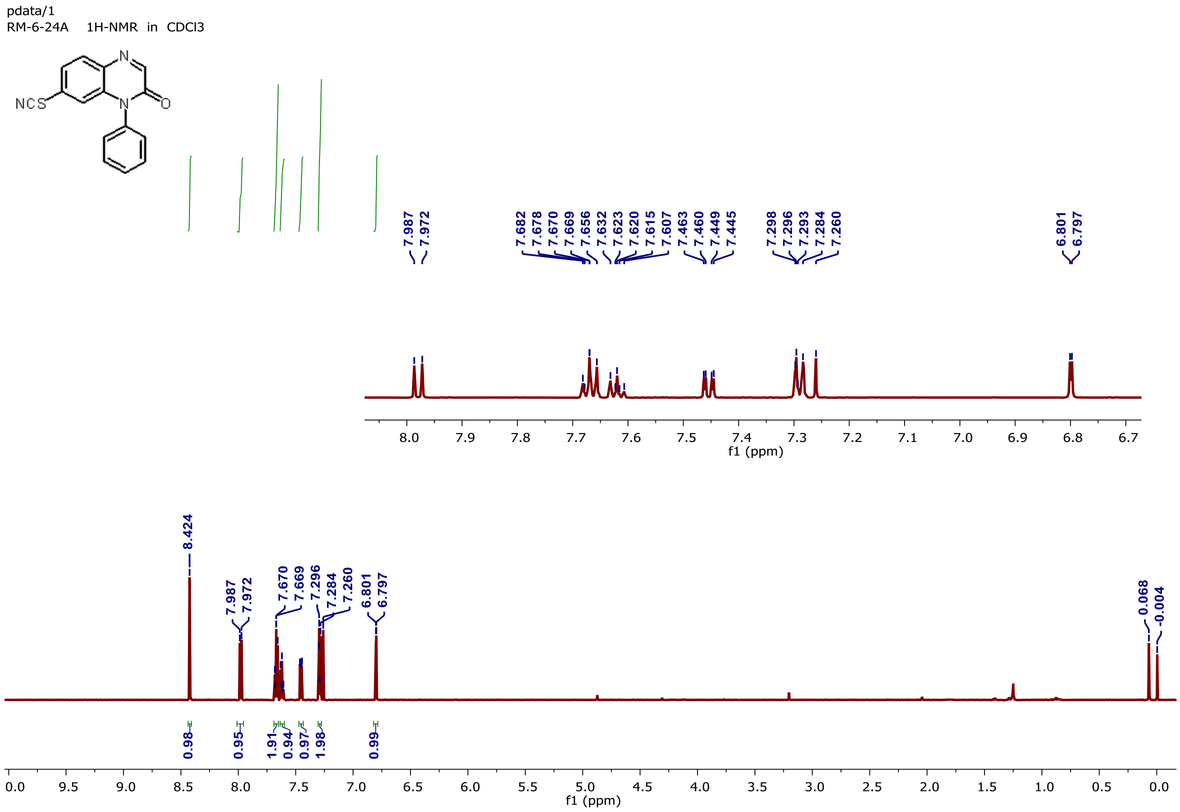
SI-12-28: Analytical and Spectral data of **4d**

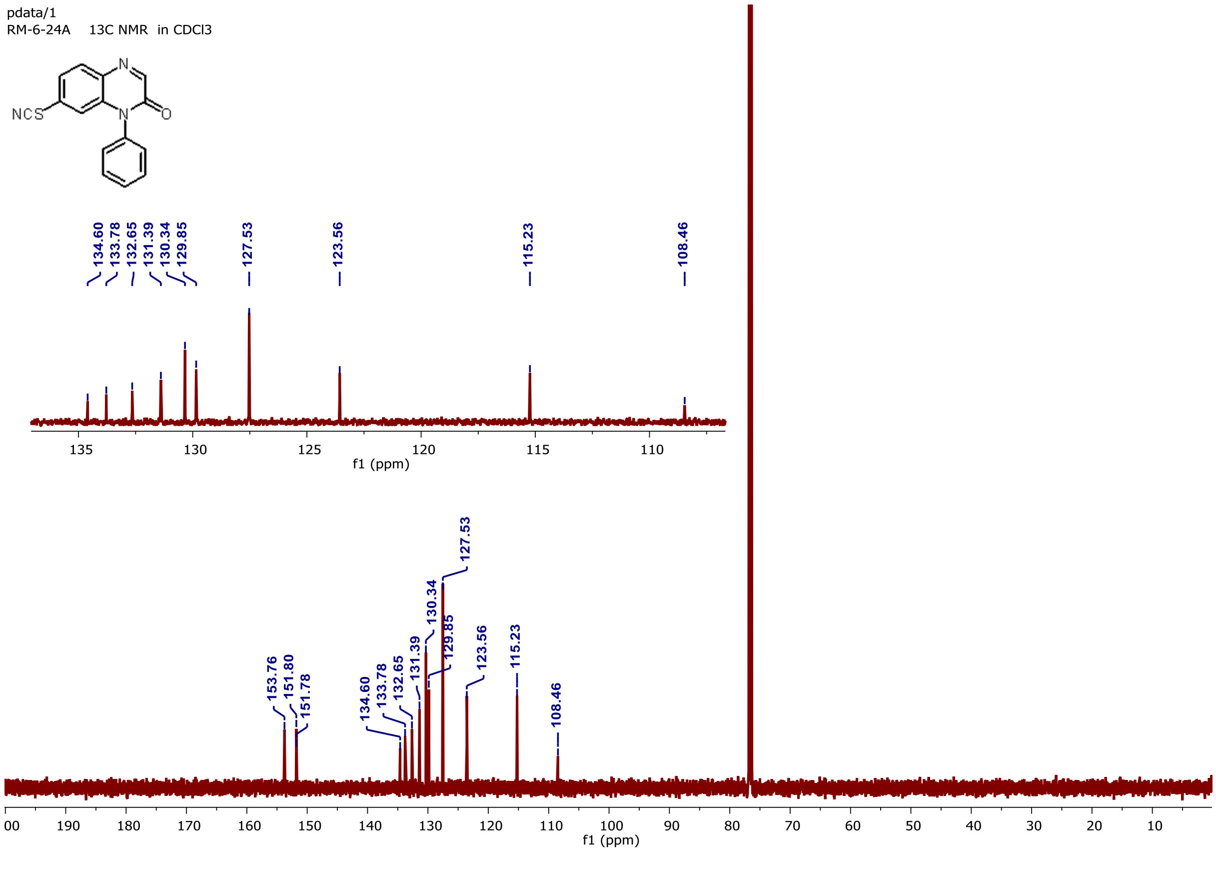


1-Phenyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4d: Prepared according to the general procedure discussed above: reaction time = 6.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (56 mg, 52%); mp 154–156 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 7.98 (d, J = 9.0 Hz, 1 H), 7.66- 7.68 (m, 2 H), 7.61-7.63 (m, 1 H), 7.45 (dd, J = 8.4, 1.8 Hz, 1 H), 7.28-7.30 (m, 2 H), 6.80 ppm (d, J = 2.4 Hz, 1 H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 153.8, 151.8, 151.8, 134.6, 133.8, 132.6, 131.4, 130.3 (2 CH), 129.8, 127.5 (2 CH), 123.6, 115.2, 108.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{15}H_{10}N_3OS$ $[M + H]^+$: 280.0544; found: 280.0541.

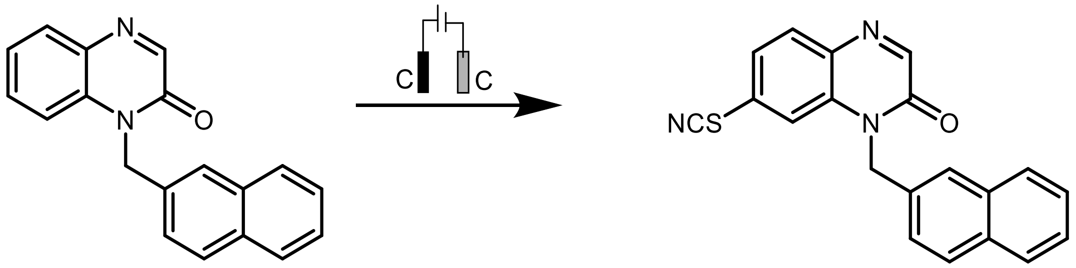


^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4d:**

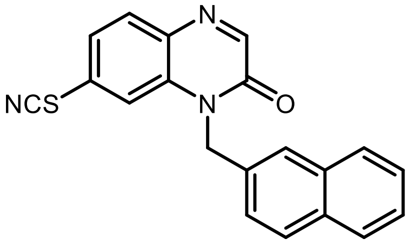




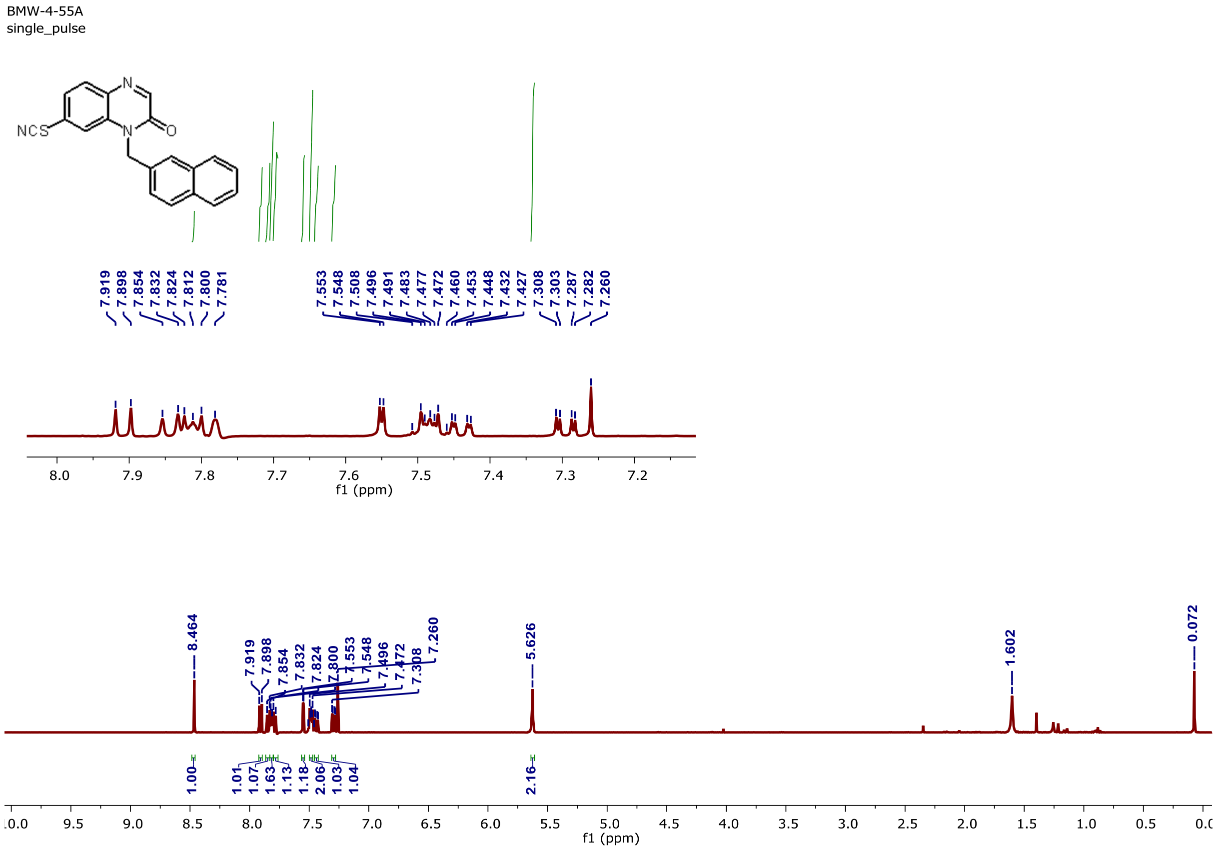
SI-12-29: Analytical and Spectral data of **4e**

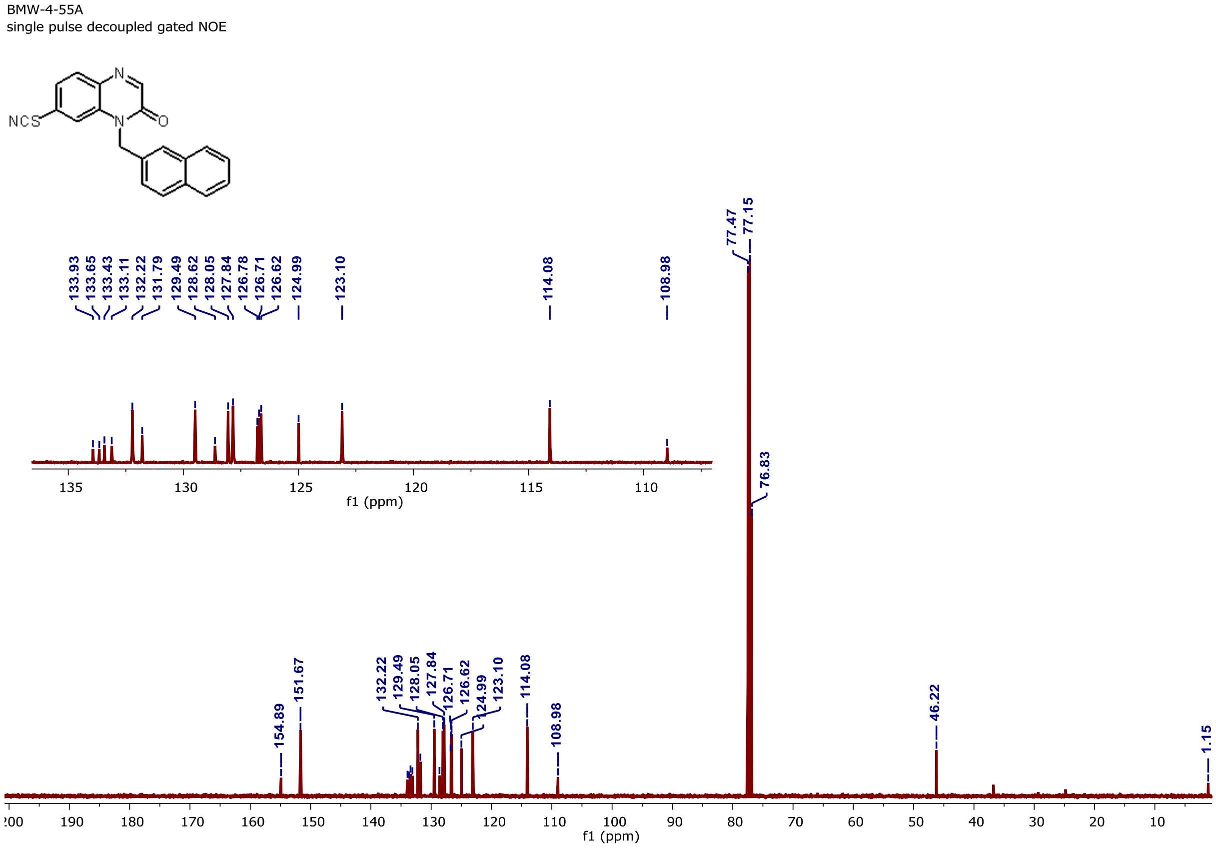


1-(Naphthalen-2-ylmethyl)-7-thiocyanatoquinoxalin-2(1*H*)-one 4e: Prepared according to the general procedure discussed above: reaction time = 6.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (80 mg, 58%); mp 140 –142 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.46 (s, 1 H), 7.91 (d, J = 8.4 Hz, 1 H), 7.84 (d, J = 8.8 Hz, 1 H), 7.80-7.82 (m, 2 H), 7.79 (d, J = 7.6 Hz, 1 H), 7.55 (d, J = 2.0 Hz, 1 H), 7.47-7.51 (m, 2 H), 7.44 (dd, J = 8.4, 2.0 Hz, 1 H), 7.30 (dd, J = 8.4, 2.0 Hz, 1 H), 5.63 (s, 2 H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 154.9, 151.7, 133.9, 133.7, 133.4, 133.1, 132.2, 131.8, 129.5, 128.6, 128.1, 127.8, 126.8, 126.7, 126.6, 125.0, 123.1, 114.1, 109.0, 46.2 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{14}N_3OS$ $[M + H]^+$: 344.0857; found: 344.0851.

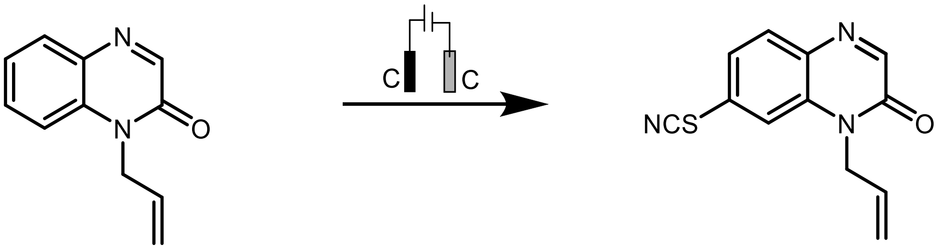


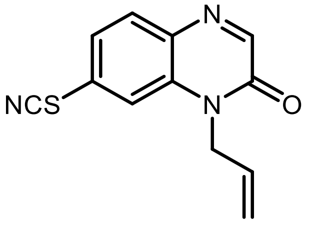
^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4e:**





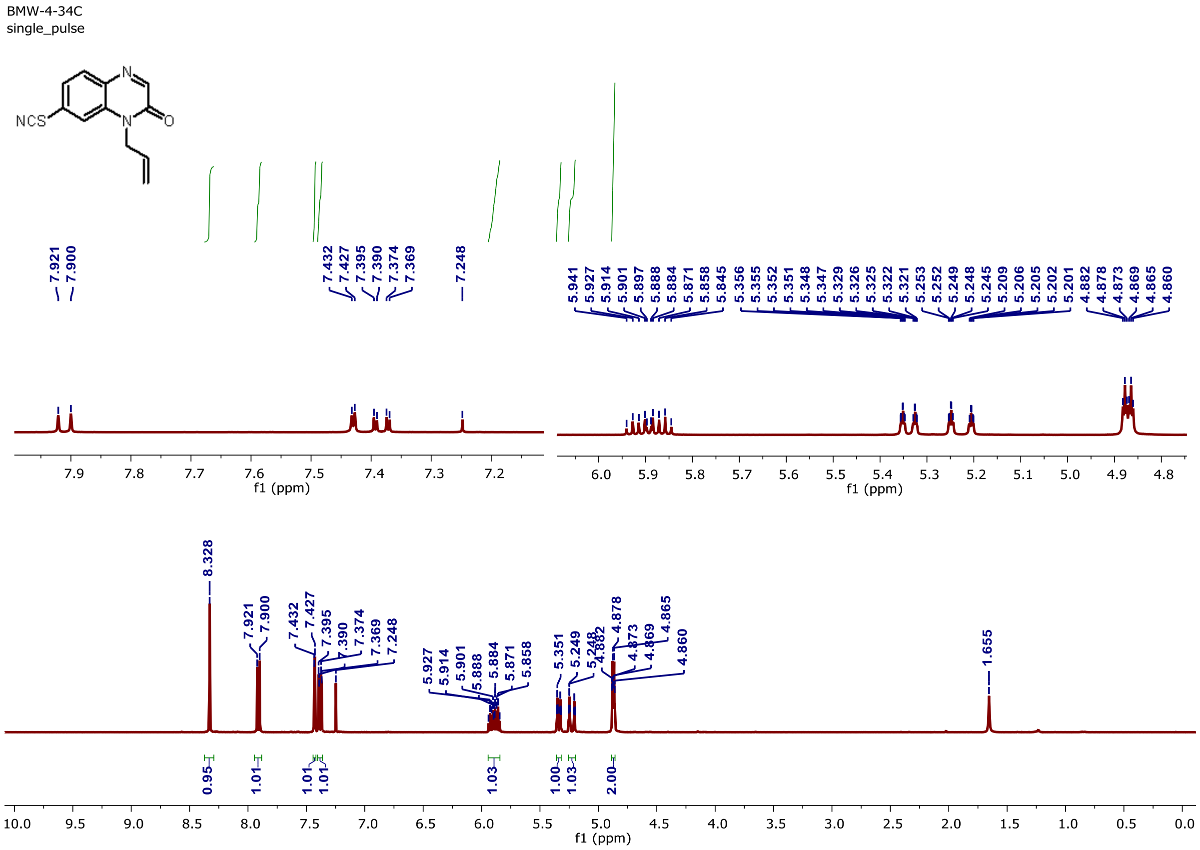
SI-12-30: Analytical and Spectral data of **4f**

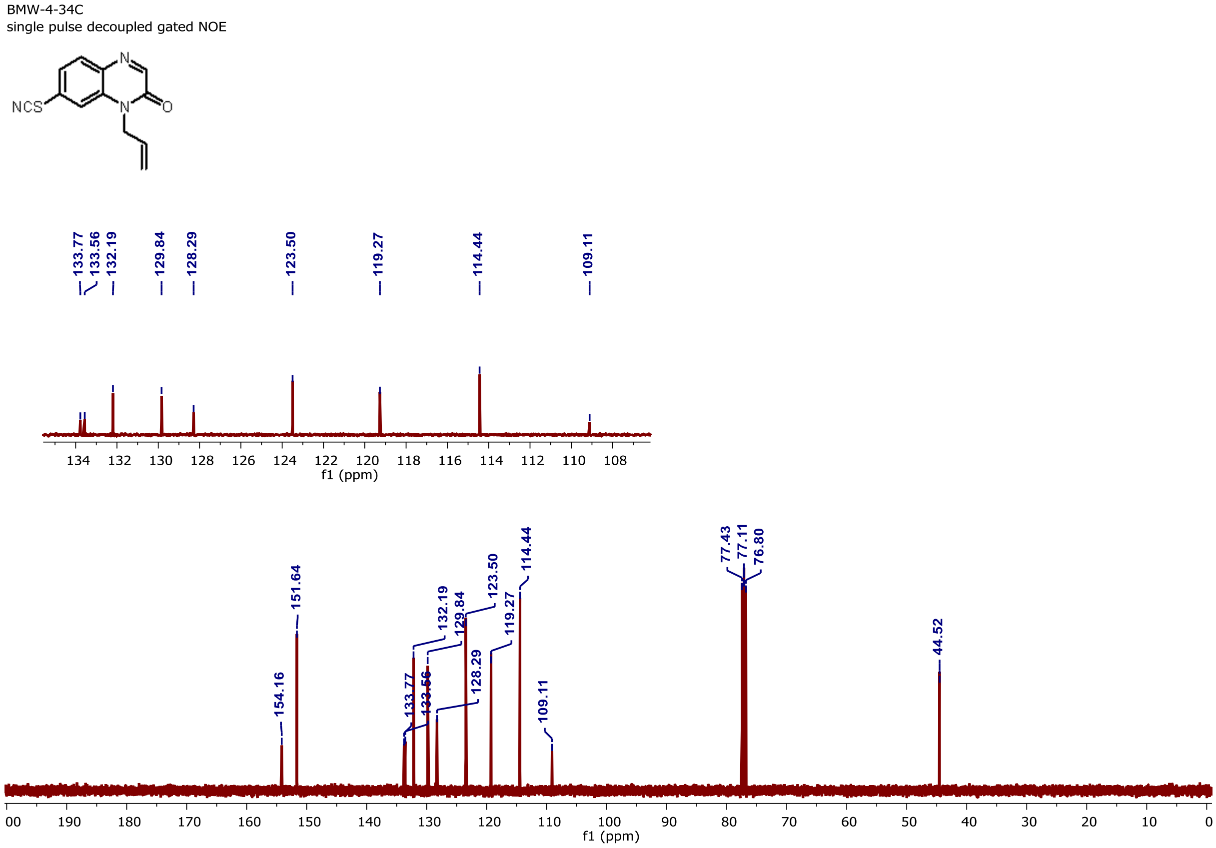




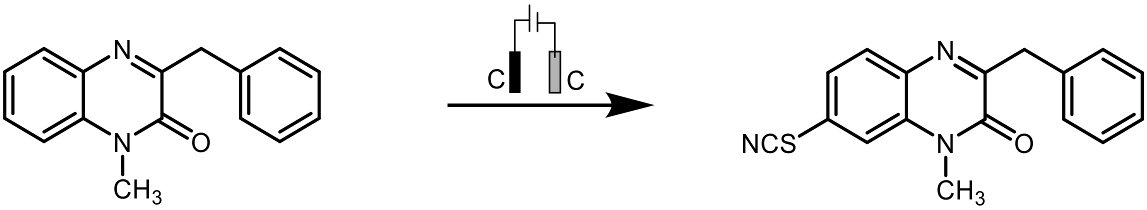
1-Allyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4f: Prepared according to the general procedure discussed above: reaction time = 6.1 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (65 mg, 70%); mp 109–111 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.43 (d, *J* = 2.0 Hz, 1 H), 7.38 (dd, *J* = 8.4, 2.0 Hz, 1 H), 5.89 (ddt, *J* = 17.2, 10.8, 5.6 Hz, 1 H), 5.32-5.36 (m, 1 H), 5.20-5.25 (m, 1 H), 4.87 ppm (dt, *J* = 5.2, 1.6 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.2, 151.6, 133.8, 133.6, 132.2, 129.8, 128.3, 123.5, 119.3, 114.4, 109.1, 44.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{12}H_{10}N_3OS$ $[M + H]^+$: 244.0544; found: 244.0543.

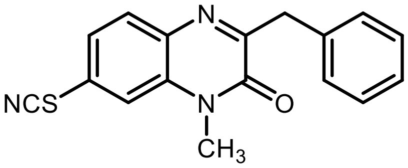
^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4f:**





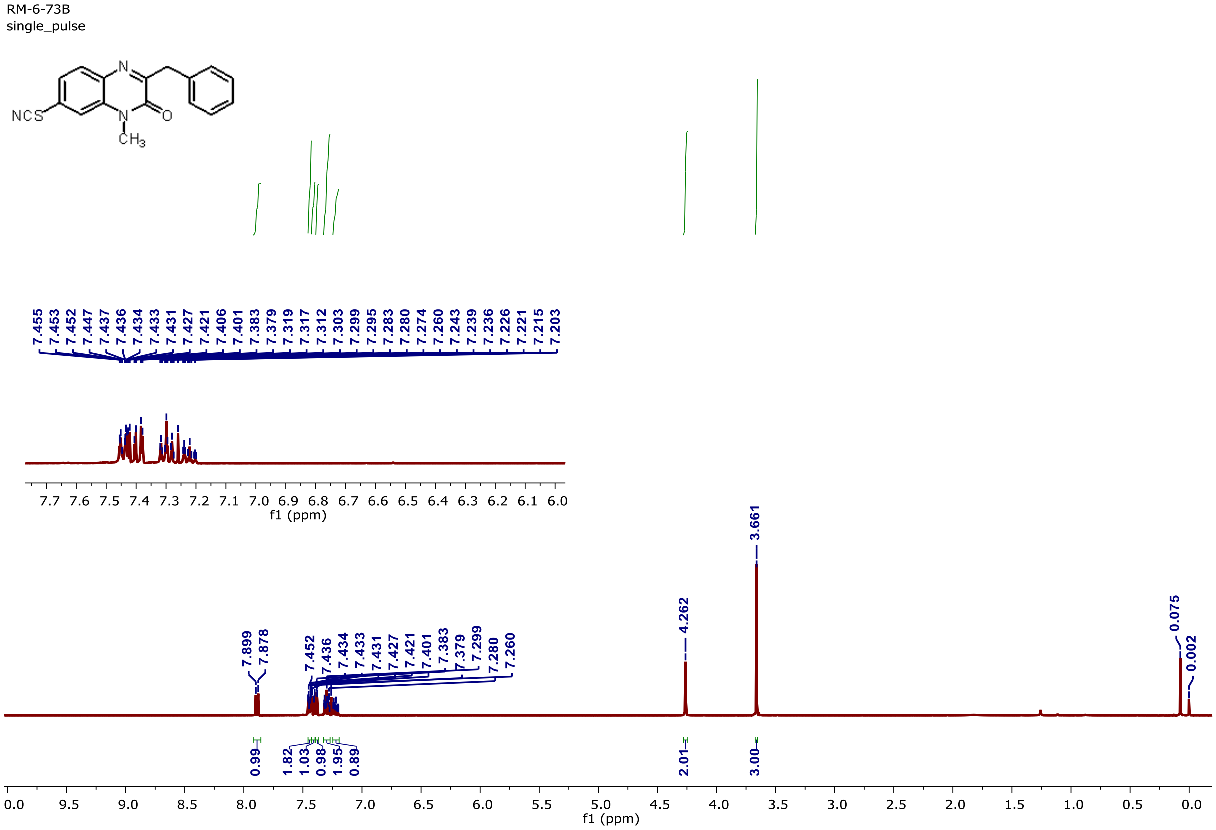
SI-12-31: Analytical and Spectral data of **4g**

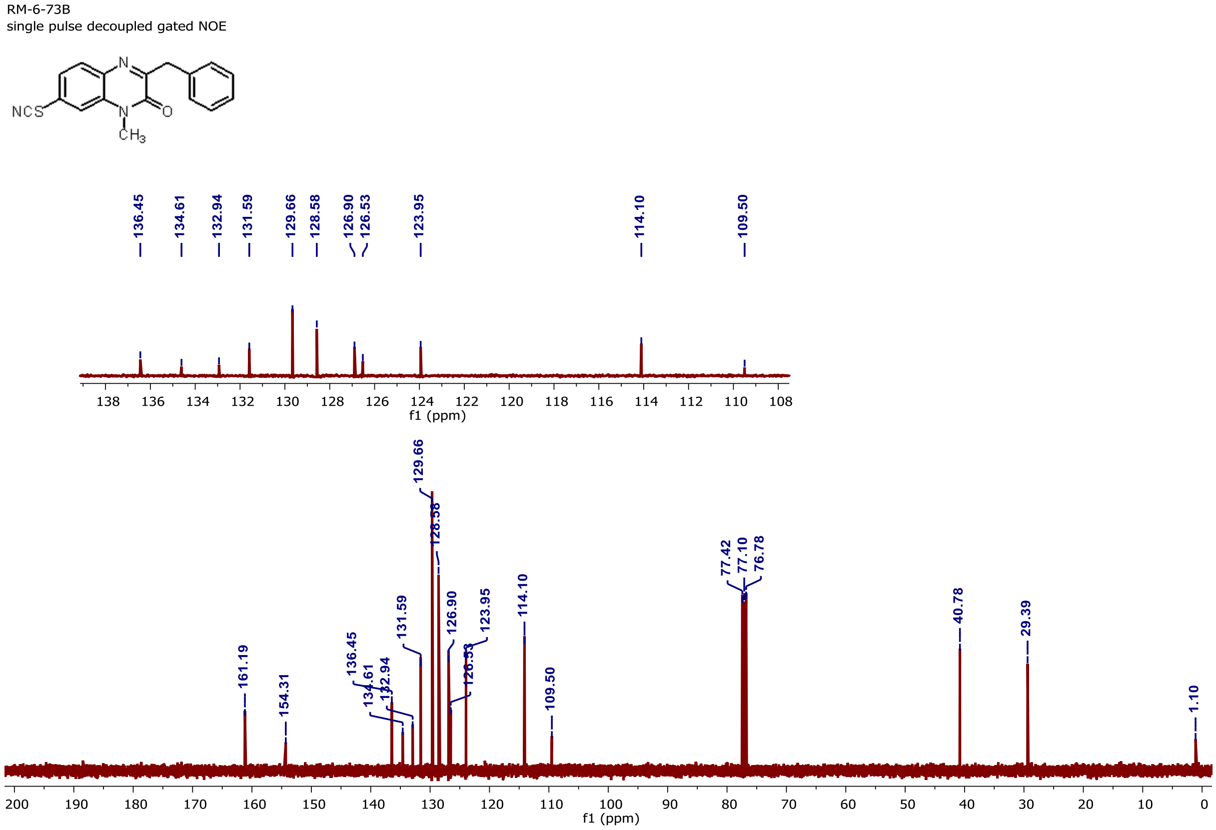




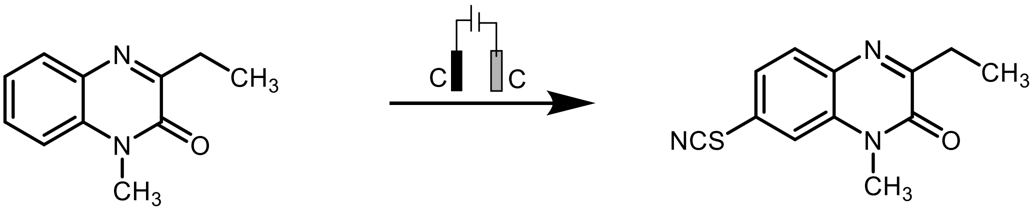
3-Benzyl-1-methyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4g: Prepared according to the general procedure discussed above: reaction time = 6.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (110 mg, 89%); mp 110–112 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.4 Hz, 1 H), 7.43-7.46 (m, 2 H), 7.41 (dd, J = 8.4, 2.4 Hz, 1 H), 7.38 (d, J = 1.6 Hz, 1 H), 7.30 (tt, J = 8.4, 1.6 Hz, 2 H), 7.20-7.24 (m, 1 H), 4.26 (s, 2 H), 3.66 (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 161.2, 154.3, 136.4, 134.6, 132.9, 131.6, 129.7 (2 CH), 128.6 (2 CH), 126.9, 126.5, 123.9, 114.1, 109.5, 40.8 (CH_2), 29.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{14}N_3OS$ [*M* + H]$^+$: 308.0857; found: 308.0857.

^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4g:**

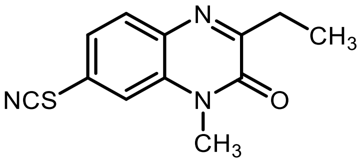


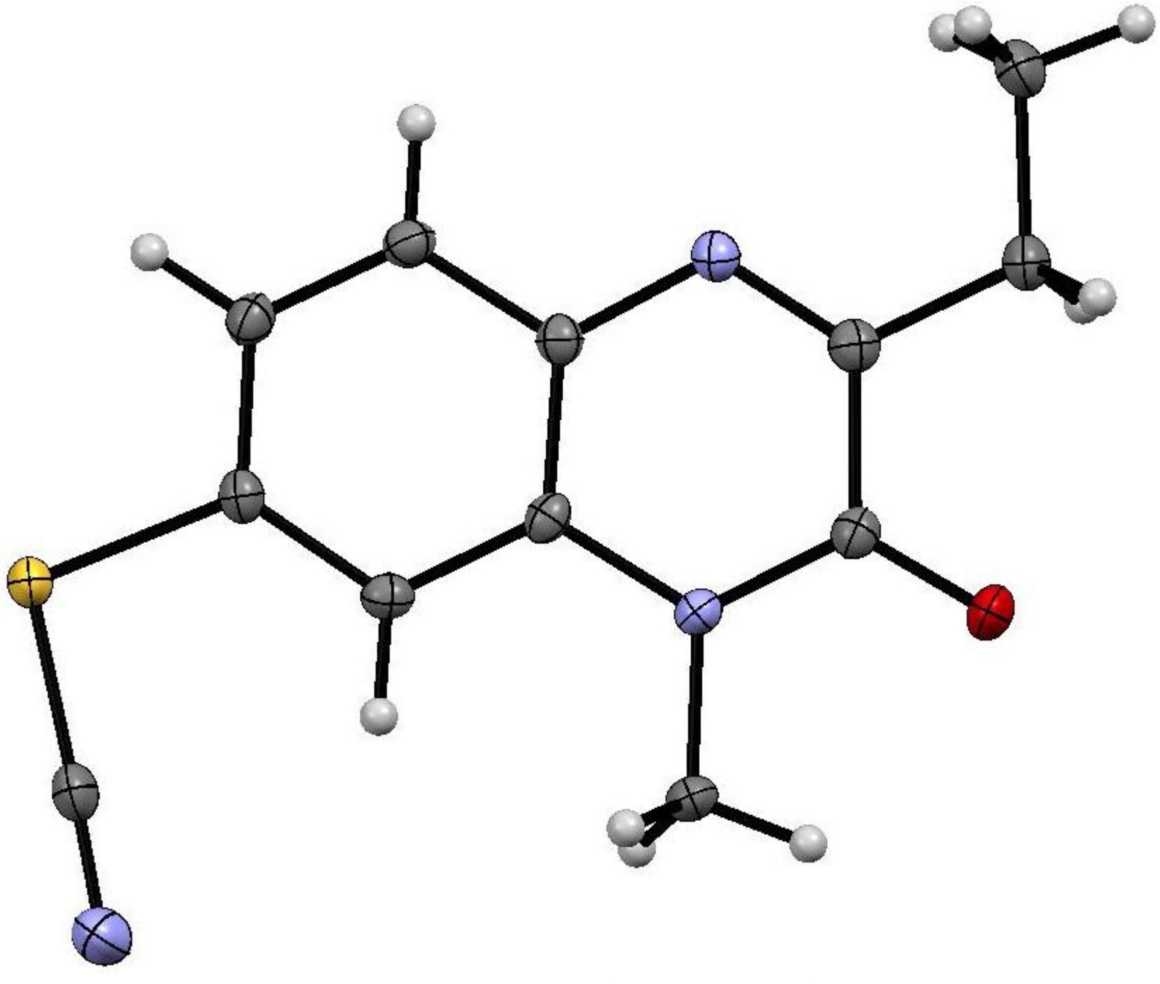


SI-12-32: Analytical and Spectral data of **4h**



3-Ethyl-1-methyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4h: Prepared according to the general procedure discussed above: time = 6.2 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (65 mg, 70%); mp 127–129 ˚C; solvent of crystallization, DCM/MeOH (1.5 mL/0.5 mL) at room temperature. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.86 (dd, *J* = 7.2, 1.6 Hz, 1 H), 7.41 (dd, *J* = 7.6, 2.0 Hz, 2 H), 3.69 (s, 3 H), 2.97 (q, *J* = 7.6 Hz, 2 H), 1.32 ppm (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 163.9, 154.4, 134.4, 133.1, 131.3, 125.9, 124.1, 114.3, 109.7, 29.3, 27.6, 10.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{12}H_{12}N_3OS$ $[M + H]^+$: 246.0701; found: 246.0692.





X-ray determined molecular structure of **4h (CCDC 2266371)**. The thermal ellipsoids are shown in 50% probability level. Solvent of crystallization, DCM/MeOH (1.5 mL:0.5 mL, *v*/*v*) at room temperature 25-30 °C.

Datablock: 4h

Bond precision: C-C = 0.0020 A Wavelength=1.54178

Cell:	a=3.9964(3)	b=8.0048(5)	c=17.9743(12)
	alpha=90.426(2)	beta=90.934(2)	gamma=98.213(2)

Temperature: 100 K

	Calculated	Reported
Volume	569.00(7)	569.00(7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C12 H11 N3 O S	C12 H11 N3 O S
Sum formula	C12 H11 N3 O S	C12 H11 N3 O S
Mr	245.30	245.30
Dx,g cm-3	1.432	1.432
Z	2	2
Mu (mm-1)	2.418	2.418
F000	256.0	256.0
F000'	257.34	
h,k,lmax	4,9,21	4,9,21
Nref	2006	1852
Tmin,Tmax	0.805,0.976	0.517,0.753
Tmin'	0.730	

Correction method= # Reported T Limits: Tmin=0.517 Tmax=0.753
AbsCorr = MULTI-SCAN

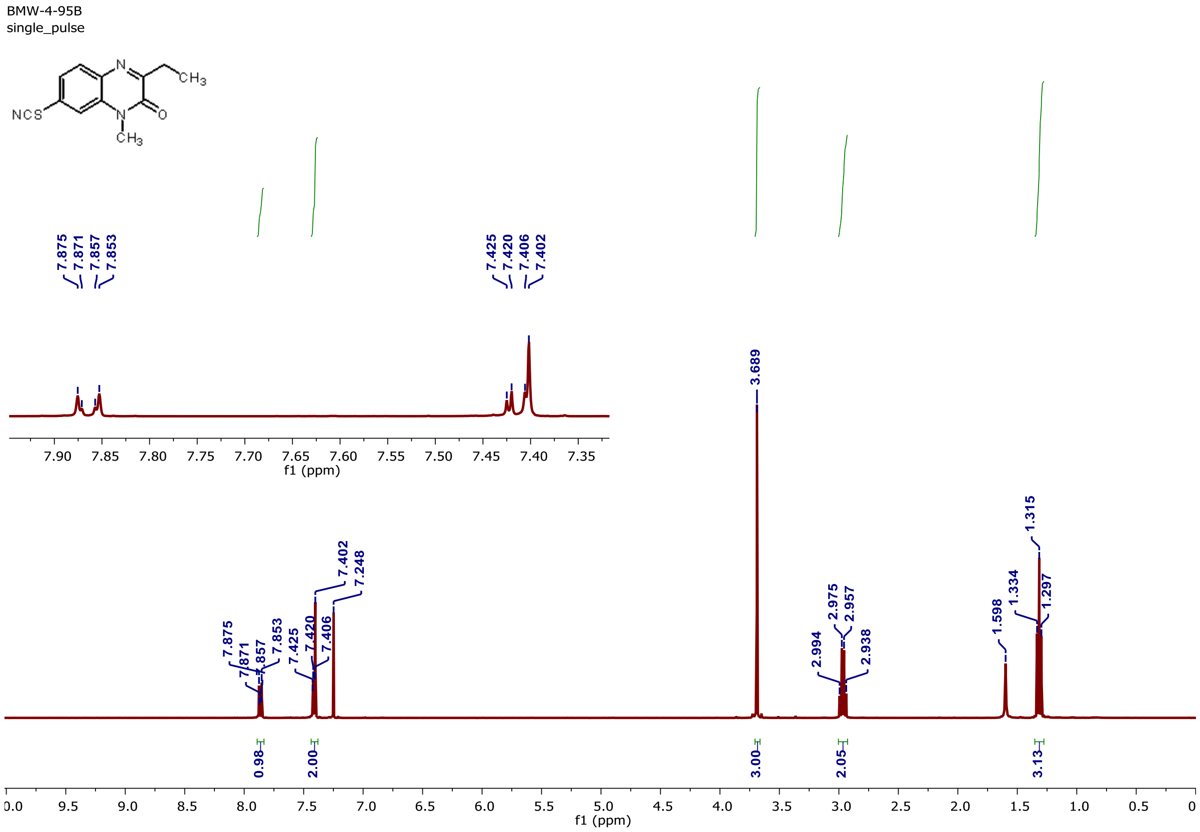
Data completeness= 0.923 Theta(max)= 66.462

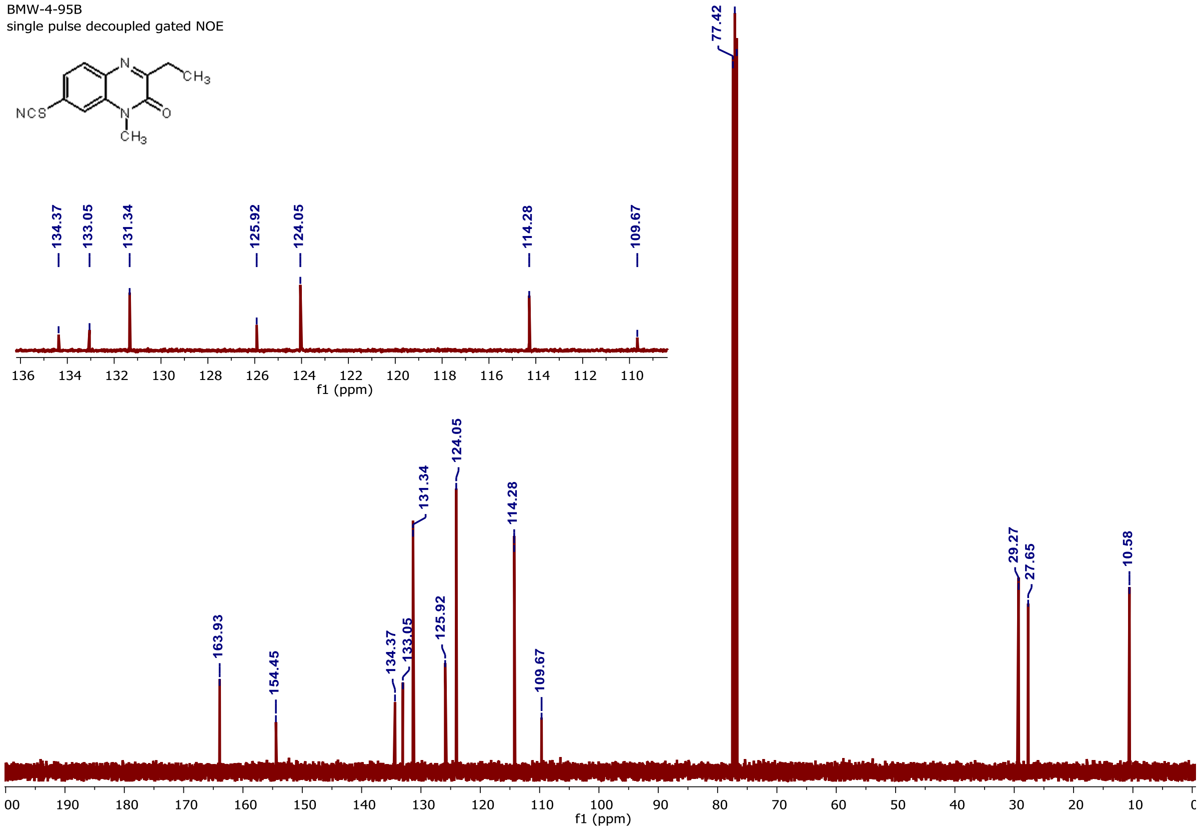
R(reflections)= 0.0350 (1849) wR2(reflections)= 0.0921 (1852)

S = 1.123 Npar= 157

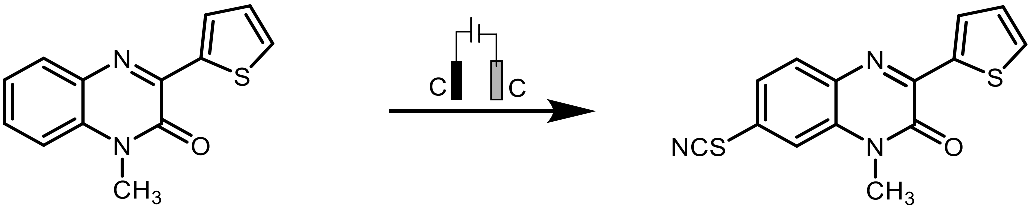
Alert level A: PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low. 0.923 Why? Author Response: The crystal diffracted poorly. No reflection was removed by intention.

^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4h:**

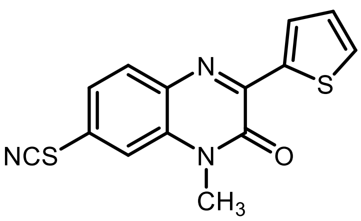




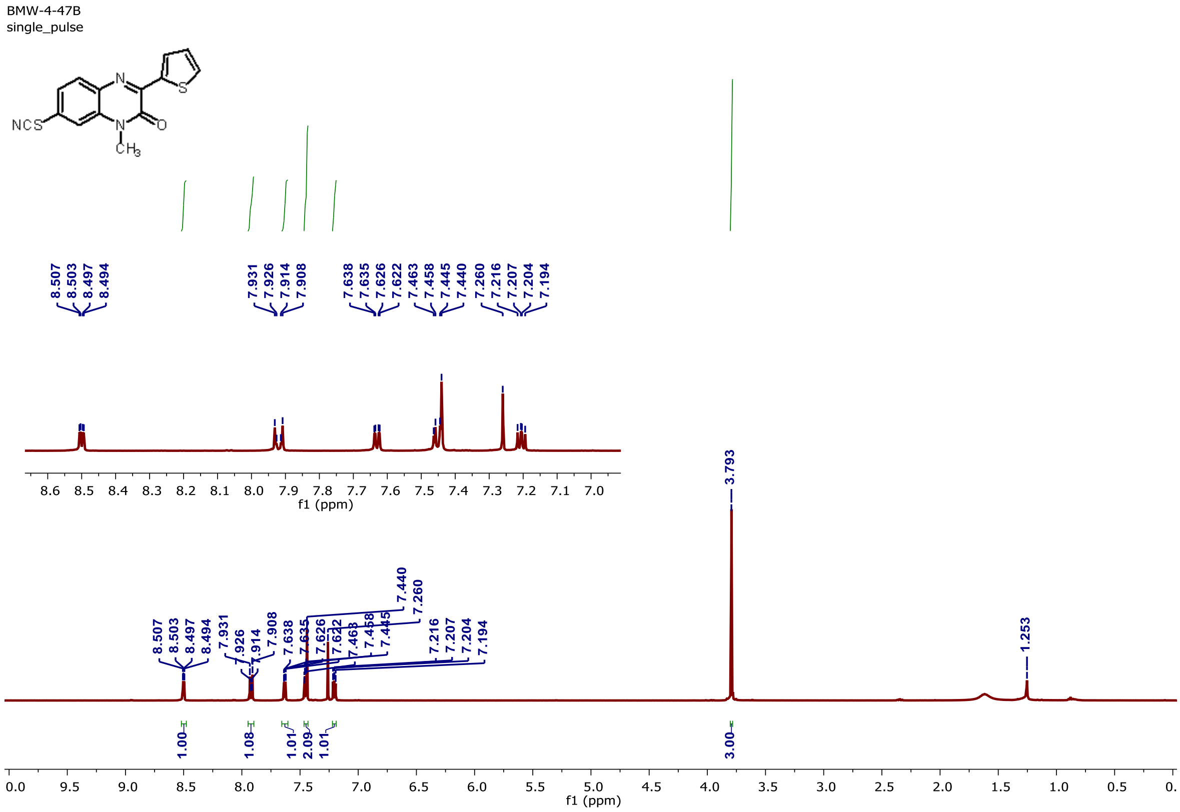
SI-12-33: Analytical and Spectral data of **4i**

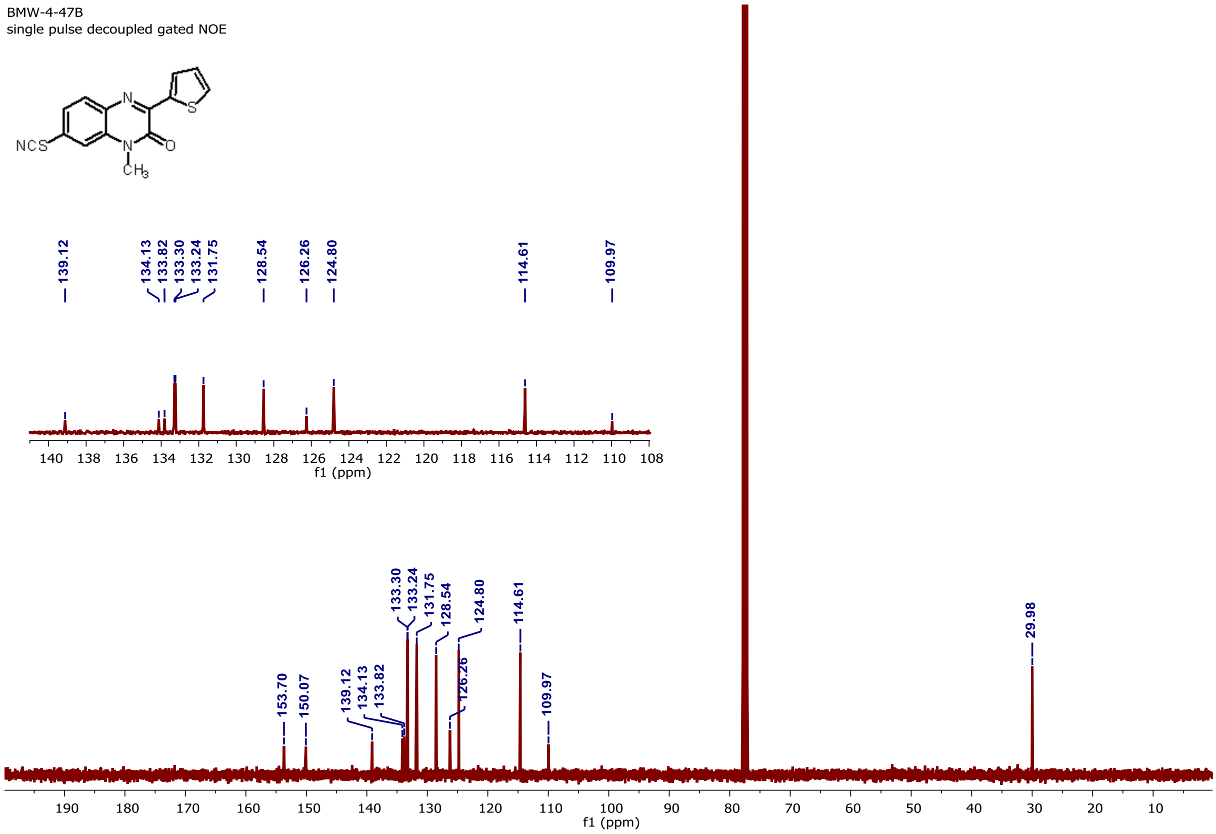


1-Methyl-7-thiocyanato-3-(thiophen-2-yl) quinoxalin-2(1*H*)-one 4i: Prepared according to the general procedure discussed above: reaction time = 6.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (48 mg, 40%); mp 187–189 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (dd, J = 4.0, 1.6 Hz, 1 H), 7.91-7.93 (m, 1 H), 7.63 (dd, J = 4.8, 1.2 Hz, 1 H), 7.44-7.46 (m, 2 H), 7.21 (dd, J = 4.8, 3.6 Hz, 1 H), 3.79 ppm (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.7, 150.1, 139.1, 134.1, 133.8, 133.3, 133.2, 131.7, 128.5, 126.3, 124.8, 114.6, 110.0, 30.0 ppm. HRMS (ESI-QTOF): *m/z* calcd for $C_{14}H_{10}N_3OS_2$ [*M* + H]$^+$: 300.0265; found: 300.0273.

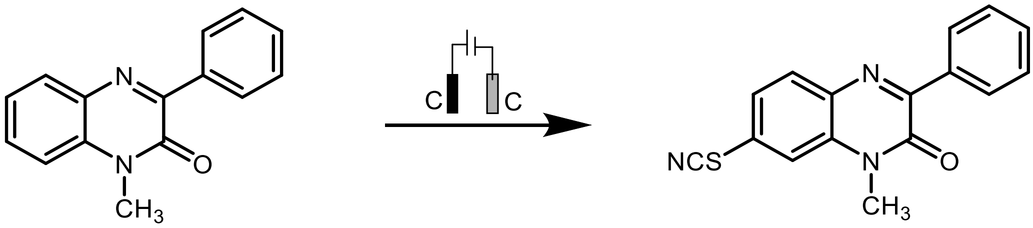


^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4i**:

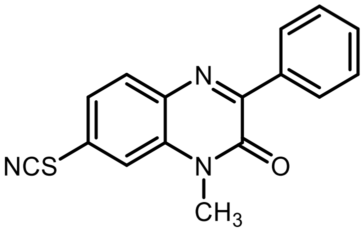




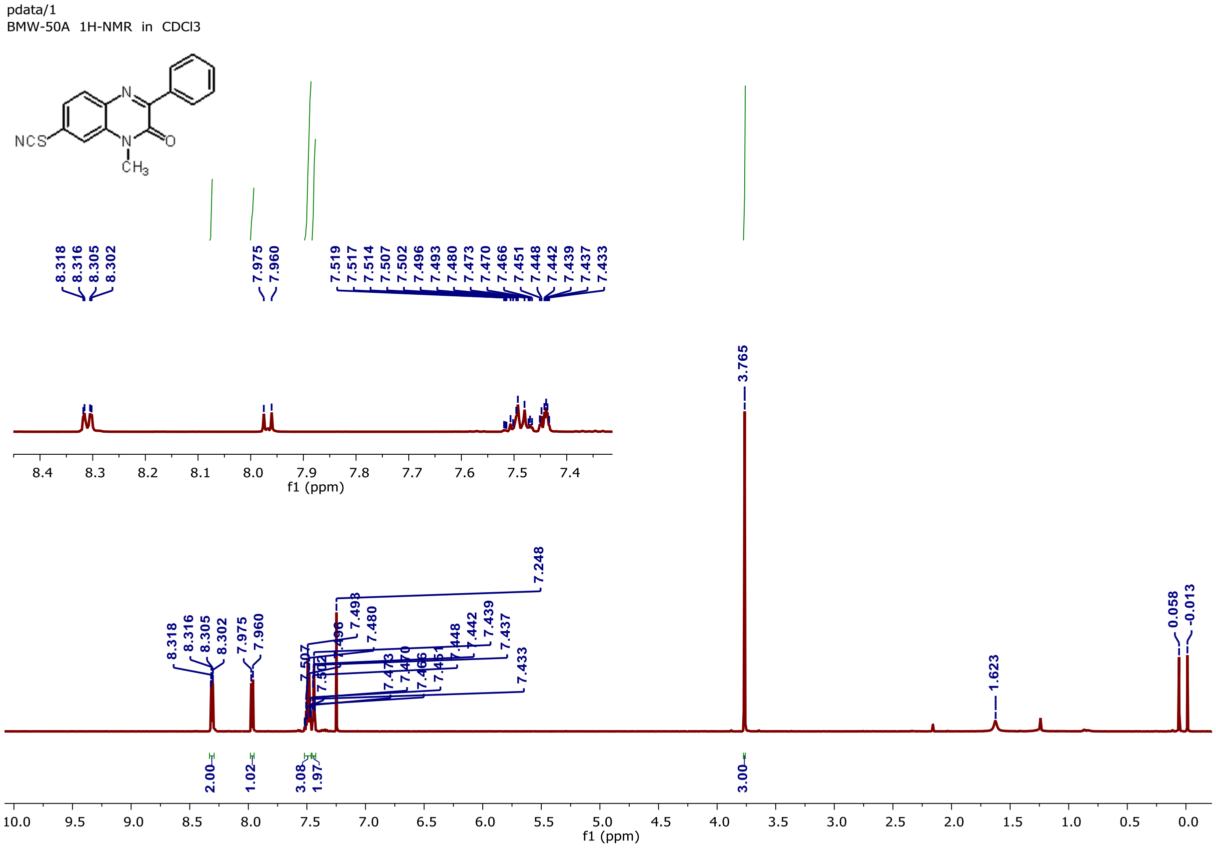
SI-12-34: Analytical and Spectral data of **4j**

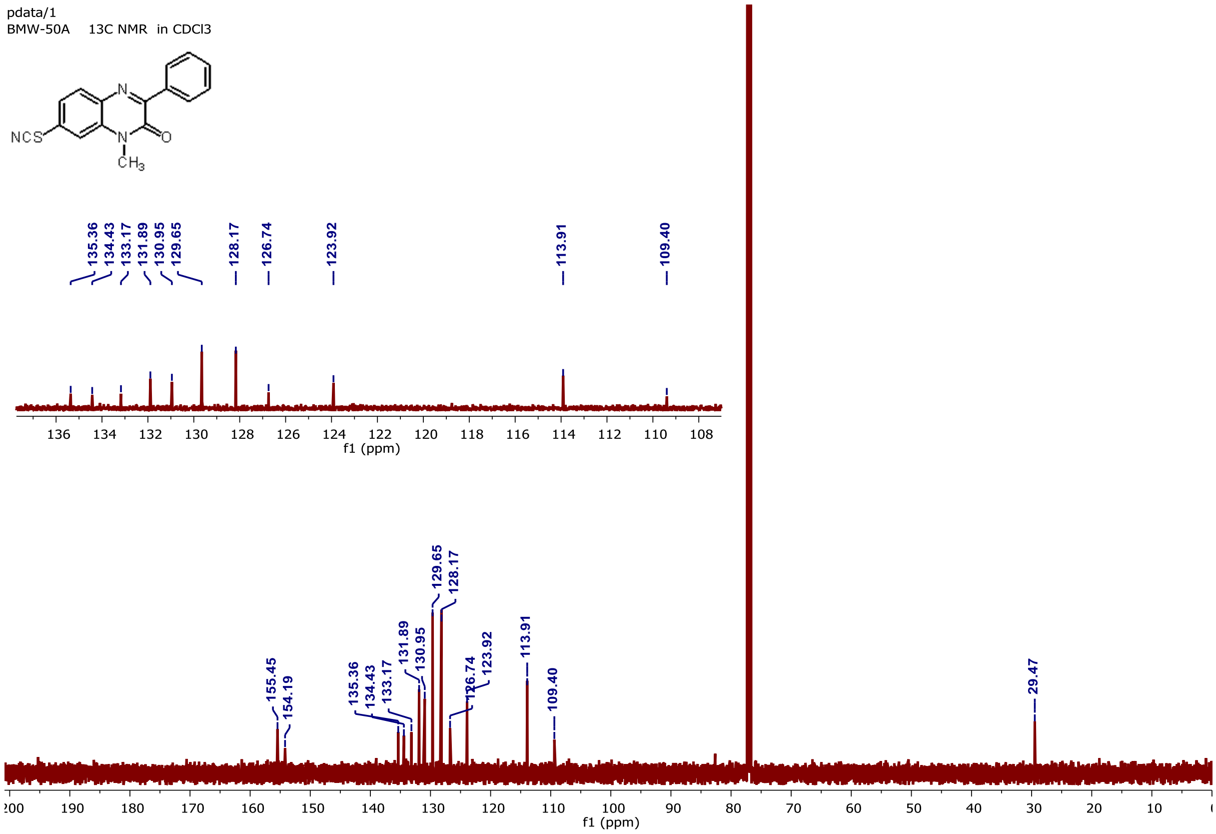


1-Methyl-3-phenyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4j: Prepared according to the general procedure discussed above: reaction time = 6.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (83 mg, 70%); mp 190–192 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.31 (dd, J = 7.8, 1.2 Hz, 2 H), 7.97 (d, J = 9.0 Hz, 1 H), 7.47-7.52 (m, 3 H), 7.43-7.45 (m, 2 H), 3.76 ppm (s, 3 H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 155.4, 154.2, 135.4, 134.4, 133.2, 131.9, 131.0, 129.7 (2 CH), 128.2 (2 CH), 126.7, 123.9, 113.9, 109.4, 29.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{12}N_3OS$ [M + H]$^+$: 294.0701; found: 294.0692.

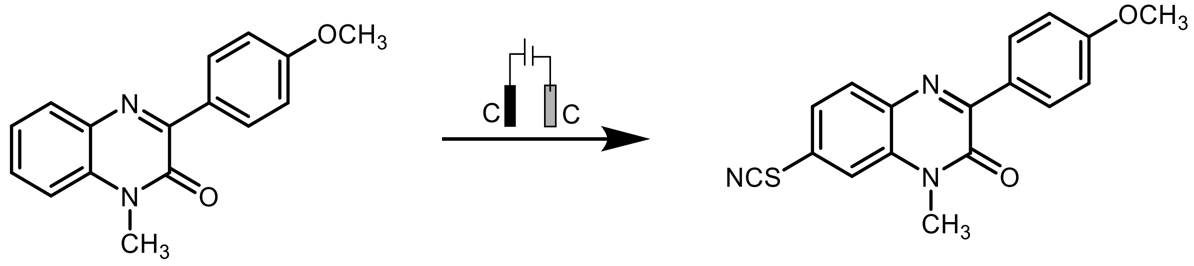


^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4j:**

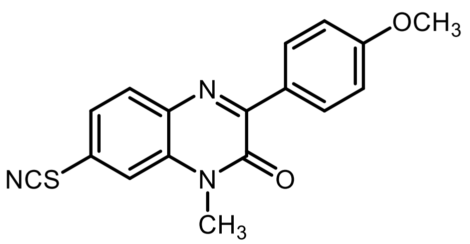




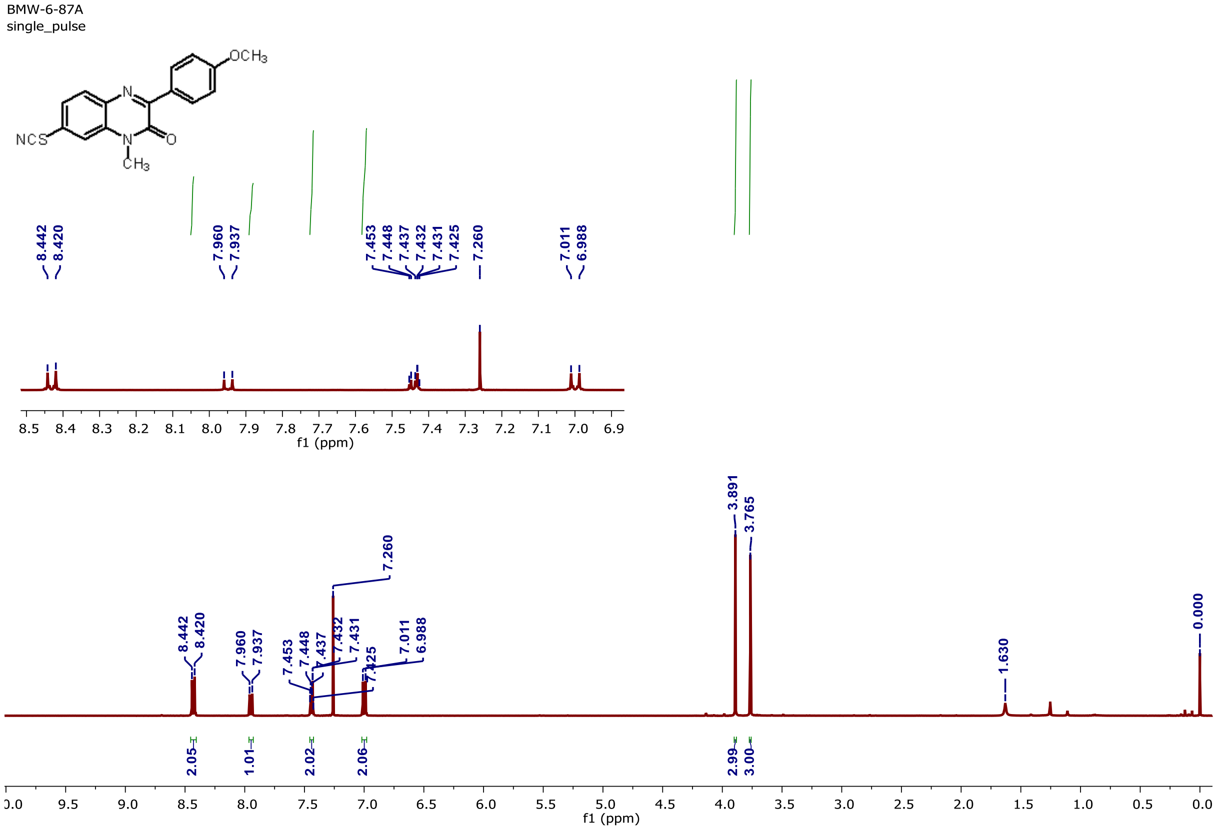
SI-12-35: Analytical and Spectral data of **4k**

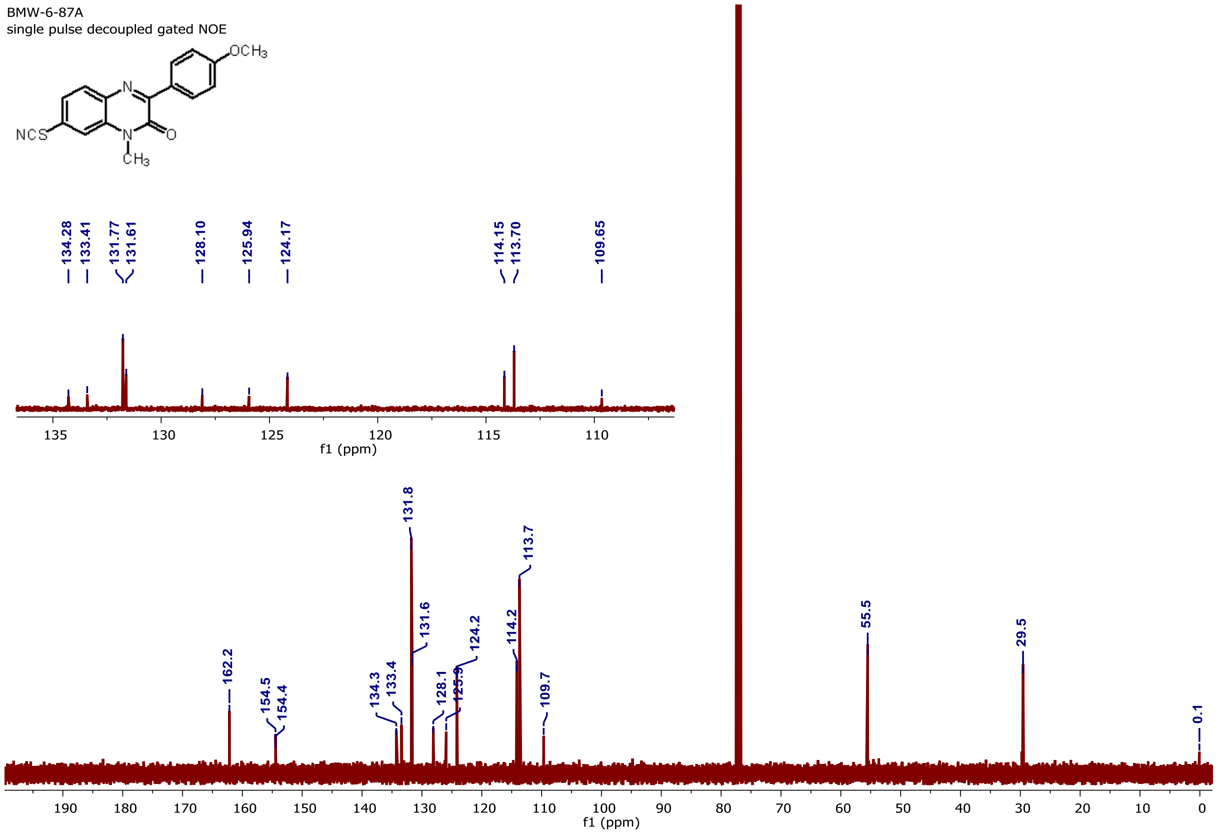


3-(4-Methoxyphenyl)-1-methyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4k: Prepared according to the general procedure discussed above: reaction time = 6.3 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (88 mg, 67%); mp 190–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 8.8 Hz, 2 H), 7.95 (d, J = 9.2 Hz, 1 H), 7.42-7.45 (m, 2 H), 7.00 (d, J = 9.2 Hz, 2 H), 3.89 (s, 3 H), 3.77 ppm (s, 3 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 162.2, 154.5, 154.4, 134.3, 133.4, 131.8 (2 CH), 131.6, 128.1, 125.9, 124.2, 114.2, 113.7 (2 CH), 109.7, 55.5, 29.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{14}N_3O_2S$ $[M + H]^+$: 324.0806; found: 324.0804.

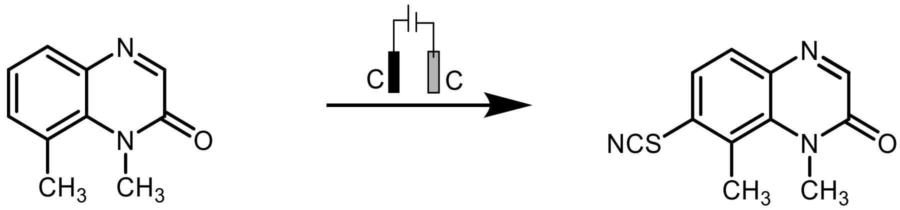


^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4k:**

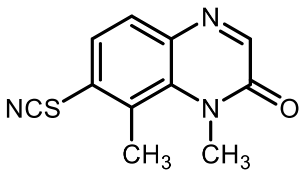




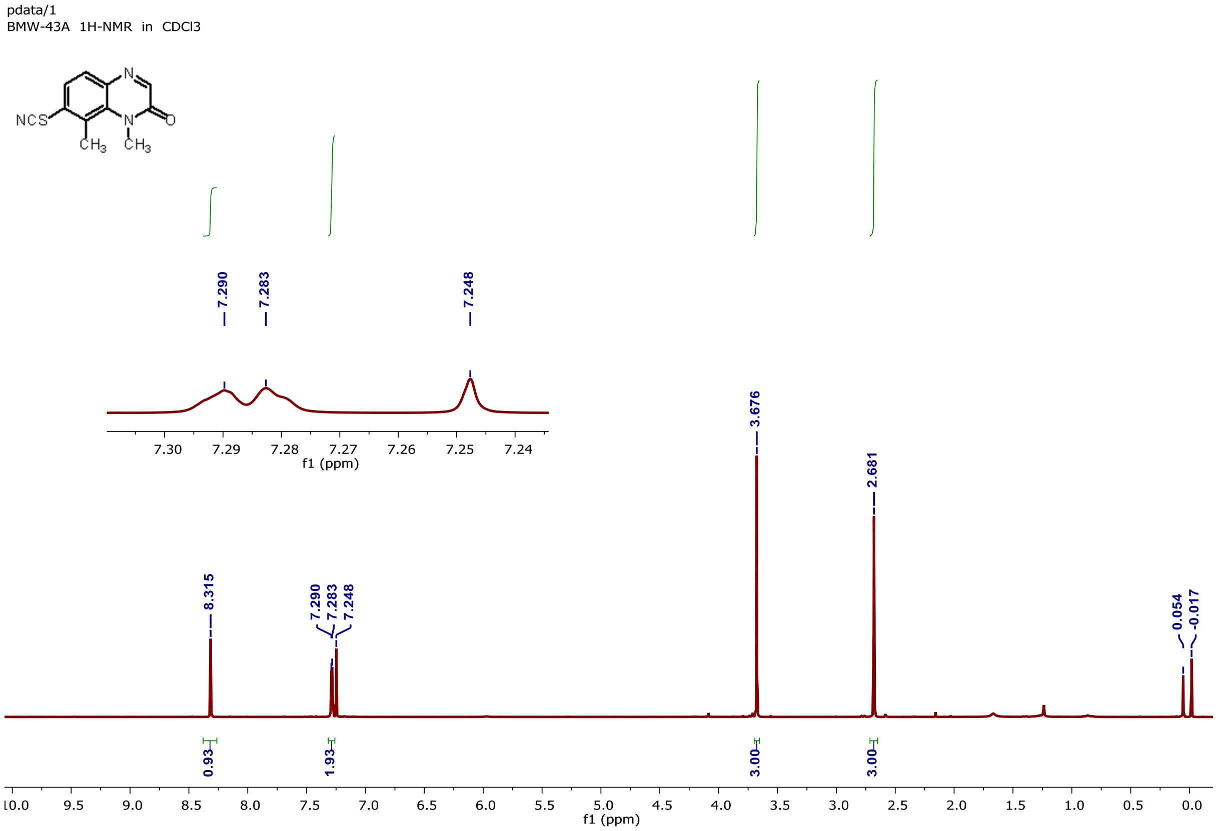
SI-12-36: Analytical and Spectral data of **4l**

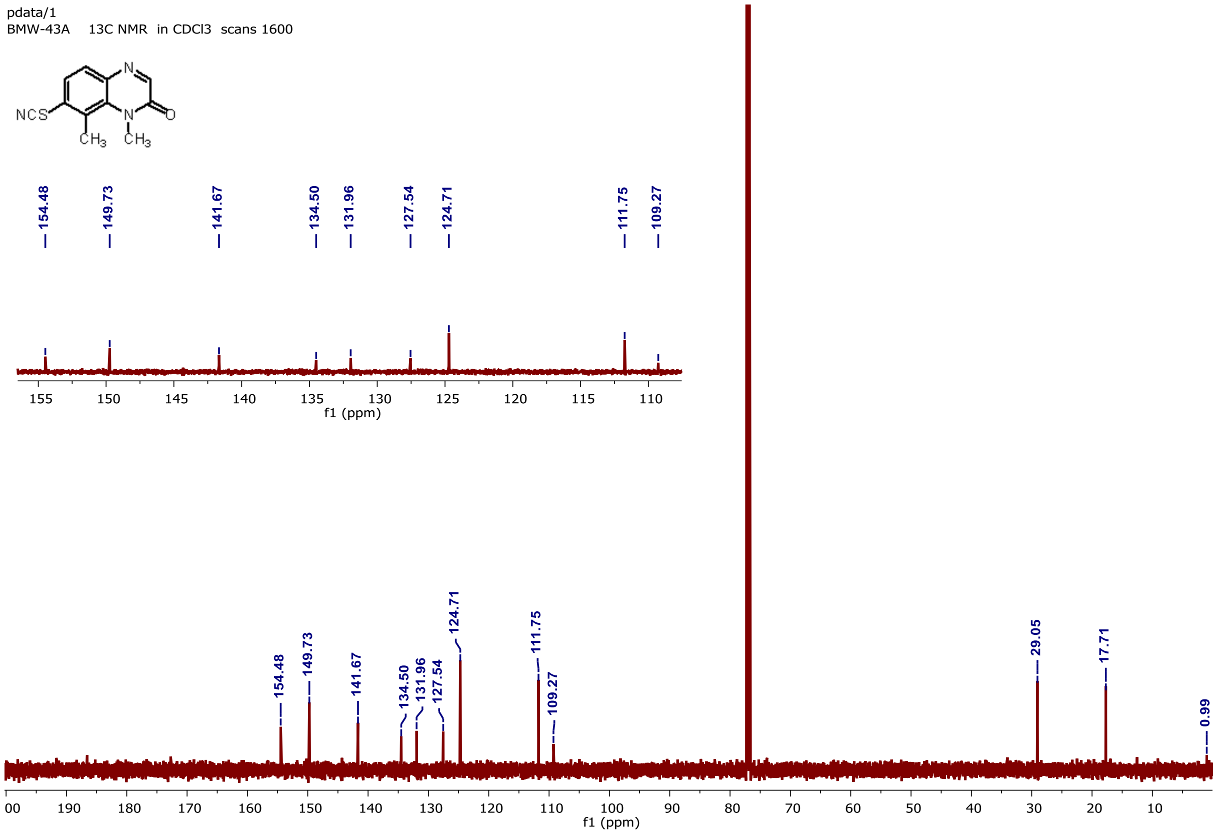


1,8-Dimethyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4l: Prepared according to the general procedure discussed above: reaction time = 6.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (73 mg, 78%); mp 186 –188 ˚C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.32 (s, 1 H), 7.29 (d, J = 4.2 Hz, 2 H), 3.68 (s, 3 H), 2.68 ppm (s, 3 H); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 154.5, 149.7, 141.7, 134.5, 132.0, 127.5, 124.7, 111.7, 109.3, 29.0, 17.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{11}H_{10}N_3OS$ [M + H]$^+$: 232.0544; found: 232.0542.

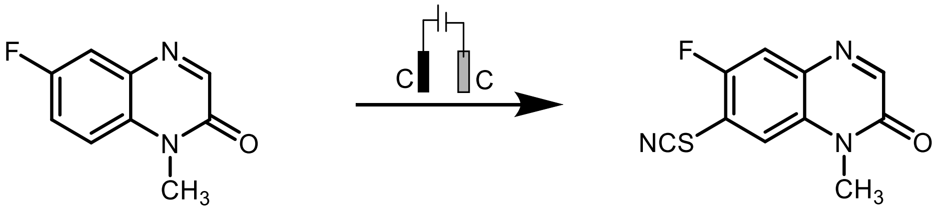


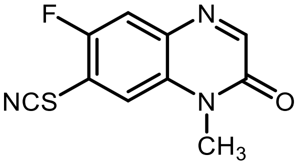
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4l:**





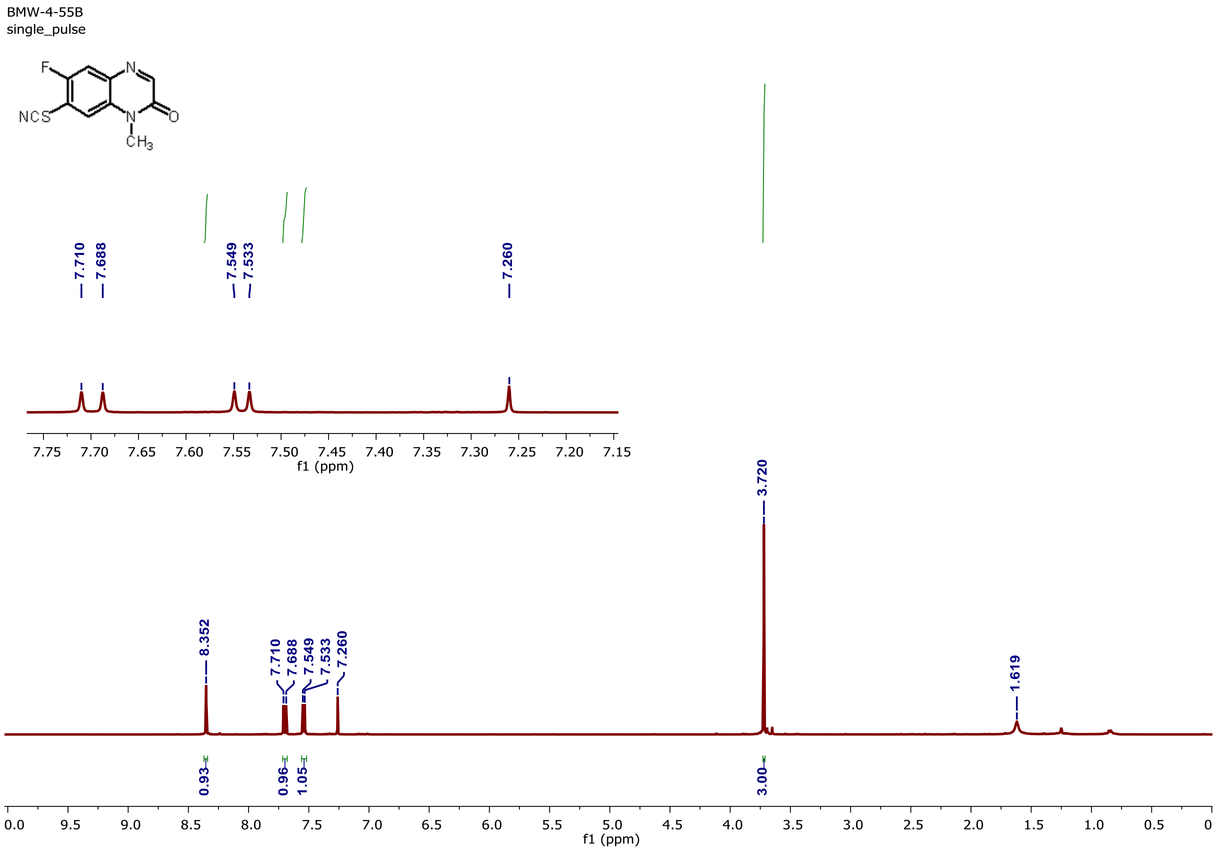
SI-12-37: Analytical and Spectral data of **4m**

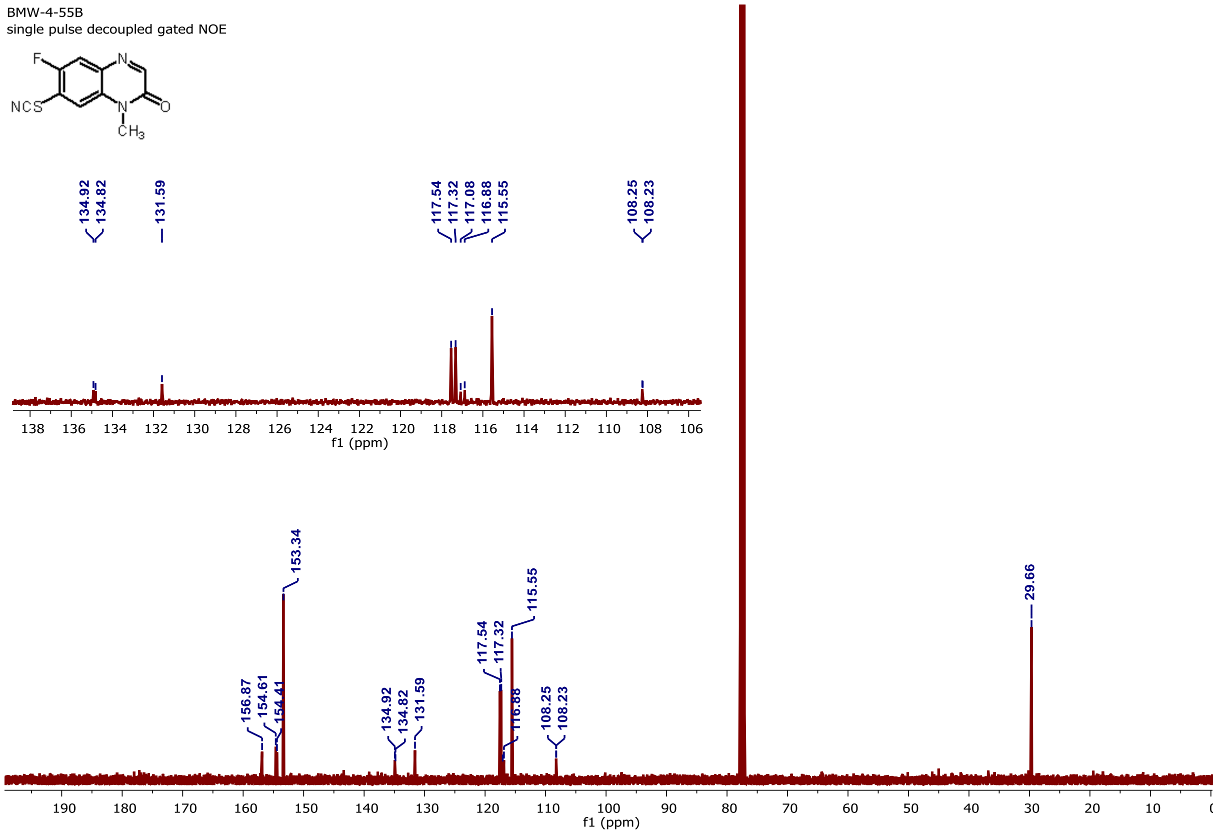


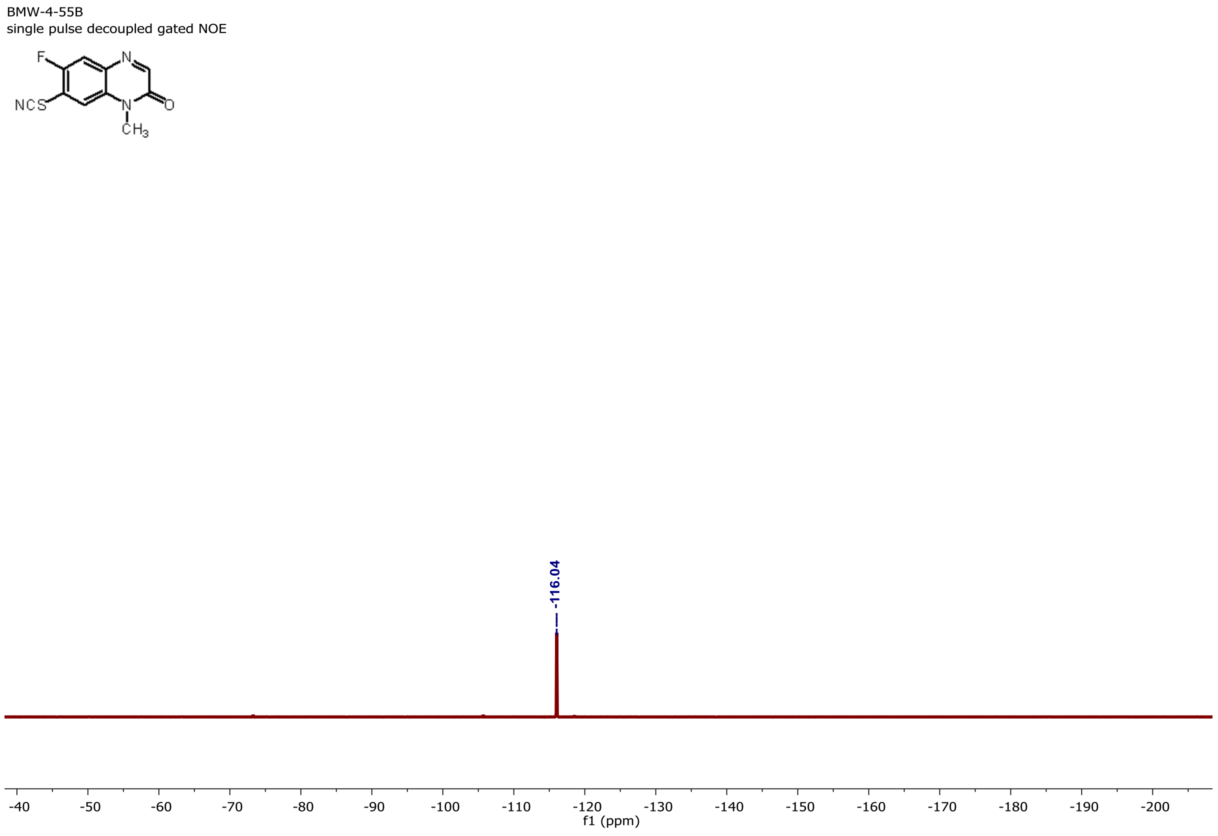


6-Fluoro-1-methyl-7-thiocyanatoquinoxalin-2(1*H*)-one 4m: Prepared according to the general procedure discussed above: reaction time = 6.2 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (71 mg, 75%); mp 187–189 ˚C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.35 (s, 1 H), 7.70 (d, J = 8.8 Hz, 1 H), 7.54 (d, J = 6.4 Hz, 1 H), 3.72 ppm (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 155.6 (d, $J_{C\text{-}F}$ = 248.5 Hz, 1 C), 154.6, 153.3, 134.9 (d, $J_{C\text{-}F}$ = 10.1 Hz, 1 C), 131.6, 117.4 (d, $J_{C\text{-}F}$ = 22.2 Hz, 1 C), 117.0 (d, $J_{C\text{-}F}$ = 20.2 Hz, 1 C), 115.6, 108.2 (d, $J_{C\text{-}F}$ = 2.0 Hz, 1 C), 29.7 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = –116.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{10}H_7FN_3OS$ $[M + H]^+$: 236.0294; found: 236.0287.

^{1}H (400 MHz, CDCl$_3$), ^{13}C{^{1}H} (101 MHz, CDCl$_3$), and ^{19}F (376 MHz, CDCl$_3$) NMR spectra of **4m**:

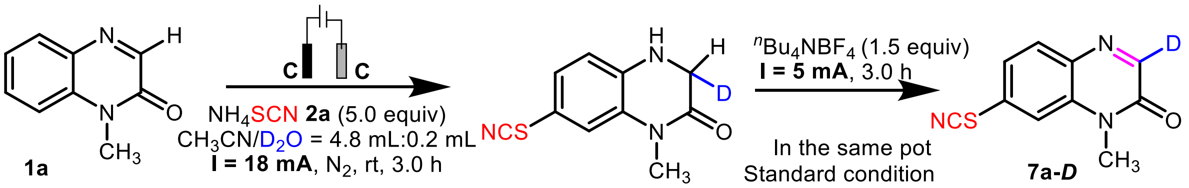



BMW-4-55B
single pulse decoupled gated NOE
F
N
NCS
N
O
CH3
134.92
134.82
131.59
117.54
117.32
117.08
116.88
115.55
108.25
108.23
138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106
f1 (ppm)
153.34
156.87
154.61
154.41
134.92
134.82
131.59
117.54
117.32
116.88
115.55
108.25
108.23
29.66
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

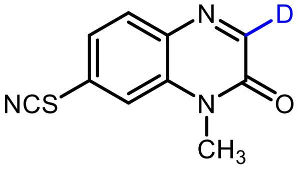

BMW-4-55B
single pulse decoupled gated NOE
F
N
NCS
N
O
CH3
-116.04
-40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

SI-12-38: Analytical and spectral data of **4a-*D***

General Procedure for the Synthesis of **4a-*D***



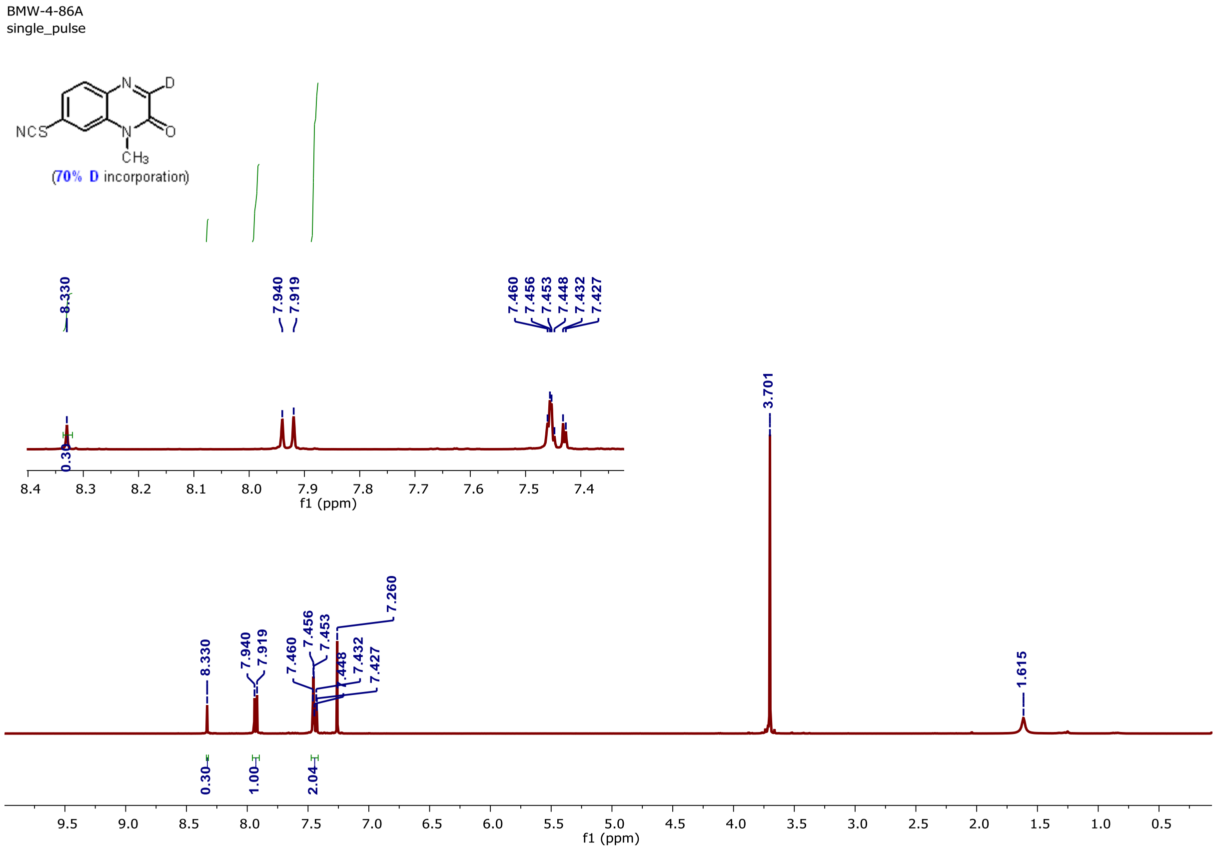
In an electrasyn undivided glass vial (10 mL) equipped with a stir bar, **1a** (64 mg, 0.4 mmol, 1.0 equiv), ammonium thiocyanate **2a** (152 mg, 2.0 mmol, 5.0 equiv), and 5.0 mL of dry CH_3CN/D_2O (4.8mL:0.2 mL) were added. The vial was equipped with graphite plate (5.0 cm x 0.8 cm x 0.2 cm, about 1.5 cm immersion depth in solution) as the anode and as well as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature until complete consumption of **1a** (3.0 h). Therefore, supporting electrolyte $^n Bu_4NBF_4$ (197 mg, 1.5 equiv) was added into the same reaction pot and electrolyzed at a constant current of 5 mA at room temperature for another 3.0 h. After completion of the reaction (TLC) and the usual work-up procedure, the crude reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate) to obtain **4a-*D***.

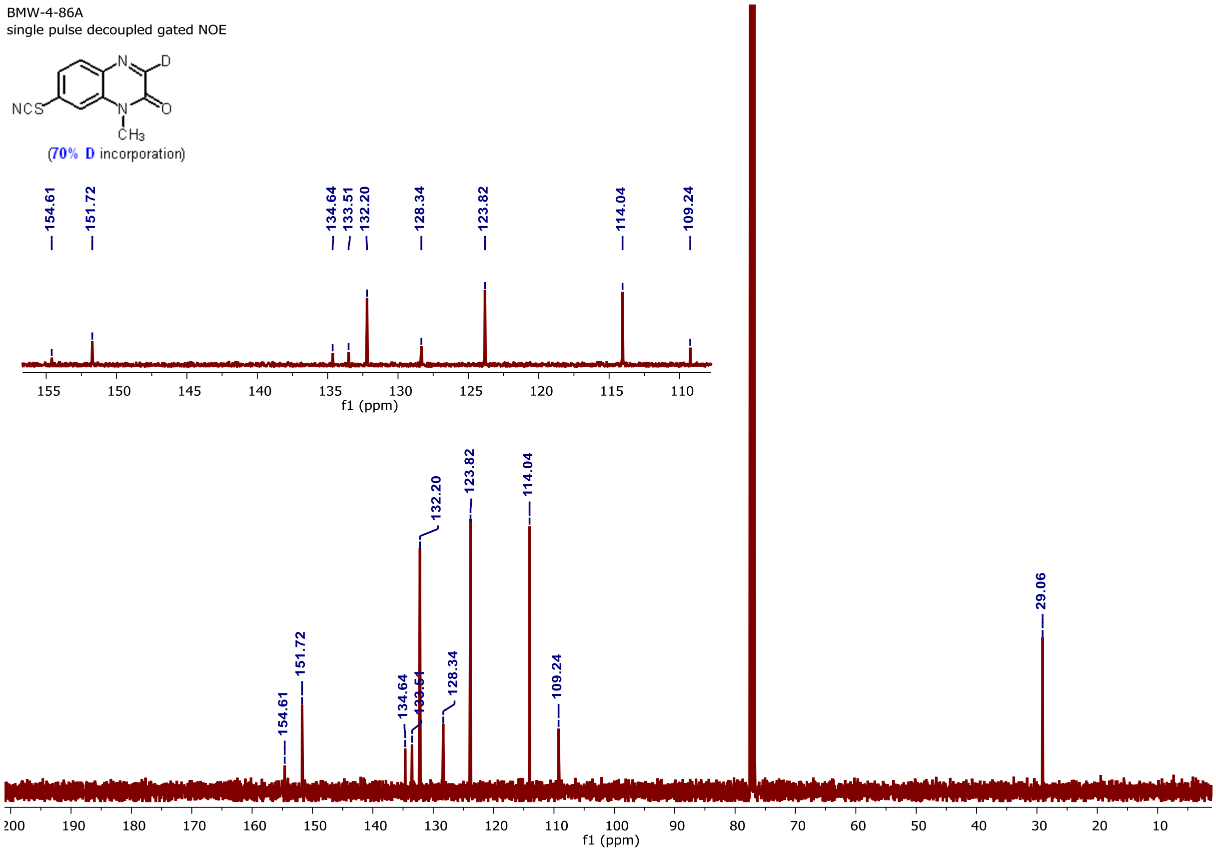


(**70% D** incorporation)

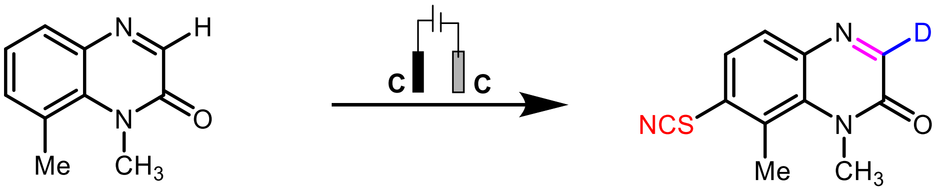
1-Methyl-7-thiocyanatoquinoxalin-2(1*H*)-one-3-*d* 4a-*D*: Prepared according to the general procedure discussed above: overall reaction time = 6.0 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (70 mg, 80%); 70% deuterium (D) incorporation, determined by ^1H NMR spectroscopy; mp 144–146 ˚C. NMR of mixtures; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 0.30 H), 7.93 (d, J = 8.4 Hz, 1 H), 7.43-7.46 (m, 2 H), 3.70 ppm (s, 3 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 154.6, 151.7, 134.6, 133.5, 132.2, 128.3, 123.8, 114.0, 109.2, 29.1 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{10}H_7DN_3OS$ $[M + H]^+$: 219.0451; found: 219.0460.

^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHZ, CDCl$_3$) NMR spectra of **4a-*D***:

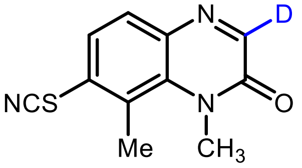




SI-12-39: Analytical and spectral data of **4l-*D***

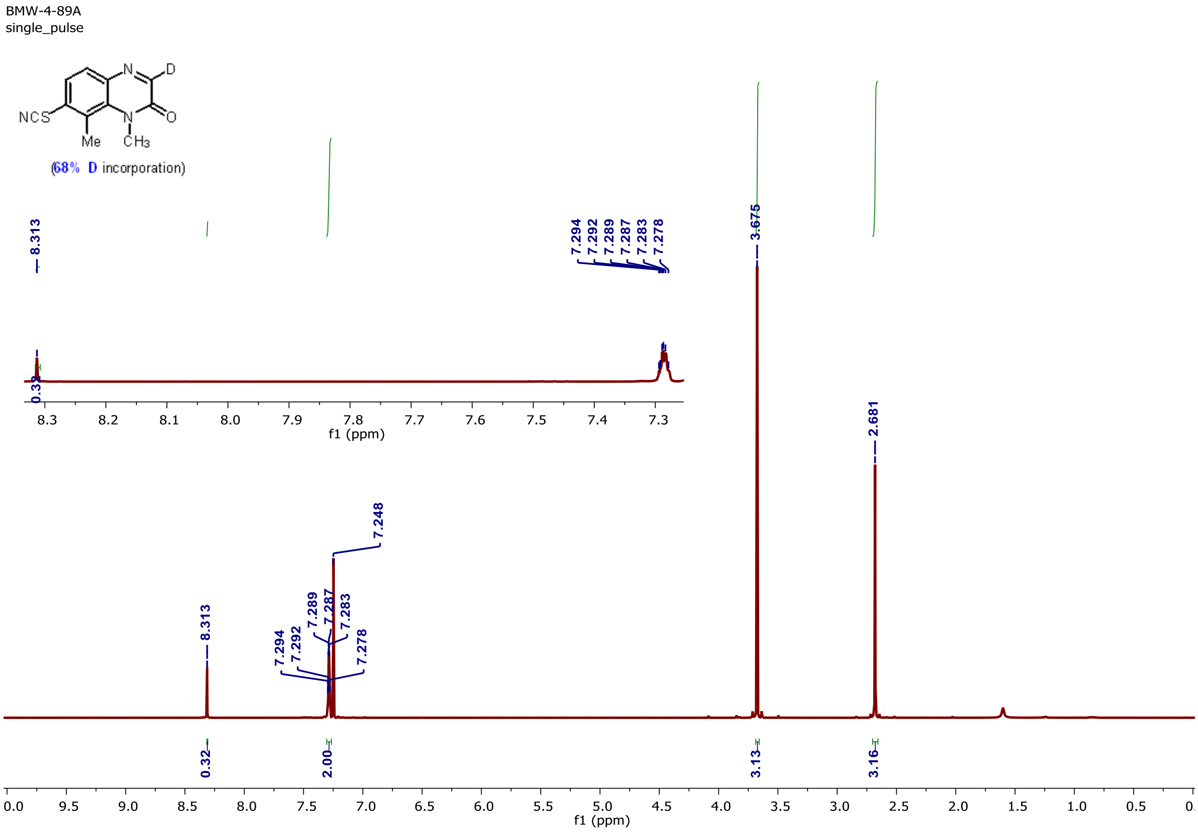


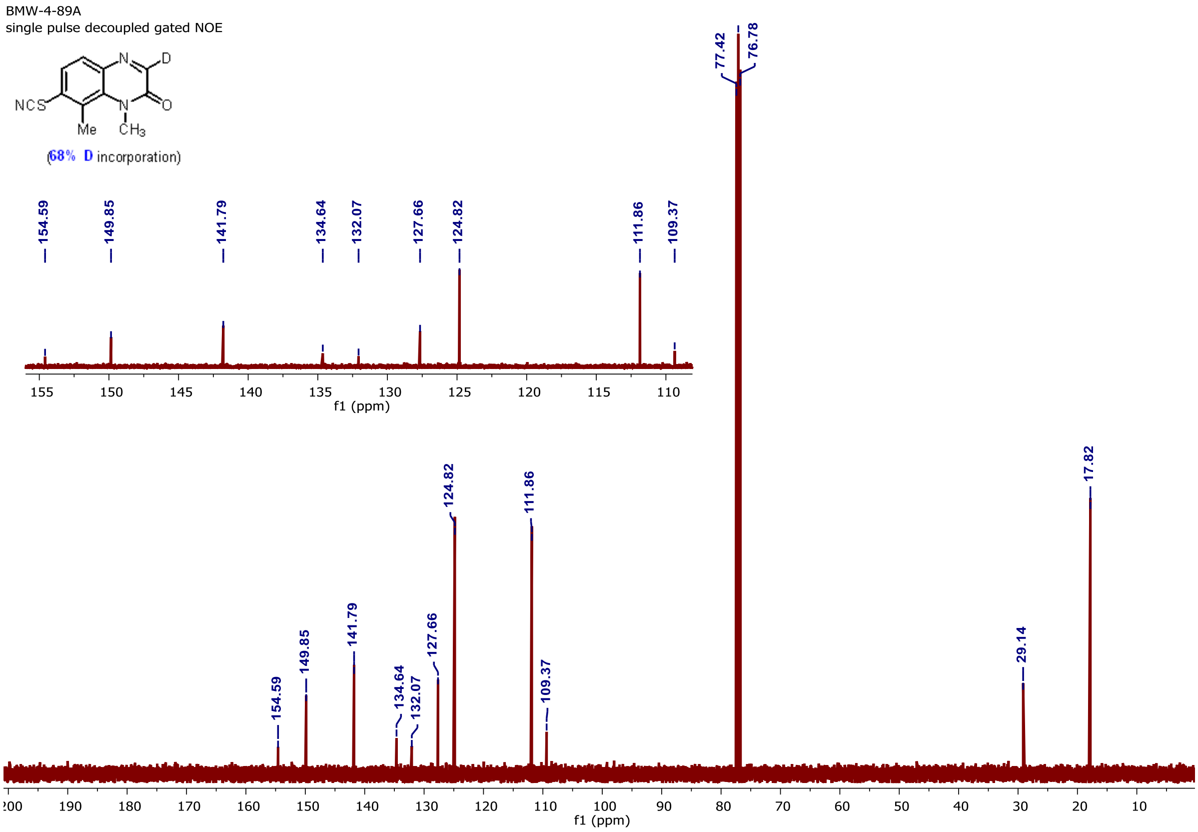
1,8-Dimethyl-7-thiocyanatoquinoxalin-2(1*H*)-one-3-*d* 4l-*D*: Prepared according to the general procedure discussed above: overall reaction time = 6.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (75 mg, 75%); 68% deuterium (D) incorporation, determined by ^{1}H NMR spectroscopy; mp 189–191 ˚C. NMR of mixtures; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 0.32 H), 7.28-7.29 (m, 2 H), 3.67 (s, 3 H), 2.68 ppm (s, 3 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 154.6, 149.8, 141.8, 134.6, 132.1, 127.7, 124.8, 111.9, 109.4, 29.1, 17.8 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{11}H_9DN_3OS$ [*M* + H]$^+$: 233.0607; found: 233.0611.



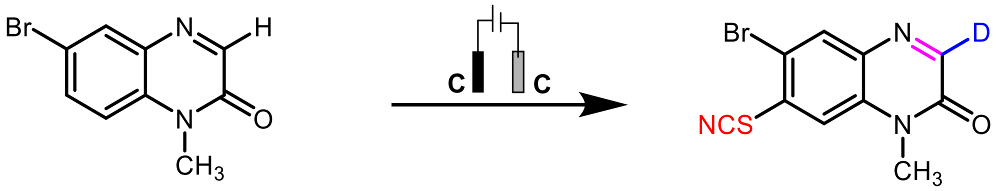
(**68% D** incorporation)

^1H (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4l-*D***:

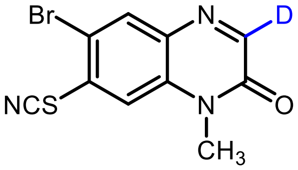




SI-12-40: Analytical and spectral data of **4n-*D***

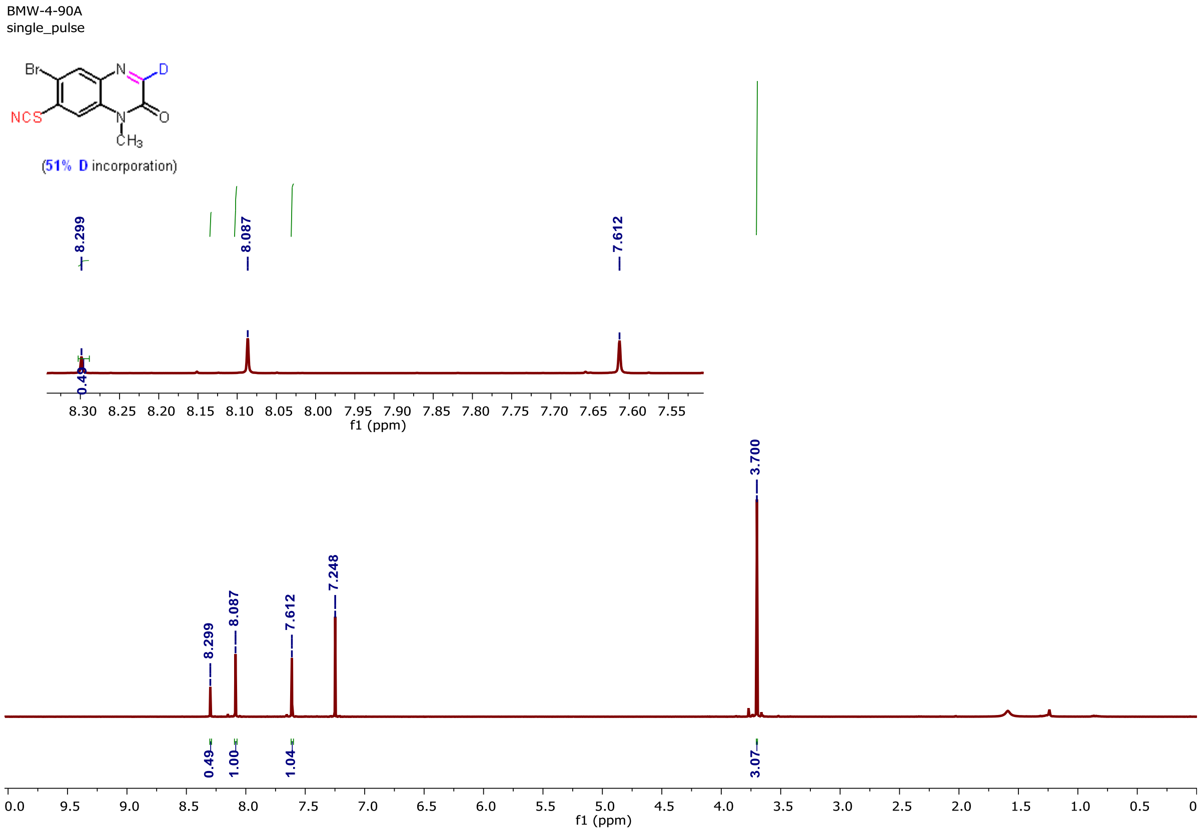


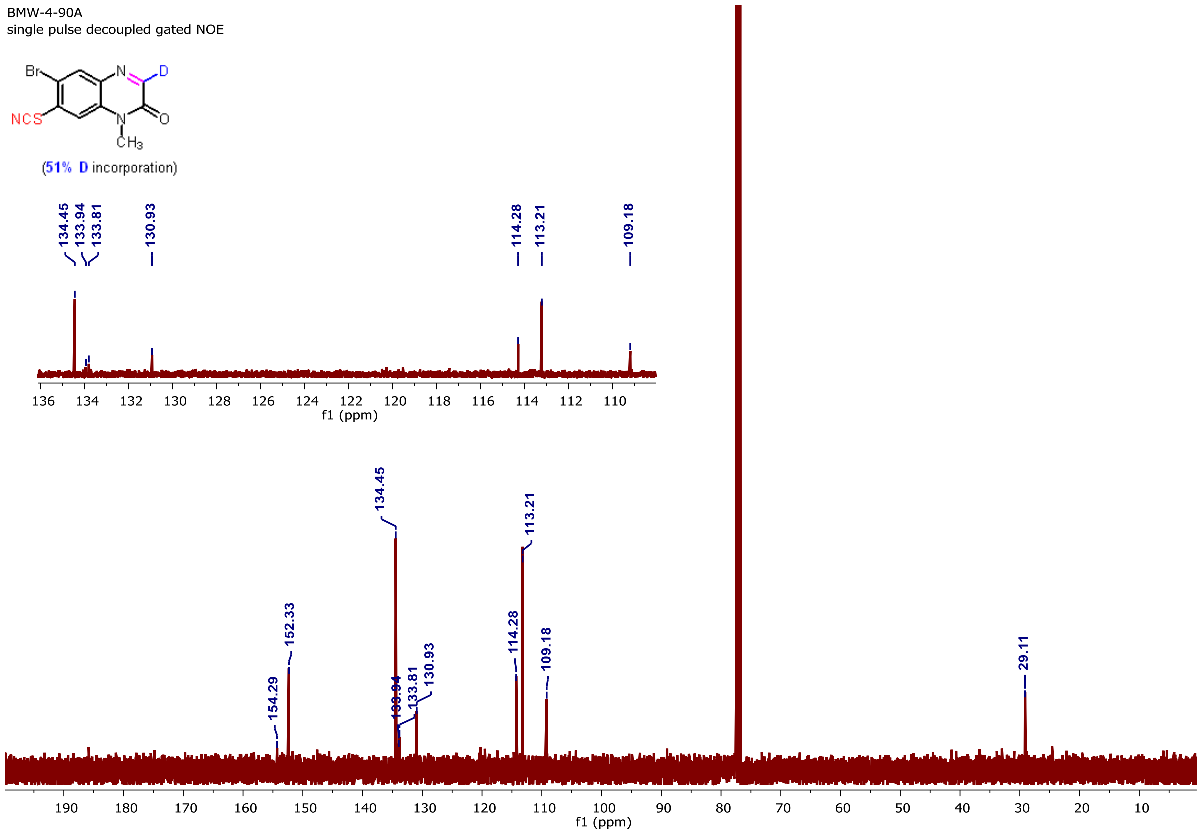
6-Bromo-1-methyl-7-thiocyanatoquinoxalin-2(1*H*)-one-3-*d* 4n-*D*: Prepared according to the general procedure discussed above: overall reaction time = 6.0 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); white solid (82 mg, 69%); 51% deuterium (D) incorporation, determined by ^{1}H NMR spectroscopy; mp 202–204 ˚C. NMR of mixtures; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* = 8.30 (s, 0.49 H), 8.09 (s, 1 H), 7.61 (s, 1 H), 3.70 ppm (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): *δ* = 154.3, 152.3, 134.4, 133.9, 133.8, 130.9, 114.3, 113.2, 109.2, 29.1 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{10}H_6DBrN_3OS$ [*M* + H]$^+$: 296.9556; found: 296.9561 and *m/z* calcd for $C_{10}H_6DBrN_3OS$ [*M* + H]$^+$: 298.9535; found: 298.9542.



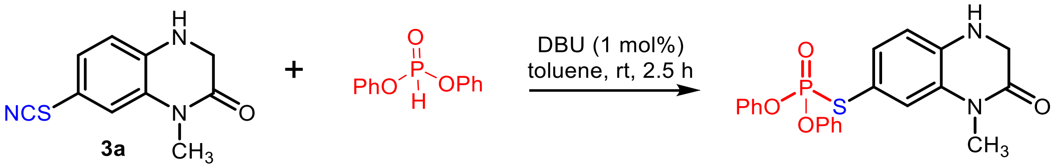
(**51% D** incorporation)

^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **4n-*D***:



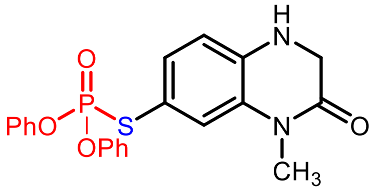


SI-12-41: Analytical and Spectral data of **6a**



3a (40 mg, 0.18 mmol, 1 equiv) was dissolved in toluene (2.0 mL), and 1 mol % of 1,8-diazabicyclo (5.4.0)undec-7-ene (DBU, 30 µL) and 1 equivalent of diphenyl phosphonate (35 µL) were subsequently added into it. The reaction mixture was stirred at room temperature for 2.5 h. After completion of the reaction (TLC), saturated ammonium chloride solution was added, and the product was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a short pad of silica gel column [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain **6a**. The reaction was carried out following the literature procedure[4].

***S*-(4-methyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-6-yl) diphenylphosphinothioate 6a:**



Prepared according to the general procedure discussed above: reaction time = 2.5 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (40%); colorless gum (30 mg, 38%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.45 (t, J = 8.0 Hz, 4 H), 7.24-7.30 (m, 6 H), 6.97 (dt, J = 8.0, 2.4 Hz, 1 H), 6.86 (t, J = 2.0 Hz, 1 H), 6.73 (d, J = 8.4 Hz, 1 H), 6.55 (s, 1 H), 3.87 (s, 2 H), 3.09 (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 165.0, 150.4 (d, $J_{C\text{-}P}$ = 8.1 Hz, 2 C), 138.9 (d, $J_{C\text{-}P}$ = 3.0 Hz, 1 C), 131.2 (d, $J_{C\text{-}P}$ = 6.1 Hz, 1 C), 130.7 (3 CH), 129.3 (d, $J_{C\text{-}P}$ = 3.0 Hz, 1 C), 126.3 (d, $J_{C\text{-}P}$ = 2.0 Hz, 1 C), 121.5 (d, $J_{C\text{-}P}$ = 4.0 Hz, 1 C), 120.7 (3 CH), 120.7 (3 CH), 114.6 (d, $J_{C\text{-}P}$ = 3.0 Hz, 1 C), 109.7 (d, $J_{C\text{-}P}$ = 8.1 Hz, 1 C), 46.5 (CH_2), 28.5 ppm; ^{31}P NMR (162 MHz, DMSO-d_6): δ = 13.8 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{21}H_{20}N_2O_4PS$ [*M* + H]$^+$: 427.0881; found: 427.0870.

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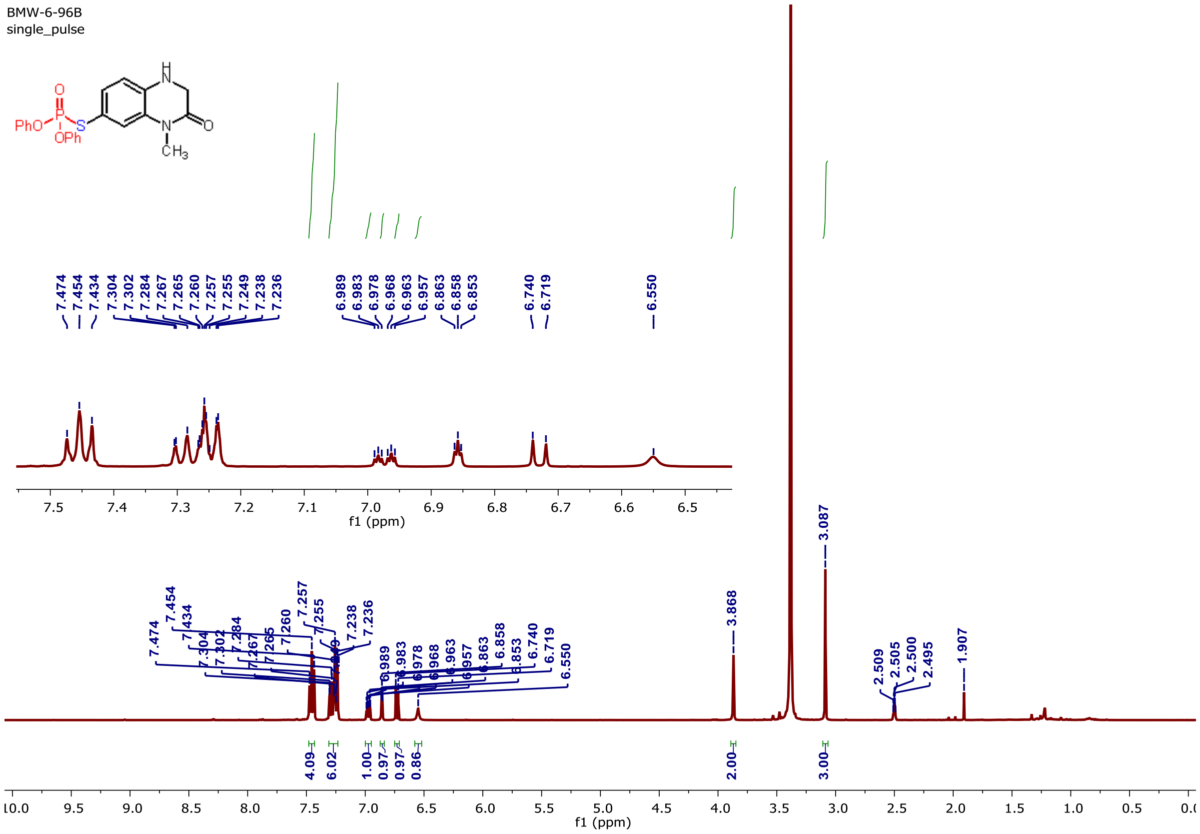
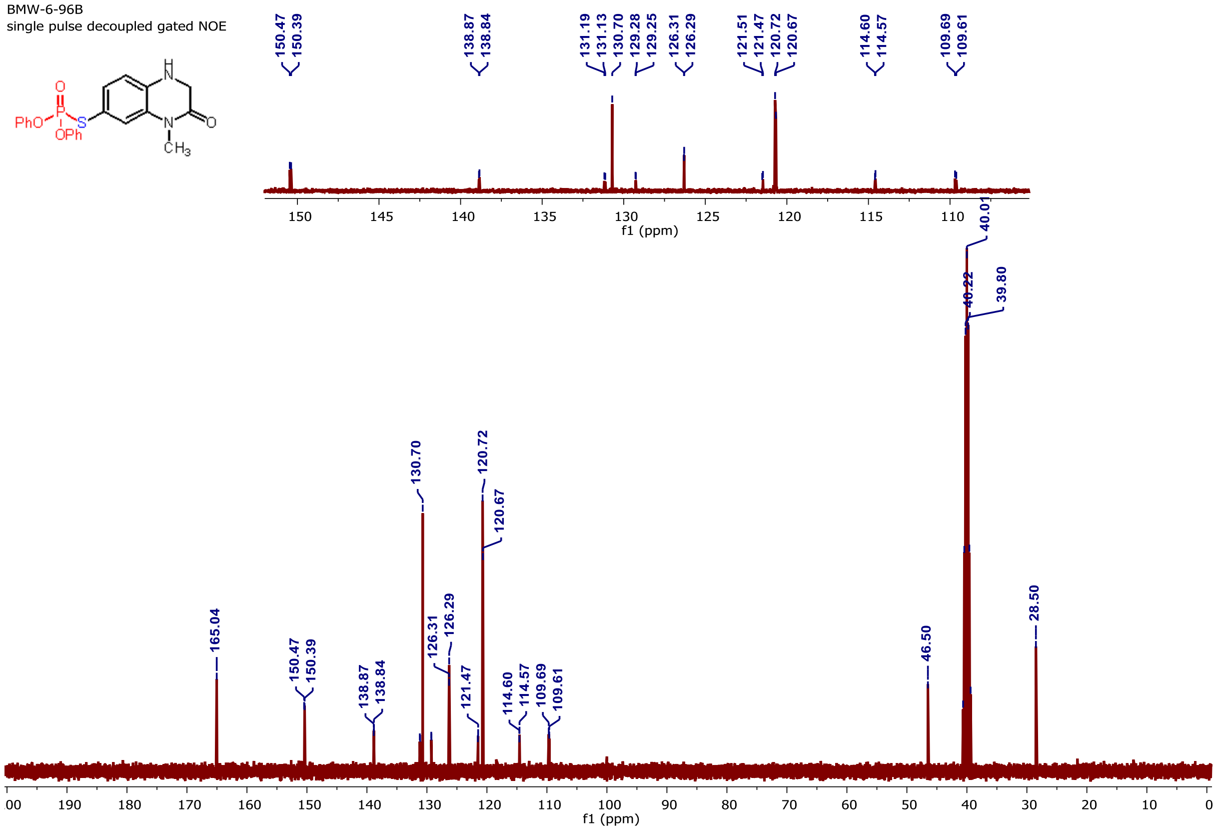
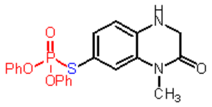
[4] P.-Y. Renard, H. Schwebel, P. Vayron, L. Josien, A. Valleix and C. Mioskowski, *Chem. Eur. J.,* 2002, **8**, 2910-2916.

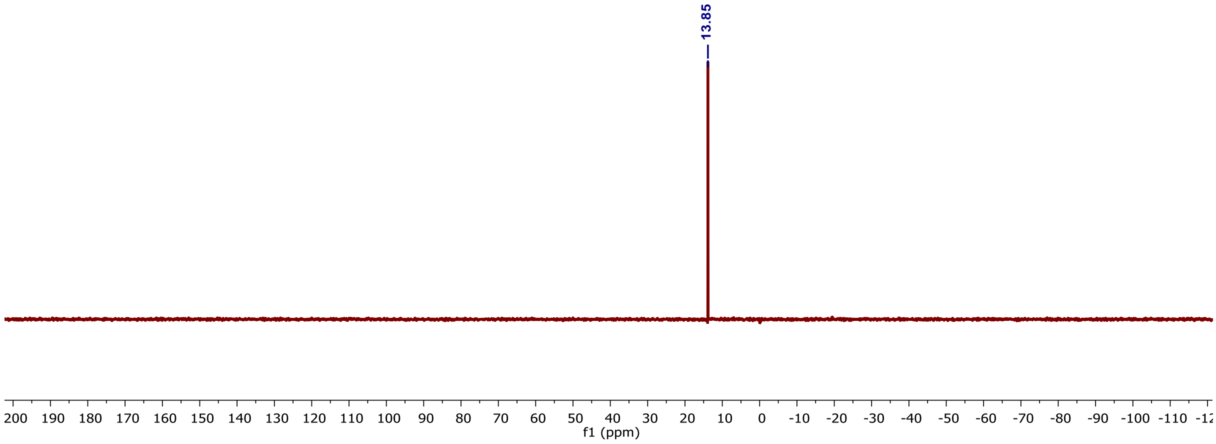
^{1}H (400 MHz, DMSO-d_6), ^{13}C{^{1}H} (101 MHz, DMSO-d_6), and ^{31}P NMR (162 MHz, DMSO-d_6) NMR spectra of **6a**:



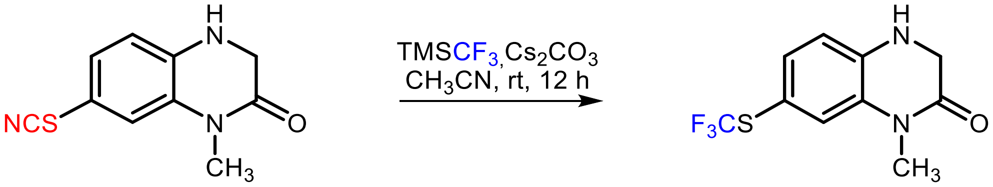


BMW-6-96B
single pulse decoupled gated NOE



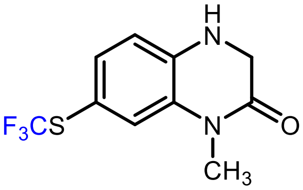


SI-12-42: Analytical and spectral data of **6b**



3a (60 mg, 0.27 mmol, 1 equiv) was dissolved in dry CH_3CN (2.0 mL), and cesium carbonate Cs_2CO_3 (178 mg, 2 equiv) and trifluoromethyltrimethylsilane $TMSCF_3$ (60 µL, 1.2 equiv) were sequentially added into it. The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (TLC), saturated ammonium chloride solution was added, and the product was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a short pad of silica gel column [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain **6b**. The reaction was carried out following the literature procedure[5].

1-Methyl-7-((trifluoromethyl)thio)-3,4-dihydroquinoxalin-2(1*H*)-one 6b: Prepared according to the general procedure discussed above: reaction time = 12 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); grey solid (30 mg, 41%); mp 108–110 ˚C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.20 (dd, J = 8.0, 1.6 Hz, 1 H), 7.16 (d, J = 2.0 Hz, 1 H), 6.67 (d, J = 8.0 Hz, 1 H), 4.05 (s, 2 H), 3.37 (s, 3 H); –NH peak in ^{1}H NMR is absent; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 164.8, 138.1, 132.6, 129.4, 122.9, 114.3, 112.9 (m, 1 C), 47.1, 28.9 ppm; One carbon peak is missing probably due to C-F coupling; ^{19}F NMR (376 MHz, CDCl$_3$): δ = –44.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{10}H_{10}N_2F_3OS$ [*M* + H]$^+$: 263.0466; found: 263.0467.



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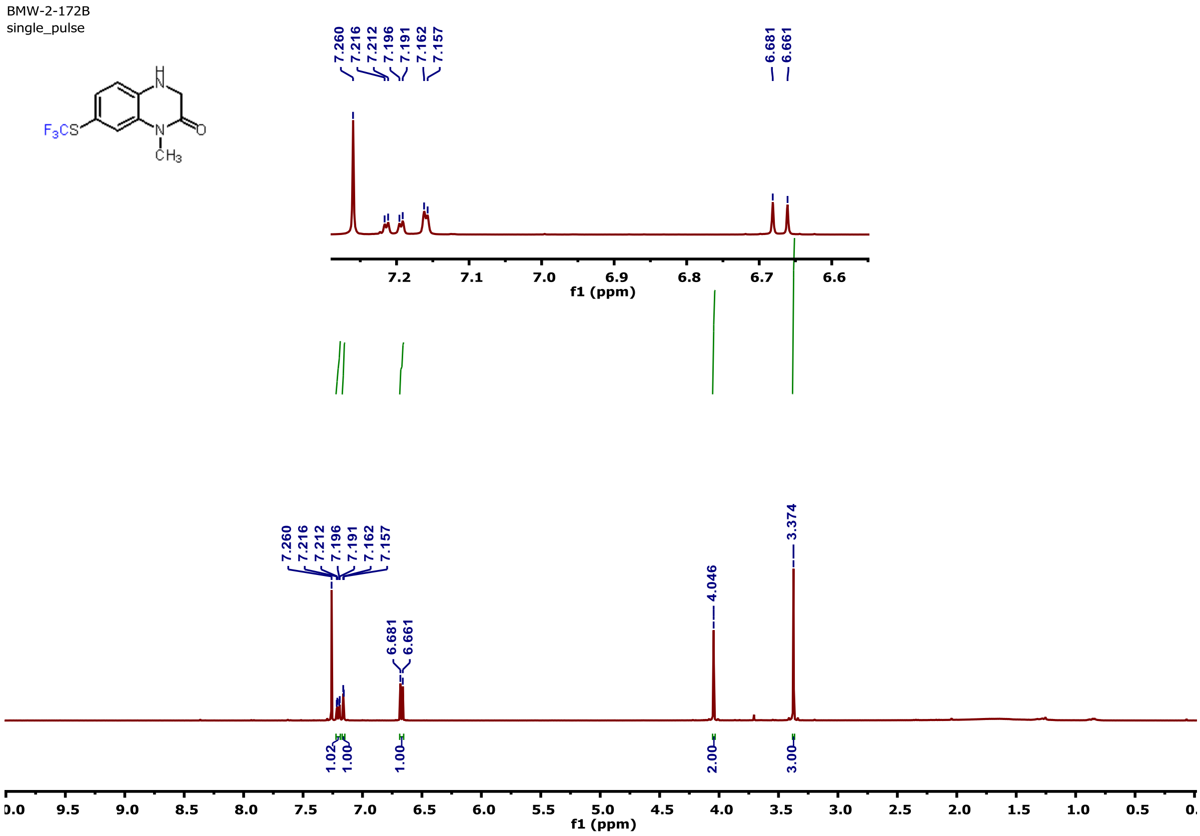
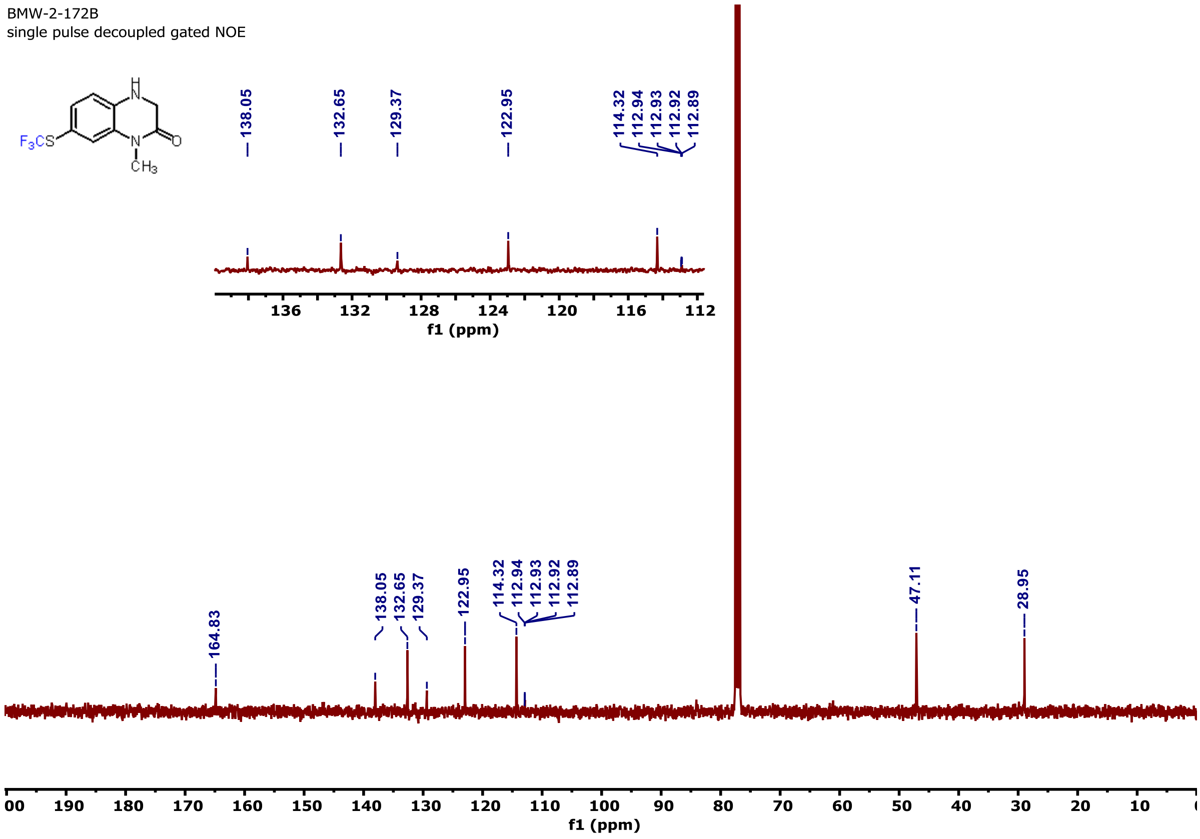
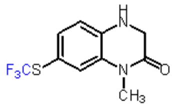
[5] K. Jouvin, C. Matheis and L. J. Goossen, *Chem. Eur. J.,* 2015, **21**, 14324–14327.

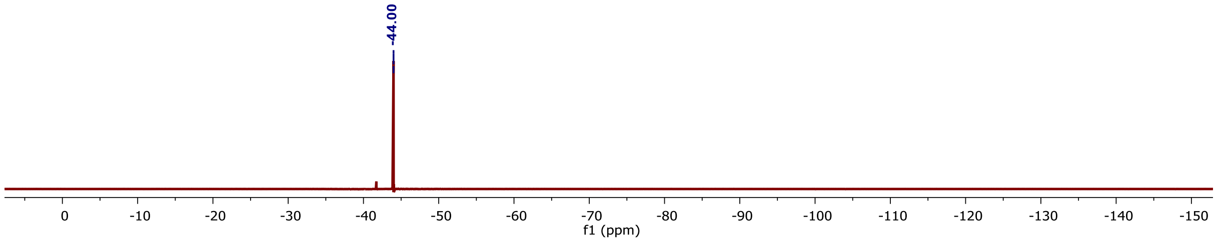
^{1}H (400 MHz, CDCl$_3$), ^{13}C{^{1}H} (101 MHz, CDCl$_3$), and ^{19}F (376 MHz, CDCl$_3$) NMR spectra of **6b**:





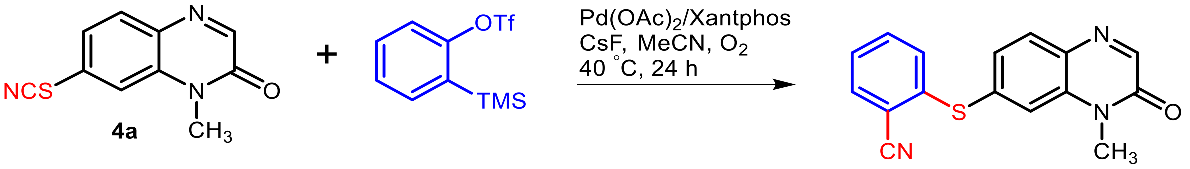
RM-6-69B
single pulse decoupled gated NOE



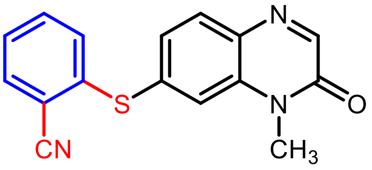


SI-12-43: Analytical and spectral data of **6c**

To Pd(OAc)$_2$ (3 mg, 0.013 mmol, 10 mol%), Xantphos (15 mg, 0.026 mmol, 20 mol%), and CsF (66 mg, 0.42 mmol, 3.3 equiv) were added acetonitrile (3 mL) saturated with oxygen and pre-stirred for 2-3 min. After that corresponding thiocyanate compound **4a** (30 mg, 0.13 mmol, 1 equiv) was added into it and stirred for 2 min. Then, aryne precursor 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (46 µL, 0.19 mmol, 1.4 equiv) was added and the reaction mixture was heated at 40 ˚C for 24 hours. After completion of the reaction (TLC), solvent was removed under reduce pressure and the crude residue was passed through a short pad of silica gel column [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain **6c**. The reaction was carried out following the literature procedure[6].



2-((4-Methyl-3-oxo-3,4-dihydroquinoxalin-6-yl)thio)benzonitrile 6c: Prepared according to the general procedure discussed above: reaction time = 24 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (30%); yellow solid (25 mg, 61%); mp 135–137 ˚C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.28 (s, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.75 (dd, J = 7.6, 1.2 Hz, 1 H), 7.57 (td, J = 8.0, 1.6 Hz, 1 H), 7.43-7.51 (m, 2 H), 7.36 (d, J = 1.6 Hz, 1 H), 7.19 (dd, J = 8.4, 2.0 Hz, 1 H), 3.62 ppm (s, 3 H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 154.9, 150.6, 138.4, 138.3, 134.4, 134.1, 133.6, 133.5, 132.8, 131.5, 128.8, 125.9, 116.8, 116.2, 115.9, 28.9 ppm; HRMS (ESI-QTOF): m/z calcd for C$_{16}$H$_{12}$N$_3$OS [M + H]$^+$: 294.0701; found: 294.0687.



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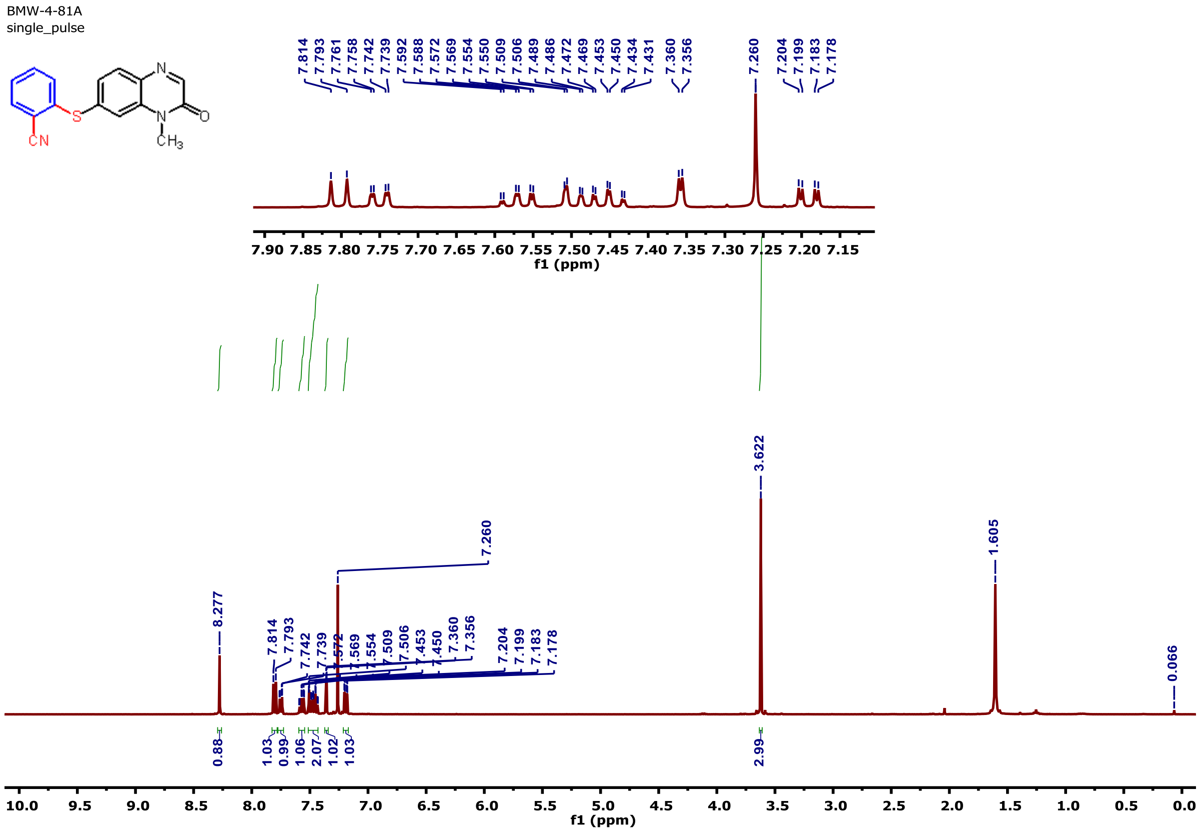
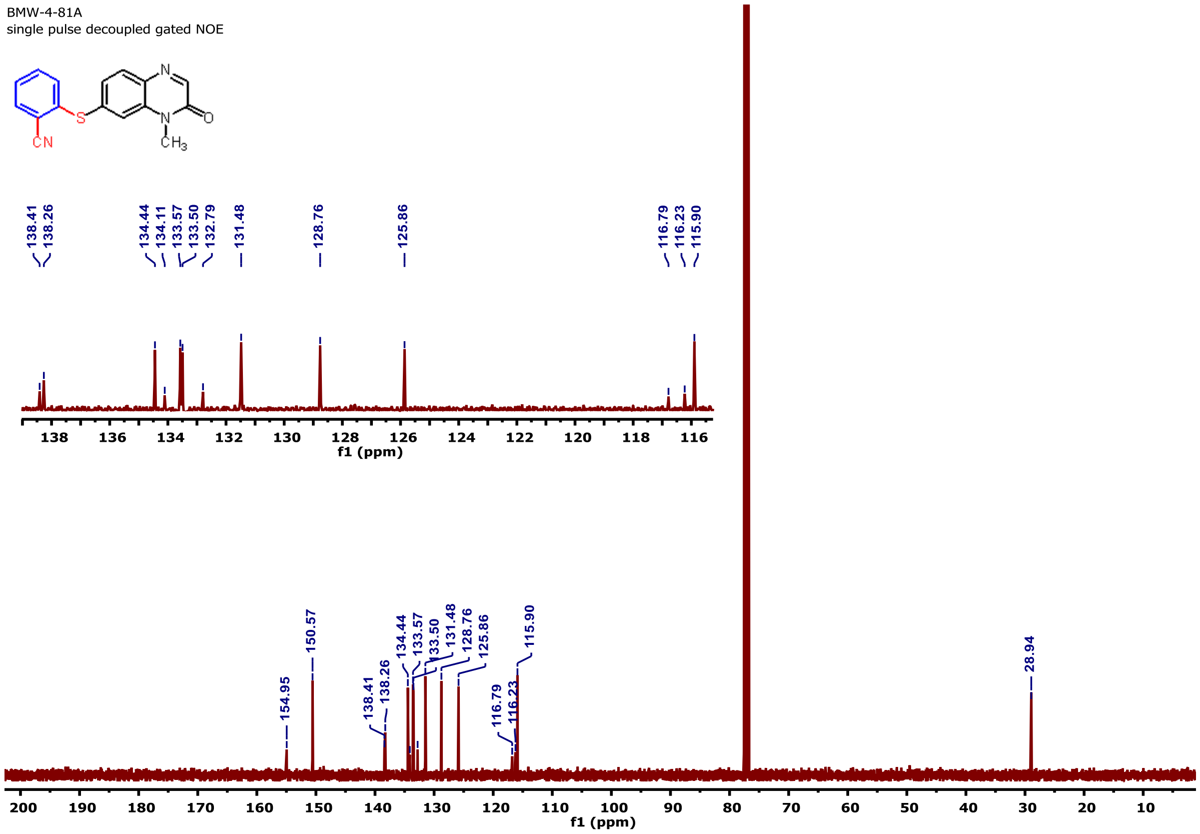
[6] M. Pawliczek, L. K. B. Garve and D. B. Werz, *Org. Lett.,* 2015, **17**, 1716–1719.

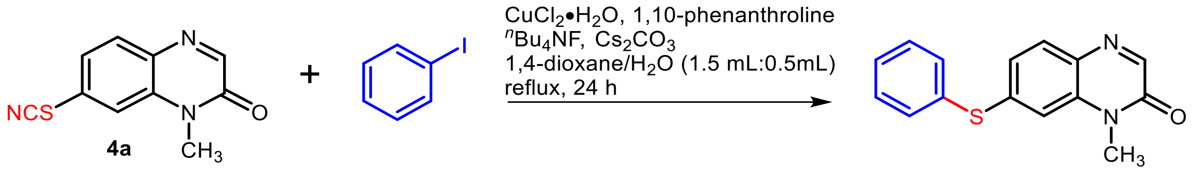
^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **6c**:

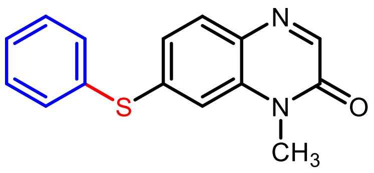




SI-12-44: Analytical and spectral data of **6d**

4a (44 mg, 0.2 mmol, 1 equiv) was dissolved in a mixture of 1,4-dioxane/H_2O (1.5 mL:0.5 mL) solvents, and iodobenzene (22 µL, 0.2 mmol, 1.0 mmol), $CuCl_2•H_2O$ (3 mg, 0.02 mmol, 10 mol%), 1,10-phenanthroline (4 mg, 0.02 mmol, 10 mol%), Cs_2CO_3 (130 mg, 0.4 mmol, 2 equiv), and $^{n}Bu_4NF$ (5 mg, 0.02 mmol, 10 mol%) were sequentially added into it, and the reaction mixture was refluxed for 24 h. After completion (TLC) of the reaction, the solvent (1,4-dioxane) was removed under reduce pressure and was diluted with DCM. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a silica gel column [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain the desired **6d**. The reaction was carried out following the literature procedure[7].





1-Methyl-7-(phenylthio)quinoxalin-2(1*H*)-one 6d: Prepared according to the general procedure discussed above: reaction time = 24 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); yellow solid (32 mg, 61%); mp 143–145 ˚C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1 H), 7.72 (d, J = 8.4 Hz, 1 H), 7.51-7.54 (m, 2 H), 7.40-7.46 (m, 3 H), 7.10-7.13 (m, 2 H), 3.54 ppm (s, 3 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 155.1, 149.3, 142.9, 133.9 (2 CH), 132.3, 131.8, 130.9, 129.9 (2 CH), 129.1, 123.6, 112.6, 28.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{15}H_{13}N_2OS$ $[M + H]^+$: 269.0748; found: 269.0742.

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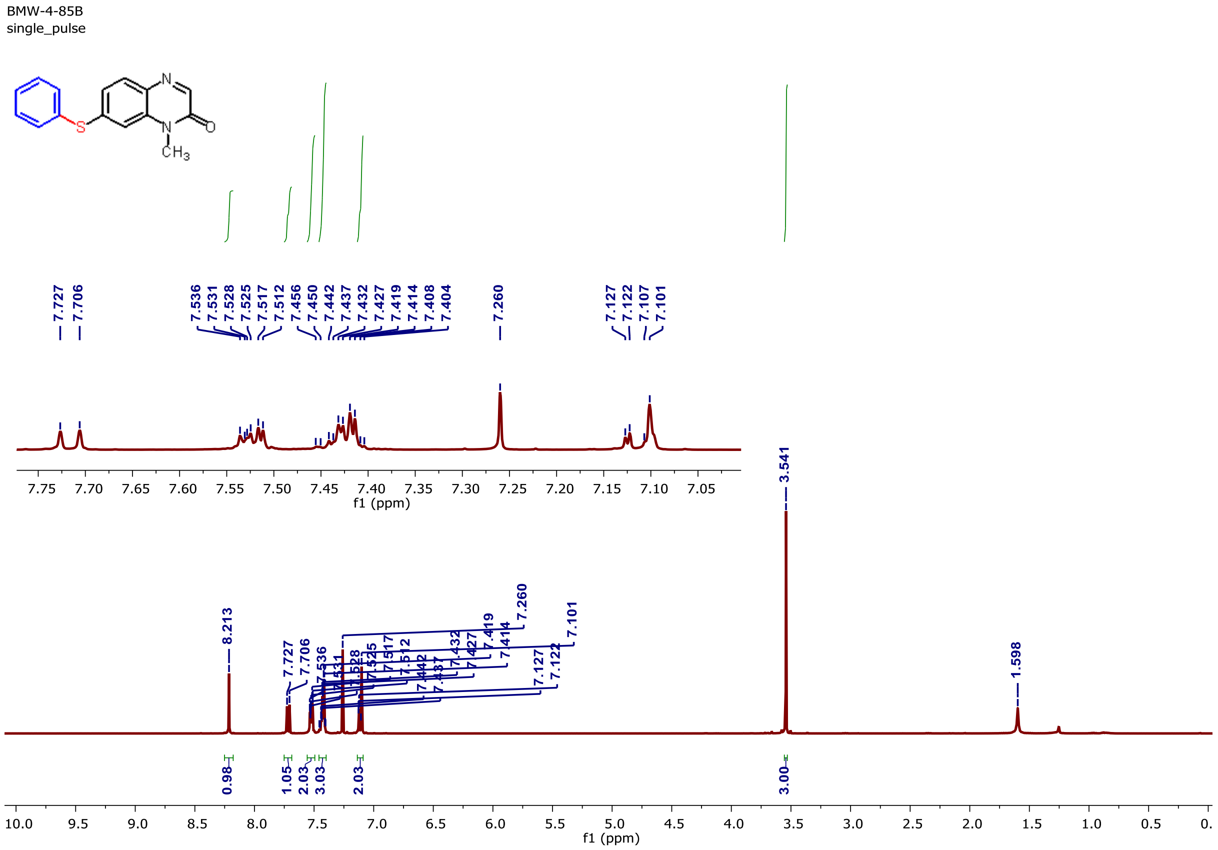
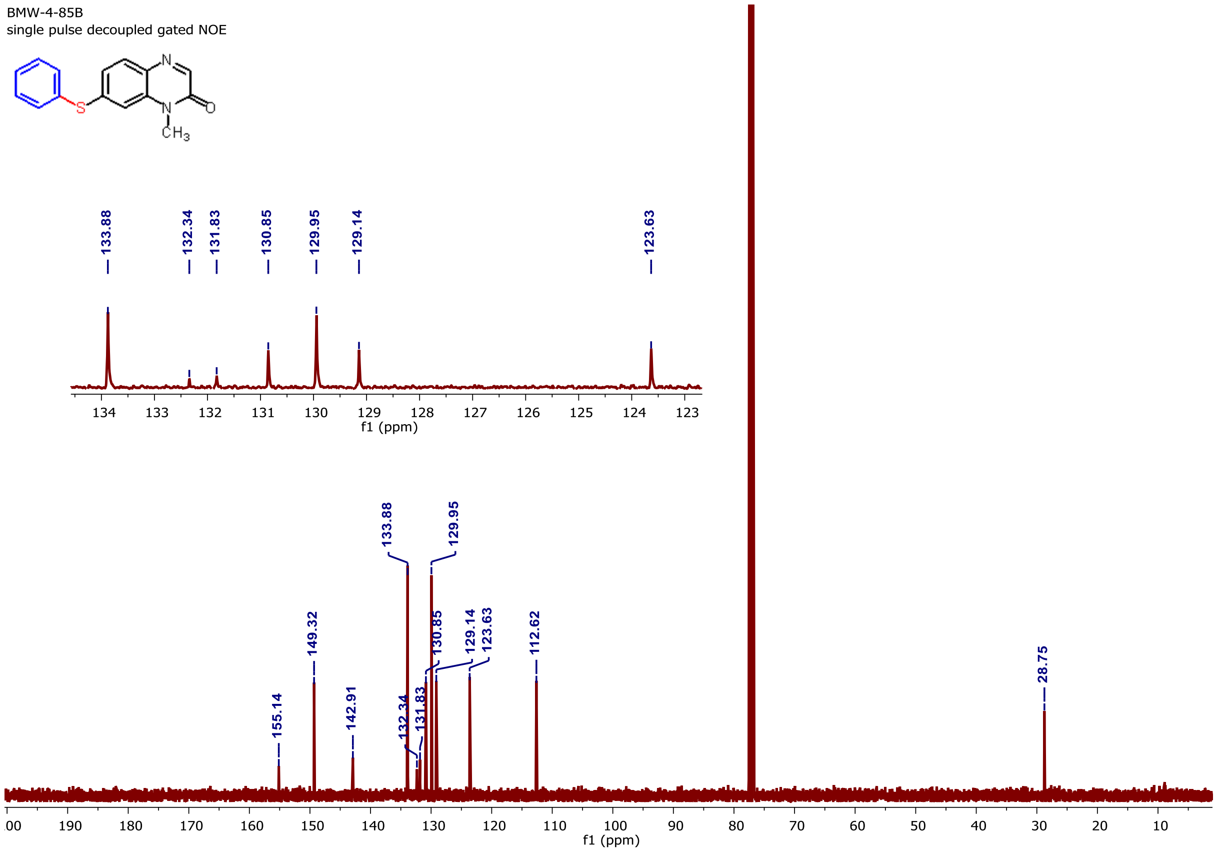
[7] F. Ke, Y. Qu, Z. Jiang, Z. Li, D. Wu and X. Zhou, *Org. Lett.,* 2011, **13**, 454–457.

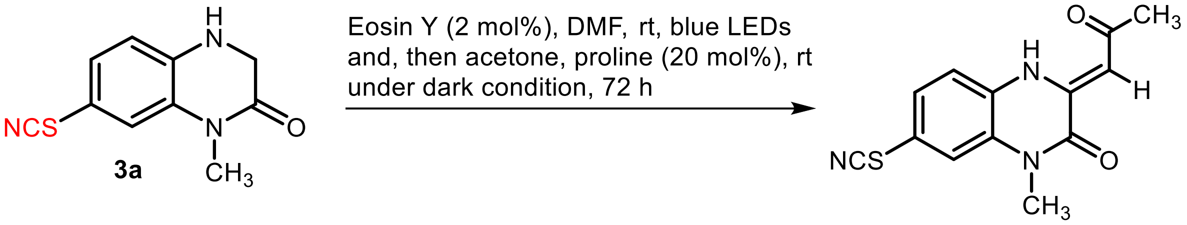
^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **6d**:



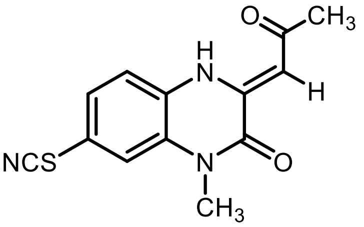


SI-12-45: Analytical and spectral data of **6e**

Compound **3a** (60 mg, 0.27 mmol, 1 equiv) was dissolved in DMF solvent (2 mL) in a two-neck round bottle flask and Eosin Y (4 mg, 2 mol%) was added into it, and the reaction mixture was irradiated under blue LEDs. After complete consumption of **3a**, acetone (1 mL) and proline (7 mg, 20 mol%) were subsequently added and stirred under dark conditions for 72 h. After completion of the reaction (TLC), a saturated ammonium chloride solution was added, and the product was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a short pad of silica gel column [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain **6e.** The reaction was carried out following the literature procedure[8].



(*Z*)-1-methyl-3-(2-oxopropylidene)-7-thiocyanato-3,4-dihydroquinoxalin-2(1*H*)-one 6e:



Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (20%); yellow solid (41 mg, 55%); mp 144–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.19 (s, 1 H), 7.32-7.34 (m, 2 H), 7.14 (dd, J = 7.6, 0.8 Hz, 1 H), 6.32 (s, 1 H), 3.63 (s, 3 H), 2.29 ppm (s, 3 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 199.9, 156.0, 141.7, 129.4, 127.4, 127.2, 117.5, 117.4, 117.3, 110.6, 96.4, 30.4, 30.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{13}H_{12}N_3O_2S$ $[M + H]^+$: 274.0650; found: 274.0653.

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[8] J. Rostoll-Berenguer, G. Blay, M. C. Muñoz, J. R. Pedro and C. Vila, *Org. Lett.,* 2019, **21**, 6011-6015.

^{1}H (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} (101 MHz, CDCl$_3$) NMR spectra of **6e:**