Supplementary Information

Persulfate-Promoted Oxidative C−N Bond Coupling of Quinoxalinones and *NH*-Sulfoximines

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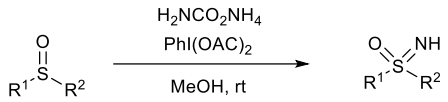
I. Substrate Preparation

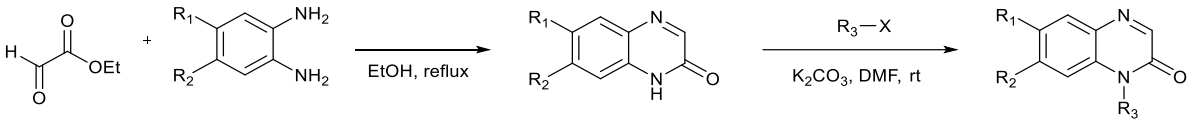
General Procedure for the Preparation of *NH*-Sulfoximine



The sulfoxide (4.0 mmol, 1.0 equiv.), $PhI(OAc)_2$ (3.87 g, 12.0 mmol, 3.0 equiv.), ammonium carbamate ($H_2NCO_2NH_4$,1.25 g, 16.0 mmol, 4.0 equiv.) and MeOH (8.0 mL) were added to a 50 mL round bottom flask equipped with a magnetic stir bar. The reaction was stirred for 30 min at room temperature in an open flask. Upon completion, a solvent was removed *in vacuo* and the crude residue was purified by flash silica gel (SiO_2) column chromatography.

(Reference: M. Zenzola, R. Doran, L. Degennaro, R. Luisi and J. A. Bull, *Angew. Chem. Int. Ed.*, 2016, **55**, 7203.)

General Procedure for the Preparation of Quinoxalinone



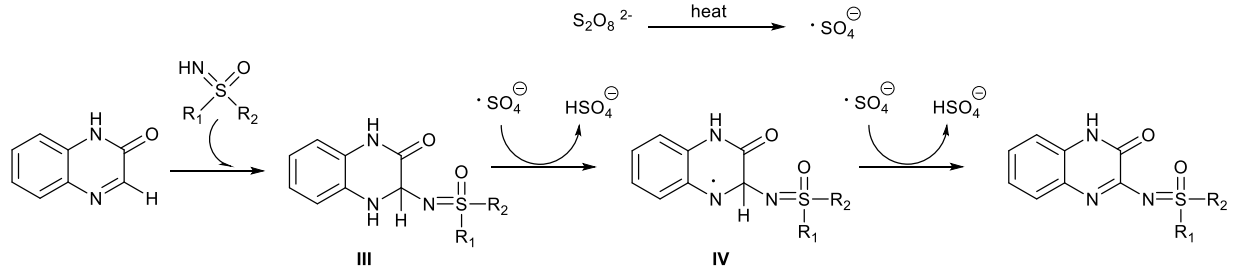
Ethyl 2- oxoacetate (1.1 equiv.) was added to a suspension of *o*-arylenediamine (4 mmol, 1 equiv.) in ethanol (1 mol/L). The reaction mixture was stirred and heated at reflux in an oil bath for 1 h, then at room temperature for 16 h. Upon completion (as monitored by TLC), the precipitate was filtered and washed with ethanol, then dried to give quinoxalinone. For alkylation, the corresponding halogenoalkane (1.6 equiv.) was added to a suspension of quinoxalinone (1 equiv.) and potassium carbonate (1.2 equiv.) in DMF (16 mL). The mixture was stirred at room temperature for 16 h. Upon completion (as monitored by TLC), the reaction mixture was washed with saturated solution of ammonium chloride (5 mL), ethyl acetate (10 mL) and water (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel (SiO_2) to afford the alkylated quinoxalinone.

Quinoxalinones **1a**−**1j** are known compounds and their ^1H NMR data agreed with the literature.

(Reference: A. Carrër, J.-D. Brion, S. Messaoudi and M. Alami, *Org. Lett*., 2013, **15**, 5606.)

II. Alternative Mechanism

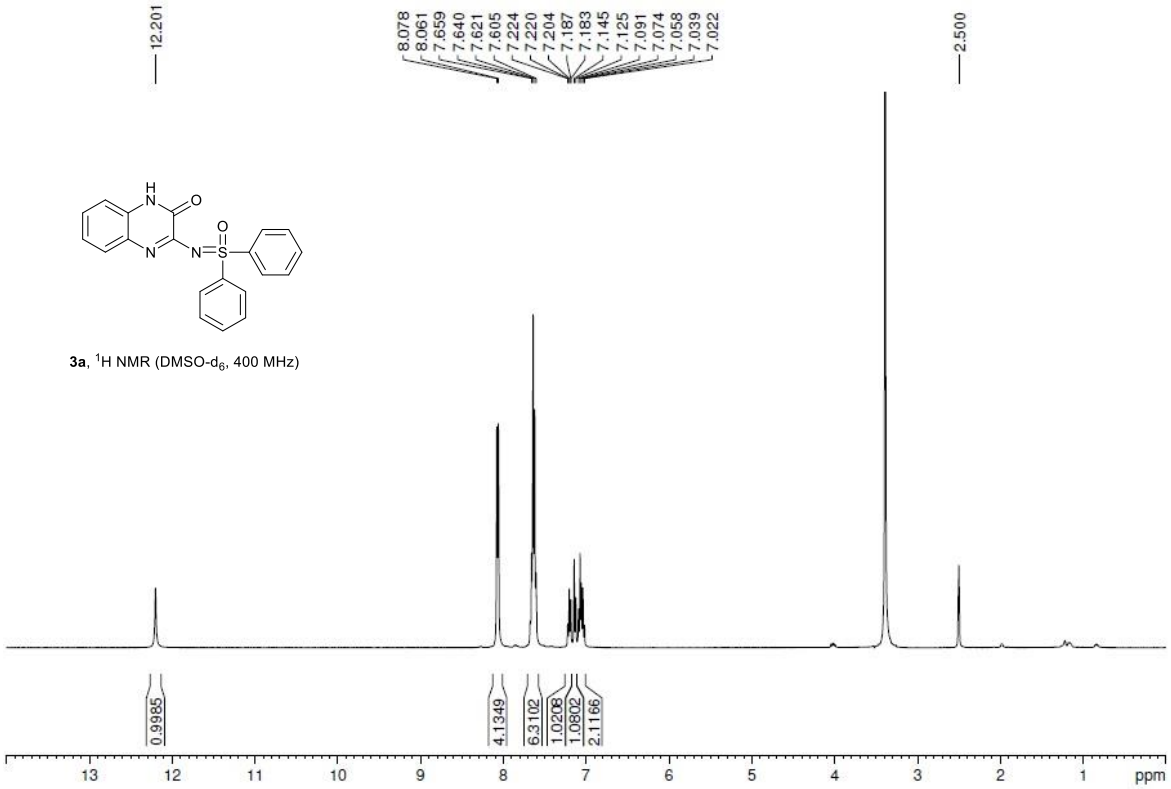
Alternative mechanism for this radical process is shown below.



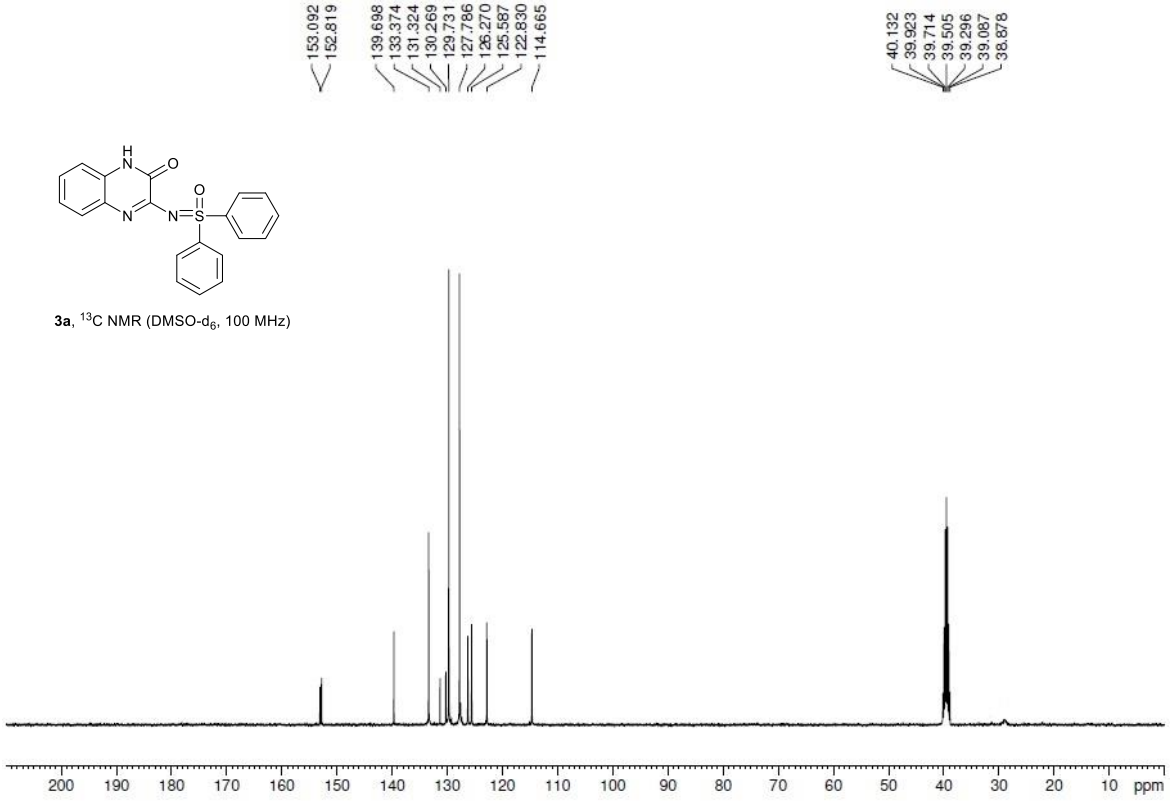
First, *NH*-sulfoximine could attack on *C3* position of quinoxalinone leading a formation of intermediate **III**. Then, a sequential hydrogen atom abstraction by sulfate radical anion ($SO_4^{-\bullet}$), which is generated by a homolytic cleavage of persulfate ($S_2O_8^{2-}$) anion, would result in a radical intermediate **IV** and eventually the corresponding sulfoximidoyl quinoxalinone product.

III. ^{1}H and ^{13}C NMR Spectra of Compounds 3a−3m and 4a−4j

3-((Oxodiphenyl-λ^{6}-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3a)

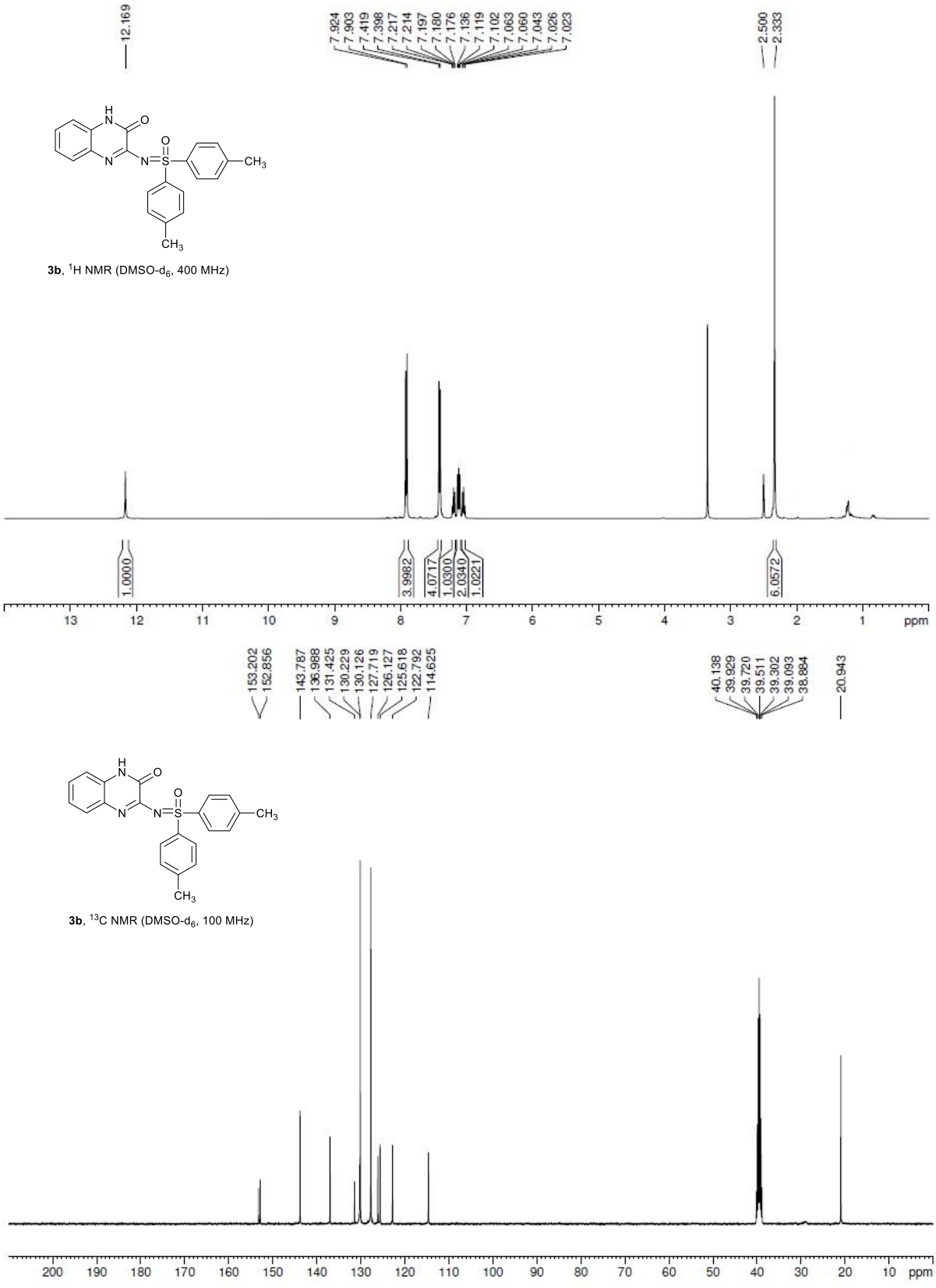


3a, ^{1}H NMR (DMSO-d_6, 400 MHz)



3a, ^{13}C NMR (DMSO-d_6, 100 MHz)

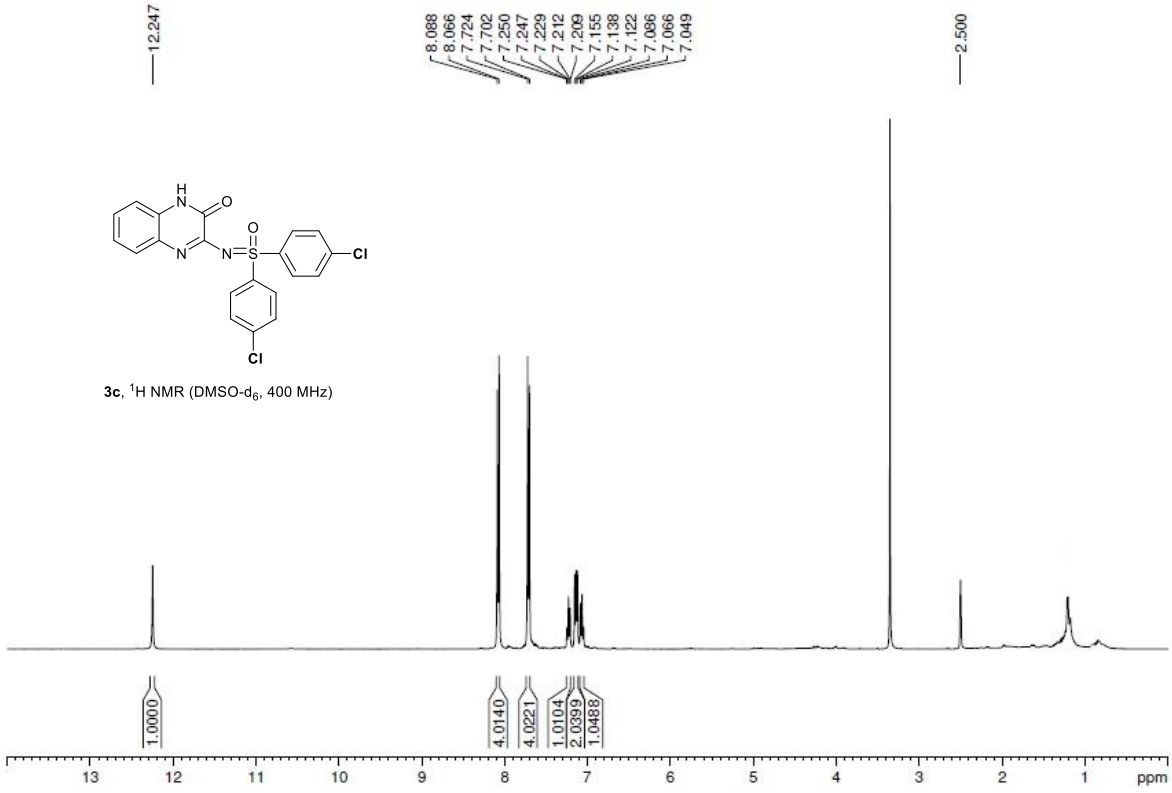
3-((Oxodi-*p*-tolyl-λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3b)



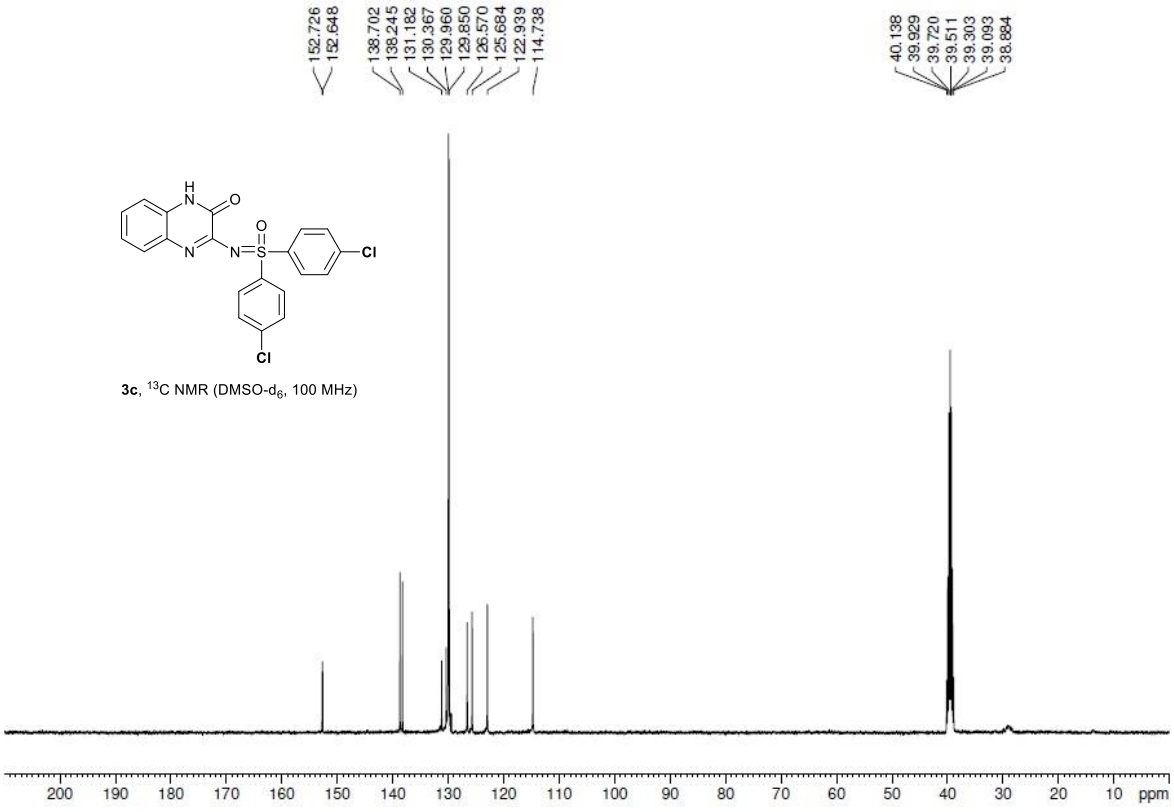
3b, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

3b, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-((Bis(4-chlorophenyl)(oxo)-λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3c)

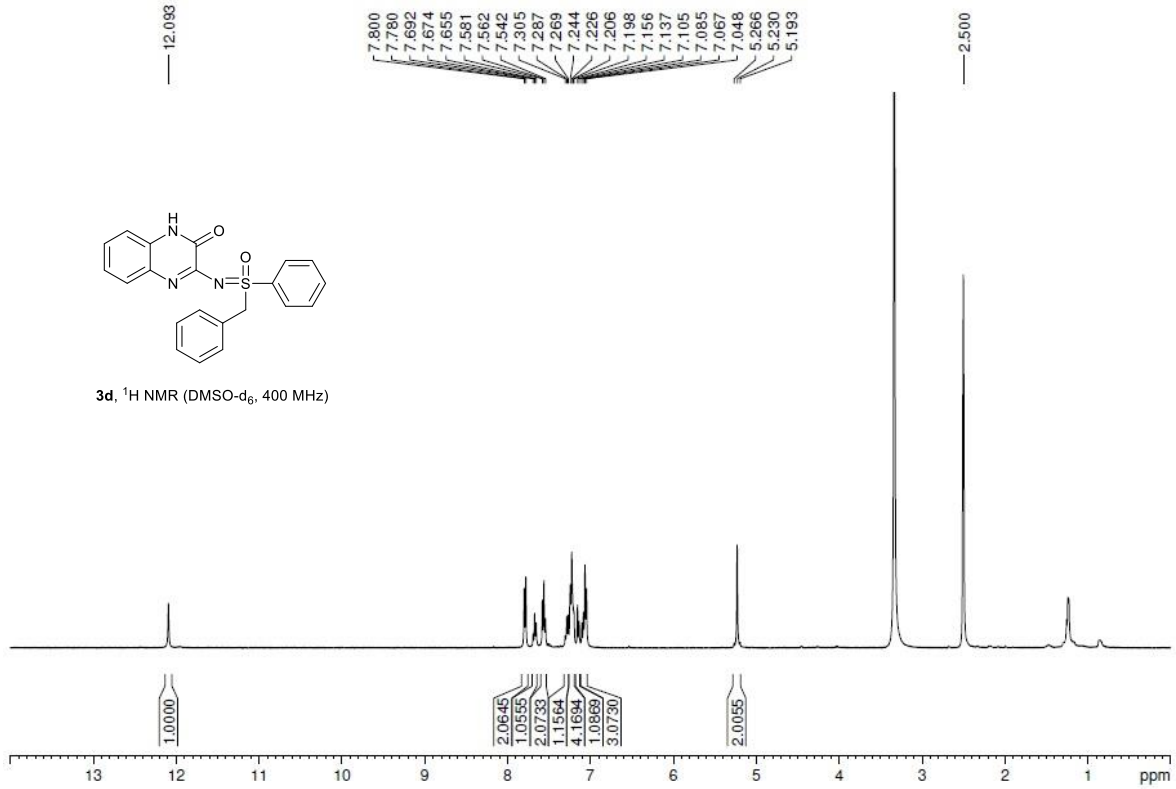


3c, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

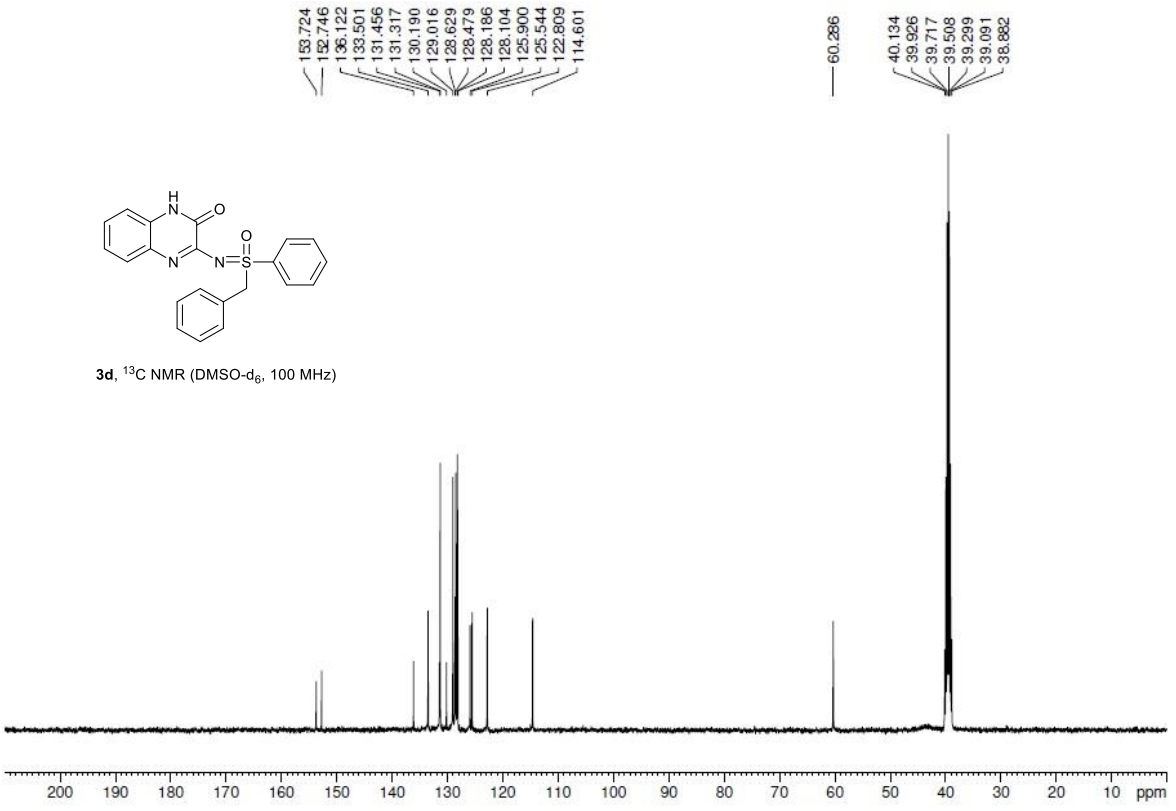


3c, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-((Benzyl(oxo)(phenyl)- λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3d)

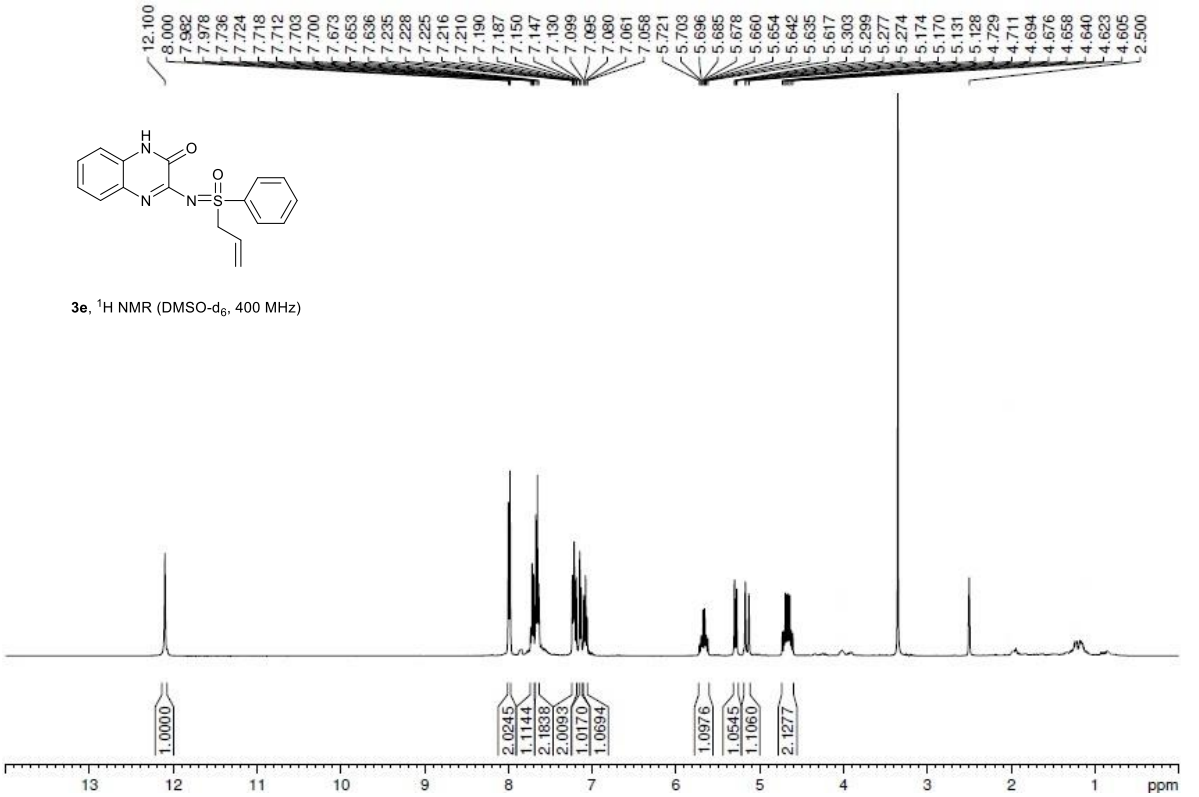


3d, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

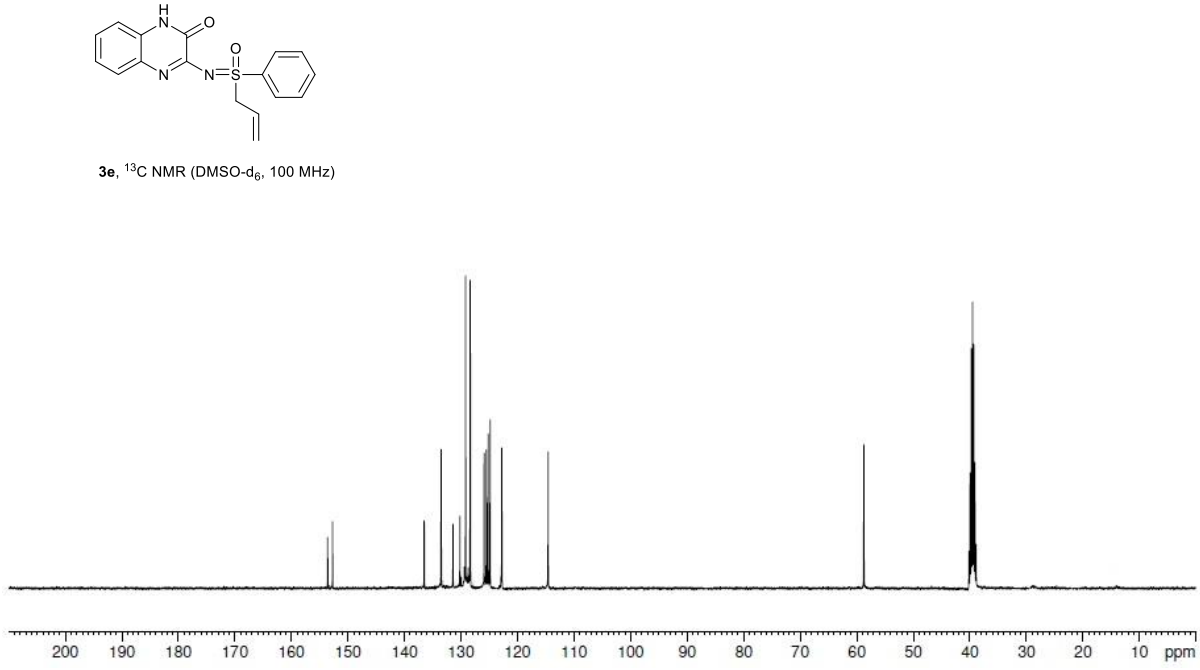


3d, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-((Allyl(oxo)(phenyl)- λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3e)

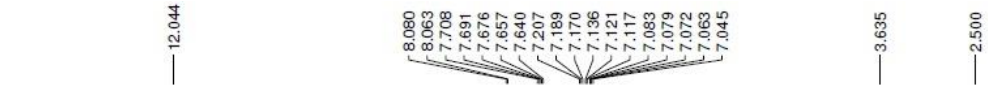


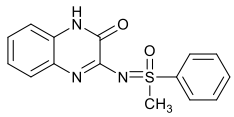
3e, ^{1}H NMR (DMSO-d$_6$, 400 MHz)



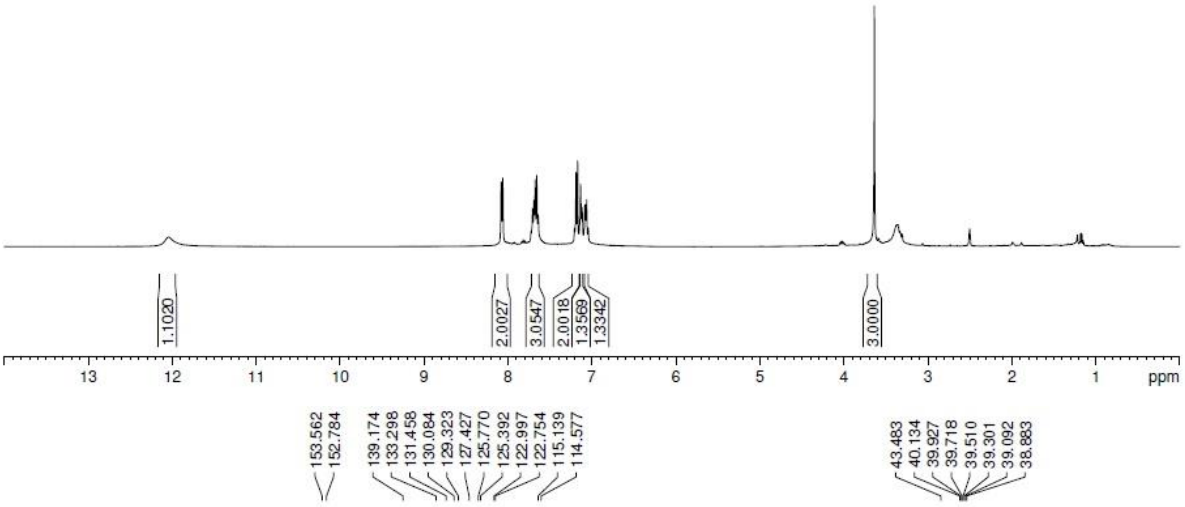
3e, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

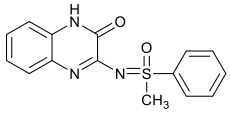
3-((Methyl(oxo)(phenyl)- λ^6-sulfanylidene)amino)quinoxalin-2 (1*H*)-one (3f)



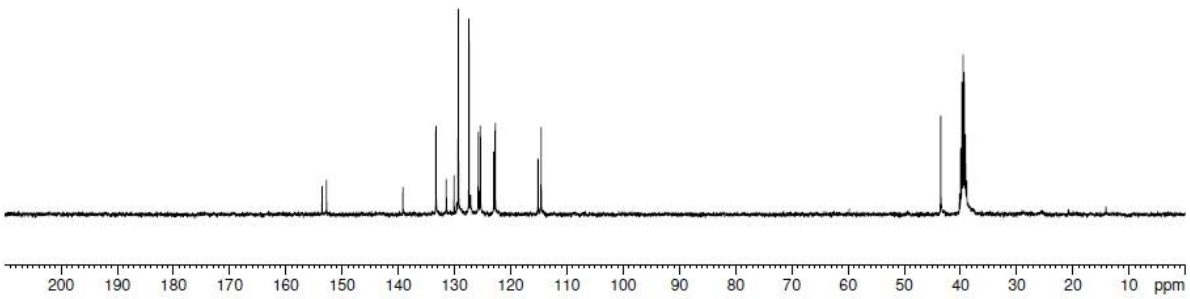


3f, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

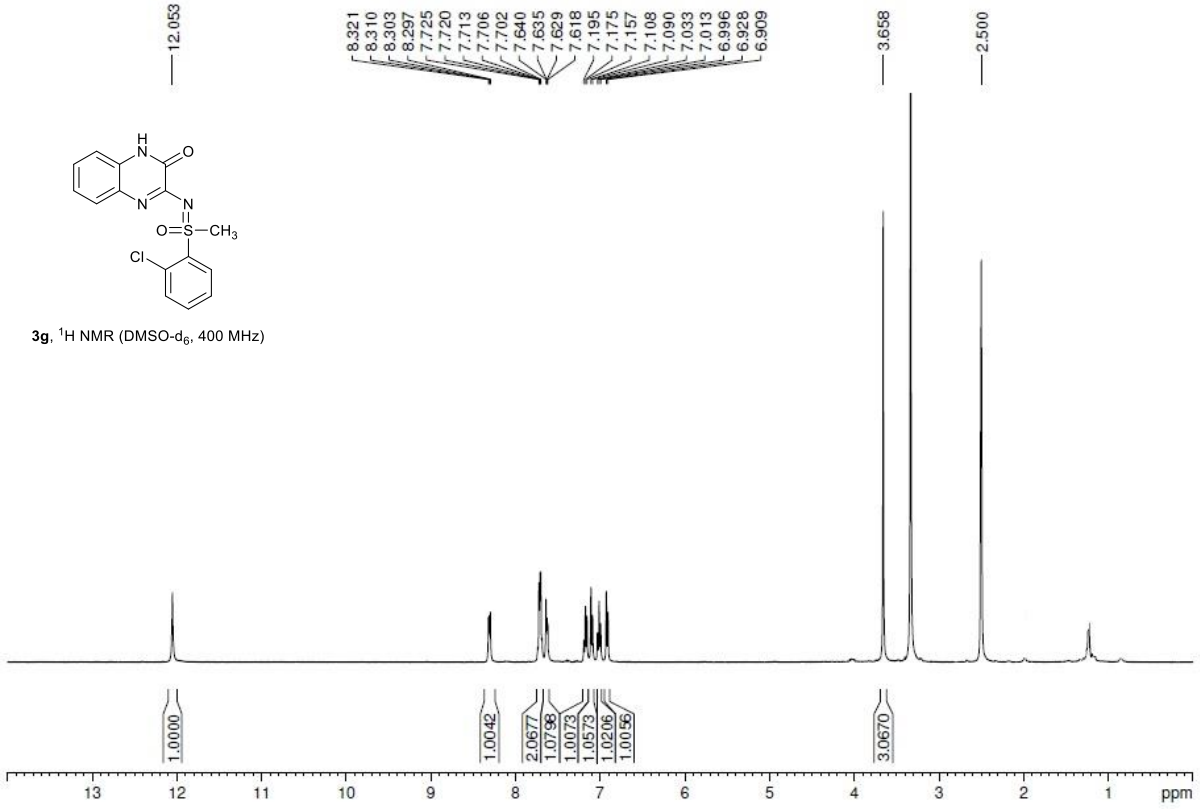




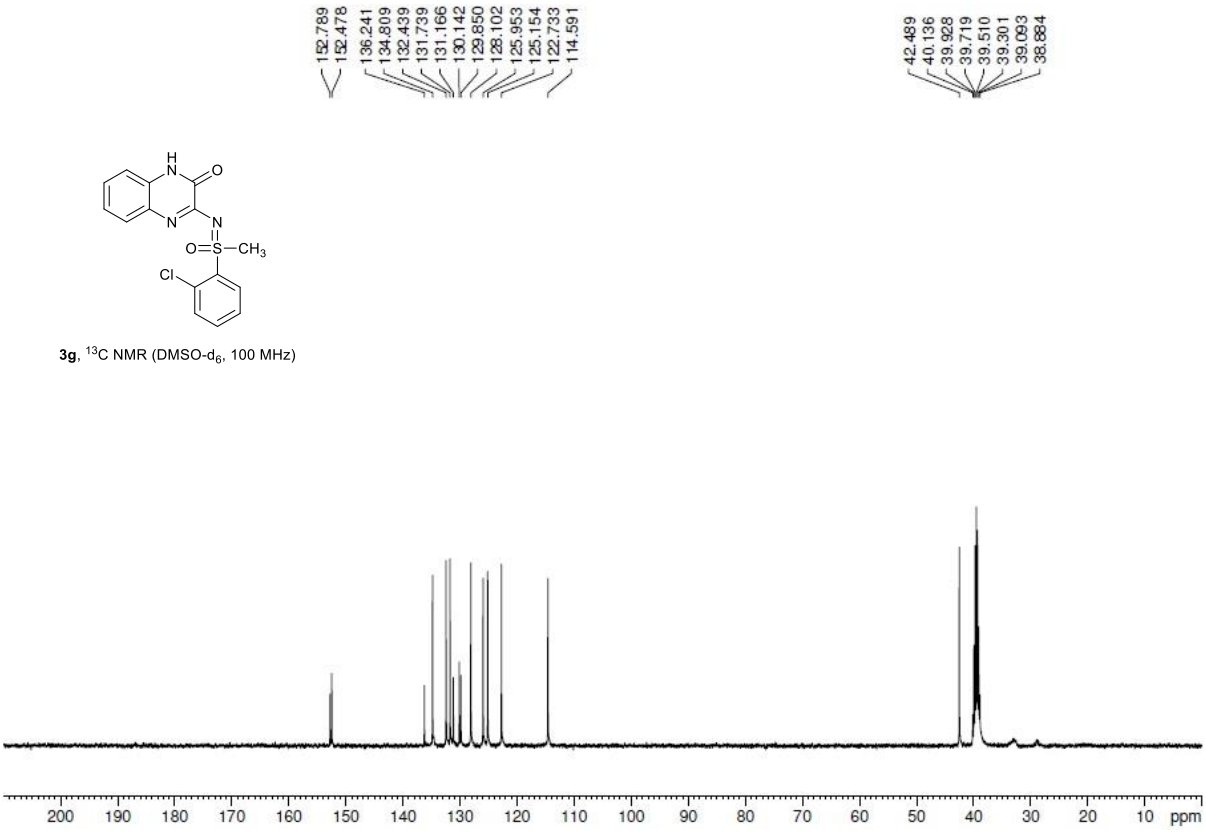
3f, ^{13}C NMR (DMSO-d$_6$, 100 MHz)



3-(((2-Chlorophenyl)(methyl)(oxo)- λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3g)

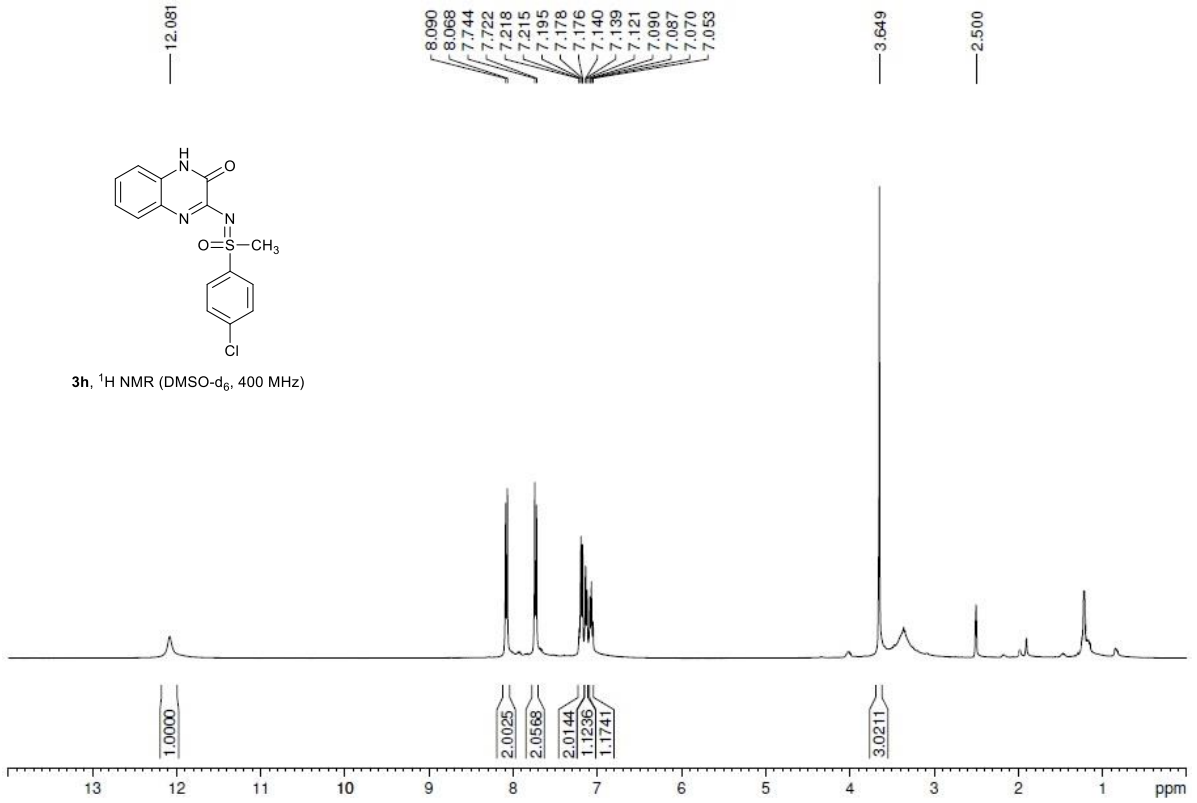


3g, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

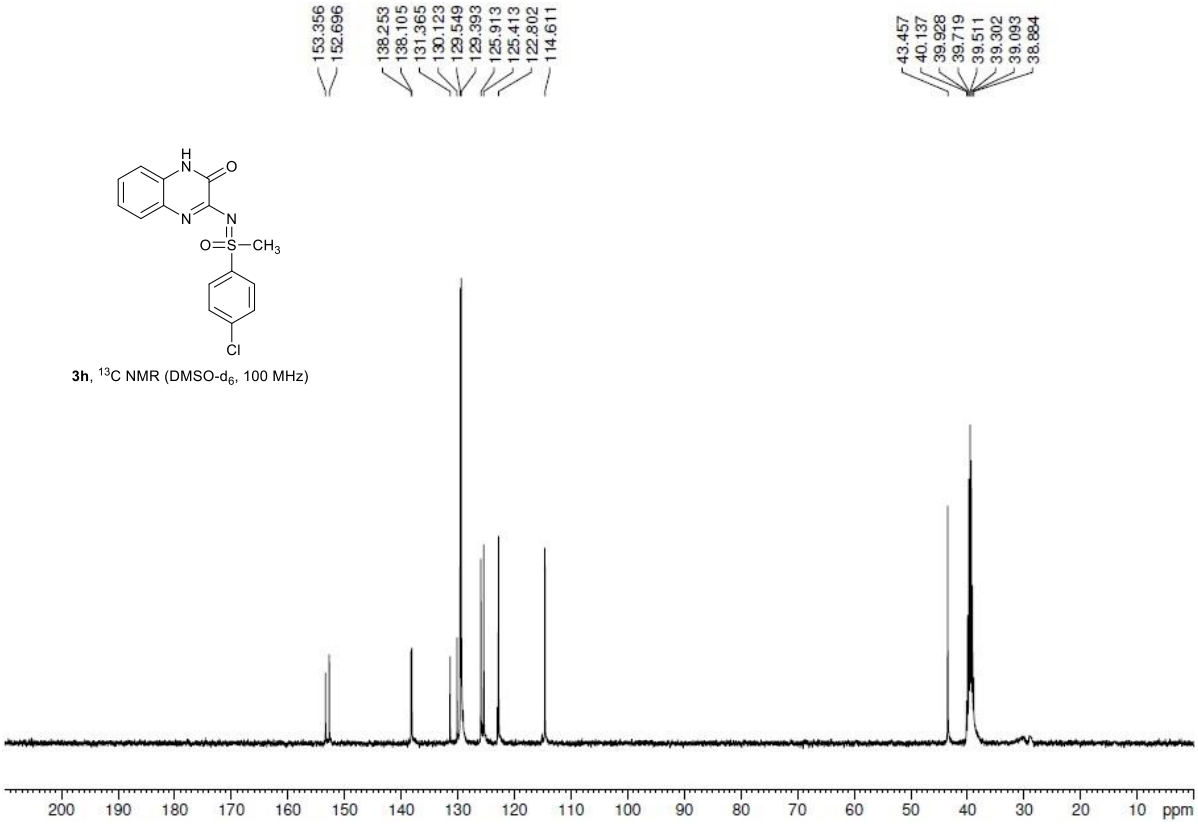


3g, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-(((4-Chlorophenyl)(methyl)(oxo)- λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3h)

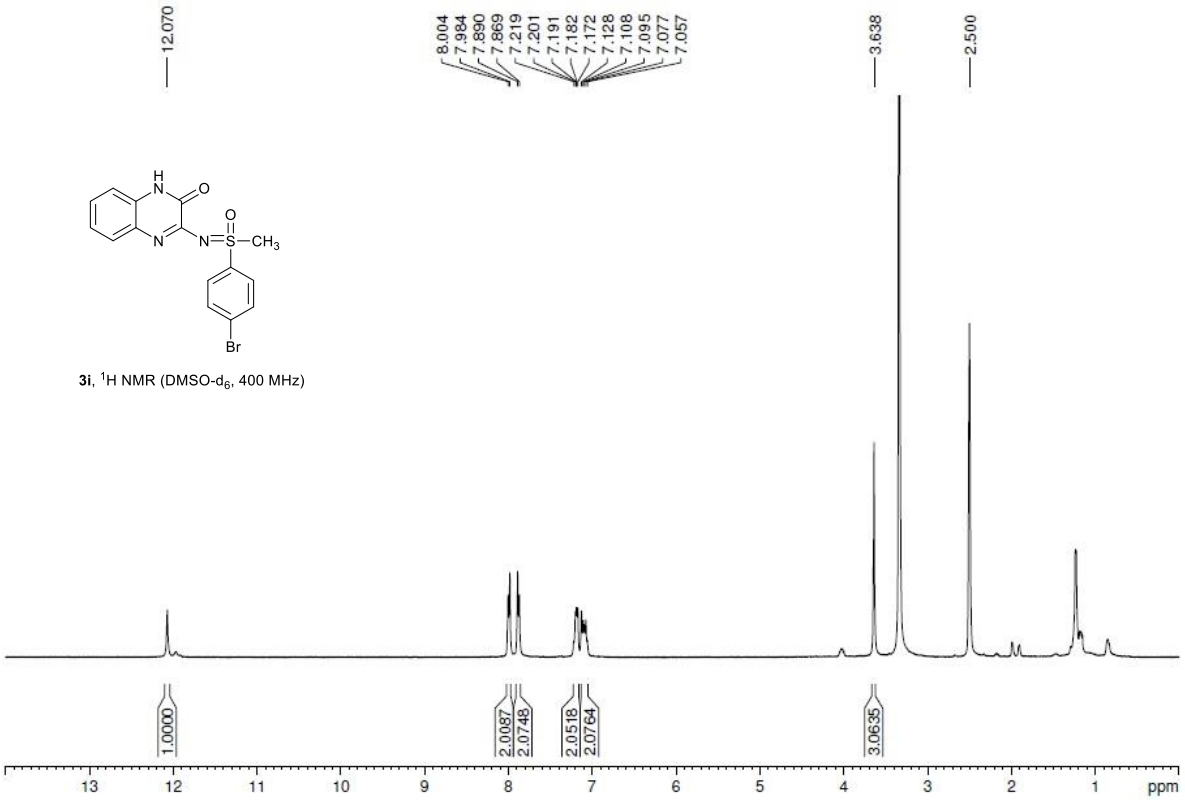


3h, ^{1}H NMR (DMSO-d_6, 400 MHz)

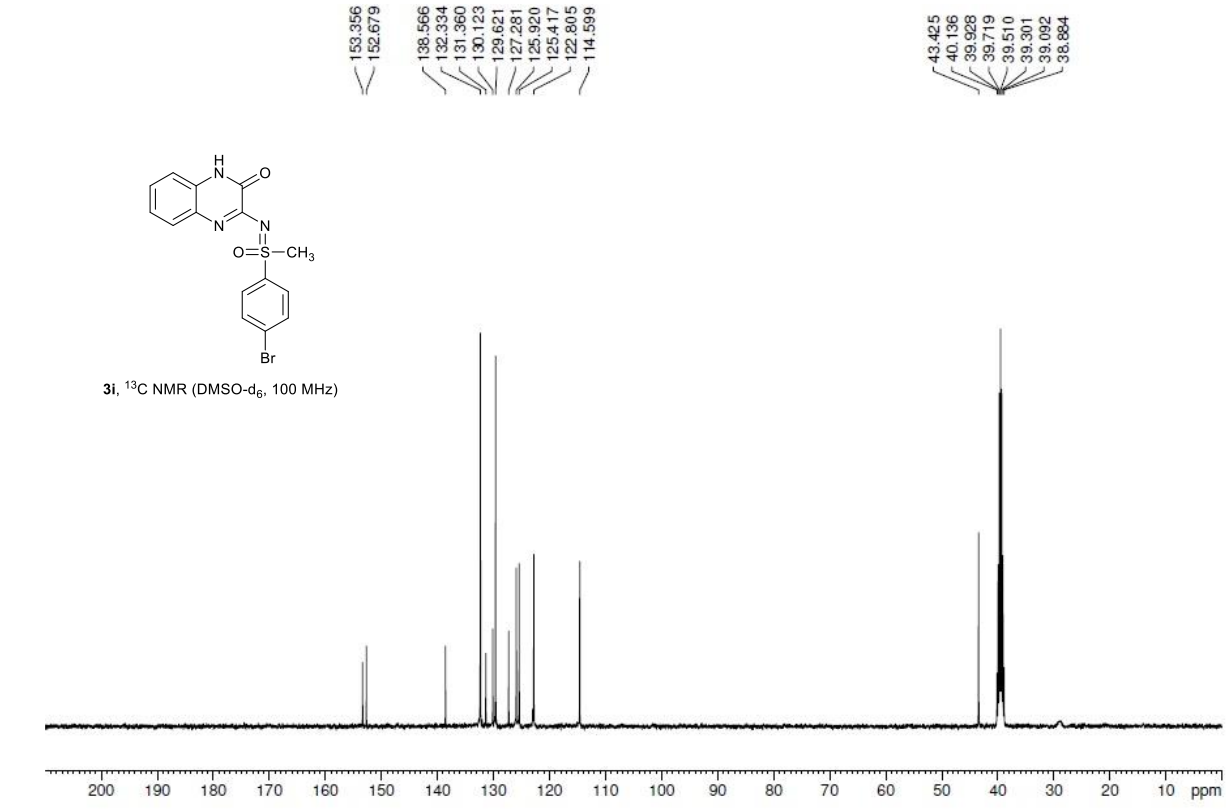


3h, ^{13}C NMR (DMSO-d_6, 100 MHz)

3-(((4-Bromophenyl)(methyl)(oxo)- λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3i)

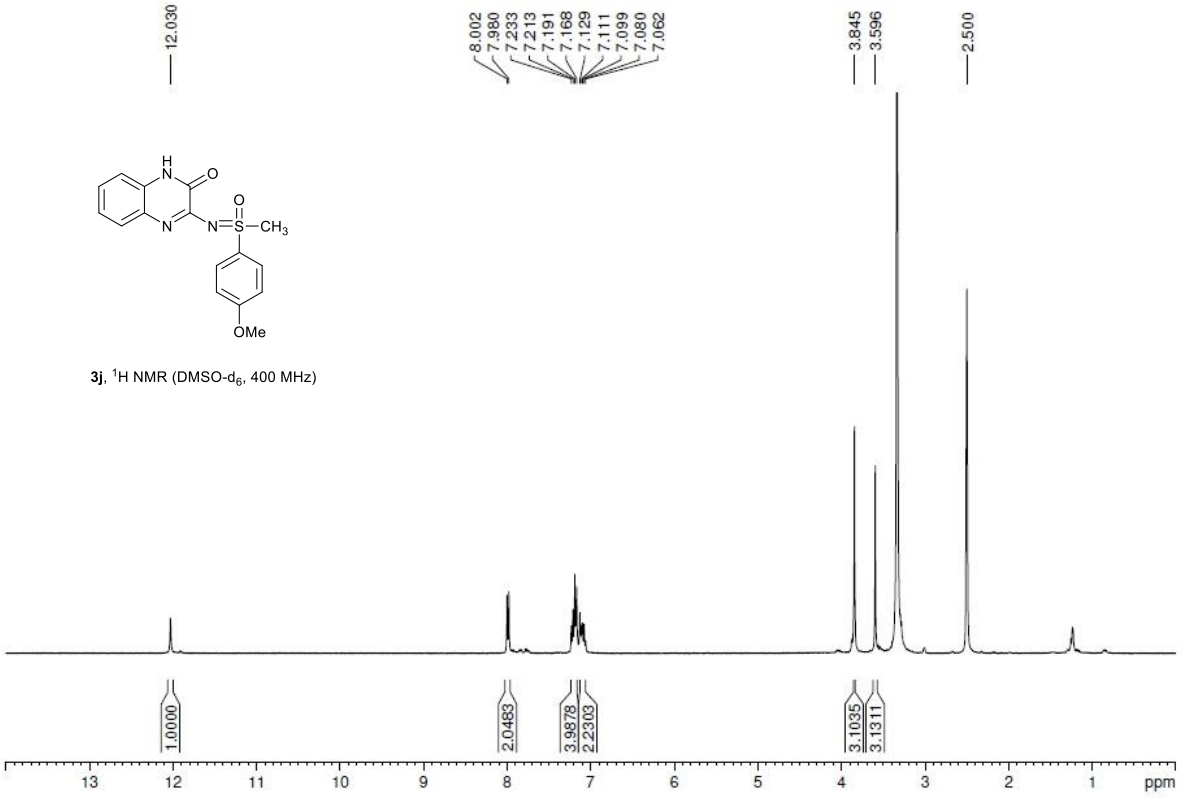


3i, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

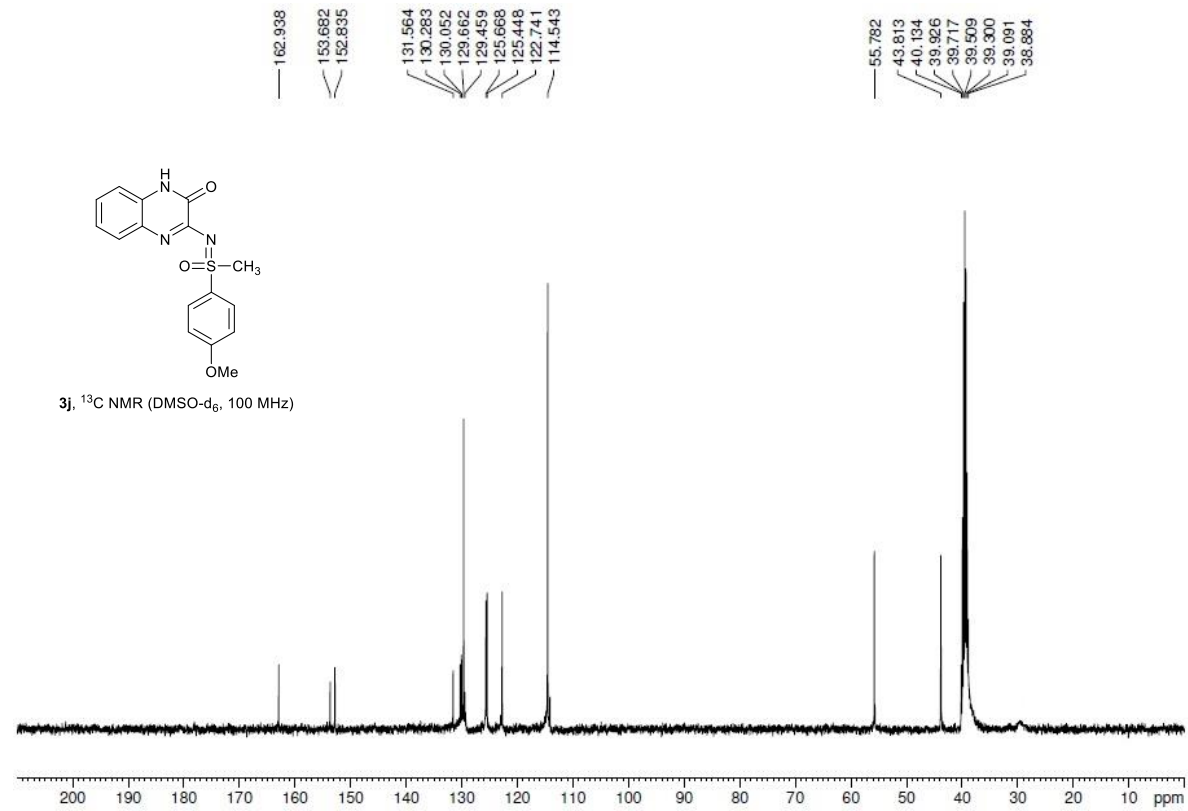


3i, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-(((4-Methoxyphenyl)(methyl)(oxo)- λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3j)

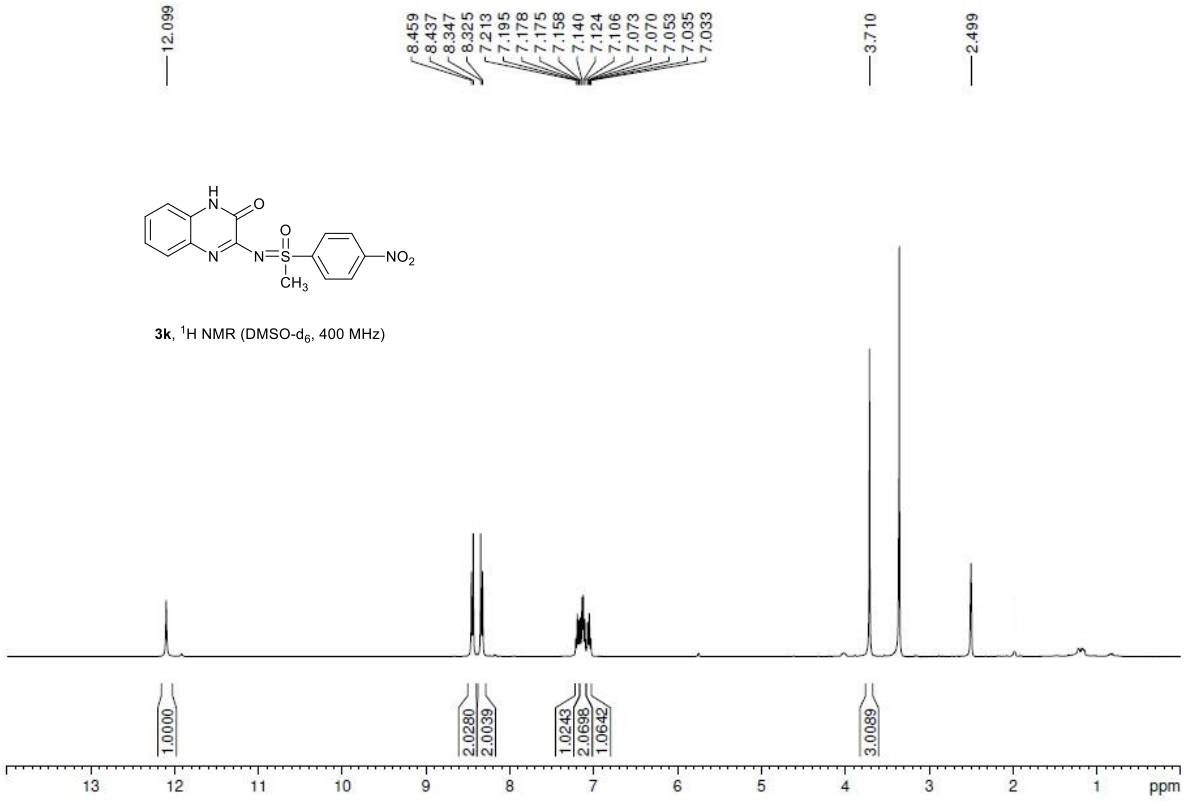


3j, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

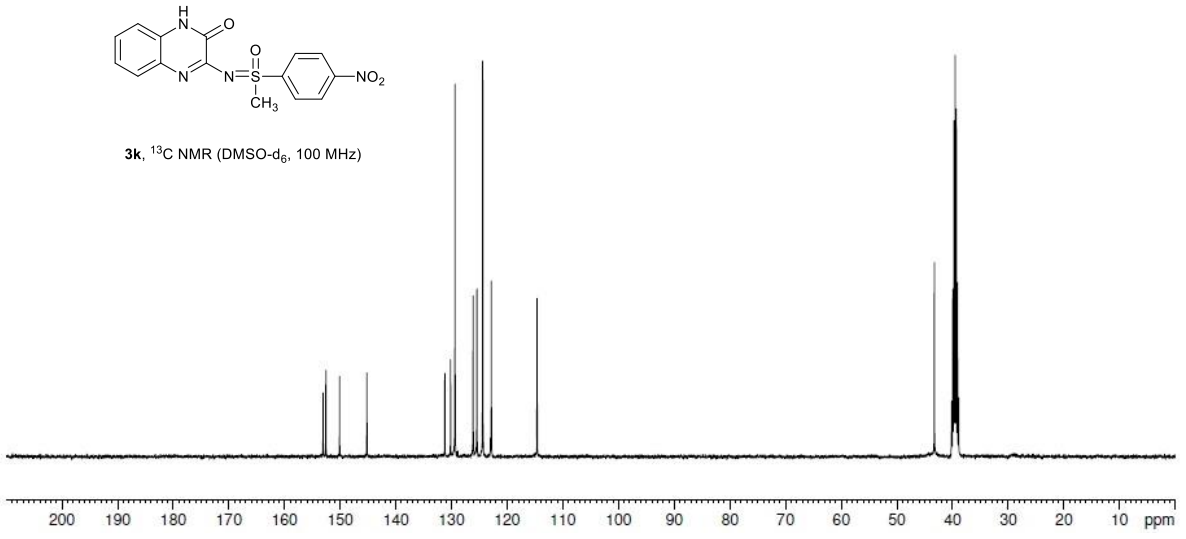


3j, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-((Methyl(4-nitrophenyl)(oxo)-λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3k)

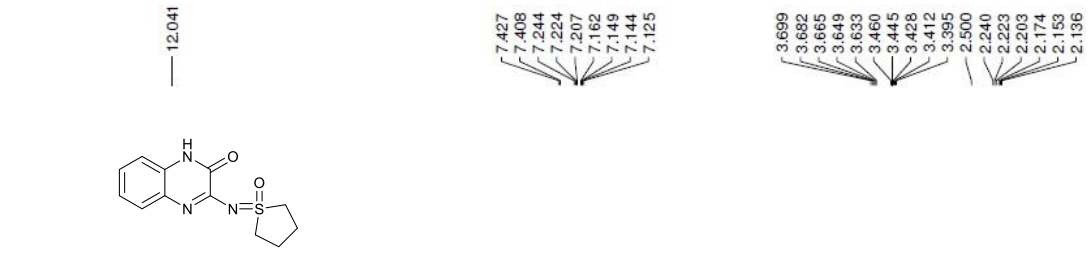


3k, ^{1}H NMR (DMSO-d_6, 400 MHz)

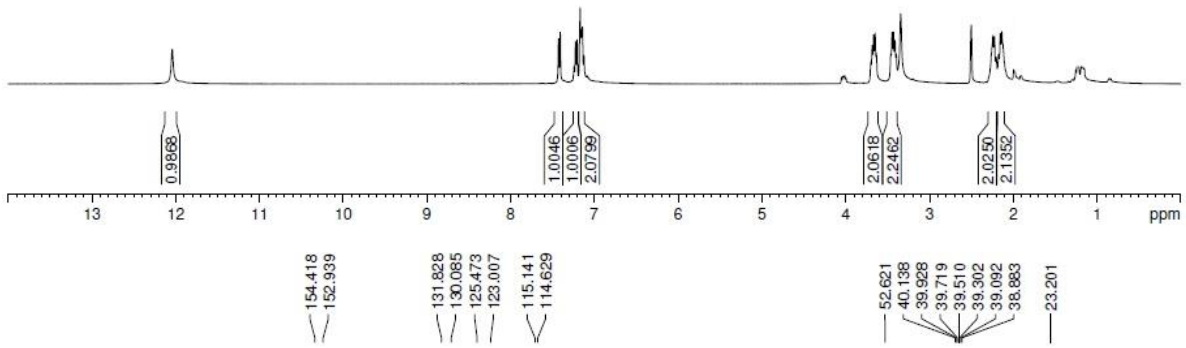


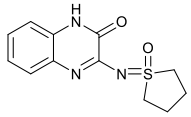
3k, ^{13}C NMR (DMSO-d_6, 100 MHz)

3-((1-Oxidotetrahydro-1 λ^6-thiophen-1-ylidene)amino)quinoxalin-2(1*H*)-one (3l)

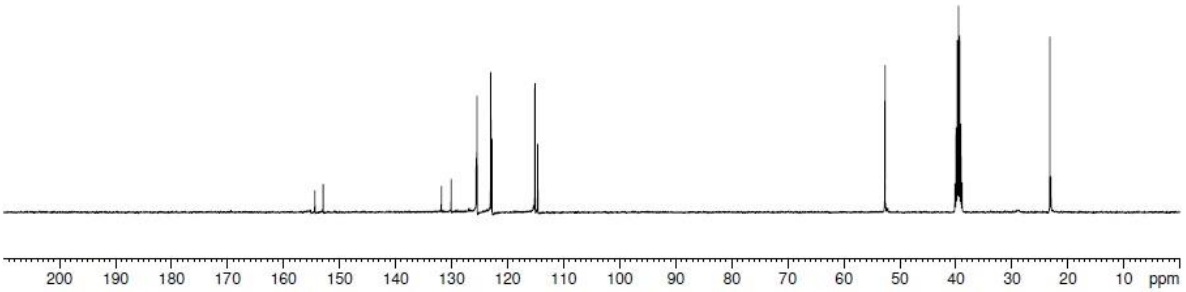


3l, ^{1}H NMR (DMSO-d_6, 400 MHz)

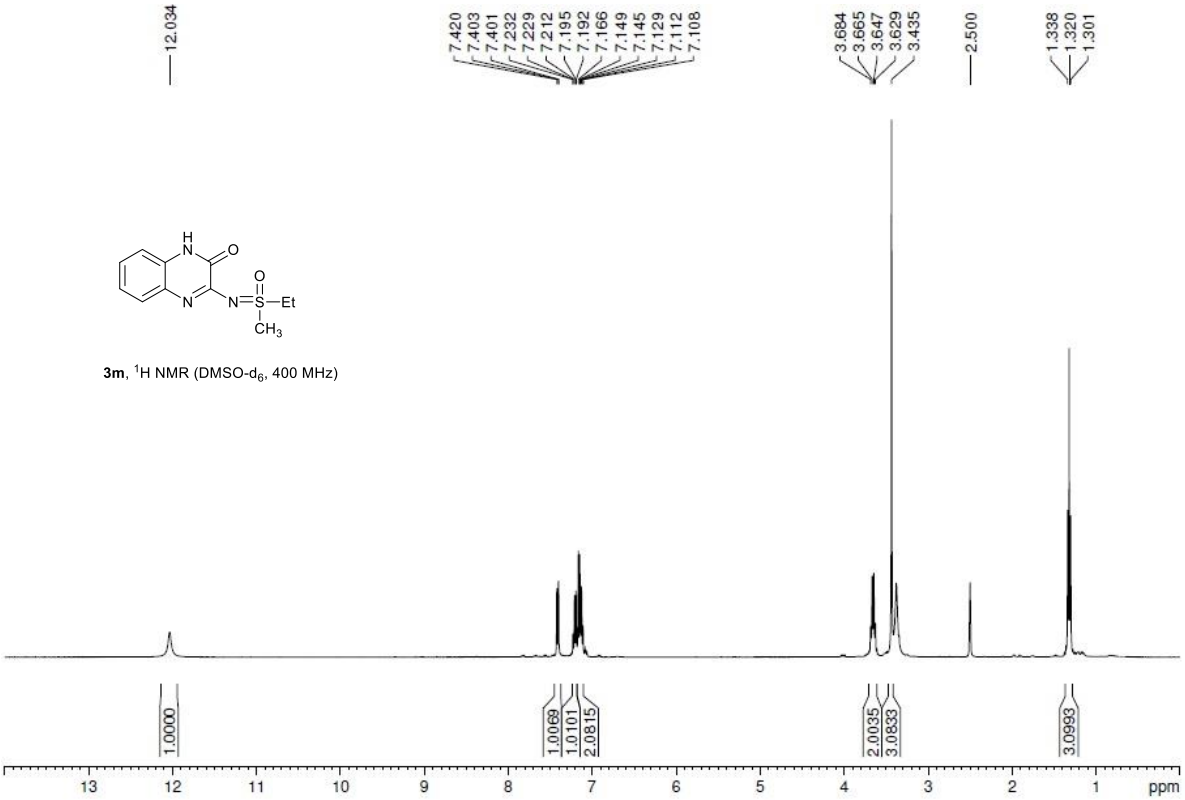




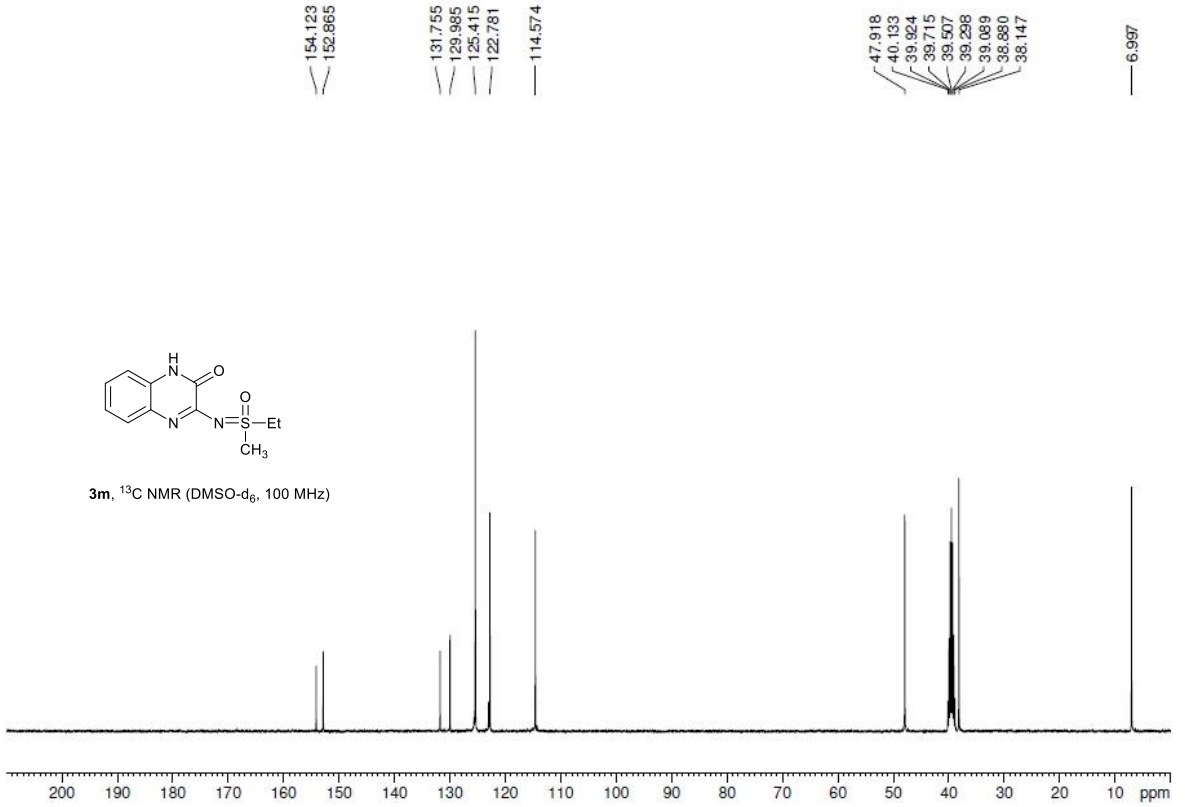
3l, ^{13}C NMR (DMSO-d_6, 100 MHz)



3-((Ethyl(methyl)(oxo)- λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (3m)

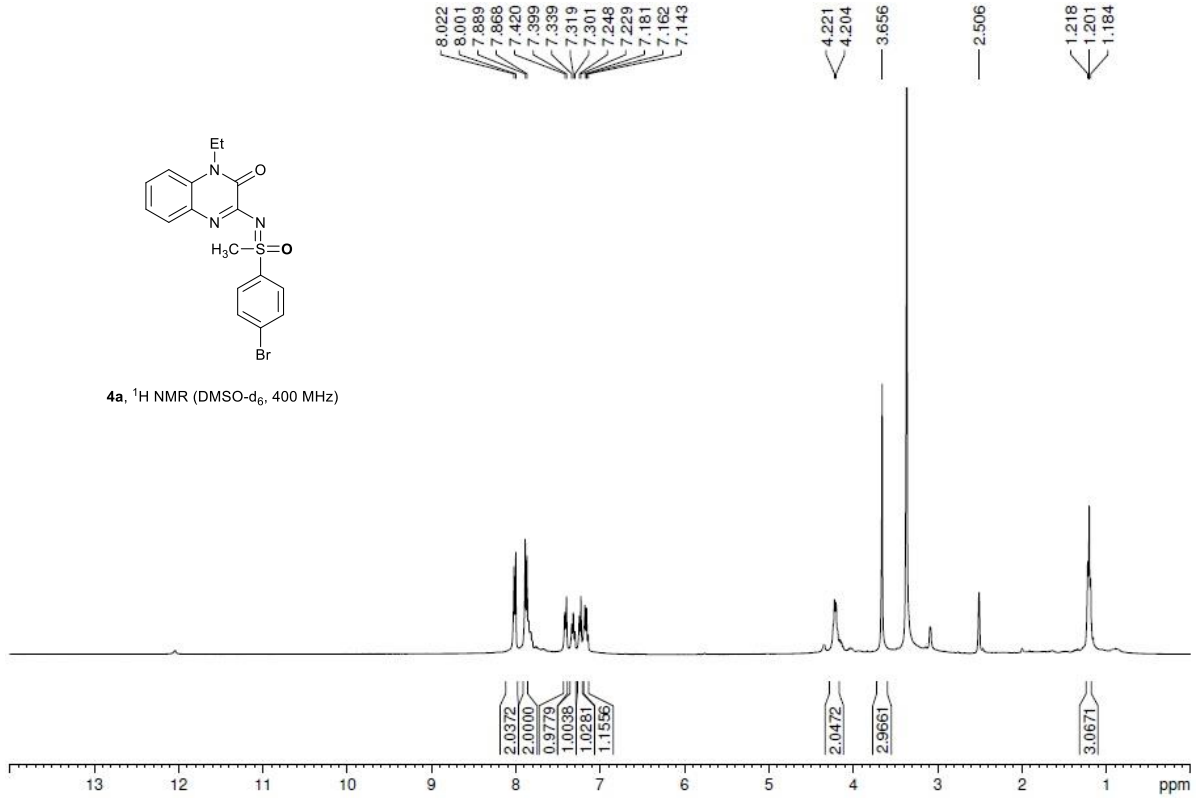


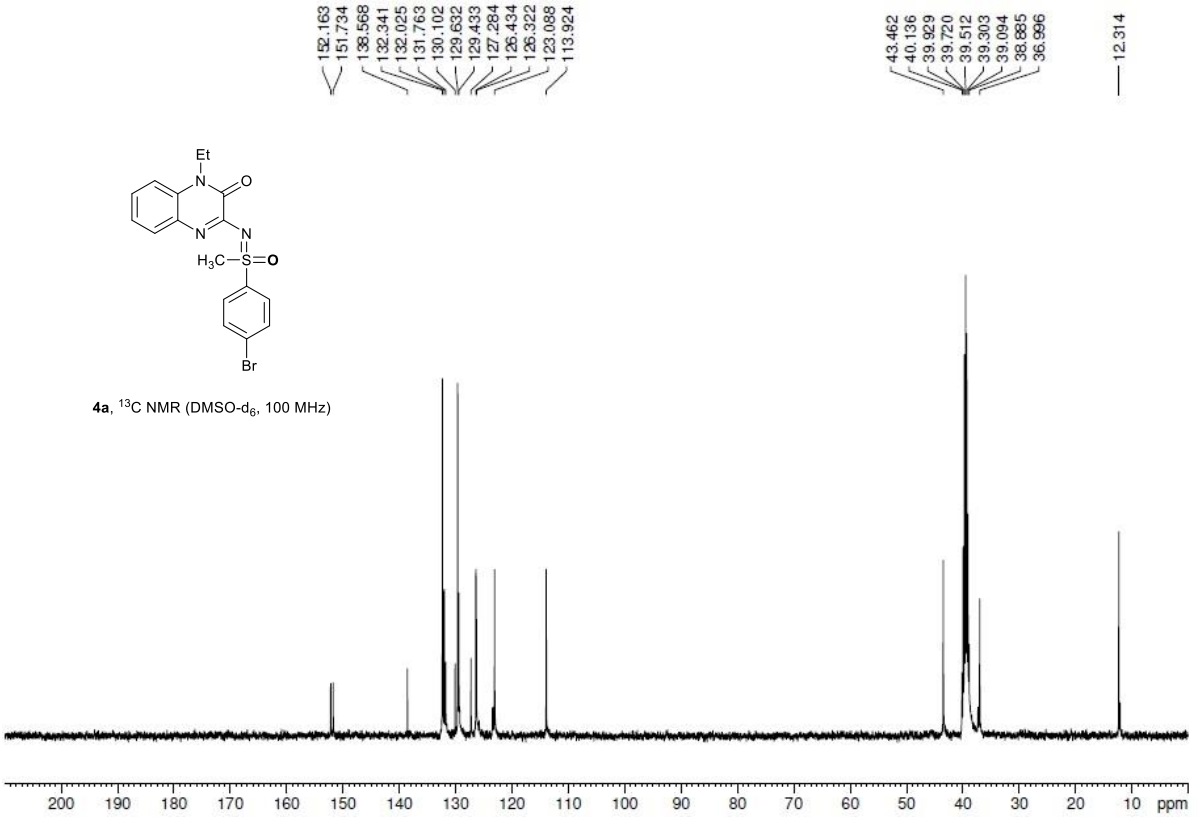
3m, ^{1}H NMR (DMSO-d$_6$, 400 MHz)



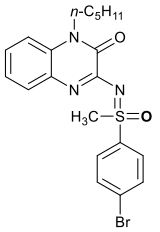
3m, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-(((4-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)-1-ethylquinoxalin-2(1*H*)-one (4a)

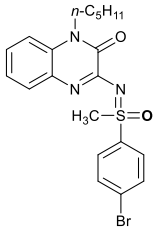




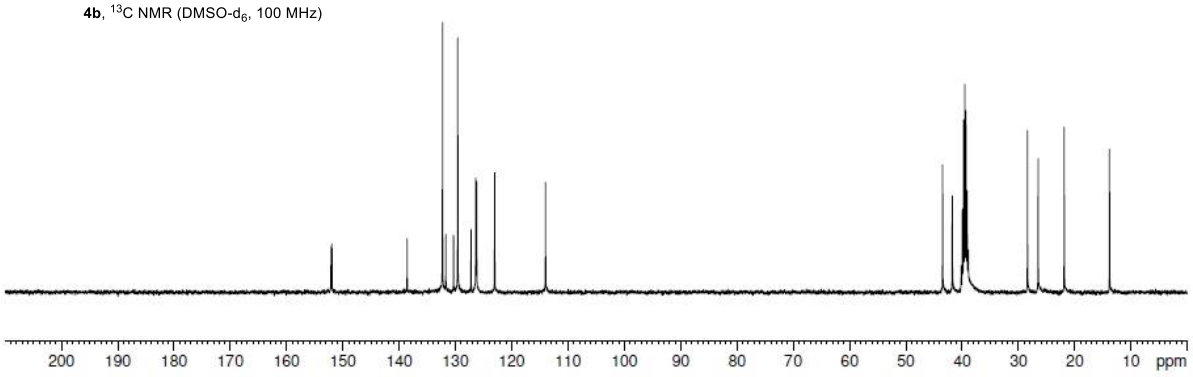
3-(((4-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)-1-pentylquinoxalin-2(1*H*)-one (4b)



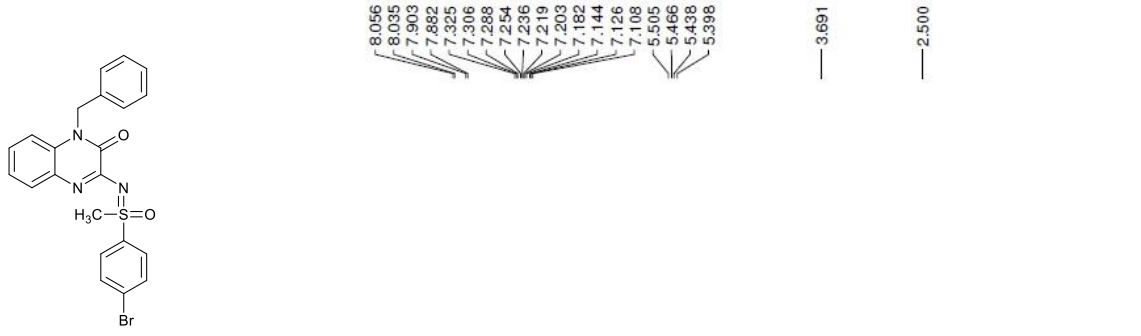
4b, ^{1}H NMR (DMSO-d$_6$, 400 MHz)



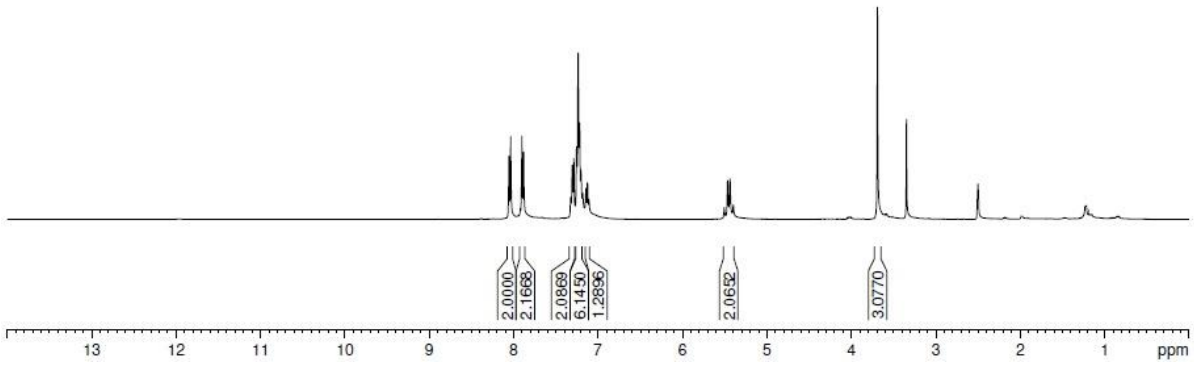
4b, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

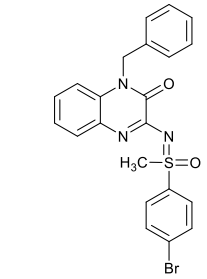


1-Benzyl-3-(((4-bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (4c)

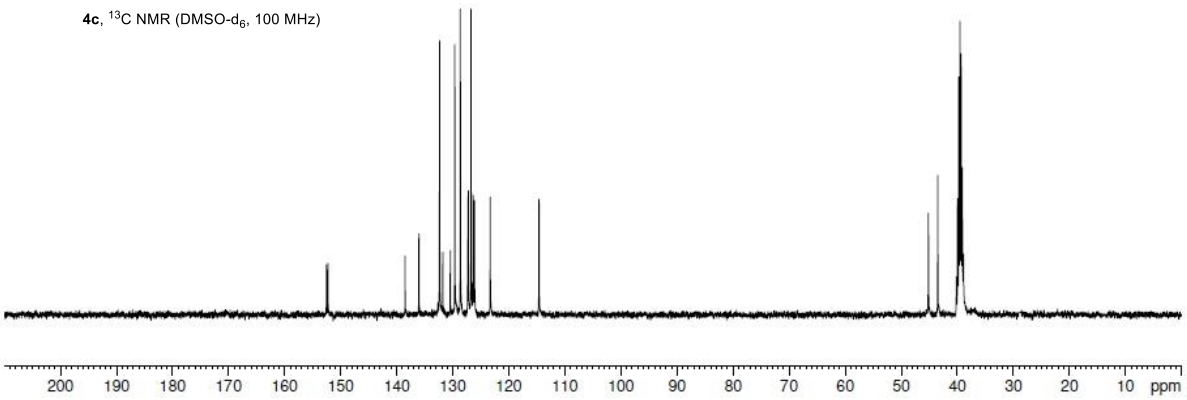


4c, ^{1}H NMR (DMSO-d_6, 400 MHz)

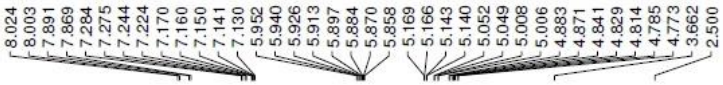


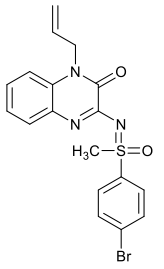


4c, ^{13}C NMR (DMSO-d_6, 100 MHz)

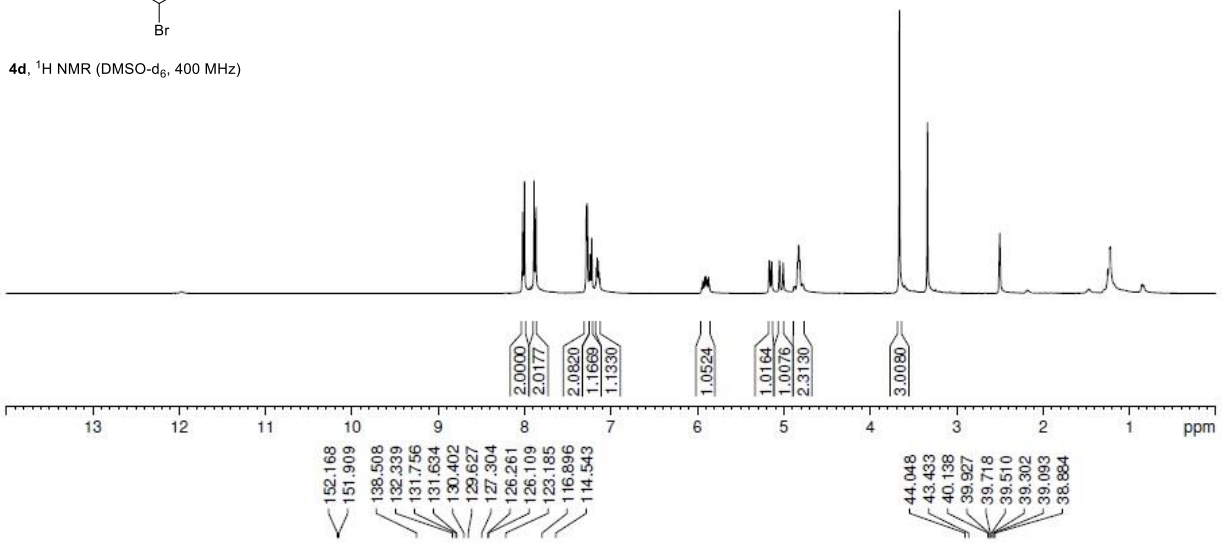


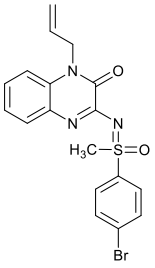
1-Allyl-3-(((4-bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (4d)





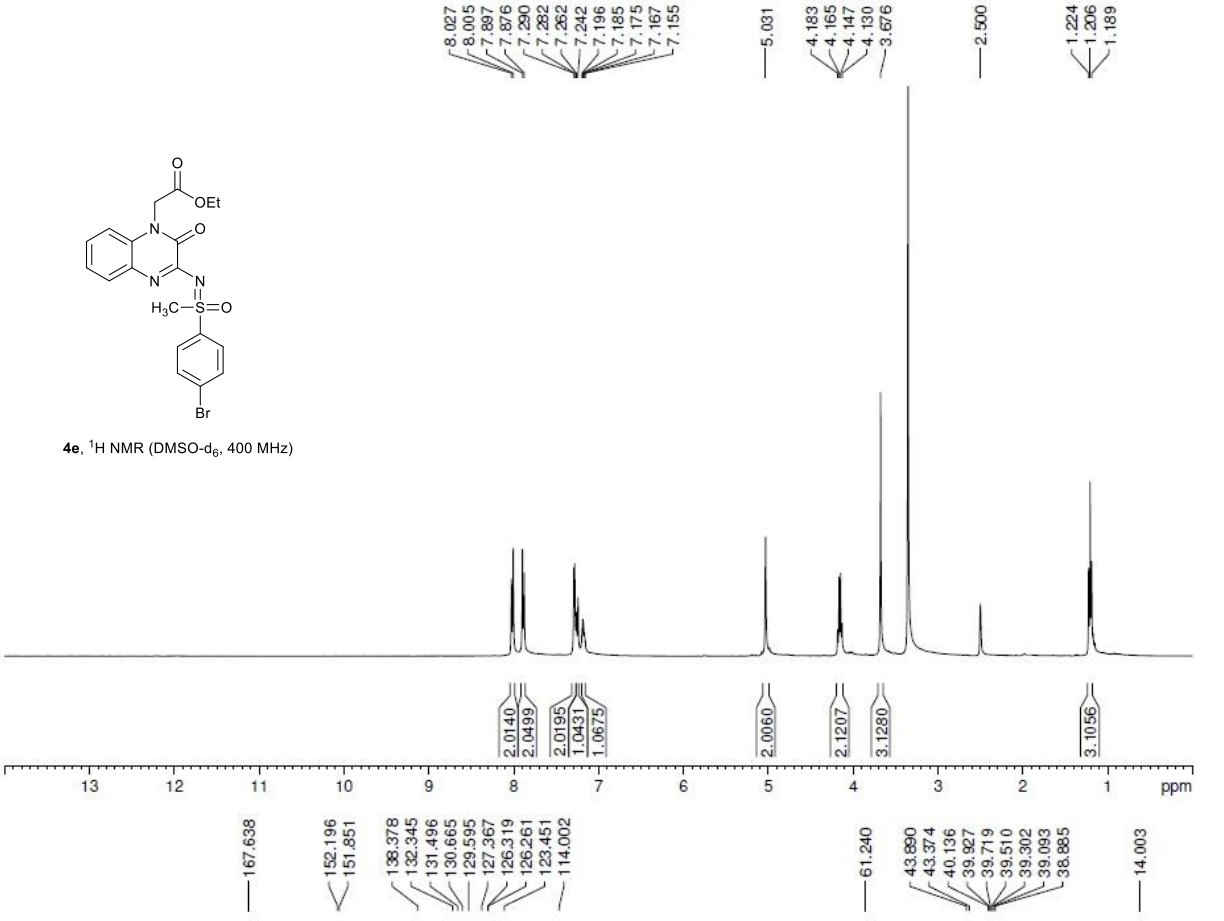
4d, ^{1}H NMR (DMSO-d$_6$, 400 MHz)





4d, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

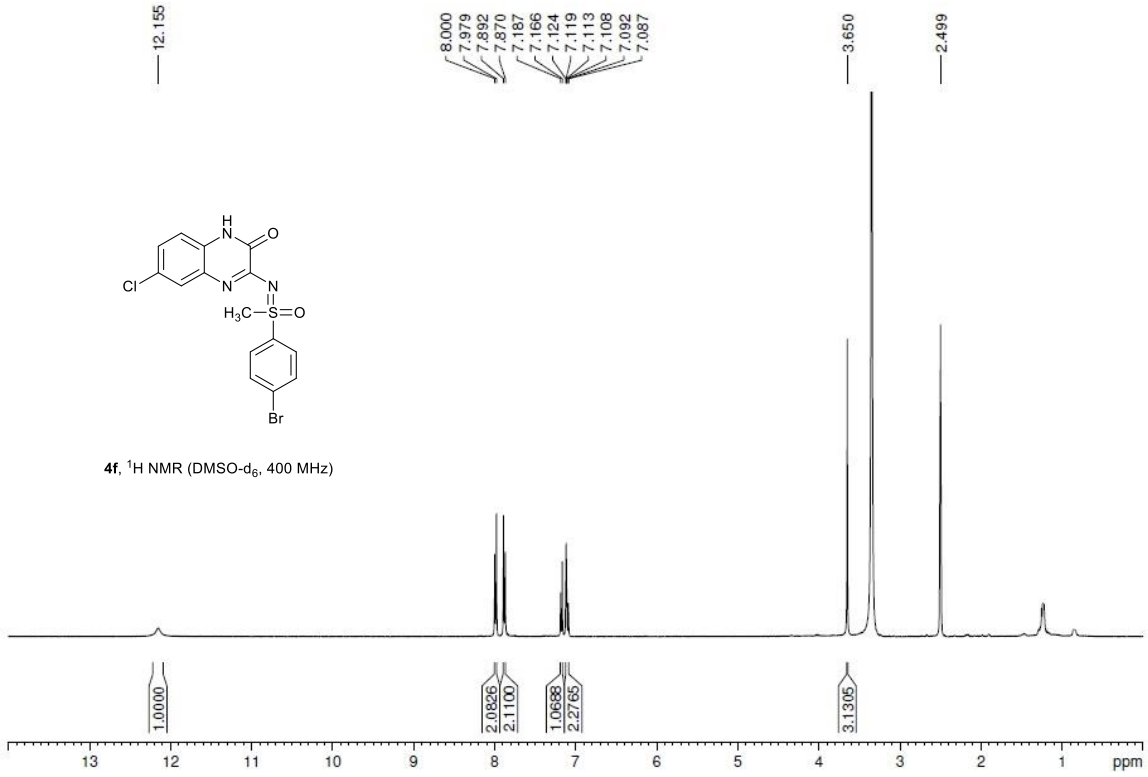
Ethyl 2-(3-(((4-bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)-2-oxoquinoxalin-1(2*H*)-yl)acetate (4e)



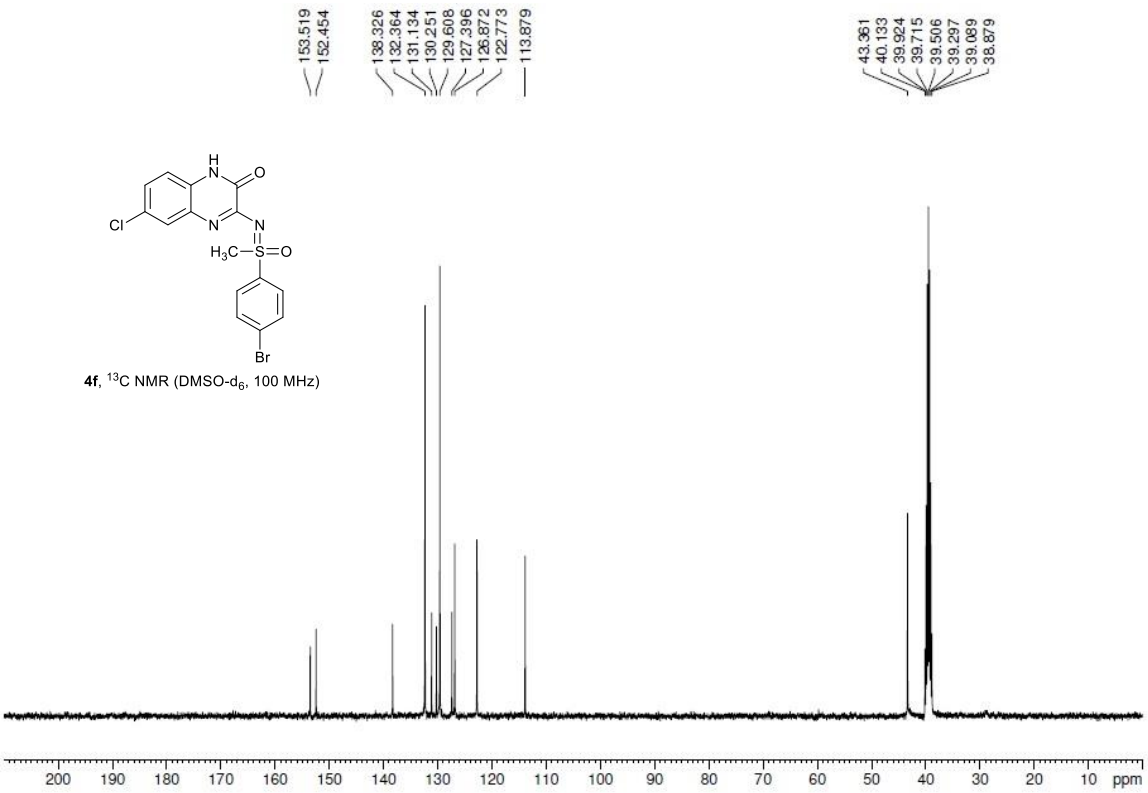
4e, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

4e, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-(((4-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)-6-chloroquinoxalin-2(1*H*)-one (4f)

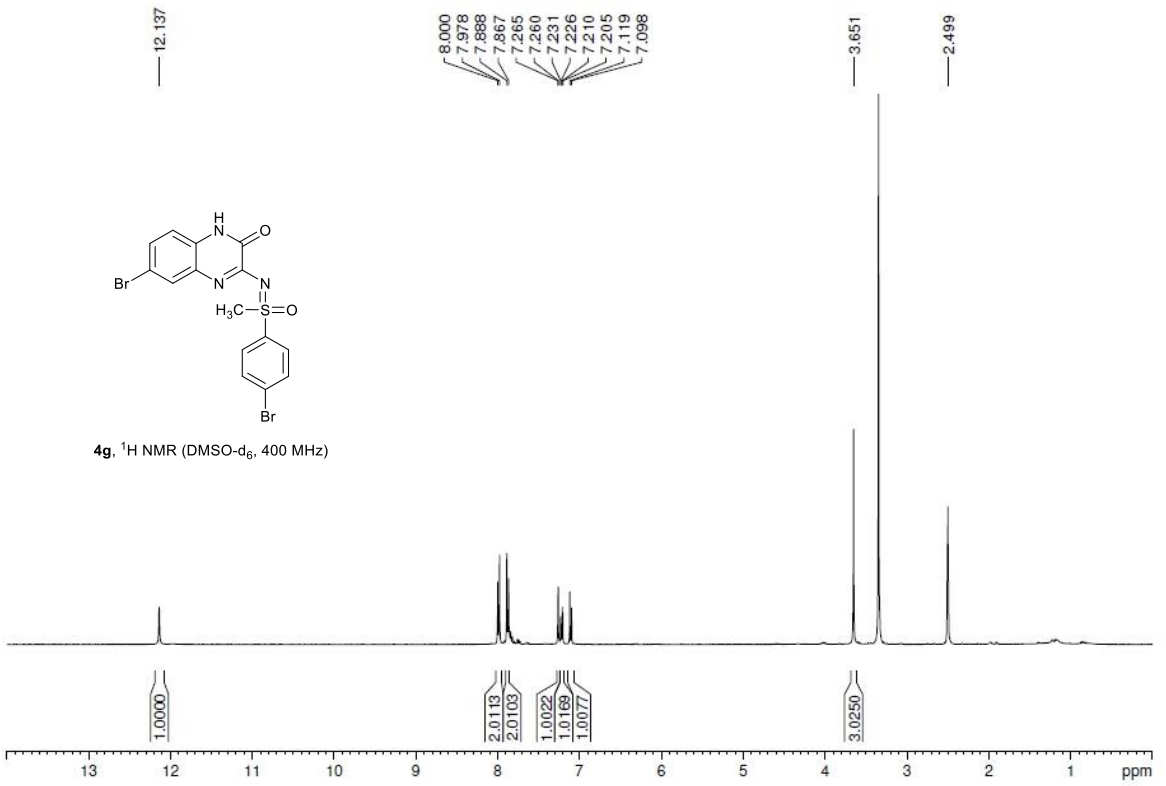


4f, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

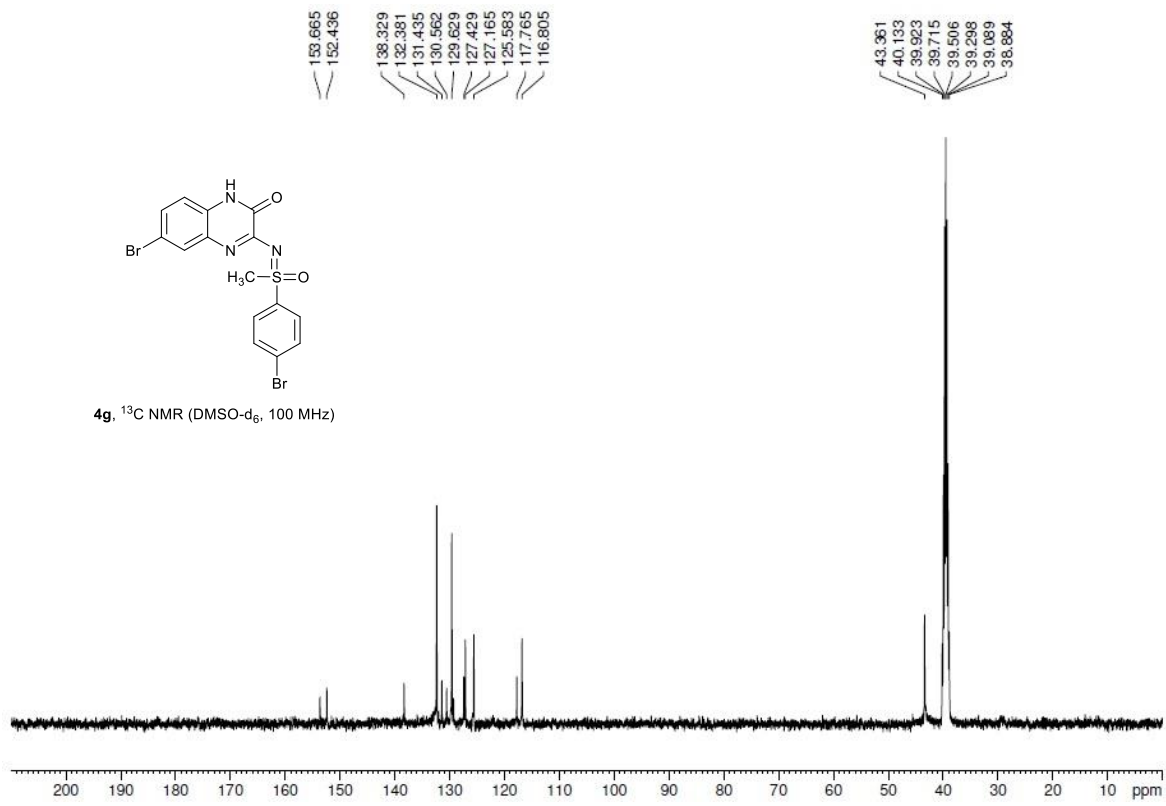


4f, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

6-Bromo-3-(((4-bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)quinoxalin-2(1*H*)-one (4g)

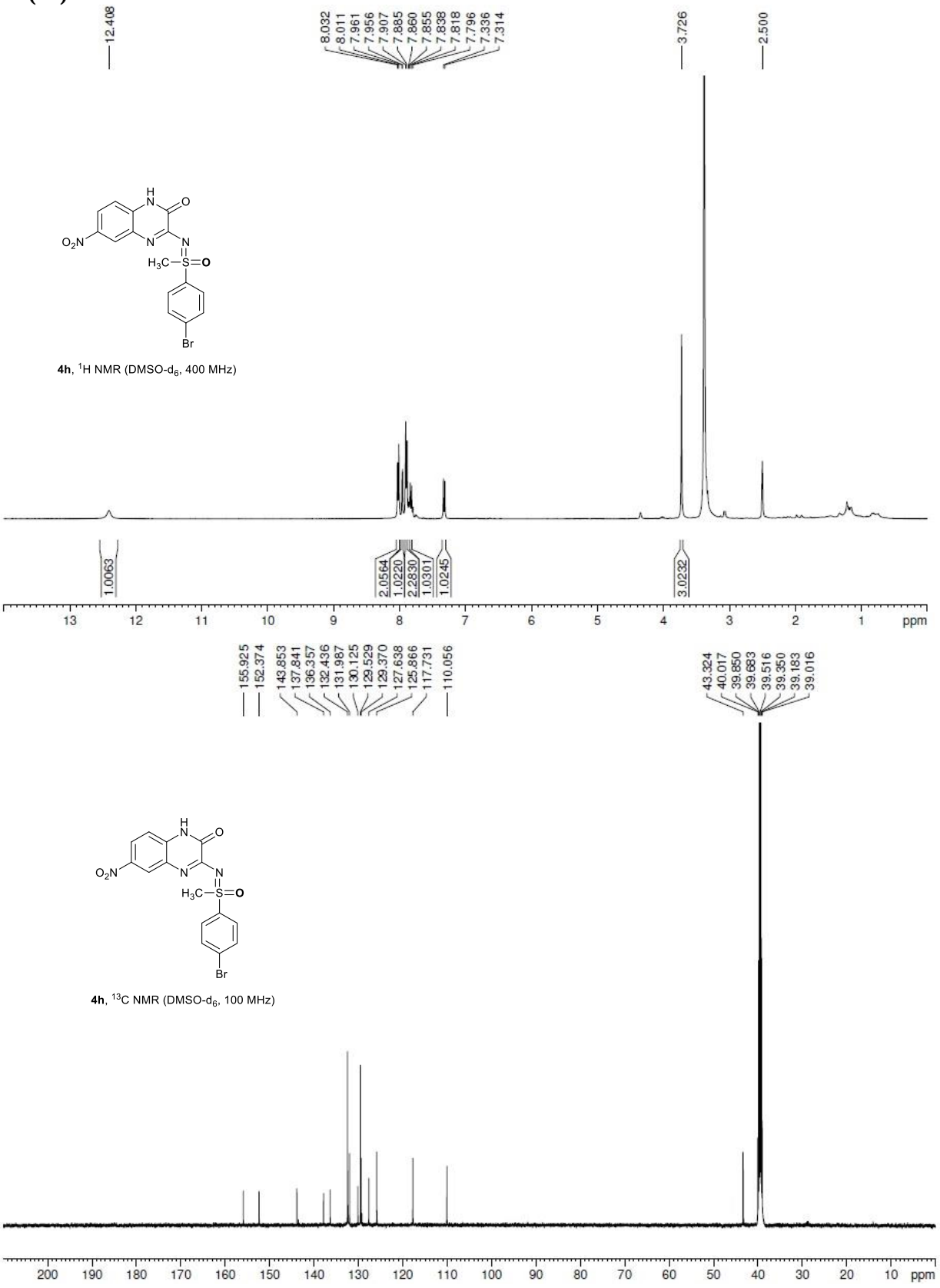


4g, ^{1}H NMR (DMSO-d_6, 400 MHz)



4g, ^{13}C NMR (DMSO-d_6, 100 MHz)

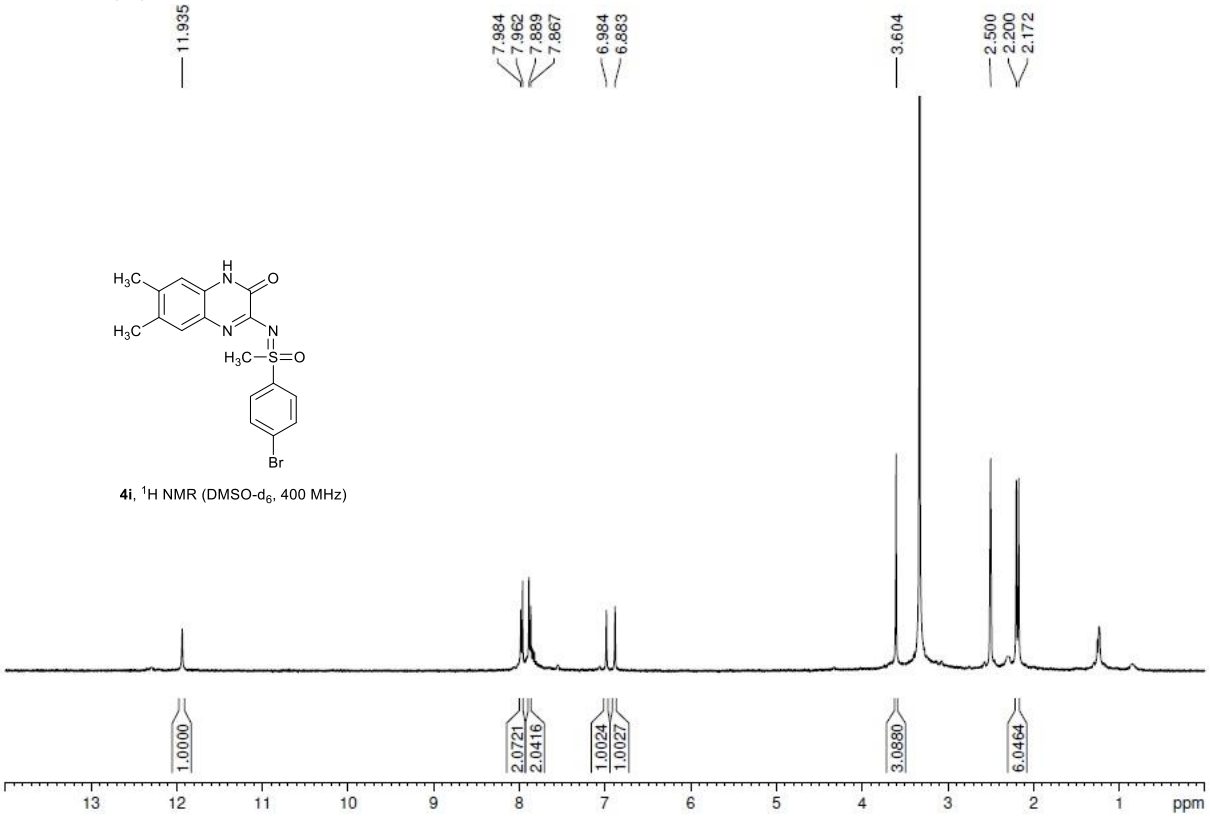
3-(((4-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)-6-nitroquinoxalin-2(1*H*)-one (4h)



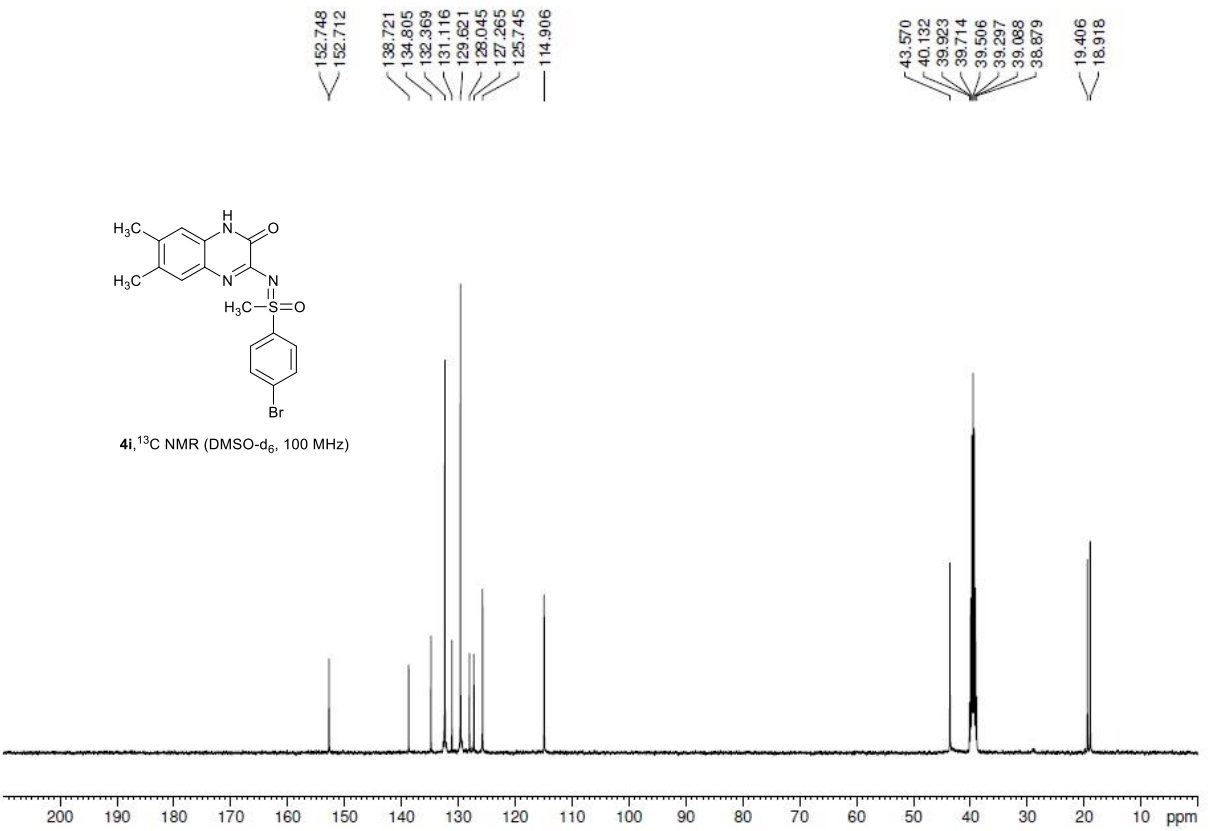
4h, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

4h, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

3-(((4-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)-6,7-dimethylquinoxalin-2(1*H*)-one (4i)

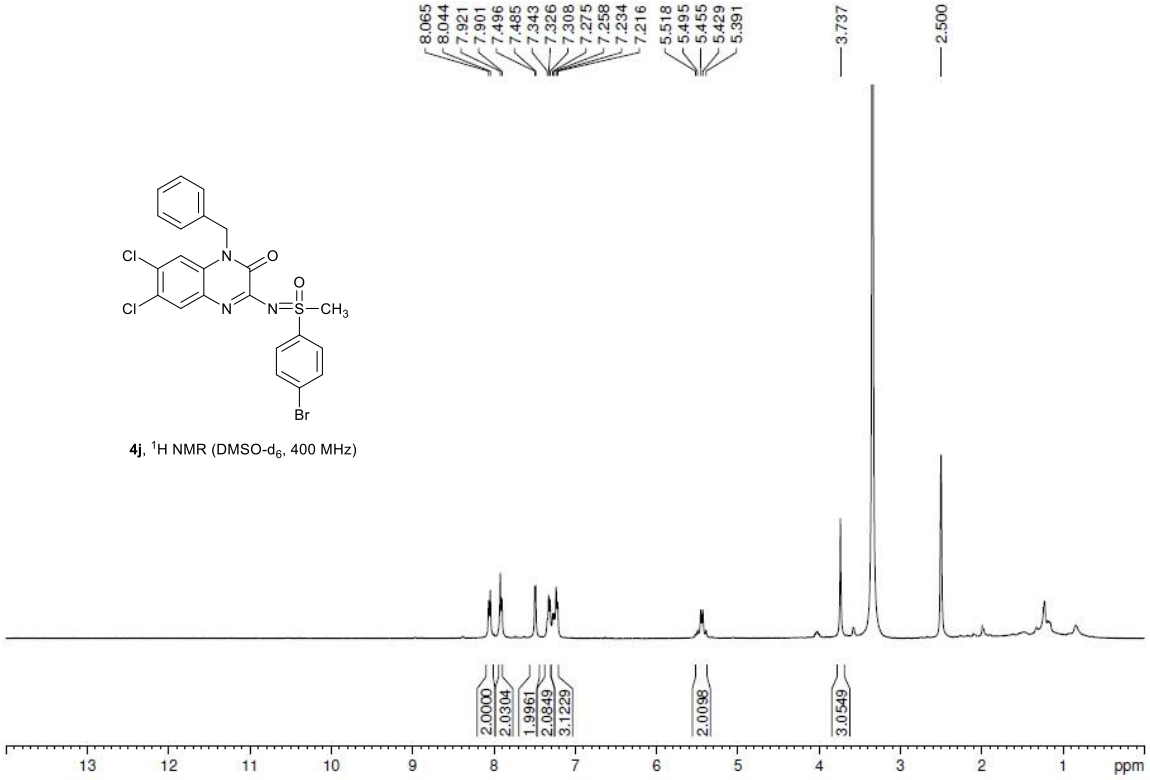


4i, ^{1}H NMR (DMSO-d$_6$, 400 MHz)

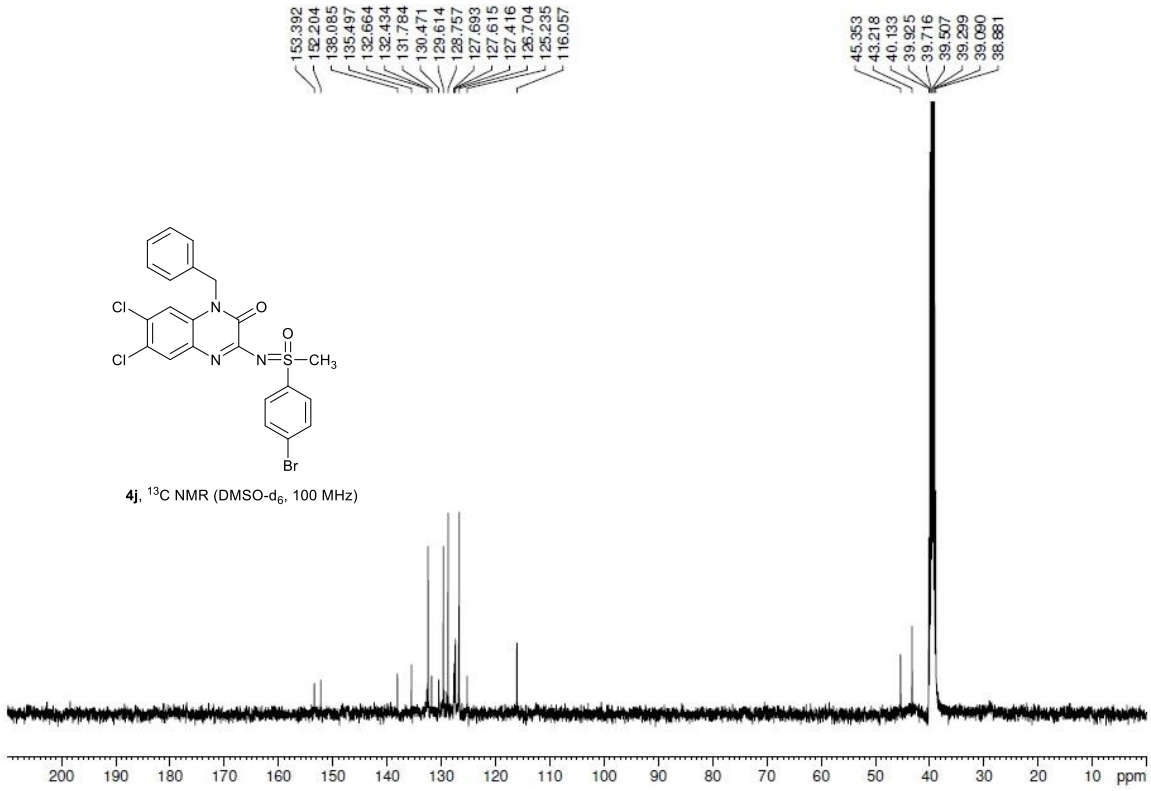


4i, ^{13}C NMR (DMSO-d$_6$, 100 MHz)

1-Benzyl-3-(((4-bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)amino)-6,7-dichloro quinoxalin-2(1*H*)-one (4j)



4j, ^{1}H NMR (DMSO-d_6, 400 MHz)



4j, ^{13}C NMR (DMSO-d_6, 100 MHz)