

SUPPORTING INFORMATION FOR

Synthesis and computationally assisted spectroscopic study of tautomerism in 3-(phenyl(2-arylhydrazineylidene)methyl)quinoxalin-2(1H)-ones

Sergey A. Katsyuba,* Liliya V. Mustakimova, Tatiana P. Gerasimova, Timur I. Burganov, Aisylu R. Sirazieva, Julia K. Voronina, Leisan R. Shamsutdinova, Il'dar Kh. Rizvanov, Vakhid A. Mamedov*

Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, Arbuzov Str. 8, 420088 Kazan, Russia

Corresponding Authors

*Sergey A. Katsyuba skatsyuba@yahoo.com

*Vakhid A. Mamedov mamedov@iopc.ru

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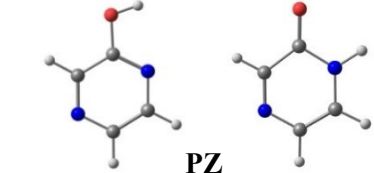
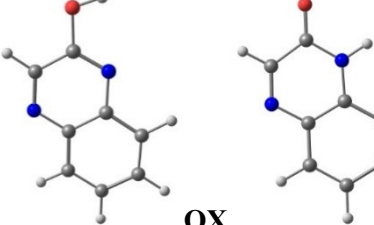
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Table S1. Experimental [1] and theoretically calculated free energy differences (ΔG , kcal·mol⁻¹) between the hydroxy and oxo tautomers of 2-pyrazinone (PZ) and quinoxaline-2-one (QX) in the gas phase.

compounds	ΔG_{exp} at T	T (K)	ΔG_{calc} at T
 <p>PZ</p>	-1.9±0.2	360	-1.7
 <p>QX</p>	3.3±0.2	450	2.8

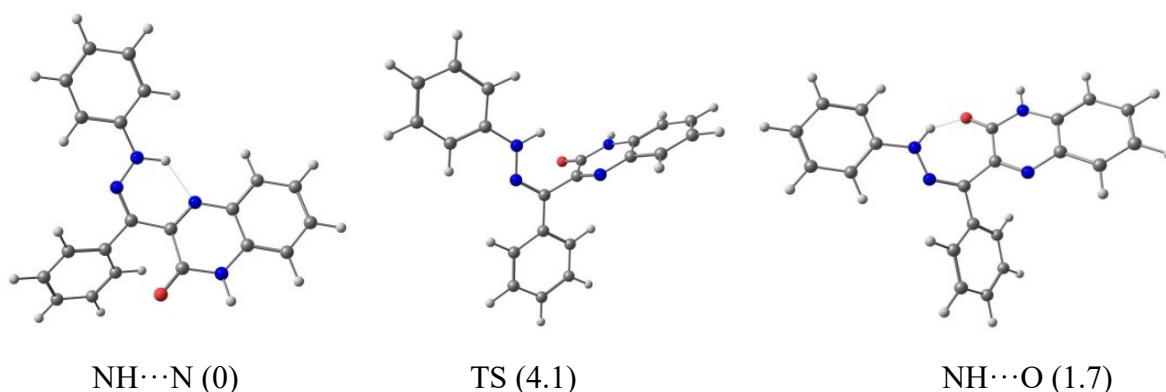


Fig. S1. NH...N, NH...O conformers and transition state (TS) of conformational transformation of **2b** and their relative free energies (kcal/mol, in parenthesis). The protocol described in [2] was used for computations. The structures are fully optimized at the TPSS-D3/def2-TZVP+COSMO (DMF) level, which combines the TPSS meta-GGA density functional [3] with the BJ-damped DFT-D3 dispersion correction [4] and the def2-TZVP basis set,[5] using the Conductor-like Screening Model (COSMO) [6] for dimethylformamide solvent. The optimized structures are characterized by frequency analysis (no imaginary frequency for true minima and only one imaginary frequency for transition state) to provide thermal free energy corrections (at 298.15 K and 1 atm) according to the modified ideal gas-rigid rotor-harmonic oscillator model.[7]

List of references:

- [1] Gerega A, Lapinski L, Nowak MJ, Furmanchuk A, Leszczynski J. *J Phys Chem A* 2007;111:4934-4943.
- [2] Zh.-W. Qu, H. Zhu, S.A. Katsyuba, V.L. Mamedova, V.A. Mamedov, S. Grimme, *Chem. Open* 2020, 9, 743-747.
- [3] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* 2003, 91, 146401.
- [4] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, 132, 154104–154119; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* 2011, 32, 1456–1465.
- [5] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, 7, 3297–3305.
- [6] A. Klamt, G. Schuurmann, *J. Chem. Soc. Perkin Trans. 2* 1993, 799–805.
- [7] S. Grimme, *Chem. Eur. J.* 2012, 18, 9955–9964.

Table S2. B97-3c computed fundamental frequencies (cm^{-1}) and IR intensities ($\text{km}\cdot\text{mol}^{-1}$, in parentheses, scaled by Boltzmann weights, ω , from Table 1 of the main text) of the bands of oxo (**A**) and hydroxy (**D**) tautomers of **2f** surrounded by 44 and 43 DCM molecules, respectively, and the corresponding experimental parameters of IR spectrum of DCM solution in the region of $1600\text{-}1700\text{ cm}^{-1}$.

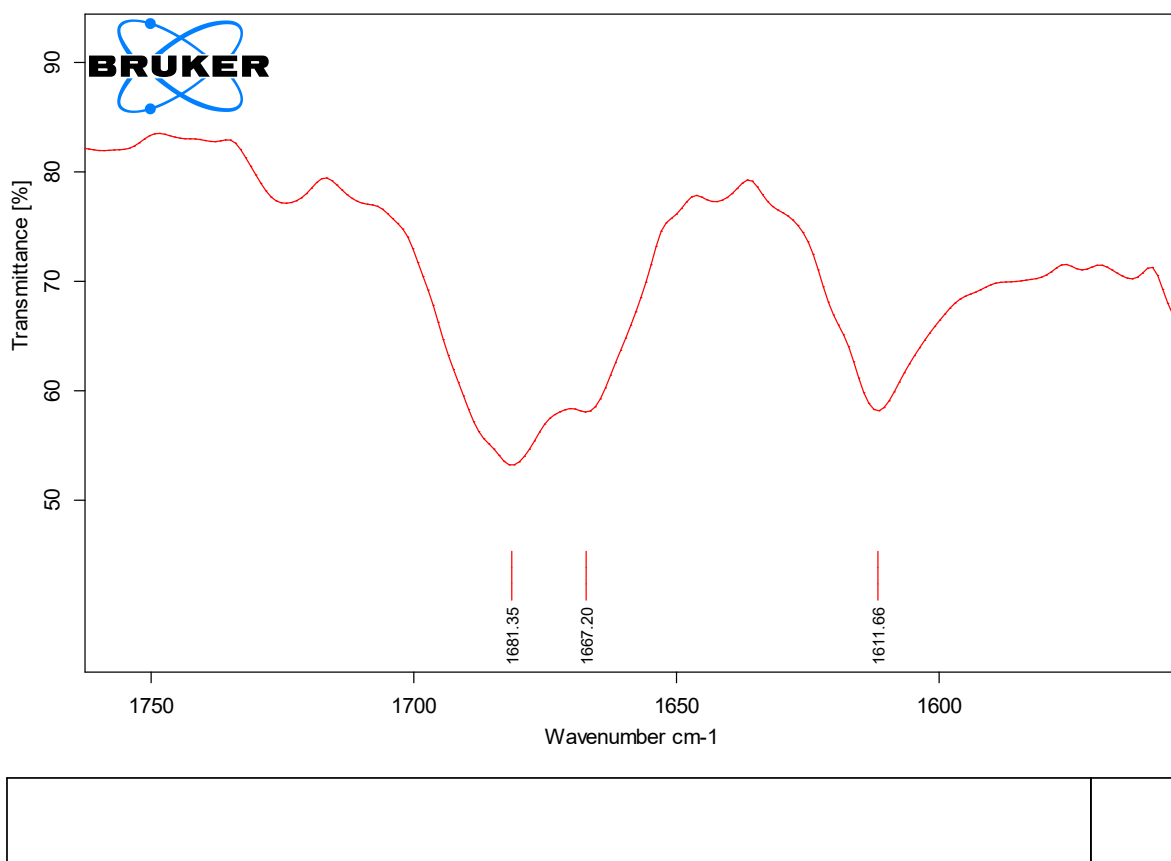
A	Observed ^a	D
Computed		Computed
1680 (92.4)	1693 vs	
1642 (4.8)	1677 w	1646 (18.9)
		1632 (2.0)
1634 (1.3)	1663 m-s	1625 (67.9)
		1608 (0.5)
1606 (0.4)		1577 (19.3)
1605 (2.2)	1611 m	1564 (37.1)
1557 (23.1)	1600 m-w	

^a w, weak; m, medium; s, strong; br, broad; v, very.

The very strong differences between the computed intensities given in black vs. those printed in different colors allow easy assignment of the experimental bands to their corresponding computed counterparts. A comparison of the colored experimental frequencies with the computed frequencies of the same color demonstrates that the latter are systematically too low, and hence can be improved by multiplying by empirical scaling factors (ESFs). ESFs obtained for each pair of frequencies of the same color, using relation

$$\text{ESF} = \nu(\text{experimental})/\nu(\text{computed})$$

vary rather moderately between 1.019 and 1.030, except the case of the pair $1693/1680 = 1.008$. Thus, for all frequencies, except the latter one, the averaged $\text{ESF} = 1.025$ was used to obtain the scaled computed frequencies collected in Table 2 and Fig. 1 in the main text.



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Fig. S2. Experimental IR spectrum of solution of **2a** in DCM

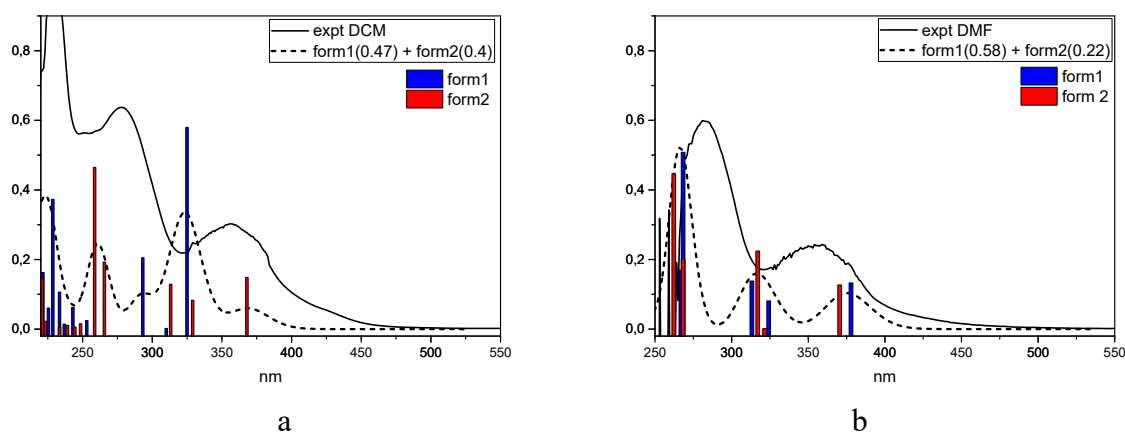


Fig. S3. Experimental electronic absorption spectra of **2a** in DCM (a) and DMF (b) and CAM-B3LYP/def2-TZVP simulated spectra of the major (red sticks) and minor (blue sticks) forms dominating in the corresponding solutions (see Table 1 in the main text for details). The simulated spectra represent the computed oscillator strengths plotted against computed wavelengths. Boltzmann weighted sums of red and blue spectra are represented as dashed lines. Boltzmann weights, ω , are taken from Table 1 in the main text.

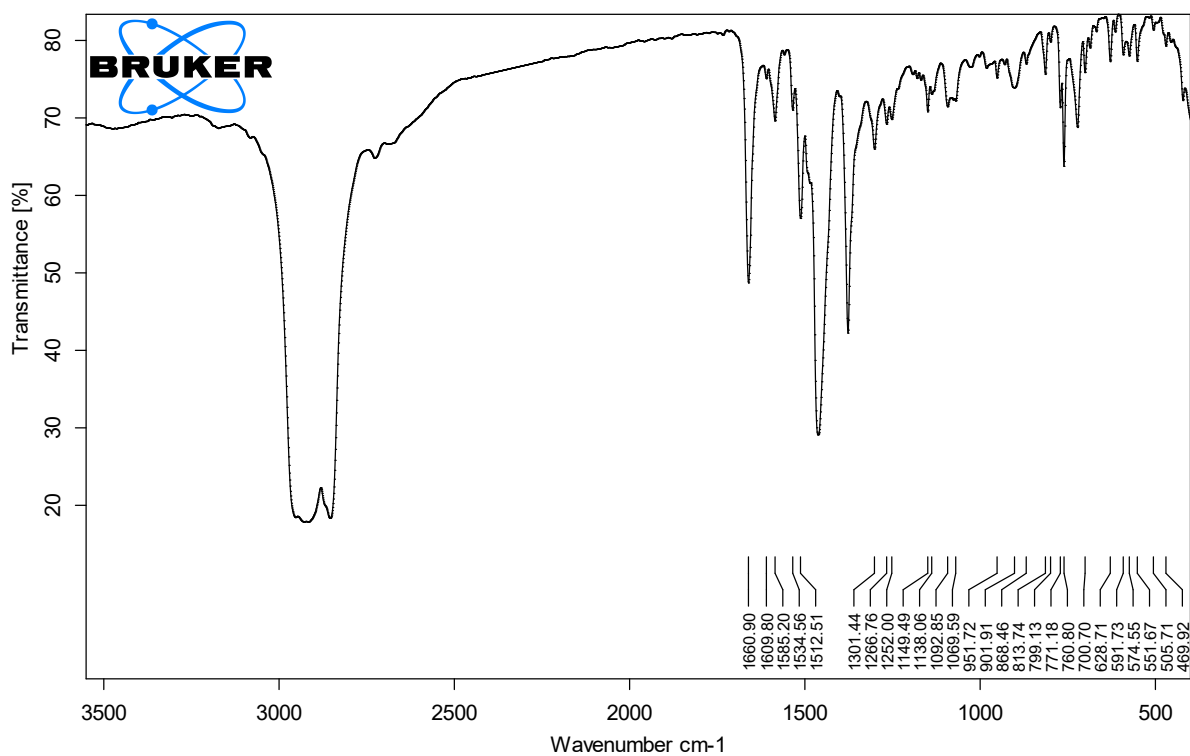


Fig. S4. Experimental IR spectrum of solid **2e** in nujol.

Crystal data for **2d**: $2(\text{C}_{21}\text{H}_{15}\text{N}_5\text{O}_3) \cdot 3(\text{C}_2\text{H}_6\text{OS})$, $M = 1005.14$, colorless crystal, Triclinic, space group P-1, $Z = 1$, $a = 8.847(3)$, $b = 12.275(4)$, $c = 13.189(4) \text{ \AA}$, $\alpha = 62.387(7)$, $\beta = 72.388(9)$, $\gamma = 73.176(8)^\circ$, $V = 1190.7(7) \text{ \AA}^3$, $\rho_{\text{calc}} = 1.402 \text{ g/cm}^3$, $\mu = 0.22 \text{ mm}^{-1}$, 9156 reflections collected (h, k, l), 4567 independent ($R_{\text{int}} 0.051$) and 3267 observed reflections [$I > 2\sigma(I)$], 335 refined parameters, $R = 0.0629$, $wR^2 = 0.1740$, max. residual electron density is $0.57 (-0.66) \text{ e \AA}^{-3}$.

Compound **2d** crystallizes as a crystal solvate with DMSO in a ratio of 1:1.5. One of the DMSO molecules is in a special position at the center of symmetry and it is disordered by two positions in an equal ratio. This is because the first DMSO molecule bonded with two molecules of the basic compound by strong $\text{NH}\dots\text{O}$ hydrogen bonds (Table 1, fig.2). In addition, these associate is stabilized by $\text{Lp}(\text{S}=\text{O})\dots\pi$ (distance O – centroid is $2.961(3) \text{ \AA}$) and $\text{O}\dots\text{S}$ interactions (distance O – S $3.322(2) \text{ \AA}$). The second DMSO molecule is bound only by $\text{CH}\dots\text{O}$ and a much weaker $\text{Lp}(\text{S}=\text{O})\dots\pi$ (distance O – centroid is $3.14(1) \text{ \AA}$) interactions. The further packing in the crystal is formed due to stacking interactions of large conjugate diarylhydrazineylidene fragments and represents infinite alternating layers consisting of compound 1 and DMSO located parallel to the plane a_0c and related to each other by van der Waals interactions (fig.3)

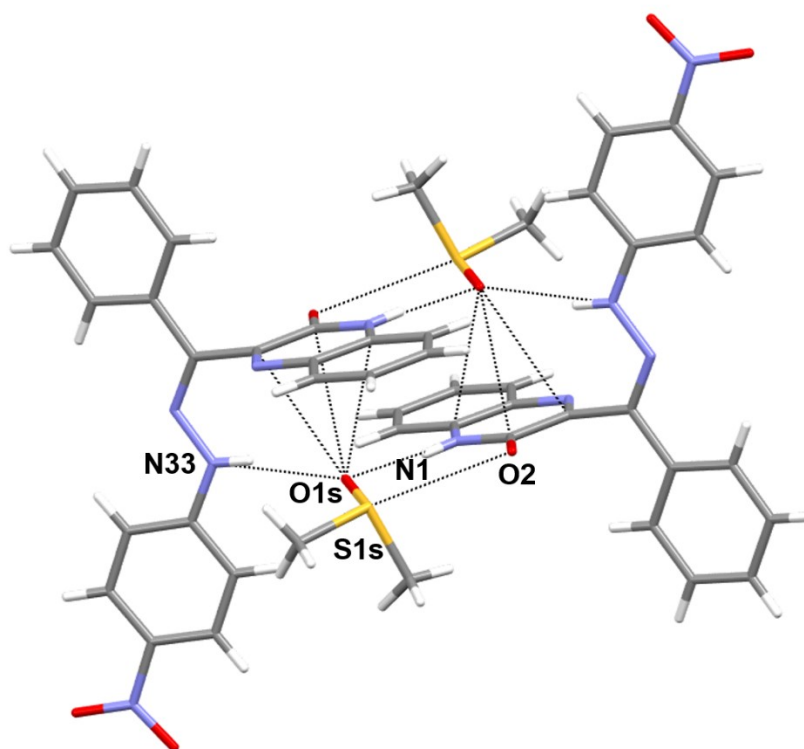


Figure S5. H-bonded associate in crystal of compound **2d**.

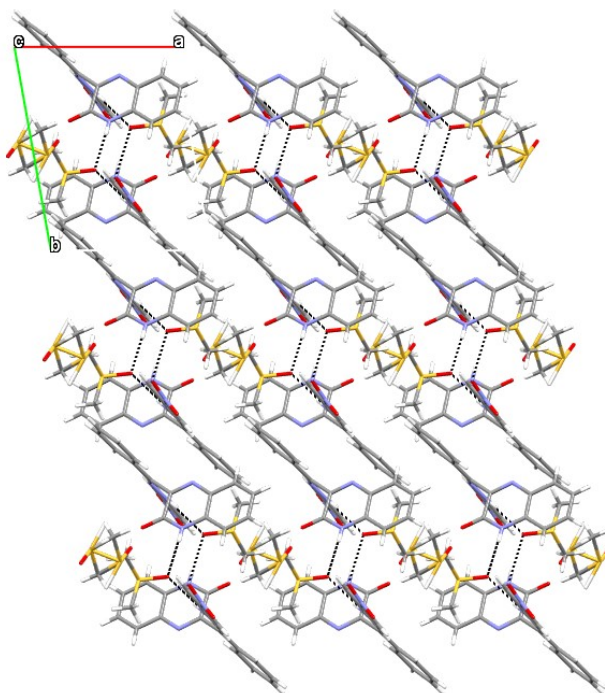


Figure S6. Crystal packing of compound **2d**.

Table S3. H-bonds in crystals of investigated compound.

H-bond	D–H, Å	H...A, Å	D...A, Å	D–H...A, °
N1–H1...O1S	0.78(4)	2.12(4)	2.884(4)	172(4)
N33–H33...O1S	0.81(4)	2.14(4)	2.926(4)	164(4)
C1S–H1SC...O2	0.96	2.47	3.348(5)	152
C7–H7...O2S	0.93	2.51	3.433(9)	173
C3S–H3SA...O2S	0.96	1.61	2.229(13)	118
C39–H39...O1S	0.93	2.59	3.348(4)	138

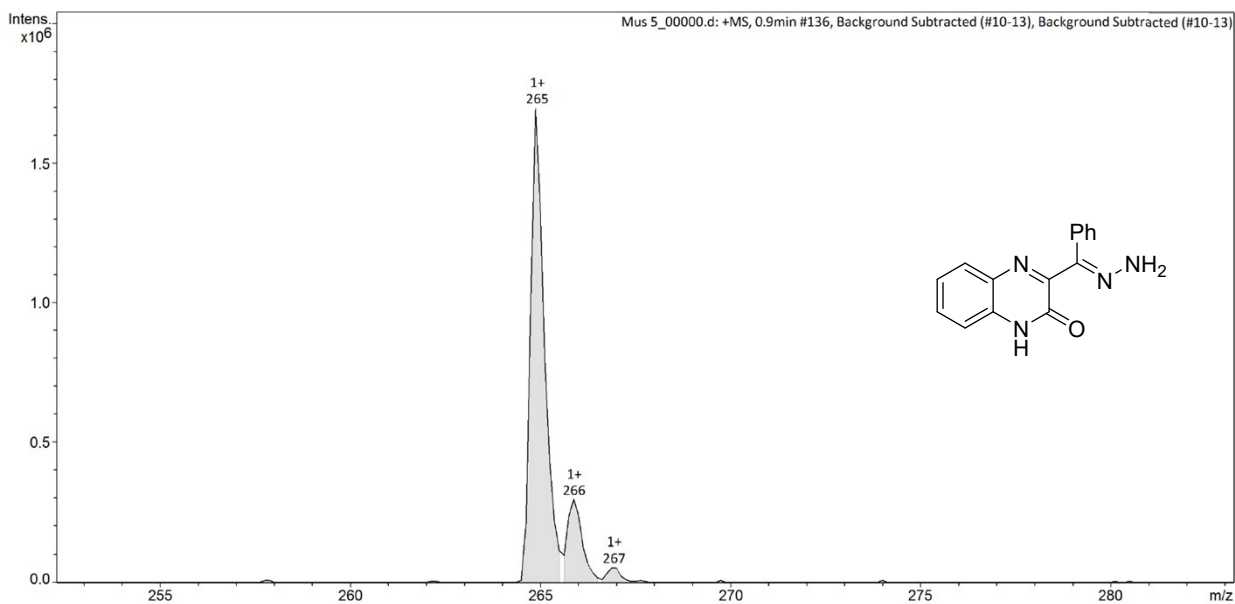


Fig. S7. MS (ESI), m/z: $[M + H]^+$ 265. Molecular weight: 264.29.

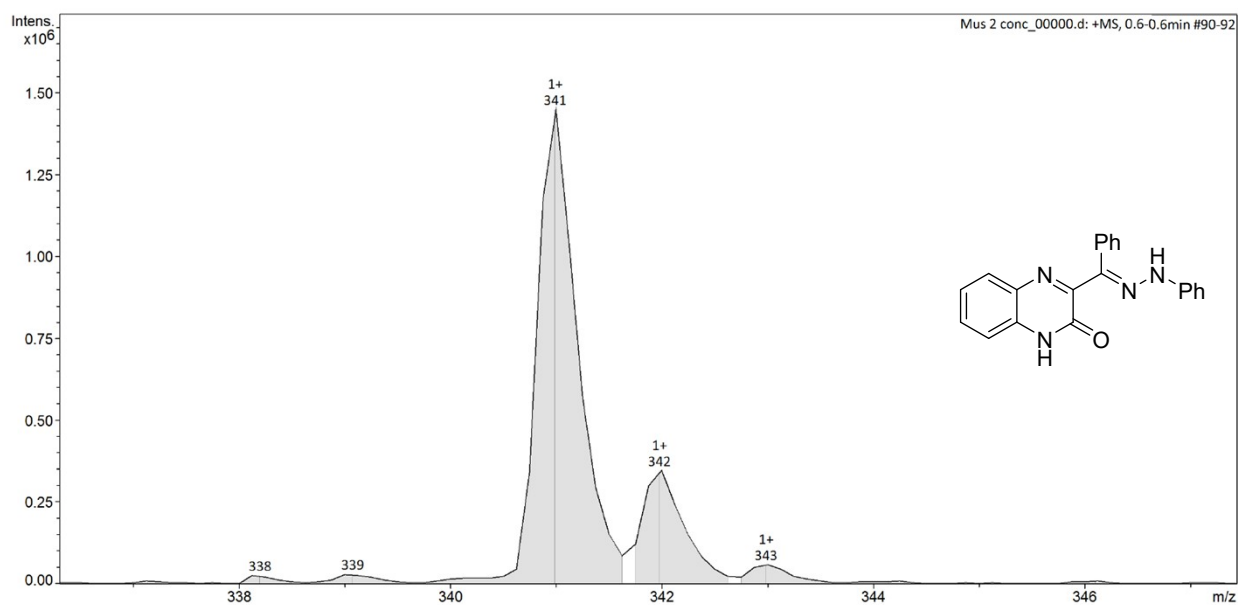


Fig. S8. MS (ESI), m/z: $[M + H]^+$ 341. Molecular weight: 340.39.

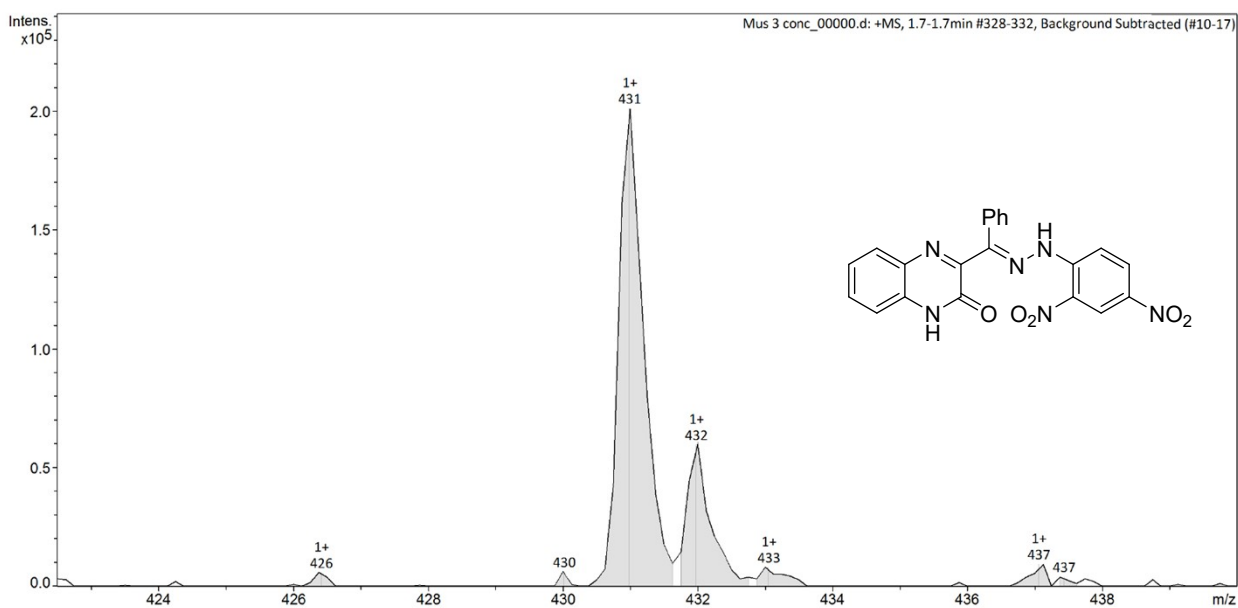


Fig. S9. MS (ESI), m/z : $[M + H]^+$ 431. Molecular weight: 430.38.

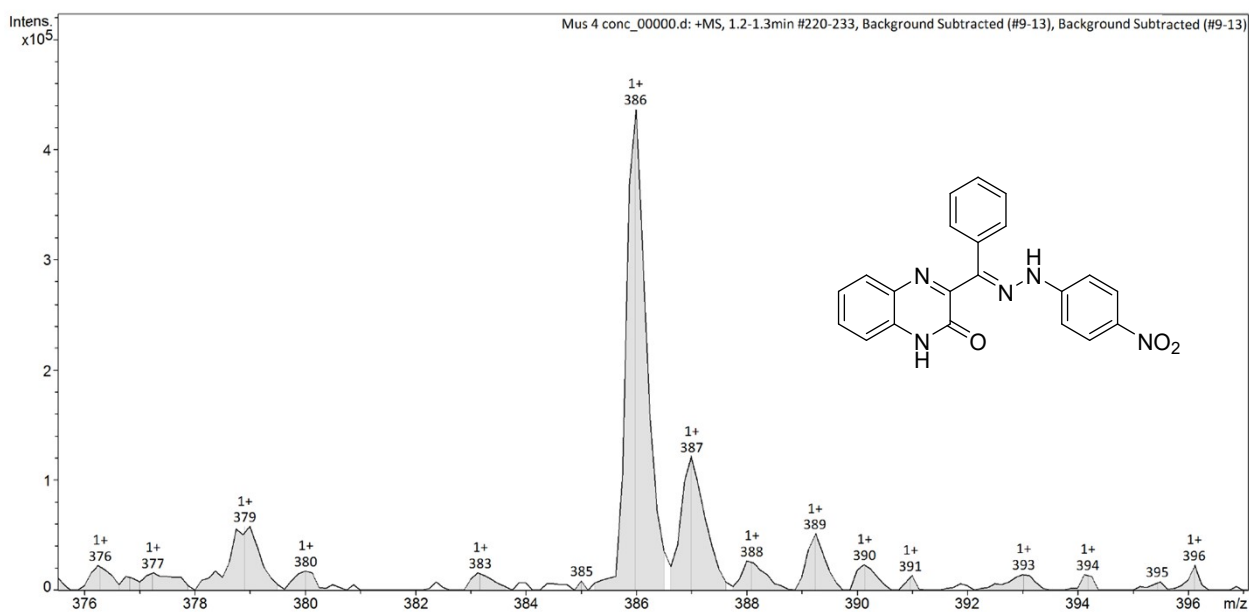


Fig. S10. MS (ESI), m/z : $[M + H]^+$ 386. Molecular weight: 385.38.

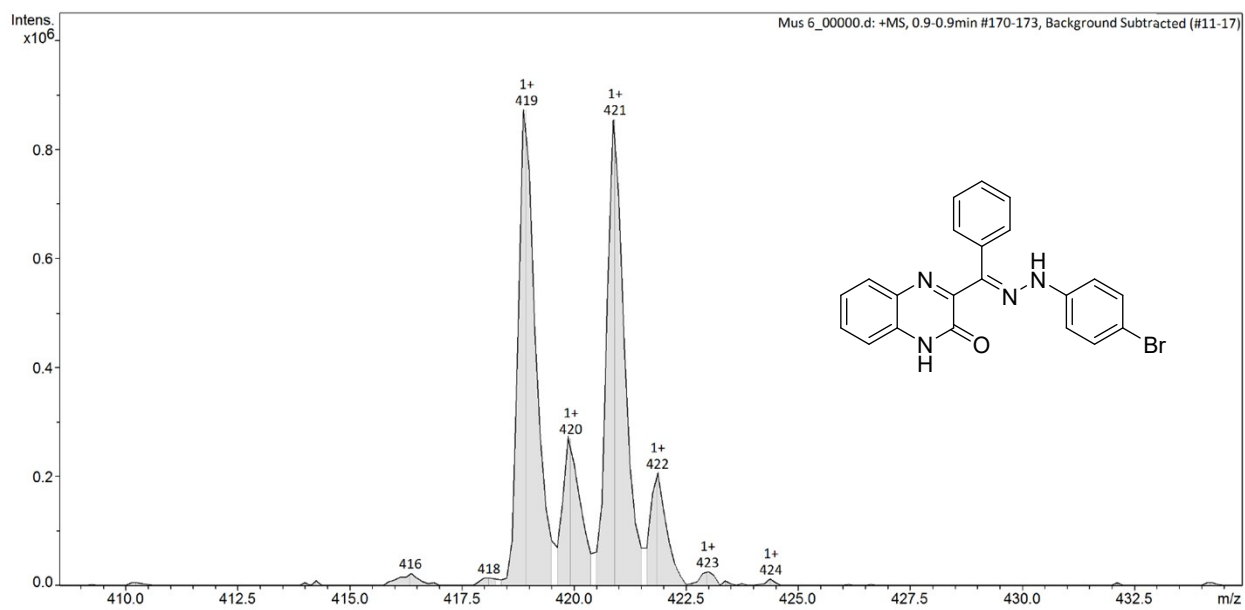


Fig. S11. MS (ESI), m/z: [M + H]⁺ 419. Molecular weight: 418.28.

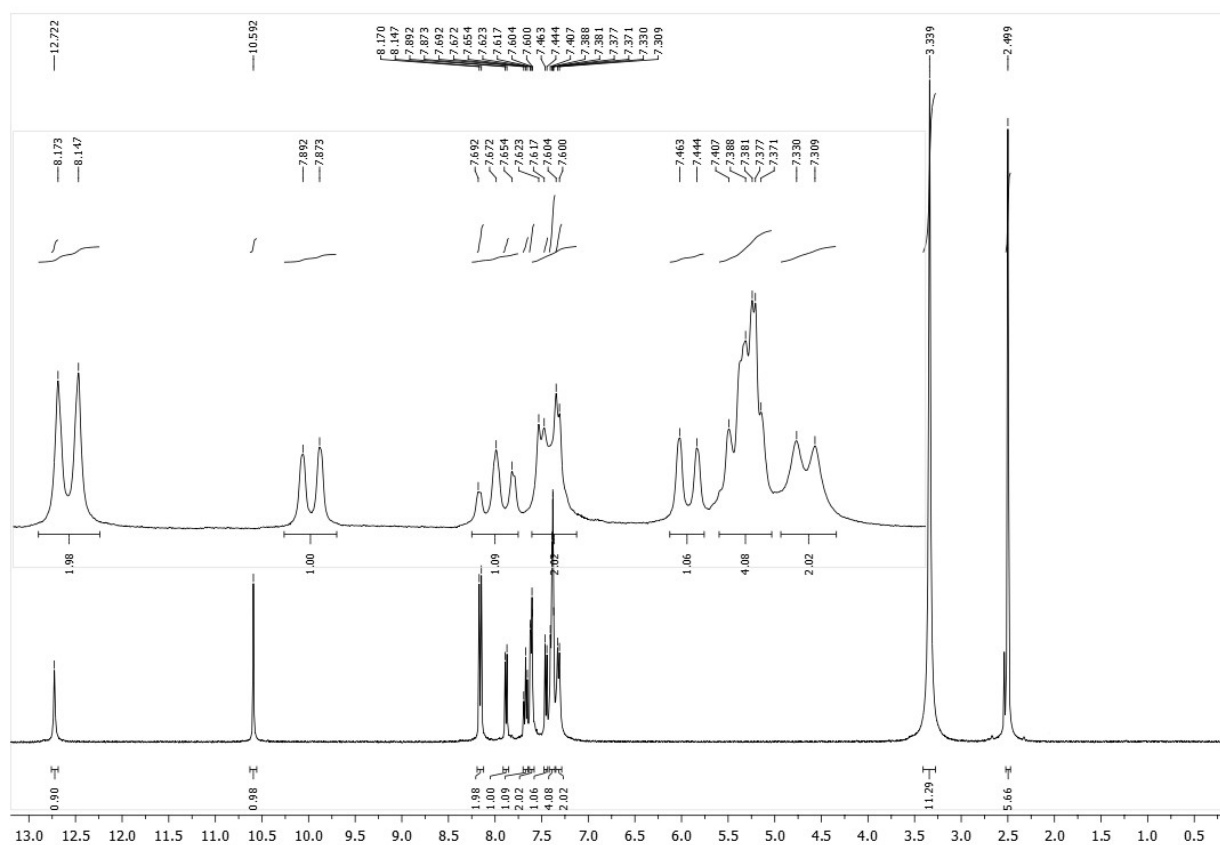


Fig. S12. 1D ^1H NMR spectrum of **2d** in DMSO-d_6 at $T = 303$ K. Chemical shifts are given in ppm (Bruker spectrometer at 500 MHz).

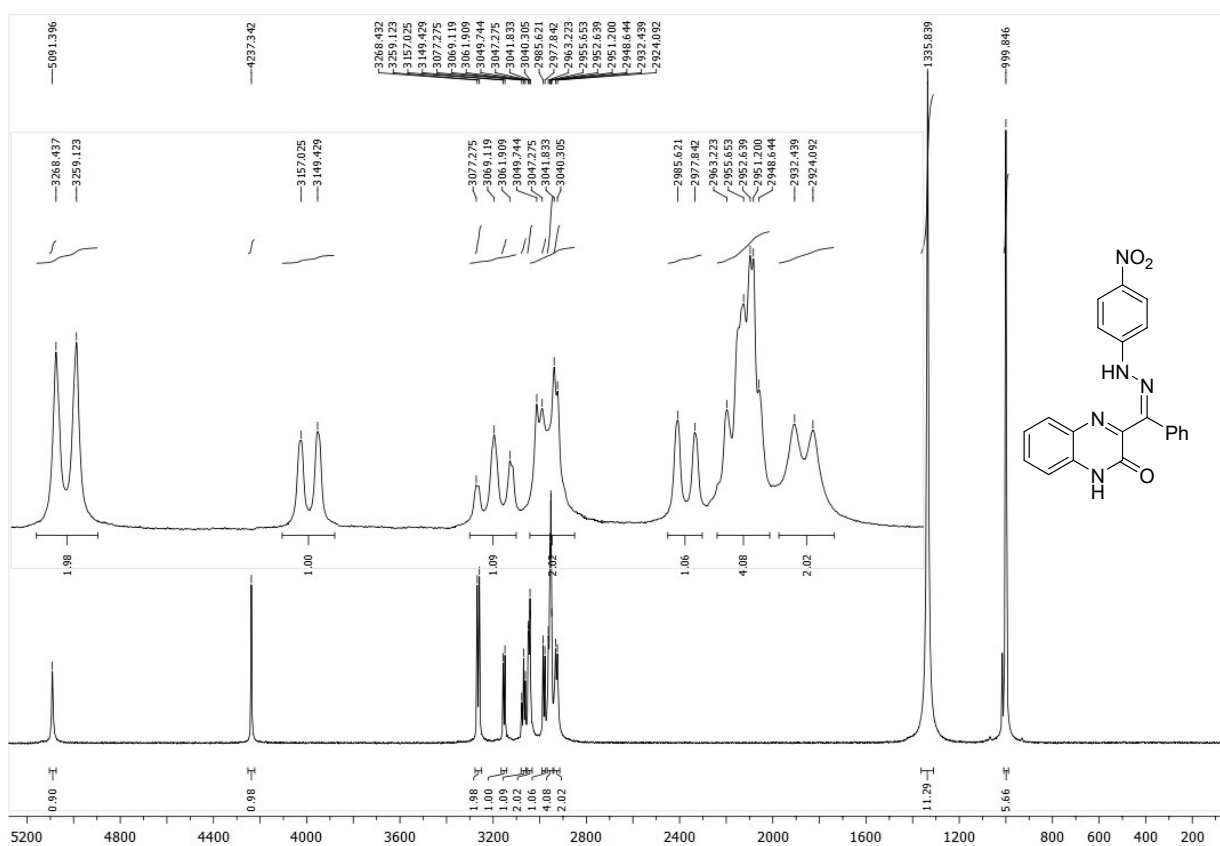


Fig. S13. 1D ^1H NMR spectrum of **2d** in DMSO-d_6 at $T = 303$ K. Chemical shifts are given in Hz (Bruker spectrometer at 500 MHz).

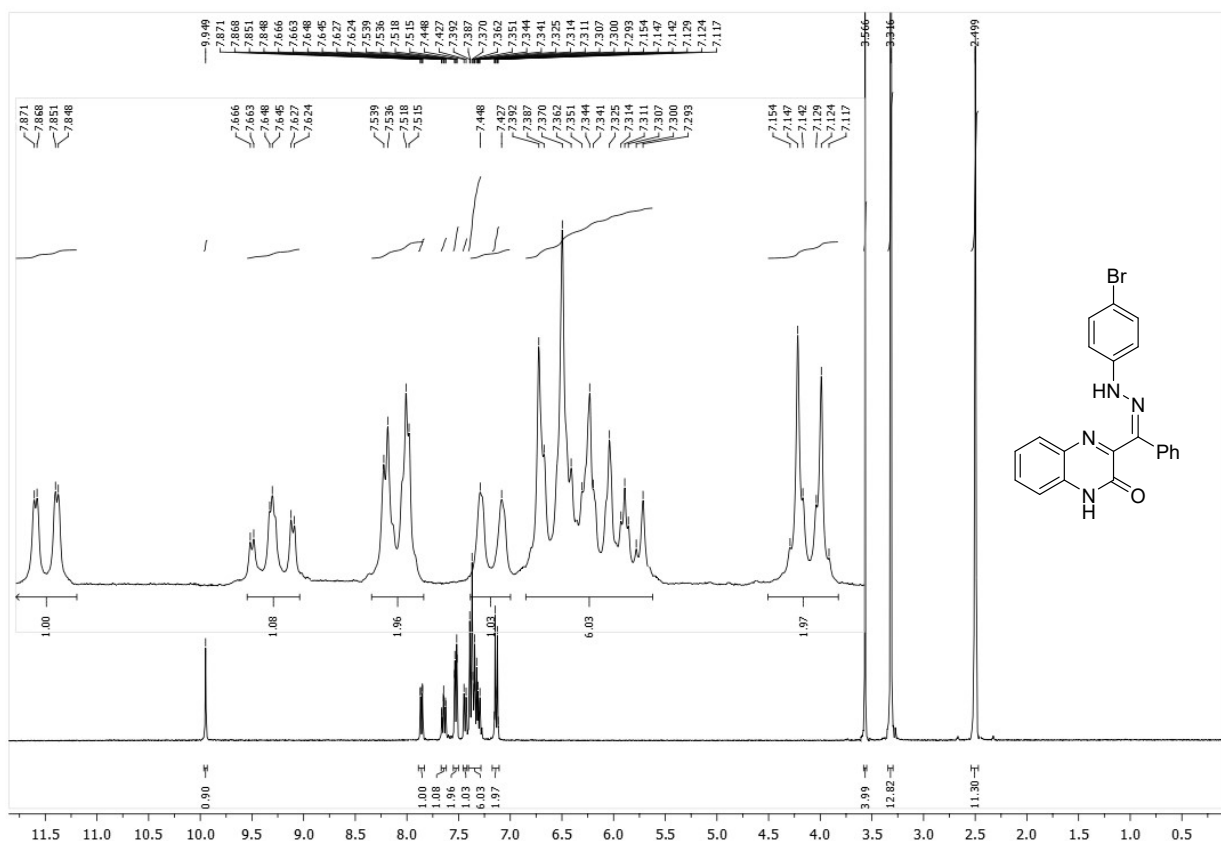


Fig. S14. 1D ^1H NMR spectrum of **2e** in DMSO-d_6 at $T = 303$ K. Chemical shifts are given in ppm (Bruker spectrometer at 500 MHz).

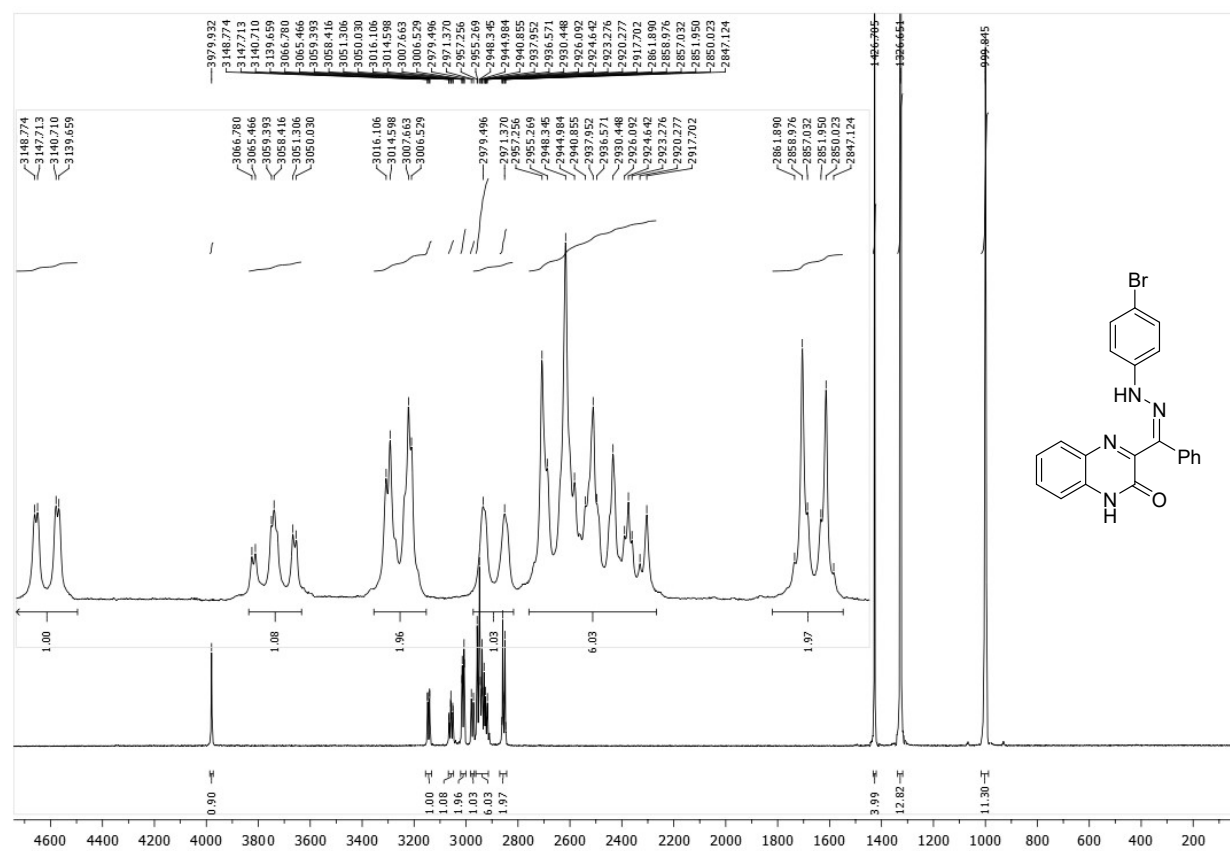


Fig. S15. 1D ^1H NMR spectrum of **2e** in DMSO-d_6 at $T = 303$ K. Chemical shifts are given in Hz (Bruker spectrometer at 500 MHz).

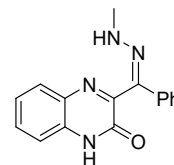
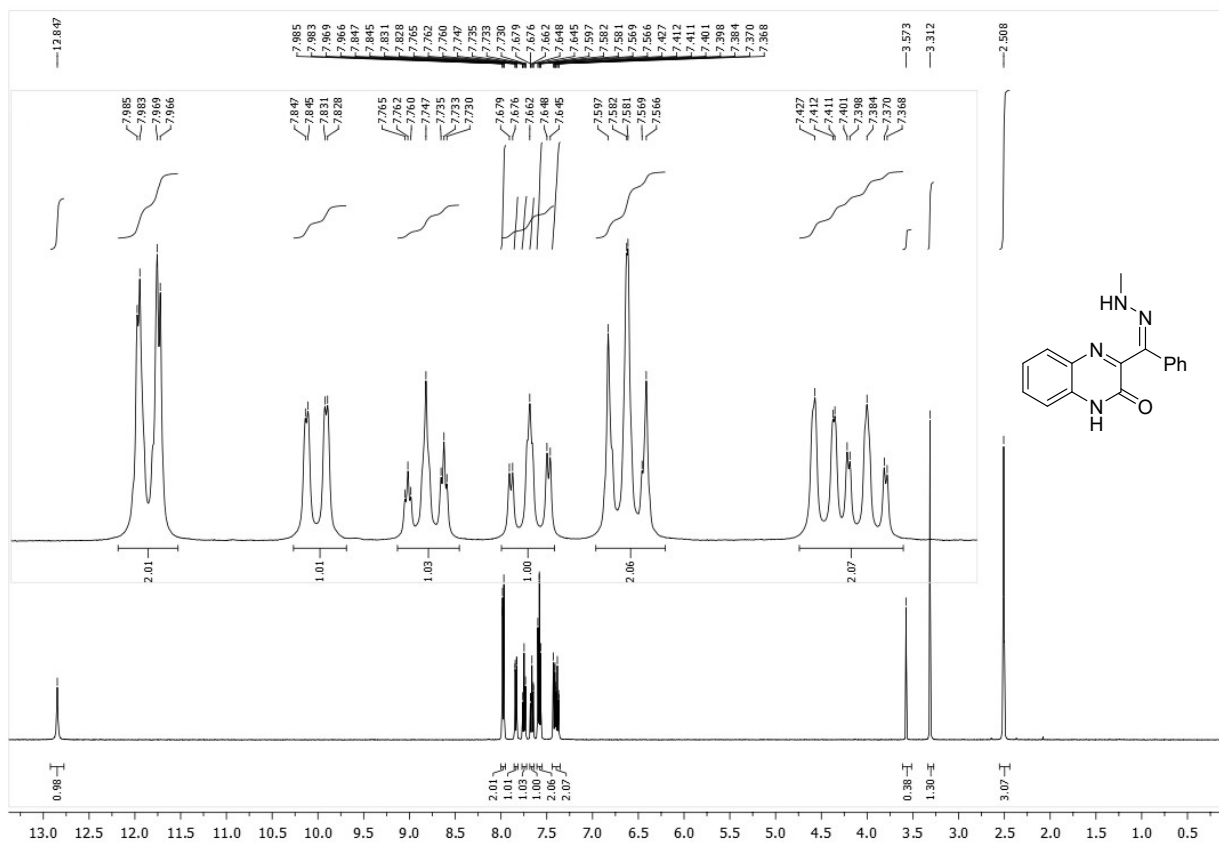


Fig. S16. 1D ^1H NMR spectrum of **2f** in DMSO-d_6 at $T = 303$ K. Chemical shifts are given in ppm (Bruker spectrometer at 500 MHz).

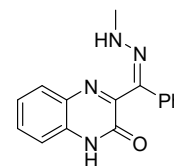
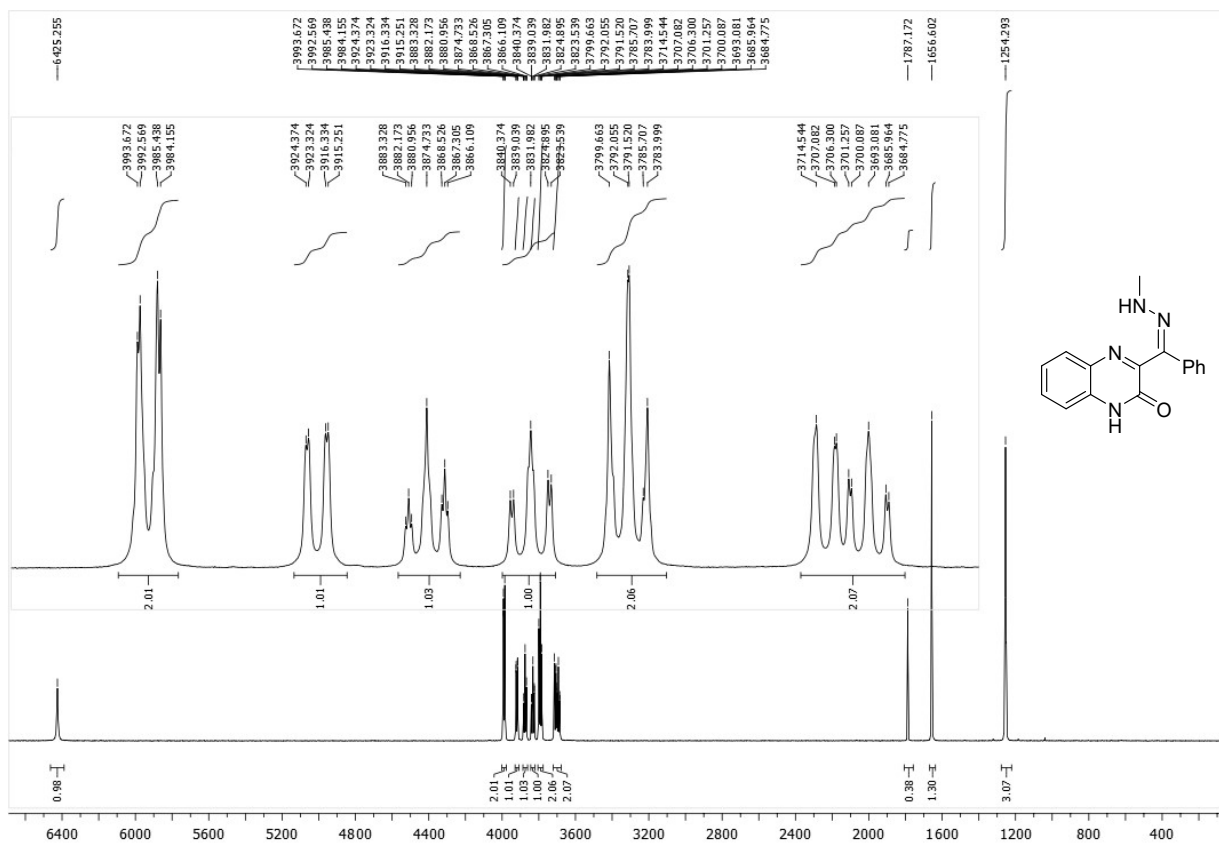


Fig. S17. 1D ^1H NMR spectrum of **2f** in DMSO-d_6 at $T = 303$ K. Chemical shifts are given in Hz (Bruker spectrometer at 500 MHz).