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Uncommon condensations of 1,2,3-triketone 2-oximes with *o*-phenylenediamine

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GENERAL INFORMATION

1D and 2D NMR spectra of compounds **6, 7b,c, 8, 10** were recorded at 20 °C on Bruker Avance 600 (600 MHz) spectrometer and Varian UNITY-300 spectrometer. Chemical shifts of nuclei ^{1}H (δ, ppm) and ^{13}C were measured relatively the residual signals of deuteron solvent (δ = 2.49 ppm for protons and 39.5 ppm for carbon nuclei). Mass spectra (EI, 70 eV) were obtained on Finnigan MAT INCOS-50 and Shimadzu GCMS-QP2010SE GC-MS instruments using direct input of sample. IR spectra were recorded on Varian Excalibur 3100 FT-IR spectrometer.

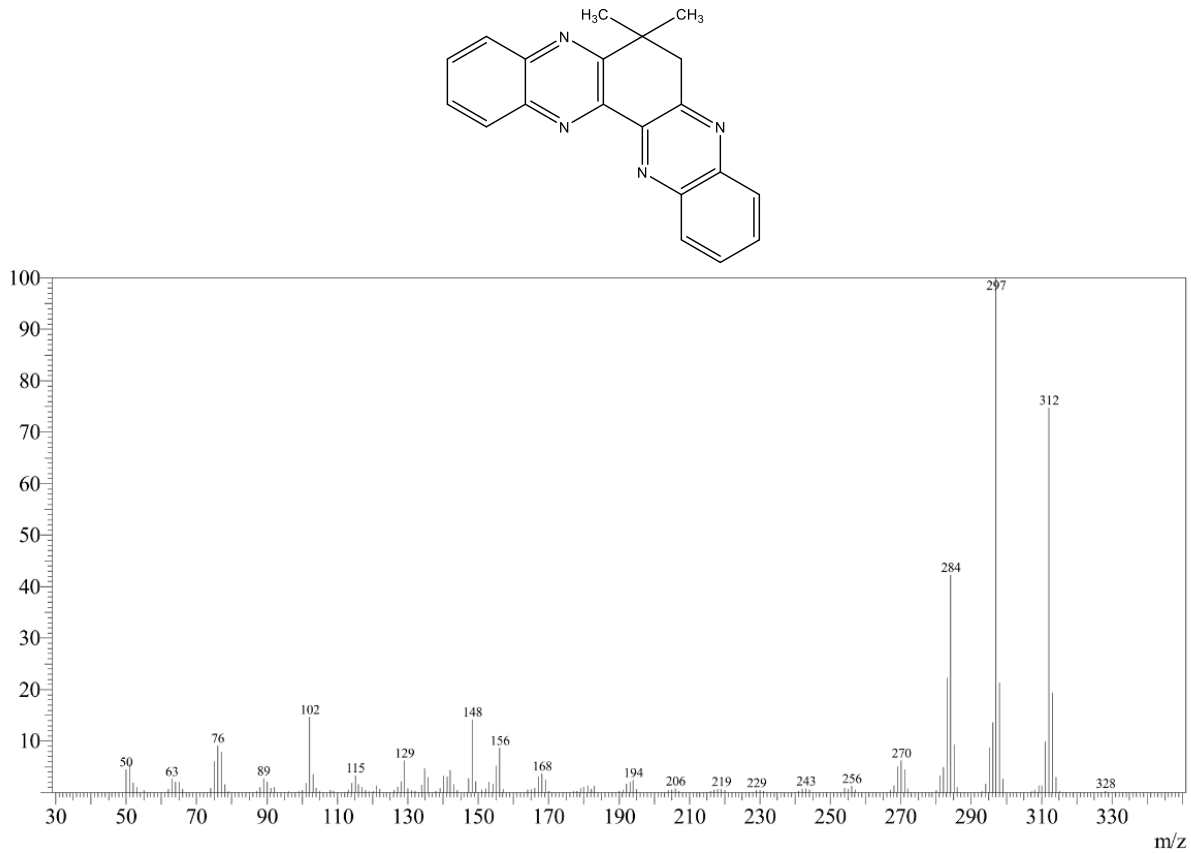


Figure S1. Mass-spectrum of 6,6-dimethyl-6,7-dihydroquinoxalino[2,3-*a*]phenazine **6**, were obtained on Shimadzu GCMS-QP2010 SE GC-MS instrument.

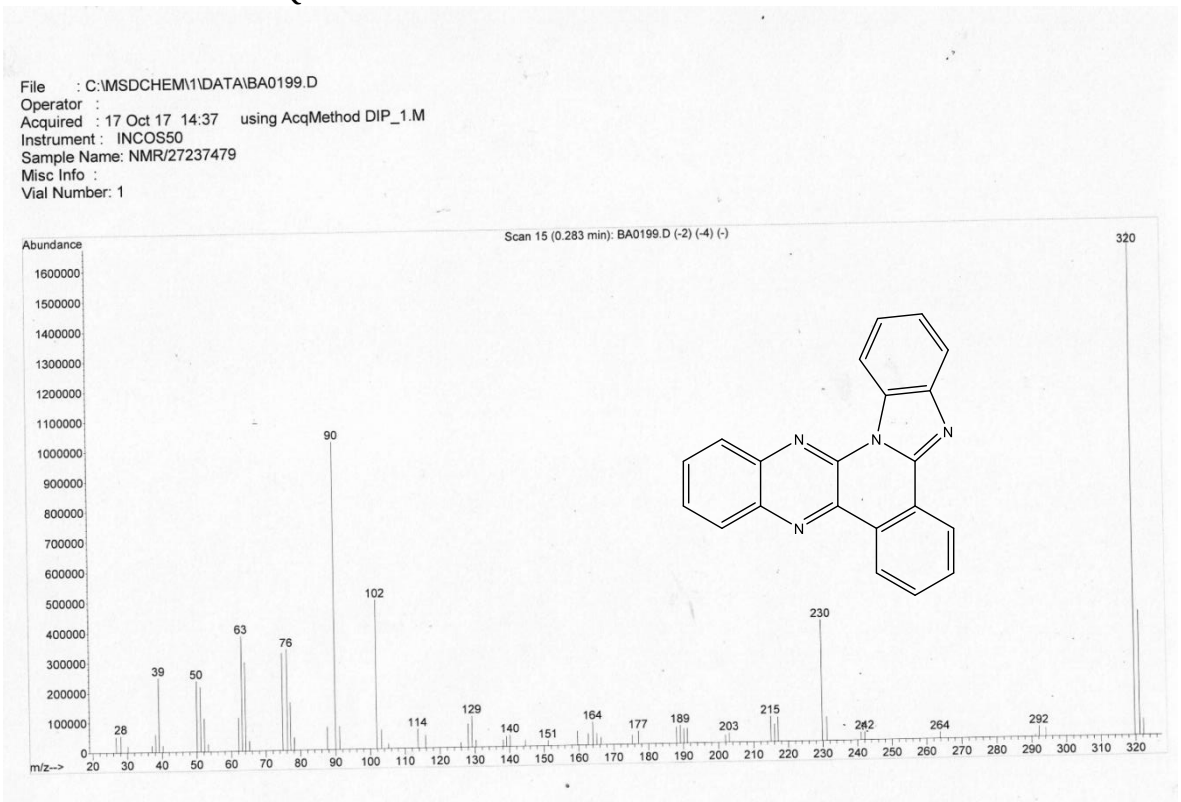


Figure S2. Mass-spectrum of benzimidazo[2',1':1,2]isoquino[3,4-*b*]quinoxaline **8**, were obtained on MAT INCOS-50 instrument.

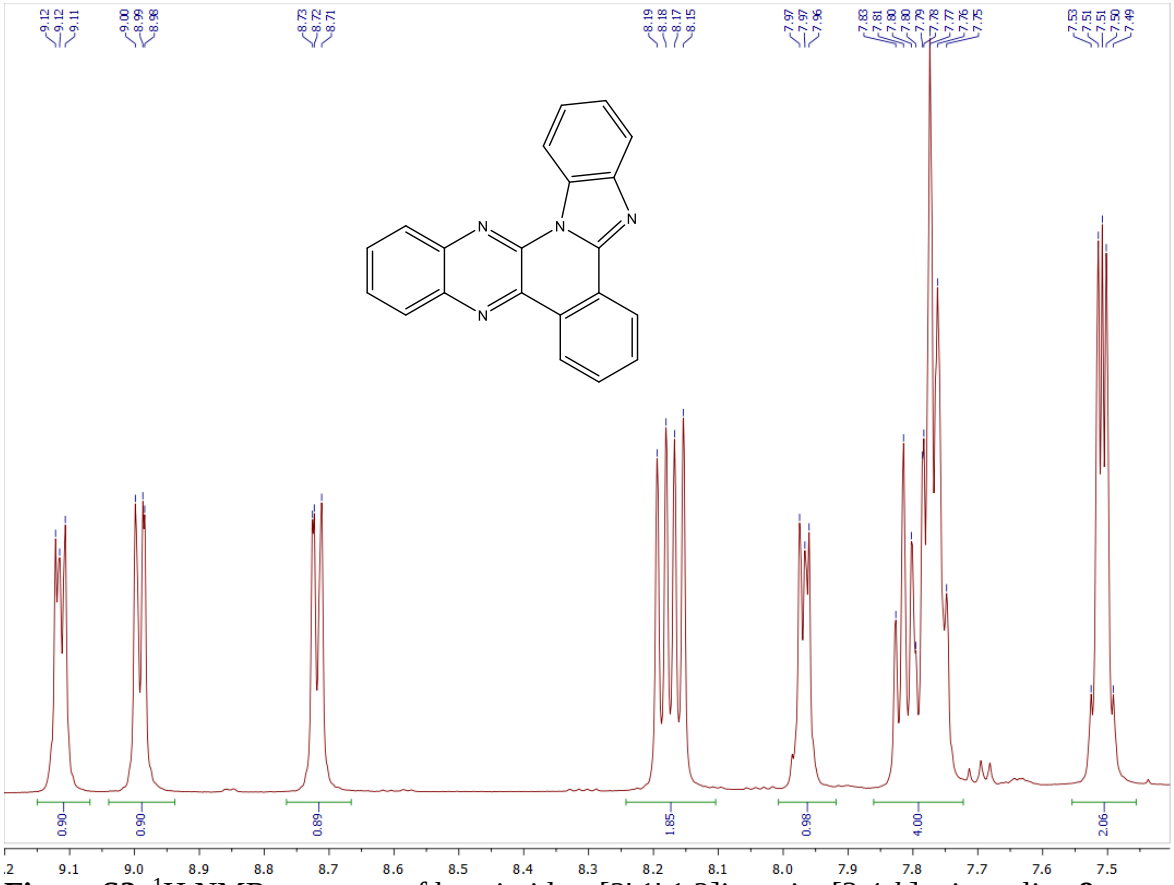


Figure S3. ^{1}H NMR spectrum of benzimidazo[2',1':1,2]isoquino[3,4-*b*]quinoxaline **8** recorded at 600 MHz (5 mg in $CDCl_3$).

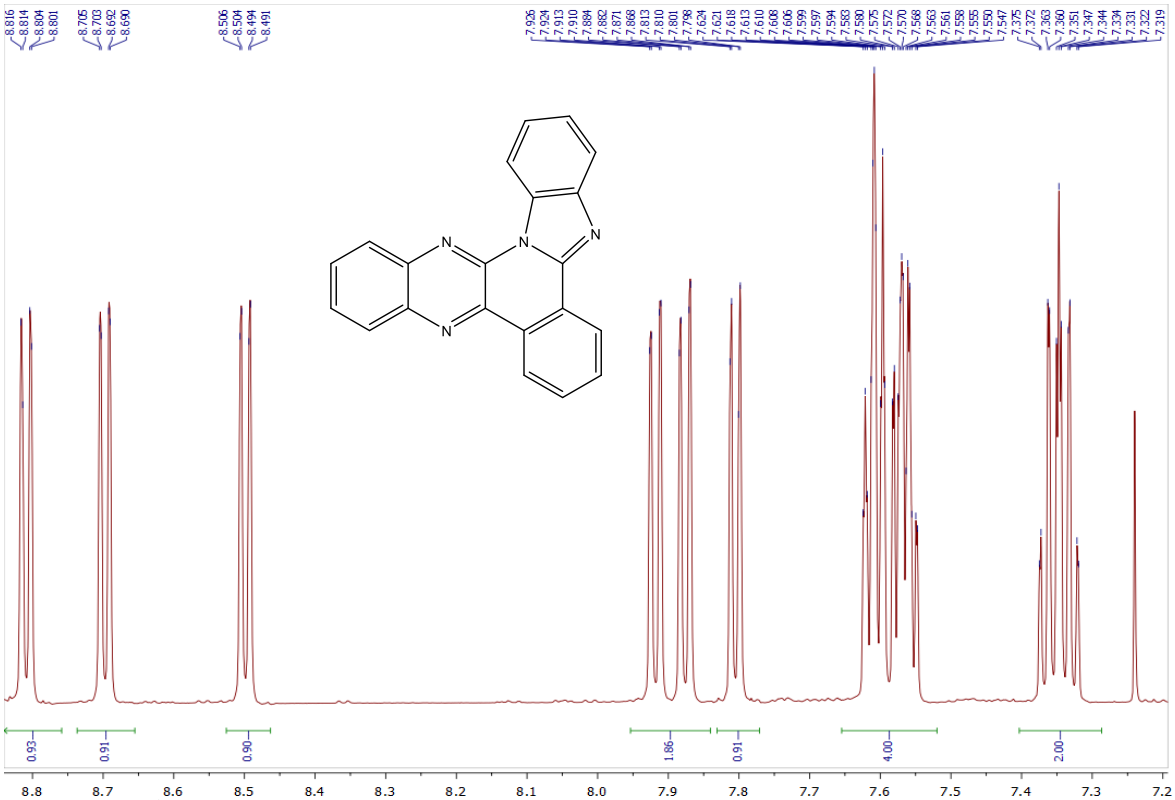


Figure S4. ^{1}H NMR spectrum of benzimidazo[2',1':1,2]isoquino[3,4-*b*]quinoxaline **8** recorded at 600 MHz (20 mg in $CDCl_3$).

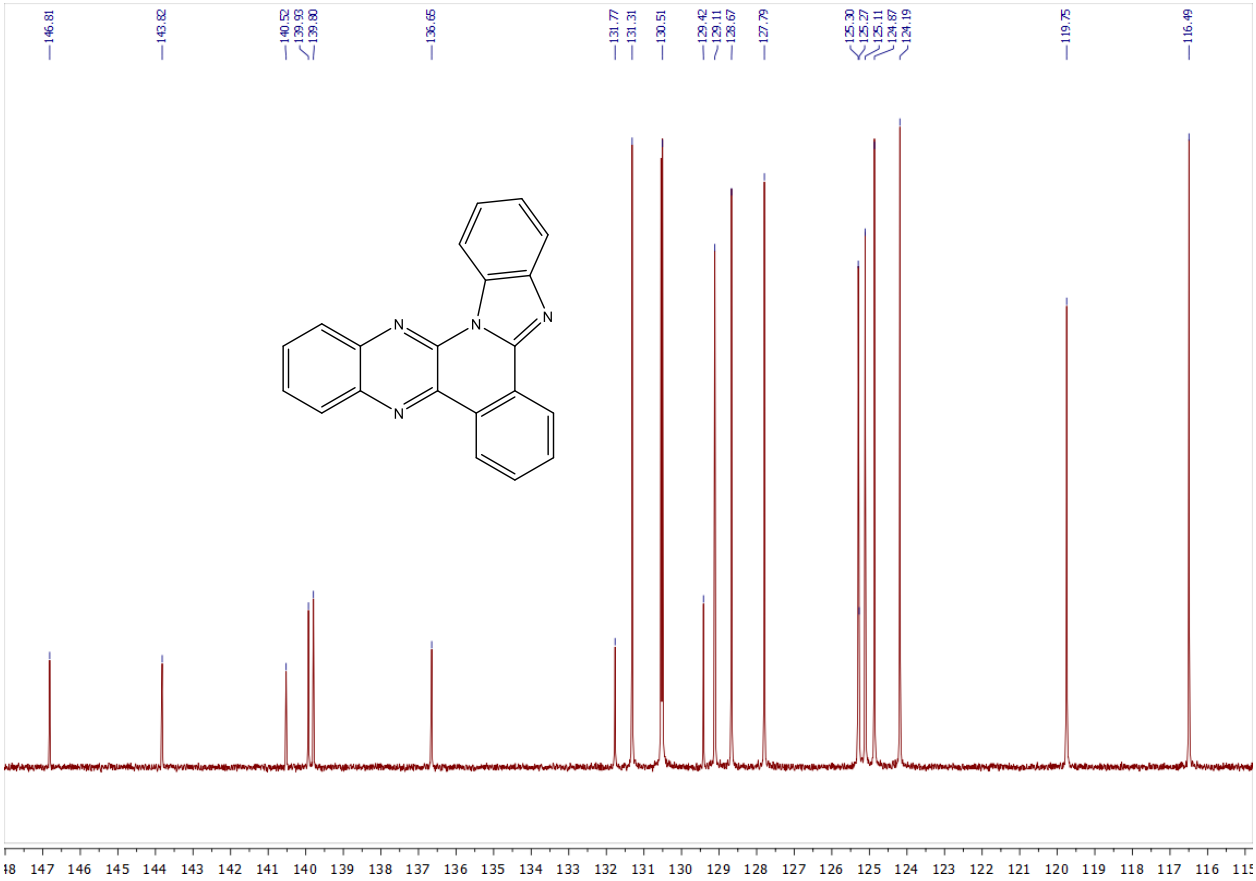


Figure S5. ^{13}C NMR spectrum of benzimidazo[2',1':1,2]isoquino[3,4-*b*]quinoxaline **8** recorded at 150 MHz (20 mg in $CDCl_3$).

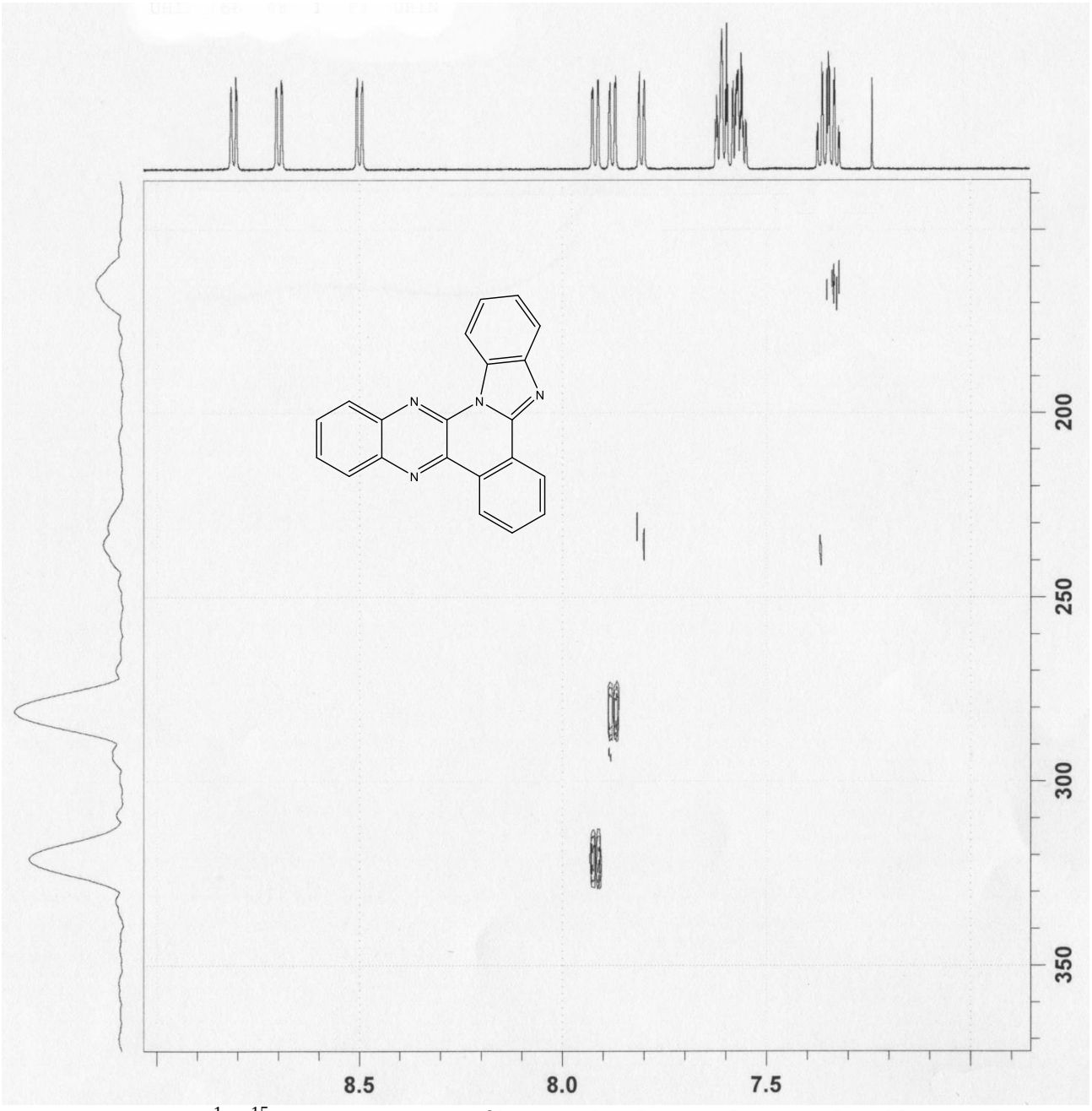
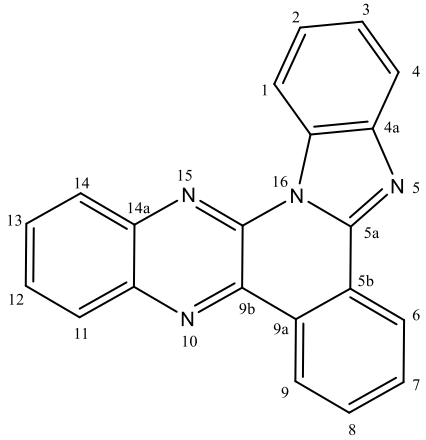


Figure S6. HMBC ^{1}H-^{15}N NMR spectrum of benzimidazo[2',1':1,2]isoquino[3,4-*b*]quinoxaline **8** recorded at 150 MHz (DMSO).

Table S1. Chemical shifts in ^{1}H, ^{13}C, ^{15}N NMR spectra for compound **8** (20 mg in $CDCl_3$).



Compound	Nucleus	1	2	3	4	4a	5(^{15}N)	5a	5b	6	7	8	9
8	^{1}H	8.80	7.33	7.36	7.80					8.50	7.59	7.56	8.70
	$^{13}C/^{15}N$	116.51	124.20	124.88	119.76	143.84	236.20	146.83	125.29	125.31	130.56	130.52	125.13

Compound	Nucleus	9a	9b	10(^{15}N)	10a	11	12	13	14	14a	15(^{15}N)	15a	16(^{15}N)	16a
8	^{1}H					7.92	7.60	7.57	7.88					
	$^{13}C/^{15}N$	129.43	136.66	321.10	139.81	129.13	128.68	131.33	127.81	139.94	281.20	140.54	165.30	131.78

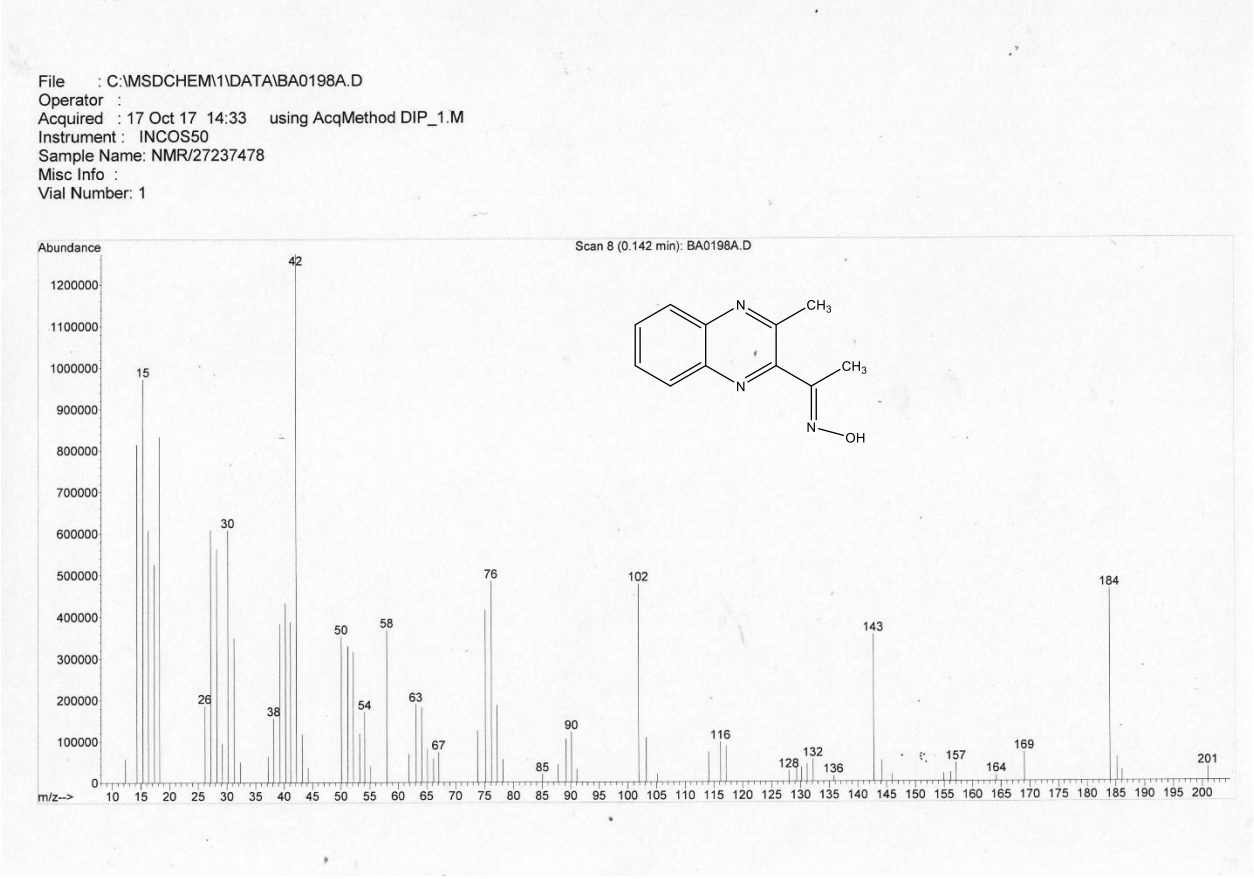


Figure S7. The mass-spectrum of 2-acetyl-3-methylquinoxaline oxime **10** were obtained on Finhigan MAT INCOS-50 instrument.

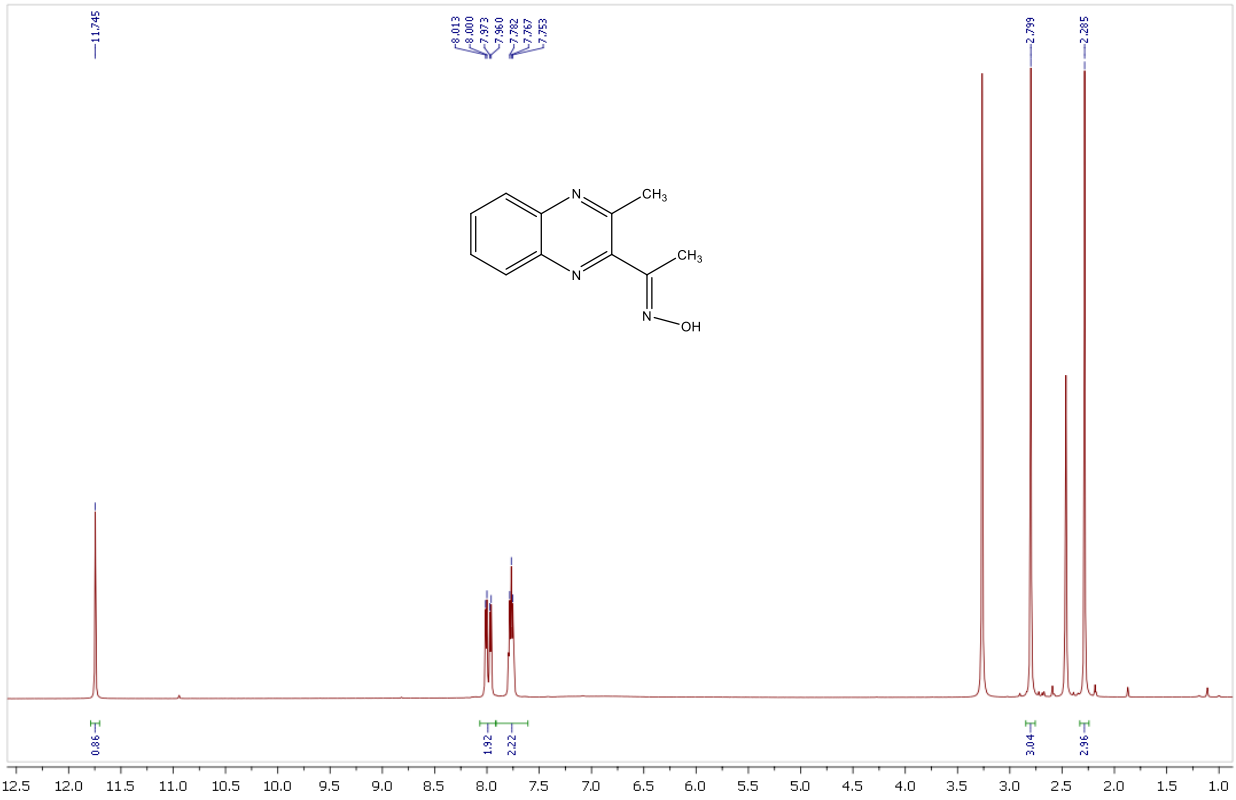


Figure S8. ^{1}H NMR spectrum of 2-acetyl-3-methylquinoxaline oxime **10** recorded at 600 MHz ($CDCl_3$).

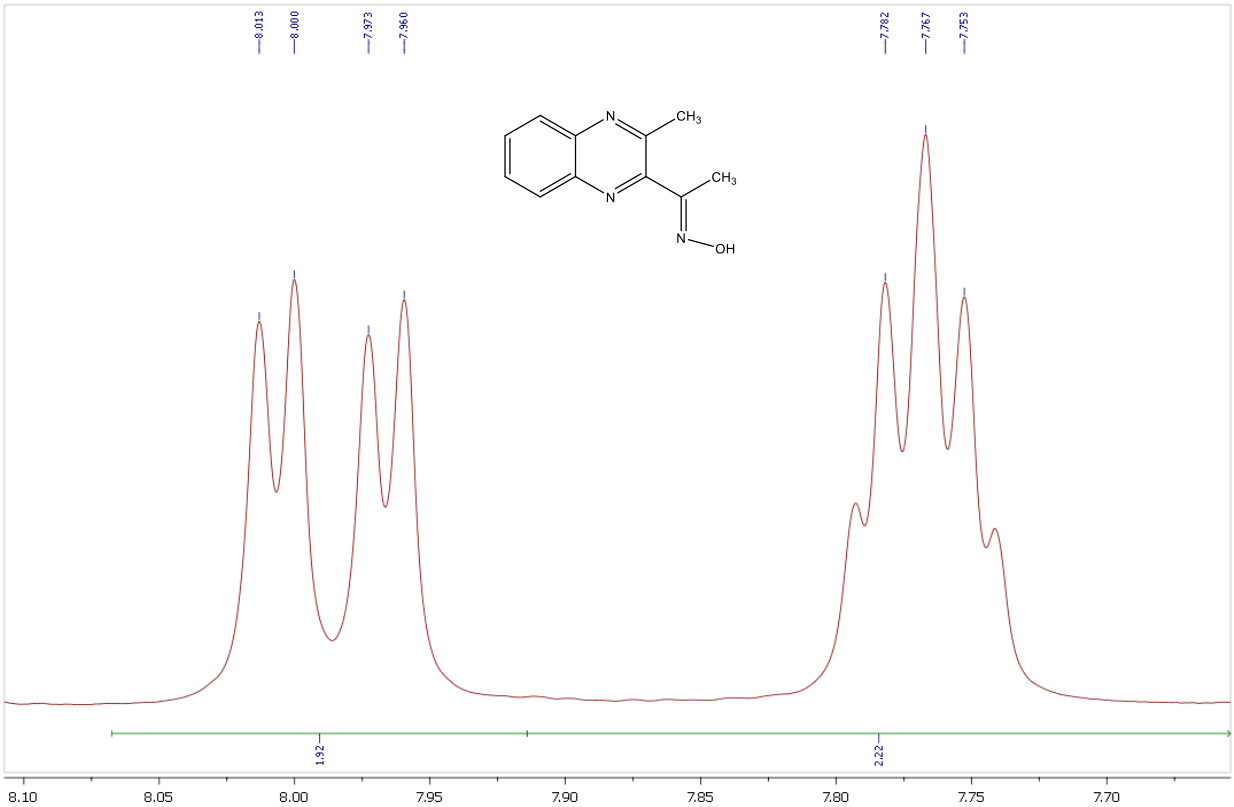


Figure S9. The aromatic protons in ^{1}H NMR spectrum of 2-acetyl-3-methylquinoxaline oxime **10** recorded at 600 MHz ($CDCl_3$).

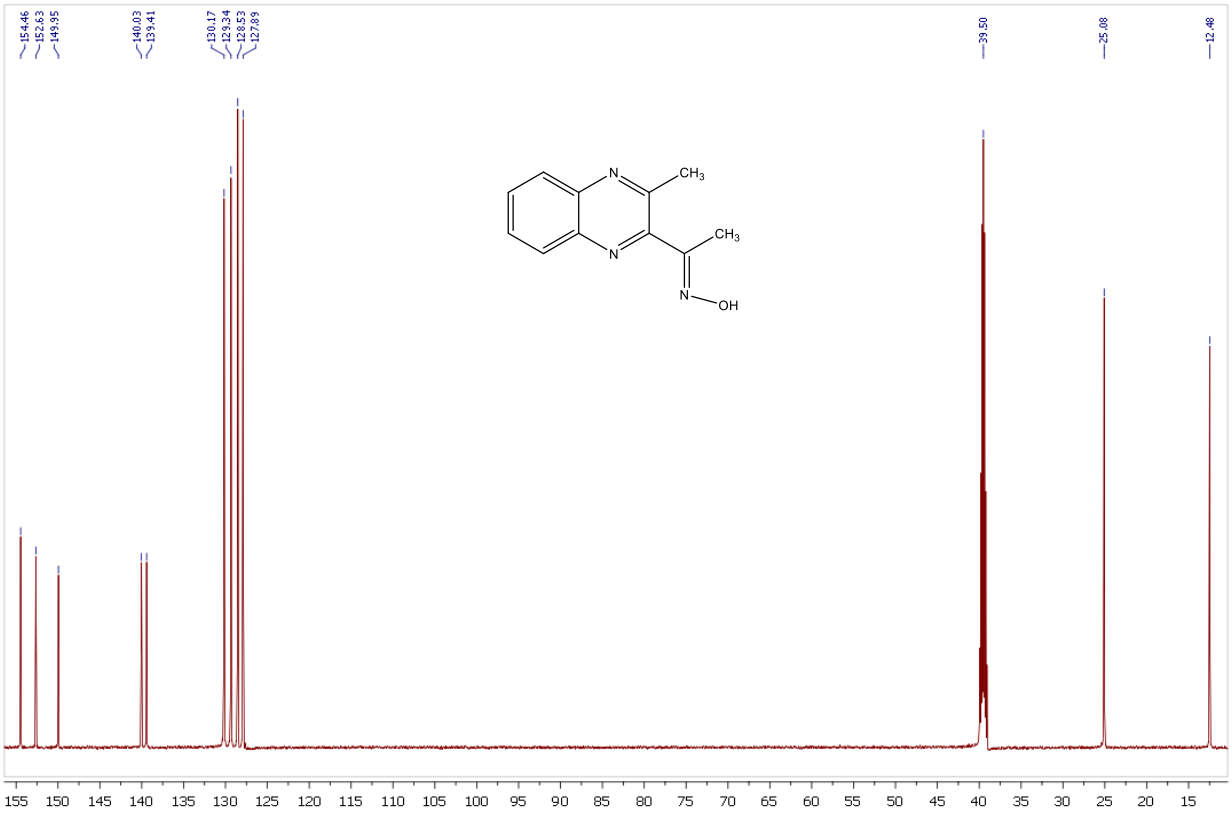


Figure S10. ^{13}C NMR spectrum of 2-acetyl-3-methylquinoxaline oxime **10** recorded at 150 MHz (30 mg in DMSO-d_6).

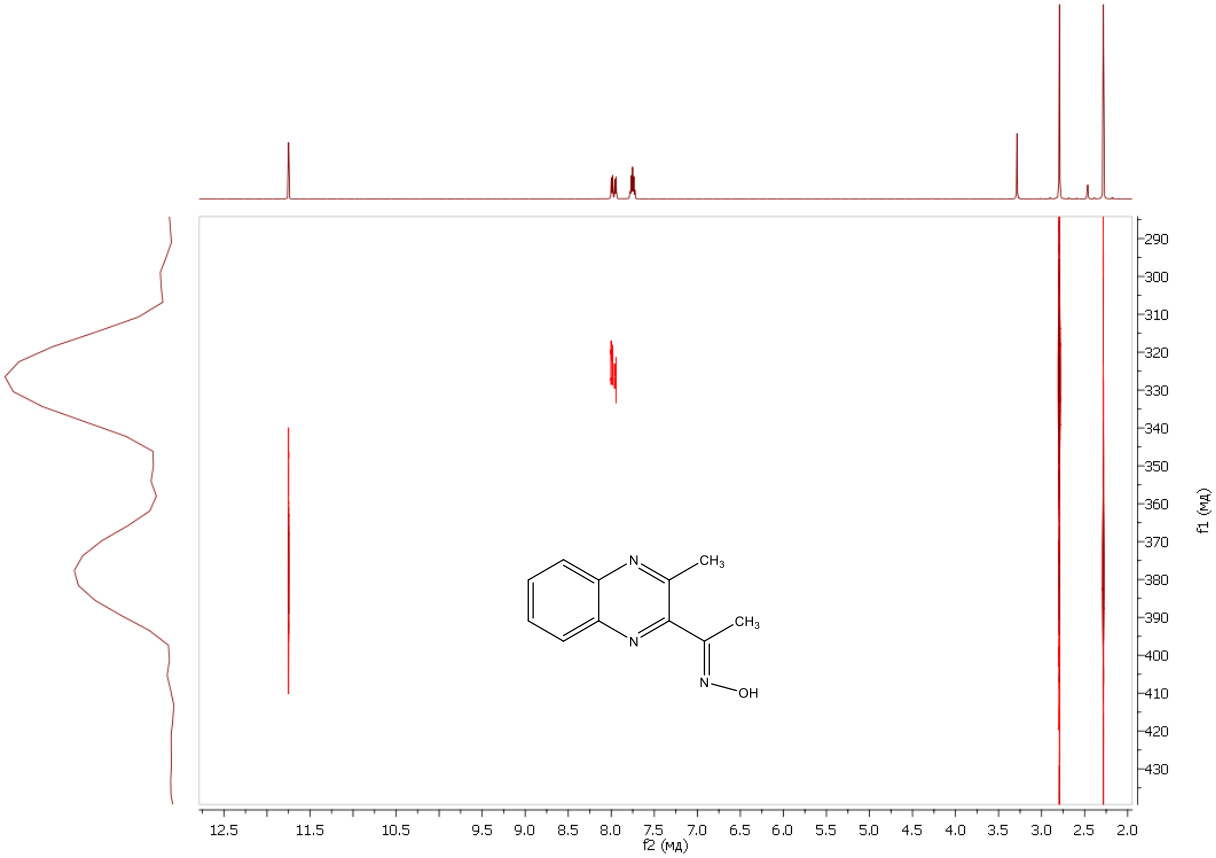


Figure S11. ^{1}H-^{15}N HMBC spectrum of 2-acetyl-3-methylquinoxaline oxime **10**

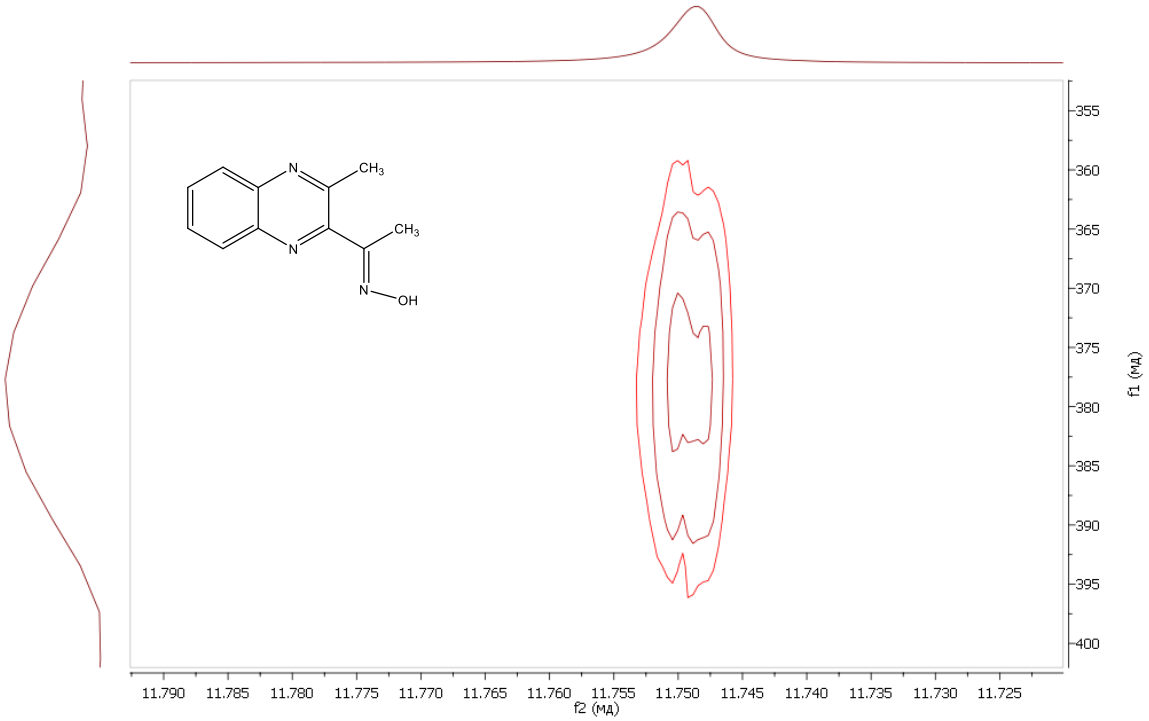
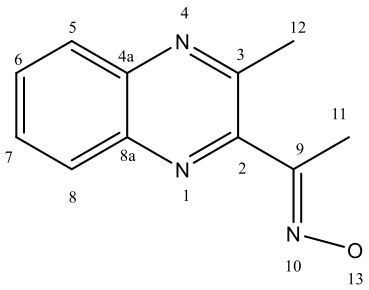


Figure S12. The fragment of ^{1}H-^{15}N HMBC spectrum of 2-acetyl-3-methylquinoxaline oxime **10**

Table S2. Chemical shifts ^{1}H, ^{13}C, ^{15}N of compound **10** in DMSO-d_6



Compound.	NUCLEUS	1(^{15}N)	2	3	4(^{15}N)	4a	5	6	7	8	8a	9	10(^{15}N)	11	12	13
10	^{1}H						7.97	7.78	7.76	8.01				2.28	2.80	11.75
	$^{13}C/^{15}N$	324.80	149.95	152.63	327.90	140.03	128.53	129.34	130.17	127.89	139.41	154.46	378.40	12.48	25.08	

Quantum chemical data

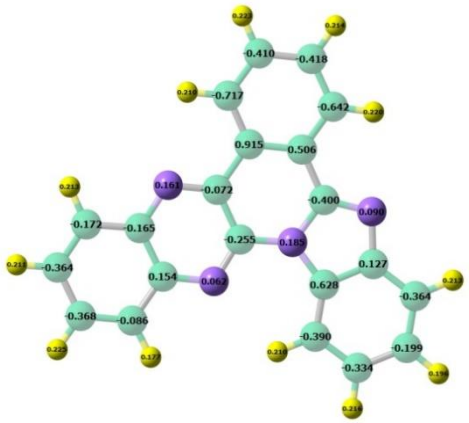
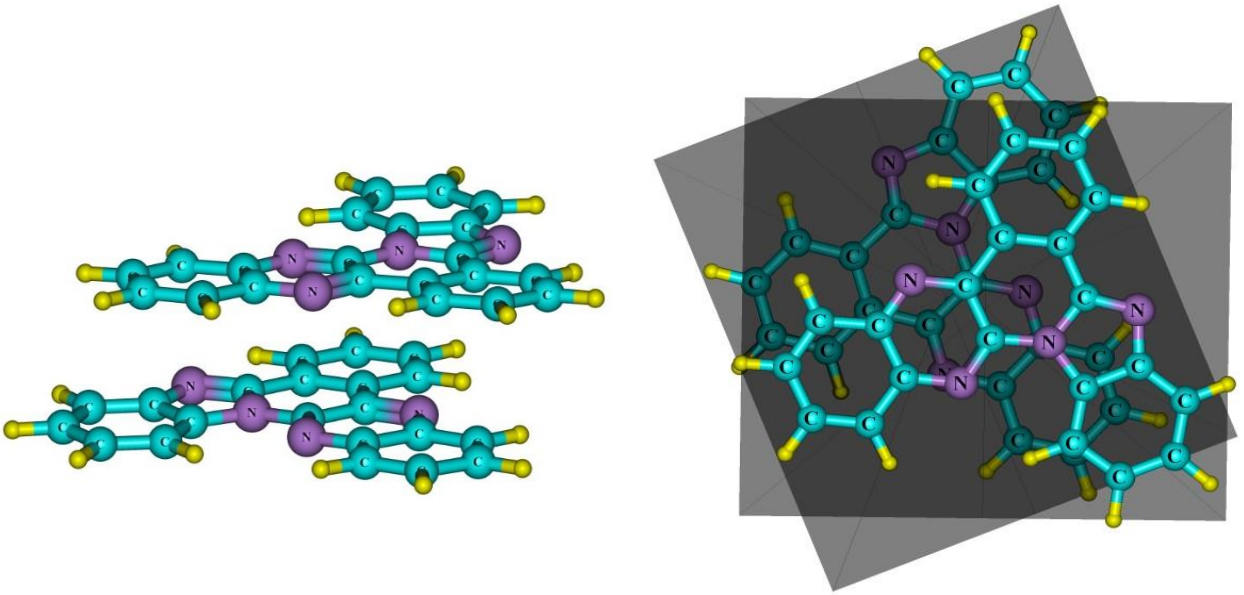


Figure S13 M06-2X/6-311++G(d,p) Mulliken charge distribution in the molecule of compound **8**.

The calculations were performed by the Gaussian 09 software package [S1] using the M06-2X functional [S2] in the 6-311++G(d,p) split-valence basis [S3]. The M062X functional has been designed specifically for investigations of nonvalent interactions and is among the best ones for studying such systems [S4,S5].

According to the calculation results, the interaction between two monomers **8** leads to the formation of stacking dimer **8'** characterized by a parallel orientation of π-systems of the monomers (**Figure S14a**) with a distance between the monomers of ~3.2 Å, which is in agreement with the results of theoretical studies on stacking complexes of various azaderivatives [S6]. The orientation of two monomer moieties in complex **8'** is not an eclipsed one: one of the monomers is shifted relative to another and rotated for about 100° around the central axis (top view is shown in **Figure S14b**). According to the calculations, complex **8'** corresponds to the energy minimum ($\lambda = 0$) on the potential energy surface (PES). The stabilization energy of the complex was calculated as the difference between the total energy of dimer and the total energy of isolated monomers and estimated as 24.3 kcal mol^{-1}.



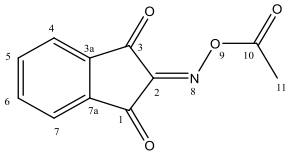
a) b)

Figure S14 The structure of dimer **8'** based on the data calculated by M06-2X/6-311++G(d,p) method.

The high energy of interaction is primarily due to the polycyclic nature of monomers and the simultaneous presence of several interacting cycles, while an increase in the number of such cycles is accompanied by a progressive increase in the stabilization energy as compared to monocyclic forms [S6]. Another factor causing the significant stabilization energy of complex **8'** is the presence of nitrogen heteroatoms: according to the reported data [S7], the energy of stacking interaction of aza-derivatives is noticeably increased in comparison with their carbon analogs.

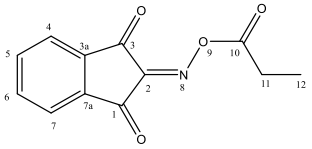
Experimental

2-Acetoxyiminoindane-1,3-dione **7b**.



Oxime **7a** (0.7 g, 4 mmol) was dissolved in boiling Ac_2O (1 ml). The reaction mixture solidified upon cooling with ice, then ether (4 ml) was added. The precipitate was filtered off and washed with ether and petroleum ether. The yield was 0.8 g (93%). Yellow crystals, m.p. 168–170 °C (literature data[8] 157–158 °C). IR (Nujol mul), ν_{max}/cm^{-1}: 1798 vs, 1743 s, 1710 vs (CO), 1621 w, 1587 m (arom). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.39 (s, 3H, CH_3), 7.90–8.00 (m, 2H, H_{Ar}), 8.05–8.15 (m, 2H, H_{Ar}). ^{1}H NMR data has not been previously reported, while the published IR data [S8] coincided with our results.

2-Propionyloxyiminoindane-1,3-dione **7c**.



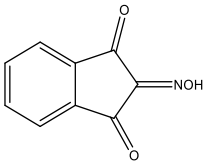
A mixture of oxime **7a** (0.35 g, 2 mmol) and propionic anhydride (0.5 ml) was refluxed until completed dissolution (~ 1 min), then the yellow solution was cooled to room temperature. The mixture solidified, and ether (3 ml) was added. The mixture was triturated, the precipitate was filtered off and washed with ether and petroleum ether. The yield was 0.34 g (74 %). Yellow crystals, m.p. 168–170 °C (EtOAc). IR (Nujol mul), ν_{max}/cm^{-1}:1780 vs, 1744 s, 1710 vs (CO), 1626 w, 1589 m (arom). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 1.28 (t, 3H, *J* 6.0 Hz, CH_3), 2.65 (q, 2H, *J* 6.0 Hz, CH_2), 7.91–7.94 (m, 2H, H_{Ar}), 8.03–8.05 (m, 1H, H_{Ar}), 8.07–8.10 (m, 1H, H_{ar}). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 8.66 (CH_3), 25.99 (CH_2), 124.72 (C5 or C6), 124.76 (C5 or C6), 136.91 (C4 or C7), 137.18 (C4 or C7), 141.42 (C3a or C7a), 141.58 (C3a or C7a), 149.09 (C2), 170.72 (C10), 178.43 (C1 or C3), 182.95 (C1 or C3).

One-pot synthesis of compounds **7b,c** *from ninhydrin*.

Compound **7b**. Ninhydrin (0.36 g, 2 mmol) was refluxed in Ac_2O (1 ml) until completed dissolution (~ 1 min). Hydroxylamine hydrochloride (0.15 g, 2.15 mmol) was added to the dark green solution, and this was refluxed until the formation of transparent light yellow solution (~ 3 min). The solution solidified upon cooling to room temperature, then ether (3 ml) was added. The precipitate was filtered off and washed with ether and petroleum ether. The yield was 0.22 g (50%). The IR spectrum coincided with the known reference sample, and the mixed sample did not exhibit m.p. depression.

Compound **7c** was prepared similarly from ninhydrin (0.36 g, 2 mmol), propionic anhydride (1 ml), when hydroxylamine hydrochloride (0.15 g, 2.15 mmol) was added to the blue-green solution. The final reflux (~ 3 min) provided a red solution. The solution solidified upon cooling, then ether (3 ml) was added. The precipitate was filtered off to isolate the desired product (0.2 g, 43%). The IR spectrum coincided with the known reference sample, and the mixed sample did not exhibit m.p. depression.

Ninhydrin oxime **7a**.



A mixture of ninhydrin (7.2 g, 4 mmol), hydroxylamine hydrochloride (3.0 g, 4.3 mmol), and H_2O (70 ml) was heated until the dissolution, refluxed until the formation of yellow precipitate (10–15 min), and cooled; the precipitate was filtered off, washed with H_2O, and dried. The yield was 0.62 g (88%), m.p. 215–217 °C.

2-Acetyl-3-methylquinoxaline oxime **10**.

3-Hydroxyiminopentane-2,4-dione **9** (0.26 g, 2 mmol) was dissolved in hot AcOH (1 ml), CF_3COOH (0.2 ml) was added, and the mixture was refluxed with air condenser for 1 min. Then *o*-phenylenediamine (0.44 g, 2 mmol) was added to initiate the exothermic reaction. The dark solution was refluxed for 1 min which solidified upon cooling. 2-Propanol (3 ml) was added; the mixture was cooled with ice and triturated, the precipitate was filtered off and washed successively with cold *i*-PrOH, ether, and petroleum ether. The yield of the crude product was 0.08 g (20%). Colorless compound, m.p. 191–193 °C (*i*-PrOH). Ref. data 196 °C (EtOH). IR (Nujol mul), ν_{max}/cm^{-1}:3167 br (OH), 1488 m, 1456 s, 1435 m, 1403 w (arom). ^{1}H NMR (600 MHz, DMSO-d_6), δ: 11.75 (s, 1H, OH), 8.00 (d, 1H, H_{Ar}, *J* 7.70 Hz), 7.96 (d, 1H, HAr, *J* 7.80), 7.72–7.82 (m, 2H, HAr), 2.80 (s, 3H, CH_3), 2.28 (s, 3H, CH_3). ^{13}C NMR (150 MHz, DMSO-d_6), δ: 12.48, 25.08, 127.89, 128.53, 129.34, 130.17, 139.41, 152.63, 154.46. MS (El, 70 eV), *m/z*(%): 201(3) [M+], 184(40) [M-OH], 143(30), 102(40), 76(40), 58(30, 42(100), 30(50), 15(80).

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