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Supplementary Information

Tautomerism in Quinoxalines Derived from the 1,4-Naphthoquinone Nucleus: Acid Mediated Synthesis, X-ray Molecular Structure of 5-Chlorobenzo[*f*]quinoxalin-6-ol and Density Functional Theory Calculations

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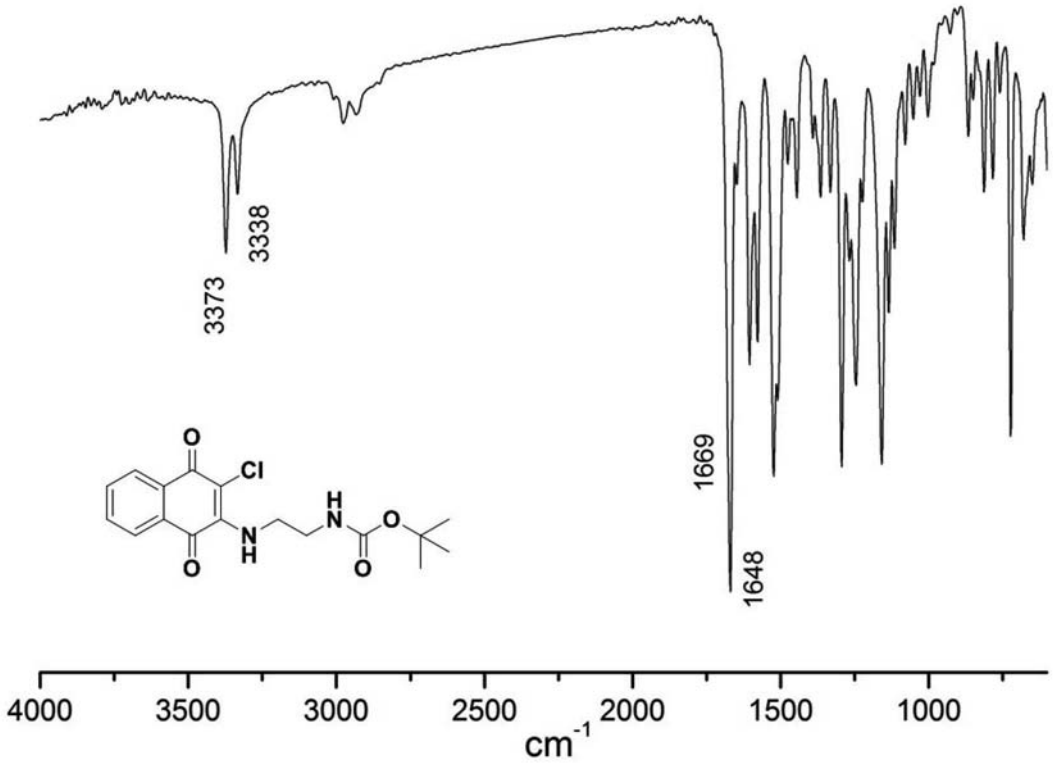

Figure S1. ATR-FTIR spectrum of **1**.

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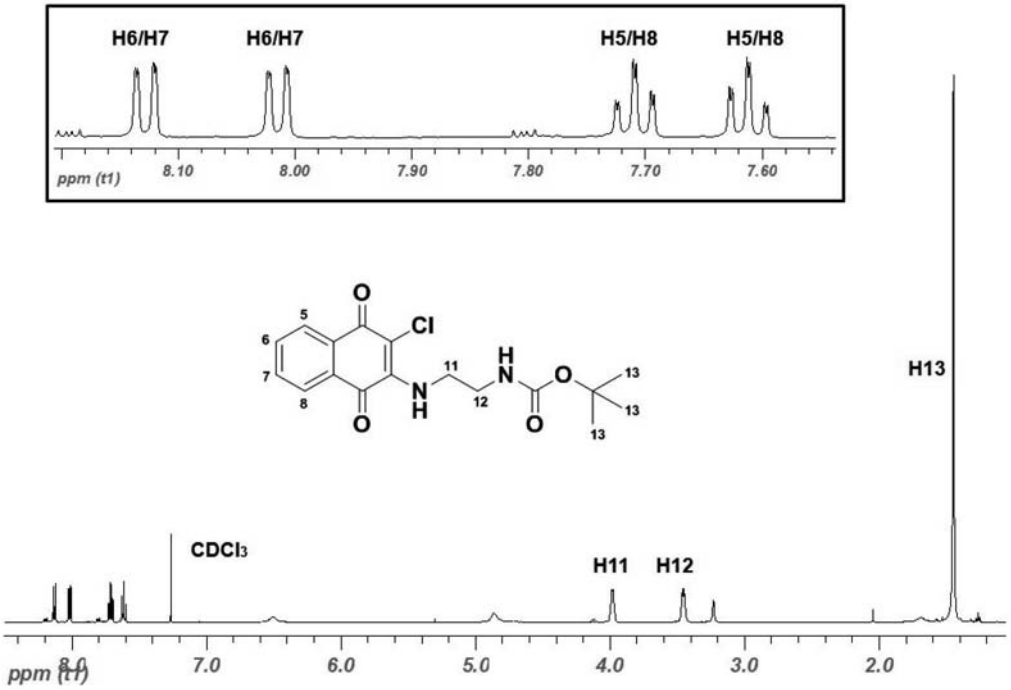


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1**.

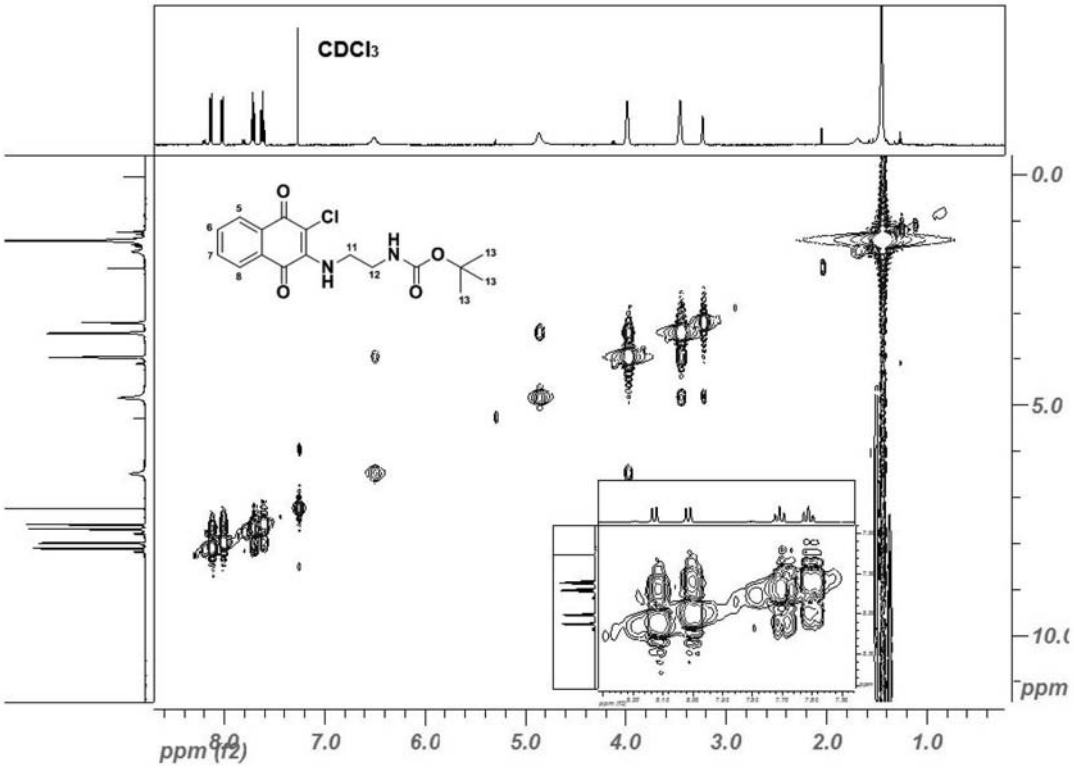


Figure S3. COSY NMR (500 MHz, $CDCl_3$) spectrum of **1**.

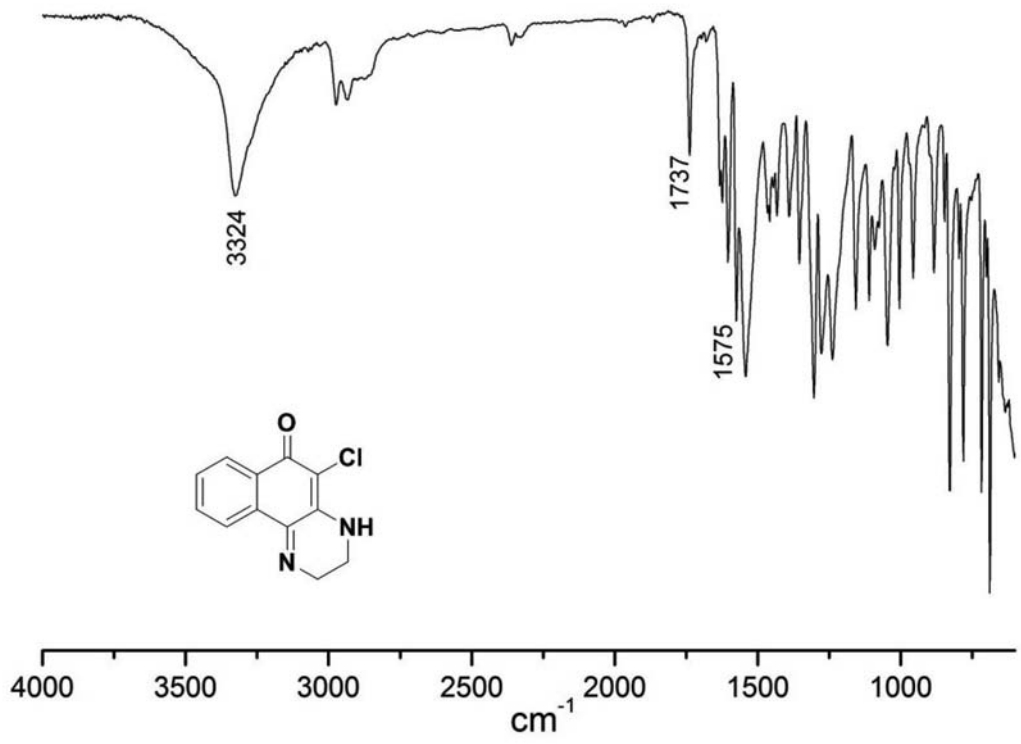


Figure S4. ATR-FTIR spectrum of **2**.

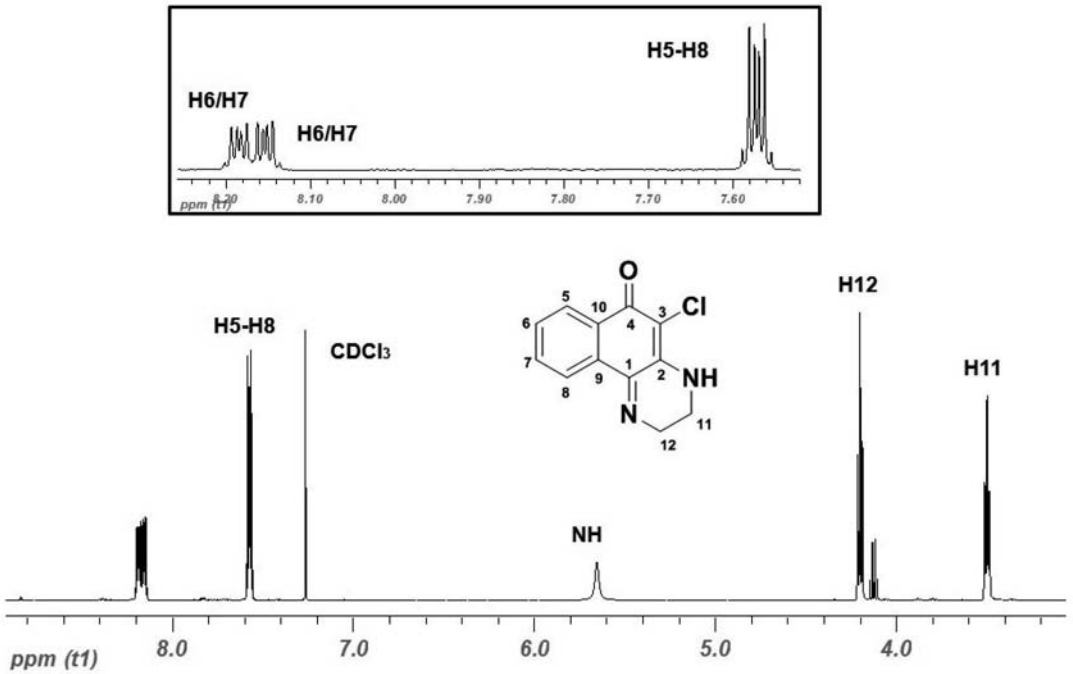


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2**.

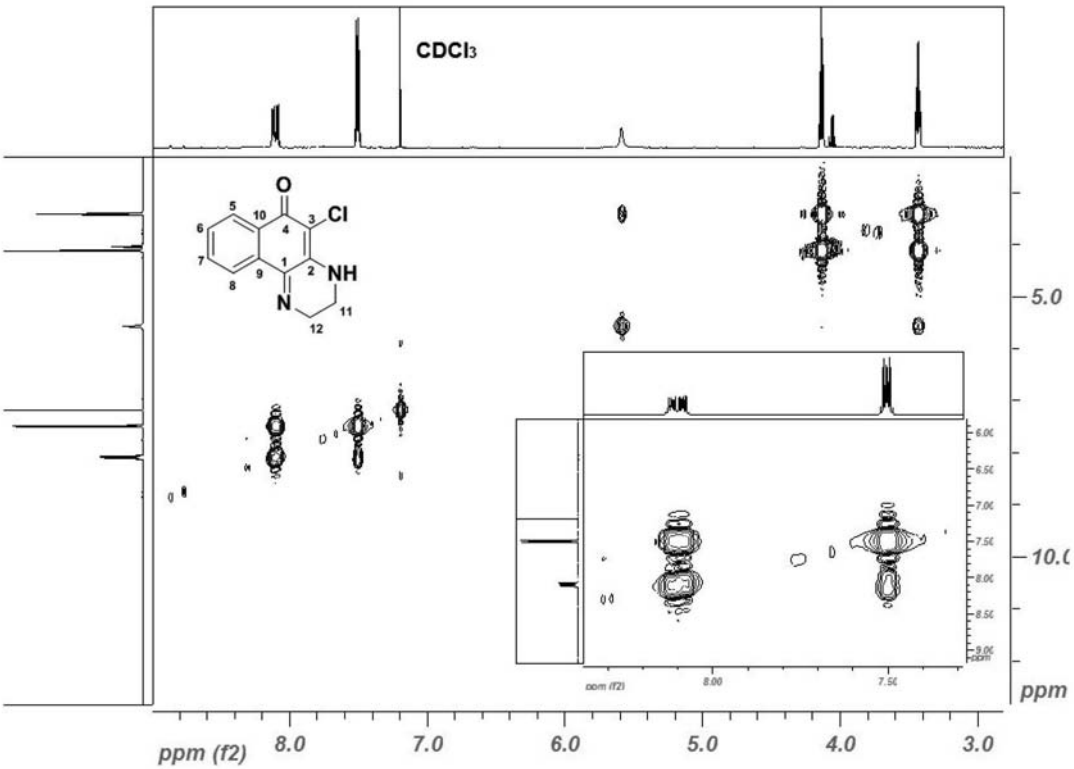
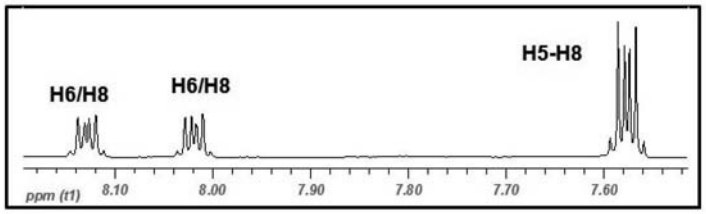


Figure S6. COSY NMR (500 MHz, $CDCl_3$) spectrum of **2**.



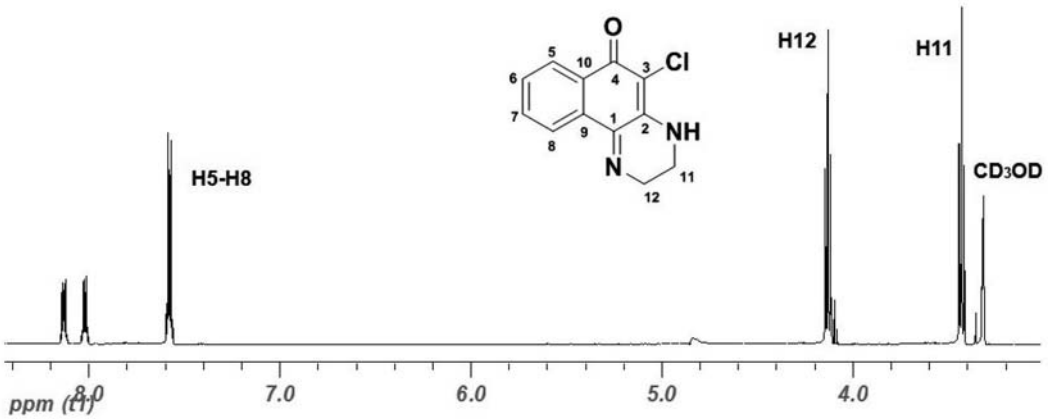


Figure S7. ^1H NMR (500 MHz, CD_3OD) spectrum of **2**.

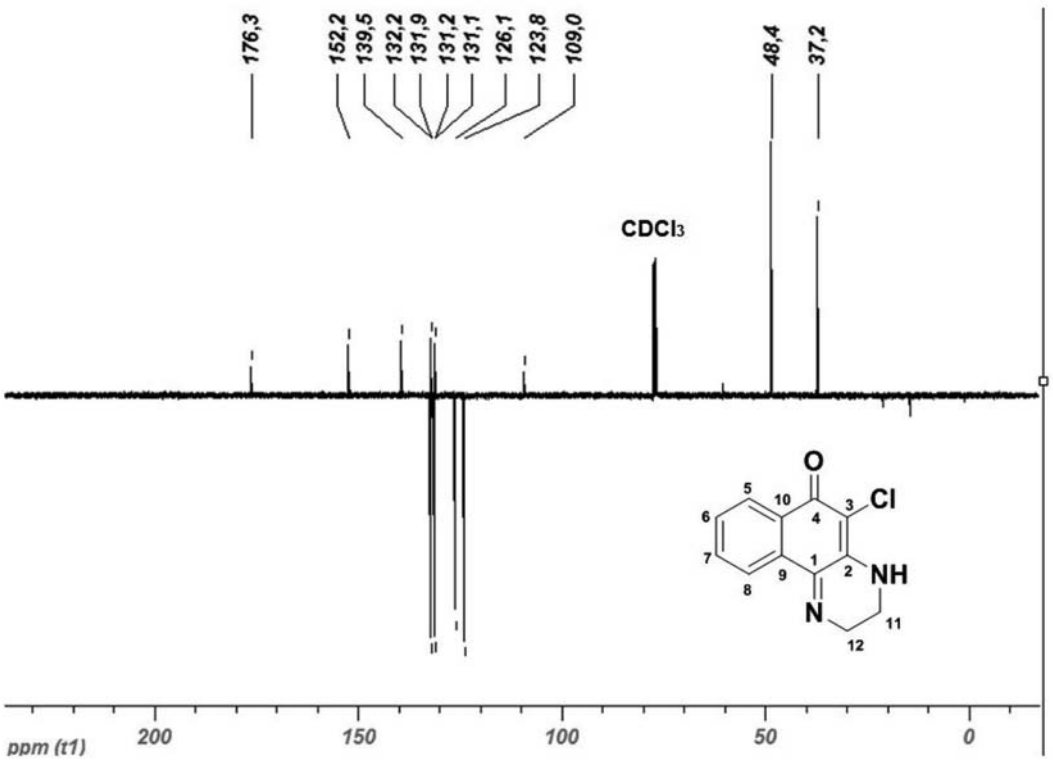


Figure S8. APT (125 MHz, $CDCl_3$) spectrum of **2** in.

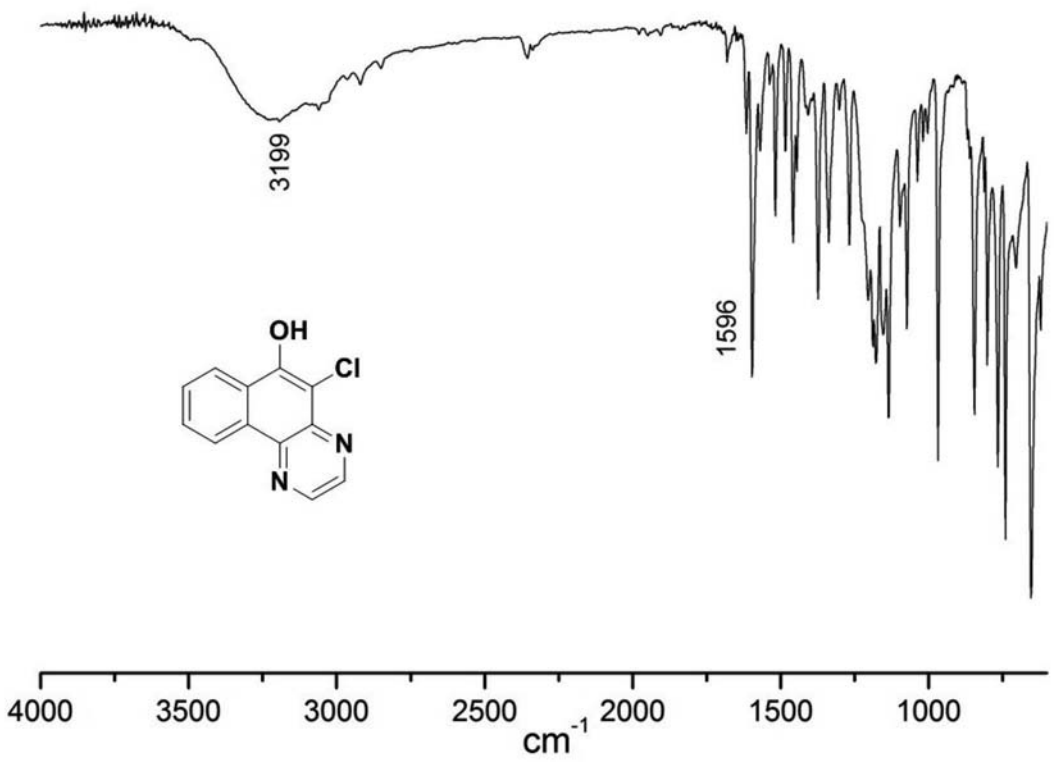


Figure S9. ATR-FTIR spectrum of **3**.

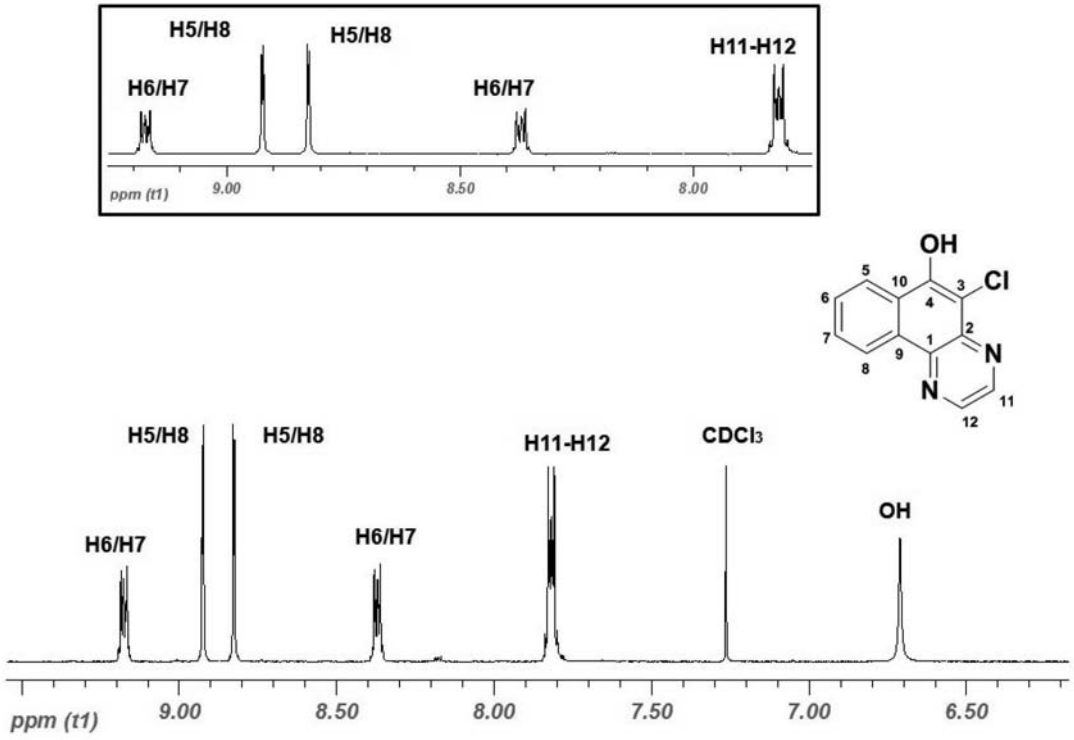


Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3**.

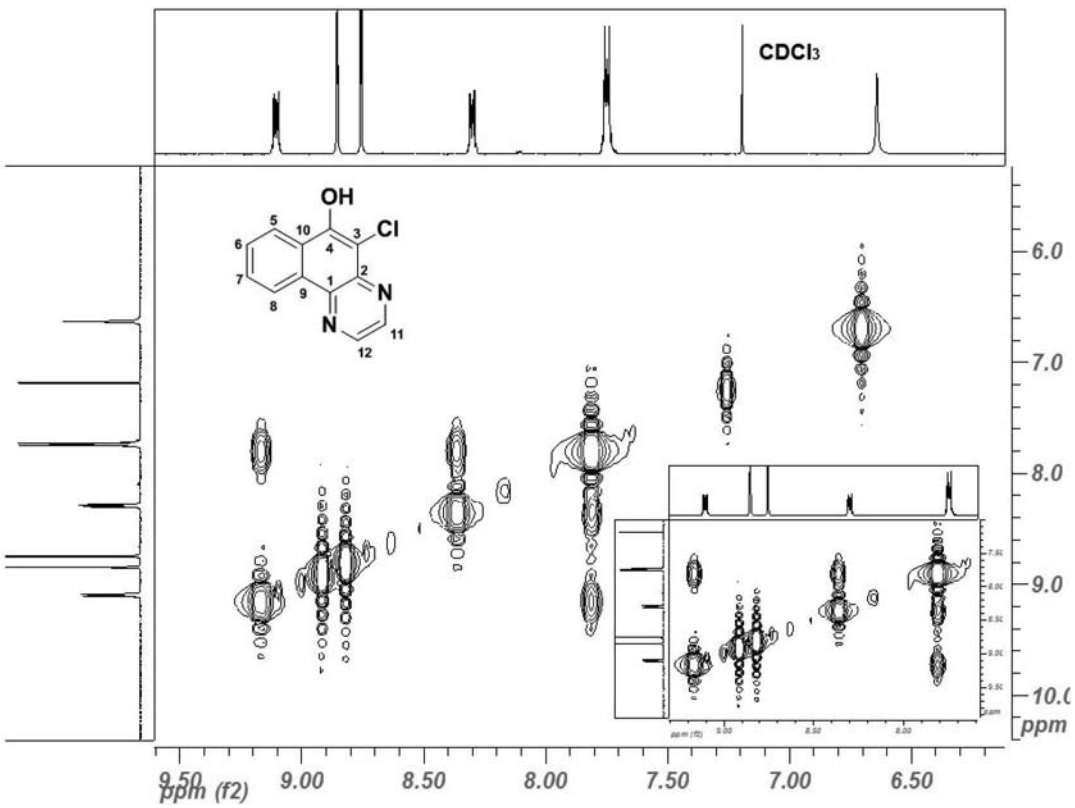


Figure S11. COSY NMR(500 MHz, $CDCl_3$) spectrum of **3**.

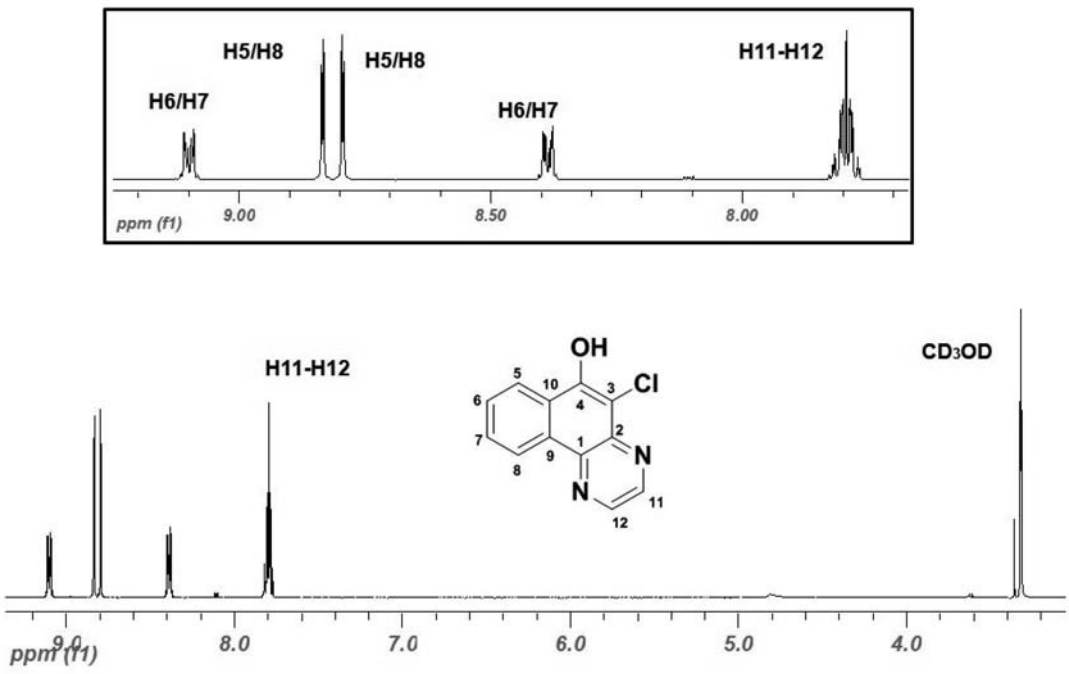


Figure S12. [1]H NMR (500 MHz, CD_3OD) spectrum of **3**.

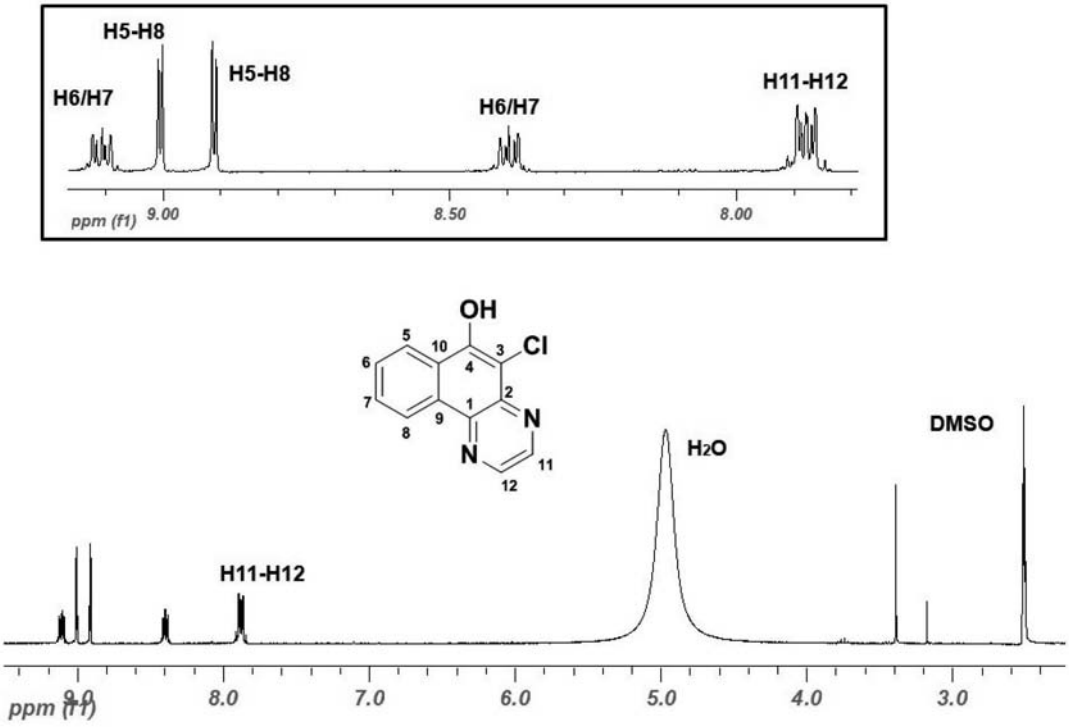


Figure S13. [1]H NMR (500 MHz, DMSO) spectrum of **3**.

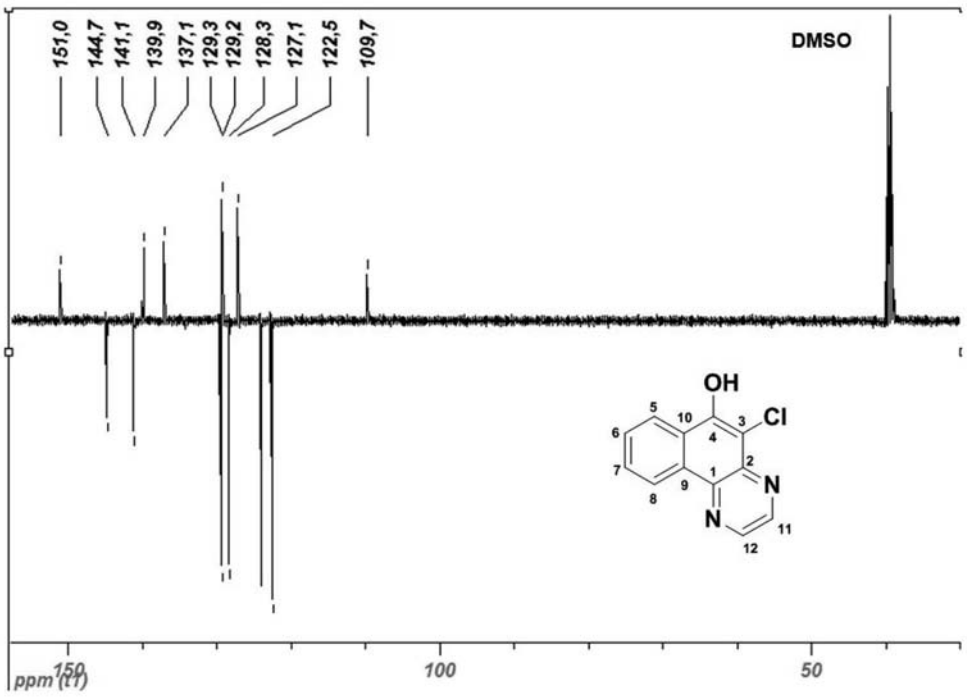


Figure S14. APT (125 MHz, DMSO) spectrum of **3**.

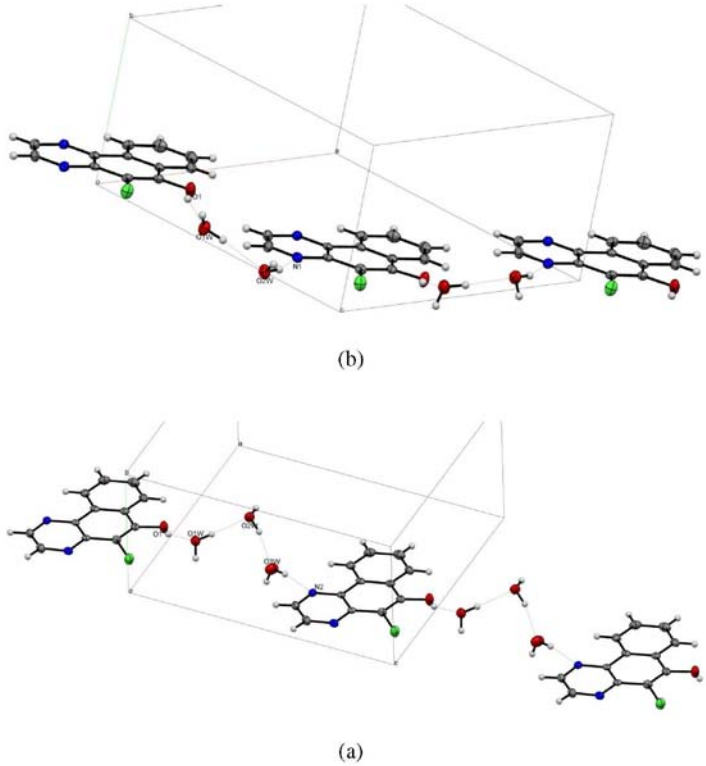


Figure S15. Views showing the hydrogen bond interactions between the water molecules: (a) along the c-axis; and (b) in the [101] direction.

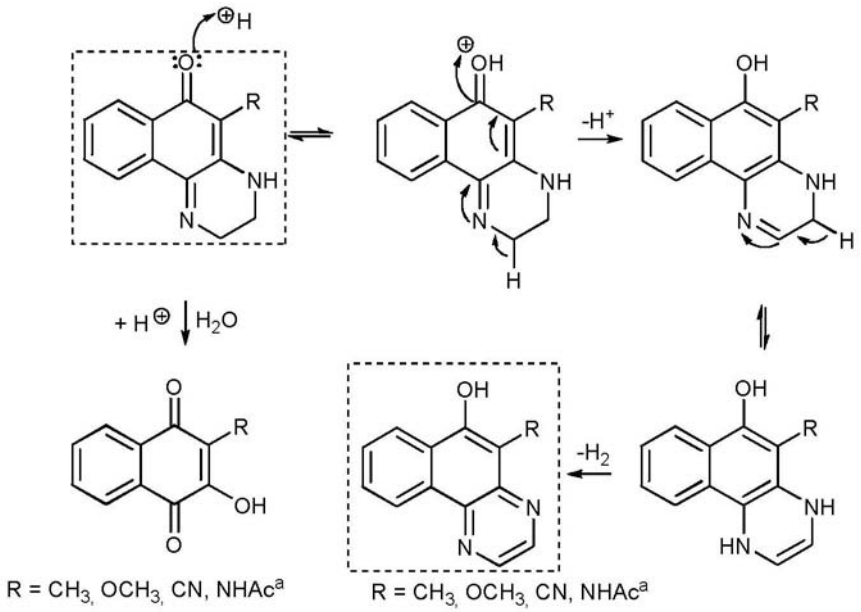


Figure S16. Path proposed by Kallmayer and Seyfang[1] for the acid promoted dehydrogenation of dihydrobenzoquinoxalines.

Table S1. Experimental (XRD) and calculated bond lengths for **3**

Bond	Experimental / Å	Calculated / Å
Cl1–C2	1.730 (3)	1.756
O1–C1	1.351 (3)	1.352
C3–N1	1.358 (4)	1.351
C3–C4	1.411 (4)	1.427
C3–C2	1.432 (4)	1.434
C1–C2	1.364 (4)	1.373
C1–C9	1.443 (4)	1.445
N1–C12	1.317 (4)	1.324
C10–C5	1.408 (4)	1.410
C10–C9	1.411 (4)	1.420
C10–C4	1.447 (4)	1.450
N2–C11	1.324 (4)	1.325
N2–C4	1.359 (3)	1.349
C8–C7	1.367 (4)	1.383
C8–C9	1.409 (4)	1.412
C11–C12	1.388 (4)	1.407
C5–C6	1.370 (4)	1.383
C6–C7	1.396 (4)	1.408

Table S2. Experimental (XRD) and calculated bond angles for **3**

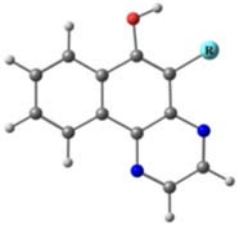
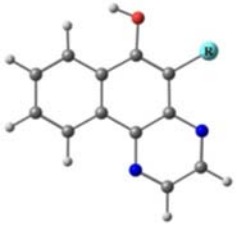
Angle / degree	Experimental (XRD)	Calculated / Å
N1–C3–C4	121.3 (2)	121.2
N1–C3–C2	119.5 (3)	120.0
C4–C3–C2	119.2 (2)	118.8
O1–C1–C2	125.0 (3)	123.3
O1–C1–C9	114.4 (2)	116.1
C2–C1–C9	120.6 (3)	120.6
C12–N1–C3	116.2 (3)	116.7
C5–C10–C9	119.1 (2)	119.1
C5–C10–C4	122.1 (3)	121.6
C9–C10–C4	118.8 (3)	119.3
C11–N2–C4	116.7 (3)	117.4
C7–C8–C9	120.6 (3)	120.5
N2–C11–C12	122.1 (3)	121.8
C1–C2–C3	121.2 (3)	121.6
C1–C2–Cl1	120.1 (2)	118.8
C3–C2–Cl1	118.7 (2)	119.5
N1–C12–C11	123.1 (3)	122.3
C8–C9–C10	119.1 (3)	119.6
C8–C9–C1	121.1 (3)	120.8
C10–C9–C1	119.9 (2)	119.5
C6–C5–C10	120.4 (3)	120.5
C6–C5–H5	119.8	121.3
C10–C5–H5	119.8	118.2
N2–C4–C3	120.7 (2)	120.5
N2–C4–C10	119.0 (3)	119.4
C3–C4–C10	120.4 (2)	120.1
C5–C6–C7	120.5 (3)	120.3
C8–C7–C6	120.3 (3)	120.3

Table S3. Hydrogen bonds in the crystal packing of **3**

D-H···*A*	*D*-H / Å	H···*A* / Å	*D*···*A* / Å	*D*-H···*A* / degree
O(1)–H(1)···O(1W)	0.82	1.94	2.686 (3)	151
O(1W)–H(1W1)···O(2W)^{i}	0.820 (10)	1.96 (1)	2.780 (3)	174 (4)
O(1W)–H(2W1)···O(2W)^{ii}	0.821 (10)	1.96 (1)	2.783 (3)	175 (4)
O(2W)–H(1W2)···N(1)	0.817 (10)	2.08 (2)	2.854 (3)	157 (3)
O(2W)–H(2W2)···O(3W)^{iii}	0.824 (10)	1.89 (1)	2.695 (3)	165 (3)
O(3W)–H(1W3)···N(2)	0.818 (10)	2.07 (1)	2.880 (3)	168 (4)
O(3W)–H(2W3)···O(1W)^{iv}	0.821 (10)	2.03 (1)	2.848 (3)	172 (4)

Symmetry codes: (*i*) −x, −y, −z+2; (*ii*) x+½, −y+½, z+½; (*iii*) x−½, −y+½, z+½; (*iv*) −x+½, y−½, −z+3/2.

Table S4. Possible conformations of benzoquinoxalines, interatomic distances between hydroxyl hydrogen and H, Cl, methyl H, and relative abundance of each conformation

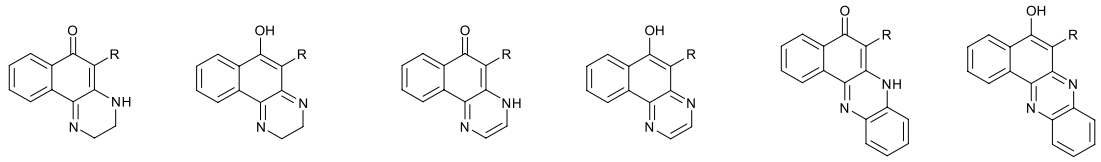
	Benzoquinoxalines conformations			
Conformations				
	Conformation 1		Conformation 2	
R	Interatomic distance / Å	Relative abundance[a]	Interatomic distance / Å	Relative abundance[a]
H	2.28	0.95	1.87	0.05
Cl	2.46	0.99	1.83	< 0.01
CH_3 (H)	2.25	0.88	2.01	0.12

[a]The relative abundances, from Boltzmann distribution, were obtained using the conformer distribution subroutine of the Spartan´06 software,[2] employing the AM1 semi-empirical method,[3] the relative abundance of which is determined by the Boltzmann distribution.

Table S5. Dipole moments (|μ| in D) of the two tautomers of dihydrobenzoquinoxaline, benzoquinoxaline and benzophenazine derivatives, calculated at the B3LYP/6-311++G(d,p) level

Derivative	R	Keto-amine tautomer	Enol-imine tautomer
Dihydrobenzoquinoxalines	H	5.18	1.00
	Cl (**2**)	5.45	1.61
	CH_3	4.76	0.93
Benzoquinoxalines	H	5.95	0.81
	Cl (**3**)	5.95	1.19
	CH_3	5.53	1.10
Benzophenazines	H	5.48	0.65
	Cl	5.85	1.23
	CH_3	4.96	1.01

Table S6. B3LYP/6-311++G(d,p) Gibbs free energies (kcal mol^{-1}) calculated for the two tautomers of dihydrobenzoquinoxalines, benzoquinoxalines and benzophenazines. The Gibbs free energy values were calculated as $G_{enol\text{-}imine} - G_{keto\text{-}amine}$ forms



Dihydrobenzoquinoxalines Benzoquinoxalines Benzophenazines

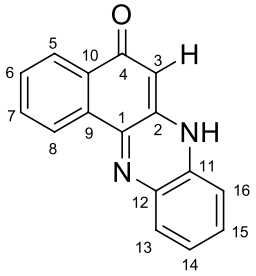
Solvent (ε)[a]	R =								
	H	Cl (**2**)	CH_3	H	Cl (**3**)	CH_3	H	Cl	CH_3
Gas phase	11.40	11.95	11.45	−9.67	−8.11	−8.68	−2.69	−1.61	−1.06
$CHCl_3$ (4.7)	13.30	14.16	13.78	−5.40	−3.82	−4.99	0.22	1.31	0.57
CH_3OH (36.2)	14.11	15.03	14.73	−3.75	−2.20	−3.56	1.29	2.37	1.56
DMSO (46.8)	14.16	15.08	14.78	−3.65	−2.10	−3.47	1.35	2.43	1.61

[a]ε: dielectric constant.

Tables S7-S15. Calculated NMR spectra of benzophenazine tautomers. All data, including the TMS reference chemical shift, were calculated using the B3LYP functional and the 6-311++G(d,p) basis set

Table S7.

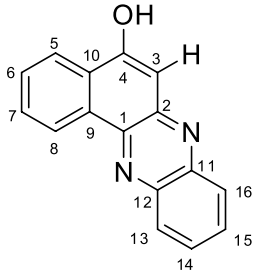
Benzophenazine (keto-amine)



^{13}C NMR data in $CHCl_3$			
Atom	Chemical shift	Atom	Chemical shift
1	155.92	**11**	137.12
2	144.29	**12**	142.95
3	104.19	**13**	138.85
4	188.15	**14**	130.55
5	132.44	**15**	139.36
6	138.59	**16**	121.03
7	137.31		
8	132.20		
9	138.59		
10	141.34		

Table S8.

Benzophenazine (enol-imine)



^{13}C NMR data in $CHCl_3$			
Atom	Chemical shift	Atom	Chemical shift
1	147.83	**11**	150.76
2	152.54	**12**	147.74
3	110.44	**13**	138.25
4	165.02	**14**	135.44
5	129.75	**15**	137.33
6	136.92	**16**	136.97
7	135.85		
8	132.91		
9	139.54		
10	134.58		

Table S9.

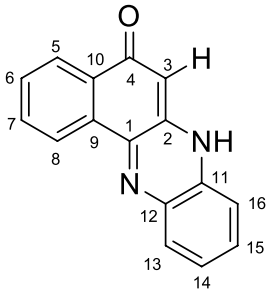
Benzophenazine (keto-amine)	^{13}C NMR data in DMSO			
	Atom	Chemical shift	Atom	Chemical shift
	**1**	155.31	**11**	137.25
	2	144.82	**12**	143.19
	3	103.94	**13**	138.82
	4	188.61	**14**	131.36
	5	132.05	**15**	140.30
	6	138.71	**16**	122.16
	7	137.72		
	8	132.42		
	9	138.84		
	10	141.37		

Table S10.

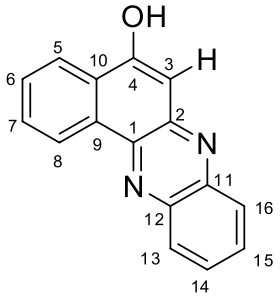
Benzophenazine (enol-imine)	^{13}C NMR data in DMSO			
	Atom	Chemical shift	Atom	Chemical shift
	**1**	148.01	**11**	150.83
	2	152.83	**12**	147.79
	3	110.53	**13**	138.27
	4	165.45	**14**	135.96
	5	129.96	**15**	137.94
	6	137.44	**16**	136.88
	7	136.28		
	8	132.83		
	9	139.47		
	10	134.80		

Table S11.

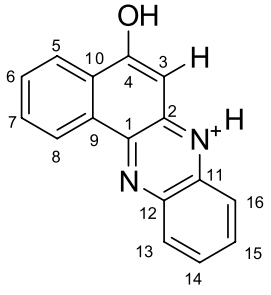
Benzophenazine (protonated)	^{13}C NMR data $CHCl_3$			
	Atom	Chemical shift	Atom	Chemical shift
	**1**	151.22	**11**	134.27
	2	140.89	**12**	147.80
	3	100.29	**13**	140.96
	4	176.32	**14**	138.55
	5	132.49	**15**	145.81
	6	161.20	**16**	124.23
	7	141.68		
	8	133.90		
	9	137.95		
	10	132.75		

Table S12.

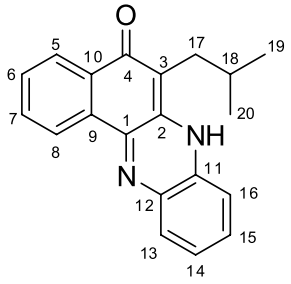
3-isobutyl-benzophenazine (keto-amine , see Figure 1a, **d**)	^{13}C NMR data in DMSO			
	Atom	Chemical shift	Atom	Chemical shift
	**1**	154.38	**11**	138.02
	2	143.19	**12**	142.48
	3	115.29	**13**	137.78
	4	187.64	**14**	131.13
	5	132.82	**15**	140.03
	6	138.69	**16**	121.46
	7	137.28	**17**	33.64
	8	131.78	**18**	38.45
	9	138.54	**19**	23.33
	10	140.24	**20**	25.51

Table S13.

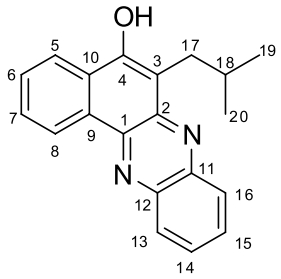
3-isobutyl-benzophenazine (enol-imine)	^{13}C NMR data in DMSO			
	Atom	Chemical shift	Atom	Chemical shift
	**1**	146.99	**11**	149.83
	2	151.61	**12**	147.33
	3	151.61	**13**	137.50
	4	162.31	**14**	136.31
	5	129.56	**15**	138.00
	6	137.36	**16**	136.47
	7	135.05	**17**	35.32
	8	132.53	**18**	36.22
	9	138.44	**19**	26.66
	10	134.50	**20**	22.98

Table S14.

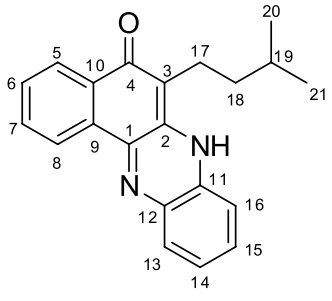
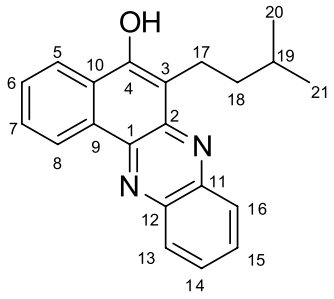
3-isopentyl-benzophenazine (keto-amine , see Figure 1a, **b**)	^{13}C NMR data in DMSO			
	Atom	Chemical shift	Atom	Chemical shift
	**1**	154.38	**12**	142.56
	2	141.67	**13**	137.96
	3	117.10	**14**	131.47
	4	187.27	**15**	140.51
	5	131.86	**16**	155.18
	6	139.20	**17**	24.01
	7	137.73	**18**	40.61
	8	131.27	**19**	33.18
	9	138.82	**20**	23.18
	10	140.12	**21**	27.19
	11	137.95		

Table S15.

3-isopentyl-benzophenazine (enol-imine)	NMR (^{13}C) data in DMSO			
	Atom	Chemical shift	Atom	Chemical shift
	**1**	147.20	**12**	147.38
	2	151.65	**13**	137.49
	3	124.50	**14**	136.15
	4	162.91	**15**	138.19
	5	129.56	**16**	136.56
	6	137.20	**17**	24.42
	7	135.03	**18**	42.69
	8	132.62	**19**	32.80
	9	138.98	**20**	26.82
	10	135.09	**21**	23.03
	11	150.14		

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