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4-Phenyldiazenyl-substituted 3,6-di-*tert*-butylcatechol: synthesis and azo–hydrazone equilibrium

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General procedures

Methanol, diethyl ether and hexane were dried using standard procedures. NMR spectra were recorded on 400 MHz Bruker AVANCE III and 300 MHz Bruker Avance Neo 300 at various temperatures. Chemical shifts are given in ppm with multiplicity (s=singlet, br.s=broad singlet, d=doublet, t=triplet, m=multiplet), coupling constants (Hz) and integration. IR spectra were recorded on a FSM-1201 FTIR spectrometer in nujol. Phenylhydrazine hydrochloride was used as purchased. 3-hydroxy-2,5-di-*tert*-butyl-1,4-benzoquinone (**OxPQ**) was synthesized according to literature procedure [S1].

Synthesis of 3,6-di-tert-butyl-2-hydroxy-4-(2-phenylhydrazono)cyclohexa-2,5-dien-1-one (**2**):
2,5-Di-*tert*-butyl-3-hydroxy-1,4-benzoquinone **1** (1.18 g, 5 mmol) and phenylhydrazine hydrochloride (0.72 g, 5 mmol) were dissolved in methanol (100 ml). The reaction mixture was maintained under reflux for 48 h. The colour of solution changed from yellow to dark-red. The progress of the reaction was monitored by TLC. After the reaction was completed, methanol was removed under reduced pressure. The dry residue was dissolved in diethyl ether, washed with water (3x50 ml), and then the ethereal layer was evaporated. The product **2** (0.70 g, 2.2 mmol, 43%) was isolated as dark-red crystals after recrystallization of crude product from hexane – diethyl ether (10:1) mixture. 4-Methoxy-3,6-di-*tert*-butylcatechol **3** (0.23 g, 0.9 mmol, 18%) was isolated as brownish powder after slow cooling of the mother liquor remaining after isolation of the target product.

3,6-Di-tert-butyl-2-hydroxy-4-(2-phenylhydrazono)cyclohexa-2,5-dien-1-one **2**: dark-red crystalline solid, mp 182°C (decomp.). IR (nujol, ν/cm^{-1}): 3273 m, 1617 w, 1600 s, 1580 s, 1520 s, 1484 m, 1423 m, 1392 w, 1356 s, 1293 m, 1246 m, 1219 w, 1160 m, 1075 w, 1050 s, 994 s, 963 m, 914 m, 889 w, 875 m, 809 w, 794 w, 752 s, 690 s, 601 s, 506 s, 492 s, 467 m. Calc. for $C_{20}H_{26}N_2O_2$ (%): C, 73.59; H, 8.03; N, 8.58; O, 9.80. Found (%): C, 69.75; H, 7.67; N, 7.86.
Tautomer **2**: ^{1}H-NMR (300 MHz, 298 K, $CDCl_3$, δ/ppm): 8.76 (s, 1H, =N-N*H*), 7.74 (s, 1H, O*H*), 7.42-7.34 (m, 2H, *Ph*), 7.31-7.27 (m, 2H, *Ph*), 7.19 (s, 1H, C-*H* of *p*-iminobenzoquinone ring), 7.06 (t, J = 7.3 Hz, 1H, *Ph*), 1.62 (s, 9H, C(C*H*$_3$)$_3$), 1.37 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C-NMR (100 MHz, 223 K, $CDCl_3$, δ/ppm): 180.63 (*C*=O), 146.62, 143.25, 142.58, 135.26, 129.90, 127.75, 123.41, 116.18, 114.55 (C=C-C of *p*-iminobenzoquinone and phenyl rings), 37.10 (*C*(CH$_3$)$_3$), 35.25 (*C*(CH$_3$)$_3$), 33.00 (C(*C*H$_3$)$_3$), 29.06 (C(*C*H$_3$)$_3$).
Tautomer **2'**: ^{1}H-NMR (300 MHz, 298 K, $CDCl_3$, δ/ppm): 7.86 (d, J = 7.7 Hz, 2H, *Ph*), 7.55 – 7.42 (m, 3H, *Ph*), 7.17 (s, 1H, C-*H* of *p*-iminobenzoquinone ring), 6.22 (s, 1H, O*H*), 5.84 (s, 1H, O*H*), 1.69 (s, 9H, C(C*H*$_3$)$_3$), 1.42 (s, C(C*H*$_3$)$_3$)
3,6-Di-tert-butyl-4-methoxycatechol **3** was previously described in [S2]**.** ^{1}H-NMR (300 MHz, 298 K, $CDCl_3$, δ/ppm): 6.43 (s, 1H, C-*H* of catechol ring), 5.37 (br.s., 2H, O*H*), 3.77 (s, 3H, OC*H*$_3$), 1.54 (s, 9H, C(C*H*$_3$)$_3$), 1.41 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C-NMR (75 MHz, 298 K, $CDCl_3$, δ/ppm): 152.24, 143.31, 137.66, 133.37, 121.38, 103.92, 56.47, 36.13, 34.34, 31.48, 29.65.

References

S1 N. Yu. Kabarova, V. K. Cherkasov, L. N. Zakharov, G. A. Abakumov, Yu. T. Struchkov and L. G. Abakumova, *Russ. Chem. Bull.*, 1992, **41**, 2224 (*Izv. Akad. Nauk, Ser. Khim.*, 1992, 2798).
S2 I. A. Novikova, V. B. Vol'eva, N. L. Komissarova, I. S. Belostotskaya and V. V. Ershov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1732 (*Izv. AN SSSR, Ser. Khim.*, 1981, 2110).

NMR spectroscopy

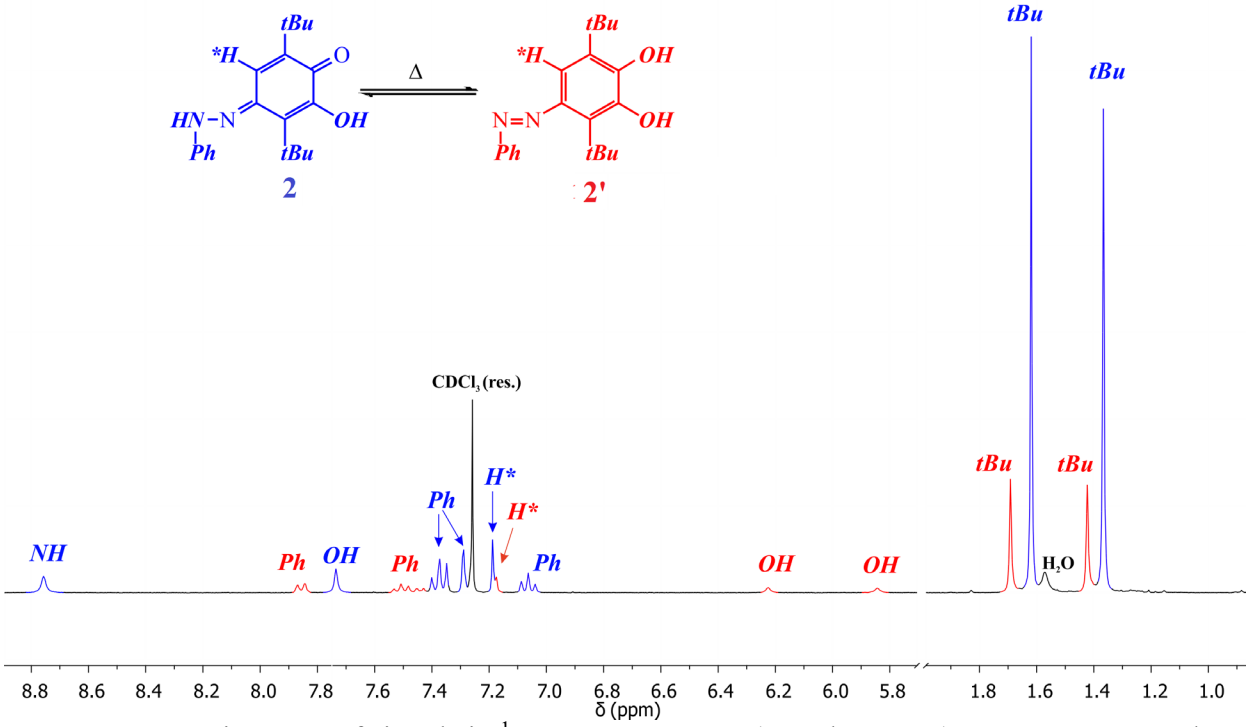

Figure S1. Assignment of signals in ^{1}H-NMR spectrum ($CDCl_3$, 298 K) to tautomers **2** and **2'**

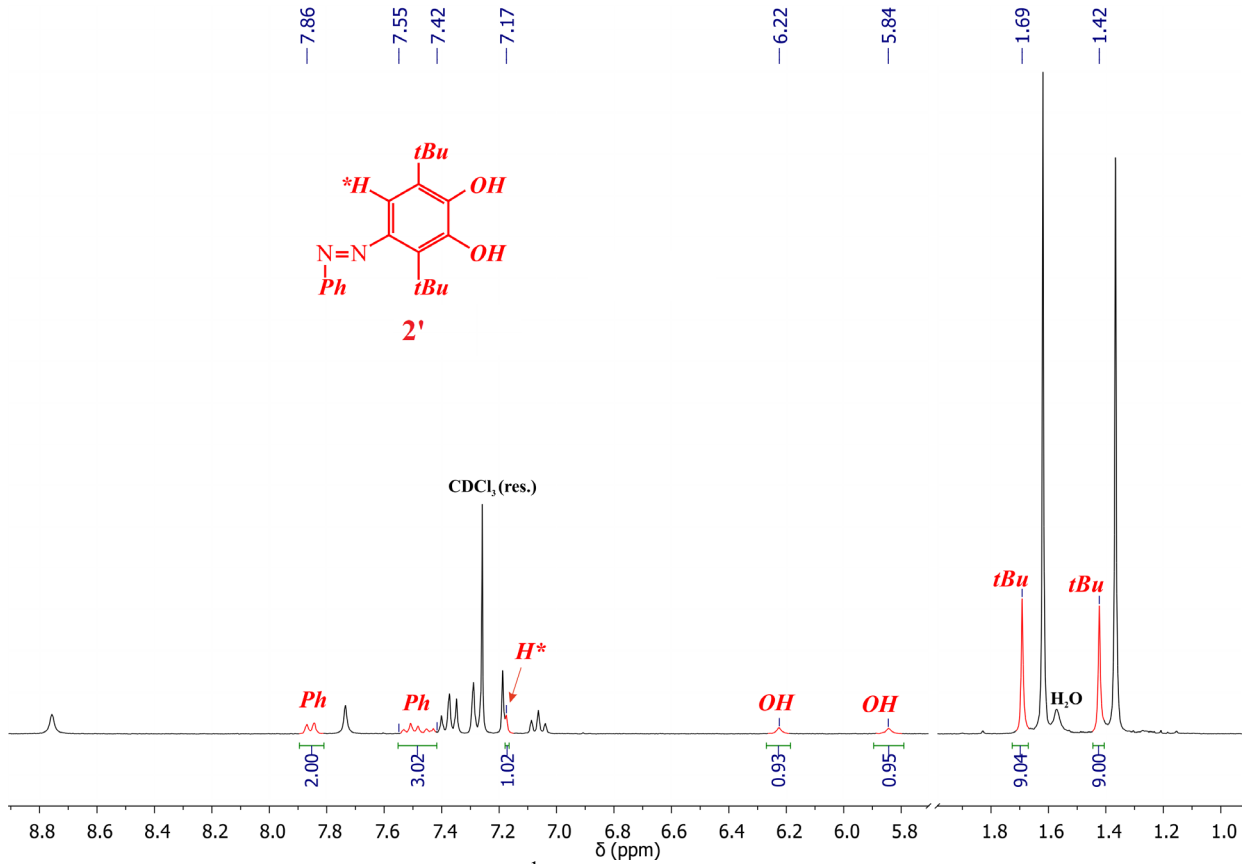

Figure S2. Integration of signals in ^{1}H-NMR spectrum ($CDCl_3$, 298 K) for tautomer **2'**

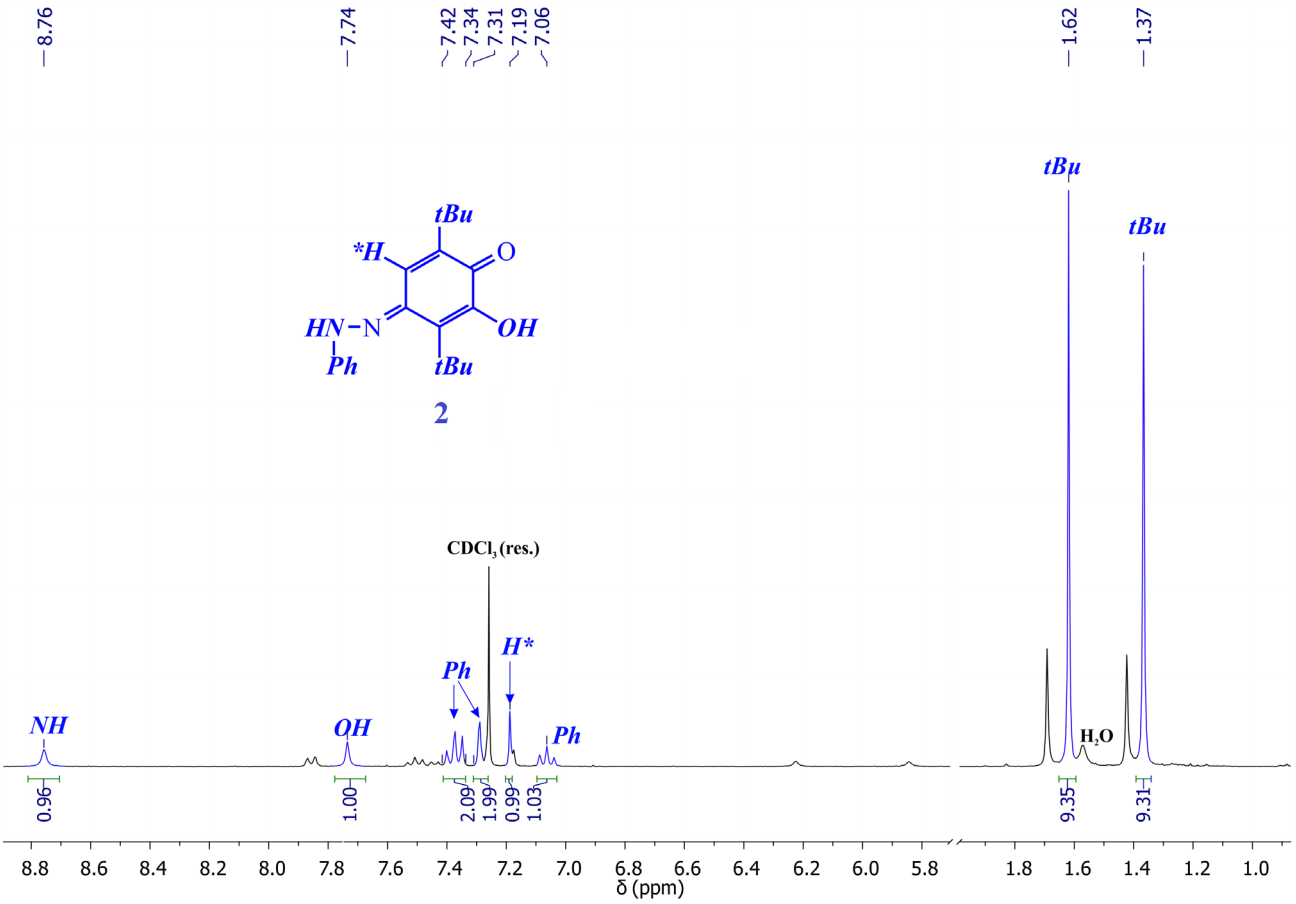

Figure S3. Integration of signals in ^{1}H-NMR spectrum ($CDCl_3$, 298 K) for tautomer **2**

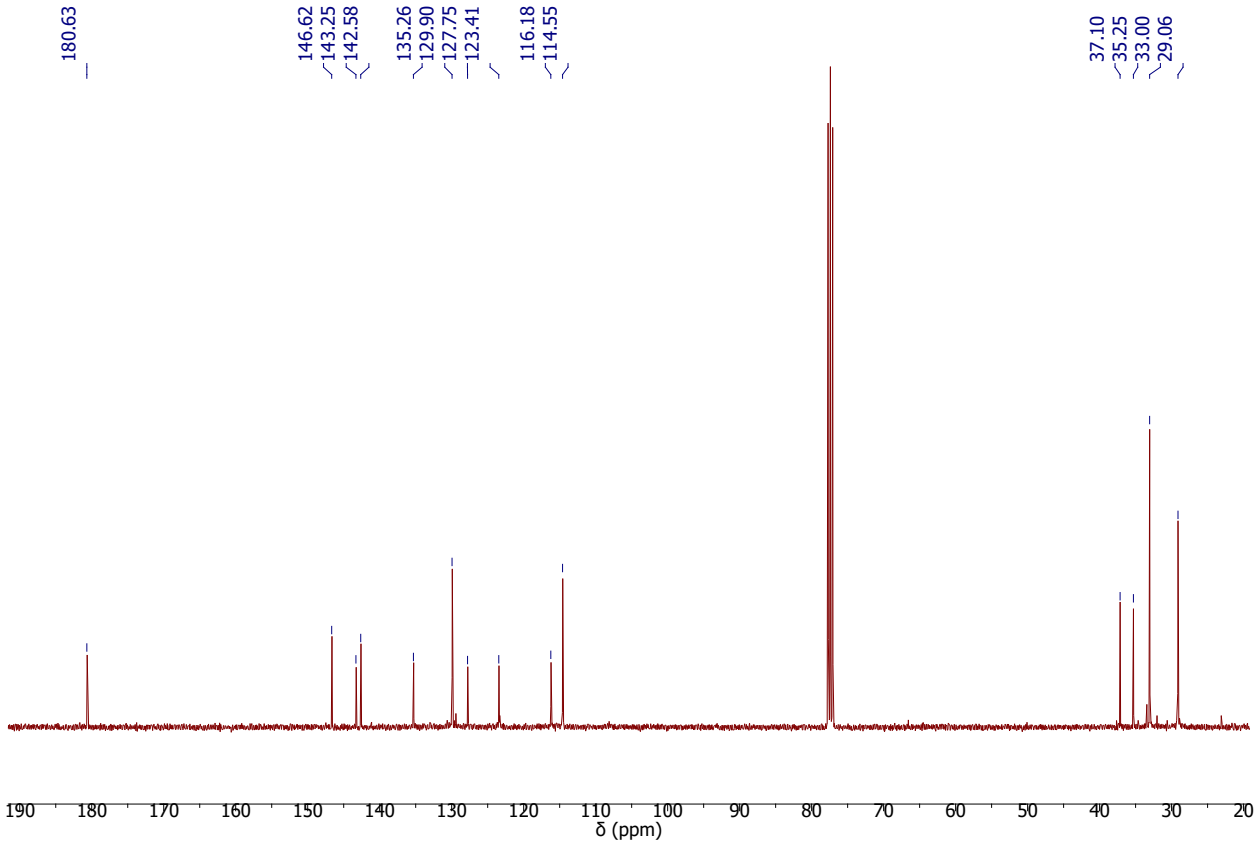

Figure S4. ^{13}C-NMR spectrum ($CDCl_3$, 223 K) of tautomer **2**

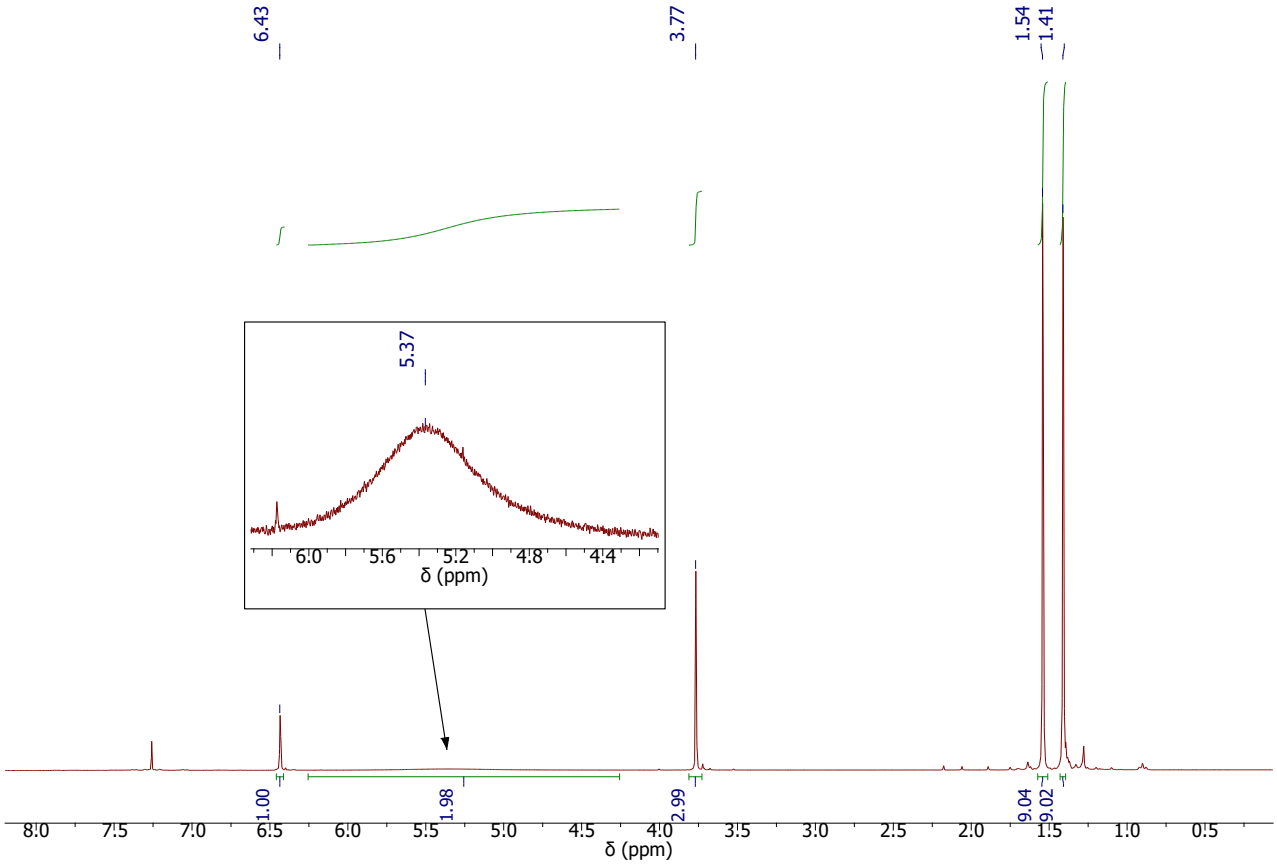

Figure S5. ^{1}H-NMR spectrum ($CDCl_3$, 298 K) of compound **3**

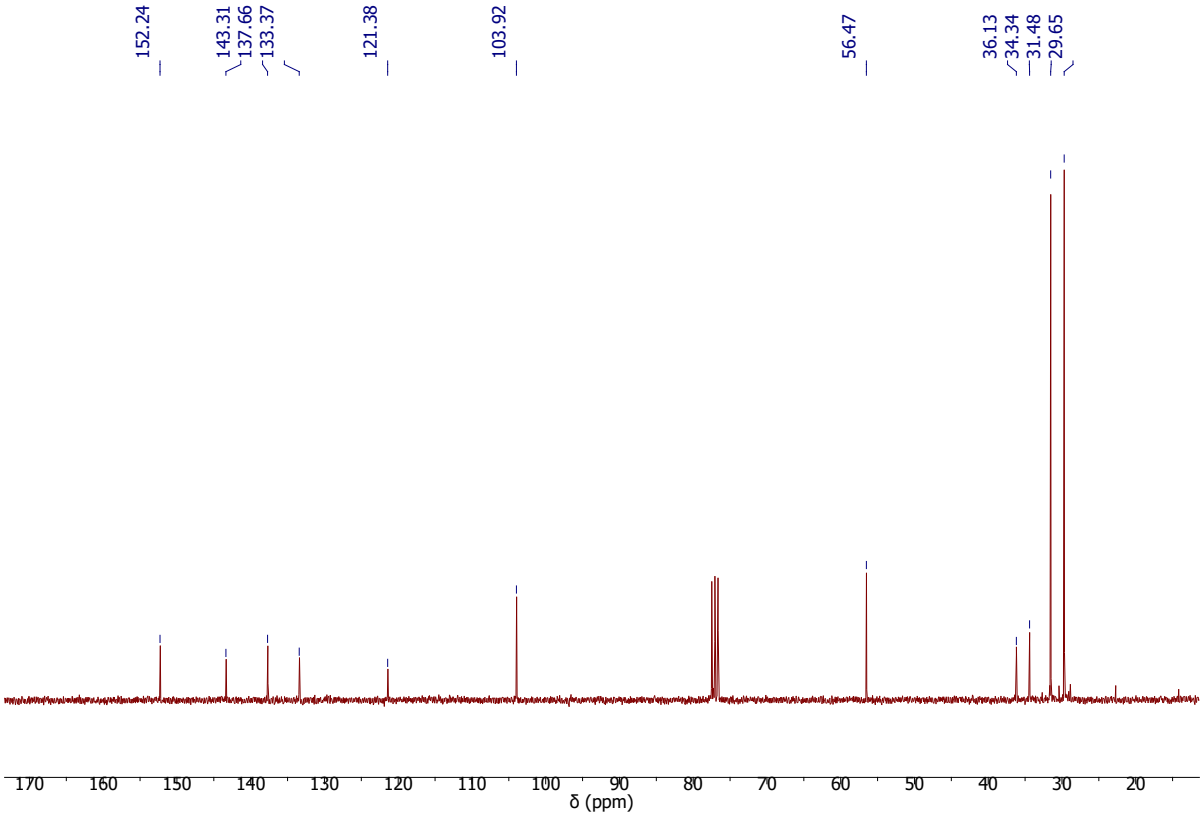

Figure S6. ^{13}C-NMR spectrum ($CDCl_3$, 298 K) of compound **3**

Thermodynamic parameters of tautomerization

Table S1. Temperature dependence of **[2]**, **[2']** and K_{eq}, estimated by ^{1}H-NMR in **$CDCl_3$**

***T*/K**	**[2]**, %	**[2']**, %	K_{eq}	**$1/T$, K^{-1}**	**$\ln K_{eq}$**
223	92.01	7.99	0.08684	0.00448	-2.44371
244	87.50	12.50	0.14286	0.0041	-1.94591
254	85.34	14.66	0.17178	0.00394	-1.76152
264	83.80	16.20	0.19332	0.00379	-1.64342
273	81.74	18.26	0.22339	0.00366	-1.49883
293	76.74	23.26	0.3031	0.00341	-1.19369
303	74.80	25.20	0.3369	0.0033	-1.08797
323	70.39	29.61	0.42066	0.0031	-0.86594

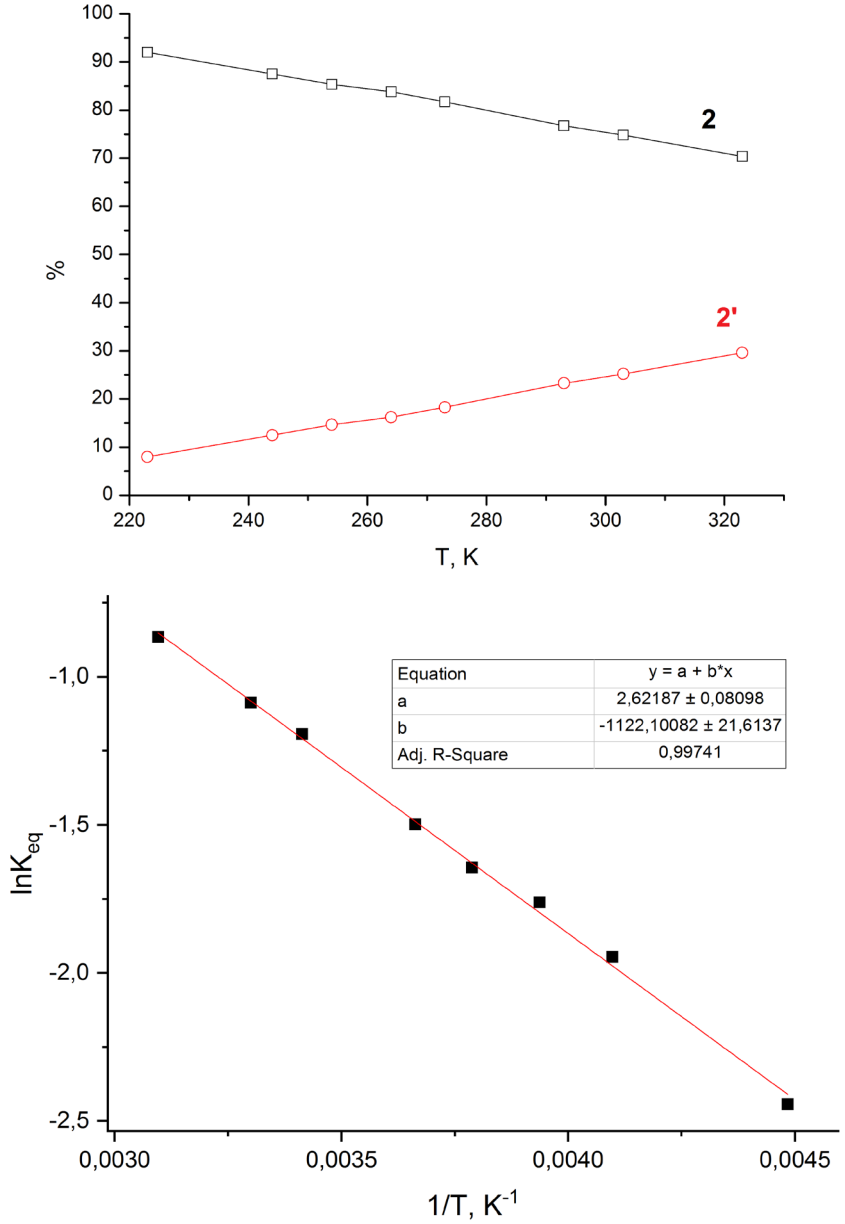

Figure S7. Relative concentrations of tautomers **2** and **2'** in $CDCl_3$ solution (C = 0.05 M) vs temperature (top) ; plot $\ln K_{eq}$ – $1/T$ for tautomerization in $CDCl_3$ (bottom)

Table S2 Temperature dependence of **[2]**, **[2']** and K_{eq}, estimated by ^{1}H-NMR in **benzene-d$_6$**

***T*, K**	**[2]**, %	**[2']**, %	K_{eq}	**1/*T*, K^{-1}**	**lnK_{eq}**
298	67.20	32.80	0.4881	0.00336	-0.71724
303	65.83	34.17	0.51906	0.0033	-0.65573
313	63.74	36.26	0.56887	0.00319	-0.5641
323	62.11	37.89	0.61005	0.0031	-0.49422
333	60.02	39.98	0.66611	0.003	-0.4063
343	58.52	41.48	0.70882	0.00292	-0.34416

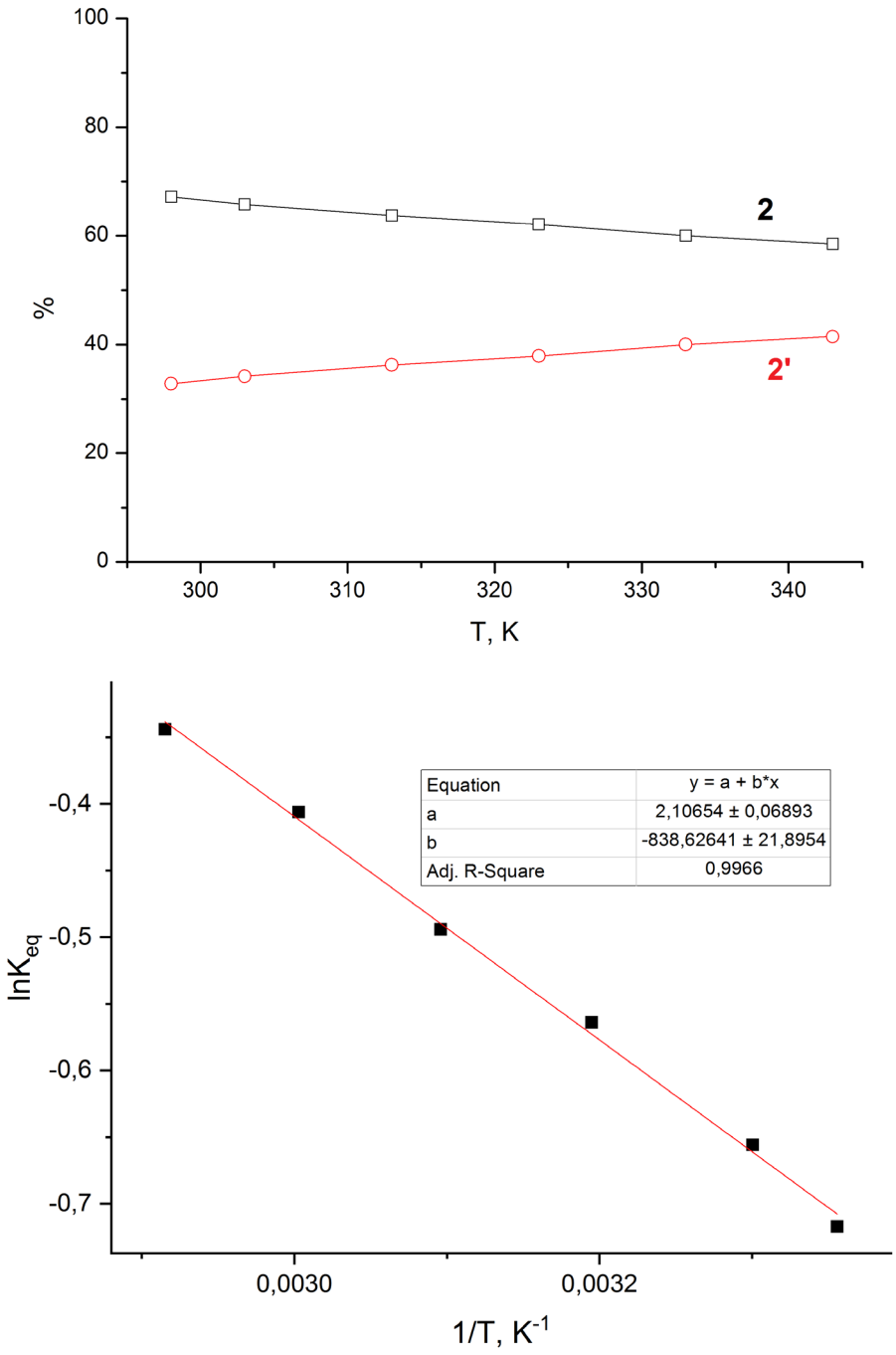

Figure S8. Relative concentrations of tautomers **2** and **2'** in benzene-d$_6$ solution (C = 0.05 M) *vs* temperature (top) ; plot ln K_{eq} – 1/T for tautomerization in benzene-d$_6$ (bottom)

Table S3. Temperature dependence of **[2]**, **[2']** and K_{eq}, estimated by ^{1}H-NMR in **toluene-d$_8$**

***T*, K**	**[2]**, %	**[2']**, %	K_{eq}	**1/*T*, K^{-1}**	**lnK_{eq}**
213	89.32	10.68	0.11963	0.00469	-2.12333
223	85.99	14.01	0.16294	0.00448	-1.8144
233	82.58	17.42	0.21102	0.00429	-1.5558
243	80.33	19.67	0.24488	0.00412	-1.40699
253	77.75	22.25	0.28626	0.00395	-1.25087
263	75.92	24.08	0.3172	0.0038	-1.14823
273	73.16	26.84	0.36687	0.00366	-1.00276
283	70.91	29.09	0.41024	0.00353	-0.89102
293	69.02	30.98	0.44886	0.00341	-0.80105
296	68.74	31.26	0.45479	0.00338	-0.78792
303	67.12	32.88	0.48983	0.0033	-0.71369
313	64.41	35.59	0.55267	0.00319	-0.59299
323	63.30	36.70	0.57973	0.0031	-0.54519
333	61.73	38.27	0.62009	0.003	-0.47789

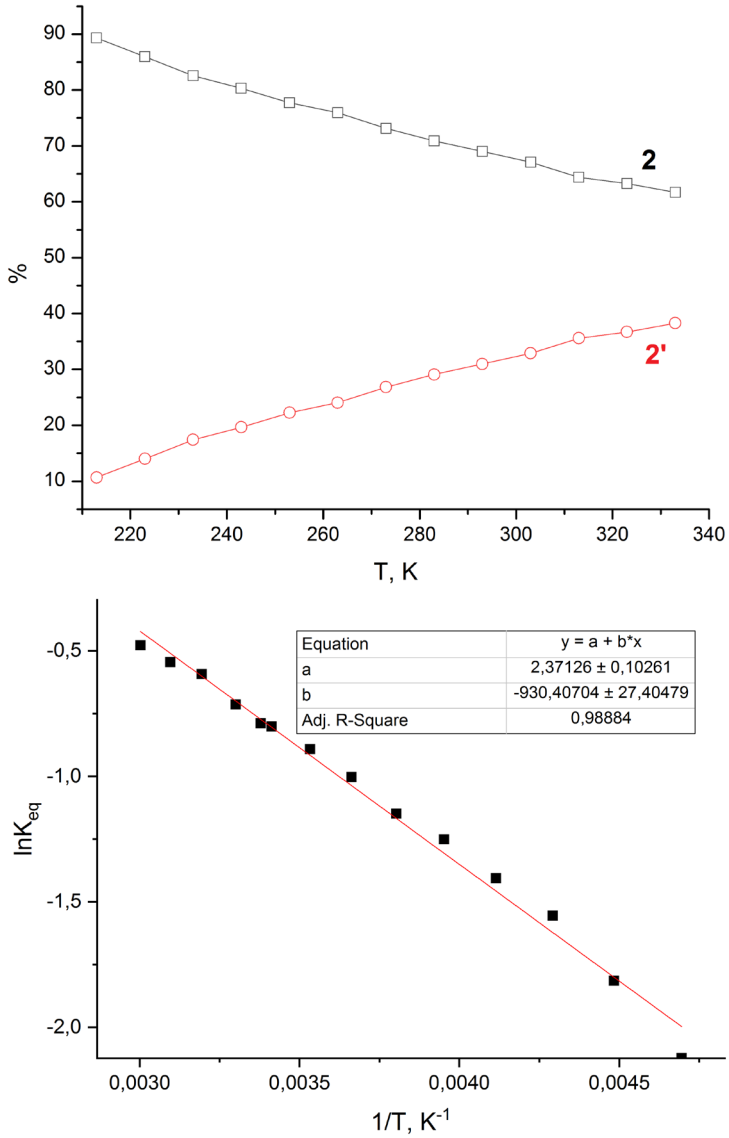

Figure S9. Relative concentrations of tautomers **2** and **2'** in toluene-d$_8$ solution (C = 0.05 M) *vs* temperature (top) ; plot ln K_{eq} – 1/T for tautomerization in toluene-d$_8$ (bottom)

Table S4. Temperature dependence of **[2]**, **[2']** and K_{eq}, estimated by ^{1}H-NMR in **CD_3CN**

***T*, K**	**[2]**, %	**[2']**, %	K_{eq}	**$1/T$, K^{-1}**	**$\ln K_{eq}$**
243	85.74	14.26	0.16628	0.00412	-1.79409
263	83.83	16.17	0.19302	0.0038	-1.64496
283	81.48	18.52	0.22736	0.00353	-1.48124
298	80.17	19.83	0.24741	0.00336	-1.39669

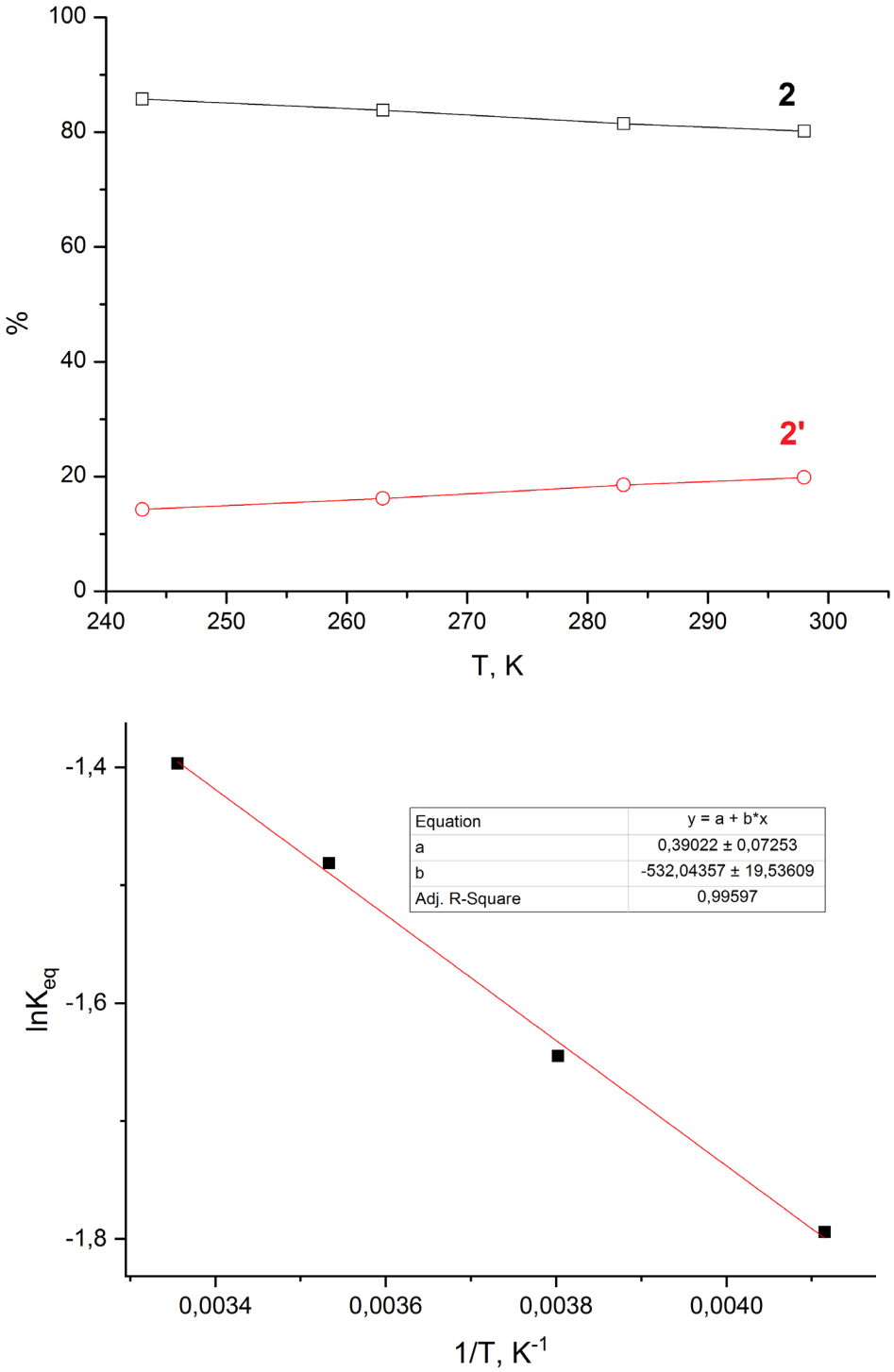

Figure S10. Relative concentrations of tautomers **2** and **2'** in CD_3CN solution (C = 0.05 M) *vs* temperature (top) ; plot ln K_{eq} – $1/T$ for tautomerization in CD_3CN (bottom)

SC XRD data

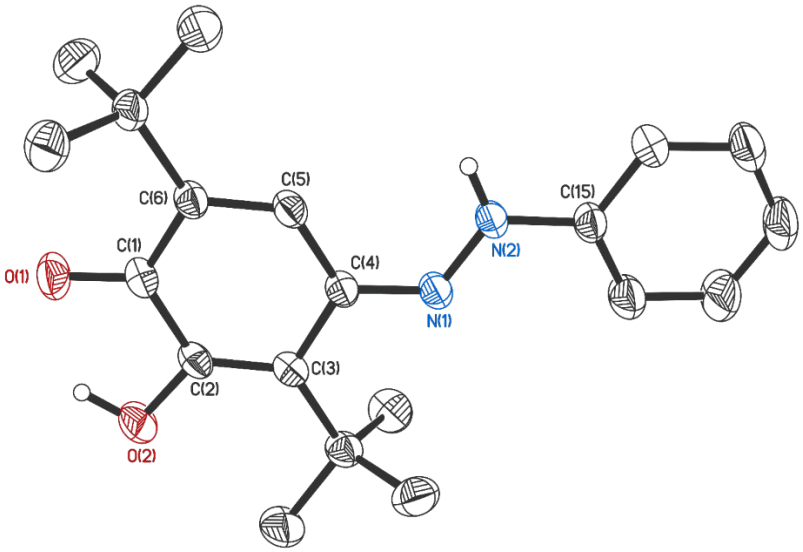

Figure S11. The molecular structure of **2**. Thermal ellipsoids are given with 30% probability level. All hydrogen atoms except H(2A). H(2B) are omitted for clarity.

Table S5. Selected bonds lengths and angles for **2**.

Bond	**Distance. Å**	**Angle**	**Value. deg.**
O(1)-C(1)	1.253(2)	O(1)-C(1)-C(2)	116.4(1)
O(2)-C(2)	1.365(2)	O(2)-C(2)-C(1)	111.3(1)
C(1)-C(2)	1.465(2)	C(4)-N(1)-N(2)	121.7(1)
C(2)-C(3)	1.355(2)	N(1)-N(2)-C(15)	120.3(1)
C(3)-C(4)	1.467(2)		
C(4)-C(5)	1.442(2)		
C(5)-C(6)	1.349(2)		
C(6)-C(1)	1.454(2)		
N(1)-N(2)	1.318(2)		
N(1)-C(4)	1.324(2)		
N(2)-C(15)	1.404(2)		

Table S6. Geometrical parameters of hydrogen bonds in **2**

Bond	**D-H. Å**	**H…A. Å**	**D…A. Å**	**D-H…A. deg.**
O(2)-H(2A)..O(1)	0.92(3)	1.83(2)	2.523(2)	131(2)
N(2)-H(2B)..O(2)	0.86(2)	2.36(2)	3.120(2)	147(2)