

Supplementary information for

***Out*-Basicity of 1,8-bis(dimethylamino)naphthalene: The experimental and theoretical challenge**

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Table of Contents

NOESY ¹ H– ¹ H and HMBC ¹ H– ¹⁵ N correlation plots for alcohol 11 (Fig. S1)	S2
¹ H NMR plots showing dynamic behavior of C ₆ H ₅ substituent in 11 (Fig. S2).....	S3
¹ H NMR plots showing dynamic behavior of N–Me groups in 11 (Fig. S3).....	S4
Selected geometrical parameters of tertiary alcohol 11 (Table S1).....	S5
Details of quantum-chemical calculations.....	S6
DFT optimized structures of conformers 11a and 11b and their total energies (Fig. S4).....	S7
Calculation of p <i>K</i> _a (<i>out</i>) value for the N ₁ atom in alcohol 11	S8
Examples of organic compounds with flat nitrogen atoms (Chart S1).....	S9
¹ H NMR plots showing dynamic behavior of salt 17 ·HBF ₄ (Fig. S5)	S10
Crystal data and structure refinement for compounds 11 , 11 ·HClO ₄ , and 17 ·HBF ₄ (Table S2)	S11
Copies of ¹ H and ¹³ C NMR spectra	S12–S16

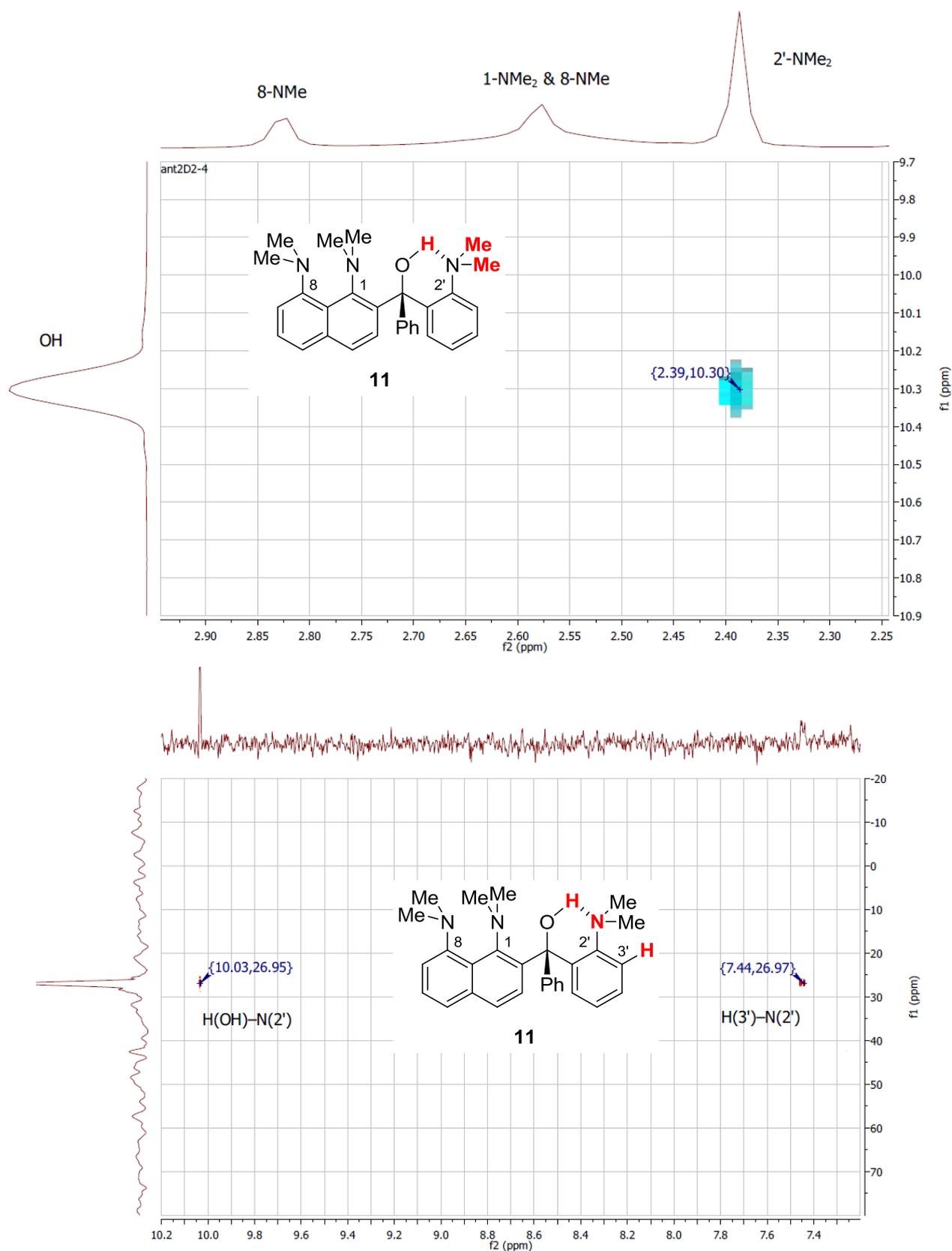


Fig. S1 NOESY ¹H-¹H (250 MHz, CDCl₃, above) and HMBC ¹H-¹⁵N (600 MHz, DMSO-d₆, below, nitrogen scale referenced to MeNO₂) correlation plots for alcohol **11**.

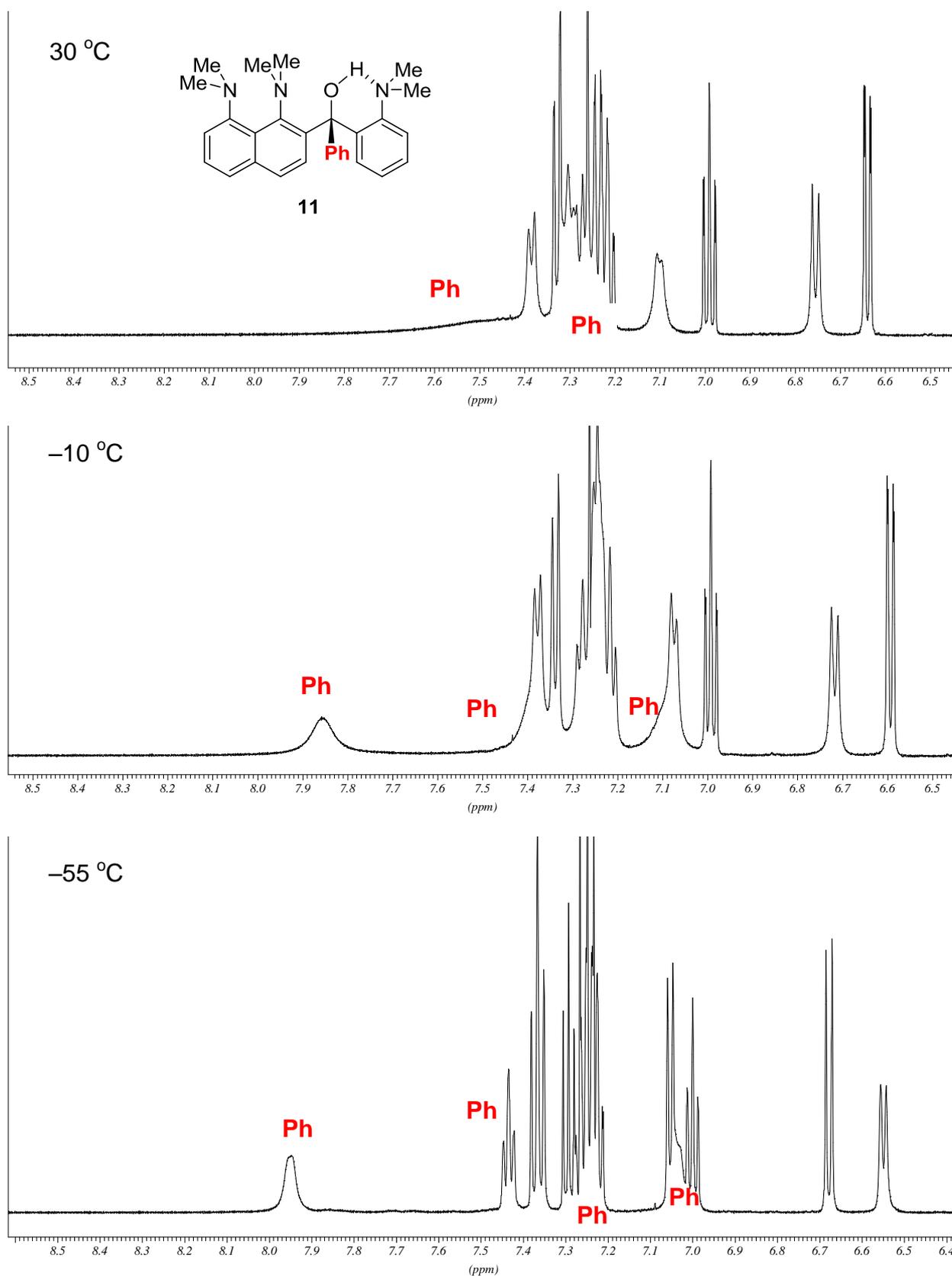


Fig. S2 ¹H NMR plots showing dynamic behavior of C₆H₅ substituent in **11** (600 MHz, CDCl₃, aromatic region at indicated temperatures).

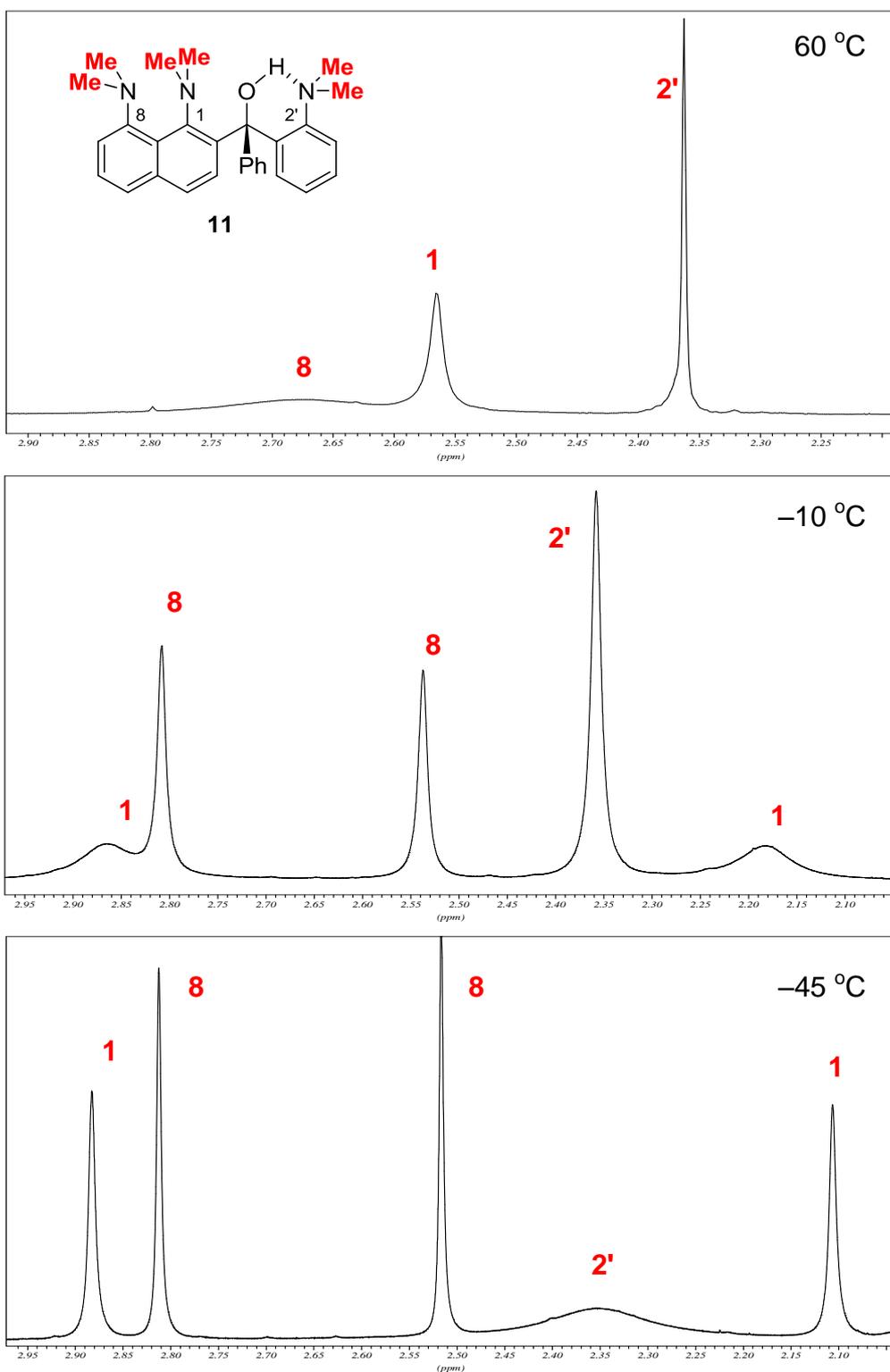
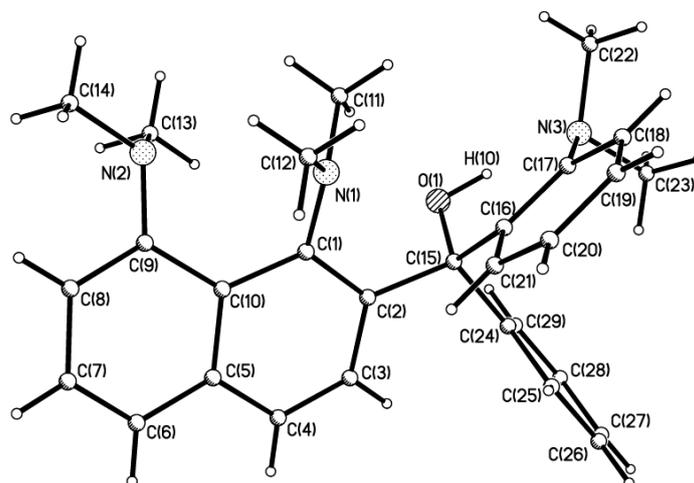


Fig. S3 ^1H NMR plots showing dynamic behavior of N-Me groups in **11** (600 MHz, CDCl_3 , aliphatic region at indicated temperatures).

Table S1 Selected geometrical parameters of tertiary alcohol **11** (X-ray diffraction, 120 K)



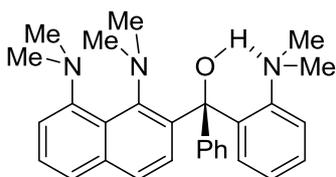
Parameter	Distances, Å and angles, (°)	Parameter	Distances, Å and angles, (°)
N ₁ ...N ₂	2.855	∠naphthalene ring–Ph	72
N ₁ ...O	3.176	∠naphthalene ring–C ₆ H ₄ NMe ₂	76
ΣN ₁	357.5	∠naphthalene ring–N(1)Me ₂	67
ΣN ₂	339.4	∠naphthalene ring–N(2)Me ₂	44
ΣN ₃	335.1	∠Ph–C ₆ H ₄ NMe ₂	86
ΔN ₁ ^a	0.640	∠C ₆ H ₄ –N(3)Me ₂	73

^a Deviation of N₁ atom from mean naphthalene plane.

Details of quantum-chemical calculations. The current consensus in the literature states that calculations of potential energy surface are a reliable source of information of hydrogen bonding, spectral characteristics and a possible reaction pathway of chemical reactions.¹ The simulations was carried out using the Gaussian 09 suite of programs.² First, the energy minimization was performed using the DFT with the B3LYP functional.^{3,4} The calculations under the non-adiabatic approach are described, that is under the full optimization of all parameters except one (NH bond length or CCNH torsion angle) which was fixed. For the method of gas-phase calculations of all potential energy minima, see lit.⁵

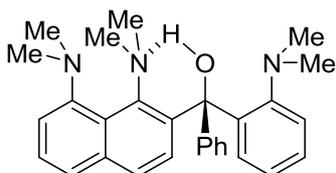
- (1) Hadži, D. *Theoretical Treatments of Hydrogen Bonding*, John Wiley & Sons: Chichester, New York, Weinheim, Brisbane, Singapore, Toronto, 1997.
- (2) M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A.Jr. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D. Fox, J. *Gaussian 09*, Revision B01, Gaussian, Inc., Wallingford CT, 2009.
- (3) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- (4) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1993, **37**, 785–789.
- (5) V. A. Ozeryanskii, A. A. Milov, V. I. Minkin, A. F. Pozharskii, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 1453–1456.

Conformer 11a



Gas $E = -1364.7253374$	CHCl_3 $E = -1364.7346569$	DMSO $E = -1364.7392029$

Conformer 11b



Gas $E = -1364.7209451$	CHCl_3 $E = -1364.7301783$	DMSO $E = -1364.7345312$

Fig. S4 DFT optimized structures of conformers **11a** and **11b** and their total energies (in a.u.).

Calculation of $pK_a(out)$ value for the N_1 atom in alcohol **11**

$$\Delta\Delta G^\circ = 2.3RT\Delta pK_a$$

$$R = 1.98726 \text{ cal K}^{-1} \text{ mol}^{-1}, \Delta\Delta G^\circ \sim 2.85 \text{ kcal mol}^{-1} \text{ (average value from Table 3), } T = 298 \text{ K}$$

$$\Delta pK_a = (2.85 \cdot 1000) / (2.3 \cdot 1.98726 \cdot 298) = 2.09$$

Using DMA as reference:

$$\text{In H}_2\text{O: } pK_a(N_1) = pK_a(\text{DMA}) - \Delta pK_a = 5.16 - 2.09 = \sim 3.1$$

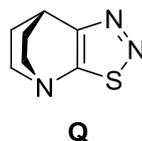
$$\text{In MeCN: } pK_a(N_1) = pK_a(\text{DMA}) - \Delta pK_a = 11.43 - 2.09 = \sim 9.3$$

In fact, the conformation of the N_3 atom in DMA residue of **11** ($\Sigma N_3 = 335.1^\circ$) is closer to benzoquinuclidine system **Q** ($\Sigma N = 319.7^\circ$) rather than to the dimethylaniline base ($\Sigma N = 352\text{--}360^\circ$).⁶ From this, it might be more justified to compare the *out*-basicity of the N_1 atom in **11** with the pK_a value of benzoquinuclidine, which is equal to 7.79.⁷

Using benzoquinuclidine as reference:

$$\text{In H}_2\text{O: } pK_a(N_1) = pK_a(\text{benzoquinuclidine}) - \Delta pK_a = 7.79 - 2.09 = \sim 5.7$$

(6) By August 2013, the Cambridge Structural Database contains no information on geometry of both benzoquinuclidine and *N,N*-dimethylaniline. The data given refer to benzoquinuclidine analogue **Q** (M. L. Petrov, V. A. Kuznetsov, *Russ. J. Org. Chem.*, 2006, **42**, 1744) and a number of DMA solvates (CCDC).



(7) A. J. Hoefnagel, M. A. Hoefnagel, B. M. Wepster, *J. Org. Chem.*, 1981, **46**, 4209–4211.

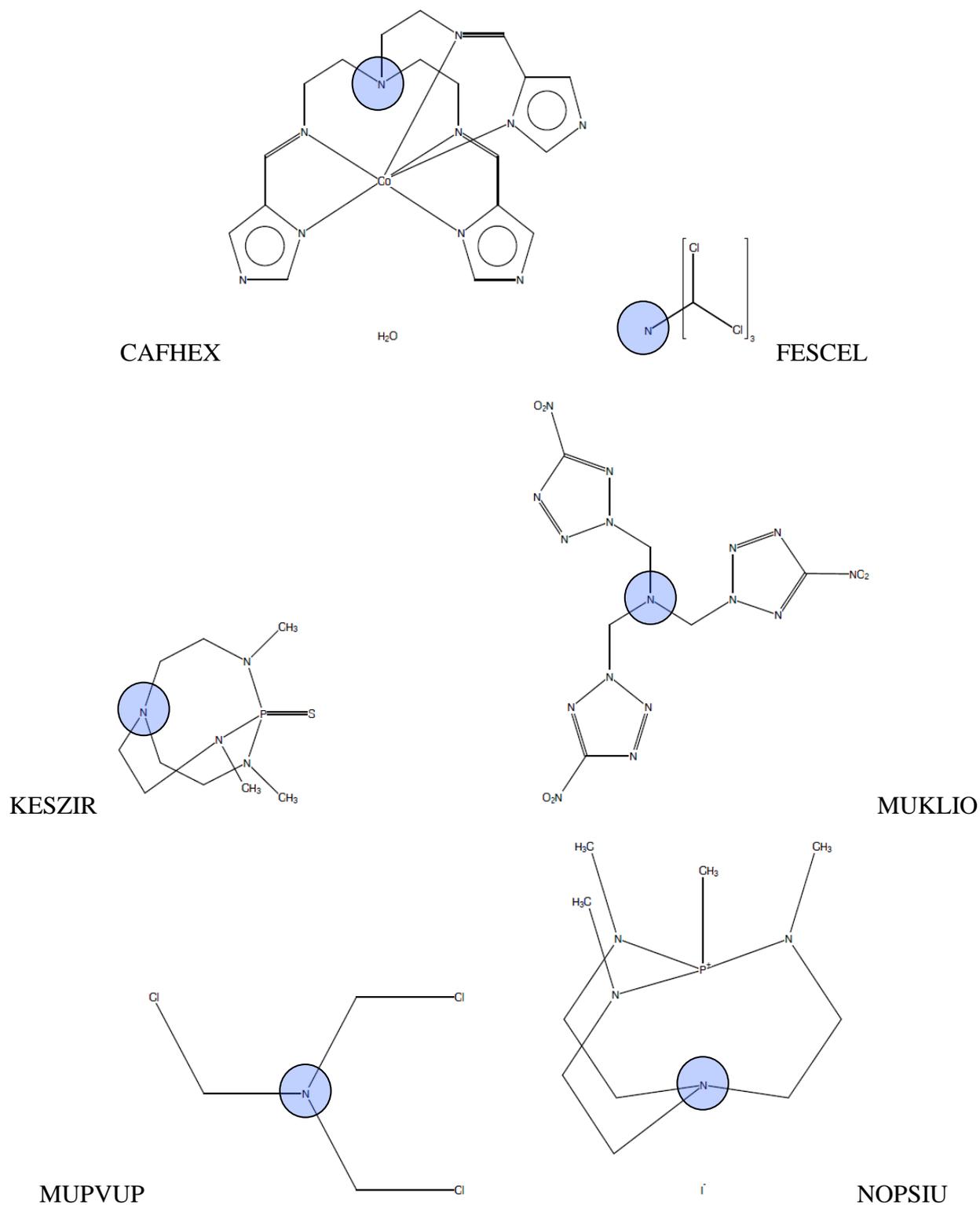


Chart S1 Examples of organic compounds with flat nitrogen atoms and their CSD entry codes.

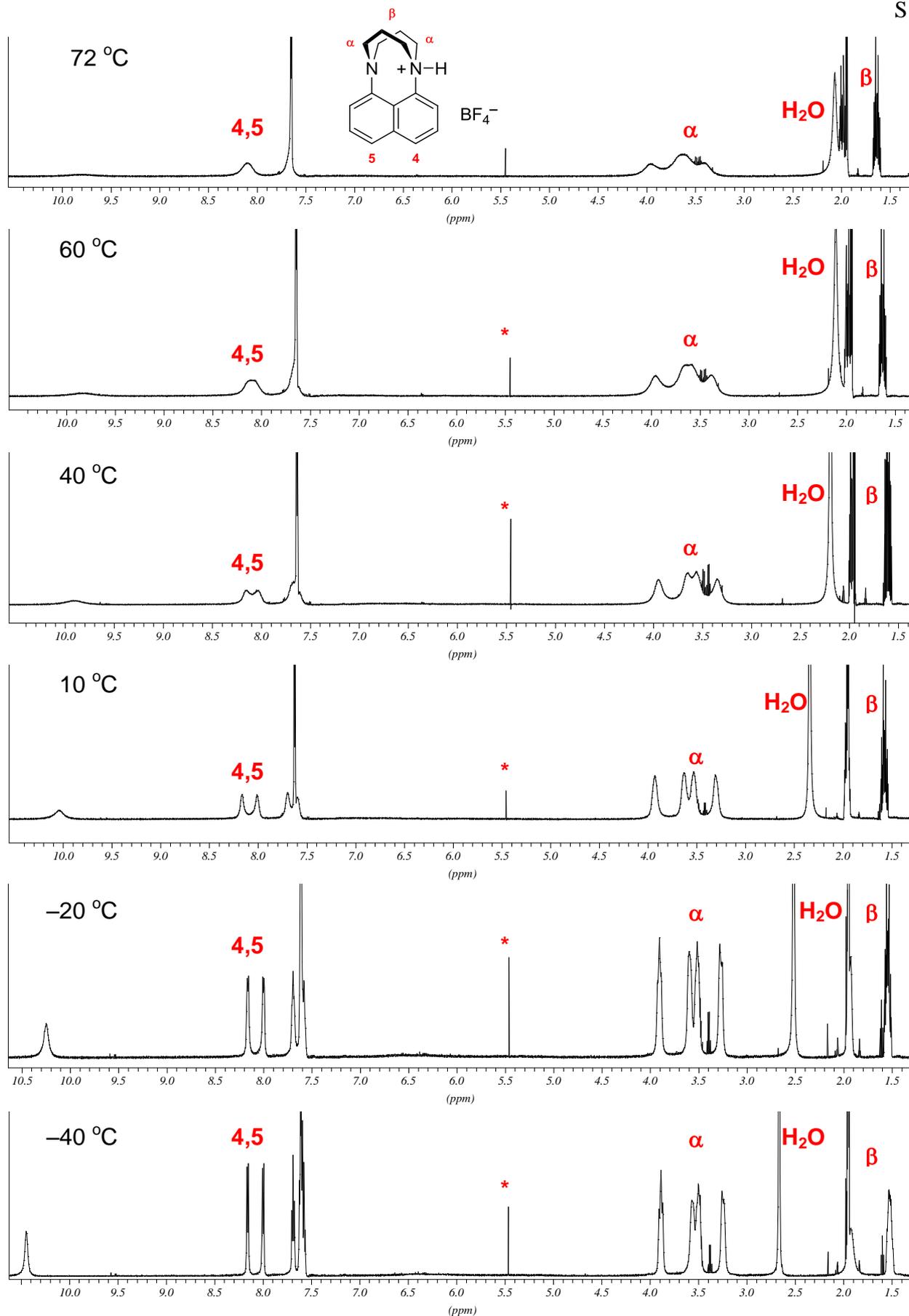


Fig. S5 ¹H NMR plots showing dynamic behavior of salt **17**·HBF₄ (600 MHz, CD₃CN).

Table S2 Crystal data and structure refinement for compounds **11**, **11**·HClO₄, and **17**·HBF₄

Parameter	11	11 ·HClO ₄	17 ·HBF ₄
Empirical formula	C ₂₉ H ₃₃ N ₃ O	C ₂₉ H ₃₄ ClN ₃ O ₅	C ₁₆ H ₁₉ BF ₄ N ₂
Formula weight	439.58	540.04	326.14
<i>T</i> (K)	120(2)	100(2)	100(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	13.8234(14)	21.5820(10)	12.8809(6)
<i>b</i> (Å)	14.4667(14)	7.8022(4)	8.8823(4)
<i>c</i> (Å)	24.486(2)	15.6198(8)	13.1761(6)
<i>β</i> (°)	90	95.6800(10)	97.9550(10)
<i>V</i> (Å ³)	4896.6(8)	2617.6(2)	1493.00(12)
<i>Z</i> , <i>D_c</i> (Mg m ⁻³)	8, 1.193	4, 1.370	4, 1.451
<i>μ</i> (mm ⁻¹)	0.073	0.192	0.120
Reflections collected/unique	39680/4770	29499/6966	14795/3948
<i>R</i> (int)	0.0810	0.0347	0.0194
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0982, 0.1239	0.0569, 0.1104	0.0417, 0.0975
<i>R</i> factor (%)	4.95	4.07	3.46

Copies of ^1H and ^{13}C NMR spectra

