Supporting information

Positively and negatively charged NHN hydrogen bonds in one molecule: synergistic strengthening effect, superbasicity and acetonitrile capture

Marina P. Vlasenko,[a] Valery A. Ozeryanskii,*[a] Alexander F. Pozharskii[a] and Olesya V. Khoroshilova[b]

[a]Department of Organic Chemistry, Southern Federal University, Zorge str. 7, 344090 Rostov-on-Don, Russian Federation. E-mail: vv_ozer2@sfedu.ru
[b]Institute of Chemistry, St. Petersburg State University, Universitetskii pr. 26, 198504 St. Petersburg, Russian Federation

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Experimental Section

Spectroscopic Measurements and General Considerations

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 (250 MHz for ^1H, 62.9 MHz for ^{13}C) and Bruker Avance-400 (400 MHz for ^1H, 100.6 MHz for ^{13}C) spectrometers with the solvent residual peaks as the internal standard (δ/ppm, ^nJ/Hz). Mass spectra were obtained from Bruker maXis mass spectrometer (electrospray ionization). Thin layer chromatography was carried out on Al_2O_3 and on silica gel (70–230 mesh, Aldrich). The progress of reactions and the purity of products were monitored by TLC on Al_2O_3; development with iodine vapor. The melting points were measured in sealed capillaries and are uncorrected. The solvents were purified and dried by standard methods. Commercial grade reagents were used in case of 1,8-bis(dimethylamino)naphthalene (**1**) (Alfa Aesar, 98+%), Pd/C 5% (Acros Organics).

Preparation of Starting Materials

Compound **9** was prepared as described previously [S1].

Tosylation was performed by analogy to a published method for 4,5-bis(dimethylamino)-1-(*p*-toluenesulfonamido)naphthalene [S2].

4,5-Bis(dimethylamino)-8-nitro-1-(*p*-toluenesulfonamido)naphthalene (10). Pyridine (0.24 mL, 3 mmol) and tosyl chloride (0.21 g, 1.1 mmol) were added to a solution of amine **9** (0.274 g, 1 mmol) in anhydrous chloroform (15 mL). The mixture was stirred for 36 h at r.t. in Ar-atmosphere until the starting amine disappeared and then neutralized with aq. KOH (1.1 mmol). The organic layer was separated, washed with the equal amount of water, dried with anhydrous Na_2SO_4 and concentrated to the minimum volume. Sulfonamide **10** was isolated by preparative thin-layer chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction (R_f=0.42). Dark red crystals with mp 163–165 °C (from EtOAc). Yield 0.248 g (58%). ^1H NMR ($CDCl_3$): δ = 2.28 (s, 3H, Me), 2.81 (s, 6H, 4-NMe_2), 3.00 (s, 6H, 5-NMe_2), 6.48 (d, *J*=9.0, 1H, 6-H), 6.92 (d, *J*=7.9, 2H, 3'-H, 5'-H), 6.97 (d, *J*=8.4, 1H, 3-H), 7.08 (s, 1H, NH), 7.14 (d, *J*=8.1, 2H, 2'-H, 6'-H), 7.62 (d, *J*=8.4, 1H, 2-H), 7.74 (d, *J*=9.0, 1H, 7-H). ^{13}C NMR ($CDCl_3$): δ = 42.8 and 43.9 (NMe_2), 60.4, 106.2, 112.1, 115.8, 121.0, 126.7, 128.4, 128.9, 130.2, 132.8, 135.4, 136.1, 142.2, 151.3, 157.2. ESI-HRMS: MH^+ = 429.1598, calc: 429.1591. IR (MeCN), ν/cm^{-1}: 3240 (NH), 3065 (CH), 2803, 1577 (*as*NO_2), 1481 (ring), 1379 (SO_2), 1304 (*s*NO_2), 1131 (SO_2).

8-Amino-4,5-bis(dimethylamino)-1-(*p*-toluenesulfonamido)naphthalene (11). A mixture consisting of nitroamide **10** (150 mg, 0.35 mmol), MeOH (10 mL) and 5% Pd/C (30 mg, about 0.2 if taken from the mass of the amide) was hydrogenated at room temperature with shaking until the starting nitroamide is consumed (controlled by TLC, Al_2O_3/MeCN). After that, the catalyst was filtered off and the solvent was removed to give amine **10** with quantitative yield as gray solid darkening in the air; mp 168–170 °C (MeCN). ^1H NMR (CD_3CN): δ = 2.32 (s, 3H, CH_3), 2.86 (d, *J*=2.2, 6H, 5-NMe_2), 2.90 (d,

J=2.6, 6H, 4-NMe_2), 6.35 (d, J=8.4, 1H, 7-H), 6.94 (d, J=8.4, 1H, 2-H), 7.21 (m, 4H, 3-H, 6-H, 3'-H, 5'-H), 7.73 (d, J=8.1, 2'-H, 6'-H), 19.28 (s, 1H, 4N···H···5N) and 2H (very br. s, NH_2); see Figure S3. ^{13}C NMR (CD_3CN): δ = 20.3 (Me), 45.3 (NMe_2), 45.5 (NMe_2), 106.2, 110.5, 121.1, 121.2, 122.5, 126.7, 128.7, 129.2, 130.9, 140.1, 143.6, 150.7, 150.9. ESI-HRMS: MH^+ = 399.1865, calc: 399.1849. IR (MeCN), ν/cm^{-1}: 3438, 3363 (NH_2), 3202 (NH), 3096 (CH), 2788, 1130 (SO_2).

4,5-Bis(dimethylamino)-1,8-bis(*p*-toluenesulfonamido)naphthalene, zwitterion (12). Freshly prepared amine **11** (0.139 g, 0.35 mmol) was reacted with tosyl chloride (0.073 g, 0.385 mmol) dissolved in pyridine (2 mL). The mixture was stirred for 24 h at r.t. in Ar-atmosphere until the starting amine disappeared and then neutralized with aq. KOH (1.1 mmol). The organic layer was separated, washed with the equal amount of water, dried with anhydrous Na_2SO_4, and concentrated to the minimum volume. Target zwitterion **12** was isolated by preparative thin-layer chromatography (Al_2O_3, MeCN). Major fraction (R_f=0.9) gave **12** as a light beige solid (its solutions possess blue fluorescence under UV-light) with 60% yield (0.116 g); mp 219–220 °C (MeCN). ^{1}H NMR (CD_3CN): δ = 2.32 (s, 6H, two CH_3), 2.87 (d, J=2.6, 12H, 4-NMe_2, 5-NMe_2), 7.22 (d, J=8.0, 4H, 3'-H, 5'-H, 3''-H, 5''-H), 7.36 (m, 4H, 2-H, 3-H, 6-H, 7-H), 7.78 (d, J=8.2, 4H, 2'-H, 6'-H, 2''-H, 6''-H), 17.56 (br. d, 1H, 1N···H···2N), 19.11 (s, 1H, 4N···H···5N). ^{13}C NMR (CD_3CN): δ = 20.4 (Me), 45.4 (NMe_2), 111.4, 121.3, 126.9, 129.1, 134.6, 140.2, 142.2, 144.3. ^{1}H NMR (DMSO-d_6): δ = 2.53 (s, 6H, two CH_3), 2.93 (br. s, 12H, 4-NMe_2, 5-NMe_2), 7.29 (m, 6H, 3'-H, 5'-H, 3''-H, 5''-H, 2-H, 3-H), 7.61 (d, J=8.5, 2H, 6-H, 7-H), 7.78 (d, 4H, J=7.6, 2'-H, 6'-H, 2''-H, 6''-H), 17.75 (br. s, 1H, 1N···H···2N), 18.88 (s, 1H, 4N···H···5N). ^{13}C NMR (DMSO-d_6): δ = 21.3 (Me), 46.0 (NMe_2), 111.2, 118.0, 122.0, 127.1, 129.7, 135.2, 140.3, 142.0, 144.0. ESI-HRMS: MH^+ = 553.1962, calc: 553.1938. IR (nujol), ν/cm^{-1}: 3227 (NH), 1310, 1125 (SO_2).

Tetrafluoroborate 12·HBF$_4$: colorless crystals decomp. above 215 °C (from MeCN). ^{1}H NMR (CD_3CN): δ = 2.41 (s, 6H, CH_3), 2.87 (d, J=2.4, 12H, 4-NMe_2, 5-NMe_2), 7.13 (d, J=8.5, 2H, 3-H, 6-H), 7.32 (d, J=8.0, 4H, 3'-H, 5'-H, 3''-H, 5''-H), 7.59 (d, J=8.2, 4H, 2'-H, 6'-H, 2''-H, 6''-H), 7.70 (d, J=8.3, 2H, 2-H, 7-H), 9.63 (s, 2H, 1,2-NH), 19.14 (br. s, 1H, 4N···H···5N). ^{13}C NMR (CD_3CN): δ = 20.5 (Me), 45.6 (NMe_2), 121.8, 122.9, 127.9, 129.7, 133.2, 134.1, 142.5, 145.2.

X-Ray Diffraction Analysis

Crystals suitable for X-ray studies were grown up by slow evaporation from solutions of compounds in appropriate solvents: **12** (MeCN), **12·HBF$_4$** (MeOH). X-Ray measurements were conducted with Bruker APEX II diffractometer (Mo-K_α line, graphite monochromator, ω-scanning) and SuperNova, Single source at offset/far, HyPix3000 (Cu-K_α line). Structure **12** was solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. Structure **12·HBF$_4$** was solved with the ShelXT structure solution program using

Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. All hydrogen atoms were placed in geometrically calculated positions and were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to n·U_{eq}(C_i) (n = 1.2 for CH and CH_2 groups and n = 1.5 for CH_3 groups), where U(C_i) are respectively the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. The main crystallographic data and some experimental details are given in Table S1. CCDC 1898534–1898535 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and structure refinement for compounds **12** and **12·HBF$_4$**

Compound	**12**·CH_3CN	**12·HBF$_4$**
Empirical formula	$C_{28}H_{32}N_4O_4S_2 \cdot CH_3CN$	$C_{28}H_{33}BF_4N_4O_4S_2$
Formula weight	593.75	640.51
T [K]	120(2)	100(5)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	9.6465(18)	11.09480(10)
b [Å]	16.788(3)	12.45500(10)
c [Å]	18.275(4)	22.3878(2)
α [°]	90	90
β [°]	91.406(3)	97.1510(10)
γ [°]	90	90
V [Å^3]	2958.8(10)	3069.61(5)
Z	4	4
D_c [g cm^{-3}]	1.333	1.386
μ [mm^{-1}]	0.224	2.140
Radiation	MoK$_\alpha$ (λ = 0.71073)	CuK$_\alpha$ (λ = 1.54184)
No. of refl. collected/ unique	7756/6586	6112/5577
No. of parameters	382	397
R indices (all data)	R_1 = 0.0398 wR_2 = 0.1007	R_1 = 0.0508 wR_2 = 0.1376
R-factor [%]	4.98	4.76
CCDC Dep. Nos.	1898535	1898534

^{1}H and ^{13}C NMR spectra of new compounds

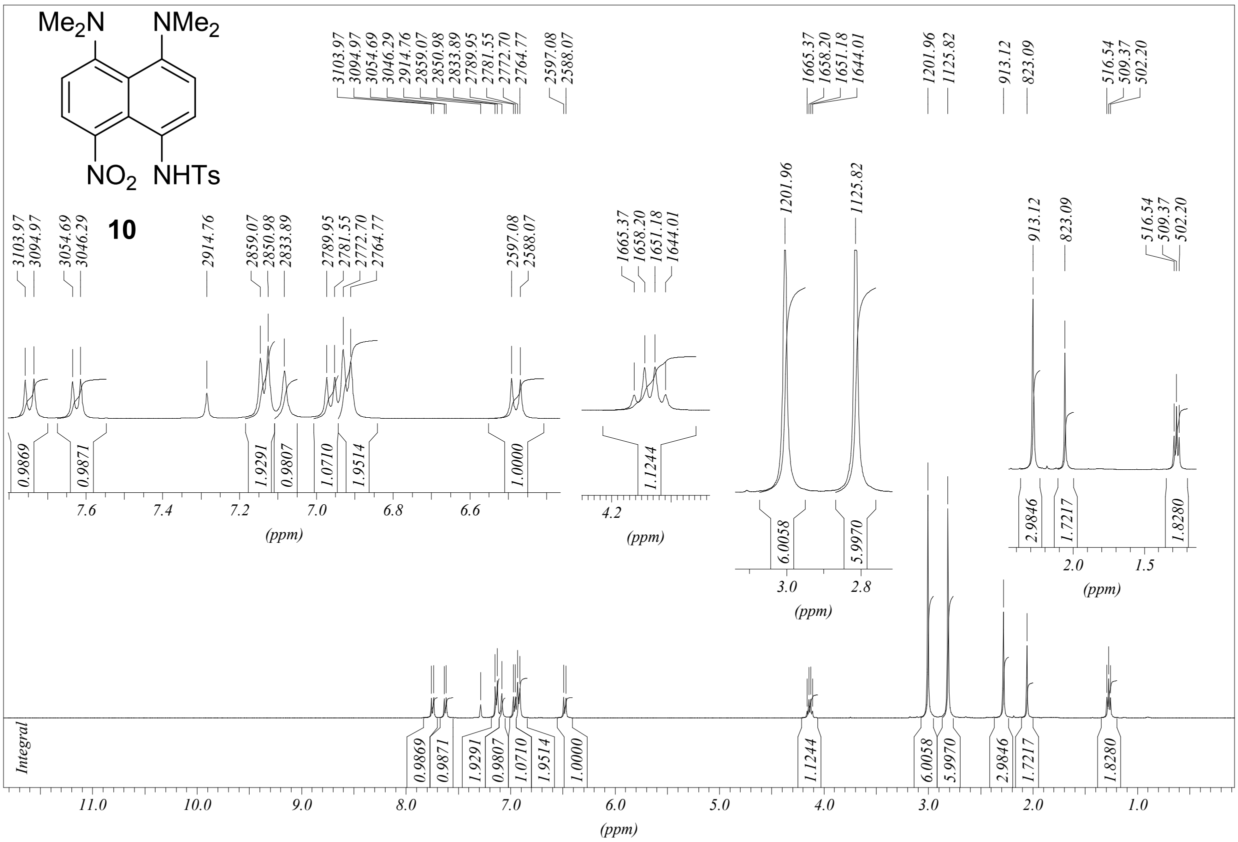


Figure S1. ^{1}H NMR spectrum of **10** ($CDCl_3$, 400 MHz).

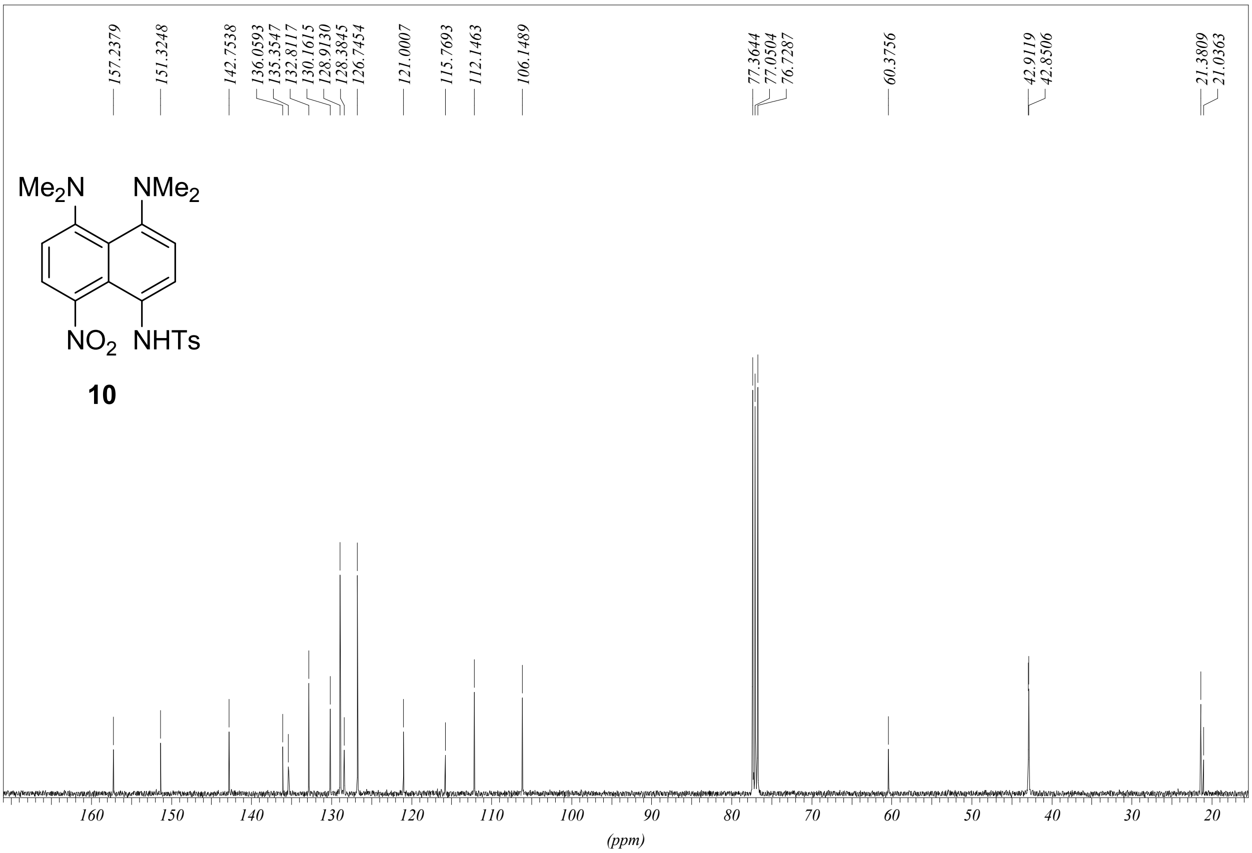


Figure S2. ^{13}C NMR spectrum of **10** ($CDCl_3$, 100.6 MHz).

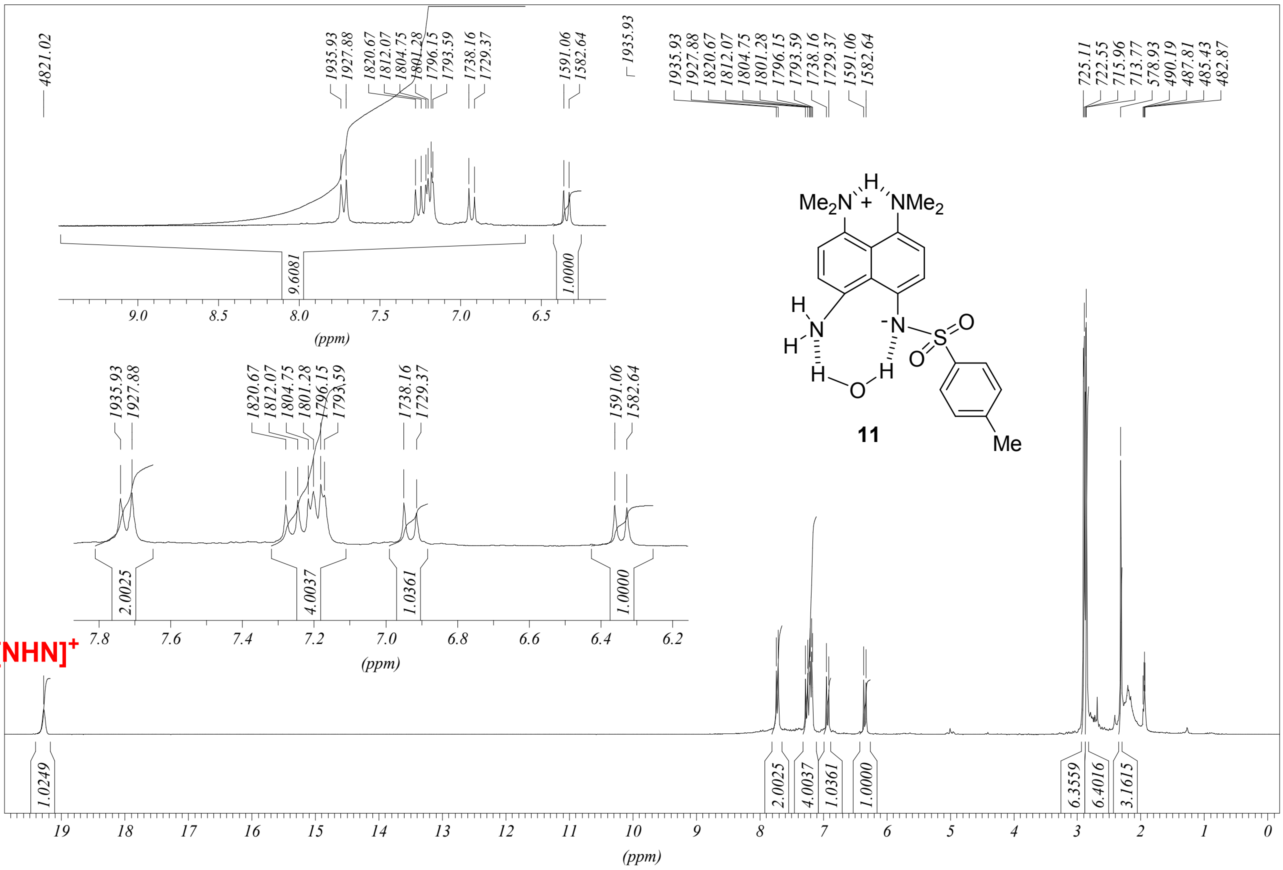


Figure S3. ^{1}H NMR spectrum of **11** (CD_3CN, 250 MHz).

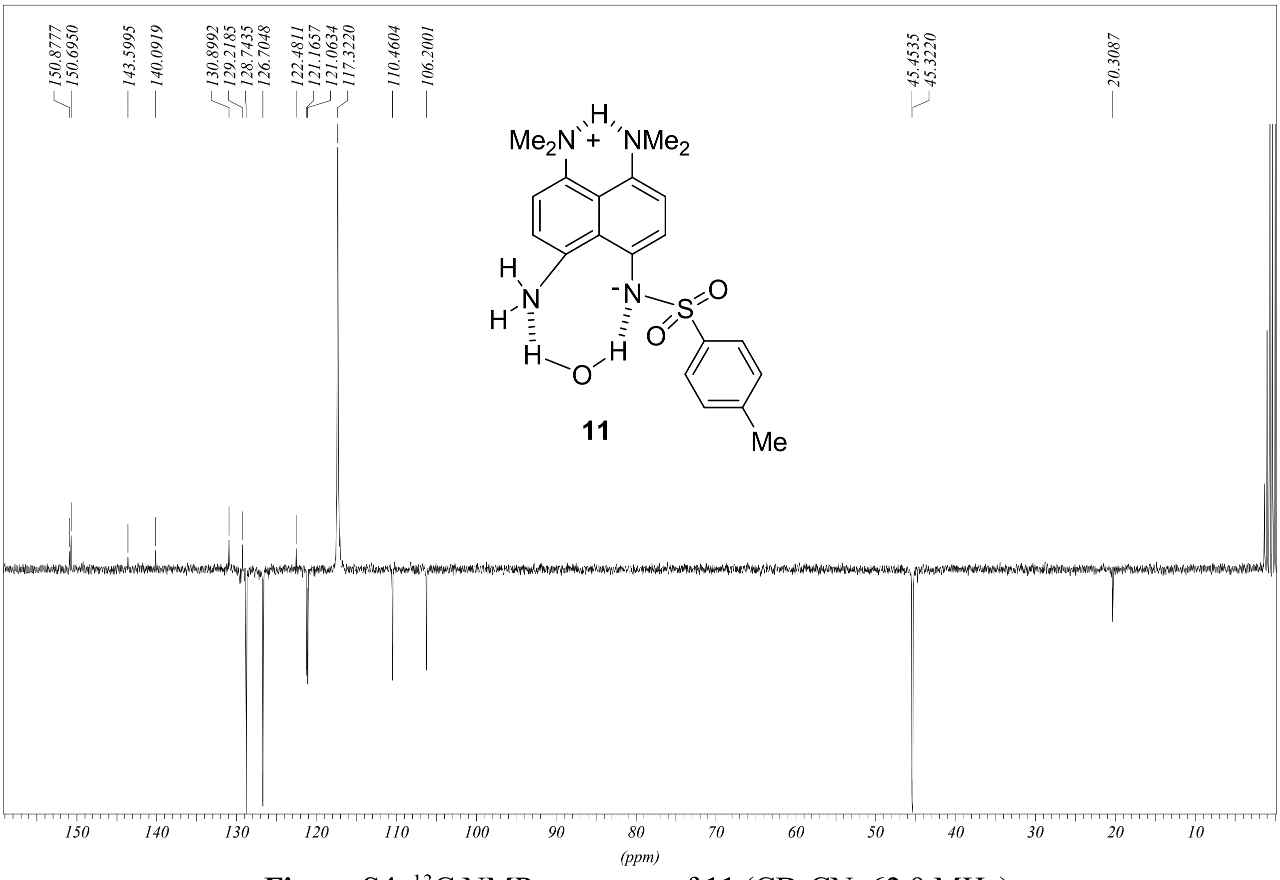


Figure S4. ^{13}C NMR spectrum of **11** (CD_3CN, 62.9 MHz).

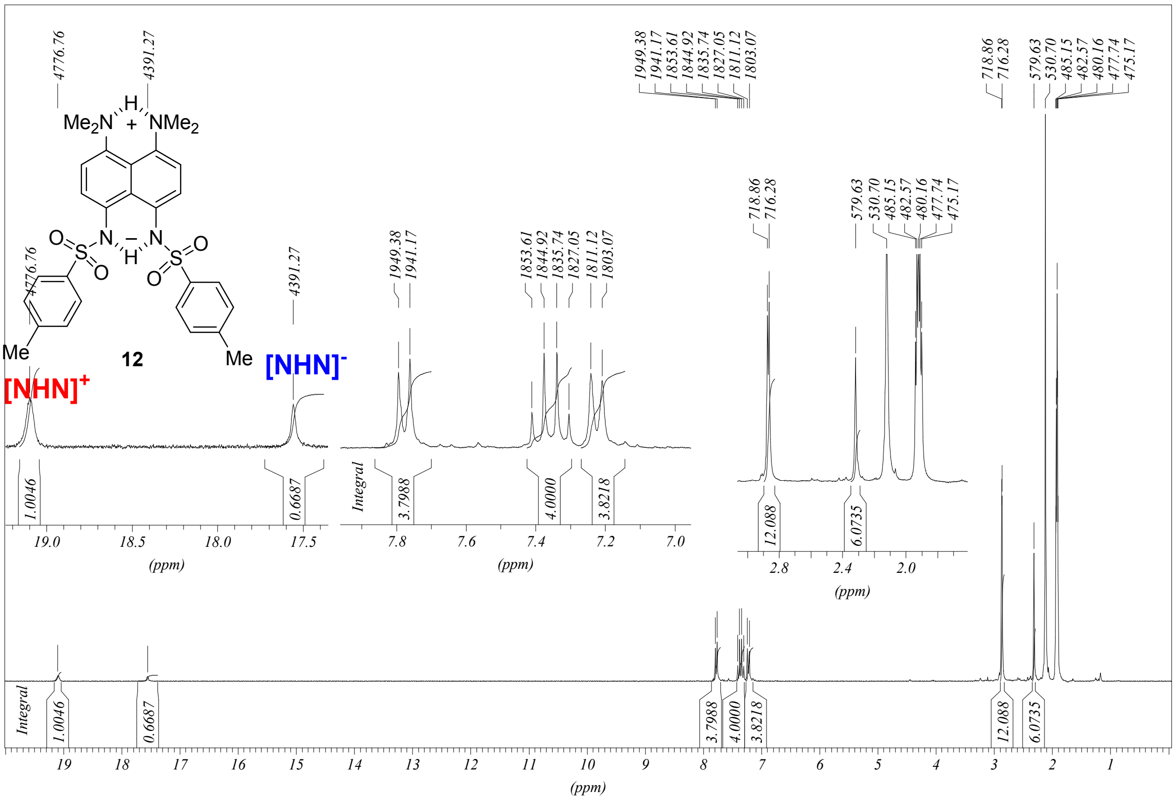


Figure S5. ^{1}H NMR spectrum of **12** (CD_3CN, 250 MHz).

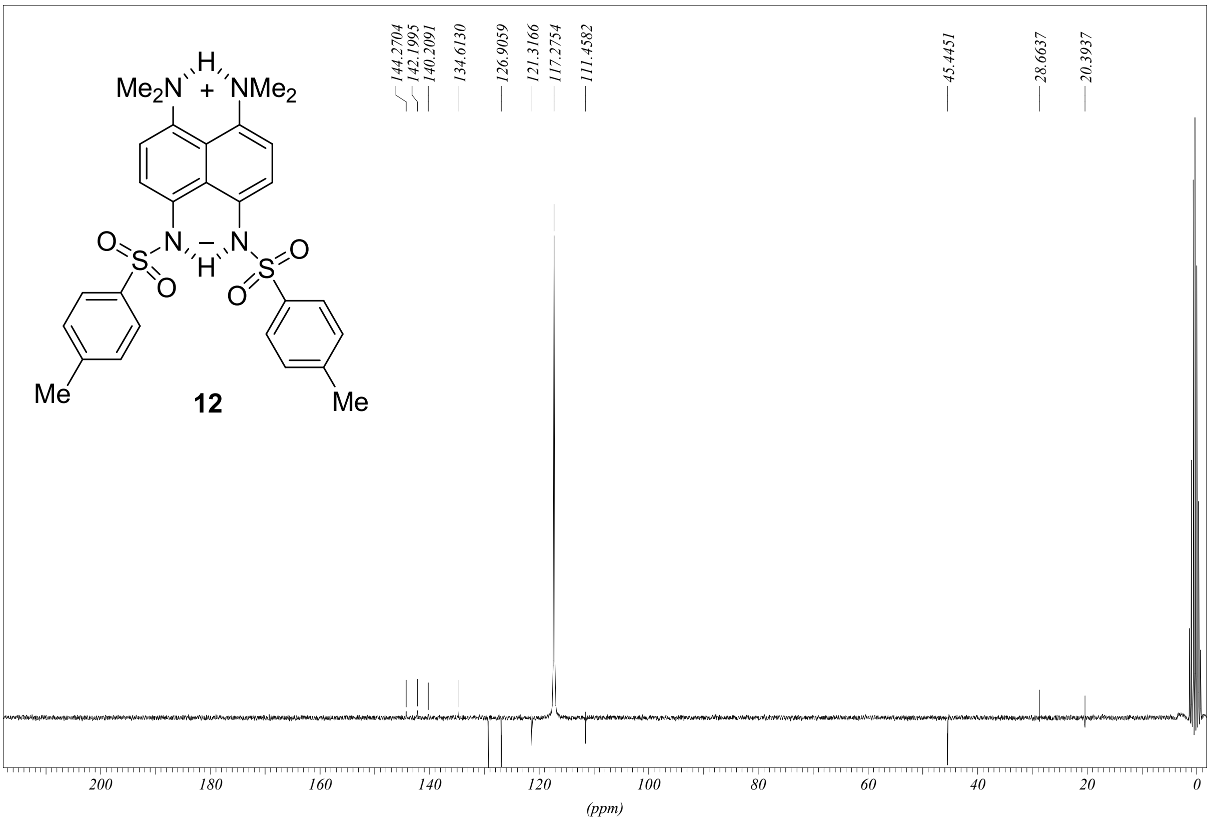


Figure S6. ^{13}C NMR spectrum of **12** (CD_3CN, 62.9 MHz).

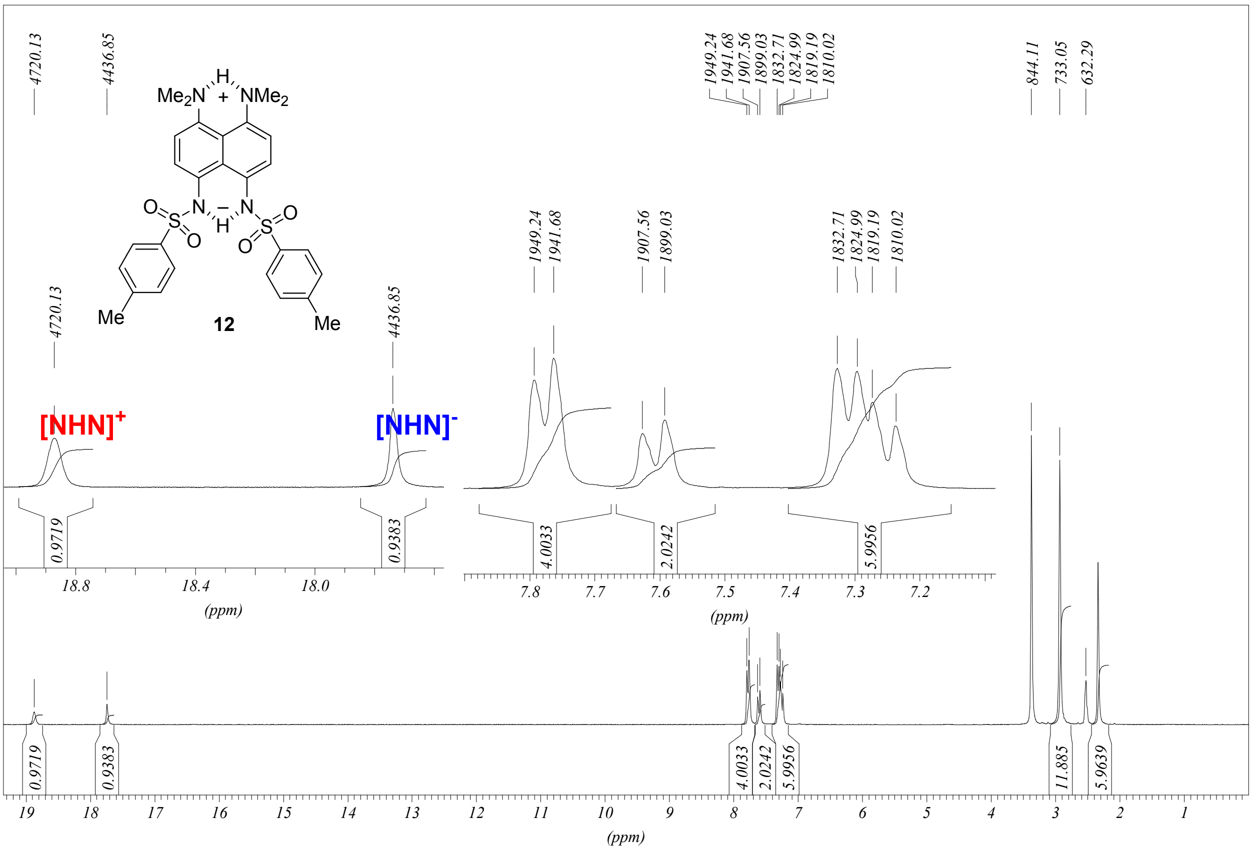


Figure S7. ^{1}H NMR spectrum of **12** (DMSO-d_6, 250 MHz).

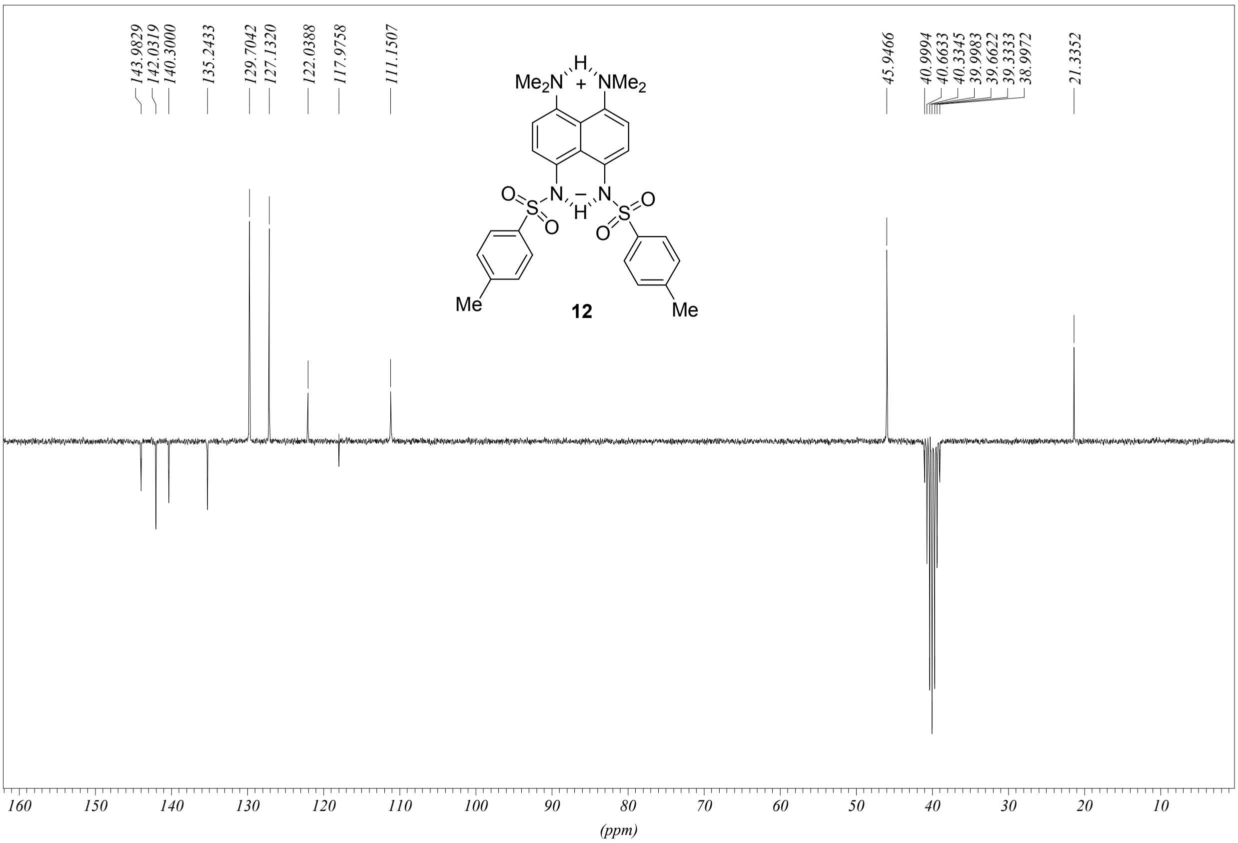


Figure S8. ^{13}C NMR spectrum of **12** (DMSO-d_6, 62.9 MHz).

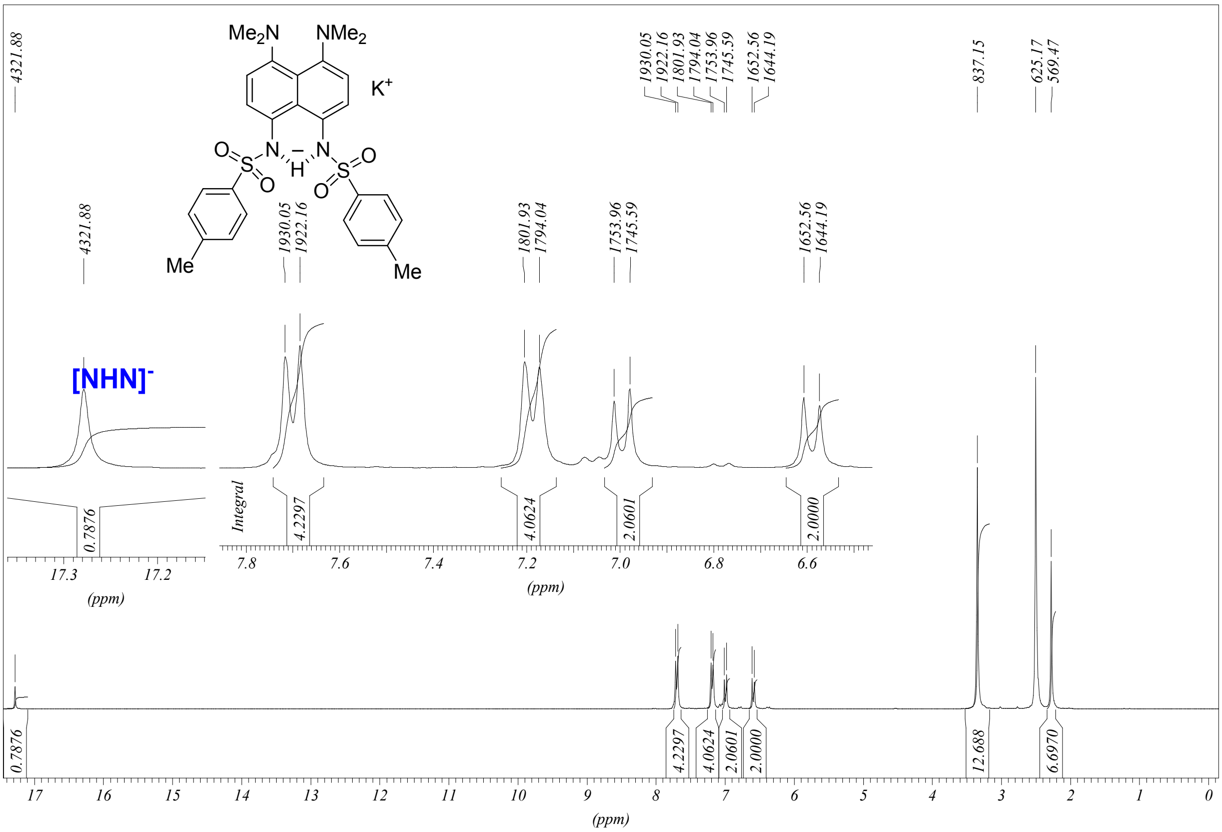


Figure S9. ^{1}H NMR spectrum of **12 + KOH** (1 eq.) (anion **18**) (DMSO-d_6, 250 MHz).

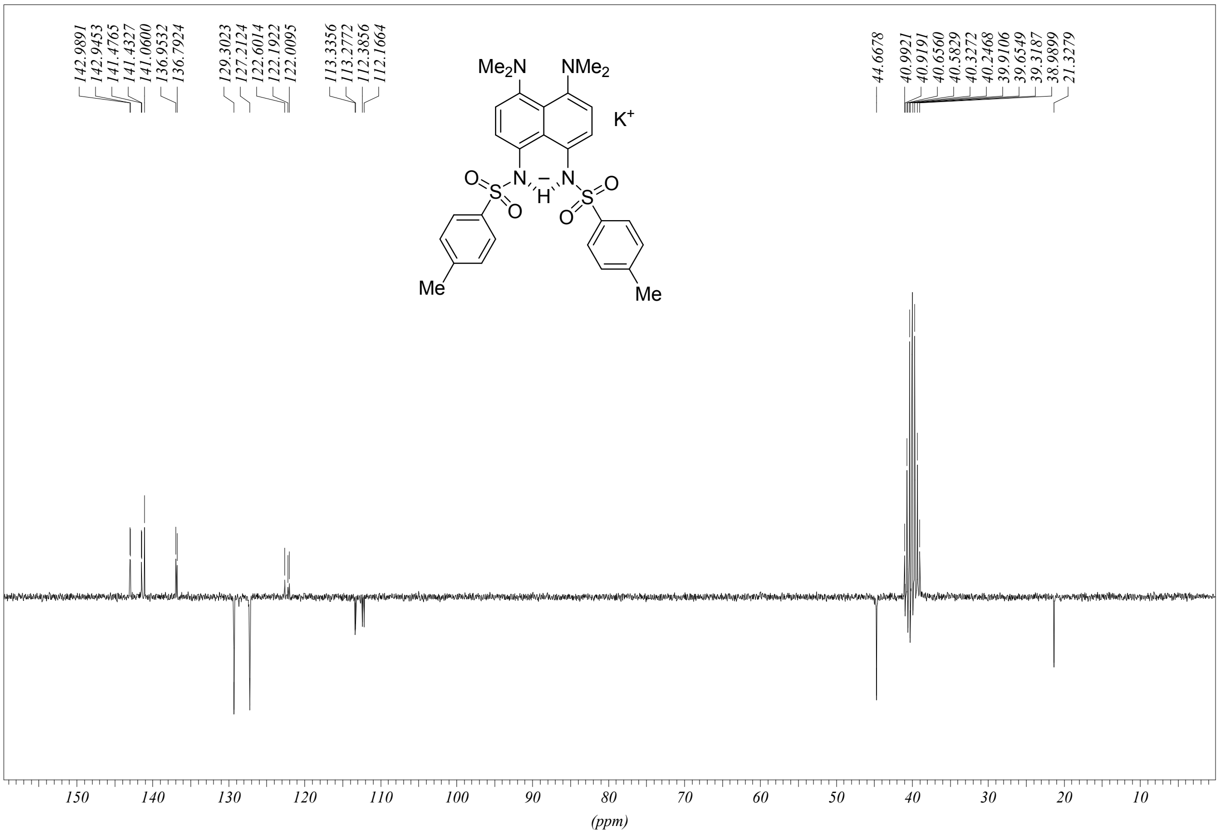


Figure S10. ^{13}C NMR spectrum of **12 + KOH** (1 eq.) (anion **18**) (DMSO-d_6, 62.9 MHz).

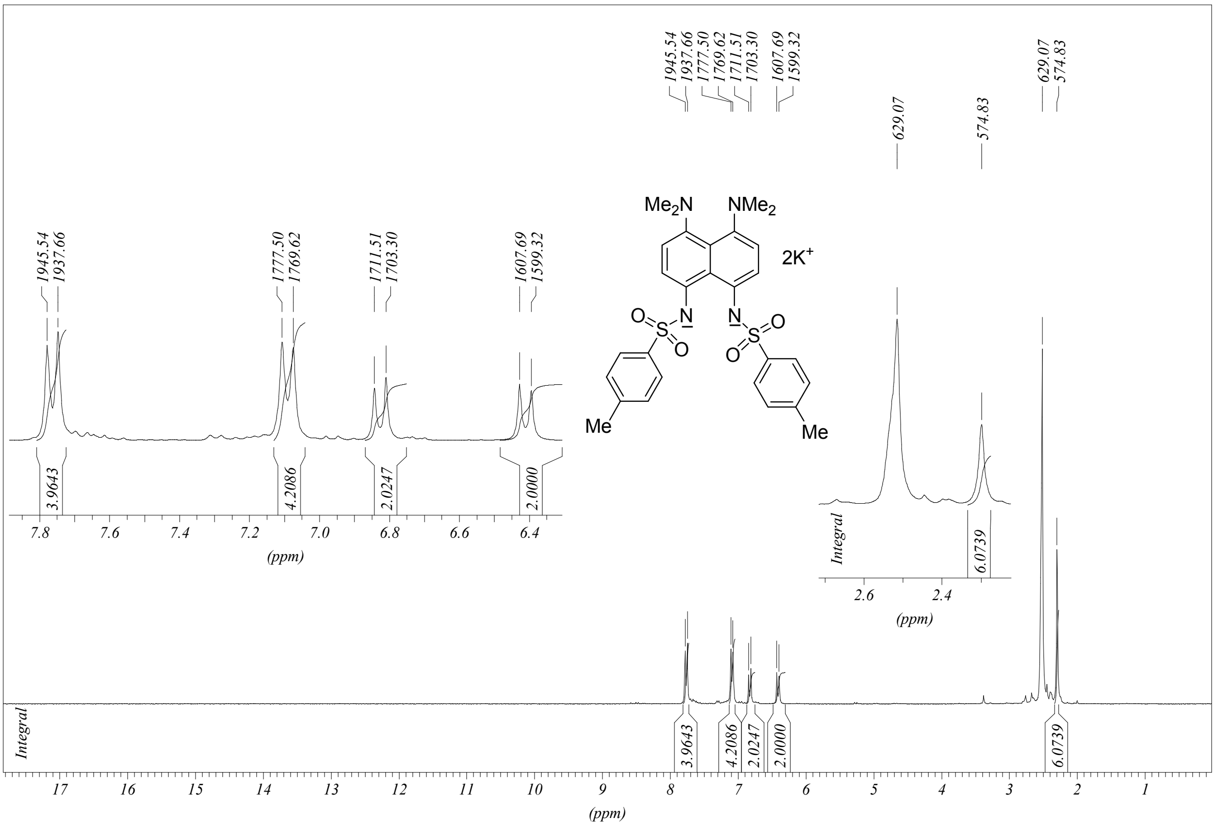


Figure S11. ^{1}H NMR spectrum of **12 + KOH** (2 eq.) (dianion **19**) (DMSO-d$_6$, 250 MHz).

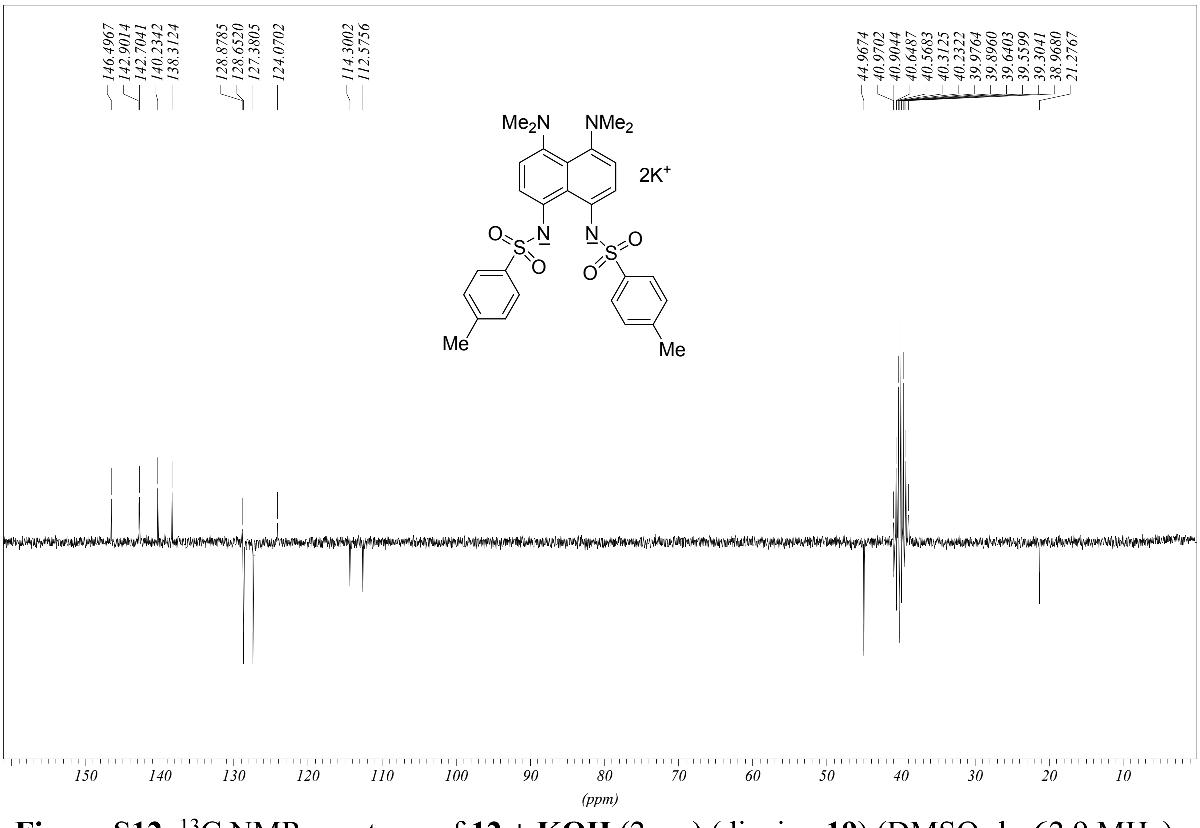


Figure S12. ^{13}C NMR spectrum of **12 + KOH** (2 eq.) (dianion **19**) (DMSO-d$_6$, 62.9 MHz).

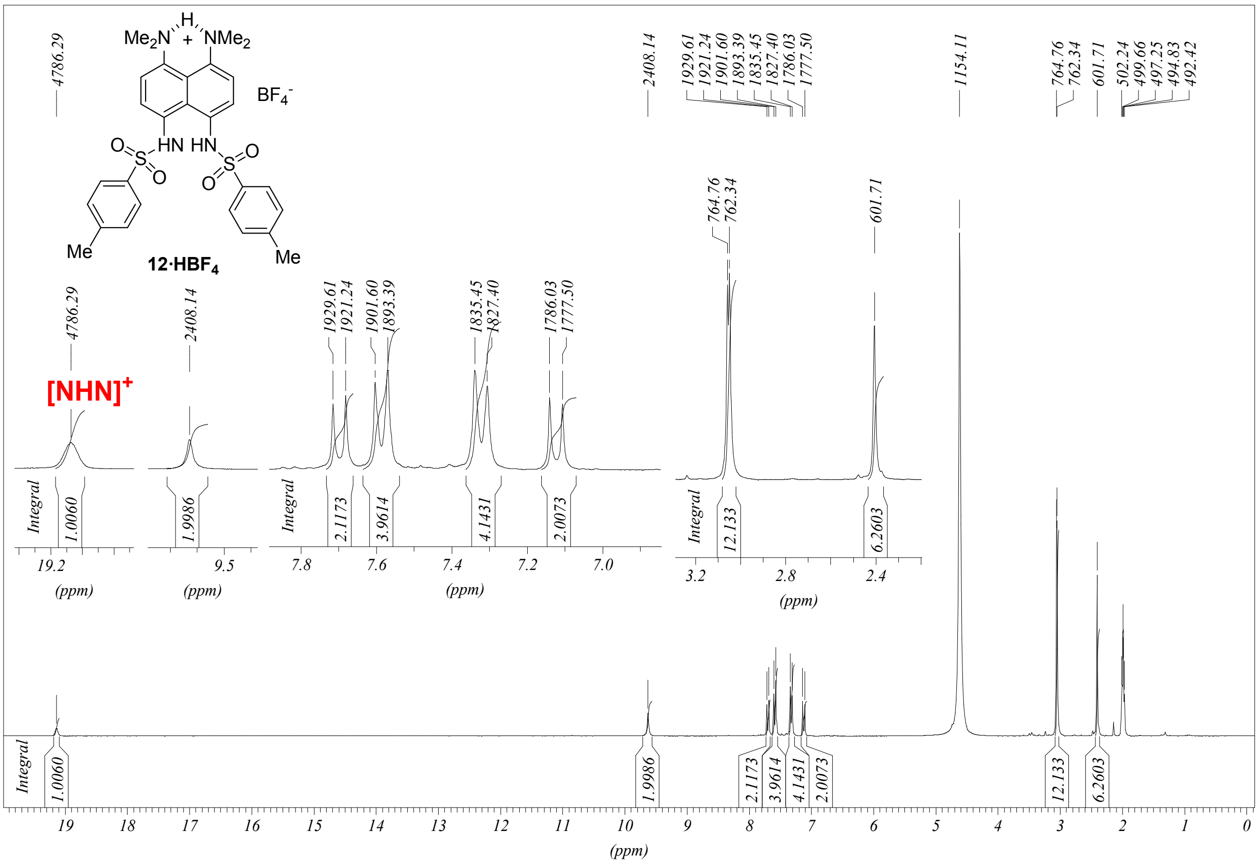


Figure S13. ^{1}H NMR spectrum of tetrafluoroborate **12**·HBF_4 (CD_3CN, 250 MHz).

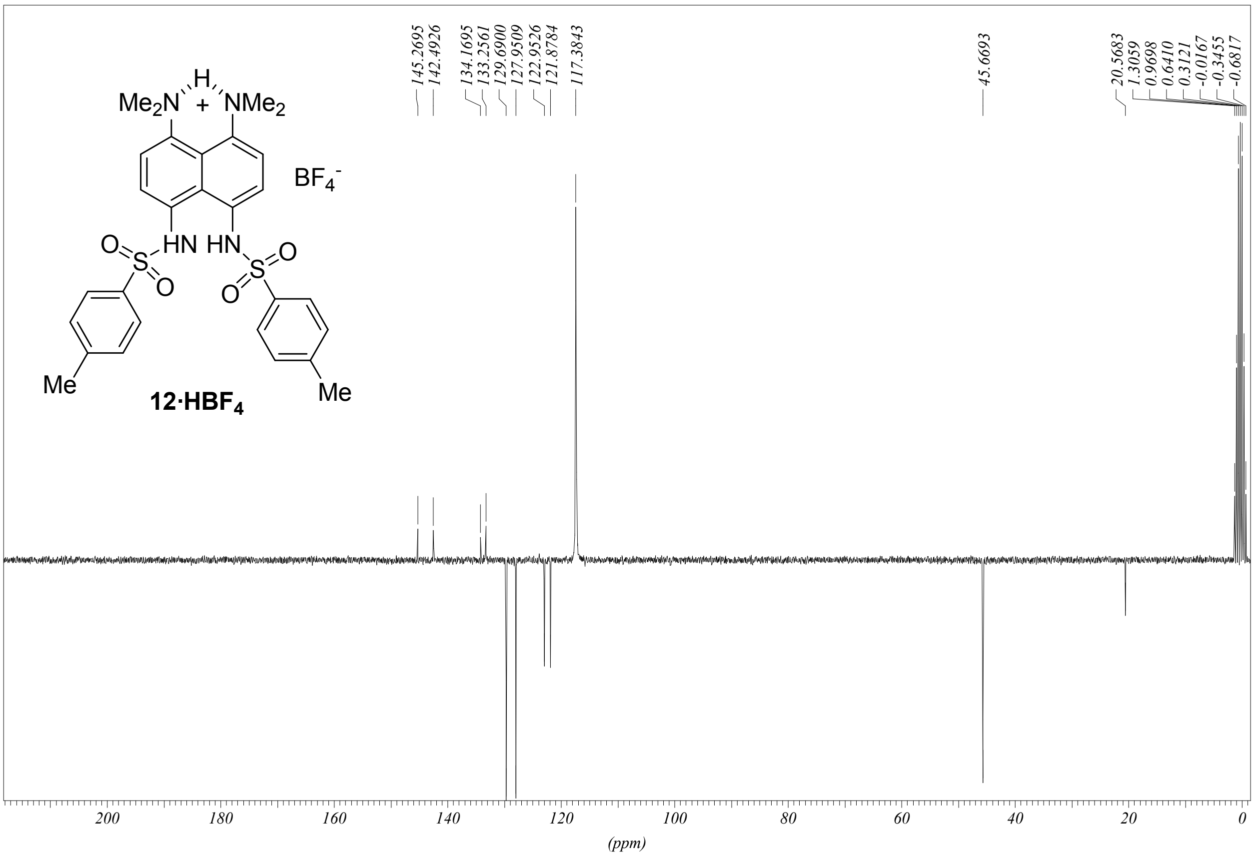


Figure S14. ^{13}C NMR spectrum of tetrafluoroborate **12·HBF_4** (CD_3CN, 62.9 MHz).

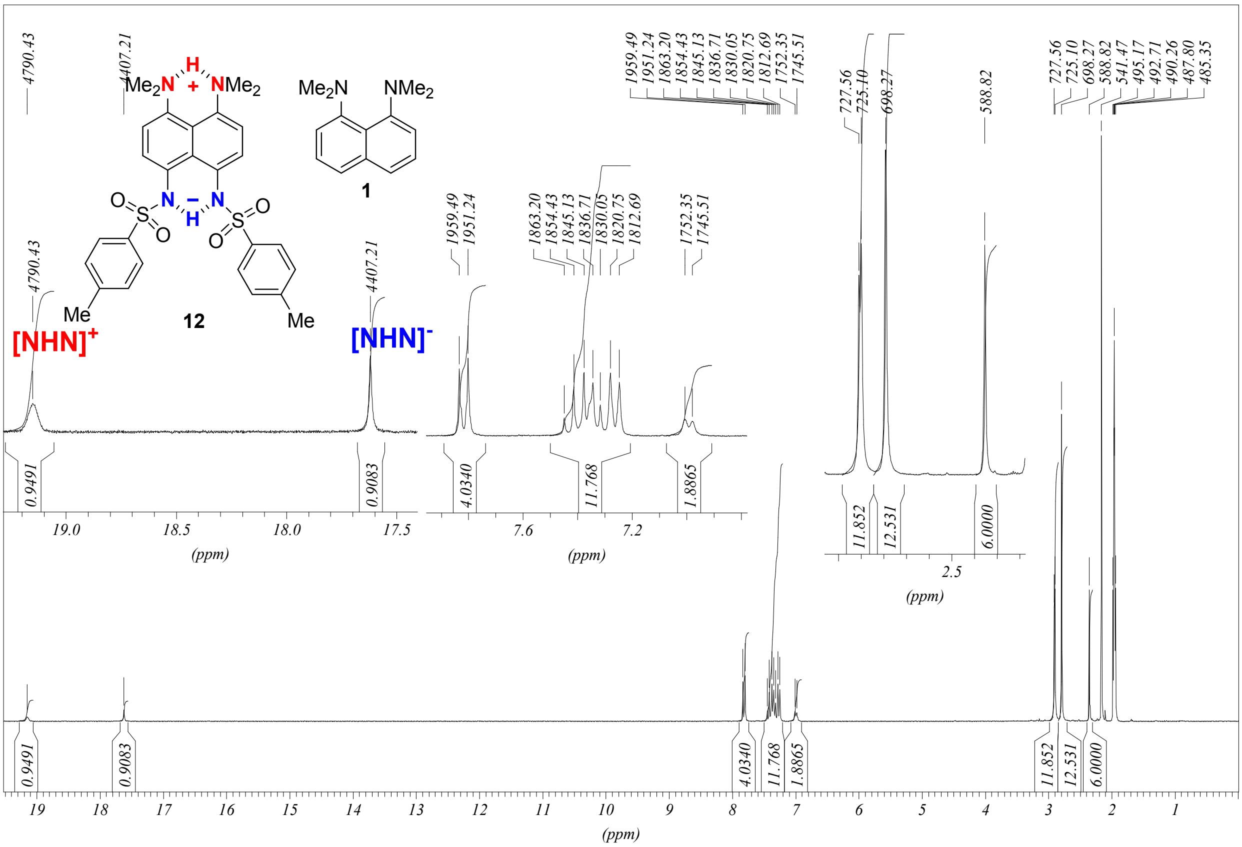


Figure S15. ^{1}H NMR spectrum of equimolar mixture of **12** and **1** (CD_3CN, 250 MHz).

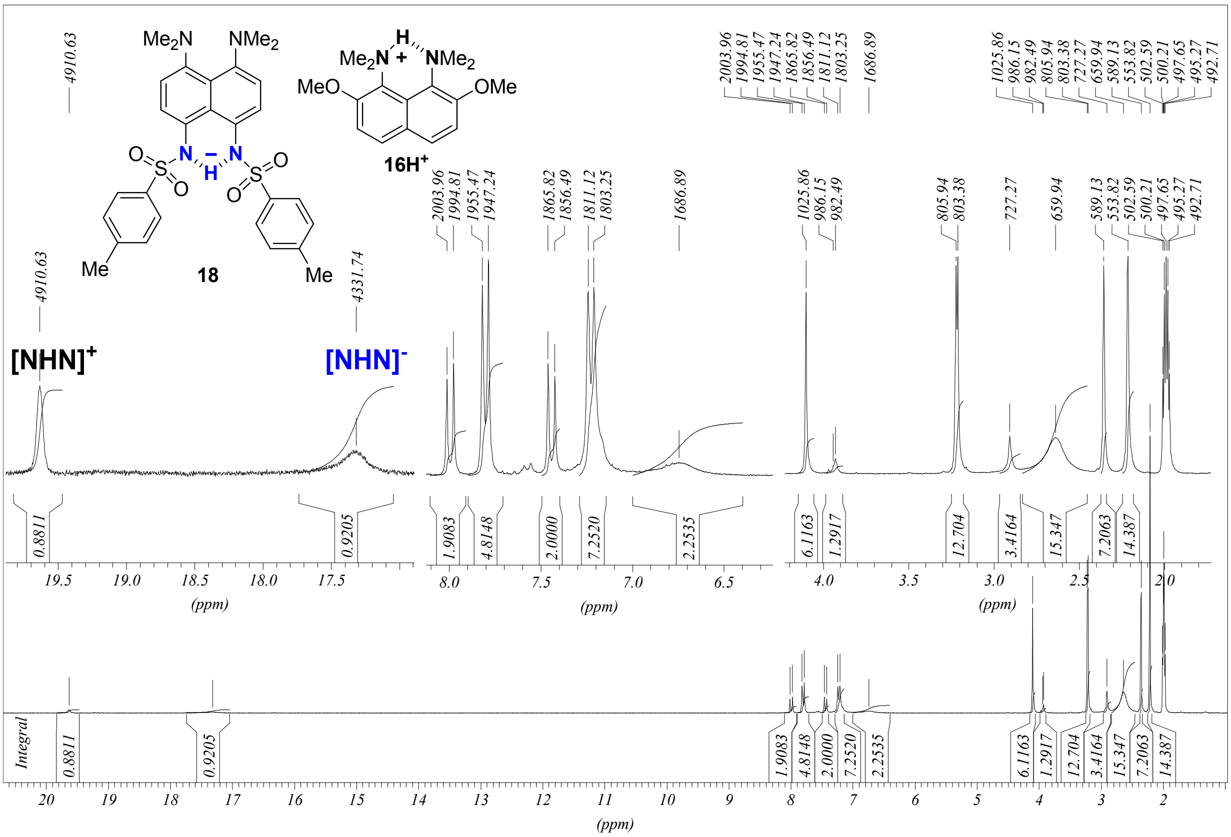


Figure S16. ^{1}H NMR spectrum of equimolar mixture of **12** and **16** (CD_3CN, 250 MHz).

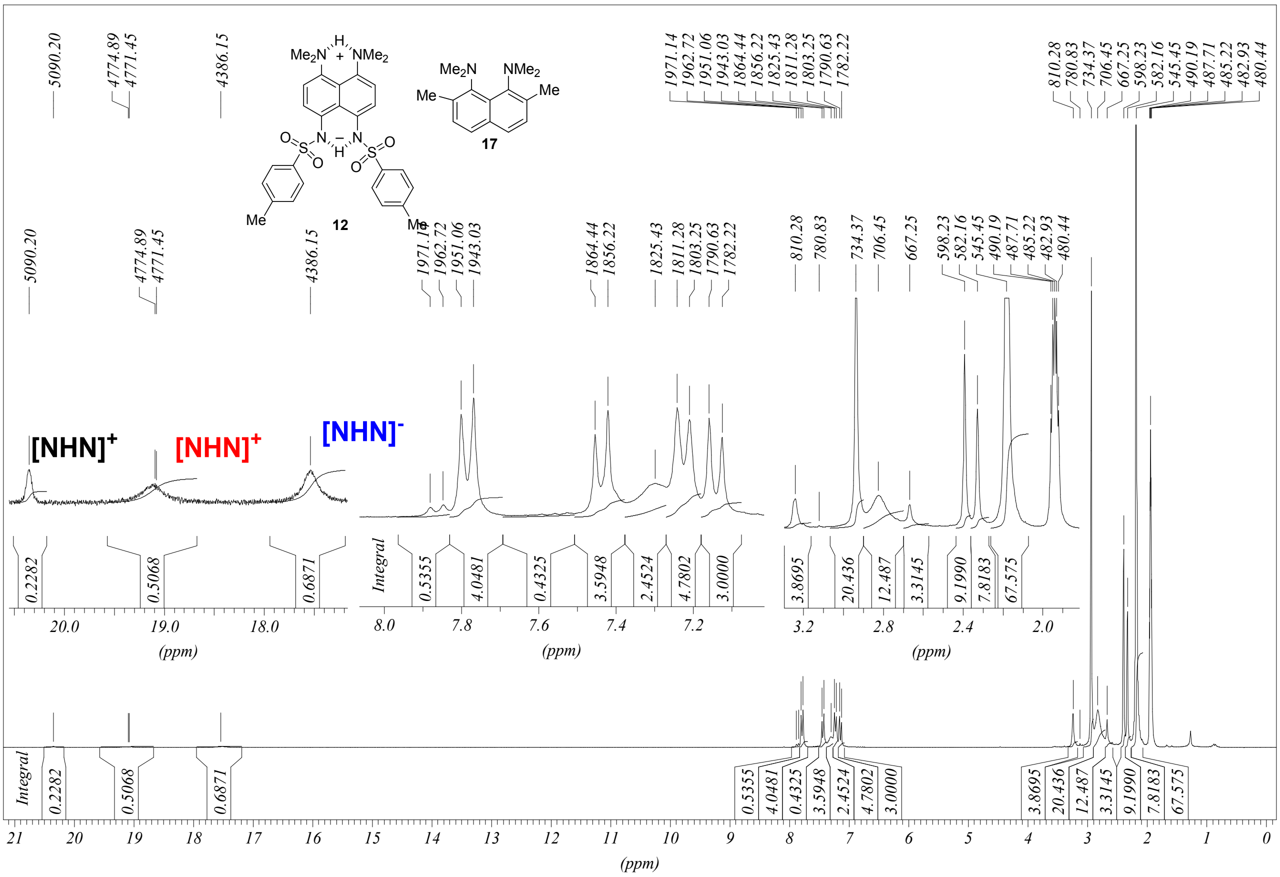


Figure S17. ^{1}H NMR spectrum of equimolar mixture of **12** and **17** (CD_3CN, 250 MHz).

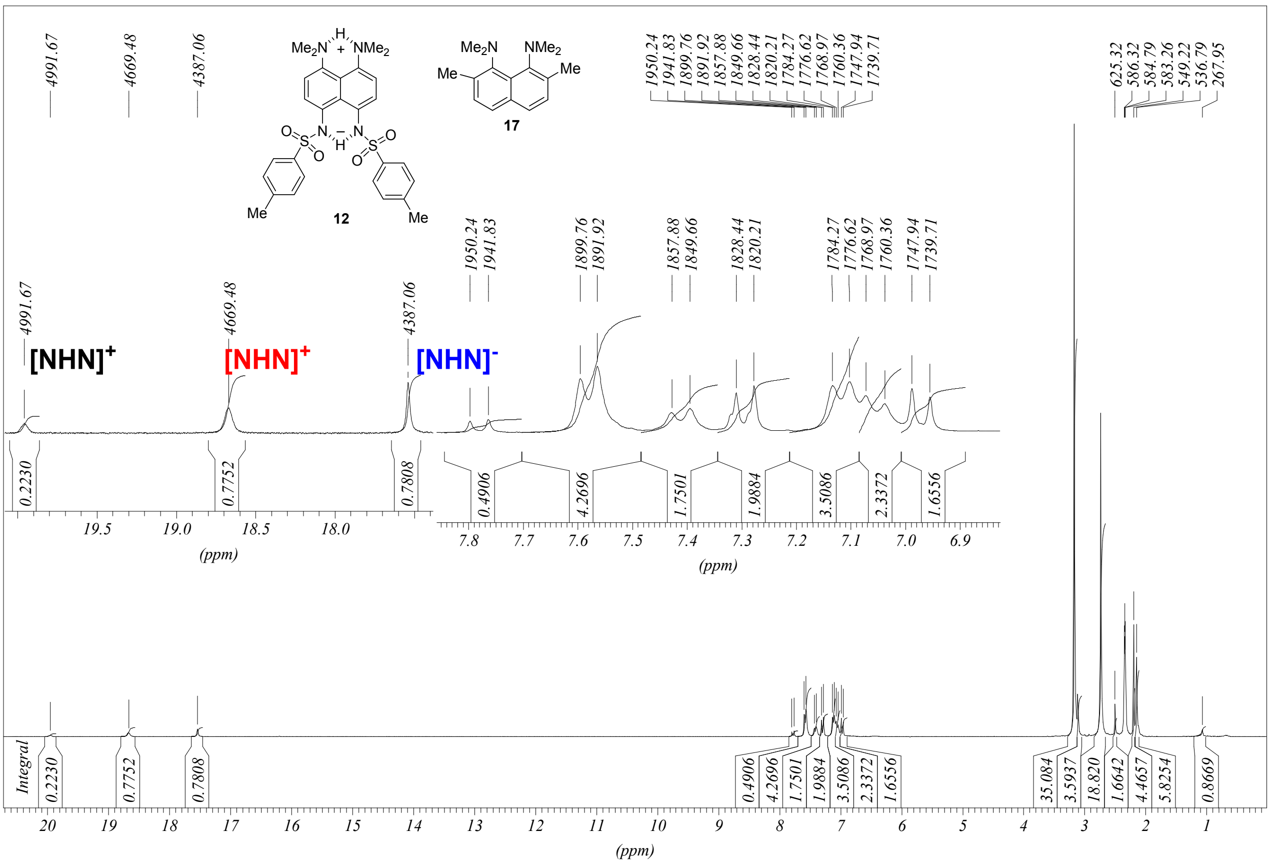


Figure S18. ^{1}H NMR spectrum of equimolar mixture of **12** and **17** (DMSO-d_6, 250 MHz).

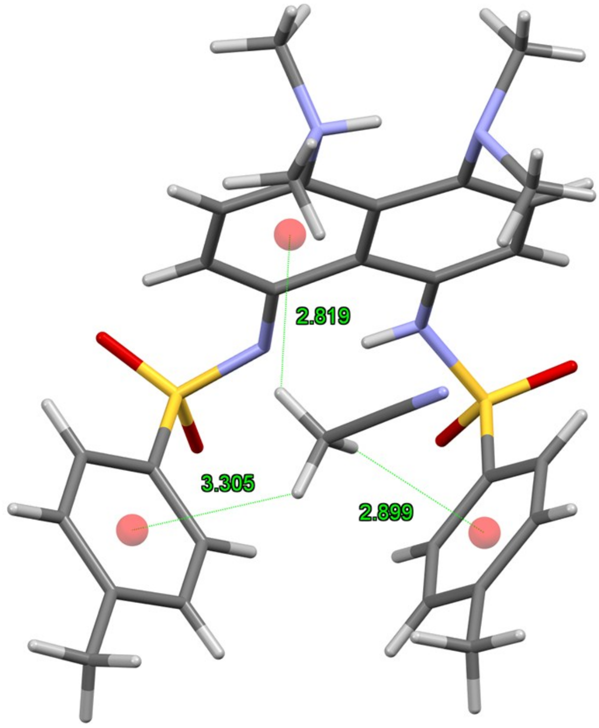


Figure S19. CH/π interactions (the shortest distances are shown) in the crystal structure of inclusion compound **12**·MeCN.

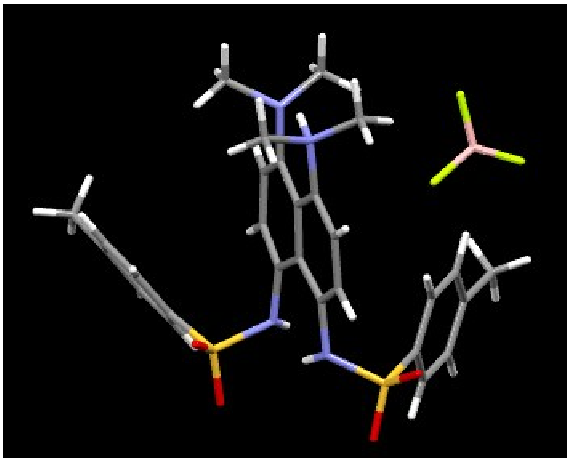
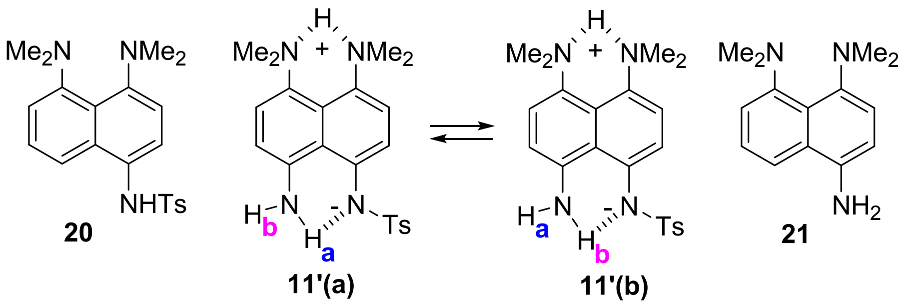


Figure S20. Mutual arrangement of the tosyl groups in X-ray structure of salt **12·HBF$_4$**.

On the formation of zwitterion from mono-tosylated tetramine 11

Some time ago [S2] we described the 4-tosylamino derivative of DMAN **20** and found that it exists as such, without transferring the proton NH onto the NMe_2 groups. However, in the present work, when obtaining its close analogue **11**, we noticed that in the ^{1}H NMR spectrum of the substance recorded in CD_3CN, a signal of the chelated $[NHN]^+$ proton appears at δ 19.28 ppm, which is consistent with the zwitterionic structure **11'**, but not **11** (Fig. S3, Scheme S1). The formation of **11'** could be explained only by the internal proton transfer from the tosylamino group to the *peri*-NMe_2 groups in **11**, since the latter was obtained in a neutral medium excluded the presence of external protons. Apparently, the stimulus for such proton transfer here might be the formation of the IHB of $[NHN]^-$ type, which is impossible in compound **20**. Regrettably, we could not perform an X-ray analysis of **20** due to its relative instability to air oxidation, resembling that of amine **21**. Therefore, the main arguments in favor of real structure of **11** were based on the ^{1}H NMR spectroscopy data and physical properties (e.g. **11** has rather high melting point and, similar to other protic salts of DMAN, is insoluble in Et_2O suggesting zwitterionic structure **11'**). Thus, if the moderately widened signals of the NH_2 group in base **21** (in $CDCl_3$) and in perchlorate **21·HClO₄** (in MeCN) are located at 3.5 and 5.1 ppm, respectively, then in compound **11'** it has a strongly diffuse appearance, extending between 6.5–8.5 ppm area (Fig. S3). This behavior is characteristic of weak and dynamically active hydrogen bonds [S3]. Based on this, we believe that zwitterion **11'** actually equilibrates between the two forms **11'(a)** and **11'(b)** (Scheme S1). Obviously, accompanying and slowed in the NMR time scale rotation of the NH_2 group around the C_{ar}–N bond causes a sharp paramagnetic shift of the NH_2 protons in **11'** as compared with the chemical shift of the chelated $[NHN]^-$ proton in the spectrum of zwitterion **12**.



Scheme S1. Possible formation of the zwitterionic structure for compound **11**.

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[S2] M. P. Vlasenko, V. A. Ozeryanskii and A. F. Pozharskii, *Russ. Chem. Bull.*, 2011, **60**, 2030–2039.

[S3] V. A. Ozeryanskii, A. F. Pozharskii, A. Filarowski and G. S. Borodkin, *Org. Lett.*, 2013, **15**, 2194–2197.