Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 1887

www.rsc.org/obc

PAPER

Naphthalene proton sponges as hydride donors: diverse appearances of the *tert*-amino-effect†

Alexander F. Pozharskii,*[a] Maria A. Povalyakhina,[a] Alexander V. Degtyarev,[a] Oxana V. Ryabtsova,[a] Valery A. Ozeryanskii,[a] Olga V. Dyablo,[a] Anna V. Tkachuk,[a] Olga N. Kazheva,[b] Anatolii N. Chekhlov[b] and Oleg A. Dyachenko[b]

Received 18th October 2010, Accepted 13th December 2010
DOI: 10.1039/c0ob00899k

It has been shown that the 1-NMe$_2$ group in the 2-substituted 1,8-bis(dimethylamino)naphthalenes (proton sponges) can intramolecularly donate a hydride ion to an appropriate electron-accepting *ortho*-substituent such as diarylcarbenium ion, β,β′-dicyanovinyl or methyleneiminium group. This produces the 1-N$^+$(Me)=CH$_2$ functionality and triggers a number of further transformations (*tert*-amino effect) including *peri*-cyclization, *ortho*-cyclization or hydrolytic demethylation. In each particular case, the course of the reaction is determined by the nature of the *ortho*-substituent and the most potent nucleophile presenting in the reaction mixture. For 2,7-disubstituted 1,8-bis(dimethylamino)naphthalenes, two types of tandem *tert*-amino effect with the involvement of both *peri*-NMe$_2$ groups have been registered. The conclusion was made that proton sponges are generally more active in the *tert*-amino reactions than the corresponding monodimethylaminoarenes. This is ascribed both to higher electron donor ability of proton sponges and markedly shortened distance between electrophilic C$_\alpha$-atom in the *ortho*-substituent and hydrogen atoms of the nearest NMe$_2$ group. Most conversions observed proceed in good to high yields and are useful for the preparation of derivatives of benzo[*h*]quinoline, quino[7,8:7′,8′]quinoline, 2,3-dihydroperimidine, *N*,*N*,*N*′-trimethyl-1,8-diaminonaphthalene and proton sponge itself.

Introduction

Some time ago one of us and co-workers had demonstrated that lithium aluminium hydride (LAH) reduction of 1,1,3-trimethyl-2,3-dihydroperimidinium salt **1a** quantitatively produces 1,8-bis(dimethylamino)naphthalene (proton sponge, **2**, Scheme 1).[1a,2] Though for the parent **2** this is not the method of choice, it can be indispensable for some proton sponge derivatives, *e.g.* those with unequal *N*-alkyl substituents[1a] or *peri*-halogen atoms.[1b] It is interesting, that unlike **1a**, the 1,1,2,2,3-pentamethyl-2,3-dihydroperimidinium salt **1b** preferably exists in the ring-opened form **3** (apparently due to a steric crowding) and even on treatment with NaBH$_4$ smoothly converts into monoisopropyl proton sponge **4**.[3]

Independently, other authors had shown that this reaction can be reversed. It was found that in the presence of transition metal (Ir^{3+}, Rh^{3+}, Ru^{3+}) complexes, the proton sponge **2** behaves as a hydride donor from one of its methyl groups.[4] The methyleneiminium cation **5** thus formed rapidly cyclizes into **1a** (Scheme 2). Thus, 2,3-dihydroperimidinium salts and naphthalene proton sponges form a redox-system interconverting through the same iminium intermediate.

In the present article a number of novel and synthetically useful cases of the hydride-donor activity of naphthalene proton sponges together with a general survey of the topic are reported.[5] The central point of this study is to demonstrate that the proton sponge *N*-methyl groups are able to donate a hydride ion not only to external acceptors as in the above examples but also intramolecularly to various *ortho*-substituents with appropriate electron deficiency that initiates a set of interesting cyclizations and transformations. This type of reactivity of tertiary aromatic amines is commonly referred to as a *tert*-amino effect.[6]

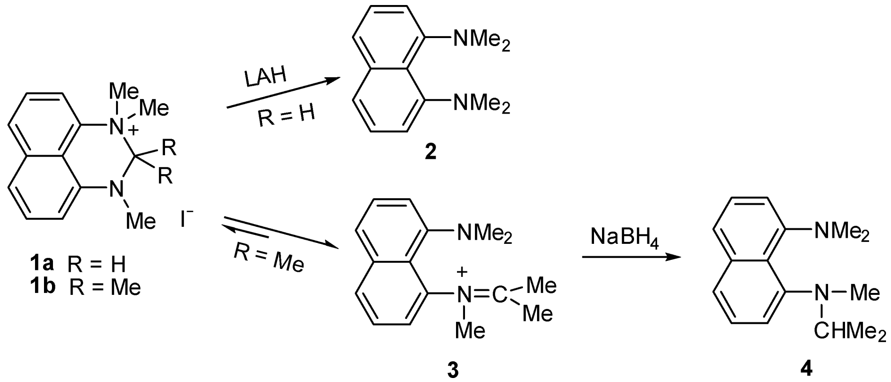
Results and discussion

Proton sponge-based 2-naphthylmethyl carbocations

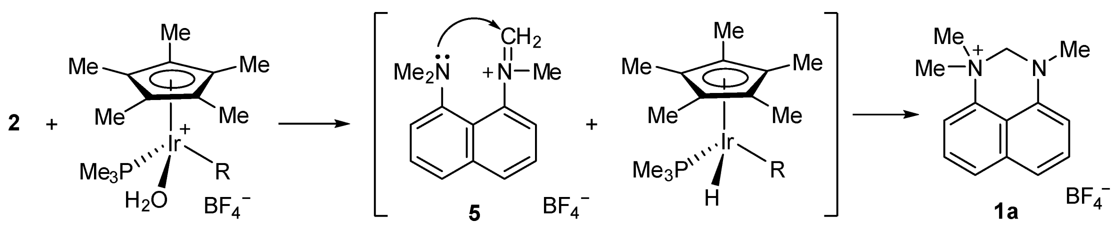
First, we have found that the *tert*-amino effect is readily displayed by proton sponge-based 2-naphthylmethyl carbocations.[5a] For example, on treatment of tertiary alcohol **6a** with conc. HCl an orange-red colour, characteristic for triarylmethyl cations, immediately develops followed by a fast discolouration and

[a]Department of Organic Chemistry, Southern Federal University, Zorge 7, 344090 Rostov-on-Don, Russian Federation. E-mail: apozharskii@sfedu.ru
[b]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Semenov 1, 142432 Chernogolovka, Moscow Region, Russian Federation

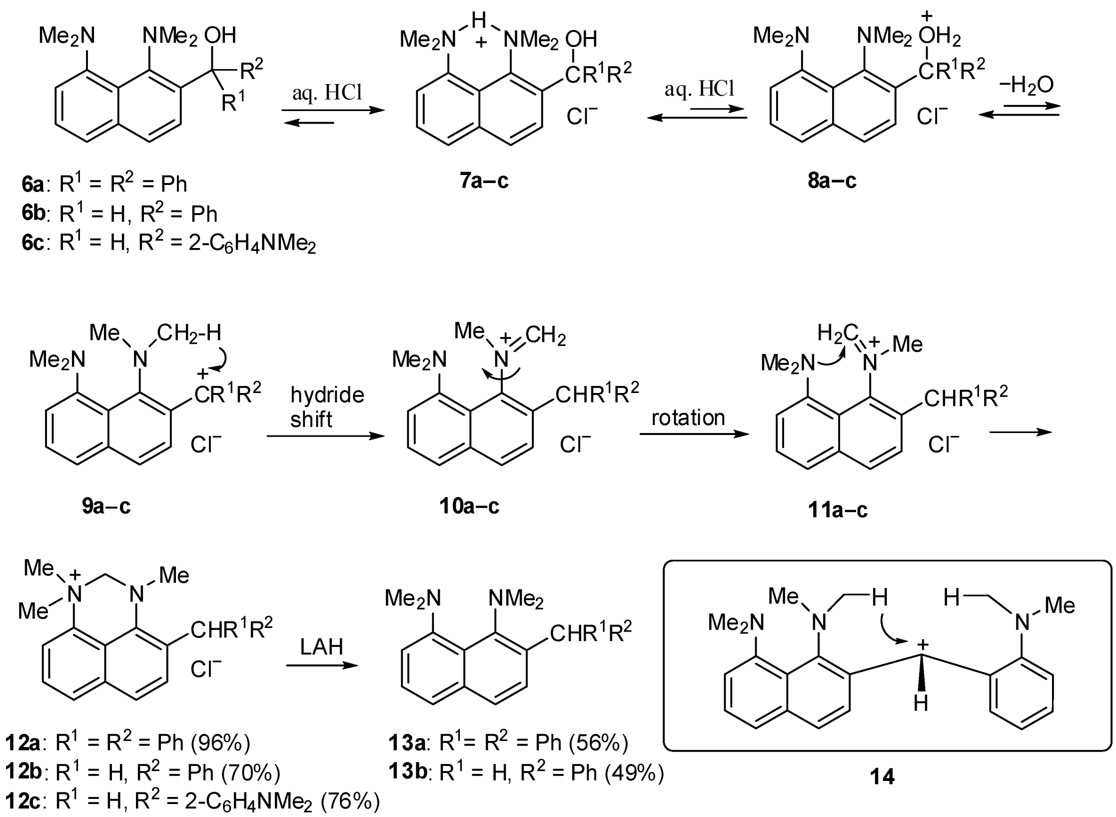
† Electronic supplementary information (ESI) available. CCDC reference numbers 804543 (**29f**), 720578 (**33**), 801823 (**35a**) and 801824 (**56**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00899k



Scheme 1



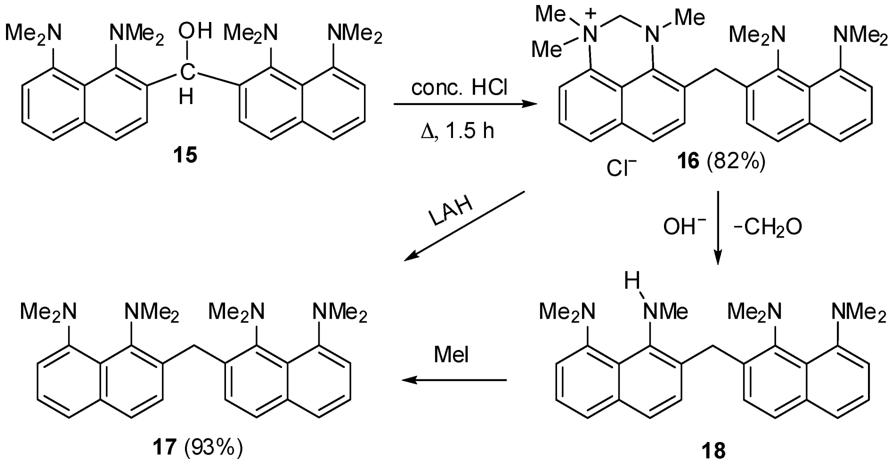
Scheme 2



Scheme 3

precipitation of 4-benzhydryl-2,3-dihydroperimidinium salt **12a** in quantitative yield. Similarly, secondary alcohols **6b,c** and **15** give chlorides **12b,c** and **16** in a good yield (Schemes 3 and 4). Reductive cleavage of salts **12** and **16** with LAH gives the proton sponge derivatives **13a,b** and **17**, respectively.

The structures of the salts **12** and **16** were proved by common spectral methods; for **12b** X-ray studies were also conducted.[5a] A plausible mechanism for the transformation is shown in Scheme 3. The process is thought to start with the formation of chelated cation **7** equilibrating with hydroxonium salt **8**, which is supposed



Scheme 4

to be direct precursor of carbocation **9**.[7] The latter immediately accepts a hydride ion from the nearest N–Me group and the iminium intermediate **10** is then cyclized into 2,3-dihydroperimidinium salt **12**. Obviously, rotation of the $N^+(Me){=}CH_2$ group around the C_{arom}–N bond (**10** → **11**) should precede the ring closure.

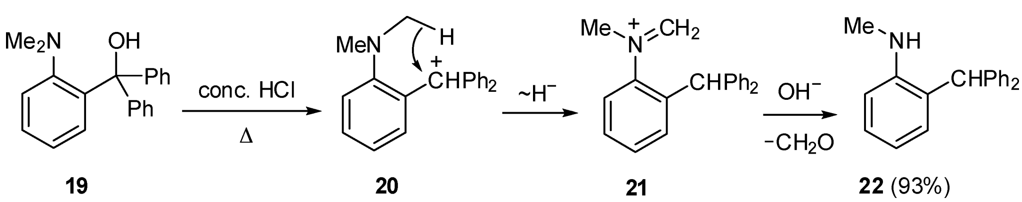
The ease, directionality and even possibility of the above *tert*-amino reactions strongly depend on stability of the intermediate carbenium ion. Thus, if in the case of tertiary alcohol **6a** the reaction ends in seconds, for the secondary alcohols, producing less stable diarylmethyl carbocations, it requires minutes (**6b**) or even hours (**6c** and **15**). The behaviour of the alcohol **6c** is of special interest since in this case a hydride ion can be donated either by the proton sponge or the *N*,*N*-dimethylaniline (DMA) residue (structure **14**). The exclusive formation of salt **12c** shows that the proton sponge is a stronger hydride donor than DMA, this is in accord with its much higher basicity and slightly lower first ionization potential (IP_1 = 7.05 eV[8] against 7.10 eV[9] for DMA). In this context, it seemed to us reasonable to test the principle ability of dimethylaniline-based carbocations to undergo the *tert*-amino reaction. With this aim, we treated 2-dimethylaminotriphenylmethanol **19**[10] with conc. HCl under reflux (Scheme 5). 2-Benzhydryl-*N*-methylaniline **22** was isolated from the reaction mixture as a single product in 93% yield. Thus, the *tert*-amino effect is also valid for the triphenylmethyl cation **20**, though its final stage is a hydrolytic cleavage of the iminium intermediate **21** with the loss of one *N*-methyl group. It is worth noting that dihydroperimidinium salts are also cleaved on alkali treatment.[1a] For example, salt **16** can be alternatively converted into the compound **17** on treatment with aqueous NaOH and a subsequent methylation of the transient tetraamine **18**.

Unlike alcohols **6** and **15**, their analogue **23a** with the α-hydroxyisopropyl *ortho*-substituent being treated with conc. HCl forms carbocation **24**, which undergoes *E*1 elimination to produce on basification 1,8-bis(dimethylamino)-2-isopropenylnaphthalene **25** in 96% yield (Scheme 6).[5a] The primary alcohol **23b** on heating with acids, *e.g.* conc. HBr, exchanges the hydroxylic group with the formation of a 2-bromomethyl derivative isolated as hydrobromide **27**.[5a] Obviously, both these reactions reflect the relatively low stability of the corresponding 2-naphthylmethyl carbenium ions.

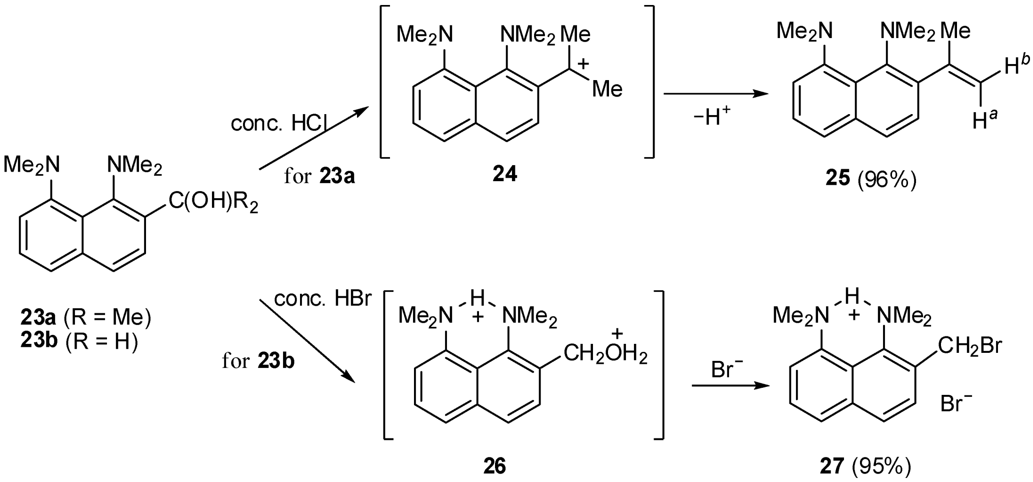
Proton sponges with electron-deficient *ortho*-vinyl groups

Next, we have found that another and more common type of the *tert*-amino effect takes place for 2-vinyl- **29** and 2,7-divinyl-1,8-bis(dimethylamino)naphthalenes **34** which have strong electron-withdrawing groups in the β-positions of the side chains. These alkenes were prepared by the Knoevenagel condensation of aldehydes **28** and **33** with malonodinitrile, dimedone, tosylacetonitrile, ethyl cyanoacetate and 2-cyanomethylbenzimidazole (Schemes 7 and 8).[5b] Monoaldehyde **28** easily reacts with these methylene-active compounds in alcohol or toluene solution; reaction in toluene demands an addition of piperidine, while in EtOH the condensation occurs without external catalyst.[11] We were able to isolate in a pure state only alkenes **29c,d,f**;[14] alkenes **29a,b** spontaneously transform into benzo[*h*]quinolines **31a,b**, though their formation as intermediates can be monitored spectrophotometrically.[15] Evidently, in this case hydride transfer produces zwitter-ions **30** which undergo subsequent cyclization (Scheme 7).

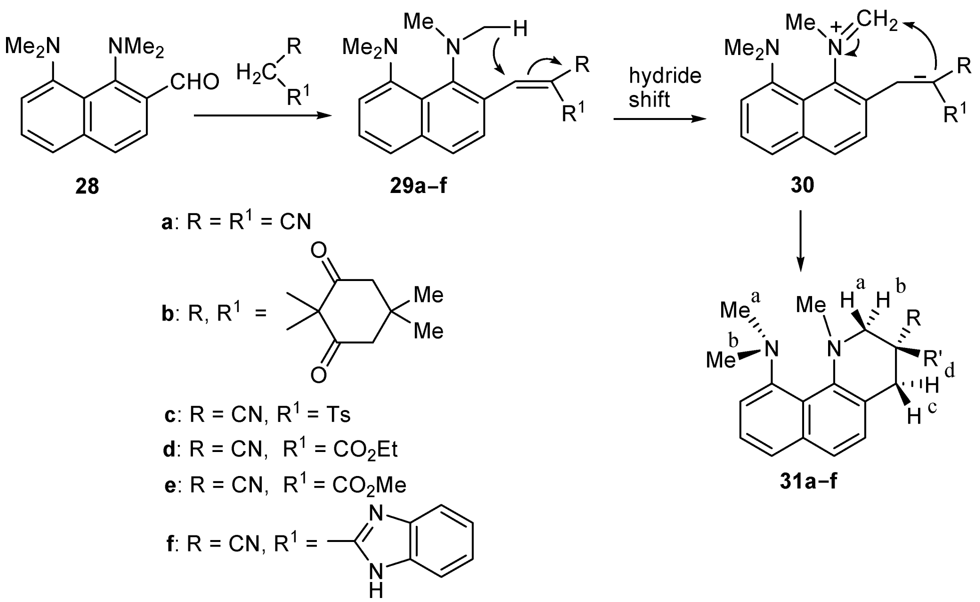
Isomerisation of alkenes **29c,d** into benzo[*h*]quinolines **31c,d** occurs rapidly and almost quantitatively on heating the solid samples or (more slowly) on incubation of their solutions in



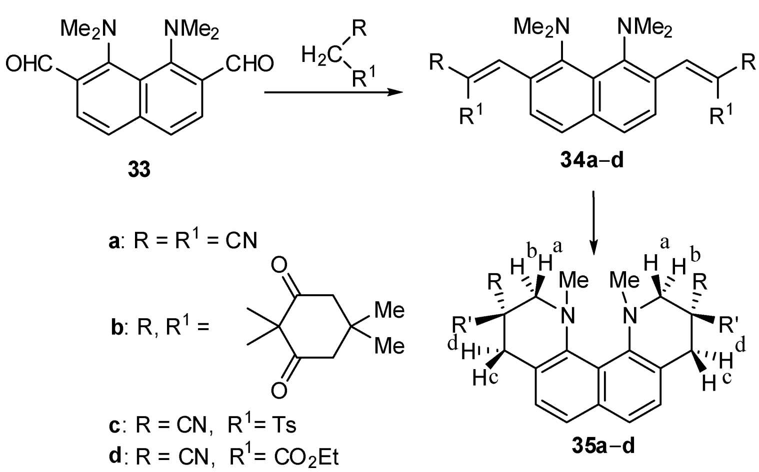
Scheme 5



Scheme 6



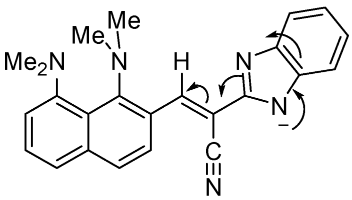
Scheme 7



Scheme 8

DMSO or ethanol at ambient temperature. On interaction of the aldehyde **28**[16] with ethyl cyanoacetate in MeOH (25 °C, 72 h) along with the condensation and subsequent *tert*-amino reaction, the complete re-esterification occurs allowing isolation of only benzo[*h*]quinoline **31e**.

The situation with benzimidazolyl-2-alkene **29f** is somewhat different: it remains intact at room temperature even in polar solvents (DMSO, DMF, EtOH) but on heating as solid or in DMSO under reflux it converts with considerable tarring into **31f** in 25% yield. Such behaviour can be attributed to enlarged NH-acidity of the benzimidazole moiety in **29f**[17] causing its conversion to anion **32** which should be more inert to a hydride reduction (see below X-ray data for **29f**).



32

The divinylic compound **34b** is especially active, self-cyclizing into **35b** even under ambient conditions. In contrast, the dialkenes **34a,c,d**[14] can be isolated; on heating in the solid state or on incubation in DMSO at room temperature they undergo double *tert*-amino cyclization giving the quino[7,8:7′,8′]quinoline derivatives **35a,c,d** in high yields (Scheme 8). The data obtained for cyclization of the mono- and dialkenes are summarized in Table 1.

Structures of **31** and **35** are confirmed by the absence in their NMR spectra of signals from one or two N–Me groups and an appearance of the two-proton peaks for the ring methylene groups. For example, in the ^{13}C and ^{1}H NMR spectra of benzoquinoline **31a** the 2- and 4-CH_2 groups resonate at δ_C 57.0 and 37.6 and δ_H 3.98 and 3.63 ppm, respectively (the assignment is based on the HETCOR experiments).[18] In the ^{1}H NMR spectra registered at 600 MHz one can see that unlike the 4-CH_2 group the 2-CH_2 hydrogens are magnetically non-equivalent due to pyramidality of the 1-NMe group (Fig. 1) and give two broadened signals at δ_H 4.07 and 3.89 ppm. In quinolines **31c–f** and **35c,d** the substituents at C-3 are different, which results in nonequivalence of the geminal hydrogens of both 2-CH_2 and 4-CH_2 groups. Their exact

Table 1 *tert*-Amino-effect in 2-vinyl- and 2,7-divinyl-1,8-bis(dimethylamino)naphthalenes

Alkene	Reaction conditions: Solvent	T/°C	Time, h	Product	Isolated yield (%)
29a[a]	PhMe	r.t.	96	**31a**	80
29b[a]	PhMe	r.t.	24	**31b**	96
29c	neat	140–180	< 0.15	**31c**	90
29c	DMSO	r.t.	48	**31c**	100
29d	DMSO	r.t.	72	**31d**	100
29f	DMSO	189	1	**31f**	25
34a	neat	145–155	< 0.15	**35a**	96
34a	DMSO	r.t.	48	**35a**	100
34b[a]	PhMe	r.t.	24	**35b**	98
34c	DMSO	r.t.	48	**35c**	100
34d	DMSO	r.t.	72	**35d**	100

[a] The alkene was not isolated in the Knovenagel condensation due to its high reactivity.

assignment has been done for compound **31e** by using correlation ^{1}H–^{13}C spectroscopy and the results obtained were applied to the other compounds of type **31**.[16] For tetrahydroquinolines **31a**[5b] and **35a** X-ray studies have been also performed (Fig. 1).

In principle, the readiness of the *tert*-amino cyclization of alkenes **29** and **34** might be caused not only by the intrinsically high hydride donacity of the proton sponge NMe_2 groups but also by the stereochemical peculiarities of these compounds such as spatial proximity of the N–Me groups and the C_α-atom of the *ortho*-substituent or their favourable orientation. Since *peri*-disubstituted naphthalenes are known to be classical objects for the testing proximity effects,[6c,f,19] we had chosen 1-dimethylamino-8-(2,2-dicyanovinyl)naphthalene **36**[6c,f] for additional study. Surprisingly, this alkene was rather inert in regard to the *tert*-amino cyclization and remained unchanged on short melting (~160 °C, <0.3 h), after prolonged heating in EtOH or incubation of its solution in DMSO at room temperature. Nevertheless, nearly quantitative cyclization of **36** into 1-methyl-3,3-dicyanonaphtho[1,8-*b*,*c*]azepine **37** occurs when a solution of **36** in DMSO was refluxed for 30 min (Scheme 9).[20]

To shed some light on factors determining higher reactivity of alkenes **29** and **34** in comparison with **36** we have performed X-ray study of compound **29f** (geometry of **36** has been reported

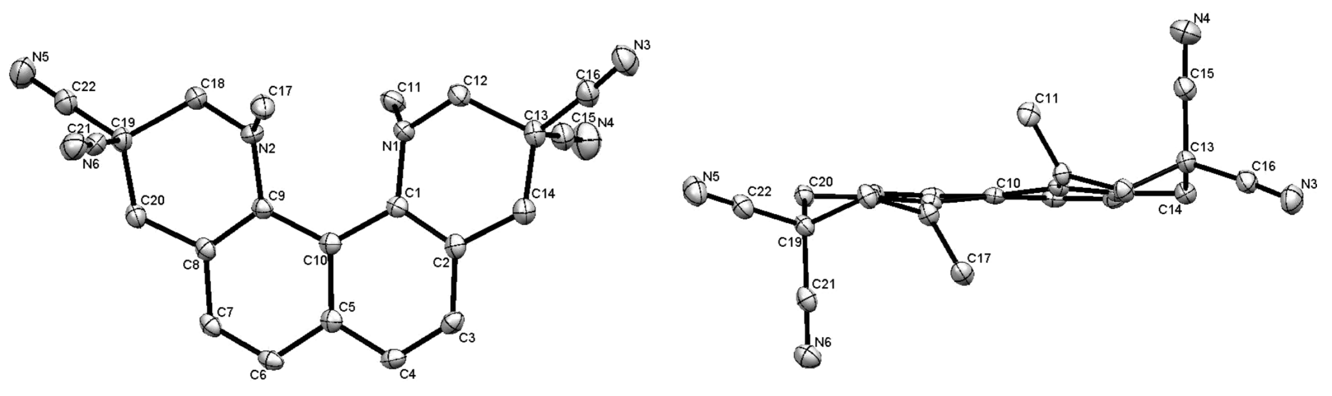
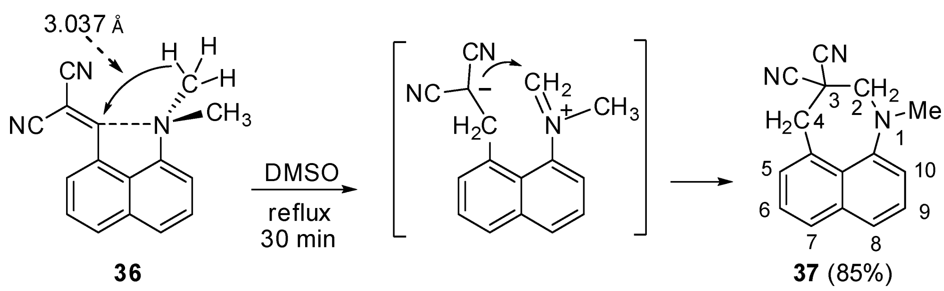


Fig. 1 Molecular structure of quino[7,8:7′,8′]quinoline **35a** (left) and view along the naphthalene plane with the N–Me groups directed to the viewer (right). Thermal ellipsoids are drawn at the 50% probability level with hydrogens being omitted for clarity.



Scheme 9

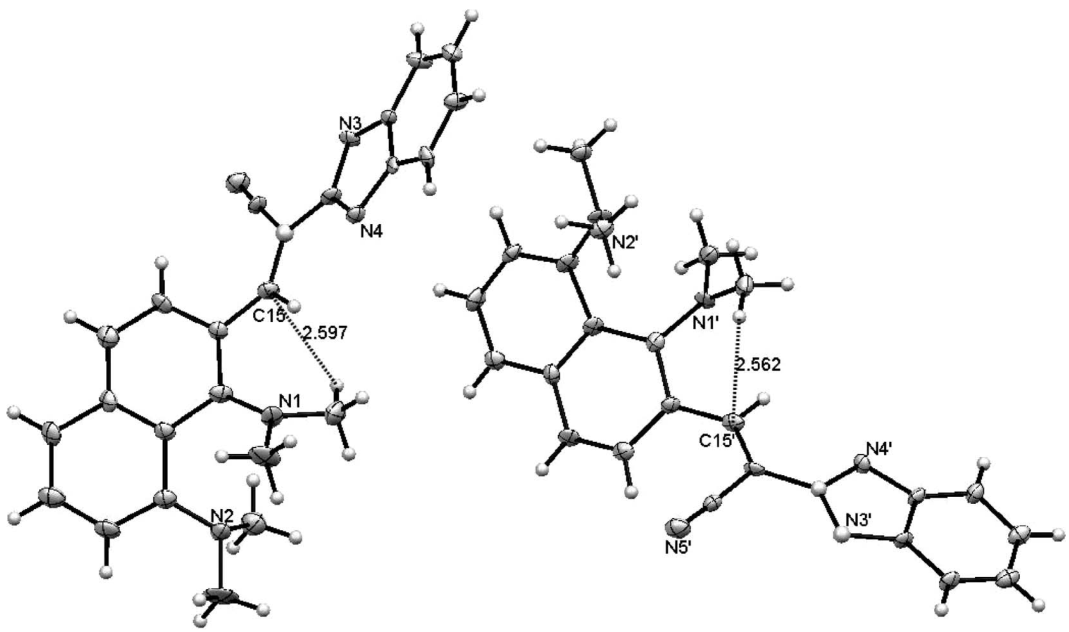
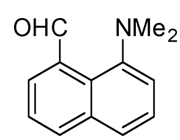


Fig. 2 Molecular structure of alkene **29f**: two independent molecules are shown. Thermal ellipsoids are drawn at the 40% probability level.

previously[19a]). The data obtained (Fig. 2) have disclosed that the nearest CH_3 hydrogen atoms in molecule **29f** are much closer (2.56–2.60 Å) to the electrophilic C_α atom of vinyl group than in alkene **36** (3.04 Å).[21] Most likely, the same should be true for proton sponge alkenes **29a–e** and **34a–d**. Since an intramolecular 1,5-hydrogen transfer (1,6 transfer for **36**) is the rate-determining step for the *tert*-amino reactions,[22] the $H_{Me}\cdots C_{CH=}$ distances can be considered as one of the most important factors influencing such processes.

Obviously, the large $H_{Me}\cdots C_{CH=}$ separation in molecule **36** results from a strong attractive interaction between the nucleophilic and electrophilic groups in the *peri*-position.[6c] This leads to a dramatic decrease of the $N\cdots C_{CH=}$ distance accompanied by strong pyramidalization and rotation of the NMe_2 group to provide better directionality of its unshared electron pair towards the electrophilic centre. Consequently, the *N*-methyl hydrogens move away from the vinyl C_α atom. Another example of such a kind is the pair 8-dimethylamino-1-naphthalenecarbaldehyde **38**[23] and 2,7-dialdehyde **33**, for which in the present work we have also performed X-ray measurements (Fig. 3). While the $H_{Me}\cdots C_{CHO}$ distance in the former molecule is equal 3.07 Å, for **33** it is much shorter (2.54 Å).



38

The geometrical specificity of *ortho*-substituted proton sponges originates from two contradictory effects: 1) the steric and electron repulsion of the *peri*-dimethylamino groups and 2) the pressure exerted by the *ortho*-substituents and causing considerable planarization of the amine nitrogen atoms.[24] Indeed, both NMe_2 groups in molecule **33** and 1-NMe_2 group in **29f** are almost flat with the sums of the valence angles at nitrogen atoms being near 358–359°. Besides, *peri*-NMe_2 groups are turned relatively to the naphthalene ring plane on *ca.* 55°. Both these factors bring the methyl hydrogens and electrophilic centre in close proximity thus facilitating the hydride shift. Since the electrophilicity of the CHO group is rather low (σ_p = 0.22),[25] aldehydes **28** and **33** do not display a *tert*-amino effect neither on heating of melted compounds nor on refluxing their solutions with $Et_2O{\cdot}BF_3$ as a catalyst. However, a transition to more electrophilic substituents such as

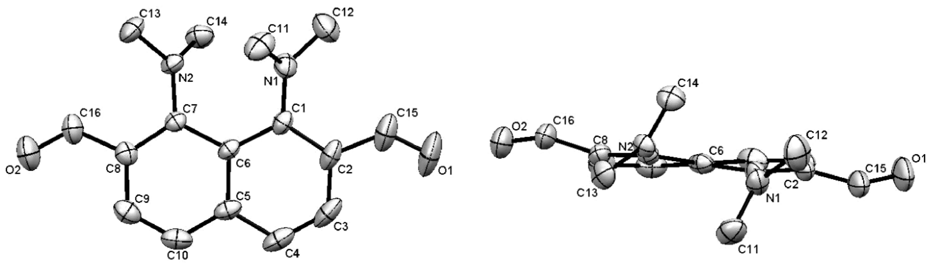
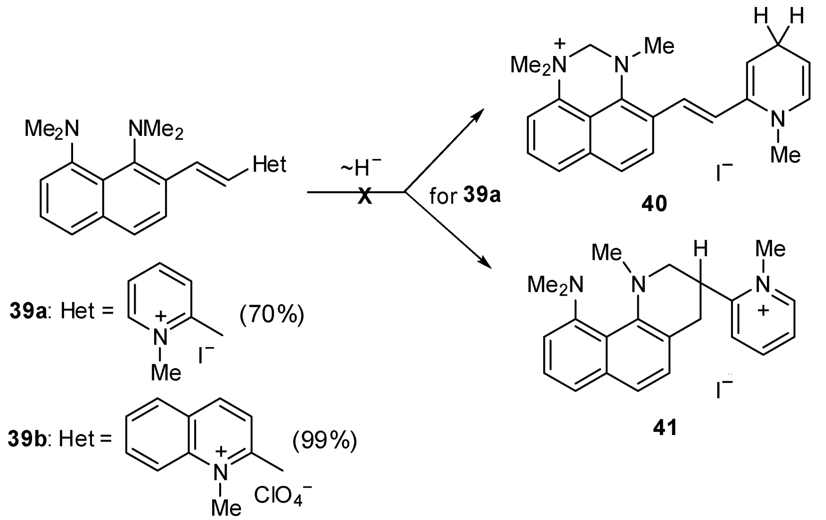


Fig. 3 Molecular structure of dialdehyde **33** (left) and view along the naphthalene plane with the NMe_2 groups directed to the viewer (right). Thermal ellipsoids are drawn at the 20% probability level with hydrogens being omitted for clarity.



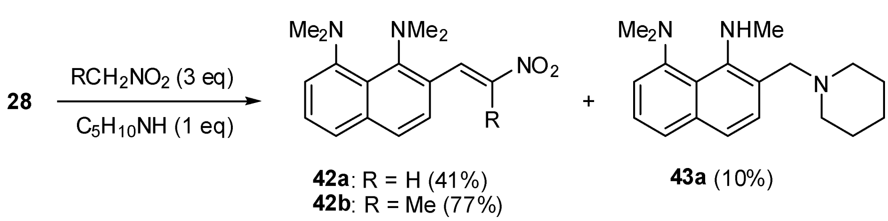
Scheme 10

2,2-dicyanovinyl makes the hydride shift possible. There is little doubt that the intrinsic hydride donor ability of the *peri*-NMe_2 groups should be also at play, favouring higher activity of the proton sponge derivatives. This follows from a comparison of the first ionization potentials of 1,8-bis(dimethylamino)naphthalene **2** ($IP_1 = 7.05$ eV) and 1-dimethylaminonaphthalene ($IP_1 = 7.50$ eV).[8]

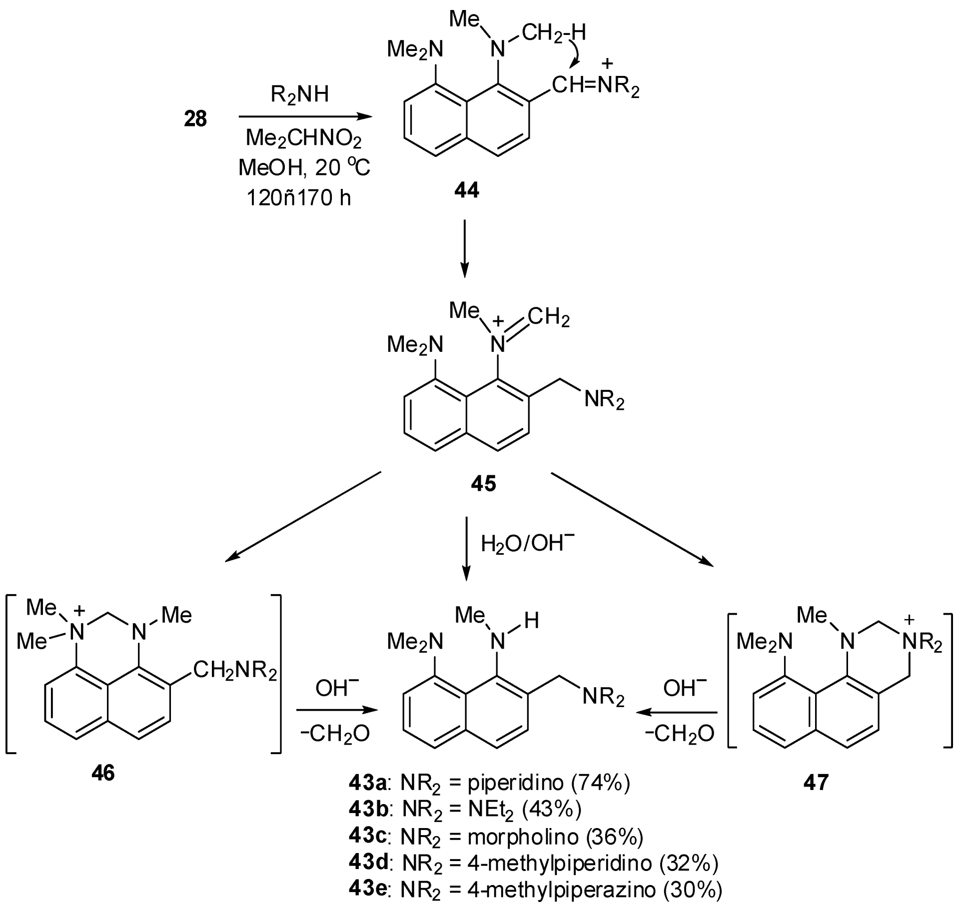
The reasons why iminium intermediates like **30** undergo *ortho*- and not *peri*-cyclization are understandable. Firstly, the nucleophilicity of the carbanion centre in **30** should be higher than that of the 8-NMe_2 group. Secondly, the *peri*-cyclization requires rotation of the N(Me)═CH_2 group around the C_{arom}–N bond (see **10** → **11**, Scheme 3), which costs some extra energy.

Further we decided to examine whether the *tert*-amino-effect can be also observed for proton sponges **39** with electron-deficient heterocyclic groups in the vinyl chain (Scheme 10). In principle, as it is shown for the salt **39a**, the hydride ion can either reduce the heterocyclic ring with subsequent *peri*-cyclization into 2,3-dihydroperimidinium salt **40** or migrate into the alkene chain ultimately producing benzo[*h*]quinoline derivative **41**. As we found, neither of these possibilities is realized. Compounds **39a,b**[14] obtained by a condensation of aldehyde **28** with 1,2-dimethylpyridinium iodide and 1,2-dimethylquinolinium perchlorate, respectively, remained unchanged on heating as solids (150–180 °C, 20 min) or in polar solvents (DMSO, 90 °C, 1 h; DMF or EtOH, reflux, 5 h).

Analogously, 2-(2-nitrovinyl)- **42a** and 2-(2-nitropropen-1-yl)-1,8-bis(dimethylamino)naphthalenes **42b** have been prepared by a condensation of aldehyde **28** with nitromethane or nitroethane in the presence of piperidine as a catalyst (Scheme 11). Interestingly, in both cases, in addition to the target compounds **42**, 1-dimethylamino-8-methylamino-7-piperidinomethyl naphthalene **43a** was isolated as a by-product in a 10% yield.



Scheme 11



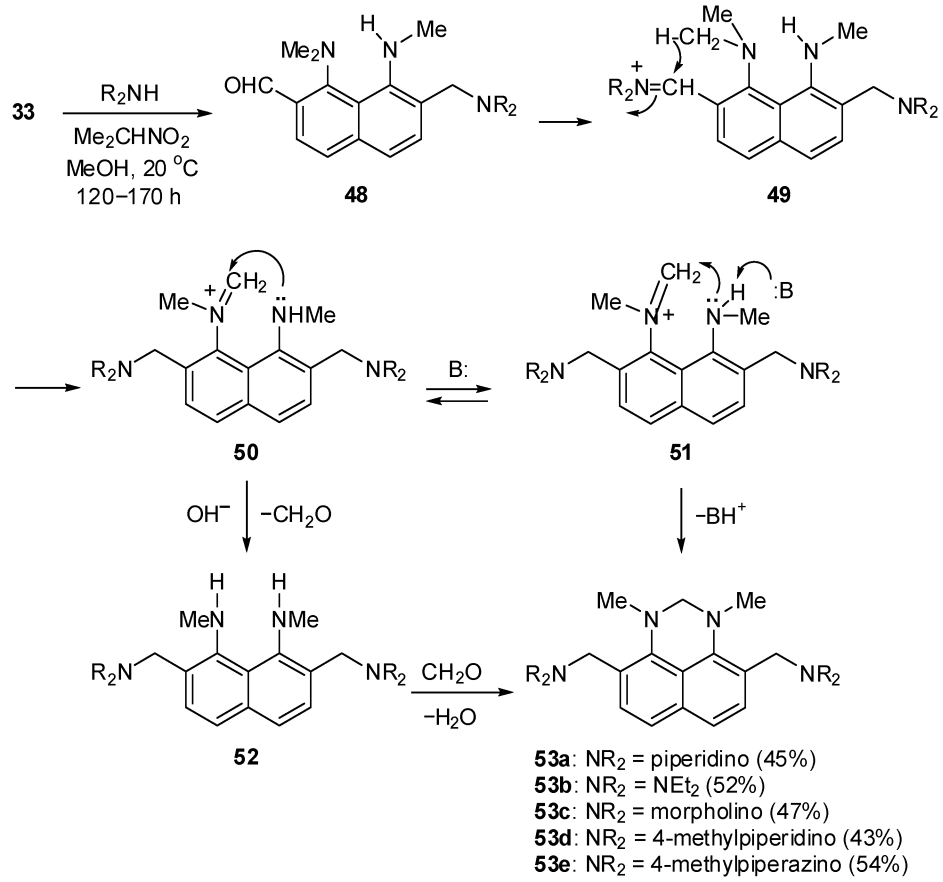
Scheme 12

The nitroalkenes **42a,b**[14] are rather stable compounds and do not enter the *tert*-amino reaction on heating as solid or under reflux in polar solvents such as DMSO (1 h), DMF or EtOH (5 h). At the same time, the formation of demethylated Mannich base **43a** clearly indicated that some kind of a *tert*-amino reaction, possibly involving 2-methyleneiminium intermediate, yet occurs. Therefore, we examined the last transformation in more detail.

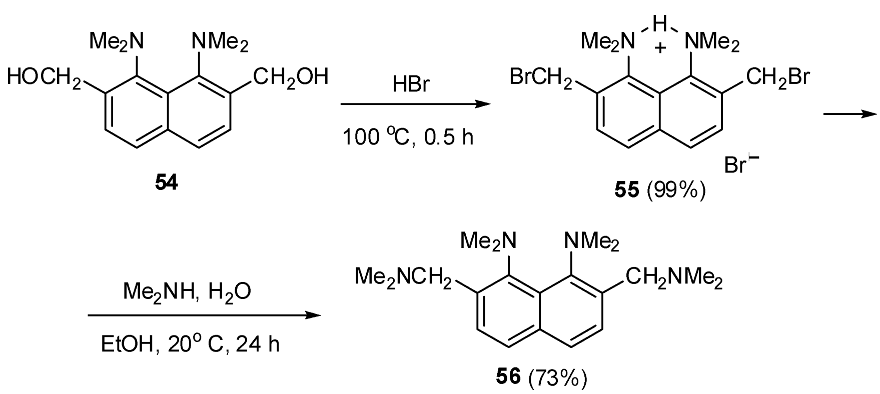
Proton sponges with methyleneiminium functionalities in *ortho*-positions

We proposed that the 2-methyleneiminium salt of type **44** (Scheme 12), which results from the nucleophilic addition of piperidine to the carbonyl group of aldehyde **28**, is the initial intermediate in the formation of Mannich base **43a**. Since **43a** is not formed in the absence of nitromethane or nitroethane, the latter appears to act as a mild acidic catalyst. To exclude the formation of nitroalkenes **42** and thus to increase the yield of **43a**, we replaced $MeNO_2$ and $EtNO_2$ by 2-nitropropane. Indeed, in this case compound **43a** became a single isolable product with a 74% yield. When some other secondary alkylamines have been used instead of piperidine, the Mannich bases **43b–e** were obtained in 30–43% non-optimized yields. Evidently, the primarily formed iminium salt **44** accepts a hydride ion from the 1-NMe_2 group producing another iminium intermediate **45**. The latter is transformed into final product **43** either by the direct hydrolytic loss of the *N*-methyl group or *via* the preliminary formation of 2,3-dihydroperimidinium **46** or benzo[*h*]quinazolinium **47** salts, which both can undergo similar basic hydrolysis. Indeed, in a special experiment we found that salt **1a** on treatment with piperidine (3 eq) in methanol (20 °C, 96 h) furnished *N*,*N*,*N*′-trimethyl-1,8-diaminonaphthalene in 59% yield.

Especially interesting results were obtained when 2,7-dialdehyde **33** reacted with secondary amines in the presence of 2-nitropropane (Scheme 13). In this case, the main reaction product was the corresponding 4,9-bis(dialkylaminomethyl)-1,3-dimethyl-2,3-dihydroperimidine **53**. Unlike the uniform tandem *tert*-amino effect, which has been described above for quino[7,8:7′,8′]quinolines **35** (Scheme 8), the formation of bis-Mannich bases **53** can be qualified as a mixed tandem *tert*-amino process (Scheme 13). As one can see, two subsequent hydride ion transfers occur from the two different *N*-methyl groups of the same molecule. On the first stage, the reaction develops similarly to monoaldehyde **28** (Scheme 12) yielding the demethylated Mannich base **48** and then the iminium intermediates **49** and **50**. However, the next stage is not the demethylation of **50** but instead the *peri*-cyclization in which the 8-$N^+(Me){=}CH_2$ and 1-NHMe functionalities participate. At the first glance, it seems strange since the nucleophilicity of the 1-NHMe group should be



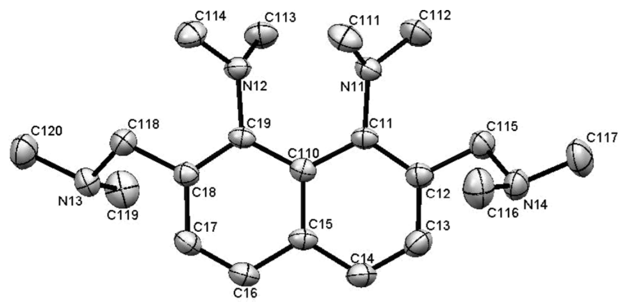
Scheme 13



Scheme 14

substantially lower than that of OH^-. A possible rationale might be the participation of OH^- or dialkylamine in the basic catalysis that sharply increases nucleophilicity of the 1-NHMe group as it is depicted in structure **51**. Apart from this, such cyclization can be promoted by the pressure of the two *ortho*-CH_2NR_2 groups ("buttressing effect")[24] which forces the *peri*-substituents to be closer to each other. Alternatively, the reaction may indeed involve hydrolytic demethylation with the loss of CH_2O molecule to give the *N*,*N*′-dimethylated diaminonaphthalene **52**, which afterwards transforms into **53**.

As we have already pointed out, in principle, the methyleneiminium cations **45** and **50** could undergo alternative cyclization producing benzo[*h*]quinazolinium salts of type **47**. Apparently, such cyclization is less favourable because of two reasons: 1) the close proximity of *peri*-substituents and 2) the unfavourable conformation of the *ortho*-CH_2NR_2 groups relative to the *peri*-substituents. To some extent both these points were resolved by an X-ray diffraction experiment for the proton sponge bis-Mannich base **56**, which was obtained in high yield from dialcohol **54**[16] as shown in Scheme 14. In all three independent molecules constituting the room-temperature solid state structure of **56** the nitrogen atoms of *peri*- and *ortho*-substituents are splayed outwards with an average separation $N_{1(8)} \cdots N_{Alk}$ equal to 4.17 Å against 2.79 Å for $N_1 \cdots N_8$ (Fig. 4).



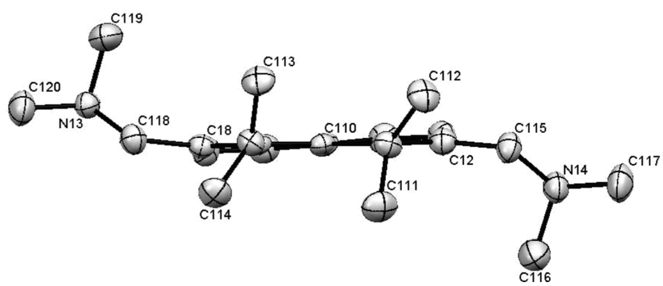


Fig. 4 Molecular structure of one of three independent molecules of bis-Mannich base **56** (left) and view along the naphthalene plane with the aromatic NMe_2 groups directed to the viewer (right). Thermal ellipsoids are drawn at the 30% probability level with hydrogens being omitted for clarity.

Conclusions

The analysis of the *tert*-amino reactions in the series of naphthalene proton sponges allows us to conclude that their course is largely determined by the nature of the *ortho*-substituent and the strongest nucleophile present in the reaction mixture. In the case of proton sponge-based 2-naphthylmethyl carbenium ions, no nucleophilic centre appears in the *ortho*-substituent after a hydride ion transfer, and the only possibility for the methyleneiminium intermediate is the *peri*-cyclization on the adjacent 8-NMe_2 group. When the hydride ion moves to a neutral *ortho*-substituent such as the electron-deficient vinyl group, the side-chain carbanion is formed, whose higher nucleophilicity determines the following *ortho*-cyclization. If the strongest nucleophile in the reaction mixture is an external base, *e.g.* OH^-, the 1-$N^+(Me){=}CH_2$ group typically undergoes hydrolytic fission into the demethylated NHMe function. For the proton sponges with electron-accepting groups in both *ortho*-positions, two types of tandem *tert*-amino effect, uniform and mixed, are possible. It has also been shown that the hydride donor ability of the proton sponge NMe_2 groups exceeds that of monodimethylaminoarenes. This can be ascribed to the lower ionization potential of proton sponges and especially to the close proximity of the *peri*-NMe_2 groups and the electrophilic centres of *ortho*-substituents. The data obtained have disclosed not only new features of the proton sponge reactivity, but also provided a convenient approach to the syntheses of such compounds as benzo[*h*]quinolines, quino[7,8:7′,8′]quinolines, 2,3-dihydroperimidinium salts, 2,3-dihydroperimidines, *N*,*N*,*N*′-trimethyl-1,8-diaminonaphthalenes, and naphthalene proton sponges bearing substituents which are otherwise difficult to introduce.

Experimental

General information

^1H and ^{13}C NMR spectra for **31a,e** were recorded on a Bruker Avance 600 (600 MHz) device, while for the rest a Bruker DPX-250 (250 MHz) spectrometer was used with the solvent as the internal standard (δ (ppm), ^nJ/Hz). IR spectra were measured in paraffin oil on a Specord IR-71 spectrometer. Mass spectra were obtained from Finnigan MAT INCOS 50 instrument (electron impact, 70 eV). UV spectra were measured in MeOH on a Varian Cary-50 spectrometer. Thin layer chromatography was carried out on Al_2O_3 with Brockmann activity III 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 and Silufol plates; development with iodine vapour. The melting points were measured in sealed capillaries and are uncorrected. The solvents were purified and dried by standard methods.

[1,8-Bis(dimethylamino)naphth-2-yl](2′-dimethylamino-phenyl)methanol (6c)

n-Butyllithium (1.6 M solution in hexane, 0.43 ml, 0.68 mmol) was added to a solution of 2-bromo-1,8-bis(dimethylamino)naphthalene[26] (0.2 g, 0.68 mmol) in dry Et_2O (5 ml) at −15 °C. After 0.5 h at −15 °C, a solution of 2-dimethylaminobenzaldehyde (0.1 g, 0.68 mmol) in dry Et_2O (2 ml) was added and the mixture was left overnight at −15 °C. The resulting solution was poured into water, the organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 2 ml). The solvents were evaporated to dryness and the residue was chromatographed on Al_2O_3 with $CHCl_3$-elution to yield **6c** (0.114 g, 46%) as brown oil. $\delta_H(CDCl_3)$ 2.68–2.88 (m, 12H, 1,8-NMe_2), 2.98 (s, 6H, 2′-NMe_2), 6.67 (br s, 1H, C*H*(OH)), 6.74 (d, 1H, H-3′, ^3J 7.61), 6.95 (t, 1H, H-4′, ^3J 7.62), 7.11–7.57 (m, 7H, H-3,4,5,6,7,5′,6′); δ_H(DMSO-d$_6$) 2.40–3.08 (m, 18H, 1,8,2′-NMe_2), 5.63 (br s, 1H, CH(O*H*)), 6.57 (s, 1H, C*H*(OH)), 6.90–7.53 (m, 9H, H-3,4,5,6,7,3′,4′,5′,6′).

General procedure for preparation of 12c, 16 and 22

A solution of **6c** (0.1 g, 0.28 mmol) or **15** (0.13 g, 0.28 mmol), or **19**[9] (0.085 g, 0.28 mmol) in conc. HCl (3 ml) was refluxed for 3 h. After evaporation of volatiles to dryness, the residue was treated with a cold solution of NH_4OH (5 ml) and then the residue was dissolved in $CHCl_3$ and filtrated. The solvent was evaporated to dryness to yield **12c** or **16**, or **22**.

4-((2-Dimethylaminophenyl)methyl)-1,1,3-trimethyl-2,3-dihydroperimidinium chloride (12c). Yield 76%. Pale beige crystals with mp 169–170 °C (from $CHCl_3$); δ_H(DMSO-d$_6$) 2.66 (s, 6H, 2′-NMe_2), 3.34 (s, 3H, 3-NMe), 3.60 (s, 6H, 1-N^+Me_2), 4.26 (s, 2H, CH_2Ar), 5.25 (br s, 2H, NCH_2N), 6.93 (m, 2H, H-3′,5′), 7.21 (m, 2H, H-4′,6′), 7.37 (d, 1H, H-5, ^3J 8.53), 7.68 (t, 1H, H-8, ^3J 7.90), 7.78 (d, 1H, H-6, ^3J 8.53), 8.10 (m, 2H, H-7,9).

4-((1,8-Bis(dimethylamino)naphth-2-yl)methyl)-1,1,3-trimethyl-2,3-dihydroperimidinium chloride (16). Yield 82%. Colourless crystals with mp 170–172 °C (from MeOH); δ_H(DMSO-d$_6$) 2.65 (s, 6H, 3′-NMe_2), 2.76 (s, 6H, 2′-NMe_2) 3.39 (s, 3H, 3-NMe), 3.59

(s, 6H, 1-N^+Me_2), 4.30 (s, 2H, CH_2Ar), 5.27 (br s, 2H, NCH_2N), 7.04–8.01 (m, 10H, H-5,6,7,8,9,4′,5′,6′,7′,8′).

2-Benzhydryl-*N*-methylaniline (22). Yield 93%. Colourless crystals with mp 214–216 °C (from MeOH); δ_H($CDCl_3$) 2.69 (s, 3H, 1-NMe), 5.43 (s, 1H, C*H*Ph_2), 6.58–7.72 (m, 3H, H-2,4,5), 7.05–7.35 (m, 11H, H-3, CHPh_2).

Bis[1,8-bis(dimethylamino)naphth-2-yl]methane (17)

A mixture of **16** (0.2 g, 0.42 mmol) and $LiAlH_4$ (0.02 g, 0.53 mmol) in dry THF (5 ml) was stirred at room temperature for 2 h, then hydrolyzed with H_2O (20 ml) and extracted with Et_2O (30 ml). The solvent was evaporated and the residue was chromatographed (Al_2O_3, $CHCl_3$) to give **17** (0.172 g, 93%) as colourless crystals with mp 107–108 °C (from *n*-hexane); δ_H($CDCl_3$) 2.75 (s, 12H, 8,8′-NMe_2), 2.93 (s, 12H, 1,1′-NMe_2), 4.26 (s, 2H, CH_2Ar), 6.97 (d, 2H, H-7,7′, ^3J 8.42), 7.06 (d, 2H, H-5,5′, ^3J 7.37), 7.24 (t, 2H, H-6,6′, ^3J 7.54), 7.36 (m, 4H, H-3,3′,4,4′); δ_H(DMSO-d_6) 2.7 (s, 12H, 8,8′-NMe_2), 2.87 (s, 12H, 1,1′-NMe_2), 4.24 (s, 2H, CH_2Ar), 6.91 (d, 2H, H-7,7′, ^3J 8.33), 7.18 (d, 2H, H-5,5′, ^3J 7.28), 7.26 (t, 2H, H-6,6′, ^3J 7.68), 7.36 (m, 4H, H-3,3′,4,4′).

General procedure for preparation of benzo[*h*]quinolines 31a,e

A mixture of aldehyde **28**[16] (0.1 g, 0.41 mmol) and the corresponding CH-acid (0.41 mmol) in 5 ml of EtOH (for **31a**) or MeOH (for **31e**) was kept at room temperature for 48 h (for **31a**) or 72 h (for **31e**). The crystals formed in the reaction mixture were filtered off and washed with cold EtOH to give pure **31a** or **31e**.

3,3-Dicyano-10-dimethylamino-1-methyl-1,2,3,4-tetrahydrobenzo[*h*]quinoline (31a). Yield 65%. Shiny colourless crystals with mp 157–158 °C (from *n*-hexane); δ_H($CDCl_3$) 2.62 (br s, 3H, 10-NMe), 2.90 (br s, 3H, 10′-NMe), 3.08 (s, 3H, 1-NMe), 3.63 (m, 2H, 4-CH_2), 3.89 (m, 1H, 2-CH_2^a), 4.07 (m, 1H, 2-CH_2^b), 6.99 (t, 1H, H-9, ^3J 4.32), 7.01 (d, 1H, H-5, ^3J 8.22), 7.35 (m, 2H, H-7,8), 7.40 (d, 1H, H-6, ^3J 8.28); δ_C($CDCl_3$) 25.8, 37.6, 41.5, 45.6, 46.5, 57.0, 113.8, 114.2, 115.4, 119.0, 121.4, 122.9, 126.1, 136.8, 141.1, 150.0.

3-Cyano-10-dimethylamino-3-methoxycarbonyl-1-methyl-1,2,3,4-tetrahydrobenzo[*h*]quinoline (31e). Yield 99%. Pale orange crystals with mp 120–122 °C (from *n*-hexane); δ_H($CDCl_3$) 2.69 (br s, 3H, 10-NMe), 2.84 (br s, 3H, 10′-NMe), 3.05 (s, 3H, 1-NMe), 3.42 (br d, 1H, 4-CH_2^a, ^2J 16.14), 3.64 (d, 1H, 4-CH_2^b, ^2J 16.50), 3.70 (d, 1H, 2-CH_2^a, ^2J 13.02), 3.88 (s, 3H, OC*H*$_3$) 3.93 (d, 1H, 2-CH_2^b, ^2J 13.02), 6.95 (d, 1H, H-9, ^3J 7.26), 7.07 (d, 1H, H-5, ^3J 8.22), 7.30 (m, 3H, H-6,7,8); δ_C($CDCl_3$) 35.8, 38.3, 41.5, 45.5, 46.0, 53.7, 56.63, 113.2, 116.9, 118.9, 119.3, 121.4, 122.0, 125.5, 126.7, 136.8, 141.6, 150.1, 168.3.

1,8-Bis(dimethylamino)-2,7-di(2-cyano-2-tosylvinyl)naphthalene (34c)

A mixture of dialdehyde **33**[16] (0.1 g, 0.37 mmol), tosylacetonitrile (0.144 g, 0.74 mmol) and piperidine (0.063 g, 0.74 mmol) in EtOH (10 ml) was kept at room temperature for 24 h. The red crystals formed in the reaction mixture were filtered off and washed with cold EtOH to give pure **34c** (0.173 g, 75%); mp 157–160 °C (from *n*-hexane); λ_{max}/nm (log ε) 490 (4.31), 312 (4.40), 228 (4.72); δ_H($CDCl_3$) 2.49 (s, 6H, 4′-CH_3), 3.23 (s, 12H, 1,8-NMe_2), 7.32 (d, 2H, H-3,6, ^3J 8.53), 7.42 (d, 2H, H-3′,5′, ^3J 8.53), 7.82 (d, 2H, H-4,5, ^3J 8.53), 7.91 (d, 2H, H-2′,6′, ^3J 8.53), 8.33 (s, 2H, C*H*=); δ_C($CDCl_3$) 22.2, 47.2, 112.9, 113.9, 123.6, 123.7, 123.9, 128.8, 128.9, 130.8, 135.8, 143.1, 146.2, 152.2, 155.8.

3,10-Dicyano-1,12-dimethyl-3,10-ditosyl-1,2,3,4,9,10,11,12-octahydroquino[7,8:7′,8′]quinoline (35c)

A solution of **34c** (0.1 g, 0.16 mmol) in DMSO (5 ml) was kept at room temperature for 48 h until its discolouration, providing after evaporation of the solvent pure **35c**. Pale beige crystals (0.98 g, 98%) with mp 252–253 °C (from EtOH); δ_H($CDCl_3$) 2.52 (m, 6H, 4′-CH_3), 2.76–3.02 (m, 12H, 1,12-NMe_2), 3.16 (m, 2H, 4,9-CH_2^a), 3.59–4.07 (m, 6H, 4,9-CH_2^b, 2,11-$CH_2^{a,b}$), 6.98 (m, 2H, H-5,8), 7.28 (m, 2H, H-6,7), 7.48 (m, 2H, H-3′,5′), 7.96 (m, 2H, H-2′,6′); δ_C($CDCl_3$) 22.3, 33.6, 45.8, 46.3, 52.8, 55.2, 117.5, 117.6, 118.1, 118.4, 123.1, 127.3, 127.6, 130.7, 130.9, 131.0, 131.2, 136.2, 136.8, 141.4, 147.4, 147.5.

3,3-Dicyano-1-methyl-1,2,3,4-tetrahydronaphth[1,8-*b*,*c*]azepine (37)

A solution of **36**[19] (0.05 g, 0.2 mmol) in DMSO (2 ml) was refluxed for 0.5 h until its discolouration, providing after evaporation of the solvent pure **37**. White crystals (0.04 g, 85%) with mp 114–115 °C (from MeOH); lit.[6f] 126.0–126.5 °C (solvent was not indicated); δ_H($CDCl_3$) 3.17 (s, 3H, 1-NMe), 3.73–3.94 (m, 4H, 2,4-CH_2), 6.86 (dd, 1H, H-10, ^3J 7.42, ^4J 1.26), 7.23 (dd, 1H, H-5, ^3J 6.95, ^4J 1.26), 7.29–7.45 (m, H-6,8,9), 7.73 (dd, 1H, H-7, ^3J 8.21, ^4J 1.26); δ_C($CDCl_3$) 36.9, 41.5, 42.4, 64.3, 110.6, 115.9, 122.3, 126.3, 126.4, 126.9, 128.6, 129.4, 129.7, 136.3, 150.3. Other analytic and spectroscopic properties are consistent with those published in ref. 6f.

General procedure for preparation of alkenes 29f and 39a,b

A mixture of aldehyde **28**[16] (0.1 g, 0.41 mmol), the corresponding CH-acid (0.41 mmol) and piperidine (0.035 g, 0.41 mmol) in EtOH (5 ml) was kept at room temperature for 24 h. The crystals formed in the reaction mixture was filtered off and washed with cold EtOH to give pure **29f**, and **39a,b**.

2-(2-(1′,8′-Bis(dimethylamino)naphth-2′-yl)-1-cyanoethenyl)-benzimidazole (29f). Yield 90%. Wine-coloured crystals, mp 181–183 °C (from EtOH); δ_H($CDCl_3$) 2.73 (s, 6H, 8′-NMe_2), 3.20 (s, 6H, 1′-NMe_2), 7.03 (m, 1H, H-7′), 7.24–7.53 (m, 6H, H-4,6,7,3′,5′,6′), 7.77 (m, 1H, H-5), 7.93 (d, 1H, H-4′, ^3J 8.53), 8.66 (s, 1H, CH=), 9.48 (br s, 1H, 1-NH); δ_H(DMSO-d_6) 2.72 (s, 6H, 8′-NMe_2), 3.13 (s, 6H, 1′-NMe_2), 7.09 (m, 1H, H-7′), 7.17–7.33 (m, 2H, H-4,7), 7.42 (m, 2H, H-5′,6′), 7.53 (m, 2H, H-3′,6), 7.70 (br d, 1H, H-5, ^3J 7.65), 7.85 (d, 1H, H-4′, ^3J 8.65), 8.35 (s, 1H, CH=), 13.08 (br s, 1H, 1-NH); δ_C(DMSO-d_6) 45.6, 46.4, 101.4, 112.3, 115.5, 117.6, 119.9, 122.8, 123.0, 123.6, 124.2, 126.1, 126.4, 128.7, 135.7, 139.6, 144.4, 147.6, 149.1, 152.4, 153.2.

1-Methyl-2-(2-(1′,8′-bis(dimethylamino)naphth-2′-yl)ethenyl)pyridinium iodide (39a). Yield 70%. Wine-coloured crystals with gold shine, mp 137–138 °C (from EtOH); λ_{max}/nm (log ε), 490 (4.17), 324 (4.57), 218 (4.73); ν_{max}/cm^{-1} 1521, 1628; δ_H(DMSO-d_6) 3.13 (s, 6H, 8′-NMe_2), 3.33 (s, 6H, 1′-NMe_2), 4.40 (s, 3H, 1-CH_3), 7.09 (dd, 1H, H-7′, ^3J 7.26, ^4J 1.26), 7.32–7.57 (m, 4H, H-3′,5′,6′, =CH$^{\alpha}$–), 7.85 (m, 2H, H-5,4′), 8.03 (d, 1H, –CH$^{\beta}$=, ^3J 15.79), 8.45 (t, 1H, H-4, ^3J 8.21), 8.60 (d, 1H, H-3, ^3J 8.21), 8.88 (d, 1H, H-6, ^3J 6.63); δ_H(CD_3OD) 2.80 (s, 6H, 8′-NMe$_2$), 3.24 (s, 6H, 1′-NMe$_2$), 4.44 (s, 3H, 1-CH$_3$), 7.18 (dd, 1H, H-7′, ^3J 6.49, ^4J 2.26), 7.36–7.57 (m, 4H, H-3′,5′,6′, –CH$^{\beta}$=), 7.82 (m, 2H, H-5,4′), 8.14 (d, 1H, –CH$^{\alpha}$=, ^3J 15.96), 8.47 (m, 2H, H-3,4), 8.78 (d, 1H, H-6, ^3J 6.31); δ_C(DMSO-d$_6$) 45.0, 45.5, 46.0, 114.8, 115.6, 122.0, 122.9, 123.4, 124.4, 124.5, 125.4, 127.4, 127.9, 138.3, 142.7, 144.1, 145.8, 150.5, 152.3, 152.8; m/z 317 (M$^+$, 44), 302 (17), 271 (10), 223 (13), 195 (16), 181 (23), 168 (15), 151 (15), 142 (100), 136 (14), 127 (32), 106 (38), 93 (13).

1-Methyl-2-(2-(1′,8′-bis(dimethylamino)naphth-2′-yl)ethenyl)-quinolinium perchlorate (39b). Yield 99%. Dark blue crystals, mp 152–153 °C (from EtOH); λ_{max}/nm (log ε), 554 (3.82), 344 (4.02); δ_H(DMSO-d$_6$) 2.75 (s, 6H, 8′-NMe$_2$), 3.20 (s, 6H, 1′-NMe$_2$), 4.56 (s, 3H, 1-CH$_3$), 7.09 (m, 1H, H-7′), 7.41 (m, 2H, H-5′,6′), 7.52 (d, 1H, H-3′, ^3J 8.53), 7.64 (d, 1H, =CH$^{\alpha}$–, ^3J 15.48), 7.93 (m, 2H, H-7,4′), 7.38–8.09 (m, 3H, H-5,6, –CH$^{\beta}$=), 8.53 (d, 1H, H-3, ^3J 8.84), 8.63 (d, 1H, H-8, ^3J 9.16), 8.95 (d, 1H, H-4, ^3J 8.84); δ_C(DMSO-d$_6$) 45.6, 46.7, 115.6, 117.5, 119.9, 121.7, 122.6, 123.1, 124.0, 126.4, 127.9, 128.3, 129.0, 129.4, 130.9, 135.5, 139.7, 140.1, 144.3, 147.7, 153.2, 153.4, 157.2.

3-(Benzimidazol-2′yl)-3-cyano-10-dimethylamino-1-methyl-1,2,3,4-tetrahydrobenzo[*h*]quinoline (31f)

A solution of **29f** (0.1 g, 0.26 mmol) in DMSO (5 ml) was refluxed for 1 h. The solvent was evaporated and the residue was purified on Al_2O_3 with $CHCl_3$ elution. Pale purple crystals of **31f** (0.025 g, 25%) with mp 82–83 °C (from *n*-hexane) were obtained. δ_H(DMSO-d$_6$) 2.78 (br s, 6H, 10-NMe$_2$), 3.08 (br s, 3H, 1-NMe), 3.71 (d, 1H, 4-CH$_2$^{a}, ^2J 15.32), 3.88 (m, 4H, 2,4-CH$_2$^{b}), 4.20 (d, 2H, 2-CH$_2$^{a}, ^2J 13.13), 6.93 (d, 1H, H-9, ^3J 6.91), 7.17–7.41 (m, 4H, H-4′,5′,6′,7′), 7.57 (d, 1H, H-7, ^3J 7.07), 7.68 (d, 1H, H-6, ^3J 7.24), 13.05 (s, 1H, N*H*).

1,8-Bis(dimethylamino)-2-(2-nitrovinyl)naphthalene (42a)

A mixture of **28**[16] (0.21 g, 0.87 mmol), CH_3NO_2 (0.159 g, 2.61 mmol) and piperidine (0.075 g, 0.87 mmol) in MeOH (10 ml) was kept at −20 °C for 48 h. The solvent was evaporated and the crude solid material was purified on Al_2O_3 (Et_2O–*n*-hexane, 1 : 1). Wine-coloured crystals of **42a** (0.102 g, 41%) with mp 112–113 °C (from EtOH) were obtained; λ_{max}/nm (log ε), 478 (3.79), 308 (4.31), 224 (4.60); ν_{max}/cm^{-1} 1613 (C=C); δ_H($CDCl_3$) 2.74 (s, 6H, 8-NMe$_2$), 3.15 (s, 6H, 1-NMe$_2$), 7.05 (br dd, 1H, H-7, ^3J 6.32, ^4J 2.11), 7.28–7.43 (m, 4H, H-3,4,5,6), 7.55 (d, 1H, =CH(NO_2), ^3J 13.68), 8.40 (d, 1H, –CH=, ^3J 13.68); δ_C($CDCl_3$) 45.8, 46.5, 115.6, 122.9, 123.4, 124.2, 124.6, 125.0, 128.5, 135.5, 139.9, 140.2, 153.3, 153.5; m/z 285 (M$^+$, 100), 268 (14), 239 (26), 223 (88), 210 (41), 198 (15), 192 (32), 180 (23), 168 (22), 152 (17), 127 (10), 58 (17), 44(20). Perchlorate **42a**·$HClO_4$ (prepared in MeOH on addition of 1 equiv of aqueous $HClO_4$): light beige crystals with mp 114–115 °C (decomp., from MeCN); δ_H(DMSO-d$_6$) 3.22 (s, 6H, 1-NMe$_2$), 3.37 (d, 6H, 8-NMe$_2$, ^3J 3.86), 7.87 (t, 1H, H-6, ^3J, 8.07), 8.07 (d, 1H, H-3, ^3J 8.77), 8.14-8.29 (m, 3H, H-4,5,7), 8.34 (d, 1H, =CH$^{\alpha}$–, ^3J 13.33), 8.44 (d, 1H, –CH$^{\beta}$=, ^3J 13.33), 17.60 (br s, 1H, H$^+$).

1,8-Bis(dimethylamino)-2-(2-nitro-2-methylvinyl)naphthalene (42b)

Method A. A mixture of **28**[16] (0.21 g, 0.87 mmol), piperidine (0.075 g, 0.87 mmol) and $C_2H_5NO_2$ (0.196 g, 2.61 mmol) in MeOH (10 ml) was kept at room temperature for 48 h. The solvent was evaporated and the residue was purified on Al_2O_3 (Et_2O–*n*-hexane, 1 : 1) to give **42b** (0.172 g, 66%) as red oil.

Method B. A mixture of **28** (0.21 g, 0.87 mmol) and piperidine (0.075 g, 0.87 mmol) in $C_2H_5NO_2$ (7 ml) was kept at room temperature for 48 h. The solvent was evaporated and the rest was purified as in *method A* to give **42b** (0.228 g, 88%); λ_{max}/nm (log ε) 446 (3.41), 296 (3.96); ν_{max}/cm^{-1} 1648 (C=C); δ_H($CDCl_3$) 2.44 (s, 3H, CH$_3$), 2.72 (s, 6H, 8-NMe$_2$), 3.08 (s, 6H, 1-NMe$_2$), 7.02 (dd, 1H, H-7, ^3J 5.37, ^4J 3.47), 7.19 (d, 1H, H-3, ^3J 8.53), 7.31–7.40 (m, 3H, H-4,5,6), 8.20 (s, 1H, –CH=); δ_C($CDCl_3$) 14.6, 45.5, 45.9, 115.0, 122.8, 123.3, 123.6, 125.2, 127.0, 127.6, 136.3, 139.0, 145.3, 151.9, 152.7; m/z 299 (M$^+$, 73), 282 (47), 265 (23), 248 (13), 237 (40), 225 (57), 210 (50), 194 (20), 181 (23), 168 (33), 139 (10), 127 (20), 119 (10), 111 (23), 104 (23), 97 (27), 91 (10), 83 (27), 77 (17), 71 (37), 65 (13), 57 (100), 41 (87). Perchlorate **42b**·$HClO_4$ (prepared in MeOH on addition of 1 equiv of aqueous $HClO_4$): light blue crystals with mp 121–123 °C (decomp., from MeCN); δ_H(DMSO-d$_6$) 2.20 (s, 3H, CH$_3$), 3.09 (s, 6H, 1-NMe$_2$), 3.30 (d, 6H, 8-NMe$_2$, ^3J 3.51), 7.57 (d, 1H, H-3, ^3J 8.42), 7.83 (t, 1H, H-6, ^3J 8.07), 8.10–8.27 (m, 3H, H-4,5,7), 8.43 (s, 1H, –CH=), 18.32 (br s, 1H, H$^+$).

General procedure for preparation of 43a–e

A mixture of **28** (0.21 g, 0.87 mmol), 2-nitropropane (0.232 g, 2.61 mmol) and the corresponding secondary amine (2.61 mmol) in MeOH (10 ml) was kept at room temperature for 120 h (for **43a,c,d,e**) or 168 h (for **43b**). After evaporation of the volatiles the residue was purified on Al_2O_3 (Et_2O–*n*-hexane, 1 : 1; then $CHCl_3$) to yield **43a–e** as pale yellow crystals.

1-Dimethylamino-8-methylamino-7-piperidinomethylnaphthalene (43a). Yield 74%. Mp 114–115 °C (from *n*-hexane); ν_{max}/cm^{-1} 3181; δ_H($CDCl_3$) 1.49 (m, 2H, 4′-CH$_2$), 1.61 (m, 4H, 3′,5′-CH$_2$), 2.45 (m, 4H, 2′,6′-CH$_2$), 2.80 (s, 6H, 1-NMe$_2$), 2.89 (s, 3H, 8-NMe), 3.65 (s, 2H, CH$_2$), 7.23 (d, 1H, H-2, ^3J 7.19), 7.33 (m, 2H, H-3,6), 7.56 (d, 1H, H-4, ^3J 7.89), 7.67 (d, 1H, H-5, ^3J 8.42); δ_C($CDCl_3$) 25.0, 26.5, 37.9, 46.3, 55.1, 60.3, 116.6, 120.3, 122.2, 124.5, 125.2, 125.9, 129.3, 136.0, 149.6, 151.5; m/z 297 (M$^+$, 34), 212 (96), 197 (84), 182 (100), 168 (70), 154 (35), 141 (23), 127 (21), 115 (28), 98 (29), 84 (54), 55 (39), 42 (59).

1-Dimethylamino-8-methylamino-7-diethylaminomethylnaphthalene (43b). Yield 43%. Mp 117–119 °C (from *n*-hexane); ν_{max}/cm^{-1} 3255; δ_H($CDCl_3$) 1.04 (t, 6H, NCH$_2$CH_3, ^3J 7.36), 2.54 (q, 4H, NCH_2CH$_3$, ^3J 7.36), 1.72–2.84 (m, 9H, 1-NMe$_2$, 8-NMe), 3.69 (s, 2H, CH$_2$), 7.19 (dd, 1H, H-2, ^3J 7.36, ^4J 1.41), 7.30 (m, 2H, H-3,6), 7.52 (dd, 1H, H-4, ^3J 7.42, ^4J 1.41), 7.70 (d, 1H, H-5, ^3J 8.42); m/z 285 (M$^+$, 20), 212 (66), 197 (67), 182 (73), 168 (49), 154 (25), 141 (16), 127 (17), 115 (22), 86 (26), 72 (34), 58 (100), 42 (80).

1-Dimethylamino-8-methylamino-7-morpholinomethylnaphthalene (43c). Yield 36%. Mp 119–120 °C (from *n*-hexane); ν_{max}/cm^{-1} 3249; δ_H($CDCl_3$) 2.48 (m, 4H, 2′,6′-CH$_2$), 2.77 (s, 6H, 1-NMe$_2$), 2.86 (s, 3H, 8-NMe), 3.67 (s, 2H, CH$_2$), 3.72 (t, 4H, 3′,5′-CH$_2$, ^3J 4.56), 7.21 (dd, 1H, H-2, ^3J 7.36, ^4J 1.41), 7.29 (m, 2H, H-3,6), 7.52 (dd, 1H, H-4, ^3J 7.72, ^4J 1.41), 7.60 (d, 1H, H-5, ^3J 8.41); *m/z* 299 (M$^+$, 33), 212 (91), 197 (97), 182 (100), 168 (65), 154 (36), 141 (23), 127 (22), 115 (31), 100 (19), 88 (17), 56 (46), 44 (54).

1-Dimethylamino-8-methylamino-7-(4-methylpiperidino)methylnaphthalene (43d). Yield 32%. Mp 123–124 °C (from *n*-hexane); ν_{max}/cm^{-1} 3255; δ_H(CDCl$_3$) 0.90 (m, 4H, 4′-CH, CH$_3$), 1.30 (m, 4H, 3′,5′-CH$_2$), 1.58 (m, 2H, 2′,6′-CH$_2$), 1.98 (m, 2H, 2′,6′-CH$_2$), 2.74 (s, 6H, 1-NMe$_2$), 2.84 (s, 3H, 8-NMe), 3.64 (s, 2H, CH$_2$), 7.18 (dd, 1H, H-2, ^3J 7.68, ^4J 1.28), 7.26 (m, 2H, H-3,6), 7.50 (dd, 1H, H-4, ^3J 7.90, ^4J 1.28), 7.61 (d, 1H, H-5, ^3J 8.32); *m/z* 311 (M$^+$, 6), 98 (21), 69 (16), 55 (63), 42 (100).

1-Dimethylamino-8-methylamino-7-(4-methylpiperazino)methylnaphthalene (43e). Yield 30%. Mp 150–152 °C (from *n*-hexane); ν_{max}/cm^{-1} 3252; δ_H(CDCl$_3$) 2.36 (s, 1H, NCH$_3$) 2.31–2.60 (m, 8H, 2′,3′,5′,6′-CH$_2$), 2.74 (s, 6H, 1-NMe$_2$), 2.84 (s, 3H, 8-NMe), 3.64 (s, 2H, CH$_2$), 7.12 (dd, 1H, H-2, ^3J 7.36, ^4J 1.28), 7.27 (m, 2H, H-3,6), 7.49 (dd, 1H, H-4, ^3J 8.00, ^4J 1.28), 7.57 (d, 1H, H-5, ^3J 8.32); *m/z* 312 (M$^+$, 10), 213 (22), 197 (33), 182 (28), 168 (18), 154 (11), 115 (10), 99 (58), 70 (27), 56 (74), 42 (100).

General procedure for preparation of 53a–e

A mixture of **33** (0.21 g, 0.78 mmol), 2-nitropropane (0.208 g, 2.34 mmol) and the corresponding secondary amine (2.34 mmol) in MeOH (10 ml) was kept at room temperature for 120 h (for **53a,c,d,e**) or 168 h (for **53b**). After evaporation of volatiles the residue was purified on Al$_2$O$_3$ (Et$_2$O–*n*-hexane, 1 : 1; then CHCl$_3$) to yield **53a–e** as pale yellow crystals.

4,9-Bis(piperidinomethyl)-1,3-dimethyl-2,3-dihydroperimidine (53a). Yield 45%. Mp 68–71 °C (from *n*-octane); δ_H(CDCl$_3$) 1.46 (m, 4H, 4′-CH$_2$), 1.59 (m, 8H, 3′,5′-CH$_2$), 2.45 (m, 8H, NCH$_2$, 2′,6′-CH$_2$), 3.18 (s, 6H, 1,3-NMe), 3.61 (s, 4H, CH$_2$), 4.32 (s, 2H, 2-CH$_2$), 7.44 (d, 2H, H-5,8, ^3J 8.53), 7.60 (d, 2H, H-6,7, ^3J 8.53); δ_C(CDCl$_3$) 25.0, 26.5, 45.7, 55.1, 59.1, 72.8, 121.7, 121.9, 124.7, 128.7, 133.6, 143.8; *m/z* 392 (M$^+$, 28), 98 (100), 84 (90), 70 (13), 55 (57), 42 (91).

4,9-Bis(diethylaminomethyl)-1,3-dimethyl-2,3-dihydroperimidine (53b). Yield 52%. Mp 43–46 °C (from *n*-hexane); δ_H(CDCl$_3$) 1.05 (t, 12H, CH$_3$, ^3J 7.27), 2.56 (q, 8H, NCH$_2$, ^3J 7.27), 3.14 (s, 6H, 1,3-NMe), 3.68 (s, 4H, CH$_2$), 4.34 (s, 2H, 2-CH$_2$), 7.47 (d, 2H, H-5,8, ^3J 8.53), 7.69 (d, 2H, H-6,7, ^3J 8.53); δ_C(CDCl$_3$) 12.3, 45.9, 47.6, 53.0, 72.8, 121.7, 122.0, 126.3, 128.3, 133.4, 143.2; *m/z* 368 (M$^+$, 7), 223 (18), 86 (100), 72 (59), 58 (48), 42 (33).

4,9-Bis(morpholinomethyl)-1,3-dimethyl-2,3-dihydroperimidine (53c). Yield 47%. Mp 112–115 °C (from *n*-octane); δ_H(CDCl$_3$) 2.52 (m, 8H, 3′,5′-CH$_2$), 3.20 (s, 6H, 1,3-NMe), 3.64 (s, 4H, CH$_2$), 3.73 (m, 8H, 2′,6′-CH$_2$) 4.32 (s, 2H, 2-CH$_2$), 7.43 (d, 2H, H-5,8, ^3J 8.53), 7.58 (d, 2H, H-6,7, ^3J 8.53); *m/z* 396 (M$^+$, 7), 100 (69), 86 (27), 70 (17), 56 (100), 42 (78), 35 (20).

4,9-Bis(4′-methylpiperidinomethyl)-1,3-dimethyl-2,3-dihydroperimidine (53d). Yield 43%. Mp 95–98 °C (from *n*-octane); δ_H(CDCl$_3$) 0.92 (m, 6H, 4′-CH$_3$), 1.30 (m, 6H, 4′-CH, 3′,5′-CH$_2$), 1.60 (m, 4H, 3′,5′-CH$_2$), 2.02 (m, 4H, 2′,6′-CH$_2$), 2.90 (m, 4H, 2′,6′-CH$_2$), 3.18 (s, 6H, 1,3-NMe), 3.61 (s, 4H, CH$_2$), 4.31 (s, 2H, 2-CH$_2$), 7.43 (d, 2H, H-5,8, ^3J 8.53), 7.60 (d, 2H, H-6,7, ^3J 8.53); *m/z* 420 (M$^+$, 11), 112 (55), 98 (65), 84 (10), 69 (21), 55 (61), 42 (100).

4,9-Bis(4′-methylpiperazinomethyl)-1,3-dimethyl-2,3-dihydroperimidine (53e). Yield 54%. Mp 95–98 °C (from *n*-octane); δ_H(CDCl$_3$) 2.28 (s, 6H, 4′-CH$_3$), 2.32–2.65 (m, 16H, 2′,3′,5′,6′-CH$_2$), 3.17 (s, 6H, 1,3-NMe), 3.60 (s, 4H, CH$_2$), 4.29 (s, 2H, 2-CH$_2$), 7.41 (d, 2H, H-5,8, ^3J 8.53), 7.54 (d, 2H, H-6,7, ^3J 8.53); δ_C(CDCl$_3$) 45.6, 46.4, 53.5, 55.7, 58.3, 72.7, 121.5, 121.9, 124.1, 128.8, 133.7, 144.0; *m/z* 422 (M$^+$, 17), 113 (30), 99 (55), 70 (61), 56 (100), 42 (89).

2,7-Bis(bromomethyl)-1,8-bis(dimethylamino)naphthalene hydrobromide (55)

A solution of alcohol **54**[16] (0.097 g, 0.35 mmol) in 46% aqueous HBr (5 ml) was kept at 100 °C for 0.5 h. The reaction mixture was then evaporated to dryness in vacuum to give hydrobromide **55** quantitatively as colourless plates with mp 315–317 °C (decomp., darkens above 250 °C, from MeCN). Anal. Calcd for $C_{16}H_{21}Br_3N_2$: C, 39.95; H, 4.40; Br, 49.83. Found: C, 39.57; H, 4.22; Br, 49.51%; δ_H(CD$_3$CN) 3.40 (d, 12H, NMe$_2$, ^4J 2.9), 4.96 (s, 4H, CH$_2$Br), 7.74 (d, 2H, H-3,6, ^3J 8.8), 8.05 (d, 2H, H-4,5, ^3J 8.8), 20.37 (br m, 1H, NH).

1,8-Bis(dimethylamino)-2,7-bis(dimethylaminomethyl)naphthalene (56)

The above hydrobromide **55** was dissolved in EtOH (2 ml) and combined with 33% aqueous dimethylamine (4 ml). The resulting mixture was kept at room temperature for 24 h, then MeCN (2 ml) was added and the mixture was made strongly basic with solid KOH. The reaction product was extracted with hexane (3 × 3 ml), dried over KOH and evaporated to dryness. This gave pure bis-Mannich compound **56** (0.085 g, 73%) as light-yellow plates with mp 79–81 °C (from *n*-hexane). Anal. Calcd for $C_{20}H_{32}N_4$: C, 73.13; H, 9.82; N, 17.05. Found: C, 73.29; H, 10.01; N, 17.34%; δ_H(300 MHz, CDCl$_3$) 2.23 (s, 12H, aliph. NMe$_2$), 2.94 (s, 12H, arom. NMe$_2$), 3.50 (s, 4H, CH$_2$N), 7.51 (d, 2H, H-3,6, ^3J 8.46), 7.55 (d, 2H, H-4,5, ^3J 8.46). Perchlorate **56**·HClO$_4$ (prepared in MeCN on addition of 1 equiv of aqueous HClO$_4$): light beige crystals with mp 256–260 °C (decomp., from MeCN); δ_H(CD$_3$CN) 2.40 (s, 12H, aliph. NMe$_2$), 3.33 (d, 12H, arom. NMe$_2$, ^4J 2.6), 3.87 (s, 4H, CH$_2$N), 7.90 (d, 2H, H-3,6, ^3J 8.8), 8.00 (d, 2H, H-4,5, ^3J 8.8), 20.36 (br m, 1H, NH).

X-Ray crystallography

X-Ray measurements were carried out with an Enraf Nonius CAD-4 (for compound **33**) and with a Bruker APEX II CCD area detector (for **29f**, **35a** and **56**), using graphite monochromated Mo-Kα radiation (γ = 0.71073 Å, $\omega/2\theta$-scanning for **33** and ω-scanning for **29f**, **35a** and **56**). The structures were solved by direct methods and subsequent Fourier syntheses using SHELXS-97 and were refined by the full-matrix least-squares technique against F^2 in anisotropic approximation for all non-hydrogen atoms with SHELXL-97. For **33**, the H atoms were determined experimentally and refined in isotropic approximation. The hydrogen atom positions for **29f**, **35a** and **56** were calculated and were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.2 $U_{eq}(C_i)$ (for Me groups the U_{iso}(H) parameters equal to 1.5 $U_{eq}(C_i)$), where $U_{eq}(C_i)$ are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded.

Crystal data for 29f. (Obtained from EtOAc): $C_{24}H_{22}N_5$, M = 380.47, space group: $P2_1/c$ (monoclinic), a = 10.247(4), b = 11.520(4), c = 34.634(13) Å, β = 102.208(7)°, V = 3996(2) Å^3, Z = 8, D_c = 1.265 g cm^{-3}, μ(Mo-Kα) = 0.078 mm^{-1}, T = 100 K, 29279 reflections collected, 5974 unique (R_{int} = 0.2366), 2961 reflections with $I > 2\sigma(I)$, 509 parameters, R_1 = 0.1712, wR_2 (all data) = 0.1612. CCDC reference number 804543. There are two independent molecules packing through the benzimidazolyl nitrogens short contacts along the a axis.

Crystal data for 33. (Obtained from $CHCl_3$): $C_{16}H_{18}N_2O_2$, M = 270.32, space group: $P2_1/c$ (monoclinic), a = 13.333(2), b = 10.094(2), c = 11.308(4) Å, β = 109.94(2)°, V = 1430.6(6) Å^3, Z = 4, D_c = 1.255 g cm^{-3}, μ(Mo-Kα) = 0.084 mm^{-1}, T = 293 K, 2635 reflections collected, 2508 unique (R_{int} = 0.0182), 1678 reflections with $I > 2\sigma(I)$, 241 parameters, R_1 = 0.0692, wR_2 (all data) = 0.1347. CCDC reference number 720578.

Crystal data for 35a. (Obtained from MeCN): $C_{22}H_{18}N_6$·0.25Me_2NH·0.75MeCN, M = 408.49, space group: $P\bar{1}$ (triclinic), a = 6.6455(7), b = 12.9280(13), c = 12.9430(13) Å, α = 101.997(2), β = 92.8910(10), γ = 94.532(2)°, V = 1083.94(19) Å^3, Z = 2, D_c = 1.252 g cm^{-3}, μ(Mo-Kα) = 0.079 mm^{-1}, T = 100 K, 10008 reflections collected, 4202 unique (R_{int} = 0.0259), 3262 reflections with $I > 2\sigma(I)$, 317 parameters, R_1 = 0.0501, wR_2 (all data) = 0.1327. CCDC reference number 801823. The crystal structure of **35a** contains channels along the a axis that are occupied by highly disordered solvent molecules including some amount of dimethylamine absorbed on crystallisation.

Crystal data for 56. (Obtained from MeOH): $C_{20}H_{32}N_4$, M = 328.50, space group: Pc (monoclinic), a = 34.582(2), b = 10.1577(6), c = 8.3390(5) Å, β = 92.8910(10)°, V = 2925.5(3) Å^3, Z = 6, D_c = 1.119 g cm^{-3}, μ(Mo-Kα) = 0.067 mm^{-1}, T = 295 K, 29486 reflections collected, 12592 unique (R_{int} = 0.0344), 7117 reflections with $I > 2\sigma(I)$, 673 parameters, R_1 = 0.1034, wR_2 (all data) = 0.1043. CCDC reference number 801824. There are three independent molecules in the unit cell.

Acknowledgements

We are grateful to Dr Zoya A. Starikova for X-ray experiments on compounds **29f**, **35a** and **56** and Dr Vladimir I. Sorokin for IR and UV measurements. The authors are also indebted to RFBR for financial support (grant No 08-03-00028).

References

1 (*a*) A. F. Pozharskii, L. A. Kurasov, V. V. Kuz'menko and L. L. Popova, *Zh. Org. Khim.*, 1981, **17**, 1005; *Chem. Abstr.*, 1981, **95**, 187185r; (*b*) N. V. Vistorobskii and A. F. Pozharskii, *Russ. J. Org. Chem.*, 1996, **32**, 61.

2 For general survey on proton sponges, see: (*a*) H. A. Staab and T. Saupe, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 865; (*b*) R. W. Alder, *Chem. Rev.*, 1989, **89**, 1215; (*c*) A. L. Llamas-Saiz, C. Foces-Foces and J. Elguero, *J. Mol. Struct.*, 1994, **328**, 297; (*d*) A. F. Pozharskii and V. A. Ozeryanskii, in *The Chemistry of Anilines*, ed. by Z. Rappoport, J. Wiley & Sons, Chichester, 2007, Part 2, Ch. 17, p. 931.

3 V. A. Ozeryanskii, E. A. Filatova, V. I. Sorokin and A. F. Pozharskii, *Russ. Chem. Bull.*, 2001, **50**, 846.

4 (*a*) S. N. Gamage, R. H. Morris, S. J. Rettig, D. C. Thackray, I. S. Thornburn and B. R. James, *Chem. Commun.*, 1987, 894; (*b*) R. P. Hughes, I. Kovacik, D. Lindner, J. M. Smith, S. Willemsen, D. Zhang, I. A. Guzei and A. L. Rheingold, *Organometallics*, 2001, **20**, 3190.

5 Preliminary reports on this topic: (*a*) O. V. Ryabtsova, A. F. Pozharskii, A. V. Degtyarev and V. A. Ozeryanskii, *Mendeleev Commun.*, 2006, **16**, 313; (*b*) M. A. Povalyakhina, A. F. Pozharskii, O. V. Dyablo, V. A. Ozeryanskii and O. V. Ryabtsova, *Mendeleev Commun.*, 2010, **20**, 36.

6 Selected articles on *tert*-amino effect: (*a*) O. Meth-Cohn and D. L. Taylor, *Chem. Commun.*, 1995, 1463 and references cited therein; (*b*) O. N. Semenova, Yu. A. Kudryavtseva, I. G. Ermolenko and L. D. Patsenker, *Russ. J. Org. Chem.*, 2005, **41**, 1100; (*c*) J. O'Leary, X. Formosa, W. Skranc and J. D. Wallis, *Org. Biomol. Chem.*, 2005, **3**, 3273; (*d*) C. Zhang, S. Murarka and D. Seidel, *J. Org. Chem.*, 2009, **74**, 419; (*e*) S. Murarka, C. Zhang and D. Seidel, *Org. Lett.*, 2009, **11**, 129; (*f*) A. A. Földi, K. Ludányi, A. C. Bényei and P. Mátyus, *Synlett.*, 2010, 2109.

7 Remarkably, that this *t*-amino reaction is completely inhibited by dimethyl sulfoxide. Thus, on treatment of alcohol **6a** in DMSO-d_6 solution in an NMR tube with 70% $HClO_4$ only the chelated cation **7a** can be registered even after prolonged standing at room temperature. Apparently, DMSO as a rather basic solvent (pK_a 0) does not allow oxonium salts **8** to be formed.

8 J. P. Maier, *Helv. Chim. Acta*, 1974, **57**, 994.

9 J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 521.

10 H. T. Al-Masri, J. Seiler, P. Lönnecke, S. Blaurock, K. Domasevitch and E. Hey-Hawkins, *Tetrahedron*, 2004, **60**, 333.

11 As it was earlier reported, both the parent proton sponge[12] and its derivatives[13] can effectively function as basic catalysts in the Knoevenagel reaction.

12 I. Rodriguez, G. Sastre, A. Corma and S. Iborra, *J. Catal.*, 1999, **183**, 14.

13 N. V. Vistorobskii and A. F. Pozharskii, *Zh. Org. Khim.*, 1991, **27**, 1543; *Chem. Abstr.*, 1992, **116**, 193866g.

14 For a discussion on stereochemistry of the proton sponge alkenes and products of their isomerisation see Fig. 2 and the special section and Table S1 in the Supporting information.

15 See Fig. S1 in the Supporting information.

16 A. F. Pozharskii, A. V. Degtyarev, O. V. Ryabtsova, V. A. Ozeryanskii, M. E. Kletskii, Z. A. Starikova, L. Sobczyk and A. Filarowski, *J. Org. Chem.*, 2007, **72**, 3006.

17 Though we did not measure NH-acidity of **29f**, one can estimate it as being between pK_a 10–11. This originates from pK_a = 11.48 (in H_2O) for 2-cyanomethylbenzimidazole (V. A. Anisimova, O. I. Askalepova, K. N. Bagdasarov and M. S. Chernov'yants, *Chem. Heterocycl. Compd.*, 1988, **24**, 281. Clearly, the NH-acidity of **29f** should be higher, especially in more polar than water DMSO, due to the presence of extra C=C bond at the C_α-atom of cyanomethyl group.

18 See Table S2 and Figs. S2 and S3 in the Supporting information.

19 (*a*) P. C. Bell and J. D. Wallis, *Chem. Commun.*, 1999, 257; (*b*) H.-B. Bürgi, J. D. Dunitz and E. Schefter, *J. Am. Chem. Soc.*, 1973, **95**, 5062.

20 Independently, cyclization of **36** into **37** has been recently reported by other authors.[6f].

21 Due to rather low quality of crystals for X-ray study of **29f** we could not directly determine the position of the NH-proton. Nevertheless, its location in the imidazole ring is unambiguous due to a specific intermolecular aggregation (see Fig. S4 and further details in the Supporting information).

22 L. C. Groenen, W. Verboom, W. H. N. Nijhuis, D. H. Reinhoudt, G. J. van Hummel and D. Feil, *Tetrahedron*, 1988, **44**, 4637.

23 D. R. W. Hodgson, A. J. Kirby and N. Feeder, *J. Chem. Soc., Perkin Trans. 1*, 1999, 949.

24 A. F. Pozharskii, O. V. Ryabtsova, V. A. Ozeryanskii, A. V. Degtyarev, O. N. Kazheva, G. G. Alexandrov and O. A. Dyachenko, *J. Org. Chem.*, 2003, **68**, 10109.

25 A. J. Gordon, R. A. Ford, *The Chemist's Companion, the Handbook of Practical Data, Techniques and References*John Wiley & Sons, New York, 1972.

26 N. J. Farrer, R. McDonald and J. S. McIndoe, *Dalton Trans.*, 2006, 4570.