1,8-Bis(bromomethyl)naphthalene in the synthesis of 1,5-diazacyclodecane and benz[de]isoquinoline proton sponges

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Dedicated to Professor Rosa M. Claramunt on the occasion of her 65th anniversary, and to recognise her outstanding contributions to heterocyclic and physical organic chemistry

Abstract
A new 1,5-diazacyclodecane-based proton sponge 9 has been prepared by treatment of 1,8-di(methylamino)naphthalene (7) with 1,8-bis(bromomethyl)naphthalene (8). Though the compound 9 is structurally related both to kinetically low-active 1,8-bis(dimethylamino)naphthalene (1, parent proton sponge) and kinetically active 1,8-bis(dimethylaminomethyl)naphthalene (2), X-ray and basicity studies have revealed that the proton sponge behavior of the former dominates. It is found that double alkylation of 1-dimethylamino-8-methylaminonaphthalene (11) with 8 touches only the NHMe functionality and leads to the substitution of the N–Me group, yielding the previously unknown benz[de]isoquinoline proton sponge 15. The reaction of 8 with 1,8-diaminonaphthalene or 2,2-dimethyl-2,3-dihydroperimidine gives, along with other products, proton sponge 18 with two benzisoquinoline fragments.

Keywords: 1,8-Diaminonaphthalenes, 1,8-bis(bromomethyl)naphthalene, 1,5-diazacyclodecane, benz[de]isoquinoline, proton sponge, basicity

Introduction
It is generally known that an organic base to be assigned to the so-called “proton sponges”, as for example 1,8-bis(dimethylamino)naphthalene (1, pKₐ = 12.1 in H₂O; 18.6 in MeCN), apart from high basicity, should possess a considerably reduced rate of proton addition-elimination (low kinetic activity).¹² When the latter criterion is not satisfied it is more appropriate to use a term ‘proton sponge-like’ compound.³⁴ A typical example is 1,8-bis(dimethylaminomethyl)
naphthalene 2, which is kinetically active despite the fact that its basicity (pK_a = 18.3 in MeCN) closely resembles that of 1.5

Some time ago one of us with co-workers tried to prepare naphthalene derivative 3, which can be considered as an interesting combination of bases 1 and 2.6 With this aim, the diamine 1 was treated with two equivalents of Eschenmoser’s salt (N,N-dimethylmethyleniminium chloride), but instead of 3 the 2-azoniaphenalene chloride 4 was isolated as the main product along with some of the mono-Mannich base 5 (Scheme 1). Notably, salt 4 is also formed by reaction of 5 with the Eschenmoser’s reagent. It was assumed that equilibrium amounts of the hydrochloride of an initially-formed bis-Mannich base 3H^+Cl^− immediately loses a dimethylamine molecule to generate the resonance-stabilized naphthylmethyl cation 6 which then cyclizes to 4.

Scheme 1. Attempted bis-aminomethylation of compound 1.

Results and Discussion

In the present work we have tried to follow up the same idea approaching it from the other side. For this, we have prepared and studied diazacyclodecane 9 in which two methylamino groups
simultaneously belong to 1,8-di(aminomethyl)- and 1,8-diaminonaphthalene fragments. This macrocycle was synthesized in 92% yield by alkylation of 1,8-di(methylamino)naphthalene (7) with 1,8-bis(bromomethyl)naphthalene (8) in the presence of triethylamine (Equation 1).

**Equation 1.** Synthesis of diazacyclodecane derivative 9.

Compound 9 forms yellowish crystals with mp 204–206 °C (from MeCN) readily dissolving in CH₂Cl₂, CHCl₃ and EtOAc. As it is depicted in Figure 1, molecule 9 is twisted along the N–CH₂ links in such a way that both naphthalene planes are settled at a 70° angle to each other. 1,8-Di(methylene)naphthalene moiety “crosses” the internitrogen space and the N-methyl groups occupy trans-positions relative to the diaminonaphthalene residue (Figure 1b).

**Figure 1.** Molecular structure of diazacyclodecane 9. (a) General view. (b) View from the side of the 1,8-di(methylene)naphthalene moiety (100 K).

In the ¹H NMR spectrum of 9 in CDCl₃, the N–CH₃ groups, due to the shielding caused by the paramagnetic component of the additional naphthalene system, resonate at δ 2.55 ppm against 2.7–2.9 ppm for ordinary protons sponges. As expected, geminal N–CH₂–Ar protons are non-equivalent and give two doublets at 3.87 and 6.23 ppm with J$_{\text{gem}}$ = 14.5 Hz. Variable temperature experiments showed that in CDCl₃ the spectrum remains unchanged up to 55 °C; the dynamics in the diastereotopic N–CH₂–Ar fragments can be registered at considerably higher temperatures. Thus, in DMSO-d₆ the doublet pattern of two CH₂ signals is smoothed at 80 °C
and coalesced at 140 °C to give one distinct peak at 175 °C (Figure 2). The estimated free energy of activation for the conformational processes giving rise to these spectral changes is $\Delta G^\neq 18.6\pm0.2$ kcal/mol. This is considerably higher than that for binaphthyl derivative 10, in which the methylene proton averaging occurs already at 70 °C.\textsuperscript{7}

**Figure 2.** $^1$H NMR patterns of the N–CH$_2$–Ar region of diazacyclodecane 9 as a function of temperature (250 MHz, DMSO-d$_6$).
Treatment of an ethyl acetate solution of 9 with one equivalent of HClO₄ followed by addition of diethyl ether leads to precipitation of the symmetric mono-perchlorate 9H⁺ClO₄⁻ in 95% yield (Equation 2).

\[
\begin{align*}
9 & \xrightarrow{\text{HClO}_4} \text{EtOAc-EtO} \\
\text{9H}^+\text{ClO}_4^- & \quad \text{ClO}_4^-
\end{align*}
\]

**Equation 2.** Synthesis of monoprotonated diazacyclodecane 9H⁺ClO₄⁻.

X-Ray measurements of this salt demonstrated that two chelate rings, six- and eight-membered, are present simultaneously in the cation, and the symmetry plane goes through both naphthalene C9–C10 bonds (chemical numbering) (Figure 3). Interestingly, that the coordination with a proton changes the molecular conformation from trans- in the parent base 9 to cis- in its salt 9H⁺ClO₄⁻. As a result, both naphthalene systems become nearly coplanar and the N–Me groups now arrange at one side of the middle molecular plane. Regrettably, the local pseudo-plane of symmetry and strong cation and anion disordering and twinning in the crystal do not allow determining exact parameters of the intramolecular hydrogen bond. Nevertheless, one can affirm that the N…N distance on protonation decreases by 7–8% (from 2.917 to 2.68–2.72 Å). In the ¹H NMR spectra of salt 9H⁺ClO₄⁻, the encircled proton is very deshielded, resonating at δ 19.55 ppm in DMSO-d₆ and at 19.95 ppm in CD₃CN. Such behavior is typical for cations of many proton sponges.

![Figure 3](image-url) General view of perchlorate 9H⁺ClO₄⁻ (the cation and the internal proton are disordered and the anion is omitted for clarity, the N atoms and the C atoms of the CH₂ links may be arbitrarily interchanged, 100 K).
Since diamine 2, in accordance with literature data,\textsuperscript{5} is kinetically active and, unlike the proton sponge 1, easily forms a dication, it was interesting to study the possibility of double protonation of base 9. Our experiments, however, show that salt $9\text{H}^+\text{ClO}_4^-$ does not undergo second protonation in low basic CD$_3$CN (more than 20 equivs of HClO$_4$ were used). Thus, in this regard compound 9 is much closer to “proton sponge” 1 rather than to Mannich base 2. The $^1$H NMR monitoring of the transprotonation process between salt $9\text{H}^+\text{ClO}_4^-$ and neutral base 1 in DMSO-$d_6$ gave for 9 $pK_a = 6.7$ (1 in DMSO has $pK_a = 7.5$, see ref. 9). The six-fold weaker basicity of 9 in comparison with 1 can be ascribed to the $-I$-effect of the second naphthalene ring.

Next, we discovered unexpectedly that the interaction of 8 with 1-dimethylamino-8-(methylamino)naphthalene (11) is accompanied by demethylation of the NHMe group, leading in 53\% yield to compound 15, which is isomeric with 9 (Scheme 2). The reaction seems to proceed in three successive S$_N$ processes involving intermediates 12–14 and is reminiscent of the proton sponge realkylation reported by us earlier.\textsuperscript{10} Undoubtedly, a key stage here is the nucleophilic attack of bromide onto the Me group in 12, which is facilitated by acidic catalysis through the formation of hydrogen bond, while the overall process is regulated by entropy factors favoring cyclization to the six-membered ring rather than the ten-membered as it would be in 9.

![Scheme 2](image_url)

**Scheme 2.** Synthesis of benz[de]isoquinoline derivative 15.
As seen from Scheme 2, the auxiliary base Et$_3$N is not involved in the key steps and is not necessary for the reaction to perform. In fact, it can really lower the yield of 15 by premature abstraction of HBr from intermediate 12. Indeed, the interaction of diamine 11 with dibromide 8 in the presence of Et$_3$N lowers the yield of benzisoquinoline 15 and requires at least 5 h for consumption of 11.

Unlike 9, methylene N–CH$_2$–Ar protons in the $^1$H NMR spectrum of 15 appear much closer in chemical shifts to give two doublets at 4.48 and 4.77 ppm with $J_{gem} = 14.5$ Hz (ABq pattern). In the gas phase, the molecular ion of 15 is more stable than that of 9 (relative intensities are 80% and 52% at 70 eV, respectively), although both undergo the same mode of fragmentation giving rise to the main [M – 185]$^+$ and [M – 169]$^+$ peaks to form protonatedacenaphthylene 16 with m/z 153 and N-methylated benzindole 17 with m/z 169. The processes associated with the loss of Me or NMe$_2$ fragments, which are typical for diamine 1 and its ring-functionalized derivatives, are observed only to a minor extent.

As expected, the reaction of dibromide 8 with unsubstituted 1,8-diaminonaphthalene gave bis(benzisoquinoline) sponge 18 (94% yield) rather than the structural isomer 19. This comes from inspection of the methylene protons region in its $^1$H NMR spectrum, which similarly to 15 contains the ABq spectral pattern centered at 4.40 ppm. The $pK_a$ values of compounds 15 and 18 in DMSO-d$_6$ measured by the competitive method (see above) turned out to be 5.6 and 4.7, respectively, displaying a further drop in basicity brought about by the benzisoquinoline fragments. The chemical shifts of the chelated NH-protons in the monoperchlorates of 15 and 18 in DMSO-d$_6$ were at $\delta$ 18.46 and 19.33 ppm, respectively.

The intriguing topology of tri(naphthalene) molecule 19 might be achieved in the sequence described by Scheme 3. Hence, we also attempted synthesis of 19 using preliminary protection of the nitrogen atoms in 1,8-diaminonaphthalene 20 with the help of an internitrogen bridge, which
could be deleted at the final step. Alkylation of 20 to 21, followed by deprotection to 22 and second alkylation should bring to 19. In the present work, Z = CMe$_2$ was tested, for which deprotection in acidic conditions is known.$^{11}$

![Scheme 3. Proposed synthesis of bicyclic derivative 19.](image)

We have found that the isopropylidene bridge in 2,2-dimethyl-2,3-dihydroperimidine (23) is too labile (and perhaps bulky) to give species of type 21. The interaction of 23 with dibromide 8 resulted in a complex mixture, from which the three main compounds, namely 27, 28, and 18, could be isolated by chromatography (Scheme 4). Of them, benzisoquinolinolino[2,1-$a$]perimidine 27 prevailed with almost 30% yield, while diamines 18 and 28 were collected in lower yields. The key steps leading to these rather unusual products are shown in Scheme 4 and were previously observed at interaction of 23 with 1,2-bis(bromomethyl)benzene providing shorter alkyldene bridge.$^{12}$ As seen, all products obtained are originated from spirocyclic intermediate 24, whose successive transformations via iminium salts 25 and 26 lead to a partial (for 27) or complete (for 28 and 18) loss of the bridge. Structure of bicyclic perimidine 27 is consistent with the mass, $^{13}$C and $^1$H NMR spectral data. Of particular interest are the prochiral Ar–CH$_2$–N methylene protons and the methyl H and C atoms of the isopropyl substituent.
Scheme 4. Alkylation of dihydroperimidine 23 by 1,8-bis(bromomethyl)naphthalene.

Finally, it is noteworthy, that compounds 9, 15 and 18 represent rather stable analogues of the N-benzylated proton sponges and we did not notice any signs of their decomposition in acidic media. Previously, English investigators failed to measure the basicity of simple representatives of such compounds due to their easy debenzylation on treatment with acids. 13,14

Experimental Section

General. 1H and 13C NMR spectra were recorded on a Bruker DPX-250 (250 MHz) spectrometer with the solvent residual peaks as the internal standard (δ ppm, J/Hz). IR spectra were measured in Nujol on a FT FSM-1202 spectrometer. Mass spectra were obtained from a Finnigan MAT INCOS 50 instrument (electron impact, 70 eV). X-Ray measurements were conducted with a Bruker APEX II diffractometer (Mo-Kα line, graphite monochromator, ω-scanning). The structures were solved by direct methods and refined by the full-matrix least-squares against F2 in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were placed in geometrically calculated positions and were refined in isotropic approximation in riding model with the Uiso(H) parameters equal to n·Ueq(Ci) (n = 1.2 for CH and CH2 groups and n = 1.5 for CH3 groups), where U(Ci) are respectively the equivalent thermal parameters of the atoms to which the corresponding H atoms are bonded. The H(N) hydrogen atoms were found in
Proton complexes with perchloric acid (hydroperchlorates) were prepared by mixing equimolar amounts of bases 9, 15, or 18 (usually 0.1 mmol) and 60% aqueous HClO₄ in a minimum volume of EtOAc (2 to 5 mL) followed by 5-fold dilution with Et₂O. The residue thus formed was washed with Et₂O, vacuum dried and recrystallized from MeCN to give the desired salts almost quantitatively.

7,16-Dimethyl-7,8,15,16-tetrahydronaphtho[1,8-bc′,8′-gh][1,5]diazecine (9). 1,8-Di(methylamino)naphthalene (0.2 g, 1.1 mmol), 1,8-bis(bromomethyl)naphthalene (0.35 g, 1.1 mmol) and triethylamine (0.3 mL, 2.2 mmol) in a mixture of toluene (3 mL) and acetonitrile (3 mL) was refluxed for two hours. The reaction mixture was poured into ice water (30 mL) and basified with a potassium hydroxide to pH 10–11. The product was extracted with dichloromethane (3 × 15 mL), the organic phase was dried over Na₂SO₄, the residue was purified by column chromatography (Al₂O₃, chloroform) to afford 1 (0.34 g, 92%) as yellowish crystals; mp 204–206 °C (MeCN). 1H NMR (CDCl₃): δ = 2.55 (s, 6 H, NMe), 3.87 (d, 2J 14.5 Hz, 2 H, 8-H, 15-H), 6.24 (d, 2J 14.5 Hz, 2 H, 8-H, 15-H), 6.99 (dd, 3J 7.6, 4J 1.0 Hz, 2 H, 1-H, 6-H), 7.33–7.48 (m, 8 H, 2-H, 3-H, 4-H, 5-H, 9-H, 10-H, 13-H, 14-H), 7.83 (dd, 3J 7.3, 4J 1.6 Hz, 2 H, 11-H, 12-H). 13C NMR (CDCl₃): δ = 39.0 (N–Me), 68.3 (N–CH₂–Ar), 114.3, 122.7, 123.3, 125.3, 126.2, 130.2, 130.4, 132.2, 137.2, 137.9, 138.6, 149.0. MS, m/z (%): 338 [M]+ (52), 323 (14), 292 (11), 197 (47), 186 (86), 169 (37), 153 (100), 127 (14), 115 (11). C₂₄H₂₂N₂ (338.45): calcd. C 85.17, H 6.55, N 8.28; found C 85.32, H 6.12, N 8.07%.

7,16-Dimethyl-7,8,15,16-tetrahydronaphtho[1,8-bc′,8′-gh][1,5]diazecine hydroperchlorate (9-HClO₄): grey to colorless crystals, mp 278–279 °C (MeCN). 1H NMR (DMSO-d₆): δ = 2.95 (d, 3J 2.1 Hz, 6 H, NMe), 4.60 (dd, 2J 14.0, 3J 4.6 Hz, 2 H, 8-H, 15-H), 5.68 (d, 2J 14.0 Hz, 2 H, 8-H, 15-H), 7.70 (t, 3J 8.1 Hz, 2 H, 10-H, 13-H), 7.83–7.91 (m, 4 H, 2-H, 5-H, 9-H, 14-H), 8.15–8.25 (m, 6 H, 1-H, 3-H, 4-H, 6-H, 11-H, 12-H), 19.55 (br s, 1 H, NHN⁺). 1H NMR (CD₃CN): δ = 2.95 (d, 3J 2.7 Hz, 6 H, NMe), 4.49 (dd, 2J 14.1, 3J 4.9 Hz, 2 H, 8-H, 15-H), 5.47 (d, 2J 14.1 Hz, 2 H, 8-H, 15-H), 7.68 (t, 3J 8.2 Hz, 2 H, 10-H, 13-H), 7.79–7.88 (m, 4 H, 2-H, 5-H, 9-H, 14-H), 8.03 (dd, 3J 7.7, 4J 0.9 Hz, 2 H, 1-H, 6-H), 8.15 (dd, 3J 8.4, 4J 0.9 Hz, 2 H, 3-H, 4-H), 8.20 (dd, 3J 8.2, 4J 1.5 Hz, 2 H, 11-H, 12-H). 19.95 (br s, 1 H, NHN⁺). C₂₄H₂₂ClN₂O₄ (438.91): calcd. C 65.68, H 5.28, N 6.38; found C 65.49, H 5.25, N 6.36%.

2-(8-Dimethylaminonaphth-1-yl)-2,3-dihydro-1H-benz[de]isoquinoline (15). 1-Dimethylamino-8-methylaminonaphthalene (0.096 g, 0.47 mmol), 1,8-bis(bromomethyl)naphthalene...
(0.150 g, 0.47 mmol) in a mixture of toluene (3 mL) and acetonitrile (3 mL) was refluxed for 3 h. The product was isolated and purified as described for compound 9. Column chromatography gave 15 as light-brown solid (0.085 g, 53%), mp 86–87 ºC (EtOAc). 1H NMR (CDCl₃): δ = 2.42 (s, 6 H, NMe₂), 4.48 (d, 3J 14.5 Hz, 2 H, 1-H, 3-H), 4.77 (d, 2J 14.5 Hz, 2 H, 1-H, 3-H), 7.05 (dd, 3J 7.4, 4J 1.0 Hz, 1 H, 7'-H), 7.24–7.31 (m, 3 H, 4-H, 9-H, 2'-H), 7.40–7.60 (m, 6 H, 3'-H, 4'-H, 5'-H, 6'-H, 5-H, 8-H), 7.82 (d, 3J 8.1 Hz, 2 H, 6-H, 7-H). 13C NMR (CDCl₃): δ = 45.0 (N-Me), 56.9 (N-CH₂-Ar), 113.9, 114.4, 121.6, 121.9, 122.3, 123.5, 125.5, 125.6, 125.7, 125.9, 128.4, 133.3, 135.0, 138.0, 149.1, 150.8. MS, mz (%): 338 [M⁺] (80), 323 (5), 292 (22), 186 (56), 170 (100), 153 (94), 140 (64), 127 (46), 115 (76), 63 (53). C₂₄H₂₂N₂O₄ (338.45): calcd. C 85.17, H 6.55, N 8.28; found C 85.28, H 6.34, N 8.19%. 2-(8-Dimethylaminonaphth-1-yl)-2,3-dihydro-1H-benz[de]isoquinoline hydroperchlorate (15·HClO₄): colorless crystals, mp 252–253 ºC (MeCN). 1H NMR (DMSO-d₆): δ = 2.74 (d, 3J 3.7 Hz, 6 H, NMe₂), 4.99 (ABq, 2J 14.8 Hz, 4 H, NCH₂Ar), 7.43 (br d, 3J 7.1 Hz, 2 H), 7.61 (dd, 3J 8.1, 4J 1.0 Hz, 2 H), 7.74–7.87 (m, 2 H), 7.99 (br d, 3J 8.1 Hz, 2 H), 8.10–8.24 (m, 4 H), 18.46 (br s, 1 H, NHN⁺). C₂₄H₂₃ClN₂O₄ (438.91): calcd. C 65.68, H 5.28, N 6.38; found C 65.52, H 5.13, N 6.24%. 1,8-Bis(2,3-dihydro-1H-benz[d]isoquinolin-2-yl)naphthalene (18). 1,8-Diaminonaphthalene (0.038 g, 0.24 mmol), 1,8-bis(bromomethyl)naphthalene (0.150 g, 0.48 mmol) and triethylamine (0.14 mL, 0.96 mmol) in a mixture of toluene (3 mL) and acetonitrile (3 mL) was refluxed for 5 h. The product was isolated and purified as described for compound 9. Column chromatography gave 18 (0.104 g, 94%) as grey crystals, mp 192–194 ºC (MeCN). 1H NMR (DMSO-d₆): δ = 4.25 (d, 3J 7.0 Hz, 4 H, 1'-H, 3'-H), 4.54 (d, 3J 14.9 Hz, 4 H, 1'-H, 3'-H), 6.90 (br d, 3J 7.0 Hz, 4 H, 4'-H, 9'-H), 7.03 (t, 3J 8.2 Hz, 4 H, 5'-H, 8'-H), 7.22 (br d, 3J 7.6 Hz, 2 H, 2'-H, 7-H), 7.32–7.42 (m, 6 H, 3-H, 6-H, 6'-H, 7'-H), 7.52 (dd, 3J 8.2, 4J 1.3 Hz, 2 H, 4-H, 5-H). 13C NMR (CDCl₃): δ = 57.3 (CH₂), 115.4, 121.5, 122.3, 124.2, 125.5, 126.1, 126.2, 127.9, 132.8, 134.1, 138.4, 149.6. MS, mz (%): 462 [M⁺] (18), 309 (100), 294 (17), 231 (10), 166 (22), 153 (38), 127 (14), 115 (24). C₃₄H₂₆N₂ (462.60): calcd. C 88.28, H 5.67, N 6.05; found C 88.51, H 5.34, N 6.15%. 1,8-Bis(2,3-dihydro-1H-benz[d]isoquinolin-2-yl)naphthalene hydroperchlorate (18·HClO₄): beige crystals, mp 252–253 ºC (MeCN). 1H NMR (DMSO-d₆): δ = 4.83–5.04 (m, 8 H, 1'-H, 3'-H), 6.86 (br d, 3J 6.8 Hz, 4 H, 4'-H, 9'-H), 7.13 (t, 3J 7.7 Hz, 4 H, 5'-H, 8'-H), 7.46 (br d, 3J 8.1 Hz, 4 H, 6'-H, 7'-H), 7.95 (t, 3J 7.9 Hz, 2 H, 3-H, 6-H), 8.26 (br d, 3J 7.5 Hz, 2 H, 2-H, 7-H), 8.36 (br d, 3J 8.4 Hz, 2 H, 4-H, 5-H), 19.33 (br s, 1 H, NHN⁺). C₃₄H₂₇ClN₂O₄ (563.05): calcd. C 72.53, H 4.83, N 4.98; found C 72.59, H 4.62, N 4.62%. Reaction of 2,2-dimethyl-2,3-dihydropyrimidine with 1,8-bis(bromomethyl)naphthalene. 2,2-Dimethyl-2,3-dihydropyrimidine (11) (0.094 g, 0.48 mmol), 1,8-bis(bromomethyl)naphthalene (0.150 g, 0.48 mmol) and triethylamine (0.06 mL, 0.48 mmol) in a mixture of toluene (3 mL) and acetonitrile (3 mL) was refluxed for 5 h. The reaction mixture was poured into ice-water (30 mL) and basified with potassium hydroxide to pH 10–11, and the products were extracted with dichloromethane (3 × 15 mL). The organic phase was dried over Na₂SO₄, evaporated to dryness
and subjected to column chromatography (silica gel, CH$_2$Cl$_2$) to afford the following products in order of elution:

**7-Isopropyl-7,7a,14,15-tetrahydrobenz[4,5,6]isoquinolino[2,1-a]perimidine (27).** Yield 27%; beige crystals with mp 205–207 °C (CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$): $\delta = 1.39$ (d, $^3J$ 6.5 Hz, 3 H, CH$_3$), 1.51 (d, $^3J$ 6.8 Hz, 3 H, CH$_3$), 4.38–4.53 (m, 1 H, CHMe$_2$), 5.02 (d, $^2J$ 16.9 Hz, 1 H, NCH$_2$Ar), 5.30 (d, $^2J$ 16.9 Hz, 1 H, NCH$_2$Ar), 6.03 (s, 1 H, NCHN), 6.64 (dd, $^3J$ 6.8, $^4J$ 1.7 Hz, 1 H), 6.96–7.06 (m, 3 H), 7.11 (dd, $^3J$ 8.0, $^4J$ 0.8 Hz, 1 H), 7.17–7.23 (m, 1 H), 7.28–7.40 (m, 3 H), 7.46–7.55 (m, 2 H), 7.57–7.63 (m, 1 H). $^{13}$C NMR (CDCl$_3$): $\delta = 21.9$ (CH$_3$), 51.3 (CCH$_3$), 55.4 (NCH$_2$), 69.2 (NCHN), 106.2, 111.6, 117.7, 118.3, 119.2, 123.5, 123.8, 125.8, 126.2, 126.7, 127.0, 127.2, 127.5, 129.6, 131.5, 133.9, 135.0, 135.9, 141.9, 142.3. MS, m/z (I(%)): 350 [M]$^+$ (29), 307 (28), 292 (11), 183 (34), 168 (25), 152 (40), 139 (26), 127 (27), 115 (12), 43 (100). C$_{25}$H$_{22}$N$_2$ (350.47): calcd. C 85.68, H 6.33, N 7.99; found C 85.32, H 6.47, N 8.06%.

**2-(8-Aminonaphth-1-yl)-2,3-dihydro-1H-benz[de]isoquinoline (28).** Yield 6%; beige crystals with mp 90–91 °C (CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$): $\delta = 4.50$ (ABq, $^2J$ 14.9 Hz, 4 H, NCH$_2$), 5.84 (br s, 2 H, NH$_2$), 6.52 (dd, $^3J$ 5.7, $^4J$ 1.6 Hz, 1 H, 7'-H), 7.13–7.23 (m, 2 H, 2'-H, 6'-H), 7.25–7.48 (m, 6 H, 4-H, 9-H, 5'-H, 3'-H, 5-H, 8-H), 7.57 (dd, $^3J$ 6.6, $^4J$ 1.3 Hz, 1 H, 4'-H), 7.77 (br d, $^3J$ 8.2 Hz, 2 H, 6-H, 7-H). $^{13}$C NMR (CDCl$_3$): $\delta = 58.1$ (CH$_2$), 110.6, 116.2, 117.7, 120.4, 122.5, 125.8, 126.2, 126.5, 126.9, 127.2, 127.9, 133.7, 134.0, 137.6, 145.6, 150.3. IR (CCl$_4$, $\nu$/cm$^{-1}$): 3474, 3318 (NH$_2$), 3058, 2959, 2928, 2867, 2857, 2788 (CH), 1586 (Ar). C$_{23}$H$_{18}$N$_2$ (310.40): calcd. C 85.13, H 5.84, N 9.03; found C 85.27, H 5.47, N 9.11%.

**1,8-Bis(2,3-dihydro-1H-benz[de]isoquinolin-2-yl)naphthalene (18).** Yield 18%; the properties are the same as described above for the compound prepared from 1,8-diaminonaphthalene.

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