ortho-Ketimines of 1,8-Bis(dimethylamino)naphthalene: Synthesis, Hydrolytic Stability and Transfer of Basicity from Proton Sponge Moiety to the Imino Function

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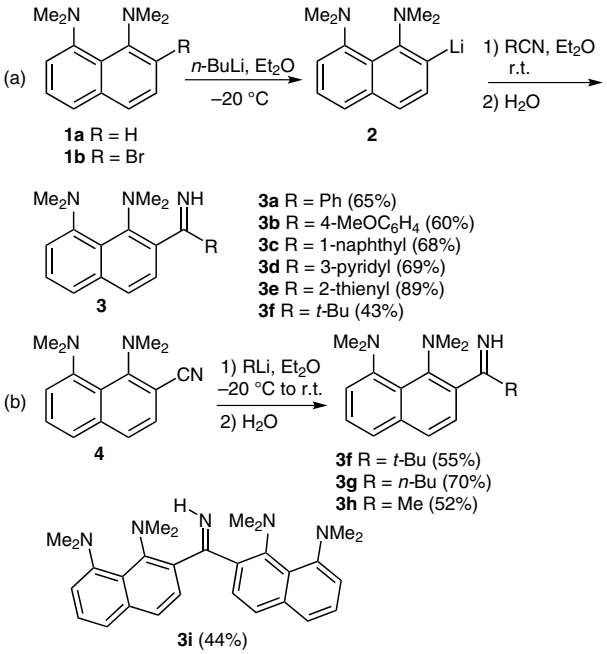
Abstract: A series of 2-ketimines and 2,7-diketimines of 1,8-bis(dimethylamino)naphthalene (proton sponge, DMAN) have been obtained and converted into the corresponding ketones via acidic hydrolysis. Investigation of structural and spectral properties of DMAN-based imines led to the conclusion that their unusual hydrolytic stability results from a combination of different factors the most important of which is a strong electron-donor effect of *peri*-dimethylamino groups.

Key words: amines, imines, hydrolysis, ketones, organometallic reagents

Imines are of common interest in organic synthesis, medicinal chemistry, and biochemistry.[1] However, in many cases handling imines, especially those with an unsubstituted NH group, is difficult due to the ease of their hydrolysis. Recently, we obtained two 2-ketimino derivatives of 1,8-bis(dimethylamino)naphthalene (**1a**, proton sponge, DMAN), namely **3a**,**b**, and turned our attention to their enhanced hydrolytic stability.[2] To shed light on the origin of this phenomenon, in the present work we have prepared a number of new representatives of these compounds with widely varied structure and studied their properties (Scheme 1). In particular, we have focused on their hydrolytic activity, molecular structure, and mutual influence of the formally conjugated *peri*-NMe_2 and imino groups.

Monoketimines **3a**–**f** were synthesized in 60–89% yields by combining aryl and hetaryl cyanides with 1,8-bis(diamino)-1-lithionaphthalene (**2**, 2-Li-DMAN) generated from bromide **1b** [Scheme 1 (a)].[3] The reaction proceeded with more difficult for alkyl cyanides, apparently due to the enhanced acidity of their α-CH bonds causing protolysis of **2** [compare with the reactions of 2-lithium and 2,7-dilithium derivatives of 1,8-bis(dimethylamino)naphthalene with acetyl chloride[3]]. Thus, on treatment of 2-Li-DMAN **2** with acetonitrile or valeronitrile the corresponding imines were not formed at all and only unsubstituted DMAN **1a** was isolated from the reaction mixture. Use of *tert*-butyl cyanide, containing no α-CH bonds, was more successful and the yield of imine **3f** reached 43%.



Scheme 1

To overcome this difficulty, we were forced to employ the reversed approach to synthesize alkyl(naphthyl)ketimines **3f**–**h** by the interaction of *ortho*-cyanide **4** with alkyllithium reagents [Scheme 1 (b); notably the use of alkylmagnesium halides for this purpose failed]. To our satisfaction, imines with butyl and methyl groups **3g**,**h** were obtained in good yields. Even for imine **3f** containing the *tert*-butyl group the protocol increased the yield by 12% to 55%. Actually, both approaches were merged when 2-Li-DMAN **2** was allowed to react with nitrile **4** to produce symmetrical binaphthylketimine **3i** (44%).

Taking into account the higher nucleophilicity of 1,8-bis(dimethylamino)-2,7-dilithionaphthalene (**6**, 2,7-Li_2-DMAN) in comparison with 2-Li-DMAN **2** and to confirm that two NMe_2 groups can stabilize two *ortho*-imino functionalities towards hydrolysis, it was also important to synthesize 2,7-diketimines of **1a**. Interaction of 2,7-Li_2-DMAN **6** with benzonitrile or 4-methoxybenzonitrile gave diimines **7a**,**b** in 14% and 11% yields, respectively, along with ~30% yield of the corresponding monoketimines **3a**,**b** (Scheme 2).

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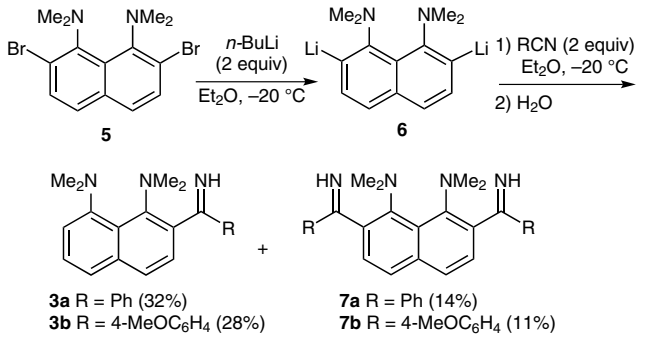
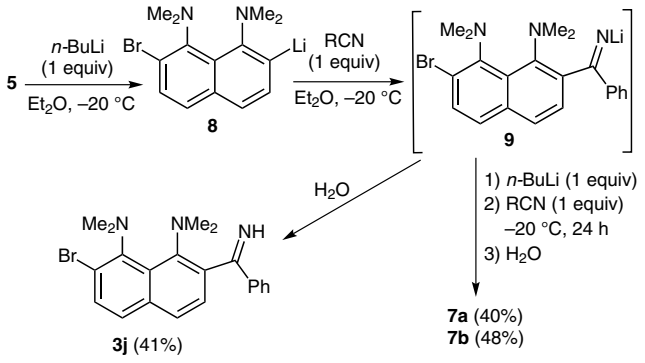


Scheme 2

These results leave no doubt that under these conditions 2,7-Li_2-DMAN **6** undergoes considerable (mono)protolysis into 2-Li-DMAN **2**, which then is converted into monoimine.

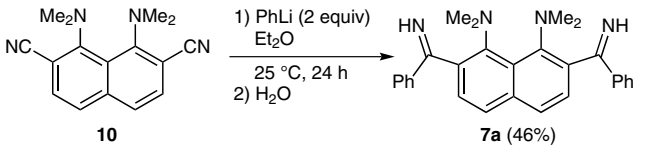
To improve the yield of compounds **7**, we tested a stepwise introduction of the imino groups. For this, dibromide **5** on treatment with one equivalent of butyllithium was transformed into less basic 2-bromo-7-lithio-1,8-bis(dimethylamino)naphthalene (**8**),[3] to which aryl cyanide, butyllithium, and again aryl cyanide were sequentially added in a one-pot mode (Scheme 3). In accord with our assumption, this protocol provided a nearly fourfold increase in the yields of diimines **7a**,**b**, although due to the low solubility of the intermediate salt **9** the introduction of the second imino group occurred under heterogeneous conditions and was accompanied by the formation of some unidentified side products. Quenching the process by water addition just after the stage **8** → **9** allowed us to isolate imine **3j** with the bromine atom in position 2 (Scheme 3) thus opening up the possibility for further functionalization of the imine structure.



Scheme 3

To check the applicability of the reversed approach (vide supra) for the synthesis of diimines we reacted 2,7-dicyano-1,8-bis(dimethylamino)naphthalene (**10**) with two equivalents of phenyllithium; the reaction gave diimine **7a** in 46% yield (Scheme 4).

The most interesting aspect in the ^{1}H NMR spectra of the obtained imines is the appearance of the NH group. In



Scheme 4

$CDCl_3$, the NH proton resonates at δ = 8.7–9.5 as a broad peak (up to 1 ppm wide) visible only at high concentrations (~0.3 M). In DMSO-d_6 this signal is considerably narrowed and shifts to a lower field (δ = 9.5–10.8, see the Supporting Information, Section SI-1). The carbon signal of the C=N group in the ^{13}C NMR spectra resonating within δ = 179–193 is also very characteristic. The IR spectra of all imines in CCl_4 solution contain a rather sharp peak ν_{NH} at 3250–3265 cm^{-1} (Table 1, see also the Supporting Information, section SI-2). These data make the engagement of the C=NH groups in hydrogen bond formation unlikely.

All proton sponge *ortho*-imines are crystalline (except **3g**,**h**) yellow-, orange-, or red-colored compounds. Their electronic spectra, as in the case of DMAN **1a**,[4] contain the long-wavelength absorption band at 350 nm (Table 1). However, unlike DMAN **1a**, this band does not tail off at 400 nm (except for **3f**) but extends into the visible region up to 440–450 nm (Supporting Information, section SI-3). This end absorption differs by low intensity and is likely caused by $n \rightarrow \pi^*$ electron transition within the imino group.

X-ray crystal structure experiments were performed for three of the obtained imines, **3b**, **3f**, and **3i**; their results are shown in Figure 1 and Table 2. All imines display considerable molecular distortions. Thus, the rotation angle of the 1-NMe_2 group relatively the average ring plane in molecules **3b**, **3f**, and **3i** varies in the limits of 53–56° while the dihedral angle C1–C2–CN changes from 37° in **3i** to 126° in **3b**. The angle between the two naphthalene planes in 2,2′-binaphthylimine **3i** is equal to 81.6° which is close to that in the proton sponge-based 2,2′-binaphthylmethanols.[5] Although such distortions should affect the interaction between the *peri*-NMe_2 and the imino groups, their conjugation is still clearly distinguishable. For example, the C=N bonds in molecules **3b** and **3i** are lengthened by 0.15–0.20 Å in comparison with imines of the benzene series.[6] Owing to the bulkiness of the *tert*-butyl group, the structure of imine **3f** reveals some specifics. First, the 1-NMe_2 group is *out*-inverted, likely because its methyls are pushed by the *tert*-butyl group into the *peri* internitrogen space; the free amine nitrogen electron pairs in **3b** and **3i** remain *in*-inverted but the 1-NMe_2 groups undergo considerable planarization with ΣN = 358.6 (359.2) and 354.5°, respectively. The nitrogen inversion in **3f** is accompanied, as in other similar cases,[3,5] by substantial increase of the N1···N8 distance: 2.90 Å in **3f** against 2.80 and 2.76 Å in **3b** and **3i**. The dihedral angle C1–C2–CN, as well as the naphthalene ring twisting (the angle between the C2–C3 and C6–C7 bonds)[7] in **3f** are also larger

than those in **3b** and **3i**. Lastly, the C=N bond in imine **3f** is shortened which makes its involvement in conjugation with the ring π-system and the NMe_2 groups unlikely.

All imines exist in the *syn* form relatively to the C=N double bond (apart from **3i**, for which the *syn* and *anti* forms are indistinguishable) with the N–H bond turned away from the 1-NMe_2 group that excludes the formation of the intramolecular hydrogen bond between them.

As the proton sponge ketimines contain two different basic centers (chelating NMe_2 groups and the imine nitrogen), the relative ease and sequence of their protonation are of importance. It would seem that the first protonation should proceed at *peri*-NMe_2 groups with the formation of the chelated cation of type **11**. Indeed, the basicity of the benzophenone imine ($pK_a = 6.82$) and even that of cyclohexanone imine ($pK_a = 9.15$)[8] is much lower than that of DMAN **1a** ($pK_a = 12.1$).[4] However, since in the proton sponge ketimines the NMe_2 and the C=NH groups are formally conjugated, some part of the electron density may be transferred towards the electron-accepting imino group, thus making the site of first protonation less unambiguous [a typical example of such a phenomenon is found for 1,3,5-tris(dialkylamino)benzenes which are protonated at ring carbon atoms[9]]. The latter assumption was partially confirmed by studying the most hydrolytically stable imine **3b**. We prepared the monoperchlorate of **3b** and recorded its ^{1}H NMR spectra in DMSO-d_6. It was found that under these conditions the salt exists as a mixture of two forms **11** and **12** with the proton localized either between the NMe_2 groups or at the imine nitrogen (Scheme 5), the second form being predominant in a ca. 2:1 ratio; this proportion can be best estimated from the relative intensity of two signals of the OMe groups at δ = 3.8–3.9. Both forms are also easily identified with regard to the position of the NH proton: in **11** the chelated proton resonates at δ = 18.6, a usual region for all proton sponge cations,[4] while the signal of the protonated imino group C=NH_2^+ in **12** appears at δ = 11.9 (Supporting Information, section SI-4a).

Table 1 Selected Spectral Characteristics of Proton Sponge Imines

Imine	IR (CCl_4) ν (NH) (cm^{-1})	^{1}H NMR δ (N*H*)		^{13}C NMR ($CDCl_3$) δ (*C*=N)	UV (MeCN) λ_{max} (nm) (log ε)
		$CDCl_3$	DMSO-d_6		
3a	3263	9.48	10.23	180.72	250 (4.47) 343 (3.79)
3b	3266	8.88	9.96	179.81	255 (4.43) 342 (3.76)
3c	3252	–[a]	10.78	180.35	282 (4.16)[b] 346 (3.79)[b]
3d	3262	9.68	10.61	178.86	248 (3.76) 342 (4.35)
3e	3273	–[a]	9.90	173.93	252 (4.50)[b] 288 (4.19)[b] 332 (3.86)[b]
3f	3253	9.35	10.04	192.77	242 (4.73)[b] 344 (4.10)
3g	3251	9.10	9.86	186.16	294 (4.34) 343 (3.81)
3h	3250	–[a]	9.69	182.4	248 (4.52)[b] 344 (3.94)
3i	3251	9.52	9.0–10.5[c]	179.31	260 (4.76) 348 (4.14)
3j	3265	9.30	10.30	180.06	254 (4.49) 337 (3.75)
7a	3264	8.69	10.39	180.39	258 (4.82) 358 (4.08)
7b	3266	–	9.86	177.49[d]	263 (4.46) 356 (3.68)

[a] The signal is extremely broad and difficult to determine.
[b] Center of shoulder.
[c] In CD_3CN.
[d] In DMSO-d_6.

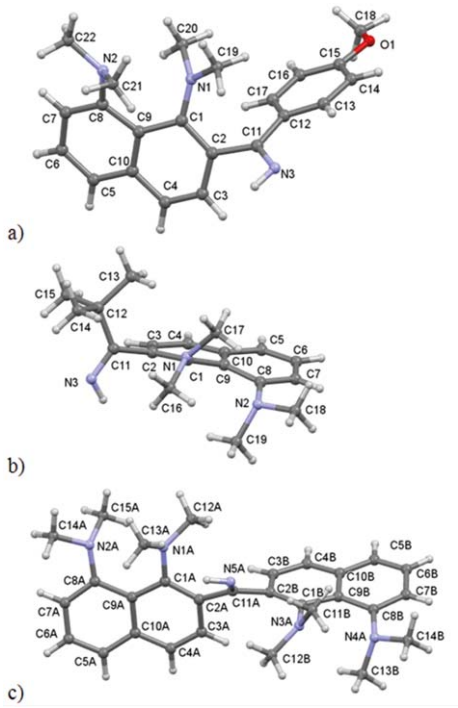
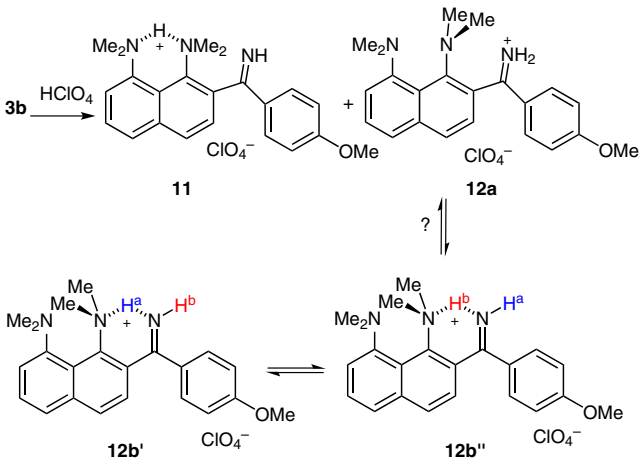


Figure 1 Molecular structures of imines **3b** (a), **3f** (b), **3i** (c)



Scheme 5

Interestingly, the intensity of the C=NH_2^+ peak for **12a** is enlarged by 25%, which almost exactly corresponds to content of form **11**. Obviously, the enlargement results from merging of signals of the C=NH and C=NH_2^+ groups in **11** and **12a** owing to their fast exchange on the NMR timescale. This is a vivid illustration of the difference in behavior of kinetically active and kinetically inert basic centers within the same molecule. One cannot exclude that cation **12** exists in two isoenergetic chelated forms **12b′** and **12b″** with slowly exchangeable NH protons and the *out*-inverted 1-NMe_2 group. Indirectly, strong broadening of the C=NH_2^+ group signals (over 1 ppm) favors this hypothesis; possibly this may reflect dynamics of the rechelation process (cf. ref.[10]). Regrettably, we have so far failed to study temperature-dependent NMR spectra of perchlorate **3b**·$HClO_4$ because of its very bad solubility in common low-freezing solvents.

Next we attempted to estimate the basicity of imine **3b** using NMR competitive proton exchange.[11] For this, the precise amount of DMAN **1a** (1 equiv) was added to a solution of **3b**·$HClO_4$ in DMSO-d_6. The ^{1}H NMR spectrum of the resulting mixture (Supporting Information, section SI-4b) showed that form **11** was completely deprotonated by DMAN **1a**. This conclusion follows from replacing peak at δ = 18.6 by that at δ = 18.3 which is characteristic for the protonated DMAN **1a**.[4] At the same time only about 40% of DMAN **1a** underwent protonation in this experiment. Both observations suggest that: (1) the basicity of the proton sponge moiety in **3b** is at least two orders of ten lower than that of the parent proton sponge and (2) basicities of **3b** as imine and as DMAN are quite comparable. Unfortunately, we failed to make more exact estimation of the pK_a values for **3b** due to a strong broadening of some peaks in the ^{1}H NMR spectra of this mixture. It is only possible to conclude that under these conditions DMAN **1a** deprotonates form **11** completely and forms **12a** partially, entering with the latter in a slow proton exchange.

Finally, we performed an acidic hydrolysis of the ketimines in 10% hydrochloric acid under reflux. As a result, a series of ketones **13** and **14** were obtained generally in good to moderate yield (Table 3). The time to complete the reaction and the yield of ketones allows the imines to be arranged in the order of their hydrolytic stability. As seen, the most stable are imines **3b**, **3e**, and **7b**. Imine **3f** containing the bulky and hydrophobic *tert*-butyl group was also hydrolyzed slowly. In contrast, imines with *n*-alkyl, phenyl, and pyridyl substituents at the C=NH group

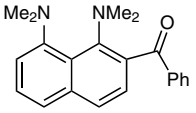
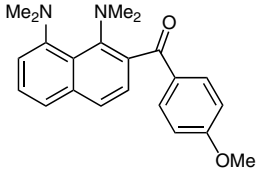
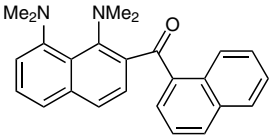
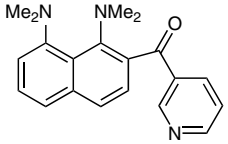
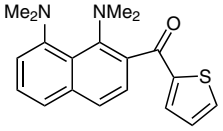
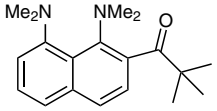
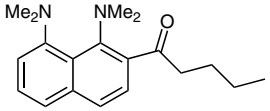
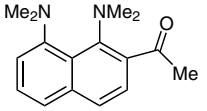
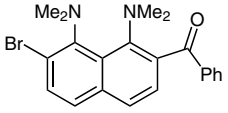
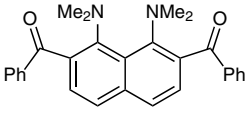
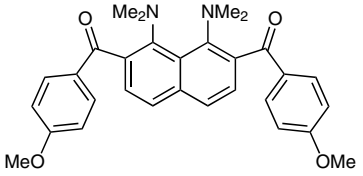
Table 2 Selected Geometrical Parameters of Some Imines (X-ray Diffraction Data)

Compound	Bond lengths and distances (Å)		ΣN for 1-NMe_2 (°)	Dihedral angles (°)			*T* (K)
	C=N	*peri*-N···N		1-NMe_2 and C1···C10	C1–C2 and C=N	C2–C3 and C6–C7	
3b	1.285 (1.293)[a]	2.817 (2.797)[a]	359.2 (358.6)[a]	50.6 (52.9)[a]	126.2 (117.0)[a]	14.4 (11.9)[a]	120
3f	1.270	2.903	355.2	55.9	90.4	15.4	100
3i	1.288	2.758 (2.754)[b]	354.5 (354.9)[b]	56.2 (57.2)[b]	36.9 (40.2)[b]	11.3 (12.1)[b]	120

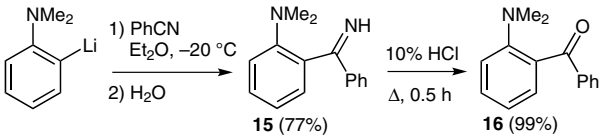
[a] For the second independent molecule.
[b] For the second proton sponge fragment.

are relatively active. The hydrolytic behavior of symmetrical imine **3i** with two DMAN moieties is very specific and will be discussed in a separate communication.

Table 3 Results of Acidic Hydrolysis of Ketimines **3** and **7** (Reflux in 10% HCl)

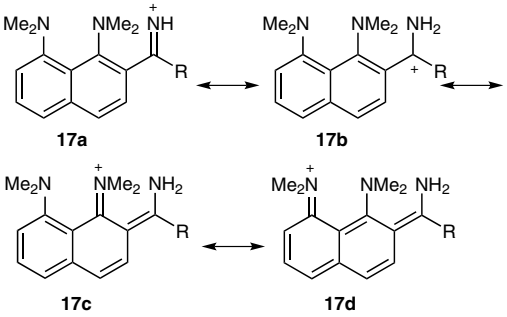
Imine	Time (h)	Product	Yield (%)
3a	2	**13a** 	99
3b	32	**13b** 	78
3c	3	**13c** 	72
3d	1	**13d** 	65
3e	12	**13e** 	56
3f	8	**13f** 	10
3g	1	**13g** 	78
3h	1	**13h** 	77
3j	1	**13j** 	85
7a	1	**14a** 	80
7b	26	**14b** 	55

It seemed reasonable to compare the hydrolytic stability of imines **3** with their benzene analogues. With this aim, 2-(dimethylamino)benzophenone imine (**15**)[12] was prepared as shown in Scheme 6 and then hydrolyzed to ketone **16**. As expected, **15** also revealed noticeable stability on heating in acids but nonetheless it was four times lower in comparison with **3a**.



Scheme 6

From the above it can be concluded that the considerable hydrolytic inertness of the proton sponge ketimines can be caused by a combination of electronic and steric factors. In our opinion, the most important of them is a pronounced electron-donor effect of the *peri*-NMe_2 groups lowering the electrophilicity of the carbon atom in the protonated imino group (see resonance structures **17a–d** in Scheme 7).



Scheme 7

Solution ^1H and ^{13}C NMR experiments were performed with a Bruker DPX-250 spectrometer (250 MHz for ^1H, 63 MHz for ^{13}C) using the solvent residual peaks as the internal reference. FT-IR spectra were measured on a FSM-1202 spectrophotometer. UV/vis spectra were measured on a Varian Cary 50 Probe spectrophotometer. MS were obtained from Finnigan MAT INCOS 50 instrument (EI, 70 eV) and on a Bruker micrOTOF II instrument (ESI). All reagents and starting materials were obtained from commercial sources and used without further purification.

X-ray diffraction analysis. Crystals suitable for X-ray studies were grown up by slow evaporation from solutions of compounds in appropriate solvents or solvent mixtures: Et_2O–hexane–acetone for **3b**, $CHCl_3$ for **3f**, MeCN–EtOH for **3i**. X-ray measurements were conducted with Bruker SMART 1000 (for **3i**, MoKα line, graphite monochromator, ω/2θ-scanning) and Bruker APEX II diffractometers (for **3b** and **3f**, Mo-Kα line, graphite monochromator, ω-scanning). The structures were solved by direct method and refined by the full-matrix least-squares against F^2 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 $U_{iso}(H)$ parameters equal to $n \cdot U_{eq}(C_i)$ ($n = 1.2$ 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 H(N) hydrogen atoms were found in difference Fourier synthesis and refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.2 U_{eq}(N_i), where U(N_i) are the equivalent thermal parameters of the N atom to which corresponding H atom is bonded. The main crystallographic data and some experimental details are given in the Supporting Information (section SI-5). CCDC 1009757–1009759 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.

Imines 3c–f,i Starting from 1,8-Bis(dimethylamino)-2-lithionaphthalene (2); General Procedure 1 (GP1)

To a solution of 1,8-bis(dimethylamino)-2-lithionaphthalene (**2**) obtained by standard techniques[3] from 2-bromo-1,8-bis(dimethylamino)naphthalene (**1b**, 1000 mg, 3.4 mmol), a solution of the corresponding nitrile in anhyd Et_2O (10 mL) was added via syringe under an argon atmosphere at –20 °C. The red-colored mixture was kept at r.t. for 24–96 h and then treated with distilled H_2O (10 mL). The yellow ether solution was separated and the aqueous phase was extracted with $CHCl_3$ (3 × 10 mL). The organic fractions were combined, evaporated, and chromatographed (alumina). The synthesis of imines **3a** and **3b** was published earlier.[2]

Imines 3f–h Starting from 2-Cyano-1,8-bis(dimethylamino)naphthalene (4); General Procedure 2 (GP2)

To a solution of 2-cyanonaphthalene **4** (1000 mg, 4.2 mmol) in abs Et_2O (20 mL), a solution of the corresponding alkyllithium was added via syringe under an argon atmosphere at –20 °C. The red-colored mixture was kept at r.t. for 24 h and treated with H_2O (10 mL). The yellow ether solution was separated and the aqueous phase was extracted with $CHCl_3$ (30 mL). The organic fractions were combined, evaporated, and chromatographed (alumina).

Imines 7a,b Starting from 2,7-Dibromo-1,8-bis(dimethylamino)naphthalene (5); General Procedure 3 (GP3)

To a solution of dibromonaphthalene **5** (1000 mg, 2.6 mmol) in anhyd Et_2O (50 mL), 1.6 M BuLi in hexanes (1.6 mL, 2.6 mmol) was added via syringe under an argon atmosphere at –20 °C. After stirring for 10 min, a solution of the corresponding nitrile (2.6 mmol) in anhyd Et_2O (10 mL) was added via syringe. The red-colored mixture was kept at –20 °C for 24 h. Then 1.6 M BuLi in hexanes (1.6 mL, 2.6 mmol) was added via syringe. Again, after stirring for 10 min, a solution of the corresponding nitrile (2.6 mmol) in anhyd Et_2O (10 mL) was added via syringe. The resulted suspension was kept at –20 °C for 24 h and treated with H_2O (10 mL). The yellow ether solution was separated and the aqueous phase was extracted with $CHCl_3$ (3 × 10 mL). The organic fractions were combined, evaporated, and chromatographed (alumina).

Ketones 13 and 14 by Hydrolysis of Imines 3 and 7; General Procedure 4 (GP4)

The imine (100 mg) was dissolved in 10% aq HCl (10 mL). The resulting solution (mostly dark red in color) was refluxed for 1–32 h and neutralized by 10% aq NH_3. The product was extracted with $CHCl_3$ and chromatographed on alumina.

2-[Imino(naphthalen-1-yl)methyl]-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (3c)

Prepared according to GP1 from 1-cyanonaphthalene (536 mg, 3.5 mmol). Reaction time: 24 h. Yellow crystals; yield: 850 mg (68%); mp 58–60 °C (*n*-hexane); R_f = 0.5 (alumina, Et_2O–*n*-hexane, 2:1). In DMSO solution **3c** exists as a mixture of *syn*- and *anti*-forms (see ^{1}H NMR in DMSO-d_6).

IR (CCl_4): 3252 (NH), 3084, 3054, 2976, 2934, 2903, 2860, 2828, 2783 cm^{-1} (CH).

^{1}H NMR ($CDCl_3$): δ = 2.70 (s, 6 H), 2.82 (s, 6 H), 7.12 (d, *J* = 7.3 Hz, 1 H), 7.64–7.34 (m, 8 H), 8.00–7.85 (m, 2 H), 8.84 (s, 1 H), 9.63 (s, 1 H).

^{1}H NMR (DMSO-d_6): δ = 2.47 (s, 6 H), 2.66 (s, 6 H), 7.04 (d, *J* = 7.5 Hz, 1 H), 7.14 (d, *J* = 5.3 Hz, 1 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 7.67–7.31 (m, 6 H), 8.03–7.89 (m, 2.2 H), 9.05 (s, 0.8 H), 10.64 (s, 0.2 H), 10.78 (s, 0.8 H).

^{13}C NMR ($CDCl_3$): δ = 44.2, 45.3, 114.5, 122.5, 123.3, 123.8, 124.4, 125.9, 126.2, 126.6, 126.9, 128.0, 128.3, 128.6, 130.4, 131.1, 134.3, 134.6, 137.8, 138.8, 147.6, 152.5, 180.4.

MS (EI): *m*/*z* (%) = 43 (22), 57 (21), 126 (24), 127 (75), 128 (27), 141 (26), 153 (51), 154 (50), 155 (27), 167 (35), 168 (59), 240 (42), 322 (34), 323 (75), 336 (57), 351 (55), 352 (73), 367 [M]$^+$ (100), 368 (28).

UV/vis (MeCN): λ_{max} (log ε) = 282 (4.16), 282 (4.16) sh, 346 nm (3.79) sh.

Anal. Calcd for $C_{25}H_{25}N_3$: C, 81.71; H, 6.86; N, 11.43. Found: C, 81.84; H, 6.75; N, 11.41.

2-[Imino(pyridin-3-yl)methyl]-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (3d)

Prepared according to GP1 from 3-cyanopyridine (396 mg, 3.8 mmol). Reaction time: 24 h. Orange crystals; yield: 740 mg (69%); mp 153–155 °C (*n*-octane); R_f = 0.2 (alumina, Et_2O–*n*-hexane, 1:1).

IR (CCl_4): 3263 (NH), 3084, 3055, 2958, 2931, 2861, 2829, 2784 cm^{-1} (CH).

^{1}H NMR ($CDCl_3$): δ = 2.60 (s, 6 H), 2.71 (s, 6 H), 7.01 (dd, *J* = 7.0, 1.1 Hz, 1 H), 7.17 (d, *J* = 8.3 Hz, 1 H), 7.42–7.21 (m, 3 H), 7.44 (d, *J* = 8.3 Hz, 1 H), 7.88 (d, *J* = 7.3 Hz, 1 H), 8.60 (dd, *J* = 4.7, 1.4 Hz, 1 H), 8.76 (d, *J* = 1.0 Hz, 1 H), 9.68 (s, 1 H).

^{1}H NMR (DMSO-d_6): δ = 2.51 (s, 6 H), 2.68 (s, 6 H), 7.04 (d, *J* = 7.4 Hz, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.48–7.30 (m, 3 H), 7.53 (d, *J* = 8.3 Hz, 1 H), 7.76 (d, *J* = 6.3 Hz, 1 H), 8.70–8.47 (m, 2 H), 10.61 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 44.7, 45.4, 77.0, 77.5, 78.0, 114.8, 122.6, 123.3, 123.4, 123.7, 127.1, 127.2, 132.0, 135.5, 135.6, 139.1, 147.7, 150.0, 151.7, 152.6, 178.9.

MS (EI): *m*/*z* (%) = 29 (26), 30 (36), 32 (86), 42 (68), 43 (27), 44 (100), 51 (36), 78 (42), 105 (35), 115 (20), 127 (35), 128 (22), 154 (23), 167 (20), 168 (42), 274 (35), 287 (45), 302 (39), 303 (27), 318 [M]$^+$ (56).

UV/vis (MeCN): λ_{max} (log ε) = 342 (3.76), 248 nm (4.35).

Anal. Calcd for $C_{20}H_{22}N_4$: C, 75.44; H, 6.96; N, 17.60. Found: C, 75.53; H, 6.88; N, 17.59.

2-[Imino(thiophen-2-yl)methyl]-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (3e)

Prepared according to GP1 from thiophene-2-carbonitrile (0.33 mL, 3.5 mmol). Reaction time: 24 h. Orange crystals; yield: 975 mg (89%); mp 117–119 °C (*n*-hexane); R_f = 0.7 (alumina, Et_2O–*n*-hexane, 2:1).

IR (CCl_4): 3273 (NH), 3078, 3056, 2976, 2935, 2904, 2868, 2860, 2829, 2782 cm^{-1} (CH).

^{1}H NMR ($CDCl_3$): δ = 2.79 (s, 6 H), 2.80 (s, 6 H), 7.07–6.98 (m, 3 H), 7.20 (d, *J* = 8.3 Hz, 1 H), 7.50–7.30 (m, 4 H).

^{1}H NMR (DMSO-d_6): δ = 2.69 (s, 6 H), 2.72 (s, 6 H), 6.80 (d, *J* = 2.6 Hz, 1 H), 7.06–6.99 (m, 2 H), 7.09 (d, *J* = 8.3 Hz, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.41 (dd, *J* = 7.9, 1.0 Hz, 1 H), 7.46 (d, *J* = 8.3 Hz, 1 H), 7.69 (d, *J* = 4.9 Hz, 1 H), 9.90 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 44.6, 44.8, 114.1, 122.6, 122.0, 122.9, 126.4, 126.5, 127.4, 129.9, 131.4, 131.7, 138.5, 145.7, 147.2, 152.1, 173.9.

MS (EI): *m*/*z* (%) = 42 (16), 44 (11), 97 (13), 110 (20), 127 (19), 139 (16), 154 (19), 167 (13), 168 (28), 195 (10), 263 (12), 279 (31), 292 (65), 293 (11), 307 (69), 308 (37), 323 [M]$^+$ (100), 324 (19).

UV/vis (MeCN): λ_{max} (log ε) = 224 (5.13), 252 (4.50), 288 (4.19) sh, 332 nm (3.86).

Anal. Calcd for $C_{19}H_{21}N_3S$: C, 70.55; H, 6.54; N, 12.99. Found: C, 70.66; H, 6.61; N, 12.91.

2-(1-Imino-2,2-dimethylpropyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (3f)

Prepared according to GP1 from pivalonitrile (0.4 mL, 3.5 mmol). Reaction time: 24 h. Beige crystals; yield: 435 mg (43%); mp 129–131 °C (*n*-heptane); R_f = 0.3 (alumina, Et_2O–*n*-hexane, 1:1).

Alternatively prepared according to GP2 from 1.7 M *t*-BuLi in pentane (3.9 mL, 7.9 mmol). Reaction time: 24 h. Yield: 690 mg (55%).

IR (CCl_4): 3253 (NH), 3082, 3056, 2965, 2932, 2903, 2869, 2827, 2783 cm^{-1} (CH).

^{1}H NMR ($CDCl_3$): δ = 1.26 (s, 9 H), 2.72 (s, 6 H), 2.87 (s, 6 H), 7.03 (d, *J* = 8.3 Hz, 2 H), 7.40–7.23 (m, 3 H), 9.35 (s, 1 H).

^{1}H NMR (DMSO-d_6): δ = 1.19 (s, 9 H), 2.72 (s, 6 H), 2.85 (s, 6 H), 7.02 (d, *J* = 8.3 Hz, 1 H), 7.10 (d, *J* = 7.4 Hz, 1 H), 7.33 (t, *J* = 7.7 Hz, 1 H), 7.45 (dd, *J* = 8.1, 2.9 Hz, 2 H), 10.04 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 30.4, 40.5, 45.3, 45.8, 114.6, 122.9, 124.5, 125.7, 126.1, 136.4, 137.9, 145.6, 152.5, 192.8.

MS (EI): *m*/*z* (%) = 32 (33), 196 (11), 225 (36), 240 (100), 241 (16), 297 [M]$^+$ (13).

UV/vis (MeCN): λ_{max} (log ε) = 242 (4.73) sh, 344 nm (4.10).

Anal. Calcd for $C_{19}H_{27}N_3$: C, 76.72; H, 9.15; N, 14.10. Found: C, 76.81; H, 9.22; N, 13.97.

2-(1-Iminopentyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (3g)

Prepared according to GP2 from 1.6 M BuLi in hexanes (2.7 mL, 6.7 mmol). Orange oil; yield: 880 mg (70%); R_f = 0.5 (alumina, Et_2O–*n*-hexane, 1:1).

IR (CCl_4): 3601 cm^{-1} (NH).

IR (thin film): 3051, 2956, 2930, 2869, 2860, 2828, 2779 (CH), 1685 (C=N), 1621, 1603, 1557, 1504 cm^{-1} (CH).

^{1}H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 7.2 Hz, 3 H), 1.45–1.27 (m, 2 H), 1.64–1.46 (m, 2 H), 2.62–2.51 (m, 2 H), 2.73 (s, 6 H), 2.90 (s, 6 H), 6.98 (dd, *J* = 7.1, 1.6 Hz, 1 H), 7.09 (d, *J* = 8.3 Hz, 1 H), 7.42–7.25 (m, 3 H), 9.10 (s, 1 H).

^{1}H NMR (DMSO-d_6): δ = 0.87 (t, *J* = 7.2 Hz, 3 H), 1.57–1.24 (m, 4 H), 2.59–2.45 (m, 2 H), 2.73 (s, 6 H), 7.04 (dd, *J* = 7.3, 1.3 Hz, 1 H), 7.11 (d, *J* = 8.3 Hz, 1 H), 7.50–7.28 (m, 3 H), 9.66 (br s, 1 H), 2.87 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 14.4, 23.1, 29.0, 40.6, 44.8, 45.5, 114.5, 122.6, 123.5, 123.6, 126.4, 126.5, 135.0, 138.5, 146.2, 152.4, 186.2.

MS (EI): *m*/*z* (%) = 29 (21), 41 (20), 225 (28), 240 (100), 241 (20), 297 [M]$^+$ (24).

UV/vis (MeCN): λ_{max} (log ε) = 343 (3.81), 249 nm (4.34).

Anal. Calcd for $C_{19}H_{27}N_3$: C, 76.75; H, 9.15; N, 14.13. Found: C, 76.84; H, 9.01; N, 14.15.

2-(1-Iminoethyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (3h)

Prepared according to GP2 from 1.6 M MeLi in Et_2O (2.6 mL, 4.2 mmol). Orange oil; yield: 557 mg (52%); R_f = 0.8 (alumina, Et_2O–*n*-hexane, 1:2).

IR (CCl_4): 3250 (NH), 3056, 2976, 2860, 2828, 2784 cm^{-1} (CH).

^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 3 H), 2.77 (s, 6 H), 2.93 (s, 6 H), 7.02 (dd, *J* = 7.0, 1.7 Hz, 1 H), 7.15 (d, *J* = 8.3 Hz, 1 H), 7.39–7.27 (m, 2 H), 7.41 (d, *J* = 8.3 Hz, 1 H).

^{1}H NMR (DMSO-d_6): δ = 2.23 (s, 3 H), 2.71 (s, 6 H), 2.84 (s, 6 H), 7.01 (d, *J* = 7.2 Hz, 1 H), 7.13 (d, *J* = 8.3 Hz, 1 H), 7.29 (t, *J* = 7.6 Hz, 1 H), 7.37 (d, *J* = 7.7 Hz, 1 H), 7.43 (d, *J* = 8.3 Hz, 1 H), 9.69 (br s, 1 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 44.3, 45.1, 114.2, 122.2, 123.2, 123.3, 125.2, 126.2, 134.8, 138.2, 145.9, 152.1, 182.0.

UV/vis (MeCN): λ_{max} (log ε) = 224 (5.07), 248 (4.52) sh, 344 nm (3.94).

Anal. Calcd for $C_{16}H_{21}N_3$: C, 75.26; H, 8.29; N, 16.46. Found: C, 75.30; H, 8.26; N, 16.45.

2,2′-(Iminomethylene)bis(*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine) (3i)

Prepared according to GP1 from 2-cyanonaphthalene **4** (894 mg, 3.7 mmol). Reaction time: 96 h. Orange crystals; yield: 723 mg (44%); mp 125–128 °C (*n*-hexane); R_f = 0.7 (alumina, Et_2O–*n*-hexane, 2:1).

IR (CCl_4): 3251 (NH), 3054, 2974, 2934, 2903, 2861, 2828, 2781 cm^{-1} (CH).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.80 (s, 12 H), 2.84 (s, 12 H), 7.03 (dd, *J* = 6.8, 1.3 Hz, 2 H), 7.42–7.25 (m, 8 H).

^{1}H NMR (250 MHz, $CDCl_3$, 212 K): δ = 3.20–2.42 (m, 24 H), 7.12–6.83 (m, 2 H), 7.48–7.07 (m, 8 H), 9.52 (s, 1 H).

^{1}H NMR (250 MHz, CD_3CN): δ = 2.17 (s, 12 H), 2.81 (s, 12 H), 7.13 (dd, *J* = 6.7, 1.6 Hz, 2 H), 7.50–7.26 (m, 8 H), 9.0–10.5 (br s, 1 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 44.7, 45.8, 77.0, 77.5, 78.0, 114.8, 122.7, 123.0, 124.7, 126.8, 128.2, 132.4, 139.2, 148.8, 153.0, 179.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{35}N_5$: 454.6282; found: 454.2937.

UV/vis (MeCN): λ_{max} (log ε) = 348 (4.14), 260 (4.76), 259 (4.77), 256 (4.75), 219 (4.71), 213 nm (4.73).

Anal. Calcd for $C_{29}H_{35}N_5$: C, 76.78; H, 7.78; N, 15.44. Found: C, 76.86; H, 7.69; N, 15.45.

2-Bromo-7-[imino(phenyl)methyl]-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (3j)

To a solution of dibromonaphthalene **5** (1000 mg, 2.6 mmol) in anhyd Et_2O (50 mL), 1.6 M BuLi in hexanes (1.6 mL, 2.6 mmol) was added via syringe under an argon atmosphere at –20 °C. After stirring for 10 min, anhyd PhCN (0.3 mL, 2.6 mmol) was added via syringe under an argon atmosphere. The red-colored mixture was kept at –20 °C for 24 h and treated with H_2O (10 mL). The yellow ether solution was separated and the aqueous phase was extracted with $CHCl_3$ (3 × 10 mL). The organic fractions were combined, evaporated and chromatographed (alumina). Yellow crystals; yield: 421 mg (41%); mp 132–134 °C (*n*-octane); R_f = 0.4 (alumina, Et_2O–*n*-hexane, 2:1).

IR (CCl_4): 3265 (NH), 3060, 3030, 2982, 2900, 2863, 2841, 2810, 2788 cm^{-1} (CH).

^{1}H NMR ($CDCl_3$): δ = 2.63 (s, 6 H), 2.97 (s, 6 H), 7.15 (d, *J* = 8.2 Hz, 1 H), 7.42–7.30 (m, 4 H), 7.45 (d, *J* = 8.3 Hz, 1 H), 7.53 (d, *J* = 8.7 Hz, 1 H), 7.62 (d, *J* = 7.2 Hz, 1 H), 9.30 (s, 1 H).

^{1}H NMR (DMSO-d_6): δ = 2.61 (s, 6 H), 2.96 (s, 6 H), 7.17 (d, *J* = 8.0 Hz, 1 H), 7.53–7.40 (m, 3 H), 7.69–7.53 (m, 5 H), 10.30 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 44.6, 45.7, 122.5, 124.4, 126.5, 127.6, 128.5, 128.6, 130.3, 131.1, 132.7, 136.6, 137.6, 139.8, 147.9, 148.2, 180.1.

MS (EI): *m*/*z* (%) = 42 (24), 58 (31), 77 (46), 104 (51), 126 (23), 127 (30), 136 (21), 152 (20), 167 (25), 168 (33), 246 (21), 248 (22), 254 (25), 255 (27), 257 (21), 320 (20), 335 (24), 336 (20), 337 (27), 349 (23), 350 (55), 351 (100), 352 (63), 353 (78), 364 (34), 365 (22), 366 (34), 379 (24), 380 (30), 381 (27), 382 (26), 395 [M]$^+$ (66), 396 (22), 397 (63), 398 (20).

UV/vis (MeCN): λ_{max} (log ε) = 337 (3.75), 254 nm (4.49).

Anal. Calcd for $C_{21}H_{22}BrN_3$: C, 63.64; H, 5.60; N, 10.60 Found: C, 63.71; H, 5.52; N, 10.69.

2,7-Bis[imino(phenyl)methyl]-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (7a)

Prepared according to GP3 from two portions of PhCN (0.3 mL, 2.6 mmol). Yellow crystals; yield: 437 mg (40%); mp 158–159 °C (*n*-heptane); R_f = 0.1 (alumina, Et_2O–*n*-hexane, 1:1).

Alternatively prepared by reaction of a solution of 2,7-dicyanonaphthalene **10** (1000 mg, 3.79 mmol) in anhyd Et_2O (100 mL) with a solution of PhLi [obtained from a solution of dry PhBr (23.6 mL, 22.3 mmol) in anhyd Et_2O (10 mL) and 1.6 M BuLi (13.9 mL, 22.3 mmol) at –20 °C under an argon atmosphere] at r.t. Reaction time: 24 h. Yield: 530 mg (46%).

IR (CCl_4): 3264 (NH), 3060, 3030, 2986, 2903, 2863, 2794 cm^{-1} (CH).

^{1}H NMR ($CDCl_3$): δ = 2.65 (s, 12 H), 7.18 (d, *J* = 8.3 Hz, 2 H), 7.42–7.30 (m, 6 H), 7.46 (d, *J* = 8.3 Hz, 2 H), 7.65 (d, *J* = 7.0 Hz, 4 H), 8.69 (s, 2 H).

^{1}H NMR (DMSO-d_6): δ = 2.55 (s, 12 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 7.47–7.38 (m, 6 H), 7.53 (d, *J* = 6.8 Hz, 4 H), 7.58 (d, *J* = 8.3 Hz, 2 H), 10.39 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 45.4, 123.5, 125.4, 128.4, 128.6, 128.7, 131.2, 134.2, 139.3, 139.7, 148.7, 180.4.

MS (EI): *m*/*z* (%) = 30 (57), 32 (100), 42 (24), 44 (37), 51 (20), 77 (97), 91 (41), 104 (100), 404 (54), 405 (27), 420 [M]$^+$ (51).

UV/vis (MeCN): λ_{max} (log ε) = 358 (4.08), 258 (4.82), 254 (4.82), 249 (4.81), 243 (4.78), 235 (4.78), 232 (4.79), 229 (4.79), 227 nm (4.79).

Anal. Calcd for $C_{28}H_{28}N_4$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.09; H, 6.62; N, 13.29.

2,7-Bis[imino(4-methoxyphenyl)methyl]-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (7b)

Prepared according to GP3 from two portions of 4-methoxybenzonitrile (358 mg, 2.7 mmol). Yellow crystals; yield: 600 mg (48%); mp 156–157 °C (*n*-octane); R_f = 0.2 (alumina, Et_2O–*n*-hexane, 1:1).

IR (CCl_4): 3266 (NH), 3076, 3055, 3003, 2957, 2931, 2904, 2872, 2861, 2838, 2794 cm^{-1} (CH).

^{1}H NMR (DMSO-d_6): δ = 2.58 (s, 12 H), 3.77 (s, 6 H), 6.95 (d, *J* = 8.6 Hz, 4 H), 7.08 (d, *J* = 8.2 Hz, 2 H), 7.60–7.45 (m, 6 H), 9.86 (s, 2 H).

^{13}C NMR (DMSO-d_6): δ = 45.3, 56.1, 114.3, 123.6, 125.0, 128.4, 130.4, 132.7, 134.6, 138.8, 148.0, 161.9, 177.5.

MS (EI): *m*/*z* (%) = 121 (73), 134 (35), 464 (73), 464 (32), 465 (51), 480 [M]$^+$ (100).

UV/vis (MeCN): λ_{max} (log ε) = 420 (2.87) sh, 356 (3.68), 263 (4.46), 225 (4.89), 222 nm (4.90).

Anal. Calcd for $C_{30}H_{32}N_4O_2$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.81; H, 6.73; N, 11.62.

2-[Imino(4-methoxyphenyl)methyl]-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine Perchlorate (3b·HClO$_4$)

An aq $HClO_4$ soln (*d* = 1.508) (0.020 mL, 0.18 mmol) was added to a solution of imine **3b** (60 mg, 0.18 mmol) in EtOAc (1 mL). The precipitate thus formed was separated by centrifugation and purified by crystallization (EtOH). Pale pink crystals; yield: 54 mg (81%); mp>193 °C dec. (EtOH).

^{1}H NMR (DMSO-d_6): δ = 2.56 (s, 6 H), 2.71 (s, 6 H), 2.99 (s, 3 H), 3.27 (d, *J* = 2.3 Hz, 3 H), 3.81 (s, 1.5 H), 3.87 (s, 3 H), 7.01 (d, *J* = 8.8 Hz, 3 H), 7.33 (d, *J* = 8.4 Hz, 0.5 H), 7.40 (d, *J* = 8.5 Hz, 1 H), 7.57–7.48 (m, 4 H), 7.71–7.60 (m, 2 H), 7.83 (t, *J* = 7.9 Hz, 0.5 H), 8.26–8.10 (m, 1.5 H), 11.93 (s, 2.5 H), 18.57 (s, 0.5 H).

[1,8-Bis(dimethylamino)naphthalen-2-yl](phenyl)methanone (13a)

Prepared according to GP4 from **3a**[2] (100 mg, 0.32 mmol). Reaction time: 1 h. Yellow crystals; yield: 99 mg (99%). Characterization data were consistent with those reported in the literature.[3]

[1,8-Bis(dimethylamino)naphthalen-2-yl](4-methoxyphenyl)methanone (13b)

Prepared according to GP4 from **3b**[2] (100 mg, 0.29 mmol). Reaction time: 32 h. Yellow crystals; yield: 78 mg (78%); mp 165–166 °C (*n*-octane); R_f = 0.6 (alumina, Et_2O–*n*-hexane, 2:1).

IR (Nujol): 1639 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 2.69 (s, 6 H), 2.75 (s, 6 H), 3.83 (s, 3 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 6.99 (dd, *J* = 6.4, 2.3 Hz, 1 H), 7.22 (d, *J* = 9.5 Hz, 1 H), 7.44–7.29 (m, 3 H), 7.68 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 30.1, 45.1, 45.2, 55.9, 77.0, 77.5, 78.0, 113.8, 114.2, 122.2, 122.6, 126.5, 127.1, 130.9, 132.0, 132.7, 139.5, 149.2, 152.6, 163.7, 167.1, 199.4.

MS (EI): *m*/*z* (%) = 121 (100), 127 (20), 135 (83), 167 (25), 168 (43), 225 (26), 304 (26), 316 (31), 331 (52), 348 [M]$^+$ (96), 349 (22).

UV/vis (MeCN): λ_{max} (log ε) = 294 (4.27), 226 (5.33), 224 (5.34), 222 nm (5.35).

Anal. Calcd for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.92; H, 6.88; N, 8.09.

[1,8-Bis(dimethylamino)naphthalen-2-yl](naphthalen-1-yl)methanone (13c)

Prepared according to GP4 from **3c** (100 mg, 0.27 mmol). Reaction time: 3 h. Yellow crystals; yield: 72 mg (72%); mp 120–121 °C (*n*-hexane); R_f = 0.8 (alumina, Et_2O–*n*-hexane, 1:1).

IR (Nujol): 1644 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 2.74 (s, 6 H), 2.81 (s, 6 H), 7.05 (dd, *J* = 6.1, 2.3 Hz, 1 H), 7.51–7.31 (m, 6 H), 7.73–7.54 (m, 2 H), 8.03–7.91 (m, 2 H), 9.02 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 44.8, 45.0, 114.0, 121.9, 122.1, 122.5, 124.1, 126.3, 126.4, 127.3, 127.4, 128.1, 128.6, 131.4, 131.6, 133.0, 134.2, 136.3, 139.7, 150.1, 152.6, 201.0.

MS (EI): *m*/*z* (%) = 126 (19), 127 (100), 128 (27), 41 (77), 155 (42), 167 (23), 168 (39), 227 (28), 368 [M]$^+$ (46).

UV/vis (MeCN): λ_{max} (log ε) = 222 (5.33), 228 (5.21) sh, 248 (4.63) sh, 252 (4.57) sh, 334 nm (4.06) sh.

Anal. Calcd for $C_{25}H_{24}N_2O$: C, 81.49; H, 6.57; N, 7.60. Found: C, 81.57; H, 6.51; N, 7.65.

[1,8-Bis(dimethylamino)naphthalen-2-yl](pyridin-3-yl)methanone (13d)

Prepared according to GP4 from **3d** (100 mg, 0.31 mmol). Reaction time: 1 h. Yellow crystals; yield: 65 mg (65%); mp 114–115 °C (*n*-hexane); R_f = 0.5 (alumina, Et_2O–*n*-hexane, 1:1).

IR (Nujol): 1650 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 2.62 (s, 6 H), 2.69 (s, 6 H), 6.99 (dd, *J* = 6.0, 2.6 Hz, 1 H), 7.46–7.24 (m, 5 H), 7.97–7.85 (m, 1 H), 8.67 (dd, *J* = 4.8, 1.6 Hz, 1 H), 8.77 (d, *J* = 1.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 45.1, 45.2, 114.7, 122.5, 122.7, 123.2, 123.5, 126.4, 127.8, 129.9, 134.7, 136.9, 140.0, 150.0, 151.5, 152.8, 153.3, 198.8.

MS (EI): *m*/*z* (%) = 32 (59), 44 (25), 78 (26), 168 (27), 287 (25), 288 (27), 302 (21), 319 [M]$^+$ (100), 320 (21).

UV/vis (MeCN): λ_{max} (log ε) = 227 (5.33), 224 (5.35), 222 nm (5.35).

Anal. Calcd for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63; N, 13.16. Found: C, 75.30; H, 6.57; N, 13.14.

[1,8-Bis(dimethylamino)naphthalen-2-yl](thiophen-2-yl)methanone (13e)
Prepared according to GP4 from **3e** (100 mg, 0.31 mmol). Reaction time: 12 h. Orange crystals; yield: 56 mg (56%); mp 130–131 °C (*n*-hexane); R_f = 0.9 (alumina, Et_2O–*n*-hexane, 1:1).

IR (Nujol): 1630 cm^{-1} (C=O).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.84 (s, 6 H), 2.85 (s, 6 H), 7.15–7.03 (m, 2 H), 7.49–7.29 (m, 5 H), 7.71 (dd, *J* = 4.9, 0.9 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 44.6, 44.9, 113.9, 121.8, 122.0, 122.3, 125.8, 127.0, 127.7, 129.9, 133.9, 134.6, 139.3, 145.9, 149.0, 152.3, 192.1.

MS (EI): *m*/*z* (%) = 39 (31), 42 (23), 44 (21), 97 (55), 111 (78), 127 (30), 167 (28), 168 (45), 182 (22), 225 (29), 292 (27), 307 (35), 324 $[M]^+$ (100), 325 (21).

UV/vis (MeCN): λ_{max} (log ε) = 260 (4.35), 282 (4.27), 350 (3.72) sh, 412 nm (3.39).

Anal. Calcd for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63. Found: C, 70.42; H, 6.16; N, 8.69.

1-[1,8-Bis(dimethylamino)naphthalen-2-yl]-2,2-dimethylpropan-1-one (13f)
Prepared according to GP4 from **3f** (100 mg, 0.34 mmol). Reaction time: 8 h. Beige crystals; yield: 10 mg (10%); mp 130–131 °C (*n*-hexane); R_f = 0.5 (alumina, Et_2O–*n*-hexane, 1:1).

IR (Nujol): 1679 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 1.23 (s, 9 H), 2.72 (s, 6 H), 2.86 (s, 6 H), 7.04 (d, *J* = 8.3 Hz, 1 H), 7.06 (dd, *J* = 7.3, 1.2 Hz, 1 H), 7.30 (t, *J* = 7.7 Hz, 1 H), 7.42–7.36 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 28.3, 44.7, 44.8, 45.5, 114.7, 122.7, 122.8, 123.1, 124.2, 126.1, 135.5, 138.0, 146.0, 152.2, 216.6.

MS (EI): *m*/*z* (%) = 29 (32), 41 (44), 57 (45), 127 (21), 167 (20), 168 (54), 182 (24), 210 (36), 225 (20), 226 (34), 241 (100), 298 $[M]^+$ (57).

UV/vis (MeCN): λ_{max} (log ε) = 244 (4.49) sh, 344 nm (3.85).

Anal. Calcd for $C_{19}H_{26}N_2O$: C, 76.47; H, 8.78; N, 9.39. Found: C, 76.52; H, 8.75; N, 9.33.

1-[1,8-Bis(dimethylamino)naphthalen-2-yl]pentan-1-one (13g)
Prepared according to GP4 from **3g** (100 mg, 0.27 mmol). Reaction time: 1 h. Yellow crystals; yield: 78 mg (78%); mp 29–30 °C (*n*-hexane); R_f = 0.9 (alumina, Et_2O–*n*-hexane, 1:1).

IR (Nujol): 1687 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3 H), 1.45–1.28 (m, 2 H), 1.74–1.57 (m, 2 H), 2.75 (s, 6 H), 2.76 (t, *J* = 7.5 Hz, 2 H), 2.92 (s, 6 H), 6.99 (dd, *J* = 6.0, 2.8 Hz, 1 H), 7.20 (d, *J* = 8.4 Hz, 1 H), 7.41–7.26 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 14.4, 23.1, 27.5, 43.3, 45.2, 45.3, 114.5, 122.4, 123.0, 123.2, 125.1, 127.2, 133.3, 139.5, 148.5, 152.7, 166.7, 209.1.

MS (EI): *m*/*z* (%) = 29 (100), 32 (29), 39 (25), 41 (76), 42 (67), 43 (51), 44 (44), 57 (34), 58 (42), 115 (20), 127 (41), 154 (31), 167 (37), 168 (70), 169 (21), 182 (38), 196 (20), 197 (20), 198 (20), 210 (60), 211 (22), 226 (22), 241 (92), 254 (34), 267 (21), 283 (38), 298 $[M]^+$ (99), 299 (23).

UV/vis (MeCN): λ_{max} (log ε) = 288 (3.74), 230 (4.72), 227 (4.75), 223 (4.75), 221 nm (4.71).

Anal. Calcd for $C_{19}H_{26}N_2O$: C, 76.47; H, 8.78; N, 9.39. Found: C, 76.52; H, 8.82; N, 9.31.

1-[1,8-Bis(dimethylamino)naphthalen-2-yl]ethanone (13h)
Prepared according to GP4 from **3h** (100 mg, 0.39 mmol). Reaction time: 1 h. Orange oil; yield: 77 mg (77%). Characterization data were consistent with those reported in the literature.[3]

[7-Bromo-1,8-bis(dimethylamino)naphthalen-2-yl](phenyl)methanone (13j)
Prepared according to GP4 from **3j** (100 mg, 0.27 mmol). Reaction time: 1 h. Yellow crystals; yield: 85 mg (85%); mp 92–93 °C (*n*-hexane); R_f = 0.4 (alumina, Et_2O–*n*-hexane, 1:1).

IR (KBr): 3060, 2977, 2918, 2897, 2882, 2861, 2838, 2790, 2783 (CH), 1666 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 2.70 (s, 6 H), 3.00 (s, 6 H), 7.20 (d, *J* = 8.3 Hz, 1 H), 7.36 (d, *J* = 8.7 Hz, 1 H), 7.47–7.38 (m, 3 H), 7.58–7.49 (m, 2 H), 7.78 (dd, *J* = 8.3, 1.2 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 44.6, 46.1, 122.3, 123.9, 126.3, 126.4, 128.8, 129.7, 130.3, 133.1, 133.4, 134.7, 138.3, 138.6, 148.4, 149.7, 199.7.

MS (EI): *m*/*z* (%) = 44 (34), 58 (36), 77 (68), 81 (35), 91 (36), 100 (26), 105 (100), 168 (27), 352 (29), 396 $[M]^+$ (37), 398 (36).

UV/vis (MeCN): λ_{max} (log ε) = 236 (4.75), 234 (4.80), 232 (4.81), 230 (4.82), 227 (4.84), 223 (4.82), 221 nm (4.81).

Anal. Calcd for $C_{21}H_{21}BrN_2O$: C, 63.48; H, 5.33; N, 7.05. Found: C, 63.95; H, 5.41; N, 6.79.

[1,8-Bis(dimethylamino)naphthalene-2,7-diyl]bis(phenylmethanone) (14a)
Prepared according to GP4 from **7a** (100 mg, 0.24 mmol). Reaction time: 1 h. Yellow crystals; yield: 80 mg (80%). Characterization data were consistent with those reported in the literature.[3]

[1,8-Bis(dimethylamino)naphthalene-2,7-diyl]bis[(4-methoxyphenyl)methanone] (14b)
Prepared according to GP4 from **7b** (100 mg (0.21 mmol). Reaction time: 26 h. Yellow crystals; yield: 55 mg (55%); yellow crystals; mp 165–166 °C (*n*-octane); R_f = 0.6 (alumina, $CHCl_3$).

IR (KBr): 2999, 2974, 2955, 2911, 2907, 2838, 2790 (CH), 1651 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 2.71 (s, 12 H), 3.85 (s, 6 H), 6.94–6.87 (m, 4 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.3 Hz, 2 H), 7.79–7.71 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 45.6, 55.9, 114.0, 122.6, 124.1, 127.6, 131.7, 131.9, 132.8, 140.5, 150.5, 163.9, 198.8.

MS (EI): *m*/*z* (%) = 77 (22), 92 (13), 107 (11), 121 (100), 122 (10), 135 (83), 437 (16), 438 (20), 465 (35), 466 (13), 482 (82) $[M]^+$, 483 (30).

UV/vis (MeCN): λ_{max} (log ε) = 371 (4.00), 284 (4.75), 229 (5.14), 224 nm (5.19).

Anal. Calcd for $C_{30}H_{30}N_2O_4$: C, 74.67; H, 6.27; N, 5.81. Found: C, 75.01; H, 6.33; N, 5.77.

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