Aminoalkylation of Electron-Rich Aromatic Compounds Using Preformed Iminium Salts Derived from Aldehydes other than Formaldehyde

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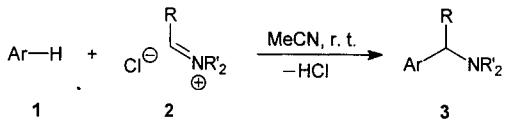
Dedicated to Prof. Dr. H. Brockmann on the occasion of his 60th birthday

Preformed iminium salts derived from aldehydes other than formaldehyde are demonstrated to be excellent reagents for the aminoalkylation of indoles, phenols and *N,N*-dimethylaniline. This method provides a simple and straightforward route to a variety of aromatic Mannich bases which are difficult to obtain by other procedures. Surprisingly, the reaction between *N*-methylindole or 2-naphthol with a preformed *N*-silyl iminium salt led to the formation of a bisindolylmethane or a dihydrooxazine derivative, respectively.

The aminomethylation of aromatic compounds by the Mannich reaction is of considerable importance for the synthesis of drugs, pesticides, and natural products. It also provides a convenient access to many useful synthetic building blocks because the amino moiety can be converted easily into a variety of other functionalities.[1,2] However, the conventional Mannich procedure which relies on the generation of the aminomethylating species through equilibria involving an amine and formaldehyde is only suitable for the aminomethylation of very electron-rich aromatic compounds.[1,2] In contrast to this, aminomethylations using preformed methylene iminium salts, which function as highly reactive Mannich reagents, have basic advantages. This methodology generally provides superior yields, the reactions are faster and require milder conditions, a factor often important in avoiding undesired byproducts and in the synthesis of complex molecules. Moreover, the scope of the aminomethylation reaction is also extended to less active substrates which are inert under classical Mannich conditions.[3]

Owing to the great utility of Mannich bases, many attempts were made to perform the Mannich reaction with aldehydes other than formaldehyde. Only a few successful reactions have been reported so far and the yields have usually been poor.[3] Therefore, alternative syntheses of aminoalkylated aromatic compounds have been developed.[4–8] However, these methods often require tedious multistep procedures, or their applications and efficiency have only limited known scope. According to the literature, even the use of preformed iminium salts generally does not provide a solution to this problem.[9] On the other hand, we had already employed preformed iminium salts derived from aldehydes other than formaldehyde (ternary iminium salts) successfully for a variety of syntheses.[10–12] The salts can be prepared readily from inexpensive bulk reagents[9,13,14] and may provide a straightforward route to the desired products. For this reason we decided to make a systematic study of the aminoalkylation of electron-rich aromatic compounds using preformed ternary iminium salts (Scheme 1).

We started our study using *N*-methylindole **(1a)** as a model owing to the fact that indoles are among the most nucleophilic aromatic compounds. Besides, indoles are easily aminomethylated in excellent yields using methylene iminium salts.[15] Ternary iminium salts **2** are typical Mannich reagents. They were chosen in order to examine the effects of structure on reactivity of iminium salts, which is an active area of research,[16] and to investigate the scope of the reaction. We were pleased to find that the use of preformed ternary iminium salts **2** actually provides an efficient and convenient access to the desired Mannich bases. Our results also indicate that arylidene iminium salts such as **2a** and **2b** are better electrophiles than alkylidene iminium salts such as **2c** (Table, Entries 1–3).



1 2 3

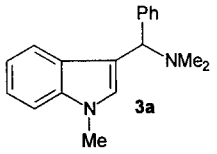
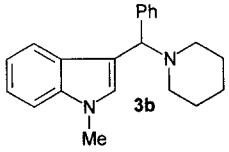
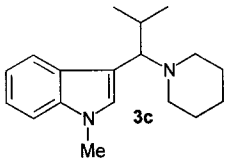
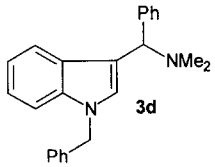
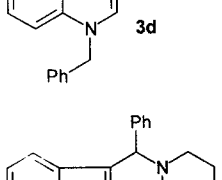
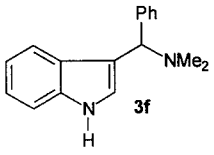
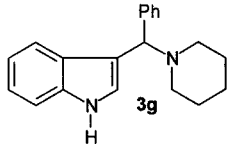
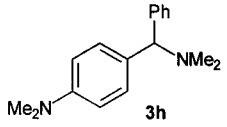
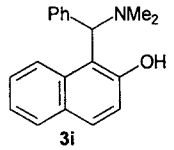
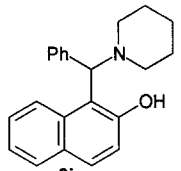
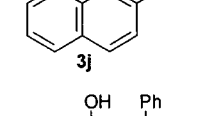
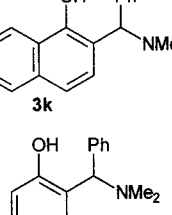
1		2	R	R′	R′
a	*N*-methylindole	**a**	Ph	Me	Me
b	*N*-benzylindole	**b**	Ph	$-(CH_2)_5-$	
c	1*H*-indole	**c**	*i*-Pr	$-(CH_2)_5-$	
d	*N,N*-dimethylaniline				
e	2-naphthol				
f	1-naphthol				
g	methyl 4-hydroxybenzoate				

Scheme 1

To our surprise the aminoalkylation of *N*-benzylindole **(1b)** took a considerably longer reaction time to afford a good yield of the product (Table, Entries 4, 5). Our methodology was also applied to the less nucleophilic *N,N*-dimethylaniline **(1d)** providing the Mannich base **3h** in moderate yield (Table, Entry 8). Preliminary attempts to aminoalkylate indole **(1c)** analogously, resulted in the formation of complex mixtures. But this problem was solved by a slight modification by using a toluene/CH_2Cl_2 mixture instead of MeCN as the solvent (Table, Entries 6, 7). This reduces the concentration of the iminium ions (iminium salts are virtually insoluble in toluene) thus preventing unwanted side reactions.

The positive results obtained so far encouraged us to extend our investigation to the aminoalkylation of phenols. 2-Naphthol **(1e)** was chosen because it is one of the most active phenols.[3] But we failed to aminoalkylate 2-naphthol **(1e)** using **2a** in analogy to indoles. Even the addition of K_2CO_3 for the in situ generation of the more nucleophilic phenolate ions furnished no better results. This came as a surprise to us because similar reaction conditions had already been used successfully for the

Table. Aminoalkylation of Aromatic Compounds **1** Using Ternary Iminium Salts **2**

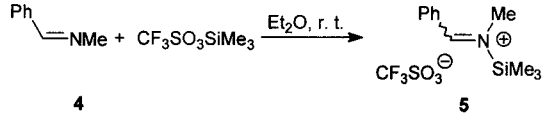
Entry	Ar-H	Iminium salt	Mannich Base	Time (h)	Yield (%)[b]
1	**1a**	**2a**	 **3a**	2	73
2	**1a**	**2b**	 **3b**	2	80
3	**1a**	**2c**	 **3c**	48	42
4	**1b**	**2a**	 **3d**	48	66
5	**1b**	**2b**	 **3e**	24	85
6	**1c**	**2a**	 **3f**	15	74
7	**1c**	**2b**	 **3g**	15	92
8	**1d**	**2a**	 **3h**	160	56
9	**1e**	**2a**	 **3i**	24	76
10	**1e**	**2b**	 **3j**	12	80
11	**1f**	**2a**	 **3k**	85	58
12	**1g**	**2a**	 **3l**	60	26

[a] Satisfactory microanalyses obtained: C ± 0.22, H ± 0.11, N ± 0.12.
[b] Yields of isolated products.

aminomethylation of phenols with preformed methylene iminium salts.[17] An obvious explanation is that methylene iminium salts are better electrophiles than ternary iminium salts. In order to overcome this drawback, we decided to employ a different base such as Et_3N to raise the concentration of the phenolate ions considerably which resulted in the desired Mannich bases **3i** and **3j**. The best results were achieved using equimolecular amounts of 2-naphthol (**1e**) and Et_3N (Table, Entries 9, 10). An excess of Et_3N led to poor yields which may be explained by the finding that iminium salts can be decomposed by bases such as Et_3N.[18] The same procedure was also employed successfully for the aminoalkylation of considerably less active phenols such as 1-naphthol (**1f**) or methyl 4-hydroxybenzoate (**1g**) (Table, Entries 11, 12).

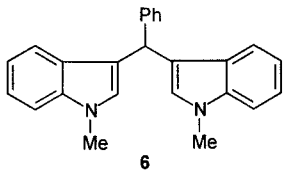
To extend our method to the synthesis of aromatic Mannich bases derived from primary amines (secondary Mannich bases) we tried to aminoalkylate *N*-methylindole (**1a**) and 2-naphthol (**1e**) analogously using the preformed *N*-trimethylsilyl iminium salt **5** which is easily accessible by reacting trimethylsilyl triflate with imine **4** (Scheme 2). But both reactions did not give the expected secondary Mannich bases. In the case of *N*-methylindole (**1a**) the bisindolylmethane derivative **6** was obtained in good yield (77%). The aminoalkylation of 2-naphthol (**1e**) furnished dihydrooxazine derivative **7** in moderate yield (32%). This reaction may be regarded as a silylogous variant of the Betti reaction.[19] As far as we know, only one preformed *N*-silyl iminium salt has been described in the literature.[20] Although *N*-silyl iminium salts have been postulated to be reactive intermediates in sev-

eral reactions,[20-23] to the best of our knowledge, these are the first syntheses using preformed *N*-silyl iminium salts. Studies are presently underway to elucidate the mechanisms and to investigate the scope of these unusual reactions.

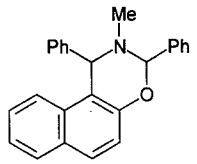


4 5

Scheme 2



6



7

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 200 spectrometer, using TMS as internal standard and $CDCl_3$ as solvent. IR spectra were recorded on a Nicolet 510 P FT-IR spectrometer. MS data were obtained from a Varian-Mat 311 A spectrometer. Elemental analyses were performed on a Perkin Elmer 240 Elemental Analyzer. Melting points were determined on a Mettler FP61 apparatus and are uncorrected. The arylidene iminium salts **2a** and **2b** were prepared according to literature,[14] the alkylidene iminium salt **2c** was prepared according to literature.[31]

Aminoalkylation of *N*-Alkylindoles; General Procedure:
The ternary arylidene iminium salt **2a** or **2b** (6 mmol)[24] was added to a solution of *N*-alkylated indole **1a** or **1b** (5 mmol) in anhyd MeCN (5 mL).[25] After stirring the mixture at r.t. under anhydrous conditions for the time required, the separated solid was collected by filtration and washed with MeCN (5 mL).[26] The residue was dissolved in CH_2Cl_2 (50–150 mL) and treated with aqueous ammonia (5%, 30 mL) at r.t. The organic layer was separated, washed neutral with water and dried ($MgSO_4$). The crude product isolated by rotary evaporation of the solvent was purified by recrystallization from propan-2-ol. The white crystals obtained were dried in vacuum.

3-(Dimethylaminophenylmethyl)-1-methylindole (**3a**):
White crystals; mp 83°C (*i*-PrOH); yield 0.96 g (73%); reaction time: 2 h.

IR (KBr): ν = 3056, 2942, 2770 cm^{-1}.

^{1}H NMR: δ = 2.26 [s, 6H, $N(CH_3)_2$], 3.70 (s, 3H, NCH_3), 4.52 (s, 1H, CH), 6.99 (s, 1 H_{arom}), 7.03–7.31 (m, 6 H_{arom}), 7.48–7.53 (m, 2 H_{arom}), 7.71–7.75 (m, 1 H_{arom}).

^{13}C NMR: δ = 33.17 (NCH_3), 44.93 [$N(CH_3)_2$], 69.68 (*C*HPh), 109.57, 117.07, 119.34, 120.48, 121.89, 127.03, 127.62, 127.79, 128.36, 128.66, 137.37, 143.94 (C_{arom}).

MS (70 eV): *m/z* (%) = 264 (M^+, 4), 221 (28), 220 (100), 204 (9), 178 (6), 144 (4), 132 (3), 77 (2).

1-Methyl-3-(phenyl-1-piperidylmethyl)indole (**3b**):
White crystals; mp 109°C (*i*-PrOH); yield: 1.21 g (80%); reaction time 2 h.

IR (KBr): ν = 3062, 2970, 2936, 2784, 1451 cm^{-1}.

^{1}H NMR: δ = 1.39–1.82 (m, 6H, 3 CH_2), 2.38–2.63 (m, 4H, CH_2NCH_2), 3.77 (s, 3H, NCH_3), 4.75 (s, 1H, CH), 6.99 (s, 1 H_{arom}), 7.11–7.39 (m, 6 H_{arom}), 7.52–7.66 (m, 2 H_{arom}), 7.86–7.90 (m, 1 H_{arom}).

^{13}C NMR: δ = 25.27 (CH_2), 26.92 (2 CH_2), 33.13 (NCH_3), 53.31 (2 CH_2), 69.00 (CH–Ph), 109.50, 116.69, 119.24, 121.00, 121.83, 126.86, 128.02, 128.51, 128.58, 137.51, 143.81 (C_{arom}).

3-(1-Isopropyl-1-piperidylmethyl)-1-methylindole (**3c**):
White crystals; mp 83°C (*i*-PrOH); yield: 0.57 g (42%); reaction time: 48 h.

IR (KBr): ν = 3051, 2948, 2922, 2858, 2803, 1445, 1365 cm^{-1}.

^{1}H NMR: δ = 0.75 (d, J = 6.5 Hz, 3H, CH_3), 1.05 (d, J = 6.5 Hz, 3H, CH_3), 1.17–1.32 (m, 2H, CH_2-piperidyl), 1.41–1.59 (m, 4H, 2 CH_2-piperidyl), 2.21–2.43 [m, 5H, 2 CH_2-piperidyl + $CH(CH_3)_2$], 3.35 (d, J = 9.7 Hz, 1H, CH), 3.75 (s, 3H, NCH_3), 6.79 (s, 1 H_{arom}), 7.03–7.36 (m, 3 H_{arom}), 7.65–7.69 (m, 1 H_{arom}).

^{13}C NMR: δ = 20.87 (CH_3), 21.45 (CH_3), 25.29 (CH_2), 27.02 (2 CH_2), 30.07 (CH), 33.21 (NCH_3), 51.39 (2 CH_2), 68.89 [$CH(CH_3)_2$], 109.36, 112.37, 118.97, 120.77, 121.45, 127.75, 130.15, 137.06 (C_{arom}).

1-Methyl-3-[(1-methylindol-3-yl)phenylmethyl]indole (**6**):
White crystals; mp 201°C (*i*-PrOH, Lit.[27] mp 202–203°C); yield: 1.41 g (77%, Lit.[27] yield: 60%); reaction time: 36 h.

IR (KBr): ν = 3054, 2935, 1621, 1474, 1329, 743 cm^{-1}.

^{1}H NMR: δ = 3.66 (s, 6H, 2 NCH_3), 5.88 (s, 1H, CH), 6.52 (s, 2 H_{arom}), 6.94–7.02 (m, 2 H_{arom}), 7.15–7.40 (m, 11 H_{arom}).

^{13}C NMR: δ = 33.11 (2 NCH_3), 40.53 (*C*HPh), 109.49, 118.70, 119.08, 120.48, 121.85, 126.46, 127.90, 128.64, 128.70, 129.13, 137.84, 144.89 (C_{arom}).

MS (70 eV): *m/z* (%) = 351 (31), 350 (M^+, 100), 349 (34), 274 (20), 273 (84), 257 (11), 220 (11), 219 (29), 218 (15), 204 (6), 175 (10), 136 (13), 129 (8), 77 (2).

1-Benzyl-3-(dimethylaminophenylmethyl)indole (**3d**):
White crystals; mp 79°C (*i*-PrOH); yield: 1.11 g (66%); reaction time: 48 h.

IR (KBr): ν = 3049, 2983, 2951, 2790, 1455 cm^{-1}.

^{1}H NMR: δ = 2.27 [s, 6H, $N(CH_3)_2$], 4.56 (s, 1H, CH), 5.23 (s, 2H, NCH_2Ph), 7.02–7.30 (m, 12 H_{arom}), 7.47–7.51 (m, 2 H_{arom}), 7.70–7.74 (m, 1 H_{arom}).

^{13}C NMR: δ = 44.86 [$N(CH_3)_2$], 50.46 (NCH_2Ph), 69.60 (*C*HPh), 110.13, 117.66, 119.64, 120.62, 122.14, 127.13, 127.97, 128.11, 128.50, 128.66, 129.18, 137.07, 138.04, 143.59 (C_{arom}).

1-Benzyl-3-(Phenyl-1-piperidylmethyl)indole (**3e**):
White crystals; mp 140°C (*i*-PrOH); yield: 1.62 g (85%); reaction time: 24 h.

IR (KBr): ν = 3058, 2959, 2934, 2803, 1480 cm^{-1}.

^{1}H NMR: δ = 1.18–1.36 (m, 2H, CH_2), 1.46–1.54 (m, 4H, 2 CH_2), 2.17–2.35 (m, 4H, CH_2NCH_2), 4.62 (s, 1H, CH), 5.10 (s, 2H, NCH_2Ph), 6.65–7.20 (m, 12 H_{arom}), 7.30–7.42 (m, 2 H_{arom}), 7.66–7.75 (m, 1 H_{arom}).

^{13}C NMR: δ = 25.33 (CH_2), 26.97 (2 CH_2), 50.44 (2 CH_2), 53.29 (NCH_2Ph), 69.06 (*C*HPh), 110.13, 117.31, 119.60, 121.26, 122.12, 126.98, 127.12, 127.65, 127.96, 128.37, 128.56, 128.76, 129.20, 137.28, 138.19, 143.46 (C_{arom}).

Aminoalkylation of Indole (1c); General Procedure:
A solution of the ternary arylidene iminium salt **2a** or **2b** (6 mmol) in anhyd CH_2Cl_2 (20 mL) was added dropwise to a solution of indole (**1c**; 0.59 g, 5 mmol) in anhyd toluene (50 mL) at 0°C. The product hydrochloride started separating on the bottom of the flask. After stirring the mixture for another 12 h at r.t., the separated solid was collected by filtration and washed with MeCN (5 mL). The Mannich base was prepared as shown in the general procedure for the aminoalkylation of *N*-alkylindoles.

3-(N,N-Dimethylaminophenylmethyl)-1H-indole (**3f**):

White crystals; mp 152°C (*i*-PrOH, Lit.[6] mp 152–154°C); yield: 0.92 g (74%); reaction time: 15 h.

IR (KBr): ν = 3418, 3061, 2824 cm^{-1}.

^1H NMR: δ = 2.28 [s, 6H, $N(CH_3)_2$], 4.55 (s, 1H, CH), 7.03–7.31 (m, 7 H_{arom}), 7.48–7.53 (m, 2 H_{arom}), 7.72–7.76 (m, 1 H_{arom}), 8.12 (br s, 1H, NH).

^{13}C NMR: δ = 44.89 [$N(CH_3)_2$], 69.74 (*C*HPh), 111.47, 118.51, 119.84, 120.43, 122.36, 122.82, 127.10, 127.29, 128.42, 128.65, 136.66, 143.58 (C_{arom}).

3-(Phenyl-1-piperidylmethyl)-1H-indole (**3g**):

White crystals; mp 61°C (*i*-PrOH); yield: 1.33 g (92%); reaction time: 15 h.

IR (KBr): ν = 3416, 3058, 2932, 2795, 1455 cm^{-1}.

^1H NMR: δ = 1.40–1.46 (m, 2H, CH_2), 1.52–1.63 (m, 4H, 2 CH_2), 2.40–2.43 (m, 4H, CH_2NCH_2), 4.69 (s, 1H, CH), 6.96–7.55 (m, 7 H_{arom}), 7.47–7.51 (m, 2 H_{arom}), 7.78–7.82 (m, 1 H_{arom}), 7.98 (br s, 1H, NH).

^{13}C NMR: δ = 25.21 (CH_2), 26.86 (2 CH_2), 53.24 (2 CH_2), 69.04 (*C*HPh), 111.37, 118.36, 119.74, 120.98, 122.29, 123.20, 126.88, 127.48, 128.47, 128.61, 136.78, 143.43 (C_{arom}).

Aminoalkylation of *N,N*-Dimethylaniline (1d); 4-(*N,N*-Dimethylaminophenylmethyl)-*N,N*-Dimethylaniline (3h):

The reaction was carried out similar to the aminoalkylation of **1a**, using a solution of **1d** (0.61 g, 5 mmol) and **2a** (10 mmol) in anhyd MeCN (5 mL); Colorless crystals; mp 90°C (*i*-PrOH); yield: 0.71 g (56%); reaction time: 160 h.

IR (KBr): ν = 2949, 2814, 1615, 1522, 1356, 802 cm^{-1}.

^1H NMR: δ = 2.27 [s, 6H, $N(CH_3)_2$], 2.95 [s, 6H, $N(CH_3)_2$], 4.05 (s, 1H, CH), 6.72 (d, J = 8.7 Hz, 2 H_{arom}), 7.17–7.37 (m, 5 H_{arom}), 7.50 (d, J = 8.7 Hz, 2 H_{arom}).

^{13}C NMR: δ = 41.05 [$N(CH_3)_2$], 45.22 [$N(CH_3)_2$], 77.84 (*C*HPh), 112.97, 126.97, 128.00, 128.80, 129.94, 131.80, 144.66, 150.01 (C_{arom}).

Aminoalkylation of Phenols; General Procedure:

The ternary arylidene iminium salt **2a** or **2b** (6 mmol)[28] was added to a solution of the phenol **1e**, **1f** or **1g** (5 mmol) in anhyd MeCN (5 mL) followed by addition of Et_3N (0.7 mL, 5 mmol). The mixture was stirred at r.t. under anhydrous conditions for the time required, then filtered and the solid washed with MeCN (5 mL). The residue was recrystallized from propan-2-ol/water (5:1). The colorless crystals were dried in vacuum.

1-(N,N-Dimethylaminophenylmethyl)-2-naphthol (**3i**):

White crystals; mp 163°C (*i*-PrOH, Lit.[29] mp 164–164.5°C); yield: 1.04 g (76%); reaction time: 24 h.

IR (KBr): ν = 3065, 2862 cm^{-1}.

^1H NMR: δ = 2.39 [s, 6H, $N(CH_3)_2$], 5.04 (s, 1H, CH), 7.21–7.94 (m, 11 H_{arom}), 13.84 (br s, 1H, OH).

^{13}C NMR: δ = 46.16 [$N(CH_3)_2$], 73.41 (*C*HPh), 116.72, 120.44, 121.51, 122.84, 126.84, 128.44, 129.09, 129.22, 129.26, 129.32, 129.96, 132.63, 140.80, 155.86 (C_{arom}).

1-(Phenyl-1-piperidylmethyl)-2-naphthol (**3j**):

White crystals; mp 196°C (*i*-PrOH, Lit.[29] mp 198–198.5°C); yield: 1.27 g (80%); reaction time: 12 h.

IR (KBr): ν = 3076, 2924, 2859, 1456 cm^{-1}.

^1H NMR: δ = 1.25–3.80 (m, 10H, 5 CH_2), 5.14 (s, 1H, CH), 7.11–7.49 (m, 6 H_{arom}), 7.60–7.80 (m, 4 H_{arom}), 7.90 (d, J = 8.6 Hz, 1 H_{arom}), 14.02 (br s, 1H, OH).

^{13}C NMR: δ = 24.62 (3 CH_2), 26.53 (2 CH_2), 72.57 (*C*HPh), 116.65, 120.46, 121.52, 122.76, 126.78, 128.31, 129.11, 129.80, 132.87, 140.17, 156.02 (C_{arom}).

2,3-Dihydro-2-methyl-1,3-diphenyl-1H-napth[1,2-e][1,3]oxazine (**7**):

White crystals; mp 135°C (*i*-PrOH, Lit.[19] mp 137°C); yield: 0.56 g (32%); reaction time: 60 h.

IR (KBr): ν = 3061, 2886, 1628, 1599, 1401, 1233 cm^{-1}.

^1H NMR: δ = 2.44 (s, 3H, NCH_3), 5.49 (s, 1H, CH), 5.85 (s, 1H, CH), 7.25–7.55 (m, 12 H_{arom}), 7.59–7.71 (m, 2 H_{arom}), 7.76–7.91 (m, 2 H_{arom}).

^{13}C NMR: δ = 35.36 (NCH_3), 63.51 (*C*HPh), 85.78 (CH), 112.42, 119.30, 123.46, 123.80, 126.95, 127.04, 127.78, 128.27, 128.53, 128.65, 129.05, 129.58, 129.89, 133.51, 138.43, 143.50, 152.70 (C_{arom}).

2-(N,N-Dimethylaminophenylmethyl)-1-naphthol (**3k**):

White crystals; mp 100°C (*i*-PrOH); yield: 0.80 g (58%); reaction time: 85 h.

IR (KBr): ν = 3427, 3068, 2961 cm^{-1}.

^1H NMR: δ = 2.33 [s, 6H, $N(CH_3)_2$], 4.45 (s, 1H, CH), 6.97–7.01 (m, 1 H_{arom}), 7.17–7.30 (m, 4 H_{arom}), 7.37–7.50 (m, 4 H_{arom}), 7.67–7.71 (m, 1 H_{arom}), 8.30–8.35 (m, 1 H_{arom}), 13.78 (br s, 1H, OH).

^{13}C NMR: δ = 44.12 [$N(CH_3)_2$], 77.91 (*C*HPh), 118.83, 118.88, 122.86, 125.24, 125.95, 126.51, 127.28, 127.71, 128.40, 129.04, 129.15, 134.11, 140.66, 152.86 (C_{arom}).

Methyl 4-Hydroxy-3-(N,N-dimethylaminophenylmethyl)benzoate (**3l**):

White crystals; mp 145°C (*i*-PrOH); yield: 0.37 g (26%); reaction time: 60 h.

IR (KBr): ν = 3404, 2967, 1713, 1321, 1289 cm^{-1}.

^1H NMR: δ = 2.31 [s, 6H, $N(CH_3)_2$], 3.82 (s, 3H, OCH_3), 4.44 (s, 1H, CH), 6.89 (J = 8.5 Hz, 1H, 5-H_{arom}), 7.28–7.45 (m, 5H, C_6H_5), 7.67 (d, J = 2.1 Hz, 1H, 2-H_{arom}), 7.84 (dd, J = 8.5, 2.1 Hz, 1H, 6-H_{arom}).

^{13}C NMR: δ = 43.81 [$N(CH_3)_2$], 52.13 (OCH_3), 77.29 (*C*HPh), 117.39, 121.40, 125.91, 128.82, 129.31, 130.99, 131.47, 139.70, 162.21 (C_{arom}), 167.33 (C=O).

***N*-Methyl-*N*-trimethylsilylbenzylidene Iminium Triflate (5):**

An equimolar amount of trimethylsilyl triflate (11.11 g, 50 mmol) was added to a solution of the imine **4**[30] (5.96 g, 50 mmol) in anhyd Et_2O (50 mL) at r.t. After 12 h the separated product was collected by filtration, washed with anhyd Et_2O and dried in vacuum; yield: 14.7 g (86%).

IR (CH_2Cl_2): ν = 3058 cm^{-1}, 2990, 2306, 1688, 1389, 1242, 1030 cm^{-1}.

^1H NMR: δ = 0.52 [s, 9H, $NSi(CH_3)_3$], 3.57 (s, 3H, NCH_3), 7.41–7.49 (m, 3 H_{arom}), 7.77–7.81 (m, 2 H_{arom}), 8.40 (s, 1H, N=*C*HPh).

^{13}C NMR: δ = 0.66 [$Si(CH_3)_3$], 47.08 (NCH_3), 129.11, 129.32, 132.35 (C_{arom}), 164.77 (N=*C*HPh).

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(24) For the aminoalkylation of **1b**, 10 mmol of iminium salt **2a** or **2b** was required. Similarly 10 mmol of **2c** or **5** was needed for the aminoalkylation of **1a** to give **3c** or **6**, respectively.
(25) For the aminoalkylation of **1b**, 2 mL of anhydr. MeCN was used.
(26) The reaction of **1a** with **5** yielded **6**, after filtration and recrystallization of the solid from propan-2-ol/water (5:1).
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