The Use of *N*,*N*-Dialkyltrimethylsilylamines in the Synthesis of Pentamethinium Salts

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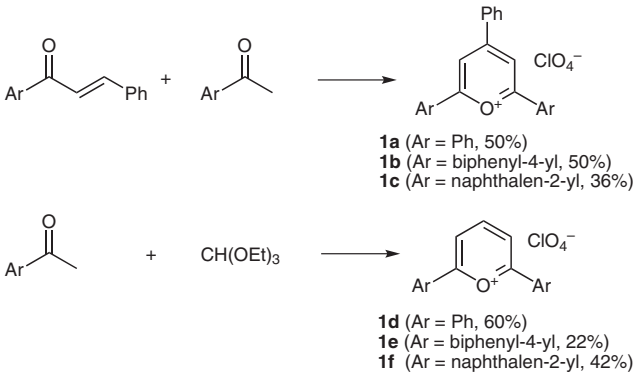
Abstract: *N*,*N*-Dialkyltrimethylsilylamines were used for the synthesis of a series of pentamethinium salts starting from 2,6-disubstituted or 2,4,6-trisubstituted pyrylium salts, N-substituted 5-aminopenta-2,4-dienals or N-substituted 5-aminopenta-2,4-dien-1-ones. The reactions proceed smoothly under mild conditions, furnishing the desired products in good yields.

Key words: cyanines, pentamethinium salts, pyrylium salts, ring opening, amino aldehydes

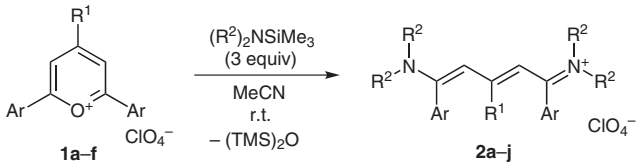
With their characteristic, positively charged π-electron system delocalized over an odd number of carbon atoms and terminal nitrogen groups, streptocyanine dyes have found numerous applications as advanced materials for optical devices, laser dyes, nonlinear optics, etc.[1] A number of synthetic procedures leading to pentamethinium salts have been developed so far, including the action of tris(dialkylamino)arsanes on pyrylium salts[2] and reactions of primary or secondary alkylamines with carboxonium salts;[3] however, simple and robust methods for facile modification of the structure and properties of pentamethinium salts are still highly desirable. Herein, we describe an efficient synthesis of pentamethinium salts employing several commercially available *N*,*N*-dialkyltrimethylsilylamines.

The starting 2,4,6-trisubstituted pyrylium salts **1a**,[4] **1b**[5] and **1c**[5] were obtained by the reaction between chalcones and aryl methyl ketones. The 2,6-disubstituted pyrylium salts **1d**,[6] **1e** and **1f** were prepared by a perchloric acid catalyzed reaction of aryl methyl ketones with triethyl orthoformate (Scheme 1).

Reaction of pyrylium salts[7] **1a–f**, bearing two or three aromatic substituents, with *N*,*N*-dialkyltrimethylsilylamines in anhydrous acetonitrile afforded the pentamethinium salts **2a–j** in very good yield (Scheme 2, Table 1). Hexamethyldisiloxane was formed as a byproduct. All reactions were carried out under an inert atmosphere at room temperature, except for the synthesis of **2c**, where refluxing of the reaction mixture was required. The reactions usually proceeded quite rapidly (1–6 h) with almost complete conversion. The use of an excess of the *N*,*N*-dialkyltrimethylsilylamine was required in order to achieve a high yield.



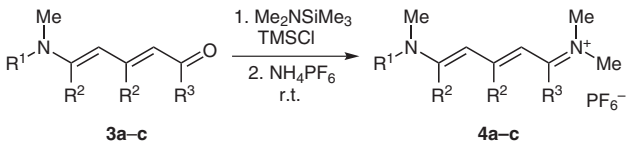
Scheme 1



Scheme 2

Thus, 3.0 equivalents of the silylated reagent seems optimal. Reactions with 2.0 or 2.5 equivalents of this reagent led to lower conversions even after prolonged reaction times; on the other hand, the application of 4.0 or 5.0 equivalents did not significantly enhance the conversion of the starting pyrylium salts.

In combination with trimethylsilyl chloride, *N*,*N*-dialkyltrimethylsilylamines could also be used for the conversion of 5-aminopenta-2,4-dienal **3a**[8] or 5-(dimethylamino)penta-2,4-dien-1-ones **3b**[9] and **3c**[10] into pentamethinium chlorides. These chlorides are known to be very hygroscopic and were therefore transformed in situ to the desired hexafluorophosphates, in very good yield (Scheme 3, Table 2). The trimethylsilyl chloride scavenges the silyl group originating from the reagent to produce hexamethyldisiloxane and supplies the chloride anion. Notably, this reaction also enables the preparation



Scheme 3

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Table 1 Prepared Pentamethinium Salts **2a–j**

Entry	Starting material	Ar	R^1	$R^2{}_2$	Time (h)	Product (yield[a])
1	**1a**	Ph	Ph	Me_2	3	**2a** (71%)
2	**1a**	Ph	Ph	$(CH_2)_4$	6	**2b** (69%)
3	**1a**	Ph	Ph	$(CH_2)_2O(CH_2)_2$	3[b]	**2c** (51%)
4	**1b**	biphenyl-4-yl	Ph	Me_2	20	**2d** (68%)
5	**1c**	naphthalen-2-yl	Ph	Me_2	24	**2e** (79%)
6	**1d**	Ph	H	Me_2	1	**2f** (82%)
7	**1d**	Ph	H	$(CH_2)_4$	3	**2g** (68%)
8	**1d**	Ph	H	$(CH_2)_2O(CH_2)_2$	4	**2h** (82%)
9	**1e**	biphenyl-4-yl	H	Me_2	2	**2i** (78%)
10	**1f**	naphthalen-2-yl	H	Me_2	6	**2j** (86%)

[a] Yield of isolated product.
[b] Under reflux.

Table 2 Prepared Pentamethinium Salts **4a–c**

Entry	Starting material	R^1	R^2	R^3	Product (yield[a])
1	**3a**	Ph	H	H	**4a** (83%)
2	**3b**	Me	H	Ph	**4b** (88%)
3	**3c**	Me	Ph	Ph	**4c** (69%)

[a] Yield of isolated product.

Table 3 Prepared Pentamethinium Salts **6a–f**

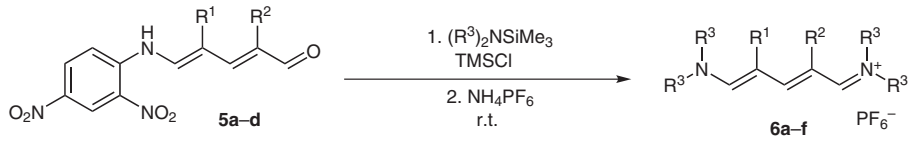
Entry	Starting material	R^1	R^2	$R^3{}_2$	Time (h)	Product (yield[a])
1	**5a**	H	H	Me_2	0.5	**6a** (87%)
2	**5a**	H	H	$(CH_2)_4$	1	**6b** (75%)
3	**5a**	H	H	$(CH_2)_2O(CH_2)_2$	0.5	**6c** (80%)
4	**5b**	H	Et	Me_2	1	**6d** (86%)
5	**5c** + **5c′**	H/Ph	Ph/H	Me_2	1	**6e** (79%)
6	**5d**	Me	Me	Me_2	2	**6f** (45%)

[a] Yield of isolated product.

of unsymmetrical pentamethinium salts bearing two different dialkylamino groups, e.g. compound **4a**.

Similarly, 5-(2,4-dinitrophenylamino)penta-2,4-dienals could serve as starting materials in the reactions with *N*,*N*-dialkyltrimethylsilylamines and trimethylsilyl chloride (Scheme 4, Table 3). In this case, both substituents at the ends of the conjugated carbon chain are displaced by the dialkylamino groups. 5-(2,4-Dinitrophenylamino)penta-2,4-dienals are easily accessible from *N*-(2,4-dinitrophenyl)pyridinium salts by a nucleophilic ring-opening reaction with aqueous sodium carbonate.[11] It should be noted that *N*-(2,4-dinitrophenyl)pyridinium salts can be transformed to pentamethinium salts in a single step upon reaction with secondary amines;[12] however, this strategy is not generally applicable. For example, attempted preparation of pentamethinium salt **6f** from *N*-(2,4-dinitrophenyl)-3,5-dimethylpyridinium chloride and dimethylamine failed. Following the two-step protocol, salt **6f** was formed in a decent yield from aldehyde **5d** and *N*,*N*-dimethyltrimethylsilylamine. In the case of compound **6e**, an inseparable mixture of regioisomers **5c** and **5c′** was used as starting material.

In conclusion, we have developed a novel and efficient synthetic procedure leading to a number of pentamethinium salts using commercially available *N*,*N*-dialkyltrimethylsilylamines. 2,6-Disubstituted or 2,4,6-trisubstituted pyrylium salts, N-substituted 5-aminopenta-2,4-dienals and N-substituted 5-aminopenta-2,4-dien-1-ones were used as starting materials. The advantages of this method are the mild reaction conditions, simple work-up and good yields. It is also noteworthy that our method enables variation of the terminal amino groups, as well as the preparation of unsymmetrical pentamethinium salts.



Scheme 4

All reactions were carried out in standard glassware under a nitrogen atmosphere. The *N*,*N*-dialkyltrimethylsilylamines are commercially available (Aldrich Chemical Company) and were used without further purification. Melting points were determined on a Kofler apparatus and are uncorrected. NMR spectra were measured on a Varian Gemini 300HC spectrometer (^{1}H at 300 MHz and ^{13}C at 75 MHz), a Bruker AMX-3 400 spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz) or a Bruker Avance DRX 500 spectrometer (^{1}H at 500 MHz and ^{13}C at 125 MHz). Chemical shifts (in ppm, δ scale) are reported relative to residual solvent signals as internal standard; coupling constants (*J*) are given in Hz. UV/Vis spectra were recorded on a HP 8452A spectrophotometer at 25 °C using $CHCl_3$ as solvent.

The syntheses of pyrylium salts **1a**,[4] **1b**,[5] **1c**[5] and **1d**,[6] aminopentadienals **3a**,[8] **5a**[11] and **5d**,[13] and aminopentadienones **3b**[9] and **3c**[10] have been described previously.

CAUTION! Although no difficulties were encountered in our laboratory, it is good to keep in mind that organic perchlorates are potentially hazardous. Pyrylium perchlorates are known to be explosive (impact sensitive). Proper safety precautions should be taken during their synthesis, storage and handling. The dry perchlorates should be handled with great care and should never be crushed, rubbed or pushed through a narrow opening.

2,6-Dibiphenyl-4-ylpyrylium Perchlorate (1e)

To a soln of 4-acetylbiphenyl (6.48 g, 33.0 mmol) and $CH(OEt)_3$ (20 mL) in Et_2O (25 mL) was added 70% $HClO_4$ (1.3 mL) in $CH(OEt)_3$ (8 mL). After 5 min at r.t., distilled H_2O (2 mL) was added and the reaction mixture was stirred for an additional 30 min and then left in a refrigerator overnight. The separated crystals were collected by filtration, washed with Et_2O, recrystallized twice from MeCN–toluene (9:1) and dried under reduced pressure.

Orange crystals; yield: 1.76 g (22%); mp 270–273 °C (MeCN–toluene).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.50 (t, *J* = 7.2 Hz, 2 H), 7.56 (t, *J* = 7.4 Hz, 4 H), 7.82 (d, *J* = 7.4 Hz, 4 H), 8.04 (d, *J* = 8.5 Hz, 4 H), 8.42 (d, *J* = 8.5 Hz, 4 H), 8.49 (d, *J* = 8.3 Hz, 2 H), 8.89 (t, *J* = 8.3 Hz, 1 H).

^{13}C NMR (125 MHz, CD_3CN): δ = 120.1 (CH), 128.3 (C), 128.4 (CH), 129.5 (CH), 130.2 (CH), 130.3 (CH), 130.4 (CH), 139.5 (C), 148.9 (C), 157.3 (CH), 172.6 (C).

Anal. Calcd for $C_{29}H_{21}ClO_5$: C, 71.83; H, 4.36. Found: C, 71.60; H, 4.42.

2,6-Dinaphthalen-2-ylpyrylium Perchlorate (1f)

To a soln of 2-acetylnaphthalene (5.62 g, 33.0 mmol) in $CH(OEt)_3$ (17 mL) was added 70% $HClO_4$ (1.3 mL). The reaction mixture was stirred at r.t. for 3 h. Then, it was concentrated to dryness on a rotatory evaporator, and the residue was crystallized from MeCN–toluene (2:1) and dried under reduced pressure.

Red crystals; yield: 2.98 g (42%); mp 262–265 °C (MeCN–toluene).

^{1}H NMR (400 MHz, CD_3CN): δ = 7.74 (t, *J* = 7.0 Hz, 2 H), 7.80 (t, *J* = 6.9 Hz, 2 H), 8.08 (d, *J* = 7.8 Hz, 2 H), 8.22–8.29 (m, 4 H), 8.35 (dd, *J* = 8.8, 1.9 Hz, 2 H), 8.60 (d, *J* = 8.3 Hz, 2 H), 8.94 (t, *J* = 8.3 Hz, 1 H), 9.02 (s, 2 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 120.5 (CH), 123.9 (CH), 126.9 (C), 129.1 (CH), 129.2 (CH), 131.1 (CH), 131.3 (CH), 131.7 (CH), 132.7 (CH), 133.8 (C), 137.4 (C), 157.3 (CH), 173.2 (C).

Anal. Calcd for $C_{25}H_{17}ClO_5$: C, 69.37; H, 3.96. Found: C, 69.45; H, 3.92.

5-(2,4-Dinitrophenylamino)-2-ethylpenta-2,4-dienal (5b) and 5-(2,4-Dinitrophenylamino)-4-ethylpenta-2,4-dienal (5b′)

A soln of *N*-(2,4-dinitrophenyl)-3-ethylpyridinium chloride[14] (1.00 g, 3.23 mmol) and K_2CO_3 (1.79 g, 12.9 mmol) in H_2O (20 mL) was stirred at 50 °C for 2 h. The precipitated orange solid was collected by filtration and washed with H_2O (60 mL). The solid product was dissolved in a small amount of CH_2Cl_2 and precipitated with hexane to yield an orange powder, which was identified as the 2-ethyl regioisomer **5b**. The mother liquor was concentrated under reduced pressure and precipitated with hexane to yield a red powder, which was identified as the 4-ethyl regioisomer **5b′**.

5b

Orange powder; yield: 590 mg (63%); mp 147–149 °C (hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 7.6 Hz, 3 H), 2.41 (q, *J* = 7.6 Hz, 2 H), 6.54 (dd, *J* = 13.1, 11.6 Hz, 1 H), 6.89 (d, *J* = 11.6 Hz, 1 H), 7.30 (dd, *J* = 13.1, 11.5 Hz, 1 H), 7.36 (d, *J* = 9.4 Hz, 1 H), 8.42 (ddd, *J* = 9.4, 2.7, 0.7 Hz, 1 H), 9.20 (d, *J* = 2.7 Hz, 1 H), 9.44 (s, 1 H), 10.51 (br d, *J* = 11.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7 (CH_3), 17.7 (CH_2), 112.1 (CH), 115.0 (CH), 124.0 (CH), 130.5 (CH), 131.9 (CH), 132.2 (C), 139.1 (C), 142.0 (C), 143.0 (C), 145.1 (CH), 193.4 (CH).

Anal. Calcd for $C_{13}H_{13}N_3O_5$: C, 53.61; H, 4.50; N, 14.43. Found: C, 53.39; H, 4.61; N, 14.24.

5b′

Red powder; yield: 150 mg (16%); mp 115–118 °C (hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.7 Hz, 3 H), 2.50 (q, *J* = 7.7 Hz, 2 H), 6.27 (ddd, *J* = 15.5, 7.7, 0.5 Hz, 1 H), 7.14 (d, *J* = 11.8 Hz, 1 H), 7.17 (d, *J* = 15.5 Hz, 1 H), 7.38 (d, *J* = 9.5 Hz, 1 H), 8.43 (ddd, *J* = 9.5, 2.6, 0.7 Hz, 1 H), 9.21 (d, *J* = 2.6 Hz, 1 H), 9.61 (d, *J* = 7.7 Hz, 1 H), 10.67 (br d, *J* = 11.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.9 (CH_3), 19.1 (CH_2), 115.0 (CH), 124.0 (CH), 126.0 (C), 126.5 (CH), 129.7 (CH), 130.6 (CH), 132.3 (C), 139.2 (C), 141.9 (C), 152.3 (CH), 193.0 (CH).

Anal. Calcd for $C_{13}H_{13}N_3O_5$: C, 53.61; H, 4.50; N, 14.43. Found: C, 53.89; H, 4.38; N, 14.16.

5-(2,4-Dinitrophenylamino)-2-phenylpenta-2,4-dienal (5c) and 5-(2,4-Dinitrophenylamino)-4-phenylpenta-2,4-dienal (5c′)

A soln of *N*-(2,4-dinitrophenyl)-3-phenylpyridinium chloride[15] (250 mg, 0.70 mmol) and K_2CO_3 (1.00 g, 7.24 mmol) in H_2O (12 mL) was heated to 50 °C and then stirred at this temperature for 1 h. After cooling, the precipitated product was collected by filtration, washed with H_2O (50 mL) and dried under reduced pressure. A mixture of regioisomers **5c** and **5c′** (7:3) was obtained.

Yield: 140 mg (59%); mp 110–114 °C (H_2O).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.83 (dd, *J* = 15.4, 7.7 Hz, 1 H, **5c′**), 6.41 (dd, *J* = 12.6, 12.1 Hz, 1 H, **5c**), 7.10–7.53 (m, 16 H, **5c** + **5c′**), 8.34 (d, *J* = 9.3 Hz, 2 H, **5c** + **5c′**), 9.02 (d, *J* = 2.8 Hz, 1 H, **5c′**), 9.06 (d, *J* = 2.7 Hz, 1 H, **5c**), 9.55 (d, *J* = 7.7 Hz, 1 H, **5c′**), 9.58 (s, 1 H, **5c**), 10.33 (br s, 2 H, **5c** + **5c′**).

Anal. Calcd for $C_{17}H_{13}N_3O_5 \cdot 0.5\ H_2O$: C, 58.62; H, 4.05; N, 12.06. Found: C, 58.88; H, 4.08; N, 12.01.

Pentamethinium Salts 2a–j; General Procedure

To a stirred soln of a pyrylium perchlorate **1a–f** (300 mg, 1.0 equiv) in anhyd MeCN (15 mL) was added a *N*,*N*-dialkyltrimethylsilylamine (3.0 equiv) under inert atmosphere. The reaction mixture was stirred at r.t. for 1–24 h (see Table 1), then concentrated to dryness on a rotatory evaporator. The residue was crystallized from the appropriate solvent.

1,5-Bis(dimethylamino)-1,3,5-triphenylpentamethinium Perchlorate (2a)[2]
Red crystals; yield: 250 mg (71%); mp 191–193 °C (*i*-PrOH) (Lit.[2] 195 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.85 (br s, 12 H), 5.32 (s, 2 H), 7.13–7.39 (m, 15 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.5 (CH_3), 109.3 (CH), 128.1 (CH), 128.8 (2 × CH), 129.4 (CH), 130.0 (CH), 130.4 (CH), 134.4 (C), 141.1 (C), 168.8 (C), 169.0 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 498 nm (32200).

1,3,5-Triphenyl-1,5-dipyrrolidin-1-ylpentamethinium Perchlorate (2b)[2]
Red crystals; yield: 270 mg (69%); mp 170–172 °C (*i*-PrOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (br s, 4 H), 2.00 (br s, 4 H), 3.08 (br s, 4 H), 3.26 (br s, 4 H), 5.26 (s, 2 H), 7.00–7.40 (m, 15 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9 (CH_2), 25.2 (CH_2), 50.8 (CH_2), 52.5 (CH_2), 108.4 (CH), 127.7 (CH), 128.5 (CH), 128.8 (CH), 129.1 (CH), 129.5 (CH), 129.6 (CH), 135.4 (C), 141.5 (C), 164.9 (C), 168.5 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 496 nm (43200).

1,5-Dimorpholin-4-yl-1,3,5-triphenylpentamethinium Perchlorate (2c)[2]
Red crystals; yield: 210 mg (51%); mp 215–218 °C (*i*-PrOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.23 (br s, 8 H), 3.69 (br s, 8 H), 5.65 (s, 2 H), 7.15–7.45 (m, 15 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.0 (CH_2), 66.1 (CH_2), 111.4 (CH), 128.3 (CH), 129.2 (CH), 129.7 (CH), 130.1 (CH), 130.6 (CH), 130.8 (CH), 133.9 (C), 140.4 (C), 168.7 (C), 170.9 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 512 nm (27100).

1,5-Dibiphenyl-4-yl-1,5-bis(dimethylamino)-3-phenylpentamethinium Perchlorate (2d)
Red crystals; yield: 230 mg (68%); mp 183–185 °C (*i*-PrOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.90 (br s, 12 H), 5.43 (s, 2 H), 7.17–7.61 (m, 23 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.5 (CH_3), 109.9 (CH), 127.0 (CH), 127.4 (CH), 128.1 (CH), 128.2 (CH), 129.0 (CH), 129.6 (CH), 130.0 (CH), 130.2 (CH), 133.1 (C), 139.5 (C), 140.9 (C), 143.3 (C), 168.9 (C), 169.0 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 502 nm (29100).

Anal. Calcd for $C_{39}H_{37}ClN_2O_4$: C, 73.98; H, 5.89; N, 4.42. Found: C, 73.62; H, 5.71; N, 4.12.

1,5-Bis(dimethylamino)-1,5-dinaphthalen-2-yl-3-phenylpentamethinium Perchlorate (2e)
Red crystals; yield: 270 mg (79%); mp 174–176 °C (*i*-PrOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.78 (br s, 12 H), 5.42 (s, 2 H), 6.96 (s, 2 H), 7.15–8.05 (m, 17 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.4 (CH_3), 109.8 (CH), 125.9 (CH), 127.0 (CH), 127.5 (CH), 127.7 (CH), 127.8 (CH), 128.5 (CH), 128.6 (CH), 129.2 (CH), 129.5 (CH), 129.9 (CH), 131.6 (C), 132.5 (C), 133.5 (C), 140.9 (C), 168.8 (C), 169.2 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 502 nm (34300).

Anal. Calcd for $C_{35}H_{33}ClN_2O_4$: C, 72.34; H, 5.72; N, 4.82. Found: C, 71.94; H, 5.86; N, 4.59.

1,5-Bis(dimethylamino)-1,5-diphenylpentamethinium Perchlorate (2f)[2]
Orange crystals; yield: 300 mg (82%); mp 235–238 °C (*i*-PrOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.96 (s, 6 H), 3.39 (s, 6 H), 6.05 (dd, *J* = 13.8, 11.8 Hz, 1 H), 6.31 (d, *J* = 12.8 Hz, 2 H), 6.96 (dd, *J* = 7.6, 1.5 Hz, 4 H), 7.19–7.32 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.1 (CH_3), 43.5 (CH_3), 106.6 (CH), 128.1 (CH), 128.4 (CH), 129.7 (CH), 132.5 (C), 161.7 (CH), 169.9 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 446 nm (95700).

1,5-Diphenyl-1,5-dipyrrolidin-1-ylpentamethinium Perchlorate (2g)
Orange crystals; yield: 280 mg (68%); mp 246–248 °C (EtOH).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.90 (quin, *J* = 7.0 Hz, 4 H), 2.15 (quin, *J* = 7.0 Hz, 4 H), 3.24 (t, *J* = 7.0 Hz, 4 H), 3.75 (t, *J* = 7.0 Hz, 4 H), 6.15–6.25 (m, 3 H), 7.02 (dd, *J* = 7.4, 1.9 Hz, 4 H), 7.18–7.30 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.8 (CH_2), 25.0 (CH_2), 49.9 (CH_2), 52.5 (CH_2), 106.6 (CH), 127.6 (CH), 128.4 (CH), 129.6 (CH), 133.2 (C), 159.6 (CH), 166.7 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 450 nm (104300).

Anal. Calcd for $C_{25}H_{29}ClN_2O_4$: C, 65.71; H, 6.40; N, 6.13. Found: C, 65.57; H, 6.10; N, 6.20.

1,5-Dimorpholin-4-yl-1,5-diphenylpentamethinium Perchlorate (2h)
Orange crystals; yield: 360 mg (82%); mp 234–235 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.27 (br s, 4 H), 3.60 (br s, 4 H), 3.90 (br s, 4 H), 3.93 (br s, 4 H), 6.19 (t, *J* = 12.7 Hz, 1 H), 6.66 (d, *J* = 12.7 Hz, 2 H), 6.99 (d, *J* = 7.2 Hz, 4 H), 7.20–7.36 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 48.8 (CH_2), 51.3 (CH_2), 66.2 (CH_2), 66.8 (CH_2), 107.8 (CH), 128.4 (CH), 128.6 (CH), 130.1 (CH), 131.9 (C), 163.3 (CH), 169.1 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 458 nm (100700).

Anal. Calcd for $C_{25}H_{29}ClN_2O_6$: C, 61.41; H, 5.98; N, 5.73. Found: C, 61.24; H, 5.81; N, 5.57.

1,5-Dibiphenyl-4-yl-1,5-bis(dimethylamino)pentamethinium Perchlorate (2i)
Yellow crystals; yield: 270 mg (78%); mp 242–245 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.02 (br s, 6 H), 3.42 (br s, 6 H), 6.26–6.44 (m, 3 H), 7.09 (d, *J* = 8.5 Hz, 4 H), 7.19–7.35 (m, 10 H), 7.45 (d, *J* = 8.5 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.2 (CH_3), 43.5 (CH_3), 107.3 (CH), 126.9 (CH), 127.0 (CH), 127.9 (CH), 128.9 (CH), 129.0 (CH), 131.4 (C), 139.3 (C), 142.9 (C), 161.8 (CH), 169.9 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 450 nm (82500).

Anal. Calcd for $C_{33}H_{33}ClN_2O_4$: C, 71.15; H, 5.97; N, 5.03. Found: C, 70.84; H, 6.15; N, 4.96.

1,5-Bis(dimethylamino)-1,5-dinaphthalen-2-ylpentamethinium Perchlorate (2j)
Yellow crystals; yield: 300 mg (86%); mp 213–216 °C (acetone–Et_2O).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.97 (s, 6 H), 3.43 (s, 6 H), 5.92–6.18 (m, 1 H), 6.38 (t, *J* = 12.5 Hz, 2 H), 6.84–7.70 (m, 14 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.9 (CH_3), 43.5 (CH_3), 106.5 (CH), 124.5 (CH), 126.9 (CH), 127.1 (CH), 127.3 (CH), 127.7 (CH), 127.9 (CH), 128.2 (CH), 129.8 (C), 131.7 (C), 132.7 (C), 162.2 (CH), 170.2 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 448 nm (87100).

Anal. Calcd for $C_{29}H_{29}ClN_2O_4$: C, 68.97; H, 5.79; N, 5.55. Found: C, 69.27; H, 5.93; N, 5.50.

Pentamethinium Salts 4a–c; General Procedure

To a stirred soln of compound **3a**,[8] **3b**[9] or **3c**[10] (300 mg, 1.0 equiv) in anhyd MeCN (10 mL), *N*,*N*-dimethyltrimethylsilylamine (1.2 equiv) and TMSCl (1.2 equiv) were added successively under inert atmosphere. After 2 h at r.t., NH_4PF_6 (1.0 equiv) in MeCN (20 mL) was added to the reaction mixture. The resulting precipitate was removed by filtration, and the solution was concentrated on a rotary evaporator and Et_2O (30 mL) was added. The precipitated product was collected by filtration and recrystallized from the appropriate solvent.

1-(Dimethylamino)-5-(*N*-methyl-*N*-phenylamino)pentamethinium Hexafluorophosphate (4a)

Orange crystals; yield: 480 mg (83%); mp 120–121 °C (EtOH).

^{1}H NMR (300 MHz, DMSO-d_6, 80 °C): δ = 3.18 (s, 3 H), 3.37 (s, 3 H), 3.49 (s, 3 H), 5.99 (t, *J* = 12.1 Hz, 1 H), 6.13 (t, *J* = 11.8 Hz, 1 H), 7.30 (t, *J* = 7.2 Hz, 1 H), 7.38–7.50 (m, 4 H), 7.64 (t, *J* = 12.6 Hz, 1 H), 7.92 (d, *J* = 11.3 Hz, 1 H), 8.02 (d, *J* = 12.1 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6, 80 °C): δ = 38.5 (CH_3), 40.3 (CH_3), 46.1 (CH_3), 105.1 (CH), 106.9 (CH), 121.4 (CH), 126.4 (CH), 129.5 (CH), 144.6 (C), 156.6 (CH), 163.0 (CH), 164.1 (CH).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 nm (93000).

Anal. Calcd for $C_{14}H_{19}F_6N_2P$: C, 46.67; H, 5.32; N, 7.78. Found: C, 46.55; H, 5.17; N, 7.68.

1,5-Bis(dimethylamino)-1-phenylpentamethinium Hexafluorophosphate (4b)

Light orange crystals; yield: 490 mg (88%); mp 206–207 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.99 (s, 3 H), 3.09 (s, 3 H), 3.22 (s, 3 H), 3.37 (s, 3 H), 5.88 (t, *J* = 12.1 Hz, 1 H), 6.17 (t, *J* = 12.6 Hz, 1 H), 6.72 (t, *J* = 12.6 Hz, 1 H), 7.07 (d, *J* = 11.5 Hz, 1 H), 7.20–7.26 (m, 2 H), 7.51–7.60 (m, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 37.8 (CH_3), 40.4 (CH_3), 42.7 (CH_3), 45.3 (CH_3), 104.0 (CH), 104.6 (CH), 128.5 (CH), 129.0 (CH), 130.1 (CH), 132.8 (C), 160.1 (CH), 162.2 (CH), 168.7 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 432 nm (96000).

Anal. Calcd for $C_{15}H_{21}F_6N_2P$: C, 48.13; H, 5.66; N, 7.49. Found: C, 48.28; H, 5.39; N, 7.51.

1,5-Bis(dimethylamino)-1,3,5-triphenylpentamethinium Hexafluorophosphate (4c)

Red crystals; yield: 310 mg (69%); mp 115–120 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.85 (br s, 12 H), 5.31 (s, 2 H), 7.15–7.28 (m, 9 H), 7.36–7.39 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.4 (CH_3), 109.3 (CH), 128.2 (CH), 128.7 (CH), 129.0 (CH), 129.5 (CH), 130.1 (CH), 130.5 (CH), 134.4 (C), 141.2 (C), 169.1 (C), 169.8 (C).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 498 nm (31000).

Anal. Calcd for $C_{27}H_{29}F_6N_2P$: C, 61.59; H, 5.55; N, 5.32. Found: C, 61.75; H, 5.78; N, 5.10.

Pentamethinium Salts 6a–f; General Procedure

An aminopentadienal **5a–d** (300 mg, 1.0 equiv) was dissolved or suspended in anhyd MeCN (10 mL). A *N*,*N*-dialkyltrimethylsilylamine (2.1 equiv) and, after 5 min, TMSCl (2.1 equiv) were added. The reaction mixture was maintained at r.t. for 0.5–2 h (see Table 3) and then NH_4PF_6 (1.0 equiv) dissolved in MeCN (10 mL) was added. The resulting inorganic precipitate was removed by filtration and the filtrate was concentrated on a rotary evaporator. The addition of Et_2O (20 mL) yielded crude product, which was purified by crystallization from the appropriate solvent (**6a–e**) or by column chromatography (**6f**; silica gel 40, CH_2Cl_2–EtOH, 1:0 → 4:1).

1,5-Bis(dimethylamino)pentamethinium Hexafluorophosphate (6a)[16]

Yellow crystals; yield: 295 mg (87%); mp 215–217 °C (*i*-PrOH) (Lit.[16] 198 °C).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.04 (s, 6 H), 3.25 (s, 6 H), 5.79 (t, *J* = 11.8 Hz, 2 H), 7.37 (t, *J* = 12.7 Hz, 1 H), 7.72 (d, *J* = 11.6 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 37.6 (CH_3), 45.3 (CH_3), 102.7 (CH), 161.6 (CH), 161.8 (CH).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 412 nm (108100).

Anal. Calcd for $C_9H_{17}F_6N_2P$: C, 36.25; H, 5.75; N, 9.39. Found: C, 36.03; H, 5.80; N, 9.29.

1,5-Dipyrrolidin-1-ylpentamethinium Hexafluorophosphate (6b)

Yellow crystals; yield: 300 mg (75%); mp 208–210 °C (EtOH).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.86–2.00 (m, 8 H), 3.41 (t, *J* = 6.6 Hz, 4 H), 3.67 (t, *J* = 6.6 Hz, 4 H), 5.70 (t, *J* = 12.1 Hz, 2 H), 7.38 (t, *J* = 12.7 Hz, 1 H), 7.90 (d, *J* = 11.6 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 24.3 (2 × CH_2), 47.7 (CH_2), 53.1 (CH_2), 103.9 (CH), 157.2 (CH), 160.9 (CH).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 424 nm (116200).

Anal. Calcd for $C_{13}H_{21}F_6N_2P$: C, 44.58; H, 6.04; N, 8.00. Found: C, 44.41; H, 6.21; N, 7.87.

1,5-Dimorpholin-4-ylpentamethinium Hexafluorophosphate (6c)

Yellow crystals; yield: 350 mg (80%); mp 195–197 °C (EtOH).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.60 (m, 8 H), 3.69 (m, 8 H), 5.95 (t, *J* = 12.2 Hz, 2 H), 7.46 (t, *J* = 12.7 Hz, 1 H), 7.79 (d, *J* = 11.8 Hz, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 46.4 (CH_2), 53.8 (CH_2), 65.3 (CH_2), 66.3 (CH_2), 102.6 (CH), 160.2 (CH), 163.0 (CH).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 418 nm (95600).

Anal. Calcd for $C_{13}H_{21}F_6N_2O_2P$: C, 40.84; H, 5.54; N, 7.33. Found: C, 41.10; H, 5.45; N, 7.25.

1,5-Bis(dimethylamino)-2-ethylpentamethinium Hexafluorophosphate (6d)

Orange crystals; yield: 290 mg (86%); mp 126–127 °C (*i*-PrOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.4 Hz, 3 H), 2.45 (q, *J* = 7.4 Hz, 2 H), 3.10 (s, 3 H), 3.31 (s, 3 H), 3.33 (s, 6 H), 5.55 (t, *J* = 12.2 Hz, 1 H), 7.19 (s, 1 H), 7.37 (d, *J* = 12.7 Hz, 1 H), 7.52 (d, *J* = 11.6 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.5 (CH_3), 18.2 (CH_2), 37.9 (CH_3), 45.6 (CH_3), 46.0 (CH_3), 99.1 (CH), 116.0 (C), 161.7 (CH), 161.9 (CH), 164.5 (CH).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 416 nm (100200).

Anal. Calcd for $C_{11}H_{21}F_6N_2P$: C, 40.49; H, 6.49; N, 8.59. Found: C, 40.47; H, 6.69; N, 8.48.

1,5-Bis(dimethylamino)-2-phenylpentamethinium Hexafluorophosphate (6e)

Yellow crystals; yield: 260 mg (79%); mp 152–154 °C (EtOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.57 (br s, 3 H), 2.86 (br s, 3 H), 3.28 (br s, 3 H), 3.31 (br s, 3 H), 5.10 (t, *J* = 11.5 Hz, 1 H), 7.15–

7.20 (m, 2 H), 7.36–7.44 (m, 3 H), 7.53 (s, 1 H), 7.61 (d, *J* = 11.5 Hz, 1 H), 7.75 (d, *J* = 12.6 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 37.4 (CH_3), 38.9 (CH_3), 45.4 (CH_3), 100.1 (CH), 115.8 (C), 127.9 (CH), 128.8 (CH), 130.4 (CH), 135.2 (C), 160.3 (CH), 161.7 (CH), 163.9 (CH).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 416 nm (105000).

Anal. Calcd for $C_{15}H_{21}F_6N_2P$: C, 48.12; H, 5.66; N, 7.49. Found: C, 47.74; H, 5.50; N, 7.45.

1,5-Bis(dimethylamino)-2,4-dimethylpentamethinium Hexafluorophosphate (6f)

Orange crystals; yield: 150 mg (45%); mp 113–116 °C (CH_2Cl_2–EtOH).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.12 (s, 6 H), 3.27 (s, 12 H), 7.04 (s, 1 H), 7.33 (br s, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 15.8 (CH_3), 44.0 (CH_3), 109.3 (C), 121.0 (CH), 127.4 (CH).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 432 nm (59000).

Anal. Calcd for $C_{11}H_{21}F_6N_2P$: C, 40.49; H, 6.49; N, 8.59. Found: C, 40.08; H, 6.03; N, 8.37.

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