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Convenient Preparation of Aromatic Aldehydes *via* DDQ Oxidation. Application in the Synthesis of a Tripodand Containing Octahydroacridine Moieties [1])

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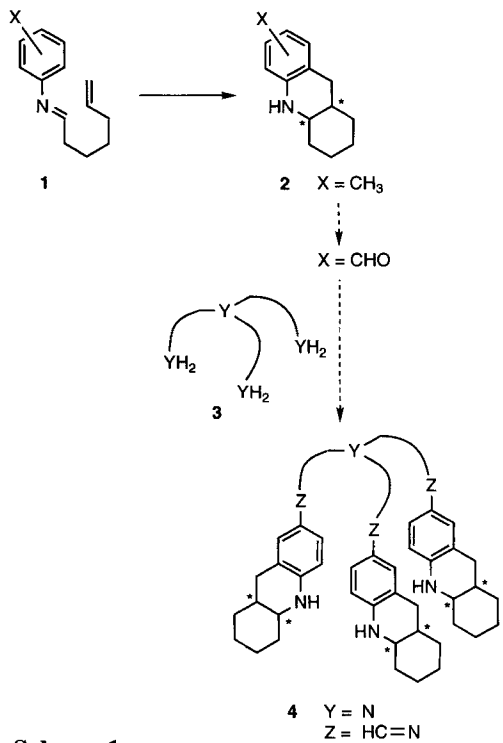
Abstract. 7-Methyloctahydroacridines **7a–d** were obtained by a one-pot imine condensation/Lewis acid-catalyzed cyclization from aniline derivatives **5a–d** and aldehyde **6**. Only those compounds **7** could be oxidized with DDQ to the corresponding octahydroacridine-7-carbaldehydes **9**, which bear a *meta*-chloro or bromo substituent (with respect to the methyl group) in addition to the *para*-amino group (*i.e.* **7c,d** → **9c,d**). Aldehyde **9c** was further converted to the novel tripodand **11** which was characterized by X-ray crystal structure analysis.

Host–guest interactions and the synthesis of novel artificial receptors are two of the most intensively studied topics in the area of supramolecular chemistry [1]. Especially semiflexible podands, cryptands and molecular tweezers have received increased interest. This is due to the fact that the combination of rigid binding pockets with flexible tethers allows precise adjustment of noncovalent interactions [2]. Based on our recent findings that octahydroacridines **2** can be easily obtained by a highly diastereoselective Lewis acid-catalyzed cyclization of *N*-arylimines **1** [3], we decided to use them as rigid substructures in novel podands **4**. As a potential coupling reaction of **2** and **3** we chose the imine condensation. This required the introduction of an aldehyde function on the aromatic moiety of **2** prior to assembly of **4**. The results towards this end and the final steps towards a novel octahydroacridine containing tripodand **4** are described in this paper.



Scheme 1

Results and Discussion

Oxidation studies were first carried out with 8-methyloctahydroacridine **7a** (X = H), which was prepared by

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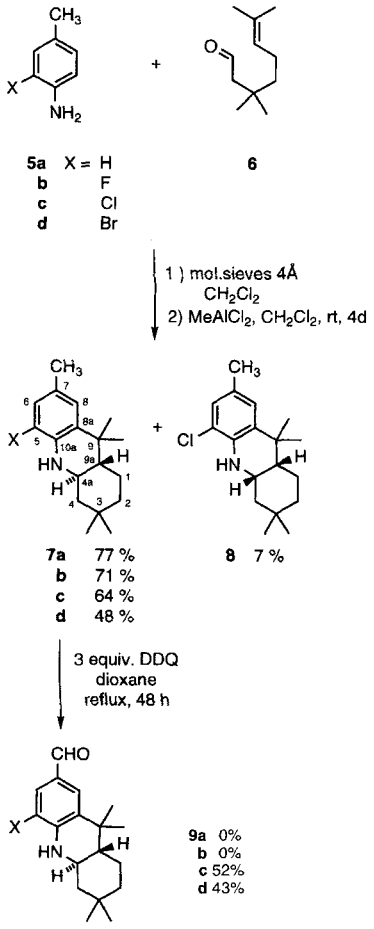
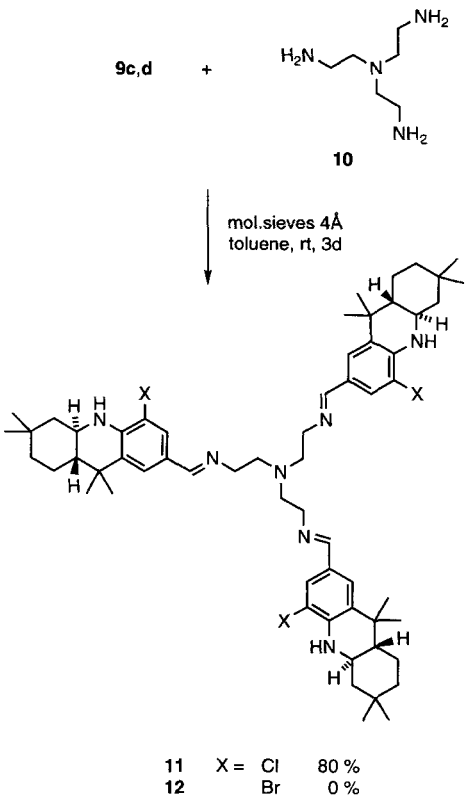
condensation of 4-methylaniline **5a** with 3,3,7-trimethyl-6-octenal **6** followed by $MeAlCl_2$-catalyzed cyclization of the *N*-arylimine [3]. Our initial attempts to obtain the aldehyde **9a** with chromyl chloride [4] lead to an inseparable mixture of various oxidation products. Cer(IV)ammonium nitrate in acetic acid is known to oxidize substituted toluenes to the corresponding benzaldehyde derivatives [5, 6]. However, this reagent was not applied to octahydroacridine **7a**, because undesired side reactions like formation of iminium ions and subsequent epimerization at C-4a might occur under acidic conditions. Rao and Naidu reported the clean conversion of 7,8-dimethoxy-5-methyl-1-phenyldihydronaphthaline to the corresponding aldehyde *via* DDQ oxidation [7]. Following their procedure a solution of compound **7a** and DDQ was refluxed in dioxane for several hours. In contrast to the literature results, no



Scheme 2

trace of the desired aldehyde **9a** was found. We reasoned that the *meta*- and *para*-oriented methoxy groups in Rao and Naidu's case enhanced the reactivity of the benzylic hydrogen atoms. Unfortunately 6-methoxy-8-methyloctahydroacridine **7** (X = OMe) could not be obtained from 2-methoxy-4-methylaniline, because the methoxy group interferes with the Lewis acid-catalyzed cyclization. In order to mimic the electron-donating effect of the methoxy group, we decided to introduce an additional halogen atom X at C-5 of the octahydroacridine **7**. Thus compounds **7b–d** (X = F, Cl, Br) were prepared by the Lewis acid-catalyzed cyclization from 2-halo-4-methyl-anilines **5b–d** as described for **7a**. In the case of aniline derivative **5c** the corresponding *cis*-configurated octahydroacridine **8** was obtained as a by-product. When submitting the octahydroacridines **7b–d** to the DDQ oxidation, we were pleased to find that both chloro and bromo derivative **7c** and **7d** were converted to the aldehydes **9c,d** in 52% and 43% yield, respectively. Treatment of the fluoro compound **7b** with DDQ under similar conditions yielded only starting material.

In order to obtain tripodands **11**, **12** octahydroacridine aldehydes **9c,d** were treated with triamine **10** in the presence of molecular sieves 4Å (Scheme 3). Whereas the chloro-substituted tripodand **11** was isolated in good yield, condensation of **10** and the bromo compound **9d** proceeded only slowly and the desired tripodand **12** could not be purified sufficiently.



Scheme 3

Fortunately, the X-ray crystal structure of tripodand **11** could be determined (Figure 1) [8]. In the solid state

11 has a noncrystallographic threefold rotational symmetry with the C_3 axis being oriented parallel to the [251] direction.

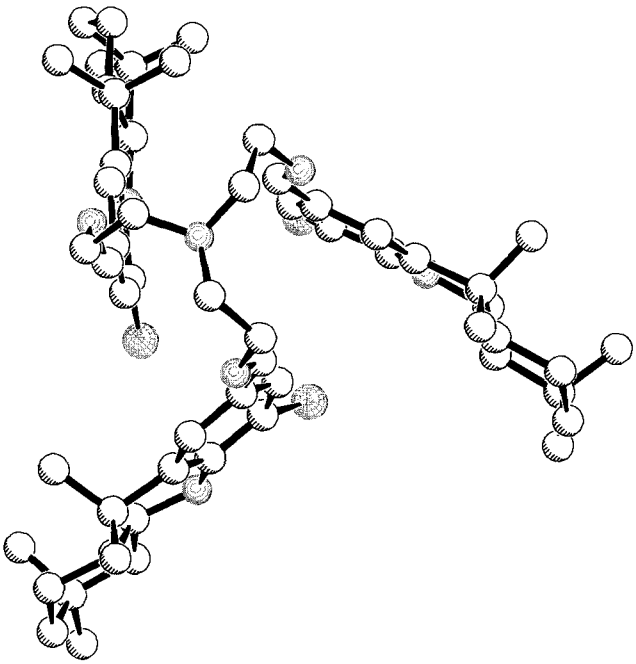


Fig. 1 X-ray crystal structure of tripodand **11**. Hydrogen atoms were omitted for clarity.

In conclusion a DDQ oxidation of 6-chloro-8-methyl-octahydroacridine **7c** and the corresponding 6-bromo derivative **7d** to the aromatic aldehydes **9b,c** has been achieved. Compound **9b** could be converted to the novel tripodand **11**. The presence of three chloro-substituents allow further functionalization of **11** *e.g.* by palladium-catalyzed coupling reactions.

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Experimental

All reactions were carried out under argon by using standard Schlenk technique. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Merck Si 254 F plates (0.25 mm thickness) and products were visualized with a solution of phosphomolybdic acid in EtOH (5%, v/v). Flash chromatography [9] was carried out with Merck silica gel 60 (230 – 400 mesh). – NMR spectra: Bruker AC 200 P (200 MHz-^{1}H, 50 MHz-^{13}C), Bruker ARX 300 (300 MHz-^{1}H, 75 MHz-^{13}C) and Varian Unity-plus (600 MHz-^{1}H, 150 MHz-^{13}C). Multiplets in ^{13}C-NMR spectra were determined by DEPT and APT experiments. – Melting points (uncorrected): Gallenkamp melting point apparatus. – IR spectra: Nicolet 5DXC FT-IR spectrometer. – Mass spectra: Finnigan Model MAT 312 (EI), Finnigan Model MAT 8230 (CI, reactand gas: NH_3). – GC-mass spectra: Varian GC 3400 coupled with a Varian Saturn 2 (ion trap) or with a Finnigan MAT 8230 (EI). – GC analysis: HP5-fused silica capillary column (ID 0.32 mm, length 25 m), HPU2-fused silica capillary column (ID 0.2 mm, length 25 m). Temperature program: 220 °C with 1 °C min^{-1} until 280 °C, then isotherm for 20 min. The following compounds were prepared according to literature procedures: 3,3,7-trimethyl-6-octenal **6** [10], triamine **10** [11].

Preparation of Octahydroacridines (7), (8) (General Procedure)

To a solution of 4-methylaniline derivative **5** (5.00 mmol) and 3,3,7-trimethyl-6-octenal **6** (840 mg, 5.00 mmol) in CH_2Cl_2 (4.5 ml) was added powdered molecular sieve 4Å (1 g) and the mixture was stirred for 10 h at room temperature. After filtration *via* Celite the solvent was removed *in vacuo* and the crude *N*-arylimine was dissolved in CH_2Cl_2 (25 ml) and cooled to –78 °C. Then were added dropwise $MeAlCl_2$ (6.0 ml, 6.00 mmol, 1M solution in CH_2Cl_2) and the resulting mixture was stirred for 4 d at room temperature. The mixture was poured slowly onto ice-cold 2N NaOH (250 ml). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 ml). The combined organic layers were dried over $MgSO_4$ and evaporated *in vacuo*.

(4aRS,9aSR)-3,3,7,9,9-Pentamethyl-1,2,3,4,4a,9,9a,10-octahydroacridine (**7a**)

The crude product was obtained as a single diastereomer. Flash chromatography on SiO_2 (hexane/ethyl acetate 75 : 1) yielded 3.96 g (15.4 mmol, 77%) of colorless crystals. *m.p.* 62 °C. – IR (KBr) ν/cm^{-1} = 3400, 3385, 3036, 2962, 2851, 1615, 1508, 807. – ^{1}H NMR (300 MHz, C_6D_6): δ/ppm = 7.20 (d, J = 1.7 Hz, 1H, 8-H), 6.93 (dd, J = 7.9/1.7 Hz, 1H, 6-H), 6.37 (d, J = 7.9 Hz, 1H, 5-H), 3.03 (ddd, J = 10.7/10.7/4.5 Hz, 1H, 4a-H), 2.34 (s, 3H, H-14), 1.63 – 1.07 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 1.35, 1.19 (s, 6H, 12-H, 13-H), 0.97, 0.92 (s, 6H, 10-H, 11-H). – ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 141.6, 131.4, 127.6, 127.4, 125.8, 114.6 (C-5, C-5a, C-6, C-7, C-8, C-8a), 48.4, 47.5, 39.6, 35.1, 33.3, 30.9, 27.7, 27.2, 25.3, 21.3, 21.1 (C-1, C-2, C-3, C-4, C-4a, C-9, C-9a, C-10, C-11, C-12, C-13, C-14). – MS (70 eV); *m/z* (%): 257 (90, M$^+$), 242 (100), 158 (53), 69 (80), 57 (64), 55 (74).

$C_{18}H_{27}N$: Calcd.: 257.2143 Found: 257.2149 (MS);
Calcd.: C 84.05 H 10.50 N 5.45
Found: C 83.98 H 10.76 N 5.50.

(4aRS,9aSR)-3,3,7,9,9-Pentamethyl-5-fluoro-1,2,3,4,4a,9,9a,10-octahydroacridine (**7b**)

The crude product was obtained as a single diastereomer. Flash chromatography on SiO_2 (hexane/ethyl acetate 100 : 1): 3.90 g (14.2 mmol, 71%) of pale yellow crystals. *m.p.* 62 °C. – IR (KBr) ν/cm^{-1} = 3417, 3042, 2988, 2847, 1630, 1585, 1510, 1458 – 1278, 495. – ^{1}H NMR (300 MHz, C_6D_6): δ/ppm = 6.92 (s, 1H, 8-H), 6.76 (d, J = 11.7 Hz, 1H, 6-H), 3.57 (s, 1H, NH), 2.97 (ddd, J = 10.9/10.9/4.3 Hz, 1H, 4a-H), 2.08

(s, 3H, 14-H), 1.58–1.00 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 1.29, 1.12 (s, 6H, 12-H, 13-H), 0.92, 0.86 (s, 6H, 10-H, 11-H). – ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 149.8 (d, J = 240 Hz, C-5), 132.8, 129.5, 128.7, 122.7, 113.4 (C-5a, C-6, C-7, C-8, C-8a), 47.2, 46.1, 38.7, 34.4, 32.4, 30.1, 26.6, 26.2, 24.4, 20.5, 20.1 (C-1, C-2, C-3, C-4, C-4a, C-9, C-9a, C-10, C-11, C-12, C-13, C-14). – MS (70 eV); *m/z* (%): 275 (100, M^+), 260 (85), 190 (58), 176 (70), 69 65), 57 (66), 55 (62).

$C_{18}H_{26}NF$ Calcd.: 275.2049 Found: 275.2056 (MS);
Calcd.: C 78.54 H 9.45 N 5.09
Found: C 78.54 H 9.54 N 5.14.

3,3,7,9,9-Pentamethyl-5-chloro-1,2,3,4,4a,9,9a,10-octahydroacridines (**7c**, **8**)

The crude product was obtained as a mixture of diastereomers (**7c** : **8** = *10* : 1 by GC). Flash chromatography on SiO_2 (eluens: hexane/ethyl acetate 200 : 1) gave 81 mg (0.28 mmol, 7%) of yellow crystals as the first fraction (**8**) and 740 mg (2.54 mmol, 64%) of pale yellow crystals as the second fraction (**7c**).

(4aRS,9aSR)-isomer (**7c**)

m.p. 100 °C. – IR (KBr) 945 cm^{-1}, 2909, 2866, 1500, 1362. – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 6.95 (d, J = 1.4 Hz, 1H, 8-H), 6.91 (d, J = 1.4 Hz, 1H, 6-H), 4.10 (s, broad, NH), 3.23 (ddd, J = 10.6/10.4/4.0 Hz, 1H, 4a-H), 2.22 (s, 3H, 14-H), 1.77–1.18 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 1.33, 1.05 (s, 6H, 12-H, 13-H), 1.00 (s, 6H, 10-H, 11-H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ/ppm = 136.9, 132.6 (C-5a, C-5), 126.9, 125.5 (C-6, C-8), 125.4, 117.3 (C-7, C-8a), 47.5, 47.2, 39.2, 35.3, 32.9, 31.0, 27.0, 26.7, 25.1, 20.9, 20.5 (C-1, C-2, C-3, C-4, C-4a, C-9, C-9a, C-10, C-11, C-12, C-13, C-14). – MS (70 eV); *m/z* (%): 291 (80, M^+), 276 (85), 192 (62), 97 (60), 69 (100), 55 (87).

$C_{18}H_{26}NCl$: Calcd.: 291.1757 Found: 291.1762 (MS);
Calcd.: C 74.18 H 8.93 N 4.80
Found: C 74.24 H 9.11 N 4.84.

(4aSR,9aSR)-isomer (**8**)

m.p. 81 °C. – IR (KBr) ν/cm^{-1} = 3433, 3037, 2978, 2843, 1612, 1506, 1452, 1363, 1298, 1267. – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 7.06 (d, J = 1.3 Hz, 1H, 8-H), 6.93 (d, J = 1.3 Hz, 1H, 6-H), 4.11 (s, NH), 3.70 (d, J = 1.7 Hz, 1H, 4a-H), 2.15 (s, 3H, 14-H), 1.39–1.05 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 1.28, 1.17 (s, 6H, 12-H, 13-H), 1.08, 0.90 (s, 6H, 10-H, 11-H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ/ppm = 135.9 (C-5), 128.9 (C-5a), 126.8, 124.7 (C-6, C-8), 124.3, 116.1 (C-7, C-8a), 46.7, 44.6 (C-4a, C-9a), 44.5, 39.1, 35.8, 29.2, 19.8 34.1, 32.7, 27.1, 26.0, 20.4 (C-1, C-2, C-3, C-4, C-9, C-10, C-11, C-12, C-13, C-14). – MS (70 eV); *m/z* (%): 291 (60, M^+), 276 (100), 69 (60), 55 (60).

$C_{18}H_{26}NCl$: Calcd.: 291.1757 Found: 291.1762 (MS);
Calcd.: C 74.18 H 8.93 N 4.80
Found: C 74.33 H 9.13 N 4.96.

(4aRS,9aSR)-3,3,7,9,9-Pentamethyl-5-bromo-1,2,3,4,4a,9,9a,10-octahydroacridine (**7d**)

The crude product was obtained as a single diastereomer. Recrystallization from benzene yielded 805 mg (2.40 mmol, 48%) of colorless crystals. *m.p.* 124 °C. – IR (KBr) ν/cm^{-1} = 3406, 3399, 3031, 2967, 2848, 1611, 1559, 1494, 1362, 495. – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.23 (s, 1H, 8-H), 7.06 (s, 1H, 6H), 4.18 (s, 1H, NH), 3.04 (ddd, J = 10.7/10.7/4.9 Hz, 1H, 4a-H), 2.15 (s, 3H, 14-H), 1.58–1.05 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 1.27, 1.09 (s, 6H, 12-H, 13-H), 0.92, 0.85 (s, 6H, 10-H, 11-H). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 138.5, 132.8, 130.7, 126.5, 126.1, 108.7 (C-5a, C-5, C-6, C-7, C-8a, C-8), 47.4, 47.0, 39.4, 35.5, 33.1, 30.8, 27.0, 26.8, 25.1, 21.1, 20.5, (C-1, C-2, C-3, C-4, C-4a, C-9, C-9a, C-10, C-11, C-12, C-13, C-14). – MS (70 eV); *m/z* (%): 335 (21, M^+), 320 (28), 149 (22), 97 (30), 83 (51), 69 (78), 57 (100), 55 (90).

$C_{18}H_{26}NBr$ Calcd.: 335.1249 Found: 335.1241 (MS);
Calcd.: C 64.30 H 7.70 N 4.20
Found: C 64.37 H 7.83 N 4.24.

Oxidation of Octahydroacridines (7c), (7d) (General Procedure)

To a solution of octahydroacridine **7c,d** (1.90 mmol) in dioxane (40 ml) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (1.30 g, 5.70 mmol) and the mixture was refluxed for 3 d. Then the mixture was cooled to room temperature, filtered and the filtrate was evaporated *in vacuo*. The remaining solid was filtered *via* neutral Al_2O_3 (eluens: benzene) and the solvent was removed.

(4aRS,9aSR)-3,3,9,9-Tetramethyl-5-chloro-1,2,3,4,4a,9,9a,10-octahydroacridine-7-carboxaldehyde (**9c**)

0.30 g (0.98 mmol, 52%) of a pale pink solid. *m.p.* 126 °C. – IR (KBr) ν/cm^{-1} = 3412, 2962, 2838, 1878, 1594, 1513, 1457. – H NMR (300 MHz, $CDCl_3$): δ/ppm = 9.70 (s, 1H, CHO), 7.80 (d, J = 1.4 Hz, 1H, 8-H), 7.65 (d, J = 1.4 Hz, 1H, 6-H), 4.61 (s, 1H, NH), 2.90 (ddd, J = 10.5/10.5/4.2 Hz, 1H, 4a-H), 1.50–0.79 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 1.14, 0.88 (s, 6H, 12-H, 13-H), 0.87, 0.79 (s, 6H, 10-H, 11-H). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 188.3 (CHO), 144.4 (C-7), 132.1, 129.7, 126.6, 126.2, 117.4, (C-5a, C-5, C-6, C-8, C-8a), 47.6, 46.6, 39.1, 35.2, 32.8, 30.9, 25.8, 25.5, 24.9, 20.8 (C-1, C-2, C-3, C-4, C-4a, C-9, C-9a, C-10, C-11, C-12, C-13). – MS (70 eV); *m/z* (%): 305 (51, M^+), 290 (92), 222 (24), 149 (26), 69 (76), 57 (100).

$C_{18}H_{24}NOCl$ Calcd.: 305.1546 Found: 305.1535 (MS);
Calcd.: C 70.82 H 7.87 N 4.59
Found: C 70.59 H 7.84 N 4.36.

(4aRS,9aSR)-3,3,9,9-Tetramethyl-5-bromo-1,2,3,4,4a,9,9a,10-octahydroacridine-7-carboxaldehyde (**9d**)

Flash chromatography on SiO_2 (hexane/ethyl acetate 50 : 1, then 25 : 1) yielded 300 mg (0.86 mmol, 43%) of a pale yellow solid. *m.p.* 120 °C. – IR (KBr) ν/cm^{-1} = 3402, 2965, 2847, 1876, 1592, 1558, 1515, 1363, 1327, 496. – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 9.68 (s, CHO), 7.84 (d, J = 1.7 Hz, 1H, 8-H), 7.80 (d, J = 1.7 Hz, 1H, 6-H), 4.68 (s, 1H, NH), 2.90 (ddd, J = 11.2/10.9/4.1 Hz, 1H, 4a-H), 1.43–0.76 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 1.12, 0.77 (s, 6a, 12H, 13-H), 0.86 (s, 6H, 10-H, 11-H). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 188.1 (CHO), 145.1 (C-7), 133.3, 132.2, 128.3, 126.6, 107.9 (C-5a, C-5, C-6, C-8a, C-8), 47.7, 46.3, 39.1, 35.2, 32.8, 30.8, 25.8, 24.8, 20.8 (C-1, C-2, C-3, C-4, C-4a, C-9a, C-9, C-10, C-11, C-12, C-13). – MS (70 eV); *m/z* (%): 351 (10, M^+), 336 (21), 86 (92), 84 (100), 51 (86).

$C_{18}H_{24}NOBr$: Calcd.: 351.1023 Found: 351.1014 (MS);
Calcd.: C 61.69 H 6.91 N 4.00
Found: C 61.61 H 7.04 N 3.93.

Tris-N-[((4aSR,9aRS)-5-chloro-3,3,9,9-tetramethyl-7-methylidene-1,2,3,4,4a,9,9a-octahydroacridinyl)2-aminoethyl] amine (**11**)

To a solution of trisamine **10** (29 mg, 0.20 mmol) in toluene (5 ml) was added molecular sieves 4Å (1 g) and then aldehyde **9c** (183 mg, 0.60 mmol) in small portions. The mixture was stirred for 3 d at room temperature and then filtered *via* Celite. The solvent was removed *in vacuo* to give 150 mg (0.16 mmol, 80%) of a yellow solid. *m.p.* 140 °C (dec.). – IR (KBr) ν/cm^{-1} = 3415 cm^{-1}, 2965, 2904, 2857, 2845, 1639, 1599, 1510, 1362, 1323, 737. – ^{1}H NMR (200 MHz, C_6D_6): δ/ppm = 7.92 (s, 3H, HC=N), 7.89 (d, J = 1.4 Hz, 3H, 8-H), 7.53 (d, J = 1.4 Hz, 3H, 6-H), 4.33 (s, 3H, NH), 3.74 (dd, J = 6.4/6.4 Hz, 6 H, $NCH_2C\underline{H}_2N$=CH), 3.03 (dd, J = 6.4/6.4 Hz, 6 H, $NC\underline{H}_2CH_2$ N=CH), 2.89 (m, 3H, 4a-H), 1.35–0.69 (m, 21H, 1-H, 2-H, 4-H, 9a-H), 1.20, 0.93 (s, 18H, 12-H, 13-H), 0.81 (s, 9H), 0.73 (s, 9H, 10-H, 11-H). – ^{13}C NMR (50 MHz, C_6D_6) δ/ppm = 160.0 (C=N), 141.3 (C-7), 132.4 (C-5), 127.9, 126.2, 124.6, 117.4 (C-5a, C-6, C-8, C-8a), 60.9 ($NCH_2\underline{C}H_2N$=CH), 56.8 ($N\underline{C}H_2CH_2N$=CH), 47.3, 46.9, 46.7, 39.2, 35.4, 33.0, 30.8, 26.5, 26.3, 25.0, 21.0 (C-1, C-2, C-3, C-4, C-4a, C-9, C-9a, C-10, C-11, C-12, C-13). – MS (70 eV); *m/z* (%): 1008 (3, M^+ + 1), 1007 (1, M^+), 690 (1), 611 (1), 308 (96), 306 (100).
$C_{60}H_{84}Cl_3N_7$ Calcd.: C 71.50 H 8.34 N 9.73
Found: C 71.35 H 8.49 N 9.61.

X-ray crystal structure analysis of 11

$C_{60}H_{84}Cl_3N_7$, M = 1009.69, 0.1 × 0.1 × 0.05 mm, a = 12.629 (7), b = 29.730(8), c = 16.240(7) Å, b = 110.09(4)°, V = 5727 (4) Å^3, $\rho_{calc.}$ = 1.171 mg m^{-3}, T = 293 K, μ = 17.73 cm^{-1}, no absorption correction, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, $\omega/2\Theta$ scans, 7638 reflections collected ($\pm h, \pm k, \pm l$), [(sinΘ)/λ] = 0.49 Å^{-1}, 7208 independent and 2917 observed reflections [$I > 2\sigma(I)$], 653 refined parameters, R = 0.079, ωR^2 = 0.189, max. residual electron density 0.85 (–0.43) e Å^{-3}. Data were collected on a Enraf-Nonius CAD4 diffractometer, programs used: MolEN, SHELXS-86, SHELXL-93, SCHAKAL-92. See ref. [8].

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