

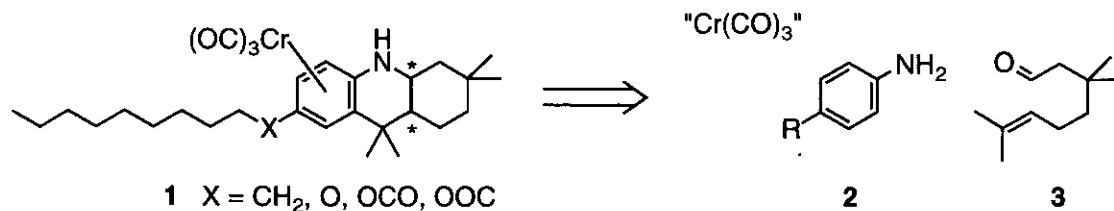
**SYNTHESIS OF η^6 -(OCTAHYDROACRIDINE)-
CHROMIUMTRICARBONYL COMPLEXES WITH NON-
POLAR TAILS VIA MOLECULAR SIEVES-CATALYZED
CYCLIZATION OF *N*-ARYLIMINES AND SUBSEQUENT
DIASTEREOSELECTIVE COMPLEXATION**

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Abstract - Molecular sieves catalyzed cyclizations of both various *N*-arylimines formed *in situ* from the corresponding arylamines and 3,3,7-trimethyl-6-octenal yielded *trans*-configured octahydroacridines. After attachment of non-polar alkyl chains these heterocycles can be complexed diastereoselectively to $\text{Cr}(\text{CO})_3$. The products were characterized by X-ray crystal structure determination.

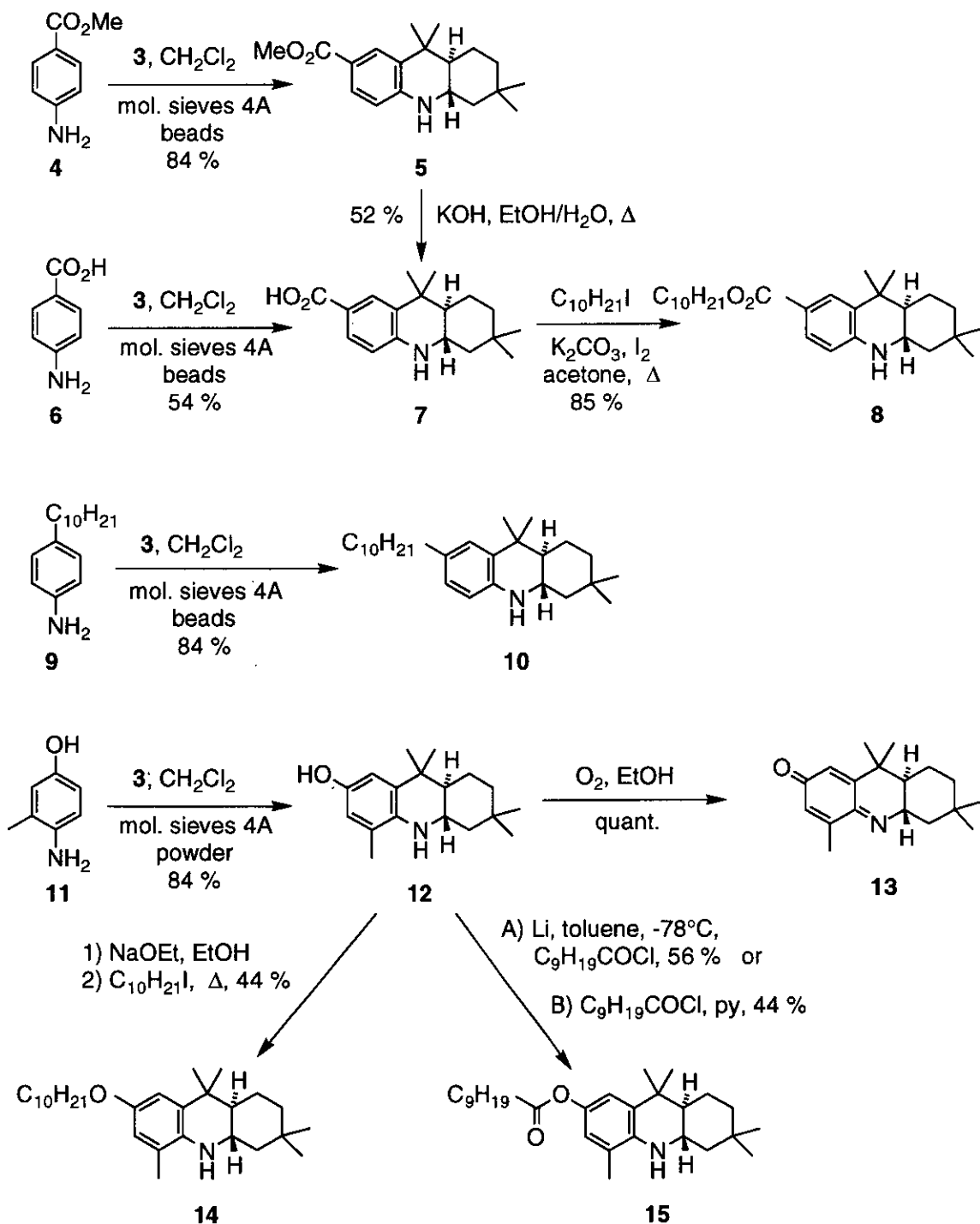
The synthesis of amphiphilic metal complexes has received increasing interest due to the unusual chemical and physical properties of the metal center in an ordered biphasic system.¹ Recent examples are the preparation of Langmuir-Blodgett films from cobalt clusters¹ and ferrocenes,² the synthesis of water-soluble palladium catalysts,³ rotaxanes,⁴ metallo porphyrin containing vesicles,⁵ ultrathin polymer films impregnated with redox catalysts,⁶ the preparation of Langmuir-Blodgett films from ruthenium(II)-bipyridine complexes⁷ and monolayers of amphiphilic ferrocenes with NLO properties.⁸ We thus reasoned, whether η^6 -(octahydroacridine)chromium complexes (**1**) with long alkyl chains could be prepared diastereoselectively. Recently we reported a highly diastereoselective Lewis acid-catalyzed cyclization of *N*-arylimines to octahydroacridines⁹ and their corresponding chromium arene complexes.¹⁰ The reaction can be treated formally as an intramolecular hetero-Diels-Alder reaction¹¹ of a 2-azadiene tethered to a non-activated alkene. In contrast to our previous approach we planned to coordinate the



chromium fragment in the final step of the synthesis of **1**. In order to vary the dipole properties of the polar head group the nonpolar tail should be attached either directly or via an ether or ester spacer. The synthesis of **1** presented another problem, which is common to most of the hetero-Diels-Alder reactions. Although a high level of stereocontrol can be achieved, in many cases the presence of a Lewis acid is required, often in stoichiometric amounts.¹¹ Therefore it would be highly desirable to achieve high diastereoselectivities under heterogeneous catalysis, without the tedious removal of Lewis acids during workup of the reaction mixture. Such a heterogeneous protocol is even more required, when chromatographic purification of the product is difficult, which was anticipated for **1**. A solution to this problem was suggested by the previous unexpected finding, that molecular sieves could induce the cyclization of *-M*-substituted *N*-arylimines.¹² We here report on the use of molecular sieves catalyzed cyclization of *N*-arylimines with both electron-donating and -withdrawing substituents for the synthesis of novel amphiphilic octahydroacridines and their chromium complexes. The physical and structural properties of these compounds are discussed as well.

As described earlier¹² treatment of 4-carbomethoxyaniline (**4**) with 3,7,7-trimethyl-6-octenal (**3**) in the presence of molecular sieve 4A beads gave *trans*-8-carbomethoxyoctahydroacridine (**5**) in 84 % yield ($\geq 99\%$ de) (Scheme 1). In order to prepare an octahydroacridine (**8**) substituted with a fatty acid ester, methyl carboxylate (**5**) was hydrolyzed to the carboxylic acid (**7**). Fortunately, the two step procedure could be circumvented by direct molecular sieve-catalyzed cyclization of 4-aminobenzoic acid (**6**) in 54 %, which again proceeded exclusively *trans* selective. Further conversion to **8** was achieved by reaction of **7** with decyl iodide and catalytic amounts of iodine in the presence of K₂CO₃ in 85 % yield.¹³ 4-Decylaniline (**9**) also cyclized cleanly to **10**. When 4-hydroxy-2-methylaniline (**11**) was employed for the cyclization, it was found that even molecular sieve powder was sufficient to induce the reaction with **3**. As shown in Scheme 1 octahydroacridine (**12**) was isolated in 84 % yield. The different acidity of molecular sieve powder and beads is related to earlier investigations by Roelofs¹⁴ and Quast.¹⁵ They reported that the increased acidity of beads as compared to powder is actually caused by acidic aluminosilicate

Scheme 1



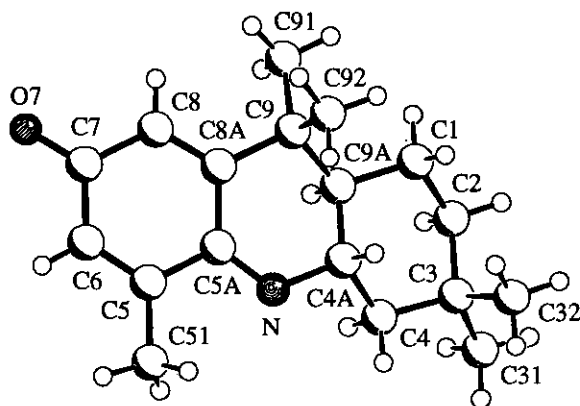
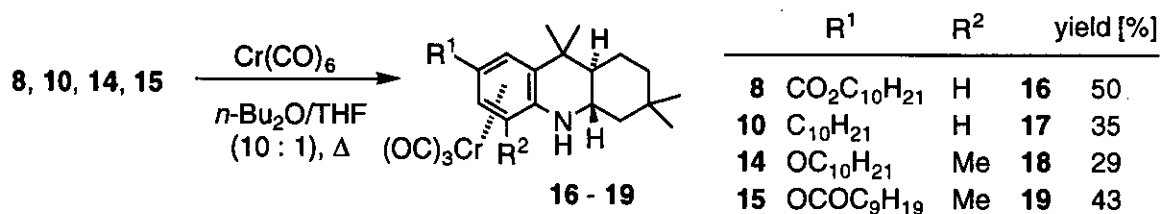


Figure 1 X-ray crystal structure of acridinone (**13**). Selected bond lengths [Å]: N-C(5) 1.280(2), C(5A)-C(8A) 1.484(2), C(5A)-C(5) 1.485(2), C(5)-C(6) 1.328(3), C(6)-C(7) 1.450(3), C(7)-O(7) 1.227 (2), C(7)-C(8) 1.468(3), C(8)-C(8A) 1.336(3).

silicate which is used as binding agent for the preparation of beads from powder. Compound (**12**) turned out to be rather sensitive towards oxygen. If oxygen was not rigorously precluded from the reaction mixture, the quinone imine (**13**) was obtained as a byproduct in 29 % yield. Stirring of **12** in EtOH in an open flask for 2 days gave **13** quantitatively. The X-ray crystal structure determination of acridinone (**13**) proved the *trans* configuration (Figure 1, Table 1).¹⁶ Bond lengths and angles of **13** are typical for a quinoid system.¹⁷ A cyclic voltammogram of **13** in MeCN showed two anodic peaks ($E_{p,a}^1 = -0.911$ V, $E_{p,a}^2 = -0.522$ V) and a cathodic peak ($E_{p,c}^1 = -1.017$ V) indicating a quasi-reversible quinonimine/4-aminophenol redox couple.¹⁸ Conversion of **12** to the ether (**14**) was achieved *via* deprotonation with NaOEt/EtOH and treatment with decyl iodide in 44 % yield. Ester (**15**) could be obtained either *via* acylation of the lithium phenolate (method A, 56 %) or direct acylation in pyridine (method B, 44 %) albeit with lower yield. The uncomplexed octahydroacridine (**15**) displays an intermediate behavior between a conglomerate and a racemate in the solid state, which was found by X-ray crystal structure

Scheme 2



determination (Table 1, Figure 2),¹⁶ that means the enantiomers (of racemic **15**) cocrystallized in an unequal amount (81 : 19) in the unit cell. The octahydroacridines (**8**, **10**, **14** and **15**) were then converted to the chromium arene complexes (**16** - **19**) by using standard conditions, i.e. heating with Cr(CO)₆ in a mixture of *n*Bu₂O/THF (10 : 1) for several hours.¹⁹ Here we were particularly concerned whether the chromium tricarbonyl moiety would be coordinated diastereoselectively or not. Examination of the crude ¹³C-nmr spectra showed that this was indeed the case for **16**, **17** and **19** (diastereomeric ratio >95 : 5). Ether (**18**) gave a second set of signals indicating a minor diastereomer (d.r. 82 : 18). As mentioned above the complexation of the chromium fragment occurred with high diastereoselectivity. However, the X-ray crystal structure determination of **17** and **19** (Table 1, Figures 3,4)^{16,20} indicated that the

Table 1. Experimental data for the structure analyses for **13**, **15**, **17** and **19**

Compound	13	15	17	19
Formula:	C ₁₈ H ₂₅ NO	C ₂₈ H ₄₅ NO	C ₃₀ H ₄₅ CrNO ₃	C ₃₀ H ₄₅ CrNO ₅ • C ₇ H ₈
M _r (g mol ⁻¹):	271.39	427.65	519.67	655.81
a (Å):	6.792(1)	9.724(1)	7.881(1)	9.663(1)
b (Å):	9.175(1)	14.101(2)	9.459(2)	14.382(2)
c (Å):	13.963(2)	19.381(1)	19.459(4)	14.642(2)
α (°):	72.17(1)	90.00	77.32(2)	93.98(2)
β (°):	76.45(1)	101.85(1)	82.30(1)	10.698(2)
γ (°):	80.33(1)	90.00	88.66(2)	106.68(1)
V (Å ³):	800.9(2)	2600.9(5)	1402.4(5)	1838.0(6)
Space group:	P 1bar	P2 ₁ /n	P 1bar	P 1bar
Diffractionmeter:	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
λ (Å):	1.54178	1.54178	0.71073	0.71073
Temperature (°C):	22	-50	-50	-50
Collected reflections:	3559	5619	5279	4037
Independent reflections:	3270	5300	4947	3750
Observed reflections:	2563	4224	2612	3108
Refined parameters:	187	394	324	401
Refinement:	on F ²	on F ²	on F ²	on F ²
R:	0.052	0.050	0.061	0.063
ω R ² :	0.150	0.145	0.148	0.167
Programs used:	SHELX-86, SHELX-93, SCHAKAL-92			

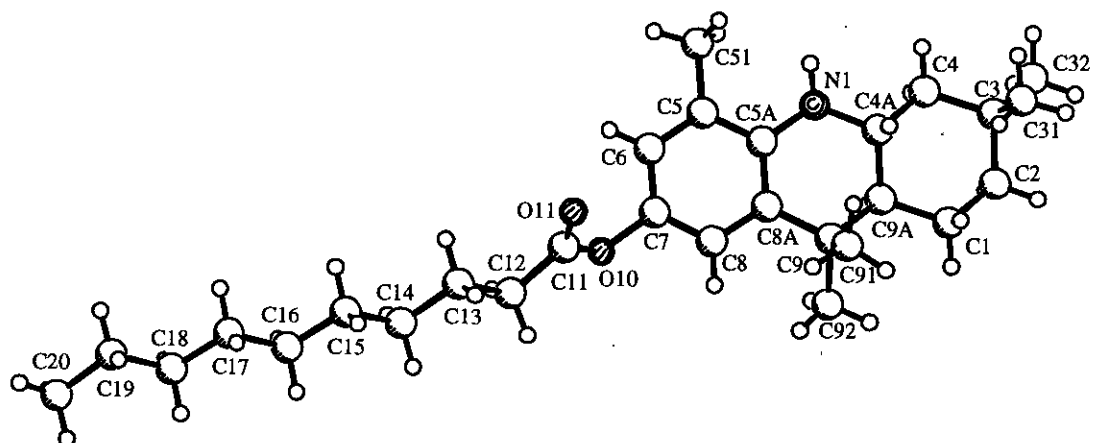


Figure 2 X-ray crystal structure of 15

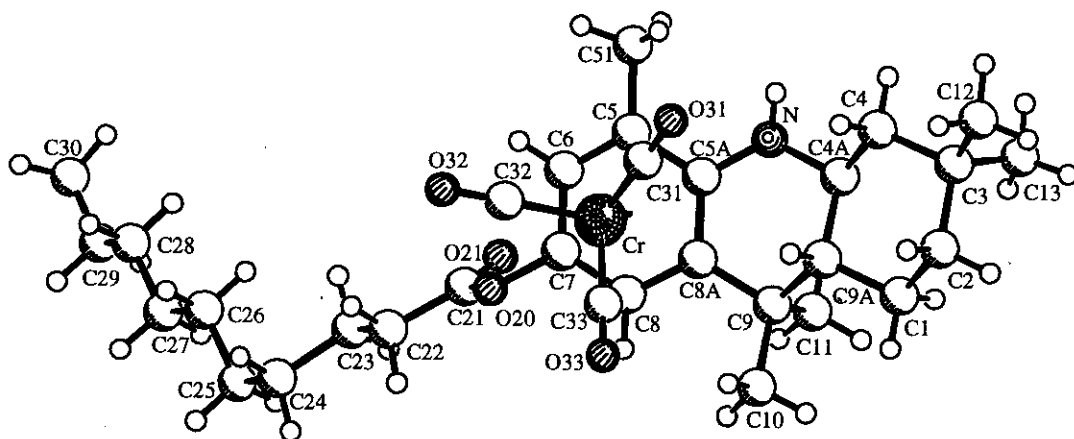


Figure 3 X-ray crystal structure of 17

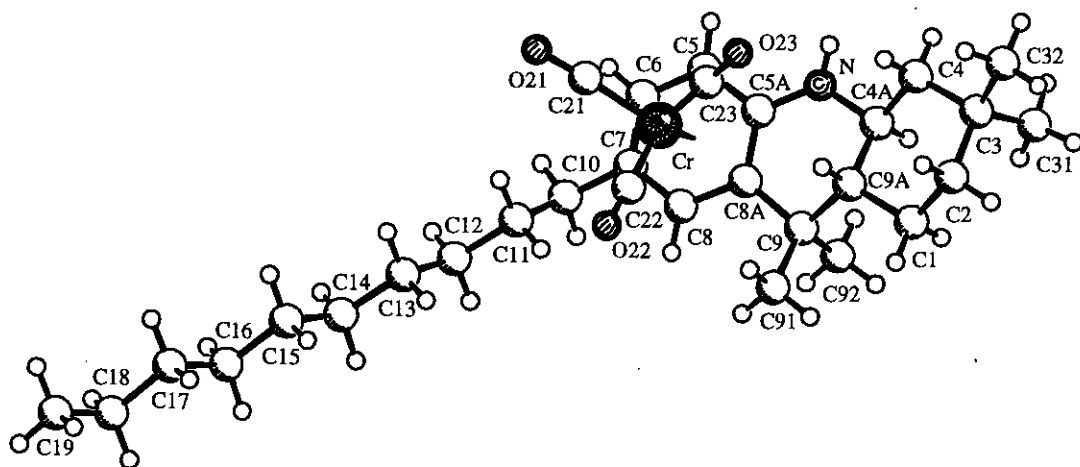


Figure 4 X-ray crystal structure of 19

chromium was attached at the opposite face of the aromatic ring as compared to the octahydroacridine chromium complexes obtained from cyclization of η^6 -(*N*-arylimino)chromium tricarbonyl.¹⁰ Whereas cyclization of an *N*-arylimine already coordinated to a chromium moiety yielded the (4*aSR*,5*RS*,8*aRS*,9*aSR*,10*aRS*)-diastereomer,²¹ the complexation of octahydroacridines (**8**, **10**, **14** and **15**) gave the (4*aSR*,5*SR*,8*aSR*,9*aSR*,10*aSR*)-diastereomers preferably.²² None of the long-chain-substituted octahydroacridines nor their chromium complexes showed mesogenic properties in the polarizing microscope or DSC. All compounds had sharp melting points, although the difference between uncomplexed octahydroacridines and chromium complexes were quite low.

In conclusion, a mild molecular sieve catalyzed cyclization of *N*-arylimines was developed. After further functionalization, the amphiphilic octahydroacridines could be complexed diastereoselectively to chromium tricarbonyl. Although the non-polar tail dominated the physical properties, no mesogenic behavior was observed.

EXPERIMENTAL

General experimental conditions are described elsewhere.⁹ Nmr spectra: Bruker ARX 300 (300 MHz, ¹H; 75 MHz, ¹³C) and a Bruker AC 200 P (200 MHz, ¹H; 50 MHz, ¹³C). Ir spectra: DIGILAB FTS-45-FTIR spectrometer. Melting points: 910 Du Pont Instruments differential scanning calorimeter. Molecular sieve 4A beads (8 - 12 mesh) and molecular sieve 4A powder (maximum grain size 50 μ m) were purchased from ACROS CHIMICA and were activated by flame drying the glass ware together with the molecular sieves immediately before adding the starting materials.

(4*aRS*,9*aSR*)-3,3,9,9-Tetramethyl-1,2,3,4,4*a*,9,9*a*,10-octahydroacridine-7-carboxylic acid (7). **Method A.** A solution of 4-aminobenzoic acid (**6**) (6.53 g, 47.6 mmol), **3** (8.00 g, 47.6 mmol) and molecular sieve 4A beads (20 g) in CH₂Cl₂ (150 ml) was stirred at room temperature for 24 h. After filtration *via* Celite the solvent was removed in vacuo and the crude product was recrystallized from acetone to give 7.37 g (54 %) of colorless crystals. **Method B.** A solution of ester (**5**) (3.00 g, 10.0 mmol) and KOH (1.10 g, 20.0 mmol) in EtOH/H₂O (2 : 1, 30 ml) was refluxed for 4 h. After removal of the solvent in vacuo the residue was diluted in H₂O (20 ml), adjusted to pH 1 with 2 N HCl, extracted with Et₂O (5 x 200 ml), dried over MgSO₄ and evaporated to give 1.50 g (52.2 %) of a colorless solid after recrystallization from acetone; mp 278°C; ir (KBr) 3392, 3200-2400, 2361, 2340, 1656, 943, 918, 837, 775 cm⁻¹; ¹H nmr (300 MHz, DMSO-D₆) δ 7.74 (d, *J* = 2.3 Hz, 1H, 8-H), 7.45 (dd, *J* = 8.3/1.9 Hz, 1H, 6-H), 6.44 (d, *J* = 8.3 Hz, 1H, 5-H), 6.34 (s, 1H, 10-H), 3.16 (ddd, *J* = 11.1/10.9/3.7 Hz, 1H, 4*a*-H), 1.73-0.88 (m, 19H); ¹³C nmr (75 MHz, DMSO-D₆) δ 167.7, 147.8, 128.5, 128.3, 127.7, 116.1, 112.1, 46.6, 46.5, 46.2, 34.2, 32.7, 30.5, 26.5, 25.8, 24.8, 20.4; ms (EI) *m/z* (%) 287 (90) [M⁺], 272 (64), 242 (8), 202 (14), 144 (12), 105 (38), 95 (30), 85

(40), 77 (36), 71 (65), 69 (100), 58 (70), 57 (90), 55 (76). HRms (EI) calcd for $C_{18}H_{25}NO_2$ 287.1885, found 287.1891. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.76; N, 4.87. Found: C, 74.97; H, 8.75; N, 4.98.

Decyl 7-((4aRS,9aSR)-3,3,9,9-Tetramethyl-1,2,3,4,4a,9,9a,10-octahydroacridine)carboxylate (8). A solution of **7** (7.00 g, 24.3 mmol), decyl iodide (6.51 g, 24.3 mmol), iodine (10 mg) and K_2CO_3 (33.5 g, 0.24 mol) in acetone (150 ml) was refluxed for 48 h. After removal of the solvent in vacuo, the solid was dissolved in H_2O (150 ml), extracted with CH_2Cl_2 (4 x 200 ml), dried over $MgSO_4$ and evaporated. Flash chromatography (hexanes/ethyl acetate/ NEt_3 200 : 1 : 5) gave 8.84 g (85 %) of a colorless solid; mp 98°C; ir (KBr) 3368, 1703, 1683, 1604, 826, 771, 740 cm^{-1} ; 1H nmr (300 MHz, C_6D_6) δ 8.25 (d, $J = 1.9$ Hz, 1H, 8-H), 7.94 (dd, $J = 8.3/1.9$ Hz, 1H, 6-H), 6.29 (d, $J = 8.4$ Hz, 1H, 5-H), 4.27 (t, $J = 6.7$ Hz, 2H, 16-H), 3.94 (s, 1H, 10-H), 2.94 (ddd, $J = 10.5/10.0/2.9$ Hz, 1H, 4a-H), 1.63-1.53 (m, 2H, 17-H), 1.50-0.75 (m, 36H); ^{13}C nmr (75 MHz, C_6D_6) δ 167.1, 147.7, 130.0, 129.2, 128.9, 118.5, 113.2, 64.3 (C-16), 47.5, 47.4, 47.1, 39.4, 34.9, 33.1, 32.3, 30.9, 29.9, 29.7, 29.4, 26.7, 26.5, 26.2, 25.2, 23.1, 21.0, 14.4; ms (EI) m/z (%) 427 (82) [M^+], 287 (21), 272 (70), 228 (22), 201 (12), 188 (20), 149 (76), 111 (46), 97 (75), 85 (80), 71 (95), 55 (100); HRms (EI) calcd for $C_{28}H_{45}NO_2$ 427.3450, found 427.3456. Anal. Calcd for $C_{28}H_{45}NO_2$: C, 78.64; H, 10.61; N, 3.28. Found: C, 78.21; H, 10.67; N, 3.45.

(4aRS,9aSR)-7-Decyl-3,3,9,9-tetramethyl-1,2,3,4,4a,9,9a,10-octahydroacridine (10). A solution of *p*-decylaniline (**9**) (467 mg, 2.00 mmol), 3,3,7-trimethyl-6-octenal (**3**) (336 mg, 2.00 mmol) and molecular sieve 4A beads (2.50 g) in CH_2Cl_2 (20 ml) was stirred at room temperature for 7 days. After filtration *via* Celite the solvent was removed in vacuo to give 641 mg (84 %) of a pale brown solid; mp 43°C; ir (KBr) 3395, 1615, 1506, 809, 721 cm^{-1} ; 1H nmr (300 MHz, C_6D_6) δ 7.18 (d, $J = 1.9$ Hz, 1H, 8-H), 6.92 (dd, $J = 8.1/1.9$ Hz, 1H, 6-H), 6.33 (d, $J = 7.9$ Hz, 1H, 5-H), 3.02 (s, 1H, 10-H), 2.96 (ddd, $J = 10.5/10.4/4.1$ Hz, 1H, 4a-H), 2.62 (t, $J = 7.4$ Hz, 2H, 15-H), 1.75-0.83 (m, 38H); ^{13}C nmr (50 MHz, $CDCl_3$) δ 140.9, 131.4, 126.4, 125.6, 121.3, 113.9, 49.0, 47.4, 47.2, 39.3, 35.5, 34.9, 33.0, 32.0, 30.9, 29.6, 29.6, 29.5, 29.4, 27.4, 27.0, 25.1, 22.7, 21.0, 14.1; ms (EI) m/z (%) 383 (60) [M^+], 368 (37), 298 (4), 284 (10), 270 (6), 256 (73), 242 (4), 149 (78), 141 (18), 127 (18), 113 (18), 105 (62), 99 (22), 92 (73), 85 (93), 69 (100), 51 (94). HRms (EI) calcd for $C_{27}H_{45}N$ 383.3552, found 383.3543. Anal. Calcd for $C_{27}H_{45}N$: C, 84.53; H, 11.83; N, 3.65. Found: C, 84.35; H, 12.04; N, 3.73.

(4aRS,9aSR)-7-Hydroxy-3,3,5,9,9-pentamethyl-1,2,3,4,4a,9,9a,10-octahydroacridine (12). A solution of 4-hydroxy-2-methylaniline (**11**) (2.46 g, 20.0 mmol), **3** (3.36 g, 20.0 mmol), powdered molecular sieves 4A (5.00 g) in CH_2Cl_2 (100 ml) were stirred for 48 h at room temperature. After evaporation of the solvent and flash chromatography (hexanes/ethyl acetate/ NEt_3 20 : 1 : 1) 4.60 g (84 %) of a colorless solid was obtained; mp 149°C; ir (KBr) 3600 - 3100, 1675, 1653, 1604, 859, 831, 738 cm^{-1} ; 1H nmr (200 MHz, C_6D_6) δ 6.79-6.65 (m, 1H, 8-H), 6.48-6.35 (m, 1H, 6-H), 3.09-2.95 (m, 2H, 4a-H, 10-H), 1.91 (s, 3H, 13-H), 1.64-0.96 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 1.22 (s, 3H, 14-H), 1.14 (s, 3H, 15-H), 0.96 (s, 3H, 11-H), 0.91 (s, 3H, 12-H); ^{13}C nmr (50 MHz, C_6D_6) δ 148.5, 135.0, 133.1, 123.0, 116.0, 112.0, 48.0, 47.1, 39.7, 39.4, 35.4, 33.2,

30.9, 27.7, 25.1, 21.3, 17.8; ms (EI) m/z (%) 273 (56) [M^+], 258 (46), 228 (18), 200 (28), 188 (40), 167 (22), 144 (31), 91 (42), 85 (38), 73 (84), 56 (100), 55 (88). HRms (EI) calcd. for $C_{18}H_{27}NO$ 273.2093, found 273.2087. Anal. Calcd for $C_{18}H_{27}NO$: C, 79.07; H, 9.95; N, 5.12. Found: C, 79.05; H, 9.95; N, 5.18.

(4aRS,9aSR)-3,3,5,9,9-Pentamethyl-1,2,3,4,4a,9,9a,10-octahydroacridin-7-one (13) was obtained as byproduct during preparation of **12** in the presence of oxygen. 781 mg (29 %) of yellow crystals; mp 87°C; ir (KBr) 1649, 1626, 929, 903 cm^{-1} ; 1H nmr (300 MHz, C_6D_6) δ 6.34 (dq, $J = 2.2/1.4$ Hz, 1H, 6-H), 6.30 (d, $J = 2.2$ Hz, 1H, 8-H), 3.37 (ddd, $J = 11.3/9.4/3.7$ Hz, 1H, 4a-H), 2.20-0.66 (m, 7H, 1-H, 2-H, 4-H, 9a-H), 2.03 (d, $J = 1.4$ Hz, 3H, 13-H), 0.91 (s, 3H, 14-H), 0.84 (s, 3H, 15-H), 0.83 (s, 3H, 11-H), 0.64 (s, 3H, 12-H); ^{13}C nmr (75 MHz, C_6D_6) δ 187.4, 157.4, 149.8, 148.6, 129.7, 125.0, 58.1, 48.0, 39.0, 35.2, 33.0, 31.8, 24.8, 23.6, 22.2, 21.1, 18.2; ms (EI) m/z (%) 271 (23) [M^+], 256 (10), 243 (36), 228 (100), 201 (6), 186 (5); HRms (EI) calcd for $C_{18}H_{25}NO$ 271.1936, found 271.1930. Anal. Calcd for $C_{18}H_{25}NO$: C, 79.66; H, 9.28; N, 5.16. Found: C, 79.25; H, 9.36; N, 5.17.

(4aRS,9aSR)-7-Decyloxy-3,3,5,9,9-pentamethyl-1,2,3,4,4a,9,9a,10-octahydroacridine (14). To a solution of Na (1.20 g, 52.2 mmol) in EtOH (100 ml) were added **12** (6.80 g, 24.9 mmol) in EtOH (20 ml) and then decyl iodide (6.70 g, 25.0 mmol) and the mixture was heated for 16 h at 80°C. Removal of the solvent, followed by hydrolysis with sat. NH_4Cl solution (50 ml), extraction with CH_2Cl_2 (4 x 100 ml), drying over $MgSO_4$, evaporation of the solvent and flash chromatography (hexanes/ethyl acetate/ NEt_3 100 : 1 : 1) gave 4.53 g (44 %) of a pale yellow solid; mp 66°C; ir (KBr) 3398, 1612, 1597, 860, 837 cm^{-1} ; 1H nmr (200 MHz, C_6D_6) δ 7.02 (d, $J = 2.7$ Hz, 1H, 8-H), 6.72 (d, $J = 2.7$ Hz, 1H, 6-H), 3.87 (t, $J = 6.4$ Hz, 2H, 16-H), 3.05 (ddd, $J = 10.9/10.1/4.3$ Hz, 1H, 4a-H), 2.87 (s, 1H, 10-H), 1.98 (s, 3H, 13-H) 1.85-0.85 (m, 38H); ^{13}C nmr (50 MHz, C_6D_6) δ 151.5, 135.8, 132.0, 121.9, 115.3, 111.8, 68.7, 48.1, 47.7, 47.4, 39.5, 35.5, 33.2, 32.3, 30.9, 30.0, 29.9, 29.8, 27.6, 26.5, 25.2, 23.1, 21.3, 17.9, 14.3; ms (EI) m/z (%) 413 (91) [M^+], 398 (54), 342 (11), 272 (83), 258 (64), 144 (32), 91 (43), 83 (80), 71 (100), 69 (72), 57 (61), 51 (80); HRms (EI) calcd for $C_{28}H_{47}NO$ 413.3658, found 413.3664. Anal. Calcd for $C_{28}H_{47}NO$: C, 81.35; H, 11.38; N, 3.39. Found: C, 81.11; H, 11.48; N, 3.49.

(4aRS,9aSR)-7-(3,3,9,9,13-Pentamethyl-1,2,3,4,4a,9,9a,10-octahydroacridinyl) decanoate (15). **Method A**. A solution of **12** (2.73 g, 10.0 mmol) in toluene (50 ml) was treated with lithium powder (100 mg, 14.4 mmol), stirred for 12 h at room temperature and cooled to -78°C. Then was added decanoyl chloride (1.90 g, 10.0 mmol) dropwise over 15 min and stirring was continued for 12 h at -78°C. Then the mixture was poured on ice, extracted with toluene (3 x 50 ml), dried over $MgSO_4$, evaporated and purified by flash chromatography (hexanes/ethyl acetate/ NEt_3 200 : 1 : 5) to give 2.41 g (56 %) of colorless crystals. **Method B**. To solution of **12** (9.15 g, 33.5 mmol) in pyridine (75 ml) was added decanoyl chloride (6.39 g, 33.5 mmol) dropwise over 15 min. After stirring for 2 d at room temperature, 1 N HCl (400 ml) was added, the precipitate was removed by filtration. The residue was azeotropically codistilled (4 x) with toluene (100 ml) and the crude product was

purified as described above to give 6.34 g (44 %) of a colorless solid; mp 97°C; ir (KBr) 3429, 3396, 1756, 1655, 747, 730 cm^{-1} ; ^1H nmr (300 MHz, C_6D_6) δ 7.10 (d, $J = 2.6$ Hz, 1H, 8-H), 6.18 (d, $J = 2.4$ Hz, 1H, 6-H), 3.07-2.96 (m, 2H, 4a-H, 10-H), 2.38 (t, $J = 7.4$ Hz, 2H, 17-H), 1.84 (s, 3H, 13-H), 1.68-1.50 (m, 2H, 18-H), 1.49-0.81 (m, 34H); ^{13}C nmr (75 MHz, C_6D_6) δ 172.2, 142.3, 139.2, 131.4, 130.6, 121.2, 117.5, 47.6, 47.4, 39.5, 35.3, 32.2, 30.9, 29.8, 29.7, 29.3, 27.2, 27.0, 25.8, 25.4, 25.2, 23.1, 21.2, 17.5, 14.3; ms (EI) m/z (%) 427 (20) [M^+], 273 (100), 258 (70), 228 (26), 149 (23), 147 (26), 105 (21), 91 (22), 79 (24), 71 (28), 69 (36); HRms (EI) calcd for $\text{C}_{28}\text{H}_{45}\text{NO}_2$ 427.3450, found 427.3460. Anal. Calcd for $\text{C}_{28}\text{H}_{45}\text{NO}_2$: C, 78.64; H, 10.61; N, 3.28; Found: C, 78.48; H, 10.89; N, 3.09.

General Procedure for the Preparation of Chromium Complexes. A solution of arene (1.00 mmol) and $\text{Cr}(\text{CO})_6$ (220 mg, 1.00 mmol) in *n*-Bu₂O/THF (10 : 1, 20 ml) was refluxed for 24 h. The solvent was removed in vacuo and the crude products were recrystallized.

Decyl tricarbonyl[7-((4*a*RS,9*a*SR)-3,3,9,9,13-tetramethyl-1,2,3,4,4*a*,9,9*a*,10-octahydroacridine)carboxylate]chromium (16). 2.55 g (50 %) of yellow crystals; mp 102°C (pentane/ CH_2Cl_2 9 : 1); ir (KBr) 3408, 3360, 1954, 1878, 1716, 1696, 1560, 1501, 773, 741, 668, 646, 623 cm^{-1} ; ^1H nmr (200 MHz, C_6D_6) δ 6.69 (s, 1H, 8-H), 6.26 (d, $J = 6.7$ Hz, 1H, 6-H), 4.16 (t, $J = 6.4$ Hz, 2H, 16-H), 3.68 (d, $J = 6.7$ Hz, 1H, 5-H), 2.67-2.55 (m, 2H, 4a-H, 10-H), 1.64-0.57 (m, 38H); ^{13}C nmr (50 MHz, C_6D_6) δ 233.9, 166.0, 132.8, 128.5, 101.1, 96.9, 95.3, 81.3, 72.7, 65.5, 47.8, 46.5, 46.4, 38.7, 34.4, 32.7, 32.3, 30.9, 29.9, 29.7, 29.6, 29.2, 26.2, 25.7, 25.4, 25.0, 23.1, 20.7, 14.4; ms (EI) m/z (%) 563 (4) [M^+], 479 (100), 427 (30), 412 (12), 338 (6), 323 (5), 294 (6), 270 (38), 227 (6), 188 (2), 158 (2), 144 (4), 130 (1), 97 (1), 69 (5); HRms (EI) calcd for $\text{C}_{31}\text{H}_{45}\text{NO}_5\text{Cr}$ 563.2703, found 563.2716. Anal. Calcd for $\text{C}_{31}\text{H}_{45}\text{NO}_5\text{Cr}$: C, 66.05; H, 8.05; N, 2.48. Found: C, 63.80; H, 8.04; N, 2.49.

Tricarbonyl[7-((4*a*RS,9*a*SR)-7-decyl-3,3,9,9,13-tetramethyl-1,2,3,4,4*a*,9,9*a*,10-octahydroacridine)chromium (17). 1.38 g (35 %) of yellow crystals; mp 125°C (pentane/ CH_2Cl_2 3 : 1); ir (KBr) 3400, 1941, 1920, 1854, 1817, 1566, 1504 cm^{-1} ; ^1H nmr (200 MHz, C_6D_6) δ 5.57 (s, 1H, 8-H), 5.15 (d, $J = 6.3$ Hz, 1H, 6-H), 3.90 (d, $J = 6.3$ Hz, 1H, 5-H), 2.75-2.61 (m, 2H, 4a-H, 10-H), 2.03 (t, $J = 6.1$ Hz, 2H, 15-H), 1.50-0.70 (m, 38H); ^{13}C nmr (50 MHz, C_6D_6) δ 236.5, 130.5, 101.6, 100.9, 97.3, 96.1, 73.1, 47.7, 46.6, 46.5, 38.9, 34.6, 34.3, 32.8, 32.4, 32.3, 30.9, 30.0, 29.8, 29.6, 26.1, 25.6, 25.1, 23.1, 20.9, 14.3; ms (EI) m/z (%) 520 (25) [M^+], 435 (88), 383 (74), 369 (62), 309 (58), 256 (100), 172 (78), 157 (85), 146 (68), 95 (79), 83 (98), 77 (96), 57 (92); HRms (EI) calcd for $\text{C}_{30}\text{H}_{45}\text{NO}_3\text{Cr}$: 519.2805; found 519.2810. Anal. Calcd for $\text{C}_{30}\text{H}_{45}\text{NO}_3\text{Cr}$: C, 69.34; H, 8.73; N, 2.70. Found: C, 68.92; H, 8.64; N, 2.78.

Tricarbonyl[7-((4*a*RS,9*a*SR)-7-decyloxy-3,3,9,9,13-pentamethyl-1,2,3,4,4*a*,9,9*a*,10-octahydroacridine)chromium (18). 1.20 g (29 %) of yellow crystals; mp 93°C (pentane/ CH_2Cl_2 10 : 1); ir (KBr) 3427, 1940, 1858, 1849, 1557, 1541, 986, 676, 634, 611 cm^{-1} ; ^1H nmr (200 MHz, C_6D_6) δ 5.50 (d, $J = 2.0$ Hz, 1H, 8-H), 5.19 (d, $J = 2.0$ Hz, 1H, 6-H), 3.54 (m, 2H, 16-H), 2.81 (ddd, $J = 11.1/10.8/4.3$ Hz, 1H, 4a-H), 2.59 (s, 1H, 10-H), 1.75-0.63 (m, 41H); ^{13}C nmr (50 MHz, C_6D_6) δ 236.9, 131.5,

102.6, 86.4, 86.1, 84.4, 81.7, 69.9, 48.7, 47.9, 47.5, 46.8, 46.2, 39.0, 38.8, 34.7, 32.7, 32.3, 31.0, 30.0, 29.7, 29.5, 26.3, 25.1, 23.1, 21.1, 17.0, 14.4; ms (EI) m/z (%) 549 (7) [M^+], 465 (100), 413 (46), 324 (14), 309 (6), 272 (26), 258 (5), 149 (11), 123 (15), 111 (20), 95 (29), 57 (48); HRms (EI) calcd for $C_{31}H_{47}NO_4Cr$ 549.2911, found 549.2893. Anal. Calcd for $C_{31}H_{47}NO_4Cr$: C, 67.73; H, 8.62; N, 2.55. Found: C, 66.97; H, 8.60; N, 2.71.

Tricarbonyl[(4aRS,9aSR)-7-(3,3,9,9,13-pentamethyl-1,2,3,4,4a,9,9a,10-octahydroacridinyl)]chromium decanoate (19). 1.73 g (25 %) of yellow crystals; mp 128°C (pentane/ CH_2Cl_2 10 : 1); ir (KBr) 3404, 1943, 1870, 1837, 1751, 1554, 1505, 972, 925, 675, 636 cm^{-1} ; 1H nmr (200 MHz, C_6D_6) δ 5.83 (d, $J = 1.9$ Hz, 1H, 8-H), 5.54 (d, $J = 1.8$ Hz, 1H, 6-H), 2.81-2.71 (m, 2H, 4a-H, 10-H) 2.15 (t, $J = 7.3$ Hz, 2H, 17-H), 1.63-0.63 (m, 39H); ^{13}C nmr (50 MHz, C_6D_6) δ 235.6, 172.5 (C-16), 127.5, 119.6, 100.3, 93.5, 88.7, 84.6, 47.9, 46.7, 46.3, 38.7, 34.6, 34.1, 32.7, 32.2, 31.0, 29.8, 29.6, 29.3, 26.0, 25.3, 25.0, 23.0, 21.0, 16.6, 14.3; ms (EI) m/z (%) 563 (4) [M^+], 479 (73), 427 (10), 324 (12), 273 (100), 258 (22), 216 (5), 174 (7), 155 (4), 95 (4), 83 (5), 69 (10); HRms (EI) calcd for $C_{31}H_{45}NO_5Cr$ 563.2703, found 563.2694. Anal. Calcd for $C_{31}H_{45}NO_5Cr$: C, 66.05; H, 8.05; N, 2.48. Found: C, 66.40; H, 8.25; N, 2.70.

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