The Synthesis of Novel Crown Ethers, Part X*, 4-Propyl-and 3-ethyl-4-methylchromenone-Crown Ethers

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Starting from ethyl propionylacetate, and ethyl 2-ethylacetoacetate we prepared 4-propyl-7,8-, 4-propyl-6,7-, 3-ethyl-4-methyl-7,8- and 3-ethyl-4-methyl-6,7-dihydroxy-2*H*-chromenones which were allowed to react with the bis-dihalides or ditosylates of glycols in DMF/Na_2CO_3 to afford the 6,7- and 7,8-chromenone derivatives of 12-crown-4, 15-crown-4 and 18-crown-6. The products were identified using ir, ^{13}C and ^{1}H nmr, ms and high resolution mass spectroscopy. The cation selectivities of chromenone crown ethers with Li^+, Na^+ and K^+ cations were estimated from the steady state emission fluorescence spectra of free and cation complexed chromenone macrocyclic ethers in acetonitrile.

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Introduction.

Substantial study has been devoted to synthesis, structural and cation binding studies on macrocylic ethers [1-3]. The effect of cations on chromophoric crown ethers investigated using fluorescence spectroscopy has recently been more interesting. Depending on the complexing macrocyclic ether, cations induce changes in triplet energy relative to excited singlet and ground state energies of the luminophore. The chromophoric part of a lumophore also has a chemical structure that transduces the interactions into a marked optical property [4-8].

We have previously synthesised various crown ethers and podands with different chromophore moieties and reported their cation-complex formation stabilities using steady state fluorescence spectroscopy in acetonitrile [9-13]. The macrocyclic ether derivatives of the 3-phenyl, 4-H, 4-methyl-6,7-dihydroxy- as well as -7,8-dihydroxy-coumarins synthesised recently showed selective cation binding effects with steady state fluorescence emission spectroscopy. The reports on macrocycles containing common aromatic groups have shown the essential cation selectivity role using fluorescence spectroscopy [14-16]. Detailed literature and explanation of optical aspects have been given in our earlier paper [13].

The present work deals with the preparation of novel molecules bearing strong chromophore moieties of 4-propyl- and 3-ethyl-4-methyl-chromenone groups which exhibit marked fluorescence intensity changes upon the cation complex formation with Li^+, Na^+ and K^+ perchlorates following the crown ether-cation binding rules [1-8].

Results and Discussion.

Organic Synthesis.

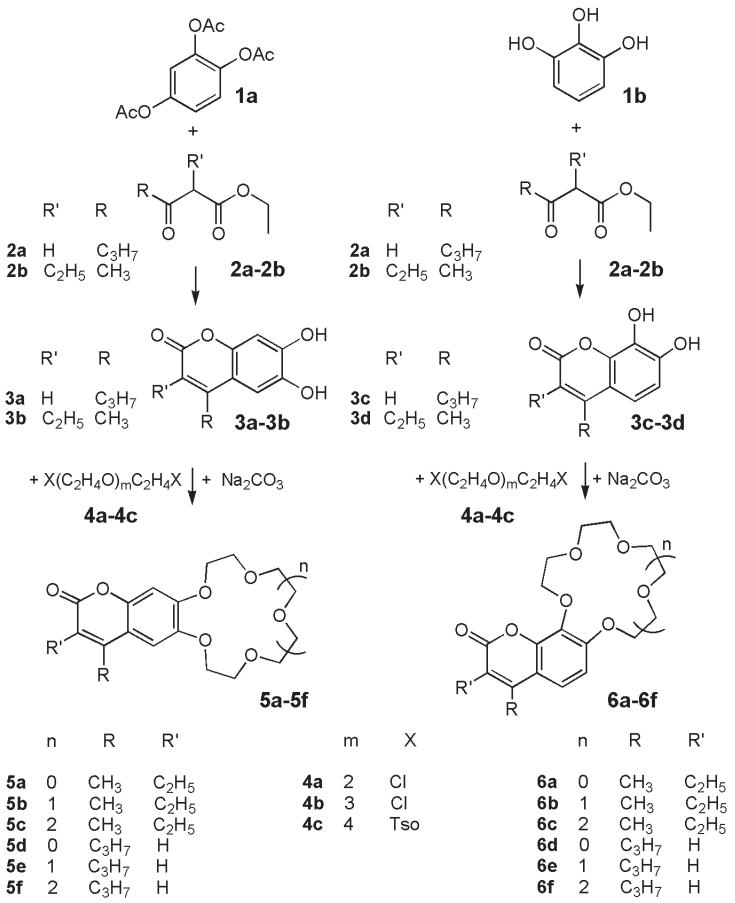
The β-keto ester **2b** was prepared from ethyl acetoacetate with ethyl iodide in THF/Na with 87 % yield. The initial coumarins were prepared *via* Pechmann reactions [17-19] in the presence of relevant Lewis acids. However, the best yields of coumarins **3a**-**3d** (67, 35, 31, 73 % respectively) were prepared from **1a, 1b** and β-ketoesters **2a**, **2b** in the presence of pure CF_3COOH in present work, (Scheme 1). The coumarin formation is rather difficult with R= H, R'= C_3H_7 types of structures, **3a** and **3c,** while the R= C_2H_5, R= CH_3 structures, **3b** and **3d**, formed much more readily even in H_2SO_4 as well as in CF_3COOH. 1,11-Dichloro-3,6,9-trioxaundecane, **4b** were available from our earlier work [8]. Compound **3a** with **4a** and **4c** afforded the crown ethers **5a** and **5c**. The reaction of **3b** with **4a**, **4b** and **4c** afforded the crown ethers **5d**, **5e** and **5f**. Compound **3c** with **4a**, **4b** and **4c** afforded the crown ethers **6a**, **6b** and **6c**. The reaction of **3d** with **4a**, **4b** and **4c** afforded the crown ethers **6d**, **6e** and **6f**, in the presence of Na_2CO_3/DMF at 80-90 °C, Scheme 1. Spectral data and fluorescence purity of the yields are reported.

Cationic Fluorescence spectroscopy Studies.

The emission fluorescence spectra of the chromenone-crowns and their complexes observed are 10^3 times more sensitive as cation sensors compared to those of dibenzocrown ethers without chromophore moieties [4,7-9]. We studied the cation association of 4-alkyl, and 3,4-dialkyl chromenone-crowns in acetonitrile (AN). The 7,8-dioxachromenone crown ethers **6a**-**6f** mostly displayed strong complexation enhanced quenching fluorescence spectra (CEQFS) when they are complexed in AN. This has been observed with other macrocyclics of 4-alkyl-coumarin derivatives due to competition between phosphorescence and fluorescence decay rates of the lumophores [8-10]. 3,4-Dialkyl chromenones, in particular, exhibited strong fluorescence emission intensities with high quantum yield due to the electron-donating role of 3-substituted alkyl groups. The fluorescence effectivities, E_{eff}, of **6b**-**6d** with, Li^+, Na^+ and K^+ perchlorates mostly showed cation selectivities in acetonitrile (Table 1). 6,7-Dioxachromenone crown ethers **5a-5f** displayed, CEQFS, upon cation complexing and the fluorescence of most of the pure macrocycles are not quenched by concentration. The products, in particular, in this work could be evaluated as cation sensi-

tizer, in particular, the 12-crown-4 derivative **5a** displayed a strong fluorescence intensity drop with Li^+, Table 1. However, the 15-crown-5 (**6e**) quenching was less and showed a marked alteration with Li^+ but no effect with Na^+ and K^+ (Table 1).

Scheme 1



	R'	R
2a	H	C_3H_7
2b	C_2H_5	CH_3

	R'	R
3a	H	C_3H_7
3b	C_2H_5	CH_3

	R'	R
3c	H	C_3H_7
3d	C_2H_5	CH_3

	n	R	R'
5a	0	CH_3	C_2H_5
5b	1	CH_3	C_2H_5
5c	2	CH_3	C_2H_5
5d	0	C_3H_7	H
5e	1	C_3H_7	H
5f	2	C_3H_7	H

	m	X
4a	2	Cl
4b	3	Cl
4c	4	Tso

	n	R	R'
6a	0	CH_3	C_2H_5
6b	1	CH_3	C_2H_5
6c	2	CH_3	C_2H_5
6d	0	C_3H_7	H
6e	1	C_3H_7	H
6f	2	C_3H_7	H

EXPERIMENTAL

Solvents and other chemicals were purchased from MERCK unless otherwise cited. Starting chemicals **2a**, **4a** and **4c** were purchased from FLUKA. Compounds **1a** and **1b** were prepared according to ref 8. IR spectra were taken as KBr pellets with a JASCO FT-IR spectrometer, model-5300. High resolution EI Mass spectra were obtained with FISONS instrument, model VG-ZABSPEC. ^{1}H nmr spectra were obtained with a BRUKER spectrometer, model AVANCE-400CPX using TMS as the internal standard. The reported mp's are uncorrected. The steady state fluorescence emission and excitation spectra were recorded using a spectrofluorometer, from JASCO, model FP-750 at room temperature in dry acetonitrile (AN).

Fluorescence Effectivities.

The 1:1 binding selectivities of the macrocycles with K^+, Na^+ and Li^+ perchlorates were estimated as a quantity of the fluorescence effectivity using the data from steady state fluorescence emission spectroscopy. The maximum fluorescence emission intensity of the free chromophore macrocycle I_{max}, and the fluorescence intensity I_o, of the macrocycle in the presence of an equivalent cation concentration $[M_0]$, are obtained at the excitation maximum wavelength, Table 1. The products were used after vacuum drying at room temperature. The cation and cation/macrocycle solutions (1/1 molar ratio of mixtures), of 1.0 x10^{-5} mol/L in AN were placed in 10-mm quartz cells in a thermostated cell compartment at 25 ^{o}C and fluorescence emission intensities were recorded at 10 nm band width [11,13], (see Table 1).

The cation complexing selectivity of the chromophoric crown ethers **5a**, **5c, 5e, 5f** and **6a-6e** were obtained from fluorescence effectivity, E_{eff}, of each macrocycle. This is calculated from quantum yields of free and complexed molecules depending on the intensities of free, I_{max} and complexed lumophore, I_o, according to Eqs 1 and 2, as displayed on Table 1.

$$E_{eff} = (\varphi_o - \varphi_{max}) / \varphi_{max} \quad (1)$$

$$E_{eff} = (I_o - I_{max}) / I_{max} \quad (2)$$

where $I_i = \xi_i C_i l_i \varphi_i$ and ξ_i values of both the free and complexed macrocycles are supposed to be identical to each other to give Eq 2.

Table 1

The Emission and Excitation Maximum, λ_{max} and Intensities, I_{max} and I_o of Free and Complexed Crown Ethers, and Cationic Fluorescence Effectivities, E_{eff} at 25 ^{0}C in AN

C.ether	Emλ_{max}	Exλ_{max}	I_{max}	I_o [Li^+]	I_o [K^+]	I_o [Na^+]	E_{eff} [Li^+]	E_{eff} [K^+]	E_{eff} [Na^+]
5a	341	407	999.0	95.4	855.5	897.7	0.90	0.14	0.10
5c	341	407	811.0	409.0	680.0	633.0	0.50	0.16	0.22
5e	341	412	196.0	95.4	193.0	181.0	0.51	0.02	0.08
5f	345	412	427.0	290.0	372.0	347.0	0.32	0.13	0.19
6a	335	393	22.0	12.7	19.4	15.2	0.42	0.12	0.31
6b	335	400	13.1	3.35	13.1	8.4	0.74	0.00	0.36
6c	335	408	999.0	13.5	9.7	5.9	0.99	0.99	0.99
6d	335	412	76.6	8.4	12.4	6.1	0.89	0.84	0.92
6e	335	411	539.0	213.1	537.5	498.0	0.60	0.00	0.08

2. Organic Procedures.

Ethyl 2-Methylacetoacetate (**2b**).

In a flask (500 mL) dry THF (200 mL), metallic Na (5.0 g, 220 mmol) and ethyl acetoacetate (30 mL, 220 mmol) reacted in few h. Ethyl iodide (35 g, 220 mmol) was added to the mixture gradually and refluxed for 18-20 h. The mixture was acidified, the THF was removed, and the resulting mixture was then extracted with ether and dried with $CaCl_2$. Distilled residue yielded **2b**, 30.0 g (87 %), bp 112 ^{o}C/20 mm; IR (KBr) 3340, 2998, 2880, 1750, 1250, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$ 250 MHz): δ 0.96 (3H, t, CH_3), 1.29 (3H, t, CH_3), 1.91 (2H, q, CH_2), 2.18 (3H, s, CH_3 CO), 3.34 (1H, t, CH), 4.22 (2H, q, CH_2); ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.2, 13.5, 17.0, 49.0, 49.3, 60.9, 166.9, 202.3; ms: m/z 158 (M^+), 143, 116, 88, 73, 43.

6,7-Dihydroxy-4-propyl-2*H*-chromen-2-one (**3a**).

Compound **1a**, (3.15 g, 25 mmol) and **2a**, (Merck, 3.96 g, 25 mmol) and CF_3COOH (20 mL, 99%) were placed in a flask (50 ml) and refluxed for 6 h and kept at -10 ^{o}C overnight. The raw product was filtered, washed with water and dried at vacuum to afford **3a**, 3.72 g (67 %), mp 184 ^{o}C (ether); IR (KBr) 3400, 2980, 1690, 1009 cm^{-1}; ^{1}H NMR ($CDCl_3$ 400 MHz): δ 0.96 (3H, t, CH_3), 1.67 (2H, m, CH_2), 2.63 (2H, t, CH_2), 3.12 (2H, s, 2OH), 6.05 (1H, s, cumH), 6.73 (1H, s, ArH), 7.05 (1H, s, ArH): ^{13}C NMR ($DMSOd_6$ 100 MHz): δ 13.8, 21.4, 33.3, 103.1, 109.4, 109.6, 110.9, 143.0, 148.3, 150.2, 156.6, 160.9: ms; m/z 220 (M^+), 205, 192, 177, 162, 77; for HRMAS Calcd, 220.0736; found, 220.0740.

6,7-Dihydroxy-4-methyl-3-ethyl-2*H*-chromen-2-one (**3b**).

Compound **1a** (3.15 g, 25 mmol) and **2b** (3.96 g, 25 mmol) and CF_3COOH, (20 mL, 99%) were placed in a flask (50 ml), refluxed for 6 h and then kept overnight at -10 ^{o}C. The raw product was collected by filtration, washed with water and dried under vacuum to afford **3b**, 1.90 g (35 %), mp 195 ^{o}C; IR (KBr) 3450, 2980, 1665, 1174, 1009 cm^{-1}; ^{1}H NMR ($CDCl_3$ 400 MHz): δ 1.11 (3H, t, CH_3), 2.35 (3H, s, CH_3), 2.63 (2H, t, CH_2), 3.37 (2H, s, 2OH), 6.04 (1H, s, cumH), 6.73 (1H, s, ArH), 7.02 (1H, s, ArH): ^{13}C NMR ($DMSOd_6$ 100 MHz): δ 13.6, 15.6, 20.3, 101.3, 103.8, 108.4, 110.9, 112.1, 122.9, 142.9, 149.6, 161.4: ms; m/z 220 (M^+), 205, 192, 177, 162, 131: for HRMAS Calcd, 220.0736; found, 220.0735.

7,8-Dihydroxy-4-propyl-2*H*-chromen-2-one (**3c**).

Compounds **1b** (3.15 g, 25 mmol), **2a** (3.96 g, 25 mmol) and CF_3COOH, (20 mL, 99 %) were placed in a flask (50 mL), refluxed for 6 h and kept overnight at -10 ^{o}C. The crystalline raw product was collected by filtration, washed with water and dried at vacuum to yield **3c**, 1.70 g (31 %), mp 198 ^{o}C, [17] (pink crystals, THF); IR (KBr) 3300, 2690, 1685, 1174 cm^{-1}; ^{1}H NMR ($CDCl_3$ 400 MHz): δ 1.00 (3H, t, CH_3), 1.69 (2H, q, CH_2), 2.72 (2H, t, CH_2), 3.20 (2H, s, 2OH), 6.10 (1H, s, cumH), 6.89 (1H, d, ArH), 7.11 (1H, d, ArH): ^{13}C NMR ($DMSOd_6$ 100 MHz): δ 13.7, 21.6, 33.3, 109.4, 112.2, 112.4, 115.4, 132.5, 143.9, 149.4, 157.4, 160.5: ms; m/z 220 (M^+), 205, 191, 177, 162, 77: for HRMAS Calcd, 220.0736; found, 220.0743.

7,8-Dihydroxy-4-methyl-3-ethyl-2*H*-chromen-2-one (**3d**).

Compound **1b** (3.15 g, 25 mmol), **2a**, (3.96 g, 25 mmol) and CF_3COOH (20 mL, 99 %) were refluxed for 6 h and kept overnight at -10 ^{o}C. The crystalline raw product was collected by filtration, washed with water and dried at vacuum to yield **3d**, 4.00 g (73 %), mp 193 ^{o}C; IR (KBr) 3350, 2970, 1676, 1055 cm^{-1}; ^{1}H NMR ($CDCl_3$ 400 MHz): δ 1.11 (3H, t, CH_3), 2.35 (3H, s, CH_3), 2.63 (2H, q, CH_2), 3.47 (2H, s, 2OH), 6.00 (1H, s, cumH), 7.06 (1H, d, ArH), 7.20 (1H, d, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 15.3, 15.8, 22.9, 113.9, 115.9, 117.1, 125.6, 133,5, 143.7, 148,6, 149.6, 163.4: ms; m/z 220 (M^+), 205, 177, 127, 97, 69: for HRMAS Calcd, 220.0736; found, 220.0736.

14-Ethyl-15-methyl-2,3,5,6,8,9-hexahydro-13*H*-[1,4,7,10]tetraoxacyclododecino[2,3-*g*]chromen-13-one (**5a**).

In a reaction flask (100 mL), **3b** (1.10 g, 5.0 mmol), **4a** (0.94 g, 5.0 mmol), Na_2CO_3 (1.06 g, 10.0 mmol) and DMF (25 mL) were placed and heated at 70-80 ^{o}C for 70-80 h while stirring, then acidified (HCl, 2 %, 40 mL) and collected by filtration. The dissolved crude product, dissolved in $CHCl_3$ (25 mL), was purified by column chromatography (Al_2O_3/CH_2Cl_2) to give **5a**, 0.3 g (18 %), mp 95 ^{o}C; IR (KBr) 2940, 1703, 1111, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$ 400 MHz): δ 1.09 (3H, t, CH_3), 2.32 (3H, s, CH_3), 2.63 (2H, q, CH_2), 3.75 (6H, m, $3CH_2$), 3.90 (2H, t, CH_2), 4.16 (4H, m, $2CH_2$), 6.82 (1H, s, ArH), 7.16 (1H, s, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.0, 14.5, 20.8, 69.6, 70.1, 70.3, 70.9, 71.8, 74.2, 103.5, 110.7, 114.9, 125.8, 145.2, 146.8, 148.9, 153.6, 161.8: ms; m/z 334 (M^+), 246 (M^+-$C_4H_8O_2$, 231, 218, 203, 190, 73; for $C_{18}H_{22}O_6$ HRMAS Calcd, 334.1416; found, 334.1416.

20-Ethyl-21-methyl-2,3,5,6,8,9,11,12,14,15-nonahydro-18*H*-[1,4,7,10,13,16]hexaoxacyclo- octadecino[2,3-*g*]chromen-18-one (**5c**).

In a reaction flask (100 mL), **3b** (1.10 g, 5.0 mmol), **4c** (2.51 g,

5.0 mmol) [18], K_2CO_3 (1.38 g, 10.0 mmol) and DMF (25 mL) reacted at 70-80 °C for 70-80 h while stirring. The crude product, treated as described above, was purified by column chromatography (Al_2O_3/CH_2Cl_2) to afford **5c**, 0.20 g (10 %), mp 90 °C; IR (KBr) 2937, 1705, 1110, 762 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.10 (3H, t, CH_3), 2.34 (3H, s, CH_3), 2.64 (2H, q, CH_2), 3.65 (4H, m, C_2H_4O), 3.69 (4H, m, $2CH_2$), 3.74 (4H, m, $2CH_2$), 3.92 (4H, t, $2CH_2$), 4.17 (4H, t, $2CH_2$), 6.75 (1H, s, Ar), 6.97 (1H, s, Ar); ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.0, 14.6, 20.8, 69.1, 69.3, 69.7, 69.8, 70.6, 70.7, 70.8, 70.8, 70.9, 71.0, 101.5, 110.0, 113.7, 125.5, 145.3, 148.2, 152.0, 161.9: ms; m/z 422(M^+), 246(M^+-$C_4H_8O_2$, 233, 203, 190; for $C_{22}H_{30}O_8$ HRMAS Calcd, 422.1941; found 422.1941.

15-Propyl-2,3,5,6,8,9-hexahydro-13*H*-[1,4,7,10]tetraoxacyclododecino[2,3-*g*]chromen-13-one (**5d**).

Compound **3a** (1.10 g, 5.0 mmol), **4a** (0.94 g, 5.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) reacted in DMF (25 mL) at 70-80 °C for 70-80 h while stirring. The crude product, treated as described above, was purified by column chromatography (Al_2O_3/CH_2Cl_2) to afford **5d**, 0.10 g (7 %), mp 115 °C; IR (KBr) 2940, 1725, 1103, 760 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.00 (3H, t, CH_3), 1.64 (2H, m, CH_2), 2.63 (2H, t, CH_2), 3.66 (4H, m, $2CH_2$), 3.82 (4H, t, $2CH_2$), 4.08 (4H, s, $2CH_2$), 5.97 (1H, s, cumH), 6.65 (1H, s, ArH), 6.88 (1H, s, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.9, 21.3, 33.8, 69.1, 69.3, 69.8, 70.7, 70.9, 71.5, 102.5, 108.7, 110.0, 119.9, 154.2, 150.5, 153.6, 155.5, 161.0: ms; m/z 334 (M^+), 246 (M^+-2x44), 231, 218, 203, 188, 73; for $C_{18}H_{22}O_6$ HRMAS Calcd, 334,1416: found 334.1411.

18-Propyl-2,3,5,6,8,9,11,12-octahydro-15*H*-[1,4,7,10,13]pentaoxacyclopentadecino[2,3-*g*]chromen-15-one (**5e**).

Compound **3a** (1.10 g, 5.0 mmol), **4b** (1.15 g, 5.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) reacted in DMF (25 mL) at 70-80 °C for 70-80 h while stirring. The crude product, treated as described above, was purified by column chromatography to afford **5e**, 0.1 g (5 %), mp 100 °C; IR (KBr) 2935, 1720, 1136, 765 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.13 (3H, t, CH_3), 1.69 (2H, m, CH_2), 2.66 (2H, t, CH_2), 3.56 (8H, m, $4CH_2$), 3.82 (4H, m, $2CH_2$), 4.06 (4H, m, $2CH_2$), 6.08 (1H, s, cumH), 6.65 (1H, s, ArH), 6.88 (1H, s, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 14.0, 21.3, 33.8, 69.4, 69.8, 70.4, 71.0, 71.2, 71.4, 71.8, 71.9, 102.3, 108.7, 110.0, 112.2, 146.1, 150.4, 153.5, 155.4, 161.7: ms; m/z 378 (M^+), 334, 246 (M^+-$C_4H_8O_2$), 218, 141, 71. for $C_{20}H_{26}O_7$ HRMAS Calcd, 378.1679; found, 378.1681.

21-Propyl-2,3,5,6,8,9,11,12,14,15-nonahydro-18*H*[1,4,7,10,13,16]hexaoxacyclooctadecino[2,3-*g*]chromen-18-one (**5f**).

Compound **3a** (1.10 g, 5.0 mmol), **4c** (2.51 g, 5.0 mmol) [18] and K_2CO_3 (1.38 g, 10.0 mmol) reacted in DMF (25 mL) at 70-80 °C for 60-70 h while stirring. The crude product, treated as described above, was purified by column chromatography to afford **5f** 0.12g (7 %), mp 85 °C, IR (KBr) 2935, 1720,1130, 850 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.05 (3H, t, CH_3), 1.70 (2H, m, CH_2), 2.65 (2H, t, CH_2), 3.70 (4H, m, $2CH_2$), 3.76 (8H, m, $2CH_2$), 3.94 (4H, t, CH_2), 4.19 (4H, t, CH_2), 6.12 (1H, s, cumH), 6.80 (1H, s, ArH), 7.01 (1H, s, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.9, 21.3, 33.8, 68.8, 69.0, 69.5, 70.1, 70.5, 70.6, 70.6, 70.7, 70.7, 70.8, 101.4, 108.9, 110.9, 111.9, 145.3, 149.7, 152.5, 155.6, 161.3: ms; m/z 422 (M^+), 334, 246 (M^+-$C_4H_8O_2$, 218, 190, 73; for $C_{22}H_{30}O_8$ HRMAS Calcd, 422,1941; found 422,1949.

14-Ethyl-15-methyl-2,3,5,6,8,9-hexahydro-13*H*-[1,4,7,10]tetraoxacyclododecino[2,3-*h*]chromen-13-one (**6a**).

Compound **3d** (1.10 g, 5.0 mmol), **4a** (0.94 g, 5.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) and DMF (25 mL) treated as described above to afford **6a**, 0.36 g (18 %), mp 120 °C; IR (KBr) 2990, 1710, 1450, 1150, 750 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.11 (3H, t, CH_3), 2.35 (3H, s, CH_3), 2.63 (2H, q, CH_2), 3.83 (6H, m, $3CH_2$), 3.96 (2H, t, CH_2), 4.20 (2H, t, CH_2), 4.35 (2H, t, CH_2), 6.82 (1H, d, Ar), 7.23 (1H, d, Ar): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.1, 14.6, 20.8, 69.4, 69.7, 69.9, 70.3, 70.6, 74.9, 109.9, 115,6, 119.0, 125.2, 136.0, 145.4, 146.3, 153.6, 160.2: ms; m/z 334 (M^+), 246 (M^+-2x44), 236, 203; for $C_{18}H_{22}O_6$ HRMAS Calcd, 334.1416; found, 334.1413.

17-Ethyl-18-methyl-2,3,5,6,8,9,11,12-octahydro-15*H*-[1,4,7,10,13]pentaoxacyclopentadecino[2,3-*h*]-chromen-15-one (**6b**).

Compound **3d** (1.10 g, 5.0 mmol), **4b** (1.15 g, 5.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) and DMF (25 mL) treated as described above to afford **6b**, 0.08 g (4 %), mp 105 °C; IR (KBr) 2985, 1725, 1107, 770 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.11 (3H, t, CH_3), 2.35 (3H, s, CH_3), 2.63 (2H, q, CH_2), 3.91 (8H, m, $2CH_2$), 4.01 (4H, m, $2CH_2$), 4.27 (2H, tCH_2), 4.37 (2H, t, CH_2), 7.06 (1H, d, ArH), 7.20 (1H, d, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.1, 14.5, 20.7, 69.3, 69.7, 69.9, 70.2, 70.6, 71.4, 72.0, 74.8, 109.9, 115.6, 119.0, 125.2, 136.0, 145.4, 146.4, 153.6, 160.2 ms; m/z 378 (M^+), 246 (M^+-$C_4H_8O_2$), 218, 196, 73; for $C_{20}H_{26}O_7$ HRMAS Calcd, 378.1679: found 378.1672.

20-Ethyl-21-methyl-2,3,5,6,8,9,11,12,14,15-nonahydro-18*H*-[1,4,7,10,13,16]hexaoxacyclooctadecino[2,3-*h*]-chromen-18-one (**6c**).

Compound **3d** (1.10 g, 5.0 mmol), **4c** (2.51 g, 5.0 mmol) [18] and K_2CO_3 (1.38 g, 10.0 mmol) and DMF (25 mL) treated as described above to afford **6c**, 0.48 g (23 %), mp 78 °C; IR (KBr) 2945, 1700, 1105, 760 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.11 (3H, t, CH_3), 2.37 (3H, s, CH_3), 2.60 (2H, q, CH_2), 3.69 (8H, m, $4CH_2$), 3.75 (4H, m, $2CH_2$), 3.90 (2H, t, CH_2) 3.97 (2H, t, CH_2), 4.19 (2H, t, CH_2), 4.28 (2H, t, CH_2), 6.83 (1H, d, ArH), 7.26 (1H, d, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.1, 14.5, 20.8, 68.6, 69.1, 69.9, 70.0, 70.1, 70.2, 70.5, 70.7, 70.8, 73.4, 108.7, 115,6, 118.9, 125.2, 135.3, 145.4, 146.3, 153.5, 160.2: ms; m/z 422 (M^+), 334, 246 (M^+-$C_4H_8O_2$), 231, 218, 190, 73; for $C_{22}H_{30}O_8$ HRMAS Calcd, 422.1941; found 422.1951.

15-Propyl-2,3,5,6,8,9-hexahydro-13*H*-[1,4,7,10]tetraoxacyclododecino[2,3-*h*]chromen-13-one (**6d**).

Compound **3c** (1.10 g, 5.0 mmol), **4a** (0.94 g, 5.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) and DMF (25 mL) treated as described above to afford **6d**, 0.39 g (23 %), mp 72 °C; IR (KBr) 2935, 1725, 1107, 770 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.02 (3H, t, CH_3), 1.71 (2H, m, CH_2), 2.67 (2H, t, CH_2), 3.80 (4H, s, $2CH_2$), 3.95 (4H, m, $2CH_2$), 4.19 (2H, t, CH_2), 4.28 (2H, t, CH_2), 6.12 (1H, s, cumH), 6.80 (1H, d, ArH), 7.10 (1H, d, ArH)): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.9, 21.5, 33.8, 69.4, 69.6, 70.2, 70.5, 70.6, 71.9, 109.9, 110.6, 114.2, 119.0, 136.4, 147.9, 154.7, 156.1, 160.4: ms; m/z 334(M^+), 306, 246 (M^+-$C_4H_8O_2$), 231, 218, 203; for $C_{18}H_{22}O_6$ HRMAS Calcd, 334.1416; found 334.1418.

18-Propyl-2,3,5,6,8,9,11,12-octahydro-15*H*-[1,4,7,10,13]pentaoxacyclopentadecino[2,3-*h*]chromen-15-one (**6e**).

Compound **3c** (1.10 g, 5.0 mmol), **4b** (1.15 g, 5.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) and DMF (25 mL) treated as described above to afford **6e**, 0.18 g (10 %), mp 113 °C; IR (KBr) 2935, 1728, 1105, 770 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.06 (3H, t, CH_3), 1.72 (2H, m, CH_2), 2.67 (2H, t, CH_2), 3.80 (8H, m, $4CH_2$), 3.89 (4H, m, $2CH_2$), 4.19 (2H, t, CH_2), 4.37 (2H, t, CH_2), 6.11 (1H, s, cumH), 6.81 (1H, d, ArH), 7.20 (1H, d, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 14.0, 21.4, 34.1, 69.0, 69.4, 70.0, 70.6, 70.8, 71.0, 71.4, 71.6, 109.6, 110.8, 113.6, 119.4, 135.9, 147.7, 155.6, 157.0, 161.0: ms: m/z 378 (M^+), 334, 246 (M^+-$C_4H_8O_2$) 218, 141, 71 for $C_{20}H_{26}O_7$ HRMAS Calcd, 378.1679; found 378.1684.

21-Propyl-2,3,5,6,8,9,11,12,14,15-nonahydro-18*H*-[1,4,7,10,13,16]hexaoxacyclooctadecino[2,3-*h*]-chromen-18-one (**6f**).

Compound **3c** (1.10 g, 5.0 mmol), **4c** (2.51 g, 5.0 mmol) [18] and K_2CO_3 (1.38 g, 10.0 mmol) and DMF (25 mL) treated as described above to afford **6f**, 0.10 g (6 %), mp 110 °C; IR (KBr) 2943, 1724, 1100, 846 cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 1.00 (3H, t, CH_3), 1.69 (2H, m, CH_2), 2.64 (2H, t, CH_2), 3.65 (4H, m, $2CH_2$), 3.74 (8H, m, $4CH_2$), 3.94 (2H, t, CH_2), 3.98 (2H, t, CH_2), 4.18 (2H, t, CH_2), 4.28 (2H, t, CH_2), 6.09 (1H, s, cumH), 6.83 (1H, d, ArH), 7.26 (1H, d, ArH): ^{13}C NMR ($CDCl_3$ 100 MHz): δ 13.9, 21.5, 33.8, 69.0, 69.4, 70.2, 70.6, 70.7, 70.8, 70.9, 71.8, 71.9, 72.9, 109.6, 111.0, 114.2, 119.1, 135.6, 148.1, 154.5, 155.2, 160.9: ms; m/z 422, 334, 246 (M^+-$C_4H_8O_2$), 218, 190, 73. for $C_{22}H_{30}O_8$ HRMAS Calcd, 422.1941; found, 422.1940.

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