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3-Phenyl- and 3-(p-methoxyphenyl)-7,8-dihydroxy and -6,7-dihydroxychromenones were prepared from ethyl 3-oxo-2-phenylpropanoate, ethyl 3-oxo-2-(4-methoxyphenyl)-propanoate and the trihydroxy benzenes in H₂SO₄. 3-Aryl-7,8- and 3-aryl-6,7-dihydroxy-2H-chromenones reacted with the bis-dihalides of polyglycols in DMF/MeCO₃ to afford 12-Crown-4, 15-Crown-4 and 18-Crown-6-chromenones. The products were identified with IR, ¹H NMR, low and high resolution mass spectroscopy and elemental analysis. Some 1:1 cation association constants, K_b, of the 3-phenyl chromenone crown ethers with Li⁺, Na⁺, K⁺ and Rb⁺ cations were studied by steady state emission fluorescence spectroscopy; K_b chromenone-crown complexes displayed crown ether-cation binding selectivity rules properly in acetonitrile.

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Introduction.

Macrocyclic ethers have been used to estimate cationic recognition and selective cation binding with different physical methods [1-3]. The effect of the cation on the chromophore crown ethers utilised fluorescence spectroscopy since the binding of cations mostly induce changes in triplet energy relative to excited singlet, S₁ → T₁ and ground state T₁ → S₀ energies of the chromophore moieties [4-7].

We have recently synthesised various crown ethers with different chromophore moieties and reported their cationic interactions using steady state fluorescence spectroscopy in acetonitrile [8-10]. The crown ether derivatives of the 4-H and 4-methyl-6,7-dihydroxy- and -7,8-dihydroxycoumarins displayed the binding effect of alkali cations on the fluorescence emission spectra. They exhibited good agreements on the cation radii and the macrocyclic molecule size as reported [8-10]. The chromophore ethers were mostly capable of displaying the effect of the cation *via* UV-VIS spectra due to the restriction on the π-electron flow [11]. The reports of Sammes *et al* [12], and Rodriguez-Ubis *et al* [13], on such structures have shown the importance of the synthesis and cation recognition role of chromofluorogenic compounds. Detailed information, on the literature was also given in our recent report [14].

The present work deals with the preparation of the novel crown ethers bearing 3-phenylchromenone moieties, which were studied with fluorescence spectroscopy to investigate cation complex formation with Li⁺, Na⁺, K⁺, and Rb⁺ perchlorates [8-11].

Results and Discussion.

Organic Synthesis.

Starting products of ethyl phenyl acetate, **1f** and ethyl (4-methoxyphenyl) acetate **1g**, were prepared from ethyl format reacting with ethyl phenyl acetate and ethyl

(4-methoxyphenyl) acetate *via* Claisen condensation. The 6,7-dihydroxychromenones, **2a** and **2b** were prepared from **1a** reacting with **1f** and **1g**. 7,8-Dihydroxychromenones, **2c** and **2d** were prepared from **1b** reacting with **1f** and **1g** in concentrated H₂SO₄, Scheme 1. The chromenone-crown ethers were obtained by cyclic condensation of the *o*-dihydroxy-chromenones with the bisdihalides and bisditosylates of polyglycols.

Namely, **2a** reacted with **1c**, **1d** and **1e** to afford the crown ethers, **3a**, **3b** and **3c**. Compound **2c** reacted with **1c**, **1d** and **1e** to afford the crown ethers, **4b**, **4c** and **4d**. Accordingly, **2d** reacted with **1c**, **1d** and **1e** to afford the crown ethers, **4d**, **4e** and **4f**, in the presence of Na₂CO₃/DMF, Scheme 1. The full spectral data of the original products are given in the experimental part while the known compounds are presented with just NMR data.

Cationic Fluorescence Measurements.

The cation binding constants, K_b of chromenone-crowns with Li⁺, Na⁺, K⁺, and Rb⁺ perchlorates obtained according to Equations 1-3 were found to be rather interesting. 3-Phenylchromenones exhibit strong fluorescence emission intensities due to their high quantum yields.



$$K_b = [M^+L]/[L][M^+] \quad (2)$$

$$(I_x - I_0)/(I_{max} - I_x) = K_b [M_0] \quad (3)$$

The association constants K_b, estimated from the emission fluorescence spectra of the chromenone-crown complexes displayed ether-cation binding selectivity rules in acetonitrile (AN), Table 1. However, 7,8-dioxa derivatives have exhibited CEFS upon cation complexing while the 6,7-dioxa-chromenones gave CEQFS as they are complexed in AN. Similar behaviours were also observed from other derivatives of such chromophore structures in our earlier studies [8-10].

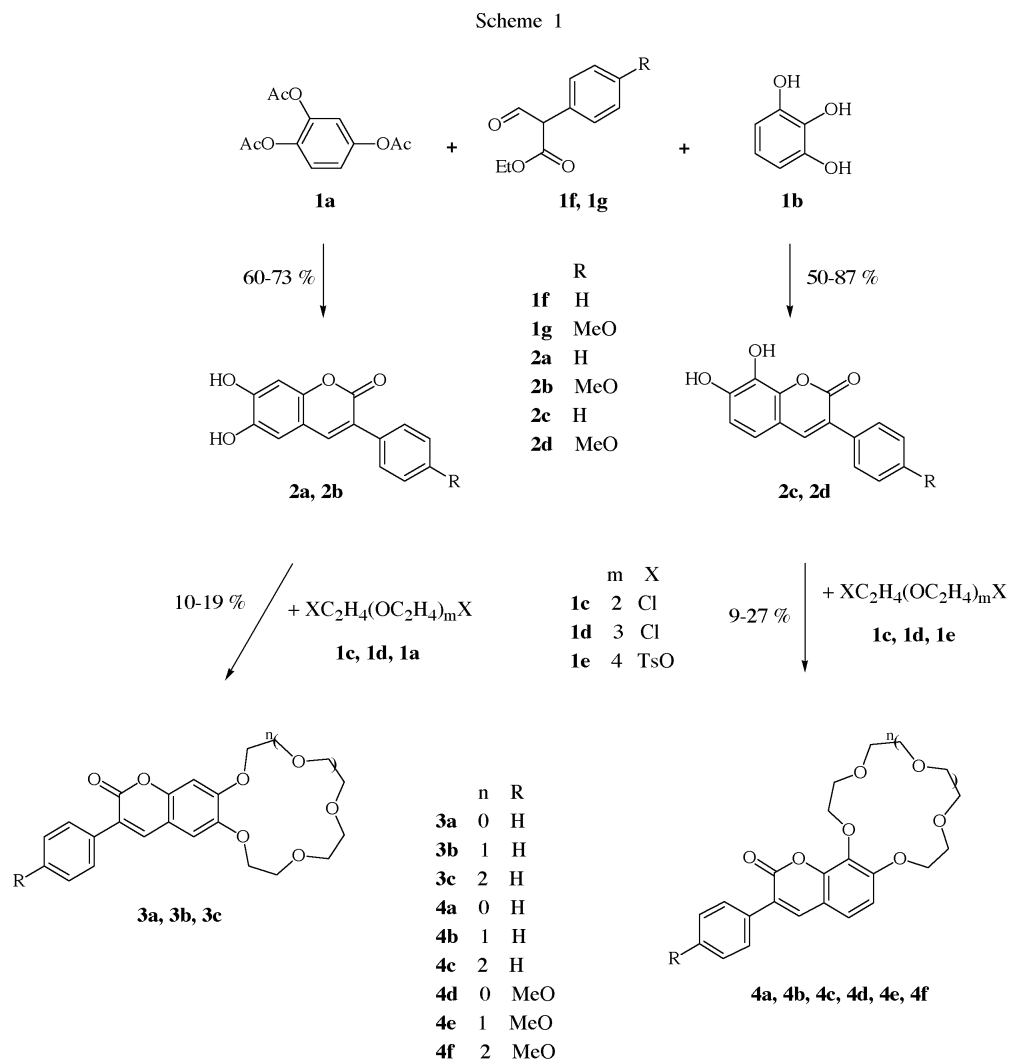


Table 1
The Fluorescence Properties and 1:1 Association, $\ln K_b$, of Crown Ethers at 25 °C in AN

Compound	λ_{ex}	λ_{em}	I_0	I_{max}	Cat.	$\ln K_b$	ΔG (kJ/mol)
3a	381	444	550	50	Li ⁺	3.75	9.2
	381	444	550	50	Na ⁺	4.39	10.8
3b	370	443	870	500	Na ⁺	6.55	16.2
	370	443	865	50	K ⁺	5.65	13.9
3c	350	440	888	700	Na ⁺	6.95	15.7
	350	443	930	690	K ⁺	7.64	18.8
	350	443	896	770	Rb ⁺	8.36	20.6
4a	367	425	270	90	Li ⁺	6.25	15.4
	367	425	295	90	Na ⁺	6.28	15.5
4b	367	425	88	266	Li ⁺	6.27	15.5
	367	425	101	280	Na ⁺	7.92	19.5
	367	425	110	180	K ⁺	7.51	18.5

EXPERIMENTAL

The starting chemicals were from MERCK or FLUKA unless otherwise cited. Initial compounds, **1c** - **1d** were available from our earlier studies [8-11]. IR spectra were taken as KBr pellets with a JASCO FT-IR spectrometer, model-5300. High resolution EI Mass spectra were obtained with FISIONS instrument, model VG-ZABSPEC. ¹H NMR spectra were obtained with a BRUKER spectrometer, model AVANCE-400CPX and TMS was the internal standard. All mp reported are uncorrected. Combustion analyses were acquired with a LECO-932 CHN analyser. The steady state fluorescence emission spectra were recorded with a JEOL spectrofluorometer, model FP-750 using the standard software at 25 °C.

The 1:1 binding constants, K_b , were estimated according to the method of de Silva *et al.*, [7] using the equation, $K_b [M_o] = [I_x - I_o] / [I_{max} - I_x]$ from the data of steady state fluorescence emission spectroscopy. The intensity of the free (uncomplexed) macrocycle is I_o and the I_x , is the fluorescence peak intensity of a crown ether in the presence of any cation concentration, $[M_o]$. I_{max} is obtained in the presence of excess of a cation concentration. The solutions of the cations in dry CH₃CN, (5.0.10⁻³ mol/L) were added stepwise to a stirred 2.00 mL solution of the macrocyclic ether, (2.5.10⁻⁴ mol/L) in dry CH₃CN in a 10-mm quartz cell placed in the spectrophotometer cell compartment. The $[I_x - I_o] / [I_{max} - I_x]$ values are plotted versus $[M_o]$ from the recorded intensity data. The slope of the least squared line gives the binding constant, K_b , (± 0.08). However, only the behaviour of compounds **3a-3c** and **4a, 4b** have been reported due to the limited solubility of others in AN.

Ethyl 3-Oxo-2-phenylpropanoate (**1f**).

A solution of dry ether (200 ml) methylformat (24.5 g, 410 mmol), ethyl phenyl acetate (76.8 g, 400 mmol) and Na (9.45 g, 410 mmol) were mixed and heated for 24 hours. The mixture was washed with water, dried (Al₂O₃) and distilled to give (**1f**), 58.0 g (30 %), bp 80 °C/0.05 torr-; IR (KBr) 3020 (Ph), 1720 (C=O) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 1.31 (t, 3H, OCH₃), 4.25 (d, H, CH), 4.31 (q, 2H, OCH₂), 7.38 (m, 3H, Ar), 7.49 (d, 2H, Ph), 12.1 (d, 1H, CHO).

Ethyl 2-(4-Methoxyphenyl)-3-oxopropanoate (**1g**).

A solution of dry ether (200 mL) methylformat (12.2 g, 205 mmol), ethyl (4-methoxyphenyl) acetate (44.4 g, 200 mmol) and Na (4.75 g, 205 mmol) were refluxed for 24 hours. The solution was washed with water, dried (Al₂O₃) and the ether was evaporated. The distilled residue yielded (**1g**), 17.0 g (38 %), bp 120 °C/0.05 torr-; IR (KBr) 3030 (Ph), 2890 (CH₃), 1735 (C=O), 1150 (CO) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 1.31 (t, 3H, CH₃), 3.77 (s, 3H, OCH₃), 4.31 (q, 2H, OCH₂), 4.26 (d, H, CH), 6.86 (d, 2H, ArH), 7.20 (d, 2H, ArH), 11.90 (d, 1H, CHO).

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

1,2,4-Triacetoxybenzene, **1a** (10.5 g, 62.5 mmol), **1f** (12 g, 62.5 mmol) and H₂SO₄ (40 mL, 85 %) were heated for 3 hours and cooled then poured into a water-ice mixture. The filtered raw product was dried and dissolved in hot methanol (100 mL) and boiled with the added charcoal then filtered to give (**2a**), 11.7 g (73 %), mp 258 °C (yellowish crystals, acetone-); IR (KBr) 3280

(OH), 1700 (C=O), 1450 (CH), 1190 (CO) cm⁻¹; ¹H NMR (acetone-d₆, 400 MHz): δ 6.78 (s, H, ArH), 6.89 (s, H, ArH), 7.42 (m, 3H, ArH), 7.67 (d, 2H, ArH), 7.69 (s, H, cumH); ms: m/z 254 (M⁺), 226 (M⁺-28), 152 (M⁺-102), 141 (M⁺-113), 113.

Anal. Calcd for C₁₅H₁₀O₄: C, 70.86; H, 3.96. Found C, 70.81; H, 4.01

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

1,2,4-Triacetoxybenzene, **1a** (4.2 g, 25 mmol), **1g** (5.5 g, 25 mmol) and H₂SO₄ (10 mL, 85 %) were heated for 2 hours to afford (**2b**), 4.26 g (60 %), mp 256 °C (pink powder, methanol); IR (KBr) 3400 (OH), 1700 (CO), 1500 (CH), 1180 (CO) cm⁻¹; ¹H NMR (acetone-d₆, 400 MHz): δ 3.60 (s, 3H, OCH₃), 6.91 (d, 2H, ArH), 7.18 (d, H, ArH), 7.60 (d, 2H, ArH), 7.68 (s, H, cumH); ms: m/z 284 (M⁺), 256 (M⁺ - 28), 155.

Anal. Calcd for C₁₆H₁₂O₅: C, 67.60; H, 4.25. Found C, 67.55; H, 4.19

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

A mixture of pyrogallol, **1b** (5.25 g, 42 mmol), ethyl α -formyl acetate, **1f** (8.0 g, 42 mmol) and H₂SO₄ (20 mL, 95 %) were heated at 85 °C for one hour to afford (**2c**), 9.0 g (87 %), mp 186 °C (acetone); IR (KBr) 3300 (OH), 1680 (C=O), 1280 (C-H), 1160 (CO) cm⁻¹; ¹H NMR (acetone-d₆, 400 MHz): δ 6.89 (s, H, Ar), 7.12 (s, H, ArH), 7.18 (m, 3H, Ph), 7.69 (d, 2H, Ph), 7.71 (s, H, cumH), 8.00 (s, 2H, OH); ms: m/z 254 (M⁺), 226 (M⁺-28), 152 (M⁺-102), 141 (M⁺-113), 113.

Anal. Calcd for C₁₅H₁₀O₄: C, 70.86; H, 3.96. Found C, 70.80; H, 3.98

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

A mixture of pyrogallol, **1a** (1.7 g, 14 mmol), **1g** (2.8 g, 14 mmol) and H₂SO₄ (10 mL, % 85) was heated at 85 °C for one hour then poured into the ice-water. It was filtered, dried and dissolved in boiling methanol with charcoal then filtered and dried to give (**2d**), 2.0 g (50 %), mp 176 °C (acetone); IR (KBr) 3491 (OH), 2872 (CH), 1722 (C=O), 1120 (C-O) cm⁻¹; ¹H NMR (acetone-d₆, 400 MHz): δ 3.53 (s, 3H, OCH₃), 6.85 (d, 2H, ArH), 6.97 (d, 2H, ArH), 7.10 (d, 2H, ArH), 7.95 (s, 2H, OH); ms: m/z 284 (M⁺), 256 (M⁺ - 28), 155.

Anal. Calcd for C₁₆H₁₂O₅: C, 67.60; H, 4.25. Found C, 67.65; H, 4.20

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

Compound **1c** (3.80 g, 20 mmol), Na₂CO₃ (4.25 g, 40 mmol), DMF (45 mL) and **2a** (5.1 g, 20 mmol) were heated at 80-90 °C for 36 hours while stirring, then acidified with HCl (2 %, 45 mL) and filtered, dried then dissolved in CHCl₃ filtered and dried on Al₂O₃. The residue was purified by column chromatography (Al₂O₃/CH₂Cl₂) to give (**3a**), 1.40 g (19 %), mp 148 °C (methanol); IR (KBr) 2990 (CH₂), 1720 (C=O), 1280 (CH), 1110 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.81 (s, 4H, 2OCH₂), 3.86 (t, 2H, OCH₂), 3.96 (t, 2H, OCH₂), 4.24 (m, 4H, 2OCH₂), 6.91 (s, H, ArH), 7.15 (s, H, ArH), 7.18 (m, 3H, Ph), 7.69 (d, 2H, Ph), 7.71 (s, H, cumH); ms: m/z 368 (M⁺), 280 (M⁺-C₄H₈O₂), 196, 168; For C₂₁H₂₀O₆ HRMAS Calcd. 368.125989; Found. 368.125643.

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

Compound **1d** (4.60 g, 20 mmol), Na₂CO₃ (4.25 g, 40 mmol), DMF (45 mL) and **2a** (5.1 g, 20 mmol) treated as outlined above to afford (**3b**), 1.23 g (15 %), mp 203 °C (acetonitril); IR (KBr) 2870 (CH₂), 1714 (C=O), 1278 (C-H), 1130 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.78 (s, 8H, 4CH₂), 3.96 (t, 4H, 2CH₂), 4.20 (m, 4H, 2OCH₂), 6.84 (s, H, ArH), 6.95 (s, H, ArH), 7.43 (m, 3H, Ph), 7.70 (d, 2H, Ph), 7.72 (s, H, cumH): ms: m/z 412 (M⁺), 280 (M⁺-C₆H₁₂O₃), 225, 199, 140; For C₂₃H₂₄O₇ HRMAS Calcd. 412.152203; Found. 412.149698.

20-Phenyl-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 (**3c**).

Compound **1e** (2.74 g 10 mmol), K₂CO₃ (2.76 g, 20 mmol), DMF (30 mL) and **2a** (2.55 g, 10 mmol) treated as described above to afford (**3c**), 0.49 g (10 %), mp 162 °C (ether); IR (KBr) 2890 (CH₂), 1720 (C=O), 1280 (C-H), 1120 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.68 (s, 4H, 2OCH₂), 3.72 (m, 4H, 2OCH₂), 3.77 (m, 4H, 2OCH₂), 3.95 (m, 4H, OCH₂), 4.20 (m, 4H, ArH) 6.83 (s, H, ArH), 6.93 (s, H, ArH), 7.40 (m, 3H, Ph), 7.69 (d, 2H, Ph), 7.71 (s, H, cumH): ms: m/z 456 (M⁺), 280 (M⁺-C₈H₁₆O₄), 196, 140; For C₂₅H₂₈O₈ HRMAS Calcd. 456.178418; Found. 412.176691

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

Compound **1c** (3.80 g, 20 mmol), Na₂CO₃ (4.25 g, 40 mmol), DMF (45 mL) and **2c** (5.1 g, 20 mmol) treated as described above to afford (**4a**), 1.61 g (22 %), mp 177 °C (acetonitril); IR (KBr) 2825 (CH₂), 1710 (C=O), 1290 (C-H), 1118 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.85 (m, 4H, OCH₂), 3.88 (t, 2H, OCH₂), 3.95 (t, 2H, 2OCH₂), 4.27 (t, 2H, OCH₂), 4.38 (t, 2H, OCH₂), 6.87 (d, 1H, ArH), 7.20 (d, 1H, ArH), 7.43 (m, 3H, Ph), 7.68 (d, 2H, Ph), 7.72 (s, H, cumH): ms: m/z 368 (M⁺), 280 (M⁺-C₄H₈O₂), 196, 168, 140; For C₂₁H₂₀O₆ HRMAS Calcd. 368.125989; Found. 368.127181.

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

Compound **1d** (4.60 g, 20 mmol), Na₂CO₃ (4.25 g, 40 mmol), DMF (45 mL) and **2c** (5.1 g, 20 mmol) treated as described above to afford (**4b**), 1.73 g (21 %), mp 138 °C (acetonitril); IR (KBr) 2830 (CH₂), 1720 (C=O), 1290 (C-H), 1120 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.83 (m, 8H, 4OCH₂), 3.87 (t, 2H, OCH₂), 3.99 (t, 2H, OCH₂), 4.25 (t, 2H, OCH₂), 4.40 (t, 2H, OCH₂), 6.89 (d, H, ArH), 7.21 (d, H, ArH), 7.42 (m, 3H, Ph), 7.70 (d, 2H, Ph), 7.75 (s, H, cumH): ms: m/z 412 (M⁺), 280 (M⁺-C₆H₁₂O₃), 225, 196, 140; For C₂₃H₂₄O₇ HRMAS Calcd. 412.152203; Found. 412.153009.

20-Phenyl-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 (**4c**).

Compound **1e** (2.74 g 10 mmol), K₂CO₃ (2.76 g, 20 mmol), DMF (30 mL) and **2c** (25.5 g, 10 mmol) treated as described above to afford (**4c**), 0.78 g (17 %), mp, 75 °C (THF); IR (KBr) 2815 (CH₂), 1715 (C=O), 1260 (C-H), 1120 (C-O) cm⁻¹; ¹H

NMR (CDCl₃, 400 MHz): δ 3.79 (m, 12H, 6OCH₂), 4.00 (m, 4H, 2OCH₂), 4.26 (t, 2H, OCH₂), 4.41 (t, 2H, OCH₂), 6.89 (d, H, ArH), 7.22 (d, H, ArH), 7.44 (m, 3H, Ph), 7.71 (d, 2H, Ph), 7.75 (s, H, cumH) ms: m/z 456 (M⁺), 280 (M⁺-C₈H₁₆O₄), 196, 140; For C₂₅H₂₈O₈ HRMAS Calcd. 456.178418; Found. 456.178598.

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

Compound **1c** (3.80 g, 20 mmol), Na₂CO₃ (4.25 g, 40 mmol), DMF (45 mL) and **2d** (5.1 g, 20 mmol) reacted as described above to afford (**4d**), 2.14 g (27 %), mp 182 °C (THF); IR (KBr) 2825 (CH₂), 1710 (C=O), 1210 (C-H), 1140 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.85 (m, 4H, 2OCH₂), 3.87 (s, 3H, OCH₃), 4.00 (t, 2H, OCH₂), 4.26 (t, 2H, OCH₂), 4.44 (t, 2H, OCH₂), 6.89 (d, 1H, ArH), 6.99 (d, 2H, ArH), 7.22 (d, 1H, ArH), 7.66 (d, 2H, ArH), 7.68 (s, 1H, cumH): ms: m/z 398 (M⁺), 310 (M⁺-C₄H₈O₂), 226, 155; For C₂₂H₂₂O₇ HRMAS Calcd. 398.136553; Found. 398.140785.

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

Compound **1d** (4.60 g, 20 mmol), Na₂CO₃ (4.25 g, 40 mmol), DMF (45 mL) and **2d** (5.1 g, 20 mmol) reacted as described above to afford (**4e**), 1.85 g (21 %), mp 134 °C (acetonitril); IR (KBr) 2810 (CH₂), 1720 (C=O), 1225 (C-H), 1140 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.76 (m, 4H, 2OCH₂), 3.86 (m, 3H, OCH₃), 3.98 (m, 4H, 2OCH₂), 4.00 (t, 2H, OCH₂), 4.39 (t, 2H, OCH₂), 6.86 (d, 2H, ArH), 6.98 (d, 2H, ArH), 7.19 (d, 1H, ArH), 7.66 (d, 2H, ArH), 7.68 (s, 1H, cumH): ms: m/z 442 (M⁺) 310 (M⁺-C₆H₁₂O₃), 284, 226, 155; For C₂₄H₂₆O₈ HRMAS Calcd. 442.162768; Found. 442.163086.

20-(4-Methoxyphenyl)-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 (**4f**).

Compound **1e** (2.74 g 10 mmol), K₂CO₃ (2.76 g, 20 mmol), DMF (30 mL) and **2d** (5.1 g, 20 mmol) reacted as described above to afford (**4f**), 0.44 g (9 %), mp 112 °C (ether); IR (KBr) 2825 (CH₂), 1715 (C=O), 1215 (C-H), 1150 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 400 Hz): δ 3.70 (m, 4H, 2OCH₂), 3.78 (m, 8H, 4OCH₂), 3.86 (s, 3H, OCH₃), 3.96 (t, 2H, OCH₂), 4.02 (t, 2H, OCH₂), 4.27 (t, 2H, OCH₂), 4.38 (t, 2H, OCH₂), 6.88 (d, 2H, ArH), 6.98 (d, 2H, ArH), 7.21 (d, 1H, ArH), 7.66 (d, 2H, ArH), 7.69 (s, 1H, cumH): ms: m/z 486 (M⁺), 310 (M⁺-C₈H₁₆O₄), 284, 226, 155; For C₂₆H₃₀O₉ HRMAS Calcd. 486.188983; Found 486.187198.

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