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SYNTHESIS OF SOME BENZO-14-CROWN-4 ETHERS SUBSTITUTED TO 7,8-DIHYDROXY-3-PHENYLCOUMARIN DERIVATIVES

Ümit Salan[a] and Mustafa Bulut[a,*]

[a]University of Marmara, Department of Chemistry, Kadıköy, 81040, İstanbul, Turkey, usalan@marmara.edu.tr, mbulut@marmara.edu.tr

Abstract – 7,8-Dihydroxy-3-phenylcoumarin derivatives reacted with 1,2-bis-(3-tosyloxypropoxy)benzene in CH_3CN/alkali carbonate to furnish 3-phenylchromenone-14-crown-4 ether derivatives, which were identified with elemental analysis, IR, ^1H NMR, ^{13}C NMR and MS spectroscopy.

INTRODUCTION

Macrocyclic molecules have attracted much attention because of their potential use in a variety of chemical processes, e.g., selective complexing agents for alkaline-earth metal ions, photo-induced electron transfer bio-mimetic studies, etc.[1-4] The coumarin nucleus is a very interesting chromophore due to its photochemical and photophysical properties and has been used to convert crown ethers and cryptands into fluorescent probes for alkaline and alkaline-earth metal ions.[5] In addition, it has been shown that 3-phenylcoumarins exhibit strong fluorescence emission intensities due to their high quantum yields.[6] We have recently synthesised various crown ethers with different chromophore moieties. The crown ether derivatives of the 4-*H* and 4-methyl-6,7-dihydroxy- and 7,8-dihydroxycoumarins displayed the binding effect of alkaline cations on the fluorescence emission spectra.[7]

This paper deals with the synthesis and structure elucidation of novel 3-phenyl-2*H*-chromenone derivatives of 14-crown-4 macrocycles.

RESULTS AND DISCUSSION

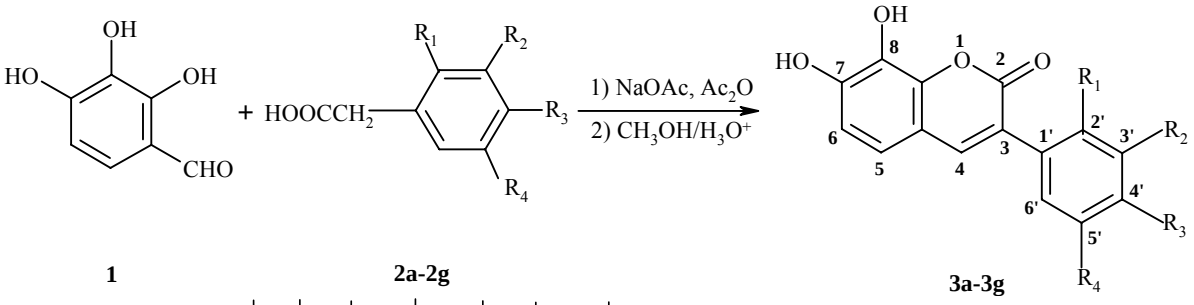
Benzo-14-crown-4 ethers **(6a-6g)** substituted to 7,8-dihydroxy-3-phenylcoumarin derivatives were synthesized from the 1,2-bis-(3-tosyloxypropoxy)benzene (**5)** and the corresponding 7,8-dihydroxy-3-phenylcoumarin derivatives (**3a-3g)** which were prepared from 2,3,4-trihydroxybenzaldehyde and corresponding phenylacetic acid in NaOAc/Ac_2O mixture.

Compound (**5)** was reacted with **3a-3g** to give the crown ethers (**6a-6g)** respectively in the presence of Na_2CO_3 in CH_3CN. The residue was chromatographed over a silica gel column eluting with $CHCl_3$. The fractions were further purified by preperative methods and the 3-phenylchromenone-14-crown-4 ethers (**6a-6g)** were obtained in 13-21% yield. The synthetic approach of benzo-14-crown-4 ethers (**6a-6g)** is shown in **Scheme 1**. The structures of the compounds (**6a-6g)** were characterized by elemental analysis, ^1H and ^{13}C NMR, MS and IR spectroscopies.

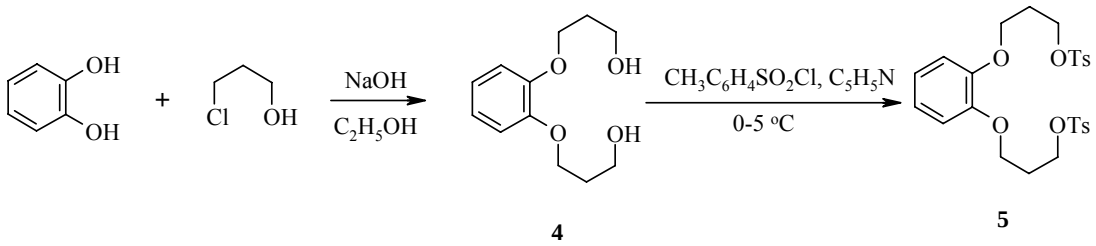
The IR spectra of **6a** showed two absorption at 2876-2927 cm^{-1} for their C-H stretching frequency. The characteristic absorptions of the carbonyl group (C=O) and benzene ring were appeared at 1720 cm^{-1} and 1625 cm^{-1} respectively. The C-O-C ether chain of the crown ether was characterized by an absorption at 1310-1090 cm^{-1}. A crown ether skeleton could also be deduced from analysis of the ^{1}HNMR spectral data. The ^{1}HNMR spectrum of compound (**6a)**, which showed two triplets for the methylene protons [-OC$\underline{H_2}$CH_2C$\underline{H_2}$O-] at δ 4.31 (J = 6 Hz) and δ 4.48 (J = 6 Hz) and one quintet for the another methylene protons [-OCH_2C$\underline{H_2}$CH_2O-] at δ 2.33 ppm (J = 6 Hz), implied the presence of 14-crown-4 ether. In addition the chemical shifts of the aromatic protons were observed in the region of δ 6.88-7.72 ppm. The structure of newly synthesized **6a** was also checked by MS spectrometry. In the MS spectrum of **6a**, we observed a molecular ion at m/z 444$[M]^+$ (calcd for $C_{27}H_{24}O_6$, M=444).

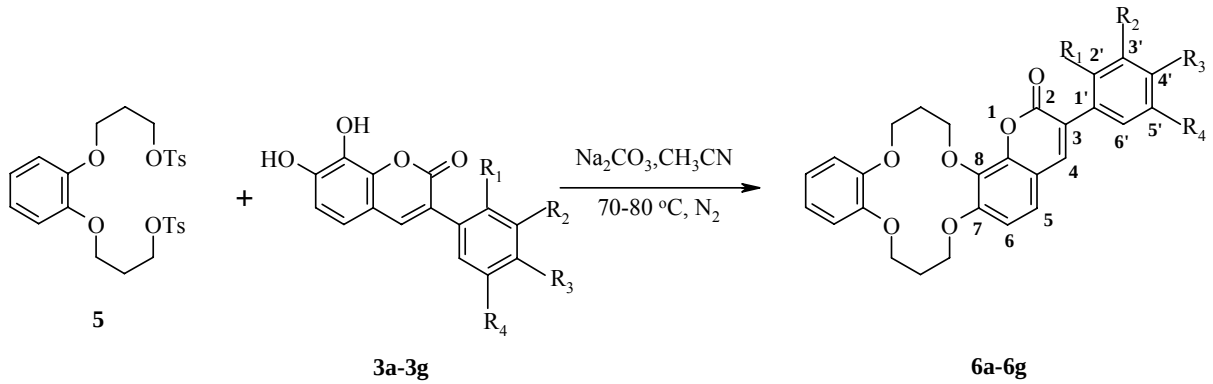
The IR spectrum of **6b-6g** showed similar absorptions compared to the spectra of compound (**6a)**. The ^{1}H NMR spectra of compound **(6b)** showed a pair of doublet at δ 7.07 (br d, J = 8 Hz, H-3' and H-5') and δ 7.58 ppm (br d, J = 8 Hz, H-2' and H-6') for aromatic protons and a singlet at δ 2.40 ppm for methyl protons. As expected, the absorptions of the C-O-C ether chain, benzene ring and carbonyl group of compound (**6b)** were appeared at 1300-1180 cm^{-1}, 1625 cm^{-1} and 1720 cm^{-1} respectively.

The IR, ^{1}H and ^{13}C NMR spectral data of **6c** and **6d** were very similar to those of compound (**6b)**. In the ^{1}HNMR spectra of **6c**, signals were easily assigned to aromatic protons at δ 6.96 (br d, J = 8 Hz, H-3' and H-5') and δ 7.64 (br d, J = 8 Hz, H-2' and H-6') ppm. The methoxy protons showed a singlet at δ 3.85 ppm. In addition, the chemical shifts of the aromatic and etheral carbons were observed around δ 114.09-160.76 ppm and δ 42.07-69.67 ppm respectively. Spectroscopic data of compound (**6d)** suggested the presence of *o*-methoxy substituted crown ethers. The structure of compound (**6e)** was elucidated by elemental analyses (C, H and N) and other spectroscopic data. The results of spectroscopy supported the structure of the new *p*-nitro substituted 14-crown-4 ether. The ^{1}H NMR spectrum of **6f** and **6g** showed the expected resonances and integrals due to the protons of these two crown ether derivatives. Also MS spectra and elemental analysis data confirmed the formation of compounds (**6f**) and (**6g)**.



	2a	2b	2c	2d	2e	2f	2g
R_1	H	H	H	OCH_3	H	H	H
R_2	H	H	H	H	H	OCH_3	OCH_3
R_3	H	CH_3	OCH_3	H	NO_2	OCH_3	OCH_3
R_4	H	H	H	H	H	H	OCH_3





	6a	6b	6c	6d	6e	6f	6g
R_1	H	H	H	OCH_3	H	H	H
R_2	H	H	H	H	H	OCH_3	OCH_3
R_3	H	CH_3	OCH_3	H	NO_2	OCH_3	OCH_3
R_4	H	H	H	H	H	H	OCH_3

Scheme 1. Synthesis of benzo-14-crown-4 ethers

EXPERIMENTAL

Melting points were measured on a Gallenkamp apparatus uncorretedly. IR spectra were recorded by using potassium bromide pellets on a Schimadzu FTIR-8300 spectrophometer as KBr pellets. Elemental

analyses were performed by the Instrumental Analysis Laboratory of Tübitak-Ankara. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuteriocholoroform or methanol with an instrument Mercury–VX 400 MHz. EI MS spectra were recorded on a Fission UG-ZABSPEC.

The starting chemicals (**1**, **2a-2g)** were purchased from Aldrich or Merck. Initial compounds (**3a-3g)** and 3-phenylchromenone-14-crown-4 ether derivatives (**6a-6g)** have been prepared according to our early studies.[8,9]

General procedure for the synthesis of 7,8-dihydroxy-3-phenylchromenones (**3a-3g**)

A mixture of (4.62 g, 30 mmol) of 2,3,4-trihydroxybenzaldehyde (**1)**, (4.08 g, 30 mmol) of phenylacetic acid and (150 mmol) of sodium acetate in 25 mL of acetic anhydride was heated with stirring at 160 ^{o}C under N_2 for 6 h. After removal of acetic acid by distillation, the resulting mixture was treated with CH_3OH/10% HCl, and the precipitates were collected by filtration. The dried product was purified by recrystallisation from ethanol.

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

A mixture of compound (**1)** (4.62 g, 30 mmol), phenylacetic acid (**2a)** (4.08 g, 30 mmol), dry sodium acetate (12.30 g 150 mmol) in acetic anhydride (25 mL) was treated as described above to afford **3a**, 6.45 g (85%), mp 254 ^{o}C (ethanol); IR (KBr) 3361-3463, 3055, 1727, 1600-1625, 1200 cm^{-1}; ^{1}H-NMR (MeOD, 400 MHz): δ 6.52 (d, *J* = 8.5 Hz, 1H, H-6), 7.13 (d, *J* = 8.5 Hz, 1H, H-5), 7.18 (br d, *J* = 8 Hz, 2H, H-2' and 6'), 7.25 (t, *J* = 8 Hz, 1H, H-4'), 7.38 (t, *J* = 8 Hz, 2H, H-3' and 5'), 7.88 (s, 1H, H-4). Anal. Calcd for $C_{15}H_{10}O_4$: C 70.86; H 3.96. Found C 70.63; H 3.77.

*7,8-Dihydroxy-3-(4'-methylphenyl)-2H-chromen-2-one (**3b**)*

Compound (**1)** (4.62 g, 30 mmol), 4-methylphenylacetic acid (**2b)** (4.50 g, 30 mmol), dry sodium acetate (12.30 g 150 mmol) in acetic anhydride (25 mL) was treated as described above to afford **3b**, 4.58 g (57%), mp 220 ^{o}C (ethanol); IR (KBr) 3400, 3120, 2850-2953, 1710, 1590-1625, 1200 cm^{-1}; ^{1}H-NMR (MeOD, 400 MHz): δ 2.41 (s, 3H, CH_3), 6.70 (d, *J* = 8.5 Hz, 1H, H-6), 6.83 (d, *J* = 8.5 Hz, 1H, H-5), 6.95 (d, *J* = 8 Hz, 2H, H-3' and H-5'), 7.18 (d, *J* = 8 Hz, 2H, H-2' and H-6'), 7.85 (s, 1H, H-4). Anal. Calcd for $C_{16}H_{12}O_4$: C 71.64; H 4.47. Found C 71.03; H 4.32.

*7,8-Dihydroxy-3-(4'-methoxyphenyl)-2H-chromen-2-one (**3c**)*

Compound (**1)** (4.62 g, 30 mmol), 4-methoxyphenylacetic acid (**2c)** (4.98 g, 30 mmol), dry sodium acetate (12.30 g 150 mmol) in acetic anhydride (25 mL) was worked up as described above to give **3c**, 8.05 g (94%), mp 244 ^{o}C (ethanol); IR (KBr) 3400, 3100, 2870-2930, 1725, 1600-1630, 1150 cm^{-1}; ^{1}H-NMR (MeOD, 400 MHz): δ 3.85 (s, 3H, OCH_3), 6.70 (d, *J* = 8.5 Hz, 1H, H-6), 6.83 (d, *J* = 8.5 Hz, 1H,

H-5), 6.95 (d, *J* = 8 Hz, 2H, H-3' and H-5'), 7.18 (d, *J* = 8 Hz, 2H, H-2' and H-6'), 7.85 (s, 1H, H-4). Anal. Calcd for $C_{16}H_{12}O_5$: C 67.60; H 4.25. Found C 67.45; H 4.02.

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

Compound (**1**) (4.62 g, 30 mmol), 2-methoxyphenylacetic acid (**2d**) (4.98 g, 30 mmol) dry sodium acetate (12.30 g, 150 mmol) in acetic anhydride (25 mL) was reacted as described above to give **3d**, 7.10 g (83%), mp 209 ^oC (ethanol); IR (KBr) 3400, 3100, 2850-2978, 1720, 1600-1620, 1180 cm^{-1}; ^1H-NMR (MeOD, 400 MHz): δ 3.70 (s, 3H, OCH_3), 6.70 (d, *J* = 8.5 Hz, 1H, H-6), 6.83 (d, *J* = 8.5 Hz, 1H, H-5), 6.93 (d, *J* = 8 Hz, 1H, H-3'), 7.18 (dd, *J* = 8 Hz, *J* =2 Hz, 1H, H-6'), 7.25 (t, *J* = 8 Hz, 2H, H-5' and H-4'), 7.63 (s, 1H, H-4). Anal. Calcd for $C_{16}H_{12}O_5$: C 67.60; H 4.23. Found C 66.20; H 3.95.

*7,8-Dihydroxy-3-(4'-nitrophenyl)-2H-chromen-2-one (**3e**)*

Compound (**1**) (4.62 g, 30 mmol), 4-nitrophenylacetic acid (**2e**) (5.43 g, 30 mmol) dry sodium acetate (12.30 g, 150 mmol) in acetic anhydride (25 mL) was treated as described above to afford **3e**, 6.10 g (68%), mp 270 ^oC (ethanol); IR (KBr) 3400, 3050, 1700, 1600-1620, 1100 cm^{-1}; ^1H-NMR (MeOD, 400 MHz): δ 6.70 (d, *J* = 8.5 Hz, 1H, H-6), 6.83 (d, *J* = 8.5 Hz, 1H, H-5), 6.85 (d, *J* = 8 Hz, 2H, H-2' and H-6'), 7.46 (d, *J*= 8 Hz, 2H, H-3' and H-5'), 7.90 (s, 1H, H-4). Anal. Calcd for $C_{15}H_9NO_6$: C 60.20; H 3.01. Found C 60.45; H 3.45.

*7,8-Dihydroxy-3-(3',4'-dimethoxyphenyl)-2H-chromen-2-one (**3f**)*

A mixture of compound (**1**) (4.62 g, 30 mmol), 3,4-dimethoxyphenylacetic acid (**2f**) (5.88 g, 30 mmol), dry sodium acetate (12.30 g, 150 mmol) in acetic anhydride (25 mL) was treated as described above to give **3f**, 7.72 g (82%), mp 220 ^oC (ethanol); IR (KBr) 3400, 3100, 2853-2950, 1700, 1580-1620, 1190 cm^{-1}; ^1H-NMR (CD_3OD, 400 MHz): δ 3.76 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.71 (d, *J* = 8.5 Hz, 1H, H-6), 6.88 (d, *J* = 8.5 Hz, 1H, H-5), 6.94 (d, *J* = 8.5 Hz, 1H, H-5'), 7.15 (dd, *J* = 8.5 and 2 Hz, 1H, H-6') 7.22 (d, *J* = 2 Hz, 1H, H-2'), 7.80 (s, 1H, H-4). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C 64.82; H 4.12.

*7,8-Dihydroxy-3-(3',4',5'-trimethoxyphenyl)-2H-chromen-2-one (**3g**)*

Compound **(1)** (4.62 g, 30 mmol), 3,4,5-trimethoxyphenylacetic acid (**2g**) (6.78 g, 30 mmol), dry sodium acetate (12.30 g, 150 mmol) in acetic anhydride (25 mL) was worked up as described above to give **3g**, 8.87g (86%), mp 238-239 ^oC (ethanol); IR (KBr) 3361-3463, 3055, 2851-2953, 1727, 1625, 1242 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ 3.69 (s, 3H, OCH_3), 3.78 (s, 6H, OCH_3), 6.72 (d, *J* = 8.5 Hz, 1H, H-6), 6.90 (br s, 2H, H-2' and H-6'), 6.96 (d, *J* = 8.5 Hz, 1H, H-5), 7.88 (s, 1H, H-4). Anal. Calcd. for $C_{18}H_{16}O_7$: C, 62.79; H, 4.68. Found: C, 61.60; H, 4.50.

Synthesis of 1,2-bis(3-tosyloxypropoxy)benzene (5)

Catachol (24.25 g, 0.22 mol) was dissolved in 220 mL of C_2H_5OH and the mixture was stirred at 50 °C under N_2. Finely ground NaOH (21.2 g, 0.53 mol) was added. After dissolving, 1-chloro-3-hydroxypropane (47 g, 0.50 mol) was added intervals over an ½ h period, the whole was stirred for 20 h at reflux temperature. The reaction mixture was worked up by filtering the undissolved salt then evaporated. The residue was dissolved in 750 mL of $CHCl_3$. The $CHCl_3$ solution was washed with 1M 100 mL of NaOH and 2 x 200 mL of H_2O. The $CHCl_3$ solution was dried over sodium sulfate and solvent stripped to yield 1,2-bis(3-hydroxypropoxy)benzene (**4)**. 32 g (64%), mp 60 °C; IR (KBr) 3388, 3085, 2871-2900, 1600-1640, 1257-1053 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.05 (quintet, *J* = 5 Hz, 4H, -$CH_2C\underline{H_2}CH_2$-), 3.85 (t, *J* = 5 Hz, 4H, -$C\underline{H_2}OH$-), 4.16 (t, *J* = 5 Hz, 4H, -$OC\underline{H_2}CH_2CH_2OH$), 6.87-6.93 (m, 4H). Anal. Calcd for $C_{12}H_{18}O_4$: C 63.70; H 7.96. Found C 63.40; H 7.80.

Compound (**4)** (5 g, 22 mmol) was dissolved in minumum amount of pyridine and cooled to -5 °C. Tosyl chloride (10.48 g, 55 mmol) in 10 mL of pyridine was added intervals over an ½ h. The reaction mixture was stirred for 2 days at 0-5 °C and then poured into the ice bath. The precipitate was filtered to yield 1,2-bis-(3-tosyloxypropoxy)benzene (**5)** 2 g (17%), mp 25 °C (ethanol); IR (KBr) 3056, 2873-2900, 1465-1590, 1386-1035 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.25 (s, 6H), 2.26 (quintet, *J* = 6 Hz, 4H, -$CH_2C\underline{H_2}CH_2$-), 3.77 (t, *J* = 6 Hz, 4H, -$C\underline{H_2}OH$-), 4.20 (t, *J* = 6 Hz, 4H, -$OC\underline{H_2}CH_2CH_2$-), 6.91-6.95 (m, 12H). Anal. Calcd for $C_{26}H_{30}O_8S_2$: C 58.43; H 5.62; S 12.00. Found C 58.30; H 5.25; S 12.44.

General procedure for the synthesis of 3-phenylchromenone-crown ethers (6a-6g)

1,2-Bis-(3-tosiloxypropoxy)benzen (**5)** (1 g, 1.8 x 10^{-3} mol), 7,8-dihydroxy-3-phenylcoumarin derivatives (**3a-3g)** (1.8 x 10^{-3} mol) and sodium carbonate (0.38 g, 3.6 x 10^{-3} mol) in 200 mL of acetonitrile were stirred for 5 days at 70-80 °C under N_2 atmosphere. The reaction mixture was acidified using 10% HCl and extracted with $CHCl_3$. The crude product was chromatographed over a silica gel column eluting with chloroform, a gradient of chloroform-methanol up to 100% methanol.

*7,8-[6,7-Benzo-1,5,8,12-tetraoxadecylene]-3-phenyl-2H-1-benzopyran-2-one (**6a**)*

Compound (**5)** (1 g, 1.8 x 10^{-3} mol), **3a** (0.457 g, 1.8 x 10^{-3} mol) and sodium carbonate (0.38 g, 3.6 x 10^{-3} mol) in acetonitrile (200 mL) was treated as describe above to afford **6a**, (0.12 g, 15%), mp 110 °C (benzene); IR (KBr) 3100, 2927-2876, 1720, 1625, 1310, 1090; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (quintet, *J* = 6 Hz, 4H, H-3 and H-10), 4.31 (t, *J* = 6 Hz, 4H, H-4 and H-9), 4.48 (t, *J* = 6 Hz, 4H, H-2 and H-11), 6.88 (d, *J* = 8 Hz, 1H, coumarin H-6), 6.90-7.00 (m, 4H, benzo), 7.18 (d, *J* = 8 Hz, 1H, coumarin H-5), 7.40 (m, 3H, coumarin H-3′, H-4′ and H-5′), 7.68 (br d, *J* = 8 Hz, 2H, coumarin H-2' and H-6'), 7.72 (s, 1H, coumarin H-4); EIMS: *m/z (rel. int.)* 444 $[M]^+$ (27%). Anal. Calcd for $C_{27}H_{24}O_6$: C 72.97; H 5.44. Found C 72.60; H 5.35.

*7,8-[6,7-Benzo-1,5,8,12-tetraoxadecylene]-3-[4'-methylphenyl]-2H-1-benzopyran-2-one (**6b**)*

Compound (**5**) (1 g, 1.8 x 10^{-3} mol), **3b** (0.482 g, 1.8 x 10^{-3} mol) and sodium carbonate (0.38 g, 3.6 x 10^{-3} mol) in acetonitrile (200 mL) was treated as describe above to afford **6b**, (0.14 g, 17%), mp 146-147 ^{o}C (benzene); IR (KBr) 3100, 2927-2876, 1720, 1625, 1300, 1180; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (quintet, *J* = 6 Hz, 4H, H-3 and H-10), 2.40 (s, 3H, -CH_3), 4.31 (t, *J* = 6 Hz, 4H, H-4 and H-9), 4.48 (t, *J* = 6 Hz, 4H, H-2 and H-11), 6.88 (d, *J* = 8 Hz, 1H, coumarin H-6), 6.88-6.95 (m, 4H, benzo), 7.07 (br d, *J* = 8 Hz, 2H, coumarin H-3' and H-5'), 7.18 (d, *J* = 8 Hz, 1H, coumarin H-5), 7.58 (br d, *J* = 8 Hz, 2H, coumarin H-2' and H-6'), 7.70 (s, 1H, coumarin H-4); EIMS: *m/z (rel. int.)* 459 $[M+H]^+$ (13%). Anal. Calcd for $C_{28}H_{26}O_6$: C 73.35; H 5.67. Found C 73.58; H 5.88.

*7,8-[6,7-Benzo-1,5,8,12-tetraoxadecylene]-3-[4'-methoxyphenyl]-2H-1-benzopyran-2-one (**6c**)*

Compound (**5**) (1 g, 1.8 x 10^{-3} mol), **3c** (0.511 g, 1.8 x 10^{-3} mol) and sodium carbonate (0.38 g, 3.6 x 10^{-3} mol) in acetonitrile (200 mL) was treated as describe above to afford **6c**, (0.18 g, 21%), mp 180-181 ^{o}C (benzene); IR (KBr) 3070, 2927-2876, 1720, 1625, 1310, 1120; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (quintet, *J* = 6 Hz, 4H, H-3 and H-10), 3.85 (s, 3H, OCH_3), 4.31 (t, *J* = 6 Hz, 4H, H-4 and H-9), 4.48 (t, *J* = 6 Hz, 4H, H-2 and H-11), 6.87 (d, *J* = 8 Hz, 1H, coumarin H-6), 6.90-7.00 (m, 4H, benzo), 6.96 (br d, *J* = 8 Hz, 2H, coumarin H-3' and H-5'), 7.18 (d, *J* = 8 Hz, 1H, coumarin H-5), 7.64 (br d, *J* = 8 Hz, 2H, coumarin H-2' and H-6'), 7.67 (s, 1H, coumarin H-4); ^{13}C NMR (400 MHz, $CDCl_3$): δ 42.07, 68.27, 69.67, 55.71, 112.94, 114.09, 122.25, 123.56, 123.97, 124.95, 139.02, 139.63, 147.22, 147.73, 148.30, 150.15, 159.94, 159.98, 160.76,; EIMS: *m/z (rel. int.)* 474 $[M]^+$ (20 %). Anal. Calcd for $C_{28}H_{26}O_7$: C 70.87; H 5.48. Found C 70.58; H 5.38.

*7,8-[6,7-Benzo-1,5,8,12-tetraoxadecylene]-3-[2'-methoxyphenyl]-2H-1-benzopyran-2-one (**6d**)*

Compound (**5**) (1 g, 1.8 x 10^{-3} mol), **3d** (0.511 g, 1.8 x 10^{-3} mol) and sodium carbonate (0.38 g, 3.6 x 10^{-3} mol) in acetonitrile (200 mL) was reacted as describe above to afford **6d**, (0.11 g, 13%), mp 175 ^{o}C (benzene); IR (KBr) 3055, 2927-2876, 1720, 1625, 1290, 1100; ^{1}H-NMR(400 MHz, $CDCl_3$): 2.20 (q, *J* = 5 Hz, 4H, H-3 and H-10), 3.80 (s, 3H, OCH_3), 4.13 (t, *J* = 5.5 Hz, 4H, H-4 and H-9), 4.51 (t, *J* = 5.5 Hz, 4H, H-2 and H-11), 6.86 (d, *J* = 8 Hz, 1H, coumarin H-6), 6.90-7.00 (m, 4H, benzo), 6.94 (br d, *J* = 8 Hz, 1H, coumarin H-6'), 7.05 (d, *J* = 8 Hz, 1H, coumarin H-5), 7.10 (dd, *J* = 7 Hz, *J* = 1.5 Hz, 1H, coumarin H-3'), 7.22 (t, *J* = 7 Hz, 1H, coumarin H-5'), 7.35 (t, *J* = 7 Hz, 1H, coumarin H-4'), 7.70 (s, 1H, coumarin H-4). Anal. Calcd for $C_{28}H_{26}O_7$: C 70.87; H 5.48. Found C 71.05; H 5.35.

*7,8-[6,7-Benzo-1,5,8,12-tetraoxadecylene]-3-[4'-nitrophenyl]-2H-1-benzopyran-2-one (**6e**)*

Compound (**5**) (1 g, 1.8 x 10^{-3} mol), **3e** (0.538 g, 1.8 x 10^{-3} mol) and sodium carbonate (0.38 g, 3.6 x 10^{-3} mol) in acetonitrile (200 mL) was treated as describe above to afford **6e**, (0.18 g, 20%), mp 206-208 ^{o}C

(benzene); IR (KBr) cm^{-1} 3100, 2927-2876, 1720, 1625, 1270, 1120; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (quintet, *J* = 6 Hz, 4H, H-3 and H-10), 4.31 (t, *J* = 6 Hz, 4H, H-4 and H-9), 4.50 (t, *J* = 6 Hz, 4H, H-2 and H-11), 6.90-7.00 (m, 4H, benzo), 6.93 (d, *J* = 8 Hz, 1H, coumarin H-6), 7.20 (d, *J* = 8 Hz, 1H, coumarin H-5), 7.81 (s, 1H, coumarin H-4), 7.83 (d, *J* = 8 Hz, 2H, coumarin H-2′ and H-6′), 8.22 (br d, *J* = 8 Hz, 2H, H-3′ and H-5′). Anal. Calcd for $C_{27}H_{23}NO_8$: C 66.25; H 4.70, N 2.86. Found C 65.75; H 4.38, N 2.83.

*7,8-[6,7-Benzo-1,5,8,12-tetraoxadecylene]-3-[3',4'-dimethoxyphenyl]-2H-1-benzopyran-2-one (**6f**)*

Compound (**5**) (1 g, 1.8 x 10^{-3} mol), **3f** (0.57 g, 1.8 x 10^{-3} mol) and sodium carbonate (0.38 g, 3.6 x 10^{-3} mol) in acetonitrile (200 mL) was treated as describe above to afford **6f**, (0.13 g, 14%), mp 182°C (benzene); IR (KBr) 3050, 2927-2876, 1720, 1625, 1350, 1150; ^{1}H-NMR (400 MHz, $CDCl_3$): 2.18 (q, *J*=6 Hz, 4H, H-3 and H-10), 3.66 (t, *J* = 6 Hz, 2H, H-9), 3.82 (s, 3H, 4'-OCH_3), 3.86 (s, 3H, 3'-OCH_3), 4.08 (t, *J* = 6 Hz, 2H, H-4), 4.26 (t, *J* = 5.5 Hz, 2H, H-11), 4.46 (t, *J* = 5.5 Hz, 2H, H-2), 6.81 (d, *J* = 8 Hz, 1H, coumarin H-6), 6.84-6.93 (m, 4H, benzo), 7.08 (d, *J* = 8 Hz, 1H, coumarin H-5), 7.56 (dd, *J* = 9 Hz, *J*=1.5 Hz, 1H, coumarin H-6'), 7.63 (s, 1H, coumarin H-4), 7.64 (d, *J* = 1.5 Hz, 1H, coumarin H-2'), 7.72 (d, *J* = 8.5 Hz, 1H, coumarin H-5'); EIMS: *m/z (rel. int.)* 505 $[M+H]^+$ (10%), 504 $[M]^+$ (25%). Anal. Calcd for $C_{29}H_{28}O_8$: C 69.04; H 5.55. Found C 69.80; H 5.38.

*7,8-[6,7-Benzo-1,5,8,12-tetraoxadecylene]-3-[3',4',5'-trimethoxyphenyl]-2H-1-benzopyran-2-one (**6g**)*

Compound (**5**) (1 g, 1.8 x 10^{-3} mol), **3g** (0.62 g, 1.8 x 10^{-3} mol) and sodium carbonate (0.38 g, 3.6 x 10^{-3} mol) in acetonitrile (200 mL) was treated as describe above to afford **6g**, (0.17 g, 18%), mp 185°C (benzene); IR (KBr) 3100, 2927-2876, 1720, 1625, 1300, 1110; ^{1}H-NMR (400 MHz, $CDCl_3$): 2.08 (q, *J* = 6 Hz, 4H, H-3 ve H-10), 3.82 (s, 3H, OCH_3), 3.84 (s, 6H, OCH_3), 4.14 (t, *J* = 6 Hz, 4H, H-4 ve H-9), 4.23 (t, *J* = 6 Hz, 2H, H-2), 4.40 (t, *J* = 6 Hz, 2H, H-11), 6.80-6.90 (m, 4H, benzo), 7.42 (d, *J* = 6 Hz, 1H, coumarin H-6), 7.44 (d, *J* = 7 Hz, 1H, coumarin H-5), 7.60 (s, 1H, coumarin H-4), 7.62 (d, *J* = 2 Hz, 2H, coumarin H-2' ve H-6'); EIMS: *m/z (rel. int.)* 535 $[M+H]^+$ (5 %), 534 $[M]^+$ (20 %). Anal. Calcd for $C_{30}H_{30}O_9$: C 67.41; H 5.62. Found C 67.15; H 5.48.

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