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## **Supporting Information for**

# Regioselective alkylation of methylene group via *meta*-bridging of calix[4]arenes

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## **Experimental procedures and characterizations**

#### **General Experimental Procedures**

All chemicals were purchased from commercial sources and used without further purification. Solvents were dried and distilled using conventional methods. Melting points were measured on Heiztisch Mikroskop – Polytherm A (Wagner & Munz, Germany). NMR spectra were performed on Varian Gemini 300 (1H: 300 MHz, 13C: 75 MHz) and on Bruker Advance DRX 500 (1H: 500 MHz, 13C: 125 MHz) spectrometers. Deuterated solvents used are indicated in each case. Chemical shifts ( $\delta$ ) are expressed in ppm and are referred to the residual peak of the solvent or TMS as an internal standard; coupling constants (J) are in Hz. The mass analyses were performed using ESI technique on Q–TOF (Micromass) spectrometer. Elemental analyses were done on Perkin–Elmer 240, Elementar vario EL (Elementar, Germany) or Mitsubishi TOX–100 instruments. All samples were dried in the desiccator over P2O5 under vacuum (1 Torr) at 80 °C for 8 hours. The IR spectra were measured on an FT–IR spectrometer Nicolet 740 or Bruker IFS66 spectrometers equipped with a heatable Golden Gate Diamante ATR–Unit (SPECAC) in KBr. 100 Scans for one spectrum were co–added at a spectral resolution of 4 cm–1. The courses of the reactions were monitored by TLC using TLC aluminium sheets with Silica gel 60 F254 (Merck). The column chromatography was performed using Silica gel 60 (Merck).

#### General remark:

## All organomercury derivatives are considered potentially hazardous and require special consideration!

#### 4-chloromercurio-25,26,27,28-tetrapropoxycalix[4]arene (2)

It was prepared on 5 g scale using procedure currently published by our group: P. Slavik, M. Dudič, K. Flídrová, J. Sýkora, I. Císařová, S. Böhm, P. Lhoták, *Org. Lett.* **2012**, *14*, 3628-3631.

#### 4-iodomercurio-25,26,27,28-tetrapropoxycalix[4]arene (3)

A mixture of calixarene 2 (6.60 g, 7.97 mmol) and iodine (2.23 g, 8.77 mmol) was dissolved in dry acetonitrile (50 ml) and dry chloroform (30 ml). The mixture was stirred overnight at room temperature. Solvent was then evaporated under reduced pressure and the residue was extracted with dichloromethane. The organic layer was extracted with solution of aq. Na<sub>2</sub>SO<sub>3</sub> (10%, 50 ml), washed with water (50 ml) and dried over magnesium sulfate. Solvent was removed under reduced pressure to yield the crude product which was purified by column chromatography on silica-gel (eluent =  $CH_2Cl_2$ :hexane 1:2, v/v). Product was obtained as white powder in 86% yield (4.93 g), mp: 163.8-165.1 °C.

<sup>1</sup>H-NMR(CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 7.48 (d, 1H, *J*= 8.0 Hz, Ar-H), 7.12 (d, 2H, *J*= 7.3 Hz, Ar-H), 6,97-6.82 (m, 2H, Ar-H), 6.28-6.05 (m, 6H, Ar-H), 4.57-4.36 (m, 4H, Ar-CH<sub>2</sub>-Ar), 4.09-3.95 (m, 4H, O-CH<sub>2</sub>), 3.75-3.60 (m, 5H, O-CH<sub>2</sub>+Ar-CH<sub>2</sub>-Ar), 3.21-3.09 (m, 3H, Ar-CH<sub>2</sub>-Ar), 2.07-1.79 (m, 8H, O- CH<sub>2</sub>-CH<sub>2</sub>), 1.17-1.06 (m, 6H, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.94-0.85 (m, 6H, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 75 MHz): 158.4, 158.3, 155.4, 155.3, 141.4, 137.8, 137.5, 137.3, 133.6, 133.4, 133.1, 132.7, 130.7, 129.3, 129.2, 127.9 (2x), 127.5, 126.8, 122.5 (2x), 122.1, 99.5, 77.8, 77.4, 77.0, 76.8, 34.9, 31.3 (2x), 31.0, 23.9 (2x), 23.3 (2x), 11.2 (2x), 10.2, 10.1 ppm. IR (KBr) v 1453.9 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>): C<sub>40</sub>H<sub>47</sub>IO<sub>4</sub>, calcd for 718.25190 [(M)<sup>+</sup>]; found: 736.28661[(M+NH<sub>4</sub><sup>+</sup>)<sup>+</sup>]. 741.24089 [(M+Na)<sup>+</sup>], 757.21412 [(M+K)<sup>+</sup>].

#### 6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (4)

Calixarene **3** (0.70 g, 0.97 mmol), tricyclohexylphosphonium tetrafluoroborate (0.071 g, 0.19 mmol), palladium acetate (0.022 g, 0.097 mmol), potassium carbonate (0.27 g, 1.94 mmol) and silver carbonate (0.13 g, 0.48 mmol) were added to an oven-dried 50 ml Schlenk flask under argon. Dry deoxygenated DMA (10 ml bubbled with argon) was added and the mixture was stirred overnight at 140 °C (conversion was monitored by TLC). After cooling down to room temperature 30 ml of dichloromethane was added and the solution was filtered. Organic layer was washed with water (30 ml) and dried over magnesium sulfate. Solvent was removed under reduced pressure to yield the crude product which was purified by column chromatography on silica gel (eluent= hexane:ethyl acetate 25:1, v/v). The title compound was then further purified by crystallization (AcOEt:DCM 1:5, v/v) to give compound as colourless crystals (0.30 g, 52%). All characteristics are fully in agreement with previously published data: Flídrová K., Slavík P., Eigner V., Dvořáková H., Lhoták P.: *Chem. Commun.* **2013**, *49*, 6749 – 6751.

#### 8-propyl-6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (5a)

Calixarene **4** (0.068 g, 0.12 mmol) was added to an oven-dried 10 ml Schlenk flask under argon. Anhydrous 2-methyltetrahydrofuran was added by syringe to the flask to form colourless solution. The solution was cooled down to -78 °C and stirred for 20 minutes. n-Butyllithium (hexane, 1.6 M, 0.3 ml, 0.48 mmol) was added dropwise to the flask while the colour gradually turned yellow. The solution was stirred for 15 min at -78 °C and then 30 min at room temperature, the colour of reaction mixture turned red. Mixture was cooled down to -78 °C and *n*-propyl iodide (0.16 g, 0.92 mmol) was added dropwise. The reaction mixture was stirred for 10 min at -78 and then 4 h at room temperature. The reaction was quenched by addition of water (3 ml). The mixture was extracted with dichloromethane (30 ml), organic layers were separated, washed with water (30 ml) and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield the crude product which was purified by preparative TLC (SiO<sub>2</sub>, eluent = dichloromethane-hexane 1/1, v/v). The title compound was obtained as a white powder in 82% yield (0.060 g), mp: 161.5-163 °C. 8-hydroxy-6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (**6**) was obtained as a side product in 13% yield (0.01 g), mp: 153-154 °C.

Compound **5a**: <sup>1</sup>H-NMR(CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.08 (d, 2H, *J*= 7.6 Hz, Ar-H), 6.89 (d, 2H, *J*= 7.3 Hz, Ar-H), 6.77-6.71 (m, 2H, Ar-H), 6.66-6.61 (m, 2H, Ar-H), 6.57-6.52 (m, 2H, Ar-H), 4.35 (t, 1H, *J*= 5.3 Hz, Ar-CH-Ar), 4.23 (d, 2H, *J*= 12.6 Hz, Ar-CH<sub>2</sub>- Ar), 4.17 (d, 1H, *J*= 13.2 Hz, Ar-CH<sub>2</sub>- Ar), 4.09-3.98 (m, 2H, O-CH<sub>2</sub>), 3.97-3.81 (m, 4H, O-CH<sub>2</sub>), 3.46-3.36 (m, 2H, O-CH<sub>2</sub>), 3.33 (d, 2H, *J* = 12.6 Hz, Ar-CH<sub>2</sub>-Ar), 2.93 (d, 1H, *J* = 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 2.21-1.78 (m, 10H, O-CH<sub>2</sub>-CH<sub>2</sub>+CH<sub>2</sub>), 1.56-1.42 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>), 1.15 (t, 6H, *J*= 7.3 Hz, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.98-0.89 (m, 9H, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>+CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 75 MHz): 157.8, 156.3, 144.1, 142.0, 138.5, 134.7, 131.1, 129.3, 129.2, 127.7, 123.0, 117.5, 77.9, 76.9, 46.1, 36.2, 34.3, 26.2, 24.0, 23.2, 19.8, 15.0, 11.1,

10.2 ppm. IR (KBr) v 1452.3 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>): calcd for  $C_{43}H_{52}O_4Na$ : 655.37578 [(M+Na)<sup>+</sup>]; found *m/z* 633.39486 [(M+H)<sup>+</sup>], 655.37712 [(M+Na)<sup>+</sup>], 671.35075 [(M+K)<sup>+</sup>].

Compound 6: <sup>1</sup>H-NMR(CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.10 (dd, 2H, *J*= 7.6, 1.8 Hz, Ar-H), 6.90 (dd, 2H, *J*= 7.3, 1.5 Hz, Ar-H), 6.78-6.72 (m, 2H, Ar-H), 6.59-6.49 (m, 4H, Ar-H), 5.60 (d, 1H, *J*= 9.1 Hz, Ar-CH-Ar), 4.39 (d, 2H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 4.34-4.26 (m, 2H, O-CH<sub>2</sub>), 4.21 (d, 1H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 4.11-4.02 (m, 2H, O-CH<sub>2</sub>), 3.99-3.90 (m, 2H, O-CH<sub>2</sub>), 3.49-3.39 (m, 2H, O-CH<sub>2</sub>), 3.27 (d, 2H, *J* = 12.6 Hz, Ar-CH<sub>2</sub>-Ar), 2.96 (d, 1H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 2.15-1.80 (m, 8H, O-CH<sub>2</sub>-CH<sub>2</sub>), 1.13 (t, 6H, *J*= 7.3 Hz, O-CH<sub>2</sub>-CH<sub>3</sub>), 0.94 (t, 6H, *J*= 7.3 Hz, O-CH<sub>2</sub>-CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 75 MHz): 158.1, 156.1, 143.0, 138.4, 137.6, 134.6, 132.5, 130.0, 129.1, 127.6, 122.9, 117.2, 77.6, 76.7, 71.7, 33.4, 29.7, 26.1, 23.7, 23.5, 23.0, 10.8, 10.0 ppm. IR (KBr) v 3533.9, 1453.0 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>): calcd for C<sub>40</sub>H<sub>46</sub>O<sub>5</sub>Na: 629.32375 [(M+Na)<sup>+</sup>]; found *m*/z 629.32397 [(M+Na)<sup>+</sup>].

#### 8-benzyl-6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (5b)

Calixarene **4** (0.064 g, 0.11 mmol) was added to an oven-dried 10 ml Schlenk flask under argon. Anhydrous 2-methyltetrahydrofuran (5 ml) was added by syringe to the flask to give colourless solution. Solution was cooled down to -78 °C and stirred for 20 min. Dropwise addition of a solution of n-butyllithium (hexane, 1.6 M, 0.4 ml, 0.64 mmol) to the flask turned the solution yellow. Solution was stirred 15 min at -78 °C and then 30 min at room temperature. The solution finally turned red. The mixture was cooled down to -78 °C and benzyl bromide (0.11 g, 0.65 mmol) was added dropwise. The solution was stirred for 10 min at -78 and then 4 h at room temperature, and finally quenched by addition of water (3 ml). Reaction mixture was extracted with dichloromethane (30 ml), organic portions were separated, washed with water (30 ml) and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield the crude product which was purified by preparative TLC (SiO<sub>2</sub>, eluent = DCM-hexane 1/1, v/v). The title compound was obtained as white powder in 64% yield (0.047 g), mp: 167-168 °C. 8-hydroxy-6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (**6**) was obtained as a side product in 12% yield (0.008 g), mp: 153-154 °C.

<sup>1</sup>H-NMR(CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.25-7.14 (m, 5H, Ar-H), 7.09 (d, 2H, *J*= 7.6 Hz, Ar-H), 6.91 (dd, 2H, *J*= 7.3, 1.5, Ar-H), 6.79-6.73 (m, 2H, Ar-H), 6.59-6.52 (m, 4H, Ar-H), 4.64 (t, 1H, *J*= 6.2 Hz, Ar-CH-Ar), 4.26-4.17 (m, 3H, Ar-CH<sub>2</sub>- Ar), 4.00-3.89 (m, 4H, O-CH<sub>2</sub>), 4.65-3.55 (m, 2H, O-CH<sub>2</sub>), 3.49-3.39 (m, 4H, O-CH<sub>2</sub> + CH<sub>2</sub>), 3.34 (d, 2H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 2.96 (d, 1H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 2.25-2.06 (m, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), 2.02-1.73 (m, 6H, O-CH<sub>2</sub>-CH<sub>2</sub>), 1.11 (t, 6H, *J*= 7.3 Hz, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.97 (t, 6H, *J*= 7.3 Hz, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 75 MHz): 157.7, 156.2, 144.1, 141.5, 140.6, 138.4, 134.7, 131.3, 130.0, 129.3, 129.3, 127.9, 127.8, 125.9, 123.0, 117.7, 77.9, 76.9, 47.2, 41.3, 34.2, 26.4, 24.1, 23.2, 11.0, 10.2 ppm. IR (KBr) v 1452.4 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>): calcd for C<sub>47</sub>H<sub>52</sub>O<sub>4</sub>Na: 703.37578 [(M+Na)<sup>+</sup>]; found *m*/*z* 681.39442 [(M+H)<sup>+</sup>], 703.37609 [(M+Na)<sup>+</sup>], 719.34901 [(M+K)<sup>+</sup>], 698.42133 [(M+NH<sub>4</sub><sup>+</sup>)<sup>+</sup>].

#### 8-allyl-6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (5c)

Calixarene 4 (0.084 g, 0.14 mmol) was added to an oven-dried 10 ml Schlenk flask under argon. Anhydrous 2-methyltetrahydrofuran (5 ml) was added by syringe to the flask to give colourless solution. Solution was cooled down to -78  $^{\circ}$ C and stirred for 20 min. Dropwise addition of a solution

of n-butyllithium (1.6 M, 0.45 ml, 0.72 mmol) to the flask turned the solution yellow. Solution was stirred 15 min at -78 °C and then 30 min at room temperature. The final colour of solution was red. Mixture was cooled down to -78 °C again and allyl bromide (0.09 ml, 1.04 mmol) was added dropwise, solution was stirred for 10 min at -78 and then 4 h at room temperature. Reaction was quenched by addition of water (3 ml). Mixture was extracted with dichloromethane (30 ml), organic portions were separated, washed with water (30 ml) and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield the crude product which was purified by preparative TLC (eluent = DCM:hexane 1/1, v/v). The title compound was obtained as a yellowish powder in 72% yield (0.065 g), mp: 146-148 °C. 8-hydroxy-6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (6) was obtained as a side product in 10% yield (0.0087 g), mp: 153-154 °C.

<sup>1</sup>H-NMR(CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.11 (dd, 2H, *J*= 7.6, 1.5 Hz, Ar-H), 6.92 (dd, 2H, *J*= 7.3, 1.8 Hz, Ar-H), 6.80-6.73 (m, 2H, Ar-H), 6.69-6.64 (m, 2H, Ar-H), 6.60-6.55 (m, 2H, Ar-H), 6.08-5.92 (m, 1H, CH<sub>2</sub>-CH-CH<sub>2</sub>), 5.05-4.91 (m, 2H, CH<sub>2</sub>-CH-CH<sub>2</sub>), 4.39 (t, 1H, *J*= 5.6 Hz, Ar-CH-Ar), 4.27 (d, 2H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 4.20 (d, 1H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 4.10-3.86 (m, 6H, O-CH<sub>2</sub>), 3.49-3.39 (m, 2H, O-CH<sub>2</sub>), 3.35 (d, 2H, *J*= 12.6 Hz, Ar-CH<sub>2</sub>-Ar), 2.99-2.90 (m, 3H, Ar-CH<sub>2</sub>-Ar + CH<sub>2</sub>-CH-CH<sub>2</sub>), 2.24-1.81 (m, 8H, O-CH<sub>2</sub>-CH<sub>2</sub>), 1.18 (t, 6H, *J*= 7.3 Hz, O-CH<sub>2</sub>-CH<sub>3</sub>), 0.95 (t, 6H, *J*= 7.3 Hz, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 75 MHz): 158.0, 156.2, 144.0, 141.0, 138.5, 136.7, 134.7, 131.3, 129.4, 129.3, 127.8, 123.0, 117.6, 115.7, 78.0, 76.9, 45.8, 38.1, 34.2, 26.2, 24.0, 23.2, 11.1, 10.2 ppm. IR (KBr) v 1452.0 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>): calcd for C<sub>43</sub>H<sub>50</sub>O<sub>4</sub>Na: 653.36013 [(M+Na)<sup>+</sup>]; found *m/z* 631.37866 [(M+H)<sup>+</sup>], 653.36073 [(M+Na)<sup>+</sup>], 669.33373 [(M+K)<sup>+</sup>], 648.40575 [(M+NH<sub>4</sub><sup>+</sup>)<sup>+</sup>].

#### 8-(ethyl-2-acetyl)-6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (5d)

Calixarene **4** (0.084 g, 0.14 mmol) was added to an oven-dried 10 ml Schlenk flask under argon. Anhydrous 2-methyltetrahydrofuran (5 ml) was added by syringe to the flask to give colourless solution. Solution was cooled down to -78 °C and stirred for 20 minutes. Dropwise addition of a solution of n-butyllithium (hexane, 1.6 M, 0.45 ml, 0.72 mmol) to the flask turned the solution yellow. Solution was stirred 15 min at -78 °C and then 30 min at room temperature. After that solution turned red. Mixture was cooled down to -78 °C again and ethyl 2-bromoacetate (0.138 g, 0.826 mmol) was added dropwise. The solution was stirred for 10 min at -78 and then 2 h at room temperature. Reaction was quenched by addition of water (3 ml). Mixture was extracted with dichloromethane (30 ml), organic portions were separated, washed with water (30 ml) and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield the crude product which was purified by preparative TLC (eluent = dichloromethane-hexane 1/1, v/v). The title compound was obtained as a white powder in 46% yield (0.0.043 g), mp: 44-46 °C. 8-hydroxy-6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (**6**) was obtained as a side product in 8% yield (0.0070 g), mp: 153-154 °C.

<sup>1</sup>H-NMR(CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.09 (d, 2H, *J*= 7.6, Ar-H), 6.90 (d, 2H, *J*= 7.6 Hz, Ar-H), 6.80-6.71 (m, 2H, Ar-H), 6.66-6.61 (m, 2H, Ar-H), 6.59-6.53 (m, 2H, Ar-H), 4.49 (t, 1H, *J*= 5.3 Hz, Ar-CH-Ar), 4.25 (d, 2H, *J*= 12.6 Hz, Ar-CH<sub>2</sub>-Ar), 4.18 (d, 1H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 4.09-3.86 (m, 8H, O-CH<sub>2</sub>), 3.47-3.37 (m, 2H, O-CH<sub>2</sub>), 3.34 (d, 2H, *J* = 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 3.15 (d, 2H, *J*= 5.3 Hz, CH<sub>2</sub>), 2.94 (d, 1H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar), 2.21-1.79 (m, 8H, O-CH<sub>2</sub>-CH<sub>2</sub>), 1.19-1.07 (m, 9H, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> + O-CH<sub>2</sub>CH<sub>3</sub>), 0.94 (t, 6H, *J*= 7.3 Hz, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 75 MHz): 172.1, 158.1, 156.2, 143.8, 139.7, 138.4, 134.7, 131.6, 129.5, 129.3, 127.7, 123.0, 117.6, 78.1, 76.9, 60.1, 42.4, 38.6, 34.3, 26.1, 24.0, 23.2, 14.4, 11.0, 10.2 ppm. IR (KBr) v 1734.9, 1452.3 cm<sup>-1</sup>.

HRMS (ESI<sup>+</sup>): calcd for  $C_{44}H_{52}O_6Na$ : 699.36561 [(M+Na)<sup>+</sup>]; found m/z 677.38400 [(M+H)<sup>+</sup>], 699.36622 [(M+Na)<sup>+</sup>], 715.33941 [(M+K)<sup>+</sup>].

#### **Dimeric calixarene** 7

Dimeric calixarene 7 was isolated during reaction of calixarene 4 with 1 eq. of BuLi in 13% yield (0,008 g, white powder), mp: 114-116 °C.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600.1 MHz):  $\delta$  7.11 (dd, 2H, *J*= 7.9, 1.5, Ar-H-*B5*), 7.06 (dd, 2H, *J*= 7.9, 1.5, Ar-H-*C5*), 6.97 (dd, 2H, *J*= 7.3, 1.5 Hz, Ar-H-*B3*), 6.86 (dd, 2H, *J*= 7.6, 1.8, Ar-H-*C3*), 6.79 (dd, 2H, *J*= 7.6, 7.6, Ar-H-*B4*), 6.72 (dd, 2H, *J*= 7.5, 7.5, Ar-H-*C4*), 6.49 – 6.45 (m, 4H, Ar-H-*A5*, *A4*), 6.42 (d, 2H, *J*= 8.1, Ar-H-*D5*), 6.38 (d, 2H, *J*= 8.1, Ar-H-*D4*), 0.96 (s, 2H, Ar-CH-Ar- *AD*), 4.79-4.69 (m, 2H, -O-CH<sub>2</sub>-*A*), 4.42 (d, 2H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar-*AB*), 4.32-4.23 (m, 2H, -O-CH<sub>2</sub>-*A*), 4.22 (d, 2H, *J*= 12.6 Hz, Ar-CH<sub>2</sub>-Ar-*BC*), 4.08-4.00 (m, 2H, -O-CH<sub>2</sub>-*B*), 3.97 (d, 2H, *J*= 12.6 Hz, Ar-CH<sub>2</sub>-Ar-*CD*), 3.86-3.80 (m, 2H, -O-CH<sub>2</sub>-*C*), 3.57-3.51 (m, 2H, -O-CH<sub>2</sub>-*B*), 3.42-3.28 (overlapped m, 4H, Ar-CH<sub>2</sub>-Ar-*CD*), 3.37 (d, 2H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar-*AB*), 3.21 (d, 2H, *J*= 12.6 Hz, Ar-CH<sub>2</sub>-Ar-*CD*), 2.96 (d, 2H, *J*= 12.9 Hz, Ar-CH<sub>2</sub>-Ar-*BC*), 2.68-2.60 (m, 2H, -O-CH<sub>2</sub>-*C*), 2.33-2.13 (m, 6H, -O-CH<sub>2</sub>-CH<sub>2</sub>-*A*,*A*,*B*), 2.11-2.00 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-*C*), 1.37 (t, 6H, *J*= 7.3 Hz, -O-CH<sub>2</sub>-CH<sub>3</sub>-*A*), 0.98 ((t, 6H, *J*= 7.6 Hz, -O-CH<sub>2</sub>-CH<sub>3</sub>-*A*), 0.98 ((t, 6H, *J*= 7.6 Hz, -O-CH<sub>2</sub>-CH<sub>3</sub>-*C*), 0.73 ((t, 6H, *J*= 7.3 Hz, -O-CH<sub>2</sub>-CH<sub>3</sub>-*C*)) ppm.

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150.9 MHz): δ 158.2 (kv. C-1 –*D*), 156.9 (kv. C-1 –*A*), 156.1 (kv. C-1 –*B*), 155.7 (kv. C-1 –*C*), 145.9, 144.4, 144.1, 148.9, 138.8, 138.4, 134.7, 134.4 (8x kv. C), 131.4 (CH -*D*), 130.5 (CH-*A*), 129.0 (CH-3–*B*), 128.8 (CH-3 -*C*), 128.4 and 128.1 (2x kv.C), 127.6 (CH-5–*B* and CH-5–*C*), 122.6 (CH-4-*B* and CH-4-*C*), 118.0 (CH -*A*), 117.3 (CH-*D*), 77.9 (OCH<sub>2</sub>-*A*), 77.6 (OCH<sub>2</sub>-*D*), 76.6 (OCH<sub>2</sub>-*B*), 76.4 (OCH<sub>2</sub>-*C*), 49.9 (Ar-CH-Ar-*AD*), 33.9 (Ar-CH<sub>2</sub>-Ar-*CD*), 33.3 (Ar-CH<sub>2</sub>-Ar-*AB*), 26.5 (Ar-CH<sub>2</sub>-Ar-*BC*), 24.1 (OCH<sub>2</sub>CH<sub>2</sub>-*A*), 23.5 (OCH<sub>2</sub>CH<sub>2</sub>-*D*), 22.9 (OCH<sub>2</sub>CH<sub>2</sub>-*B* and OCH<sub>2</sub>CH<sub>2</sub>-*C*), 11.1 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-*A*), 10.0 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-*D*), 9.9 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-*B*), 9.7 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-*C*) ppm.

IR (KBr) v 1452.8 cm<sup>-1</sup>. HRMS (ESI+): calcd for  $C_{80}H_{90}O_8Na$ .: 1201.65279 [(M+Na)<sup>+</sup>]; found m/z 1179.67175 [(M+H)<sup>+</sup>], 1201.65390 [(M+Na)<sup>+</sup>], 1217.62720 [(M+K)<sup>+</sup>].







### **Compound 5a**



#### **Compound 5a**





## **Compound 5b**



**Compound 5b** 



## Compound 5c



**Compound 5c** 



## Compound 5d



**Compound 5d** 























## HMBC







#### **Crystallographic information**

#### Compound 5a C<sub>43</sub>H<sub>52</sub>O<sub>4</sub>:

 $M = 632.88 \text{ g.mol}^{-1}$ , triclinic system, group P-1, space a = 10.0808 (3) Å,b = 12.8064 (3) Å, c = 15.1154 (3) Å,  $\alpha = 89.880$  (2)°,  $\beta = 75.473$  (2)°,  $\gamma = 75.260$  (2)°, Z = 2, V = 1822.85 (9) Å<sup>3</sup>, Dc = 1.153 g.cm<sup>-3</sup>,  $\mu$ (Cu-K $\alpha$ ) = 0.56 mm<sup>-1</sup>, crystal dimensions of 0.42 × 0.31 × 0.24 mm. Data were collected at 180 (2) K on a Xcalbur Onyx CCD diffractometer with graphite monochromated Cu-Ka radiation. The structure was solved by direct methods<sup>1</sup> and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs<sup>2</sup> to final value R = 0.054 and  $R_w = 0.145$  using 7316 independent reflections ( $\Theta_{max}$  = 76.0°), 449 parameters and 28 restrains. The positions of disordered propoxy group were found from the electron density maps and then placed in appropriate positions. All distances between neighboring atoms and angles were fixed. Site occupancies were refined with the overall sum of the position constrained to full occupation. The hydrogen atoms were placed in calculated positions. The structure was deposited into Cambridge Structural Database under number CCDC 1006510.



The figure of compound **5a** structure and numbering the hydrogen atoms were omitted for sake of clarity except for the hydrogen atoms propyl.

#### Compound 5b C<sub>47</sub>H<sub>52</sub>O<sub>4</sub>:

 $M = 680.9 \text{ g.mol}^{-1}$ , triclinic P-1, system, space group a = 12.3671(7) Å, b = 12.6350 (8) Å, c = 13.8467 (9) Å,  $\alpha = 77.854$  (5)°,  $\beta = 63.909$  (6)°,  $\gamma = 80.759$  (5)°, Z = 2, V = 1894.0 (2) Å<sup>3</sup>, Dc = 1.194 g.cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.07 mm<sup>-1</sup>, crystal dimensions of 0.44 × 0.21 × 0.14 mm. Data were collected at 120 (2) K on a Gemini Atlas CCD diffractometer with graphite monochromated Mo-Ka radiation. The structure was solved by charge flipping methods<sup>3</sup> and anisotropically refined by full matrix least squares on F squared using the Jana2006 suite of programs<sup>4</sup> to final value R = 0.048 and  $R_w = 0.133$  using 8450 independent reflections ( $\Theta_{max}$  = 29.2°), 460 parameters and 0 restrains. The hydrogen atoms were placed in calculated positions. The structure was deposited into Cambridge Structural Database under number CCDC 1006512.



The figure of compound **5b** structure and numbering the hydrogen atoms were omitted for sake of clarity.

#### Compound 5c C<sub>43</sub>H<sub>50</sub>O<sub>4</sub>:

 $M = 630.87 \text{ g.mol}^{-1}$ , triclinic system, space group P-1, *a* = 9.8496 (3) Å, b = 12.9700 (5) Å, c = 14.9932 (5) Å,  $\alpha = 89.965$  (3)°,  $\beta = 77.360$  (3)°,  $\gamma = 74.040$  (3)°, Z = 2,  $V = 1793.30 (12) Å^3$ , Dc = 1.168 g.cm<sup>-3</sup>,  $\mu$ (Cu-K $\alpha$ ) = 0.57 mm<sup>-1</sup>, crystal dimensions of 0.37 × 0.25 × 0.21 mm. Data were collected at 120 (2) K on a Gemini Atlas CCD diffractometer with mirror collimated Cu-Ka radiation. The structure was solved by direct methods<sup>1</sup> and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs<sup>2</sup> to final value R = 0.064 and  $R_w = 0.206$  using 6201 independent reflections ( $\Theta_{max} = 67.0^{\circ}$ ), 443 parameters and 18 restrains. The positions of disordered propoxy group were found from the electron density maps and then placed in appropriate positions. All distances between neighboring atoms and angles were fixed. Site occupancies were refined with the overall sum of the position constrained to full occupation. The hydrogen atoms were placed in calculated positions. The structure was deposited into Cambridge Structural Database under number CCDC 1006513.



The figure of compound **5c** structure and numbering the hydrogen atoms were omitted for sake of clarity except for the hydrogen atoms allyl.

#### Compound 7 2(C<sub>80</sub>H<sub>90</sub>O<sub>8</sub>)·CH<sub>2</sub>Cl<sub>2</sub>:

M = 2444.11 g.mol<sup>-1</sup>, monoclinic system, space group  $P2_1/c$ , *a* = 13.22632 (10) Å, *b* = 25.83704 (17) Å, *c* = 20.88126 (15) Å, β = 99.7860 (7)°, Z = 2, V = 7031.90 (9) Å<sup>3</sup>, Dc = 1.168 g.cm<sup>-3</sup>, µ(Cu-Kα) = 0.57 mm<sup>-1</sup>, crystal dimensions of 0.37 × 0.25 × 0.21 mm. Data were collected at 190 (2) K on a Xcalibur Onyx CCD diffractometer with graphite monochromated Cu-Kα radiation. The structure was solved by direct methods<sup>1</sup> and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs<sup>2</sup> to final value R = 0.072 and R<sub>w</sub> = 0.138 using 14412 independent reflections ( $\Theta_{max} = 76.0^{\circ}$ ), 961 parameters and 278 restrains. The positions of disordered solvent and propoxy groups were found from the electron density maps and then placed in appropriate positions. All distances between neighboring atoms and angles were fixed. Site occupancies were refined with the overall sum of the position constrained to full occupation. The hydrogen atoms were placed in calculated positions. The structure was deposited into Cambridge Structural Database under number CCDC 1006511.



The figure of compound **7** structure and numbering the hydrogen atoms and propyl groups were omitted for sake of clarity.