Electronic Supplementary Informations

Nicolas Zigon, Aurélie Guenet, Ernest Graf and Mir Wais Hosseini

Laboratoire de Chimie de Coordination Organique (UMR 7140), Université de Strasbourg,
Institut Le Bel, 4 rue Blaise Pascal, 67000 Strasbourg, France

Tel: +33 3 68 85 13 23
Fax: +33 3 68 85 13 25
E-mail: hosseini@unistra.fr
Experimental section

THF, CH₂Cl₂ and triethylamine were distilled over sodium, CaH₂ and KOH, respectively. Analytical grade MeOH, toluene and CH₃CN were used without further purification. ¹H- ³¹P- and ¹³C-NMR spectra were acquired at 25°C on either Bruker AV 300, Brucker AV 400, Brucker AV 500, or Brucker AV 600 spectrometers in deuterated solvents and residual solvent peak was used as the internal reference. Absorption spectra were recorded on an Uvikon XL spectrophotometer. MS was performed by the Service de Spectrométrie de Masse, University of Strasbourg.

2,6-bis(chloromethyl)pyridine 2,¹² 4-ethynlypyridine 9 and 2-(2-(2-((tetrahydro-2H-pyran-2-yl)oxy)ethoxy)ethoxy)ethoxy)ethanol 3¹ were synthesized according to published procedures.

2,6-bis(13-((tetrahydro-2H-pyran-2-yl)oxy)-2,5,8,11-tetraoxatridecyl)pyridine 4: A solution of compound 3 (6.12 g, 22 mmol, 2.2 eq.) in dry THF (50 mL) was added dropwise over 30 min to a suspension of NaH (60 % in oil, 0.875 g, 22 mmol, 2.2 eq.) in dry THF (150 mL). After 40 min, a solution of compound 2 (1.75 g, 10 mmol, 1 eq.) in dry THF (90 mL) was added over a period of one hour. The reaction mixture was then refluxed for 5 days. After evaporation of the solvent, the resulting oil was dissolved in CH₂Cl₂ (200 mL), washed with distilled water (3x200 mL) and brine (100 mL). The organic layer was dried over MgSO₄, evaporated and purified by column chromatography (Al₂O₃, petroleum ether/EtOAc 1:1 to 3:7) to yield compound 4 (3.9 g, 59 %) as a yellow oil.

¹H-NMR (CDCl₃, 300 MHz): δ (ppm) = 1.47-1.87 (m, 12H, CH₂), 3.45-3.90 (m, 36H, OCH₂), 4.62 (m, 2H, CH), 4.68 (s, 4H, OCH₂), 7.39 (d, 2H, J = 8.0 Hz), 7.72 (t, 1H, J = 8.0 Hz)

¹³C-NMR (CDCl₃, 75 MHz): δ (ppm) = 19.6, 25.6, 30.7, 62.4, 66.8, 70.4, 70.7, 70.8, 70.8, 74.0, 99.1, 120.1, 137.5, 157.9

Elemental analysis calcd (%) for C₃₅H₅₇NO₁₂: C 60.07 H 8.71 N 2.12; found: C 59.95 H 9.07 N 1.88

1,1'-(pyridine-2,6-diyl)bis(2,5,8,11-tetraoxatridecan-13-ol) 5: 2.6 mL of a 37 % HCl aqueous solution were added dropwise to a solution of compound 4 (3.9 g, 5.9 mmol, 1 eq.) in MeOH (300 mL). The resulting solution was stirred at RT for one day. NaHCO₃ was then added until pH 7 was reached. After evaporation of the solvent, the resulting solid was suspended in Et₂O (500 mL), filtrated on a sintered glass-funnel, and evaporated to dryness to afford 5 (2.6 g, 90 %) as a yellow oil.

¹H-NMR (CDCl₃, 300 MHz): δ (ppm) = 2.83 (br, 2H, OH), 3.58-3.75 (m, 32H, OCH₂), 4.67 (s, 4H, OCH₂), 7.38 (d, 2H, J = 8.0 Hz), 7.72 (t, 1H, J = 8.0 Hz)
UV-Vis (CH2Cl2) \( \lambda_{\text{max}} \) (e, mol\(^{-1}\)·L·cm\(^{-1}\)):

- 230 (1.8·10^4), 270 (9.7·10^3)
General procedure for the titration experiment: To a solution of compound 1 (1 eq.) in dry and degassed CH₂Cl₂ (2 mL), a solution of AgSbF₆ (0.25 eq.) in dry CH₃CN (1 mL) was added. The reaction mixture was stirred at RT in the dark for 2 h. After removal of the solvent, the desired product was obtained quantitatively as a yellow solid. The same experimental procedure was repeated with 0.5, 0.75, 1, 2, and 3 eq. of AgSbF₆.
References