Supporting Information


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General experimental methods

Proton, $^{19}$F and $^{13}$C NMR spectroscopies were carried out on a Bruker ARX 300 spectrometer at 300.14, 282.41 and 75.5 MHz respectively. The highly coupled $^{13}$C signals of the fluorinated carbons are not listed below. $^{1}H,^{1}H,^{2}H,^{3}H,^{3}H$-perfluorodecyl triflate,$^{21}$ $^{1}H,^{1}H,^{2}H,^{3}H,^{3}H$-perfluoroundecyl iodide$^{11}$ and $^{1}H,^{1}H,^{2}H,^{2}H,^{3}H,^{3}H$-perfluorotridecyl iodide$^{22}$ were prepared by the literature methods. Fluoroflash® silica gel (40 µm) was purchased from Fluorous Technologies. GC analyses were performed using a Perkin Elmer Clarus 500 GC and a Perkin Elmer-Elite Series PE-5 column (30 m x 0.25 mm, 5 % diphenyl, 95 % dimethylpolysiloxane).

$^{1}H,^{1}H,^{2}H,^{3}H,^{3}H$-perfluoro-2-iodo-$n$-tridecan-1-ol

Perfluorodecyl iodide (7.00 g, 26.12 mmol), allyl alcohol (3 mL, 44.11 mmol) and AIBN (400 mg, 2.43 mmol) were heated at 80 °C under an inert atmosphere for 24 h. The yellow solid obtained was recrystallized from hexane (20 mL). The resulting mixture was purified by column chromatography on
silica gel (petroleum ether/diethyl ether = 6/4) affording the pure product as a white solid (6.52 g, 60%). mp 121-123 °C; Anal. Calcd for C\textsubscript{13}H\textsubscript{6}F\textsubscript{21}O: C, 22.18; H, 0.86 %. Found: C, 22.03; H, 0.76 %; HRMS (EI) Calcd for C\textsubscript{13}H\textsubscript{6}F\textsubscript{21}O: 703.91280; found: 703.91281; δ\textsubscript{H} (CDCl\textsubscript{3}) 4.39 (1H, m), 3.78 (2H, m), 2.96 (1H, m), 2.71 (1H, m), 1.95 (1H, br s); δ\textsubscript{F} (CDCl\textsubscript{3}) -80.68 (3F, t, 4\textsubscript{JFF} 9.9), -112.94 (1F, m\textsubscript{AB}), -114.63 (1F, m\textsubscript{AB}), -121.71 (10F, m), -122.63 (2F, m), -123.44 (2F, m), -126.05 (2F, m). δ\textsubscript{C} (CDCl\textsubscript{3}) 67.9 (CH\textsubscript{2}), 37.5 (t, 2\textsubscript{JCF} 21.3, CH\textsubscript{2}), 21.8 (CH).

1H,1H,2H,2H,3H,3H-perfluorotridecan-1-ol

1H,1H,2H,2H,3H,3H-perfluoro-2-iodo-\textit{n}-tridecanol (4.30 g, 6.10 mmol) and AIBN (45 mg, 0.27 mmol) were suspended in dry benzotrifluoride (40 mL). Tributyltin hydride (3.30 mL, 12.20 mmol) was then added dropwise and the reaction mixture heated to 85 °C under an inert atmosphere for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting residue was redissolved in diethyl ether and washed with water and brine. The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and filtered. KF (710 mg, 12.20 mmol) was dispersed in the organic layer and stirred for 12 h. After filtration and removing the solvent, the resulting solid was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 1/1) to give the product as a white solid (2.29 g, 65%). mp 85-87 °C (lit.,\textsuperscript{23} 86-89 °C); Anal. Calcd for C\textsubscript{13}H\textsubscript{7}F\textsubscript{21}O: C, 27.09; H, 1.04 %. Found: C, 27.01; H, 1.22 %; HRMS (EI) Calcd for C\textsubscript{13}H\textsubscript{7}F\textsubscript{21}O: 578.01612; found: 578.01616; δ\textsubscript{H} (CDCl\textsubscript{3}) 3.71 (2H, m), 2.16 (2H, m), 1.82 (2H, m), 1.48 (1H, br s); δ\textsubscript{F} (CDCl\textsubscript{3}) -80.73 (3F, t, 4\textsubscript{JFF} 9.5), -114.24 (2F, t, 4\textsubscript{JFF} 16.1), -121.70 (10F, m), -122.65 (2F, m), -123.45 (2F, m), -126.06 (2F, m). δ\textsubscript{C} (CDCl\textsubscript{3}) 61.4 (CH\textsubscript{2}), 27.6 (t, 2\textsubscript{JCF} 23.4, CH\textsubscript{2}), 23.0 (CH\textsubscript{2}).
**N,N’-Dioctyl-4,13-diaza-18-crown-6 (2)**

N,N’-Dioctyl-4,13-diaza-18-crown-6 was prepared by a procedure analogous to that for 3 and the resultant oil was purified by Kugelröhr distillation (0.1 mmbar, 2 h, 75 °C) to give the pure product as a brown oil (288 mg, 78%). It has been prepared previously by acylation followed by reduction.²⁴ Anal. Calcd for C₂₈H₅₈N₂O₄: C, 69.07; H, 12.03; N, 5.75 %. Found: C, 69.16; H, 11.84; N, 5.64 %. m/z (FAB) 486.43968 (M⁺. C₂₈H₅₈N₂O₄ requires 486.43966); δ_H (CDCl₃) 3.55 (16H, m), 2.72 (8H, t, 3_J_HH 6.5), 2.43 (4H, t, 3_J_HH 7.1), 1.38 (4H, m), 1.19 (20H, br s), 0.81 (6H, t, 3_J_HH 6.5); δ_C (CDCl₃) 70.7 (CH₂), 69.6 (CH₂), 55.8 (CH₂), 53.8 (CH₂), 31.8 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 27.5 (CH₂), 26.8 (CH₂), 22.7 (CH₂), 14.1 (CH₃).

**N,N’-Bis(1H,1H,2H,2H-perfluorodecyl)-4,13-diaza-18-crown-6 (5)**

A mixture of 4,13-diaza-18-crown-6 (250 mg, 0.95 mmol), 1H,1H,2H,2H-perfluoroundecyl triflate (1.43 g, 2.4 mmol),²¹ Na₂CO₃ (250 mg, 2.4 mmol) and dry ethyl acetate (30 mL) was refluxed under an inert atmosphere for 72 h. After cooling to room temperature, the solvent was removed under reduced pressure and water was added. The aqueous mixture was extracted with dichloromethane and the dichloromethane extracts were combined, dried over MgSO₄ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ and then with EtOAc as eluants. The EtOAc fractions were combined and evaporated *in vacuo* to give a white solid, which was recrystallised from MeOH (583 mg, 53%). mp 62-64 °C (lit.,¹² 60-62 °C); Anal. Calcd for C₃₂H₃₂F₃₄N₂O₄: C, 33.29; H, 2.79; N, 2.43 %; Found: C, 33.14; H, 2.58; N, 2.29 %; m/z (FAB) 1155 (M⁺, 100%); δ_H (CDCl₃) 3.54 (16H, m), 2.83 (4H, t, 3_J_HH 7.9), 2.73 (8H, t, 3_J_HH 5.5), 2.21 (4H, m); δ_F (CDCl₃) -80.93 (3F, t, 4_J_FF 9.9), -114.00 (2F, t, 4_J_FF 15.6), -122.02 (6F, m), -122.81 (2F, m), -123.51
(2F, m), -126.21 (2F, m); $\delta_C$ (CDCl$_3$) 70.8 (CH$_2$), 69.9 (CH$_2$), 54.0 (CH$_2$), 46.7 (CH$_2$), 29.0 (t, $^2J_{CF}$ 21.5, CH$_2$).

**Partition coefficients**

The organic solvent (2 mL) and perfluoro-1,3-dimethylcyclohexane (2 mL) were added to a vial containing macrocycle 5 (0.100 g) and a magnetic stirrer bar. The samples were stirred at 18.5 °C for 0.5 h and allowed to stand for 0.5 h for the phases to separate. An aliquot was removed from each phase (1 mL). The solvent was removed and the residue was dried under oil pump vacuum (0.01 mmHg) and then weighed.

**Potassium picrate extractions (Table 2)$^4,13$**

Equal volumes of a dichloromethane (10 mL) or benzotrifluoride solution (10 mL) of the required macrocycle (0.1 mM) and an aqueous solution of the potassium picrate (0.1 mM) were introduced into a stoppered flask and stirred for 30 min at 21 ± 1 °C. The mixture was allowed to stand for 2 h at the same temperature to allow complete phase separation. The absorbance of the picrate in the aqueous phase was measured at 356 nm with a Shimadzu UV-visible spectrophotometer. The percentage extraction was calculated by:

$$\text{% Extraction} = 100 \frac{(\text{Abs}_{\text{before}} - \text{Abs}_{\text{after}})}{\text{Abs}_{\text{before}}}$$

where $\text{Abs}_{\text{before}}$ is the absorbance of a similarly diluted sample of the unextracted potassium picrate solution and $\text{Abs}_{\text{after}}$ is the absorbance of the potassium picrate solution after extraction. Three independent extractions were performed for each combination of potassium picrate and ionophore, and the results were averaged.
General procedure for the separation and recovery of macrocycle 3 without an aqueous wash

After 12 h the reaction mixture was cooled to room temperature and was filtered to remove the excess potassium salts. The clear organic phase was passed through a short column of fluorous reverse phase silica gel (~ 2.7 g, 2.5 cm long, 1.5 cm diameter) and the column was eluted with benzotrifluoride (40 mL) to obtain the clean organic products. The fluorinated phase transfer catalyst was then recovered (91-99 %) by eluting with trifluoroethanol (60 mL). After removing the trifluoroethanol, the phase transfer catalyst was dried in vacuo for 2 h at 60 °C before being reused in another aliphatic nucleophilic substitution (Table S1).

<table>
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<th>Catalyst Used (g)</th>
<th>Catalyst Recovered (g)</th>
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References


$^{1}H$ NMR

$^{19}F$ NMR
S12