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Monofunctional Chiral Crowns. Part 1

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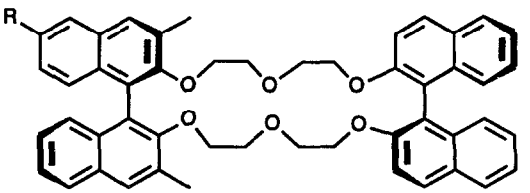
Abstract: A siloxane oligomer bearing a chiral crown with high affinity for α-amino acids has been synthesised. The host is a modified form of a coronand first prepared by Cram, in which two 1,1′-binaphthol systems are linked through the oxygen atoms at the 2,2′-positions to form a 22-membered ring system containing six ether oxygen atoms attached to each other by four ethylene units. This was selectively mono-alkenylated to form an undec-10-en-1-yl derivative, which was bonded to linear siloxanes [$HSiMe_2O(SiMe_2O)_nSiMe_2H$] and [$Me_3SiO(Me_2SiO)_x(MeHSiO)_ySiMe_3$] with total chain lengths of *ca* 4 and 200 Si atoms respectively, *via* a Pt catalysed hydrosilylation reaction.

α-Amino acids occupy a pivotal role in both biology and organic chemistry, and provide the building blocks for many biologically important compounds. As a consequence, considerable efforts have been made in the last decade to develop new methodologies for the synthesis of proteinogenic amino acids in homochiral form.[1] Complementary techniques based on the resolution of racemic mixture, particularly using chromatographic methods, provide alternative means of accessing both antipodal forms of α-amino acids.[2] Our interest is centred in the use of supported liquid membranes to effect the selective separation of biogenic materials and, in order to overcome the carrier partitioning problem which contributes to the instability of conventional liquid membrane systems consisting of a carrier dissolved in a solvent, we have linked chemically various carriers to fluid poly(organosiloxanes) of low viscosity. The products then function as integrated carrier/solvent systems.[3]

For the resolution of α-amino acids we have targeted unnatural D-amino acids as they are key starting materials for several major drugs in current use, and we have chosen the chiral crown ether (1) as the active carrier since it exhibits selectivity for α-amino acids of this configuration.[4,5]

In order to link the receptor to the polymer we have identified the derivative (2) which bears an alkenyl spacer unit capable of bonding through the unsaturated terminus to a siloxane polymer ("SiO"), thereby affording a functionalised polymer (3).

The key intermediate *en route* our target molecule is the homochiral bromobinaphthol (7) which we have synthesised through the implementation of the first three steps summarised in scheme 1, utilising the bis(methylmethoxy) (MEM) derivative (4) of chiral 2,2′-dihydroxybinaphthol as the starting compound.



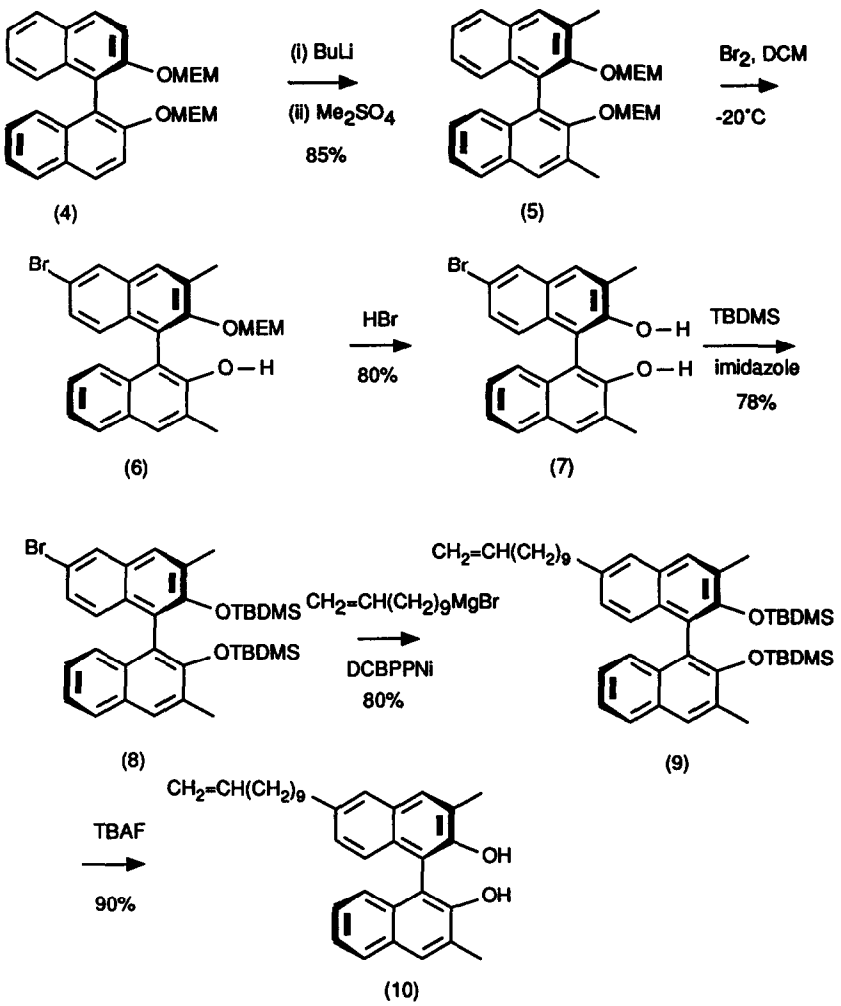
(1) R=H
(2) R=$(CH_2)_9CH{=}CH_2$
(3) R=$(CH_2)_9CH_2CH_2$"SiO"

Initially we found that bromination of the diether (5) at *ca* 0°C gave a 6,6′-dibromo derivative,[6] but by maintaining the reaction temperature at -20°C the partly protected monobromonaphthol (6) could be isolated. However, it was more convenient to deprotect this compound *in situ* thus affording the (+) *R*-binaphthol (7). This product was reprotected as the di-^{t}butyldimethylsilyl (TBDMS) ether (8, R=Br).

Alkenylation was achieved by reacting the ether (8) with undec-10-en-1-yl magnesium bromide in the presence of a catalytic amount of dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) (DCBDPNi) giving the desired product (9) in 80% yield and ≥95 % ee. The optical purity of this key product was confirmed by N.M.R. spectral analysis of its Mosher ester. Compound (9) was deprotected by treatment with tetrabutylammonium fluoride to afford the alkenyl binaphthol (10).

It should be pointed out that attempts to introduce the alkenyl side chain in the protected bromobinaphthol (11) using the standard methods of metal halogen exchange,[7] followed by treatment of the metallic derivative with a suitable alkenyl bromide, all failed. Acylation reactions were also investigated and attempts to form Grignard reagents from the protected bromobinaphthol were made. Such ventures either failed, or were inefficient. When the reactions failed the usual product was the debromobinaphthol (5) and we discovered that treatment of the bromobinaphthol with butyl lithium, followed by the addition of deuterium oxide did not lead to the deuterated binaphthol (13). Thus we conclude that the lithiated binaphthol is very reactive and effects immediate dehydrobromination of the butyl bromide liberated from the metal halogen exchange process. It follows that the lithium derivative (12) is destroyed before a follow-up reaction with an added alkenyl bromide, or acyl halide, can be accomplished. Alkylations using organo-copper and organo-cerium species also failed.

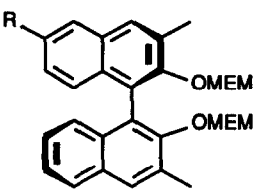
To complete the synthesis of the functionalised crown the chiral tosylate (14) was prepared following a literature procedure[8] and this was heated in KOH/tetrahydrofuran with the alkenylbinaphthol (10). After 7 days at reflux, the reaction was worked up to afford the target molecule (2) in 65% yield (see scheme 2).



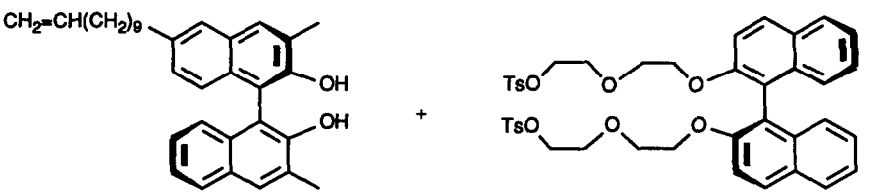
Scheme 1. Synthesis of the alkenylbinaphthol (7)

In previous studies[9] we have shown that crown ethers can be chemically linked to one or more silicon centres *via* a catalytic hydrosilylation procedure which generally affords single addition products in high yields under mild conditions.[10]

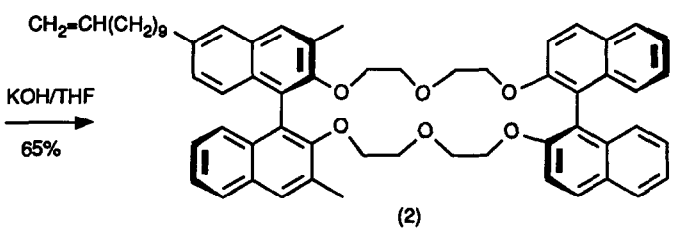
$$\equiv SiH + L\text{-}(CH_2)_nCH{=}CH_2 \xrightarrow{Pt} L\text{-}(CH_2)_{n+2}Si\equiv$$



(11) R=Br
(12) R=Li
(13) R=D



(10) (14)



(2)

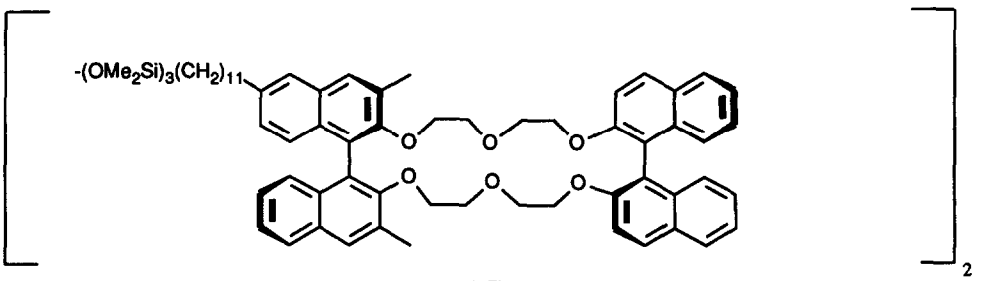
Scheme 2. Synthesis of the crown (2)

Our work now required an extension of this methodology towards the bonding of the crown (2) to the silicon centres of short- and long-chain H-functionalised siloxanes, $HSiMe_2O(SiMe_2O)_nSiMe_2H$ (n = *ca* 4) and $Me_3SiO(Me_2SiO)_x(MeHSiO)_ySiMe_3$ (x + y = *ca* 200, x = *ca* 6). This afforded small quantities of the homochiral silylated derivatives (15) and (16) respectively.

Both the model complex (15) and the longer chain functionalised siloxane (16) were obtained as very viscous liquids. The former was characterised by analysis, infrared, ^1H- and ^{19}Si N.M.R. methods, which showed that hydrosilylation had occurred almost quantitatively without fragmentation or rearrangement of the polymer chain. Complete functionalisation of the longer chain commercial polymer was also apparent from the spectroscopic data derived from (16). Thus the feasibility of tethering this chiral crown to a siloxane

polymer has been established, but we have not, as yet, obtained a sufficiently mobile fluid which can be readily used as a supported liquid membrane.

As part of this study we have extended, using N.M.R. methods, previous investigations[5] of the enantioselectivity of chiral crowns towards amino acid derivatives. Cram *et al.*[5] established that the crown (1) complexes some salts of amino acids and esters with a high enantiomeric selectivity, recognition occurring through a combination of the macrocyclic effect, complementarity and pre-organisation.[11] The favoured combinations are (*SS*)-crown (1) with amino acids of the L-configuration, and (*RR*)-crown (1) with D-amino acids. In almost all such investigations the amino acid salts used have contained non H-bonding anions such as ClO_4^- or PF_6^- in order to minimise anion - H_3N^+R interactions and facilitate the formation of suitable crystalline forms of the host-guest complex. Our studies have centred on Cl^- salts as these are more relevant to the separation process we are pursuing, even though the H-bonding capability of this anion may tend to reduce the stereoselective interactions between guest and host.



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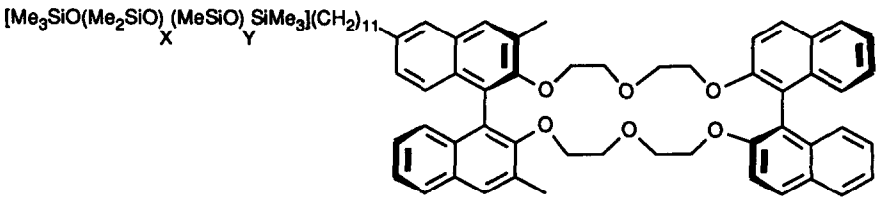


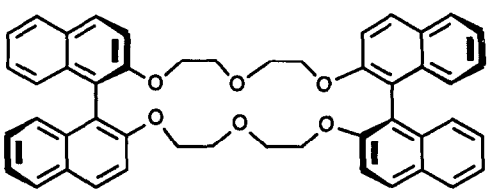
(16)

We studied the degree of recognition through ^1H N.M.R. measurements on solutions of the hydrochlorides of (*R*)- and (*S*)-phenylglycine ethyl ester, and (*R*)- and (*S*)-phenylalanine ethyl ester, each in combination in a 1:1 molar ratio with the known chiral crown (17) (this compound was synthesised by the literature procedure[8]). The effects of complexation were most clearly evidenced by small chemical shift changes of *ca* 0.4 ppm in the $-N^+H_3$ proton signals in the phenylglycine adducts, and of *ca* 0.1 ppm in the ester methylene proton resonances in the phenylalanine derivatives. Unlike salts containing non-H-bonding anions where

significant differences are observed between the two enantiomers in the presence of the chiral crown, *both* enantiomers of each hydrochloride salt exhibited similar (but not identical) chemical shifts (Table 1).
Attempts to grow crystal of any of the four crown (17) - amino ester hydrochloride complexes for X-ray analysis were unsuccessful, but we believe that chiral resolution of amino acids and their derivatives is likely to be highly anion dependent.

Table 1. Selected ^1H N.M.R. Data on $CDCl_3$ Solutions of Amino Acid Ester Hydrochlorides and Chiral Crown (17) in a 1:1 Molar Ratio

Chemical Shifts (δ)	$-CO_2CH_2CH_3$	$-CO_2CH_2CH_3$	$=CHCO_2Et$	$-N^+H_3$
18a/b	1.05 (t)	4.04 (q)	5.09 (s)	8.79
19a/b	1.04 (t)	4.01 (q)	4.31 (s)	8.66
18a/17	1.25 (t)	4.11 (q)	5.11 (br)	9.14
18b/17	1.16 (t)	4.17 (q)	5.10 (br)	9.14
19a/17	1.16 (t)	4.18 (q)	4.35 (br)	8.76
19b/17	1.08 (t)	4.07 (q)	4.28 (br)	8.66



(17)

(R)-Phenylglycine ethyl ester hydrochloride (18a)
(S)-Phenylglycine ethyl ester hydrochloride (18b)
(R)-Phenylalanine ethyl ester hydrochloride (19a)
(S)-Phenylalanine ethyl ester hydrochloride (19b)

Experimental

Petrol refers to petroleum ether b.p. 60-80°C. Merck DC-alufolien Kieselgel 60 F_{254} sheets containing a fluorescent indicator were used in TLC analyses, and flash column chromatography was carried out using Amicon Matrex or Merck 9385 silica gel. Melting points were determined on a commercially available apparatus (Electrothermal MK III) and are uncorrected. Infra red spectra were recorded on a Perkin-Elmer 1310 instrument using 0.5mm path length sodium chloride cells. Data on siloxanes were collected from thin

films of these fluids held between NaCl discs. N.M.R. spectra were recorded on JEOL GX 270 and 400 MHz spectrometers. The deuterated solvent signal was used as the internal standard and chemical shifts are quoted on the δ-scale relative to tetramethylsilane. Mass spectra were recorded using a VG 7070E instrument equipped with a VG 2000 data system. Chemical ionisation was employed using isobutane as the reagent gas.

(+)-2,2′-Di(2-methoxyethoxymethyloxy)binaphthyl (4)

Optically pure (+)-2,2′-binaphthol[8,12] (5.94g, 20.7mmol) in dry tetrahydrofuran (60cm^3) was added by means of a syringe to a stirred solution of NaH (4.15g, 60%, 62.1mmol) in tetrahydrofuran (20cm^3) at -5°C protected by a nitrogen atmosphere. After the addition, 2-methoxyethoxymethyl chloride (5.69cm^3, 49.7mmol) was added, the mixture was stirred under nitrogen for 3h at -5°C and then was allowed to warm to room temperature (14°C) during the course of 8h. Water (60cm^3) was introduced and the product was extracted into dichloromethane (3 x 150cm^3). The extracts were dried over anhydrous magnesium sulphate, then filtered and the solvent removed. The oil that remained was chromatographed, eluting with ethyl acetate:petrol (3:7), to afford the title compound (8.6g, 90%) as a viscous liquid; $[\alpha]_D^{20}$ + 61.8° (c 1.00, tetrahydrofuran); ν_{max}cm^{-1}(neat) 2940, 1120; δ_H 3.24-3.73 (14H, m), 5.20 (4H, d, J = 2.3 Hz), 7.11-7.15 (2H, m) 7.18-7.24 (2H, m), 7.30-7.38 (2H, m), 7.62 (2H, d, J = 10.0 Hz), 7.84-7.89 (2H, d, J = 8.0 Hz), 7.94 (2H, d, J = 8.0 Hz); m/z (%) (C.I.) 463 (1 M+1$^+$), 462 (3 M$^+$), 89 (100), m/z [FAB (+)] (%) 462 (6 M$^+$), 89 (100).

(-)-2,2′-Di(2-methoxyethoxymethyloxy)-3,3′-dimethylbinaphthyl (5)

(+)-2,2′-Di(2-methoxyethoxymethyloxy)binaphthyl (4) (0.50g, 1.08mmol) in dry tetrahydrofuran (10cm^3) under an atmosphere of nitrogen was treated with n-butyl lithium (2.02cm^3, 1.6M in hexane, 3.22mmol) and the mixture was stirred at 0°C for 45 min. It was then allowed to warm to room temperature (20°C) and dimethyl sulphate (0.31cm^3, 3.22mmol) was added. After a further 16h at ambient temperature, saturated ammonium chloride solution (30cm^3) was added. The product was extracted into ethyl acetate (3 x 25cm^3), and the combined organic fractions were washed with brine (30cm^3) and with water (30cm^3). The solvent was removed and the crude product was purified by chromatography, eluting with ethyl acetate:petrol (1:3). This afforded the title compound (5) as an oil (0.5g, 85%); $[\alpha]_D^{20}$ - 53.8° (c 1.00, tetrahydrofuran); ν_{max}cm^{-1} (neat), 2940 (C-H), 1120 (OCH_2), 1060 (OCH_2); δ_H 2.46 (6H, s,), 2.83 (4H, m), 3.10 (2H, m), 3.38 (2H, m), 3.20 (6H, s), 4.58 (2H, d, J = 6.1 Hz), 4.72 (2H, d, J = 6.1 Hz), 7.10-7.40 (6H, m), 7.80 (4H, m); m/z (C.I.) (%), 490 (2, M$^+$), 322 (32), 89 (100).

(+)-6-Bromo-2,2′-dihydroxy-3,3′-dimethylbinaphthyl (7)

A solution of (-)-2,2′-di(2-methoxyethoxymethyloxy)-3,3′-dimethylbinaphthyl (5) (0.32g, 0.67mmol) in dry dichloromethane (15cm^3) was cooled to -20°C under a positive pressure of nitrogen, and a portion (0.63cm^3, 1.40mmol) of a solution of bromine (1cm^3) in dichloromethane (20cm^3) was added slowly over a period of 15 min. The mixture was allowed to warm to 0°C over a period of 1.5h and then to room temperature. The solvent was removed, and tetrahydrofuran (20cm^3) and hydrogen bromide solution (1cm^3) were added,

followed by water (10cm^3). Extraction with dichloromethane (2 x 40cm^3) and chromatography, eluting with ethyl acetate:petrol (1:49) yielded the title compound (7) as a colourless crystalline solid (0.21g, 80%), m.p. 97°C; $[\alpha]^{20}D$ + 11.5° (c 1.00, tetrahydrofuran); ν_{max}cm^{-1} (Nujol) 3400 (OH), 2940 (C-H); δ_H 2.50 (6H, s), 5.03 (1H, s), 5.14 (1H, s), 6.87 (1H, d, J = 9.0 Hz), 7.02 (1H, d, *J* = 8.2 Hz), 7.2-7.4 (3H, m), 7.70 (1H, s), 7.82 (2H, m), 7.97 (1H, d, *J* = 1.8 Hz); m/z (C.I.) (%) 394 (7, M$^+$), 392 (7, M$^+$), 135 (100), 83 (33) [Found: C, 67.4; H, 4.6 $C_{22}H_{17}O_2Br$ requires: C, 67.2; H, 4.4%].

(-)-6-Bromo-2,2′-di(^{t}butyldimethylsilyloxy)-3,3′-dimethylbinaphthyl (8)

(+)-6-Bromo-2,2′-dihydroxy-3,3′-dimethylbinaphthyl(7) (0.81g, 2.06 mmol) in dimethylformamide (50cm^3) containing imidazole (0.62g, 9.10mmol) was treated with ^{t}butyldimethylsilyl chloride (1.37g, 9.1mmol). The reaction mixture was stirred at room temperature under nitrogen for 4 days, then washed with saturated sodium bicarbonate solution. The product was extracted into ethyl acetate (4 x 30cm^3) and the combined extracts evaporated to afford an oil which was chromatographed eluting with petrol. In this way the title compound (0.9g, 78%) was obtained as a viscous colourless liquid; $[\alpha]_D^{20}$ - 210.5° (c, 1.00 tetrahydrofuran); ν_{max}cm^{-1} (film) 2940 (C-H), 1260 ($SiCH_3$), 1065 (Si-O); δ_H -1.2 (6H, s), -1.1 (6H, s), 0.91 (18H, s), 2.60 (6H, s), 7.10 (1H, d, *J* = 8.4 Hz), 7.15 (1H, d, *J* = 8.3 Hz), 7.20-7.43 (3H, m), 7.74 (1H, s), 7.86 (2H, d), 8.20 (1H, d, *J* = 1.9 Hz); m/z (C.I.) (%) 622 (51 M$^+$), 620 (47 M$^+$), 565 (45), 115 (100);

(-)-2,2′-Di(^{t}butyldimethylsilyloxy)-3,3′-dimethyl-6-(undec-10-enyl)binaphthyl (9)

A two-necked round bottomed flask (10cm^3) containing magnesium turnings (200mg, 8.23mmol) was equipped with a magnetic stirrer and a reflux condenser. The reaction vessel and the magnesium were dried under a rapid stream of nitrogen with a heat gun. After the flask had cooled to room temperature, the rate of nitrogen flow was reduced, and anhydrous diethyl ether (2cm^3) and undec-10-enyl-1-bromide (0.76g, 3.26mmol) in ether (3cm^3) were added slowly by means of a syringe. The reaction mixture was stirred at room temperature, and within a few minutes an exothermic reaction occurred. After cooling, the mixture was transferred, with concomitant filtration, to another flask containing a solution of (-)-6-bromo-2,2′-di(^{t}butyldimethylsilyloxy)-3,3′-dimethylbinaphthyl (8) (0.67g, 1.09mmol) and dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) (0.02g, 10.0mmol) in diethyl ether (5cm^3). The reaction mixture was then heated at reflux under nitrogen for 4 days, cooled and hydrolysed with 2M hydrochloric acid (5cm^3). The organic layer was separated and the aqueous layer extracted with ethyl acetate (2 x 20cm^3). The combined organic layer and extracts were washed with water (2 x 20cm^3), saturated sodium bicarbonate solution (20cm^3), and again with water (20cm^3). The solvents were then removed and the crude product was purified by chromatography, eluting with hexane to give (9) as a colourless oil (0.63g, 83%); $[\alpha]^{20}_D$ - 198.2° (c 1.00, tetrahydrofuran); δ_H -1.07 (6H, s), 0.01 (6H, s), 0.90 (18H, s), 1.30-1.50 (12H, m), 1.52 (2H, m), 2.20 (2H, m), 2.53 (3H, s), 3.54 (3H, s), 2.80 (2H, m), 5.00-5.20 (2H, m), 5.90-6.00 (1H, m), 7.00-7.10 (1H, m), 7.20-7.30 (2H, m), 7.38-7.42 (1H, m), 7.63-7.70 (1H, m), 7.77 (1H, s), 7.80-7.90 (2H, m); m/z (C.I.) (%) 695 (3 M+1$^+$), 149 (80), 73 (100).

1-Bromo-10-undecene

An ice/acetone-cooled solution of 10-undecene-1-ol (3.0cm^3, 15mmol) in dry pyridine (27 cm^3) was treated with 4-toluenesulphonyl chloride (2.95g, 15.5mmol) in small proportions, so that the temperature did not exceed 0°C. The mixture was allowed to stand at 0°C overnight (16h), then it was poured into ice-water (50cm^3), and extracted with diethyl ether (3 x 100cm^3). The combined extracts were washed with cold 6M sulphuric acid (2 x 100cm^3) and then with 2% sodium bicarbonate (200cm^3). Removal of the solvent gave a colourless solid which was purified by chromatography, eluting with diethyl ether:petrol 1:19 to give undec-10-enyl 4-methylbenzenesulphonate (5.2g, 78%); δ_H 1.22 (12H, m), 1.65 (2H, m), 2.02 (2H, m), 2.44 (3H, s), 4.01 (2H, t, J = 6.5 Hz), 4.97 (2H, dt, J = 17.1, 2.7 Hz), 6.82 (1H, m), 7.39 (2H, d, J = 8.1 Hz), 7.80 (2H, d, J = 8.1 Hz). This compound (2.61g, 8mmol) in dry acetone (7 cm^3) containing anhydrous lithium bromide (1.57g, 18mmol) was heated under reflux with protection from moisture for 16h. Dichloromethane (40cm^3) and water (60cm^3) were added to the cooled reaction mixture and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 30cm^3) and the combined organic phases dried and evaporated at less than 20°C giving the title compound as a colourless oil (1.82g, 94%), b.p. 85°C/1 mm Hg (lit., b.p.[13] 83-84°C/1 mmHg); δ_H 1.29 (12H, m), 1.85 (2H, m), 2.07 (2H, m), 3.41 (2H, t, J = 6.8 Hz), 4.97 (2H, dt, J = 17.1 Hz, 2.7 Hz), and 5.83 (1H, m).

(-)-2,2′-Dihydroxy-3,3′-dimethyl-6-(undec-10-enyl)binaphthyl (10)

A solution of tetrabutylammonium fluoride in tetrahydrofuran (1M, 1cm^3) was added to +(R)-2,2′-di(^{t}butyldimethylsilyloxy)-3,3′-dimethyl-6-(undec-10-enyl)binaph thyl (9) (0.30g, 0.043mmol) in dry tetrahydrofuran under nitrogen. After 1h, water (5cm^3) was introduced and the reaction mixture was extracted with ethyl acetate (3 x 20cm^3). The combined extracts were dried and evaporated, and the residue chromatographed eluting with dichloromethane. This gave the title compound as an oil (0.19g, 82%); $[\alpha]^{20}_D$ + 19.9 (c 1.00, tetrahydrofuran); ν_{max}cm^{-1} (neat), 3500 br (OH), 2910 (C-H), 1645 (HC=CH$_2$); δ_H 1.2 (12H, m), 1.62 (2H, m), 2.00 (2H, m), 2.50 (6H, s), 2.70 (2H, t, J = 7.5 Hz), 4.95 (2H, m), 5.05 (1H, s), 5.15 (1H, s), 5.8 (1H, m), 6.95 (1H, d, J = 8.5 Hz), 7.07 (2H, m), 7.23 (1H, m), 7.33 (1H, m), 7.58 (1H, s), 7.72 (1H, s), 7.8 (2H, m); m/z (C.I.) (%) 647 (100 MH$^+$), 466 (97 M$^+$), 371 (12), 97 (32) [Found: C, 85.1; H, 8.5 $C_{23}H_{38}O_2$ requires: C, 84.9 ; H, 8.2%].

Mosher ester of the binaphthol (10)

A solution of (+)-binaphthol (10) (15mg, 2.75 x 10^{-2} mmol) in dry dichloromethane (2cm^3), DMAP (0.435g) was protected by an atmosphere of nitrogen gas and treated with the (+)-(R)-enantiomer of Mosher's acid chloride (0.025g). The mixture was stirred at 20°C for 14h, and then the product was collected by filtration (19mg, 82%); δ_H 1.15 (12H, m), 1.6 (2H, m), 2.00 (2H, m), 2.23 (3H, s), 2.25 (3H, s), 2.70 (2H, t, J = 7.9 Hz), 2.95 (6H, s, OCH_3), 4.95 (2H, m), 5.05 (1H, m), 6.8-7.9 (9H, m). This compound was unstable and decomposed when left at room temperature over a period of 3 days.

(+)-6-Bromo-2,2′-di(2-methoxyethoxymethoxy)-3,3′-dimethylbinaphthyl (11)

Sodium hydride (0.032g, 0.98mmol) was added to a stirred solution of the substrate (7) (0.14g, 0.45mmol) in dry tetrahydrofuran at 0°C under a positive pressure of nitrogen. After 15 min, methoxyethoxymethyl chloride (0.125cm^3, 1.11mmol) was added. The mixture was stirred at 0°C for 4h and water (4 cm^3) was then added to the mixture. The crude product was extracted from this mixture with ethyl acetate(3 x 30cm^3) and the combined, dry extracts were evaporated to leave an oil. This was purified by chromatography, eluting with ethyl acetate:petrol (2:8), to obtain the the title compound (11) (0.22g, 86%) as a colourless oil; $[\alpha]^{20}_D$ +45.5°(c 1.00, tetrahydrofuran); ν_{max}cm^{-1}(neat), 2940 (C-H), δ_H 2.55 (6H, s), 2.80 (4H, m), 3.10 (2H, m), 3.20 (6H, m), 3.25 (2H, m), 3.35 (2H, m), 4.60 (2H, m), 4.69 (2H, m), 7.02 (1H, d, J = 8.4 Hz), 7.1 (1H, d, J = 8.2 Hz), 7.18-7.42 (3H, m), 7.69 (1H, s), 7.80 (2H, m), 7.96 (1H, d, J = 1.8 Hz); m/z (C.I.)(%) 751 (22 M+1$^+$), 750 (58 M$^+$), 569 (22 M+1$^+$), 568 (58 M$^+$), 447 (57), 89 (100).

Deuteration of (11)

n-Butyl lithium (1.3M in hexane, 0.035cm^3, 1.2eq.) was added dropwise to a solution of (+)-6-bromo--2,2′-di(2-methoxyethoxymethoxy)-3,3′-dimethylbinaphthyl (11) (0.024g, 4.9 x 10^{-2}mmol) in dry tetrahydrofuran (5cm^3), protected under nitrogen and maintained at -78°C. After 1h, the mixture was warmed to -4°C, and then D_2O (0.5cm^3) was added. After maintaining the mixture at -40°C for 0.5h, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature over a period of *ca* 1h. It was extracted into ethyl acetate (2 x 10cm^3), and the dry extracts were evaporated. The residue was purified by chromatography, eluting with ethyl acetate:petrol (1:9). The product (0.02g, 84%) was a viscous liquid; δ_H 2.46 (6H, s), 2.83 (4H, m), 3.10 (2H, m), 3.38 (2H, m), 320 (6H, s), 4.58 (2H, d, J = 6.1 Hz), 4.72 (2H, d, J = 6.1 Hz), 7.10-7.40 (6H, m), 7.80 (4H, m); m/z (C.I.) (%) 490 (2 M$^+$), 332 (32), 89 (100); $[\alpha]^{20}_D$ - 53.8° (c 1.00 tetrahydrofuran).

Preparation of the crown (2)

A mixture of dry tetrahydrofuran (10cm^3), optically pure binaphthol (10) (0.05g, 0.11mmol) and potassium hydroxide (85%) (0.04g, 0.21mmol) was heated at reflux under an atmosphere of nitrogen for 5h. The (R)-ditosylate (14) (0.074g, 0.11 mmol) in dry tetrahydrofuran (5cm^3) was then added slowly to the solution which was boiled for a further 175h. The reaction mixture was then cooled and the solvent removed. The residue was partitioned between with water (25cm^3) and dichloromethane (25cm^3), the organic layer collected, and, after drying, the solvent was removed. This gave an oil which was chromatographed on neutral alumina, eluting first with dichloromethane:petrol (1:1), and then with neat dichloromethane. The dichloromethane fractions were combined and evaporated to yield the crown (2) (0.06g, 58%) as a viscous oil which slowly crystallised to give colourless prisms, m.p. 53°C; ν_{max}cm^{-1}(film) 2910 (C-H), 1440, (C-H), 1640 (C=C), 1065 (OCH$_2$) cm^{-1}. δ_H 1.25 (12H, m), 1.52 (2H, m), 1.95 (2H, m), 2.35 (6H, s), 2.60 (2H, t, J = 8.0 Hz), 3.0 (2H, m), 3.12 (2H, m), 3.40 (6H, m), 3.62 (2H, m), 3.82 (2H, m), 4.00 (2H, m), 4.88 (2H, m), 5.74

(1H, m), 6.80-7.85 (2H, m); m/z [FAB (+)] (%) 892 (12 M^+), 493 (48), 461 (56), 368 (33), 309 (57), 269 (72), 239 (58), 171 (61), 115 (42), 81 (100), $[\alpha]^{20}_D$ + 132.8° (c 1.00, tetrahydrofuran) [Found: C, 81.8; H, 7.6; $C_{68}H_{66}O_6$ requires: C, 82.0; H, 7.2%].

Purification of hydride terminated dimethylsiloxane polymer $HSiMe_2O(SiMe_2O)_nSiMe_2H$

The hydride terminated polymer (purchased from ABCR) was distilled under reduced pressure (1mm Hg). The first fraction b.p. 42-43°C was collected and analysed by ^1H N.M.R. and ^{29}Si N.M.R. δ_H 0-0.6 (30H, m, SiMe), 0.19 (6H, d, J = 3.7Hz, $SiMe_2H$), 4.70 (2H, h, J = 3.7Hz, $SiMe_2H$); δ_{si} - 6.8 (2Si, $SiMe_2H$), -19.8 (2Si, $SiMe_2$), -21.5 (2Si, $SiMe_2$). The N.M.R. intensities indicate that the average degree of polymerisation of the siloxane (n) was 4.

Hydrosilylation of the crown (2) - Preparation of (15)

To the crown (2) (0.11 g, 0.13 mmol) in dry tetrahydrofuran (10 cm^3), under nitrogen, was added [$Me_2HSiO(Me_2SiO)_nSiMe_2H$] (0.04g, 0.84 mmol, 1.4 equiv) in dry tetrahydrofuran (3cm^3), and 3 drops of a 0.001M solution of bis(cyclooctadiene)platinum dichloride in acetone. The mixture was heated under reflux for 3 days. Every 24h an extra 3 drops of the acetone catalyst solution was added to the reaction mixture and after this time the solvent was removed. Chromatography of the residue on neutral alumina, gave the hydrosilylated crown (15) (0.15g, 97%) as a viscous liquid; $\nu_{max}cm^{-1}$ (thin film) 2920 (C-H), 1260 ($SiCH_3$), 1060 (SiO and OCH_2). δ_H 0.00 (20H, m), 1.25 (12H, m), 1.52 (2H, m), 2.35 (6H, s), 2.60 (2H, t, J = 8.0 Hz), 3.00 (2H, m), 3.12 (2H, m), 3.40 (6H, m), 3.62 (2H, m), 3.82 (2H, m), 4.00 (2H, m), 6.8-7.85 (2H, m). δ_{si} -21.29, -21.75, -21.98, -22.17, and -22.29 ($SiMe_2$) [Found: C, 80.1; H, 8.6 $C_{148}H_{170}Si_6O_{17}$ requires: C, 79.9; H, 8.1%].

Hydrosilylation of the crown (2) - Preparation of (16)

The polymer [$Me_3SiO(Me_2SiO)_x(MeHSiO)_ySiMe_3$] (0.30 g, 1.63 x 10^{-2} mmol) in dry tetrahydrofuran (5cm^3), 3 drops of a 0.001M solution of hydrogen hexachloroplatinate(IV) hydrate in acetone was added to the crown (2) (0.03mg, 1.63 x 10^{-5} mol) in dry tetrahydrofuran (10cm^3) protected by an atmosphere of nitrogen. The mixture was heated under reflux for 24h, a further few drops of the platinum catalyst solution were added, and the heating continued for another 48h. The mixture was then cooled, the solvent was removed, and the catalyst was removed by passing the residue redissolved in dichloromethane:petrol (1:1) through a neutral alumina column. The column was eluted with dichloromethane:petrol (1:1). This gave (16) as a viscous oil (0.06 g 92%); $\nu_{max}cm^{-1}$ (film) 3010 (C-H), 1260 ($SiCH_3$), 1060 (SiO and OCH_2). δ_H 0.10 (152H, m), 1.25 (12H, m), 1.52 (2H, m), 2.35 (6H, s), 2.60 (2H, t, J = 8.0 Hz), 3.00 (2H, m), 3.12 (2H, m), 3.40 (6H, m), 3.62 (2H, m), 3.82 (2H, m), 4.00 (2H, m), 6.8-7.85 (21H, m).

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