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Towards peptide versions of Cram's host–guest chemistry: the synthesis of $C^{\alpha,\alpha}$-disubstituted glycines with binaphthol-based crowned side-chains

Jean-Paul Mazaleyrat,* Karen Wright, Maria-Vittoria Azzini, Anne Gaucher and Michel Wakselman

SIRCOB, UMR CNRS 8086, Bâtiment Lavoisier, University of Versailles, F-78000 Versailles, France

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We wish to dedicate this paper to the memory of Donald J. Cram

Abstract—Dietherification of the hydroxy groups of various α,α-disubstituted α-amino acids or their precursors, possessing either an achiral frame derived from α-hydroxymethylserine, or a 2,2′,6,6′-tetrasubstituted biphenyl frame with only an axial chirality, or a frame with α-carbon chirality derived from α-methyl-(*L*)-DOPA, using (*R*)-2,2′-bis-(5-tosyloxy-3-oxa-1-pentyloxy)-1,1′-binaphthyl as alkylating agent, gave a new series of amino acids bearing binaphthol-based crown-ethers, as building blocks for the construction of short-chain peptide helices with topologically well-localized receptors.

Considering the well-documented high tendency of α-amino acids disubstituted at their α-carbon to induce β-bends and $\alpha/3_{10}$-helical secondary structures in polypeptides,[1] we have previously designed *crown-carrier $C^{\alpha,\alpha}$-disubstituted glycines*[2,3] as interesting targets allowing control of the spatial organization of the crown-ether receptors in short-chain peptide structures, for the construction of new molecular receptors and supramolecular devices using peptidic frameworks.[4] We have recently reported the synthesis of crowned amino acids derived from α-methyl-(*L*)-DOPA,[3] as well as the synthesis of [20-C-6]-Bip,[2] another $C^{\alpha,\alpha}$-disubstituted glycine possessing a 2,2′,6,6′-tetrasubstituted biphenyl frame with only an axial dissymmetry, related to the 1,1′-binaphthyl-crown-ether series developed by Cram et al.[5,6] In such receptors, the presence of extended steric and chiral barriers imparted complementary binding features in host–guest chemistry. In the same view,

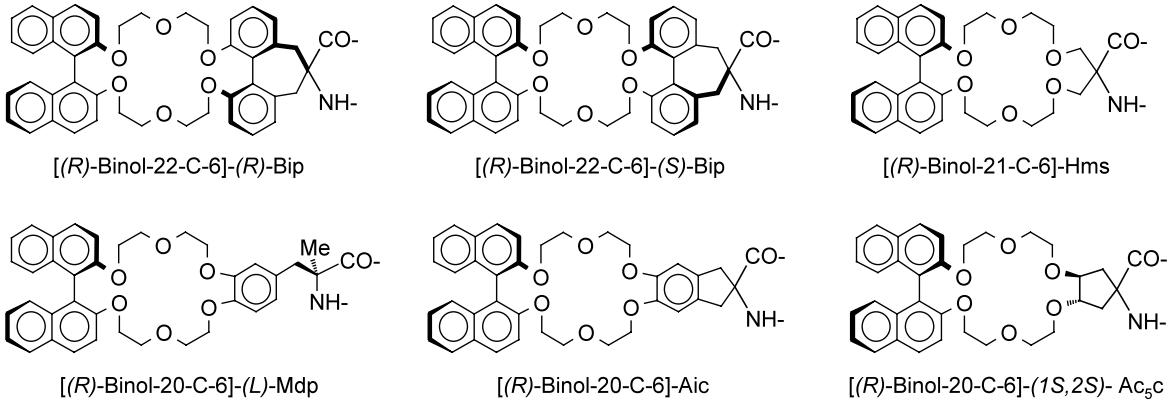

Figure 1. Structure of some 2,2′-dihydroxy-1,1′-binaphthyl (Binol)-based crown-carrier $C^{\alpha,\alpha}$-disubstituted glycines.

Keywords: binaphthol; crown-ethers; $C^{\alpha,\alpha}$-disubstituted glycines; modified α-amino acids.
* Corresponding author. Fax: +33-01-3925-4452; e-mail: jean-paul.mazaleyrat@chimie.uvsq.fr

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we have now designed a new series of *$C^{\alpha,\alpha}$-disubstituted glycines containing binaphthol-based crown-ether side-chain receptors* (Fig. 1).

Various architectures have been considered, involving either achiral frames derived from α-hydroxymethylserine (Hms)[7,8] and 2-amino-5,6-dihydroxyindan-2-carboxylic acid (Aic),[9,10] or a cyclic Ac_7c frame with only axial chirality,[11] derived from [20-C-6]-Bip,[2] or a cyclic frame with chiral γ,γ′-carbons, derived from (1*S*,2*S*)-dihydroxy-substituted α-aminocyclopentane carboxylic acid (Ac_5c),[12] or an acyclic frame with α-carbon chirality derived from α-methyl-(*L*)-DOPA (Mdp).[3] In the present paper, we report our preliminary results on the synthesis of some of these compounds: [(*R*)-Binol-22-C-6]-(*R*)-Bip, [(*R*)-Binol-22-C-6]-(*S*)-Bip, [(*R*)-Binol-21-C-6]-Hms and [(*R*)-Binol-20-C-6]-(*L*)-Mdp (Fig. 1).

Introduction of a 2,2′-dihydroxy-1,1′-binaphthyl (Binol) unit on the crown-ether side chains of these different amino acids may result in several interesting features: (i) *transformation of achiral architectures to chiral analogues* as in the case of [(*R*)-Binol-21-C-6]-Hms compared to [19-C-6]-Hms,[8] (ii) *presence of supplementary steric and chiral barriers* as in the case of [(*R*)-Binol-20-C-6]-(*L*)-Mdp compared to [18-C-6]-(*L*)-Mdp,[3] which may allow additive asymmetric interactions with chiral guests, (iii) *possibility of resolution of otherwise scarcely accessible structures*, illustrated here by the synthesis and the chromatographic separation of the [(*R*)-Binol-22-C-6]-(*R*)-Bip and [(*R*)-Binol-22-C-6]-(*S*)-Bip diastereomers, resulting in resolution of the [C-6]-Bip part of the molecule (vide infra) which could not be obtained in an enantiomerically pure state for the parent [20-C-6]-Bip structure in previous studies,[2c] and (iv) *opportunity for photophysical studies* involving intramolecular energy transfer[13] or intramolecular spin polarization[14] in designed peptides, because of the presence of the photoactive 1,1′-binaphthyl chromophore.

Access to all these compounds required the initial synthesis of 2,2′-bis(5-tosyloxy-3-oxa-1-pentyloxy)-1,1′-binaphthyl (+)-(*R*)-**1** which was readily obtained in ca. 60% overall yield from optically pure (+)-(*R*)-Binol, as previously described (Fig. 2).[15]

For the synthesis of the [(*R*)-Binol-21-C-6]-Hms residue, we used 2,2′-bis(hydroxymethyl)-1-aza-4-oxaspirodecane **2**[16] as a convenient starting material, to apply a reaction pathway similar to the one reported very recently in the case of achiral crowned Hms.[8]

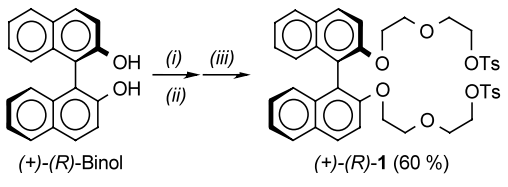

Figure 2. Synthesis of the ditosylate (+)-(*R*)-**1**: (i) NaH; DMF; Cl-$(CH_2)_2$-O$(CH_2)_2$-OTHP; 70°C; 48 h. (ii) MeOH; HCl; CH_2Cl_2; 25°C; 2 h. (iii) TsCl; pyridine; −15°C; 16 h.

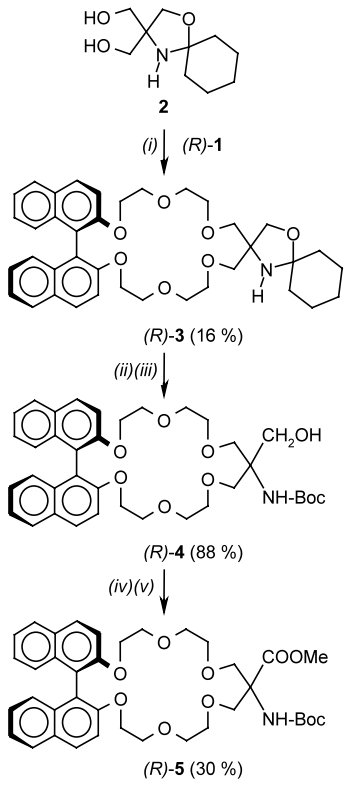

Figure 3. Synthesis of Boc-[(*R*)-Binol-21-C-6]-Hms-OH (*R*)-**5**: (i) KH; THF; 70°C; 24 h. (ii) 2N HCl; 60°C; 3 h. (iii) Boc_2O; MeCN; rt; 24 h. (iv) CrO_3; aq. H_2SO_4; acetone; 0°C; 1 h. (v) CH_2N_2; CH_2Cl_2/Et_2O.

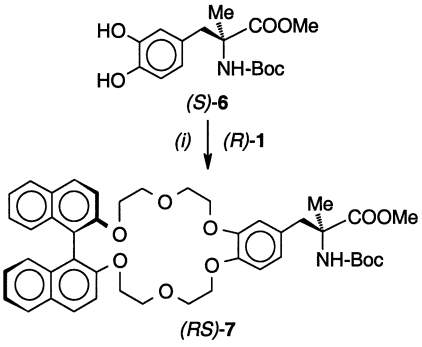

Figure 4. Synthesis of Boc-[(*R*)-Binol-20-C-6]-(*L*)-Mdp-OMe (*RS*)-**7**: (i) Cs_2CO_3; DMF; 60°C; 20 h.

Etherification of the two hydroxymethyl groups of **2** with potassium hydride in THF at 70°C and the ditosylate (*R*)-**1** as alkylating agent, in highly diluted conditions, gave (*R*)-**3**[17] (Fig. 3) in 16% yield, which upon acidolysis followed by *N*-protection using Boc_2O in acetonitrile,[18] gave (*R*)-**4**[17] in 88% yield. Finally, oxidation of (*R*)-**4** with Jones reagent, followed by esterification of the resulting crude *N*-protected amino acid with diazomethane, gave Boc-[(*R*)-Binol-21-C-6]-Hms-OMe (*R*)-**5**[17] in 30% yield (not optimized).

The (*RS*) isomer of the [Binol-20-C-6]-Mdp residue was also prepared from the terminally protected amino acid Boc-(*L*)-Mdp-OMe (*S*)-**6** (Fig. 4).[3] Applying similar

experimental conditions as those previously reported by Voyer et al.[19a,d] and then by us,[2,3,20] a DMF solution (ca. 0.05 mol/l) of the dicesium salt of (*S*)-**6** was reacted at 60°C with a DMF solution (ca. 0.1 mol/l) of the ditosylate (*R*)-**1** (1.1 equiv. mol/mol) which was added dropwise during a 1 h period. The reaction mixture was stirred at 60°C for 20 h, DMF was evaporated in vacuo and the crude product was purified by preparative TLC on silica gel with eluent CH_2Cl_2/MeOH/AcOH 98:1:1, to afford Boc-[(*R*)-Binol-20-C-6]-(*L*)-Mdp-OMe (*RS*)-**7**[17] in 32% yield.

In the same manner, treatment of racemic methyl 6-*tert*-butyloxycarbonylamino - 1,11 - dihydroxy - 6,7 - dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-6-carboxylate Boc-$[HO]_2$-Bip-OMe (*R*+*S*)-**8** (Fig. 5), previously obtained in five steps from 2-amino-3-methoxybenzoic acid,[2c] by the ditosylate (*R*)-**1** in similar experimental conditions as above, allowed access to the [Binol-22-C-6]-Bip residue.

Furthermore, the obtained ca. 1:1 mixture of diastereomers presented close but distinct TLC spots on silica gel (eluent CH_2Cl_2/MeOH 99:1) and could be separated using preparative TLC after several consecutive elutions, leading to Boc-[(*R*)-Binol-22-C-6]-(*R*)-Bip-OMe (*RR*)-**9**[17] in 25% yield (50% of theoretical yield) and Boc-[(*R*)-Binol-22-C-6]-(*S*)-Bip-OMe (*RS*)-**9**[17] in 26% yield (52% of theoretical yield).[21] Such separation represents a *resolution of the Bip part of the molecule after crown formation*, with access to both of its enantiomers, which is especially interesting since we have previously observed that racemization was an inherent process during the etherification of the dicesium salt of Boc-$[HO]_2$-Bip-OMe **8** in DMF at 60°C, with partly racemized protected amino esters Boc-[20-C-6]-(*R*)-Bip-OMe and Boc-[20-C-6]-(*S*)-Bip-OMe being respectively obtained from nearly enantiomerically pure (*R*)-**8** and (*S*)-**8**.[2c]

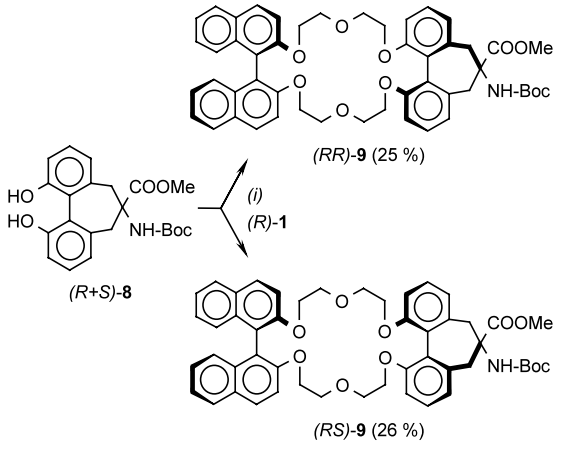

Figure 5. Synthesis of the diastereomeric Boc-[(*R*)-Binol-22-C-6]-(*R*)-Bip-OMe (*RR*)-**9** and Boc-[(*R*)-Binol-22-C-6]-(*S*)-Bip-OMe (*RS*)-**9** from racemic Boc-$[HO]_2$-Bip-OMe (*R*+*S*)-**8**: (i) Cs_2CO_3; DMF; 60°C; 20 h.

The absolute configuration of the diastereomers (*RR*)-**9** and (*RS*)-**9** could be attributed with a reasonable degree of confidence by considering the optical rotations of both compounds. Indeed, according to the known (+)-(*R*) absolute configuration of the common fragment of both molecules: (*R*)-Binol[O-$(CH_2)_2$-$O(CH_2)_2$-OR]$_2$ (R = H or Ts), with for example $[\alpha]^{25}_{578} = +31$ (*c* 1; THF) for (*R*)-**1**,[15c] and the previously established (−)-(*R*)/(+)-(*S*) absolute configuration of the Boc-$[HO]_2$-Bip-OMe part, with $[\alpha]^{25}_{436} = -394$ (*c* 0.1; MeOH) for (*R*)-**8**[2c] and $[\alpha]^{25}_{436} = +403$ (*c* 0.1; MeOH) for (*S*)-**8**,[2c] one would expect a positive rotation for (*RS*)-**9** and either a negative rotation or a positive one with a lower absolute value for (*RR*)-**9**. Therefore, the isomer with $[\alpha]^{25}_{436} = -7$ (*c* 0.1; MeOH) could be assumed to be (*RR*)-**9** while the other isomer with $[\alpha]^{25}_{436} = +567$ (*c* 0.1; MeOH) was assumed to be (*RS*)-**9**.

This attribution was unambigously confirmed by chemical derivation: cleavage of the ArO–R ether bonds of the postulated (*RR*)-**9** isomer by treatment with a large excess of boron tribromide in dichloromethane,[22] followed by re-esterification of the crude product with thionyl chloride in methanol (Fig. 6), allowed the recovery of (+)-(*R*)-Binol with $[\alpha]^{25}_{D} = +29$ (*c* 0.84; THF)[23] and of H-$[HO]_2$-Bip-OMe **10** with $[\alpha]^{25}_{436} = -93$ (*c* 0.14; MeOH),[23] corresponding to the previously established (−)-(*R*) absolute configuration.[2c]

The presently described small-scale synthesis of $C^{\alpha,\alpha}$-disubstituted glycines with binaphthol-based crown-ether side-chain receptors, is to be extended to other structures such as [(*R*)-Binol-20-C-6]-Aic or [(*R*)-Binol-20-C-6]-(1*S*,2*S*)-Ac_5c (Fig. 1). Binaphthol is likely to be introduced as well into crowned (*L*)-DOPA itself,[19] and into crowned β^3-(*L*)-DOPA[20] with, in the latter case, the aim of favoring stable 3_{14}-helical secondary structures in derived polycrown peptides. The easy access to the (*R*) and (*S*) enantiomers of binaphthol (both commercially available) will be exploited to prepare a variety of isomers such as the protected [(*S*)-Binol-20-C-6]-(*L*)-Mdp residue (*SS*)-**7** to be compared with (*RS*)-**7**. Larger [Binol-C-8]-crowned amino acids will also be prepared as interesting targets for the study of new peptidic pseudorotaxanes which could result from host–guest complexes between bis-crown peptides and diammonium ions.[19i]

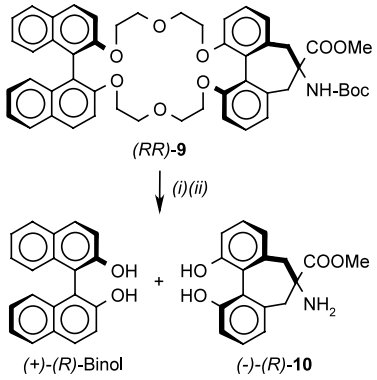

Figure 6. Cleavage of the postulated (*RR*)-**9** isomer to (+)-(*R*)-Binol and H-$[HO]_2$-Bip-OMe (−)-(*R*)-**10**: (i) BBr_3; CH_2Cl_2; −10°C to rt; 48 h. (ii) MeOH; $SOCl_2$; rt; 1 week.

As the feasibility of solution synthesis of peptides based on crowned $C^{\alpha,\alpha}$-disubstituted glycines has previously been evaluated,[2c,3] there seems to be no obstacle to the construction of a variety of binaphthol-crowned derived polypeptides, in which 3_{10}-helical secondary structures should be favored in principle, even in the case of short-chain oligomers. In such molecules, the crown-ether receptors should be in a topologically well-defined and predictable spatial situation relative to the helical main chain in the case of the α,α-cyclic frames present in Bip (i.e. **9**), Hms (i.e. **5**), Aic or Ac_5c, while more flexibility is expected for the α,α-acyclic frame present in Mdp derivatives (i.e. **7**).

Altogether, as pointed out earlier, the presence of a binaphthyl unit in the crown-ether moiety of these $C^{\alpha,\alpha}$-disubstituted glycines makes them amino acid analogs of the very famous binaphthyl crown-ether series previously designed by Cram[5] in order to impart structural chiral recognition properties to hosts. Here, hopefully, the chirality of the binaphthyl unit could function in synergy with the chirality of the peptidic chain in new crown or poly-crown catalysts with enhanced chiral recognition properties.[6] Finally, the binaphthyl unit is subject to structural modifications, especially at the 3,3′-, 4,4′- and 7,7′-positions,[5d,24] which might be of interest for introducing extra functionalities in view of designed peptidic supramolecular devices.[25]

References

1. For reviews on α,α-disubstituted α-amino acids and their peptides, see: (a) Benedetti, E. *Biopolymers* **1996**, *40*, 3–44; (b) Karle, I. L. *Biopolymers* **1996**, *40*, 157–180; (c) Toniolo, C.; Crisma, M.; Formaggio, F.; Benedetti, E.; Santini, A.; Iacovino, R.; Saviano, M.; Di Blasio, B.; Pedone, C.; Kamphuis, J. *Biopolymers* **1996**, *40*, 519–522; (d) Karle, I. L. *Acc. Chem. Res.* **1999**, *32*, 693–701; (e) Andrews, M. J. I.; Tabor, A. B. *Tetrahedron* **1999**, *55*, 11711–11743; (f) Toniolo, C.; Crisma, M.; Formaggio, F.; Peggion, C. *Biopolymers* **2001**, *60*, 396–419.
2. (a) Mazaleyrat, J. P.; Gaucher, A.; Goubard, Y.; Šavrda, J.; Wakselman, M. *Tetrahedron Lett.* **1997**, *38*, 2091–2094; (b) Mazaleyrat, J.-P.; Goubard, Y.; Azzini, M.-V.; Wakselman, M.; Crisma, M.; Formaggio, F.; Toniolo, C. In *Peptides* 2000; Martinez, J.; Fehrentz, J.-A., Eds.; EDK: Paris, France, 2001; pp. 185–186; (c) Mazaleyrat, J.-P.; Goubard, Y.; Azzini, M.-V.; Wakselman, M.; Peggion, C.; Formaggio, F.; Toniolo, C. *Eur. J. Org. Chem.* **2002**, 1232–1247.
3. Wright, K.; Melandri, F.; Cannizzo, C.; Wakselman, M.; Mazaleyrat, J.-P. *Tetrahedron* **2002**, *58*, 5811–5820.
4. For leading references on the use of peptidic frameworks for the construction of molecular receptors and devices, see: (a) Voyer, N.; Lamothe, J. *Tetrahedron* **1995**, *51*, 9241–9284; (b) Voyer, N. *Topics in Current Chemistry*, Springer: Berlin, 1996; Vol. 184, pp. 1–37.
5. For review articles, see: (a) Cram, D. J.; Cram, J. M. *Science* **1974**, *183*, 803–809; (b) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8–14; (c) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009–1020.
6. For a review on molecular recognition, asymmetric catalysis and new materials involving 1,1′-binaphthyl dimers, oligomers and polymers, see: Pu, L. *Chem. Rev.* **1998**, *98*, 2405–2494.
7. For the synthesis of Hms, see: (a) O'Connor, M. J.; Brush, J. R.; Theo, S.-B. *Aust. J. Chem.* **1977**, *30*, 683–684; (b) Stasiak, M.; Wolf, W. M.; Leplawy, M. T. *J. Pept. Sci.* **1998**, *4*, 46–57. For the conformational analysis of Hms(Ipr) homooligomers, see: (c) Wolf, W. M.; Stasiak, M.; Leplawy, M. T.; Bianco, A.; Formaggio, F.; Crisma, M.; Toniolo, C. *J. Am. Chem. Soc.* **1998**, *120*, 11558–11566.
8. For the synthesis of achiral crowned Hms, see: Bělohradský, M.; Císařová, I.; Holý, P.; Pastor, J.; Závada, J. *Tetrahedron* **2002**, *58*, 8811–8823.
9. Aic: 2-aminoindan-2-carboxylic acid.
10. For the synthesis of achiral crowned Aic, see: Kotha, S.; Brahmachary, E. *Indian J. Chem.* **2001**, *40B*, 1–4.
11. For the conformational analysis of peptides based on the Ac_7c residues Bip and Bin possessing only an axial chirality, see: (a) Formaggio, F.; Crisma, M.; Toniolo, C.; Tchertanov, L.; Guilhem, J.; Mazaleyrat, J. P.; Gaucher, A.; Wakselman, M. *Tetrahedron* **2000**, *56*, 8721–8734; (b) Formaggio, F.; Peggion, C.; Crisma, M.; Toniolo, C.; Tchertanov, L.; Guilhem, J.; Mazaleyrat, J. P.; Goubard, Y.; Gaucher, A.; Wakselman, M. *Helv. Chim. Acta* **2001**, *84*, 481–501.
12. For the conformational analysis of Ac_5c homooligomers, see: Toniolo, C.; Benedetti, E. *Macromolecules* **1991**, *24*, 4004–4009.
13. Toniolo, C.; Formaggio, F.; Crisma, M.; Mazaleyrat, J. P.; Wakselman, M.; George, C.; Deschamps, J. R.; Flippen-Anderson, J. L.; Pispisa, B.; Venanzi, M.; Palleschi, A. *Chem. Eur. J.* **1999**, *5*, 2254–2264.
14. Corvaja, C.; Sartori, E.; Toffoletti, A.; Formaggio, F.; Crisma, M.; Toniolo, C.; Mazaleyrat, J. P.; Wakselman, M. *Chem. Eur. J.* **2000**, *6*, 2775–2782.
15. (a) Helgeson, R. C.; Timko, J. M.; Moreau, P.; Peacock, S. C.; Mayer, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 6762–6763; (b) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 2564–2571; (c) Kyba, E. P.; Gokel, G. W.; de Jong, F.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173–4184.
16. Pierce, J. S.; Lunsford, C. D.; Raiford, R. W., Jr.; Rush, J. L.; Riley, D. W. *J. Am. Chem. Soc.* **1951**, *73*, 2595–2596.
17. All new compounds gave satisfactory analytical data ($^1H/^{13}C$ NMR, C,H,N analysis and/or ESI^+/MS). Further experimental details of synthesis will be given in a full account of this study. Optical rotations $[\alpha]^{25}_{436}$ are reported next: (*R*)-**3**: +225 (*c* 0.25; CH_2Cl_2). (*R*)-**4**: +212 (*c* 0.1; CH_2Cl_2). (*R*)-**5**: +219 (*c* 0.08; CH_2Cl_2). (*RS*)-**7**: +220 (*c* 0.2; MeOH). (*RR*)-**9**: −7 (*c* 0.1; MeOH). (*RS*)-**9**: +567 (*c* 0.1; MeOH).
18. (a) Kemp, D. S.; Curran, T. P. *J. Org. Chem.* **1988**, *53*, 5729–5731; (b) Kemp, D. S.; Carey, R. I. *J. Org. Chem.* **1989**, *54*, 3640–3646.
19. (a) Voyer, N. *J. Am. Chem. Soc.* **1991**, *113*, 1818–1821; (b) Voyer, N.; Roby, J. *Tetrahedron Lett.* **1991**, *32*, 331–334; (c) Voyer, N.; Deschênes, D.; Bernier, J.; Roby, J. *J. Chem. Soc., Chem. Commun.* **1992**, 134–136; (d)

Voyer, N.; Roby, J.; Deschênes, D.; Bernier, J. *Supramol. Chem*. **1995**, *5*, 61–69; (e) Voyer, N.; Guérin, B. *J. Chem. Soc., Chem. Commun*. **1997**, 2329–2330; (f) Voyer, N.; Potvin, L.; Rousseau, E. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1469–1471; (g) Meillon, J.-C.; Voyer, N. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 967–969; (h) Biron, E.; Voyer, N.; Meillon, J.-C.; Cormier, M.-E.; Auger, M. *Biopolymers* **2000**, *55*, 364–372; (i) Meillon, N.; Voyer, J.-C.; Biron, E.; Sanschagrin, F.; Stoddart, J. F. *Angew. Chem., Int. Ed*. **2000**, *39*, 143–145; (j) Voyer, N.; Côté, S.; Biron, E.; Beaumont, M.; Chaput, M.; Levac, S. *J. Supramol. Chem*. **2001**, *1*, 1–5.

20. Gaucher, A.; Barbeau, O.; Hamchaoui, W.; Vandromme, L.; Wright, K.; Wakselman, M.; Mazaleyrat, J.-P. *Tetrahedron Lett*. **2002**, *43*, 8241–8244.
21. Chromatographic separation of the diastereoisomers (*RR*)-**9** and (*RS*)-**9** by preparative TLC was realized only on small scale. HPLC might be necessary when the synthesis is scaled-up.
22. Felix, A. M. *J. Org. Chem*. **1974**, *39*, 1427–1429.
23. According to the reported maximum values $[\alpha]_D^{25}=+34$ (*c* 1.1; THF)[15c] for (+)-(*R*)-Binol and $[\alpha]_{436}^{25}=-137$ (*c* 0.1; MeOH)[2c] for (−)-(*R*)-**10**, these compounds were presently obtained from enantiomerically pure (*RR*)-**9** with only ca. 85% and ca. 68% ee, respectively. However, this result does not question the enantiomeric purity of the starting (*RR*)-**9**, but rather reflects a racemization of the dihydroxy-substituted binaphthyl and biphenyl skeletons, in the acidic conditions required for both ether cleavage and re-esterification, as previously reported.[2c]
24. For a review article on synthetic approaches to binaphthyl derivatives, see: Putala, M. *Enantiomer* **1999**, *4*, 243–262.
25. For review articles on fluorescent sensors and artificial molecular machines, mentioning the use of binaphthyl crown-ethers, see: (a) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev*. **1997**, *97*, 1515–1566; (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed*. **2000**, *39*, 3348–3391.