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Efficient Synthesis of 2-Methyl Derivatives of 1,1′-Bi(2-naphthol) and 1,1′-Bi(2-phenols)

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Reaction of 1,1′-binaphthol and structurally related 1,1′-biphenols with sulfonylating reagents [RSO_2Cl; R = 4-Tol, Ph] leads to clean, ultraselective monoderivatisation, shown crystallographically in one case (2-OH–2′-OTs–1,1′-binaphthyl). Reaction of the remaining 2-hydroxy function with either Tf_2O or NfF [Nf = nonaflate, $CF_3(CF_2)_3SO_2$-] affords the protected/activated cores (2-R^1O–2′-R^2O–1,1′-biaryl) [R^1,R^2 pairs = Tf,Ts (X-ray); Tf,SO_2Ph; Nf,Ts (on 1,1′-binaphthyl core); Tf,Ts; Nf,Ts (on 1,1′-biphenyl core); Tf,Ts; Nf,Ts (on 3,3′,5,5′-tetramethyl-1,1′-biphenyl core)]. Reaction of the Tf,Ts species with either MeMgBr/$NiCl_2$(dppe) (for the 1,1′-binaphthyl) or $(AlMe_3)_2$(DABCO)/$Pd_2(dba)_3$ (for the 1,1′-biphenyl) affords 2-OH–2′-Me–1,1′-biaryl units on subsequent hydrolysis (crystallographically characterised in the binaphthyl case). The latter methyl/hydroxy compounds are doubly deprotonated by either *n*BuLi/TMEDA or *n*BuLi/*t*BuOK to afford dianions that react cleanly with Cl_2SiPh_2 (two X-ray structures). The equivalent reaction of the 2-OH–2′-Me–1,1′-binaphthyl with $Ph(O)Cl_2$ is less clean due to the absence of a strong Thorpe–Ingold effect.

Introduction

1,1′-Binaphthyl and 1,1′-biphenyl units are the subject of growing interest due to a number of useful structural cores that find application in materials,[1] natural products,[2] polymers synthesis[1] and chiral stationary phases for chromatographic applications.[3] For example, biphenyl units are present in important antibiotics such as biphenomycin and vancomycin[4] and in potent antitumor agents such as ellagitannins.[5] Polyhydroxylated derivatives have also found use as antioxidants in food preservatives.[6] Most commonly, 1,1′-binaphthyl and biphenyl scaffolds have found use in the production of highly effective chiral ligands, especially those with C_2 symmetry,[7] of which BINAP[8] is probably the best known. More recently, 1,1′-bi(2-naphthol) **1** has been used for hybrid materials in the preparation of supported catalysts in heterogeneous asymmetric catalysis.[9] Despite these large number of applications, modular preparation of C_1 1,1′-binaphthyl and biphenyl units is often hindered by the need to prepare appropriate aryl coupling partners, followed (in chiral cases) by resolution when the direct stereoselective synthesis is not possible.[10] Such species could have numerous uses e.g. in ligand preparation or as precursors to chiral acids.[11] Given the ready availability of the parent enantiopure 1,1′-bi(2-naphthol) (**1b**), regioselective functionalisation of the ring positions is an attractive strategy. While this has been achieved in the 6-,[12] 3-[13] and 2-positions[14] for C_2 symmetric 1,1′-binaphthyl compounds, clean very highly selective (>98%) monofunctionalisation of the 2-position of **1** is often problematic. We set about to find a solution to this problem and to extend these ideas to suitable 1,1′-biphenol compounds leading to a family of interesting dissymmetric 1,1′-biaryl compounds.

Results and Discussions

We are interested in the synthesis of C_1-symmetric ligands prepared from 1,1′-bi(2-naphthol) (**1**) by selective functionalisation of just one of the 2-hydroxy groups.[15] To maximise the synthetic utility of any new approach to such species, it is important to realise a preparation that is: (i) technically simple, (ii) succinct and not reliant on extensive chromatographic purification and (iii) can be extended readily to the 1,1′-biphenol analogues. There are already a number of literature monoprotections of 1,1′-bi(2-naphthol) (**1**), of which methylation and triflation are the most common.[14b,16] While quite selective, none of these reactions are completely monoselective and chromatographic separation of unreacted starting material and bis-alkylated products is subsequently required. Previously, we had shown that carbamoyl chlorides and related acid chlorides reacted with 1,1′-bi(2-naphthol) (**1**) to give monoacylated binol derivatives.[15] In this case, careful control of the reaction conditions was often required to give excellent monoselectivity. We had speculated that the origin of the selectivity for the monoacylation was due to the presence of intramo-

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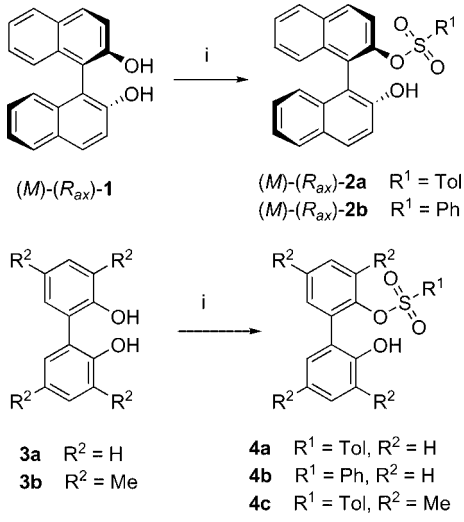
lecular hydrogen bonds between the installed carbonyl and the remaining hydroxy group. We expected similar factors to operate in the reaction of **1** with tosyl chloride (4-TsCl, 4-$MeC_6H_4SO_2Cl$) and other sulfonyl chlorides. We were therefore delighted to discover that the reaction of (R_{ax})-1,1′-bi(2-naphthol) (**1**) with *p*-toluenesulfonyl chloride is extremely selective and proceeds readily to completion even when only 1.0 equiv. of TsCl is present. The reaction could be readily extended to other sulfonyl chlorides and 1,1′-biphenol analogues (Scheme 1). The reactions were typically complete within 8 h but could be stirred overnight without harm. For clarity only transformations from (R_{ax})-binol (**1**) are shown in Scheme 1. This corresponds to an (*M*) axis of chirality which is used throughout this paper, as the peculiarities of the CIP rules[17] can result in an apparent stereochemical inversion upon replacement of the 2-OH group (see later). This remarkably simple TsCl procedure does not seem to have been commonly employed before, although there is a passing reference to a similar observation in a more substituted case.[18] A crystallographic investigation of **2a** (Figure 1) revealed the formation of an *intermolecular* hydrogen-bonded motif as opposed to the *intramolecular* interactions we had observed previously in carbamate derivatives.[15] Typically, the compounds **2** and **4** were highly crystalline and easily obtained in high purity (>99%) and excellent yield (90–100%). Only compound **4b** was isolated in less than 90% recrystallised yield (73%). However, the conversion to **4b** was still essentially quantitative. In fact, all of the reaction mixtures were so clean, containing essentially single sulfonyl compounds, that they could be used directly in one-pot procedures without the need for isolation in all cases.



Scheme 1. Synthesis of mono-tosylated and mono-sulfonylated biaryl derivatives. Reagents and conditions: (i) TsCl or $PhSO_2Cl$ (1.01 equiv.), DMAP (15 mol-%), NEt_3 (1.1 equiv.), dichloromethane, room temperature, 8 h.

The reaction of the tosylated 1,1′-binaphthyl species **2a**–**b**, or any of its 1,1′-biphenyl analogues **4a**–**c**, with trifluoromethanesulfonic anhydride (Tf_2O)[16b] led to the clean formation of the triflate derivatives **5a**–**b**/**6a**–**b** in high yield

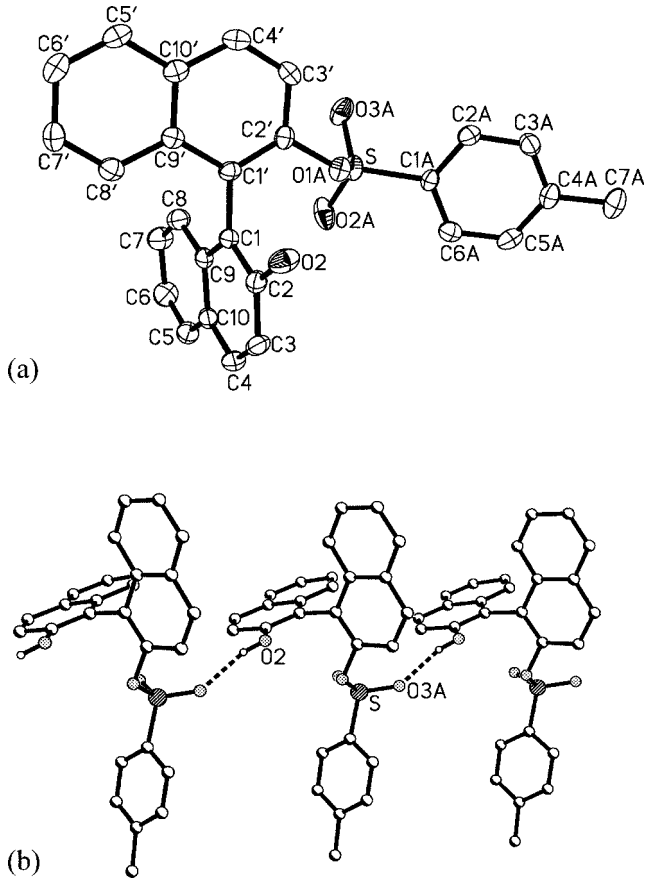
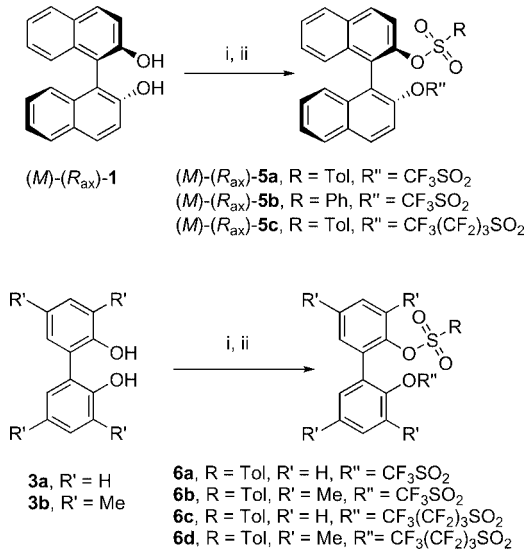


Figure 1. (a) Molecular structure of (*P*)-(S_{ax})-**2a**. Solvent molecule and hydrogen atoms omitted for clarity. Displacement ellipsoids drawn at 50% probability level. Selected inter atomic distances [Å] and angles [°]: O(2)···O(3a)^{i} (*i* = *x* – *1*, *y*, *z*) 2.795(2), H(2O)···O(3a)^{i} 1.97, O(2)–H(2O)–O(3a)^{i} 166, O(2)–C(2) 1.373(3), S–O(3a) 1.4359(15); (b) View showing hydrogen bonding interaction in (*P*)-(S_{ax})-**2a,** forming a chain parallel to the crystallographic *a* axis.

(80–99%) after overnight stirring at ambient temperature. These preparations could easily be extended to the nonaflate [Nf = $CF_3(CF_2)_3SO_2$-] derivatives by use of NfF (**5c**/**6c**–**d**). The selectively protected/activated 1,1′-binaphthyl **5** and 1,1′-biphenyl **6** derivatives could be obtained by a two-step one-pot procedure without the need to isolate **2** or **4** simply by adding Tf_2O at the end of the first step (Scheme 2). This procedure is extremely simple and highly robust: no inert atmosphere is required and normal (undried) technical grade dichloromethane and NEt_3 can be used without a reduction in yields. These technically simple preparations may be carried out on a large scale (although we normally restricted our reactions to a 5 g upper limit). The only complication to arise in the one-pot process was the need to wash the crude products with copious warm water to completely remove the significant amounts of the NEt_3·HCl by-product that is formed on a large scale. All of the products **5** and **6** were found to be highly crystalline negating the use of chromatographic purification. In the case of **5a** the molecular connectivity was confirmed by a crystallographic study (Figure 2).



Scheme 2. One-pot synthesis of activated/protected binaphthyl and biphenyl derivatives. Reagents and conditions: (i) TsCl or $PhSO_2Cl$ (1.01 equiv.), DMAP (15 mol-%), NEt_3 (2.2 equiv.), dichloromethane, room temperature, 8 h. (ii) Tf_2O or $CF_3(CF_2)_3SO_2F$ (1.1 equiv.), dichloromethane, room temperature, 16 h.

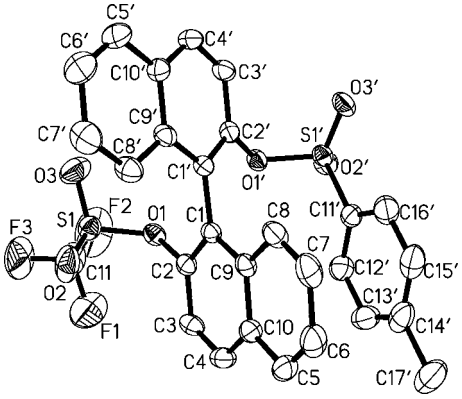
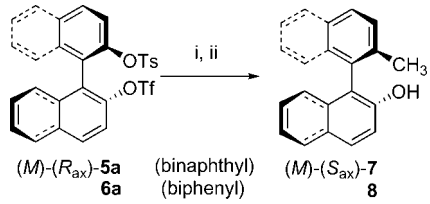


Figure 2. Molecular structure of (*M*)-(R_{ax})-**5a**. Hydrogen atoms omitted for clarity, displacement ellipsoids drawn at 50% probability level. Selected inter atomic distances [Å] and angles [°]: S(1)–O(1) 1.566(2), S(1′)–O(1′) 1.604(2); torsion angle C(2)–C(1)–C(1′)–C(2′) –70.2(3).

The 1,1′-binaphthyl compound **5a** was converted to its methyl derivative **7** via selective $NiCl_2$(dppe)-catalysed coupling with MeMgBr. Only the triflate group reacts under these homogeneous conditions. Only at extended reaction times (where the reaction turns from orange to black) were traces of the 2,2′-dimethylated species observed. We suspect the subsequent tosyl-coupling is promoted by the heterogeneous "nickel-black" that is ultimately formed in this reaction. To minimise the number of steps required to prepare mono methyl **7**, the intermediate tosyl ester was hydrolysed in situ with excess KOH (aq), after quenching the excess MeMgBr with methanol (Scheme 3). A significant excess of KOH (20 equiv.) is required to promote the hydrolysis as the by-product magnesium salts sequester significant amounts of the hydroxide, however, the reaction again proceeds cleanly. One-pot preparation of **7** was the only step in the synthetic sequence to require chromatography. While **7** is crystalline (Figure 3) its direct precipitation from the crude product could not be routinely attained. Nevertheless, **7** is obtained with a 60–65% isolated yield from (*M*)-(R_{ax})-binol (**1**) after just two two-step, one-pot procedures. This is a significant improvement on literature routes to this potentially useful chiral fragment. Traditionally, **7** has been prepared from **A** by exhaustive reduction of the carbonyl group (4 steps) and subsequent BBr_3-induced demethylation.[19] As **A** itself has to be prepared either by a two-step carbonylation route[20] or a multi-step C–C coupling reaction[20] use of **7** has, thus far, not proved popular.



Scheme 3. One-pot methylation. Reagents and conditions: (i) either: **5a** (1 equiv.), MeMgBr (3 equiv.), $NiCl_2$(dppe) (7 mol-%), THF 60 °C, 12 h, or: **6a** (1 equiv.), $(AlMe_3)_2$(DABCO) (0.8 equiv.), $Pd_2(dba)_3$ (3 mol-%), X-Phos (5 mol-%), THF 70 °C, 16 h; (ii) $KOH_{(aq.)}$ (20 equiv.).

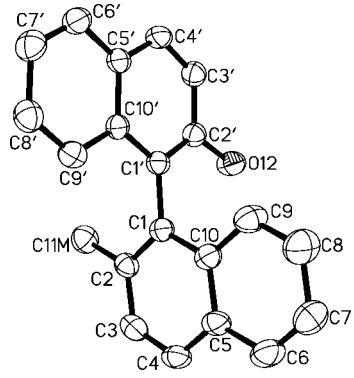
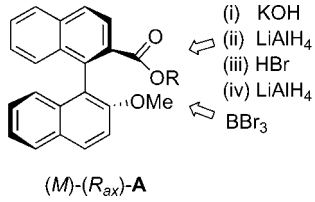


Figure 3. Molecular structure of (*M*)-(S_{ax})-**7** [derived from (R_{ax})-binol]. Only one of the two crystallographically independent molecules is shown, hydrogen atoms omitted for clarity; displacement ellipsoids drawn at 50% probability level. Selected inter atomic distances [Å] and angles [°]: C(2)–C(11M) 1.504(3), C(12)–C(21M) 1.499(3), O(12)–C(2′) 1.368(3), O(22)–C(12′) 1.372(3); torsion angle C(2)–C(1)–C(1′)–C(2′) –87.7(3), C(12)–C(11)–C(11′)–C(12′) –75.0(3).



A different approach was used for the preparation of 2-OH–2′-Me–1,1′-biphenyl **8** involving the use of palladium-catalysed alkylation. While the coupling with the alkyl Grignard for substrate **5a** consistently gave 60–65% yield, and <3% of the 2,2′-dimethyl-1,1′-binaphthyl by-product,

the equivalent performance in the 1,1′-biphenyl series was inferior. Optimal preparation of the substrate **8** was attained by palladium-catalysed C–OTf coupling with $(AlMe_3)_2$(DABCO) in the presence of a monophosphane ligand from the X-Phos[21] family (85%) under conditions recently disclosed by us.[22] Interestingly, the palladium-catalysed coupling of **5a** and $(AlMe_3)_2$(DABCO) did not give high yields. Even for prolonged reaction times, the coupling product was obtained in <25% yield. We believe that the increased steric hindrance in substrate **5a** is responsible for this poor performance. In the case of **7** the required connectivity could be demonstrated crystallography (Figure 3). Finally, optical rotation data showed that the *M* chirality of the (R_{ax})-1,1′-bi(2-naphthol) (**1**) is retained throughout its transformation into (*M*)-(S_{ax})-**7** (The change in the axial stereochemistry descriptor is purely a CIP artefact).

We believed that the proximity of the 2-OH function in **7** would allow for a directed and selective lithiation of the 2-methyl group. This goal could be realised through a short study of the required lithiation conditions using either *n*BuLi/TMEDA (method A) or *n*BuLi/KO*t*Bu (method B).[23] Under the optimised conditions, **7** was converted into its insoluble dark red dilithium salt using 2.5 equiv. of *n*BuLi in the presence of TMEDA as a solution in Et_2O at 0 °C for 24 h. A similar procedure carried out on substrate **8** led to an equally insoluble bright yellow 1,1′-biphenyl-derived dianion. D_2O quenching of the highly moisture-sensitive dianion of **7** provided evidence that >90% dilithiation had occurred (Ar–CH_2D 1:1:1 triplet at δ = 2.17 ppm, J_{HD} = 2.2 Hz). Figure 4 shows the extent of deuterium incorporation in **7** by lithiation under method **A** conditions (*n*BuLi/TMEDA,1:1, see experimental for details) after 3 and 24 h reaction time. An alternative route leading to the dilithiated compound was envisaged by using a modification of Schlosser's "super-base" method (*n*BuLi/*t*BuOK, 1:1, method B). In this case much shorter reaction times are required (3 h compared with >20 h for method A). In the case of the super-base, 95% lithiation is obtained within 3 h with 2.5 equiv. of *n*BuLi/*t*BuOK, however, temperatures of –40 °C or below are required to avoid undesired quenching of the reaction mixture by the solvent (normally Et_2O). Using method A, it was safe to perform the lithiation in Et_2O at 0 °C, although attempts to increase the rate of reaction by carrying it out at ambient temperature led to a less clean reaction due to minor aryl C–H lithiation. Method A was generally preferred for further functionalisation of 2-OH-2′-Me-1,1′-binaphthyl **7** and 1,1′-biphenyl **8** due to the absence of additional *tert*-butoxide-derived by-products in the reaction mixture.

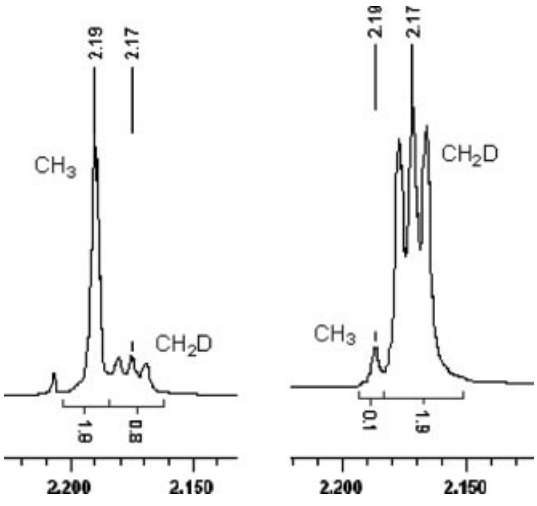
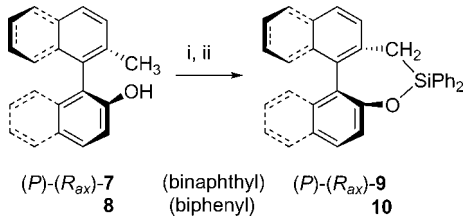


Figure 4. Deuterium incorporation observed in **7** after short (3 hours) and prolonged (24 h) lithiation times with *n*BuLi/TMEDA (3.0 equiv.).

The dilithium species attained from **7**–**8** contain two anionic sites that may be expected to have quite different reactivities. The benzylic (CH_2^-) anionic moiety is expected to not only be more basic, but also more nucleophilic than its hydroxylic counterpart. For this reason, in order to avoid undesired mixed alkylation products, initial reactions of the dilithium salts of **7** and **8** were carried out with dichlorodiphenylsilane. The formation of the desired chelate compound is expected to be favoured not only by the formation of a strong Si–O bond (ca. 120 kcal mol^{-1}) but by the presence of a large Thorpe–Ingold effect[24] engendered by the large $SiPh_2$ fragment, favouring closure of the 7-ring chelate. We were delighted to discover that the reaction of the dilithium salts of both **7** and **8** led to clean formation of **9** and **10** respectively in good yields (Scheme 4).



Scheme 4. Synthesis of silane derivatives **9**-**10**. Reagents and conditions: (i): **7** or **8** (1 equiv.), *n*BuLi (3 equiv.), TMEDA (3 equiv.), Et_2O, 0 °C, 24 h. (ii) Cl_2SiPh_2, –60 °C for 3 h followed by warming to 0 °C (2 h).

Compounds **9** and **10** are both highly crystalline and were obtained in 55–60% isolated yield as colourless rods. Crystallographic investigation of **9**–**10** revealed very similar structures (Figure 5–Figure 6).

The importance of using bis-electrophiles deploying a large steric (i.e. Thorpe–Ingold) effect to promote closure of the chelate is reinforced by the reaction of the dilithio species derived from **7** with phenylphosphonic dichloride. After **7** had been doubly deprotonated by 3 equiv. of *n*BuLi/TMEDA, successive quenching with $Cl_2P(O)Ph$ afforded the formation of a single diastereomer of the expected phosphorus(V) compound **11a** (Scheme 5). Compound **11a** is stable to hydrolysis and easily isolated by column chromatography. The absolute stereochemistry of all elements of chirality in the molecule was assigned using crystallographic analysis of a sample derived from (S_{ax})-binol **1**. The favoured diastereoisomer is (*P*)-(S_{ax},R_P)-**11a** with an *R* configuration at the phosphorus atom (Figure 7). Although essentially complete diastereoselectivity is seen, the yield of this compound is poor (up to 17%). Inspection of

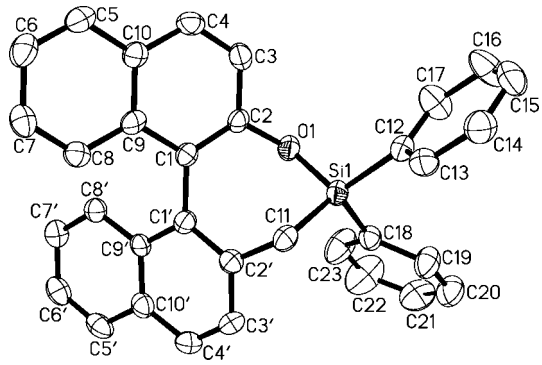


Figure 5. Molecular structure of (*P*)-(R_{ax})-**9** [derived from (S_{ax})-binol]. Hydrogen atoms omitted for clarity; displacement ellipsoids drawn at 50% probability level. Selected inter atomic distances [Å] and angles [°]: Si(1)–O(1) 1.667(2), Si(1)–C(11) 1.866(3), O(1)–Si(1)–C(11) 104.45(10), C(18)–Si(1)–C(12) 110.37(10); torsion angle C(2)–C(1)–C(1′)–C(2′) 57.9(3).

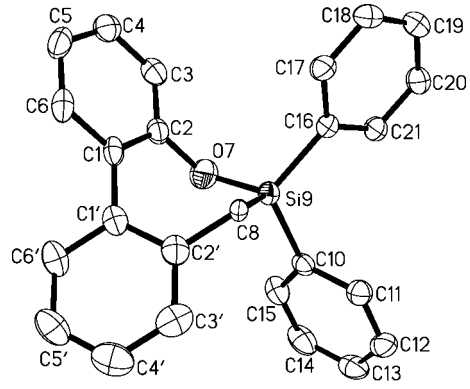
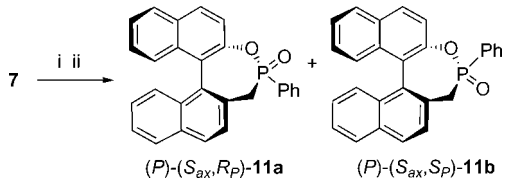


Figure 6. Molecular structure of **10**. Only one of the two crystallographically independent molecules shown. Hydrogen atoms omitted for clarity; displacement ellipsoids drawn at 50% probability level. Selected inter atomic distances [Å] and angles [°]: O(7)–Si(9) 1.691(2), O(7a)–Si(9a) 1.6656(14), C(8)–Si(9) 1.759(2), C(8a)–Si(9a) 1.844(2). O(7)–Si(9)–C(8) 103.84(9), O(7a)–Si(9a)–C(8a) 104.34(7), C(10)–Si(9)–C(16) 110.52(8), C(10a)–Si(9a)–C(16a) 109.62(8); torsion angle C(2)–C(1)–C(1′)–C(2′) 51.5(3), C(2a)–C(1a)–C(1′a)–C(2′a)–52.6(3).

the ^{31}P NMR spectrum of the reaction mixture is informative. A resonance at δ_P 53.51 ppm is observed for (*P*)-(S_{ax},R_P)-**11a** along with traces of a closely related species at δ_P 53.35 ppm, proposed to be the phosphorus epimer (*P*)-(S_{ax},S_P)-**11b**. This was confirmed by lithiation using *n*BuLi/*t*BuOK (method B) which led to a 16–18% isolated yield of **11a/b**. However, in this case a mixture of both possible diastereomers was realised with a S_P:R_P ratio of 5:6. The two diastereomers could be separated by careful chromatography, but attempts to crystallise the minor diastereomer were unsuccessful. As both lithiation methods A and B resulted in poor yields, attempts were made to identify the mass balance of the reaction. The majority of the crude reaction mixture consisted of a very polar yellow compound that could only be eluted from the chromatography columns with neat methanol. The ^{31}P NMR spectrum of this component displayed a broad signal at δ_P 11.5 ppm, which was also present in the crude reaction mixture. Mass spectrometry (FAB) studies of this polar band revealed the presence of mass ions consistent with the formula $(\mathbf{11})_n$ (n = 2, 3) with the possibility of higher oligomers being present as well. Consistent with the presence of mixed stereoisomers, the ^{1}H and ^{13}C NMR spectra of the mixture were broad and uninformative. We believe that the failure of $PhP(O)Cl_2$ electrophile to form chelate **11** effectively is due to the presence of the smaller oxo phenyl moiety [P(=O)Ph] which displays a considerably smaller steric demand than a $SiPh_2$ unit. This trend is born out in reactions of the dianion derived from **7** (either method A or B) with sterically less demanding $PhPCl_2$. While ^{31}P-NMR studies of the reaction mixture revealed the presence of the desired ligand the reaction is even less clean than transformations using $PhP(O)Cl_2$. Isolation of the derived ligand is complicated by its oxidative and hydrolytic instability.



Scheme 5. Preparation of phosphane oxide **11a**. Reagents and conditions: (i): a) **7** (1 equiv.), *n*BuLi (3 equiv.), TMEDA (3 equiv.), Et_2O, 0 °C, 24 h. [leads to (*P*)-(S_{ax},R_P)-**11a** only]; or b) **7** (1 equiv.), *n*BuLi (2.5 equiv.), *t*BuOK (2.5 equiv.), Et_2O, –40 °C, 3 h [leads to a 5:6 mixture of (*P*)-(S_{ax},R_P)-**11a** and its S_p epimer **11b**] (ii) $PhP(=O)Cl_2$ (2.0 or 1.5 equiv.), –60 °C, 3 h.

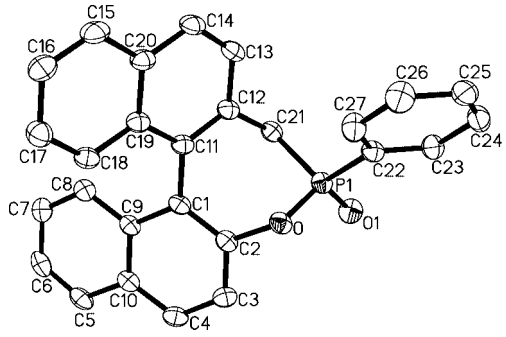


Figure 7. Molecular structure of (*P*)-(S_{ax},R_P)-**11a** derived from (S_{ax})-binol. Hydrogen atoms omitted for clarity; displacement ellipsoids drawn at 50% probability level. Selected inter atomic distances [Å] and angles [°]: P(1)–O 1.691(2), P(1)–O(1) 1.4732(12), P(1)–C(21) 1.813(2), P(1)–C(22) 1.793(2), C(21)–P(1)–O 102.45(7), C(22)–P(1)–O(1) 113.45(8); torsion angle C(2)–C(1)–C(11)–C(12) 54.8(2).

Conclusions

We have developed an ultraselective monosulfonylation of 1,1′-binaphthol (**1**) and structurally related 1,1′-biphenol derivatives and their subsequent reaction with Tf_2O or NfF to afford the protected/activated cores **5**–**6**. Chemoselective methylation of these cores and subsequent hydrolysis allows rapid access to the 2-OH–2′-Me species **7**–**8** in a highly expedient process compared to published approaches. Double

deprotonation of the 1,1′-binaphthyl methyl compound **7** with either *n*BuLi/TMEDA or *n*BuLi/*t*BuOK, followed by reaction with Cl_2SiPh_2 leads to 7-ring silanoxanes **9**–**10** in good overall yield (38-42%). Using sterically less demanding electrophiles (i.e. those lacking the strong Thorpe–Ingold effect present in Cl_2SiPh_2), such as $PhP(=O)Cl_2$, poorer yields were evidenced in the reaction of the equivalent dianion derived from **7**.

Experimental Section

General Methods: Procedures involving air- or moisture-sensitive reagents/intermediates were performed under a positive pressure of argon using standard Schlenk techniques. Flash chromatography was performed using a forced flow with the solvent indicated in the relevant experimental procedures. Silica gel 60 (220–240 mesh) was used as the stationary phase (Fluka). Thin-layer chromatography was performed on pre-coated plates (0.25 mm) silica, with visualisation by UV, $KMnO_4$ or PMA staining. ^1H, ^{13}C, ^{19}F and ^{31}P NMR were recorded with a Bruker (AV400, DPX 300 or DRX 500). All chemical shifts (δ) were referenced to chloroform and are reported in parts per million (ppm). Coupling constants (J) are given in Hz. Assignments to binaphthyl or biphenyl untis are abbreviated "Ar", those to tosyl groups "Ts" and to phenylsulfonyl groups "Ph". IR spectra were recorded as a solution in chloroform or as specified. MS were recorded at high resolution with a micromass LCT or VG micromass 70E mass spectrometer using electrospray ionisation (ESI), electron impact (EI) or fast atom bombardment (FAB). Elemental analyses were performed with an Exeter Analytical CE-440. Optical rotations were measured with a JASCO DIP370 Digital polarimeter and are quoted as 10^{-1} deg cm^2 g^{-1}. Concentration (c) is given as g/100 cm^3. Organic solvents were used as supplied or distilled from suitable drying agents and stored over 4-Å molecular sieves under argon.[25] (*R*)- and (*S*)-binol were purchased from Reuter Chemischer Apparatebau KG, 3,3′,5,5′-tetramethylbiphenol was synthesised according to the literature,[26] 2-(di-*tert*-butylphosphanyl)-2′,4′,6′-triisopropyl-1,1′-biphenyl (X-Phos) was purchased from Strem.

(*P*)-(*S*$_{ax}$)-2-Hydroxy-2′-tosyloxy-1,1′-binaphthyl (2a): (S_{ax})-Binol (1.00 g, 3.50 mmol), *p*-toluenesulfonyl chloride (0.67 g, 3.53 mmol) and DMAP (0.069 g, 0.57 mmol) were dissolved in 10 mL of freshly distilled CH_2Cl_2 and the resulting solution cooled to 0 °C. Neat NEt_3 (0.6 mL, 3.85 mmol) was added dropwise to the solution, which was then stirred at ambient temperature. After 8 h quantitative yield was obtained (white solid, 1.54 g, 3.50 mmol, 100%). R_f = 0.45 in CH_2Cl_2. M.p. 61–62 °C. $[\alpha]_D^{25}$ = –46.2 (c = 1.00, $CHCl_3$). Compound **2a** could be crystallised as colourless plates of a toluene monosolvate from toluene/light petroleum. The toluene was removed under prolonged drying. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.06 (d, J = 9.0 Hz, 1 *H*, $Ar_{4or4'}$), 7.97 (d, J = 8.2 Hz, 1 *H*, $Ar_{5or5'}$), 7.84 (d, J = 9.0 Hz, 1 *H*, $Ar_{4or4'}$), 7.78 (d, J = 9.0 Hz, 1 *H*, $Ar_{3or3'}$), 7.73 (d, J = 9.2 Hz, 1 *H*, $Ar_{3or3'}$), 7.51 (approx. t, J = 7.5 Hz plus unresolved long-range coupling, 1*H*, $Ar_{6,6',7or7'}$), 7.33 (approx. t, J = 7.5 plus unresolved long-range coupling, 1*H*, $Ar_{6,6',7or7'}$), 7.40–7.28 (m, 5*H*, toluene), 7.23 (d, J = 8.2 Hz, 2*H*, Ts) overlapped by 7.22–7.14 (m, 4*H*, $Ar_{8or8'}$, $Ar_{6,6',7or7'}$, $Ar_{3or3'}$), 6.91 (d, J = 8.2 Hz, 2*H*, Ts), 6.83 (d, J = 8.4 Hz, plus unresolved long-range coupling, 1*H*, $Ar_{8or8'}$), 5.05 (s, 1*H*, O*H*), 2.40 (s, 3*H*, CH_3), 2.33 (s, 3*H*, toluene). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): non solvate: δ = 151.6 (*C*, Ar), 146.4 (*C*, Ar), 144.7 (*C*, Ar), 133.4 (2 *C*, Ar), 132.7 (*C*, Ar), 132.5 (*C*, Ar), 131.0 (*C*H, Ar), 130.4 (*C*H, Ar), 129.3 (2 *C*H, Ts), 128.9 (*C*, Ar), 128.3 (*C*H, Ar), 127.8 (CH, Ar), 127.6 (*C*H, Ar), 127.5 (2 *C*H, Ts), 126.7 (*C*H, Ar), 126.6 (*C*H, Ar), 126.3 (*C*H, Ar), 124.7 (*C*H, Ar), 123.9 (*C*, Ar), 123.4 (*C*H, Ar), 121.7 (*C*H, Ar), 118.2 (*C*H, Ar), 113.8 (*C*, Ar), 21.6 (*C*H_3, Ts*C*H_3) ppm. IR (CCl_4 solution): $\tilde{\nu}$ = 3555 (OH), 3061 (CH, Ar), 1382, 1361 (SO_2), 1177 (SO_2) cm^{-1}. HRMS (EI): *m*/*z* found 440.1082 required 440.1082. $C_{27}H_{20}O_4S$ (440.10): calcd. C 73.62 H 4.58 found C 73.59 H 4.70%.

(*M*)-(*R*$_{ax}$)-2-Hydroxy-2′-(phenylsulfonyloxy)-1,1′-binaphthyl (2b): Prepared as for **2a** starting from (R_{ax})-binol and benzenesulfonyl chloride, to give **2b** as a colourless solid, 1.34 g, 90%. R_f = 0.27 in CH_2Cl_2. M.p. 61–64 °C. $[\alpha]_D^{25}$ = +44.0 (c = 1.0 in $CHCl_3$). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.08 (d, J = 9.0 Hz, 1 *H*, $Ar_{4or4'}$), 7.98 (d, J = 8.3 Hz, 1 *H*, $Ar_{5or5'}$), 7.84 (d, J = 8.8 Hz, 1 *H*, $Ar_{4or4'}$), 7.78 (d, J = 8.1 Hz, 1 *H*, $Ar_{5or5'}$), 7.72 (d, J = 9.0 Hz, 1 *H*, $Ar_{3or3'}$), 7.53 (ddd, J_1 = 8.1 Hz, J_2 = 6.8 Hz, J_3 = 1.3 Hz, 1 *H*, $Ar_{6,6',7or7'}$), 7.40 (tt, J_1 = 8.7 Hz, J_2 = 1.2 Hz, 1 *H*, Ph-*p*), overlapping with 7.36 (ddd, J_1 = 6.9 Hz, J_2 = 5.5 Hz, J_3 = 1.2 Hz, 1 *H*, $Ar_{6,6',7or7'}$), 7.31 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2 *H*, Ph-*o*), overlapping with 7.31–7.27 (m, 2 *H*, $Ar_{3or3'}$, $Ar_{6,6',7or7'}$), 7.24 (d, J = 8.9 Hz, 1 *H*, $Ar_{8or8'}$), 7.18–7.14 (m, 3 *H*, Ph-*m*, $Ar_{6,6'7or7'}$), 6.88 (d, J = 8.4 Hz, 1 *H*, $Ar_{8or8'}$), 4.98 (s, 1 *H*, O*H*) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 151.6 (*C*, Ar), 146.3 (*C*, Ar), 135.8 (*C*, Ar), 133.7 (*C*, Ar), 133.4 (*C*, Ar), 133.3 (*C*, Ar), 132.5 (*C*, Ar), 131.0 (*C*H, Ar), 130.5 (*C*, Ar), 128.9 (*C*, Ar), 128.6 (2 *C*H, Ar), 128.3 (*C*H, Ar), 127.9 (*C*H, Ar), 127.7 (*C*H, Ar), 127.4 (2 *C*H, Ar), 126.8 (*C*H, Ar), 126.7 (*C*H, Ar), 126.2 (*C*H, Ar), 124.6 (*C*H, Ar), 124.0 (*C*H, Ar), 123.5 (*C*H, Ar), 121.6 (*C*H, Ar), 118.0 (*C*H, Ar), 113.7 (*C*H, Ar) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3684 (OH), 3035 (CH, Ar), 3010, 1239 (SO_2), 1194 (SO_2) cm^{-1}. HRMS (EI): *m*/*z* found 426.0940, $C_{26}H_{18}O_4S$ required 426.0926.

2-Hydroxy-2′-tosyloxy-1,1′-biphenyl (4a): Prepared as for **3a** starting from biphenol to give **4a** as a colourless solid, 1.64 g, 90%. R_f = 0.33 in CH_2Cl_2. M.p. 115–117 °C. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.51 (dd, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 1 *H*, Ar), 7.43 (approx. td, J_1 = 8.1 Hz, J_2 = 1.9 Hz, 1*H*, Ar), 7.37 (approx. td, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1*H*, Ar), 7.31 (d, J = 1.8 Hz, 1*H*, Ar), 7.28 (d, J = 8.3 Hz, 2*H*, Ts), 7.21 (ddd, J_1 = 9.0 Hz, J_2 = 6.9 Hz, J_3 = 2.3 Hz, 1*H*, Ar), 7.06 (d, J = 8.0 Hz, 2*H*, Ts), 6.86 (d, J = 6.0 Hz, 1*H*, Ar), 6.83 (approx. td, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 1*H*, Ar), 4.93 (s, O*H*), 2.38 (s, 3*H*, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 152.6 (*C*, Ar), 146.9 (*C*, Ar), 145.0 (*C*, Ar), 132.1 (*C*, Ar), 132.0 (*C*H, Ar), 131.1 (*C*H, Ar), 131.0 (*C*, Ar), 129.5 (*C*H, Ar), 129.5 (2 *C*H, Ts), 129.4 (*C*H, Ar), 127.9 (2 *C*H, Ts), 127.7 (*C*H, Ar), 123.9 (*C*H, Ar), 123.6 (*C*, Ar), 120.5 (*C*H, Ar), 116.4 (*C*H, Ar), 21.6 (*C*H_3, Ts) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3565 (OH), 3069 (CH, Ar), 1474, 1376 (SO_2), 1166 (SO_2) cm^{-1}. HRMS (EI): *m*/*z* found 340.0768 required 340.0769. $C_{19}H_{16}O_4S$ (340.08): calcd. C 67.04 H 4.74; found C 66.87 H 4.73.

2-Hydroxy-2′-(phenylsulfonyloxy)-1,1′-biphenyl (4b): Prepared as for **3a** to give **4b** as a colourless solid, 1.28 g, 73%. R_f = 0.33 in CH_2Cl_2. M.p. 110–111 °C. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.53 (tt, J_1 = 8.8 Hz, J_2 = 1.2 Hz, 1 *H*, Ar), 7.52 (dd, J_1 = 8.4 Hz, J_2 = 1.0 Hz, 1 *H*, Ar), 7.44 (ddd, J_1 = 8.1 Hz, J_2 = 7.3 Hz, J_3 = 1.9 Hz, 1 *H*, Ar), 7.42 (dd, J_1 = 6.6 Hz, J_2 = 1.4 Hz, 2 *H*, Ar), 7.38 (approx. td, J_1 = 7.4 Hz, J_2 = 1.4 Hz, 1 *H*, Ar), 7.32–7.27 (m, 3 *H*, Ts, Ar), 7.21 (ddd, J_1 = 9.0 Hz, J_2 = 6.9 Hz, J_3 = 2.2 Hz, 1 *H*, Ar), 6.87–6.84 (m, 2 *H*, Ar), 6.82 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1 *H*, Ar), 4.87 (s, 1 *H*, O*H*) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 152.6 (*C*, Ar), 146.9 (*C*, Ar), 135.3 (*C*, Ar), 133.8 (*C*H, Ar), 132.1 (*C*H, Ar), 131.1 (*C*H, Ar), 131.0 (*C*, Ar), 129.6 (*C*H, Ar), 129.5 (*C*H, Ar), 128.9 (2 *C*H, Ts), 127.9 (2 *C*H, Ts), 127.8 (*C*H, Ar), 123.9 (*C*H, Ar), 123.4 (*C*, Ar), 120.7 (*C*H, Ar), 116.4 (*C*H, Ar)

ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3564 (OH), 1450, 1377 (SO_2), 1165 (SO_2) cm^{-1}. HRMS (EI): *m/z* found 326.0609 required 326.0613. $C_{18}H_{14}O_4S$ (326.06): calcd. C 66.25 H 4.32; found C 65.94 H 4.31.

2-Hydroxy-3,3′,5,5′-tetramethyl-2′-tosyloxy-1,1′-biphenyl (4c): Prepared as for **2a** starting from 3,5,3′,5′-tetramethyl-1,1′-biphenol to give **4c** as a colourless solid, 1.63 g, 99%. R_f = 0.25 in CH_2Cl_2/light petroleum ether, 1:1. M.p. 115–116 °C. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.26 (approx. d, J = 8.2 Hz, 2 *H*, Ts), 7.12 (dd, J_1 = 1.6 Hz, J_2 = 0.7 Hz, 1 *H*, Ar), 7.04 (approx. d, J = 8.2 Hz, 2 *H*, Ts), 6.93 (approx. d, J = 2.2 Hz, 1 *H*, Ar), 6.73 (dd, J_1 = 1.5 Hz, J_2 = 0.7 Hz, 1 *H*, Ar), 6.59 (approx. d, J = 2.1 Hz, 1 *H*, Ar), 4.83 (br. s, 1 *H*, O*H*), 2.49 (s, 3 *H*, Ts-CH_3), 2.37 (s, 3 *H*, CH_3), 2.32 (s, 3 *H*, CH_3), 2.11 (s, 3 *H*, CH_3), 2.09 (s, 3 *H*, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 148.5 (*C*, Ar), 144.5 (*C*, Ar), 144.1 (*C*, Ar), 137.3 (*C*, Ar), 133.8 (*C*, Ar), 133.7 (*C*, Ar), 132.3 (*C*H, Ar), 131.3 (*C*, Ar), 131.0 (*C*H, Ar), 130.3 (*C*H, Ar), 129.0 (2 *C*, Ar), 128.9 (*C*, Ar), 128.8 (*C*H, Ar), 127.3 (2 *C*, Ar), 124.8 (*C*, Ar), 124.0 (*C*, Ar), 21.6 (Ts-*C*H_3), 20.8 (*C*H_3), 20.3 (*C*H_3), 17.8 (*C*H_3), 16.1 (*C*H_3) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3556 (OH), 2923 (CH, Ar), 1462, 1321 (SO_2), 1146 (SO_2) cm^{-1}. HRMS (EI): *m/z* found 396.1386 required 396.1395. $C_{23}H_{24}O_4S$ (396.14): calcd. C 69.67 H 6.10; found C 69.39 H 6.12.

(*P*)-(S_{ax})-2-(Trifluoromethoxy)-2′-tosyloxy-1,1′-binaphthyl (5a): (S_{ax})-Binol *ent*-**1a** (5.11 g, 17.86 mmol), *p*-toluenesulfonyl chloride (3.40 g, 17.89 mmol) and DMAP (0.35 g, 2.85 mmol) were dissolved in 50 mL of freshly distilled CH_2Cl_2 and the resulting solution cooled to 0 °C. Neat NEt_3 (8.4 mL, 53.7 mmol) was added dropwise to the solution. The reaction mixture was stirred for 12 h at ambient temperature. After this time, trifluoromethanesulfonic anhydride (5.54 g, 19.65 mmol) was added slowly at 0 °C to the reaction mixture and stirring continued for another 12 h. The organic layer was washed with 1 M HCl (3 × 100 mL) and with water (3 × 100 mL), dried with $MgSO_4$ and the solvent removed in vacuo. Crystallization from boiling MeOH or from CH_2Cl_2/hexane (1:6) afforded **5a** as colourless microneedles (9.89 g, 17.28 mmol, 97%). R_f = 0.51 in CH_2Cl_2/light petroleum ether, 1:1. M.p. 159–161 °C. $[a]_D^{25}$ = +108.0 (c = 1.00, $CHCl_3$). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.07 (d, J = 9.0 Hz, 1 *H*, $Ar_{4or4'}$), 7.97 (d, J = 8.8 Hz, 1 *H*, $Ar_{5or5'}$), 7.95 (d, J = 8.5 Hz, 1 *H*, $Ar_{4or4'}$), 7.89 (d, J = 8.2 Hz, 1 *H*, $Ar_{5or5'}$), 7.78 (d, J = 9.0 Hz, 1 *H*, $Ar_{3or3'}$), 7.53–7.46 (m, 2 *H*, $Ar_{6,6',7or7'}$) overlapped by 7.48 (d, J = 8.5 Hz, 1 *H*, $Ar_{3or3'}$), 7.28 (ddd, J_1 = 8.5 Hz, J_2 = 6.9 Hz, J_3 = 1.3 Hz, 1 *H*, $Ar_{6,6',7or7'}$), 7.22 (ddd, J_1 = 8.5 Hz, J_2 = 6.9 Hz, J_3 = 1.2 Hz, 1 *H*, $Ar_{6,6',7or7'}$) 7.08 (approx. d, J = 8.2 Hz, 2 *H*, Ts), 7.05 (d, J = 8.5 Hz, plus unresolved long-range couplings,1 *H*, $Ar_{8or8'}$), 6.98 (d, J = 8.5 Hz, plus unresolved long-range couplings,1 *H*, $Ar_{8or8'}$), 6.74 (approx. d, J = 8.2 Hz, 2 *H*, Ts), 2.22 (s, 3 *H*, TsCH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 145.9 (*C*, Ar), 145.2 (*C*, Ar), 144.4 (*C*, Ar), 133.1 (*C*, Ar), 132.9 (*C*, Ar), 132.7 (*C*, Ar), 132.0 (*C*, Ar), 131.8 (*C*, Ar), 131.2 (*C*H, Ar), 130.8 (*C*H, Ar), 129.1 (2 *C*H, Ts), 129.0 (*C*H, Ar), 128.2 (*C*H, Ar), 127.9 (*C*H, Ar), 127.4 (*C*H, Ar), 127.2 (2 *C*H, Ts), 127.1 (*C*H, Ar), 126.6 (*C*H, Ar), 126.5 (*C*H, Ar), 126.3 (*C*H, Ar), 124.6 (*C*, Ar), 122.1 (*C*, Ar), 121.4 (*C*H, Ar), 119.3 (*C*H, Ar), 118.0 (q, J_{CF} = 320 Hz, *C*F_3), 21.6 (*C*H_3, Ts) ppm. $^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$): δ = –75.7 (s, CF_3) ppm. IR (CCl_4 solution): $\tilde{\nu}$ = 3060 (CH, Ar), 3018 (CH, Ar), 1625, 1172 (SO_2), 1365 (SO_2) cm^{-1}. HRMS (FAB): *m/z* found 572.0579 required 572.0575. $C_{28}H_{19}F_3O_6S_2$ (572.06): calcd. C 58.73 H 3.34;found C 58.67 H 3.19.

On this and larger scales, solid crude **5a** could also be isolated directly by removal of the CH_2Cl_2 reaction solvent followed by addition of MeOH/water (1:1, 100 mL per 15 mmol of **5a**) to the chilled residual oil, followed by agitation, filtration and further washing in 1:1 MeOH/water.

(*M*)-(R_{ax})-2-(Trifluoromethoxy)-2′-(phenylsulfonyloxy)-1,1′-binaphthyl (5b): Prepared as for **5a** starting from (R_{ax})-binol and benzenesulfonyl chloride to give **5b** as a colourless solid, 1.64 g, 84%. R_f = 0.46 in CH_2Cl_2/light petroleum ether, 1:1. M.p. 100–102 °C. $[a]_D^{25}$ = –101.9 (c = 1.0, $CHCl_3$). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.07 (d, J = 9.0 Hz, 1 *H*, $Ar_{4or4'}$), 7.95 (d, J = 8.9 Hz, 1 *H*, $Ar_{5or5'}$) overlapped by 7.95 (d, J = 9.2 Hz, 1 *H*, $Ar_{4or4'}$), 7.88 (d, J = 8.2 Hz, 1 *H*, $Ar_{5or5'}$), 7.75 (d, J = 9.0 Hz, 1 *H*, $Ar_{3or3'}$), 7.51 (ddd, J_1 = 7.8 Hz, J_2 = 5.3 Hz, J_3 = 1.3 Hz, 1 *H*, $Ar_{6,6',7or7'}$), overlapping with 7.49 (ddd, J_1 = 8.2 Hz, J_2 = 5.3 Hz, J_3 = 1.2 Hz, 1 *H*, $Ar_{6,6',7or7'}$), 7.45 (d, J = 9.2 Hz, 1 *H*, $Ar_{3or3'}$), 7.30 (ddd, J_1 = 8.9, J_2 = 6.8, J_3 = 1.2 Hz, 1 *H*, $Ar_{6,6',7or7'}$) overlapping with 7.28 (ddd, J_1 = 7.8, J_2 = 6.9, J_3 = 1.3 Hz, 1 *H*, $Ar_{6,6',7or7'}$), 7.27-7.24 (m, 1 *H*, Ph-*p*), 7.22 (approx. d, J_1 = 8.4, J_2 = 1.2 Hz, 2 *H*, Ph-*o*), 7.06 (approx. t, J = 8.7 Hz, 2 *H*, Ph-*m*), 7.02 (d, J = 7.8 Hz, 1 *H*, $Ar_{8or8'}$), 7.00 (d, J = 7.8 Hz, 1 *H*, $Ar_{8or8'}$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 145.8 (*C*, Ar), 145.2 (*C*, Ar), 135.8 (*C*, Ar), 133.4 (*C*H, Ar), 133.2 (*C*, Ar), 133.0 (*C*, Ar), 132.0 (*C*, Ar), 131.8 (*C*, Ar), 131.2 (*C*H, Ar), 130.9 (*C*H, Ar), 128.4 (2 *C*, Ph), 128.2 (*C*H, Ar), 128.0 (*C*H, Ar), 127.6 (*C*H, Ar), 127.2 (*C*H, Ar), 127.1 (*C*H, Ar), 127.1 (2 *C*, Ph), 126.8 (*C*H, Ar), 126.5 (*C*H, Ar), 126.4 (*C*H, Ar), 124.5 (*C*, Ar), 122.2 (*C*, Ar), 131.2 (*C*H, Ar), 119.2 (*C*H, Ar), 118.0 (q, J_{CF} = 320.3 Hz, *C*F_3) ppm. $^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$): δ = –74.82 (s, CF_3) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 1376 (SO_2), 1140 (SO_2), 1093, 1067, 969 cm^{-1}. HRMS (EI): *m/z* found 558.0426 required 558.0419. $C_{27}H_{17}F_3O_6S_2$ (558.55): calcd. C 58.06, H 3.07; found C 57.92, H 3.01.

(*M*)-(R_{ax})-2-Nonaflyloxy-2′-tosyloxy-1,1′-binaphthyl (5c): Prepared as for **5a** from (R_{ax})-binol and $CF_3(CF_2)_3SO_2F$ to give **5c** as a colourless powder, 11.5 g, 91%. R_f = 0.54 in CH_2Cl_2/light petroleum ether, 1:1. M.p. 128–131 °C. $[a]_D^{25}$ = –94.6 (c = 1.0, $CHCl_3$). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.06 (d, J = 9.1 Hz, 1 *H*, $Ar_{4or4'}$), 7.97 (d, J = 8.6 Hz, 1 *H*, $Ar_{5or5'}$), 7.94 (d, J = 9.2 Hz, 1 *H*, $Ar_{4or4'}$), 7.88 (d, J = 8.8 Hz, 1 *H*, $Ar_{5or5'}$), 7.76 (d, J = 9.1 Hz, 1 *H*, $Ar_{3or3'}$), 7.52–7.46 (m, 2 *H*, $Ar_{6,6',7or7'}$) overlapped by 7.50 (d, J = 9.2 Hz, 1 *H*, $Ar_{3or3'}$), 7.28 (ddd, J_1 = 8.6 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1 *H*, $Ar_{6,6',7or7'}$), 7.22 (ddd, J_1 = 8.6 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1 *H*, $Ar_{6,6',7or7'}$), 7.07 (approx. d, J = 8.4 Hz, 2 *H*, Ts-*o*), 7.05 (dd, J_1 = 8.6, J_2 = 0.5 Hz, 1 *H*, $Ar_{8or8'}$), 6.98 (dd, J_1 = 8.5 Hz, J_2 = 0.7 Hz, $Ar_{8or8'}$), 6.74 (approx. d, J_1 = 8.0 Hz, 2 *H*, Ts-*m*), 2.23 (s, 3 *H*, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 146.0 (*C*, Ar), 145.4 (*C*, Ar), 144.4 (*C*, Ar), 133.1 (*C*, Ar), 133.0 (*C*, Ar), 132.8 (*C*, Ar), 132.0 (*C*, Ar), 131.8 (*C*, Ar), 131.1 (*C*H, Ar), 130.9 (*C*H, Ar), 129.1 (2 *C*H, Ts), 128.1 (*C*H, Ar), 127.9 (*C*H, Ar), 127.4 (*C*H, Ar), 127.2 (*C*H, Ar), 127.1 (3 *C*H, Ts, Ar), 126.6 (*C*H, Ar), 126.5 (*C*H, Ar), 126.3 (*C*H, Ar), 124.7 (*C*, Ar), 122.1 (*C*, Ar), 121.4 (*C*H, Ar), 119.3 (*C*H, Ar) 21.5 (*C*H_3, Ts) ppm. $^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$): δ = –81.2 (t, J = 9.0 Hz, CF_2), –110.6 (q, J = 14.9 Hz, CF_3), –121.6 (approx. s, CF_2), –126.4 (t, J = 14.5 Hz, CF_2) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 1376 (SO_2), 1173 (SO_2), 1145 (CF_3), 969, 942 cm^{-1}. HRMS (EI): *m/z* found: 722.0462 required 722.0479. $C_{31}H_{19}F_9O_6S_2$ (722.60): calcd. C 51.53, H 2.65; found C 51.32, H 2.46.

2′-Tosyloxy-2-(trifluoromethoxy)-1,1′-biphenyl (6a): Prepared as for **5a** from 1,1′-biphenol to give **6a** as a colourless solid 12.4 g, 98%. R_f = 0.51 in CH_2Cl_2/light petroleum ether, 1:1. M.p. 64–66 °C. ^1H NMR ($CDCl_3$): δ = 7.45 (ddd, J_1 = 8.8 Hz, J_2 = 7.1 Hz, J_3 = 1.8 Hz, 1 *H*, Ar), 7.43–7.39 (m, 2 *H*, Ar), 7.38 (ddd, J_1 = 7.6 Hz, J_2 = 7.2 Hz, J_3 = 1.5 Hz, 1 *H*, Ar), 7.32 (approx. d, J = 8.3 Hz, 2 *H*, Ts-*o*), 7.29–7.25 (m, 3 *H*, Ar), 7.11 (approx. d, J = 8.3 Hz, 2 *H*,

Ts-*m*), 7.06 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 1 *H*, Ar) 2.43 (s, 3 *H*, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 146.8 (*C*, Ar), 146.7 (*C*, Ar), 145.0 (*C*, Ar), 132.7 (*C*, Ar), 132.4 (*C*H, Ar), 131.9 (*C*H, Ar), 130.5 (*C*, Ar), 130.2 (*C*H, Ar), 129.6 (2 *C*H, Ts), 129.6 (*C*H, Ar), 129.4 (*C*, Ar), 127.9 (2 *C*H, Ts, Ar), 127.2 (*C*H, Ar), 123.1 (*C*H, Ar), 121.2 (*C*H, Ts), 21.7 (*C*H$_3$, Ts-*C*H$_3$) ppm. $^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$): δ = –75.4 (s, C*F*$_3$) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 1401, 1377 (SO_2), 1139 (SO_2), 1090 (CF), 892 cm^{-1}. HRMS (EI): *m*/*z* found: 472.0275 required 472.0262. $C_{20}H_{15}F_3O_6S_2$ (472.46): calcd. C 50.84, H 3.20; found C 50.89, H 3.09.

3,3′,5,5′-Tetramethyl-2′-tosyloxy-2-(trifluoromethoxy)-1,1′-biphenyl (6b): Prepared as for **5a** starting from 3,3′,5,5′-tetramethyl-1,1′-biphenol **3b** to give **6b** as a colourless solid, 1.64 g, 75%. R_f = 0.53 in CH_2Cl_2/light petroleum ether, 1:1. M.p. 84–86 °C. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.33 (approx. d, *J* = 8.2 Hz, 2 *H*, Ts-*o*), 7.12 (dd, J_1 = 1.6 Hz, J_2 = 0.7 Hz, 1 *H*, Ar), 7.08 (approx. d, *J* = 8.2 Hz, 2 *H*, Ts-*m*), 6.95 (approx. d, *J* = 2.2 Hz, 1 *H*, Ar), 6.88–6.86 (m, 2 *H*, Ar), 2.42 (s, 3 *H*, Ts-C*H*$_3$), 2.39 (s, 3 *H*, C*H*$_3$), 2.33 (s, 3 *H*, C*H*$_3$), 2.26 (s, 3 *H*, C*H*$_3$), 2.16 (s, 3 *H*, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 144.1 (*C*, Ar), 144.0 (*C*, Ar), 143.1 (*C*, Ar), 137.7 (*C*, Ar), 136.7 (*C*, Ar), 134.4 (*C*, Ar), 132.9 (*C*, Ar), 132.6 (*C*H, Ar), 131.9 (*C*H, Ar), 131.7 (*C*, Ar), 130.9 (*C*H, Ar), 130.9 (*C*, Ar), 130.3 (*C*H, Ar), 130.2 (*C*, Ar), 129.0 (2 *C*H, Ts), 127.1 (2 *C*H, Ts), 118.0 (q, J_{CF} = 320.4 Hz, *C*F$_3$), 21.5 (*C*H$_3$, Ts), 20.7 (*C*H$_3$), 20.7 (*C*H$_3$), 17.5 (*C*H$_3$), 17.0 (*C*H$_3$) ppm. $^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$): δ = –75.1 (s, C*F*$_3$) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 2924 (CH, Ar), 1402, 1367 (SO_2), 1170 (SO_2) cm^{-1}. HRMS (EI) found 528.0912 required 528.0888. $C_{24}H_{23}F_3O_6S_2$ (528.09): calcd. C 54.54 H 4.39; found C 54.25 H 4.26.

2′-Nonaflyloxy-2-(trifluoromethoxy)-1,1′-biphenyl (6c): Prepared as for **5c** starting from 1,1′-biphenol to give **6c** as a colourless solid, 3.0 g, 90%. R_f 0.56 in CH_2Cl_2/light petroleum ether, 1:1. M.p. 68–70 °C. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.44 (ddd, J_1 = 8.4 Hz, J_2 = 7.1 Hz, J_3 = 1.8 Hz, 1 *H*, Ar), overlapped with 7.43–7.40 (m, 1 *H*, Ar), 7.41 (ddd, J_1 = 7.4 Hz, J_2 = 1.6 Hz, J_3 = 1.2 Hz, 1 *H*, Ar), 7.37 (dd, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1 *H*, Ar), 7.33 (approx. d, *J* = 8.0 Hz, 2 *H*, Ts-*o*), 7.28 (dd, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 2 *H*, Ar), 7.28 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1 *H*, Ar), 7.11 (approx. d, *J* = 8.0 Hz, 2 *H*, Ts-*m*), 7.06 (dd, J_1 = 7.6 Hz, J_2 = 1.7 Hz, 1 *H*, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 146.9 (*C*, Ar), 146.8 (*C*, Ar), 144.9 (*C*, Ar), 132.7 (*C*, Ar), 132.3 (*C*H, Ar), 131.8 (*C*H, Ar), 130.6 (*C*, Ar), 130.1 (*C*H, Ar), 129.6 (2 *C*H, Ts), 129.6 (*C*H, Ar), 129.5 (*C*, Ar), 127.9 (*C*H, Ar), 127.9 (2 *C*H, Ts), 127.1 (*C*H, Ar), 123.0 (*C*H, Ar), 121.2 (*C*H, Ar), 21.5 (*C*H$_3$, Ts) ppm. $^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$): δ = –81.2 (t, *J* = 8.3 Hz, C*F*$_2$), –110.5 (approx. s, C*F*$_3$), –121.5 (approx. s, C*F*$_2$), –126.4 (t, *J* = 13.7 Hz, C*F*$_2$) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 1598, 1401, 1378 (SO_2), 1139 (SO_2), 1090 (CF_2 or CF_3) cm^{-1}. HRMS (EI) found 622.0164 required 622.0166. $C_{27}H_{23}F_9O_6S_2$ (622.02): calcd. C 44.37 H 2.43; found C 44.33 H 2.45.

3,3′,5,5′-Tetramethyl-2′-tosyloxy-2-(trifluoromethoxy)-1,1′-biphenyl (6d): Prepared as for **5c** starting from 3,3′,5,5′-tetramethyl-1,1′-biphenol **3b** to give **6d** as a colourless solid, 1.24 g, 93%. R_f 0.32 in CH_2Cl_2/light petroleum ether, 1:1. M.p. 100–101 °C. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.33 (approx. d, *J* = 8.2 Hz, 2 *H*, Ts-*o*), 7.12 (dd, J_1 = 1.6, J_2 = 0.7 Hz, 1 *H*, Ar), 7.08 (approx. d, *J* = 8.2 Hz, 2 *H*, Ts-*m*), 6.95 (approx. d, *J* = 2.2 Hz, 1 *H*, Ar), 6.88–6.86 (m, 2 *H*, Ar), 2.42 (s, 3 *H*, Ts-C*H*$_3$), 2.39 (s, 3 *H*, C*H*$_3$), 2.33 (s, 3 *H*, C*H*$_3$), 2.26 (s, 3 *H*, C*H*$_3$), 2.16 (s, 3 *H*, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 144.1 (*C*, Ar), 144.0 (*C*, Ar), 142.8 (*C*, Ar), 137.8 (*C*, Ar), 136.7 (*C*, Ar), 134.4 (*C*, Ar), 132.8 (*C*, Ar), 132.5 (*C*H, Ar), 132.0 (*C*H, Ar), 131.9 (*C*, Ar), 131.0 (*C*H, Ar), 131.0 (*C*, Ar), 130.4 (*C*, Ar), 130.2 (*C*H, Ar), 129.0 (2 *C*H, Ts), 127.0 (2 *C*H, Ts) 21.5 (*C*H$_3$, Ts), 20.6 (2 *C*H$_3$), 17.4 (*C*H$_3$), 17.0 (*C*H$_3$) ppm. $^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$): δ = –81.2 (d, *J* = 8.8 Hz, C*F*$_2$), –111.3 (t, *J* = 13.7 Hz, C*F*$_3$), –121.5 (approx. s, C*F*$_2$), –126.5 (t, *J* = 13.9 Hz, C*F*$_2$) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 2925 (Ar CH), 1598, 1367 (SO_2), 1170 (SO_2), 1137 (CF_2 or CF_3) cm^{-1}. HRMS (EI) found 678.0769 required 678.0792. $C_{23}H_{15}F_9O_6S_2$ (678.08): calcd. C 47.79 H 3.42 found C 47.54 H 3.29%.

(*P*)-(S_{ax})-2-Hydroxy-2′-methyl-1,1′-binaphthyl (7): To a solution of **5a** (5.5 g, 9.61 mmoL) and Ni(dppe)Cl_2 (0.355 g, 0.67 mmol) in 100 mL of freshly distilled THF, a solution of MeMgBr in Et_2O (28.8 mmol) was added dropwise at 0 °C. The reaction mixture was warmed to ambient temperature and then stirred at 60 °C for 20 h. Completion of the coupling was indicated by the reaction mixture turning deep orange-brown from its original lemon yellow colour and by TLC analysis. Unreacted MeMgBr was quenched with methanol (10 mL). An aqueous solution of KOH (11 g in 75 mL of H_2O) was then added and the reaction mixture stirred at 80 °C for 12 h. The reaction mixture was acidified with diluted HCl (1 M) and extracted with CH_2Cl_2. The organic layers were dried with $MgSO_4$ and the solvent removed in vacuo. The crude product was purified by column chromatography to give **7** as a colourless solid (1.8 g, 6.34 mmol, 66%) R_f = 0.33 Et_2O/light petroleum ether, 1:5. M.p. 125–127 °C. $[\alpha]_D^{25}$ = +87.0 (*c* = 1.00, $CHCl_3$). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.5 Hz, 1 *H*, Ar$_{4or4'}$), 7.91 (approx. d, *J* = 8.8 Hz, 2 *H*, Ar$_{5or5'}$ overlapped by Ar$_{4or4'}$), 7.87 (d, *J* = 8.1 Hz, 1 *H*, Ar$_{5or5'}$), 7.56 (d, *J* = 8.5 Hz, 1 *H*, Ar$_{3or3'}$), 7.45 (ddd, J_1 = 8.1 Hz, J_2 = 6.7 Hz, J_3 = 1.3 Hz, 1 *H*, Ar$_{6,6',7or7'}$), 7.35 (d, *J* = 8.8 Hz, 1 *H*, Ar$_{3or3'}$) overlapped by 7.34–7.20 (m, 5 *H*, Ar$_{6,6',7or7'}$ and Ar$_{8or8'}$), 6.98 (d, *J* = 8.4 Hz plus unresolved long-range coupling, 1 *H*, Ar$_{8,8'}$), 4.77 (s, 1 *H*, O*H*), 2.15 (s, 3 *H*, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 150.7 (*C*, Ar), 137.2 (*C*, Ar), 133.3 (*C*, Ar), 133.2 (*C*, Ar), 132.5 (*C*, Ar), 129.8 (*C*H, Ar), 129.1 (*C*, Ar), 129.0 (*C*H, Ar), 128.9 (*C*, Ar), 128.6 (*C*H, Ar), 128.1 (2 *C*H, Ar), 126.8 (*C*H, Ar), 126.7 (*C*H, Ar), 125.5 (*C*H, Ar), 125.4 (*C*H, Ar), 124.5 (*C*H, Ar), 123.4 (*C*H, Ar), 117.5 (*C*, Ar), 117.4 (*C*H, Ar), 20.1 (*C*H$_3$, Bz) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3534 (OH), 1620, 1597 (Ar C=C), 1346, 1128 cm^{-1}. HRMS (EI) found 284.1203, $C_{21}H_{16}O$ required 284.1201. These values are concordant with those published for **7** obtained by alternative routes.[27]

2-Hydroxy-2′-methyl-1,1′-biphenyl (8): To a solution of **6a** (0.472 g, 1.0 mmol), $Pd_2(dba)_3$ (0.027 g, 0.03 mmol) and X-Phos (0.021, 0.05 mmol) in freshly distilled THF (8 mL) under argon, was added $(AlMe_3)_2$(DABCO) (0.0205 g, 0.8 mmol) in THF (8 mL). The reaction was then heated to reflux overnight. The reaction mixture was then cooled to ambient temperature and a solution of KOH (0.561 g, 10.0 mmol) in MeOH (5 mL) and water (5 mL) was added. The reaction mixture was then left to reflux for 4 h. After this time, the reaction mixture was acidified with diluted HCl (1 M) and extracted with CH_2Cl_2. The organic phase was dried with $MgSO_4$, filtered and the solvent removed in vacuo. The crude product was purified by column chromatography to give **6a** as a pale yellow viscous oil (0.156 g, 0.85 mmol, 85%). R_f = 0.31 CH_2Cl_2/light petroleum ether, 1:1. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 5 *H*, Ar), 7.14 (dd, J_1 = 7.3 Hz, J_2 = 1.6 Hz, 1 *H*, Ar), 7.01 (ddd, J_1 = 8.6 Hz, J_2 = 7.4 Hz, J_3 = 1.1 Hz, 1 *H*, Ar) overlapped with 7.01 (ddd, J_1 = 8.6 Hz, J_2 = 7.4 Hz, J_3 = 1.1 Hz, 1 *H*, Ar), 4.81 (s, 1 *H*, O*H*), 2.20 (s, 3 *H*, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 152.5 (*C*, Ar), 137.4 (*C*, Ar), 135.7 (*C*, Ar), 130.7 (*C*H, Ar), 130.4 (*C*H, Ar), 130.1 (*C*H, Ar), 129.1 (*C*H,

Ar), 128.5 (*C*H, Ar), 127.7 (*C*, Ar), 126.4 (*C*H, Ar), 120.4 (*C*H, Ar), 115.3 (*C*H, Ar), 19.7 (*C*H$_3$, Bz) ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3544 (OH), 2925 (Ar CH), 1476 (Ar C=C), 1337, 1152 cm^{-1}. HRMS (ESI) found 183.0815, $C_{13}H_{11}O$ (M – H) required 183.0877 (M – H).

Lithiation of 7 and 8. Method A: To a solution of **7** or **8** (0.2 mmol) in Et_2O (2 mL), *n*-butyllithium (0.24 mL of a 2.5 M solution in hexanes) was added dropwise at 0 °C. To this pale yellow solution *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was added (70 mg, 0.6 mmol) and the reaction mixture was stirred at 0 °C for 24 h. The dark red slurry was then cooled to –60 °C and the appropriate amount of electrophile (2.0 equiv.) was added to the mixture (in the case of the D_2O experiment, 0.3 mL were used). The organic layer was washed with 1 M HCl (3 × 5 mL) and dried with $MgSO_4$. The solvent was removed in vacuo and the crude reaction mixture was analysed by ^{1}H NMR spectroscopy. 97% of the corresponding [D$_1$]-**7** (δ = 2.17 ppm, t, J_{HD} = 2.2 Hz) was confirmed by NMR studies.

Lithiation of 7 and 8. Method B: A solution of **7** or **8** (0.2 mmol) and *t*BuOK (56 mg, 0.5 mmol) in Et_2O (2 mL) was cooled to –40 °C. *n*-Butyllithium (0.2 mL of a 2.5 M solution in hexanes) was added dropwise and the reaction mixture stirred for 3 h. The dark red slurry was then cooled to –60 °C and the appropriate amount of electrophile (1.5 equiv.) was added to the mixture (in the case of the D_2O experiment, 0.3 mL were used). The organic layer was washed with 1 M HCl (3 × 5 mL) and dried with $MgSO_4$. The solvent was removed in vacuo and the crude reaction mixture was analysed by ^{1}H NMR spectroscopy. 95% of the corresponding [D$_1$]-**7** (δ = 2.17 ppm, t, J_{HD} = 2.2 Hz) was confirmed by NMR studies.

(*P*)-(*S*$_{ax}$)-4,5-Dihydro-4,4-diphenyl-3-oxa-4-silacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (9): A slurry of the red dilithium salt of **7** (0.29 g, 1.0 mmol), prepared according to method **A**, was cooled to –60 °C and dichlorodiphenylsilane (0.44 mL, 2.1 mmol) was added. The reaction mixture was stirred for 4 h while warming to ambient temperature. The crude reaction mixture was filtered through a small plug of silica and the product purified by column chromatography (pentane/EtOAc, 9.5:0.5) to give **9** as a colourless solid (0.28 g, 0.6 mmol, 60%). R_f = 0.62. $[a]_D^{25}$ = –37.7 (c = 1.00, $CHCl_3$). M.p. 251–253 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.88 (approx. d, J = 8.0 Hz, 2 *H*, 2 × Ar$_{5or5'}$), 7.83 (d, J = 8.8 Hz, 1 *H*, Ar$_{4or4'}$), 7.75 (d, J = 8.4 Hz, 1 *H*, Ar$_{4or4'}$), 7.68–7.65 (m, 2 *H*, Ph$_o$), 7.51–7.33 (m, 6 *H*, Ar and Ph), 7.28 (d, J = 14 Hz, 1 *H*, Ar$_{3or3'}$), 7.23–7.18 (m, 9 *H*, Ar and Ph), 2.93 (d, J = 14 Hz, 1 *H*, C$H_{2\alpha}$), 2.60 (d, J = 14 Hz, 1 *H*, C$H_{2\beta}$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 150.8 (*C*–O, Ar), 134.8 (2 *C*H, Ph), 134.5 (2 *C*H, Ph), 133.7 (2 *C*, Ar), 132.9 (2 *C*, Ar), 131.9 (*C*, Ar), 131.8 (*C*, Ar), 130.6 (*C*H, Ar), 130.4 (*C*H, Ar), 130.1 (2 *C*, Ar), 129.6 (*C*H, Ar), 128.1 (5 *C*H, Ph and Ar), 127.9 (*C*H, Ar), 127.6 (2 *C*H, Ar), 126.8 (2 *C*H, Ar), 125.9 (*C*H, Ar), 125.7 (*C*H, Ar), 124.4 (*C*H, Ar), 124.0 (*C*H, Ar), 123.8 (*C*, Ar), 122.7 (*C*H, Ar), 22.8 (*C*H$_2$) ppm. The Ar and Ph substituents could not be easily distinguished. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 2958 (Ar CH), 1125 ($SiPh_2$), 984 (Si–O–Ar), 948 (Si–O–Ar) cm^{-1}. HRMS (EI) found 464.1596 required 464.1599. $C_{33}H_{24}OSi$ (464.16): calcd. C 85.31, H 5.21; found C 85.27, H 5.38.

6,7-Dihydro-6,6-diphenyl-5-oxa-6-siladibenzo[*a*,*c*]cycloheptene (10): A slurry of the yellow-green dilithium salt of **8** (0.34 g, 1.8 mmol), prepared according to method **A**, was cooled to –60 °C and dichlorodiphenylsilane (0.80 mL, 3.78 mmol) was added. The reaction mixture was stirred for 4 h while warming to ambient temperature. The crude reaction mixture was filtered through a small plug of silica and the product crystallised from CH_2Cl_2/pentane (1:5) to give **10** as a colourless solid (0.36 g, 1.0 mmol, 56%). M.p. 146–148 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.41 (approx. d, J = 6.5 Hz, 2 *H*, Ar$_{4and4'}$), 7.52–7.23 (m, 10 *H*, Ar and Ph), 7.19 (approx. td, J_1 = 7.5 Hz, J_2 = 1.4 Hz, 1 *H*, Ar$_{5or5'}$), 7.15 (approx. td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1 *H*, Ar$_{5or5'}$), 7.03 (t, J = 8.1 Hz plus unresolved long-range couplings, 2 *H*, Ph$_p$), 2.82 (d, J = 14.1 Hz, 1 *H*, C$H_{2\alpha}$), 2.52 (d, J = 14.1 Hz, 1 *H*, C$H_{2\beta}$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 152.3 (*C*–O), 137.7 (*C*–CH_2), 135.8 (*C*, Ar), 134.7 (*C*H, Ar), 134.3 (*C*H, Ar), 132.7 (*C*, Ar), 131.3 (*C*H, Ar), 130.5 (*C*, Ar), 130.4 (*C*, Ar), 129.1 (*C*H, Ar), 128.9 (*C*H, Ar), 128.1 (*C*H, Ar), 127.6 (2 *C*H, 2 × Ph$_p$), 125.6 (*C*H, Ar), 122.8 (*C*H, Ar), 121.6 (*C*H, Ar), 22.3 (*C*H$_2$) ppm. The Ar and Ph substituents could not be easily distinguished. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 2936 (Ar CH), 1492, 1121 (d for $SiPh_2$), 905 (Si–O–Ar) cm^{-1}. HRMS (EI) found 364.1297 required 364.1283. $C_{25}H_{20}OSi$ (364.12): calcd. C 82.38, H 5.53; found C 81.98, H 5.55.

(*P*)-(*S*$_{ax}$,*S*$_P$)-4-Phenyl-5*H*-3-oxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]-dinaphthalene 4-Oxide (11a): A slurry of the red dilithium salt of **7** (0.52 g, 1.8 mmol), prepared according to method A, was cooled to –60 °C and phenylphosphonic dichloride (0.78 g, 4.0 mmol) was added. The reaction mixture was stirred for 3 h while warming to ambient temperature. The crude reaction mixture was then filtered through celite and washed with water. The organic layers were extracted with CH_2Cl_2, dried with $MgSO_4$ and the solvent removed in vacuo. The solid obtained was then purified by column chromatography (CH_2Cl_2/Et_2O, 8.5:1.5) to give **11a** as one distereomer (white solid, 0.12 g, 0.30 mmol, 17%). R_f = 0.38. M.p. 200–202 °C. $[a]_D^{25}$ = + 203.0 (c = 0.17, $CHCl_3$). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.8 Hz, 1 *H*, Ar$_{4,4',5,or5'}$), 7.98 (d, J = 8.2 Hz, 1 *H*, Ar$_{4,4',5,or5'}$), 7.93 (d, J = 8.2 Hz, 1 *H*, Ar$_{4,4',5,or5'}$), 7.80 (d, J = 8.4 Hz, 1 *H*, Ar$_{4,4',5,or5'}$), 7.68 (d, J = 8.8 Hz, 1 *H*, Ar$_{3or3'}$), 7.48 (br., 3 *H*, Ar and Ph), 7.39 (d, J = 8.4 Hz, 1 *H*, Ar$_{3or3'}$), overlapped by 7.40–7.22 (m, 7 *H*, Ar and Ph), 7.06 (d, J = 8.3 Hz, 1 *H*, Ar$_{8or8'}$), 3.57 (dd, J_{HH} = 15.3 Hz, J_{HP} = 25.6 Hz, 1 *H*, C$H_{2\alpha}$), 3.32 (dd, J_{HH} = 15.3 Hz, J_{HP} = 7.8 Hz, 1 *H*, C$H_{2\beta}$) ppm. ^{13}C{^{1}H} (125.1 MHz, $CDCl_3$) δ = 146.5 (d, $^2J_{CP}$ = 9.7 Hz, *C*, Ar$_2$), 132.8 (d, J_{CP} = 2.5 Hz, *C*H, Ar), 132.7 (*C*, Ar), 132.6 (C, Ar), 132.5 (*C*, Ar), 132.3 (*C*H, Ar), 132.2 (*C*H, Ar), 131.5 (*C*, Ar), 130.9 (*C*H, Ar), 130.5 (d, J_{CP} *C* = 5.0 Hz, *C*, Ar), 130.2 (d, J_{CP} = 10.1 Hz, *C*, Ar), 129.0 (*C*H, Ar), 128.7 (d, $^1J_{CP}$ = 135.1 Hz, *C*, Ph$_i$), 128.4 (*C*H, Ar), 128.3 (*C*H, Ar), 128.2 (d, J_{CP} = 12.5 Hz, *C*H, Ph$_m$), 127.6 (d, J_{CP} = 5.0 Hz, *C*H, Ph$_p$), 127.1 (d, J_{CP} = 5.0 Hz, *C*H, Ph$_o$), 126.6 (*C*H, Ar), 126.4 (*C*H, Ar), 125.8 (*C*H, Ar), 125.5 (*C*H, Ar), 124.6, 122.2 (*C*H, Ar), 36.5 (d, $^1J_{CP}$ = 85.1 Hz, *C*H$_2$) ppm. The Ar and Ph substituents could not be easily distinguished. ^{31}P{^{1}H} (202.4 MHz, $CDCl_3$) δ = 53.51 ppm. IR (CCl_4 solution): $\tilde{\nu}$ = 3059 (CH, Ar), 2961 (CH_2 Bz), 1252 (P=O), 1217 (P=O) cm^{-1}. HRMS (EI) found 406.1131, $C_{27}H_{19}O_2P$ required 406.1123.

Crystallographic Data: Colourless crystals of **2a** were grown from toluene, **5a**, **7**, **9**, and **10** from CH_2Cl_2/hexane, **11a** from CH_2Cl_2/Et_2O. All single crystals were attained by either liquid–liquid diffusion techniques or by cooling to 4 °C. Single crystal diffraction data was collected using graphite-monochromated Mo-K_α X-radiation using either a Bruker APEX (**2a**, **5a**, **9** and **10**) or SMART1000 (**7**, **11a**) CCD area detector diffractometer, each equipped with an Oxford Cryostream cooling device. All data was collected at 150 K. Details of the individual data collections and refinements are given in Table 1. All structures were solved by direct methods using SHELXS-97, except **5a** which was solved using SIR-92. All structures were refined by least-squares full-matrix refinements against F^2 using SHELXL-97, and all non-H atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were geometrically placed and included as part of a riding model

Table 1. Summary of crystal data.

	2a	**5a**	**7**
Chemical formula	$C_{27}H_{20}O_4S{\cdot}C_7H_8$	$C_{28}H_{19}F_3O_6S_2$	$C_{21}H_{16}O$
M_r	532.62	572.55	284.34
Cell setting, space group	orthorhombic, $P2_12_12_1$	monoclinic, $P2_1$	tetragonal, $P4_1$
Temperature [K]	150(2)	150(2)	150(2)
a, b, c [Å]	7.4803(6), 17.8177(14), 19.953(2)	10.1291(11), 9.3320(10), 14.1204(14)	8.9239(11), 8.9239(11), 37.956(9)
α, β, γ [°]	90.00, 90.00, 90.00	90.00, 99.242(2), 90.00	90.00, 90.00, 90.00
V [Å^3]	2659.4(4)	1317.4(4)	3023(2)
Z	4	2	8
D_x [Mg·m^{-3}]	1.330	1.443	1.250
μ [mm^{-1}]	0.16	0.27	0.08
Crystal form, colour	column, colourless	trigonal tablet, colourless	tablet, colourless
Crystal size [mm]	$0.64\times0.18\times0.15$	$0.77\times0.67\times0.08$	$0.53\times0.38\times0.11$
T_{min}, T_{max}	–	0.440, 0.744	–
No. of measured, independent and observed [$I>2\sigma(I)$] reflections	16733, 6089, 5095	7285, 5312, 4909	15176, 3150, 2658
R_{int}	0.049	0.033	0.044
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.075, 0.96	0.038, 0.094, 1.00	0.034, 0.079, 1.10
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.25, –0.29	0.35, –0.19	0.15, –0.15
Flack parameter	0.03(6)	0.00(6)	
	9	**10**	**11a**
Chemical formula	$C_{33}H_{24}OSi$	$C_{25}H_{20}OSi$	$C_{27}H_{19}O_2P$
M_r	464.61	364.50	406.39
Cell setting, space group	monoclinic, $P2_1$	monoclinic, $P2_1/c$	orthorhombic, $P2_12_12_1$
Temperature [K]	150(2)	150(2)	150(2)
a, b, c [Å]	9.4434(13), 11.0517(15), 11.7216(16)	15.5742(11), 18.9111(14), 12.9999(9)	10.2706(11), 10.7256(11), 18.393(2)
α, β, γ [°]	90.00, 92.571(3), 90.00	90.00, 96.122(1), 90.00	90.00, 90.00, 90.00
V [Å^3]	1222.1(3)	3807.0(5)	2026.2(6)
Z	2	8	4
D_x [Mg·m^{-3}]	1.263	1.272	1.332
μ [mm^{-1}]	0.12	0.14	0.16
Crystal form, colour	plate, colourless	block, colourless	column, colourless
Crystal size [mm]	$0.34\times0.24\times0.06$	$0.49\times0.48\times0.21$	$0.90\times0.20\times0.18$
T_{min}, T_{max}	–	–	0.781, 1.000
No. of measured, independent and observed [$I>2\sigma(I)$] reflections	7546, 5160, 3954	22703, 8651, 6597	15566, 4591, 4251
R_{int}	0.033	0.090	0.025
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.098, 0.92	0.052, 0.147, 1.04	0.035, 0.095, 1.07
$(\Delta/\sigma)_{max}$	<0.0001	0.001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.37, –0.24	0.49, –0.33	0.55, –0.25
Flack parameter	0.22(13)		0.02(7)

except the Me hydrogen atoms in **2a** and **5a** and the hydroxy hydrogen atoms in **2a** and **7**, which were all located from difference Fourier syntheses and refined as part of rigid rotating groups. The absolute configuration has been determined in all cases and Flack parameters are reported except for **7**, which conatins no atoms heavier than Si so a Flack parameter cannot be reliably determined using Mo-K_α X-radiation and **10**, which crystallises in a centrosymmetric space group. Crystallographic data for all compounds are summarised in Table 1.[28]

CCDC-626072 to -626077 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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