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# Reversible aromatic bromination induced by buttressing; 1-bromo- and 8-bromo-3,6-di-*tert*-butyl-2-methoxynaphthalene†

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**Summary** — Convenient syntheses of 3,6-di-*tert*-butylnaphthalen-2-ol and 3,3′,6,6′-tetrakis-*tert*-butyl-[1,1′-binaphthalene]-2,2′-diol **1** are described. The methyl ether of the former is brominated most rapidly at the 1-position, similarly to 2-methoxynaphthalene. Unlike the parent compound, there is a rapid proton-catalysed reversible reaction leading ultimately to the formation of 8-bromo-3,6-di-*tert*-butyl-2-methoxynaphthalene by an intermolecular route. This difference in reactivity is due to steric buttressing by the 3-*tert*-butyl group which destabilises the initial 1-bromo adduct towards 1-protonation leading to facilitated loss of bromonium ion; this explanation is in accord with a molecular mechanics analysis. The reactivity of the 1-bromo ether or its derivatives is strikingly different from that of its unsubstituted precursor, and exemplified by their responses to palladium-catalysed biaryl synthesis.

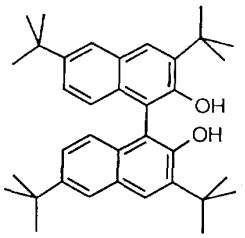
**binaphthyl / bromination / reversibility / Suzuki cross-coupling**

**Résumé — Bromation aromatique réversible induite par effet stérique ; 1-bromo et 8-bromo-3,6-di-*tert*-butyl-2-méthoxynaphtalène.** Les synthèses des 3,6-di-*tert*-butylnaphtalén-2-ol **4a** et 3,3′,6,6′-tétrakis-*tert*-butyl-[1,1′-binaphtalène]-2,2′-diol **1** sont décrites. Comme pour le 2-méthoxynaphtalène, l'éther méthylique de **4a** est bromé en position 1 le plus rapidement, mais en définitive, une réaction protocatalysée réversible et rapide conduit au 8-bromo-3,6-di-*tert*-butyl-2-méthoxynaphtalène, par voie intermoléculaire. Cette différence de réactivité est due à un effet stérique du groupe 3-*tert*-butyle, qui déstabilise l'adduit initial 1-bromé par rapport à la 1-protonation, conduisant à une perte facile de l'ion bromonium ; cette explication est en accord avec une analyse de mécanique moléculaire. La réactivité de l'éther 1-bromé ou de ses dérivés est remarquablement différente de celle de son précurseur non substitué et est mise en évidence par leur comportement dans la synthèse de biaryles pallado-catalysée.

**binaphtyle / bromation / réversibilité / couplage Suzuki**

## Introduction

The object of the work was to synthesise a series of binaphthols exemplified by **1** and **2a** using Friedel–Crafts methods, as precursors for enantiomerically pure Lewis acids with a sterically encumbered donor group. A single di-*tert*-butylated adduct is the major product from the reaction of $\beta$-naphthol with isobutene [1]. Some controversy existed in the earlier literature as to the structure of the derived adduct which was initially assigned as 1,6-bis(1,1-dimethylethyl)-2-naphthalenol **3** [2]. Later work showed that the product was in fact 3,6-bis(1,1-dimethylethyl)naphthalen-2-ol **4a** [3]. This was the starting point for much of the work to be described.

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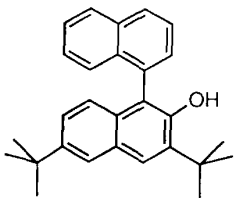
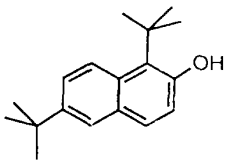



2a

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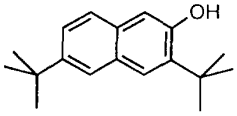


4a

## Discussion

*Synthesis of precursors*

After considerable experimentation based on prior work, a more satisfactory route to the desired inter-

† This paper is dedicated to Professor Henri Kagan in recognition of his many seminal contributions to organic chemistry.

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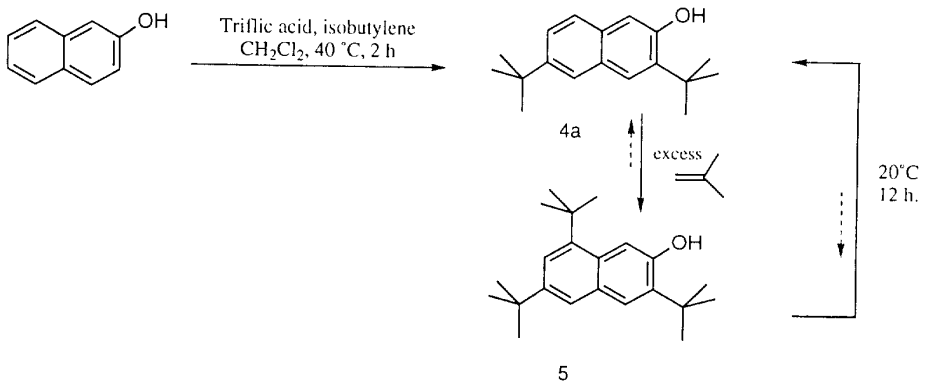



**Fig 1.** Kinetic and thermodynamic control in the *tert*-butylation of β-naphthol.

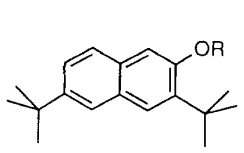
mediate **4a** was developed [4]. Isobutene was passed into a mixture of β-naphthol and a catalytic quantity of $CF_3SO_3H$ in dry dichloromethane heated at reflux. Over a period of two hours the contents of the flask approximately doubled in volume (acid-catalysed isobutene polymerisation products). The isobutene source was removed, the solution was allowed to cool to room temperature over 24 h and the organics isolated via basic aqueous workup. 3,6-Bis(1,1-dimethylethyl)naphthalen-2-ol **4a** was isolated as fine white needles by recrystallisation from pentane (5 crops, 85% in total). Removing the isobutene source and leaving the solution to stand for 24 h before quenching was found to be crucial for the success of the operation. If the reaction was quenched hot in the presence of isobutene, a second naphthalene species was found to be the major component (90%). This was assigned as 3,6,8-tris-(1,1-dimethylethyl)naphthalen-2-ol **5** on the basis of work performed by Chasar [5]. He found that under conditions identical to those employed by Layer [1], with the exception of a lower reaction temperature (90–95 vs 110 °C) 3,6,8-tris(1,1-dimethylethyl)naphthalen-2-ol **5** was essentially the only product and was isolated in 60% yield. It would seem that tri-*tert*-butylnaphthol **5** is the kinetic product, but at higher temperatures di-*tert*-butylnaphthol **4a** becomes the thermodynamically preferred product even in the presence of isobutene. Reversible butylation at the 8-position can be rationalised, since the *tert*-butyl group at the 8-position in tri-*tert*-butylnaphthol **5** has a strong steric interaction with the 1-H proton (fig 1).

By way of explanation, when a stronger acid catalyst ($CF_3SO_3H$) is used in a lower boiling solvent (dichloromethane) tri-*tert*-butylnaphthol **5** is both the kinetic and thermodynamic product. When the isobutene source is removed and its effective concentration becomes zero, the equilibrium position is affected, and acid catalysed dealkylation occurs to give di-*tert*-butylnaphthol **4a**, isolated in 85% yield. Replacing $CF_3SO_3H$ by *p*-TsOH led merely to efficient synthesis of the *tert*-butyl ether of β-naphthol. Interestingly, the IR spectrum of compound **4a** showed the OH stretch as a sharp absorption (3 519 $cm^{-1}$) whereas the IR spectrum of β-naphthol shows the OH stretch as a broad band (3 600–2 800 $cm^{-1}$) characteristic of an H-bonded hydroxyl functionality. Similarly, the hydroxyl resonance of **4a** is a a sharp singlet ($\delta_H$ 4.98 ppm) in the $^1H$ NMR spectrum. The lack of hydrogen bonding in di-*tert*-butylnaphthol **4a** is rationalised by the steric bulk of the *tert*-butyl group at the neighbouring 3-position which prevents intermolecular association.

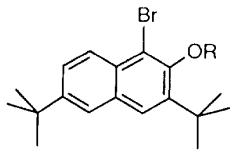
Successful alkylation encouraged us to apply the same conditions to 2,2′-binaphthol. (±)-3,3′,6,6′-Tetrakis(1,1-dimethylethyl)-[1,1′-binaphthalene]-2,2′-diol **1** is a well-known compound and has been previously prepared by the symmetrical oxidative coupling of 3,6-bis-(1,1-dimethylethyl)naphthalen-2-ol **4a** [6]. The direct *tert*-butylation of BINOL **6** had not been reported. Isobutene was passed into a mixture of (±)-BINOL **6** and a catalytic quantity of $CF_3SO_3H$ in dry $CH_2Cl_2$ heated at reflux. Over a period of 2 h the contents of the flask approximately doubled in volume (acid-catalysed isobutene polymerisation adducts). The resulting crude mixture consisted of an off-white solid in a red viscous oil. The solid was filtered at the pump and washed repeatedly with pentane to give a white solid which proved to be spectroscopically pure (±)-3,3′,6,6′-tetrakis (1,1-dimethylethyl)-[1,1′-binaphthalene]-2,2′-diol **1** in 93% yield. Aside from the superior yield and convenience, the advantage of this method over the oxidative coupling of 3,6-bis(1,1-dimethylethyl)naphthalen-2-ol **4a** is that enantiomerically pure *tert*-butylated BINOL derivatives should be readily accessible by this method. Indeed, it was found that attempted resolution of (±)-3,3′,6,6′-tetrakis(1,1-dimethylethyl)-[1,1′-binaphthalene]-2,2′-diol **1** via diastereomeric phosphate salt formation, as used succesfully in the resolution of (±)-BINOL **6** itself, was ineffective [7]. Interestingly, when the same conditions were applied to 2-hydroxy-1,1′-binaphthyl **7a**, itself prepared by a Suzuki coupling reaction between 1-naphthylboronic acid and 1-bromo-2-methoxynaphthalene followed by demethylation, the reactant was recovered unchanged.

*Bromination of tert-butylated ether*

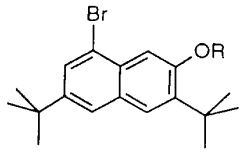
At this point we required functionality at the 1-position in di-*tert*-butylnaphthol **4a** in order to perform a palladium-catalysed Suzuki coupling with an appropriately substituted 1-naphthalene. Methylation gave 3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene



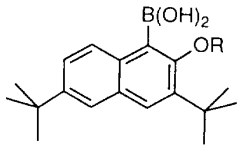

**4b** R = Me
**4c** R = Et



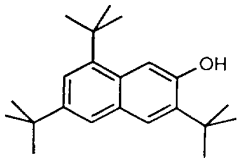

**8a** R = Me
**8b** R = Et



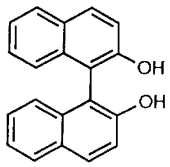

**9a** R = Me
**9b** R = Et




**4d** R = Me




**5**

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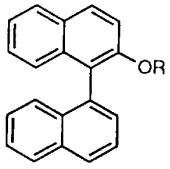


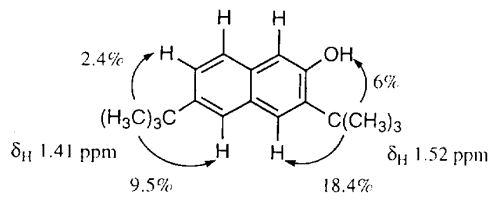

**7a**, R = H
**7b**, R = Me

**4b** (92%) without complication and this product was treated with bromine in acetic acid; after 5 min the reaction was essentially complete. Under these conditions 2-methoxynaphthalene gives exclusively 1-bromo-2-methoxynaphthalene more slowly but well within 24 h [8]. $^1$H NMR analysis of the crude reaction mixture from **4b** showed two products, separated by flash column chromatography and identified as 1-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **8a** (47%) and 8-bromo-bis(1,1-dimethylethyl)-2-methoxynaphthalene **9a** (27%) respectively.

The $^1$H NMR spectrum of the 1-bromoadduct **8a** showed the characteristic coupling pattern of the 5-H, 7-H and 8-H protons ($J$ 1.9, $J$ 8.9 Hz). The methoxy group was observed as a singlet at 4.04 ppm. The $^{13}$C/DEPT spectrum showed the now quaternary C1 bromine-bearing carbon resonance downfield at $\delta_C$ 116.2 ppm compared with C1 in the parent **4b** ($\delta_C$ 106.2 ppm). The structural assignment of the minor product as 8-bromoadduct **9a** was based on the following spectral data: The mass spectrum gave two peaks of equal intensity with $m/z$ values of 351 (M + 1$^+$) and 349 (M + 1$^+$) Daltons consistent with a monobrominated adduct (RMM = 349). The $^1$H NMR spectrum displayed two distinct *tert*-butyl resonances as sharp singlets ($\delta_H$ 1.47, 1.40 ppm) and the methoxy resonance as a singlet ($\delta_H$ 4.01 ppm) showing that bromination had occurred in the ring. Inspection of the aromatic signals, integrating for four protons, revealed that the coupling pattern displayed by the 5-H, 7-H and 8-H protons characteristic in this series of 2,3,6-trisubstituted naphthalenes had been destroyed. Only a single *meta* coupling was apparent between the 5-H and 7-H protons. This unambiguously places the bromine atom in the 8-position. This was further confirmed by a $^1$H NMR nuclear Overhauser effect (nOe) experiment of which the results are displayed in figure 2.

The ratio of the two bromoadducts **8a** and **9a** was found to be dependent on the reaction time. When the reaction was monitored by $^1$H NMR the methoxy resonance for the 8-bromoadduct **9a** intensified at the expense of the corresponding resonance for the 1-bromoadduct **8a** with time. Hence bromination is ultimately under thermodynamic control.

1-Bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **8a** is stable once it is isolated from the reaction mixture. It was recovered unchanged when treated with 1 equiv of bromine in acetic acid for 24 h. The by-product from bromination is hydro-



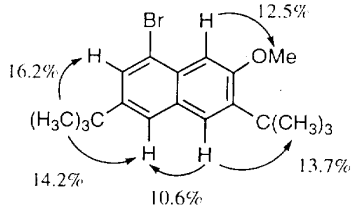




**Fig 2.** $^1$H nOe effects in compounds **4a** and **9a**.

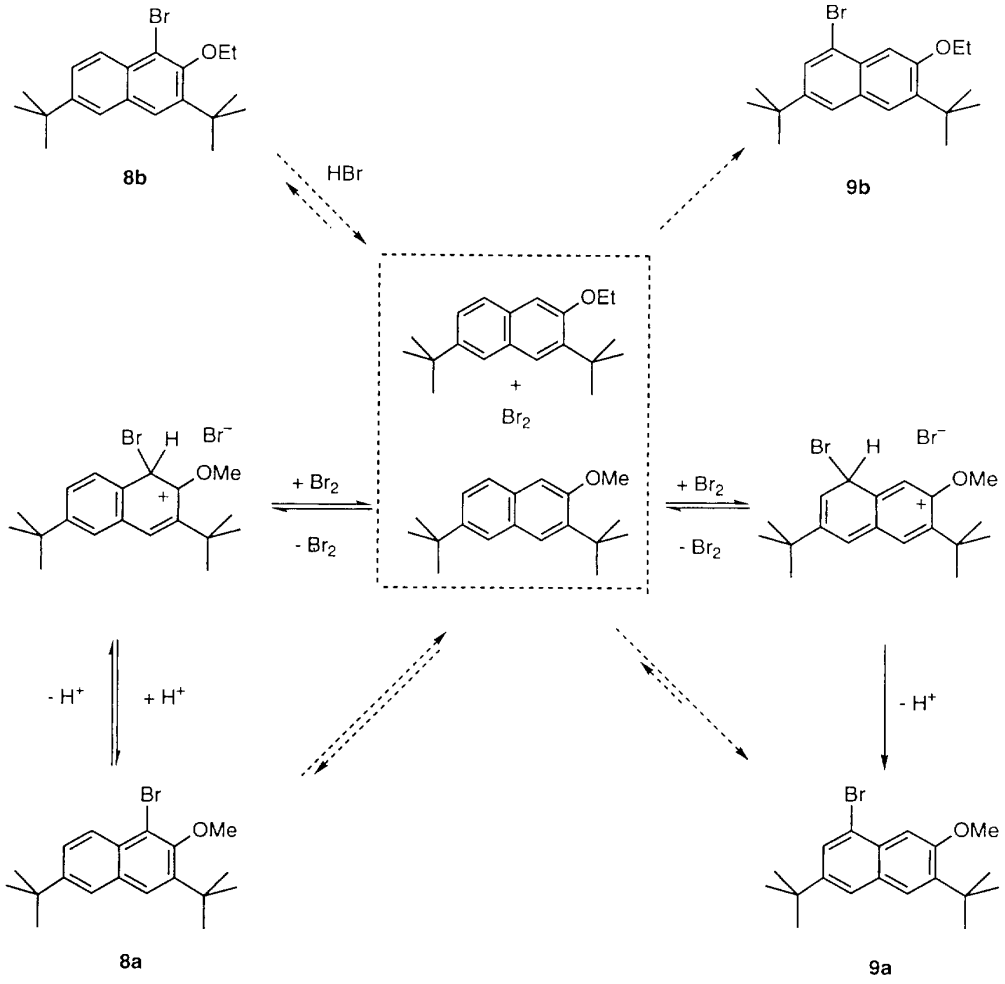



**Fig 3.** The intermolecular mechanism for the observed reversible bromination.

bromic acid. When 1-bromoadduct **8a** was treated with 1 equiv of hydrobromic acid in acetic acid it was converted into 8-bromoadduct **9a** at approximately the same rate as in the bromination reaction. But starting from compound **9a**, under these conditions none of the isomer **8a** product was observed after 48 h. That the isomerisation was catalysed by hydrobromic acid was demonstrated by treating di-*tert*-butylmethoxynaphthalene **4b** with bromine in $d_4$-acetic acid. The reaction was monitored directly by $^1$H NMR and after 96 h showed a single species which was assigned as 8-bromo-1-deutero-3,6-bis-(1,1-dimethylethyl)-2-methoxynaphthalene, demonstrating the addition of a formal $D^+$ to the 1-position in the course of rearrangement.

One aspect of this isomerisation process remained unresolved. The isomerisation may proceed via a tight ion-pair like intermediate whereby the bromine atom is transferred from the 1-position to the 8-position in the same molecule. Alternatively, intermolecular transfer may occur via liberation of free bromine into the reaction mixture, as in figure 3.

To differentiate between these, a bromine trapping experiment was devised. The ethyl ether, 3,6-bis(1,1-dimethylethyl)-2-ethoxynaphthalene **4c** was synthesised via alkylation of di-*tert*-butylnaphthol **4** with iodoethane. Ethyl ether **4c** was treated with bromine in acetic acid in order to generate authentic samples of 1-bromo-3,6-bis(1,1-dimethylethyl)-2-ethoxynaphthalene **8b** and 8-bromo-3,6-bis(1,1-dimethylethyl)-2-ethoxynaphthalene **9b** which could be formed in the trap experiments. The ethyl derivative **4c** was found to exhibit the same reactivity as methyl ether **4b** in its reaction with bromine and the two bromoadducts **8b** and **9b** were formed in a 3:1 ratio respectively after 5 min and were separated by preparative TLC. Inspection of the $^1$H NMR spectra of the various ethyl and methyl ether adducts **4c**, **8b**, **9b**, **4b**, **8a**, **9a** showed that the ether resonances had chemical shifts sufficiently different from each other to allow meaningful integration of the possible products derived from the trap experiments.

A 1:1 mixture of 1-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **8a** and 3,6-bis(1,1-dimethylethyl)-2-ethoxynaphthalene **4c** was treated with hydrobromic acid in acetic acid for 24 h. After the normal aqueous work-up the crude reaction mixture was analysed by $^1$H NMR. The results show that bromine

transfer is intermolecular, since the relative ratio of the various compounds indicates a statistical intermolecular distribution of bromine undistorted by any intramolecular process (table I).

**Table I.** Reaction of compound **8a** with HBr in the presence of an equimolar amount of ether **4c**.

| *Ether* | ***4b*** | ***8a*** | ***9a*** | ***4c*** | ***8b*** | ***9b*** |
|---|---|---|---|---|---|---|
| $\delta_H$, ppm | 3.95 | 4.04 | 4.01 | 4.19 | 4.23 | 4.25 |
| Relative integral % | *25* | *12* | *13* | *25* | Trace | *25* |

The bromine liberated from 1-bromoadduct **8a** by the action of hydrobromic acid can be trapped by ethyl ether **4c** in the 1- or 8-position. At $t = 0$, only the ethyl ether **4c** is present in significant concentration. As the reaction proceeds and methyl ether **4b** is generated, that too can act as a trap. Bromination in the 8-positions of either of these leads to irreversible removal of bromine from the system as demonstrated in the 'inverse' trap experiment below. Ethyl ether **4c** is present in higher concentration than methyl ether **4b** and the 2:1 ratio of their derived 8-bromoethers **9b** and **9a** reflects their summed effective concentrations and the corresponding unselective attack of bromine overall up to the point where the reaction was quenched (75% loss of bromine from 1-bromomethyl ether **8a**). Bromine transfer to the 1-position of ethyl ether **4c** results in the formation of **8b**, and bromination is also reversible at this site. Assuming that the relative rates of reversible bromination are approximately the same in both 1-bromoether derivatives **8a** and **8b**, then the low concentration of free bromine is insufficient to create significant quantities of **8b** and just a trace (as observed) will result.

The interpretation of the above experiment is valid only if reversible bromine addition does not occur at the 8-position. An 'inverse' trap experiment was performed to demonstrate this. A 1:1 mixture of 8-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **9a** and 3,6-bis(1,1-dimethylethyl)-2-ethoxynaphthalene **4c** were treated with hydrobromic acid in acetic acid for 24 h. After the normal aqueous work-up the crude reaction mixture was analysed by $^1$H NMR. Bromine transfer had not occurred and the two naphthalene derivatives were recovered unchanged.

The overall mechanism for the reversible acid-catalysed bromination reaction of 3,6-bis(1,1-dimethylethyl)naphthalen-2-ol with bromine in acetic acid, in the presence and absence of ethyl ether as competing bromine scavenger, is shown in figure 3.

*Molecular mechanics analysis of buttressing*

The origin of the distinct reactivity of compound **4b** in bromination lies in the destabilising effect of the 3-*tert*-butyl group, which operates against the conjunction of three adjacent substituents. The MMX energies of the various compounds involved, and appropriate models, are shown in figure 4 [9]. It seems apparent (a) that the 6-*tert*-butyl group exerts only a secondary effect on the overall structures and energies, (b) the methoxy group in **4b** is forced out of the plane of conjugation, and (c) that the destabilising effect involved in driving the 1-bromo to 8-bromo rearrangement is of the order of 2.5 kcal mol$^{-1}$. The enhanced rate of reversal of the bromination step is also a consequence of the gain in energy on rehybridisation of the 1-carbon on protonation, through the loss of torsional strain. According to the model, strain relief in **8a** occurs mainly through an out-of-plane twist of C2 and C3 of the naphthalene so that the relevant exocyclic torsional angles are ca $\pm 165°$ and the endocyclic torsional angles $\pm 15°$.

*Biaryl synthesis; a comparison*

Palladium-catalysed Suzuki coupling between 1-bromo-2-methoxynaphthalene and 1-naphthylboronic acid gave the methoxybiaryl **7b** in 83% yield [10]. When 1-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **8a** was treated with an equivalent of 1-naphthylboronic acid under the same conditions only 21% conversion to 3,6-bis(1,1-dimethylethyl)-2-methoxy-[1,1′-binaphthalene] **2b** occurred. The remaining species were found to be unreacted 1-bromo-3,6-bis(dimethylethyl)-2-methoxynaphthalene **8a** and 3,6-bis(dimethylethyl)-2-methoxynaphthalene **4b** (34 and 45% respectively). All of the boronic acid had been consumed to generate naphthalene or 1,1′-binaphthyl (19 and 60% respectively based on boronic acid) (fig 5). When a twofold excess of the boronic acid was employed, the improved yields shown in square brackets were obtained.

In contrast, 8-bromoadduct **9a** with the bromine atom in the electronically similar but sterically much less encumbered pseudo-*ortho* position coupled with 1-naphthylboronic acid to give exclusively 3,6-bis-(dimethylethyl)-7-methoxy-[1,1′-binaphthalene] **10** (98% isolated yield) (fig 6).

The Suzuki coupling may of course be performed in the reverse sense. Attempts to synthesise boronic acid **4d** from 1-bromoadduct **8a** were troublesome, again due to the buttressing effect of the *tert*-butyl group in the 3-position. The optimum procedure involved treatment of 1-bromoadduct **8a** with *n*-butyllithium at $-78$ °C, followed by an immediate trimethyl borate quench. This gave a 4:1 mixture of borate ester and naphthalene **4b** in good isolated yield. Normally the first formed boronate ester is readily hydrolysed during work-up to the required boronic acid. In this case the enhanced stability of an intermediate, tentatively identified by $^1$H NMR as the boronate hemi-ester ArB(OMe)OH, meant that vigorous overnight stirring was necessary to liberate boronic acid **4d**. It proved possible to obtain a sample of the boronic acid that was clean by $^1$H NMR by pentane washing, but this procedure was accompanied by a significant loss of product due to decomposition to the 1-H naphthalene. Hence the unpurified reaction mixture was used directly in Suzuki coupling procedures thereafter.

Boronic acid **4d** (as a mixture with di-*tert*-butylmethoxynaphthalene **4b**) was treated with 1-iodonaphthalene under standard Suzuki-coupling conditions. All of the boronic acid **4d** was consumed and the $^1$H NMR spectrum of the crude reaction mixture showed the desired biaryl in an approximate 1:8 ratio with di-*tert*-butylmethoxynaphthalene **4b**. The re-

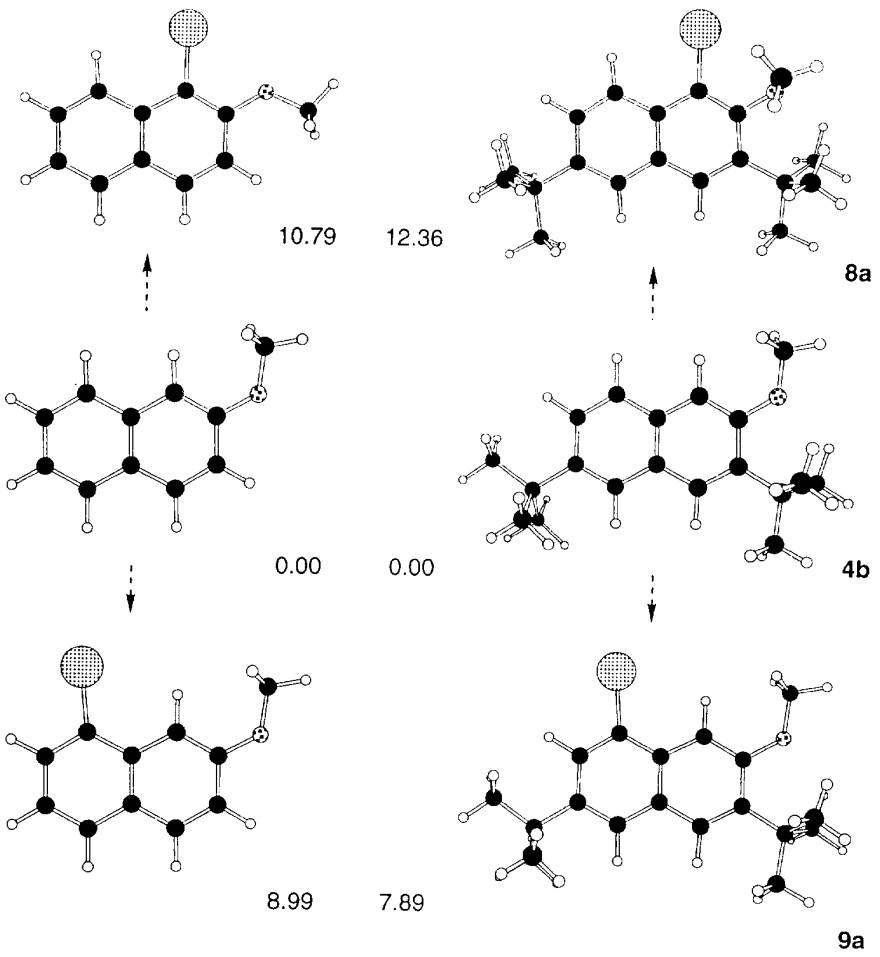



**Fig 4.** MMX-minimised structures and energies relevant to the bromination chemistry, relative to the corresponding 3,6-unsubstituted compounds. The numbers are heats of formation $\Delta H_f$ in Kcal $mol^{-1}$.

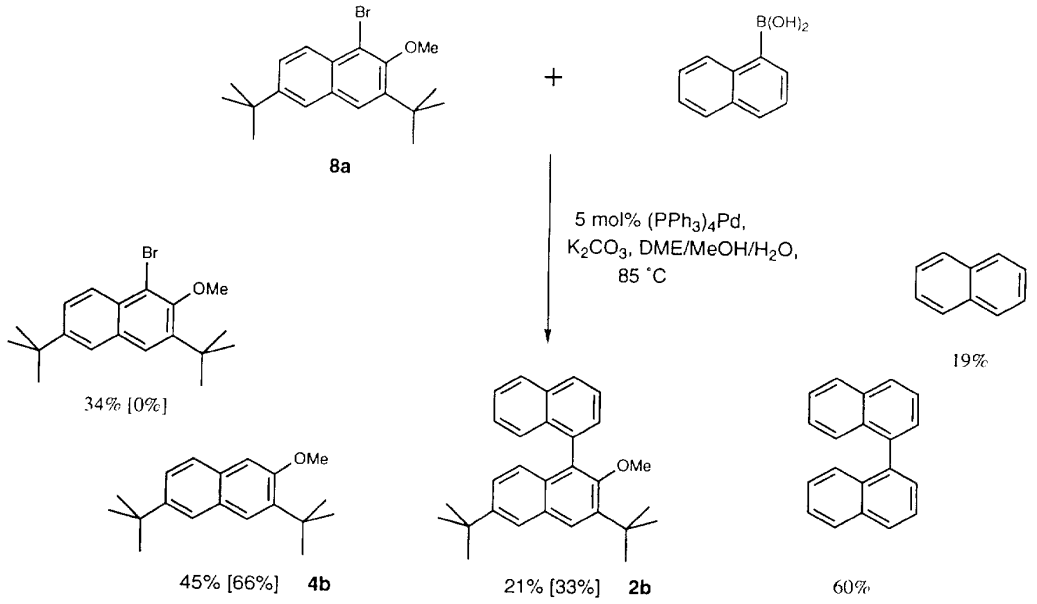
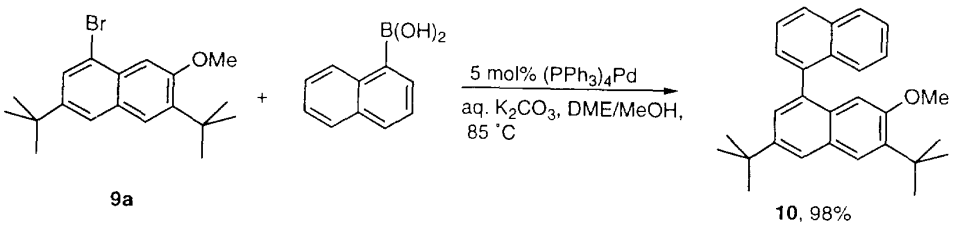
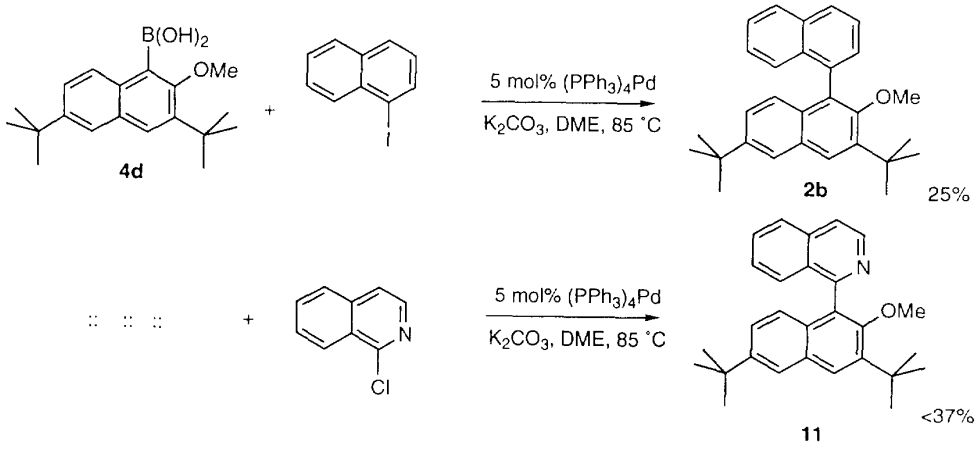



**Fig 5.** Product distributions in Suzuki cross-coupling from the buttressed halide **8a**.




**9a** **10**, 98%

**Fig 6.** Efficient Suzuki coupling with the 8-bromo compound **9a**.




**4d** **2b** 25%

**11** <37%

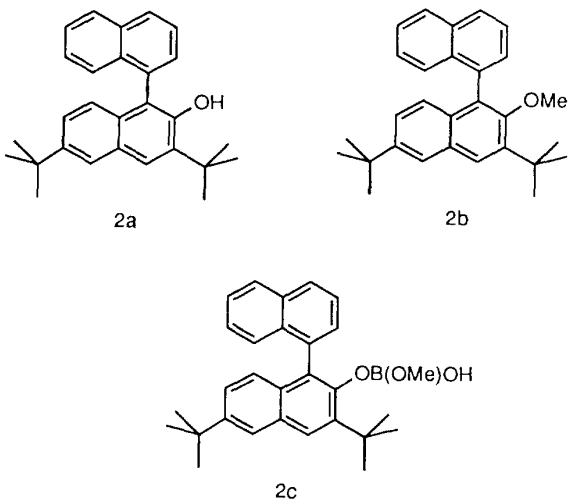
**Fig 7.** Optimum cross-couplings with the boronic acid **4d**.

mainder of the material was found to be unreacted 1-iodonaphthalene. Only traces of naphthalene and 1,1′-binaphthyl were observed in the $^1$H NMR spectrum. The 1:8 ratio represents a 25% conversion of boronic acid **4d** into biaryl, rather worse than the 33% conversion obtained in the Suzuki coupling of 1-bromoadduct **8a** with 1-naphthylboronic acid but in considerably poorer overall yield (12%) (fig 7).

Similar conditions were employed in the coupling reaction between boronic acid **4d** [as a 4:1 mixture with 3,6-bis(dimethylethyl)-2-methoxynaphthalene] and 1-chloroisoquinoline. The crude reaction mixture indicated a 37% conversion into biaryl **11**, isolated as a white crystalline solid by flash chromatography [11].

Various other Suzuki-type palladium-catalysed coupling procedures were attempted, following literature protocols [12–14]. None of these procedures gave any more than a trace of desired biaryl as judged by $^1$H NMR analysis of the crude reaction mixture.

Boron tribromide cleaves the methyl group from 2-methoxy-[1,1′-binaphthalene] in 1 h at room temperature in quantitative yield. The reaction between boron tribromide and di-*tert*-butylmethoxybiaryl **2b** is complete after 24 h as judged by TLC. No starting material remained but two spots were observed by quenching of UV fluorescence. One spot was assumed to be the desired biaryl product **2a** and the second was tentatively assigned as the derived boronic ester **2c**. 'Normal' work-up of these reactions involves quenching with an aqueous base, which instantaneously destroys the boronic ester. Here vigorous stirring of the reaction mixture with aqueous base for 2 h was required to cleave the sterically hindered boron–oxygen bond, however. The hydroxybiaryl **2a** was isolated as a white solid (73%) by preparative TLC, whose $^1$H NMR spectrum shows the OH resonance as a sharp singlet at $\delta_H$ 5.07 ppm; the OH stretch appeared as a sharp and strong absorption at 3 533 cm$^{-1}$ in the IR spectrum.




**2a** **2b**

**2c**

## Experimental section

### *General*

Infrared spectra were recorded on a Perkin-Elmer 1750 Fourier Transform spectrometer. $^1$H NMR spectra were recorded on Varian Gemini 200 (200 MHz), Bruker WH 300 (300 MHz) or Bruker AM 500 (500 MHz) spectrometers. Chemical shifts ($\delta_H$) are quoted in parts per million (ppm) and are referenced to the residual solvent peak [$CDCl_3$, $\delta_H$ = 7.27; $CD_2Cl_2$, $\delta_H$ = 5.32; $CD_3CO_2D$, $\delta_H$ = 2.18, $C_6D_6$, $\delta_H$ = 7.16]. COSY, nOe and decoupling experiments were carried out on a Bruker AM 500 (500 MHz) spectrometer. $^{13}$C NMR spectra were recorded on Varian Gemini 200 (50.3 MHz) or Bruker AM 500 (125.6 Hz) spectrometers using DEPT editing on the former. Quaternary carbons were assigned from a broad-band decoupled analysis used in conjunction with the DEPT program. Chemical shifts ($\delta_C$) are quoted in ppm and are internally referenced to the solvent [$CDCl_3$, $\delta_C$ = 77.0; $CD_2Cl_2$, $\delta_C$ = 53.8; $CD_3CO_2D$, $\delta_C$ = 28.9, $C_6D_6$, $\delta_C$ = 128.0]. Mass spectra were recorded on a Trio-1 GCMS (Hewlett Packard GC) spectrometer by chemical ionisation with ammonia gas.

All manipulations of air or moisture sensitive materials were carried out under a dry argon atmosphere using standard vacuum line and Schlenk techniques. Solvents were deoxygenated where necessary by repeated freeze–thaw cycles, in which the solvent was frozen in liquid nitrogen, allowed to warm to room temperature in vacuo and flushed with argon. Transfers and filtrations were carried out using stainless-steel cannula wire. 1-Bromo-2-methoxynaphthalene [8] and 2-methoxy-1-naphthylboronic acid [11] were prepared according to literature procedures.

Commercial samples of *n*-butyllithium were titrated against freshly recrystallised diphenylacetic acid immediately before use [15]. Powdered molecular sieves were activated by drying at 80 °C for 24 h and then heated at 300 °C for 0.5 h under vacuum immediately before use. Magnesium turnings were activated by dry stirring for 24 h under argon [16].

### *Preparation of 3,6-bis(1,1-dimethylethyl)naphthalen-2-ol* **4a**

Isobutene gas was passed into a stirred solution of *β*-naphthol (10.0 g, 6.9 mmol) and $CF_3SO_3H$ (0.6 mL, 0.34 mmol) in dichloromethane (50 mL) at reflux for 2 h. The black solution was allowed to cool to room temperature over 24 h and was then washed with saturated aqueous sodium hydrogen carbonate solution (20 mL). The organic layer was dried ($MgSO_4$), filtered and the solvent evaporated to give a dark red 'wet' solid. Recrystallisation from pentane (5 crops) gave the title compound **4a** as fine white needles (15.0 g, 85%). Mp 138–141 °C ([2] 139 °C).

IR (KBr): 3 519s (OH), 3 051w ($sp^2$ CH), 2 998w ($sp^3$ CH), 2 955s ($sp^3$ CH), 2 867s ($sp^3$ CH), 1 605m (C=C), 1 392m ($sp^3$ CH), 1 364s ($sp^3$ CH), 1 183s (OH), 909s, 860s $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 7.70 (2H, s, 4-H and 5-H); 7.57 (1H, d, *J* 8.6, 8-H); 7.48 (1H, dd *J* 8.6, 1.9, 7-H); 6.98 (1H, s, 1-H); 4.99 (1H, s, OH); 1.52 (9H, s, *tert*-butyl); 1.41 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 152.9 (C2); 146.2 (C6); 138.2 (C3); 131.1 (C8a); 128.8 (C4a); 126.0 (C4); 124.9 (C8); 124.7 (C7); 122.8 (C5); 110.3 (C1); 35.0 (C9); 34.6 (C11); 31.3 (C10); 29.8 (C12).

MS (APCI$^+$, $NH_3$): 257 (M + 1$^+$, 100%), 241 (23), 201 (6).

Anal calc for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.01; H, 9.21%.

If the reaction mixture was quenched hot immediately after the removal of the isobutene source, a 1:9 mixture of 3,6-bis(1,1-dimethylethyl)naphthalen-2-ol **4a** and 3,6,8-tris(1,1-dimethylethyl)naphthalen-2-ol **5** was obtained:

For the latter – $^1$H NMR ($CDCl_3$) $\delta$ ppm: 7.72 (1H, s, 4-H or 1-H), 7.59 (2H, br s, 5-H or 7-H and 4-H or 1-H), 7.53 (1H, d, *J* 1.9, 5-H or 7-H), 1.63 (9H, s, *tert*-butyl), 1.52 (9H, s, *tert*-butyl), 1.42 (9H, s, *tert*-butyl).

### *Preparation of 3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene* **4b**

3,6-bis(1,1-dimethylethyl)naphthalen-2-ol (2.0 g, 7.9 mmol) was treated with finely divided potassium hydroxide flakes (1.25 g, 31 mmol) in vigorously stirred DMSO (10 mL). After 10 min a deep blue colour developed and methyl iodide (4.9 mL, 79 mmol) was added. The blue colour discharged immediately to give a pale yellow solution. The mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 50 mL). The combined organics were washed with water (4 × 100 mL), dried ($MgSO_4$), filtered and the solvent evaporated to give a pale yellow oil which solidified on standing. Purification by flash chromatography on silica gel (5% ethyl acetate in pentane) gave the title compound **4b** as a white solid (1.97 g, 92%). Mp 93 °C ([3] 81–82 °C).

IR (KBr): 3 061w ($sp^2$ CH), 3 005w ($sp^2$ CH), 2 958vs ($sp^3$ CH), 2 869s ($sp^3$ CH), 1 607m (Ar C=C), 1 504m, 1 462s ($sp^3$ CH), 1 436m, 1 389m ($sp^3$), 1 362s ($sp^3$), 1 318m, 1 252s, 1 205vs (OMe), 1 172m, 1 074s (OMe), 903s, 850s $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 7.76 (1H, d, *J* 1.9, 5-H); 7.74 (1H, s, 4-H); 7.70 (1H, d, *J* 8.6, 8-H); 7.55 (1H, dd, *J* 8.6, 1.9, 7-H); 7.16 (1H, s, 1-H); 3.99 (3H, s, OMe); 1.54 (9H, s, *tert*-butyl); 1.47 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 157.9 (C2); 146.7 (C6); 140.2 (C3); 131.6 (C4a or C8a); 128.9 (C4a or C8a); 126.0 (Ar–CH); 125.9 (Ar–CH); 125.0 (Ar–CH); 123.2 (Ar–CH); 106.2 (C1); 55.4 (C13); 35.7 (C9); 35.1 (C11); 31.9 (C10); 30.4 (C12).

MS (CI$^+$, $NH_3$) 271 (M + 1$^+$; 100%), 255 (16), 215 (8).

Anal calc for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.15; H, 9.95%.

### *Preparation of 3,6-bis(1,1-dimethylethyl)-2-ethoxynaphthalene* **4c**

As above for **4b** but with EtI in place of MeI to give the title compound **4c** as a white solid (96%). Mp 151–152 °C.

IR (KBr): 3 067w ($sp^2$ CH), 3 005w ($sp^2$ CH), 2 963s ($sp^3$ CH), 2 939s ($sp^3$ CH), 2 868m ($sp^3$ CH), 1 605m (C=C), 1 459s, 1 449s ($sp^3$ CH def), 1 388m ($sp^3$ CH def), 1 363s ($sp^3$ CH def), 1 253m, 1 205s ($OCH_2$), 1 179m, 1 068s ($OCH_2$), 904s, 852s, 835s $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 7.69 (1H, d, *J* 1.9, 5-H); 7.68 (1H, s, 4-H); 7.63 (1H, d, *J* 8.6, 8-H); 7.48 (1H, dd, *J* 8.6, 1.9, 7-H); 7.09 (1H, s, 1-H); 4.18 (2H, q, *J* 7.0, OMe); 1.54 (3H, t, *J* 7.0, *tert*-butyl); 1.50 (9H, s, *tert*-butyl); 1.41 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 156.5 (C2); 146.0 (C6); 139.7 (C3); 131.1 (C4a or C8a); 128.3 (C4a or C8a); 125.5 (Ar–CH); 125.3 (Ar–CH); 124.4 (Ar–CH); 122.6 (Ar–CH); 106.1 (C1); 63.3 (C13); 35.2 (C9); 34.6 (C11); 31.4 (C10); 30.0 (C12); 14.9 (C14).

MS (CI$^+$, $NH_3$): 285 (M + 1$^+$, 100%), 269 (12), 229 (5).

*Attempted preparation of 1-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene* **8a**

Following a modification of the procedure of Fuson and Chadwick [8] a solution of bromine (0.45 mL, 8.7 mmol) in acetic acid (10 mL) was added dropwise to a solution of 3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **4b** (2.1 g, 7.9 mmol) in acetic acid (20 mL) at room temperature. After 10 min the acetic acid was removed under reduced pressure and the residue washed with saturated aqueous sodium hydrogen carbonate solution (30 mL). The organics were extracted with dichloromethane (3 × 30 mL), dried ($MgSO_4$), filtered and the solvent evaporated to give a brown oil (2.3 g). $^1$H NMR analysis of the crude reaction mixture showed a 3:1 mixture of the title compound **8a** and 8-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **9a** (integration of methoxy resonances at $\delta_H$ 4.04, 4.01 ppm; **8a**, **9a**). Purification by flash chromatography on silica gel gave first 8-bromo-3,6-bis-(1,1-dimethylethyl)-2-methoxynaphthalene **9a** as a colourless oil (0.75 g, 27%).

IR (film): 2 995w ($sp^2$ CH), 2 961s ($sp^3$ CH), 2 869s ($sp^3$ CH), 1 599m (C=C), 1 488m ($sp^3$ CH def), 1 464m ($sp^3$ CH def), 1 428m, 1 390w, 1 361w, 1 307w, 1 280w, 1 229s, 1 203s (OMe), 1 168m, 1 078s (OMe), 905w, 877w, 842w, 765w.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 7.77 (1H, d, *J* 1.7, 7-H); 7.66 (2H, br s, 5-H and 4-H); 7.42 (1H, s, 1-H); 4.01 (3H, s, OMe); 1.47 (9H, s, *tert*-butyl); 1.40 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 158.5 (C2); 147.0 (C6); 140.7 (C3); 129.9 (C4a or C8a); 129.4 (C4a or C8a); 128.3; (Ar–CH); 126.0 (Ar–CH); 122.9 (Ar–CH); 120.6 (C8); 105.2 (C1); 55.0 (C13); 35.2 (C9); 34.7 (C11); 31.3 (C10); 29.8 (C12).

MS ($CI^+$, $NH_3$): 351 (M + $1^+$, 67%), 349 (M + $1^+$, 100), 335 (12), 333 (12), 271 (49), 215 (5).

Further elution gave 1-bromo-3,6-bis(dimethylethyl)-2-methoxynaphthalene **8a** (1.28 g, 47%). Mp 93–95 °C.

IR (thin film): 3 069w ($sp^2$ CH), 2 962s ($sp^3$ CH), 2 869s ($sp^3$ CH), 1 591m (C=C), 1 557m, 1 488m ($sp^3$ CH def), 1 457m ($sp^3$ CH def), 1 412m, 1 392m, 1 362m, 1 315m, 1 265m, 1 228m, 1 214m (OMe), 1 160m, 1 066s (OMe), 995s, 949s, 901s, 844s, 820s $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 8.13 (1H, d, *J* 8.9, 8-H); 7.73 (1H, s, 4-H); 7.71 (1H, d, *J* 1.9, 5-H); 7.62 (1H, dd, *J* 8.9, 1.9, 7-H); 4.04 (3H, s, OMe); 1.51 (9H, s, *tert*-butyl); 1.42 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 155.9 (C2); 148.3 (C6); 144.0 (C3); 130.9 (C4a or C8a); 130.4 (C4a or C8a); 125.9 (Ar–CH); 125.7 (Ar–CH); 125.6 (Ar–CH); 123.1 (Ar–CH); 116.2 (C1); 61.9 (C13); 35.7 (C9); 34.7 (C11); 31.2 (C10); 30.9 (C12).

MS ($CI^+$, $NH_3$): 368 (M + $18^+$, 2%), 366 (M + $18^+$, 2), 351 (M + $1^+$, 11), 349 (M + $1^+$, 11), 335 (2), 333 (2), 295 (3), 293 (3), 271 (100), 255 (13), 215 (7).

Anal calc for $C_{19}H_{25}BrO$: C, 65.33; H, 7.21. Found: C, 65.17; H, 7.43%.

*Crossover experiment*

The 1- and 8-bromo-3,6-bis(1,1-dimethylethyl)-2-ethoxynaphthalenes **8b** and **9b** were prepared using the bromination procedure for the preparation of 1- and 8-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalenes **8a** and **9a** (above). The title compounds were purified by flash chromatography on silica gel to give first 8-bromo-3,6-bis-(1,1-dimethylethyl)-2-ethoxynaphthalene **9b** as a colourless oil which solidified on standing (25%). Mp 106–108 °C.

IR (KBr): 2 961s ($sp^3$ CH), 1 599m (C=C), 1 488m ($sp^3$ CH def), 1 465m ($sp^3$ CH def), 1 439m, 1 391w ($sp^3$ CH def), 1 360w ($sp^3$ CH def), 1 229s ($OCH_2$), 1 202s, 1 075s ($OCH_2$) $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 7.76 (1H, d, *J* 1.8, 7-H); 7.66 (1H, s, 4-H); 7.65 (1H, d, *J* 1.8, 5-H); 7.41 (1H, s, 1-H); 4.25 (2H, q, *J* 7.0, $OCH_2CH_3$); 1.57 (3H, t, *J* 7.0, $OCH_2CH_3$); 1.50 (9H, s, *tert*-butyl); 1.40 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 157.7 (C2); 146.8 (C6); 140.7 (C3); 129.9 (C4a or C8a); 129.3 (C4a or C8a); 128.3 (Ar–CH); 126.0 (Ar–CH); 122.9 (Ar–CH); 120.5 (C8); 105.6 (C1); 63.5 (C13); 35.2 (C9); 34.7 (C11); 31.3 (C10); 29.9 (C12); 14.8 (C14).

MS ($CI^+$, $NH_3$): 382 (M + $18^+$, 2%), 365 (M + $1^+$, 18), 363 (M + $1^+$, 16), 349 (2), 347 (2), 336 (2), 334 (2), 321 (7), 319 (7), 309 (8), 307 (8), 285 (100), 269 (24), 229 (8).

Further elution gave 1-bromo-3,6-bis(dimethylethyl)-2-ethoxynaphthalene **8b** as a colourless oil (55%).

IR (film): 2 962s ($sp^3$ CH), 1 593m (C=C), 1 429m ($sp^3$ CH def), 1 388w ($sp^3$ CH def), 1 362w ($sp^3$ CH def), 1 349m, 1 225s ($OCH_2$), 1 213s, 1 065s ($OCH_2$), 1 027s $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 8.13 (1H, d, *J* 8.9, 8-H); 7.74 (1H, s, 4-H); 7.71 (1H, d, *J* 1.9, 5-H); 7.61 (1H, dd, *J* 8.9, 1.9, 7-H); 4.23 (2H, q, *J* 7.0, $OCH_2CH_3$); 1.54 (3H, t, *J* 7.0, $OCH_2CH_3$); 1.51 (9H, s, *tert*-butyl); 1.42 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 154.4 (C2); 148.2 (C6); 144.1 (C3); 130.8 (C4a or C8a); 130.3 (C4a or C8a); 126.0 (Ar–CH); 125.8 (Ar–CH); 125.7 (Ar–CH); 123.0 (Ar–CH); 116.8 (C1); 69.1 (C13); 35.8 (C9); 34.7 (C11); 31.2 (C10); 30.9 (C12); 15.2 (C14).

MS ($CI^+$, $NH_3$): 382 (M + $18^+$, 9%), 380 (M + $18^+$, 11), 365 (M + $1^+$, 49), 363 (M + $1^+$, 88), 362 (100), 349 (19), 347 (20), 336 (10), 334 (9), 321 (50), 319 (50), 309 (34), 307 (36), 285 (34), 283 (44), 267 (13), 211 (12).

*Preparation of (±)-2-methoxy-[1,1′-binaphthalene]* **7b**

Tetrakis(triphenylphosphine)palladium[0] (61 mg, 0.05 mmol) was added as a solid to a solution of 1-bromo-2-methoxynaphthalene (250 mg, 1.1 mmol) in DME (18 mL). After stirring for 10 min 1-naphthylboronic acid (220 mg, 1.3 mmol) in methanol (ca 0.2 mL) and potassium carbonate (320 mg, 2.3 mmol) in water (1.2 mL) were added. The solution was heated at reflux for 16 h, the resulting solution cooled to room temperature and poured into water. The organics were extracted with diethyl ether, dried ($MgSO_4$), filtered and the solvent evaporated. *This protocol is subsequently referred to as the general Suzuki procedure.* The resulting yellow oil was purified by flash chromatography on silica gel (15% dichloromethane in pentane) to give the title compound as a white solid (192 mg, 75%). Mp 107–108 °C.

IR (KBr): 2 935m ($sp^3$ CH), 2 837w ($sp^3$ CH), 1 620w (Ar C=C), 1 592m (Ar C=C), 1 507s, 1 263vs (C–O), 1 250s, 1 086m, 804s, 780s $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 8.00 (1H, d, *J* 9.0, 4-H); 7.97 (1H, br d, *J* 8.2, 2′-H or 4′-H); 7.95 (1H, br d, *J* 8.2, 8′-H or 8-H); 7.88 (1H, br d, *J* 8.0, 8-H or 8′-H); 7.63 (1H, dd, *J* 8.2, 7.0, 3′-H); 7.46 (3H, m, 3-H, 2′-H or 4′-H, 7′-H or 7-H); 7.34 (1H, ddd, *J* 8.0, 6.7, 1.2, 7-H or 7′-H); 7.34 (1H, br d, *J* 8.0, 5′-H or 5-H); 7.29 (1H, ddd, *J* 8.0, 6.6, 1.2, 6′-H or 6-H); 7.23 (1H, ddd, *J* 8.4, 6.7, 1.3, 6-H or 6′-H); 7.17 (1H, br d, *J* 8.4, 5-H or 5′-H); 3.77 (3H, s, OMe).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 154.6 (C2); 134.5 (Ar–C); 134.3 (Ar–C); 133.7 (Ar–C); 133.0 (Ar–C); 129.5 (Ar–CH); 129.0 (Ar–C); 128.4 (Ar–CH); 128.2 (Ar–CH); 127.8 (Ar–CH); 127.7 (Ar–CH); 126.4 (Ar–CH); 126.2 (Ar–CH); 125.8 (Ar–CH); 125.7 (Ar–CH); 125.5 (Ar–CH); 125.5

(Ar–CH); 123.6 (Ar–CH); 123.3 (Ar–C); 113.9 (Ar–CH); 56.8 (C9).

MS ($CI^+$, $NH_3$): 302 (M + $18^+$, 100%), 285 (M + $1^+$, 72), 239 (7).

*Preparation of (±)-[1,1′-binaphthalen]-2-ol* **7a**

A solution of boron tribromide (1M, 1.0 mL, 1.0 mmol) in dichloromethane was added dropwise to a solution of (±)-2-methoxy-[1,1′-binaphthalene] (138 mg, 0.51 mmol) in dichloromethane (2 mL). The mixture was quenched after 1 h by the addition of saturated aqueous sodium hydrogen carbonate solution (5 mL). The organics were extracted with dichloromethane (3 × 10 mL), dried ($MgSO_4$), filtered and the solvent evaporated to give the title compound as a white solid (126 mg, 93%). Mp 91–94 °C ([17] 90–93 °C).

IR (KBr): 3 660–3 300s (OH), 3 057w ($sp^2$ CH), 1 620m (Ar C=C), 1 595m (Ar C=C), 1 385s, 1 194vs (C–O), 805s, 781s $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) δ ppm: 8.04 (1H, br d *J* 8.1, 2′-H or 4′-H); 7.99 (1H, br d, *J* 8.0, 8′-H or 8-H); 7.92 (1H, d, *J* 8.9, 4-H); 7.88 (1H, br d, *J* 8.1, 8-H or 8′-H); 7. 68 (1H, dd, *J* 8.1, 7.0, 3′-H); 7.56 (1H, br d, *J* 2′-H or 4′-H); 7.54 (1H, ddd, *J* 8.1, 6.9, 1.4, 7-H or 7′-H); 7.41 (1H, br d, *J* 8.3, 5-H or 5′-H); 7.36 (1H, ddd, *J* 8.0, 6.8, 1.0, 7′-H or 7-H); 7.35 (1H, d, *J* 8.9, 3-H); 7.34 (1H, ddd, *J* 8.3, 6.9, 1.1, 6-H or 6′-H); 7.25 (1H, ddd, *J* 8.1, 6.8, 1.2, 6′-H or 6-H); 7.11 (1H, br d, *J* 8.1, 5′-H or 5-H).

$^{13}C$ NMR ($CDCl_3$) δ ppm: 150.9 (C2); 134.2 (Ar–C); 133.9 (Ar–C); 132.8 (Ar–C); 131.4 (Ar–C); 129.9 (Ar–CH); 129.6 (Ar–CH); 129.2 (Ar–CH); 128.9, 128.5 (Ar–CH); 128.0 (Ar–CH); 126.8 (Ar–CH); 126.5 (Ar–CH × 2); 126.0 (Ar–CH); 125.8 (Ar–CH); 125.0 (Ar–CH); 123.3 (Ar–CH); 118.8 (Ar–C); 117.4 (Ar–CH).

MS ($CI^+$, $NH_3$): 288 (M + $18^+$, 100%), 271 (M + $1^+$, 42), 270 (51).

*Preparation of 3,3′,6,6′-tetrakis(1,1-dimethylethyl)-[1,1′-binaphthalene]-2,2′-diol* **1**

Isobutene was passed through a solution of (±)-[1,1′-binaphthalene]-2,2′-diol **6** (5 g, 17 mmol) and $CF_3SO_3H$ (0.15 mL, 0.09 mmol) in dichloromethane (50 mL) heated at reflux. After 2 h the contents of the flask had approximately doubled in volume (acid catalysed isobutene polymerisation products). The dark red solution was allowed to cool and quenched with saturated aqueous sodium hydrogen carbonate solution (50 mL). The organic layer was dried ($MgSO_4$), filtered and the solvent evaporated to give a pink solid in a red solution. The solid was filtered at the pump and washed repeatedly with pentane to give the title compound **1** as a spectroscopically pure white solid (8.1 g, 93%). Mp > 300 °C (literature: 332–334 °C).

IR (KBr): 3 516s (OH), 3 069w ($sp^2$ CH), 3 003 ($sp^2$ CH), 2 967s ($sp^3$ CH), 2 923s ($sp^3$ CH), 2 897s ($sp^2$ CH), 1 601m (Ar C=C), 1 505m, 1 487m, 1 469m, 1 440s, 1 425s, 1 396s ($sp^3$ CH def), 1 367s ($sp^3$ CH def), 1 213s, 1 180vs, 1 161vs, 905s, 832s $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) δ ppm: 7.93 (2H, s, 4-H); 7.67 (2H, d, *J* 2.0, 5-H); 7.32 (2H, dd, *J* 8.8, 2.0, 7-H); 6.95 (2H, d, *J* 8.8, 8-H); 5.34 (2H, s, OH); 1.56 (18H, s, *tert*-butyl); 1.37 (18, s, *tert*-butyl).

$^{13}C$ NMR ($CDCl_3$) δ ppm: 152.3 (C2); 146.4 (C6); 138.3 (C6); 130.2 (C4a or C8a); 129.0 (C4a or C8a); 127.4 (Ar C–H); 125.4 (Ar C–H); 123.5 (Ar C–H); 123.4 (Ar C–H); 111.4 (C1); 35.5 (C9); 34.6 (C11); 31.3 (C10); 29.8 (C12).

MS ($CI^+$, $NH_3$): 511 (M + $1^+$, 100%).

Anal calc for $C_{36}H_{46}O$: C, 84.66; H, 9.08. Found: C, 84.77; H, 9.05%.

*Preparation of (±)-3,6-bis(1,1-dimethylethyl)-2-methoxy-[1,1′-binaphthalene]* **2b**

Using the general palladium-catalysed Suzuki cross-coupling procedure (above). The following quantities of reagents were used: Tetrakis(triphenylphosphine)palladium[0] (73 mg, 0.06 mmol). 1-Bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **8a** (440 mg, 1.26 mmol) in DME (20 mL). 1-Naphthylboronic acid (430 mg, 2.5 mmol) in methanol (1 mL) and potassium carbonate (659 mg, 4.8 mmol) in water (2.4 mL) to give a yellow oil (500 mg). $^1H$ NMR analysis showed 33% conversion to the title compound based on 1-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene. The remainder of the material was 3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene [integration of methoxy resonances $\delta_H$ 3.10, 3.99 ppm]. Purification by flash chromatography on silica gel (5% dichloromethane in pentane) gave the title compound as a colourless oil (125 mg, 25%).

IR (KBr): 3 044w ($sp^2$ CH), 2 960vs ($sp^3$ CH), 2 867m ($sp^3$ CH), 1 590 (Ar C=C), 1 464m, 1 410m, 1 390m ($sp^3$ CH def), 1 365s ($sp^3$ CH def), 1 233s, 1 214s (OMe), 799s, 779s $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) δ ppm: 7.99 (1H, br d, *J* 8.0, 4′-H); 7.96 (1H, br d, *J* 8.0, 8′-H); 7.89 (1H, s, 4-H); 7.79 (1H, d, *J* 2.0, 5-H); 7.64 (1H, dd, *J* 8.2, 7.0, 3′-H); 7.53 (1H, dd, *J* 7.0, 1.2, 2′-H); 7.48 (1H, ddd, *J* 8.0, 6.7, 1.2, 7′-H); 7.40 (1H, br d, *J* 8.1, 5′-H); 7.32 (1H, ddd, *J* 8.1, 6.7, 1.3, 6′-H); 7.26 (1H, dd, *J* 8.9, 2.0, 7-H); 7.03 (1H, br d, *J* 8.9, 8-H); 3.10 (3H, s, OMe); 1.53 (9H, s, *tert*-butyl); 1.37 (9H, s, *tert*-butyl).

$^{13}C$ NMR ($CDCl_3$) δ ppm: 157.1 (C2); 152.0 (Ar–C); 147.6 (Ar–C); 143.2 (Ar–C); 135.6 (Ar–C); 134.3 (Ar–C); 133.5 (Ar–C); 131.5 (Ar–C); 130.6 (Ar–C); 129.7 (Ar–CH); 128.6 (Ar–CH); 128.3 (Ar–CH); 126.8 (Ar–CH); 126.4 (Ar–CH); 126.3 (Ar–CH); 126.2 (Ar–CH); 126.0 (Ar–CH); 124.9 (Ar–CH); 124.7 (Ar–CH); 123.5 (Ar–CH); 61.1 (C13); 35.8 (C9); 34.9 (C11); 31.4 (C10); 31.0 (C12).

MS ($CI^+$, $NH_3$): 414 (M + $18^+$, 13%), 397 (M + $1^+$, 100), 358 (23), 341 (37).

*Preparation of (±)-3,6-bis(1,1-dimethylethyl)-7-methoxy-[1,1′-binaphthalene]* **10**

Using the general palladium-catalysed Suzuki cross-coupling procedure. The following quantities of reagents were used: Tetrakis(triphenylphosphine)palladium[0] (20 mg, 0.016 mmol). 8-Bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **9a** (120 mg, 0.34 mmol) in DME (5 mL). 1-Naphthylboronic acid (70 mg, 0.41 mmol) in methanol (ca 0.1 mL) and potassium carbonate (104 mg, 0.75 mmol) in water (0.38 mL) to give a yellow oil. Purification by preparative TLC gave the title compound as a colourless oil (132 mg, 98%).

IR (KBr): 3 044w ($sp^2$ CH), 2 960s ($sp^3$ CH), 2 868m ($sp^3$ CH), 1 603m (C=C), 1 490m, 1 462s, 1 430m, 1 389w ($sp^3$ CH def), 1 360m ($sp^3$ CH def), 1 226s, 1 203s (C–O), 802s, 780s $cm^{-1}$.

$^1H$ NMR ($CDCl_3$) δ ppm: 7.96 (2H, br d, *J* 8.1, 4′-H and 8′-H); 7.82 (1H, d, *J* 2.0, 5-H); 7.78 (1H, s, 4-H); 7.62 (1H, dd, *J* 8.2, 7.0, 3′-H); 7.53 (1H, dd, *J* 7.0, 1.2, 2′-H); 7.51 (1H, d, *J* 2.0, 7-H); 7.49 (2H, m, 5′-H and 7′-H); 7.33 (1H, ddd, *J* 8.1, 6.8, 1.2, 6′-H); 6.66 (1H, s, 1-H); 3.45 (3H, s, OMe); 1.47 (9H, s, *tert*-butyl); 1.44 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 157.8 (C2); 146.2 (C3 or C6); 140.1 (C3 or C6); 139.6 (Ar–C); 136.4 (Ar–C); 134.2 (Ar–C); 133.2 (Ar–C); 130.9 (Ar–C); 129.3 (Ar–C); 128.5 (Ar–CH); 128.3 (Ar–CH); 128.0 (Ar–CH); 127.1 (Ar–CH); 127.0 (Ar–CH); 126.2 (Ar–CH); 126.2 (Ar–CH); 126.1 (Ar–CH); 125.9 (Ar–CH); 123.2 (Ar–CH); 105.0 (C1); 54.9 (C13); 35.5 (C9 or C11); 35.0 (C9 or C11); 31.6 (C10 or C12); 30.1 (C10 or C12).

MS ($CI^+$, $NH_3$): 397 (M + $1^+$, 100%), 382 (73), 342 (36).

*Preparation of 3,6-bis(1,1-dimethylethyl)-2-methoxy-1-naphthylboronic acid* ***4d***

*n*-Butyllithium (2.5 M, 0.4 mL) was added to a stirred solution of 1-bromo-3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene **8a** (0.35 g, 1 mmol) in THF (2.5 mL) under argon at −78 °C. The yellow solution was quenched immediately by addition of $B(OMe)_3$ (0.57 mL, 5 mmol) and stirred for 1 h at room temperature. Water (2 mL) was added and the mixture transferred to a separatory funnel, and the upper layer concentrated to give an oil which was stirred in $CH_2Cl_2$ (50 mL) with water (50 mL) overnight. The organic layer was dried ($MgSO_4$) and the solvent removed to give an off-white solid (0.331 g). $^1$H NMR analysis revealed a 4:1 mixture of boronic acid **4d** and 1-H naphthalene **8a**, from which the latter could be removed by washing with pentane, albeit with significant decomposition of the boronic acid. In this way a pure sample of boronic acid was isolated (0.080 g, 25%), Mp 108–110 °C.

IR (KBr): 3 600–3 000 (OH), 2 959s, 2 870s, 1 568m, 1 412s (B–O), 1 360s (B–O), 1 267s (C–O), 1 212s (C–O), 1 079m, 1 004m, 904s, 806s (Ar–H) $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 8.24 (1H, d, *J* 8.9, 8-H); 7.79 (1H, s, 4-H); 7.71 (1H, d, *J* 2.2, 5-H); 7.54 (H, dd, *J* 8.9, 2.2, 7-H); 5.45 (2H, s, B–OH); 3.95 (3H, s, OMe); 1.48 (9H, s, *tert*-butyl); 1.40 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 163.7 (C2); 147.2 (C6); 141.5 (C3); 133.4, 130.2 (C4a, C8a); 128.6, 126.2, 124.9, 123.2 (Ar–C); 63.1 (C13); 35.2 (C9); 34.6 (C11); 31.2 (C10); 30.8 (C12).

MS (APCI, $NH_3$): 349 (M + $Cl^-$, 100%), 217 (13%).

*Preparation of 1-(3,6-bis(1,1-dimethylethyl)-2-methoxy-1-naphthyl)isoquinoline* ***11***

Using the general palladium-catalysed Suzuki cross-coupling procedure (above), with the quantities of reagents as follows: $Pd(PPh_3)_4$ (0.644 g, 0.56 mmol), 1-chloroisoquinoline (1.83 g, 11 mmol) in DME (50 mL), together with 3,6-bis-(1,1-dimethylethyl)-2-methoxy-1-naphthylboronic acid (8.4 g, 4:1 mixture with 3,6-bis(1,1-dimethylethyl)-2-methoxynaphthalene, 22 mmol) in MeOH (20 mL) and $K_2CO_3$ (30% solution in $H_2O$, 11 mL, 22 mmol). There was thus obtained a yellow oil (3.85 g, with 37% of the desired product by $^1$H NMR). Purification by flash chromatography (silica gel, $CH_2Cl_2$) gave the title compound as a white solid (1.31 g, Mp 87–88 °C, 30%).

IR (KBr): 3 050w, 2 960s, 2 867s, 1 621w, 1 583m, 1 557m (Ar C=C), 1 411s, 1 237s, 1 193s, 825vs, 747s (Ar C–H).

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 8.79 (1H, d, *J* 5.7, 3′-H); 7.93, (1H, s, 4-H); 7.92 (1H, d, *J* 6.3, 8′-H); 7.81 (1H, d, *J* 2.0, 5-H); 7.78 (1H, d, 4′-H); 7.69 (1H, ddd, *J* 8.4, 1,1, 7′-H); 7.62 (1H, d, *J* 8.4, 5′-H); 7.44 (1H, ddd, *J* 8.4, 1, 1, 6′-H); 7.35 (1H, dd, *J* 8.9, 2.0, 7-H); 7.12 (1H, d, *J* 8.9, 8-H); 3.17 (3H, s, OMe); 1.56 (9H, s, *tert*-butyl); 1.38 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 158.8 (C2); 156.5 (C1′); 147.2 (C3); 142.5 (C3′); 142.3 (C6); 136.4, 130.8, 130.3, 128.6 (C4a, C4′a, C8a, C8′a); 127.6 (C4); 127.4 (C5); 126.7 (C6′); 126.7 (C8′); 126.5 (C1); 124.9 (C7); 124.0 (C8); 122.9 (C5); 120.2 (C4′); 61.6 (C13); 35.4 (C9); 35.4 (C11); 31.2 (C10); 30.7 (C12).

MS ($APCI^+$, $NH_3$): 398 (100%, M + 1).

Anal calc for $C_{28}H_{31}NO$: C, 84.59; H, 7.86; N, 3.52. Found: C, 84.46; H, 7.66; N, 3.57%.

*Preparation of (±)-3,6-bis(1,1-dimethylethyl)-[1,1′-binaphthalen]-2-ol* ***2a***

A solution of boron tribromide (1 M, 0.5 mL, 0.5 mmol) in dichloromethane was added dropwise to a solution of (±)-3,6-bis(1,1-dimethylethyl)-2-methoxy-[1,1′-binaphthalene] (100 mg, 0.25 mmol) in dichloromethane (2 mL). The mixture was quenched after 24 h by vigorous stirring with saturated aqueous sodium hydrogen carbonate solution (5 mL) for 2 h. The organics were extracted with dichloromethane (3 × 10 mL), dried ($MgSO_4$), filtered and the solvent evaporated to give a yellow oil. Purification by preparative TLC gave the title compound as a white solid (71 mg, 73%). Mp 85–86 °C.

IR (KBr): 3 533s (OH), 3 058w ($sp^2$ CH), 2 960vs ($sp^3$ CH), 2 909s ($sp^3$ CH), 2 870m ($sp^3$ CH), 1 602m (Ar C=C), 1 434w, 1 418w, 1 389m ($sp^3$ C–H def), 1 366m ($sp^3$ C–H def), 1 191s (C–O), 1 157s, 801s, 779s $cm^{-1}$.

$^1$H NMR ($CDCl_3$) $\delta$ ppm: 8.03 (1H, br d, *J* 8.3, 4′-H); 7.99 (1H, br d, *J* 8.1, 8′-H); 7.85 (1H, s, 4-H); 7.78 (1H, d, *J* 2.0, 5-H); 7.67 (1H, dd, *J* 8.3, 7.0, 3′-H); 7.57 (1H, dd, *J* 7.0, 1.1, 2′-H); 7.53 (1H, ddd, *J* 8.1, 6.7, 1.3, 7′-H); 7.41 (1H, br d, *J* 8.1, 5′-H); 7.35 (1H, ddd, *J* 8.1, 6.7, 1.2, 6′-H); 7.27 (1H, dd, *J* 8.9, 2.0, 7-H); 6.93 (1H, br d, *J* 8.9, 8-H); 5.07 (1H, s, OH); 1.56 (9H, s, *tert*-butyl); 1.38 (9H, s, *tert*-butyl).

$^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 150.3 (Ar–C); 145.8 (Ar–C); 138.0 (Ar–C); 134.3 (Ar–C); 133.0 (Ar–C); 132.0 (Ar–C); 130.6 (Ar–C); 130.0 (Ar–CH); 129.2 (Ar–CH); 128.4 (Ar–CH); 128.3 (Ar–C); 126.8 (Ar–CH); 126.5 (Ar–CH); 126.0 (Ar–CH); 125.9 (Ar–CH × 2); 124.6 (Ar–CH); 124.1 (Ar–CH); 123.0 (Ar–CH); 119.2 (C1); 35.4 (C9); 34.5 (C11); 31.3 (C10); 29.8 (C12).

MS ($CI^+$, $NH_3$): 383 (M + $1^+$, 100%), 382 (52), 367 (31), 327 (39), 311 (7), 271 (4), 252 (3), 183 (4), 155 (4), 128 (5), 57 (14).

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