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Asymmetric synthesis of 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine catalysed by palladium(0)-complexes

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Summary — The cyclisation of *N*-substituted 2-aminophenol **1** with (*Z*)-1,4-bis[(methoxycarbonyl)oxy]but-2-ene **2** catalysed by palladium(0) complexes associated with chiral ligands leads to 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazines with ee up to 79%.

aminophenol / benzomorpholine / cyclisation / palladium / chirality

Résumé — Synthèse asymétrique de la 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine catalysée par les complexes du palladium(0). La cyclisation de 2-aminophénols *N*-substitués **1** avec le (*Z*)-1,4-bis[(méthoxycarbonyl)oxy]but-2-ène **2** catalysée par les complexes du palladium(0) associé à des ligands chiraux conduit aux 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazines avec des énantiosélectivités de 79 %.

aminophénol / benzomorpholine / cyclisation / palladium / chiralité

Introduction

3,4-Dihydro-2*H*-1,4-benzoxazine derivatives or benzomorpholine derivatives have aroused considerable interest owing to the presence of this heterocyclic skeleton in a number of structures of compounds having important therapeutic and biological activities [1–4]. Catalytic asymmetric synthesis of such heterocycles seems difficult and only a few methods have been reported to date. The construction of morpholine skeletons was first reported by Saegusa et al [5] by reacting 2-buten-1,4-ylene diesters with 2-aminoethanols in the presence of a palladium catalyst. This reaction was extended to the catalytic asymmetric cyclisation by Hayashi and co-workers [6] using a palladium complex coordinated with BINAP where enantiomeric excesses up to 65% were obtained. More recently Achiwa and co-workers [7, 8] also prepared chiral 2-vinylmorpholine with 83% enantioselectivity by reaction of (*Z*)-1,4-diacetoxybut-2-ene with 2-(benzylamino)phenol in the presence of a palladium catalyst associated with BHMP-β-Ala and extended their cyclisation to chiral 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine with ee up to 71%.

In a previous paper [9], we reported the asymmetric synthesis of 2-vinyl-1,4-benzodioxanes in the presence of a catalytic amount of palladium(0) associated with BINAP with ee up to 45%. Here we wish to report the extension of our methodology for the construction of 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine.

Results and discussion

Initial cyclisation experiments were carried out with various *N*-substituted 2-aminophenols **1** and (*Z*)-1,4-bis[(methoxycarbonyl)oxy]but-2-ene **2** in THF in the presence of a palladium complex generated in situ by mixing 1,4-bis(diphenylphosphino)butane (DPPB) with $Pd_2(dba)_3$ as catalyst and the results are summarized in scheme 1 and table I.

Table I. Palladium-catalysed reaction of **1** with **2**[a].

Entry	*1*	*[1]/[2]*	*Compounds (yields)*[b]
1	**1a**	1/1.5	**3a** (13%) + **5** (39%)
2	**1a**	1/1	**3a** (38%) + **5** (28%)
3	**1a**	2/1[c]	**3a** (45%) + **5** (10%)
4	**1b**	1/1.5	**3b** (78%)
5	**1c**	1/1.5	**4** (25%)
6	**1d**	1/1.5	No reaction

[a] Conditions: [**1**]/[palladium]/[DPPB] = 20:1:1; [**1**] = 0.2 M; solvent THF; 25 °C; 24 h. [b] Isolated yields after column chromatography and not optimized. [c] [**1**] = 0.4 M.

In the reaction of 2-(tosylamino)phenol **1b** with **2**, benzomorpholine **3b**, bearing a vinyl group at the C-2 position, was obtained as a single regioisomer and in quite good yield (entry 4). The plausible reaction pathway for this regiospecific formation is shown in

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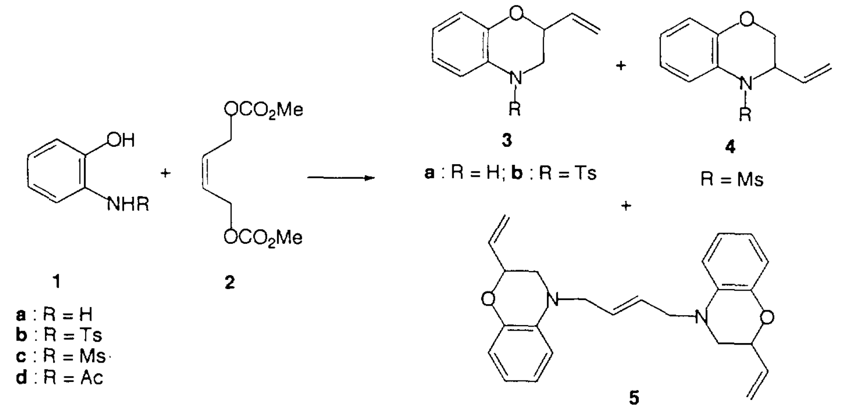
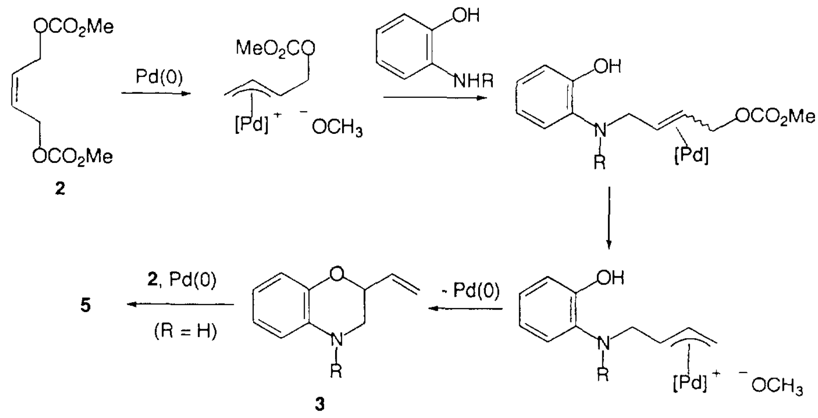


Scheme 1



Scheme 2

scheme 2. Reaction of 1,4-bis[(methoxycarbonyl)oxy]-but-2-ene **2** with palladium(0) gives a cationic π-allyl intermediate with a methoxy anion; the nucleophilic substitution takes place at the less hindered termini of the π-allyl system with the amino group of **1b** to give an allylic amine. The formation of the π-allyl palladium intermediate followed by intramolecular attack of the phenoxide obtained by abstraction of the acidic hydrogen by methoxide anion on this π-allyl system produces benzomorpholine **3b**. This regiospecificity is in agreement with the fact that the nitrogen nucleophile is generally more reactive than the oxygen nucleophile towards π-allyl palladium complexes [10].

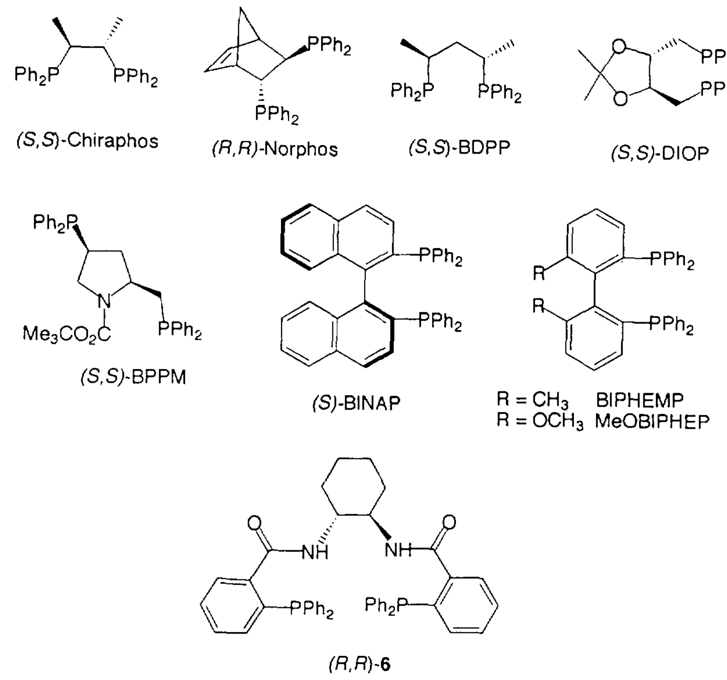
2-(Mesylamino)phenol **1c** reacted also with **2** to give a single product **4** in lower chemical yield (entry 5) and bearing the vinyl group at the C-3 position α to the nitrogen atom as shown by ^{1}H NMR and ^{13}C NMR. The signal of H-2 appeared at δ 3.76 ppm for **3b** and of H-3 at δ 4.99 ppm for **3a**; however more characteristic are the signals of $-OCH_2-$ and $-NCH<$ for compound **4** at δ 67.35 and 55.08 ppm respectively compared to the signals of $-NCH_2-$ and $-OCH<$ for compound **3b** at 48.32 and 78.11. It seems from this surprising result that the phenoxide obtained by abstraction of the acidic hydrogen of the phenol by exchange with the methoxy anion is more nucleophilic than the compound mesylamino **1c** in this case.

Reaction of 2-aminophenol **1a** (entries 1–3) with dicarbonate **2** in the presence of palladium catalyst also gave the cyclic compound **3a** together with **5**. The structure of this latter product was determined by ^{1}H and ^{13}C NMR and mass spectrometry with a molecular peak at 374. This compound is obtained by two successive nucleophilic substitutions of compound **3a** on the dicarbonate **2** in the presence of palladium (scheme 2). As expected, increasing the relative amount of the 2-aminophenol favored the formation of the desired cyclic compound **3a**.

Under similar reaction conditions, cyclisation with **1d** did not take place and only the formation of a small amount of by-products was observed.

We then focused on the catalytic cyclisation between **1a–b** and **2** in THF at 25 °C in the presence of chiral-phosphine palladium catalysts. The phosphines used are shown in scheme 3 and the results are summarized in table II.

Palladium complexes of (*S*,*S*)-Chiraphos (entry 1), (*R*,*R*)-Norphos (entry 2) and (*S*,*S*)-BDPP (entry 3) showed very low activities and selectivities in the cyclisation of 2-(tosylamino)phenol **1b** with



Scheme 3

Table II. Palladium-catalysed asymmetric synthesis of **3b** from **1** and **2**[a].

Entry	**1**	*Ligand*	*Yield of* **3b** *(%)*[b]	*ee (%)*[c]	*Configuration*
1	**1b**	(*S*,*S*)-Chiraphos	4	14	(*S*)
2	**1b**	(*R*,*R*)-Norphos	0	–	–
3	**1b**	(*S*,*S*)-BDPP	4	14	(*R*)
4	**1b**	(*S*,*S*)-DIOP	59	8	(*S*)
5	**1b**	(2*S*,4*S*)-BPPM	28	32	(*S*)
6	**1b**	(*S*)-BINAP	32	24	(*S*)
7	**1a**	(*S*)-BINAP[d]	20[e]	78	(*S*)
8	**1b**	(*R*)-BIPHEMP	17	32	(*R*)
9	**1a**	(*R*)-BIPHEMP[d]	26[e]	37	(*R*)
10	**1b**	(*S*)-MeOBIPHEP	22	16	(*S*)
11	**1a**	(*S*)-MeOBIPHEP[d]	25[e]	53	(*S*)
12	**1b**	(*R*,*R*)-**6**	30	79	(*S*)

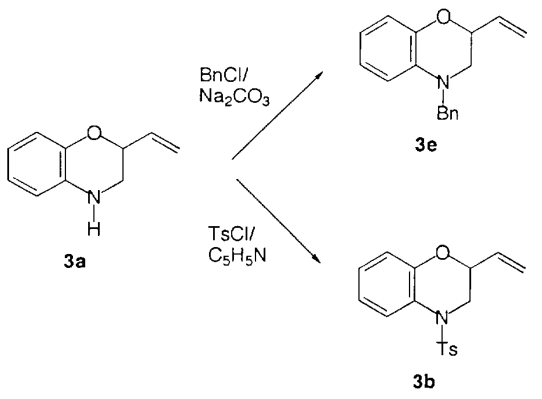
[a] Conditions: [**1**]/[**2**]/[palladium]/[ligand] = 22:20:1:1; [**1**] = 0.2 M; solvent THF; 25 °C; 24 h. [b] Isolated yields after column chromatography and not optimized. [c] Determined by HPLC analysis with a chiral stationary phase column (CHIRALPAK AD, *n*-hexane/propan-2-ol 95:5). [d] [**1**]/[**2**]/[palladium]/[ligand] = 40:20:1:1. [e] Isolated yield after transformation to **3b** by tosylation of **3a**.

2. Such behaviour was also noticed by Hayashi and co-workers [6] and Achiwa and co-workers [8] in the reaction of aminoalcohols with (*Z*)-1,4-bis[(methoxycarbonyl)oxy]but-2-ene **2**. The use of (*S*,*S*)-DIOP as the ligand gave higher chemical yields but again very disappointing enantioselectivity (entry 4). The diphosphines (*S*,*S*)-BPPM, (*S*)-BINAP, (*R*)-BIPHEMP and (*S*)-MeOBIPHEP gave higher enantioselectivities, up to 32% for (*S*,*S*)-BPPM and (*R*)-BIPHEMP. It is to be noticed that an ee of only 8% was obtained using (*S*)-BINAP as the ligand in the cyclisation of 2-(benzylamino)phenol and **2** under the same conditions [8], indicating the very important influence of the substituent at the nitrogen on the enantioselectivity [6]. Finally the most enantioselective phosphine ligand in this cyclisation was Trost's ligand which gave ee up to 79% (entry 12), which is the highest value obtained to date in this cyclisation reaction.

We also performed the cyclisation on the free 2-aminophenol **1a** using (*S*)-BINAP, (*R*)-BIPHEMP and (*S*)-MeOBIPHEP as the chiral ligands, the chemical yields and enantioselectivities being determined after transformation into the *N*-tosyl derivative **3b**. We noticed a huge increase in enantioselectivity for (*S*)-BINAP and (*S*)-MeOBIPHEP going from the *N*-tosyl derivative **1b** to the amino derivative **1a**: 16 to 53% for (*S*)-MeOBIPHEP and 24 to 78% for (*S*)-BINAP. On the other hand, (*R*)-BIPHEMP gave the same selectivities with **1a** and **1b**. These results indicated again the crucial influence of the substituent at the nitrogen on the enantioselectivity of the cyclisation.

It is to be noticed that the cyclisation of 2-(mesylamino)phenol **1c** with **2** in the presence of palladium(0) complex associated with (*S*)-BINAP gave the cyclised compound **4** in 20% chemical yield and only 6% enantioselectivity, against 24% for the *N*-tosyl derivative.

The absolute configuration of 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazines **3a** and **3b** was determined by correlation with the known 4-benzyl-2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine **3e** (scheme 4) [8]. Compound **3a** obtained from cyclisation reaction in the presence of (*R*)-BIPHEMP was readily converted into the *N*-benzyl derivative **3e** by refluxing with benzyl chloride in the presence of sodium carbonate in water. The obtained compound turned out to be the (*R*) isomer by measurement of the optical rotation [**3e**: $[\alpha]_{\mathrm{D}}^{20}$ −6.6 (*c* 0.5, chloroform); lit [8] for (*R*) **3e** $[\alpha]_{\mathrm{D}}^{23}$ −10.5 (*c* 1, chloroform)]. It follows that vinyl benzomorpholine **3a** obtained by the asymmetric cyclisation using (*R*)-BIPHEMP as the chiral ligand has the absolute configuration (*R*). The same 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine **3a** of configuration (*R*) was then transformed to the *N*-tosyl derivative by treatment by TsCl in pyridine for the determination of the configuration of compound **3b**.



Scheme 4

In conclusion we have shown that asymmetric palladium(0) catalysed cyclisation of *N*-substituted 2-aminophenol with (*Z*)-1,4-bis[(methoxycarbonyl)oxy]-but-2-ene occurred with ee up to 79% by a judicious choice of the substituent at the nitrogen and the chiral ligand.

Experimental section

^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were measured on a Brüker AM 200 spectrometer in $CDCl_3$ solution. Chemical shifts are reported in δ ppm referred to $SiMe_4$ as an internal standard. Optical rotations were determined on a Perkin-Elmer 241 polarimeter. EI-mass spectra were recorded on a Nermag R10 spectrometer at an ionization voltage of 70 eV. Silica gel column chromatography was carried out using Merck silica gel 60 Gerudan (40–63 μm). Analytical HPLC was performed on a Shimadzu instrument and a UV detector. Cyclisation reactions were carried out in Schlenk tubes under an inert atmosphere. Tetrahydrofuran (THF) was distilled from sodium-benzophenone and stored under argon and all chromatography solvents were distilled prior to use.

2-Aminophenol, tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$], 1,4-bis(diphenylphosphino)butane (DPPB), (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane (CHIRAPHOS), (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (BDPP), (2*S*,3*S*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP), (2*S*,4*S*)-1-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-pyrrolidine (BPPM), and (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphtyl (BINAP) were purchased from the Aldrich Chemical Co. (2*R*,3*R*)-2,3-bis(diphenylphosphino)bicyclo-[2.2.1]hept-5-ene (NORPHOS) was a gift from Prof Brunner (Regensburg, Germany). (*R*)-2,2′-bis(diphenylphosphino)-6,6′-dimethyl-1,1′-biphenyl (BIPHEMP) and (*S*)-2,2′-bis-(diphenylphosphino)-6,6′-dimethoxy-1,1′-biphenyl (MeO-BIPHEP) were gifts from Dr Schmidt (Hofmann la Roche, Bale, Swizerland); **6** was prepared according to the Trost procedure [11]. *N*-tosyl 2-aminophenol **1b** [12], 2-(mesylamino)phenol **1c** [13] and (*Z*)-1,4-bis[(methoxycarbonyl)oxy]but-2-ene **2** [14] were prepared according to the literature methods.

Typical procedure for the cyclisation of 2-aminophenol **1a** *with (Z)-1,4-bis[(methoxycarbonyl)oxy]but-2-ene* **2**

To a solution of $Pd_2(dba)_3$ (11.2 mg, 0.012 mmol, 1 equiv) and the diphosphine (0.025 mmol, 1 equiv) in THF (3 mL) was added a solution of 2-aminophenol **1a** (133 mg, 1.22 mmol, 50 equiv) and (*Z*)-1,4-bis[(methoxycarbonyl)oxy]but-2-ene **2** (124.7 mg, 0.61 mmol, 25 equiv) in THF (3 mL). After stirring at room temperature for 24 h the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (hexane/ethyl acetate 3:1) to give the cyclised product **3a** and compound **5**.

2-Vinyl-3,4-dihydro-2H-1,4-benzoxazine **3a**

Oil; R_f 0.5 (hexane/ethyl acetate 3:1).
IR (film): 3 500–3 300, 3 080, 3 020, 1 645, 1 260 cm^{-1}.
^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.15 (dd, J = 11.7 and 7.7 Hz, 1H, H-3), 3.35 (dd, J = 11.7 and 2.6 Hz, 1H, H-3), 3.70 (bs, 1H, NH), 4.55 (dddt, J = 7.7, 5.7, 2.6 and 1.3 Hz, 1H, H-2), 5.22 (dd, J = 10.5 and 1.3 Hz, 1H, =CH_2), 5.42 (dd, J = 17.3 and 1.3 Hz, 1H, =CH_2), 5.90 (ddd, J = 17.3, 10.5 and 5.7 Hz, 1H, -CH=CH_2), 6.50–6.90 (m, 4H, arom).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 45.44, 74.39, 115.47, 116.82, 117.67, 118.92, 121.21, 132.98, 134.95, 149.66.
Anal calc for $C_{10}H_{11}NO$: C, 74.51; H, 6.88. Found: C, 74.56; H, 6.82.

(E)-1,4-Bis(2-vinyl-3,4-dihydro-2H-1,4-benzoxazin-4-yl)but-2-ene **5**

Oil; R_f 0.65 (hexane/ethyl acetate 3:1).
IR (film): 3 080, 3 020, 1 645, 1 260 cm^{-1}.
^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.07 (dd, J = 11.7 and 7.8 Hz, 2H, H-3), 3.22 (dd, J = 11.7 and 2.7 Hz, 2H, H-3), 3.85 (m, 4H, H-1, H-4), 4.62 (dddt, J = 7.8, 5.8, 2.7 and 1.3 Hz, 2H, H-2, H-3), 5.27 (ddd, J = 10.5, 1.3 and 1.3 Hz, 2H, =CH_2), 5.45 (ddd, J = 17.3, 1.3 and 1.3 Hz, 2H, =CH_2), 5.70 (m, 2H, H-2, H-3), 5.92 (ddd, J = 17.3, 10.5 and 5.8 Hz, 2H, -CH=CH_2), 6.55–6.90 (m, 8H, arom).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 51.23, 52.78, 73.84, 112.50, 116.50, 117.75, 118.00, 121.42, 127.99, 134.37, 134.91, 143.82.

MS (EI, 70 eV): m/z (%) 374 ($M^{+\cdot}$, 76), 214 (49), 213 (14), 174 (11), 172 (12), 160 (27), 159 (10), 158 (11), 132 (13), 131 (10), 130 (12), 120 (29), 117 (11), 115 (10), 93 (11), 91 (10), 79 (10), 77 (20), 65 (19), 55 (30), 54 (14), 53 (16), 51 (13), 41 (100).

Anal calc for $C_{24}H_{26}N_2O$: C, 76.95; H, 6.99. Found: C, 77.23; H, 6.89.

Typical procedure for the cyclisation of 2-(tosyl or mesylamino)phenol **1b** *and* **1c** *with (Z)-1,4-bis[(methoxycarbonyl)oxy]but-2-ene* **2**

To a solution of $Pd_2(dba)_3$ (11.2 mg, 0.012 mmol, 1 equiv) and the diphosphine (0.025 mmol, 1 equiv) in THF (3 mL) was added a solution of 2-(tosylamino)phenol **1b** (160 mg, 0.61 mmol, 25 equiv) or of 2-(mesylamino)phenol **1c** (114 mg, 0.61 mmol, 25 equiv) and (*Z*)-1,4-bis[(methoxycarbonyl)oxy]but-2-ene **2** (124.7 mg, 0.61 mmol, 25 equiv) in THF (3 mL). After stirring at room temperature for 24 h, the solvent was removed in vacuo and the residue was chromatographed on silica gel to give the cyclised product **3b** or **4**. The enantiomeric excess of compound **3b** was determined by HPLC analysis (CHIRALPAK AD, *n*-hexane/propan-2-ol = 95:5, flow rate 0.5 mL/mn, concentration 0.2 mg/mL, detection UV-225 nm).

4-Tosyl-2-vinyl-3,4-dihydro-2H-1,4-benzoxazine **3b**

Solid; Mp 143–145 °C; R_f 0.6 (hexane/ethyl acetate 2:1); $[\alpha]_D^{20}$ +22.7 (*c* 1, chloroform) for entry 7 for 78% ee.

IR (film): 3 080, 3 020, 1 645, 1 260 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.40 (s, 3H, CH_3), 3.15 (dd, J = 14.5 and 10.0 Hz, 1H, H-3), 3.70–3.84 (m, 1H, H-2), 4.27 (dd, J = 14.5 and 2.5 Hz, 1H, H-3), 5.28 (d, J = 10.4 Hz, 1H, $=CH_2$), 5.32 (d, J = 17.3 Hz, 1H, $=CH_2$), 5.75 (ddd, J = 17.3, 10.4 and 5.8 Hz, 1H, $-CH=CH_2$), 6.80–7.85 (m, 8H, arom).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 21.54, 48.32, 78.11, 118.72, 117.51, 120.92, 123.39, 124.49, 126.24, 127.20 (double intensity), 129.92 (double intensity), 133.24, 135.51, 144.35, 146.75.

Anal calc for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43. Found: C, 64.35; H, 5.45.

4-Mesyl-3-vinyl-3,4-dihydro-2H-1,4-benzoxazine **4**

Oil; R_f 0.6 (hexane/ethyl acetate 3:1).

IR (film) 3 080, 3 020, 1 645, 1 600, 1 330, 1 170 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.01 (s, 3H, CH_3), 4.18 (dd, J = 11.2 and 2.8 Hz, 1H, H-2), 4.39 (dd, J = 11.2 and 1.8 Hz, 1H, H-2), 4.99 (m, 1H, H-3), 5.27 (dd, J = 10.3 and 1.0 Hz, 1H, $=CH_2$), 5.39 (dd, J = 17.2 and 1.0 Hz, 1H, $=CH_2$), 5.85 (ddd, J = 17.2, 10.3 and 5.7 Hz, 1H, $-CH=CH_2$), 6.90–7.70 (m, 4H, arom).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 39.55, 55.08, 67.35, 117.88, 119.23, 121.79, 121.82, 123.44, 125.28, 132.64, 145.52.

MS (EI, 70 eV): m/z (%) 239 ($M^{+\cdot}$, 49), 160 (100), 132 (19), 77 (20), 51 (16), 41 (32).

Determination of the configuration of compounds **3a** *and* **3b**

The 2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine **3a** (50 mg, 0.31 mmol, 1 equiv) obtained by cyclisation reaction using (*R*)-BIPHEMP as the chiral ligand, was mixed with $NaHCO_3$ (688 mg, 8.2 mmol, 25 equiv), H_2O (1 mL) and benzyl chloride (64.8 mg, 0.51 mmol, 1.6 equiv) and refluxed for 1 h. After cooling, the solution was washed with water and dried. Evaporation of the solvent gave the 4-benzyl-2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine **3e** in 52% yield (40 mg). The observed rotation $[\alpha]_D^{20}$ −6.6 (*c* 0.5, chloroform) allowed us to ascribe the (*R*) configuration to the major enantiomer of **3a**.

Alternatively, compound **3a** (50 mg, 0.31 mmol, 1 equiv) and pyridine (60 mg, 0.76 mmol, 2.5 equiv) were dissolved in dichloromethane (2 mL). After addition of tosyl chloride (60 mg, 0.31 mmol, 1 equiv) at 0 °C and stirring for 3 h, the solution was hydrolysed with water (1 mL) and the organic phase was washed with water and dried. Evaporation of the solvent gave 81 mg of 4-tosyl-2-vinyl-3,4-dihydro-2*H*-1,4-benzoxazine **3b** (71% yield), the configuration of the major enantiomer being (*R*).

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