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An Organocatalyst Bearing Stereogenic Carbon and Sulfur Centers as an Efficient Promoter for Enantioselective Hydrosilylation of 1,4-Benzooxazines

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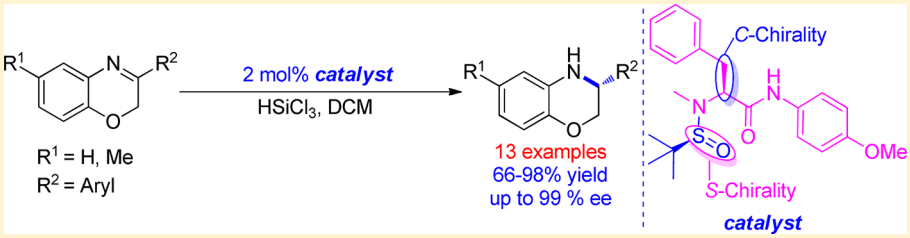
Supporting Information



ABSTRACT: The efficient and enantioselective hydrosilylation of 3-aryl-1,4-benzooxazines was achieved using an L-phenyl alanine derived new Lewis base catalyst bearing stereogenic carbon and sulfur centers. In the presence of 2 mol % of catalyst, a broad range of 3-aryl-1,4-benzooxazines were hydrosilylated to afford the corresponding chiral 3-aryl-3,4-dihydro-2*H*-1,4-benzooxazine products with good to high yields (66−98%) and enantioselectivities (70−99% ee). This method provides an alternative approach with great practical application potential to access chiral 3-aryl-3,4-dihydro-2*H*-1,4-benzooxazines.

Chiral 3-substituted 3,4-dihydro-2*H*-1,4-benzooxazine is an important structural motif that has been frequently seen in biologically interesting natural products such as Obscurinervidine and Niblinine and synthetic chiral drugs such as Levofloxacin (Figure 1).[1,2] The development of methods for the preparation of such types of compounds has attracted remarkable attention in the past few decades.[3−5] The currently available methods to access enantioenriched 3-substituted 3,4-dihydro-2*H*-1,4- benzooxazines mainly rely on kinetic resolution[3] and stoichiometric synthesis.[4] There are only a few catalytic asymmetric versions. Satoh[5a] and Zhou[5b−d] developed transition-metal-catalyzed asymmetric reduction of 1,4-benzooxazines as an efficient method, which furnished various 3-substituted 3,4-dihydro-2*H*-1,4-benzooxazines in excellent enantioselectivity. Rueping[6a,b] and Thomas[6c] devised an organocatalytic version using chiral phosphoric acids as catalysts and Hantszch esters as reductants and also achieved excellent results. Recently, Zhang has tried to implement similar transformations via the more cost-efficient organocatalytic hydrosilylation approach that utilizes trichlorosilane as the reductant and *trans*-4-hydroxy-L-proline derived Lewis base **3** (Figure 1) as the catalyst.[7] This method, however, was found to only afford low to moderate enantioselectivities (<76% ee in most cases, 87% ee in only one case) after a range of 1,4-benzooxazine substrates (**1**) were examined. An earlier attempt by Malkov and Kočovský using L-valine derived Lewis base **4** to catalyze the hydrosilylation of **1a** (R^1 = H, R^2 = Ph) also resulted in low enantioselectivity (25% ee).[8]

Given the attractiveness of organocatalytic asymmetric hydrosilylation from the viewpoints of practical application and economy, it is desirable to search for catalysts that could furnish high enantioselectivity for the hydrosilylation of 1,4-benzooxazine, ideally with low catalyst loading. In recent years, we have made quite good progress in devising Lewis base organocatalysts for asymmetric hydrosilylations.[9,10] As part of our continuing efforts in this field, we have successfully developed a highly efficient new catalyst that could promote the hydrosilylation of a broad range of 1,4-benzooxazines and afford the corresponding 3-substituted 3,4-dihydro-2*H*-1,4-benzooxazines in high yield and good to high enantioselectivity (Scheme 1). Herein, we wish to report the results.

Since our previously developed *S*-chiral sulfinamide type catalysts have shown exceptional reactivity and enantioselectivity,[9a,f−h,j] we first checked the efficacies of these catalysts in a model reaction of **1a**. The *N*-sulfinyl L-prolinamide **5**, a hybridized catalyst that bears both chiral carbon and sulfur centers and has been demonstrated to be highly enantioselective for the hydrosilylation of *β*-enamino esters,[9i] was found to give promising results. It smoothly drove the reaction to completion and afforded the desired product **2a** with 92% yield and 59% ee (Table 1, entry 1). Although such results are on the same mediocre level as those obtained with Zhang's catalyst **3**,[7] we anticipated that a highly efficient catalyst might be developed out of this special type of catalyst if a stereochemi-

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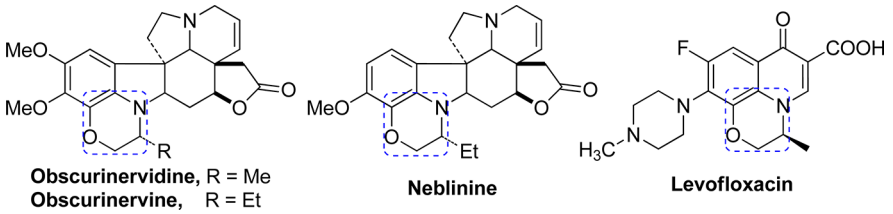

Figure 1. Natural products and drugs containing a chiral benzooxazine scaffold.

Scheme 1. Lewis Base Catalyzed Asymmetric Hydrosilylation of 1,4-Benzooxazines

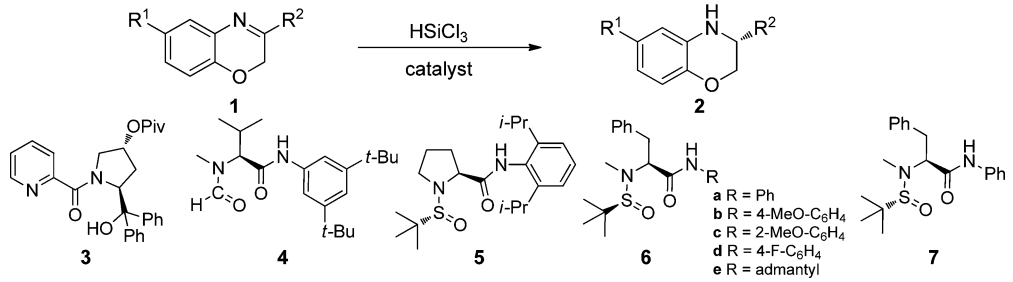

Table 1. Asymmetric Hydrosilylation of 1,4-Benzooxazine 1a[a]

entry	catalyst (amt (mol %))	temp (°C)	solvent	yield (%)[b]	ee (%)[c]
1	**5** (20)	−20	DCM	92	59
2	**6a** (20)	−20	DCM	97	89
3	**6b** (20)	−20	DCM	98	91
4	**6c** (20)	−20	DCM	64	25
5	**6d** (20)	−20	DCM	96	90
6	**6e** (20)	−20	DCM	87	70
7	**7** (20)	−20	DCM	87	22
8	**6b** (20)	−10	DCM	70	72
9	**6b** (20)	−40	DCM	96	93
10	**6b** (10)	-40	**DCM**	**90**	**93**
11[d]	**6b** (2)	−40	DCM	96	93
12[d]	**6b** (2)	−40	$CHCl_3$	90	90
13[d]	**6b** (2)	−40	toluene	92	79
14[d]	**6b** (2)	−40	CH_3CN	79	49

[a]Unless otherwise noted, the reactions were performed with **1a** (0.1 mmol) and $HSiCl_3$ (0.3 mmol) in solvent at the designated temperature for 36 h. [b]Isolated yield. [c]Determined by HPLC with a chiral stationary phase. The product **2a** was determined to have an *R* configuration by comparison of the optical rotation with the literature data. [d]The reaction time is 48 h. If the reaction time is 24 h, the yield is lower by about 20%, albeit with unaffected ee.

cally better matching skeleton was used. We first turned to the noncyclic L-phenylalanine skeleton and prepared the analogous new catalyst **6a** (see the Supporting Information for its synthesis and the absolute stereochemistry determination by X-ray crystallography). Delightfully, it exhibited significantly enhanced enantioselectivity. The ee value reaches 89% (entry 2). The set of analogues **6b−e** derived from different amines were then prepared to explore if the catalytic efficacy could be further improved by changing the side amide group. **6b**, bearing a *p*-methoxyphenyl group, brought the ee value up to 91% (entry 3). When the *p*-methoxyphenyl group was switched to an *o*-methoxyphenyl group (**6c**), a substantial drop in enantioselectivity was observed (entry 4). When this group was further replaced with an aliphatic adamantyl group (**6e**), both the enantioselectivity and the reactivity were dramatically decreased (entry 6). Notably, catalyst **7**, the diastereomer of **6a** with opposite stereochemistry on the sulfur atom, exhibited much lower enantioselectivity (entry 7), indicating that a stereochemical match between the carbon center and the sulfur center in the catalyst is crucial for the enantiocontrol.

Next, we tested different reaction conditions in the **6b**-catalyzed hydrosilylation of **1a** to optimize the catalytic performance. While raising the reaction temperature from −20 to −10 °C caused significant loss of reactivity and enantioselectivity (entry 8),[11] a slight increase in enantioselectivity was observed when the temperature was lowered from −20 to −40 °C (entry 9). The reaction proceeded equally well when the catalyst loading was decreased from 20 to 10 mol % (entry 10). *Even with a further lowered catalyst loading of 2 mol %, the reaction could still retain the excellent enantioselectivity* and only needs slightly longer time for completion (entry 11). Solvent screening indicated that chloroform is almost as good as dichloromethane (entry 12), whereas toluene and acetonitrile are much less effective (entries 13 and 14).

With the optimized conditions in hand, we then explored the substrate scope of the present reaction system. A broad range of 3-aryl-1,4-benzooxazines **1** were tested in the presence of 2 mol % of **6b**. The results are summarized in Table 2. Substrates **1a−j**, bearing 3-aryl groups (R^2) with different electronic properties, were smoothly hydrosilylated to give the desired 3-aryl-3,4-dihydro-2*H*-1,4-benzooxazine products (**2a−j**) in good to high yield (66−98%) and good to high enantioselectivity (81−99% ee, entries 1−10). For the substrate **1k** bearing a relatively electron deficient 3-*p*-(trifluoromethyl)-phenyl group, only moderate yield and enantioselectivity were achieved (entry 11). Notably, **1l** with a 3,2′-thienyl group also proved to be a good substrate, affording 97% yield and 90% ee (entry 12). In addition, substrates bearing a substituent such as methyl on the 6-position (**1m**) were also found to be tolerable, furnishing 79% yield and 90% ee (entry 13). It should be pointed out that substrates bearing a 3-alkyl group such as 3-methyl- and 3-isopropyl-1,4-benzooxazines proved to be not suitable substrates, due to their poor stablility under the present reaction conditions.

Although further experiments are still needed to rationalize the high efficiency of the present catalyst system for the

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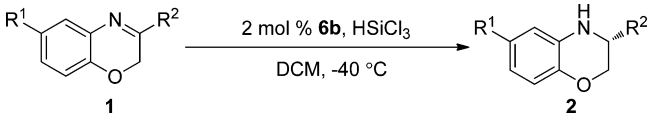
Table 2. 6b-Catalyzed Asymmetric Hydrosilylation of Various 1,4-Benzooxazines[a]



entry	substrate R[1]	substrate R[2]		yield (%)[b]	ee (%)[c]
1	H	Ph	**1a**	96	93
2	H	*p*-MeO-Ph	**1b**	93	83
3	H	*p*-Me-Ph	**1c**	97	92
4	H	*p*-BnO-Ph	**1d**	88	92
5	H	*p*-F-Ph	**1e**	97	86
6	H	*p*-Cl-Ph	**1f**	91	80
7	H	*m*-Cl-Ph	**1g**	98	83
8	H	*o*-Cl-Ph	**1h**	93	99
9	H	1-naphthyl	**1i**	66	95
10	H	2-naphthyl	**1j**	68	92
11	H	*p*-CF_3-Ph	**1k**	74	70
12	H	2-thienyl	**1l**	97	90
13	6-Me	Ph	**1m**	79	97

[a]Unless otherwise noted, the reactions were performed with **1** (0.1 mmol), **6b** (0.02 mol), and $HSiCl_3$ (0.3 mmol) in DCM (1 mL) at −40 °C for 48 h. [b]Isolated yield. [c]Determined by HPLC with a chiral stationary phase.

hydrosilylation of 3-aryl-1,4-benzooxazines in comparison to others, the following structural features of the catalyst are certainly critical contributors: (1) the Lewis basic *S*-chiral *tert*-butylsulfinyl group, which has been previously demonstrated to be an exceptionally powerful Lewis base activator,[9g,h] (2) the combination of the chiral sulfur and carbon centers, which endows the catalyst with excellent asymmetric induction capability, and (3) the acyclic L-phenylalanine backbone, which matches well with the cyclic structure of the substrate, in contrast to catalyst **5** bearing a cyclic L-proline backbone, which was previously shown to be an excellent catalyst for acyclic substrates[9c,f−h,j] but is apparently much less suitable for the present cyclic substrate system.

In conclusion, we have developed the asymmetric hydrosilylation of 3-aryl-1,4-benzooxazines into a highly efficient and enantioselective method for the construction of chiral 3-aryl-3,4-dihydro-2*H*-1,4-benzooxazines using a newly synthesized catalyst based on L-phenylalanine with both chiral carbon and sulfur centers. With a remarkably low catalyst loading, a broad range of 3-aryl-1,4-benzooxazines were hydrosilylated to afford the corresponding chiral 3-aryl-3,4-dihydro-2*H*-1,4-benzooxazine products with generally high yields and enantioselectivities. This method provides an alternative approach with great practical application potential to access chiral 3-aryl-3,4-dihydro-2*H*-1,4-benzooxazines.

EXPERIMENTAL SECTION

General Experimental Methods. All starting materials were of the highest commercially available grade and were used without further purification. All reactions were performed under an argon (Ar) atmosphere unless otherwise specified. All solvents used in the reactions were dried and distilled according to the standard procedure prior to use, and other chemicals were purchased and used as received. Substrates **1a**,[5c,d,6a,7] **1b**,[6a,7] **1c**,[5c,d,6a,7] **1d**,[7] **1e**,[5c,d,6a,7] **1f**,[5c,d] **1g**,[5d,6a,7] **1h**,[7] **1j**,[5c] **1k**,[5d] and **1l**,[7] products **2a**,[5c,d,6a,7] **2b**,[6a,7] **2c**,[5c,d,6a,7] **2d**,[7] **2e**,[5c,d,6a,7] **2f**,[5c,d] **2g**,[5d,7] **2h**,[7] **2j**,[5c] **2k**,[5d] and **2l**,[7] and catalyst **5**[9g,h] are known compounds.

General Procedure for the Synthesis of Catalysts 6 and 7. Catalysts **6** and **7** were synthesized according to our previously reported procedures.[9g,h]

*(S)-2-((S)-N-2-Dimethylpropan-2-ylsulfinamido)-N-3-diphenylpropanamide (**6a**):* white solid, mp 90−92 °C; $[\alpha]_D^{20}$ = −144.0° (*c* = 0.416, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.44 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.34−7.18 (m, 7H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.45 (dd, *J* = 4.3, 11.5 Hz, 1H), 3.71 (dd, *J* = 4.3, 14.8 Hz, 1H), 2.89 (dd, *J* = 11.5, 14.8 Hz, 1H), 2.69 (s, 3H), 0.91 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 168.5, 138.5, 138.2, 129.1, 128.9, 128.6, 126.6, 124.3, 119.6, 72.7, 59.1, 35.2, 27.2, 23.5; ESI HRMS exact mass calcd for $(C_{20}H_{26}N_2O_2S + Na)^+$ *m*/*z* 381.1607, found *m*/*z* 381.1613; IR (KBr) 3267 (m), 3060 (m), 2961 (m), 1691 (s), 1626 (m), 1557 (m), 1498 (m), 1428 (m), 1132 (m), 1045 (m), 877 (s), 843 (s), 754 (s), 712 (s) cm^{-1}.

*(S)-2-((S)-N-2-Dimethylpropan-2-ylsulfinamido)-N-(4-methoxyphenyl)-3-phenylpropanamide (**6b**):* yellow solid, mp 120−122 °C; $[\alpha]_D^{20}$ = −120.8° (*c* = 0.36, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.30 (s, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.32−7.18 (m, 5H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.44 (dd, *J* = 4.2, 11.5 Hz, 1H), 3.79 (s, 3H), 3.71 (dd, *J* = 4.2, 14.8 Hz, 1H), 2.88 (dd, *J* = 11.6, 14.7 Hz, 1H), 2.68 (s, 3H), 0.90 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 168.1, 156.3, 138.6, 131.4, 129.1, 128.6, 126.6, 121.2, 114.0, 72.5, 59.1, 55.5, 35.2, 27.1, 23.5; ESI HRMS exact mass calcd for $(C_{21}H_{28}N_2O_3S + Na)^+$ *m*/*z* 411.1713, found *m*/*z* 411.1712; IR (KBr) 3249 (m), 3330 (m), 2952 (m), 1679 (s), 1595 (m), 1538 (m), 1453 (m), 1305 (m), 1033 (m), 940 (s), 918 (s), 880 (s), 745 (s), 705 (s) cm^{-1}.

*(S)-2-((S)-N-2-Dimethylpropan-2-ylsulfinamido)-N-(2-methoxyphenyl)-3-phenylpropanamide (**6c**):* yellow solid, mp 90−92 °C; $[\alpha]_D^{20}$ = −86.3° (*c* = 0.454, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.74 (s, 1H), 8.23 (dd, *J* = 1.3, 7.9 Hz, 1H), 7.30−7.20 (m, 5H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.38 (dd, *J* = 6.1, 8.8 Hz, 1H), 3.86 (s, 3H), 3.58 (dd, *J* = 6.1, 14.3 Hz, 1H), 2.99 (dd, *J* = 8.8, 14.2 Hz, 1H), 2.79 (s, 3H), 0.99 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 168.6, 149.1, 138.4, 129.3, 128.6, 127.2, 126.6, 124.5, 121.0, 120.7, 110.4, 69.4, 58.8, 55.9, 36.2, 28.6, 23.2; ESI HRMS exact mass calcd for $(C_{21}H_{28}N_2O_3S + Na)^+$ *m*/*z* 411.1713, found *m*/*z* 411.1719; IR (KBr) 3311 (m), 2930 (m), 1680 (s), 1626 (m), 1600 (m), 1557 (m), 1429 (m), 1334 (s), 1230 (m), 1116 (m), 1030 (m), 883 (s), 746 (s), 712 (s) cm^{-1}.

*(S)-2-((S)-N-2-Dimethylpropan-2-ylsulfinamido)-N-(4-fluorophenyl)-3-phenylpropanamide (**6d**):* yellow solid, mp 80−85 °C; $[\alpha]_D^{20}$ = −125.9° (*c* = 0.686, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.49 (s, 1H), 7.64−7.59 (m, 2H), 7.32−7.21 (m, 5H), 7.00 (t, *J* = 8.7 Hz, 2H), 4.44 (dd, *J* = 4.3, 11.5 Hz, 1H), 3.69 (dd, *J* = 4.3, 14.8 Hz, 1H), 2.88 (dd, *J* = 11.6, 14.8 Hz, 1H), 2.68 (s, 3H), 0.91 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 168.40, 159.3 (*J* = 241.6), 138.4, 134.2, 129.1, 128.6, 126.7, 121.2 (*J* = 7.8 Hz), 115.5 (*J* = 22.3 Hz), 72.6, 59.1, 35.2, 27.1, 23.5; ESI HRMS exact mass calcd for $(C_{20}H_{25}FN_2O_2S + Na)^+$ requires *m*/*z* 399.1513, found *m*/*z* 399.1516; IR (KBr) 3273 (m), 3063 (m), 2960 (m), 2927 (m), 1690 (s), 1557 (m), 1434 (m), 1213 (s), 1157(m), 1101 (m), 1044 (m), 923 (s), 747 (s), 712 (s) cm^{-1}.

*(S)-N-((3R,5R,7R)-Adamantan-1-yl)-2-((S)-N-2-dimethylpropan-2-ylsulfinamido)-3-phenylpropanamide (**6e**):* white solid, mp 85−86 °C; $[\alpha]_D^{20}$ = −106.8° (*c* = 0.56, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.26−7.14 (m, 5H), 7.04 (s, 1H), 4.19 (dd, *J* = 4.4, 11.4 Hz, 1H), 3.57 (dd, *J* = 4.4, 14.7 Hz, 1H), 2.77 (dd, *J* = 11.6, 14.8 Hz, 1H), 2.61 (s, 3H), 2.05 (s, 9H), 1.67 (s, 6H), 0.84 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 168.8, 139.0, 129.1, 128.5, 126.4, 72.1, 59.0, 52.3, 41.3, 36.4, 35.2, 29.4, 26.8, 23.4; ESI HRMS exact mass calcd for $(C_{24}H_{36}N_2O_2S + Na)^+$ *m*/*z* 439.2390, found *m*/*z* 439.2385; IR (KBr) 3460 (w), 3270 (s), 2901 (s), 2850 (m), 1674 (s), 1557 (m), 1434 (m), 1359 (s), 1186(m), 1102 (m), 1042 (m), 864 (s), 703 (m) cm^{-1}.

*(S)-2-((R)-N,2-dimethylpropan-2-ylsulfinamido)-N,3-diphenylpropanamide (**7**):* white solid; $[\alpha]_D^{20}$ = −124.0° (*c* = 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.63 (s, 1H), 7.58−7.57 (m, 2H), 7.29−7.27 (m, 6H), 7.22−7.19 (m, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 4.45 (dd, *J* = 5.3, 9.2 Hz, 1H), 3.65 (dd, *J* = 9.2, 14.0 Hz, 1H), 2.89 (s, 3H),

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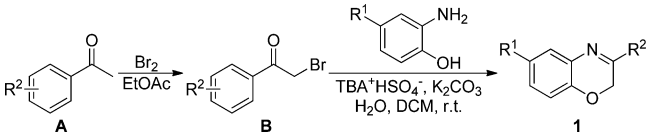
2.88 (dd, J = 5.3, 14.1 Hz, 1H), 1.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm); 167.4, 138.3, 137.8, 129.6, 128.8, 128.5, 126.7, 123.9, 119.3, 59.1, 36.1, 35.1, 22.7; ESI HRMS exact mass calcd for $(C_{20}H_{26}N_2O_2S + Na)^+$ m/z 381.1607, found m/z 381.1613; IR (KBr) 3274 (m), 3061 (m), 2960 (s), 1683 (s), 1557 (s), 1497 (m), 1313 (s), 1251(s), 1135 (m), 1037 (s), 879(s), 754 (s), 711 (m) cm^{-1}.

General Procedure for the Synthesis of Substrates 1.[12] To a solution of aryl methyl ketone **A** (10 mmol) in ethyl acetate (20 mL)



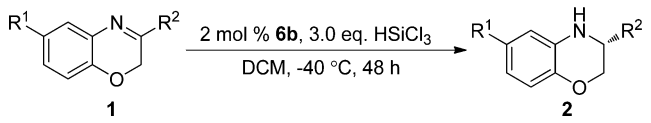
was slowly added a solution of bromine (0.51 mL, 10 mmol) in ethyl acetate (20 mL) at ambient temperature. After completion of the reaction, the mixture was extracted with DCM. The combined extracts were washed with water and dried over anhydrous sodium sulfate. Solvents were evaporated under vacuum. Purification by flash column chromatography (silica gel, hexane/EtOAc) afforded pure product **B**.

To a stirred biphasic solution of *o*-aminophenol (10 mmol), sodium carbonate (2.12 g, 20 mmol), and tetra-*n*-butylammonium hydrosulfate (169.77 mg, 0.5 mmol) in DCM and H_2O (50 and 20 mL, respectively) was added a solution of α-brominated aryl methyl ketone (10 mmol) in DCM (20 mL) at room temperature. The reaction mixture was stirred for 24 h at the same temperature and was then extracted with DCM. The combined extracts were washed with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was purified by flash column chromatography to afford pure product **1**.

*3-(Naphthalen-1-yl)-2H-benzo[b][1,4]oxazine (**1i**):* yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.43 (d, J = 7.6 Hz, 1H), 7.94 (t, J = 7.6 Hz, 2H), 7.61−7.46 (m, 5H), 7.10 (t, J = 7.9 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H), 4.97 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 161.8, 146.4, 134.4, 133.9, 130.6, 130.4, 129.7, 128.9, 128.6, 127.8, 127.2, 126.3, 126.1, 125.4, 124.9, 122.5, 115.7, 65.6; ESI HRMS exact mass calcd for $(C_{18}H_{13}NO + H)^+$ m/z 260.1070, found m/z 260.1070; IR (KBr) 2923 (m), 1609 (m), 1499 (m), 1312 (s), 1277 (s), 1211 (s), 1057 (m), 884 (s), 753 (s) cm^{-1}.

*6-Methyl-3-phenyl-2H-benzo[b][1,4]oxazine (**1m**):* yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.96−7.92 (m, 2H), 7.51−7.50 (m, 3H), 7.29 (s, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 5.05 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 158.7, 144.0, 135.5, 133.5, 131.7, 131.0, 129.1, 128.7, 128.1 126.4, 115.1, 62.9, 20.6; ESI HRMS exact mass calcd for $(C_{15}H_{13}NO + H)^+$ m/z 224.1070, found m/z 224.1070; IR (KBr) 2924 (m), 1606 (m), 1480 (m), 1313 (s), 1256 (s), 1184 (s), 1065 (s), 1026 (s), 884 (s), 753 (s) cm^{-1}.

General Procedure for the Asymmetric Hydrosilylation of Benzooxazines 1. To a stirred solution of benzooxazine **1** (0.1



mmol) and catalyst **6b** (0.8 mg, 0.002 mmol) in anhydrous DCM (1.0 mL) was added trichlorosilane (30 μL, 0.3 mmol) dropwise via syringe at −40 °C. The mixture was stirred at the same temperature for 48 h. The reaction mixture was then quenched with water and extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was purified through column chromatography to afford the desired product **2**. The ee values were determined using established HPLC techniques with chiral columns.

*(R)-3-(Naphthalen-1-yl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2i**):* yellow oil; 14.6 mg (56% yield); $[\alpha]_D^{20}$ = −32.1° (c = 0.19, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.19 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 7.1 Hz, 1H), 7.60−7.49 (m, 3H), 6.93−6.84 (m, 2H), 6.78−6.73 (m, 2H), 5.37 (dd, J = 2.3, 8.3 Hz, 1H), 4.53 (dd, J = 2.5, 10.7 Hz, 1H), 4.13 (dd, J = 8.5, 10.7 Hz, 1H), 4.05 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.7, 134.4, 134.1, 133.9, 130.9, 129.2, 128.6, 126.6, 125.8, 125.6, 124.5, 122.3, 121.5, 119.1, 116.7, 115.6, 70.2, 50.1; ESI HRMS exact mass calcd for $(C_{18}H_{15}NO + H)^+$ m/z 262.1226, found m/z 262.1221; IR (KBr) 3363 (w), 2923 (m), 1609 (m), 1499 (m), 1312 (s), 1277 (s), 1211 (s), 1057 (m), 884 (s), 753 (s) cm^{-1}. The enantiomers were analyzed by HPLC using a chiral OD-H column (*n*-hexane/2-propanol 90/10, flow rate 1.0 mL/min, λ 254 nm): minor enantiomer, t_R = 38.5 min; major enantiomer, t_R = 24.1 min; 95% ee.

*(R)-6-Methyl-3-phenyl-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2m**):* yellow oil; 17.8 mg (79% yield); $[\alpha]_D^{20}$ = −31.0° (c = 0.258, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.41−7.34 (m, 5H), 6.75 (d, J = 8.7 Hz, 1H), 6.51 (d, J = 8.7 Hz, 1H), 6.50 (s, 1H), 4.51 (dd, J = 2.9, 8.5 Hz, 1H), 4.27 (dd, J = 2.9, 10.6 Hz, 1H), 3.97 (dd, J = 8.5, 10.6 Hz, 1H), 3.95 (br s, 1H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 141.4, 139.3, 133.5, 130.9, 128.8, 128.3, 127.1, 119.4, 116.3, 115.9, 71.00, 54.3, 20.7; ESI HRMS exact mass calcd for $(C_{15}H_{15}NO + H)^+$ m/z 226.1226, found m/z 226.1222; IR (KBr) 2924 (m), 1606 (m), 1480 (m), 1313 (s), 1256 (s), 1184 (s), 1065 (s), 1026 (s), 884 (s), 753 (s) cm^{-1}. The enantiomers were analyzed by HPLC using a chiral IC column (*n*-hexane/2-propanol 98/2, flow rate 1.0 mL/min, λ 254 nm): minor enantiomer, t_R = 7.7 min; major enantiomer, t_R = 6.8 min; 97% ee.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving experimental details and ^{1}H and ^{13}C NMR and HPLC spectra of the products and a CIF file giving the X-ray structure of compound **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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