Asymmetric Allylation

Quinox, a Quinoline-Type *N*-Oxide, as Organocatalyst in the Asymmetric Allylation of Aromatic Aldehydes with Allyltrichlorosilanes: The Role of Arene–Arene Interactions**

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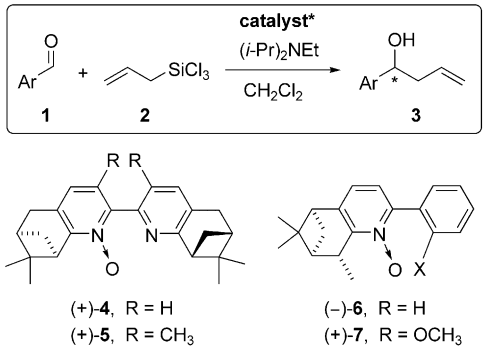
Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday

Activation of allylsilane reagents **2** by a catalytic amount of a chiral Lewis base has been shown to effect asymmetric allylation of aromatic and heteroaromatic aldehydes **1** (Scheme 1).[1–4] The highest enantioselectivities were reported

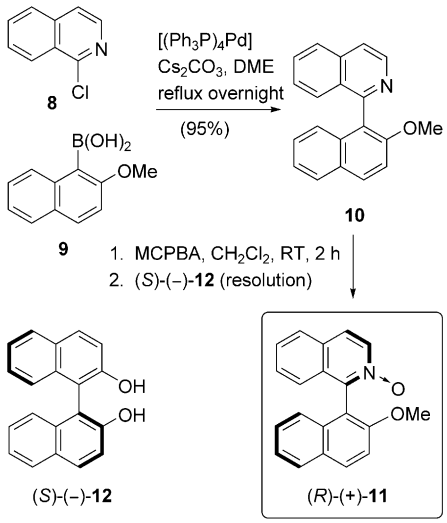


Scheme 1. Asymmetric allylation of aromatic and heteroaromatic aldehydes with a Lewis base catalyst.

by us for pindox **4** ($\leq$92% *ee*) and its dimethyl analogue **5** ($\leq$98% *ee*) as catalysts (**3**, Ar = Ph).[5] We also proposed a mechanism consistent with the available data, in which we postulated the chelation of the silicon atom by the oxygen atom of the *N*-oxide and the nitrogen atom of the second pyridine ring of **4**/**5**. However, in a subsequent study, we demonstrated that the second nitrogen is not a prerequisite for good asymmetric induction, as the simple phenyl derivative **6** and its *o*-methoxy analogue **7** (each of 87% enantiopurity) induced the formation of the allylation product **3** in 41% and 69% *ee*, respectively (**3**, Ar = Ph).[6]

The latter behavior seems to suggest that arene–arene interactions (e.g., π-stacking)[7] of the incoming benzaldehyde and the second aromatic nucleus may be involved in the reaction.[8] Furthermore, the *N*-oxide catalysts are only effective with aromatic and heteroaromatic aldehydes,[3–6] which appears to lend additional credence to this rationalization. Hence, if the catalyst contains an electron-rich aromatic system, such as the *o*-methoxy-phenyl in **7**, it should be most effective with electron-poor aromatic aldehydes (i.e., with electron-withdrawing substituent) and vice versa. In line with this hypothesis, we have endeavored to synthesize a new electron-rich catalyst and explore its activity toward electron-rich and electron-poor aromatic aldehydes. Moreover, benzaldehyde derivatives containing electron-withdrawing groups were reported to produce only modest enantioselectivities in the allylation reaction,[3–6] so that development of an effective catalyst for this class of compounds would be desirable.

We have chosen the isoquinoline *N*-oxide derivative **11** as the candidate catalyst (Scheme 2), the synthesis of which was inspired by the simplicity of the initial steps toward the well-known heterobidentate ligand quinap.[9] Thus, the Suzuki–Miyaura coupling of 1-chloro-isoquinoline (**8**)[9b] with boronic acid **9**[9b,10] afforded the biaryl derivative **10**[9] (95%), whose treatment with *m*-chloroperoxybenzoic acid provided racemic *N*-oxide (±)-**11** (99%).



Scheme 2. Synthesis of the isoquinoline *N*-oxide derivative **11**.

Racemic **11** was resolved by cocrystallization with (*S*)-(−)-binol (**12**; binol = 2,2'-dihydroxy-1,1'-biphenyl),[11] which gave the crystalline material containing binol and (+)-**11** (in a 1:1 ratio), while (−)-**11** remained in the solution. This cocrystallization, followed by a chromatographic separation of (+)-**11** from (*S*)-binol, furnished pure (+)-**11** of 98% *ee* (as revealed by chiral HPLC) in 89% yield of the isolated product.[12] The absolute configuration of **11** was found to be (*R*)-(+)-**11** by crystallographic analysis of the molecular

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crystal of (+)-**11** with (*S*)-(−)-**12** (Figure 1),[13] the absolute configuration of which is known. In line with the accepted acronym quinap,[9] we propose the new acronym quinox for **11**.

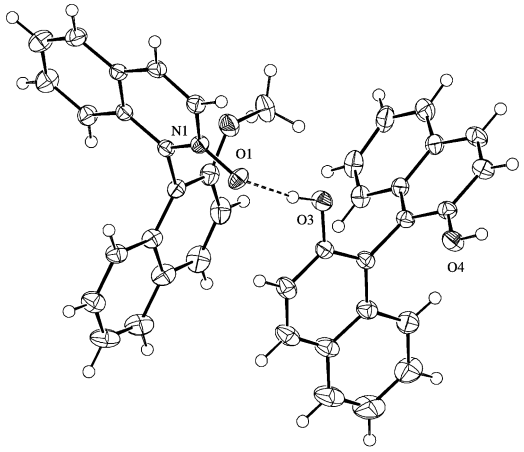


Figure 1. An ORTEP diagram illustrating the interaction of (*R*)-(+)-**11** (on the left) with (*S*)-(−)-**12** (right), in particular the hydrogen bonding N–O···H–O. Displacement parameters are shown at the 50% probability level.

The addition of allyltrichlorosilane (**2**) to benzaldehyde (**1a**) (Scheme 1), carried out in the presence of (*R*)-(+)-**11** (5 mol%) at −40 °C for 2 h in CH_2Cl_2, produced (*R*)-(+)-**3a** of 87% *ee* (Table 1, entry 1). When the catalyst load was lowered to 1 mol% the reaction slowed (to ~12 h) but the enantioselectivity was not altered (entry 2).[14] In MeCN, the reaction was slower and rather less enantioselective (entry 3). A further decrease of the enantioselectivity was observed for the reaction in $CHCl_3$ (63% *ee*, entry 4) but the reaction was much faster (30 min at −40 °C and ~1 h at −60 °C; Table 1, entries 4 and 5). Cinnamyl derivatives **1b** and **1c** had good reactivity with modest enantioselectivity (entries 6 and 7).

Table 1: The Allylation of Aldehydes **1** with **2** Catalyzed by (*R*)-(+)-**11** (Scheme 1).[a]

entry	aldehyde	Ar	solvent	*t* [h]	yield [%][b]	*ee* [%][c,d]
1	**1a**	Ph	CH_2Cl_2	2	60	87
2	**1a**	Ph	CH_2Cl_2[e]	12	55	87
3	**1a**	Ph	MeCN	12	60	70
4	**1a**	Ph	$CHCl_3$	0.5	80	63
5	**1a**	Ph	$CHCl_3$[f]	1	79	62
6	**1b**	Cinnamyl	CH_2Cl_2	12	86	51
7	**1c**	α-Methylcinnamyl	CH_2Cl_2	12	71	55
8	**1d**	4-MeO-C_6H_4	CH_2Cl_2	12	70	12
9	**1e**	2-Furyl	CH_2Cl_2	12	68	5
10	**1f**	2-Thiophenyl	CH_2Cl_2	12	59	6
11	**1g**	2-Pyridyl	CH_2Cl_2	12	25[g]	–
12	**1h**	4-Pyridyl	CH_2Cl_2	12	trace	–
13	**1i**	4-NO_2-C_6H_4	CH_2Cl_2	2	73	89
14	**1j**	4-Cl-C_6H_4	CH_2Cl_2	2	65	93
15	**1k**	4-F-C_6H_4	CH_2Cl_2	2	79	91
16	**1l**	4-CF_3-C_6H_4	CH_2Cl_2	2	85	96

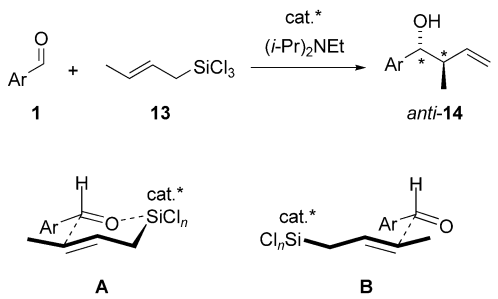
[a] The reaction was carried out at 0.4 mmol scale with 1.1 equiv of **2**, in the presence of (*R*)-(+)-**11** (5 mol%, 98% *ee*) as catalyst and (*i*-Pr)$_2$NEt (1 equiv) as base at −40 °C. [b] Yield of the isolated product (note that some of the products are fairly volatile). [c] Determined by chiral HPLC or GC. [d] All products **3** were of (*R*)-(+)-configuration, as revealed by the comparison of their optical rotations (measured in $CHCl_3$) and their GC and HPLC retention times with the literature data and with the behavior of authentic samples.[3a,b,16,17] [e] With 1 mol% of the catalyst. [f] At −60 °C. [g] For product identification, see reference [18, 19].

Electron-rich *p*-methoxybenzaldehyde (**1d**) and the 2-furyl and 2-thiophenyl analogues **1e** and **1f** gave almost racemic products in good yields (Table 1, entries 8–10), while pyridyl aldehydes **1g** and **1h** proved to be practically unreactive (entries 11 and 12).

By contrast, the introduction of electron-withdrawing substituents into *p*-position resulted in a dramatic increase in both reactivity and enantioselectivity. Thus, *p*-nitrobenzaldehyde **1i** afforded the corresponding product in better yield and with slightly higher *ee* than benzaldehyde (compare entries 1 and 13), and the *p*-halo derivatives **1j** and **1k** both gave >90% *ee* (Table 1, entries 14 and 15). The highest conversion and enantioselectivity (96% *ee*) was attained with the *p*-trifluoromethyl derivative **1l** (entry 16).

The observed trend in the reaction rate and enantioselectivity, with best results obtained for the electron-poor benzaldehydes **1i–l**, is fully compatible with the original hypothesis of the arene–arene interaction of the catalyst with the incoming aldehyde. The acceleration in chloroform appears to lend further support to these interactions as the driving force for the reaction.[15]

The allylation with *trans*-crotyltrichlorosilane **13** (prepared as an 87:13 *trans*/*cis* mixture by the CuCl-catalyzed reaction of crotyl chloride with $HSiCl_3$)[2b] was briefly explored to assess the scope of the reaction and to shed more light on the mechanism (Scheme 3). With pindox (**4**) as catalyst, the reaction in CH_2Cl_2 produced mainly *anti*-**14** (Table 2, entry 1), which is compatible with the generally accepted cyclic transition state **A**.[1,3] By contrast, a 2:1 *anti*/*syn* mixture (entry 2) was produced in the presence of quinox (**11**), suggesting a participation of the open-chain transition state **B**. In MeCN, the enantioselectivity was significantly reduced but the *anti*/*syn* ratio was increased (entry 3). A further drop in enantioselectivity and simultaneous increase of diastereoselectivity was observed for the electron-rich aldehyde **1d** (entry 4). By contrast, the electron-poor aldehyde **1l** (entries 5 and 6), whose arene–arene interactions with the catalyst are assumed to be stronger, exhibited high enantioselectivity and lower diastereoselectivity. This trend suggests that, in the case of quinox (**11**), the cyclic transition



Scheme 3. Proposed reaction transition states, cat.* = chiral catalyst.

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Table 2: The Allylation of Aldehydes **1** with **13** (Scheme 3).[a]

entry	aldehyde	Ar	catalyst	solvent	yield [%][b]	*anti*:*syn*	*ee* [%][c,d] *anti*, *syn*
1	**1a**	Ph	(+)-**4**[e]	CH_2Cl_2	54	93:7	87[g]
2	**1a**	Ph	(+)-**11**[f]	CH_2Cl_2	70	68:32	65, 78
3	**1a**	Ph	(+)-**11**[f]	MeCN	51	76:24	56, 60
4	**1d**	4-MeO-C_6H_4	(+)-**11**[f]	MeCN	53	82:18	50, 37
5	**1l**	4-CF_3-C_6H_4	(+)-**11**[f]	CH_2Cl_2	76	70:30	92, 95
6	**1l**	4-CF_3-C_6H_4	(+)-**11**[f]	MeCN	62	60:40	80, 84

[a] The reaction was carried out in the same way as shown in Table 1. at −40 °C. [b] Isolated yield (note that some of the products are fairly volatile). [c] Determined by chiral HPLC or GC. [d] The products **14** had the absolute configuration shown in Scheme 3, as revealed by the comparison of their optical rotations (measured in $CHCl_3$) and their GC retention times with the literature data[3a] and with the behavior of authentic samples. [e] At −60 °C for 24 h. [f] At −40 °C for 12 h. [g] Enantiomer of *anti*-**14** was formed with (+)-**4** as catalyst.

state **A** is less favored when arene–arene interactions operate (Table 2, entries 2 and 5), and more favored when the latter interactions are minimal (entry 4). Note that **1d** has the more Lewis basic carbonyl oxygen and should be more prone to coordinate to the Lewis acidic silicon, which should favor **A**. On the other hand, the less Lewis basic **1a** and **1l** are less suitable for this coordination, leaving **B** as an option, which is compatible with the experimental results.[20]

In conclusion, quinox (*R*)-(+)-**11** has been synthesized and shown to exercise an unusually high level of enantiocontrol in the Sakurai–Hosomi–Denmark-type allylation of electron-poor aromatic aldehydes ($\leq$96 % *ee*, the highest value reported to date). An arene–arene interaction between the catalyst and the substrate aldehyde has been proposed as a rationale for this observation.[21] These reactions require low catalyst loading ($\leq$5 mol %) and are characterized by a substantial solvent effect upon the rate (typically 12 h in MeCN, 2 h in CH_2Cl_2, and 30 min in $CHCl_3$).

Experimental Section

(±)-1-(2-Methoxy-1-naphthyl)-isoquinoline-*N*-oxide (±)-**11**: *m*-Chloroperoxybenzoic acid (70 %, 2.2 g, 9.3 mmol) was added to a solution of 1-(2-methoxy-1-naphthyl)isoquinoline **10**[9b] (1.32 g, 4.6 mmol) in dichloromethane (20 mL) at 0 °C and the mixture was stirred at room temperature for 2 h. The mixture was then extracted with saturated $NaHCO_3$ (10 mL), the organic solution was washed with brine (5 mL), dried over Na_2SO_4, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (1 × 20 cm) with an ethyl acetate/methanol mixture (4:1) to afford (±)-**11** as white solid (1.37 g, 98 %): mp 107–110 °C (ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.75 (s, 3H), 6.96 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.20–7.32 (m, 3H), 7.37 (d, J = 8.8 Hz, 1H), 7.43–7.47 (m, 1H), 7.67 (d, J = 6.8 Hz, 1H), 7.76–7.82 (m, 2H), 8.10 (d, J = 8.8 Hz, 1H), 8.39 ppm (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 57.03 (CH_3), 113.91 (CH), 113.96 (C), 123.96 (CH), 124.23 (CH), 124.42 (CH), 125.88 (CH), 127.27 (CH), 127.90 (CH), 128.64 (CH), 128.80 (CH), 129.20 (C), 129.53 (CH), 129.57 (CH), 130.73 (C), 132.23 (CH), 132.94 (C), 138.03 (CH), 143.84 (C), 155.91 ppm (C); IR (KBr): $\tilde{\nu}$ = 3054 (w), 1319 (s), 1268 (s), 1251 cm^{-1} (s); MS (EI, 70 eV) *m*/*z* (%) 301.4 (35) [$M^{\cdot+}$], 284.4 (87), 270.3 (100), 242.3 (47), 241.3 (40), 120.7 (19); HRMS (EI) 301.1102 ($C_{20}H_{15}O_2N$ requires 301.1103).

(*R*)-(+)-1-(2-Methoxy-1-naphthyl)-isoquinoline-*N*-oxide (*R*)-(+)-**11**: Solid (*S*)-(−)-binol (*S*)-(−)-**12** (475 mg, 1.66 mmol) was added to a hot solution of racemic 1-(2-methoxy-1-naphthyl)-isoquinoline-*N*-oxide (±)-**11** (500 mg, 1.66 mmol) in dichloromethane (20 mL) and the resulting clear solution was allowed to cool to room temperature. The molecular complex (*R*)-**11**·(*S*)-**12** thus formed as a white precipitate over the period of about 30 min was collected by suction filtration and the individual components were separated by column chromatography on silica gel (1 × 20 cm) with dichloromethane, which eluted (S)-(−)-**12** (235 mg, 49 %), followed by a dichloromethane/methanol mixture (93:7), which eluted (*R*)-(+)-**11** (223 mg, 45 %, or 89 % when calculated for a single enantiomer): mp 178–181 °C (ethyl acetate-hexane); $[\alpha]_D^{20}$ = +134 (c = 1.33 in $CHCl_3$) (lit.[3d] gives mp 180.5 °C and $[\alpha]_D$ = +132.1 (c = 0.9, $CHCl_3$); chiral HPLC (Chiralcel AD-H, hexane/2-propanol 75:25, 1 mL min^{-1}) showed 96–98 % *ee*, depending on the batch (t_S = 12.36 min, t_R = 19.17 min). The filtrate from the original crystallization was evaporated and the components of the residue were separated by chromatography in the same manner as that shown for the molecular crystal to furnish (*S*)-(−)-**12** (224 mg, 47 %), followed by (*S*)-(−)-**11** (215 mg, 43 %, or 86 % calculated for a single enantiomer), which was of 70 % *ee*.

General procedure for the asymmetric allylation of aldehydes **1** with allyltrichlorosilane (**2**)**:** Allyltrichlorosilane (75 μL, 0.47 mmol) was added to a solution of catalyst (*R*)-(+)-**11** (6 mg, 0.02 mmol or 1.2 mg, 0.004 mmol), diisopropylethylamine (46 μL, 0.5 mmol), and aldehyde (0.4 mmol) in dichloromethane (2 mL) under nitrogen at −40 °C. The reaction mixture was stirred at −40 °C for 0.5–12 h (see Table 1). The reaction was quenched with saturated aqueous $NaHCO_3$ (1 mL), the layers were separated, and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The combined organic extracts were washed with saturated aqueous NaCl (3 mL) and dried over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (1 × 20 cm) with a petroleum ether/ethyl acetate mixture (9:1). The yields and enantioselectivities are given in Table 1.

Experimental procedures, analytical and spectral data, crystallographic data, and copies of the NMR spectra for the key compounds are available in the Supporting Information.

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Keywords: allylation · arenes · asymmetric catalysis · O ligands · organocatalysis

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[12] While this work was in progress, Nakajima published the same synthesis of (+)-**11**, including the resolution with (*S*)-(−)-binol.[3d] However, this synthesis was mentioned as a footnote without specifying the conditions and the absolute configuration of (+)-**11** was not determined.

[13] Crystal data for (*R*)-**11**·(*S*)-**12**: colorless crystals, space group $P2_12_12_1$, $a = 8.5583(1)$ Å, $b = 11.9097(1)$ Å, $c = 29.0481(4)$ Å, $V = 2960.78(6)$ Å^3, $Z = 4$, $d_{calcd} = 1.318$ g cm^{-3}, $\mu = 0.085$ mm^{-1}, $R_F(\text{obs}) = 0.0395$.

[14] Investigation of the allylation of **1a** with **2**, catalyzed by (*R*)-(+)-**11** of 29%, 50%, and 75% *ee*, respectively, has demonstrated a fully linear relationship between the enantiopurity of the catalyst and the product. In these experiments, the resulting product **3a** was of 27%, 45%, and 71% *ee*, respectively.

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[21] Hayashi has proposed π–π stacking of **1** and the catalysts but, in his case, the variation of the enantioselectivity was less dramatic (94% *ee* for **1d** and 56% *ee* for **1l** as the extremes of the scale).[4] Furthermore, his catalyst gave the best results in MeCN, which is known not to support arene–arene interactions,[15] thus suggesting that his and our catalyst may operate through a different mode of interactions.

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