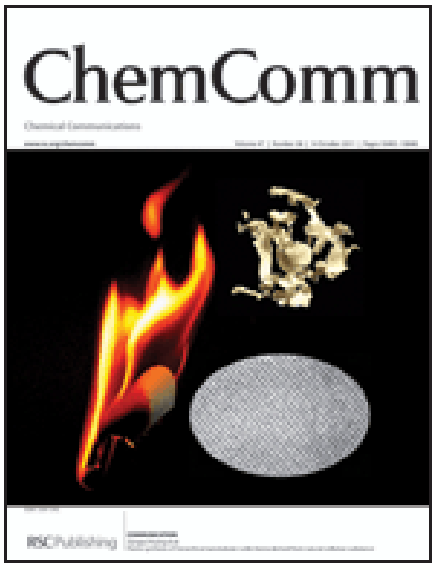

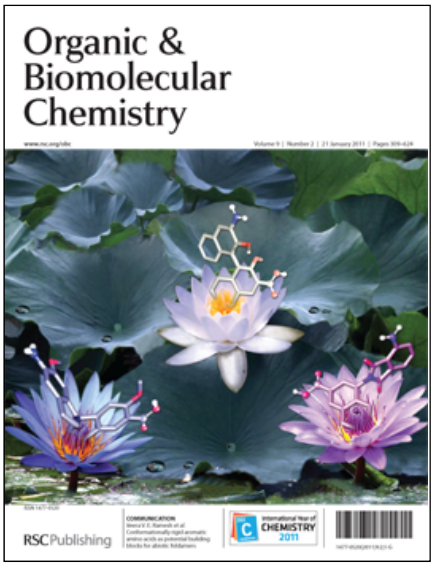

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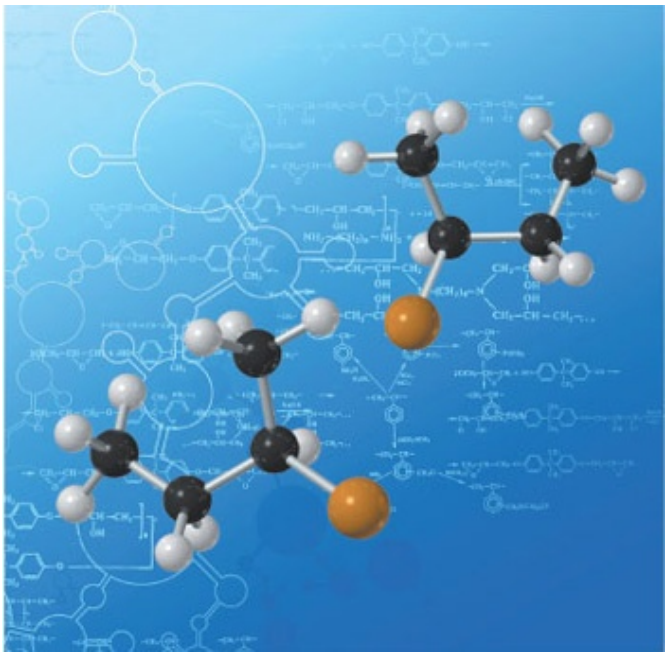

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PAPER

A new synthetic route for axially chiral secondary amines with binaphthyl backbone and their applications in asymmetric Michael reaction of aldehydes to nitroalkenes†‡

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A new synthetic route for binaphthyl-based secondary amines has been developed. The key features of this route include the selective direct esterification of the binaphthyl structure at the 3- or 3,3′-position and the methylation by a Negishi cross-coupling reaction. Based on the new approach, a series of 3-monosubstituted and 3,3′-disubstituted chiral secondary amines with a binaphthyl backbone were synthesized and screened in the Michael reaction of aldehydes to various nitroalkenes. 3-Monosubstituted secondary amine **7c** was proved to be the best catalyst, affording high yields (up to 95%), good to excellent enantioselectivities (up to 99%) and diastereoselectivities (*syn*/*anti* up to 99 : 1) under the optimized conditions.

Introduction

The uses of chiral secondary amines as asymmetric catalysts in many carbon–carbon bond-forming reactions have seen tremendous development in recent years.[1] In this area, proline and its derivatives have proven to be highly effective organocatalysts.[2] However, these factors such as the difficulties in the modification of the pyrrolidine ring when designing structurally new proline catalysts, sometimes high catalyst loading, the possible side products caused by the decarboxylation between the proline catalyst and aldehyde substrate (Scheme 1),[3,4b] have limited their applications in asymmetric catalysis. It is still highly desirable to develop other structurally and electronically tunable organocatalysts.

Maruoka and co-workers have designed and synthesized a series of binaphthyl-based chiral secondary amine organocatalysts **1–5**, and applied them successfully in several asymmetric reactions *via* enamine intermediates,[4] such as asymmetric Aldol reactions,[4a,b,d] cross-Aldol reactions,[4l] Mannich reactions,[4d] aminoxylation reactions,[4g–i] hydroxyamination reactions,[4c] iodination reactions[4i] and bromination reactions.[4f] In most cases these secondary amine catalysts exhibit unique reactivities and selectivities in comparison with proline and its derivatives (Fig. 1).

We were quite interested in these axially chiral secondary amines with binaphthyl backbones. They possess some special features (Fig. 2),[4e] such as larger space between the secondary-amino nitrogen and the functional group at the 3-position, the absence of an α-substituent, ease of introducing various functional groups at the 3-position, mild basicity and nucleophilicity, and may be developed into a promising universal catalyst. We also noticed that the current preparation for these chiral ligands suffers from either the use of expensive starting material or the long reaction procedures.[4a–c,5] Herein we describe a new synthetic approach towards these binaphthyl-based secondary amines, featuring the selective direct esterification at the 3-position and the methylation by a Negishi cross-coupling reaction.

On the other hand, asymmetric Michael reactions of aldehydes to nitroalkenes are among the most useful synthetic methods for the preparation of γ-nitro aldehydes as versatile synthetic intermediates.[6,7] However, few binaphthyl-based secondary amines have been used in this transformation.[8,9] We envisioned that the variation of the functional group at the 3-position and on the C_2 symmetry of the ligand may exert significant influences on the reaction activity and stereoselectivity.[10] For this purpose, 3-monosubstituted and 3,3′-disubstituted binaphthyl-based amino alcohol derivatives **6–7** were designed, synthesized and screened for the asymmetric Michael reaction of aldehydes to nitroalkenes. 3-Monosubstituted secondary amine **7c** exhibited the best catalytic activities, enantioselectivities and diastereoselectivities.

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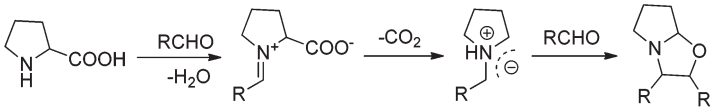
‡ Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data for all new compounds. See DOI: 10.1039/c2ob07110j



Scheme 1 Possible decarboxylation between proline and aldehyde.

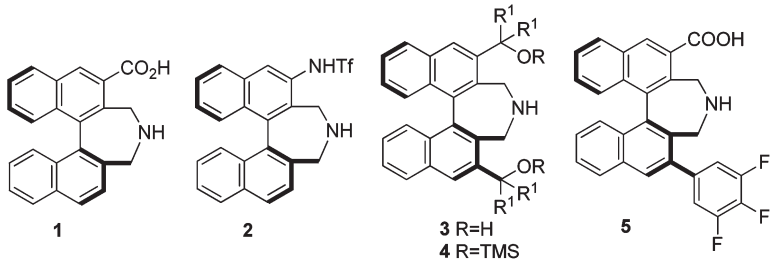


Fig. 1 Some efficient binaphthyl-based secondary amines.

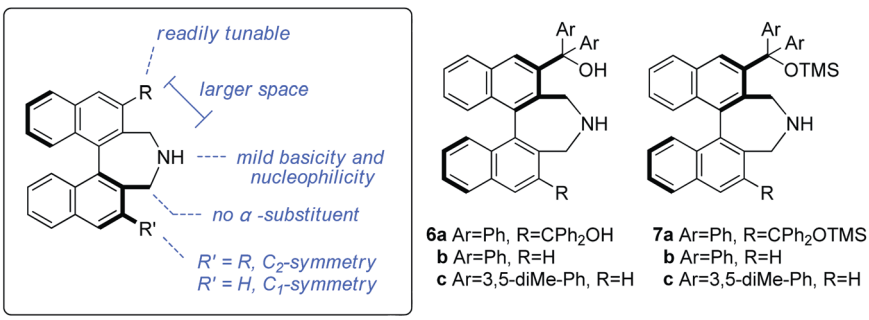


Fig. 2 Binaphthyl-based bifunctional secondary amine catalysts.

Results and discussion

Although Maruoka *et al.* have already established a synthetic route for the key intermediate **8** from chiral 1,1′-binaphthyl-2,2′-dicarboxylic acid (Fig. 3 Route A),[4a,b] the starting material was expensive and not commercially available, besides, the yield was disappointing (22% yield for 6 steps). Maruoka's group also reported another approach starting from chiral 1,1′-binaphthyl-2,2′-diol, but this route suffered from long procedure and tedious operations (Fig. 3 Route B).[4c,5]

These results strongly encouraged us to develop an entirely new route for the synthesis of the catalyst. Initially we planned to synthesize key intermediate **8** from MOM protected (*R*)-BINOL, first introducing diphenylhydroxy group at the 3-position, then forming the carbon–carbon bond at the 2,2′-position (Fig. 4, Route C). But we encountered a serious problem in generating bistriflate at the 2,2′-position, only monotriflate was obtained, we attributed this to the existence of a sterically bulky substituent on the 3-position.

So we think about reducing the steric hindrance of the 3-substituent with a smaller ester group. Usually ester functionality was generated by indirect esterification, which means first introducing functional moieties as aldehyde, triflate or boronate, then converting them to ester.[4c,11,12] To simplify the procedure, we adopted a direct esterification of the binaphthyl structure as illustrated in Fig. 4 (Route D). Compound **11a** was synthesized from MOM-protected chiral BINOL **10** by treatment with 1.2 equiv. of n-BuLi in anhydrous THF, followed by 1.5 equiv. of $ClCO_2Et$ at −78 °C. It is worth commenting that diester **11b** can also be selectively obtained when using 2.5 equiv. of n-BuLi and 4.0 equiv. of $ClCO_2Et$. After removal of the MOM-protecting group under acidic conditions **12** can be converted to bistriflate **13** smoothly by treatment with Tf_2O and DMAP. For the methylation of the OTf moiety, the well-established Kumada coupling reaction with MeMgI was not suitable due to the incompatibility between the ester substituent and the Grignard reagent, hence the more general and milder Negishi coupling reaction was adopted to synthesize **14**.[13] Several different palladium and nickel catalysts have been screened and $Pd(dppf)Cl_2$ was proved to be the best reagent to afford **14** in high yield (95%). Subsequent radical bromination of **14** with NBS proceeded cleanly to give **15** in 88% yield. Finally treatment of **15** with allylamine afforded the requisite tertiary amine intermediate **8** in 75% yield.

Compared with Maruoka's strategies, Route D is more efficient and economical, 7 steps with 42% overall yield for the key intermediate **8**. Its key features include: (1) selective direct esterification of the binaphthyl structure at the 3- or 3,3′-position and (2) methylation at the 2,2′-position of binaphthyl structure by a Negishi cross-coupling reaction. This procedure could also facilitate large-scale access to this type of compound.

With building block **8** in hand, both 3,3′-disubstituted and 3-monosubstituted binaphthyl-based amino alcohol derivatives

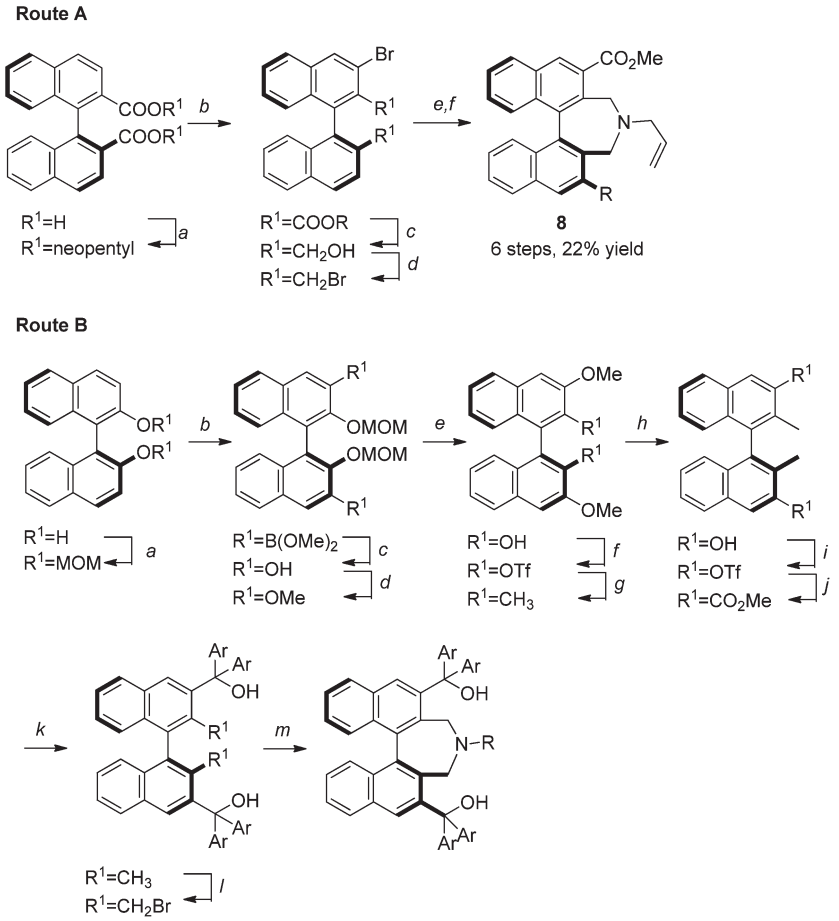


Fig. 3 Maruoka's procedures for the synthesis of chiral secondary amine intermediate.

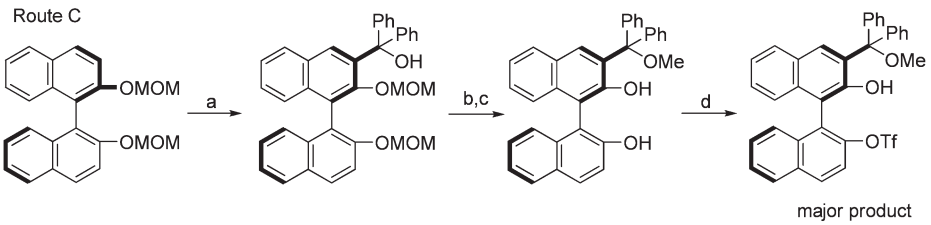
6–7 can be easily prepared according to literature procedures (Fig. 5).[4c,j] The synthetic procedures and spectroscopic data were summarized in the ESI.‡

The efficiencies of these binaphthyl-based secondary amines were evaluated in the direct asymmetric Michael reaction and the results were summarized in Table 1. In the presence of 10 mol% 3,3′-disubstituted amino alcohol **6a**, the reaction of propanal with *trans*-β-nitrostyrene in CH_2Cl_2 at room temperature afforded the corresponding Michael adduct in low yield and low stereoselectivity (Table 1 entry 1, 32% yield, 57 : 43 dr, 37% ee). 3-Monosubstituted amino alcohol **6b** showed significantly improved effects (entry 2, 77% yield, 85 : 15 dr, 73% ee). Highly hindered 3,5-dimethylphenyl derivative **6c** was found to be more efficient, not only enhancing the reaction rate, but also exhibiting excellent enantioselectivity (entry 3, 89% yield, 70 : 30 dr, 99% ee).

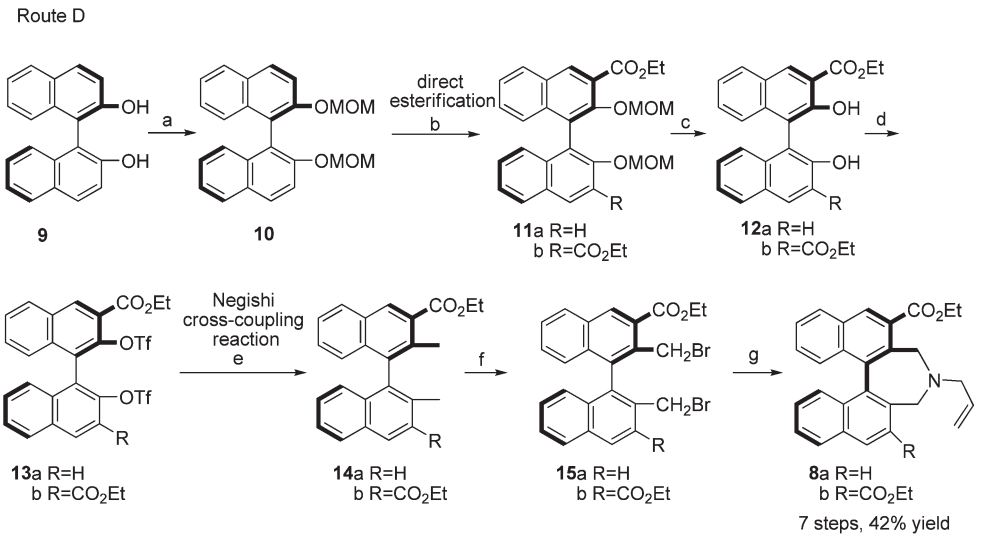
To further improve the reactivity, the hydroxyl group of **6a** was converted to a siloxy group,[4f,7d] and the resulting catalyst **7a** showed significantly higher yield and ee (entry 4, 80% yield, 88% ee for *syn* adduct). It is quite interesting that **7a** can afford the *anti* product in 96% ee, which was seldom obtained in previous research. 3-Monosubstituted diarylmethanol silyl ethers **7b** and **7c** appeared to play an important role in this catalytic asymmetric process, the reactivity along with the diastereoselectivity increased dramatically (entry 5 *versus* 4, entry 2 *versus* 1). In particular, the reaction can be completed within 3 hours at room temperature in the presence of **7c** to afford the adduct in good yield (89%), nearly optically pure form (>99% ee) and high diastereoselectivity (dr 85 : 15) (entry 6). The diastereoselectivity can be further improved without a significant loss in the yield when performing the reaction at 0 °C (entry 7), although a prolonged time was required.

Next, the Michael reaction of propanal and *trans*-β-nitrostyrene was carried out in various solvents at room temperature. As shown in Table 2, the reaction rate exhibited a strong solvent dependence. For example, the reaction proceeded rapidly in polar aprotic solvents as CH_2Cl_2 and $CHCl_3$, affording high chemical yields (85–89%), diastereoselectivity (85 : 15) and excellent enantioselectivities (97–99% ee) (entries 4–5). Modest yields and diastereoselectivities were achieved in Et_2O and THF (entries 3 and 6). Substantial improvement in yield can be observed when the reaction was carried out in hexane and toluene at ambient temperature (entries 1–2). Although the reactivity was improved, unsatisfactory yield and dr were observed for polar protic solvent as MeOH (entry 7). It is worth noting that when performing the reaction in brine, high chemical yield was achieved along with high *syn*-diastereoselectivity and ee (entry 9).

Having established **7c** as an effective catalyst, CH_2Cl_2 as the solvent for the enantioselective Michael reaction of propanal, we

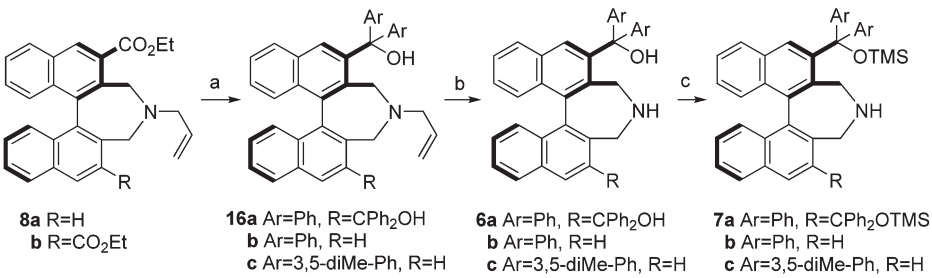


Reagents and conditions: a) *n*-BuLi, $Ph_2C{=}O$, THF, r.t.; b) 3N HCl, THF, reflux; c) CF_3COOH, CH_3OH/CH_2Cl_2, 0 °C-r.t.; d) 20 mol% DMAP, Tf_2O, Et_3N, DCM, 0 °C-r.t.



Reagents and conditions: a) NaH, MOMCl, THF, 0 °C to r.t.; b) *n*-BuLi, THF; then $ClCO_2Et$, -78 °C; c) 6N HCl, THF, 60 °C; d) 20 mol% DMAP, Tf_2O, pyridine, 0 °C to r.t.; e) 7 mol% $Pd(dppf)Cl_2$, Me_2Zn, 0 to 120 °C; f) 10 mol% AIBN, NBS, *n*-hexane, 80 °C; g) allylamine, MeCN, 0 to 50 °C.

Fig. 4 Our new synthetic route for chiral secondary amine intermediate.



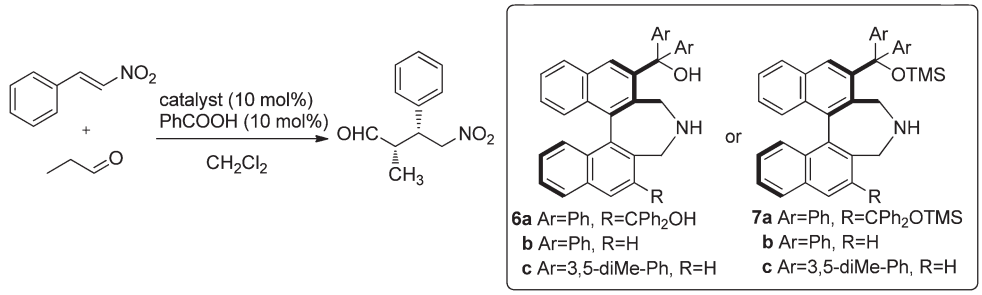
Reagents and conditions: a) ArLi, Et_2O, -78 °C; b) NDMBA, $Pd(OAc)_2$, Ph_3P, CH_2Cl_2, r.t.; c) TMSOTf, Et_3N, CH_2Cl_2, 0 °C to r.t.

Fig. 5 Synthesis of binaphthyl-based secondary amine catalysts.

next investigated the scope of the substrates (Table 3). Various aromatic substituted nitroalkenes reacted well with propanal to give the desired Michael products with 88–95% yields, high enantioselectivities (92–99% ee) and good diastereoselectivities (entries 1–4). The dr was sensitive to the steric hindrance of aryl substituent, for example, 85 : 15 dr was obtained for (*E*)-(2-nitrovinyl)benzene, while 75 : 25 dr was observed for bulky (*E*)-1-(2-nitrovinyl)naphthalene. In the case of heteroaromatic nitroalkenes, the corresponding Michael adducts were achieved with reasonable good chemical yields and stereoselectivities (Table 3, entries 5–6). Significant improvement in the enantioselectivity can be observed when the reaction was carried out under lower temperatures (entries 5–6). The aliphatic nitroalkenes were also excellent Michael acceptors for this catalytic system, although longer reaction time was needed, which can be explained by the lower electrophilic activity of aliphatic nitroalkenes (entry 7).

In addition to propanal, other linear aldehydes, such as butyraldehyde, pentanal and hexanal can also be employed successfully as the Michael donors to give the Michael adducts with

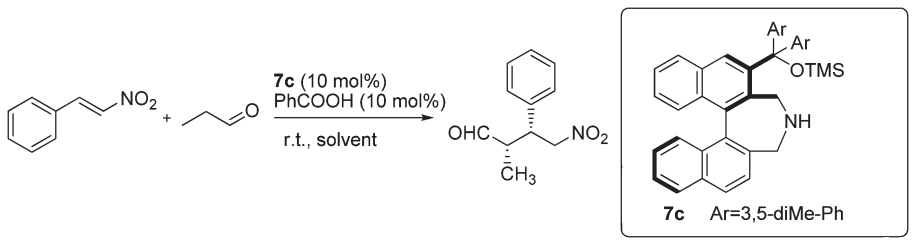
Table 1 Effects of the catalysts in the Michael reaction of propanal and (*E*)-(2-nitrovinyl)-benzene[a]



Entry	Cat.	*t* [h]	*T*	Yield[b] [%]	*syn*/*anti*[c]	ee[d] [%] (*syn*)
1	**6a**	24	r.t.	32	57 : 43	37
2	**6b**	24	r.t.	77	85 : 15	73
3	**6c**	15	r.t	89	70 : 30	99
4	**7a**	20	r.t	80	37 : 63	88 (96[e])
5	**7b**	6	r.t.	85	75 : 25	98
6	**7c**	3	r.t.	89	85 : 15	>99
7	**7c**	10	0 °C	86	87 : 13	>99

[a] Unless otherwise shown, the reaction was performed with (*E*)-(2-nitrovinyl)-benzene (0.5 mmol), propanal (5.0 mmol), catalyst (10 mol%) and PhCOOH (10 mol%) in CH_2Cl_2 (2.0 mL) at room temperature. [b] Yield of isolated product. [c] Determined by ^{1}H NMR spectroscopy (400 MHz). [d] The ee values were determined by HPLC analysis on a chiral column (Chiralcel OD-H). [e] ee [%] (*anti*).

Table 2 Influences of solvents on the Michael addition of propanal and (*E*)-(2-nitrovinyl)-benzene[a]



Entry	Solvent	Time [h]	Yield[b] [%]	*syn*/*anti*[c]	ee[d] [%] (*syn*)
1	Hexane	72	82	64 : 36	98
2	Toluene	100	80	78 : 22	97
3	Et_2O	120	30	65 : 35	98
4	$CHCl_3$	4	85	85 : 15	97
5	CH_2Cl_2	3	89	85 : 15	>99
6	THF	120	16	61 : 39	98
7	MeOH	120	56	71 : 29	93
8	MeCN	120	n.d.	n.d.	n.d.
9	Brine	7	83	87 : 14	92

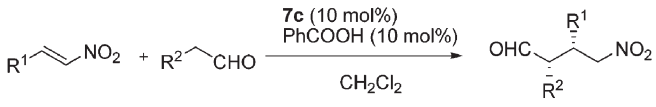
[a] Unless otherwise shown, the reaction was performed with (*E*)-(2-nitrovinyl)-benzene (0.5 mmol), propanal (5.0 mmol), **7c** (10 mol%) and PhCOOH (10 mol%) in solvent (2.0 mL) at room temperature. [b] Yield of isolated product. [c] Determined by ^{1}H NMR spectroscopy. [d] The ee values were determined by HPLC analysis on a chiral column (Chiralcel OD-H).

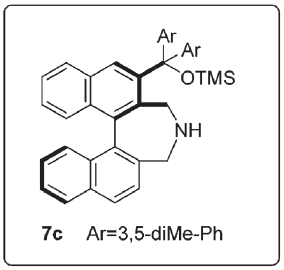
high chemical yields (85–95%) and good enantioselectivities (95–97%), but long reaction time (40 hours) was needed to ensure complete conversion (entries 8–10). Higher diastereoselectivity can usually be observed for aldehyde with longer carbon chain. Unfortunately, the branched aldehyde reacts sluggishly in the presence of organocatalyst, only 30% yield was obtained even after 120 hours, but the large steric hindrance around the α-position of aldehyde seems to be helpful for high stereoselectivity (entry 11, 97 : 3 dr, 95% ee).

In our research 3-monosubstituted organocatalyst showed significantly improved effects compared to 3,3′-disubstituted catalyst. Plausible transition-state models have been proposed to account for the observed absolute configuration of the Michael adduct (Fig. 6).

The azepine moieties of organocatalysts **7a** and **7b** reacts with the unmodified aldehyde to form nucleophilic *anti*-enamine.[4f,g] The neighbouring rigid 3-substituent served as an efficient stereocontrolling element. For 3-monosubstituted **7b**, the

Table 3 Catalytic asymmetric Michael reaction of aldehydes and nitroalkenes[a]





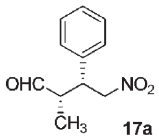
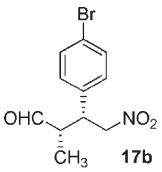
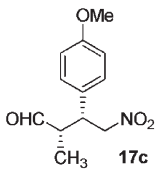
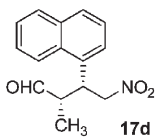
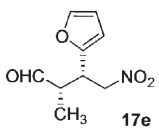
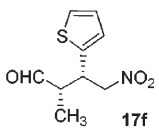
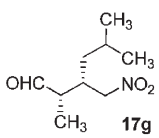
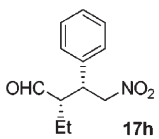
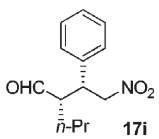
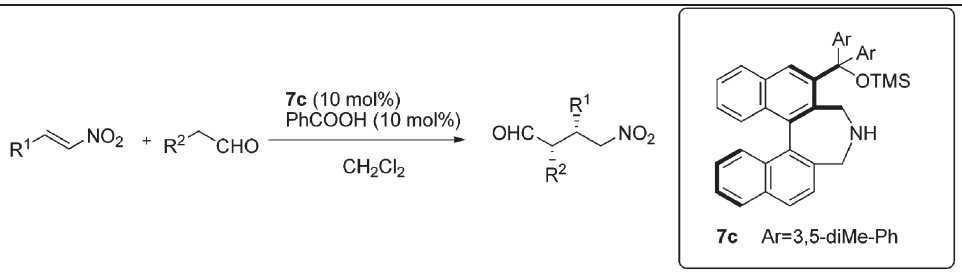
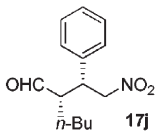
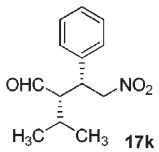
Entry	Product	*T*	Time [h]	Yield[b] [%]	*syn*/*anti*[c]	ee[d] [%](*syn*)
1	 **17a**	r.t.	3	89	85 : 15	>99
2	 **17b**	r.t.	3	90	80 : 20	94
3	 **17c**	r.t.	3	95	84 : 16	>99
4	 **17d**	r.t.	4	88	75 : 25	92
5	 **17e**	r.t.	3	94	84 : 16	86
		0 °C	12	92	85 : 15	98
6	 **17f**	r.t.	4	94	76 : 24	88
		0 °C	24	94	85 : 15	97
7	 **17g**	r.t.	24	82	90 : 10	95
8	 **17h**	r.t.	40	90	88 : 12	97
9	 **17i**	r.t.	40	85	92 : 8	97

Table 3 *(Contd.)*



Entry	Product	*T*	Time [h]	Yield[b] [%]	*syn*/*anti*[c]	ee[d] [%](*syn*)
10	 **17j**	r.t.	40	95	99 : 1	95
11	 **17k**	r.t.	120	30	97 : 3	94

[a] Unless otherwise shown, the reaction was performed with (*E*)-nitrostyrene (0.5 mmol), aldehyde (5.0 mmol), **7c** (10 mol%) and PhCOOH (10 mol %) in CH_2Cl_2 (2.0 mL) at room temperature. [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy (400 MHz). [d] The ee values were determined by HPLC analysis on a chiral phase (Chiralcel OD-H, Chiralpak AS-H and AD-H).

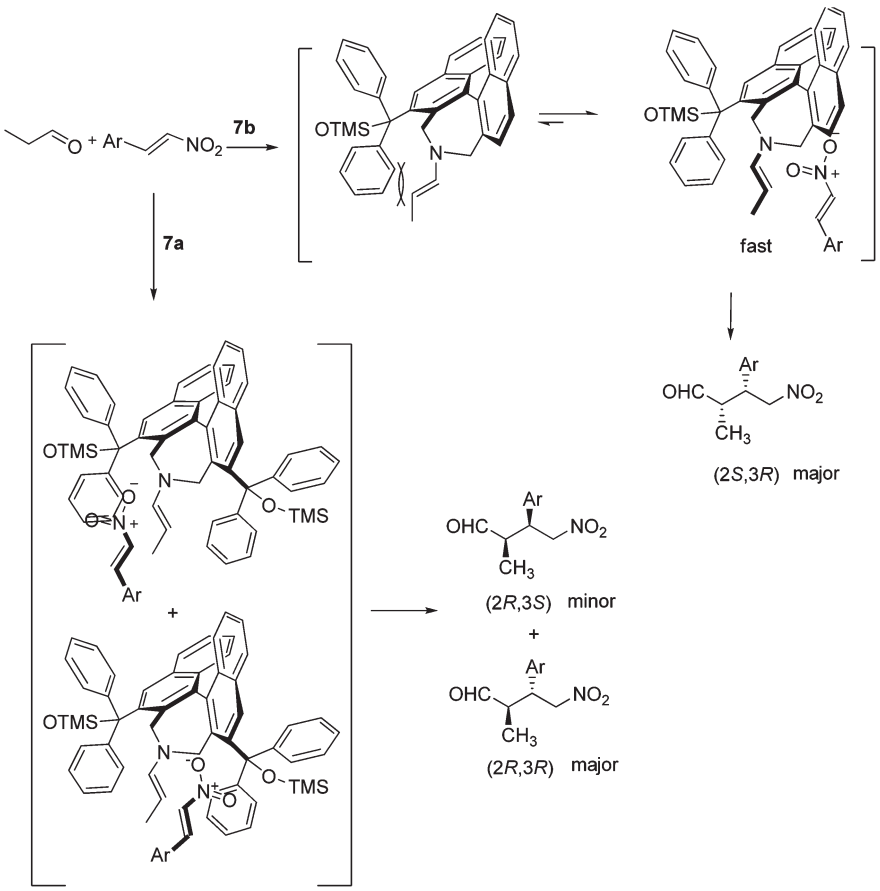


Fig. 6 Plausible transition state models for the direct asymmetric Michael reaction of (*R*)-**7a** and **7b**.

nitrostyrene might approach from the lower side, *i.e. Re* face of *anti* enamine to *Re* face of nitrostyrene, to avoid the steric repulsion from the 3-diphenylmethanol silyl ether functionality, resulting in *syn* Michael adduct with (2*S*,3*R*) absolute configuration. But for 3,3′-disubstituted **7a**, the existence of two bulky 3-substituents did retard the approach of the nitroolefin, caused a significant drop in reactivity and a reversal in stereoselectivity.

Conclusions

In summary, a new synthetic route for binaphthyl-based secondary amines was developed. The unique features of this route include: (1) selective direct esterification of the binaphthyl structure at the 3- or 3,3′-position and (2) methylation at the 3,3′-position of the binaphthyl structure by a Negishi cross-coupling reaction. This procedure could facilitate the large-scale production and utilization of these chiral catalysts in asymmetric catalysis. We also demonstrated the practical application of novel 3-monosubstituted binaphthyl-based secondary amines for the direct asymmetric Michael addition of aldehydes to nitroalkenes. The products were obtained with high to excellent chemical yields and enantioselectivities under optimized conditions. Further investigations concerning the effectiveness of **7c** and related catalysts in other asymmetric reactions, as well as a more detailed mechanism study, are currently underway.

Experimental section

General

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200–300 mesh). ^{1}H NMR spectra were recorded on a Bruker XL 400 (400 MHz) spectrometer and the spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ = 7.26 ppm), or with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. Chemical shifts were reported as parts per million (ppm) in the δ scale downfield from TMS. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublet), bs (broad singlet). ^{13}C NMR spectra were recorded on Bruker (100 MHz) spectrometer with complete proton decoupling, and chemical shifts were reported in ppm from TMS with the solvent as the internal reference ($CDCl_3$, δ = 77.0 ppm). HPLC analyses were conducted on an Agilent instrument using Daicel Chiralcel OD-H, Chiralpak AD-H or AS-H columns (0.46 cm diameter × 25 cm length). Optical rotations were recorded on a Perkin-Elmer polarimeter (Model 341). High resolution mass was recorded on an ESI-ion trap mass spectrometer (Shimadzu, LCMS-IT-TOF). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

Typical procedure for the Michael reaction of aldehydes to nitroolefins

Propanal (0.36 mL, 5.0 mmol) was added to a solution of (*E*)-(2-nitrovinyl)-benzene (75 mg, 0.5 mmol), PhCOOH (6 mg, 0.05 mmol) and catalyst **7c** (30 mg, 0.05 mmol) in CH_2Cl_2 (2.0 mL) at room temperature. After the reaction mixture had been stirred for 3 hours at that temperature, it was concentrated under vacuum and the crude mixture was purified by flash chromatography to afford the Michael adduct as clear oil (121 mg, 87% yield). Assignment of the stereoisomers was performed by comparison with literature data. The value of *syn*/*anti* ratio was determined by ^{1}H NMR by comparing different integrations of hydrogens of the aldehyde group. The enantiomeric excess was measured by HPLC with Chiralcel OD-H columns.

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