CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200501109

One-Pot Enantioselective Aziridination of Olefins Catalyzed by a Copper(I) Complex of a Novel Diimine Ligand by Using $PhI(OAc)_2$ and Sulfonamide as Nitrene Precursors

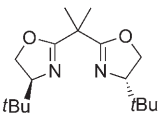
Xisheng Wang and Kuiling Ding*[a]

Abstract: A novel chiral C_2-symmetric 1,4-diamine with multistereogenic centers at the backbone of the ligand has been synthesized from cheap natural product D-mannitol through multistep transformations. Its diimine derivative (**3a**) was found to be highly effective for the enantioselective control of the copper-catalyzed asymmetric aziridination of olefin derivatives with PhI=NTs as the nitrene source, affording the corresponding *N*-sulfonylated azirindine derivatives in good to excellent yields with up to 99% *ee* (*ee* = enantiomeric excess). The catalyst system discovered in the present work was also extended to a one-pot enantioselective aziridination by using sulfonamide/iodobenzene diacetate as the nitrene source. In this case, most reactions proceeded smoothly to give the corresponding products in moderate yields with good to excellent enantiomeric excesses (75–96% *ee*).

Keywords: asymmetric catalysis · aziridination · copper · diimine · D-mannitol · one-pot reaction

Introduction

The enantioselective aziridination of olefins catalyzed by transition-metal complexes represents one of the important C–N bond-forming reactions in asymmetric catalysis,[1] and its products, optically active aziridines, have been found to be very useful intermediates in the synthesis of natural or biologically important products.[2] Although a variety of chiral catalysts including Fe, Mn, and Cu complexes have been developed in the past two decades,[1,3–5] the field of asymmetric aziridination catalysis has remained relatively undeveloped. The most promising catalyst systems developed so far are the Cu^I complexes of C_2-symmetric bidentate N,N-ligands (for example, **1**–**2**) and [*N*-(4-tolylsulfonyl)-imino]phenyliodinane (PhI=NTs) was usually used as the nitrene source.[4,5] However, Dauban and Dodd have revised this reaction in a one-pot fashion[6a] by using sulfonamide and iodosylbenzene in the presence of molecular sieves to avoid the preparation and purification of unstable and explosive PhI=NTs.[7] Very recently, Che and co-workers reported an alternative procedure for the in situ formation of nitrene by using iodobenzene diacetate [$PhI(OAc)_2$] and sulfonamides.[6b] However, in both cases, the substrates were limited to the highly reactive electron-rich styrene derivatives and the enantioselectivity of the reaction was only moderate (<75% *ee*). In the present work, we will report our results on the development of the new chiral C_2-symmetric 1,4-diimine ligand **3a** containing a bicyclic backbone, which produced excellent enantioselectivity and activity in the Cu^I-catalyzed enantioselective aziridination of electron deficient olefin derivatives by using either PhI=NTs or sulfonamide/iodosylbenzene diacetate as the nitrene source.



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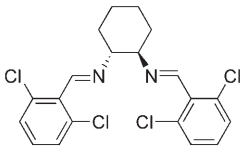

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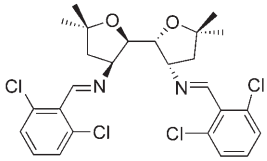

3a

Results and Discussion

To develop efficient and enantioselective catalysts for asymmetric reactions, the search for a well-designed chiral ligand

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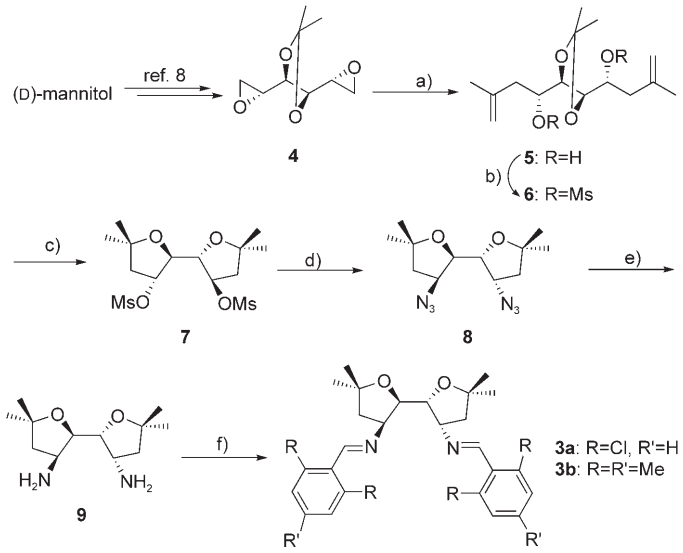
with a new structural skeleton is highly desirable. The common practice for the synthesis of chiral diimine ligands is the use of the corresponding diamines as the precursors, including 1,2-diaminocyclohexane, 1,2-diarylethylenediamine, and axially chiral 1,4-diamines, such as 1,1′-binaphthyl-2,2′-diamine or 1,1′-biphenyl-2,2′-diamine derivatives.[1,3–5] (2*R*,2′*R*,3*S*,3′*S*)-5,5,5′,5′-Tetramethyloctahydro-2,2′-bifuranyl-3,3′-diamine (**9**, Scheme 1) is a C_2-symmetric chiral 1,4-diamine with four stereogenic carbon centers and contains relatively rigid five-membered rings at the backbone. We envisioned that the multistereogenic centers and conformational rigidity of the backbone, and the more basic properties of chelating nitrogen atoms (in comparison with the diimine ligands derived from 1,1′-biaryl-2,2′-diamine)[5] in **3** might be favorable for the enantioselective discrimination of its complexes in the catalysis.



Scheme 1. Synthesis of chiral 1,4-diamine **9** and its diimine derivatives (**3a–b**): a) C_3H_5MgBr, CuI (20%), THF, −30°C, 93%; b) MsCl, Et_3N, 10°C, >99%; c) CH_2Cl_2, $HClO_4$ (70% aq), 70%; d) NaN_3, DMF, 65%; e) 10% Pd/C, H_2 (1 atm), >99%; f) 2,6-dichlorobenzaldehyde or 2,4,6-trimethylbenzaldehyde, MeOH, reflux, 24 h, **3a**: 93%, **3b**: 75%.

Synthesis of chiral C_2-symmetric 1,4-diimine ligands 3: 2,2-Dimethyl-4,5-bis-oxiranyl-[1,3]dioxolane **4** can be easily prepared by starting from naturally occurring and commercially available compound D-mannitol according to the literature procedure (Scheme 1).[8] Grignard addition of 2-methyl ethenyl mangnesium bromide[9] to **4** afforded **5** in 93% yield. Treatment of **5** with methanesulfonyl chloride (MsCl) in the presence Et_3N gave the corresponding methanesulfonic acid ester **6** in quantitative yield. Cyclization of **6** catalyzed by aqueous $HClO_4$[9] gave **7** in good yield, which can be transformed to **8** with a 65% yield upon reaction with NaN_3 in DMF (5 equiv, 100°C). Hydrogenation of diazide **8** occurred by catalysis on Pd/C (10%) in methanol (25°C, 1 atm H_2) and gave the diamine **9** in >99% yield. Finally, two diimine ligands **3a–b** were prepared from diamine **9** by simple condensation in refluxing methanol with 2,6-dichlorobenzaldehyde and 2,4,6-trimethylbenzaldehyde, respectively. The molecular structure of **3a** determined by X-ray crystal structural analysis is shown in Figure 1.[10]

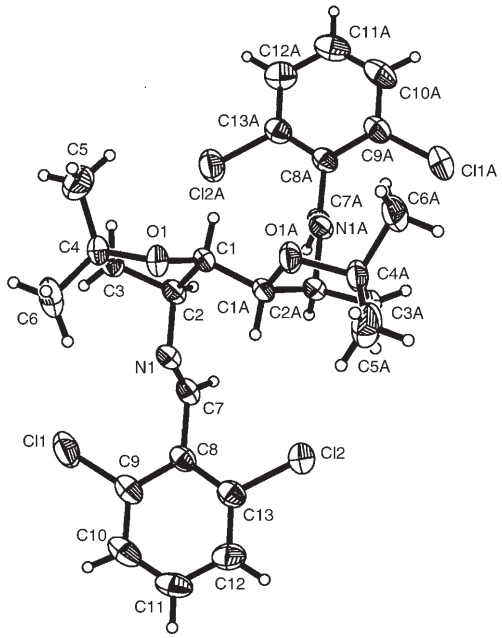
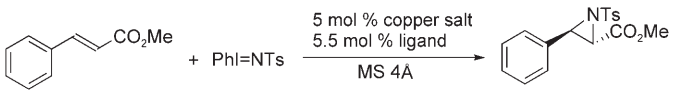


Figure 1. Molecular structure of ligand **3a**.

Asymmetric aziridination of olefin derivatives catalyzed by 3/Cu complexes: With ligands **3a–b** in hand, we started to first investigate their asymmetric induction capability in the Cu^I-catalyzed aziridination of the methyl cinnamate **10a** by employing PhI=NTs as the nitrene source. Under the experimental conditions (Table 1, entries 1–7) $[Cu(MeCN)_4]ClO_4$ turns out to be the best copper source (entry 4) in the presence of ligand **3a**. Cu^I salts are obviously superior to Cu^{II} (entries 6–7) in terms of both activity and enantioselectivity of the catalysis. Although the reactions proceeded very well in benzene and acetonitrile, the enantioselectivities of the reactions dropped significantly in these solvents (entry 8–9). By decreasing the reaction temperature to −75°C, the enantioselectivity of the reaction could be improved to 80.4% *ee* (entry 10). When **3b** was employed as the chiral ligand, the enantiomeric excess of product **11a** was only 69.5% with a poor yield (entry 11), indicating the significant impact of the benzylidene moieties of the ligand. Increasing the catalyst loading from 5 to 10% resulted in a further improvement in the enantioselectivity of the reaction to 87.6% *ee* with a high yield (entry 12). To compare the catalytic properties of the catalysts composed of newly developed ligand **3** with those of ligand **2**, reported previously by Jacobsen, the aziridinations of **10a** with PhI=NTs were carried out in the presence of in situ prepared catalysts **3**/Cu^I or **2**/Cu^I under the same experimental conditions, respectively. It is obvious that in this reaction the catalyst **3**/Cu^I is comparable to **2**/Cu^I in

Table 1. Asymmetric aziridination of methyl cinnamate.[a]



10a 11a

Entry	Ligand	Copper salt	Solvent	T [°C]	t [h]	Yield [%][b]	*ee* [%][c]
1	**3a**	CuOTf	CH_2Cl_2	0	24	4	n.d
2	**3a**	$[Cu(MeCN)_4]BF_4$	CH_2Cl_2	0	24	78	54.9
3	**3a**	$[Cu(MeCN)_4]PF_6$	CH_2Cl_2	0	24	92	67.8
4	**3a**	$[Cu(MeCN)_4]ClO_4$	CH_2Cl_2	0	24	93	70.6
5	**3a**	$[Cu(OTf)_2]$	CH_2Cl_2	0	24	19	24.5
6	**3a**	$[Cu(H_2O)_4][BF_4]_2$	CH_2Cl_2	0	24	trace	n.d
7	**3a**	$[Cu(H_2O)_6][ClO_4]_2$	CH_2Cl_2	0	24	trace	n.d
8	**3a**	$[Cu(MeCN)_4]ClO_4$	CH_3CN	0	24	93	<5
9	**3a**	$[Cu(MeCN)_4]ClO_4$	C_6H_6	0	24	90	27.9
10	**3a**	$[Cu(MeCN)_4]ClO_4$	CH_2Cl_2	−75	48	67	80.4
11	**3b**	$[Cu(MeCN)_4]ClO_4$	CH_2Cl_2	−75	48	29	69.5
12	**3a**[d]	$[Cu(MeCN)_4]ClO_4$	CH_2Cl_2	−75	48	97	87.6
13	**3a**[d,e]	$[Cu(MeCN)_4]PF_6$	CH_2Cl_2	0	24	99	73.6
14	**2**[d,e]	$[Cu(MeCN)_4]PF_6$	CH_2Cl_2	0	24	60	73.4

[a] The reactions were carried out with the ratio of **10a**/PhI=NTs/**3**/Cu 5:1:0.055:0.05 in a 0.125 mmol scale of PhI=NTs (0.042 M) in the presence of 100 mg of MS 4 Å. [b] The yield of isolated product. [c] The enantiomeric excess was determined by HPLC on Chiralcel columns and the absolute configuration was determined to be (2*S*,3*R*) by comparison of their optical rotations with that of literature data.[4b] n.d. = not determined. [d] The catalyst loading was 10 mol%. [e] In the absence of MS 4 Å.

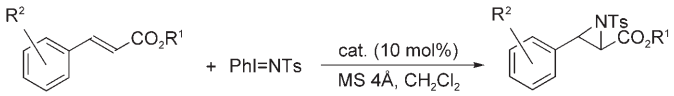
terms of both catalytic activity and enantioselectivity (entry 13 versus 14).

Encouraged by the preliminary results obtained above, the asymmetric aziridination reactions of a variety of alkenes (most are cinnamates) were then investigated by using the optimized reaction conditions. The size of the ester alkyl substituent R^1 has a significant impact on the enantioselectivity of the reaction (Table 2, entries 1–3). The bulky *tert*-butyl ester **10c** afforded the best enantioselectivity with up to >99% *ee* being obtained (entry 3). The other *tert*-butyl cinnamate esters **10c–j** were then used in the catalysis reaction. It is obvious that the substrate adaptability of the catalyst composed of ligand **3a** is excellent (entries 3–10, 94–99% *ee*, 63–99% yield) with the exception of substrate **10h**, which contains an electron-donating group (95% yield, 80% *ee*). The absolute configuration of (−)-**10f** was determined to be (2*S*,3*R*) unambiguously by X-ray crystallographic analysis, by using the Bijvoet method based on the anomalous dispersion of the Br heavy atom (Figure 2) with a Flack parameter of −0.001(12).[10]

Under the same experimental conditions, aziridination of electron-rich *cis*-olefin 2,2-dimethylchromene **10k** also gave an excellent enantiomeric excess of azrindine derivative **11k** with quantitative yield, despite the poor enantioselectivity (28.5% *ee*) for the reactions of simple olefins, such as styrene (Scheme 2).[4c–d]

One-pot procedure for the asymmetric aziridination of olefin derivatives catalyzed by 3/Cu^I complexes: On the basis of the results obtained above, we switched our attention to the development of a one-pot procedure for the asymmetric alkene aziridination with sulfonamide and iodobenzene diacetate or idosylbenzene instead of PhI=NTs as

Table 2. Asymmetric aziridination of olefin derivatives.[a]



10a-j 11a-j

Entry	Substrate	R^1	R^2	Yield [%][b]	*ee* [%][c]	Config.[d]
1	**10a**	Me	H	97	87.6	2*S*,3*R* (−)
2	**10b**	Ph	H	96	87.1	2*S*,3*R* (−)
3	**10c**	*t*Bu	H	99	>99	2*S*,3*R* (−)
4	**10d**	*t*Bu	4-F	99	97.8	(−)
5	**10e**	*t*Bu	4-Cl	97	98.1	(−)
6	**10f**	*t*Bu	4-Br	97	98.3	2*S*,3*R* (−)
7	**10g**	*t*Bu	4-Me	86	94.4	(−)
8	**10h**	*t*Bu	4-MeO	95	80.1	(+)
9	**10i**	*t*Bu	2-NO_2	63	98.6	(+)
10	**10j**	*t*Bu	2,3-MeO	67	97.0	(+)

[a] The reactions were carried out with the ratio of **10**/PhI=NTs/**3a**/Cu 5:1:0.11:0.1 in a 0.125 mmol scale of PhI=NTs (0.042 M) in the presence of 100 mg of MS 4 Å. [b] The yield of isolated product. [c] The enantiomeric excess was determined by HPLC on Chiralcel columns. [d] The absolute configurations of **11a–c** and **11k–l** were determined by comparison of their optical rotations with those of literature data.[4b] The absolute configuration of (−)-**11f** was determined to be (2*S*,3*R*) by the Bijvoet method based on the anomalous dispersion of Br heavy atom.[10]

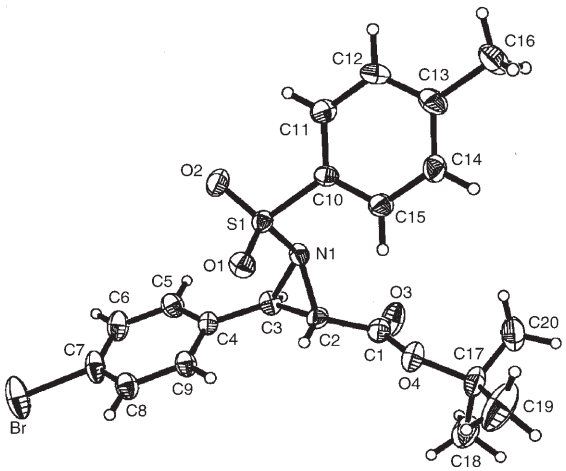
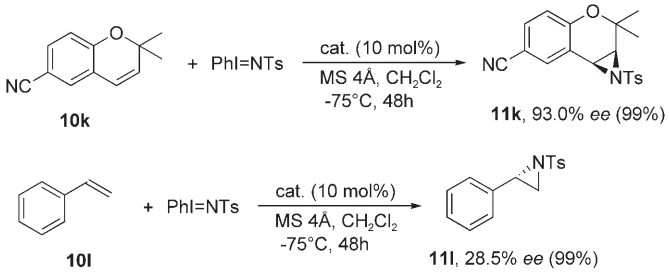


Figure 2. Molecular structure of product **11f**.



Scheme 2. Aziridination of electron-rich olefin derivatives.

the nitrene source in the presence of the **3a**/Cu^I catalyst. The reaction of **10f** proceeded at 0 °C in the presence of MS 4 Å to give the corresponding aziridine **11f** in 34% yield with high enantioselectivity (89.7% *ee*, Table 3, entry 1). On the contrary, the reaction catalyzed by **2**/Cu^I under the same experimental conditions afforded a much lower yield (11%) and enantioselectivity (75.7% *ee*, entry 2). Decreasing the reaction temperature to −75 °C produced comparable enantioselectivity, but with a very low yield (14%, entry 3). Fortunately, when the reaction temperature was adjusted to −30 °C, both the yield and enantioselectivity of the reaction could be significantly improved (44% yield, 95.8% *ee*, entry 4). Although the yield of the reaction could be slightly improved by using PhI=O instead of $PhI(OAc)_2$ as the oxidant, the enantioselectivity dropped to some extent (entry 5 versus 2). Therefore, the subsequent extension of the substrates was carried out under the experimental conditions shown by entry 4. Again, all the cinnamate substrates examined in Table 3, except **10i**, afforded good to excellent enantiomeric excesses of the aziridine derivatives (75–95% *ee*) with moderate yields (entries 6–10). Although the enantioselectivity for the reaction of **10i** was very high (entry 11), the yield of the product was very modest (19%). The low reactivity of this substrate might be attributed to the reduced electron density of the reactive site due to the presence of the electron-withdrawing NO_2 group in the substrate. The much higher yield of the reaction for electron-rich olefin **10k** (entry 12) further supported the above-mentioned speculation. Generally speaking, the yields for this one-pot reaction system are lower than those obtained by using isolated PhI=NTs as nitrene source. This may be attributed to the lower efficiency in the in situ formation of PhI=NTs at a lower temperature (−30 °C) in the reaction system, the instability of the Cu-nitrene intermediate, and the electron-deficient (less reactive) nature of most of the substrates. In fact, the preparation of PhI=NTs from sulfonamide and iodobenzene diacetate requires reaction conditions of room temperature and the presence of KOH.[11]

Table 3. One-pot asymmetric olefin aziridination.[a]

Entry	Substrate	Oxidant	T [°C]	t [h]	Yield [%][b]	*ee* [%][c]
1	**10f**	$PhI(OAc)_2$	0	24	34	89.7 (2*S*,3*R*)
2[d]	**10f**	$PhI(OAc)_2$	0	24	11	75.7 (2*S*,3*R*)
3	**10f**	$PhI(OAc)_2$	−75	48	14	89.6 (2*S*,3*R*)
4	**10f**	$PhI(OAc)_2$	−30	36	44	95.8 (2*S*,3*R*)
5	**10f**	PhI=O	−30	24	46	91.8 (2*S*,3*R*)
6	**10c**	$PhI(OAc)_2$	−30	36	49	96.1 (−)
7	**10d**	$PhI(OAc)_2$	−30	36	55	95.5 (−)
8	**10e**	$PhI(OAc)_2$	−30	36	45	95.3 (−)
9	**10g**	$PhI(OAc)_2$	−30	36	39	88.3 (−)
10	**10h**	$PhI(OAc)_2$	−30	36	41	74.3 (+)
11	**10i**	$PhI(OAc)_2$	−30	36	19	97.4 (+)
12	**10k**	$PhI(OAc)_2$	−30	36	86	75.0 (3*S*,4*S*)

[a] The reaction was carried out with the ratio of **10**/$TsNH_2$/oxidant/**3a**/Cu 5:1:1:0.11:0.1 in a 0.125 mmol scale of $TsNH_2$ (0.042 M). [b] The yield of isolated product. [c] The enantiomeric excess was determined by HPLC on Chiralcel columns. The absolute configuration was determined by comparison of optical rotations with those of literature data.[4b,10] [d] By using ligand **2** instead of **3a** under otherwise identical conditions.

The origin of enantioselectivity: By comparing the structures of ligands **2** and **3a**, it is obvious that the distance between the two imino nitrogen atoms in **3a** is longer than that in **2**, which might result in the formation of a larger bite angle (N-Cu-N) in the **3a**/Cu^I complex. On the other hand, the bite angle in the **3a**/Cu^I complex could be easily adjusted as a result of the relative flexibility of the C1−C1A single bond in ligand **3a** (Figure 1) upon the approach of the substrates. These structural features of ligand **3a** might be responsible for its excellent performance in the Cu^I-catalyzed enantioselective azirination of olefin derivatives. On the basis of the absolute configuration of the products observed in the experiment (Figure 2), the crystal structure of ligand **3a** (Figure 1), and the transition state previously proposed by Scott for the catalysis,[5c] a possible model for asymmetric induction in the aziridination of cinnamates under the present catalytic system has been constructed (Figure 3). After the complexation of **3a** with Cu^I, the sterically bulky 2,6-dichlorophenyl moieties significantly extend forward in the quadrants II and IV, and as a result, the nitrene will bind to Cu^I in quadrant III and the π–π-stacking interaction between one of the 2,6-dichlorophenyl moieties and the tosyl group might further stabilize the orientation of the nitrene species. Accordingly, the olefin substrate will approach the Cu-bound nitrene intermediate from quadrant IV, in which the CO_2R group in the olefin substrate can facilitate the coordination of carbonyl oxygen to three-coordinated copper, giving the product with (2*S*,3*R*) configuration. The sense of asymmetric induction expected according to this model is consistent with that observed in the experiment. On the basis of this asymmetric induction model, it can be also expected that the increase in the steric demand of the alkoxy group in the α,β-unsaturated ester substrate will be favorable for enantioface discrimination in the catalysis, accounting for the results observed in the experiment (entries 1–3 in Table 2).

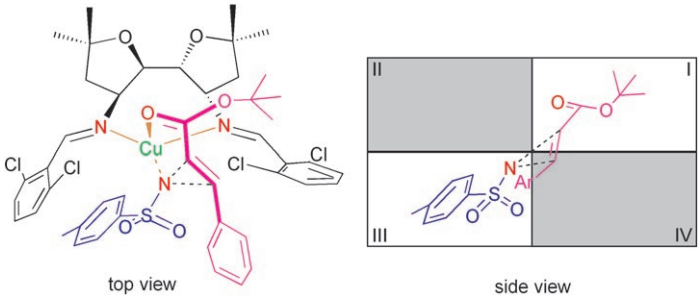


Figure 3. Schematic representation of the proposed asymmetric induction pathway for **3a**/Cu^I-catalyzed aziridination of cinnamate derivatives.

Conclusion

A novel chiral C_2-symmetric 1,4-diamine with multistereogenic centers at the backbone of the ligand has been designed and synthesized from the cheap commercially available natural product D-mannitol, and its diimine derivative **3a** was found to be highly effective for the enantioselective control of the copper-catalyzed asymmetric aziridination of olefin derivatives by using either PhI=NTs or sulfonamide/iodobenzene diacetate as the nitrene source in a one-pot fashion. The research on the application of this novel diamine and its derivatives as the chiral ligands in other asymmetric reactions[12] is currently underway in our laboratory.

Experimental Section

General remarks: NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 spectrometer (^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively). Chemical shifts are reported in ppm relative to an internal standard: TMS ($\delta=0$ ppm) for ^{1}H NMR and $CDCl_3$ ($\delta=77.0$ ppm) for ^{13}C NMR spectra. Coupling constants, *J*, are listed in Hz. Melting points were measured on a XT-4 microscopic instrument and are uncorrected. Optical rotation was measured with a PE-341 automatic polarimeter. Liquid chromatographic analyses were conducted on a JASCO 1580 system. EIMS (70 eV) and ESIMS were obtained on HP5989 A and Mariner LC-TOF spectrometers, respectively. HRMS were determined on a Kratos Concept instrument, Q-Tof micro instrument, or APEXIII 7.0 TESLA FTMS. IR spectra were measured with a BIO-Rad FIS-185 instrument. Elemental analysis was performed with an Elemental VARIO EL apparatus. All the experiments sensitive to moisture or air were carried out under an argon atmosphere by using standard Schlenk techniques. Commercial reagents were used as received without further purification unless otherwise noted. Benzene and THF were freshly distilled over sodium benzophenone ketyl. Dichloromethane, *N*,*N*-dimethylformamide, and acetonitrile were distilled from calcium hydride, and methanol from magnesium prior to use. The key intermediate, 2,2-dimethyl-4,5-bis-oxiranyl-1,3-dioxolane **4** was synthesized from natural D-mannitol following a literature method.[8] 3-Arylacrylic esters **10a–h** were prepared from corresponding acid derivatives by following literature methods.[5e]

(4*R*,5*R*)-4,5-Bis[(1*R*)-1-hydroxy-3-methylbut-3-enyl]-2,2-dimethyl-1,3-dioxolane (5): A solution of the 2-methylvinyl magnesium bromide, prepared from the reaction of 2-bromopropene (5.3 mL, 59.7 mmol) with magnesium ribbon (1.45 g, 60 mmol) in dry THF (25 mL) was added dropwise to a stirred solution of CuI (1.14 g, 6 mmol) in dry THF (30 mL) at −30 °C. After the resulting mixture had been stirred for 15 min at −30 °C, a solution of **4** (2.7 g, 13.4 mmol) in dry THF (20 mL) was added dropwise over 30 min. Stirring was continued for 1 h at −30 °C and an additional 1 h at 0 °C. After this time, the reaction was quenched first by the addition of MeOH (4 mL) and then by being poured into saturated NH_4Cl solution (150 mL). The mixture was extracted with EtOAc (3×150 mL) and the combined organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography (hexane/EtOAc 8:1–7:1) to give **5** (3.6 g, 93%) as a colorless oil. $[\alpha]_D^{20}=+1.1$ ($c=0.8$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=4.93$–4.87 (m, 4H), 3.78–3.76 (m, 4H), 3.25 (br, 2H), 2.57 (d, $J=14.1$ Hz, 2H), 2.21–2.01 (m, 2H), 1.68 (s, 6H), 1.28 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=142.5$, 113.7, 109.2, 83.1, 70.5, 42.7, 27.1, 22.7 ppm; FTIR (KBr pellet): $\tilde{\nu}=3369$, 2938, 1651, 1455, 1373, 1239, 1070, 880 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 271 (0.6) $[M+1]^+$, 255 (11), 215 (6), 157 (17), 115 (29), 109 (37), 81 (57), 59 (100); HRMS (EI): calcd for $C_{15}H_{20}O_4$: 270.1831; found: 270.1811 $[M]^+$.

(4*S*,5*S*)-4,5-Bis[(1*R*)-1-methanesulfonyloxy-3-methylbut-3-enyl]-2,2-dimethyl-1,3-dioxolane (6): To a solution of **5** (3.24 g, 12 mmol) in CH_2Cl_2 (50 mL) was added NEt_3 (4 mL, 28.8 mmol) at 0 °C under argon. After stirring for 10 min, MsCl (4 mL, 28.8 mmol) in CH_2Cl_2 (50 mL) was added at 0 °C and the reaction temperature was then increased to RT. After the mixture had been stirred at RT overnight, the mixture was quenched with H_2O (40 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by flash-column chromatography on silica gel (hexane/EtOAc 4:1–2:1) to afford **6** (5.1 g, >99%) as a colorless oil. $[\alpha]_D^{20}=+14.3$ ($c=1.1$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=4.95$–4.91 (m, 6H), 4.25–4.24 (m, 2H), 3.06 (s, 6H), 2.55–2.52 (m, 4H), 1.83 (s, 6H), 1.45 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.9$, 115.3, 111.0, 79.5, 78.7, 38.8, 38.7, 27.0, 22.2 ppm; FTIR (KBr pellet): $\tilde{\nu}=2987$, 2942, 1651, 1456, 1358, 1340, 1174, 1083, 952, 910, 798, 527 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 426 (0.6) $[M]^+$, 411 (136), 371 (2), 291 (13), 177 (15), 159 (19), 109 (77), 81 (100), 55 (51), 43 (48); HRMS (MALDI-DHB): calcd for $C_{17}H_{30}O_8S_2Na$: 449.1279; found: 449.1274 $[M+Na]^+$.

(2*S*,2′*S*,3*R*,3′*R*)-3,3′-Dimethanesulfonyloxy-5,5,5′,5′-tetramethyloctahydro-2,2′-bifuranyl (7): Aqueous perchloric acid solution (20 mL, 70%) was added dropwise to a solution of **6** (3.5 g, 8.2 mmol) in CH_2Cl_2 (50 mL) at −10 °C. After stirring for 0.5 h at −10 °C, the reaction mixture was neutralized with saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (2×150 mL) and the combined organic extracts were washed with H_2O and brine, and were then dried over Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by flash-column chromatography on silica gel (hexane/EtOAc 3:1–2:1) to afford **7** (2.4 g, 75%) as a white solid. M.p. 94–95 °C $[\alpha]_D^{20}=-60.4$ ($c=1.0$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=5.17$–5.15 (m, 2H), 4.29 (d, $J=2.4$ Hz, 2H), 3.04 (s, 6H), 2.08 (d, $J=4.2$ Hz, 4H), 1.31 (s, 6H), 1.29 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=82.7$, 82.4, 82.3, 44.9, 38.3, 28.7, 27.4 ppm; FTIR (KBr pellet): $\tilde{\nu}=2979$, 2941, 2864, 1435, 1357, 1181, 1164, 1116, 1052, 964, 942, 890 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 193 (6), 137 (2), 98 (100), 83 (9), 79 (15), 69 (14), 57 (9), 43 (23); elemental analysis (%) calcd for $C_{14}H_{26}O_8S_2$: C 43.51, H 6.78%; found: C 43.49, H 6.85.

(2*R*,2′*R*,3*S*,3′*S*)-3,3′-Diazido-5,5,5′,5′-tetramethyloctahydro-2,2′-bifuranyl (8): A solution of **7** (100 mg, 0.26 mmol) and NaN_3 (84.2 mg, 1.4 mmol) in dry DMF (5 mL) was heated at 100 °C for 12 h, and then another equivalent of NaN_3 (84.2 mg, 1.4 mmol) was added. The resulting mixture was then stirred for 12 h at this temperature before being cooled to RT. After removing the solvent in vacuo, the residue was diluted with H_2O (5 mL) and extracted with EtOAc (3×5 mL). The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by flash-column chromatography on silica gel (hexane/EtOAc 12:1) to afford **8** (40 mg, 65% Yield) as a colorless oil. $[\alpha]_D^{20}=+212.8$ ($c=1.0$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=4.27$–4.24 (m, 2H), 3.99–3.98 (m, 2H), 2.20–2.04 (m, 4H), 1.39 (s, 6H), 1.31 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=80.5$, 80.3, 63.3, 44.1, 29.2, 28.5 ppm; FTIR (KBr pellet): $\tilde{\nu}=2974$, 2936, 2895, 2512, 2105, 1760, 1736, 1687, 1450, 1368, 1268, 1135, 1062, 1014, 885, 790, 734 cm^{-1}; MS (MALDI-TOF): 303.2 $[M+Na]^+$; HRMS (MALDI-DHB): calcd for $C_{12}H_{20}N_6O_2Na$: 303.1546; found: 303.1540 $[M+Na]^+$.

(2*R*,2′*R*,3*S*,3′*S*)-5,5,5′,5′-Tetramethyloctahydro-2,2′-bifuranyl-3,3′-diamine (9): Pd/C (10%, 140 mg) was added to a stirred solution of **8** (700 mg, 2.5 mmol) in MeOH (15 mL) under argon. The argon gas was replaced with a stream of hydrogen, and then the mixture was stirred at 25 °C under 1 atm of hydrogen for 24 h. After this time, the catalyst was removed by filtration through a Celite pad. The solution obtained was then concentrated under reduced pressure to give **9** (570 mg, >99%) as a white solid, which could be used without further purification. This compound can be recrystallized from hexane. M.p. 40–41 °C; $[\alpha]_D^{20}=-110.2$ ($c=0.6$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=4.04$ (d, $J=6.0$ Hz, 2H), 3.75 (q, $J=6.9$ Hz, 2H), 2.02 (dd, $J=4.8$, 7.2 Hz, 2H), 1.67 (dd, $J=4.8$, 7.2 Hz, 2H), 1.63 (br, 4H), 1.37 (s, 6H), 1.20 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=79.2$, 78.7, 54.9, 49.0, 29.2, 28.0 ppm; FTIR (KBr pellet): $\tilde{\nu}=3352$, 3264, 3189, 2969, 2932, 2907, 1600, 1450, 1381, 1362, 1312, 1249, 1131, 1095, 1048, 969, 898, 863, 794, 535 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 229 $[M+1]^+$ (1), 211 (7), 155 (6), 144 (11), 114 (6), 98 (13), 84

(39), 70 (100), 58 (30), 43 (15); HRMS (MALDI-DHB): calcd for $C_{12}H_{24}N_2O_2Na$: 251.1735; found: 251.1730 $[M+Na]^+$.

(2*R*,2′*R*,3*S*,3′*S*)-5,5,5′,5′-Tetramethyl-3*N*,3′*N*-bis(2,6-dichlorobenzylidene)octahydro-2,2′-bifuranyl-3,3′-diamine (3a): A solution of **9** (510 mg, 2.2 mmol) and 2,6-dichlorobenzaldehyde (783 mg, 4.5 mmol) in dry MeOH (15 mL) was heated to reflux for 24 h. After removal of part of the solvent by evaporation, the concentrated solution was cooled to RT to give **3a** (1130 mg, 93%) as colorless crystals. M.p. 197–198°C; $[\alpha]_D^{20}=+139.8$ ($c=0.6$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.49$ (s, 2H), 7.40–7.37 (m, 4H), 7.30–7.25 (m, 2H), 4.31–4.32 (m, 2H), 4.19 (d, $J=6.6$ Hz, 2H), 2.19 (q, $J=6.9$ Hz, 2H), 1.89 (dd, $J=1.2$, 12.0 Hz, 2H), 1.49 (s, 6H), 1.35 ppm (s, 6H); FTIR (KBr pellet): $\tilde{\nu}=2968$, 2934, 2891, 1651, 1585, 1561, 1447, 1435, 1377, 1369, 1330, 1301, 1173, 1130, 1092, 1055, 1031, 963, 938, 857, 791, 774 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 543 (44) $[M]^+$, 367 (21), 311 (100), 270 (224), 242 (40), 226 (55), 185 (34), 174 (35), 159 (46), 123 (28), 98 (37), 69 (22), 55 (21), 43 (43), 41 (51); elemental analysis (%) calcd for $C_{26}H_{28}Cl_2N_2O_2$: C 57.58, H 5.20, N 5.17; found: C 57.74, H 5.15, N 5.15.

X-ray crystallographic analysis of 3a:[10] A single crystal of **3a** was obtained by slow evaporation of the solvent (MeOH) at room temperature. X-ray crystallographic analysis was performed with a Bruker SMART CCD-APEX at 20°C by using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). A total of 4095 reflections were measured and 2796 were unique ($R_{int}=0.0385$). The structure was solved by direct methods (SHELX-97) and refined by full-matrix least-squares to $R=0.0436$ and $R_w=0.0533$. Crystal data for **3a**: $C_{26}H_{28}N_2O_2Cl_4$, formula weight: 542.30, monoclinic, space group: C2, $a=20.193(3)$, $b=6.8532(9)$, and $c=11.2737(14)$ Å, $V=1343.2(3)$ Å^3, $Z=2$, $\rho_{calcd}=1.341$ g cm^{-3}, $F(000)=564$, μ ($Mo_{K\alpha}$) $=0.466$ mm^{-1}.

(2*R*,2′*R*,3*S*,3′*S*)-5,5,5′,5′-Tetramethyl-3*N*,3′*N*-bis(2,4,6-trimethylbenzylidene)octahydro-2,2′-bifuranyl-3,3′-diamine (3b): Following a similar procedure for the preparation of **3a**, **3b** was obtained in 75% yield. M.p.: 168–169°C; $[\alpha]_D^{20}=+228.4$ ($c=0.5$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.51$ (s, 2H), 6.90 (s, 4H), 4.33–4.35 (m, 2H), 3.79–3.81 (m, 2H), 2.46 (s, 12H), 2.31 (s, 6H), 2.12 (dd, $J=6.0$, 6.9 Hz, 2H), 1.73 (dd, $J=1.8$, 8.1 Hz, 2H), 1.47 (s, 6H), 1.33 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.0$, 139.3, 138.3, 129.9, 82.3, 80.5, 73.5, 49.0, 30.0, 29.2, 21.6, 21.1 ppm; FTIR (KBr pellet): $\tilde{\nu}=2978$, 2922, 2888, 1635, 1610, 1484, 1450, 1427, 1378, 1360, 1338, 1295, 1237, 1179, 1136, 1077, 1044, 1029, 966, 952, 857, 786, 767 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 488 (3) $[M]^+$, 404 (3), 355 (3), 341 (487), 326 (14), 285 (59), 244 (30), 187 (28), 159 (100), 148 (67), 133 (56), 117 (30), 98 (27), 41 (23); elemental analysis (%) calcd for $C_{32}H_{44}N_2O_2$: C 78.65, H 9.07, N 5.73; found: C 78.36, H 9.08, N 5.37.

***tert*-Butyl-3-(2-nitrophenyl)acrylate (10i)**: Thionyl chloride (40 mL) was added to 3-(2-Nitrophenyl)acrylic acid (2.9 g, 15.0 mmol) in a 100 mL round-bottomed flask. The mixture was heated to reflux and kept at the corresponding temperature for 60 min. After this time, the hot solution was poured into cold hexane (100 mL) and the solution was distilled until a minimum amount of liquid remained. Hexane (50 mL) was again added and the solution redistilled. Finally, the solvent was removed in vacuo to leave a pale yellow solid, which was dissolved in *t*-butanol (60 mL) and pyridine (6 mL). The reaction mixture was heated to reflux for 10 h and then cooled to RT and quenched with a solution of saturated $NaHCO_3$ (5.69 g, 28.3 mmol). The resulting mixture was extracted with diethyl ether (3×50 mL) and the combined organic extracts were dried over $MgSO_4$. After removal of the solvent under vacuum, the residue was purified by flash-column chromatography on silica gel (hexane/EtOAc 30:1) to afford **10i** (1.87 g, 50%) as a white solid. M.p. 69–70°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.05$–7.99 (m, 2H), 7.65–7.52 (m, 3H), 6.30 (d, $J=15.9$ Hz, 1H), 1.55 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=165.0$, 148.2, 138.7, 133.4, 130.7, 130.0, 129.1, 125.2, 124.8, 81.1, 28.0 ppm; FTIR (KBr pellet): $\tilde{\nu}=3072$, 2983, 1702, 1639, 1606, 1571, 1525, 1475, 1442, 1368, 1341, 1291, 1213, 1159, 984, 867, 854, 792, 749, 719 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 194 (29), 147 (9), 130 (39), 120 (106), 102 (14), 92 (9), 77 (8), 65 (9), 57 (100), 41 (28); HRMS (MALDI-DHB): calcd for $C_{13}H_{15}NO_4SNa$: 272.0898; found: 272.0893 $[M+Na]^+$; elemental analysis (%) calcd for $C_{13}H_{15}NO_4S$: C 62.64, H 6.07, N 5.62; found: C 63.10, H 6.10, N 5.26.

***tert*-Butyl-3-(2,3-dimethoxyphenyl)acrylate (10j)**: Concentrated H_2SO_4 (1.1 mL, 20 mmol) was added dropwise to a stirred suspension of $MgSO_4$ (9.62 g, 80 mmol) in CH_2Cl_2 (80 mL). After stirring for 15 min, 3-(2,3-dimethoxyphenyl)acrylic acid (4.16 g, 20 mmol) and *tert*-butanol (9.56 mL, 100 mmol) were added. The reaction mixture was stirred for 24 h at RT, and then quenched with saturated $NaHCO_3$ solution (100 mL). The resultant mixture was extracted with diethyl ether (3×100 mL) and the combined organic extracts were dried over $MgSO_4$. After removal of the solvent under vacuum, the residue was purified by flash-column chromatography on silica gel (hexane/EtOAc 30:1) to afford **10j** (2.17 g, 41%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.92$ (d, $J=16.2$ Hz, 1H), 7.15 (dd, $J=1.8$, 6.2 Hz, 1H), 7.05 (t, $J=8.1$ Hz, 1H), 6.92 (dd, $J=1.8$, 6.2 Hz, 1H), 6.41 (d, $J=16.2$ Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 1.56 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.5$, 153.1, 148.2, 138.2, 128.8, 124.1, 121.3, 119.0, 113.5, 80.4, 61.3, 55.8, 28.2 ppm; FTIR (KBr pellet): $\tilde{\nu}=3007$, 2933, 1706, 1630, 1595, 1581, 1520, 1467, 1456, 1367, 1342, 1255, 1147, 1134, 1019, 984, 861, 846, 804, 759 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 264 (54) $[M]^+$, 208 (89), 191 (70), 177 (100), 148 (19), 133 (15), 121 (31), 105 (19), 91 (18), 77 (25), 65 (6), 57 (44), 41 (31); HRMS (MALDI-DHB): calcd for $C_{15}H_{20}O_4SNa$: 287.1255; found: 287.1254 $[M+Na]^+$.

General procedure for 3a/Cu^I-catalyzed aziridinations: Dry CH_2Cl_2 (3 mL) was added to a Schlenk tube containing the copper salt (0.0125 mmol) and the chiral diimine ligand (0.014 mmol) under argon, The mixture was then stirred at room temperature for 1 h. After this time, the reaction system was cooled to −75°C and the olefin (0.625 mmol) and PhI=NTs (47 mg, 0.125 mmol) were added sequentially to the stirred solution against a slow positive flow of argon. The reaction was monitored by TLC. After the completion of reaction, the mixture was concentrated to dryness and the residue was purified by flash chromatography on silica gel (EtOAc/hexane 1:4–1:6) to give the corresponding aziridine derivatives **11**.

Compound 11a: 87.6% *ee*, $[\alpha]_D^{20}=-27.8$ ($c=1.3$ in CH_2Cl_2); lit.[4b] 96% *ee* (2*R*,3*S*); $[\alpha]_D^{25}=+33.1$ ($c=1.00$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.77$ (d, $J=8.7$ Hz, 2H), 7.32–7.24 (m, 7H), 4.44 (d, $J=3.9$ Hz, 1H), 3.86 (s, 3H), 3.53 (d, $J=3.9$ Hz, 1H), 2.41 ppm (s, 3H); EIMS (70 eV): *m*/*z* (%): 331 (0.3) $[M]^+$, 300 (2), 272 (2), 155 (6), 176 (59), 144 (19), 116 (100), 91 (37), 77 (11), 65 (20), 49 (15). The enantiomeric excess of **11a** was determined by HPLC on a Chiralcel AS-H column (hexane/2-propanol 60:40; flow rate: 0.6 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=21.8$ min (major isomer), $t_{R2}=35.7$ min (minor isomer)).

Compound 11b: 87.0% *ee*, $[\alpha]_D^{20}=-41.5$ ($c=1.1$ in CH_2Cl_2); lit.[4b] 97% *ee* (2*R*,3*S*), lit.[4b] $[\alpha]_D^{25}=+44.4$ ($c=1.03$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.85$ (d, $J=8.4$ Hz, 2H), 7.45–7.23 (m, 12H), 4.63 (d, $J=3.9$ Hz, 1H), 3.71 (d, $J=3.9$ Hz, 1H), 2.44 ppm (s, 3H); EIMS (70 eV): *m*/*z* (%): 300 (39), 238 (71), 183 (27), 155 (38), 139 (66), 116 (54), 91 (100), 77 (28), 65 (39). The enantiomeric excess of **11b** was determined by HPLC on a Chiralcel OJ-H column (hexane/2-propanol 60:40; flow rate: 0.6 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=57.1$ min (major isomer), $t_{R2}=92.2$ min (minor isomer)).

Compound 11c: >99% *ee*, $[\alpha]_D^{20}=-22.9$ ($c=1.0$ in CH_2Cl_2); lit.[4b] 96% *ee* (2*R*,3*S*), $[\alpha]_D^{25}=+27.5$ ($c=1.03$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.80$ (d, $J=8.4$ Hz, 2H), 7.32–7.26 (m, 7H), 4.39 (d, $J=3.9$ Hz, 1H), 3.41 (d, $J=3.9$ Hz, 1H), 2.42 (s, 3H), 1.55 ppm (s, 9H); ESIMS (*m*/*z*): 396.1 $[M+Na]^+$. The enantiomeric excess of **11c** was determined by HPLC on a Chiralcel OJ-H column (hexane/2-propanol 70:30; flow rate: 0.7 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=16.0$ min (major isomer), $t_{R2}=20.7$ min (minor isomer)).

Compound 11d: 97.8% *ee*, $[\alpha]_D^{20}=-37.8$ ($c=0.7$ in CH_2Cl_2); lit.[5c] 98% *ee*; $[\alpha]_D^{30}=-42.2$ ($c=0.25$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.75$ (d, $J=8.1$ Hz, 2H), 7.25 (d, $J=8.1$ Hz, 2H), 7.23–7.16 (m, 2H), 6.98–6.93 (m, 2H), 4.32 (d, $J=3.6$ Hz, 1H), 3.37 (d, $J=3.6$ Hz, 1H), 2.39 (s, 3H), 1.51 ppm (s, 9H); EIMS (70 eV): *m*/*z* (%): 336 (30), 318 (21), 292 (18), 180 (31), 155 (6), 136 (16), 108 (15), 91 (24), 57 (100). The enantiomeric excess of **11d** was determined by HPLC on a Chiralcel OD column (hexane/2-propanol 97:3; flow rate: 1.0 mL min^{-1}; UV detection

at $\lambda=230$ nm; $t_{R1}=11.6$ min (major isomer), $t_{R2}=13.0$ min (minor isomer)).

Compound 11e: 98.1% *ee*, $[\alpha]_D^{20}=-39.6$ ($c=0.6$ in CH_2Cl_2); lit.[5c] 93% *ee*; $[\alpha]_D^{26}=-41.0$ ($c=0.66$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.80$ (d, $J=8.7$ Hz, 2H), 7.31–7.27 (m, 4H), 7.19–7.17 (m, 2H), 4.35 (d, $J=3.9$ Hz, 1H), 3.39 (d, $J=3.9$ Hz, 1H), 2.43 (s, 3H), 1.60 ppm (s, 9H); ESIMS *m/z*: 430.0 $[M+Na]^+$. The enantiomeric excess of **11e** was determined by HPLC on a Chiralcel OD column (hexane/2-propanol 97:3; flow rate: 1.0 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=12.2$ min (major isomer), $t_{R2}=14.3$ min (minor isomer)).

Compound 11f: 98.3% *ee*, $[\alpha]_D^{20}=-40.4$ ($c=0.6$ in CH_2Cl_2); lit.[5c] 98% *ee*, $[\alpha]_D^{30}=-41.8$ ($c=0.33$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.79$ (d, $J=8.7$ Hz, 2H), 7.29 (d, $J=8.7$ Hz, 2H), 7.28 (d, $J=8.4$ Hz, 2H), 7.10 (d, $J=8.4$ Hz, 2H), 4.33 (d, $J=3.9$ Hz, 1H), 3.38 (d, $J=3.9$ Hz, 1H), 2.42 (s, 3H), 1.54 ppm (s, 9H); ESIMS *m/z*: 474.0 $[M+Na]^+$. The enantiomeric excess of **11f** was determined by HPLC on a Chiralcel OD column (hexane/2-propanol 97:3; flow rate: 1.0 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=12.7$ min (major isomer), $t_{R2}=16.1$ min (minor isomer)).

X-ray crystallographic analysis of (−)-11f:[10] A single crystal of (−)-**11f** was obtained by slow evaporation of the solvent (dichloromethane/hexane) at room temperature. X-ray crystallographic analysis was performed by using a Bruker SMART CCD-APEX at 20°C with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). A total of 6175 reflections were measured and 4404 were unique ($R_{int}=0.0931$). The structure was solved by direct methods (SHELX-97) and refined by full-matrix least-squares to $R=0.0582$ and $R_w=0.0875$. Crystal data for (−)-**11f**: $C_{20}H_{22}BrN_2O_4S$, formula weight = 452.32, monoclinic, space group $P2_1$, $a=6.113(10)$, $b=20.414(3)$, and $c=8.4961(13)$ Å, $V=1058.7(3)$ Å^3, $\rho_{calcd}=1.419$ g cm^{-3}, $Z=2$, $F(000)=464$, μ ($Mo_{K\alpha}$) = 2.064 mm^{-1}. The absolute configuration of (−)-**11f** was determined by the Bijvoet method, based on the anomalous dispersion of Br heavy atom, to be unambiguously (2*S*,3*R*) with a Flack parameter of −0.001(12).

Compound 11g: 94.4% *ee*, $[\alpha]_D^{20}=-16.3$ ($c=1.1$ in CH_2Cl_2); lit.[5c] 88% *ee*, $[\alpha]_D^{30}=-18.9$ ($c=0.84$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.80$ (d, $J=6.6$ Hz, 2H), 7.31–7.27 (m, 2H), 7.18–7.11 (m, 4H), 4.36 (d, $J=3.9$ Hz, 1H), 3.46 (d, $J=3.9$ Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 1.55 ppm (s, 9H); EIMS (70 eV): *m/z* (%): 387 (0.3) $[M]^+$, 332 (13), 314 (17), 288 (8), 176 (100), 158 (13), 130 (83), 117 (17), 91 (32), 77 (13), 65 (16), 57 (74), 41 (26). The enantiomeric excess of **11g** was determined by HPLC on a Chiralcel OD column (hexane/2-propanol 98:2; flow rate: 1.0 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=11.4$ min (major isomer), $t_{R2}=13.2$ min (minor isomer)).

Compound 11h: 80.1% *ee*, $[\alpha]_D^{20}=+5.9$ ($c=0.7$ in CH_2Cl_2); lit.[5c] 93% *ee*, $[\alpha]_D^{26}=+30.4$ ($c=1.06$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.93$ (d, $J=8.1$ Hz, 2H), 7.36 (d, $J=8.1$ Hz, 2H), 7.23 (d, $J=8.7$ Hz, 2H), 6.80 (d, $J=8.7$ Hz, 2H), 4.03 (d, $J=7.5$ Hz, 1H), 3.76 (s, 3H), 3.57 (d, $J=7.5$ Hz, 1H), 2.45 (s, 3H), 1.18 ppm (s, 9H); EIMS (70 eV): *m/z* (%): 403 (0.5) $[M]^+$, 348 (15), 330 (8), 304 (5), 192 (100), 174 (10), 146 (40), 91 (33), 77 (11), 65 (11), 57 (64), 41 (21). The enantiomeric excess of **11h** was determined by HPLC on a Chiralcel OD column (hexane/2-propanol 97:3; flow rate = 1.0 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=12.3$ min (major isomer), $t_{R2}=13.8$ min (minor isomer)).

Compound 11i: M.p. 110–111°C; 98.6% *ee*; $[\alpha]_D^{20}=+15.9$ ($c=0.7$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.15$ (d, $J=7.5$ Hz, 1H), 7.90 (d, 2H, $J=8.1$ Hz), 7.51–7.47 (m, 2H), 7.36 (d, $J=8.1$ Hz, 2H), 7.22–7.19 (m, 1H), 4.97 (d, $J=3.9$ Hz, 1H), 3.21 (d, $J=3.9$ Hz, 1H), 2.46 (s, 3H), 1.59 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=163.8$, 148.0, 144.4, 137.5, 134.1, 130.2, 129.7, 129.5, 128.9, 127.5, 125.1, 83.8, 49.0, 46.4, 29.3, 27.8 ppm; FTIR (KBr pellet): $\tilde{\nu}=2924$, 2854, 1743, 1597, 1528, 1344, 1164, 1086, 930, 843, 816, 687, 598 cm^{-1}; ESIMS *m/z*: 419.1 $[M+1]^+$; HRMS (MALDI-DHB): calcd for $C_{20}H_{22}N_2O_6SNa$: 441.1096; found: 441.1091 $[M+Na]^+$.

The enantiomeric excess of **11i** was determined by using HPLC on a Chiralcel AS-H column (hexane/2-propanol 70:30; flow rate = 0.8 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=22.5$ (minor isomer), $t_{R2}=27.6$ min (major isomer)).

Compound 11j: M.p. 53–54°C; 97.0% *ee*; $[\alpha]_D^{20}=+4.0$ ($c=1.30$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.85$ (d, $J=8.1$ Hz, 2H), 7.29 (d, $J=8.1$ Hz, 2H), 6.97–6.85 (m, 2H), 6.60 (d, $J=6.6$ Hz, 1H), 4.65 (d, $J=4.2$ Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.40 (d, $J=4.2$ Hz, 1H), 2.43 (s, 3H), 1.55 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=164.6$, 152.5, 148.4, 144.0, 137.6, 129.5, 127.5, 127.3, 124.0, 118.5, 112.7, 83.28, 61.0, 55.8, 48.3, 43.7, 27.8, 21.6 ppm; FTIR (KBr pellet): $\tilde{\nu}=2926$, 2844, 1734, 1582, 1481, 1337, 1223, 1161, 1087, 912, 840, 815, 713, 676 cm^{-1}; EIMS (70 eV): *m/z* (%): 433 (1) $[M]^+$, 360 (6), 222 (100), 204 (11), 176 (28), 162 (17), 147 (12), 91 (13), 77 (4), 57 (18), 41 (6); HRMS (ESI): calcd for $C_{22}H_{27}NO_6SNa$: 456.1457; found: 446.1451 $[M+Na]^+$. The enantiomeric excess of **11j** was determined with HPLC on a Chiralcel AS-H column (hexane/2-propanol 80:20; flow rate = 0.6 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=21.8$ (minor isomer), $t_{R2}=25.6$ min (major isomer)).

Compound 11k: 93.0% *ee*, $[\alpha]_D^{20}=-110.8$ ($c=1.25$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.81$ (d, $J=8.7$ Hz, 2H), 7.55 (d, $J=2.4$ Hz, 1H), 7.47 (dd, $J=1.8$, 6.6 Hz, 1H), 7.32 (d, $J=8.1$ Hz, 2H), 6.81 (d, $J=8.7$ Hz, 1H), 3.86 (d, $J=7.2$ Hz, 1H), 3.37 (d, $J=7.2$ Hz, 1H), 2.43 (s, 3H), 1.29 (s, 3H), 1.25 ppm (s, 3H); EIMS (70 eV): *m/z* (%): 354 (0.5) $[M]^+$, 199 (100), 184 (5), 157 (8), 145 (16), 130 (22), 91 (43), 77 (9), 65 (24), 55 (22), 41 (17). The enantiomeric excess of **11k** was determined by using HPLC on a Chiralcel OJ column (hexane/2-propanol 80:20; flow rate = 1.0 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=32.5$ (major isomer, *S*,*S*), $t_{R2}=43.3$ min (minor isomer, *R*,*R*)).[4c]

Compound 11l: 28.5% *ee*, $[\alpha]_D^{20}=+26.7$ ($c=0.7$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.88$ (d, $J=8.1$ Hz, 2H), 7.35–7.21 (m, 7H), 3.79 (dd, $J_1=3.0$ Hz, $J_2=4.5$ Hz, 1H), 2.99 (d, $J=7.2$ Hz, 1H), 2.44 (s, 3H), 2.40 ppm (d, $J=4.5$ Hz, 1H); EIMS (70 eV): *m/z* (%): 273 (0.5) $[M]^+$, 180 (8), 155 (2), 134 (3), 118 (70), 91 (100), 77 (3), 65 (26), 57 (13), 41 (77). The enantiomeric excess of **11l** was determined by using HPLC on a Chiralcel OJ column (hexane/2-propanol 90:10; flow rate = 0.8 mL min^{-1}; UV detection at $\lambda=230$ nm; $t_{R1}=33.4$ (major isomer, *R*), $t_{R2}=41.2$ min (minor isomer, *S*)).[4c]

General procedure for the one-pot procedure of the asymmetric alkene aziridinations: Dry CH_2Cl_2 (3 mL) was added to a Schlenk tube containing $[Cu(CH_3CN)_4]ClO_4$ (4.2 mg, 0.0125 mmol) and the chiral diimine ligand **3a** (7.7 mg, 0.014 mmol) under argon, and the resultant mixture was stirred at RT for 1 h. After the reaction system was cooled to −30°C, the olefin (0.625 mmol, 5 equiv) was added to the solution under a slow positive flow of argon and the mixture was stirred for an additional 30 min. $TsNH_2$ (21.4 mg, 0.125 mmol) and $PhI(OAc)_2$ (40.3 mg, 0.125 mmol) were then added in one portion to the stirred solution. After the reaction was completed, the mixture was concentrated to dryness and the residue was purified by flash chromatography on silica gel (EtOAc/hexane 1:4–1:6). The product was identified by ^{1}H NMR spectroscopy and its enantiomeric excess was determined by HPLC on a Chiracel column.

Acknowledgements

Financial support from the National Natural Science Foundation of China, the Chinese Academy of Sciences, the Major Basic Research Development Program of China (Grant no. G2000077506), and the Science and Technology Committee of Shanghai Municipality is gratefully acknowledged.

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Received: September 7, 2005
Revised: February 20, 2006
Published online: April 6, 2006

