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Asymmetric Catalysis via Chiral Aziridines*

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The chiral bis(aziridines) **4**, **6** and **7** have been synthesized and evaluated as chelating ligands for a variety of asymmetric transformations mediated by metals. The processes studied were the asymmetric addition of osmium tetroxide to olefins, copper-catalyzed asymmetric cyclopropanation and aziridination, palladium-catalyzed asymmetric allylic alkylation and asymmetric 1,2-addition of organolithium reagents to imines. In the best cases an enantiomeric excess >95% was obtained.

Our long-standing interest in the chemistry of chiral aziridines[1,2] has led us to prepare a new class of chiral ligands suitable for metal-mediated asymmetric synthesis. The general structure of these ligands is shown in Fig. 1 and is characterized by the following features: (*i*) C_2-symmetry, (*ii*) easy availability in both enantiomeric forms and with different tether lengths, (*iii*) as will be shown below, they are useful for both stoichiometric and catalytic asymmetric synthesis mediated by a range of metals (Os, Cu, Pd, Li).

In a recent preliminary communication[3] we reported on the use of one such ligand in the stoichiometric asymmetric addition of osmium tetroxide to olefins, as well as catalytic asymmetric cyclopropanation and aziridination reactions. We have now developed an alternative route to a number of new ligands of this type and in this paper we present full experimental details for their use in the transformations listed above. A new application of these ligands to enantioselective additions of organolithium reagents to imines will also be described. Mechanistic studies of palladium-catalyzed asymmetric allylic alkylation[3] have been reported in detail elsewhere.[4]

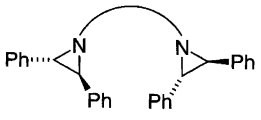

Fig. 1. Schematic representation of the C_2-symmetric bis(aziridine) ligands.

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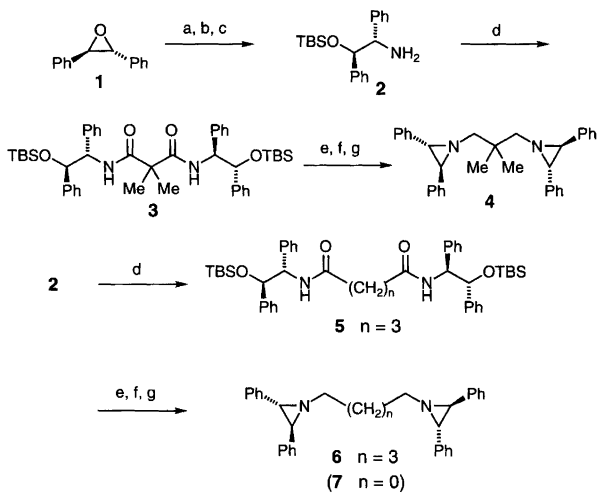
Results and discussion

Ligand synthesis. The route previously used[4] for the synthesis of ligand **7** was found to be less suitable for the new ligands **4** and **6**, and their synthesis is shown in Scheme 1.

(*R,R*)-2,3-Diphenyloxirane **1**[5] was ring-opened by sodium azide, the resultant azido alcohol was protected as the *tert*-butyldimethylsilyl (TBS) ether, and the azide



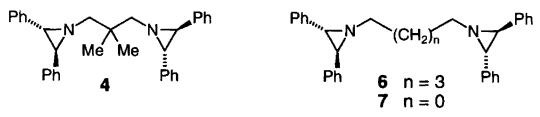
Scheme 1. Synthesis of ligands **4** and **6**. TBS = $SiMe_2{}^tBu$. (a) NaN_3, NH_4Cl, 2-methoxyethanol–H_2O, 90 °C, 93%; (b) TBSCl, imidazole, DMF, room temp., 94%; (c) Ph_3P, THF–H_2O, reflux, 93%; (d) dimethylmalonyl dichloride or glutaryl dichloride, toluene–pyridine, room temp., 91% for **3**, 92% for **5**; (e) BH_3·THF, reflux, 84% from **3**, 72% from **5**; (f) Bu_4NF, THF, room temp.; (g) Ph_3P, diethyl azodicarboxylate, THF, room temp., 55% (two steps) for **4**, 74% (two steps) for **6**.

was reduced to the primary amine **2**. This was then reacted with the appropriate bis(acyl chloride) to give **3** or **5**, followed by a sequence of reduction, deprotection and ring-closure to give **4** and **6**, respectively. Overall yields were good, and the sequence obviously lends itself to the preparation of the enantiomeric series.

Ligand structure and dynamics. The C_2-symmetry of ligands **4**, **6** and **7** is apparent from their ^1H and ^{13}C NMR spectra (see Experimental). As expected[4] for such aziridines, pyramidal inversion at nitrogen is relatively slow on the NMR timescale and the room temperature spectra show broadened signals for the aziridine ring protons. These signals sharpen to singlets at higher temperatures, and split into AB patterns (J=ca. 3 Hz) when the samples are cooled. The barriers to nitrogen inversion, calculated by the coalescence temperature method, are summarized in Fig. 2. It should be noted that owing to the non-stereogenic nature of the (chirotopic) nitrogen atoms, the inversion process does not alter the ligand structure.

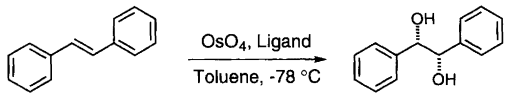
Stoichiometric asymmetric addition of osmium tetroxide to olefins. We chose the *syn*-dihydroxylation of (*E*)-stilbene via osmium tetroxide addition as a standard reaction to compare the performance of ligands **4** and **7** in terms of enantioselectivity. The former ligand is presumed to form a six-membered chelate with the metal, while the latter should give a five-membered ring. The results are shown in Scheme 2.

A dramatic difference was noted, the ligand **4**, forming the larger chelate, giving essentially racemic product, while use of **7** gave the 1,2-diol of 95% enantiomeric excess (*ee*). This result may be compared with the best literature values reported for the stoichiometric reaction (e.g., 97% *ee*, Tomioka,[6a] 99% *ee*, Hanessian[6b]). Both of our ligands were recovered quantitatively after work-up.



Ligand	T_c / K	$\Delta\nu$ / Hz	$\Delta G^{\ddagger}$ / kJ mol^{-1}
4	320	48	66
6	316	118	63
7	294	58	60

Fig. 2. Dynamic NMR data for pyramidal inversion at nitrogen in ligands **4**, **6** and **7**.



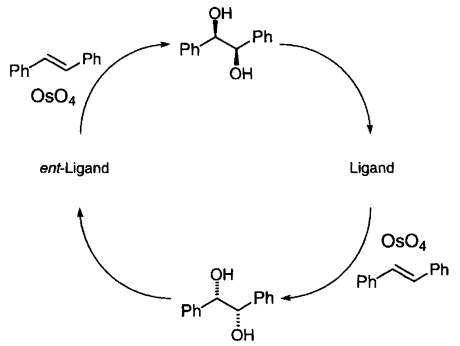
Ligand	Yield	*ee*
7	90%	95%
4	51%	<5%

Scheme 2. Stoichiometric asymmetric dihydroxylation using ligands **4** and **7**.

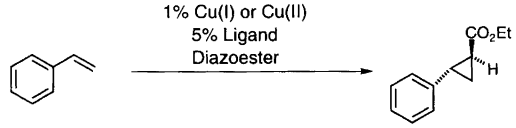
The fact that the reactions took place rapidly at −78 °C is indicative of ligand acceleration.[7] While we have not investigated the mechanism in detail,[8] we presume that the five-membered chelate is more rigid and leads to a more ordered transition state in which the phenyl groups on ligand **7** have a greater influence on the orientation of the substrate with respect to the osmium.

As far as the sense of chiral induction with ligand **7** is concerned, the diol product formed has the *S,S*-configuration. It should be noted that this diol can be used to synthesize[5] the enantiomer of epoxide **1** (Scheme 1) and, thus, the enantiomer of ligand **7**. This amusing turn of events is shown schematically below (Scheme 3).

Copper-catalyzed asymmetric cyclopropanation. The next reaction tested was that shown in Scheme 4, with styrene as the standard substrate.[9] The ligands used were **4**, **6** and **7**, and the results are shown below. These results parallel those obtained with osmium, in that increasing the size of the presumed chelate leads to a substantial drop in enantioselectivity. Chemical yields also decrease with increasing tether length in the ligand. The greater flexibility of the larger chelates probably allows reaction via a number of ligand–copper–substrate arrays. It is noteworthy that both copper(I) and copper(II) species can be used as catalyst precursors, in contrast with the case with other ligands.[9a,c] The mechanism of this reaction has been suggested[10] to involve a discrete carbenoid intermediate and, possibly, a metallacyclobutane species.[9a] However, rationalisation of the observed sense of asymmetric induction is no simple task.

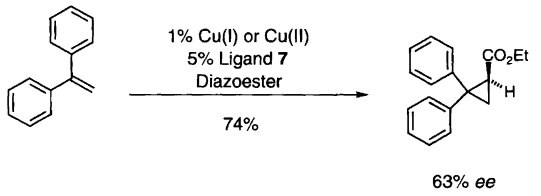


Scheme 3. Scheme for 'interconversion' of the enantiomers of chiral ligand **7**.



Ligand	Chelate size	Yield	*trans* / *cis*	*ee* *trans* / *cis*
7	5	82%	3 : 1	60% / 52%
4	6	60%	2 : 1	19 % / 20%
6	8	43%	2 : 1	8% / 5%

Scheme 4. Copper-catalyzed asymmetric cyclopropanation of styrene using chiral bis(aziridine) ligands.

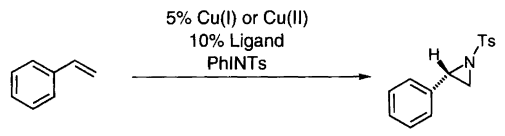


Scheme 5. Copper-catalyzed asymmetric cyclopropanation of 1,1-diphenylethene using ligand **7**.

The best enantiomeric excess we have obtained so far is that shown in Scheme 5 and ligand **7** was again the one of choice. The best literature value for the *ee* from this reaction is >99% *ee*, reported by Evans.[9a]

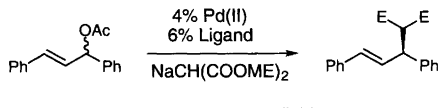
Copper-catalyzed asymmetric aziridination. Since chiral aziridines are useful 'building blocks' in organic synthesis[1,2] we next tested the reaction[11] shown in Scheme 6. Once more, the five-membered chelate proved to be the more efficient inducer of chirality. Jacobsen[12] has recently drawn a mechanistic analogy between this aziridination reaction and the cyclopropanation process described above, and suggested the intermediacy of a Cu-nitrenoid species for the former. For both reaction types, however, it cannot be excluded that the actual catalytic species are non-monomeric, thus making mechanistic rationalisation difficult. The lack of detailed mechanistic information for these two reaction types makes the development of new chiral ligands subject to much trial and error. Our results compare favourably with the best literature value reported by Jacobsen[12] (66% *ee*).

Palladium-catalyzed asymmetric alkylation. We earlier reported[4] on the excellent enantiomeric excess obtained for ligand **7** in the reaction shown below (Scheme 7). This is to our knowledge the best *ee* value obtained by the use of *N,N*-bidentate ligands. While this result was gratifying, the corresponding reaction involving a cyclohexenyl acetate would be of greater synthetic utility.



Ligand	Chelate size	Yield	*ee*
7	5	68%	33%
4	6	60%	8%

Scheme 6. Copper-catalyzed asymmetric aziridination of styrene using chiral bis(aziridine) ligands.



Ligand	Chelate size	Yield	*ee*
7	5	89%	>99%
4	6	5%	n. d.

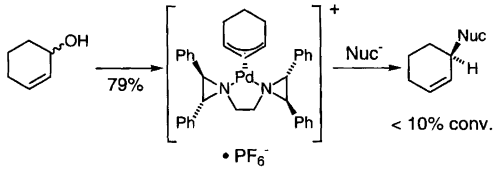
Scheme 7. Palladium-catalyzed asymmetric allylic substitution using chiral bis(aziridine) ligands.

However, no reaction occurred. We reasoned that this surprising lack of reactivity was due either to the fact that the π-allyl–palladium complex, which is the catalytic intermediate, did not form, or that, once formed, it simply did not react.

The latter explanation proved to be the correct one, since we were able to synthesize and characterize the putative catalytic intermediate without difficulty. However, in a stoichiometric reaction with the sodium salt of dimethyl malonate very little reaction occurred even under forcing conditions (Scheme 8).

We believe that the complex is unreactive mainly for steric reasons, and we have performed molecular modelling on the π-allyl complex (Fig. 3). Note that the complex shown is that of *ent*-**7**. As can be seen, the cyclohexenyl moiety lies embedded in the chiral cleft defined by the ligand, and approach of the nucleophile is hindered by the two flanking phenyl rings. It should also be noted that the geometry at palladium is square planar, in contrast with the corresponding 1,3-diphenylallyl–palladium complex described earlier.[4] The present complex (as the hexafluorophosphate salt) was characterized by a variety of NMR spectroscopic techniques (cf., Ref. 4). The ^{1}H NMR spectrum shows some interesting features, in particular substantial shift differences between the terminal allylic protons (H-3 at δ 4.25 and H-1 at δ 2.95) and also an unusually high-field shift for H-4_{eq} (δ −0.42). The high-field shifts of protons H-1 and H-4_{eq} are explained by anisotropic shielding by phenyl rings B and A, respectively, and the proximity of the relevant protons and aromatic moieties is particularly apparent in the space-filling representation shown in Fig. 3. We have earlier noted[4] similar effects in complexes of **7**, and the use of such 'intrusive' ligands for the investigation of other chiral π-allyl species relevant to palladium-mediated asymmetric catalysis is currently being studied.[13]

It was also instructive to compare ligands **4** and **7** in the palladium-catalyzed reaction shown in Scheme 7. With the 1,3-diphenylallyl system, ligand **4** unexpectedly led to only very low conversion (<10%) and no attempt was made to determine the enantiomeric excess of the product. We therefore decided to prepare and study the π-allyl intermediate, but bis(aziridine) **4** obviously has a very low binding constant for palladium, since it proved impossible to synthesize the desired complex by the usual route.[14] To overcome these problems, we are currently



Scheme 8. Attempted stoichiometric allylic substitution on a cyclohexenyl π-allyl palladium complex of ligand *ent*-**7**. Nuc = $NaCH(COOMe)_2$; conditions: THF, reflux.

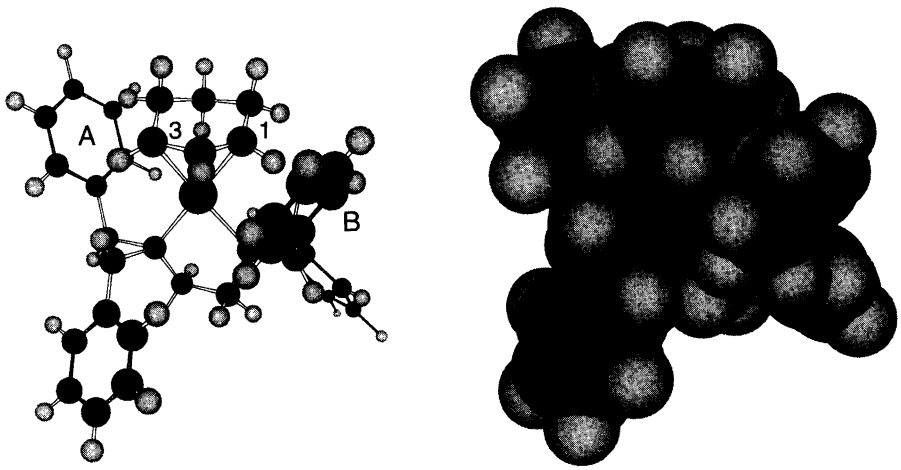


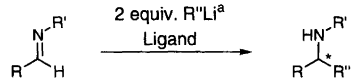
Fig. 3. Optimized (MM2) structure of the cyclohexenyl π-allyl palladium complex of ligand *ent*-**7**.

engaged in the synthesis of mixed N, P ligands based on chiral aziridines.

Catalytic asymmetric addition of organolithium reagents to imines. In a recent paper, Denmark[15] described a new method for the asymmetric synthesis of amines via 1,2-addition of alkyllithiums to imines (Scheme 9). The chiral inducers were either bis(oxazolines) or sparteine and these could be used in either stoichiometric or catalytic amounts. The highest enantiomeric excess for the catalytic process was 82%, when 20 mol% of a chiral bis(oxazoline) was used. Employing the bis(aziridines) as ligands in this reaction gave the results shown below. While the stoichiometric process was quite promising in terms of asymmetric induction, the highest enantiomeric excess obtained so far for the catalytic reaction is only 14%. Further studies of this reaction are under way.

Conclusions

We have shown that the easily available bis(aziridines) shown in Fig. 1 are useful ligands for a variety of metal-mediated asymmetric transformations; in the best cases, enantiomeric excesses of >95% can be achieved. For those reaction types which so far have not yielded useful levels of chiral induction, improvements can hopefully be made by 'fine-tuning' of the ligand structure. The results described above show that ligands capable of forming five-membered chelates are probably the optimum, and the synthetic strategy shown in Scheme 1 should be flexible enough to allow steric and/or electronic modification of the substituents on the aziridine rings.



R = phenyl, R' = 4-methoxyphenyl, R" = Me

Ligand	Mol%[a]	Yield	%*ee*	Abs. conf.
7	100	47%	67	*R*
7	10	70%	14	*R*
6	10	44%	0	
4	10	12%	0	

[a] with respect to imine

Scheme 9. Asymmetric 1,2-addition of organolithium reagents to imines in the presence of chiral ligands.

Experimental

^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) spectra were run on a Varian XL 300 or Varian Unity 400 spectrometer. Chloroform-*d* was used as the solvent unless otherwise stated, and tetramethylsilane (for ^{1}H) or the chloroform signal at 77.0 ppm (for ^{13}C) was used as reference. For ^{13}C NMR signals the superscripts + and − denote odd and even numbers of attached protons, respectively. IR spectra were obtained for thin films or CH_2Cl_2 solutions on a Perkin-Elmer 1600 FT-IR instrument, and only the strongest/structurally most important peaks are listed. Optical rotations were measured at 25 °C on a Perkin-Elmer 241 polarimeter. Elemental analyses were performed by Analytische Laboratorien GMBH, Germany. Mass spectra were obtained on a Kratos MS890 system at the University of Cambridge, UK. Melting points were determined on a Leitz apparatus, and are uncorrected. Chloroform and dichloromethane were dried and distilled immediately before use. Tetrahydrofuran (THF) was distilled under nitrogen from purple solutions of Na–benzophenone. Toluene and pyridine were dried over calcium hydride and distilled under nitrogen. *N*,*N*-Dimethylformamide (DMF) was distilled at reduced pressure from calcium hydride. Merck silica gel 60 (240–400 mesh) was used for flash chromatography. Commercial copper(I) and copper(II) triflates (Fluka) were handled and stored under argon. Solutions of organolithium reagents were titrated with diphenylacetic acid immediately before use.

Synthesis of ligands **4** *and* **6**. *[Steps (a)–(g) refer to Scheme 1].* (*a*) (*R*,*R*)-Stilbene oxide (7.57 g, 36.2 mmol),

NaN_3 (10.0 g, 154 mmol), NH_4Cl (3.3 g), 2-methoxyethanol (160 ml) and water (20 ml) were stirred together at 90 °C for 20 h. The reaction mixture was allowed to cool then poured into water (300 ml) and the mixture was extracted with Et_2O (4 × 200 ml). The combined organic extracts were dried ($MgSO_4$) and purified by flash chromatography, eluting with 1:9 EtOAc–pentane. The resulting product contained residual 2-methoxyethanol which was removed by dissolution in Et_2O (100 ml) and extraction with brine (3 × 40 ml). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give (1*R*, 2*S*)-1,2-diphenyl-2-azidoethanol (8.61 g, 93%).[16]

(*b*) Dry (1*R*, 2*S*)-1,2-diphenyl-2-azidoethanol (1.0 g, 4.18 mmol) and imidazole (426 mg, 6.27 mmol) were dissolved in dry DMF (10 ml). (1,1-Dimethylethyl)dimethylsilyl chloride (1.26 g, 8.36 mmol) was dissolved in DMF (15 ml) and added to the mixture via cannula. After 64 h the mixture was poured into a mixture of water (50 ml) and Et_2O (100 ml). The organic layer was washed with saturated NH_4Cl (2 × 25 ml), dried ($MgSO_4$) and the solvents were removed. The residue was purified by flash chromatography, eluting with 2:98 Et_2O–pentane followed by 5:95 Et_2O–pentane, to give (1*R*, 2*S*)-1,2-diphenyl-2-azido-1-[(1,1-dimethylethyl)dimethylsiloxy]ethane (1.39 g, 94%) as an oil, R_f(Et_2O–pentane, 1:19) 0.59; ν_{max}(liquid film)/cm^{-1} 2956 (SiC–H_3), 2929 (SiC–H_3), 2105 (N_3), 1603 (Ph), 1493 (Ph), 1362 (CMe_3) and 1256 (SiMe); ^1H NMR (300 MHz; $CDCl_3$) 7.29–7.17 (10 H, m), 4.68 (1 H, d, *J* 6.6, PhCH_A), 4.54 (1 H, d, *J* 6.6, PhCH_B), 0.71 (9 H, s, CMe_3), −0.25 (3 H, s, Si$Me_A$$Me_B$) and −0.32 (3 H, s, $SiMe_A$$Me_B$); ^{13}C NMR (75.5 MHz; $CDCl_3$) 140.9$^-$, 137.0$^-$, (128.2–127.2)$^+$ (several lines), 78.7$^+$ (PhC$_A$C$_B$Ph), 72.1$^+$ (PhC$_A$C$_B$Ph), 25.6$^+$(CMe_3), 18.0$^-$ (CMe_3), −5.0$^+$ (Si$Me_A$$Me_B$) and −5.6$^+$ ($SiMe_A$$Me_B$); *m/z* 338 (8.7%, M^+−Me), 311 (58, M−N_3), 296 (64, *M*−Me−N_3) and 221 (100, *M*−^{t}BuMe$_2$SiOH) (Found: M^+−Me, 338.1690. $C_{20}H_{27}N_3OSi$ requires *M*−Me, 338.1688); $[\alpha]_D$ +4.36 (*c* 1.01, CH_2Cl_2).

(*c*) (1*R*, 2*S*)-1,2-Diphenyl-2-azido-1-[(1,1-dimethylethyl)dimethylsiloxy]-ethane (2.04 g, 5.78 mmol) and Ph_3P (2.0 g, 7.63 mmol) were dissolved in THF (25 ml) before the addition of 1:2 water–THF (30 ml). The mixture was refluxed for 1 h. Additional Ph_3P (0.40 g, 1.53 mmol) and water (10 ml) were added to the mixture which was then refluxed overnight. After cooling, THF was removed under reduced pressure and the remaining mixture extracted with CH_2Cl_2 (3 × 20 ml). The combined organics were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography, eluting with 1:9 EtOAc–pentane followed by 2:3 EtOAc–pentane, to give (1*S*, 2*R*)-1,2-diphenyl-2-[(1,1-dimethylethyl)dimethylsiloxy]-ethylamine (**2**). (1.77 g, 93%) as an oil; R_f(EtOAc–pentane, 1:9) 0.12; ν_{max}(liquid film)/cm^{-1} 2954 ($SiCH_3$), 2928 ($SiCH_3$), 1603 (Ph), 1493 (Ph), 1361 (CMe_3) and 1251 (SiMe); ^1H NMR (300 MHz; $CDCl_3$) 7.30–7.17 (10 H, m, 2 × Ph), 4.63 (1 H, d, *J* 6.5, PhC*H*O), 4.01 (1 H, d, *J* 6.5, PhC*H*N), 1.42 (2 H, br s, NH_2), 0.74 (9 H, s, $SiMe_3$), −0.26 (3 H, s, Si$Me_A$$Me_B$) and −0.33 (3 H, s, $SiMe_A$$Me_B$); ^{13}C NMR (75.5 MHz; $CDCl_3$) 142.6$^-$, 141.9$^-$, (127.8–126.9)$^+$ (several lines), 80.1$^+$(PhCO), 62.9$^+$ (PhCN), 25.7$^+$ (CMe_3), 18.1$^-$ (CMe_3), −4.8$^-$ (Si$Me_A$$Me_B$) and −5.6$^-$ ($SiMe_A$$Me_B$); *m/z* 328 (0.3%, M^++H) and 106 (100, $PhCHN_3$) (Found: M^++H 328.2101. $C_{20}H_{29}NOSi$ requires *M*+H, 328.2097); $[\alpha]_D$ −36.1 (*c* 1.09, CH_2Cl_2).

(*d*) (1*S*, 2*R*)-1,2-Diphenyl-2-[(1,1-dimethylethyl)dimethylsiloxy]-ethylamine (**2**) (4.03 g, 12.3 mmol) and dry pyridine (2.60 ml, 32.2 mmol) were dissolved in dry toluene (150 ml). The mixture was cooled to 0 °C and dimethylmalonyl dichloride (860 µl, 6.50 mmol) added dropwise. The mixture was allowed to warm to room temperature and stirred for 3 days. The mixture was diluted with EtOAc (200 ml) and washed with HCl (100 ml of a 1 M solution). The aqueous phase was further extracted with EtOAc (2 × 100 ml). The combined organics were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography eluting with 1:9 EtOAc–pentane, followed by 1:4 EtOAc–pentane, to yield *N*,*N*′-bis{(1*S*, 2*R*)-1,2-diphenyl-2-[(1,1–dimethylethyl)-dimethylsiloxy]-ethyl}dimethylmalonamide **3** (4.19 g, 91%), m.p. 106–107.5 °C (from EtOH); R_f(EtOAc–pentane 1:4) 0.29; ν_{max}(KBr)/cm^{-1} 3442 (NH), 3408 (NH), 1666 (C=O), 1604 (Ph), 1587 (Ph) and 1496 (C=O); ^1H NMR (400 MHz; $CDCl_3$) 7.36 (2 H, d, *J* 8.4, 2 × NH), 7.19–7.12 (8 H, m), 7.07 (4 H, t, *J* 7.2), 6.99–6.96 (4 H, m), 6.87–6.85 (4 H, m), 4.98 (2 H, dd, *J* 8.4 and 4.8, 2 × PhC*H*NH), 4.89 (2 H, d, *J* 4.8, 2 × PhC*H*OSi), 1.31 (6 H, s, CMe_2), 0.85 (18 H, s, 2 × CMe_3), −0.03 (6 H, s, 2 × Si$Me_A$$Me_B$) and −0.30 (6 H, s, 2 × $SiMe_A$$Me_B$); ^{13}C NMR (75.5 MHz; $CDCl_3$) 172.2$^-$ (C=O), 140.5$^-$ (*ipso*-Ph_A), 137.7$^-$ (*ipso*-Ph_B), (127.8–126.6)$^+$ several lines (Ph), 77.3$^+$ (PhCHOSi), 60.0$^+$ (PhCHN), 49.2$^-$ (CMe_2), 25.8$^+$ (CMe_3), 24.0$^+$ (CMe_2), 18.1$^-$ (CMe_3), −4.6$^-$ (Si$Me_A$$Me_B$) and −5.2$^-$ ($SiMe_A$$Me_B$); $[\alpha]_D$ −51.4 (*c* 1.09, CH_2Cl_2).

(*e*) *N*,*N*′-Bis{(1*S*, 2*R*)-1,2-diphenyl-2-[(1,1-dimethylethyl)dimethylsiloxy]ethyl}dimethylmalonamide (**3**) (94 mg, 0.125 mmol) was dissolved in dry THF (7 ml) under nitrogen before BH_3·THF (980 µl of a 1 M solution in THF) was added dropwise. The mixture was refluxed for 14 h. The THF was removed under reduced pressure and the residue was purified by flash chromatography eluting with 3% EtOAc in pentane to yield *N*,*N*′-bis{(1*S*, 2*R*)-1,2-diphenyl-1-[(1,1-dimethylethyl)dimethylsiloxy] ethyl 2,2-dimethylpropane-1,3-diamine (76 mg, 84%) as an oil, R_f(pentane–Et_2O 9:1) 0.32; ν_{max}(liquid film)/cm^{-1} 3345 (NH), 1602 (Ph) and 1493 (Ph); ^1H NMR (300 MHz; $CDCl_3$) 7.24–7.12 (20 H, m, 4 × Ph), 4.52 (2 H, d, *J* 6.6, 2 × PhC*H*O), 3.44 (2 H, d, *J* 6.6, 2 × PhC*H*N), 1.95 (2 H, d, *J* 11.3, 2 × NHC$H_A$$H_B$), 1.90 (2 H, d, *J* 11.3, 2 × NHCH_ACH_B), 0.73 (18 H, s,

$2\times CMe_3$), 0.57 (6 H, s, CMe_2), −0.32 (6 H, s, $2\times SiMe_AMe_B$) and −0.37 (6 H, s, $2\times SiMe_AMe_B$); ^{13}C NMR (75.5 MHz; $CDCl_3$) 142.7$^-$ (*ipso*-Ph_A), 141.3$^-$ (*ipso*-Ph_B), 128.8$^+$, 127.6$^+$, 127.3$^+$, 127.2$^+$, 127.0$^+$, 126.6$^+$, 79.3$^+$ (Ph*C*HOSi), 70.7$^+$ (Ph*C*HN), 56.6$^-$ (NCH_2), 34.9$^-$ (*C*Me_2), 25.8$^+$ (C*Me*$_3$), 24.3$^+$ (C*Me*$_2$), 18.1$^-$ (*C*Me_3), −4.8$^+$ (Si*Me*$_A$$Me_B$) and −5.4$^+$ ($SiMe_A$*Me*$_B$); *m/z* 722 (0.1%, *M*), 665 (3, *M*−^{t}Bu) and 501 (100, *M*−$Me_2{}^t$BuSiOCHPh) (Found by EI: M^+, 722.4653. $C_{45}H_{66}N_2O_2Si_2$ requires *M*, 722.4663); $[\alpha]_D$ −29.7 (*c* 2.41, CH_2Cl_2).

(*f*, *g*) *N*,*N*′-Bis{(1*S*, 2*R*)-1,2-diphenyl-2-[(1,1-dimethylethyl)dimethylsiloxy]ethyl-2,2-dimethylpropane-1,3-diamine (1.53 g, 2.12 mmol) was dissolved in THF (20 ml) and tetrabutylammonium fluoride (10 ml of a 1 M solution in THF, 10.0 mmol) was added and the mixture stirred at room temperature for 4 days before the THF was removed under reduced pressure. Water (10 ml) was added to the residue which was extracted with CH_2Cl_2 (3 × 15 ml). The combined organics were dried ($MgSO_4$) and evaporated under reduced pressure to yield a solid containing desilylated starting material. The solid was added to Ph_3P (1.55 g, 5.92 mmol) and any water removed as an azeotrope with toluene (50 ml). The residue was dissolved in dry THF (60 ml) under nitrogen and cooled to 0 °C before diethyl azodicarboxylate (DEAD) (945 µl, 6.01 mmol) was added dropwise to the stirred mixture. The mixture was stirred at room temperature for 2 days and the THF removed under reduced pressure. The residue was purified by flash chromatography eluting with 3% EtOAc in pentane followed by recrystallization from hexane (13 ml) to give 1,1′-(2,2-dimethylpropane-1,3-diyl)bis[(2*R*, 3*R*)-2,3-diphenylaziridine] **4** (534 mg, 55%) as rectangular prisms, m.p. 137–138.5 °C (from hexane); R_f(EtOAc–pentane, 1:9) 0.35; ν_{max}(KBr)/cm^{-1} 1600 (Ph) and 1497 (Ph); ^1H NMR (300 MHz; $CDCl_3$) 7.40–7.18 (20 H, m, 4 × Ph), 3.07 (2 H, br s, $2\times PhCH_ACH_BPh$), 2.95 (2 H, br s, $2\times PhCH_ACH_BPh$), 2.26 (2 H, d, *J* 12.2, $2\times NCH_AH_B$), 2.11 (2 H, d, *J* 12.2, $2\times NCH_AH_B$) and 0.85 (6 H, s, CMe_2); ^{13}C NMR (75.5 MHz; $CDCl_3$) 140.5$^-$ (*ipso*-Ph_A), 134.4$^-$ (*ipso*-Ph_B), (129.8–126.0)$^+$ several lines (Ph), 60.3$^-$ (NCH_2), 50.7$^+$ (NC_AHPh), 46.5$^+$ (NC_BHPh), 37.0$^-$ (*C*Me_2) and 25.1$^+$ (C*Me*$_2$); *m/z* 458 (0.4%, M^+), 278 (2, *M*−PhCHCHPh) and 180 (100, PhCHCHPh) (Found: M^+ 458.2723. $C_{33}H_{34}N_2$ requires *M*, 458.2722); $[\alpha]_D$ −136.1 (*c* 1.02, CH_2Cl_2).

(*d*) (1*S*, 2*R*)-1,2-Diphenyl-2-[(1,1-dimethylethyl)dimethylsiloxy]-ethylamine (**2**) (1.00 g, 3.06 mmol) and dry pyridine (590 µl, 7.29 mmol) were dissolved in dry toluene (40 ml). The mixture was cooled to 0 °C and glutaryl dichloride (210 µl, 1.65 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 45 min and then allowed to warm to room temperature and stirring was continued for 3 days. The mixture was then added to EtOAc (150 ml) and washed with $CuSO_4$ (2 × 50 ml of a 0.1 M solution) and water (20 ml). The combined aqueous layers were extracted with EtOAc (2 × 50 ml) and the combined organics dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography, eluting with 2:3 EtOAc–pentane, followed by 19:1 EtOAc–MeOH, to yield *N*,*N*′-bis{(1*S*, 2*R*)-1,2-diphenyl-2-[(1,1-dimethylethyl)dimethylsiloxy]eth}glutaramide **5** (1.05 g, 91%) as needles, m.p. 162–164 °C (from EtOAc); R_f(EtOAc–pentane 2:3) 0.26; ν_{max}(KBr)/cm^{-1} 3300 br (NH), 1644 (C=O), 1604 (Ph) and 1544 (C=O); ^1H NMR (300 MHz; $CDCl_3$) 7.32–7.08 (20 H, m, 4 × Ph), 6.56 (2 H, d, *J* 8.5, 2 × NH), 5.20 (2 H, dd, *J* 8.5 and 4.8, 2 × PhC*H*NH), 5.08 (2 H, d, *J* 4.8, 2 × PhC*H*OSi), 2.16 (4 H, t, *J* 6.9, $CCH_2CH_2CH_2C$), 1.86 (2 H, quintet, *J* 6.9, $CCH_2CH_2CH_2C$), 0.96 (18 H, s, $2\times CMe_3$), 0.06 (6 H, s, $2\times SiMe_AMe_B$) and −0.14 (6 H, s, $2\times SiMe_AMe_B$); ^{13}C NMR (75.5 MHz; $CDCl_3$) 171.2$^-$ (C=O), 140.7$^-$ (*ipso*-Ph_A), 138.0$^-$ (*ipso*-Ph_B), (128.9–126.6)$^+$ several lines (Ph), 77.3$^+$ (Ph*C*HOSi), 59.5$^+$ (Ph*C*HN), 35.2$^-$ ($CH_2CH_2CH_2$), 25.8$^+$ (C*Me*$_3$), 21.9$^-$ ($CH_2CH_2CH_2$), 18.2$^-$ (*C*Me_3), −4.7$^-$ (Si*Me*$_A$$Me_B$) and −5.1$^-$ ($SiMe_A$*Me*$_B$); $[\alpha]_D$ −55.0 (*c* 1.36, CH_2Cl_2).

(*e*) *N*,*N*′-Bis{(1*S*, 2*R*)-1,2-diphenyl-2-[(1,1-dimethylethyl)dimethylsiloxy]ethyl}glutaramide (**5**) (253 mg, 0.337 mmol) was dissolved in THF (16 ml) under nitrogen before BH_3·THF (2.6 ml of a 1 M solution in THF) was added dropwise. The mixture was refluxed for 2 days. The THF was removed under reduced pressure and water (10 ml) and EtOAc (10 ml) were added to the residue. The layers were separated and the aqueous phase was further extracted with CH_2Cl_2 (2 × 10 ml). The combined organics were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography eluting with 2:3 EtOAc–pentane, to yield *N*,*N*′-bis{(1*S*, 2*R*)-1,2-diphenyl-2-[(1,1-dimethylethyl)dimethylsiloxy]ethyl}pentane-1,5-diamine (175 mg, 72%) as an oil, R_f(EtOAc–pentane, 2:3) 0.26; ν_{max}($CDCl_3$)/cm^{-1} 3263 (NH), 1600 (Ph) and 1500 (Ph); ^1H NMR (400 MHz; $CDCl_3$) 7.25–7.16 (20 H, m, 4 × Ph), 4.63 (2 H, d, *J* 6.8, 2 × PhC*H*O), 3.64 (2 H, d, *J* 6.8, 2 × PhC*H*N), 2.21 (2 H, dt, *J* 12.0 and 7.4, $2\times NHCH_AH_B$), 2.13 (2 H, dt, *J* 12 and 6.8, $2\times NHCH_AH_B$), 1.22–1.09 (4 H, m, $CH_2CH_2CH_2CH_2CH_2$), 0.89 (2 H, quintet, *J* 7.6, $CH_2CH_2CH_2CH_2CH_2$), 0.71 (18 H, s, $2\times CMe_3$), −0.31 (6 H, s, $2\times SiMe_AMe_B$) and −0.38 (6 H, s, $2\times SiMe_AMe_B$); ^{13}C NMR (100.6 MHz; $CDCl_3$) 142.5 (*ipso*-Ph_A), 141.0 (*ipso*-Ph_B), 128.9, 127.8, 127.6, 127.4, 127.1, 126.9, 79.3 (Ph*C*HO), 66.9 (Ph*C*HN), 47.1 ($NCH_2CH_2CH_2$), 29.5 ($NCH_2CH_2CH_2$), 25.7 (C*Me*$_3$), 24.4 ($NCH_2CH_2CH_2$), 18.0 (*C*Me_3), −5.0 (Si*Me*$_A$$Me_B$) and −5.6 ($SiMe_A$*Me*$_B$); *m/z* 722 (0.2%, M^+) and 501 (100, *M*−PhCHOSi$Me_2{}^t$Bu) (Found: M^+ 722.4667. $C_{45}H_{66}N_2O_2Si_2$ requires *M*, 722.4663); $[\alpha]_D$ −19.4 (*c* 1.13, CH_2Cl_2).

(*f*, *g*) *N*,*N*′-Bis{(1*S*, 2*R*)-1,2-diphenyl-2-[(1,1-dimethylethyl)dimethyl-siloxy]ethyl}pentane-1,5-diamine (110 mg, 0.152 mmol) was dissolved in THF (1.5 ml) and tetrabutylammonium fluoride (680 µl of a 1 M solu-

tion in THF, 0.680 mmol) was added to the stirred solution at room temperature. The mixture was stirred overnight. The THF was removed under reduced pressure. Water (10 ml) was added to the residue which was extracted with CH_2Cl_2 (2 × 10 ml). The combined organics were dried ($MgSO_4$) and evaporated under reduced pressure to give a solid containing desilylated starting material. The solid was added to Ph_3P (119 mg, 0.454 mmol) and any water removed as an azeotrope with toluene. The residue was suspended in dry THF (7 ml) under nitrogen and DEAD (85 µl, 0.540 mmol) was added dropwise to the stirred mixture. The mixture was stirred at room temperature for 2 days and the THF removed under reduced pressure. The residue was purified by flash chromatography eluting with 1:9 EtOAc–pentane, followed by 1:4 EtOAc–pentane, to yield 1,1′-(pentane-1,5-diyl)bis[(2*R*, 3*R*)-2,3-diphenylaziridine] **6** (52 mg, 74%) as prisms, m.p. 103–105 °C (from hexane); R_f(EtOAc–pentane) 0.22; ν_{max}(KBr)/cm^{-1} 1602 (Ph), 1495 (Ph), 752 (Ph) and 697 (Ph); ^{1}H NMR (400 MHz; $CDCl_3$) 7.42–7.25 (20 H, m, 4 × Ph), 3.27 (2 H, br s, 2 × PhCH_ACH$_B$Ph), 2.97 (2 H, br s, 2 × PhCH$_A$CH_BPh), 2.39 (2 H, ddd, *J* 11.6, 8.4 and 6.4, NCH_AH$_B$), 2.02 (2 H, ddd, *J* 11.6, 8.0 and 6.6, NCH$_A$$H_B$), 1.49–1.37 (4 H, m, NCH$_2$CH_2) and 1.20 (2 H, quintet, *J* 7.5, NCH$_2$CH$_2$CH_2); ^{13}C NMR (100.6 MHz; $CDCl_3$) (130.1–126.0)$^+$ (several lines), 52.5$^-$ (NCH_2), 50.3$^+$ (br, PhCH_ACH$_B$Ph), 45.6$^+$ (br, PhCH$_A$CH_BPh), 29.7$^-$ (NCH_2CH_2) and 25.0$^-$ ($NCH_2CH_2CH_2$); *m/z* 458 (5.6%, M^+), 278 (83, *M* − PhCHCHPh), 194 (100, PhCHCHPhN) and 180 (78, PhCHCHPh) (Found: M^+ 458.2726. $C_{33}H_{34}N_2$ requires *M*, 458.2722); $[\alpha]_D$ −112 (*c* 1.05, CH_2Cl_2).

Stoichiometric asymmetric addition of osmium tetroxide to trans-*stilbene.* Ligand **7** (0.333 g, 0.8 mmol) was dissolved with stirring under nitrogen in dry toluene (5 ml) and the solution was cooled to −78 °C. A solution of osmium tetroxide (0.060 g, 0.24 mmol) in toluene (1.5 ml) was added and the resultant mixture was stirred at −78 °C for 2 h before addition of a solution of (*E*)-stilbene (0.036 g, 0.2 mmol) in toluene (0.75 ml). Stirring was continued for 5 h at −78 °C, at which point TLC analysis indicated complete consumption of the olefin. The toluene was removed *in vacuo* and the residue was taken up in a 1:1 mixture of aqueous $NaHSO_3$ and THF and the solution refluxed for 2 h. The cooled reaction mixture was made basic by addition of $NaHCO_3$ and the mixture was extracted with ethyl acetate (2 × 10 ml). The combined organics were dried over $MgSO_4$, the solvents were removed, and the residue purified by flash chromatography (ether–pentane, 1:1) to yield (*S*, *S*)-hydrobenzoin (0.038 g, 90%). The chiral ligand was also recovered in near-quantitative yield. The diol product had spectral and physical data in accord with those in the literature[5a] and was shown to be of 95% *ee* by polarimetric comparison with an authentic sample.[5a] (Enantiomerically pure material was obtained after a single recrystallization from ethanol). The same procedure was used for the reaction with ligand **4**.

General procedure for copper-catalyzed asymmetric cyclopropanation. The bis(aziridine) ligand **7** (18 mg, 0.044 mmol) and copper(I) triflate (4.4 mg, 0.018 mmol) were dissolved in dry chloroform (2 ml) under an atmosphere of argon. The resulting solution was cooled to 0 °C and styrene (0.91 g, 8.76 mmol) was added via syringe. Ethyl diazoacetate (100 mg, 0.87 mmol dissolved in 2 ml dry chloroform) was then slowly added (5 h addition time) via a syringe pump. After complete addition, the ice bath was removed and the reaction mixture stirred overnight at r.t. Ether (10 ml) was added and the resulting solution was subsequently washed with water (5 ml), sat. aqueous NH_4Cl (2 × 5 ml) and brine (5 ml). After drying ($MgSO_4$), the solvent was removed and the residue flash chromatographed (10% ether in pentane) to give the cyclopropanes. For yields, stereo- and enantioselectivity, see Scheme 4. The enantiomeric excess was determined by chiral HPLC using a Chiralcel OD-H column (10% isopropyl alcohol in hexane as the eluent gave baseline separation). The spectral and physical data of the products were in excellent agreement with published values [see the supplementary material in Ref. 9(a)] and absolute configurations of the *trans* and *cis* isomers were assigned by polarimetry (comparison with literature values).[9a] A similar procedure was used for the reactions involving copper(II) triflate.

The same procedure was used for the cyclopropanation of 1,1-diphenylethene. The product was purified by flash chromatography (5% ether in pentane). For yields and enantioselectivity, see Scheme 5. The enantiomeric excess and absolute configuration of the product were determined after basic hydrolysis to the corresponding carboxylic acid, as described.[9a]

General procedure for copper-catalyzed asymmetric aziridination. The bis(aziridine) ligand **7** (17 mg, 0.058 mmol) and copper(I) triflate (10 mg, 0.048 mmol) were dissolved in dry methylene chloride (3 ml) under an atmosphere of argon. The resulting mixture was stirred until clear, then styrene (100 mg, 0.96 mmol) was added at 0 °C followed by PhINTs (0.54 g, 1.44 mmol) and the stirred reaction mixture was allowed to reach room temperature overnight. Ether (10 ml) was added and the resulting solution was subsequently washed with water (5 ml), sat. aqueous NH_4Cl (2 × 5 ml) and brine (5 ml). After drying ($MgSO_4$) the solvent was removed and the residue flash chromatographed (25% ether in pentane) to give the aziridine. For yields and enantioselectivity, see Scheme 6. A similar procedure was used for the reactions with copper(II) triflate. The enantiomeric excess and absolute configuration were determined by correlation with an authentic sample of the enantiomer, prepared from commercially available (*R*)-(−)-2-phenylglycinol [via *N*-tosylation followed by ring closure,[17] see also Ref. 11(b)]. The enantiomerically pure material showed $[\alpha]_D$ −97.9 (*c* 1.0, CH_2Cl_2). ^{1}H NMR: δ 7.88

(AA′ of AA′BB′, J_{AB} 8.2 Hz, 2 H), 7.35–7.19 (m, 7 H), 3.78 (dd, *J* 7.0 and 4.0 Hz, 1 H), 2.98 (d, *J* 7.0, 1 H), 2.42 (s, 3 H), 2.38 (d, *J* 4.0, 1 H).

Palladium-catalyzed allylic alkylation. The reaction was carried out and the products were characterized as previously described.[4] The stoichiometric reaction between the cyclohexenyl π-allyl palladium complex (PF_6^- salt) and sodium dimethylmalonate was run in an NMR tube, with tetrahydrofuran-d_8 as the solvent. The reaction was monitored by ^{1}H NMR spectroscopy at temperatures between 25 and 65 °C.

Synthesis of the cyclohexenyl π-allyl palladium complex of ent-7. The general method of Bosnich[14] was used to prepare di-μ-chloro-bis(cyclohexenyl-π-allyl)dipalladium. This complex (30 mg, 0.067 mmol) was slurried in methanol (2 ml) and ligand *ent*-**7** (56 mg, 0.134 mmol) was added. The resultant mixture was stirred at room temperature until a clear solution was obtained (ca. 4 h). Silver hexafluorophosphate (34 mg, 0.134 mmol) was added and a white precipitate formed immediately. After 15 min the mixture was filtered through a pad of Celite and the filtrate was evaporated to dryness. The residue was recrystallized from chloroform–diethyl ether. 79 mg (79%) of the complex were obtained (as the PF_6^- salt) as a near-colorless microcrystalline solid which was air-stable but which slowly decomposed upon being heated above 135 °C. $[\alpha]_D$ −125 (*c* 0.52, CH_2Cl_2). ^{1}H NMR: δ 7.61–7.30 (m, 20 H), 4.85 (app. t, J=7.0 Hz, 1 H), 7.25 (m, 1 H), 4.10 (m, 2 H), 3.73 (m, 2 H), 2.95 (m, 1 H), 2.66 (m, 2 H), 2.42 (m, 2 H), 1.47 (m, 1 H), 1.06 (m, 2 H), 0.80 (m, 1 H), 0.49 (m, 1 H), −0.42 (m, 1 H). Anal. $C_{36}H_{37}F_6N_2PPd$: C, H, N.

General procedure for the asymmetric addition of organolithiums to imines. To a solution of the imine (0.192 mmol) and ligand (0.192 or 0.0192 mmol) in toluene (3.5 ml) at −78 °C under an argon atmosphere, was added MeLi (0.383 mmol, 1.2 M in ether) over 1 h. The reaction was followed by TLC (15% ether–pentane). After 1–12 h the reaction was quenched by addition of methanol at −78 °C. The reaction mixture was allowed to reach room temperature. Water was added and the layers were separated. The aqueous phase was extracted three times with ether and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*. Flash chromatography of the residue on silica (ether–pentane 5–15%) gave the product. The enantiomeric excess was determined by chiral HPLC using a Chiralcel OD-H column (2% isopropyl alcohol in hexane as the eluent gave baseline separation). The physical and spectral data were in accord with those reported (see the supplementary material, Ref. 15). For yields and enantioselectivity, see Scheme 9.

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