An Approach to a Chiral Cycloalkanone-Mediated Asymmetric Epoxidation of Stilbene with Oxone®

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Chiral and C2-symmetric seven-membered cycloalkanones 2—6 bearing 1,2-diphenylethane-1,2-diamine and cyclohexane-1,2-diamine backbones were synthesized and evaluated their asymmetry inductive behaviours in an asymmetric epoxidation of stilbene with oxone®. Although the reaction of the ketones 2 and 3 of a 1,2-diphenylethane-1,2-diamine backbone gave stilbene oxide in trace to 31% yield, those of the ketones 4—6 of a cyclohexane-1,2-diamine backbone gave the epoxide in satisfactorily high yield up to 98%. It is noteworthy that both reactions with use of stoichiometric and substoichiometric amounts of a ketone 4 gave the epoxide in the essentially same enantioselectivity, 17 and 18%. Eleven-membered cyclic ketones 7 and 8 bearing a binaphthalene backbone were also synthesized and examined their behaviours, while the enantioselectivity turned out to be marginal.

Key words epoxidation; olefin; oxone®; ketone; asymmetric synthesis; stilbene

In these years we have been involved in the development of external chiral ligands effective for a variety type of catalytic asymmetric reactions.[1,2] As an approach toward asymmetric epoxidation of an olefin with oxone®,[3] we designed a chiral ketone **1** for a precursor to a dioxilane (Fig. 1).[4] The chiral ketone **1** is characteristic by a 1,2-diphenylethane-1,2-diamine backbone[5] and benzenesulfonamide moiety as an electron-withdrawing group for electrophilic activation of a ketone carbonyl group as well as prevention of Baeyer–Villiger oxidative rearrangement of a dioxilane.[6] However, enantioselectivity was relatively low, 30% ee for epoxidation of stilbene, even though the sense of enantiofacial differentiation was exactly the same as we predicted.[7] The corresponding dioxilane A, generated from **1** and oxone®, is anticipated to take a rigid conformation B due to steric reason, of which chiral environment is expected to be good for enantiofacial selection (Fig. 2). Since modification of the benzene ring of arylsulfonamide is one possibility to tune up the structure **1**, new chiral ketones **2** and **3** bearing bulky 2,4,6-trimethyl and 2,4,6-triisopropylbenzenesulfonamides were synthesized and examined their efficiency. Three cyclohexyl versions **4**—**6** were also prepared and evaluated in an epoxidation of stilbene. Other than seven-membered cycloalkanones, the 11-memberd cycloalkanones **7** and **8** bearing a binaphthyl backbone were prepared and also examined their attitudes toward an asymmetric epoxidation of stilbene. It is noteworthy that epoxidation of stilbene with **4** gave stilbene oxide in reasonably high yield and almost the same enantioselectivity, regardless of whether stoichiometric (1.0 eq) or substoichiometric (0.3 eq) amount of **4** was used.

Synthesis of the 7-Membered Chiral and C2 Symmetric Cycloalkanones 2—6 The ketones **2** and **3** were readily prepared in three steps starting from commercially available (*S*,*S*)-diamine **9** (Chart 1). According to the reported procedure, **9** was arylsulfonated with the corresponding chlorides in methylene chloride giving **10a**, **b**.[8] Cyclization of **10** was carried out with 3-iodo-2-iodomethylpropene in *N*,*N*-dimethylformamide (DMF) to afford olefins **11a**, **b**, which were then ozonolyzed to the ketones **2** and **3** (Chart 1).

The chiral ketones **4**—**6** bearing a cyclohexanediamine backbone were prepared by the same reaction sequence from (*R*,*R*)-diamine **12**[9] (Chart 2). The phosphonamide **6** was designed expecting more bulkiness than **4** and **5** around the nitrogen.

Synthesis of the 11-Membered Chiral Cycloalkanones 7 and 8 The ketone **7** was readily prepared from a binaph-

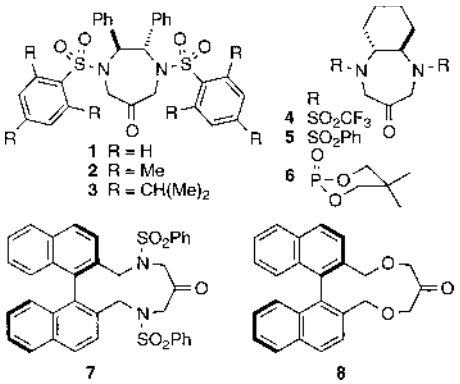

Fig. 1. Chiral Ketones for Asymmetric Epoxidation

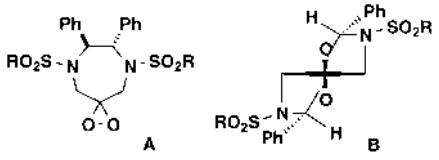

Fig. 2. Anticipated Structures of Dioxilane A and B of **1**—**3**

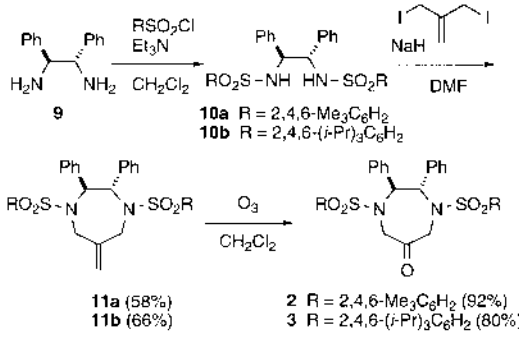

Chart 1. Synthesis of **2** and **3** from a Diamine **9**

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thalenedicarboxylic acid **15**[10] under the standard conditions (Chart 3). The diacid was converted to a diamine **16b** in 69% yield, which was then subjected to the standard three-step procedure for the preparation of cycloalkanone. The target ketone **7** was obtained in satisfactorily high yield.

On the other hand, the reaction of a diol **19**[11] with diiodide did not proceed to cyclize. However, reaction with dichloride gave mono-alkylation product **20** in 92% yield (Chart 4). Treatment of **20** with sodium hydride in DMF gave the desired cyclized-olefin **21** in 15% yield, which was then converted to an alkanone **8** in 99% yield.

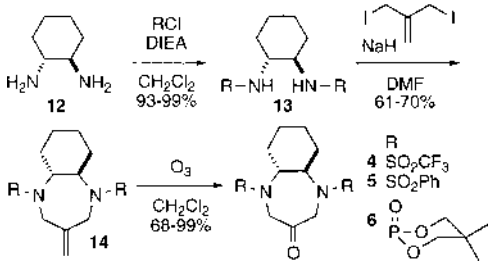


Chart 2. Three Step Synthesis of the Chiral Ketones **4**—**6**

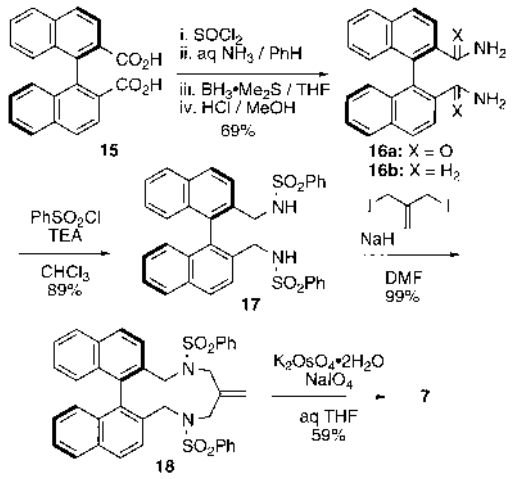


Chart 3. Synthesis of Chiral Ketone **7** from a Carboxylic Acid **15**

Asymmetric Epoxidation of Stilbene with Oxone® Using Chiral Cycloalkanones 2—8 The cycloalkanones **2** and **3** were evaluated as the precursors of the dioxilane A in the asymmetric epoxidation reaction of *trans*-stilbene. According to the previously reported reaction of **1**,[7] we first examined the reaction using one equivalent of **2** in 1,4-dioxane and acetonitrile as a solvent (Table 1, entries 1—3). The chemical yield of stilbene oxide was not improved and more surprisingly the enantioselectivity was quite marginal. The ketone **3** bearing more bulky triisopropylbenzenesulfonyl group did not mediated the epoxidation and gave only a trace amount of the epoxide (entry 4). On the other hand, the ketones **4**—**6** bearing a cyclohexyl backbone behaved more favourably (entries 5—10). Trifluoromethanesulfonylamide **4** promoted the reaction and gave the epoxide in 49 and 98% yields in dioxane and acetonitrile, respectively (entries 5, 6). The enantioselectivities were 14 and 17%. More interestingly, substoichiometric (0.3 eq) amount of **4** gave stilbene oxide in 78% yield and 18% ee (entry 7). Benezenesulfonamide **5** gave the product in 53% chemical yield and 7% ee (entry 8). Phosphonylamide **6** expecting more bulkiness gave the product in 71% chemical yield and 20% ee.

The ketones **7** and **8** bearing a binaphthyl and 11-membered backbone mediated the epoxidation reaction and gave the epoxide in relatively high chemical yields (entries 11, 12). However, the enantioselectivity was far away from our satisfaction. It is also very disappointing to find that Baeyer–

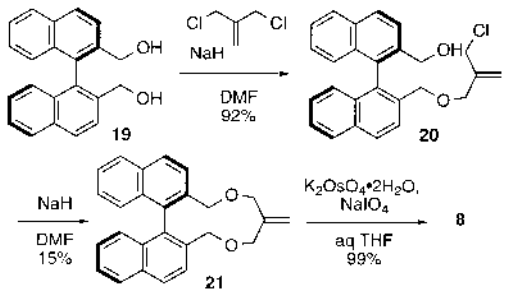
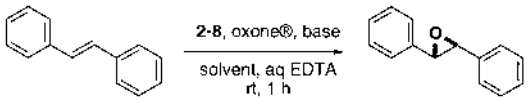


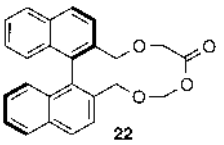
Chart 4. Synthesis of Chiral Ketone **8** from a Diol **19**

Table 1. Asymmetric Epoxidation of Stilbene with Oxone®–Ketone **2**—**8**[a]



Entry	Ketone	eq	Oxone/eq	Solvent	Base	eq	Yield/%	ee/%
1	**1**	1.0	1.4	Dioxane	K_2CO_3	6	27	30
2	**2**	1.0	5.0	Dioxane	$NaHCO_3$	16	16	0
3	**2**	1.0	1.4	MeCN	K_2CO_3	6	31	0
4	**3**	1.0	1.4	Dioxane	K_2CO_3	6	Trace	nd
5	**4**	1.0	5.0	Dioxane	$NaHCO_3$	16	49	14
6	**4**	1.0	5.0	MeCN	$NaHCO_3$	16	98	17
7	**4**	0.3	5.0	MeCN	$NaHCO_3$	16	78	18
8	**5**	1.0	5.0	MeCN	$NaHCO_3$	16	53	7
9	**6**	1.0	5.0	MeCN	$NaHCO_3$	16	Trace	nd
10	**6**	1.0	1.4	MeCN	K_2CO_3	6	71	20
11	**7**	1.0	1.4	MeCN	K_2CO_3	6	46	2
12	**8**	1.0	1.4	MeCN	K_2CO_3	6	73	0

a) The data in entry 1 is quoted from ref. 7 for comparison purpose. Oxone® was added over a period of 1 h using a syringe drive, excepting 3 h for entry 10. The mixture was then stirred at room temperature for another 1 h, excepting 9 h for entry 1. In entry 4, acetonitrile could not be used because of insolubility of **4**. nd: not determined.



22

Fig. 3. Baeyer–Villiger Product **22**

Villiger rearrangement occurred quite easily from the ketone **8** and gave a lactone **22** in 55% chemical yield (entry 12).

Discussions on Catalytic Behaviour of the Cycloalkanones The asymmetric epoxidation with cycloalkanones **2** and **3** did not proceed smoothly, probably because of Baeyer–Villiger type degradation of the ketone. This indicates that bulky arylsulfonylamide group is not effective for activation of dioxilane and prevention of Bayer–Villiger oxidative rearrangement. The situation is also same in the reactions using **7** and **8** though the relative epoxidation rate seemed to be faster than rearrangement. Hence, it is quite important to know that the ketones **4**—**6**, especially trifluoromethanesulfonamide **4** in 0.3 eq, catalyzed the reaction giving the epoxide in the same enantioseletivity and 78% yield. Since the trifluoromethanesulfonyl group is highly electron-withdrawing in nature, the electrophilic reactivity of the ketone is significantly high in converting to a dioxilane, and the electron-withdrawing character of the amide retards Baeyer–Villiger oxidative rearrangement. These strongly indicated that electrophilic activation of ketone is possible by attaching electron-withdrawing sulfonylamide groups on both α-methylene carbons of the ketone, but not by bulky sulfonylamide (**2**, **3**, **7**) and ether group (**8**).

Conclusion

The chiral and C2 symmetric seven- and eleven-membered cycloalkanones **2**—**8** bearing a 1,2-diphenylethane-1,2-diamine, cyclohexane-1,2-diamine, and binaphthalene backbones were prepared from the corresponding diamines **9**, **12**, **16**, and diol **19**. Asymmetric epoxidation of stilbene with oxone® was examined using these new cycloalkanones and was effectively catalyzed especially by the ketone **4** bearing trifluoromethanesulfonylamide group giving stilbene oxide in reasonably high 78—98% chemical yield and 18% ee.

Experimental[12)]

(2*S*,3*S*)-6-Methylene-2,3-diphenyl-1,4-bis(2,4,6-trimethylbenzenesulfonyl)[1,4]diazepane (11a) A solution of **10a**[8)] (8.1 g, 14 mmol) in DMF (24 ml) was added to a suspension of sodium hydride (60%, 1.1 g, 28 mmol) in DMF (4.0 ml) at 0 °C. The mixture was stirred at 80 °C for 1 h. To the mixture was added 3-iodo-2-iodomethylpropene (5.2 g, 17 mmol) at 0 °C. The whole was stirred at 80 °C for 1.5 h and was quenched with saturated (satd) NH_4Cl. The mixture was extracted with benzene (100 ml). The combined organic layers were washed with 10% HCl, satd $NaHCO_3$, and brine. Concentration and column chromatography (AcOEt/hexane=1/5) gave **11a** (5.0 g, 58%) as a white amorphous of $[\alpha]_D^{25}$ −162.1° (c=1.51, $CHCl_3$). ^{1}H-NMR: 1.93 (6H, s, CH_3), 2.36 (12H, s, CH_3), 4.65 (2H, d, J=16.8 Hz, CH_2), 4.71 (2H, d, J=16.8 Hz, CH_2), 5.15 (2H, s, CH_2), 5.19 (2H, s, CH_2), 6.50 (4H, s, ArH), 6.58 (4H, d, J=7.3 Hz, ArH), 6.72 (4H, dd, J=7.3, 7.3 Hz, ArH). 6.81 (2H, d, J=7.3 Hz, ArH). ^{13}C-NMR: 20.5, 22.8, 26.9, 49.6, 65.1, 111.7, 126.8, 127.0, 127.2, 131.5, 133.3, 138.6, 139.5, 142.2, 144.6. IR (Nujol): 1605, 1470 cm^{-1}. MS (FAB) *m/z*: 629 (M^++H). High resolution (HR)-MS *m/z*: Calcd for $C_{36}H_{41}N_2O_4S_2$: 629.2508. Found: 629.2512.

(2*S*,3*S*)-2,3-Diphenyl-1,4-bis(2,4,6-trimethylbenzenesulfonyl)[1,4]diazepan-6-one (2) A solution of **11a** (4.1 g, 6.5 mmol) in chloroform (65 ml) was ozonized at −60 °C by passing the O_3/O_2 stream until the solution was saturated with O_3. Excess O_3 was removed by O_2 stream, and triphenylphosphine (2.6 g, 9.7 mmol) was added portionwise to the reaction mixture. The whole was stirred at room temperature for 1 h. Concentration and column chromatography (AcOEt/hexane=1/1) gave **2** (3.0 g, 92%) as colourless needles of mp 179.5—180.5 °C (*tert*-butyl methyl ether (TBME)) and $[\alpha]_D^{25}$ −5.9° (c=1.52, $CHCl_3$). ^{1}H-NMR: 2.28 (6H, s, CH_3), 2.31 (12H, s, CH_3), 3.83 (2H, d, J=17.6 Hz, CH_2), 4.69 (2H, d, J=17.6 Hz, CH_2), 6.05 (2H, s, CH_2), 6.87 (4H, s, CH_2), 7.16—7.17 (4H, m, ArH). 7.23—7.31 (6H, m, ArH). ^{13}C-NMR: 20.9, 23.1, 51.9, 64.1, 127.5, 127.9, 128.6, 131.7, 132.3, 138.0, 140.5, 143.1, 206.4. IR (Nujol): 1740, 1430 cm^{-1}. MS (FAB) *m/z*: 632 (M^++H). HR-MS *m/z*: Calcd for $C_{35}H_{39}N_2O_5S_2$: 631.2300. Found: 631.2288.

(2*S*,3*S*)-6-Methylene-2,3-diphenyl-1,4-bis(2,4,6-triisopropylbenzenesulfonyl)[1,4]diazepane (11b) Prepared from **10b**[8)] and 3-iodo-2-iodomethylpropene, according to the procedure for **11a**. Column chromatography (AcOEt/hexane=1/10) gave **11b** in 66% yield as a white amorphous of $[\alpha]_D^{25}$ −50.4° (c=1.10, $CHCl_3$). ^{1}H-NMR: 1.11 (24H, d, J=5.2 Hz, CH_3 2.82 (2H, seqt, J=6.9 Hz, CH), 3.75 (4H, seqt, J=6.9 Hz, CH), 4.28 (2H, d, J=16.7 Hz, CH_2), 4.70 (2H, d, J=16.7 Hz, CH_2), 5.02 (2H, s, CH_2), 5.62 (2H, s, CH_2), 7.00—7.10 (14H, m, ArH). ^{13}C-NMR: 23.50, 23.53, 24.75, 24.8, 29.5, 34.1, 48.2, 64.5, 123.8, 127.4, 127.9, 128.2, 131.8, 139.9, 145.6, 151.4, 153.1. IR (Nujol): 1600, 1460 cm^{-1}. MS (FAB) *m/z*: 797 (M^++H). HR-MS *m/z*: Calcd for $C_{48}H_{65}N_2O_4S_2$: 797.4386. Found: 797.4393.

(2*S*,3*S*)-2,3-Diphenyl-1,4-bis(2,4,6-triisopropylbenzenesulfonyl)[1,4]-diazepan-6-one (3) Prepared from **11b**, according to the procedure for **2**. Column chromatography (TBME/hexane=1/10) gave **3** in 80% yield as a white powder of mp 198.5—200.5 °C and $[\alpha]_D^{25}$ +18.9° (c=0.54, $CHCl_3$). ^{1}H-NMR: 0.96 (12H, d, J=6.7 Hz, CH_3), 1.06 (12H, d, J=6.7 Hz, CH_3), 1.24 (12H, d, J=7.0 Hz, CH_3), 2.88 (2H, seqt, J=6.7 Hz, CH), 3.62 (4H, seqt, J=6.7 Hz, CH), 3.88 (2H, d, J=17.7 Hz, CH_2), 4.81 (2H, d, J=17.7 Hz, CH_2), 6.09 (2H, s, CH_2), 7.11 (4H, s, ArH), 7.26—7.35 (10H, m, ArH). ^{13}C-NMR: 23.50, 23.53, 24.75, 24.78, 29.7, 34.1, 51.4, 63.4, 124.3, 127.8, 127.9, 128.9, 130.3, 138.9, 151.9, 153.7, 206.4. IR (Nujol): 1740 cm^{-1}. MS (FAB) *m/z*: 799 (M^++H). HR-MS *m/z*: Calcd for $C_{47}H_{63}N_2O_5S_2$: 799.4178. Found: 799.4189.

(6*R*,7*R*)-3-Methylene-1,5-bistrifluoromethanesulfonyldecahydrobenzo-[*b*][1,4]diazepine (14: R=CF_3SO_2) Prepared from **13** (R=CF_3SO_2)[13)] and 3-iodo-2-iodomethylpropene, according to the procedure for **11**. Column chromatography (AcOEt/hexane=1/5) and recrystallization gave **14** (CF_3SO_2) in 61% yield as a white powder of mp 145—146 °C (diethyl ether) and $[\alpha]_D^{25}$ −12.3° (c=1.30, $CHCl_3$). ^{1}H-NMR: 1.33—1.42 (2H, m, CH_2), 1.80—2.11 (6H, m, CH_2), 3.83 (2H, br s, CH), 4.17—4.28 (4H, m, CH_2), 5.15 (2H, s, CH_2). ^{13}C-NMR: 25.0, 31.1, 65.9, 66.1, 119.3 (q, J=321 Hz), 119.8, 137.4. IR (Nujol): 3400, 1180 cm^{-1}. MS (FAB) *m/z*: 431 (M^++H). *Anal.* Calcd for $C_{12}H_{16}F_6N_2O_4S_2$: C, 33.49; H, 3.75; N, 6.51. Found: C, 33.37; H, 3.71; N, 6.53.

(6*R*,7*R*)-1,5-Bistrifluoromethanesulfonyldecahydrobenzo[*b*][1,4]diazepin-3-one (4) Prepared from **14** (R=CF_3SO_2), according to the procedure for **2**. Column chromatography (AcOEt/hexane=1/1) and recrystallization gave **4** in 76% yield as colourless granules of mp 126.5 °C (dec.) ($CHCl_3$–hexane) and $[\alpha]_D^{25}$ −23.9° (c=1.76, MeOH). ^{1}H-NMR: 1.39—2.14 (8H, m, CH_2), 3.78 (2H, m, CH), 4.21 (2H, d, J=18.5 Hz, CH_2), 4.44 (2H, d, J=18.5 Hz, CH_2). ^{13}C-NMR: 24.7, 29.5, 59.4, 65.4, 119.3 (q, J=323 Hz), 199.3. IR (Nujol): 1725 cm^{-1}. MS (FAB) *m/z*: 433 (M^++H). *Anal.* Calcd for $C_{11}H_{14}F_6N_2O_5S_2$: C, 30.56; H, 3.26 Found: C, 30.48; H, 3.27.

(6*R*,7*R*)-1,5-Bisbenzenesulfonyl-3-methylenedecahydrobenzo[*b*][1,4]-diazepine (14: R=$PhSO_2$) Prepared from **13** (R=$PhSO_2$) and 3-iodo-2-iodomethylpropene, according to the procedure for **11a**. Column chromatography (AcOEt/hexane=1/2) and recrystallization gave **14** (R=$PhSO_2$) in 84% yield as colorless cubes of mp 165—166 °C (benzene) and $[\alpha]_D^{25}$ +18.7° (c=1.68, $CHCl_3$). ^{1}H-NMR: 1.25 (2H, m, CH_2), 1.73 (4H, m, CH_2), 1.93 (2H, m, CH_2), 3.57 (2H, m, CH), 3.99 (2H, d, J=15.6 Hz, CH_2), 4.07 (2H, d, J=15.6 Hz, CH_2), 4.90 (2H, s, CH_2), 7.44—7.52 (6H, m, ArH), 7.83—7.86 (4H, m, ArH). ^{13}C-NMR: 25.4, 31.3, 52.0, 64.1, 116.5, 127.1, 128.8, 132.1, 139.8, 142.3. IR (Nujol): 1650, 1320 cm^{-1}. MS (FAB) *m/z*: 447 (M^++H). *Anal.* Calcd for $C_{22}H_{26}N_2O_4S_2$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.07; H, 5.86; N, 6.11.

(6*R*,7*R*)1,5-Bisbenzenesulfonyldecahydrobenzo[*b*][1,4]diazepin-3-one (5) Prepared from **14** (R=$PhSO_2$) according to the procedure for **2**. Column chromatography (AcOEt/hexane=1/2) and recrystallization gave **5** in 99% yield as colourless needles of mp 195—196 °C (benzene–hexane) and $[\alpha]_D^{25}$ −26.2° (c=1.55, $CHCl_3$). ^{1}H-NMR: 1.21—1.30 (2H, m, CH_2), 1.74—1.83 (6H, m, CH_2), 3.66—3.68 (2H, m, CH), 4.15 (2H, d, J=18.3 Hz, CH_2), 4.21 (2H, d, J=18.3 Hz, CH_2), 7.49—7.52 (4H, m, ArH), 7.55—7.58 (2H, m, ArH), 7.82—7.84 (4H, m, ArH). ^{13}C-NMR: 25.0, 29.9, 56.3, 63.9, 126.7,

129.2, 132.7, 141.6, 204.2. IR (Nujol): 1720 cm^{-1}. MS (FAB) *m/z*: 449 (M^++H). *Anal.* Calcd for $C_{21}H_{24}N_2O_5S_2$: C, 56.23; H, 5.39. Found: C, 56.04; H, 5.36.

(1*R*,2*R*)-*N*,*N*′-Bis(5,5-dimethyl-2-oxo-2λ^5-[1,3,2]dioxaphosphinan-2-yl)cyclohexane-1,2-diamine (13: R=PO(OCH$_2$C(Me)$_2$CH$_2$O)) A solution of 2-chloro-5,5-dimethyl[1,3,2]dioxaphosphinane 2-oxide (11 g, 57 mmol) in CH_2Cl_2 (60 ml) was added to a solution of **12** in CH_2Cl_2 (24 ml) containing *N*,*N*-diisopropylethylamine (20 ml, 110 mmol) at 0 °C. The mixture was stirred at room temperature for 12 h, and was poured onto 10% HCl (100 ml), and then extracted with $CHCl_3$ (100 ml). The combined organic layers were washed with satd $NaHCO_3$, brine. Concentration and recrystallization from AcOEt–$CHCl_3$ afforded **13** (R=PO(OCH$_2$C(Me)$_2$CH$_2$O)) in 64% yield as a white powder of mp 185—188 °C and $[\alpha]_D^{25}$ +8.3° (*c*=1.44, $CHCl_3$). ^{1}H-NMR: 1.01, 1.09 (each 6H, s, CH_3), 1.26 (4H, m, CH_2), 1.69, 2.17 (each 2H, m, CH_2), 2.86 (2H, m, CH), 3.51 (2H, m, NH), 3.91 (1H, dd, *J*=11.6, 11.6 Hz, CH_2), 3.91 (1H, dd, *J*=10.1, 10.1 Hz, CH_2), 3.94 (1H, dd, *J*=11.6, 11.6 Hz, CH_2), 3.94 (1H, dd, *J*=10.1, 10.1 Hz, CH_2), 4.13 (2H, dd, *J*=10.1, 10.1 Hz, CH_2), 4.14 (2H, dd, *J*=10.1, 10.1 Hz, CH_2). ^{13}C-NMR ($CDCl_3$): 21.1, 21.5, 24.7, 32.0 (d, *J*=5.2 Hz), 34.7, 56.4 (*J*=7.2 Hz), 76.3 (d, *J*=6.2 Hz), 76.5 (d, *J*=6.2 Hz). IR (Nujol): 3200, 1275 cm^{-1}. MS *m/z*: 410 (M^+). HR-MS *m/z*: Calcd for $C_{16}H_{32}N_2O_6P_2$: 410.1736. Found: 410.1733.

(6*R*,7*R*)-1,5-Bis(5,5-dimethyl-2-oxo-λ^5-[1,3,2]dioxaphosphin-2-yl)-decahydrobenzo[*b*][1,4]diazepin-3-one (6) Prepared from **13** (R=PO(OCH$_2$C(Me)$_2$CH$_2$O)), according to the procedure for **11a** and **2**. Column chromatography (EtOH/AcOEt=1/20) and recrystallization gave **6** in 48% two-step yield as pale yellow granules of mp 155—156 °C (AcOEt) and $[\alpha]_D^{25}$ +17.2° (*c*=1.33, $CHCl_3$). ^{1}H-NMR: 0.93, 1.18 (each 6H, s, CH_3), 1.34, 1.78 (each 2H, m, CH_2), 1.88 (2H, m, CH_2), 2.00 (2H, m, CH_2), 3.43 (2H, m, CH), 3.81 (2H, dd, *J*=7.7, 18.0 Hz, CH_2), 3.96 (2H, dd, *J*=18.3, 18.3 Hz, CH_2), 3.98 (2H, dd, *J*=18.3, 18.3 Hz, CH_2), 4.03 (2H, dd, *J*=10.7, 18.0 Hz, CH_2), 4.19 (2H, dd, *J*=11.0, 11.0 Hz, CH_2), 4.20 (2H, dd, *J*=11.0, 11.0 Hz, CH_2). ^{13}C-NMR: 21.0, 21.9, 25.3, 30.6, 31.8 (d, *J*=5.2 Hz), 55.6, 62.5, 76.3 (d, *J*=6.3 Hz), 76.4 (d, *J*=6.3 Hz), 206.4. IR (Nujol): 1715 cm^{-1}. MS *m/z*: 464 (M^+). HR-MS (FAB) *m/z*: Calcd for $C_{19}H_{35}N_2O_7P_2$: 465.1919. Found: 465.1910.

(*R*)-[1,1′]Binaphthalenyl-2,2′-dicarboxylic Acid Diamide (16a) A solution of (*R*)-**15** (1.69 g, 4.94 mmol) in thionyl chloride (5.0 ml) was refluxed with stirring for 1 h. After the whole was concentrated, benzene (5.0 ml) and aqueous NH_3 (28%, 5.0 ml) were added. The mixture was stirred at room temperature for 0.5 h, and then poured onto 10% HCl, and was extracted with AcOEt (100 ml). The organic layer was washed with brine. Concentration, column chromatography (hexane/AcOEt=9/1, then AcOEt), and recrystallization gave **16a** (1.53 g, 91%) as colourless cubes of mp 222.5—224.0 °C (benzene) and $[\alpha]_D^{25}$ +237.5° (*c*=0.80, $CHCl_3$). ^{1}H-NMR: 5.44 (2H, br s, NH_2), 7.04 (2H, br s, NH_2), 7.11 (2H, d, *J*=8.6 Hz, ArH), 7.25—7.28 (2H, m, ArH), 7.47—7.50 (2H, m, ArH), 7.73 (2H, d, *J*=8.6 Hz, ArH), 7.92 (2H, d, *J*=8.3 Hz, ArH), 8.01 (2H, d, *J*=8.3 Hz, ArH). ^{13}C-NMR: 123.7, 126.4, 127.2, 127.3, 128.2, 128.3, 129.0, 132.3, 133.1, 134.2, 172.4. IR (Nujol): 3300, 3150, 1660 cm^{-1}. MS *m/z*: 340 (M^+). HR-MS *m/z*: Calcd for $C_{22}H_{16}N_2O_2$: 340.1212. Found: 340.1217.

(*R*)-*N*,*N*′-Bisbenzenesulfonyl-1,1′-binaphthyl-2,2′-bis(methylamine) (17) A solution of **16a** (525 mg, 1.54 mmol) in tetrahydrofuran (THF) (2.5 ml) was added to $BH_3 \cdot Me_2S$ in THF (2.5 ml, 10 M) and refluxed for 2 d with stirring. To the mixture were added MeOH (8.0 ml) and aqueous HCl (35%, 1.0 ml) at 0 °C and then the mixture was concentrated. The residue was poured onto 15% NaOH (15 ml) and extracted with TBME (30 ml). Combined organic layers were washed with satd $NaHCO_3$ (15 ml) and brine. Concentration gave (*R*)-**16b** (360 mg, 75%) as a pale yellow oil, which was used in the next step without any purification.

To a solution of **16b** (100 mg, 0.29 mmol) in CH_2Cl_2 (3.0 ml) containing triethylamine (TEA, 0.12 ml, 0.87 mmol) was added benzenesulfonyl chloride (0.09 ml, 0.73 mmol) at 0 °C. The whole was stirred for 1 h at room temperature. After addition of water (10 ml), the mixture was extracted with benzene (30 ml). The extract was washed with 10% HCl, satd $NaHCO_3$ and brine. Concentration and column chromatography (AcOEt/hexane=1/2) gave **17** (150 mg, 89%) as a white amorphous of mp 85—89 °C and $[\alpha]_D^{25}$ +86.9° (*c*=0.72, $CHCl_3$). ^{1}H-NMR: 3.68, 3.73 (each 2H, dd, *J*=6.0, 14.4 Hz, CH_2), 4.69 (2H, dd, *J*=6.0, 6.0 Hz, NH), 6.92 (2H, d, *J*=8.6 Hz, ArH), 7.24—7.26 (2H, m, ArH), 7.32—7.36 (6H, m, ArH), 7.46—7.49 (4H, m, ArH), 7.52 (2H, d, *J*=8.0 Hz, ArH), 7.64 (2H, d, *J*=8.6 Hz, ArH), 7.92 (4H, dd, *J*=8.6, 8.6 Hz, ArH). ^{13}C-NMR ($CDCl_3$): 45.1, 125.5, 126.4, 126.5, 126.7, 127.1, 128.31, 128.33, 129.0, 132.51, 132.53, 133.0, 133.1, 133.6, 139.3. IR (Nujol): 3250, 1325 cm^{-1}. MS (FAB) *m/z*: 593 (M^++H). HR-MS *m/z*: Calcd for $C_{34}H_{29}N_2O_4S_2$: 593.1569. Found: 593.1577.

(*R*)-10-Methylene-8,12-bis(phenylsulfonyl)-8,9,10,11,12,13-hexahydro-7*H*-dinaphtho[2,1-*g*:1,2-*i*][1,5]diazacycloundecine (18) Prepared from **17** and 3-iodo-2-iodomethylpropenein, according to the procedure for **11a**. Recrystallization gave **18** in 72% yield as colourless needles of mp 203.5—205 °C (AcOEt) and $[\alpha]_D^{25}$ +182° (*c*=0.98, $CHCl_3$). ^{1}H-NMR: 3.38 (2H, d, *J*=15.9 Hz, CH_2), 3.53 (2H, d, *J*=14.7 Hz, CH_2), 3.55 (2H, d, *J*=15.9 Hz, CH_2), 4.44 (2H, d, *J*=14.7 Hz, CH_2), 4.65 (2H, s, CH_2), 7.01 (2H, d, *J*=8.6 Hz, ArH). 7.25—7.30 (2H, m, ArH), 7.43—7.49 (6H, m, ArH), 7.52—7.55 (2H, m, ArH), 7.68—7.73 (6H, m, ArH) 7.90—7.94 (4H, m, ArH). ^{13}C-NMR: 49.3, 50.8, 118.5, 125.9, 126.3, 126.7, 127.0, 127.1, 128.2, 129.0, 132.7, 132.9, 133.0, 133.1, 134.2, 136.3, 138.9. IR (Nujol): 1640 cm^{-1}. MS (FAB) *m/z*: 645 (M^++H). HR-MS *m/z*: Calcd for $C_{38}H_{33}N_2O_4S_2$: 645.1882. Found: 645.1901.

(R)-8,12-Bis(phenylsulfonyl)-7,8,9,11,12,13-hexahydro-10*H*-dinaphtho[2,1-*g*:1,2-*i*][1,5]diazacycloundecine-10-one (7) To a suspension of **18** (64 mg, 0.1 mmol) and $K_2OsO_4 \cdot 2H_2O$ (3 mg, 0.01 mmol in THF (1.5 ml) was added a solution of sodium metaperiodate (63 mg, 0.3 mmol) in water (0.5 ml). The whole was stirred at room temperature for 2.5 d. After addition of water (10 ml), the mixture was extracted with AcOEt. The extract was washed with 10% HCl, satd $NaHCO_3$ and brine. Concentration and column chromatography (benzene) gave **7** (38 mg, 59%) as a solid of mp 146—148 °C and $[\alpha]_D^{25}$ +216.6° (*c*=0.27, $CHCl_3$). ^{1}H-NMR: 3.24 (2H, d, *J*=16.2 Hz, CH_2), 3.57 (2H, d, *J*=13.2 Hz, CH_2), 4.05 (2H, d, *J*=16.2 Hz, CH_2), 4.30 (2H, d, *J*=13.2 Hz, CH_2), 7.25 (2H, d, *J*=8.3 Hz, ArH). 7.36—7.39 (4H, m, ArH), 7.46—7.49 (4H, m, ArH), 7.54—7.59 (8H, m, ArH), 7.99—7.03 (4H, m, ArH). ^{13}C-NMR δ: 52.6, 53.9, 125.3, 126.6, 127.1, 127.9, 128.3, 128.4, 128.6, 129.1, 130.5, 132.6, 133.1, 134.2, 135.2, 136.2, 201.1. IR (Nujol): 1735 cm^{-1}. MS (FAB) *m/z*: 647 (M^++H). HR-MS *m/z*: Calcd for $C_{37}H_{31}N_2O_5S_2$: 647.1674. Found: 647.1668.

(*R*)-[2′-(2-Chloromethylallyloxymethyl)[1,1′]binaphthalenyl-2-yl]methanol (20) A solution of a diol **19** (443 mg, 1.41 mmol) in DMF (11 ml) was added to a suspension of sodium hydride (60%, 57 mg, 1.43 mmol) in DMF (130 ml) at 0 °C. The mixture was stirred at room temperature for 1 h. To the mixture was added 3-chloro-2-chloromethylpropene (4.90 ml, 42.3 mmol) at −40 °C. The whole was stirred at −40 °C for 24 h and was quenched with satd NH_4Cl. The mixture was extracted with benzene (30 ml). The combined organic layers were washed with brine. Concentration and column chromatography (AcOEt/hexane=1/6) gave **20** (520 mg, 92%) as a colourless gum of $[\alpha]_D^{25}$ +104.4° (*c*=0.43, $CHCl_3$). ^{1}H-NMR: 2.94 (1H, dd, *J*=3.7, 9.4 Hz, OH), 3.87 (1H, d, *J*=11.9 Hz, CH_2), 3.89 (1H, d, *J*=12.4 Hz, CH_2), 3.92 (1H, d, *J*=11.9 Hz, CH_2), 3.96 (1H, d, *J*=12.4 Hz, CH_2), 4.07 (1H, d, *J*=10.7 Hz, CH_2), 4.16 (1H, dd, *J*=3.7, 12.2 Hz, CH_2), 4.20 (1H, d, *J*=10.7 Hz, CH_2), 4.28 (1H, dd, *J*=9.4, 12.2 Hz, CH_2), 5.06 (1H, s, CH_2), 5.19 (1H, s, CH_2), 7.04 (1H, d, *J*=8.5 Hz, ArH), 7.07 (1H, d, *J*=8.5 Hz, ArH), 7.24 (2H, m, ArH), 7.47 (2H, m, ArH), 7.69 (1H, d, *J*=8.5 Hz, ArH), 7.79 (1H, d, *J*=8.5 Hz, ArH), 7.94 (1H, d, *J*=8.5 Hz, ArH), 7.94 (1H, d, *J*=8.5 Hz, ArH), 8.02 (2H, m, ArH). ^{13}C-NMR: 44.9, 63.2, 71.0, 71.1, 117.6, 126.0, 126.1, 126.29, 126.34, 126.5, 126.7, 127.4, 127.6, 128.06, 128.08, 128.5, 128.7, 132.7, 133.0, 133.1, 133.3, 133.5, 133.8, 135.4, 138.1, 141.2. IR (Nujol): 3400, 1595 cm^{-1}. MS *m/z*: 402 (M^+). HR-MS *m/z*: Calcd for $C_{26}H_{23}ClO_2$: 402.1387. Found: 402.1381.

(*R*)-10-Methylene7,10,11,13-tetrahydro-9*H*-dinaphtho[2,1-*g*:1,2-*i*][1,5]dioxacycloundecine (21) A solution of **20** (470 mg, 1.20 mmol) in DMF (45 ml) was added to a suspension of sodium hydride (60%, 56 mg, 1.40 mmol) in DMF (140 ml) at 0 °C over a period of 5 h. The whole was stirred at room temperature for 24 h and was quenched with satd NH_4Cl. The mixture was extracted with benzene (30 ml). The combined organic layers were washed with brine. Concentration and column chromatography (acetone/hexane=1/20) gave **21** (69 mg, 15%) as a white amorphous of $[\alpha]_D^{25}$ +278° (*c*=0.18, $CHCl_3$). ^{1}H-NMR: 3.76 (2H, d, *J*=11.9 Hz, CH_2), 4.08 (2H, d, *J*=11.9 Hz, CH_2), 4.23 (2H, *J*=11.8 Hz, CH_2), 4.46 (2H, *J*=11.8 Hz, CH_2), 4.87 (2H, s, CH_2), 7.04 (2H, d, *J*=8.0 Hz, ArH), 7.22 (2H, dd, *J*=7.3, 7.3 Hz, ArH), 7.44 (2H, dd, *J*=7.3, 7.3 Hz, ArH), 7.68 (2H, d, *J*=8.4 Hz, ArH), 7.92 (2H, d, *J*=8.0 Hz, ArH), 7.98 (2H, d, *J*=8.4 Hz, ArH). ^{13}C-NMR: 70.6, 71.2, 113.6, 125.8, 125.9, 126.0, 126.4, 128.0, 128.1, 128.2, 132.8, 133.3, 135.2, 145.0. IR (Nujol): 1640 cm^{-1}. MS *m/z*: 366 (M^+). HR-MS *m/z*: Calcd for $C_{26}H_{22}O_2$: 366.1620. Found: 366.1626.

(*R*)-7,13-Dihydro-9*H*-dinaphtho[2,1-*g*:1,2-*i*][1,5]dioxacycloundecine-10(11*H*)-one (8) To a suspension of **21** (42 mg, 0.1 mmol) and $K_2OsO_4 \cdot 2H_2O$ (4 mg, 0.01 mmol) in THF (2.4 ml) was added a solution of sodium metaperiodate (99 mg, 0.5 mmol) in water (0.8 ml). The whole was stirred at room temperature for 1 d. After addition of water (10 ml), the mixture was extracted with TBME (10 ml). The extract was washed with brine. Concen-

tration and column chromatography (AcOEt/hexane/TEA=2/20/1) gave **8** (42 mg, 99%) as a solid of mp 171.0—172.5 °C and $[\alpha]_D^{25}$ +257° (c=0.32, $CHCl_3$). ^{1}H-NMR: 3.86 (2H, d, J=14.1 Hz, CH_2), 4.07 (2H, d, J=14.1 Hz, CH_2), 4.30 (2H, d, J=10.5 Hz, CH_2), 4.55 (2H, d, J=10.5 Hz, CH_2), 7.02 (2H, d, J=8.6 Hz, ArH), 7.23 (2H, ddd, J=1.1, 8.6, 8.6 Hz, ArH), 7.47 (2H, ddd, J=1.1, 8.3, 8.3 Hz, ArH), 7.68 (2H, d, J=8.6 Hz, ArH), 7.94 (2H, d, J=8.3 Hz, ArH), 8.01 (2H, d, J=8.6 Hz, ArH). ^{13}C-NMR: 73.0, 73.4, 126.2, 126.3, 126.6, 128.0, 128.2, 128.4, 132.9, 133.4, 134.0, 135.4, 208.6. IR (Nujol): 1725 cm^{-1}. MS m/z: 368 (M^+). HR-MS m/z: Calcd for $C_{25}H_{20}O_3$: 368.1412. Found: 368.1402.

Asymmetric Epoxidation of Stilbene Catalyzed by 4 (Table 1, Entry 7) To an acetonitrile solution (7.5 ml) of *trans*-stilbene (90 mg, 0.50 mmol), **4** (65 mg, 0.15 mmol), and an aqueous Na_2EDTA solution (3 ml, 4×10^{-4} M) was added a mixture of oxone® (922 mg, 1.5 mmol) and sodium bicarbonate (391 mg, 4.7 mmol) in portions over a period of 1 h at room temperature (r.t.). After stirring for 1 h, the mixture was poured onto water (20 ml), and extracted with $CHCl_3$ (60 ml). The combined organic layers were washed with brine. Concentration and column chromatography (hexane, then hexane/AcOEt=9/1) gave *trans*-stilbene epoxide (74 mg, 78%) of $[\alpha]_D^{25}$ −47.6° (c=1.19, $CHCl_3$) in 18 % ee. ^{1}H-NMR, IR, and MS were identical with those reported.[14] The ee was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralcel OD-H, hexane/iso-PrOH= 9 : 1, 0.5 ml/min, 15.0 min (major enantiomer), 26.9 min (miner enantiomer).

In entry 12, column chromatography gave (*R*)-7,14-dihydrodinaphtho[2,1-*h*:1,2-*j*][1,3,6]trioxacyclododecin-11(12*H*)-one 22 as a white gum in 55% yield: ^{1}H-NMR: 3.85 (1H, d, J=12.5 Hz, CH_2), 3.89 (1H, d, J=16.2 Hz, CH_2), 4.23 (1H,d, J=16.2 Hz, CH_2), 4.30 (1H, J=12.2 Hz, CH_2), 4.67 (1H, J=12.5 Hz, CH_2), 4.77 (1H, J=12.2 Hz, CH_2), 4.78 (1H, J=5.8 Hz, CH_2), 5.73 (1H, J=5.8 Hz, CH_2), 6.95 (1H, d, J=8.6 Hz, ArH), 6.95 (1H, d, J=8.6 Hz, ArH), 7.23 (2H, m, ArH), 7.45 (1H, d, J=7.3 Hz, ArH), 7.47 (1H, d, J=7.3 Hz, ArH), 7.75 (1H, d, J=8.6 Hz, ArH), 7.87 (1H, d, J=8.6 Hz, ArH), 7.92 (1H, d, J=8.6 Hz, ArH), 7.94 (1H, d, J=8.3 Hz, ArH), 8.01 (1H, d, J=8.5 Hz, ArH), 8.06 (1H, d, J=8.6 Hz, ArH). ^{13}C-NMR: 69.2, 69.4, 71.3, 88.7, 126.4, 126.8, 127.0, 127.1, 127.4, 127.5, 127.76, 127.83, 129.3, 129.4, 129.6, 129.7, 133.3, 134.3, 134.39, 134.42, 134.47, 134.53, 134.6, 135.9, 172.0. IR ($CHCl_3$): 1740 cm^{-1}. MS m/z: 384 (M^+). HR-MS m/z: Calcd for $C_{25}H_{20}O_4$: 384.1362. Found: 384.1368.

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References and Notes

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