Asymmetric opening of the epoxide ring in cyclohexene oxide by thiophenol using homochiral phosphinamide catalysts

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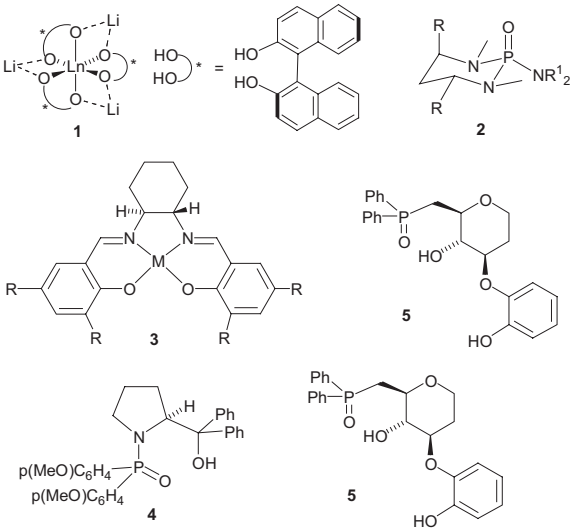
Enantiomerically pure phosphinamides containing a pendant hydroxyl group catalyse the Al(III)-promoted ring opening of the *meso* epoxide in cyclohexene oxide with thiophenol in up to 80% enantiomeric excess.

Keywords: epoxide ring, cyclohexene oxide, thiophenol, homochiral phosphinamide catalyst

The enantioselective ring-opening of *meso* epoxides provides a useful method for the asymmetric synthesis of alcohols.[1-6] The catalysts reported for this application include BINOL/lanthanide complexes **1**,[2] and chiral phosphoramide catalysts **2**.[3] The phosphoramide catalysts promote the reaction by engaging in a Lewis-base interaction with the nucleophile and subsequently activating its addition to the epoxide. Jacobsen and co-workers have employed Salen catalysts **3** for enantioselective *meso* epoxide opening, and for kinetic resolution of racemic epoxides.[4]

In studies in our own group, and others, the use of homochiral phosphinamides for the asymmetric catalysis of the reduction of ketones by borane has been investigated.[7] This reaction is promoted by the *donation* of electron density from the phosphinamide to borane, thus sharply increasing its reactivity. Our best results were obtained using catalysts of general structure **4** containing a hydroxyl group. It is believed that the hydroxy generates an electron-poor (Lewis acid) catalyst site on the molecule, which forms a bond to the ketone substrate and thus 'locks' it in close proximity to the activated, nearby borane molecule (Fig. 1). In view of this explanation, we felt that the same process could be applied to the control of epoxide opening, *i.e.* to create a 'two-site' bifunctional[8] catalyst in which the epoxide is opened by a Lewis acid and the nucleophilic addition is driven by a Lewis base phosphinamide (Fig. 2).

The bifunctional, combined phosphine oxide.diol catalyst **5**, developed by Shibasaki,[9] has structural similarities to our own, and has been employed successfully for the asymmetric catalysis of hydrocyanation reactions. The related, asymmetric phosphoramides such as **2** act as effective Lewis base catalysts in a number of applications.[10]



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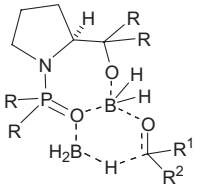


Fig. 1

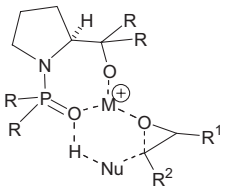
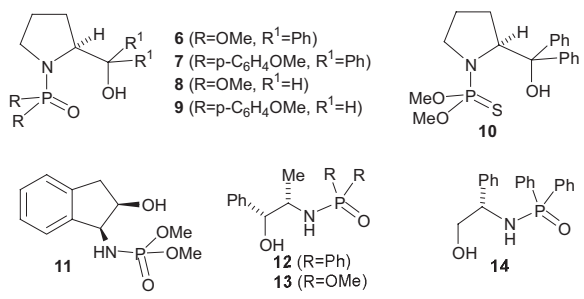


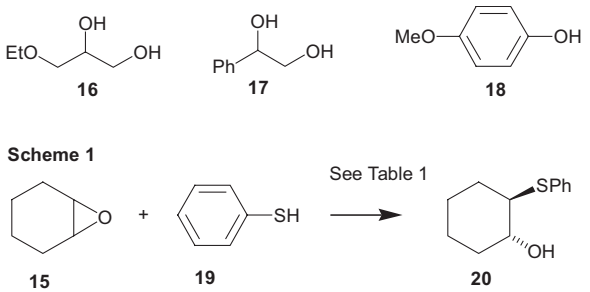
Fig. 2

Results and discussion

We prepared a small series of initial catalyst candidates **6–14**, all derived from amino alcohols. The dimethylphosphoryl derivatives were prepared by direct reaction of the aminoalcohol (O-protection was not generally required) with dimethylphosphite in the presence of carbon tetrachloride. The diarylphosphinamide derivatives were made either from the dimethylphosphoryl precursor or by direct reaction of the amino alcohols with the appropriate diarylphosphoryl choride. In our previous work on borane reductions,[7] we had found that proline-derived amino alcohols were particularly effective, presumably due to their stereochemically well-defined structure. For our initial studies, we therefore included several pyrrolidine ring-containing compounds containing both aminophosphate and phosphinamide groups respectively.

Initially we examined the ring-opening of cyclohexene oxide **15** using alcohol nucleophiles **16–18**, and thiophenol **19**. In these studies, none of the alcohol nucleophiles were able to ring-open the epoxide, using $Ti(OiPr)_4$, $Al(OiPr)_3$, Et_2Zn and $Ln(OTf)_3$. However the more nucleophilic thiophenol was successful in furnishing product **20** and therefore we chose to focus on this reaction in optimisation studies (Scheme 1). Previous examples of asymmetric epoxide opening using





Scheme 1

thiol nucleophiles[2c,6] include those which make use of a zinc tartrate catalyst[6d] and gallium/lithium BINOL derivatives.[2c] Although e.e.s of up to 98% were obtained by Shibasaki,[2c] the reaction most successful when a hindered thiol, such as tBuSH, was employed as the nucleophile.

In initial studies on the epoxide opening shown in Scheme 1, we varied the metal ($Ti(OiPr)_4$, $Al(OiPr)_3$, Me_3Al, $Zn(OtBu)_2$, Et_2Zn and $Ln(OTf)_3$) and the solvent (THF, DCM, Toluene, MeCN). In all cases, the proline-derived ligands **6**–**10** gave products in moderate to good yields with no more than 14% e.e. In the case of the acyclic ligands, only **14** gave promising results. Using 10 mol% of this ligand along with 10 mol% of $AlCl_3$ in DCM resulted in the formation of the product of ring opening in 64% isolated yield and 70% e.e. (Table 1) The choice of Lewis acid was important; using the other metal salts, including $Al(OiPr)_3$, the product was formed with essentially no enantioselectivity. The choice of solvent was also important; in THF under the same conditions, **20** was formed in only 17% e.e., whilst in toluene the product was essentially racemic, although the conversions were good.

We conducted some investigations into the effects of additives, which often have dramatic effects on catalysis. For example, Inanaga[11a] and Shibasaki[11b,c] have both reported that the performance of lanthanum metal catalysts were improved by Ph_3PO and Ph_3AsO respectively. We examined a number of additives (Table 1) and found that the effects were generally moderate, although HMPA did provide a small improvement. We also examined the effect of the mol% of $AlCl_3$ on the reaction, which proved to be highly revealing. At 8 mol%, the e.e. dropped to just 9%, whilst at 12% the e.e. (67%) remained close to that observed at the 10 mol% level. Too much $AlCl_3$ was also detrimental; product being formed in 26% e.e. and 3% e.e. respectively using 15 and 20 mol% metal salt. Figure 3 shows a graphical representation of the variation. Our best result (72% isolated yield, 80% e.e.) was obtained using 12 mol% of both $AlCl_3$ and HMPA with 10 mol% **14**. It therefore appears that the best results are obtained through close matching of the levels of metal and additive. In the absence of aluminium trichloride, essentially no conversion was observed.

At lower temperatures the e.e. surprisingly did not improve and even dropped (to 54%) at –20ºC. The low temperature reaction also revealed an unexpected dependence on the thiophenol for catalyst formation; when the thiophenol was added last to the reaction (after cooling) an essentially racemic product was formed. The speculated importance of the thiophenol to catalyst formation was also supported by the reduction in e.e. to 29% (at rt) when slow, dropwise, addition of thiophenol was carried out (normally this is added rapidly in one portion).

Finally, as a control experiment, the performances of the parent amino alcohols in the reaction were examined under the reaction conditions described in Scheme 1 and Table 1. However, the addition products were essentially racemic (<1% e.e.). Some revealing results were, however, obtained for certain amino alcohols in toluene solvent and $Ti(iPr)_4$. Using 10 mol% of the metal salt and ligand, **20** was formed in 33% and 24% e.e. respectively using diphenylprolinol and *cis*-aminoindanol respectively.

Conclusion

In conclusion, we have demonstrated that enantiomerically pure phosphinamides containing a nearby hydroxyl group are capable of directing the asymmetric nucleophilic ring opening of cyclohexene oxide to give products in up to 80% enantiomeric excess. Extended studies of the reaction revealed a very precise relationship between the choice of solvent, metal salt and mol% of the latter. Of the phosphinylated amino alcohols we examined, one of them, compound **14** gave significantly improved results over the others.

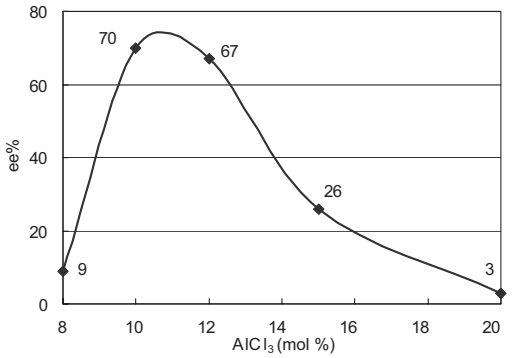


Fig. 3 Effect of mol% of $AlCl_3$ on ee in addition of **19** to cyclohexene oxide.

Table 1 Addition of **19** to cyclohexene oxide (Scheme 1)

Entry	$AlCl_3$/mol%	Solvent	Additive/mol%	t/h	Yield/%	ee/%
1	10	DCM	–	44	64	70
2	10	THF	–	66	91	17
3	10	Toluene	–	66	85	<1
4	10	DCM	Bu_3PO (10)	69	56	63
5	10	DCM	DPPE (10)	4	67	62
6	10	DCM	Et_3N (12)	64	82	56
7	10	DCM	HMPA (10)	44	81	74
8	8	DCM	–	40	12	9
9	12	DCM	–	64	65	67
10	15	DCM	–	40	62	26
11	20	DCM	–	40	52	3
12	0	DCM	–	64	0.6	3.5
13	12	DCM	HMPA (12)	88	72	80

Conditions: 10 mol% ligand **14**, rt.

Experimental

General

The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded at 300, 75 and 121 MHz, respectively, using $CDCl_3$ as a solvent, and are reported in ppm relative to $CHCl_3$ (δ 7.26) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ 77.00) for ^{13}C NMR. Flash chromatography(FC) was carried out with silicagel 60 (230–400 mesh). The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC on a Chiralcel OD 0.46 × 25 cm column, hexane/EtOH = 99/1. All solvents and commercially available chemicals, including amino acid precursors were used as received. Compounds **6, 7** and **10** were prepared as previously described.[7b,12] The characterisations of novel compounds **8**, **9** and **11** must formally be regarded as tentative in the absence of complete data but are well supported by the data that are available.

N-(O,O-dimethylphosphoryl)-(S)-2-pyrrolidine-methanol **(8)**: Carbon tetrachloride (2.42 ml, 25.0 mmol) was added dropwise to an ice-cold stirred solution of (S)-(+)-2-pyrrolidinemethanol (1.02 g, 10.0 mmol), dimethyl phosphite (1.20 ml, 1.00 g, 12.0 mmol) and triethylamine (1.80 ml, 12.0 mmol) in anhydrous DCM (20 ml). The resulting solution was allowed to slowly warm to rt and then stirred for a further 24 h. After this period, the reaction was quenched with water and the organic layer separated. The aqueous layer was extracted with DCM, the combined organic layers were washed with saturated NH_4Cl, water, and then brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography using EtOAc-IPA (4: 1) and then IPA as eluant. This gave **8** (0.51 g, 24%) as a slightly yellow oil: ^{1}H NMR (300 MHz; $CDCl_3$) δ 1.55–1.70 (1H, m), 1.70–2.10 (3H, m), 3.00–3.25 (2H, m), 3.45–3.53 (2H, m), 3.62–3.85 (7H, m), 4.25–4.55 (1H, bs); ^{13}C NMR (75 MHz; $CDCl_3$) δ 27.4 (d, J = 7.9 Hz), 29.7 (d, J = 8.8 Hz), 47.8, 53.3 (d, J = 5.3 Hz), 53.6 (d, J = 5.7 Hz), 61.5, 67.1; ^{31}P NMR (121 MHz; $CDCl_3$) δ 13.8. $[\alpha]_d^{17}$= –29.2 (c 1.1, DCM). *m/z* (EI+) 210 (M+H), 178, 109.

N-(Di-p-Anisylphosphoryl)-(S)-2-pyrrolidine-methanol **(9)**: *p*-Anisylmagnesium bromide 0.5 M in THF (14.7 ml, 7.35 mmol) was added dropwise to a stirred solution of *N*-(*O*,*O*-dimethylphosphoryl)-(*S*)-2-pyrrolidinemethanol **8** (0.35 g, 1.67 mmol) in anhydrous THF (5 ml) at –78°C under a nitrogen atmosphere. The resulting mixture was allowed to slowly warm to rt over a 3 h period and was then heated at 60°C for a further 90 min whereupon the reaction was complete as assayed by thin-layer chromatography. The solution was allowed to cool to rt and diluted with water and the THF removed under reduced pressure. The residue was acidified with saturated NH_4Cl and the aqueous phase extracted with EtOAc. The combined organic layers were washed with water and brine and dried ($MgSO_4$), and the solvent removed under reduced pressure. The residue was purified by column chromatography using EtOAc-IPA (4: 1) This gave **9** (0.61 g, 25%) as a slightly yellow oil. ^{1}H NMR (300 MHz; $CDCl_3$) δ 1.60–1.95 (3H, m), 1.95–2.10 (1H, m), 3.00–3.15 (2H, m), 3.35–3.50 (2H, m), 3.60–3.75 (1H, m), 3.84 (3H, s), 3.88 (3H, s), 5.10–5.20 (1H, bs), 6.85–7.00 (4H, m), 7.40–7.60 (4H, m); ^{13}C NMR (62.9 MHz; $CDCl_3$) δ 25.8 (d, J = 8.3 Hz), 29.9 (d, J = 7.3 Hz) 48.8 (d, J = 3.7 Hz), 55.7, 65.5, 67.5, 114.2 (d, J = 21.4 Hz), 114.6(d, J = 21.4 Hz), 122.5 (d, J = 49.3 Hz), 124.3 (d, J = 50.9 Hz), 134.0 (d, J = 11.1 Hz), 134.5 (d, J = 10.6 Hz), 162.8 (d, J = 3.1 Hz); ^{31}P NMR (162 MHz; $CDCl_3$) δ 28.9. $[\alpha]_D^{17}$= +47.9 (c 1.1, DCM) *m/z* (EI+) 362 (M+H), 330, 261, 178. HR–MS (EI+) found 361.144201, $C_{19}H_{24}NO_4P$ requires 361.144297.

N-(O,O-Dimethylphosphoryl)-(1S,2R)-(-)-cis-amino-2-indanol **(11)**: To a stirred solution of (1*S*,2*R*)-(-)-*cis*-amino-2-indanol (1.0 g, 6.7 mmol) in anhydrous DCM (30 ml) under nitrogen was added triethylamine (1.03 ml, 7.4 mmol) and trimethylsilylchloride (0.94 ml, 7.4 mmol). The resulting mixture was stirred at rt overnight. Then triethylamine (1.12 ml, 8.0 mmol) and dimethylphosphite (0.74 ml, 8.0 mmol) was added to mixture then carbon tetrachloride (1.62 ml, 16.8 mmol) was added dropwise to an ice-cold stirred solution of the resulting mixture. The solution was allowed to slowly warm to rt and then stirred for 6 h. After this period, the reaction was quenched with water and the organic layer separated. [Note; TMS deprotects *in situ*.] The aqueous layer was extracted with DCM, the combined organic layers were washed with saturated NH_4Cl, water, and then brine and dried ($MgSO_4$), and the solvent was removed under reduced pressure. This gave **11** (2.16 g, 98%) as a slightly yellow powder: ^{1}H NMR (300 MHz; CDCN) δ 1.17–1.82 (1H, brs), 2.67 (1H, d, J = 16.2 Hz), 2.87–2.93 (1H, m), 3.58 (6H, two overlapping doublets, J = 11.1, 9.2 Hz), 4.36–4.45 (2H, m), 7.07–7.28 (4H, m); ^{13}C NMR (75 MHz; CDCN) δ –1.2, 39.2, 52.4 (d J = 7.5 Hz), 59.2, 74.9 (d, J = 3.8 Hz), 123.8, 124.6, 126.2, 127.1; ^{31}P NMR (121 MHz; CDCN) δ 12.42. $[\alpha]_D^{17}$ = –15.2 (c 1.2, DCM). *m/z* (EI+), 239 (M–H_2O, 225 (M–MeOH), 130.

N-(Diphenylphosphoryl)-(1R, 2S)-(-)-norephedrine **(12)**:[13] Diphenylphosphinylchloride (0.65 ml, 3.3 mmol) was added dropwise to an ice-cold stirred solution of (1*R*, 2*S*)-(-)-norephedrine (453 mg, 3.0 mmol) and triethylamine (0.84 ml, 6.0 mmol) in anhydrous DCM (5 ml). The resulting solution was allowed to slowly warm to rt and was then stirred for 20 h. After this period, the reaction was quenched with water and the organic layer separated. The aqueous layer was extracted with DCM, the combined organic layers were washed with saturated NH_4Cl, water, and then brine and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified by column chromatography using EtOAc. This gave **12** (0.94 g, 89%) as a white powder: ^{1}H NMR (300 MHz; $CDCl_3$) δ 1.06 (1H, d, J = 6.6 Hz), 3.10–3.50 (2H, m), 4.85 (1H, bs), 5.97 (1H, bs), 7.15–8.00 (15H, m); ^{13}C NMR (75 MHz; $CDCl_3$) δ 18.0 (d, J = 9.0 Hz), 53.7, 76.6, 126.7, 126.9, 127.7, 128.3, 128.4, 128.4, 128.6, 130.0, 131.1, 131.3, 131.5, 131.8, 132.3, 132.4, 132.8, 140.8 (doublets observed, but poorly defined due to overlaps); ^{31}P NMR (121 MHz; $CDCl_3$) δ 26.2.

N-(O,O-Dimethylphosphoryl)-(1R, 2S)-(-)-norephedrine **(13)**:[14] Carbon tetrachloride (0.70 ml, 7.2 mmol) was added dropwise to an ice-cold stirred solution of (1*R*, 2*S*)-(-)-norephedrine (453 mg, 3.0 mmol), dimethylphosphite (0.30 ml, 3.3 mmol), and triethylamine (0.54 ml, 3.9 mmol) in anhydrous DCM (5 ml). The resulting solution was allowed to slowly warm to rt and then stirred for 20 h. After this period, the reaction was quenched with water and the organic layer separated. The aqueous layer was extracted with DCM, the combined organic layers were washed with saturated NH_4Cl, water, brine and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified by column chromatography using EtOAc. This gave **13** (0.29 g, 38%) as a white powder: ^{1}H NMR (300 MHz; $CDCl_3$) δ 0.98 (1H, d, J = 6.6 Hz), 3.30–3.50 (1H, m), 3.67 (6H, 2 overlapping doublets, J = 12.0, 12.5 Hz) 3.70–3.90 (1H, m), 4.30–4.70 (1H, br), 4.83 (1H, d J = 6.6 Hz), 7.15–7.45 (5H, m); ^{13}C NMR (75 MHz; $CDCl_3$) δ 16.3 (d, J = 4.7 Hz), 53.5 (d, J = 5.6 Hz), 53.8, 77.1, 125.9, 126.1, 126.5, 127.5, 128.5, 128.8, 141.9; ^{31}P NMR (121 MHz; $CDCl_3$) δ 12.2.

N-(Diphenylphosphoryl)-(R)-(-)-2-phenylglycinol **(14)**: To a stirred solution of (*R*)-(-)-2-phenylglycinol (824 mg, 6.0 mmol) in anhydrous DCM (20 ml) under nitrogen was added triethylamine (0.92 ml, 6.6 mmol) and trimethylsilylchloride (0.84 ml, 6.6 mmol). The resulting mixture was stirred at rt overnight. Triethylamine (1.68 ml, 12.0 mmol) was added to mixture then diphenylphosphinylchloride (1.30 ml, 6.6 mmol) was added dropwise to an ice-cold stirred solution of the resulting mixture. The solution was allowed to slowly warm to rt and then stirred for 20 h. The reaction was quenched with water and the organic layer separated. The aqueous layer was extracted with DCM, the combined organic layers were washed with saturated NH_4Cl, water, brine, dried ($MgSO_4$), and the solvent was removed under reduced pressure. To a stirred solution of the TMS protected product in MeOH (10–15 ml) was added acetic acid (15–20 drops) and water (5 drops) overnight. After this period, the solvent was removed under reduced pressure. The residue was purified by column chromatography using EtOAc/DCM = 9/1. This gave **14** (1.64 g, 81%) as a white powder: ^{1}H NMR (300 MHz; $CDCl_3$) δ 3.70–4.00 (3H, m), 4.15–4.35 (1H, m), 5.00–5.30 (1H, m), 7.20–7.50 (11H, m), 7.75–7.95 (4H, m); ^{13}C NMR (75 MHz; $CDCl_3$) δ 59.3, 68.8, 126.8, 128.1, 128.9, 129.1, 131.7, 132.0, 132.2, 132.6, 133.1, 133.2, 133.4, 140.8; ^{31}P NMR (121 MHz; $CDCl_3$) δ 28.1. *m/z* (EI +) 338 (M + H), 306, 218, 201, 106 HR-MS (EI +) found 338.131849, $C_{20}H_{21}NO_2P$ requires 338.130993.

General procedure for the catalytic asymmetric epoxide ring opening of cyclohexeneoxide by thiophenol

To a stirred solution of chiral ligand (10 mol%) in the solvents under nitrogen was added the metal salt. The resulting mixture was stirred at rt for 1 h, then cyclohexene oxide and thiophenol (1.2 eq.) were added. The reaction mixture was stirred at rt until it was complete. After this period, the reaction was quenched with water and diluted with hexane then filtered through a Celite pad, washed with brine and dried by $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to furnish the corresponding product **20**: ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.45–7.50 (2H, m), 7.20–7.30 (3H, m), 3.31 (1H, td, J = 9.0, 2.5 Hz), 3.20 (1H, brs), 2.70–2.82 (1H, m), 2.02–2.15 (2H, m),1.68–1.77 (2H, m), 1.05–1.35 (4H,m); ^{13}C NMR (75 MHz; $CDCl_3$) δ 24.2, 25.8, 32.4, 33.7, 55.8, 72.0, 127.4, 128.6, 132.7, 133.4. The conversion was determined either by NMR analysis or by GC using an external

standard. The enantiomeric purity was determined by HPLC analysis using a chiral column (ChiralCel OD, 250 × 4.6 mm, Hexane: EtOAc 99: 1, 0.5 ml/min, retention times 7.08. 8.69 min), whilst the configuration was confirmed by optical rotation comparison with published data.[6c,e]

Optimised reaction conditions for asymmetric epoxide ring opening of cyclohexeneoxide by thiophenol

To a stirred solution of **14** (33.7 mg, 0.1 mmol) in anhydrous DCM (2.0 ml) under nitrogen was added $AlCl_3$ (16.0 mg, 0.12 mmol) and hexamethylphosphoramide (21.0µl, 0.12 mmol). The resulting mixture was stirred at rt for 3.5 h, then cyclohexene oxide (101.2 µl, 1.0 mmol) and thiophenol (0.5 ml: 2.4 M in DCM, 1.2 mmol) were added. The reaction mixture was stirred at rt for 88 h, After this period, the reaction was quenched with water and diluted hexane and filtered through a celite pad, and washed with brine and dried by $MgSO_4$. The solvent was removed under reduced pressure to give crude product **20** which was purified by flash chromagraphy on silica gel. The enantiomeric purity was determined by HPLC analysis as described above (80.0% *e.e.,* 72% yield).

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