Tetrahedron 67 (2011) 4378–4384

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of C_3- and C_2-symmetric tris- and bis-sulfoxide ligands by asymmetric oxidation

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ARTICLE INFO

Article history:
Received 13 December 2010
Received in revised form 2 February 2011
Accepted 9 February 2011
Available online 3 March 2011

Keywords:
Sulfoxide
Tridentate ligand
Asymmetric oxidation
1,4-Addition
Hydroacylation

ABSTRACT

A series of tris- and bis-sulfoxides were synthesized by multiple asymmetric oxidation of the corresponding sulfides. High enantioselectivities were obtained based on Horeau-type amplification of selectivity. Naphthyl-substituted sulfoxides allowed for higher selectivity and greater ease of purification. These sulfoxides were tested as ligands in rhodium-catalyzed olefin hydroacylation and 1,4-addition of phenyl boronic acid to 2-cyclohexen-1-one. While no enantioinduction was observed in hydroacylation, up to 80% ee was obtained for a tris-sulfoxide and a bis-sulfoxide ligand in the 1,4-addition. Bis-sulfoxides with flexible backbones gave lower and inversed enantioselectivity, suggesting backbone rigidity plays a key role in enantioinduction.

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1. Introduction

Incorporating symmetry in the design of chiral ligands has resulted in a large number of privileged ligand architectures for asymmetric catalysis.[1] While C_2 symmetry has dominated the field, there is growing evidence that C_3-symmetric ligands can favorably decrease the number of possible stereoisomeric intermediates/transition states in octahedral environments.[2–4] The synthesis of C_3-symmetric chiral ligands is challenging due to the scarcity of chiral C_3-symmetric scaffolds on which to build ligands. Herein, we present the design and synthesis of C_3-symmetric tripodal sulfoxide ligands and a series of related C_2-symmetric sulfoxide ligands. In initial studies, we tested these ligands in rhodium-catalyzed hydroacylation and conjugate addition reactions. Although enantioinduction was not observed for hydroacylation, these novel ligands promote conjugate addition with good levels of enantiocontrol (up to 80% ee).

Sulfoxide ligands[5] are increasingly attractive targets in asymmetric transition metal catalysis. Early work in this field demonstrated modest levels of enantioselectivity in hydrogenation,[6] Diels–Alder,[7] and allylic substitution[8,9] reactions. Recently, Dorta,[10,11] Liao,[12] and Li[13] have shown that bis-sulfoxide ligands can induce excellent levels of enantioselectivity in 1,4-additions of aryl boronic acids to α,β-unsaturated ketones. It has been proposed that a favorable interaction between the substrate and the oxygen of the sulfoxide leads to high levels of enantioselectivity.[11] White has used bis-sulfoxide ligands in palladium-catalyzed allylic C–H activation.[14] Moreover, our group has shown that sulfoxides are excellent directing groups in diastereoselective rhodium-catalyzed intramolecular olefin hydroacylation (Fig. 1).[15]

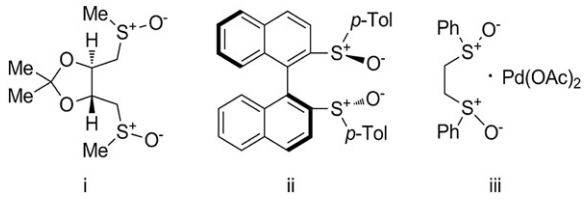

Fig. 1. Representative bis-sulfoxide ligands; (i) James' dios ligand for asymmetric olefin hydrogenation[6] (ii) Dorta's *p*-tol-BINASO ligand for asymmetric 1,4-additions of aryl boronic acids[10] (iii) White's palladium bis-sulfoxide catalyst for allylic C–H activation.[14]

A common strategy for the synthesis of chiral bis-sulfoxides is the nucleophilic substitution of chiral sulfinate esters with organometallic reagents.[16] Licini[17] and Siedlecka[18] have reported, however, promising results in the synthesis of chiral bis-sulfoxides via double catalytic asymmetric oxidation of the corresponding bis-sulfide. In this approach, only a catalytic amount of chiral material is needed and Horeau-type[19] amplification of enantioselectivity can in principle give highly enantioenriched material.

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doi:10.1016/j.tet.2011.02.023

In considering possible designs for a C_3-symmetric chiral ligand, we imagined using sulfoxides as a simple way to incorporate chirality into a tripodal scaffold (Fig. 2). An alkylation of commercially available trichloride **3** followed by a triple asymmetric oxidation would provide the chiral C_3-symmetric tris-sulfoxide. Together with the growing utility of sulfoxide ligands in transition metal catalysis, this ligand could have multiple applications. This synthetic strategy can also be applied to the synthesis of analogous bis-sulfoxides in order to probe the effect of the third arm of the ligand.

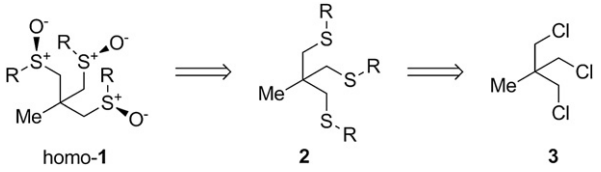


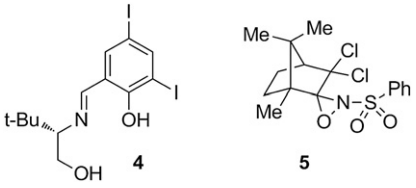
Fig. 2. Retrosynthesis of tris-sulfoxide **1**.

2. Results and discussion

2.1. Design and synthesis of a C_3-symmetric ligand

Enhancing enantiomeric excess by preparing and then separating diastereomeric mixtures was first demonstrated by Horeau in 1973.[19] Inspired by this concept, we postulated that upon asymmetric oxidation of tris-sulfide **2**, the formation of three chiral centers would lead to significant enhancements of enantioselectivity with respect to the enantioselectivity of a single oxidation. The resulting homochiral diastereomer (*RRR* and *SSS*) could then be separated from the undesired heterochiral diastereomer (*RRS* and *SSR*), and material resulting from undesired catalyst selectivity could be removed by chromatography.

We prepared a series of tridentate sulfoxides with various substituents (Table 1). These ligands varied in their ease of isolation and scalability. We began our studies by examining the oxidation of phenyl tris-sulfide **2a** (readily available by alkylation of the corresponding trichloride with thiophenol, see Supplementary data). With an achiral oxidant, and assuming each oxidation is independent, one would expect the statistical diastereomeric ratio to be 1:3 homo/hetero. Using *m*CPBA as the oxidant, a dr of 1:2.5 homo/hetero was observed (Table 1, entry 1). This diastereoselectivity validates the independent nature of the oxidations because the stereochemistry of a sulfoxide in an intermediate does not significantly influence the stereochemical outcome of the next sulfide oxidation. Next, we applied Jackson's sulfide oxidation catalyst using ligand **4** derived from *tert*-leucinol and 3,5-diiodosalicylaldehyde.[20,21] We were pleased to find that this asymmetric oxidation system reversed the dr to 1.8:1 with the major homo diastereomer being formed in 94% ee. Under the assumption of an independent oxidation mechanism, 94% ee would be obtained with a dr of 0.8:1 homo/hetero. The deviation from this dr indicates a small amount of substrate control in subsequent oxidations, however the oxidation is still largely catalyst controlled (see Supplementary data for details). Unfortunately, the separation of the diastereomers was not possible on large scale. Furthermore, the product was a viscous liquid and recrystallization was not an option to further upgrade the optical purity.



The oxidation of cyclohexyl tris-sulfide **2b** (Table 1, entry 2) was poorly enantioselective (32% ee), despite non-statistical diastereoselectivity (1.8:1 homo/hetero). The Davis oxaziridine **5** is known to give high levels of enantioselectivity for certain dialkyl sulfides, which are typically problematic substrates for asymmetric sulfide oxidation.[22,23] Only a modest improvement in enantioselectivity was observed in this case (35% ee).

Next we examined naphthyl substituents in the synthesis of tris-sulfoxides. Both 1-naphthyl and 2-naphthyl derivatives (**2c** and **2d**) gave high levels of enantioselectivity (97% and 99% ee, respectively) with good dr (3.1:1 homo/hetero in both cases). Moreover, both products were isolable by column chromatography and could be obtained in 40–60% yield. The synthesis requires only two steps, with the first being a high yielding alkylation (>90%), and thus represents a practical synthesis of a C_3-symmetric chiral ligand. A single crystal of **1c** suitable for X-ray diffraction confirmed the (*S*) absolute stereochemistry of the sulfoxides in accordance with literature precedence for asymmetric oxidation of alkyl aryl sulfides (Fig. 3).[20] The naphthyl based ligands **1c** and **1d** thus resulted in the most scalable ligand synthesis.

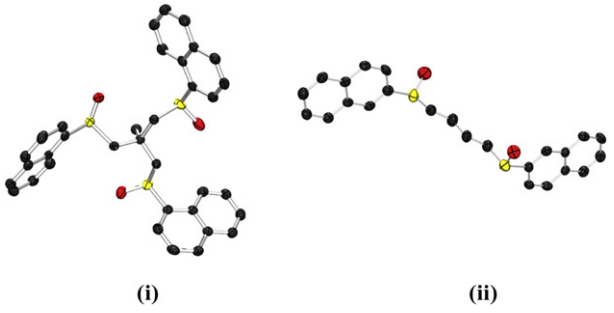
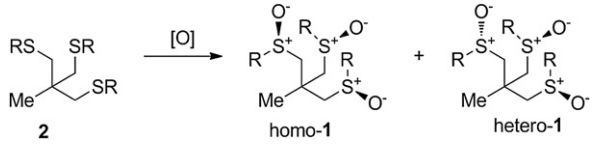


Fig. 3. (i) Molecular structure of **1c**. (ii). Molecular structure of **7d**. The thermal ellipsoids are drawn at the 50% probability level.

Table 1
Synthesis of tris-sulfoxides by triple oxidation of tris-sulfides



Entry	R	1	Yield homo-**1** (%)	dr[a]	ee (%)
1	Ph	**1a**	21	1.8:1 (1:2.5)	94
2	Cy	**1b**	44[b]	1.8:1 (1:2.6)	32[b]
3[c]	Cy	**1b**	76[d]	3.7:1 (1:2.6)	35
4	1-Nap	**1c**	40	3.7:1 (1:1.8)	97
5	2-Nap	**1d**	60	3.1:1 (1:2.5)	99

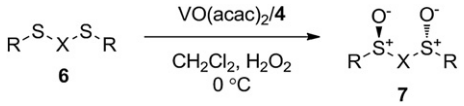
[a] Homo-**3**:hetero-**3**, dr with *m*CPBA in parentheses.
[b] See Section 4.3.2.2.
[c] Using **5** as oxidant.
[d] Mixture of diastereomers.

2.2. C_2-Symmetric bis-sulfoxide ligands

In addition to the C_3-symmetric tris-sulfoxides, we decided to investigate C_2-symmetric bis-sulfoxides to compare their efficiencies and selectivities as ligands. Because the third sulfoxide arm and the methyl group in ligands **1a** and **1b** reduce the flexibility of the three-carbon backbone linker between the sulfoxides, a ligand was devised to have a similar rigidity, in order to make a direct comparison between the tris-sulfoxide and bis-sulfoxide series. Ligand

7a, which contains a quaternary carbon center, was synthesized in an analogous fashion to **1a**. The enantiomeric excess of the reaction mixture in this double asymmetric oxidation was 95% (Table 2, **7a**), which is slightly less than for the single asymmetric oxidation of 2-naphthylmethylsulfide (98% ee, under identical oxidation conditions). This decrease in stereoselectivity is likely due to the presence of the quaternary carbon center, which increases the steric bulk of the alkyl side. Column chromatography was successful in separating the diastereomers, and one recrystallization resulted in an upgrade of the enantiomeric excess from 95% to >99% ee, but a modest overall yield (38%).

Table 2
Synthesis of bis-sulfoxides by double oxidation of bis-ssulfides



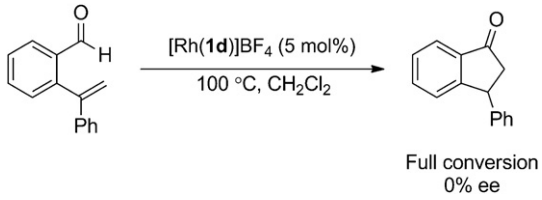
Entry	R	X	7	Yield homo-7 (%)	dr[a,b]	ee[b] (%)
1	2-Nap	$CH_2C(Me)_2CH_2$	**7a**	38	9.8:1 (1:1.8)	95
2	Ph	CH_2CH_2	**7b**	9	5.2:1 (1:4.0)	99
3	2-Nap	$(CH_2)_3$	**7c**	12	4.0:1 (1:1.2)	98
4	2-Nap	$(CH_2)_4$	**7d**	49	4.6:1 (1:1.0)	98
5	2-Nap	$(CH_2)_5$	**7e**	22	4.3:1 (1:1.0)	98

[a] Homo-**7**:hetero-**7**, dr with *m*CPBA in parentheses.
[b] Stereoselectivities are reported for the crude material—purification by column chromatography and recrystallization yielded enantio- and diastereo-pure material.

To probe the effect of backbone flexibility, ligands with linear alkane backbones were synthesized (Table 2, **7b**–**e**). While the ligands were all obtained in high enantioselectivities (98–99% ee), they varied significantly in their ease of isolation. Diastereomers were not separable by column chromatography: two recrystallizations were generally necessary to obtain diastereomerically pure ligand. Because the *meso* diastereomers tended to crystallize more easily than the desired homo diastereomer, low mass recovery of the desired diastereomer was obtained. A single crystal of **7d** suitable for X-ray diffraction confirmed the (*S*) absolute stereochemistry of the sulfoxide, which matches the stereochemistry of **1c** (Fig. 3). Therefore, the asymmetric oxidation occurs with the same sense of enantioinduction for the tris-sulfoxides and bis-sulfoxides.

2.3. Sulfoxide ligands in catalysis

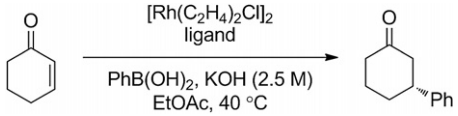
Tris-sulfoxide **1d** and bis-sulfoxide **7d** were tested in the rhodium-catalyzed intramolecular hydroacylation of 2-(1-phenylvinyl) benzaldehyde (Scheme 1). Morehead has previously reported that using 2 mol % [Rh((*R*)-BINAP)]ClO_4 in dichloromethane at room temperature, a 98% yield of the indanone product could be obtained in 98% ee.[24] Both ligands resulted in full conversion to the desired hydroacylation product after 20 h, with no decarbonylation. However, no enantioenrichment of the products could be detected.



Scheme 1. Intramolecular olefin hydroacylation with tris-sulfoxide **1d**.

We next examined the rhodium-catalyzed 1,4-addition of phenyl boronic acid to 2-cyclohexen-1-one. While ligand **1d** was able to achieve product in 80% ee and 72% yield, ligand **1c** gave only 50% ee and low yield (15%) (Table 3, entries 1 and 2), despite possessing a bulkier aryl group on the sulfoxide. Perhaps steric clash between arms of the ligand in **1c** contributed to an unfavorable coordination geometry. Ligand **7a**, which was designed to have a similar backbone rigidity to **1d**, gave identical enantioselectivity to **1d**. This result supports the idea that the third arm of the tris-sulfoxide ligand is a spectator in this particular reaction. Ligands **7b**–**e** provided lower levels of enantioselectivity (0–43% ee), however, there was a reversal of the observed sense of enantioinduction despite having the same sulfoxide configuration. Moreover, the enantioselectivity increased as the bite angle increased. The reason for this inversion of selectivity is not known at present, however, we speculate that flexibility in the backbone might lead to alternative coordination geometries (O- vs S-binding).

Table 3
Rhodium-catalyzed 1,4-addition reaction[a]



Entry	Ligand	Time	Yield (%)	ee (%)
1	**1c**	24	15	50
2	**1d**	24	72	80
3	**7a**	18	89	80
4	**7b**	18	82	0
5	**7c**	18	66	−20
6	**7d**	18	35	−31
7	**7e**	18	15	−43

[a] Conditions: 2-cyclohexen-1-one (1.0 equiv), phenyl boronic acid (4 equiv), $[Rh(C_2H_4)_2Cl]_2$ (1.5 mol %), ligand (3.6 mol %), KOH (2.5 M, 50 mol %), EtOAc, 40 °C.

3. Conclusion

In summary, a series of chiral tridentate and bidentate sulfoxide ligands have been synthesized by multiple asymmetric oxidation. The synthesis of naphthyl tris-sulfoxides was particularly efficient due to the high intrinsic enantioselectivity of the oxidation and the ease of separating the resulting diastereomers by column chromatography. The ligands were tested in a rhodium-catalyzed intramolecular olefin hydroacylation and a rhodium-catalyzed 1,4-addition of phenyl boronic acid to 2-cyclohexen-1-one. No enantioselectivity was observed in hydroacylation. On the other hand, ligands **1d** and **7a** provided good levels of enantioinduction (80% ee) in the 1,4-addition. An interesting reversal of enantioinduction in the 1,4-addition was observed in the case of flexible bis-sulfoxides. Future work in this area will include exploring the use of these readily available sulfoxide ligands for other catalytic applications.

4. Experimental section

4.1. General considerations

Commercial reagents were purchased from Sigma–Aldrich, Strem or Alfa Aesar and used without further purification. All reactions were carried out under an argon atmosphere unless otherwise indicated. Reactions were monitored using thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates and a Waters 2795 LC–MS. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300, Varian Mercury 400, VRX-S (Unity) 400, or Bruker AV-III 400 spectrometer. NMR spectra were internally referenced to the residual solvent signal or TMS. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s=singlet, d=doublet,

t=triplet, q=quartet, m=multiplet, br=broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm).

High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI). Infrared (IR) spectra were obtained on a Perkin–Elmer Spectrum 1000 FT-IR Systems and are reported in wavenumber (cm^{-1}). Melting point ranges were determined on a Fisher-Johns Melting Point Apparatus. Enantiomeric excesses (ee's) were ascertained on an Agilent 1100 Series HPLC. Diastereomeric ratios were determined by integration of crude ^1H NMR spectra. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Automatic Polarimeter. Column chromatography was performed with Silicycle Silia-P Flash Silica Gel, using either glass columns or a Biotage SP-1 system. All salts were purchased from Aldrich and used without purification. Solvents were purchased from Caledon and were purified according to standard procedures.

4.2. Synthesis of sulfides

4.2.1. General procedure for synthesis of tris-sulfides. Sodium hydride (6 equiv, 60% dispersion in oil) and sodium iodide (1 equiv) were dissolved in N,*N*-dimethylformamide (0.1 M) in a flame dried round bottom flask. The appropriate thiol (6 equiv) was added dropwise, followed by 2,2,2-tris(chloromethyl)-ethane (1 equiv). The mixture was stirred at 100 °C for 24 h. The crude mixture was diluted with ethyl acetate, washed twice with 1:1 1 M NaOH/brine and the combined organic extracts were dried over Na_2SO_4. The solvent was removed in vacuo. The tris-sulfide product was purified as described below for each entry.

4.2.1.1. 2,2,2-Tris((phenylthio)methyl)-ethane ***2a***. Prepared according to the general procedure for tris-sulfides. The product was isolated as a clear oil (480 mg, 95%) by column chromatography eluting with 2–5% ethyl acetate in hexanes (R_f=0.5 in 5% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (s, 3H), 3.17 (s, 6H), 7.15 (t, J=7.2 Hz, 3H), 7.24 (t, J=7.4 Hz, 6H), 7.33 (d, J=8.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 41.5, 43.6, 126.1, 128.9, 129.7, 137.0; IR (neat): 2961, 1582, 1479, 1438, 1088, 1024, 733, 688 cm^{-1}; HRMS (EI) calcd for $[C_{23}H_{24}S_3]^+$ 396.1040, found 396.1039.

4.2.1.2. 2,2,2-Tris((cyclohexylthio)methyl)-ethane ***2b***. Prepared according to the general procedure for tris-sulfides. The product was isolated as a clear oil (1.1 g, 93%) by column chromatography eluting with 5% ethyl acetate in hexanes (R_f=0.9 in 10% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 3H), 1.20–1.37 (m, 15H), 1.56–1.64 (m, 3H), 1.71–1.79 (m, 6H), 1.93–2.02 (m, 6H), 2.58–2.66 (m, 3H), 2.66 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 24.3, 26.2, 26.3, 34.3, 40.1, 40.1, 45.3; IR (neat): 2924, 2850, 1447, 1262, 1200, 999 cm^{-1}; HRMS (EI) calcd for $[C_{23}H_{42}S_3]^+$ 414.2449, found 414.2443.

4.2.1.3. 2,2,2-Tris((2-naphthylthio)methyl)-ethane ***2d***. Prepared according to the general procedure for tris-sulfides. Upon addition of 1:1 diethyl ether/acetone to the crude concentrated mixture after aqueous workup, a white solid precipitated. This solid was isolated by filtration and washed with diethyl ether to yield the product as a white solid (2.83 g, 91%); mp 89–92 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 3H), 3.33 (s, 6H), 7.35–7.44 (m, 9H), 7.53–7.58 (m, 3H), 7.62–7.67 (m, 6H), 7.70–7.74 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 41.8, 43.4, 125.6, 126.4, 127.0, 127.3, 127.6, 127.6, 128.3, 131.7, 133.6, 134.3; IR (neat): 3054, 1584, 1499, 1131, 1071, 808, 734 cm^{-1}; HRMS (EI) calcd for $[C_{35}H_{30}S_3]^+$ 546.1510, found 546.1489.

4.2.2. General procedure for synthesis of bis-sulfides. To a stirred solution of diol (19.7 mmol) in CH_2Cl_2 in a water bath at room temperature were added triethylamine (59.1 mmol, 5.98 g, 8.24 mL) and methanesulfonyl chloride (49.3 mmol, 5.64 g, 3.84 mL). The cloudy red solution was stirred for 12 h, then quenched with aqueous 1 M HCl (20 mL). The aqueous phase was extracted twice with CH_2Cl_2 (50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to yield the bismesylate, which was used without further purification. To a solution of the bismesylate (4.07 mmol) in acetone (20 mL) were added 2-thionaphthol (9.36 mmol, 1.5 g) and potassium carbonate (12.2 mmol, 1.7 g). The resulting thick slurry was stirred for 12 h at room temperature. The crude mixture was then diluted with ethyl acetate (50 mL) and the organic extracts were washed with aqueous 1 M NaOH (20 mL) and brine (2×20 mL). The organic phase was dried over Na_2SO_4 and concentrated to dryness. The resulting solid was triturated with ether (2×5 mL) to yield the title compound as a white solid.

4.2.2.1. 1,3-Bis(naphthalen-2-ylthio)propane ***6c***. Prepared according to the general procedure for bis-sulfides. Propane-1,3-diol bismethanesulfonate was synthesized from propane-1,3-diol to yield a red oil (4.05 g, 88%). Alkylation then yielded the title compound as a white solid (1.06 g, 72%); mp 85–88 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.06 (quint, J=7.0 Hz, 2H), 3.18 (t, J=7.0 Hz, 4H), 7.37–7.47 (m, 6H), 7.64–7.79 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 32.3, 125.7, 126.5, 127.0, 127.2, 127.4, 127.7, 128.4, 131.8, 133.5, 133.7; IR (neat): 1499, 1133, 1071, 852, 816, 737 cm^{-1}; HRMS (EI) calcd for $[C_{23}H_{20}S_2]^+$ 360.1006, found 360.1010.

4.2.2.2. 1,4-Bis(naphthalen-2-ylthio)butane ***6d***. Prepared according to the general procedure for bis-sulfides. Butane-1,4-diol bismethanesulfonate was prepared from butanediol to yield a brown solid (2.57 g, 55%). Alkylation then provided the title compound as a white solid (945 mg, 70%); mp 168–170 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 1.85–1.95 (m, 4H), 3.01–3.07 (m, 4H), 7.38–7.49 (m, 6H), 7.70–7.80 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1, 33.1, 125.6, 126.5, 126.9, 127.0, 127.4, 127.7, 128.4, 131.7, 133.8, 144.6; IR (neat): 2931, 1584, 1498, 1453, 1129, 1068, 849, 812, 737 cm^{-1}; HRMS (EI) calcd for $[C_{24}H_{22}S_2]^+$ 374.1163, found 374.1160.

4.2.2.3. (2,2-Dimethylpropane-1,3-diyl)bis(naphthalen-2-ylsulfane) ***6a***. To a solution of 2,2-dimethyl-1,3-propanediol (29 mmol, 3.0 g) in CH_2Cl_2 (25 mL) were added pyridine (4 mL) and toluenesulfonyl chloride (72 mmol, 13.7 g). The mixture was stirred at room temperature for 24 h. Another 5.5 g (29 mmol) of tosyl chloride was added and the reaction was stirred for another 24 h. The crude mixture was diluted with ethyl acetate (75 mL) and washed with aqueous 1 M HCl (2×20 mL), and brine (20 mL). The organic phase was dried over Na_2SO_4 and concentrated to dryness. 2,2-dimethyl-1,3-propanediol bistosylate was isolated by column chromatography eluting with 30% ethyl acetate in hexanes as a white solid (3.15 g, 26%). To a flame dried round bottom flask were added NaH (60% dispersion in mineral oil) (8 mmol, 321 mg) and NaI (1.6 mmol, 242 mg). A solution of 2-thionaphthol (7.3 mmol, 1.17 g) in DMF (20 mL) was then added, followed by 2,2-dimethyl-1,3-propanediol bistosylate (2.4 mmol, 1.0 g). The mixture was stirred at 100 °C for 24 h. The crude mixture was diluted with ethyl acetate (100 mL) and washed with aqueous 1 M NaOH (20 mL). The organic phase was then washed with brine (20 mL), and the aqueous phase was extracted with ethyl acetate (40 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated to dryness. The product was purified by column chromatography eluting with 0–10% ethyl acetate in hexanes to yield a white solid (733 mg, 79%); mp 79–81 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 6H), 3.18 (s, 4H), 7.36–7.46 (m, 6H), 7.60–7.76 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 26.9, 37.2, 45.7, 125.5, 126.4, 126.8, 127.0, 127.5, 127.6, 128.3, 131.6, 133.7, 135.0; IR (neat): 1587, 1132, 1072, 846, 820, 812, 737 cm^{-1}; HRMS (EI) calcd for $[C_{25}H_{24}S_2]^+$ 388.1319, found 388.1329.

4.3. Synthesis of sulfoxides

4.3.1. General procedure for racemic oxidation for the development of chiral assays. Sulfide (1 equiv) was dissolved in CH_2Cl_2 (1 M) and the solution was cooled to 0 °C. *m*CPBA (3.05 equiv for tris-sulfides, 2.05 equiv for bis-sulfides; 74% by weight) was then added, and the reaction mixture was stirred at 0 °C for 30 min. The crude mixture was poured into brine and aqueous 1 M NaOH was added to basify. This mixture was extracted twice with CH_2Cl_2 and the organic extracts were dried over Na_2SO_4. The solvent was removed in vacuo. The homochiral diastereomer was isolated by preparative TLC. For ligands **7b**–**e**, the *meso* diastereomer could not be removed by chromatography, but separation was achieved during HPLC analysis.

4.3.2. General procedure for asymmetric oxidation. Ligand **4** (8 mol % for tris-sulfides, 5 mol % for bis-sulfides; synthesized according to Pelotier[20]), was dissolved in one third of total volume CH_2Cl_2 to give a yellow solution. $VO(acac)_2$ (4 mol % for tris-sulfides, 2.5 mol % for bis-sulfides) was dissolved in another equal portion of CH_2Cl_2, and this solution was added to the first solution. The mixture was initially greenish-blue, and after stirring at room temperature for 30 min, the solution turned green-brown. The tris-sulfide (1 equiv, 0.17 M final concentration) was added in the final portion of CH_2Cl_2, and this was stirred at room temperature for 30 min. The reaction mixture was then cooled to 0 °C and 30% H_2O_2 was added dropwise (3.2 equiv for tris-sulfides, 2.4 equiv for bis-sulfides). The reaction mixture was stirred at 0 °C until the first appearance of over-oxidation as judged by LC–MS analysis. The reaction mixture was quenched by addition of sodium thiosulfate, and extracted twice with CH_2Cl_2. The organic layer was dried over Na_2SO_4, and the solvent was removed in vacuo.

4.3.2.1. 2,2,2-Tris((phenylsulfinyl)methyl)-ethane ***1a***. Synthesized according to the general procedure for asymmetric oxidation (reaction time: 3 h, 0.151 mmol tris-sulfide). The product was isolated by column chromatography (90% ethyl acetate in hexanes) to give a viscous semi-solid (14 mg, 21%). ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 3.14 (d, *J*=14.0 Hz, 3H), 3.53 (d, *J*=14.0 Hz, 3H), 7.47–7.56 (m, 9H), 7.72 (dd, *J*=8.0, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 39.5, 67.5, 124.1, 129.5, 131.2, 143.9; IR (neat): 3056, 2912, 1477, 1443, 1084, 1032, 998, 748, 688 cm^{-1}; MS (ESI^+) calcd for $[C_{23}H_{24}O_3S_3H]^+$ 445.10, found 445.32. $[\alpha]_{D^{25}}$ −237 (*c* 0.42, $CHCl_3$). HPLC analysis: 94% ee (OD-H, 1:9 isopropanol/hexanes, 1 mL/min, 254 nm, t_{R1}=34.3 min, t_{R2}=41.9 min).

4.3.2.2. 2,2,2-Tris((cyclohexylsulfinyl)methyl)-ethane ***1b***. Synthesized according to the general procedure for asymmetric oxidation (reaction time: 2.3 h, 0.723 mmol tris-sulfide). A small aliquot of the crude material was purified by preparative TLC (8% MeOH in CH_2Cl_2) to give material with 32% ee. The remaining crude material was purified by recrystallization from ethyl acetate/methanol. The resulting crystals were washed three times with cold ethyl acetate and dried under vacuum to give light pink crystals (148 mg, 44%) of low optical purity (5% ee). Mp 189–191 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 1.20–1.50 (m, 15H), 1.69 (d, *J*=11.1 Hz, 3H), 1.81 (s, 3H), 1.82–1.95 (m, 9H), 2.11 (*t*, *J*=13.5 Hz, 3H), 2.60 (tt, *J*=11.6 Hz, 3.4 Hz, 3H), 2.81 (d, *J*=13.9 Hz, 3H), 3.54 (d, *J*=13.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 24.7, 25.1, 25.4, 25.4, 26.5, 38.2, 59.4, 60.2; IR (neat): 2935, 2854, 1441, 1398, 1070, 1023, 996 cm^{-1}; HRMS (ESI^+) calcd for $[C_{23}H_{42}O_3S_3H]^+$ 463.2368, found 463.2351. $[\alpha]_{D^{25}}$ −2.9 (*c* 1.3, $CHCl_3$, 32% ee). HPLC analysis: 32% ee (OD-H, 6% isopropanol in hexanes, 1 mL/min, 210 nm, t_{R1}=19.0 min, t_{R2}=24.0 min).

4.3.2.3. 2,2,2-Tris((1-naphthylsulfinyl)methyl)-ethane ***1c***. 2,2,2-Tris((1-naphthylthio)methyl)-ethane was synthesized according to general procedure for the synthesis of tris-sulfides (reaction time: 2.5 days, 0.78 mmol 2,2,2-tris(chloromethyl)-ethane). Purification was difficult, therefore the crude material was subjected to asymmetric oxidation directly according to the general procedure for asymmetric oxidation (reaction time: 6 h, 287 mg crude, 0.535 mmol (assuming pure tris-sulfide)). The product was isolated by column chromatography (60% ethyl acetate in hexanes) to give a white solid (110 mg, 35% over two steps). A single crystal suitable for X-ray diffraction was grown by slow evaporation from a solution of 60% ethyl acetate in hexanes. Mp 190 °C (decomposed). ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.36 (d, *J*=14.0 Hz, 3H), 3.75 (d, *J*=14.0 Hz, 3H), 7.66–7.56 (m, 9H), 7.95 (d, *J*=8.3Hz, 3H), 7.97 (d, *J*=8.2 Hz, 3H), 8.09 (d, *J*=8.4 Hz, 3H), 8.14 (d, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 40.4, 65.2, 121.9, 123.7, 126.0, 127.1, 127.9, 128.8, 129.3, 131.8, 133.8, 140.1; IR (neat): 3049, 2955, 1503, 1379, 1045, 808, 772, 743 cm^{-1}; HRMS (ESI^+) calcd for $[C_{35}H_{30}S_3O_3H]^+$ 595.1429, found 595.1406. $[\alpha]_{D^{25}}$ −783 (*c* 0.24, $CHCl_3$). HPLC analysis: 97% ee (AD-H, 4:6 isopropanol/hexanes, 1 mL/min, 254 nm, t_{R1}=17.5 min (minor, *R*), t_{R2}=41.9 min (major, *S*)).

4.3.2.4. 2,2,2-Tris((2-naphthylsulfinyl)methyl)-ethane ***1d***. Synthesized according to the general procedure for asymmetric oxidation (reaction time: 3 h, 1.41 mmol tris-sulfide). The product was isolated by column chromatography (65% ethyl acetate in hexanes) to give a white solid (500 mg, 60%); mp 87–90 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 3.21 (d, *J*=14.0 Hz, 3H), 3.71 (d, *J*=13.9 Hz, 3H), 7.55–7.63 (m, 6H), 7.74 (dd, *J*=8.6, 1.8 Hz, 3H), 7.89–7.95 (m, 6H), 8.00 (d, *J*=8.6 Hz, 3H), 8.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.3, 39.6, 67.5, 120.0, 124.6, 127.3, 127.9, 128.0, 128.6, 129.8, 132.9, 134.5, 140.9; IR (neat): 2957, 1714, 1504, 1345, 1066, 1032, 812, 744 cm^{-1}; HRMS (ESI^+) calcd for $[C_{35}H_{30}S_3O_3H]^+$ 595.1429, found 595.1434. $[\alpha]_{D^{25}}$ −383 (*c* 1.1, $CHCl_3$). HPLC analysis: 99% ee (AD-H, 4:6 isopropanol/hexanes, 1 mL/min, 254 nm, t_{R1}=49.8 min (minor), t_{R2}=54.1 min (major)).

4.3.2.5. 2,2′-(2,2-Dimethylpropane-1,3-diyldisulfinyl)dinaphthalene ***7a***. The title compound was prepared according to the general procedure for asymmetric oxidation (reaction time: 6 h, 2.78 mmol bis-sulfide) to give a white solid. This solid was purified by column chromatography (65% ethyl acetate in hexanes) and then recrystallized from boiling ethyl acetate to give a white solid (441 mg, 38%); mp 155–157 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 6H), 3.06 (d, *J*=13.9 Hz, 2H), 3.12 (d, *J*=13.9 Hz, 2H), 7.56–7.62 (m, 4H), 7.64 (dd, *J*=8.6, 1.8 Hz, 2H), 7.89–7.96 (m, 4H), 7.99 (d, *J*=8.7 Hz, 2H), 8.24 (d, *J*=1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 36.0, 70.3, 119.9, 124.4, 127.3, 127.8, 128.0, 128.5, 129.6, 133.0, 134.4, 141.7; IR (neat): 1503, 1061, 1033, 812, 744 cm^{-1}; HRMS (ESI^+) calcd for $[C_{25}H_{24}O_2S_2+H]^+$ 421.1290, found 421.1293. $[\alpha]_{D^{25}}$ −270 (*c* 1.1, $CHCl_3$). HPLC analysis: >99% ee (AD-H, 4:6 isopropanol/hexanes, 1 mL/min, 254 nm, t_{R1}=13.2 min (minor), t_{R2}=24.1 min (major)).

4.3.2.6. 1,3-Bis(phenyl-2-sulfinyl)ethane ***7b***. The title compound was prepared from 1,2-bis(thiophenyl)ethane according to the general procedure for asymmetric oxidation (reaction time: 3 h, 1.62 mmol bis-sulfide; one extra equivalent of H_2O_2 (0.98 mmol) was added after 2 h) to give a white solid. This solid was purified by column chromatography (90% ethyl acetate in hexanes) and then twice recrystallized from boiling acetone to give a crystalline white solid (41 mg, 9%). This compound has been synthesized previously.[18,25] Spectral data are in agreement with the literature. HPLC analysis: >99% ee (AD-H, 4:6 isopropanol/hexanes, 1 mL/min, 233 nm, t_{R1}=6.4 min (major), t_{R2}=7.2 min (*meso*), t_{R3}=8.1 min (minor)).

4.3.2.7. 1,3-Bis(naphthalen-2-ylsulfinyl)propane ***7c***. The title compound was prepared according to the general procedure for asymmetric oxidation from 1,3-bis(naphthalen-2-ylthio)propane (2.32 mmol bis-sulfide, reaction time=4.5 h, one extra equivalent (2.32 mmol) H_2O_2 was added after 3 h). The product was isolated by column chromatography in 70% ethyl acetate in hexanes, followed by two recrystallizations from boiling acetone to yield a white solid (105 mg, 12%); mp 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (quint, J=7.4 Hz, 2H), 2.93 (dt, J=14.0, 7.1 Hz, 2H), 3.11 (dt, J=13.6, 7.7 Hz, 2H), 7.45 (dd, J=8.6, 1.8 Hz, 2H), 7.55–7.63 (m, 4H), 7.84–7.89 (m, 6H), 8.09 (d, J=1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 54.7, 119.8, 124.9, 127.6, 128.0, 128.3, 128.7, 129.7, 133.0, 134.6, 140.2; HRMS (ESI$^+$) calcd for $[C_{23}H_{20}O_2S_2+H]^+$ 393.0983, found 393.0972. $[\alpha]_{D^{25}}$ −240 (*c* 0.9, $CHCl_3$). HPLC analysis: >99% ee (AD-H, 4:6 isopropanol/hexanes, 1 mL/min, 254 nm, t_{R1}=16.3 min (major), t_{R2}=18.1 min (minor), t_{R3}=20.5 min (*meso*)).

4.3.2.8. 1,4-Bis(naphthalen-2-ylsulfinyl)butane ***7d***. The title compound was prepared according to the general procedure for asymmetric oxidation from 1,4-bis(naphthalen-2-ylthio)butane (2.32 mmol bis-sulfide, reaction time=4.5 h). The product was isolated by column chromatography in 70% ethyl acetate in hexanes, followed recrystallization from boiling acetone to yield a white solid (460 mg, 49%). A single crystal suitable for X-ray diffraction was grown by layering hexanes onto a dichloromethane solution. Mp 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65–1.78 (m, 2H), 1.92–2.04 (m, 2H), 2.75–2.84 (m, 2H), 2.86–2.95 (m, 2H), 7.51 (dd, J=8.6, 1.8 Hz, 2H), 7.55–7.62 (m, 4H), 7.87–7.93 (m, 4H), 7.95 (d, J=8.7 Hz, 2H), 8.14 (d, J=1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 56.0, 119.7, 124.6, 127.4, 127.8, 128.0, 128.5, 129.5, 132.8, 134.4, 140.5; IR(neat): 1588, 1345, 1066, 1040, 818, 750 cm^{-1}; HRMS (ESI$^+$) calcd for $[C_{24}H_{22}O_2S_2+H]^+$ 407.1134, found 407.1142. $[\alpha]_{D^{25}}$ −173 (*c* 1.1, $CHCl_3$). HPLC analysis: >99% ee (AD-H, 2:8 isopropanol/hexanes, 1.5 mL/min, 233 nm, t_{R1}=35.7 min (major), t_{R2}=37.3 min (minor), t_{R3}=44.1 min (*meso*)).

4.3.2.9. 1,5-Bis(naphthalen-2-ylsulfinyl)pentane ***7e***. To 1,5-pentanediol (2.0 g, 0.019 mol) was added 4 mL of pyridine and the solution was stirred and cooled to 0 °C. *p*-Toluenesulfonyl chloride (7.2 g, 0.038 mol, 2 equiv) in 12 mL pyridine was added by addition funnel over 30 min. The reaction mixture was stirred at 0 °C for 4 h. Addition of 20 mL of cold water precipitated a white solid. The desired product was separated from the mono-tosylate (3:1 ratio) by recrystallization from hot methanol, affording 2.54 g (32%) of pentane-1,5-diyl bis(*p*-toluenesulfonate), as clear long crystals whose characterization data are in agreement with literature.[26] Pentane-1,5-diyl bis(p-toluenesulfonate) (2.54 g, 0.0061 mol), 2-thionaphthol (2.44 g, 0.015 mol, 2.5 equiv), and potassium carbonate (2.5 g, 0.018 mol, 3 equiv) were dissolved in 50 mL of acetone and stirred at 45 °C for 24 h. The mixture was then filtered, concentrated, taken up in dichloromethane, and washed with 1 M NaOH and brine. The aqueous layer was washed twice with dichloromethane. Combined organic layers were dried over Na_2SO_4, and evaporated to afford a beige solid. ^{1}H NMR analysis indicated a 3:1 ratio of the desired bis-sulfide to the disulfide resulting from oxidation of 2-thionaphthol, which was carried through to the oxidation step without further purification.

The title compound was prepared according to the general procedure for asymmetric oxidation from the crude mixture of 1,3-bis(naphthalen-2-ylthio)pentane (1.0 g crude material, reaction time: 3.75 h). The off-white product was isolated by column chromatography eluting with ethyl acetate. Two recrystallizations from boiling acetone yielded a white solid (181 mg, 22%, calculated based on the NMR determined ratio of bis-sulfide added in the oxidation reaction); mp 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52–1.67 (m, 4H), 1.77–1.86 (m, 2H), 2.76–2.90 (m, 4H), 7.52 (dd, J=8.6, 1.7 Hz, 2H), 7.55–7.60 (m, 4H), 7.87–7.92 (m, 4H), 7.94 (d, J=8.6 Hz, 2H), 8.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 27.7, 56.2, 119.7, 124.6, 127.3, 127.8, 128.0, 128.5, 129.5, 132.8, 134.4, 140.7. IR(neat): 3050, 2935, 1070, 1029, 867, 813, 755, 742 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{24}O_2S_2+H]^+$ 421.1290, found 421.1286. $[\alpha]_{D^{25}}$ −193 (*c* 0.27, $CHCl_3$). HPLC analysis: >99% ee (AD-H, 4:6 isopropanol/hexanes, 1 mL/min, 210 nm, t_{R1}=17.4 min (minor), t_{R2}=20.4 min (major), t_{R3}=21.6 min (*meso*)).

4.3.3. Procedure for the oxidation of ***2b*** *with the Davis oxaziridine.* The Davis oxaziridine, *N*-(phenylsulfonyl)(3,3-dichlorocamphoryl)oxaziridine, was synthesized according to a literature procedure.[22,23] Since the final step of the synthesis was low yielding, a 0.97:1 mixture of the oxaziridine/sulfonylimine was used as the oxidant. The oxidant mixture (200 mg, 100.4 mg oxaziridine, 0.276 mmol) was dissolved in 2.5 mL CH_2Cl_2 and cooled to 0 °C. 2,2,2-Tris((cyclohexylthio)methyl)-ethane (41 mg, 0.099 mmol) was dissolved in 2.5 mL CH_2Cl_2, and this was added to the first flask. The solution was stirred at 0 °C for 40 h. The solvent was removed under reduced pressure and 2,2,2-tris((cyclohexylsulfinyl)methyl)-ethane was isolated by preparative TLC eluting with 8% MeOH in CH_2Cl_2 as a 3.7:1 (homo/hetero) mixture of diastereomers (35 mg, 76%).

4.4. Rhodium-catalyzed olefin hydroacylation

4.4.1. Procedure for olefin hydroacylation. 2-(1-Phenylvinyl)benzaldehyde was synthesized according to the procedure of Morehead.[24] Inside a glovebox, **1d** (0.005 mmol, 3.0 mg) was dissolved in CH_2Cl_2 (1 mL) and added to $[Rh(NBD)_2]BF_4$ (0.005 mmol, 1.9 mg). This solution was added to a Schlenk tube (AF-0096-01 from Chemglass) containing a magnetic stir bar and the tube was sealed. The tube was removed from the glovebox and placed on a Schlenk line. The headspace in the tube was removed by one freeze-pump-thaw cycle, and then H_2 was flowed into the tube for 30 min. The solution was then degassed by three freeze-pump-thaw cycles and taken back into the glovebox. A solution of 2-(1-phenylvinyl) benzaldehyde (0.1 mmol, 20.8 mg) was then added to the catalyst solution, and the reaction was stirred at 100 °C for 20 h. The crude mixture was concentrated in vacuo and purified by column chromatography. Spectral data of the purified material are in agreement with the literature.[27]

4.5. Rhodium-catalyzed 1,4-addition

4.5.1. Procedure for asymmetric 1,4-addition of phenyl boronic acid to cyclohex-2-ene-1-one. In a glovebox, the sulfoxide ligand (0.0136 mmol) was dissolved in ethyl acetate and added to $[Rh(C_2H_4)_2Cl]_2$ (2.2 mg, 0.006 mmol) in ethyl acetate (3 mL total). The resulting mixture was allowed to stir at room temperature for 20 min, upon which degassed 2-cyclohexen-1-one (36 mg, 0.375 mmol) and phenyl boronic acid (183 mg, 1.5 mmol, 4 equiv) were added. The reaction flask was sealed with a rubber stopper and brought out of the glovebox, upon which 2.5 M $KOH_{(aq)}$ (0.075 mL, degassed) was added via syringe. The reaction was performed under argon at 40 °C and monitored by LC–MS. Upon completion, the mixture was filtered through Celite, concentrated, and purified by preparative TLC (eluent 30% ethyl acetate in hexanes). HPLC analysis: OD-H, 1:99 isopropanol:hexanes, 0.5 mL/min, 254 nm, t_{R1}=34.5 min (*R*), t_{R2}=38.9 min (*S*).

Acknowledgements

We thank the University of Toronto, Canadian Foundation for Innovation, Ontario Ministry of Research and Innovation, Boehringer Ingelheim Ltd. Canada, and Natural Sciences and Engineering Research Council of Canada (NSERC) for funding. V.M.D is grateful

for an Alfred P. Sloan Fellowship and P.K.D for an NSERC Vanier Canada Graduate Scholarship. We thank Dr. Alan Lough for X-ray structure analysis.

Supplementary data

NMR spectra and HPLC traces for all new compounds can be found in the supplementary data available in the online version. Crystallographic data for compounds **1c** and **7d** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 797193 and CCDC 802122. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.Uk). Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.02.023.

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