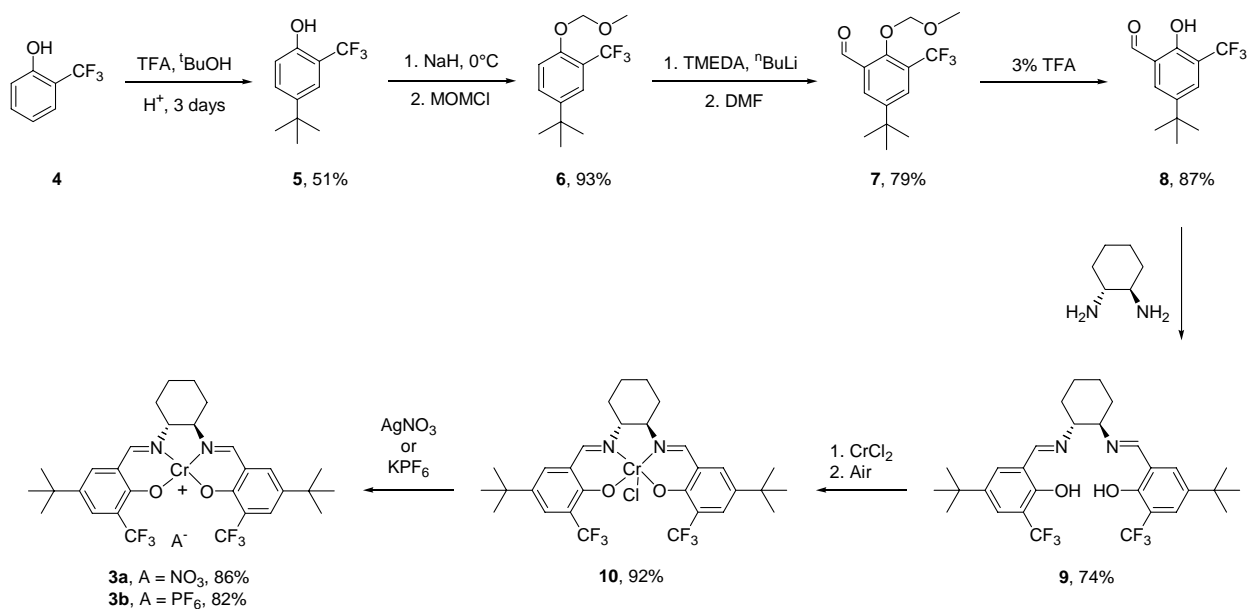




We have reported detailed studies of the effect on AE of various substituents at all positions on the arene ring of the salen ligand<sup>40</sup> which culminated in complex **1a**.<sup>41, 42</sup> Recently, an exploration of salen substituent effects led to the discovery of complex **2b**, which was also an effective mediator of epoxidation.<sup>43</sup> We envisaged that, by incorporating the beneficial substituents from **1a** and **2b** into a new catalyst **3**, we could obtain further improvements in the asymmetric epoxidation of unfunctionalised alkenes. The new catalyst was expected to be a less reactive but more selective epoxidising agent. We now describe the synthesis of **3a,b** and their use in the AE of a variety of classes of alkenes

## Results and Discussion

Scheme 1 shows the synthetic route adopted for the synthesis of **3a,b**. After unsuccessful attempts to introduce the trifluoromethyl group into the benzene ring late in the synthesis, we adopted the methods previously used for the synthesis of 3-trifluoromethylsalicylaldehyde.<sup>41</sup> The synthesis of phenol **5** had been described previously by Stokker *et al*.<sup>44</sup> The protection, formylation, and deprotection steps proceeded in good yield.<sup>45</sup> Contrary to our previous experience,<sup>41</sup> the use of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was found to be essential to achieve a selective formylation – a complicated mixture resulted in its absence. Care had to be taken also to prevent decomposition of the delicate trifluoromethyl phenol derivative **7** which is sensitive to acid and base.<sup>46, 47</sup> After some experimentation, we found that 3% TFA in CH<sub>2</sub>Cl<sub>2</sub> removed the protecting group without causing the product to decompose.



**Scheme 1.** Synthesis of Cr(salen) complexes (overall yield = 18–19%).

With the requisite salicylaldehyde **8** in hand, the synthesis of **3a,b** was achieved in good yield using standard methods.<sup>41</sup> The paramagnetic complexes were characterised by IR and ES-MS. Elemental analyses were not satisfactory, however this is not unusual for these complexes<sup>26</sup> and epoxidation results were reproducible from batch to batch.

We first tested our new catalysts in the stoichiometric epoxidation of *trans*- $\beta$ -methylstyrene (our standard test substrate) by O=Cr(salen) (see Table 1). Gratifyingly, the catalysts lived up to our expectations, exhibiting higher enantioselectivity than any previous Cr(salen) catalyst in the epoxidation of this substrate. The epoxide is stable in the presence of Cr<sup>III</sup>(salen)<sup>+</sup> and O=Cr<sup>V</sup>(salen)<sup>+</sup>, thus enantioselectivity is not a result of kinetic resolution. The effect of changing counterion was unusually large, nitrate was found to be significantly better than hexafluorophosphate. The addition of Ph<sub>3</sub>PO was found to improve the ees obtained, in line with previous results. The yields in stoichiometric mode were low, however this is not unexpected.<sup>43</sup>

**Table 1.** Epoxidation of *trans*- $\beta$ -methylstyrene in acetonitrile with PhIO as oxidant at 0°C<sup>a</sup>

No.	Catalyst	Additive	Stoichiometric <sup>b</sup>		Catalytic <sup>c</sup>	
			Ee (yield)	Time (h)	Ee (yield)	Time (h)
1	<b>3a</b>	None	92 (15)	24	76 (8)	42
2	<b>3a</b>	Ph <sub>3</sub> PO	94 (23)	24	88 (16)	42
3	<b>3a</b>	Ph <sub>3</sub> PO	–	24	-15 (3) <sup>d</sup>	18
4	<b>3b</b>	None	79 (18)	3	–	
5	<b>3b</b>	Ph <sub>3</sub> PO	89 (27)	3	–	

<sup>a</sup>See experimental section for full details. <sup>b</sup>1.0 equiv. of O=Cr(salen) w.r.t. substrate. <sup>c</sup>0.10 equiv. of Cr(salen) and 1.5 equiv. of PhIO w.r.t. substrate. <sup>d</sup>with 5.0 equiv. of NaOCl (0.55M in 0.05M NaHPO<sub>4</sub>) as oxidant.

The most notable result in Table 1 is that obtained in catalytic mode (10 mol% Cr<sup>III</sup>(salen)) with Ph<sub>3</sub>PO additive, which is the highest ee (88%) obtained thus far under catalytic conditions with Cr(salen) complexes. However it is still slightly lower than in stoichiometric mode, as had been observed previously with **1a**.<sup>41</sup> Also the yields were unexpectedly low, usually the yield in catalytic mode is significantly higher than in stoichiometric mode (71% vs 45% with **1a**). The very low catalytic yield is probably due to disproportionation of PhIO over the extended reaction times necessary for this slower catalyst.<sup>48</sup> In line with previous results,<sup>41</sup> the use of NaOCl as terminal oxidant resulted in a poor ee (entry 3), however, the sense of the enantioselectivity was reversed suggesting a different oxidation pathway.<sup>43</sup> We have also rationalised the reduction in ee relative to stoichiometric mode in terms of a second oxidation cycle being in operation under catalytic conditions.<sup>41,43</sup> Evidence for the presence of multiple oxidation cycles has been reported for Mn(salen)-, Mn(corrole)- and Fe(porphyrin)-catalysed epoxidations.<sup>49-53</sup> Bryliakov and Talsi<sup>10</sup> have recently reported evidence supporting the presence of two discrete (salen)chromium-oxo species starting from Cr(salen) chloride complexes and iodosylbenzene: a

monomeric  $[(\text{salen})\text{Cr}^{\text{V}}=\text{O}]^+$  and a dimeric mixed valent  $\text{Cr}^{\text{III}}\text{Cr}^{\text{V}}$ -oxo species. They proposed that only the former species was acting as an oxidant under their conditions, while the latter species acted as a reservoir.<sup>10</sup> The nature of the proposed second oxidant and/or oxidation cycle in our system is currently under investigation in our laboratory and will be the focus of a future report.

Having established that **3a** was the better catalyst we then examined its substrate scope. Examples of terminal mono-substituted, terminal di-substituted, *cis*- and *trans*-1,2-disubstituted alkenes, were all examined. Table 2 shows results for those substrates where epoxide was formed as product. Unfortunately, the excellent selectivity of the catalyst in the case of *trans*- $\beta$ -methylstyrene did not extend to other substrates. Only *trans*-stilbene and *cis*- $\beta$ -methylstyrene gave ees greater than 50%, which is a significant improvement for the latter substrate in Cr(salen)-mediated AE. Yields were poor in all cases. The attempted epoxidation of  $\alpha$ -methylstyrene resulted in a complicated mixture with no epoxide or starting material present. *trans*-Methyl cinnamate was recovered unchanged after 48 hours under stoichiometric conditions.

**Table 2.** Epoxidation of alkenes using **3a** and PhIO in acetonitrile at 0°C<sup>a</sup>

No.	Substrate	Additive	Stoichiometric		Catalytic	
			Ee (yield)	Time (h)	Ee (yield)	Time (h)
1	<i>trans</i> - $\beta$ -Methylstyrene	None	92 (15)	24	76 (8)	42
2	<i>trans</i> - $\beta$ -Methylstyrene	Ph <sub>3</sub> PO	94 (23)	24	88 (16)	42
3	<i>cis</i> - $\beta$ -Methylstyrene	None	57 (1)	24	44 (17)	42
4	<i>cis</i> - $\beta$ -Methylstyrene	Ph <sub>3</sub> PO	51 (3)	24	41 (21)	42
5	Styrene	None	NR <sup>b</sup>	42	–	–
6	Styrene	Ph <sub>3</sub> PO	7 (ND <sup>c</sup> )	42	–	–
7	<i>trans</i> -Stilbene	None	50 (<10)	42	–	–
8	<i>trans</i> -Stilbene	Ph <sub>3</sub> PO	58 (10)	42	–	–

<sup>a</sup> See Table 1 for general details. Entries 1 & 2 are taken from Table 1. <sup>b</sup>NR = no reaction. <sup>c</sup>ND = not determined.

## Conclusions

A rationally designed, novel Cr(salen) complex has been synthesised and tested in the epoxidation of a range of alkenes. The highest ever selectivity for the AE of *trans*- $\beta$ -methylstyrene by a Cr(salen) complex was achieved but only moderate to poor selectivity with other substrates. The differences in results between catalytic and stoichiometric modes are suggested to be due to the presence of a second oxidation cycle.

## Experimental Section

**General Procedures.** All chemicals were available from Aldrich and used as received unless stated. 2-Trifluoromethylphenol was obtained from Fluorochem Ltd. and used as received. *trans*-Cyclohexane-1,2-diamine was purchased in racemic form and resolved using literature methods.<sup>54</sup> Iodosylbenzene was synthesised using literature procedures.<sup>55</sup>

**4-*tert*-Butyl-2-trifluoromethylphenol (5).** A modified version of the procedure of Stokker *et al.* was used.<sup>44</sup> To a solution of 2-trifluoromethylphenol (24.0 g, 148 mmol) and *tert*-butanol (11.5 g, 155 mmol) in trifluoroacetic acid (TFA) (100 ml) was added concentrated sulphuric acid (2 ml). The colourless solution was stirred for 3 days at room temperature, during which time a dark yellow colour developed. The reaction mixture was concentrated under vacuum to yield a dark green oil (26.4 g) which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (150 ml). This solution was then washed with water (150 ml), saturated sodium bicarbonate (3 × 150 ml) and brine (150 ml). After drying over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed under vacuum to yield a light green coloured oil which solidified on standing. The resulting solid was recrystallised from pet. spirits (40–60°C) to yield white crystals (16.48 g, 51%): Mp 57–61°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.49 (d, 1H, *J* = 2.3 Hz, ArH), 7.43 (dd, 1H, *J* = 8.6 Hz, 2.3 Hz, ArH), 6.88 (d, 1H, *J* = 8.6 Hz, ArH), 5.62 (s, 1H, OH), 1.30 (s, 9H, <sup>t</sup>Bu); MS (GCMS) *m/z* (% relative intensity) 218.2 (M<sup>+</sup>, 40), 203.2 (M-CH<sub>3</sub>, 100), 183.2 (90), 155.1 (30), 127.1 (20).

**4-*tert*-Butyl-1-methoxymethoxy-2-trifluoromethylbenzene (6).** Sodium hydride (1.38 g of a 60% dispersion in mineral oil, 34.5 mmol) was washed with hexane and transferred to a 3-neck 100 ml RB flask under an atmosphere of N<sub>2</sub>. After addition of anhydrous DMF (11 ml), the slurry was cooled with stirring to 0°C. To the resulting grey suspension, a solution of **5** (5.00 g, 22.9 mmol) in anhydrous DMF (6 ml) was added dropwise at such a rate that the evolution of hydrogen did not become too vigorous. After complete addition the ice bath was removed and the reaction mixture was stirred for 1 h. Chloromethylmethyl ether (2.6 ml, 34 mmol) was then added dropwise and the resulting solution was stirred overnight. Ice/water (50 ml) was added cautiously and the mixture extracted with Et<sub>2</sub>O (3 × 50 ml). The combined Et<sub>2</sub>O extracts were washed with NaOH solution (2M, 50 ml), hydrochloric acid (2M, 50 ml), and brine (50 ml). The solution was dried over MgSO<sub>4</sub> and the solvent was removed *in vacuo* to yield a colourless liquid (5.57 g, 93%) which was used in the next step without further purification: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.57 (d, 1H, *J* = 2.3 Hz, ArH), 7.47 (dd, 1H, *J* = 2.3 Hz, *J* = 8.6 Hz, ArH), 7.15 (d, 1H, *J* = 8.6 Hz, ArH), 5.24 (s, 2H, CH<sub>2</sub>), 3.50 (s, 3H, CH<sub>3</sub>), 1.31 (s, 9H, <sup>t</sup>Bu); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 152.9, 143.2, 130.2, 123.9 (q, -CF<sub>3</sub>, *J*<sub>C-F</sub> = 272 Hz), 124.0, 119.0 (q, *J*<sub>C-F</sub> = 30.5) 115.2, 94.5 (-CH<sub>2</sub>-), 56.4 (-OCH<sub>3</sub>), 34.5 (-CMe<sub>3</sub>), 31.5 (-CH<sub>3</sub>); MS (GCMS) *m/z* (% relative intensity) 262.2 (M<sup>+</sup>, 50), 247.2 (25), 232.2 (10), 217.2 (M-C<sub>2</sub>H<sub>5</sub>O, 100), 201.2 (10) 183.1 (20); IR (KBr, cm<sup>-1</sup>) 2961, 1619, 1589, 1508, 1423, 914, 741;

**5-*tert*-Butyl-2-methoxymethoxy-3-trifluoromethylbenzaldehyde (7).** To a solution of **6** (8.41 g, 32.1 mmol) in dry hexane (75 ml) under an atmosphere of N<sub>2</sub> was added TMEDA

(4.9 ml, 32 mmol) via syringe. The solution was then cooled to 0°C and *n*BuLi (20 ml of a 1.6M solution in hexanes, 32 mmol) was added dropwise via syringe. The resulting thick grey solution was stirred for 2 h at 0°C followed by addition of dry DMF (2.72 ml, 35.1 mmol). The solution was then stirred for 0.5 h at 0°C followed by 1 h at room temperature. Following the addition of 1M HCl (50 ml) the mixture was extracted with Et<sub>2</sub>O (3 × 50 ml). The combined ether extracts were then washed with brine (50 ml), dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure to yield a clear liquid, which was distilled under vacuum (7.39 g, 79%): Bp 95–96°C (0.1 mm Hg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 10.31 (s, 1H, CHO), 8.06 (d, 1H, *J* = 8.6 Hz, ArH), 7.86 (d, 1H, *J* = 8.6 Hz, ArH), 5.10 (s, 2H, CH<sub>2</sub>), 3.63 (s, 3H, CH<sub>3</sub>), 1.36 (s, 9H, <sup>t</sup>Bu); IR (KBr, cm<sup>-1</sup>) 2965, 1697, 1608, 1481, 1326, 924; Anal. calcd for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>O<sub>3</sub>: C, 57.93; H, 5.90; F, 19.63. Found: C, 58.19; H, 6.06; F, 20.07.

**5-*tert*-Butyl-2-hydroxy-3-trifluoromethylbenzaldehyde (8).** Aldehyde **7** (7.07 g, 24.4 mmol) was dissolved in a 3% solution of TFA in CH<sub>2</sub>Cl<sub>2</sub> (180 ml). The solution was stirred and monitored by TLC for the disappearance of starting material. When no starting material remained, the solvent was removed *in vacuo* to yield a clear solution which, on standing, solidified to yield a low melting solid (5.19 g, 87%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 11.56 (s, 1H, OH), 9.97 (s, 1H, CHO), 7.84 (d, 1H, *J* = 1.9 Hz, ArH), 7.76 (d, 1H, *J* = 1.9 Hz, ArH), 1.38 (s, 9H, <sup>t</sup>Bu); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.8 (ArCHO), 157.7, 142.8, 134.0 (ArCH), 131.5 (q, *J*<sub>C-F</sub> = 5.0 Hz, ArCH), 123.4 (q, -CF<sub>3</sub>, *J*<sub>C-F</sub> = 273 Hz), 121.1, 118.8 (q, *J*<sub>C-F</sub> = 31 Hz, ArC<sub>3</sub>), 34.5 (-CMe<sub>3</sub>), 31.3 (-CH<sub>3</sub>); GC-MS *m/z* (% relative intensity): 247 (2), 246 (16, **M**<sup>+</sup>), 232 (13), 231 (100, **M**<sup>+</sup>-CH<sub>3</sub>), 227 (6), 212 (7), 211 (52, **M**<sup>+</sup>-CH<sub>3</sub>-HF), 183 (13), 155 (5), 127 (7), 91 (5); IR (KBr, cm<sup>-1</sup>) 2972, 2866, 1668, 1618, 1482, 1367, 1339, 1259, 1142, 733; Anal. calc'd for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>O<sub>2</sub>: C, 58.54; H, 5.32; F, 23.15. Found: C, 58.52; H, 5.52; F, 23.36.

**(*R,R*)-(-)-*N,N'*-Bis(5-*tert*-butyl-3-trifluoromethylsalicylidene)-*trans*-cyclohexane-1,2-diamine (9).** (*R,R*)-(-)-*trans*-Cyclohexane-1,2-diamine (0.23 g, 2.0 mmol) was dissolved in EtOH (15 ml) and **8** (1.0 g, 4.1 mmol) was added to the solution. The resulting bright yellow solution was refluxed for 2 h, cooled and the solvent removed *in vacuo* to yield a solid which was recrystallised from a water/EtOH mixture to give bright yellow crystals. (0.84 g, 74%): Mp 130–131°C; [ $\alpha$ <sub>D</sub>]<sup>25</sup> = -216 (c = 1.01, CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr, cm<sup>-1</sup>) 2967, 2867, 1636 (C=N), 1606, 1481, 1367, 1333, 1285, 1261, 1127, 895, 827, 691; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 14.23 (br s, 2H, OH), 8.30 (s, 2H, N=CH), 7.54 (d, 2H, *J* = 2.1 Hz, ArH), 7.31 (d, 2H, *J* = 2.1 Hz, ArH), 3.37–3.28 (m, 2H, C=NCH), 1.99–1.29 (m, 8H, cyclohexyl-CH<sub>2</sub>), 1.23 (s, 9H, <sup>t</sup>Bu); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.2 (C=N), 157.9, 140.8, 132.1 (ArCH), 127.0 (q, *J*<sub>C-F</sub> = 4.6 Hz, ArCH), 124.1 (q, *J*<sub>C-F</sub> = 272 Hz, CF<sub>3</sub>), 118.9, 117.5 (q, *J*<sub>C-F</sub> = 30 Hz, C-CF<sub>3</sub>), 72.6 (cyclohexyl-CH), 34.3 (-CMe<sub>3</sub>), 33.2 (-CH<sub>2</sub>-), 31.4 (-CH<sub>3</sub>), 24.4 (-CH<sub>2</sub>-). MS-MS (Electrospray): Daughter-MS of 571 *m/z* (% relative intensity): 571 (100, **M**+H<sup>+</sup>), 551 (30, **M**-F), 511 (5), 447 (5), 326 (5), 306 (5), 125 (90, **M**-C<sub>23</sub>H<sub>23</sub>F<sub>6</sub>O<sub>2</sub>), 98 (7); Anal. calc'd for C<sub>30</sub>H<sub>36</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>: C, 63.15; H, 6.36; N, 4.91; F, 19.98; Found: C, 63.26; H, 6.26; N, 4.91; F, 19.90.

**CAUTION: There is evidence that Cr(III)salen and O=Cr(V)salen complexes are genotoxic and carcinogenic and thus due care should be taken to avoid contact.**<sup>56, 57</sup>

**(*R,R*)-(-)-*N,N'*-Bis(5-*tert*-butyl-3-trifluoromethylsalicylidene)-*trans*-cyclohexane-1,2-diamine chromium(III) chloride (10).** Complex **10** was prepared using the procedure described in the supplementary information of Daly *et al.*<sup>41</sup> starting from CrCl<sub>3</sub>. Ligand **9** (4.0 g, 7.0 mmol) gave **10** as a brown precipitate (4.23 g, 92%): Mp > 230°C; IR (KBr, cm<sup>-1</sup>) 2962, 2862, 1631 (C=N), 1553, 1457, 1395, 1352, 1308, 1260, 1147, 1028, 924, 892, 864, 839, 780, 734, 697, 547; MS (Electrospray) *m/z* (% relative intensity): 678.0 (**M+Na**, 5), 662.1 (15), 661.1 (**M-Cl**+**H<sub>2</sub>O+Na**, 40), 622.2 (10), 621.1 (40), 620.1 (**M-Cl**, 100), 618.1 (5).

**[(*R,R*)-(-)-*N,N'*-Bis(5-*tert*-butyl-3-trifluoromethylsalicylidene)-*trans*-cyclohexane-1,2-diamine chromium(III)] nitrate (3a).** Complex **10** (500 mg, 762 μmol) was dissolved in MeOH (20 ml) and a solution of silver nitrate (194 mg, 1.14 mmol) in water (5 ml) was added. The resulting suspension was stirred for 30 minutes and the white precipitate of silver chloride was removed by filtration. The filtrate was concentrated under vacuum to yield a brown precipitate which was collected by filtration and dried under vacuum (445 mg, 86%): Mp > 230°C; IR (KBr, cm<sup>-1</sup>) 2962, 2877, 1631 (C=N), 1553, 1457, 1393 (N-O), 1259, 1144, 1028, 924, 892, 864, 839, 781, 734, 697, 548; MS (Electrospray) *m/z* (% relative intensity) 705.0 (**M+Na**, 3), 688.1 (5), 663.1 (10), 662.1 (15), 661.1 (**M-NO<sub>3</sub>+H<sub>2</sub>O+Na**, 38), 621.1 (57), 620.1 (**M-NO<sub>3</sub>**, 100).

**[(*R,R*)-(-)-*N,N'*-Bis(5-*tert*butyl-3-trifluoromethylsalicylidene)-*trans*-cyclohexane-1,2-diamine chromium(III)] hexafluorophosphate (3b).** Complex **10** (500 mg, 762 μmol) was dissolved in the minimum amount of MeOH (20 ml) and a solution of potassium hexafluorophosphate (211 mg, 1.14 mmol) in water (5 ml) was added. The resulting solution was stirred overnight at room temperature and concentrated to yield a brown precipitate (480 mg, 82%): Mp > 230°C; IR (KBr, cm<sup>-1</sup>) 2942, 1627 (C=N), 1557, 1469, 1454, 1397, 1350, 1313, 1226, 1086, 1014, 845, 736, 559; MS (Electrospray) *m/z* (% relative intensity) 663.2 (10), 662.2 (20), 661.1 (40, **M-PF<sub>6</sub>+H<sub>2</sub>O+Na**), 622.2 (10), 621.1 (50), 620.1 (**M-PF<sub>6</sub>**, 100), 618.1 (5).

**General epoxidation procedure.** Details of procedures for epoxidations are given in the supplementary information of Daly *et al.*<sup>41</sup> Daly *et al.* have described conditions for the analysis of reaction mixtures by chiral GC or HPLC except:  $\alpha$ -methylstyrene and styrene oxide which were analysed by chiral GC (Supelco cyclodextrin- $\beta$  capillary column (betadex 120), 30 m  $\times$  0.25 mm i.d., 0.25 μm film.) with column temperatures of 80°C and 100°C, respectively.

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