Pergamon

SCIENCE DIRECT®

Tetrahedron: *Asymmetry* 14 (2003) 791–816

TETRAHEDRON: *ASYMMETRY*

Asymmetric rhodium carbene insertion into the Si–H bond: identification of new dirhodium(II) carboxylate catalysts using parallel synthesis techniques

Richard T. Buck,[a,b] Diane M. Coe,[c] Martin J. Drysdale,[c] Leigh Ferris,[a] David Haigh,[c] Christopher J. Moody,[b,*] Neil D. Pearson[d] and J. Bobby Sanghera[a]

[a]*Department of Chemistry, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK*
[b]*School of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, UK*
[c]*GlaxoSmithKline, Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire SG1 2NY, UK*
[d]*GlaxoSmithKline, New Frontiers Science Park, Coldharbour Road, Harlow, Essex CM19 5AD, UK*

Received 6 November 2002; accepted 6 December 2002

Abstract—Decomposition of methyl 2-diazophenylacetate in the presence of silanes and a chiral dirhodium(II) catalyst results in Si–H insertion of the intermediate carbenoid with varying degrees of enantioselectivity. New chiral dirhodium(II) carboxylate catalysts were identified using solution phase parallel synthesis techniques.

1. Introduction

The development of chiral catalysts for asymmetric reactions of metal carbenoids has been widely studied since the first report by Nozaki et al. that decomposition of ethyl diazoacetate in the presence of a copper(II) complex with a chiral Schiff base ligand resulted in enantioselective cyclopropanation of styrene.[1] Although copper based catalysts are extremely effective in cyclopropanation reactions, dirhodium(II) compounds, first introduced by Teyssié et al.,[2] are generally superior catalysts for diazo compound decomposition since they mediate a wider range of carbenoid processes such as insertion.[3] Although enantioselective C–H insertion reactions using chiral dirhodium(II) carboxylates and carboxamides as catalysts are now fairly commonplace,[4] attempts to effect enantioselective carbenoid X–H (X = heteroatom) have been less successful. Thus Brunner et al. observed up to 12% ee in the S–H insertion reaction of 3-diazo-2-butanone with thiophenol,[5] and McKervey et al. have described an intramolecular N–H insertion reaction which proceeds in 45% ee using dirhodium(II) mandelate as catalyst.[6] Our own work was initially directed at O–H insertion reactions,[7] and although we showed that diastereoselectivity was possible using chiral diazoesters,[8] all attempts to effect enantioselective O–H insertions with chiral dirhodium(II) carboxylates failed.[9] Although, recently, Doyle et al. have shown that chiral rhodium catalysts can enhance the diastereocontrol in the O–H insertion reactions of chiral diazoesters,[10] the general lack of enantioselectivity observed in insertions into polar X–H bonds is thought to be associated with a stepwise mechanism involving initial attack of the heteroatom X on the electrophilic metal carbene to form an ylide followed by hydrogen transfer.[3] In contrast, carbene insertions into less polar X–H bonds, such as Si–H, are thought to be concerted, and therefore much more likely to be influenced by chiral catalysts. We now report the full details of a study on asymmetric insertions into the Si–H bond.[11,12]

2. Results and discussion

The rhodium(II) catalysed reaction of diazoesters with silanes resulting in the formation of α-silylcarbonyl compounds by Si–H insertion, was first reported by Doyle et al. in 1988,[13] although examples of copper catalysed processes had been described earlier.[14] The reaction has recently been the subject of renewed interest,[15,16] and diastereoselective Si–H insertion was achieved by using diazoesters of chiral alcohols.[15b] Since the publication of our preliminary results,[11] fur-

* Corresponding author.

0957-4166/03/$ - see front matter
PII: S0957-4166(03)00035-1

ther papers have appeared. Thus, asymmetric Si–H insertions have been carried out using *N*-(arenesulfonyl)prolinates[17] and *N*-phthaloyl-amino acids[18] as chiral ligands for rhodium; copper(I) catalysts bearing chiral Schiff base ligands have also been used.[19,20] The mechanism of the rhodium carbene insertion into Si–H bonds has also been discussed.[21–23]

Our initial work focused on the asymmetric synthesis of methyl 2-(silyl)phenylacetates **2** from methyl diazophenylacetate **1**, a reaction that works well for a range of silanes using dirhodium(II) acetate **3** as catalyst (Table 1, entry 1). Thus a dichloromethane solution of methyl diazophenylacetate **1** and the silane was treated with the catalyst to give the Si–H insertion products **2** in good yield and in varying enantioselectivity (ee) (Table 1). The ee was determined by HPLC analysis on a chiral stationary phase by comparison with the racemic methyl 2-(silyl)phenylacetates obtained from the dirhodium(II) acetate catalysed reaction. A range of known catalysts was used in the first instance: our recently described catalysts[9] based on phthalate half esters **4** and 1-substituted pyrroles **5** gave relatively poor results with ee's in the range 8–23% (Table 1). However, the known *N*-(benzenesulfonyl)proline derived catalyst **6**[24] gave significantly better results, particularly with the bulkier silanes. Dirhodium(II) mandelate **7**,[25] on the other hand, proved a poor catalyst, although the *O*-alkyl derivatives **8**–**11** were somewhat better. Also significantly better was the catalyst **12** derived from 2-methoxy-2-(trifluoromethyl)phenylacetic acid.[26] Dirhodium(II) camphanate **13**[27] also gave >30% ee with the bulky silane, whereas the related camphenate ligand **14** was a poor catalyst. Finally, in this initial screen, carboxamidate ligands were investigated: Doyle's catalyst, $Rh_2(MEPY)_4$ **15**[28] consistently gave 40–50% ee, but our recently prepared difluoro-version **16**,[29] whilst exhibiting significantly greater catalytic activity in terms of reduced reaction times, gave poorer enantioselectivity (Table 1).

The achievement of catalytic asymmetric Si–H insertion using these diverse sets of chiral dirhodium(II) catalysts suggested that Si–H insertion occurs in the same concerted fashion as has been demonstrated for C–H insertion reactions. Evidence for the concerted nature of these insertions has been provided subsequently.[21] The higher reactivity of the Si–H bond towards insertion makes possible a range of intermolecular insertion that are uncharacteristic of C–H insertion using the same catalysts, but this higher reactivity dictates an earlier transition state that limits catalyst control of enantioselectivity. That enantiomeric excesses approaching 50% were achieved encouraged us to continue these studies as described below.

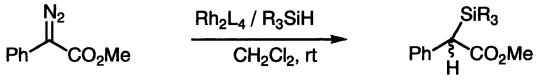
In order to enhance further the enantioselectivity of the rhodium carbene silane insertion reactions, a systematic search for alternative chiral carboxylic acid ligands was required, and therefore we decided to adopt parallel array technology to evaluate a wide variety of acids. The principles of combinatorial and parallel synthetic techniques have rapidly found application beyond the confines of the pharmaceutical industry and the search for new therapeutic agents. The benefits of parallel techniques in the identification of new catalysts are clear, since this methodology improves efficiency without introducing complex analysis and a deconvolution process to identify the catalyst of interest. A number of groups have now published studies involving the preparation of ligands on a solid-support or in solution, and evaluation of their potential as ligands for asymmetric synthesis.[30]

A set of 80 carboxylic acids ligands, **L1**–**L80**, was selected for study; acetic acid was deliberately included as **L80** to act as control. The other ligands were chosen by a cluster analysis of available acids. Thus the commercially available carboxylic acids, ca. 30,000 compounds (of which ca. 10,000 possess a 'chiral flag'), contained within the Available Chemical Directory were identified and filtered to identify the mono-carboxylic acids. Compounds containing additional functional groups which we reasoned might be incompatible because of their ability to compete for the dirhodium centre were then excluded; examples of such groups were primary amines, amidines, phosphonic acids, and nitriles. The resulting set, ca. 2000 compounds, was then clustered and the centroid of each of 80 clusters selected as a representative acid. The singletons produced during the process were not evaluated further because of the self-evident limitation on second generation arrays.

The representative chiral carboxylic acid ligand from one of each of the 79 clusters then underwent ligand exchange with a previously prepared dirhodium(II) carbonate species.[31] Typically, 20 chiral acids were subjected to the reaction conditions in parallel. Subsequent parallel vacuum filtration followed by drying allowed the isolation of the desired chiral dirhodium(II) carboxylate catalysts. Although no further purification was carried out, the structures were confirmed by automated ^1H NMR and mass spectrometry analysis. From the original 80 acids used, 70 chiral dirhodium(II) carboxylate catalysts were isolated in this manner, the remaining 10 chiral carboxylic acid ligands were recovered as unreacted starting material; these 10 ligands are shown in Fig. 1. It is not clear why these ligands did not form dirhodium(II) carboxylate species; although some contain sites (e.g. sulfides, basic nitrogens) which might also bind to the metal centre, this does not necessarily prevent complex formation (cf. the ligands in Fig. 2 and Table 2).

Subsequently a dichloromethane solution of methyl 2-diazophenylacetate **1** (10 mg) and one of 3 silanes, with a varying degree of steric bulk, was then treated with one of each of the 70 previously prepared chiral dirhodium(II) carboxylate catalysts to effect the carbenoid Si–H insertion reaction. Of the 70 chiral dirhodium(II) carboxylate catalysts used, 48 catalysed the desired Si–H insertion and gave the expected product, the remaining 22 rhodium species showing no catalytic activity (Fig. 2). The fact that these 22 rhodium species did not cause decomposition of the

Table 1. Dirhodium(II) catalysed asymmetric Si–H insertion reactions of methyl diazophenylacetate: initial screening of catalysts



1

2a $R_3 = PhMe_2$
2b $R_3 = t\text{-}BuMe_2$
2c $R_3 = i\text{-}Pr_3$
2d $R_3 = i\text{-}Bu_3$

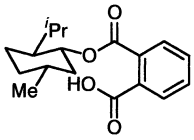
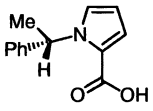
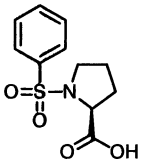
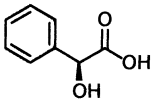
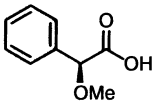
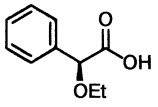
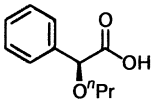
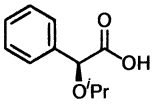
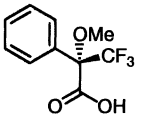
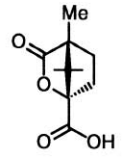
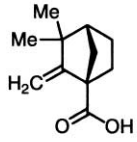
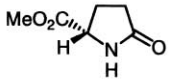
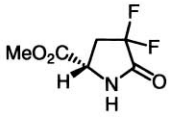
Cat	Chiral Carboxylic Acid Ligand L	Enantioselectivity/% [a] (Yield/%) 2a	2b	2c
3		0 (93)	0 (85)	0 (85)
4		10 (90)	23 (71)	18 (60)
5		8 (88)	18 (76)	23 (71)
6		12 (77)	25 (76)	38 (63)
7		8 (86)	20 (76)	16 (69)
8		27 (78)	31 (81)	26 (62)
9		29 (76)	30 (78)	29 (65)
10		27 (77)	27 (70)	24 (68)
11		14 (80)	19 (83)	15 (70)
12		29 (88)	35 (73)	42 (68)

Table 1. (*Continued*)

13		15 (84)	23 (71)	31 (65)
14		6 (89)	9 (75)	10 (66)
15		47 (69)	40 (58)	-
16		38 (79)	18 (66)	58 (51)[b]

[a] Determined by HPLC analysis (see Experimental Section); [b] Using tri-isobutylsilane to give **2d**.

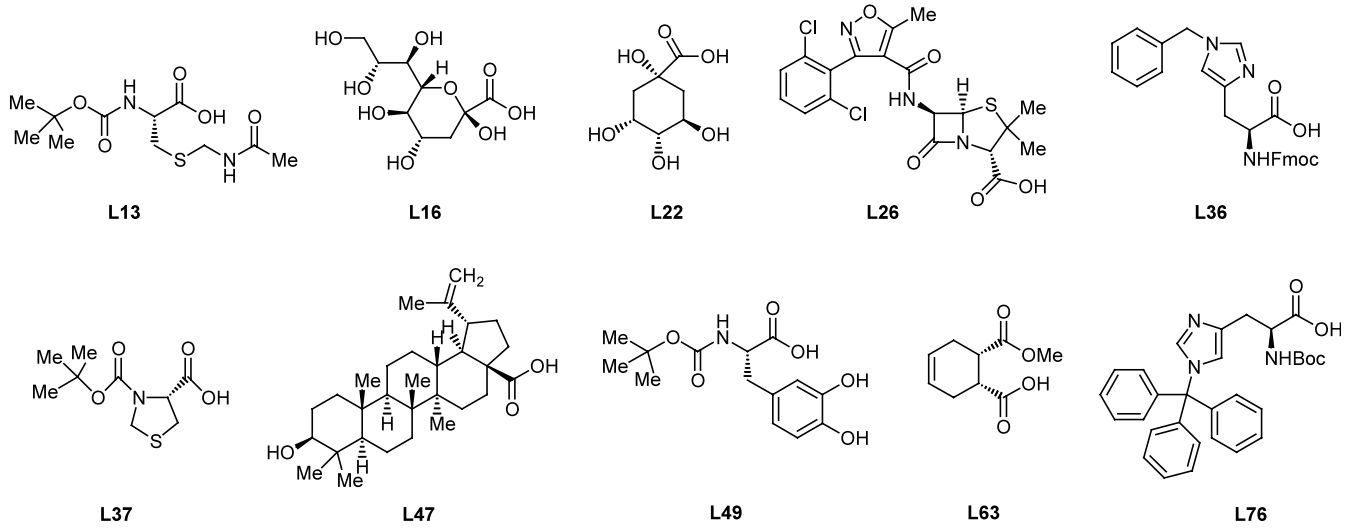


Figure 1. Ten chiral carboxylic acids **L** which did not form isolable dirhodium(II) carboxylates.

diazo ester **1** casts doubt on their structure, and suggests that the desired dirhodium(II) carboxylate was either not formed in these cases, or was isolated in an impure state from the parallel synthesis reactions.

With 48 catalytically active dirhodium(II) carboxylates, one of which was the dirhodium(II) acetate control, and using three silanes, 144 samples for analysis were generated. Parallel purification of these silane insertion products **2** through a small silica column (BondElut®) allowed the isolation of sufficient material for the determination of the enantioselectivities of the Si–H insertion products by automated HPLC on a chiral stationary phase. The results are summarised in Table 2, along with the spectroscopic characterisation data for the catalysts.

General relationships in this first set of parallel reactions can be systematically deduced with regards to chiral carboxylic acid ligand. For the majority of the chiral dirhodium(II) carboxylate catalysts applied to the enantioselective Si–H insertion reaction it was apparent that in most cases there was a significant increase in enantioselectivity on increasing the steric bulk of the silane, i.e. the use of tri-isopropylsilane generally gave the greatest enantioselectivities. Some other significant relationships were the presence of an *N*-(1-dimethylamino-5-naphthalenesulfonyl) group

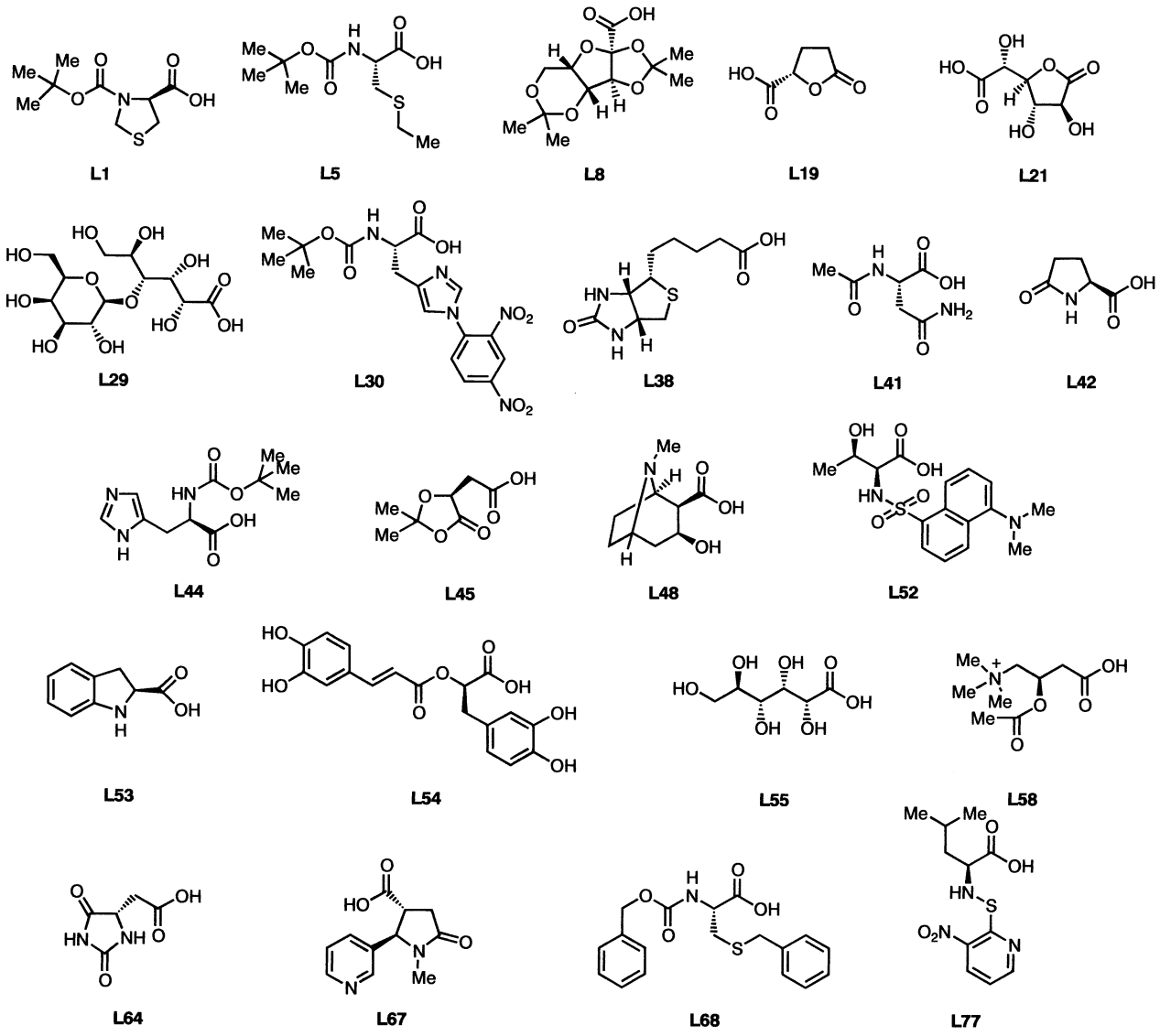


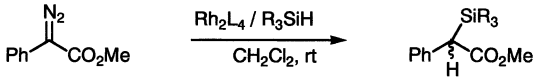
Figure 2. 22 Chiral carboxylic acids **L** which did not give dirhodium(II) species that were catalytically active in silane insertion reactions with diazoester **1**.

which generally gave good enantioselectivity, for example the chiral carboxylic acid ligand *N*-(1-dimethylamino-5-naphthalenesulfonyl)phenylalanine **L4** in an enantioselectivity of 48% and also *N*-(1-dimethylamino-5-naphthalenesulfonyl)proline **L6** in 47% ee. Chiral carboxylic acid ligands containing the *N*-(9-fluorenylmethoxycarbonyl) (Fmoc) protecting group also showed good enantioselectivities, for example *N*-(9-fluorenylmethoxycarbonyl)-(4*R*)-*tert*-butoxy-(*S*)-proline **L32** with an enantioselectivity of 46% and also *N*-(9-fluorenylmethoxycarbonyl)-*N*-methylphenylalanine **L35** in 44% ee.

Chiral carboxylic acid ligands based on proline are well documented in inducing enantioselectivity in a range of asymmetric rhodium carbene transformations. This is shown here for example with Davies' *N*-(4-*tert*-butylphenylsulfonyl)proline **L61** chiral carboxylic acid ligand,[32,33] which achieved an enantioselectivity of 41% and the valine-prolinate ligand **L72** in 47% ee. Davies subsequently reported that use of dirhodium(II) *N*-[(4-dodecylphenyl)sulfonyl]prolinate in the catalysed decomposition of diazoester **1** in the presence of dimethylphenylsilane resulted in the formation of **2a** in 51% ee, increased to 85% at −78°C.[17] *N*-Phthaloyl containing chiral carboxylic acid ligands are also well documented. In the enantioselective Si–H insertion reactions they also induced reasonable enantioselectivities, for example with Ikegami's *N*-phthaloyl-(*S*)-phenylalanine **L28** chiral carboxylic acid ligand,[34] with an enantioselectivity of 33% and *N*-phthaloyl-(*S*)-leucine **L24** in 41% ee. Recent work by the Japanese group has showed that the enantioselectivity exhibited by ligand **L28** increases to 74% if the reaction is conducted at −90°C.[18]

There were also the more unusual chiral carboxylic acid ligands that parallel synthesis methods allow to be screened because of the diversity of the technique, for example *N*-α-(benzyloxycarbonyl)-*N*′-ε-(4-toluenesulfonyl)lysine **L46** with an enantioselectivity of 41%. More interestingly though, this first set of parallel reactions also identified two chiral dirhodium(II) carboxylate catalysts of significant interest (shaded in Table 2). Firstly, the chiral carboxylic acid ligand based

Table 2. Parallel screening of chiral dirhodium(II) carboxylate catalysts in Si–H insertion reactions of methyl diazophenylacetate



1

2a $R_3 = PhMe_2$
2b $R_3 = t\text{-}BuMe_2$
2c $R_3 = i\text{-}Pr_3$

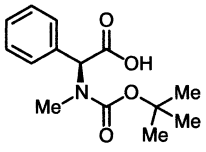
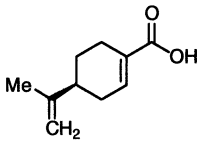
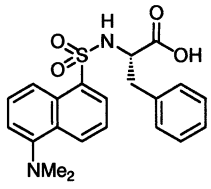
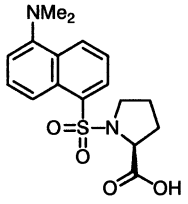
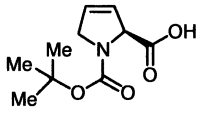
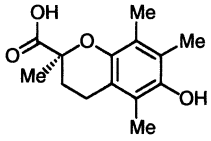
Cat	Chiral Carboxylic Acid Ligand L	Dirhodium(II) Carboxylate Catalyst (Rh_2L_4) Yield and spectroscopic data[a]	Enantioselectivity/% 2a	2b	2c
L2		16% yield δ_H (250 MHz; $CDCl_3$) 7.31 (12H, m, ArH), 7.17 (8H, m, ArH), 4.86 (4H, m, CH), 2.64 (12H, s, Me) and 1.26 (36H, s, CMe_3) *m/z* (LC-MS) 1281 (MNH_4^+).	2	15	18
L3		40% yield *m/z* (LC-MS) 867 (MH^+).	3	16	21
L4		47% yield δ_H (300 MHz; CD_3OD) 8.16 (12H, m, ArH), 7.41 (12H, m, ArH), 6.83 (20H, m, ArH), 3.92 (4H, dd, *J* 9.0, 5.0, CH), 2.91 (4H, dd, *J* 13.7, 5.1, CHH), 2.84 (24H, s, Me) and 2.68 (4H, dd, *J* 13.7, 9.1, CHH), NH not observed *m/z* (LC-MS) 1797 (MH^+).	25	43	48
L6		13% yield δ_H 8.40 (12H, m, ArH), 7.39 (12H, m, ArH), 4.53 (4H, t, *J* 6.1, CH), 3.46 (8H, m, CH_2), 2.88 (24H, s, Me), 2.13 (8H, m, CH_2) and 1.92 (8H, m, CH_2) *m/z* (LC-MS) 1596 (MH^+).	23	36	47
L7		12% yield *m/z* (LC-MS) 1073 (MNH_4^+).	8	17	25
L9		79% yield δ_H (250 MHz; DMSO) 2.39 (36H, m, Me), 2.05 (16H, m, CH_2), 1.98 (4H, m, OH) and 1.50 (12H, s, Me) *m/z* (LC-MS) 1221 (MNH_4^+).	32	38	32

Table 2. (*Continued*)

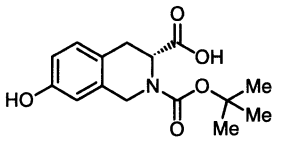
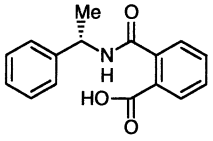
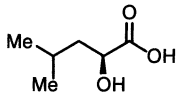
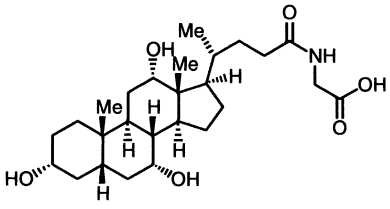
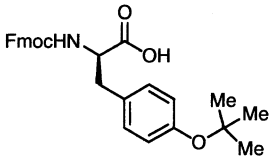
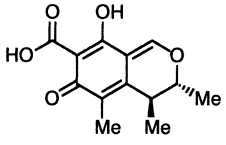
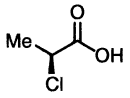
L10		53% yield δ_H (250 MHz; CD_3OD) 6.70 (12H, m, ArH), 4.98 (4H, m, CH), 4.35 (8H, m, CH_2), 2.98 (8H, m, $CHC\underline{H}_2$) and 1.38 (36H, s, CMe_3, OH not observed *m/z* (LC-MS) 1393 (MNH_4^+).	8	15	31
L11		75% yield δ_H 7.46 (36H, m, ArH), 4.12 (4H, q, *J* 7.1, CH) and 1.18 (12H, d, *J* 6.9, Me), NH not observed *m/z* (LC-MS) 1280 (MH^+).	8	2	10
L12		94% yield δ_H (250 MHz; CD_3OD) 3.82 (4H, m, CH), 1.52 (4H, m, $C\underline{H}Me_2$)), 1.23 (8H, m, CH_2) and 0.81 (24H, d, *J* 6.9, Me), OH not observed *m/z* (LC-MS) 748 (MNH_4^+).	23	39	53
L14		78% yield δ_H (250 MHz; CD_3OD) 3.98 (4H, m, CH), 3.82 (4H, m, CH), 3.70 (4H, m, CH), 3.48 (8H, m, CH_2), 2.38-1.25 (72H, m, CH_2), 1.04 (12H, m, Me), 0.96 (12H, s, Me) and 0.75 (12H, s, Me), OH not observed *m/z* (LC-MS) 2065 (MH^+).	1	1	0
L15		35% yield δ_H (250 MHz; $CDCl_3$) 7.72-6.78 (48H, m, ArH), 5.38 (4H, s, NH), 4.73 (4H, m, $CHCO_2$), 4.58 (4H, d, *J* 7.1, C$\underline{H}$H), 4.48 (4H, d, *J* 7.2, CH$\underline{H}$), 4.22 (4H, t, *J* 6.8, CH), 3.06 (8H, m, $CHC\underline{H}_2$) and 1.28 (36H, s, CMe_3) *m/z* (LC-MS) 2058 (MNH_4^+).	17	29	28
L17		52% yield δ_H (250 MHz; CD_3OD) 5.51 (4H, s, CH), 3.92 (4H, m, CH), 2.77 (4H, m, CH), 2.04 (12H, s, Me), 1.29 (12H, d, *J* 6.8, Me) and 1.15 (12H, d, *J* 6.9, Me), OH not observed *m/z* (LC-MS) 1281 [M+Formic]$^-$.	3	3	0
L18		95% yield δ_H 4.45 (4H, q, *J* 7.1, CH) and 1.74 (12H, d, *J* 6.8, Me) *m/z* (LC-MS) 637 (MH^+).	3	9	10

Table 2. (*Continued*)

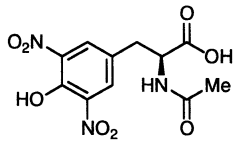
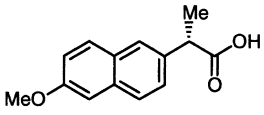
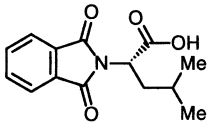
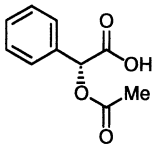
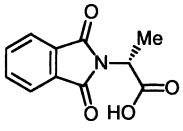
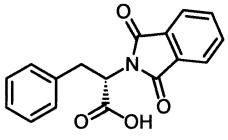
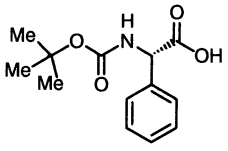
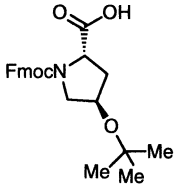
L20		69% yield δ_H 8.15 (8H, m, ArH), 4.11 (4H, m, CH), 2.71 (8H, m, CH_2) and 1.78 (12H, s, Me), OH and NH not observed *m/z* (LC-MS) 1472 (MNH_4^+).	0	32	48
L23		76% yield δ_H (300 MHz; DMSO) 7.43 (24H, m, ArH), 3.84 (12H, s, OMe), 3.48 (4H, m, CH) and 1.06 (12H, d, *J* 7.1, Me) *m/z* (LC-MS) 1140 (MNH_4^+).	3	11	15
L24		12% yield δ_H 7.68 (16H, m, ArH), 3.82 (4H, m, CH), 1.86 (4H, m, C<u>H</u>Me_2), 1.38 (8H, m, CH_2), 0.92 (12H, d, *J* 6.3, Me) and 0.87 (12H, d, *J* 6.5, Me) *m/z* (LC-MS) 1248 (MH^+).	23	32	41
L25		81% yield δ_H (300 MHz; CD_3OD) 7.26 (12H, m, ArH), 7.14 (8H, m, ArH), 5.74 (4H, s, CH) and 2.07 (12H, s, Me) *m/z* (FAB) 978 (M^+).	15	17	15
L27		72% yield δ_H 7.82 (8H, m, ArH), 7.61 (8H, m, ArH), 5.08 (8H, q, *J* 7.0, CH) and 1.53 (12H, d, *J* 7.2, Me) *m/z* (LC-MS) 1096 (MNH_4^+).	7	7	9
L28		99% yield δ_H 7.69 (20H, m, ArH), 7.09 (16H, m, ArH), 5.20 (4H, t, *J* 8.0, CH) and 3.51 (8H, d, *J* 8.1, CH_2) *m/z* (LC-MS) 1427 [M+Formic]$^-$.	22	37	33
L31		14% yield δ_H (250 MHz; $CDCl_3$) 7.29 (12H, m, ArH), 7.13 (8H, m, ArH), 4.82 (4H, m, CH) and 1.23 (36H, s, CMe_3), NH not observed *m/z* (LC-MS) 1225 (MNH_4^+).	2	4	5
L32		22% yield δ_H 7.82-7.21 (32H, m, ArH), 4.50 (8H, m, CH_2), 4.28 (4H, t, *J* 6.9, CH), 4.13 (4H, m, CH), 3.73 (8H, m, CH_2), 3.35 (4H, m, C<u>H</u>CO_2), 2.22 (8H, m, CH_2) and 1.21 (36H, s, CMe_3) *m/z* (LC-MS) 1858 (MNH_4^+).	37	42	46

Table 2. (*Continued*)

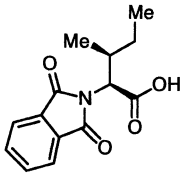
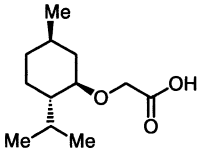
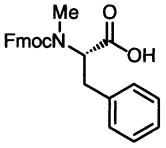
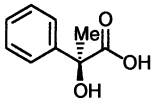
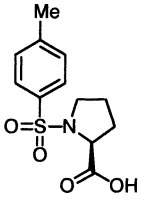
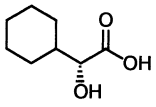
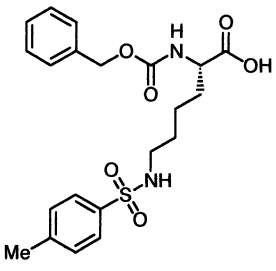
L33		35% yield δ_H (250 MHz; $CDCl_3$) 7.62 (4H, m, ArH), 4.62 (1H, d, J 7.1, C<u>H</u>CO_2), 2.21 (1H, m, CH), 1.29 (2H, m, CH_2), 0.84 (3H, d, *J* 6.9, CHMe) and 0.70 (3H, m, CH_2Me) *m/z* (LC-MS) 1265 (MNH_4^+).	4	25	31
L34		6% yield *m/z* (LC-MS) 1060 (MH^+).	1	7	32
L35		4% yield δ_H (250 MHz; $CDCl_3$) 7.81-6.85 (52H, m, ArH), 4.65 (4H, m, $CHCO_2$), 4.51 (8H, m, OCH_2), 4.22 (4H, m, CH), 2.89 (8H, m, $CHCH_2$) and 2.68 (12H, s, Me) *m/z* (LC-MS) 1809 (MH^+).	23	27	44
L39		74% yield δ_H (300 MHz; CD_3OD) 7.30 (8H, m, ArH), 7.17 (12H, m, ArH) and 1.25 (12H, s, Me), OH not observed *m/z* (FAB) 866 (M^+).	4	2	0
L40		12% yield δ_H (250 MHz; CD_3OD) 7.87 (8H, d, *J* 8.1, ArH), 7.48 (8H, d, *J* 8.2, ArH), 4.07 (4H, m, CH), 3.60 (8H, m, CH_2), 2.50 (12H, s, Me), 1.92 (8H, m, CH_2) and 1.55 (8H, m, CH_2) *m/z* (LC-MS) 1297 (MNH_4^+).	0	34	0
L43		70% yield δ_H (300 MHz; CD_3OD) 3.75 (4H, d, *J* 7.1 Hz, CH), 3.08 (4H, d, *J* 7.1 Hz, CH), 1.70 (8H, m, CH_2), 1.62 (16H, m, CH_2) and 1.20 (16H, m, CH_2), OH not observed *m/z* (FAB) 835 (MH^+).	7	18	9
L46		44% yield δ_H (250 MHz; $CDCl_3$) 7.68 (8H, m, ArH), 7.30 (8H, m, ArH), 7.20 (20H, m, ArH), 4.90 (8H, s, OCH_2), 4.18 (4H, m, C<u>H</u>CO_2), 2.78 (8H, m, C<u>H</u>$_2$NH), 2.28 (12H, s, Me) and 1.32 (24H, m, CH_2), NH not observed *m/z* (LC-MS) 1940 (M^+).	15	31	41

Table 2. (*Continued*)

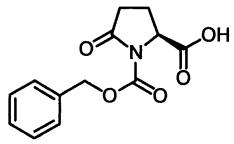
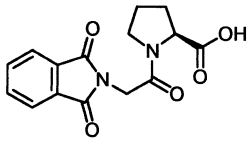
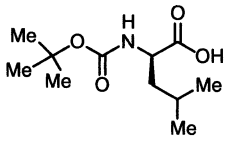
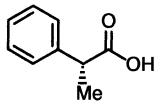
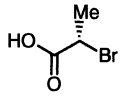
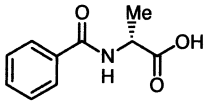
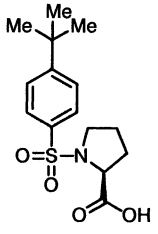
L50		75% yield δ_H 7.34 (20H, m, ArH), 4.93 (8H, s, CH_2), 4.70 (4H, m, CH) and 2.50 (16H, m, CH_2) *m/z* (LC-MS) 1272 (MNH_4^+).	27	32	35
L51		65% yield δ_H 7.80 (16H, m, ArH), 4.37 (8H, s, CH_2), 4.09 (4H, s, CH), 2.90 (16H, m, CH_2) and 1.80 (8H, m, CH_2) *m/z* (LC-MS) 1428 (MNH_4^+).	17	30	32
L56		9% yield δ_H (250 MHz; $CDCl_3$) 1.78 (4H, m, CH), 1.53 (8H, m, CH_2), 1.21 (36H, s, CMe_3), 0.86 (12H, d, *J* 6.9, Me) and 0.84 (12H, d, *J* 6.8, Me), NH not observed *m/z* (LC-MS) 1128 (MH^+).	16	15	18
L57		83 % yield δ_H (300 MHz; CD_3OD) 7.12 (12H, m, ArH), 7.02 (8H, m, ArH), 3.39 (4H, m, CH) and 1.18 (12H, d, *J* 7.1, Me) *m/z* (FAB) 802 (M^+).	1	2	6
L59		94% yield δ_H (300 MHz; CD_3OD) 4.18 (4H, q, *J* 6.8, CH) and 1.58 (12H, d, *J* 6.8, Me) *m/z* (LC-MS) 831 (MNH_4^+).	5	8	3
L60		49% yield δ_H (300 MHz; CD_3OD) 7.68 (8H, m, ArH), 7.41 (4H, m, ArH), 7.27 (8H, m, ArH), 4.38 (4H, q, *J* 7.3, CH) and 1.22 (12H, d, *J* 6.7, Me), NH not observed *m/z* (LC-MS) 975 (MH^+).	25	23	28
L61		7% yield δ_H (250 MHz; CD_3OD) 7.85 (8H, d, *J* 8.0, ArH), 7.53 (8H, d, *J* 8.1, ArH), 4.10 (4H, m, CH), 3.60 (8H, m, CH_2), 1.92 (8H, m, CH_2), 1.58 (8H, s, CH_2) and 1.32 (36H, m, CMe_3) *m/z* (LC-MS) 1447 (M^+).	8	34	41

Table 2. (*Continued*)

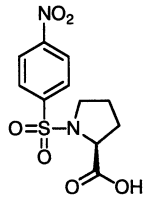
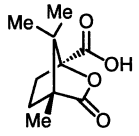
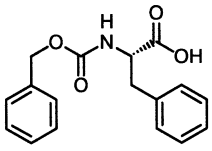
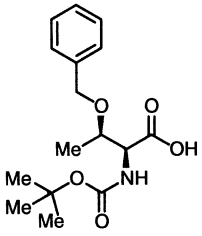
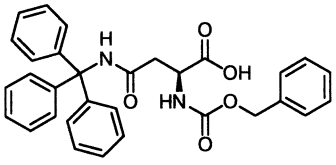
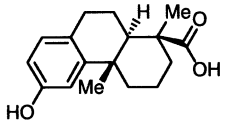
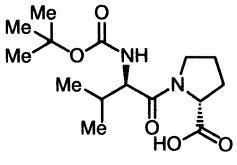
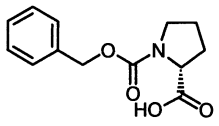
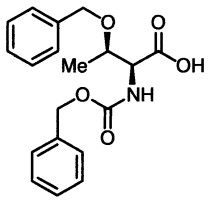
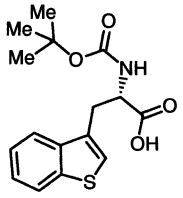
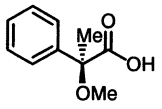
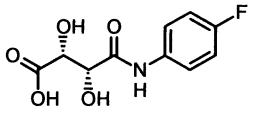
L62		65% yield δ_H (250 MHz; CD_3OD) 8.18 (8H, d, *J* 7.0, ArH), 7.80 (8H, d, *J* 7.1, ArH), 4.17 (4H, s, CH), 3.62 (8H, m, CH_2), 1.94 (8H, m, CH_2) and 1.61 (8H, m, CH_2) *m/z* (LC-MS) 1420 (MNH_4^+).	14	29	33
L65		33% yield *m/z* (LC-MS) 1012 (MNH_4^+)	13	12	15
L66		13% yield δ_H 7.31 (40H, m, ArH), 4.47 (8H, s, OCH_2), 4.20 (4H, m, CH) and 3.07 (8H, m, CH_2), NH not observed *m/z* (LC-MS) 1400 (MH^+).	32	41	43
L69		17% yield δ_H (250 MHz; $CDCl_3$) 7.21 (20H, m, ArH), 5.12 (4H, m, CH), 4.45 (4H, m, CH), 4.31 (8H, s, CH_2), 1.72 (12H, m, Me) and 1.28 (36H, s, CMe_3), NH not observed *m/z* (LC-MS) 1440 (MH^+).	5	4	20
L70		58% yield δ_H 7.21 (80H, m, ArH), 5.10 (8H, s, OCH_2), 4.50 (4H, t, *J* 6.2, CH) and 2.84 (8H, d, *J* 6.5, CH_2), NH not observed *m/z* (LC-MS) 2236 (M^+).	18	1	6
L71		27% yield δ_H (300 MHz; CD_3OD) 6.81 (4H, m, ArH), 6.69 (4H, m, ArH), 6.49 (4H, m, ArH), 2.70 (8H, m, CH_2), 2.22 (8H, m, CH_2), 2.14 (4H, m, CH_2), 1.98 (8H, m, CH_2), 1.58, (8H, m, CH_2), 1.37 (8H, m, CH_2), 1.28 (12H, s, Me) and 1.14 (12H, s, Me), OH not observed *m/z* (LC-MS) 1317 (MNH_4^+).	18	7	29
L72		48% yield δ_H 7.81 (4H, bs, NH), 5.42 (4H, m, CH), 4.58 (4H, m, C<u>H</u>Me_2), 4.28 (4H, m, CH), 3.74 (8H, m, CH_2), 2.19 (8H, m, CH_2), 2.02 (8H, m, CH_2), 1.43 (36H, s, CMe_3), 1.00 (12H, d, *J* 6.7, Me) and 0.93 (12H, d, *J* 6.7, Me) *m/z* (LC-MS) 1477 (MNH_4^+).	38	45	47

Table 2. (*Continued*)

L73		65% yield δ_H 7.37 (20H, m, ArH), 5.13 (8H, s, CH_2), 4.43 (4H, m, CH), 3.35 (8H, m, CH_2), 2.30 (8H, m, CH_2) and 1.62 (8H, m, CH_2) *m/z* (LC-MS) 1272 (MNH_4^+).	24	14	35
L74		68% yield δ_H 7.28 (40H, m, ArH), 5.11 (4H, m, CH), 4.50 (4H, m, CH), 4.26 (8H, s, OCH_2), 2.87 (8H, s, CH_2) and 1.76 (12H, m, Me), NH not observed *m/z* (LC-MS) 1593 (MNH_4^+).	4	23	33
L75		22% yield δ_H 7.83 (4H, s, ArH), 7.38 (16H, s, ArH), 4.60 (4H, m, CH), 3.09 (8H, m, CH_2) and 0.97 (36H, s, CMe_3), NH not observed *m/z* (LC-MS) 1488 (MH^+).	19	18	16
L78		64% yield δ_H 7.28 (8H, m, ArH), 7.16 (12H, m, ArH), 2.77 (12H, s, OMe) and 1.34 (12H, s, Me) *m/z* (FAB) 922 (M^+).	4	12	16
L79		52% yield δ_H 7.60 (8H, m, ArH), 7.05 (8H, m, ArH) and 4.49 (8H, m, CH), OH and NH not observed *m/z* (LC-MS) 1175 (MH^+).	15	14	17
L80		commercially available catalyst (control experiment)	0	0	0

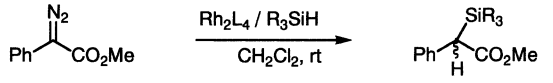
[a] NMR spectra recorded at 300 MHz in $CDCl_3$ unless otherwise stated.

on an *N*-arenesulfonyl α-amino acid substructure, *N*-(1-dimethylamino-5-naphthalenesulfonyl)phenylalanine **L4**, gave enantioselectivities up to 48% using the most sterically hindered silane, tri-isopropylsilane. The chiral carboxylic acid ligand based on an α-hydroxy acid substructure, (*S*)-α-hydroxy-isocaproic acid **L12**, gave enantioselectivities up to 53%, also with tri-isopropylsilane. Already these results are an improvement on those initially reported in Table 1, and therefore formed the basis of the second generation parallel screen.

Having now identified these two chiral carboxylic acid ligands, **L4** and **L12**, a second generation array was then constructed to improve further the enantioselectivity of the Si–H insertion reaction by utilising a substructure search. This involved looking back over the array at the specific sub-groups from which these two chiral carboxylic acid ligands were identified from and then to synthesise further catalysts from these chiral ligands containing the *N*-arenesulfonyl α-amino acid and α-hydroxy acid substructures. The results of these second sets of parallel reactions are shown in Table 3 for the *N*-arenesulfonyl α-amino acid ligands **L4/1**–**L4/5** and Table 4 for the α-hydroxy acid ligands **L12/1**–**L12/8**. The dirhodium(II) carboxylates derived from ligands **L4/2**, **L4/3** and **L4/5** were also prepared conventionally, as were three additional catalysts from ligands **L4/6**–**L4/8**.[35]

These second sets of parallel reactions identified further chiral dirhodium(II) carboxylate catalysts capable of effecting enantioselective Si–H insertion reactions, and although the α-hydroxy acid ligands gave generally poor results in silane insertion reactions (Table 4), the *N*-arenesulfonyl α-amino acid ligands generally showed greater promise (Table 3). In an attempt to improve enantioselectivity, the Si–H insertion reactions were then repeated at −78°C in dichloromethane, with the most hindered

Table 3. Second generation parallel screening of chiral dirhodium(II) *N*-arenesulfonyl α-aminocarboxylates in Si–H insertion reactions of methyl diazophenylacetate



1

2a $R_3 = PhMe_2$
2b $R_3 = t\text{-}BuMe_2$
2c $R_3 = i\text{-}Pr_3$

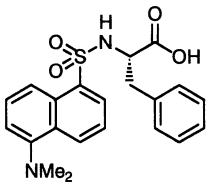
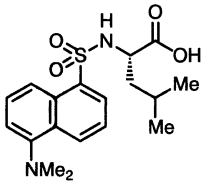
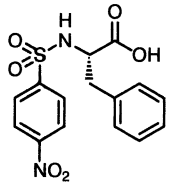
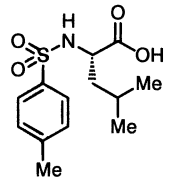
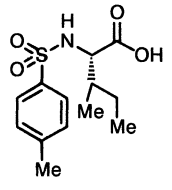
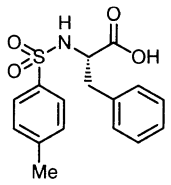
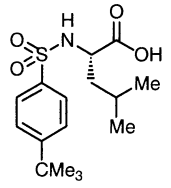
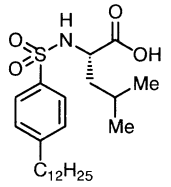
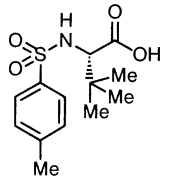
Cat	Chiral Carboxylic Acid Ligand L	Dirhodium(II) Carboxylate Catalyst (Rh_2L_4) Yield and spectroscopic data	Enantioselectivity/% (Yield/%) 2a	2b	2c
L4		as Table 2	25	43	48 LT; 52 (11)
L4/1		19% yield δ_H (250 MHz; $CDCl_3$) 8.42 (12H, m, ArH), 8.02 (12H, m, ArH), 5.50 (4H, s, NH), 4.02 (4H, m, CH), 2.82 (24H, s, Me), 1.52 (4H, m, C<u>H</u>Me_2), 1.28 (8H, m, CH_2), 0.88 (12H, d, *J* 6.6, $CHMe_2$) and 0.84 (12H, d, *J* 6.7, $CHMe_2$) *m/z* (FAB) 1661 (M^+)	32	57	61
L4/2		78% yield (parallel synthesis) 95% yield (conventional synthesis) For spectroscopic data, see Experimental Section.	23 P; 21 (22)	48	55 LT; 64 (31) P; 36 (1)
L4/3		15% yield (parallel synthesis) 81% yield (conventional synthesis) For spectroscopic data, see Experimental Section.	21 P; 27 (47)	44	49 LT; 76 (52) P; 40 (2)
L4/4		35% yield δ_H (250 MHz; $CDCl_3$) 7.70 (8H, d, *J* 8.6, ArH), 7.21 (8H, d, *J* 8.5, ArH), 5.73 (4H, m, NH), 3.54 (4H, m, CH), 2.42 (12H, s, Me), 1.61 (4H, m, C<u>H</u>Me), 0.89 (8H, m, CH_2) and 0.61 (24H, m, Me) *m/z* (FAB) 1343 (MH^+).	7	27	42 LT; 73 (19)

Table 3. (*Continued*)

L4/5		40% yield (parallel synthesis) 94% yield (conventional synthesis) For spectroscopic data, see Experimental Section.	21	35	39 LT; 56 (25)
L4/6		98% yield (conventional synthesis) For spectroscopic data, see ref 35.	13 (79) P; 28 (61)	32 (82)	31 (44) LT; 52 (27) P; 39 (9)
L4/7		21% yield (conventional synthesis) For spectroscopic data, see ref 35.	32 (76) P; 31 (68)	40 (78)	42 (40) LT; 49 (37) P; 44 (21)
L4/8		91% yield (conventional synthesis) For spectroscopic data, see ref 35.	31 (83) P; 21 (63)	38 (75)	40 (17) LT; 59 (7) P; 29 (4)

LT = low temperature (-78 °C); P = pentane as solvent at -78 °C

silane, tri-isopropylsilane. As can be seen from Tables 3 and 4, in some, but not all cases, carrying out the reactions at −78°C resulted in further improvement of the enantioselectivity. The *N*-arenesulfonyl α-amino acids all showed improvements in enantioselectivity under these conditions, although no further improvement was observed upon changing the solvent to pentane (Table 3). The chiral carboxylic acid ligand *N*-(4-toluenesulfonyl)-(*S*)-leucine **L4/3** proved the best, improving from 49 to 76% ee at low temperature; this compares very favourably with enantioselectivities observed in other studies,[17,18] although we have not fully optimised the reaction conditions (temperature, solvent). The resulting silylester **2c** (76% ee) was reduced with DIBAL to give the alcohol **17**; acylation with 4-bromobenzoyl chloride gave the ester **18**, obtained in 94% ee after a single recrystallisation (Scheme 1)

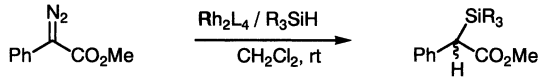
Other silanes were also screened in the enantioselective Si–H insertion reaction, tri-isobutylsilane, tris(trimethylsilyl)silane and 1,1,1,3,5,5,5-heptamethylsiloxane, in the presence of the diazoester **1**, and one of each of the chiral dirhodium(II) carboxylate catalysts from the first and second sets of parallel reactions, to yield the expected Si–H insertion products **2d–f** in each case. The catalyst derived from the chiral carboxylic acid ligand, *N*-(4-toluenesulfonyl)-(*S*)-phenylalanine **L4/5**, gave consistently the greatest enantioselectivities for the Si–H insertion product, **2d** in 50% ee, **2e** in 55% ee and **2f** in 44% ee respectively (Scheme 2).

Finally, the diazolactone, dihydro-3-diazo-4,4-dimethyl-2-furanone **19**, was also screened in the enantioselective Si–H insertion reaction with the previous silanes. Although the racemic silane insertion products **20a** and **20b** could be obtained in reasonable yield using dirhodium(II) acetate as catalyst (Scheme 3), the system was not suitable for parallel screening due to the non-trivial purification of the Si–H insertion products.

2.1. Determination of the absolute stereochemistry of the Si–H insertion product 2a

In order to determine the stereochemical outcome of the silane insertion reactions, i.e. does an (*S*) chiral dirhodium(II) carboxylate catalyst induce (*S*) or (*R*) enantioselectivity in the Si–H insertion product, the conversion of the methyl 2-(silyl)phenylacetates **2** into compounds of known absolute configuration was investigated. This was most conveniently done on the phenyldimethylsilyl derivative **2a** and involved reduction of the ester to alcohol **21** followed by Tamao–Fleming oxidation of the C–Si bond using the procedure published by Landais and Planchenault[36] to give phenyl-1,2-ethanediol (Scheme 4).

Table 4. Second generation parallel screening of chiral dirhodium(II) α-hydroxycarboxylates in Si–H insertion reactions of methyl diazophenylacetate



1

2a $R_3 = PhMe_2$
2b $R_3 = t\text{-}BuMe_2$
2c $R_3 = i\text{-}Pr_3$

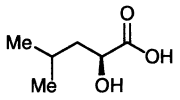
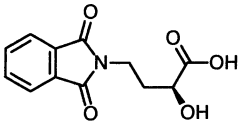
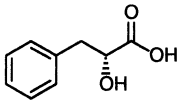
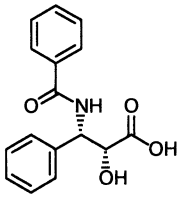
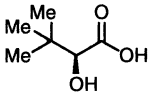
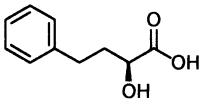
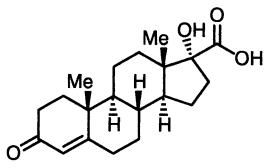
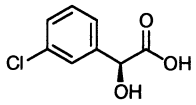
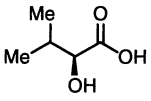
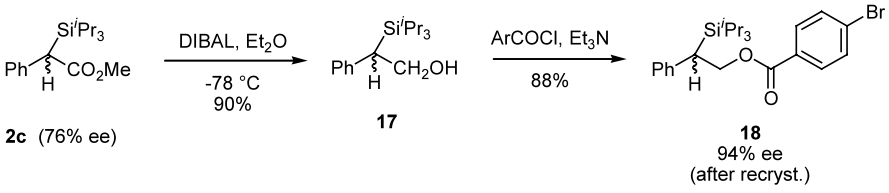
Cat	Chiral Carboxylic Acid Ligand L	Dirhodium(II) Carboxylate Catalyst (Rh_2L_4) Yield and spectroscopic data	Enantioselectivity/% (Yield/%) 2a	2b	2c
L12		as Table 2.	23	39	53 LT; 38 (31)
L12/1		79% yield δ_H (300 MHz; CD_3OD) 7.84 (16H, m, ArH), 4.21 (4H, m, CH), 3.86 (8H, m, CH_2), 2.10 (8H, m, CH_2), OH not observed *m/z* (FAB) 1199 (MH^+).	29	42	46 LT; 54 (27)
L12/2		59% yield δ_H (300 MHz; CD_3OD) 7.19 (8H, m, ArH), 7.13 (12H, m, ArH), 4.05 (4H, m, CH), 2.89 (4H, dd, *J* 13.7, 4.2, CHH), 2.61 (4H, dd, *J* 13.9, 8.1, CHH), OH not observed *m/z* (FAB) 866 (M^+).	15	26	41 LT; 30 (40)
L12/3		67% yield δ_H (300 MHz; CD_3OD) 7.68 (8H, m, ArH), 7.30 (12H, m, ArH), 7.11 (20H, m, ArH), 5.18 (4H, m, CH), 3.79 (4H, m, CH), OH and NH not observed *m/z* (FAB) 1344 (MH^+).	30	32	39 LT; 31 (44)
L12/4		19% yield δ_H (250 MHz; $CDCl_3$) 4.22 (4H, s, CH), 1.22 (36H, s, CMe_3), OH not observed *m/z* (FAB) 731 (MH^+).	11	24	34 LT; 30 (11)
L12/5		72% yield δ_H (250 MHz; CD_3OD) 7.21 (20H, m, ArH), 4.07 (4H, m, CH), 2.89 (8H, m, CH_2), 2.59 (8H, t, *J* 7.1, CH_2), OH not observed *m/z* (LC-MS) 923 (MH^+).	6	28	29 LT; 33 (30)

Table 4. (*Continued*)

L12/6		22% yield δ_H (250 MHz; DMSO) 5.62 (4H, m, CH), 2.40-0.87 (76H, m, 3CH and 8CH_2), 1.12 (12H, s, Me), 0.70 (12H, s, Me), OH not observed *m/z* (LC-MS) 1532 (MH^+).	9	23	26 LT; 20 (5)
L12/7		80% yield δ_H (250 MHz; CD_3OD) 7.18 (12H, m, ArH), 7.00 (4H, m, ArH), 4.66 (4H, s, CH), OH not observed *m/z* (LC-MS) 966 (MNH_4^+).	4	6	10 LT; 17 (27)
L12/8		26% yield δ_H (250 MHz; CD_3OD) 3.70 (4H, m, CH), 1.76 (4H, m, C<u>H</u>$(CH_3)_2$), 1.09 (12H, d, *J* 6.8, Me), 0.97 (12H, d, *J* 6.7, Me), OH not observed *m/z* (LC-MS) 692 (MNH_4^+).	1	2	10 LT; 12 (19)

LT = low temperature (-78 °C)



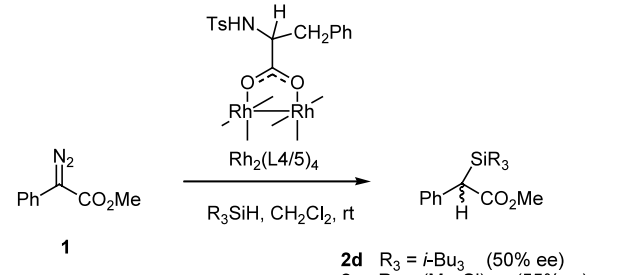
2c (76% ee) **17** **18** 94% ee (after recryst.)

Scheme 1.

Hence the absolute configuration of the major enantiomer of was readily determined by comparison of known specific rotations of the product 1,2-diol. In common with other studies,[17,18] we find that there is no general pattern; (*S*)-configured catalysts often give (*S*)-configured silylester **2a** but not always.

3. Conclusion

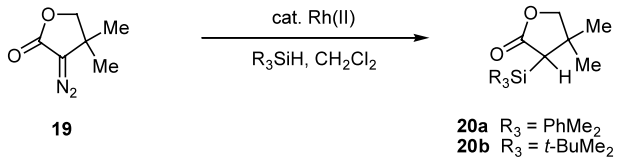
This parallel synthesis technique has enabled us to identify several chiral dirhodium(II) carboxylates capable of effecting enantioselective Si–H insertion reactions using methyl diazophenylacetate **1**. It is interesting that catalysts based on α-hydroxyacids and *N*-arenesulfonyl α-amino acids emerged as the most generally useful families; such catalysts were among the earliest chiral dirhodium-(II) carboxylate catalysts investigated, although the first studied ligands, mandelic acid and *N*-benzenesulfonyl-prolinate, give relatively poor results in our silane insertion reactions (8 and 12% ee, respectively, for Me_2PhSiH). Although the reactions have not been fully optimised in terms of temperature and solvent, the use of parallel synthesis techniques has resulted in the rapid identification of improved catalysts for enantioselective Si–H insertion reaction of diazoesters with silanes.



1

2d R_3 = *i*-Bu_3 (50% ee)
2e R_3 = $(Me_3Si)_3$ (55%ee)
2f R_3 = $Me(Me_3SiO)_2$ (44%ee)

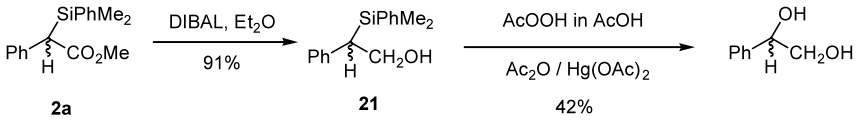
Scheme 2.



19

20a R_3 = $PhMe_2$
20b R_3 = *t*-$BuMe_2$

Scheme 3.



2a 21

Scheme 4.

4. Experimental

4.1. General information

Commercially available solvents and reagents were utilised throughout with no further purification, other than of those detailed below. 'Light petroleum' refers to the fraction boiling between 40 and 60°C and was distilled from calcium chloride through a 36 cm Vigreux column before use. Diethyl ether and ethyl acetate were purified in the same manner prior to use. Dichloromethane was purified and dried by distillation from phosphorus pentoxide. Toluene was distilled over calcium hydride before being stored under nitrogen and over activated 4 Å molecular sieves. Tetrahydrofuran was distilled from sodium benzophenone ketyl whilst under nitrogen prior to use.

Analytical thin-layer chromatography (TLC) was carried out using aluminium backed plates coated with Merck Kieselgel 60 GF_{254}. All developed plates were visualised under UV light at 254 nm and/or by staining with ammonium molybdate and permanganate dips. Flash silica gel chromatography was carried out using Merck Kieselgel 60 H silica and pressure was applied at the column head using hand bellows. Samples were applied to the separation column either pre-adsorbed onto silica or as a saturated solution in an appropriate solvent. Chiral high performance liquid chromatography (HPLC) was performed using either a Thermo Separation Products instrument or a Gilson automated system at 265 nm. The Thermo Separation Products chromatographic system used a Daicel Chemical Industries, Ltd. Chiralpak AD or a Chiralcel OD HPLC column (diameter 0.46 cm, length 25 cm). The Gilson automated chromatographic system used an (*S*,*S*)-WHELK-01 HPLC column (diameter 0.46 cm, length 25 cm).

IR spectra were recorded in the range 4000–600 cm^{-1} using a Nicolet FT-205 spectrometer with internal calibration. Spectra were recorded using potassium bromide disks or as either solutions in chloroform or thin films using sodium chloride plates. ^1H NMR spectra were recorded using Bruker AC-250 (250 MHz), Bruker AC-300 (300 MHz) and Bruker DPX-400 (400 MHz) instruments. ^{13}C NMR spectra were recorded on Bruker AC-250 (62.9 MHz) and Bruker DPX-400 (100.6 MHz) instruments. ^1H NMR spectra were referenced against tetramethylsilane at 0.00 ppm and residual chloroform at 7.27 ppm. Chemical shift values δ_H and δ_C are accurate to ±0.01 ppm and ±0.10 ppm respectively. Signals are described as being broad (br), singlets (s), doublets (d), triplets (t), quartets (q), multiplets (m), double doublets (dd), double triplets (dt), etc. High-resolution mass spectra were recorded on a Kratos MS80 instrument by electron impact (EI), unless otherwise. Liquid chromatography–mass spectra (LC–MS) were recorded on an automated Micromass Platform LC instrument.

4.1.1. Methyl 2-diazophenylacetate 1. Prepared using the Bamford–Stevens reactions.[37]

4.1.2. Dihydro-3-diazo-4,4-dimethyl-2-furanone 19. To a stirred solution of dihydro-4,4-dimethyl-2,3-furandione (2.50 g, 19.51 mmol) in dry toluene (100 mL) was added 4-toluenesulfonylhydrazide (3.63 g, 19.51 mmol). After heating under Dean and Stark conditions overnight the reaction mixture was allowed to cool and triethylamine (19.74 g, 195.11 mmol) was added dropwise. After stirring overnight the solvent was removed under reduced pressure to yield a golden yellow oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (4:1) as eluant to yield the *title compound* as a bright yellow oil (0.63 g, 23%); (Found: M^+, 140.0585. $C_6H_8N_2O_2$ requires 140.0586); ν_{max} (film)/cm^{-1} 2968, 2093, 1734, 1464, 1145; δ_H (400 MHz; $CDCl_3$) 4.05 (2H, s, CH_2), 1.42 (6H, s, Me); δ_C (100.6 MHz; $CDCl_3$) 169.1 (C=O), 78.5 (CH_2), 59.0 (C=N_2), 38.9 (C), 25.9 (Me); *m*/*z* 140 (M^+, 77%), 125 (76), 82 (20), 71 (11), 67 (100), 55 (52), 53 (62).

4.2. Catalysts: dirhodium(II) tetrakis(carbonate)

Prepared by the literature procedure.[31] A stirred suspension of dirhodium(II) acetate (0.50 g, 1.13 mmol) in 2 M aqueous sodium carbonate solution (13.33 mL) was heated at 85°C for 30 min during which time the green colour changed to a blue purple. Cooling and filtration gave a purple solid which was subsequently washed with water (25 mL), methanol (25 mL) and ether (25 mL) and then dried to yield the *title compound* as a purple powdery solid (0.63 g, 1.02 mmol, 90%). This was then used in subsequent reactions without further purification.

4.2.1. Dirhodum(II) tetrakis((1*R*,2*S*,5*R*)-(−)-menthyl (2-carboxy)benzoate) 4. (a) To a stirred solution of (−)-menthol (0.62 g, 3.97 mmol), phthalic anhydride (1.00 g, 6.75 mmol) and 4-dimethylaminopyridine (0.10 g, 0.81 mmol) in dioxane (5 mL) under a nitrogen atmosphere was added triethylamine (0.60 g, 5.95 mmol) dropwise. After stirring overnight ether (50 mL) was added and the reaction mixture washed with aqueous hydrochloric acid (2 M) (50 mL). The aqueous phase was then extracted with ether (2×50 mL). The organic extracts were combined, dried ($MgSO_4$) and the solvent was then removed under reduced pressure to yield a

colourless oily residue. Carbon tetrachloride (20 mL) was added and the solution filtered. Removal of the solvent under reduced pressure yielded a colourless solid. Recrystallisation from chloroform and light petroleum yielded *(1R,2S,5R)-(−)-menthyl (2-carboxy)benzoate* as a colourless solid (0.58 g, 48%), mp 108–109°C (lit.,[38] mp 111°C); $[\alpha]_D^{20} = -90.0$ (*c* 1.0, $CHCl_3$) (lit.,[38] $[\alpha]_D^{20} = -89.2$ (*c* 5.0, $CHCl_3$)); (Found: C, 70.7; H, 8.1. $C_{18}H_{24}O_4$ requires C, 71.0; H, 8.0%); (Found: M^+, 304.1668. $C_{18}H_{24}O_4$ requires 304.1674); ν_{max} ($CHCl_3$)/cm^{-1} 3500–2500, 3023, 2957, 1703, 1600, 1453, 1291, 739; δ_H (250 MHz; $CDCl_3$) 11.25–10.75 (1H, bs, OH), 7.91 (2H, m, ArH), 7.59 (2H, m, ArH), 4.98 (1H, m, 1-H_{ax}), 2.23 (1H, m, 6-H_{eq}), 1.98 (1H, m, 6-H_{ax}), 1.71 (2H, m, 3-H_{eq} and 4-H_{eq}), 1.50 (2H, m, 3-H_{ax} and 4-H_{ax}), 1.48 (2H, m, 2-H_{ax} and 5-H_{ax}), 1.10 (1H, m, C$\underline{H}Me_2$), 0.94 (3H, d, *J* 6.5, 5-Me), 0.90 (3H, d, *J* 7.0, $CHMe_2$), 0.84 (3H, d, *J* 7.0, $CHMe_2$); δ_C (62.9 MHz; $CDCl_3$) 172.4 (C=O), 167.6 (C=O), 134.1 (C), 134.0 (C), 132.1 (ArC), 130.5 (ArC), 129.7 (ArC), 128.5 (ArC), 75.9 (1-CH), 47.0 (2-CH), 40.2 (6-CH_2), 34.1 (4-CH_2), 31.4 ($\underline{C}HMe_2$), 26.1 (5-CH), 23.3 (3-CH_2), 21.9 (5-Me), 20.7 ($CHMe_2$), 16.1 ($CHMe_2$); *m*/*z* 305 (M^+, 24%), 167 (98), 149 (100), 138 (67), 123 (36), 95 (74), 81 (57), 55 (30).

(b) Dirhodium(II) acetate (100 mg, 0.23 mmol) and (1*R*,2*S*,5*R*)-(−)-menthyl (2-carboxy)benzoate (825 mg, 2.71 mmol) were fused together at 160°C for a period of 48 h in the absence of solvent. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (4:1) as eluant to yield the *title compound* as a green powdery solid (195 mg, 61%), mp 165–166°C; $[\alpha]_D^{22} = -90.0$ (*c* 0.1, $CHCl_3$); (Found: C, 60.7; H, 6.3. $C_{72}H_{92}O_{16}Rh_2$ requires C, 60.9; H, 6.5%); (Found: M^+, 1418.4544. $C_{72}H_{92}O_{16}Rh_2$ requires 1418.4539); ν_{max} ($CHCl_3$)/cm^{-1} 3020, 2957, 1724, 1598, 1453, 1216, 739; δ_H (250 MHz; $CDCl_3$) 7.90–7.33 (16H, m, ArH), 4.55 (4H, m, 1-H_{ax}), 2.05 (4H, m, 6-H_{eq}), 1.89 (4H, m, 6-H_{ax}), 1.59 (8H, m, 3-H_{eq} and 4-H_{eq}), 1.33–0.93 (20H, m, 2-H_{ax}, 3-H_{ax}, 4-H_{ax}, 5-H_{ax} and C$\underline{H}Me_2$), 0.85 (12H, d, *J* 7.2, 5-Me), 0.82 (12H, d, *J* 6.9, $CHMe_2$), 0.75 (12H, d, *J* 6.9, $CHMe_2$); δ_C (62.9 MHz; $CDCl_3$) 187.3 (C=O), 166.3 (C=O), 135.4 (C), 131.3 (ArC), 130.3 (ArC), 129.4 (ArC), 129.1 (ArC), 127.7 (C), 75.2 (1-CH), 47.1 (2-CH), 40.3 (6-CH_2), 34.3 (4-CH_2), 31.4 ($\underline{C}HMe_2$), 26.3 (5-CH), 23.4 (3-CH_2), 22.0 (5-Me), 20.9 ($CHMe_2$), 16.3 ($CHMe_2$); *m*/*z* (FAB) 1418 (M^+, 9%), 849 (50), 701 (42), 481 (99), 459 (99), 414 (100), 345 (84).

4.2.2. Dirhodium(II) tetrakis((*S*)-1-(1-phenylethyl)-pyrrole-2-carboxylate) 5. (a) To a stirred solution of (*S*)-(−)-1-phenylethylamine (5.00 g, 41.26 mmol) in toluene (70 mL) was added acetic acid (70 mL) followed by 2,5-dimethoxy tetrahydrofuran (6.54 g, 49.51 mmol). After heating under reflux for 24 h the solvent was removed under reduced pressure to yield a black oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (97:3) as eluant to yield *(S)-1-(1-phenylethyl)pyrrole* as a colourless oil (6.62 g, 94%), $[\alpha]_D^{20} = +40.0$ (*c* 1.0, EtOH) (lit.,[39] $[\alpha]_D^{25} = +46.0$ (*c* 0.9, EtOH)); (Found: M^+, 171.1046. $C_{12}H_{13}N$ requires 171.1048); ν_{max} (film)/cm^{-1} 3029, 2980, 1491, 1450, 725; δ_H (250 MHz; $CDCl_3$) 7.27 (3H, m, ArH), 7.08 (2H, m, ArH), 6.75 (2H, m, 2-H and 5-H), 6.18 (2H, m, 3-H and 4-H), 5.25 (1H, q, *J* 7.0, CH), 1.82 (3H, d, *J* 7.0, Me); δ_C (62.9 MHz; $CDCl_3$) 143.5 (C), 128.6 (ArC), 127.4 (ArC), 125.8 (ArC), 119.4 (2-CH and 5-CH), 108.0 (3-CH and 4-CH), 58.1 (CH), 22.1 (Me); *m*/*z* 171 (M^+, 70%), 117 (22), 105 (100), 77 (32), 67 (75).

(b) To a stirred solution of (*S*)-1-(1-phenylethyl)pyrrole (5.00 g, 29.20 mmol) in dry tetrahydrofuran (100 mL) under a nitrogen atmosphere at 0°C was added trifluoroacetic anhydride (14.72 g, 70.08 mmol) dropwise. After stirring for 2 h the solvent was removed under reduced pressure to yield a yellow oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (19:1) as eluant to yield *(S)-1-(1-phenylethyl)-2-trifluoroacetylpyrrole* as a pale yellow oil (5.84 g, 75%), $[\alpha]_D^{20} = -96.4$ (*c* 1.0, $CHCl_3$); (Found: M^+, 267.0872. $C_{14}H_{12}F_3NO$ requires 267.0871); ν_{max} (film)/cm^{-1} 3032, 2985, 1668, 1495, 1450, 736; δ_H (250 MHz; $CDCl_3$) 7.29 (5H, m, Ph), 7.16 (2H, m, 3-H and 5-H), 6.53 (1H, q, *J* 7.0, CH), 6.31 (1H, m, 4-H), 1.80 (3H, d, *J* 7.1, Me); δ_C (62.9 MHz; $CDCl_3$) 169.9 (C=O), 141.4 (C), 130.9 (3-CH), 128.7 (ArC), 127.7 (ArC), 126.3 (ArC), 124.9 (5-CH), 124.8 (C), 110.5 (4-CH), 56.7 (CH), 22.0 (Me), CF_3 not observed; *m*/*z* 267 (M^+, 23%), 198 (8), 105 (100), 77 (12).

(c) To a stirred solution of (*S*)-1-(1-phenylethyl)-2-trifluoroacetylpyrrole (1.00 g, 3.74 mmol) in *N*,*N*-dimethylformamide (50 mL) was added lithium hydroxide (0.90 g, 37.42 mmol). After stirring at 70°C overnight the reaction mixture was partitioned between water (100 mL) and ether (100 mL). The organic phase was removed and the aqueous phase was acidified to pH 1 with aqueous hydrochloric acid (2 M) and then extracted with ethyl acetate (3×100 mL). The organic extracts were combined, washed with saturated brine (100 mL), dried ($MgSO_4$) and the solvent was removed under reduced pressure to yield a pale brown oil. Ether (50 mL) was added and the reaction mixture was subsequently washed with water (3×50 mL), dried ($MgSO_4$) and the solvent was then removed under reduced pressure to yield a pale yellow solid. Recrystallisation from ethyl acetate and light petroleum yielded *(S)-1-(1-phenylethyl)pyrrole-2-carboxylate* as colourless crystals (0.55 g, 68%), mp 85–86°C; $[\alpha]_D^{20} = -195.2$ (*c* 1.0, $CHCl_3$); (Found: M^+, 215.0944. $C_{13}H_{13}NO_2$ requires 215.0946); (Found: C, 72.5; H, 6.1; N, 6.4. $C_{13}H_{13}NO_2$ requires C, 72.5; H, 6.1; N, 6.5%) ν_{max} ($CHCl_3$)/cm^{-1} 3420, 3054, 2985, 1668, 1494, 1430, 739; δ_H (250 MHz; $CDCl_3$) 7.30 (2H, m, ArH), 7.25 (1H, m, 5-H), 7.14 (3H, m, ArH), 7.03 (1H, m, 3-H), 6.56 (1H, q, *J* 7.1, CH), 6.21 (1H, m, 4-H), 1.80 (3H, d, *J* 7.0, Me); δ_C (62.9 MHz; $CDCl_3$) 165.9 (C=O), 142.6 (C), 128.5 (5-CH), 127.3 (ArC), 126.7 (ArC), 126.2 (ArC), 121.3 (C), 120.5 (3-CH), 108.8 (4-CH), 55.4 (CH), 21.9 (Me); *m*/*z* 215 (M^+, 14%), 155 (2), 111 (13), 105 (100), 104 (38), 93 (3), 77 (19), 51 (7).

(d) To a stirred solution of (*S*)-1-(1-phenylethyl)-pyrrole-2-carboxylate (584 mg, 2.71 mmol) in chlorobenzene (60 mL) was added rhodium(II) acetate (100 mg, 0.23 mmol). After heating under reflux for 24 h the solvent was then removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (1:1) as eluant to yield the *title compound* as a green powdery solid (176 mg, 72%), mp 130–131°C (dec.); $[\alpha]_D^{21} = -70.0$ (*c* 0.1, $CHCl_3$); (Found: C, 58.7; H, 4.4; N, 5.3. $C_{52}H_{48}N_4O_8Rh_2$ requires C, 58.8; H, 4.6; N, 5.3%); (Found: M^+, 1062.1593. $C_{52}H_{48}N_4O_8Rh_2$ requires 1062.1582); ν_{max} ($CHCl_3$)/cm^{-1} 3054, 2987, 1731, 1493, 1430, 737; δ_H (250 MHz; $CDCl_3$), 6.92 (20H, m, ArH), 6.70 (4H, m, 5-H), 6.64 (4H, m, 3-H), 6.23 (4H, q, *J* 7.5, CH), 5.92 (4H, m, 4-H), 1.58 (12H, d, *J* 7.5, Me); δ_C (62.9 MHz; $CDCl_3$) 179.1 (C=O), 142.7 (C), 128.5 (5-CH), 128.5 (ArC), 128.2 (ArC), 123.2 (ArC), 118.8 (C), 117.7 (3-CH), 108.9 (4-CH), 55.1 (CH), 21.3 (Me); *m*/*z* (FAB) 1062 (M^+, 26%), 546 (48), 476 (5), 441 (12), 412 (4), 374 (17), 345 (4), 308 (21), 271 (7), 218 (14), 198 (10), 156 (11), 121 (5).

4.2.3. Dirhodium(II) tetrakis(*N*-phenylsulfonyl-(*S*)-prolinate) 6. Prepared by the literature procedure.[24]

4.2.4. Dirhodium(II) tetrakis((*S*)-(+)-mandelate) 7. Prepared by the literature procedure.[25]

4.2.5. Dirhodium(II) tetrakis((*S*)-(+)-α-methoxyphenylacetate) 8. A stirred suspension of dirhodium(II) tetrakis(carbonate) (50 mg, 0.08 mmol) and (*S*)-(+)-α-methoxyphenylacetic acid (108 mg, 0.64 mmol) in water (5 mL) was heated at 85°C for 1 h. During this time the initial deep blue colour faded and the green product precipitated out. Cooling and filtration gave a green solid which was subsequently washed with water (10 mL) and dried under vacuum to yield the *title compound* as a green powdery solid (54 mg, 77%), mp 250°C (dec.); $[\alpha]_D^{23} = +60.0$ (*c* 0.1, $CHCl_3$); (Found: C, 49.8; H, 4.1. $C_{36}H_{36}O_{12}Rh_2$ requires C, 49.9; H, 4.2%); (Found: M^+, 866.0303. $C_{36}H_{36}O_{12}Rh_2$ requires 866.0317); ν_{max} ($CHCl_3$)/cm^{-1} 3055, 2989, 1606, 1455, 1095, 740; δ_H (400 MHz; CD_3OD) 7.17 (20H, m, ArH), 4.25 (4H, s, CH), 2.84 (12H, s, OMe); δ_C (100.6 MHz; CD_3OD) 190.0 (C=O), 137.1 (C), 127.8 (ArC), 127.7 (ArC), 126.5 (ArC), 82.8 (CH), 56.1 (Me); *m*/*z* (FAB) 866 (M^+, 6%), 388 (11), 211 (15), 152 (29), 121 (100), 107 (69).

4.2.6. Dirhodium(II) tetrakis((*S*)-(+)-α-ethoxyphenylacetate) 9. (a) To a stirred solution of (*S*)-(+)-mandelic acid (1.00 g, 6.57 mmol) in iodoethane (103 g, 657 mmol) was added silver(I) oxide (3.05 g, 13.14 mmol). After stirring overnight the reaction mixture was filtered and the solvent was removed under reduced pressure to yield a colourless oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (9:1) as eluant to yield *(S)-(+)-ethyl 2-ethoxy-2-phenylacetate* as a colourless oil (0.75 g, 55%), $[\alpha]_D^{23} = +77.0$ (*c* 1.0, $CHCl_3$); (Found: M^+, 208.1101. $C_{12}H_{16}O_3$ requires 208.1099); ν_{max} (film)/cm^{-1} 3065, 2980, 1735, 1495, 1455, 1178, 753; δ_H (400 MHz; $CDCl_3$) 7.46 (2H, m, ArH), 7.35 (3H, m, ArH), 4.87 (1H, s, CH), 4.21 (1H, dq, *J* 10.8, 7.1, CO_2CHHMe), 4.15 (1H, dq, *J* 10.8, 7.1, CO_2CHHMe), 3.61 (1H, dq, *J* 9.1, 7.0, $OCHHMe$), 3.52 (1H, dq, *J* 9.1, 7.0, $OCHHMe$), 1.28 (3H, t, *J* 7.0, OCH_2Me), 1.22 (3H, t, *J* 7.1, CO_2CH_2Me); δ_C (100.6 MHz; $CDCl_3$) 171.0 (C=O), 136.8 (C), 128.5 (ArC), 128.5 (ArC), 127.1 (ArC), 81.0 (CH), 65.3 (OCH_2Me), 61.1 (CO_2CH_2Me), 15.1 (OCH_2Me), 14.1 (CO_2CH_2Me); *m*/*z* 208 (M^+, 1%), 163 (10), 135 (100), 107 (90), 105 (41), 79 (90), 77 (61), 51 (30).

(b) To a stirred solution of (*S*)-(+)-ethyl 2-ethoxy-2-phenylacetate (0.50 g, 2.40 mmol) in methanol/water (5:1) (36 mL) was added lithium hydroxide monohydrate (0.50 g, 12.00 mmol). After stirring overnight the reaction mixture was then partitioned between water (100 mL) and ether (100 mL). The organic phase was removed and the aqueous phase was then acidified to pH 1 with aqueous hydrochloric acid (2 M) and extracted with ethyl acetate (3×100 mL). The organic extracts were combined, washed with saturated brine (100 mL), dried ($MgSO_4$) and the solvent was then removed under reduced pressure to yield *(S)-(+)-α-ethoxyphenylacetic acid* as a pale yellow oil (0.42 g, 97%), $[\alpha]_D^{21} = +102.0$ (*c* 1.0, acetone) (lit.,[40] $[\alpha]_D^{15} = +88.5$ (*c* 3.0, acetone)); (Found: M^+, 180.0781. $C_{10}H_{12}O_3$ requires 180.0786); ν_{max} (film)/cm^{-1} 3500–2500, 3065, 2980, 1724, 1495, 1455, 1175, 761; δ_H (400 MHz; $CDCl_3$) 8.41 (1H, bs, OH), 7.45 (2H, m, ArH), 7.36 (3H, m, ArH), 4.89 (1H, s, CH), 3.61 (1H, dq, *J* 9.2, 7.0, $OCHHMe$), 3.55 (1H, dq, *J* 9.2, 7.0, $OCHHMe$), 1.28 (3H, t, *J* 9.0, Me); δ_C (100.6 MHz; $CDCl_3$) 174.6 (C=O), 135.8 (C), 128.9 (ArC), 128.7 (ArC), 127.2 (ArC), 80.4 (CH), 65.4 (CH_2), 15.0 (Me); *m*/*z* 180 (M^+, 1%), 135 (100), 107 (81), 79 (51), 77 (25).

(c) A stirred suspension of dirhodium(II) tetrakis(carbonate) (50 mg, 0.08 mmol) and (*S*)-(+)-α-ethoxyphenylacetic acid (117 mg, 0.64 mmol) in water (5 mL) was heated at 85°C for 1 h. During this time the initial deep blue colour faded and the green product precipitated out. Cooling and filtration gave a green solid which was subsequently washed with water (10 mL) and dried under vacuum to yield the *title compound* as a green crystalline solid (29 mg, 39%), mp 250°C (dec.); $[\alpha]_D^{24} = +40.0$ (*c* 0.1, $CHCl_3$); (Found: C, 52.0; H, 4.6. $C_{40}H_{44}O_{12}Rh_2$ requires C, 52.1; H, 4.8%); (Found: M^+, 922.0919. $C_{40}H_{44}O_{12}Rh_2$ requires 922.0933); ν_{max} ($CHCl_3$)/cm^{-1} 3056, 2986, 1610, 1587, 1455, 1108, 746; δ_H (400 MHz; $CDCl_3$) 7.19 (20H, m, ArH), 4.43 (4H, s, CH), 3.07 (4H, m, $OCHHMe$), 2.93 (4H, m, $OCHHMe$), 1.05 (12H, t, *J* 9.3, Me); δ_C (100.6 MHz; $CDCl_3$) 191.1 (C=O), 137.3 (C), 128.2 (ArC), 127.9 (ArC), 126.6 (ArC), 81.4 (CH), 65.1 (CH_2), 15.0 (Me); *m*/*z* (FAB) 922 (M^+, 6%), 376 (10), 295 (8), 255 (15), 181 (8), 152 (6), 135 (100), 133 (8), 107 (100).

4.2.7. Dirhodium(II) tetrakis((*S*)-(+)-α-″propoxyphenylacetate) 10. (a) To a stirred solution of (*S*)-(+)-mandelic acid (1.00 g, 6.57 mmol) in 1-iodopropane (111 g, 657 mmol) was added silver(I) oxide (3.05 g, 12.14 mmol).

After stirring overnight the reaction mixture was filtered and the solvent was removed under reduced pressure to yield a colourless oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (9:1) as eluant to yield *(S)-(+)-^{n}propyl 2-^{n}propoxy-2-phenylacetate* as a colourless oil (0.82 g, 53%), $[\alpha]_D^{23}=+65.0$ (*c* 1.0, $CHCl_3$); (Found: M^+, 236.1410. $C_{14}H_{20}O_3$ requires 236.1412); ν_{max} (film)/cm^{-1} 3033, 2967, 1732, 1496, 1455, 1177, 754; δ_H (400 MHz; $CDCl_3$) 7.47 (2H, m, ArH), 7.33 (3H, m, ArH), 4.86 (1H, s, CH), 4.08 (2H, t, *J* 6.7, $CO_2CH_2CH_2Me$), 3.52 (1H, dt, *J* 9.0, 6.7, $OCHHCH_2Me$), 3.41 (1H, dt, *J* 9.0, 6.7, $OCHHCH_2Me$), 1.68 (2H, sextet, *J* 6.9, OCH_2CH_2Me), 1.61 (2H, sextet, *J* 6.8, $CO_2CH_2CH_2Me$), 0.94 (3H, t, *J* 7.4, OCH_2CH_2Me), 0.84 (3H, t, *J* 7.4, $CO_2CH_2CH_2Me$); δ_C (100.6 MHz; $CDCl_3$) 171.2 (C=O), 137.0 (C), 128.5 (ArC), 128.4 (ArC), 127.1 (ArC), 81.1 (CH), 71.6 (OCH_2CH_2Me), 66.6 ($CO_2CH_2CH_2Me$), 22.8 (OCH_2CH_2Me), 21.9 ($CO_2CH_2CH_2Me$), 10.5 (OCH_2CH_2Me), 10.2 ($CO_2CH_2CH_2Me$); *m*/*z* 236 (M^+, 1%), 177 (2), 149 (62), 107 (100), 91 (9), 79 (27), 77 (17), 51 (5).

(b) To a stirred solution of (*S*)-(+)-^{n}propyl 2-^{n}propoxy-2-phenylacetate (0.50 g, 2.12 mmol) in methanol/water (5:1) (32 mL) was added lithium hydroxide monohydrate (0.44 g, 10.58 mmol). After stirring overnight the reaction mixture was then partitioned between water (100 mL) and ether (100 mL). The organic phase was removed and the aqueous phase was then acidified to pH 1 with aqueous hydrochloric acid (2 M) and extracted with ethyl acetate (3×100 mL). The organic extracts were combined, washed with saturated brine (100 mL), dried ($MgSO_4$) and the solvent was then removed under reduced pressure to yield *(S)-(+)-α-^{n}propoxyphenylacetic acid* as a pale yellow oil (0.41 g, 99%), $[\alpha]_D^{20}=+96.0$ (*c* 1.0, $CHCl_3$); (Found: M^+, 194.0946. $C_{11}H_{14}O_3$ requires 194.0943); ν_{max} (film)/cm^{-1} 3500–2500, 3033, 2965, 1724, 1496, 1455, 1186, 723; δ_H (400 MHz; $CDCl_3$) 7.44 (2H, m, ArH), 7.37 (3H, m, ArH), 4.88 (1H, s, CH), 3.51 (1H, dt, *J* 9.0, 6.6, $OCHHCH_2Me$), 3.45 (1H, dt, *J* 9.0, 6.8, $OCHHCH_2Me$), 1.68 (2H, sextet, *J* 6.8, OCH_2CH_2Me), 0.94 (3H, t, *J* 7.4, Me), OH not observed; δ_C (100.6 MHz; $CDCl_3$) 174.2 (C=O), 135.8 (C), 128.9 (ArC), 128.7 (ArC), 127.1 (ArC), 80.5 (CH), 71.7 (OCH_2), 22.7 (CH_2), 10.4 (Me); *m*/*z* 194 (M^+, 1%), 149 (100), 135 (5), 122 (6), 107 (76), 91 (13), 79 (81), 63 (7), 51 (14).

(c) A stirred suspension of dirhodium(II) tetrakis(carbonate) (50 mg, 0.08 mmol) and (*S*)-(+)-α-^{n}propoxyphenylacetic acid (126 mg, 0.64 mmol) in water (5 mL) was heated at 85°C for 1 h. During this time the initial deep blue colour faded and the green product precipitated out. Cooling and filtration gave a green solid which was subsequently washed with water (10 mL) and dried under vacuum to yield the *title compound* as a green crystalline solid (40 mg, 51%), mp 250°C (dec.); $[\alpha]_D^{23}=+50.0$ (*c* 0.1, $CHCl_3$); (Found: C, 54.0; H, 5.6. $C_{44}H_{52}O_{12}Rh_2$ requires C, 54.0; H, 5.4%); (Found: M^+, 978.1522. $C_{44}H_{52}O_{12}Rh_2$ requires 978.1539); ν_{max} ($CHCl_3$)/cm^{-1} 3058, 2966, 1682, 1599, 1454, 1194, 738; δ_H (400 MHz; $CDCl_3$) 7.17 (20H, m, ArH), 4.41 (4H, s, CH), 3.03 (4H, m, $OCHHCH_2Me$), 2.87 (4H, m, $OCHHCH_2Me$), 1.48 (8H, sextet, *J* 9.1, OCH_2CH_2Me), 0.84 (12H, t, *J* 9.8, Me); δ_C (100.6 MHz; $CDCl_3$) 191.1 (C=O), 137.4 (C), 128.2 (ArC), 127.9 (ArC), 126.6 (ArC), 81.5 (CH), 71.3 (OCH_2), 22.8 (CH_2), 10.6 (Me); *m*/*z* (FAB) 978 (M^+, 1%), 323 (6), 295 (7), 239 (13), 218 (6), 181 (7), 149 (55), 133 (17), 107 (100).

4.2.8. Dirhodium(II) tetrakis((*S*)-(+)-α-isopropoxyphenylacetate) 11. (a) To a stirred solution of (*S*)-(+)-mandelic acid (0.50 g, 3.29 mmol) in 2-iodopropane (55 g, 329 mmol) was added silver(I) oxide (1.52 g, 6.57 mmol). After stirring overnight the reaction mixture was filtered and the solvent was removed under reduced pressure to yield a colourless oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (9:1) as eluant to yield *(S)-(+)-isopropyl 2-isopropoxy-2-phenylacetate* as a colourless oil (228 mg, 29%), $[\alpha]_D^{20}=+68.0$ (*c* 1.0, $CHCl_3$); (Found: M^+, 236.1415. $C_{14}H_{20}O_3$ requires 236.1412); ν_{max} (film)/cm^{-1} 3032, 2978, 1727, 1581, 1455, 1176, 724; δ_H (400 MHz; $CDCl_3$) 7.46 (2H, m, ArH), 7.32 (3H, m, ArH), 5.03 (1H, h, *J* 6.2, CO_2CHMe_2), 4.93 (1H, s, CH), 3.69 (1H, h, *J* 6.1, $OCHMe_2$), 1.26 (3H, d, *J* 6.2, $OCHMe_2$), 1.21 (3H, d, *J* 6.2, $OCHMe_2$), 1.19 (3H, d, *J* 6.2, CO_2CHMe_2), 1.13 (3H, d, *J* 6.2, CO_2CHMe_2); δ_C (100.6 MHz; $CDCl_3$) 171.1 (C=O), 137.4 (C), 128.4 (ArC), 128.2 (ArC), 127.0 (ArC), 78.7 (CH), 71.0 ($OCHMe_2$), 68.5 (CO_2CHMe_2), 22.2 ($OCHMe_2$), 22.0 (CO_2CHMe_2), 21.7 ($OCHMe_2$), 21.5 (CO_2CHMe_2); *m*/*z* 236 (M^+, 1%), 177 (9), 149 (68), 107 (100), 104 (15), 79 (24), 77 (12), 51 (2).

(b) To a stirred solution of (*S*)-(+)-isopropyl 2-isopropoxy-2-phenylacetate (178 mg, 0.75 mmol) in methanol/water (5:1) (12 mL) was added lithium hydroxide monohydrate (158 mg, 3.77 mmol). After stirring overnight the reaction mixture was then partitioned between water (50 mL) and ether (50 mL). The organic phase was removed and the aqueous phase was then acidified to pH 1 with aqueous hydrochloric acid (2 M) and extracted with ethyl acetate (3×50 mL). The organic extracts were combined, washed with saturated brine (50 mL), dried ($MgSO_4$) and the solvent was then removed under reduced pressure to yield a colourless solid. Recrystallisation from ethyl acetate and light petroleum yielded *(S)-(+)-α-isopropoxyphenylacetic acid* as a colourless solid (140 mg, 96%), mp 53–54°C (lit.,[40] mp 53–57°C); $[\alpha]_D^{20}=+98.0$ (*c* 1.0, $CHCl_3$); (Found: C, 67.8; H, 7.3. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.3%); (Found: M^+, 194.0946. $C_{11}H_{14}O_3$ requires 194.0943); ν_{max} ($CHCl_3$)/cm^{-1} 3500–2500, 3065, 2975, 1724, 1582, 1456, 1177, 723; δ_H (400 MHz; $CDCl_3$) 7.45 (2H, m, ArH), 7.36 (3H, m, ArH), 4.99 (1H, s, CH), 3.74 (1H, h, *J* 6.1, CH), 1.26 (3H, d, *J* 6.1, Me), 1.20 (3H, d, *J* 6.1, Me), OH not observed; δ_C (100.6 MHz; $CDCl_3$) 174.1 (C=O), 136.3 (C), 128.8 (ArC), 128.7 (ArC), 127.1 (ArC), 77.9 (CH), 71.4 ($CHMe_2$), 22.4 (Me), 21.6 (Me); *m*/*z* 194 (M^+, 1%), 149 (39), 135 (10), 107 (100), 79 (39), 77 (22).

(c) A stirred suspension of dirhodium(II) tetrakis(carbonate) (50 mg, 0.08 mmol) and (*S*)-(+)-α-isopropoxyphenylacetic acid (126 mg, 0.64 mmol) in water (5 mL) was heated at 85°C for 1 h. During this time the initial deep blue colour faded and the green product precipitated out. Cooling and filtration gave a green solid which was subsequently washed with water (10 mL) and dried under vacuum to yield the *title compound* as a green powdery solid (31 mg, 39%), mp 250°C (dec.); $[\alpha]_D^{24}=+60.0$ (*c* 0.1, $CHCl_3$); (Found: C, 53.9; H, 5.6. $C_{44}H_{52}O_{12}Rh_2$ requires C, 54.0; H, 5.4%); (Found: M^+, 978.1566. $C_{44}H_{52}O_{12}Rh_2$ requires 978.1569); ν_{max} ($CHCl_3$)/cm^{-1} 3055, 2984, 1607, 1418, 1089, 738; δ_H (400 MHz; $CDCl_3$) 7.21 (20H, m, ArH), 4.52 (4H, s, CH) 3.17 (4H, h, *J* 6.0, CH), 1.03 (12H, d, *J* 6.1, Me), 0.95 (12H, d, *J* 6.1, Me); δ_C (100.6 MHz; $CDCl_3$) 191.5 (C=O), 137.8 (C), 128.2 (ArC), 127.8 (ArC), 126.8 (ArC), 79.0 (CH), 70.9 (C̲HMe$_2$), 22.1 (Me), 21.9 (Me); *m*/*z* (FAB) 978 (M^+, 3%), 922 (4), 785 (6), 400 (9), 376 (31), 323 (15), 295 (21), 239 (23), 208 (11), 181 (19), 149 (66), 108 (31), 107 (100).

4.2.9. Dirhodium(II) tetrakis((*S*)-(−)-α-methoxy-α-trifluoromethylphenylacetate) 12. Prepared by the literature procedure.[26]

4.2.10. Dirhodium tetrakis((1*R*)-(+)-camphanate) 13. Prepared by the literature procedure.[27]

4.2.11. Dirhodium tetrakis((*R*)-(+)-camphene-1-carboxylate) 14. A solution of dirhodium(II) acetate (100 mg, 0.23 mmol) and (+)-camphene-1-carboxylic acid (652 mg, 3.62 mmol) in chlorobenzene (50 ml) was heated under reflux for a period of 96 h. The chlorobenzene and residual acetic acid were removed under high vacuum and the reaction mixture was taken up in dichloromethane (100 ml). This was washed with saturated sodium hydrogen carbonate solution (100 ml) followed by water (2×100 ml). After drying over sodium sulfate the mixture was concentrated and purified by flash chromatography (light petroleum/diethyl ether 5.7:1) to give the *title compound* as a dark green solid (201 mg, 96%), mp >280°C; $[\alpha]_D^{24}=+107.6$ (*c* 0.20, $CHCl_3$); (Found: C, 57.3; H, 6.6. $C_{44}H_{60}O_8Rh_2$:requires C, 57.3; H, 6.5%); ν_{max} ($CHCl_3$)/cm^{-1} 1605 (C=O), 1216 (CO); δ_H (250 MHz; $CDCl_3$) 4.51 and 4.47 (each 1 H, s, camphene-2=CH_2), 1.99–1.37 (7 H, m, camphene-4, camphene-5,-6,-7), 1.02 and 1.00 (each 3 H, s, camphene-3-Me$_2$); δ_C (62.9 MHz; $CDCl_3$) 163.1 (C=O), 143.0 (camphene-2), 100.3 (camphene-2=CH_2), 61.7 (camphene-1), 46.8 (camphene-4), 42.4 (camphene-3), 40.7 (camphene-7), 31.8 (camphene-6), 29.5 and 25.9 (camphene-3-Me$_2$), 24.4 (camphene-5).

4.2.12. Dirhodium tetrakis[methyl 2-oxopyrrolidine-(5*S*)-carboxylate] 15. Prepared by the literature procedure.[28]

4.2.13. Dirhodium tetrakis[methyl 3,3-difluoro-2-oxopyrrolidine-(5*S*)-carboxylate] 16. Prepared by the literature procedure.[29]

4.3. General procedure for the synthesis of chiral dirhodium(II) carboxylate catalysts by parallel synthesis

A stirred suspension of dirhodium(II) tetrakis(carbonate) (30.9 mg, 0.05 mmol) and a chiral carboxylic acid ligand (0.40 mmol) in distilled water (3 mL) was heated at 85°C for 1 h. Cooling and filtration gave a solid which was subsequently washed with water (10 mL) and dried under vacuum to yield the desired rhodium species.

The structures of the formed chiral dirhodium(II) carboxylate catalysts were confirmed by automated ^1H NMR and mass spectrometry analysis where possible (Tables 2–4).

4.3.1. Dirhodium(II) tetrakis(*N*-(4-nitrophenylsulfonyl)-(*S*)-phenylalaninate) L4/2. A stirred suspension of dirhodium(II) tetrakis(carbonate) (50 mg, 0.08 mmol) and *N*-(4-nitrophenylsulfonyl)-(*S*)-phenylalanine (227 mg, 0.64 mmol) in water (5 mL) was heated at 85°C for 1 h. During this time the initial deep blue colour faded and the green product precipitated out. Cooling and filtration gave a green solid which was subsequently washed with water (10 mL) and dried under vacuum to yield the *title compound* as a green powdery solid (123 mg, 95%), mp 250°C (dec.); $[\alpha]_D^{24}=-110.0$ (*c* 0.1, MeOH); (Found: C, 44.8; H, 3.4; N, 6.5. $C_{60}H_{52}N_8O_{24}Rh_2S_4$ requires C, 44.9; H, 3.3; N, 6.7%); (Found: MH^+, 1603.0165. $C_{60}H_{53}N_8O_{24}Rh_2S_4$ requires 1603.0166); ν_{max} (KBr)/cm^{-1} 3281, 3055, 2987, 1730, 1603, 1533, 1454, 1351, 1310, 1163, 1093, 739; δ_H (400 MHz; CD_3OD) 8.18 (8H, d, *J* 7.0, ArH), 7.80 (8H, d, *J* 7.0, ArH), 7.12 (20H, m, ArH), 4.12 (4H, dd, *J* 9.5, 4.9, CH), 3.10 (4H, dd, *J* 13.8, 4.9, CH̲H), 2.81 (4H, dd, *J* 13.8, 9.5, CHH̲), NH not observed; δ_C (100.6 MHz; CD_3OD) 172.7 (C=O), 149.7 (C), 146.6 (C), 136.5 (C), 129.0 (ArC), 128.0 (ArC), 127.7 (ArC), 126.4 (ArC), 123.6 (ArC), 57.7 (CH), 38.3 (CH_2); *m*/*z* (FAB) 1603 (MH^+, 6%), 664 (61), 483 (27), 413 (89), 391 (100), 373 (64), 232 (65).

4.3.2. Dirhodium(II) tetrakis(*N*-(4-toluenesulfonyl)-(*S*)-leucinate) L4/3. A stirred suspension of dirhodium(II) tetrakis(carbonate) (50 mg, 0.08 mmol) and *N*-(4-toluenesulfonyl)-(*S*)-leucine (185 mg, 0.64 mmol) in water (5 mL) was heated at 85°C for 1 h. During this time the initial deep blue colour faded and the green product precipitated out. Cooling and filtration gave a green solid which was subsequently washed with water (10 mL) and dried under vacuum to yield the *title compound* as a green powdery solid (88 mg, 81%), mp 250°C (dec.); $[\alpha]_D^{24}=-90.0$ (*c* 0.1, $CHCl_3$); (Found: C, 46.7; H, 5.3; N, 4.1. $C_{52}H_{72}N_4O_{16}Rh_2S_4$ requires C, 46.5; H, 5.4; N, 3.9%); (Found: MH^+, 1343.2013. $C_{52}H_{73}N_4O_{16}Rh_2S_4$ requires 1343.2015); ν_{max} ($CHCl_3$)/cm^{-1} 3287, 3055, 2961, 1725, 1599, 1455, 1324, 1160, 1094, 740; δ_H (400 MHz; $CDCl_3$) 7.73 (8H, d, *J* 8.6, ArH), 7.27 (8H, d, *J* 8.5, ArH), 5.33 (4H, s, NH), 3.90 (4H, m, CH), 2.41 (12H, s, Me), 1.74 (4H, m, C̲HMe$_2$), 1.50 (8H, m, CH_2), 0.88 (12H, d, *J* 6.6, CHMe$_2$), 0.80 (12H, d, *J* 6.5, CHMe$_2$); δ_C (100.6 MHz; $CDCl_3$) 177.4 (C=O), 143.9 (C), 136.6 (C), 129.7 (ArC), 127.3 (ArC), 54.0 (CH), 42.0 (CH_2), 24.3 (C̲HMe$_2$), 22.7 (CHMe$_2$), 21.6 (Me), 21.2 (CHMe$_2$); *m*/*z* (FAB) 1343 (MH^+, 4%), 1102 (14), 1058 (20), 729 (39), 309 (60), 240 (100).

4.4. Dirhodium(II) tetrakis(*N*-(4-toluenesulfonyl)-(*S*)-phenylalaninate) L4/5

A stirred suspension of dirhodium(II) tetrakis(carbonate) (50 mg, 0.08 mmol) and *N*-(4-toluenesulfonyl)-(*S*)-phenylalanine (207 mg, 0.64 mmol) in water (5 mL) was heated at 85°C for 1 h. During this time the initial deep blue colour faded and the green product precipitated out. Cooling and filtration gave a green solid which was subsequently washed with water (10 mL) and dried under vacuum to yield the *title compound* as a green powdery solid (113 mg, 94%), mp 250°C (dec.); $[\alpha]_D^{24} = -80.0$ (*c* 0.1, MeOH); (Found: C, 51.7; H, 4.5; N, 3.8. $C_{64}H_{64}N_4O_{16}Rh_2S_4$ requires C, 51.9; H, 4.4; N, 3.8%); (Found: MH^+, 1479.1388. $C_{64}H_{65}N_4O_{16}S_4Rh_2$ requires 1479.1389); ν_{max} (KBr)/cm^{-1} 3283, 3054, 2987, 1730, 1598, 1455, 1325, 1157, 1092, 739; δ_H (400 MHz; CD_3OD) 7.54 (8H, d, *J* 8.3, ArH), 7.22 (8H, d, *J* 8.6, ArH), 7.15 (12H, m, ArH), 7.11 (8H, m, ArH), 4.01 (4H, dd, *J* 6.1, 4.2, CH), 3.03 (4H, dd, *J* 10.3, 4.2, CHH), 2.83 (4H, dd, *J* 10.3, 6.1, CHH), 2.37 (12H, s, Me), NH not observed; δ_C (100.6 MHz; CD_3OD) 172.9 (C=O), 143.0 (C), 137.7 (C), 136.4 (C), 129.1 (ArC), 129.0 (ArC), 128.0 (ArC), 126.6 (ArC), 126.3 (ArC), 57.4 (CH), 38.5 (CH_2), 20.0 (Me); *m*/*z* (FAB) 1479 (MH^+, 32%), 1388 (25), 1204 (31), 946 (26), 727 (30), 705 (100), 533 (35).

4.4.1. Dirhodium(II) tetrakis(*N*-(4-*tert*-butylphenylsulfonyl)-(*S*)-leucinate) L4/6. Prepared as described previously.[35]

4.4.2. Dirhodium(II) tetrakis(*N*-(4-dodecylphenylsulfonyl)-(*S*)-leucinate) L4/7. Prepared as described previously.[35]

4.4.3. Dirhodium(II) tetrakis(*N*-(4-toluenesulfonyl)-(*S*)-*tert*-leucinate) L4/8. Prepared as described previously.[35]

4.5. Silane insertions: conventional method

4.5.1. Methyl 2-(dimethylphenylsilyl)phenylacetate 2a. To a stirred solution of methyl 2-diazophenylacetate (100 mg, 0.57 mmol) in dry dichloromethane (2 mL) under a nitrogen atmosphere was added dimethylphenylsilane (85 mg, 0.63 mmol) followed by a chiral dirhodium(II) catalyst (2 mol%). After stirring for 30 min the solvent was removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (19:1) as eluant to yield the *title compound* as a colourless oil; (Found: M^+, 284.1235. $C_{17}H_{20}O_2Si$ requires 284.1233); ν_{max} (film)/cm^{-1} 3025, 2951, 1719, 1599, 1453, 1149, 736; δ_H (250 MHz; $CDCl_3$) 7.37 (5H, m, ArH), 7.17 (5H, m, ArH), 3.60 (1H, s, CH), 3.54 (3H, s, OMe), 0.35 (3H, s, Me), 0.32 (3H, s, Me); δ_C (62.9 MHz; $CDCl_3$) 173.1 (C=O), 136.0 (C), 135.5 (C), 134.0 (ArC), 129.6 (ArC), 128.4 (ArC), 128.0 (ArC), 127.7 (ArC), 125.7 (ArC), 51.3 (OMe), 46.1 (CH), –4.1 (Me), –4.5 (Me); *m*/*z* 284 (M^+, 13%), 151 (10), 135 (60), 118 (100), 105 (8), 90 (14), 77 (4), 43 (10).

4.5.2. Methyl 2-(*tert*-butyldimethylsilyl)phenylacetate 2b. To a stirred solution of methyl 2-diazophenylacetate (100 mg, 0.57 mmol) in dry dichloromethane (2 mL) under a nitrogen atmosphere was added *tert*-butyldimethylsilane (73 mg, 0.63 mmol) followed by a chiral dirhodium(II) catalyst (2 mol%). After stirring for 30 min the solvent was removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (19:1) as eluant to yield the *title compound* as a colourless oil; (Found: M^+, 264.1546. $C_{15}H_{24}O_2Si$ requires 264.1546); ν_{max} (film)/cm^{-1} 3026, 2953, 1723, 1600, 1453, 1148, 756; δ_H (250 MHz; $CDCl_3$) 7.37 (2H, m, ArH), 7.25 (2H, m, ArH), 7.17 (1H, m, ArH), 3.67 (3H, s, OMe), 3.56 (1H, s, CH), 0.88 (9H, s, CMe_3), 0.12 (3H, s, Me), –0.11 (3H, s, Me); δ_C (62.9 MHz; $CDCl_3$) 173.7 (C=O), 137.0 (C), 128.7 (ArC), 128.0 (ArC), 125.6 (ArC), 51.3 (OMe), 42.9 (CH), 26.5 (CMe_3), 17.7 ($\underline{C}Me_3$), –6.6 (Me), –7.0 (Me). *m*/*z* 264 (M^+, 18%), 207 (50), 118 (100), 89 (99), 73 (58), 59 (20).

4.5.3. Methyl 2-(tri-isopropylsilyl)phenylacetate 2c. To a stirred solution of methyl 2-diazophenylacetate (100 mg, 0.57 mmol) in dry dichloromethane (2 mL) under a nitrogen atmosphere was added tri-isopropylsilane (99 mg, 0.63 mmol) followed by a chiral dirhodium(II) catalyst (2 mol%). After stirring for 30 min the solvent was removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (19:1) as eluant to yield the *title compound* as a colourless oil; (Found: M^+, 306.2019. $C_{18}H_{30}O_2Si$ requires 306.2015); ν_{max} (film)/cm^{-1} 3058, 2948, 1728, 1604, 1453, 1147, 782; δ_H (400 MHz; $CDCl_3$) 7.42 (2H, m, ArH), 7.25 (2H, m, ArH), 7.18 (1H, m, ArH), 3.70 (1H, s, CH), 3.66 (3H, s, OMe), 1.19 (3H, h, *J* 7.1, $C\underline{H}Me_2$), 1.07 (9H, d, *J* 7.3, Me), 1.00 (9H, d, *J* 7.4, Me); δ_C (100.6 MHz; $CDCl_3$) 174.0 (C=O), 136.8 (C), 129.5 (ArC), 128.0 (ArC), 125.7 (ArC), 51.4 (OMe), 41.5 (CH), 18.6 (Me), 18.5 (Me), 11.6 ($\underline{C}HMe_2$); *m*/*z* 306 (M^+, 28%), 263 (12), 156 (35), 145 (100), 118 (49), 103 (11), 89 (51), 75 (52), 59 (93).

4.5.4. 2-(Tri-isopropylsilyl)-2-phenylethanol 17. To a stirred solution of methyl 2-(tri-isopropylsilyl)-phenylacetate **2c** (0.53 g, 1.72 mmol) in dry ether (20 mL) under a nitrogen atmosphere at –78°C was added di-isobutylaluminium hydride (1 M solution in toluene) (3.44 mL, 3.44 mmol) dropwise. After allowing the reaction mixture to stir for 30 min it was then allowed to warm to room temperature where aqueous hydrochloric acid (1 M) (20 mL) was added. After stirring for a further 30 min the organic layer was removed and the aqueous phase was then extracted with ether (3×50 mL). The organic extracts, including the removed organic layer, were combined, washed with saturated brine (50 mL), dried ($MgSO_4$) and the solvent was then removed under reduced pressure to yield a pale brown oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (4:1) as eluant to yield a the *title compound* as a colourless oil (0.43 g, 90%), $[\alpha]_D^{22} = +15.0$ (*c* 1.0, $CHCl_3$);

(Found: M^+, 278.2068. $C_{17}H_{30}OSi$ requires 278.2066); ν_{max} (film)/cm^{-1} 3383, 3025, 2944, 1599, 1464, 1078, 765; δ_H (400 MHz; $CDCl_3$) 7.28 (2H, m, ArH), 7.23 (2H, m ArH), 7.15 (1H, m, ArH), 4.26 (1H, dd, *J* 11.9, 11.5, C<u>H</u>H), 4.02 (1H, m, CH<u>H</u>), 2.78 (1H, dd, *J* 11.9, 3.6, CH), 1.13 (3H, h, *J* 7.6, C<u>H</u>Me$_2$), 1.04 (9H, d, *J* 6.9, Me), 0.99 (9H, d, *J* 7.1, Me), OH not observed; δ_C (100.6 MHz; $CDCl_3$) 141.0 (C), 129.0 (ArC), 128.6 (ArC), 125.5 (ArC), 64.2 (CH_2), 38.9 (CH), 18.8 (Me), 18.7 (Me), 11.0 (<u>C</u>HMe$_2$); *m*/*z* 278 (M^+, 1%), 261 (23), 219 (25), 157 (100), 131 (74), 104 (69), 91 (38), 75 (58), 61 (52).

4.5.5. (2-Phenyl-2-tri-isopropylsilyl)ethyl 4-bromobenzoate 18. To a stirred solution of 2-(tri-isopropylsilyl)-2-phenylethanol **17** (100 mg, 0.36 mmol) in dry dichloromethane (4 mL) under a nitrogen atmosphere was added 4-bromobenzoylchloride (86 mg, 0.39 mmol) followed by triethylamine (40 mg, 0.39 mmol) dropwise. After stirring at room temperature overnight the solvent was then removed under reduced pressure to yield a pale yellow solid. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (19:1) as eluant to yield the *title compound* as a colourless solid (146 mg, 88%), mp 78–79°C; $[\alpha]_D^{23} = -18.0$ (*c* 1.0, $CHCl_3$); (Found: C, 62.8; H, 7.3. $C_{24}H_{33}BrO_2Si$ requires C, 62.5; H, 7.2%); (Found: M^+, 460.1430. $C_{24}H_{33}BrO_2Si$ requires 460.1433); ν_{max} ($CHCl_3$)/cm^{-1} 3028, 2946, 1716, 1591, 1451, 1082, 757; δ_H (400 MHz; $CDCl_3$) 7.64 (2H, d, *J* 6.7, ArH), 7.46 (2H, d, *J* 6.8, ArH), 7.23 (4H, m, ArH), 7.12 (1H, m, ArH), 4.85 (2H, m, CH_2), 3.01 (1H, dd, *J* 9.7, 6.6, CH), 1.23 (3H, h, *J* 7.4, C<u>H</u>Me$_2$), 1.08 (9H, d, *J* 7.3, Me), 1.04 (9H, d, *J* 7.3, Me); δ_C (100.6 MHz; $CDCl_3$) 166.0 (C=O), 141.0 (C), 131.5 (ArC), 130.9 (ArC), 129.4 (C), 128.5 (ArC), 128.3 (ArC), 127.7 (C), 125.2 (ArC), 67.1 (CH_2), 34.5 (CH), 18.8 (Me), 18.7 (Me), 11.1 (<u>C</u>HMe$_2$); *m*/*z* 460 (M^+, 1%), 356 (16), 274 (25), 131 (54), 91 (34), 77 (24), 54 (12). HPLC conditions: column: Chiralpak AD; retention times (min): 4.84, 6.97; solvent ratio: hexane:2-propanol (99:1); flow rate (mL/min): 1.0.

4.5.6. Methyl 2-(tri-isobutylsilyl)phenylacetate 2d. To a stirred solution of methyl 2-diazophenylacetate (100 mg, 0.57 mmol) in dry dichloromethane (2 mL) under a nitrogen atmosphere was added tri-isobutylsilane (125 mg, 0.63 mmol) followed by a chiral dirhodium(II) carboxylate catalyst (2 mol%). After stirring for 30 min the solvent was removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (19:1) as eluant to yield the *title compound* as a colourless oil; (Found: M^+, 348.2491. $C_{21}H_{36}O_2Si$ requires 348.2485); ν_{max} (film)/cm^{-1} 3056, 2954, 1725, 1598, 1464, 1147, 771; δ_H (400 MHz; $CDCl_3$) 7.32 (2H, m, ArH), 7.26 (2H, m, ArH), 7.18 (1H, m, ArH), 3.67 (3H, s, OMe), 3.55 (1H, s, CH), 1.77 (1H, h, *J* 6.6, C<u>H</u>Me$_2$), 0.91 (9H, d, *J* 6.6, CHMe$_2$), 0.90 (9H, d, *J* 6.6, CHMe$_2$), 0.67 (3H, dd, *J* 15.1, 6.6, C<u>H</u>H), 0.62 (3H, dd, *J* 15.1, 6.6, CH<u>H</u>); δ_C (100.6 MHz; $CDCl_3$) 173.7 (C=O), 136.9 (C), 128.8 (ArC), 128.1 (ArC), 125.6 (ArC), 51.3 (OMe), 44.4 (CH), 26.6 (CHMe$_2$), 26.5 (CHMe$_2$), 24.3 (<u>C</u>HMe$_2$), 23.2 (CH_2); *m*/*z* 348 (M^+, 42%), 291 (9), 257 (11), 218 (14), 193 (17), 173 (43), 143 (79), 118 (100), 101 (25), 75 (35), 59 (28).

4.5.7. Methyl 2-(tris(trimethylsilyl)silyl)phenylacetate 2e. To a stirred solution of methyl 2-diazophenylacetate (100 mg, 0.57 mmol) in dry dichloromethane (2 mL) under a nitrogen atmosphere was added tris(trimethylsilyl)silane (155 mg, 0.63 mmol) followed by a chiral dirhodium(II) carboxylate catalyst (2 mol%). After stirring for 30 min the solvent was removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (19:1) as eluant to yield a colourless solid. Recrystallisation from ethyl acetate and light petroleum yielded the *title compound* as a colourless solid, mp 145–146°C; (Found: C, 54.8; H, 9.4. $C_{18}H_{36}O_2Si_4$ requires C, 54.5; H, 9.1%); (Found: M^+, 396.1794. $C_{18}H_{36}O_2Si_4$ requires 396.1792); ν_{max} (film)/cm^{-1} 3054, 2951, 1720, 1598, 1453, 1151, 739; δ_H (400 MHz; $CDCl_3$) 7.33 (2H, m, ArH), 7.26 (2H, m, ArH), 7.17 (1H, m, ArH), 3.68 (1H, s, CH), 3.65 (3H, s, OMe), 0.13 (27H, s, Me); δ_C (100.6 MHz; $CDCl_3$) 174.6 (C=O), 139.1 (C), 129.3 (ArC), 128.3 (ArC), 125.9 (ArC), 51.5 (OMe), 38.3 (CH), 1.2 (Me); *m*/*z* 396 (M^+, 1%), 381 (4), 263 (98), 205 (32), 175 (9), 147 (12), 117 (18), 83 (100), 73 (43), 51 (19).

4.5.8. Methyl 2-(1,1,1,3,5,5,5-heptamethyltrisiloxyl)-phenylethanote 2f. To a stirred solution of methyl 2-diazophenylacetate (100 mg, 0.57 mmol) in dry dichloromethane (2 mL) under a nitrogen atmosphere was added 1,1,1,3,5,5,5-heptamethylsiloxane (139 mg, 0.63 mmol) followed by a chiral dirhodium(II) carboxylate catalyst (2 mol%). After stirring for 30 min the solvent was removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (19:1) as eluant to yield the *title compound* as a colourless oil; (Found: M^+, 370.1456. $C_{16}H_{30}O_4Si_3$ requires 370.1452); ν_{max} (film)/cm^{-1} 3027, 2958, 1729, 1598, 1454, 1149, 756; δ_H (400 MHz; $CDCl_3$) 7.35 (2H, m, ArH), 7.24 (2H, m, ArH), 7.18 (1H, m, ArH), 3.68 (1H, s, OMe), 3.41 (1H, s, CH), 0.10 (3H, s, Me), 0.03 (18H, s, SiMe$_3$); δ_C (100.6 MHz; $CDCl_3$) 172.5 (C=O), 135.8 (C), 128.9 (ArC), 128.0 (ArC), 125.7 (ArC), 51.4 (OMe), 47.5 (CH), 1.5 (Me), −1.6 (SiMe$_3$); *m*/*z* 370 (M^+, 15%), 237 (34), 221 (31), 207 (15), 118 (94), 84 (100), 83 (62), 73 (33), 51 (16).

4.5.9. Dihydro-4,4-dimethyl-3-(dimethylphenylsilyl)-2-furanone 20a. To a stirred solution of dihydro-3-diazo-4,4-dimethyl-2-furanone (100 mg, 0.71 mmol) in dry dichloromethane (2 mL) under a nitrogen atmosphere was added dimethylphenylsilane (107 mg, 0.78 mmol) followed by dirhodium(II) acetate (2 mol%). After stirring for 30 min the solvent was removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (9:1) as eluant to yield a colourless solid. Recrystallisation from ethyl acetate

and light petroleum yielded the *title compound* as a colourless solid (134 mg, 76%), mp 50–51°C; (Found: C, 67.7; H, 8.3. $C_{14}H_{20}O_2Si$ requires C, 67.7; H, 8.1%); (Found: M^+, 248.1233. $C_{14}H_{20}O_2Si$ requires 248.1233); ν_{max} ($CHCl_3$)/cm^{-1} 3049, 2960, 1751, 1598, 1456, 1167, 757; δ_H (400 MHz; $CDCl_3$) 7.58 (2H, m, ArH), 7.39 (3H, m, ArH), 3.73 (1H, d, *J* 8.5, CHH), 3.62 (1H, d, *J* 8.5, CHH), 2.09 (1H, s, CH), 1.04 (3H, s, CMe_2), 1.03 (3H, s, CMe_2), 0.52 (6H, s, Me); δ_C (100.6 MHz; $CDCl_3$) 179.0 (C=O), 136.4 (C), 134.0 (ArC), 129.7 (ArC), 128.0 (ArC), 79.1 (CH_2), 44.2 (CH), 40.6 (C), 28.6 (CMe_2), 24.3 (CMe_2), −2.0 (Me), −2.9 (Me); *m*/*z* 248 (M^+, 1%), 233 (76), 161 (13), 135 (100), 105 (8), 91 (5).

4.5.10. Dihydro-3-(*tert*-butyldimethylsilyl)-4,4-dimethyl-2-furanone 20b. To a stirred solution of dihydro-3-diazo-4,4-dimethyl-2-furanone (100 mg, 0.71 mmol) in dry dichloromethane (2 mL) under a nitrogen atmosphere was added *tert*-butyldimethylsilane (91 mg, 0.78 mmol) followed by dirhodium(II) acetate (2 mol%). After stirring for 30 min the solvent was removed under reduced pressure to yield a green oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (9:1) as eluant to yield the *title compound* as a colourless oil (84 mg, 52%); (Found: M^+, 228.1545. $C_{12}H_{24}O_2Si$ requires 228.1546); ν_{max} (film)/cm^{-1} 2958, 1758, 1467, 1124; δ_H (400 MHz; $CDCl_3$) 3.89 (1H, d, *J* 8.4, CHH), 3.81 (1H, d, *J* 8.4, CHH), 1.92 (1H, s, CH), 1.20 (6H, s, CMe_2), 0.97 (9H, s, CMe_3), 0.19 (3H, s, Me), 0.17 (3H, s, Me); δ_C (100.6 MHz; $CDCl_3$) 178.8 (C=O), 79.6 (CH_2), 41.0 (C), 40.8 (CH), 27.3 (CMe_2), 27.1 (CMe_3), 24.2 (CMe_2), 17.3 (CMe_3), −4.1 (Me), −5.2 (Me); *m*/*z* 228 (M^+, 1%), 213 (25), 171 (100), 129 (18), 99 (31), 75 (30), 59 (10).

4.6. Silane insertions: parallel synthesis method

To methyl 2-diazophenylacetate (10 mg, 0.057 mmol) in dry dichloromethane (0.1 mL) was added a silane (0.062 mmol) in dichloromethane (0.1 mL) followed by a chiral dirhodium(II) carboxylate catalyst (2 mol%). After the solvent and any unreacted silane were removed, this crude product was then subjected to flash silica gel chromatography through a BondElut® column with hexane and ethyl acetate as eluant, to yield the desired Si–H insertion product, which was subjected to automated HPLC analysis to determine the enantioselectivity of the reaction.

4.7. Determination of enantiomeric excess

The enantiomeric purity of the (silyl)phenylacetates **2** was determined by compariosn with the racemate by HPLC on a chiral stationary phase; the conditions for each product are summarised below.

Methyl 2-(dimethylphenylsilyl)phenylacetate **2a**: column: Chiralpak AD; retention times (min): 11.62, 12.69; solvent ratio: hexane:2-propanol (199:1); flow rate (mL/min): 0.5, *or* column: (*S*,*S*)-WHELK-O1; retention times (min): 6.11, 7.30; solvent ratio: heptane:ethyl acetate (19:1); flow rate (mL/min): 1.0.

Methyl 2-(tert-butyldimethylsilyl)phenylacetate **2b**: column: Chiralpak AD; retention times (min): 8.41, 9.01; solvent ratio: hexane:2-propanol (199:1); flow rate (mL/min): 0.5, *or* column: *S*,*S*)-WHELK-O1; retention times (min): 4.38, 5.50; solvent ratio: heptane:ethyl acetate (19:1); flow rate (mL/min): 1.0.

Methyl 2-(tri-isopropylsilyl)phenylacetate **2c**: column: Chiralpak AD; retention times (min): 8.58, 9.08; solvent ratio: hexane:2-propanol (199:1); flow rate (mL/min): 0.5, *or* column: (*S*,*S*)-WHELK-O1; retention times (min): 4.16, 5.21; solvent ratio: heptane:ethyl acetate (19:1); flow rate (mL/min): 1.0.

Methyl 2-(tri-isobutylsilyl)phenylacetate **2d**: column: (*S*,*S*)-WHELK-O1; retention times (min): 5.23, 6.34; solvent ratio: heptane:ethyl acetate (49:1); flow rate (mL/min): 1.0.

Methyl 2-(tris(trimethylsilyl)silyl)phenylacetate **2e**: column: (*S*,*S*)-WHELK-O1; retention times (min): 4.57, 5.64; solvent ratio: heptane:ethyl acetate (49:1); flow rate (mL/min): 1.0.

Methyl 2-(1,1,1,3,5,5,5-heptamethyltrisiloxyl)phenylethanote **2f**: column: (*S*,*S*)-WHELK-O1; retention times (min): 4.72, 5.76; solvent ratio: heptane:ethyl acetate (49:1); flow rate (mL/min): 1.0.

4.7.1. 2-(Dimethylphenylsilyl)-2-phenylethanol 21. To a stirred solution of methyl 2-(dimethylphenylsilyl)-phenylacetate (0.98 g, 3.45 mmol) in dry ether (40 mL) under a nitrogen atmosphere at −78°C was added diisobutylaluminium hydride (1 M solution in toluene) (6.90 mL, 6.90 mmol) dropwise. After allowing the reaction mixture to stir for 30 min it was then allowed to warm to room temperature where aqueous hydrochloric acid (1 M) (40 mL) was added. After stirring for a further 30 min the organic phase was removed and the aqueous phase was then extracted with ether (3×100 mL). The organic extracts, including the removed organic phase, were combined, washed with saturated brine (100 mL), dried ($MgSO_4$) and the solvent was then removed under reduced pressure to yield a pale brown oil. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (4:1) as eluant to yield a colourless solid. Recrystallisation from ethyl acetate and light petroleum yielded the *title compound* as a colourless solid (0.80 g, 91%), mp 56–57°C; (Found: C, 74.6; H, 7.9. $C_{16}H_{20}OSi$ requires C, 74.9; H, 7.9%); (Found: M^+, 256.1290. $C_{16}H_{20}OSi$ requires 256.1283); ν_{max} ($CHCl_3$)/cm^{-1} 3500–3100, 3024, 2956, 1599, 1450, 1112, 736; δ_H (400 MHz; $CDCl_3$) 7.38 (5H, m, ArH), 7.24 (2H, m, ArH), 7.16 (1H, m, ArH), 7.02 (2H, m, ArH), 4.09 (1H, dd, *J* 11.2, 11.1, CHH), 3.95 (1H, dd, *J* 11.2, 4.5, CHH), 2.66 (1H, dd, *J* 11.1, 4.5, CH), 0.28 (3H, s, Me), 0.24 (3H, s, Me), OH not observed; δ_C (100.6 MHz; $CDCl_3$) 139.9 (C), 136.7 (C), 134.0 (ArC), 129.3 (ArC), 128.5 (ArC), 128.1 (ArC), 127.8 (ArC), 125.4 (ArC), 63.2 (CH_2), 41.6 (CH), −3.7 (Me), −4.9 (Me); *m*/*z* 256 (M^+, 1%), 223 (17), 155 (20), 137 (45), 104 (100), 91 (35), 71 (41), 57 (78).

4.7.2. Phenyl-1,2-ethanediol. To a stirred solution of 2-(dimethylphenylsilyl)-2-phenylethanol (0.77 g, 3.00 mmol) in peracetic acid (18 mL of a 32% solution in acetic acid) and acetic anhydride (2.5 mL) was added mercuric acetate (1.65 g, 5.15 mmol). After stirring for 2 h the solvent was removed under reduced pressure and ether (100 mL) was added to the residue which was filtered and the solvent was then removed under reduced pressure to yield a pale grey solid. This crude product was then subjected to flash silica gel chromatography using light petroleum and ethyl acetate (3:7) as eluant to yield a colourless solid. Recrystallisation from ethyl acetate and light petroleum yielded the *title compound* as colourless needles (0.17 g, 42%), mp 64–65°C (lit.,[41] mp 64°C); ν_{max} ($CHCl_3$)/cm^{-1} 3500–3100, 3032, 1602, 1448, 1192, 739; δ_H (400 MHz; $CDCl_3$) 7.31 (5H, m, ArH), 4.78 (1H, dd, *J* 8.1, 3.6, CH), 3.75 (1H, dd, *J* 11.3, 3.6, CHH), 3.66 (1H, dd, *J* 11.3, 8.1, CHH), 3.03 (1H, bs, exch D_2O, OH), 2.61 (1H, bs, exch D_2O, OH); δ_C (100.6 MHz; $CDCl_3$) 140.5 (C), 128.52 (ArC), 128.0 (ArC), 126.1 (ArC), 74.7 (CH), 68.0 (CH_2).

Acknowledgements

We thank GlaxoSmithKline for support, partly through the Asymmetric Synthesis Link Programme, and partly through the CASE Scheme; we also thank the EPSRC for support, the EPSRC Mass Spectrometry Centre at Swansea for mass spectra, and Dr Darko Butina for help with the cluster analysis.

References

1. Nozaki, H.; Moriuti, S.; Takaya, H.; Noyori, R. *Tetrahedron Lett*. **1966**, *7*, 5239–5244.
2. Paulissen, R.; Reimlinger, H.; Hayez, E.; Hubert, A. J.; Teyssié, P. *Tetrahedron Lett*. **1973**, *14*, 2233–2236.
3. (a) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley: New York, 1998; (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev*. **1998**, *98*, 911–935; (c) Forbes, D. C.; McMills, M. C. *Curr. Org. Chem*. **2001**, *5*, 1091–1105.
4. For recent examples, see: (a) Doyle, M. P.; Davies, S. B.; May, E. J. *J. Org. Chem*. **2001**, *66*, 8112–8119; (b) Doyle, M. P.; Hu, W. H.; Valenzuela, M. V. *J. Org. Chem*. **2002**, *67*, 2954–2959; (c) Davies, H. M. L.; Hansen, T.; Hopper, D. W.; Panaro, S. A. *J. Am. Chem. Soc*. **1999**, *121*, 6509–6510; (d) Davies, H. M. L.; Antoulinakis, E. G. *Org. Lett*. **2000**, *2*, 4153–4156.
5. Brunner, H.; Wutz, K.; Doyle, M. P. *Monatsh. Chem*. **1990**, *121*, 755–764.
6. García, C. F.; McKervey, M. A.; Ye, T. *J. Chem. Soc., Chem. Commun*. **1996**, 1465–1466.
7. Miller, D. J.; Moody, C. J. *Tetrahedron* **1995**, *51*, 10811–10843.
8. Aller, E.; Brown, D. S.; Cox, G. G.; Miller, D. J.; Moody, C. J. *J. Org. Chem*. **1995**, *60*, 4449–4460.
9. Ferris, L.; Haigh, D.; Moody, C. J. *Tetrahedron Lett*. **1996**, *37*, 107–110.
10. Doyle, M. P.; Yan, M. *Tetrahedron Lett*. **2002**, *43*, 5929–5931.
11. Buck, R. T.; Doyle, M. P.; Drysdale, M. J.; Ferris, L.; Forbes, D. C.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Zhou, Q.-L. *Tetrahedron Lett*. **1996**, *37*, 7631–7634.
12. Buck, R. T.; Coe, D. M.; Drysdale, M. J.; Moody, C. J.; Pearson, N. D. *Tetrahedron Lett*. **1998**, *39*, 7181–7184.
13. Bagheri, V. B.; Doyle, M. P.; Taunton, J.; Claxton, E. E. *J. Org. Chem*. **1988**, *53*, 6158–6160.
14. (a) Rijkens, F.; Janssen, M. J.; Drenth, W.; VanDerKerk, G. J. M. *J. Organometal. Chem*. **1964**, *2*, 347–356; (b) Watanabe, H.; Kakano, T.; Araki, K.; Matsumoto, H.; Nagai, Y. *J. Organomet. Chem*. **1974**, *69*, 389–396; (c) Baikov, V. E.; Danilkina, L. P.; Oglobin, K. A. *J. Gen. Chem. USSR* **1981**, *51*, 1858.
15. (a) Andrey, O.; Landais, Y.; Planchenault, D. *Tetrahedron Lett*. **1993**, *34*, 2927–2930; (b) Landais, Y.; Planchenault, D. *Tetrahedron Lett*. **1994**, *35*, 4565–4568; (c) Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron Lett*. **1994**, *35*, 9549–9552; (d) Andrey, O.; Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron* **1995**, *51*, 12083–12096.
16. Sengupta, S.; Das, D.; Sensarma, D. *Tetrahedron Lett*. **1996**, *37*, 8815–8818.
17. Davies, H. M. L.; Hansen, T.; Rutberg, J.; Bruzinski, P. R. *Tetrahedron Lett*. **1997**, *38*, 1741–1744.
18. Kitagaki, S.; Kinoshita, M.; Takeba, M.; Anada, M.; Hashimoto, S. *Tetrahedron: Asymmetry* **2000**, *11*, 3855–3859.
19. Dakin, L. A.; Schaus, S. E.; Jacobsen, E. N.; Panek, J. S. *Tetrahedron Lett*. **1998**, *39*, 8947–8950.
20. Dakin, L. A.; Ong, P. C.; Panek, J. S.; Staples, R. J.; Stavropoulos, P. *Organometallics* **2000**, *19*, 2896–2908.
21. Landais, Y.; ParraRapado, L.; Planchenault, D.; Weber, V. *Tetrahedron Lett*. **1997**, *38*, 229–232.
22. Bulugahapitiya, P.; Landais, Y.; ParraRapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem*. **1997**, *62*, 1630–1641.
23. Qu, Z. H.; Shi, W. F.; Wang, J. B. *J. Org. Chem*. **2001**, *66*, 8139–8144.
24. Kennedy, M.; McKervey, M. A.; Maguire, A. R.; Roos, G. H. P. *J. Chem. Soc., Chem. Commun*. **1990**, 361–362.
25. Agaskar, P. A.; Cotton, F. A.; Falvello, L. R.; Han, S. *J. Am. Chem. Soc*. **1986**, *108*, 1214–1223.
26. Brunner, H.; Kluschanzoff, H.; Wutz, K. *Bull. Soc. Chim. Belg*. **1989**, *98*, 63–72.
27. The structure of dirhodium(II) camphanate has been reported although no uses of it as a chiral catalyst were described. See: Kojic-Prodic, B.; Marcec, R.; Nigovic, B.; Raza, Z.; Sunjic, V. *Tetrahedron: Asymmetry* **1992**, *3*, 1–4.
28. Doyle, M. P.; Winchester, W. R.; Hoorn, J. A. A.; Lynch, V.; Simonsen, S. H.; Ghosh, R. *J. Am. Chem. Soc*. **1993**, *115*, 9968–9978.
29. Doyle, M. P.; Hu, W.; Phillips, I. M.; Moody, C. J.; Pepper, A. G.; Slawin, A. M. Z. *Adv. Synth. Catal*. **2001**, *343*, 112–117.
30. For example, see: (a) Reetz, M. T.; Becker, M. H.; Klein, H. W.; Stockigt, D. *Angew. Chem., Int. Ed*. **1999**, *38*, 1758–1761; (b) Dahmen, S.; Brase, S. *Synthesis* **2001**, 1431–1449; (c) Chataigner, I.; Gennari, C.; Ongeri, S.; Piarulli, U.; Ceccarelli, S. *Chem. Eur. J*. **2001**, *7*, 2628–2634; (d) Reetz, M. T. *Angew. Chem., Int. Ed*. **2001**, *40*, 284–310.

31. Roos, G. H. P.; McKervey, M. A. *Synth. Commun.* **1992**, *22*, 1751–1756.
32. Davies, H. M. L. *Aldrichim. Acta* **1997**, 107–114.
33. Davies, H. M. L. *Eur. J. Org. Chem.* **1999**, 2459–2469.
34. Hashimoto, S.; Watanabe, N.; Ikegami, D. *Tetrahedron Lett.* **1990**, *31*, 5173–5174.
35. Buck, R. T.; Moody, C. J.; Pepper, A. G. *ARKIVOC* **2002**, 16–32. http://arkat-usa.org/ark/journal/2002/Padwa/AP-2391H/2391H.htm.
36. Landais, Y.; Planchenault, D. *Tetrahedron* **1997**, *53*, 2855–2870.
37. Regitz, M.; Maas, G. *Diazo Compounds. Properties and Synthesis*; Academic Press: Orlando, FL, 1986.
38. Höfle, G.; Steglich, W. *Synthesis* **1972**, 619–621.
39. Smith, H. E.; Orr, R. K.; Chen, F.-M. *J. Am. Chem. Soc.* **1975**, *97*, 3126–3130.
40. McKenzie, A. *J. Chem. Soc.* **1899**, *75*, 753–770.
41. Kotsuki, H.; Kataoka, M.; Nishizawa, H. *Tetrahedron Lett.* **1993**, *34*, 4031–4034.