Developing asymmetric iron and ruthenium-based cyclone complexes; complex factors influence the asymmetric induction in the transfer hydrogenation of ketones.

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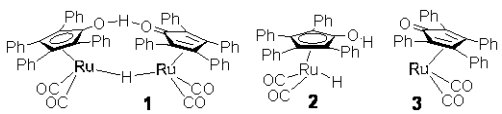
The preparation of a range of asymmetric iron and ruthenium-cyclone complexes, and their application to the asymmetric reduction of a ketone, are described. The enantioselectivity of of ketones reduction is influenced by a single chiral centre in the catalyst, as well as by the planar chirality in the catalyst. This represents the first example of asymmetric ketone reduction using an iron cyclone catalyst.

Introduction

The ruthenium complex **1** (the Shvo catalyst)[1-4] reversibly splits to give hydride **2** and the unsaturated species **3**.



By 'shuttling' between **2** and **3**, the Shvo catalyst transfers pairs of hydrogen atoms between secondary alcohols and ketones and has been used to good effect in dynamic kinetic resolution (DKR) reactions of alcohols and amines.[2,3] There is evidence,[4] largely based on kinetic isotope effects, that the hydrogen transfer to ketones and aldehydes, by the Shvo catlyst, takes place via a *concerted* 'outer sphere' mechanism (Figure 1a). This is analogous to that of of ketone reduction by the Noyori catalyst **4** (Figure 1b).[5]

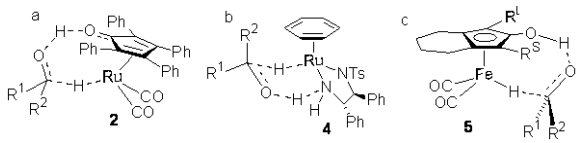
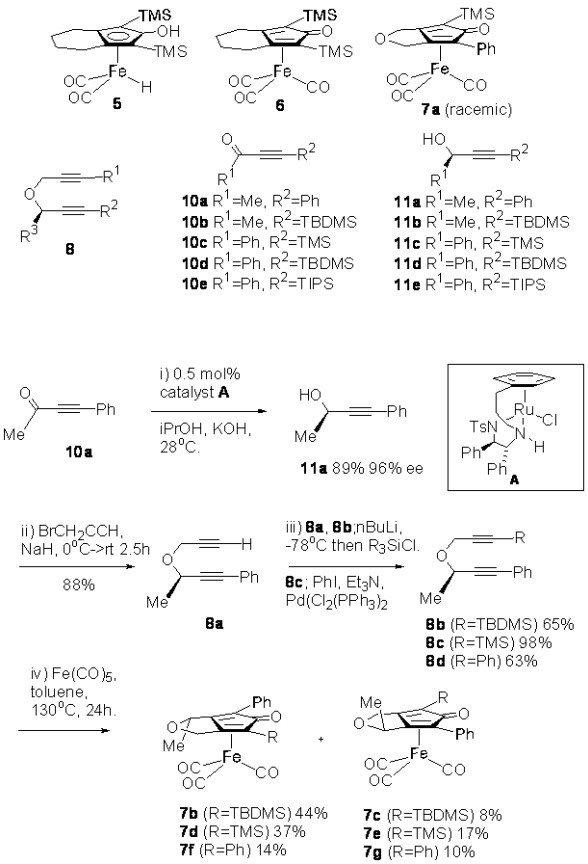


Figure 1; Comparison of mechanisms of hydrogen transfer by a) ruthenium hydride **2**, b) Noyori catalyst **4** and c) iron hydride **5**. In c, the potential for substituents R^L (large) and R^S (small) to influence the enantioselectivity is illustrated.

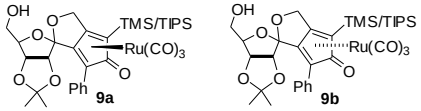
The Shvo catalyst is also an efficient ketone reducing agent when using an excess of an alcohol (usually iPrOH) or formic acid as hydrogen source,[1d] and can also catalyse hydrogenation reactions.[1b,c,4d,6] The closely related iron complex **5** has recently been prepared from the tricarbonyl precursor **6**[7] and employed in catalytic reduction reactions of ketones by Casey and Guan.[8] The mechanism appears to be analogous to that of the Shvo catalyst **2** (Figure 1c). In recent studies, complex **5** has been applied to the oxidation of alcohols using acetone as an acceptor, and a number of its derivatives have been reported and evaluated in this role.[9] In our own studies,[10] we reported the synthesis and applications of racemic complexes **7a**-**7g** in alcohol oxidations. The complexes were formed by an intramolecular cyclisation from a linear dialkyne precursor **8**, followed by diastereoisomer separation.[7,11]



Scheme 1; Synthesis of iron catalysts **7b**-**7g**.

However, given their proposed mechanism for reduction of ketones, we reasoned that asymmetric derivatives of **7b**-**7g** complexes should be capable of enantioselective ketone reduction reactions. Asymmetric induction would be predicted

to be achieved by the steric and/or electronic effects of the groups flanking the central 'C-O' bond of the cyclone ligand (Figure 1c).



Since the start of our studies in this area, Yamamoto has reported the synthesis of the asymmetric Shvo-type catalyst precursors **9a/9b**, which are capable of asymmetric hydrogenation (35 atm H_2) of acetophenone in 14-21% ee and up to 100% conversion.[12a] As far as we are aware this is the first example of an asymmetric Shvo-type catalyst, although Berkessel has very recently published a closedly related system based on chiral-at-Fe complexes which catalysed pressure hydrogenation (i.e. with H_2 gas) of acetophenone in up to 31% ee.[12b] Despite the difference in planar chirality, it was found that the same enantiomer of alcohol product (*R*) was formed by both **9a** and **9b**. Herein we disclose our own results in the area of asymmetric Shvo-type reduction catalysts using both iron- and ruthenium-based cyclone catalysts in asymmetric transfer hydrogenation (ATH) reactions (Table 1).

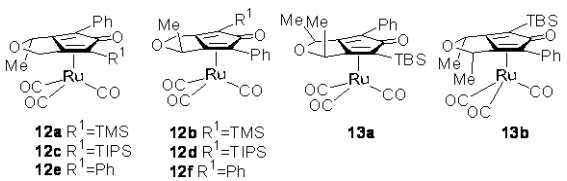
Racemic complex **7a**[10] was first tested and was found to work efficiently in a formic acid/triethylamine (FA/TEA) system, as commonly used in ATH reactions (Table 1).[5] At low temperature only a trace of formate byproduct was observed. Raising the temperature to 60 ^{o}C resulted in essentially complete reduction although some formate co-product was formed. The use of 10 mol% catalyst was required, along with 10 mol% of trimethylamine N-oxide to initiate hydride formation.[9b,10,13] An inferior result was observed in iPrOH.[5] Enantiopure complexes **7b** – **7g** were prepared (Scheme 1) from alcohol (*R*)-**11a** (made in 96% ee by reduction of the precursor ketone **10a** by ATH using an established catalyst[14]**).** Elaboration of (*R*)-**11a** following the reported route[10] gave in each case (i.e. from **8b-d** where R^1= TBDMS, TMS and Ph respectively) two enantiomerically-enriched complexes which were separated by chromatography on silica gel. In our previous studies on the racemic series, we had established the relative configuration of the chiral centres via an X-ray crystallographic solution of **7c**; the other iron complexes are assigned by analogy with **7b/c.**[10] The enantiomeric purity of catalyst **7d** was established using a shift reagent and was established to be ca. 92% ee, indicating a small loss of ee relative to the alcohol but a high enough level to be meaningful in these investigations (see supporting information). Conversions were in all cases measured by integrating the product peaks in the GC against the starting material peaks.

The new catalysts were tested in the ATH of acetophenone (Table 1). In the case of **7b/c**, the catalyst proved to be of low activity and a reduction product of low ee was formed in the same major enantiomeric form. Each purified, enantiomerically-pure diastereoisomer of **7d/e** was found to be a more effective catalyst for ketone reduction in 5:2 FA/TEA, giving almost complete transformation within 48-96 hours at 40^{o}C. Again, both gave reduction products of the same absolute configuration, mirroring the activity of the ruthenium complexes reported by Yamamoto.[12] More interestingly, catalysts **7f/g**, which bear identical (phenyl) groups flanking the central C=O function in the cyclone, also gave the same alcohol enantiomers. The chiral centre on the backbone of the cyclone clearly has a significant effect on the catalyst enantioselectivity, possibly due to an influence on the conformation of the phenyl rings.. Although the ees are low, the isomer with the methyl group positioned proximal to the $Fe(CO)_3$ group gave a higher ee in each case (**7b,d,f** vs **7c,e,g** respectively). The effect may arise via an influence on the positions of the CO ligands which subsequently communicates to the reduction transition state.

Monitoring the reductions over time indicated that the ees did not change significantly over time, even after several days (e.g. **7d** after 48 and 96h), indicating that product racemisation is not taking place. Although the conversions appear to level out over time, it is at present unclear as to whether this may be due to catalyst deactivation or a solvent effect. Formic acid/triethylamine was used in the traditional azeotrope ratio of 5:2 throughout. A ratio of 1:1 FA:TEA gave a conversion of 25% in 96h and 21% ee when **7d** was used as catalyst. A 1:2 FA:TEA mixture was not homogeneous, whilst a 5:1 FA:TEA mixture gave only 11% conversion after 96h, in 26% ee. These results indicate that the FA:TEA ratio effects the rate but not the ee of the reaction, with 5:2 being the best ratio of those tested.

As far as we are aware, this represents the first application of any iron cyclone complex to the asymmetric reduction of ketones by transfer hydrogenation,[12] and also reveals an unusual effect of a backbone chiral centre on the observed enantiocontrol.

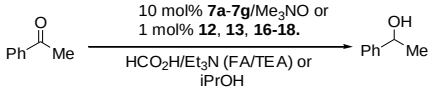
We also wished to establish whether the analogous ruthenium-based catalysts would exhibit a similar pattern of enantioselectivity. To this end, complexes **12a-12f** were prepared and evaluated, using the corresponding diyne precursors.[15]



Alcohol (*R*)-**11a** (96% ee) was converted to the three derivatives **12a** – **12f** following the precendent for the iron complexes[10] but with the use of $Ru_3(CO)_{12}$ in the complexation step.[15] Complexes **12a/b**, were formed as a mixture of two separable diastereoisomers of product in 27 and 12% isolated yields respectivity. Although the relative position of the Me group has not been established, we have assumed that, in analogy with the iron series, that the major enantiomer is that in which the Me on the backbone is proximal to the $Ru(CO)_3$ group. Both **12a** and **12b** were effective in catalysing the reduction of acetophenone, again in the same absolute sense (Table 1). Unlike the Fe series, there was evidence of racemisation during extended reaction times; for example in the case of **12a**, the ee was 20% after 10 h. For the Ru complexes, in situ formation of the hydride using

NaOH in THF followed by phosphoric acid was completed prior to the reduction,[7a] and Me_3NO was not required. The ruthenium catalysts were also used at lower loadings (1 mol%) than the iron complexes (10 mol%). In the case of **12c/d**, only one isomer was isolated, and in low yield, from the cyclisation, and was assumed to be of the configuration shown in **12c**. This complex promoted reduction but in poor enantioselectivity.

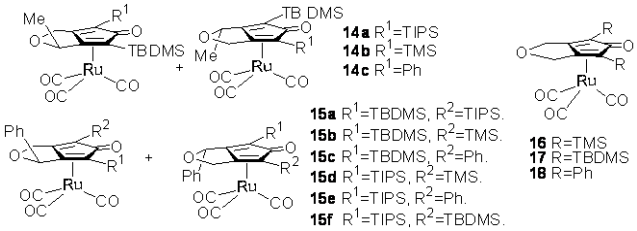
Table 1; Asymmetric reduction of acetophenone using iron and ruthenium cyclone complexes[a]



Com-plex	Conditions	Time /h	Conv/%[b] (alcohol)	Ee (*R/S*)
7a	FA/TEA 28°C 1M	18	60 (<1 form)	n/a
7a	FA/TEA 40°C 1M	18	90 (+2 form)	n/a
7a	FA/TEA 60°C 1M	18	89 (+10 form.)	n/a
7a	iPrOH 28°C 0.2M	18	6.8	n/a
7a	iPrOH 60°C 0.2M	18	52	n/a
7b	FA/TEA 28°C 1M	48	25	15 (*R*)
7b	FA/TEA 40°C 1M	48	36	10 (*R*)
7c	FA/TEA 40°C 1M	96	10	10 (*R*)
7d	FA/TEA 28°C 1M	48	40	25 (*R*)
7d	FA/TEA 28°C 1M	96	69	23 (*R*)
7e	FA/TEA 28°C 1M	48	46	11 (*R*)
7d	FA/TEA 40°C 1M	96	80 (+5 form)	23 (*R*)
7e	FA/TEA 40°C 1M	48	91 (+5 form.)	11 (*R*)
7f	FA/TEA 40°C 1M[d]	96	66 (+10 form.)	25 (*R*)
7g	FA/TEA 40°C 1M[d]	96	17	5 (*R*)
12a	FA/TEA 60°C 1.6M	160	50	12 (*R*)[c]
12a	iPrOH 60°C 0.18M	160	28	11 (*R*)
12b	FA/TEA 60°C 1.6M	160	61	3 (*R*)
12b	iPrOH 60°C 0.18M	160	35	4 (*R*)
12c	FA/TEA 60°C1.6M	150	48	5 (*R*)
12c	iPrOH 60°C 0.18M	150	58	3 (*R*)
12e	FA/TEA 60°C 1.6M	18	31	17 (*R*)
12e	iPrOH 60°C 0.18M	18	13	11 (*R*)
13a/b	FA/TEA 60°C 1.6M	150	19	15 (*S*)
13a/b	iPrOH 60°C 0.18M	150	20	5 (*S*)
16	FA/TEA 60°C 1.6M	168	35 (+5 form.)	n/a
16	iPrOH 60°C 0.18M	184	17	n/a
17	FA/TEA 60°C 1.6M	168	80 (+7 form.)	n/a
17	iPrOH 60°C 0.18M	168	90	n/a
18	FA/TEA 60°C 1.6M	168	12.5	n/a
18	iPrOH 60°C 0.18M	168	21	n/a

a. 10 mol% iron catalyst was used, with 10 mol% Me_3NO. b. form. = formate byproduct. c. ee was 20% (*R*) at 10h and decreased with time. d. Reactions at 28°C, 1M with **7c**; 48h, 5% conv, 10% ee (*R*), **7f**; 96h, 2% conv, 29% ee, **7g**; 96h, trace conversion.

Complexes **12e/f** have two identical groups flanking the central C=O group, analogous to **7c/d**. The cyclisation to form **12e/f** was achieved in low yield, however only one diastereoisomer, assumed to be **12e**, could be isolated. This was capable of reduction of acetophenone in up to 17% ee (*R*), which, although low, confirms that for the Ru catalysts as well as the iron ones, planar asymmetry is not required for the asymmetric reduction. In order to eliminate the effect of one backbone chiral centre, complexes **13a/b** were selected for study – in this case containing two methyl groups in a *cis* arrangement. This was prepared by reacting alcohol (*R*)-**11b** (see below) with mesylated (*R*)-**11a**, resulting in inversion of configuration. Cyclisation of the resulting diyne with $Ru_3(CO)_{12}$ gave a mixture from which one isomer of **13** was isolated in pure form. Although the relative positions of the methyl groups to the $Ru(CO)_3$ centre are not known, this catalyst will rely on planar chirality alone in the reduction reaction. The result was that acetophenone was reduced in up to 15% ee, and in this case unexpected (*S*) configuration (Table 1). Taken together, these results indicate that asymmetric induction by cyclone catalysts arises from a combination of control by backbone chiral centres and planar chirality.



The synthesis of catalysts **14a-c** was investigated. The TBS-substituted alcohol (*R*)-**11b** was prepared from **10b** in quantitative conversion, 88% isolated yield and over 99% ee using the same ATH catalyst as was used for **11a**.[14] Unfortunately, separation of the diastereomers of these complexes could not be achieved and these were not evaluated in reductions.

In studies directed at improving the d.e.s of the cyclisation through the use of a larger group on the chiral centre, we examined derivatives of **8** where R^3=Ph. Ru/TsDPEN catalysts are less effective at reduction of aryl/propargylic ketones **10c-10e**,[16] therefore these were reduced using (*R*)-Alpine borane.[17] For variation of group R^1, we prepared alcohols (*R*)-**11c-11e** however the TMS derivative (*R*)-**11c** was prone to loss of the silyl group in the subsequent alcohol alkylation step. Reaction of the dialkyne derivatives of (*R*)-**11d** (96% ee) and (*R*)-**11e** (97% ee) with $Ru_3(CO)_{12}$ led to the formation of Ru cyclone complexes **15a-f**, all of which were formed as inseparable mixtures of diastereoisomers and proved to be poor catalysts (see SI). For comparison of relative reactivity, symmetrical complexes **16-18** were also prepared and tested in ATH reactions; the TBDMS-substituted catalyst **17** proved to be the most active (Table 1).

In conclusion, a series of enantiomerically enriched iron and ruthenium cyclone complexes have been prepared and applied to the ATH of ketones to alcohols. The iron complexes, in their first reported role as ATH catalysts, are as effective in terms of asymmetric induction as the ruthenium complexes, although higher loadings are required. Other iron-based catalysts have recently been reported to give higher activities and enantioselectivities.[18] The results also indicate that the control of enantioselectivity in the reductions, whilst modest, appears to rely on a novel means of asymmetric induction by a remote chiral centre in addition to the planar symmetry of the catalysts.

Experimental section.

Procedures for starting material ketones, racemic reductions, synthesis of **16-18**, Tables for reductions using **15a-f** and NMR spectra may be found in the Electronic Supporting Information.

(*R*)-4-Phenyl-3-butyne-2-ol 11a.[14]

(*R,R*)-Tethered Ru(II) catalyst (43 mg, 0.07 mmol)[14b] was dissolved in iPrOH (135 cm^3) at 28 °C. KOH (0.1M in iPrOH, 3.46 cm^3, 0.0346 mmol) was added and the solution was observed to initially turn dark purple and the gradually become lighter in colour. After stirring for 30 min at 28 °C, 4-phenyl-3-butyne-2-one **10a** (2.00 g, 13.88 mmol) was added and again the mixture turned dark purple. After 15 h the solvent was removed in vacuo to afford a dark oil which was purified by short path distillation (125 °C, 5.8 mbar) to afford the alcohol as a colourless oil (1.80 g, 12.32 mmol, 89%); $[\alpha]_D^{28}$ +32.4 (c 0.966 in $CHCl_3$) (lit.[14a] $[\alpha]_D^{23}$ -35.0 (c 1.0 in $CHCl_3$) 97% ee (*S*); *m/z* (ESI) 169 $[M+23]^+$; (Found (ESI): M+Na 169.0630, $C_{10}H_{10}NaO$ requires 169.0624); ν_{max} 3298, 2978, 2927, 2870, 2225, 1595 and 1490 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.46-7.41 (2H, m, Ar), 7.34-7.28 (3H, m, Ar), 4.77 (1H, m, C*H*(OH)CH_3), 2.00 (1H, d, *J* 5.13, O*H*), 1.57 (3H, d, *J* 7.03, CH_3); δ_C (100 MHz, $CDCl_3$) 131.68 (CH, Ar), 128.42 (CH, Ar), 128.42 (CH, Ar), 122.61 (ipso, Ar), 90.96 (C≡C), 84.05 (C≡C), 58.91 (*C*H(OH)CH_3), 24.42 (CH(OH)*C*H_3); The ee was determined using chiral GC of the acetyl derivative of the alcohol synthesised from reacting a sample of the alcohol (<10 mg) with acetic anhydride (<50 μL) and DMAP (<1 mg) in DCM (*ca.* 1 cm^3) overnight; cyclodextrin CB column; 96 % ee, 115 °C, H_2, 15 psi, 62.72 (*S*), 64.18 min (*R*).[14b]

(*R*)-Dipropargylic ether 8a (**8;** R^1=H, R^2=Ph, R^3=Me).[19]

Sodium hydride (0.190 g, 60% on mineral oil, 4.746 mmol, 1.1 eq) was added to (*R*)-4-phenyl-3-butyne-2-ol (0.630 g, 4.315 mmol, 1 eq.) in THF (8 cm^3) at 0 °C. After 30 min, propargylic bromide (0.55 cm^3, 0.7695 g, 80% in toluene, 5.178 mmol, 1.2 eq.) was added at 0 °C and the reaction was left to warm to room temperature over 2.5 h. The mixture was quenched using saturated $NH_4Cl_{(aq)}$ (30 cm^3) and extracted with ether (3 x 30 cm^3). The combined organic fractions were dried over $MgSO_4$ and the solvent removed in vacuo to afford a yellow oil. Purification by column chromatography (EtOAc/pet. Ether (40-60) 1:20) afforded propagylic ether **8a** (**8;** R^1=H, R^2=Ph, R^3=Me) as a yellow oil (0.70 g, 3.804 mmol, 88%); $[\alpha]_D^{28}$ +289.04 (c 0.762 in $CHCl_3$); *m/z* (ESI) 207 (M^+ +23); (Found (ESI): M+Na 207.0788, $C_{13}H_{12}NaO$ requires 207.0780); ν_{max} 3289, 2985, 2932, 2853, 2361, 2223, 2198, 2115, 1958, 1888, 1724, 1671, 1596, 1489, 1439, 1368 and 1325 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.51-7.45 (2H, m, Ar), 7.38-7.32 (3H, m, Ar), 4.68 (1H, q, *J* 6.5, OC*H*CH_3), 4.44 (1H, dd, *J* 15.6, 2.0, OC*H*H), 4.36 (1H, dd, *J* 15.6, 2.0 OCH*H*), 2.49 (1H, t, *J* 2.0, C≡C*H*), 1.59 (3H, d, *J* 6.5, CH_3); δ_C (100 MHz, $CDCl_3$) 131.73 (CH, Ar), 128.43 (CH, Ar), 128.25 (CH, Ar), 122.45 (ipso, Ar), 87.88 (C≡C), 85.62 (C≡C), 79.56 ((C≡*C*H), 74.42 (C≡C), 64.62 (O*C*H), 55.74 (OCH_2), 22.00 (CH_3).

(*R*)-Dipropargylic ether 8c (**8;** R^1=Me_3Si, R^2=Ph, R^3=Me).[10]

To **8a** (**8;** R^1=H, R^2=Ph, R^3=Me) (0.350 g, 1.9022 mmol, 1 eq.) in THF (12.5 cm^3) was added nBuLi (1.6M in hexanes, 1.3 cm^3, 2.092 mmol, 1.1 eq.) at -78 °C. After 1 h at -78 °C, trimethylsilylchloride (0.29 cm^3, 0.248 g, 2.283 mmol, 1.2 eq.) was added and the mixture stirred at -78 °C for 1 h before being allowed to warm to room temperature overnight. The reaction was quenched using saturated $NH_4Cl_{(aq)}$ (15 cm^3) and extracted using Et_2O (3 x 15 cm^3). The combine organics were dried over $MgSO_4$ and the solvent removed in vacuo to afford the product as a dark yellow oil (0.4800 g, 1.86 mmol, 98 %) and used without further purification; $[\alpha]_D^{28}$ +160.04 (c 0.57 in $CHCl_3$); *m/z* (ESI) 279 $[M+23]^+$; (Found (ESI): M+Na 279.1176 $C_{16}H_{20}NaOSi$ requires 279.1176); ν_{max} 2985, 2954, 2927, 2890, 2843, 2168, 1763, 1595 and 1487 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.48-7.45 (2H, m, Ar), 7.34-7.30 (3H, m, Ar), 4.62 (1H, q, *J* 6.5, OC*H*CH_3), 4.42 (1H, d, *J* 15.6, OC*H*H), 4.32 (1H, d, *J* 15.6, OCH*H*), 1.57 (3H, d, *J* 6.5, CH_3), 0.20 (9H, s, Si$(CH_3)_3$); δ_C (100 MHz, $CDCl_3$) 131.73 (CH, Ar), 128.39 (CH, Ar), 128.24 (CH, Ar), 122.55 (ipso, Ar), 101.29 (C≡C), 91.35 (C≡C), 88.12 (C≡C), 85.53 (C≡C), 64.66 (OCH), 55.61 (OCH_2), 22.02 (CH*C*H_3), -0.10 (Si(*C*$H_3)_3$).

(*R*)-Dipropargylic ether 8 (R^1=$(iPr)_3Si$, R^2=Ph, R^3=Me).

To **8a** (**8**: R^1=H, R^2=Ph, R^3=Me) (0.350 g, 1.9022 mmol, 1 eq.) in THF (12.5 cm^3) was added nBuLi (1.6M in hexanes, 1.3 cm^3, 2.092 mmol, 1.1 eq.) at -78 °C. After 1 h at -78 °C triisopropylsilylchloride (0.49 cm^3, 0.440 g, 2.283 mmol, 1.2 eq.) was added and the mixture stirred at -78 °C for 1 h before being allowed to warm to room temperature overnight. The reaction was quenched using saturated $NH_4Cl_{(aq)}$ (15 cm^3) and extracted using Et_2O (3 x 15 cm^3). The combined organics were dried over $MgSO_4$ and the solvent removed in vacuo to afford the product as a dark orange oil in quantative yield and used without further purification; $[\alpha]_D^{28}$ +150.35 (c 0.20 in $CHCl_3$); *m/z* (ESI) 363 $[M+23]^+$; (Found (ESI): M+Na 363.2115 $C_{22}H_{32}NaOSi$ requires 363.2115); ν_{max} 2937, 2890 and 2863 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.47-7.44 (2H, m, Ar), 7.34-7.30 (3H, m, Ar), 4.74 (1H, q, *J* 6.5, (OC*H*CH_3)), 4.41 (2H, s, OCH_2), 1.57 (3H, d, *J* 6.5, CHCH_3), 1.12-1.08 (21H, m, Si(C*H*(C$H_3)_2)_3$); δ_C (100 MHz, $CDCl_3$) 131.82 (CH, Ar), 128.39 (CH, Ar), 128.27 (CH, Ar), 122.67 (ipso, Ar), 103.14 (C≡C), 88.30 (C≡C), 87.73 (C≡C), 85.34 (C≡C), 64.01 (O*C*H), 56.58 (*C*H_2), 22.03, 18.61, 17.72, 12.31, 11.19.

(*R*)-Dipropargylic ether 8b (**8:** R^1=$(tBu)_3SiMe_2$, R^2=Ph, R^3=Me).[10]

Compound **8a** (**8:** R^1=H, R^2=Ph, R^3=Me) (0.195 g, 1.06 mmol) was dissolved in dry THF (15 cm^3) and cooled to -78 °C. n-Butyllithium in hexanes (1.6 M, 0.79 cm^3, 1.26 mmol) was added dropwise and the mixture was allowed to stir for 1 h after which time *tert*-butyldimethylsilylchloride (0.207 g, 1.37 mmol) in dry THF (5 cm^3) was added. After 17 h the reaction was quenched with H_2O (20 cm^3), the THF was removed under reduced pressure and the product was extracted into Et_2O (3 x 20 cm^3). The combined organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to give the product as a brown oil which was purified by column chromatography on silica with a gradient elution from 100 % petroleum ether to 80:20 petroleum ether:ethyl acetate to give the product **8** as a yellow oil (0.206 g, 0.69 mmol, 65 %). The measured data is in agreement with that previously reported for

the racemic compound.[10] $[\alpha]_D^{24}$ +150.7 (c 1.0 in $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 7.42-7.46 (2H, m, Ar), 7.28-7.34 (3H, m, Ar), 4.64 (1H, q, *J* 6.8, CC*H*(CH_3)O), 4.41 (1H, d, *J* 15.8, CCH_2O), 4.33 (1H, d, *J* 15.8, CCH_2O), 1.55 (3H, d, *J* 6.8 Hz, (CCH(CH_3)O), 0.95 (9H, s, Si(CH_3)$_2$C(CH_3)$_3$) 0.12 (6H, s, Si(CH_3)$_2$C(CH_3)$_3$.

(*R*)-Dipropargylic ether 8d (**8:** R^1=Ph, R^2=Ph, R^3=Me).
To **8a** (**8:** R^1=H, R^2=Ph, R^3=Me) (0.400 g, 2.1739 mmol, 1eq.), phenyliodide (0.29 cm^3, 0.5322 g, 2.6087 mmol, 1.2 eq.) in triethylamine (7 cm^3) at 50 °C was added $Pd(Cl_2)(PPh_3)$ (0.031 g, 0.043 mmol, 0.02 eq.) After stirring for 5 min, CuI (0.04 g, 0.0217 mmol, 0.01 eq.) was added and the mixture kept at 50 °C for 18 h. The mixture was then hot filtered to remove the amide salts. Removal of the remaining amine in vacuo afforded a yellow oil which was purified by column chromatography to afford the product as a light yellow oil (0.358 g, 1.3769 mmol, 63%); $[\alpha]_D^{28}$ +180.00 (c 0.16 in $CHCl_3$); *m/z* (ESI) 261 $[M+1]^+$, 283 $[M+23]^+$; (Found (ESI): M+Na 283.1093 $C_{19}H_{16}NaO$ requires 283.1093); ν_{max} 3052, 2981, 2934, 2843, 2219 and 1716 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.50-7.46 (4H, m, Ar), 7.35-7.30 (6H, m, Ar), 4.73 (1H, q, *J* 6.5, OC*H*CH_3), 4.65 (1H, d, *J* 15.6, OC*H*H), (R^1=Ph, R^2=Ph, R^3=Me).[10,19] 4.73 (1H, q, *J* 6.5, OC*H*CH_3), 4.65 (1H, d, *J* 15.6, OC*H*H), 4.57 (1H, d, *J* 15.6, OCH*H*), 1.61 (3H, d, *J* 6.5, OCHCH_3); δ_C (100 MHz, $CDCl_3$) 131.81 (CH, Ar), 131.76 (CH, Ar), 128.42 (CH, Ar), 128.40 (CH, Ar), 128.25 (CH, Ar), 128.23 (CH, Ar), 122.61 (ipso, Ar), 122.54 (ipso, Ar), 88.18 (C≡C), 86.22 (C≡C), 85.61 (C≡C), 84.92 (C≡C), 64.66 (O*C*H), 56.60 (O*C*H_2), 22.08 (OCH*C*H_3).

(*R*)-alcohol 11b.[20]
Tethered-TsDPEN (*R,R*) Ru(II) catalyst[14b] (31 mg, 0.005 mmol, 0.5 mol%) was dissolved in anhydrous iPrOH (97 cm^3) and warmed to 28 °C. On addition of KOH (in iPrOH, 0.1M, 2.5 cm^3, 0.25 mmol) the colourless solution turned dark purple and was stirred at 28 °C for 30 min before TBDMS-3-butyn-2-one **10b** (1.840 g, 10 mmol) was added. After 18 h at 28 °C the solvent was removed in vacuo and the resulting alcohol was purified by column chromatography (EtOAc/Hexane 5%) to afford a yellow oil (1.630 g, 8.76 mmol, 88%); *m/z* (ESI) 207 $[M+23]^+$; $[\alpha]_D^{28}$; +26.29 (c 0.978 in $CHCl_3$); ν_{max} 3315, 2954, 2924, 2887, 2853, 2168, 1470 1358, 1251, 1112, 1072, 1041 and 940 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 4.52 (1H, dq, *J* 6.6, 5.3, C*H*(OH)CH_3), 1.77 (1H, d, J 5.3, O*H*), 1.45 (3H, d, *J* 6.6, CH(OH)CH_3), 0.93 (9H, s, SiC(CH_3)$_3$), 0.10 (6H, s, Si(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 108.35 (quat., C≡C), 86.64 (quat., C≡C), 58.75 (*C*H(OH)CH_3), 26.00 (CH_3), 24.35 (CH_3), 16.42 (quat., Si*C*(CH_3)$_3$), -4.71 (CH_3, Si(*C*H_3)$_2$). The ee was determined using the acetyl derivative of the alcohol synthesised from reacting a trace amount of the alcohol (<10 mg) with acetic anhydride (<50 µL) and DMAP (<1 mg) in DCM (ca. 1 cm^3) overnight. cyclodextrin CB column; 99 % ee, 115 °C, H_2, 15 psi, 14.19 (*S*), 14.51 min (*R*).

(*R*)-Mesyl derivative of (*R*)-4-phenyl-3-butyne-2-ol 11a.[21]
To (*R*)-4-phenyl-3-butyne-2-ol **11a** (1.00g, 1.00 cm^3, 6.833 mmol, 1 eq.) and triethylamine (1.90 cm^3, 13.46 mmol, 2 eq.) in DCM (10 cm^3) at -78 °C was slowly added methanesulfonyl chloride (0.80 cm^3, 10.13 mmol, 1.5 eq.) after 1 h the mixture was allowed to warm to room temperature and quenched with $NaHCO_{3(aq)}$ (15 cm^3), extracted with DCM (3 x 10 cm^3) and dried over Na_2SO_4. Removal of the solvent in vacuo afforded the mesylate as a colourless oil in quantitative yield and was used immediately without further purification; δ_H (400 MHz, d_6-DMSO) 7.50-7.46 (2H, m, Ar), 7.43-7.34 (3H, m, Ar), 5.55 (1H, q, J 6.5, C*H*CH_3), 3.18 (3H, s, SO_2CH_3), 1.77 (3H, d, J 6.5, CHCH_3).

(*R,S*)-Dipropargyl ether precursor of ligand 13a/b.
To (*R*)-4-(t-butyldimethylsilyl)-3-butyne-2-ol **11b** (0.3852 g, 2.0710 mmol, 1 eq.) in THF (5 cm^3) was added sodium hydride (0.083 g, 2.0710 mmol, 60% in mineral oil, 1 eq.) at 0 °C. After 30 min the mesyl derivative of (*R*)-4-phenyl-3-butyne-2-ol **11a** (0.46 g, 2.0710 mmol, 1 eq.) was added and the reaction was allowed to warm to room temperature over 18 h. After quenching the mixture using saturated aqueous sodium bicarbonate (5 cm^3) the mixture was extracted with Et_2O (3 x 7 cm^3) and dried over $NaSO_4$, removal of the solvent in vacuo afforded a yellow oil which was purified by column chromatography (EtOAc/hexane gradient 1:100 to 1:10) yielding the product as a colourless oil (0.1911 g, 0.6125 mmol, 30%); $[\alpha]_D^{28}$ +0.19 (c 0.78 in $CHCl_3$); *m/z* (ESI) 335.2 $[M+23]^+$; (Found (ESI): M+Na 335.1801 $C_{20}H_{28}NaOSi$ requires 335.1802); ν_{max} 2983, 2952, 2929, 2880 and 2853 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.48-7.42 (2H, m, Ar), 7.33-7.28 (3H, m, Ar), 4.72 (1H, q, *J* 6.5, C*H*), 4.51 (1H, q, *J* 6.5, C*H*), 1.55 (3H, d, *J* 6.5, CH_3), 1.50 (3H, d, *J* 6.5, CH_3), 0.95 (9H, s, SiC(CH_3)$_3$), 0.10 (6H, s, SiCH_3); δ_C (100 MHz, $CDCl_3$) 131.76 (Ar), 131.70 (Ar), 128.29 (Ar), 128.19 (Ar), 128.14 (Ar), 106.30 (C≡C), 89.35 (C≡C), 84.73 (C≡C), 63.47 (C≡C), 63.45 (C≡C), 26.04, 22.10, 21.79. -4.70 (Si(CH_3)$_2$).

Iron cyclone complexes 7b/c.
(*R*)-Dipropargylic ether **8b** (**8:** R^1=$(tBu)_3SiMe_2$, R^2=Ph, R^3=Me, 96% ee) (0.206 g, 0.69 mmol) and $Fe(CO)_5$ (0.27 cm^3, 2.05 mmol) were dissolved in dry toluene (3 cm^3) and heated at 130 °C for 24 h after which time the solution was allowed to cool to room temperature and the solvent was removed under reduced pressure. The brown residue was filtered through celite using a 9:1 mixture of hexane:ethyl acetate and subsequent purification by column chromatography on silica with a gradient elution from 100 % petroleum ether to 40:60 petroleum ether:ethyl acetate gave two diastereomers of product, which were separated. The measured data is in agreement with that previously reported for the racemic compound.[10] Minor diastereomer, yellow solid (0.026 g, 0.056 mmol, 8 %); $[\alpha]_D^{26}$ -47.0 (c 0.05 in $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 7.99-8.05 (2H, m, Ar), 7.29-7.39 (3H, m, 3H, Ar), 5.56 (1H, q, *J* 6.8 Hz, CC*H*(CH_3)O), 4.81 (1H, d, *J* 13.2 Hz, CH_2), 4.71 (1H, d, *J* 13.2 Hz, CH_2), 1.53 (3H, d, *J* 6.8 Hz, CH_3), 1.01 (9H, s, SiC(CH_3)$_3$) 0.47 (3H, s, Si(*C*H_3)$_2$C(CH_3)$_3$), 0.08 (3H, s, Si(CH_3)$_2$C(CH_3)$_3$). Major diastereomer, brown oil (0.140 g, 0.300 mmol, 44 %); $[\alpha]_D^{28}$ +20.0 (c 0.05 in $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 7.47-7.53 (2H, m, Ar), 7.29-7.41 (3H, m, Ar), 5.38 (1H, q, *J* 6.0 Hz, CC*H*(CH_3)O), 4.79 (1H, d, *J* 13.2 Hz, CH_2), 4.73 (1H, d, *J* 13.2 Hz, CH_2), 1.65 (3H, d, *J* 6.0 Hz, CH_3), 0.97 (9H, s, SiC(CH_3)$_3$) 0.51 (3H, s, Si(CH_3)$_2$C(CH_3)$_3$), 0.06 (3H, s, Si(CH_3)$_2$C(CH_3)$_3$).

Iron cyclone complexes 7d/e.

These complexes (two diastereomers) were synthesised by the same procedure as for **7d/e** using (*R*)-dipropargylic ether **8c** (**8:** R^1=TMS, R^2=Ph, R^3=Me, 96% ee) (0.390 g, 1.53 mmol) and $Fe(CO)_5$ (0.60 cm^3, 4.56 mmol) and were purified by column chromatography on silica gel with a gradient elution from 100 % petroleum ether to 80:20 petroleum ether:ethyl acetate to give two diastereomers of product which were separated, as brown oils. The measured data is in agreement with that previously reported for the racemic material.[10] Minor diastereomer (0.111 g, 0.262 mmol, 17 %); $[\alpha]_D^{28}$ -166.0 (c 0.05 in $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 7.99-8.03 (2H, m, Ar), 7.29-7.40 (3H, m, Ar), 5.57 (1H, q, *J* 6.4 Hz, CC*H*(CH_3)O), 4.81 (1H, d, *J* 12.8 Hz, CH_2), 4.71 (1H, d, *J* 12.8 Hz, CH_2), 1.52 (3H, d, *J* 6.4 Hz, CH_3), 0.33 (9H, s, Si(CH_3)$_3$). Major diastereomer (0.240 g, 0.566 mmol, 37 %); $[\alpha]_D^{28}$ +101.0 (c 0.05 in $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 7.48-7.52 (2H, m, Ar), 7.30-7.40 (3H, m, Ar), 5.36 (1H, q, *J* 6.4 Hz, CC*H*(CH_3)O), 4.79 (1H, d, *J* 13.2 Hz, CH_2), 4.71 (1H, d, *J* 13.2 Hz, CH_2), 1.65 (3H, d, *J* 6.4 Hz, CH_3), 0.31 (9H, s, Si(CH_3)$_3$).

Iron cyclone complexes 7f/g.

These complexes (two diastereomers) were synthesised by the same procedure as for **7b/c** using (*R*)-dipropargylic ether **8d** (**8:** R^1=Ph, R^2=Ph, R^3=Me, 96% ee) (0.165 g, 0.63 mmol) and $Fe(CO)_5$ (0.25 cm^3, 1.90 mmol) and were purified by column chromatography on silica with a gradient elution from 100 % petroleum ether to 80:20 petroleum ether:ethyl acetate to give two diastereomers of product, which were separated. The measured data is in agreement with that previously reported for the racemic material.[10] Minor diastereomer; brown powder (0.026 g, 0.061 mmol, 10 %); $[\alpha]_D^{28}$ -75.0 (c 0.01 in $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 8.06-8.11 (2H, m, Ar), 7.86-7.93 (2H, m, Ar), 7.32-7.45 (6H, m, Ar), 5.64 (1H, q, *J* 6.4 Hz, (CC*H*(CH_3)O), 5.17 (2H, s, CH_2), 1.54 (3H, d, *J* 6.4 Hz, (CCH(CH_3)O). A broad resonance exists from 6.5-7.6 ppm in the ^{1}H NMR spectrum that has not been assigned; this may be due to paramagnetic impurities. Major diastereomer; brown powder (0.039 g, 0.091 mmol, 14 %); $[\alpha]_D^{28}$ +23.0 (c 0.05 in $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 7.90-7.96 (2H, m, Ar), 7.53-7.59 (2H, m, Ar), 7.32-7.45 (6H, m, Ar), 5.40 (1H, q, *J* 6.0 Hz, (CC*H*(CH_3)O), 5.25 (1H, d, *J* 13.2 Hz, CH_2), 5.03 (1H, d, *J* 13.2 Hz, CH_2) 1.67 (3H, d, *J* 6.0 Hz, (CCH(CH_3)O). A broad resonance exists from 6.6-7.8 ppm in the ^{1}H NMR spectrum that has not been assigned; this may be due to paramagnetic impurities.

Ruthenium cyclone complex 12a/b.

A sealed tube was charged with **8c** (**8:** R^1=Me_3Si, R^2=Ph, R^3=Me) (0.3813 g, 1.4894 mmol, 3eq.) and $Ru_3(CO)_{12}$ (0.3173 g, 0.4965 mmol, 1 eq.) in acetonitrile (5 cm^3) and the reaction heated to 100 ^{o}C over 2 days. The solvent was removed in vacuo and redissolved in DCM then filtered to remove any unreacted $Ru_3(CO)_{12}$ and purified by column chromatography (EtOAc/pet. ether (40-60) 1:10) to afford the major **12a** (0.1787, 0.404 mmol, 27%) and minor **12b** (0.0768 g, 0.1738 mmol, 12%) diastereoisomers. Configurations assigned by analogy with Fe complexes; **Major;** *m/z* (ESI) 471 $[M+1]^+$, 493 $[M+23]^+$; $[\alpha]_D^{28}$ +79.20 (c 0.11 $CHCl_3$); (Found (ESI): M+H 471.0218 $C_{20}H_{21}O_5RuSi$ requires 471.0201); (Found (ESI): M+Na 493.0039 $C_{20}H_{20}NaO_5RuSi$ requires 493.0021); ν_{max} 2075, 2006 and 1626 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.43 (2H, d, *J* 7.0, Ar), 7.35 (2H, t, *J* 7.5, Ar), 7.30-7.25 (1H, m, Ar), 5.29 (1H, q, *J* 6.0, OC*H*CH_3), 4.83-4.73 (2H, m, OCH_2), 1.59 (3H, d, *J* 6.0, OCHCH_3), 0.32 (9H, s, Si(CH_3)$_3$); δ_C (100 MHz, $CDCl_3$) 193.82 (C=O), 179.00 (C=O), 130.44 (ipso, Ar), 129.80 (CH, Ar), 128.35 (CH, Ar), 127.64 (CH, Ar), 114.40, 112.85, 80.04, 74.81 (O*C*HCH$_3$), 67.27, 62.54, 23.73 (OCH*C*H$_3$), -0.51 (Si(*C*H$_3$)$_3$); **Minor** $[\alpha]_D^{28}$ -8.30 (c 0.112 $CHCl_3$); *m/z* (ESI) 471 $[M+1]^+$, 493 $[M+23]^+$; (Found (ESI): M+H 471.0200 $C_{20}H_{21}O_5RuSi$ requires 471.0201); (Found (ESI): M+Na 493.0019 $C_{20}H_{20}NaO_5RuSi$ requires 493.0021); ν_{max} 2080, 2020 and 1989 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.97 (2H, d, *J* 7.5, Ar), 7.35 (2H, t, *J* 7.5, Ar),7.29-7.25 (1H, m, Ar), 5.60 (1H, q, *J* 6.5, OC*H*CH_3), 4.89 (1H, dd, *J* 12.6, 1.0, OC*H*H), 4.78 (1H, d, *J* 12.6, OCH*H*), 1.43 (3H, d, *J* 6.5, OCHCH_3), 0.33 (9H, s, Si(CH_3)$_3$); δ_C (100 MHz, $CDCl_3$) 193.94 (C=O), 180.55 (C=O), 132.74 (ipso, Ar), 128.72 (CH, Ar), 127.36 (CH, Ar), 126.54 (CH, Ar), 110.96, 109.65, 76.48 (O*C*HCH$_3$), 75.74, 70.64, 66.33, 63.86, 27.90, 19.06, -0.40 (Si(CH$_3$)$_3$).

Ruthenium cyclone complex 12c/d.

A sealed tube was charged with **8** (R^1=(iPr)$_3$Si, R^2=Ph, R^3=Me) (0.5898 g, 1.798 mmol, 3eq.) and $Ru_3(CO)_{12}$ (0.3830 g, 0.5994 mmol, 1 eq.) in acetonitrile (6 cm^3) and the reaction heated to 100 ^{o}C over 2 days. The solvent was removed in vacuo and redissolved in DCM and filtered to remove any unreacted $Ru_3(CO)_{12}$ and purified by column chromatography (EtOAc/pet. ether (40-60) 1:10) to afford only one diastereoisomer cleanly (0.1197 g, 0.2213 mmol, 12%); $[\alpha]_D^{28}$ +39.11 (c 0.140 $CHCl_3$); *m/z* (ESI) 555 $[M+1]^+$, 577 $[M+23]^+$; (Found (ESI): M+H 555.1148 $C_{22}H_{33}O_5RuSi$ requires 555.1142); ν_{max} 2944, 2860, 2077, 2023, 1999 and 1622 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.37-7.32 (2H, m, Ar), 7.29-7.24 (2H, m, Ar), 7.21-7.15 (1H, m, Ar), 5.22 (1H, q, *J* 6.0, OC*H*CH_3), 4.74 (2H, s, OCH_2), 1.53 (3H, d, *J* 6.0, OCHCH_3), 1.32 (3H, sept., *J* 7.5, Si(C*H*(CH$_3$)$_2$)$_3$), 1.15-1.08 (18H, m Si(CH(CH_3)$_2$)$_3$); δ_C (100 MHz, $CDCl_3$) 193.83 (C=O), 178.95 (C=O), 130.38 (ipso, Ar), 129.89 (CH, Ar), 128.37 (CH, Ar), 127.62 (CH, Ar), 116.19, 111.69, 79.37, 74.72 (O*C*HCH$_3$), 68.36, 62.42, 23.66, 19.12, 12.32.

Ruthenium cyclone complex 12e/f.

A sealed tube was charged with **8d** (**8:** R^1=Ph, R^2=Ph, R^3=Me) (0.3580 g, 1.3769 mmol, 3eq.) and $Ru_3(CO)_{12}$ (0.2933 g, 0.4586 mmol, 1 eq.) in acetonitrile (5 cm^3) and the reaction was heated to 100 ^{o}C over 2 days. The solvent was removed in vacuo and redissolved in DCM and filtered to remove any unreacted $Ru_3(CO)_{12}$ and purified by column chromatography (EtOAc/pet. ether (40-60) 1:20) to afford only one diastereoisomer cleanly (0.1371 g, 0.2898 mmol, 21%); $[\alpha]_D^{28}$ -61.96 (c 0,092 $CHCl_3$); *m/z* (ESI) 475 $[M+1]^+$, 497 $[M+23]^+$; (Found (ESI): M+H 475.0123 $C_{23}H_{17}O_5Ru$ requires 475.0120); ν_{max} 2074, 1999 and 1622 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.87 (2H, d, *J* 7.5, Ar), 7.50 (2H, d, *J* 7.0, Ar), 7.43-7.36 (4H, m, Ar), 7.35-7.28 (2H, m, Ar), 5.34 (1H, dq, *J* 1.5, 6.0, C*H*CH$_3$), 5.25 (1H, d, *J* 12.6, C*H*H), 5.07 (1H, dd, *J* 2.0, 12.6, CH*H*), 1.61 (3H, d, *J* 6.0, CHCH_3); δ_C (100 MHz, $CDCl_3$) 193.80 (C=O), 132.39 (ipso, Ar), 130.08 (ipso, Ar), 128.88 (CH, Ar), 128.47 (CH, Ar), 127.85 (CH, Ar), 127.76 (CH,

Ar), 127.00 (CH, Ar), 109.03 (quat.), 107.13 (quat.), 77.98 (quat.), 74.92 (CH), 74.06 (quat.), 67.75 (quat.), 23.74 (CH_3).

Ruthenium cyclone complex 13a/b.

A sealed tube was charged with the dipropargyl ether precursor of ligand **13a/b** (0.083 g, 0.26 mmol, 3eq.) and $Ru_3(CO)_{12}$ (0.056 g, 0.0.887 mmol, 1 eq.) in acetonitrile (1 cm^3) and the reaction heated to 100 °C over 2 days. The solvent was removed in vacuo and redissolved in DCM and filtered to remove any unreacted $Ru_3(CO)_{12}$ and purified by column chromatography (EtOAc/hexane 1:20) to afford only one diastereoisomer cleanly (0.040 g, 0.0805 mmol, 31%); $[\alpha]_D^{28}$ +38.60 (c 0.020 $CHCl_3$); *m/z* (ESI) 527 $[M]^+$; (Found (ESI): M+H 527.0822 $C_{24}H_{29}O_5RuSi$ requires 527.0828); ν_{max} 2075, 1999 and 1638 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.44-7.40 (2H, m, Ar), 7.37-7.32 (2H, m, Ar), 7.29-7.26 (1H, m, Ar), 5.22 (1H, qd, *J* 6.0, 1.5, C*H*CH_3) 5.00 (1H, qd, *J* 6.0, 1.5, C*H*CH_3), 1.58 (3H, d, *J* 6.0, CHC*H*$_3$), 1.55 (3H, d, *J* 6.0, CHC*H*$_3$), 0.99 (9H, s, SiC(C*H*$_3$)$_3$), 0.51 (3H, s, SiC*H*$_3$), 0.18 (3H, s, SiC*H*$_3$); δ_C (100 MHz, $CDCl_3$) 193.91 (C=O), 180.04 (C=O), 130.34 (ipso, Ar), 130.07 (CH, Ar) 128.38 (CH, Ar), 127.70 (CH, Ar), 119.99, 116.40, 78.22, 74.82, 73.51, 60. 83, 31.56, 28.06, 27.23, 23.76, 22.63, 18.81, -2.04, -3.67.

(*R*)-Alcohol 11d.

A flask was charged with (*R*)-Alpine borane solution (45.08 cm^3, 22.54 mmol, 0.5M in THF) and the solvent was removed in vacuo. The flask was cooled to 0 °C and 3-(t-butyldimethylsilyl)-1-phenyl-prop-2-ynone **10d** (5.00 g, 20.49 mmol) was added dropwise. After 4 days acetylaldehyde (5 cm^3) was added. After 1 h, $NaOH_{(aq)}$ (10 cm^3, 5N), THF (10 cm^3) and hydrogen peroxide (11.5 cm^3, 30 %wt) added. CAUTION: addition of peroxide is very exothermic. After heating to 40 °C for 4 h, in air, the reaction was extracted using Et_2O (3 x 30 cm^3) and the combined organic phases washed using brine (30 cm^3), dried over $MgSO_4$ and the solvent removed in vacuo. Purification by column chromatography (EtOAc/ hexane 0.5%-5%) afforded a colourless oil (Rf 0.13 (10% EtOAc/hexane), 3.67 g, 14.918 mmol, 73 %, 96 % ee); $[\alpha]_D^{28}$ +4.2 (c 1.054 in $CHCl_3$); *m/z* 269.2 $[M+ 23]^+$; (Found (ESI): M+Na 269.1333. $C_{15}H_{22}NaOSi$ requires 269.1332); ν_{max} 3362 (OH), 2926, 2857, 1671, 1446 and 1003 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.56 (2H, d, *J* 7.1, Ar), 7.36 (3H, m, Ar), 5.47 (1H, s, Ar), 0.99 (9H, s, SiC(C*H*$_3$)$_3$), 0.17 (6H, s, Si(C*H*$_3$)$_2$); δ_C (100 MHz, $CDCl_3$) 140.36 (ipso, Ar), 128.49 (CH, Ar), 128.26 (CH, Ar), 126.70 (CH, Ar), 105.69 (quat., C≡C), 89.81 (quat., C≡C), 64.90 (*C*H(OH)), 26.03 (SiC(*C*H$_3$)$_3$), 16.50 (quat., Si*C*(CH$_3$)$_3$), -4.71 (Si(*C*H$_3$)$_2$); δ_{Si} (99 MHz, $CDCl_3$) -7.64 (s, Si(CH$_3$)$_2$C(CH$_3$)$_3$). The ee was determined by chiral GC; cyclodextrin CB column; 96 % ee, 100 °C, H_2, 15 psi, 83.70 min (*S*), 85.99 min (*R*).[17]

(*R*)-Dipropargylic ether 8 (R^1=H, R^2=Si(tBu)Me_2, R^3=Ph).

To a solution of (*R*)-alcohol **11d** (1.1606 g, 6.0976 mmol 1 eq.) in THF (20 cm^3) at 0 °C was added NaH (0.2881 g, 60 % in mineral oil, 7.2019 mmol, 1.1 eq.). The reaction mixture was stirred for 30 min at 0 °C after which propargylic bromide was added (0.85 cm^3, 80%wt in toluene, 1.17 g, 7.86 mmol, 1.2 eq.) and the ice bath removed. After 4 h the reaction was quenched using saturated $NaHCO_{3(aq)}$ solution (20 cm^3) and extracted using Et_2O (3 x 10 cm^3). The combined organic fractions were dried over $MgSO_4$ and the solvent removed in vacuo. Purification column chromatography (EtOAc/ hexane 0 % to 1 %) afforded a colourless oil (1.121 g, 3.948 mmol, 60 %); $[\alpha]_D^{28}$ +27.3 (c 0.68 in $CHCl_3$); *m/z* 307.2 $[M+ 23]^+$; (Found (ESI): M+Na 307.1483, $C_{18}H_{24}NaOSi$ requires 307.1489); ν_{max} 2952, 2927, 2884, 2855, 1250 and 1059 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.56 (2H, d, *J* 7.2, Ar), 7.41-7.34 (3H, m, Ar), 5.45 (1H, s, ArC*H*), 4.41 (1H, dd, ^4J 2.3, *J* 15.7, OC*H*H), 4.29 (1H, dd, ^4J 2.3, *J* 15.7, OCH*H*), 2.48 (1H, t, ^4J 2.3, C≡C*H*), 0.98 (9H, s, SiC(C*H*$_3$)$_3$), 0.17 (6H, s, Si(C*H*$_3$)$_2$); δ_C (100 MHz, $CDCl_3$) 137.65 (ipso, Ar), 128.69 (CH, Ar), 128.44 (CH, Ar), 126.75 (CH, Ar), 102.50 (quat., C≡C), 91.77 (quat., C≡C), 74.82 (quat. C≡C), 70.44 (Ar*C*H), 55.26 (O*C*H$_2$), 26.05 (SiC(*C*H$_3$)$_3$), 16.55 (Si*C*(CH$_3$)$_3$), -4.70 (Si(*C*H$_3$)$_2$); δ_{Si} (99 MHz, $CDCl_3$) -7.51 (s, Si(CH$_3$)$_2$C(CH$_3$)$_3$).

(*R*)-Dipropargylic ether 8 (R^1=TMS, R^2=Si(tBu)Me_2, R^3=Ph).

A flask was charged with (*R*)-dipropargylic ether **8** (R^1=H, R^2=Si(tBu)Me_2, R^3=Ph) (0.500 g, 1.7606 mmol) in THF (12 cm^3) and cooled to -78 °C. Addition of nBuLi (1.21 cm^3, 1.94 mmol, 1.6 M in hexane, 1.1 eq.) affording a dark green solution. After 1 h TMSCl (0.27 cm^3, 2.11 mmol, 1.2 eq.) was added and the ice bath removed after 5 min. After 30 min the reaction mixture colour had changed from green to yellow. After 3 h the reaction was quenched using water (10 cm^3) and extracted with Et_2O (3 x 10 cm^3), the organic fractions combined and dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a yellow oil which was purified using column chromatography (EtOAc/Hexane 0 to 20%) to afford a pale yellow oil (0.4300 g, 1.208 mmol, 69 %); $[\alpha]_D^{28}$ +27.3 (c 0.68 in $CHCl_3$); *m/z* (ESI) 379.2 $[M+ 23]^+$; (Found (ESI): M+Na 379.1881. $C_{21}H_{32}NaOSi_2$ requires 379.1884); ν_{max} 2954, 2928, 2898, 2856, 2173, 1249 and 1059 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.56 (2H, d, *J* 7.5, Ar), 7.40-7.31 (3H, m, Ar), 5.45 (1H, s, ArC*H*), 4.40 (1H, d, *J* 15.8, OC*H*H), 4.28 (1H, d, *J* 15.8, OCH*H*), 0.98 (9H, s, SiC(C*H*$_3$)$_3$), 0.21 (9H, s, Si(C*H*$_3$)$_3$), 0.17 (6H, s, Si(C*H*$_3$)$_2$); δ_C (100 MHz, $CDCl_3$) 137.77 (ipso, Ar), 128.50 (CH, Ar), 128.41 (CH, Ar), 127.83 (CH, Ar), 102.70 (quat., C≡C), 101.11 (quat., C≡C), 91.81 (quat. C≡C), 91.60 (quat. C≡C), 70.39 (Ar*C*H), 56.07 (O*C*H$_2$), 26.08 (SiC(*C*H$_3$)$_3$), 16.56 (Si*C*(CH$_3$)$_3$), -0.16 (Si(*C*H$_3$)$_3$, -4.70 (Si(*C*H$_3$)$_2$); δ_{Si} (99 MHz, $CDCl_3$) -7.57 (s, *Si*(CH$_3$)$_2$C(CH$_3$)$_3$), -17.73 (s, *Si*(CH$_3$)$_3$).

(*R*)-Dipropargylic ether 8 (R^1=TIPS, R^2=Si(tBu)Me_2, R^3=Ph.

A flask was charged with (*R*)-dipropargylic ether **8** (R^1=H, R^2=Si(tBu)Me_2, R^3=Ph) (0.500 g, 1.7606 mmol) in THF (10 cm^3) and cooled to -78 °C. Addition of nBuLi (1.35 cm^3, 2.17 mmol, 1.6 M in hexane, 1.2 eq.) afforded a dark green solution. After 30 min TIPSCl (0.50 cm^3, 2.36 mmol, 1.3 eq.) was added and the ice bath removed after 30 mins. After 5 h the reaction was quenched using water (10 cm^3) and extracted with Et_2O (3 x 10 cm^3), the organic fractions combined and dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a yellow oil which was purified using column chromatography (EtOAc/Hexane 0 to 5%) to afford a bright yellow oil (0.219 g, 0.53 mmol, 30 %); $[\alpha]_D^{28}$ +50.1 (c 0.825 in $CHCl_3$); *m/z* (ESI) 463.3 $[M+ 23]^+$; (Found (ESI): M+Na 463.2821. $C_{27}H_{44}NaOSi_2$ requires 463.2823); ν_{max} 2928, 2889, 2863, 1462, 1249, 1060,

1038,1027 and 1007 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.56-7.53 (2H, m, Ar), 7.40-7.32 (3H, m, Ar), 5.55 (1H, s, ArC*H*), 4.51 (1H, d, *J* 16.1, OC*H*H), 4.31 (1H, d, *J* 16.1, OCH*H*), 1.08 (21H, m, Si(C*H*(CH_3)$_2$)$_3$) (0.97 (9H, s, SiC(CH_3)$_3$), 0.17 (6H, s, Si(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 137.97 (ipso, Ar), 128.49 (CH, Ar), 128.44 (CH, Ar), 127.87 (CH, Ar), 102.74 (quat., C≡C), 102.70 (quat., C≡C), 91.49 (quat. C≡C), 88.42 (quat., C≡C), 69.75 (Ar*C*H), 56.22 (OCH_2), 26.09 CH_3, SiC(*C*H_3)$_3$), 18.61 (Si(*C*H(CH_3)$_2$)$_3$), 16.58 (Si*C*(CH_3)$_3$), 11.18 (CH_3, Si(CH(*C*H_3)$_2$)$_3$), -4.68 (Si(*C*H_3)$_2$); δ_{Si} (99 MHz, $CDCl_3$) -1.86 (s, *Si*(CH(CH_3)$_2$)$_3$), -7.57 (s, *Si*(CH_3)$_2$C(CH_3)$_3$).

(*R*)-Dipropargylic ether 8 (R^1=Ph, R^2=Si(tBu)Me_2, R^3=Ph).
A flask was charged with (*R*)-dipropargylic ether **8** (R^1=H, R^2=Si(tBu)Me_2, R^3=Ph) (0.500 g, 1.7606 mmol), PhI (0.26 cm^3, 2.34 mmol, 1.3 eq.) and Et_3N (6.3 cm^3). To this mixture was added $PdCl_2(PPh_3)_2$ (27.4 mg, 0.0391 mmol, 0.02 eq.) and after 5 min CuI (3.7 mg, 0.0195 mmol, 0.01 eq.) was added and the reaction heated to 50 ^oC for 20 h. The reaction mixture was then filtered and the remaining amine removed in vacuo. Purification by column chromatography (EtOAc/Hexane 0 to 2 %) afforded a light yellow oil (0.3693 g, 1.03 mmol, 58%); $[\alpha]_D^{28}$ +58.0 (c 1.02 in $CHCl_3$); *m/z* (ESI) 361.2 $[M+1]^+$; 383.1 $[M+23]^+$; (Found (ESI): M+Na, 383.1802. $C_{24}H_{28}NaOSi$ requires 383.1802); ν_{max} 2952, 2927, 2884, 2855 and 1057 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.56 (2H, d, *J* 7.6, Ar), 7.50-7.48 (2H, m, Ar), 7.41-7.31 (6H, m, Ar), 5.53 (1H, s, ArC*H*), 4.63 (1H, d, *J* 15.7, OC*H*H), 4.51 (1H, d, *J* 15.7, OCH*H*), 1.05 (9H, s, SiC(CH_3)$_3$), 0.18 (6H, s, Si(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 137.82 (ipso, Ar), 131.81 (CH, Ar), 128.57 (CH, Ar), 128.53 (CH, Ar), 128.45 (CH, Ar), 128.25(CH, Ar), 127.81 (CH, Ar), 122.60 (ipso, Ar), 102.83 (quat., C≡C), 91.70 (quat., C≡C), 86.62 (quat., C≡C), 84.71 (quat., C≡C), 70.50 (Ar*C*H), 56.10 (OCH_2), 26.08 (SiC(*C*H_3)$_3$), 16.56 (Si*C*(CH_3)$_3$), -4.67 (Si(*C*H_3)$_2$); δ_{Si} (99 MHz, $CDCl_3$) -7.52 (s, Si(CH_3)$_2$C(CH_3)$_3$).

(*R*)-Alcohol 11e.
(*R*)-Alpine borane solution (0.5M, in THF, 22 mmol, 44 cm^3) was introduced to a flask and the solvent removed in vacuo. The flask was cooled to 0 ^oC and 3-(tri(isopropyl)silyl)-1-phenyl-prop-2-yn-1-one **10e** (5.72 g, 20.0 mmol) was added dropwise. The ice bath was removed and after 4 days the reaction was quenched using acetaldehyde (4.5 cm^3). After 1 h THF (10 cm^3) and $NaOH_{(aq)}$ (5N, 10 cm^3) were added and the reaction mixture put in a water bath and H_2O_2 (30 wt%, 11.5 cm^3) was added carefully. CAUTION: very exothermic. After complete addition of the peroxide the reaction was heated for 4 h in air followed by extraction with Et_2O (3 x 30 cm^3). The combined organic fractions were then washed with brine (30 cm^3) and dried over $MgSO_4$. Removal of the solvent in vacuo afforded a colourless oil which on purification by column chromatography (hexane/EtOAc) afforded a colourless oil (2.6031 g, 9.0385 mmol, 45% yield, 97% ee); $[\alpha]_D^{28}$ +5.81 (c 1.32, $CHCl_3$); *m/z* 287.2 [M-1], 309.2 [M+23]; (Found (ESI): M-H 287.1816 $C_{18}H_{27}OSi$ requires 287.1826, M+Na 309.1631 $C_{18}H_{26}NaOSi$ requires 309.1645); ν_{max} 3354 (OH), 2941, 2891, 2864 and 2169 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.6-7.56 (2H, m, Ar) 7.42-7.29 (3H, m, Ar), 5.49 (1H, d, *J* 6.3, ArC*H*), 2.17 (1H, d, *J* 6.3, O*H*), 1.09 (21H, m, Si(C*H*(CH_3)$_3$); δ_C (75 MHz, $CDCl_3$) 128.54 (ipso, Ar), 128.51 (CH, Ar), 128.30 (CH, Ar), 126.77 (CH, Ar), 106.87 (quat., C≡C), 98.02 (quat., C≡C), 65.11 (*C*H(OH)), 18.59 (Si(CH(*C*H_3)$_2$)$_3$), 11.15 (Si(*C*H(CH_3)$_2$)$_3$); The ee was determined by GC using cyclodextrin CB column; 97 % ee, 170 ^oC, H_2, 15 psi, 61.96 min (*S*), 63.68 min (*R*).[17]

(*R*)-Dipropargylic ether 8 (R^1=H, R^2=Si(iPr)$_3$, R^3=Ph).
To a solution of (*R*)-alcohol **11e** (1.000 g, 3.472 mmol 1 eq.) in THF (11 cm^3) at 0 ^oC was added NaH (0.1527 g, 60 % on mineral oil, 3.8194 mmol, 1.1 eq.). The reaction mixture was stirred for 30 min at 0 ^oC after which propargylic bromide was added (0.45 cm^3, 80%wt in toluene, 0.619 g, 4.166 mmol, 1.2 eq.) and the ice bath removed. After 4 h the reaction was quenched using saturated $NHCO_{3(aq)}$ solution (20 cm^3) and extracted using Et_2O (3 x 10 cm^3). The combined organic fractions were dried over $MgSO_4$ and the solvent removed in vacuo. Purification by column chromatography (EtOAc/ hexane 0 to 1 %) afforded a colourless oil (0.9155 g, 2.8083 mmol, 81 %); $[\alpha]_D^{28}$ +24.25 (c 1.048, $CHCl_3$); *m/z* 349.2 $[M+23]^+$; (Found (ESI): 349.1953 M+Na $C_{21}H_{30}NaOSi$ requires 349.1958); ν_{max} 2941, 2924, 2864, 2169, 2031 and 1461 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.59-7.56 (2H, m, Ar) 7.40-7.31 (3H, m, Ar), 5.48 (1H, s, ArC*H*), 4.44 (1H, dd, ^4J 2.4, *J* 15.6, OC*H*H), 4.31 (1H, dd, ^4J 2.4, *J* 15.6, OCH*H*), 2.47 (1H, t, ^4J 2.4, C≡C*H*), 1.10 (21H, m, Si(C*H*(CH_3)$_3$); δ_C (100 MHz, $CDCl_3$) 137.79 (ipso, Ar), 128.47 (CH, Ar), 128.38 (CH, Ar), 127.75 (CH, Ar), 103.62 (quat., C≡C), 89.95 (quat., C≡C), 79.35 (C≡CH), 74.72 (quat., C≡C), 70.50 (Ar*C*H), 55.19 (OCH_2), 18.58 (Si(CH(*C*H_3)$_2$)$_3$), 11.16 (Si(*C*H(CH_3)$_2$)$_3$); δSi (99 MHz, $CDCl_3$) -1.53 (s, Si(CH(CH_3)$_2$)).

(*R*)-Dipropargylic ether 8 (R^1=Me_3Si, R^2=Si(iPr)$_3$, R^3=Ph).
To a solution of (*R*)-dipropargylic ether **8** (R^1=H, R^2=Si(iPr)$_3$, R^3=Ph) (0.190 g, 0.582 mmol) in THF (3 cm^3) cooled to -78 ^oC was added nBuLi (0.4 cm^3, 0.6404 mmol, 1.6 M in hexane, 1.1 eq.) affording a dark green solution. After 1 h TMSCl (0.089 cm^3, 0.699 mmol, 1.2 eq.) was added and the ice bath removed after 5 min. After 6 h the reaction was quenched using water (3 cm^3) and extracted with Et_2O (3 x 4 cm^3), the organic fractions were combined and dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a yellow oil which was purified using column chromatography (EtOAc/Hexane 0 to 1%) to afford a yellow oil (0.1362 g, 0.3424 mmol, 59 %); $[\alpha]_D^{28}$ +42.2 (c 1.106, $CHCl_3$); *m/z* 421.2 $[M+23]^+$; (Found (ESI): 421.2354 M+Na $C_{24}H_{38}NaOSi_2$ requires 421.2353); ν_{max} 2944, 2893, 2865, 1719 and 1250 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.58 (2H, d, *J* 7.04, Ar), 7.41-7.31 (3H, m, Ar), 5.49 (1H, s, ArC*H*), 4.44 (1H, d, *J* 15.8, OC*H*H), 4.31 (1H, d, *J* 15.8, OCH*H*), 1.10 (21H, m, Si(C*H*(CH_3)$_3$), 0.20 (6H, s, Si(CH_3)$_3$); δ_C (100 MHz, $CDCl_3$) 137.92 (ipso, Ar), 128.44 (CH, Ar), 128.38 (CH, Ar), 127.85 (CH, Ar), 103.78 (quat., C≡C), 101.17 (quat., C≡C), 91.77 (C≡CH), 89.85 (quat., C≡C) 70.43 (Ar*C*H) 56.02 (OCH_2) 18.62 (Si(CH(*C*H_3)$_2$)$_3$), 11.19 (CH, Si(*C*H(CH_3)$_2$)$_3$), -0.16 (Si(*C*H_3)$_3$).

(*R*)-Dipropargylic ether 8 (R^1=Si(tBu)Me_2, R^2=Si(iPr)$_3$, R^3=Ph).
To a solution of (*R*)-*dipropargylic* ether **8** (R^1=H, R^2=Si(iPr)$_3$, R^3=Ph) (0.400 g, 1.227 mmol) in THF (7 cm^3) cooled to -78 ^oC was added nBuLi (0.84 cm^3, 1.3497 mmol, 1.6 M in hexane, 1.1

eq.) affording a dark green solution. After 1 h TBDMSCl (0.222 g, 1.472 mmol, 1.2 eq.) was added and the ice bath removed after 5 min. After 16 h the reaction was quenched using water (10 cm^3) and extracted with Et_2O (3 x 10 cm^3), the organic fractions were combined and dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a crude yellow oil (0.4263 g, 0.9689 mmol, 79%); $[\alpha]_D^{28}$ +65.9 (c 0.50, $CHCl_3$); *m/z* 463.2 $[M+23]^+$; (Found (ESI): M+Na 463.2819 $C_{27}H_{44}NaOSi_2$ requires 463.2823); ν_{max} 2942, 2927, 2891, 2863, 2173, 1461 and 1063cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.58 (2H, d, *J* 7.04, Ar) 7.41-7.31 (3H, m, Ar), 5.49 (1H, s, ArC*H*), 4.44 (1H, d, *J* 15.8, OC*H*H) 4.31 (1H, d, *J* 15.8, OCH*H*) 1.10 (21H, m, Si(C*H*(CH_3)$_3$) 0.20 (6H, s, Si(CH_3)$_3$); δ_C (100 MHz, $CDCl_3$) 137.92 (ipso, Ar), 128.44 (CH, Ar), 128.38 (CH, Ar), 127.85 (CH, Ar), 103.78 (quat., C≡C), 101.17 (quat., C≡C), 91.77 (CH, C≡*C*H), 89.85 (quat., C≡C) 70.43 (*C*H(OH)) 56.02 (OCH_2) 18.62 (Si(CH(*C*H_3)$_2$)$_3$), 11.19 (Si(*C*H(CH_3)$_2$)$_3$), -0.16 (Si(*C*H_3)$_3$);

(*R*)-Dipropargylic ether 8 (R^1=Ph, R^2=Si(iPr)$_3$, R^3=Ph).

A flask was charged with (*R*)-dipropargylic ether **8** (R^1=H, R^2=Si(iPr)$_3$, R^3=Ph) (0.500 g, 1.534 mmol), PhI (0.21 cm^3, 1.84 mmol, 1.2 eq.) and Et_3N (6 cm^3). To this mixture was added $PdCl_2(PPh_3)_2$ (21.5 mg, 0.0306 mmol, 0.02 eq.) and after 5 min CuI (2.9 mg, 0.0153 mmol, 0.01 eq.) was added and the reaction heated to 50 ^oC for 20 h. The reaction mixture was then filtered and the remaining amine removed in vacuo. Purification by column chromatography (EtOAc/Hexane 0 to 0.5 %) afforded a light yellow oil (0.5874 g, 1.461 mmol, 95 %); $[\alpha]_D^{28}$ +45.0 (c 1.088, $CHCl_3$); *m/z* 403.2 $[M+1]^+$, 425.2 $[M+23]^+$; ν_{max} 2942, 2890, 2864, 1762, 1644, 1450 and 1240cm^{-1}; (Found (ESI): 425.2265 M+Na $C_{27}H_{34}NaOSi$ requires 425.2271); δ_H (400 MHz, $CDCl_3$) 7.50 (2H, d, *J* 7.50, Ar), 7.49-7.45 (2H, m, Ar), 7.40-7.31 (6H, m, Ar), 5.56 (1H, s, ArC*H*), 4.67 (1H, d, *J* 15.7, OC*H*H), 4.54 (1H, d, *J* 15.7, OCH*H*), 1.12 (21H, m, Si(CH(CH_3)$_3$); δ_C (100 MHz, $CDCl_3$) 138.00 (ipso, Ar), 131.83 (CH, Ar), 128.47 (CH, Ar), 128.45 (CH, Ar), 128.42(CH, Ar), 128.25 (CH, Ar), 127.84 (CH, Ar), 122.65 (ipso, Ar), 103.87 (quat., C≡C), 90.05 (quat., C≡C), 86.54 (quat., C≡*C*), 84.07 (quat., C≡C) 70.57 (*C*H(OH)) 56.04 (OCH_2) 18.63 (Si(CH(*C*H_3)$_2$)$_3$), 11.20 (Si(*C*H(CH_3)$_2$)$_3$); δ_{Si} (99 MHz, $CDCl_3$) -1.53 (s).

Ruthenium cyclone complex 15b.

A pressure tube was charged with (*R*)-dipropargylic ether **8** (R^1=TMS, R^2=Si(tBu)Me_2, R^3=Ph), (1.000 g, 2.808 mmol 3 eq.), acetonitrile (10 cm^3) and $Ru_3(CO)_{12}$ (0.5986 g, 0.9363 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 100 ^oC. After 2 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (4 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAc/Hexane 0 to 10 %) to afford a yellow solid (0.4522 g, 0.7947 mmol, 28 %). The metal complex was characterised as a mixture of two diasteroisomers in an approximate ratio of 3:1; *m/z* 571.0 $[M+1]^+$; (Found (ESI): 571.0918 M+H $C_{25}H_{33}O_5RuSi_2$ requires 571.0911); ν_{max} 2951, 2927, 2894, 2881, 2853, 2077, 2019, 1197 and 1632cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.49-7.44 (1.5H, m, Ar) 7.41-7.36 (3H, m, Ar), 7.20-7.16 (0.5H, m, Ar), 5.85 (1H, s, ArC*H*), 4.98 (1H, d, *J* 12.1), 4.85 (0.75H, dd, 2.3, 12.8, OCH_2, major) 4.90 (0.25H, d, *J* 12.5, OCH_2, minor), 0.99 (6H, s, SitBu), 0.62 (3H, s, Si(CH_3)$_2$), 0.34 (3H, s, Si(CH_3)$_2$), 0.30 (6H, s, Si(CH_3)$_3$), 0.22 (3H, s, Si(CH_3)$_2$), -0.75 (3H, s, Si(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 193.80 (quat., C=O), 185.80 (quat., C=O), 138.75 (ipso, Ar), 138.48 (ipso, Ar), 129.59 (CH, Ar), 129.41 (CH, Ar), 129.14 (CH, Ar), 128.42 (CH, Ar), 128.32 (CH, Ar), 127.67 (CH, Ar), 119.91 (quat.), 119.29 (quat.), 117.12 (quat.), 82.56 (CH, ArCH), 81.33 (CH, ArCH), 67.13 (quat./CH_2), 66.92 (quat./CH_2), 64.33 (quat./CH_2), 64.20 (quat./CH_2), 27.67 (CH/CH_3), 27.25 (CH/CH_3), 19.00 (quat./CH_2), 17.74 (quat./CH_2), 14.10 (CH/CH_3), -0.28 (CH/CH_3), -0.45 (CH/CH_3), -3.15 (CH/CH_3), -4.66 (CH_3), -4.78 (CH_3); δ_{Si} (99 MHz, $CDCl_3$), 4.03 (s, TBS), 3.20 (s, TBS), -3.72 (s, TMS).

Ruthenium cyclone complex 15a.

A pressure tube was charged with (*R*)-dipropargylic ether **8** (R^1=TIPS, R^2=Si(tBu)Me_2, R^3=Ph) (0.1395 g, 0.3170 mmol 2 eq.), acetonitrile (1 cm^3) and $Ru_3(CO)_{12}$ (0.1013 g, 0.1585 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 100 ^oC. After 2 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (2 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAc/Hexane 0 to 10 %) to afford a yellow solid (0.1404 g, 0.2151 mmol, 68 %). The metal complex was characterised as a mixture of two diasteroisomers in an approximate ratio of 3:1; *m/z* 655.1 $[M+1]^+$, 677.1 $[M+23]^+$; (Found (ESI): 655.1861 M+H $C_{31}H_{45}O_5RuSi_2$ requires 655.1851); ν_{max} 2946, 2926, 2862, 2077, 2019, 1998 and1629 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.50-7.47 (1.5H, m, Ar), 7.42-7.37 (3H, m, Ar), 7.22-7.20 (0.5H, m, Ar), 5.85 (1H, s, ArC*H*), 5.00 (1H, d, *J* 12.8, OC*H*H), 4.88 (0.75H, dd, *J* 2.1, 12.8, OCH*H*, major), 4.79 (0.25H, d, *J* 12.5, OCH*H*, minor), 1.41 (3H, septet, *J* 7.2, SiC*H*(CH_3)$_2$), 1.18 (18H, pseudo t, *J* 7.2, SiCH(CH_3)$_2$), 0.98 (9H, s, SitBu), 0.24 (3H, s, Si(CH_3)$_2$), -0.71 (3H, s, Si(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 193.76 (quat., C=O), 185.60 (quat., C=O), 138.53 (ipso, Ar), 129.62 (CH, Ar), 129.41 (CH, Ar), 129.14 (CH, Ar), 128.95 (CH, Ar), 128.54 (CH, Ar), 128.51 (CH, Ar), 128.32 (CH, Ar), 127.70 (CH, Ar), 121.93 (quat.), 118.11 (quat.), 82.02 (CH), 81.25 (CH), 67.88 (quat./CH_2), 64.91 (quat./CH_2), 64.01 (quat./CH_2), 27.81 (CH/CH_3), 27.39 (CH/CH_3), 19.67 (CH_3), 19.33 (CH_3), 19.20 (CH_3), 19.15 (CH_3), 19.07 (quat.), 15.46 (CH/CH_3), 12.37 (CH/CH_3), 12.29 (CH/CH_3), -3.08 (CH_3), -4.40 (CH_3); δ_{Si} (99 MHz, $CDCl_3$), 4.22 (s, TBS), 3.31 (s, TBS), 2.51 (s, TIPS).

Ruthenium cyclone complex 15c.

A pressure tube was charged with (*R*)-dipropargylic ether **8** (R^1=Ph, R^2=Si(tBu)Me_2, R^3=Ph), (0.250 g, 0.6944 mmol 2 eq.), acetonitrile (1.5 cm^3) and $Ru_3(CO)_{12}$ (0.2219 g, 0.3472 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 100 ^oC. After 3 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (2 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAc/Hexane; 0 to 10 %) to afford a yellow solid (0.1799 g, 0.3139 mmol, 45 %). The metal complex was

characterised as a mixture of two diasteroisomers in an approximate ratio of 4:1; *m/z* 575.0 $[M+1]^+$; (Found (ESI): M+H 575.0832 $C_{28}H_{29}O_5RuSi$ requires 575.0829); (Found (ESI): M+Na 597.0654 $C_{28}H_{28}NaO_5RuSi$ requires 597.0649); ν_{max} 2952, 2928, 2883, 2854, 2064, 2020 and 2009cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.87 (0.3H, d, *J* 7.3, Ar), 7.83 (1.6H, d, *J* 7.3, Ar), 7.54-7.51 (1.5H, m, Ar), 7.44-7.35(5H, m, Ar), 7.32-7.24 (1.5H, m, Ar) 5.90 (1H, s, ArC*H*), 5.40 (0.85H, dd, *J* 0.9, 12.9, OC*H*H, major), 5.34 (0.15H, dd, *J* 1.4, 12.5, OC*H*H, minor) 5.23 (0.15H, d, *J* 12.5, OCH*H*, minor), 5.15 (0.85H, dd, *J* 2.4, 12.9, OCH*H*, major), 1.03(7.65H, s, SitBu, major), 0.66 (1.35H, s, SitBu, minor), 0.35 (2.35H, s, $Si(CH_3)_2$, major), 0.33 (0.65H, s, $Si(CH_3)_2$, minor), -0.03(0.5H, s, $Si(CH_3)$, minor), -0.74 (2.5H, s, $Si(CH_3)$, major); δ_C (100 MHz, $CDCl_3$) 193.78 (quat, C=O), 193.72 (quat C=O), 180.08 (quat, C=O), 138.32 (ipso, Ar), 138.08 (ipso, Ar), 132.20 (ipso, Ar), 132.15 (ipso, Ar), 129.78 (CH, Ar), 129.56 (CH, Ar), 129.19 (CH, Ar), 128.88 (CH, Ar), 128.86 (CH, Ar), 128.54 (CH, Ar), 128.38 (CH, Ar), 127.79 (CH, Ar), 127.76 (CH, Ar), 127.13 (CH, Ar), 127.11 (CH, Ar), 115.10 (quat.), 113.14 (quat.), 82.62 (CH), 81.46 (CH), 75.53 (quat./CH_2), 67.63 (quat./CH_2), 67.30 (quat./CH_2), 62.34 (quat./CH_2), 34.64 (quat./CH_2), 31.56 (quat./CH_2), 27.72 (CH/CH_3), 27.26 (CH/CH_3), 25.26 (quat./CH_2), 22.63 (quat./CH_2), 19.00 (quat./CH_2), 14.10 (CH_3), -2.96 (CH_3), -4.64 (CH_3), -4.72 (CH_3, $SiCH_3$); δ_{Si} (99 MHz, $CDCl_3$), 4.22 (s, TBS), 3.31 (s, TBS), 2.51 (s, TIPS).

Ruthenium cyclone complex 15e.

A pressure tube was charged with (*R*)-dipropargylic ether **8** (R^1=Ph, R^2=Si(iPr)$_3$, R^3=Ph) (0.3906 g, 0.9716 mmol 2 eq.), acetonitrile (3 cm^3) and $Ru_3(CO)_{12}$ (0.3104 g, 0.4858 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 100 ^oC. After 2 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (2 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAc/Hexane 0 to 5 %) to afford a yellow solid (Rf 0.2, 0.1994 g, 0.3242 mmol, 33 %). Found to be a 3:2 mixture of diastereoisomers; *m/z* 617.1 $[M+1]^+$; (Found (ESI): M+H 617.1307 $C_{31}H_{35}O_5RuSi$ requires 617.1300); (Found (ESI): M+Na 639.1128 $C_{31}H_{34}NaO_5RuSi$ requires 639.1119); ν_{max} 2944, 2864, 2076, 2001 and 1636 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.87-7.81 (2H, m, Ar), 7.53-7.48 (1.3H, m, Ar), 7.41-7.35 (4.5H, m, Ar), 7.31-7.23 (2.2H, m, Ar), 5.97 (0.4H, s, ArC*H*, minor), 5.92 (0.6H, s, ArC*H*, major), 5.43 (0.6H, d, *J* 12.8, OC*H*H, major), 5.27 (0.4H, d, *J* 12.4, OC*H*H, minor), 5.21 (0.4H, d, *J* 12.4, OCH*H*, minor), 5.15 (0.6H, dd, *J* 2Hz, 12.8, OCH*H*, major), 1.10 (7.5H, s, SiC*H*(CH_3)$_2$), 1.05 (3.75H, d, *J* 7.2, SiC*H*(CH_3)$_2$), 1.00 (3.75H, d, *J* 7.2, SiC*H*(CH_3)$_2$), 0.94 (6H, d, *J* 6.0, SiC*H*(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 193.89 (quat., C=O), 193.80 (quat., C=O), 180.18 (quat., C=O), 179.75 (quat., C=O), 138.44 (ipso, Ar), 137.96 (ipso, Ar), 132.22 (ipso, Ar), 132.20 (ipso, Ar), 129.67 (CH, Ar), 129.53 (CH, Ar), 129.06 (CH, Ar), 128.87 (CH, Ar), 128.39 (CH, Ar), 128.22 (CH, Ar)127.73 (CH, Ar), 127.54(CH, Ar), 127.19 (CH, Ar), 127.16 (CH, Ar), 113.27 (quat.), 113.11 (quat.), 107.34 (quat.), 83.00 (Ar*C*H), 81.85 (Ar*C*H), 75.36 (quat.), 67.13 (quat.), 67.08 (quat.), 61.88 (quat.), 19.76 (CH_3/CH), 19.24 (CH_3/CH), 19.18 (CH_3/CH), 19.11 (CH_3/CH), 12.86 (CH_3/CH), 12.78 (CH_3/CH); δSi (99 MHz, $CDCl_3$), 4.22 (s, TBS), 3.31 (s, TBS), 2.51 (s, TIPS).

Ruthenium cyclone complex 15d.

A pressure tube was charged with (*R*)-dipropargylic ether **8** (R^1=TMS, R^2=Si(iPr)$_3$, R^3=Ph) (0.400 g, 1.005 mmol 3 eq.), acetonitrile (3 cm^3) and $Ru_3(CO)_{12}$ (0.2141 g, 0.3350 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 100 ^oC. After 3 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (2 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAC/Hexane 0 to 5 %) to afford a yellow solid (0.1542 g, 0.2524 mmol, 25 %). The metal complex was characterised as a mixture of two diasteroisomers in an approximate ratio of 7:3; *m/z* 613.1 $[M+1]^+$; (Found (ESI): MH+ 613.1375 $C_{28}H_{39}O_5RuSi_2$ requires 613.1381); ν_{max} 2943, 2891, 2864, 2047 and 1195 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.48-7.43 (1.5H, m, Ar), 7.39-7.33 (3H, m, Ar), 7.19-7.14 (0.5H, m, Ar), 5.92 (0.3H, s, ArC*H*, minor), 5.86 (0.7H, s, ArC*H*, major), 5.00 (0.7H, s, *J* 12.8, OC*H*H, major), 4.92 (0.3H, d, *J* 12.5, OC*H*H, minor), 4.83 (0.7H, dd, *J* 2.1, *J* 12.8, OCH*H*, major), 4.78 (0.3H, d, *J* 12.5, OCH*H*, minor), 1.13-1.02 (11H, m, SiiPr), 0.99-0.94 (5H, m, SiiPr), 0.90-0.86 (5H, m, SiiPr), 0.33 (2.7H, s, TMS, minor), 0.29 (6.3H, s, TMS, major); δ_C (100 MHz, $CDCl_3$) 193.85 (quat., C=O), 185.98 (quat., C=O), 185.91 (quat., C=O), 138.44 (quat., Ar), 138.79(quat., Ar), 138.67 (quat., Ar), 129.49 (CH, Ar), 129.38 (CH, Ar), 128.26 (CH, Ar), 128.13 (CH, Ar), 127.43 (CH, Ar), 119.85 (quat.), 118.49 (quat.), 116.93 (quat.), 114.58 (quat.), 82.90 (Ar*C*H), 81.69 (Ar*C*H), 67.12 (quat.), 66.64 (quat.), 66.58 (quat.), 65.77 (quat.), 64.43 (quat.), 64.05 (quat.), 19.69 (CH_3/CH), 19.18 (CH_3/CH), 19.12 (CH_3/CH), 19.00 (CH_3/CH), 17.68 (CH_3/CH), 12.80 (CH_3/CH), 12.76 (CH_3/CH) 12.27(CH_3/CH), -0.42 (CH_3, TMS), -0.51 (CH_3, TMS); δSi (99 MHz, $CDCl_3$), 4.22 (s, TBS), 3.31 (s, TBS), 2.51 (s, TIPS).

Ruthenium cyclone complex 15f.

A pressure tube was charged with (*R*)-dipropargylic ether **8** (R^1=TBDMS, R^2=Si(iPr)$_3$, R^3=Ph) (0.3331 g, 0.7571 mmol 3 eq.), acetonitrile (3 cm^3) and $Ru_3(CO)_{12}$ (0.1613 g, 0.2523 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 100 ^oC. After 3 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (2 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAc/Hexane 0 to 5 %) to afford a sticky red solid (0.104 g, 0.1596 mmol, 21%). The metal complex was characterised as a mixture of two diasteroisomers in an approximate ratio of 3:2; *m/z* 655.1 $[M+1]^+$; (Found (ESI): M+H 655.1850 $C_{31}H_{45}O_5RuSi_2$ requires 655.1851); ν_{max} 2945, 2927, 2890, 2863, 2079, 2022, 2002 and1620 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.47-7.43 (1 H, m, Ar), 7.39-7.34 (3H, m, Ar), 7.20-7.16 (1H, m, Ar), 5.93 (0.45H, s, ArC*H*, minor), 5.86 (0.55H, s, ArC*H*, major), 5.01 (0.55H, dd, *J* 0.8, 12.8, OC*H*H, major), 4.93 (0.45H, dd, *J* 1.2, 12.5, OC*H*H, minor), 4.85 (0.55H, dd, *J* 2.2, 12.8 , OCH*H*, major), 4.78 (0.45H, d, *J* 12.5, OCH*H*, minor), 1.19-0.6 (30H, m, Si^iPr_3 and Si^tBu), 0.43 (1.35H, s, $SiCH_3$, minor), 0.41 (1.65H, s, $SiCH_3$, major), 0.12 (1.35H, s, $SiCH_3$,

minor), 0.10 (1.65H, s, $SiCH_3$, major); δ_C (100 MHz, $CDCl_3$) 193.84 (quat., C=O), 185.43 (quat., C=O), 185.34 (quat., C=O), 138.68 (ipso, Ar), 138.31 (ipso, Ar), 129.53 (CH, Ar), 129.37 (CH, Ar), 129.00 (CH, Ar), 128.56 (CH, Ar), 128.51 (CH, Ar), 128.34 (CH, Ar), 128.14 (CH, Ar), 127.54 (CH, Ar), 127.39 (CH, Ar), 121.64 (quat.), 117.79 (quat.), 82.74 (Ar*C*H), 81.70 (Ar*C*H), 66.97 (quat./CH_2), 66.85 (quat./CH_2), 66.82 (quat./CH_2), 65.65 (quat./CH_2), 63.91 (quat./CH_2), 61.87 (quat./CH_2), 27.42 (CH_3), 27.37 (CH_3), 19.67 (CH_3/CH), 19.20 (CH_3/CH), 19.03 (CH_3/CH), 18.84 (quat.), 18.78 (quat.), 18.56 (CH_3/CH), 12.76 (CH_3/CH), 12.63 (CH_3/CH) 11.20 (CH_3/CH), 11.12 (CH_3/CH), 10.95 (CH_3/CH), -4.34 (CH_3, TBS), -4.70 (CH_3, TBS) -4.81; δSi (99 MHz, $CDCl_3$), 4.22 (s, TBS), 3.31 (s, TBS), 2.51 (s, TIPS).

Reduction of Acetophenone using iron catalysts and FA/TEA. Complex **7a** (7.8 mg, 19.1 μmol), trimethylamine-N-oxide (2.1 mg, 18.9 μmol) and acetophenone (23.0 mg, 0.191 mmol) were dissolved in 5:2 formic acid:triethylamine (0.2 cm^3) and heated at 28 °C for 18 h. The reaction was monitored over time by GC (Chrompac cyclodextrin-β-236M 50M column, T = 130 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas). R_T: Acetophenone: 13.4 minutes. 1-Phenylethyl formate: 15.1 (*S*), 15.5 (*R*) min. 1-Phenylethanol: 17.4 (*R*), 18.0 (*S*) min.[1] The above procedure was repeated using other complexes, temperatures and reaction times. The product configurations were assigned by comparison to previously quoted data[1] and use of authentic reference samples.

Reduction of Acetophenone using iron catalysts and ^{i}PrOH. Complex **7a** (7.8 mg, 19.1 μmol), trimethylamine-N-oxide (2.1 mg, 18.9 μmol) and acetophenone (23.0 mg, 0.191 mmol) were dissolved in ^{i}PrOH (0.96 cm^3) and heated at 28 °C for 18 h. The reaction was monitored over time by GC (Chrompac cyclodextrin-β-236M 50M column, T = 130 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas). R_T: Acetophenone: 13.4 min. 1-Phenylethanol: 17.4 (R), 18.0 (S) min.[1] The above procedure was repeated using other temperatures and concentrations.

General ruthenium-hydride synthesis prior to use in reductions.[12]

To Ru(TMS-TMS) (22.6 mg, 0.05 mmol) in THF (1 cm^3) was added aqueous sodium hydroxide (0.5 cm^3, 1M, 0.50 mmol) and stirred for 2.5 h. An excess of H_3PO_4 (0.3 cm^3) was then added and the reaction extracted using Et_2O (3 x 10 cm^3), dried over $MgSO_4$ and the solvent removed all under a nitrogen atmosphere to afford the hydride species as a yellow oil which was used immediately without further purification. Selected data for each hydride this formed is given below.

Reduction of acetophenone using ruthenium hydride complexes.

Method A- iPrOH: The ruthenium hydride (0.01 mmol, 0.5 mol%) was dissolved in anhydrous iPrOH (10 cm^3) and heated at 60 °C over 30 min. Acetophenone (0.22 cm^3, 0.2266 g, 1.89 mmol) was then added and the reaction stirred at 60 °C over 7 days and the reaction was monitored by GC.

Method B- HCOOH/Et_3N: The ruthenium hydride (0.02 mmol, 0.25 mol%) was dissolved in formic acid triethylamine complex (5:2, 4 cm^3) and heated at 60 °C over 30 min. Acetophenone (0.92 cm^3, 0.9476 g, 7.90 mmol) was then added and the reaction stirred at 60 °C over 7 days and the reaction was monitored by GC.

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Notes and references

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