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Stereoselective conjugate addition reactions of lithium amides to α,β-unsaturated chiral iron acyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHR)]$

Stephen G. Davies *, Jairton Dupont, Robert J. C. Easton, Osamu Ichihara, Jeffrey M. McKenna, Andrew D. Smith, José A. A. de Sousa

Department of Organic Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford, OX1 3TA, UK

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Abstract

Conjugate addition of achiral lithium dimethylamide to the chiral iron cinnamoyl complexes (*S*,*E*)- and (*S*,*Z*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHPh)]$ proceeds with high diastereoselectivity, with this protocol being used to establish unambiguously the absolute configuration of Winterstein's acid (3-*N*,*N*-dimethylamino-3-phenylpropanoic acid) as (*R*). The highly diastereoselective conjugate addition of lithium *N*-benzyl-*N*-trimethylsilylamide to a range of α,β-unsaturated iron acyl complexes, followed by in-situ elaboration of the derived enolate by either alkylation or aldol reactions is also demonstrated, facilitating the stereoselective synthesis of both *cis*- and *trans*-β-lactams. This methodology has been used to effect the formal asymmetric syntheses of (±)-olivanic acid and (±)-thienamycin. Addition of chiral lithium amides derived from primary and secondary amines to the iron crotonyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHMe)]$ indicates that lithium *N*-α-methylbenzylamide shows low levels of enantiorecognition, while lithium *N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamide and lithium *N*-benzyl-*N*-α-methylbenzylamide show high levels of enantiodiscrimination. The high level of observed enantiorecognition was used to facilitate a kinetic resolution of (*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHMe)]$ with homochiral lithium (*R*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamide. Further mechanistic studies show that conjugate additions of (*RS*)-lithium *N*-benzyl-*N*-α-methylbenzylamide to either the (*RS*)- or homochiral iron crotonyl complex show 2:1 stoicheiometry, while homochiral lithium *N*-benzyl-*N*-α-methylbenzylamide shows 1:1 stoicheiometry.
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Keywords: Enantiorecognition; Conjugate addition; Iron acyl auxiliary

1. Introduction

The iron chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ has been used extensively within organic synthesis for the asymmetric synthesis of a variety of organic molecules. Remarkable levels of stereocontrol are observed upon reaction of alkyl and acyl ligands attached to $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ for a range of transformations including alkylations, aldol reactions, conjugate addition reactions and Diels–Alder reactions [1]. The high levels of control observed using this auxiliary indicate that it is able to control effectively both the three dimensional space around attached alkyl and acyl ligands and the orientation of these ligands within that space. Structural and conformational analyses of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R]$ complexes derived from complexation of an organic fragment (R = acyl, alkyl) to the iron auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ indicate that they adopt a geometry close

* Corresponding author. Tel.: +44-1865-275695; fax: +44-1865-275633.
E-mail address: steve.davies@chem.ox.ac.uk (S.G. Davies).

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to octahedral [2], in which the triphenylphosphine, carbon monoxide and the organic ligand R occupy three adjacent sites of the pseudo-octahedral structure, with each lying approximately orthogonal to the plane formed by the other two and the metal. The remaining three co-ordination sites on iron are occupied by the cyclopentadienyl ligand. The iron acetyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3]$ (**1**) is chiral, and adopts a conformation that places the acetyl oxygen *anti* to the carbon monoxide ligand, with one of the triphenylphosphine phenyl groups approximately parallel to the plane of the acetyl ligand, shielding one face of the acetyl (Fig. 1) [3,4].

Iron acetyl complex **1** is readily deprotonated upon treatment with *n*-BuLi, and treatment of the derived enolate with MeI generates the corresponding propanoyl complex **2** in essentially quantitative yield [5]. Further deprotonation to generate the corresponding lithium enolate **3**, and alkylation with alkyl halides generates iron complexes **4** with high levels of diastereoselectivity (typically >96% d.e.) [6]. The high diastereoselectivity observed in these transformations may be rationalised by deprotonation of the acyl ligand being completely stereoselective for formation of the (*E*)-enolate (iron *trans* to R), with alkylation occuring only from the unhindered face (away from the triphenylphosphine) in the conformation with the enolate oxygen *anti* to the carbon monoxide ligand (Fig. 2) [7].

Additions of aldehydes to the lithium enolates derived from both the acetyl and propanoyl complexes **1** and **2** generate the corresponding β-hydroxy acyl complexes with essentially no stereocontrol [8]. However, transmetallation to an aluminium enolate prior to addition of the aldehyde leads to excellent stereocontrol [9,10]. In the acetyl series, complementary stereoselectivity has been observed by Liebeskind for the corresponding tin enolate [11], while in the propionyl series

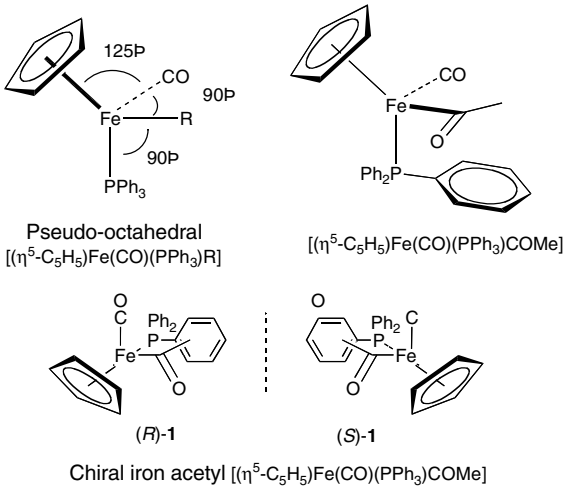


Fig. 1. Chiral acetyl $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COMe)]$.

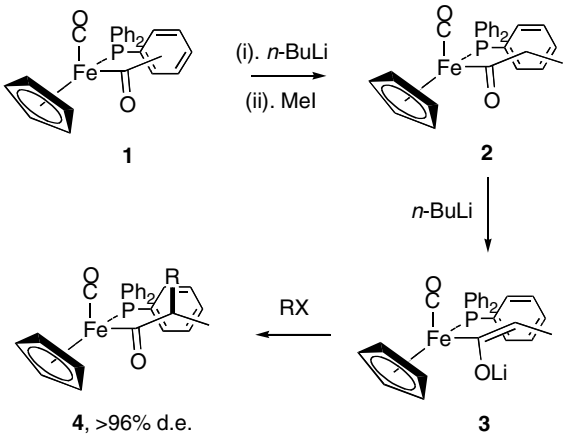


Fig. 2. Diastereoselective alkylation of complexes derived from the iron acyl auxiliary.

complementary control at the β-centre may be achieved via the corresponding copper enolate [12], demonstrating that the iron auxiliary acyls may be considered as convenient chiral acetate and propionate enolate equivalents (Fig. 3).

The high stereoselectivity observed upon reaction of acetyl complex **1** with electrophiles has been used to discriminate between the two enantiomers of racemic substrates. For instance, treatment of the lithium enolate derived from (*RS*)-**1** with (*RS*)-*tert*-butyl 2-bromopropi-

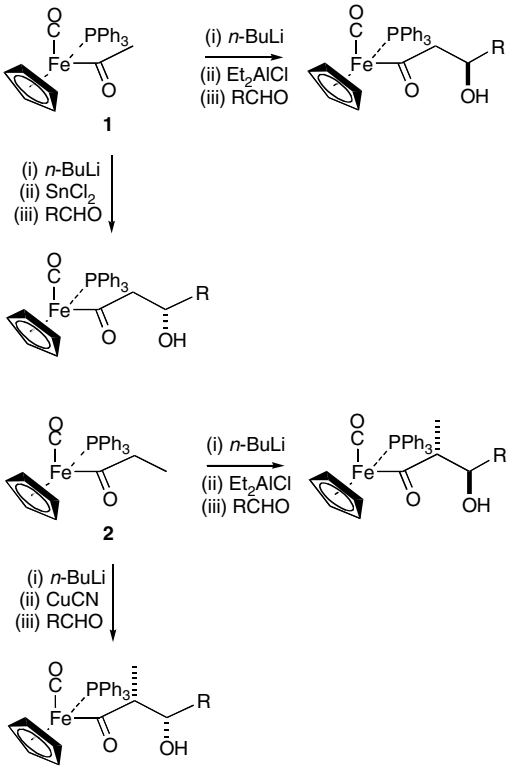


Fig. 3. Stereoselective aldol reactions of the iron acetyl and propanoyl complexes **1** and **2**.

onate gave a 97.5:2.5 mixture of the β-methyl succinoyl complexes (*RS*,*SR*)-**5** and (*RR*,*SS*)-**6**, consistent with one enantiomer of the enolate preferring to react forty times faster with one of the enantiomers of the α-bromoester than with the other [13]. Similarly, treatment of the lithium enolate of (*S*)-**1** with (*RS*)-propylene oxide in the presence of diethyl aluminium chloride leads to the selective formation of (*S*,*R*)-γ-hydroxyacyl complex **7**, which upon oxidative decomplexation produces homochiral (*R*)-4-methylbutyrolactone **8** (Fig. 4) [14].

Conjugate addition reactions to readily available (*E*)-α,β-unsaturated iron acyl complexes **9** have also been explored, with addition of a range of alkyllithium reagents proceeding with high stereoselectivity. The configuration of the newly formed β-stereogenic centre in these reactions is consistent with the nucleophile adding to the α,β-unsaturated acyl ligand in its *cisoid* conformation from the unhindered face to give **10** [15]. Furthermore, addition of alkyllithiums to the (*E*)-α,β-unsaturated acyl complexes and subsequent trapping of the intermediate with alkyl halides results in the highly stereoselective formation of two new stereogenic centres, giving **11** in high d.e. (Fig. 5) [16].

In an extension of this methodology, we have demonstrated previously that the iron crotonyl complex **12** undergoes highly diastereoselective conjugate additions of lithium amides derived from primary amines. For

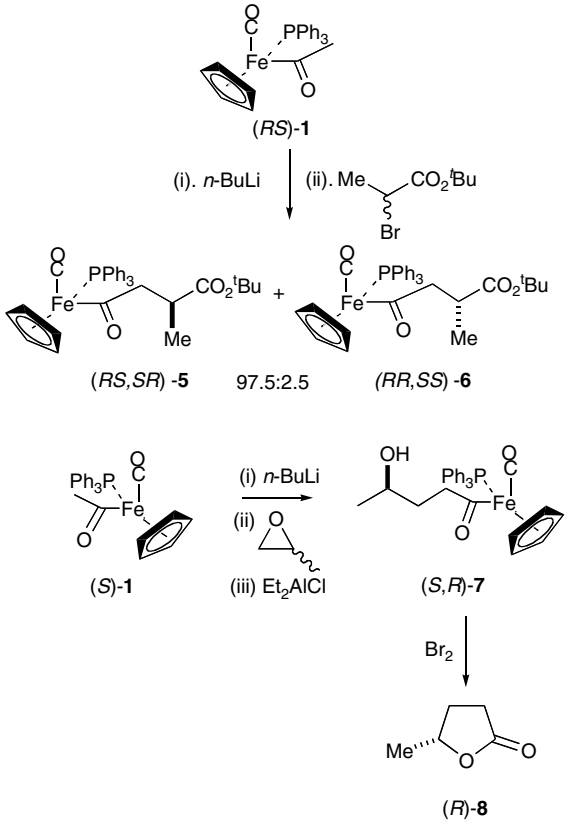


Fig. 4. Enantiodiscrimination reactions using the iron chiral auxiliary.

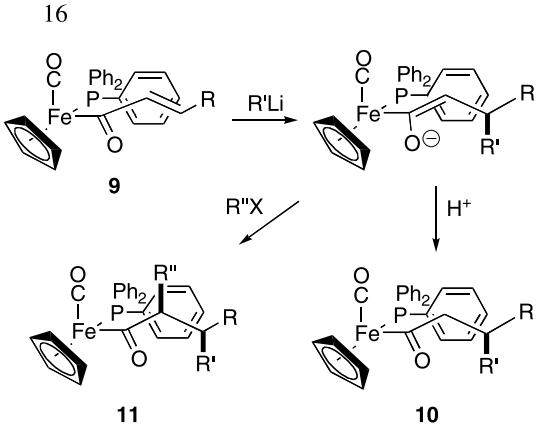
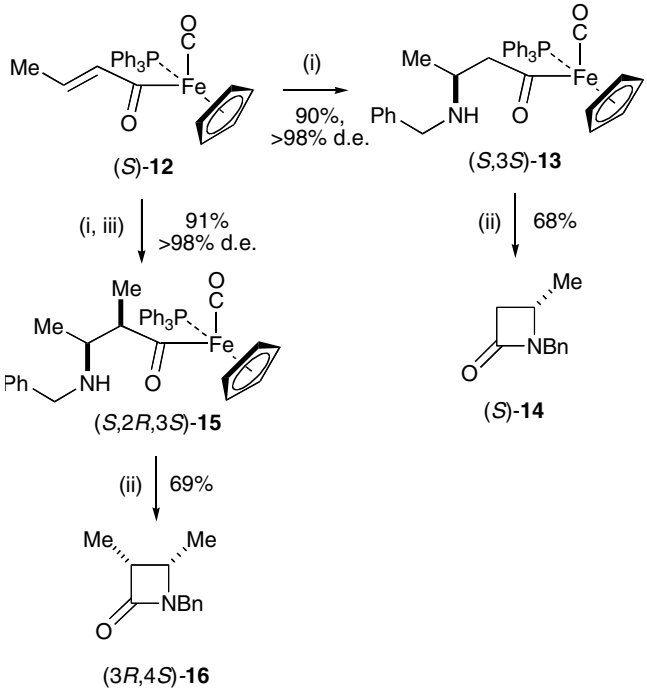


Fig. 5. Conjugate addition of alkyllithium reagents to (*E*)-α,β-unsaturated iron acyls.

instance, conjugate addition of lithium benzylamide to the (*S*)-iron crotonyl complex **12** affords the (*S*,3*S*)-β-amino complex-**13** in 90% yield as a single diastereoisomer, which upon oxidative decomplexation with bromine affords homochiral (*S*)-4-methyl-*N*-benzylazetidin-2-one **14**. Furthermore, conjugate addition of lithium benzylamide to **12** and tandem methylation gives (*S*,2*R*,3*S*)-β-amino-α-methyl complex-**15** in 91% yield as a single diastereoisomer, with oxidative decomplexation yielding the *cis*-β-lactam (3*R*,4*S*)-**16** (Scheme 1) [16–18].



Scheme 1. Reagents and conditions: (i) BnNHLi (1.2 eq), THF, −78 °C; (ii) Br_2 (2 eq), DCM, −78 °C then NEt_3, −78 °C to rt; (iii) MeI (4 eq), THF, −78 °C to rt.

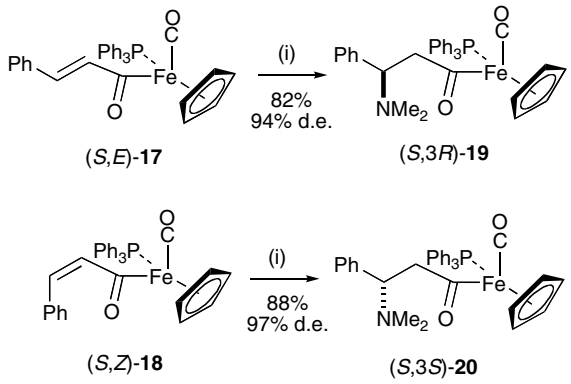
As an extension of this methodology, we report herein our full investigations concerning the conjugate additions of chiral and achiral lithium amides derived from a range of primary and secondary amines to chiral α,β-unsaturated iron acyl complexes [(η^5-C_5H_5)Fe(CO)(PPh_3)(COC=CHR)], and the stereoselective in-situ elaboration of the derived β-amino enolates. Parts of this work have been communicated previously [19,20].

2. Results and discussion

2.1. Conjugate addition of achiral secondary lithium amides: asymmetric synthesis of Winterstein's acid

Winterstein's acid (3-*N*,*N*-dimethylamino-3-phenylpropanoic acid) has been identified as the carboxylate side chain of the diterpene taxine B [21], and although synthetic homochiral Winterstein's acid has been prepared by resolution [22], its absolute configuration is yet to be established unambiguously. Having demonstrated previously that high levels of asymmetric induction are observed upon conjugate addition of lithium benzylamide to (*S*,*E*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COC=CHMe)] [16,17], the conjugate addition of a secondary lithium amide was investigated to probe the generality of this procedure. Lithium dimethylamide was chosen as the nucleophile of choice, as it was proposed that stereoselectivity in this procedure would facilitate the preparation, and allow unambiguous assignment, of the absolute configuration of Winterstein's acid. Conjugate addition of lithium dimethylamide to the diastereoisomeric iron acyl complexes (*S*,*E*)- and (*S*,*Z*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CHPh)] [23] **17** and **18** respectively at −100 °C proceeded to complete conversion in each case, giving the diastereoisomeric (*S*,*R*)- and (*S*,*S*)-β-*N*,*N*-dimethylamino iron complexes **19** and **20** in 82% and 88% isolated yields and 94% and 97% d.e. respectively. In each case, fractional crystallisation gave (*S*,3*R*)-**19** and (*S*,3*S*)-**20** in >97% d.e., with the configuration of the β-centres within (*S*,3*R*)-**19** and (*S*,3*S*)-**20** assigned relative to the iron centre by analogy with the known sense of asymmetric induction upon conjugate addition of lithium dibenzylamide to the (*E*)-crotonoyl complex [17], and by the characteristic ^{1}H NMR chemical shifts of the α-protons [24]. The observed stereocontrol in these reactions is consistent with a mechanism involving lithium co-ordination to the acyl oxygen and subsequent delivery of the dimethylamide to the unhindered face of the cinnamoyl ligand in the *s-cis* conformation (Scheme 2).

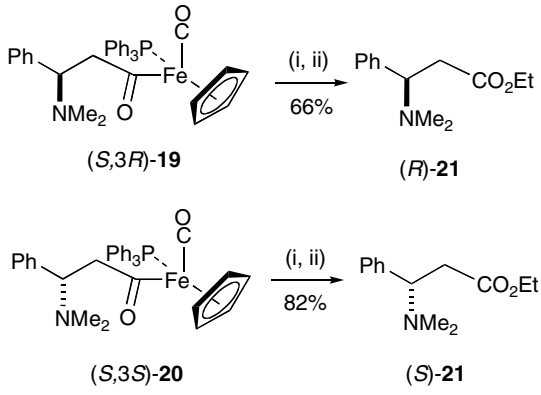
Oxidative decomplexation of **19** and **20** with NBS gave, after filtration through alumina and ion exchange chromatography, the corresponding enantiomeric *N*,*N*-dimethyl β-amino acids, which were converted directly



Scheme 2. Reagents and conditions: (i) $LiNMe_2$, THF, −100 °C.

to their ethyl ester derivatives **21** and subsequently characterized as their hydrochloride salts in 82% and 66% yields, respectively. The e.e. of the hydrochloride salts of (*S*)-**21** and (*R*)-**21** was shown to be >98% and 97%, respectively, by ^{1}H NMR spectroscopic analysis in the presence of (−)-2,2,2-trifluoro-1-(9-anthryl)ethanol and comparison with an authentic racemic sample. These salts were subsequently used to regenerate pure (*S*)- and (*R*)-ethyl 3-dimethylamino-3-phenyl-propanoate **21**, with measurement of the specific rotation of **21** {for (*S*)-**21**; $[\alpha]_D^{20}$ +13.9 (c 0.5, $CHCl_3$), $[\alpha]_{436}^{20}$ +31.5 (c 0.5, $CHCl_3$); for (*R*)-**21**; $[\alpha]_{436}^{20}$ −31.1 (c 0.5, $CHCl_3$)} and comparison with the ethyl ester derived from Winterstein's acid {$[\alpha]_D^{18}$ −15.5 (neat);[22] $[\alpha]_D^{20}$ −9.58 (c 9.0, $CHCl_3$)[22]} unambiguously establishing the absolute configuration of Winterstein's acid as (*R*) (Scheme 3).

To probe further the utility of these transformations, the tandem conjugate addition and alkylation of iron complex (*S*,*Z*)-**18** was investigated, with conjugate addition of lithium dimethylamide and alkylation of the resultant enolate with MeI giving (*S*,2*R*,3*S*)-**22** in >98% d.e. after chromatographic purification and recrystallisation in 65% yield. The configuration at C(2) within



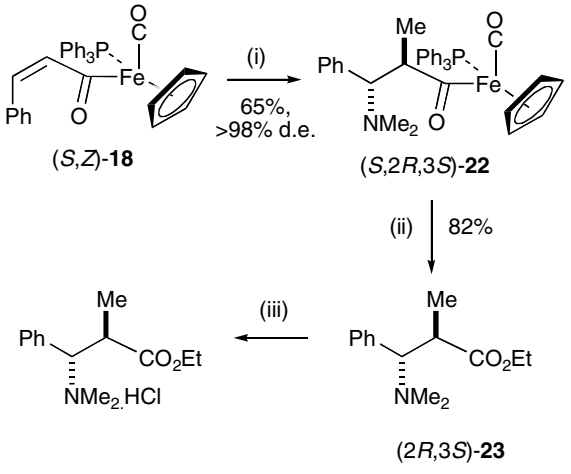
Scheme 3. Reagents and conditions: (i) NBS, HCl, H_2O, −78 °C to rt then Dowex ion exchange chromatography; (ii) HCl, EtOH, Δ.

22 relative to the iron centre was assumed by analogy with the known sense of asymmetric induction upon alkylation of the enolates of iron acyl complexes. Subsequent oxidative decomplexation with NBS and conversion to the corresponding ethyl ester gave (2*R*,3*S*)-**23** in 82% yield and >98% d.e., which was converted to its hydrochloride salt for analysis (Scheme 4).

2.2. Tandem conjugate addition-aldol reactions of achiral secondary lithium amides: a formal synthesis of (±)-olivanic acid and (±)-thienamycin

Having demonstrated the asymmetric synthesis of Winterstein's acid, extension of this conjugate addition methodology to the tandem conjugate addition-aldol manifold was investigated, as this protocol could be used for the stereoselective preparation of β-lactam derivatives with a hydroxyethyl side chain via an aldol reaction with acetaldehyde. Such structural frameworks have been synthesised previously for the stereoselective synthesis of carbapenem antibiotics such as thienamycin and olivanic acid (Fig. 6).

The (*RS*)-crotonoyl iron complex **12** was chosen for initial studies, with conjugate addition of lithium bis-(3,4-dimethoxybenzyl)amide followed by addition of acetaldehyde generating an 89:11 mixture of two diastereoisomers **24**:**25** in 78% yield, with recrystallisation of this diastereoisomeric mixture yielding **24** as a single diastereoisomer. Similarly, conjugate addition of lithium *N*-benzyl-*N*-trimethylsilylamide (LSA) to (*RS*)-**12** followed by in situ reaction with acetaldehyde gave an 83:17 mixture of diastereoisomers **26**:**27** in 81% yield, with recrystallisation giving **26** as a single diastereoisomer. The observation of only two diastereoisomers in these reactions from a possible eight is consistent with the iron auxiliary controlling both the formation of the β-centre



Scheme 4. Reagents and conditions: (i) $LiNMe_2$, THF, −100 °C then MeI, −100 °C to rt; (ii) NBS, HCl, H_2O, −78 °C to rt then Dowex ion exchange chromatography; (iii) HCl, EtOH, Δ.

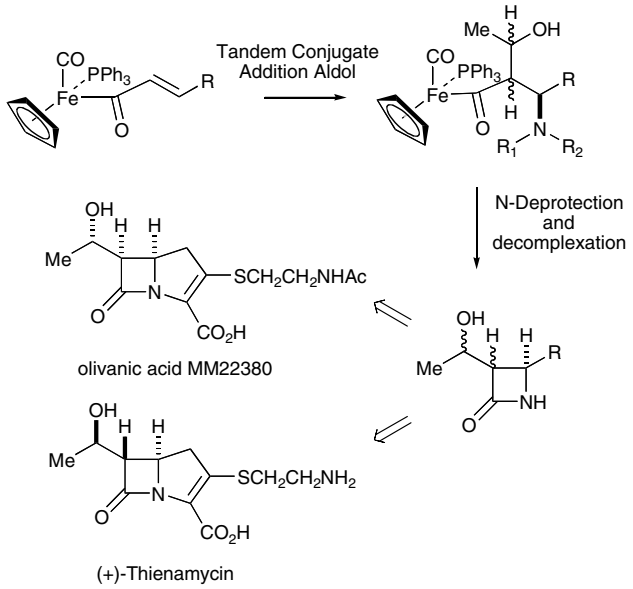
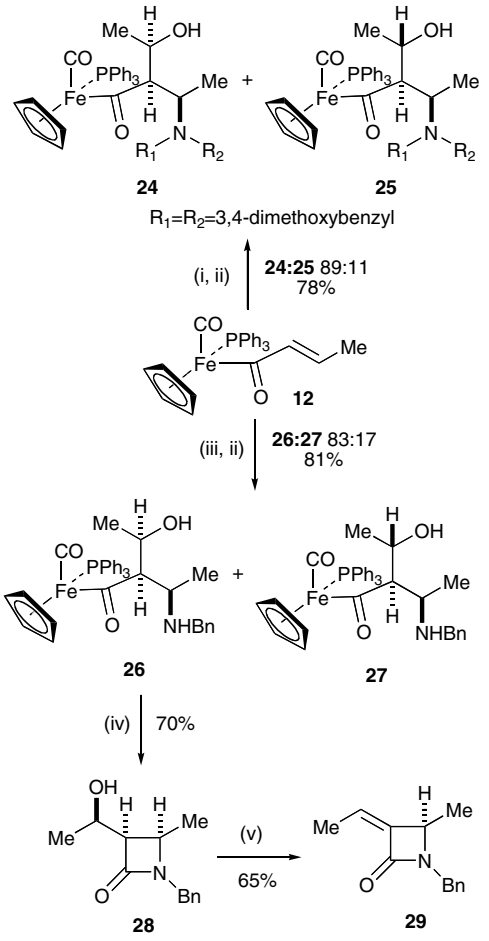


Fig. 6. Retrosynthetic analysis of olivanic acid and thienamycin.

upon conjugate addition of the lithium amide and the α-centre upon aldol reaction with acetaldehyde, with the mixture of diastereoisomers having different relative configurations at the alcohol stereocentre. The relative configuration within diastereoisomer **26** was assigned by decomplexation with bromine at −78 °C, generating *cis*-β-lactam **28** in 70% yield, as indicated by the coupling constant between C(3)H and C(4)H (*J*5.3 Hz) [25]. Subsequent transformation of the hydroxy-β-lactam to the ethylidene-β-lactam **29** via the mesylate gave (*Z*)-**29** exclusively in 65% isolated yield [26], with nOe difference studies confirming the (*Z*)-olefin geometry, consistent with the configuration within *syn*-aldol **26**. The observed relative configuration within **26** is consistent with conjugate addition of LSA to the least hindered face of the α,β-unsaturated acyl complex in the *anti-s-cis* conformation, with subsequent approach of acetaldehyde to the resultant (*E*)-enolate in the *anti* conformation, again from the unhindered face. The configuration within *N*-bis-(3,4-dimethoxybenzyl)-**24** was assigned by analogy to that of **26** (Scheme 5).

With the ability of the iron auxiliary to impart high levels of stereocontrol in the conjugate addition-aldol manifold for the preparation of *cis*-β-lactams demonstrated, the application of this strategy to natural product synthesis was investigated. Kametani et al. [27] have previously utilised *cis*-β-lactam **30** in the preparation of (±)-olivanic acid MM22380, and this product was identified as a viable target to demonstrate the synthetic utility of the conjugate addition/aldol approach using the chiral iron auxiliary. This approach necessitated the stereoselective synthesis of δ-functionalised-α,β-unsaturated acyl complex **31**, with conjugate addition-aldol reaction utilised to create the required *cis*-β-lactam skeleton (Fig. 7).



Scheme 5. Reagents and conditions: (i) Lithium bis-(3,4-dimethoxybenzyl)amide, THF, −78 °C; (ii) MeCHO, THF, −78 °C to rt; (iii) Lithium *N*-benzyl-*N*-trimethylsilylamide, THF, −78 °C; (iv) Br_2, DCM, −78 °C then NEt_3, −78 °C to rt; (v) MsCl, NEt_3, 0 °C then $NaHCO_3$, Δ.

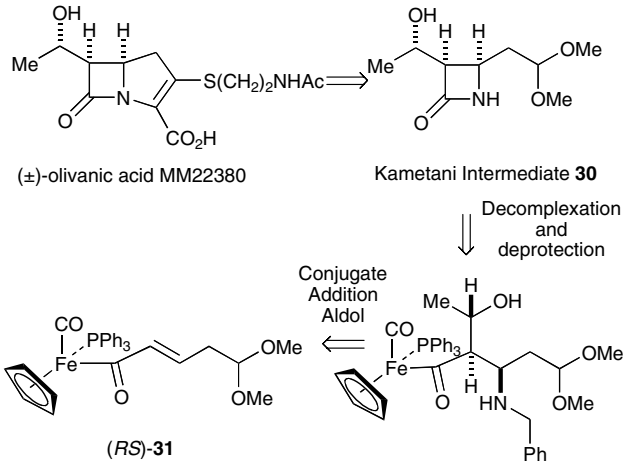
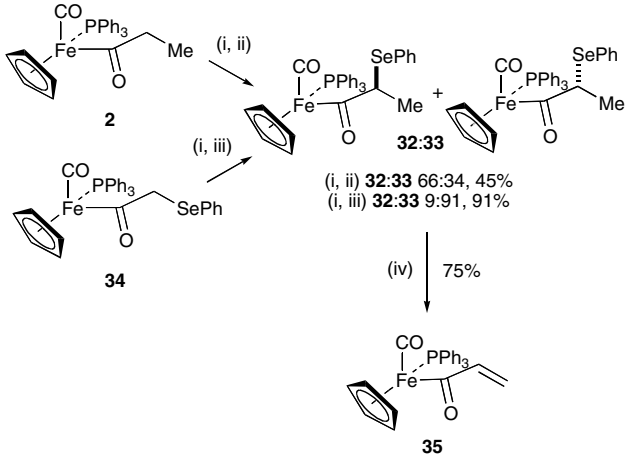


Fig. 7. Proposed formal synthesis of (±)-olivanic acid.

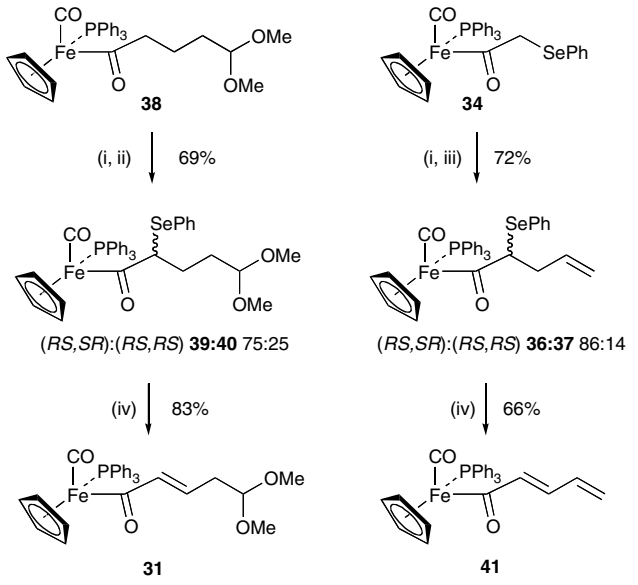


Scheme 6. Reagents and conditions: (i) *n*-BuLi, THF, −78 °C, 2h; (ii) $(SePh)_2$, THF, −78 °C, 1 h then MeOH, −78 °C to rt; (iii) MeI, THF, −78 °C to rt; (iv) *m*CPBA, DCM, −78 °C 1 h then $(iPr)_2NH$, −78 °C to rt.

Although routes to functionalised α,β-unsaturated acyl complexes have been reported previously via Peterson olefination or aldol-methylation-elimination [23], an alternative tactic, via selenoxide *syn*-elimination, was investigated [28]. In a model system, selenenylation was achieved following deprotonation of the propanoyl complex **2** and addition of diphenyl diselenide, giving the desired complex as a 66:34 mixture of diastereoisomers **32**:**33** and in low isolated yield (45%), with ^1H NMR spectroscopic analysis allowing assignment of the relative configuration of the two diastereoisomers. Methylation of the selenyl complex **34** proved more successful, giving **32**:**33** in an 9:91 ratio and in 91% isolated yield. Elimination of the 9:91 mixture of selenides **32**:**33** through oxidation with *m*CPBA yielded the known iron acryloyl complex **35** in 75% yield (Scheme 6).

This methodology was then applied to the synthesis of the desired δ-functionalised-α,β-unsaturated acyl complex **31**. Unfortunately, the inherent reactivity of the enolate derived from selenide **34** limited its utility to alkylation with activated electrophiles, with alkylation with allyl iodide giving a 86:14 mixture of diastereoisomers **36**:**37** in 72% yield. However, selenenylation of **38** gave a 75:25 mixture of diastereoisomers **39**:**40** in 69% yield, with subsequent *syn*-elimination of the diastereoisomeric mixtures **36**:**37** and **39**:**40** furnishing α,β-unsaturated complexes **41** and **31** respectively in high yields (Scheme 7).

With (*RS*)-acceptor **31** in hand, its ability to direct the course of asymmetric conjugate addition reactions was assessed via reaction with lithium benzylamide, giving β-amino iron acyl complex (*RS*,3*RS*)-**42** in >96% d.e. and in 82% yield. Furthermore, conjugate addition of lithium benzylamide and subsequent alkylation with MeI gave (*RS*,2*SR*,3*RS*)-**43** in >96% d.e., and in 76% isolated yield as a single diastereoisomer after purification,

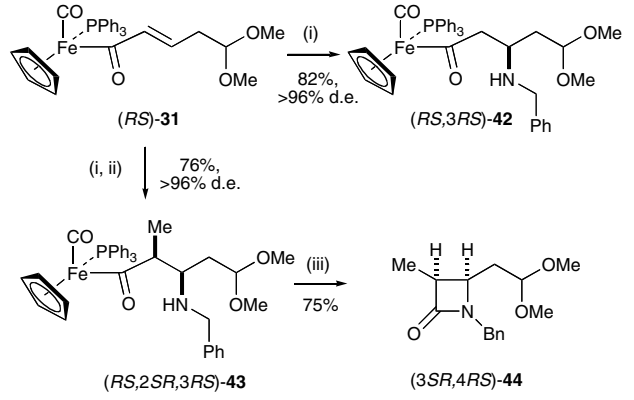


Scheme 7. Reagents and conditions: (i) *n*-BuLi, THF, −78 °C, 2h; (ii) $(SePh)_2$, THF, −78 °C, 1 h then MeOH, −78 °C to rt; (iii) allyl iodide, THF, −78 °C to rt; (iv) *m*CPBA, DCM, −78 °C 1 h then $(iPr)_2NH$, −78 °C to rt.

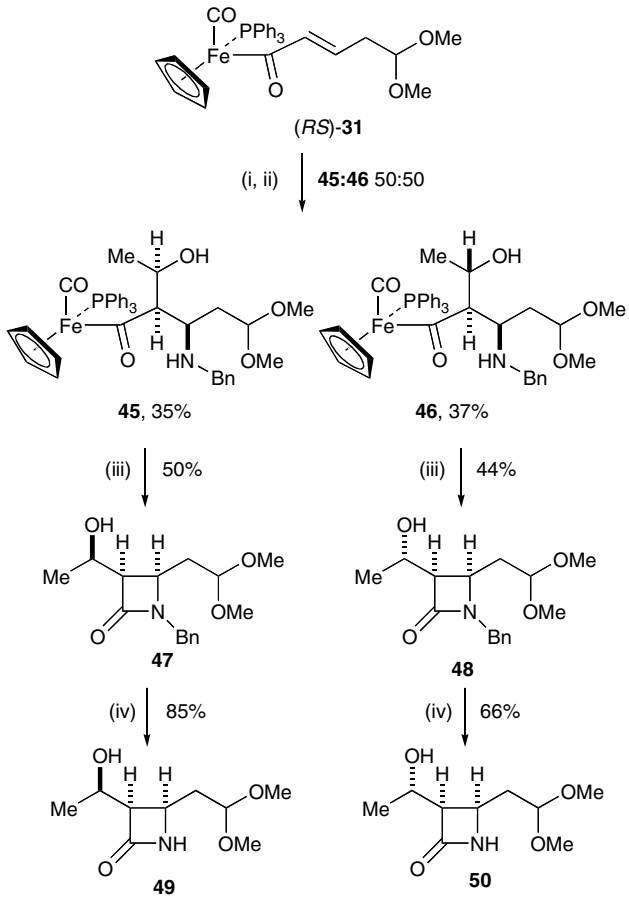
with decomplexation giving *cis*-β-lactam **44** in 75% yield. The configuration at C(3) within **42** and **43** upon conjugate addition relative to the iron centre was assigned upon the basis of addition to the least hindered face of the α,β-unsaturated acyl complex in the *anti-s-cis* conformation, while that at C(2) within **43** was assumed by analogy with the known sense of asymmetric induction upon alkylation of the enolates of the iron acyl complex (Scheme 8).

Having shown that conjugate addition and alkylation reactions of iron acyl complex **31** proceed stereoselectively, the conjugate addition of LSA to **31** and tandem aldol reaction with acetaldehyde was investigated, giving high conversion to the desired β-amino aldol diastereoisomers **45**:**46**, but as a 1:1 mixture of diastereoisomers. Separation via chromatographic purification gave the homogenous β-amino complexes **45** and **46** in 35% and 37% isolated yield respectively. In order to confirm the relative configuration within each diastereoisomer, decomplexation and *N*-debenzylation was undertaken. Treatment of **45** and **46** with bromine gave *cis*-β-lactams **47** and **48** in 50% and 44% yield respectively, with subsequent removal of the *N*-benzyl protecting groups achieved by dissolving metal reduction, giving **49** and **50** in 85% and 66% yield respectively. ^1H NMR spectroscopic analysis confirmed that β-lactam **50** had spectroscopic properties consistent with those described by Kametani et al. [27] in the preparation of (±)-olivanic acid MM22380, confirming the relative configuration within complexes **45** and **46**, and achieving the desired formal synthesis (Scheme 9).

The further application of this methodology for the diastereoselective synthesis of *trans*-β-lactams was next investigated. Lithium amide conjugate addition to a (*Z*)-α,β-unsaturated iron acyl complex and subsequent aldol reaction was proposed to lead, after decomplex-



Scheme 8. Reagents and conditions: (i) NHBnLi, THF, −78 °C; (ii) MeI, THF, −78 °C to rt; (iii) Br_2, DCM, −78 °C then NEt_3, −78 °C to rt.



Scheme 9. Reagents and conditions: (i) LSA, THF, −78 °C; (ii) MeCHO, THF, −78 °C to rt; (iii) Br_2, DCM, −78 °C then NEt_3, −78 °C to rt; (iv) Na, NH_3, EtOH, −78 °C.

ation, to a *trans*-β-lactam. To facilitate conjugate addition, rather than γ-deprotonation, the preparation of a (*Z*)-α,β-unsaturated iron acyl complex with sp^2-hybridisation at the γ-position was investigated, which would lead to a formal asymmetric synthesis of thienamycin via the preparation of *trans*-β-lactam **51** (Fig. 8).

Following a known protocol [23], Peterson olefination of the iron trimethylsilyl complex **52** with (*E*)-3-trimethylsilylpropenal [29] gave a 60:40 mixture of the separable (*E*,*E*)- and (*Z*,*E*)-dienoyl complexes **53** and **54** in 55% and 37% yield respectively. The conjugate addition of lithium benzylamide to (*E*,*E*)-**53** and (*Z*,*E*)-**54**, and the known dienoyl complexes (*E*)-**55** and (*Z*)-**56**, was next investigated. Addition of lithium benzylamide to (*E*,*E*)-**53** and (*E*)-**55** gave (*RS*,3*SR*)-**57** and (*RS*,3*SR*)-**58** in 97% d.e. in each case and in 90% and 92% yield respectively, while conjugate addition to (*Z*,*E*)-**54** and (*Z*)-**56** gave (*RS*,3*RS*)-**59** and (*RS*,3*RS*)-**60** in 98% d.e. in each case and in 54% and 66% yield respectively (Scheme 10).

Following the high diastereoselectivity observed upon conjugate addition of lithium benzylamide to the (*Z*)-dienoyl complexes, the tandem addition of LSA to (*Z*)-**56** followed by addition of acetaldehyde was undertaken, giving an 89:11 mixture of only two diastereoisomers by ^{1}H NMR spectroscopic analysis. Chromatographic purification and subsequent recrystallisation allowed the isolation of **61** as a single diastereoisomer in 62% yield. Decomplexation of **61** with Br_2 and subsequent treatment with TBDMSCl gave *O*-silyl-β-lactam **62**, and confirmed the *trans*-C(3)–C(4) configuration within **62** {C(3)H–C(4)H *J*2.1 Hz}. *N*-Debenzylation of *O*-silyl-β-lactam **62** using sodium in liquid ammonia gave β-lactam **63** in 83% yield and with spectroscopic properties identical to those of the literature, further confirming the relative configuration within **61**, and completing a formal synthesis of (±)-thienamycin (Scheme 11) [30].

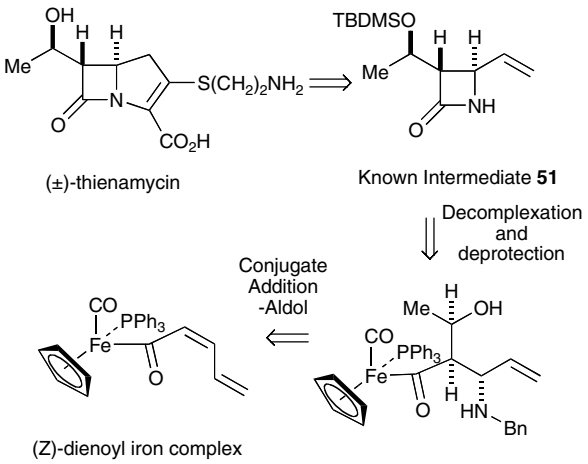
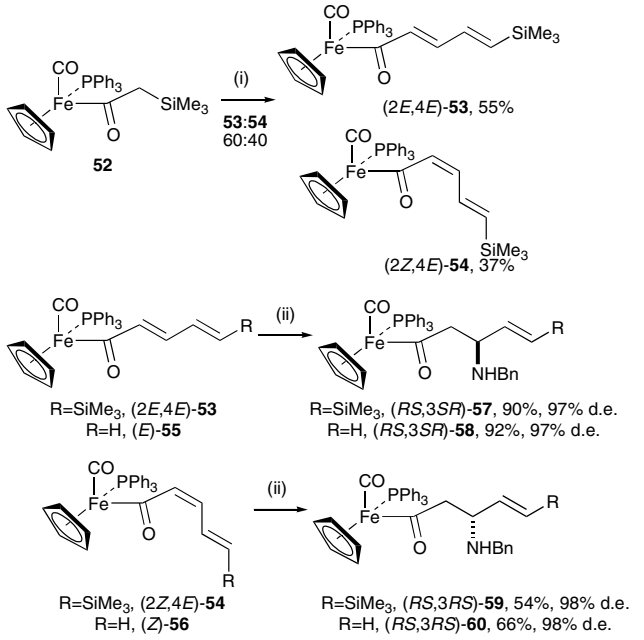


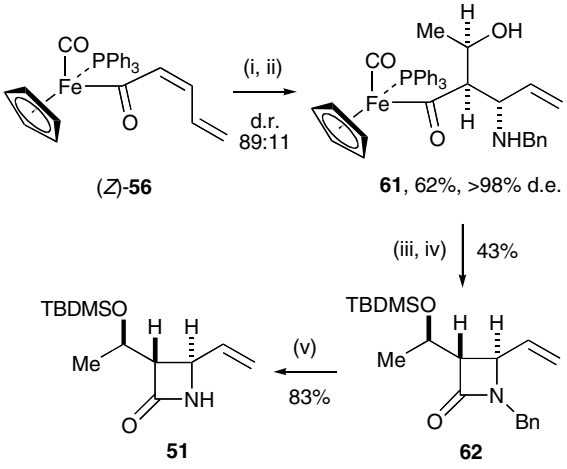
Fig. 8.



Scheme 10. Reagents and conditions: (i) *n*-BuLi, THF, −78 °C then (*E*)-3-trimethylsilylpropenal, THF, −78 °C to rt; (ii) NHBnLi, THF, −78 °C.

2.3. Enantiorecognition between chiral iron acyl complex and chiral lithium amides

Having demonstrated that achiral lithium amides derived from primary and secondary amines undergo efficient and highly diastereoselective conjugate addition to α,β-unsaturated iron acyl complexes, and that the enolates arising from these conjugate additions may react with alkylating agents and aldehydes, further studies con-



Scheme 11. Reagents and conditions: (i) LSA, THF, −78 °C; (ii) MeCHO, THF, −78 °C to rt; (iii) Br_2, DCM, −78 °C then NEt_3, −78 °C to rt; (iv) TBDMSCl, imidazole, DMF, rt; (v) Na, NH_3, EtOH, −78 °C.

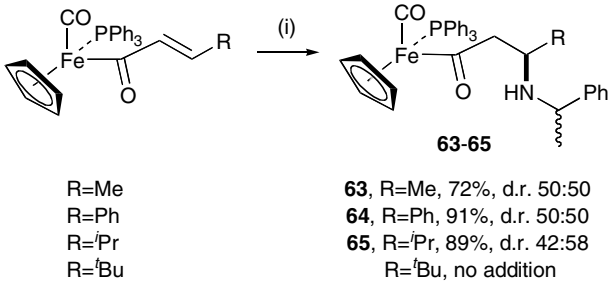
centrated upon ascertaining the levels of chiral recognition observed in the conjugate addition of chiral lithium amides to iron acyl complexes. The conjugate addition of lithium (*RS*)-*N*-α-methylbenzylamide to the iron crotonoyl complex (*RS*)-**12** furnished a 50:50 mixture of inseparable diastereoisomers **63** in 72% yield. The relative configuration within these diastereoisomers was assumed to arise from complete stereocontrol by the iron complex in the formation of the β-stereocentre, but with no discrimination observed between the enantiomers of lithium (*RS*)-α-methylbenzylamide. This is consistent with the reaction proceeding under the stereochemical dominance of the chiral iron auxiliary, unsurprising given that α-methylbenzylamine generally undergoes conjugate addition reactions with poor levels of stereocontrol to α,β-unsaturated acceptors [31]. In an attempt to enhance the observed levels of recognition, the effect of the introduction of a more bulky substituent to the β-position of the iron complex was tested. Conjugate addition of lithium (*RS*)-*N*-α-methylbenzylamide to (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CHPh)] and (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CH^{i}Pr)] furnished the inseparable products of conjugate addition **64** and **65** in high yields (91% and 89% yield respectively) but with low levels of stereocontrol (d.r. 50:50 and 42:58, respectively), while no addition was seen to (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CH^{t}Bu)] (Scheme 12).

To probe further the possibility of chiral recognition in the iron acyl system, it was proposed that the introduction of a second substituent onto the nitrogen atom of the lithium amide would restrict the conformational lability of the reacting species, and lead to improved levels of enantiorecognition. Thus, reductive amination of (*RS*)-*N*-α-methylbenzylamine with 3,4-dimethoxybenzaldehyde gave (*RS*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamine. Conjugate addition of two equivalents of lithium (*RS*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamide to the (*RS*)-**12** gave a crude product containing three diastereoisomers **68**:**69**:**70** in a 94:3:3 ratio (Scheme 13).

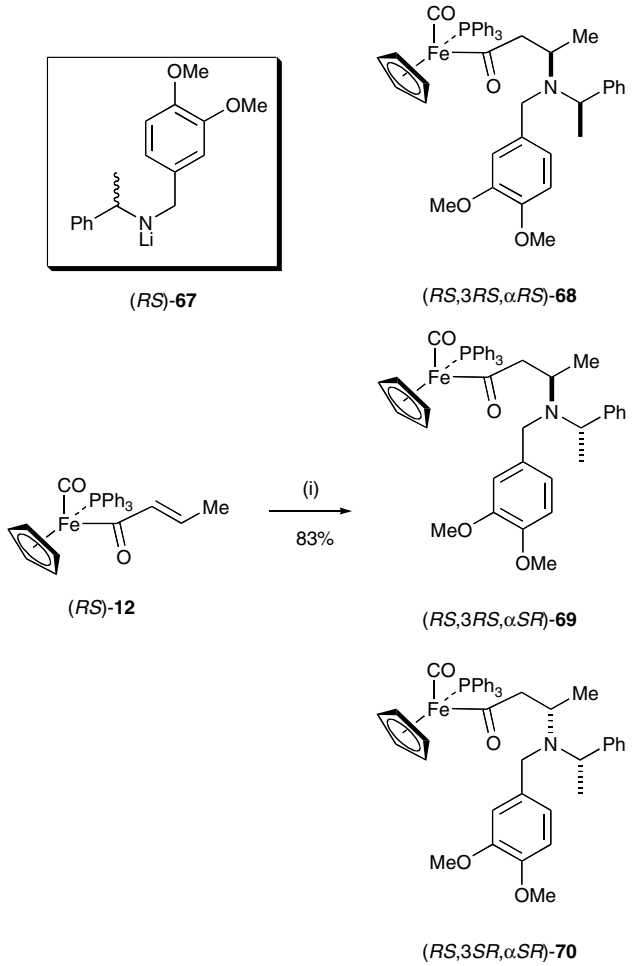
The configuration of each of the three diastereoisomers (*RS*,3*RS*,α*RS*)-**68**, (*RS*,3*RS*,α*SR*)-**69** and (*RS*,3*SR*,α*SR*)-**70** was unambiguously identified by separate reactions of homochiral lithium amide (*R*)-**67** with homochiral (*R*)- and (*S*)-**12**. Addition of lithium amide (*R*)-**67** to (*R*)-**12** afforded (*R*,3*R*,α*R*)-**68** as a single diastereoisomer in 92% yield (Scheme 14).

In contrast, addition of lithium amide (*R*)-**67** to (*S*)-**12** afforded an inseparable 50:50 mixture of (*S*,3*S*,α*R*)-**69** and (*S*,3*R*,α*R*)-**70** in 55% yield (Scheme 15).

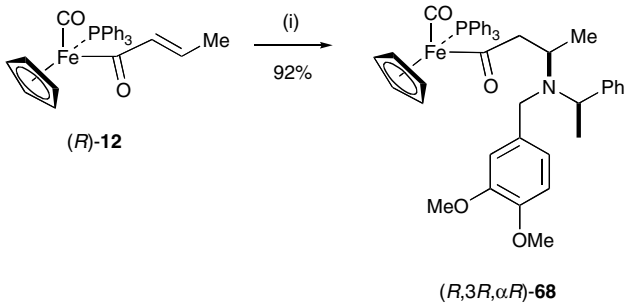
The loss of stereocontrol observed in the reaction of the (*S*)-iron auxiliary with lithium (*R*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamide suggests that the stereodirecting capabilities of the chiral iron auxiliary is effectively cancelled by the stereocontrol imposed by the chiral lithium amide upon conjugate addition. Furthermore, the 94:3:3 ratio of diastereoisomers resulting from the reaction of the (*RS*)-iron auxiliary with the (*RS*)-amide suggests a >15:1 rate difference between the addition of the matched pair {lithium amide (*R*)-**67** and (*R*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CHMe)] **12**} and the mismatched pair {lithium amide (*R*)-**67**



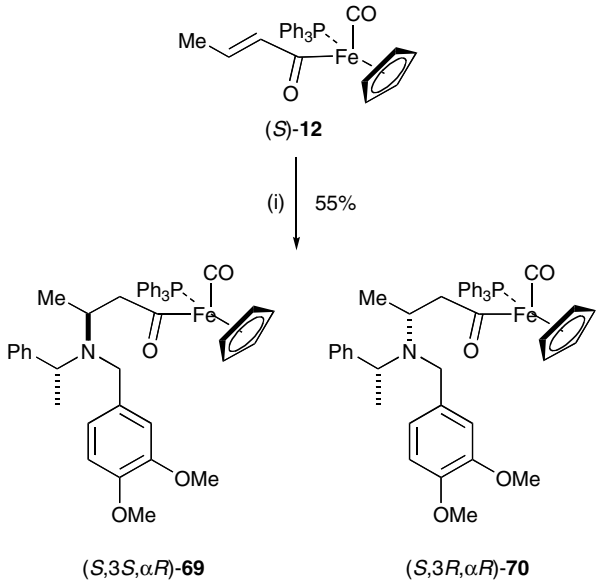
Scheme 12. Reagents and conditions: (i) Lithium (*RS*)-*N*-α-methylbenzylamide (2.5 eq), THF, −78 °C.



Scheme 13. Reagents and conditions: (i) Lithium (*RS*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamide (2.0 eq), THF, −78 °C.



Scheme 14. Reagents and conditions: (i) Lithium (*R*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamide (2.0 eq), THF, −78 °C.

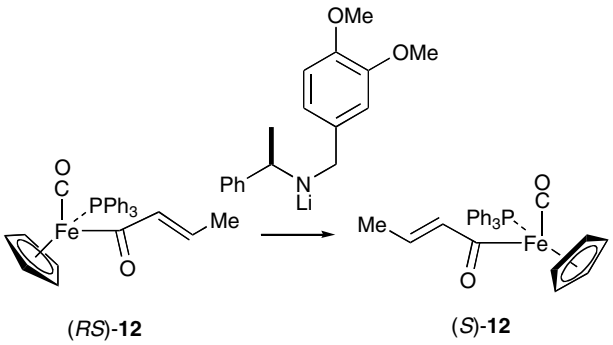


Scheme 15. Reagents and conditions: (i) Lithium (*R*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamide (2.0 eq), THF, −78 °C.

and (*S*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CHMe)] **12**}. This rate difference was used as the basis for a kinetic resolution of (*RS*)-**12** by homochiral lithium amide (*R*)-**67**. Thus, addition of various equivalents of lithium amide (*R*)-**67** to (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)-(COCH=CHMe)] **12** and measurement of the reaction conversion and specific rotation of the recovered iron complex showed that at conversions >70% the recovered (*S*)-iron complex **12** was essentially homochiral (>95% e.e.), consistent with a stereoselectivity factor, E for the resolution process of 15 (Scheme 16).

2.4. Probing the reaction stoicheiometry in the conjugate addition of chiral lithium amides to the chiral iron auxiliary

During these investigations, the stoicheiometry of the reaction between (*RS*)-lithium amide **67** and (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CHMe)] **12** was probed, with two equivalents of (*RS*)-lithium amide **67** required



Conversion (%)	SpecificRotation (c 0.15, benzene)	e.e (%)
4	+6.3	4
18	+33.5	19
34	+73.8	42
56	+145.0	83
70	+181.4	>95
80	+178.1	>95

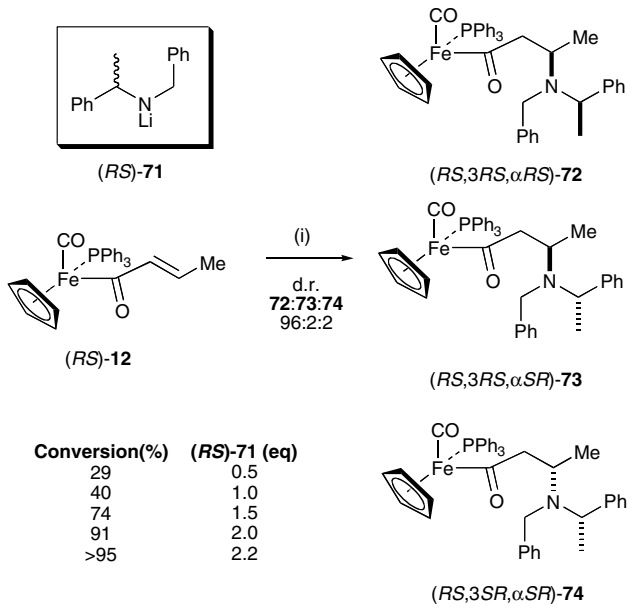
authentic (*S*)-**12** $[\alpha]_D^{23}$ +175.3 (c 0.15, benzene)

Scheme 16. Reagents and conditions: (i) Lithium (*R*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamide (2.0 eq), THF, −78 °C.

for the conjugate addition to the (*RS*)-iron complex to proceed to completion. For instance, with 0.5 equivalents of lithium (*RS*)-amide **67** the reaction proceeds to ~25% conversion [32]; with 1.0 equivalent the conversion is ~50%, while with 2.0 equivalents the conversion is >90%. To investigate further this observation, the stoicheiometry of the addition of the related lithium amide *N*-benzyl-*N*-α-methylbenzylamide **71** to the [(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CHMe)] iron complex was studied in detail. Conjugate addition of lithium (*RS*)-*N*-benzyl-*N*-α-methylbenzylamide to (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CHMe)] consistently gave a 96:2:2 diastereoisomeric mixture of (*RS*,3*RS*,-α*RS*)-**72**, (*RS*,3*RS*,α*SR*)-**73** and (*RS*,3*SR*,α*SR*)-**74** independent of the reaction conversion [33]. The reaction proceeded to 40% conversion with 1.0 equivalent of (*RS*)-lithium amide, and to >90% conversion with 2.0 equivalents of (*RS*)-lithium amide, indicating that the 2:1 lithium amide: acceptor stoicheiometry is observed in this reaction pairing (Scheme 17).

The 2:1 amide:acceptor stoicheiometry was also observed in the addition of lithium (*RS*)-**71** to homochiral (*R*)-iron crotonoyl **12**, giving an 87:7:6 mixture of (*R*,3*R*,α*R*)-**72**, (*R*,3*R*,α*S*)-**73** and (*R*,3*S*,α*S*)-**74** at 54% conversion with 1.0 equivalent of amide, and an 89:6:5 mixture of **72**:**73**:**74** at >90% conversion with 2.0 equivalents of amide (Scheme 18).

Reaction of the 'matched' homochiral pair of lithium (*R*)-amide **71** with (*R*)-**12** showed 1:1 stoicheiometry, furnishing (*R*,3*R*,α*R*)-**72** as a single diastereoisomer at 46% conversion with 0.5 equivalents of amide, and >95% conversion with 1.0 equivalent of amide. In the 'mismatched'



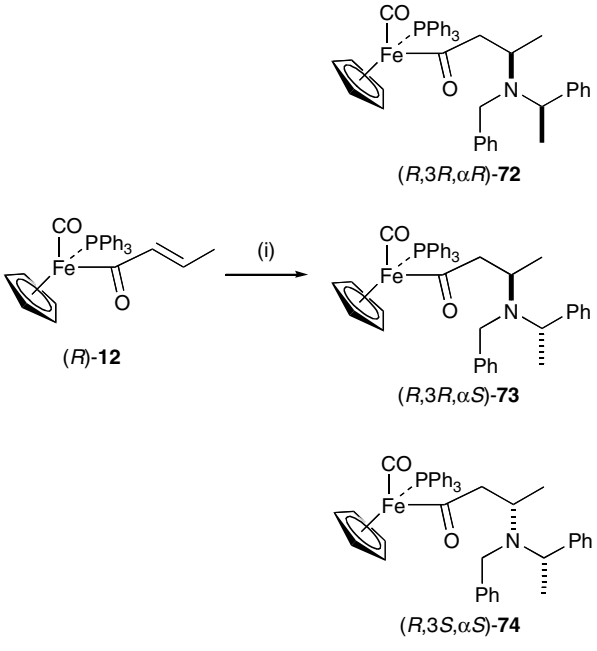
Conversion(%)	(*RS*)-71 (eq)
29	0.5
40	1.0
74	1.5
91	2.0
>95	2.2

Scheme 17. Reagents and conditions: (i) Lithium (*RS*)-*N*-benzyl-*N*-α-methylbenzylamide-**71**, THF, −78 °C.

case, addition of lithium (*S*)-amide **71** to iron complex (*R*)-**12** gave, upon addition of 1.0 equivalent of lithium (*S*)-amide **71** to (*R*)-**12**, 61% conversion to a 50:50 mixture of (*R*,3*R*,α*S*)-**73**:(*R*,3*S*,α*S*)-**74**, consistent with, as expected, the 'mismatched' reaction proceeding at a much slower rate than the 'matched' reaction. 1:1 stoicheiometry in this 'mismatched' manifold was assumed as the reaction had proceeded to >50% conversion with 1 equivalent of amide (Scheme 19).

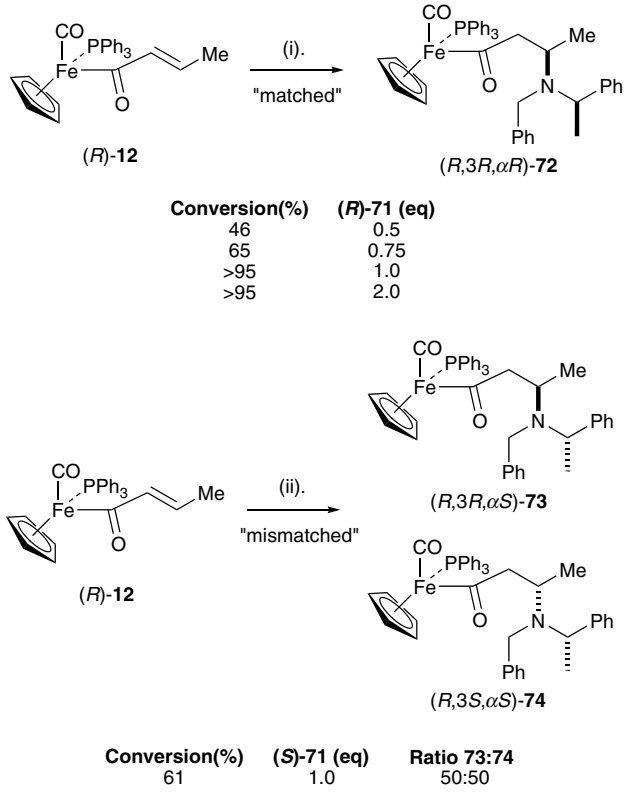
Furthermore, conjugate addition of homochiral (*R*)-lithium amide **71** to the (*RS*)-iron crotonyl complex **12** also showed 1:1 stoicheiometry, giving an 82:9:9 mixture of (*R*,3*R*,α*R*)-**72**, (*S*,3*S*,α*R*)-**73** and (*S*,3*R*,*SR*)-**74** at 48% conversion with 0.5 equivalents of amide, and a 55:25:20 mixture of **72:73:74** at >95% conversion with 1.0 equivalent of amide (Scheme 20).

It is therefore clear that the reaction of (*RS*)-lithium amide **71** with either (*RS*)- or homochiral iron acyl complex **12** shows 2:1 stoicheiometry, while the homochiral lithum amide **71** shows 1:1 stoicheiometry with either (*RS*)- or homochiral iron acyl complex **12**. The wide applicability of lithium amides within organic synthesis has ensured that both the solid phase and solution phase structures of lithium amides have been the subject of many investigations, with the aim of understanding the factors which affect both the reactivity and selectivity of these agents [34]. Studies of lithium amide complexes in a range of solvents have shown that a variety of aggregation states co-exist in solution [35], with the degree of aggregation dependent upon solvent, temperature



Conversion(%)	(*RS*)-71 (eq)	d.r. (72:73:74)
54	1.0	87:7:6
>90	2.0	89:6:5

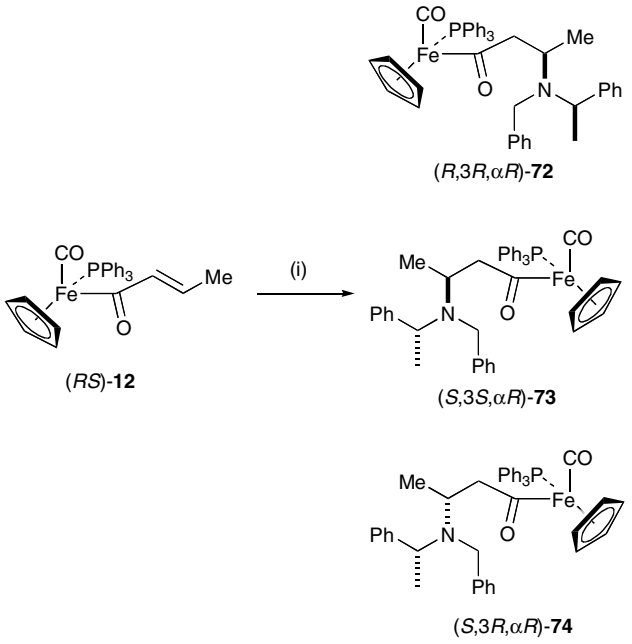
Scheme 18. Reagents and conditions: (i) Lithium (*RS*)-*N*-benzyl-*N*-α-methylbenzylamide **71**, THF, −78 °C.



Conversion(%)	(*R*)-71 (eq)
46	0.5
65	0.75
>95	1.0
>95	2.0

Conversion(%)	(*S*)-71 (eq)	Ratio 73:74
61	1.0	50:50

Scheme 19. Reagents and conditions: (i) Lithium (*R*)-*N*-benzyl-*N*-α-methylbenzylamide-**71**, THF, −78 °C; (ii) Lithium (*S*)-*N*-benzyl-*N*-α-methylbenzylamide-**71**, THF, −78 °C.



Conversion(%)	(*RS*)-71 (eq)	d.r. (72:73:74)
48	0.5	82:9:9
>95	1.0	50:25:25

Scheme 20. Reagents and conditions: (i) Lithium (*R*)-*N*-benzyl-*N*-α-methylbenzylamide-**71**, THF, −78 °C.

and concentration [36], although a lithium amide dimer is perhaps the most widely recognised aggregation state in the literature. While the pink/red solution colouration seen upon deprotonation of dibenzylamines has been attributed to charge transfer in the unsolvated monomer [37], the actual aggregation state of lithium *N*-benzyl-*N*-α-methylbenzylamide **71** in THF solution has, to the best of our knowledge, not yet been fully determined, although in the solid phase, two groups have independently published dimeric crystal structures of lithium *N*-benzyl-*N*-α-methylbenzylamide [38]. The rate of deprotonation of ketones by lithium amides have also been investigated, with the kinetic studies of Collum et al. [39] and Majewski et al. [40] indicating a fractional order with respect to LDA $\{k \propto [\mathrm{LDA}]^{0.5}\}$, consistent with a dimer–monomer pre-equilibrium and deprotonation with a disolvated monomer, while similar studies with LHMDS in the presence of NEt_3 implicate a dimer based mechanism [41]. Upon the assumption that in THF solution chiral lithium amides such as **67** and **71** react predominantly as dimeric complexes, conjugate addition reactions involving a single enantiomer of lithium amide can involve only homochiral [(*R*,*R*) or (*S*,*S*)] dimers, while in the racemic series both homochiral [(*R*,*R*) and (*S*,*S*)] and heterochiral [(*R*,*S*)] dimers can be formed. The differences in the reaction stoicheiometry for racemic and homochiral lithium amides upon addition to the iron crotonyl complex implies that heterochiral [(*R*,*S*)] lithium amide dimers play an essential role in the conjugate addition reaction of the racemic amide. Assuming that each dimeric lithium amide complex can potentially react with two α,β-unsaturated acceptors, addition to both reactive sites of a homochiral dimer upon the opposite faces of the complex will be allowed, while in the case of the heterochiral lithium amide dimer reacting with the extremely bulky iron acyl acceptors, the second addition is blocked by the first formed complexed iron acyl enolate, as shown schematically in Fig. 9. Using homochiral (*R*)-amide **71**, only homochiral [(*R*,*R*)] dimers are possible, which react, in the matched case, with the iron complex (*R*)-**12** with high stereoselectivity upon both reaction sites of the dimeric complex, resulting in 1:1 stoicheiometry, giving a single β-amino complex. Similarly, for addition of (*R*)-**71** to the (*RS*)-auxiliary **12**, conjugate addition from opposite faces of the homochiral [(*R*,*R*)] dimer is possible, resulting in 1:1 stoicheiometry and a loss of stereocontrol upon addition to the (*S*)-enantiomer of the chiral iron auxiliary. With conjugate additions using racemic (*RS*)-amide **71**, the observed 2:1 stoicheiometry in these reactions is consistent with the formation of a heterochiral (*R*,*S*)-lithium amide dimer with a *mono*-complexed iron acyl enolate that is unreactive to further conjugate addition. In such an iron enolate-lithium amide complex, the second conjugate addition is required by the configuration of the constituent amide components to proceed on the same face of the dimer-complex as the bound iron enolate, which will be precluded by the steric constraints of the reaction manifold, resulting in the observed 2:1 stoicheiometry upon addition to either the (*R*)- or the (*RS*)-auxiliary **12**.

Three distinct mechanistic portfolios may be considered that are compatible with the predominant formation of an (*R*,*S*) lithium amide dimer with a *mono*-complexed iron acyl enolate that is inert to further conjugate addition. One plausible explanation is that the lithium amides react as non-equilibrating dimers in solution, *a priori* homochiral dimers in the case of the homochiral lithium amide, but only heterochiral dimers for the racemic lithium amide. After one conjugate addition, the homochiral dimer-*mono*-enolate complex may undergo further addition, but the heterochiral dimer-*mono*-enolate complex is inert to further reaction. Alternatively, with the (*RS*)-lithium amide a mixture of rapidly equilibrating homochiral [(*R*,*R*) and (*S*,*S*)] and heterochiral (*R*,*S*) lithium amide dimers may be formed. If the rate of the first conjugate addition of the heterochiral lithium amide dimer is fast relative to that of the homochiral dimers, the selective formation of the required unreactive (*R*,*S*)-dimer-*mono*-enolate, and thus the 2:1 stoicheiometry, may be realized (Curtin–Hammett). Finally, fast *mono*-conjugate addition to a mixture of rapidly equilibrating homo- and heterochiral lithium amide dimers may occur to give a mixture

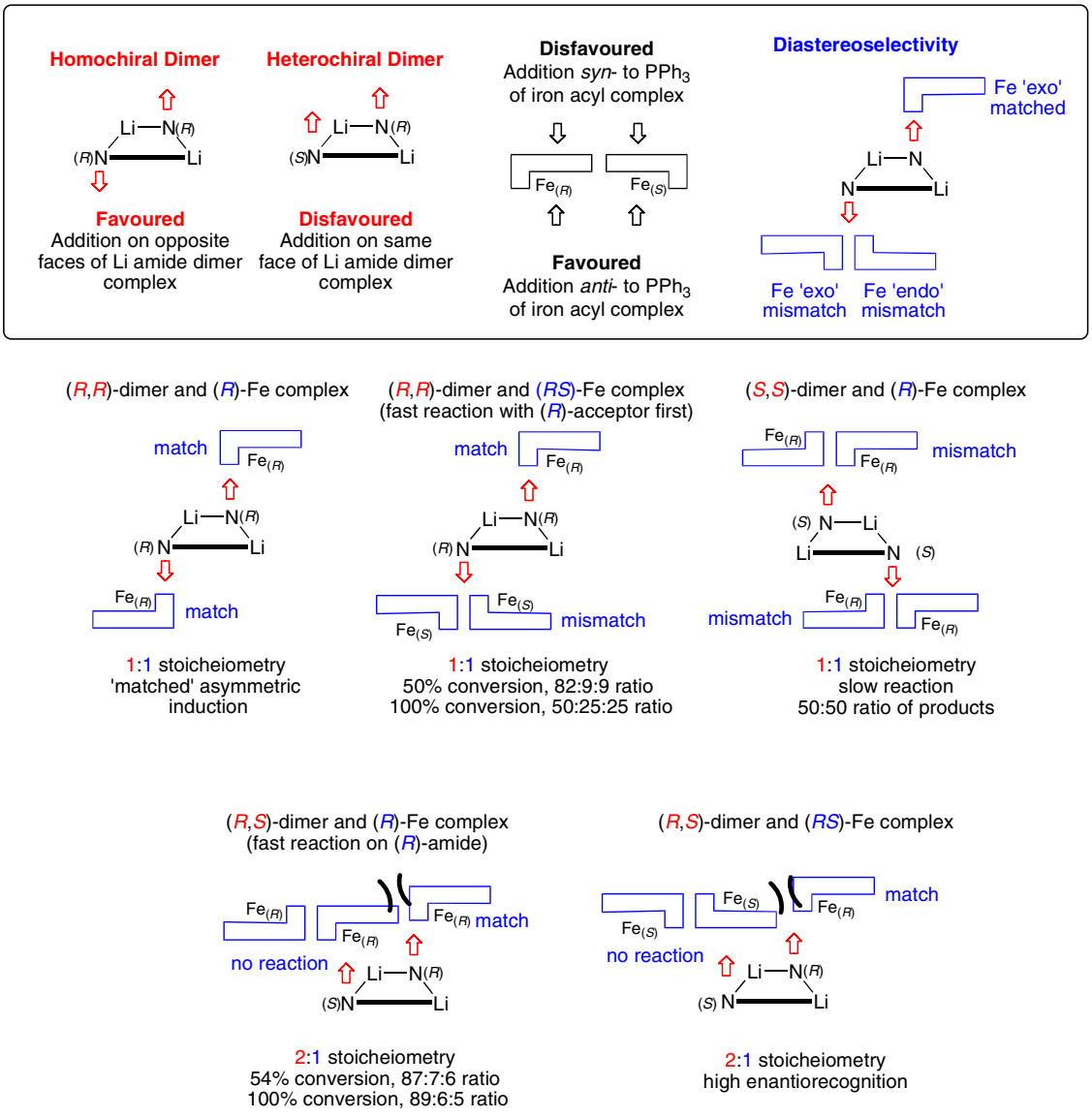


Fig. 9. Schematic representation of homo- and heterochiral lithium amides aggregates and conjugate addition to the iron crotonyl complex.

of iron acyl enolate-lithium amide dimer complexes. Assuming that the rate of the second conjugate addition to the dimer-*mono*-enolate complex is much slower than the first, rapid equilibration to form only the stable (*R*,*S*)-dimer-*mono*-enolate complex, which is inert to further conjugate addition, resulting in 2:1 stoicheiometry, may occur. With the data in hand it is not currently possible to distinguish between these possibilities.

In conclusion, conjugate addition of both primary and secondary achiral lithium amides to α,β-unsaturated iron acyl complexes proceed with high diastereoselectivity, with the addition of lithium dimethylamide to (*S*,*Z*)- and (*S*,*E*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COCH=CHPh)] used to determine unambiguously the absolute configuration of Winterstein's acid. In-situ elaboration of the enolates derived from the conjugate additions via alkylation or aldol reaction facilitates the stereoselective synthesis of both *cis*- and *trans*-β-lactams via addition to the corresponding (*E*)- or (*Z*)-iron acyl complex and oxidative decomplexation. This methodology has been applied to the formal synthesis of (±)-olivanic acid and (±)-thienamycin. Upon conjugate addition of chiral lithium amides to α,β-unsaturated iron acyl complexes, lithium α-methylbenzylamide shows low levels of enantiorecognition whereas homochiral secondary lithium amides derived from α-methylbenzylamine show significant enantiodiscrimination. Conjugate additions of (*RS*)-lithium amides **67** and **71** with either the (*RS*)- or homochiral iron crotonyl complex **12** show 2:1 stoicheiometry, while homochiral lithum amides **67** and **71** show 1:1 stoicheiometry. This stoicheiometry may be explained only by the formation of a heterochiral lithium

dimer-*mono*-enolate complex, which is inert to further reaction. Further investigations from this laboratory regarding the application of homochiral lithium amides in enantiorecognition protocols and further mechanistic studies upon the aggregation state of lithium amides in these conjugate addition protocols will be reported in due course.

3. Experimental

3.1. General experimental

All reactions involving organometallic or other moisture sensitive reagents were performed under an atmosphere of nitrogen and in deoxygenated solvents via standard vacuum line techniques. All glassware was flame-dried and allowed to cool under vacuum. THF was distilled under an atmosphere of dry nitrogen from sodium benzophenone ketyl. *n*-Butyllithium was used as a solution in hexanes at the molarity stated. All other solvents and reagents were used as supplied (Analytical or HPLC grade), without prior purification. Reactions were dried with $MgSO_4$. Flash chromatography was performed on Kieselgel 60 silica or alumina (grade as stated). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AMX 500 (^{1}H: 500 MHz and ^{13}C: 125.3 MHz), Bruker W-H 300 (^{1}H: 300 MHz), Bruker AM-250 (^{31}P 100 MHz), Varian 200 (^{1}H: 200 MHz) and Bruker AC200 (^{1}H: 200 MHz and 13C 50 MHz) spectrometers in the deuterated solvent stated. All chemical shifts (δ) are quoted in ppm and coupling constants (J) in Hz. Residual protio signals from the solvents were used as an internal reference. ^{13}C multiplicities were assigned using a DEPT sequence. In all cases, the reaction diastereoselectivity was assessed by peak integration of the ^{1}H NMR spectrum of the crude reaction mixture. Infrared spectra were recorded on a Perkin–Elmer 1750 IR Fourier Transform spectrophotometer, with only the characteristic peaks quoted. Low resolution mass spectra (*m*/*z*) were recorded on a VG MassLab ZAB 1F using field desorption techniques, or VG MassLab 20–250 instrument. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter with a water-jacketed 10 cm cell and specific rotations given in units of 10^{-1} deg cm^2 g^{-1}. Concentrations are quoted in g/100 ml. Melting points were recorded on a Leica VMTG Galen III apparatus and are uncorrected. Elemental analyses were performed by the microanalysis service of the Dyson Perrins Laboratory, Oxford.

3.2. Representative procedure 1

n-Butyllithium (2.5 eq) was added dropwise to a stirred solution of the amine (3.0 eq) in anhydrous THF at −78 °C under nitrogen. After 30 min, a solution of the iron crotonyl complex **12** (1.0 eq) in anhydrous THF was added dropwise via cannula and stirred at −78 °C for the specified time prior to the addition of methanol and warmed to RT. After concentration in vacuo, the residue was extracted with DCM, filtered through alumina and concentrated in vacuo before purification by column chromatography.

3.3. Preparation of (*S*,3*R*)-(η^5-C_5H_5)Fe(CO)(PPh_3)-$COCH_2CH(Ph)NMe_2$ (**19**)

n-BuLi (2.5 M, 1.3 ml, 3.3 mmol) was added dropwise to a stirred solution of the dimethylamine (0.55 ml, 8.3 mmol) in anhydrous THF (5 ml) at −20 °C under nitrogen. After 1 h, the solution was cooled to −78 °C and added dropwise to a solution of the iron complex (*S*,*E*)-**17** (0.9 g, 1.7 mmol) in anhydrous THF (60 ml) at −100 °C. After 1 h methanol was added and the solution allowed to warm to rt. Concentration in vacuo, dissolution of the resultant oil in DCM and filtration through alumina (grade I) and further concentration in vacuo gave, after chromatographic purification (DCM:EtOAc:MeOH 60:39:1) **19** (808 mg, 81%, 94% d.e.); $C_{35}H_{34}NO_2FeP$ requires C, 71.6; H, 5.8; N, 2.4%; Found C, 71.5; H, 5.9; N, 2.3%; $[\alpha]_{546}^{20}$ +129.2 (c 0.05, benzene); $\nu_{max}(CH_2Cl_2)$ 1899 (C≡O), 1611 (C=O); δ_H (300 MHz, $CDCl_3$) 2.08 (6H, s, NMe_2), 2.67 (1H, dd, $J_{2A,2B}$16.1, $J_{2A,3}$6.2, C(2)H_A), 3.41 (1H, dd, $J_{2B,2A}$16.1, $J_{2B,3}$6.2, C(2)H_B), 3.74 (1H, t, *J*6.2, C(3)*H*), 4.37 (5H, d, J_{PH}1.0, C_5H_5), 7.08–7.52 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 42.3, 64.6, 67.9, 85.4, 126.4, 127.7, 127.9, 128.7, 129.6, 133.3, 136.3, 140.6, 220.4; δ_P (100 MHz, $CDCl_3$) 71.9; *m*/*z* (FAB) 587 (M^+).

3.4. Preparation of (*S*,3*S*)-(η^5-C_5H_5)Fe(CO)(PPh_3)-$COCH_2CH(Ph)NMe_2$ (**20**)

n-BuLi (2.5 M, 1.3 ml, 3.3 mmol) was added dropwise to a stirred solution of the dimethylamine (0.55 ml, 8.3 mmol) in anhydrous THF (5 ml) at −20 °C under nitrogen. After 1 h, the solution was cooled to −78 °C and added dropwise to a solution of the iron complex (*S*,*Z*)-**18** (0.9 g, 1.7 mmol) in anhydrous THF (60 ml) at −100 °C. After 1 h methanol was added and the solution allowed to warm to rt. Concentration in vacuo, dissolution of the resultant oil in DCM and filtration through alumina (grade I) and further concentration in vacuo gave, after chromatographic purification (DCM:EtOAc:MeOH 60:39:1) **20** (86%, >97% d.e.). Subsequent recrystallisation (DCM:hexane) gave **20** as a single diastereoisomer; (878 mg, 82%); $C_{35}H_{34}NO_2FeP$ requires C, 71.6; H, 5.8; N, 2.4%; Found C, 71.3; H, 5.8; N, 2.1%; $[\alpha]_{546}^{20}$ +358.4 (c 0.05, benzene); ν_{max} (CH_2Cl_2) 1900 (C≡O), 1622 (C=O); δ_H (300 MHz, $CDCl_3$) 1.95 (6H, s, NMe_2), 2.53 (1H, dd, $J_{2A,2B}$15.4, $J_{2A,3}$4.0, C(2)H_A), 3.41 (1H, dd, $J_{2B,2A}$15.4, $J_{2B,3}$4.0, C(2)H_B),

3.74 (1H, t, *J*4.0, C(3)*H*), 4.04 (5H, d, J_{PH}1.0, C_5H_5), 7.18–7.59 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 42.5, 66.0, 67.6, 85.1, 126.5, 127.6, 127.7, 128.6, 129.4, 133.1, 136.6, 141.7, 220.5; δ_P (100 MHz, $CDCl_3$) 71.7; *m*/*z* (FAB) 587 (M^+).

3.5. Preparation of (*S*)-ethyl 3-*N*,*N*-dimethylamino-3-phenyl-propanoate (**21**)

Iron complex **20** (0.8 g, 1.36 mmol), NBS (1.3 eq, 1.77 mmol) and 2.5 M HCl (2.5 eq) were combined at −78 °C in THF (100 ml) and allowed to warm to rt. Concentration in vacuo gave a green oil, which was extracted into water (50 ml). Filtration gave a green solid containing (η^5-C_5H_5)Fe(CO)(PPh_3)Br, while concentration of the water filtrate gave a yellow oil which was purified by Dowex ion exchange chromatography. After concentration in vacuo the intermediate was dissolved in EtOH saturated with HCl and heated at reflux for 8 h before concentration in vacuo. The residue was treated with 2 M NEt_3 in EtOH until basic, with subsequent chromatographic purification giving the free ester **21** (247 mg, 82%) as a colourless oil; $[\alpha]_{436}^{20}$ +31.5 (c 1.6, MeOH); δ_H (300 MHz, $CDCl_3$) 1.11 (3H, t, *J*7.2, OCH_2CH_3), 2.18 (6H, s, NMe_2), 2.69 (1H, dd, $J_{2A,2B}$14.7, $J_{2A,3}$6.9, C(2)H_A), 2.95 (1H, dd, $J_{2B,2A}$14.7, $J_{2B,3}$8.2, C(2)H_B), 3.86 (1H, app t, *J*7.2, C(3)*H*), 4.01 (2H, q, *J*7.2, OCH_2CH_3), 7.23–7.34 (5H, m, *Ph*); treatment with HCl (aq) and concentration in vacuo gave the HCl salt, which was crystallised from $CHCl_3$:EtOAc, giving **21**·HCl as white needles; m.p. 176–178 °C; $C_{13}H_{20}ClNO_2$ requires C, 60.6; H, 7.8; N, 5.4%; Found C, 60.3; H, 8.0; N, 5.4%; $[\alpha]_{436}^{20}$ +23.1 (c 0.5, $CHCl_3$); ν_{max} (CH_2Cl_2) 3380 (NH), 1735 (C=O); δ_H (300 MHz, $CDCl_3$) 1.12 (3H, t, *J*7.2, OCH_2CH_3), 2.69 (6H, br s, NMe_2), 3.25 (1H, dd, $J_{2A,2B}$16.6, $J_{2A,3}$4.7, C(2)H_A), 3.69 (1H, dd, $J_{2B,2A}$16.6, $J_{2B,3}$9.3, C(2)H_B), 4.04 (2H, m, OCH_2CH_3), 4.54 (1H, m, C(3)*H*), 7.47–7.59 (5H, m, *Ph*); *m*/*z* (DCI-NH_3) 222 (M^+).

3.6. Preparation of (*R*)-ethyl 3-*N*,*N*-dimethylamino-3-phenyl-propanoate (**21**)

Iron complex **21** (0.8 g, 1.36 mmol), NBS (1.3 eq, 1.77 mmol) and 2.5 M HCl (2.5 eq) were combined at −78 °C in THF (100 ml) and allowed to warm to rt. Concentration in vacuo gave a green oil, which was extracted into water (50 ml). Filtration gave a green solid containing (η^5-C_5H_5)Fe(CO)(PPh_3)Br, while concentration of the water filtrate gave a yellow oil which was purified by Dowex ion exchange chromatography. After concentration in vacuo the intermediate was dissolved in EtOH saturated with HCl and heated at reflux for 8 h before concentration in vacuo. The residue was treated with 2 M NEt_3 in EtOH until basic, with subsequent chromatographic purification giving the free ester **21** (199 mg, 66%) as a colourless oil; $[\alpha]_{436}^{20}$ −31.1 (c 1.6, MeOH); treatment with HCl (aq) and concentration in vacuo gave the HCl salt, which was crystallised from hexane:EtOH, giving **21**·HCl as white needles; $C_{13}H_{20}ClNO_2$ requires C, 60.6; H, 7.8; N, 5.4%; Found C, 60.3; H, 8.0; N, 5.3%; $[\alpha]_{436}$ [20] −22.7 (c 0.5, $CHCl_3$).

3.7. Preparation of (*S*,2*R*,3*S*)-(η^5-C_5H_5)Fe(CO)(PPh_3)COCH(Me)CH(Ph)NMe_2 (**22**)

n-BuLi (2.5 M, 1.3 ml, 3.3 mmol) was added dropwise to a stirred solution of the dimethylamine (0.55 ml, 8.3 mmol) in anhydrous THF (5 ml) at −20 °C under nitrogen. After 1 h, the solution was cooled to −78 °C and added dropwise to a solution of the iron complex (*S*,*Z*)-**18** (0.9 g, 1.7 mmol) in anhydrous THF (60 ml) at −100 °C. After 1 h MeI (5 eq) was added and the solution allowed to warm to rt. Concentration in vacuo, dissolution of the resultant oil in DCM and filtration through alumina (grade I) further concentration in vacuo gave, after chromatographic purification (DCM:EtOAc:MeOH 60:39:1) **22** 664 mg, (65%, >97% d.e.). Subsequent recrystallisation (DCM:hexane) gave **22** as a single diastereoisomer; $C_{35}H_{34}NO_2FeP$ requires C, 72.1; H, 6.0; N, 2.3%; Found C, 72.1; H, 6.1; N, 2.1%; $[\alpha]_{546}^{20}$ +225.2 (c 0.05, benzene); ν_{max} (CH_2Cl_2) 1902 (C≡O), 1610 (C=O); δ_H (300 MHz, $CDCl_3$) 0.73 (3H, d, *J*4.0, C(2)*Me*), 2.05 (6H, s, NMe_2), 3.41 (1H, d, *J*7.6, C(3)*H*), 3.55 (1H, m, C(2)*H*), 4.39 (5H, d, J_{PH}1.0, C_5H_5), 6.94–7.71 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 14.3, 42.7, 65.6, 71.3, 84.9, 126.3, 127.1, 127.8, 129.5, 130.0, 133.7, 137.1, 137.4, 221.5; δ_P (100 MHz, $CDCl_3$) 72.0; *m*/*z* (FAB) 601 (M^+).

3.8. Preparation of ethyl (2*R*,3*S*)-2-methyl-3-*N*,*N*-dimethylamino-3-phenyl-propanoate (**23**)

Iron complex **22** (0.8 g, 1.33 mmol), NBS (1.3 eq, 1.73 mmol) and 2.5 M HCl (2.5 eq) were combined at −78 °C in THF (100 ml) and allowed to warm to rt. Concentration in vacuo gave a green oil, which was extracted into water (50 ml). Filtration gave a green solid containing (η^5-C_5H_5)Fe(CO)(PPh_3)Br, while concentration of the water filtrate gave a yellow oil which was purified by Dowex ion exchange chromatography. After concentration in vacuo the intermediate was dissolved in EtOH saturated with HCl and heated at reflux for 8 h before concentration in vacuo. The residue was treated with 2 M NEt_3 in EtOH until basic, with subsequent chromatographic purification giving the free ester **23** (258 mg, 82%) as a colourless oil; δ_H (300 MHz, $CDCl_3$) 0.92 (3H, d, *J*7.0, C(2)*Me*), 1.27 (3H, t, *J*7.1, OCH_2CH_3), 2.09 (6H, s, NMe_2), 3.16 (1H, m, C(2)*H*), 3.67 (1H, d, *J*11.0, C(3)*H*), 4.19 (2H, q, *J*7.1, OCH_2CH_3), 7.13–7.78 (5H, m, *Ph*); treatment with HCl (aq) and

concentration in vacuo gave the HCl salt, which was crystallised from EtOH:hexane, giving **23**·HCl as white needles; m.p. 166–168 °C; $C_{14}H_{22}ClNO_2$ requires C, 61.9; H, 8.1; N, 5.2%; Found C, 61.7; H, 8.3; N, 5.4%; $[\alpha]_{436}^{20}$ +135.0 (c 0.5, $CHCl_3$); ν_{max} (CH_2Cl_2) 3320 (NH), 1732 (C=O); δ_H (300 MHz, $CDCl_3$) 1.03 (3H, d, *J*7.2, C(2)*Me*), 1.29 (3H, t, *J*7.1, OCH_2CH_3), 2.73 (6H, s, NMe_2), 3.49 (1H, m, C(2)*H*), 4.25 (2H, q, *J*7.1, OCH_2CH_3), 4.45 (1H, br d, C(3)*H*), 7.44–7.63 (5H, m, *Ph*); *m*/*z* (DCI-NH_3) 236 (M^+).

3.9. Preparation of (RS,RS,RS,RS)-(η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH[CH(OH)CH$_3$]CH{N[CH$_2$Ph(3,4-OMe)$_2$]$_2$}CH$_3$ (24)

n-BuLi (1.50 ml, 2.40 mmol) was added to a solution of bis-(3,4-dimethoxybenzyl)amine (0.860 g, 2.70 mmol) in THF (10 ml) at 0 °C and stirred for 1 h before cooling to −78 °C. A solution of **12** (0.480 g, 1.00 mmol) in THF (5 ml) was added via cannula, and after 14 h a solution of acetaldehyde (0.500 ml, 9.0 mmol) in THF (5 ml) was added via cannula and stirred for 3 h at −78 °C before warming to rt. After concentration in vacuo, the resultant oil was extracted into $CHCl_3$ (3×20 ml) and filtered through alumina (grade V). Concentration in vacuo and chromatographic purification of the residue on alumina (grade I) [EtOAc/CH_2Cl_2 (1:9)] gave **24**:**25** as a mixture of diastereoisomers (89:11; 0.490 g, 78%). Crystallisation (Et_2O:hexane) gave **24** as a single diastereoisomer as orange plates; Found: C, 68.55; H, 6.05; N, 2.0%; $C_{48}H_{52}FeNO_7P$ requires C, 68.5; H, 6.3; N, 2.1%; ν_{max} (CH_2Cl_2) 1900 (C≡O), 1602 (C=O); δ_H (300 MHz, $CDCl_3$) −0.08 (3H, d, *J*6.6, $CHCH_3$), 0.44 (3H, d, *J*6.5, $CH(OH)CH_3$), 2.83 (1H, br s, C(3)*H*), 3.15 (1H, m, C(2)*H*), 3.50 (4H, m, NCH_2Ph), 3.84 (12H, s, 4×O*Me*), 4.32 (5H, d, J_{PH}1.1, C_5H_5), 4.92 (1H, m, $CH(OH)CH_3$), 6.96–6.73 (6H, m, *Ar*), 7.52–7.18 (15H, m, PPh_3); δ_C (50 MHz, $CDCl_3$) 7.5, 17.9, 52.0, 53.0, 55.8, 68.0, 76.8, 86.2, 110.8, 113.2, 122.3, 128.1, 129.7, 131.0, 133.3, 136.6, 148.3, 149.0, 221.0; *m*/*z* (FAB+) 842 (MH^+, 100%); δ_P (100 MHz) 69.3.

3.10. Preparation of (RS,RS,RS,RS) and (RS,RS,RS,SR)-(η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH[CH(OH)-CH$_3$]CH{NHCH$_2$Ph}CH$_3$ (26 and 27)

n-BuLi (1.60 ml, 2.40 mmol) was added to a solution of (*N*-trimethylsilyl)benzylamine (0.520 g, 2.90 mmol) in THF (5 ml) at 0 °C and stirred for 1 h before cooling to −78 °C. A cooled solution of **12** (0.46 g, 0.96 mmol) in THF (5 ml) at −95 °C was added via cannula, and after 3 h a solution of acetaldehyde (0.500 ml, 9.0 mmol) in THF (5 ml) was added via cannula and stirred for 3 h at −95 °C before the addition of methanol (1 ml) and the reaction allowed to warm to rt. After concentration in vacuo, the resultant oil was extracted into $CHCl_3$ (3×20 ml) and filtered through alumina (grade V). Concentration in vacuo and chromatographic purification of the residue on alumina (grade I) [EtOAc/CH_2Cl_2 (1:9)] gave **26**:**27** as a mixture of diastereoisomers (87:13; 0.490 g, 81%). Crystallisation (Et_2O:DCM) gave a single diastereoisomer **26** as orange plates; Found: C, 70.3; H, 5.9; N, 2.2%; $C_{37}H_{38}FeNO_3P$ requires C, 70.5; H, 6.1; N, 2.2%); ν_{max} (CH_2Cl_2) 1914 (C≡O), 1593 (C=O); δ_H (300 MHz, $CDCl_3$) 0.12 (3H, d, *J*6.2, $CH(OH)CH_3$), 1.18 (3H, d, *J*6.5, $CHCH_3$), 2.65 (1H, m, C(3)*H*), 3.15 (1H, dd, *J*8.7, *J*2.4, C(2)*H*), 3.44 (1H, AB, *J*12.6, NCH_AHPh), 3.67 (1H, AB, *J*12.6, NCH_BHPh), 4.40 (5H, d, J_{PH}1.3, C_5H_5), 4.85 (1H, m, $CH(OH)CH_3$), 6.85 (1H, br s, N*H*), 7.10–7.69 (15H, m, PPh_3); δ_C (50 MHz, $CDCl_3$) 17.6, 19.9, 51.0, 51.9, 67.5, 81.2, 86.4, 127.0, 128.2, 129.8, 133.3, 136.5, 139.6, 221.1, 279.9; *m*/*z* (FAB+) 632 (MH^+, 40%); δ_P (100 MHz) 72.9.

Selected data for **27**; δ_H (300 MHz, $CDCl_3$) 0.78 (3H, d, *J*6.5, $CH(OH)CH_3$), 1.50 (3H, d, *J*6.5, $CHCH_3$), 4.45 (5H, d, J_{PH}1.3, C_5H_5).

3.11. Preparation of (3RS,4RS,1′RS)-1-benzyl-3-(1′-hydroxyethyl)-4-methylazetidin-2-one (28)

To a solution of 2**6** (0.300 g, 0.47 mmol) in DCM (5 ml) at −78 °C was added a solution of bromine (0.050 ml, 1.0 mmol) in DCM (5 ml) via cannula. The resultant solution was stirred for 2 h at −78 °C before NEt_3 (0.1 ml) was added. After 1 h at −78 °C the reaction was allowed to warm to rt and concentrated in vacuo. The residue was triturated with Et_2O, and the filtrate concentrated in vacuo to give an oil which was purified by column chromatography on silica gel (EtOAc) to give **28** as an oil (0.072 g, 70%); ν_{max} (film) 1737s (C=O); δ_H (300 MHz, $CDCl_3$) 1.21 (3H, d, *J*6.5, C(4)HCH_3), 1.27 (3H, d, *J*6.2, $CH(OH)CH_3$), 2.07 (1H, br s, O*H*), 3.08 (1H, dd, *J*7.5, *J*5.3, C(3)*H*), 3.67 (1H, m, C(4)H), 4.10 (1H, AB, J_{AB}15.3, NCH_AHPh), 4.12 (1H, m, C(1′)*H*), 4.61 (1H, AB, J_{AB}15.3, CH_BHPh), 7.36–7.23 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 13.6, 22.4, 43.9, 50.3, 58.5, 64.7, 127.7, 128.1, 128.8, 135.8, 168.7; 168.7 (CO), *m*/*z* (CI, NH_3) 220 (MH^+, 100%).

3.12. Preparation of (Z,RS)-1-benzyl-3-ethylidene-4-methylazetidin-2-one (29)

Methanesulphonyl chloride (0.024 g, 0.18 mmol) was added dropwise to a solution of **28** (0.040 g, 0.18 mmol) and NEt_3 (0.025 ml, 0.18 mmol) in DCM (1 ml) at 0 °C. The resulting solution was stirred for 30 min, then washed with water, 1 M pH 3 phosphate buffer, sodium hydrogen carbonate solution, brine and dried. Following evaporation, the residue was dissolved in methanol (5 ml), sodium hydrogen carbonate (0.090 g, 1.0 mmol) added, and the solution heated at reflux for 30 min, cooled, filtered and evaporated to yield **29** as an oil

(0.024 g, 65%); δ_H (300 MHz, $CDCl_3$) 1.18 (3H, d, *J*6.1, C(4)HCH_3), 2.01 (3H, d, *J*7.2, C=CHCH_3), 3.88 (1H, q, *J*6.1, C(4)*H*), 4.18 (1H, AB, J_{AB}15.3, NCH_AHPh), 4.68 (1H, AB, J_{AB}15.3, CH_BHPh), 5.54 (1H, q, *J*7.2, C=CHCH_3), 7.35–7.25 (5H, m, *Ph*); *m*/*z* (CI, NH_3) 202 (MH^+, 100%).

3.13. Preparation of (RS,SR) and (RS,RS)-(η^5-C_5H_5)Fe(CO)(PPh_3)COCH(SePh)CH_3 (**32** and **33**)

(i) To a solution of **2** (0.525 g, 1.12 mmol) in THF (10 ml) at −78 °C was added *n*-BuLi (1.57 M, 0.800 ml, 1.26 mmol). After 2 h a solution of diphenyl diselenide (0.405 g, 1.30 mmol) in THF (10 ml) was added via cannula. After 6 h at −78 °C the reaction was quenched by addition of methanol (1 ml), warmed to rt and concentrated in vacuo. The residue was extracted using DCM (2×20 ml) and filtered through alumina (grade V), and the filtrate evaporated to an oil which was purified by column chromatography on alumina (grade I) yielding starting material **2** (0.140 g, 27%) and an inseparable 66:34 mixture of diastereoisomers **32** and **33** {(0.230 g, 33%), 45% based on recovered starting material}; **32** δ_H (300 MHz, $CDCl_3$) 0.73 (3H, d, *J*6.8, C(3)H_3), 4.29 (1H, q, *J*6.8, C(2)*H*), 4.55 (5H, d, J_{PH}1.3, C_5H_5), 7.67–7.22 (20H, m, *Ph*), **33**; δ_H (300 MHz, $CDCl_3$) 1.60 (3H, d, *J*6.8, C(3)H_3), 4.20 (1H, q, *J*7.9, C(2)*H*), 4.52 (5H, d, J_{PH}1.3, C_5H_5), 7.68–7.18 (20H, m, *Ph*).

(ii) To a solution of **34** (0.610 g, 1.00 mmol) in THF (20 ml) at −78 °C was added *n*-BuLi (1.6 M, 0.750 ml, 1.20 mmol), before the addition of MeI (0.100 ml, 1.52 mmol) via syringe after 1 h. The reaction mixture was allowed to warm to rt over 4 h and the solvent removed in vacuo. The resulting oil was extracted with DCM (2×20 ml) and filtered through alumina (grade V). Concentration in vacuo and purification by column chromatography on silica gel [Et_2O/40–60 (1:4)] afforded an 9:91 mixture of **32**:**33** (0.570 g, 91%).

3.14. Preparation of (RS)-(η^5-C_5H_5)Fe(CO)(PPh_3)-$COCH_2SePh$ (**34**)

To acetyl complex **1** (1.00 g, 2.20 mmol) in THF (30 ml) at −78 °C was added *n*-BuLi (1.6 M, 1.50 ml, 2.40 mmol), before the addition of a solution of diphenyl diselenide (0.825 g, 2.60 mmol) in THF (10 ml) was added via cannula after 2 h. The solution was stirred for 1 h, methanol (1 ml) added and the reaction mixture warmed to rt before being concentrated in vacuo. Extraction of the resulting oil using DCM (3×30 ml), filtration through alumina (grade V) and further evaporation gave the crude product, which was purified by column chromatography on silica gel [Et_2O/40–60 (1:4)] to give the selenide. Crystallisation from DCM/hexane yielded **34** as red blocks (1.00 g, 75%); Found: C, 63.2; H, 4.6%; $C_{32}H_{27}FeO_2PSe$ requires C, 63.1; H, 4.5%; ν_{max} (CH_2Cl_2) 1920 (C≡O), 1593 (C=O); δ_H (300 MHz, CD_2Cl_2) 3.78 (1H, AB, J_{AB}14.4, CH_AHSePh), 4.30 (1H, AB, J_{AB}14.4, CH_BHSePh), 4.45 (5H, d, J_{PH}1.1, C_5H_5), 7.55–7.23 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 55.8, 85.5, 126.3, 128.4, 128.9, 129.7, 132.2, 132.3, 133.4, 136.0, 220.5, 270.0; *m*/*z* (FAB+) 611 (MH^+, 25%), 383 (100%); δ_P 76.9 (PPh_3).

3.15. Preparation of (RS)-(η^5-C_5H_5)Fe(CO)(PPh_3)-$COCH{=}CH_2$ (**35**)

To a solution of **32**:**33** (9:91; 0.570 g, 0.91 mmol) in DCM (20 ml) at −78 °C was added a solution of 55% *m*-chloroperbenzoic acid (0.290 g, 0.91 mmol) in DCM (10 ml) via cannula. After 1 h, diisopropylamine (0.510 ml, 3.60 mmol) at was added using a syringe and the reaction mixture allowed to warm to rt over 4 h, before being filtered through alumina (grade V) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel [Et_2O/40–60 (1:2)] and crystallised from Et_2O to give **35** as yellow needles (0.320 g, 75%) with identical spectroscopic properties to those reported previously [23].

3.16. Preparation of (RS,SR)- and (RS,RS)-(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH(SePh)CH_2CH{=}CH_2$ (**36** and **37**)

To a solution of **34** (0.500 g, 0.82 mmol) in THF (10 ml) at −78 °C was added *n*-BuLi (1.6 M, 0.62 ml, 0.96 mmol), before the addition of allyl iodide (0.160 ml, 1.60 mmol) after 2 h. The reaction mixture was allowed to warm to rt over 16 h, before concentration in vacuo and the residual oil extracted with DCM (2×20 ml). After filtration of this solution through alumina (grade V) and removal of the solvent, the crude products were purified by column chromatography [Et_2O/40–60 (1:4)] to give the title compounds as an 86:14 mixture of diastereoisomers **36**:**37**. Recrystallisation of the mixture from DCM/hexane yielded **36** as orange needles (0.400 g, 72%); Found: C, 64.4; H, 4.7%; $C_{35}H_{31}FeO_2PSe$ requires C, 64.7; H, 4.8%; ν_{max} (CH_2Cl_2) 1919 (C≡O), 1582 (C=O); δ_H (300 MHz, $CDCl_3$) 2.48 (1H, m, CH_AHCH=CH_2); 2.89 (1H, m, CH_BHCH=CH_2), 4.23 (1H, t, *J*5.4, C(2)*H*), 4.46 (5H, d, J_{PH}1.1, C_5H_5), 5.06–5.00 (2H, m, CH=CH_2), 5.96 (1H, m, C*H*=CH_2), 7.12–7.58 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 35.0, 71.7, 85.7, 116.0, 126.6, 128.2, 129.0, 129.9, 130.7, 134.5, 136.0, 136.5, 220.6, 273.2; *m*/*z* (FAB+) 651 (MH^+, 10%), 383 (100%); δ_P 74.2 (PPh_3).

3.17. Preparation of (E,RS)-(η^5-C_5H_5)Fe(CO)(PPh_3)-COCH=CHCH=CH_2 (**41**)

To a mixture of **36**:**37** (86:14; 0.160 g, 0.25 mmol) in DCM (5 ml) at −78 °C was added a solution of 55% *m*-chloroperbenzoic acid (0.080 g, 0.25 mmol) in DCM (2 ml) via cannula and after 1 h diisopropylamine (0.160 ml, 1.00 mmol) was added using syringe. After 1 h, the reaction mixture was allowed to warm to rt over 4 h, before being filtered through alumina (grade V) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel [Et_2O/40–60 (1:4)] to give the (*E*)-isomer **41** and some of the less polar (*Z*)-isomer in the ratio (93:7). Recrystallisation of this mixture from Et_2O yielded the title compound **41** as red needles (0.080 g, 66%) with identical spectroscopic properties to those described in the literature [23].

3.18. Preparation of (RS)-(η^5-C_5H_5)Fe(CO)(PPh_3)-CO(CH_2)$_3$CH(OMe)$_2$ (**38**)

To a solution of acetyl complex **1** (1.40 g, 3.08 mmol) in THF (15 ml) at −78 °C was added *n*-BuLi (1.5 M, 2.15 ml, 3.22 mmol), before the addition of 3-bromo-1,1-dimethoxypropane (0.510 ml, 3.36 mmol) by syringe after 2 h. The reaction mixture was then to warm to rt over 6 h, methanol (1 ml) added and the solvents removed in vacuo. Extraction into DCM (3×20 ml) and filtration through alumina (grade V) and subsequent purification by column chromatography on silica gel [Et_2O/40–60 (1:2)], then crystallisation from Et_2O afforded **38** as orange needles (1.34 g, 78%); Found: C, 66.7; H, 5.9%; $C_{31}H_{33}FeO_4P$ requires C, 66.9; H, 6.0%; ν_{max} (CH_2Cl_2) 1914 (C≡O), 1605 (C=O); δ_H (300 MHz, $CDCl_3$) 1.32–1.05 (4H, m, C(3)H_2C(4)H_2), 2.55 (1H, m, C(2)H_A), 2.88 (1H, m, COCH_B), 3.24 (3H, s, O*Me*), 3.26 (3H, s, O*Me*), 4.21 (1H, t, *J*5.3, C*H*(OMe)$_2$), 4.41 (5H, d, J_{PH}1.1, C_5H_5), 7.36–7.59 (15H, m, P*Ph*$_3$); δ_C (50 MHz, $CDCl_3$) 20.2, 31.7, 52.1, 52.6, 65.4, 85.2, 104.5, 128.2, 129.8, 133.5, 136.6, 221.0, 277.2; *m*/*z* (FAB+) 557 (MH^+, 10%), 525 (100%), 383 (100%); δ_P 76.2 (PPh_3).

3.19. Preparation of (RS,SR) and (RS,RS)-(η^5-C_5H_5)-Fe(CO)(PPh_3)COCH(SePh)CH_2CH_2CH(OMe)$_2$ (**39** and **40**)

To a solution of **38** (3.00 g, 5.40 mmol) in THF (60 ml) at −78 °C was added *n*-BuLi (1.5 M, 4.2 ml, 6.0 mmol) before the addition of a solution of diphenyl diselenide (2.0 g, 6.5 mmol) in THF (10 ml) after 2 h. The reaction was allowed to warm to −10 °C over 5 h before the addition of methanol (1 ml). After concentration in vacuo, the crude products were extracted into DCM (2×20 ml) and filtered through alumina (grade V) before removal of the solvent and purification by column chromatography on silica gel [Et_2O/40–60 (3:7)] that gave partial separation of the diastereoisomers. The less polar fraction was obtained as a 50:50 mixture of **39**:**40**, the more polar fraction gave **39** as a single diastereoisomer which was then crystallised from Et_2O to yield red blocks (overall yield 2.63 g, 69%); **39**. Found: C, 62.5; H, 5.1%; $C_{37}H_{37}FeO_4PSe$ requires C, 62.5; H, 5.2%; ν_{max} (CH_2Cl_2) 1912 (C≡O), 1584 (C=O); δ_H (500 MHz, $CDCl_3$) 0.75, 1.12, 1.23, 1.56 (4×1H, m, CH_2CH_2), 3.11 (3H, s, O*Me*), 3.19 (3H, s, O*Me*), 3.98 (1H, t, *J*5.7, C*H*(OMe)$_2$), 4.04 (1H, dd, *J*10.1, *J*3.1, C(2)*H*), 4.49 (5H, d, J_{PH}1.1, C_5H_5), 7.22–7.57 (20H, m, *Ph*), δ_C (50 MHz, $CDCl_3$) 25.4, 30.4, 51.8, 52.6, 74.1, 85.8, 104.2, 127.0, 128.1, 128.9, 129.8, 130.7, 133.4, 133.7, 136.4, 220.5, 272.1; *m*/*z* (FAB+) 713 (MH^+, 3%), 383 (100%); δ_P 74.5 (PPh_3). Selected data for **40**; δ_H (300 MHz, $CDCl_3$) 3.23 (3H, s, O*Me*), 3.23 (3H, s, O*Me*), 4.47 (5H, d, J_{PH}1.3, C_5H_5); δ_C (50 MHz, $CDCl_3$) 29.5, 52.4, 53.3, 85.8, 104.9.

3.20. Preparation of (E,RS)-(η^5-C_5H_5)Fe(CO)(PPh_3)-COCH=$CHCH_2$ CH(OMe)$_2$ (**31**)

To a mixture of **39**:**40** (75:25; 2.4 g, 3.4 mmol) in DCM (10 ml) at −78 °C was added a solution of 55% *m*-chloroperbenzoic acid (1.1 g, 3.4 mmol) in DCM (10 ml) via cannula and after 1 h diisopropylamine (2.0 ml, 14.3 mmol) was added using syringe. After 1 h, the reaction mixture was allowed to warm to rt over 4 h, before being filtered through alumina (grade V) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel [Et_2O/40–60 (2:5)] and subsequently crystallised from Et_2O to give **31** as red needles (1.55 g, 83%); Found: C, 67.1; H, 5.4%; $C_{31}H_{31}FeO_4P$ requires C, 67.2; H, 5.6%; ν_{max} (CH_2Cl_2) 1918 (C≡O), 1566 (C=O); δ_H (300 MHz, $CDCl_3$) 2.24 (2H, app t, *J*6.5, CH_2) 3.31 (6H, s, 2×O*Me*), 4.37 (1H, t, *J*5.9, C*H*(OMe)$_2$), 4.43 (5H, d, J_{PH}1.2, C_5H_5), 5.41 (1H, dt, *J*15.3, *J*7.2, COCH=C*H*), 6.50 (1H, d, *J*15.3, COC*H*), 7.31–7.52 (15H, m, PPh_3); δ_C (50 MHz, $CDCl_3$) 34.9, 52.6, 52.8, 85.4, 103.5, 123.0, 127.9, 129.6, 133.3, 136.3, 146.6, 220.6, 271.3; *m*/*z* (FAB+) 555 (MH^+, 15%), 383 (100%); δ_P 76.9 (PPh_3).

3.21. Preparation of (RS,RS)-(η^5-C_5H_5)Fe(CO)-(PPh_3)COCH$_2$CH(NHCH$_2$Ph)CH$_2$CH(OMe)$_2$ (**42**)

To benzylamine (0.580 g, 5.40 mmol) in THF (10 ml) at −78 °C was added *n*-BuLi (1.6 M, 2.40 ml, 3.85 mmol) at −78 °C and stirred for 1 h before being added via cannula to a solution of **31** (1.00 g, 1.80 mmol) in THF (20 ml) at −78 °C. After 5 h and then quenched by the addition of methanol (1 ml). After warming and evaporation of the solvent under reduced pressure the residue was extracted into $CHCl_3$ (2×20 ml) and

filtered through alumina (grade V). Purification by flash chromatography on alumina (grade I) [DCM/EtOAc (3:7)] yielded **42** which was subsequently crystallised from Et_2O as orange needles (0.970 g, 82%); Found: C, 69.1; H, 6.1; N, 2.0%; $C_{38}H_{40}NO_4P$ requires C, 69.0; H, 6.1; N, 2.1%; ν_{max} (CH_2Cl_2) 1914 (C≡O), 1603 (C=O); δ_H (300 MHz, $CDCl_3$) 1.22–1.42 (2H, m, C(4)H_2), 2.67 (1H, dd, *J*16.2, *J*6.2, C(2)H_AH), 2.75 (1H, m, C(3)*H*), 3.22 (1H, dd, *J*16.2, *J*4.8, C(2)H_BH), 3.22 (3H, s, O*Me*), 3.25 (3H, s, O*Me*), 3.58 (1H, AB, J_{AB}13.2, NCH_AHPh), 3.60 (1H, AB, J_{AB}13.2, NCH_BHPh), 4.37 (1H, t, *J*5.5, C*H*(OMe)$_2$), 4.40 (5H, d, J_{PH}1.1, C_5H_5), 7.51–7.17 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 36.9, 50.8, 50.9, 52.7, 52.8, 69.8, 85.3, 103.5, 126.7, 128.2, 129.9, 133.2, 136.6, 141.9, 220.9, 278.3; *m*/*z* (FAB+) 662 (MH^+, 25%), 383 (100%); δ_P 76.1 (PPh_3).

3.22. Preparation of (*RS,2SR,3RS*)-(η^5-C_5H_5)Fe(CO)(*PPh*$_3$)COCH(*Me*)CH(NHCH$_2$*Ph*)CH$_2$CH(*OMe*)$_2$ (*43*)

To benzylamine (0.15 g, 1.35 mmol) in THF (10 ml) at −78 °C was added *n*-BuLi (1.4 M, 0.8 ml, 1.12 mmol) at −78 °C and stirred for 1 h before being added via cannula to a solution of **31** (0.25 g, 0.45 mmol) in THF (10 ml) at −78 °C. After 3 h MeI (0.150 ml, 2.40 mmol) was added via syringe before the addition of methanol (1 ml) after a further 3 h. After warming and evaporation of the solvent under reduced pressure the residue was extracted into $CHCl_3$ (2×20 ml) and filtered through alumina (grade V). Purification by flash chromatography on alumina (grade I) [DCM/EtOAc (4:1)] yielded **43** which was subsequently crystallised from Et_2O as orange needles (0.230 g, 76%); Found: C, 69.4; H, 6.2; N, 1.9%; $C_{39}H_{42}FeNO_4P$ requires C, 69.3; H, 6.3; N, 2.1%; ν_{max} (CH_2Cl_2) 1914 (C≡O), 1595 (C=O); δ_H (300 MHz, $CDCl_3$) 1.08 (3H, d, *J*7.3, C(2)CH_3) 1.36 (1H, ddd, *J*14.2, *J*7.4, *J*5.5, C(4)H_AH), 1.52 (1H, dt, *J*14.2, *J*5.5, C(4)H_BH), 2.39 (1H, ddd, *J*7.4, *J*5.5, *J*4.8, C(3)*H*), 3.13 (1H, AB, J_{AB}12.9, NCH_AHPh), 3.27 (3H, s, O*Me*), 3.28 (3H, s, O*Me*), 3.28 (1H, dq, *J*7.3, *J*2.7, C(2)*H*), 3.43 (1H, AB, J_{AB}12.9, NCH_BHPh), 4.37 (1H, t, *J*5.5, C*H*(OMe)$_2$), 4.43 (5H, d, J_{PH}1.3, C_5H_5), 7.16–7.55 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 11.7, 35.1, 51.6, 52.5, 54.1, 69.8, 85.1, 103.1, 126.3, 128.1, 129.7, 133.4, 136.9, 141.1, 221.0, 282.9; *m*/*z* (FAB+) 676 (MH^+, 30%), 383 (100%); δ_P 75.7 (PPh_3).

3.23. Preparation of (3*SR*,4*RS*)-1-benzyl-4-(2′, 2′-dimethoxyethyl)-3-methylazetidin-2-one (*44*)

To a solution of **43** (0.410 g, 0.61 mmol) in DCM (10 ml) was cooled to −78 °C and a solution of bromine (0.062 ml, 1.20 mmol) in DCM (2 ml) was added dropwise via cannula. The reaction was stirred for 1 h then NEt_3 (0.500 ml) was added. After 2 h at −78 °C, the solution was allowed to warm to rt and the solvent removed in vacuo. Trituration with Et_2O, filtration and evaporation of the filtrate gave an oil which was subjected to column chromatography on silica gel [EtOAc/40–60 (1:1)], giving **44** as a pale yellow oil (0.120 g, 75%); Found: C, 68.4; H, 8.3%; $C_{15}H_{21}NO_3$ requires C, 68.4; H, 8.0%; ν_{max} (film) 1747 (C=O); δ_H (300 MHz, $CDCl_3$) 1.21 (3H, d, *J*7.6, C(3)HCH_3), 1.78 (2H, m, C(4)CH_2), 3.18 (3H, s, O*Me*), 3.21 (3H, s, O*Me*), 3.27 (1H, dq, *J*7.6, *J*5.3, C(3)H), 3.66 (1H, m, C(4)*H*), 4.18 (1H, AB, *J*15.4, NCH_AHPh), 4.29 (1H, t, *J*5.6, C*H*(OMe)$_2$), 4.57 (1H, AB, *J*15.4, NCH_BHPh), 7.22–7.35 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 9.6, 32.2, 44.5, 47.2, 51.6, 53.0, 53.4, 102.5, 127.5, 127.9, 128.7, 136.4, 171.5; *m*/*z* (CI, NH_3) 264 (MH^+, 100%).

3.24. Preparation of (*RS,RS,RS,RS*) and (*RS,RS,RS,SR*)-(η^5-C_5H_5)Fe(CO)(*PPh*$_3$)COCH[CH(OH)CH$_3$]CH(NHCH$_2$*Ph*)CH$_2$CH(*OMe*)$_2$ (*45* and *46*)

To a solution of (*N*-trimethylsilyl)benzylamine (1.30 g, 7.30 mmol) in THF (5 ml) at −78 °C was added *n*-BuLi (1.5 M, 4.30 ml, 6.45 mmol) and stirred for 1 h before being added to a solution of **31** (1.00 g, 1.80 mmol) in THF (15 ml) at −95 °C. After 4 h a solution of acetaldehyde (1.0 ml, 18.0 mmol) in THF (15 ml) was added via cannula and after 3 h at −95 °C methanol (1 ml) was added. After warming to rt the reaction mixture was concentrated in vacuo and the resultant oil extracted into $CHCl_3$ (3×20 ml), filtered through alumina (grade V), concentrated in vacuo and the residue purified by column chromatography on alumina (grade I) [EtOAc/40–60(3:7)-EtOAc] to give **45** and **46** as a 50:50 mixture of diastereoisomers. Further column chromatography on silica gel [$CHCl_3$/MeOH/AcOH (90:4:2)] gave the less polar diastereoisomer **45**, which was subsequently crystallised from DCM/Et_2O, giving **45** as orange needles (0.450 g, 35%); Found: C, 61.2; H, 5.8; N, 1.7%; $C_{40}H_{44}FeNO_5P$ (1.2 CH_2Cl_2) requires C, 61.2; H, 5.8; N, 1.7%; ν_{max} (CH_2Cl_2) 1915 (C≡O), 1591 (C=O); δ_H (500 MHz, $CDCl_3$) 0.54 (1H, br m, C(4)CH_AH), 0.90 (1H, br m, C(4)CH_BH), 1.23 (3H, d, *J*6.6, CHCH_3), 2.99 (1H, br m, C(3)*H*), 3.25 (3H, s, O*Me*), 3.28 (3H, s, O*Me*), 3.35 (1H, dd, *J*8.7, *J*2.6, C(2)*H*), 3.52 (1H, AB, J_{AB}12.6, NCH_AHPh), 3.64 (1H, AB, J_{AB}12.6, NCH_BHPh), 4.26 (1H, t, *J*5.4, C*H*(OMe)$_2$), 4.42 (5H, d, J_{PH}1.0, C_5H_5), 4.91 (1H, br m, C*H*(OH)Me), 6.80 (1H, br s, N*H*), 7.19–7.50 (20H, m, *Ph*), δ_C (50 MHz, $CDCl_3$) 20.2, 35.6, 50.8, 52.5, 53.0, 53.9, 67.6, 78.6, 86.4, 103.9, 127.0, 128.2, 128.4, 129.9, 133.3, 134.0, 136.5, 220.3 *m*/*z* (FAB+) 706 (MH^+, 50%), 383 (100%); δ_P 73.3 (PPh_3). Further elution and subsequent crystallisation (Et_2O) gave **46** as orange needles (0.465 g, 37%); Found: C, 67.8; H, 6.6; N, 2.05%; $C_{40}H_{44}FeNO_5P$ requires C, 68.1; H, 6.3; N, 2.0%; ν_{max} (CH_2Cl_2) 1911

(C≡O), 1601 (C=O); δ_H (500 MHz, $CDCl_3$) 1.40 (1H, br m, C(4)CH_AH), 1.41 (3H, d, *J*6.7, CHCH_3), 1.82 (1H, br m, C(4)CH_BH), 2.63 (1H, d, *J*7.6, C(3)*H*), 2.65 (1H, d, *J*3.4, C(2)*H*), 3.24 (3H, s, O*Me*), 3.25 (3H, s, O*Me*), 3.30 (1H, AB, J_{AB}12.6, NCH_AHPh), 3.69 (1H, AB, J_{AB}12.6, NCH_BHPh), 4.16 (1H, dd, *J*7.0, *J*3.4, C*H*(OMe)$_2$), 4.53 (5H, d, J_{PH}1.2, C_5H_5), 4.53 (1H, dq, *J*10.4, *J*6.6, C*H*(OH)Me), 7.20–7.70 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 24.5, 39.9, 51.6, 52.4, 53.5, 54.6, 67.8, 80.5, 86.8, 104.3, 126.6, 128.0, 128.2, 129.7, 133.4, 136.8, 140.7, *m*/*z* (FAB+) 706 (MH^+, 40%), 383 (100%); δ_P 74.8 (PPh_3).

3.25. Preparation of (3RS,4RS,1″RS)-1-benzyl-4-(2′,2′-dimethoxyethyl)-3-(1″-hydroxyethyl)azetidin-2-one (**47**)

To a solution of **45** (0.150 g, 0.21 mmol) in DCM (5 ml) at −78 °C was added a solution of bromine (0.022 ml, 0.42 mmol) in DCM (5 ml) via cannula. The resultant solution was stirred for 2 h at −78 °C before NEt_3 (0.1 ml) was added. After 1 h at −78 °C the reaction was allowed to warm to rt and concentrated in vacuo. The residue was triturated with Et_2O, and the filtrate concentrated in vacuo to give an oil which was purified by column chromatography on silica gel (EtOAc) to give **47** as an oil (0.031 g, 50%); δ_H (300 MHz, $CDCl_3$) 1.39 (3H, d, *J*6.4, CHCH_3), 2.00 (1H, ddd, *J*14.6, *J*7.1, *J*5.1, C(4)CH_AH), 2.08 (1H, dt, *J*14.6, *J*5.8, C(4)CH_BH), 2.34 (1H, br s, Me(O*H*)CH), 3.19 (3H, s, O*Me*), 3.20 (1H, obscured, C(1)*H*), 3.21 (3H, s, O*Me*), 3.71 (1H, dt, *J*7.1, *J*5.4, C(3)*H*), 4.12 (1H, dq, *J*6.4, *J*4.4, C*H*(OH)Me), 4.23 (1H, app t, *J*5.8, C*H*(OMe)$_2$), 4.24 (1H, AB, J_{AB}15.5, NCH_AHPh), 4.62 (1H, AB, J_{AB}15.5, NCH_BHPh), 7.24–7.35 (5H, m, *Ph*), δ_C (50 MHz, $CDCl_3$) 23.1, 32.2, 44.6, 51.5, 53.1, 53.5, 58.6, 64.5, 102.8, 127.5, 127.8, 128.7, 136.2, 168.8.

3.26. Preparation of (3RS,4RS,1″SR)-1-benzyl-4-(2′,2′-dimethoxyethyl)-3-(1″-hydroxyethyl)azetidin-2-one (**48**)

To a solution of **46** (105 mg, 0.15 mmol) in DCM (2 ml) at −78 °C was added a solution of bromine (0.016 ml, 0.31 mmol) in DCM (5 ml) via cannula. The resultant solution was stirred for 2 h at −78 °C before NEt_3 (0.1 ml) was added. After 1 h at −78 °C the reaction was allowed to warm to rt and concentrated in vacuo. The residue was triturated with Et_2O, and the filtrate concentrated in vacuo to give an oil which was purified by column chromatography on silica gel (EtOAc) to give **48** as an oil (19 mg, 44%); δ_H (300 MHz, $CDCl_3$) 1.43 (3H, d, *J*6.1, CHCH_3), 1.90 (1H, dt, *J*14.9, *J*3.4, C(4)CH_AH), 2.12 (1H, ddd, *J*14.9, *J*9.0, *J*6.7, C(4)CH_BH), 3.18 (1H, dd, *J*10.2, *J*5.0, C(3)*H*), 3.29 (3H, s, O*Me*), 3.31 (3H, s, O*Me*), 3.71 (2H, m, CH(O*H*)Me and C(4)*H*), 4.12 (1H, AB, J_{AB}15.3, NCH_AHPh), 4.14 (1H, m, C*H*(OH)Me), 4.36 (1H, dd, *J*6.6, *J*3.7, C*H*(OMe)$_2$), 4.62 (1H, AB, J_{AB}15.3, NCH_AHPh), 7.24–7.39 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 21.3, 30.6, 44.1, 51.3, 52.9, 54.9, 61.1, 63.5, 103.0, 127.8, 128.1, 128.8, 135.8, 167.3; *m*/*z* (CI, NH_3) 294 (MH^+, 5%), 186 (100%).

3.27. Preparation of (3RS,4RS,1″SR)-4-(2′,2′-dimethoxyethyl)-3-(1″-hydroxyethyl)azetidin-2-one (**50**)

NH_3 (10 ml) was condensed at −78 °C and sodium (25 mg, 1.10 mmol) added. The resulting blue solution was warmed and the dried ammonia re-condensed at −78 °C. Ethanol (0.10 ml) was added via syringe, followed by sodium (10 mg, 0.43 mmol) and the blue solution was stirred for 5 min at −78 °C before a solution of **48** (11 mg, 0.04 mmol) in THF (1 ml) was added via syringe. Following a further addition of sodium (10 mg, 0.43 mmol) the reaction mixture maintained a blue colour, and after stirring for a further 10 min at −78 °C the reaction was quenched by the addition of solid ammonium chloride (0.10 g). On warming, and after evaporation of the ammonia, the residue was dissolved in DCM (5 ml) and filtered. Concentration in vacuo, and purification by column chromatography on silica gel [$CHCl_3$/MeOH (9:1)] gave **50** as an oil (5 mg, 66%); δ_H (300 MHz, $CDCl_3$) 1.42 (3H, d, *J*6.2, CHCH_3), 1.96 (1H, ddd, *J*14.4, *J*8.1, *J*5.4, C(4)CH_AH), 2.29 (1H, dt, *J*14.4, *J*4.8, C(4)CH_BH), 3.20 (1H, ddd, *J*10.1, *J*5.2, *J*1.5, C(3)*H*), 3.37 (3H, s, O*Me*), 3.39 (3H, s, O*Me*), 3.88 (1H, dt, *J*8.1, *J*5.0, C(4)*H*), 4.16 (1H, dq, *J*10.1, *J*6.2, C*H*(OH)Me), 4.50 (1H, app t, *J*5.1, C*H*(OMe)$_2$), 5.99 (1H, br s, N*H*); δ_C (50 MHz, $CDCl_3$) 22.1, 33.6, 48.2, 53.8, 54.1, 60.8, 63.9, 104.0, 167.7; *m*/*z* 189 (M+NH_4^+-MeOH, 5%), 96 (100%); M+NH_4^+-MeOH exact mass calculated 189.1239, Found 189.1246.

3.28. Preparation of (3RS,4RS,1″RS)-4-(2′,2′-dimethoxyethyl)-3-(1″-hydroxyethyl)azetidin-2-one (**49**)

NH_3 (10 ml) was condensed at −78 °C and sodium (25 mg, 1.10 mmol) added. The resulting blue solution was warmed and the dried ammonia re-condensed at −78 °C. Ethanol (0.10 ml) was added via syringe, followed by sodium (10 mg, 0.43 mmol) and the blue solution was stirred for 5 min at −78 °C before a solution of **47** (22 mg, 0.07 mmol) in THF (1 ml) was added via syringe. Following a further addition of sodium (10 mg, 0.43 mmol) the reaction mixture maintained a blue colour, and after stirring for a further 10 min at −78 °C the reaction was quenched by the addition of solid ammonium chloride (0.10 g). On warming, and after evaporation of the ammonia, the residue was dissolved in DCM (5 ml) and filtered. Concentration in vacuo, and purification by column chromatography on silica gel [$CHCl_3$/MeOH (9:1)] gave **49** as an oil (13 mg, 85%); δ_H (300 MHz, $CDCl_3$) 1.32 (3H, d, *J*6.2, CHCH_3),

1.93 (1H, ddd, *J*14.1, *J*4.1, *J*2.6, C(4)CH_AH), 2.11 (1H, dd, *J*14.1, *J*10.8, *J*6.0, C(4)CH_BH), 3.19 (1H, app t, *J*5.9, C(3)*H*), 3.35 (3H, s, O*Me*), 3.36 (3H, s, O*Me*), 3.85 (1H, ddd, *J*10.8, *J*5.4, *J*2.6, C(4)*H*), 4.11 (1H, m, C*H*(OH)Me), 4.47 (1H, dd, *J*6.0, *J*4.1, C*H*(OMe)$_2$), 6.19 (1H, br s, N*H*); δ_C (50 MHz, $CDCl_3$) 22.7, 33.0, 47.7, 53.5, 54.0, 59.0, 64.4, 104.0, 169.3; *m*/*z* (CI, NH_3) 204 (MH^+, 30%), 155 (100%); MH^+ exact mass calculated 204.1236, Found 204.1236.

3.29. Preparation of (E,E,RS)- and (Z,E,RS)-(η^5-C_5H_5)Fe(CO)(PPh_3)COCH=CHCH=CHSiMe$_3$ (**53** and **54**)

To a solution of trimethylsilyl complex **52** (3.10 g, 5.90 mmol) in THF (100 ml) at −78 °C was added *n*-BuLi (1.6 M, 4.40 ml, 7.00 mmol). After 1 h a solution of (*E*)-3-trimethylsilylpropenal (1.60 g, 12.40 mmol) in THF (10 ml) was added via cannula, and the reaction then stirred at −78 °C for 4 h before warming to rt. The reaction mixture was evaporated to an oil which was extracted into DCM (2×20 ml), filtered through alumina (grade V) and concentrated in vacuo before purification by column chromatography on silica gel (DCM) giving (*Z*,*E*,*RS*)-**54** as a red foam (1.22 g, 37%); Found: C, 68.2; H, 5.8%; $C_{32}H_{33}FeO_2PSi$ requires C, 68.1; H, 5.9%; ν_{max} (CH_2Cl_2) 1917 (C≡O), 1582 (C=O); δ_H (300 MHz, $CDCl_3$) 0.02 (9H, s, Si*Me*$_3$), 4.44 (5H, d, J_{PH}1.1 C_5H_5), 5.13 (1H, app t, *J*10.8, COCH=C*H*), 5.89 (1H, d, *J*18.4, C*H*Si), 6.37 (1H, d, *J*11.1, COC*H*), 6.51 (1H, dd, *J*18.4, *J*10.8, C*H*=CHSi), 7.52–7.31 (15H, m, PPh_3); δ_C (50 MHz, $CDCl_3$) −1.4, 85.5, 123.0, 128.1, 129.7, 133.2, 136.2, 139.4, 141.4, 141.5, 220.3, 273.3; *m*/*z* (FAB+) 565 (MH^+, 5%), 383 (100%); δ_P 76.8 (PPh_3); further elution gave (*E*,*E*,*RS*)-**53** which was crystallised from Et_2O as beige needles (1.82 g, 55%); Found: C, 67.9; H, 5.9%; $C_{32}H_{33}FeO_2PSi$ requires C, 68.1; H, 5.9%; ν_{max} (CH_2Cl_2) 1917 (C≡O), 1549 (C=O); δ_H (300 MHz, $CDCl_3$) 0.09 (9H, s, Si*Me*$_3$), 4.44 (5H, d, J_{PH}1.1 C_5H_5), 5.80 (1H, dd, *J*14.9, *J*10.3, COCH=C*H*), 6.11 (1H, d, *J*18.3, C*H*Si), 6.36 (1H, dd, *J*18.3, *J*10.3, C*H*=CHSi), 6.47 (1H, d, *J*14.9, COC*H*), 7.50–7.31 (15H, m, PPh_3), δ_C (50 MHz, $CDCl_3$) −1.4, 85.5, 127.0, 128.0, 129.7, 133.1, 136.3, 141.6, 143.1, 143.3, 220.7; *m*/*z* (FAB+) 565 (MH^+, 5%), 383 (100%); δ_P 76.8 (PPh_3).

3.30. Preparation of (RS,3SR,4E)-(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH(NHCH_2Ph)CH$=CHSiMe$_3$ (**58**)

n-BuLi (11.20 ml, 18.0 mmol) was added to a solution of benzylamine (2.03 g, 19.0 mmol) in THF (25 ml) at −78 °C and stirred for 2 h. A solution of **55** (2.67 g, 4.73 mmol) in THF (25 ml) at −78 °C was added via cannula, and after 3 h methanol (1 ml) was added and the reaction allowed to warm to rt. After concentration in vacuo, the resultant oil was extracted into $CHCl_3$ (3×20 ml) and filtered through alumina (grade V). Concentration in vacuo and chromatographic purification of the residue on alumina (grade I) [EtOAc/DCM (1:1)] gave **58** as an orange foam (2.85 g, 90%); Found: C, 69.9, H, 6.5, N, 1.9%; $C_{39}H_{42}FeNO_2PSi$ requires C, 69.7, H, 6.3, N, 2.1%; ν_{max} (CH_2Cl_2) 1917 (C≡O), 1604 (C=O); δ_H (500 MHz, $CDCl_3$) 0.05 (9H, s, Si*Me*$_3$), 2.66 (1H, dd, *J*17.1, *J*2.7, C(2)H_AH), 2.98 (1H, m, C(3)*H*), 3.10 (1H, dd, *J*17.1. *J*9.0, C(2)H_BH), 3.47 (1H, AB, J_{AB}13.3, NCH_AHPh), 3.59 (1H, AB, J_{AB}13.3, NCH_BHPh), 4.40 (5H, d, J_{PH}1.0, C_5H_5), 5.51 (1H, d, *J*18.6, CH=C*H*Si), 5.67 (1H, dd, *J*18.6, *J*7.2, C*H*=CHSi), 7.19–7.50 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) −1.2, 51.6, 60.9, 72.5, 85.4, 126.4, 128.0, 129.7, 130.1, 133.3, 136.3, 141.0, 148.4, 220.3, 277.3; *m*/*z* (FAB+) 672 (MH^+, 5%), 383 (100%); δ_P 75.95 (PPh_3).

3.31. Preparation of (RS,3SR)-(η^5-C_5H_5)Fe(CO)(PPh_3) $COCH_2CH(NHCH_2Ph)CH$=CH_2 (**57**)

n-BuLi (1.6 M, 1.81 ml, 2.9 mmol) was added to a solution of benzylamine (0.32 g, 3.0 mmol) in THF (5 ml) at −78 °C and stirred for 2 h. A solution of **53** (0.50 g, 1.01 mmol) in THF (15 ml) at −78 °C was added via cannula, and after 3 h methanol (1 ml) was added and the reaction allowed to warm to rt. After concentration in vacuo, the resultant oil was extracted into chloroform (3×20 ml) and filtered through alumina (grade V). Concentration in vacuo and chromatographic purification of the residue on alumina (grade I) [EtOAc/DCM (1:1)] and recrystallisation from Et_2O gave **57** as orange needles (0.555 g, 92%); Found: C, 72.0, H, 6.0, N, 2.3%; $C_{36}H_{34}FeNO_2P$ requires C, 72.1, H, 5.7, N, 2.3%; ν_{max} (CH_2Cl_2) 1910 (C≡O), 1600 (C=O); δ_H (300 MHz, $CDCl_3$) 2.75 (1H, dd, *J*17.1, *J*3,1, C(2)H_AH), 2.97 (1H, m, C(3)*H*), 3.13 (1H, dd, *J*17.1, *J*8.6, C(2)H_BH), 3.48 (1H, AB, J_{AB}13.2, NCH_AHPh), 3.63 (1H, AB, J_{AB}13.2, NCH_BHPh), 4.40 (5H, d, J_{PH}1.2, C_5H_5), 4.88–4.96 (2H, m, CH=CH_2), 5.45 (1H, ddd, *J*14.6, *J*10.3, *J*7.9, C*H*=CH_2), 7.19–7.51 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 51.5, 58.4, 70.9, 85.4, 114.0, 126.0, 128.1, 128.4, 129.7, 133.2, 136.3, 140.0, 141.0, 220.3, 276.7; *m*/*z* (FAB+) 599 (M^+, 5%), 383 (100%).

3.32. Preparation of (RS,3RS,E)-(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH(NHCH_2Ph)CH$=CHSiMe$_3$ (**59**)

n-BuLi (1.6 M, 8.1 ml, 13.0 mmol) was added to a solution of benzylamine (1.64 g, 15.0 mmol) in THF (15 ml) at −78 °C and stirred for 2 h. A solution of **54** (0.78 g, 1.38 mmol) in THF (25 ml) at −78 °C was added via cannula, and after 3 h methanol (1 ml) was added and the reaction allowed to warm to rt. After concentration in vacuo, the resultant oil was extracted into

chloroform (3×20 ml) and filtered through alumina (grade V). Concentration in vacuo and chromatographic purification of the residue on alumina (grade I) [EtOAc/DCM (1:1)] gave **59** as an orange foam (0.500 g, 54%); Found: C, 69.6, H, 6.2, N, 1.9%; $C_{39}H_{42}FeNO_2PSi$ requires C, 69.7, H, 6.3, N, 2.1%; ν_{max} (CH_2Cl_2) 1916 (C≡O), 1605 (C=O); δ_H (500 MHz, $CDCl_3$) 0.06 (9H, s, Si*Me*$_3$), 2.85 (1H, dd, *J*17.0, *J*8.5, C(2)H_AH), 3.10 (1H, dd, *J*17.0, *J*3.5, C(2)H_BH), 3.28 (1H, ddd, *J*8.5, *J*7.2, *J*3.5, C(3)*H*), 3.40 (1H, AB, J_{AB}13.0, NCH_AHPh), 3.52 (1H, AB, J_{AB}13.0, NCH_BHPh), 4.38 (5H, d, J_{PH}1.0, C_5H_5), 5.68 (1H, d, *J*18.6, CH=C*H*Si), 5.79 (1H, dd, *J*18.6, *J*7.2, C*H*=CHSi), 7.16–7.48 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) −1.1, 51.8, 60.4, 71.0, 85.1, 126.5, 128.0, 128.0, 128.4, 129.7, 130.3, 133.2, 136.4, 140.8, 148.8, 220.3, 277.6; *m*/*z* (FAB+) 672 (MH^+, 5%), 383 (100%); δ_P 76.6 (PPh_3).

3.33. Preparation of (*RS*,3*RS*)-(η^5-C_5H_5)Fe(CO)-(PPh_3)$COCH_2CH(NHCH_2Ph)CH$=CH_2 (**60**)

n-BuLi (1.6 M, 43.8 ml, 70.0 mmol) was added to a solution of benzylamine (7.7 g, 71.8 mmol) in THF (160 ml) at −78 °C and stirred for 2 h. A solution of **56** (3.50 g, 7.11 mmol) in THF (40 ml) at −78 °C was added via cannula, and after 30 h methanol (5 ml) was added and the reaction allowed to warm to rt. After concentration in vacuo, the resultant oil was extracted into chloroform (3×30 ml) and filtered through alumina (grade V). Concentration in vacuo and chromatographic purification of the residue on alumina (grade I) [EtOAc/DCM (1:1)] and recrystallisation from Et_2O gave **60** as orange needles (2.80 g, 66%); Found: C, 72.0, H, 6.05, N, 2.3%; $C_{36}H_{34}FeNO_2P$ requires C, 72.1, H, 5.7, N, 2.3%; ν_{max} (CH_2Cl_2) 1910 (C≡O), 1600 (C=O); δ_H (300 MHz, $CDCl_3$) 2.86 (1H, dd, *J*17.1, *J*8.2, C(2)H_AH), 3.12 (1H, dd, *J*17.1, *J*3.5, C(2)H_BH), 3.25 (1H, dt, *J*8.2, *J*3.5, C(3)*H*), 3.41 (1H, AB, J_{AB}13.0, NCH_AHPh), 3.57 (1H, AB, J_{AB}13.0, NCH_BHPh), 4.40 (5H, d, J_{PH}0.8, C_5H_5), 4.99–5.09 (2H, m, CH=CH_2), 5.57 (1H, ddd, *J*17.2, *J*10.0, *J*8.2, C*H*=CH_2), 7.16–7.49 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 51.6, 58.2, 71.2, 85.1, 115.3, 126.5, 128.1, 128.4, 129.7, 133.2, 136.3, 140.7, 141.0, 220.3, 277.1; *m*/*z* (FAB+) 599 (M^+, 5%), 383 (100%).

3.34. Preparation of (*RS*,2*RS*,3*RS*,1′*SR*)-(η^5-C_5H_5)-Fe(CO)(PPh_3)$COCH[CH(OH)CH_3]CH(NHCH_2Ph)$-$CH$=$CH_2$ (**61**)

n-BuLi (1.6 M, 8.8 ml, 14.1 mmol) was added to a solution of (*N*-trimethylsilyl)benzylamine (2.6 g, 14.60 mmol) in THF (5 ml) at −78 °C. After 1 h, a solution of (*Z*)-**56** (0.74 g, 1.50 mmol) in THF (15 ml) at −78 °C was added via cannula, and stirred for 30 h before a solution of acetaldehyde (5.0 ml) in THF (15 ml) was added via cannula and stirred for 8 h at −78 °C before the addition of methanol (1 ml) and the reaction allowed to warm to rt. After concentration in vacuo, the resultant oil was extracted into chloroform (3×20 ml) and filtered through alumina (grade V). Concentration in vacuo and chromatographic purification of the residue on alumina (grade I) [EtOAc/CH_2Cl_2 (1:1)] gave **61** which was crystallised (Et_2O:DCM) to give **61** as a single diastereoisomer and as orange plates (0.60 g, 62%); Found: C, 70.7, H, 5.95, N, 2.2%; $C_{38}H_{38}FeNO_3P$ requires C, 70.9, H, 5.95, N, 2.2%; ν_{max} (CH_2Cl_2) 1914 (C≡O), 1600 (C=O); δ_H (500 MHz, $CDCl_3$) 1.22 (3H, d, *J*6.5, CH(OH)CH_3), 2.54 (1H, br m, CH(O*H*)Me); 2.70 (1H, br m, C(3)*H*), 2.93 (1H, br m, C(2)*H*), 3.32 (1H, AB, J_{AB}12.6, NCH_AHPh), 3.54 (1H, AB, J_{AB}12.6, NCH_BHPh), 4.44 (2H, m, CH=CH_2), 4.55 (5H, d, J_{PH}1.0, C_5H_5), 4.65 (1H, m, C*H*=CH_2), 5.12 (1H, dq, *J*6.6, *J*2.0, CH(OH)*Me*), 7.21–7.62 (20H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 23.3, 50.4, 60.3, 68.4, 86.2, 116.1, 126.9, 128.2, 129.0, 132.0, 133.2, 136.1, 136.5, 139.5, 221.3; *m*/*z* (FAB+) 644 (MH^+, 5%), 383 (100%); δ_P 70.6 (PPh_3).

3.35. Preparation of (3*RS*,4*SR*,1′*SR*)-1-benzyl-3-[(1′-tert-butyldimethylsilyloxy)ethyl]-4-vinylazetidin-2-one (**45**)

A solution of **61** (0.230 g, 0.36 mmol) in DCM (5 ml) was cooled to −78 °C and a solution of bromine (0.040 ml, 0.72 mmol) in DCM (5 ml) was added dropwise via cannula. The green solution was stirred for 2 h before NEt_3 (0.30 ml) was added by syringe. Stirring was continued for 1 h at −78 °C and then the reaction mixture was allowed to warm to rt. This mixture was evaporated, and the residue triturated with Et_2O. The filtrate was evaporated to an oil and subjected to purification by flash chromatography on silica gel (EtOAc) gave (3*RS*,*SR*,1′*SR*)-1-benzyl-3-(1′-hydroxyethyl)-4-vinylazetidin-2-one as an oil (0.042 g, 51%) contaminated 5with triphenylphosphine (*ca.* 10%); ν_{max} (film) 1747 (C=O); δ_H (300 MHz, $CDCl_3$) 1.25 (3H, d, *J*6.4, CH(OH)CH_3), 2.10 (1H, br s, CH(O*H*)CH_3), 2.97 (1H, m, C(3)*H*), 4.00 (2H, comprising 1H, AB, J_{AB}15.2, NCH_AHPh, and obscured C(4)*H*), 4.22 (1H, br m, C*H*(OH)CH_3), 4.68 (1H, AB, J_{AB}15.2, NCH_BHPh), 5.21 (1H, m, CH=CH_AH), 5.27 (1H, m, CH=CH_BH), 5.78 (1H, m, C*H*=CH_2), 7.24–7.38 (5H, m, *Ph*). To a solution of (3*RS*,*SR*,1′*SR*)-1-benzyl-3-(1′-hydroxyethyl)-4-vinylazetidin-2-one (12 mg, 0.05 mmol) in DMF (0.20 ml) was added *tert*-butyldimethylsilyl chloride (35 mg, 0.23 mmol) followed by imidazole (40 mg, 0.59 mmol). After 30 h at rt the reaction mixture was partitioned between 0.1 M HCl and EtOAc. The combined organic phases were washed with sodium hydrogen carbonate solution, water, brine and dried. The residue was purified by col-

umn chromatography on silica gel [EtOAc/40–60 (1:4)], giving **62** as a colourless oil (15 mg, 84%; 43% over two steps); ν_{max} (film) 1747 (C=O); δ_H (300 MHz, $CDCl_3$) 0.02, 0.05 (2×3H, s, $Si(CH_3)_2$), 0.82 (9H, s, $SiC(CH_3)_3$), 1.17 (3H, d, *J*6.2, $CH(OH)CH_3$), 2.89 (1H, dd, *J*4.6, *J*2.1, C(3)*H*), 4.00 (1H, dd, *J*8.5, *J*2.1, C(4)*H*), 4.05 (1H, AB, J_{AB}15.1, NCH_AHPh), 4.20 (1H, dq, *J*6.2, *J*4.6, $CH(OH)CH_3$), 4.58 (1H, AB, J_{AB}15.1, NCH_BHPh), 5.18 (1H, m, $CH=CH_AH$), 5.25 (1H, m, $CH=CH_BH$), 5.75 (1H, ddd, *J*17.0, *J*10.2, *J*8.5, $CH=CH_2$), 7.34–7.23 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) −4.8, −4.6, 17.9, 22.4, 25.7, 44.4, 55.8, 64.6, 65.2, 119.1, 127.4, 128.4, 128.6, 135.8, 136.2, 167.6; *m*/*z* (CI, NH_3) 346 (MH^+, 100%); MH^+ exact mass calculated 346.2202, Found 346.2202.

3.36. Preparation of (3RS,4SR,1′SR)-3-[(1′-tert-butyldimethylsilyloxy)ethyl]-4-vinylazetidin-2-one (**51**)

NH_3 (10 ml) was condensed at −78 °C and sodium (25 mg, 1.10 mmol) added. The resulting blue solution was warmed and the dried ammonia re-condensed at −78 °C. Ethanol (0.05 ml) was added via syringe, followed by sodium (10 mg, 0.43 mmol) and the blue solution was stirred for 5 min at −78 °C before a solution of **62** (13 mg, 0.04 mmol) in THF (1 ml) was added via syringe. After stirring for 20 min at −78 °C the reaction was quenched by the addition of solid ammonium chloride (100 mg). On warming, and after evaporation of the ammonia, the residue was dissolved in DCM (5 ml) and filtered. Concentration in vacuo, and purification by column chromatography on silica gel [EtOAc/40–60 (1:4)] gave **51** as a white solid (0.008 g, 83%); δ_H (lit.[31]; 300 MHz, $CDCl_3$) 0.08 (6H, s, $Si(CH_3)_2$), 0.89 (9H, s, $SiC(CH_3)_3$), 1.22 (3H, d, *J*6.2, $CH(OH)CH_3$), 2.89 (1H, dd, *J*4.3, *J*2.5, C(3)*H*), 4.20–4.27 (2H, m, C(4)*H* and C*H*(OH)Me), 5.18 (1H, d, *J*10.3, $CH=CH_AH$), 5.32 (1H, d, *J*17.1, $CH=CH_BH$), 5.86 (1H, br s, N*H*), 5.96 (1H, ddd, *J*17.1, *J*10.3, *J*6.9, $CH=CH_2$); δ_C (50 MHz, $CDCl_3$) −5.1, −4.3, 17.9, 22.4, 25.7, 52.1, 65.2, 65.8, 116.5, 137.6, 168.4.

3.37. Preparation of (RS,3RS,αRS)- and (RS,3RS,αSR)-(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH${NH[CH(CH_3)Ph]}Me (**63**)

Following representative procedure 1, *n*-BuLi (1.6 M, 0.82 ml, 0.51 mmol) and (*RS*)-α-methylbenzylamine (60 mg, 0.52 mmol) in THF (10 ml) and (*RS*)-**12** in THF (10 ml) gave, after chromatography on alumina (Et_2O), an inseparable mixture of diastereoisomers **63** (90 mg, 72%) as an orange solid; $C_{36}H_{36}NO_2FeP$ requires C, 71.9; H, 6.0; N, 2.3%; Found C, 71.8; H, 5.8; N, 2.3%; ν_{max} (CH_2Cl_2) 1910 (C≡O), 1600 (C=O); δ_H (200 MHz, $CDCl_3$) 0.54, 0.58 (2×3H, d, *J*6.2, CH_3CHCH_2), 1.23 (3H, d, *J*6.4, C(α)*Me*), 1.23 (3H, d, *J*6.6, C(α)*Me*), 1.84 (2×1H, br s, N*H*), 2.30 (1H, m, CH_3CHCH_2), 2.54–2.56 (3H, m, CH_3CHCH_2 and CH_3CHCH_2), 2.88 (1H, dd, $J_{A,B}$17.4, $J_{A,CH}$6.7, CH_3CHCH_2), 3.20–3.27 (1H, m, CH_3CHCH_2), 3.67–3.77 (2×1H, m, C(α)*H*), 4.37 (2×5H, s, C_5H_5), 7.20–7.56 (2×20H, m, *Ph*); δ_P (100 MHz, $CDCl_3$) 72.4, 72.0; *m*/*z* (FAB) 602 (MH^+, 37%).

3.38. Preparation of (RS,3RS,αRS)- and (RS,3RS,αSR)-(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH${NH[CH(CH_3)Ph]}Ph (**64a** and **64b**)

Following representative procedure 1, *n*-BuLi (1.6 M, 3.1 ml, 4.92 mmol) and (*RS*)-α-methylbenzylamine (608 mg, 5.03 mmol) in THF (10 ml) and (*RS*)-(η^5-C_5H_5)Fe(CO)(PPh_3)COCH=CHPh (1.09 g, 2.01 mmol) in THF (10 ml) gave, after chromatography on alumina (Et_2O), a partially separable mixture of diastereoisomers, arbitrarily assigned as **64a** and **64b** (1.1 g, 91% overall); data for **64a**: $C_{41}H_{38}NO_2FeP$ requires C, 74.2; H, 5.8; N, 2.1%; Found C, 74.1; H, 5.5; N, 1.9%; ν_{max} (CH_2Cl_2) 1915 (C≡O), 1600 (C=O); δ_H (200 MHz, $CDCl_3$) 1.23 (3H, d, *J*6.5, C(α)*Me*), 1.98 (1H, br s, N*H*), 2.78 (1H, dd, *J*16.9, *J*3.3, $PhCHCH_A$), 3.30–3.72 (2H, m, C(α)*H* and $PhCHCH_B$), 3.74 (1H, m, $PhCHCH_2$), 4.36 (5H, s, $C_{5\ H5}$), 7.07–7.53 (20H, m, *Ph*); δ_P (100 MHz, $CDCl_3$) 76.2; δ_C (50 MHz, $CDCl_3$) 21.9, 54.5, 57.2, 72.6, 85.5, 126.4, 126.6, 126.9, 127.5, 128.4, 130.0, 133.5, 133.7, 136.7, 144.5, 147.0, 220.3; *m*/*z* (electrospray) 664 (MH^+, 100%). Data for **64b**: $C_{41}H_{38}NO_2FeP$ requires C, 74.2; H, 5.8; N, 2.1%; Found C, 74.2; H, 6.05; N, 2.0%; ν_{max} (CH_2Cl_2) 1915 (C≡O), 1600 (C=O); δ_H (200 MHz, $CDCl_3$) 1.21 (3H, d, *J*6.8, C(α)*Me*), 1.60 (1H, br s, N*H*), 2.78 (1H, m, $PhCHCH_A$), 3.06–3.14 (2H, m, C(α)H and $PhCHCH_B$), 3.27 (1H, m, $PhCHCH_2$), 4.41 (5H, s, C_5H_5), 6.92–7.50 (20H, m, *Ph*); δ_P (100 MHz, $CDCl_3$) 75.6; δ_C (50 MHz, $CDCl_3$) 25.2, 55.1, 57.4, 73.0, 85.5, 126.6, 127.2, 127.8, 128.2, 129.2, 130.4, 133.6, 133.7, 135.9, 143.9, 146.0, 220.5'; *m*/*z* (electrospray) 664 (MH^+, 100%).

3.39. Preparation of (RS,3RS,αRS)- and (RS,3RS,αSR)-(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH${NH[CH(CH_3)Ph]}^{i}Pr (**65a** and **65b**)

Following representative procedure 1, *n*-BuLi (1.6 M, 2.3 ml, 3.8 mmol) and (*RS*)-α-methylbenzylamine (466 mg, 3.85 mmol) in THF (10 ml) and (*RS*)-(η^5-C_5H_5)Fe(CO)(PPh_3)COCH=CHiPr (782 mg, 1.54 mmol) in THF (20 ml) gave, after chromatography on alumina (Et_2O), a partially separable mixture of diastereoisomers **65a** and **65b** (863 mg, 89% overall); data for **65a**: $C_{38}H_{40}NO_2FeP$ requires C, 72.5; H, 6.4; N, 2.2%; Found C, 72.7; H, 6.7; N, 2.1%; ν_{max} (CH_2Cl_2)

1915 (C≡O), 1605 (C=O); δ_H (200 MHz, $CDCl_3$) 0.61, 0.68 (2×3H, d, *J*6.8, $(CH_3)_2CH$), 1.19 (3H, d, *J*6.5, C(α)*Me*), 1.25 (1H, br s, N*H*), 1.30 (1H, m, $(CH_3)_2CH$), 2.34 (1H, br s, $COCH_2CH$), 2.52 (1H, dd, *J*16.0, *J*6.1, $COCH_A$), 3.20 (1H, dd, *J*16.0, *J*4.7, $COCH_B$), 3.65 (1H, q, *J*6.5, C(α)*H*), 4.36 (5H, s, C_5H_5), 7.18–7.55 (20H, m, *Ph*); δ_P (100 MHz, $CDCl_3$) 76.2; δ_C (50 MHz, $CDCl_3$) 17.6, 18.9, 25.2, 29.5, 55.3, 56.9, 66.6, 85.4, 126.7, 127.2, 128.2, 128.4, 129.9, 133.5, 133.7, 136.8, 147.3, 221.1; *m/z* (electrospray) 630 (MH^+, 100%). Data for **65b**: $C_{41}H_{38}NO_2FeP$ requires C, 72.5; H, 6.4; N, 2.2%; Found C, 72.6; H, 6.8; N, 2.2%; ν_{max} (CH_2Cl_2) 1910 (C≡O), 1600 (C=O); δ_H (200 MHz, $CDCl_3$) 0.47, 0.75 (2×3H, d, *J*6.9, $(CH_3)_2CH$), 1.27 (3H, d, *J*6.7, C(α)*Me*), 1.40 (1H, m, $(CH_3)_2CH$), 1.65 (1H, br s, N*H*), 2.74 (1H, m, $COCH_2CH$), 2.67 (1H, dd, *J*17.1, *J*7.0, $COCH_A$), 2.78 (1H, dd, *J*17.1, *J*5.0, $COCH_B$),3.70 (1H, m, C(α)*H*), 4.35 (5H, s, C_5H_5), 7.18–7.54 (20H, m, *Ph*); δ_P (100 MHz, $CDCl_3$) 76.3; δ_C (50 MHz, $CDCl_3$) 17.3, 17.8, 24.9, 28.3, 55.6, 56.0, 67.5, 85.4, 126.6, 127.1, 127.2, 128.1, 128.3, 129.8, 133.4, 133.6, 136.6, 146.7, 221.0; *m/z* (electrospray) 630 (MH^+, 100%).

*3.40. Preparation of (RS,3RS,αRS)-, (RS,3RS,αSR)-, and (RS,3SR,αSR)-(η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH$_2$CH{N[CH(CH$_3$)Ph]-[CH$_2$((OMe)$_2$Ph)]}Me (**68**, **69** and **70**)*

Following representative procedure 1, *n*-BuLi (1.6 M, 0.8 ml, 1.24 mmol) and (*RS*)-*N*-3,4-dimethoxy benzyl-*N*-α-methylbenzylamine (267 mg, 1.26 mmol) in THF (10 ml) and (*RS*)-**12** (200 mg, 0.42 mmol) in THF (5 ml) gave, after chromatography on alumina (Et_2O), an inseparable mixture of diastereoisomers **68**:**69**:**70** (260 mg, 83%) in a 94:3:3 ratio. The ^1H NMR spectrum of the mixture was readily assigned by comparison with those of homochiral **68, 69** and **70** prepared separately.

*3.41. Preparation of (R,3R,αR)-(η^5-C_5H_5)Fe(CO)-(PPh$_3$)COCH$_2$CH{N[CH(CH$_3$)Ph]-[CH$_2$((OMe)$_2$-Ph)]}Me (**68**)*

Following representative procedure 1, *n*-BuLi (1.6 M, 1.2 ml, 1.86 mmol), (*R*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamine (400 mg, 1.89 mmol) in THF (10 ml) and (*R*)-**12** (300 mg, 0.63 mmol) in THF (5 ml) gave, after work up and chromatography on alumina (DCM:E-t_2O 1:1), **68** (430 mg, 92%) as an orange solid; $C_{45}H_{46}NO_4FeP$ requires C, 71.9; H, 6.2; N, 1.9%; Found C, 72.3; H, 6.3; N, 1.8%; ν_{max} (CH_2Cl_2) 1905 (C≡O), 1600 (C=O); δ_H (300 MHz, $CDCl_3$) 0.50 (3H, d, *J*6.4, CH_3CHCH_2), 1.25 (3H, d, *J*6.8, C(α)*Me*), 2.47 (1H, dd, $J_{A,B}$16.4, $J_{A,CH}$10.0, CH_3CHCH_A), 2.87 (1H, d, *J*16.4, CH_3CHCH_B), 3.55 (2H, m, NCH_2), 3.79 (1H, q, *J*6.8, C(α)*H*), 3.88, 3.89 (2×3H, s, O*Me*), 4.20 (5H, s, C_5H_5), 6.78–7.00 (3H, m, *Ph*), 7.23–7.68 (20H, m, *Ph*); δ_C (63 MHz) 18.9, 19.0, 47.8, 49.8, 55.8, 56.0, 57.7, 71.4, 85.1, 111.0, 111.6, 119.9, 126.4, 127.7, 129.6, 128.0, 128.4, 133.3, 135.4, 136.6, 144.9, 147.7, 149.0, 220.5, 275.0; δ_P (100 MHz, $CDCl_3$) 72.4; *m/z* (FAB) 752 (MH^+, 3%).

*3.42. Preparation of (S,3S,αR)- and (S,3R,αR)-(η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH$_2$CH{N[CH(CH$_3$)Ph]-[CH$_2$((OMe)$_2$Ph)]}Me (**69** and **70**)*

Following representative procedure 1, *n*-BuLi (1.6 M, 1.2 ml, 1.86 mmol) and (*R*)-*N*-3,4-dimethoxybenzyl-*N*-α-methylbenzylamine (400 mg, 1.89 mmol) in THF (10 ml) and (*S*)-**12** (300 mg, 0.63 mmol) in THF (5 ml) gave, after chromatography on alumina (DCM:Et_2O 1:1), **69** and **70** (260 mg, 55%) as an inseparable 50:50 mixture of diastereoisomers; $C_{45}H_{46}NO_4FeP$ requires C, 71.9; H, 6.2; N, 1.9%; Found C, 71.6; H, 6.3; N, 2.2%; ν_{max} (CH_2Cl_2) 1907 (C≡O), 1604 (C=O); δ_H (300 MHz, $CDCl_3$) 0.52 (3H, d, *J*6.4, CH_3CHCH_2), 0.95 (3H, d, *J*6.4, CH_3CHCH_2), 1.19 (3H, d, *J*6.7, C(α)*Me*), 1.27 (3H, d, *J*6.7, C(α)*Me*), 2.36 (1H, dd, $J_{A,B}$13.4, $J_{A,CH}$9.9, CH_3CHCH_A), 2.71 (1H, d, *J*13.4, CH_3CHCH_B),3.02 (1H, m, CH_3CHCH_2), 3.03-3.33 (3H, m, CH_3CHCH_2 and CH_3CHCH_2), 3.57–3.72 (2×1H, m, C(α)*H*), 3.85, 3.86, 3.87 (4×3H, s, O*Me*), 4.26, 4.32 (2×5H, s, C_5H_5), 6.99–6.77 (2×3H, m, *Ph*), 7.21–7.49 (2×20H, m, *Ph*); δ_P (100 MHz, $CDCl_3$) 73.1, 72.0; *m/z* (FAB) 602 (MH^+, 3%).

*3.43. Preparation of (RS,3RS,αRS)-, (RS,3RS,αSR)-, and (RS,3SR,αSR)-(η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH$_2$CH{N[CH(CH$_3$)Ph]-[CH$_2$Ph]}Me (**72**, **73** and **74**)*

Following representative procedure 1, *n*-BuLi (1.6 M, 0.5 ml, 0.80 mmol), (*RS*)-*N*-benzyl-*N*-α-methylbenzylamine (180 mg, 0.84 mmol) in THF (25 ml) and (*RS*)-**12** (200 mg, 0.42 mmol) in THF (5 ml) gave, after chromatography on silica gel (petrol:Et_2O 4:1), an inseparable mixture of diastereoisomers **72**:**73**:**74** (190 mg, 67%) in a 96:2:2 ratio. The ^1H NMR spectrum of the mixture was readily assigned by comparison with those of homochiral **72**, **73** and **74** prepared separately.

*3.44. Preparation of (R,3R,αR)-(η^5-C_5H_5)Fe(CO)-(PPh$_3$)COCH$_2$CH{N[CH(CH$_3$)Ph]-[CH$_2$Ph]}Me (**72**)*

Following representative procedure 1, *n*-BuLi (1.6 M, 0.28 ml, 0.46 mmol), (*R*)-*N*-benzyl-*N*-α-methylbenzylamine (110 mg, 0.52 mmol) in THF (10 ml) and (*R*)-**12** (100 mg, 0.21 mmol) in THF (5 ml) gave, after chromatography on alumina (DCM:Et_2O 1:1), **72** (119

mg, 82%); $C_{43}H_{42}NO_2FeP$ requires C, 74.7; H, 6.1; N, 2.0%; Found C, 75.0; H, 6.0; N, 1.9%; $[\alpha]_D^{20}$ −43.2 (c 0.1, benzene); υ_{max} (CH_2Cl_2) 1913 (C≡O), 1601 (C=O); δ_H (300 MHz, $CDCl_3$) 0.52 (3H, d, *J*6.6, CH_3CHCH_2), 1.26 (3H, d, *J*6.9, C(α)*Me*), 2.48 (1H, dd, $J_{A,B}$16.2, $J_{A,CH}$10.5, CH_3CHCH_A), 2.93 (1H, d, *J*16.2, CH_3CHCH_B), 3.20 (1H, m, CH_3CHCH_2), 3.62 (2H, ABq, *J*16.2, NCH_2), 3.80 (1H, q, *J*6.8, C(α)*H*), 4.22 (5H, d, J_{PH}0.8, C_5H_5), 7.23–7.45 (25H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 19.1, 19.2 48.0, 50.3, 58.1, 71.1, 85.1, 126.4, 126.6, 127.8, 127.9, 128.1, 128.3, 129.8, 133.3, 133.5, 136.3, 137.1, 143.0, 145.0, 221.3, 276.2; δ_P (100 MHz, $CDCl_3$) 72.5; *m*/*z* (FAB) 692 (MH^+, 10%).

3.45. Preparation of (R,3R,αS)- and (R,3S,αS)-(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH${N[CH(CH_3)Ph]-[CH_2Ph]}Me (**73** and **74**)

Following representative procedure 1, *n*-BuLi (1.6 M, 0.57 ml, 0.92 mmol) and (*S*)-*N*-benzyl-*N*-α-methylbenzylamine (220 mg, 1.0 mmol) in THF (5 ml) and (*R*)-**12** (200 mg, 0.42 mmol) in THF (5 ml) gave a 50:50 mixture of diastereoisomers **73**:**74**. Recrystallisation from crude (petrol:DCM) gave a sample enriched in one diastereoisomer; $C_{43}H_{42}NO_2FeP$ requires C, 74.7; H, 6.1; N, 2.0%; Found C, 74.5; H, 6.2; N, 1.9%; δ_H (300 MHz, $CDCl_3$) 0.49 (3H, d, *J*6.3, CH_3CHCH_2), 1.28 (3H, d, *J*6.8, C(α)*Me*), 2.40 (1H, dd, $J_{A,B}$14.8, $J_{A,CH}$10.0, CH_3CHCH_A), 3.19–3.33 (2H, m, $CH_3CHCH_2$and CH_3CHCH_B), 3.62 (2H, ABq, *J*15.4, NCH_2), 3.84 (1H, q, *J*6.8, C(α)*H*), 4.29 (5H, s, C_5H_5), 7.20–7.41 (25H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 16.8, 19.1 48.7, 50.2, 58.2, 72.3, 85.2, 126.2, 126.3, 127.6, 127.7, 128.0, 128.4, 129.6, 133.3, 133.4, 136.3, 136.7, 142.9, 145.6, 220.5, 275.7; δ_P (100 MHz, $CDCl_3$) 72.2; *m*/*z* (FAB) 692 (MH^+, 15%); selected data for other diastereoisomer; δ_H (300 MHz, $CDCl_3$) 0.94 (3H, d, *J*6.2, CH_3CHCH_2), 1.16 (3H, d, *J*6.7, C(α)*Me*), 4.32 (5H, d, J_{PH}0.8, C_5H_5); δ_P (100 MHz, $CDCl_3$) 73.1.

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