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Unsymmetrical Iron P-NH-P' Catalysts for the Asymmetric Pressure Hydrogenation of Aryl Ketones

Samantha A. M. Smith^{[+][a]}, Paraskevi O. Lagaditis^{[+][a]}, Anne Lüpke^[b], Alan J. Lough^[a], Robert H. Morris^{*[a]}

Celebrating 100 years of CSC conferences in Canada and 150 years of the GDCh in Germany.

Abstract: The reductive amination of α -dialkylphosphine acetaldehydes with enantiopure β -aminophosphines is a new, versatile route to unsymmetrical tridentate (pincer) ligands P-NH-P'. Four new ligands $\text{PR}_2\text{CH}_2\text{CH}_2\text{NHCHR}'\text{CHR}''\text{PPh}_2$ ($\text{R} = \text{iPr}, \text{Cy}, \text{R}' = \text{Ph}, \text{CH}(\text{CH}_3)_2, \text{R}'' = \text{Ph}, \text{H}$) prepared in this way are used to make the iron(II) complexes $\text{mer-FeCl}_2(\text{CO})(\text{P-NH-P}')$ and $\text{mer-FeCl}(\text{H})(\text{CO})(\text{P-NH-P}')$. The hydride complex with the rigid ligand with $\text{R}' = \text{R}'' = \text{Ph}$ is an efficient and highly enantioselective homogeneous asymmetric pressure hydrogenation (APH) catalyst. Prochiral aryl ketones are reduced under mild conditions (THF, 0.1 mol% catalyst, 1 mol% KOtBu, 5–10 bar, 50 °C) to the (S)-alcohols, usually in enantiomeric excess (e.e.) greater than 90%. DFT calculations provide transition state structures for the enantiodetermining hydride transfer step.

The homogeneous asymmetric pressure hydrogenation of prochiral ketones provides an efficient route to valuable non-racemic alcohols.^[1] While the best catalysts are based on ruthenium, osmium and iridium,^[2] more sustainable iron-based systems show much promise.^[3] The most enantioselective reductions to date (over 95% e.e. in the alcohol product) were reported by the Gao group who used a mixture of $\text{Fe}_3(\text{CO})_{12}$ and an enantiopure 22-membered –PNNPN– macrocycle to catalyze the complete reduction of several aryl ketones.^[4] Our group reported the first well defined Fe(II) precatalysts for the APH of ketones, $\text{trans-[Fe(L)(CO)(PNNP)]}^{n+}$ containing enantiopure PNNP ligands but the e.e. and activity were low to moderate;^[5] such complexes are excellent for the asymmetric transfer hydrogenation (ATH) of ketones^[6] but cause a reduction in e.e. of the product alcohol at reaching the conversion determined by the equilibrium. An advantage of the irreversibility of the APH process is that complete conversion can be obtained with no degradation in the e.e. of the alcohol. Iron complexes with functionalized cyclopentadienyl and chiral ligands have so far displayed low activity

and selectivity for the APH of ketones^[7] but more promising results for the APH of imines.^[8]

Pincer iron complexes $\text{Fe}(\text{CO})\text{X}(\text{Y})(\text{PNP})$ (**A**, Figure 1), X, Y = halide, hydride, borohydride, PNP achiral ligand with trialkylphosphine and pyridyl donors, have excellent activity for the pressure hydrogenation of ketones as discovered by Milstein and coworkers.^[9] Similar complexes with achiral PNP ligands with trialkylphosphine and secondary amine donors (**B**) were shown by several groups to efficiently catalyze other hydrogenation and dehydrogenation applications.^[10]

Our group reported the first such pincer complex (**C**) with an enantiopure ligand as a precursor for the APH of ketones to alcohols with e.e. up to 89% and an imine to amine in 90% e.e.^[11] The mixed phosphine imine-type PNP' ligand of **C**, which forms in an iron-templated reaction, requires LiAlH_4 reduction while on the metal to produce the N-H functionality required for ketone activation and enantioselectivity.^[12] Some decomposition products were identified in this reaction including undesired $\text{Fe}(\text{CO})_2(\text{PNP}')$ complexes as a consequence of the dicarbonyl precursor structure.^[11, 13] Thus a monocarbonyl precursor complex was targeted. We also found that ligands forming five membered rings –Fe-NH-C-C-PR₂ form more active complexes than those that form 6-membered rings and that R = alkyl may provide more active catalysts than R = aryl.^[13] Zirakzadeh et al. have recently described the synthesis of similar complexes with enantiopure ferrocenylphosphine ligands; e.e. up to 81% were observed for the APH of aryl ketones.^[14] Kirchner's group has also prepared chiral iron complexes with unsymmetrical PNP' ligands for the hydrogenation of ketones but no e.e. was reported.^[15] Based on these developments, we targeted the synthesis of a new family of chiral pincer ligands and their iron APH catalysts as described here.

Figure 1. Iron hydrogenation and dehydrogenation catalysts with pincer ligands.

Reductive amination has proven to be a successful method for the synthesis of the new ligands **1** to **4** (Scheme 1).

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Supporting information for this article is given via a link at the end of the document. CCDC 1525651 (S-7), 1538240 (S-8) and 1525652 (S-10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Scheme 1. Synthesis of new chiral P-NH-P' ligands.

Two equivalents of the hydride reagent are added, the first to release the α -diisopropylphosphine acetaldehyde by deprotonation of the phosphonium dimer,^[16] and the second to reduce the imine formed by the condensation of this aldehyde with the primary amino group of the β -aminophosphine. Normally this method would yield tertiary amine products;^[17] however we find that the substituent α to the amine of the starting material lends enough steric bulk to protect the secondary amine from further reaction. Due to the availability of a range of enantiopure β -aminophosphines^[18] and our air- and moisture-stable phosphonium dimers,^[19] a large variety of these ligands can be synthesized in this manner. The characterization of ligands **1-4** is discussed in the Supporting Information.

Ligands **1-4** were stirred with anhydrous iron dichloride in tetrahydrofuran (THF) under CO gas to yield the complexes (**S,S**)-**5**, (**S,S**)-**6**, (**S**)-**7**, and (**S**)-**8** in high yields as purple solids (Scheme 2). They are synthesized as a single *trans*-dichloro isomer as signalled by a characteristic set of doublets with a large $^2J_{PP}$ coupling constant (177 Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The crystal structures of (**S**)-**7** (Figure 2) and (**S**)-**8** (Supporting Information) shows that they have the expected *mer* configuration with the C-H on the chiral carbon *anti* with respect to the N-H group. A very similar structure with the symmetrical $(\text{PiPr}_2\text{CH}_2\text{CH}_2)_2\text{NH}$ ligand has been reported.^[20]

Scheme 2. Synthesis of $\text{Fe}(\text{Cl})_2(\text{CO})(\text{P-NH-P}')$ complexes.

Figure 2. Structure of (**S**)-**7** (molecule A) with thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: Fe1-P1 2.279(1), Fe1-P2 2.254(1), Fe1-Cl1 2.329(1), Fe1-Cl2 2.316(1), Fe1-C29 1.757(5), Fe1-N1 2.081(4), N1-H 0.86(4), C29-O1 1.129(5); N1-Fe1-P1 85.2(1), N1-Fe1-P2 84.7(1), P2-Fe1-P1 169.99(5), Cl2-Fe1-Cl1 171.02(5), C29-Fe1-N1 177.8(2).

The monohydride complexes are prepared by treating the dichloro complexes with Superhydride (LiHBEt_3) at -30° (Scheme 3). (**S,S**)-**9** exists as predominantly (87%) one isomer in solution, with characteristic $^{31}\text{P}\{^1\text{H}\}$ spectra displaying two doublets with a large coupling constant $^2J_{PP}$ (138 Hz), again suggesting a *mer* configuration of the complex. The major isomer has an associated doublet of doublet pattern in the hydride region of the ^1H NMR spectrum with a chemical shift of -21.5 ppm. Minor amounts of two other isomers are present (see SI). Complex (**S,S**)-**6** was reacted with Superhydride, however the reaction produced a mixture of free ligand and several unidentified phosphorus-containing species. The spectra of (**S**)-**10** are complex because of the presence of four isomers with doublet of doublet or triplet hydride resonances at -20.47 ppm (5%), -20.96 (22%), -21.40 (31%) and -22.05 ppm (42%). Clearly the extra phenyl group in (**S,S**)-**9** is needed to restrict the number of diastereomers. One of the isomers of (**S**)-**10** has been crystallographically characterized as shown in Figure 3. The N-H and Fe-H bonds are almost parallel with a dihedral angle H-N1-Fe1-H of 7.0° . In the crystal structure with the symmetrical $(\text{PiPr}_2\text{CH}_2\text{CH}_2)_2\text{NH}$ ligand, the N-H is found instead parallel to the Fe-Cl unit.^[20] The synthesis of (**S**)-**11** was not selective with a mixture of up to six hydride complexes shown in the ^1H NMR spectrum. This complex was not tested due to the complicated mixture of isomers.

Scheme 3. Synthesis of iron chloro(hydrido) complexes.

Figure 3 Crystal structure of **(S)-10**. Selected bond lengths [Å] and angles [°]: Fe1-H 1.40(4), Fe1-C29 1.717(4), Fe1-N1 2.093(3), Fe1-P2 2.189(1), Fe1-P1 2.218(1), Fe1-Cl1 2.4116(1), O1-C29 1.164(5), N1-H 0.90(6); N1-Fe1-P1 85.8(1), N1-Fe1-P2 83.7(1), H-Fe1-N1 84.1(16), C29-Fe1-N1 171.89(2), P2-Fe1-P1 164.79(5), H-Fe1-Cl1 170(1), C29-Fe1-Cl1 100.1(2), N1-Fe1-Cl1 87.7(1).

The chloro(hydrido) complexes **(S,S)-9** and **(S)-10** were tested as catalysts for the APH of selected ketones in THF in the presence of base (Scheme 4). These systems were found to be very active under the conditions of 10 bar of H₂, 50 °C, of ketone: catalyst: KOtBu = 1000:1:10; oxygen must be rigorously excluded in the preparation of the catalyst solution and its injection into the purged pressure reactor. The complex **(S)-10** containing one substituent on the backbone of the ligand when tested for the APH of acetophenone gave low to moderate enantioselectivity depending on the reaction conditions (50–80%). Fortunately **(S,S)-9** with two phenyl groups on the backbone yields excellent results, quantitatively reducing a variety of ketones to the (S)-alcohols in high e.e. (Table 1, Figure 4). The second phenyl substituent on the ligand backbone of this complex is clearly important to lock the PPh₂ group into a rigid, asymmetric structure; the complex **C** (Figure 1) also has this feature, and both **(S,S)-9** and **C** have similar activity and are much more enantioselective than **(S)-10** and other complexes that just have one substituent next to the NH.^[13]

Scheme 4. The APH of ketones

Table 1. Results of ketone APH as in Scheme 4 with catalyst **(S,S)-9**.^[a]

Entry	R	R'	Conversion (%) ^[b]	Time (min)	e.e. (S) (%) ^[b]
1	CH ₃	H	>99	90	95
2	CH ₂ CH ₃	H	>99	120	96
3	CH ₃	<i>o</i> -Cl	>99	90	93
4	C ₆ H ₁₁	H	38	90	62
5	CH ₃	<i>m</i> -(CF ₃) ₂	8	60	86
6	CH ₃	<i>p</i> -Cl	>99	60	90
7	CH ₃	<i>p</i> -CH ₃	>99	60	94

[a] reaction conditions for **(S,S)-9**: 10 bar H₂, 0.1 mol% catalyst, 1 mol% KOtBu, 50 °C, 10 mL THF; [b] conversion and e.e. determined by chiral GC.

The APH of acetophenone (entry 1, Table 1) using **(S,S)-9** produced (S)-1-phenylethanol in much higher e.e. (95%) than our previously reported system based on catalyst **C** (89%),^[11] Gao's system gave 97% e.e. but at longer reaction times, higher pressure, higher catalyst and base loading. Similar results are obtained when acetophenone is hydrogenated using **(S,S)-9** with 5 bar H₂. The hydrogenation of propiophenone (entry 2) took longer than the standard 90 min. reaction, but resulted in quantitative conversion at 120 min. with 96% e.e. (S). The *ortho*-chloro substituted ketone (entry 3) is considered a challenging substrate for asymmetric reduction^[21] but it is efficiently and selectively reduced by this catalyst system. The product, (S)-1-(2-chlorophenyl)ethanol, has been identified as a key chiral intermediate in the synthesis of a new class of chemotherapeutic drugs.^[22] Cyclohexyl phenyl ketone (entry 4) proved to be a difficult substrate to reduce, with less than 40% conversion and low e.e. The APH of 3',5'-bis(trifluoromethyl)acetophenone (entry 5) resulted in a very low conversion, possibly because the acidic alcohol product deactivates the catalyst. *Para*-methylacetophenone (entry 7) is reduced with somewhat higher enantioselectivity (94% (S)) than *para*-chloroacetophenone (90%, entry 6). This suggests that the enantioselectivity can be influenced by the electronics of the ketone substrate, perhaps by affecting the strength of the NH-O(ketone) hydrogen bond which orients the ketone in the hydride transfer step.^[12]

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Figure 4. Other ketones reduced by the (*S,S*)-**9** system (except **16**).

The difference in position of the acetyl functionality in acetylnaphthone substrates **12** and **13** affected the number of turnovers in 90 min., 1000 TON for **12** vs 610 for **13**, while both were reduced in high e.e. (*R*)-1-(1-naphthyl)ethanol has been used to desymmetrize prochiral 3-substituted glutaric anhydrides, giving the chiral building blocks for (+)-compactin, an HMG-CoA-reductase inhibitor.^[23] 2-Acetylfuran (**14**) was reduced quantitatively to the alcohol with 95% e.e. (*S*). This chiral product can be used for the synthesis of macrosphelide B, shown to be a strong inhibitor for the adhesion of human leukemia HL-60 cells to human umbilical-vein cells.^[24] 3-Methylbutan-2-one (**15**), a challenging aliphatic ketone, was successfully reduced quantitatively but with low enantioselectivity, and surprisingly, with the (*R*)-alcohol in excess. Oddly the very similar system with catalyst **C** provided the (*S*)-alcohol in 46% e.e.^[11] The even more challenging 3,3-dimethylbutan-2-one (**16**) proved to be too sterically crowded for (*S,S*)-**9** to reduce. Further exploration of the activity and enantioselectivity of (*S,S*)-**9** is currently in progress.

Previous work has provided strong evidence for a *mer* FeH₂(CO)L structure with *trans* dihydrides, where L is a P-NH-P ligand, as the active catalyst that transfers a hydride to the ketone.^[10b, 10e, 10g, 12c] The transition state structure producing (*S*)-1-phenylethanol by attack of a hydride in *trans*-FeH₂(CO)((*S,S*)-**1**) on acetophenone was calculated using DFT (Figure 5) and found to be 1.6 kcal/mol lower in energy than that producing the (*R*) alcohol (Supporting information). In this structure the phenyl group of the ketone lies over the isopropyl groups while the smaller methyl group is against a phenyl of the PPh₂, that is locked into position by the adjacent asymmetric array of phenyl groups which also lock the five-membered -PCHPhCHPhNHFe- ring by taking the favourable equatorial positions.

Figure 5. The transition state structure of the transfer of a hydride from the dihydride of the (*S,S*)-**9** system to acetophenone to give the (*S*) alcohol. Hydrogens on the ketone and on the ligand other than the NH have been deleted for clarity.

In conclusion, a new method of ligand synthesis has been successfully utilized to produce four new iron dichloride complexes and four new iron hydride complexes, one of which shows great promise for the enantioselective reduction of ketones. The use of the well defined precatalyst (*S,S*)-**9** allows the quantitative APH of a variety of ketones to enantiomerically enriched alcohols in up to 96% e.e. *Ortho*-chloroacetophenone, 1-acetylnaphthone, and 2-acetylfuran have been reduced quantitatively with high enantioselectivities to alcohols of interest to the pharmaceutical industry. We have disclosed a versatile method that allows the synthesis of a wide range of catalyst structures, a flexibility often needed when matching the catalyst with the substrate to attain high levels of enantioselection.

Experimental Section

See the Supporting Information.

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Highly enantioselective and active iron catalyst.

The reductive amination of α -dialkylphosphine acetaldehydes with enantiopure β -aminophosphines is a new, versatile route to unsymmetrical tridentate (pincer) ligands P-NH-P'. Several prochiral aryl ketones are reduced to the (S)-alcohols, usually in e.e. greater than 90%, using 0.1 mol% of an iron complex *mer*-FeCl(H)(CO)(P-NH-P') at 5 to 10 bar H₂ and 50 °C.

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Synthesis of (S,S)-(Cy) ₂ PCH ₂ CH ₂ N(H)CH(Ph)CH ₂ P(Ph) ₂ 2 :	S5
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Synthesis of (S)-(iPr) ₂ PCH ₂ CH ₂ N(H)CH(CH(CH ₃) ₂)CH ₂ P(Ph) ₂ 4 :	S11
Synthesis of <i>trans</i> -Fe(Cl) ₂ (CO)[(S,S)-(iPr) ₂ PCH ₂ CH ₂ N(H)CH(Ph)CH(Ph)P(Ph) ₂] (S,S)-5 :	S15
Synthesis of <i>trans</i> -Fe(Cl) ₂ (CO)[(S,S)-(Cy) ₂ PCH ₂ CH ₂ N(H)CH(Ph)CH(Ph)P(Ph) ₂] (S,S)-6 :	S19
Synthesis of <i>trans</i> -Fe(Cl) ₂ (CO)[(S)-(iPr) ₂ PCH ₂ CH ₂ N(H)CH(Ph)CH ₂ P(Ph) ₂] (S)-7 :	S22
Synthesis of <i>trans</i> -Fe(Cl) ₂ (CO)[(S)-(iPr) ₂ PCH ₂ CH ₂ N(H)CH(CH(CH ₃) ₂)CH ₂ P(Ph) ₂] (S)-8 :	S27
Synthesis of Fe(H)(Cl)(CO)[(S,S)-(iPr) ₂ PCH ₂ CH ₂ N(H)CH(Ph)CH(Ph)P(Ph) ₂] (S,S)-9 :	S30
Synthesis of Fe(H)(Cl)(CO)[(S,S)-(Cy) ₂ PCH ₂ CH ₂ N(H)CH(Ph)CH(Ph)P(Ph) ₂]:	S33
Synthesis of Fe(H)(Cl)(CO)[(S)-(iPr) ₂ PCH ₂ CH ₂ N(H)CH(Ph)CH ₂ P(Ph) ₂] (S)-10 :	S35
Synthesis of Fe(H)(Cl)(CO)[(S)-(iPr) ₂ PCH ₂ CH ₂ N(H)CH(iPr)CH ₂ P(Ph) ₂] (S)-11 :	S37
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Pro-(<i>R</i>)-ketone adduct with dihydride	S58
(<i>R</i>)-transition state	S61
(<i>R</i>)-alkoxide adduct	S63

General procedures.

All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. All solvents were degassed and dried using standard procedures prior to all manipulations and reactions unless stated otherwise. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma Aldrich, degassed, and dried over activated molecular sieves prior to use. (1*S*,2*S*)-2-(diphenylphosphino)-1,2-diphenylethylamine was purchased from ACROS Organics, (S)-1-(diphenylphosphino)-2-phenylethylamine, and (S)-1-(diphenylphosphino)-3-methyl-2-butylamine was purchased from Alfa Aesar. All other reagents were purchased from commercial sources and utilized without further purification. NMR spectra were recorded at ambient temperature and pressure using a Agilent 500 MHz spectrometer with a OneNMR H/F{X} Probe (500 MHz for ^1H , 126 MHz for ^{13}C and 202 MHz for ^{31}P), or an Agilent DD2-600 MHz spectrometer (600 MHz for ^1H , 151 MHz for ^{13}C and 243 MHz for ^{31}P) unless stated otherwise. The ^1H and ^{13}C NMR were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). All ^{31}P chemical shifts were measured relative to 85% phosphoric acid as an external reference. Gas Chromatography was done on a Shimadzu GC-2014 Gas Chromatograph equipped with a chiral column (CP chirasil-Dex CB 25 m x 2.5 mm x 2.5 μm) to determine substrate conversion and enantiopurity. Hydrogen and nitrogen gases were used as the mobile phase. All of the hydrogenation reactions were performed in a 50 mL stainless steel Parr Hydrogenation reactor at constant temperatures and pressures. The temperature was maintained at 50 $^\circ\text{C}$ using a constant temperature water bath and was purged of oxygen by flushing the reactor several times with 10 atm of $\text{H}_{2(\text{g})}$. The elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

Synthesis of (S,S)-(iPr) $_2$ PCH $_2$ CH $_2$ N(H)CH(Ph)CH(Ph)P(Ph) $_2$ 1:

(1*S*,2*S*)-2-(diphenylphosphino)-1,2-diphenylethylamine (100 mg, 2.62×10^{-4} mol), iPr-phosphonium dimer (76 mg, 1.57×10^{-4} mol, 0.6 eq.), and sodium(trisacetoxo)borohydride (117 mg, 5.50×10^{-4} mol, 2.1 eq.) were mixed in THF (10 mL) and stirred over 3 Å MS for 16 hours. Solvent was removed in vacuo and the residue was redissolved in dichloromethane. The solution was transferred into a Schlenk flask and placed on a Schlenk line under argon. A solution of saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ and a second solution of distilled water were degassed and placed under argon. An air-free wash with the NH_4Cl solution (2x10 mL) then with water (2x10 mL). The solution was dried over MgSO_4 , then filtered. The solvent was removed to give a colourless solid. Yield 80 mg (58%). ^1H NMR (600 MHz, CD_2Cl_2) δ : 0.87-0.96 (m, 12 H, $\text{C}(\text{CH}_3)_2$), 1.57 ppm (m, 2 H, $\text{CH}(\text{CH}_3)_2$), 2.34 ppm (d, 1H, CH), 2.46 ppm (s, 1 H, CH), 4.05 ppm (m, 2 H, CH_2), 6.87-7.80 (m, 20 H). ^{31}P { ^1H } NMR (242 MHz, CD_2Cl_2) δ : -2.04 ppm (s, iPr_2P), -8.50 (s, Ph_2P). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[\text{C}_{34}\text{H}_{42}\text{NP}_2]^+$: 526.2787, found: 526.2788.

Figure S1: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (242 MHz, CD_2Cl_2) of $(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2$ **1**

Figure S2: ^1H NMR spectrum (600 MHz, CD_2Cl_2) of $(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2$ **1**

Figure S3: gCOSY (600 MHz, CD_2Cl_2) of $(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2$ **1**

Synthesis of $(S,S)\text{-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH}_2\text{P(Ph)}_2$ **2**:

Follows the procedure above with $(1S,2S)\text{-2-(diphenylphosphino)-1,2-diphenylethylamine}$ (250 mg, 6.55×10^{-4} mol), and Cy-phosphonium dimer (211 mg, 3.28×10^{-4} mol). This reaction yielded a colourless powder. Yield 108 mg, 54%. ^1H NMR (500 MHz, CD_2Cl_2) δ : 1.01-1.73 (m, 24 H, $\text{C}_6\text{H}_{11} + \text{CH}_2\text{PCy}_2$), 2.36 (bm, 1 H, CHNH), 2.45 (m, 1 H, CHNH), 4.08 (bm, 2H, overlapping $\text{CH(Ph)} \times 2$), 6.90-7.21 (m, 14 H, Ar-H), 7.46 (m, 3H, Ar-H), 7.83 (m, 3 H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 124 MHz): 133.93 (d, $^2J_{\text{CP}} = 20$ Hz, C_{Ar}), 133.76 (d, $J_{\text{CP}} = 20$ Hz, C_{Ar}), 130.5 (C_{Ar}), 130.4 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 128.3 (C_{Ar}), 128.0 (C_{Ar}), 127.7 (C_{Ar}), 127.4 (C_{Ar}), 127.3 (PC_{Ar}), 126.7 (C_{Ar}), 125.9 (C_{Ar}), 65.6 (d, $J_{\text{CP}} = 20$ Hz, CHPh), 51.9 (d, $J_{\text{CP}} = 16$ Hz, CHPh), 46.3 (d overlapped, $\text{CH}_2\text{CH}_2\text{PiPr}_2$), 46.3 (d overlapped, $\text{CH}_2\text{CH}_2\text{PiPr}_2$), 33.2 (m, C_{Cy}), 30.2 (m, C_{Cy}), 28.9 (C_{Cy}), 27.3 (d, $J_{\text{CP}} = 12$ Hz, C_{Cy}), 27.2 (CH_2PCy_2), 26.5 (C_{Cy}). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2) δ : -8.55 ppm (bs, Cy_2P), -10.73 (s, Ph_2P). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[\text{C}_{40}\text{H}_{50}\text{NP}_2]^+$: 607.3447, found: 607.3430.

Figure S4: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, CD_2Cl_2) of $(S,S)\text{-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2$ **2**

Figure S5: ^1H NMR spectrum (500 MHz, CD_2Cl_2) of $(S,S)\text{-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2$ **2**

Figure S6: ^1H gCOSY (500 MHz, CD_2Cl_2) of $(S,S)\text{-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2$ **2**

Figure S7: $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CD_2Cl_2) of $(S,S)\text{-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2$ **2**

Synthesis of $(S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH}_2\text{P(Ph)}_2$ **3**:

Follows the procedure above with $(S)\text{-1-(diphenylphosphino)-2-phenylethylamine}$ (100 mg, 3.27×10^{-4} mol), and $\text{iPr-phosphonium dimer}$ (95 mg, 1.96×10^{-4} mol, 0.6 eq.). This reaction yielded a colourless, viscous oil. Yield 110 mg (75%). ^1H NMR (600 MHz, CD_2Cl_2) δ : 0.87-0.95 (m, 12 H, $\text{C(CH}_3)_2$), 1.3 (m, 1 H, $\text{CH(CH}_3)_2$), 1.56 (m, 3 H, 2 CH plus $\text{CH(CH}_3)_2$), 2.66 (bm, 1H, CH), 2.79 (bm, 2 H, CH), 3.4 (bm, 1H, CH), 4.03 (bm, 1 H, CH_2), 7.21-7.51 (m, 15 H). $^{31}\text{P}\{^1\text{H}\}$ NMR (242 MHz, CD_2Cl_2) δ : -0.71 ppm (bs, iPr_2P), -22.76 (s, Ph_2P). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[\text{C}_{28}\text{H}_{38}\text{NP}_2]^+$: 450.2474, found: 450.2472.

Figure S8: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (242 MHz, CD_2Cl_2) of $(S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH}_2\text{P(Ph)}_2$ **3**

Figure S9: ^1H NMR spectrum (600 MHz, CD_2Cl_2) of $(S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH}_2\text{P(Ph)}_2$ **3**.

Synthesis of $(S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(CH(CH}_3)_2)\text{CH}_2\text{P(Ph)}_2$ **4**:

Follows the procedure above with (S) -1-(diphenylphosphino)-3-methyl-2-butylamine (300 mg, 1.11 mmol), $i\text{Pr}$ -phosphonium dimer (267 mg, 0.553 mmol), and trisacetoxy borohydride (469 mg, 2.21 mmol). This reaction yielded a colourless, viscous oil. Yield 320 mg (70%). ^1H NMR (500 MHz, CD_2Cl_2) δ : 0.97-1.13 (m, 18 H, $\text{C(CH}_3)_2 \times 3$), 1.73 (sept, 3 H, $\text{CH(CH}_3)_2 \times 3$), 1.86 (bm, 1 H, CHPiPr_2), 2.31 (bm, 1 H, CHPiPr_2), 2.47 (dd, 1 H, CH(iPr)), 2.53 (bm, 1 H, CHPPH_2), 2.75 (bm, 1 H, CHPPH_2), 3.01 (bm, 1 H, CHNH), 3.15 (bm, CHNH), 7.35-7.49 (m, 10 H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 124 MHz): 134.9 (d, $J_{\text{CP}} = 20$ Hz, C_{Ar}), 134.6 (d, $^2J_{\text{CP}} = 19$ Hz, C_{Ar}), 132.9 (d, $^2J_{\text{CP}} = 9$ Hz, C_{Ar}), 132.6 (d, $^2J_{\text{CP}} = 10$ Hz, C_{Ar}), 131.0 (C_{Ar}), 130.9 (C_{Ar}), 130.8 (C_{Ar}), 62.7 (d, $^2J_{\text{CP}} = 16$ Hz, CHPPH_2), 48.6 (d, $^2J_{\text{CP}} = 35$ Hz, CHNH), 32.4 (d, $^2J_{\text{CP}} = 7$ Hz, CH(iPr)), 30.3 (m, CHPiPr_2), 25.1 (dd, $^2J_{\text{CP}} = 12$, 8 Hz, C_{iPr}), 21.7 (dd, $^2J_{\text{CP}} = 16$, 2 Hz, C_{iPr}), 20.6 (m, C_{iPr}), 20.4 (d, $J_{\text{CP}} = 9$ Hz, C_{iPr}), 19.4 (d, $J_{\text{CP}} = 54$ Hz, C_{iPr}). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2) δ : 0.21 (s, iPr_2P), -21.98 ppm (s, Ph_2P). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[\text{C}_{25}\text{H}_{40}\text{NP}_2]^+$: 416.2630, found: 416.2628.

Figure S10: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, CD_2Cl_2) of $(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(CH(CH}_3)_2)\text{CH}_2\text{P(Ph)}_2$ **4**

Figure S12: ^1H -gCOSY (500 MHz, CD_2Cl_2) of $(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(CH(CH}_3)_2\text{)CH}_2\text{P(Ph)}_2$ **4**

Figure S13: $^{13}\text{C}\{^1\text{H}\}$ (126 MHz, CD_2Cl_2) of $(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(CH(CH}_3)_2\text{)CH}_2\text{P(Ph)}_2\text{ 4}$

Synthesis of $\text{trans-Fe}(\text{Cl})_2(\text{CO})[(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2]$ (S,S)-5:

A Schlenk flask was charged with $(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2$ (80 mg, 0.153 mmol), FeCl_2 (19 mg, 0.153 mmol) and THF (15 mL). The flask was degassed and exposed to $\text{CO}_{(\text{g})}$ (1 atm). The colourless slurry immediately turned dark purple. After 1h, the solvent was removed and the purple residue was dissolved with benzene, filtered and dried. (66 mg, 64 %). ^1H NMR (C_6D_6 , 600 MHz): 7.91 (m, 2H, PArH), 7.80 (m, 2H, PArH), 7.48 (m, 1H, ArH), 7.15 (m, 1H, ArH), 7.02 (m, 2H, PArH), 6.89 (m, 2H, ArH), 6.81 (m, 3H, ArH), 6.74 (m, 2H, PArH), 6.70 (m, 1H, ArH), 6.62 (m, 2H, ArH), 6.55 (m, 1H, ArH), 5.75 (m, 1H, NH), 5.28 (t, $J_{\text{HH}} = 12$ Hz, 1H, NHCHPh), 4.91 (dd, $J_{\text{HH}} = 12$ Hz, $J_{\text{HP}} = 7$ Hz, 1H, CH(Ph)PPh_2), 3.13 (m, 1H, $\text{CH}_2\text{CH}_2\text{PiPr}_2$), 2.87 (dd, $J_{\text{HH}} = 12$ Hz, $J_{\text{HP}} = 35$ Hz, 1H, $\text{CH}_2\text{CH}_2\text{PiPr}_2$), 2.66 (m, 2H, $\text{PCH(CH}_3)_2$), 1.77 (t, $J_{\text{HH}} = 14$ Hz, 1H, CH_2PiPr_2), 1.67 (m, $J_{\text{HH}} = 14$ Hz, 1H, CH_2PiPr_2), 1.49 (dd, $J_{\text{HH}} = 7$ Hz, $J_{\text{HP}} = 14$ Hz, 3H, $\text{PCH(CH}_3)_2$), 1.38 (dd, $J_{\text{HH}} = 7$ Hz, $J_{\text{HP}} = 14$ Hz, 3H, $\text{PCH(CH}_3)_2$), 1.28 (dd, $J_{\text{HH}} = 7$ Hz, $J_{\text{HP}} = 12$ Hz, 3H, $\text{PCH(CH}_3)_2$), 1.14 (dd, $J_{\text{HH}} = 7$ Hz, $J_{\text{HP}} = 12$ Hz, 3H, $\text{PCH(CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 124 MHz): 223.9 (t, $^2J_{\text{CP}} = 22$ Hz, CO), 138.1 (d, $J_{\text{CP}} = 9$ Hz, PC_{Ar}), 132.5 (d, $J_{\text{CP}} = 8$ Hz, PC_{Ar}), 131.2 (C_{Ar}), 130.5 (PC_{Ar}), 129.6 (C_{Ar}), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 128.4 (C_{Ar}), 127.9 (C_{Ar}), 127.6 (PC_{Ar}), 126.8 (d, $J_{\text{CP}} = 9$ Hz, PC_{Ar}), 126.4 (C_{Ar}), 123.4 (C_{Ar}), 71.3 (dd, $J_{\text{CP}} = 3, 13$ Hz,

CHPh), 55.7 (d, $J_{CP} = 5$ Hz, CH(Ph)PPh₂), 47.6 (m, CH₂CH₂PiPr₂), 26.2 (d, $J_{CP} = 12$ Hz, CH₂PiPr₂), 23.3 (d, $J_{CP} = 21$ Hz, CH(CH₃)₂), 21.2 (d, $J_{CP} = 17$ Hz, CH(CH₃)₂), 20.2 (CH₃), 19.5 (CH₃), 18.9 (CH₃), 18.3 (CH₃). ³¹P{¹H} NMR (C₆D₆, 242 MHz): 71.1 (d, $^2J_{PP} = 177$ Hz, PiPr₂), 69.5 (d, $^2J_{PP} = 177$ Hz, PPh₂) ppm. EA: Calc. for C₃₅H₄₁Cl₂FeNOP₂·0.5C₆H₆: Expected C, 63.4; H, 6.2; N, 1.9. Found: C, 63.6, H, 5.6, N, 1.8. AT-IR 1940 cm⁻¹ ν(CO).

Figure S14: ¹H NMR spectrum (600 MHz, C₆D₆) of *trans*-Fe(Cl)₂(CO)[(S,S)-(iPr)₂PCH₂CH₂N(H)CH(Ph)CH(Ph)P(Ph)₂] (**S,S**)-**5**.

Figure S15: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (242 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2)]$ (***S,S***)-5.

Figure S16: ^1H COSY NMR spectrum (600 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2]$ (**S,S**)-**5**.

Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (124 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2]$ (**(S,S)-5**).

Synthesis of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(S,S)\text{-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2]$ (**(S,S)-6**):

The procedure above was followed with (*S,S*)-(*Cy*)₂PCH₂CH₂N(H)CH(Ph)CH(Ph)P(Ph)₂ (216 mg, 0.357 mmol) and FeCl₂ (33 mg, 0.206 mmol). Yielded a purple solid (203 mg, 74%). ^1H NMR (CD_2Cl_2 , 600 MHz): 7.86-6.79 (m, 20H, *PARH*), 5.54 (td, $J_{\text{HH}}=12$, 4 Hz, 1H, *NH*), 5.13 (td, $J_{\text{HH}}=12$, 3 Hz, 1H, *NHCH(Ph)*), 4.86 (dd, $J_{\text{HH}}=12$ Hz, $J_{\text{HH}}=7$ Hz, 1H, *CH(Ph)PPh*₂), 3.21-3.06 (m, 2H, *CH*₂CH₂PCy₂), 2.43 (q, $J_{\text{HH}}=12$, 8 Hz, 2H, *CH*₂CH₂Pr₂), 2.28-1.12 (m, 22H, PC₆H₁₁). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 242 MHz): 70.1 (d, $^2J_{\text{PP}}=173$ Hz, *PiPr*₂), 61.5 (d, $^2J_{\text{PP}}=173$ Hz, *PPh*₂) ppm. AT-IR 1946 cm^{-1} $\nu_{(\text{CO})}$. EA Calc. for C₄₁H₄₉Cl₂FeNOP₂·0.7C₆H₆: C, 66.59; H, 6.59; N, 1.72. Found: C, 66.88; H, 6.65; N, 1.74.

Figure S18: ^1H NMR spectrum (500 MHz, CD_2Cl_2) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(S,S)\text{-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2]$ (*S,S*)-6.

Figure S19: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, CD_2Cl_2) of *trans*-Fe(Cl)₂(CO)[(S,S)-(Cy)₂PCH₂CH₂N(H)CH(Ph)CH(Ph)P(Ph)₂] (**(S,S)-6**).

Figure S20: ^1H COSY NMR spectrum (600 MHz, CD_2Cl_2) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(\text{S},\text{S})-(\text{Cy})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{P}(\text{Ph})_2]$ (**S,S**)-**6**.

Synthesis of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(\text{S})-(i\text{Pr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-**7**:

A Schlenk flask was charged with (*S*)-(*i*Pr) $_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}_2\text{P}(\text{Ph})_2$ (50 mg, 0.114 mmol), FeCl_2 (15 mg, 0.114 mmol) and THF (15 mL). The flask was degassed and exposed to CO (1 atm). The colourless slurry immediately turned dark purple. After 1h, the solvent was removed and the purple residue was dissolved with benzene, filtered and dried. (40 mg, 60%). Crystals suitable for X-ray crystallography were obtained from a slow diffusion of pentane into benzene. ^1H NMR (C_6D_6 , 500 MHz): 8.03 (m, 2H, *PARH*), 7.79 (m, 2H, *PARH*), 7.05 (m, 6H, *PARH*), 6.97 (m, 3H, *ArH*), 5.30 (m, 1H, *NH*), 4.73 (m, 1H, *CHPh*), 3.05 (m, 3H, $\text{CH}_2\text{CH}_2\text{PiPr}_2$, CH_2PPh_2), 2.72 (m, 2H, $\text{CH}(\text{CH}_3)_2$, $\text{CH}_2\text{CH}_2\text{PiPr}_2$), 2.51 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.75 (m, $J_{\text{HH}} = 14$ Hz, 1H, CH_2PiPr_2), 1.55 (dd, $J_{\text{HH}} = 7$ Hz, $J_{\text{HP}} = 15$ Hz, 3H, CH_3), 1.39 (dd, $J_{\text{HH}} = 7$ Hz, $J_{\text{HP}} = 15$ Hz, 4H, CH_3 , CH_2PiPr_2), 1.31 (dd, $J_{\text{HH}} = 7$ Hz, $J_{\text{HP}} = 15$ Hz, 3H, CH_3), 1.14 (dd, $J_{\text{HH}} = 7$ Hz, $J_{\text{HP}} = 15$ Hz, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 124 MHz): 224.8 (t, $J_{\text{CP}} = 25$ Hz, CO), 134.0 (d, $J_{\text{CP}} = 9$ Hz, PC_{Ar}), 132.2 (d, $J_{\text{CP}} = 8$ Hz, PC_{Ar}), 129.9 (s, C_{Ar}), 129.2 (s, C_{Ar}), 127.9 (PC_{Ar} , C_{Ar}), 64.3 (dd, $J_{\text{CP}} = 3$, 8 Hz, *CHPh*), 47.1 (m, $\text{CH}_2\text{CH}_2\text{PiPr}_2$), 37.3 (d, $J_{\text{CP}} = 15$ Hz, CH_2PPh_2), 26.7 (d, $J_{\text{CP}} = 13$ Hz, CH_2PiPr_2), 23.9 (d, $J_{\text{CP}} = 22$ Hz, $\text{CH}(\text{CH}_3)_2$), 22.5 (d, $J_{\text{CP}} = 19$ Hz, $\text{CH}(\text{CH}_3)_2$), 20.3 (s, CH_3), 19.9 (s, CH_3), 19.2 (s, CH_3), 18.6 (s, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): 71.2 (d, $J_{\text{PP}} = 177$ Hz, PiPr_2), 52.8 (d, $J_{\text{PP}} = 177$ Hz, PPh_2) ppm. AT-IR 1941 cm^{-1} $\nu_{(\text{CO})}$. EA: Expected 57.64 C%, 6.17 H%, 2.32 N%. Found: 57.50 C%, 5.89 H%, 2.04 N%

Figure S21: ^1H NMR spectrum (500 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH}_2\text{P(Ph)}_2]$ (**S**)-**7**.

Figure S22: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(\text{S})-(\text{iPr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-**7**.

Figure S23: ^1H COSY NMR spectrum (500 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH}_2\text{P(Ph)}_2]$ (**S**)-**7**.

Figure S24: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (124 MHz, C₆D₆) of *trans*-Fe(Cl)₂(CO)[(S)-(iPr)₂PCH₂CH₂N(H)CH(Ph)CH₂P(Ph)₂] (**S**)-**7**.

Figure S25: H-P HMBC (500 MHz, C₆D₆) of *trans*-Fe(Cl)₂(CO)[(S)-(iPr)₂PCH₂CH₂N(H)CH(Ph)CH₂P(Ph)₂] (**S**)-7.

Synthesis of *trans*-Fe(Cl)₂(CO)[(S)-(iPr)₂PCH₂CH₂N(H)CH(CH(CH₃)₂)CH₂P(Ph)₂] (**S**)-8:

Follows the procedure above with (S)-(iPr)₂PCH₂CH₂N(H)CH(iPr)CH₂P(Ph)₂ (55 mg, 0.132 mmol), FeCl₂ (17 mg, 0.132 mmol) and THF (10 mL). Yielded a purple solid (40 mg, 60%). Crystals suitable for X-ray crystallography were obtained from a slow diffusion of pentane into benzene. ¹H NMR (C₆D₆, 500 MHz): 8.09 (m, 2H, ArH), 7.80 (m, 2H, ArH), 6.99 (m, 6H, ArH), 4.77 (m, 1H, NH), 3.83 (m, 1H, CHiPr), 3.00 (m, 3H, CH₂CH₂PiPr₂, CH₂PPh₂), 2.77 (m, 1H, PCH(CH₃)₂), 2.56 (m, 2H, CH₂PPh₂, PCH(CH₃)₂), 2.21 (m, 1H, CH(CH₃)₂), 2.02 (m, 1H, CH₂PiPr₂), 1.64 (m, 1H, CH₂PiPr₂), 1.57 (m, 3H, PCH(CH₃)₂), 1.43 (m, 3H, PCH(CH₃)₂), 1.37 (m, 3H, PCH(CH₃)₂), 1.21 (m, 3H, PCH(CH₃)₂), 0.89 (m, 3H, CH₃), 0.70 (m, 3H, CH₃). ¹³C{¹H} NMR (C₆D₆, 124 MHz): 224.7 (t, ²J_{CP} = 24 Hz, CO), 134.2 (d, J_{CP} = 9 Hz, C_{Ar}), 132.3 (d, J_{CP} = 8 Hz, C_{Ar}), 129.9 (C_{Ar}), 129.1 (C_{Ar}), 128.4 (C_{Ar}), 63.3 (d, J_{CP} = 8 Hz, CH(iPr)), 45.3 (CH₂CH₂PiPr₂), 28.1 (d, J_{CP} = 18 Hz, CH₂PPh₂), 27.3 (CH₂PiPr₂), 27.2 (CH(CH₃)₂), 23.9 (d, J_{CP} = 22 Hz, PCH(CH₃)₂), 22.5 (d, J_{CP} = 19 Hz, PCH(CH₃)₂), 21.6 (CH(CH₃)₂), 20.4 (PCH(CH₃)₂), 20.1 (PCH(CH₃)₂), 19.4 (PCH(CH₃)₂), 18.8 (PCH(CH₃)₂), 13.5 (CH(CH₃)₂). ³¹P{¹H} NMR (C₆D₆, 202 MHz): 69.3 (d, ²J_{PP} = 177 Hz, PiPr₂), 53.3 (d, ²J_{PP} = 177 Hz, PPh₂); AT-IR 1933 cm⁻¹ ν_(CO).

Figure S26: ^1H NMR spectrum (500 MHz, C_6D_6) of $\text{trans-Fe}(\text{Cl})_2(\text{CO})[(\text{S},\text{S})-(\text{iPr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{CH}(\text{CH}_3)_2)\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-**8**.

Figure S27: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, C_6D_6) of *trans*-Fe(Cl)₂(CO)[(S,S)-(iPr)₂PCH₂CH₂N(H)CH(CH(CH₃)₂)CH₂P(Ph)₂] (**S**)-**8**.

Figure S28: ^1H COSY NMR spectrum (500 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{Cl})_2(\text{CO})[(\text{S},\text{S})-(\text{iPr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{CH}(\text{CH}_3)_2)\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-**8**.

Synthesis of $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(\text{S},\text{S})-(\text{iPr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{P}(\text{Ph})_2]$ (**S,S**)-**9**:

A vial was charged with (**S,S**)-**5** (83 mg, 0.122 mmol), THF (10 mL) placed in a freezer (-30°C) for 20 min. The vial was removed and LiHBEt_3 (135 μL , 1 M THF solution, 0.134 mmol) was added. The colour of the solution immediately changed from purple to red-orange. The reaction was allowed to stir to room temperature. The solvent was removed, taken up with benzene and subsequently filtered into a pre-weighed vial. Benzene was removed by lyophilization to yield an orange-brown solid (70 mg, 89 %). ^1H NMR (THF-d_8 , 500 MHz): -20.46 (dd, $^2J_{\text{HP}} = 47, 56$ Hz, FeH , minor hydride 9%), -21.48 (dd, $^2J_{\text{HP}} = 47, 56$ Hz, FeH , major hydride 87%), -22.12 (dd, $^2J_{\text{HP}} = 57, 60$ Hz, FeH , minor hydride 4%). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-d_8 , 202 MHz): 94.5 (dd, $^2J_{\text{PP}} = 138$ Hz, $^2J_{\text{HP}}^{\text{residual}} = 33$ Hz, PiPr_2), 92.2 (dd, $^2J_{\text{PP}} = 138$ Hz, $^2J_{\text{HP}}^{\text{residual}} = 26$ Hz, PPh_2). AT-IR 2115 cm^{-1} $\nu_{(\text{Fe-H})}$, 1900 cm^{-1} $\nu_{(\text{CO})}$. EA Calc. for $\text{C}_{35}\text{H}_{42}\text{ClFeNOP}_2\cdot\text{C}_6\text{H}_6$: C, 68.0; H, 6.7; N, 1.9. Found: C, 67.6; H, 6.9; N, 2.3. The hydride regions of the ^1H NMR spectra were simulated to obtain accurate populations of the 3 isomers.

Figure S29: ^1H NMR spectrum (500 MHz, THF-d_8) of $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{P}(\text{Ph})_2]\text{-9}$.

Figure S30: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, THF- d_8) of $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(S,S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{P}(\text{Ph})_2]$ (***S,S***)-**9**

Figure S31: H-P HMBC (500 MHz, THF- d_8) of $\text{Fe(H)(Cl)(CO)[(S,S)-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2\text{] (S,S)-9$.

Synthesis of $\text{Fe(H)(Cl)(CO)[(S,S)-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N(H)CH(Ph)CH(Ph)P(Ph)}_2\text{] :$

Follows the procedure above with **(S,S)-6** (44 mg, 5.77×10^{-2} mmol) and LiHBEt_3 (64 μL , 1 M THF solution, 6.35×10^{-2} mmol). Yielded a red solid (42 mg, quant.). ^1H NMR (C_6D_6 , 500 MHz): -21.57 (dd, $^2J_{\text{HP}} = 48, 56$ Hz, FeH). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): 94.3 (dd, $^2J_{\text{PP}} = 137$ Hz, $^2J_{\text{HP}}^{\text{residual}} = 18$ Hz, PiPr_2), 87.8 (dd, $^2J_{\text{PP}} = 141$ Hz, $^2J_{\text{HP}}^{\text{residual}} = 22$ Hz, PPh_2). AT-IR 1898 cm^{-1} $\nu_{(\text{CO})}$. EA Calc. for $\text{C}_{41}\text{H}_{50}\text{ClFeNOP}_2 \cdot 2.0\text{ C}_6\text{H}_6$: C, 72.14; H, 7.10; N, 1.59. Found: C, 72.32; H, 7.40; N, 1.81.

Figure S32: ^1H NMR spectrum (500 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(\text{S},\text{S})-(\text{Cy})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{P}(\text{Ph})_2]$.

Figure S33: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(S,S)\text{-(Cy)}_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{P}(\text{Ph})_2]$.

Synthesis of $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(S)\text{-(iPr)}_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-10:

A vial was charged with (**S**)-**7** (40 mg, 0.066 mmol), THF (10 mL) and placed in a freezer (-30°C) for 20 min. The vial was removed and LiHBEt_3 (73 μL , 1 M THF solution, 0.073 mmol) was added. The colour of the solution immediately changed from purple to red-orange. The reaction was allowed to stir to room temperature. The solvent was removed, taken up with benzene and subsequently filtered into a pre-weighed vial. Benzene was removed by lyophilization to yield an orange-brown solid (40 mg, quant.). Crystals suitable for X-ray diffraction were obtained from slow diffusion of pentane into benzene. Four isomers were detected by NMR spectroscopy as determined by four separate hydride signals. ^1H NMR (C_6D_6 , 500 MHz): -20.47 (t, $^2J_{\text{HP}} = 55$ Hz, *FeH*, 5%), -20.96 (dd, $^2J_{\text{HP}} = 52, 56$ Hz, *FeH*, 22%), -21.40 (t, $^2J_{\text{HP}} = 54$ Hz, *FeH*, 31%), -22.05 (dd, $^2J_{\text{HP}} = 53, 55$ Hz, *FeH*, 42%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz, overlapping multiplets): 65-66 (m, *PPh*₂, 3 isomers), 68.9 (dd, $^2J_{\text{PP}} = 136$, $^2J_{\text{HP}}^{\text{residual}} = 33$ Hz, *PPh*₂, 1 isomer), 93-95 ppm (m, *PiPr*₂, 4 isomers). AT-IR 1897 cm^{-1} $\nu_{(\text{CO})}$. EA Found Calcd. for $\text{C}_{29}\text{H}_{38}\text{ClFeNOP}_2 \cdot 0.5\text{C}_6\text{H}_6$: C, 63.1; H, 6.8; N, 2.3. Found C, 62.7; H, 6.9; N, 2.2. The hydride regions of the ^1H NMR spectra were simulated to obtain accurate populations of the 4 isomers.

Figure S34: ^1H NMR spectrum (500 MHz, C_6D_6), hydride region of $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(\text{S})-(\text{iPr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-**10**.

Figure S35: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, C_6D_6) of $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(\text{S})-(\text{iPr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-**10**.

Synthesis of $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(\text{S})-(\text{iPr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{iPr})\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-**11**:

Follows the procedure above with (**S**)-**8** (75 mg, 0.131 mmol) and LiHBEt_3 (131 μL , 1 M THF solution, 0.131 mmol). Yielded an orange-brown solid (70 mg, quant.). Crystals suitable for X-ray diffraction were obtained from slow diffusion of pentane into benzene. At least 6 isomers were detected by NMR spectroscopy as determined by seven separate hydride signals, two of which are correlated in ^1H - ^1H COSY NMR. ^1H NMR (C_6D_6 , 500 MHz): - 8.11 (m, FeH , 7%), -8.41 (m, FeH , 14%), -13.41 (bm, FeH , 11%), -14.51 (bm, FeH , 9%), -20.96 (dd, $^2J_{\text{HP}} = 56.9, 52.5$ Hz, FeH , 17%), -22.04 (dd, $^2J_{\text{HP}} = 55.8, 53$ Hz, FeH , 21%), -22.78 (t, $^2J_{\text{HP}} = 60.3$ Hz, FeH , 17%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz, extracted from HMBC): 64.68 (d, PPh_2 , correlated to FeH at -20.96), 64.62 (d, PPh_2 , correlated to FeH at -22.05), 91.20 (d, PiPr_2 , correlated to FeH at -20.96), 92.08 (d, PiPr_2 , correlated to FeH at -22.03).

Figure S36: ^1H NMR spectrum (500 MHz, C_6D_6) of *trans*-Fe(H)(Cl)(CO)[(S)-(iPr)₂PCH₂CH₂N(H)CH(CH(CH₃)₂)CH₂P(Ph)₂] (**S**)-**11**.

Figure S37: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, C_6D_6) of *trans*-Fe(H)(Cl)(CO)[(S)-(iPr)₂PCH₂CH₂N(H)CH(CH(CH₃)₂)CH₂P(Ph)₂] (**S**)-**11**.

Figure S38: ^1H COSY NMR spectrum (500 MHz, C_6D_6) of *trans*-Fe(H)(Cl)(CO)[(S)-(iPr) $_2$ PCH $_2$ CH $_2$ N(H)CH(CH(CH $_3$) $_2$)CH $_2$ P(Ph) $_2$] (**S**)-**11**.

Figure S39: ^1H - ^{31}P HMBC NMR spectrum (500 MHz, C_6D_6) of *trans*- $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(\text{S})-(\text{iPr})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{CH}(\text{CH}_3)_2)\text{CH}_2\text{P}(\text{Ph})_2]$ (**S**)-**11**.

Catalysis with $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(\text{S},\text{S})-(\text{Cy})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{P}(\text{Ph})_2]$

Table S1 Preliminary results for use of catalyst $\text{Fe}(\text{H})(\text{Cl})(\text{CO})[(\text{S},\text{S})-(\text{Cy})_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{P}(\text{Ph})_2]$ ^[a]

Entry	$\text{R}^{[\text{b}]}$	$\text{R}'^{[\text{b}]}$	Conversion (%) ^[c]	Time (min)	e.e. (S) ^[c] (%)
1	CH_3	H	> 99	120	91
2	CH_2CH_3	H	> 99	120	91
3	CH_3	<i>o</i> -Cl	> 97	120	83
4	CH_3	<i>p</i> -Cl	> 99	120	83

[a] conditions: 10 bar H_2 , 0.2 mol% catalyst, 2 mol% KO^tBu , 50 °C, 10 mL THF; [b] refer to Scheme 4 [c] conversion and e.e. determined by chiral GC.

Gas Chromatography Traces

Acetophenone

Figure S40: GC trace for entry 1, Table 1

GC analysis conditions: Oven temperature 130 °C

Retention time: (*R*)-isomer = 6.693; (*S*)-isomer = 7.193; starting material = 4.093.

Propiophenone

Figure S41: GC trace for entry 2, Table 1

GC analysis conditions: Oven temperature 120 °C

Retention time: (*R*)-isomer = 10.966; (*S*)-isomer = 11.992; starting material = 5.349

***o*-Chloroacetophenone**

Figure S42: GC trace for entry 3, Table 1

GC analysis conditions: Oven temperature 145 °C

Retention time: (*R*)-isomer = 5.654; (*S*)-isomer = 6.924; starting material = 2.752.

Cyclohexylphenyl ketone

Figure S43: GC trace for entry 4, Table 1

GC analysis conditions: Oven temperature 170 °C

Retention time: (*R*)-isomer = 8.924; (*S*)-isomer = 8.642; starting material = 5.723.

***p*-Chloroacetophenone**

Figure S44: GC trace for entry 6, Table 1

GC analysis conditions: Oven temperature 145 °C

Retention time: (*R*)-isomer = 4.737; (*S*)-isomer = 5.213; starting material = 2.588.

***p*-Methylacetophenone**

Figure S45: GC trace for entry 7, Table 1

GC analysis conditions: Oven temperature 130 °C

Retention time: (*R*)-isomer = 7.194; (*S*)-isomer = 7.677; starting material = 4.142.

2-Acetonaphthone

Figure S46: GC trace for entry 1, Table 2

GC analysis conditions: Oven temperature 150 °C

Retention time: (*R*)-isomer = 6.119; (*S*)-isomer = 6.378; starting material = 4.403.

1-Acetonaphthone

Figure S47: GC trace for entry 2, Table 2

GC analysis conditions: Oven temperature 150 °C

Retention time: (*R*)-isomer = 22.786; (*S*)-isomer = 20.001; starting material = 8.640.

2-Acetylfuran

Figure S48: GC trace for entry 3, Table 2

GC analysis conditions: Oven temperature 90 °C

Retention time: (*R*)-isomer = 11.335; (*S*)-isomer = 11.476; starting material = 5.227.

3-Methylbutan-2-one

Figure S49: GC trace for entry 4, Table 2

GC analysis conditions: Oven temperature 50 °C

Retention time: (*R*)-isomer = 9.471; (*S*)-isomer = 10.105; starting material = 3.74.

DFT calculations

Calculations

DFT calculations were performed using Gaussian 09 (Rev. D.01)¹ at the M11L²/6-31G* level except SDD for Fe. Normal (opt) convergence criteria were met using a pruned (99,590) integration grid (grid = ultrafine). Optimizations were performed in a THF solvent continuum (1 atm, 298 K) using the integral equation formalism polarizable continuum model (IEF-PCM)^{3,4} with radii and non-electrostatic terms from the SMD solvation model (scrf = smd).⁵ Full vibrational and thermochemical analyses were performed on optimized structures to obtain solvent-corrected free energies (G°) and enthalpies (H°). Optimized ground states were found to have zero imaginary frequencies while transition states had one imaginary frequency. Calculations were performed using the facilities of the Shared Hierarchical Academic Research Computing Network (SHARCNET)⁶ and Scinet of Compute/Calcul Canada.⁷

The transition state energies (Figure S50) are higher than those reported for a similar system^[8] because of the larger basis set employed in the current work which gives more reliable results. The *S* transition state is 31.5 kcal/mol at 323 K relative to the separate dihydride and ketone species while the *R*-transition state is 33.1 kcal/mol, consistent with the fact that warming to 323 K is required for reaction.

[1] Gaussian 09, Revision or B.01 or D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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Reaction coordinate diagram for hydride transfer to the ketone.

Figure S50. The reaction coordinate diagram for hydride transfer.

Optimized coordinates

Acetophenone

delta H (Hartrees) -384.658 delta S (cal/mol/K) 87.745

delta G (kcal/mol) (323) -241401.3464

6	-0.207422000	-0.053000000	-0.000162000
6	0.426003000	1.189114000	-0.000325000
6	0.569004000	-1.211624000	0.000189000
6	-1.690822000	-0.204317000	-0.000127000
6	1.809017000	1.268752000	-0.000245000
1	-0.162729000	2.113871000	-0.000485000
6	1.948590000	-1.132614000	0.000317000
1	0.058526000	-2.181271000	0.000424000
6	2.570769000	0.109459000	0.000065000
1	2.300023000	2.248267000	-0.000396000
1	2.551794000	-2.047548000	0.000656000
1	3.665039000	0.174099000	0.000174000
6	-2.530531000	1.036496000	0.000568000
8	-2.192703000	-1.300344000	-0.000541000
1	-2.322546000	1.661188000	0.885242000
1	-3.593124000	0.758558000	0.000678000
1	-2.322995000	1.661991000	-0.883648000

Dihydride *trans*-FeH₂(CO)(*mer*-(*S,S*)-1)

delta H (Hartrees) -2295.234072 delta S (cal/mol/K) 241.77

delta G (kcal/mol) (323) -1440337.472

1	-5.841578000	0.090269000	-1.889635000
1	-5.124188000	1.365536000	2.150778000
1	3.745371000	-1.268508000	2.513200000
6	4.713973000	-0.883797000	2.149781000
6	-0.555563000	1.665151000	0.042374000
15	-0.607705000	-1.035001000	-0.052268000
6	3.122113000	2.173429000	-0.355123000
1	-0.939575000	-3.892916000	0.149114000
1	-1.659521000	-2.726122000	-4.610898000
6	-3.386780000	1.042856000	0.933240000
7	0.829319000	1.428506000	-0.372988000
1	-3.305196000	-2.221854000	0.264714000
6	-1.801862000	-1.754702000	3.793067000
1	-0.039366000	-1.019793000	2.793117000
6	-5.638525000	0.725644000	0.159020000
6	2.031466000	-2.090568000	0.402377000
1	1.601705000	-0.708875000	-1.508710000
1	-1.219764000	-0.948278000	-2.987768000
6	4.550841000	0.496168000	1.549834000
6	-1.576655000	-1.574505000	1.396285000
6	-1.269388000	-1.983701000	-2.634343000
6	-3.082100000	-2.258091000	3.645788000
6	1.725626000	2.464139000	0.123899000

1	-1.372660000	-1.625475000	4.792325000
1	-3.674065000	-2.524760000	4.527802000
6	-4.750257000	1.072117000	1.164287000
26	1.502735000	-0.469100000	0.042661000
1	4.651812000	1.426923000	3.486940000
15	3.509769000	0.429559000	0.021986000
1	1.664670000	2.441468000	1.227295000
1	-6.717294000	0.746760000	0.344604000
1	5.396795000	-0.848210000	3.016024000
6	-3.785437000	0.336226000	-1.314892000
1	3.941268000	2.484650000	2.257142000
1	-1.256992000	0.611841000	-1.665388000
6	3.998903000	1.438309000	2.597068000
6	-1.053454000	-1.416826000	2.675805000
1	5.546602000	0.875435000	1.244962000
6	-2.866550000	-2.091822000	1.261210000
6	-2.881723000	0.669848000	-0.310321000
1	-3.406400000	0.047088000	-2.302964000
8	2.349533000	-3.170375000	0.642525000
6	-1.414496000	0.559875000	-0.569707000
6	-1.082334000	-2.283407000	-1.287481000
6	-5.150269000	0.358465000	-1.083825000
1	-0.551044000	1.570384000	1.147803000
6	-1.324510000	-4.627871000	-1.827662000
1	-1.717277000	-5.105696000	-3.892034000
1	1.404798000	3.471599000	-0.203805000
1	2.992792000	1.129631000	2.927371000
1	3.162052000	2.294170000	-1.454865000
1	-1.333891000	-5.672513000	-1.499791000
6	-1.535440000	-4.312800000	-3.159484000
6	-1.101083000	-3.623838000	-0.901600000
1	5.120947000	-1.625568000	1.444760000
1	-2.702267000	1.292040000	1.752701000
6	-1.504106000	-2.987325000	-3.558882000
1	-4.624899000	-2.825261000	2.250094000
1	3.843052000	2.896728000	0.061510000
6	-3.612029000	-2.428548000	2.375559000
6	4.675613000	0.015964000	-1.352154000
1	6.654956000	0.503294000	-0.583374000
6	4.969825000	-1.461005000	-1.477174000
6	5.951613000	0.826673000	-1.369224000
1	4.051688000	-2.070444000	-1.487286000
1	4.071043000	0.303593000	-2.237414000
1	5.507430000	-1.663621000	-2.419275000
1	5.614601000	-1.827301000	-0.660898000
1	5.779404000	1.908411000	-1.239532000
1	6.474569000	0.695356000	-2.332195000
1	0.852670000	1.476562000	-1.396510000

6	-1.066635000	3.037659000	-0.317991000
6	-1.441122000	3.932226000	0.675275000
6	-1.155044000	3.439591000	-1.646653000
6	-1.901687000	5.198397000	0.353114000
6	-1.609116000	4.705310000	-1.972493000
6	-1.986714000	5.588046000	-0.972572000
1	-1.367254000	3.626304000	1.726470000
1	-0.858364000	2.752970000	-2.450110000
1	-2.195187000	5.890331000	1.149336000
1	-1.671605000	5.007048000	-3.023304000
1	-2.348967000	6.588289000	-1.231027000
1	1.403013000	-0.083520000	1.546063000

Pro-(S)-ketone adduct with dihydride

delta H (Hartrees)	-2679.89	delta S (cal/mol/K)	289.894
delta G (kcal/mol) (323)	-1681723.575		
1	5.343978000	2.733402000	2.035293000
1	5.495689000	1.967950000	-2.190564000
1	-1.345534000	-3.687000000	-2.775977000
6	-2.445775000	-3.746444000	-2.716584000
6	0.646065000	1.211722000	-1.088121000
15	1.458954000	-0.978613000	0.259315000
6	-2.962049000	0.308673000	-1.481482000
1	2.696516000	-3.292039000	1.478523000
1	1.472031000	-0.228896000	5.172892000
6	3.654932000	1.477612000	-1.201345000
7	-0.670435000	0.639074000	-0.784010000
1	4.345616000	-0.994231000	0.919389000
6	3.932413000	-2.592912000	-2.573180000
1	1.813194000	-2.307145000	-2.300028000
6	5.570460000	2.396640000	-0.080758000
6	-0.454151000	-3.093385000	-0.087826000
1	-1.105621000	-1.093386000	1.049124000
1	1.041968000	0.445217000	2.860685000
6	-3.058135000	-2.360555000	-2.718618000
6	2.938087000	-1.599725000	-0.610153000
6	1.520479000	-0.522734000	3.046388000

6	5.194179000	-2.432286000	-2.028935000
6	-1.657388000	0.987574000	-1.797474000
1	3.812945000	-3.049703000	-3.561367000
1	6.079849000	-2.756013000	-2.585997000
6	4.953788000	1.951743000	-1.239145000
26	-0.584125000	-1.387089000	-0.408338000
1	-2.865176000	-2.214016000	-4.858198000
15	-2.650816000	-1.457543000	-1.154446000
1	-1.254985000	0.652131000	-2.771287000
1	6.599816000	2.768368000	-0.111609000
1	-2.791759000	-4.318001000	-3.595032000
6	3.569159000	1.905981000	1.149321000
1	-3.096195000	-0.638308000	-4.082587000
1	1.082286000	1.268206000	0.993024000
6	-2.614223000	-1.621382000	-3.961420000
6	2.811824000	-2.180824000	-1.867871000
1	-4.161632000	-2.461343000	-2.756565000
6	4.216681000	-1.452903000	-0.068219000
6	2.943975000	1.441537000	-0.003939000
1	3.017930000	1.895784000	2.097917000
8	-0.335495000	-4.216556000	0.136906000
6	1.567387000	0.868903000	0.079928000
6	1.875919000	-1.357569000	1.989466000
6	4.871638000	2.374479000	1.114786000
1	0.985021000	0.683474000	-2.002976000
6	2.635918000	-2.993564000	3.599958000
1	2.477713000	-2.445433000	5.678560000
1	-1.800760000	2.084406000	-1.861406000
1	-1.521071000	-1.470934000	-3.969187000
1	-3.372808000	0.732106000	-0.545845000
1	3.068909000	-3.977588000	3.808416000
6	2.304400000	-2.142584000	4.640864000
6	2.424334000	-2.604816000	2.288422000
1	-2.694349000	-4.339318000	-1.822263000
1	3.196160000	1.104193000	-2.124840000
6	1.744045000	-0.908486000	4.357561000
1	6.328340000	-1.731575000	-0.333999000
1	-3.711690000	0.507844000	-2.265780000
6	5.333321000	-1.863280000	-0.771767000
6	-4.041951000	-1.858259000	-0.006040000
1	-5.753660000	-2.112946000	-1.337159000
6	-4.030101000	-3.293991000	0.464470000
6	-5.415586000	-1.470584000	-0.506149000
1	-3.041749000	-3.608201000	0.838853000
1	-3.798555000	-1.218185000	0.867485000
1	-4.750388000	-3.433427000	1.288705000
1	-4.328796000	-3.991143000	-0.337087000
1	-5.474998000	-0.423839000	-0.846985000

1	-6.159705000	-1.589643000	0.301280000
1	-0.987152000	1.056398000	0.098273000
6	0.619567000	2.690898000	-1.382527000
6	0.824953000	3.143968000	-2.679208000
6	0.375532000	3.624019000	-0.379431000
6	0.782201000	4.496543000	-2.975309000
6	0.328180000	4.976107000	-0.673250000
6	0.530894000	5.416887000	-1.971813000
1	1.023377000	2.415279000	-3.475528000
1	0.219480000	3.292754000	0.655357000
1	0.948443000	4.835282000	-4.003304000
1	0.138323000	5.698567000	0.127850000
1	0.498001000	6.486997000	-2.201045000
1	-0.125731000	-1.537767000	-1.886265000
6	-3.023975000	1.932432000	2.144526000
6	-4.204752000	1.212116000	2.311974000
6	-2.992348000	2.978680000	1.223059000
6	-1.787877000	1.630343000	2.915337000
6	-5.327843000	1.529396000	1.567490000
1	-4.251167000	0.383781000	3.026956000
6	-4.114395000	3.298319000	0.483535000
1	-2.066015000	3.551286000	1.106765000
6	-5.284461000	2.571647000	0.654400000
1	-6.251886000	0.958024000	1.703852000
1	-4.081280000	4.126264000	-0.231908000
1	-6.176237000	2.824459000	0.071260000
6	-1.857703000	0.612279000	4.004151000
8	-0.755465000	2.205436000	2.658234000
1	-2.710292000	0.783790000	4.679059000
1	-0.925549000	0.628528000	4.583688000
1	-1.980624000	-0.395585000	3.571861000

(S)-transition state

delta H (Hartrees)

-2679.87

delta S (cal/mol/K)

275.815

delta G (kcal/mol) (323) -1681707.365

v imag 621.4i cm⁻¹

1	-6.234989000	1.210825000	-2.217777000
1	-5.959430000	0.608364000	2.027837000
1	1.501271000	-1.031029000	3.920381000
6	2.551718000	-0.709140000	4.021389000
6	-1.310658000	1.611292000	0.314001000
15	-1.129969000	-1.103116000	0.042029000
6	2.253325000	2.368018000	1.066987000
1	0.277222000	-3.480224000	-0.660930000
1	-2.923863000	-2.679528000	-4.353571000
6	-4.116729000	0.503992000	0.931712000
7	0.144004000	1.472012000	0.246139000
1	-3.741039000	-2.426188000	-0.246424000
6	-2.590467000	-2.948092000	3.402671000
1	-0.834930000	-1.822818000	2.869900000
6	-6.254771000	0.913943000	-0.084022000
6	1.451952000	-1.949246000	1.093008000
1	-2.885599000	-1.152706000	-2.434115000
6	2.752322000	0.675215000	3.438864000
6	-2.190488000	-2.024085000	1.209404000
6	-2.186874000	-1.995466000	-2.454822000
6	-3.802047000	-3.463351000	2.977490000
6	0.763128000	2.557695000	1.003918000
1	-2.256106000	-3.106056000	4.433437000
1	-4.434960000	-4.027032000	3.670891000
6	-5.485704000	0.670367000	1.042588000
26	0.842839000	-0.364944000	0.684858000
1	1.999351000	1.620037000	5.218368000
15	2.595604000	0.662892000	1.591813000
1	0.314545000	2.551707000	2.013752000
1	-7.337956000	1.045384000	0.005669000
1	2.790692000	-0.703626000	5.098901000
6	-4.270481000	0.836986000	-1.429772000
1	1.968968000	2.692721000	3.807814000
1	-1.731356000	0.587700000	-1.509253000
6	1.824550000	1.648834000	4.128880000
6	-1.790193000	-2.232182000	2.525735000
1	3.794004000	0.992757000	3.651030000
6	-3.405304000	-2.566144000	0.787881000
6	-3.488168000	0.571726000	-0.310203000
1	-3.786459000	0.937377000	-2.409633000
8	1.837204000	-2.990947000	1.397122000
6	-1.997516000	0.466105000	-0.437118000
6	-1.289630000	-2.194882000	-1.410381000
6	-5.641298000	1.000959000	-1.321993000
1	-1.575564000	1.537240000	1.388287000
6	-0.472335000	-4.165607000	-2.546499000

1	-1.376760000	-4.621890000	-4.449101000
1	0.522804000	3.539300000	0.552607000
1	0.765867000	1.382331000	3.966858000
1	2.670407000	2.468663000	0.046157000
1	0.208550000	-5.022738000	-2.572933000
6	-1.355724000	-3.942890000	-3.590536000
6	-0.438518000	-3.296753000	-1.470568000
1	3.177713000	-1.483886000	3.552741000
1	-3.525071000	0.311880000	1.834978000
6	-2.214717000	-2.858709000	-3.538551000
1	-5.162206000	-3.679313000	1.318359000
1	2.727112000	3.146693000	1.688879000
6	-4.207508000	-3.270968000	1.665663000
6	4.336985000	0.406918000	1.036401000
1	5.369495000	1.795182000	2.382014000
6	4.943057000	-0.879751000	1.548502000
6	5.255852000	1.577795000	1.305471000
1	4.305987000	-1.758764000	1.353775000
1	4.236867000	0.307754000	-0.055834000
1	5.908602000	-1.062823000	1.045760000
1	5.151255000	-0.842316000	2.632116000
1	4.924931000	2.503862000	0.809047000
1	6.265870000	1.352584000	0.919172000
1	0.447812000	1.599909000	-0.734624000
6	-1.815058000	2.932921000	-0.214040000
6	-2.666971000	3.721022000	0.547038000
6	-1.469719000	3.357876000	-1.493783000
6	-3.169709000	4.909959000	0.044173000
6	-1.964272000	4.549673000	-1.994077000
6	-2.818645000	5.327748000	-1.228188000
1	-2.946937000	3.390331000	1.555048000
1	-0.787814000	2.753587000	-2.108115000
1	-3.843234000	5.518698000	0.656586000
1	-1.678507000	4.876027000	-2.999737000
1	-3.212378000	6.268225000	-1.627282000
1	0.204076000	-0.181747000	2.063130000
1	1.453979000	-0.336600000	-0.864764000
6	1.803029000	0.409137000	-2.282479000
6	3.268856000	0.054450000	-2.277824000
6	3.735622000	-1.245618000	-2.108602000
6	4.186520000	1.081274000	-2.462607000
6	5.093175000	-1.508027000	-2.099230000
1	3.021482000	-2.060188000	-1.929740000
6	5.547822000	0.820205000	-2.458185000
1	3.806994000	2.100090000	-2.595358000
6	6.004933000	-0.473921000	-2.269620000
1	5.450260000	-2.532160000	-1.944991000
1	6.262317000	1.638656000	-2.600095000

1	7.079943000	-0.682837000	-2.256775000
6	0.951562000	-0.456872000	-3.177836000
8	1.494970000	1.608784000	-2.175251000
1	1.097213000	-1.539342000	-3.053950000
1	1.211894000	-0.197506000	-4.220866000
1	-0.111506000	-0.215878000	-3.034547000

(S)-alkoxide adduct

delta H (Hartrees)	-2679.88	delta S (cal/mol/K)	278.422
delta G (kcal/mol) (323)	-1681714.683		
1	-6.057904000	1.209971000	-2.447935000
1	-6.048486000	0.591215000	1.804366000
1	1.697738000	-1.068060000	3.984319000
6	2.747281000	-0.732360000	4.036446000
6	-1.273252000	1.568557000	0.382380000
15	-1.123730000	-1.133971000	0.098101000
6	2.291798000	2.344208000	1.098543000
1	0.472866000	-3.402553000	-0.649261000
1	-2.796546000	-2.749616000	-4.312288000
6	-4.141441000	0.485454000	0.824738000
7	0.182390000	1.425874000	0.322703000
1	-3.647920000	-2.596114000	-0.273227000
6	-2.755880000	-2.753673000	3.482423000
1	-0.996533000	-1.622944000	2.978089000
6	-6.211630000	0.903919000	-0.320708000
6	1.428524000	-1.989967000	1.270311000
1	-2.847521000	-1.256229000	-2.364961000
6	2.903229000	0.653618000	3.445798000
6	-2.219495000	-2.020075000	1.248289000
6	-2.096659000	-2.051833000	-2.405687000
6	-3.915831000	-3.348900000	3.018374000
6	0.797060000	2.510187000	1.083793000
1	-2.497682000	-2.805274000	4.545252000

1	-4.582375000	-3.870674000	3.712917000
6	-5.514644000	0.654411000	0.850406000
26	0.861758000	-0.395830000	0.783942000
1	2.206147000	1.590056000	5.250027000
15	2.674870000	0.646356000	1.609202000
1	0.374723000	2.495505000	2.105733000
1	-7.297993000	1.037646000	-0.297666000
1	3.032850000	-0.720568000	5.102138000
6	-4.147842000	0.827762000	-1.540528000
1	2.100047000	2.659278000	3.840850000
1	-1.611275000	0.572530000	-1.470752000
6	1.986411000	1.614130000	4.168826000
6	-1.911712000	-2.093197000	2.604144000
1	3.947056000	0.989233000	3.614030000
6	-3.384693000	-2.634740000	0.789950000
6	-3.437120000	0.556052000	-0.375434000
1	-3.602920000	0.928802000	-2.488048000
8	1.749578000	-3.018945000	1.663796000
6	-1.942416000	0.445129000	-0.417415000
6	-1.183021000	-2.210721000	-1.367453000
6	-5.522053000	0.994716000	-1.517674000
1	-1.560405000	1.463661000	1.450280000
6	-0.235609000	-4.095763000	-2.546422000
1	-1.121409000	-4.579797000	-4.450213000
1	0.535471000	3.492038000	0.645291000
1	0.926686000	1.329475000	4.050446000
1	2.665152000	2.446294000	0.060739000
1	0.503061000	-4.902393000	-2.593667000
6	-1.141113000	-3.916514000	-3.579502000
6	-0.255368000	-3.247653000	-1.453162000
1	3.363740000	-1.498913000	3.542857000
1	-3.608287000	0.294383000	1.763737000
6	-2.072520000	-2.895100000	-3.503994000
1	-5.140837000	-3.761042000	1.292980000
1	2.780946000	3.127555000	1.701681000
6	-4.227230000	-3.289440000	1.668917000
6	4.371935000	0.379216000	0.940330000
1	5.530380000	1.686577000	2.262954000
6	4.981076000	-0.934865000	1.371677000
6	5.324669000	1.526589000	1.190337000
1	4.314968000	-1.795618000	1.189448000
1	4.200563000	0.324025000	-0.148111000
1	5.909127000	-1.119792000	0.803850000
1	5.255298000	-0.936461000	2.440919000
1	4.965435000	2.478795000	0.769037000
1	6.294694000	1.310375000	0.709083000
1	0.508359000	1.574884000	-0.682112000
6	-1.778380000	2.903221000	-0.112873000

6	-2.636268000	3.665064000	0.667920000
6	-1.434151000	3.358771000	-1.383113000
6	-3.148488000	4.862339000	0.194902000
6	-1.940332000	4.559253000	-1.851064000
6	-2.801037000	5.312506000	-1.067294000
1	-2.914020000	3.308005000	1.667743000
1	-0.739587000	2.772042000	-2.002210000
1	-3.826634000	5.450986000	0.821811000
1	-1.657842000	4.913416000	-2.848516000
1	-3.202334000	6.259249000	-1.443885000
1	0.288467000	-0.228286000	2.161645000
1	1.214101000	-0.291061000	-1.322598000
6	1.528499000	0.359724000	-2.249027000
6	3.024043000	0.072132000	-2.351100000
6	3.540773000	-1.208715000	-2.182879000
6	3.902593000	1.117073000	-2.599003000
6	4.904638000	-1.439066000	-2.242394000
1	2.854028000	-2.042716000	-1.970574000
6	5.270301000	0.893332000	-2.660960000
1	3.479774000	2.121258000	-2.715586000
6	5.776783000	-0.384049000	-2.477550000
1	5.297747000	-2.451446000	-2.092907000
1	5.954539000	1.729265000	-2.848707000
1	6.856890000	-0.562020000	-2.517961000
6	0.816698000	-0.289409000	-3.437886000
8	1.223288000	1.622891000	-2.099241000
1	0.973663000	-1.379385000	-3.529006000
1	1.180142000	0.186167000	-4.366301000
1	-0.267368000	-0.096548000	-3.375412000

Pro-(*R*)-ketone adduct with dihydride

delta H (Hartrees)	-2679.89	delta S (cal/mol/K)	288.334
delta G (kcal/mol) (323)	-1681723.548		
1	-5.347129000	1.832862000	-2.940436000
1	-6.130685000	1.357447000	1.258299000
1	1.772142000	-3.184651000	3.280849000

6	2.832738000	-2.907555000	3.413090000
6	-1.095008000	1.284172000	1.025640000
15	-1.333702000	-1.098563000	-0.230824000
6	2.536850000	1.064240000	1.904044000
1	-2.231298000	-3.544398000	-1.570045000
1	-0.356150000	-0.569569000	-5.058827000
6	-4.095272000	1.081001000	0.634371000
7	0.322822000	0.916182000	0.958185000
1	-4.105534000	-1.497897000	-1.238297000
6	-3.853651000	-3.153104000	2.244590000
1	-1.791773000	-2.523873000	2.239707000
6	-5.891997000	1.619034000	-0.866549000
6	0.802124000	-2.837720000	0.608990000
1	1.251854000	-0.838700000	-0.630070000
1	-0.425555000	0.196032000	-2.737411000
6	3.003802000	-1.404558000	3.363495000
6	-2.810335000	-1.930438000	0.442264000
6	-0.838528000	-0.790399000	-2.979530000
6	-5.052174000	-3.168745000	1.553824000
6	1.102512000	1.502471000	2.038734000
1	-3.778277000	-3.628744000	3.228123000
1	-5.932990000	-3.652215000	1.989781000
6	-5.433169000	1.355453000	0.414063000
26	0.609836000	-1.114475000	0.768706000
1	2.479882000	-1.205648000	5.441242000
15	2.570890000	-0.749770000	1.688579000
1	0.661669000	1.146706000	2.987983000
1	-6.951641000	1.833686000	-1.039297000
1	3.152735000	-3.299486000	4.393935000
6	-3.658502000	1.349809000	-1.701591000
1	2.347728000	0.320691000	4.552464000
1	-1.184512000	1.118089000	-1.090631000
6	2.192762000	-0.767077000	4.469838000
6	-2.740438000	-2.538725000	1.691782000
1	4.069543000	-1.157513000	3.540993000
6	-4.023372000	-1.963990000	-0.249082000
6	-3.188166000	1.068826000	-0.422161000
1	-2.952838000	1.353054000	-2.542231000
8	0.895010000	-3.980031000	0.496023000
6	-1.752021000	0.714074000	-0.228379000
6	-1.385222000	-1.598122000	-1.982311000
6	-4.998396000	1.616730000	-1.925071000
1	-1.489019000	0.772483000	1.927536000
6	-1.745355000	-3.316440000	-3.644770000
1	-1.179317000	-2.837389000	-5.667851000
1	1.032102000	2.608111000	2.037185000
1	1.113373000	-0.949633000	4.335928000
1	2.972678000	1.513129000	0.988488000

1	-2.094636000	-4.323643000	-3.895243000
6	-1.233147000	-2.491421000	-4.630522000
6	-1.822046000	-2.873965000	-2.334099000
1	3.413224000	-3.441190000	2.644065000
1	-3.756524000	0.848088000	1.651218000
6	-0.776825000	-1.227822000	-4.291014000
1	-6.078389000	-2.583620000	-0.250384000
1	3.144229000	1.431668000	2.748774000
6	-5.133774000	-2.574205000	0.303309000
6	4.093461000	-0.963865000	0.663199000
1	5.703933000	-1.264366000	2.103024000
6	4.226810000	-2.332494000	0.037322000
6	5.380889000	-0.542628000	1.333140000
1	3.325063000	-2.620405000	-0.526679000
1	3.888182000	-0.255094000	-0.163766000
1	5.072533000	-2.340452000	-0.672993000
1	4.433681000	-3.120207000	0.781249000
1	5.315725000	0.450073000	1.810875000
1	6.196206000	-0.491291000	0.589610000
1	0.690045000	1.299599000	0.080847000
6	-1.339035000	2.764707000	1.178135000
6	-1.826221000	3.268135000	2.377284000
6	-1.068127000	3.652541000	0.141416000
6	-2.037544000	4.626831000	2.544920000
6	-1.274041000	5.011259000	0.307860000
6	-1.759830000	5.503015000	1.509422000
1	-2.044890000	2.574103000	3.198895000
1	-0.685412000	3.280753000	-0.818231000
1	-2.425127000	5.005212000	3.496627000
1	-1.060220000	5.698100000	-0.518486000
1	-1.927867000	6.577444000	1.636498000
1	-0.018073000	-1.244618000	2.190540000
6	3.345719000	1.717509000	-2.185454000
6	4.627291000	2.045468000	-1.744748000
6	3.144533000	0.515320000	-2.861839000
6	2.171071000	2.589553000	-1.938991000
6	5.687736000	1.189861000	-1.985638000
1	4.808550000	2.982632000	-1.207724000
6	4.202007000	-0.340004000	-3.098031000
1	2.130737000	0.258079000	-3.187199000
6	5.475691000	-0.001869000	-2.661813000
1	6.692771000	1.455586000	-1.642604000
1	4.034214000	-1.286395000	-3.621649000
1	6.315676000	-0.679071000	-2.851026000
6	2.372164000	3.850604000	-1.158962000
8	1.076752000	2.278334000	-2.350483000
1	2.684670000	3.629742000	-0.123326000
1	1.437936000	4.425785000	-1.130272000

1 3.163602000 4.479759000 -1.595398000

(R)-transition state

delta H (Hartrees) -2679.87

delta S (cal/mol/K)

274.487

delta G (kcal/mol) (323) -1681705.751

v imag 683.882i cm⁻¹

1	5.801408000	-0.000911000	-2.003503000
1	5.305096000	-2.560684000	1.411457000
1	-3.505038000	-0.540830000	3.160245000
6	-4.463537000	-0.896869000	2.744613000
6	0.652863000	-1.810615000	-0.468086000
15	0.636544000	0.427067000	0.976259000
6	-3.018313000	-2.250846000	-1.029079000
1	0.023592000	2.563547000	2.710895000
1	3.514916000	4.299508000	-0.341857000
6	3.522550000	-1.641563000	0.647356000
7	-0.743524000	-1.435383000	-0.724498000
1	3.045598000	1.167055000	2.505825000
6	1.455753000	-1.863188000	4.290206000
1	-0.108632000	-1.744268000	2.822842000
6	5.712645000	-1.291757000	-0.280268000
6	-2.138822000	1.309875000	1.453357000
1	2.691079000	2.006652000	-0.626999000
6	-4.238030000	-1.828964000	1.574768000
6	1.380618000	-0.217416000	2.520573000
6	2.273056000	2.624627000	0.171837000
6	2.638777000	-1.322775000	4.763720000
6	-1.577706000	-2.629640000	-0.804386000
1	1.002962000	-2.723965000	4.793749000
1	3.129746000	-1.753709000	5.642598000
6	4.884726000	-1.886940000	0.657405000
26	-1.484761000	0.017762000	0.473649000
1	-4.022391000	-3.532190000	2.862112000

15	-3.462885000	-0.935579000	0.149829000
1	-1.454037000	-3.178875000	0.146995000
1	6.789712000	-1.487923000	-0.269270000
1	-4.995756000	-1.422677000	3.555859000
6	3.800562000	-0.218964000	-1.250229000
1	-3.383253000	-3.819348000	1.237134000
1	1.269804000	0.063259000	-1.284244000
6	-3.480095000	-3.056806000	2.026377000
6	0.831121000	-1.313617000	3.182355000
1	-5.222408000	-2.179995000	1.210050000
6	2.574538000	0.315980000	3.009689000
6	2.958286000	-0.785369000	-0.296912000
1	3.366518000	0.419195000	-2.031579000
8	-2.580267000	2.147759000	2.105702000
6	1.483760000	-0.525376000	-0.365618000
6	1.292189000	2.119411000	1.016264000
6	5.163149000	-0.460465000	-1.241610000
1	0.659803000	-2.328128000	0.515280000
6	1.240153000	4.242675000	2.169689000
1	2.596727000	5.755481000	1.449870000
1	-1.233634000	-3.304345000	-1.611383000
1	-2.470170000	-2.811059000	2.393947000
1	-3.134464000	-1.837931000	-2.049459000
1	0.826796000	4.874822000	2.962476000
6	2.226012000	4.732538000	1.327421000
6	0.780707000	2.948055000	2.016475000
1	-5.063721000	-0.010152000	2.485081000
1	2.886898000	-2.135345000	1.391705000
6	2.739435000	3.920187000	0.332283000
1	4.130560000	0.206530000	4.484023000
1	-3.669985000	-3.140795000	-0.978390000
6	3.194256000	-0.229215000	4.120055000
6	-4.899976000	-0.106412000	-0.680384000
1	-6.679315000	-0.907321000	0.296898000
6	-5.138588000	1.305294000	-0.192732000
6	-6.187422000	-0.899460000	-0.690507000
1	-4.223776000	1.918915000	-0.215658000
1	-4.555669000	-0.035133000	-1.728419000
1	-5.885947000	1.806633000	-0.831569000
1	-5.530900000	1.332674000	0.837611000
1	-6.045932000	-1.946980000	-1.006006000
1	-6.902835000	-0.443017000	-1.396030000
1	-0.750015000	-0.975947000	-1.653693000
6	1.215918000	-2.767739000	-1.489056000
6	1.584556000	-4.051768000	-1.111655000
6	1.373591000	-2.385191000	-2.817864000
6	2.097549000	-4.944555000	-2.038575000
6	1.882288000	-3.277928000	-3.745395000

6	2.246024000	-4.558972000	-3.359798000
1	1.465462000	-4.357500000	-0.064203000
1	1.087413000	-1.373401000	-3.131334000
1	2.384849000	-5.953367000	-1.723846000
1	2.001512000	-2.966236000	-4.788677000
1	2.651295000	-5.260768000	-4.096108000
1	-1.476849000	-0.939482000	1.648677000
1	-1.460968000	0.947807000	-0.889051000
6	-0.405995000	2.551652000	-2.239312000
6	-0.882084000	3.584961000	-1.439236000
6	0.722231000	2.770740000	-3.020261000
6	-0.251599000	4.815260000	-1.431019000
6	1.347915000	4.007689000	-3.024661000
6	0.858460000	5.034096000	-2.235261000
1	-1.751514000	3.409425000	-0.791240000
1	1.086531000	1.950401000	-3.649457000
1	-0.626143000	5.616338000	-0.784268000
1	2.227917000	4.173231000	-3.656304000
1	1.353104000	6.011432000	-2.231972000
6	-1.137802000	1.244594000	-2.423301000
6	-2.560417000	1.443035000	-2.898725000
1	-3.054688000	0.467002000	-3.003345000
1	-2.512072000	1.894856000	-3.906956000
1	-3.167571000	2.106275000	-2.265217000
8	-0.510715000	0.277898000	-2.899835000

(R)-alkoxide adduct

delta H (Hartrees)	-2679.88	delta S (cal/mol/K)	277.634
delta G (kcal/mol) (323)	-1681712.661		
1	5.815746000	-0.354679000	-1.917174000
1	5.010249000	-3.198261000	1.201649000
1	-3.405237000	-1.499840000	3.049880000
6	-4.424966000	-1.406006000	2.639624000

6	0.492709000	-1.741247000	-0.674392000
15	0.685597000	0.224785000	1.129784000
6	-3.153874000	-1.624194000	-1.435374000
1	0.086241000	2.325255000	2.946560000
1	3.676293000	4.057414000	0.007087000
6	3.345552000	-2.013929000	0.543356000
7	-0.843386000	-1.168401000	-0.865881000
1	3.180725000	0.702427000	2.586994000
6	1.380970000	-2.234715000	4.333589000
1	-0.198354000	-1.948813000	2.903113000
6	5.569406000	-1.806523000	-0.343977000
6	-2.042757000	0.844014000	2.075157000
1	2.785103000	1.805966000	-0.375613000
6	-4.469637000	-1.861359000	1.195490000
6	1.414071000	-0.547740000	2.608482000
6	2.373989000	2.407096000	0.439424000
6	2.616844000	-1.809125000	4.788862000
6	-1.773898000	-2.206561000	-1.291692000
1	0.867894000	-3.065049000	4.829873000
1	3.088467000	-2.302942000	5.644825000
6	4.672725000	-2.406260000	0.524940000
26	-1.488190000	-0.064480000	0.670439000
1	-4.590264000	-3.929043000	1.768374000
15	-3.551052000	-0.707031000	0.080540000
1	-1.751047000	-3.021883000	-0.544287000
1	6.618870000	-2.118015000	-0.355222000
1	-5.083414000	-2.044179000	3.253247000
6	3.795085000	-0.433018000	-1.190197000
1	-4.046423000	-3.716625000	0.095522000
1	1.309721000	0.156917000	-1.155606000
6	-3.979843000	-3.289564000	1.108126000
6	0.781300000	-1.608529000	3.252793000
1	-5.524068000	-1.839447000	0.851413000
6	2.657358000	-0.124599000	3.079880000
6	2.887934000	-1.005602000	-0.302895000
1	3.440556000	0.327734000	-1.898474000
8	-2.392995000	1.358276000	3.038695000
6	1.448917000	-0.589474000	-0.340978000
6	1.365958000	1.902348000	1.253678000
6	5.123401000	-0.821735000	-1.208970000
1	0.430469000	-2.433505000	0.194010000
6	1.364710000	3.980787000	2.484488000
1	2.780118000	5.472785000	1.841739000
1	-1.457324000	-2.649757000	-2.254795000
1	-2.934616000	-3.378887000	1.451122000
1	-3.137518000	-0.886711000	-2.260620000
1	0.960037000	4.596382000	3.294465000
6	2.378969000	4.467583000	1.676054000

6	0.865504000	2.708247000	2.276679000
1	-4.748165000	-0.365125000	2.791154000
1	2.652257000	-2.510537000	1.232369000
6	2.879515000	3.678572000	0.655516000
1	4.229826000	-0.406230000	4.512947000
1	-3.894842000	-2.392568000	-1.713616000
6	3.252230000	-0.750307000	4.159998000
6	-4.818192000	0.516385000	-0.468167000
1	-6.462621000	-0.850774000	-0.908376000
6	-5.468341000	1.242535000	0.687516000
6	-5.863353000	-0.062441000	-1.395510000
1	-4.735488000	1.672778000	1.390489000
1	-4.224408000	1.259320000	-1.035639000
1	-6.082254000	2.076912000	0.309304000
1	-6.143885000	0.584801000	1.260598000
1	-5.433499000	-0.488656000	-2.315413000
1	-6.569264000	0.727114000	-1.705282000
1	-0.760948000	-0.477269000	-1.680813000
6	0.996571000	-2.534611000	-1.854833000
6	1.325510000	-3.874057000	-1.702036000
6	1.157897000	-1.936270000	-3.101922000
6	1.807983000	-4.612687000	-2.770503000
6	1.634091000	-2.676639000	-4.170063000
6	1.962357000	-4.014429000	-4.009094000
1	1.202027000	-4.348350000	-0.719921000
1	0.884897000	-0.880462000	-3.235540000
1	2.064664000	-5.668408000	-2.632720000
1	1.753170000	-2.199473000	-5.148987000
1	2.341471000	-4.594161000	-4.857265000
1	-1.491920000	-1.283035000	1.540155000
1	-1.457275000	1.497769000	-1.061827000
6	-0.183231000	2.885080000	-2.064690000
6	-0.443734000	3.987300000	-1.256596000
6	0.951755000	2.903340000	-2.863612000
6	0.393526000	5.088995000	-1.263956000
6	1.793330000	4.005810000	-2.877662000
6	1.511742000	5.106669000	-2.085681000
1	-1.325669000	3.978975000	-0.599849000
1	1.148661000	2.022969000	-3.486810000
1	0.177275000	5.945939000	-0.615295000
1	2.680524000	4.009341000	-3.522181000
1	2.174603000	5.979018000	-2.094316000
6	-1.140329000	1.700355000	-2.169252000
6	-2.418724000	2.197621000	-2.853457000
1	-3.137651000	1.367829000	-2.965202000
1	-2.167641000	2.546550000	-3.871021000
1	-2.920458000	3.028351000	-2.324494000
8	-0.634921000	0.643274000	-2.758006000