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Flexible C_2-Symmetric Bis-Sulfoxides as Ligands in Enantioselective 1,4-Addition of Boronic Acids to Electron-Deficient Alkenes

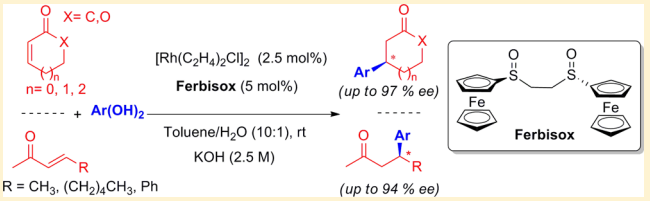
Noureddine Khiar,*[,†] Álvaro Salvador,[†,§] Victoria Valdivia,[†,‡] Ahmed Chelouan,[‡] Ana Alcudia,[‡] Eleuterio Álvarez,[†] and Inmaculada Fernández*[,‡]

[†]Instituto de Investigaciones Químicas, CSIC-Universidad de Sevilla, c/. Américo Vespucio, 49., Isla de la Cartuja, 41092 Sevilla, Spain

[‡]Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad de Sevilla, 41012 Sevilla, Spain

Supporting Information

ABSTRACT: The application of acyclic C_2-symmetric chelating bis-sulfoxide ligands in the Rh(I)-catalyzed enantioselective 1,4-addition of boronic acids to electron-deficient alkenes is reported. Among the acyclic ethane-bridged bis-sulfoxides tested, the ligand Ferbisox (**11**), bearing ferrocenyl moieties as substituents at the sulfinyl sulfurs, has exhibited the best results in terms of chemical yield (up to 96%) and enantioselectivity (up to 97% ee). The conjugate addition takes place smoothly in toluene at room temperature in short reaction times (typically 2 h). The reaction scope, including the use of different boronic acids, five-, six-, and seven-membered cyclic enones, an unsaturated lactone, and the most challenging acyclic ketones, is reported. An X-ray diffraction study of the [Ferbisox·RhCl]$_2$ precatalyst clearly exhibits a dimeric structure with an S coordination of the sulfoxide to rhodium. On the basis of the X-ray data and on structural studies conducted in solution by ^{1}H NMR, a model explaining the high enantioselection observed is proposed.



INTRODUCTION

Enantioselective conjugate addition is one of the most powerful tools for the construction of C−C bonds in modern asymmetric synthesis.[1] Since the pioneering works of Hayashi[2] and Miyaura,[3] a wide number of methodologies have been successfully developed for this transformation and very high levels of sophistication and efficiency have been achieved so far.[4] Successful Rh(I)-catalyzed additions of arylboronic acids to activated alkenes were traditionally achieved using chiral phosphorus-containing ligands.[1d] In sharp contrast with the case for phosphines, chiral bis-sulfoxide ligands have been scarcely studied in the framework of asymmetric catalysis, despite their undeniable advantages.[5] In this sense, sulfoxides are air and moisture stable and are ideally suited for the construction of diverse metal−ligand complexes with a well-defined chiral environment, as a result of the close proximity of the chiral sulfur atom to the coordination sphere of the metal.[6] On the other hand, the past decade has witnessed a genuine revolution in the synthesis of chiral sulfoxides, enabling the design and synthesis of a large number of sulfoxides with varied steric and electronic character in both enantiomeric forms.[5b,7] First employed in the late 1970s, bis-sulfoxides have shown increasingly good performance in different enantioselective transformations (ruthenium-catalyzed hydrogenations (1977),[8] iron-catalyzed Diels−Alder reaction (1993),[9] palladium-catalyzed allylic substitution (1995),[10] Reissert reactions (2004),[11] and organocatalytic allylation of benzoylhydrazine (2007)[12]) (Figure 1). However, it was not until the late 2000s that their interesting metal-coordinating abilities toward transition metals were rewarded with enantioselectivities that can compete with those of good standard catalysts used in the literature. Indeed, in 2008, the Dortás group found that C_2-symmetric atropoisomeric sulfoxides were among the best ligands for the Rh-catalyzed 1,4-addition of arylboronic acids to cyclohexenones.[13] This behavior,[14] which can compete with the excellent performance of the state of the art for chiral dienes,[15] was recently confirmed by other research groups and triggered the search of novel C_1-[16] and C_2-symmetric chiral sulfoxide ligands (Figure 1). Important contributions in this area have been achieved by the groups of Zhou[17] and Liao[18] through the development of a wide variety of chelating bis-sulfoxide ligands and also their application in Rh(I)-catalyzed enantioselective 1,4-addition. The ligands reported by Liao are based on a simple benzene backbone that acts as a rigid scaffold for the formation of sulfoxides in relative 1,2-positions. This chelating mode has been exploited by the authors to prepare, in a very efficient manner, C_2-symmetric ligands as well as the related C_1-symmetric hetero bis-sulfoxides.[19]

As a part of an ongoing and traditionally established project in our laboratories based on the synthesis and later application of sulfoxide-containing molecular entities in asymmetric catalysis (both organocatalyzed[12,20] and metal catalyzed[21]), herein we report the application of acyclic ethane-bridged bis-sulfoxides of type **I** (Figure 2) in the enantioselective 1,4-

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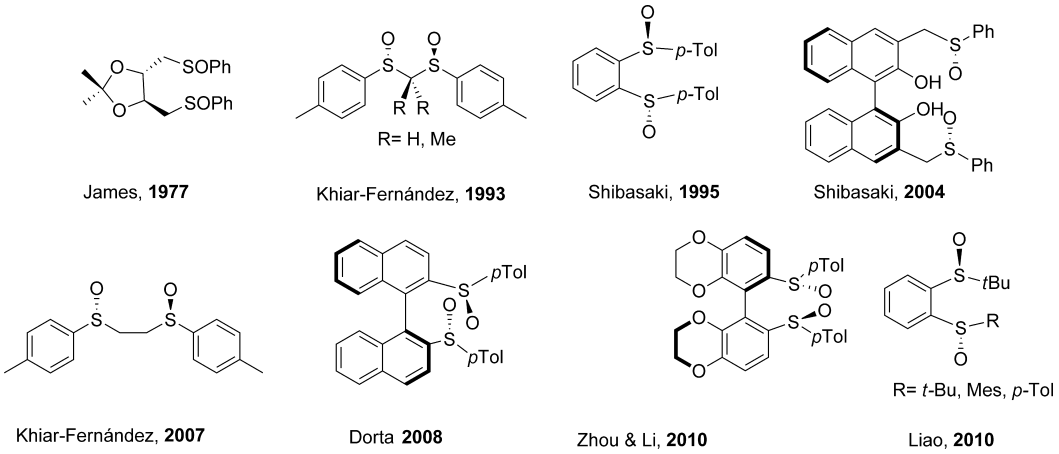


Figure 1. Representative examples of chiral chelating bis-sulfoxides.

addition of arylboronic acids to α,β-unsaturated carbonyl compounds.

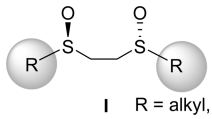


Figure 2. General structure of C_2-symmetric ligands studied in this work.

As a feature distinguishing them from the previously described rigid ligands, our C_2-symmetric ligands have their sulfoxide-coordinating functions placed on a flexible, less conformationally restricted ethane fragment. On the other hand, the design of our ligands relies on the presence of the sulfur atoms as sole source of chirality, which will permit the assessment of their exact contribution to the stereochemical outcome of the process.

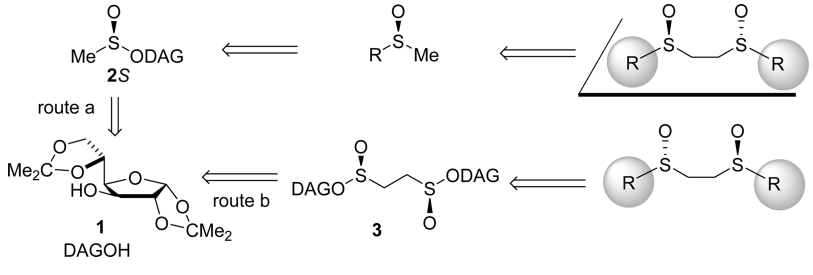
RESULTS AND DISCUSSION

Synthesis of the C_2-Symmetric Ligands. In order to fine tune the steric and electronic characters of the bis-sulfoxide ligands, we have applied our highly modular diacetone-D-glucose (DAG) methodology (Scheme 1).[22] It is worth mentioning that in addition to taking place with a dynamic kinetic transformation of the starting racemic sulfinyl chlorides, the DAG methodology is able to give both enantiomers[22c,d] of the final bis-sulfoxides using diacetone-D-glucose **1** as a single chiral auxiliary following two different pathways. The first approach (route a, Scheme 1) is based on the use of DAG methanesulfinate **2**, as a common intermediate for the synthesis of various optically pure methyl sulfoxides, followed by a copper-catalyzed oxidative coupling of the corresponding lithium anions.[23] The second approach (route b, Scheme 1) is based on the condensation of Grignard reagents on diastereomerically pure C_2-symmetric DAG bis-sulfinate esters **3**, obtained by dynamic kinetic resolution of 1,2-ethane bis-sulfinyl chloride.[24] While both routes are able to give both enantiomers of the final sulfoxides with high ee, the former is preferred when the methyl sulfoxide intermediate has no other acidic proton, as in the case of bis-sulfoxides designed for this work.

A selected variety of methyl sulfoxides with different substituents, including *p*-tolyl (**4**), mesityl (**5**), *tert*-butyl (**6**), and ferrocenyl (**7**), has been easily prepared in high yields (typically 85% yields; Scheme 2) by treatment of the diastereomerically pure methyl sulfinylating agent $2R_S$ or $2S_S$ with an organometallic reagent (both organolithium and Grignard reagents). In this manner, the reaction of $2R_S$ or $2S_S$ at low temperature (0 °C) with the corresponding nucleophile (see Scheme 2) cleanly affords the desired methyl sulfoxides **4**–**7**, with inversion of the configuration at the sulfur atom. The obtained enantiopure methyl sulfoxides are transformed into the final ligands by copper-catalyzed oxidative dimerization of the corresponding α anions (generated by treatment of **4**–**7** with *n*-BuLi at −78 °C). Under these conditions, the acyclic C_2-symmetric ligands **8**–**11** were obtained in high yields and high enantiopurities (Scheme 2).

It is worth mentioning that the enantiopurity of the bis-sulfoxides is higher than the enantiopurity of the parent methyl sulfoxide intermediates due to a statistical amplification, a consequence of the Horeau principle.[25] In this sense, starting from an *x*:1 enantiomeric ratio of a given sulfoxide (ee: $x - 1$), the dimerization process (which does not alter the configuration at the sulfinyl sulfur) will give the corresponding bis-

Scheme 1. DAG Sulfinate Based Retrosynthetic Analysis of Flexible Ethane-Bridged C_2-Symmetric Ligands



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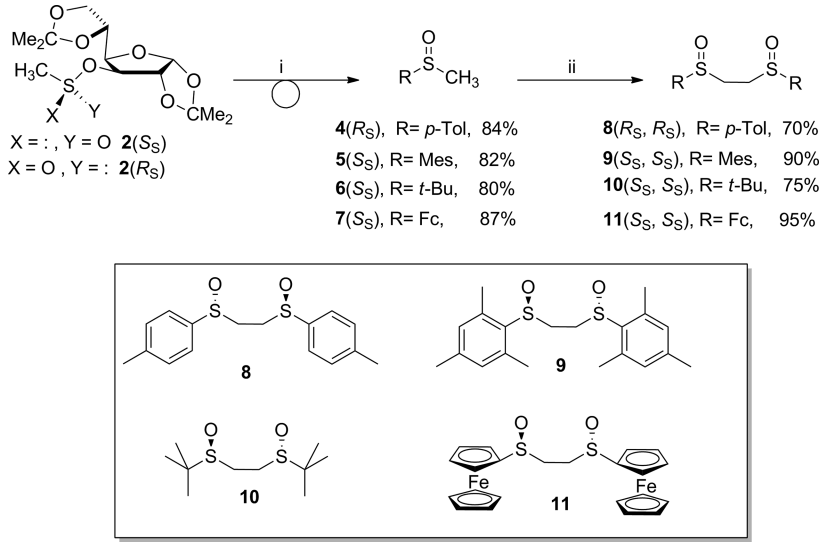
Scheme 2. Synthesis of C_2-Symmetric Bis-Sulfoxides 8−11 by Cu-Catalyzed Dimerization of Lithiomethyl Sulfoxides Using the DAG Methodology[a]



[a]Reagents and conditions: (i) RM, THF, −78 °C. (ii) (1) *n*-BuLi, THF, −78 °C, (2) $CuCl_2$, THF, −78 °C to room temperature.

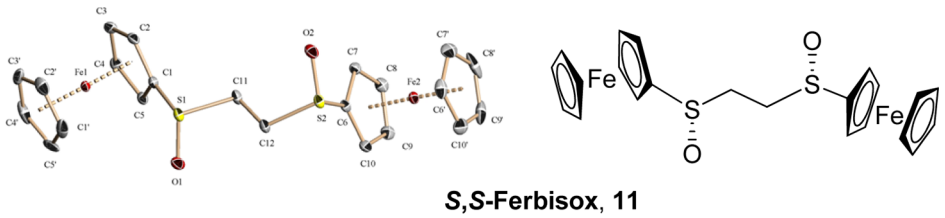


Figure 3. ORTEP drawing of the ligand Ferbisox **11**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity.

sulfoxide with an x^2:1 enantiomeric ratio (ee: $x^2 - 1$), together with a 2x quantity of the *meso* bis-sulfoxide, which can be easily eliminated by column chromatography. Considering that the methyl sulfoxide intermediates are obtained with inversion of configuration at the sulfinyl sulfur and generally in high enantiomeric purity from the starting DAG methanesulfinate **2**, the reported method allows the synthesis of both enantiomers of a wide range of enantiopure bis-sulfoxides in a rapid and predictable manner. Thus, the epimeric DAG methanesulfinate **2**R_S leads to the final bis-sulfoxide **8** with an R_S,R_S absolute configuration at the sulfurs, while DAG methanesulfinate **2**S_S gives ligands **9**−**11** with an S_S,S_S absolute configuration at the sulfurs. Additional confirmation of the stereochemical outcome of the whole process came from an X-ray study of the interesting electron-rich C_2-symmetric bis-ferrocenyl ligand Ferbisox **11**, obtained in 83% overall yield from the starting DAG methanesulfinate **2**S_S and ferrocenyllithium. X-ray diffraction quality crystals were obtained by a slow vapor diffusion technique from ligand **11** (Figure 3), which allowed the determination of the absolute configuration in both sulfur atoms as S_S.

As is usual in ferrocenyl sulfoxide compounds, the orientation of the substituent at sulfur is *anti* to the iron atom (Fe−C1−S1−C11 torsion angle 177.26°), forcing the sulfinyl oxygen to face the pro-*S* position (O2−S2−C6−C7 torsion angle −1.52°). This interesting conformation opens the way for the synthesis of new ligands which combine central and planar chirality through a diastereoselective ortho-lithiation/substitution pathway.[26]

Enantioselective 1,4-Addition of Boronic Acids to Olefins. Once the ligands **8**−**11** were in hand, we assayed them in the model reaction of 2-cyclohexenone **12** and phenylboronic acid **13** (Table 1), under previously reported conditions: toluene/KOH (2.5 M in H_2O) (10/1) and 5 mol % of a combination of ligand and $[Rh(C_2H_4)_2Cl]_2$.[14] All of the reactions reached full conversion, affording 3-phenylcyclohexanone **14** in short reaction times with good yields (typically 77−94% in less than 2 h). The amount of boronic acid plays an important role in the reaction, since compound **14** is obtained in 66% yield and 20% ee with 1.2 equiv of **13** (entry 1), while the use of 2 equiv (entry 2) substantially increases the yield (77%) and enantioselectivity (42% ee). As shown in Table 1, the enantioselectivity depends not only on the steric but also on the electronic nature of the substituents at the sulfinyl sulfur. In this sense, an increase of the steric hindrance, from the *p*-Tol group (entry 2) to a *t*-Bu group (entry 8), is translated into an increase of the enantioselectivity from 42% ee to 78% ee, respectively. On the other hand, ligand **9** with a sterically demanding aromatic mesityl group afforded the addition compound **14** with a deceiving 26% ee (entry 6). The highest enantioselection, 86% ee in favor of **14***R*, was obtained with the Ferbisox ligand **11** having a sterically demanding and electronically rich ferrocene moiety (entry 9).

On the basis of the enantioselective performance exhibited by the studied ligands, we dismissed ligands **8** and **9** to focus

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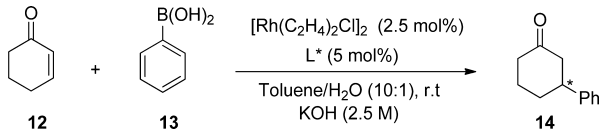
Table 1. Effect of the Ligand Structure on the Enantioselective Conjugate Addition of Phenylboronic Acid 13 to Cyclohexenone 12[a]



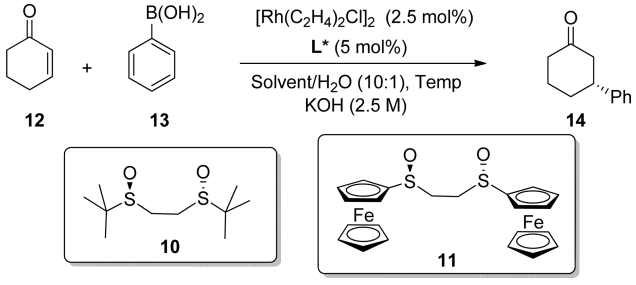
entry	amt of **13** (equiv)	L*	time (h)	yield[b] (%)	er[c] (%)
1	1.2	**8**	1.5	66	40/60
2	2	**8**	1.5	77	29/71
3	2	**8**[d]	2.5	80	44/56
4	2	**8**[e]	2.5	80	47/53
5	2	**8**	0.25[f]	76	40/60
6	2	**9**	20	77	63/37
7	2	**9**	2[g]	85	66/34
8	2	**10**	7[g]	92	89/11
9	2	**11**	48[g]	96	93/7

[a]All reactions were conducted using 5 mol % of the ligand together with 2.5 mol % of $[Rh(C_2H_4)Cl]_2$. [b]Isolated yield of pure compound **14** after column chromatographic purification. [c]Determined by chiral stationary phase HPLC with an OD-H column: hexane/*i*PrOH 98/2, flow 0.5 mL/min. [d]Reaction done in DMF. [e]Reaction done in 1,4-dioxane. [f]Reaction done at 0 °C. [g]Reaction done at 40 °C.

our attention on the successful ligand **10**, with a sterically demanding *t*-Bu group, and ligand **11**, with an electronically rich ferrocenyl moiety. The results of a detailed study on the influence of the temperature and solvents on the catalytic performance of the aforementioned ligands are collected in Table 2.

While both ligands exhibited similar reactivities, the enantioselectivity obtained with ligand **11** was slightly better

Table 2. Temperature Effect on the Enantioselective Conjugate Addition of Phenylboronic Acid 13 to Cyclohexenone 12 Using Ligands 10 and 11[a]



entry	L*	solvent	temp (°C)	time (h)	yield[b] (%)	er[c] (%*R*/%*S*)
1	**10**	toluene	0	2.5	83	91/9
2	**11**	toluene	0	2.5	91	92/8
3	**10**	toluene	rt	2	92	89/11
4	**11**	toluene	rt	2	93	93/7
5	**10**	toluene	40	1	90	87/13
6	**11**	toluene	40	1	91	89/11
7	**11**	toluene	80	0.5	87	73/27
8	**10**	DCM	rt	3	92	89/11
9	**11**	MeOH	rt	1.5	94	90/10

[a]All reactions were conducted using 5 mol % of the ligand together with 2.5 mol % of $[Rh(C_2H_4)Cl]_2$. [b]Isolated yield of pure compound **14** after column chromatographic purification. [c]Determined by chiral stationary phase HPLC with an OD-H column: hexane/*i*PrOH 98/2, flow 0.5 mL/min.

(compare entries 3 and 4). When the temperature is increased, the reaction takes place more quickly but to the detriment of the enantioselectivity, room temperature being the best reactivity−enantioselectivity compromise (entries 3 and 4). The use of other solvents such as methylene chloride (entry 8) and methanol (entry 9) afforded the final adduct **14***R* with good yields and enantioselectivities but did not improve upon the results obtained in toluene. On the basis of the results compiled in Table 2, we can conclude that the optimized reaction conditions are as follows: 1 equiv of an α,β-unsaturated compound reacts with 2 equiv of phenylboronic acid in the presence of 5 mol % of the "in situ" prepared precatalyst system formed by $[Rh(C_2H_4)_2Cl]_2$ and Ferbisox **11**, in a toluene/KOH mixture (2.5 M aqueous) (10/1), at room temperature.

Reaction Scope. Subsequently, we started the study of the reaction scope, first by the addition of different boronic acids to cyclohexenone **12** (Table 3, entries 2−7). The reaction is independent of the electronic factors, as electron-donating and electron-withdrawing substituents on the aryl group of the boronic acids gave the products of addition **18**−**22** with good yields (compare entries 1−9). Both *para*- and *meta*-substituted aryls could be introduced with acceptable enantioselectivities and high yields (entries 2−5). In contrast, addition of an *ortho*-substituted aryl proceeded with excellent yield but with a considerable drop in enantioselectivity (entry 6). On the addition of *p*-tolyl, *p*-methoxyphenyl, and *p*-chlorophenyl groups, the corresponding ketones **18**−**20** were obtained with high yields and enantioselectivities of 82%, 74%, and 64%, respectively (entries 2−4), while the *m*-tolyl substituted ketone **21** was obtained in high yield with 78% ee (entry 5). Next, we studied the addition of phenylboronic acid to other cyclic enones and enoates, including the five-membered-ring 2-cyclopentenone **15**, the seven-membered-ring cycloheptenone **16**, and the unsaturated cyclic lactone **17**. To our delight, the 3-phenylcyclopentanone **23***R* (Table 3, entry 7) was isolated in good yield (83%) and high enantioselectivity (92% ee), improving upon all the previous efforts employed in the model reaction of 2-cyclohexenone **12**. This result points out that the system formed by Ferbisox **11** and $[Rh(C_2H_4)_2Cl]_2$ may not be quite as specific for the 2-cyclohexenone substrate **12** but very efficient for other unsaturated systems. Satisfyingly, this hypothesis was confirmed by the result obtained with the seven-membered-ring enone **16** (Table 3, entry 8), giving the corresponding addition product **24***R* in high yield (87%) and high enantioselectivity (96%). An equally satisfying result was reached with the six-memberred-ring unsaturated lactone **17** (entry 9), giving the addition product **25***R* in high yield (95%) and excellent enantioselectivity (97% ee).

With these results in hand, we then turned our attention to the 1,4-adition of phenylboronic acid **13** to the more challenging acyclic unsaturated ketones. It is worth mentioning that, until quite recently, only a few catalyst systems gave good results in this transformation.[27] Nevertheless, the synthetic efforts undertaken in the last years have led to the discovery of highly efficient catalysts able to give high enantioselectivities with both cyclic and acyclic substrates.[28] Encouraged by the good results obtained with cyclic substrates, we decided to determine the catalytic efficiency of ligand **11** with acyclic substrates, including 3-pentenone **26**, non-3-en-2-one **27**, and (*E*)-4-phenylbut-3-en-2-one **28**. Pleasingly, we found that the system is very efficient, as the final aryl ketones **29**−**34** were obtained with high yields and high enantioselectivities (Table 4, entries 1−6). First, the addition of phenylboronic acid to 3-

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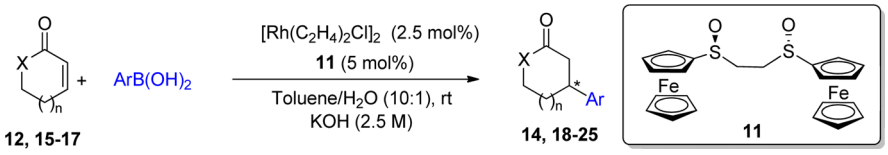
Table 3. Reaction Scope of Ferbisox 11 Catalyzed 1,4-Addition of Arylboronic Acids to Cyclic Activated Alkenes[a]



12, 15-17 — 14, 18-25 — 11

Entry	Starting alkene	Product	Yield[b] (%)	e.r.[c] (%*R*:%*S*)
1	**12**	**14** (Ar = Ph)	87	93 : 7
2	**12**	**18** (Ar = 4-MeC$_6$H$_4$)	96	91 : 9
3	**12**	**19** (Ar = 4-OMeC$_6$H$_4$)	86	86 : 14
4	**12**	**20** (Ar = 4-ClC$_6$H$_4$)	87	82 : 18
5	**12**	**21** (Ar = 3-MeC$_6$H$_4$)	99	89 : 11
6	**12**	**22** (Ar = 2-MeC$_6$H$_4$)	90	75 : 25
7	**15**	**23** (Ar = Ph)	83	96 : 4
8	**16**	**24** (Ar = Ph)	87	98 : 2
9	**17**	**25** (Ar = Ph)	95	98.5 : 1.5

[a]All reactions were conducted using 5 mol % of the ligand together with 2.5 mol % of $[Rh(C_2H_4)Cl]_2$. [b]Isolated yield of pure addition compounds after column chromatographic purification. [c]Determined by chiral stationary phase HPLC.

pentenone **26** gave the desired 4-phenylpentan-2-one **29***S* in 87% yield and an interesting 90% ee (Table 4, entry 1). The addition of other boronic acids to 3-pentenone **26** (Table 4, entries 2−4) shows once again that the reaction is independent of the electronic factors, as both electron-donating and electron-withdrawing substituents on the aryl group of the boronic acids gave the products of addition with good yields (compare entries 1−4). In the addition of *p*-tolyl, *p*-methoxyphenyl, and *p*-chloroyphenyl groups, the corresponding ketones **30**−**32** were obtained with high yields and enantioselectivities of 94%, 90%, and 94%, respectively (entries 2−4). Equally successful was the addition of phenylboronic acid to non-3-en-2-one **27**, which afforded the desired 4-phenylnoan-2-one **33***S* in 92% yield and an remarkable 94% ee. Interestingly enough, in the addition of phenylboronic acid to the hindered (*E*)-4-phenylbut-3-en-2-one **28**, the desired product **34** was obtained with a moderate 64% yield and an excellent 94% ee (Table 1, entry 6).

Preliminary Studies on the Mechanism of the Enantioselective 1,4-Addition of Arylboronic Acid to Cyclic and Acyclic Ketones. The catalytic cycle of Rh(I)-catalyzed 1,4-addition of arylboronic acids to activated alkenes has been well studied and involves (i) transmetalation of arylboronic acid to the HO−[Rh] species **35**, giving the Ar−[Rh] intermediate **36**, (ii) insertion of alkene **37** into the Ar−[Rh] bond of **38** to yield the rhodium enolate **39**, and finally (iii) formation of the addition product **40** and regeneration of **35** via hydrolysis of the rhodium enolate intermediate with water (Scheme 3).[29]

Thus, with one exception,[14] in most reported systems the enantioselectivity and the absolute configuration of the final product is set at the insertion step of alkene **37** into the arylrhodium(I)−ligand intermediate **38**. Taking into account that our ligand is a sulfoxide, a preliminary step before discussing the observed enantioselectivity and the sense of the same is the determination of the structure of the precatalyst.

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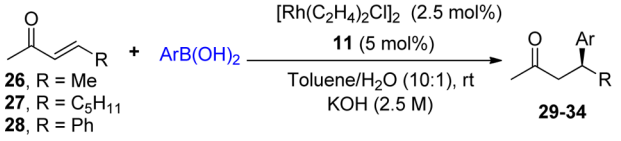
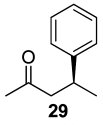
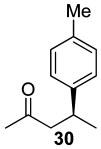
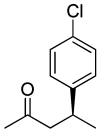
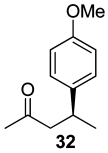
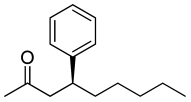
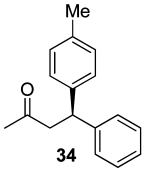
Table 4. Study on the Ferbisox·Rh(I)-Catalyzed 1,4-Addition of Arylboronic Acids to Linear Unsaturated Ketones 26−28[a]

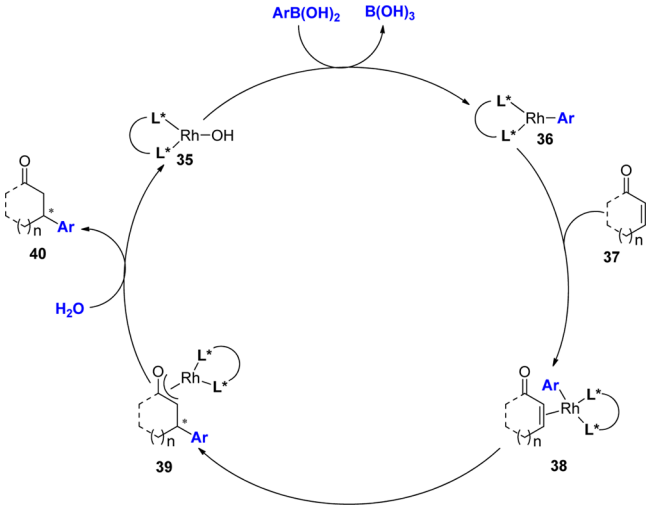


Entry	Product	Yield[b] (%)	e.r.[c] (%*S*:%*R*)
1	 **29**	87	95 : 5
2	 **30**	76	97: 3
3	 **31**	99	97: 3
4	 **32**	56	95 : 5
5	 **33**	92	97: 3
6	 **34**	60	3: 97

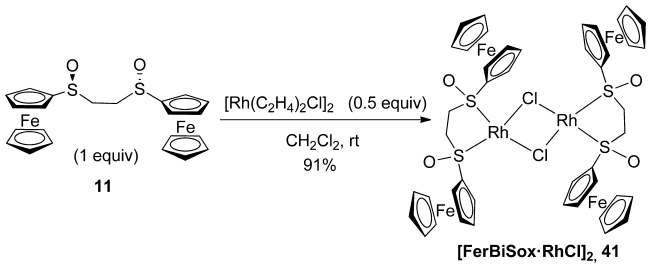
[a]All reactions were conducted using 5 mol % of the ligand **11** together with 2.5 mol % of $[Rh(C_2H_4)Cl]_2$. [b]Isolated yield of pure addition compounds after column chromatographic purification. [c]Determined by chiral stationary phase HPLC.

Indeed, sulfoxide ligands can coordinate metals through either the sulfur or oxygen atom, according to steric and electronic demands.[5,6,30] A number of complexes of chelating bis-sulfoxides (mostly racemic) are currently known, including those with ruthenium,[23,31] platinum,[31] palladium,[10,32c,33] and rhodium.[10,13,32c,33a,34] The main coordination mode of bis-sulfoxide ligands to rhodium is through the sulfur, eventhough an O coordination has been observed in the case of the seterically demanding racemic ligand **10**.[32] To determine the coordination mode of Ferbisox ligand **11** to the rhodium, we decided to synthesize the corresponding Rh(I) complex to further study its structural characteristics using ^{1}H NMR. Condensation of 0.5 equiv of $[Rh(C_2H_4)_2Cl]_2$ and 1 equiv of ligand **11** in CH_2Cl_2 for 16 h afforded complex **41** in 91% yield as orange crystals (Scheme 4).

Scheme 3. Catalytic Cycle for the Miyaura−Hayashi Reaction



Scheme 4. Reaction Scheme for the Synthesis of Complex 41



Generally, O bonding in sulfoxides results in small downfield chemical shifts of the α protons, while larger downfield chemical shifts are seen for coordination through the S atom. In the case of complex **41**, ^{1}H NMR analysis shows that it has a C_2 symmetry and that it exhibits a signal pattern similar to that of the free ligand **11** (Figure 4), except for the chemical shifts and the nonequivalency of the methylenic and the ferrocenyl protons α to the sulfur. There is a large nonequivalence of the α methylene protons (1 ppm) in the Rh complex **41** in comparison with the free ligand **11** (0.6 ppm) and a deshielding of the cyclopentadienyl proton α to the sulfur by 1.2 ppm.

Taken altogether, these data point out that the Rh complex **41** is S coordinated with a fixed conformation in solution.

Next, the molecular structure of the dimeric complex **41** was confirmed by X-ray studies. Layering a methylene chloride solution with THF afforded shiny red crystals suitable for their X-ray diffraction analysis. The solid-state structure of the complex shows that the rhodium atom is located in a slightly distorted square plane containing the bis-ferrocenyl ligand **11** and two bridging chlorines (Figure 5). Ligand **11** coordinates to the rhodium via the sulfur atoms, forming a five-membered ring with an S−Rh−S angle of 87.57(4)°, and as expected the S−O bond length is significantly shorter in the complex **41** (1.476(3) Å) relative to that in the free ligand (1.494(1) Å). Significantly, the Rh−Rh distance observed in complex **41** (3.203(1) Å) is longer in comparison with similar dimeric Rh(I) complexes derived from ligand **8** with a *p*-tolylsulfinyl group (3.019 Å) and from ligand **10** with a *tert*-butylsulfinyl group (3.161 Å), indicating a higher electron density on the metal center in complex **41**. In the S-coordinated complex, the

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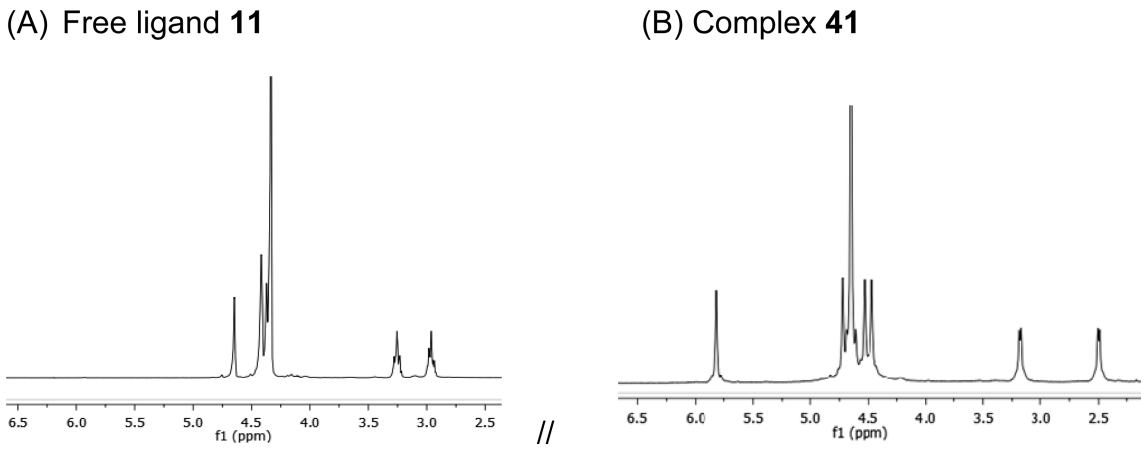

Figure 4. ^{1}H NMR ($CDCl_3$, 500 MHz) of free ligand **11** and complex **41**.

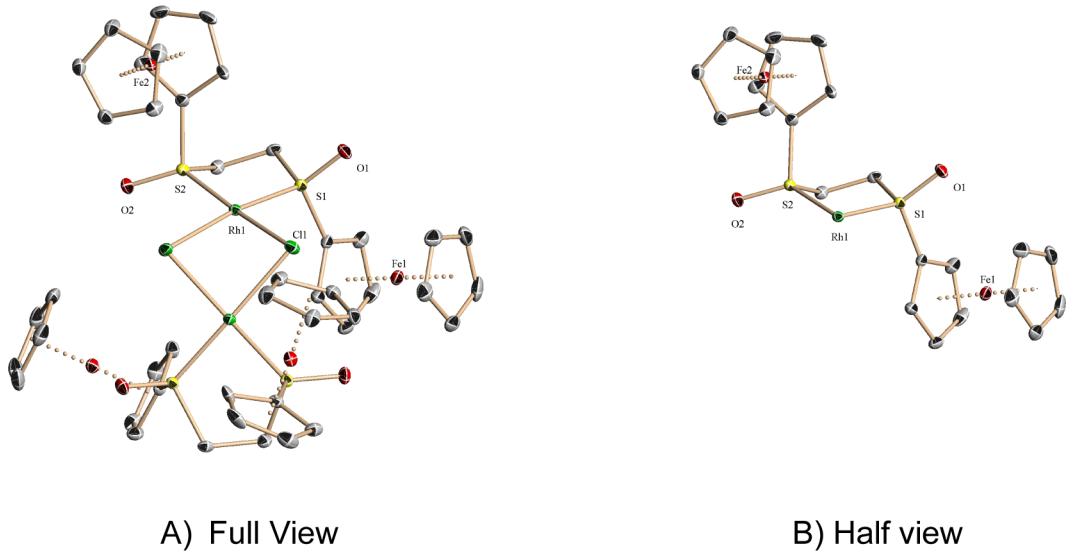

Figure 5. ORTEP drawing of complex **41** (A, full view; B, half view). Thermal ellipsoids are represented at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected angles (deg) and bond lengths (Å): S(1)−Rh(1)−Cl(1)#1, 171.89(4); S(2)−Rh(1)−Cl(1), 174.24(4); S(2)−Rh(1)−S(1), 87.57(4); S(2)−Rh(1)−Cl(1)#1, 95.45(4); Rh(1)−S(2), 2.1632(13); Rh(1)−S(1), 2.1784(12); Rh(1)−Cl(1)#1, 2.3976(13); Rh(1)−Cl(1), 2.4017(13).

five-membered metallacycle formed shows a half-chair conformation with both ferrocenyl moieties occupying pseudoaxial positions.

Therefore, the rhodium complex **41** creates an effective C_2-symmetric environment with the pseudoaxial ferrocenyl substituents located at the upper left and the lower right positions, as shown in the half-view of the complex (Figure 5). This conformation points out that the ferrocenyl group will play a determining role in the facial discrimination of the olefinic face upon coordination to the rhodium. In this sense, at the addition of a phenylrhodium species to enones in the catalytic cycle, the olefinic double bond coordinates to the rhodium so as to minimize the steric repulsion between the protruding ferrocenyl moiety and the carbonyl group of the enones. The alkyl substituents at the β position of the enone are located far from the ligand and do not play a decisive role in controlling the enantioface coordination of the olefins. Thus, both cyclic and linear enones undergo the phenyl addition from the α-re face, affording the 1,4-phenylation products with the observed absolute configurations (Scheme 5).

Thus, in contrast to the rigid atropoisomeric bis-sulfoxides,[14] the enantiodiscrimination step with the flexible bis-sulfoxide **11** must be the insertion of the alkenes into the arylrhodium(I)−**11** intermediate, as is the case for the majority of the systems reported for the enantioselective Miyaura−Hayashi reaction.

■ CONCLUSIONS

In summary, chiral bis-sulfoxide Ferbisox **11** proved to be effective in Rh(I)-catalyzed asymmetric 1,4-addition. The application of the DAG methodology allows the quick and high-yielding synthesis of C_2-symmetric ligands with the particularity of the sole presence of sulfur chirality, as opposed to the usual carbon-backbone chirality. Ferbisox **11**, with two ferrocenyl groups bridged by a flexible ethane chain, smoothly catalyzes in combination with $[Rh(C_2H_4)_2Cl]_2$ the addition of arylboronic acids to activated olefins. The generality of the reported method was demonstrated by the addition of sterically and electronically different arylboronic acids to five-, six-, and seven-membered cyclic enones to cyclic enoates and to the more challenging acyclic enones. The X-ray structure of the successful ligand **11** and the precatalyst dimeric Rh(I) complex

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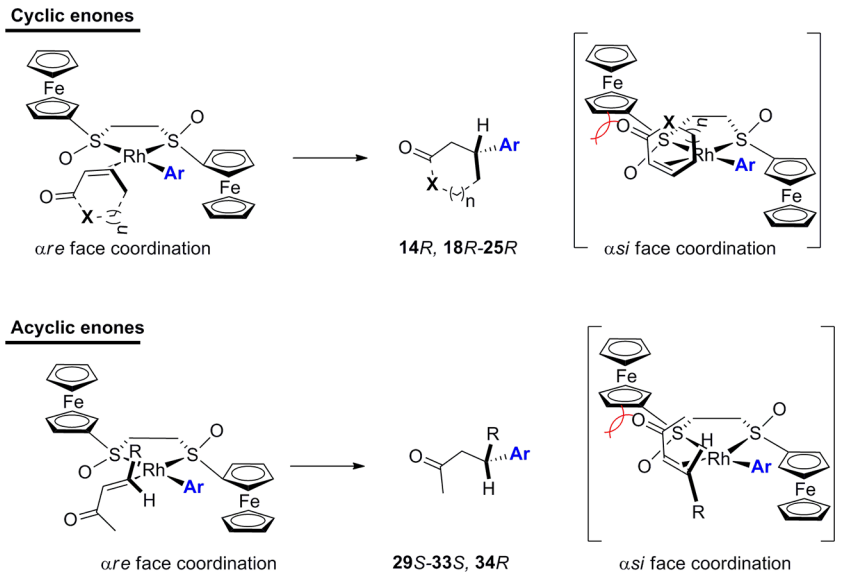
Scheme 5. Model Explaining the Origin of the Enantioselectivity Obtained with Ferbisox 11 in the 1,4-Addition of Phenylboronic Acids to Cyclic and Acyclic Activated Ketones



41 have also been reported, revealing an S coordination to the sulfur leading to a dimeric chlorine-bridged complex with a square-planar geometry around the rhodium atoms. On the basis of the X-ray data and on structural studies conducted in solution by ^{1}H NMR, a model explaining the high enantioselection observed and the origin of the preference of the formed enantiomer is proposed. Together with the work aimed at applying Ferbisox to other catalytic processes, the collected structural results are being used to modulate the ligand structure in order to optimize the enantiodifferentiation of the olefinic face upon coordination to the rhodium. The results of these studies will be reported in due course.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were conducted under an atmosphere of dry argon using oven-dried glassware and freshly distilled and dried solvents. Chromatographic columns (silica gel 230−400 mesh) were eluted with positive air pressure, and eluents are given as volume to volume ratios (v/v). ^{1}H NMR (400 and 500 MHz, internal Me_4Si) spectra were recorded from solutions in $CDCl_3$. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. High-resolution mass spectra (HRMS) were measured with an ESI-Qtrap mass spectrometer. Enantiomeric excesses were determined by chiral stationary phase HPLC.

General Method for the Synthesis of Methyl Sulfoxides. Over a solution of the corresponding sulfinate **2***R* or **2***S* (6.20 mmol, 1 equiv) in toluene (25 mL), cooled to 0 °C and under an argon atmosphere, was added 1.2 equiv of the appropriate organometallic reagent. After it was stirred at this temperature for 1 h, the reaction mixture was quenched with an aqueous saturated solution of NH_4Cl (8 mL) and extracted with EtOAc (4 × 25 mL). The collected organic phase was washed with brine (2 × 10 mL) and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The resulting residue was purified by recrystallization or by flash chromatography.

*(R)-4-Methylphenyl Methyl Sulfoxide (**4**).* This compound was prepared from DAG methanesulfinate **2***R* and a 1 M solution of (4-methylphenyl)magnesium bromide in ether. Yield: 802 mg, 84%. White solid. Mp: 74−75 °C. $[\alpha]_D^{20}$ = +145.0° (*c* 1.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 and 7.35 (4H), 2.70 (s, 3H), 2.45 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.7, 139.0, 127.4, 123.8, 47.7, 21.3. MS: calcd for $C_8H_{10}OS$: 154.23, found 154.05.

*(S)-(2,4,6)-Trimethylphenyl Methyl Sulfoxide (**5**).* This compound was prepared from DAG methanesulfinate **2***S* and a 1 M solution of 2,4,6-trimethyphenyl magnesium bromide in ether. Yield: 925 mg, 82%. $[\alpha]_D^{20}$ = −390.0° (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.8 (s, 2H), 2.78 (s, 3H), 2.49 (s, 6H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.8, 137.6, 130.7, 38.2, 20.8, 18.7. HRMS: calcd for $C_{10}H_{14}OS$: 183.0843, found 183.0838.

*(S)-1,1-Dimethylethyl Methyl Sulfoxide (**6**).* This compound was prepared from DAG methanesulfinate **2***S* and a 2 M solution of *tert*-butylmagnesium chloride in ether. Yield: 596.2 mg, 80%. $[\alpha]_D^{20}$ = +19.0° (*c* 1.0, MeOH), +8.7° (*c* 1.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.6, 31.5, 22.5. HRMS: calcd for $C_5H_{12}OS$ 120.0608, found 120.0608.

*(S)-Ferrocenyl Methyl Sulfoxide (**7**).* This compound was prepared from DAG methanesulfinate **2***S* and a freshly prepared 1 M suspension of ferrocenyllithium in THF. Yield: 1.42 g, 87%. Yellow solid. Mp: 101−103 °C. $[\alpha]_D^{20}$ = +143.0° (*c* 1.0, $CHCl_3$). HPLC: 99% ee, Chiralcel OD-H column (*n*-hexane/2-propanol, 90/10, 0.5 mL/min); t_R = 31.3 min (*S* isomer), 42.9 min (*R* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.71 (s, 1H), 4.48 (s, 1H), 4.43−4.40 (m, 2H), 4.34 (s, H), 2.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 92.6, 69.8, 69.7, 69.4, 66.0, 65.7, 59.2, 41.9. HRMS: calcd for $C_{11}H_{12}OSFe$ 247.9958, found 247.9963. Anal. Calcd for $C_{11}H_{12}FeOS$: C, 53.25; H, 4.87; S, 12.92. Found: C, 53.21; H, 4.62; S, 13.08.

General Method for the Oxidative Cu(II) Dimerization of Enantiopure Methylsulfinyl Anion. Bis-sulfoxides **8**−**11** were prepared by addition of $CuCl_2$ (16 mmol, 2.1 g, 1.6 equiv) to a solution of the corresponding alkyl or aryl methylsulfinyl lithium carbanion (10 mmol, 1 equiv, generated by treatment of the corresponding methyl sulfoxide with LDA at low temperature) in THF at −78 °C. After it was stirred for 15 min, the reaction mixture was stirred at room temperature in the presence of oxygen for 1 h, quenched with 10% H_2SO_4 aqueous solution (10 mL), and extracted with chloroform and the extract was sequentially washed with aqueous NH_3 solution (2 × 10 mL) and brine (1 × 10 mL). The product was purified by flash chromatography.

*(R,R)-Bis(p-tolylsulfinyl)ethane (**8**).* This compound was prepared from sulfoxide **4***R*. Yield: 2.14 g, 70%. $[\alpha]_D$ = +272.0° (*c* 0.5, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 and 7.26 (arom, 8H), 3.27−3.34 (m, 2H), 2.68−2.75 (m, 2H), 2.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.7, 139.0, 130.0, 123.8, 47.7, 21.3. HRMS: calcd for $C_{16}H_{18}O_2S_2$ 306.0748, found 306.0754.

*(S,S)-Bis(Mesitylsulfinyl)ethane (**9**).* This compound was prepared from sulfoxide **5***S*. Yield: 3.25 g, 90%. $[\alpha]_D$ = −369.0° (*c* 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (s, 4H), 3.45−3.60 (m, 2H), 3.10−3.25 (m, 2H), 2.49 (s, 12H), 2.24 (s, 6H) ppm. ^{13}C NMR

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($CDCl_3$, 125 MHz): δ 18.9, 20.9, 45.5, 131.0, 133.7, 138.2, 141.5. HRMS: calcd for $C_{20}H_{27}O_2S_2$ 363.1452, found 363.1446.

*(S,S)-Bis(tert-butylsulfinyl)ethane (**10**).* This compound was prepared from sulfoxide **6***S*. Yield: 1.75 g, 75%. White solid. Mp: 154−156 °C. $[\alpha]_D$ = −245.0° (*c* 0.5, EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.00−2.84 (m, 4H), 1.29 (s, 18H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.7, 39.3, 53.8. HRMS: calcd for $C_{10}H_{23}O_2S_2$ $(M + H)^+$ 239.1139, found 239.1137.

*(S,S)-Bis(ferrocenyl)ethane (**11**).* This compound was prepared from sulfoxide 7*S*. Yield: 4.99 g, 95%. Yellow solid. Mp: 111−113 °C. $[\alpha]_D^{20}$ = +89.1° (*c* 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.65 (s, 2H), 4.43−4.35 (m, 16H), 3.28−3.23 (m, 2H), 3.00−2.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 89.9, 70.4, 70.0, 69.9, 67.0, 65.3, 48.3. HRMS: calcd for $C_{22}H_{22}O_2S_2Fe_2$ 493.9760, found 493.9748.

Bis(μ-chloro)bis{(*S,S*)-[diferrocenylethane]rhodium(I)} (41). A solution of $[Rh(C_2H_4)_2Cl]_2$ (5.9 mg, 0.015 mmol) in CH_2Cl_2 (0.5 mL) was added over a solution of ligand **11** (15 mg, 0.03 mmol) in CH_2Cl_2 (0.5 mL) previously stirred for 5 min at room temperature. The reaction mixture turned an intense red after 30 min and was stirred for 16 h at room temperature. The crude reaction mixture was filtered through a pad of Celite. The Celite was washed with CH_2Cl_2, and the solvent was evaporated. The complex was obtained as an intense red solid. The compound was dissolved in 1 mL of CH_2Cl_2, the solution was layered with THF (10 mL), and the crystallizer was kept at room temperature for 48 h to yield bright carmine crystals. Yield: 19.4 mg, 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.82 (s, 4H), 4.80−4,30 (m, 32H), 3.20−3.16 (m, 4H), 2.52−2.48 (d, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 96.1, 73.8, 70.9, 70.5, 69.4, 64.1, 57.1. For crystallographic data see the Supporting Information.

Typical Procedure for the 1,4-Addition of Boronic Acids to Cyclic Enones. A mixture of ligand **11** (7.1 mg, 0.03 mmol) and $[Rh(C_2H_4)_2Cl]_2$ (6.0 mg, 0.015 mmol) was stirred for 0.5 h in 1.2 mL of degassed toluene. $PhB(OH)_2$ (146 mg, 1.2 mmol) was added over the catalyst and sequentially the α,β-unsaturated carbonyl compound (0.6 mmol) and an aqueous solution of KOH (120 μL, 2.5 M). The reaction was followed by TLC, and once the starting material was consumed, the crude reaction mixture was charged into a column chromatograph. The eluents are indicated for each case.

*(R)-3-Phenylcyclohexanone (**14**).* Following the typical procedure for the 1,4-addition, the reaction of 2-cycloheptenone **12** (58 μL, 0.6 mmol) and phenyl boronic acid **13** (146 mg, 1.2 mmol) gave, after flash chromatography (hexane/Et_2O, 9/1), the product **14** as a colorless oil. Yield: 97.1 mg, 85%. $[\alpha]_D^{20}$ = +11.2° (*c* 0.9, $CHCl_3$). HPLC: 85% ee, Chiralcel OD-H column (*n*-hexane/2-propanol, 90/10), 0.5 mL/min; t_R = 27.5 min (minor), 28.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.36 (m, 2H), 7.21−7.26 (m, 3H), 3.05−2.95 (m, 1H), 2.37−2.59 (m, 4H), 2.07−2.16 (m, 2H), 1.80−1.89 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9, 144.3, 128.6, 126.6, 126.5, 48.9, 44.7, 41.1, 32.7, 25.5.

*(R)-3-(p-Tolyl)cyclohexanone (**18**).* This compound was synthesized following the general procedure. Flash chromatography on silica gel (eluting with AcOEt/hexane 1/10) afforded the product as a colorless oil. Yield: 54 mg, 96%. $[\alpha]_D^{20}$ = −21.5° (*c* 0.5, CH_2Cl_2). HPLC: 82% ee, Chiralcel AS-H column (*n*-hexane/2-propanol, 60/40), 0.6 mL/min; t_R = 9.3 min (minor), 17.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10−7.01 (m, 4H), 2.93−2.84 (m, 1H), 2.51−2.29 (m, 4H), 2.22 (s, 3H), 2.08−1.96 (m, 2H), 1.82−1.64 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.0, 141.4, 136.2, 129.3, 126.4, 49.0, 44.3, 41.1, 32.8, 25.5, 20.9 ppm. HRMS: calcd for $C_{13}H_{16}O$ 188.1201, found 188.1203.

*(R)-3-(4-Methoxyphenyl)cyclohexanone (**19**).* This compound was synthesized following the general procedure. Flash chromatography on silica gel (eluting with AcOEt/hexane 0.5/20) afforded the product as a colorless oil. Yield: 53 mg, 86%. $[\alpha]_D^{20}$ = −17.9° (*c* 0.3, CH_2Cl_2). HPLC: 74% ee, Chiralcel AS-H column (*n*-hexane/2-propanol, 70/30), 0.6 mL/min; t_R = 25.5 min (major), 29.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.99−2.90 (m, 1H), 2.59−2.30 (m, 4H), 2.17−1.95 (m, 2H), 1.85−1.65 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.1, 158.1, 136.4, 127.4, 113.9, 55.1, 49.1, 43.8, 41.0, 32.9, 25.3 ppm. HRMS: calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1145.

*(R)-3-(4-Chlorophenyl)cyclohexanone (**20**).* This compound was synthesized following the general procedure. Flash chromatography on silica gel (eluting with AcOEt/hexane, 0.5/20) afforded the product as a white solid. Yield: 45 mg, 72%. $[\alpha]_D^{20}$ = −11.3° (*c* 0.6, CH_2Cl_2). HPLC: 64% ee, Chiralcel AS-H column (*n*-hexane/2-propanol, 80/20), 0.7 mL/min; t_R = 19.9 min (minor), 20.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 9 Hz, 2H), 7.07 (d, *J* = 9 Hz, 2H), 2.96−2.86 (m, 1H), 2.52−2.23 (m, 4H), 2.09−1.96 (m, 2H), 1.81−1.65 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.4, 142.7, 132.2, 128.7, 127.8, 48.7, 44.0, 41.0, 32.6, 25.3 ppm. HRMS: calcd for $C_{12}H_{13}OCl$ 208.0655, found 208.0657.

*(R)-3-(m-Tolyl)cyclohexanone (**21**).* This compound was synthesized following the general procedure. Flash chromatography on silica gel (eluting with AcOEt/hexane 1/20) afforded the product as a colorless oil. Yield: 56 mg, 99%. $[\alpha]_D^{20}$ = −15.4° (*c* 0.5, CH_2Cl_2). HPLC: 78% ee, Chiralcel OD-H column (*n*-hexane/2-propanol, 90/10), 0.7 mL/min; t_R = 13.9 min (minor), 15.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20−7.26 (m, 1H), 7.01−7.07 (m, 3H), 2.92−3.01 (m, 1H), 2.35−2.62 (m, 4H), 2.35 (s, 3H), 2.05−2.18 (m, 2H), 1.75−1.91 (m, 2H). ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.1, 144.0, 138.0, 128.4, 127.3, 123.4, 48.9, 44.6, 41.1, 32.7, 25.5, 21.3 ppm. HRMS: alcd for $C_{13}H_{16}O$ 188.1201, found 188.1197.

*(R)-3-(o-Tolyl)cyclohexanone (**22**).* This compound was synthesized following the general procedure. Flash chromatography on silica gel (eluting with AcOEt/hexane, 1/10) afforded the product as a colorless oil. Yield: 51 mg, 90%. $[\alpha]_D^{20}$ = −21.5° (*c* 0.5, CH_2Cl_2). HPLC: 50% ee, Chiralcel AS-H column (*n*-hexane/2-propanol, 60/40), 0.6 mL/min; t_R = 9.3 min (minor), 17.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11−7.01 (m, 4H), 2.94−2.83 (m, 1H), 2.52−2.28 (m, 4H), 2.23 (s, 3H), 2.09−1.95 (m, 2H), 1.83−1.62 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.0, 141.4, 136.2, 129.3, 126.4, 49.0, 44.3, 41.1, 32.8, 25.5, 20.9 ppm. HRMS: calcd for $C_{13}H_{16}O$ 188.1201, found 188.1203.

*(R)-3-Phenylcyclopentanone (**23**).* Following the typical procedure for the 1,4-addition, the reaction of 2-cyclopentenone **15** (50 μL, 0.6 mmol) and phenylboronic acid **13** (146 mg, 1.2 mmol) gave, after flash chromatography (hexane/Et_2O, 9/1), the product **23** as a colorless oil. Yield: 79.8 mg, 83%. $[\alpha]_D^{20}$ = +71.3° (*c* 0.5, $CHCl_3$). HPLC: 92% ee, Chiralcel OD-H column (*n*-hexane/2-propanol, 90:10, 0.5 mL/min); t_R = 26.8 min (minor), 27.7 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.38 (m, 2H), 7.23−7.28 (m, 3H), 3.40−3.48 (m, 1H), 2.62−2.71 (m, 1H), 2.30−2.49 (m, 4H), 1.98−2.02 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.1, 142.9, 128.5, 126.5, 126.5, 45.6, 42.0, 38.7, 31.0 ppm.

*(R)-3-Phenylcycloheptanone (**24**).* Following the typical procedure for the 1,4-addition, the reaction of 2-cyclohexeptenone **16** (67 μL, 0.6 mmol) and phenyl boronic acid **13** (146 mg, 1.2 mmol) gave, after flash chromatography (Hexane:Et_2O, 9:1), the product **24** as a colorless oil. Yield: 92.2 mg, 87%. $[\alpha]_D^{20}$ = +49.1° (*c* 0.8, $CHCl_3$). HPLC: 96% ee, Chiralcel OD-H column (*n*-hexane/2-propanol, 90/10), 0.5 mL/min; t_R = 30.5 min (minor), 34.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.32 (m, 2H), 7.16−7.22 (m, 3H), 2.90−2.94 (m, 2H), 2.57−2.67 (m, 3H), 2.03−2.07 (m, 3H), 1.72−1.75 (m, 2H), 1.55−1.45 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.3, 146.8, 128.5, 126.3, 126.2, 51.2, 43.8, 42.6, 39.1, 29.1, 24.1 ppm.

*(R)-4-Phenyltetrahydropyran-2-one (**25**).* Following the typical procedure for the 1,4-addition, the reaction of 5,6-dihydro-2*H*-pyran-2-one **17** (58.8 μL, 0.6 mmol) and phenylboronic acid **13** (146 mg, 1.2 mmol) gave, after flash chromatography (hexane/AcOEt, 2/1), the product **25** as a colorless oil. Yield: 100.4 mg, 95%. $[\alpha]_D^{20}$ = −6.0° (*c* 0.7, $CHCl_3$). HPLC: 97% ee, Chiralcel OD-H column (*n*-hexane/2-propanol, 90/10), 0.5 mL/min; t_R = 48.9 min (minor), 50.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20−7.39 (m, 5H), 4.38−4.52 (m, 2H), 3.22−3.26 (m, 1H), 2.88−2.96 (m, 1H), 2.64 (dd, *J* = 10.6 Hz and 17.6 Hz, 1H), 2.00−2.16 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 142.8, 128.9, 127.2, 126.4, 68.6, 37.4, 37.4, 30.3 ppm.

*(S)-4-Phenylpentan-2-one (**29**).* Following the typical procedure for the 1,4-addition, the reaction of 3-penten-2-one **26** (83.1 μL, 0.6 mmol) and phenylboronic acid **13** (146 mg, 1.2 mmol) gave, after flash chromatography (hexane/Et_2O, 9/1), the product **13** as a colorless oil. Yield: 84.6 mg, 87%. $[\alpha]_D^{20}$ = +1.8° (*c* 0.8, $CHCl_3$). HPLC: 90% ee, Chiralcel OD-H column (*n*-hexane/2-propanol, 90/10), 0.5 mL/min; t_R = 14.0 min (minor), 15.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17−7.32 (m, 5H), 3.28−3.34 (m, 1H), 2.61−2.80 (m, 2H), 2.06 (s, 3H), 2.01 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 146.1, 128.5, 126.7, 126.2, 51.9, 35.4, 30.5, 21.9 ppm.

*(S)-4-(p-Tolyl)pentan-2-one (**30**).* Following the typical procedure for the 1,4-addition, the reaction of (*E*)-3-penten-2-one **26** (42 μL, 0.6 mmol) and *p*-tolylboronic acid (81.5 mg, 0.6 mmol) gave, after flash chromatography (hexane/AcOEt, 20/1), the product **30** as a colorless oil. Yield: 40 mg, 76%. $[\alpha]_D^{20}$ = +20.8° (*c* 0.5, $CHCl_3$). HPLC: 94% ee, Chiralcel AS-H column (n-hexane/2-propanol, 98/2), 1 mL/min; t_R = 7.5 min (major), 8.7 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14−7.12 (m, 4H), 3.32−3.28 (m, 1H), 2.80−2.60 (m, 2H), 2.34 (s, 3H), 2.09 (s, 3H), 1.28 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.02, 143.20, 135.84, 129.27, 126.68, 52.16, 35.15, 30.60, 22.18, 21.03 ppm. HRMS: calcd for $C_{12}H_{16}O$ 192.1150, found 192.1154.

*(S)-4-(Methoxyphenyl)pentan-2-one (**31**).* Following the typical procedure for the 1,4-addition, the reaction of (*E*)-3-penten-2-one **26** (42 μL, 0.6 mmol) and (4-methoxyphenyl)boronic acid (91.2 mg, 0.6 mmol) gave, after flash chromatography (hexane/AcOEt, 20/1), the product **31** as a colorless oil. Yield: 31 mg, 54%. $[\alpha]_D^{20}$ = +18.5° (*c* 0.5, $CHCl_3$). HPLC: 90% ee, Chiralcel AS-H column (*n*-hexane/2-propanol, 98/2), 1 mL/min; t_R = 19.2 min (major), 25.2 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16−7.15 (m, 2H), 7.87−7.86 (m, 2H), 3.81 (s, 3H), 3.29−3.28 (m, 1H), 2.76−2.64 (m, 2H), 2.08 (s, 3H), 1.27 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.17, 158.14, 138.34, 127.76, 114.02, 55.36, 52.39, 34.84, 30.72, 22.33 ppm. HRMS: calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1154.

*(S)-4-(Chlorophenyl)pentan-2-one (**32**).* Following the typical procedure for the 1,4-addition, the reaction of (*E*)-3-penten-2-one **26** (42 μL, 0.6 mmol) and (4-chlorophenyl)boronic acid (93.8 mg, 0.6 mmol) gave, after flash chromatography (hexane/AcOEt, 10/1), the product **32** as a colorless oil. Yield: 59 mg, 99%. $[\alpha]_D^{20}$ = +20.2° (*c* 0.5, $CHCl_3$). HPLC: 94% ee, Chiralcel AS-H column (*n*-hexane/2-propanol, 98/2), 1 mL/min; t_R = 9.5 min (major), 11.3 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28−7.26 (m, 2H), 7.17−7.15 (m, 2H), 3. 32−3.30 (m, 1H), 2.76−2.64 (m, 2H), 2.08 (s, 3H), 1.26 (d, *J* = 5.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.36, 144.72, 131.94, 128.67, 128.23, 51.81, 34.80, 30.60, 22.01 ppm. HRMS: calcd for $C_{11}H_{13}ClO$ 196.0655, found 196.0655.

*(S)-4-Phenylnonan-2-one (**33**).* Following the typical procedure for the 1,4-addition, the reaction of 3-nonan-2-one **27** (99.2 μL, 0.6 mmol) and phenylboronic acid **13** (146 mg, 1.2 mmol) gave, after flash chromatography (hexane/Et_2O, 9/1), the product **33** as a colorless oil. Yield: 120.5 mg, 92%. $[\alpha]_D^{20}$ = +26.3° (*c* 0.7, $CHCl_3$). HPLC: 94% ee, Chiralcel OD-H column (n-hexane/2-propanol, 90/10), 0.5 mL/min; t_R = 30.5 min (minor), 34.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17−7.32 (m, 5H), 3.28−3.34 (m, 1H), 2.61−2.80 (m, 2H), 2.06 (s, 3H), 2.01 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 146.1, 128.5, 126.7, 126.2, 51.9, 35.4, 30.5, 21.9 ppm.

*(S)-4-Phenyl-4-(p-tolyl)butan-2-one (**34**).* Following the typical procedure for the 1,4-addition, the reaction of (*E*)-4-phenyl-3-buten-2-one **28** (43.9 mg, 0.6 mmol) and *p*-tolylboronic acid (81.5 mg, 0.6 mmol) gave, after flash chromatography (hexane/AcOEt, 20/0.5), the product **34** as a colorless oil. Yield: 43 mg, 60%. $[\alpha]_D^{20}$ = −6.8° (*c* 0.5, $CHCl_3$). HPLC: 92% ee, Chiralcel OD-H column (*n*-hexane/2-propanol, 98/2), 1 mL/min; t_R = 13.1 min (minor), 15.7 min (major). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30−7.26 (m, 4H), 7.21−7.20 (m, 1H), 7.14−7.12 (m, 4H), 4.58 (t, *J* = 6.5 Hz, 1H), 3.19 (d, *J* = 7 Hz, 2H), 2.32 (s, 3H), 2.11 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.05, 144.16, 140.90, 136.04, 129.34, 128.63, 127.71, 127.62, 126.43, 49.83, 45.77, 30.70, 21.02 ppm. HRMS: calcd for $C_{17}H_{18}O$ 238.1358, found 238.1353.

X-ray Structural Analysis of Compounds 11 and 31. Crystals of suitable size for X-ray diffraction analysis were coated with dry perfluoropolyether, mounted on glass fibers, and fixed in a cold nitrogen stream (*T* = 100 K) to the goniometer head. Data collections were performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromated radiation (λ(Mo Kα) = 0.71073 Å), by means of ω and φ scans with a width of 0.50°. The data were reduced (SAINT)[35] and corrected for absorption effects by the multiscan method (SADABS).[36] The structures were solved by direct methods (SIR-2002)[37] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)[38] minimizing $w[F_o^2 - F_c^2]^2$. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and allowed to ride on the attached atoms with the isotropic temperature factors (U_{iso} values) fixed at 1.2 times (1.5 times for methyl groups) those U_{eq} values of the corresponding attached atoms.

*Crystal data for **11**:* $C_{22}H_{22}Fe_2O_2S_2$, *M* = 494.22, orthorhombic, *a* = 5.8114(5) Å, *b* = 10.6834(9) Å, *c* = 32.091(3) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 1992.4(3) Å^3, *T* = 173(2) K, space group $P2_12_12_1$, *Z* = 4, μ(Mo Kα) = 1.682 mm^{-1}, 39414 reflections measured, 6058 independent reflections (R_{int} = 0.0326). The final R1 value was 0.0241 ($I > 2\sigma(I)$). The final wR2(F^2) value was 0.0571 ($I > 2\sigma(I)$). The final R1 values was 0.0270 (all data). The final wR2(F^2) value was 0.0584 (all data). The goodness of fit on F^2 was 1.052. The Flack parameter was 0.008(10).

*Crystal data for **41**:* $C_{44}H_{44}Cl_2Fe_4O_4Rh_2S_4$, *M* = 1265.15, tetragonal, *a* = 11.118(3) Å, *b* = 11.118(3) Å, *c* = 34.896(13) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 4314(2) Å^3, *T* = 173(2) K, space group $P4_32_12$, *Z* = 4, μ(Mo Kα) = 2.419 mm^{-1}, 43469 reflections measured, 6554 independent reflections (R_{int} = 0.0729). The final R1 value was 0.0362 ($I > 2\sigma(I)$). The final wR2(F^2) value was 0.0652 ($I > 2\sigma(I)$). The final R1 value was 0.0631 (all data). The final wR2(F^2) value was 0.0878 (all data). The goodness of fit on F^2 was 1.146. The Flack parameter was −0.01(3).

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving ^{1}H and ^{13}C NMR spectra of compounds **4**−**7**, ligands **8**−**11**, and the adducts **14**, **18**−**25**, and **29**−**34**, crystallographic data for compounds **11** and **41**, HPLC chromatograms of the adducts are given, and positional and thermal parameters for **11** and **31** with bond distances and angles for the non-hydrogen atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*N.K.: fax, +34954460565; tel, +34954489559; e-mail, khiar@iiq.csic.es. I.F.: e-mail, inmaff@us.es.

Present Address

§University of Zürich, Institute of Organic Chemistry, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland.

Notes

The authors declare no competing financial interest.

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