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Enantioselective Synthesis of Chiral Sulfones by Ir-Catalyzed Asymmetric Hydrogenation: A Facile Approach to the Preparation of Chiral Allylic and Homoallylic Compounds

Taigang Zhou,[†] Byron Peters,[†] Matías F. Maldonado,[†] Thavendran Govender,[‡] and Pher G. Andersson*[,†,‡]

[†]Department of Chemistry-BMC, Uppsala University, Box 576, S-75123 Uppsala, Sweden
[‡]Department of Pharmacy, University of KwaZulu-Natal, Durban 4000, South Africa

Supporting Information

ABSTRACT: A highly efficient and enantioselective Ir-catalyzed hydrogenation of unsaturated sulfones was developed. Chiral cyclic and acyclic sulfones were produced in excellent enantioselectivities (up to 98% ee). Coupled with the Ramberg–Bäcklund rearrangement, this reaction offers a novel route to chiral allylic and homoallylic compounds in excellent enantioselectivities (up to 97% ee) and high yields (up to 94%).

Chiral sulfones are present in, and can be used as synthetic intermediates for the preparation of, many biologically active compounds and natural products, such as those shown in Figure 1.[1,2] Furthermore, one of their most important

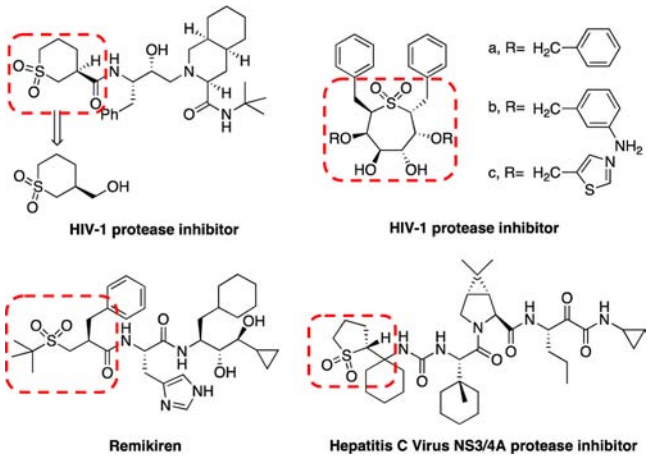

Figure 1. Biologically active compounds with chiral sulfone moieties.

applications is their conversion to chiral olefins through the Ramberg–Bäcklund rearrangement.[3] Chiral olefins, especially chiral allylic and homoallylic compounds, are common structural moieties in natural products and pharmaceutical compounds.[4] Thus the production of chiral sulfones is key to numerous organic syntheses. Despite the well-known importance of chiral allylic and homoallylic compounds in organic synthesis, no single, facile preparation of both chiral allylic and homoallylic compounds has been developed. Asymmetric allylic substitution is one of the most widely used methods of producing chiral allylic entities,[5] but it cannot be applied in homoallylic chiral induction. Conversely, methods that selectively introduce homoallylic chirality cannot be used to synthesize chiral allylic compounds.[6]

Transition-metal-catalyzed asymmetric hydrogenation is one of the most efficient, straightforward, and well-established methods for preparing enantiomericially enriched compounds.[7] In recent decades, the transition-metal-catalyzed hydrogenations using Ir, Ru, and Rh compounds have proven effective in the asymmetric reduction of many types of olefins, such as α,β-unsaturated acids, ketones, imines, phosphonates, and heterocyclic compounds.[8] However, to our knowledge, the asymmetric hydrogenation of unsaturated cyclic sulfones is still unknown in the literature, and only a few examples involving unsaturated acyclic sulfones have been reported. Paul and Palmer have reported the rhodium-catalyzed asymmetric hydrogenation of acyclic β,β-disubstituted vinyl phenyl sulfones in high enantioselectivities.[9a] Unfortunately, the reaction required the substrate to have a coordinating group, e.g. an ester or amide, next to the C=C bond. Yuasa et al. hydrogenated an acyclic allyl sulfone in 84% ee using a Ru-BINAP catalyst.[9b]

Over the past few years, our group has developed several classes of chiral N,P-ligated iridium complexes that are efficient catalysts for the asymmetric hydrogenation of various substrates.[8d,g,i,10] We tested these catalysts in the asymmetric hydrogenation of prochiral unsaturated sulfones and converted the resulting chiral sulfones into chiral allylic and homoallylic compounds via the Ramberg–Bäcklund rearrangement (Scheme 1). Herein we report the first examples of the Ir-catalyzed asymmetric hydrogenation of acyclic sulfones, as well as the first asymmetric hydrogenation of cyclic sulfones with varying substitution patterns, in excellent enantioselectivities (up to 98% ee). When coupled with the Ramberg–Bäcklund rearrangement, this method constitutes a novel approach to both chiral allylic and homoallylic compounds in high yield and excellent enantioselectivities.

We chose two model substrates to hydrogenate, the seven-membered cyclic sulfone **1** and the acyclic β,β-disubstituted vinyl sulfone **2** (Table 1) with Ir complexes bearing our chiral ligands **A**–**F** (Scheme 2).[10] $[(\mathbf{C})\mathrm{Ir}(\mathrm{COD})]^+[\mathrm{BAr_F}]^-$ (COD =

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Scheme 1. Strategy for Asymmetric Synthesis of Chiral Sulfone and Chiral Allylic, Homoallylic Compounds

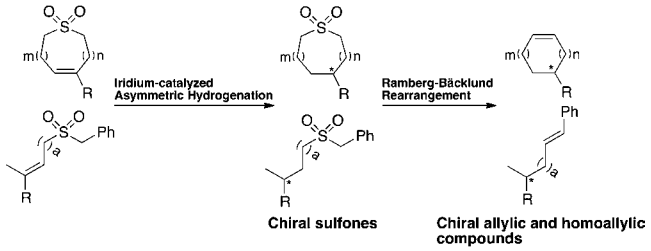
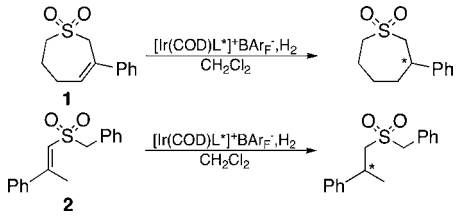


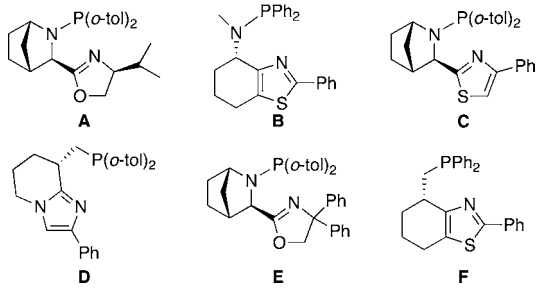
Table 1. Catalyst Screening for Asymmetric Hydrogenation of Cyclic and Acyclic Unsaturated Sulfones[a]



entry	ligand	substrate	conv. (%)[b]	ee (%)[c,d]
1	**A**	**1**	25	14 (*S*)
		2	45	76 (*S*)
2	**B**	**1**	42	97 (*S*)
		2	27	50 (*R*)
3	**C**	**1**	>99	96 (*R*)
		2	>99	96 (*S*)
4	**D**	**1**	>99	83 (*S*)
		2	>99	27 (*R*)
5	**E**	**1**	30	87 (*R*)
		2	24	41 (*S*)
6	**F**	**1**	49	96 (*S*)
		2	90	74 (*R*)

[a]Reaction conditions: 0.25 mmol of substrate, 0.5 mol % catalyst, 2 mL of CH_2Cl_2, 50 bar of H_2, 17 h, rt. [b]Conversion, determined by ^1H NMR spectroscopy. No side products were detected. [c]Determined by chiral HPLC or GC analyses. [d]Absolute configuration determined by analogy with corresponding alkenes obtained from Ramberg–Bäcklund rearrangement.

Scheme 2. Ligands Tested in Asymmetric Hydrogenation of Unsaturated Sulfones[a]

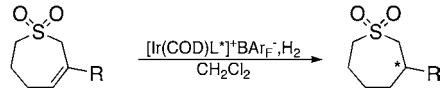


[a]*o*-tol = 2-methylphenyl.

1,4-cyclooctadiene; BAr_F^- = tetrakis(3,5-bis-trifluoromethylphenyl)borate) performed best, hydrogenating both **1** and **2** to full conversion and in 96% ee.

In light of this success, *β*-substituted *β*,*γ*-unsaturated seven-membered cyclic sulfones bearing various aliphatic and aromatic substituents were hydrogenated to the corresponding chiral products using [(**C**)Ir(COD)]$^+$[BAr_F]$^-$. Excellent enantioselectivities (90–98% ee, Table 2, entries 1–8) were obtained. When the substituent was an aryl ring, *para* substituents on the ring had little influence on hydrogenation selectivity (entries 1–7). However, an *o*-methyl substituent on the aryl ring (entry 2) gave poorer conversion, likely due to the steric bulk of the substrate. Despite the fact that [(**C**)Ir(COD)]$^+$[BAr_F]$^-$ hydrogenated the hydroxymethyl-substituted compound in 92% ee (entry 8), it gave only moderate selectivity (41% ee) for the methyl-substituted variant. However, [(**E**)Ir(COD)]$^+$[BAr_F]$^-$ hydrogenated this compound in 96% ee (entry 9).

Table 2. Asymmetric Hydrogenation of *β*-Substituted *β*,*γ*-Unsaturated Seven-Membered Cyclic Sulfones[a]



entry	substrate	ligand	conv. (%)[b]	ee (%)[c,d]
1	Ph	**C**	>99	98 (−)(*R*)
2	2-MeC_6H_4	**C**	23	93 (−)
3	3-MeC_6H_4	**C**	>99	98 (−)
4	4-MeC_6H_4	**C**	>99	96 (−)(*R*)
5	4-MeOC_6H_4	**C**	>99	97 (−)
6	4-FC_6H_4	**C**	91	95 (−)
7	4-ClC_6H_4	**C**	>99	90 (−)
8	CH_2OH	**C**	>99	92 (−)[e]
9	Me	**E**	>99	96 (−)(*S*)

[a]Reaction conditions: 0.25 mmol of substrate, 0.5 mol % catalyst, 2 mL of CH_2Cl_2, 50 bar of H_2, 17 h, rt. [b]Conversion, determined by ^1H NMR spectroscopy. No side products were detected. [c]Determined by chiral HPLC or GC analyses. [d]Absolute configuration determined by analogy with corresponding alkenes obtained from Ramberg–Bäcklund rearrangement. [e]Determined by chiral GC after conversion to 1-(2-cyclohexenyl)methanol and then into its acetate, 1-(2-cyclohexenyl)methyl ethanoate.

Next, we evaluated substrates with different substitution patterns and ring sizes (Table 3). Six-membered cyclic sulfones (Table 3, entries 1–3) were hydrogenated in good to excellent enantioselectivities (85–93% ee) using [(**C**)Ir(COD)]$^+$[BAr_F]$^-$. Substrates with seven-membered rings were hydrogenated in good to excellent enantioselectivities and full conversions (89–93%; entries 4–8) using the same catalyst that was effective for their isomers in Table 2. Most substrates gave excellent results with [(**C**)Ir(COD)]$^+$[BAr_F]$^-$ (entries 4–7), but the 4-methyl-4-5-unsaturated seven-membered ring was hydrogenated most selectively with [(**E**)Ir(COD)]$^+$[BAr_F]$^-$ (entry 8) and [(**A**)Ir(COD)]$^+$[BAr_F]$^-$ was the best catalyst for the five-membered cyclic sulfone, giving good enantioselectivity (87% ee, entry 9).

We carried out the asymmetric reduction of several acyclic, *E*-*β*,*β*-disubstituted vinyl sulfones (Table 4, entries 1–7). Full conversions and high enantioselectivities (90–96% ee) were achieved for all vinyl sulfones with [(**C**)Ir(COD)]$^+$[BAr_F]$^-$, demonstrating the utility of the reaction for a series of different aryl substitutions as well as a dialkyl substrate. An allylic sulfone was also reduced in full conversion and excellent enantioselectivity (97% ee, entry 8) with the same catalyst. These results complement those obtained with the cyclic substrates, demonstrating the utility of our N,P-ligated iridium catalysts in the asymmetric hydrogenation of prochiral sulfones.

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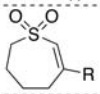
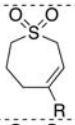
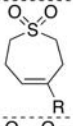
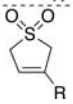
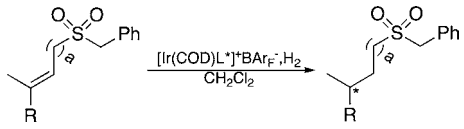
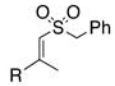
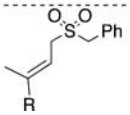
Table 3. Asymmetric Hydrogenations of Cyclic Unsaturated Sulfones Having Five-, Six-, and Seven-Membered Rings by $[Ir(COD)L^*]^+BAr_F^-$ Catalysts[a]

entry	substrate	R	ligand	conv. (%)[b]	ee (%)[c,d]
1		Ph	C	43	90 (−)(*R*)
2		CH_2OH	C	>99	93 (−)[f]
3		Me	C	>99	85 (−)(*S*)[e]
4		Ph	C	>99	93 (+)(*S*)
5		Ph	C	>99	89 (−)
6		Ph	C	>99	89 (+)
7		CH_2OH	C	>99	90 (−)(*S*)[g]
8		Me	E	>99	90 (+)(*S*)
9		Ph	A	78	87 (−)

[a]Reaction conditions: 0.25 mmol of substrate, 0.5 mol % catalyst, 2 mL of CH_2Cl_2, 50 bar of H_2, 17 h, rt. [b]Conversion, determined by ^1H NMR spectroscopy. No side products were detected. [c]Determined by chiral HPLC or GC analyses. [d]Absolute configuration determined by analogy with corresponding alkenes obtained from Ramberg–Bäcklund rearrangement. [e]Determined by comparing optical rotation with a literature value.[11] [f]Determined by GC after conversion to corresponding acetate. [g]Determined by GC after conversion to 1-(3-cyclohexenyl)methanol.

Table 4. Asymmetric Hydrogenation of Acyclic Sulfones[a]

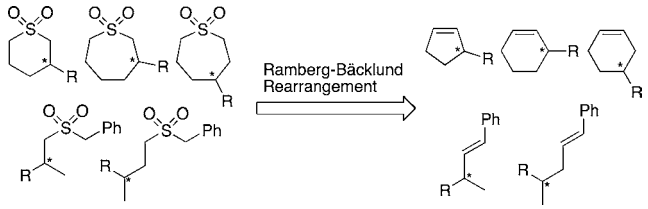


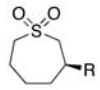
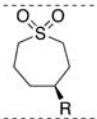
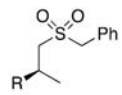
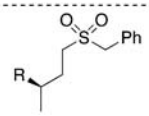
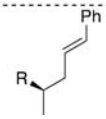
entry	substrate	R	ligand	conv. (%)[b]	ee (%)[c,d]
1		Ph	C	>99	96 (+)(*S*)
2		4-MeC_6H_4	C	>99	90 (+)
3		4-$MeOC_6H_4$	C	>99	92 (+)
4		4-ClC_6H_4	C	>99	96 (+)
5		4-BrC_6H_4	C	>99	96 (+)
6		4-$CF_3C_6H_4$	C	>99	95 (+)
7		*n*-Bu	C	>99	93 (+)(*R*)
8		Ph	C	>99	97 (−)

[a]Reaction conditions: 0.25 mmol of substrate, 0.5 mol % catalyst, 2 mL of CH_2Cl_2, 50 bar of H_2, 17 h, rt. [b]Conversion, determined by ^1H NMR spectroscopy. No side products were detected. [c]Determined by chiral HPLC analyses. [d]Absolute configuration determined by analogy with corresponding alkenes obtained from Ramberg–Bäcklund rearrangement.

By coupling asymmetric hydrogenation with Ramberg–Bäcklund rearrangement, we converted the chiral sulfone into chiral allylic and homoallylic compounds. As shown in Table 5, the Ramberg–Bäcklund rearrangements of the chiral acyclic and seven-membered cyclic sulfones produced here afforded the corresponding alkenes in good to excellent yields (75–94%, entries 2–14). The cyclic substrates ring-contracted to the

Table 5. Transformation of Chiral Sulfones to Chiral Allylic and Homoallylic Compounds by the Ramberg–Bäcklund Rearrangement



entry	substrate	product	R	yield (%)[a]	ee (%)[b]
1			Ph	30	90 (−)(*S*)[c]
2			Me	>99[d]	96 (−)(*S*)[c,e]
3			Ph	88	96 (−)(*S*)[c]
4			4-MeC_6H_4	85	96 (−)(*S*)[c]
5			4-$MeOC_6H_4$	90	97 (−)
6			CH_2OH	82	92 (−)
7			Me	>99[d]	90 (−)(*S*)[c,e]
8			Ph	90	89 (−)
9			CH_2OH	80	90 (−)(*S*)[c]
10			Ph	91[f]	96 (+)(*R*)[c]
11			4-BrC_6H_4	94[f]	96 (+)
12			4-$MeOC_6H_4$	93[f]	92 (+)
13			*n*-Bu	78[f]	93 (+)(*S*)[c]
14			Ph	75[f]	>97 (−)

[a]Isolated yields. [b]Determined by chiral HPLC or GC analyses. [c]Absolute configuration determined by comparing optical rotation with a literature value. [d]Not an isolated yield but a conversion determined by GC. [e]Ee determined from the chiral sulfone. See Supporting Information for reaction conditions. [f]Only the trans (*E*) isomer was observed.

corresponding cyclic alkenes, and the acyclic substrates underwent rearrangement with complete trans selectivity.

Inherent ring strain was likely a factor in the poor conversion obtained for the rearrangement of the six-membered cyclic sulfone to the five-membered cyclic alkene (entry 1). No erosion of enantiometric excess was observed during the Ramberg–Bäcklund rearrangement of the substrates tested.

We developed a Selectivity Model to explain the stereoselectivity of our catalysts in the hydrogenation (Figure 2).[10b,12] The catalyst is drawn in its Ir^{3+} form, which is present after H_2 and the substrate have been added,[12] from the perspective of the olefin. This is superimposed on a two-by-two grid to separate the environment around Ir into four quadrants, as shown in Figure 2. In this orientation, three of the quadrants are occupied by the steric bulk of the ligand; quadrant 2 is fully encumbered, and quadrants 1 and 4 are partially occupied. Quadrant 3 is relatively free. In the most stable configuration, the substrate will be oriented to have its least bulky substituent (in the substrates described here, a proton) in the most hindered quadrant (2, Figure 2).[12] Thus the stereochemical outcome of hydrogenation can be predicted assuming that hydride is delivered from the iridium center. Little information on the absolute configurations of the saturated sulfones described here exists in the literature; however, absolute

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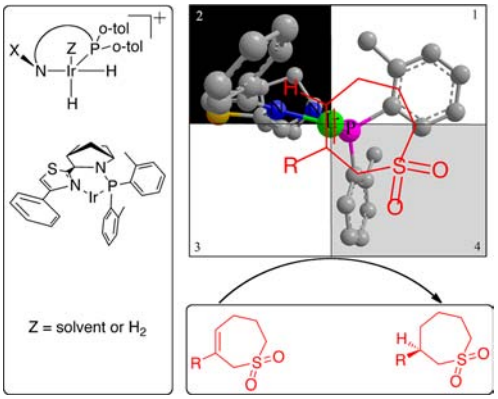

Figure 2. Selectivity model applied in predicting the absolute configuration of the products from the asymmetric hydrogenation.

stereochemistry could be determined after converting the sulfones to the corresponding chiral olefins using the Ramberg–Bäcklund rearrangement (Tables 2–4).

The stereochemical outcomes of the hydrogenations shown in Tables 2–4 conformed to those predicted by the Selectivity Model in cases where absolute stereochemistry could be assigned. Thus the model proved to be a useful and convenient method for predicting the stereoselectivity of the hydrogenation of an unsaturated sulfone by $[Ir(COD)\ L^*]^+[BAr_F]^-$.

In conclusion, we have developed a highly efficient and enantioselective hydrogenation of both cyclic and acyclic unsaturated sulfones; the reaction was catalyzed by N,P-ligated iridium catalysts. When coupled with the Ramberg–Bäcklund rearrangement, this method constitutes a novel approach to both chiral allylic and homoallylic compounds in high yield and excellent enantioselectivities. We are currently exploring this method as a route to chiral drug intermediates for biologically active target molecules.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

Pher.Andersson@biorg.uu.se

Notes

The authors declare no competing financial interest.

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