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Ru(salen)-catalyzed asymmetric sulfimidation using arylsulfonyl azide

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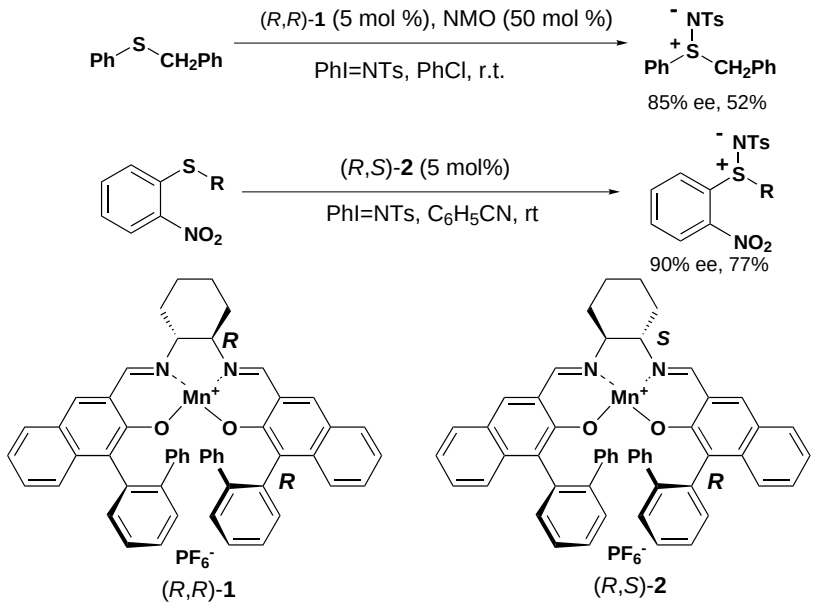
Abstract—An (OC)Ru(II)(salen) complex was found to catalyze imidation of alkyl aryl sulfides in the presence of arylsulfonyl azide with high enantioselectivity as well as good chemical yield.

Optically active sulfoxides are widely used as chiral auxiliaries in organic synthesis and many excellent methodologies for asymmetric sulfoxidation have been developed.[1,2] In contrast, use of sulfimides, nitrogen equivalents of sulfoxides, in organic synthesis is rather limited, because of lack of convenient synthetic method of optically active sulfimides. Optically active sulfimides were first prepared by conversion from the corresponding optically active sulfoxides[3] and then by kinetic resolution of racemic sulfimides using an optically active base.[4] Recently, highly diastereoselective sulfimidations have also been reported by Gaggero et al. and Uemura et al.[5] On the other hand, Uemura et al. reported that the imidation of alkyl aryl sulfides using a chiral copper(I)-bis(oxazoline) complex as a catalyst showed moderate enantioselectivity.[6] We also found that optically active Mn(salen)s **1** and **2** served as efficient catalysts for enantioselective sulfimidation showing good enantioselectivity (Scheme 1).[7] However, there is still room for improvement, espe-



Scheme 1.

Keywords: (OC)Ru(salen) complex; asymmetric catalysis; sulfimidation; sulfide; toluenesulfonyl azide.

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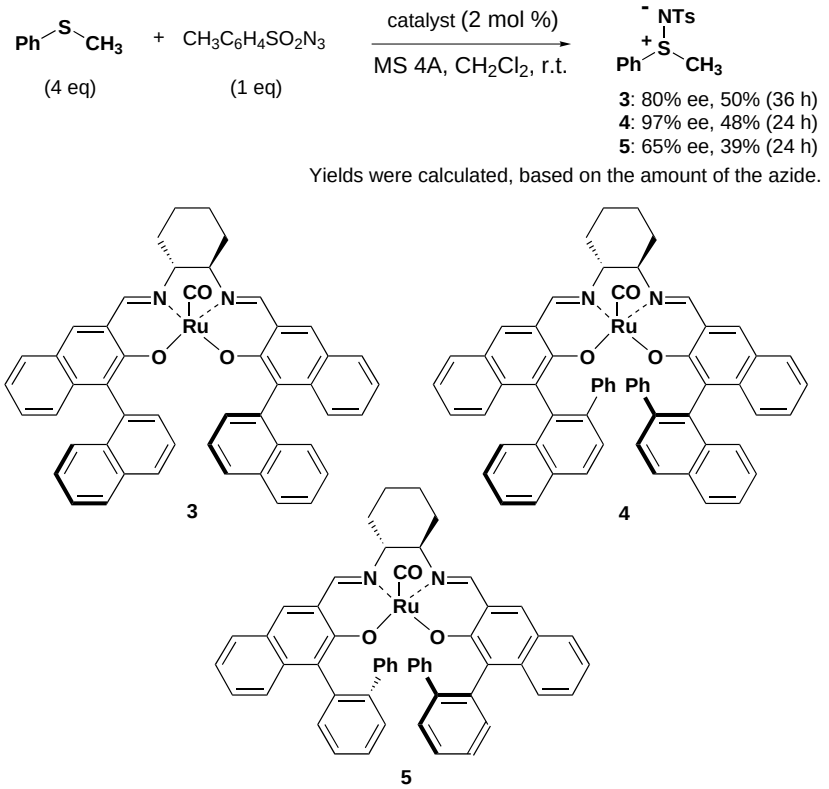
cially in respect of enantioselectivity and the nitrene precursor.

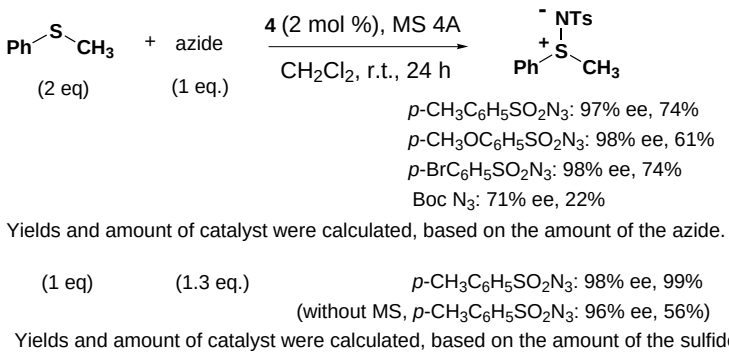
Jacobsen et al. reported that arylsulfonyl azide served as a nitrene precursor for asymmetric aziridination in the presence of copper ion under photo-irradiation.[8] During our study on asymmetric sulfimidation, we found that arylsulfonyl azides could be used as a nitrene precursor in the presence of (OC)Ru(II)(salen) complexes [hereafter, abbreviated as Ru(salen)][9] without photo-irradiation. Arylsulfonyl azides are readily prepared from commercially available arylsulfonyl chlorides in one step. Thus, we examined asymmetric imidation of methyl phenyl sulfide with toluenesulfonyl azide by using Ru(salen)s (**3**–**5**) as the catalyst (Scheme 2) and found that the reaction with complex **4** as the catalyst showed high enantioselectivity. Complex **5**, the ruthenium equivalent of Mn(salen) **1**, showed only moderate enantioselectivity.

We next examined sulfimidation with complex **4** as the catalyst in the presence of various azides (Scheme 3). All the arylsulfonyl azides used showed a similar high level of enantioselectivity and no electronic effect on enantioselectivity was observed, though chemical yields were moderate. However, we found that the chemical yield was improved when the amount of the sulfide was reduced and a slight excess amount of azide was used. *t*-Butoxycarbonyl azide (Boc N_3) was a poor precursor.

With these results in hand, we examined imidation of various sulfides with complex **4** as the catalyst in the presence of toluenesulfonyl azide (Table 1). Imidation of alkyl aryl sulfides proceeded smoothly with excellent

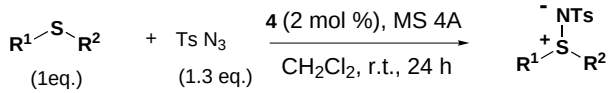


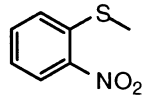
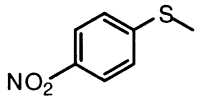
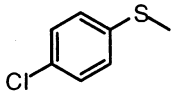
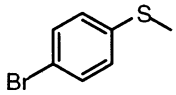
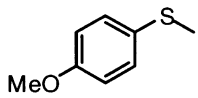
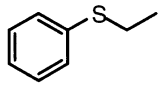
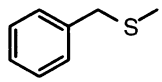
Scheme 2.



Scheme 3.

Table 1. Asymmetric imidation of various sulfides using Ru(salen) **4** as the catalyst



Entry	Substrate	Yield	% ee	sign of $[\alpha]_D$[a)]
1		98	99[b)]	+
2		99	99[c)]	+
3		81	99[d)]	+
4		93	99[d)]	+
5		90	93[b)]	+
6		99	95[e)]	+
7		36	66[f)]	+

a) Optical rotation was measured in chloroform.
b) Determined by HPLC analysis using DAICEL CHIRALCEL OJ column (hexane/2-propanol= 1 : 1).
c) Determined by HPLC analysis using DAICEL CHIRALCEL AD column (hexane/2-propanol= 1 : 1).
d) Determined by HPLC analysis using DAICEL CHIRALCEL OJ-H column (hexane/2-propanol= 3 : 1).
e) Determined by HPLC analysis using DAICEL CHIRALCEL OJ column (hexane/2-propanol= 3 : 1).
f) Determined by HPLC analysis using DAICEL CHIRALCEL OD-H column (hexane/2-propanol= 3 : 1).

enantioselectivity. On the other hand, the imidation of dialkyl sulfide, benzyl methyl sulfide, showed moderate enantioselectivity of 66% ee (entry 7). The low chemical yield in this reaction may be attributable to strong coordination of the sulfide to complex **4**.

Typical experimental procedure for imidation of sulfides was exemplified by the reaction of methyl *o*-nitrophenyl sulfide with **4** as the catalyst (Table 1, entry 1): (*R*,*R*)-complex **4** (1.9 mg, 2.0 μmol) was dissolved in dry toluene (1 ml), concentrated azeotropically in vacuo, and re-dissolved in dichloromethane (0.5 ml). To this solution were added methyl *o*-nitrophenyl sulfide (16.9 μl, 0.1 mmol) and MS 4 Å (20 mg), and the suspension was stirred for half an hour at room temperature. To this suspension was added *p*-toluenesulfonyl azide (19.7 μl, 0.13 mmol), and the whole mixture was stirred for another 24 h at the temperature. The mixture was chromatographed on silica gel (hexane:ethyl acetate = 7:3–3:7) to give *S*-methyl *S*-(*o*-nitrophenyl) *p*-toluenesulfimide (33.3 mg, 98%). The enantiomeric excess of the sulfimide was determined to be 99% by HPLC analysis using DAICEL CHIRALCEL OJ (hexane:*i*-PrOH = 1:1).

In conclusion, we were able to demonstrate that chiral ruthenium(II)(salen) complex **4** bearing an apical CO ligand is an excellent catalyst for asymmetric sulfimidation. Study on the mechanism of this reaction is in progress in our laboratory.

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