Tetrahedron: *Asymmetry* 19 (2008) 1304–1309

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Ruthenium(II) and rhodium(III) catalyzed asymmetric transfer hydrogenation (ATH) of acetophenone in isopropanol and in aqueous sodium formate using new chiral substituted aromatic monosulfonamide ligands derived from (1*R*,2*R*)-diaminocyclohexane

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ARTICLE INFO

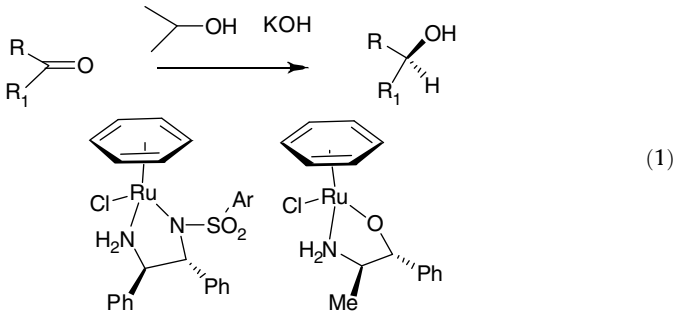
Article history:
Received 23 January 2008
Accepted 24 April 2008
Available online 10 June 2008

ABSTRACT

A series of aromatic monosulfonamide ligands derived from (1*R*,2*R*)-diaminocyclohexane were synthesized with electron withdrawing and donating groups. These were complexed with Rh(Cp*) or Ru(arene) and their catalytic efficiencies were compared in the ATH of acetophenone using sodium formate/water or isopropanol/KOH as the hydrogen source. Results suggest that substituents on the benzene ring of the sulfonamide have very little electronic impact on the enantioselectivity and mechanism of the reaction.

1. Introduction

Noyori et al. reported the use of monotosylated diamines and 1,2-aminoalcohols as ligands for the ruthenium(II) catalyzed asymmetric transfer hydrogenation (ATH) of ketones (Eq. 1).[1] Since this discovery, a significant number of new ligand-ruthenium(II), rhodium(III), and iridium(I) complexes have been used as catalysts in the ATH of ketones.[2–4]



(1)

Recently, a number of researchers have shown that catalytic ATH of ketones can be carried out efficiently using water under noninert atmospheric conditions, increasing the potential industrial applications.[5] Water is inexpensive, readily available, and environmentally benign, which has inspired the synthesis of novel water soluble ligands for the ATH of ketones. We recently reported a C_2-symmetric water soluble bis(sulfonamide) ligand derived from *trans*-1,2-cyclohexanediamine. When used with Ru(II) and Rh(III) complexes as catalysts in the ATH of ketones,[6a] the resulting secondary alcohol was formed in >90% enantioselectivity and yield. In the hope of discovering a more active and enantioselective catalyst, we investigated the role of substituents on the ligand $ArSO_2$ group, the influence of different hydrogen sources and the catalytic ability of different metals [ruthenium(II) or rhodium(III)]. Noyori et al. have shown that the ligand $ArSO_2$ group is important for maintaining reactivity; analogues with CF_3SO_2, C_6H_5CO, and CH_3CO were much less reactive.[1] We found that replacing the $ArSO_2$ group with heterocyclic substituents on the sulfonamide, complexed to $Rh^{III}(Cp^*)$ led to excellent water soluble catalysts for ATH, resulting in secondary alcohols with >90% enantioselectivity and yield.[6b] Noyori's work further shows that the effect of electron donor alkyl groups (CH_3, i-C_3H_7) on the η^6-arene can also increase the catalytic activity.[1a] A similar study with electron withdrawing groups on the arene ring was reported by Süss-Fink et al. They showed that the rate of ATH is dramatically decreased by an electron withdrawing methyl carboxylate group on the arene ring in **2** (Fig. 1), compared

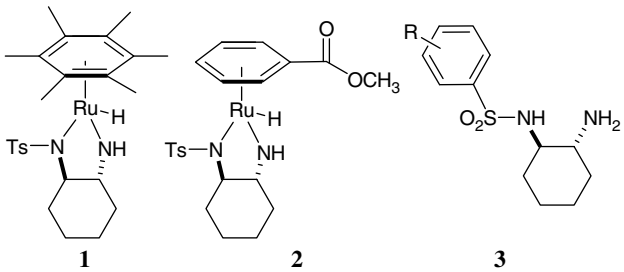


Figure 1. Monosulfonamide ligand and metal complex.

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doi:10.1016/j.tetasy.2008.04.036

to electron donating methyl group in **1** (Fig. 1). When aqueous sodium formate is used as the hydrogen source,[10] the latter is ten times more reactive. A systematic study involving electron attractors and donors on the $ArSO_2$, however, has not been reported. In a recent study Mioskowski and Mohar reported the ATH of ketones with electron withdrawing groups on the Ru^{II} (monosulfonamide-1,2-diphenylethane) complex.[7] In this work, the authors claimed that electron withdrawing groups such as, *p*-trifluoromethylbenzene, pentafluorobenzene, and nonaflate sulfonyl substituents enhance the enantioselectivity of the catalyst by increasing the acidity of the N–H and decreasing the basicity on the adjacent $–NH_2$. They also reported a number of sulfonamide ligands with electron withdrawing (NO_2, Cl) and donating groups (OCH_3), which were used in the ATH of ketones.[8a,b] All of these reactions were performed using $HCOOH/Et_3N$ as the hydrogen source, and not isopropanol/KOH or aqueous sodium formate. Xiao et al. demonstrated that the pH of the medium plays a major role in the rate, TOF, and enantioselectivity, when $HCOOH–NEt_3$ in water is used as the hydrogen source in the ATH of ketones.[9] Similarly, studies have shown that electron attractors on the ketone substrate also favor rate enhancement and selectivity in the ATH.[1–6,8c]

These observations prompted us to explore the electronic role of the substituents on the aryl sulfonamide of ligand **3** (R = electron withdrawing or donating group). Ru^{II}(arene), $Rh^{III}(Cp^*)$ complexes, and electron donor or electron withdrawing groups in particular, can relay the electronic effect through the sulfonamide bond to the metal center (Fig. 2). Herein, we report the effect of these substituents on the rate, enantioselectivity, and yield in the ATH of ketones, in the presence of aqueous sodium formate or isopropanol as the hydrogen source. The secondary alcohol was obtained in good yield and enantioselectivity.

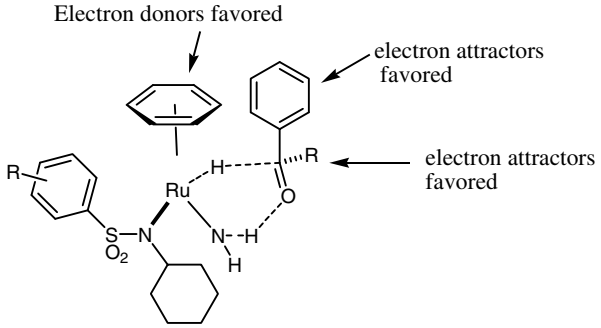


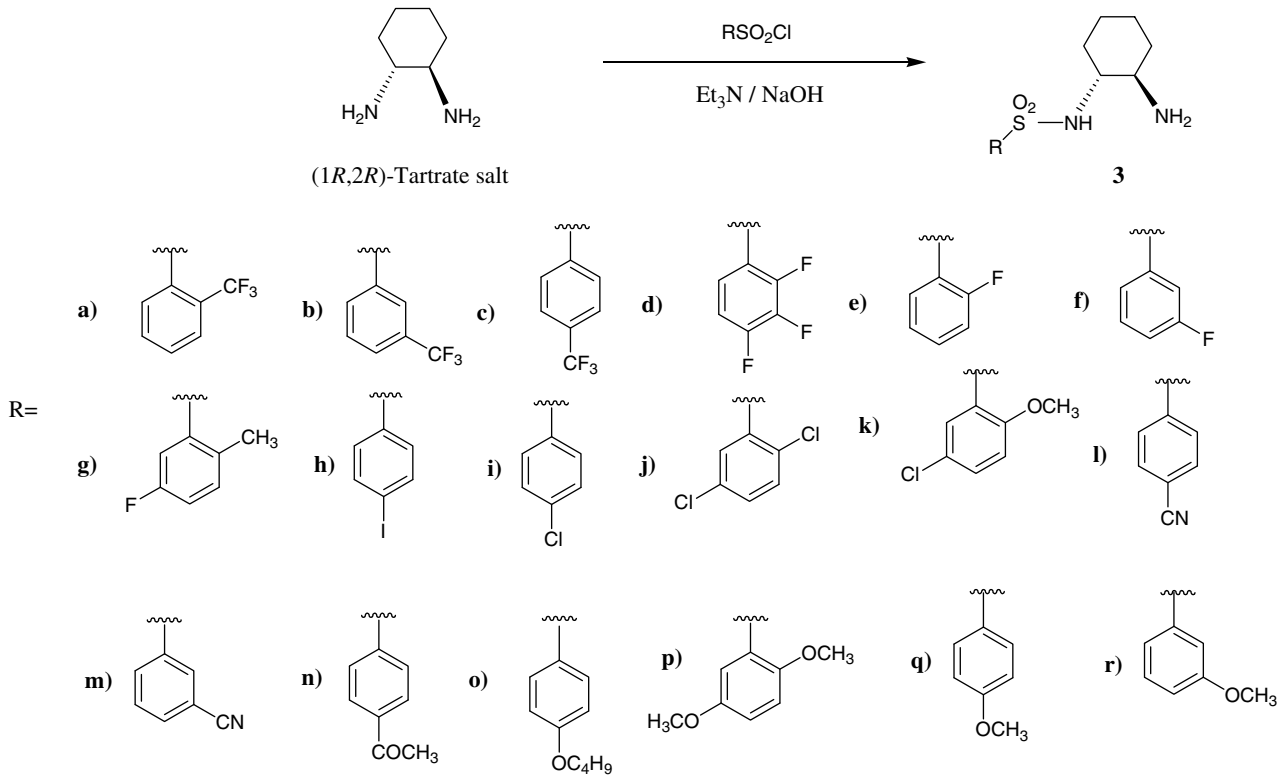
Figure 2. Substituent effects in the asymmetric transfer hydrogenation of ketones.

2. Results and discussion

To explore the electronic effects on ATH catalysts, we synthesized a series of monosulfonamide ligands with electron withdrawing and donating groups **3a**–**r** derived from *trans*-(1*R*,2*R*)-1,2-cyclohexanediamine using our previously reported method (Scheme 1).[11] The new ligands were fully characterized as outlined in Section 4.

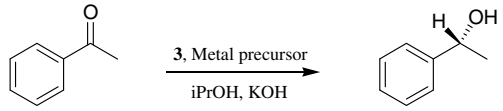
The ligands **3a**–**h** were then reacted with $[RuCl_2(arene)]_2$ and the resulting complexes were tested as catalysts in the ATH of acetophenone with isopropanol/KOH as the hydrogen source. The results are shown in Table 1.

Catalysts with both electron withdrawing and donating groups exhibited high enantioselectivities (82–94%) (Table 1) in the ATH of acetophenone, when Ru^{II}(benzene) was used as the catalyst



Scheme 1. Chiral monosulfonamide ligands.

Table 1
Asymmetric transfer hydrogenation of acetophenone in isopropanol/KOH, catalyzed by $Ru^{II}(arene)L^*$ complexes



Metal precursor: I = $[RuCl_2(\eta^6\text{-benzene})]_2$ II = $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$

Entry	Metal complex	Ligand[a]	Yield (%)	ee[b] (%)
1	I	**3a**	89	88
2	II	**3a**	67	86
3	I	**3b**	66	86
4	I	**3c**	73	84
5	II	**3c**	46	88
6	I	**3d**	76	82
7	I	**3e**	56	88
8	I	**3f**	78	85
9	I	**3g**	90	85
10	II	**3g**	57	93
11	I	**3h**	73	84
12	II	**1h**	32	81
13	I	**3i**	49	82
14	II	**3i**	31	86
15	I	**3j**	57	84
16	I	**3k**	76	88
17	I	**3l**	77	85
18	II	**3l**	46	65
19	I	**3m**	43	85
20	I	**3n**	86	84
21	I	**3o**	53	84
22	I	**3p**	64	89
23	I	**3q**	68	91
24	I	**3r**	49	94

Absolute configurations are all (*R*), assigned by comparing the specific rotations with the literature values.[6a,b]

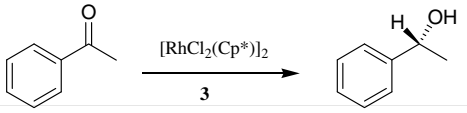
[a] Reaction conditions: 25 °C using a mixture of isopropanol/KOH, 5 h, S/C 33.

[b] Measured by GC analysis of the acetylated alcohol with chiral capillary column β-DEX™ 120.

and isopropanol as the source of hydrogen. Overall, however, ligands with electron withdrawing groups (entries 1, 3, 4, 6,7, 8, 9, 11, 16, 17, and 20) gave slightly better yields (66–90%), compared to ligands with electron donating groups (49–68%) (entries 21–24). Replacing Ru^{II}(benzene) with Ru^{II}(cymene) under the same reaction conditions resulted in high enantioselectivities, but in lower yields, probably due to steric interference from the isopropyl group of the cymene.

Interestingly, when Ru^{II}(arene) was replaced with $Rh^{III}(Cp^*)$ in the chiral ligand-complex, excellent enantioselectivities (90–97%) and yields (90–99%) were obtained using identical reaction conditions, irrespective of the nature of the substituent on the benzenesulfonamide ring (Table 2). When the source of hydrogen was changed to aqueous sodium formate, the rate of the reaction was enhanced, and high enantioselectivities (90–95%) and yields (86–100%) were maintained. In addition, using $Rh(Cp^*)L^*$ with aqueous sodium formate, resulted in complete reduction in 45 min, compared to 5 h using isopropanol/KOH, representing a sixfold rate enhancement. Our data suggest that with $Rh(Cp^*)L^*$ as catalyst, the effect of substituents on the enantioselectivity and yields is minimal. As in our previous work,[6b] we found that the use of a surfactant, along with sodium formate, had little or no effect on the rate of ATH of ketones. The low yields observed with some ligands in Table 1 may be attributed to the low solubility of the $Ru^{II}(arene)L^*$ complex in isopropanol; this is inferred since the reaction mixture showed catalyst adhering to the walls of the vessel, while with aqueous sodium formate a clear solution was observed.

Table 2
Asymmetric transfer hydrogenation of acetophenone in isopropanol/KOH, catalyzed by $Rh^{III}(Cp^*)L^*$ complexes



Entry	Ligand	*t* (h)	HCOONa, H_2O[a]		*t* (h)	*i*-PrOH, KOH[b]	
			Yield (%)	ee[c] (%)		Yield (%)	ee[c] (%)
1	**3a**	0.45	100	99	5	96	92
2	**3b**	0.45	98	94	5	99	96
3	**3d**	0.45	91	90	5	—	—
4	**3f**	0.45	100	91	5	94	93
5	**3g**	0.45	>99	94	5	95	97
6	**3h**	0.45	100	92	5	92	95
7	**3j**	0.45	86	93	5	79	96
8	**3k**	0.45	>99	95	5	52	96
9	**3l**	0.45	100	92	5	67	77
10	**3m**	0.45	94	94	5	96	100
13	**3p**	0.45	>99	96	5	98	97

Absolute configurations are all (*R*), assigned by comparing the specific rotations with the literature values.[6a,b]

[a] 40 °C using a mixture of water/sodium formate under air.

[b] Reaction conditions: 25 °C using a mixture of isopropanol/KOH, S/C 33.

[c] Measured by GC analysis of the acetylated alcohol with chiral capillary column β-DEX™ 120.

In summary, comparing the results from Tables 1 and 2 suggests that $Rh^{III}(Cp^*)L^*$ exhibits a better catalyst in terms of rate and enantioselectivity than $Ru^{II}(arene)L^*$-based catalysts.[1k] The rate enhancement in aqueous sodium formate observed with a variety of $Rh(Cp^*)L^*$-based catalysts,[2e,f,5a–c] highly favors the mechanism hypothesized by Ogo, Süss-Fink, and Xiao.[5c,o,10,12] In their proposed mechanism, the $Rh^{III}(Cp^*)$ complex reacts with sodium formate, to give a formato intermediate species, which dissolves in the hydrophobic ketone, and the reaction then takes place in the substrate, leading to the catalytically, active metal hydride species. Since we did not see any dramatic difference in rate, enantioselectivity, or yield with electron donor or attractor groups, we presume these groups are too far removed from the metal center to have any significant electronic impact in the transition state.

3. Conclusion

In conclusion, we have synthesized a series of ligands with electron withdrawing and electron donating SO_2Ar groups, and tested their Ru(II) and Rh(III) complexes in the ATH of acetophenone to study the effects of substituents on both enantioselectivity and yield. Results suggest that, when used with the Ru^{II}(arene) complex and isopropanol as the hydrogen source, electron withdrawing groups, such as $-CF_3$, and –F on the ligand tend to give slightly higher yields compared to other groups, with the enantioselectivity showing little or no change. Replacing the Ru^{II}(arene) moiety with $Rh^{III}(Cp^*)$ and using ligands **3a**–**r** resulted in excellent enantioselectivities and yields in both isopropanol and aqueous sodium formate. In these cases, no electronic effects on the selectivity were observed. In summary, our results suggest that substituents on the benzene ring of the sulfonamide have minimal electronic impact on the enantioselectivity on the ATH.

4. Experimental

Monosulfonamide ligands **3a**–**r** were prepared by the reported methodology,[11] from the corresponding commercially available

substituted benzenesulfonyl chloride with chiral (1*R*,2*R*)-1,2-cyclohexanediamine.

4.1. Characterization of 3a–r

4.1.1. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-2-(trifluoromethyl)-benzenesulfonamide 3a

Yellow oil (0.4 g, 97%); $[\alpha]_D^{25} = -25$ (*c* 0.13, CH_2Cl_2); IR (film): ν_{max} = 3593, 3367, 3064, 2935, 2857, 1853, 1587, 1445, 1346, 1178, 1028, 972, 774 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.3 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.7–7.65 (m, 2H), 3.11 (br s, 3H), 2.80 (dt, *J* = 4.03, 10.4 Hz, 1H), 2.48 (dt, *J* = 4.3, 10.9 Hz, 1H), 1.96–1.93 (m, 1H), 1.62–1.54 (m, 3H), 1.22–1.10 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 132.6, 131.4, 128.4 (q, J_{CF} = 7.4 Hz), 127.4 (q, J_{CF} = 32.9 Hz), 123.0 (q, J_{CF} = 273.8 Hz), 60.6, 54.7, 34.9, 32.5, 24.9, 24.6; Anal. Calcd for $C_{13}H_{17}F_3N_2O_2S$: C, 48.44, H, 5.32. Found: C, 48.48, H, 5.34.

4.1.2. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-3-(trifluoromethyl)-benzenesulfonamide 3b

Yellow crystals (0.45 g, 95%); mp 90–92 °C; $[\alpha]_D^{25} = -34$ (*c* 0.52, CH_2Cl_2); IR (KBr): ν_{max} = 3359, 3272, 3064, 2936, 2862, 1607, 1450, 1326, 1162, 1130, 1070, 915, 806, 720, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 3.40 (br s, 3H), 2.78 (td, *J* = 4.0, 10.6 Hz, 1H), 2.54 (td, *J* = 4.0, 10.9 Hz, 1H), 1.95–1.65 (m, 4H), 1.59–1.10 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6, 131.6 (q, J_{CF} = 33.3 Hz), 129.9, 129.1 (q, J_{CF} = 3.5 Hz), 124.4, 124.0 (q, J_{CF} = 3.91 Hz), 123.3 (q, J_{CF} = 273.0 Hz), 60.2, 54.64, 35.3, 32.5, 24.8, 24.7; Anal. Calcd for $C_{13}H_{17}F_3N_2O_2S$: C, 48.44; H, 5.32. Found: C, 48.49; H, 5.36.

4.1.3. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-4-(trifluoromethyl)-benzenesulfonamide 3c

White powder (0.55 g, 96%); mp 149–152 °C; $[\alpha]_D^{25} = -57$ (*c* 0.26, CH_2Cl_2); IR (KBr): ν_{max} = 3352, 3287, 3057, 2933, 2860, 1607, 1449, 1403, 1324, 1164, 1131, 1062, 1017, 952, 915, 845, 711 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.18 Hz, 2H), 7.78, (d, *J* = 8.30 Hz, 2H), 2.76 (br s, 3H), 2.71 (dt, *J* = 4.0, 10.4 Hz, 1H), 2.43 (dt, *J* = 3.6, 10.6 Hz, 1H), 1.95–1.92 (m, 1H), 1.88–1.86 (m, 1H), 1.67–1.63 (m, 2H), 1.24–1.1 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.7, 134.3 (q, J_{CF} = 32.7 Hz), 127.6, 126.1 (q, J_{CF} = 3.9 Hz), 123.1 (q, J_{CF} = 273.0 Hz), 60.3, 54.8, 35.9, 32.7, 24.8; Anal. Calcd for $C_{13}H_{17}F_3N_2O_2S$: C, 48.44; H, 5.32. Found: C, 48.45; H, 5.33.

4.1.4. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-2,3,4-(trifluoro)benzenesulfonamide 3d

Yellow crystals (0.18 g, 85%); mp 122–124 °C; $[\alpha]_D^{25} = -46$ (*c* 0.56, CH_2Cl_2); IR (KBr): ν_{max} = 3361, 3294, 3063, 2934, 2860, 1607, 1504, 1466, 1336, 1244, 1161, 1076, 1037, 949, 819, 736, 660, 610 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.78–7.64 (m, 2H), 7.18–7.04 (m, 2H), 3.35 (s, 3H), 2.88–2.7 (m, 1H), 2.58–2.42 (m, 1H), 2.15–1.92 (m, 1H), 1.88–1.72 (m, 1H), 1.69–1.60 (m, 2H), 1.32–1.1 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154 (dd, J_{CF} = 13.5, 260.1 Hz), 149 (dd, J_{CF} = 10.0, 262.2 Hz), 140 (dt, J_{CF} = 14.3, 256.6 Hz), 127.1 (d, J_{CF} = 12.0 Hz), 124.2 (dd, J_{CF} = 3.7, 18.0 Hz), 60.4, 54.6, 35.3, 32.5, 24.8, 24.7. Anal. Calcd for $C_{12}H_{15}F_3N_2O_2S$: C, 46.75; H, 4.87. Found: C, 46.80; H, 4.93.

4.1.5. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-2-fluorobenzenesulfonamide 3e

Yellow solid (0.15 g, 75%); mp 110–112 °C; $[\alpha]_D^{25} = -30$ (*c* 0.66, CH_2Cl_2); IR (KBr): ν_{max} = 3348, 3289, 3057, 2931, 2859, 1597, 1474, 1448, 1329, 1264, 1163, 1078, 946, 827, 765, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (dt, *J* = 2.0, 8.0 Hz, 1H), 7.63–7.51 (m, 2H), 7.16–7.32 (m, 2H), 2.89 (br s, 3H), 2.78 (dt, *J* = 4.1, 10.4 Hz, 1H), 2.45 (dt, *J* = 4.0, 10.9 Hz, 1H), 2.02–1.7 (m, 1H), 1.84–1.72 (m, 1H), 1.68–1.54 (m,2H), 1.28–1.0 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158 (J_{CF} = 225.0 Hz), 134.4 (J_{CF} = 6.0 Hz), 130.2, 128.5 (J_{CF} = 7.5 Hz), 124.2 (J_{CF} = 1.0 Hz), 116.4 (J_{CF} = 10.1 Hz), 61.8, 54.5, 34.4, 32.2, 24.4, 24.9. Anal. Calcd for $C_{12}H_{17}FN_2O_2S$: C, 52.92; H, 6.29. Found: C, 52.99; H, 6.35.

4.1.6. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-3-fluorobenzenesulfonamide 3f

Yellow crystals (0.42 g, 55%); mp 118–120 °C; $[\alpha]_D^{25} = -64$ (*c* 0.52, CH_2Cl_2); IR (KBr): ν_{max} = 3348, 3259, 3083, 2933, 2854, 1590, 1476, 1328, 1223, 1156, 1083, 780, 679 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.70 (ddd J_H = 1.0, 1.3, J_{H-F} = 7.8 Hz, 1H), 7.61 (ddd J_H = 3.4, 1.7, J_{H-F} = 8.2 Hz, 1H), 7.51 (ddd J_H = 8.1, 7.9, J_{H-F} = 5.3 Hz, 1H), 7.27 (dddd, J_H = 1.0, 1.7, J_{H-F} = 7.3, J_H = 1.0 Hz, 1H), 2.67 (dt, *J* = 4.3, 10.9 Hz, 1H), 2.58 (br s, 1H), 2.37 (dt, *J* = 4.2, 11.0 Hz, 1H), 1.95–1.91 (m, 1H), 1.87–1.84 (m, 1H), 1.67–1.62 (m, 2H), 1.27–1.1 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.49 (d, J_{CF} = 251.3 Hz), 143.1 (d, J_{CF} = 36.7 Hz), 130.8 (d, J_{CF} = 7.6 Hz), 122.8 (d, J_{CF} = 3.2 Hz), 119.7 (d, J_{CF} = 21.2 Hz) 114.6 (d, J_{CF} = 24.2 Hz), 60.5, 54.8, 35.84, 32.7, 24.9, 24.8; Anal. Calcd for $C_{12}H_{17}FN_2O_2S$: C, 52.92; H, 6.29. Found: C, 52.95; H, 6.30.

4.1.7. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-5-fluoro-2-methyl-benzenesulfonamide 3g

White crystals (0.22 g, 98%); mp 123–125 °C; $[\alpha]_D^{25} = -63$ (*c* 0.41, CH_2Cl_2); IR (KBr): ν_{max} = 3584, 3288, 3076, 2934, 2859, 1604, 1484, 1450, 1392, 1322, 1268, 1228, 1183, 1157, 1071, 946, 885, 822, 747, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 8.7 and *J* = 2.8 Hz, 1H), 7.29–7.26 (m, 1H), 7.15 (ddd, *J* = 2.8, 5.3, 8.1 Hz, 1H), 2.64 (s, 3H), 2.61 (td, *J* = 4.0, 10.7 Hz, 1H), 2.37 (td, *J* = 4.2, 10.0 Hz, 1H), 1.94–1.87 (m, 2H), 1.66–1.60 (m, 2H), 1.25–1.10 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2 (J_{CF} = 248.0 Hz), 140.3 (J_{CF} = 6.2 Hz), 133.1 (J_{CF} = 7.2 Hz), 132.0 (J_{CF} = 3.7 Hz), 119.5 (J_{CF} = 20.7 Hz), 116.8 (J_{CF} = 24.9 Hz), 60.38, 54.7, 36.1, 32.5, 24.9, 24.8, 19.6; Anal. Calcd for $C_{13}H_{19}FN_2O_2S$: C, 54.52; H, 6.69. Found: C, 54.56; H, 6.70.

4.1.8. *N*-((1*R*,2*R*)-2-Aminocyclohexyl)-4-iodobenzenesulfonamide 3h

Yellow crystals (0.61 g, 90%); mp 105–108 °C; $[\alpha]_D^{25} = -39$ (*c* 0.42, CH_2Cl_2); IR (KBr): ν_{max} = 3749, 3358, 3264, 2931, 2854, 1643, 1562, 1448, 1322, 1159, 1083, 815, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 2.65 (td, *J* = 4.3, 10.0 Hz, 1H), 2.39 (td, *J* = 4.0, 10.0 Hz, 1H), 1.95–1.89 (m, 1H), 1.83–1.79 (m, 1H), 1.66–1.60 (m, 2H), 1.30–1.10 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.9, 138.3, 128.5, 99.7, 60.4, 54.7, 35.7, 32.6, 24.9, 24.8; Anal. Calcd for $C_{12}H_{17}IN_2O_2S$: C, 37.90; H, 4.51. Found: C, 37.94; H, 4.55.

4.1.9. *N*-(1*R*,2*R*)-2-(Aminocyclohexyl)-4-chloro-benzenesulfonamide 3i

Yellow oil (0.22 g, 88%); $[\alpha]_D^{25} = -22$ (*c* 0.31, CH_2Cl_2); IR (film): ν_{max} = 3348, 3287, 3065, 2933, 2858, 1585, 1476, 1448, 1393, 1325, 1161, 1088, 1013, 942, 915, 829, 752, 705, 623 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.87, (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 3.6 (br d, 3H), 2.76 (dt, *J* = 4.0, 10.2 Hz, 1H), 2.55 (dt, *J* = 4.2, 10.2 Hz, 1H), 1.96–1.94 (m, 1H), 1.74–1.5 (m, 3H), 1.22–1.1 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 138.7, 129.2, 128.4, 60, 54.4, 34.7, 32.3, 25.2, 24.8, 24.5. Anal. Calcd for $C_{12}H_{17}ClN_2O_2S$: C, 49.91; H, 5.93. Found: C, 49.98; H, 6.01.

4.1.10. *N*-(1*R*,2*R*)-2-(Aminocyclohexyl)-2,5-dichlorobenzenesulfonamide 3j

Pale brown solid (0.48 g, 94%); mp 146–149 °C; $[\alpha]_D^{25} = -29$ (*c* 0.11, CH_2Cl_2); IR (KBr): ν_{max} = 3350, 3290, 3085, 2932, 2854, 1643, 1450, 1330, 1240, 1163, 1100, 1039, 947, 896, 824 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.1 (d, *J* = 2.2 Hz, 1H), 7.48–7.44 (m, 2H), 2.71 (dt, *J* = 4.0, 10.4 Hz, 1H), 2.45 (dt, *J* = 4.0, 10.9 Hz, 1H), 1.96–1.94 (m, 1H), 1.81–1.79 (m, 1H), 1.67–1.61 (m, 2H), 1.27–1.09 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.7, 133.5, 13.4, 132.7, 130.9, 129.8, 60.9, 54.9, 35.3, 32.4, 24.8, 24.6; Anal. Calcd for $C_{12}H_{16}Cl_2N_2O_2S$: C, 44.59, H, 4.99. Found: C, 44.64, H, 5.04.

4.1.11. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-4-chloro-2-methoxybenzenesulfonamide 3k

Pale brown solid (0.40 g, 91%); mp 159–161 °C; $[\alpha]_D^{25} = -33$ (*c* 0.57, CH_2Cl_2); IR (KBr): ν_{max} = 3361, 3286, 2930, 2855, 1588, 1477, 1389, 1322, 1269, 1158, 1066, 1017, 895, 812, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 2.8 Hz, 1H), 7.48 (dd, *J* = 2.6, 8.8 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 3.97 (s, 3H), 2.62 (dt, *J* = 4.1, 10.0 Hz, 1H), 2.38 (dt, *J* = 4.0, 10.4 Hz, 1H), 1.96–1.90 (m, 1H), 1.82–1.72 (m, 1H), 1.67–1.58 (m, 2H), 1.25–1.02 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.7, 133.9, 129.7, 125.7, 113.4, 60.9, 56.6, 54.9, 35.3, 32.3, 24.9, 24.7; Anal. Calcd for $C_{13}H_{19}ClN_2O_3S$: C, 48.97; H, 6.01. Found: C, 49.00; H, 6.04.

4.1.12. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-4-cyano-benzenesulfonamide 3l

Yellow crystals (0.22 g, 91%); mp 126–128 °C; $[\alpha]_D^{25} = -47$ (*c* 0.45, CH_2Cl_2); IR (KBr): ν_{max} = 3356, 3268, 3057, 2934, 2859, 2232, 1589, 1449, 1330, 1161, 1091, 836, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 3.16 (br s, 3H), 2.74–2.70 (m, 1H), 2.52–2.4 (m, 1H), 1.97–1.92 (m, 1H), 1.82–1.78 (m, 1H), 1.65–1.62 (m, 2H), 1.26–1.16 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8, 127.5, 126.3, 126.2, 60.2, 54.7, 35.6, 32.6, 24.8, 24.7; Anal. Calcd for $C_{13}H_{17}N_3O_2S$: C, 55.89; H, 6.13. Found: C, 55.90; H, 6.15.

4.1.13. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-3-cyano-benzenesulfonamide 3m

Yellow crystals (0.25 g, 88%); mp 104–106 °C; $[\alpha]_D^{25} = -63$ (*c* 0.42, CH_2Cl_2); IR (KBr): ν_{max} = 3339, 3277, 3066, 2932, 2854, 2233, 1581, 1445, 1328, 1156, 1089, 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.22 (sa, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.8, 8.0 Hz, 1H), 2.84 (br s, 3H), 2.72 (dt, *J* = 4.0, 10.1 Hz, 1H), 2.40 (dt, *J* = 3.6, 10.2 Hz, 1H), 2.0–1.82 (m, 2H), 1.56–1.74 (m, 2H), 1.38–1.04 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 150.1, 129.1, 120, 114.4, 113.6, 61, 56.7, 56, 55, 35, 32.1, 24.9, 24.7; Anal. Calcd for $C_{13}H_{17}N_3O_2S$: C, 55.89; H, 6.13. Found: C, 55.84; H, 6.09.

4.1.14. 4-Acetyl-*N*-(1*R*,2*R*)-(2-aminocyclohexyl)benzenesulfonamide 3n

Pale brown solid (0.41 g, 78%); 200–203 °C dec; $[\alpha]_D^{25} = -28$ (*c* 0.22, CH_2Cl_2); IR (KBr): 3350, 3287, 3056, 2933, 2856, 1635, 1587, 1450, 1393, 1325, 1159, 1091, 910, 835, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.24 Hz, 2H), 3.57–3.34 (m, 4H), 2.31–2.09 (m, 1H), 2.05 (s, 3H), 1.80–1.65 (m, 2H), 1.56–1.35 (m, 2H), 1.18–1.0 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9, 142.9, 142.2,125.9, 124.8, 63.03, 58.52, 34.89, 32.08, 24.7, 23.3. Anal. Calcd for $C_{14}H_{20}N_2O_3S$: C, 56.73; H, 6.80. Found: C, 56.66; H, 6.76.

4.1.15. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-4-butoxy-benzenesulfonamide 3o

Yellow oil (0.29 g, 94%); $[\alpha]_D^{25} = -33$ (*c* 0.44, CH_2Cl_2); IR (film): ν_{max} = 3352, 3258, 2920, 2854, 1589, 1495, 1299, 1253, 1145, 1066, 1094, 832 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 2.63 (dt, *J* = 4.0, 10.6 Hz, 1H), 2.37 (dt, *J* = 4.1, 11.1 Hz, 1H), 1.94–1.90 (m, 1H), 1.82–1.76 (m, 3H), 1.65–1.60 (m, 2H), 1.53–1.46 (m, 2H), 1.24–1.02 (m, 4H), 0.98 (t, *J* = 17.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.4, 132.3, 129.1, 114.6, 68.2, 60.4, 54.9, 35.5, 32.7, 31.1, 25.0, 24.8, 19.2, 13.8.; Anal. Calcd for $C_{16}H_{26}N_2O_3S$: C, 58.87; H, 8.03. Found: C, 58.82, H, 7.99.

4.1.16. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-2,5-dimethoxybenzenesulfonamide 3p

Pale brown crystals (0.32 g, 99%); mp 108–110 °C; $[\alpha]_D^{25} = -15$ (*c* 0.81, CH_2Cl_2); IR (KBr): ν_{max} = 3294, 3071, 2933, 2856, 1583, 1493, 1440, 1322, 1274, 1222, 1157, 1041, 816, 736, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 2.4 Hz, H), 7.07 (dd, *J* = 4.0, 8.8 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, H), 3.93 (s, 3H), 3.82 (s, 3H), 2.64 (dt, *J* = 4.0, 11.0 Hz, 1H), 2.38 (dt, *J* = 4.0, 10.9 Hz, 1H), 1.98–1.90 (m, 2H), 1.78–1.60 (m, 2H), 1.24–1.04 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1, 150.1, 129.2, 120.0, 114.4, 113.6, 61.0, 56.7, 55.0, 35.0, 32.1, 24.9, 24.7. Anal. Calcd. for $C_{14}H_{22}N_2O_4S$: C, 53.48; H, 7.05. Found: C, 52.91; H, 7.00.

4.1.17. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-4-methoxy-benzenesulfonamide 3q

Yellow solid (0.2 g, 80%); mp 96–98 °C; $[\alpha]_D^{25} = -57$ (*c* 0.26, CH_2Cl_2); IR(KBr): ν_{max} = 3356, 3281, 3048, 2931, 2857, 1695, 1497, 1321, 1258, 1154, 1093, 1026, 912, 834, 734, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 9.2 Hz, 2H), 6.97 (d, *J* = 9 Hz, 2H), 3.7 (s, 3H), 2.65 (dt, *J* = 4.5, 10.4 Hz, 1H), 2.40 (dt, *J* = 4.0, 10.7 Hz, 1H), 1.95–1.91 (m, 1H), 1.83–1.81 (m, 1H), 1.66–1.60 (m, 2H), 1.25–1.10 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8, 132.6, 129.2, 114.2, 60.2, 55.6, 54.8, 35.5, 32.7, 25, 24.8; Anal. Calcd for $C_{13}H_{20}N_2O_3S$: C, 54.91; H, 7.09. Found: C, 54.95, H, 7.12.

4.1.18. *N*-(1*R*,2*R*)-(2-Aminocyclohexyl)-3-methoxy-benzenesulfonamide 3r

Light yellow solid (0.18 g, 80%); $[\alpha]_D^{25} = -85$ (*c* 1.0, CH_2Cl_2); IR (KBr); ν_{max} = 3358, 3288, 3068, 2931, 2858, 1596, 1481, 1315, 1246, 1157, 1075, 1039, 944, 788, 735, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.53–7.36 (m, 3H), 7.12–7.01 (m, 1H), 3.83 (s, 3H), 3.3 (br s, 3H), 2.72 (dt, *J* = 3.9, 10.0 Hz, 1H), 2.47 (dt, *J* = 4.0, 10.2 Hz, 1H), 1.98–1.92 (m, 1H), 1.70–1.53 (m, 3H), 1.28–1.06 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 142.3, 130.0, 118.9, 118.7, 111.6, 60.3, 55.6, 54.5, 34.8, 32.3, 24.8, 24.5; Anal. Calcd for $C_{13}H_{20}N_2O_3S$: C, 54.91; H, 7.09. Found: C, 54.88; H, 7.05.

4.2. Procedure for catalytic reactions

4.2.1. General procedure for the asymmetric transfer hydrogenation of ketones in isopropanol

A mixture of the metal precursor $[RuCl_2(arene)]_2$ or $[RhCl_2Cp^*]_2$ (0.0039 mmol), and the chiral ligand (0.0075 mmol) in freshly distilled 2-propanol was stirred at 80 °C for 30 min under an argon atmosphere. A solution of potassium hydroxide in 2-propanol was stirred at 50 °C for 30 min. Then the prochiral ketone in 2-propanol was added to the catalyst solution, followed by KOH solution, and stirred at room temperature for the time indicated in Table 1 for each individual reaction. Water was added to the reaction mixture and then extracted with dichloromethane (3 × 10 mL). The dichloromethane layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure, and passed through a short silica gel path. The residue containing the alcohol was acetylated using acetic anhydride.

4.2.2. General procedure for the asymmetric transfer hydrogenation of ketones in water (S/C 100)

A mixture of the metal precursor $[RhCl_2Cp^*]_2$ (0.0039 mmol) and the chiral ligand (0.0075 mmol) was heated in water (2 mL) at 40 °C for 1 h in air without a base. HCOONa (5.7 mmol) and the substrate were subsequently added (1.14 mmol). The reaction mixture was stirred at 40 °C in air for the time indicated in Table 1 for each individual reaction. The reaction mixture was extracted with ether (3 × 10 mL). The ether layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue containing the alcohol was acetylated using acetic anhydride.

Acknowledgments

We gratefully acknowledge support for this project by CONACYT (Grant 37827-E), COSNET (Grants 498.01P and 414.03P), DGEST (grant 310.06-P), and graduate scholarship from CONACYT for N.A.C.

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