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Tetrahedron: *Asymmetry* 18 (2007) 1103–1107

Iridium-catalyzed asymmetric transfer hydrogenation of quinolines with Hantzsch esters

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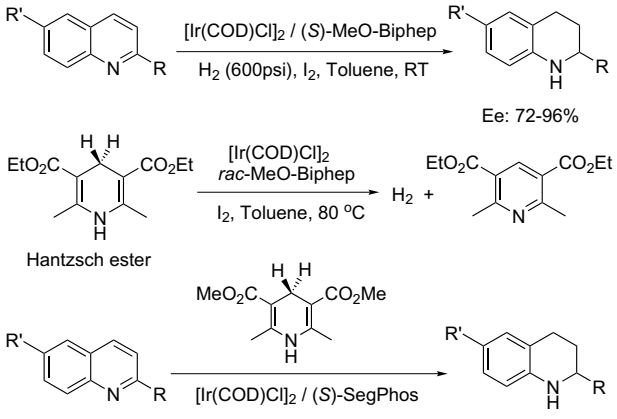
Received 22 March 2007; accepted 25 April 2007
Available online 1 June 2007

Abstract—The iridium-catalyzed enantioselective transfer hydrogenation of quinolines with Hantzsch esters was developed with up to 88% ee using $[Ir(COD)Cl]_2$/(*S*)-SegPhos/I_2 as a catalyst.

1. Introduction

Recently, the biomimetic highly enantioselective organocatalyzed transfer hydrogenation of α,β-unsaturated carbonyl compounds and imines has been realized by List, MacMillan, and Rueping using Hantzsch esters as the hydrogen source.[1] A copper-catalyzed asymmetric hydrogenation of α-ketoesters was reported with up to 94% ee by List et al. using Hantzsch esters,[2] which avoided some of the technical and safety concerns associated with using compressed hydrogen gas. In 2006, Rueping extended this strategy to the asymmetric transfer hydrogenation of heteroaromatic compounds, quinolines, and realized the first example of a metal-free reduction of heteroaromatic compounds.[3] The catalysts are sterically congested chiral phosphoric acids derived from BINOL. Excellent enantioselectivities (87–>99% ee) were obtained for 2-substituted quinolines.

Recently, we developed the highly enantioselective Ir-catalyzed asymmetric hydrogenation of quinoline derivatives using $[Ir(COD)Cl]_2$/MeO-BiPhep as a catalyst in the presence of iodine,[4–6] and this methodology has been successfully applied to the synthesis of tetrahydroquinoline alkaloids.[7] Furthermore, over the course of studying the quinoline hydrogenation mechanism, we found that the dehydroaromatization reactions of 1,4-dihydropyridines (Hantzsch esters) could be realized when using the above asymmetric hydrogenation catalytic system, hydrogen gas was produced in this reaction.[8] As a result, we explored the iridium-catalyzed asymmetric transfer hydrogenation of quinolines using Hantzsch esters as hydrogen source by combination of the above two reactions (Scheme 1). A mild asymmetric transfer hydrogenation of quinolines was realized smoothly using $[Ir(COD)Cl]_2$/(*S*)-SegPhos/I_2 in the presence of Hantzsch esters.



Scheme 1. Asymmetric transfer hydrogenation of quinolines.

2. Results and discussion

In our initial investigation, we found the $[Ir(COD)Cl]_2$/(*S*)-SynPhos/I_2 system could catalyze the transfer hydrogenation of 2-methylquinoline in THF with moderate activity and enantioselectivity (Table 1, entry 1). To evaluate the effect of solvents and other factors, 2-methylquinoline **1a**

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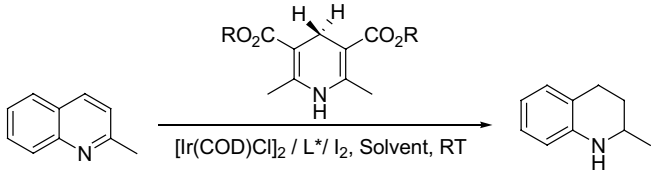
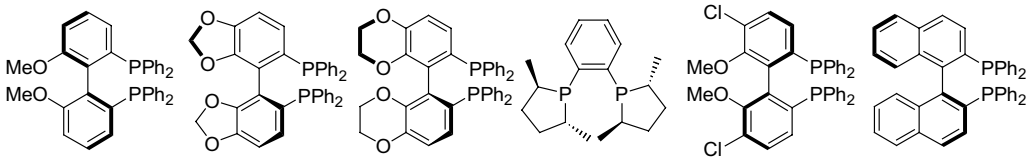
0957-4166/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.tetasy.2007.04.028

Table 1. Ir-catalyzed asymmetric transfer hydrogenation of 2-methylquinoline[a]



1a **2a**

Entry	R	Ligand	Solvent	Time (h)	Yield[b] (%)	ee[c] (%)
1	Et	(*S*)-SynPhos	THF	22	53	52
2	Et	(*S*)-SynPhos	CH_2Cl_2	21	80	2
3	Et	(*S*)-SynPhos	DME	30	38	49
4	Et	(*S*)-SynPhos	Toluene[d]	5	71	8
5	Et	(*S*)-SynPhos	Dioxane	24	43	68
6	Et	(*S*)-BINAP	Dioxane	42	96	54
7	Et	(*S*)-MeO-BiPhep	Dioxane	20	77	78
8	Et	(*R*,*R*)-Me-DuPhos	Dioxane	20	73	4
9	Et	(*R*)-Cl-MeOBiPhep	Dioxane	40	92	79
10	Et	(*S*)-SegPhos	Dioxane	42	96	79
11	Me	(*S*)-SegPhos	Dioxane	20	97	82
12	*i*-Pr	(*S*)-SegPhos	Dioxane	20	97	59
13	*t*-Bu	(*S*)-SegPhos	Dioxane	24	90	23
14	Me	(*S*)-SegPhos	Toluene	90	68	91
15	Me	(*S*)-SegPhos	Toluene/dioxane (2/1)	42	86	87



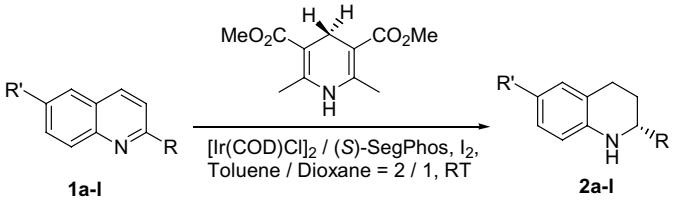
[a] Conditions: 0.25 mmol quinoline, $[Ir(COD)Cl]_2$ (1 mol %), ligand (2.2 mol %), I_2 (5 mol %), 2.5 mL solvent, Hantzsch ester (2.0 equiv).
[b] Isolated yields based on 2-methylquinoline.
[c] Determined by HPLC analysis using a chiralpak OJ-H column.
[d] The reaction was carried out at 60 °C.

was chosen as the model substrate. First, the effect of solvents on reactivity and enantioselectivity were studied; this reaction is highly solvent dependent. For dichloromethane, the reactivity is high and the enantioselectivity is very low (2% ee, entry 2). For dioxane, high enantioselectivity and low reactivity were obtained. Moderate reactivity and enantioselectivity were obtained in THF and DME. For our previously developed Ir-catalyzed asymmetric hydrogenation of quinolines in the presence of iodine, toluene is the best solvent; the reaction was carried out in toluene at room temperature. The reactivity was very low, when the temperature was raised to 60 °C; a very low enantioselectivity was obtained (8% ee, entry 4). Next, the effect of chiral ligands was also investigated using dioxane as solvent. Some commercially available ligands (Table 1, entries 5–10) were screened: (*S*)-MeO-BiPhep (78% ee), (*R*,*R*)-Me-DuPhos (4% ee), (*S*)-BINAP (54% ee), (*R*)-Cl-MeOBiPhep (79% ee), (*S*)-SegPhos (79% ee), (*R*)-Cl-MeOBiPhep, and (*S*)-SegPhos gave the best results (79% ee, entries 9 and 10).

A survey of various Hantzsch esters (entries 10–13) for the transfer hydrogenation revealed that dimethyl Hantzsch ester provided the highest reaction rate and enantioselectivity at room temperature (82% ee, entry 11). This can be explained by the relative size of the ester moieties.[1e] Subsequently, we reevaluated the solvent effect using the dimethyl Hantzsch ester as a hydrogen source. Gratifyingly, the transfer hydrogenation can proceed in toluene with 91% ee, but the reactivity is moderate (entry 14). For the above optimized conditions, high enantioselectivity was obtained in toluene, while high reactivity was obtained in dioxane. To obtain better activity and enantioselectivity, we screened the effect of the toluene/dioxane mixed solvents on the reactivity and enantioselectivity; the results showed that toluene/dioxane ratio (2/1) is the best conclusion. It should be noted that transfer hydrogenation cannot take place in the absence of iodine.

Having established the optimal conditions, we explored the scope of this new Ir-catalyzed asymmetric transfer hydrogenation of quinolines, the results are summarized in Table 2. 2-Alkyl substituted quinolines were hydrogenated smoothly with good yields, although, enantioselectivities were obviously influenced by the length of the side chain (Table 2, entries 1–4). Substrates with a short chain gave better enantioselectivities. The reactions were sensitive to the substituents at the 6-position (Table 2, entries 5–7),

Table 2. Ir-catalyzed asymmetric transfer hydrogenation of quinolines[a]



Entry	R′/R	Yield[b] (%)	Time (h)	ee[c] (%)	Config.
1	H/Me	86 (**2a**)	42	87	(*S*)
2	H/Et	92 (**2b**)	42	87	(*S*)
3	H/*n*-Bu	98 (**2c**)	42	81	(*S*)
4	H/*n*-Pentyl	94 (**2d**)	45	68	(*S*)
5	F/Me	90 (**2e**)	45	86	(*S*)
6	Me/Me	82 (**2f**)	56	86	(*S*)
7	MeO/Me	43 (**2g**)	74	81[d]	(*S*)
8	H/Phenethyl	88 (**2h**)	45	87	(*S*)
9	H/3,4-Methylenedioxyphenethyl	87 (**2i**)	46	87	(*S*)
10	H/3,4-$(MeO)_2C_6H_3(CH_2)_2$–	92 (**2j**)	46	88	(*S*)
11	H/$Ph_2CH(OH)CH_2$–	76 (**2k**)	79	78	(*R*)
12	H/Ph	90 (**2l**)	69	10	(*R*)

[a] Conditions: 0.25 mmol quinoline, $[Ir(COD)Cl]_2$ (1 mol %), ligand (2.2 mol %), I_2 (5 mol %), 2.5 mL solvents, Hantzsch ester (2.0 equiv).
[b] Isolated yields based on **1**.
[c] Determined by HPLC.
[d] 48% recovered starting material.

with low reactivity being obtained for substrates with electron-donating groups, which is probably attributable to the electronic effect. 2-(2-Arylethyl)-substituted quinolines can also be hydrogenated with good asymmetric induction (Table 2, entries 8–10). Interestingly, this transfer hydrogenation system can tolerate a hydroxyl group, and moderate enantioselectivity can be achieved for **1k** (Table 2, entry 11). For 2-aryl substituted quinoline (entry 12), only 10% enantioselectivity was obtained, although the reason for this is unclear.

3. Conclusions

In conclusion, we have developed the asymmetric transfer hydrogenation of quinolines with the $[Ir(COD)Cl]_2$/(*S*)-SegPhos/I_2 system under mild reaction conditions, and up to 88% ee was obtained. This system provides an efficient and convenient route to synthesize tetrahydroquinolines and their derivatives. Further investigation on the mechanism and the range of substrates is currently in progress.

4. Experimental

4.1. General

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on Bruker DRX 400 instrument with tetramethylsilane (TMS) as the internal standard. Enantiomeric excesses were determined by HPLC analysis, using a Chiral column described below in detail. Optical rotations were measured with JASCO P-1020 polarimeter. Flash column chromatography was performed on silica gel (200–300 mesh). All reactions were monitored by TLC analysis. Transfer hydrogenation reactions were performed in a Schlenk tube.

4.2. Experimental data for the tetrahydroquinoline derivatives 2a–2l

Typical procedure: A mixture of $[Ir(COD)Cl]_2$ (1.7 mg, 0.0025 mmol) and (*S*)-SegPhos (3.4 mg, 0.0055 mmol) in solvent (1 mL) was stirred at room temperature for 10 min in a Schlenk tube, after which I_2 (3.2 mg, 0.0125 mmol) was added and stirred for another 10 min, the substrate (0.25 mmol) and Hantzsch dihydropyridine (0.50 mmol) were then added. The resulting mixture was allowed to stir at rt for 20–90 h. The solvent was removed under reduced pressure. The enantiomeric excesses were determined by chiral HPLC (OJ-H, OD-H, or AS-H) after the purification by column chromatography on silica gel (ethyl acetate/hexane).

4.2.1. 2-Methyl-1,2,3,4-tetrahydroquinoline 2a. (Known compound, see Ref. 4). 87% ee, $[\alpha]_D^{RT} = -73.2$ (*c* 0.56, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.21 (t, $J = 6.2$ Hz, 3H), 1.60 (m, 1H), 1.93 (m, 1H), 2.75 (m, 1H), 2.81 (m, 1H), 3.40 (m, 1H), 3.68 (br, 1H), 6.47 (d, $J = 8.5$ Hz, 1H), 6.60 (m, 1H), 6.95 (m, 2H); HPLC (OJ-H, elute: hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 1.0 mL/min), (*S*) $t_1 = 10.6$ min, (*R*) $t_2 = 11.8$ min.

4.2.2. 2-Ethyl-1,2,3,4-tetrahydroquinoline 2b. (Known compound, see Ref. 4). 87% ee, $[\alpha]_D^{RT} = -70.9$ (*c* 0.66, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 0.98 (t, $J = 7.5$ Hz, 3H), 1.52 (m, 3H), 1.95 (m, 1H), 2.76 (m, 2H), 3.15 (m, 1H), 3.75 (br, 1H), 6.46 (d, $J = 7.9$ Hz, 1H), 6.59 (t, $J = 7.3$ Hz, 1H), 6.95 (m, 2H); HPLC (OJ-H, elute:

hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 0.6 mL/min), (*S*) $t_1 = 15.0$ min, (*R*) $t_2 = 16.4$ min.

4.2.3. 2-Butyl-1,2,3,4-tetrahydroquinoline 2c. (Known compound, see Ref. 4). 81% ee, $[\alpha]_D^{RT} = -72.2$ (*c* 0.92, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 0.95 (t, $J = 6.9$ Hz, 3H), 1.36 (m, 4H), 1.50 (m, 3H), 1.96 (m, 1H), 2.75 (m, 2H), 3.22 (m, 2H), 3.76 (br, 1H), 6.48 (d, $J = 7.6$ Hz, 1H), 6.59 (m, $J = 7.3$ Hz, 1H), 6.95 (m, 2H); HPLC (OJ-H, elute: hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate 0.6 mL/min), (*S*) $t_1 = 11.9$ min, (*R*) $t_2 = 13.7$ min.

4.2.4. 2-Pentyl-1,2,3,4-tetrahydroquinoline 2d. (Known compound, see Ref. 4). 68% ee, $[\alpha]_D^{RT} = -41.3$ (*c* 0.92, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 0.91 (t, $J = 6.7$ Hz, 3H), 1.42 (m, 8H), 1.48 (m, 1H), 1.95 (m, 1H), 2.76 (m, 2H), 3.23 (m, 1H), 3.74 (br, 1H), 6.47 (d, $J = 7.5$ Hz, 1H), 6.59 (t, J = 7.3 Hz, 1H), 6.95 (m, 2H); HPLC (OJ-H, elute: hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate 0.6 mL/min), (*S*) $t_1 = 11.2$ min, (*R*) $t_2 = 12.2$ min.

4.2.5. 6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline 2e. (Known compound, see Ref. 4). 86% ee, $[\alpha]_D^{RT} = -54.4$ (*c* 0.70, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.20 (d, $J = 6.2$ Hz, 3H), 1.55 (m, 1H), 1.91 (m, 1H), 2.72 (m, 1H), 2.80 (m, 1H), 3.35 (m, 1H), 3.75 (br, 1H), 6.40 (m, 1H), 6.67 (m, 2H); HPLC (OD-H, elute: hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 0.8 mL/min), (*S*) $t_1 = 6.6$ min, (*R*) $t_2 = 7.9$ min.

4.2.6. 2,6-Dimethyl-1,2,3,4-tetrahydroquinoline 2f. (Known compound, see Ref. 4). 87% ee, $[\alpha]_D^{RT} = -65.3$ (*c* 0.62, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.20 (d, $J = 6.2$ Hz, 3H), 1.58 (m, 2H), 1.92 (m, 1H), 2.20 (s, 3), 2.70 (m, 1), 2.78 (m, 1), 3.35 (m, 1H), 3.56 (br, 1H), 6.41 (d, $J = 7.8$ Hz, 1H), 6.78 (m, 2H); HPLC (OJ-H, elute: hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 1.0 mL/min), (*S*) $t_1 = 13.1$ min, (*R*) $t_2 = 16.3$ min.

4.2.7. 6-Methoxy-2-methyl-1,2,3,4-tetrahydroquinoline 2g. (Known compound, see Ref. 4). 81% ee, $[\alpha]_D^{RT} = -63.5$ (*c* 0.36, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.21 (t, $J = 6.2$ Hz, 3H), 1.57 (m, 1H), 1.93 (m, 1H), 2.73 (m, 1H), 2.83 (m, 1H), 3.33 (m, 1H), 3.73 (s, 3H), 6.46 (d, $J = 8.3$ Hz, 1H), 6.60 (m, 2H); HPLC (OJ-H, elute: hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min), (*S*) $t_1 = 14.7$ min, (*R*) $t_2 = 17.8$ min.

4.2.8. 2-Phenethyl-1,2,3,4-tetrahydroquinoline 2h. (Known compound, see Ref. 4). 87% ee, $[\alpha]_D^{RT} = -67.2$ (*c* 1.14, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.68 (m, 1H), 1.83 (m, 2H), 1.98 (m, 1H), 2.78 (m, 4H), 3.29 (m, 1H), 3.74 (br, 1H), 6.45 (d, $J = 7.4$ Hz, 1H), 6.60 (t, J = 7.3 Hz, 1H), 6.95 (m, 2H), 7.21 (m, 3H), 7.30 (m, 2H); HPLC (AS-H, elute: hexanes/*i*-PrOH = 94/6, detector: 254 nm, flow rate 0.8 mL/min), (*S*) $t_1 = 6.4$ min, (*R*) $t_2 = 7.0$ min.

4.2.9. 2-(3′,4′-Methylenedioxyphenethyl)-1,2,3,4-tetrahydroquinoline 2i. (Known compound, see Ref. 4). 87% ee, $[\alpha]_D^{RT} = -50.0$ (*c* 1.19, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.21 (m, 1H), 1.66 (m, 1H), 1.76 (m, 2H), 1.98 (m, 1H), 2.65 (m, 2H), 2.78 (m, 2H), 3.27 (m, 1H), 3.75 (br, 1H), 5.92 (s, 2H), 6.46 (d, $J = 7.8$ Hz, 1H), 6.60 (m, 2H), 6.70 (m, 2H), 6.95 (m, 2H); HPLC (AS-H, elute: hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.8 mL/min), (*S*) $t_1 = 16.7$ min, (*R*) $t_2 = 20.3$ min.

4.2.10. 2-(3′,4′-Dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline 2j. (Known compound, see Ref. 4). 88% ee, $[\alpha]_D^{RT} = -43.8$ (*c* 1.34, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.68 (m, 1H), 1.81 (m, 2H), 1.98 (m, 1H), 2.69 (m, 2H), 2.79 (m, 2H), 3.30 (m, 1H), 3.86 (s, 3H), 3.87 (s, 3H), 6.45 (d, $J = 7.7$ Hz, 1H), 6.60 (m, 1H), 6.74 (m, 3H), 6.96 (m, 2H); HPLC (AS-H, elute: hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate 0.8 mL/min), (*R*) $t_1 = 9.9$ min, (*S*) $t_2 = 10.5$ min.

4.2.11. 1,1-Diphenyl-2-(1,2,3,4-tetrahydroquinolin-2-yl)-ethanol 2k. (Known compound, see Ref. 4). 78% ee, $[\alpha]_D^{RT} = -82.6$ (*c* 1.18, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 0.87 (m, 1H), 1.71 (m, 2H), 2.46 (m, 2H), 2.69 (m, 2H), 3.29 (m, 2H), 4.41 (br, 1H), 6.38 (d, $J = 7.8$ Hz, 1H), 6.60 (m, 1H), 6.91 (m, 2H), 7.24 (m, 2H), 7.33 (m, 4H), 7.45 (m, 4H); HPLC (OD-H, elute: hexanes/*i*-PrOH = 94/6, detector: 254 nm, flow rate: 1.0 mL/min), (*S*) $t_1 = 11.3$ min, (*R*) $t_2 = 13.4$ min.

4.2.12. 2-Phenyl-1,2,3,4-tetrahydroquinoline 2l. (Known compound, see Ref. 3a). 10% ee, $[\alpha]_D^{RT} = +7.6$ (*c* 0.88, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.99 (m, 1H), 2.12 (m, 1H), 2.75 (m, 1H), 2.90 (m, 1H), 4.01 (br, 1H), 4.43 (m, 1H), 6.38 (d, $J = 7.9$ Hz, 1H), 6.88 (m, 1H), 6.90 (m, 2H), 7.35 (m, 6H), 7.41 (m, 4H); HPLC (AS-H, elute: hexanes/*i*-PrOH = 94/6, detector: 254 nm, flow rate 1.0 mL/min), (*S*) $t_1 = 5.2$ min, (*R*) $t_2 = 11.9$ min.

Acknowledgment

We are grateful for the financial support from the National Science Foundation of China (20302005).

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