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Highly enantioselective hydrogenation of new 2-functionalized quinoline derivatives

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ABSTRACT

The asymmetric hydrogenation of a new series of 2-functionalized quinolines has been developed in the presence of in situ generated catalysts obtained from $[Ir(cod)Cl]_2$/(*R*)-bisphosphine/I_2 combinations. The enantioselectivity levels were as high as 84–94% ee for the synthesis of 1,2,3,4-tetrahydroquinolines.

Optically active substituted tetrahydroquinolines constitute the principal structural unit of many natural alkaloids which display a wide range of physiological activities.[1] In addition, they are very useful synthetic intermediates for the preparation of biologically active compounds for pharmaceutical, agrochemical, and fine chemical industries.[2] (−)-Angustureine and (−)-Galipinine (Fig. 1) which show, for example, antiplasmodial and cytotoxic activities, respectively, are two members of the array of chiral 2-substituted tetrahydroquinolines of interest.[2,3] The catalytic asymmetric hydrogenation of quinolines provides a very convenient and straightforward access to non-racemic substituted tetrahydroquinolines.[4–8] Successful asymmetric hydrogenation of quinoline derivatives with iridium catalysts modified by chiral diphosphines and assisted by iodine has been demonstrated.[5] Other efficient chiral iridium[6] as well as ruthenium[7] hydrogenation catalysts and organometallic and organic based transfer hydrogenation processes[8] have also been reported. Regardless of the recent progresses, highly enantioselective hydrogenation of various functionalized quinolines still remains a challenge. Previous reports have focused generally on aryl, alkyl, and benzyl 2-substituted quinolines. However, a

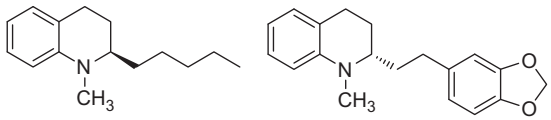
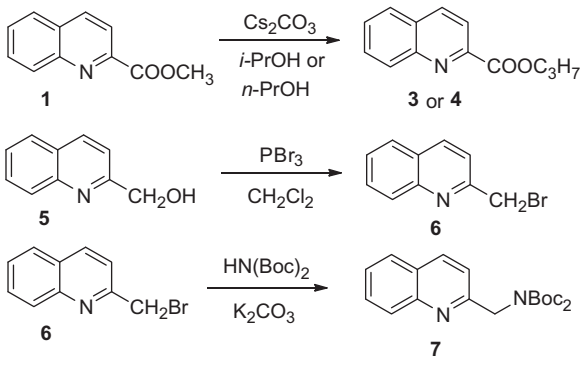


Figure 1. Selected bioactive quinoline derivatives isolated from *Galipea officinalis*.



Scheme 1. Synthesis of the new substrates.

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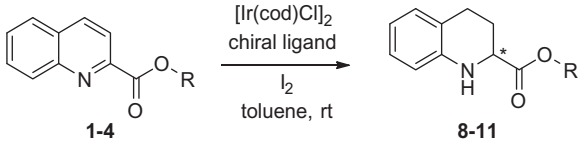
larger substrates scope is desirable in order to increase the promise applications of this methodology.

Following our interest in the asymmetric hydrogenation of aromatic heterocycles,[9] we sought to examine new 2-substituted quinolines which would present a high synthetic potential for further elaboration into valuable molecules. For this purpose, we explored 2-substituted quinolines bearing esters (**1–4**), hydroxymethyl (**5**), bromomethyl (**6**), and protected amine (**7**) groups which represent especially convenient functionalities for organic synthesis.

The syntheses of the new 2-functionalized quinolines are shown in Scheme 1. They have been performed from commercial methyl quinoline 2-carboxylate **1**. The *n*-propyl quinoline 2-carboxylate **3** and *iso*propyl quinoline 2-carboxylate **4** esters were obtained by transesterification of methyl ester **1** in the presence of a catalytic amount of cesium carbonate in the appropriate alcohol. As already described, quinolin-2-yl methanol **5** was obtained by classical reduction of methyl ester **1** in the presence of sodium borohydride.[5a] Substitution of the hydroxy moiety by a bromide in the presence of PBr_3 led to 2-(bromomethyl)quinoline **6**. The synthesis of the amino protected quinoline **7** has been performed from 2-(bromomethyl)quinoline **6** by reaction with di-*tert*-butylimino-dicarboxylate in the presence of potassium carbonate affording the *N*,*N*-diBoc-quinolin-2ylmethanamine **7**.

Table 1
Asymmetric hydrogenation of quinoline-2-carboxylates **1-4**[a]



Entry	Substrate	Ligand	Conv.[b] (%)	Yield[c] (%)	ee[c] (%)
1[d]	R = Me, **1**	**L1**	100	88	66
2[d,e]		**L1**	100	88	53
3		**L2**	98	97	49
4		**L3**	75	70	38
5		**L4**	99	99	21
6		**L5**	97	91	50
7[d]		**L6**	100	98	25
8		**L7**	100	95	74
9		**L8**	88	82	72
10[e]		**L8**	94	89	72
11		**L9**	95	87	55
12	R = Et, **2**	**L7**	99	94	94
13		**L8**	99	94	88
14[e]		**L7**	100	100	85
15	R = *n*-Pr, **3**	**L7**	100	100	90
16	R = *i*-Pr, **4**	**L7**	100	100	75

[a] All reactions were performed on a 1 mmol scale; S/Ir/L/I_2 = 100/1/1.1/5; P_{H2} = 50 bar; 20 °C; toluene 7 mL; 17 h.
[b] Conversion determined by GC and RMN.
[c] Yield determined by HPLC analysis on Chiralcel OJ-H column (hexane/*i*-PrOH 70:30, 1 mL/min).
[d] 30 h.
[e] The catalyst was prepared under air.

For our preliminary hydrogenation experiments, we chose methyl quinoline 2-carboxylate 1 as the substrate and varied the chiral ligand under the standard reaction conditions (toluene as the solvent, I_2 as the additive, 50 bar H_2, 20 °C) (Table 1).[5a,5l] Among the large array of ligands employed for screening, members of MeO-Biphep family **L1**–**L5**, Synphos **L6**, Difluorphos **L7**, and P-Phos **L8** and **L9** furnished the most promising results (Fig. 2, Table 1). The reactions proceeded smoothly with high conversions. The highest enantioselectivities of 72–74% ee were achieved by applying ligands **L7** and **L8** (entries 8 and 9). The transfer of the chiral information is related to the dihedral angle of the biaryl and the stereoelectronic properties of the *P*-substituents of the ligands. As already highlighted by Chan,[5g] the catalysts bearing P-Phos ligand **L8** could be prepared under air without pre-degassing and drying of the solvent, it displayed similar activity and enantioselectivity as if prepared under inert atmosphere (entry 10 vs 9). However, an erosion of the enantioselectivity was observed when the catalyst bearing L1 was prepared under air (entry 2 vs 1).[5g,5l]

Next, we examined the hydrogenation of three other esters **2–4** with bulkier groups in the presence of Difluorphos **L7** and P-Phos **L8** ligands (entries 12–16). The selectivity of hydrogenation of ethyl ester **2** increased significantly compared to results obtained with the methyl congener **1** (from 74 to 94% ee in the presence of **L7**) (entries 8 and 12). Nonetheless, a further increase of the bulkiness of the ester from ethyl to propyl groups resulted in a substantial erosion of the enantioselectivity. Actually, the hydrogenation of *n*- and *i*-propyl esters **3** and **4** proceeded with 90% and 75% ee, respectively (entries 15 and 16).

It is important to mention that for methyl (**8**) and ethyl (**9**) ester hydrogenation products, we observe the slow dehydrogenative

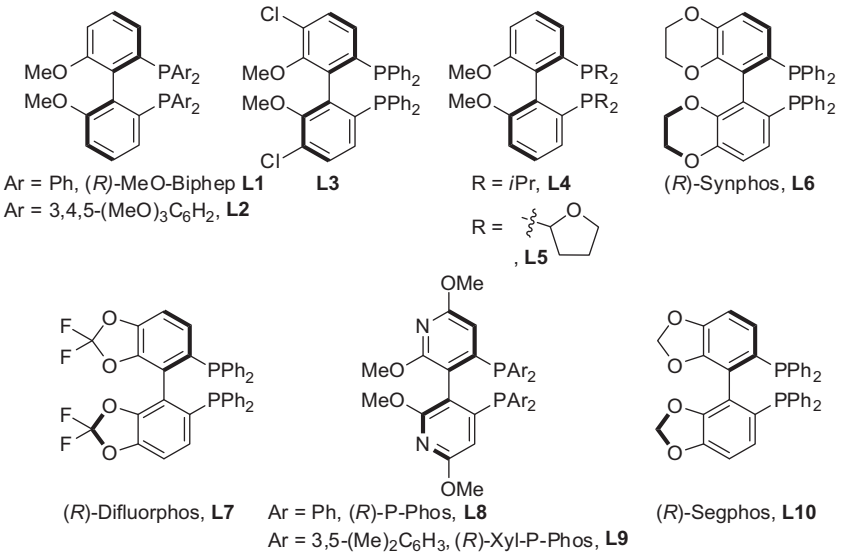
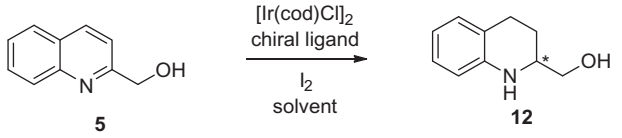


Figure 2. Bisphosphine ligands used.

Table 2
Asymmetric hydrogenation of **5**[a]



5 **12**

Entry	Ligand	Solvent	Conv. (%)[b]	Yield (%)[c]	ee (%)[c]
1	**L7**	Toluene	4	4	nd
2[d]		Toluene	100	100	83
3		Toluene/MeOH	100	100	75
4		Toluene/*i*-PrOH	97	97	84
5[e]		Toluene/*i*-PrOH	77	77	81
6[f]	**L9**	Toluene/*i*-PrOH	100	100	70
7	**L2**	Toluene/*i*-PrOH	99	99	70
8[f]	**L8**	Toluene/*i*-PrOH	97	97	78
9[f]	**L10**	Toluene/*i*-PrOH	100	100	80

[a] All reactions were performed on a 1 mmol scale; S/Ir/L/I_2 = 100/1/1.1/5; P_{H2} = 50 bar; 20 °C; 17 h; solvent 7 mL, toluene/MeOH or toluene/*i*-PrOH = 8/1.
[b] Conversion determined by GC and RMN.
[c] Yield determined by HPLC analysis on a Chiralcel OD column (hexane/*i*-PrOH 90:10, 1 mL/min).
[d] 20 °C, 10 days;
[e] 10 °C, 17 h;
[f] 30 °C; 17 h

aromatization of the nitrogen heterocycle leading back to substrates **1** and **2** when the products were stored in solution under the light.[10]

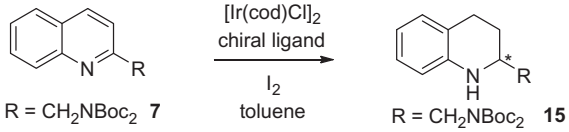
Afterward, we considered the asymmetric hydrogenation of 2-hydroxymethyl quinoline **5** under our standard reaction conditions (Table 2).

Due to the low solubility of **5**, the hydrogenation in neat toluene was sluggish and required about 10 days to go to completion. The hydrogenation product was however obtained with 83% ee (entry 2 vs 1). The addition of methanol allowed improving the solubility of **5** and consequently the efficiency of the hydrogenation into **12** (entry 3). Thus, when varying the ratio of toluene and methanol, we found an optimal combination of 8:1. Even if the reaction could go to completion within 17 h, the selectivity into **12** dropped from 83 to 75% ee compared to results obtained in neat toluene (entry 3 vs 2). The substitution of MeOH by *i*PrOH allowed an increase of the enantioselectivity from 75% to 84% ee (entry 4). This result is the best among all attempts while varying further the chiral ligand (entries 6–9 vs 4). The hydrogenation of **5** has been reported only once by Zhou in neat *i*PrOH but with a lower enantioselectivity (75% ee).[5a] A lowering of the reaction temperature to 10 °C had a slight influence on the enantioselectivity and the reaction slowed down as 77% yield was obtained within 17 h (entry 5). It is not straightforward to observe a likely harmful effect on the stability of the catalyst especially in the presence of *iso*propanol as the yield and ee remained high.[5a,5e]

We then explored the hydrogenation of the 2-bromomethyl substituted quinoline **6** (Table 3). Beside the expected hydrogenation product **13**, we observed the formation of the 2-methyl-1,2,3,4-tetrahydroquinoline **14** resulting from bromide cleavage. The result exhibiting the best compromise between yield and enantioselectivity into **13** was obtained in the presence of ligand **L8** (entry 2). The reaction provided **13** in 100% yield and with 81% of ee. The constant higher ee obtained for **14** suggests that the cleavage of the bromide is occurring most probably prior to hydrogenation of the quinoline heterocycle. Indeed, the results are close to those obtained for the hydrogenation of 2-methyl substituted quinoline.[5k] When using the corresponding 2-chloroethyl substituted quinoline as a substrate, we observed a systematic cleavage of the chloride and could not find conditions providing selectively the hydrogenated chloroethyl product.

Finally, we concentrated on the nitrogen substituted quinoline **7** which could be of interest for preparing chiral aminoquinolines (Table 4). The *N,N*-diBoc protected substrate **7** was easily synthesized from the bromo substituted quinoline **6** (Scheme 1) and provides a direct access to the corresponding amino tetrahydroquinoline after hydrogenation and deprotection. The hydrogenations were carried out under our standard conditions with different ligands. Thus, the hydrogenation of **7** could be performed

Table 4
Asymmetric hydrogenation of **7**[a]

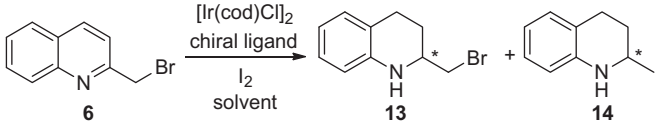


R = CH_2NBoc_2 **7** R = CH_2NBoc_2 **15**

Entry	Substrate	Ligand	Conv. (%)[b]	Yield (%)[c]	ee (%)[c]
1	**7**	**L7**	100	100	83
2		**L8**	100	100	85
3		**L10**	100	100	87
4[d]			100	100	91

[a] All reactions were performed on a 1 mmol scale; S/Ir/L/I_2 = 100/1/1.1/5; P_{H2} = 50 bar; 20 °C; toluene 7 mL; 17 h.
[b] Conversion determined by GC and RMN.
[c] Yield determined by HPLC analysis: Chiralcel OD column (hexane/*i*-PrOH 98:2, 0.2 mL/min).
[d] 0 °C, 80 bar.

Table 3
Asymmetric hydrogenation of **6**[a]



6 **13** **14**

Entry	Ligand	Conv. (%)[b]	Yield **13** (%)[c]	Yield **14** (%)[c]	ee **13** (%)[c]	ee **14** (%)[c]
1[d]	**L7**	100	65	30	69	90
2	**L8**	100	100	—	81	—
3[e]		100	55	45	45	82
4	**L10**	100	44	56	79	84

[a] All reactions were performed on a 1 mmol scale; S/Ir/L/I_2 = 100/1/1.1/5; P_{H2} = 30 bar; 20 °C; 17 h; toluene/*i*-PrOH 8:1; 7 mL.
[b] Conversion determined by GC and RMN.
[c] Yield determined by HPLC analysis on Chiralcel OD column (hexane/*i*-PrOH 98:2, 1.5 mL/min).
[d] 50 bar H_2.
[e] 20 bar H_2.

in an excellent yield (100%) and with a high enantioselectivity of 87% with Segphos **L10** (entry 3). By lowering temperature to 0 °C, the ee could be increased up to 91% with always a complete conversion (entry 4).

In conclusion we have developed the highly enantioselective asymmetric hydrogenation of a range of 2-functionalized quinolines using Ir/bisphosphine/I_2 based catalytic systems. It has been shown that this type of catalytic system tolerates esters and hydroxy groups. We demonstrate here that it is also the case for nitrogen and bromide substituents. This methodology provides an access to synthetically useful chiral tetrahydroquinolines with excellent enantioselectivities especially for substrates **2** and **7**, the latter providing interesting building blocks for synthesis. Further investigations on 2-functionalized quinolines will be reported in due course.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.06.114.

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