Asymmetric Catalysis

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A Highly *cis*-Selective and Enantioselective Metal-Free Hydrogenation of 2,3-Disubstituted Quinoxalines**

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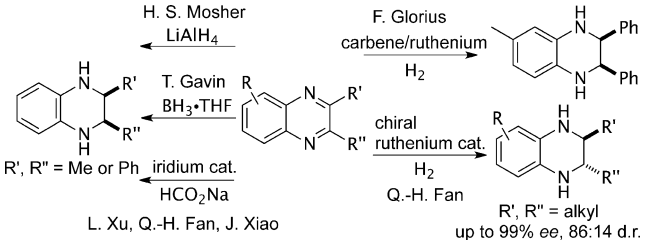
Abstract: *A wide range of 2,3-disubstituted quinoxalines have been successfully hydrogenated with H_2 using borane catalysts to produce the desired tetrahydroquinoxalines in 80–99% yields with excellent cis selectivity. Significantly, the asymmetric reaction employing chiral borane catalysts generated by the in situ hydroboration of chiral dienes with $HB(C_6F_5)_2$ under mild reaction conditions has also been achieved with up to 96% ee, and represents the first catalytic asymmetric system to furnish optically active cis-2,3-disubstituted 1,2,3,4-tetrahydroquinoxalines.*



Scheme 1. Reductions of 2,3-disubstituted quinoxalines. THF = tetrahydrofuran.

Tetrahydroquinoxalines are very useful moieties and present in a wide range of biologically and medicinally active compounds, and a lot of methods have been developed to access them.[1] The direct reduction of quinoxalines is one of the most efficient approaches among these methodologies.[2] In particular, the catalytic hydrogenation with H_2 as well as its asymmetric version has attracted attention and great advances have been made.[3] Since the first asymmetric hydrogenation of 2-methylquinoxaline with chiral rhodium catalysts reported by Murata and co-workers in 1987,[4a] a variety of chiral transition metal catalysts have been developed for the enantioselective hydrogenation of 2-substituted quinoxalines.[4] However, in sharp contrast, the reduction of 2,3-substituted quinoxalines has been rarely reported.[5,6] For example, Deselms and Mosher reported a noncatalytic lithium aluminium hydride reduction of 2,3-dimethylquinoxaline to give a *cis* product in 1960 (Scheme 1).[5a] Gavin and co-workers described the reduction of 2,3-dimethyl- and 2,3-diphenylquinoxaline with borane in THF solution (Scheme 1).[5b] Recently, Xu, Fan, and Xiao reported an iridium-catalyzed transfer *cis*-selective hydrogenation of 2,3-dimethylquinoxaline (Scheme 1).[5c] Glorius and co-workers described a ruthenium/carbene-catalyzed *cis*-selective hydrogenation of 2,3-diphenyl-6-methylquinoxaline. In 2011, Fan and co-workers disclosed the first and the only asymmetric hydrogenation of 2,3-dialkylquinoxalines with chiral cationic ruthenium diamine catalysts to give the desired *trans* products with up to 99% *ee* and 86:14 d.r. (Scheme 1).[5e] Therefore, the development of highly stereoselective hydrogenations of 2,3-disubstituted quinoxalines under mild reaction conditions with a good substrate scope, especially the corresponding asymmetric reactions, still remains a challenge in the field of catalytic hydrogenation.

The recently emerging frustrated Lewis pair (FLP) chemistry provides a breakthrough approach for metal-free hydrogenation with molecular H_2 since catalytic hydrogenation has long been dominated by transition-metal catalysis.[7–9] A wide range of unsaturated compounds have proven to be effective substrates for the FLP-catalyzed hydrogenations.[9,10] Significantly, some promising advances have also been made for FLP-catalyzed asymmetric reactions,[11,12] but the asymmetric hydrogenation of silyl enol ethers is the only example to proceed with more than 90% *ee*.[11f] In 2013, Stephan and co-workers described the hydrogenation of 2,3-dimethyl- and 2,3-diphenylquinoxaline using an equivalent of the Lewis acid $B(C_6F_5)_3$. Interestingly, decahydro- instead of tetrahedroquinoxaline derivatives were obtained.[10c] As part of our general interest in exploring novel FLP catalytic systems, we recently reported the asymmetric hydrogenation of imines[11e] and silyl enol ethers,[11f] and the *cis*-selective hydrogenation of simple pyridines,[10d] using an in situ catalyst generation strategy involving the hydroboration of alkenes with $HB(C_6F_5)_2$ (Piers' borane).[13,14] Our attempts on other challenging substrates for the hydrogenation show that 2,3-disubstituted quinoxalines can be highly *cis*-selectively and enantioselectively hydrogenated under FLP catalysis. Herein, we report our preliminary efforts on this subject.

Initially, the metal-free hydrogenation of 2,3-dimethyl quinoxaline (**1a**) under H_2 (20 bar) at 100 °C in toluene was examined using 10 mol% of $B(C_6F_5)_3$ (**3a**)[15a] or $B(p\text{-}HC_6F_4)_3$ (**3b**).[15b] These reactions went well to give *trans*-**2a** as a major product (Table 1, entries 1 and 2). Further lowering the temperature can obviously improve the *cis* selectivities (entries 3–6), and up to 98:2 d.r. was obtained at 60 °C using **3b**. Reducing the catalyst loading to 5 mol% gave a similar

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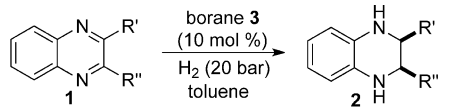
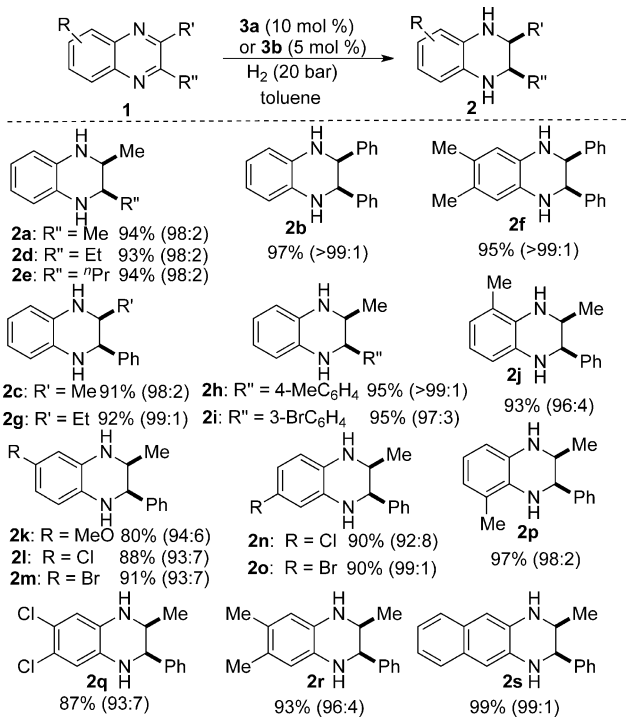
Table 1: Hydrogenation of 2,3-disubstituted quinoxalins.[a]



1a: R' = R'' = Me **3a**: $B(C_6F_5)_3$ **3c**: $HB(C_6F_5)_2$
1b: R' = R'' = Ph **3b**: $B(p\text{-}HC_6F_4)_3$ **3d**: $HB(p\text{-}HC_6F_4)_2$
1c: R' = Me, R'' = Ph

Entry	1	3	*T* [°C]	*t* [h]	Conv. [%][b]	*cis*/*trans*[b]
1	**1a**	**3a**	100	24	>99	27:73
2	**1a**	**3b**	100	24	>99	32:68
3	**1a**	**3a**	80	20	>99	63:37
4	**1a**	**3b**	80	20	>99	79:21
5	**1a**	**3a**	60	20	>99	92:8
6	**1a**	**3b**	60	20	>99	98:2
7[c]	**1a**	**3b**	60	20	>99	98:2
8	**1b**	**3a**	100	24	>99	>99:1
9	**1b**	**3b**	100	24	95	>99:1
10	**1b**	**3c**	100	24	48	>99:1
11	**1b**	**3d**	100	24	21	>99:1
12[c]	**1b**	**3a**	100	24	75	>99:1
13	**1b**	**3a**	80	24	85	>99:1
14	**1c**	**3a**	100	20	>99	92:8
15	**1c**	**3a**	60	20	>99	98:2
16	**1c**	**3a**	40	20	83	>99:1

[a] All reactions were carried out with 2,3-disubstituted quinoxalines (0.10 mmol), borane (10 mol%), and H_2 (20 bar) in toluene (0.5 mL) unless otherwise noted. [b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] 5 mol% of borane was used.

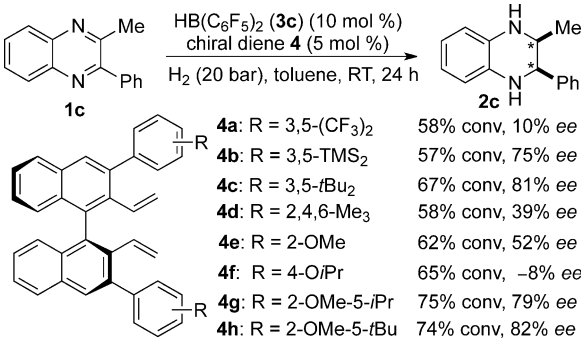


Scheme 2. Stereoselective hydrogenation of 2,3-disubstituted quinoxalines: a) dialkylquinoxalines, **3b** (5 mol%), 60°C; b) diarylquinoxalines, **3a** (10 mol%), 100°C; c) 2-aryl-3-alkylquinoxalines, **3a** (10 mol%), 60°C.

result without loss of any reactivity and selectivity (entry 7). For the hydrogenation of 2,3-diphenylquinoxaline (**1b**), *cis*-tetrahydroquinoxaline (**2b**) was obtained as an exclusive product using the boranes **3a–d**. The borane **3a** gave a quantitative conversion, but **3c**[13] and **3d**[15c] gave a much lower conversion (entries 8–13). The borane **3a** was also an efficient catalyst for the hydrogenation of 2-methyl-3-phenylquinoxaline (**1c**), and a quantitative conversion with 98:2 d.r. was afforded at 60°C (entries 14 and 15). Further decreasing the temperature to 40°C gave better *cis* selectivity but a lower reactivity (entry 16).

With the optimal reaction conditions in hand, a variety of 2,3-disubstituted quinoxalines were subjected to this metal-free hydrogenation using either **3a** or **3b** as the catalyst. As shown in Scheme 2, different types of substituents at the 2- and 3-positions of quinoxalines are all well tolerated to give the desired products **2a–i** in 91–97% yields with d.r. values of 98:2–>99:1. Moreover, 2-phenyl-3-methylquinoxalines bearing different substituents were also effective substrates for furnishing the products **2j–s** in 80–99% yields with d.r. values of 92:8–99:1.

After achieving the highly *cis*-selective hydrogenation of 2,3-disubstituted quinoxalines, its asymmetric version was next investigated using chiral borane catalysts generated in situ by the hydroboration of chiral dienes with the borane **3c**. As shown in Scheme 3, several chiral dienes (**4a–h**)[16] were subjected to the asymmetric hydrogenation of the quinoxaline **1c** at room temperature. It was found that all these reactions can furnish *cis*-**2c** as the exclusive product, but substituents at the 3,3′-positions of the binaphthyl framework



Scheme 3. Evaluation of chiral dienes for hydrogenation of the quinoxaline **1c**.

had an influence on the enantioselectivies. The chiral diene **4h** gave a better *ee* value.

The reaction conditions were further optimized. As shown in Table 2, solvents were found to have an obvious impact on both reactivity and enatioselectivity (entries 1–7). Using *n*-hexane as solvent, *cis*-**2c** can be obtained in 89% conversion with 88% *ee* (entry 6). Moreover, the reaction concentration can also affect the enantioselectivity, and 89% *ee* was obtained at a concentration of 0.067 M (entries 8–11). Reducing the catalyst loading to 5 mol% resulted in low conversion and *ee* value (entry 12).

A variety of 2,3-disubstituted quinoxalines were subsequently examined for the metal-free asymmetric hydrogenation in *n*-hexane under H_2 (20 bar) using **4h** (5 mol%) and

Table 2: Optimization of the asymmetric hydrogenation.[a]

Entry	Solvent	Conc [M]	Conv [%][b]	*cis*/*trans*[c]	*Ee* [%][c]
1	toluene	0.1	74	>99:1	82
2	mesitylene	0.1	60	95:5	80
3	benzene	0.1	87	>99:1	84
4	CH_2Cl_2	0.1	91	>99:1	84
5	Et_2O	0.1	trace	–	–
6	*n*-hexane	0.1	89	>99:1	88
7	cyclohexane	0.1	56	>99:1	77
8	*n*-hexane	0.4	91	>99:1	80
9	*n*-hexane	0.2	89	>99:1	82
10	*n*-hexane	0.067	87	>99:1	89
11	*n*-hexane	0.05	82	>99:1	87
12[d]	*n*-hexane	0.5	45	>99:1	76

[a] All reactions were carried out with **1c** (0.10 mmol), $HB(C_6F_5)_2$ (10 mol%), chiral diene **4h** (5 mol%), and H_2 (20 bar) at room temperature. [b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] Determined by HPLC using a Chiralcel OD-H column. [d] 5 mol% of catalyst.

$HB(C_6F_5)_2$ (10 mol%). As shown in Table 3, all these reactions proceeded efficiently to furnish the desired tetrahydroquinoxaline products in 71–99% yields with d.r. values of 98:2–>99:1, and 67–96% *ee* (entries 1–14). The substituents at the 2,3-positions of the quinoxalines influenced the enantioselectivity (entries 1–4). When 2-phenyl-3,5-dimethylquinoxaline was employed as a substrate, only 67% *ee* was obtained (entry 5). In contrast, substituents at the 6-, 7-, and 8-positions gave much higher *ee* values (entries 6–14). The absolute configuration of the compound **2l** was determined to be (2*R*,3*S*) by its X-ray structure (Figure 1).[17] However, 2,3-dialkyl- and diaryl-substituted quinoxalines were not suitable

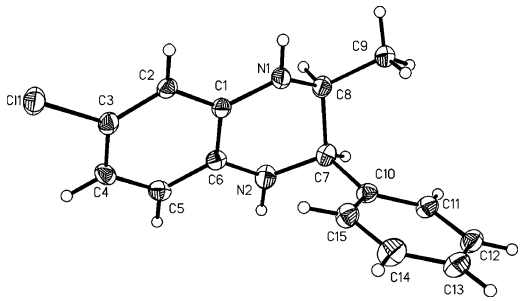
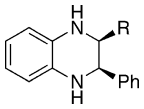
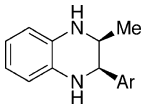
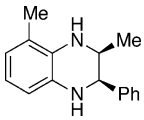
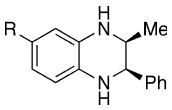
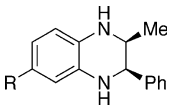
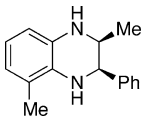
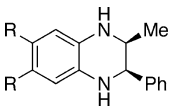
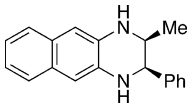


Figure 1. X-ray structure of the compound (2*R*,3*S*)-**2l**. Thermal ellipsoids shown at 30% probability.

substrates for the current catalytic systems, and still awaits further effort on the search for more efficient chiral catalysts. Moreover, the asymmetric hydrogenation can be carried out on a relatively large scale. For example, 0.8977 grams of the tetrahydroquinoxaline **2m** was obtained in 89% yield with greater than 99:1 d.r. and 90% *ee* (Scheme 4).

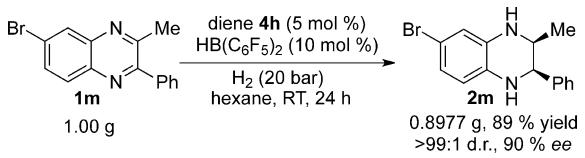
In summary, a metal-free *cis*-selective hydrogenation of a broad range of 2,3-disubstituted quinoxalines using borane catalysts has been successfully realized to furnish 2,3-disubstituted 1,2,3,4-tetrahydroquinoxalines in 80–99% yields with d.r. values of 92:8–>99:1. Significantly, the highly desirable asymmetric reaction using chiral borane catalysts generated

Table 3: Asymmetric hydrogenation of 2,3-disubstituted quinoxalines.[a]

Entry	Product (**2**)	Yield [%][b]	*cis*/*trans*[c]	*ee* [%][c]
				
1	**2c**: R = Me	82	>99:1	89
2	**2g**: R = Et	71	>99:1	77
				
3	**2h**: Ar = 4-MeC_6H_4	91	>99:1	96
4[d]	**2i**: Ar = 3-BrC_6H_4	91	98:2	81
				
5	**2j**	72	99:1	67
				
6	**2k**: R = OMe	87	>99:1	92
7	**2l**: R = Cl	85	>99:1	94
8	**2m**: R = Br	85	>99:1	90
				
9[d]	**2n**: R = Cl	75	98:2	96
10[d]	**2o**: R = Br	85	98:2	86
				
11[d]	**2p**	93	>99:1	77
				
12[d]	**2q**: R = Cl	87	99:1	86
13	**2r**: R = Me	89	>99:1	92
				
14	**2s**	99	>99:1	92

[a] All reactions were carried out with 2,3-disubstituted quinoxaline (0.25 mmol), $HB(C_6F_5)_2$ (10 mol%), chiral diene **4h** (5 mol%), and H_2 (20 bar), in *n*-hexane (3.7 mL) at room temperature for 24 h unless other noted. [b] Yield of isolated product. [c] Determined by HPLC using a Chiralcel OD-H column, except for that in entry 12 for which a Chiralpak IC column was used). [d] At 50°C.

by the in situ hydroboration of the chiral diene **4h** with $HB(C_6F_5)_2$ under mild reaction conditions has been achieved to furnish optically active products with up to 96% *ee*. Further



Scheme 4. Asymmetric hydrogenation on a gram scale.

study for efficient catalysts and their application for the metal-free hydrogenation of other unsaturated compounds is underway in our laboratory.

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[17] CCDC 1026035 (**21**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

