



Literature presentation

Chiral Boron-Bridged Bisoxazolines : Readily Available Anionic Ligands for Asymmetric Catalysis

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Angew. Chem. Int. Ed. 2005, 44, 4888-4891

Hu, Gang

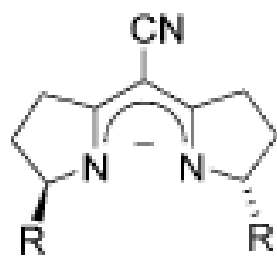
Department of Chemistry

Michigan State University

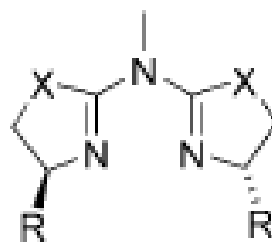
September 8, 2005



Analogues of Semicorrins

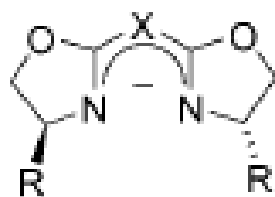


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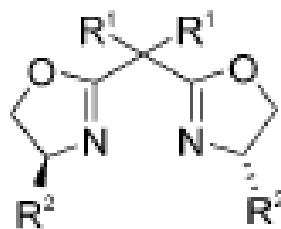
2: X = CH₂

3: X = O



4: X = CH

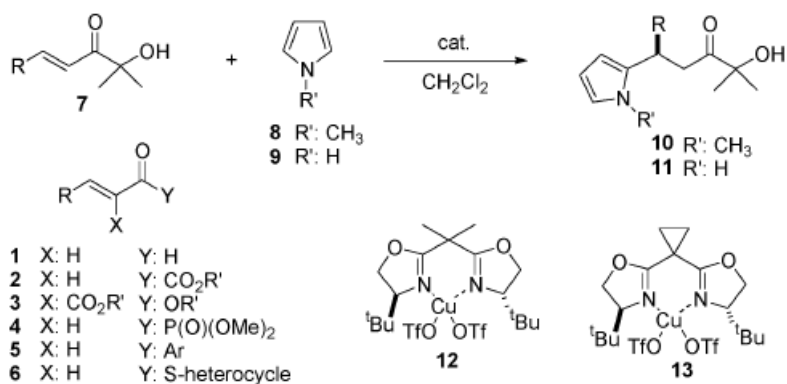
5: X = N



6



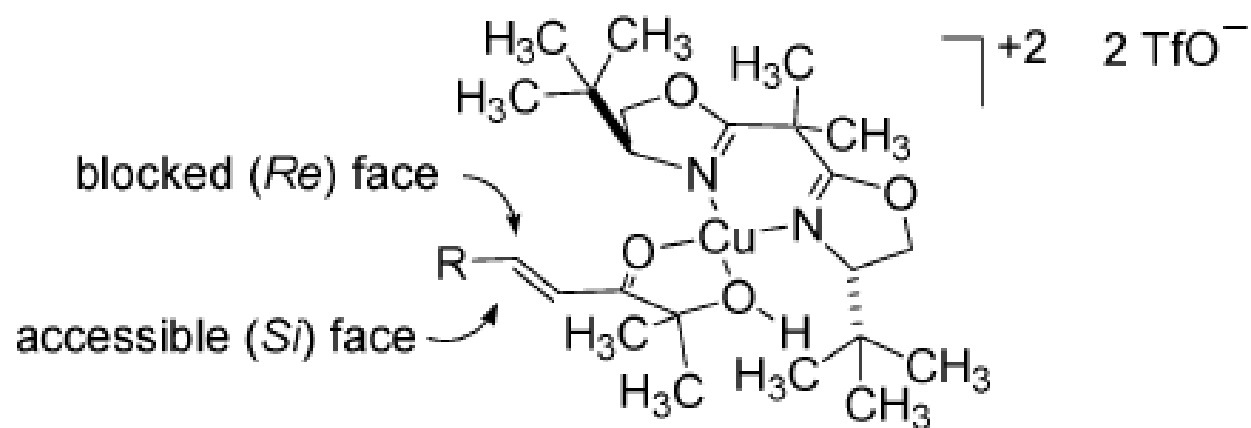
Recent application of bisoxazolines (box) 6



enone 7	R	T_1 , °C	time, h	product	yield, % ^b	ee, % ^c
a	PhCH ₂ CH ₂	25	2	10a	86	92
		25	2	10a	80	91 ^d
		-20	2	11a	83	90
b	CH ₃ (CH ₂) ₅	-20	6	10b	82	96
		-20	0.5	11b	87	91 ^e
c	(CH ₃) ₂ CH	0	20	10c	86	95
d	<i>c</i> -C ₆ H ₁₁	25	4	10d	84	97 ^f
e	CH ₃ CH ₂	-20	18	10e	88	94
f	(CH ₃) ₂ CHCH ₂	-20	12	10f	86	94 ^f
g	Ph	25	24	10g	95	68 ^d

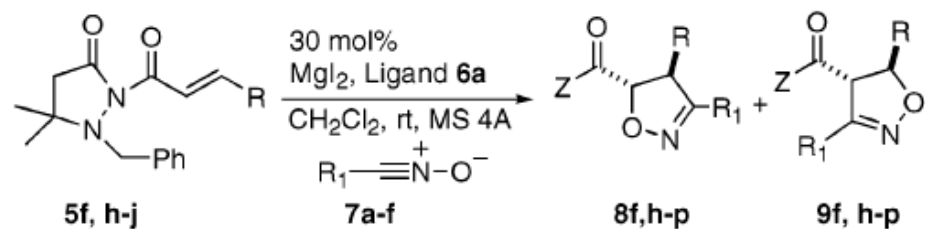


Stereochemical model





Intermolecular Carben Transfer

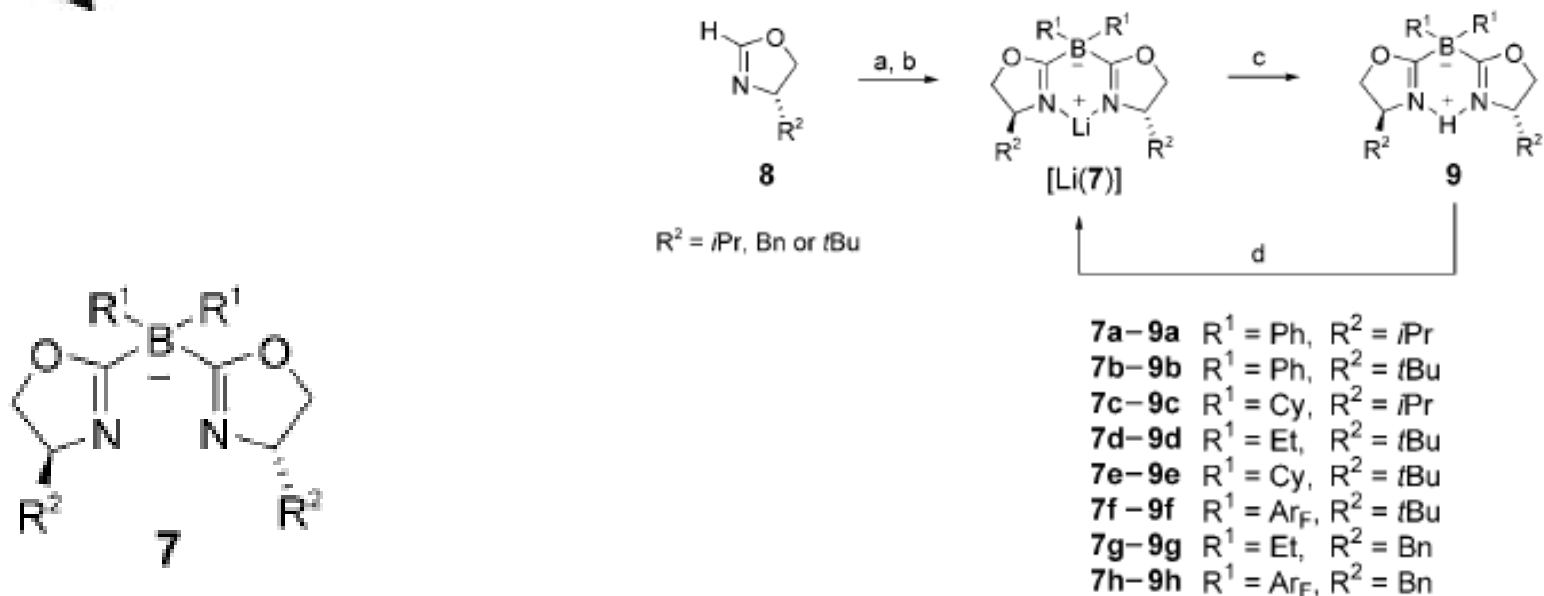


ent	sub. R	nitrile oxide R ₁	prod	yld, % ^a	8:9 ^b	8 ee, % ^c
1	R = Me 5f	7a	8f, 9f	84	99:1	99
2	R = Et 5h	7a	8h, 9h	86	99:1	99
3	R = Ph 5i	7a	8i, 9i	85	99:1	99
4	R = CO ₂ Et 5j	7a	8j, 9j	75	99:1	99
5	R = Me 5f	R ₁ = Ph 7b	8k, 9k	75	99:1	99
6	R = Me 5f	R ₁ = 2-Cl-Ph 7c	8l, 9l	78	99:1	86
7	R = Me 5f	R ₁ = 4-Cl-Ph 7d	8m, 9m	70	99:1	96
8	R = Me 5f	R ₁ = 4-MeOPh 7e	8n, 9n	61	10:1	99
9	R = Me 5f	R ₁ = <i>t</i> -Bu 7f	8o, 9o	44	99:1	92
10	R = Me 5f	R ₁ = <i>i</i> -Bu 7g	8p, 9p	63	33:1	79





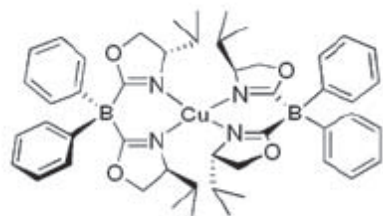
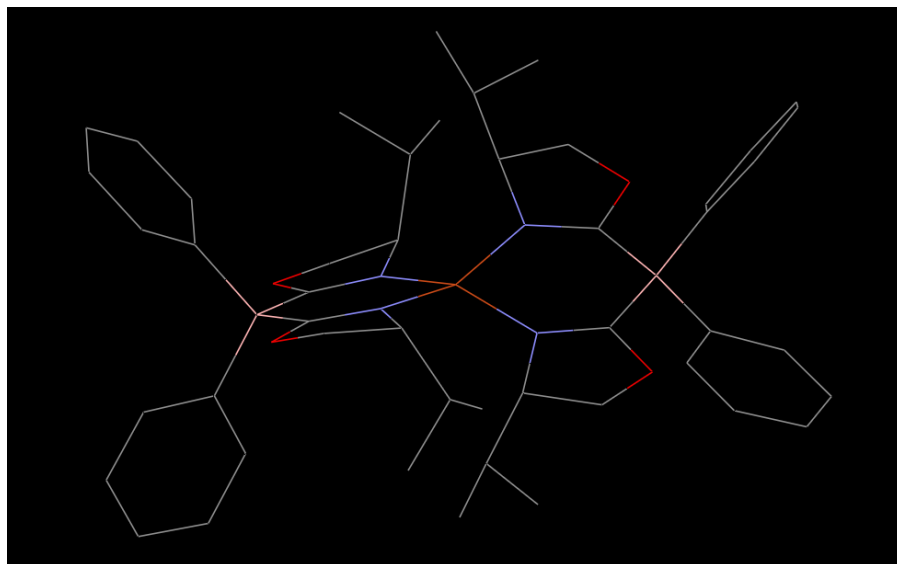
Borabox ligands developed



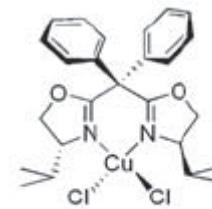
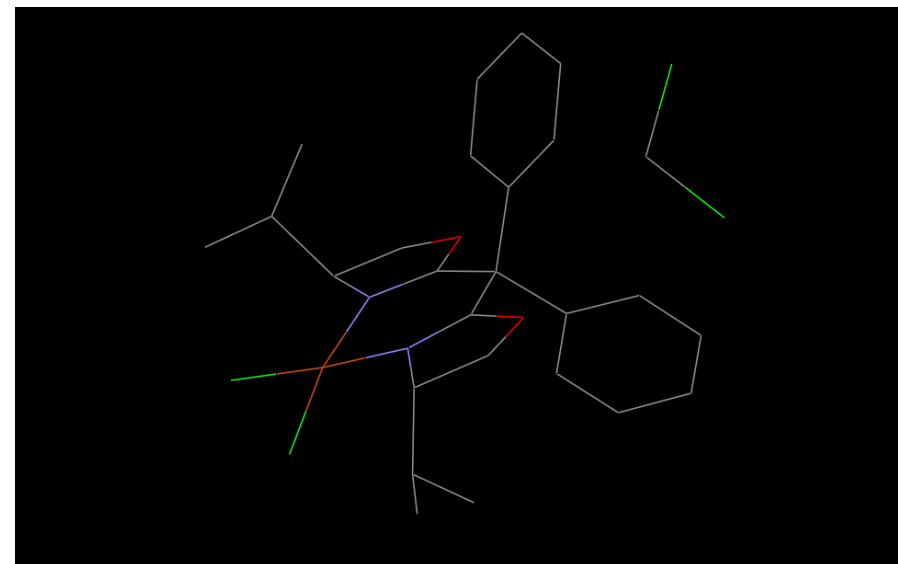
Scheme 1. Synthesis of borabox ligands as the lithium salts of **7a–f** (34–98%) or in their protonated form **9a–f** (44–89%). a) $tBuLi$, $-78^\circ C$, THF; b) $(R^1)_2BX$ ($X = Cl, Br$), toluene, $-78^\circ C$; c) hexanes/ $EtOAc/Et_3N, SiO_2$; d) $nBuLi$, THF, $0^\circ C$. $Ar_F = 3,5$ -bis(trifluoromethyl)-phenyl, Cy = cyclohexyl, Bn = benzyl.



X-Ray structure of borobox-Cu complex



[Cu(7a)₂]



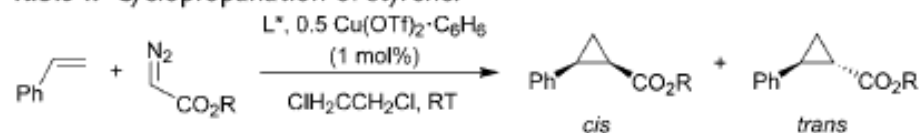
[Cu(6a)]

Barluenga, J.; Rubio, E.; Lopez, J. A.; Tomas, M. *Angew. Chem. Int. Ed.* **1999**, 38(8), 1091

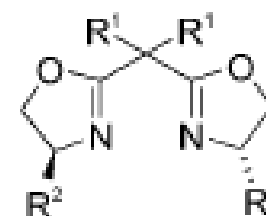


Test of these borobox ligands in the cyclopropanation reactions

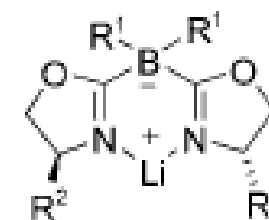
Table 1: Cyclopropanation of styrene.



Entry	Ligand	R ¹	R ²	Diazo ester (R)	<i>cis</i> / <i>trans</i>	<i>cis</i> ^[a] <i>ee</i> [%]	<i>trans</i> ^[a] <i>ee</i> [%]	Yield [%] ^[b] (<i>cis</i> + <i>trans</i>)
1	6a ^[c]	Ph	<i>i</i> Pr	Et	36:64	54	51	85
2	6b ^[d]	Ph	<i>t</i> Bu	Et	33:67	91	89	72
3	6d ^[d]	Me	<i>t</i> Bu	Et	27:73	97	99	77
4	7a	Ph	<i>i</i> Pr	Et	29:71	58	65	77
5	7b	Ph	<i>t</i> Bu	Et	30:70	66	70	84
6	7c	Cy	<i>i</i> Pr	Et	32:68	24	33	68
7	7d	Et	<i>t</i> Bu	Et	28:72	59	72	75
8	7e	Cy	<i>t</i> Bu	Et	28:72	78	66	79
9	7f	Ar _F	<i>t</i> Bu	Et	32:68	68	77	89
10	6b	Ph	<i>t</i> Bu	<i>t</i> Bu	21:79	93	90	70
11	6d ^[e]	Me	<i>t</i> Bu	<i>t</i> Bu	19:81	93	96	75
12	7b	Ph	<i>t</i> Bu	<i>t</i> Bu	15:85	77	67	77
13	7d	Et	<i>t</i> Bu	<i>t</i> Bu	13:87	76	73	65
14	7e	Cy	<i>t</i> Bu	<i>t</i> Bu	9:91	82	73	63
15	7f	Ar _F	<i>t</i> Bu	<i>t</i> Bu	17:83	86	92	65
16	6d ^[d]	Me	<i>t</i> Bu	BHT	4:96 ^[f]	–	99	85
17	7f	Ar _F	<i>t</i> Bu	BHT	1:99 ^[f]	–	98	89



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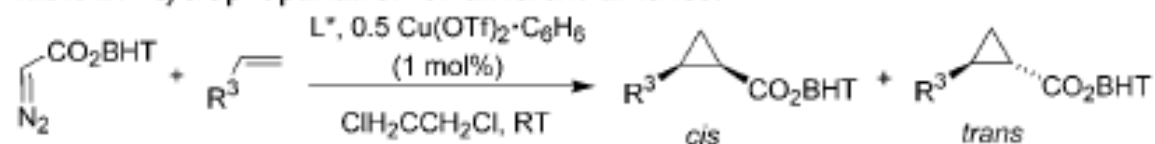


[Li(7)]



Cyclopropanation of different alkene

Table 2: Cyclopropanation of different alkenes.



Entry	Ligand	R ¹	R ²	R ³	<i>cis/trans</i> ^[a]	<i>trans</i> ^[b] <i>ee</i> [%]	Yield ^[c] [%] (<i>cis+trans</i>)
1	6 d	Me	<i>t</i> Bu	Ph	4:96	99	85
2	7 f	Ar _F	<i>t</i> Bu	Ph	1:99	98	89
3	6 d	Me	<i>t</i> Bu	<i>p</i> -MeOC ₆ H ₄	4:96	96	35 ^[d]
4	7 f	Ar _F	<i>t</i> Bu	<i>p</i> -MeOC ₆ H ₄	4:96	97	65 ^[d]
5	6 d	Me	<i>t</i> Bu	<i>p</i> -FC ₆ H ₄	4:96	99.4	89
6	7 f	Ar _F	<i>t</i> Bu	<i>p</i> -FC ₆ H ₄	1:99	99.5	91
7	6 d	Me	<i>t</i> Bu	PhCH ₂	7:93	99	ng ^[e]
8	7 f	Ar _F	<i>t</i> Bu	PhCH ₂	8:92	97	66
9	6 d	Me	<i>t</i> Bu	<i>n</i> -hexyl	2:98	99	51 ^[d]
10	7 f	Ar _F	<i>t</i> Bu	<i>n</i> -hexyl	1:99	95	68 ^[d]

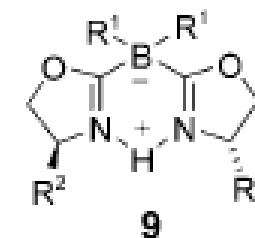
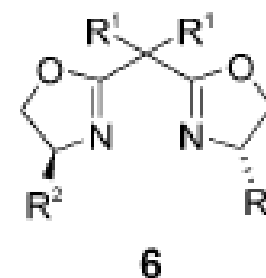
[a] Determined by ¹H NMR spectroscopic analysis. [b] Determined by HPLC (see the Supporting Information). [c] After chromatography; average of two runs. [d] Reaction time not optimized. [e] ng = not given; results taken from reference [11a].



Enantioselective monobenzoylation of *meso* 1,2-diols

Table 3: Enantioselective monobenzoylation of *meso* 1,2-diols.

Entry	Ligand	R ¹	R ²	<i>meso</i> 1,2-diol	Yield [%] ^[a]	<i>ee</i> [%] ^[b]
1	6c	Me	Bn		70	33 ^[c]
2	6e	Me	Ph		58	13
3	9g	Et	Bn		79	40
4	9h	Ar _F	Bn		73	76
5	6c	Me	Bn		74	85 ^[c]
6	6e	Me	Ph		62	22
7	9g	Et	Bn		75	47
8	9h	Ar _F	Bn		83	90
9	6c	Me	Bn		68	84 ^[c]
10	6e	Me	Ph		58	86
11	9g	Et	Bn		62	92
12	9h	Ar _F	Bn		65	94



[a] Average of two runs. [b] *ee* and absolute configuration values were determined by HPLC according to the literature data (see the Supporting Information). [c] The enantiomer of **6c** was used in this case and, therefore, a product of opposite configuration was obtained.