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ENANTIOSELECTIVE HYDROBORATIONS CATALYZED BY RHODIUM(+1) COMPLEXES

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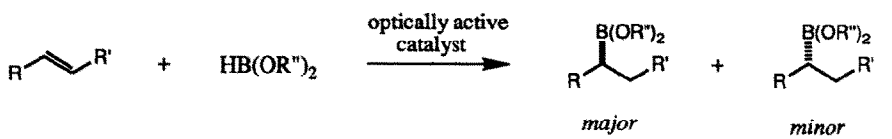
Abstract: *Enantioselective* hydroborations of alkenes **1** - **4** with catecholborane were performed via catalysis with complexes containing the chiral ligands **DIOP**, **BINAP**, **CHIRAPHOS**, **DIPAMP**, **BDPP**, **2-MeODIOP**, and **3-MeODIOP**. Alkenes **1** - **3** were also hydroborated with catecholborane derivatives **5** - **8** in the presence of Rh(+1)/**DIOP** catalysts. Trends in the observed optical purities are discussed.

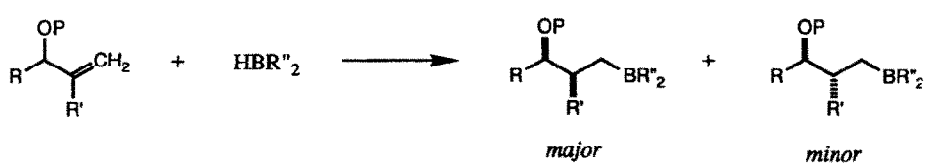
Three years ago two of us reported the first *enantioselective* hydroborations in which optically active rhodium catalysts were used to add the boron-hydride bond of catecholborane to prochiral alkenes with control of absolute stereochemistry.[1] This process is unique insofar as it is the only asymmetric hydroboration of alkenes which affords enantiomers directly, all other procedures give diastereomeric boranes via either substrate- or reagent-control.[2]

enantioselectivity in hydroborations



reagent-controlled diastereoselectivity in hydroborations (L* = chiral auxiliary)

substrate-controlled diastereoselectivity in hydroborations (P = protecting group)

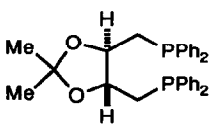


The more established methods for asymmetric hydroborations of prochiral alkenes, reactions which proceed via reagent-controlled diastereoselectivity, are not practical for all substrates; poor optical yields are obtained in some cases, e.g. for 1,1-disubstituted alkenes. Moreover, stoichiometric quantities of air- and water- sensitive reagents must be prepared for these transformations, and separation of by-products formed from the chiral auxiliaries can be problematic.[3]

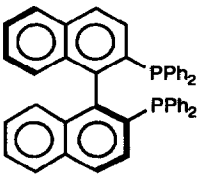
Enantioselective hydroborations of prochiral alkenes are mediated by catalytic quantities of optically active transition-metal catalysts, and the typical by-product, catechol, can be removed via partitioning with aqueous base. Highly enantioselective hydroborations would be an attractive alternative to methods which rely upon reagent-controlled diastereoselectivity. At present, however, enantiomeric excesses of over 95 % have only been obtained in catalyzed hydroborations of phenylethene (styrene) derivatives.[4,5] The challenge in this area is to understand the factors which control enantioselective hydroborations, and to use this knowledge to optimize the optical yields obtained for other substrate types.[6,7]

This paper presents a systematic study of enantioselective hydroborations using readily available phosphine ligands (Figure 1)[8] and structurally diverse substrates. In the first phase of this research seven optically active ligands were used in catalyzed hydroborations of three (in some cases more) alkenes. Subsequent work focussed on the effect of the boron-hydride derivative on the enantioselectivity of the reaction. The primary objective of these experiments was to correlate trends in the data with catalyst type, and to explore effects of some obvious variables one might manipulate to obtain higher enantioselectivities.

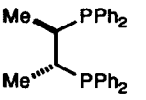
Figure 1. Chiral phosphine ligands which can be used in catalyzed hydroborations.



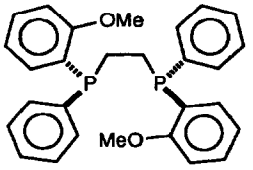
R,R-DIOP



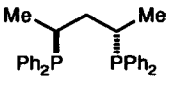
S-BINAP



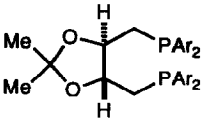
R,R-CHIRAPHOS



S,S-DIPAMP



S,S-BDPP



R,R-2-MeODIOP
Ar = 2-$MeOC_6H_4$

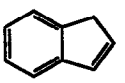
R,R-3-MeODIOP
Ar = 3-$MeOC_6H_4$

Enantioselective Hydroborations Using Readily Available Bisphosphine Ligands

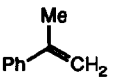
Norbornene, indene, and 2-phenylpropene were selected as substrates since these materials have different structural features. In some cases 2,3,3-trimethylbut-1-ene was also screened, but it reacts slowly, presumably due to steric hindrance, hence it was not convenient to test this substrate with all the ligands. Temperature effects were examined in a few examples. In most cases, however, the reaction components were mixed at -78 °C, warmed to -25 °C, and allowed to stand at this temperature; if no appreciable reaction occurred within 24 h, the reaction mixture was allowed to stand at -5 °C until the reaction was complete (TLC). Optical purities of the products were measured via HPLC with a chiral column, NMR analyses of 2-methoxy-3,3,3-trifluoropropanoate derivatives,[9] or NMR/chiral shift experiments. The solvent employed was usually THF but a few reactions were run using benzene or toluene for comparison. Table 1 lists data for hydroborations of substrates **1** - **4** in the presence of the ligands shown in Figure 1.

substrates

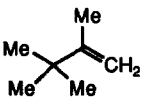
1



2

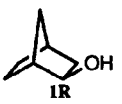


3

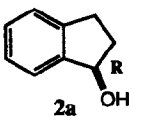


4

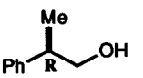
product alcohols



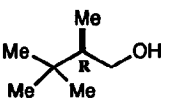
1a



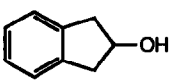
2a



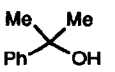
3a



4a



2b

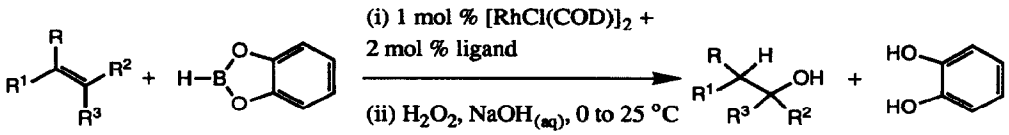


3b

In general, optical yields in these reactions increase as the reaction temperature is decreased (c.f. hydroborations of norbornene with **DIOP**- and **2-MeODIOP**-based systems). Solvent changes between THF, benzene, and toluene have no profound effect.

Comparison of results obtained indicates **R,R-DIOP** is slightly more effective than **BINAP**; this is perhaps surprising because the binapthyl ligand is superior in many other reactions. The results with **CHIRAPHOS** and **DIPAMP** are relatively poor implying five-membered ring chelate structures are not favored for asymmetric induction in this process. The ligand **BDPP** is structurally analogous to **CHIRAPHOS** except that it forms six-membered ring chelates; catalysts based upon this give higher optical yields for each of the substrates **1** - **3**. In view of these results, **2-MeODIOP**[10,11] and **3-MeODIOP**[11] were also screened in an attempt to improve on the selectivities obtained with the parent ligand **DIOP**. The *ortho*-substituted ligand **(2-MeODIOP)** was generally more effective giving 82 % e.e. with norbornene, the maximum observed in this series.

Table 1. Enantioselective Hydroborations[a] Using Readily Available Chiral Phosphine Ligands.



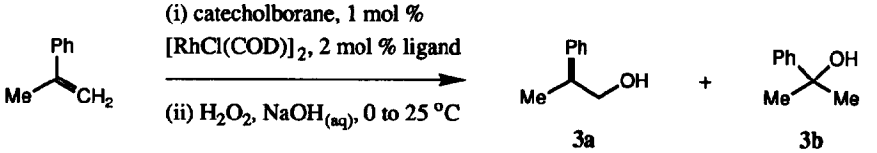
ligand	substrate	solvent	temp. (°C)	product	e.e. (%)	method to determine e.e.
R,R-DIOP	**1**	C_6H_6[b]	40	**1R-1a**	23	MPTA[c]
	1	C_6H_6	5	**1R-1a**	31	MPTA
	1	THF	-5	**1R-1a**	49	$Eu(hfc)_3$[d]
	1	THF	-25	**1R-1a**	60	$Eu(hfc)_3$
	1	THF	-40	**1R-1a**	55	MPTA
	2	MePh[e]	-30	**S-2a**	74	MPTA
	3	THF	-5	**R-3a**	27	$Eu(hfc)_3$
	4	THF	25	**R-4a**	53	$Eu(hfc)_3$
	4	THF	-5	**R-4a**	69	$Eu(hfc)_3$
R-BINAP	**1**	C_6H_6[f]	5	**1R-1a**	43	$Eu(hfc)_3$
	1	THF[f]	-25	**1R-1a**	65	$Eu(hfc)_3$
	2	DME[g]	-40	**2a**	19	$Eu(hfc)_3$
	3	THF	-25	**S-3a**	25	$Eu(hfc)_3$
	4	THF	-5	-	0	$Eu(hfc)_3$
S,S-CHIRAPHOS	**1**	THF	-25	**1S-1a**	4	$Eu(hfc)_3$
	2	THF	-25	-[h]	0	HPLC[i]
	3	THF	-25	**R-3a**	25	$Eu(hfc)_3$
	4	THF	-5	-	0	$Eu(hfc)_3$
R,R-DIPAMP	**1**	THF	-25	-	0	$Eu(hfc)_3$
	2	THF	-5	**S-2a**[j]	7	HPLC
	3	THF	-5	-	0	$Eu(hfc)_3$
S,S-BDPP	**1**	THF	-25	**1R-1a**	80	$Eu(hfc)_3$
	2	THF	-5	**S-2a**	4	HPLC
	3	THF	-5	**R-3a**	27	$Eu(hfc)_3$
R,R-2-MeODIOP	**1**	THF	25	**1R-1a**	76	$Eu(hfc)_3$
	1	THF	-25	**1R-1a**	82	$Eu(hfc)_3$
	1	MePh	-25	**1R-1a**	82	$Eu(hfc)_3$
	2	MePh	-25	**S-2a**	59	$Eu(hfc)_3$
	3	THF	25	**R-3a**	15	$Eu(hfc)_3$
	4	MePh	-5	-	0	$Eu(hfc)_3$
R,R-3-MeODIOP	**1**	THF	-25	**1R-1a**	69	$Eu(hfc)_3$
	2	THF	-25	**S-2a**	55	HPLC
	3	THF	-5	**3b**[k]	-	-

[a] Catalyst is 1 mol % $[RhCl(COD)]_2$. + 2 mol % ligand unless otherwise noted. [b] Catalyst is 2.5 mol % $[RhCl(COD)]_2$. + 5 mol % ligand. [c] Methoxy(trifluoromethyl)phenylacetic acid derivative. [d] Chiral shift NMR experiment. [e] Result from Suzuki and co-workers[6] using 1 mol % $[Rh(C_2H_4)_2Cl]_2$ + 2 mol % ligand. [f] Catalyst is 0.5 mol % $[RhCl(COD)]_2$. + 1 mol % ligand. [g] Result from Dai and co-workers[5] using 2 mol % of $[RhCl(COD)]_2$ with ligand (mol % of ligand not specified). [h] 1-Indanol (**2a**) and 2-indanol (**2b**) were formed in a ratio of 1:1. [i] Chiralcel OB column from Daicel Industries. [j] 1-Indanol (**2a**) and 2-indanol (**2b**) were formed in a ratio of 2:1. [k] Less than 20 % of the primary alcohol is formed, see Table 2.

Throughout, norbornene (**1**) seems particularly amenable to asymmetric hydroboration. This substrate reacts relatively fast, the hydroboration processes are generally complete within 2 h at -25 °C. It may be significant that chiral induction in reactions of norbornene arises because the ends of the alkene linkage are enantiotopic, not via enantioface selectivity as for substrates **2** - **4**. Enantioselectivities obtained for indene (**2**) vary widely with the nature of the chiral ligand. High optical yields are obtained in hydroborations of this substrate using **DIOP**-based catalysts, whereas trivial induction is observed when a **BDPP**-based system is used, *even though this same system gives high optical yields with norbornene (1)*. The widest variations of this kind are observed for 2,3,3-trimethylbut-1-ene (**4**); this substrate gives 69 % e.e. with **DIOP** but no optical induction at all with the *ortho*-substituted analogue, **2-MeODIOP**. Again this is in contrast with norbornene which gives good induction with **DIOP**, but even better optical yields with **2-MeODIOP**.

Analysis of the product mixtures from the catalyzed hydroborations of 2-phenylpropene revealed significant, and in some cases predominant, formation of tertiary alcohols (Table 2). Formation of secondary alcohols in the hydroboration of phenylethene has been reported by others,[4,5] selective formation of tertiary alcohols in preference to primary ones is even more remarkable. We[12] and others[5] have observed the ratio of secondary to primary alcohol in catalyzed hydroborations of phenylethene is dependant upon the concentration and nature of phosphine ligands present. Similar considerations seem to be applicable to catalyzed hydroborations of 2-phenylpropene (**3**); ratios of primary to tertiary alcohol products **3a**:**3b** are dependent upon the phosphine used. Data given in Table 2 indicates no correlation between chelate-ring size and product distribution; the exact features which govern formation of tertiary alcohols remain open for investigation. We are currently examining enantioselective hydroborations that give chiral tertiary alcohols.

Table 2. Regiochemistry of Enantioselective Hydroborations of 2-Phenylpropene (**3**).



3a **3b**

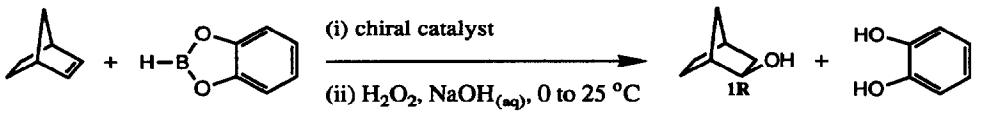
entry	ligand	ratio **3a**:**3b**[a]	e.e. of **3a** (%)[b]
1	**R,R-DIOP**	90:10	27
2	**R-BINAP**	85:15	25
3	**S,S-CHIRAPHOS**	>95:5	25
4	**R,R-DIPAMP**	85:15	0
5	**S,S-BDPP**	48:52	27
6	**3-MeODIOP**	19:81	n.d.

[a] .Determined via ^{1}H NMR analyses. [b] See Table 1 for method of e.e. determination.

Other experiments (Table 3) were performed to test the effect of different catalyst systems based upon the same ligand. The first two entries in Table 3 indicate cationic catalysts may be superior to the corresponding neutral systems at comparable reaction temperatures (c.f. Table 1, first three entries). It may be important that the [RhCl(COD)]$_2$/**DIOP**/NaBPh$_4$ system could contain zwitterionic complexes with one phenyl of the BPh$_4^-$

the [RhCl(COD)]$_2$/**DIOP**/NaBPh$_4$ system could contain zwitterionic complexes with one phenyl of the BPh$_4^-$ entity complexed.[13,14] The results indicated in Table 3 for **BINAP**- and **2-MeODIOP**-based systems indicate cationic catalysts formed from these ligands are comparable, or slightly inferior to, the corresponding neutral systems.

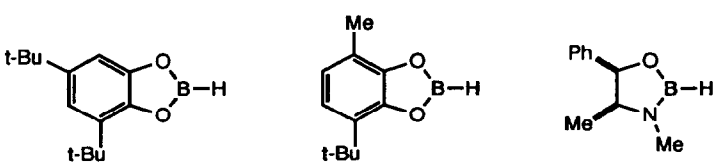
Table 3. Enantioselective Hydroborations Using Alternative Catalyst Systems.



catalyst system	solvent	temp. (°C)	product configuration	e.e. (%)	method to determine e.e.
1 mol % [RhCl(COD)]$_2$, 2 mol % **R,R-DIOP**, 4 mol % NaBPh$_4$	THF	25	**1R**	53	Eu(hfc)$_3$
1 mol % [RhCl(COD)]$_2$, 2 mol % **R,R-DIOP**, 4 mol % NaBPh$_4$	THF	-25	**1R**	54	Eu(hfc)$_3$
1 mol % [RhCl(COD)]$_2$, 2 mol % **R,R-DIOP**, 2 mol % AgBF$_4$	THF	-25	**1R**	59	Eu(hfc)$_3$
0.5 mol %, [Rh(COD)(**R,R-DIOP**)][BF$_4$]	C$_6$H$_6$	5	**1R**	48	MPTA
0.5 mol %, [Rh(COD)(**R-BINAP**)][BF$_4$]	C$_6$H$_6$	5	**1R**	46	Eu(hfc)$_3$
0.5 mol %, [Rh(COD)(**R-BINAP**)][BF$_4$]	THF	-25	**1R**	42	Eu(hfc)$_3$
1 mol % [RhCl(COD)]$_2$, 2 mol % **S,S-BDPP**, 2 mol % NaBPh$_4$	THF	-25	**1R**	52	Eu(hfc)$_3$
1 mol % [RhCl(COD)]$_2$, 2 mol % **R,R-2-MeODIOP**, 4 mol % NaBPh$_4$	THF	25	**1R**	65	Eu(hfc)$_3$

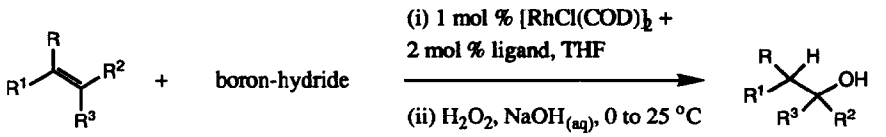
Enantioselective Hydroborations Using Boron-Hydrides Other Than Catecholborane

It is reasonable to assume that steric effects play a significant role in determining the sense and magnitude of asymmetric induction in catalyzed hydroboration reactions involving optically active ligands. Increasing the size of the boron-hydride component accentuates steric effects, hence compounds **5**,[15] **6**, and **7**[16] were screened (Table 4) to probe the effect of this change upon induction in catalyzed hydroborations.



5 **6** **7**

Table 4. Enantioselective Hydroborations Using Alternative Boron-Hydride Compounds.



boron-hydride	substrate	ligand	temp. (°C)	product	e.e. (%)	method to determine e.e.
5	**1**	**R,R-DIOP**	-25	**1R-1a**	18	$Eu(hfc)_3$
5	**2**	**R,R-DIOP**	-5	**2b**[a]	-	-
6	**1**	**R,R-DIOP**	-25	**1R-1a**	25	GC[a]
6	**2**	**R,R-DIOP**	-5	**S-2a**	30	HPLC
7	**1**	**R,R-DIOP**	25	**1S-1a**	19	$Eu(hfc)_3$
7	**1**	**S,S-DIOP**	25	**1R-1a**	16	$Eu(hfc)_3$
7	**1**	**S,S-CHIRAPHOS**	25	**1R-1a**	25	$Eu(hfc)_3$

[a] Estimated via GC analysis on a Cyclodex-B column; base-line resolution was not obtained.

In the event the highest enantiomeric excess obtained in this series was 30 %. The most surprising observation in this series of experiments was for the ephidrine derivatives 7; here the catalyst formed from **R,R-DIOP** gave the 1S-norbornene **(1a)** whereas catecholborane under the same conditions gave the 1R product. When **S,S-DIOP** was used in conjunction with reagent **7**, the sense of the asymmetric induction was opposite, i.e. the 1R-product was formed. Consequently , we conclude the ligand, not the ephidrine chirality, is the dominant feature in determining the outcome of the reaction, and the reversal of selectivity is a consequence of the structural properties of the hydroborating reagent. A recent report[7] has outlined similar observations for ephidrine-based oxazaborolidines. Further modifications of the boron-hydride source may prove to be beneficial to the development of asymmetric hydroborations, but the compounds examined here are clearly not ideal. Moreover, there were some practical problems associated with these reagents: the reactions were relatively slow, presumably due to increased hindrance, and the relatively hydrophobic phenolic residues were difficult to separate from the products via simple base extractions.

Conclusions

This work clearly shows enantioselective hydroborations of alkenes are possible; chiral induction obtained depends upon substrate structure, ligand type, and, to a lesser extent, catalyst type (i.e. neutral or cationic rhodium complexes). Better optical yields are obtained at lower temperatures.

None of the seven ligands tested here give uniformly good results with respect to asymmetric synthesis, but the combined data provides pointers to ligand designs that may be more successful. Ligands that give five-

membered chelate rings (assuming of course the catalyst has only one metal center per molecule) do not seem to be favorable for good chiral induction in these reactions. The cheap, readily available, tartrate-based ligand **DIOP** is often as effective as **BINAP**,[17] a much less accessible compound. Ligands which are simple modifications of **DIOP**, here **2-MeODIOP** and **3-MeODIOP**, may provide some surprisingly good results; more work is required to understand the subtle stereoelectronic features which constitute an effective ligand for these purposes.

Experimental

General Procedures. High field NMR spectra were recorded on a Bruker AF300 or a Bruker AC250. ^1H chemical shifts are reported in δ ppm relative to $CHCl_3$ (7.25 ppm), ^{13}C chemical shifts are reported relative to the central peak of $CDCl_3$ (77.10 ppm), ^{11}B chemical shifts are reported relative to $BF_3.Et_2O$. Low resolution (EI) mass spectra were determined on a Finnigan 3300 mass spectrometer. HPLC was performed on a Rainin Rabbit HP using a Chiralcel OB column from Daicel Chemical Industries. Gas chromatography was carried out on a Shimadzu GC9A using a Cyclodex-B capillary column from J&W Scientific. Thin layer chromatography was performed on silica gel 60 F_{254} plates from Whatman. Flash chromatography was performed on SP Silica Gel 60 (230-400 mesh ASTM). Tetrahydrofuran, benzene and toluene was distilled immediately before use from sodium benzophenone ketal. Catecholborane was purchased from Aldrich Chemical Co. and distilled under reduced pressure before use, (4S,5R)-3,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine (**7**)[16] and 4,6-di-t-butyl-1,3,2-benzodioxaborole (**5**)[15] were prepared according to literature procedures; **R-BINAP** and **S,S-CHIRAPHOS** were purchased from Aldrich, **S,S-BDPP** was purchased from Strem Chemicals and **R,R-DIOP** was prepared according to a literature procedure.[18] **3-MeO-(R,R)-DIOP**[11] was prepared analogous to a published procedure for **2-MeO-(R,R)-DIOP**.[10,11] Organic solutions were dried over anhydrous magnesium sulfate.

General Procedure for Catalyzed Hydroboration. A Schlenk tube charged with a catalytic amount of $[Rh(COD)Cl]_2$ and chiral phosphine (1:2) was three times evacuated/flushed with N_2. Solvent (2 mL) was added, followed by 1 mmol of substrate in 2 mL of solvent. The yellow solution was cooled to -78 °C, stirred for 10 min, and 2 equiv. of neat borane was added. The reaction mixture was stirred at this temperature for 30 min and then stored at a constant temperature (see Tables). The reaction was followed by TLC and upon completion of the reaction (typical reaction times at -25 °C: for substrate **1**, 6 h; **2**, 3 d; and, **3**, 2 d), 1 mL of ethanol was added at 0 °C followed by 1.7 mL of 3 M NaOH solution and 1 mL of 30% H_2O_2. The mixture was stirred for 6 h at 20 °C and then diluted with 10 mL of 1 M NaOH solution. Extraction with diethyl ether (3 x 75 mL), washing of the combined organic fractions with 1 M NaOH solution (50 mL), water (50 mL) and saturated NaCl solution (50 mL) and evaporating the solvent after drying provided the crude products. Analyses of the crude reaction mixtures indicated quantitative formation of the products in >95 % purity; the optical purities of the crude products were analyzed without further purification.

Synthesis of 4-t-Butyl-7-methyl-1,3,2-benzodioxaborole (6). The title compound was prepared following the method used for benzodioxaborole (catecholborane). A solution of 3-t-butyl-6-methylcatechol (4 g, 22 mmol) in 30 mL of THF was added under argon at 0 °C to 23 mL of a 1.0 M solution of BH_3 in THF. The reaction mixture was stirred for 2 h at this temperature, then the THF was distilled off under Ar. The remaining brown oil was distilled under vacuum (0.3 Torr, b.p. 68 °C) yielding a colorless oil. ^1H NMR (250

MHz, $CDCl_3$) δ 6.83-6.95 (m, 2H), 2.37 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 146.29 (C), 145.09 (C), 133.86 (C), 123.86 (CH), 120.79 (C), 119.57 (CH), 34.04 (C), 29.82 (CH_3), 14.45 (CH_3); ^{11}B NMR (96.3 MHz, $CDCl_3$) δ 28.55 (br d, J_{BH} = 235 Hz); MS (EI) M^+ 190 (22), 175 (100); Anal.for $C_{11}H_{15}O_2B$: Calcd: C, 69.52 % ; H, 7.95 %. Found: C, 69.66 %; H, 7.87 %.

Catalyzed Hydroborations Using 4,6-Di-t-butyl-1,3,2-benzodioxaborole (5) and 4-t-Butyl-7-methyl-1,3,2-benzodioxaborole (6). The general procedure for catalyzed hydroboration as described above was followed. Typical reaction times: for substrate **1**, 6 h at -25 °C; **2**, 9 d at -5 °C. Unfortunately it was not possible to remove the catechol derivatives that are formed during the oxidation by simple alkaline work-up, hence the crude products were purified via flash chromatography.[19]

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