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pseudo Enantiomeric Carbohydrate Olefin Ligands – Case Study and Application in Kinetic Resolution in Rhodium(I)-Catalysed 1,4-Addition

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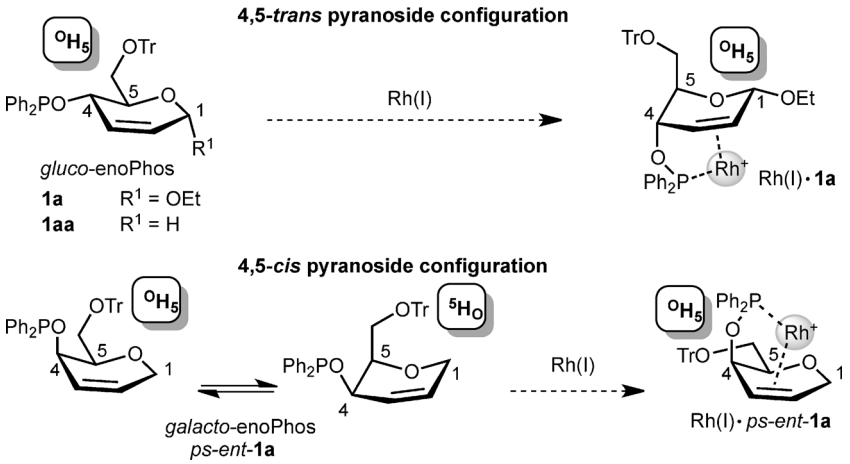
Abstract: In order to investigate significant differences in asymmetric induction for *pseudo* enantiomeric carbohydrate olefin ligands in rhodium(I)-catalysed 1,4-addition reactions, we designed a set of new olefin ligands differing in relative configuration and pyranoside conformation. With these, we have successfully elucidated structural requirements for metal binding and also identified an improved alternative for one *pseudo* enantiomer. Furthermore, we report the efficient kinetic resolution of a racemic 4-hydroxycyclopentenone derivative by 1,4-addition.

Keywords: asymmetric catalysis; carbohydrates; conjugate addition; kinetic resolution; ligand design

Due to the increasing demand for chiral building blocks in natural product and medicinal chemistry, the design of new chiral ligands for asymmetric metal catalysis is an active research field. Chiral olefin ligands,[1] introduced independently by Hayashi[2] and Carreira,[3] are the ligands of choice for rhodium(I)-mediated 1,4-additions of boronic acids to enones.[4]

Carbohydrates are attractive, inexpensive starting materials for the design of novel ligands.[5] With *gluco*-enoPhos (**1a**, **1aa**)[6] and *galacto*-enoPhos (*ps-ent*-**1a**),[7] we have introduced a set of *pseudo* enantiomeric[8] olefin-phosphinite ligands derived from D-glucose and D-galactose (Scheme 1), giving 1,4-addition products in opposite configurations and typically above 90% ee. Significantly lower selectivity was observed for the *gluco*-ligands **1a** and **1aa** with bulky arylboronic and alkenylboronic acids, while high *ee*s were retained with *galacto*-ligand *ps-ent*-**1a**.[7] This finding prompted us to investigate the origin of the differing asymmetric induction exerted by **1a** and **1aa** on the one hand and *ps-ent*-**1a** on the other hand, as well as to develop an improved alternative to *gluco*-ligands **1a** and **1aa**.

An obvious explanation for the different efficiency of the *gluco*-ligands (**1a**, **1aa**) and *galacto*-ligand (*ps-*



Scheme 1. Ligands *gluco*-enoPhos (**1a** and **1aa**) and *galacto*-enoPhos (*ps-ent*-**1a**): proposed coordination to Rh(I).

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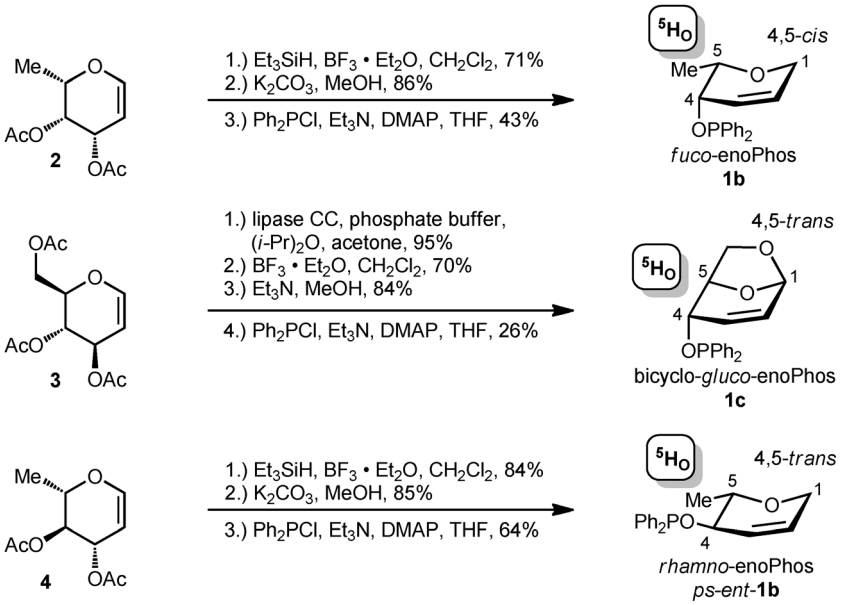

Scheme 2. Preparation of *fuco*-enoPhos (**1b**), bicyclo-*gluco*-enoPhos (**1c**) and *rhamno*-enoPhos (*ps-ent*-**1b**).

ent-**1a**) may lie in the relative configuration of their pyranose scaffolds – 4,5-*trans* for **1a** and **1aa** but 4,5-*cis* for *ps-ent*-**1a** – which will impact the preferred conformations of the free ligands (*cf.* Scheme 1). In general, 2,3-unsaturated pyranosides prefer half chair conformations $^{O}\mathbf{H}_{5}$ and $^{5}\mathbf{H}_{O}$, namely.[9] The ^{1}H NMR data for free **1a** (4,5-*trans*) prove a $^{O}\mathbf{H}_{5}$ conformation ($^{3}J_{4,5}=9.5$ Hz, diaxial H-4 and H-5) with equatorial 4-phosphinite and 5-trityloxymethyl groups.[6a] In free *ps-ent*-**1a** (4,5-*cis*) either the trityloxymethyl residue or the phosphinite is in an unfavourable axial position, thus neither $^{O}\mathbf{H}_{5}$ nor $^{5}\mathbf{H}_{O}$ is specially favoured. Bidentate coordination to Rh(I) requires proximity of olefin and phosphinite, and we reasoned that only conformers with axial phosphinites will effectively bind to Rh(I). Therefore, we expected a $^{5}\mathbf{H}_{O}$ conformation for **1a** in its rhodium complex with both trityloxymethyl group and phosphinite forced into unfavourable axial positions (Scheme 1). Ligand *ps-ent*-**1a** with no significant conformational preference in its free state can be expected to adopt a $^{O}\mathbf{H}_{5}$ conformation in its Rh(I) complex with the bulky trityloxymethyl residue in a favourable equatorial position (Scheme 1). These putative differences in the coordination mode may result in reduced complex stability and efficiency for **1a** and **1aa**. Bidentate coordination of **1a** was unequivocally established in ^{1}H and ^{31}P NMR studies of its Rh(I) complex,[6a] but overlapping signals in the ^{1}H NMR spectrum prevented elucidation of the pyranose conformation, and no single crystals of the complex could be obtained.

In order investigate the interplay of relative pyranoside configuration and conformation of our ligands in Rh(I) complexes, we prepared the new olefin ligands shown in Scheme 2. The 4,5-*cis* configured ligand *fuco*-enoPhos (**1b**) is closely related to *galacto*-ligand *ps-ent*-**1a** but lacking the trityloxy group. Ligand bicyclo-*gluco*-enoPhos (**1c**) is 4,5-*trans* configured but permanently locked in a $^{5}\mathbf{H}_{O}$ conformation with an axial phosphinite. Ligand *rhamno*-enoPhos (*ps-ent*-**1b**) is 4,5-*trans* configured but has no trityloxy group. Syntheses of the new ligands started from glycals **2**,[10] **3** and **4**[11] (Scheme 2) which are accessible from L-fucose and L-rhamnose (**2**, **4**) or commercially available (**3**). Ligands **1b** and *ps-ent*-**1b** were prepared *via* Ferrier rearrangement, deacetylation and phosphinite introduction, and for the synthesis of bicyclic **1c**, glucal **3** was subjected to 6-*O* deacetylation,[12] intramolecular Ferrier rearrangement[13] and phosphinite introduction.

NMR studies on 4,5-*trans* configured *rhamno*-enoPhos (*ps-ent*-**1b**) and its rhodium complex gave direct evidence for a major conformational change upon metal binding. After addition of a Rh(I) salt, *ps-ent*-**1b** showed all characteristics of bidentate coordination: the H-2/H-3 multiplet experienced an upfield shift in the ^{1}H NMR, while the ^{31}P NMR showed a downfield shift for the phosphinite signal, which was split into a doublet by ^{31}P,^{103}Rh coupling (Table 1). This is in accordance with our previous findings[6a] and Rh(I) complexes of other ligands.[14] The H-5 signal hardly shifted upon complexation, but the vicinal H-5/H-4 coupling changed drastically. Free *ps-ent*-**1b** adopts a $^{5}\mathbf{H}_{O}$ conformation with equatorial orientation of phosphinite and methyl group ($^{3}J_{4,5}=7.6$ Hz), but binding to Rh(I) induced a ring flip to the $^{O}\mathbf{H}_{5}$ conformer with diaxial orientation of the substituents ($^{3}J_{4,5}<1.0$ Hz) (Table 1). This finding verifies

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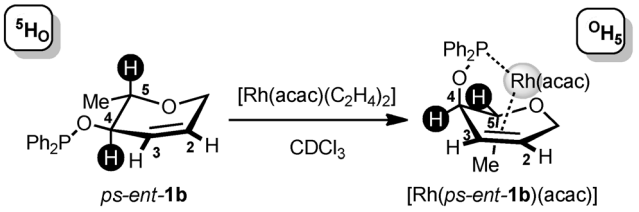
Table 1. NMR studies on *ps-ent*-**1b** and its Rh(I) complex.



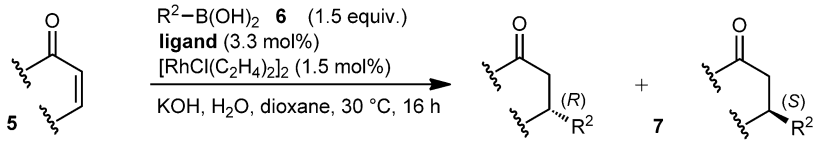
	ps-ent-**1b**		[Rh(*ps-ent*-**1b**)(acac)]	
	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]
H-2[a]	5.75–5.86	n.d.	4.46–4.55	n.d.
H-3[a]			4.08–4.15	n.d.
H-5[a]	3.59 (qd)	$^3J_{4,5}=7.6$, $^3J_{5,6}=6.2$	3.77 (q)	$^3J_{4,5}<1.0$, $^3J_{5,6}=6.2$
Ph_2P[b]	111.56 (s)	–	157.03 (d)	$^1J_{P,Rh}=194.9$

[a] From ^{1}H NMR (400 MHz).
[b] From ^{31}P NMR (162 MHz).

that complexation will trigger a ring flip to conformers with axial phosphinites, even if this forces other bulky residues into axial positions.

Next, we evaluated the new ligands in 1,4-addition reactions and compared the results to those obtained with *gluco*- and *galacto*-enoPhos[7] (Table 2). In the benchmark reaction with cyclohexenone (**5a**) and phenylboronic acid (**6a**), **1b**, **1c** and *ps-ent*-**1b** gave excellent *ee* values (entries 1, 2, and 4) just like **1a** and *ps-ent*-**1a** (entries 3 and 5). Therefore, the bulky trityloxy residue of **1a**, **1aa** and *ps-ent*-**1a**, is not a prerequisite for efficient asymmetric induction.[15] The direction of asymmetric induction is determined by the orientation of the 4-phosphinite relative to the plane of the pyranoside. Ligands with a phosphinite oriented below the pyranoside plane (*fuco*-ligand **1b**, *gluco*-ligands **1c** and **1a**) produced *R*-**7aa** (entries 1–3), *rhamno*- and *galacto*-ligands *ps-ent*-**1b** and *ps-ent*-**1a** with a phosphinite above the pyranoside plane yielded *S*-**7aa** (entries 4 and 5).

Table 2. 1,4-Additions of boronic acids to enones in the presence of **1a–c** and *ps-ent*-**1a**, **1b**.



Entry	Ligand	Enone **5**	R^2 in **6**	Adduct **7** No.	Yield [%][a]	*ee* [%][b]
1	**1b**	**5a**	**6a**	**7aa**	92	97 *R*
2	**1c**				80	98 *R*
3[c]	**1a**				80	99 *R*
4	*ps-ent*-**1b**				88	98 *S*
5[c]	*ps-ent*-**1a**				92	99 *S*
6	**1b**		**6b**	**7ab**	96	**95** *R*
7	**1c**				78	87 *R*
8[c]	**1aa**				94	60 *R*
9	*ps-ent*-**1b**				80	66 *S*
10[c]	*ps-ent*-**1a**				96	93 *S*
11	**1b**		**6c**	**7ac**	98	**86** (−)
12[c]	**1a**				54	78 (−)
13	*ps-ent*-**1b**				88	80 (+)
14[c]	*ps-ent*-**1a**				90	**96** (+)
15	**1b**	**5b**	**6d**	**7bd**	**76**	**92** (+)
16[c]	**1a**				37	89 (+)
17	*ps-ent*-**1b**				49	90 (−)
18[c]	*ps-ent*-**1a**				**77**	**94** (−)
19	**1b**		**6e**	**7be**	**63**	**92** *R*
20[c]	**1a**				34	79 *R*
21	*ps-ent*-**1b**				30	93 *S*
22[c]	*ps-ent*-**1a**				**66**	**92** *S*

[a] Isolated yield.
[b] Determined by GC.
[c] Results from ref.[7]

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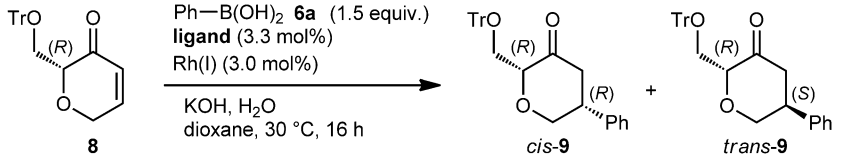
Table 3. 1,4-Addition of boronic acid **6a** to enone **8**.



Entry	Ligand	Rh(I) salt	Adduct **9**	
			Yield [%][a]	*cis/trans*[b]
1[c]	–	$[Rh(cod)OH]_2$	93	20:**80**
2	**1b**	$[RhCl(C_2H_4)_2]_2$	**92**	**95**:5
3[c]	**1a**		78	**89**:11
4	*ps-ent*-**1b**		79	7:**93**
5[c]	*ps-ent*-**1a**		**86**	6:**94**

[a] Combined yield of *cis*- and *trans*-**9**.
[b] Determined by ^{1}H NMR.
[c] Results from ref.[7]

Striking differences were seen for sterically encumbered 2-methoxyphenylboronic acid (**6b**), for which *gluco*-ligand **1aa** (4,5-*trans*) had led to 60% *ee*. The *fuco*-ligand **1b** (4,5-*cis*) gave 95% *ee*, while 4,5-*trans* configured but conformationally locked *gluco*-ligand **1c** led to a smaller yet significant improvement (87% *ee*) (entries 6–8). On the other hand, *rhamno*-ligand *ps-ent*-**1b** (4,5-*trans*) turned out to be inferior (66% *ee*) to 4,5-*cis* configured *galacto*-ligand *ps-ent*-**1a** (93% *ee*) (entries 9 and 10). Similar trends were observed with alkenylboronic acid **6c** (entries 11–14). 1,4-Addition of boronic acids **6d** and **6e** to cyclopentenone **5b** in the presence of **1a** had resulted in modest yields (entries 16 and 20). These were improved using *fuco*-ligand **1b** (entries 15 and 19), while *rhamno*-ligand *ps-ent*-**1b** was inferior to *ps-ent*-**1a** (entries 17 and 18 as well as 21 and 22).

These results clearly show that *fuco*- and *galacto*-ligands **1b** and *ps-ent*-**1a** with 4,5-*cis* pyranoside scaffolds are superior to 4,5-*trans* configured *gluco*- and *rhamno*-ligands **1a**, **1aa** and *ps-ent*-**1b**. The example of bicyclic **1c** highlights the complex interplay of pyranoside configuration and ligand conformation affecting asymmetric induction. While 4,5-*trans* configured **1a** and *ps-ent*-**1b** have to undergo conformational changes upon complexation, 4,5-*trans* configured **1c** is locked in a favourable conformation for Rh(I) binding. This results in improved stereoselectivity compared to **1a** and *ps-ent*-**1b**. Yet **1c** is inferior to 4,5-*cis* configured **1b** and *ps-ent*-**1a**.

With improved *pseudo* enantiomers **1b** and *ps-ent*-**1a**, we turned to 1,4-additions involving chiral enones. These may either yield diastereomeric products, with stereoselectivity depending on the relative efficiency of substrate and catalyst control or result in kinetic resolution[16] of racemic enones. Previous studies with racemic 6-alkyl[17] and 5-TMS[18] cyclohexenones by others had led to complete conversion of the starting material giving *trans*- and *cis*-configured products in moderate to high *ee*. We started our studies with enantiopure enone **8**,[7,19] (Table 3). Under substrate control, the addition of boronic acid **6a** predominantly yielded *trans*-**9** (entry 1). The *fuco*-ligand **1b** as well as *gluco*-ligand **1a** favour formation of *cis*-**9**, leading to a mismatched combination of substrate and catalyst control. Both ligands override substrate control but *fuco*-ligand **1b** proved yet again to be superior by significantly improving the *cis/trans* ratio (entries 2 and 3). Reaction in the presence of *ps-ent*-**1a** and *ps-ent*-**1b** constitutes a matched combination of reagent and catalyst control. While the *cis/trans* ratio of **9** was almost identical for both ligands, *galacto*-enoPhos (*ps-ent*-**1a**) gave a higher yield (entries 4 and 5).

Next, we investigated *O*-TBS-protected 4-hydroxycyclopentenone (**10**), an attractive material in sustainable chemistry, prepared from furfuryl alcohol,[20] which is accessible from hemicellulose of agricultural wastes.[21] Non-racemic **10**, an important building block in the synthesis of many bioactive compounds,[22] is mainly prepared from *cis*-3,5-dihydroxycyclopentene *via* enzymatic desymmetrisation in six steps.[23,24] Methods for kinetic resolution of *rac*-**10** by enzymatic and Pd-catalysed processes have recently received attention,[25] but 1,4-addition has as yet not been explored for this purpose.[26]

The results on kinetic resolution of *rac*-**10** are summarised in Table 4. Reaction with boronic acid **6a** in the presence of an achiral Rh catalyst and CsF as the base yielded exclusively known *trans*-configured compound **11**.[27] After reacting *rac*-**10** with 0.6 equiv. of **6a** in the presence of **1a**, the remaining *R*-**10** was isolated in excellent *ee* and 36% yield, while *ps-ent*-**1a** yielded *S*-**10** in modest *ee* (entries 1 and 2). Apart from addition products **11**, we observed **12**, formed *via* a Heck-type side reaction.[28] Using 0.4 equiv. of **6a**, ligands **1a**, and *ps-ent*-**1a** gave products *S,R*-**11** and

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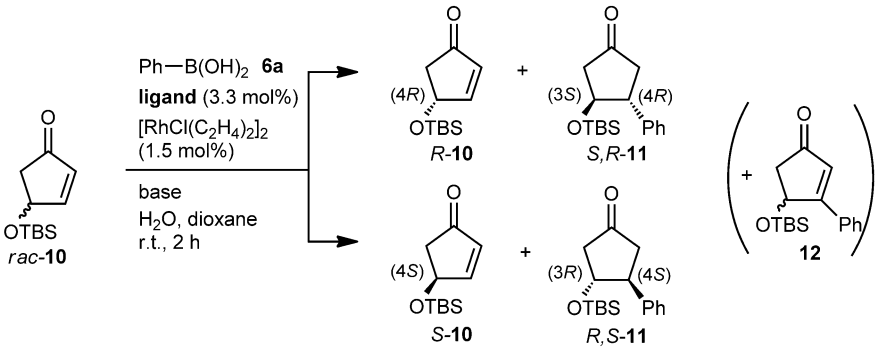
Table 4. Kinetic resolution of *rac*-**10** by 1,4-addition.



	Ligand	Base	Boronic Acid **6a** [equiv.]	Enone **10** Yield [%]	Enone **10** *ee*[a]	Adduct **11** Yield [%]	Adduct **11** *ee*[a]	s[e]
1[b]	**1a**	CsF[d]	0.6	**36**	**98** *R*	39	n.d.	–
2[b]	*ps-ent*-**1a**	CsF[d]	0.6	**37**	38 *S*	20	n.d.	–
3[b]	**1a**	CsF[d]	0.4	26	n.d.	**29**	**88** *S,R*	–
4[b]	*ps-ent*-**1a**	CsF[d]	0.4	79	n.d.	**19**	**92** *R,S*	–
5[c]	**1b**	Et_3N	0.6	**40**	**99** *R*	52	72 *S,R*	31
6[c]	*ps-ent*-**1a**	Et_3N	0.6	**40**	**99** *S*	55	79 *R,S*	44
7[c]	**1b**	Et_3N	0.4	42	86 *R*	**39**	86 *S,R*	57
8[c]	*ps-ent*-**1a**	Et_3N	0.4	40	78 *S*	**38**	**92** *R,S*	57

[a] Determined by GC.
[b] Yields after separation of **10** and **11**.
[c] Yields determined from the **10**/**11** ratio in the ^{1}H NMR spectrum of the product mixture.
[d] **12** in 4–20% yield.
[e] Calculation of s value according to ref.[29]

R,S-**11** respectively in good *ee* but unsatisfactory yields (entries 3 and 4). To overcome low yields and by-product formation, we re-investigated the reaction conditions and substituted ligand **1b** for **1a**. To our delight, Et_3N as a base improved yield and *ee* and suppressed formation of **12**. A yield of 40% and 99% *ee* for *R*-**10** and *S*-**10** were achieved using **1b** and *ps-ent*-**1a** with 0.6 equiv. of **6a** (entries 5 and 6), while decreasing the amount of **6a** to 0.4 equiv. yielded addition products *S,R*-**11** and *R,S*-**11** in fair *ee* (entries 7 and 8).

In conclusion, we have elucidated the interplay of pyranoside configuration and conformation in Rh(I) complexes of carbohydrate olefin ligands and its consequences for asymmetric induction in 1,4-additions. During our studies, we have identified *fuco*-ligand **1b** as an improved alternative to **1a**, leading to substantially increased *ee* values. The *pseudo* enantiomeric ligand pair **1b** and *ps-ent*-**1a** now gives consistently high *ee* values for both achiral enones and bulky boronic acids and chiral enones. Furthermore, we successfully employed our ligands in the kinetic resolution of a racemic *O*-TBS-protected 4-hydroxycyclopentenone, allowing the recovery of the starting material in excellent *ee*.

Experimental Section

Synthesis of Enantioenriched *R*-10

In a glove box $[Rh(C_2H_4)_2Cl]_2$ (2.7 mg, 7.1 μmol) and *fuco*-enoPhos (**1b**) (4.6 mg, 15.5 μmol) were placed into a flame-dried Schlenk flask. Under a nitrogen atmosphere, degassed 1,4-dioxane (1 mL) was added and the solution was stirred for 15 min at room temperature. An aqueous solution of Et_3N (65 μL, 471 μmol in 0.5 mL degassed H_2O) was added and the mixture was stirred for additional 15 min. Enone *rac*-**10** (100 mg, 471 μmol, 1.0 equiv.) was added and the reaction mixture was stirred for additional 15 min. Next phenylboronic acid **6a** (34.5 mg, 283 μmol, 0.6 equiv.) and degassed 1,4-dioxane (1 mL) were added and the resulting mixture was stirred for 2 h at room temperature. After completion of the reaction Et_2O (10 mL) and H_2O (10 mL) were added and the aqueous layer was extracted with Et_2O (2×, 15 mL). The organic phase was dried over Na_2SO_4, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (PE/EtOAc, 10:1). The products (113 mg) were isolated in one fraction, comprising enantioenriched enone *R*-**10** and 1,4-addition product *S,R*-**11**. The product ratio was determined from the ^{1}H NMR spectrum: *R*-**10**/*S,R*-**11** = 43:57, *R*-**10** (188 μmol, 40% yield; *S,R*-**11**: 248 μmol, 52% yield). Enantiomeric excesses were determined from the product mixture in a single run: *R*-**10** 99% *ee*; *S,R*-**11** 72% *ee*.

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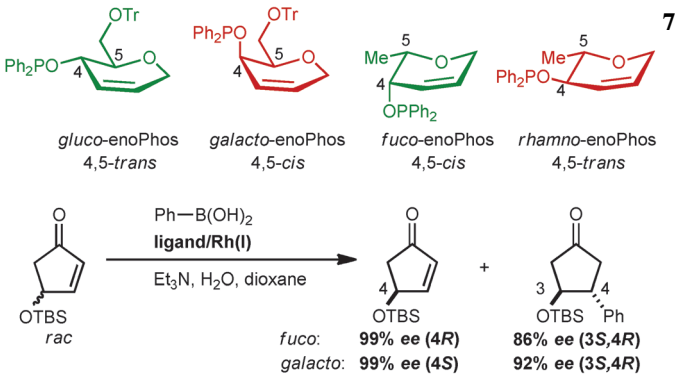

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