JOC*Note*

Asymmetric Synthesis of 2°- and 3°-Carbinols via *B*-Methallyl-10-(TMS and Ph)-9-borabicyclo[3.3.2]decanes†

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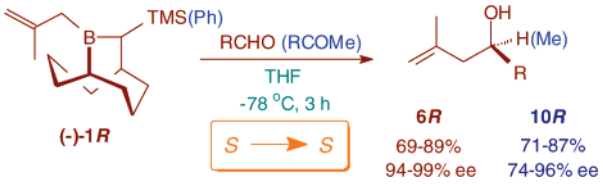

Simple Grignard procedures provide methallylboranes **1a** and **1b** in enantiomerically pure form from air-stable precursors in 98% and 95% yields, respectively. These reagents add smoothly to aldehydes and methyl ketones, respectively, providing branched 2°- (**6**, 69−89%, 94−99% ee) and 3°- (**10**, 71−87%, 74−96% ee) homoallylic alcohols.

The asymmetric allylboration of aldehydes remains as one of the most powerful processes for the preparation of nonracemic 2°-homoallylic alcohols.[1] In 1978, Hoffmann[1a,c] reported the first enantioselective synthesis of branched 2°-homoallylic alcohols employing a methallyl derivative of his camphor-derived boronic esters. Unfortunately, low enantioselectivity is generally observed with these reagents (40−76% ee). Brown's diisopinocampheylborane reagents proved to be more selective (90−96% ee), but the preparation of these reagents from high-purity air-sensitive organoborane precursors through organolithium procedures presents operational difficulties.[1d,o] Moreover, these reagents are ineffective for the allylation of ketones.[1e] A variety of alternative processes are now available for these types of "allylation" processes,[2] but for ketone substrates, the only successful methallylation was recently reported employing tetrakis(methallyl)tin and a (*R*)-H_8-BINOL/Ti catalyst.[3] This method uses 6 equiv of the toxic methallyltin moiety, a large catalyst loading (30 mol %), and exhibits modest to good enantioselectivity (46−90% ee). Since asymmetric methallylation is an important synthetic process,[4] we felt that a better, more selective and user-friendly process would represent an important advance. We envisaged that the methallylation of both aldehydes and ketones could be markedly improved through the use of the 10-substituted-9-borabicyclo[3.3.2]decanes which are easy to handle, effectively recovered and recycled, and available in both enantiomeric forms.

Recently, we reported the synthesis of the *B*-allyl-10-TMS- and -10-Ph-BBD systems (**2**) and their highly selective additions to aldehydes[5] and ketones,[6] respectively. The corresponding *B*-methallyl reagents **1** were envisaged as very attractive alternatives for the methallylboration of either aldehydes or ketones, depending upon the choice of the 10-substituent employed.

The air-stable crystalline pseudoephedrine (PE) complexes **4a** serve as efficient precursors to **2a** (98%) through simple Grignard procedures.[5] However, the analogous process with **4a** and methallylmagnesium chloride (0.5 M in THF) proved to be both sluggish and inefficient. Fortunately, the more reactive *B*-OMe derivatives **3a**, which are readily prepared from **2a** (87%),[5a] provide an efficient entry to **1a** through this Grignard method (98%) (Scheme 1).

Reagents **1a** react smoothly with aldehydes to yield pure 3-methyl homoallylic alcohols **6** efficiently (69−89%) with excellent selectivities (94−99% ee) (Scheme 2, Table 1). The product ee values were determined by their conversion to their Alexakis esters and analysis through ^{31}P NMR.[7] Similar to allylboration,[5] this process is quite general, being effective for alkyl, aryl, substituted aryl, heteroaryl, and unsaturated aldehydes. Our protocol includes the isolation of the borinic ester intermediates **5** in essentially quantitative yields following the removal of the solvents. A non-oxidative workup procedure was employed that permits the recovery of the air-stable pseudoephedrine (PE) complexes **4a** (62−78%), which can be converted back to **1a** (Scheme 1).

The competitive reaction of **1a** and **2a** with benzaldehyde (1:1:1) was conducted at −78 °C. This reveals that **2a** is only

† This work is dedicated to Professor Alfred Hassner on the occasion of his 77th birthday.

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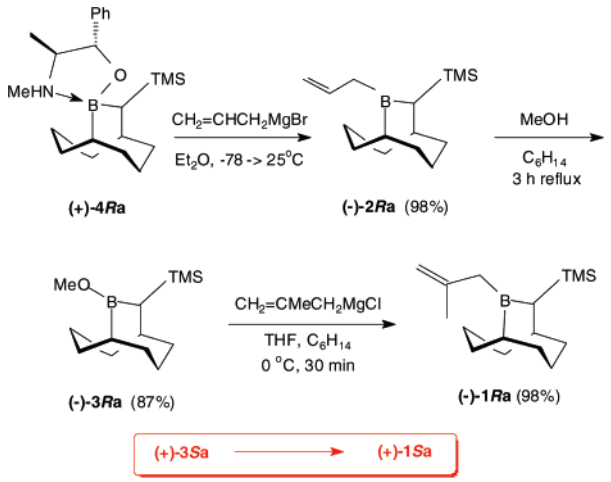
TABLE 1. Methallylboration of Aldehydes with 1a

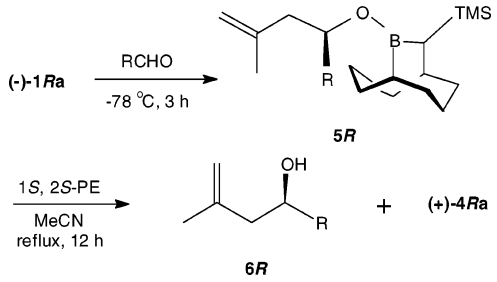
R in RCHO	series	**1a**	**4a** (%)	**6**, %	ee,[a] % abs config[c]
Ph[d]	**a**	*S*, *R*	73, 75	78, 80	95; (*S*),(*R*)
4-$MeOC_6H_4$	**b**	*S*	66	78	98;[b] (*S*)
4-$NO_2C_6H_4$	**c**	*R*	66	69	99; (*R*)
2-ClC_6H_4	**d**	*R*	70	89	94; (*R*)
pyridyl	**e**	*R*	62	88	96; (*R*)
i-Pr	**f**	*S*	74	75	97; (*S*)
t-Bu	**g**	*R*	65	73	94; (*R*)
trans-crotyl	**h**	*R*	78	85	94; (*R*)

[a] Enantiomeric excesses were determined by conversion to Alexakis esters and ^{31}P NMR analysis.[7] [b] Enantiomeric excess was determined by ^{13}C NMR analysis of the Mosher ester. [c] The absolute configuration of the alcohols was determined by a direct comparison of optical rotations obtained to those reported in the literature.[1c,d,2b] [d] This run was performed with both (+)-**1*Sa*** and (−)-**1*Ra***.

SCHEME 1. Preparation of Methallylborane 1



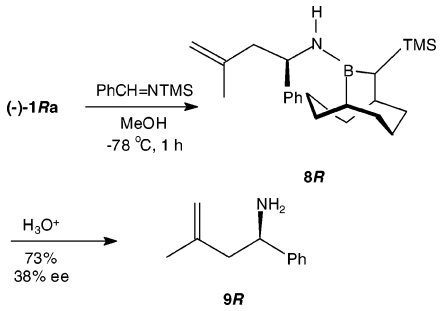
SCHEME 2. Asymmetric Allylboration of Aldehydes with 1a



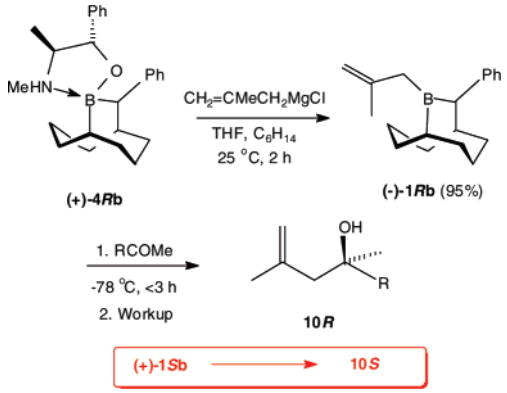
slightly more reactive than **1a** (i.e., 1.3:1.0), a result that is likely to be steric in origin.

Homoallylic amines provide important building blocks for the synthesis of numerous nitrogen-containing natural products.[8] While the methallylboration of *N*-metallo imines is unknown,[9] the corresponding allylboration process has been extensively studied.[10−12] We chose to examine this process through the generation of *N*-H benzaldimine with MeOH (1 equiv) from its *N*-TMS precursor in the presence of **1a** in THF at −78 °C. After

SCHEME 3. Asymmetric Allylboration of Benzaldimine with 1a



SCHEME 4. Asymmetric Allylboration of Ketones with 1b



1 h, the formation of the aminoborane **8** was complete as determined by ^{11}B NMR (δ 46). Acidic hydrolysis (2 M HCl) followed by a basic workup affords the homoallylic amine **9** (73%), in only modest enantioselectivity (38% ee) (Scheme 3). While disappointing, the lowered observed selectivities for this and related additions to aldimines vs aldehydes appears to be a general phenomenon attributable to the larger relative size of NH vs O.[12]

In contrast to the sluggish reaction of methallylmagnesium chloride with **4a**, this Grignard reagent does readily add to the crystalline pseudoephedrine complex,[6] (+)-**4*Rb***, to provide pure *B*-methallyl-10-Ph-9-BBD ((−)-**1*Rb***) directly in excellent yield (95%) (Scheme 4). The enantiomer, (+)-**1*Sb***, was similarly prepared from the corresponding *N*-methylpseudoephedrine complex, (+)-**4′*Sb***.[6] The asymmetric methallylboration of representative methyl ketones was examined with **1b**. These reagents (−)-**1*Rb*** and (+)-**1*Sb*** undergo clean addition even to hindered methyl ketones (entry 3d) in ≤3 h at −78 °C providing the desired 3°-carbinols **10** with excellent enantioselectivities (74−96% ee) (Table 2). An oxidative workup (NaOH, H_2O_2) was normally used in this protocol. A non-oxidative procedure employing *N*-methylpseudoephedrine was developed for the **10*Sa*** example resulting in a 76% yield of recovered (+)-**4′*Sb***. Similarly, for **10*Rb***, a pseudoephedrine workup gave crystalline (+)-**4*Rb*** in 71% yield.

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TABLE 2. Methallylboration of Ketones with 1b

R in $RCOCH_3$	10	1b	yield, %	ee,[a] % abs config[b]
Ph	**a**	*S*	87 (80)[c]	88; *S*
4-$NO_2C_6H_4$	**b**	*R*	71 (69)[c]	93; *R*
trans-PhCH=CH	**c**	*S*	81	74; *S*
t-Bu	**d**	*S*	75	96; *S*

[a] Enantiomeric excesses were determined by conversion to Alexakis esters and ^{31}P NMR.[7] [b] The absolute configuration of the alcohols was determined by a direct comparison of optical rotations obtained to those reported in the literature.[3a] [c] Yields in parentheses for **10*S*a** and **10*R*b** were obtained employing a non-oxidative workup (the complexes (+)-**4′*S*b** and (+)-**4*R*b** were also recovered in 76% and 71% yield, respectively).

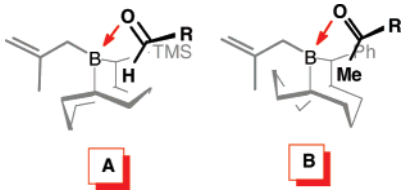
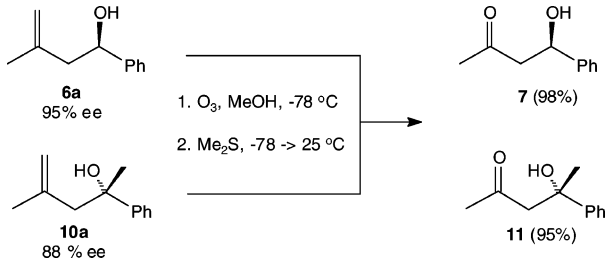


FIGURE 1. Proposed models for the most energetically favorable pre-transition state complexes which explain the observed stereochemistry in the methallylboration of RCHO with **1a** (A) and RCOMe with **1b** (B).

SCHEME 5. Ozonolysis of *β*-Methyl Homoallylic Alcohols



The asymmetric addition of acetone-derived enolates to aldehydes occurs with low enantioselectivity.[13] The product *β*-hydroxy methyl ketones are valuable intermediates in the total synthesis of macrolide and polyether antibiotics.[14] An alternative to the ineffective aldol route to *β*-hydroxy methyl ketones with acetone enolates was introduced by Hoffmann[1b] through the ozonolysis of **6**. Very recently, Walsh showed that this process was effective for **10**.[3a] With the higher selectivities observed with **1** and **10**, we chose to demonstrate the synthetic value of this transformation further with simple examples and to reconfirm the absolute stereochemistry of **6** and **10** (Scheme 5).

In summary, the new BBD reagents **1** are efficiently prepared in either enantiomeric form through simple Grignard procedures that employ air-stable organoborane precursors. Exceeding the selectivities observed with other reagents and processes, **1** provides either enantiomer of branched 2° (**6**, 69−89%) and 3°-homoallylic alcohols (**10**, 71−87%) with predictable stereochemistry (see Figure 1)[5,6] and remarkable enantioselectivity (94−99% and 74−96% ee, respectively). Thus, for the first time, one system can be modified for the effective methallylation of either aldehydes or ketones. This new method can be used with either an oxidative or non-oxidative workup, the latter process providing the recovered chiral borane as an air-stable and recyclable complex **4**. Ozonolysis of **6** and **10** provides *β*-hydroxyalkyl methyl ketones **7** and **11** efficiently in high enantiomeric purity.

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Experimental Section

B*-Methallyl-10*R*-trimethylsilyl-9-borabicyclo[3.3.2]decane-((−)-1*R*a).** A solution of (−)-**3*R (0.71 g, 3.0 mmol) in hexane (12 mL) was cooled to 0 °C and a solution of methallylmagnesium chloride (7.8 mL , 0.5 M in THF) was added dropwise. The solution was allowed to reach room temperature and was stirred for 1 h. Then the reaction mixture was cooled to −78 °C and quenched with TMSCl (0.5 equiv). With use of standard techniques to prevent the exposure of the borane to the open atmosphere, the solution was concentrated under vacuum, the residue was washed with pentane (4 × 10 mL), and these washings were filtered through a celite pad. Concentration gives 0.77 g (98%) of (−)-**1*R*a**: ^1H NMR (C_6D_6, 300 MHz) *δ* 0.23 (s, 9H), 1.02−1.76 (m, 15H), 1.80 (s, 3H), 2.23 (m, 3H), 4.75 (s, 1H), 4.92 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6) *δ* 1.9, 22.2, 25.4, 25.9, 26.2, 29.2, 31.5, 34.2, 34.9, 40.0, 40.9, 110.0, 145.0; ^{11}B NMR ($CDCl_3$) *δ* 83.7; $[\alpha]^{23}_D$ −22.6 (*c* 1.24, C_6D_6). *B*-Methallyl-10*S*-trimethylsilyl-9-borabicyclo[3.3.2]decane ((+)-**1*S*a**) is prepared by the same procedure starting with (+)-**3*S***. $[\alpha]^{23}_D$ +22.3 (*c* 1.24, C_6D_6). HRMS $[M + H]^+$ calcd for $C_{16}H_{31}BSi$ 263.2368, found 263.2369 *m/z*.

Representative Procedure for the Allylboration of Aldehydes with 1a. (−)-(*R*)-3-Methyl-1-(2-chlorophenyl)-3-buten-1-ol (6*R*d): A solution of (−)-**1*R*a** (0.79 g, 3 mmol) in THF (3 mL) was cooled to −78 °C and 2-chlorobenzaldehyde (0.42 g, 3.0 mmol) was added dropwise. After 3 h, the solvents were removed under vacuum to yield 1.15 g (95%) of the corresponding borinate **5*R*d**. The (1*S*,2*S*)-(−)-pseudoephedrine (0.50 g, 3.0 mmol) and acetonitrile (7 mL) were added and the mixture was heated at reflux temperature for 2 h. The crystals were separated and washed with pentane (3 × 10 mL) to yield 0.78 g (70%) of (+)-**4*R*a**. The residue was purified by column chromatography on silica gel (9:1, hexane:Et_2O) to obtain 0.52 g (88%) of 3-methyl-1-(2-chlorophenyl)-3-buten-1-ol (**6*R*d**). ^1H NMR ($CDCl_3$, 300 MHz) *δ* 1.86 (s, 3H), 2.23 (dd, *J* = 13.9 Hz, *J* = 9.7 Hz, 1H), 2.52−2.60 (m, 2H), 4.92 (d, *J* = 18.7 Hz, 2H), 5.21 (dd, *J* = 9.7 Hz, *J* = 2.7 Hz, 1H), 7.16−7.34 (m, 3H), 7.61 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 22.0, 46.6, 67.9, 114.2, 126.9, 127.1, 128.3, 129.3, 131.5, 141.4, 142.5. HRMS $[M + H - H_2O]^+$ calcd for $C_{11}H_{12}Cl_1$ 179.0622, found 179.0622. The enantiomeric purity was determined by the CDA reagent developed by Alexakis, using the reported procedures (^{31}P NMR *δ* 131 (97, **6*R*d**), 144 (3, **6*S*d**)).[7] $[\alpha]^{25}_D$ +58.54 (*c* 1.11, $CHCl_3$, 94% ee).

Representative Ozonolysis. (*S*)-4-Hydroxy-4-phenyl-2-butanone (7): 6*S*a (0.14 g, 0.86 mmol) was diluted in MeOH (10 mL) and cooled to −78 °C. To this solution was bubbled ozone until a blue color persisted (10 min) in the reaction mixture. The reaction mixture was allowed to reach room temperature and the excess of ozone was removed under a N_2 purge. The solution was cooled to −78 °C, dimethyl sulfide (0.13 mL) was added dropwise, and the mixture was stirred overnight slowly reaching room temperature. The mixture was washed with water (3 × 5 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 0.14 g of **7** (98%). ^1H NMR ($CDCl_3$, 300 MHz) *δ* 2.20 (s, 3H), 2.81 (dd, *J* = 3.6 Hz, 18.0 Hz, 1H), 2.90 (dd, *J* = 8.7 Hz, *J* = 18.0 Hz, 1H), 3.32 (s, broad OH, 1H), 5.15 (dd, *J* = 3.7 Hz, *J* = 8.7 Hz, 1H), 7.26−7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 30.7, 51.9, 69.8, 125.6, 127.7, 142.7, 209.0. $[\alpha]^{24}_D$ −53.2 (*c* 2.20, $CHCl_3$) {lit.[13] (*R*) $[\alpha]^{53}_D$ +40.9 (*c* 10.3, $CHCl_3$, 57% ee) +57.1 (*c* 1.10, $CHCl_3$)}.

(*R*)-3-Methyl-1-phenyl-3-buten-1-amine (9*R*): A solution of (−)-**1*R*a** (0.79 g, 3 mmol) in THF (3 mL) was cooled to −78 °C. To this solution was added *N*-TMS benzaldimine (0.62 g, 3.0 mmol)[11] followed by dry MeOH (0.16 mL, 4 mmol). After 1 h, the reaction was warmed to room temperature and the solvents were removed under vacuum to afford the intermediate aminoborane. A solution of aqueous HCl (10 mL, 2 M) was added. The mixture was stirred at room temperature for 1 h. The aqueous phase was washed with Et_2O (2 × 5 mL). The resulting aqueous phase was neutralized with Na_2CO_3 followed by Et_2O extractions (3 × 15 mL). The organic phase was then dried over $MgSO_4$. Removal of solvent in vacuo afforded the homoallylic amine **9*R*** (38% ee, 73% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.81 (s, 3H), 2.40 (ddq, J = 13.8 Hz, J = 9.2 Hz, J = 4.0 Hz, 2H), 2.42 (s, broad OH, 1H), 4.85−4.86 (m, 1H), 4.90 (dd, J = 9.2 Hz, J = 4.1 Hz, 1H), 4.95−4.97 (m, 1H), 7.54 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 48.3, 114.9, 123.5, 126.4, 141.3, 147.1, 151.5. The enantiomeric purity was determined by the ^{31}P NMR CDA reagent developed by Alexakis, using the reported procedures.[7] $[\alpha]^{29}_D$ +6.71 (*c* 1.31, $CHCl_3$, 38% ee). HRMS [M + H]$^+$ calcd for $C_{11}H_{16}N_1$ 162.1277, found 162.1277.

(+)-*B*-Methallyl-(10*S*)-phenyl-9-borabicyclo[3.3.2]decane (1*S*b). To a solution of (+)-**4′*S*b**[6] (1.17 g, 3.0 mmol) in hexane (12 mL) was added freshly prepared methallylmagnesium chloride (9.0 mL, 0.66 M in THF) dropwise. The solution was allowed to stir for 2 h. The reaction mixture was cooled to −78 °C and quenched with 1.0 equiv of TMSCl. With use of standard techniques to prevent the exposure of the borane to the open atmosphere, the solution was concentrated under vacuum, the residue was washed with pentane (3 × 20 mL), and these washings were filtered through a celite pad. Concentration gives 0.76 g (95%) of **1*S*b**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60−2.71 (m, 20H), 4.57 (s, 1H), 4.80 (s, 1H), 7.15−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 23.6, 25.4, 26.6, 27.9, 29.1, 29.8, 34.2, 39.9, 40.4, 53.3, 109.6, 124.71, 128.1, 129.9, 144.5, 146.7. $[\alpha]^{27}_D$ +45.2 (*c* 2.03, C_6D_6). HRMS [M]$^+$ calcd for $C_{19}H_{27}B$ 266.2206, found 266.2206 *m/z*. (-)-*B*-Methallyl-10*R*-phenyl-9-borabicyclo[3.3.2]decane **(1*R*b)** is prepared by the same procedure starting with (+)-**4*R*b** (9-(1*S*,2*S*-pseudoephedrinyl)-(10*R*)-phenyl-9-borabicyclo[3.3.2]decane).[6] $[\alpha]^{27}_D$ −42.3 (*c* 1.91, C_6D_6). Other data are essentially identical with those for **1*S*b**.

Representative Procedure for the Allylboration of Ketones with 1b. (−)-(*S*)-4-Methyl-2-phenyl-4-penten-2-ol (10*S*a): A solution of (+)-**1*S*b** (0.80 g, 3.0 mmol) in THF (3 mL) was cooled to −78 °C and acetophenone (0.36 g, 3.0 mmol) was added dropwise. After 3 h, the temperature of the reaction mixture was raised to 25 °C and NaOH (2.0 mL, 3 M solution in water) was added followed by H_2O_2 (0.9 mL, 30 wt % in water). The biphasic mixture was refluxed for 2 h followed by an aqueous workup (3 × 15 mL of brine solution). The combined organic phase was dried over $MgSO_4$ and filtered. The crude product was then purified by silica gel column chromatography (4:1, hexane:ethyl acetate) to obtain 0.46 g of **10*S*a** (87%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.44 (s, 3H), 1.59 (s, 3H), 2.50 (s, broad OH, 1H), 2.60 (dd, J = 13.3 Hz, J = 4.6 Hz, 2H), 4.84 (d, J = 4.4 Hz, 2H), 7.22−7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 30.5, 51.9, 73.1, 115.5, 124.7, 126.4, 127.9, 142.4, 147.8. $[\alpha]^{27}_D$ −31.2 (*c* 1.00, CH_2Cl_2, 88% ee). The enantiomeric purity was determined by the CDA reagent developed by Alexakis, using the reported procedures (^{31}P NMR δ 136.5 (94, **10*S*a**), 138.0 (6, **10*R*a**)).[7] These data were in complete agreement with literature values.[3a]

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Supporting Information Available: Full experimental procedures, characterization data, and selected spectra for **1**−**10** and derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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