Synthesis of Chiral Esters of (*E*)-3-(Silyloxy)-2-propenylboronic Acid via the Iridium-Catalyzed Isomerization of the Double Bond

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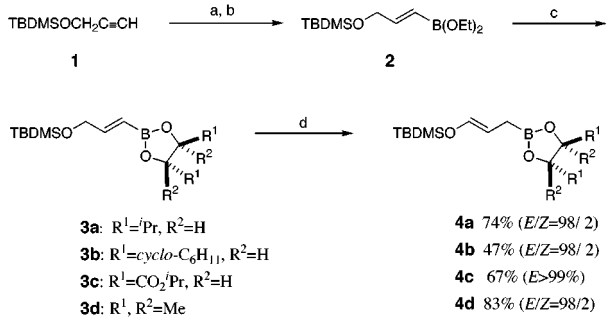
Allylboronic esters have been prepared by transmetalation of allyllithium, -magnesium, and -tin reagents with boron alkoxides and halides.[1] The approaches are experimentally simple, but they often suffer from a general lack of regio- and stereoselectivity in the preparation of the allyl anion precursors. For example, the synthesis of (*E*)-(*γ*-alkoxyallyl)boronates has not met with much success, in part because of the configurational instability of the (*E*)-*γ*-alkoxyallyl anions, though they are an excellent reagent for the diastereoselective synthesis of *anti*-1,2-diols from carbonyl compounds.[2] Thus, an alternative and indirect method using (*E*)-*γ*-silyl-substituted allylmetal reagents has recently been developed.[3] We wish to report herein an alternative and direct method for the synthesis of (*γ*-(silyloxy)allyl)boronic esters (**4**) by the transition metal-catalyzed isomerization of the double bond (Schemes 1 and 2).[4] The cationic iridium complex[5] obtained via hydrogenation of $[Ir(cod)(PPh_2Me)_2]PF_6$ was recognized to be an excellent catalyst for the isomerization of various 3-(silyloxy)-1-propenylboronates (**3** and **5**) under mild conditions.

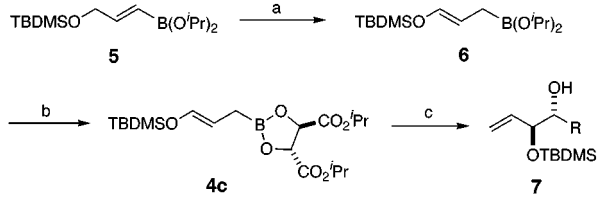
The hydroboration of propargyl silyl ether (**1**) with diisopinocampheylborane followed by dealkylation of the isopinocampheyl group with a large excess of acetaldehyde gave the 3-(silyloxy)-1-propenylboronate (**2**) which was in situ converted to a chiral diol ester **3** (TBDMS = ^{t}Bu$_2$MeSi).[6] The positional isomerization of the double bond was carried out at room temperature for 20 min in the presence of 3 mol % of $[IrH_2(thf)_2(PPh_2Me)_2]PF_6$ (**3**), which was in situ generated by passing a stream of H_2 into a THF solution of the precatalyst $[Ir(cod)(PPh_2Me)_2]$-PF_6.[5] High *E*-selectivities exceeding 98% and high conversions in a range of 60−90% were achieved for various cyclic esters of vinylboronic acid **3a**−**d**. Although the reaction gave an inseparable mixture of **3** and **4**, the reagents thus obtained can be used in situ for the next allylboration because the allylic derivatives **4** selectively participate in the addition to aldehydes.

Scheme 1[a]



[a] (a) $HB(ipc)_2$ in THF at −35 °C to r.t.; (b) CH_3CHO at reflux for 12 h; (c) diol at r.t. for 3 h; (d) $[IrH_2(thf)_2(PPh_2Me)]PF_6$ (3 mol %) inTHF for 20 min. at. r.t.

Scheme 2[a]



[a] (a) $[IrH_2(AcOEt)_2(PPh_2Me)_2]PF_6$ (3 mol %) in AcOEt for 10 min at r.t., yield 94% (*E*/*Z* = 98/2). (b) L(+)-diisopropyl tartarate in toluene. (c) RCHO and MS-4A in toluene at −78 °C for 5 h.

Alternatively, the diisopropyl allylboronate (**6**), which is readily convertible to various chiral esters (**4**) via the ester exchange with diol, was stereoselectively obtained by the isomerization of **5** (Scheme 2). The reaction in THF was very fast, and the initial reaction was highly selective, but it was still not suited for a practical procedure because of accompanying *E*/*Z* isomerization on prolongation of the reaction time. In contrast, an almost quantitative isomerization (94% conversion) without the stereochemical isomerization (*E*, 98%) was achieved when the reaction was carried out in ethyl acetate for 10 min. The isomerization of **5** with 3 mol % catalyst resulted in the conversions and the *E*/*Z* selectivities shown in Table 1.

The utility of the present reaction was demonstrated by an asymmetric allylboration of the representative aldehydes with **4c** to give the *anti*-1,2-diol **7**.[7] For operational convenience, the in situ preparation of the diisopropyl boronic ester (**6**) was followed by the ester exchange with a chiral diol for the allylboration of aldehydes. Thus, a sequence of the addition of diisopropyl tartrate (1 equiv) to the crude **6** (1 equiv), the evaporation of 2-propanol and ethyl acetate in vacuo to give **4c**, and finally the addition of an aldehyde at −78 °C afforded an *anti*-1,2-diol with high diastereoselectivity (>99%) and enantioselectivities (Table 2). The enantiomer excess (% ee) in a range of 67−91% thus achieved was comparable

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Table 1. Isomerization of 5 to 6[a]

entry	solvent	time/min	conversion/%	E/Z
1	THF	5	70	*E* > 99
2		10	76	99/1
3		20	97	80/20
4		30	99	67/33
5	CH_3CO_2Et	5	64	*E* >99
6		10	94	98/2
7		20	96	96/4
8		30	97	95/5
9		60	98	92/8

[a] A mixture of **5** (1 mmol) and catalyst (0.03 mmol) in solvent (5 mL) was stirred at room temperature.

Table 2. Asymmetric *Anti*-α-Hydroxyallylation of Aldehydes with 4c

entry	aldehyde	product no.	yield/%	% ee[a]
1	*c*-$C_6H_{11}CHO$	**7a**	85	91
2	$C_5H_{11}CHO$	**7b**	86	82
3	PhCHO	**7c**	82	67
4	$(CH_3)_2C{=}CHCHO$	**7d**	84	69
5	$PhCH{=}CHCHO$	**7e**	98	73

[a] The % ee was determined by ^{1}H NMR of the correspoding Mosher's esters.

to that obtained with diisopinocampheyl(3-silyl-2-propenyl)borane.[3]

Experimental Section

(*E*)-3-(*tert*-Butyldimethylsilyloxy)-1-propenylboronic Esters (3 and 5). The boronates were synthesized by the reported procedure.[6b] A 100 mL-flask was charged with THF (9 mL) and $BH_3{\cdot}SMe_2$ (32 mmol). α-Pinene (72 mmol) was then dropwise added at 0 °C. The mixture was stirred for 1 h at 0 °C and an additional 2 h at room temperature to give a white suspension of diisopinocampheylborane. After being cooled to −35 °C, 3-(*tert*-butyldimethylsilyloxy)propyne (**1**) (30 mmol) was slowly added, and the resulting mixture was stirred for 1.5 h at −35 °C, slowly warmed to room temperature, and stirred for an additional 4 h. Acetaldehyde (28 mL, 501 mmol) was added at 0 °C, and the mixture was then refluxed for 12 h. The evaporation of the excess acetaldehyde and other volatile in vacuo (10 mmHg) gave an oil of the crude **2**. The residue was directly treated with a diol (30 mmol) in THF (12 mL) for 3 h at room temperature. The evaporation of the solvent followed by Kugelrohr distillation gave **3**.

3a: 80%; bp 96 °C/0.1 mmHg; ^{1}H NMR δ 0.07 (s, 6 H), 0.92 (s, 9 H), 0.92 (d, 12 H, *J* = 6.6 Hz), 1.66−1.73 (dqq, 2 H), 3.85 (dd, 2 H, *J* = 8.2 and 4.3 Hz), 4.26 (dd, 2 H, *J* = 3.7 and 2.0 Hz), 5.76 (dt, 1 H, *J* = 17.8 and 2.1 Hz), 6.70 (dt, 1 H, *J* = 17.8 and 3.6 Hz); ^{13}C NMR δ, 152.2, 84.0, 64.6, 33.1, 25.9, 17.8, 16.7, −5.4; ^{11}B NMR δ 29.4; exact mass calcd for $C_{17}H_{35}BO_3Si$ *m/e* 326.2449, found *m/e* 326.2430.

3b: 86%; bp 160 °C/0.1 mmHg; ^{1}H NMR δ 0.07 (s, 6 H), 0.91 (s, 9 H), 0.70−2.60 (m, 22 H), 3.87 (d, 2 H, *J* = 4.6 Hz)), 4.24 (dd, 2 H, *J* = 3.5 and 2.0 Hz), 5.76 (dt, 1 H, *J* = 17.8 and 2.1 Hz), 6.70 (dt, 1 H, *J* = 18.0 and 3.6 Hz); ^{13}C NMR δ 152.1, 83.3, 64.6, 43.0, 30.8, 28.3, 27.3, 26.4, 25.9, −5.4; ^{11}B NMR δ 29.5; exact mass calcd for $C_{23}H_{43}BO_3Si$ *m/e* 406.3075, found *m/e* 406.3069.

3c: 53%; bp 173 °C/0.1 mmHg; ^{1}H NMR δ 0.07 (s, 6 H), 0.921 (s, 9 H), 0.92 (d, 12 H, *J* = 6.6 Hz), 1.66−1.73 (dqq, 2H), 3.85 (dd, 2H, *J* = 8.2 and 4.3 Hz), 3.85 (dd, 2H, *J* = 8.2 and 2.0 Hz), 4.26 (dd, 2 H, *J* = 3.7 and 2.0 Hz), 5.76 (dt, 1 H, *J* = 17.8 and 2.1 Hz), 6.70 (dt, 1 H, *J* = 17.8 and 3.6 Hz); ^{13}C NMR δ 169.0, 154.8, 77.6, 69.8, 64.3, 25.8, 21.5, 18.3, −5.5; ^{11}B NMR δ 31.3; exact mass calcd for $C_{19}H_{35}BO_7Si$ *m/e* 399.2011 ($M^+ - 15$), found *m/e* 399.2008.

3d: 53%; bp 91 °C/0.3 mmHg; ^{1}H NMR δ 0.07 (s, 6 H), 0.92 (s, 9 H), 0.92 (d, 12H, *J* = 6.6 Hz), 1.66−1.73 (dqq, 2H), 3.85 (dd, 2H, *J* = 8.2 and 4.3 Hz), 3.85 (dd, 2H, *J* = 8.2 and 4.3 Hz), 4.26 (dd, 2 H, *J* = 3.7 and 2.0 Hz), 5.76 (dt, 1 H, *J* = 17.8 and 2.1 Hz), 6.70 (dt, 1 H, *J* = 17.8 and 3.6 Hz); ^{13}C NMR δ 152.1, 83.1, 64.5, 47.9, 28.4, 25.9, 24.7, −5.4; ^{11}B NMR δ 29.6; exact mass calcd for $C_{15}H_{31}BO_3Si$ *m/e* 297.2057 ($M^+ - 1$), found *m/e* 297.2038.

The crude **2** obtained by the above procedure was directly treated with 2-propanol (38 mL) at refluxing temperature for 12 h. The evaporation of the volatile gave an oil which was then subjected to distillation to give the diisopropyl ester (**5**).

5: 68%, bp 73 °C/0.1 mmHg; ^{1}H NMR δ 0.07 (s, 6 H), 0.92 (s, 9 H), 1.17 (d, 12 H, *J* = 6.1 Hz), 4.25 (dd, 2 H, *J* = 3.8 and 2.1 Hz), 4.46 (qq, 2 H, *J* = 6.1 Hz), 5.84 (dt, 1 H, *J* = 17.6 and 2.1 Hz), 6.58 (dt, 1 H, *J* = 17.6 and 3.8 Hz); ^{13}C NMR δ 149.2, 65.2, 64.8, 25.9, 24.6, −5.3; ^{11}B NMR δ 26.5; exact mass calcd for $C_{15}H_{33}BO_3Si$ *m/e* 299.2214 ($M^+ - 1$), found *m/e* 299.2226.

3-(*tert*-Butyldimethylsilyloxy)-2-propenylboronic Esters (4). The bubbling hydrogen into a red solution of $[Ir(cod)(PPh_2Me)_2]PF_6$ (0.03 mmol) in THF (5 mL) at room temperature gave a light yellow solution of $[IrH_2(thf)_2(PPh_2Me)_2]PF_6$. After removal of the excess hydrogen by bubbling argon, the boronic ester (**3**) was added and the mixture was then stirred for 20 min at room temperature. Concentration in vacuo, followed by Kugelrohr distillation, gave **4**. The complete separation of viscous oil of **3** and **4** was rather difficult by Kugelrohr distillation. Thus, the following compounds are accompanied with 5−15% of **3**.

4a: 74%; bp 94 °C/0.1 mmHg; ^{1}H NMR δ 0.07 (s, 6 H), 0.92 (s, 9 H), 0.92 (d, 12 H, *J* = 6.6 Hz), 1.66−1.73 (dqq, 2 H), 3.85 (dd, 2 H, *J* = 8.2 and 4.3 Hz), 3.85 (dd, 2H, *J* = 8.2 and 4.3 Hz), 4.26 (dd, 2H, *J* = 3.7 and 2.0 Hz), 5.76 (dt, 1 H, *J* = 17.8 and 2.1 Hz), 6.70 (dt, 1 H, *J* = 17.8 and 3.6 Hz); ^{13}C NMR δ 140.1, 106.5, 84.1, 33.0, 25.7, 17.8, 16.6, −5.2; ^{11}B NMR δ 32.8; exact mass calcd for $C_{17}H_{35}BO_3Si$ *m/e* 326.2448, found *m/e* 326.2452.

4b: 47%; bp 146 °C/0.1 mmHg; ^{1}H NMR δ 0.07 (s, 6 H), 0.92 (s, 9 H), 0.92 (d, 12H, *J* = 6.6 Hz), 1.66−1.73 (m, 2H), 3.85 (dd, 2 H, *J* = 8.2 and 4.3 Hz), 4.26 (dd, 2H, *J* = 3.7 and 2.0 Hz), 5.76 (dt, 1 H, *J* = 17.8 and 2.1 Hz), 6.70 (dt, 1H, *J* = 17.8 and 3.6 Hz); ^{13}C NMR δ 140.1, 129.0, 106.6, 83.4, 43.0, 28.3, 27.3, 26.0, 25.9, 25.7, −5.2; ^{11}B NMR δ 32.7; exact mass calcd for $C_{23}H_{43}BO_3Si$ *m/e* 406.3075, found *m/e* 406.3074.

4c: 67%; bp 165 °C/0.4 mmHg; ^{1}H NMR δ 0.12 (s, 6 H), 0.91 (s, 9 H), 1.30 (d, 12 H, *J* = 6.7 Hz), 1.68 (d, 2 H, *J* = 6.4 Hz), 4.77 (s, 2 H), 5.04 (dt, 1 H, *J* = 12.0 and 7.5 Hz), 5.12 (qq, 2 H, *J* = 6.3 Hz), 6.26 (dt, 1 H, *J* = 12.0 and 1.3 Hz); ^{13}C NMR δ 169.3, 140.8, 104.9, 77.7, 76.2, 69.9, 25.4, 21.6, −5.4; ^{11}B NMR δ 36.0; exact mass calcd for $C_{19}H_{35}BO_7Si$ *m/e* 414.2245, found *m/e* 414.2245.

4d: 83%; bp 80 °C/0.15 mmHg; ^{1}H NMR δ 0.07 (s, 6 H), 0.92 (s, 9 H), 0.92 (d, 12H, *J* = 6.6 Hz), 1.66−1.73 (m, 2H), 3.85 (dd, 2H, *J* = 8.2 and 4.3 Hz), 4.26 (dd, 2H, *J* = 3.7 and 2.0 Hz), 5.76 (dt, 1 H, *J* = 17.8 and 2.1 Hz), 6.70 (dt, 1 H, *J* = 17.8 and 3.6 Hz); ^{13}C NMR δ 140.1, 106.3, 83.1, 25.8, 24.8, −5.2; ^{11}B NMR δ, 33.1; exact mass calcd for $C_{15}H_{31}BO_3Si$ *m/e* 298.2136, found *m/e* 298.2125.

Asymmetric *Anti*-α-Hydroxyallylation of Aldehydes (Table 2). A 25 mL flask charged with $[Ir(cod)(PPh_2Me)_2]PF_6$ (0.03 mmol) was flushed with argon. The catalyst was dissolved in ethyl acetate (5 mL), and then the hydrogen was bubbled into the solution through a syringe needle to give a light yellow solution of $[IrH_2(AcOEt)_2(PPh_2Me)_2]PF_6$. Argon was bubbled into the solution to remove the excess hydrogen, and the boronic ester (**5**, 1 mmol) was then added. After being stirred for 10 min at room temperature, the mixture was treated with ethylenediamine (0.06 mmol) to deactivate the catalyst. (L)-(+)-Diisopropyl tartarate (1.1 mmol) in toluene (5 mL) was added, and 2-propanol and solvents were then evaporated in vacuo (0.1 mmHg for 1 h) to give a viscous oil of **4c**. ^{1}H NMR analysis revealed the formation of *E*-**4c** with over 98% isomeric purity. The residue was disolved in toluene (5 mL). Molecular sieves 4A (0.05 g/mL) and cyclohexanecarboxaldehyde (0.5 mmol) were added at −78 °C. After being stirred for 5 h at −78 °C, the reaction mixture was quenched with 1 M aqueous HCl. The product was extracted with hexane, washed with aqueous Na_2CO_3, and finally dried over $MgSO_4$. Chromatography over silica gel with CH_2Cl_2 gave **7**. The enantiomeric excess value was determined to be 91% ee by ^{1}H NMR analysis of its (*R*)-(+)-MTPA ester.[8] The charac-

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teristic peak appeared at $\delta = 3.60$ (s, 3 H), while the minor peak apperared at $\delta = 3.53$ (s, 3 H).

A sequence of the isomerization of **5** and the Kugelrohr distillation gave the diisopropyl boronate **6** in a yield of 75%. **6** (*E*/*Z* = 99/1): bp 64 °C/0.1 mmHg; ^{1}H NMR δ 0.12 (s, 6 H), 0.91 (s, 9 H), 1.14 (d, 12 H, *J* = 6.1 Hz), 1.43 (d, 2 H, *J* = 7.6 Hz), 4.83 (qq, 2 H, *J* = 6.1 Hz), 5.05 (dt, 1 H, *J* = 12.0 and 7.5 Hz), 6.17 (dt, 1 H, *J* = 12.1 and 1.5 Hz); ^{13}C NMR δ 139.5, 108.0, 65.2, 25.8, 24.6, −5.2; ^{11}B NMR δ 31.4; exact mass calcd for $C_{15}H_{33}BO_3Si$ *m*/*e* 300.2292, found *m*/*e* 300.2288.

7a: ^{1}H NMR δ 0.06 (d, 6 H, *J* = 7.6 Hz), 0.90 (s, 9 H), 0.96−2.03 (m, 11 H), 2.37 (d, 1 H, *J* = 2.0 Hz), 3.29 (ddd, 1 H, *J* = 7.9, 4.0 and 2.0 Hz), 4.19 (dd, 1 H, *J* = 6.3 and 4.4 Hz), 5.22 (d, 1 H, *J* = 10.4 Hz), 5.25 (d, 1 H, *J* = 17.2 Hz), 5.87 (ddd, 1 H, *J* = 17.2, 10.4 and 6.8 Hz); ^{13}C NMR δ 136.2, 117.1, 78.6, 74.8, 39.0, 28.9, 28.8, 26.5, 26.0, 25.8, 18.2, −4.3, −5.0; exact mass calcd for $C_{12}H_{23}O_2Si$ ($M^+ - t$-Bu) *m*/*e* 227.1467, found *m*/*e* 227.1466; $[\alpha]^{17}_D$= −7.9° (*c*=1.00, $CHCl_3$).

7b: ^{1}H NMR δ 0.06 (d, 6 H, *J* = 9.5 Hz), 0.89 (t, 3 H, *J* = 7.1 Hz), 0.90 (s, 9 H), 1.26−1.58 (m 8 H), 2.19 (d, 1 H, *J* = 3.4 Hz), 3.56 (dt, 1 H, *J* = 12.0 and 3.9 Hz), 4.03 (dd, 1 H, *J* = 6.7 and 4.0 Hz), 5.20 (d, 1 H, *J* = 10.5 Hz), 5.22 (d, 1 H, *J* = 17.3 Hz), 5.83 (ddd, 1 H, *J* = 17.3, 10.5 and 7.0 Hz); ^{13}C NMR δ −4.9, −4.3, 14.0, 18.2, 22.6, 25.5, 25.8, 31.9, 74.7, 77.2, 117.0, 136.8; exact mass calcd for $C_{11}H_{23}O_2Si$ ($M^+ - t$-Bu) *m*/*e* 215.1468, found *m*/*e* 215.1476; $[\alpha]^{17}_D = +0.9°$ (*c* = 1.01, $CHCl_3$).

7c: ^{1}H NMR δ −0.03(d, 6 H, *J* = 18.8 Hz), 0.87 (s, 9 H), 2.56 (d, 1 H, *J* = 2.7 Hz), 4.24 (dd, 1 H, *J* = 6.1 and 5.1 Hz), 4.65 (dd, 1 H, *J* = 5.0 and 3.0 Hz), 5.16 (d, 1 H, *J* = 10.5 Hz), 5.21 (d, 1 H, *J* = 17.3 Hz), 5.70 (ddd, 1 H, *J* = 17.1, 10.5 and 6.2 Hz), 7.23−7.34 (m, 5 H); ^{13}C NMR δ −5.2, −4.6, 18.2, 25.8, 78.1, 117.3, 126.8, 127.5, 128.0, 136.7, 140.2; exact mass calcd for $C_{12}H_{17}O_2Si$ ($M^+ - t$-Bu) *m*/*e* 221.0998, found *m*/*e* 221.1000; $[\alpha]^{25}_D = -20.2°$ (*c* = 0.70, $CHCl_3$).

7d: ^{1}H NMR δ 0.07 (d, 6 H, *J* = 8.8 Hz), 0.91 (s, 9 H), 1.69 (s, 3 H), 1.74 (s, 3 H), 2.15 (d, 1H, *J* = 3.2 Hz), 4.06 (dd, 1 H, *J* = 6.0 and 5.9 Hz), 4.29 (ddd, 1 H, *J* = 10.2, 5.9 and 3.7 Hz), 5.15 (d, 1 H, *J* = 8.8 Hz), 5.19 (d, 1 H, *J* = 10.5 Hz), 5.24 (d, 1 H, *J* = 17.3 Hz), 5.83 (ddd, 1 H, *J* = 17.1, 10.5 and 6.5 Hz); ^{13}C NMR δ −4.9, −4.4, 18.2, 18.5, 25.8, 28.9, 71.8, 116.8, 123.4, 136.7, 137.1; exact mass calcd for $C_{14}H_{27}OSi$ (M^+-OH) 239.1831, found 239.1829; $[\alpha]^{17}_D = -15.5°$ (*c* = 1.07, $CHCl_3$).

7e: ^{1}H NMR δ 0.09 (d, 6 H, *J* = 9.5 Hz), 0.92 (s, 9 H), 2.39 (d, 1 H, *J* = 3.9 Hz), 4.20 (dd, 1 H, *J* = 6.3 and 4.4 Hz), 4.24 (ddd, 1 H, *J* = 6.5, 4.4 and 3.8 Hz), 5.23 (d, 1 H, *J* = 10.5 Hz), 5.28 (d, 1 H, *J* = 17.1 Hz), 5.87 (ddd, 1 H, *J* = 17.2, 10.6 and 6.5 Hz), 6.19 (dd, 1 H, *J* = 16.0 and 6.5 Hz), 6.64 (d, 1 H, *J* = 16.0 Hz), 7.21−7.39 (m, 5 H); ^{13}C NMR δ −4.9, −4.4, 18.2, 25.8, 75.8, 77.3, 117.2, 126.5, 127.6, 127.8, 128.5, 131.9, 136.9; exact mass calcd for $C_{14}H_{19}O_2Si$ ($M^+ - t$-Bu) *m*/*e* 247.1154, found *m*/*e* 247.1174; $[\alpha]^{24}_D = +2.3°$ (*c* = 0.66, $CHCl_3$).

Supporting Information Available: ^{1}H NMR spectra of **3**−**7** (15 pages). The material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal and can be ordered from the ACS; see any current masthead page for ordering information.

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