Experimental Section

Melting points are uncorrected. NMR spectra were taken of solutions in $CDCl_3$ on a Bruker WP 200SY or AC 80 and IR spectra of solutions in $CHCl_3$ on a Perkin-Elmer 681. A UV spectrum in ethanol was taken on a Perkin-Elmer 550 SE. Mass spectra were determined on a VG ZAB-2F.

Reaction of Precocene II (2) with Iron(III) Chloride/Acetic Acid. Precocene II (**2**, 40 mg) was treated with ferric trichloride (80 mg) in acetic acid (0.5 mL) at room temperature for 4 h. The usual workup and chromatography of the residue eluting with light petroleum ether/ethyl acetate (4:1) afforded **5**: 26 mg; IR 3010, 3000, 2920, 2820, 1610, 1500, 1460, 1450, 1440, 1270,1130, 1010 cm^{-1}; UV, 236 nm, 286, 337; ^1H NMR (200 MHz) δ 1.52 (12 H, s), 3.82 and 3.84 (each 6 H, s), 6.19, 6.45, and 6.55 (each 2 H, s); MS, m/z (rel intens) 438 (M^+, 60), 423 (100), 219.5 (2), 219 (9), 211.5 (2), 211 (1), 204.5 (10), 204 (38), 196.5 (2), 196 (6); mass spectrum, exact mass calcd for $C_{26}H_{30}O_6$ 438.2034, found m/z 438.2042.

Reaction of Dimer B (3) with Iron(III) Chloride/Acetic Acid. Dimer B (**3**, 23 mg) was treated with ferric trichloride/acetic acid as above. Chromatography of the mixture of products obtained eluting with light petroleum ether/ethyl acetate (4:1) afforded dimer C (**4**, 20 mg) and the 3,3'-dimer (**5**, 3 mg).

Treatment of Dimer C (4) with Acetic Anhydride/Perchloric Acid. The dimer C (**4**, 300 mg) in benzene (1 mL) was treated with acetic acid (1 mL), acetic anhydride (1 mL), and perchloric acid (one drop) for 2 h. Usual workup and chromatography gave **5** (217 mg).

Treatment of the Dimer 6 with DDQ. The dimer **6** (150 mg)[15] in benzene (50 mL) was treated with DDQ (150 mg) at reflux for 5 h. The solution was filtered, washed with 2 M sodium hydroxide solution, and evaporated. The residue was crystallized from methanol affording **7**: 90 mg; mp 150–152 °C, IR 3000, 2980, 2960, 2810, 1610, 1500, 1460, 1450, 1440, 1400, 1380, 1350, 1290, 1270, 1240, 1190, 1130, 1080, 1010, 950, 900, 840 cm^{-1}; ^{1}NMR (200 MHz) δ 1.39 (3 H, s), 1.41 (9 H, s), 3.73, 3.81, 3.83, and 3.84 (each 3 H, s), 5.34 (1 H, s, H-4), 6.20 (1 H, s, H-3'), 6.44, 6.47, 6.57, and 6.72 (each 1 H, s, Ph-H); MS, m/z (rel intens) 438 (M^+, 70), 423 (100), 269 (13), 243 (33), 232 (14), 219 (9), 211.5 (5), 204 (52); mass spectrum, exact mass calcd for $C_{26}H_{30}O_6$ 438.2042, found m/z 438.2029.

Acknowledgment. We thank the CAICYT (Madrid) for financial support.

Registry No. **2**, 644-06-4; **3**, 89004-21-7; **4**, 89064-12-0; **5**, 110271-54-0; **6**, 17678-76-1; **7**, 110271-55-1.

Preparation of (3*S*,4*S*)-2,5-Dimethyl-3,4-hexanediol [(*S*)-DIPED] from (*R*,*R*)-Tartaric Acid via Trimethylsilyl Chloride Catalyzed Acetylation of a Hindered 1,4-Diol

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Directed asymmetric synthesis via α-chloro boronic esters is a powerful new synthetic tool.[1-3] The original chiral director used was pinanediol derived from α-pinene, and it was noted that oxygenated chiral directors such as diacetone mannitol or tartrate esters failed.[1] Pinanediol boronic esters are sterically hindered and difficult to hydrolyze.[1]

(*R*,*R*)-2,3-Butanediol boronic esters can be hydrolyzed and have desirable C_2 symmetry, though limited diastereoselectivity (20:1).[4] More recently we have reported 30:1 diastereomeric ratios from the use of (3*S*,4*S*)-2,5-dimethyl-3,4-hexanediol (diisopropylethanediol, DIPED, **7**) as chiral director.[5] The reagent was made efficiently by our previous diol synthesis,[2] but prior preparation of pinanediol was required. In view of the potential utility of DIPED in the α-chloro boronic ester synthesis, as well as in other syntheses which utilize simple chiral diols as directors,[6,7] we undertook the synthesis of DIPED from tartaric acid.

The quantitative conversion of L-tartaric acid to the methyl ester acetonide[8] (**1**) was followed by straightforward methylation with methylmagnesium bromide to yield the bis(tertiary diol) **2**.[9] After brief attempts to convert **2** to diolefin **5** via a methanesulfonate,[10] we undertook the acetate pyrolysis route.

Attempted acetylation of the very hindered diol **2** by standard means yielded mixtures containing substantial amounts of monoacetylated diol. Thus, acetyl chloride and dimethylaniline with **2** in ether refluxed overnight, conditions which convert *tert*-butyl alcohol to the acetate,[11] yielded the monoacetate of **2**. Acetic anhydride, 4-(dimethylamino)pyridine (1 equiv), and triethylamine (1.7 equiv) with **2** at 25 °C for 48 h[12] yielded a 2:1 mixture of the diacetate **3** and the monoacetate, but an attempt to improve the conversion to **3** by refluxing failed.

Trimethylsilyl chloride in acetic anhydride has been reported to be an efficient acetylating agent.[13] This combination with **2** at 25 °C overnight yielded a 3:2 mixture of monoacetate to diacetate **3** but gave exclusively **3** within a few hours at 85 °C. The original rationale for this process was a postulated formation of acetylium ion, CH_3CO^+,[13] and our results are perhaps consistent with the formation of a low equilibrium concentration of this intermediate. However, the large excess of reactants originally specified[13] is not necessary, and trimethylsilyl chloride is not consumed in the reaction. Nearly quantitative diacetylation was achieved with only a catalytic amount (10 mol %) of trimethylsilyl chloride. Without trimethylsilyl chloride, acetic anhydride reacted very slowly with **2** to form a small amount of monoacetate barely detectable by TLC.

Ester pyrolysis of **3** proved efficient at the optimum temperature and flow rate, but as the temperature rose

(1) Matteson, D. S.; Ray, R.; Rocks, R. R.; Tsai, D. J. *Organometallics* **1983**, *2*, 1536-1543.
(2) Matteson, D. S.; Sadhu, K. M.; Peterson, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 812-819.
(3) Matteson, D. S.; Sadhu, K. M.; Ray, R.; Peterson, M. L.; Majumdar, D.; Hurst, G. D.; Jesthi, P. K.; Tsai, D. J. S.; Erdik, E. *Pure Appl. Chem.* **1985**, *57*, 1741-1748.
(4) Sadhu, K. M.; Matteson, D. S.; Hurst, G. D.; Kurosky, J. M. *Organometallics* **1984**, *3*, 804-806.
(5) Matteson, D. S.; Kandil, A. A. *Tetrahedron Lett.* **1986**, *27*, 3831-3834.
(6) Johnson, W. S.; Harbert, C. A.; Stipanovic, R. D. *J. Am. Chem. Soc.* **1968**, *90*, 5279-5280.
(7) (a) Mash, E. A.; Nelson, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 8256-8258. (b) Nelson, K. A.; Mash, E. A. *J. Org. Chem.* **1986**, *51*, 2721-2724.
(8) Carmack, M.; Kelley, C. J. *J. Org. Chem.* **1968**, *33*, 2171-2173.
(9) **2** has also been made by: Mash, E. A.; Nelson, K. A.; Heidt, P. C. *Tetrahedron Lett.* **1987**, *28*, 1865-1868. The yield was nearly quantitative on a small scale at much higher dilution than our procedure (Mash, E. A., personal communication, 1987).
(10) Treatment of **2** with methanesulfonyl chloride and triethylamine [Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195-3196] yielded black tar. With methanesulfonyl chloride and pyridine, **2** yielded an unidentified unsymmetrical product which contained no SO_2CH_3 or OH peaks in NMR spectrum.
(11) Hauser, C. R.; Hudson, B. E.; Abramovitch, B.; Shivers, J. C. *Organic Synthesis*; Wiley: New York, 1955; Collect. Vol. 3, 142-144.
(12) Höfle, G.; Steglich, W. *Synthesis* **1972**, 619-621.
(13) Barua, N. C.; Sharma, R. P.; Baruah, J. N. *Tetrahedron Lett.* **1983**, *24*, 1189-1190.

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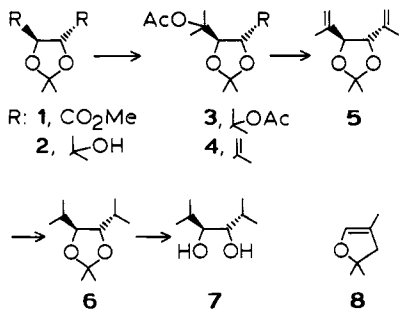

above the point where some recycling of the monoelimination product 4 was necessary, a byproduct identified as 2,2,4-trimethyl-2,3-dihydrofuran (8) began to appear in substantial quantities. Formation of 8 may be initiated by cleavage of the doubly allylic ring bond, followed by loss of 2-methylpropenal (not detected) and ring closure. It is very difficult to separate 8 from 5 by fractional distillation, and it is not necessary. Large amounts of 8 can lead to minor loss of 7 during purification.

Hydrogenation of 5 over rhodium was followed by hydrolysis of 6, which required extended reflux with aqueous ethanolic acid. DIPED (7) is volatile with steam, and careful fractionation of the ethanol from the aqueous hydrolysis medium proved necessary in order to concentrate the DIPED efficiently.

Experimental Section

General Data. Methylmagnesium bromide was purchased from Aldrich Chemical Company. Instruments used included a Nicolet NT-200 and a JEOL FX-90Q NMR spectrometer, a VG Instruments 7070 EHF mass spectrometer, a Jasco DIP-181 digital polarimeter, and a Thomas-Hoover melting point apparatus (glass capillary tubes, uncorrected). Microanalyses were done by Galbraith Laboratories, Knoxville TN.

(4*R*,5*R*)-2,2-Dimethyl-4,5-bis(1-hydroxy-1-methylethyl)-1,3-dioxolane (2). A solution of 218 g (1.00 mol) of dimethyl (2*R*,3*R*)-2,3-*O*-isopropylidenetartrate (1) prepared from L-tartaric acid[8]) in 300 mL of diethyl ether was added dropwise to a vigorously stirred solution of 5 mol of methylmagnesium bromide in 3.2 L of diethyl ether (or preferably more, to reduce gum formation).[9] The vigorously exothermic reaction was coontrolled with an ice–water bath and a reflux condenser. Toward the end of the addition, a gummy phase separated, making stirring difficult. After standing overnight, the mixture was treated with excess saturated aqueous ammonium chloride (*CAUTION*:methane evolution) and stirred until all was dissolved (2 h). The ether extracts were dried over sodium sulfate and concentrated. The solid was washed with light petroleum (bp 30–60 °C) and filtered: 148–179 g (68–82%); mp 152–154 °C; 90-MHz ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 6), 1.32 (s, 6), 1.37 (s, 6), 3.74 (s, 2), 3.87 (br s, 2 O*H*). Anal. Calcd for $C_{11}H_{22}O_4$: C, 60.52; H, 10.16. Found: C, 60.41; H, 10.24.

(4*R*,5*R*)-2,2-Dimethyl-4,5-bis(1-acetoxy-1-methylethyl)-1,3-dioxolane (3). To 186.4 g (0.854 mol) of 2 in 930 mL of acetic anhydride was added 8.2 mL (0.086 mol) of chlorotrimethylsilane. The mixture was stirred 16–24 h in a bath at 85–95 °C. Thin-layer chromatography indicated that the reaction was complete. The acetic anhydride was distilled at 15–30 Torr and finally at 1 Torr. The residue of 3 was used directly in the next step or was distilled rapidly at 105–120 °C (0.02 Torr), 252.8 g (98%), crystallized on standing or seeding. The analytical sample was recrystallized from light petroleum (bp 30–60 °C); mp 58–60 °C; 200-MHz ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6), 1.53 (s, 6), 1.60 (s, 6), 2.01 (s, 6), 4.05 (s, 2). Anal. Calcd for $C_{15}H_{26}O_6$: C, 59.58; H, 8.67. Found: C, 59.68; H, 8.69.

(4*R*,5*R*)-2,2-Dimethyl-4-(1-hydroxy-1-methylethyl)-5-(1-acetoxy-1-methylethyl)-1,3-dioxolane ("Monoacetate"). Attempted preparation of 3 by acetylation of 2 with acetyl chloride/pyridine yielded a mixture of the diacetate 3 together with the monoacetate, which was isolated by chromatography on silica with 3:1 light petroleum/diethyl ether: 200-MHz NMR ($CDCl_3$) δ 1.25 (s, 3), 1.29 (s, 3), 1.44 (s, 6), 1.57 (s, 3), 1.59 (s, 3), 2.00 (s, 3), 2.19 (s, 1, OH) 3.97 (s, 2); mass spectrum (70 eV) [molecular ion not observed], calcd for $C_{12}H_{21}O_5$ (M – 15) 245.1389, found, 245.1407.

(4*S*,5*S*)-2,2-Dimethyl-4,5-bis(1-methylvinyl)-1,3-dioxolane (5). A 2.5 cm diameter Vycor pyrolysis tube packed with a 20-cm section of quartz chips was mounted vertically in a tube furnace and heated under a 5–20 mL/min flow of argon to 450–470 °C measured by a thermocouple at the center of the heated zone in a well down the center of the tube. Small-scale runs were carried out first to optimize conditions for the particular apparatus used. A solution of 250 g (0.83 mol) of 3 in 100–250 mL of acetone was added at the rate of 20 drops/min to the top of the tube. The product was trapped at −78 °C, and a very small amount was collected in a second trap. The product was concentrated under vacuum, then dissolved in ether, and washed twice with water followed by aqueous sodium bicarbonate. The organic layer was dried over sodium sulfate, concentrated, and distilled to yield 117–137 g of crude diene 5, bp 51–65 °C (4 Torr). If the pyrolysis temperature/time was a little too low, as indicated by the presence of NMR peaks characteristic of the monoacetoxy alkene 4 (next paragraph), the higher boiling residue was repyrolyzed, and the total yield of 5 was as high as 85%. If the pyrolysis temperature was a little too high, the product contained a substantial amount (15–20%) of the byproduct 8: most prominent ^{1}H NMR peak at δ 1.1 (s), bp slightly lower than that of 5. A 74-g sample of 98% pure 5 was obtained by distillation through a 30-cm column packed with stainless steel helices: bp 46–47 °C (2.0 Torr); 200-MHz ^{1}H NMR ($CDCl_3$) δ 1.11 (impurity, s, 2% of 6), 1.46 (s, 6, C(CH_3)$_2$), 1.77 (m, 6, C=CC*H*$_3$), 4.19 (s, 2, OC*H*), 4.97 (m, 2, C=C*H*H), 5.04 (m, 2, C=CH*H*); 22.6-MHz ^{13}C NMR ($CDCl_3$) δ 17.52, 27.05, 83.13, 108.81, 114.30, 141.47; d^{20} 0.909; $[\alpha]^{25}_{546}$ +27.1° (neat); $[\alpha]^{25}_{365}$ +89.5° (neat); $[\alpha]^{25}_{546}$ −12.4° (*c* 1.4, toluene); $[\alpha]^{25}_{365}$ −33.1° (*c* 1.4, toluene). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.51; H, 9.62.

2,2-Dimethyl-4-(1-methylethenyl)-5-(1-acetoxy-1-methylethyl)-1,3-dioxolane (4). This compound, bp 104–108 °C (3.5 Torr), was obtained as a byproduct when the temperature of pyrolysis of 3 was a little low: 90-MHz NMR ($CDCl_3$) δ 1.43 (s, 6), 1.52 (s, 6), 1.82 (s, 3), 2.00 (s, 3), 4.16 (d, J = 8 Hz, C*H*OR), 4.41 (d, J = 8 Hz, C'*H*OR), 4.9–5.2 (m, 2, C=CH_2). No further characterization was attempted, but repyrolysis of the neat liquid yielded 5.

(3*S*,4*S*)-2,5-Dimethyl-3,4-hexanediol (DIPED, 7). A solution of 73.9 g (0.405 mol) of dioxolane 5 (purity 98%) in 300–400 mL of absolute ethanol was hydrogenated at 1 atm in the presence of 7.4 g of 5% rhodium on alumina catalyst overnight. The catalyst was filtered and rinsed with ethanol. The ethanol solution was mixed with 420 mL of 2 M aqueous hydrochloric acid, and the mixture was refluxed for 43 h. The acetone and ethanol were distilled through a 30-cm fractionating column packed with glass helices until most of the ethanol had been recovered, and the mixture in the still pot was separated into two phases. The mixture was cooled, saturated with sodium chloride (100 g), and extracted with three 100–200-mL portions of ether. The ether solution was washed with aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated. The residue of DIPED (7) sublimed at 65 °C (0.01 Torr): 53.1 g (89%); mp 74–76 °C (lit.[5] mp 72–74 °C); 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.95 (d, J = 6.6 Hz, 12, CH(CH_3)$_2$), 1.70–1.91 (m, 2, C*H*(CH_3)$_2$), 2.15 (br s, 2, O*H*), 3.31 (m, 2 C*H*OH) (lit.[5] 90-MHz spectrum similar); 22.6-MHz ^{13}C NMR ($CDCl_3$), similar to that reported[5] but shifted δ 0.7–1.3 upfield. $[\alpha]^{25}_{546}$ +1.3°, $[\alpha]^{25}_{365}$ +8.2° (*c* 2.7 toluene); $[\alpha]^{25}_{D}$ −2.6° (*c* 2.4, methanol); $[\alpha]^{25}_{577}$ −3.4°, $[\alpha]^{25}_{546}$ −3.78°, $[\alpha]^{25}_{435}$ −6.1°, $[\alpha]^{25}_{365}$ −8.3° (*c* 4.2, methanol). Similar hydrogenation and hydrolysis of a 71/29 mixture (by weight) of 5 and 8 (28.1 g) yielded 12.3 g (77%) of 7, mp 68–72 °C.

(4*S*,5*S*)-2,2-Dimethyl-4,5-bis(1-methylethyl)-1,3-dioxolane (6). For synthetic purposes, this intermediate was normally not isolated. For partial characterization, hydrogenation of 5 was followed by fractional distillation of ethanol and 6: bp 62–70 °C (9 Torr); 89%; 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.92 (d, J = 2.9 Hz, 6), 1.00 (d, J = 2.9 Hz, 6), 1.38 (s, 6), 1.6–1.9 (m, 2), 3.45–3.67 (m, 2); 22.6-MHz ^{13}C NMR ($CDCl_3$) δ 17.52, 19.84, 27.71, 31.40, 84.26, 108.10. Hydrolysis of 6 in 1 M hydrochloric acid in 1:1 ethanol/water overnight yielded 88% DIPED (7).

Identification of 2,2,4-Trimethyl-2,3-dihydrofuran (8). Forerun from the pyrolysis of **3** at above the optimum temperture was fractionated to yield a small amount of unidentified yellow distillate, bp 35–44 °C (2 Torr), and a fraction, bp 43–44 °C (2.0 Torr), which contained a 70/30 mol ratio of **8** and **5** by NMR analysis: 200-MHz ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 6, CCH_3), 2.12 (m, J = 1 Hz, 3, C=$CCH)_3$, 2.44 (m, J = 1 Hz, 2, CH_2), 5.86 (m, J small, C=CH); GC–M, m/e calcd for $C_7H_{12}O$ 112.0888, found, 112.062 (±0.015).

Acknowledgment. We thank the National Institutes of Health for support (Grant GM33801) and the Boeing Corporation for partial support of purchase of the departmental Nicolet NT-200 NMR instrument.

Registry No. **1**, 37031-29-1; (4*R*,5*R*)-**2**, 81706-69-6; (4*R*,5*R*)-**3**, 110373-86-9; (4*R*,5*R*)-**3** (monoacetate), 110373-88-1; **4**, 110373-87-0; (4*S*,5*S*)-**5**, 110454-08-5; (4*S*,5*S*)-**6**, 110454-09-6; (3*S*,4*S*)-**7**, 109785-53-7; **8**, 102548-10-7.

Vinyl Triflate Syntheses Using Polymer-Bound 2,6-Di-*tert*-butylpyridine

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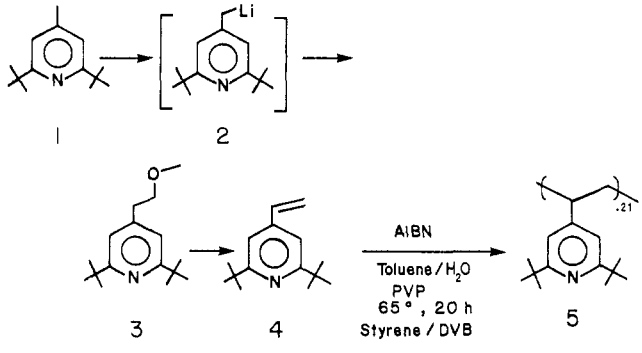
Polymer-bound organic reagents often provide advantages over their homogeneous counterparts.[1] For instance, ease of workup, higher yields, and sometimes enhanced product selectivity have largely contributed to their popularity. In the case of expensive reagents, recovery of the reagent is important from an economical viewpoint.

Nonnucleophilic organic bases represent an important class of reagents which have been utilized in a variety of applications.[2] Surprisingly, only two examples have been reported where a sterically hindered nonnucleophilic base has been incorporated into a polymer.[3,4] In the most recent case, we presented a new and improved synthesis of 4-vinyl-2,6-di-*tert*-butylpyridine (**4**) and its suspension copolymerization with styrene and divinylbenzene.[4]



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(4) Wright, M. E.; Pulley, S. R. *J. Org. Chem.* **1987**, *52*, 1623.

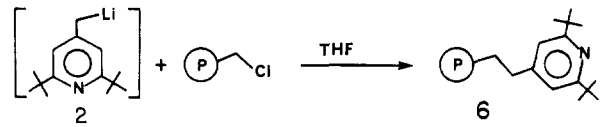
Table I. Vinyl Triflate Synthesis Using 6

ketone	solvent	time, h	temp, °C	products (% yield)
ref 5	CH_2Cl_2	24	25	**7** (57), **8** (18)
	pentane	24	25	**7** (40), **8** (14)
	CCl_4	24	25	**7** (86)
ref 10	CCl_4	48	40	OTf (58)
ref 11	CCl_4	24	25	OTf + OTf (90) (10)[a]

[a] Isolated yield of both isomers, 83%.

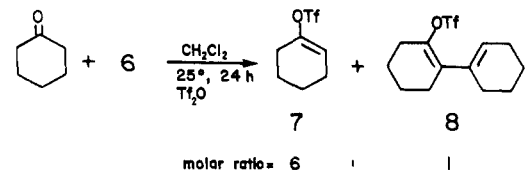
In this paper we wish to report a two-step, quantitative, incorporation of 2,6-di-*tert*-butylpyridine into polystyrene (1% cross-linked) beads and the unique reactivity pattern which we have observed from the polymer-bound base.

Treatment of porous chloromethylated polystyrene beads (1% cross-linked) with **2** gave a quantitative conversion to the copolymer **6**. The copolymer beads are clear



and colorless, and retain excellent swelling properties in benzene, tetrahydrofuran (THF), and methylene chloride. It is noteworthy to mention that copolymer **6** is quite different from copolymer **5** in that the pyridine moiety in the former is located considerably farther from the polymer backbone.

Since **1** has been shown to be the base of choice in vinyl triflate syntheses when using Tf_2O,[5-7] we decided to explore the use of the polymer-bound version. Not only did the reaction of cyclohexanone with triflic anhydride and **6** in methylene chloride produce the expected vinyl triflate **7** but a new product was isolated, which we have assigned the structure of **8**.[8] Compound **8** would appear to be



formed from a sequence of reactions, first of which is an aldol condensation of cyclohexanone, then a "dehydration step", and finally reaction of the unsaturated ketone with Tf_2O to form the diene triflate. Diluting the reaction one-fold caused the ratio of **7**/**8** to increase to 12. In addition, if the ratio of base to ketone was increased we also observed an increase in the ratio of **7**/**8**. In examining the formation of **7** using **1**, we do find minor (≤5%) amounts of **8** are present in the crude product. However,

(5) Stang, P. J.; Treptow, W. *Synthesis*, **1980**, 283.

(6) The pyridine base **I** can be recovered using a slightly modified procedure: Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438.

(7) Vinyl triflates can also be prepared in high yield, however, under strongly basic conditions, from the reaction of metal-enolates and $PhNTf_2$: McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979. Crisp, G. T.; Scott, W. J. *Synthesis* **1985**, 335.

(8) Spectroscopic data for **8**: ^{1}H NMR ($CDCl_3$) 5.63 (m, 1 H), 2.32 (m, 2 H), 2.18 (m, 2 H), 2.03 (m, 4 H), 1.75 (m, 2 H), 1.60 (m, 6 H); ^{13}C NMR ($CDCl_3$) 141.9, 133.6, 133.5, 127.3, 118.3 (CF_3, q, J = 319 Hz), 29.0, 27.7, 26.9, 25.1, 23.0, 22.6, 21.83, 21.80.

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