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RUTHENIUM-CATALYZED ALLYLIC SUBSTITUTION OF ALLYLIC CYCLIC CARBONATES

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Abstract: Allylic substitution of allylic cyclic carbonates with PhSH or PhOH in the presence of $CpRu(PPh_3)_2Cl$ (5 mol %) afforded (*E*)-allylic alcohol and *erythro*-β-hydroxy thiophenoxide or phenoxide respectively, *via* external attack of nucleophiles to π-allyl ruthenium complex.

Although palladium-catalyzed allylic substitution with carbon, nitrogen, oxygen, and sulfur nucleophiles *via* π-allyl complexes has been carried out extensively,[1] so far little has been known for ruthenium-catalyzed allylic substitution. Recently, Watanabe reported[2] Ru(cod)(cot)-catalyzed allylic alkylation of allylic carbonates with acetoacetates. As a part of our program to utilize allylic cyclic carbonates as substrates for metal-catalyzed reactions, we were interested in Ru-catalyzed allylic substitution of allylic and dienylic cyclic carbonates with oxygen and sulfur nucleophiles, which resulted in highly diastereoselective substitution.

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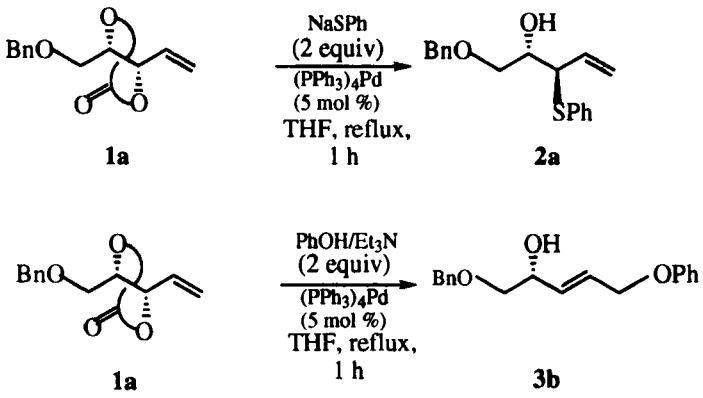
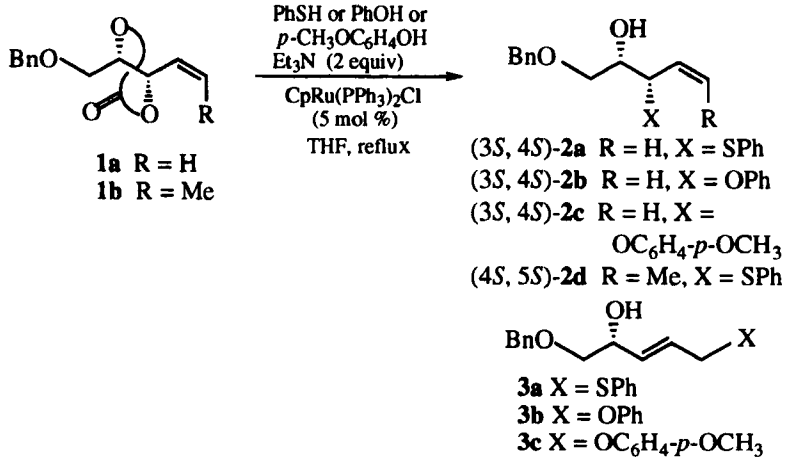


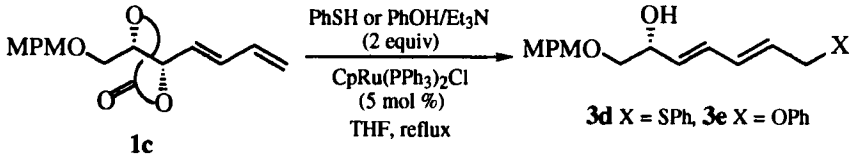
Scheme 1

Recently, we have reported $(PPh_3)_4Pd$-catalyzed substitution of NaSPh and PhOH with allylic and dienylic cyclic carbonates.[3] In the reaction of NaSPh with allylic cyclic carbonates **1a**, *threo*-β-hydroxy sulfide **2a** was obtained by internal transfer of thiophenoxide to carbon via π-allyl palladium complex. However, with PhOH and **1a**, (*E*)-allylic alcohol **3b** was afforded (Scheme 1).

To obtain different products which can be obtained from palladium catalysts, we have explored the Ru-catalyzed allylic substitution. Different from the results of Pd-catalyzed allylation of allylic cyclic carbonates, the reaction of allylic cyclic carbonates with PhSH and PhOH afforded a mixture of α- and γ-substituted products depending on the substrates, which are easily separable by SiO_2 column chromatography (Sheme 2).

In the reaction of **1a** with thiophenol, in addition to (*E*)-allylic alcohol **3a**, *erythro*-β-hydroxy sulfide **2a** was obtained which is in contrast to the diastereoselectivity associated with palladium-catalyzed *S*-alkylation of allylic cyclic carbonates. Presumably, in this system the substitution was proceeded by external attack of



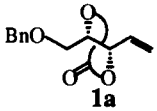
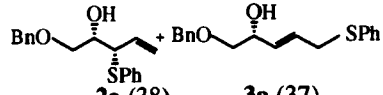
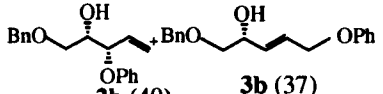
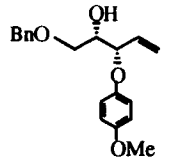
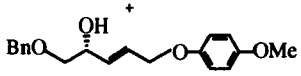
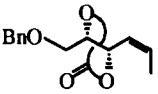
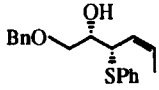
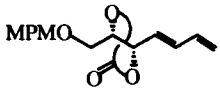
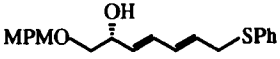
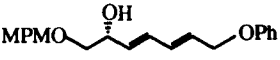


Scheme 2

thiophenol to carbon *via* π-allyl ruthenium complex with net retention. The results are summarized in Table 1.

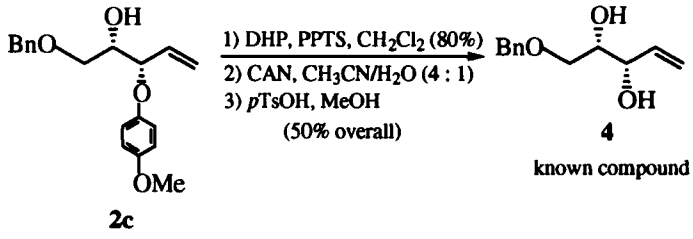
The optically active cyclic carbonate **1a** reacted with PhSH in the presence of Et_3N in refluxing THF for 1 h with $CpRu(PPh_3)_2Cl$ (5 mol %) as catalyst to give the *erythro*-β-hydroxy sulfide **2a** together with (*E*)-allylic alcohol **3a** in the ratio of ~1 : 1 in 75 % yield, which were easily separable by column chromatography (entry 1 in Table 1). In our hands, $RuH_2(PPh_3)_4$ and $RuCl_2(PPh_3)_3$ did not give the products. Treatment of **1a** with PhOH under the same conditions afforded *erythro*-

Table 1. Ruthenium [$CpRu(PPh_3)_2Cl$]-mediated Substitution of Allylic and Dienylic Cyclic Carbonates

Entry	Substrate	Nucleophile[a]	Reaction time (h)[b]	Product (Yield %)[c]
1	 **1a**	A	1	 **2a** (38) **3a** (37)
2	**1a**	B	1	 **2b** (40) **3b** (37)
3	**1a**	C	1	 **2c** (40) +  **3c** (40)
4	 **1b**	A	48	 **2d** (60)
5	 **1c**	A	4	 **3d** (71)
6	**1c**	B	6	 **3e** (55)

[a]A: PhSH, Et_3N; B: PhOH, Et_3N; C: *p*-methoxyphenol, Et_3N.[b]All the reactions were run in the presence of $CpRu(PPh_3)_2Cl$ (5 mol %) as catalyst in THF at reflux.[c]$[\alpha]_D^{25}$ values in $CHCl_3$. **3**: -25.2 (*c* 2.10); **5**: -3.90 (*c* 0.25); **7**: -4.80 (*c* 0.06); **6**: -8.41 (*c*1.13); **10**: -5.38 (*c* 0.59); **11**: -1.63 (*c*1.47); **12**: -85.6 (*c* 0.43); **13**: -2.22(*c* 0.32); **14**: +1.7 (*c* 0.20).

[d]The yields are isolated yields.

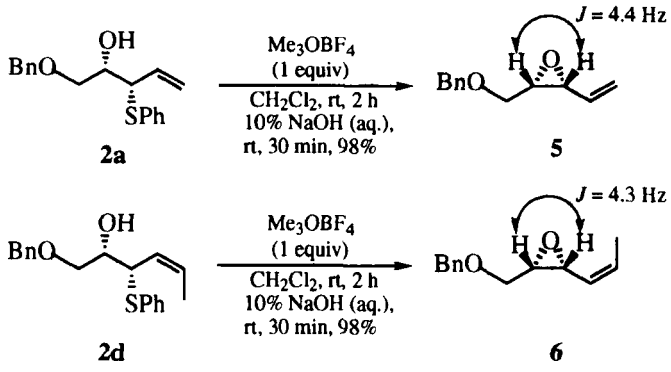


Scheme 3

β-hydroxy phenoxide **2b** and (*E*)-allylic alcohol **3b** (entry 2). Similarly, *p*-methoxyphenol was added to **1a** to afford a mixture of **2c** and **3c** (entry 3). To establish the stereochemistry of phenoxide introduced in **2c**, the compound **2c** was converted to the corresponding diol **4**, which is shown in Scheme 3. The alcohol **2c** was protected with DHP to furnish THP ether which was subsequently subjected to oxidative deprotection[4] of THP group afforded for *p*-methoxy group followed by deprotection afforded **4**.[5]

For the methyl-substituted allylic cyclic carbonate **1b**, only β-hydroxy sulfide **2d** was obtained after refluxing for 48 h, which suggested that the substitution reaction was very sensitive to steric effect (entry 4). To confirm the relative stereochemistry of the newly introduced C-S bonds in **2a** and **2d**, the β-hydroxy sulfides **2a** and **2d** were converted to the corresponding vinyl *cis*-epoxides **5** and **6**, respectively, by treating with trimethyloxonium tetrafluoroborate followed by treatment of 10% aqueous NaOH.[6] The *cis*-epoxide was inferred from ^{1}H NMR (300 MHz) coupling constants of the two vicinal protons of the epoxides (Scheme 4).

Finally, for dienylic cyclic carbonate **1c** with the nucleophiles PhOH and PhSH, ε-substituted (*E*,*E*)-dienylic alcohols **3d** and **3e** were afforded as the sole products (Scheme 2). In the case of PhSH, this result is in contrast to α-substituted product obtained with Pd catalyst.[3]



Scheme 4

Experimental Section

Typical procedures: Preparation of (3*S*, 4*S*)-5-Benzyloxy-*syn*-4-hydroxy-3-thiophenoxy-1-pentene (**2a**) and (4*S*)-5-Benzyloxy-4-hydroxy-1-thiophenoxy -(2*E*) -pentene (**3a**). To a stirred solution of the allylic cyclic carbonate **1b**(104 mg, 0.42 mmol), $CpRu(PPh_3)_2Cl$ (15.2 mg, 0.022 mmol) in dry THF (3 mL) under nitrogen atmosphere was added PhSH (94 mg, 0.86 mmol). After stirring for 1 h at reflux, the reaction mixture was cooled and THF was evaporated. The crude product was purified by SiO_2 column chromatography using EtOAc/hexanes (1 : 3, R_f = 0.56 and 0.44) to give **2a** (47.4 mg, 38%) and **3a**(46.8 mg, 37%). (**2a**): ^1H NMR (300 MHz, $CDCl_3$) δ2.78(bd, 1H, *J* = 3.8 Hz), δ 3.56 (dd, 1H, *J* = 9.8, 6.2 Hz), δ 3.67 (dd, 1H, *J* = 9.8, 3.4 Hz), δ 3.76 (dd, 1H, *J* = 16.1, 9.0 Hz) δ 3.85 (m, 1H) δ 4.51 (s, 2H) δ 5.01 (dd, 1H, *J* = 16.9, 1.1 Hz), δ 5.75 (ddd, 1H, *J* = 16.9, 10.2, 9.0 Hz), δ 6.88 (d, 2H, J = 8.5 Hz), δ 7.26 (m, 5H), δ 7.45 (m, 2H) IR (neat) 3442, 3062cm^{-1}. MS (m/e) 191,149, 110, 91 (base peak). $[\alpha]_D^{25}$ = -25.2 (*c* 2.10,

$CHCl_3$). (**3a**): ^1H NMR (200 MHz, $CDCl_3$) δ2.32 (bd, 1H, J = 2.9Hz), δ 3.25 (dd, 1H, J = 9.7, 7.6 Hz), δ 3.48 (dd, 1H, J = 9.7, 3.3 Hz) δ 3.54 (d, 2H, J = 6.9 Hz), δ 4.42 (m, 1H), δ 4.54 (s, 2H) δ 5.49 (dd, 1H, J = 15.3, 6.2 Hz), δ 5.83 (m, 3H) δ 7.30 (m, 7H). IR (neat) 3442, 3050, 1241cm^{-1}. MS (m/e) 300 (M^+), 160, 145, 133, 94, 91 (base peak). $[\alpha]_D^{25}$ = -8.41 (*c* 1.13, $CHCl_3$).

(3*S*, 4*S*)-5-Benzyloxy-*syn*-hydroxy-3-phenoxy-1-pentene (**2b**): TLC, SiO_2, EtOAc/hexanes 1 : 3, R_f = 0.37. ^1H NMR (300 MHz, $CDCl_3$) δ2.60 (bd, 1H, J = 4.7 Hz), δ 3.65 (m, 2H), δ 3.95 (m, 1H) δ 4.54 (s, 2H) δ 4.80 (dd, 1H, J = 6.0, 5.7 Hz), δ 5.31 (dd, 1H, J = 10.6, 1.3 Hz) δ 5.36 (dd, 1H, J = 17.4, 1.3 Hz) δ 5.89 (ddd, 1H, J = 17.4, 10.6, 6.0 Hz) δ 6.94 (m, 3H) δ 7.30 (m, 7H). IR (neat) 3375, 3061, 1238cm^{-1}. MS (m/e) 134, 94, 91 (base peak). $[\alpha]_D^{25}$ = -4.80 (*c* 0.06, $CHCl_3$).

(2*E*, 4*S*)-5-Benzyloxy-4-hydroxy-1-phenoxy-2-pentene (**3b**): TLC, SiO_2, EtOAc /hexanes 1 : 3, R_f = 0.22. ^1H NMR (300 MHz, $CDCl_3$) δ1.82 (bs, 1H), δ 3.40 (dd, 1H, J =9.6, 8.0 Hz), δ 3.57 (dd, 1H, J = 9.6, 3.4 Hz) δ 4.42 (m, 1H) δ 4.54 (d, 2H, J = 5.2 Hz), δ 4.58 (s, 2H) δ 5.88 (dd, 1H, J = 16.2, 6.3 Hz) δ 6.03 (dt, 1H, J = 16.2, 6.3 Hz) δ 6.92 (m, 3H) δ 7.33 (m, 7H). IR (neat) 3454, 3059, 1241cm^{-1}. MS (m/e) 184, 160, 145, 133, 94, 91 (base peak). $[\alpha]_D^{25}$ = -3.90 (*c* 0.25, $CHCl_3$).

(3*S*, 4*S*)-5-Benzyloxy-*syn*-hydroxy-3-(4-methoxyphenoxy)-1-pentene (**2c**): TLC, SiO_2, EtOAc/hexanes 1 : 3, R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$) δ2.60 (bd, 1H, J = 4.6 Hz), δ 3.61 (dd, 1H, J = 9.8, 5.6 Hz), δ 3.68 (dd, 1H, J = 9.8, 4.3 Hz), δ 3.95 (m, 1H) δ 4.55 (s, 2H), 4.75 (dd, 1H, J = 6.0, 5.7 Hz) δ 5.28 (dd, 1H, J = 10.6, 1.2 Hz), δ 5.31 (dd, 1H, J = 10.6, 1.3 Hz) δ 5.33 (dd, 1H, J = 17.4, 1.2 Hz) δ 5.87 (ddd, 1H, J = 17.4, 10.6, 6.0 Hz) δ 6.78 (m, 2H) δ 6.85 (m, 2H), 7.32 (m,

5H). IR (neat) 3465, 3064, 1506, 1226cm^{-1}. MS (m/e) 172, 128, 107, 91 (base peak) $[\alpha]_D^{25}$ = -5.38 (*c* 0.59, $CHCl_3$).

(2*E*, 4*S*)-5-Benzyloxy-4-hydroxy-1-(4-methoxyphenoxy)-2-pentene (**3c**): TLC, SiO_2, EtOAc/hexanes 1 : 3, R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (bd, OH, *J* = 3.4 Hz), δ 3.37 (dd, 1H, *J* =9.6, 7.9 Hz), δ 3.55 (dd, 1H, *J* = 9.6, 3.4 Hz), δ 3.76 (s, 3H), δ 4.42 (m, 1H) δ 4.47 (d, 2H, *J* = 5.3 Hz), δ 4.56 (s, 2H) δ 5.83 (dd, 1H, *J* = 15.6, 5.7 Hz) δ 6.04 (dt, 1H, *J* = 15.6, 5.3 Hz) δ 6.82 (m, 4H) δ 7.35 (m, 5H). IR (neat) 3457, 3031, 1507, 1230cm^{-1}. MS (m/e) 214, 124, 91 (base peak), 84. $[\alpha]_D^{25}$ = -1.63 (*c* 1.47, $CHCl_3$).

(2*Z*, 4*S*, 5*S*)-6-Benzyloxy-*syn*-hydroxy-4-thiophenoxy-2-hexene (**2d**): TLC, SiO_2, EtOAc/hexanes 1 : 2, R_f = 0.33. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.40 (d, 3H, *J* = 6.8 Hz) δ 2.90 (bd, 1H, *J* = 3.5 Hz), δ 3.48 (dd, 1H, *J* =9.8, 5.9 Hz), δ 3.53 (dd, 1H, *J* = 9.8, 2.9 Hz) δ 3.75 (m, 1H), δ 4.12 (dd, 1H, *J* = 10.5, 8.1 Hz), δ 4.50 (s, 2H), δ5.25 (dd, 1H, *J* = 10.6, 10.5 Hz), δ 5.53 (m, 1H), δ 7.32 (m, 8H), δ 7.48 (m, 2H). IR (neat) 3452, 3061, 1582cm^{-1}. MS (m/e) 314 (M^+), 164, 110, 91 (base peak). $[\alpha]_D^{25}$ = -85.58 (*c* 0.43, $CHCl_3$).

(2*E*, 4*E*, 6*S*)-7-*O*-(4-Methoxybenzyl)-6-hydroxy-1-thiophenoxy-(2, 4)-heptadiene (**3d**): TLC, SiO_2, EtOAc/hexanes 1 : 2, R_f = 0.27. ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.47 (bs, 1H), δ 3.30 (dd, 1H, *J* = 9.5, 8.4 Hz), δ 3.47 (dd, 1H, *J* = 9.5, 3.3 Hz), δ 3.59 (d, 2H, *J* = 7.6 Hz), δ 3.80 (s, 3H), δ 4.42 (m, 1H), δ 4.50 (s, 2H), δ 5.55 (dd, 1H, *J* = 14.8, 6.0 Hz), δ 5.70 (dt, 1H, *J* = 14.8, 7.6 Hz), δ 6.26 (dd, 1H, *J* = 14.8, 10.3 Hz), δ 6.90 (m, 3H), δ 7.28 (m,7H). IR (neat) 3434, 3000, 1612cm^{-1}. MS (m/e) 247, 137, 121(base peak), 110. $[\alpha]_D^{25}$ = -2.22 (*c* 0.32, $CHCl_3$).

(2*E*, 4*E*, 6*S*)-7-*O*-(4-Methoxybenzyl)-6-hydroxy-1-phenoxy-(2, 4)-heptadiene (**3e**): TLC, SiO_2, EtOAc/hexanes 1 : 3, R_f= 0.21. ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (bd, 1H, *J* = 2.8 Hz), δ 3.32 (dd, 1H, *J* = 9.7, 8.1 Hz), δ 3.49 (dd, 1H, *J* = 9.7, 3.4 Hz) δ 3.80 (s, 3H), δ 4.58 (d, 2H, *J* = 5.3 Hz), δ 5.62 (dd, 1H, *J* = 15.1, 4.2 Hz), δ 5.78 (m, 1H), δ 6.32 (d, 2H, *J* = 15.1 Hz), δ 6.85 (m, 3H), δ 7.24 (m, 5H). IR (neat) 3450, 1600, 1585cm^{-1}. MS (m/e) 180, 136, 121(base peak), 77. $[\alpha]_D^{25}$ = +1.7 (*c* 0.20, $CHCl_3$).

(3*S*, 4*S*)-5-Benzyloxy-*syn*-3, 4-dihydroxy-1-pentene (**4**): TLC, SiO_2, EtOAc/ hexanes 1 : 3, R_f= 0.17. ^1H NMR (400 MHz, $CDCl_3$) δ 2.55 (bd, 1H, *J* = 5.2 Hz), δ 2.60 (bd, 1H, *J* = 4.0 Hz) δ 3.57 (dd, 1H, *J* = 9.8, 5.8 Hz), δ 3.64 (dd, 1H, *J* = 9.8, 3.6 Hz), δ 3.68 (m, 1H), δ 4.18 (m, 1H), δ 4.53 (d, 1H, *J* =11.9 Hz), δ 5.23 (dd, 1H, *J* = 11.8, 1.5 Hz), δ 5.35 (dd, 1H, *J* = 16.8, 1.5 Hz), δ 5.23 (ddd, 1H, *J* = 16.8, 11.8, 4.4 Hz) δ 7.33 (m, 5H). IR (neat) 3396, 2897cm^{-1}. MS (m/e) 147, 119, 91 (base peak). $[\alpha]_D^{25}$ = -10.81 (*c* 0.18, $CHCl_3$).

(3*R*, 4*S*)-5-Benzyloxy-cis-3, 4-epoxy-1-pentene (**5**): TLC, SiO_2, EtOAc/ hexanes 1 : 3, R_f = 0.68. ^1H NMR (300 MHz, $CDCl_3$) δ 3.36 (dt, 1H, *J* = 5.6, 4.4 Hz), δ 3.57 (dd, 1H, *J* = 5.6, 4.4 Hz), δ 3.69 (dd, 1H, *J* = 11.3, 4.4 Hz), 3.74 (dd, 1H, *J* = 8.3, 4.3 Hz), δ 4.18 (m, 1H), δ 4.54 (d, 1H, J =12.0 Hz), δ 4.64 (d, 1H, *J* = 12.0 Hz), δ 5.35 (dd, 1H, *J* = 11.5, 1.1 Hz), δ 5.49 (dd, 1H, *J* = 16.6, 1.1 Hz), δ 5.68 (ddd, 1H, *J* = 16.6, 11.5, 6.9 Hz) δ 7.32 (m, 5H). IR (neat) 3031, 2925, 1453, 1097cm^{-1}. MS (m/e) 107, 91 (base peak), 84. $[\alpha]_D^{25}$ = -9.17 (*c* 0.1, $CHCl_3$).

(2*Z*, 4*R*, 5*S*)-6-Benzyloxy-*cis*-4, 5-epoxy-2-hexene (**6**): TLC, SiO_2, EtOAc/ hexanes 1 : 3, R_f= 0.70. ^1H NMR (300 MHz, $CDCl_3$) δ 1.80 (dd, 3H, *J* = 7.1, 1.7 Hz),δ

3.38 (dt, 1H, J = 6.4, 4.3 Hz), δ 3.55 (dd, 1H, J = 10.8, 6.4 Hz), δ 3.70 (dd, 1H, J = 10.8, 4.3 Hz), δ 3.74 (dd, 1H, J = 8.3, 4.3 Hz) δ 4.54 (d, 1H, J = 12.0 Hz), δ 4.64 (d, 1H, J = 12.0 Hz), δ 5.19 (ddt, 1H, J = 11.2, 8.3, 1.7 Hz), δ 5.84 (m, 1Hz), δ 7.35 (m, 5H). IR (neat) 3087, 2859, 1453, 1097cm^{-1}. MS (m/e) 107, 98, 91 (base peak). $[\alpha]_D^{25}$ = -9.17 (*c* 0.1, $CHCl_3$).

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References and Notes

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