DOI 10.5012/bkcs.2010.31.7.2057

An Efficient Synthesis of Functionalized 1,6-Dienes from Baylis-Hillman Adducts *via* a Pd-Catalyzed Decarboxylative Protonation Protocol

Bo Ram Park, Ko Hoon Kim, and Jae Nyoung Kim*

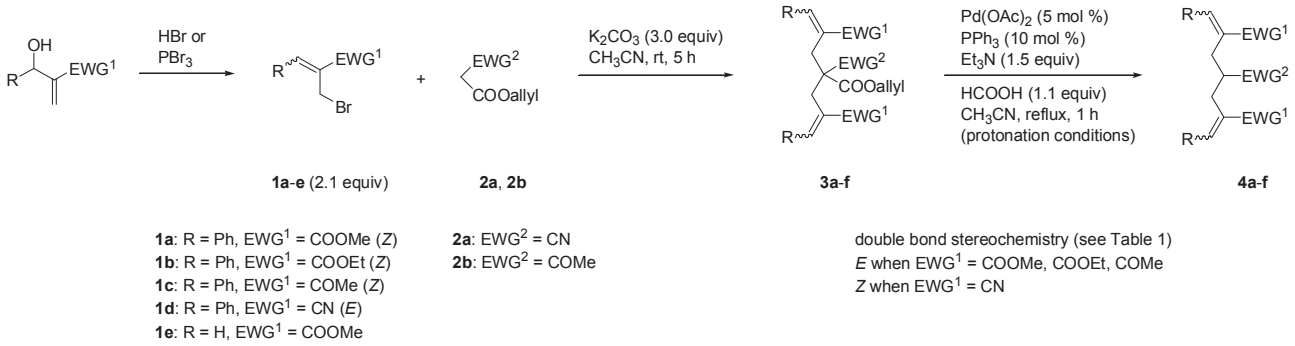
Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea
**E-mail: kimjn@chonnam.ac.kr*
Received April 4, 2010, Accepted May 10, 2010

Key Words: Palladium, 1,6-Dienes, Baylis-Hillman adducts, Decarboxylative protonation

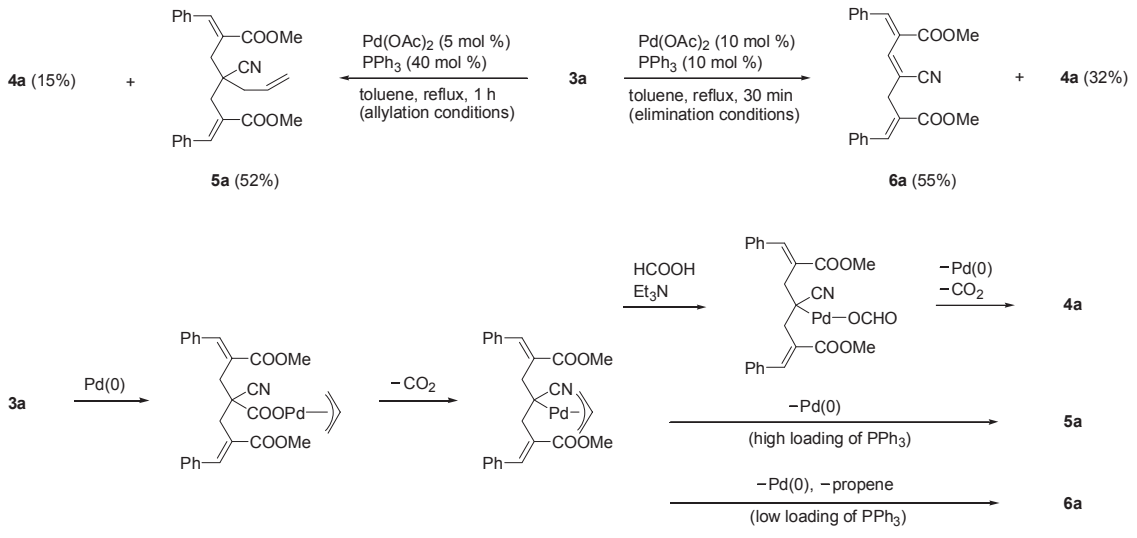
Functionalized 1,6-dienes is a synthetically important skeleton[1,2] and has been used for the synthesis of various carbocycles *via* a ring-closing metathesis (RCM) reaction[1a] and a Pd-catalyzed cyclization/hydrosilylation.[1b,c] In addition, symmetric bis-cinnamic acid derivatives have been used for the synthesis of C_2-symmetric core units of HIV protease inhibitors,[2a] spiro glutarimides and spiro bisglutarimides,[2b] and propellano bislactone derivatives.[2c] These functionalized 1,6-dienes are most commonly prepared by diallylation of active methylene compounds with allylic halides under basic conditions.[1e,2b,2c] Recently, a palladium-catalyzed allylation of active methylene compounds are using widely.[1a,3] Cinnamyl bromides, derived from the Baylis-Hillman adducts, has also been used in this way for the synthesis of symmetric bis-cinnamic acid derivatives.[2b-e]

During our recent studies on Pd-catalyzed decarboxylative protonation, allylation, and elimination reactions with modified Baylis-Hillman adducts,[4] we envisioned that synthetically interesting 1,6-diene derivatives **4** could be synthesized, as shown in Scheme 1.

The starting materials **3a-f** were prepared by the reactions of various cinnamyl bromides **1a-e**, prepared from the corresponding Baylis-Hillman adducts stereoselectively,[5] and active methylene compounds **2a** or **2b** under the influence of K_2CO_3 in CH_3CN at room temperature. Bis-cinnamylated products

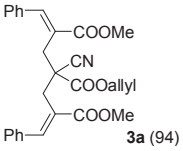
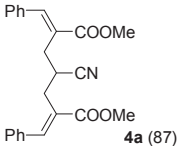
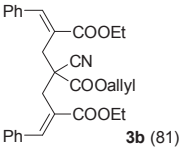
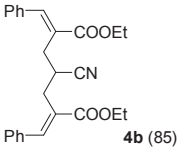
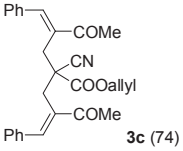
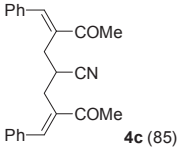
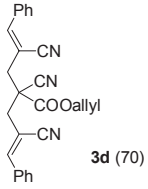
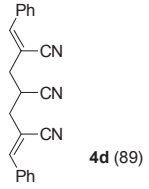
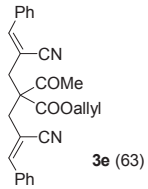
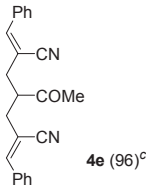
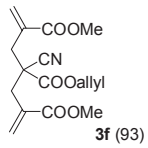
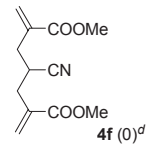


Scheme 1



Scheme 2

Table 1. Synthesis of **3** and Pd-catalyzed decarboxylative protonation to **4**

Entry	Substrates	**3** (%)[a]	**4** (%)[b]
1	**1a** + **2a**	 **3a** (94)	 **4a** (87)
2	**1b** + **2a**	 **3b** (81)	 **4b** (85)
3	**1c** + **2a**	 **3c** (74)	 **4c** (85)
4	**1d** + **2a**	 **3d** (70)	 **4d** (89)
5	**1d** + **2b**	 **3e** (63)	 **4e** (96)[c]
6	**1e** + **2a**	 **3f** (93)	 **4f** (0)[d]

[a]Conditions: compound **1** (2.1 mmol), compound **2** (1.0 mmol), K_2CO_3 (3.0 equiv), CH_3CN, rt, 5 h. [b]$Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), Et_3N (1.5 equiv), HCOOH (1.1 equiv), CH_3CN, reflux, 1 h. [c]Run at rt, 30 min. [d]Severe decomposition of **3f** to intractable mixtures and failed to obtain **4f**.

3a-f were obtained as the major products (63 - 94%) along with trace amounts of mono-cinnamylated compounds. The stereochemistry around the double bond is *E* for **3a-c** and *Z* for **3d** and **3e**.[5] The next Pd-catalyzed decarboxylative protonation reaction of **3a-f** was carried out under the typical conditions involving the use of $Pd(OAc)_2$ (5 mol %)/PPh_3 (10 mol %) and Et_3N (1.5 equiv)/HCOOH (1.1 equiv) in CH_3CN (reflux, 1 h).[4,6] Desired products **4a-e** were isolated in 85 - 96% yields and the results are summarized in Table 1. It is interesting to note that the reaction of acetyl derivative **3e** (entry 5) showed very fast and clean reaction even at room temperature within short time (30 min). As shown in Table 1, the stereochemistry around the double bond is *E* for **4a-c** and *Z* for **4d** and **4e**. The reaction of methylene derivative **3f** (entry 6) did not produce the desired compound **4f** in an appreciable amount, unexpectedly. Severe decomposition of **3f** to intractable side products was observed.

As a next trial, we examined Pd-catalyzed decarboxylative allylation[4b,6] and decarboxylation-elimination,[4b,e,6] with compound **3a** as a representative example as shown in Scheme 2. Decarboxylative allylation was carried out under the conditions of high loading of PPh_3 (Pd/PPh_3, 1:8),[4b,6] and allyl derivative **5a** was isolated in 52% yield along with a protonation product **4a** (15%).[7] Decarboxylation-elimination reaction was performed under the conditions of low loading of PPh_3 (Pd/PPh_3, 1:1), as reported in a similar system,[4b,e,6] and desired product **6a** was obtained in 55% along with **4a** (32%).[7] All of the mechanisms for the Pd-catalyzed decarboxylative protonation, allylation, and elimination reactions are summarized in Scheme 2.[4,6]

In summary, we disclosed an efficient synthesis of functionalized 1,6-diene derivatives starting from the Baylis-Hillman adducts *via* the Pd-catalyzed decarboxylative protonation as the key step.

Experimental Section

Typical procedure for the preparation of compound 3a.[4e] A solution of cinnamyl bromide **1a** (536 mg, 2.1 mmol), allyl cyanoacetate **2a** (125 mg, 1.0 mmol), and K_2CO_3 (415 mg, 3.0 mmol) in CH_3CN (4 mL) was stirred at room temperature for 5 h. After the usual aqueous workup and column chromatographic purification process (hexanes/ether, 4:1) compound **3a** was obtained as colorless oil, 445 mg (94%). Other compounds were prepared similarly and the spectroscopic data of **3a-f** are as follows.

Compound 3a:[4e] 94%; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.15 (s, 4H), 3.77 (s, 6H), 4.49 (dt, *J* = 5.4 and 1.5 Hz, 2H), 5.22-5.37 (m, 2H), 5.82-5.91 (m, 1H), 7.21-7.25 (m, 4H), 7.31-7.40 (m, 6H), 7.88 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 33.54, 48.80, 52.09, 67.03, 117.17, 118.49, 127.13, 128.56, 128.71, 128.87, 130.98, 134.54, 144.29, 167.63, 167.99.

Compound 3b: 81%; colorless oil; IR (film) 2246, 1748, 1709, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (t, *J* = 7.2 Hz, 6H), 3.14 (s, 4H), 4.24 (q, *J* = 7.2 Hz, 4H), 4.48 (dt, *J* = 5.4 and 1.5 Hz, 2H), 5.21-5.37 (m, 2H), 5.80-5.91 (m, 1H), 7.21-7.24 (m, 4H), 7.31-7.40 (m, 6H), 7.87 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.13, 33.53, 48.84, 61.33, 67.08, 117.29, 118.47, 127.58, 128.62, 128.71, 128.96, 131.12, 134.76, 144.01, 167.33, 168.15; ESIMS *m/z* 524 (M^++Na). Anal. Calcd for $C_{30}H_{31}NO_6$: C, 71.84; H, 6.23; N, 2.79. Found: C, 71.57; H, 6.51; N, 2.88.

Compound 3c: 74%; colorless oil; IR (film) 2246, 1744, 1671, 1246 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.40 (s, 6H), 3.05 (d, *J* = 13.8 Hz, 2H), 3.21 (d, *J* = 13.8 Hz, 2H), 4.47 (dt, *J* = 5.7 and 1.5 Hz, 2H), 5.22-5.37 (m, 2H), 5.83-5.96 (m, 1H), 7.26-7.31 (m, 4H), 7.33-7.43 (m, 6H), 7.66 (s, 2H); ^{13}C NMR

($CDCl_3$, 75 MHz) δ 25.83, 32.79, 49.19, 67.22, 117.68, 118.67, 128.71, 128.88, 129.01, 131.38, 134.74, 137.48, 143.76, 168.04, 199.66; ESIMS *m/z* 464 (M^++Na). Anal. Calcd for $C_{28}H_{27}NO_4$: C, 76.17; H, 6.16; N, 3.17. Found: C, 76.46; H, 6.34; N, 3.02.

Compound 3d:[4e] 70%; white solid, mp 86 - 88 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.00 (d, *J* = 13.8 Hz, 2H), 3.16 (d, *J* = 13.8 Hz, 2H), 4.79 (dt, *J* = 6.0 and 1.2 Hz, 2H), 5.21-5.41 (m, 2H), 5.86-5.99 (m, 1H), 7.24 (s, 2H), 7.38-7.45 (m, 6H), 7.73-7.79 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.92, 50.70, 68.24, 102.41, 116.17, 117.82, 120.36, 128.83, 129.08, 130.16, 131.09, 132.48, 150.24, 165.81.

Compound 3e:[4e] 63%; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3H), 3.14 (d, *J* = 15.0 Hz, 2H), 3.21 (d, *J* = 15.0 Hz, 2H), 4.73 (dt, *J* = 6.3 and 1.2 Hz, 2H), 5.25-5.40 (m, 2H), 5.87-6.00 (m, 1H), 7.15 (s, 2H), 7.37-7.44 (m, 6H), 7.67-7.73 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.61, 37.61, 63.36, 67.11, 104.27, 118.45, 120.32, 128.90, 128.95, 130.76, 130.78, 132.91, 149.27, 169.50, 201.85.

Compound 3f: 93%; colorless oil; IR (film) 2246, 1744, 1724, 1442, 1284, 1216, 1162 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.90 (d, *J* = 14.1 Hz, 2H), 3.05 (d, *J* = 14.1 Hz, 2H), 3.77 (s, 6H), 4.62 (dt, *J* = 5.7 and 1.5 Hz, 2H), 5.26-5.40 (m, 2H), 5.83-5.96 (m, 1H), 5.86 (s, 2H), 6.43 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.85, 49.63, 52.25, 67.28, 117.44, 119.44, 130.49, 130.69, 134.11, 166.55, 167.14; ESIMS *m/z* 344 (M^++Na). Anal. Calcd for $C_{16}H_{19}NO_6$: C, 59.81; H, 5.96; N, 4.36. Found: C, 60.11; H, 6.18; N, 4.29.

Typical procedure for the synthesis of compound 4a. A solution of **3a** (237 mg, 0.5 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), PPh_3 (13 mg, 10 mol %), Et_3N (76 mg, 0.75 mmol), and HCOOH (25 mg, 0.55 mmol) in CH_3CN (1.5 mL) was heated to reflux for 1 h under N_2 atmosphere. After the usual aqueous workup and column chromatographic purification process (hexanes/EtOAc, 7:1) compound **4a** was obtained as colorless oil, 170 mg (87%). Other compounds were prepared similarly and the spectroscopic data of **4a-e** are as follows.

Compound 4a: 87%; colorless oil; IR (film) 2239, 1711, 1266 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.74 (dd, *J* = 13.5 and 6.9 Hz, 2H), 2.88 (dd, *J* = 13.5 and 9.3 Hz, 2H), 3.39-3.48 (m, 1H), 3.83 (s, 6H), 7.22-7.42 (m, 10H), 7.90 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.72, 29.79, 52.22, 120.90, 128.24, 128.65, 128.81, 128.91, 134.71, 143.18, 167.56; ESIMS *m/z* 412 (M^++Na). Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.60. Found: C, 74.41; H, 5.79; N, 3.33.

Compound 4b: 85%; colorless oil; IR (film) 2239, 1705, 1224 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (t, *J* = 7.2 Hz, 6H), 2.73 (dd, *J* = 13.8 and 6.9 Hz, 2H), 2.87 (dd, *J* = 13.8 and 9.3 Hz, 2H), 3.42-3.53 (m, 1H), 4.27 (q, *J* = 6.9 Hz, 4H), 7.28-7.42 (m, 10H), 7.90 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.18, 29.77, 29.87, 61.20, 120.95, 128.58, 128.63, 128.72, 128.91, 134.83, 142.87, 167.09; ESIMS *m/z* 440 (M^++Na). Anal. Calcd for $C_{26}H_{27}NO_4$: C, 74.80; H, 6.52; N, 3.35. Found: C, 74.69; H, 6.89; N, 3.47.

Compound 4c: 85%; white solid, mp 108 - 110 °C; IR (KBr) 2238, 1666, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 6H), 2.69 (dd, *J* = 13.2 and 6.6 Hz, 2H), 2.80 (dd, *J* = 13.2 and 9.6 Hz, 2H), 3.21-3.32 (m, 1H), 7.38-7.41 (m, 10H), 7.70 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.72, 28.57, 29.30, 121.06, 128.68, 128.86, 128.92, 134.65, 137.99, 143.40, 199.29; ESIMS *m/z* 380 (M^++Na). Anal. Calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.87; H, 6.57; N, 3.79.

Compound 4d: 89%; white solid, mp 99 - 102 °C; IR (KBr) 2243, 2211, 1449 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.82 (d, *J* = 7.2 Hz, 4H), 3.33-3.42 (m, 1H), 7.20 (s, 2H), 7.41-7.46 (m, 6H), 7.74-7.80 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.57, 37.89, 104.96, 118.18, 118.97, 129.30, 129.32, 131.36, 132.95, 148.51; ESIMS *m/z* 346 (M^++Na). Anal. Calcd for $C_{22}H_{17}N_3$: C, 81.71; H, 5.30; N, 12.99. Found: C, 81.45; H, 5.76; N, 12.63.

Compound 4e: 96%; colorless oil; IR (film) 2209, 1714, 1448 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 3H), 2.56 (dd, *J* = 14.1 and 6.0 Hz, 2H), 2.80 (dd, *J* = 14.1 and 8.1 Hz, 2H), 3.38-3.47 (m, 1H), 6.99 (s, 2H), 7.38-7.43 (m, 6H), 7.69-7.73 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.64, 37.70, 49.51, 107.40, 118.46, 129.05, 129.20, 130.86, 133.34, 146.61, 209.08; ESIMS *m/z* 363 (M^++Na). Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 80.96; H, 6.04; N, 8.11.

Typical procedure for the synthesis of compound 5a. A solution of **3a** (237 mg, 0.5 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), PPh_3 (52 mg, 40 mol %) in toluene (1.5 mL) was heated to reflux for 1 h under N_2 atmosphere. After the usual aqueous workup and column chromatographic purification process (hexanes/CH_2Cl_2/ether, 15:10:1) compound **5a** was obtained as colorless oil, 112 mg (52%) along with **4a** (29 mg, 15%).

Compound 5a: 52%; colorless oil; IR (film) 2233, 1718, 1232 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.04 (d, *J* = 7.2 Hz, 2H), 2.76 (d, *J* = 13.8 Hz, 2H), 2.85 (d, *J* = 13.8 Hz, 2H), 3.82 (s, 6H), 4.96 (d, *J* = 17.1 Hz, 1H), 5.07 (d, *J* = 9.3 Hz, 1H), 5.52-5.65 (m, 1H), 7.22-7.25 (m, 4H), 7.31-7.40 (m, 6H), 7.86 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.86, 41.94, 42.47, 52.46, 120.54, 121.37, 128.83, 128.91, 129.01, 129.22, 132.00, 135.48, 143.60, 168.76; ESIMS *m/z* 452 (M^++Na). Anal. Calcd for $C_{27}H_{27}NO_4$: C, 75.50; H, 6.34; N, 3.26. Found: C, 75.77; H, 6.58; N, 3.41.

Typical procedure for the synthesis of compound 6a. A solution of **3a** (237 mg, 0.5 mmol), $Pd(OAc)_2$ (11 mg, 10 mol %), PPh_3 (13 mg, 10 mol %) in toluene (1.5 mL) was heated to reflux for 30 min under N_2 atmosphere. After the usual aqueous workup and column chromatographic purification process (hexanes/$CHCl_3$/ether, 20:10:1) compound **6a** was obtained as colorless oil, 107 mg (55%) along with **4a** (62 mg, 32%).

Compound 6a: 55%; colorless oil; IR (film) 2216, 1717, 1256 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.60 (d, *J* = 2.1 Hz, 2H), 3.87 (s, 3H), 3.88 (s, 3H), 6.78 (m, 1H), 7.21-7.46 (m, 10H), 7.81 (d, *J* = 1.2 Hz, 1H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.67, 52.38, 52.50, 116.69, 117.15, 126.15, 128.62, 128.84 (2C), 129.18, 129.47, 130.06, 130.54, 134.11, 134.35, 138.59, 143.85, 143.89, 166.37, 167.52; ESIMS *m/z* 410 (M^++Na). Anal. Calcd for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.62. Found: C, 74.67; H, 5.76; N, 3.59.

Acknowledgments. This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0070633). Spectroscopic data were obtained from the Korea Basic Science Institute, Gwangju branch.

References and Notes

1. For the synthesis of functionalized 1,6-dienes and their synthetic applications, see: (a) Bassindale, M. J.; Edwards, A. S.; Hamley, P.; Adams, H.; Harrity, J. P. A. *Chem. Commun*. **2000**, 1035-1036. (b) Pei, T.; Widenhoefer, R. A. *Org. Lett*. **2000**, *2*, 1469-1471. (c) Widenhoefer, R. A.; Perch, N. S. *Org. Lett*. **1999**, *1*, 1103-1105. (d) Nayak, M.; Batra, S. *Eur. J. Org. Chem*. **2009**, 3505-3507. (e) Bhar, S.; Chaudhuri, S. K.; Sahu, S. G.; Panja, C. *Tetrahedron* **2001**, *57*, 9011-9016. (f) Schuster, M.; Blechert, S. *Angew. Chem. Int. Ed*. **1997**, *36*, 2036-2056. (g) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413-4450. (h) Patil, N. T.; Kadota, I.; Shibuya, A.; Gyoung, Y. S.; Yamamoto, Y. *Adv. Synth. Catal*. **2004**, *346*, 800-804.
2. For the synthesis of bis-cinnamic acid derivatives and their synthetic applications, see: (a) Doi, T.; Hirabayashi, K.; Kokubo, M.; Komagata, T.; Yamamoto, K.; Takahashi, T. *J. Org. Chem*. **1996**, *61*, 8360-8361. (b) Basavaiah, D.; Reddy, R. J. *Org. Biomol. Chem*. **2008**, *6*, 1034-1039. (c) Basavaiah, D.; Satyanarayana, T. *Org. Lett*. **2001**, *3*, 3619-3622. (d) Lee, H. S.; Kim, S. J.; Kim, J. N. *Bull. Korean Chem. Soc*. **2006**, *27*, 1063-1066. (e) Kim, S. J.; Lee, H. S.; Kim, J. N. *Tetrahedron Lett*. **2007**, *48*, 1069-1072.
3. For the Pd-catalyzed allylations of active methylene compounds, see: (a) Gan, K.-H.; Jhong, C.-J.; Yang, S.-C. *Tetrahedron* **2008**, *64*, 1204-1212. (b) Ranu, B. C.; Chattopadhyay, K.; Adak, L. *Org. Lett*. **2007**, *9*, 4595-4598. (c) Giambastiani, G.; Poli, G. *J. Org. Chem*. **1998**, *63*, 9608-9609.
4. For our recent papers on Pd-catalyzed decarboxylative protonation, allylation, and elimination reactions, see: (a) Gowrisankar, S.; Kim, K. H.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett*. **2008**, *49*, 6241-6244. (b) Kim, S. H.; Lee, H. S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett*. **2009**, *50*, 3038-3041. (c) Kim, J. M.; Kim, S. H.; Lee, H. S.; Kim, J. N. *Tetrahedron Lett*. **2009**, *50*, 1734-1737. (d) Kim, S. H.; Kim, E. S.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett*. **2009**, *50*, 6256-6260. (e) Kim, K. H.; Kim, E. S.; Kim, J. N. *Tetrahedron Lett*. **2009**, *50*, 5322-5325. For the Pd-catalyzed reactions of Baylis-Hillman adducts, see: (f) Gowrisankar, S.; Lee, H. S.; Kim, S. H.; Lee, K. Y.; Kim, J. N. *Tetrahedron* **2009**, *65*, 8769-8780.
5. For the synthesis of cinnamyl bromide derivatives in a stereoselective manner from Baylis-Hillman adducts, see: (a) Gowrisankar, S.; Kim, S. H.; Kim, J. N. *Bull. Korean Chem. Soc*. **2009**, *30*, 726-728 and further references cited therein. (b) Basavaiah, D.; Reddy, K. R.; Kumaragurubaran, N. *Nature Protocols* **2007**, *2*, 2665-2676. (c) Das, B.; Banerjee, J.; Ravindranath, N. *Tetrahedron* **2004**, *60*, 8357-8361. (d) Fernandes, L.; Bortoluzzi, A. J.; Sa, M. M. *Tetrahedron* **2004**, *60*, 9983-9989. (e) Sa, M. M.; Ramos, M. D.; Fernandes, L. *Tetrahedron* **2006**, *62*, 11652-11656. (f) Deng, J.; Hu, X.-P.; Huang, J.-D.; Yu, S.-B.; Wang, D.-Y.; Duan, Z.-C.; Zheng, Z. *J. Org. Chem*. **2008**, *73*, 2015-2017. (g) Lee, K. Y.; Lee, Y. J.; Kim, J. N. *Bull. Korean Chem. Soc*. **2007**, *28*, 143-146. (h) Lee, K. Y.; Park, D. Y.; Kim, J. N. *Bull. Korean Chem. Soc*. **2006**, *27*, 1489-1492.
6. For the leading references on Pd-catalyzed decarboxylative protonation, allylation, and elimination reactions, see: (a) Tsuji, J.; Nisar, M.; Shimizu, I. *J. Org. Chem*. **1985**, *50*, 3416-3417. (b) Mandai, T.; Imaji, M.; Takada, H.; Kawata, M.; Nokami, J.; Tsuji, J. *J. Org. Chem*. **1989**, *54*, 5395-5397. (c) Tsuji, J. *Pure Appl. Chem*. **1986**, *58*, 869-878. (d) Marinescu, S. C.; Nishimata, T.; Mohr, J. T.; Stoltz, B. M. *Org. Lett*. **2008**, *10*, 1039-1042. (e) Ragoussis, V.; Giannikopoulos, A. *Tetrahedron Lett*. **2006**, *47*, 683-687. (f) Tsuji, J.; Yamada, T.; Minami, I.; Yuhara, M.; Nisar, M.; Shimizu, I. *J. Org. Chem*. **1987**, *52*, 2988-2995. (g) Waetzig, S. R.; Tunge, J. A. *J. Am. Chem. Soc*. **2007**, *129*, 4138-4139. (h) Waetzig, S. R.; Rayabarapu, D. K.; Weaver, J. D.; Tunge, J. A. *Angew. Chem. Int. Ed*. **2006**, *45*, 4977-4980. (i) Waetzig, S. R.; Tunge, J. A. *J. Am. Chem. Soc*. **2007**, *129*, 14860-14861. (j) You, S.-L.; Dai, L.-X. *Angew. Chem. Int. Ed*. **2006**, *45*, 5246-5248. (k) Imao, D.; Itoi, A.; Yamazaki, A.; Shirakura, M.; Ohtoshi, R.; Ogata, K.; Ohmori, Y.; Ohta, T.; Ito, Y. *J. Org. Chem*. **2007**, *72*, 1652-1658. (l) Nakamura, M.; Hajra, A.; Endo, K.; Nakamura, E. *Angew. Chem. Int. Ed*. **2005**, *44*, 7248-7251. (m) Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M. *Angew. Chem. Int. Ed*. **2005**, *44*, 6924-6927.
7. Decarboxylative protonation product **4a** must be formed due to trace amounts of moisture in the reaction mixture.[4]