Synthesis of β-Aryl Substituted *N*-Tosyl *Aza*-Baylis-Hillman Adducts: Heck Reaction of *N*-Tosyl *Aza*-Baylis-Hillman Adducts

Jeong Mi Kim, Sung Hwan Kim, Se Hee Kim, and Jae Nyoung Kim*

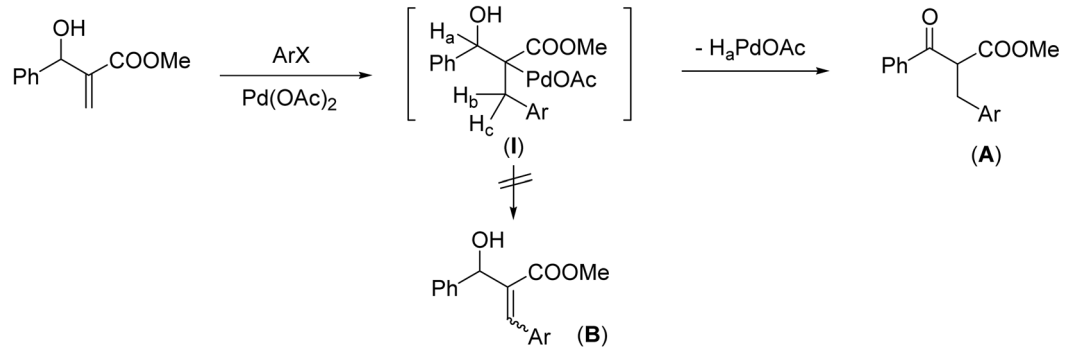
Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea
**E-mail: kimjn@chonnam.ac.kr*
Received February 15, 2008

Key Words : Baylis-Hillman adducts, Heck reaction, *Aza*-Baylis-Hillman adducts

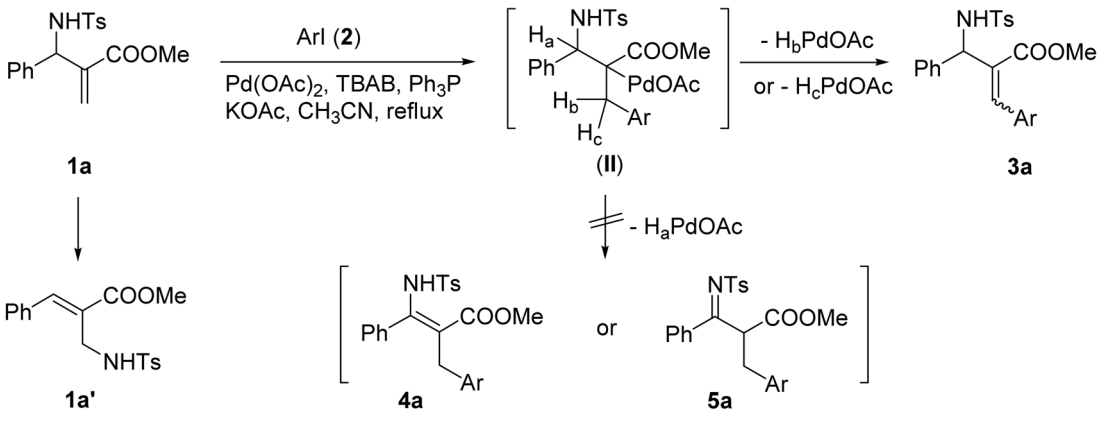
During the last two decades notable improvements in Baylis-Hillman chemistry have been achieved in view of the reaction rate and synthetic applications of Baylis-Hillman or *aza*-Baylis-Hillman adducts.[1] However, the general and efficient synthesis of β-branched *aza*-Baylis-Hillman adducts has remained unsolved. Although many approaches have been examined, most of the methods suffer from low yields and lack of generality.[2,3] Thus, development of an efficient synthetic method of these compounds would be helpful in chemical transformations of Baylis-Hillman adducts.[1-4]

The most simple and convenient method for the preparation of β-aryl-substituted Baylis-Hillman adducts could be the palladium-mediated Heck reaction with aryl halides. Actually intermolecular Heck type arylation of Baylis-Hillman adducts has been examined by some research groups.[5] However, the reaction gave benzyl-substituted β-keto ester (**A**) as the major product instead of β-aryl-substituted Baylis-Hillman type adduct (**B**) as shown in Scheme 1.[5] The compound (**A**) was generated *via* the *syn*-elimination of H_aPdOAc from the intermediate (**I**) and the following keto-enol tautomerization.[5c] This unfavorable result might be the principle reason for the lack of any trials on the synthesis of β-aryl *aza*-Baylis-Hillman adducts *via* the Heck type arylation strategy.

Three types of compounds including **3a**, **4a** and **5a** could be produced from the Heck reaction of *N*-tosyl *aza*-Baylis-Hillman adduct **1a** as in Scheme 2. However, we expected that the conformation of the intermediate (**II**, Scheme 2) might be differ with that of the corresponding intermediate



Scheme 1



Scheme 2

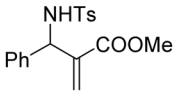
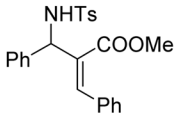
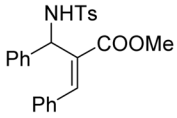
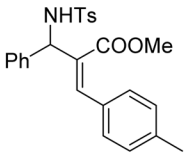
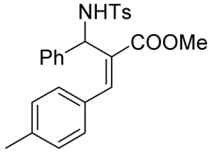
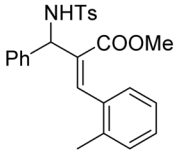
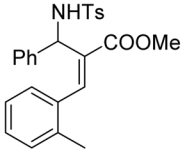
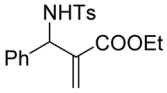
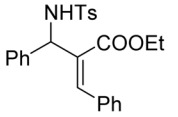
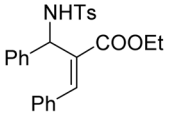
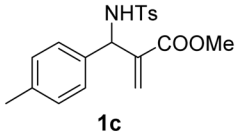
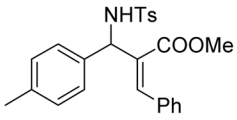
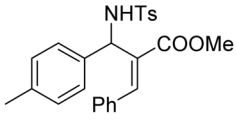
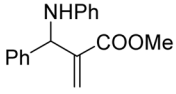
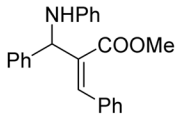
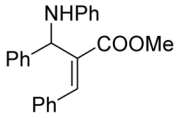
of Baylis-Hillman alcohol (**I**, Scheme 1) due to the increased steric hindrance around H_a. Thus, we expected that the final *syn*-elimination of palladium could occur with H_b/H_c instead of H_a to produce desired **3a** as the major product. With the expectation we examined the reaction of **1a** and iodobenzene (**2a**). To our delight we obtained β-phenyl *N*-tosyl *aza*-Baylis-Hillman adduct **3a** in good yield (67%) as *E/Z* mixture and we wish to report herein the results. To the best

Table 1. Optimization of reaction conditions for the synthesis of **3a**

Entry	Conditions	Results (% Yield)[a]
1	$Pd(OAc)_2$ (5 mol%), Et_3N (3.0 equiv), PPh_3 (20 mol%), DMF, 90-100 °C, 5 h	**3a** (45), **1a** (33)
2	$Pd(OAc)_2$ (10 mol%), Et_3N (3.0 equiv), PPh_3 (20 mol%), CH_3CN, reflux, 25 h	**3a** (50), **1a** (20)
3	$Pd(OAc)_2$ (10 mol%), *n*-Bu_4NBr (0.5 equiv), Et_3N (3.0 equiv), PPh_3 (20 mol%), CH_3CN, reflux, 20 h	**3a** (60), **1a** (15)
4	$Pd(OAc)_2$ (5 mol%), *n*-Bu_4NBr (1.0 equiv), KOAc (2.0 equiv), PPh_3 (10 mol%), CH_3CN, reflux, 18 h	**3a** (73), **1a** (11)
5	$Pd(OAc)_2$ (5 mol%), *n*-Bu4NBr (1.0 equiv), K_2CO_3 (3.0 equiv), H_2O/DMF, 50-60 °C, 5 h	**3a** (0), **1a'** (95)
6	$Pd(OAc)_2$ (5 mol%), K_2CO_3 (3.0 equiv), PPh_3 (20 mol%), CH_3CN, reflux, 20 h	**3a** (30), **1a'** (25)

[a]The yield of **3a** is a combined yield of *E* and *Z* isomers. In some cases **3a** was contaminated with small amount of **1a**.

Table 2. Synthesis of β-aryl *aza*-Baylis-Hillman adducts

Entry	Substrate	Conditions[a]	Products (%)	
1	 **1a**	1. C_6H_5I (**2a**), 18 h 2. K_2CO_3, reflux, 8 h	 **3a**-*Z* (31)	 **3a**-*E* (36)
2	**1a**	1. 4-MeC_6H_4I (**2b**), 24 h 2. K_2CO_3, reflux, 8 h	 **3b**-*Z* (37)	 **3b**-*E* (41)
3	**1a**	1. 2-MeC_6H_4I (**2c**), 15 h	 **3c**-*Z* (26)	 **3c**-*E* (48)
4	 **1b**	1. **2a**, 20 h 2. K_2CO_3, reflux, 8 h	 **3d**-*Z* (32)	 **3d**-*E* (40)
5	 **1c**	1. **2a**, 20 h 2. K_2CO_3, reflux, 8 h	 **3e**-*Z* (35)	 **3e**-*E* (41)
6	 **1d**	1. **2a**, 10 h 2. K_2CO_3, reflux, 6 h	 **3f**-*Z* (27)	 **3f**-*E* (31)

[a]Conditions: step 1: compound **1** (1.0 mmol), compound **2** (2.0 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), TBAB (1.0 mmol), KOAc (2.0 mmol), CH_3CN, reflux; step 2: K_2CO_3 (1.0 mmol), reflux.

of our knowledge this is the first successful results for the synthesis of β-aryl *aza*-Baylis-Hillman adduct *via* palladium-mediated Heck reaction.[5]

The reactions of **1a** and **2a** under various Pd-mediated Heck reaction conditions were examined and the results are summarized in Table 1. In most cases (entries 1-4 and 6) we observed the formation of desired product **3a** in variable yields (30-73%) with some remaining starting material **1a**. When we used Et_3N the reaction was sluggish (entries 1-3). Among the conditions the use of $Pd(OAc)_2$/TBAB/KOAc/PPh_3 in refluxing CH_3CN (entry 4) was found to be the best. It is interesting to note that rearranged tosylamide derivative **1a'** was obtained almost quantitatively when we used K_2CO_3 as a base (entry 5).[6,7]

Initially, we isolated **3a**-*E* (35%) and **3a**-*Z* (38%) under the conditions of entry 4 in Table 1. However, unfortunately, **3a**-*Z* was contaminated with small amount of starting material **1a**, which could not be separated easily by column chromatography due to their similar mobility. Thus we used K_2CO_3 in order to convert remaining **1a** into **1a'** completely according to the results of entry 5 in Table 1. In this manner we obtained analytically pure **3a**-*E* (36%) and **3a**-*Z* (31%), which were identified by comparison with the reported data (vide infra, entry 1 in Table 2).[2]

Encouraged by the successful results, we prepared starting materials **1b-d** according to the reported methods,[8] and synthesized analogous compounds **3b-f** similarly under the optimized conditions and the results are summarized in Table 2. 4-Iodotoluene (**2b**) and 2-iodotoluene (**2c**) showed similar reactivity (entries 2 and 3). Other *N*-tosyl- (**1b** and **1c**) and *N*-phenyl- (**1d**) derivatives also showed same reactivity (entries 4-6). In most cases except entry 3, we observed some remaining starting materials **1a-d** and we treated the reaction mixture with K_2CO_3 before separation (vide supra).

In summary, we prepared some β-aryl *N*-tosyl *aza*-Baylis-Hillman adducts *via* the Heck type reaction of *aza*-Baylis-Hillman adduct and aryl iodide under the influence of $Pd(OAc)_2$/TBAB/KOAc/PPh_3 in refluxing CH_3CN in moderate yield as *E*/*Z* mixture.

Experimental Section

Typical procedure for the synthesis of 3a: A mixture of **1a** (345 mg, 1.0 mmol), **2a** (408 mg, 2.0 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), *n*-Bu_4NBr (322 mg, 1.0 mmol), KOAc (196 mg, 2.0 mmol), PPh_3 (26 mg, 0.1 mmol) in CH_3CN (3 mL) was heated to reflux for 18 h. To the reaction mixture K_2CO_3 (138 mg, 1.0 mmol) was added and maintained refluxing for 8 h. After the usual aqueous workup and column chromatographic purification process (hexanes/CH_2Cl_2/ether, 5:1:2) we obtained **3a**-*Z* (131 mg, 31%) and **3a**-*E* (152 mg, 36%) as white solids. The selected spectroscopic data of prepared compounds **3a** and **3f** are as follows.

Compound **3a**-*Z*: 31%; white solid, mp 117-119 °C; IR (film) 3290, 2924, 1711, 1163 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, 3H), 3.39 (s, 3H), 5.32 (d, *J* = 9.3 Hz, 1H), 5.99 (d, *J* = 9.3 Hz, 1H), 6.63 (s, 1H), 6.94-6.97 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.21-7.33 (m, 8H), 7.72 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.24, 51.62, 61.52, 126.46, 127.20, 127.81, 127.94, 128.33, 128.55 (2C), 129.53, 130.18, 134.58, 137.74, 138.12, 138.22, 143.34, 168.22; ESIMS *m/z* 422 (M^++1). Anal Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32. Found: C, 68.58; H, 5.77; N, 3.23.

Compound **3a**-*E*: 36%; white solid, mp 153-155 °C; IR (film) 3292, 3061, 1718, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3H), 3.66 (s, 3H), 5.85 (d, *J* = 10.5 Hz, 1H), 6.34 (d, *J* = 10.5 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.16-7.19 (m, 2H), 7.26-7.43 (m, 10H), 7.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.46, 52.09, 53.94, 126.26, 127.02, 127.57, 128.57, 128.78, 128.94 (2C), 129.23, 129.56, 133.65, 137.68, 139.07, 142.75, 142.92, 166.89; ESIMS *m/z* 422 (M^++1). Anal Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32. Found: C, 68.64; H, 5.46; N, 3.15.

Compound **3b**-*Z*: 37%; white solid, mp 126-128 °C; IR (film) 3292, 2960, 2918, 1699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, 3H), 2.33 (s, 3H), 3.41 (s, 3H), 5.29 (d, *J* = 9.3 Hz, 1H), 5.94 (d, *J* = 9.3 Hz, 1H), 6.57 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.05-7.16 (m, 4H), 7.22-7.32 (m, 5H), 7.71 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.26 (2C), 51.61, 61.70, 126.46, 127.21, 127.76, 128.47, 128.53, 128.67, 129.18, 129.52, 131.61, 137.79, 138.29, 138.44, 138.75, 143.29, 168.39; LCMS *m/z* 435 (M^+).

Compound **3b**-*E*: 41%; white solid, mp 161-163 °C; IR (film) 3309, 2952, 2924, 1697 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 3H), 2.39 (s, 3H), 3.64 (s, 3H), 5.88 (d, *J* = 10.5 Hz, 1H), 6.35 (d, *J* = 10.5 Hz, 1H), 7.06-7.10 (m, 4H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.27-7.43 (m, 7H), 7.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.40, 21.49, 52.02, 54.08, 126.34, 127.05, 127.55, 128.05, 128.57, 129.10, 129.19, 129.56, 130.84, 137.83, 139.17, 140.00, 142.89, 142.96, 167.03; LCMS *m/z* 435 (M^+).

Compound **3c**-*Z*: 26%; white solid, mp 146-148 °C; IR (film) 3288, 2924, 1707cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, 3H), 2.29 (s, 3H), 3.30 (s, 3H), 5.37 (d, *J* = 9.3 Hz, 1H), 5.99 (d, *J* = 9.3 Hz, 1H), 6.56-6.59 (m, 1H), 6.86 (s, 1H), 7.00-7.05 (m, 1H), 7.12-7.22 (m, 4H), 7.23-7.34 (m, 5H), 7.75 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.84, 21.34, 51.51, 61.22, 125.13, 126.41, 127.17, 127.79 (2C), 128.38, 128.60, 129.62, 129.66, 131.23, 134.62, 135.67, 137.93, 138.50, 138.81, 143.39, 167.87; LCMS *m/z* 435 (M^+).

Compound **3c**-*E*: 48%; white solid, mp 140-142 °C; IR (film) 3309, 2952, 1703 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.17 (s, 3H), 2.35 (s, 3H), 3.70 (s, 3H), 5.69 (d, *J* = 10.2 Hz, 1H), 6.35 (d, *J* = 10.2 Hz, 1H), 7.05-7.12 (m, 4H), 7.21-7.29 (m, 7H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.86, 21.40, 52.17, 53.82, 126.13, 126.22, 126.92, 127.38, 127.75, 128.44, 129.30, 129.40, 129.95, 130.32, 132.90, 137.30, 137.69, 139.48, 141.59, 142.87, 167.00; LCMS *m/z* 435 (M^+).

Compound **3d**-*Z*: 32%; white solid, mp 88-90 °C; IR (film) 3292, 2918, 1699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz)

δ 0.83 (t, J = 7.2 Hz, 3H), 2.21 (s, 3H), 3.81-3.93 (m, 2H), 5.31 (d, J = 9.3 Hz, 1H), 5.99 (d, J = 9.3 Hz, 1H), 6.62 (s, 1H), 6.95-6.98 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.23-7.33 (m, 8H), 7.73 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.33, 21.26, 60.87, 61.64, 126.50, 127.22, 127.77, 127.84, 128.40, 128.45, 128.49, 129.53, 130.54, 134.69, 137.81, 138.02, 138.20, 143.33, 167.72.

Compound **3d**-*E*: 40%; white solid, mp 148-149 °C; IR (film) 3311, 2964, 1693, 1261 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.19 (t, J = 7.2 Hz, 3H), 2.39 (s, 3H), 4.06-4.16 (m, 2H), 5.85 (d, J = 10.2 Hz, 1H), 6.37 (d, J = 10.2, 1H), 7.09 (d, J = 8.4 Hz, 2H), 7.16-7.19 (m, 2H), 7.23-7.43 (m, 10H), 7.67 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.02, 21.47, 53.99, 61.15, 126.27, 127.02, 127.52, 128.53, 128.77, 128.94, 129.19, 129.24, 129.50, 133.72, 137.75, 139.20, 142.48, 142.87, 166.43.

Compound **3e**-*Z*: 35%; white solid, mp 86-88 °C; IR (film) 3294, 2924, 1703 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3H), 2.33 (s, 3H), 3.44 (s, 3H), 5.31 (d, J = 9.3 Hz, 1H), 5.88 (d, J = 9.3 Hz, 1H), 6.66 (s, 1H), 6.97-7.00 (m, 2H), 7.10-7.22 (m, 7H), 7.28-7.30 (m, 2H), 7.75 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.01, 21.27, 51.64, 61.36, 126.37, 127.25, 127.94, 128.35, 128.52, 129.28, 129.53, 130.32, 134.67, 135.15, 137.60, 137.79, 138.03, 143.32, 168.30.

Compound **3e**-*E*: 41%; white solid, mp 142-143 °C; IR (film) 3311, 2952, 1699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3H), 2.39 (s, 3H), 3.66 (s, 3H), 5.80 (d, J = 10.5 Hz, 1H), 6.31 (d, J = 10.5 Hz, 1H), 7.07-7.18 (m, 6H), 7.25 (d, J = 7.8 Hz, 2H), 7.32-7.42 (m, 5H), 7.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.98, 21.48, 52.07, 53.77, 126.20, 127.05, 128.77, 128.97, 129.06, 129.21, 129.31, 129.53, 133.72, 136.07, 137.31, 137.74, 142.63, 142.88, 166.94.

Compound **3f**-*Z*: 27%; pale yellow oil; IR (film) 3402, 3026, 1712, 1601 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.53 (s, 3H), 4.27 (br s, 1H), 5.41 (s, 1H), 6.66-6.74 (m, 3H), 6.92 (s, 1H), 7.12-7.19 (m, 2H), 7.22-7.45 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 51.72, 61.66, 113.52, 118.03, 127.70, 127.99, 128.12, 128.15, 128.28, 128.82, 129.19, 133.85, 134.29, 135.48, 139.89, 146.62, 169.32; ESIMS *m/z* 344 (M^++1). Anal Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.67; H, 6.05; N, 3.93.

Compound **3f**-*E*: 31%; pale yellow oil; IR (film) 3402, 3057, 1709, 1601 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.70 (s, 3H), 5.17 (br s, 1H), 5.91 (s, 1H), 6.37-6.41 (m, 2H), 6.62-6.68 (m, 1H), 7.02-7.09 (m, 2H), 7.25-7.43 (m, 10H), 7.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 51.88, 53.99, 113.42, 117.59, 126.44, 127.05, 128.44, 128.74, 128.91, 129.08, 129.21, 132.17, 134.82, 141.20, 141.72, 146.81, 167.26; ESIMS *m/z* 344 (M^++1). Anal Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.76; H, 6.35; N, 4.02.

References and Notes

1. For the general review on Baylis-Hillman reaction, see: (a) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811-891. (b) Ciganek, E. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1997; Vol. 51, pp 201-350. (c) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001-8062. (d) Kim, J. N.; Lee, K. Y. *Curr. Org. Chem.* **2002**, *6*, 627-645. (e) Lee, K. Y.; Gowrisankar, S.; Kim, J. N. *Bull. Korean Chem. Soc.* **2005**, *26*, 1481-1490 and further references cited therein.
2. For the synthesis of β-branched *aza*-Baylis-Hillman adducts, see: (a) Li, Q.; Shi, M.; Lyte, J. M.; Li, G. *Tetrahedron Lett.* **2006**, 7699-7702. (b) Shi, Y.-L.; Xu, Y.-M.; Shi, M. *Adv. Synth. Catal.* **2004**, *346*, 1220-1230. (c) Back, T. G.; Rankic, D. A.; Sorbetti, J. M.; Wulff, J. E. *Org. Lett.* **2005**, *7*, 2377-2379. (d) Shi, Y.-L.; Shi, M. *Tetrahedron* **2006**, *62*, 461-475. (e) Utsumi, N.; Zhang, H.; Tanaka, F.; Barbas, C. F., III. *Angew. Chem. Int. Ed.* **2007**, *46*, 1878-1880.
3. For the other synthesis of β-branched *aza*-Baylis-Hillman adducts and their synthetic applications, see: (a) Yamaguchi, A.; Aoyama, N.; Matsunaga, S.; Shibasaki, M. *Org. Lett.* **2007**, *9*, 3387-3390. (b) Vitis, L. D.; Troisi, L.; Granito, C.; Pindinelli, E.; Ronzini, L. *Eur. J. Org. Chem.* **2007**, 356-362.
4. For our recent chemical transformations involving Baylis-Hillman adducts, see: (a) Gowrisankar, S.; Lee, H. S.; Lee, K. Y.; Lee, J.-E.; Kim, J. N. *Tetrahedron Lett.* **2007**, *48*, 8619-8622. (b) Park, D. Y.; Lee, K. Y.; Kim, J. N. *Tetrahedron Lett.* **2007**, *48*, 1633-1636. (c) Park, D. Y.; Gowrisankar, S.; Kim, J. N. *Tetrahedron Lett.* **2006**, *47*, 6641-6645. (d) Park, D. Y.; Kim, S. J.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2006**, *47*, 6315-6319. (e) Park, D. Y.; Lee, M. J.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2005**, *46*, 8799-8803. (f) Kim, H. S.; Kim, S. H.; Kim, J. N. *Bull. Korean Chem. Soc.* **2007**, *28*, 1841-1843. (g) Gowrisankar, S.; Kim, H. S.; Lee, H. S.; Kim, J. N. *Bull. Korean Chem. Soc.* **2007**, *28*, 1844-1846.
5. For the intermolecular palladium-mediated Heck type reaction of Baylis-Hillman adducts, see: (a) Basavaiah, D.; Muthukumaran, K. *Tetrahedron* **1998**, *54*, 4943-4948. (b) Sundar, N.; Bhat, S. V. *Synth. Commun.* **1998**, *28*, 2311-2316. (c) Perez, R.; Veronese, D.; Coelho, F.; Antunes, O. A. C. *Tetrahedron Lett.* **2006**, *47*, 1325-1328. (d) Kumareswaran, R.; Vankar, Y. D. *Synth. Commun.* **1998**, *28*, 2291-2302. (e) Kabalka, G. W.; Venkataiah, B.; Dong, G. *Org. Lett.* **2003**, *5*, 3803-3805. Intramolecular Heck reaction of Baylis-Hillman adducts was also studied, please see: (f) Park, J. B.; Ko, S. H.; Hong, W. P.; Lee, K.-J. *Bull. Korean Chem. Soc.* **2004**, *25*, 927-930.
6. Secondary tosylamide **1a** was changed into the primary derivative **1a'** readily with K_2CO_3 in CH_3CN in the absence of Pd catalyst (reflux, 18 h, quantitative). However, we could not observe the formation of any trace amounts of **1a'** when we used KOAc as a base in CH_3CN in the absence of Pd catalyst (reflux, 18 h).
7. The reaction of **1a** and bromobenzene under the optimized conditions (entry 4 in Table 1) was examined, but we observed no reaction. Most of the starting material **1a** was remained (70-80%) and we observed the formation of small amounts (< 20%) of **1a'**, which might be produced *via* the Pd-mediated rearrangement. For the related reference, please see: Park, J. B.; Ko, S. H.; Kim, B. G.; Hong, W. P.; Lee, K.-J. *Bull. Korean Chem. Soc.* **2004**, *25*, 27-28.
8. For the synthesis of starting materials, see: (a) Kim, J. N.; Lee, H. J.; Lee, K. Y.; Gong, J. H. *Synlett* **2002**, 173-175. (b) Lee, C. G.; Lee, K. Y.; Lee, S.; Kim, J. N. *Tetrahedron* **2005**, *61*, 1493-1499.