Recently numerous chemical transformations of Baylis-Hillman adducts have been published involving the synthesis of cyclic and acyclic compounds. Among the reactions introduction of allyl, vinyl and aryl moiety at the primary position of the Baylis-Hillman adducts can be regarded as an important transformation due to the usefulness of the compounds thereof as synthetic intermediates.

Introduction of allyl group at the primary position of Baylis-Hillman adduct was studied by Yadav and coworkers. They reported the synthesis of 1,5-diene derivatives involving the type reaction under various acidic conditions. However, the regioselectivity is the principle problem in this case. As an example, Friedel-Crafts reaction with toluene produced a mixture of ortho- and para-isomers (vide infra, Scheme 2). In addition, various Pd- and Rh-catalyzed introduction of aryl moiety has been studied. Kabalka group reported a Pd-catalyzed cross-coupling of Baylis-Hillman acetate and organosilane or potassium organotrifluoroborate. Genet and coworkers examined a Rh-catalyzed arylation with arylboronic acid or potassium aryltrifluoroborate.

Although various methods have been reported and most of the methods provided moderate yields of products, development of an efficient and general method for the introduction of carbon nucleophile at the primary position of Baylis-Hillman adduct is still highly required, especially in a stereoselective manner. Thus we decided to examine the cross-coupling reactions between the bromide of Baylis-Hillman adduct and allyl-, aryl-, and vinylstannane as a continuous manner. Thus we decided to examine the cross-coupling reactions between the bromide of Baylis-Hillman adduct and allyl-, aryl-, and vinylstannane (Scheme 1) as a continuous work on our recent Pd-mediated reactions with Baylis-Hillman adducts. Although cross-couplings involving the use of allyl bromides and organostannanes have been studied extensively, this is the first trial in the Baylis-Hillman chemistry to the best of our knowledge. Fortunately we obtained good results and wish to report herein the results. The results are summarized in Scheme 1.

We decided to use the bromides of Baylis-Hillman adducts and chose three representative Baylis-Hillman adducts, 2a-c. The starting materials 2a-c were prepared in pure form (Z for 2a and 2b, E for 2c) as shown in Scheme 1. The reaction of cinnamyl bromide 2a and allyltributylstannane (1.2 equiv) in the presence of Pd(Ph₃P)₄/LiCl (0.5 equiv) in THF afforded desired product 3a in 96% yield. As a palladium catalyst, Pd(Ph₃P)₄ was superior than Pd(OAc)₂ and only 2

![Scheme 1](image-url)
mol% of catalyst was sufficient. The reaction time can be shortened by raising the reaction temperature with 5 mol% of Pd(0) catalyst. Similarly, 3b and 3c were prepared in high yields also (81-93%). The arylation and vinylination of 2a-c were examined with phenyltributylstannane, 2-(tributylstannyl)furan, and tetravinylstannane. The corresponding products 4a-c, 5a-c, and 6a-c were obtained in good yields (73-95%). The yields of nitrile-containing compounds were comparatively lower than those of the ester- or acetyl-containing compounds. The reaction of phenyltributylstannane required elevated temperature (50 °C).

Tolyl-substituted products 4d and 4e were synthesized in good yields (74-78%) similarly by the reactions of 2a and ortho-tolyltributylstannane and para-tolyltributylstannane, which were prepared from Pd-mediated reactions between n-tbutyltin hydride and 2-iodo- and 4-iodotoluene, respectively, while the traditional Friedel-Crafts reaction of 3a gave 6a in low yield (48%). Similarly the Pd-mediated reaction of 2a in 66% yield as in Scheme 2. As a next trial we prepared tributylstannyl derivative 7a by the Pd-mediated reaction of 2a and hexabutylditin in the presence of Pd(0) in 66% yield as in Scheme 3. The reaction of 7a and allyl bromide under the influence of Pd(Ph3P)4/LiCl produced 3a in low yield (48%). Similarly the reaction of 7a and bromobenzene afforded 4a in low yield (43%) also together with some self-coupling product 8a (10%).

In summary, we disclosed an efficient synthetic method of allyl-, aryl and vinyl-attached Baylis-Hillman adducts via the Pd-mediated cross-coupling reactions between the bromide of Baylis-Hillman adduct and the corresponding organostannane compounds.

**Experimental Section**

**Typical experimental procedure for the preparation of 3a.**

To a stirred mixture of 2a\(^{10}\) (128 mg, 0.5 mmol) and allyltributylstannane (200 mg, 0.6 mmol) in dry THF (2 mL) was added Pd(Ph3P)4 (12 mg, 0.2 mol%) and LiCl (11 mg, 0.25 mmol) and the reaction mixture was stirred at room temperature for 12 h. After removal of solvent and column chromatographic purification process (hexanes/EtOAc, 95:5) analytically pure product 3a was obtained as colorless oil, \(^{24}\) 104 mg (96%). Other compounds were synthesized similarly and the known compounds, 3a, 4a, 4b, 4c, 5a, 5b, 5c, 6a, 6b, 6c\(^{16}\) and 8a\(^{15}\) were identified by comparison with their \(^1\)H NMR and IR spectroscopic data with the reported. The spectroscopic data of unknown compounds, 3b, 3c, 5a, 5b, 5c, 6b and 7a, are as follows.

**Compound 3b: 93%; colorless oil; IR (film) 3077, 2927, 1667 cm\(^{-1}\); \(^1\)H NMR (CDCl3, 300 MHz) \(\delta\) 2.20-2.24 (m, 2H), 2.45 (s, 3H), 2.60-2.63 (m, 2H), 4.95-5.05 (m, 2H), 5.78-5.87 (m, 1H), 7.34-7.43 (m, 5H), 7.51 (s, 1H); \(^13\)C NMR (CDCl3, 75 MHz) \(\delta\) 25.61, 26.07, 33.00, 114.77, 128.56, 128.60, 129.20, 135.57, 137.88, 140.02, 142.06, 200.06.

**Compound 3c: 81%; colorless oil; IR (film) 3080, 2924, 2209 cm\(^{-1}\); \(^1\)H NMR (CDCl3, 300 MHz) \(\delta\) 2.37-2.54 (m, 4H), 5.04-5.16 (m, 2H), 5.75-5.88 (m, 1H), 6.94 (s, 1H), 7.26-7.44 (m, 3H), 7.69-7.74 (m, 2H); \(^13\)C NMR (CDCl3, 75 MHz) \(\delta\) 32.27, 35.64, 110.66, 116.45, 118.65, 128.55, 128.78, 129.93, 133.67, 136.04, 143.84.

**Compound 5a: 84%; yellow oil; IR (film) 2951, 1715 cm\(^{-1}\); \(^1\)H NMR (CDCl3, 300 MHz) \(\delta\) 3.80 (s, 3H), 3.88 (s, 2H), 6.06-6.08 (m, 1H), 6.30-6.31 (m, 1H), 7.33-7.47 (m, 6H), 7.87 (s, 1H); \(^13\)C NMR (CDCl3, 75 MHz) \(\delta\) 26.89, 27.25, 110.60, 116.45, 118.65, 128.55, 128.78, 129.93, 133.67, 136.04, 143.84.

**Compound 5b: 86%; yellow oil; IR (film) 2957, 2924, 1669 cm\(^{-1}\); \(^1\)H NMR (CDCl3, 300 MHz) \(\delta\) 2.46 (s, 3H), 3.87 (s, 2H), 6.00-6.02 (m, 1H), 6.27-6.29 (m, 1H), 7.32-7.49 (m, 6H), 7.87 (s, 1H); \(^13\)C NMR (CDCl3, 75 MHz) \(\delta\) 25.61, 26.07, 33.00, 114.77, 128.56, 128.60, 129.20, 135.57, 137.88, 140.02, 142.06, 200.06.
Compound 5c: 82%; yellow oil; IR (film) 2913, 2212 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 3.73 (s, 2H), 6.26-6.27 (m, 1H), 6.35-6.36 (m, 1H), 6.99 (s, 1H), 7.38-7.43 (m, 5H), 7.72-7.74 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 34.58, 112.73, 135.73, 139.20, 141.03. 199.54.

Compound 6b: 93%; colorless oil; IR (film) 3079, 2978, 1668 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.47 (s, 3H), 3.26-3.29 (m, 2H), 4.99-5.11 (m, 2H), 5.91-6.03 (m, 1H), 7.32-7.46 (m, 5H), 7.64 (s, 1H), ¹³C NMR (CDCl₃, 75 MHz) δ 26.05, 30.57, 115.51, 128.48, 128.82, 129.28, 135.34, 137.73, 139.20, 141.30, 199.54.

Compound 7a: 66%; colorless oil; IR (film) 2956, 2925, 1709 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.84-0.94 (m, 15H), 1.23-1.31 (m, 6H), 1.37-1.46 (m, 6H), 2.29 (s, 2H), 3.80 (s, 3H), 7.35-7.37 (m, 5H), ¹³C NMR (CDCl₃, 75 MHz) δ 10.22, 11.80, 13.67, 27.33, 28.95, 51.98, 127.47, 128.30, 129.25, 131.78, 133.89, 136.88, 169.46; ESI-MS m/z 465 (M+1).


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References and Notes


