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Tetrahedron Letters
Tetrahedron Letters 46 (2005) 8799–8803

Regioselective construction of polysubstituted pyridine ring from Baylis–Hillman adducts via sequential introduction of tosylamide, Michael reaction, aldol condensation, and elimination of TsH

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Received 14 September 2005; accepted 7 October 2005
Available online 26 October 2005

Abstract—Facile synthetic method of polysubstituted pyridine derivatives was developed starting from the Baylis–Hillman adducts. The reaction involved sequential introduction of tosylamide, Michael addition, aldol condensation, elimination of *p*-toluenesulfinic acid, and isomerization process.

Recently, syntheses of a variety of heterocyclic compounds[1a,b] from Baylis–Hillman adducts have been reported including the synthesis of quinolines,[1c] pyrazoles,[1d] and furans.[1e] However, to the best of our knowledge, synthesis of pyridine derivatives from Baylis–Hillman adducts has not been reported. The prevalence of pyridines in nature and their central role as versatile building blocks in the synthesis of natural products as well as biologically active compounds have led to a continued interest in the practical synthesis of pyridine derivatives.[2] In these respects, we now wish to report the first synthesis of highly substituted pyridine scaffold starting from the Baylis–Hillman adducts.[3]

The Baylis–Hillman adducts derived from methyl vinyl ketone or ethyl vinyl ketone were converted into their acetates **1** (Ac_2O, DMAP) and transformed to **2** by the S_N2' reaction with *p*-toluenesulfonamide as reported.[4,5] Initially, we tried the synthesis of pyridine **6a** starting from **2a** (Scheme 1). The reaction of **2a** and methyl vinyl ketone (MVK) under the influence of DBU in THF produced two major components on TLC, which were very difficult to separate. Later, it was found that the two spots corresponded to the two diastereomers of **4a**, which might be formed via Michael reaction of **2a** and MVK and the following aldol cyclization reaction of **3a**.[6] Thus, we did not try to separate the diastereomers **4a** in pure states.[7] Instead, we tried the next dehydration reaction with crude mixtures of **4a** after simple aqueous workup. Dehydration was conducted in benzene with catalytic amounts of *p*-TsOH under refluxing conditions. We could obtain the expected compound **5a** in pure state by column chromatography after the reaction.[8] With this compound **5a** in our hands we examined a variety of conditions to convert **5a** into the final pyridine derivative **6a**.[9] The use of Cs_2CO_3 in DMF at around 120–130 °C gave the best yield of product. The use of K_2CO_3 (DMF, 90–100 °C, 30 h, 39%), DBU (dioxane, reflux, 24 h, low yield), *t*-BuOK (THF, rt, 30 h, 44%), *n*-Bu_4NF (THF, reflux, 5 h, 47%) all gave lower yields than Cs_2CO_3 (DMF, 120 °C, 1 h, 56%) conditions.

By using the optimized reaction conditions we synthesized pyridine derivatives **6b–f** as shown in Table 1 in reasonable yields. We prepared **6b** and **6c** without any problems (entries 2 and 3). However, we found an interesting isomerization during the synthesis of **5d** (entry 4). We obtained **5d** in 38% yield. Instead we could isolate another compound **5d′** in 31% yield and the structure was confirmed by using various spectroscopic data including NOE experiments as shown in Scheme 2.

Keywords: Pyridines; Baylis–Hillman adducts; Michael reaction; Cyclization.
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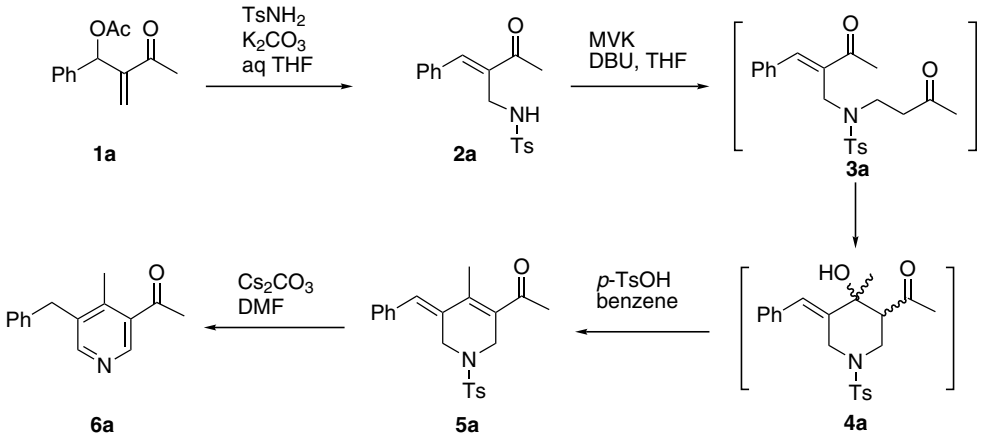
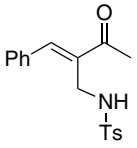
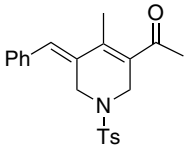
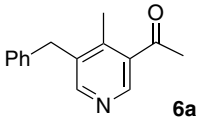
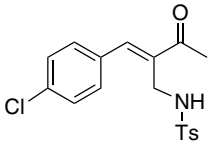
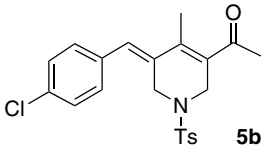
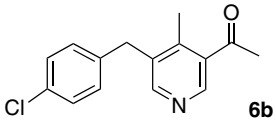
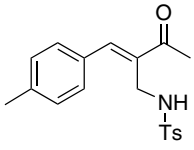
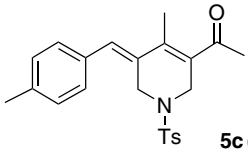
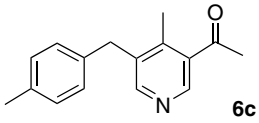
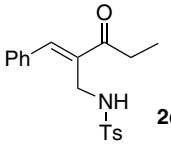
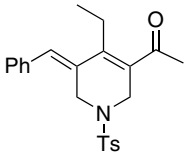
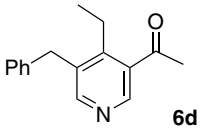
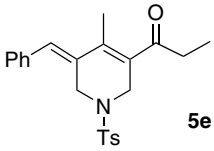
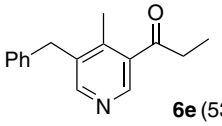
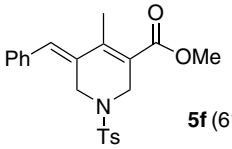
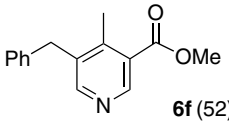
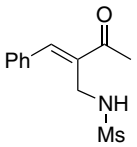
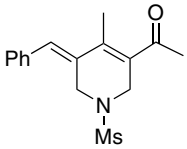
0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.10.034

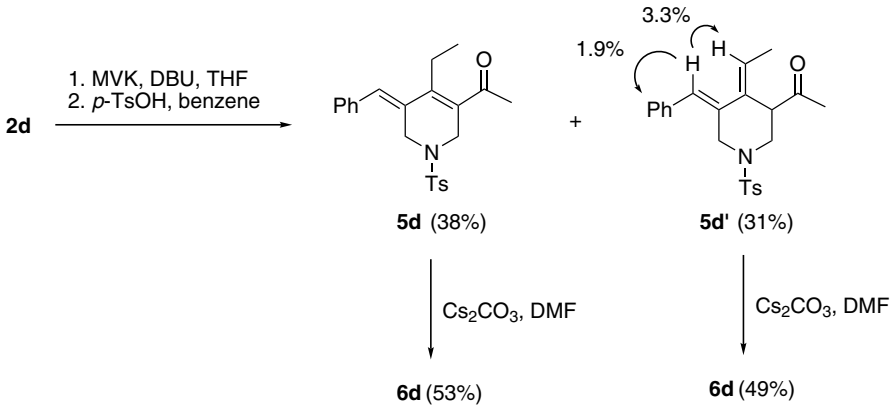


Scheme 1.

Table 1. Synthesis of 3,4,5-trisubstituted pyridines

Entry	Substrate **2**[a] (%)	Intermediate **5**[b] (%)	Pyridine **6**[c] (%)
1	 **2a** (66)	 **5a** (87)	 **6a** (56)
2	 **2b** (64)	 **5b** (72)	 **6b** (60)
3	 **2c** (64)	 **5c** (80)	 **6c** (64)
4	 **2d** (51)	 **5d** (38)[d]	 **6d** (53)
5	**2a**	 **5e** (85)	 **6e** (53)
6	**2a**	 **5f** (61)	 **6f** (52)
7	 **2e** (53)	 **5g** (67)	**6a** (53)

[a] Substrate **1**, $TsNH_2$, or $CH_3SO_2NH_2$ (1 equiv), aq THF, K_2CO_3 (1.2 equiv), reflux, 5–16 h.
[b] (1) Michael acceptor (1.5 equiv), DBU (0.5 equiv), THF, rt, 3–24 h, (2) aq workup, (3) benzene, *p*-TsOH (0.1 equiv), reflux, 1–5 h.
[c] DMF, Cs_2CO_3 (3 equiv), 120–130 °C, 0.5–3 h.
[d] The corresponding *exo*-ethylidene compound **5d′** was isolated in 31% yield.



Scheme 2.

Fortunately, however, the two compounds **5d** and **5d′** could be changed to **6d** in similar yields. The use of ethyl vinyl ketone or methyl acrylate as the Michael acceptors did not show any differences during the whole steps to give **6e** and **6f** (entries 5 and 6) in moderate yields. As the last entry, the use of methanesulfonamide instead of *p*-toluenesulfonamide showed similar results (entry 7).

In summary, we developed an efficient synthetic route for 3,4,5-trisubstituted pyridine derivatives starting from the Baylis–Hillman adducts of methyl vinyl ketone and ethyl vinyl ketone. The synthesis was achieved by following the successive steps: (i) introduction of tosylamide, (ii) Michael addition, (iii) aldol condensation, (iv) elimination of *p*-toluenesulfinic acid, and finally isomerization of double bond.

References and notes

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2. For recent synthesis of pyridine derivatives, see: (a) Suzuki, D.; Nobe, Y.; Watai, Y.; Tanaka, R.; Takayama, Y.; Sato, F.; Urabe, H. *J. Am. Chem. Soc.* **2005**, *127*, 7474; (b) Xi, Z.; Sato, K.; Gao, Y.; Lu, J.; Takahashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9568; (c) Charette, A. B.; Grenon, M.; Lemire, A.; Pourashraf, M.; Martel, J. *J. Am. Chem. Soc.* **2001**, *123*, 11829; (d) Palacios, F.; Herran, E.; Rubiales, G.; Ezpeleta, J. M. *J. Org. Chem.* **2002**, *67*, 2131; (e) Beccalli, E. M.; Contini, A.; Trimarco, P. *Tetrahedron Lett.* **2004**, *45*, 3447; (f) Heller, B.; Sundermann, B.; Buschmann, H.; Drexler, H.-J.; You, J.; Holzgrabe, U.; Heller, E.; Oehme, G. *J. Org. Chem.* **2002**, *67*, 4414; (g) Pal, M.; Batchu, V. R.; Dager, I.; Swamy, N. K.; Padakanti, S. *J. Org. Chem.* **2005**, *70*, 2376, and further references cited therein.
3. For our recent publications on the chemical transformations of Baylis–Hillman adducts, see: (a) Gowrisankar, S.; Lee, K. Y.; Kim, J. N. *Tetrahedron Lett.* **2005**, *46*, 4859; (b) Lee, K. Y.; Gowrisankar, S.; Kim, J. N. *Tetrahedron Lett.* **2005**, *46*, 5387; (c) Lee, C. G.; Lee, K. Y.; Lee, S.; Kim, J. N. *Tetrahedron* **2005**, *61*, 1493, and further references cited therein.
4. Synthesis of starting materials **2a–e** was carried out by the reaction of tosylamide and the Baylis–Hillman acetates in the presence of K_2CO_3 in aq THF under refluxing conditions according to the previous paper. (a) Kim, J. N.; Chung, Y. M.; Im, Y. J. *Tetrahedron Lett.* **2002**, *43*, 6209; (b) Kim, J. N.; Lee, H. J.; Lee, K. Y.; Kim, H. S. *Tetrahedron Lett.* **2001**, *42*, 3737.
5. *Typical procedure for the synthesis of starting materials* **2a**: To a stirred mixture of the Baylis–Hillman acetate (436 mg, 2.0 mmol) of benzaldehyde and methyl vinyl ketone and *p*-toluenesulfonamide (342 mg, 2.0 mmol) in aq THF (5 mL) was added K_2CO_3 (332 mg, 2.4 mmol) and heated to reflux for 16 h. After the usual workup and column chromatographic purification process (hexanes/ether, 5:2) we obtained **2a** as a white solid, 433 mg (66%). The other compounds were synthesized analogously and the spectroscopic data are as follows.
Compound **2a**: 66%; white solid, mp 120–121 °C; IR (KBr) 3271, 1658, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.33 (s, 3H), 2.41 (s, 3H), 3.89 (d, $J = 6.6$ Hz, 2H), 5.29 (t, $J = 6.6$ Hz, 1H), 7.24–7.67 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.44, 25.41, 39.95, 127.20, 128.79, 129.55, 129.57, 129.71, 133.77, 135.73, 136.46, 143.33, 144.11, 200.45.
Compound **2b**: 64%; white solid, mp 88–89 °C; IR (KBr) 3271, 1662, 1327, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.34 (s, 3H), 2.43 (s, 3H), 3.82 (d, $J = 6.6$ Hz, 2H), 5.29 (t, $J = 6.6$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.40 (s, 4H), 7.53 (s, 1H), 7.67 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.49, 25.41, 39.92, 127.23, 129.13, 129.67, 130.91, 132.22, 135.91, 136.25, 136.31, 142.70, 143.53, 200.21.
Compound **2c**: 64%; white solid, mp 114–115 °C; IR (KBr) 3271, 2924, 1658, 1327, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.33 (s, 3H), 2.40 (s, 3H), 2.42 (s, 3H), 3.90 (d, $J = 6.6$ Hz, 2H), 5.23 (t, $J = 6.6$ Hz, 1H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.54 (s, 1H), 7.67 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.42, 21.48, 25.39, 40.11, 127.26, 129.61 (2C), 129.73, 130.97, 135.00, 136.55, 140.27, 143.34, 144.39, 200.47.
Compound **2d**: 51%; white solid, mp 135–137 °C; IR (KBr) 3275, 2924, 1662, 1331, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.10 (t, $J = 7.2$ Hz, 3H), 2.42 (s, 3H), 2.70 (q, $J = 7.2$ Hz, 2H), 3.89 (d, $J = 6.6$ Hz, 2H), 5.24 (t, $J = 6.6$ Hz, 1H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.37–7.47 (m, 5H), 7.60 (s, 1H), 7.67 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 8.29, 21.48, 30.31, 40.29, 127.24, 128.84, 129.56, 129.63 (2C), 133.92, 135.30, 136.54, 142.79, 143.36, 203.10.

Compound **2e**: 53%; white solid, mp 63–65 °C; IR (KBr) 3282, 1662, 1319, 1149 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.49 (s, 3H), 2.95 (s, 3H), 4.10 (d, $J = 6.3$ Hz, 2H), 5.08 (t, $J = 6.3$ Hz, 1H), 7.41–7.53 (m, 5H), 7.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.58, 39.52, 39.58, 128.89, 129.45, 129.85, 133.72, 135.96, 144.51, 200.31.

6. For the applications of aldol type condensation reaction in the transformations of Baylis–Hillman adducts, see: (a) Kim, J. N.; Kim, J. M.; Lee, K. Y. *Synlett* **2003**, 821; (b) Im, Y. J.; Lee, C. G.; Kim, H. R.; Kim, J. N. *Tetrahedron Lett.* **2003**, *44*, 2987; (c) Kim, J. N.; Im, Y. J.; Kim, J. M. *Tetrahedron Lett.* **2002**, *43*, 6597.
7. One of the major components of **4a** was separated by column chromatography in pure state as a white solid in 60% yield: mp 128–130 °C; IR (KBr) 3491, 2924, 1701, 1346, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.24 (s, 3H), 2.31 (s, 3H), 2.43 (s, 3H), 2.45 (s, 1H, OH), 2.81–3.03 (m, 3H), 3.80–3.87 (m, 1H), 4.68 (dd, $J = 13.2$ and 2.1 Hz, 1H), 6.88 (s, 1H), 7.20–7.59 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.55, 22.52, 32.50, 44.83, 45.34, 58.42, 73.33, 124.66, 127.33, 127.68, 128.54, 128.84, 129.83, 132.96, 135.93, 138.59, 143.93, 208.78. However, we did not determine the stereochemistry of this major component.
8. *Typical procedure for the synthesis of intermediate* **5a**: To a stirred mixture of tosylamide derivative **2a** (329 mg, 1.0 mmol) and methyl vinyl ketone (105 mg, 1.5 mmol) in THF (4 mL) was added DBU (76 mg, 0.5 mmol) and stirred at room temperature for 6 h. After the reaction we could observe two major components on TLC, which must be the corresponding two diastereoisomers resulting from the consecutive Michael addition and aldol reaction. The separation was not carried out. Instead, desired portion was separated by simple aq workup and removal of solvent as a crude state. The crude mixtures was dissolved in benzene and subjected to dehydration conditions, *p*-TsOH (19 mg, 0.1 mmol), reflux, 1 h. The desired dehydration product **5a** was separated after aq workup and column chromatographic purification process (hexanes/EtOAc, 5:1), 332 mg (87%) as a white solid. The other compounds were synthesized analogously (reaction time is mentioned in the parenthesis: the first refer to the cyclization and the second dehydration) and the spectroscopic data are as follows.

   Compound **5a** (6/1 h): 87%; white solid, mp 79–80 °C; IR (KBr) 1682, 1350, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.93 (s, 3H), 2.31 (s, 3H), 2.42 (s, 3H), 4.06 (s, 2H), 4.16 (s, 2H), 6.75 (s, 1H), 7.17–7.56 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.60, 21.46, 30.55, 44.98, 46.12, 127.70, 127.87, 128.57, 129.03, 129.44, 130.19, 131.64, 132.48, 133.95, 135.86, 135.91, 143.69, 201.45.

   Compound **5b** (3/1 h): 72%; white solid, mp 70–71 °C; IR (KBr) 2927, 1682, 1350, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.93 (s, 3H), 2.31 (s, 3H), 2.42 (s, 3H), 4.04 (s, 2H), 4.10 (s, 2H), 6.69 (s, 1H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.55 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.55, 21.44, 30.51, 44.80, 46.06, 127.65, 128.67, 128.78, 129.48, 130.27, 132.35, 132.93, 133.72, 133.78, 134.32, 135.42, 143.81, 201.38.

   Compound **5c** (5/2 h): 80%; white solid, mp 119–121 °C; IR (KBr) 1678, 1350, 1242, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.93 (s, 3H), 2.31 (s, 3H), 2.39 (s, 3H), 2.42 (s, 3H), 4.06 (s, 2H), 4.18 (s, 2H), 6.73 (s, 1H), 7.08 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.55 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.65, 21.26, 21.49, 30.57, 45.09, 46.17, 127.75, 129.05, 129.32, 129.43, 130.37, 131.03, 132.07, 133.01, 134.07, 136.32, 137.94, 143.66, 201.40.

   Compound **5d** (24/2 h): 38%; clear oil; IR (film) 1682, 1597, 1350, 1246,1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 0.94 (t, $J = 7.2$ Hz, 3H), 2.30 (s, 3H), 2.38 (q, $J = 7.2$ Hz, 2H), 2.41 (s, 3H), 4.09 (s, 2H), 4.18 (s, 2H), 6.77 (s, 1H), 7.18–7.55 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.47, 21.47, 22.01, 30.20, 44.91, 46.12, 127.64, 127.91, 128.61, 129.07, 129.52, 129.58, 130.23, 131.55, 134.28, 135.96, 141.76, 143.77, 200.96.

   Compound **5d′**: 31%; clear oil; IR (film) 1712, 1597, 1346, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.69 (d, $J = 6.9$ Hz, 3H), 2.19 (s, 3H), 2.42 (s, 3H), 2.92 (dd, $J = 12.0$ and 5.1 Hz, 1H), 3.49 (dd, $J = 13.5$ and 2.1 Hz, 1H), 3.60 (t, $J = 4.2$ Hz, 1H), 4.03 (dd, $J = 12.0$ and 3.3 Hz, 1H), 4.46 (d, $J = 13.5$ Hz, 1H), 5.95 (q, $J = 6.9$ Hz, 1H), 6.65 (s, 1H), 7.13–7.63 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.96, 21.50, 28.38, 46.17, 47.32, 50.11, 125.84, 127.05, 127.39, 127.72, 128.47, 129.00, 129.67, 133.31, 134.62, 134.94, 136.06, 143.71, 206.23.

   Compound **5e** (6/1 h): 85%; clear oil; IR (film) 2927, 1693, 1342, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.12 (t, $J = 7.5$ Hz, 3H), 1.86 (s, 3H), 2.42 (s, 3H), 2.57 (q, $J = 7.5$ Hz, 2H), 4.03 (s, 2H), 4.16 (s, 2H), 6.70 (s, 1H), 7.16–7.57 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 8.15, 15.84, 21.79, 36.17, 45.25, 46.39, 128.05, 128.08, 128.87, 129.31, 129.74, 129.81, 131.77, 133.12, 134.26, 134.27, 136.23, 143.99, 205.69.

   Compound **5f** (24/5 h): 61%; white solid, mp 108–110 °C; IR (KBr) 1716, 1350, 1250, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 3H), 2.41 (s, 3H), 3.77 (s, 3H), 4.11 (s, 2H), 4.15 (s, 2H), 6.82 (s, 1H), 7.18–7.56 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.26, 21.46, 44.91, 46.20, 51.72, 123.02, 127.70, 127.95, 128.57, 129.09, 129.41, 130.97, 131.91, 134.14, 135.83, 142.11, 143.57, 166.73.

   Compound **5g** (6/1 h): 67%; yellow solid, mp 125–127 °C; IR (KBr) 1682, 1335, 1153 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.18 (s, 3H), 2.38 (s, 3H), 2.74 (s, 3H), 4.21 (s, 2H), 4.33 (s, 2H), 7.00 (s, 1H), 7.23–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.89, 30.53, 37.36, 44.62, 45.93, 128.10, 128.70, 129.09, 130.76, 131.60, 133.01, 135.59, 136.07, 201.49.
9. *Typical procedure for the synthesis of pyridine* **6a**: To a stirred solution of **5a** (191 mg, 0.5 mmol) in dry DMF (2 mL) was added Cs_2CO_3 (490 mg, 1.5 mmol) and heated to 120–130 °C for 1 h. After the usual workup and column chromatographic purification process (hexanes/EtOAc, 5:1) we obtained **6a** as clear oil, 63 mg (56%). The other compounds were synthesized analogously (reaction time is mentioned in the parenthesis) and the spectroscopic data are as follows.

   Compound **6a** (1 h): 56%; clear oil; IR (film) 1689, 1454, 1281 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 3H), 2.62 (s, 3H), 4.05 (s, 2H), 7.07–7.32 (m, 5H), 8.47 (s, 1H), 8.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.20, 30.28, 36.75, 126.49, 128.40, 128.66, 134.81, 135.81, 138.53, 145.76, 148.04, 152.88, 200.99.

   Compound **6b** (20 min): 60%; clear oil; IR (film) 1689, 1493, 1281 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.34 (s, 3H), 2.62 (s, 3H), 4.02 (s, 2H), 7.02 (d, $J = 8.7$ Hz, 2H), 7.25 (d, $J = 8.7$ Hz, 2H), 8.45 (s, 1H), 8.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.19, 30.25, 36.12, 128.79, 129.69, 132.37, 134.84, 135.30, 137.04, 145.70, 148.26, 152.80, 200.84.

   Compound **6c** (30 min): 64%; clear oil; IR (film) 1689, 1281 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.31 (s, 3H), 2.35 (s, 3H), 2.61 (s, 3H), 4.00 (s, 2H), 6.97 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 8.46 (s, 1H), 8.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.16, 20.91, 30.27, 36.32, 128.28, 129.31, 134.78, 135.45, 136.04 (2C), 145.68, 147.95, 152.84, 201.00.

Compound **6d** (30 min): 53%; clear oil; IR (film) 1689, 1277 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.07 (t, $J = 7.5$ Hz, 3H), 2.62 (s, 3H), 2.82 (q, $J = 7.5$ Hz, 2H), 4.08 (s, 2H), 7.08–7.32 (m, 5H), 8.45 (s, 1H), 8.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.55, 22.41, 30.49, 35.88, 126.54, 128.50, 128.68, 134.29, 135.14, 139.22, 148.33, 151.41, 153.62, 200.94.

Compound **6e** (1 h): 53%; clear oil; IR (film) 1693, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.21 (t, $J = 7.2$ Hz, 3H), 2.30 (s, 3H), 2.92 (q, $J = 7.2$ Hz, 2H), 4.05 (s, 2H), 7.08–7.32 (m, 5H), 8.45 (s, 1H), 8.67 (s, 1H); ^{13}C NMR ($CDCl_3$,75 MHz): δ 8.11, 16.13, 35.99, 36.80, 126.51, 128.45, 128.68, 135.44, 135.76, 138.57, 145.22, 146.97, 152.48, 204.51.

Compound **6f** (3 h): 52%; clear oil; IR (film) 1724, 1288 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.45 (s, 3H), 3.91 (s, 2H), 4.06 (s, 3H), 7.06–7.31 (m, 5H), 8.48 (s, 1H), 8.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.29, 36.78, 52.18, 126.47, 126.86, 128.37, 128.65, 135.31, 138.62, 147.62, 149.71, 153.26, 167.12.