Synthesis of 4-Benzylidene-2,5-dimethyl-3,4-dihydro-2*H*-pyrrole Derivatives from Baylis-Hillman Adducts and Their Chemical Transformations

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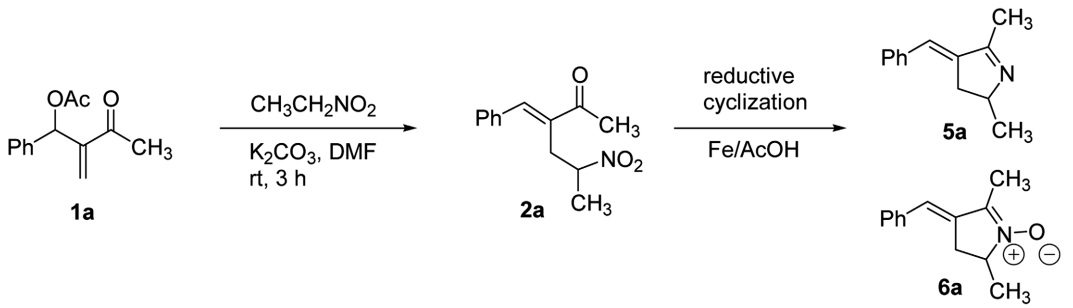
Recently, Basavaiah and Rao reported the synthesis of substituted γ-lactams by the reductive cyclization of γ-nitroesters, which were prepared from the reaction of the acetates of Baylis-Hillman adducts and nitro compounds.[1] γ-Nitrocarbonyl compounds could be transformed into cyclic nitrones or pyrroline derivatives depending upon the reduction conditions and the nature of the carbonyl groups.[1,2] Various reduction conditions have been used for the reductive cyclization of γ-nitrocarbonyl compounds including Fe/AcOH,[1] Zn/NH_4Cl,[2a-d] and catalytic hydrogenation.[2e,2f]

Suitably substituted pyrrolines[3] or cyclic nitrone derivatives[4] have been prepared and used as important synthetic intermediates.[1-4] During the investigation on the chemical transformations of Baylis-Hillman adducts,[5] we intended to examine the reductive cyclization of γ-nitroketone derivatives **2** derived from the acetates of Baylis-Hillman adducts as shown in Scheme 1. The starting materials **2a-e** were easily prepared by the S_N2' reaction of primary nitroalkanes and the acetates of the Baylis-Hillman adducts according to the previous method.[1,5] We tried the reductive cyclization of **2a** under various conditions and the results are summarized in Table 1 (entries 1-3). As shown in Table 1, we obtained mixtures of 4-benzylidene-2,5-dimethyl-3,4-dihydro-2*H*-pyrrole (**5a**) and cyclic nitrone derivative **6a** in variable yields. The use of Fe/AcOH gave the pyrroline derivative **5a** as the major product under refluxing conditions (entry 1). Whereas, we obtained the cyclic nitrone derivative **6a** as the major product when we use Zn/NH_4Cl at low temperature (entry 3). The use of Fe/AcOH (entry 2) at lower temperature and Zn/NH_4Cl at room temperature (not shown) showed diminished selectivity. In spite of our extensive efforts we failed to obtain higher selectivity. Similarly, we synthesized **5b-e** and **6b-e** from the reaction of **2b-e** under Fe/AcOH/reflux conditions and the results are summarized in Table 1.

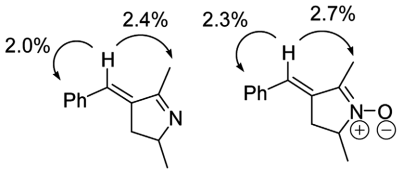
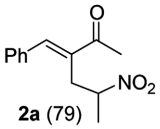
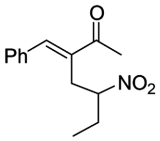
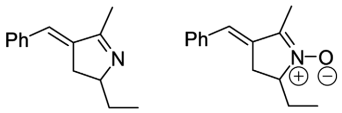
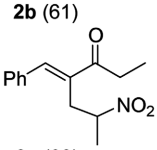
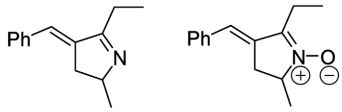
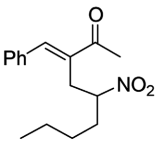
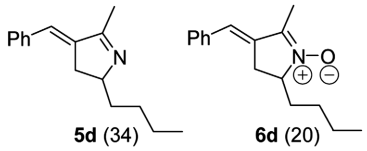
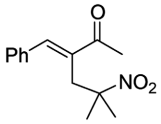
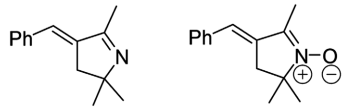
For the substrates **2b-d**, pyrroline derivatives **5b-d** were isolated as the major products. However, nitrone **6e** was obtained as the major product in the case of dimethyl-substituted starting material **2e** (entry 7). Structure identification of the synthesized products was carried out by their ^1H and ^{13}C NMR, IR, mass, and chemical transformations (vide infra). The stereochemistry of the double bond of **5a** and **6a** was confirmed as *E* based on NOE experiments (shown in Table 1).[1,5] The mechanism for the formation of **5** and **6** was proposed as in Scheme 2 with **5a** and **6a** as the representative examples. Reduction of the nitro group into amino group to form **3a** and the following condensation gave **5a**. Partial reduction to hydroxylamine derivative **4a** and the following cyclization and dehydration afforded **6a**.

In order to verify the usefulness of the prepared pyrroline compounds **5**, we examined the Michael addition reaction of the acidic methyl group at the 5-position of **5a** toward acrylonitrile or methyl acrylate (Scheme 3).[6] The reaction of pyrroline **5a** and acrylonitrile in THF in the presence of catalytic amounts of base (DBU or NaOMe) produced intractable mixtures of products. Fortunately, we could obtain **8a** in moderate yield (59%) by refluxing **5a** in acrylonitrile without any base and solvent for long time (60 h). First introduction of acrylonitrile to the methyl group of **5a** produced the corresponding mono adduct (**I**), which reacted once more with acrylonitrile to produce **8a**. But, the third introduction of acrylonitrile to **8a** did not occur presumably due to the steric hindrance. The Michael addition reaction was thought to occur *via* the imine-enamine tautomerization as shown.[7] Similarly, we obtained **7a** from the reaction of **5a** and methyl acrylate in 58% yield. The

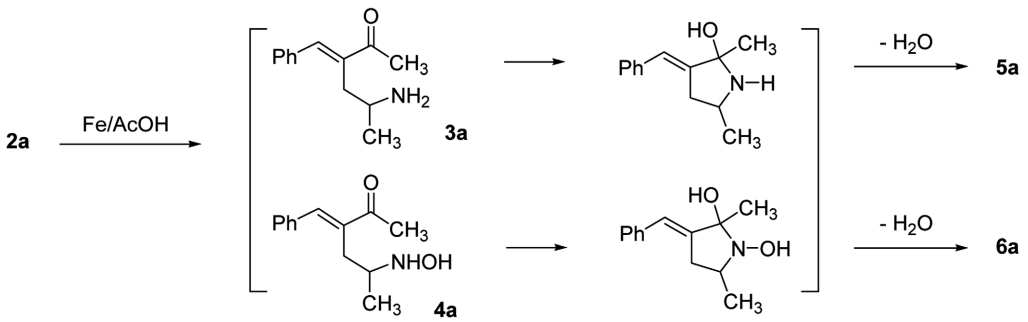


Scheme 1

Table 1. Reductive cyclization of **2**

Entry	Substrates **2**[a]	Conditions	Products (% yield)
			
1	 **2a** (79)	Fe (8 equiv) AcOH, reflux, 2 h	**5a** (54) **6a** (27)
2		Fe (10 equiv) AcOH, 80 °C, 2 h	**5a** (32) **6a** (40)
3		Zn (8 equiv) NH_4Cl (2 equiv) aq. THF, - 10 °C, 2 h	**5a** (14) **6a** (58)
4	 **2b** (61)	Fe (10 equiv) AcOH, reflux, 4 h	 **5b** (38) **6b** (24)
5	 **2c** (82)	Fe (8 equiv) AcOH, reflux, 2 h	 **5c** (37) **6c** (21)
6	 **2d** (79)	Fe (8 equiv) AcOH, reflux, 4 h	 **5d** (34) **6d** (20)
7	 **2e** (75)	Fe (8 equiv) AcOH, reflux, 2 h	 **5e** (36) **6e** (46)

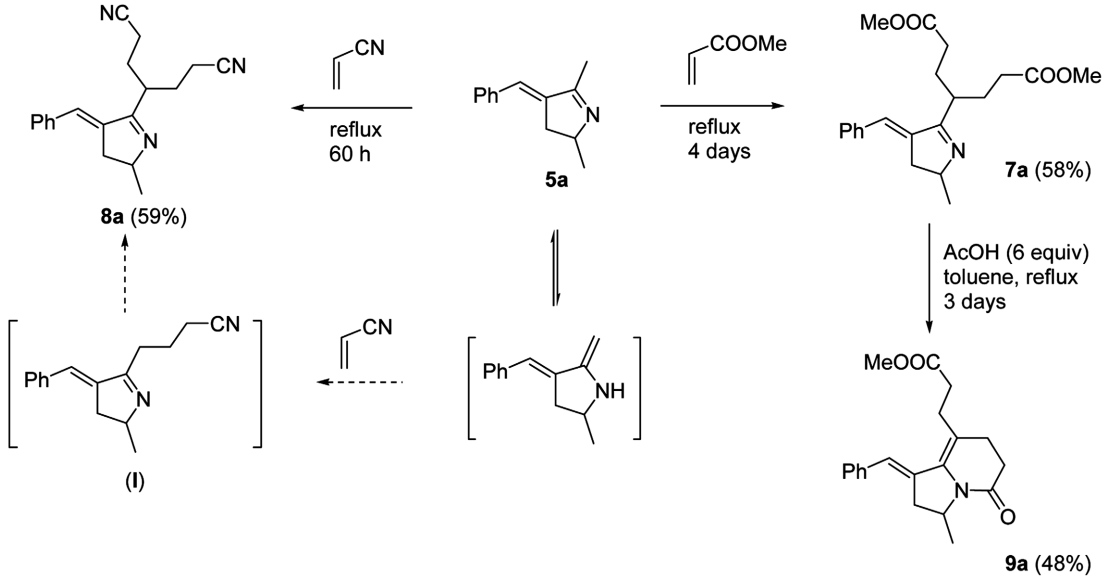
[a]Yields in parenthesis. Conditions: Baylis-Hillman acetate **1**, nitroalkane (2 equiv), K_2CO_3 (3 equiv), DMF, rt, 3 h.



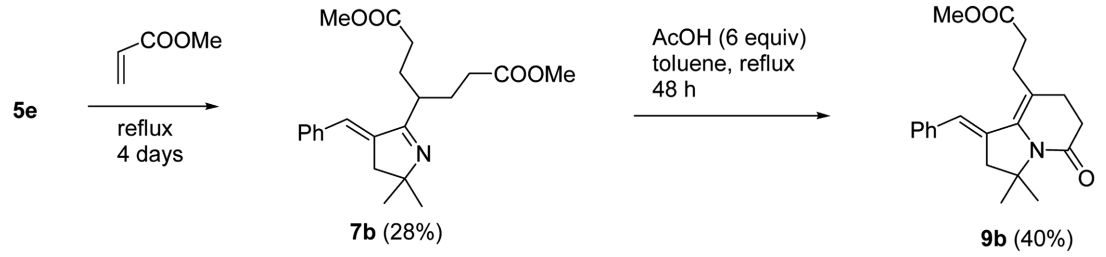
Scheme 2

compound **7a** could be transformed to bicyclic lactam derivative **9a** in refluxing toluene in the presence of acetic acid in 48% yield.[8,9] We also tried the reactions of **5e** and **5c** and obtained the corresponding tetrahydroindolizinone derivatives **9b** and **9c** *via* the corresponding intermediates **7b** and **7c** although the yields were relatively low (Schemes 4 and 5).

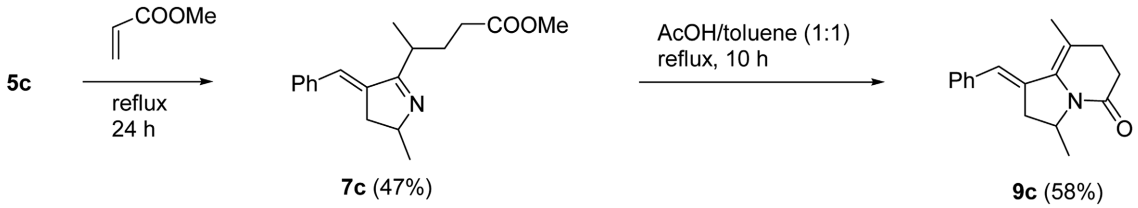
In summary, we disclosed the reductive cyclization of *γ*-nitrocarbonyl compounds derived from Baylis-Hillman adducts into cyclic nitrone and pyrroline derivatives.



Scheme 3



Scheme 4



Scheme 5

Selective double Michael addition reaction of the pyrroline compounds was observed for the first time. Further studies on the synthesis of bicyclic lactam derivatives and transformation into natural alkaloid derivatives are underway.[9]

Experimental Section

Typical procedure for the synthesis of starting material 2a: A solution of Baylis-Hillman acetate **1a** (436 mg, 2 mmol), nitroethane (300 mg, 4 mmol), and K_2CO_3 (830 mg, 6 mmol) in DMF (5 mL) was stirred at room temperature for 3 h. After the normal aqueous workup and column chromatographic purification process (hexanes/ether, 10 : 1) we obtained **2a**, 370 mg (79%). Other starting materials **2b-e** were synthesized similarly and the spectroscopic data are as follows.

Compound **2a**: 79%; oil; IR (neat) 1666, 1550 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.44 (d, J = 6.6 Hz, 3H), 2.48 (s, 3H), 2.93 (ddd, J = 14.1, 5.7, and 0.9 Hz, 1H), 3.15 (dd, J = 14.1 and 9.0 Hz, 1H), 4.77-4.89 (m, 1H), 7.27-7.46 (m, 5H), 7.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.80, 25.84, 31.92, 81.45, 128.65, 128.73, 129.01, 134.48, 137.00, 143.85, 199.64.

Compound **2b**: 61%; oil; IR (neat) 1666, 1547 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J = 7.2 Hz, 3H), 1.67-1.76 (m, 1H), 1.86-1.97 (m, 1H), 2.47 (s, 3H), 2.93 (dd, J = 14.1 and 4.5 Hz, 1H), 3.13 (dd, J = 14.1 and 9.6 Hz, 1H), 4.60-4.71 (m, 1H), 7.28-7.44 (m, 5H), 7.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.12, 25.84, 26.77, 30.52, 88.27, 128.63, 128.66, 128.94, 134.47, 136.98, 143.80, 199.63.

Compound **2c**: 82%; oil; IR (neat) 1670, 1547 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18 (t, J = 7.2 Hz, 3H), 1.43 (d, J = 6.7 Hz, 3H), 2.77-2.96 (m, 3H), 3.11-3.19 (m, 1H), 4.78-4.88 (m, 1H), 7.26-7.45 (m, 5H), 7.71 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.65, 18.87, 30.74, 32.23, 81.57, 128.65,

128.74, 128.91, 134.64, 136.63, 142.45, 202.43.

Compound **2d**: 79%; IR (neat) 1670, 1550 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, J = 7.2 Hz, 3H), 1.14-1.35 (m, 4H), 1.57-1.70 (m, 1H), 1.81-1.95 (m, 1H), 2.47 (s, 3H), 2.91 (dd, J = 14.1 and 4.8 Hz, 1H), 3.13 (dd, J = 14.1 and 9.6 Hz, 1H), 4.66-4.76 (m, 1H), 7.25-7.45 (m, 5H), 7.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.65, 21.98, 25.88, 27.72, 30.82, 33.19, 86.88, 128.65, 128.69, 128.96, 134.53, 137.08, 143.81, 199.68.

Compound **2e**: 75%; oil; IR (neat) 1674, 1539 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.37 (s, 6H), 2.48 (s, 3H), 3.30 (s, 2H), 7.27-7.44 (m, 5H), 7.71 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.81, 26.00, 34.55, 87.88, 128.50, 128.75, 128.78, 135.04, 137.79, 143.24, 199.62.

Typical procedure for the synthesis of pyrroline 5a and cyclic nitrone 6a: To a stirred mixture of **2a** (233 mg, 1 mmol) in AcOH (3 mL) was added Fe powder (447 mg, 8 mmol) and heated to reflux for 2 h. After cooling the reaction mixtures to room temperature, dilution with ether, filtration over Celite pad, normal aqueous workup with ether, and column chromatographic purification process (hexanes/CH_2Cl_2/EtOAc, 2 : 1 : 1) we obtained pyrroline **5a** and nitrone **6a**, 100 mg (54%), 55 mg (27%), respectively. Other experiments for the synthesis of **5b-e** and **6b-e** were carried out similarly and the spectroscopic data of prepared compounds are as follows.

Compound **5a**: 54%; oil; IR (neat) 2962, 1601 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.32 (d, J = 6.9 Hz, 3H), 2.22 (d, J = 1.8 Hz, 3H), 2.43 (dt, J = 17.7 and 3.0 Hz, 1H), 3.08 (ddd, J = 17.7, 7.2, and 3.0 Hz, 1H), 4.18-4.28 (m, 1H), 6.70 (t, J = 3.0 Hz, 1H), 7.25-7.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.05, 22.50, 37.65, 65.36, 124.98, 127.75, 128.56, 128.71, 136.90, 143.08, 171.17; ESIMS m/z 186.40 (M^++H).

Compound **6a**: 27%; white solid, mp 64-65 °C; IR (neat) 1550, 1269 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.53 (d, J = 6.9 Hz, 3H), 2.17 (d, J = 1.5 Hz, 3H), 2.76 (ddd, J = 16.5, 3.9, and 2.4 Hz, 1H), 3.35 (ddd, J = 16.5, 8.4, and 2.4 Hz, 1H), 4.17-4.27 (m, 1H), 6.50 (t, J = 2.4 Hz, 1H), 7.22-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.22, 19.54, 33.39, 66.62, 122.17, 127.25, 128.49, 128.65, 135.03, 136.50, 145.27; ESIMS m/z 202.06 (M^++H).

Compound **5b**: 38%; oil; IR (neat) 2958, 2924, 1601 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02 (t, J = 7.2 Hz, 3H), 1.42-1.57 (m, 1H), 1.72-1.87 (m, 1H), 2.21 (d, J = 1.8 Hz, 3H), 2.47 (dt, J = 17.7 and 2.7 Hz, 1H), 3.00 (ddd, J = 17.7, 6.9, and 2.7 Hz, 1H), 4.01-4.12 (m, 1H), 6.68 (t, J = 2.7 Hz, 1H), 7.25-7.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.64, 16.05, 29.53, 35.30, 71.57, 124.58, 127.65, 128.51, 128.66, 136.93, 142.94, 171.24.

Compound **6b**: 24%; oil; IR (neat) 2966, 2931, 1547, 1273 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (t, J = 7.2 Hz, 3H), 1.72-1.83 (m, 1H), 2.09-2.22 (m, 1H), 2.18 (d, J = 1.2 Hz, 3H), 2.82 (dt, J = 16.8 and 2.7 Hz, 1H), 3.25 (ddd, J = 16.8, 8.4, and 2.7 Hz, 1H), 4.09-4.18 (m, 1H), 6.50 (t, J = 2.4 Hz, 1H), 7.23-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.36, 9.10, 25.55, 30.49, 71.60, 122.17, 127.29, 128.54, 128.69, 135.32, 136.54, 146.09.

Compound **5c**: 37%; oil; IR (neat) 2970, 1601, 1450 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, J = 7.5 Hz, 3H), 1.31 (d, J = 6.9 Hz, 3H), 2.43 (dt, J = 17.4 and 2.7 Hz, 1H), 2.57 (qd, J = 7.5 and 1.5 Hz, 2H), 3.07 (ddd, J = 17.4, 6.9, and 2.7 Hz, 1H), 4.19-4.28 (m, 1H), 6.71 (t, J = 2.7 Hz, 1H), 7.24-7.47 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.26, 22.59, 22.69, 38.01, 65.31, 124.21, 127.60, 128.50, 128.69, 136.99, 142.34, 174.99.

Compound **6c**: 21%; oil; IR (neat) 1539, 1273 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20 (t, J = 7.5 Hz, 3H), 1.52 (d, J = 6.6 Hz, 3H), 2.66 (q, J = 7.5 Hz, 2H), 2.71-2.79 (m, 1H), 3.35 (ddd, J = 16.5, 8.4, and 2.7 Hz, 1H), 4.17-4.25 (m, 1H), 6.53 (t, J = 2.7 Hz, 1H), 7.22-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.66, 16.67, 19.59, 33.40, 66.56, 121.91, 127.24, 128.52, 128.66, 134.06, 136.59, 149.70.

Compound **5d**: 34%; IR (neat) 2954, 2927, 1601 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (t, J = 6.9 Hz, 3H), 1.33-1.47 (m, 5H), 1.72-1.83 (m, 1H), 2.24 (d, J = 1.8 Hz, 3H), 2.49 (dt, J = 17.4 and 2.7 Hz, 1H), 3.01 (ddd, J = 17.4, 7.2, and 2.7 Hz, 1H), 4.10-4.19 (m, 1H), 6.72 (t, J = 2.7 Hz, 1H), 7.20-7.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.98, 15.70, 22.72, 28.49, 35.56, 36.37, 69.71, 125.48, 127.84, 128.55, 128.76, 136.71, 142.56, 171.69.

Compound **6d**: 20%; oil; IR (neat) 2954, 1550, 1269 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (t, J = 6.9 Hz, 3H), 1.23-1.43 (m, 5H), 1.58-1.71 (m, 1H), 2.17 (d, J = 1.5 Hz, 3H), 2.82 (dt, J = 16.5 and 2.7 Hz, 1H), 3.26 (ddd, J = 16.5, 8.4, and 2.7 Hz, 1H), 4.08-4.19 (m, 1H), 6.51 (t, J = 2.7 Hz, 1H), 7.06-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.18, 13.91, 22.53, 26.63, 31.17, 32.52, 70.80, 122.43, 127.35, 128.59, 128.72, 135.30, 136.54, 146.23.

Compound **5e**: 36%; oil; IR (neat) 2962, 2924, 1601 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (s, 6H), 2.20 (s, 3H), 2.71 (d, J = 2.7 Hz, 2H), 6.68 (t, J = 2.7 Hz, 1H), 7.25-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.99, 29.46, 43.81, 70.08, 125.38, 127.76, 128.53, 128.69, 136.88, 143.22, 168.84.

Compound **6e**: 46%; white solid, mp 87-89 °C; IR (neat) 2974, 2931, 1543, 1265 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 6H), 2.17 (s, 3H), 3.05 (d, J = 2.1 Hz, 2H), 6.52 (t, J = 2.1 Hz, 1H), 7.22-7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.40, 26.42, 40.70, 72.25, 121.98, 127.16, 128.47, 128.64, 134.07, 136.67, 143.55.

Typical procedures for the synthesis of Michael adduct 7a and bicyclic lactam derivative 9a: A solution of **5a** (185 mg, 1 mmol) in methyl acrylate (3 mL) was heated to reflux for 4 days. After removal of methyl acrylate and column chromatographic purification process (hexanes/EtOAc, 2 : 1) we obtained **7a**, 208 mg (58%). To a stirred solution of **7a** (179 mg, 0.5 mmol) in toluene (3 mL) was added AcOH (180 mg, 3 mmol) and the reaction mixture was heated to reflux for 3 days. After removal of solvent and column chromatographic purification process (hexanes/CH_2Cl_2/EtOAc, 2 : 1 : 2) we obtained **9a**, 78 mg (48%). The compounds **7b**, **7c**, **8a**, **9b**, and **9c** were synthesized analogously and the spectroscopic data are as follows.

Compound **7a**: 58%; oil; IR (neat) 2954, 1736, 1439 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, J = 6.8 Hz, 3H), 1.95-2.50 (m,

9H), 2.85-3.00 (m, 1H), 3.09 (ddd, J = 17.4, 7.2, and 2.7 Hz, 1H), 3.65 (s, 6H), 4.27-4.33 (m, 1H), 6.75 (t, J = 2.7 Hz, 1H), 7.26-7.49 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.84, 28.48, 31.36, 31.52, 35.95, 38.09, 51.53, 65.53, 124.62, 127.87, 128.57, 128.93, 136.81, 142.63, 173.82, 175.40; ESIMS *m/z* 358.09 (M^++H).

Compound **7b**: 28%; IR (neat) 2958, 1736, 1169 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.31 (s, 6H), 1.90-2.17 (m, 4H), 2.22-2.47 (m, 4H), 2.73 (d, J = 2.7 Hz, 2H), 2.89-2.95 (m, 1H), 3.64 (s, 6H), 6.73 (t, J = 2.7 Hz, 1H), 7.20-7.47 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.54, 29.56, 31.39, 35.76, 44.33, 51.49, 70.33, 124.86, 127.85, 128.54, 128.91, 136.82, 142.92, 173.13, 173.78.

Compound **7c**: 45% (1 : 1 mixture of two diastereomers); IR (neat) 2962, 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.25 (d, J = 6.9 Hz, 1.5H), 1.26 (d, J = 6.9 Hz, 1.5 Hz), 1.29 (d, J = 6.9 Hz, 1.5H), 1.30 (d, J = 6.9 Hz, 1.5 Hz, 1.5H), 1.85-1.95 (m, 1H), 2.08-2.22 (m, 1H), 2.28-2.48 (m, 3H), 2.90-2.97 (m, 1H), 3.07 (ddd, J = 17.4, 6.9, and 2.4 Hz, 1H), 3.66 (s, 3H), 4.24-4.30 (m, 1H), 6.75 (t, J = 2.4 Hz, 1H), 7.25-7.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.94, 19.10, 22.67, 22.82, 29.96, 30.12, 31.59, 31.69, 31.77, 38.12, 38.19, 51.46, 65.30, 65.41, 124.14, 124.22, 127.68, 128.53, 128.83, 136.98, 142.04, 174.01, 176.86, 177.00.

Compound **8a**: 59%; oil; IR (neat) 2927, 2245, 1589 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32 (d, J = 6.6 Hz, 3H), 1.92-2.05 (m, 2H), 2.14-2.55 (m, 7H), 3.10-3.23 (m, 2H), 4.28-4.38 (m, 1H), 6.87 (t, J = 2.7 Hz, 1H), 7.22-7.51 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.81, 14.98, 22.66, 29.12, 35.21, 38.03, 65.81, 119.21, 125.43, 128.33, 128.67, 129.13, 136.16, 141.99, 173.39; ESIMS *m/z* 292.10 (M^++H).

Compound **9a**: 48%; oil; IR (neat) 2954, 1732, 1666 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.17 (d, J = 6.3 Hz, 3H), 2.22-2.60 (m, 7H), 2.66-2.89 (m, 2H), 2.95-3.04 (m, 1H), 3.70 (s, 3H), 4.37-4.48 (m, 1H), 6.90 (s, 1H), 7.24-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.04, 26.74, 27.95, 30.86, 32.79, 36.57, 50.98, 51.74, 112.17, 126.84, 127.25, 128.35, 128.92, 133.93, 134.72, 137.00, 167.59, 173.16.

Compound **9b**: 40%; oil; IR (neat) 2924, 1736, 1651 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 6H), 2.30-2.37 (m, 2H), 2.40-2.47 (m, 2H), 2.52-2.59 (m, 2H), 2.71-2.77 (m, 4H), 3.69 (s, 3H), 6.78 (s, 1H), 7.19-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.72, 26.08, 28.05, 32.69, 33.15, 45.54, 51.77, 61.39, 112.44, 126.14, 127.22, 128.37, 128.96, 132.75, 136.70, 137.01, 168.18, 173.25.

Compound **9c**: 58%; oil; IR (neat) 1651, 1404 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18 (d, J = 6.3 Hz, 3H), 2.08 (s, 3H), 2.26-2.35 (m, 1H), 2.45-2.58 (m, 4H), 3.00 (ddd, J = 15.3, 8.7, and 3.3 Hz, 1H), 4.39-4.50 (m, 1H), 6.84 (s, 1H), 7.22-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.37, 20.11, 29.58, 30.75, 36.45, 50.93, 109.83, 126.98, 127.03, 128.34, 128.77, 133.36, 134.67, 137.29, 167.47.

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