DOI 10.5012/bkcs.2010.31.6.1765

An Efficient Synthesis of α,α-Diallyl Carbinols from Esters Activated with Amides *via* an In-Mediated Barbier Type Allylation

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Received March 27, 2010, Accepted April 14, 2010

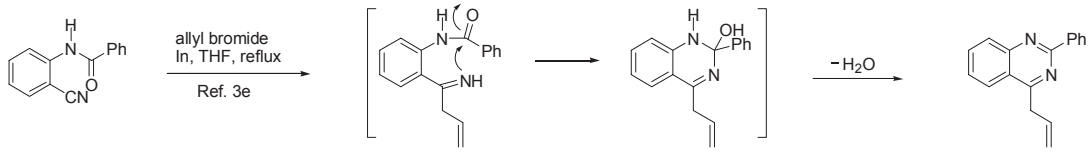
Key Words: Indium, Barbier reaction, Amide-Esters, Diallyl carbinols

Allylindium reagents have been used extensively for the introduction of allyl group in a Barbier type manner to various electrophiles.[1-3] Although many reactive electrophiles such as aldehydes and imines have been used in the indium-mediated allylations,[1] the reactions of allylindium reagents with less reactive nitriles and esters have not been reported much.[2,3]

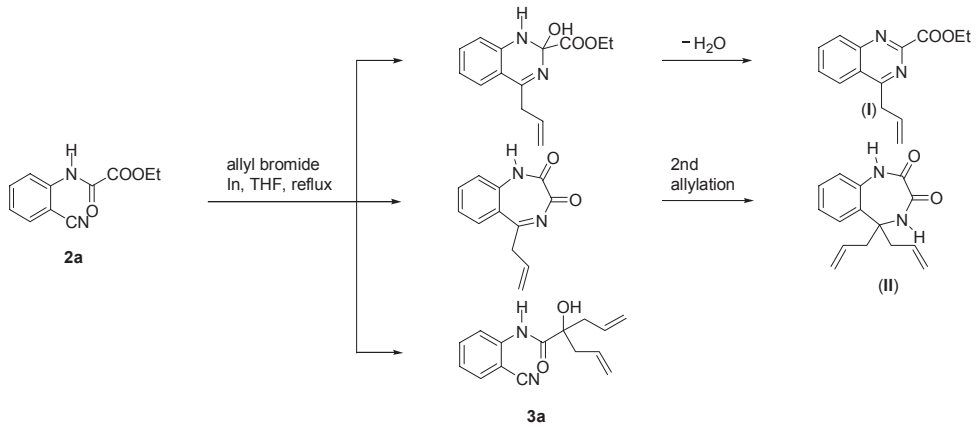
Recently, we reported a series of indium-mediated Barbier type allylations of nitrile groups in γ-cyanoesters,[3a] γ-ketonitriles,[3b] δ-ketonitriles,[3c] and *ortho*-cyanobenzoates.[3d] During the studies we found that allylindium reagents, generated *in situ* from indium powder and allyl bromide in THF, can react with nitrile when the molecule has a suitable electrophilic quencher such as an ester,[3a,d] another nitrile,[3c] and a sterically hindered ketone.[3b,c] Very recently, we found that an amide group can also be used as an effective quencher for the imine intermediate to produce quinazoline derivative in good yield, as shown in Scheme 1.[3e]

During the synthesis of quinazolines we examined the reaction of allylindium reagents and oxalic amide-ester derivative **2a**, prepared from 2-aminobenzonitrile (**1a**) and monoethyl oxalyl chloride.[4] Three types of compounds could be expected as shown in Scheme 2. The first candidate is a quinazoline derivative (**I**) that can be formed according to the process in Scheme 1. The second possibility is the formation of a seven-membered ring and the following second allylation to form a benzo[*e*]diazepine scaffold (**II**). The last one is a diallylation of ester moiety to produce diallyl carbinol **3a**.[5]

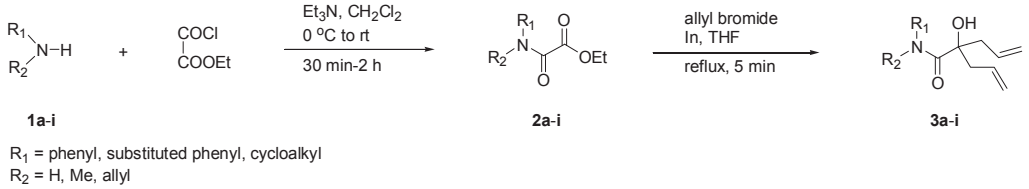
Actually, the reaction of **2a** and allylindium reagents, generated from allyl bromide and indium powder in THF, afforded diallyl carbinol **3a** (71%) as the major product within 5 min at refluxing temperature. We could not observe the formation of quinazoline (**I**) and benzo[*e*]diazepine derivative (**II**). The results stated that the reactivity of an activated ester with amide group is larger than that of the nitrile moiety toward allylindium reagents. To the best of our knowledge the reaction of ester and allylindium reagents has not been reported,[6] although the ester of **2a** is an activated one with nearby amide group. Zinc-mediated diallylation of diethyl oxalate has been reported;[5b,c] however, an In-mediated diallylation has not been reported (*vide infra*, Scheme 4). Encouraged by the results we decided to



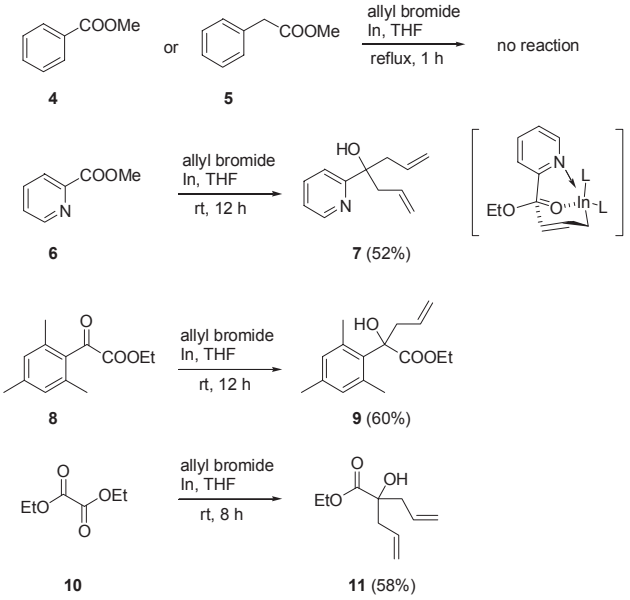
Scheme 1



Scheme 2



Scheme 3



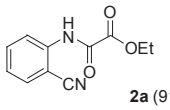
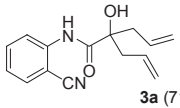
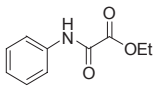
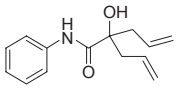
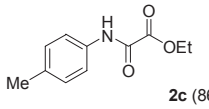
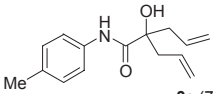
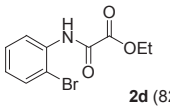
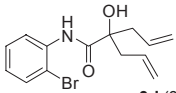
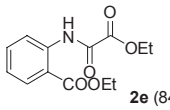
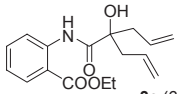
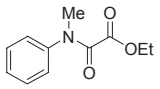
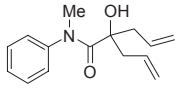
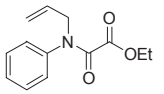
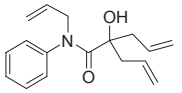
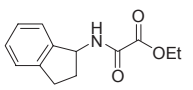
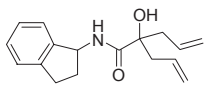
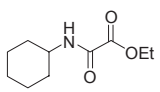
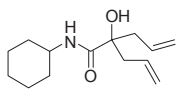
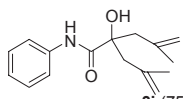
Scheme 4

examine the In-mediated allylation of oxalic amide-esters.

The starting materials **2a-i** were prepared from the corresponding amines **1a-i** and monoethyl oxalyl chloride (Et_3N, CH_2Cl_2, 0 °C to rt, 2 h) in good yields (81 - 91%).[4] The reaction of **2b**, as a representative ester, with allylindium reagents produced **3b** in a reasonable yield (75%) within 5 min at refluxing temperature. The reaction required 60 min for the completion at 40 - 45 °C while 12 h at room temperature. The use of other solvents such as DMF, aqueous THF, and aqueous DMF showed similar reactivity. Thus we carried out the reactions of **2c-i** in THF at refluxing temperature in the presence of allyl bromide (4.0 equiv) and indium powder (2.0 equiv), and the results are summarized in Table 1. Irrespective of the *N*-substituents the corresponding diallyl carbinols **3c-i** were obtained in good yields (66 - 79%). It is interesting to note that the reaction of **2e** (entry 5) showed the participation only at the activated ester part to produce **3e**. Methallyl bromide could be used successfully in the reaction (entry 10).

As a next experiment, we examined the reactions of allylindium reagents with five representative esters, methyl benzoate (**4**), methyl phenylacetate (**5**), ethyl 2-picolinate (**6**), ethyl mesitylglyoxylate (**8**), and diethyl oxalate (**10**), as shown in Scheme 4. The reactions of **4** and **5** failed even at refluxing temperature. The reaction of **6** produced the corresponding diallyl carbinol **7** in moderate yield (52%). The increased reactivity of compound **6** as compared to compound **4** must be ascribed to the pre-

Table 1. Synthesis of amide-esters **2a-i** and their In-mediated allylation.

entry	substrate (%)[a]	product (%)[b]
1	 **2a** (91)	 **3a** (71)
2	 **2b** (87)	 **3b** (75)
3	 **2c** (86)	 **3c** (79)
4	 **2d** (82)	 **3d** (67)
5	 **2e** (84)	 **3e** (69)
6	 **2f** (85)	 **3f** (68)
7	 **2g** (87)	 **3g** (67)
8	 **2h** (85)	 **3h** (72)
9	 **2i** (81)	 **3i** (66)
10[c]	**2b**	 **3j** (75)

[a]Conditions: amine **1** (1.0 equiv), monoethyl oxalyl chloride (1.1 equiv), Et_3N (1.1 equiv), CH_2Cl_2, 0 °C (10 min), rt (2 h). [b]Conditions: amide-ester **2** (1.0 equiv), allyl bromide (4.0 equiv), In powder (2.0 equiv), THF, reflux, 5 min. [c]Methallyl bromide was used.

sence of an electron-withdrawing 2-pyridyl moiety in part. In addition, there could be a favorable chelation effect between the nitrogen atom and indium metal in the transition state.[1] The reaction of α-keto ester **8** produced **9** in moderate yield (60%) at room temperature. Ketone group showed higher reactivity than the ester even though the ketone is sterically hindered.[7] The reaction of diethyl oxalate (**10**) showed similar reactivity as that of oxalic amide-ester **2**, and produced diallyl carbinol **11** in 58% yield.

In summary, we prepared various α,α-diallyl carbinols *via* the indium-mediated Barbier type allylation of amide-esters. From the results we found that allylindium reagents can react effectively with ester groups activated by amide or another ester group.

Experimental Section

Typical procedure for the synthesis of amide-ester 2a. To a stirred solution of 2-aminobenzonitrile (**1a**, 118 mg, 1.0 mmol) and Et_3N (111 mg, 1.1 mmol) in CH_2Cl_2 (2 mL) was added a solution of monoethyl oxalyl chloride (150 mg, 1.1 mmol, in 1 mL of CH_2Cl_2) at 0 °C (10 min) and the reaction mixture was stirred at room temperature for 2 h. After the usual aqueous workup and column chromatographic purification process (hexanes/CH_2Cl_2/EA, 10:1:1), **2a** was obtained as a white solid, 198 mg (91%).[4b] Other compounds were prepared similarly as reported,[4a-d] and the spectroscopic data of unknown compounds **2e**, **2g** and **2h** are as follows.

Compound 2e: 84%; white solid, mp 91 - 92 °C; IR (KBr) 3242, 1728, 1687, 1585, 1516 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (t, J = 7.2 Hz, 3H), 1.45 (t, J = 7.2 Hz, 3H), 4.44 (q, J = 7.2 Hz, 2H), 4.45 (q, J = 7.2 Hz, 2H), 7.19 (t, J = 8.4 Hz, 1H), 7.60 (t, J = 8.1 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 8.75 (d, J = 8.4 Hz, 1H), 12.63 (br s, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.92, 14.11, 61.65, 63.51, 116.44, 120.36, 123.88, 131.02, 134.49, 139.50, 154.64, 160.57, 167.59; ESIMS *m/z* 266 (M^++1).

Compound 2g: 87%; colorless oil; IR (film) 1743, 1671, 1596, 1495, 1410 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.98 (t, J = 7.2 Hz, 3H), 4.01 (q, J = 7.2 Hz, 2H), 4.37 (d, J = 6.3 Hz, 2H), 5.15-5.18 (m, 1H), 5.20-5.22 (m, 1H), 5.80-5.92 (m, 1H), 7.21-7.26 (m, 2H), 7.33-7.38 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.54, 51.23, 61.59, 118.91, 127.48, 128.47, 129.36, 131.59, 140.00, 161.51, 162.47; ESIMS *m/z* 234 (M^++1).

Compound 2h: 85%; colorless oil; IR (film) 3354, 1691, 1681 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.40 (t, J = 7.2 Hz, 3H), 1.85-1.97 (m, 1H), 2.58-2.69 (m, 1H), 2.85-3.09 (m, 2H), 4.35 (q, J = 7.2 Hz, 2H), 5.50 (dt, J = 7.8 and 7.5 Hz, 1H), 7.19-7.31 (m, 4H+NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.96, 30.23, 35.51, 55.08, 63.26, 124.14, 124.90, 126.90, 128.36, 141.78, 143.40, 156.26, 160.68; ESIMS *m/z* 234 (M^++1).

Typical procedure for the synthesis of diallyl carbinol 3a. A stirred mixture of **2a** (109 mg, 0.5 mmol), allyl bromide (242 mg, 2.0 mmol), and indium powder (114 mg, 1.0 mmol) in THF (0.5 mL) was heated to reflux for 5 min under nitrogen atmosphere. After the usual aqueous workup and column chromatographic purification process (hexanes/CH_2Cl_2/EA, 15:2:1), **3a** was obtained as a white solid, 91 mg (71%). Other compounds were prepared similarly and the spectroscopic data of unknown compounds **3a-j**, **7** and **9** are as follows.

Compound 3a: 71%; white solid, mp 78 - 79 °C; IR (KBr) 3316, 2221, 1679, 1525 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.42-2.49 (m, 2H), 2.73-2.81 (m, 2H), 2.96 (s, OH), 5.19-5.26 (m, 4H), 5.79-5.93 (m, 2H), 7.16-7.22 (m, 1H), 7.57-7.63 (m, 2H), 8.41 (d, J = 8.7 Hz, 1H), 9.31 (br s, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.14, 77.50, 102.50, 116.02, 120.50, 120.77, 124.25, 131.61, 132.26, 134.03, 139.74, 173.00; ESIMS *m/z* 257 (M^++1). Anal. Calcd. For $C_{15}H_{16}N_2O$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.61; H, 6.45; N, 10.59.

Compound 3b: 75%; white solid, mp 38 - 39 °C; IR (KBr) 3369, 1664, 1529, 1445 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.36-2.43 (m, 2H), 2.68 (s, OH), 2.77-2.83 (m, 2H), 5.18-5.23 (m, 4H), 5.76-5.90 (m, 2H), 7.12 (t, J = 8.4 Hz, 1H), 7.33 (t, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 8.60 (br s, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.29, 77.04, 119.66, 120.29, 124.42, 128.96, 132.15, 137.17, 172.23; ESIMS *m/z* 232 (M^++1). Anal. Calcd. For $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.87; H, 7.66; N, 5.89.

Compound 3c: 79%; white solid, mp 50 - 51 °C; IR (KBr) 3373, 1660, 1593, 1523 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.31 (s, 3H), 2.35-2.42 (m, 2H), 2.58 (s, OH), 2.76-2.83 (m, 2H), 5.18-5.23 (m, 4H), 5.76-5.90 (m, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 8.51 (br s, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.84, 43.31, 77.00, 119.70, 120.23, 129.45, 132.24, 134.05, 134.67, 172.04; ESIMS *m/z* 246 (M^++1).

Compound 3d: 67%; white solid, mp 72 - 73 °C; IR (KBr) 3424, 3342, 1672, 1524, 1438 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.39-2.46 (m, 2H), 2.76-2.83 (m, 2H), 2.77 (s, OH), 5.18-5.25 (m, 4H), 5.78-5.92 (m, 2H), 6.98 (t, J = 8.1 Hz, 1H), 7.31 (t, J = 8.1 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 8.37 (d, J = 8.1 Hz, 1H), 9.19 (br s, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.25, 77.40, 113.83, 120.33, 121.47, 125.28, 128.22, 131.95, 132.26, 135.22, 172.55; ESIMS *m/z* 310 (M^++1), 312 (M^++3).

Compound 3e: 69%; white solid, mp 93 - 94 °C; IR (KBr) 3297, 3239, 1703, 1661, 1584 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (t, J = 6.9 Hz, 3H), 2.46-2.53 (m, 2H), 2.76-2.84 (m, 2H), 2.91 (s, OH), 4.44 (q, J = 6.9 Hz, 2H), 5.18-5.26 (m, 4H), 5.81-5.95 (m, 2H), 7.15 (t, J = 7.8 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.79 (d, J = 7.8 Hz, 1H), 11.91 (br s, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.21, 43.43, 61.39, 77.31, 116.04, 119.94, 120.21, 122.80, 130.94, 132.24, 134.38, 140.60, 167.80, 173.69; ESIMS *m/z* 304 (M^++1). Anal. Calcd. For $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.43; H, 7.08; N, 4.44.

Compound 3f: 68%; colorless oil; IR (film) 3395, 1630, 1594, 1356 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.25 (br s, 4H), 3.31 (s, 3H), 4.30 (br s, OH), 5.05-5.16 (m, 4H), 5.76-5.89 (m, 2H), 7.25-7.28 (m, 2H), 7.33-7.45 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.07, 43.51, 77.36, 118.24, 127.86, 128.47, 129.30, 132.90, 143.58, 174.03; ESIMS *m/z* 246 (M^++1).

Compound 3g: 67%; colorless oil; IR (film) 3403, 1628, 1594, 1369 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.20 (d, J = 6.0 Hz, 4H), 4.26 (d, J = 8.0 Hz, 2H), 4.27 (s, OH), 4.96-5.16 (m, 6H), 5.75-5.93 (m, 3H), 7.23-7.27 (m, 2H), 7.37-7.42 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.52, 56.10, 77.31, 118.31, 118.54, 128.71, 129.00 (2C), 132.36, 132.86, 141.74, 173.54; ESIMS *m/z* 272 (M^++1).

Compound 3h: 72%; colorless oil; IR (film) 3393, 3314, 1650, 1524 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.72-1.86 (m, 1H), 2.31-2.40 (m, 2H), 2.52-2.61 (m, 1H), 2.62 (s, OH), 2.67-2.77 (m, 2H), 2.80-3.05 (m, 2H), 5.14-5.23 (m, 4H), 5.43 (dt, J = 8.1 and 7.8 Hz, 1H), 5.73-5.92 (m, 2H), 6.93 (d, J = 8.1 Hz, NH), 7.16-7.29 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.19, 34.00, 43.36, 43.42, 54.34, 76.64, 119.74, 119.86, 123.99, 124.73, 126.68, 127.88, 132.39, 132.47, 142.98, 143.32, 173.69; ESIMS *m*/*z* 272 (M^++1).

Compound 3i: 66%; colorless oil; IR (film) 3396, 3334, 1646, 1530 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.10-1.23 (m, 3H), 1.28-1.43 (m, 2H), 1.58-1.74 (m, 3H), 1.84-1.89 (m, 2H), 2.27-2.35 (m, 2H), 2.64-2.72 (m, 2H), 2.72 (s, OH), 3.67-3.80 (m, 1H), 5.12-5.21 (m, 4H), 5.71-5.84 (m, 2H), 6.62 (d, J = 7.8 Hz, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.71, 25.42, 33.04, 43.33, 47.90, 76.34, 119.48, 132.50, 172.85; ESIMS *m*/*z* 238 (M^++1). Anal. Calcd. For $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.96; H, 9.65; N, 5.77.

Compound 3j: 75%; white solid, mp 75 - 77 °C; IR (KBr) 3438, 3373, 1665, 1600, 1527, 1444 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.77 (s, 6H), 2.34 (d, J = 13.5 Hz, 2H), 2.83 (s, OH), 2.86 (d, J = 13.5 Hz, 2H), 4.86 (s, 2H), 4.96 (s, 2H), 7.11 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 8.1 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 8.72 (br s, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.68, 47.19, 76.40, 116.33, 119.65, 124.36, 128.98, 137.40, 141.39, 172.71; ESIMS *m*/*z* 260 (M^++1). Anal. Calcd. For $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.42; H, 8.36; N, 5.13.

Compound 7: 52%; colorless oil; IR (film) 3391, 1640, 1592, 1435, 1393 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.62 (dt, J = 7.2 and 1.2 Hz, 4H), 4.91 (s, OH), 4.96-5.03 (m, 4H), 5.58-5.72 (m, 2H), 7.18 (ddd, J = 12.3, 5.1 and 1.2 Hz, 1H), 7.33 (dt, J = 8.1 and 1.2 Hz, 1H), 7.69 (td, J = 8.1 and 1.8 Hz, 1H), 8.51-8.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 46.08, 75.54, 118.15, 120.03, 121.81, 133.50, 136.56, 147.49, 162.85; ESIMS *m*/*z* 190 (M^++1). Anal. Calcd. For $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.23; H, 8.16; N, 7.29.

Compound 9: 60%; colorless oil; IR (film) 3485, 1729 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (t, J = 7.2 Hz, 3H), 2.23 (s, 3H), 2.37 (s, 6H), 2.84-3.03 (m, 2H), 2.88 (s, OH), 4.22 (q, J = 7.2 Hz, 2H), 5.11-5.18 (m, 2H), 5.80-5.94 (m, 1H) 6.80 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.89, 20.41, 22.87, 42.45, 61.60, 80.49, 119.17, 131.55, 133.07, 135.25, 136.12, 136.44, 174.14; ESIMS *m*/*z* 263 (M^++1). Anal. Calcd. For $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.44; H, 8.29.

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 was obtained from the Korea Basic Science Institute, Gwangju branch.

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