Expedient Synthesis of 3-Benzoylflavones by PCC Oxidation of 3-Benzylideneflavanones

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Received July 29, 2008

Key Words : Baylis-Hillman adducts, Flavanones, PCC, Flavones

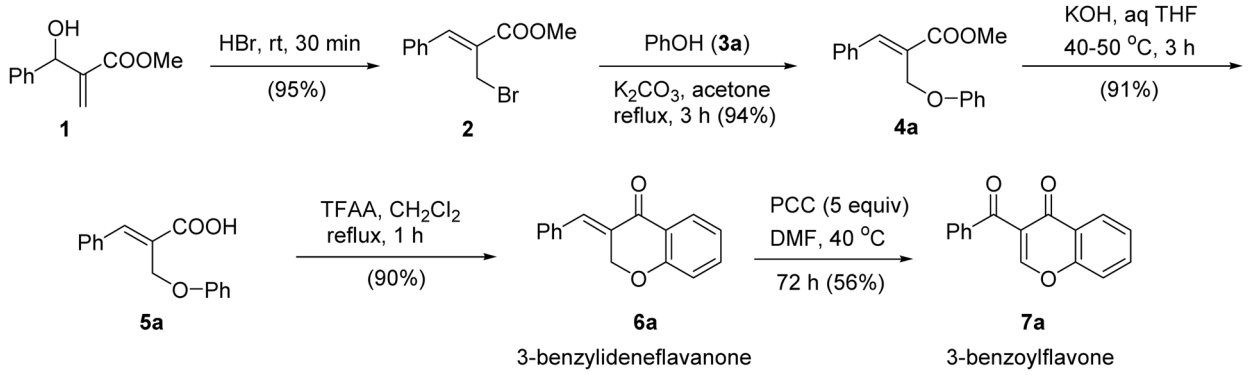
The synthesis and chemical transformation of 3-arylideneflavanones (3-arylidenechroman-4-ones) and related compounds received much attention due to the abundance of this moiety in many natural products and biologically active substances.[1-3] Many 3-arylideneflavanones showed interesting biological activities including anti-HIV, anti-mutagenic, anti-inflammatory, anti-bacterial, anti-fungal and antiviral activities.[1-3] In addition, oxidation of 3-arylideneflavanones into 3-aroylflavones (3-aroylchromones)[3] is also regarded as an important transformation in this respect.

In this paper, we described the synthesis of various 3-benzylideneflavanones **6** and the following oxidation with pyridinium chlorochromate (PCC) to make the corresponding 3-benzoylflavones **7** (Scheme 1 and Table 1). The synthesis of 3-arylideneflavanones **6** was carried out by following the method of Basavaiah[1c] from the Baylis-Hillman adducts[4,5] *via* the following three-step sequence comprised of (i) introduction of phenol at the primary position of the Baylis-Hillman adduct, (ii) hydrolysis of the ester group and (iii) Friedel-Crafts type cyclization.[1b-d]

The starting material **4a** was synthesized in pure *E*-form in good yield (94%) by the reaction of phenol (**3a**) and the cinnamyl bromide **2**,[1b-d,4] which was easily prepared from **1** and HBr, under the influence of K_2CO_3 in acetone. Hydrolysis of **4a** was carried out in aqueous KOH to produce the corresponding acid **5a**. Without further purification, treatment of **5a** with trifluoroacetic anhydride (TFAA) produced 3-benzylideneflavanone **6a** in 90% yield.[1c] With this compound in our hand we examined the oxidation of **6a** with PCC which was found as an effective oxidant in a similar system by us recently.[6] As expected, treatment of **6a** with PCC (5.0 equiv) in DMF afforded 3-benzoylflavone **7a**[3,7] in moderate yield (56%), although long reaction time (72 h) was required for the oxidation.

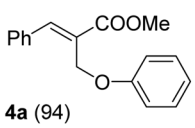
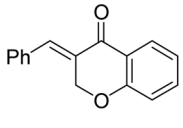
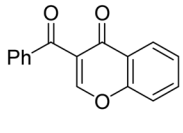
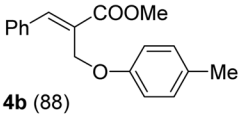
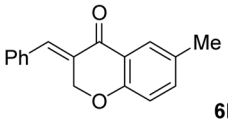
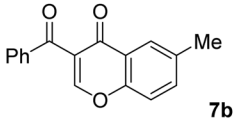
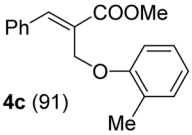
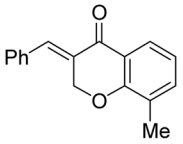
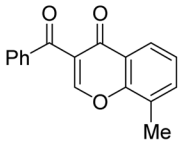
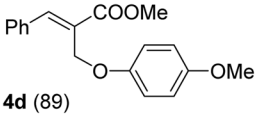
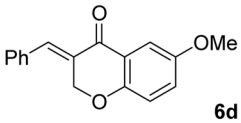
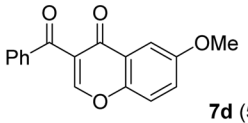
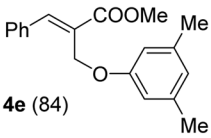
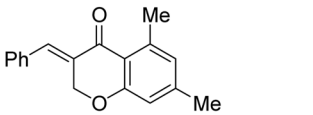
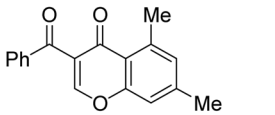
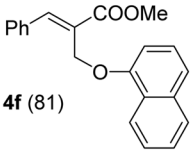
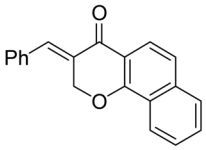
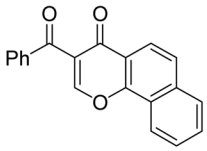
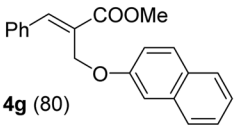
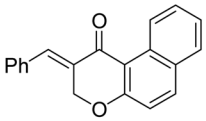
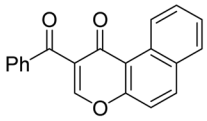
Encouraged by the results we prepared starting materials **4b-g** (80-91%) from the reactions of **2** and 4-methylphenol (**3b**), 2-methylphenol (**3c**), 4-methoxyphenol (**3d**), 3,5-dimethylphenol (**3e**), 1-naphthol (**3f**), and 2-naphthol (**3g**). By following the same procedure of **6a** we synthesized various 3-benzylideneflavanones **6b-g** as summarized in Table 1. As shown in entry 7, the cyclization reaction of compound **4g** occurred at the 1-position of naphthalene moiety selectively and produced **6g**. PCC oxidation of **6b-g** was also carried out and desired 3-benzoylflavones **7b-g** were prepared in 46-70% yields. Similarly, we synthesized nitrogen analog **8** with *N*-tosylaniline as in Scheme 2. Compound **9** was synthesized by using the same protocol of **6a-g**, however, the oxidation of **9** was failed. Double bond isomerization of **6a** from the *exo*- to the *endo*-position was also examined (Scheme 3). Initially, we tried the isomerization under catalytic hydrogenation conditions[8a-c] and obtained desired compound 3-benzylflavone (**10**)[8b] in low yield (37%) due to the formation of fully reduction compound **11** (32%).[8b] In addition, the ratio of **10**/**11** was highly dependent on the reaction conditions and it was difficult to make **10** as the major product. After many trials, we found that **10** can be prepared from **6a** in good yield (71%) under the influence of DBU (1.2 equiv) in CH_3CN (40 °C, 12 h).

In summary, we disclosed a facile synthesis of 3-benzylideneflavanones and 3-benzoylflavones from Baylis-Hillman adducts. The biological activities of synthesized compounds will be examined and published in due course.

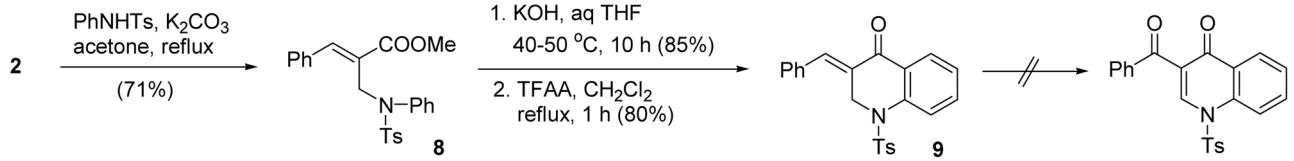


Scheme 1

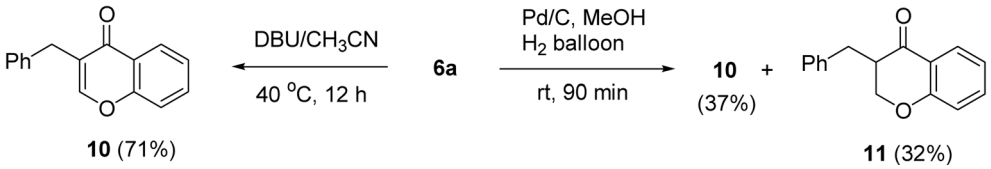
Table 1. Synthesis of 3-benzylideneflavanones and 3-benzoylflavones

Entry	Compound **4** (%)	Product **6** (%)[a]	Product **7** (%)
1	 **4a** (94)	 **6a** (91/90)	 **7a** (56)
2	 **4b** (88)	 **6b** (90/87)	 **7b** (53)
3	 **4c** (91)	 **6c** (95/82)	 **7c** (50)
4	 **4d** (89)	 **6d** (87/89)	 **7d** (58)
5	 **4e** (84)	 **6e** (83/84)	 **7e** (46)
6	 **4f** (81)	 **6f** (96/82)	 **7f** (54)
7	 **4g** (80)	 **6g** (98/93)[b]	 **7g** (70)

[a]First yields refer to hydrolysis stage to compounds **5a-g** and the second yields to cyclization step to **6a-g**. [b]The structure was confirmed by the splitting pattern of aromatic protons in ^{1}H NMR (Experimental)



Scheme 2



Scheme 3

Experimental Section

Typical procedure for the synthesis of 4a. Baylis-Hillman adduct **1** (384 mg, 2.0 mmol) was treated with aqueous HBr (48%, 2.0 mL) at room temperature for 30 min. After the usual extractive workup with ether and column chromatographic purification (hexanes/EtOAc, 8:1) process, cinnamyl bromide **2** was obtained as colorless oil, 485 mg (95%).

The reaction mixture of **2** (255 mg, 1.0 mmol), phenol (**3a**, 104 mg, 1.1 mmol), and K_2CO_3 (207 mg, 1.5 mmol) in acetone (5 mL) was heated to reflux for 3 h. After the usual extractive workup with ether and column chromatographic purification (hexanes/EtOAc, 5:1) process, compound **4a** was obtained as colorless oil, 252 mg (94%). Other products including **8** were prepared analogously and the spectroscopic data of **4c**, **4d**, **4f**, **4g**, and **8** are as follows. Compounds **4a**,[1c] **4b**,[9a] and **4e**[9a] were known.

Compound 4c: 91%; colorless oil; IR (film) 1718, 1495, 1234, 1117 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.22 (s, 3H), 3.84 (s, 3H), 4.84 (s, 2H), 6.87-6.91 (m, 2H), 7.13-7.17 (m, 2H), 7.35-7.37 (m, 3H), 7.49-7.51 (m, 2H), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.27, 52.22, 62.89, 111.80, 120.79, 126.74, 127.33, 127.59, 128.66, 129.51, 129.69, 130.68, 134.52, 145.32, 156.68, 167.77.

Compound 4d: 89%; colorless oil; IR (film) 1718, 1508, 1225 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.77 (s, 3H), 3.84 (s, 3H), 4.78 (s, 2H), 6.85 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 7.35-7.38 (m, 3H), 7.48-7.50 (m, 2H), 8.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 52.24, 55.66, 63.52, 114.60, 116.09, 127.44, 128.65, 129.53, 129.74, 134.43, 145.45, 152.58, 154.15, 167.67.

Compound 4f: 81%; colorless oil; IR (film) 1716, 1267, 1235, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.85 (s, 3H), 5.01 (s, 2H), 6.87 (d, J = 7.5 Hz, 1H), 7.31-7.39 (m, 4H), 7.43-7.55 (m, 5H), 7.81 (d, J = 7.5 Hz, 1H), 8.13 (s, 1H), 8.27 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.34, 63.00, 105.24, 120.64, 122.25, 125.23, 125.83, 126.42, 127.33, 127.38, 128.55, 128.75, 129.60, 129.73, 134.48, 134.52, 145.82, 154.25, 167.77.

Compound 4g: 80%; colorless oil; IR (film) 1717, 1629, 1256, 1234, 1214 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.86 (s, 3H), 4.96 (s, 2H), 7.18-7.25 (m, 2H), 7.32-7.37 (m, 4H), 7.41-7.51 (m, 3H), 7.70 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.35, 62.78, 107.23, 119.15, 123.75, 126.38, 126.79, 127.17, 127.63, 128.75, 129.15, 129.43, 129.64, 129.76, 134.42, 134.47, 145.83, 156.36, 167.67.

Compound 8: 71%; colorless oil; IR (film) 1716, 1352, 1253, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 3H), 3.65 (s, 3H), 4.71 (s, 2H), 6.73 (d, J = 7.5 Hz, 2H), 7.08-7.40 (m, 12H), 7.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.54, 46.16, 52.09, 126.81, 127.90, 128.05, 128.44 (2C), 129.17 (2C), 129.29, 129.81, 134.25, 134.48, 138.58, 143.48, 143.80, 167.83.

Typical procedure for the synthesis of 6a. A mixture of **4a** (268 mg, 1.0 mmol) and KOH (190 mg, 3.0 mmol) in aqueous THF (3 mL) was heated to 40-50 °C for 3 h. After acidification with aqueous HCl solution and the usual extractive workup with EtOAc, crude acid **5a** was obtained in 91% yield (232 mg). The acid **5a** was used without further purification. A stirred solution of **5a** (232 mg, 0.91 mmol) and TFAA (390 mg, 1.86 mmol) in CH_2Cl_2 (5 mL) was heated to reflux for 1 h. After the usual extractive workup with ether and column chromatographic purification (hexanes/EtOAc, 4:1) process, compound **6a** was obtained as yellow oil, 193 mg (90%). Other compounds including **9** were prepared analogously and the spectroscopic data of **6c**, **6e-g**, and **9** are as follows. Compounds **6a**,[1c] **6b**,[9b] and **6d**[9c] were known.

Compound 6c: 82%; yellow oil; IR (film) 1672, 1601, 1479, 1304 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.22 (s, 3H), 5.37 (d, J = 2.0 Hz, 2H), 6.96 (t, J = 7.5 Hz, 1H), 7.31-7.35 (m, 3H), 7.38-7.46 (m, 3H), 7.87 (s, 1H), 7.88 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.46, 67.43, 121.26, 121.61, 125.49, 127.08, 128.64, 129.34, 129.92, 131.02, 134.42, 136.67, 137.13, 159.30, 182.62.

Compound 6e: 84%; yellow solid, mp 74-76 °C; IR (KBr) 1668, 1614, 1321, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.30 (s, 3H), 2.69 (s, 3H), 5.23 (d, J = 1.5 Hz, 2H), 6.65 (s, 1H), 6.69 (s, 1H), 7.29 (d, J = 7.5 Hz, 2H), 7.37-7.45 (m, 3H), 7.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.65, 22.70, 67.20, 116.05, 118.69, 126.61, 128.61, 129.12, 129.80, 132.39, 134.70, 136.25, 142.59, 145.83, 162.40, 182.99; ESIMS *m/z* 265.46 (M^++1).

Compound 6f: 82%; yellow solid, mp 78-80 °C; IR (KBr) 1665, 1625, 1101 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.59 (d, J = 1.8 Hz, 2H), 7.34-7.65 (m, 8H), 7.80 (d, J = 8.4 Hz, 1H), 7.93 (t, J = 1.8 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 68.29, 116.35, 121.53, 122.54, 123.43, 124.82, 126.22, 127.88, 128.72, 129.36, 129.65, 129.94, 130.49, 134.49, 137.01, 137.40, 159.26, 181.83.

Compound 6g: 93%; yellow solid, mp 66-68 °C; IR (KBr) 1663, 1617, 1597, 1511, 1434, 1241 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.39 (d, J = 1.8 Hz, 2H), 7.09 (d, J = 9.3 Hz, 1H), 7.32-7.49 (m, 6H), 7.67 (t, J = 8.1 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.94 (s, 1H), 9.45 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 67.46, 114.30, 118.72, 125.02, 126.46, 128.47, 128.69, 129.23, 129.51, 129.61, 129.83, 131.92, 132.17, 134.70, 136.76, 137.41, 163.18, 182.54; ESIMS *m/z* 287.44 (M^++1).

Compound 9:[9d] 80%; yellow solid, mp 135-137 °C; IR (KBr) 1674, 1607, 1356, 1167 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3H), 5.06 (d, J = 1.8 Hz, 2H), 6.97-7.04 (m, 4H), 7.32-7.54 (m, 7H), 7.61-7.68 (m, 1H), 7.83 (d, J = 8.7 Hz, 1H), 7.95 (dd, J = 7.8 and 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.58, 47.93, 127.13, 127.34, 127.40, 128.19, 128.85, 128.95, 129.49, 129.58, 129.88, 130.01, 134.14, 134.19, 134.42, 138.39, 141.34, 144.19, 182.57; ESIMS *m/z* 390.49 (M^++1).

Typical procedure for the synthesis of 7a. A mixture of **6a** (118 mg, 0.5 mmol) and PCC (540 mg, 2.5 mmol) in DMF (2 mL) was heated to 40 °C for 72 h. The reaction mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite. After the usual aqueous extractive workup with CH_2Cl_2 and column chromatographic purification (hexanes/EtOAc, 4:1) process, compound **7a** was obtained as a white solid, 70 mg (56%). Other compounds were prepared analogously and the spectroscopic data of synthesized compounds **7a-g** are as follows.

Compound 7a:[7b] 56%; white solid, mp 128-130 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.44-7.63 (m, 5H), 7.72-7.78 (m,

1H), 7.85-7.88 (m, 2H), 8.27 (dd, J = 9.0 and 1.2 Hz, 1H), 8.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 118.31, 124.99, 125.18, 126.12, 126.49, 128.41, 129.58, 133.51, 134.38, 137.15, 156.07, 158.63, 174.70, 191.89.

Compound 7b: 53%; white solid, mp 129-130 ºC; IR (KBr) 1651, 1618, 1481, 1319 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.47 (s, 3H), 7.42-7.48 (m, 3H), 7.52-7.61 (m, 2H), 7.84-7.88 (m, 2H), 8.03 (m, 1H), 8.27 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.94, 118.01, 124.59, 124.92, 125.72, 128.32, 129.55, 133.39, 135.52, 136.22, 137.16, 154.29, 158.51, 174.74, 192.01; ESIMS *m/z* 265.40 (M^++1).

Compound 7c: 50%; white solid, mp 98-100 ºC; IR (KBr) 1651, 1577, 1340, 1319 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.53 (s, 3H), 7.36 (t, J = 7.5 Hz, 1H), 7.43-7.49 (m, 2H), 7.56-7.62 (m, 2H), 7.85-7.88 (m, 2H), 8.08-8.11 (m, 1H), 8.34 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.48, 124.01, 124.90, 124.92, 125.60, 127.85, 128.37, 129.55, 133.43, 135.33, 137.20, 154.58, 158.36, 175.03, 192.03.

Compound 7d: 58%; white solid, mp 137-138 ºC; IR (KBr) 1718, 1508, 1225 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.90 (s, 3H), 7.32 (dd, J = 9.5 and 3.5 Hz, 1H), 7.45-7.49 (m, 3H), 7.58-7.62 (m, 2H), 7.85-7.87 (m, 2H), 8.29 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.96, 105.57, 119.70, 124.31 (2C), 125.72, 128.37, 129.55, 133.41, 137.27, 150.86, 157.61, 158.42, 174.56, 192.12.

Compound 7e: 46%; white solid, mp 153-155 ºC; IR (KBr) 1658, 1637, 1596 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H), 2.78 (s, 3H), 7.01 (s, 1H), 7.15 (s, 1H), 7.44-7.47 (m, 2H), 7.56-7.60 (m, 1H), 7.85-7.87 (m, 2H), 8.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.57, 22.78, 116.10, 120.98, 126.09, 128.40, 129.48, 130.06, 133.35, 137.38, 141.53, 144.57, 156.60, 157.65, 176.65, 192.42.

Compound 7f: 54%; white solid, mp 182-184 ºC (decomp.); IR (KBr) 1662, 1641, 1392 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45-7.51 (m, 2H), 7.59-7.64 (m, 1H), 7.70-7.79 (m, 2H), 7.84 (d, J = 8.7 Hz, 1H), 7.90-7.93 (m, 2H), 7.96-7.99 (m, 1H), 8.19 (d, J = 8.7 Hz, 1H), 8.47 (s, 1H), 8.53 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 120.89, 121.52, 122.23, 123.77, 126.22, 126.44, 127.58, 128.21, 128.46, 129.64, 129.77, 133.59, 136.11, 137.08, 153.64, 157.46, 174.56, 191.92.

Compound 7g: 70%; white solid, mp 165-167 ºC; IR (KBr) 1667, 1637, 1592, 1299 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45-7.51 (m, 2H), 7.54-7.67 (m, 3H), 7.70-7.76 (m, 1H), 7.91-7.95 (m, 3H), 8.15 (d, J = 9.0 Hz, 1H), 8.28 (s, 1H), 9.94 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 117.32, 118.47, 127.12, 127.22, 127.86, 128.32, 128.50, 129.53, 129.62, 130.48, 130.89, 133.56, 136.28, 137.18, 155.20, 157.47, 176.67, 192.31; ESIMS *m/z* 301.42 (M^++1).

Acknowledgments. This study was financially supported by Chonnam National University, 2007. Spectroscopic data was obtained from the Korea Basic Science Institute, Gwangju branch.

References and Notes

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