Supplementary data

CuI Catalyzed *N*-Arylation of Amide as A Key Step for the Preparation of 3-Aryl β-Carbolin-1-ones

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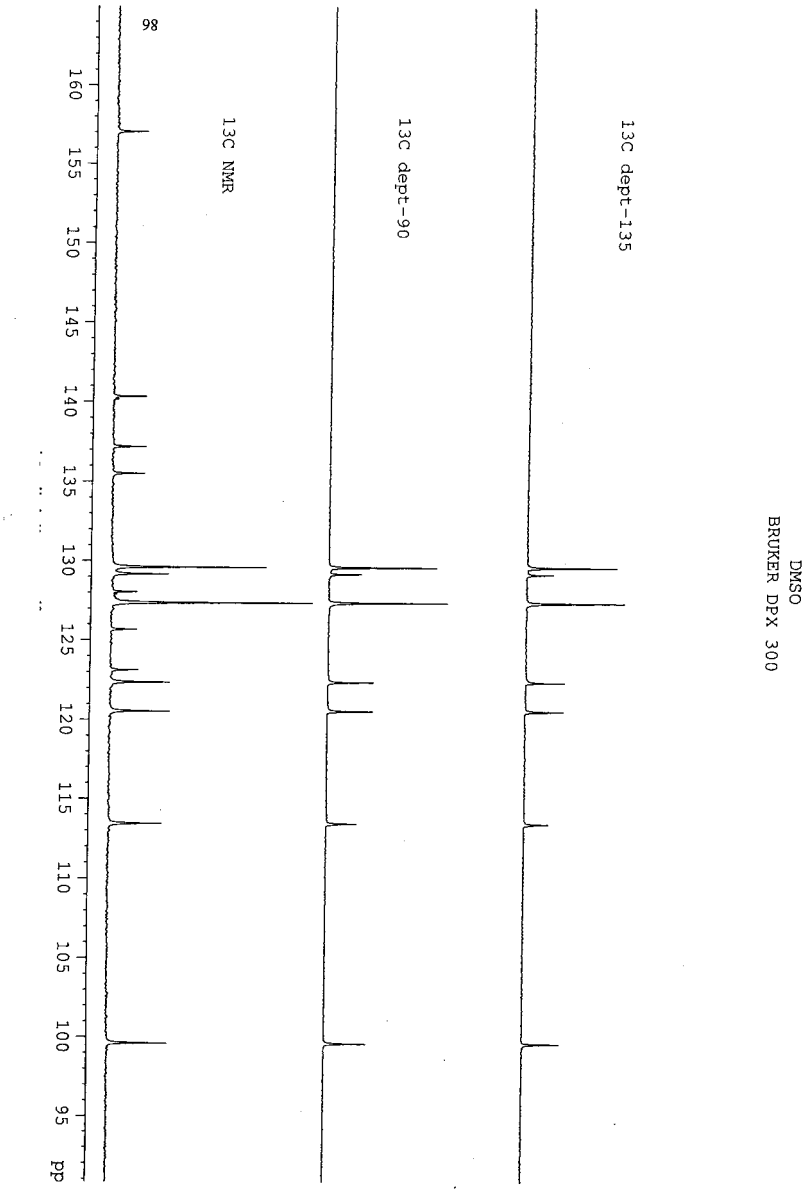

Fig. 1. Spectra of ^{13}C DEPT of Compound **2a** (90 °C, 135 °C).

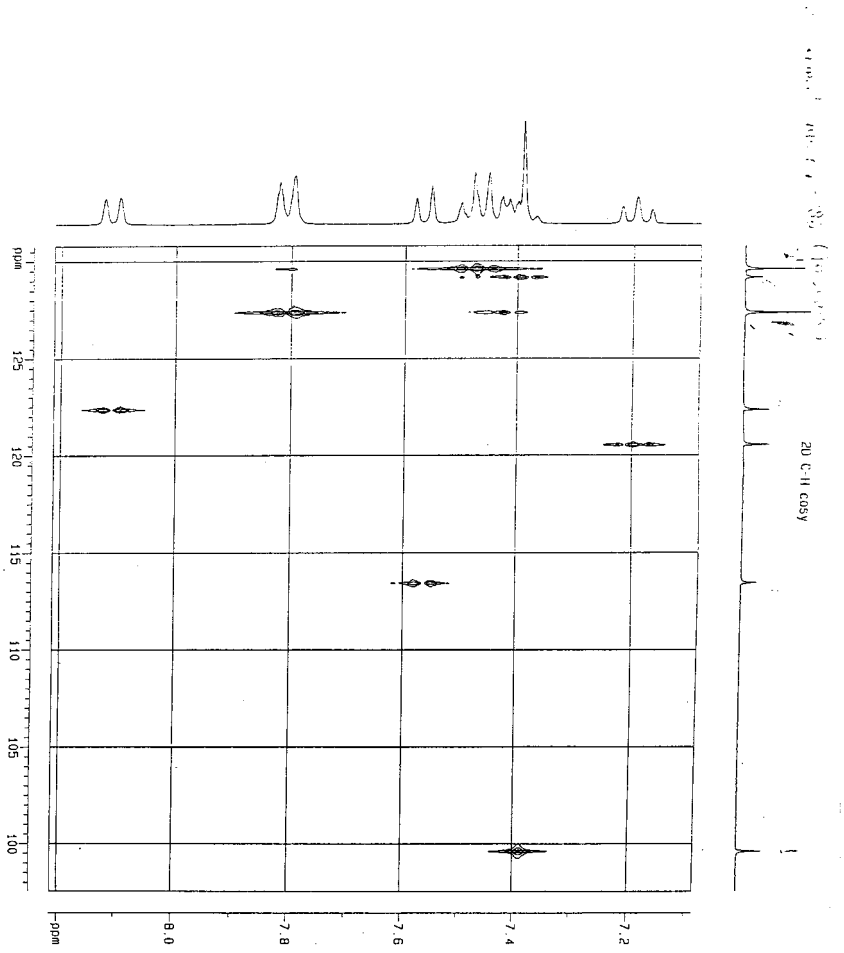

Fig. 2. Spectra of ^{13}C-^{1}H COSY of Compound **2a**.

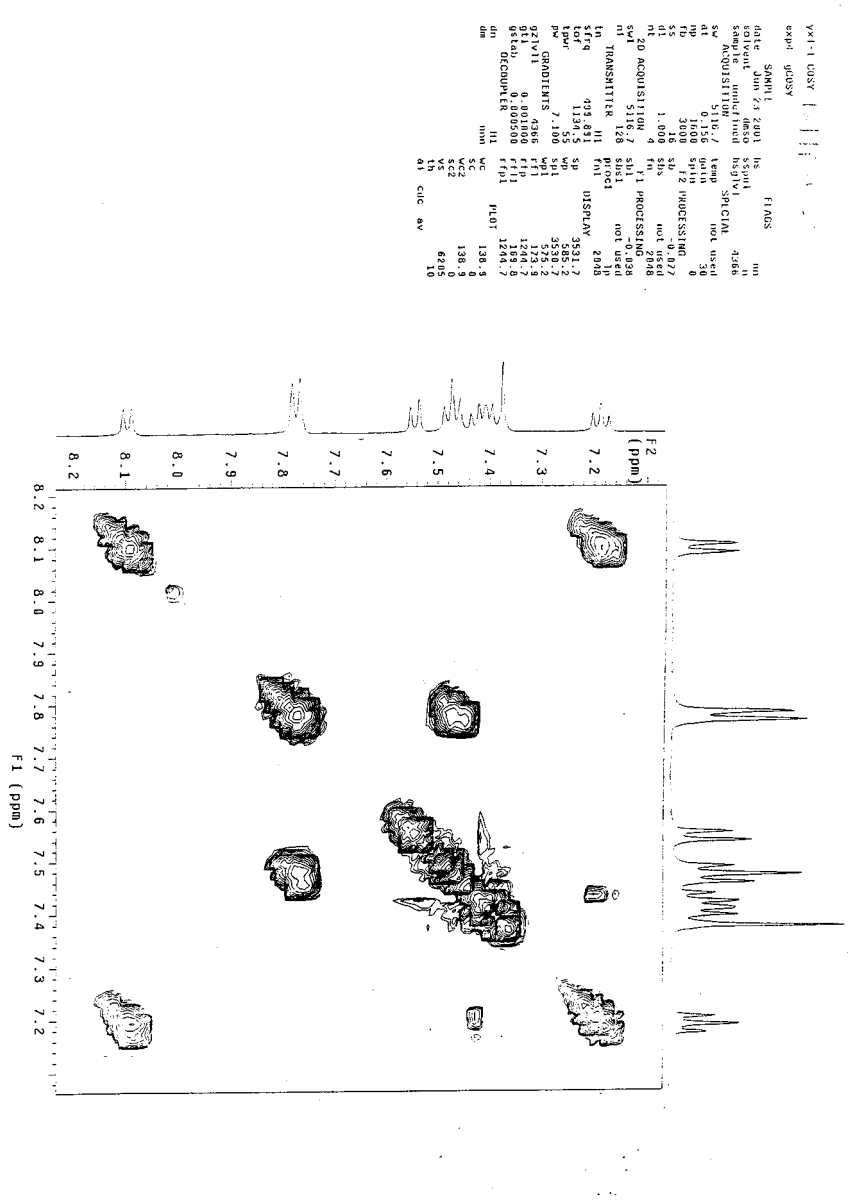

Fig. 3. Spectra of ^{1}H-^{1}H COSY of Compound **2a**.

Experimental

Comment:

The IR spectra were recorded on a Nicolet FT-IR 5DX spectrometer as KBr pellets. The ^{1}H NMR spectra were recorded on a Bruker ACF-300 spectrometer in $CDCl_3$ with TMS as internal reference. The *J* values are given in Hz. MS spectra were obtained on a VG-ZAB-HS mass spectrometer with 70 eV. The elemental analyses were performed on a Perkin-Elmer 240C instrument.

A General Procedure for the Preparation of 5a-i by Michael Addition. To a cold solution (ice-water bath) of ethyl acetamidocyanoacetate (**3**, 3.4 g, 20 mmol) and chalcone (**4**, 10 mmol) in anhydrous THF (50 mL) was added solid *t*-BuONa (96 mg, 1.0 mmol) in one portion. After the resultant mixture was stirred at room temperature for 4 h (monitored by TLC), the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and washed with saturated aq. solution of Na_2CO_3. The organic layer was dried over Na_2SO_4 and removal of the solvent gave the crude product, which was purified by chromatography [silica gel, 50% EtOAc in petroleum ether (60-90 ^oC)] to yield pure compound **5**.

Ethyl 2-acetamido-2-cyano-3-(2-bromophenyl)-5-oxo-5-phenylpentanate (5a): mp 166-170 ^oC (EtOH); IR: ν 3360, 2981, 2247, 1757, 1689, 1673, 1596 cm^{-1}; ^{1}H NMR: δ 8.35 (1H, s), 8.01-7.88 (3H, m), 7.65-7.44 (5H, m), 7.23-7.20 (1H, m), 4.83 (1H, dd, *J* = 8.0, 2.9), 4.14-3.90 (3H, m), 3.72 (1H, dd, *J* = 19.3, 2.8), 2.12 (3H, s), 0.95 (3H, t, *J* = 7.2); MS: m/z (%) 458 (M+2, 0.1), 105 (100). Anal. Calcd. for $C_{22}H_{21}BrN_2O_4$: C, 57.78%; H, 4.63%; N, 6.13%. Found: C, 57.71%; H, 4.85%; N, 6.15%.

Ethyl 2-acetamido-2-cyano-3-(2-bromophenyl)-5-oxo-5-(4-chlorophenyl) pentanate (5b): mp 152-156 ^oC (EtOH); IR: ν 3252, 2972, 2246, 1762, 1685, 1665 cm^{-1}; ^{1}H NMR: δ 8.18 (1H, s), 7.97-7.94 (2H, m), 7.88 (1H, dd, *J* = 7.9, 1.4), 7.59 (1H, dd, *J* = 8.0, 1.3), 7.50-7.48 (2H, m), 7.44-7.39 (1H, m), 7.23-7.19 (1H, m), 4.81 (1H, dd, *J* = 7.9, 3.1), 4.09-3.91 (3H, m), 3.68 (1H, dd, *J* = 19.1, 3.1), 2.12 (3H, s), 0.95 (3H, t, *J* = 7.1); MS: m/z (%) 492 (M^+, 1.2), 241 (100). Anal. Calcd. for $C_{22}H_{20}BrClN_2O_4$: C, 53.73%; H, 4.10%; N, 5.70%. Found: C, 53.74%; H, 4.14%; N, 5.75%.

Ethyl 2-acetamido-2-cyano-3-(2-bromophenyl)-5-oxo-5-(4-methylphenyl)

pentanate (5c): mp 146-148 ^{o}C (EtOH); IR: ν 3371, 2987, 2247, 1760, 1692, 1669, 1604 cm^{-1}; ^{1}H NMR: δ 8.41 (1H, s), 7.92-7.89 (3H, m), 7.58 (1H, dd, *J* = 8.0, 1.3), 7.44-7.39 (1H, m), 7.31-7.28 (2H, m), 7.23-7.17 (1H, m), 4.81 (1H, dd, *J* = 8.2, 2.7), 4.10-3.91 (3H, m), 3.68 (1H, dd, *J* = 19.2, 2.8), 2.45 (3H, s), 2.11 (3H, s), 0.92 (3H, t, *J* = 7.1); MS: m/z (%) 470 (M^{+}, 0.9), 119 (100). Anal. Calcd. for $C_{23}H_{23}BrN_2O_4$: C, 58.61%; H, 4.92%; N, 5.94%. Found: C, 58.62%; H, 4.73%; N, 6.06%.

Ethyl 2-acetamido-2-cyano-3-(2-bromo-4,5-methylenedioxy)-5-oxo-5-phenylpentanate (5d): mp 196-200 ^{o}C (EtOH); IR: ν 3251, 3030, 2246, 1758, 1682, 1654, 1598 cm^{-1}; ^{1}H NMR: δ 8.24 (1H, s), 8.02 (2H, d, *J* = 7.3), 7.69-7.62 (1H, m), 7.52 (2H, t, *J* = 7.5), 7.35 (1H, s), 7.07 (1H, s), 6.03 (2H, s), 4.75 (1H, dd, *J* = 8.1, 2.7), 4.09-4.0 (3H, m), 3.67 (1H, dd, *J* = 19.2, 2.7), 2.12 (3H, s), 1.08 (3H, t, *J* = 7.1); MS: m/z (%) 502 (M+2, 4.4), 500 (M^{+}, 4.7), 105 (100). Anal. Calcd. for $C_{23}H_{21}BrN_2O_6$: C, 55.10%; H, 4.22%; N, 5.59%. Found: C, 55.15%, H, 4.28%; N, 5.57%.

Ethyl 2-acetamido-2-cyano-3-(2-bromo-4,5-methylenedioxy)-5-oxo-5-(4-chlorophenyl)pentanate (5e): mp 168-172 ^{o}C (EtOH); IR: ν 3251, 3035, 2246, 1760, 1684, 1655, 1589 cm^{-1}; ^{1}H NMR: δ 8.07 (1H, s), 7.97-7.93 (2H, m), 7.51-7.47 (2H, m), 7.31 (1H, s), 7.00 (1H, s), 6.03 (2H, s), 4.73 (1H, dd, *J* = 7.9, 3.2), 4.09-3.95 (3H, m), 3.62 (1H, dd, *J* = 19.1, 3.2), 2.06 (3H, s), 1.08 (3H, t, *J* = 7.1); MS: m/z (%) 536 (M+2, 0.1), 139 (100). Anal. Calcd. for $C_{23}H_{20}BrClN_2O_6$: C, 51.56%; H, 3.76%; N, 5.23%. Found: C, 51.53 %, H, 3.76%; N, 5.43%.

Ethyl 2-acetamido-2-cyano-3-(2-bromo-4,5-methylenedioxy)-5-oxo-5-(4-methylphenyl)pentanate (5f): mp 180-184 ^{o}C (EtOH); IR: ν 3257, 3035, 2247, 1761, 1678, 1655, 1607 cm^{-1}; ^{1}H NMR: δ 8.33 (1H, s), 7.91 (2H, d, *J* = 8.2), 7.36 (1H, s), 7.31 (2H, d, *J* = 8.0), 7.00 (1H, s), 6.03 (2H, s), 4.73 (1H, dd, *J* = 8.2, 2.7), 4.09-3.95 (3H, m), 3.63 (1H, dd, *J* = 19.1, 2.8), 2.43 (3H, s), 2.10 (3H, s), 1.07 (3H, t, *J* = 7.1); MS: m/z (%) 516 (M+2, 0.1), 514 (M^{+}, 0.2), 119 (100); Anal. Calcd. for $C_{24}H_{23}BrN_2O_6$: C, 55.94%; H, 4.50%; N, 5.44%. Found: C, 55.90%; H, 4.69%; N, 5.25%.

Ethyl 2-acetamido-2-cyano-3-(2-bromo-4,5-dimethoxyphenyl)-5-oxo-5-phenyl pentanate (5g): mp 214-216 ^{o}C (EtOH); IR: ν 3377, 2987, 2248, 1757, 1683, 1665,

1602 cm^{-1}; ^1H NMR: δ 8.36 (1H, s), 8.03-8.0 (2H, m), 7.66 (1H, t, J = 7.2), 7.52 (2H, J = 7.9), 7.43 (1H, s), 6.98 (1H, s), 4.70 (1H, dd, J = 8.1, 2.7), 4.14-3.95 (6H, m), 3.87 (3H, s), 3.70 (1H, dd, J = 19.1, 2.7), 2.11 (3H, s), 1.01 (3H, t, J = 7.1); MS: m/z (%) 518 (M+2, 1.3), 516 (M^+, 1.2), 403 (0.2), 349 (16.3), 347 (16.6), 267 (99), 251 (16.6), 190 (4.4), 105 (100), 98 (17.6), 77 (50.7), 56 (25.7), 43 (69.6). Anal. Calcd. for $C_{24}H_{25}BrN_2O_6$: C, 55.72%; H, 4.87%; N, 5.41%. Found: C, 55.61%; H, 5.00%; N, 5.46%.

Ethyl 2-acetamido-2-cyano-3-(2-bromo-4,5-dimethoxyphenyl)-5-oxo-5-(4-chlorophenyl)pentanate (5h): mp 196-198 ^oC (EtOH); IR: ν 3265, 3068, 2247, 1758, 1688, 1660, 1590 cm^{-1}; ^1H NMR: δ 8.22 (1H, s), 7.97 (2H, d, J = 8.5), 7.50 (2H, d, J = 8.4), 7.42 (1H, s), 6.99 (1H, s), 4.68 (1H, dd, J = 8.1, 2.5), 4.05-3.91 (6H, m), 3.87 (3H, s), 3.65 (1H, dd, J = 19.1, 2.5), 2.11 (3H, s), 1.02 (3H, t, J = 7.1); MS: m/z (%) 552 (M+2, 0.5), 139 (100). Anal. Calcd. for $C_{24}H_{24}BrClN_2O_6$: C, 52.24%; H, 4.38%; N, 5.08%. Found: C, 52.13%; H, 4.32%; N, 5.28%.

Ethyl 2-acetamido-2-cyano-3-(2-bromo-4,5-dimethoxyphenyl)-5-oxo-5-(4-methylphenyl)pentanate (5i): mp 184-188 ^oC (EtOH); IR: ν 3268, 2995, 2247, 1760, 1682, 1661, 1606 cm^{-1}; ^1H NMR: δ 8.45 (1H, s), 7.92 (2H, d, J = 8.0), 7.44 (1H, s), 7.31 (2H, d, J = 8.0), 6.98 (1H, s), 4.68 (1H, dd, J = 6.8, 2.5), 4.04-3.95 (6H, m), 3.87 (3H, s), 3.67 (1H, dd, J = 19.1, 1.6), 2.45 (3H, s), 2.11 (3H, s), 1.01 (3H, t, J = 7.1); MS: m/z (%) 532 (M+2, 1.3), 530 (M^+, 1.2), 119 (100). Anal. Calcd. for $C_{25}H_{27}BrN_2O_6$: C, 56.51%; H, 5.12%; N, 5.27%. Found: C, 56.57%; H, 5.10%; N, 5.40%.

A General Procedure for the Preparation of Pyridone 6a-i. To a cold solution (ice-water bath) of aq. HCl (37%, 5 mL) and HOAc (50 mL) was added solid compound **5** (10 mmol) in one portion. After the resultant mixture was stirred at room temperature for 7 h (monitored by TLC), it was poured into ice-water. The mixture was neutralized to pH = 7 by solid $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and dried over Na_2SO_4. The solvent was removed to yield a residue, which was purified by recrystallization to give pure compound **6**.

Ethyl 3-acetamido-4-(2-bromophenyl)-6-phenyl-1,2,3-trihydro-2-pyridone-

3-carboxylate (6a): mp 212-216 ^{o}C (EtOAc); IR: ν 3416, 3373, 1734, 1704, 1674, 1599 cm^{-1}; ^{1}H NMR: δ 7.62 (1H, s), 7.59 (1H, s), 7.55-7.46 (2H, m), 7.45-7.40 (3H, m), 7.27-7.25 (2H, m), 7.19-7.15 (1H, m), 6.72 (1H, s), 5.57 (1H, d, *J* = 2.5), 5.26 (1H, s), 4.27-4.06 (2H, m), 2.13 (3H, s), 1.27 (3H, t, *J* = 7.2); MS: m/z (%) 458 (M+2, 0.2), 456 (M^{+}, 0.2), 290 (100). Anal. Calcd. for $C_{22}H_{21}BrN_2O_4$: C, 57.78%; H, 4.63%; N, 6.13%. Found: C, 57.62%; H, 4.59%; N, 6.08%.

Ethyl 3-acetamido-4-(2-bromophenyl)-6-(4-chlorophenyl)-1,2,3-trihydro-2-pyridone-3-carboxylate (6b): mp 228-230 ^{o}C (EtOAc); IR: ν 3409, 3266, 1740, 1704, 1660 cm^{-1}; ^{1}H NMR: δ 7.62 (1H, d, *J* = 1.0), 7.59 (1H, s), 7.41-7.38 (4H, m), 7.27-7.16 (3H, m), 6.69 (1H, s), 5.56 (1H, d, *J* = 2.5), 5.25 (1H, s), 4.27-4.09 (2H, m), 2.12 (3H, s), 1.28 (3H, t, *J* = 7.2); MS: m/z (%) 492 (M+2, 0.4), 490 (M^{+}, 0.4), 324 (100). Anal. Calcd. for $C_{22}H_{20}BrClN_2O_4$: C, 53.73%; H, 4.10%; N, 5.70%. Found: C, 53.81%; H, 4.10%; N, 5.72%.

Ethyl 3-acetamido-4-(2-bromophenyl)-6-(4-methylphenyl)-1,2,3-trihydro-2-pyridone-3-carboxylate (6c): mp 246-248 ^{o}C (EtOAc); IR: ν 3414, 3368, 1733, 1704, 1675 cm^{-1}; ^{1}H NMR: δ 7.62-7.59 (1H, m), 7.39-7.33 (3H, m), 7.27-7.20 (4H, m), 7.18-7.12 (1H, m), 6.70 (1H, s), 5.56 (1H, d, *J* = 2.5), 5.23 (1H, s), 4.25-4.09 (2H, m), 2.40 (3H, s), 2.13 (3H, s), 1.27 (3H, t, *J* = 7.2); MS: m/z (%) 472 (M+2, 0.2), 470 (M^{+}, 0.2), 304 (100). Anal. Calcd. for $C_{23}H_{23}BrN_2O_4$: C, 58.61%; H, 4.92%; N, 5.94%. Found: C, 58.53%; H, 4.80%; N, 5.79%.

Ethyl 3-acetamido-4-(2-bromo-4,5-methylenedioxyphenyl)-6-phenyl-1,2,3-trihydro-2-pyridone-3-carboxylate (6d). mp 248-250 ^{o}C (EtOAc); IR: ν 3421, 3239, 1748, 1703, 1676, 1651 cm^{-1}; ^{1}H NMR: δ 7.50-7.41 (6H, m), 7.03 (1H, s), 6.73 (1H, s), 6.72 (1H, s), 5.98 (2H, s), 5.46 (1H, d, *J* = 2.5), 5.21 (1H, s), 4.30-4.13 (2H, m), 2.13 (3H, s), 1.30 (3H, t, *J* = 7.2); MS: m/z (%) 502 (M+2, 0.1), 500 (M^{+}, 0.1), 334 (100). Anal. Calcd. for $C_{23}H_{21}BrN_2O_6$: C, 55.10%; H, 4.22%; N, 5.59%. Found: C, 55.22%; H, 4.28%; N, 5.67%.

Ethyl 3-acetamido-4-(2-bromo-4,5-methylenedioxyphenyl)-6-(4-chlorophenyl)-1,2,3-trihydro-2-pyridone-3-carboxylate (6e): mp 256-260 ^{o}C (EtOAc); IR: ν 3404,

3297, 1739, 1704, 1658 cm^{-1}; ^1H NMR: δ 7.48-7.41 (5H, m), 7.03 (1H, s), 6.71 (1H, s), 6.69 (1H, s), 5.98 (2H, s), 5.45 (1H, d, J = 2.5), 5.20 (1H, s), 4.30-4.11 (2H, m), 2.13 (3H, s), 1.27 (3H, t, J = 7.1); MS: m/z (%) 538 (M+4, 0.3), 537 (M+3, 0.3), 536 (M+2, 0.3), 535 (M+1, 0.2), 534 (M^+, 0.3), 368 (100); Anal. Calcd. for $C_{23}H_{20}BrClN_2O_6$: C, 51.56%; H, 3.76%; N, 5.23%. Found: C, 51.65%; H, 3.93%; N, 5.25%.

Ethyl 3-acetamido-4-(2-bromo-4,5-methylenedioxyphenyl)-6-(4-methylphenyl)-1,2,3-trihydro-2-pyridone-3-carboxylate (6f): mp 214-216 ^oC (EtOAc); IR: ν 3384, 3223, 1730, 1703, 1662 cm^{-1}; ^1H NMR: δ 7.38-7.35 (3H, m), 7.24 (2H, d, J = 8.0), 7.03 (1H, s), 6.72 (1H, s), 6.71 (1H, s), 5.98 (2H, s), 5.45 (1H, d, J = 2.5), 5.17 (1H, s), 4.31-4.10 (2H, m), 2.40 (3H, s), 2.13 (3H, s), 1.27 (3H, t, J = 7.1); MS: m/z (%) 516 (M+2, 0.2), 514 (M^+, 0.2), 348 (100). Anal. Calcd. for $C_{24}H_{23}BrN_2O_6$: C, 55.93%; H, 4.50%; N, 5.44%. Found: C, 55.85%; H, 4.46%; N, 5.62%.

Ethyl 3-acetamido-4-(2-bromo-4,5-dimethoxyphenyl)-6-phenyl-1,2,3-trihydro-2-pyridone-3-carboxylate (6g). mp 216-220 ^oC (EtOAc); IR: ν 3366, 3219, 1746, 1704, 1658 cm^{-1}; ^1H NMR: δ 7.48-7.40 (6H, m), 7.04 (1H, s), 6.73 (1H, s), 6.71 (1H, s), 5.47 (1H, d, J = 2.5), 5.24 (1H, d, J = 6.3), 4.32-4.09 (2H, m), 3.89 (3H, s), 3.79 (3H, s), 2.13 (3H, s), 1.27 (3H, t, J = 7.2); MS: m/z (%) 518 (M+2, 4.0), 516 (M^+, 4.5), 378 (100). Anal. Calcd. for $C_{24}H_{25}BrN_2O_6$: C, 55.72%; H, 4.87%; N, 5.41%. Found: C, 55.74%; H, 4.84%; N, 5.51%.

Ethyl 3-acetamido-4-(2-bromo-4,5-dimethoxyphenyl)-6-(4-chlorophenyl)-1,2,3-trihydro-2-pyridone-3-carboxylate (6h): mp 238-242 ^oC (EtOAc); IR: ν 3369, 3219, 1756, 1704, 1664 cm^{-1}; ^1H NMR: δ 7.46 (1H, s), 7.38(4H, s), 7.03 (1H, s), 6.72 (1H, s), 6.42 (1H, s), 5.67 (1H, s), 5.23 (1H, d, J = 6.1), 4.32-4.26 (2H, m), 3.86 (3H, s), 3.75 (3H, s), 1.88 (3H, s), 1.27 (3H, t, J = 7.1); MS: m/z (%) 554 (M+4, 3.4), 552 (M+2, 11.2), 550 (M^+, 8.4), 412 (100). Anal. Calcd. for $C_{24}H_{24}BrClN_2O_6$: C, 52.24%; H, 4.38%; N, 5.08%. Found: C, 52.19%; H, 4.44%; N, 5.07%.

Ethyl

3-acetamido-4-(2-bromo-4,5-dimethoxyphenyl)-6-(4-methylphenyl)-1,2,3-trihydro-2-pyridone-3-carboxylate (6i): mp 228-230 ^{o}C (EtOAc); IR: ν 3364, 3242, 1749, 1705, 1662 cm^{-1}; ^{1}H NMR: δ 7.34-7.32 (3H, m), 7.22 (2H, d, J = 8.0), 7.04 (1H, s), 6.75 (1H, s), 6.39 (1H, s), 5.67 (1H, d, J = 5.7), 5.22 (1H, d, J = 6.2), 4.36-4.24 (2H, m), 3.88 (3H, s), 3.75 (3H, s), 2.38 (3H, s), 1.90 (3H, s), 1.27 (3H, t, J = 7.1); MS: m/z (%) 532 (M+2, 7.0), 530 (M^{+}, 6.1), 392 (100). Anal. Calcd. for $C_{25}H_{27}BrN_2O_6$: C, 56.51%; H, 5.12%; N, 5.27%. Found: C, 56.53%; H, 5.28%; N, 5.47%.

A General Procedure for the Preparation of 3-Phenyl-2,9-dihydro-1*H*-pyrido [3,4-*b*]indol-1-one (2a-i): A mixture of **6** (5 mmol), CuI (1.9 g, 10 mmol) and NaH (480 mg, 20 mmol) in anhydrous DME (100 mL) was heated to reflux under N_2 for 7 h (minitored by TLC). After the most of DME was removed under vacuum, 10% aq. solution of NH_4OH (100 mL) was added. The resultant mixture was stirred for 2 h at room temperature and the solid was collected. The crude product was purified by chromatography (silica gel, 10% MeOH in EtOAc) to give pure compound **2**.

3-Phenyl-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (2a): mp 300-302 ^{o}C (MeOH); IR: ν 3110, 3051, 1636, 1620, 1598 cm^{-1}; ^{1}H NMR: (500 Mz, DMSO-d_6) δ 11.96 (1H, s), 11.60 (1H, s), 8.10 (1H, d, J = 8.0), 7.77 (2H, d, J = 7.5), 7.54 (1H, d, J = 8.5), 7.47 (2H, t, J = 8.5), 7.47 (2H, t, J = 7.0), 7.43-7.39 (2H, m), 7.37 (1H, s), 7.19 (1H, t, J = 7.5); ^{13}C NMR: (DMSO-d_6) δ 157.0, 140.3, 137.2, 135.5, 129.6, 129.2, 128.0, 127.4, 125.7, 123.1, 122.4, 120.5, 113.4, 99.6; MS: m/z (%) 262 (M+2, 6.2), 261 (M+1, 60.5), 260 (M^{+}, 100). Anal. Calcd. for $C_{17}H_{12}N_2O$: C, 78.44%; H, 4.65%; N, 10.76%. Found: C, 78.44%; H, 4.65%; N, 10.61%.

3-(4-Chlorophenyl)-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (2b): mp 344-346 ^{o}C (MeOH); IR: ν 3115, 2971, 1635 cm^{-1}; ^{1}H NMR: (DMSO-d_6) δ 12.05 (1H, s), 11.66 (1H, s), 8.11 (1H, d, J = 7.9), 7.83 (2H, dd, J = 6.8, 1.9), 7.56-7.53 (3H, m), 7.46-7.42 (2H, m), 7.23 (1H, t, J =7.2); MS: m/z (%) 297 (M+3, 5.8), 296 (M+2, 33.1), 294 (M^{+}, 100). Anal. Calcd. for $C_{17}H_{11}ClN_2O$: C, 69.28%; H, 3.76%; N, 9.50%. Found: C, 69.26%; H, 3.77%; N, 9.40%.

3-(4-Methylphenyl)-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (2c): mp 326-328 ^{o}C (MeOH); IR: ν 3141, 2972, 1635 cm^{-1}; ^{1}H NMR: (DMSO-d_6) δ 11.98 (1H,

s), 11.55 (1H, s), 8.11 (1H, d, *J* = 7.9), 7.70 (2H, d, *J* = 8.1), 7.53 (1H, d, *J* = 8.3), 7.43 (1H, t, *J* = 7.2), 7.37 (1H, s), 7.30 (2H, d, *J* = 8.1), 7.20 (1H, t, *J* = 7.2), 2.37 (3H, s); MS: m/z (%) 276 (M+2, 1.6), 275 (M+1, 19.8), 274 (M^+, 100). Anal. Calcd. for $C_{18}H_{14}N_2O$: C, 78.81%; H, 5.14%; N, 10.21%. Found: C, 78.80%; H, 5.05%; N, 10.00%.

3-Phenyl-6,7-methylenedioxy-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (2d): mp 342-344 ^oC (MeOH); IR: ν 3084, 2893, 1635, 1613 cm^{-1}; ^1H NMR: (DMSO-d_6) δ 11.85 (1H, s), 11.41 (1H, s), 7.79-7.76 (2H, m), 7.57 (1H, d, *J* = 0.2), 7.51-7.41 (3H, m), 7.28 (1H, s), 6.97 (1H, s), 6.06 (2H, s); MS: m/z (%) 306 (M+2, 2.7), 305 (M+1, 20.8), 304 (M^+, 100). Anal. Calcd. for $C_{18}H_{12}N_2O_3$: C, 71.05%; H, 3.97%; N, 9.21%. Found: C, 71.03%; H, 3.91%; N, 9.08%.

3-(4-Chlorophenyl)-6,7-methylenedioxy-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1 - one (2e): mp 334-336 ^oC (MeOH); IR: ν 3181, 3101, 29751635, 1619 cm^{-1}; ^1H NMR: (DMSO-d_6) δ 11.90 (1H, s), 11.48 (1H, s), 7.79 (2H, dd, *J* = 8.5, 1.4), 7.56-7.52 (3H, m), 7.31 (1H, d, *J* = 1.4), 6.97 (1H, s), 6.06 (2H, s); MS: m/z (%) 341 (M+3, 7.0), 340 (M+2, 35.0), 339 (M+1, 22.3), 338 (M^+, 100). Anal. Calcd. for $C_{18}H_{11}ClN_2O_3$: C, 63.82%; H, 3.27%; N, 8.27%. Found: C, 64.05%; H, 3.51%; N, 8.16%.

3-(4-Methylphenyl)-6,7-methylenedioxy-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1 - one (2f): mp 338-340 ^oC (MeOH); IR: ν 3092, 2972, 1638 cm^{-1}; ^1H NMR: (DMSO-d_6) δ 11.84 (1H, s), 11.37 (1H, s), 7.66 (2H, dd, *J* = 7.9, 1.2), 7.57 (1H, d, *J* = 1.3), 7.28 (2H, d, *J* =7.4), 7.24 (1H, d, *J* = 1.5), 6.96 (1H, d, *J* =1.3), 6.06 (2H, s), 2.35 (3H, s); MS: m/z (%) 320 (M+2, 3.2), 319 (M+1, 21.2), 318 (M^+, 100). Anal. Calcd. for $C_{19}H_{14}N_2O_3$: C, 71.69%; H, 4.43%; N, 8.80%. Found: C, 71.71%; H, 4.49%; N, 8.57%.

3-Phenyl-6,7-dimethoxy-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (2g): mp 306-308 ^oC (MeOH); IR: ν 3392, 3174, 1635, 1596 cm^{-1}; ^1H NMR: (DMSO-d_6) δ 11.75 (1H, s), 11.40 (1H, s), 7.79 (2H, d, *J* = 7.3), 7.64 (1H, s), 7.51-7.46 (2H, m), 7.42-7.37 (1H, m), 7.35 (1H, s), 6.98 (1H, s), 3.85 (3H, s), 3.84 (3H, s); MS: m/z (%) 322 (M+2, 2.2), 321 (M+1, 22.6), 320 (M^+, 100). Anal. Calcd. for $C_{19}H_{16}N_2O_3$: C, 71.24%; H, 5.03%; N, 8.74%. Found: C, 71.24%; H, 5.08%; N, 8.56%.

3-(4-Chlorophenyl)-6,7-dimethoxy-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (2h): mp 316-318 ^{o}C; IR: ν 3114, 1633, 1607 cm^{-1}; ^{1}H NMR: (DMSO-d_6) δ 11.79 (1H, s), 11.47 (1H, s), 7.81 (2H, dd, J = 8.6, 1.8), 7.63 (1H, s), 7.54 (2H, dd, J = 8.7, 1.8), 7.38 (1H, s), 6.97 (1H, s), 3.85 (3H, s), 3.84 (3H, s); MS: m/z (%) 357 (M+3, 7.0), 356 (M+2, 33.2), 355 (M+1, 26.1), 354 (M^+, 100). Anal. Calcd. for $C_{19}H_{15}ClN_2O_3$: C, 64.30%; H, 4.26%; N, 7.89%. Found: C, 64.40%; H, 4.25%; N, 7.75%.

3-(4-Methylphenyl)-6,7-dimethoxy-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (2i): mp 330-332 ^{o}C (MeOH); IR: ν 3166, 1630, 1603 cm^{-1}; ^{1}H NMR: (DMSO-d_6) δ 11.72 (1H, s), 11.36 (1H, s), 7.69 (2H, d, J = 7.9), 7.63 (1H, s), 7.31-7.27 (3H, m), 6.97 (1H, s), 3.84 (6H, s), 2.39 (3H, s); MS: m/z (%) 336 (M+2, 3.3), 335 (M+1, 23.0), 334 (M^+, 100). Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84%; H, 5.43%; N, 8.38%. Found: C, 71.79%; H, 5.45%; N, 8.32%.

Ethyl 4-(2-bromophenyl)-6-phenyl-2-oxo-3-pyridinecarboxylate (8). A mixture of **6a** (457 mg, 1 mmol) and Cs_2CO_3 (652 mg, 2 mmol) in toluene (10 mL) was stirred at 100 ^{o}C for 10 h and cooled to room temperature. Then it was poured into 2% aqueous solution of HCl and extracted with diethyl ether. The combined organic layers were washed with H_2O and dried over Na_2SO_4. The solvent was removed to give crude product, which was purified by chromatography to give 350 mg (88%) of pure product **8**, mp 200-202 ^{o}C (EtOAc/PE); IR: ν 1738, 1627, 1608 cm^{-1}; ^{1}H NMR: δ 7.97-7.93 (2H, m), 7.67 (1H, d, J = 7.8), 7.51-7.49 (3H, m), 7.36 (1H, d, J = 1.1), 7.31-7.28 (2H, m), 6.78 (1H, s), 4.12-4.04 (2H, m), 0.92 (3H, t, J = 7.1); MS: m/z (%) 399 (M+2, 1.6), 397 (M^+, 1.6), 290 (100). Anal. Calcd for $C_{20}H_{16}BrNO_3$: C, 60.32%; H, 4.05%; N, 3.53%. Found: C, 60.30%; H, 4.00%; N, 3.60%.

3-Acetamido-4-(2-bromophenyl)-6-phenyl-2-pyridone (9): It was separated as an intermediate compound from the conversion of compound **6a** to **2a**. mp 228-230 ^{o}C (EtOAc/PE); IR: ν 3261, 2924, 2853, 1640, 1529, 759 cm^{-1}; ^{1}H NMR: (DMSO-d_6) δ 1.75 (s, 3H), 6.45 (s, 1H), 7.31 (d, 2H, J = 4.9), 7.40 (d, 1H, J = 7.4), 7.45- 7.47 (m, 3H), 7.69 (d, 1H, J = 7.9), 7.77 (t, 2H, J = 3.6), 9.05 (s, 1H), 12.16 (s, 1H); ^{13}C NMR: δ 169.3, 161.7, 148.4, 144.3, 139.2, 134.0, 133.4, 130.9, 130.7, 130.5, 129.7, 128.1, 127.6, 124.9, 122.0, 107.2, 23.3. MS: m/z (%): 384 (M+2, 14.3), 382 (M^+, 13.6), 342

(100). Anal. Calcd for $C_{19}H_{15}BrN_2O_2$: C, 59.55; H, 3.95; N, 7.31. Found: C, 59.56%; H, 4.04%; N, 7.33%.