Regioselective Synthesis of Bioactive Spiro Heterocyclic Compounds Containing Both Indoline and Quinolone Moieties by Aryl Radical Cyclization

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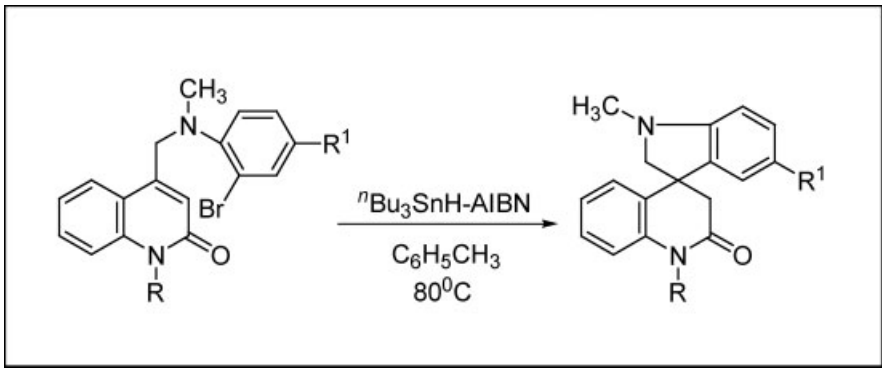

The tin hydride-mediated aryl radical cyclization of a number of 4-(2′-bromo-*N*-methylanilino)-methyl-1-alkylquinolin-2(1*H*)-ones under mild neutral condition afforded 1-alkyl-3,4-dihydroquinolin-2(1*H*)-one-4-spiro-3′-(1-methylindolines) in excellent yield. The starting materials, amines were derived from 4-bromomethyl-*N*-methyl quinolin-2(1*H*)-ones and 2-bromo-*N*-methyl anilines by refluxing in acetone in the presence of anhydrous potassium carbonate and sodium iodide (Finkelstein condition).

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INTRODUCTION

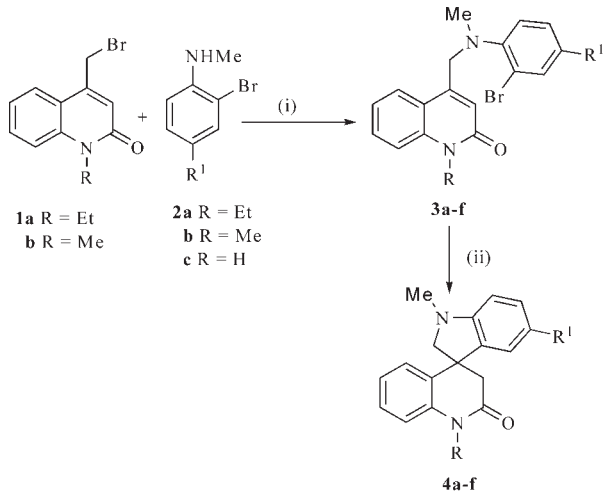
Nitrogen-containing heterocycles as recognized pharmacophores have received great attention in drug discovery and lead optimization [1–3]. In addition to traditional cycloadditions, cyclizations of nitrogen radicals or nitrogen-containing carbon radicals are the new approaches to *N*-heterocyclics [4–11]. Between these two radical reactions, the latter one is more general because carbon radicals are easy to generate and carbon–carbon bond formation by radical cyclization is a well-established process [12–16]. In our continuous effort on the development of free-radical reactions, we recently reported the 5-exo cyclization [17–20] and 6-endo cyclization [21,22] of oxygen heterocycles. We also recently reported the cyclization of 4-(2′-bromothioarylmethyl)-1-methylquinolin-2(1*H*)-one by $^{n}Bu_3SnH$ and AIBN, where a 6-endo ring closure took place to generate a six-membered sulfur heterocycle [23]. Several methodologies based on free-radical cyclization for the construction of five- [24–26] and six-membered [27–31] nitrogen heterocycles are available. In contrast, formation of spiro nitrogen heterocycles is almost rarely reported in literature [32–34].

Zhang and Pugh [35] demonstrated that intramolecular free-radical Michael-type addition facilitates the spiro cyclization process when an aryl radical is attached at the β-carbon of an α,β-unsaturated lactone system. Stabilization of the intermediate radical by the carbonyl group controls this regioselectivity [35]. It is also well documented that a 5-hexenyl radical cyclizes preferentially to the cyclopentylmethyl radical *via* 5-exo cyclization and not to the more stable cyclohexyl radical *via* 6-endo cyclization [36,37]. In this context, we undertook a study on the radical cyclizations of 4-(2′-bromo-*N*-methylanilinomethyl)-1-alkylquinolin-2(1*H*)-ones where these very criteria are present. Also quinolones fused with other heterocycles are known to have interesting biological activities and medicinal properties. Quinolone derivatives are biologically significant [38–42] because of their antibacterial activity, DNA-gyrase inhibition and marked cytotoxicity against animal and plant tumors. Keeping these biological activities in mind a number of attempts have been made over the last few decades to synthesize various biologically active quinolone derivatives many of which are abundant in nature [43]. Herein, we report the regioselective formation of spiro quinolone heterocycles by $^{n}Bu_3SnH$ mediated radical cyclization.

RESULTS AND DISCUSSION

The amines **3a–f** required for the present study were readily prepared in 89–95% yield from *o*-bromoanilines

Scheme 1. Reagents and conditions: (i) Acetone, K_2CO_3, NaI, reflux, 8h; (ii) $^nBu_3SnH$, toluene, 80°C N_2 atm, 1h.



3, 4	R	R^1	Yield (%) (Compound **3**)	Yield (%) (Compound **4**)
a	Et	H	95	90
b	Et	Me	90	95
c	Et	Et	89	92
d	Me	H	95	95
e	Me	Me	92	92
f	Me	Et	92	90

2a–c and 4-bromomethyl-1-alkylquinolin-2(1*H*)-ones **1a,b** in refluxing acetone for 8 h in the presence of anhydrous potassium carbonate and sodium iodide. The amines were subjected to $^nBu_3SnH$-AIBN induced radical cyclization. Compound **3a** when heated at 80°C in dry degassed toluene under nitrogen with $^nBu_3SnH$ in the presence of catalytic amount of AIBN for 1 h afforded the cyclic product **4a** in 90% yield (Scheme 1). The structure of the compound **4a** was readily confirmed by ^1H NMR spectroscopy which exhibited one proton doublet at δ 2.83 (J = 16 Hz), another one proton doublet at δ 2.90 (J = 16 Hz) due to —COCH_2, —N(CH$_3$)CH_2 protons appear as two one proton doublet each at δ 3.21 and 3.39 (J = 8.8 Hz). Further confirmation of the structure **4a** came from its COSY, HETCOR and ^{13}C NMR spectrum. COSY spectrum of compound **4a** showed that —COCH_2 protons at δ 2.83 and 2.90 correlate with each other and —N(CH$_3$)CH_2 protons at δ 3.21 and 3.39 correlate with each other. The ^{13}C NMR spectrum of **4a** also strongly supported its structure. The ^{13}C chemical shifts of the compound **4a** are assigned by DEPT experiment. DEPT showed thirteen protonated carbons, two —CH$_3$, three >CH$_2$ and eight >CH— moieties. Protonated carbon resonances are established by direct correlation with proton resonance by HETCOR experiment (normal one bond C—H coupling). Methylene protons resonance at δ 2.83 and 2.90 (CH_2CO) are related with carbon resonance at δ 42.34 and the methylene protons at δ 3.21 and 3.39 (—N(CH$_3$)CH_2) are related with carbon resonance at δ 67.42 respectively. Mass spectrum of the compound **4a** showed a molecular ion peak at m/z = 293 (M^+ + 1). These clearly indicated the formation of a spiro heterocyclic compound.

The other substrates **3b–f** were also treated similarly to afford exclusively compounds **4b–f** in 90–95% yield.

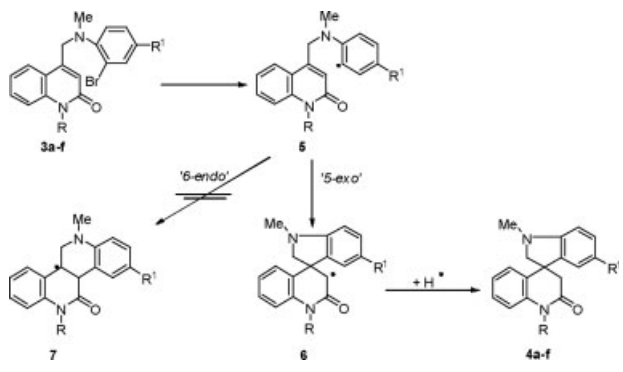
FMO theory can rationalize the regioselective formation of the spiro heterocyclic ring. Aryl radicals are high energy species and hence are nucleophilic in character. The highly electron withdrawing carbonyl group confers considerable electrophilic character to the C-4 position of the quinolone moiety. Thus in the case of nucleophilic radical **5**, FMO theory suggests that the mode of ring closure is largely determined by the interaction between the radical SOMO (≡HOMO) and the alkene LUMO of the acceptor (electron deficient centre) and accordingly more favorable bond formation occurs between the radical centre (nucleophilic) and C-4 of the quinolone ring for 5-exo product **4a–f** (Scheme 2) containing both the quinolone and indoline moieties which are known to be present in biologically active compounds.

In conclusion, we can say that the exclusive formation of 5-membered spiro heterocyclic pyrrole ring in excellent yield occurs because of two driving forces: first, the stabilization of the radical intermediate and second, stereoelectronically favored 5-exo pathway. This gives a simple and straightforward synthesis for spiro heterocyclic compounds. The methodology described here is mild and attractive because of its simplicity.

EXPERIMENTAL

Melting points were determined in an open capillary and are uncorrected. IR spectra were recorded on a Perkin–Elmer L

Scheme 2



120-000A spectrometer (ν_{max} in cm^{-1}) using samples as neat liquids and solid samples were recorded on KBr disks. UV absorption spectra were recorded in EtOH on a Shimadzu UV-2401PC spectrophotometer (λ_{max} in nm). ^1H NMR (400 MHz, 500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DPX-400 and Bruker DPX-500 spectrometer in $CDCl_3$ (chemical shift in δ) with TMS as internal standard. Elemental analyses and mass spectra were recorded on a Leco 932 CHNS analyzer and on a JEOL JMS-600 instrument respectively. Silica gel [60–120 mesh, Spectrochem, India] was used for chromatographic separation. Silica gel G [E-Merck, India] was used for TLC. Petroleum ether refers to the fraction boiling between 60 and 80°C.

General procedure for the preparation of 4-(2′-bromo-*N*-methylanilino)methyl-1-alkylquinolin-2(1*H*)-ones 3a–f. A mixture of 4-bromomethyl-*N*-alkylquinolone (**1a,b,**5 mmol), 2-bromoaniline (**2a–f**, 5 mmol), anhydrous potassium carbonate (5 g) and sodium iodide (20 mg) was heated under reflux in dry acetone (125 mL) for 8 h. The reaction mixture was cooled, filtered and concentrated. The residual mass was extracted with CH_2Cl_2(3 × 50 mL), washed with 10% Na_2CO_3 solution (2 × 25 mL), brine (3 × 50 mL) and dried (Na_2SO_4). The residual mass after the removal of solvent was subjected to column chromatography on silica gel using petroleum ether EtOAc (4:1) as eluant to give compounds **3a–f** which were recrystallized from $CHCl_3$-petroleum ether.

Compound (3a). Yield 95%, Viscous liquid; IR (Neat) υ_{max}: 2922 (Aromatic CH stretching), 1652 (CO δ lactum), 1590 (C=C) cm^{-1}; UV (EtOH) λ_{max}(log ε): 213 (4.44), 232 (4.49), 329 (3.76) nm; ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.35 (t, J = 7.1 Hz, 3H, NCH_2CH_3), 2.75 (s, 3H, NCH_3), 4.35 (s, 2H, CH_2NCH_3), 4.36 (q, J = 7.1 Hz, 2H, NCH_2CH_3), 6.91–6.96 (m, 1H, Ar*H*), 7.04 (s, 1H, =C*H*), 7.17–7.85 (m, 7H, Ar*H*); MS (*m*/*z*): 395 (M^+ + 23, 20%), 393 (M^+ + 23, 20%), 373 (M^+ + 1, 91%), 371 (M^+ + 1, 100%), 291 (15%). *Anal.* Calcd for $C_{19}H_{19}BrN_2O$: C, 61.46; H, 5.15; N, 7.54%. Found: C, 61.75; H, 4.95; N, 7.42%.

Compound (3b). Yield 90%, Viscous liquid; IR (Neat) υ_{max}: 2920 (Aromatic CH stretching), 1652 (CO δ lactum), 1591 (C=C) cm^{-1}; UV (EtOH) λ_{max}(log ε): 214 (4.36), 330 (3.51) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.36 (t, J = 7.1 Hz, 3H, NCH_2CH_3), 2.29 (s, 3H, $ArCH_3$), 2.73 (s, 3H, CH_2NCH_3), 4.32 (s, 2H, CH_2NCH_3), 4.36 (q, J = 7.1 Hz, 2H, NCH_2CH_3), 7.02 (s, 1H, =C*H*), 7.08–7.91 (m, 7H, Ar*H*); MS (*m*/*z*): 409 (M^+ + 23, 22%), 407 (M^+ + 23, 21%), 387 (M^+ + 1, 100%), 385 (M^+ + 1, 92%), 305 (15%). *Anal.* Calcd for $C_{20}H_{21}BrN_2O$: C, 62.34; H, 5.49; N, 7.27%. Found: C, 62.12; H, 5.68; N, 7.15%.

Compound (3c). Yield 89%, Viscous liquid; IR (Neat) υ_{max}: 2922 (Aromatic CH stretching), 1652 (CO δ lactum), 1592 (C=C) cm^{-1}; UV (EtOH) λ_{max}(log ε): 215 (3.62), 231 (3.67), 330 (2.83) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.19 (t, J = 7.5 Hz, 3H, $ArCH_2CH_3$), 1.35 (t, J = 7.1 Hz, 3H, NCH_2CH_3), 2.55 (q, J = 7.5 Hz, 2H, $ArCH_2CH_3$), 2.72 (s, 3H, NCH_3), 4.31 (s, 2H, CH_2NCH_3), 4.34 (q, J = 7.1 Hz, 2H, NCH_2CH_3), 7.01 (s, 1H, =C*H*), 7.09–7.89 (m, 7H, Ar*H*); MS (*m*/*z*): 401 (M^+ + 1, 100%), 399 (M^+ + 1, 86%), 319 (7%), 317 (17%), 309 (57%), 293 (25%). *Anal.* Calcd for $C_{21}H_{23}BrN_2O$: C, 63.16; H, 5.80; N, 7.01%. Found: C, 63.28; H, 6.03; N, 7.20%.

Compound (3d). Yield 95%, Viscous liquid;. IR (Neat) υ_{max}: 2924 (Aromatic CH stretching), 1656 (CO δ lactum), 1590 (C=C) cm^{-1}; UV (EtOH) λ_{max}(log ε): 215 (4.73), 229 (4.77), 330 (3.96) nm; ^1H NMR (400 MHz, $CDCl_3$): δ_H 2.75 (s, 3H, CH_2NCH_3), 3.74 (s, 3H, $CONCH_3$), 4.35 (s, 2H, NCH_2), 6.91–6.95 (m, 1H, Ar*H*), 7.03 (s, 1H, =C*H*), 7.19–7.85 (m, 7H, Ar*H*); MS (*m*/*z*): 381 (M^+ + 23, 21%), 379 (M^+ + 23, 26%), 359 (M^+ + 1, 96%), 357 (M^+ + 1, 89%), 309 (100%), 277 (31%). *Anal.* Calcd for $C_{18}H_{17}BrN_2O$: C, 60.51; H, 4.79; N, 7.84%. Found: C, 60.76; H, 4.68; N, 7.65%.

Compound (3e). Yield 92%, White solid, mp 100–102°C; IR (KBr) υ_{max}: 2922 (Aromatic CH stretching), 1654 (CO δ lactum), 1588 (C=C) cm^{-1}; UV (EtOH) λ_{max}(log ε): 218 (4.63), 230 (4.66), 330 (3.85) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.29 (s, 3H, $ArCH_3$), 2.73 (s, 3H, CH_2NCH_3), 3.73 (s, 3H, $CONCH_3$), 4.32 (s, 2H, NCH_2), 7.00 (s, 1H, =C*H*), 7.07–7.89 (m, 7H, Ar*H*); MS (*m*/*z*): 395 (M^+ + 23, 21%), 393 (M^+ + 23, 21%), 373 (M^+ + 1, 89%), 371 (M^+ + 1, 100%), 291 (17%). *Anal.* Calcd for $C_{19}H_{19}BrN_2O$: C, 61.46; H, 5.15; N, 7.54%. Found: C, 61.68; H, 5.30; N, 7.31%.

Compound (3f). Yield 92%, White solid, mp 101–102°C; IR (KBr) υ_{max}: 2922 (Aromatic CH stretching), 1651 (CO δ lactum), 1591 (C[dond]C) cm^{-1}; UV (EtOH) λ_{max} (log ε): 215 (4.45), 232 (4.48), 330 (3.87) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.19 (t, J = 7.5 Hz, 3H, $ArCH_2CH_3$), 2.55 (q, J = 7.5 Hz, 2H, $ArCH_2CH_3$), 2.72 (s, 3H, CH_2NCH_3), 3.72 (s, 3H, $CONCH_3$), 4.31 (s, 2H, NCH_2), 7.01 (s, 1H, =C*H*), 7.09–7.88 (m, 7H, Ar*H*); MS (*m*/*z*): 409 (M^+ + 23, 14%), 407 (M^+ + 23, 14%), 387 (M^+ + 1, 100%), 385 (M^+ + 1, 85%), 305 (11%); *Anal.* Calcd for $C_{20}H_{21}BrN_2O$: C, 62.34; H, 5.49; N, 7.27%. Found: C, 62.08; H, 5.71; N, 7.11%.

General procedure for the preparation of 1-alkyl-3,4-dihydroquinolin-2(1*H*)-one-4-spiro-3′-(1-methylindoline) 4a–f. Tributyltin hydride (1.1 mmol) was added to a stirred solution of (**3a–f**, 1 mmol) and azobisisobutyronitrile (0.5 mmol) in dry degassed toluene (5 mL) under nitrogen. The mixture was heated at 80°C for 1 h and concentrated. The residue was dissolved in ether (10 mL) and stirred with a 10% aq. potassium fluoride solution (10 mL) for 45 min. The white precipitate was filtered and the aqueous phase was extracted with ether (10 mL). The combined ether extract was washed with brine and dried (Na_2SO_4). The residual mass after the removal of solvent was subjected to column chromatography using petroleum ether-ethyl acetate (4:1) as eluant to give cyclized product **4a–f**.

Compound (4a). Yield 90%, Viscous liquid; IR (Neat) υ_{max}: 2974 (Aromatic CH stretching), 1673 (CO δ lactum) cm^{-1}; UV (EtOH) λ_{max} (log ε): 212 (4.47), 253 (4.19), 305 (3.42) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.28 (t, J = 7.1 Hz, 3H, NCH_2CH_3), 2.75 (s, 3H, NCH_3), 2.83 (d, J = 16 Hz, 1H, COC*H*), 2.90 (d, J = 16 Hz, 1H, COC*H*), 3.21 (d, J = 8.8 Hz, 1H, NC*H*), 3.39 (d, J = 8.8 Hz, 1H, NC*H*), 4.03 (q, J = 7.1 Hz, 2H, NCH_2CH_3), 6.59–7.25 (m, 8H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 12.70 (NCH_2CH_3), 35.52 (NCH_3), 37.16 (NCH_2CH_3), 42.34 ($COCH_2$), 46.55 (CH_2C), 67.42 (CH_2NCH_3), 107.85 (Ar*C*H), 115.02 (Ar*C*H), 118.41 (Ar*C*H), 123.09 (Ar*C*H), 123.52 (Ar*C*H), 127.00 (Ar*C*H), 128.02 (Ar*C*H), 128.82 (Ar*C*H), 131.93 (Ar*C*), 132.55 (Ar*C*), 138.65 (Ar*C*), 153.04 (Ar*C*), 168.05 (*C*O); MS (*m*/*z*): 315 (M^+ + 23, 25%), 293 (M^+ + 1, 100%), 289 (20%), 251 (50%). *Anal.* Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.89; N, 9.54%. Found: C, 77.90; H, 6.63; N, 9.80%.

Compound (4b). Yield 95%, White solid, mp 124–126°C; IR (KBr) υ_{max}: 2921 (Aromatic CH stretching), 1674 (CO δ

lactum) cm^{-1}; UV (EtOH) λ_{max} (log ε): 211 (4.51), 253 (4.18), 313 (3.34) nm; ^1H NMR (500 MHz, $CDCl_3$,): δ_H 1.28 (t, J = 7.1 Hz, 3H, NCH_2CH_3), 2.26 (s, 3H, $ArCH_3$), 2.71 (s, 3H, NCH_3), 2.82 (d, J = 16 Hz, 1H, COCH), 2.90 (d, J = 16 Hz, 1H, COCH), 3.18 (d, J = 8.8 Hz, 1H, NCH), 3.33 (d, J = 8.8 Hz, 1H, NCH), 4.01 (q, J = 7.1 Hz, 2H, NCH_2CH_3), 6.51–7.29 (m, 7H, ArH); MS (*m*/*z*): 329 (M^+ + 23, 50%), 307 (M^+ + 1, 100%), 303 (11%), 265 (39%). *Anal*. Calcd for $C_{20}H_{22}N_2O$: C, 78.39; H, 7.23; N, 9.14%. Found: C, 78.60; H, 7.04; N, 9.02%.

Compound (4c). Yield 92%, Viscous liquid; IR (Neat) υ_{max}: 2926 (Aromatic CH stretching), 1676 (CO δ lactum) cm^{-1}; UV (EtOH) λ_{max} (log ε): 211 (3.85), 253 (3.57), 312 (3.37) nm; ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.15 (t, J = 7.5 Hz, 3H, $ArCH_2CH_3$), 1.27 (t, J = 7.1 Hz, 3H, NCH_2CH_3), 2.52 (q, J = 7.5 Hz, 2H, $ArCH_2CH_3$), 2.71 (s, 3H, NCH_3), 2.82 (d, J = 16 Hz, 1H, COCH), 2.90 (d, J = 16 Hz, 1H, COCH), 3.17 (d, J = 8.8 Hz, 1H, NCH), 3.33 (d, J = 8.8 Hz, 1H, NCH), 3.99 (q, J = 7.1 Hz, 2H, NCH_2CH_3), 6.52–7.29 (m, 7H, ArH); MS (*m*/*z*): 343 (M^+ + 23, 14%), 321 (M^+ + 1, 84%), 317 (100%), 289 (38%), 279 (27%). *Anal*. Calcd for $C_{21}H_{24}N_2O$: C, 78.71; H, 7.54; N, 8.74%. Found: C, 78.48; H, 7.69; N, 8.90%.

Compound (4d). Yield 95%, White solid, mp 120–122°C; IR (KBr) υ_{max}: 2952 (Aromatic CH stretching), 1676 (CO δ lactum) cm^{-1}; UV (EtOH) λ_{max} (log ε): 211 (4.72), 251 (4.19), 305 (3.40) nm; ^1H NMR (400 MHz, $CDCl_3$): δ_H 2.74 (s, 3H, CH_2NCH_3), 2.85 (d, J = 16 Hz, 1H, COCH), 2.90 (d, J = 16 Hz, 1H, COCH), 3.21 (d, J = 8.8 Hz, 1H, NCH), 3.40 (d, J = 8.8 Hz, 1H, NCH), 3.42 (s, 3H, $CONCH_3$), 6.58–7.30 (m, 8H, ArH); MS (*m*/*z*): 301 (M^+ + 23, 20%), 279 (M^+ + 1, 100%), 375 (25%), 237 (17%). *Anal*. Calcd for $C_{18}H_{18}N_2O$: C, 77.66; H, 6.51; N, 10.06%. Found: C, 77.90; H, 6.35; N, 9.86%.

Compound (4e). Yield 92%, White solid, mp 99–101°C; IR (KBr) υ_{max}: 2988 (Aromatic CH stretching), 1676 (CO δ lactum) cm^{-1}; UV (EtOH) λ_{max} (log ε): 211 (4.51), 253 (4.14), 313 (3.36) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.26 (s, 3H, $ArCH_3$), 2.72 (s, 3H, CH_2NCH_3), 2.86 (d, J = 16 Hz, 1H, COCH), 2.90 (d, J = 16 Hz, 1H, COCH), 3.20 (d, J = 8.8 Hz, 1H, NCH), 3.35 (d, J = 8.8 Hz, 1H, NCH), 3.44 (s, 3H, $CONCH_3$), 6.52–7.28 (m, 7H, ArH); MS (*m*/*z*): 315 (M^+ + 23, 14%), 293 (M^+ + 1, 100%), 289 (21%), 251 (50%). *Anal*. Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.89; N, 9.58%. Found: C, 77.78; H, 7.08; N, 9.43%.

Compound (4f). Yield 90%, Viscous liquid, IR (Neat) υ_{max}: 2917 (Aromatic CH stretching), 1674 (CO δ lactum) cm^{-1}; UV (EtOH) λ_{max} (log ε): 214 (4.32), 254 (4.11), 311 (3.40) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.15 (t, J = 7.5 Hz, 3H, $ArCH_2CH_3$), 2.52 (q, J = 7.5 Hz, 2H, $ArCH_2CH_3$), 2.71 (s, 3H, CH_2NCH_3), 2.85 (d, J = 16 Hz, 1H, COCH), 2.90 (d, J = 16 Hz, 1H, COCH), 3.18 (d, J = 8.8 Hz, 1H, NCH), 3.35 (d, J = 8.8 Hz, 1H, NCH), 3.42 (s, 3H, $CONCH_3$), 6.53–7.30 (m, 7H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 15.41 ($ArCH_2CH_3$), 27.75 ($ArCH_2CH_3$), 28.92 (CH_2NCH_3), 35.49 ($CONCH_3$), 41.54 ($COCH_2$), 46.00 (CH_2C), 67.44 (CH_2NCH_3), 107.41 (ArCH), 114.46 (ArCH), 122.47 (ArCH), 122.67 (ArCH), 126.24 (ArCH), 127.42 (ArCH), 127.51 (ArCH), 131.04 (ArC), 132.14 (ArC), 134.13 (ArC), 139.27 (ArC), 150.72 (ArC), 168.21 (CO); MS (*m*/*z*): 329 (M^+ + 23, 18%), 307 (M^+ + 1, 100%), 303 (50%), 265 (50%). *Anal*. Calcd for $C_{20}H_{22}N_2O$: C, 78.39; H, 7.23; N, 9.14%. Found: C, 78.21; H, 7.45; N, 8.96%.

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