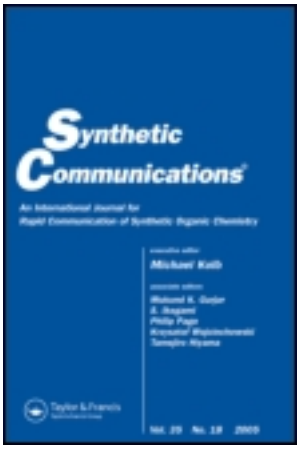

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Regioselective Synthesis of Coumarin and Quinolone-Annulated Spiro Heterocycles via Aryl Radical Cyclization

K. C. Majumdar [a] , P. P. Mukhopadhyay [a] & P. K. Basu [a]

[a] Department of Chemistry, University of Kalyani, Kalyani, India

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K. C. Majumdar, P. P. Mukhopadhyay, and P. K. Basu
Department of Chemistry, University of Kalyani, Kalyani, India

Abstract: 3-(2′-Bromobenzyloxy)quinolin-2-ones and 3-(2′-bromobenzyloxy)benzopyran-7-ones undergo aryl radical cyclization in the presence of $^{n}Bu_3SnCl$-$Na(CN)BH_3$-AIBN to give spiro-quinolone and coumarin derivatives.

Keywords: 5-*Exo-trig*, organotin reagent, radical cyclization, regioselection, spiro heterocycles

INTRODUCTION

Aryl radical cyclization reactions have become an important tool in the development of modern carbo- and heterocyclic chemistry[1] and the synthesis of polycyclic natural products. In particular, the intramolecular addition of aryl radicals to double bonds is well documented in literature[2] and the addition of aryl radicals to cyclic rings to form spiro heterocycles followed by reduction has also been reported.[3] In contrast to carbocycles, there are relatively few reports dealing with the intramolecular addition of aryl radicals to heterocyclic rings. Several examples, by Da Mata et al.,[4] Shankaran et al.,[5] and Harrowven,[6] involve the addition of aryl radicals onto quinoline, thiophene, and pyridine derivatives. One reported example of an indony[7] radical was offered by Sundberg[7c] in the synthesis of iboga alkaloids. Furo[3,2-*c*]quinolin-4(5*H*)-one and 2*H*-pyrano[3,2-*c*]quinolin-5(6*H*)-one

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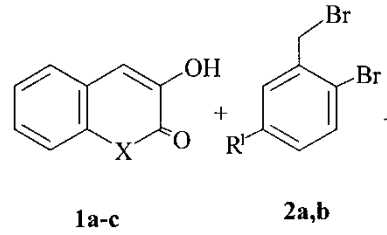
Address correspondence to K. C. Majumdar, Department of Chemistry, University of Kalyani, Kalyani 741235, W. B., India. Tel.: +91-33-2582-7521; Fax: +91-33-25828282; E-mail: kcm@klyuniv.ernet.in

derivatives are abundantly distributed in nature[8] and a number of syntheses[9] of these heterocycles, including those from our own work,[10] have been reported. Coumarins and quinolones fused with other heterocycles are known to have interesting biological and photodynamic properties,[11] that in turn, have encouraged research with regard to procedures for the preparation of families of these compounds. Thus, a number of methodologies have been reported[12] for the synthesis of various 3,4-fused furo- and pyranocoumarins, as some members belongs to these two families have shown[13] useful levels of biological activities such as antihelminthic, hypnotic, insecticidal, and antifungal activities; anticoagulant effects on blood; diuretic properties; and also their occurrence in nature.[14] As not much work has been published on the generation of radicals in heteroatomic systems, we became interested in undertaking, the synthesis of various heterocycles incorporating 3-hydroxyquinolone and 3-hydroxycoumarin moieties by aryl radical cyclization.

RESULTS AND DISCUSSION

3-Hydroxyquinolin-2(1*H*)-ones **1a** and 2-bromobenzyl bromide **2** in refluxing acetone in the presence of anhydrous potassium carbonate afforded 3-(2′-bromobenzyloxy)quinolin-2-ones **3a** (Scheme 1). Similar results were obtained when the other 3-hydroxy compounds (**1b,c**) and different 2-bromobenzyl bromides (**2a,b**) are subjected to same reaction conditions to produce the radical precursors **3b–f**.



1a-c **2a,b** **3a-f**

1. a) X = -NC_2H_5
   b) X = -NCH_3
   c) X = -O-

2. a) R^1 = H
   b) R^1 = -OCH_3

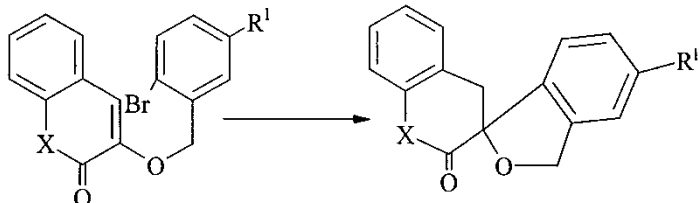
3.	X	R^1	Yield(%)
a	NC_2H_5	H	90
b	NC_2H_5	OCH_3	88
c	NCH_3	H	80
d	NCH_3	OCH_3	85
e	-O-	H	80
f	-O-	OCH_3	84

Scheme 1. Reagents and conditions: acetone, K_2CO_3, reflux, 6–8 h.

Compounds **3a–f** were characterized from their elemental analyses and spectroscopic data. The substrate **3a** was then refluxed in dry degassed benzene under a nitrogen atmosphere with tri-*n*-butyltin chloride and sodium cyanoborohydride in the presence of azobisisobutyronitrile (AIBN) for 4 h to give the cyclic product **4a** (Scheme 2).

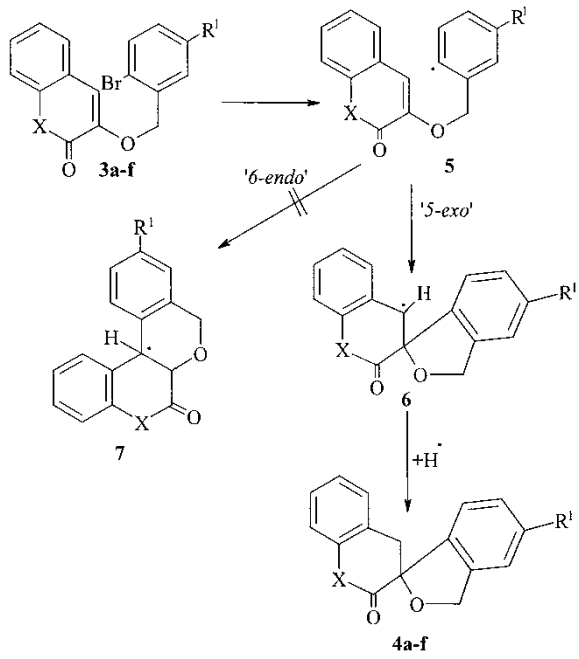
The ^{13}C NMR spectrum supports the proposed structure. The ^{13}C NMR chemical shift as well as the multiplicity of compound **4a** was established by distortionless enhancement by polarization transfer (DEPT) experiment. DEPT shows twelve protonated carbons: one CH_3, three CH_2, and eight CH. To test the generality of the reaction, similar treatment of compounds **3b–f** with $^{n}Bu_3SnCl$ and $Na(CN)BH_3$ in the presence of AIBN afforded the corresponding cyclized products **4b–f** in 80–85% yield.

The mechanism for the radical transformation is outlined in Scheme 3. The regioselectively exclusive formation of spiroheterocyclic ring in products **4a–f** from the starting material **3a–f** may be explained by the generation of aryl radical **5**. Subsequent 5-*exo* cyclization may give spiroheterocyclic radical **6**, which then readily abstracts the hydrogen atom from the in situ formed $^{n}Bu_3SnH$ to produce spiroheterocycles **4a–f**. At this instance, the exclusive formation of five-membered heterocyclic compounds **4a–f** from the substrates **3a–f** suggests that the benzylic radicals **6a–f** generated by 5-*exo-trig* ring closure of radicals **5** might be more stable than the radical **7**, generated from 6-*endo-trig* ring closure. Inspection of the molecular models indicates that the radical intermediate **6** should be much more stabilized because of the excellent overlapping of the p-orbital of the radical center with the neighboring aromatic π-system.



	X	R^1	Yield(%)
4.a	NC_2H_5	H	80
b	NC_2H_5	OCH_3	82
c	NCH_3	H	84
d	NCH_3	OCH_3	80
e	-O-	H	85
f	-O-	OCH_3	84

Scheme 2. Reagents and conditions: $^{n}Bu_3SnCl$, $Na(CN)BH_3$, AIBN, benzene, reflux, 4–5 h, N_2 atms.



Scheme 3.

In conclusion, we can say that the exclusive formation of 5-membered spiro heterocyclic furan ring in excellent yield occurs because of two driving forces: first, the stabilized radical intermediate and second, the stereoelectronically favored 5-*exo* pathway. This gives a simple straightforward synthesis for spiro heterocyclic compounds. The methodology described here is mild and is attractive because of its simplicity. Thus, we have demonstrated that the combined alkylation and radical cyclization is a viable strategy for the synthesis of some potentially bioactive furanopyran-annulated coumarins and quinolones.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer (ν_{max} in cm^{-1}) using samples as neat liquids, solid samples were recorded in KBr disks, and UV absorption spectra were, recorded in EtOH on a Shimadzu UV-2401PC spectrophotometer (λ_{max} in nm). ^1H NMR (300 MHz, 500 MHz) and ^{13}C NMR (125.7 MHz) spectra were recorded on a Bruker DPX-300 and Bruker DRX-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 analyser and on a JEOL JMS600 instrument respectively. ^{1}H NMR and ^{13}C NMR spectra were recorded at the Indian Institute of Chemical Biology, Kolkata, India, and Bose Institute, Kolkata, India. 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 3-(2′-Bromobenzyloxy) quinolin-2-ones (3a–d) or 3-(2′-Bromobenzyloxy)benzopyran-7-ones (3e–f)

3-hydroxy compounds (**1**) (4 mmol) and 2-bromobenzyl bromide (**2**) (1.0 g, 4 mmol) were refluxed in acetone (100 mL) in the presence of anhydrous potassium carbonate (4 g) for 8 h. The reaction mixture was then cooled and filtered, and the solvent was removed. The residual mass was extracted with CH_2Cl_2 (3×50 mL) and the extract was washed with 10% Na_2CO_3 solution to remove unreacted 3-hydroxycompound, then with brine (3×50 mL), and dried (Na_2SO_4). The residual mass after removal of the solvent (CH_2Cl_2) was subjected to column chromatography over silica gel using petroleum ether–ethyl acetate (19 : 1) as eluent to give compounds **3**, which were then recrystallized from chloroform–petroleum ether.

Compound 3a: Yield: 90%; white solid; mp: 140°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.37$ (t, 3H, $J = 7$ Hz, C**H**$_3$), 4.40 (q, 2H, $J = 7$ Hz, *N*C**H**$_2$), 5.25 (s, 2H, OC**H**$_2$), 6.93 (s, 1H, =C**H**), 7.16 (m, 2H, Ar**H**), 7.31 (m, 2H, Ar**H**), 7.41 (m, 2H, Ar**H**), 7.57 (m, 1H, Ar**H**), 7.67–7.70 (m, 1H, Ar**H**) ppm; IR (KBr): $\nu = 3050$, 1703, 1644, 1461 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 331$ ($\log\varepsilon = 3.47$), 286 ($\log\varepsilon = 3.46$), 276 ($\log\varepsilon = 3.49$), 222 ($\log\varepsilon = 4.28$) nm; MS: $m/z = 357$, 359 (M^+); Anal. calcd. for $C_{18}H_{16}NO_2Br$: C, 60.35; H, 4.50; N, 3.91; found: C, 60.24; H, 4.39; N, 4.02.

Compound 3b: Yield: 88%; white solid; mp: 120°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.36$ (t, 3H, $J = 7$ Hz, C**H**$_3$), 3.76 (s, 3H, *N*C**H**$_3$), 4.39 (q, 2H, $J = 7$ Hz, *N*C**H**$_2$), 5.15 (s, 2H, OC**H**$_2$), 6.71 (m, 2H, Ar**H**), 6.95 (s, 1H, =C**H**), 7.17 (m, 1H, Ar**H**), 7.22 (m, 1H, Ar**H**), 7.30 (m, 1H, Ar**H**), 7.42 (m, 2H, Ar**H**) ppm; IR (KBr): $\nu = 3045$, 1702, 1640, 1446 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 332$ ($\log\varepsilon = 3.39$), 286 ($\log\varepsilon = 3.49$), 277 ($\log\varepsilon = 3.44$), 223 ($\log\varepsilon = 4.24$) nm; MS: $m/z = 387$, 389 (M^+); Anal. calcd. for $C_{19}H_{18}NO_3Br$: C, 58.78; H, 4.67; N, 3.61; found: C, 58.84; H, 4.58; N, 3.52.

Compound 3c: Yield: 80%; white solid; m.p. 148°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 3.80$ (s, 3H, *N*C**H**$_3$), 5.27 (s, 2H, OC**H**$_2$), 6.92 (s, 1H, =C**H**), 7.16 (m, 2H, Ar**H**), 7.31 (m, 2H, Ar**H**), 7.42 (m, 2H, Ar**H**), 7.57 (m, 1H, Ar**H**), 7.63 (m, 1H, Ar**H**) ppm; IR (KBr): $\nu = 3050$, 1700, 1620, 1440 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 332$ ($\log\varepsilon = 3.59$), 286 ($\log\varepsilon = 3.55$),

276 ($\log\varepsilon = 3.58$), 222 ($\log\varepsilon = 4.4$) nm; MS: $m/z = 343$, 345 (M^+); Anal. calcd. for $C_{17}H_{14}NO_2Br$: C, 59.32; H, 4.09; N, 4.07; found: C, 59.49; H, 4.20; N, 3.98.

Compound 3d: Yield: 85%; white solid; mp: 124°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 3.77$ (s, 3H, NCH_3), 3.80 (s, 3H, OCH_3), 5.24 (s, 2H, OCH_2), 6.73 (m, 1H, ArH), 6.91 (s, 1H, =CH), 7.19–7.24 (m, 2H, ArH), 7.32–7.34 (m, 1H, ArH), 7.42 (m, 3H, ArH) ppm; IR (KBr): $\nu = 3052$, 1710, 1620, 1445 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 332$ ($\log\varepsilon = 3.36$), 286 ($\log\varepsilon = 3.45$), 277 ($\log\varepsilon = 3.45$), 222 ($\log\varepsilon = 4.2$) nm; MS: $m/z = 373$, 375 (M^+); Anal. calcd. for $C_{18}H_{16}NO_3Br$: C, 57.77; H, 4.31; N, 3.74; found: C, 57.84; H, 4.20; N, 3.80.

Compound 3e: Yield: 80%; white solid; mp: 110°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 5.19$ (s, 2H, OCH_2), 6.90 (s, 1H, =CH), 7.28 (m, 2H, ArH), 7.35 (m, 3H, ArH), 7.41 (m, 2H, ArH), 7.60 (m, 1H, ArH) ppm; IR (KBr): $\nu = 3030$, 1720, 1620, 1350 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 293$ ($\log\varepsilon = 3.65$), 228 ($\log\varepsilon = 3.87$), 209 ($\log\varepsilon = 4.16$) nm; MS: $m/z = 330$, 332 (M^+); Anal. calcd. for $C_{16}H_{11}O_3Br$: C, 58.03; H, 3.35. Found: C, 58.09; H, 3.26.

Compound 3f: Yield: 85%; white solid; mp: 122°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\lambda_H = 3.79$ (s, 3H, OCH_3), 5.20 (s, 2H, OCH_2), 6.75–6.79 (dd, $J = 9$, 3 Hz, 1H, ArH), 6.89 (s, 1H, =CH), 7.15 (d, $J = 3$ Hz, 1H, ArH), 7.22 (m, 2H, ArH), 7.36 (m, 2H, ArH), 7.45 (d, $J = 9$ Hz, 1H, ArH) ppm; IR (KBr): $\nu = 3030$, 1724, 1620, 1380 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 290$ ($\log\varepsilon = 3.91$), 227 ($\log\varepsilon = 4.00$), 206 ($\log\varepsilon = 4.36$) nm; MS: $m/z = 360$, 362 (M^+); Anal. calcd. for $C_{17}H_{13}O_4Br$: C, 56.53; H, 3.63. Found: C, 56.36; H, 3.79.

General Procedure for the Preparation of Compounds 4a–f

A suspension of the compounds **3** (0.08 mmol), $^nBu_3SnCl$ (0.08 mL, 0.296 mmol), $Na(CN)BH_3$ (250 mg, 3.98 mmol), and AIBN (15 mg) in dry degassed benzene (7 mL) were refluxed for 4–5 h under N_2 atmosphere. Solvent was evaporated under reduced pressure and the residue was taken in H_2O (10 mL) and was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extract was washed with 1% aqueous NH_4OH (2 × 10 mL), brine, and dried (Na_2SO_4). The residual mass after removal of the solvent was magnetically stirred with saturated solution of potassium fluoride for 24 h. It was then extracted with CH_2Cl_2 (3 × 10 mL), washed several times with water, and dried (Na_2SO_4). The residual mass after removal of the solvent (CH_2Cl_2) was subjected to column chromatography using petroleum ether–ethyl acetate (4 : 1) as eluent to give cyclized products **4**, which were then recrystallized from chloroform–petroleum ether.

Compound 4a: Yield: 80%; white solid; mp: 112°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.20$ (t, $J = 7$ Hz, 3H), 3.18 (d, $J = 15.5$ Hz, 1H), 3.49 (d, $J = 15.5$ Hz, 1H), 3.92 (q, $J = 7$ Hz, 2H), 5.21 (d, $J = 12$ Hz, 1H), 5.42 (d, $J = 12$ Hz, 1H), 6.58 (m, 1H), 7.11 (m, 3H), 7.27–7.37 (m, 4H) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta_C = 12.87$ (**C**H_3), 38.20 (-*N***C**H_2), 39:08 (-**C**H_2), 73.98 (O**C**H_2), 85.92 (CO**C**), 114.82, 114.89, 121.61, 121.70, 123.58, 127.65, 128.53, 129.07, 129.88, 139.15, 140.28, 140.68 (Ar**C**), 170.09 (-**C**O) ppm; IR (KBr): $\nu = 3050$, 1703, 1608, 1444 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 334$ (log$\varepsilon = 3.62$), 278 (log$\varepsilon = 3.58$), 268 (log$\varepsilon = 3.81$), 210 (log$\varepsilon = 4.34$) nm; MS: $m/z = 279$ (M^+); Anal. calcd. for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.58; H, 5.89; N, 4.88.

Compound 4b: Yield: 82%; white solid; mp: 82°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.20$ (t, $J = 7$ Hz, 3H), 3.13 (d, $J = 15.5$ Hz, 1H), 3.48 (d, $J = 15.5$ Hz, 1H), 3.84 (s, 3H), 3.95 (q, $J = 7$ Hz, 2H), 5.16 (d, $J = 12$ Hz, 1H), 5.38 (d, $J = 12$ Hz, 1H), 6.41 (m, 1H), 6.59 (m, 3H), 7.27 (m, 3H) ppm; IR (KBr): $\nu = 3052$, 1709, 1610, 1450 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 331$ (log$\varepsilon = 3.58$), 275 (log$\varepsilon = 3.77$), 269 (log$\varepsilon = 3.76$), 222 (log$\varepsilon = 4.44$) nm; MS: $m/z = 309$ (M^+); Anal. calcd. for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.65; H, 6.31; N, 4.62.

Compound 4c: Yield: 84%; white solid; mp: 118°C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta_H = 3.24$ (d, $J = 15.5$ Hz, 1H), 3.40 (s, 3H), 3.50 (d, $J = 15.5$ Hz, 1H), 5.21 (d, $J = 12$ Hz, 1H), 5.42 (d, $J = 12$ Hz, 1H), 6.58 (m, 2H), 7.09 (m, 3H), 7.28 (m, 3H) ppm; IR (KBr): $\nu = 3052$, 1704, 1610, 1440 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 334$ (log$\varepsilon = 3.65$), 283 (log$\varepsilon = 3.67$), 265 (log$\varepsilon = 3.82$), 224 (log$\varepsilon = 4.30$) nm; MS: $m/z = 265$ (M^+); Anal. calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.69; N, 5.28. Found: C, 76.71; H, 5.91; N, 5.42.

Compound 4d: Yield: 80%; white solid; mp: 106°C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta_H = 3.21$ (d, $J = 15.5$ Hz, 1H), 3.26 (s, 3H), 3.48 (d, $J = 15.5$ Hz, 1H), 3.76 (s, 3H), 5.16 (d, $J = 12$ Hz, 1H), 5.39 (d, $J = 12$ Hz, 1H), 6.55 (m, 2H), 7.00 (m, 3H), 7.27 (m, 2H) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta_C = 30.79$ (*N***C**H_3), 39.04 (**C**H_2), 55.88 (O**C**H_3), 73.85 (O**C**H_2), 86.92 (CO**C**), 109.19, 113.55, 115.62, 123.52, 123.93, 125.91, 128.80, 129.46, 130.58, 135.39, 139.53, 159.14 (Ar**C**), 167.69 (-**C**O) ppm; IR (KBr): $\nu = 3045$, 1700, 1615, 1435 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 335$ (log$\varepsilon = 3.65$), 279 (log$\varepsilon = 3.54$), 266 (log$\varepsilon = 3.87$), 228 (log$\varepsilon = 4.30$) nm; MS: $m/z = 295$ (M^+); Anal. calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.45; H, 5.51; N, 4.62.

Compound 4e: Yield: 85%; white solid; mp: 142°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 2.90$ (d, $J = 15$ Hz, 1H), 3.41 (d, $J = 15$ Hz, 1H), 5.13 (d, $J = 12$ Hz, 1H), 5.20 (d, $J = 12$ Hz, 1H), 6.93 (m, 1H), 7.08 (m, 2H), 7.31 (m, 3H) 7.39 (m, 2H) ppm; IR (KBr): $\nu = 3035$, 1722, 1615, 1380 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 279$ (log$\varepsilon = 3.34$), 271 (log$\varepsilon = 3.40$),

265 ($\log\varepsilon = 3.32$), 205 ($\log\varepsilon = 4.27$) nm; MS: $m/z = 252$ (M^+); Anal. calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.05; H, 4.89.

Compound 4f: Yield: 84%; white solid; mp: 149°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_H = 3.02$ (d, $J = 15$ Hz, 1H), 3.31 (d, $J = 15$ Hz, 1H), 3.77 (s, 3H), 5.03 (d, $J = 12$ Hz, 1H), 5.09 (d, $J = 12$ Hz, 1H), 6.65 (m, 2H), 6.80 (m, 3H), 7.34 (m, 2H) ppm; IR (KBr): $\nu = 3030$, 1730, 1622, 1375 cm^{-1}; UV/Vis (EtOH): $\lambda_{max} = 279$ ($\log\varepsilon = 3.38$), 274 ($\log\varepsilon = 3.37$), 268 ($\log\varepsilon = 3.32$), 204 ($\log\varepsilon = 4.23$) nm; MS: $m/z = 282$ (M^+); Anal. calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 4.99. Found: C, 72.46; H, 4.84.

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