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A novel tandem reaction of 3-substituted coumarins with two equivalents of dimethylsulfoxonium ylide to 2-substituted cyclopenta[*b*]benzofuran-3-ol derivatives

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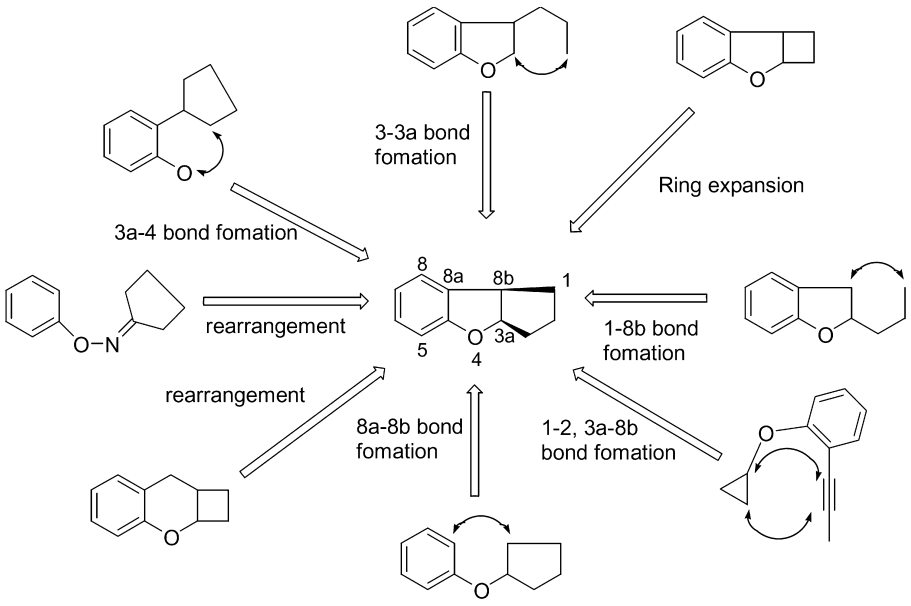
Abstract—When the coumarins (**4**) having an electron-withdrawing group at the 3 position were treated with 2.4 equiv. of dimethylsulfoxonium methylide at room temperature in DMF or DMSO, novel tricyclic 2-substituted cyclopenta[*b*]benzofuran-3-ols (**5**) were obtained in moderate to good yields. The intermediates, 1a-substituted benzo[*b*]cyclopropa[*d*]pyran-2(1a*H*)-ones (**3**), of this tandem reaction were isolated and derived to the corresponding 2-substituted cyclopenta[*b*]benzofuran-3-ols (**5**) by treatment with 1.1 equiv. of dimethylsulfoxonium methylide.

The cyclopenta[*b*]benzofuran system is a basic skeleton appearing in natural products such as aplysins[1] and rocaglamides,[2] etc. and in useful architectures such as benzoprostacyclins[3] which are analogues of biologically active prostaglandins. Many methods for construction of the skeleton by 1–8b bond formation,[4] 3–3a bond formation,[5] 3a–4 bond formation,[6] 8a–8b bond formation,[7] 1–2;3a–8b bonds formation,[8] ring expansion,[9] and rearrangements[10] have been developed up to today (Scheme 1).

We have investigated cyclopropane ring cleavage of 2-substituted cyclopropane-1,1-dicarboxylates (**1**), which



Scheme 1.

Keywords: benzofurans; coumarins; ylides; cyclopropanation.
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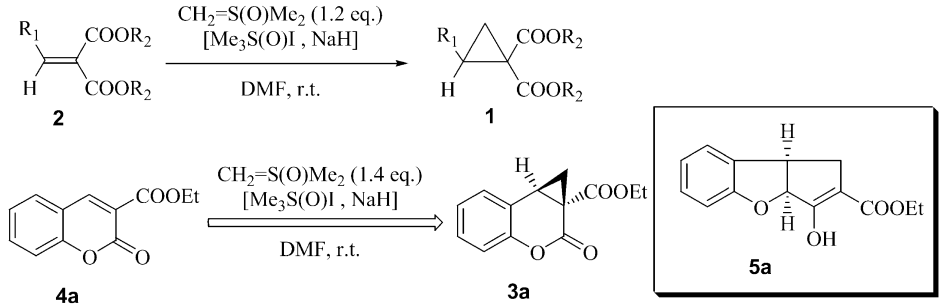


Scheme 2.

were prepared from appropriate 3-substituted 1-alkoxycarbonylacrylic esters (**2**) by treatment with dimethylsulfoxonium methylide (CH_2=S(O)Me_2).[11] During this investigation, to prepare ethyl 2-oxobenzo[*b*]cyclopropa[*d*]pyran-1a(2*H*)-carboxylate (**3a**), 3-ethoxycarbonylcoumarin (**4a**)[12] was treated with 1.4 equiv. of CH_2=S(O)Me_2 in the usual manner.[11] The isolated product, however, was not the desired cyclopropane compound (**3a**) but an unexpected novel tricyclic compound (**5a**) (Scheme 2). In the previous communication, we described the one-pot reaction of the 2-substituted coumarin derivatives (**4**) to the corresponding 2-substituted cyclopenta[*b*]benzofuran-2-ol derivatives (**5**).[13] This paper deals with the details of this novel transformation of **4** and 1a-substituted benzo[*b*]-cyclopropa[*d*]pyran-2(1a*H*)-one derivatives (**3**) to **5**. Consideration of the reaction route to **5** from **4** is also reported.

The crystalline product (**5a**), mp 86.5–87.5°C, was found to have a molecular formula $C_{14}H_{14}O_4$ on the basis of elementary analysis and high-resolution mass spectrometry (M^+; *m/z* 246.0950). The molecular weight of **5a** increases by 14 and 28 comparing with those of the desired cyclopropane compound (**3a**) and the starting material (**4a**), respectively. These increases would be attributable to one CH_2 and two CH_2, which would be incorporated from CH_2=S(O)Me_2. This means that 2 equiv. of CH_2=S(O)Me_2 would be theoretically necessary for the present transformation of **4a** to **5a**. Thus, the coumarin (**4a**) was again treated with 2.4 equiv. of CH_2=S(O)Me_2 to increase, as expected, the yield of **5a** to 64% (run 2 in Table 1). The structure of **5a** was determined as ethyl (3a*R**,8b*S**)-3a,8b-dihydro-3-hydroxy-1*H*-cyclopropa[*b*]benzofuran-2-carboxylate on the basis of its spectral and X-ray crystallographic analysis.[13]

Other solvents for the present reaction were tried, and the results are shown in Table 1. The reaction to **5a** took place in aprotic polar solvents such as DMF, DMSO, and 1,3-dimethyl-2-imidazolidinone (DMI) in 58–68% yields (runs 2–4), but no or low yields (0–26%) were afforded in nonpolar solvents such as THF, chloroform, dichloromethane, and toluene (runs 5–8).

In order to examine the usefulness of this reaction, several coumarin derivatives (**4b**–**k**) were prepared and subjected to the reaction conditions of runs 2 and 3 in Table 1. These results are summarized in Table 2. As shown in Table 2, the coumarins (**4**) bearing an electron-withdrawing group such as ester, ketone, nitrile, and sulfone were transformed to the corresponding cyclopenta[*b*]benzofuranes (**5**) in 26–89% yields. However, the coumarin derivatives which have hydrogen, trifluoromethyl, nitro, sulphenyl, and sulfinyl groups on the 3-position were not reacted at all. The nature of the substituent at the 3-position of **4** and the 1a-position of **3** would influence very much on the ring-opening ability of the cyclopropane portion as well as on the approach of CH_2=S(O)Me_2 to the carbonyl group at the 2-position.

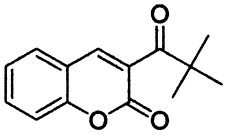
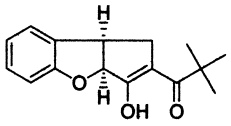
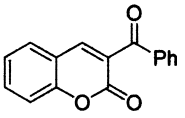
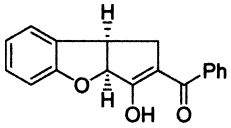
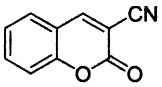
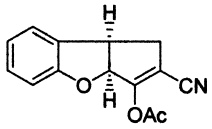
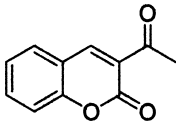
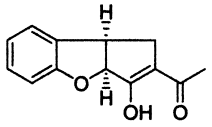
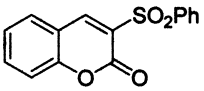
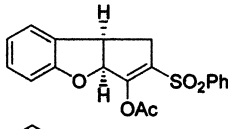
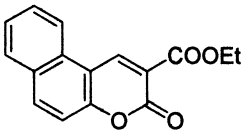
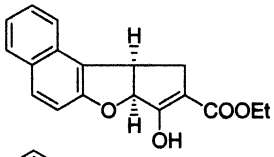
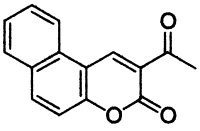
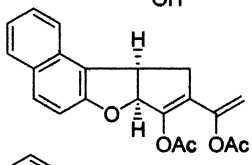
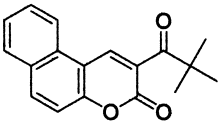
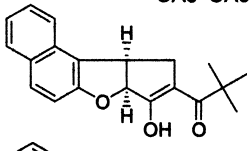
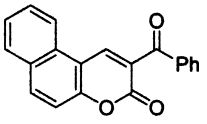
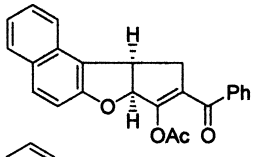
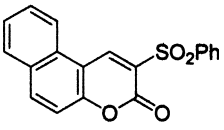
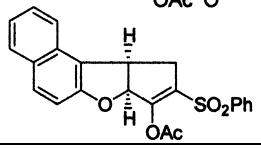
Next, our attention was focused on isolation of a possible intermediate in this tandem reaction. As shown above, 2 equiv. of CH_2=S(O)Me_2 are needed theoretically in this reaction. We assumed that the first 1 equiv. of CH_2=S(O)Me_2 would be used for cyclopropanation of the coumarin derivatives (**4**), and the second 1 equiv. of CH_2=S(O)Me_2 would be used for transformation of the cyclopropane derivatives (**3**) to the cyclopenta[*b*]benzofurane derivatives (**5**) as shown in Scheme 3. In order to clarify this assumption, we planned the isolation of the cyclopropane intermediates (**3**) and their conversion to **5** (Scheme 3). To isolate the cyclopropane intermediate (**3**), 3-ethoxycarbonylcoumarin (**4a**: WG=COOEt) was treated

Table 1. Reaction of **4a** with CH_2=S(O)Me_2 in various solvents

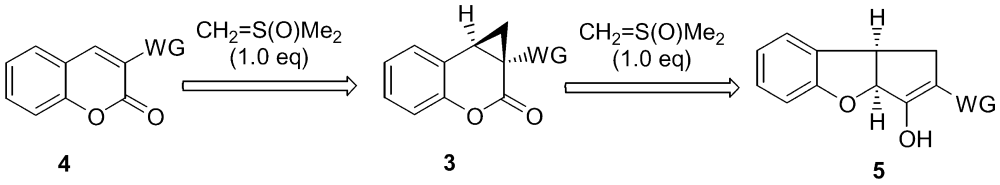
Run	Solvent	CH_2=S(O)Me_2 (equiv.)	Time (h)	Temperature (°C)	Isolated yield of **5a** (%)
1	DMF	1.4	2	rt	47
2	DMF	2.4	2	rt	64
3	DMSO	2.4	2	rt	58
4	DMI	2.4	24	rt	68
5	THF	2.4	72	rt	18[a]
6	$CHCl_3$	2.4	50	rt	0[b]
7	CH_2Cl_2	2.4	98	rt	26[a]
8	Toluene	2.4	100	rt	0[b]

[a] Small amount of **5a** was obtained together with many unidentified products.
[b] A complex mixture was obtained.

Table 2. Conversion of coumarins (**4**) to 1*H*-cyclopenta[*b*]benzofuran derivatives (**5**)

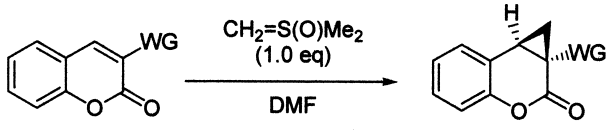
Run		Starting material		Product	Isolated yield (%)[a]
1	**4b**		**5b**		54 (DMF)
2	**4c**		**5c**		54 (DMF), 64 (DMSO)
3	**4d**		**5d**		52 (DMF)[b]
4	**4e**		**5e**		31 (DMF), 26 (DMSO)
5	**4f**		**5f**		62 (DMF)[b], 45 (DMSO)[b]
6	**4g**		**5g**		61 (DMF), 59 (DMSO)
7	**4h**		**5h**		58 (DMF)[b]
8	**4i**		**5i**		89 (DMF)
9	**4j**		**5j**		74 (DMF)[b]
10	**4k**		**5k**		67 (DMF)[b]

[a] Reaction solvent is shown in parentheses.
[b] The product (**5**) was isolated after acetylation because of the easy separation.



Scheme 3.

Table 3. Cyclopropanation of 2-substituted coumarins (**4**)



4 **3**

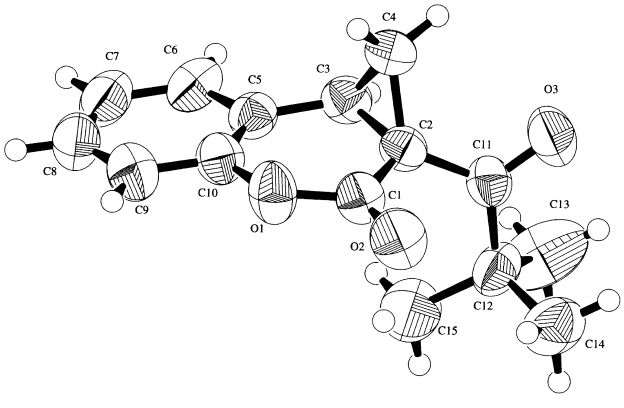
Run	Starting material (**4**)	Temperature (°C)	Reaction time (h)	Product	Isolated yield (%)[a]
1	**4a** (WG=COOEt)	0	1	**3a** (WG=COOEt)	28 (45)
2	**4b** (WG=CO*t*-Bu)	0	2	**3b** (WG=CO *t*-Bu)	62
3	**4c** (WG=COPh)	−40	2	**3c** (WG=COPh)	50 (58)
4	**4d** (WG=CN)	0	1	**3d** (WG=CN)	17 (28)
5	**4e** (WG=$COCH_3$)	−40	3	**3e** (WG=$COCH_3$)	43 (48)

[a] Yield in parentheses was calculated on the basis of recovery of the starting material (**4**).

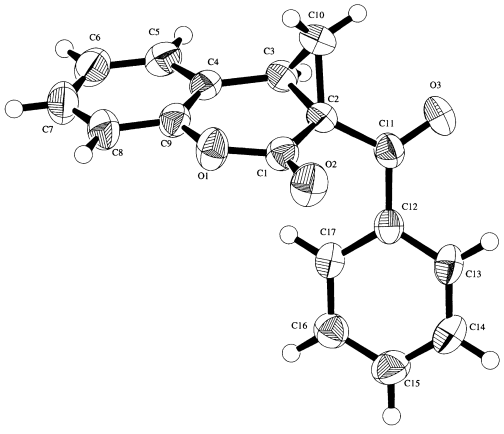
with 1 equiv. of CH_2=S(O)Me_2 in DMF at room temperature,[11] but only **5a** (WG=COOEt) was obtained as a product together with the starting material (**4a**). The desired **3a** (WG=COOEt) would be reactive under these conditions; therefore, the produced **3a** would immediately react with another CH_2=S(O)Me_2 to afford **5a**. Next, we again treated **4a** with 1 equiv. of CH_2=S(O)Me_2 in DMF at 0°C, and the cyclopropane intermediate (**3a**) could be obtained in only 28% yield together with the recovered **4a** (17%). The structure of **3a** was confirmed on the basis of its spectral data. The molecular formula of the cyclopropane compound (**3a**) was found to correspond to $C_{13}H_{12}O_4$ by high-resolution mass spectrometry (M^+; *m*/*z* 232.0728). The IR spectrum showed ester and lactone band absorptions at 1756 and 1722 cm^{-1}. The ^1H NMR spectrum showed the existence of an ethyl ester group (1.32 ppm (t, 3H) and 4.28 ppm (q, 2H)), three protons on the cyclopropane ring (1.37 ppm (dd, 1H), 2.47 ppm (dd, 1H), and 2.91 ppm (dd, 1H)), and four protons on the phenyl group (7.03 ppm (dd, 1H), 7.14 ppm (dt, 1H), 7.26 (ddd, 1H), and 7.37 ppm (dd, 1H)).

Several 3-substituted coumarins (**4b**–**e**) could be also derived to the corresponding cyclopropane derivatives (**3b**–**e**) in low to moderate yields as shown in Table 3. The structures of **3b**–**e** were determined on the basis of analogy of their spectral data with **3a**, and especially, those of **3b** and **3c** were also established by X-ray crystallographic analyses (Fig. 1).

These cyclopropane derivatives (**3a**–**e**) were treated with 1.1 equiv. of CH_2=S(O)Me_2 in DMF at room temperature, and the corresponding cyclopenta[*b*]benzofuran derivatives (**5a**–**e**) were obtained in low to moderate yields (Scheme 4). The physical and spectral data of the obtained

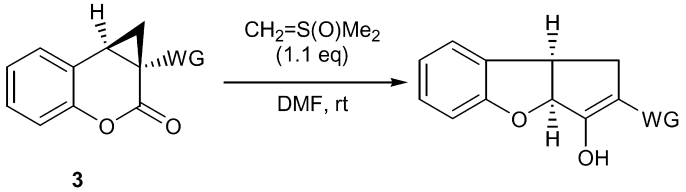


ORTEP drawing of **3b**



ORTEP drawing of **3c**

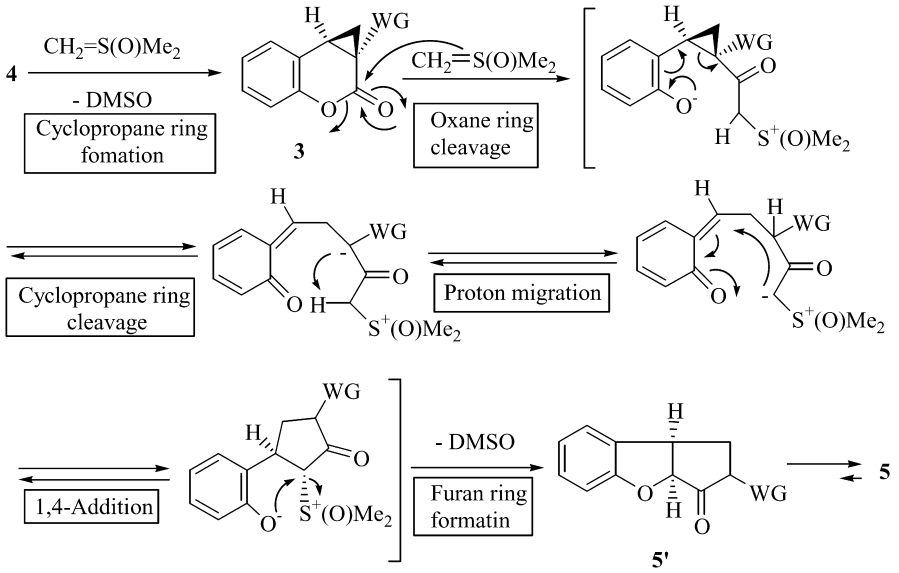
Figure 1.



3

5a: WG = COOEt, 32%
5b: WG = CO *t*-Bu, 37%
5c: WG = COPh, 68%
5d: WG = CN, 17%
(yield after acetylation)
5e: WG = $COCH_3$, 8%

Scheme 4.



Scheme 5.

products (**5a**–**e**) were consistent with those of the compounds produced in the above-mentioned one-pot manner from the coumarin derivatives (**4**) (Table 2). From these results, it was proved that the cyclopropane compound (**3**) was the important intermediate in the present transformation.

We now assume a plausible reaction mechanism as shown in Scheme 5. The cyclopropane ring was formed by 1 equiv. of CH_2=S(O)Me_2, and the formed cyclopropane compound (**3**) would be unstable at room temperature because of the strained cyclopropane ring activated by two electron-withdrawing groups. One more equivalent of CH_2=S(O)Me_2 attacked the carbonyl carbon on the coumain ring to effect further ring-opening of the cyclopropane ring. After migration of the acidic proton, conjugate addition of the produced sulfur ylide portion to the quinonemethide function produces the cyclopentane ring under elimination of dimethylsulfoxide to afford cyclopenta[*b*]benzofuran derivatives (**5**).

In conclusion, we have found a novel tandem reaction of the coumarin derivatives (**4**) bearing an electron-withdrawing group on the 3-position with 2 equiv. of CH_2=S(O)Me_2 to afford the cyclopenta[*b*]benzofurans (**5**), and proposed a reaction mechanism as shown in Scheme 5.

As an application of the present reaction, we have already communicated the first total synthesis of (±)-linderol A,[14] a tricyclic hexahydrodibenzofuran constituent of *Lindera umbellata* bark, with potent inhibitory activity on melanin biosynthesis of cultured B-16 melanoma cells,[15] and further applications are in progress.

1. Experimental

Melting points were measured with a Yanaco MP micro-melting point apparatus and are uncorrected. NMR spectra were measured on a Varian XL-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz), a JEOL AL-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz) and a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) with tetramethylsilane as an internal standard and chemical shifts are reported in ppm. IR spectra were taken with a Shimadzu IR-435 spectrophotometer. A Shimadzu GCMS-QP 1000 and a JEOL JMS-SX 102A QQ spectrometers for low-resolution EIMS (LR-EIMS) and HR-EIMS were used. A JEOL JMS-SX 102A QQ spectrometer for low-resolution FABMS (LR-FABMS) and HR-FABMS was used. All solvents were removed under reduced pressure in the usual work-up procedure. Silica gel 60 (grade 7734, 60–230 mesh, Merck) for column chromatography and silica gel 60 PF_{254} (Nacalai Tesque Inc.) for preparative TLC (PTLC) were used. The coumarin derivatives (**4**) were prepared by Knoevenagel condensation of salicylaldehyde or 2-hydroxy-1-naphthoaldehyde with the corresponding malonate or an appropriate active methylene compound in the presence of catalytic amounts of piperidine and acetic acid.[12]

1.1. General procedure of 3-substituted coumarin (4) to cyclopenta[*b*]benzofuran (5)

Trimethylsulfoxonium iodide (528 mg, 2.4 mmol) was added in one portion to a suspension of NaH (60% in mineral oil, 96 mg, 2.4 mmol) in DMF (3 ml) or DMSO (3 ml) at room temperature and the whole was stirred for 30 min under an N_2 atmosphere. To the reaction mixture was added dropwise a solution of **4** (1.0 mmol) in DMF (1 ml) or DMSO (1 ml) at room temperature and the whole was stirred for additional 2 h. After acidification with 3% HCl solution under ice-cooling, the mixture was extracted with ether (10 ml×4). The organic layers were washed with water, dried over sodium sulfate, and evaporated. The residue was purified by column chromatography to give the product (**5**). If necessary, acetylation was carried out as follows. A solution of the crude product, acetic anhydride (204 mg, 2.0 mmol), triethylamine (202 mg, 2.0 mmol), and 4-(dimethylamino)pyridine (6.0 mg, 0.05 mmol) in chloroform (3 ml) was stirred at room temperature

for 12 h. After acidification with 3% HCl solution under ice-cooling, the mixture was extracted with ether (10 ml×4). The combined organic layer was washed with water, dried over sodium sulfate, and evaporated. The residue was purified by column chromatography to give the acetylated product.

1.1.1. Ethyl (3a*R,8b*S**)-3a,8b-dihydro-3-hydroxy-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (5a).** Colourless needles (ethanol). Mp 86.5–87.5°C.[13]

1.1.2. (3a*R,8b*S**)-3a,8b-Dihydro-2-pivaloyl-1*H*-cyclopenta[*b*]benzofuran-3-ol (5b).** Colourless needles (*n*-hexane), mp 86.0–88.0°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.17 (s, 9H, $C(CH_3)_3$), 2.98 (td, 1H, *J*=1.3, 13.9 Hz, 1-CH_2), 3.33 (dd, 1H, *J*=8.3, 14.2 Hz, 1-CH_2), 4.04 (t, 1H, *J*=8.3 Hz, 8b-H), 5.51 (d, 1H, *J*=8.9 Hz, 3a-H), 6.86 (d, 1H, *J*=7.9 Hz, Ar-H), 6.91 (dt, 1H, *J*=1.0, 7.6 Hz, Ar-H), 7.14 (d, 1H, *J*=7.9 Hz, Ar-H), 7.20 (t, 1H, *J*=7.3 Hz, Ar-H), 14.28 (s, 1H, OH). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 26.1, 35.6, 40.4, 42.3, 86.4, 107.4, 110.2, 121.3, 124.3, 128.8, 130.0, 158.6, 180.5, 205.3. IR ($CHCl_3$): 1624, 1584, 1570 cm^{-1}. LR-EIMS *m*/*z*: 258 (M^+), 77 (100). HR-EIMS calcd for $C_{16}H_{18}O_3$: 258.1256. Found: 258.1260. Anal. calcd for $C_{16}H_{18}O_3$: C; 74.39, H; 7.02. Found: C; 74.34, H; 7.11.

1.1.3. (3a*R,8b*S**)-2-Benzoyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-3-ol (5c).** Colourless needles (benzene), mp 141.5–143.0°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 3.04 (dd, 1H, *J*=1.3, 14.5 Hz, 1-CH_2), 3.52 (dd, 1H, *J*=8.3, 14.5 Hz, 1-CH_2), 4.17 (t, 1H, *J*=8.3 Hz, 8b-H), 5.48 (d, 1H, *J*=8.9 Hz, 3a-H), 6.85–6.92 (m, 2H, Ar-H), 7.10–7.20 (m, 2H, Ar-H), 7.35–7.56 (m, 3H, Ar-H), 7.76–7.81 (m, 2H, Ar-H), 14.67 (br, 1H, OH). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 34.5, 40.8, 86.3, 107.7, 110.2, 121.4, 124.5, 128.3, 128.5, 128.9, 129.4, 132.2, 135.6, 158.8, 182.8, 191.8. IR ($CHCl_3$): 1620, 1592, 1564, 1507 cm^{-1}. LR-EIMS *m*/*z*: 278 (M^+, 100). HR-EIMS calcd for $C_{18}H_{14}O_3$: 278.0943. Found: 278.0935. Anal. calcd for $C_{18}H_{14}O_3$: C; 77.68, H; 5.07. Found: C; 77.50, H; 4.99.

1.1.4. (3a*R,8b*S**)-3-Acetoxy-2-cyano-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran (5d).** Colourless needles (benzene–*n*-hexane), mp 88.5–89.5°C. ^{1}H NMR(270 MHz, $CDCl_3$) δ: 2.33 (s, 3H, $COCH_3$), 2.73 (td, 1H, *J*=1.7, 15.8 Hz, 1-CH_2), 3.19 (ddd, 1H, *J*=1.0, 7.9, 15.8 Hz, 1-CH_2), 4.19 (br-t, 1H, *J*=8.3 Hz, 8b-H), 6.04 (ddd, 1H, *J*=1.3, 2.3, 8.6 Hz, 3a-H), 6.83 (d, 1H, *J*=7.9 Hz, Ar-H), 6.95 (dt, 1H, *J*=1.0, 7.6 Hz, Ar-H), 7.16–7.22 (m, 2H, Ar-H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 20.7, 36.4, 41.9, 85.7, 100.7, 110.5, 113.2, 121.7, 124.5, 128.8, 129.4, 157.7, 159.8, 166.3. IR ($CHCl_3$): 3004, 2210, 1777, 1658, 1595 cm^{-1}. LR-EIMS *m*/*z*: 241 (M^+), 199 (100). HR-EIMS calcd for $C_{14}H_{11}NO_3$: 241.0739. Found: 241.0724. Anal. calcd for $C_{14}H_{11}NO_3$: C; 69.70, H; 4.60, N; 5.81. Found: C; 69.88, H; 4.66, N; 5.85.

1.1.5. (3a*R,8b*S**)-2-Acetyl-3a,8b-dihydro-1*H*-cyclopenta-[*b*]benzofuran-3-ol (5e).** Colourless prisms (benzene–*n*-hexane), mp 114.0–115.0°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 2.10 (s, 3H, $COCH_3$), 2.74 (dd, 1H, *J*=1.2, 14.2 Hz, 1-CH_2), 3.16 (dd, 1H, *J*=8.3, 14.2 Hz, 1-CH_2), 4.07 (t, 1H, *J*=8.6 Hz, 8b-H), 5.52 (d, 1H, *J*=8.9 Hz, 3a-H), 6.85 (d, 1H, *J*=7.9 Hz, Ar-H), 6.91 (t, 1H, *J*=7.3 Hz, Ar-H), 7.15 (t, 1H, *J*=7.8 Hz, Ar-H), 7.22 (d, 1H, *J*=7.3 Hz, Ar-H), 12.0–13.0 (br, 1H, OH). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 25.9, 33.6, 40.3, 87.0, 109.7, 110.2, 121.3, 124.4, 128.9, 129.8, 158.5, 178.3, 195.8. IR ($CHCl_3$): 1653, 1591 cm^{-1}. LR-EIMS *m*/*z*: 216 (M^+, 100). HR-EIMS calcd for $C_{13}H_{12}O_3$: 216.0786. Found: 216.0796. Anal. calcd for $C_{13}H_{12}O_3$: C; 72.21, H; 5.59. Found: C; 72.35, H; 5.68.

1.1.6. (3a*R,8b*S**)-3-Acetoxy-2-benzenesulfonyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran (5f).** Viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.23 (s, 3H, CH_3), 2.78 (ddd, 1H, *J*=1.7, 2.5, 15.9 Hz, 1-CH_2), 3.14 (ddd, 1H, *J*=1.0, 8.0, 15.9 Hz, 1-CH_2), 4.07 (t, 1H, *J*=8.2 Hz, 8b-H), 5.83 (ddd, 1H, *J*=1.0, 2.5, 8.6 Hz, 3a-H), 6.78 (dd, 1H, *J*=0.4, 8.1 Hz, Ar-H), 6.87 (dt, 1H, *J*=0.9, 7.4 Hz, Ar-H), 7.08–7.16 (m, 2H, Ar-H), 7.45–7.52 (m, 2H, Ar-H), 7.60 (tt, 1H, *J*=1.6, 7.4 Hz), 7.82–7.87 (m, 2H, Ar-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 20.6, 35.9, 40.2, 87.3, 110.3, 121.5, 124.4, 127.9, 128.7, 128.8, 129.08, 129.10, 133.9, 139.3, 151.7, 157.8, 167.2. IR ($CHCl_3$): 1770, 1645, 1592 cm^{-1}. LR-EIMS *m*/*z*: 356 (M^+), 314 (100). HR-EIMS calcd for $C_{19}H_{16}O_5S$: 356.0718. Found: 356.0717.

1.1.7. Ethyl (3a*R,10c*S**)-3a,10c-dihydro-3-hydroxy-1*H*-cyclopenta[*b*]naphtho[1,2-*d*]furan-2-carboxylate (5g).** Colourless needles (AcOEt–*n*-hexane), mp 131.5–134.0°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.24 (t, 3H, *J*=7.3 Hz, CH_2CH_3), 2.90 (td, 1H, *J*=2.0, 14.9 Hz, 1-CH_2), 3.19 (dd, 1H, *J*=8.3, 14.5 Hz, 1-CH_2), 4.19 (q, 2H, *J*=7.3 Hz, CH_2CH_3), 4.42 (dt, 1H, *J*=2.0, 8.6 Hz, 10c-H), 5.82 (dd, 1H, *J*=2.0, 8.9 Hz, 3a-H), 7.15 (d, 1H, *J*=8.6 Hz, Ar-H), 7.31 (t, 1H, *J*=8.3 Hz, Ar-H), 7.49 (dt, 1H, *J*=1.3, 8.6 Hz, Ar-H), 7.65 (d, 1H, *J*=8.9 Hz, Ar-H), 7.70 (d, 1H, *J*=8.9 Hz, Ar-H), 7.82 (d, 1H, *J*=7.9 Hz, Ar-H), 10.1 (s, 1H, OH). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 14.2, 33.3, 39.8, 60.5, 88.4, 103.0, 112.5, 121.1, 122.2, 123.1, 126.9, 129.0, 129.8, 129.9, 130.1, 155.7, 167.8, 169.3. IR ($CHCl_3$): 3500–3000, 1670, 1630, 1598 cm^{-1}. LR-EIMS *m*/*z*: 296 (M^+), 168 (100). HR-EIMS calcd for $C_{18}H_{16}O_4$: 296.1049. Found: 296.1023. Anal. calcd for $C_{18}H_{16}O_4$: C; 72.96, H; 5.44. Found: C; 73.09, H; 5.50.

1.1.8. (3a*R,10c*S**)-3-Acetoxy-2-(1-acetoxyvinyl)-3a,10c-dihydro-1*H*-cyclopenta[*b*]naphtho[1,2-*d*]furan (5h).** Pale yellow plates (benzene–*n*-hexane), mp 175.0–177.5°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 2.16 (s, 3H, $COCH_3$), 2.28 (s, 3H, $COCH_3$), 2.92 (dt, 1H, *J*=15.5, 2.2 Hz, 1-CH_2), 3.29 (dd, 1H, *J*=15.5, 8.4 Hz, 1-CH_2), 4.48 (dt, 1H, *J*=1.7, 8.7 Hz, 10c-H), 4.95 (d, 1H, *J*=2.0 Hz, =CH_2), 5.06 (d, 1H, *J*=2.2 Hz, =CH_2), 6.11 (dd, 1H, *J*=8.9, 2.1 Hz, 3a-H), 7.09 (d, 1H, *J*=8.7 Hz, Ar-H), 7.32 (dt, 1H, *J*=1.2, 7.5 Hz, Ar-H), 7.49 (dt, 1H, *J*=1.0, 7.5 Hz, Ar-H), 7.62 (d, 1H, *J*=8.2 Hz, Ar-H), 7.69 (d, 1H, *J*=8.9 Hz, Ar-H), 7.82 (d, 1H, *J*=8.2 Hz, Ar-H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 20.8, 21.0, 36.4, 39.7, 88.8, 108.0, 112.6, 121.1, 121.9, 122.9, 123.0, 126.8, 129.0, 129.6, 129.9, 130.0, 143.6, 147.7, 155.5, 167.5, 168.4. IR ($CHCl_3$): 1752, 1670, 1627 cm^{-1}. LR-EIMS *m*/*z*: 350 (M^+, 29), 266 (100). HR-EIMS calcd for $C_{21}H_{18}O_5$: 350.1154. Found: 350.1158. Anal. calcd for $C_{21}H_{18}O_5$: C; 71.99, H; 5.18. Found: C; 72.26, H; 5.42.

1.1.9. (3a*R,10c*S**)-3a,10c-Dihydro-2-pivaloyl-1*H*-cyclopenta[*b*]naphtho[1,2-*d*]furan-3-ol (5i).** Colourless needles (benzene–*n*-hexane), mp 130.0–132.0°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.15 (s, 9H, $C(CH_3)_3$), 3.18 (d, 1H, *J*=13.9 Hz, 1-CH_2), 3.50 (dd, 1H, *J*=8.5, 13.9 Hz, 1-CH_2), 4.45 (t, 1H, *J*=8.5 Hz, 10c-H), 5.72 (d, 1H, *J*=9.5 Hz, 3a-H), 7.15 (d, 1H, *J*=8.8 Hz, Ar-H), 7.34 (t, 1H, *J*=7.6 Hz, Ar-H), 7.51 (t, 1H, *J*=7.5 Hz, Ar-H), 7.69 (t, 2H, *J*=9.1 Hz, Ar-H), 7.83 (d, 1H, *J*=7.9 Hz, Ar-H), 14.32 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 26.1, 35.2, 39.9, 42.5, 87.4, 107.8, 112.5, 121.0, 122.0, 123.1, 127.0, 129.2, 129.9, 130.2, 156.1, 179.5, 206.0. IR ($CHCl_3$): 3500–3100, 1626, 1594, 1575 cm^{-1}. LR-EIMS *m/z*: 308 (M^+, 100). HR-EIMS calcd for $C_{20}H_{20}O_3$: 308.1412. Found: 308.1414. Anal. calcd for $C_{20}H_{20}O_3$: C; 77.90, H; 6.54. Found: C; 77.93, H; 6.65.

1.1.10. (3a*R,10c*S**)-3-Acetoxy-2-benzoyl-3a,10c-dihydro-1*H*-cyclopenta[*b*]naphtho[1,2-*d*]furan (5j).** Colourless needles (benzene–*n*-hexane), mp 142.5–144.5°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.81 (s, 3H, $COCH_3$), 3.22 (dt, 1H, *J*=16.3, 2.3 Hz, 1-CH_2), 3.52 (ddd, 1H, *J*=16.3, 8.2, 0.6 Hz, 1-CH_2), 4.59 (dt, 1H, *J*=8.6, 2.0 Hz, 10c-H), 6.22 (dd, 1H, *J*=8.9, 2.0 Hz, 3a-H), 7.15 (d, 1H, *J*=8.8 Hz, Ar-H), 7.30–7.42 (m, 3H, Ar-H), 7.46–7.54 (m, 2H, Ar-H), 7.63–7.70 (m, 3H, Ar-H), 7.73 (d, 1H, *J*=9.0 Hz, Ar-H), 7.83 (d, 1H, *J*=8.3 Hz, Ar-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 20.3, 36.7, 40.4, 89.1, 112.4, 121.1, 122.2, 123.2, 127.1, 127.9, 128.3, 128.6, 129.0, 129.8, 130.1, 132.8, 137.4, 149.3, 155.5, 167.6, 192.6. IR ($CHCl_3$): 1767, 1644, 1595, 1575 cm^{-1}. LR-EIMS *m/z*: 370 (M^+, 9.9), 105 (100). HR-EIMS calcd for $C_{24}H_{18}O_4$: 370.1205. Found: 370.1211. Anal. calcd for $C_{24}H_{18}O_4$: C; 77.82, H; 4.90. Found: C; 77.86, H; 5.09.

1.1.11. (3a*R,10c*S**)-3-Acetoxy-2-benzenesulfonyl-3a,10c-dihydro-1*H*-cyclopenta[*b*]naphtho[1,2-*d*]furan (5k).** Colourless prisms (AcOEt), mp 202.5–205.0°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.26 (s, 3H, $COCH_3$), 3.01 (dt, 1H, *J*=16.0, 2.3 Hz, 1-CH_2), 3.28 (dd, 1H, *J*=16.0, 8.3 Hz, 1-CH_2), 4.43 (t, 1H, *J*=8.5 Hz, 10c-H), 5.99 (dd, 1H, *J*=9.2, 2.6 Hz, 3a-H), 7.05 (d, 1H, *J*=8.8 Hz, Ar-H), 7.30 (dt, 1H, *J*=1.7, 7.3 Hz, Ar-H), 7.41–7.58 (m, 5H, Ar-H), 7.66 (d, 1H, *J*=8.8 Hz, Ar-H), 7.78 (d, 1H, *J*=8.1 Hz, Ar-H), 7.84 (d, 1H, *J*=9.0 Hz, Ar-H), 7.85 (d, 1H, *J*=8.3 Hz, Ar-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 20.6, 35.3, 39.7, 88.3, 112.2, 119.8, 121.8, 123.3, 127.1, 127.9, 129.0, 129.1, 129.5, 129.7, 130.3, 133.9, 139.2, 151.3, 155.4, 167.3. IR ($CHCl_3$): 1774, 1648, 1625 cm^{-1}. LR-EIMS *m/z*: 406 (M^+, 64), 222 (100). HR-EIMS calcd for $C_{23}H_{18}O_5S$: 406.0875. Found: 406.0869. Anal. calcd for $C_{23}H_{18}O_5S$: C; 67.97, H; 4.46. Found: C; 68.00, H; 4.43.

1.2. General procedure of 3-substituted coumarin (4) to benzo[*b*]cyclopropa[*d*]pyran (3)

Trimethylsulfoxonium iodide (220 mg, 1.0 mmol) was added in one portion to a suspension of NaH (60% in mineral oil, 40 mg, 1.0 mmol) in DMF (2 ml) at room temperature and the whole was stirred for 30 min under an N_2 atmosphere. The reaction mixture was cooled to 0 or −40°C. A solution of **4** (1.0 mmol) in DMF (1 ml) was added dropwise to the reaction mixture and the whole was stirred for additional hours. After acidification with 3% HCl solution under ice-cooling, the mixture was extracted with ether (30 ml×4). The organic layers were washed with water, dried over sodium sulfate, and evaporated. The residue was purified by column chromatography or PTLC to give a cyclopropane product (**3**).

1.2.1. Ethyl (1a*R,7b*S**)-1,7b-dihydro-2-oxobenzo[*b*]cyclopropa[*d*]pyran-1a(2*H*)-carboxylate (3a).** Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.32 (t, 3H, *J*=7.1 Hz, CH_2CH_3), 1.37 (dd, 1H, *J*=6.4, 4.9 Hz, cyclopropane-H), 2.47 (dd, 1H, *J*=9.0, 4.9 Hz, cyclopropane-H), 2.91 (dd, 1H, *J*=9.0, 6.4 Hz, cyclopropane-H), 4.28 (q, 2H, *J*=7.1 Hz, CH_2CH_3), 7.03 (dd, 1H, *J*=8.1, 1.3 Hz, Ar-H), 7.14 (dt, 1H, *J*=1.3, 7.5 Hz, Ar-H), 7.26 (ddd, 1H, *J*=1.7, 7.5, 8.1 Hz, Ar-H), 7.37 (dd, 2H, *J*=7.5, 1.7 Hz, Ar-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 14.0, 20.9, 28.7, 28.9, 62.3, 117.1, 120.1, 124.5, 127.6, 128.4, 149.4, 162.3, 167.3. IR ($CHCl_3$): 1756, 1722, 1586 cm^{-1}. LR-EIMS *m/z*: 232 (M^+, 30), 159 (100). HR-EIMS calcd for $C_{13}H_{12}O_4$: 232.0735. Found: 232.0728.

1.2.2. (1a*R,7b*S**)-1,7b-Dihydro-1a-pivaloylbenzo[*b*]cyclopropa[*d*]pyran-2(1a*H*)-one (3b).** Colourless needles (ethanol), mp 130.5–132.0°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.16 (t-like, 1H, *J*=4.8 Hz, cyclopropane-H), 1.26 (s, 9H, $C(CH_3)_3$), 2.44 (dd, 1H, *J*=8.7, 4.3 Hz, cyclopropane-H), 2.50 (dd, 1H, *J*=8.8, 5.1 Hz, cyclopropane-H), 7.08 (dd, 1H, *J*=8.2, 0.9 Hz, Ar-H), 7.15 (dt, 1H, *J*=1.1, 7.5 Hz, Ar-H), 7.28 (dt, 1H, *J*=1.6, 7.8 Hz, Ar-H), 7.36 (dd, 2H, *J*=7.5, 1.6 Hz, Ar-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 17.9, 27.6, 28.0, 35.2, 44.8, 117.3, 120.0, 124.7, 127.9, 128.4, 149.7, 164.8, 207.1. IR ($CHCl_3$): 1738, 1694, 1584 cm^{-1}. LR-FABMS *m/z*: 245 $(M+H)^+$. HR-FABMS calcd for $C_{15}H_{16}O_3$+H: 245.4478. Found: 245.1187. Anal. calcd for $C_{15}H_{16}O_3$: C; 73.75, H; 6.60. Found: C; 73.87, H; 6.67.

1.2.3. (1a*R,7b*S**)-1a-Benzoyl-1,7b-dihydrobenzo[*b*]cyclopropa[*d*]pyran-2(1a*H*)-one (3c).** Colourless needles (ethanol), mp 122.5–124.0°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.39 (dd, 1H, *J*=5.9, 4.9 Hz, cyclopropane-H), 2.69 (dd, 1H, *J*=8.8, 4.9 Hz, cyclopropane-H), 2.82 (dd, 1H, *J*=8.8, 5.9 Hz, cyclopropane-H), 7.10–7.60 (m, 7H, Ar-H), 7.70–7.79 (m, 2H, Ar-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 18.7, 29.1, 34.6, 117.5, 120.1, 124.8, 128.0, 128.5, 128.6, 128.7, 133.4, 135.4, 149.7, 164.9, 191.9. IR ($CHCl_3$): 1739, 1679, 1596 cm^{-1}. LR-FABMS *m/z*: 265 $(M+H)^+$. HR-FABMS calcd for $C_{17}H_{12}O_3$+H: 265.0865. Found: 265.0869. Anal. calcd for $C_{17}H_{12}O_3$: C; 77.26, H; 4.58. Found: C; 77.51, H; 4.67.

1.2.4. (1a*R,7b*S**)-1a-Cyano-1,7b-dihydrobenzo[*b*]cyclopropa[*d*]pyran-2(1a*H*)-one (3d).** Colourless needles (ethanol), mp 130.0–131.0°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.66 (dd, 1H, *J*=5.7, 6.6 Hz, cyclopropane-H), 2.41 (dd, 1H, *J*=5.6, 9.1 Hz, cyclopropane-H), 3.29 (dd, 1H, *J*=6.7, 8.9 Hz, cyclopropane-H), 7.05 (dd, 1H, *J*=8.3 Hz, Ar-H), 7.20 (dt, 1H, *J*=1.0, 7.5 Hz, Ar-H), 7.32 (dt, 1H, *J*=1.6, 7.8 Hz, Ar-H), 7.41 (dd, 1H, *J*=1.6, 7.4 Hz, Ar-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ:17.4, 23.2, 29.0, 116.2, 117.7, 118.3, 125.3, 127.7, 129.3, 149.0, 160.6. IR ($CHCl_3$): 2240, 1754 cm^{-1}. LR-EIMS *m/z*: 185 (M^+, 100).

HR-EIMS calcd for $C_{11}H_7NO_2$: 185.0477. Found: 185.0478. Anal. calcd for $C_{11}H_7NO_2$: C; 71.35, H; 3.81, N; 7.56. Found: C; 71.02, H; 3.91, N; 7.30.

1.2.5. (1a*R,7b*S**)-1a-Acetyl-1,7b-dihydrobenzo[*b*]cyclopropa[*d*]pyran-2(1a*H*)-one (3e).** Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.38 (dd, 1H, J=6.5, 4.2 Hz, cyclopropane-H), 2.47 (dd, 1H, J=9.0, 4.3 Hz, cyclopropane-H), 2.62 (s, 3H, $COCH_3$), 2.92 (dd, 1H, J=8.9, 6.6 Hz, cyclopropane-H), 7.06 (dd, 1H, J=8.1, 1.2 Hz, Ar-H), 7.14 (dt, 1H, J=1.3, 7.5 Hz, Ar-H), 7.27 (dt, 1H, J=1.8, 7.8 Hz, Ar-H), 7.36 (dd, 1H, J=7.6, 1.7 Hz, Ar-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 23.9, 30.0, 31.8, 35.5, 117.1, 120.7, 124.6, 127.6, 128.4, 149.4, 165.1. IR ($CHCl_3$): 1741, 1697, 1617, 1586 cm^{-1}. LR-FABMS m/z: 203 $(M+H)^+$. HR-FABMS calcd for $C_{12}H_{10}O_3$+H: 203.0709. Found: 203.0714.

1.3. General procedure of benzo[*b*]cyclopropa[*d*]pyran (3) to cyclopenta[*b*]benzofuran (5)

Conversion to cyclopenta[*b*]benzofuran (**5**) from the corresponding benzo[*b*]cyclopropa[*d*]pyran (**3**) was performed in a similar manner as that from 3-substituted coumarin (**4**) except for use of 1.1 equiv. of dimethylsulfoxonium methylide. The physical and spectral data of the obtained products (**5**) agreed with those given by the earlier-mentioned one-pot reaction.

1.4. Crystallography of 3b and 3c

Diffraction data for **3b** and **3c** were measured on a Rigaku AFC7R four-circle diffractometer with filtered Cu Kα radiation (λ=1.54178 Å) and a rotating anode generator. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

1.4.1. Crystal data of 3b

Formula $C_{15}H_{16}O_3$, formula weight=244.29, triclinic, space group P-1 (#2), a=10.2962(6), b=10.8328(8), c=6.5414(7) Å, α=105.962(7), β=92.499(7), γ=110.354(5)°, V=649.78(10) Å^3, Z=2, D_{calc}=1.248 g/cm^3, F_{000}=260.00, μ(Cu Kα)=7.01 cm^{-1}. Of the total of 1939 unique reflections (complete for $2\theta<120°$), 1173 satisfied the criterion $I>3.00\sigma(I)$ and only these were used in the solution and refinement of structure. The structure was solved by a direct method using SIR88,[16] and the final refinement was done by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms, and hydrogen atoms were included but not refined. The final R value was 0.058 (R_w=0.093).

1.4.2. Crystal data of 3c

Formula $C_{17}H_{12}O_3$, formula weight=264.28, orthorhombic, space group $P2_12_12_1$ (#19), a=6.528(1), b=33.655(2), c=5.965(2) Å, V=1310.6(4) Å^3, Z=4, D_{calc}=1.339 g/cm^3, F_{000}=552.00, μ(Cu Kα)=7.49 cm^{-1}. Of the total of 1189 reflections (complete for $2\theta<120°$), 1142 satisfied the criterion $I>3.00\sigma(I)$ and only these were used in the solution and refinement of structure. The structure was solved by a direct method using SAPI91,[17] and the final refinement was done by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms, and hydrogen atoms were included but not refined. The final R value was 0.026 (R_w=0.047).

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