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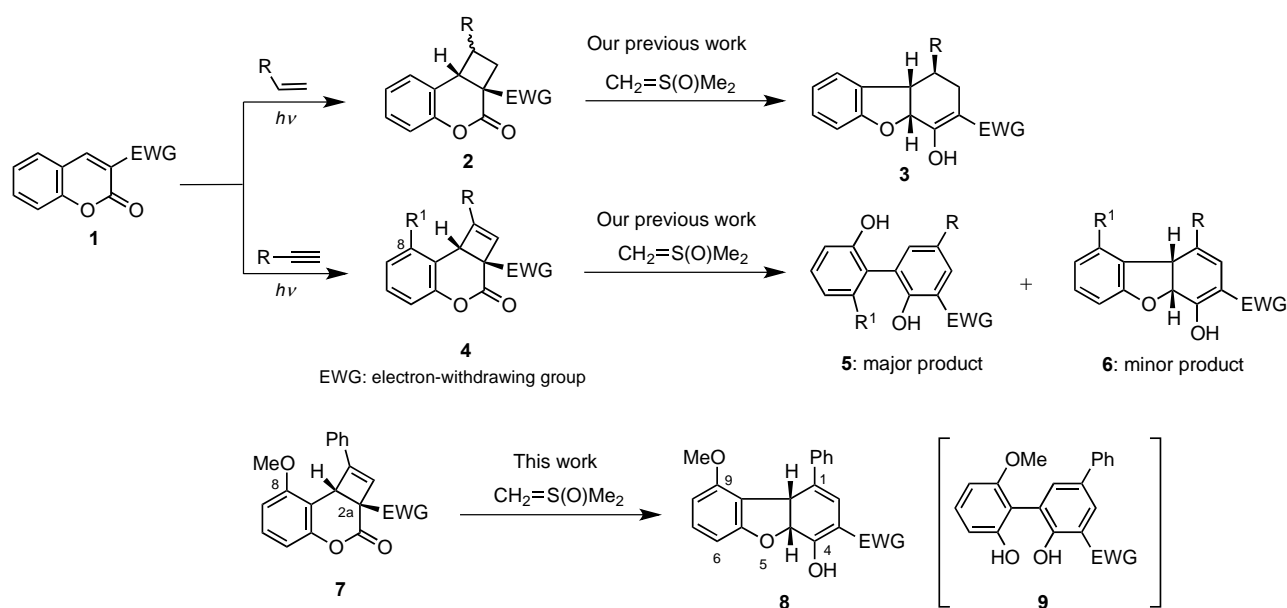
SKELETAL TRANSFORMATION OF 2a,8b-DIHYDROBENZO[b]-CYCLOBUTE[d]PYRAN-3-ONES INTO DIHYDRODIBENZOFURANS

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Abstract – Using dimethylsulfoxonium methylide as the methylene-transfer reagent, 8-methoxy-2a,8b-dihydrobenzo[b]cyclobute[d]pyran-3-ones were exclusively converted into the corresponding dihydrodibenzofuran derivatives. The use of a methoxy group as the substituent and its position are crucial to the success of this transformation.

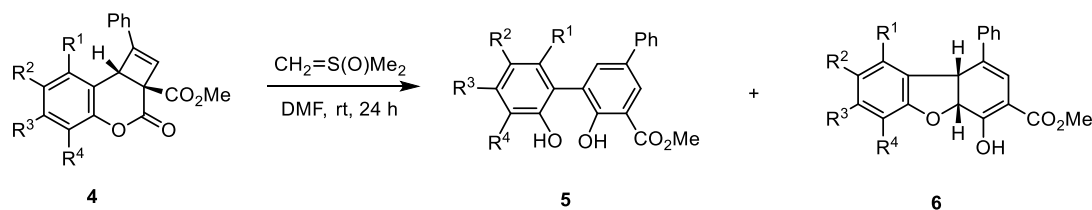
Cyclopropanes and cyclobutanes have ring strain. In this regard, their cycloalkanes are unstable and have high reactivity, and play an important role in organic synthesis.¹ Motivated by our strong interest in their reactivity, we have developed several reactions involving cyclopropane and cyclobutane ring opening reactions.² In a previous study, we found that benzo[b]cyclobuta[d]pyran-3-ones **2**, prepared by the [2+2]photocycloaddition reaction of 3-substituted coumarins **1** with monosubstituted alkenes, could be stereoconvergently transformed into tetrahydrodibenzofuran derivatives **3** by using more than 2 equiv. of dimethylsulfoxonium methylide ($\text{CH}_2=\text{S}(\text{O})\text{Me}_2$), the methylene-transfer reagent in the Corey-Chaykovsky cyclopropanation reaction (Scheme 1).^{3,4} The transformation of **2** into **3** was applied to the syntheses of dibenzofuran-type natural products.⁵ In anticipation of the formation of dihydrodibenzofuran derivatives **6** from 2a-substituted 2a,8b-dihydrobenzo[b]cyclobute[d]pyran-3-one derivatives **4**, which are cyclobutene derivatives that have more strain than **2**, we treated **4** with $\text{CH}_2=\text{S}(\text{O})\text{Me}_2$ in the usual manner. However, contrary to our expectation, the main products were 2,2'-biphenols **5** ($\text{R}^1=\text{H}$).⁶ In our continuous studies of the reaction of small cycloalkanes with $\text{CH}_2=\text{S}(\text{O})\text{Me}_2$, we contrived to obtain **6** as the main product. In this paper, we describe the skeletal transformation of 8-methoxy-2a,8b-dihydrobenzo[b]cyclobute[d]pyran-3-ones **7** into dihydrodibenzofuran derivatives **8** using $\text{CH}_2=\text{S}(\text{O})\text{Me}_2$.



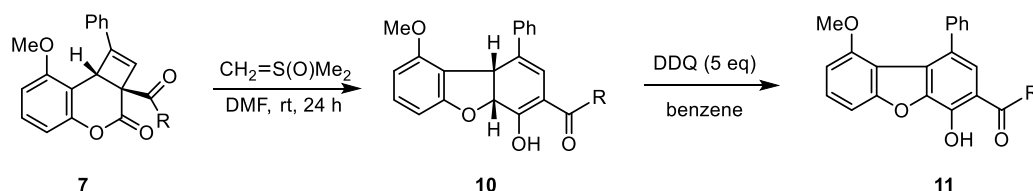
Scheme 1. Skeletal transformation of cyclobutane **2** and cyclobutenes **4** and **7**

At first, the substituent effect of a methoxy (OMe) group on the phenyl group of the coumarin ring in **4** was investigated (Table 1). Substrate **4a** having a OMe group at the 8-position was treated with $\text{CH}_2=\text{S}(\text{O})\text{Me}_2$ under the same conditions as the previous transformation [$\text{CH}_2=\text{S}(\text{O})\text{Me}_2$ (2.0 eq) in DMF at rt].⁶ Surprisingly, expected product **6a** was obtained in high yield without **5a** (entry 1). However, substrates having a OMe group at the 7-position **4b**, the 6-position **4c**, and the 5-position **4d** gave **5b-d** as the major or sole product (entries 2-4). The substituent position on **4** would be important for the production of **6**: when substrates **4e** and **4f** having a methyl and a trimethylsilyl (TMS) group at the 8-position were used, the products were only **5e** and **5f** in 36% and 63% yields, respectively (entries 5 and 6). As a result, the formation of **6** would be strongly influenced by the functional group and the position of the substituent on the phenyl group of the coumarin ring. The structures of **5** and **6** were confirmed by comparing their spectral data with those of similar compounds prepared previously.⁶

Next, we examined the scope of the reaction for substrates having 3-acyl groups in the presence of an 8-OMe group (Table 2). Substrates **7a-e** with alkylcarbonyl or arylcarbonyl groups at the 2a-position were subjected to the same reaction conditions as those mentioned above. Although the obtained products were expectedly dihydrodibenzofurans **10**, several of them were unstable. Therefore, all products **10** except **10d** were isolated as dibenzofurans **11a-c** and **11e** after oxidation with DDQ.⁷

Table 1. Substituent effect on phenyl group of coumarin ring

| Entry | R ¹ | R ² | R ³ | R ⁴ | Yield of 5 (%) ^a | Yield of 6 (%) ^a |
|-------|----------------|----------------|----------------|----------------|------------------------------------|------------------------------------|
| 1 | 4a | OMe | H | H | 5a : N.D. ^b | 6a : 87 |
| 2 | 4b | H | OMe | H | 5b : 48 | 6b : 17 |
| 3 | 4c | H | H | OMe | 5c : 56 | 6c : N.D. |
| 4 | 4d | H | H | OMe | 5d : 70 | 6d : N.D. |
| 5 | 4e | Me | H | H | 5e : 36 | 6e : N.D. |
| 6 | 4f | TMS | H | H | 5f : 63 | 6f : N.D. |

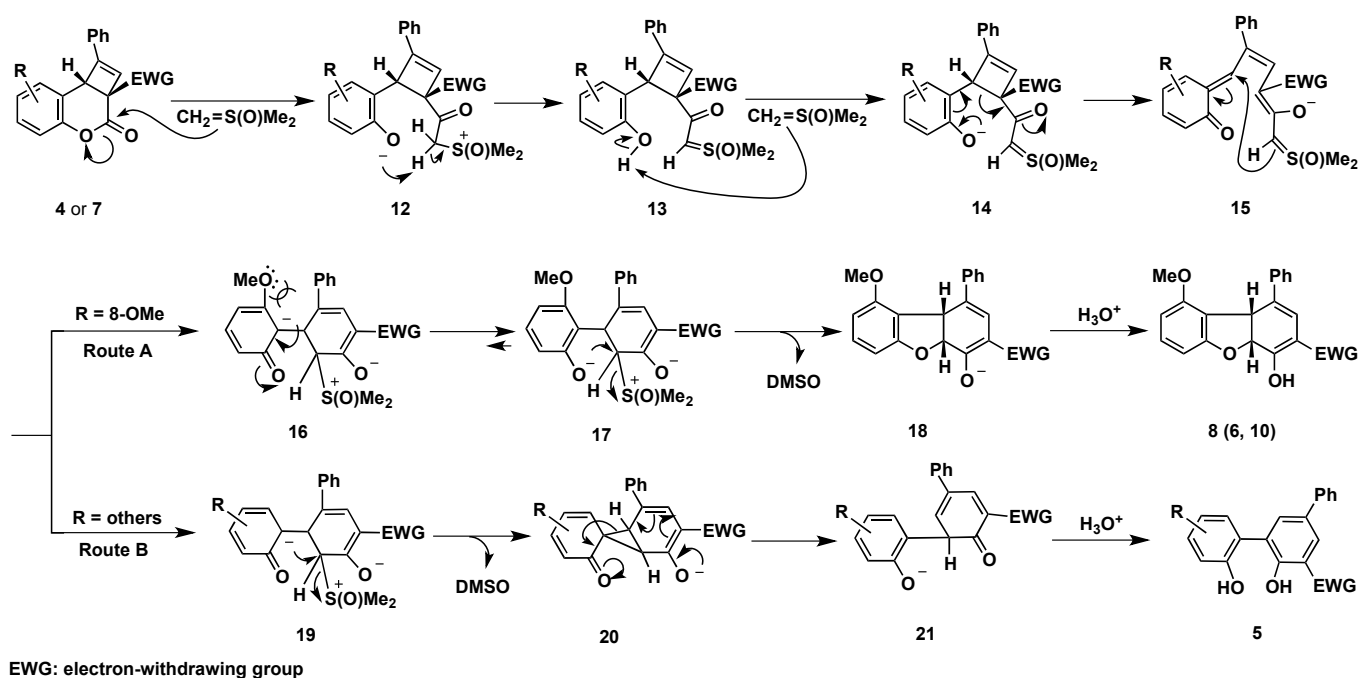
^a Isolated yield.^b Not detected.**Table 2.** Substituent effect of 3-acyl group in the presence of 8-OMe group

| Entry | R | Yield of 10 (%) ^a | Yield of 11 (%) ^a |
|-------|-----------|-------------------------------------|-------------------------------------|
| 1 | 7a | Me | - |
| 2 | 7b | <i>n</i> -Pr | - |
| 3 | 7c | <i>i</i> -Pr | - |
| 4 | 7d | <i>t</i> -Bu | 10d : 48 |
| 5 | 7e | Ph | - |

^a Isolated yield.

A plausible reaction mechanism is shown in Scheme 2. Similar to the previously reported skeletal transformation reaction of benzo[*b*]cyclobuta[*d*]pyran-3-ones **2** and benzo[*b*]cyclobuta[*d*]pyran-3-ones **4**,^{3,6} one equivalent of CH₂=S(O)Me₂ would attack the lactone carbonyl group of **4** or **7** to initiate ring opening to form **12**. The use of one more equivalent of CH₂=S(O)Me₂ as the base would promote the cyclobutene ring opening to give intermediate **15**. At next stage, the type and position of the substituent would divide the fate of **5** or **8**. When the substituent is an 8-methoxy group, **17** would be preferred over

16 because there is repulsion between the carbanion of the enolate moiety and the unshared electron pair on the methoxy oxygen in **16**, and a C-O bond would be formed between the oxygen of the enolate moiety and the methine carbon linked to the dimethylsulfoxonium group to give **8** (**6**, **10**) (Route A). On the other hand, when the substituent is not an 8-methoxy group, **19** would take precedence similarly to the previous reaction.⁶ Therefore, a C-C bond would be formed between the carbon of the enolate moiety and the methine carbon linked to the dimethylsulfoxonium group in **19**, and this would be followed by aromatization accompanying the cleavage of the cyclopropane ring to give **5** (Route B).



Scheme 2. Plausible reaction mechanism

In conclusion, we have achieved the skeletal transformation of 2a-carbonyl-8-methoxy-2a,8b-dihydrobenzo[*b*]cyclobute[*d*]pyran-3-ones into dihydrodibenzofurans with $\text{CH}_2=\text{S}(\text{O})\text{Me}_2$ in DMF at rt. The use of a methoxy group as the substituent and its position are crucial to the success of the reaction. Further studies, including other substituent effects and theoretical calculations, are in progress.

EXPERIMENTAL

General: Melting points were measured with a Yanaco MP micro-melting point apparatus and uncorrected. NMR spectra were measured on JEOL AL-300 (^1H : 300 MHz; ^{13}C : 75.5 MHz), and Varian INOVA 400NB (^1H : 400 MHz; ^{13}C : 100 MHz) spectrometers with tetramethylsilane as the internal standard. Chemical shifts are reported in ppm. IR spectra were measured with Shimadzu IR-435 and

Shimadzu FTIR-8400 spectrophotometer. A JEOL JMS-GC mate spectrometer was used for low-resolution and high-resolution electron ionizations MS (LR-EIMS and HR-EIMS). Silica gel 60 (grade 7734, 60-230 mesh, Merck) and Silica gel 60N (Kanto Chemical Co., Inc.) for column chromatography and Silica gel 60 F₂₅₄ plate (0.5 mm and 1 mm in thickness, Merck) for preparative TLC were used.

Typical procedure for the synthesis of dihydrodibenzofurans: Methyl (4aRS,9bSR)-4a,9b-dihydro-4-hydroxy-9-methoxy-1-phenyldibenzofuran-3-carboxylate (6a). To a suspension of trimethylsulfoxonium iodide (440 mg, 2.00 mmol) in DMF (2.0 mL), NaH (60% in mineral oil, 80 mg, 2.00 mmol) was added under ice-cooling and the whole was stirred for 30 min at rt under N₂ atmosphere. To the stirred mixture, **4** (336 mg, 1.00 mmol) was added to the reaction mixture, and the stirring was continued overnight. After acidification with 5% HCl aq., the mixture was extracted with Et₂O. The combined extracts were washed with water and sat. NaCl aq., dried over Na₂SO₄, and evaporated. The residue was purified by silica gel column chromatography with AcOEt-*n*-hexane (1:3) to give **6a** (305 mg, 87%) as pale yellow amorphous. ¹H-NMR (400 MHz, CDCl₃) δ: 3.15 (3H, s), 3.81 (3H, s), 4.91 (1H, d, *J* = 10.1 Hz), 5.50 (1H, d, *J* = 10.1 Hz), 6.24 (1H, dd, *J* = 0.5, 7.7 Hz), 6.36 (1H, d, *J* = 1.3 Hz), 6.56 (1H, d, *J* = 7.9 Hz), 7.05 (1H, dt, *J* = 0.7, 8.1 Hz), 7.22 – 7.25 (1H, m), 7.28 – 7.32 (4H, m), 12.3 (1H, s). ¹³C-NMR (100 MHz, CDCl₃) δ: 44.1, 52.1, 54.5, 80.9, 100.7, 103.0, 104.3, 114.1, 117.6, 126.5, 127.0, 127.5, 129.7, 129.8, 141.5, 156.9, 159.4, 165.2, 170.7. IR (CHCl₃): 1659, 1604 cm⁻¹. LR-EIMS *m/z*: 350 (M⁺, 43.6), 318 (36.9), 317 (20.7), 237 (100.0). HR-EIMS calcd for C₂₁H₁₈O₅: 350.1154. Found: 350.1149.

Methyl 2,2'-dihydroxy-5'-methoxy-5-phenylbiphenyl-3-carboxylate (5b). Yield 48%. Pale yellow amorphous. ¹H-NMR (400 MHz, CDCl₃) δ: 3.80 (3H, s), 4.04 (3H, s), 6.24 (1H, s), 6.87 (1H, d, *J* = 2.9 Hz), 6.90 – 6.94 (1H, m), 7.04 (1H, d, *J* = 8.8 Hz), 7.34 – 7.38 (1H, m), 7.43 – 7.47 (2H, m), 7.57 – 7.59 (2H, m), 7.82 (1H, d, *J* = 2.0 Hz), 8.17 (1H, d, *J* = 2.4 Hz), 12.0 (1H, s). ¹³C-NMR (100 MHz, CDCl₃) δ: 52.9, 55.8, 113.0, 115.2, 116.0, 119.4, 126.2, 126.8, 127.5, 128.0, 128.1, 128.9, 133.7, 136.9, 139.4, 147.8, 154.1, 156.4, 171.1. IR (CHCl₃): 1669 cm⁻¹. LR-EIMS *m/z*: 350 (M⁺, 39.1), 318 (100.0), 303 (49.6). HR-EIMS calcd for C₂₁H₁₈O₅: 350.1154. Found: 350.1149.

Methyl (4aRS,9bSR)-4a,9b-dihydro-4-hydroxy-8-methoxy-1-phenyldibenzofuran-3-carboxylate (6b). Yield 17%. Pale yellow amorphous. ¹H-NMR (400 MHz, CDCl₃) δ: 3.51 (3H, s), 3.83 (3H, s), 4.99 (1H, dd, *J* = 0.9, 11.7 Hz), 5.69 (1H, d, *J* = 11.7 Hz), 6.18 (1H, dd, *J* = 1.0, 2.7 Hz), 6.59 (1H, d, *J* = 0.7

Hz), 6.62 (1H, ddd, $J = 0.8, 2.7, 8.8$ Hz), 6.81 (1H, d, $J = 8.8$ Hz), 7.29 – 7.50 (5H, m), 12.4 (1H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ : 44.2, 52.1, 55.7, 80.3, 100.3, 109.6, 111.1, 113.2, 116.0, 126.1, 127.5, 127.9, 128.7, 129.0, 139.2, 151.7, 154.4, 165.8, 170.7. IR (CHCl_3): 1659, 1593 cm^{-1} . LR-EIMS m/z : 350 (M^+ , 42.6), 318 (100.0), 303 (38.4). HR-EIMS calcd for $\text{C}_{21}\text{H}_{18}\text{O}_5$: 350.1154. Found: 350.1158.

Methyl 2,2'-dihydroxy-4'-methoxy-5-phenylbiphenyl-3-carboxylate (5c). Yield 56%. Brown yellow amorphous. ^1H -NMR (400 MHz, CDCl_3) δ : 3.83 (3H, s), 4.02 (3H, s), 6.62 – 6.74 (3H, m), 7.33 – 7.37 (1H, m), 7.42 – 7.47 (3H, m), 7.56 – 7.76 (2H, m), 7.77 (1H, d, $J = 2.2$ Hz), 8.12 (1H, d, $J = 2.0$ Hz), 12.0 (1H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ : 52.9, 55.4, 103.3, 108.0, 112.9, 117.7, 126.8, 127.4, 127.5, 127.8, 128.9, 131.8, 133.7, 136.9, 139.5, 155.1, 156.3, 161.2, 171.1. IR (CHCl_3): 1668, 1614 cm^{-1} . LR-EIMS m/z : 350 (M^+ , 51.0), 318 (100.0), 301 (27.9). HR-EIMS calcd for $\text{C}_{21}\text{H}_{18}\text{O}_5$: 350.1154. Found: 350.1151.

Methyl 2,2'-dihydroxy-3'-methoxy-5-phenylbiphenyl-3-carboxylate (5d). Yield 70%. Pale yellow amorphous. ^1H -NMR (400 MHz, CDCl_3) δ : 3.94 (3H, s), 4.00 (3H, s), 6.01 (1H, s), 6.91 – 6.98 (3H, m), 7.30 – 7.35 (1H, m), 7.40 – 7.45 (2H, m), 7.57 – 7.60 (2H, m), 7.81 (1H, dd, $J = 0.5, 2.4$ Hz), 8.13 (1H, d, $J = 2.6$ Hz), 11.4 (1H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ : 52.6, 56.1, 110.5, 112.7, 119.8, 123.4, 123.9, 126.7, 127.1, 127.2, 127.7, 128.8, 132.2, 136.5, 139.8, 143.3, 147.3, 158.1, 171.0. IR (CHCl_3): 1670 cm^{-1} . LR-EIMS m/z : 350 (M^+ , 57.0), 318 (100.0), 272 (26.5). HR-EIMS calcd for $\text{C}_{21}\text{H}_{18}\text{O}_5$: 350.1154. Found: 350.1149.

Methyl 2,2'-dihydroxy-6'-methyl-5-phenylbiphenyl-3-carboxylate (5e). Yield 36%. Yellowish oil. ^1H -NMR (300 MHz, CDCl_3) δ : 2.36 (3H, s), 4.02 (3H, s), 6.37 (1H, s), 6.94 (1H, t, $J = 7.5$ Hz), 7.15 (1H, dd, $J = 1.7$ Hz, 7.5 Hz), 7.20 – 7.24 (1H, m), 7.34 – 7.46 (3H, m), 7.55 – 7.58 (2H, m), 7.80 (1H, d, $J = 2.4$ Hz), 8.15 (1H, d, $J = 2.4$ Hz), 11.9 (1H, s). ^{13}C -NMR (75 MHz) δ : 16.5, 52.9, 112.9, 120.9, 124.9, 126.8, 127.1, 127.4, 127.9, 128.1, 128.8, 128.9, 131.1, 133.6, 137.2, 139.5, 152.0, 156.6, 171.1. IR (CHCl_3): 3660–3300, 1715, 1634, 1597 cm^{-1} . LR-EIMS m/z : 334 (M^+ , 37.8), 302 (100.0), 285 (39.7), 101 (22.0). HR-EIMS calcd for $\text{C}_{21}\text{H}_{18}\text{O}_4$: 334.1205. Found: 334.1200.

Methyl 2,2'-dihydroxy-5-phenyl-6'-trimethylsilylbiphenyl-3-carboxylate (5f). White crystals ($\text{AcOEt} / n\text{-Hexane}$), mp 118.6 – 121.3 $^\circ\text{C}$. ^1H -NMR (300 MHz, CDCl_3) δ : 0.35 (9H, s), 4.03 (3H, s), 6.65 (1H, s), 7.01 – 7.08 (1H, m), 7.28 – 7.49 (5H, m), 7.56 – 7.64 (2H, m), 7.80 (1H, d, $J = 2.4$ Hz), 8.15 (1H, d, $J = 2.4$ Hz), 12.0 (1H, s). ^{13}C -NMR (75 MHz, CDCl_3) δ : -0.80, 52.7, 112.8, 121.0, 124.5, 126.7, 127.3, 127.8, 128.2, 128.4, 128.8, 132.5, 133.6, 135.4, 137.2, 139.4, 156.5, 158.5, 171.0. IR (CHCl_3): 3650–3300, 1668

cm⁻¹. LR-EIMS *m/z*: 392 (M⁺, 32.4), 360 (23.2), 345 (100.0), 302 (18.7). HR-EIMS calcd for C₂₃H₂₄O₄Si: 392.1444. Found: 392.1436.

Typical Procedure for the Oxidation of Dihydrodibenzofurans:⁷ After work-up of above reaction, the crude product in benzene was oxidized with excess of DDQ at room temperature. After completion of the reaction, benzene was evaporated and the crude product was purified by silica gel column chromatography to give dibenzofuran derivatives **11**.

1-(4-Hydroxy-9-methoxy-1-phenyldibenzofuran-3-yl)-1-ethanone (11a). Yield 50%. Yellowish powder (AcOEt / *n*-hexane), mp 190.2 – 192.7 °C, ¹H-NMR (300 MHz, CDCl₃) δ: 2.69 (3H, s), 3.28 (3H, s), 6.59 (1H, d, *J* = 8.1 Hz), 7.25 – 7.28 (2H, m), 7.39 – 7.45 (5H, m), 7.54 (1H, s), 12.7 (1H, s). ¹³C-NMR (75 MHz) δ: 27.1, 55.0, 104.1, 104.6, 113.1, 116.8, 126.5, 126.7, 126.9, 128.4, 129.2, 129.8, 129.9, 142.4, 143.4, 147.7, 155.6, 159.1, 204.7. IR (CHCl₃): 3000, 1651, 1614 cm⁻¹. LR-EIMS *m/z*: 332 (M⁺, 100.0), 317 (97.1). HR-EIMS calcd for C₂₁H₁₆O₄: 332.1049. Found: 332.1050.

1-(4-Hydroxy-9-methoxy-1-phenyldibenzofuran-3-yl)-1-butanone (11b). Yield 45%. Yellowish crystals (AcOEt / *n*-hexane), mp 187.5 – 190.4 °C, ¹H-NMR (300 MHz, CDCl₃) δ: 1.02 (3H, t, *J* = 7.4 Hz), 1.81 (2H, sext, *J* = 7.3 Hz), 3.02 (2H, t, *J* = 7.3 Hz), 3.27 (3H, s), 6.56 (1H, d, *J* = 8.1 Hz), 7.24 (1H, d, *J* = 5.5 Hz), 7.38 – 7.43 (6H, m), 7.56 (1H, s), 12.9 (1H, s). ¹³C-NMR (75 MHz) δ: 13.8, 17.9, 40.6, 55.0, 104.0, 104.6, 113.1, 116.5, 125.7, 126.7, 126.8, 128.2, 128.9, 129.8, 129.8, 142.5, 143.5, 147.8, 155.6, 159.0, 207.0. IR (CHCl₃): 1650, 1613 cm⁻¹. LR-EIMS *m/z*: 360 (M⁺, 55.0), 317 (100.0). HR-EIMS calcd for C₂₃H₂₀O₄: 360.1361. Found: 360.1362.

1-(4-Hydroxy-9-methoxy-1-phenyldibenzofuran-3-yl)-2-methyl-1-propanone (11c). Yield 48%. White crystals (AcOEt / *n*-hexane), mp 124.1 – 125.9 °C, ¹H-NMR (300 MHz, CDCl₃) δ: 1.28 (6H, d, *J* = 7.5 Hz), 3.28 (3H, s), 3.65 (1H, hept, *J* = 6.8 Hz), 6.58 (1H, d, *J* = 8.1 Hz), 6.27 (1H, d, *J* = 7.1 Hz), 7.38 – 7.44 (6H, m), 7.60 (1H, s), 13.0 (1H, s). ¹³C-NMR (75 MHz) δ: 19.4, 35.3, 55.0, 104.0, 104.6, 113.1, 115.3, 125.6, 126.7, 126.8, 128.2, 128.9, 129.8, 142.5, 143.7, 148.4, 155.6, 159.0, 211.1. IR (CHCl₃): 1646, 1614 cm⁻¹. LR-EIMS *m/z*: 360 (M⁺, 31.2), 317 (100.0). HR-EIMS calcd for C₂₃H₂₀O₄: 360.1361. Found: 360.1357.

1-[(4*aR**S*,9*b**S**R*)-4-hydroxy-9-methoxy-1-phenyl-4*a*,9*b*-dihydrodibenzofuran-3-yl]-2,2-dimethyl-1-propanone (10d).** Yield 48%. Yellowish oil. ¹H-NMR (300 MHz, CDCl₃) δ: 1.32 (9H, s), 3.19 (3H, s),

4.87 (1H, d, $J = 9.5$ Hz), 5.33 (1H, d, $J = 9.8$ Hz), 6.26 (1H, d, $J = 8.2$ Hz), 6.57 (1H, d, $J = 7.9$ Hz), 6.68 (1H, s), 7.05 (1H, t, $J = 8.1$ Hz), 7.23 – 7.33 (5H, m), 17.0 (1H, s). ^{13}C -NMR (75 MHz) δ : 27.7, 41.3, 43.1, 54.6, 81.6, 103.2, 104.4, 106.4, 114.3, 120.1, 126.5, 127.0, 127.2, 127.7, 129.7, 142.3, 156.9, 159.8, 183.7, 201.2. IR (CHCl_3): 1698, 1596 cm^{-1} . LR-EIMS m/z : 376 (M^+ , 9.7), 319 (100.0), 57 (33.1). HR-EIMS calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4$: 376.1674. Found: 376.1679.

(4-Hydroxy-9-methoxy-1-phenyldibenzofuran-3-yl) phenyl ketone (11e). Yield 48%. Yellowish crystals (AcOEt / *n*-hexane), mp 177.4 – 181.1 °C, ^1H -NMR (300 MHz, CDCl_3) δ : 3.28 (3H, s), 6.60 (1H, d, $J = 7.9$ Hz), 7.29 (1H, dd, $J = 0.7, 8.3$ Hz), 7.35 (5H, s), 7.41 – 7.56 (5H, m), 7.73 – 7.76 (2H, m), 12.6 (1H, s). ^{13}C -NMR (75 MHz) δ : 55.0, 104.1, 104.7, 116.3, 126.6, 126.8, 127.3, 127.7, 128.1, 128.4, 129.19, 129.22, 129.5, 129.7, 130.0, 131.9, 138.1, 142.2, 148.5, 155.7, 159.2, 201.6. IR (CHCl_3): 1721, 1641 cm^{-1} . LR-EIMS m/z : 394 (M^+ , 100.0), 317 (30.6). HR-EIMS calcd for $\text{C}_{26}\text{H}_{18}\text{O}_4$: 394.1205. Found: 394.1204.

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