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Reactions of 2-hydroxyaryl-α,β-unsaturated ketones with dimethylsulfonium carbonylmethylides: a new and facile diastereoselective synthesis of 2,3-disubstituted dihydrobenzofurans

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ABSTRACT

A simple, efficient, and general method has been developed for the diastereoselective synthesis of 2,3-disubstituted dihydrobenzofurans through reactions of 2-hydroxyaryl-α,β-unsaturated ketones with dimethylsulfonium carbonylmethylides.

1. Introduction

Natural products possessing 2,3-dihydrobenzofuran moiety have been found to exhibit useful biological activities.[1,2] Hence, the synthesis of 2,3-dihydrobenzofuran derivatives continues to attract considerable attention. Several approaches for the synthesis of 2,3-dihydrobenzofuran have been developed, such as cyclodehydration,[3] cycloaddition,[4] TBAF, Lewis acid, and transition metal-catalyzed reactions,[5] and anionic, electrocyclic, and free radical cyclizations.[6] However, for the synthesis of 2,3-disubstituted dihydrobenzofurans, the Sakurai reaction[7] and the (2+3)-cycloaddition reaction[8] between 1,4-benzoquinone monoimides and alkenes have been utilized. Recently, Barret and coworkers have shown that the use of azadienes as dipolarophiles improves the yield of 2,3-disubstituted dihydrobenzofurans.[9] These reactions involve use of expensive starting materials, which are not easily accessible.

Although, the methylene group transfer from sulfur ylides to α,β-unsaturated carbonyl compounds has been extensively studied, only very few reports are available where the application of this important reaction in the synthesis of 2,3-dihydrobenzofuran system has been demonstrated. Bravo and co-workers have earlier shown that the reaction of dimethylsulfoxonium methylides on 2-hydroxyaryl-α,β-unsaturated ketones gives 2,3-dihydrobenzofurans.[10] However, to our knowledge, the synthetic potential of this reaction for the diastereoselective synthesis of 2,3-disubstituted dihydrobenzofurans has not been explored. As there has been considerable interest in the synthesis of 2,3-disubstituted dihydrobenzofuran systems due to the presence of this moiety in many biologically active natural products such as (±)-obtusafuran,[11] (±)-liliflol-B,[12] (±)-kadsurinone,[13] (±)-denudatin,[14] (±)-conocarpan,[15] and (+)-lithospermic acid,[16] we considered it worthwhile to investigate the scope and utility of this methylene group transfer reaction for the diastereoselective synthesis of such systems.

We report herein the reactions of 2-hydroxyaryl-α,β-unsaturated ketones with dimethylsulfonium carbonylmethylides, which lead to the formation of 2,3-disubstituted dihydrobenzofurans in good yields with high diastereoselectivity.

2. Results and discussion

The methylene group transfer reactions of 2-hydroxyaryl-α,β-unsaturated ketones **1a**–**f** with dimethylsulfonium carboethoxymethylide **2** and dimethylsulfonium phenacylide **3** were carried out in dry benzene at 80 °C, which gave corresponding 2,3-dihydrobenzofurans **4a**–**f** and **5a**–**f** along with cyclopropane derivatives **6a**–**f** (Scheme 1). Although, in the former case, diastereoisomeric mixtures of *trans* and *cis* isomers (*trans*≫*cis*) of 2,3-dihydrobenzofuran derivatives were obtained, in the latter case, exclusively the *trans* isomers were formed. The geometry of these diastereomers was assigned on the basis of their ^{1}H NMR signals. In compounds

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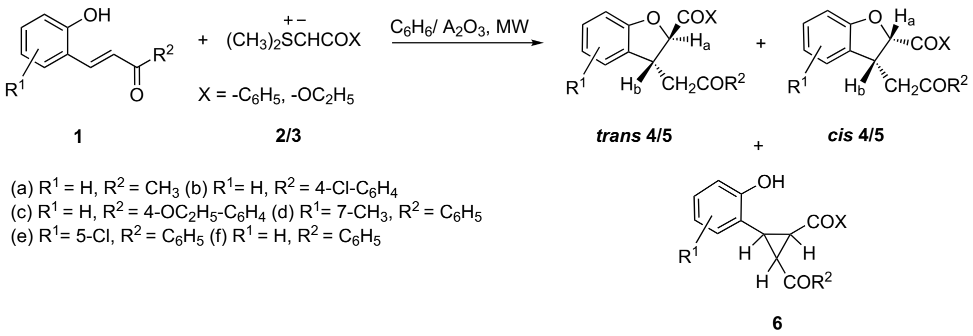
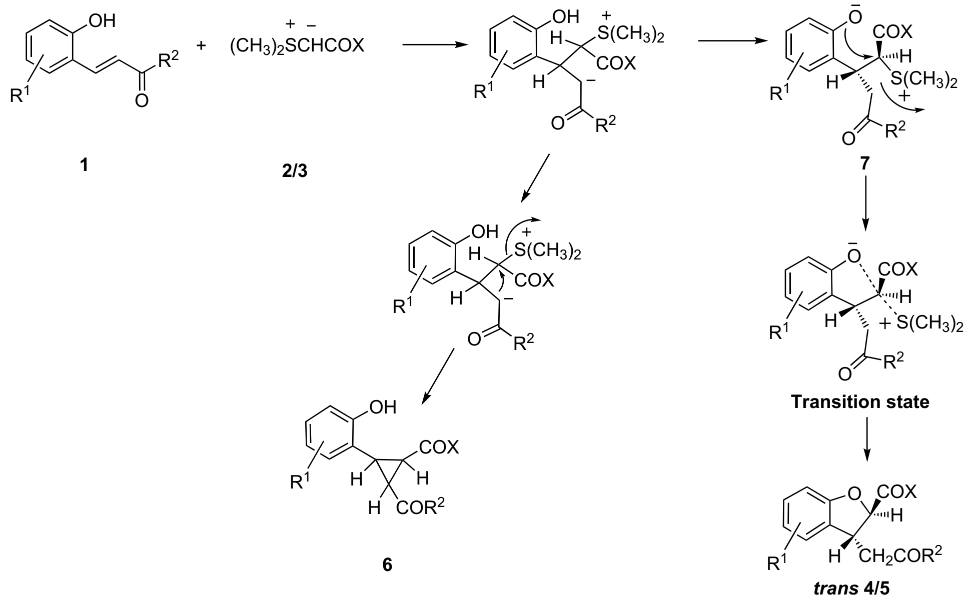


Scheme 1. Synthesis of *trans*/*cis* dihydrobenzofurans **4**/**5** and **6**.



Scheme 2. Plausible mechanism for the formation of *trans* **4**/**5** and **6**.

4a–**f**, the C2-protons of *trans* isomers appear at *δ* 4.88–4.76, whereas in *cis* isomers, these appear at *δ* 5.38–5.26. Hence, the protons in the *trans* isomers appear ≈0.5–0.6 ppm upfield as compared to the *cis* isomers. The coupling constants of these 2,3-*trans*-protons ($J_{Ha\text{-}Hb}$=5–6 Hz) were less than that of the *cis*-protons ($J_{Ha\text{-}Hb}$=9 Hz).[17] In the ^{13}C NMR spectra, the carbons bearing the *cis*-substituents appear upfield than the *trans*-substituted carbons (signals for the *trans* isomer appear at around *δ* 84.70, 44.20, whereas for the *cis* isomer they are obtained at around *δ* 82.59, 40.17).

The formation of the 2,3-dihydrobenzofurans can be envisaged as shown in Scheme 2. The reaction may presumably be proceeding through the initial formation of the intermediate **7** by the attack of the ylide on the double bond, which undergoes elimination–cyclization to give the dihyrobenzofuran derivatives. As our results show the predominance of the formation of the *trans* isomers in both cases, the intermediate **7** seems to adopt more stable transition state (*trans*-geometry) for the attack of the phenoxide ion and leads to the preferential formation of the *trans* isomers. The formation of the cyclopropane derivatives in these reactions is not surprising as the formation of cyclopropane ring through the reaction of α,β-unsaturated ketones and stabilized sulfur ylides is well-known.[18–22]

Table 1

The *trans*/*cis* ratio and yields of 2,3-disubstituted dihydrobenzofurans

Compd no.[a]	R1	R2	Conventional heating[b]		Microwave activation[c]	
			trans/*cis*[d]	Yield %[e]	*trans*/*cis*[d]	Yield %[e]
4a	H	CH_3	75:25	82	85:15	93
4b	H	4-Cl-C_6H_4	73:27	80	87:13	95
4c	H	4-OC_2H_5-C_6H_4	76:24	81	82:18	93
4d	7-CH_3	C_6H_5	78:22	78	91:9	95
4e	5-Cl	C_6H_5	73:27	75	87:13	90
4f	H	C_6H_5	73:27	82	86:14	90
5a	H	CH_3	100:0	58	100:0	82
5b	H	4-Cl-C_6H_4	100:0	54	100:0	79
5c	H	4-OC_2H_5-C_6H_4	100:0	55	100:0	84
5d	7-CH_3	C_6H_5	100:0	58	100:0	80
5e	5-Cl	C_6H_5	100:0	56	100:0	78
5f	H	C_6H_5	100:0	52	100:0	72

[a] Products were characterized by NMR, IR, and HRMS.

[b] All reactions were carried out in dry benzene at 80 °C for 2–3 h.

[c] All reactions were carried out on Al_2O_3, initially at 160 W/5 min/90 °C then 320 W/2 min/110 °C.

[d] Ratio of isomers were determined by ^{1}H NMR spectroscopic analysis of the reaction mixture.

[e] Isolated, unoptimized yields.

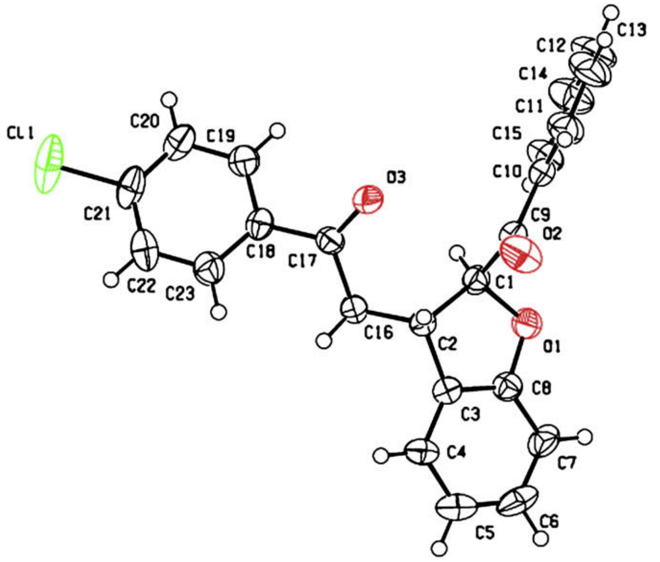


Figure 1. ORTEP diagram of *trans*-2-benzoyl-3-(4-chloro)benzoylmethyl-2,3-dihydrobenzofuran **5b** showing labeling scheme.

However, we found that the reactions leading to the formation of 2,3-dihydrobenzofuran and cyclopropane were competitive and their ratio was dependent on the substituents of the sulfur ylides. In the case of dimethylsulfonium carboethoxymethylide, the average ratio of dihydrobenzofuran to cyclopropane was 90:10 as compared to the case of dimethylsulfonium phenacylide where it was found to be 55:45. The possibility of the formation of the dihydrobenzofurans through the opening of the initially formed cyclopropanes was ruled out, as there was no change in their ratio even after prolonging the reaction time for additional 2 h.

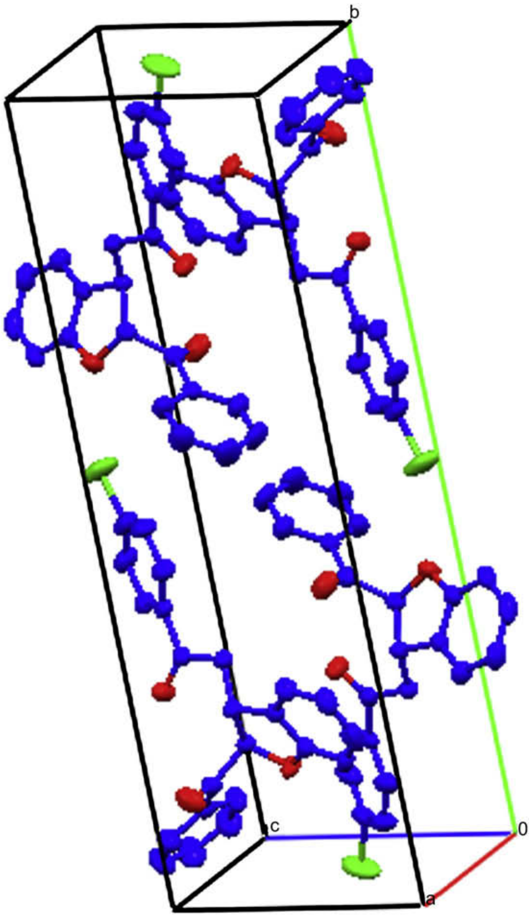


Figure 2. Unit cell packing of **5b** showing four molecules in one unit cell (hydrogen atoms omitted for clarity).

In view of increasing the efficiency and selectivity of these reactions, we carried out these reactions under solvent-free microwave conditions. Interestingly, we found that the microwave activation not only made the reactions much cleaner, faster, and more diastereoselective for the *trans* isomers, it also substantially decreased the formation of the cyclopropane derivatives. In the case of phenacylide, the dihydrobenzofuran to cyclopropane ratio changed to 80:20, whereas no significant formation of the cyclopropane derivatives was observed in the case of dimethylsulfonium carboethoxymethylide. Hence, the microwave condition makes these reactions more synthetically useful. The reaction conditions and the yields for the formation of **4a**–**f** and **5a**–**f** are given in Table 1.

3. X-ray crystallographic studies of *trans*-2-benzoyl-3-(4-chloro)benzoylmethyl-2,3-dihydrobenzofuran 5b

The geometry of compound **5b** has also been confirmed by single crystal X-ray as shown in Figure 1. Its unit cell packing diagram is given in Figure 2. Colorless needle-shaped crystals of **5b** were grown by slow evaporation of its ethyl acetate/hexane solution. The crystal system of **5b** is monoclinic and reveals *trans*-geometry of C1–C2 protons. All the bond lengths and bond angles are normal and lie within the expected ranges, i.e., O1–C1=1.463(5), C1–C2=1.537(6), C2–C3=1.500(6), C2–C16=1.521(6), C1–C9=1.539(6), C1–H1 and C2–H2=0.9800 Å. Torsion angle between H2–C1–C2–H1=128.22° confirms the *trans*-geometry, and C9–C1–C2–C16=118.54° shows that the phenyl ring of 2-benzoyl group and phenyl ring of 3-(4-chloro)benzoylmethyl group are completely staggered.

It also forms an intermolecular O···H bond between oxygen of 2-positioned benzoyl group and a *meta*-hydrogen of 3-positioned phenyl ring of (4-chloro)benzoylmethyl group within a distance of 2.822 Å (Fig. 3). There is also an intermolecular CH···π interaction between an *ortho*-hydrogen of 3-positioned phenyl ring of (4-chloro)benzoylmethyl group and π-cloud of phenyl ring of dihydrobenzofuran unit within a distance of 2.856 Å (Fig. 4). These two major interactions cause the aggregation of molecules in the solid state.

4. Conclusion

In summary, we have described the potential of the reactions of 2-hydroxyaryl-α,β-unsaturated ketones with dimethylsulfonium carbonylmethylides as a general synthetic methodology for the diastereoselective synthesis of 2,3-disubstituted dihydrobenzofurans. This may find its useful applications in the synthesis of many natural products containing 2,3-disubstituted dihydrobenzofuran moiety.

5. Experimental

5.1. General

All the reagents used in this study were purchased from Sigma–Aldrich or Merck and were chemically pure. All the heating reactions were carried out under a nitrogen atmosphere and the solvents used were dried and distilled. Benzene was dried over sodium and benzophenone, and distilled before use. For all microwave-induced reactions, focused microwave reactor Pelco was used. All reactions have been carried out in reaction vials with control of power, temperature and time. The reaction

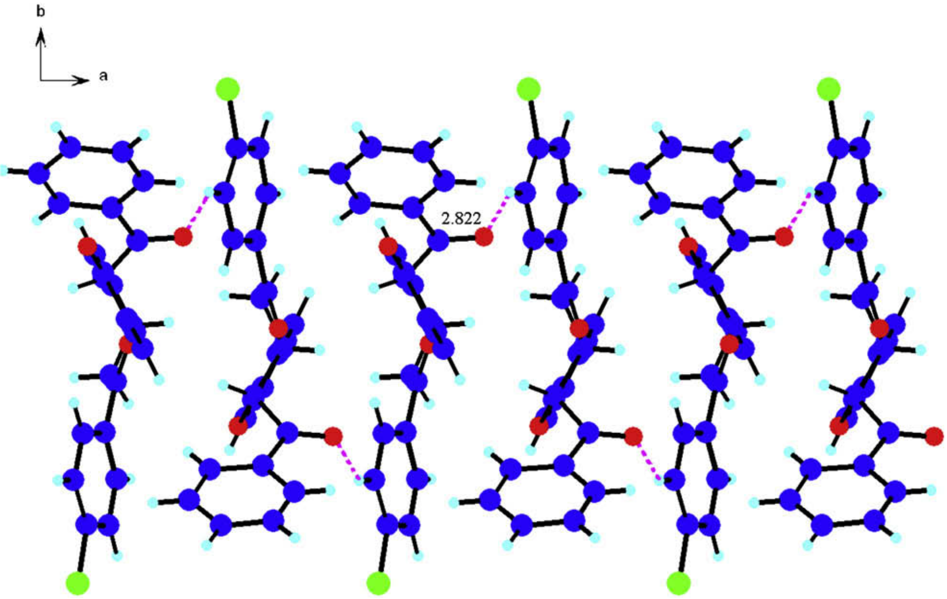


Figure 3. Ball and stick model of $\mathbf{C_{23}H_{17}O_{3}Cl}$ (**5b**) showing intermolecular O···H bonding interaction (2.822 Å) along *c* axis in the solid state.

vials were placed in the MW reactor supplied with a safety valve for release of overpressure. After reaching the set temperature, the power regulates itself to maintain the reaction temperature. Monitoring of the reaction was carried out on silica gel TLC plates (Silica Merck 60 F_{254}) using hexane/EtOAc (9:1) as solvent. Column chromatography was performed using silica gel (60–120 mesh). Unless otherwise specified, anhydrous Na_2SO_4 was used as the drying agent. Melting points were determined using an ELECTRON Bombay micro melting point apparatus and are uncorrected. IR absorption spectra were recorded on Nicolet 5DX FTIR instrument and values are reported in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a DPX-300 Brucker spectrometer. X-ray data was recorded using a Brucker SMART CCD single crystal diffractometer. High-resolution mass spectra (HRMS) were recorded on QSTAR EXCEL APPLIED BIOSYSTEM spectrometer, at IIT Delhi.

5.2. General method of synthesis of 2-hydroxyaryl-α,β-unsaturated ketones and dimethylsulfonium carboethoxymethylide/dimethylsulfonium phenacylide

2-Hydroxyaryl-α,β-unsaturated ketones **1a**–**f** were prepared from aldol condensation of appropriate ketones with salicylaldehyde.[23] Dimethylsulfonium carboethoxymethylide **2** and dimethylsulfonium phenacylide **3** were prepared by the methods of Payne[18] and Trost,[21] respectively.

5.3. General method for the synthesis of 4, 5, and 6 in solution phase

2-Hydroxyaryl-α,β-unsaturated ketone **1** (1 mmol) was taken in dry benzene (25 ml) and the solution was stirred at 80 °C under nitrogen atmosphere for 15 min. Thereafter, a solution of dimethylsulfonium carboethoxymethylide **2** (3 mmol)/dimethylsulfonium phenacylide **3** (3 mmol) in benzene was added and the stirring continued for 2–3 h at the same temperature under nitrogen atmosphere. The reaction was quenched by addition of cold water. Organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product obtained was purified by column chromatography on silica gel (eluent, hexane/EtOAc, 98:2), which gave *cis* isomers of **4** (R_f=0.85–0.80), further elution with the same solvent gave *trans* isomers of **4** (R_f=0.82–0.78). Similarly, column chromatography of the reaction product **5** on silica gel (eluent, hexane/EtOAc, 98:2) gave *trans* isomers of **5** (R_f=0.80–0.78). Elution with (hexane/EtOAc, 98:4) gave **6** (R_f=0.68–0.66) (yield of **6**, 42–46%).

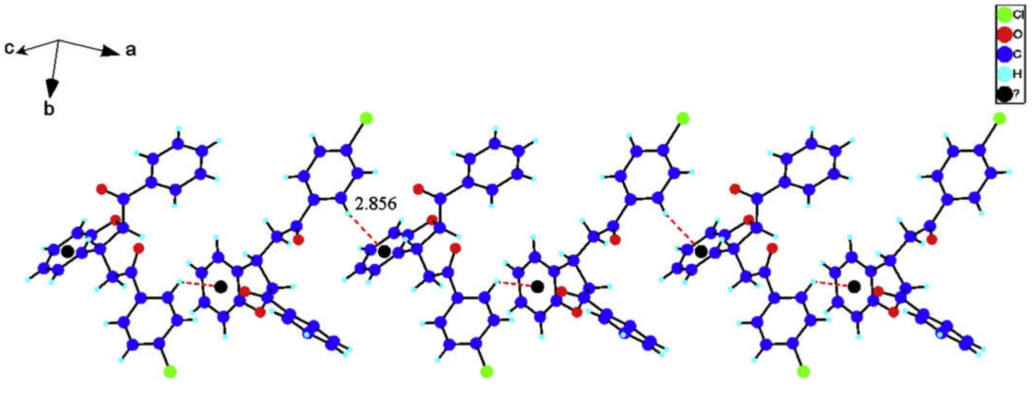


Figure 4. Ball and stick model of $\mathbf{C_{23}H_{17}O_{3}Cl}$ (**5b**) showing intermolecular CH···π interaction (2.856 Å) in 3D.

5.4. General method for the synthesis of 4, 5, and 6 under microwave activation

2-Hydroxyaryl-α,β-unsaturated ketone **1** (1 mmol) and dimethylsulfonium carboethoxymethylide **2** (3 mmol)/dimethylsulfonium phenacylide **3** (3 mmol) were loaded on neutral alumina (0.5 mmol). This mixture was irradiated with microwaves for the specified time (Table 1). The reaction was quenched by addition of cold water. The product was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude products obtained were purified by column chromatography on silica gel as described above (Section 5.3) (yield of **6**, 18–21%).

5.4.1. *trans-3-Acetylmethyl-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4a***

Viscous liquid. R_f 0.78 (hexane/EtOAc 9:1), yield 83%. IR: ν_{max} (cm^{-1}) 1744.12, 1668.52 (CO). δ_H (300 MHz, $CDCl_3$): 7.19–6.81 (m, 4H, ArH), 4.76 (d, J=6.3 Hz, 1H, C2-H), 4.27 (q, 2H, J=7.0 Hz, $-COOCH_2$), 4.10–4.06 (m, 1H, C3-H), 3.10–2.80 (m, 2H, $-CH_2CO$), 2.21 (s, 3H, $-CH_3$), 1.29 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 205.98, 170.34, 158.60, 128.81–109.87 (ArC), 84.42, 61.60, 48.81, 41.48, 30.15, 14.03. HRMS: m/z calcd for $C_{14}H_{16}O_4K$: 287.0686 $[M+K]^+$, found: 287.0689.

5.4.2. *cis-3-Acetylmethyl-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4a***

White crystalline solid, mp 103–105 °C. R_f 0.80 (hexane/EtOAc 9:1), yield 10%. IR: ν_{max} (cm^{-1}) 1744.12, 1668.52 (CO). δ_H (300 MHz, $CDCl_3$): 7.19–6.86 (m, 4H, ArH), 5.25 (d, J=9.0 Hz, 1H, C2-H), 4.29–4.14 (m, 3H, $-COOCH_2$ and C3-H), 2.86–2.71 (m, 2H, $-CH_2CO$), 2.15 (s, 3H, $-CH_3$), 1.31 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 205.78, 169.43, 158.58, 128.87–110.01 (ArC), 82.41, 61.66, 44.80, 39.64, 30.26, 14.14. HRMS: m/z calcd for $C_{14}H_{16}O_4K$: 287.0686 $[M+K]^+$, found: 287.0688.

5.4.3. *trans-3-(4-Chloro)benzoylmethyl-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4b***

Viscous liquid. R_f 0.81 (hexane/EtOAc 9:1), yield 84%. IR: ν_{max} (cm^{-1}) 1745.20, 1685.07 (CO). δ_H (300 MHz, $CDCl_3$): 7.92–6.86 (m, 8H, ArH), 4.86 (d, J=6.0 Hz, 1H, C2-H), 4.31–4.24 (m, 3H, $-COOCH_2$ and C3-H), 3.55–3.34 (m, 2H, $-CH_2CO$), 1.30 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 196.22, 170.40, 158.78, 140.02–110.05 (ArC), 84.70, 61.74, 44.23, 41.82, 14.12. HRMS: m/z calcd for $C_{19}H_{17}O_4ClNa$: 367.0713 $[M+Na]^+$, found: 367.0713.

5.4.4. *cis-3-(4-Chloro)benzoylmethyl-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4b***

White crystalline solid, mp 88–89 °C. R_f 0.83 (hexane/EtOAc 9:1), yield 11%. IR: ν_{max} (cm^{-1}) 1745.20, 1685.07 (CO). δ_H (300 MHz, $CDCl_3$): 7.88–6.86 (m, 8H, ArH), 5.36 (d, J=9.0 Hz, 1H, C2-H), 4.52–4.44 (m, 1H, C3-H), 4.23–4.12 (m, 1H, $-COOCHH$), 4.07–3.97 (m, 1H, $-COOCHH$), 3.39–3.22 (m, 2H, $-CH_2CO$), 1.17 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 196.10, 169.45, 158.72, 139.96–110.13 (ArC), 82.59, 61.48, 40.17, 39.96, 14.05. HRMS: m/z calcd for $C_{19}H_{18}O_4Cl$: 345.0894 $[M+H]^+$, found: 345.0897.

5.4.5. *trans-3-(4-Ethoxy)benzoylmethyl-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4c***

Viscous liquid. R_f 0.82 (hexane/EtOAc 9:1), yield 80%. IR: ν_{max} (cm^{-1}) 1748.07, 1673.43 (CO). δ_H (300 MHz, $CDCl_3$): 7.97–6.87 (m, 8H, ArH), 4.87 (d, J=6.6 Hz, 1H, C2-H), 4.33–4.27 (m, 3H, $-COOCH_2$ and C3-H), 4.15–4.00 (q, J=6.9 Hz, 2H, $-OCH_2$), 3.55–3.32 (m, 2H, $-CH_2CO$), 1.44 (t, J=6.9 Hz, 3H, $-OCH_2CH_3$), 1.30 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 195.85, 170.50, 163.21, 158.81, 131.06–109.94 (ArC), 84.85, 63.80, 61.64, 43.90, 42.03, 14.63, 14.12. HRMS: m/z calcd for $C_{21}H_{22}O_5$: 354.1467 $[M]^+$, found: 354.1462.

5.4.6. *cis-3-(4-Ethoxy)benzoylmethyl-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4c***

White crystalline solid, mp 81–83 °C, R_f 0.85 (hexane/EtOAc 9:1), yield 13%. IR: ν_{max} (cm^{-1}) 1748.07, 1673.43 (CO). δ_H (300 MHz, $CDCl_3$): 7.92–6.87 (m, 8H, ArH), 5.38 (d, J=9.0 Hz, 1H, C2-H), 4.56–4.48 (m, 1H, C3-H), 4.23–3.96 (m, 4H, $-OCH_2$ and $-COOCH_2$), 3.37–3.22 (m, 2H, $-CH_2CO$), 1.45 (t, J=6.9 Hz, 3H, $-OCH_2CH_3$), 1.15 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 195.69, 169.53, 163.16, 158.77, 130.28–109.99 (ArC), 82.75, 63.79, 61.39, 40.09, 39.76, 14.62, 14.00. HRMS: m/z calcd for $C_{21}H_{23}O_5$: 355.1545 $[M+H]^+$, found: 355.1545.

5.4.7. *trans-3-Benzoylmethyl-2-ethoxycarbonyl-7-methyl-2,3-dihydrobenzofuran* ***4d***

Viscous liquid. R_f 0.81 (hexane/EtOAc 9:1), yield 84%. IR: ν_{max} (cm^{-1}) 1750.50, 1683.73 (CO). δ_H (300 MHz, $CDCl_3$): 8.04–6.77 (m, 8H, ArH), 4.86 (d, J=6.0 Hz, 1H, C2-H), 4.31–4.23 (m, 3H, $-COOCH_2$ and C3-H), 3.59–3.31 (m, 2H, $-CH_2CO$), 2.27 (s, 3H, $-CH_3$), 1.30 (t, J=7.0 Hz, 3H, $COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 197.32, 170.46, 157.10, 136.26–119.92 (ArC), 84.74, 61.09, 44.10, 42.07, 14.98, 13.92. HRMS: m/z calcd for $C_{20}H_{21}O_4$: 325.1440 $[M+H]^+$, found: 325.1427.

5.4.8. *cis-3-Benzoylmethyl-2-ethoxycarbonyl-7-methyl-2,3-dihydrobenzofuran* ***4d***

Viscous liquid. R_f 0.83 (hexane/EtOAc 9:1), yield 9%. IR: ν_{max} (cm^{-1}) 1750.50, 1683.73 (CO). δ_H (300 MHz, $CDCl_3$): 7.92–6.87 (m, 8H, ArH), 5.38 (d, J=9.0 Hz, 1H, C2-H), 4.64–4.48 (m, 1H, C3-H), 4.25–4.01 (m, 2H, $-COOCH_2$), 3.22–3.31 (m, 2H, $-CH_2CO$), 2.29 (s, 3H, $-CH_3$), 1.16 (t, J=7.0 Hz, 3H, $COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 197.30, 169.88, 157.02, 136.20–118.47 (ArC), 82.41, 60.97, 40.26, 30.38, 14.12, 13.89. HRMS: m/z calcd for $C_{20}H_{20}O_4K$: 363.0999 $[M+K]^+$, found: 363.0991.

5.4.9. *trans-3-Benzoylmethyl-5-chloro-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4e***

Viscous liquid. R_f 0.79 (hexane/EtOAc 9:1), yield 79%. IR: ν_{max} (cm^{-1}) 1745.20, 1685.07 (CO). δ_H (300 MHz, $CDCl_3$): 7.92–6.86 (m, 8H, ArH), 4.86 (d, J=6.0 Hz, 1H, C2-H), 4.31–4.24 (m, 3H, $-COOCH_2$ and C3-H), 3.55–3.34 (m, 2H, $-CH_2CO$), 1.30 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 196.22, 170.40, 158.78, 140.02–110.05 (ArC), 84.70, 61.74, 44.23, 41.82, 14.12. HRMS: m/z calcd for $C_{19}H_{17}O_4ClNa$: 367.0713 $[M+Na]^+$, found: 367.0699.

5.4.10. *cis-3-Benzoylmethyl-5-chloro-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4e***

White crystalline solid, mp 92–93 °C. R_f 0.81 (hexane/EtOAc 9:1), yield 11%. IR: ν_{max} (cm^{-1}) 1745.20, 1685.07 (CO). δ_H (300 MHz, $CDCl_3$): 7.88–6.86 (m, 8H, ArH), 5.36 (d, J=9.0 Hz, 1H, C2-H), 4.52–4.44 (m, 1H, C3-H), 4.23–4.12 (m, 1H, $-COOCHH$), 4.07–3.97 (m, 1H, $-COOCHH$), 3.39–3.22 (m, 2H, $-CH_2CO$), 1.17 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 196.10, 169.45, 158.72, 139.96–110.13 (ArC), 82.59, 61.48, 40.17, 39.96, 14.05. HRMS: m/z calcd for $C_{19}H_{18}O_4Cl$: 345.0894 $[M+H]^+$, found: 345.0896.

5.4.11. *trans-3-Benzoylmethyl-2-ethoxycarbonyl-2,3-dihydrobenzofuran* ***4f***

Viscous liquid. R_f 0.80 (hexane/EtOAc 9:1), yield 79%. IR: ν_{max} (cm^{-1}) 1745.9, 1683.48 (CO). δ_H (300 MHz, $CDCl_3$): 7.99–6.86 (m, 9H, ArH), 4.88 (d, J=6.3 Hz, 1H, C2-H), 4.32–4.25 (m, 3H, $-COOCH_2$ and C3-H), 3.60–3.38 (m, 2H, $-CH_2CO$), 1.26 (t, J=7.0 Hz, 3H, $-COOCH_2CH_3$). δ_C (75 MHz, $CDCl_3$): 197.32, 170.36, 158.74, 136.34–109.10 (ArC), 84.72, 61.57, 44.19, 41.81, 14.04. HRMS: m/z calcd for $C_{19}H_{18}O_4Na$: 333.1103 $[M+Na]^+$, found: 333.1117.

5.4.12. cis-3-Benzoylmethyl-2-ethoxycarbonyl-2,3-dihydrobenzofuran ***4f***

White crystalline solid, mp 64–65 °C. R_f 0.83 (hexane/EtOAc 9:1), yield 11%. IR: ν_{max} (cm^{-1}) 1745.9, 1683.48 (CO). δ_H (300 MHz, CDCl$_3$): 7.94–6.86 (m, 9H, ArH), 5.38 (d, J=9.0 Hz, 1H, C2-H), 4.55–4.47 (m, 1H, C3-H), 4.23–4.14 (m, 1H, –COOC*H*H), 4.06–3.95 (m, 1H, –COOCH*H*), 3.47–3.27 (m, 2H, –CH$_2$CO), 1.15 (t, J=7.0 Hz, 3H, –COOCH$_2$C*H*$_3$). δ_C (75 MHz, CDCl$_3$): 197.27, 169.51, 158.80, 136.50–110.07 (ArC), 82.70, 61.46, 40.21, 40.02, 14.02. HRMS: m/z calcd for $C_{19}H_{18}O_4K$: 349.0842 [M+K]$^+$, found: 349.0842.

5.4.13. trans-2-Benzoyl-3-acetylmethyl-2,3-dihydrobenzofuran ***5a***

White crystalline solid, mp 95–96 °C. R_f 0.83 (hexane/EtOAc 9:1), yield 82%. IR: ν_{max} (cm^{-1}) 1693.06 (CO). δ_H (300 MHz, CDCl$_3$): 8.00–6.83 (m, 9H, ArH), 5.51 (d, J=5.7 Hz, 1H, C2-H), 4.37–4.31 (m, 1H, C3-H), 3.09–2.85 (m, 2H, –CH$_2$CO), 2.18 (s, 3H, –CH$_3$). δ_C (75 MHz, CDCl$_3$): 206.65, 195.02, 158.47, 137.75–110.03 (ArC), 87.50, 47.95, 39.53, 26.93. HRMS: m/z calcd for $C_{18}H_{16}O_3Na$: 303.0997 [M+Na]$^+$, found: 303.0998.

5.4.14. trans-2-Benzoyl-3-(4-chloro)benzoylmethyl-2,3-dihydrobenzofuran ***5b***

White crystalline solid, mp 125–126 °C. R_f 0.84 (hexane/EtOAc 9:1), yield 79%. IR: ν_{max} (cm^{-1}) 1683.88 (CO). δ_H (300 MHz, CDCl$_3$): 8.09–6.84 (m, 13H, ArH), 5.63 (d, J=5.5 Hz, 1H, C2-H), 4.58–4.51 (m, 1H, C3-H), 3.63–3.34 (m, 2H, –CH$_2$CO). δ_C (75 MHz, CDCl$_3$): 197.74, 194.73, 158.57, 136.39–109.95 (ArC), 87.61, 44.08, 39.58. HRMS: m/z calcd for $C_{23}H_{17}O_3ClNa$: 399.0764 [M+Na]$^+$, found: 399.0768.

5.4.15. trans-2-Benzoyl-3-(4-ethoxy)benzoylmethyl-2,3-dihydrobenzofuran ***5c***

White crystalline solid, mp 97–98 °C. R_f 0.85 (hexane/EtOAc 9:1), yield 84%. IR: ν_{max} (cm^{-1}) 1663.42 (CO). δ_H (300 MHz, CDCl$_3$): 8.10–6.85 (m, 13H, ArH), 5.65 (d, J=5.4 Hz, 1H, C2-H), 4.55–4.51 (m, 1H, C3-H), 4.12–4.05 (q, J=6.9 Hz, 2H, –OCH$_2$), 3.62–3.32 (m, 2H, –CH$_2$CO), 1.43 (t, J=6.9 Hz, 3H, –OCH$_2$C*H*$_3$). δ_C (75 MHz, CDCl$_3$): 196.19, 194.81, 163.20, 158.60, 134.97–109.91 (ArC), 87.64, 63.79, 43.70, 39.80, 14.63. HRMS: m/z calcd for $C_{25}H_{22}O_4Na$: 409.1416 [M+Na]$^+$, found: 409.1409.

5.4.16. trans-2-Benzoyl-3-benzoylmethyl-7-methyl-2,3-dihydrobenzofuran ***5d***

White crystalline solid, mp 103–104 °C. R_f 0.84 (hexane/EtOAc 9:1), yield 80%. IR: ν_{max} (cm^{-1}) 1677.48 (CO). δ_H (300 MHz, CDCl$_3$): 8.12–6.79 (m, 13H, ArH), 5.62 (d, J=5.4 Hz, 1H, C2-H), 4.57–4.51 (m, 1H, C3-H), 3.67–3.38 (m, 2H, –CH$_2$CO), 2.21 (s, 3H, –CH$_3$). δ_C (75 MHz, CDCl$_3$): 197.82, 195.21, 157.01, 136.46–120.18 (ArC), 87.60, 44.14, 40.13, 15.13. HRMS: m/z calcd for $C_{24}H_{20}O_3Na$: 379.1310 [M+Na]$^+$, found: 379.1322.

5.4.17. trans-2-Benzoyl-3-benzoylmethyl-5-chloro-2,3-dihydrobenzofuran ***5e***

White crystalline solid, mp 128–129 °C. R_f 0.84 (hexane/EtOAc 9:1), yield 78%. IR: ν_{max} (cm^{-1}) 1683.88 (CO). δ_H (300 MHz, CDCl$_3$): 8.09–6.84 (m, 13H, ArH), 5.63 (d, J=5.5 Hz, 1H, C2-H), 4.58–4.51 (m, 1H, C3-H), 3.63–3.34 (m, 2H, –CH$_2$CO). δ_C (75 MHz, CDCl$_3$): 197.74, 194.73, 158.57, 136.39–109.95 (ArC), 87.61, 44.08, 39.58. HRMS: m/z calcd for $C_{23}H_{17}O_3ClNa$: 399.0764 [M+Na]$^+$, found: 399.0769.

5.4.18. trans-2-Benzoyl-3-benzoylmethyl-2,3-dihydrobenzofuran ***5f***

White crystalline solid, mp 95–96 °C. R_f 0.85 (hexane/EtOAc 9:1), yield 72%. IR: ν_{max} (cm^{-1}) 1689.17 (CO). δ_H (300 MHz, CDCl$_3$): 8.10–6.85 (m, 14H, ArH), 5.65 (d, J=5.1 Hz, 1H, C2-H), 4.59–4.53 (m, 1H, C3-H), 3.68–3.39 (m, 2H, –CH$_2$CO). δ_C (75 MHz, CDCl$_3$): 197.74, 194.73, 158.57, 136.39–109.95 (ArC), 87.61, 44.08, 39.58. HRMS: m/z calcd for $C_{23}H_{18}O_3K$: 381.0893 [M+K]$^+$, found: 381.0892.

5.4.19. Benzoyl-2-(4-chloro)benzoyl-3-(2-hydroxyphenyl)-cyclopropane ***6b***

White crystalline solid, mp 110–112 °C. R_f 0.67 (hexane/EtOAc 9:1), yield 18%. IR: ν_{max} (cm^{-1}) 3419.6 (OH), 1664.7, 1649.4 (CO). δ_H (300 MHz, CDCl$_3$): 8.02–6.88 (m, 13H, ArH), 5.02 (br s, 1H, –OH), 4.23 (t, J=4.8 Hz, 1H, –CHCOAr), 3.82 (dd, J=10.0 and 4.8 Hz, 1H, –ArCH), 3.54 (dd, J=10.0 and 4.8 Hz, 1H, –CHCOAr). δ_C (75 MHz, CDCl$_3$): 197.57, 193.81, 154.78, 139.50–115.22 (ArC), 36.31, 34.22, 29.73. HRMS: m/z calcd for $C_{23}H_{17}O_3ClNa$: 399.0764 [M+Na]$^+$, found: 399.0770.

5.4.20. 1,2-Dibenzoyl-3-(2-hydroxyphenyl)cyclopropane ***6f***

White crystalline solid, mp 152–153 °C. R_f 0.68 (hexane/EtOAc 9:1), yield 20%. IR: ν_{max} (cm^{-1}) 3403.9 (OH), 1672.6, 1649.8 (CO). δ_H (300 MHz, CDCl$_3$): 8.21–6.58 (m, 14H, ArH), 5.49 (br s, 1H, –OH), 4.24 (t, J=4.8 Hz, 1H, –CHCOAr), 3.77 (dd, J=10.0 and 4.8 Hz, 1H, –ArCH), 3.62 (dd, J=10.0 and 4.8 Hz, 1H, –CHCOAr). δ_C (75 MHz, CDCl$_3$): 197.48, 193.21, 154.28, 142.36–108.92 (ArC), 43.08, 41.24, 37.72. HRMS: m/z calcd for $C_{23}H_{18}O_3K$: 381.0893 [M+K]$^+$, found: 381.0912.

5.5. Crystal data for 5b

Colorless crystals with dimension of 0.42×0.16×0.11 mm were obtained by slow evaporation of compound **5b** in ethyl acetate/hexane solution, having molecular formula $C_{23}H_{17}O_3Cl$, MW=376.82, monoclinic, space group $P21/n$, a=8.6018(16), b=23.854(5), c=9.8911(19) Å, α=90.00°, β=115.229(3)°, γ=90.00°, V=1835.9(6) Å^3, T=273 K, D_x=1.363 g cm^{-3}, Z=4, λ=0.71073 Å, ω and ϕ scans, 3410 reflections collected and, 2709 [$I \geq 2\sigma(I)$] were considered, observed and used in the structure analysis and refinement. R_1/wR_2 ($I \geq 2\sigma(I)$)=0.1140/0.2235 and R_1/wR_2 (all data)=0.1470/0.2227. Although value of R_1 is slightly higher than 0.10 but low e.s.d.'s for all other atoms suggest that the overall geometry and accuracy of the structure is not compromised to any significant extent. Crystallographic data for the structure have been deposited with Cambridge Crystallographic Database Center as supplementary publication number CCDC 675499.

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Supplementary data

^{1}H and ^{13}C NMR spectra of representative compounds are available in Supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.041.

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