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SYNTHESIS AND UNAMBIGUOUS STEREOCHEMICAL DETERMINATION OF 1-*exo*- AND 1-*endo*-1-ARYL-1,2,2a,8b-TETRAHYDRO-3*H*-BENZO[*b*]CYCLOBUTA[*d*]PYRAN-3-ONES

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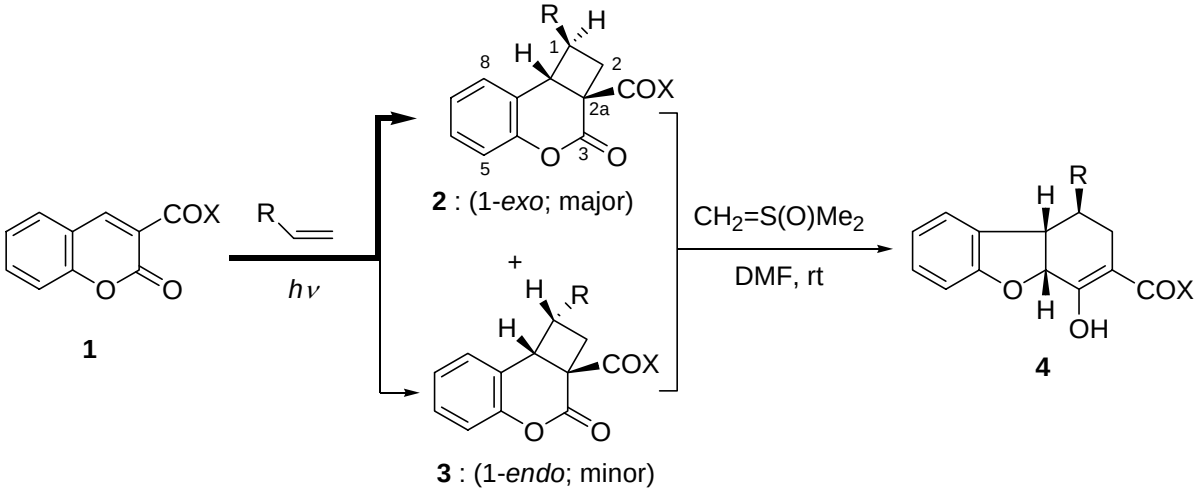
Abstract – Stereoselective preparation of 1-*exo*-substituted 1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**2**) was achieved by photo [2+2] cycloaddition of olefins to 3-substituted coumarins (**1**). 1-*endo*-Substituted 1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**3**) were stereoselectively prepared by hydrogenation over the Pd-carbon of 2a,8b-dihydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**5**), which were obtained by photo [2+2] cycloaddition of the coumarins (**1**) to acetylenes. The stereochemistry of 1-*exo*- and 1-*endo*-arylcyclobutanes (**2** and **3**) could be easily determined on the basis of the ^{1}H-NMR spectrum, in which the C8-proton in **3** was strongly shielded by the 1-aryl ring but that in **2** was not.

INTRODUCTION

The photo [2+2] cycloaddition of alkenes has been a highly useful methodology for preparation of cyclobutane compounds in organic synthesis because of two new carbon-carbon bond formations introducing four new stereocenters at the maximum.[1] With respect to the photocycloaddition of the coumarins having an appropriate electron-withdrawing group at the 3-position (**1**) to olefins, there have been several reports, to the best of our knowledge.[2] In the cases of the photocycloaddition of the coumarins (**1**) and monosubstituted olefins, only or mainly 1-*exo*-substituted 1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**2**) were obtained. It could be clearly assigned on the basis of the ^{1}H-NMR spectra that the R group in **2** and **3** located at the 1-position, but

their stereochemistries were vague.

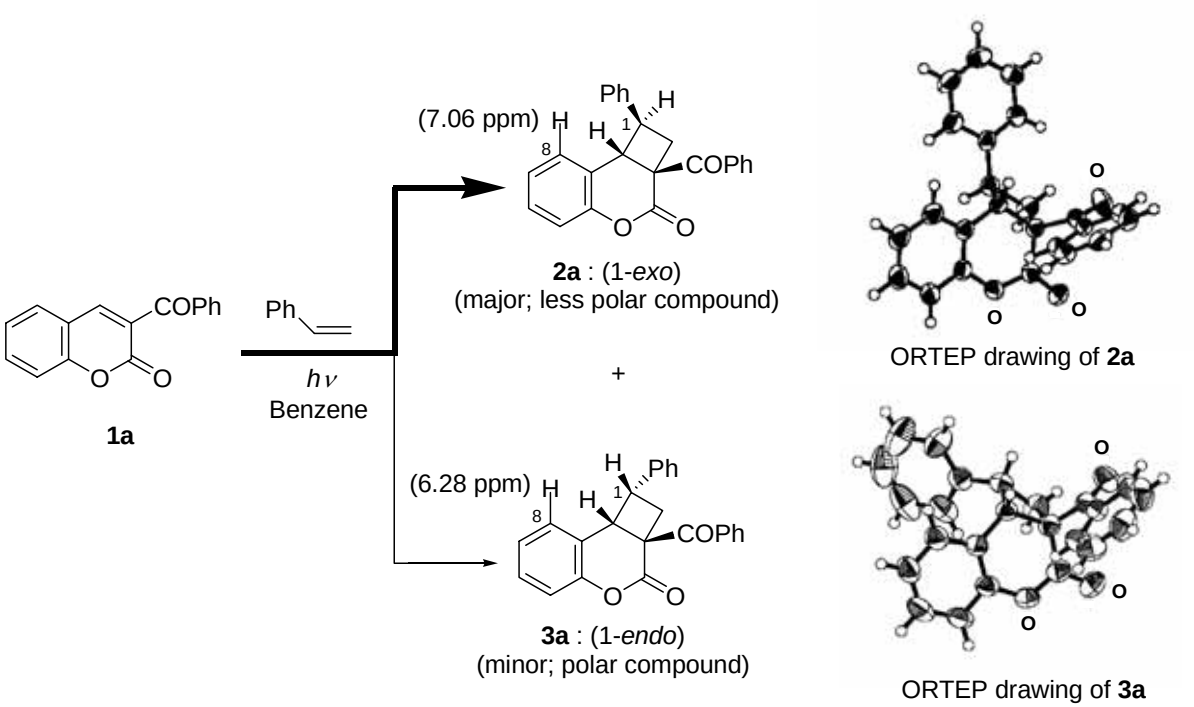


Scheme 1

In a previous study, we found that benzocyclobutapyranones such as **2** and **3** can be readily transformed to tetrahydrodibenzofuran derivatives (**4**),[3] which could be convertible to a series of biologically interesting tricyclic monoterpene-polyketides such as linderol A,[3,4,5] adunctin E[6] and their analogues (Scheme 1). In the course of the study, we needed unambiguous determination of the stereochemistry at the 1-position in **2** and **3**. In this paper, we describe the stereoselective synthesis of 1-*exo*- (**2**) and 1-*endo*-substituted 1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**3**), and their stereochemical determination by the ^{1}H-NMR spectra of **2** and **3** with an aryl substituent at the 1-position.

RESULTS AND DISCUSSION

A solution of the 3-benzoylcoumarin (**1a**) and 6 equivalents of styrene in benzene was irradiated with a high-pressure Hg lamp (400W) to afford a mixture of [2+2] adducts (**2a** and **3a**) in 99% yield (Scheme 2).[2e] These diastereomeric isomers (**2a** and **3a**) were isolated with medium-pressure liquid chromatography (MPLC). The ^{1}H-NMR spectra of the polar product showed the characteristic resonance of a doublet at 6.28 ppm, which would be assumed to be shielded by the phenyl group at the 1-position. In order to clarify this assumption, X-Ray crystallographic analysis of **2a** and **3a** was performed (Scheme 2).[7] As shown in Scheme 2, it is obvious that the phenyl group at the 1-position of the *endo*-isomer (**3a**; polar product) strongly shields the C8-proton, but that of the *exo*-isomer (**2a**; less polar product) is far from C8-H. Each C8-H of **2a** and **3a** was assigned on the basis of the detailed ^{1}H-NMR spectral analysis including heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond coherence (HMBC). The C8-H of **2a** was observed at 7.06 ppm as a double doublet. On the other hand, that of **3a** appeared at 6.28 ppm as a doublet. As a result, we concluded that the less polar compound (**2a**), the major product, was the *exo*-form and the polar compound (**3a**), the minor product, was the *endo*-form.

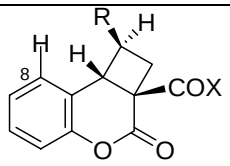
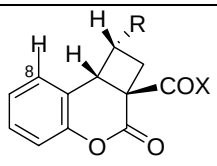


Scheme 2

In order to confirm the generality of this observation, various cyclobutanes (**2** and **3**) were prepared (*vide post*), and the ^{1}H-NMR spectra of the products (**2** and **3**) were taken. Chemical shifts of C8-H were carefully assigned, and the results are given in Table 1. In all cases of **3a**–**k** having 1-aryl and 1-heteroaryl groups, the chemical shifts of C8-H were observed at lower δ value than those of **2a**–**k**. X-Ray crystallographic analysis showed that **2j** and **3j** had almost the same conformation as **2a** and **3a**, respectively.[3] This means that the predominant conformation of **3** in solution would be maintained as it was in solid state. As a matter of course, low δ value of C8-H was not observed at all in the cases of 1-aliphatic groups (**2m**–**q** and **3m**–**q**). This was ascertained by X-Ray crystallographic analysis of **2q** and **3q** as shown in Figure 1.[8] It is noteworthy that this stereochemical determination methodology for **2** and **3** is simple and useful though the substituent groups at the 1-position of **2** and **3** are limited to aryl groups.

Figure 1

Table 1. C8-H Chemical shift of **2** and **3**.

X	R	C8-H chemical shift in ^{1}H-NMR	
			
		2 : *exo*-form	**3** : *endo*-form
Ph	Ph	**2a** : 7.06[a]	**3a** : 6.28[a]
Ph	2-pyridyl	**2b** : -[c]	**3b** : 6.52[b]
4-F-C_6H_4	Ph	**2c** : -[c]	**3c** : 6.29[b]
Ph	4-Br-C_6H_4	**2d** : 7.03[b]	**3d** : 6.29[b]
Ph	4-MeO-C_6H_4	**2e** : 7.04[b]	**3e** : 6.30[b]
4-MeO-C_6H_4	Ph	**2f** : 7.05[b]	**3f** : 6.28[b]
Me	Ph	**2g** : 7.01[b]	**3g** : 6.45[b]
i-Pr	Ph	**2h** : 7.00[b]	**3h** : 6.45[b]
t-Bu	Ph	**2i** : 7.01[b]	**3i** : 6.27[b]
EtO	Ph	**2j** : 6.99[a]	**3j** : 6.45[a]
MeO	Ph	**2k** : 6.99[a]	**3k** : 6.48[a]
Ph	*n*-Bu	**2m** : -[c]	**3m** : 7.08[b]
Ph	$AcOCH_2$	**2n** : -[c]	**3n** : -[c]
Ph	cyclohexyl	**2p** : -[c]	**3p** : -[c]
EtO	$AcOCH_2$	**2q** : -[c]	**3q** : -[c]

[a] The chemical shift was assigned on the basis of ^{1}H-NMR spectra with HMQC and HMBC.
[b] The chemical shift was assigned by comparison with ^{1}H-NMR spectra of **2a**, **j**, **k** and **3a**, **j**, **k**.
[c] The chemical shift could not be assigned due to complexity in the aromatic region; however, no aromatic peaks were observed below 6.9 ppm.

In the cases of the photocycloaddition of coumarins (**1**) to monosubstituted olefins, *exo*-products (**3**) were predominantly obtained as shown above and described in the literature (Method A).[2] In order to prepare the *endo*-products mainly, we planned selective preparation of the *endo*-products (**3**) *via* cyclobutene derivatives (**5**).[9] Hydrogenation of the cyclobutene derivative (**5**) would occur from the *exo* face, the sterically less hindered side, to give exclusively the *endo*-product (**3**) as shown in Figure 2.

A solution of 3-benzoylcoumarin (**1a**) and 3 equivalents of phenylacetylene in benzene was irradiated with a high-pressure Hg lamp (400W) to afford successfully the cyclobutene (**5a**) in 94% yield as a single product. The phenyl group should attach at the 1-position because 2-H and 8b-H were each observed as a singlet in the ^{1}H-NMR spectrum. The cyclobutene (**5a**) was hydrogenated under several conditions as shown in Table 2 to give a mixture of **2a** and **3a** (Scheme 3, Method B). Hydrogenation over Pd-C in EtOH gave the best ratio (**2a**/**3a** = 1/10) and the main product was *endo*-**3a** as we had expected.

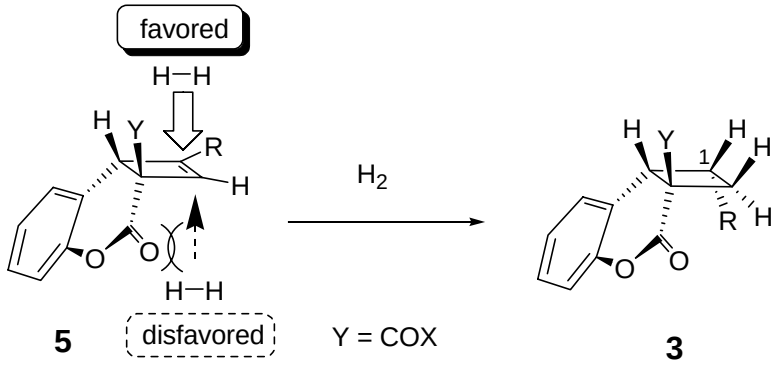
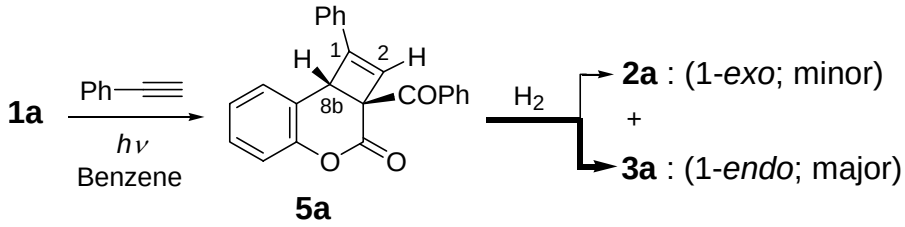


Figure 2



Scheme 3

Table 2. Hydrogenation of **5a**

Run	Catalyst	Solvent	Total Yield (%)	Ratio of **2a**/**3a**
1	5% Pd-C	EtOH	60	1/10
2	5% Pd-C	AcOEt	82	1/4
3	PtO_2	AcOEt	28	1/1
4	$(Ph_3P)_3RhCl$	C_6H_6	0[a]	-

[a] Hydrogenation did not proceed at all.

Mixtures of **2** and **3** having various ratios were prepared according to Method A or B as shown in Table 3, and **2** and **3** were isolated by recrystallization or MPLC.

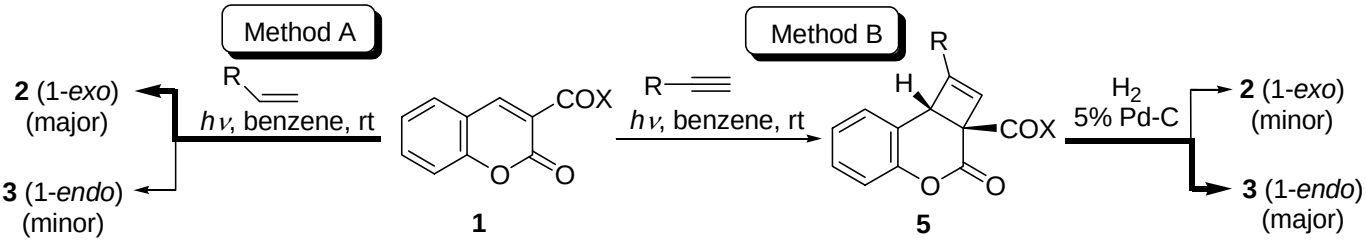
In Method A, the main products were the *exo*-form (**2**), and the ratio of **2**/**3** increased in the cases of the 3-acylcoumarins (**1a**–**i** and **m**–**q**) rather than those in the cases of 3-alkoxycarbonylcoumarins (**1j** and **k**). In Method B, the *endo*-form (**3**) was obtained as the main products. The ratio of **2**/**3** depended on the bulkiness of the electron-withdrawing group (COX) in **5**, and as X in **5** was bulkier, the ratio of **2**/**3** became smaller (**3g**, **h**, and **i**).

CONCLUSION

In conclusion, we have succeeded in the stereoselective preparation of 1-*exo*- and 1-*endo*-substituted 1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**2** and **3**). The former could be prepared as a main product by photo [2+2] cycloaddition of the 3-substituted coumarins (**1**) and olefins; the latter were prepared as a main product by hydrogenation over the Pd-carbon of the cyclobutenes (**5**), which were obtained by photo [2+2] cycloaddition of the coumarins (**1**) and acetylenes. It was also found that the stereochemistry of 1-*exo*- and 1-*endo*-arylcyclobutanes (**2** and **3**) could be easily determined by comparing their ^{1}H-NMR spectra, in which the C8-proton of **3** was strongly shielded by the 1-aryl ring

compared with that of **2**.

Table 3. Stereoselective preparation of **2** and **3**



Product	Preparation Method	Yield (%)[c,d]	Ratio (**2**/**3**)[g]	Product	Preparation Method	Yield (%)[c,d]	Ratio (**2**/**3**)[g]
2a	A[a]	99	5.0/1	**2i**	A[a]	93	5.0/1
3a	B[a]	(94 : 60[e])	1/10	**3i**	B[a]	(40 : 95[f])	1/1.3
2b **3b**	A[b]	92	5.0/1	**2j**	A[a]	78	1.5/1
				3j	B[a]	(71 : 85[e])	1/1.4
2c **3c**	A[b]	93	3.0/1	**2k**	A[a]	83	2.0/1
				3k	B[a]	(92 : 55[e])	1/2.2
2d **3d**	A[b]	98	3.0/1	**2m** **3m**	A[b]	93	6.0/1
2e	A[a]	97	3.6/1	**2n** **3n**	A[b]	80	3.9/1[h]
3e	B[a]	(68 : 35[e])	1/5.7				
2f **3f**	A[b]	93	3.0/1	**2p** **3p**	A[b]	83	8.4/1[h]
2g	A[a]	92	4.5/1	**2q** **3q**	A[b]	89	3.7/1
3g	B[a]	(91 : 83[e])	1/3.5				
2h	A[a]	99	5.2/1				
3h	B[a]	(85 : 98[f])	1/1.8				

[a] Isolation by recrystallization. [b] Isolation with MPLC. [c] Total yield of mixture of *exo*- and *endo*-**1** before recrystallization or MPLC. [d] The yields in parentheses are those of Method B (photochemical reaction : hydrogenation). [e] EtOH was used as solvent. [f] AcOEt was used as solvent because of insolubility of **5** in EtOH. [g] The ratio was estimated from ^{1}H-NMR spectrum before isolation. [h] The ratio was obtained by isolation yield.

EXPERIMENTAL

Melting points were measured with a Yanaco MP micro-melting point apparatus and are uncorrected. NMR spectra were measured on a Varian INOVA 400 NB (^{1}H : 400 MHz, ^{13}C : 100 MHz), a JEOL AL-300 (^{1}H; 300 MHz, ^{13}C; 75.5MHz) and a Varian Gemini 200 (^{1}H; 200 MHz, ^{13}C; 50 MHz) with tetramethylsilane as an internal standard and chemical shifts are reported in ppm. IR spectra were taken with a Shimadzu IR-435 spectrophotometer. Low-resolution (MS) and high-resolution (HRMS)

electron impact ionization MS spectra were measured on Shimadzu GCMS-QP 1000 and Shimadzu GC/MS-5050A spectrometers. Shimadzu GCMS-QP 1000 for low-resolution [MS(CI)] and high-resolution [HRMS(CI)] chemical ionization MS, and JEOL JMS-SX 102AQQ for low-resolution [MS(FAB)] and high-resolution FABMS [HRMS(FAB)] were used. The elemental analyses were established using Perkin Elmer Series II CHNS/O Analyzer 2400. Photochemical reaction was performed on UV-HT400 (Ishii laboratory warks Co. LTD). All solvents were removed under reduced pressure in the usual work-up procedure. Silica gel 60 (Merck, 0.063 – 0.200 mm) for column chromatography and silica gel packed in a glass column (Yamazen Corporation, 0.040 mm) for MPLC were used. X-Ray crystallography was performed on a Rigaku AFC7R diffractometer with filtered Cu-Kα radiation and rotating anode generator, and a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-Kα radiation. The coumarin derivatives (**1**) were prepared by Knoevenagel condensation of salicylaldehyde with the corresponding malonate or an appropriate active methylene compound in the presence of catalytic amounts of piperidine and acetic acid.[10]

General procedure: Method A A solution of **1** and 6 equivalents of monosubstituted alkene in benzene was added in a photochemical reactor vessel with a 400-W high-pressure mercury lamp in a water-cooled quartz immersion well, and the stirred solution was irradiated until **1** was consumed. The solvent was evaporated, and the obtained residue was purified by column chromatography to give a mixture of **2** and **3**. 1-*exo*-**2** was obtained by recrystallization or 1-*exo*-**2** and 1-*endo*-**3** were isolated with MPLC.

General procedure: Method B Preparation of cyclobutene derivatives (5) A solution of **1** and 3 or 6 equivalents of monosubstituted acetylene in benzene was added in a photochemical reactor vessel with a 400-W high-pressure mercury lamp in a water-cooled quartz immersion well, and the stirred solution was irradiated until **1** was consumed. The solvent was evaporated, and the obtained residue was purified by column chromatography to give **5**. **Hydrogenation of 5** An ethanol or AcOEt solution of **5** was hydrogenated over catalytic amounts of 5% Pd-C under hydrogen atmosphere until **5** was consumed. The Pd-C was filtered off, and the filtrate was evaporated. The residue was purified by column chromatography to give a mixture of **2** and **3**. Recrystallization of the mixture gave only 1-*endo*-**3**.

***rel*-(1*R*,2a*R*,8b*R*)-2a-Benzoyl-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (2a)** (from Method A) Polar compound. Colorless columns (AcOEt - *n*-hexane), mp 112.1 - 113.7 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.26 (1H, ddd, *J* = 11.9, 8.8, 0.6 Hz, 2-H), 3.45 (1H, dd, *J* = 11.9, 10.3 Hz,

2-H), 3.66 (1H, dt, *J* = 9.9, 8.8 Hz, 1-H), 3.95 (1H, d, *J* = 8.8 Hz, 8b-H), 7.06 (1H, dd, *J* = 7.5, 1.7 Hz, 8-H), 7.13 (1H, dt, *J* = 1.1, 7.3 Hz, Ar-H), 7.14 - 7.41 (9H, m, Ar-H), 7.49 - 7.56 (1H, m, Ar-H), 7.87 - 7.90 (2H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 38.2, 44.5, 48.8, 53.0, 117.4, 122.3, 125.3, 126.5, 127.2, 127.4, 128.67, 128.75, 129.2, 129.3, 133.6, 133.8, 141.1, 151.4, 167.6, 194.3. IR ($CHCl_3$): 1741, 1668, 1595 cm^{-1}. MS *m/z* (relative intensity, %): 354 (M^+, 0.4), 104 (100). HRMS *m/z*: Calcd for $C_{24}H_{18}O_3$; 354.1256. Found; 354.1258. *Anal.* Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.23; H, 5.20. Crystal data (RAXIS RAPID) $C_{24}H_{18}O_3$, *M* = 354.40, monoclinic, *a* = 8.8895(6), *b* = 22.9681(16), *c* = 8.8931(7) Å, *β* = 102.095(5)°, V = 1775.4(2) Å^3, T = 93 K, space group $P2_1/a$ (no. 14), *Z* = 4, D_{calc} = 1.326 g/cm^3, F_{000} = 744.00, *μ*(Cu-kα) = 6.955 cm^{-1}, 7816 reflections measured, 2268 unique (R_{int} = 0.043). The structure was solved by direct methods (SIR92)[11] and expanded using Fourier techniques (DIRDIF99).[12] The final R_1 was 0.042.

***rel*-(1*R*,2a*S*,8b*S*)-2a-Benzoyl-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3a)** (from Method A and B) Less polar compound. Colorless columns (AcOEt - *n*-hexane), mp 202.0 - 202.8 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.96 (1H, dd, *J* = 11.6, 11.1 Hz, 2-H), 3.62 (1H, ddd, *J* = 12.3, 8.8, 3.3 Hz, 2-H), 4.10 (1H, dt, *J* = 10.4, 9.0 Hz, 1-H), 4.22 (1H, dd, *J* = 9.2, 3.3 Hz, 8b-H), 6.28 (1H, d, *J* = 7.7 Hz, 8-H), 6.80 (1H, dt, *J* = 1.3, 7.5 Hz), 6.83 - 6.88 (2H, m, Ar-H), 7.12 - 7.16 (4H, m, Ar-H), 7.21 - 7.26 (1H, m, Ar-H), 7.39 - 7.44 (2H, m, Ar-H), 7.52 - 7.57 (1H, m, Ar-H), 7.80 - 7.83 (2H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 32.8, 42.6, 45.7, 49.9, 116.6, 117.3, 124.5, 127.2, 128.0, 128.1, 128.9, 129.0 (x 2), 130.7, 133.0, 133.6, 137.5, 151.0, 165.4, 192.8. IR ($CHCl_3$): 1737, 1685, 1595, 1580 cm^{-1}. MS *m/z* (relative intensity, %): 354 (M^+, 1.3), 104 (100). HRMS *m/z*: Calcd for $C_{24}H_{18}O_3$; 354.1256. Found; 354.1249. *Anal.* Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.30; H, 5.17. Crystal data (AFC7R): $C_{24}H_{18}O_3$, *M* = 354.40, monoclinic, *a* = 11.749(5), *b* = 9.913(3), *c* = 15.705(3) Å, *β* = 91.63(2)°, V = 1828.4(9) Å^3, T = 296 K, space group $P2_1/n$ (no. 14), *Z* = 4, D_{calc} = 1.287 g/cm^3, F_{000} = 744.00, *μ*(Cu-kα) = 6.75 cm^{-1}, 3696 reflections measured, 3472 unique (R_{int} = 0.009). The structure was solved by direct methods (SIR88)[13] and expanded using Fourier techniques (DIRDIF94).[14] The final R_1 was 0.042 (2421 reflections were used).

***rel*-(1*R*,2a*R*,8b*R*)-2a-Benzoyl-1-(2-pyridyl)-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (2b)** (from Method A) Polar compound. Colorless plates (AcOEt - *n*-hexane), mp 131.4 - 132.8 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ : 3.26 (1H, dd, *J* = 11.6, 8.4 Hz, 2-H), 3.58 (1H, dd, *J* = 11.6, 9.7 Hz, 2-H), 3.72 (1H, q, *J* = 8.9 Hz, 1-H), 4.38 (1H, d, *J* = 8.4 Hz, 8b-H), 7.04 - 7.15 (5H, m, Ar-H), 7.25 - 7.40 (3H, m, Ar-H), 7.48 - 7.65 (2H, m, Ar-H), 7.94 (2H, d, *J* = 7.3 Hz), 8.57 (1H, br d, *J* = 4.0 Hz, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 37.4, 45.7, 46.3, 53.0, 117.1, 121.8, 122.0, 122.3, 125.2, 127.6,

128.5, 128.9, 129.4, 133.5, 133.7, 136.4, 149.7, 151.4, 159.4, 167.4, 194.4. IR ($CHCl_3$) : 1739, 1667, 1588 cm^{-1}. MS *m/z* (relative intensity, %): 355 (M^+, 1.3), 105 (100). HRMS *m/z*: Calcd for $C_{23}H_{17}NO_3$: 355.1208. Found: 355.1210. *Anal.* Calcd for $C_{23}H_{17}NO_3$: C ; 77.73, H ; 4.82, N ; 3.94. Found : C ; 76.72, H ; 4.79, N ; 3.88.

***rel*-(1*R*,2a*S*,8b*S*)-2a-Benzoyl-1-(2-pyridyl)-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3b)** (from Method A) Less polar compound. Colorless amorphous. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.44 (1H, ddd, *J* = 12.1, 7.9, 0.7 Hz, 2-H), 3.58 (1H, ddd, *J* = 12.1, 8.8, 2.0 Hz, 2-H), 4.09 (1H, q, *J* = 8.7 Hz, 1-H), 4.43 (1H, d, *J* = 9.4 Hz, 8b-H), 6.51 (1H, d, *J* = 7.0 Hz, 8-H), 6.77 (1H, td, *J* = 7.5, 1.1 Hz, Ar-H), 6.86 - 7.01 (3H, m, Ar-H), 7.12 (1H, td, *J* = 8.5, 1.6 Hz, Ar-H), 7.36 - 7.46 (3H, m, Ar-H), 7.53 (1H, tt, *J* = 7.3, 1.1 Hz, Ar-H), 7.87 - 7.91 (2H, m, Ar-H), 8.37 (1H, dd, *J* = 4.8, 0.7 Hz, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 32.8, 43.3, 44.8, 51.7, 117.0, 117.7, 121.6, 122.9, 124.2, 128.6, 128.8, 129.0, 129.2, 133.2, 133.5, 135.9, 149.1, 151.6, 157.8, 165.8, 194.0. IR ($CHCl_3$); 1738, 1685, 1588 cm^{-1}. MS *m/z* (relative intensity, %): 355 (M^+, 1.6), 105 (100). HRMS *m/z*: Calcd for $C_{23}H_{17}NO_3$: 355.1208. Found : 355.1212.

***rel*-(1*R*,2a*R*,8b*R*)-2a-(4-Fluorobenzoyl)-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (2c)** (from Method A) Polar compound. Colorless amorphous. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.29 (1H, dd, *J* = 11.9, 8.8 Hz, 2-H), 3.38 (1H, dd, *J* = 11.9, 10.3 Hz, 2-H), 3.68 (1H, q, *J* = 9.3 Hz, 1-H), 3.98 (1H, d, *J* = 9.2 Hz, 8b-H), 6.95 - 7.17 (5H, m, Ar-H), 7.20 - 7.28 (3H, m, Ar-H), 7.32 - 7.36 (3H, m, Ar-H), 7.97 - 8.01 (2H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 38.8, 44.4, 48.6, 53.1, 115.9 (d, *J* = 22.1 Hz), 117.3, 122.1, 125.4, 126.5, 127.3, 127.4, 128.8, 129.2, 130.3 (d, *J* = 3.1 Hz), 132.4 (d, *J* = 9.2 Hz), 140.9, 151.3, 166.0 (d, *J* = 256.7 Hz), 167.5, 192.9. IR ($CHCl_3$): 1739, 1666, 1594 cm^{-1}. MS *m/z* (relative intensity, %): 372 (M^+, 0.4), 104 (100). HRMS *m/z*: Calcd for $C_{24}H_{17}O_3F$: 372.1162. Found: 372.1165.

***rel*-(1*R*,2a*S*,8b*S*)-2a-(4-Fluorobenzoyl)-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (3c)** (from Method A) Less polar compound. Colorless needles (AcOEt / n-hexane), mp 150.3 - 152.1 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.98 (1H, ddd, *J* = 12.2, 10.4, 0.5 Hz, 2-H), 3.61 (1H, ddd, *J* = 12.2, 8.7, 3.4 Hz, 2-H), 4.10 (1H, q, *J* = 9.4 Hz, 1-H), 4.21 (1H, dd, *J* = 9.2, 3.3 Hz, 8b-H), 6.29 (1H, dd, *J* = 7.7, 0.9 Hz, 8-H), 6.81 (1H, td, *J* = 7.5, 1.3 Hz, Ar-H), 6.84 - 6.88 (2H, m, Ar-H), 7.07 - 7.17 (5H, m, Ar-H), 7.21 - 7.30 (2H, m, Ar-H), 7.82 - 7.88 (2H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 32.9, 42.6, 45.7, 50.0, 116.3 (d, *J* = 22.1 Hz), 116.5, 117.4, 124.6, 127.3, 128.1, 129.1, 129.5 (d, *J* = 3.4 Hz), 130.7, 131.6 (d, *J* = 9.5 Hz), 137.3, 150.9, 165.4, 165.8 (d, *J* = 256.7 Hz), 191.4. IR ($CHCl_3$): 1737,

1685, 1595 cm^{-1}. MS *m/z* (relative intensity, %): 372 (M^+, 0.2), 104 (100). HRMS *m/z*: Calcd for $C_{24}H_{17}O_3F$: 372.1162. Found: 372.1170. *Anal.* Calcd for $C_{24}H_{17}O_3F$: C, 77.41; H; 4.60. Found: C, 77.44; H, 4.77.

***rel*-(1*R*,2a*R*,8b*R*)-2a-Benzoyl-1-(4-bromophenyl)-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (2d)** (from Method A) Polar compound. Colorless amorphous. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.25 (1H, ddd, *J* = 12.1, 8.8, 0.9 Hz, 2-H), 3.42 (1H, dd, *J* = 12.1, 10.3 Hz, 2-H), 3.62 (1H, dt, *J* = 10.3, 8.8 Hz, 1-H), 3.89 (1H, d, *J* = 8.8 Hz, 8b-H), 7.03 (1H, dd, *J* = 7.5, 1.6 Hz, 8-H), 7.08 - 7.19 (4H, m, Ar-H), 7.33 - 7.48 (5H, m, Ar-H), 7.55 (1H, tt, *J* = 7.4, 1.3 Hz, Ar-H), 7.87 - 7.90 (2H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 38.0, 44.0, 48.8, 52.9, 117.5, 121.1, 121.9, 125.4, 127.3, 128.3, 128.8, 129.3, 129.4, 131.9, 133.7, 133.8, 140.0, 151.3, 167.4, 194.2. IR ($CHCl_3$): 1739, 1667, 1610, 1579 cm^{-1}. MS *m/z* (relative intensity, %): 434 (M^++2, 0.4), 432 (M^+, 0.3), 182 (100). HRMS *m/z*: Calcd for $C_{24}H_{17}O_3Br$: 432.0361. Found: 432.0354.

***rel*-(1*R*,2a*S*,8b*S*)-2a-Benzoyl-1-(4-bromophenyl)-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (3d)** (from Method A) Less polar compound. Colorless amorphous. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.89 (1H, dt, *J* = 11.4, 0.7 Hz, 2-H), 3.63 (1H, ddd, *J* = 12.3, 8.6, 3.3 Hz, 2-H), 4.05 (1H, q, *J* = 9.5 Hz, 1-H), 4.22 (1H, dd, *J* = 9.1, 3.2 Hz, 8b-H), 6.29 (1H, d, *J* = 7.7 Hz, 8-H), 6.72 (2H, dt, *J* = 8.4, 2.2 Hz, Ar-H), 6.88 (1H, td, *J* = 7.5, 1.3 Hz, Ar-H), 7.15 - 7.60 (7H, m, Ar-H), 7.79 - 7.82 (2H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 33.0, 42.1, 45.6, 49.9, 116.3, 117.6, 121.3, 124.8, 128.9, 129.1, 129.3, 129.9, 130.7, 131.3, 132.9, 133.8, 136.6, 151.0, 165.2, 192.7. IR ($CHCl_3$): 1739, 1686 cm^{-1}. MS *m/z* (relative intensity, %): 434 (M^++2, 0.4), 432 (M^+, 0.4), 182 (100). HRMS *m/z*: Calcd for $C_{24}H_{17}O_3Br$: 432.0361. Found: 432.0366.

***rel*-(1*R*,2a*R*,8b*R*)-2a-Benzoyl-1-(4-methoxyphenyl)-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (2e)** (from Method A) Polar compound. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.25 (1H, ddd, *J* = 12.1, 8.8, 0.9 Hz, 2-H), 3.41 (1H, dd, *J* = 12.1, 10.3 Hz, 2-H), 3.60 (1H, dt, *J* = 10.3, 8.8 Hz, 1-H), 3.79 (3H, s, OCH_3), 3.89 (1H, d, *J* = 8.8 Hz, 8b-H), 6.84 - 6.89 (2H, m, Ar-H), 7.04 (1H, dd, *J* = 7.5, 1.7 Hz, 8-H), 7.11 - 7.18 (4H, m, Ar-H), 7.31 - 7.42 (3H, m, Ar-H), 7.51 - 7.57 (1H, m, Ar-H), 7.88 - 7.91 (2H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 38.7, 44.0, 49.2, 52.9, 55.3, 114.1, 117.4, 122.3, 125.3, 127.4, 127.7, 128.7, 129.1, 129.3, 133.2, 133.6, 133.9, 151.3, 158.8, 167.7, 194.5. IR ($CHCl_3$): 1739, 1667, 1608 cm^{-1}. MS(CI) *m/z* (relative intensity, %): 385 [$(M + H)^+$, 2.9], 134 (100). HRMS(CI) *m/z*: Calcd for $C_{25}H_{20}O_4$ + H: 385.1440. Found: 385.1443.

***rel*-(1*R*,2a*S*,8b*S*)-2a-Benzoyl-1-(4-methoxyphenyl)-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (3e)** (from Method A and B) Less polar compound. Colorless powder (AcOEt - *n*-hexane), mp 146.0 - 147.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.89 (1H, ddd, *J* = 12.1, 10.8, 0.6 Hz, 2-H), 3.61 (1H, ddd, *J* = 12.1, 8.8, 3.3 Hz, 2-H), 3.74 (3H, s, OCH_3), 4.05 (1H, dt, *J* = 10.5, 8.8 Hz, 1-H), 4.18 (1H, dd, *J* = 9.0, 3.3 Hz, 8b-H), 6.30 (1H, d, *J* = 7.5 Hz, 8-H), 6.66 - 6.70 (2H, m, Ar-H), 6.73 - 6.77 (2H, m, Ar-H), 6.85 (1H, dt, *J* = 1.3, 7.4 Hz, Ar-H), 7.17 (1H, dd, *J* = 8.3, 1.2 Hz, Ar-H), 7.23 - 7.29 (1H, m, Ar-H), 7.40 - 7.46 (2H, m, Ar-H), 7.53 - 7.58 (1H, m, Ar-H), 7.81 - 7.84 (2H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 33.4, 42.1, 45.9, 49.9, 55.2, 113.5, 116.7, 117.4, 124.6, 128.9, 128.96, 129.00, 129.3, 129.7, 130.9, 133.0, 133.6, 151.0, 158.7, 165.5, 192.9. IR ($CHCl_3$): 1737, 1685, 1608 cm^{-1}. MS(FAB) *m/z*: 385 $(M + H)^+$. HRMS(FAB) *m/z*: Calcd for $C_{25}H_{20}O_4$ + H: 385.1440. Found: 385.1435. *Anal.* Calcd for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 77.99; H, 5.21.

***rel*-(1*R*,2a*R*,8b*R*)-2a-(4-Methoxybenzoyl)-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (2f)** (from Method A) Polar compound. Colorless plates (*i*-Pr_2O), mp 120.0 - 122.0 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.27 (1H, dd, *J* = 11.7, 8.8 Hz, 2-H), 3.40 (1H, dd, *J* = 11.7, 10.1 Hz, 2-H), 3.64 (1H, q, *J* = 9.3 Hz, 1-H), 3.82 (3H, s, OCH_3), 3.97 (1H, d, *J* = 9.2 Hz, 8b-H), 6.87 (2H, d, *J* = 8.8 Hz, Ar-H), 7.05 (1H, dd, *J* = 7.3, 1.8 Hz, 8-H), 7.12 (1H, td, *J* = 7.3, 1.1 Hz, Ar-H), 7.14 (1H, d, *J* = 8.1 Hz, Ar-H), 7.19 - 7.32 (6H, m, Ar-H), 7.92 (2H, d, *J* = 8.8 Hz, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 38.7, 44.4, 48.7, 52.9, 55.4, 113.9, 117.2, 122.4, 125.2, 126.4, 126.5, 127.1, 127.4, 128.7, 129.0, 132.0, 141.1, 151.4, 163.9, 167.7, 192.6. IR ($CHCl_3$): 1738, 1657, 1595, 1570, 1505 cm^{-1}. MS *m/z* (relative intensity, %): 384 (M^+, 0.6), 135 (100). HRMS *m/z*: Calcd for $C_{25}H_{20}O_4$: 384.1362. Found: 384.1360. *Anal.* Calcd for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 78.27, H, 5.34.

***rel*-(1*R*,2a*S*,8b*S*)-2a-(4-Methoxybenzoyl)-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (3f)** (from Method A) Less polar compound. Colorless column (*i*-Pr_2O), mp 220.0 - 222.0 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.94 (1H, dd, *J* = 12.1, 10.6 Hz, 2-H), 3.61 (1H, ddd, *J* = 12.1, 8.8, 3.3 Hz, 2-H), 3.81 (3H, s, OCH_3), 4.08 (1H, q, *J* = 9.3 Hz, 1-H), 4.20 (1H, dd, *J* = 9.2, 2.9 Hz, 8b-H), 6.28 (1H, d, *J* = 7.7 Hz, 8-H), 6.79 (1H, td, *J* = 7.3, 1.1 Hz, Ar-H), 6.75 - 6.91 (2H, m, Ar-H), 6.89 (2H, d, *J* = 8.8 Hz, Ar-H), 7.08 - 7.20 (4H, m, Ar-H), 7.22 (1H, t, *J* = 8.4 Hz, Ar-H), 7.79 (2H, d, *J* = 8.8 Hz, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 32.8, 42.6, 45.8, 49.8, 55.5, 114.2, 116.8, 117.3, 124.4, 125.8, 127.1, 128.0, 128.1, 128.9, 130.6, 131.2, 137.6, 151.0, 163.8, 165.6, 191.4. IR ($CHCl_3$): 1737, 1673, 1597, 1573, 1506 cm^{-1}. MS *m/z* (relative intensity, %): 384 (M^+, 0.4), 280 (100). HRMS *m/z*: Calcd for $C_{25}H_{20}O_4$: 384.1362. Found: 384.1357. *Anal.* Calcd for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 77.82; H, 5.37.

***rel*-(1*R*,2a*R*,8b*R*)-2a-Acetyl-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (2g)** (from Method A) Polar compound. Colorless plates (AcOEt - *n*-hexane), mp 107.9 - 108.5 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.26 (3H, s, C(=O)CH_3), 3.00 (1H, dd, *J* = 11.5, 9.4 Hz, 2-H), 3.05 (1H, dd, *J* = 11.5, 10.3 Hz, 2-H), 3.56 (1H, dt, *J* = 9.7, 9.4 Hz, 1-H), 3.87 (1H, d, *J* = 9.4 Hz, 8b-H), 7.01 (1H, dd, *J* = 7.5, 1.8 Hz, 8-H), 7.08 (1H, dt, *J* = 1.3, 7.3 Hz, Ar-H), 7.11 (1H, d, *J* = 7.5 Hz, Ar-H), 7.20 - 7.37 (6H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 26.5, 37.3, 43.8, 47.0, 54.6, 117.2, 121.6, 125.1, 126.5, 127.2, 127.6, 128.7, 129.2, 140.8, 151.3, 168.2, 200.5. IR ($CHCl_3$): 1744, 1707, 1585 cm^{-1}. MS *m/z* (relative intensity, %): 292 (M^+, 0.2), 104 (100). HRMS *m/z*: Calcd for $C_{19}H_{16}O_3$: 292.1099. Found: 292.1093. *Anal.* Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.91; H, 5.59.

***rel*-(1*R*,2a*S*,8b*S*)-2a-Acetyl-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3g)** (from Method A and B) Less polar compound. Colorless needles (AcOEt - *n*-hexane), mp 98.6 - 100.8 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.41 (3H, s, C(O)CH_3), 2.95 (1H, ddd, *J* = 12.6, 8.4, 0.9 Hz, 2-H), 3.27 (1H, ddd, *J* = 12.6, 9.0, 2.4 Hz, 2-H), 3.99 (1H, q, *J* = 8.9 Hz, 1-H), 4.24 (1H, dd, *J* = 9.3, 2.0 Hz, 8b-H), 6.45 (1H, d, *J* = 7.5 Hz, 8-H), 6.81 (1H, dt, *J* = 1.3, 7.5 Hz, Ar-H), 6.87 - 6.90 (2H, m, Ar-H), 6.96 (1H, dd, *J* = 8.2, 1.1 Hz, Ar-H), 7.10 - 7.16 (4H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 26.4, 33.1, 42.0, 43.5, 53.5, 116.9, 117.7, 124.4, 127.1, 128.0, 128.1, 128.8, 129.8, 137.4, 151.0, 166.2, 201.2. IR ($CHCl_3$): 1737, 1715 cm^{-1}. MS(CI) *m/z* (relative intensity, %): 293 [$(M + H)^+$, 3.7], 104 (100). HRMS(CI) *m/z*: Calcd for $C_{19}H_{16}O_3$ + H: 293.1178. Found: 293.1184. *Anal.* Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.95; H, 5.58.

***rel*-(1*R*,2a*R*,8b*R*)-2a-Isobutyryl-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (2h)** (from Method A) Polar compound. Colorless plates (AcOEt - *n*-hexane), mp 139.0 - 139.9 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.96 (3H, d, *J* = 6.8 Hz, C(O)CH(C$\underline{H}_3$)$_2$), 1.13 (3H, d, *J* = 6.8 Hz, C(O)CH(C$\underline{H}_3$)$_2$), 2.97 (1H, hept, *J* = 6.8 Hz, C(O)C$\underline{H}$(CH$_3$)$_2$), 2.98 (1H, dd, *J* = 11.2, 8.8 Hz, 2-H), 3.15 (1H, t, *J* = 11.0 Hz, 2-H), 3.57 (1H, dt, *J* = 10.7, 8.9 Hz, 1-H), 3.84 (1H, d, *J* = 9.4 Hz, 8b-H), 7.00 (1H, dd, *J* = 7.5, 1.7 Hz, 8-H), 7.08 (1H, dt, *J* = 1.1, 7.4 Hz, Ar-H), 7.13 (1H, dd, *J* = 8.3, 0.7 Hz, 8-H), 7.20 - 7.37 (6H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 18.7, 19.1, 37.4, 37.6, 44.0, 47.7, 53.9, 117.2, 121.7, 125.1, 126.5, 127.2, 127.4, 128.7, 129.2, 140.9, 151.4, 168.7, 207.0. IR ($CHCl_3$): 1742, 1704 cm^{-1}. MS *m/z* (relative intensity, %): 320 (M^+, 0.1), 104 (100). HRMS *m/z*: Calcd for $C_{21}H_{20}O_3$: 320.1412. Found: 320.1413. *Anal.* Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.98; H, 6.44.

***rel*-(1*R*,2a*S*,8b*S*)-2a-Isobutyryl-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3h)** (from Method A and B) Less polar compound. Colorless needles (AcOEt), mp 128.4 - 130.2 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.17 (3H, d, *J* = 7.0 Hz, C(O)CH(C<u>H</u>$_3$)$_2$), 1.22 (3H, d, *J* = 6.8 Hz, C(O)CH(C<u>H</u>$_3$)$_2$), 2.90 (1H, ddd, *J* = 12.6, 8.4, 0.9 Hz, 2-H), 3.06 (1H, hept, *J* = 6.8 Hz, C(O)C<u>H</u>(CH$_3$)$_2$), 3.37 (1H, ddd, *J* = 12.6, 9.2, 2.4 Hz, 2-H), 4.00 (1H, q, *J* = 9.0 Hz, 1-H), 4.21 (1H, dd, *J* = 9.5, 1.6 Hz, 8b-H), 6.45 (1H, d, *J* = 7.3 Hz, 8-H), 6.81 (1H, dt, *J* = 1.3, 7.5 Hz, Ar-H), 6.87 - 6.90 (2H, m, Ar-H), 6.96 (1H, dd, *J* = 8.2. 1.1 Hz, Ar-H), 7.10 - 7.16 (4H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 19.7, 19.9, 33.3, 38.4, 42.0, 43.9, 53.0, 116.9, 117.7, 124.4, 127.0, 128.0, 128.1, 128.8, 129.8, 137.5, 151.1, 166.5, 207.9. IR ($CHCl_3$): 1735, 1704 cm^{-1}. MS(CI) *m/z* (relative intensity, %): 321 [(M + H)$^+$, 2.8], 104 (100). HRMS(CI) *m/z*: Calcd for $C_{21}H_{20}O_3$ + H: 321.1491. Found: 321.1494. *Anal.* Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.72; H, 6.46.

***rel*-(1*R*,2a*R*,8b*R*)-2a-(2,2-Dimethylpropionyl)-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta-[*d*]pyran-3-one (2i)** (from Method A and B) Polar compound. Colorless needles (AcOEt - *n*-hexane), mp 159.0 - 161.5 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.14 (9H, s, C(O)C(CH$_3$)$_3$), 2.90 - 2.99 (1H, m, 1-H), 3.45 - 3.58 (2H, m, 2-H and 1-H), 3.67 - 3.71 (1H, m, 8b-H), 7.01 (1H, dd, *J* = 7.5, 1.7 Hz, 8-H), 7.11 (1H, d, *J* = 1.1, 7.3 Hz, Ar-H), 7.15 - 7.37 (7H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 27.6, 37.2, 43.9, 45.2, 49.1, 52.9, 117.4, 122.5, 125.2, 126.5, 127.06, 127.14, 128.8, 129.1, 141.4, 151.5, 168.5, 207.2. IR ($CHCl_3$): 1740, 1688 cm^{-1}. MS *m/z* (relative intensity, %): 334 (M$^+$, 0.2), 104 (100). HRMS *m/z*: Calcd for $C_{22}H_{22}O_3$: 334.1569. Found: 334.1562. *Anal.* Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.87; H, 6.64.

***rel*-(1*R*,2a*S*,8b*S*)-2a-(2,2-Dimethylpropionyl)-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta-[*d*]pyran-3-one (3i)** (from Method A and B) Less polar compound. Colorless needles. mp 173.3 - 174.0 °C (AcOEt - *n*-hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.30 (9H, s, C(O)(CH$_3$)$_3$), 2.73 (1H, ddd, *J* = 12.3, 10.3, 0.7 Hz, 2-H), 3.52 (1H, ddd, *J* = 12.3, 9.0, 3.3 Hz, 2-H), 3.95 (1H, q, *J* = 9.5 Hz, 1-H), 4.06 (1H, dd, *J* = 9.3, 2.9 Hz, 8b-H), 6.27 (1H, d, *J* = 7.5 Hz, 8-H), 6.77 (1H, dt, *J* = 1.3, 7.4 Hz, Ar-H), 6.82 - 6.85 (2H, m, Ar-H), 7.07 (1H, dt, *J* = 1.3, 8.2 Hz, Ar-H), 7.11 - 7.20 (4H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 28.6, 33.1, 41.9, 44.4, 44.6, 51.3, 116.7, 117.2, 124.4, 127.1, 128.1, 128.2, 128.9, 130.4, 137.6, 151.0, 165.6, 208.0. IR ($CHCl_3$): 1736, 1697 cm^{-1}. MS(CI) *m/z* (relative intensity, %): 335 [(M + H)$^+$, 4.6], 104 (100). HRMS(CI) *m/z*: Calcd for $C_{22}H_{22}O_3$ + H: 335.1647. Found: 335.1651. *Anal.* Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 79.27; H, 6.79.

Methyl *rel*-(1*R*,2a*R*,8b*R*)-3-Oxo-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-2a-carboxylate (2k) (from Method A) Polar compound. Colorless needles (AcOEt - *n*-hexane), mp 119.0 - 119.8 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.00 (1H, ddd, *J* = 11.7, 8.2, 0.7 Hz, 2-H), 3.27 (1H, t, *J* =

11.2 Hz, 2-H), 3.57 (1H, dt, *J* = 11.2, 8.6 Hz, 1-H), 3.74 (3H, s, OCH_3), 3.83 (1H, d, *J* = 9.3 Hz, 8b-H), 6.99 (1H, dd, *J* = 7.5, 1.6 Hz, 8-H), 7.08 (1H, dt, *J* = 1.1, 7.4 Hz, Ar-H), 7.14 (1H, dd, *J* = 8.2, 1.1 Hz, Ar-H), 7.24 - 7.38 (6H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 36.1, 44.6, 47.6, 49.0, 53.3, 117.4, 121.1, 124.9, 126.6, 127.3, 127.5, 128.8, 129.3, 140.7, 151.5, 167.4, 169.3. IR ($CHCl_3$): 1753, 1730, 1584 cm^{-1}. MS *m/z* (relative intensity, %): 308 (M^+, 0.3), 104 (100). HRMS *m/z*: Calcd for $C_{19}H_{16}O_4$: 308.1048. Found: 308.1044. *Anal.* Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.74; H, 5.17.

Methyl *rel*-(1*R*,2a*S*,8b*S*)-3-Oxo-1-phenyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-2a-carboxylate (3k) (from Method A and B) Less polar compound. Colorless needles (AcOEt - *n*-hexane), mp 117.1 - 117.9 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.01 (1H, ddd, *J* = 12.8, 8.1, 0.9 Hz, 2-H), 3.40 (1H, ddd, *J* = 12.8, 9.0, 2.4 Hz, 2-H), 3.85 (3H, s, OCH_3), 4.13 (1H, q, *J* = 8.9 Hz, 1-H), 4.29 (1H, dd, *J* = 9.3, 2.0 Hz, 8b-H), 6.48 (1H, d, *J* = 7.7 Hz, 8-H), 6.82 (1H, dt, *J* = 1.3, 7.5 Hz, Ar-H), 6.85 - 6.95 (3H, m, Ar-H), 7.08 - 7.16 (4H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 33.1, 42.5, 45.3, 48.0, 53.4, 116.9, 117.5, 124.3, 127.0, 128.0, 128.1, 128.7, 129.5, 137.1, 151.1, 165.5, 170.4. IR ($CHCl_3$): 1745, 1584 cm^{-1}. MS *m/z* (relative intensity, %): 308 (M^+, 0.2), 104 (100). HRMS *m/z*: Calcd for $C_{19}H_{16}O_4$: 308.1048. Found: 308.1053. *Anal*. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.79; H, 5.19.

***rel*-(1*R*,2a*R*,8b*R*)-2a-Benzoyl-1-butyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (2m)** (from Method A) Polar compound. Colorless prisms (*n*-hexane), mp 89.0 – 90.5 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.86 (3H, t, *J* = 6.8 Hz, CH_3), 1.20 - 1.30 (4H, m, $C\underline{H}_2C\underline{H}_2CH_3$), 1.42 - 1.54 (1H, m, 1-CH_2), 1.55 - 1.65 (1H, m, 1-CH_2), 2.40 (1H, sext, *J* = 7.9 Hz, 1-H), 2.89 (1H, dd, *J* = 12.1, 8.8 Hz, 2-H), 2.96 (1H, dd, *J* = 12.1, 9.2 Hz, 2-H), 3.52 (1H, d, *J* = 7.7 Hz, 8b-H), 7.10 - 7.20 (3H, m, Ar-H), 7.25 - 7.40 (3H, m, Ar-H), 7.51 (1H, tt, *J* = 7.5, 1.3 Hz, Ar-H), 7.81 - 7.85 (2H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 13.9, 22.4, 28.7, 35.1, 37.2, 40.8, 46.6, 52.9, 117.3, 122.7, 125.2, 127.6, 128.6, 128.7, 129.2, 133.4, 133.7, 151.0, 167.5, 194.4. IR ($CHCl_3$): 1737, 1666, 1594, 1580 cm^{-1}. MS *m/z* (relative intensity, %): 334 (M^+, 2.1), 105 (100). HRMS *m/z*: Calcd for $C_{22}H_{22}O_3$; 334.1569. Found; 334.1568. *Anal.* Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.93; H, 6.61.

***rel*-(1*R*,2a*S*,8b*S*)-2a-Benzoyl-1-butyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3m)** (from Method A) Less polar compound. Colorless needles (*i*-Pr_2O), mp 133.0 - 134.5 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.81 (3H, t, *J* = 7.0 Hz, CH_3), 0.86 - 1.35 (6H, m, $(C\underline{H}_2)_3CH_3$), 2.26 (1H, ddd, *J* = 12.1, 8.4, 0.7 Hz, 2-H), 2.63 - 2.77 (1H, m, 1-H), 3.46 (1H, ddd, *J* = 12.1, 8.8, 2.4 Hz, 2-H), 4.00 (1H, dd, *J* = 9.2, 1.5 Hz, 8b-H), 7.08 (1H, ddd, *J* = 7.3, 1.8, 0.7 Hz, 8-H), 7.13 - 7.23 (2H, m, Ar-H), 7.33

- 7.41 (3H, m, Ar-H), 7.48 - 7.54 (1H, m, Ar-H), 7.74 - 7.79 (2H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 13.9, 22.4, 28.5, 31.6, 35.4, 36.6, 43.1, 51.1, 117.6, 118.1, 124.8, 128.8, 128.9, 129.0, 129.9, 133.2, 133.4, 151.3, 166.1, 193.3. IR ($CHCl_3$): 1737, 1682 cm^{-1}. MS *m/z* (relative intensity, %): 334 (M^+, 5.3), 105 (100). HRMS *m/z*: Calcd for $C_{22}H_{22}O_3$; 334.1569. Found; 334.1574. *Anal.* Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 79.11; H, 6.65.

***rel*-(1*R*,2a*R*,8b*R*)-1-Acetoxymethyl-2a-benzoyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (2n)** (from Method A) Polar compound. Colorless needles (AcOEt), mp 111.0 - 112.0 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.04 (3H, s, $COCH_3$), 2.67 - 2.80 (1H, m, 1-H), 2.91 (1H, dd, *J* = 12.3, 9.0 Hz, 2-H), 3.13 (1H, dd, *J* = 12.3, 8.6 Hz, 2-H), 3.78 (1H, d, *J* = 7.3 Hz, 8b-H), 4.11 (1H, dd, *J* = 11.7, 6.6 Hz, OCH_2), 4.21 (1H, dd, *J* = 11.4, 5.1 Hz, OCH_2), 7.11 - 7.22 (3H, m, Ar-H), 7.30 - 7.41 (3H, m, Ar-H), 7.53 (1H, t, *J* = 7.3 Hz, Ar-H), 7.82 (2H, d, *J* = 7.3 Hz, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 20.7, 32.8, 38.9, 43.2, 52.4, 65.3, 117.4, 121.6, 125.4, 127.7, 128.7, 129.1, 129.2, 133.3, 133.6, 150.9, 166.7, 170.7, 193.5. IR ($CHCl_3$): 1735, 1667, 1593, 1580 cm^{-1}. MS *m/z* (relative intensity, %): 350 (M^+, 1.3), 105 (100). HRMS *m/z*: 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, 71.99; H, 5.20.

***rel*-(1*R*,2a*S*,8b*S*)-1-Acetoxymethyl-2a-benzoyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3n)** (from Method A) Less polar compound. Colorless column (*i*-PrOH), mp 89.0 - 92.0 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.94 (3H, s, $COCH_3$), 2.63 (1H, dd, *J* = 12.5, 7.5 Hz, 2-H), 2.94 - 3.07 (1H, m, 1-H), 3.46 (1H, dd, *J* = 12.5, 9.2 Hz, 2-H), 3.87 (1H, dd, *J* = 11.7, 4.6 Hz, OCH_2), 3.94 (1H, dd, *J* = 11.7, 5.9 Hz, OCH_2), 4.20 (1H, d, *J* = 9.5 Hz, 8b-H), 7.10 - 7.21 (3H, m, Ar-H), 7.28 - 7.48 (3H, m, Ar-H), 7.53 (1H, td, *J* = 7.3, 1.1 Hz, Ar-H), 7.82 (2H, d, *J* = 7.7 Hz, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 20.5, 31.9, 34.5, 41.6, 51.9, 63.3, 117.4, 125.1, 128.8, 129.1, 129.4, 133.0, 133.6, 151.4, 165.7, 170.3, 193.3. IR ($CHCl_3$): 1736, 1683, 1595, 1581 cm^{-1}. MS *m/z* (relative intensity, %): 350 (M^+, 1.9), 105 (100). HRMS *m/z*: Calcd for $C_{21}H_{18}O_5$; 350.1154. Found; 350.1153. *Anal.* Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 72.21; H, 5.26.

***rel*-(1*R*,2a*R*,8b*R*)-2a-Benzoyl-1-cyclohexyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (2p)** (from Method A) Polar compound. Colorless prisms (*i*-PrOH), mp 142.0 - 144.0 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.70 - 0.89 (2H, m, cyclohexyl-H), 1.03 - 1.42 (4H, m, cyclohexyl-H), 1.55 - 1.90 (5H, m, cyclohexyl-H), 2.16 (1H, quint, *J* = 8.8 Hz, 1-H), 2.71 (1H, dd, *J* = 12.1, 8.8 Hz, 2-H), 2.98 (1H, dd, *J* = 12.1, 9.2 Hz, 2-H), 3.63 (1H, d, *J* = 7.7 Hz, 8b-H), 7.12 (1H, d, *J* = 8.1 Hz, Ar-H), 7.13 - 7.20 (2H, m, Ar-H), 7.25 - 7.40 (3H, m, Ar-H), 7.51 (1H, t, *J* = 7.7 Hz, Ar-H), 7.81 (2H, d, *J* = 7.8 Hz,

Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 25.68, 25.72, 26.2, 29.4, 30.2, 35.3, 43.3, 45.1, 46.1, 52.3, 117.4, 123.1, 125.2, 128.1, 128.7, 129.1, 133.4, 133.8, 151.1, 167.7, 194.3. IR ($CHCl_3$): 1737, 1665, 1595, 1578 cm^{-1}. MS *m/z* (relative intensity, %): 360 (M^+, 2.7), 255 (100). HRMS *m/z*: Calcd for $C_{24}H_{24}O_3$; 360.1725. Found; 360.1729. *Anal.* Calcd for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71. Found: C, 80.00; H, 6.58.

***rel*-(1*R*,2a*S*,8b*S*)-2a-Benzoyl-1-cyclohexyl-1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3p)** (from Method A) Less polar compound. Colorless column (*i*-PrOH), mp 129.0 - 130.5 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.70 - 0.90 (2H, m, cyclohexyl-H), 0.95 - 1.28 (4H, m, cyclohexyl-H), 1.45 - 1.85 (5H, m, cyclohexyl-H), 2.33 (1H, t, *J* = 10.8 Hz, 2-H), 2.48 (1H, quint,d, *J* = 8.4, 1.5 Hz, 1-H), 3.24 (1H, ddd, *J* = 11.4, 8.1, 3.3 Hz, 2-H), 4.04 (1H, dd, *J* = 8.6, 3.1 Hz, 8b-H), 7.17 - 7.26 (3H, m, Ar-H), 7.33 - 7.42 (3H, m, Ar-H), 7.52 (1H, tt, *J* = 7.5, 1.5 Hz, Ar-H), 7.72 - 7.75 (2H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 25.5, 25.7, 26.2, 28.5, 32.1, 32.7, 37.7, 43.5, 50.5, 118.0, 124.8, 128.8, 128.9, 129.1, 130.2, 133.1, 133.5, 151.3, 165.9, 193.1. IR ($CHCl_3$): 1738, 1685, 1594, 1580 cm^{-1}. MS *m/z* (relative intensity, %): 360 (M^+, 5.9), 255 (100). HRMS *m/z*: Calcd for $C_{24}H_{24}O_3$; 360.1725. Found; 360.1720. *Anal.* Calcd for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71. Found: C, 79.69; H, 6.74.

Ethyl *rel*-(1*R*,2a*R*,8b*R*)-1-Acetoxymethyl-1,2,2a,8b-tetrahydro-3-oxo-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-2a-carboxylate (2q) (from Method A) Polar compound. Colorless plates (AcOEt - *n*-hexane), mp 84.3 - 85.6 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.20 (3H, t, *J* = 7.2 Hz, $OCH_2C\underline{H}_3$), 2.09 (3H, s, $COCH_3$), 2.68 (1H, dd, *J* = 14.2, 7.8 Hz, 2-CH_2), 2.69 (1H, m, 1-CH), 2.86 (1H, dd, *J* = 14.6, 13.8 Hz, 2-H), 3.65 (1H, d, *J* = 7.9 Hz, 8b-H), 4.10 - 4.28 (4H, m, $C\underline{H}_2$OAc and $OC\underline{H}_2CH_3$), 7.07 - 7.14 (3H, m, Ar-H), 7.26 - 7.32 (1H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 13.8, 20.6, 31.7, 38.8, 43.6, 47.8, 62.2, 65.0, 117.2, 120.7, 124.8, 127.5, 129.1, 151.2, 166.8, 168.5, 170.7. IR ($CHCl_3$): 1749, 1728, 1612, 1584 cm^{-1}. MS *m/z* (relative intensity, %): 318 (M^+, 1.7), 146 (100). HRMS *m/z*: Calcd for $C_{17}H_{18}O_6$: 318.1103. Found: 318.1099. *Anal.* Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.09; H, 5.84. Crystal data (AFC7R): $C_{17}H_{18}O_6$, *M* = 318.33, orthorhombic, *a* = 12.8067(8), *b* = 14.5180(8), *c* = 8.7113(8) Å, V = 1619.7(2) Å^3, T = 296 K, space group $P2_12_12_1$ (no. 19), *Z* = 4, D_{calc} = 1.305 g/cm^3, F_{000} = 672.00, μ(Cu-kα) = 8.33 cm^{-1}, 1427 reflections measured, 1407 unique (R_{int} = 0.000). The structure was solved by direct methods (MITHRIL84)[15] and expanded using Fourier techniques (DIRDIF94).[14] The final R_1 was 0.037 (1050 reflections were used).

Ethyl *rel*-(1*R*,2a*S*,8b*S*)-1-Acetoxymethyl-1,2,2a,8b-tetrahydro-3-oxo-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-2a-carboxylate (3q) (from Method A) Less polar compound. Colorless plates (AcOEt -

n-hexane), mp 83.6 - 84.4 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.23 (3H, t, *J* = 7.2 Hz, $OCH_2C\underline{H}_3$), 1.94 (3H, s, $COCH_3$), 2.55 (1H, ddd, *J* = 13.0, 4.6, 0.9 Hz, 2-H), 2.93 - 3.04 (1H, m, 1-H), 3.30 (1H, dd, *J* = 13.0, 9.6 Hz, 2-H), 3.83 (1H, dd, *J* = 11.8, 3.6 Hz, 8b-H), 4.05 (1H, dd, *J* = 11.8, 5.0 Hz, -$C\underline{H}_2OCOCH_3$), 4.17 (1H, dq, *J* = 10.6, 7.2 Hz, $OC\underline{H}_2CH_3$), 4.19 (1H, dd, *J* = 9.5, 7.2 Hz, -$C\underline{H}_2OCOCH_3$), 4.25 (1H, dq, *J* = 10.6, 7.2 Hz, $COOC\underline{H}_2CH_3$), 7.02 - 7.14 (3H, m, Ar-H), 7.24 - 7.31 (1H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 13.8, 20.4, 31.0, 34.5, 41.3, 48.4, 62.3, 62.8, 116.9, 117.7, 124.5, 128.3, 129.1, 151.8, 166.2, 169.5, 170.3. IR ($CHCl_3$): 1749, 1728, 1612, 1584 cm^{-1}. MS *m/z* (relative intensity, %): 318 (M^+, 1.3), 146 (100). HRMS *m/z*: Calcd for $C_{17}H_{18}O_6$: 318.1103. Found: 318.1101. *Anal.* Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.15; H, 5.78. Crystal data (AFC7R): $C_{17}H_{18}O_6$, *M* = 318.33, monoclinic, *a* = 11.6911(5), *b* = 9.3077(4), *c* = 14.9175(7) Å, β = 97.696(4)°, V = 1608.7(1) Å^3, T = 296 K, space group $P2_1/c$ (no. 14), *Z* = 4, D_{calc} = 1.314 g/cm^3, F_{000} = 672.00, μ(Cu-kα) = 8.39 cm^{-1}, 2676 reflections measured, 2502 unique (R_{int} = 0.029). The structure was solved by direct methods (MITHRIL84)[15] and expanded using Fourier techniques (DIRDIF94).[14] The final R_1 was 0.048 (2137 reflections were used).

***rel*-(2a*R*,8b*R*)-2-Benzoyl-2a,8b-dihydro-1-phenyl-*3H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (5a)**

Yellow amorphous. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.66 (1H, s, 8b-H), 6.71 (1H, s, 2-H), 7.21 (1H, dd, *J* = 8.1, 1.3 Hz, Ar-H), 7.23 (1H, dt, *J* = 1.3, 7.5 Hz, Ar-H), 7.30 - 7.40 (6H, m, Ar-H), 7.43 - 7.47 (2H, m, Ar-H), 7.49 (1H, dd, *J* = 7.5, 1.6 Hz, Ar-H), 7.51 - 7.56 (1H, m, Ar-H), 7.71 - 7.74 (1H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 47.7, 57.8, 118.2, 119.7, 125.3, 125.7, 127.1, 128.4, 128.6, 129.0, 129.46, 129.51, 129.53, 131.5, 133.7, 134.0, 151.1, 151.3, 165.9, 193.5. IR ($CHCl_3$): 1734, 1676 cm^{-1}. MS *m/z* (relative intensity, %): 352 (M^+, 7.0), 105 (100). HRMS *m/z*: Calcd for $C_{24}H_{16}O_3$: 352.1099. Found: 352.1107.

***rel*-(2a*R*,8b*R*)-2a-Benzoyl-2a,8b-dihydro-1-(4-methoxybenzoyl)-*3H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (5e)** Colorless needles (AcOEt - *n*-hexane), mp 182.0 - 183.7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.79 (3H, s, OCH_3), 4.61 (1H, s, 8b-H), 6.57 (1H, s, 2-H), 6.84 - 6.88 (2H, m, Ar-H), 7.21 (1H, dd, *J* = 8.1, 1.3 Hz, Ar-H), 7.22 (1H, dt, *J* = 7.5, 1.3 Hz, Ar-H), 7.33 - 7.41 (5H, m, Ar-H), 7.47 (1H, dd, *J* = 7.5, 1.6 Hz, Ar-H), 7.51 - 7.56 (1H, m, Ar-H), 7.71 - 7.74 (2H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 47.7, 55.3, 57.7, 114.0, 118.2, 119.9, 124.4, 124.6, 125.2, 127.2, 128.4, 129.0, 129.46, 129.47, 133.7, 134.1, 150.8, 151.1, 160.5, 166.2, 193.8. IR ($CHCl_3$): 1733, 1676, 1620, 1598 cm^{-1}. MS *m/z* (relative intensity, %): 382 (M^+, 33), 105 (100). HRMS *m/z*: Calcd for $C_{25}H_{18}O_4$: 382.1205. Found: 382.1207. *Anal.* Calad for $C_{25}H_{18}O_4$: C, 78.52; H, 4.74. Found: C, 78.54; H, 4.90.

***rel*-(2a*R*,8b*R*)-2a-Acetyl-2a,8b-dihydro-3-oxo-1-phenyl-*3H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (5g)**
Pale yellow amorphous. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.45 (3H, s, $COCH_3$) 4.68 (1H, s, 8b-H), 6.55 (1H, s, 2-H), 7.08 (1H, dd, *J* = 8.1, 1.1 Hz, Ar-H), 7.15 (1H, dt, *J* = 7.5, 1.3 Hz, Ar-H), 7.27 (1H, dt, *J* = 1.7, 7.8 Hz, Ar-H), 7.32 - 7.40 (3H, m, Ar-H), 7.42 - 7.47 (3H, m, Ar-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 27.8, 46.5, 60.2, 117.7, 119.7, 124.9, 125.7, 126.9, 128.7, 129.2, 129.3, 129.6, 131.4, 150.9, 153.3, 166.0, 202.0. IR ($CHCl_3$): 1733, 1709, 1645 cm^{-1}. MS *m/z* (relative intensity, %): 290 (M^+, 21), 247 (100). HRMS *m/z*: Calcd for $C_{19}H_{14}O_3$: 290.0943. Found: 290.0948.

***rel*-(2a*R*,8b*R*)-2a,8b-Dihydro-2a-isobutyryl-1-phenyl-*3H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (5h)**
yellow amorphous. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.16 (6H, d, *J* = 7.0 Hz, $CH(C\underline{H}_3)_2$), 3.11 (1H, hept, *J* = 7.0 Hz, $C\underline{H}(CH_3)_2$), 4.54 (1H, s, 8b-H), 6.57 (1H, d, *J* = 0.4 Hz, 2-H), 7.09 (1H, dd, *J* = 8.1, 1.3 Hz, Ar-H), 7.16 (1H, dt, *J* = 1.3, 7.5 Hz, Ar-H), 7.25 - 7.29 (1H, m, Ar-H), 7.30 - 7.39 (3H, m, Ar-H), 7.43 - 7.46 (3H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 18.5, 18.6, 38.3, 47.3, 59.5, 117.8, 119.7, 124.9, 125.7, 127.1, 128.7, 129.26, 129.27, 129.6, 131.5, 151.0, 152.6, 166.3, 208.4. IR ($CHCl_3$): 1734, 1702 cm^{-1}. MS *m/z* (relative intensity, %): 318 (M^+, 7.6), 247 (100). HRMS *m/z*: Calcd for $C_{21}H_{18}O_3$: 318.1256. Found: 318.1264.

***rel*-(2a*R*,8b*R*)-2a-(2,2-Dimethylpropionyl)-2a,8b-dihydro-1-phenyl-*3H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (5i)** Colorless needles (AcOEt), mp 171.5 - 172.8 °C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.22 (9H, s, $COC(CH_3)_3$), 4.47 (1H, s, 8b-H), 6.60 (1H, s, 2-H), 7.11 (1H, dd, *J* = 7.8, 1.2 Hz, Ar-H), 7.18 (1H, dt, *J* = 1.5, 7.3 Hz, Ar-H), 7.29 - 7.50 (7H, m, Ar-H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 27.7, 44.4, 47.6, 58.8, 117.9, 119.9, 125.0, 125.5, 127.9, 128.5, 129.0, 129.2, 129.3, 131.4, 150.0, 151.1, 166.0, 209.3. IR ($CHCl_3$): 1732, 1691 cm^{-1}. MS *m/z* (relative intensity, %): 332 (M^+, 3.1), 57 (100). HRMS *m/z*: Calcd for $C_{22}H_{20}O_3$: 332.1412. Found: 332.1418. *Anal.* Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.37; H, 6.23.

Ethyl *rel*-(2a*R*,8b*R*)-2a,8b-Dihydro-3-oxo-1-phenyl-*3H*-benzo[*b*]cyclobuta[*d*]pyran-2a-carboxylate (5j) Pale yellow amorphous, ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.30 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$), 4.27 (1H, dq, *J* = 10.8, 7.1 Hz, $OC\underline{H}_2CH_3$), 4.31 (1H, dq, *J* = 10.8, 7.1 Hz, $OC\underline{H}_2CH_3$), 4.66 (1H, s, 8b-H), 6.50 (1H, s, 2-H), 7.09 (1H, dd, *J* = 8.2, 1.3 Hz, 8-H), 7.16 (1H, dt, *J* = 1.3, 7.5 Hz, Ar-H), 7.25 - 7.31 (1H, m, Ar-H), 7.32 - 7.38 (3H, m, Ar-H), 7.43 - 7.47 (3H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.0, 47.8, 53.8, 62.3, 117.8, 119.6, 124.9, 125.8, 126.0, 128.7, 129.2 (x 2), 129.6, 131.5, 151.0, 152.6, 165.4, 168.4. IR ($CHCl_3$): 1744, 1584 cm^{-1}. MS *m/z* (relative intensity, %): 320 (M^+, 12.4), 247 (100). HRMS *m/z*: Calcd for $C_{20}H_{16}O_4$: 320.1048. Found: 320.1045.

Methyl *rel*-(2a*R*,8b*R*)-2a,8b-Dihydro-3-oxo-1-phenyl-*3H*-benzo[*b*]cyclobuta[*d*]pyran-2a-carboxylate (5k) Pale yellow amorphous. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.82 (3H, s, OCH_3), 4.67 (1H, s, 8b-H), 6.50 (1H, d, *J* = 0.4 Hz, 2-H), 7.09 (1H, dd, *J* = 8.2, 1.3 Hz, Ar-H), 7.16 (1H, dt, *J* = 1.3, 7.5 Hz, Ar-H), 7.20 - 7.31 (1H, m, Ar-H), 7.32 - 7.42 (3H, m, Ar-H), 7.43 - 7.47 (3H, m, Ar-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 47.9, 53.1, 53.7, 117.8, 119.5, 124.9, 125.7, 125.9, 128.7, 129.2, 129.3, 129.6, 131.5, 151.0, 152.7, 165.3, 168.8. IR ($CHCl_3$): 1736, 1661 cm^{-1}. MS *m/z* (relative intensity, %): 306 (M^+, 24), 247 (100). HRMS *m/z*: Calcd for $C_{19}H_{14}O_4$: 306.0892. Found: 306.0902.

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