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

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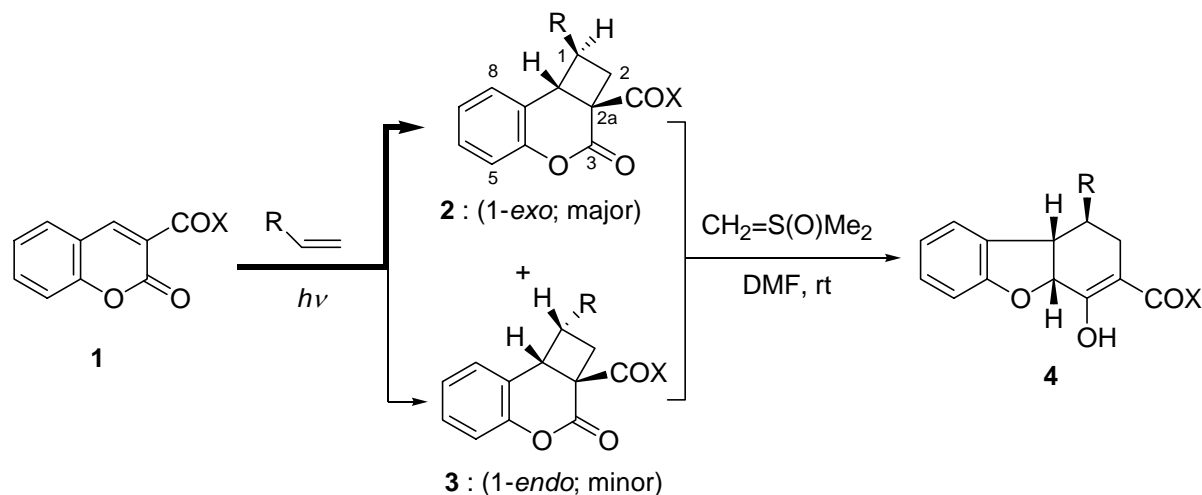
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Abstract – Stereoselective preparation of 1-*exo*-substituted 1,2,2a,8b-tetrahydro-3H-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**2**) was achieved by photo [2+2] cycloaddition of olefins to 3-substituted coumarins (**1**). 1-*endo*-Substituted 1,2,2a,8b-tetrahydro-3H-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**3**) were stereoselectively prepared by hydrogenation over the Pd-carbon of 2a,8b-dihydro-3H-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 ¹H-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-3H-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**2**) were obtained. It could be clearly assigned on the basis of the ¹H-NMR spectra that the R group in **2** and **3** located at the 1-position, but

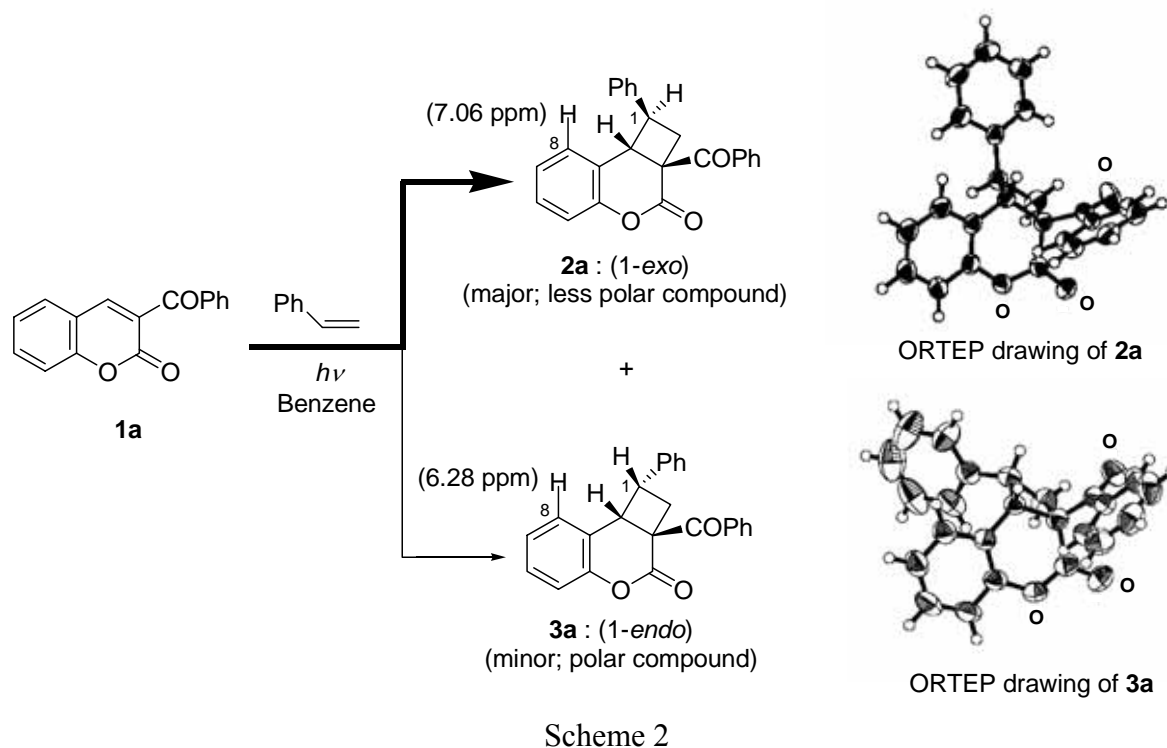
their stereochemistries were vague.



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 E⁶ 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 ¹H-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 ¹H-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 ¹H-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.



In order to confirm the generality of this observation, various cyclobutanes (**2** and **3**) were prepared (*vide post*), and the $^1\text{H-NMR}$ 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.

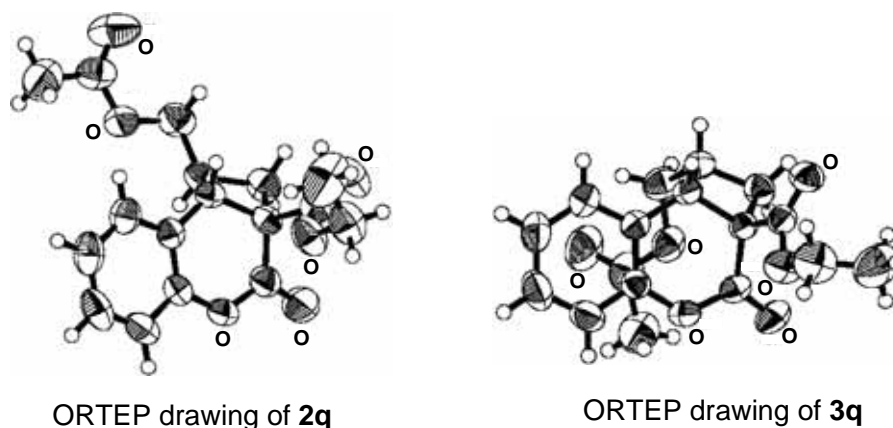
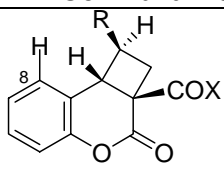
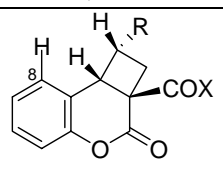


Figure 1

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

X	R	C8-H chemical shift in $^1\text{H-NMR}$	
		 2 : <i>exo</i> -form	 3 : <i>endo</i> -form
Ph	Ph	2a : 7.06 ^a	3a : 6.28 ^a
Ph	2-pyridyl	2b : - ^c	3b : 6.52 ^b
4-F-C ₆ H ₄	Ph	2c : - ^c	3c : 6.29 ^b
Ph	4-Br-C ₆ H ₄	2d : 7.03 ^b	3d : 6.29 ^b
Ph	4-MeO-C ₆ H ₄	2e : 7.04 ^b	3e : 6.30 ^b
4-MeO-C ₆ H ₄	Ph	2f : 7.05 ^b	3f : 6.28 ^b
Me	Ph	2g : 7.01 ^b	3g : 6.45 ^b
<i>i</i> -Pr	Ph	2h : 7.00 ^b	3h : 6.45 ^b
<i>t</i> -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	<i>n</i> -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

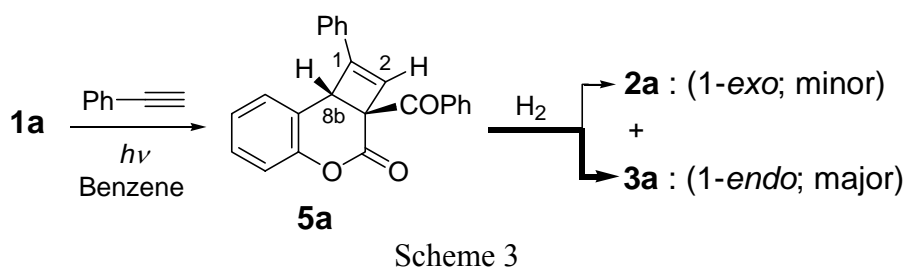
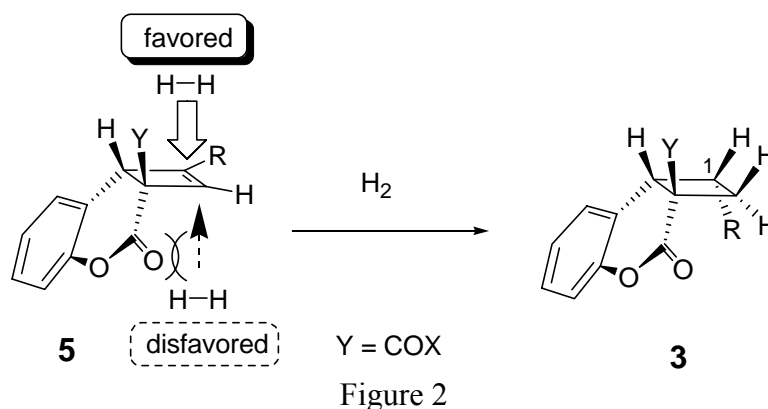
^a The chemical shift was assigned on the basis of $^1\text{H-NMR}$ spectra with HMQC and HMBC.

^b The chemical shift was assigned by comparison with $^1\text{H-NMR}$ 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 $^1\text{H-NMR}$ 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.

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 ₃ P) ₃ RhCl	C ₆ H 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.

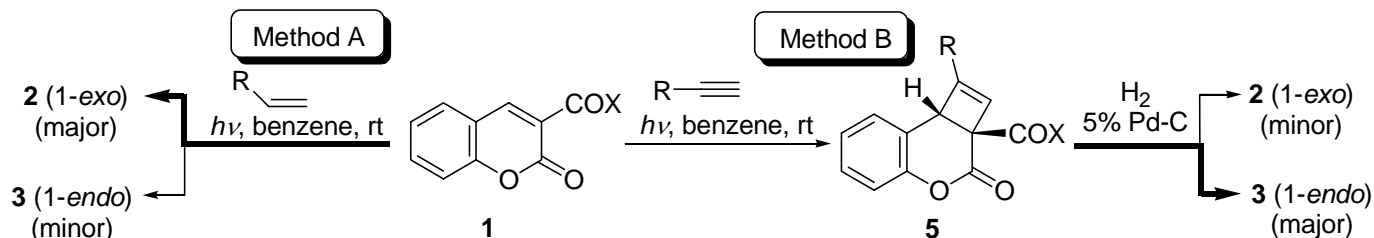
In Method A, the main products were the *exo*-form (**2**), and the ratio of **2/3** increased in the cases of the 3-acylcoumarins (**1a–i** and **m–q**) rather than those in the cases of 3-alkoxycarbonylcoumarins (**1j** and **k**). In Method B, the *endo*-form (**3**) was obtained as the main products. 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 ¹H-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	A ^b	92	5.0/1	2j	A ^a	78	1.5/1
3b				3j	B ^a	(71 : 85 ^e)	1/1.4
2c	A ^b	93	3.0/1	2k	A ^a	83	2.0/1
3c				3k	B ^a	(92 : 55 ^e)	1/2.2
2d	A ^b	98	3.0/1	2m	A ^b	93	6.0/1
3d				3m	A ^b	93	6.0/1
2e	A ^a	97	3.6/1	2n	A ^b	80	3.9/1 ^h
3e	B ^a	(68 : 35 ^e)	1/5.7	3n			
2f	A ^b	93	3.0/1	2p	A ^b	83	8.4/1 ^h
3f				3p	A ^b	83	8.4/1 ^h
2g	A ^a	92	4.5/1	2q	A ^b	89	3.7/1
3g	B ^a	(91 : 83 ^e)	1/3.5	3q			
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 ¹H-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 (¹H : 400 MHz, ¹³C : 100 MHz), a JEOL AL-300 (¹H; 300 MHz, ¹³C; 75.5MHz) and a Varian Gemini 200 (¹H; 200 MHz, ¹³C; 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 works 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-K α radiation and rotating anode generator, and a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-K α 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*,2*aR*,8*bR*)-2a-Benzoyl-1-phenyl-1,2,2*a*,8*b*-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. ¹H-NMR (300 MHz, CDCl₃) 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). $^{13}\text{C-NMR}$ (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 $\text{C}_{24}\text{H}_{18}\text{O}_3$; 354.1256. Found; 354.1258. Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_3$: C, 81.34; H, 5.12. Found: C, 81.23; H, 5.20. Crystal data (RAXIS RAPID) $\text{C}_{24}\text{H}_{18}\text{O}_3$, $M = 354.40$, monoclinic, $a = 8.8895(6)$, $b = 22.9681(16)$, $c = 8.8931(7)$ Å, $\beta = 102.095(5)^\circ$, $V = 1775.4(2)$ Å³, $T = 93$ K, space group $\text{P2}_1/a$ (no. 14), $Z = 4$, $D_{\text{calc}} = 1.326$ g/cm³, $F_{000} = 744.00$, $\mu(\text{Cu-K}\alpha) = 6.955$ cm⁻¹, 7816 reflections measured, 2268 unique ($R_{\text{int}} = 0.043$). The structure was solved by direct methods (SIR92)¹¹ and expanded using Fourier techniques (DIRDIF99).¹² The final R_I was 0.042.

***rel*-(1*R*,2*aS*,8*bS*)-2*a*-Benzoyl-1-phenyl-1,2,2*a*,8*b*-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. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{24}\text{H}_{18}\text{O}_3$; 354.1256. Found; 354.1249. Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_3$: C, 81.34; H, 5.12. Found: C, 81.30; H, 5.17. Crystal data (AFC7R): $\text{C}_{24}\text{H}_{18}\text{O}_3$, $M = 354.40$, monoclinic, $a = 11.749(5)$, $b = 9.913(3)$, $c = 15.705(3)$ Å, $\beta = 91.63(2)^\circ$, $V = 1828.4(9)$ Å³, $T = 296$ K, space group $\text{P2}_1/n$ (no. 14), $Z = 4$, $D_{\text{calc}} = 1.287$ g/cm³, $F_{000} = 744.00$, $\mu(\text{Cu-K}\alpha) = 6.75$ cm⁻¹, 3696 reflections measured, 3472 unique ($R_{\text{int}} = 0.009$). The structure was solved by direct methods (SIR88)¹³ and expanded using Fourier techniques (DIRDIF94).¹⁴ The final R_I was 0.042 (2421 reflections were used).

***rel*-(1*R*,2*aR*,8*bR*)-2*a*-Benzoyl-1-(2-pyridyl)-1,2,2*a*,8*b*-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. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 (CHCl₃) : 1739, 1667, 1588 cm⁻¹. MS *m/z* (relative intensity, %): 355 (M⁺, 1.3), 105 (100). HRMS *m/z*: Calcd for C₂₃H₁₇NO₃: 355.1208. Found: 355.1210. *Anal.* Calcd for C₂₃H₁₇NO₃: C ; 77.73, H ; 4.82, N ; 3.94. Found : C ; 76.72, H ; 4.79, N ; 3.88.

***rel*-(1*R*,2*aS*,8*bS*)-2*a*-Benzoyl-1-(2-pyridyl)-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3*b*)** (from Method A) Less polar compound. Colorless amorphous. ¹H-NMR (300 MHz, CDCl₃) 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, 8*b*-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). ¹³C-NMR (75.5 MHz, CDCl₃) 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 (CHCl₃): 1738, 1685, 1588 cm⁻¹. MS *m/z* (relative intensity, %): 355 (M⁺, 1.6), 105 (100). HRMS *m/z*: Calcd for C₂₃H₁₇NO₃ : 355.1208. Found : 355.1212.

***rel*-(1*R*,2*aR*,8*bR*)-2*a*-(4-Fluorobenzoyl)-1-phenyl-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (2*c*)** (from Method A) Polar compound. Colorless amorphous. ¹H-NMR (400 MHz, CDCl₃) 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, 8*b*-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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1739, 1666, 1594 cm⁻¹. MS *m/z* (relative intensity, %): 372 (M⁺, 0.4), 104 (100). HRMS *m/z*: Calcd for C₂₄H₁₇O₃F: 372.1162. Found: 372.1165.

***rel*-(1*R*,2*aS*,8*bS*)-2*a*-(4-Fluorobenzoyl)-1-phenyl-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3*c*)** (from Method A) Less polar compound. Colorless needles (AcOEt / n-hexane), mp 150.3 - 152.1 °C. ¹H-NMR (400 MHz, CDCl₃) 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, 8*b*-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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1737,

1685, 1595 cm^{-1} . MS m/z (relative intensity, %): 372 (M^+ , 0.2), 104 (100). HRMS m/z : Calcd for $\text{C}_{24}\text{H}_{17}\text{O}_3\text{F}$: 372.1162. Found: 372.1170. Anal. Calcd for $\text{C}_{24}\text{H}_{17}\text{O}_3\text{F}$: C, 77.41; H, 4.60. Found: C, 77.44; H, 4.77.

***rel*-(1*R*,2*aR*,8*bR*)-2*a*-Benzoyl-1-(4-bromophenyl)-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (2*d*)** (from Method A) Polar compound. Colorless amorphous. $^1\text{H-NMR}$ (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, 8*b*-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). $^{13}\text{C-NMR}$ (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 $\text{C}_{24}\text{H}_{17}\text{O}_3\text{Br}$: 432.0361. Found: 432.0354.

***rel*-(1*R*,2*aS*,8*bS*)-2*a*-Benzoyl-1-(4-bromophenyl)-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (3*d*)** (from Method A) Less polar compound. Colorless amorphous. $^1\text{H-NMR}$ (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, 8*b*-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). $^{13}\text{C-NMR}$ (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 $\text{C}_{24}\text{H}_{17}\text{O}_3\text{Br}$: 432.0361. Found: 432.0366.

***rel*-(1*R*,2*aR*,8*bR*)-2*a*-Benzoyl-1-(4-methoxyphenyl)-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]-pyran-3-one (2*e*)** (from Method A) Polar compound. Colorless oil. $^1\text{H-NMR}$ (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, 8*b*-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). $^{13}\text{C-NMR}$ (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 [$(\text{M} + \text{H})^+$, 2.9], 134 (100). HRMS(CI) m/z : Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_4 + \text{H}$: 385.1440. Found: 385.1443.

rel-(1R,2aS,8bS)-2a-Benzoyl-1-(4-methoxyphenyl)-1,2,2a,8b-tetrahydro-3H-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. ¹H-NMR (400 MHz, CDCl₃) 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, OCH₃), 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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1737, 1685, 1608 cm⁻¹. MS(FAB) *m/z*: 385 (M + H)⁺. HRMS(FAB) *m/z*: Calcd for C₂₅H₂₀O₄ + H: 385.1440. Found: 385.1435. *Anal.* Calcd for C₂₅H₂₀O₄: C, 78.11; H, 5.24. Found: C, 77.99; H, 5.21.

rel-(1R,2aR,8bR)-2a-(4-Methoxybenzoyl)-1-phenyl-1,2,2a,8b-tetrahydro-3H-benzo[b]cyclobuta[d]-pyran-3-one (2f) (from Method A) Polar compound. Colorless plates (*i*-Pr₂O), mp 120.0 - 122.0 °C. ¹H-NMR (300 MHz, CDCl₃) 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, OCH₃), 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). ¹³C-NMR (75.5 MHz, CDCl₃) 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 (CHCl₃): 1738, 1657, 1595, 1570, 1505 cm⁻¹. MS *m/z* (relative intensity, %): 384 (M⁺, 0.6), 135 (100). HRMS *m/z*: Calcd for C₂₅H₂₀O₄: 384.1362. Found: 384.1360. *Anal.* Calcd for C₂₅H₂₀O₄: C, 78.11; H, 5.24. Found: C, 78.27, H, 5.34.

rel-(1R,2aS,8bS)-2a-(4-Methoxybenzoyl)-1-phenyl-1,2,2a,8b-tetrahydro-3H-benzo[b]cyclobuta[d]-pyran-3-one (3f) (from Method A) Less polar compound. Colorless column (*i*-Pr₂O), mp 220.0 - 222.0 °C. ¹H-NMR (300 MHz, CDCl₃) 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, OCH₃), 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). ¹³C-NMR (75.5 MHz, CDCl₃) 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 (CHCl₃): 1737, 1673, 1597, 1573, 1506 cm⁻¹. MS *m/z* (relative intensity, %): 384 (M⁺, 0.4), 280 (100). HRMS *m/z*: Calcd for C₂₅H₂₀O₄: 384.1362. Found: 384.1357. *Anal.* Calcd for C₂₅H₂₀O₄: C, 78.11; H, 5.24. Found: C, 77.82; H, 5.37.

***rel*-(1*R*,2*aR*,8*bR*)-2*a*-Acetyl-1-phenyl-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one**

(2*g*) (from Method A) Polar compound. Colorless plates (AcOEt - *n*-hexane), mp 107.9 - 108.5 °C. ¹H-NMR (300 MHz, CDCl₃) δ: 2.26 (3H, s, C(=O)CH₃), 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, 8*b*-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). ¹³C-NMR (75.5 MHz, CDCl₃) 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 (CHCl₃): 1744, 1707, 1585 cm⁻¹. MS *m/z* (relative intensity, %): 292 (M⁺, 0.2), 104 (100). HRMS *m/z*: Calcd for C₁₉H₁₆O₃: 292.1099. Found: 292.1093. *Anal.* Calcd for C₁₉H₁₆O₃: C, 78.06; H, 5.52. Found: C, 77.91; H, 5.59.

***rel*-(1*R*,2*aS*,8*bS*)-2*a*-Acetyl-1-phenyl-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3*g*)**

(from Method A and B) Less polar compound. Colorless needles (AcOEt - *n*-hexane), mp 98.6 - 100.8 °C. ¹H-NMR (400 MHz, CDCl₃) δ: 2.41 (3H, s, C(O)CH₃), 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, 8*b*-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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1737, 1715 cm⁻¹. MS(CI) *m/z* (relative intensity, %): 293 [(M + H)⁺, 3.7], 104 (100). HRMS(CI) *m/z*: Calcd for C₁₉H₁₆O₃ + H: 293.1178. Found: 293.1184. *Anal.* Calcd for C₁₉H₁₆O₃: C, 78.06; H, 5.52. Found: C, 77.95; H, 5.58.

***rel*-(1*R*,2*aR*,8*bR*)-2*a*-Isobutyryl-1-phenyl-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (2*h*)**

(from Method A) Polar compound. Colorless plates (AcOEt - *n*-hexane), mp 139.0 - 139.9 °C. ¹H-NMR (300 MHz, CDCl₃) δ: 0.96 (3H, d, *J* = 6.8 Hz, C(O)CH(CH₃)₂), 1.13 (3H, d, *J* = 6.8 Hz, C(O)CH(CH₃)₂), 2.97 (1H, hept, *J* = 6.8 Hz, C(O)CH(CH₃)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, 8*b*-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). ¹³C-NMR (75.5 MHz, CDCl₃) 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 (CHCl₃): 1742, 1704 cm⁻¹. MS *m/z* (relative intensity, %): 320 (M⁺, 0.1), 104 (100). HRMS *m/z*: Calcd for C₂₁H₂₀O₃: 320.1412. Found: 320.1413. *Anal.* Calcd for C₂₁H₂₀O₃: C, 78.73; H, 6.29. Found: C, 78.98; H, 6.44.

***rel*-(1*R*,2*aS*,8*bS*)-2*a*-Isobutyryl-1-phenyl-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (3*h*)**

(from Method A and B) Less polar compound. Colorless needles (AcOEt), mp 128.4 - 130.2 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.17 (3H, d, $J = 7.0$ Hz, $\text{C(O)CH}(\underline{\text{C}}\text{H}_3)_2$), 1.22 (3H, d, $J = 6.8$ Hz, $\text{C(O)CH}(\underline{\text{C}}\text{H}_3)_2$), 2.90 (1H, ddd, $J = 12.6, 8.4, 0.9$ Hz, 2-H), 3.06 (1H, hept, $J = 6.8$ Hz, $\text{C(O)CH}(\underline{\text{C}}\text{H}_3)_2$), 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). $^{13}\text{C-NMR}$ (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 $\text{C}_{21}\text{H}_{20}\text{O}_3 + \text{H}$: 321.1491. Found: 321.1494. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3$: C, 78.73; H, 6.29. Found: C, 78.72; H, 6.46.

***rel*-(1*R*,2*aR*,8*bR*)-2*a*-(2,2-Dimethylpropionyl)-1-phenyl-1,2,2*a*,8*b*-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 $^\circ\text{C}$. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 1.14 (9H, s, $\text{C(O)C}(\text{CH}_3)_3$), 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). $^{13}\text{C-NMR}$ (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 $\text{C}_{22}\text{H}_{22}\text{O}_3$: 334.1569. Found: 334.1562. Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_3$: C, 79.02; H, 6.63. Found: C, 78.87; H, 6.64.

***rel*-(1*R*,2*aS*,8*bS*)-2*a*-(2,2-Dimethylpropionyl)-1-phenyl-1,2,2*a*,8*b*-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 $^\circ\text{C}$ (AcOEt - *n*-hexane). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.30 (9H, s, $\text{C(O)C}(\text{CH}_3)_3$), 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). $^{13}\text{C-NMR}$ (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 $\text{C}_{22}\text{H}_{22}\text{O}_3 + \text{H}$: 335.1647. Found: 335.1651. Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_3$: C, 79.02; H, 6.63. Found: C, 79.27; H, 6.79.

Methyl *rel*-(1*R*,2*aR*,8*bR*)-3-Oxo-1-phenyl-1,2,2*a*,8*b*-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-2*a*-carboxylate (2k) (from Method A) Polar compound. Colorless needles (AcOEt - *n*-hexane), mp 119.0 - 119.8 $^\circ\text{C}$. $^1\text{H-NMR}$ (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, OCH₃), 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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1753, 1730, 1584 cm⁻¹. MS m/z (relative intensity, %): 308 (M⁺, 0.3), 104 (100). HRMS m/z : Calcd for C₁₉H₁₆O₄: 308.1048. Found: 308.1044. Anal. Calcd for C₁₉H₁₆O₄: C, 74.01; H, 5.23. Found: C, 73.74; H, 5.17.

Methyl *rel*-(1R,2aS,8bS)-3-Oxo-1-phenyl-1,2,2a,8b-tetrahydro-3H-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. ¹H-NMR (400 MHz, CDCl₃) 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, OCH₃), 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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1745, 1584 cm⁻¹. MS m/z (relative intensity, %): 308 (M⁺, 0.2), 104 (100). HRMS m/z : Calcd for C₁₉H₁₆O₄: 308.1048. Found: 308.1053. Anal. Calcd for C₁₉H₁₆O₄: C, 74.01; H, 5.23. Found: C, 73.79; H, 5.19.

***rel*-(1R,2aR,8bR)-2a-Benzoyl-1-butyl-1,2,2a,8b-tetrahydro-3H-benzo[*b*]cyclobuta[*d*]pyran-3-one (2m)** (from Method A) Polar compound. Colorless prisms (*n*-hexane), mp 89.0 - 90.5 °C. ¹H-NMR (300 MHz, CDCl₃) δ : 0.86 (3H, t, $J = 6.8$ Hz, CH₃), 1.20 - 1.30 (4H, m, CH₂CH₂CH₃), 1.42 - 1.54 (1H, m, 1-CH₂), 1.55 - 1.65 (1H, m, 1-CH₂), 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). ¹³C-NMR (75.5 MHz, CDCl₃) 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 (CHCl₃): 1737, 1666, 1594, 1580 cm⁻¹. MS m/z (relative intensity, %): 334 (M⁺, 2.1), 105 (100). HRMS m/z : Calcd for C₂₂H₂₂O₃: 334.1569. Found: 334.1568. Anal. Calcd for C₂₂H₂₂O₃: C, 79.02; H, 6.63. Found: C, 78.93; H, 6.61.

***rel*-(1R,2aS,8bS)-2a-Benzoyl-1-butyl-1,2,2a,8b-tetrahydro-3H-benzo[*b*]cyclobuta[*d*]pyran-3-one (3m)** (from Method A) Less polar compound. Colorless needles (*i*-Pr₂O), mp 133.0 - 134.5 °C. ¹H-NMR (300 MHz, CDCl₃) δ : 0.81 (3H, t, $J = 7.0$ Hz, CH₃), 0.86 - 1.35 (6H, m, (CH₂)₃CH₃), 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 $\text{C}_{22}\text{H}_{22}\text{O}_3$; 334.1569. Found; 334.1574. Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_3$: C, 79.02; H, 6.63. Found: C, 79.11; H, 6.65.

rel-(1R,2aR,8bR)-1-Acetoxyethyl-2a-benzoyl-1,2,2a,8b-tetrahydro-3H-benzo[b]cyclobuta[d]pyran-3-one (2n) (from Method A) Polar compound. Colorless needles (AcOEt), mp 111.0 - 112.0 $^{\circ}\text{C}$. ^1H -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 $\text{C}_{21}\text{H}_{18}\text{O}_5$; 350.1154. Found; 350.1158. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_5$: C, 71.99; H, 5.18. Found: C, 71.99; H, 5.20.

rel-(1R,2aS,8bS)-1-Acetoxyethyl-2a-benzoyl-1,2,2a,8b-tetrahydro-3H-benzo[b]cyclobuta[d]pyran-3-one (3n) (from Method A) Less polar compound. Colorless column (*i*-PrOH), mp 89.0 - 92.0 $^{\circ}\text{C}$. ^1H -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 $\text{C}_{21}\text{H}_{18}\text{O}_5$; 350.1154. Found; 350.1153. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_5$: C, 71.99; H, 5.18. Found: C, 72.21; H, 5.26.

rel-(1R,2aR,8bR)-2a-Benzoyl-1-cyclohexyl-1,2,2a,8b-tetrahydro-3H-benzo[b]cyclobuta[d]pyran-3-one (2p) (from Method A) Polar compound. Colorless prisms (*i*-PrOH), mp 142.0 - 144.0 $^{\circ}\text{C}$. ^1H -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). $^{13}\text{C-NMR}$ (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 $\text{C}_{24}\text{H}_{24}\text{O}_3$; 360.1725. Found; 360.1729. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_3$: C, 79.97; H, 6.71. Found: C, 80.00; H, 6.58.

rel-(1R,2aS,8bS)-2a-Benzoyl-1-cyclohexyl-1,2,2a,8b-tetrahydro-3H-benzo[b]cyclobuta[d]pyran-3-one (3p) (from Method A) Less polar compound. Colorless column (*i*-PrOH), mp 129.0 - 130.5 °C. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{24}\text{H}_{24}\text{O}_3$; 360.1725. Found; 360.1720. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_3$: C, 79.97; H, 6.71. Found: C, 79.69; H, 6.74.

Ethyl rel-(1R,2aR,8bR)-1-Acetoxyethyl-1,2,2a,8b-tetrahydro-3-oxo-3H-benzo[b]cyclobuta[d]pyran-2a-carboxylate (2q) (from Method A) Polar compound. Colorless plates (AcOEt - *n*-hexane), mp 84.3 - 85.6 °C. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 1.20 (3H, t, $J = 7.2$ Hz, OCH_2CH_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, CH_2OAc and OCH_2CH_3), 7.07 - 7.14 (3H, m, Ar-H), 7.26 - 7.32 (1H, m, Ar-H). $^{13}\text{C-NMR}$ (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 $\text{C}_{17}\text{H}_{18}\text{O}_6$; 318.1103. Found: 318.1099. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_6$: C, 64.14; H, 5.70. Found: C, 64.09; H, 5.84. Crystal data (AFC7R): $\text{C}_{17}\text{H}_{18}\text{O}_6$, $M = 318.33$, orthorhombic, $a = 12.8067(8)$, $b = 14.5180(8)$, $c = 8.7113(8)$ Å, $V = 1619.7(2)$ Å³, $T = 296$ K, space group $\text{P}2_12_12_1$ (no. 19), $Z = 4$, $D_{\text{calc}} = 1.305$ g/cm³, $F_{000} = 672.00$, $\mu(\text{Cu-K}\alpha) = 8.33$ cm⁻¹, 1427 reflections measured, 1407 unique ($R_{\text{int}} = 0.000$). The structure was solved by direct methods (MITHRIL84)¹⁵ and expanded using Fourier techniques (DIRDIF94).¹⁴ The final R_I was 0.037 (1050 reflections were used).

Ethyl rel-(1R,2aS,8bS)-1-Acetoxyethyl-1,2,2a,8b-tetrahydro-3-oxo-3H-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. ¹H-NMR (300 MHz, CDCl₃) δ: 1.23 (3H, t, *J* = 7.2 Hz, OCH₂CH₃), 1.94 (3H, s, COCH₃), 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, -CH₂OCOCH₃), 4.17 (1H, dq, *J* = 10.6, 7.2 Hz, OCH₂CH₃), 4.19 (1H, dd, *J* = 9.5, 7.2 Hz, -CH₂OCOCH₃), 4.25 (1H, dq, *J* = 10.6, 7.2 Hz, COOCH₂CH₃), 7.02 - 7.14 (3H, m, Ar-H), 7.24 - 7.31 (1H, m, Ar-H). ¹³C-NMR (75.5 MHz, CDCl₃) 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 (CHCl₃): 1749, 1728, 1612, 1584 cm⁻¹. MS *m/z* (relative intensity, %): 318 (M⁺, 1.3), 146 (100). HRMS *m/z*: Calcd for C₁₇H₁₈O₆: 318.1103. Found: 318.1101. *Anal.* Calcd for C₁₇H₁₈O₆: C, 64.14; H, 5.70. Found: C, 64.15; H, 5.78. Crystal data (AFC7R): C₁₇H₁₈O₆, *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) Å³, *T* = 296 K, space group P2₁/c (no. 14), *Z* = 4, *D*_{calc} = 1.314 g/cm³, *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*_{*I*} was 0.048 (2137 reflections were used).

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

Yellow amorphous. ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1734, 1676 cm⁻¹. MS *m/z* (relative intensity, %): 352 (M⁺, 7.0), 105 (100). HRMS *m/z*: Calcd for C₂₄H₁₆O₃: 352.1099. Found: 352.1107.

***rel*-(2aR,8bR)-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. ¹H-NMR (400 MHz, CDCl₃) δ: 3.79 (3H, s, OCH₃), 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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1733, 1676, 1620, 1598 cm⁻¹. MS *m/z* (relative intensity, %): 382 (M⁺, 33), 105 (100). HRMS *m/z*: Calcd for C₂₅H₁₈O₄: 382.1205. Found: 382.1207. *Anal.* Calcd for C₂₅H₁₈O₄: C, 78.52; H, 4.74. Found: C, 78.54; H, 4.90.

rel-(2aR,8bR)-2a-Acetyl-2a,8b-dihydro-3-oxo-1-phenyl-3H-benzo[b]cyclobuta[d]pyran-3-one (5g)

Pale yellow amorphous. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{19}\text{H}_{14}\text{O}_3$: 290.0943. Found: 290.0948.

rel-(2aR,8bR)-2a,8b-Dihydro-2a-isobutyryl-1-phenyl-3H-benzo[b]cyclobuta[d]pyran-3-one (5h)

yellow amorphous. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.16 (6H, d, $J = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.11 (1H, hept, $J = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 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). $^{13}\text{C-NMR}$ (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 $\text{C}_{21}\text{H}_{18}\text{O}_3$: 318.1256. Found: 318.1264.

rel-(2aR,8bR)-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 $^\circ\text{C}$. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ : 1.22 (9H, s, $\text{COC}(\text{CH}_3)_3$), 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). $^{13}\text{C-NMR}$ (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 $\text{C}_{22}\text{H}_{20}\text{O}_3$: 332.1412. Found: 332.1418. Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_3$: C, 79.50; H, 6.06. Found: C, 79.37; H, 6.23.

Ethyl rel-(2aR,8bR)-2a,8b-Dihydro-3-oxo-1-phenyl-3H-benzo[b]cyclobuta[d]pyran-2a-carboxylate (5j)

Pale yellow amorphous, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.30 (3H, t, $J = 7.1$ Hz, OCH_2CH_3), 4.27 (1H, dq, $J = 10.8, 7.1$ Hz, OCH_2CH_3), 4.31 (1H, dq, $J = 10.8, 7.1$ Hz, OCH_2CH_3), 4.66 (1H, s, 8b-H), 6.50 (1H, s, 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), 7.25 - 7.31 (1H, m, Ar-H), 7.32 - 7.38 (3H, m, Ar-H), 7.43 - 7.47 (3H, m, Ar-H). $^{13}\text{C-NMR}$ (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 $\text{C}_{20}\text{H}_{16}\text{O}_4$: 320.1048. Found: 320.1045.

Methyl *rel*-(2a*R*,8b*R*)-2a,8b-Dihydro-3-oxo-1-phenyl-3*H*-benzo[*b*]cyclobuta[*d*]pyran-2a-carboxylate

(**5k**) Pale yellow amorphous. ¹H-NMR (400 MHz, CDCl₃) δ: 3.82 (3H, s, OCH₃), 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). ¹³C-NMR (100 MHz, CDCl₃) 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 (CHCl₃): 1736, 1661 cm⁻¹. MS *m/z* (relative intensity, %): 306 (M⁺, 24), 247 (100). HRMS *m/z*: Calcd for C₁₉H₁₄O₄: 306.0892. Found: 306.0902.

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