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Intramolecular Hetero-*Diels-Alder* Reactions of Functionalized α,β-Unsaturated Carbonyl Compounds: Polycyclic 2*H*-Pyran Derivatives

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Summary. The reaction of benzoylacetonitrile, methyl cyanoacetate, and ethyl benzoylacetate with 2-allyloxy- and 2-(3-methyl-2-butenyloxy)-benzaldehyde as well as 2-(3-methyl-2-butenyloxy)-1-naphthaldehyde afforded the corresponding *Knoevenagel* condensation products. Some of those underwent spontaneous intramolecular cycloaddition to give *cis*-fused 2*H*-pyran derivatives as major products. One-pot reactions of 1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione with 2-(3-methyl-2-butenyloxy)-benzaldehyde and 2-(3-methyl-2-butenyloxy)-1-naphthaldehyde resulted in *Diels-Alder* cycloadducts.

Keywords. Intramolecular hetero-*Diels-Alder* reaction; α,β-Unsaturated ketones; 2*H*-Pyrans.

Intramolekulare Hetero-*Diels-Alder*-Reaktionen von funktionalisierten α,β-ungesättigten Carbonylverbindugen: Polycyclische 2*H*-Pyranderivate

Zusammenfassung. Reaktion von Benzoylacetonitril, Methylcyanoacetat and Ethylbenzoylacetat mit 2-Allyloxy- und 2-(3-Methyl-2-butenyloxy)-benzaldehyd sowie mit 2-(3-Methyl-2-butenyloxy)-1-naphthaldehyd ergab das entsprechende *Knoevenagel*-Derivat. Einige dieser letzteren Produkte unterlagen einer spontanen intramolekularen Cycloaddition zu *cis*-verknüpfen 2*H*-Pyranderivaten als Hauptprodukt. Eintopfreaktionen von 1,3-Cyclohexandion und 5,5-Dimethyl-1,3-cyclohexandion mit 2-(3-Methyl-2-butenyloxy)-benzaldehyd und 2-(3-Methyl-2-butenyloxy)-1-naphthaldehyd resultierten in *Diels-Alder*-Cycloaddukten.

Introduction

The hetero-*Diels-Alder* reaction of α,β-unsaturated carbonyl compounds – which can be formally treated as 1-oxa-1,3-butadienes – with electron-rich dienophiles, *e.g.* enol ethers, is an important synthetic method for the construction of 3,4-dihydro-2*H*-pyran derivatives which are present in many natural products [1–4]. These reactions belong to the class of $4\pi+2\pi$ cycloadditions with an inverse electron demand. Simple 1-oxa-1,3-butadienes show only low reactivity in cycloadditions with enol ethers. The introduction of the electron-withdrawing groups at positions

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2 or 3 in heterodienes, however, changes their reactivity. This is due to a strong decrease of the LUMO energy of the diene which then can more easily overlap with the HOMO of the dienophile. This type of cycloadditions can be performed *via* inter- or intramolecular modes. Several examples of intramolecular hetero-*Diels-Alder* reactions of 1-oxa-1,3-butadienes possessing alkene substituents have been reported [5–8], dealing with condensations of cyclic 1,3-dicarbonyl compounds with aldehydes bearing dienophile moieties and affording 2-alkylidene- or 2-arylidene-1,3-dioxo compounds that subsequently underwent $4\pi+2\pi$ cycloaddition to give cycloadducts. In all reported syntheses, 1,3-dicarbonyl groups were incorporated in cyclic molecules such as *Meldrum*'s acid [5], N,N-dimethylbarbituric acid [6], pyrazolone, izoxazolone [7], and oxazepandione [8]. These types of processes belong to the tandem *Knoevenagel* – hetero-*Diels-Alder* reactions and have been applied for the syntheses of several natural products [4].

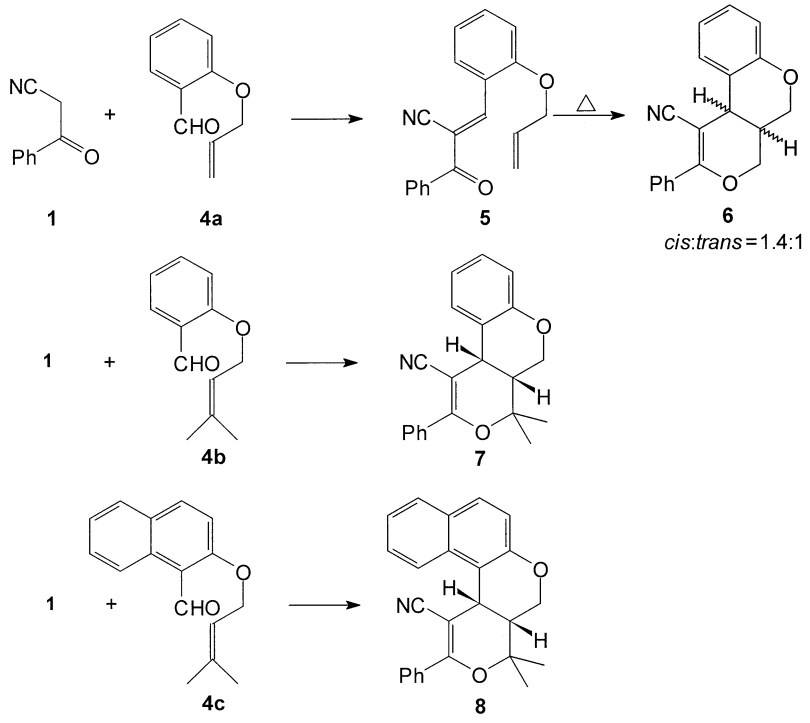
Recently, we have reported the efficient synthesis of polyfunctionalized 3,4-dihydro-2*H*-pyrans *via* intermolecular hetero-*Diels-Alder* reactions of cyano substituted α,β-unsaturated ketones with enol ethers [9, 10]. The efficiency of these cycloadditions prompted us to extend these reactions to intramolecular cases.

Results and Discussion

The aim of this work was to investigate intramolecular hetero *Diels-Alder* reactions of acyclic *o*-alkenyloxyarylidene carbonyl compounds containing electron-withdrawing groups and to compare their reactivity with those of cyclic analogues.

In our investigations, we applied the following active methylene compounds as substrates: benzoylacetonitrile (**1**) methyl cyanoacetate (**2**), ethyl benzoylacetate (**3**), benzaldehydes **4a**,**b**, and 1-naphthaldehyde **4c**. The aldehydes contained allyloxy- (**4a**) and 2-(3-methyl-2-butenyloxy)- (**4b**,**c**) groups, in *o*-position to the carbonyl function which should act as dienophiles in cycloadditions. Aldehydes **4a–c** were condensed with **1**, **2**, and **3** yielding 2-arylidene derivatives as intermediates. Their intramolecular hetero-*Diels-Alder* reaction should give the desired fused pyrans. We studied these reactions taking into account the character of the substituents in the diene and in dienophile moieties. All reactions were carried out in acetonitrile solution in the presence of catalytic amounts of ethylene diammonium diacetate (*EDDA*). The progress of the reactions was monitored by TLC.

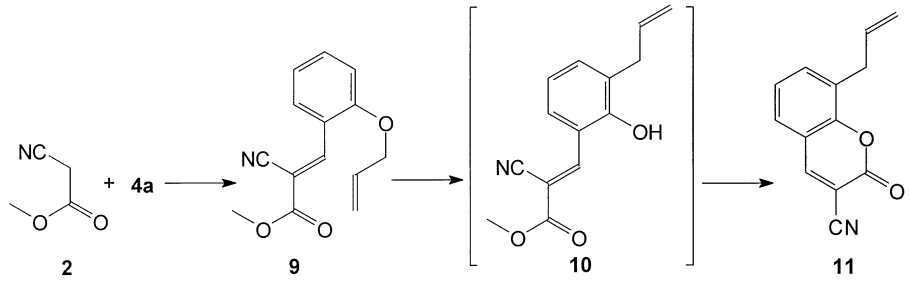
The reaction of **1** and **4a**, carried out at room temperature, gave rise to the formation of the *Knoevenagel* educt **5** in good yield (Scheme 1). The intramolecular hetero-*Diels-Alder* cycloaddition of **5** was accomplished in boiling xylene and afforded a mixture of the annulated cycloadducts *cis*-**6** and *trans*-**6**. The ratio of two diastereoisomers (1.4:1) in the crude product was determined by ^{1}H NMR spectroscopy. The configuration of the *cis* and *trans*-annulated compounds was deduced from chemical shift values and coupling constants of the vicinal protons attached to C-4a and C-10b. For the *cis*-adduct, the proton at C-10b appeared as a doublet at $\delta = 3.88$ ppm with a small coupling constant of 5.4 Hz. For the *trans*-diastereoisomer, the signal of the proton at C-10b was a doublet at $\delta = 3.73$ ppm with a large coupling constant of 11.2 Hz. In the spectra of both



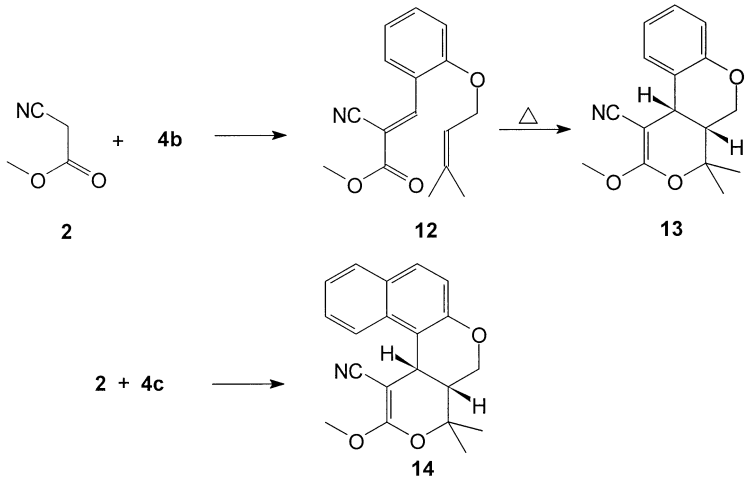
Scheme 1

diastereoisomers, the resonances of the protons at C-4a was observed as a multiplet in the range of 2.45–2.54 ppm.

The reaction of **1** with aldehydes **4b** and **4c**, carried out at room temperature, yielded exclusively the *cis*-annulated cycloadducts **7** and **8**, respectively (Scheme 1). Thus, the condensation-cycloaddition sequence was run as an one-pot reaction. The stereochemistry of the products was confirmed by their ^{1}H NMR spectra. For **7**, the signal of the proton at C-10b appeared as a doublet at $\delta = 3.78$ ppm with $^3J = 5.5$ Hz; the signal of proton 12c-H of **8** was a doublet at $\delta = 4.55$ ppm with $^3J = 4.1$ Hz. It is interesting to note that during the reactions an intensive yellow colour appeared which faded as the cycloadducts were formed. The condensation of **2** with aldehyde **4a** in acetonitrile in the presence of *EDDA* furnished the condensation product **9** that was thermally stable at room temperature (Scheme 2).



Scheme 2



Scheme 3

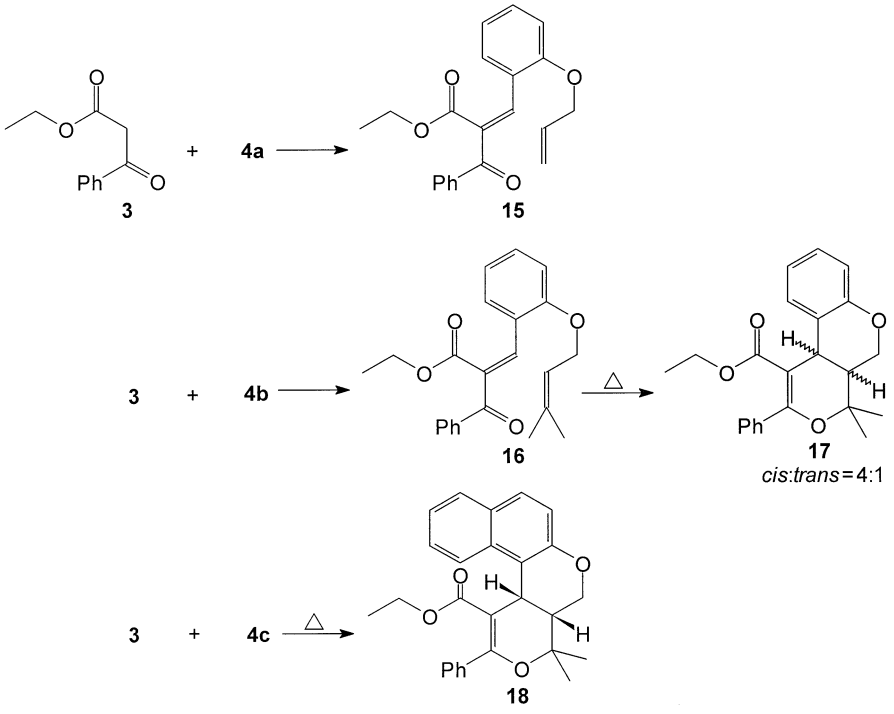
However, heating of **9** in boiling xylene resulted in the formation of lactone **11**. The formation of **11** can be rationalized as depicted in Scheme 2. It consists in a 3,3-sigmatropic shift of the allyl group and formation of the *o*-phenol derivative **10** which subsequently undergoes ring closure with elimination of methanol to give **11**. The structure of **11** was confirmed by analytical and IR, ^{1}H, ^{13}C NMR, and MS data.

The reaction of **2** with **4b**, performed at room temperature, yielded the yellowish coloured condensation product **12** exclusively (Scheme 3). Its cycloaddition was accomplished in boiling xylene giving the *cis*-annulated cycloadduct **13** as the sole product. In contrast, the reaction of **2** with **4c** occurred at room temperature, leading directly to the *cis*-fused compound **14**.

In further experiments we studied the reactions of **3** with **4a–c**. In these reactions we expected to observe the influence of the 3-ethoxycarbonyl group in the 1-oxa-1,3-butadiene intermediates on the intramolecular cycloaddition. *Knoevenagel* condensation of **3** with **4a**,**b**, carried out at room temperature, led to products **15** and **16**, respectively (Scheme 4). Prolonged heating of **15** in xylene did not afford the expected cycloadduct, whereas compound **16** underwent cycloaddition yielding a mixture of the *cis*/*trans*-annulated cycloadducts **17** in a ratio of 4:1 under these conditions. The reaction of **3** with aldehyde **4c** at room temperature gave rise to the formation of a mixture of the *Knoevenagel* condensation product and the *Diels-Alder* cycloadduct. To complete the cycloaddition, the reaction mixture was heated in xylene, and the *cis* cycloadduct **18** was obtained as the sole product (Scheme 4).

Next we investigated the reactions of cyclic 1,3-dicarbonyl compounds such as 1,3-cyclohexanedione (**19**) and 5,5-dimethyl-1,3-cyclohexanedione (dimedone **20**) with **4a–c**. To our knowledge, the intramolecular cycloaddition of 1,3-cyclohexanedione with (*R*)-citronellal catalyzed by sodium methoxide leading to the corresponding *trans*-cycloadduct has been reported [11].

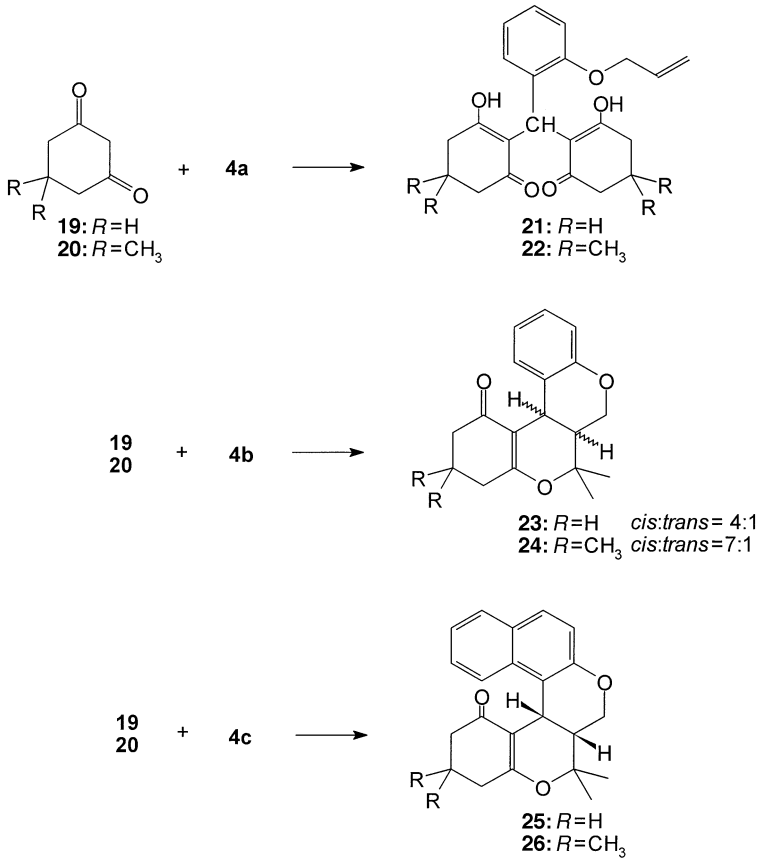
The reactions of **4a** with **19** and **20**, carried out at room temperature in acetonitrile in the presence of *EDDA*, involved the formation of condensation



Scheme 4

products **21** and **22**. Their analytical and spectroscopic data showed that they were formed by condensation of two molecules of 1,3-dicarbonyl compounds **19** or **20** with one molecule of **4a** (Scheme 5). Changing of the reaction condition, *e.g.* the sequence of addition of the reagents or lowering of the temperature, did not influence the course of these reactions. Similar reactions of **20** with aliphatic or aromatic aldehydes have already been reported [12]. In contrast to **4a**, **4b** reacted with **19** and **20** to afford the *Diels-Alder* cycloducts **23** and **24** in one-pot reactions. The ^{1}H NMR analysis of the crude products showed that they consisted of a mixture of *cis*/*trans*-annulated cycloadducts. In both reactions the *cis*-cycloadducts were the major products (Table 1). The reaction of **4c** with **19** and **20**, carried out at room temperature, led exclusively to formation of *cis*-fused cycloadducts **25** and **26**, respectively (Scheme 5). The results of the reactions leading to the cycloadducts obtained are given in Table 1.

In conclusion, we have shown, that the reactions of the activated methylene compounds with aromatic 2-alkenyloxy aldehydes involved, in the first step, formation of α,β-unsaturated carbonyl compounds that were prone to undergo intramolecular hetero-*Diels-Alder* cycloadditions. It is worth to note that all one-pot reactions occurring at room temperature led to the exclusive formation of *cis*-annulated cycloadducts. In contrast, the cycloaddition of isolated *Knoevenagel* intermediates required heating and furnished a mixture of *cis*/*trans*-cycloadducts with predominant formation of *cis*-products. The cyclic 1,3-dicarbonyl compounds underwent the tandem *Knoevenagel*-hetero-*Diels-Alder* reactions easier than the activated acyclic carbonyl compounds. We did not notice a striking difference



Scheme 5

Table 1. Yields and diastereomeric ratios of cycloadducts in reactions of **1**–**3** and **19**, **20** with **4a**–**c**

Substrates	Cycloadducts	Yield (%)	Ratio of *cis:trans*
1 and **4a**	**6**-*cis*/**6**-*trans*	86	1.4:1
4b	**7**-*cis*	60	>100:1
4c	**8**-*cis*	66	>100:1
2 and **4b**	**13**-*cis*	65	>100:1
4c	**14**-*cis*	69	>100:1
3 and **4b**	**17**-*cis*/**17**-*trans*	70	4:1
4c	**18**-*cis*	67	>100:1
19 and **4b**	**23**-*cis*/**23**-*trans*	73	4:1
4c	**24**-*cis*	70	>100:1
20 and **4b**	**25**-*cis*/**25**-*trans*	73	7:1
4c	**26**-*cis*	60	>100:1

between the reactivity of acyclic carbonyl compounds possessing cyano or ethoxycarbonyl groups. The methyl groups attached to the terminal dienophile systems influenced their reactivity, since the reactions with aldehydes **4b** and **4c** were more effective than with **4a** and led almost exclusively to the *cis*-

cycloadducts. We assume that the formation of the *cis*-diastereoisomers depends on the structure of the intermediate α,β-unsaturated carbonyl compounds. Their ^{1}H NMR spectra (compounds **5**, **9**, **12**, **15**, **16**) indicated that they were single isomers, since the signals of the vinyl protons in α,β-unsaturated systems appeared as one proton singlets. Their chemical shift values strongly suggest that these compounds are the *E*-isomers [13]. Thus, due to the *cis*-linkage of the newly formed rings, we assume that the hetero-*Diels-Alder* reaction occurred *via* an energetically favoured *endo-E-syn* transition state [4].

Experimental

Melting points were determined on a Boetius hot stage apparatus; IR spectra: Bruker IFS 48, KBr pellets; ^{1}H and ^{13}C NMR spectra: Bruker AMX 500 (500.14 MHz for ^{1}H and 125.77 MHz for ^{13}C), $CDCl_3$, *TMS* as internal standard, ^{13}C signal assignments were confirmed by DEPT methods; MS: Finningan Mat 95 (70 eV); Microanalyses: Perkin Elmer Analyser 240, Regional Laboratory of Physicochemical Analyses in Kraków; their results were in satisfactory agreement with the calculated values. 2-Allyloxy-and 2-(3-methyl-2-butenyloxy)-benzaldehydes (**4a**–**b**) and 2-(3-methyl-2-butenyloxy)-1-naphthaldehyde (**4c**) were obtained according to Ref. [14].

Reactions of compounds **1**–**3** *and* **20** *with aromatic 2-alkenyloxy aldehydes* **4a**-**c**; *Synthesis of condensation products* **5**, **9**, **12**, **15**, **16**, **21**, **22**, *and cycloadducts* **7**-*cis*, **8**-*cis*, **14**-*cis*, **18**-*cis*, **23**-(*cis*/*trans*), **24**, **25**-(*cis*/*trans*) *and* **26**-*cis*

To a solution of the compounds **1**–**3**, **19**, **20** (0.01 mol) in 20 ml of dry acetonitrile, aldehydes **4a**–**c** (0.01 mol) and 60 mg ethylene diammonium diacetate (*EDDA*) were added. The solution was stirred for several hours and left for 24–72 h at room temperature. The progress of the reactions was monitored by TLC. The solvent was evaporated, and the residue was purified by column chromatography on silica gel using petrol ether and *t*-butyl-methyl ether (1:1) as eluent. Recrystallization from petrol ether and *t*-butyl-methyl ether (3:1) mixture afforded pale yellow or colourless crystals of the condensation products or the appropriate cycloadducts.

Synthesis of cycloadducts **6** *(cis/trans),* **13** *cis,* **17** *(cis/trans) and* **18** *cis*

A solution of the arylidene carbonyl compound **5**, **12**, or **16** (0.005 mol) in 10 ml anhydrous xylene was refluxed for 24–48 h. The progress of the reactions was monitored by TLC. The solvent was evaporated, and the mixture was separated and purified by column chromatography on silica gel using petrol ether and *t*-butyl-methyl ether (1:1 or 2:1) as eluent. Recrystallization from a mixture of petrol ether and *t*-butyl-methyl ether (3:1) gave colourless crystals.

3-(2-Allyloxyphenyl)-2-benzoyl-2-propenecarbonitrile (**5**; $C_{19}H_{15}NO_2$)

Pale yellow crystals (83%); m.p.: 140°C; IR (KBr): $\nu = 3067$, 2910, 2857 (CH), 2220 (C≡N), 1645 (C=O), 1594 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 4.60 (d, $J = 5.0$ Hz, 2H, 1″-H), 5.27 (dd, $J = 1.1$ Hz, 10.6 Hz, 1H, 3″-H), 5.32 (dd, $J = 1.1$ Hz, 17.3 Hz, 1H, 3″-H), 5.99 (m, 1H, 2″-H), 6.95–8.39 (m, 9H, CH_{arom}), 8.60 (s, 1H, 3-H) ppm; ^{13}C NMR ($CDCl_3$, δ): 69.27 (C-1″), 109.99 (C-2), 112.37 (C-2″), 116.93 (CN), 118.02 (C-3″), 121.29 (*i*-Ph), 121.23, 128.55, 129.31, 129.35, 132.12, 133.07, 134.92 (C_{arom}), 136.09 (*i*-Ph), 150.44 (C-3), 158.24 (*i*-Ph), 189.72 (C=O) ppm; MS: *m*/*z* (%) = 289.0 (34) $[M]^{+\cdot}$, 260.0 (100) $[M\text{-}CHO]^{+\cdot}$, 232.0 (21) $[M\text{-}C_3H_5O]^{+\cdot}$, 105.0 (29) $[C_6H_5CO]^{+\cdot}$, 77.0 (28) $[C_6H_5]^{+\cdot}$.

(4aRS,10bRS)-4a,10b-Dihydro-2-phenyl-4H,5H-pyrano[3,4-c][1]benzopyran-1-carbonitrile (**6**-*cis*; $C_{19}H_{15}NO_2$)

Colourless crystals (50%); m.p.: 180°C; IR (KBr): $\nu = 3055$, 2979, 2872 (CH), 2201 (C≡N), 1605 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 2.54 (m, 1H, 4a-H), 3.88 (d, J(4a-H,10b-H) = 5.4 Hz, 1H, 10b-H), 4.16 (dd, J(5-H_{ax},4a-H) = 8.0 Hz, J_{gem} = 11.1 Hz, 1H, 5-H_{ax}), 4.30 (dd, J(5-H_{eq},4a-H) = 2.3 Hz, J_{gem} = 11.2 Hz, 1H, 5-H_{eq}), 4.38 (dd, J(4-H_{ax},4a-H) = 6.0 Hz, J_{gem} = 11.3 Hz, 1H, 4-H_{ax}), 4.44 (dd, J(4-H_{eq},4a-H) = 2.1 Hz, J_{gem} = 11.2 Hz, 1H, 4-H_{eq}), 6.87–7.7 (m, 9H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3$, δ): 29.53 (C-4a), 32.79 (C-10b), 64.46 (C-5), 67.44 (C-4), 86.86 (C-1), 117.1 (CN), 120.56, 121.14, 121.29, 128.26, 128.34, 128.85, 130.72, 130.90, 132.95 (C_{arom}), 153.07 (*i*-Ph), 164.76 (C-2) ppm; MS: *m/z* (%) = 289.2 (100) $[M]^{+\cdot}$, 288.2 (45) $[M\text{-}H]^{+\cdot}$, 260.2 (17) $[M\text{-}CHO]^{+\cdot}$, 105.0 (67) $[C_6H_5CO]^{+\cdot}$, 77.0 (25) $[C_6H_5]^{+\cdot}$.

(4aRS,10bRS)-4a,10b-Dihydro-2-phenyl-4H,5H-pyrano[3,4-c][1]benzopyran-1-carbonitrile (**6**-*trans*; $C_{19}H_{15}NO_2$)

Colourless crystals (36%); ^1H NMR ($CDCl_3$, δ): 2.45 (m, 1H, 4a-H), 3.73 (d, J(4a-H,10b-H) = 11.2 Hz, 1H, 10b-H), 3.99 (dd, J(4a-H,5-H_{ax}) = 11.7 Hz, J_{gem} = 10.2 Hz, 1H, 5-H_{ax}), 4.01 (dd, J(4a-H,4-H_{ax}) = 11.45 Hz, J_{gem} = 10.4 Hz, 1H, 4-H_{ax}), 4.41 (dd, J(4a-H,5-H_{eq}) = 5.7 Hz, J_{gem} = 10.2 Hz, 1H, 5-H_{eq}), 4.56 (dd, J(4a-H,4-H_{eq}) = 3.6 Hz, J_{gem} = 10.4 Hz, 1H, 4-H_{eq}), 6.88–8.07 (m, 9H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3$, δ): 35.62 (C-4a), 35.81 (C-10b), 66.93 (C-5), 68.39 (C-4), 84.00(C-1), 117.15 (CN), 120.61, 121.03, 123,05, 125.63, 128.39, 128.56, 128.85, 131.29, 132.91 (C_{arom}), 154.09 (*i*-Ph), 168.84 (C-2) ppm.

(4aRS,10bRS)-4a,10b-Dihydro-4,4-dimethyl-2-phenyl-4H,5H-pyrano[3,4-c][1]benzopyran-1-carbonitrile (**7**-*cis*; $C_{21}H_{19}NO_2$)

Colourless crystals (60%); m.p.: 223°C; IR (KBr): $\nu = 3061$, 2986, 2885 (CH), 2201 (C≡N), 1599 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.55 (s, 3H, 4-CH_3), 1.6 (s, 3H, 4-CH_3), 2.26 (ddd, J(10b-H,4a-H) = 5.6 Hz, J(5-H_{ax},4a-H) = 11.5 Hz, J(5-H_{eq},4a-H) = 3.7 Hz, 1H, 4a-H), 3.78 (d, J(4a-H, 10b-H) = 5.5 Hz, 1H, 10b-H), 3.83 (t, J(4a-H, 5-H_{ax} = 11.4 Hz, J_{gem} = 11.4 Hz, 1H, 5-H_{ax}), 4.43 (ddd, J(4a-H, 5-H_{eq}) = 3.7 Hz, J_{gem} = 11.2 Hz, J(10b-H, 5-H_{eq}) = 1.7 Hz, 1H, 5-H_{eq}), 6.87–7.65 (m, 9H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3$, δ): 25.52 (C-4a), 25.67 (C-10b), 31.97 (CH_3), 36.63 (CH_3), 62.53 (C-5), 77.85 (C-4), 86.28 (C-1), 119.51 (CN), 116.48, 120.65, 128.28, 129.05, 130.76, 131.96, 133.37 (C_{arom}), 153.82 (*i*-Ph), 162.64 (C-2); MS: *m/z*(%) = 317.1(97) $[M]^{+\cdot}$, 248.1(27) $[M\text{-}C_5H_9]^{+\cdot}$, 220.1 (100), 173.1 (33) $[M\text{-}C_6H_5CO(CN)CH]^{+\cdot}$, 105.0(61) $[C_6H_5CO]^{+\cdot}$, 77.1 (36) $[C_6H_5]^{+\cdot}$, 69.1 (37) $[C_5H_9]^{+\cdot}$, 41.0 (27) $[C_3H_5]^{+\cdot}$.

(4aRS,12cRS)-4a,12c-Dihydro-4,4-dimethyl-2-phenyl-4H,5H-naphtho[2,1-b]pyrano[3,4-d]-pyran-1-carbonitrile (**8** *cis*; $C_{25}H_{21}NO_2$)

Yellow crystals (66%); m.p.: 245°C; IR (KBr): $\nu = 3061$, 2979, 2892 (CH), 2208 (C≡N), 1645, 1625, 1603 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.59 (s, 3H, 4-CH_3), 1.65 (s, 3H, 4-CH_3), 2.26 (ddd, J(12c-H,4a-H) = 4.3 Hz, J(5-H_{ax},4a-H) = 12.1 Hz, J(5-H_{aq},4a-H) = 4.3 Hz, 1H, 4a-H), 4.09 (t, J(4a-H, 5-H_{ax}) = 11.5 Hz, J_{gem} = 11.5 Hz, 1H, 5-H_{ax}), 4.52 (dd, J(4a-H,5-H_{eq}) = 2.5 Hz, J_{gem} = 11.0 Hz, 1H, 5-H_{eq}), 4.55 (d, J(4a-H,12c-H) = 4.1 Hz, 1H, 12c-H), 7.06–8.1 (m, 11H, C_{arom}) ppm; MS: *m/z* (%) = 367.2 (100) $[M]^{+\cdot}$, 298.1 (21) $[M\text{-}C_5H_9]^{+\cdot}$, 270.1 (61), 182.1 (15) $[M\text{-}C_6H_5CO,CH_3,CH_3]^{+\cdot}$, 105.0 (29) $[C_6H_5CO]^{+\cdot}$, 77.0 (20) $[C_6H_5]^{+\cdot}$, 69.1 (11) $[C_5H_9]^{+\cdot}$, 41.1 (15) $[C_3H_5]^{+\cdot}$.

Methyl 3-(2-allyloxy-phenyl)-2-cyano-2-propenylate (**9**; $C_{14}H_{13}NO_3$)

Yellow crystals (81%); m.p.: 72°C; IR (KBr): $\nu = 2954$, 2848 (CH), 2232 (C≡N), 1743 (C=O), 1599 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 3.94 (s, 3H, OCH_3), 4.65 (dt, J(2″-H, 1″-H) = 5.15 Hz, J(3″-

H,1″-H) = 1.5 Hz, 2H, 1″-H), 5.34 (ddd, J(2″-H,3″-H$_{cis}$) = 10.6 Hz, J(1″-H,3″-H$_{cis}$) = 1.4 Hz, J_{gem} = 2.7 Hz, 1H, 3″-H$_{cis}$), 5.44 (ddd, J(2″-H,3″-H$_{trans}$) = 17.3 Hz, J(1″-H,3″-H$_{cis}$) = 1.6 Hz, J_{gem} = 2.9 Hz, 1H, 3″-H$_{trans}$), 6.06 (ddt, J(1″-H,2″-H) = 5.15 Hz, J(3″-H$_{cis}$,2″-H) = 12.1 Hz, J(3″-H$_{trans}$, 2″-H) = 17.3 Hz, 1H, 2″-H), 6.95 (d, J = 8.4 Hz, 1H, Ph-H), 7.07 (t, J = 7.5 Hz, 1H, CH$_{arom}$), 7.50 (t, J = 7.9 Hz, 1H, CH$_{arom}$), 8.31 (d, J = 7.9 Hz, 1H, CH$_{arom}$), 8.83 (s, 1H, 3-H) ppm; ^{13}C NMR ($CDCl_3$, δ): 53.18 (OCH_3), 69.39 (C-1″), 102.03 (C-2″), 112.49 (C-3″), 115.83 (CN), 118.17, 120.96, 121.14, 129.42, 132.28, 134.92 (C$_{arom}$), 150.04 (C-2) 158.30 (C-3), 163.29 (C=O) ppm; MS: m/z(%) = 243.1 (53) [M]$^{+\cdot}$, 211.1 (62) [M-CH_3OH]$^{+\cdot}$, 184.1 (90) [M-CH_3OCO]$^{+\cdot}$, 183.1 (51), 182.1 (100), 156.1 (19) [M-C_3H_4O, CH_3O]$^{+\cdot}$, 145.1 (27) [M-$CH_3OCO(CN)CH$]$^{+\cdot}$, 143.1 (36) [M-CH_3OCO, C_3H_5]$^{+\cdot}$, 41.1 (88) [C_3H_5]$^{+\cdot}$.

8-Allyl-2-oxo-2H-1-benzopyran-3-carbonitrile (**11**; $C_{13}H_9NO_2$)

Lactone **11** was obtained by heating **9** (0.005 mol) in 10 ml anhydrous xylene for 24 h. The progress of the reaction was monitored by TLC. The solvent was evaporated, and the residue was purified by column chromatography on silica gel using a mixture of petrol ether and *t*-butyl-methyl ether (1:1) as eluent. Recrystallization from a mixture of petrol ether and *t*-butyl-methyl ether (3:1) gave colourless crystals.

Yield: 76%; m.p.: 131°C; IR (KBr): ν = 3086, 3042, 2973 (CH), 2232 (C≡N), 1731 (C=O), 1599 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 3.62 (d, J(2′-H,1′-H) = 6.6 Hz, 2H, 1′-H), 5.15 (dd, J(2′-H, 3′-H$_{cis}$ = 10.1 Hz, J_{gem} = 1.5 Hz, 1H, 3′-H$_{cis}$), 5.16 (dd, J(2′-H,3′-H$_{trans}$) = 16.9 Hz, J_{gem} = 1.3 Hz, 1H, 3′-H$_{trans}$), 5.98 (tdd, J(1′-H,2′-H) = 6.6 Hz, J(3′-H$_{cis}$, 2′-H) = 10.2 Hz, J(3′-H$_{trans}$, 2′-H) = 16.9 Hz, 1H, 2′-H), 7.36 (t, J = 7.6 Hz, 1H, CH$_{arom}$), 7.48 (dd, J = 7.75 Hz, 1.3 Hz, 1H, CH$_{arom}$), 7.59 (d, J = 7.5 Hz, 1H, CH$_{arom}$), 8.28 (s, 1H, 4-H) ppm; ^{13}C NMR ($CDCl_3$, δ): 32.95 (C-1′), 103.00 (C-2′), 113.00 (C-3′), 117.09 (CN), 117.52, 125.41, 127.45, 129.19, 134.37, 136.12 (C$_{arom}$), 152.12 (C-4), 152.42 (C-3), 156.38 (C-2) ppm; MS: m/z (%) = 211.1 (100) [M]$^{+\cdot}$, 183.1 (76) [M-CO]$^{+\cdot}$, 182.1 (55), 167.1 (7) [M-CO_2]$^{+\cdot}$, 154.1 (31).

Methyl 2-cyano-3-(2-(3-methyl-2-butenyloxy)phenyl)-2-propenylate (**12**; $C_{16}H_{17}NO_3$)

Pale yellow crystals (81%); m.p.: 71°C; IR (KBr): ν = 3049, 2948, 2866 (CH), 2220 (C≡N), 1724 (C=O), 1599 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.75 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 3.93 (s, 3H, OCH_3), 4.62 (d, J = 6.6 Hz, 2H, 1″-H), 5.47 (t, J = 6 Hz, 1H, 2″-H), 6.97 (d, J = 8.4 Hz, 1H, CH$_{arom}$), 7.04 (t, J = 7.7 Hz, 1H, CH$_{arom}$), 7.49 (t, J = 7.9 Hz, 1H, CH$_{arom}$), 8.30 (d, J = 7.9 Hz, 1H, CH$_{arom}$) 8.79 (s, 1H, 3-H) ppm; MS: m/z (%): 271.1 (34) [M]$^{+\cdot}$, 212.1 (10) [M-CH_3OCO]$^{+\cdot}$, 203.1 (13) [M-C_5H_8]$^{+\cdot}$, 171.0 (48) [M-CH_3OCO, CN, CH_3]$^{+\cdot}$, 145.1 (68) [M-CH_3OCO, C_5H_7]$^{+\cdot}$, 69.1 (100) [C_5H_9]$^{+\cdot}$.

(4aRS, 10bRS)-4a,10b-Dihydro-2-methyloxy-4H,5H-pyrano [3,4-c][1]benzopyran-1-carbonitrile (**13**-*cis*; $C_{16}H_{17}NO_3$)

Colourless crystals (65%); m.p.: 109°C; IR (KBr): ν = 3073, 2998, 2866 (CH), 2195 (C≡N), 1618 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.49 (s, 3H, 4-CH_3), 1.51 (s, 3H, 4-CH_3), 2.14 (m, 1H, 4a-H), 3.75 (s, 3H, OCH_3), 3.77 (m, 2H, 5-H), 4.35 (d, J(4a-H, 10b-H) = 10.85 Hz, 1H, 10b-H), 6.81 (d, J = 7.9 Hz, 1H, CH$_{arom}$), 6.95 (t, J = 6.9 Hz, 1H, CH$_{arom}$), 7.17 (t, J = 6.6 Hz, 1H, CH$_{arom}$), 7.41 (d, J = 7.3 Hz, 1H, CH$_{arom}$); ^{13}C NMR ($CDCl_3$, δ): 25.18 (CH_3), 25.93 (CH_3), 30.22 (C-10b), 37.12 (C-4a), 54.85 (OCH_3), 61.98 (C-5), 62.57 (C-4), 81.22 (C-1), 118.89 (CN), 116.37, 120.42, 120.71, 128.73, 131.30, 131.39 (C$_{arom}$), 163.49 (C-2) ppm; MS: m/z (%) = 271.1 (87) [M]$^{+\cdot}$, 212.1 (13) [M-CH_3OCO]$^{+\cdot}$, 196.1 (29), 171.0 (55) [M-CH_3OCO, CN, CH_3]$^{+\cdot}$, 145.1 (88) [M-CH_3OCO, C_5H_7]$^{+\cdot}$, 69.1 (100) [C_5H_9]$^{+\cdot}$.

(4aRS, 12cRS)-4a, 12c-Dihydro-4,4-dimethyl-2-methyloxy-4H,5H-naphtho [2,1-b] pyrano [4,3-d]pyran-1-carbonitrile (**14**-*cis*; $C_{20}H_{19}NO_3$)

Pale yellow crystals (69%); m.p.: 198°C; IR (KBr): $\nu = 3067$, 2986, 2860 (CH), 2208 (C≡N), 1618 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.55 (s, 3H, 4-CH_3), 1.58 (s, 3H, 4-CH_3), 2.13 (ddd, J(12c-H,4a-H) = 4.2 Hz, J(5-H_{ax},4a-H) = 11.9 Hz, J(5-H_{eq}, 4a-H) = 4.2 Hz, 1H, 4a-H), 3.77 (s, 3H, OCH_3), 3.99 (t, J(4a-H, 5-H_{ax}) = 11.5 Hz, J_{gem} = 11.5 Hz, 5-H_{ax}), 4.41 (br, 2H, 5-H_{eq}, 12c-H), 7.01–8.04 (m, 6H, CH_{arom}) ppm; MS: *m/z* (%): 321.2 (90) $[M]^{+\cdot}$, 253.1 (52) $[M\text{-}C_5H_8]^{+\cdot}$, 246.1 (20) $[M\text{-}CH_3O, CH_2(CH_3)_2]^{+\cdot}$, 221.1 (100) $[M\text{-}CH_3O, C_5H_9]^{+\cdot}$, 193.1 (49) $[M\text{-}CH_3OCO, C_5H_9]^{+\cdot}$, 195.1 (67) $[M\text{-}CH_3O, C_5H_9,CN]^{+\cdot}$, 182.1 (57), 139.1 (21), 69.1 (47) $[C_5H_9]^{+\cdot}$, 41.1 (56) $[C_3H_5]^{+\cdot}$.

Ethyl 3-(2-allyloxyphenyl)-2-benzoyl-2-propenylate (**15**; $C_{21}H_{20}O_4$)

Colourless crystals (78%); m.p.: 60°C; IR (KBr): $\nu = 3080$, 3061, 2986 (CH), 1718, 1668 (C=O), 1618 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.16 (t, J = 7.1 Hz, 3H, OC_2H_5), 4.20 (q, J = 7.1 Hz, 2H, OC_2H_5), 4.52 (dd, J(2″-H, 1-H″) = 5.0 Hz, J(3″-H, 1-H″) = 1.5 Hz, 2H, 1″-H), 5.27 (dd, J(2″-H, 3″-H_{cis}) = 10.6 Hz, J(1″-H, 3″-H_{cis}) = 1.4 Hz, 1H, 3″-H_{cis}), 5.38 (dd, J(2″-H, 3″-H_{trans}) = 17.3 Hz, J(1″-H,3″-H_{trans}) = 1.5 Hz, 1H, 3″-H_{trans}), 6.00 (ddt, J(1″-H, 2″-H) = 5.0 Hz, J(3″-H_{cis}, 2″-H) = 12.0 Hz, J(3″-H_{trans}, 2″-H) = 17.3 Hz, 1H, 2″-H), 7.17–7.92 (m, 9H, CH_{arom}), 8.36 (s, 1H, 3-H) ppm; ^{13}C NMR ($CDCl_3$, δ): 13.99 (*C*H_3CH_2O), 61.26 (CH_3*C*H_2O), 69.01 (C-1″), 112.19 (C-2″), 117.49 (C-3″), 120.66, 122.64, 128.55, 129.09, 130.34, 131.09, 131.61, 132.83, 133.40, 136.60 (C_{arom}), 138.41 (C-3), 156.99 (C-2), 165.24 (*C*OOEt), 195.39 (*C*OPh) ppm; MS: *m/z* (%) = 336.2 (14.3) $[M]^{+\cdot}$, 290.1 (63) $[M\text{-}C_2H_5OH]^{+\cdot}$, 279.1 (100) $[M\text{-}C_3H_5O]^{+\cdot}$, 263.1 (13) $[M\text{-}C_6H_5CO]^{+\cdot}$, 249.1 (24) $[M\text{-}C_3H_5, C_2H_5OH]^{+\cdot}$, 173.0 (39) $[M\text{-}C_6H_5CO,C_3H_5O, H]^{+\cdot}$, 105.0 (89) $[C_6H_5CO]^{+\cdot}$, 77.0 (31) $[C_6H_5]^{+\cdot}$.

Ethyl 2-benzoyl-3-(2-(3-methyl-2-butenyloxy)phenyl)-2-propenylate (**16**; $C_{23}H_{24}O_4$)

Colourless crystals (81%); m.p.: 62°C; IR (KBr): $\nu = 3055$, 2986, 2892 (CH), 1718, 1668 (C=O), 1605 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.16 (t, J = 7.1 Hz, 3H, OC_2H_5), 1.74 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 4.21 (q, J = 7.1 Hz, 2H, OC_2H_5), 4.52 (d, J = 6.4 Hz, 2H, 1″-H), 5.44 (t, J = 6.5 Hz, 1H, 2″-H), 6.68–7.95 (m, 9H, CH_{arom}), 8.35 (s, 1H, 3-H) ppm; MS: *m/z* (%) = 296.1 (17) $[M\text{-}C_5H_8]^{+\cdot}$, 250.1 (33) $[M\text{-}C_5H_9, C_2H_5O]^{+\cdot}$, 221.1 (49) $[M\text{-}C_2H_5OCO, C_5H_9,H]^{+\cdot}$, 219.1 (96) $[M\text{-}C_5H_8, C_6H_5]^{+\cdot}$, 191.1 (41) $[M\text{-}C_6H_5CO, C_5H_8]^{+\cdot}$, 173.0 (48), 105.0 (100) $[C_6H_5CO]^{+\cdot}$, 69.1 (49) $[C_5H_9]^{+\cdot}$, 41.0 (30) $[C_3H_5]^{+\cdot}$.

(4aRS, 10bRS)-4a,10b-Dihydro-4,4-dimethyl-2-phenyl-4H,5H-pyrano[3,4-c][1]benzopyran-1-ethyl carboxylate (**17**-*cis*; $C_{23}H_{24}O_4$)

Oil (56%); IR (KBr): $\nu = 3061$, 2986, 2898 (CH), 1711 (C=O), 1649 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.79 (t, J = 7.2 Hz, 3H, OC_2H_5), 1.38 (s, 3H, 4-CH_3), 1.51 (s, 3H, 4-CH_3), 2.17 (ddd, J(10b-H, 4a-H) = 6.5 Hz, J(5-H_{ax}, 4a-H) = 8.5 Hz, J(5-H_{eq}, 4a-H) = 3.85 Hz, 1H, 4a-H), 385 (m, 2H, OC_2H_5), 4.19 (d, J(4a-H, 10b-H) = 5.4 Hz, 1H, 10b-H), 4.21 (dd, 4a-H, 5-H_{ax}) = 8.5 Hz, J_{gem} = 11.3 Hz, 1H, 5-H_{ax}), 4.45 (dd, J(4a-H, 5-H_{eq}) = 3.8 Hz, J_{gem} = 11.3 Hz, 1H, 5-H_{eq}), 6.76–7.39 (m, 9H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3$, δ): 13.48 (OCH_2*C*H_3), 24.78 (CH_3), 26.59 (CH_3), 32.11 (C-10b), 37.84 (C-4a), 60.29 (O*C*H_2CH_3), 63.83 (C-5), 107.01 (C-4), 116.01, 120.29, 121.86, 127.81, 127.97, 128.09, 128.75, 130.39 (C_{arom}), 136.55 (*i*-Ph), 154.09 (C-1), 154.23 (C-2), 169.31 (C=O) ppm; MS: *m/z* (%) = 364.2 (54) $[M]^{+\cdot}$, 318.2 (59) $[M\text{-}C_2H_5OH]^{+\cdot}$, 291.2 (34) $[M\text{-}C_2H_5OCO]^{+\cdot}$, 173.1 (34), 105.0 (100) $[C_6H_5CO]^{+\cdot}$, 69.1 (16) $[C_5H_9]^{+\cdot}$, 41.0 (18.1) $[C_3H_5]^{+\cdot}$.

(4aRS, 12cRS)-4a,12c-Dihydro-4,4-dimethyl-2-phenyl-4H,5H-naphtho[2,1-b]-pyrano[4,3-d]pyran-1-ethyl carboxylate (**18**-*cis*; $C_{23}H_{24}O_4$)

Colourless crystals (67%); m.p.: 170°C; IR (KBr): $\nu = 3061$, 2979, 2890 (CH), 1705 (C=O), 1624 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.42 (t, $J = 7.15$ Hz, 3H, OC_2H_5), 1.52 (s, 3H, 4-CH_3), 1.68 (s, 3H, 4-CH_3), 2.18 (ddd, J(12c-H, 4a-H) = 4.4 Hz, J(5-H_{ax}, 4a-H) = 4.4 Hz, J(5-H_{eq}, 4a-H) = 11.9 Hz, 1H, 4a-H), 3.14 (dq, $J(CH_3, OCH_2) = 7.1$ Hz, $J_{gem} = 10.8$ Hz, 1H, OC_2H_5), 3.41 (dq, $J(CH_3,OCH_2) = 7.1$ Hz, $J_{gem} = 10.8$ Hz, 1H, OC_2H_5), 4.28 (t, (4a-H, 5-H_{ax}) = 11.4 Hz, $J_{gem} = 11.4$ Hz, 1H, 5-H_{ax}), 4.50 (dd, J(4a-H, 5-H_{eq} = 2.7 Hz, $J_{gem} = 10.8$ Hz, 1H, 5-H_{eq}), 7.07–7.88 (m, 11H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3$, δ): 13.48 (OCH_2CH_3), 24.78 (CH_3), 26.59 (CH_3), 32.11 (C-10b), 37.84 (C-4a), 60.29 (OCH_2CH_3), 63.83 (C-5), 107.01 (C-4), 116.01, 120.29, 121.86, 127.81, 127.97, 128.09, 128.75, 130.39 (C_{arom}), 136.55 (*i*-Ph), 154.09 (C-1), 154.23 (C-2), 169.31 (C=O) ppm; MS: *m/z* (%) = 414.2 (100) $[M]^{+\cdot}$, 341.2 (13) $[M\text{-}C_2H_5OCO]^{+\cdot}$, 223.1 (17) [M-$C_2H_5OCOCH$, $C_6H_5CO]^{+\cdot}$, 105.0 (31) $[C_6H_5CO]^{+\cdot}$.

(2-Allyloxyphenyl)-bis-(2-hydroxy-6-oxo-1-cyclohexenyl)-methane (**21**; $C_{22}H_{24}O_5$)

Colourless crystals (50%); m.p.: 186°C; IR (KBr): $\nu = 3230$ (OH), 3061, 2961 (CH), 1711 (C=O), 1636, 1605 (C=C) cm^{-1}, ^1H NMR ($CDCl_3$, δ): 1.71–3.29 (m, 13H, CH, CH_2), 3.67 br, 0.15H, OH), 4.44 (s, 0.85H, OH), 4.53 (m, 2H, OCH_2CHCH_2), 4.95 (s, 0.55H, OH), 5.23 (m, 1H, OCH_2CHCH_2), 5.32 (m, 1H, OCH_2CHCH_2), 5.55 (s, 0.45H, OH), 6.0 (m, 1H, OCH_2CHCH_2), 6.76–7.18 (m, 4H, CH_{arom} ppm; MS: *m/z* (%) = 368.2 (46) $[M]^{+\cdot}$, 309.1 (73) $[M\text{-}C_3H_5O, 2H]^{+\cdot}$, 213.1 (22) [M-$C_3H_6$, $C_6H_7O_2$, 2H]$^{+\cdot}$, 199.1 (100) [M-C_3H_5O, $C_6H_7O_2$, H]$^{+\cdot}$, 55.0 (30), 41.0 (17) $[C_3H_5]^{+\cdot}$.

(2-Allyloxyphenyl)-bis-(2-hydroxy-4, 4-dimethyl-6-oxo-1-cyclohexenyl)-methane (**22**: $C_{26}H_{32}O_5$)

Colourless crystals (56%); m.p.: 190°C, IR (KBr): $\nu = 3387$ (OH), 3042, 2947 (CH), 1718 (C=O), 1642, 1609 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 0.94 (s, 3H, CH_3), 1.08 (s, 9H, CH_3), 2.11–2.48 (m, 9H, CH, CH_2), 4.43 (t, $J = 5.5$ Hz, 2H, OCH_2CHCH_2), 5.30 (m, 2H, OCH_2CHCH_2), 5.62 (s, 1H, OH), 6.02 (m, 1H, OCH_2CHCH_2), 6.70–7.5 (m, 4H, CH_{arom}), 12.0 (br, 1H, OH) ppm; ^{13}C NMR ($CDCl_3$, δ): 29.25, 31.51 42.83, 46.77, 53.54 (CH, CH_2, CH_3, $C(CH_3)$), 69.04 (C-1′′), 111.50 (C-2′′), 117.38 (C-3′′), 116.39, 120.27, 127.34, 128.27, 128.57, 133.63 (C=C-OH, C_{arom}), 154.0, 156.19 (*i*-Ph), 189.19 (C=O) ppm; MS: *m/z* (%) = 424.0 (14) $[M]^{+\cdot}$, 365.1 (32) $[M\text{-}C_3H_5O, 2H]^{+\cdot}$, 243.1 (12) [M-$C_3H_6$, $C_8H_{11}O_2]^{+\cdot}$, 227.1 (100) [M-C_3H_5O, $C_8H_{12}O_2]^{+\cdot}$, 83.1 (31).

(6aRS, 12bRS)-1,2,3,4,6a,12b-Hexahydro-6,6-dimethyl-6H,7H-[1]benzopyrano [3,4-c] [1]benzopyran-1-one (**23**-*cis*; $C_{18}H_{20}O_3$)

Colourless crystals (58%); m.p.: 153°C; IR (KBr): $\nu = 3086$, 2979, 2872 (CH), 1640 (C=O), 1601 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.15 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 2.0 (m, 3H, 2-H, 3-H, 4-H), 2.4 (m, 3H, 2-H, 3-H, 4-H), 2.59 (dt, J(12b-H, 6a-H) = 5.7 Hz, 1H, 6a-H), 4.20 (d, J(6a-H, 12b-H) = 5.7 Hz, 1H, 12b-H), 4.33 (dd, J(6a-H, 7-H) = 3.3 Hz, $J_{gem} = 11.9$ Hz, 1H, 7-H), 4.42 (dd, J(6A-H, 7-H) = 3.7 Hz, $J_{gem} = 11.9$ Hz, 1H, 7-H), 6.68–7.19 (m, 4H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3$, δ): 20.57 (C-6a), 23.96 (C-12b), 27.91, 27.98, 29.56 (C-2, C-3, C-4), 37.25 (CH_3), 38.70 (CH_3), 64.98 (C-7), 79.84 (C-6), 112.81 (C-12c), 115.69, 120.71, 123.14, 127.44, 129.92, 153.77 (C_{arom}), 170.77 (C-4a), 198.47 (C-1) ppm; MS: *m/z* (%) = 284.2 (57) $[M]^{+\cdot}$, 241.1 (100) $[M\text{-}(CH_3)_2CH]^{+\cdot}$, 173.1 (15) $[M\text{-}C_6H_7O_2]^{+\cdot}$.

(6aRS,12bSR)-1,2,3,4,6a,12b-Hexahydro-6,6-dimethyl-6H,7H-[1]benzopyrano[3,4-c][1]-benzopyran-1-one (**23**-*trans*; $C_{18}H_{20}O_3$)

Colourless crystals (15%); m.p.: 176°C; ^1H NMR ($CDCl_3$, δ): 1.20 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 2.02–2.65 (m, 6H, 2-H, 3-H, 4-H), 2.12 (ddd, J(12b-H, 6a-H) = 11.9 Hz, J(7-H_{ax}, 6a-H) = 11.9 Hz,

J(7-H_{eq}, 6a-H) = 5.4 Hz, 1H, 6a-H), 3.52 (d, J(6a-H,12b-H) = 11.5 Hz, 1H, 12b-H), 4.03 (dd, J(6a-H, 7-H_{ax}) = 12.1 Hz, J_{gem} = 9.65 Hz, 1H, 7-H_{ax}), 4.35 (dd, J(6a-H, 7-H_{eq}) = 5.45 Hz, J_{gem} = 9.65 Hz, 1H, 7-H_{eq}), 6.82–7.09 (m, 4H, CH_{arom}) ppm.

(6aRS,12bRS)-1,2,3,4,6a,12b-Hexahydro-3,3,6,6-tetramethyl-6H,7H-[1]benzopyrano[3,4-c][1]-benzopyran-1-one (**24**-*cis*; $C_{20}H_{24}O_3$)

Colourless crystals (73%); m.p.: 137°C; IR (KBr): v = 3086, 2961, 2872, (CH), 1636 (C=O), 1605 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.08 (s, 3H, 3-CH_3), 1.11 (s, 6H, 3-CH_3, 6-CH_3), 1.49 (s, 3H, 6-CH_3), 2.02 (ddd, J(12b-H, 6a-H) = 5.7 Hz, J(7-H, 6a-H) = 3.0 Hz, J(7-H, 6a-H) = 3.0 Hz, 1H, 6a-H), 2.25–2.47 (m, 4H, 2-H, 4-H), 4.21 (d, J(6a-H, 7-H) = 5.7 Hz, 1H, 12b-H), 4.36 (dd, J(6a-H, 7-H) = 3.0 Hz, J_{gem} = 12.0 Hz, 1H, 7-H), 4.42 (dd, J(6a-H, 7-H) = 3.7 Hz, J_{gem} = 12.0 Hz, 1H, 7-H), 6.68 (d, J = 7.9 Hz, 1H, CH_{arom}), 6.81 (t, J = 7.2 Hz, 1H, CH_{arom}), 7.05 (t, J = 7.0 Hz, 1H, CH_{arom}), 7.15 (d, J = 7.4 Hz, 1H, CH_{arom}) ppm; MS: m/z (%) = 312.2 (54) $[M]^{+\cdot}$, 297.2 (15) $[M\text{-}CH_3]^{+\cdot}$, 269.1 (100) $[M\text{-}(CH_3)_2CH]^{+\cdot}$, 173.1 (14) $[M\text{-}C_8H_{10}O_2, H]^{+\cdot}$.

(6aRS,14cRS)-1,2,3,4,6a,14c-Hexahydro-6,6-dimethyl-6H,7H-naphtho[1′,2′:5,6]pyrano[3,4-c][1]-benzopyran-1-one (**25**-*cis*; $C_{22}H_{22}O_3$)

Colourless crystals (61%); m.p.: 203°C; IR (KBr): v = 3067, 2979, 2937 (CH), 1649 (C=O), 1599 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.42 (s, 3H, 6-CH_3), 1.48 (s, 3H, 6-CH_3), 1.87 (m, 2H, 2-H, 3-H), 2.11 (ddd, J(14c-H, 6a-H) = 4.8 Hz, J(7-H_{ax}, 6a-H) = 11.0 Hz, J(7-H_{eq}, 6a-H) = 6.1 Hz, 1H, 6a-H), 2.19 (t, J = 6.5 Hz, 2H, 4-H), 2.36–2.48 (m, 2H, 2-H, 3-H), 4.12 (t, J(6a-H, 7-H_{ax}) = 10.95 Hz, J_{gem} = 10.95 Hz, 1H, 7-H_{ax}), 4.35 (dd, J(6a-H, 7-H_{eq}) = 6.1 Hz, J_{gem} = 10.4 Hz, 1H, 7-H_{eq}), 4.53 (br, 1H, 14c-H), 6.97 (d, J = 8.8 Hz, 1H, CH_{arom}), 7.32 (t, J = 8.6 Hz, 1H, CH_{arom}), 7.50 (t, J = 7.2 Hz, 1H, CH_{arom}), 7.61 (d, J = 8.8 Hz, 1H, CH_{arom}), 7.72 (d, J = 7.9 Hz, 1H, CH_{arom}), 8.15 (d, J = 8.6 Hz, 1H, CH_{arom}) ppm; MS: m/z (%) = 334.2 (96) $[M]^{+\cdot}$, 317.2 (100) $[M\text{-}OH]^{+\cdot}$, 291.1 (42) $[M\text{-}(CH_3)_2CH]^{+\cdot}$, 249.1 (21) $[M\text{-}C_5H_9O]^{+\cdot}$, 223.1 (60), 210.1 (39), 181.1 (18) $[M\text{-}C_6H_6O_2,(CH_3)_2CH]^{+\cdot}$, 69.1 (22) $[C_5H_9]^{+\cdot}$, 57.1 (26)$^{+\cdot}$, 41.1 (42) $[C_3H_5]^{+\cdot}$.

(6aRS,14cRS)-1,2,3,4,6a,14c-Hexahydro-3,3,6,6-tetramethyl-6H,7H-naphtho[1′,2′:5,6]pyrano[3,4-c][1]benzopyran-1-one (**26**-*cis*; $C_{24}H_{26}O_3$)

Colourless crystals (60%); m.p.: 225°C; IR (KBr): v = 3073, 2973, 2866 (CH), 1649 (C=O), 1592 (C=C); ^{1}H NMR ($CDCl_3$, δ): 0.98 (s, 3H, 3-CH_3), 1.03 (s, 6H, 3-CH_3), 1.42 (s, 3H, 6-CH_3), 1.48 (s, 3H, 6-CH_3), 2.11 (m, 1H, 6a-H), 2.03 (d, J = 16.2 Hz, 1H, 4-H), 2.10 (d, J = 16.2 Hz, 1H, 4-H), 2.29 (s, 2H, 2-H), 4.09 (t, J(6a-H, 7-H_{ax}) = 10.85 Hz, J_{gem} = 10.85 Hz, 1H, 7-H_{ax}), 4.35 (dd, J(6a-H,7-H_{eq}) = 6.3 Hz, J_{gem} = 10.7 Hz, 1H, 7-H_{eq}), 4.52 (br, 1H, 14c-H), 6.97–8.15 (m, 6H, Ch_{arom}) ppm; MS: m/z (%) = 362.2 (100) $[M]^{+\cdot}$, 345.2 (56) $[M\text{-}OH]^{+\cdot}$, 319.1 (52) $[M\text{-}(CH_3)_2CH]^{+\cdot}$, 277.1 (15) $[M\text{-}C_5H_9O]^{+\cdot}$, 223.1 (57) $[M\text{-}C_8H_{10}O_2, H]^{+\cdot}$, 41.1 (18) $[C_3H_5]^{+\cdot}$,

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