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[4+2] Cycloaddition reactions of coumarin quinone methide with pentafulvenes: facile synthesis of novel polycyclic pyran derivatives

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Dedicated with best wishes to Professor Dr Binne Zwanenburg

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Abstract—The quinone methide generated in situ by the Knoevenagel condensation of formaldehyde and 4-hydroxycoumarin underwent facile Diels–Alder reactions with pentafulvenes to afford novel pyranocoumarin derivatives in good yields.

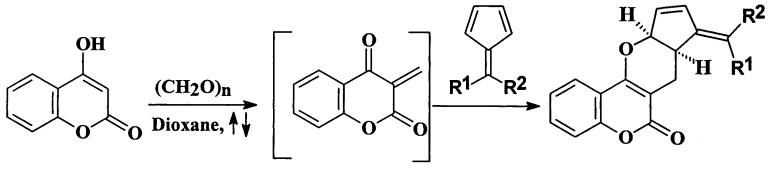
1. Introduction

o-Quinone methides[1] constitute a class of highly reactive intermediates and their cycloaddition chemistry has invoked considerable interest. Much less attention, however, has been paid to heterocyclic quinone methides.[2,3] This may be attributed to their relative inaccessibility and considerably amplified reactivity. In the context of our general interest in the cycloaddition chemistry of *o*-quinones[4] and *o*-thioquinones,[5] the cycloadditions of *o*-quinone methides, especially those derived from 4-hydroxycoumarin appeared attractive from the vantage point of constructing polycyclic oxygen heterocycles. Generally, polycyclic systems having a pyranopyrone skeleton display interesting biological properties.[6] In this context, we have explored the reactivity of pentafulvenes,[7] which can act as 2π, 4π, or 6π components in cycloaddition reactions, towards a coumarin quinone methide and the results are presented here. It is noteworthy that except for isolated reports,[3] the cycloaddition chemistry of the coumarin quinone methide is largely uninvestigated.

2. Results and discussion

Our investigations were initiated with the reaction of 4-hydroxy coumarin **1**, paraformaldehyde and 6,6-diphenyl fulvene in refluxing 1,4-dioxane leading to the pyranocoumarin derivative **3** in 85% yield (Scheme 1). Interestingly, only one regioisomer was formed in this reaction.

The structure of **3** was established by spectroscopic analysis. The IR spectrum of the product **3** showed a strong peak at 1701 cm^{-1}. This value is typical for a coumarin carbonyl group, thus indicating that the product is an angular adduct. In the ^1H NMR spectrum, one of the methylene H-atoms of



1 **2** **3**

$R^1=R^2=Ph$ 85%

Scheme 1.

Keywords: quinones; Diels–Alder reactions; heterocycles.
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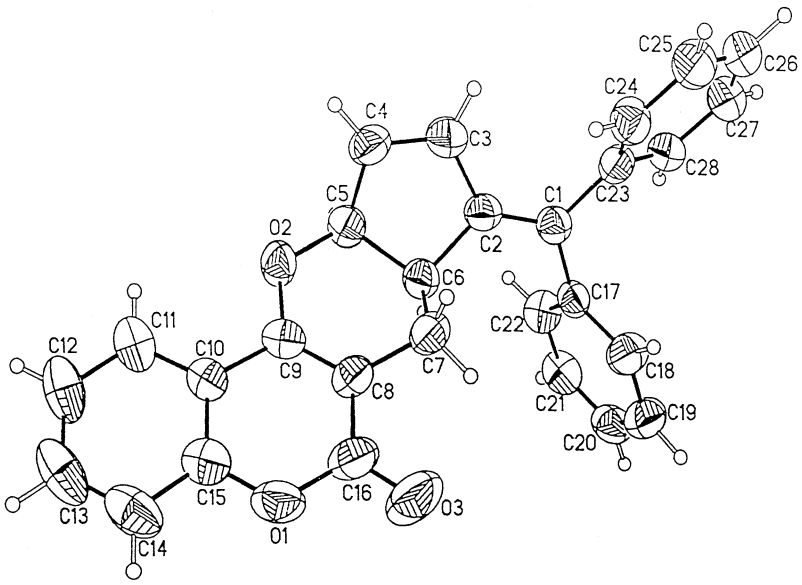
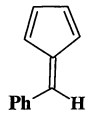
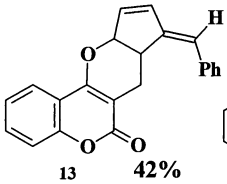
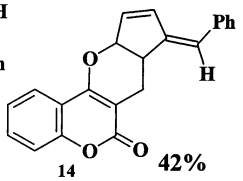
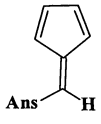
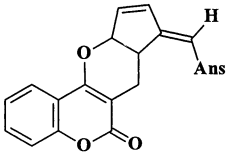
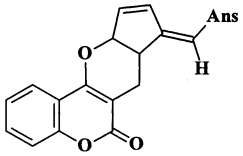
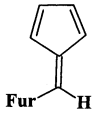
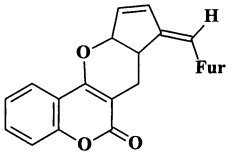
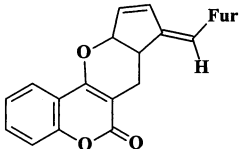
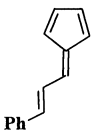
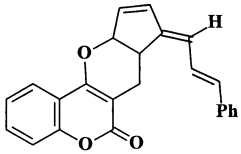
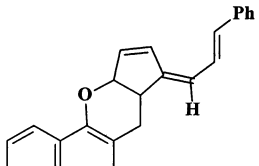


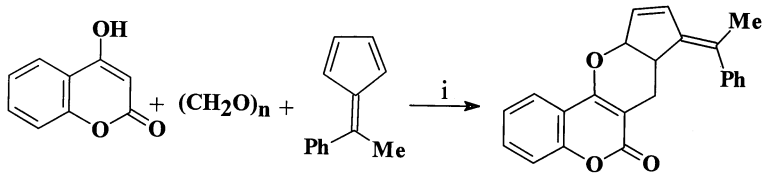
Figure 1. Single crystal X-ray structure of **3**.

the pyran ring appeared as a double doublet (J=16.5 and 8.1 Hz) at δ 2.18 due to the geminal and vicinal couplings respectively. The signal due to the other proton appeared as a double doublet (J=16.5 and 8.4 Hz) at δ 2.64. This large difference in the δ value for these protons can be attributed to the influence of phenyl group of the fulvene moiety. This strongly supported the regiochemistry of the product. In the ^{13}C NMR spectrum, the carbonyl carbon resonated at δ

Table 1.

Entry	Fulvene	Reaction conditions[a]	Product(s), Yield(s)	
1	 4	6 h	 13 42%	 14 42%
2	 5	5 h	 15 45%	 16 40%
3	 6	4 h	 17 40%	 18 40%
4	 7	4 h	 19 40%	 20 40%

[a] 1,4-Dioxane, reflux

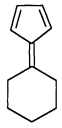
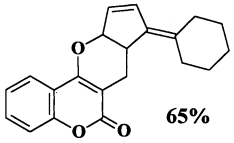
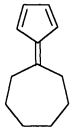
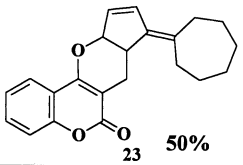


8 21

i) 1,4-Dioxane, reflux, 6 h, 84%

Scheme 2.

Table 2.

Entry	Fulvene	Reaction conditions[a]	Product(s), Yield(s)
1	 9	2 h	 22 65%
2	 10	2.5 h	 23 50%

[a] 1,4-Dioxane, reflux

162.30. Ultimately, the structure was confirmed by single crystal X-ray analysis (Fig. 1).

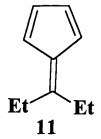
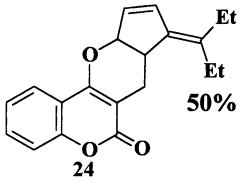
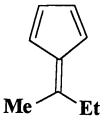
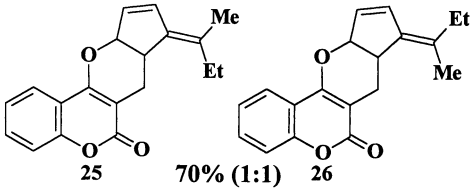
A similar reactivity was shown by other 6-aryl fulvenes and the results are summarized in Table 1. Not surprisingly, unsymmetrically substituted fulvenes afforded both the *Z* and *E* isomers; these were separated by column chromatography.

Even though 6-methyl-6-phenyl fulvene **8** is an unsymmetrically substituted one, the cycloaddition reaction with the coumarin quinone methide afforded only the *Z* isomer (Scheme 2).

A similar mode of cycloaddition was also observed in the reactions of the coumarin quinone methide with various cycloalkyl fulvenes. These results are summarized in Table 2.

The cycloaddition reactions of coumarin quinone methide

Table 3.

Entry	Fulvene	Reaction conditions[a]	Product(s), Yield(s)
1	 11	4 h	 24 50%
2	 12	3 h	 25 70% (1:1) 26

[a] 1,4-Dioxane, reflux

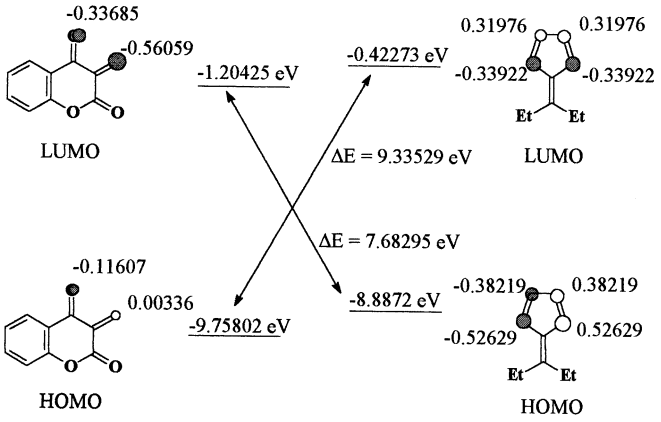


Figure 2.

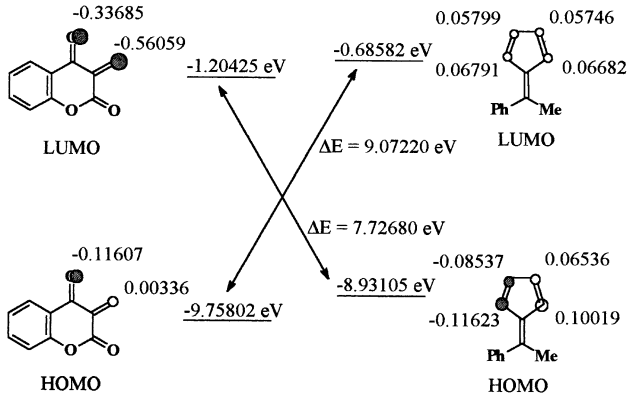


Figure 3.

with dialkyl fulvenes under similar conditions afforded [4+2] adducts in good yields. As expected, unsymmetrically substituted fulvene **12** on cycloaddition gave a mixture of *Z* and *E* isomers; these were inseparable. The results are given in Table 3.

3. Theoretical considerations

In order to gain some insight into the above reactions and the selectivity observed with some systems, we have carried out AM1 calculations using PC SPARTAN Graphical Interface Package for Molecular Mechanics and Molecular Orbital Models.[8]

As a representative example, the correlation diagram for the reaction of **2** with 6,6-diethylfulvene is illustrated in Fig. 2.

It is evident from the correlation diagram that the LUMO (diene) and HOMO (dienophile) interaction is allowed in terms of energetics and symmetry. The observed regiochemistry of the product can be clearly understood on the basis of matching of signs and sizes of the orbital coefficients.

It may be recalled that the Diels–Alder reaction of coumarin quinone methide **2** with 6-methyl-6-phenyl fulvene afforded only the *Z*-isomer. This can also be clearly explained on the basis of matching of signs of the orbital coefficients (Fig. 3).

4. Conclusion

In conclusion, we have found that pentafulvenes serve as very efficient dienophiles in the inverse electron demand Diels–Alder reaction with quinone methides derived from α-hydroxycoumarin leading to pyranopyrone derivatives. It is noteworthy that pyranopyrones constitute the basic skeleton of a number of biopotent natural products such as warfarin, pyripyropene and arisugasin.

5. Experimental

5.1. Data for compounds

5.1.1. 8-[(Diphenyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [3]. A solution of 4-hydroxycoumarin (0.162 g, 1.00 mmol), paraformaldehyde (0.240 g, 8.00 mmol) and 6,6-diphenyl fulvene (0.460 g, 2.00 mmol) in dry 1,4-dioxane (4 mL) was refluxed (100°C) under argon atmosphere for 5 h. The solvent was removed in vacuo and the residue was extracted with chloroform (3×20 mL). The organic layer was washed with aqueous sodium carbonate solution and brine and dried over anhydrous sodium sulfate. The chloroform was evaporated off and the residue was subjected to chromatography on silica gel using 10% ethyl acetate–hexane as eluent to afford 0.343 g (85%) of product as a colorless crystalline solid; recrystallized from dichloromethane–hexane solvent system (mp: 155–157°C); IR (KBr) ν_{max}: 3059, 2913, 1701, 1640, 1612, 1495, 1409, 1361, 1276, 1175, 1114, 1051, 1606, 895 cm^{-1}. ^1H NMR: δ 2.18 (dd, J=16.5, 8.1 Hz, 1H), 2.64 (dd, J=16.5, 8.4 Hz, 1H), 3.32–3.40 (m, 1H), 5.57 (dt, J=6.9, 2.4 Hz, 1H), 6.17 (dd, J=6.0, 3.0 Hz, 1H), 6.53 (dd, J=5.1, 3.0 Hz, 1H), 7.15–7.44 (m, 13H), 7.73 (d, J=6.3 Hz, 1H). ^{13}C NMR: δ 21.99, 38.28, 83.07, 101.26, 116.00, 116.71, 122.47, 123.92, 127.37, 127.64, 128.27, 128.67, 129.42, 129.83, 131.51, 135.31, 135.99, 136.27, 141.54, 141.73, 144.17, 159.76, 162.30. Anal. Calcd for $C_{28}H_{20}O_3$: C, 83.15; H, 4.98. Found: C, 83.23; H, 4.79. X-Ray crystal data $C_{28}H_{20}O_3$, Fw 404.44, 0.42×0.40×0.25 mm^3,

orthorhombic, space group *Pbca*, unit cell dimensions: a=9.9051(1) Å, α=90°, b=16.0715(2) Å, β=90°, c=25.3875(4) Å, γ=90°. R indices (all data) $R1$=0.1368, $wR2$=0.2195. Volume=4041.43(9) Å^3, Z=8. D_{calc}=1.329 Mg/m^3. $F(000)$=1696. Absorption coefficient 0.086 mm^{-1}, reflections collected 67771.[†]

5.1.2. 8-(*Z*)-[(Phenyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [13] and 8-(*E*)-[(phenyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [14]. 13 (42%), a colorless solid; recrystallized from dichloromethane–hexane solvent system (mp: 153–155°C) and **14** (42%), a colorless solid; (mp: 148–151°C) recrystallized from dichloromethane–hexane solvent system.

*Spectral data for **13***: IR (KBr) ν_{max}: 3059, 2915, 1701, 1647, 1418, 1189, 764 cm^{-1}. ^{1}H NMR: δ 2.21 (dd, J=16.5, 8.4 Hz, 1H), 3.11 (dd, J=16.5, 7.4 Hz, 1H), 3.68–3.75 (m, 1H), 5.68 (d, J=6.3 Hz, 1H), 6.19 (d, J=3.4 Hz, 1H), 6.46 (s, 1H), 7.25–7.53 (m, 9H), 7.81 (d, J=7.9 Hz, 1H). ^{13}C NMR: δ 20.87, 37.43, 84.01, 101.33, 116.62, 122.36, 123.82, 127.32, 128.33, 128.83, 131.46, 136.42, 138.39, 147.11, 152.39, 159.85, 162.50. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.45; H, 4.68.

*Spectral data for **14***: IR (KBr) ν_{max}: 3020, 2910, 1701, 1647, 1411, 1067, 771 cm^{-1}. ^{1}H NMR: δ 2.77 (dd, J=16.6, 5.1 Hz, 1H), 2.97 (dd, J=16.7, 7.4 Hz, 1H), 3.37–3.41 (m, 1H), 5.48 (d, J=6.4 Hz, 1H), 6.38 (dd, J=5.3, 1.9 Hz, 1H), 6.47 (s, 1H), 6.96 (d, J=5.4 Hz, 1H), 7.18–7.50 (m, 8H), 7.73 (d, J=7.8 Hz, 1H). ^{13}C NMR: δ 20.85, 40.70, 81.87, 100.65, 116.68, 122.39, 123.70, 128.40, 128.46, 131.36, 134.82, 136.39, 145.36, 152.42, 160.35, 162.64. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.60; H, 4.80.

5.1.3. 8-(*Z*)-[(4-Methoxyphenyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]-benzopyran-6-one [15] and 8-(*E*)-[(4-methoxyphenyl)-methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta-[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [16]. 15 (45%), a colorless solid; recrystallized from dichloromethane–hexane solvent system (mp: 144–147°C) and **16** (40%), a colorless solid; recrystallized from dichloromethane–hexane solvent system (mp: 139–143°C).

*Spectral data for **15***: IR (KBr) ν_{max}: 3070, 2955, 2935, 2847, 1708, 1647, 1411, 1263, 1182, 1047, 879, 764, 528 cm^{-1}. ^{1}H NMR: δ 2.18 (dd, J=16.5, 8.6 Hz, 1H), 3.12 (dd, J=16.5, 7.3 Hz, 1H), 3.65–3.67 (m, 1H), 3.82 (s, 3H), 5.67 (d, J=5.6 Hz, 1H), 6.12 (d, J=3.8 Hz, 1H), 6.38 (s, 1H), 6.42 (d, J=4.3 Hz, 1H), 6.87 (d, J=8.5 Hz, 2H), 7.24–7.52 (m, 5H), 7.79 (d, J=7.6 Hz, 1H). ^{13}C NMR: δ 20.73, 37.51, 55.29, 84.32, 101.50, 113.96, 114.39, 116.02, 116.69, 122.43, 123.38, 123.82, 129.73, 131.46, 132.82, 138.67, 145.08, 152.47, 158.91, 159.88, 162.39. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.68; H, 5.30. Found: C, 80.30; H, 5.10.

*Spectral data for **16***: IR (KBr) ν_{max}: 3070, 2955, 2935, 2840, 1708, 1640, 1512, 1398, 1256, 1182, 1108, 1034, 838, 764, 542 cm^{-1}. ^{1}H NMR: δ 2.75 (dd, J=16.7, 4.9 Hz, 1H), 2.94 (dd, J=16.7, 7.3 Hz, 1H), 3.35–3.37 (m, 1H), 3.78 (s, 3 H), 5.44 (dd, J=6.4, 1.5 Hz, 1H), 6.34–6.38 (m, 2H), 6.80 (d, J=8.6 Hz, 2H), 6.95 (d, J=5.5 Hz, 1H), 7.18–7.49 (m, 5H), 7.72 (d, J=7.8 Hz, 1H). ^{13}C NMR: δ 20.71, 40.57, 55.19, 81.87, 100.50, 113.90, 116.04, 116.60, 122.13, 122.40, 123.70, 129.58, 129.84, 131.33, 134.86, 135.67, 143.54, 152.33, 158.75, 160.38, 162.70. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.68; H, 5.30. Found: C, 80.93; H, 5.51.

5.1.4. 8-(*Z*)-[(2-Furanyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [17] and 8-(*E*)-[(2-furanyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [18]. 17 (40%), a colorless solid; recrystallized from dichloromethane–hexane solvent system (mp: 139–142°C) and **18** (40%), a colorless solid; recrystallized from dichloromethane–hexane solvent system (mp: 136–138°C).

*Spectral data for **17***: IR (KBr) ν_{max}: 3070, 1715, 1634, 1411, 757 cm^{-1}. ^{1}H NMR: δ 2.13 (dd, J=16.4, 7.5 Hz, 1H), 3.29 (dd, J=16.4, 7.5 Hz, 1H), 3.75–3.83 (m, 1H), 5.67 (d, J=6.5 Hz, 1H), 6.18 (d, J=3.5 Hz, 1H), 6.25 (s, 1H), 6.31 (d, J=3.0 Hz, 1H), 6.42, (s, 2H), 7.26–7.33 (m, 2H), 7.46–7.53 (m, 2H), 7.82 (d, J=7.8 Hz, 1H). ^{13}C NMR: δ 21.63, 38.21, 84.00, 101.61, 110.42, 110.58, 111.64, 116.64, 122.35, 123.79, 131.37, 134.72, 136.84, 142.75, 145.00, 152.21, 152.36, 159.89, 162.68. Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.20; H, 4.70.

*Spectral data for **18***: IR (KBr) ν_{max}: 3050, 1708, 1627, 1404, 764 cm^{-1}. ^{1}H NMR: δ 2.78 (dd, J=16.6, 4.3 Hz, 1H), 2.91 (dd, J=16.5, 7.1 Hz, 1H), 3.39 (d, J=5.7 Hz, 1H), 5.44 (d, J=4.7 Hz, 1H), 6.13 (s, 1H), 6.24 (d, J=2.8 Hz, 1H), 6.36 (s, 1H), 7.20–7.98 (m, 6H), 7.71 (d, J=7.0 Hz, 1H). ^{13}C NMR: δ 20.28, 40.36, 81.65, 100.38, 109.70, 109.96, 111.37, 115.94, 116.49, 122.25, 123.57, 131.23, 135.37, 136.46, 142.17, 152.24, 152.80, 160.37, 162.56. Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.67; H, 4.20.

5.1.5. 8-(*Z*)-[(2-phenylethenyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [19] and 8-(*E*)-[(2-phenylethenyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [20]. 19 (40%), a colorless solid; recrystallized from dichloromethane–hexane solvent system (mp: 143–145°C) and **20** (40%), a colorless solid; recrystallized from dichloromethane–hexane solvent system (mp: 136–139°C).

*Spectral data for **19***: IR (KBr) ν_{max}: 3050, 3030, 2950, 1701, 1640, 1418, 1128, 764 cm^{-1}. ^{1}H NMR: δ 2.23 (dd, J=16.3, 9.1 Hz, 1H), 3.20 (dd, J=16.3, 7.6 Hz, 1H), 3.46–3.51 (m, 1H), 5.64 (d, J=6.5 Hz, 1H), 6.19 (d, J=5.1 Hz, 1H), 6.26 (d, J=11.4 Hz, 1H), 6.41 (d, J=5.5 Hz, 1H), 6.59

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(d, J=15.2 Hz, 1H), 6.93–6.97 (m, 1H), 7.24–7.55 (m, 8H), 7.82 (d, J=7.7 Hz, 1H). ^{13}C NMR: δ 22.48, 37.26, 83.64, 101.25, 115.94, 116.66, 123.86, 124.80, 126.59, 127.84, 128.69, 134.82, 136.71, 148.01, 152.41, 160.32, 162.64. Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.33; H, 5.12. Found: C, 80.99; H, 5.37.

Spectral data for ***20***: IR (KBr) ν_{max}: 3063, 2950, 1701, 1640, 1418, 778 cm^{-1}. ^{1}H NMR: δ 2.71–2.97 (m, 2H), 3.35–3.37 (m, 1H), 5.43–5.45 (m, 1H), 6.21–6.58 (m, 3H), 6.92–7.70 (m, 11H). ^{13}C NMR: δ 20.06, 39.89, 81.98, 101.30, 115.92, 116.50, 122.24, 122.37, 123.58, 124.62, 126.32, 127.55, 127.76, 128.52, 131.24, 132.94, 134.36, 137.13, 145.63, 152.22, 160.31, 162.57. Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.33; H, 5.12. Found: C, 81.69; H, 4.87.

5.1.6. 8-(*Z*)-[(1-Methyl-1-phenyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [21]. 21 (75%), a colorless solid; recrystallized from dichloromethane–hexane solvent system (mp: 148–150°C).

Spectral data for ***21***: IR (KBr) ν_{max}: 3070, 2955, 2935, 1701, 1647, 1492, 1398, 1128, 1047, 764 cm^{-1}. ^{1}H NMR: δ 2.16–2.25 (m, 4H), 3.17 (dd, J=16.1, 7.3 Hz, 1H), 3.29–3.35 (m, 1H), 5.68 (d, J=6.3 Hz, 1H), 6.07 (d, J=4.8 Hz, 1H), 6.38 (dd, J=5.5, 1.5 Hz, 1H), 7.20–7.36 (m, 7H), 7.48–7.54 (m, 1H), 7.83 (d, J=7.8 Hz, 1H). ^{13}C NMR: δ 21.38, 30.90, 38.52, 83.74, 101.06, 116.64, 122.39, 123.83, 126.97, 128.09, 128.20, 134.12, 142.61, 152.38, 160.15, 162.80. Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.62; H, 4.99.

5.1.7. 8-[(Cyclohexyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [22]. 22 (65%), a pale yellow semi-solid.

Spectral data for ***22***: IR (neat) ν_{max}: 2935, 2860, 1708, 1643, 1452, 1407, 1304, 1276, 1180, 1115, 1052, 1010, 902, 756, 732 cm^{-1}. ^{1}H NMR: δ 1.53–1.59 (m, 6H), 2.03 (dd, J=16.1, 9.4 Hz, 1H), 2.24–2.34 (m, 4H), 2.94 (dd, J=16.2, 7.1 Hz, 1H), 3.14–3.22 (m, 1H), 5.56 (d, J=6.9 Hz, 1H), 6.01 (d, J=5.6 Hz, 1H), 6.48 (m, 1H) 7.23–7.30 (m, 2H), 7.45–7.51 (m, 1H), 7.78 (d, J=7.8 Hz, 1H). ^{13}C NMR: δ 22.02, 26.59, 28.07, 31.40, 32.00, 37.11, 83.76, 101.24, 104.77, 115.99, 116.54, 122.31, 123.64, 131.21, 132.28, 132.38, 134.20, 136.90, 152.30, 160.13, 162.51. HRMS: 320.1412 (Calcd.), 320.1396 (found).

5.1.8. 8-[(Cycloheptyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [23]. 23 (50%), a pale yellow semi-solid.

Spectral data for ***23***: IR (neat) ν_{max}: 3058, 2921, 2854, 1708, 1640, 1452 cm^{-1}. ^{1}H NMR: δ 1.55–1.69 (m, 8H), 2.02 (dd, J=15.8, 9.1 Hz, 1H), 2.37–2.43 (m, 4H), 3.01–3.16 (m, 2H), 5.55 (d, J=5.9 Hz, 1H), 6.02 (d, J=4.5 Hz, 1H), 6.54 (d, J=3.9 Hz, 1H) 7.23–7.51 (m, 3H), 7.79 (d, J=7.7 Hz, 1H). ^{13}C NMR: δ 21.53, 27.78, 28.21, 28.95, 29.78, 32.06, 32.94, 37.61, 83.81, 101.23, 115.99, 116.56, 122.33, 123.64, 131.22, 132.29, 132.70, 135.57, 139.58, 152.33, 159.99, 162.51. HRMS: 334.1569 (Calcd.), 334.1673 (found).

5.1.9. 8-[(Diethyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [24]. 24 (50%), a pale yellow semi-solid.

Spectral data for ***24***: IR (neat) ν_{max}: 3353, 3030, 2969, 1708, 1640, 1418, 1061, 771 cm^{-1}. ^{1}H NMR: δ 0.77–1.01 (m, 6H), 1.89–1.98 (m, 1H), 2.04–2.11 (m, 4H), 2.85 (dd, J=16.1, 7.0 Hz, 1H), 3.00–3.05 (m, 1H), 5.45 (d, J=6.3 Hz, 1H), 5.94 (d, J=4.0 Hz, 1H), 6.43 (d, J=3.8 Hz, 1H), 7.12–7.21 (m, 2H), 7.35–7.40 (m, 1H), 7.67 (d, J=7.6 Hz, 1H). ^{13}C NMR: δ 13.20, 13.63, 21.81, 23.79, 25.24, 36.90, 83.51, 100.72, 115.69, 122.16, 123.60, 131.14, 132.28, 132.38, 132.49, 137.39, 138.79, 151.98, 159.97, 162.66. HRMS: 308.1412 (Calcd.), 308.1631 (found).

5.1.10. 8-(*Z*)-[(1-Ethyl-1-methyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [25] and 8-(*E*)-[(1-ethyl-1-methyl)methylene]-7,7a,8,10a-tetrahydro-6*H*-*cis*-cyclopenta[5,6]pyrano[3,2-*c*][1]benzopyran-6-one [26]. Inseparable mixture of **25** and **26** (70%), a pale yellow semi-solid.

Spectral data for ***25*** *and* ***26***: IR (neat) ν_{max}: 3050, 2968, 1698, 1495, 1401, 1176, 1108, 1039, 746 cm^{-1}. ^{1}H NMR: δ 0.99–1.04 (t, J=7.5 Hz, 3H), 1.08–1.18 (t, J=7.5 Hz, 3H), 1.78 (s, 3H), 1.85 (s, 3H), 2.01–2.08 (m, 2H), 2.12–2.21 (m, 4H), 3.00–3.17 (m, 4H), 5.55 (s, 2H), 6.00–6.04 (m, 2H), 6.53 (s, 2H), 7.21–7.28 (m, 4H), 7.44–7.49 (m, 2H), 7.76–7.79 (m, 2H). ^{13}C NMR: δ 12.97, 13.18, 17.55, 18.50, 21.36, 21.92, 27.75, 28.19, 29.63, 37.38, 37.68, 88.69, 101.17, 116.92, 116.45, 122.25, 131.13, 131.43, 132.22, 132.40, 132.56, 132.90, 139.16, 139.43, 152.27, 159.90, 162.31, 162.38. HRMS: 294.1256 (Calcd.), 294.2156 (found).

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