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Topochemical photodimerization of (*E*)-3-benzylidene-4-chromanone derivatives from β-type structures directed by halogen groups

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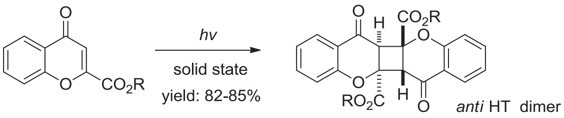
ABSTRACT

Halogen substituent plays an important role in the crystalline packing of aromatic compounds. The [2+2] photocycloaddition of (*E*)-3-benzylidene-4-chromanones in the crystalline state was investigated, and halogen substitution has been adopted to organize molecules with proper arrangement for photodimerization. Not halogen bonds, but the electron-withdrawing property of halogen atoms can enhance the face-to-face π–π interactions. Therefore, F, Cl or Br substitution at the *para* position of phenyl gave rise to almost the same β-structures with face-to-face π-stacking. Only resulted β-structures can undergo photodimerization, which gave the *syn*-HH (*syn*-head-to-head) products with high regio-/stereoselectivity.

1. Introduction

In the past several decades, [2+2] photocyclodimerization in the crystalline state has been investigated extensively.[1] The seminal study of Schmidt and Wegner established the fundamental topochemical postulate for the field of crystal engineering directed reaction, which requires that the potentially reactive double bonds must be aligned parallel to each other, and that the distance between them should be less than 4.2 Å.[2] A variety of innovative approaches have been adopted to organize molecules with proper arrangement for photodimerization, which include molecular templates, host–guest complexes, coordination polymers, microenvironment, and directing crystal packing.[3] Among these elaborate strategies, crystal engineering is a valuable tool to construct the desired architecture in the solid state.[4] For example, hydrogen bonding has been successfully used to direct molecular arrangement for [2+2] photodimerization in the crystal.[3j] Weak face-to-face π–π interaction was also considered for this topochemical transformation. But due to the sensitivity of the crystal structure to molecular information, more cooperative intermolecular interactions are needed. Therefore, fluoro,[5] chloro,[6] bromo,[7] methoxy,[8] acetoxy,[1b] and trifluoromethy[9] have been used as steering groups for the arrangement of aromatic rings in the crystal engineering. These substituents tend to steer the crystal packed in a photoactive form (β-structure) characterized by a short axis ca. 4 Å.[10]

Recently, Sakamoto et al. reported two examples of photodimerization of chromane derivatives in solution and solid state.[11] Solid-state photolysis of chromone-2-carboxylic esters selectively gave *anti*-head-to-tail photodimers (Scheme 1). It has been known that (*E*)-3-benzylidene-4-chromanones (homoiso-flavonoids) related to flavonoids has good biological activity.[12] Here, we report their solid photodimerization behaviors. The halogen has been introduced in the phenyl moiety to control the arrangement of the substrates in the crystalline state, which promoted the occurring and regio-/stereoselectivity of the photodimerization. Moreover, the effect of halogen substitution at different positions on the crystal packing has been systematically investigated.



Scheme 1.

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2. Results and discussion

Viewing the crystal structure of (*E*)-3-benzylidene-4-chromanone (**1a**),[13] the C=C bonds are parallel, but the nearest distance between them is 5.270 Å, more than 4.2 Å (Fig. 1). According to the Schmidt's postulate, it could not undergo photodimerization, which was confirmed by our experiment. Therefore, we considered to introduce a halogen group onto the phenyl for realizing the β-structure packing by using the additional halogen···halogen interaction.[10]

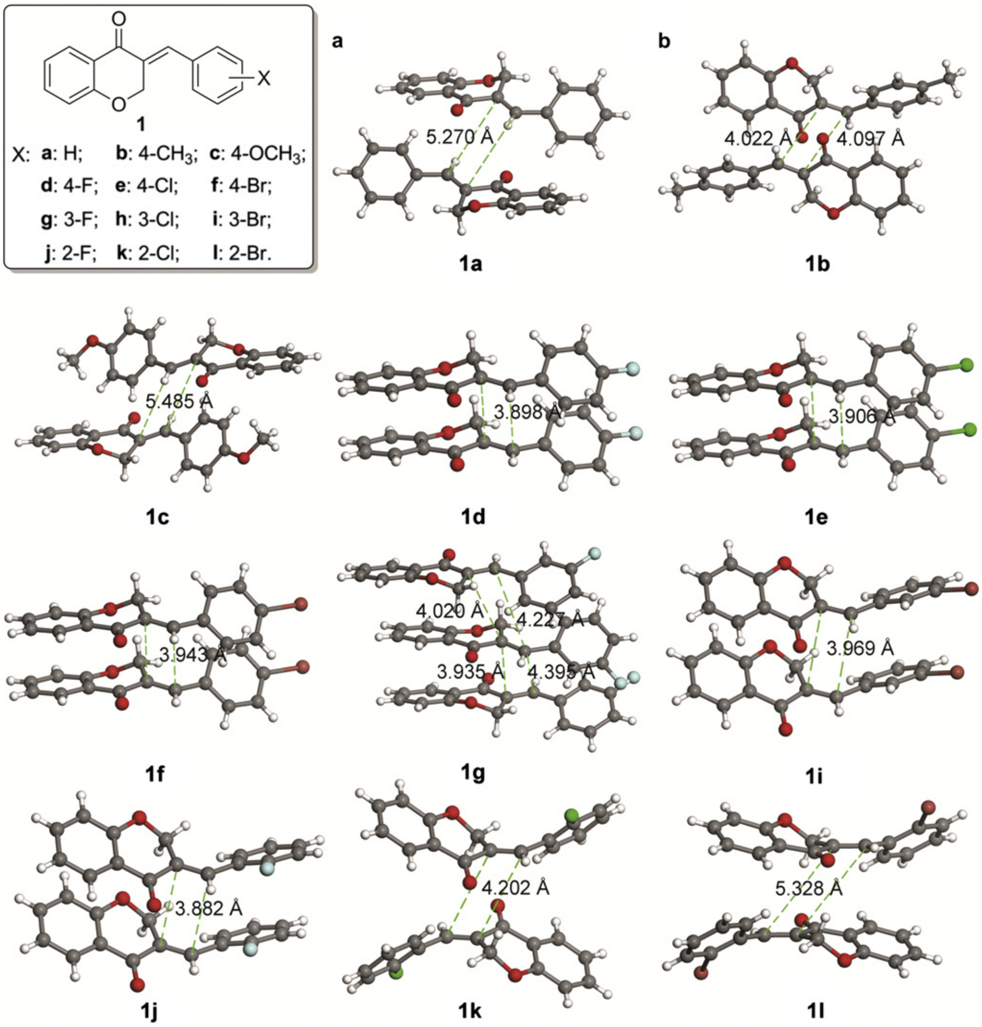


Fig. 1. The chemical structure of substituted (*E*)-3-benzylidene-4-chromanones **1a**–**l** and arrangement of closest neighbors in their crystal structures except **1h**.

The reactants **1a**–**l** were synthesized,[14] and their crystals were grown from a mixture of light petroleum, ethyl acetate, and methanol. Except **1h**, that we could not get a single crystal suitable for X-ray analysis, all structures were determined and the arrangements of closest neighbors in these crystals are shown in Fig. 1.

Actually, in contrast with compounds **1a**–**c**, halogen (F, Cl or Br) substitution at the *para* position of phenyl (**1d**–**f**) gave rise to almost the same β-structures with face-to-face π-stacking. But in most β-structures crystals, halogen···halogen interaction can be ignored (Tables 1–5) because the shortest halogen···halogen distances are more than the sum of the van der Waals radii. The favorable π-stacking could be attributed to the electron-withdrawing property of halogen atoms. According to the Hunter–Sanders model, electron-withdrawing substituents diminish the electron density in the π-cloud of the substituted ring, and result in stronger π–π interaction than unsubstituted dimer.[15] However, the situations for halogen substitution at other positions of phenyl are little complicated, and only **1i**, **1j** gave the β-structures. Unfavorable π–π interaction among the non-β-structures may be due to the stronger electron density and lower symmetry of phenyl group.

All molecules of **1d**–**f**, **1i**, and **1j** in the crystal structures are arranged in a *syn*-head-to-head β manner with a slight offset (Table 6). These parameters basically conform to the topochemical postulate. Although we did not get the crystal structure of **1h**, the later photoreaction indicated that it should have similar packing as **1i**.

Table 1
Weak intermolecular contacts in **1d**

	H···O or H···C/Å	C–H···O or C–H···C/°	C···O or C···C/Å
C12–H12A···O2	2.689	162.98	3.608
C9–H9B···O2	2.395	139.18	3.209
C9–H9A···O1	2.578	135.30	3.355
C16–H16A···C4	2.761	144.42	3.577
	O···C or C···C/Å	C–O···C or C–C···C/°	C···C or C···C/Å
C7–O2···C9	3.209	153.41	4.339
C3–C2···C3	3.386	100.92	3.898
C5–C6···C5	3.399	100.07	3.898
	H···F/Å	C–H···F/°	C···F/Å
C3–H3A···F1	2.669	141.25	3.461

Table 2
Weak intermolecular contacts in **1e**

	H···O or H···C/Å	C–H···O or C–H···C/°	C···O or C···C/Å
C13–H13A···C2	2.888	151.75	3.752
C16–H16A···C5	2.833	140.61	3.618
C12–H12A···O2	2.589	155.07	3.474
C7–H7A···O2	2.465	145.90	3.331
C7–H7B···O1	2.551	138.21	3.355

Table 3
Weak intermolecular contacts in **1f**

	H···O or H···C/Å	C–H···O or C–H···C/°	C···O or C···C/Å
C12–H12A···C2	2.840	140.05	3.619
C15–H15A···C5	2.864	153.68	3.739
C9–H9B···O2	2.571	138.15	3.374
C9–H9A···O1	2.487	146.77	3.359
C16–H16A···O1	2.578	153.69	3.456
	H···Br/Å	C–H···Br/°	C···Br/Å
C3–H3A···Br1	3.032	147.24	3.865

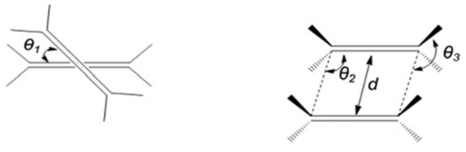
Table 4
Weak intermolecular contacts in **1i**

	H···O or H···C/Å	C–H···O or C–H···C/°	C···O or C···C/Å
C12–H12A···C2	2.859	161.53	3.623
C15–H15A···C5	2.869	123.88	3.489
C16–H16A···O1	2.667	165.12	3.594
C9–H9A···O1	2.616	140.55	3.439
C9–H9B···O1	2.700	135.61	3.477
C9–H9B···O2	2.669	134.38	3.435
	C···C/Å	C–C···C/°	C···C/Å
C4–C1···C4	3.392	104.35	3.969
C1–C2···C5	3.341	83.22	3.466
	H···Br/Å	C–H···Br/°	C···Br/Å
C4–H4A···Br1	2.945	124.88	3.575

Table 5
Weak intermolecular contacts in **1j**

	H···O or H···C/Å	C–H···O or C–H···C/°	C···O or C···C/Å
C9–H9A···O2	2.572	142.35	3.224
C13–H13A···O1	2.719	126.05	3.303
C14–H14A···O1	2.667	120.46	3.594
	H···F or H···H/Å	C–H···F or C–H···H/°	C···F or C···H/Å
C15–H15A···F1	2.540	126.50	3.198
C3–H3A···F1	2.613	154.06	3.492
C3–H5A···H5A	2.396	132.95	3.122

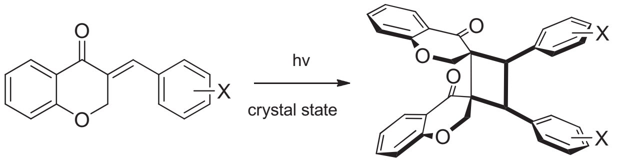
Table 6
The geometric parameters of photoactive compounds[a]



No	Compd	d (Å)	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)
1	**1d**	3.898	0	92.36	75.52
2	**1e**	3.906	0	90.97	75.35
3	**1f**	3.943	0	90.89	75.47
4	**1i**	3.969	0	92.03	73.37
5	**1j**	3.882	0	90.90	79.83

[a] The structure of **1h** was not determined. θ_3 is the angle between the >C=C<and C=C···C=C plane.

Powder crystals were placed between two quartz slides and irradiated with a 500 W high-pressure mercury lamp under argon and Pyrex filter at room temperature. For those β-form arranged compounds, **1d–f**, **1h–j**, a clean photodimerization occurred (Scheme 2, Table 7).



Scheme 2.

Table 7
The irradiation of (E)-3-benzylidene-4-chromanones **1a–l** in the solid state

Entry	Compd	Time[a] (h)	Conv[b] (%)	Yield (%)
1	**1a**	40	—	—
2	**1b**	40	—	—
3	**1c**	40	—	—
4	**1d**	10	82	72
5	**1e**	30	97	38
6	**1f**	30	98	37
7	**1g**	40	—	—
8	**1h**	6	89	60
9	**1i**	30	93	47
10	**1j**	40	95	54
11	**1k**	40	—	—
12	**1l**	40	—	—

[a] The reaction was reached at the photostationary state in the cited irradiation.
[b] The conv and the yield were determined by ^{1}H NMR.

The progress of the reaction was monitored by ^{1}H NMR spectroscopy and thin layer chromatography. The dimers were purified by column chromatography and the crystals were grown from a mixture of light petroleum and ethyl acetate. X-ray structure and ^{1}H NMR spectroscopy analysis indicated the stereochemistry of products is *syn*-HH (*syn*-head-to-head) (Fig. 2). The low yield was due to deformation of the substrates in the reaction and the lack of molecular flexibility. It is obvious that high regio-/stereoselectivity in forming photodimers is attributed to the constricted arrangement in the crystalline state.

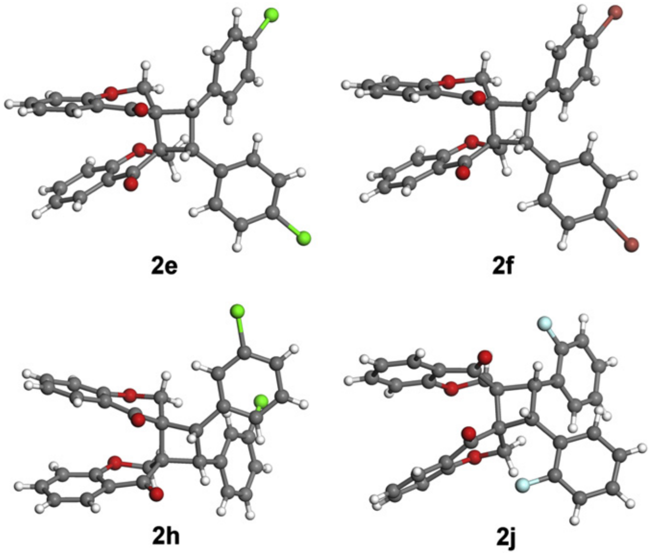

2e **2f** **2h** **2j**

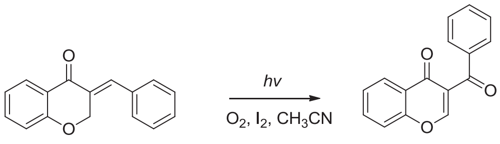
Fig. 2. Crystal structures of the photodimerization products.

It is easy to understand why **1c**, **1g**, and **1l** could not undergo dimerization from Fig. 1. The nearest double bonds of **1c** and **1l** are parallel and the distance between them is 5.485, 5.328 Å, respectively, more than 4.2 Å. The double bonds of **1g** are not parallel

(θ_1=53.67°), although the nearest distance between them is 3.935 Å.

A few examples were reported that double bonds are within 4.2 Å, but photochemically inert.[16] Both of **1b**, **1k** are arranged in α form (*anti*-head-to-tail) with potentially reactive double bonds (Fig. 1). In contrast to the above photoactive compounds, the neighboring moieties of the C=C bonds in **1b**, **1k** are not parallel. Probably due to the steric compression, these moieties hamper close movement of double bonds toward each other. Thus unparallel groups act as stationary impediments to the photodimerization.

The photochemistry of (*E*)-3-benzylidene-4-chromanones in solution was also examined. Same as reported before,[17] photodimerization was not observed. However, we isolated product **3a**[18] when irradiating the solution of **1a** in acetonitrile (Scheme 3), which is similar to Chawla and Marathe's reports.[19] The isolated yield of this reaction is 45% in the presence of oxygen and iodine. The mechanism may include the $^1O_2$ initiated ene reaction, then elimination of H_2O.



1a **3a**

Scheme 3.

3. Conclusion

In summary, we present here the [2+2] photocycloaddition of (*E*)-3-benzylidene-4-chromanones in the crystalline state. Halogen substituent in phenyl group plays an important role in crystal packing. Not halogen bonds, but the electron-withdrawing property of halogen atoms can enhance the face-to-face π–π interactions. Therefore, F, Cl or Br substitution at the *para* position of phenyl gave rise to almost the same β-structures with face-to-face π-stacking. Only resulted β-structures can undergo photodimerization, which gave the *syn*-HH (*syn*-head-to-head) products with high regio-/stereoselectivity. This work will inspire more ideas about photodimerization in organic synthesis.

4. Experimental section

4.1. General

Melting points were determined on a Laboratory Devices X-4 apparatus and are uncorrected. IR spectra were taken on a Nicolet 380 FT-IR spectrometer in KBr film and reported in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker DMX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in parts per million relative to TMS as internal standard. HRMS (EI) was determined by using Micromass GCT MS instrument (Waters). X-ray crystallographic analysis was performed with a Rigaku R-AXIS RAPID IP.

4.2. General procedure for the synthesis of 3-benzylidene-4-chromanones derivatives

A round-bottom flask was charged with the 4-chromanone (3.4 mmol) and aromatic-aldehyde (3.6 mmol). This was dissolved in methanol (20 mL), and concentrated hydrochloride (10 mL). The mixture was refluxed for 24 h and then diluted with water. Filtration afforded the crude product, which was crystallized from methanol to give the pure product.

4.2.1. (E)-3-Benzylidene-4-chromanone ***1a***[20]. Colorless crystal, yield 79%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, *J*=7.6, 1.6 Hz, 1H, ArH), 7.89 (s, 1H, CH), 7.51–7.41 (m, 4H, ArH), 7.33–7.30 (m, *J*=1.2 Hz, 2H, ArH), 7.10–7.06 (m, 1H, ArH), 6.97 (d, *J*=8.0 Hz, 1H, ArH), 5.36 (d, *J*=1.6 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.37, 161.34, 137.62, 136.02, 134.60, 131.14, 130.16, 129.63, 128.91, 128.14, 122.24, 122.09, 118.10, 67.80. HRMS (EI): calcd for $C_{16}H_{12}O_2$ (M^+): 236.0837; found: 236.0835.

*4.2.2. (E)-3-(4-Methylbenzylidene)-4-chromanone****1b***[20]. Colorless crystal, yield 51%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, *J*=8, 2 Hz, 1H, ArH), 7.86 (s, 1H, CH), 7.51–7.46 (m, 1H, ArH), 7.27–7.21 (m, 5H, ArH), 7.09–7.05 (m, 1H, ArH), 6.97 (d, *J*=8.4 Hz, 1H, ArH), 5.37 (d, *J*=2 Hz, 2H, CH_2), 2.41 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.47, 161.31, 140.14, 137.81, 135.97, 131.82, 130.35, 129.70, 128.15, 122.31, 122.07, 118.08, 67.95, 21.68. HRMS (EI): calcd for $C_{17}H_{14}O_2$ (M^+): 250.0994; found: 250.0990.

4.2.3. (E)-3-(4-Methoxybenzylidene)-4-chromanone ***1c***[20]. Colorless crystal, yield 69%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, *J*=8, 1.6 Hz, 1H, ArH), 7.84 (s, 1H, CH), 7.50–7.46 (m, 1H, ArH), 7.28 (d, *J*=8.8 Hz, 2H, ArH), 7.09–7.05 (m, 1H, ArH), 6.98–6.95 (m, 3H, ArH), 5.38 (dd, *J*=2 Hz, 2H, CH_2), 3.86 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.38, 161.19, 160.95, 137.52, 135.86, 132.26, 129.13, 128.10, 127.25, 122.35, 122.04, 118.03, 114.49, 68.00, 55.62. HRMS (EI): calcd for $C_{17}H_{14}O_3$ (M^+): 266.0943; found: 266.0947.

4.2.4. (E)-3-(4-Fluorobenzylidene)-4-chromanone ***1d***[21]. Colorless crystal, yield 61%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, *J*=7.6, 1.6 Hz, 1H, ArH), 7.83 (s, 1H, CH), 7.52–7.48 (m, 1H, ArH), 7.32–7.29 (m, 2H, ArH), 7.17–7.06 (m, 2H, ArH), 6.97 (d, *J*=8.4 Hz, 1H, ArH), 5.33 (d, *J*=1.6 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.23, 164.65, 162.15, 161.27, 136.40, 136.12, 132.20, 132.12, 130.97, 130.73, 128.14, 122.18, 118.11, 116.26, 116.05, 67.67. HRMS (EI): calcd for $C_{16}H_{11}O_2F$ (M^+): 254.0743; found: 254.0746.

4.2.5. (E)-3-(4-Chlorobenzylidene)-4-chromanone ***1e***[22]. Colorless crystal, yield 70%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, *J*=8, 1.6 Hz, 1H, ArH), 7.81 (s, 1H, CH), 7.52(m, 1H, ArH), 7.44–7.42 (m, 2H, ArH), 7.24 (s, 1H, ArH), 7.10–7.06 (m, 1H, ArH), 6.98 (d, *J*=8.4 Hz, 1H, ArH), 5.31 (d, *J*=1.6 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.15, 161.31, 136.20, 135.80, 133.01, 131.63, 131.39, 129.26, 128.18, 122.24, 122.13, 118.15, 67.66. HRMS (EI): calcd for $C_{16}H_{11}O_2Cl$ (M^+): 270.0448; found: 270.0451.

4.2.6. (E)-3-(4-Bromobenzylidene)-4-chromanone ***1f***[22]. Colorless crystal, yield 75%, ^1H NMR (400 MHz, CDCl3): δ 8.02 (dd, *J*=8, 1.6 Hz, 1H, ArH), 7.79 (s, 1H, CH), 7.59 (d, *J*=8.4 Hz, 2H, ArH), 7.52–7.48 (m, 1H, ArH), 7.18 (d, *J*=8.4 Hz, 2H, ArH), 7.10–7.06 (m, 1H, ArH), 6.98 (d, *J*=8.4 Hz, 1H, ArH), 5.30 (d, *J*=2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.16, 161.33, 136.25, 136.23, 133.46, 132.23, 131.73, 131.58, 128.19, 124.10, 122.25, 122.13, 118.16, 67.66. HRMS (EI): calcd for $C_{16}H_{11}O_2^{79}Br$ (M^+): 313.9942; found: 313.9940; calcd for $C_{16}H_{11}O_2^{81}Br$ (M^+): 315.9922; found: 315.9926.

4.2.7. (E)-3-(3-Fluorobenzylidene)-4-chromanone ***1g***[23]. Colorless crystal, yield 70%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, *J*=8, 1.6 Hz, 1H, ArH), 7.81 (s, 1H, CH), 7.52–7.48 (m, 1H, ArH), 7.45–7.40 (m, 1H, ArH), 7.14–7.06(m, 3H, ArH), 7.02–6.97 (m, 2H, ArH), 5.32 (d, *J*=2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.15, 164.15, 161.69, 161.38, 136.70, 136.62, 136.26, 136.11, 136.09, 132.18, 130.60, 130.52, 128.19, 125.88, 125.85, 122.25, 122.10, 118.18, 116.85, 116.69, 116.63, 116.48, 67.63. HRMS (EI): calcd for $C_{16}H_{11}O_2F$ (M^+): 254.0743; found: 254.0746.

4.2.8. (E)-3-(3-Chlorobenzylidene)-4-chromanone ***1h***[24]. White solid, yield 65%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, J=8, 1.2 Hz, 1H, ArH), 7.79 (s, 1H, CH), 7.52–7.48(m, 1H, ArH), 7.40 (s, 1H, ArH), 7.38 (s, 1H, ArH),7.29 (s, 1H, ArH), 7.19 (t, J=4.4 Hz, 1H, ArH), 7.09 (t, 7.2 Hz, 1H, ArH), 6.98(d, J=8.4 Hz, 1H, ArH), 5.31 (d, J=1.2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.13, 161.39, 136.34, 136.29, 135.92, 134.98, 132.33, 130.22, 129.84, 129.63, 128.21, 128.15, 122.28, 122.10, 118.20, 67.61. HRMS (EI): calcd for $C_{16}H_{11}O_2Cl$ (M^+): 270.0448; found: 270.0451.

4.2.9. (E)-3-(3-Bromobenzylidene)-4-chromanone ***1i***[22]. Colorless crystal, yield 75%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, J=8, 1.6 Hz, 1H, ArH), 7.78 (s, 1H, CH), 7.55–7.48 (m, 2H, ArH), 7.45 (s, 1H, ArH), 7.33 (t, J=8 Hz, 1H, ArH), 7.23(d, J=7.6 Hz, 1H, ArH), 7.11–7.07 (m, 1H, ArH), 6.98 (d, J=8.4 Hz, 1H, ArH), 5.31 (d, J=2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.10, 161.40, 136.64, 136.29, 135.80, 132.72, 132.53, 132.38, 130.45, 128.57, 128.21, 123.06, 122.28, 122.11, 118.20, 67.59. HRMS (EI): calcd for $C_{16}H_{11}O_2^{79}Br$ (M^+): 313.9942; found: 313.9939; calcd for $C_{16}H_{11}O_2^{81}Br$ (M^+): 315.9922; found: 315.9927.

4.2.10. (E)-3-(2-Fluorobenzylidene)-4-chromanone ***1j***[20]. Colorless crystal, yield 55%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J=8, 1.6 Hz, 1H, ArH), 7.85 (d, J=1.2 Hz, 1H, CH), 7.52–7.48 (m, 1H, ArH), 7.44–7.38 (m, 1H, ArH), 7.23–7.14 (m, 3H, ArH), 7.10–7.06 (m, 1H, ArH), 7.12–7.04 (m, 1H, ArH), 6.97 (d, J=8.4 Hz, 1H, ArH), 5.19 (t, J=1.6 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.09, 161.98, 161.60, 159.49, 136.18, 133.09, 131.65, 131.57,131.13, 131.10, 130.51, 130.49, 128.23, 124.43, 124.39, 122.67, 122.52, 122.18, 118.18, 116.42, 116.20, 68.14, 68.09. HRMS (EI): calcd for $C_{16}H_{11}O_2F$ (M^+): 254.0743; found: 254.0746.

4.2.11. (E)-3-(2-Chlorobenzylidene)-4-chromanone ***1k***[22]. Colorless crystal, yield 61%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, J=8, 1.6 Hz, 1H, ArH), 7.96 (s, 1H, CH), 7.52–7.48 (m, 2H, ArH), 7.36–7.32 (m, 2H, ArH), 7.24 (s, 1H, ArH), 7.14–7.07 (m, 2H, ArH), 6.97 (d, J=8.4 Hz, 1H, ArH), 5.31(d, J=1.6 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.29, 161.53, 136.24, 135.17, 134.71, 133.14, 132.69, 130.71, 130.53, 130.30, 128.24, 126.84, 122.22, 118.19, 67.75. HRMS (EI): calcd for $C_{16}H_{11}O_2Cl$ (M^+): 270.0448; found: 270.0451.

4.2.12. (E)-3-(2-Bromobenzylidene)-4-chromanone ***1l***[22]. Colorless crystal, yield 50%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, J=8, 1.6 Hz, 1H, ArH), 7.90 (s, 1H, CH), 7.68 (dd, J=8.0, 0.8 Hz, 1H, ArH), 7.52–7.48 (m, 1H, ArH), 7.40–7.36 (m, 1H, ArH), 7.29–7.25 (m, 1H, ArH), 7.13–7.07 (m, 2H, ArH), 6.97 (d, J=8 Hz, 1H, ArH), 5.17 (d, J=2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.28, 161.54, 136.84, 136.25, 134.98, 133.49, 132.40, 130.79, 130.50, 128.23, 127.44, 125.09, 122.22, 118.20, 67.67. HRMS (EI): calcd for $C_{16}H_{11}O_2^{79}Br$ (M^+): 313.9942; found: 313.9946; calcd for $C_{16}H_{11}O_2^{81}Br$ (M^+): 315.9922; found: 315.9926.

4.3. Procedure for photoreaction of (*E*)-3-benzylidene-4-chromanone

A quartz tube was charged with a solution of (*E*)-3-benzylidene-4-chromanone (50 mg, 0.2 mmol) and catalytic amount of I_2 in acetonitrile saturated with oxygen (10 mL). The mixture was irradiated with a high-pressure mercury lamp (500 W) for 24 h. The reaction mixture was then concentrated under vacuum and the residue was purified by silica gel column chromatography using petroleum ether:EtOAc (2:1) as eluent.

4.3.1. 3-Benzoyl-chromone ***3a***[18]. White solid, yield 45%, ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H, CH), 8.26 (dd, J=8, 1.6 Hz, 1H, ArH), 7.85 (t, J=7.6 Hz, 2H, ArH), 7.77–7.72(m, 1H, ArH), 7.61–7.53 (m, 2H, ArH), 7.50–7.45(m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.09, 174.92, 158.84, 156.30, 137.40, 134.60, 133.72, 129.80, 128.63, 126.72, 126.34, 125.43, 125.23, 118.53; APCI-MS: m/z 251.28 $[M+H]^+$. HRMS (EI): calcd for $C_{16}H_{10}O_3$ (M^+): 250.0630; found: 250.0626.

4.4. General procedure for the photodimerization of 3-benzylidene-4-chromanone derivatives

Powdered 3-benzylidene-4-chromanone derivatives **1a–l** sandwiched two quartz plates charged in Pyrex tube were irradiated with a 500-W high-pressure mercury lamp in argon. Crude photolysate was subjected to silica gel column chromatography using petroleum ether: dichloromethane (1:2). Solid dimers were recrystallized from a mixture of petroleum ether and EtOAc.

4.4.1. syn-HH dimer ***2d***. Colorless crystal, mp: 255–256 °C; IR (KBr film): ν 1689, 1608, 1510, 1480, 1462, 1308, 1220, 756, 731, 409 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, J=8, 1.6 Hz, 2H, ArH), 7.22–7.18 (m, 2H, ArH), 6.97–6.92 (m, 8H, ArH), 6.73 (t, J=7.6 Hz, 2H, ArH), 6.56 (d, J=8.4 Hz, 2H, ArH), 5.20 (s, 2H, CH), 4.76 (d, J=13.2 Hz, 2H, CH_2), 4.46 (d, J=13.2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl3): δ 190.38, 162.94, 161.15, 160.49, 136.17, 131.38, 131.31, 131.04, 127.64, 121.18, 119.74, 117.01, 115.50, 115.29, 68.78, 54.09, 39.21. HRMS (EI): calcd for $C_{32}H_{22}O_4F_2$ (M^+): 508.1486; found: 508.1494.

4.4.2. syn-HH dimer ***2e***. Colorless crystal, mp: 288–289 °C; IR (KBr film): ν 1688, 1607, 1491, 1479, 1460, 1307, 754, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, J=7.6, 1.2 Hz, 2H, ArH), 7.24–7.18 (m, 6H, ArH), 6.93 (d, J=8.4 Hz, 4H, ArH), 6.73 (t, J=7.2 Hz, 2H, ArH), 6.56 (d, J=8.4 Hz, 2H, ArH), 5.19 (s, 2H, CH), 4.75 (d, J=12.8 Hz, 2H, CH_2), 4.43 (d, J=12.8 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.23, 161.14, 136.23, 133.84, 132.95, 131.08, 128.64, 127.63, 121.20, 119.66, 117.03, 68.66, 54.10, 39.28. HRMS (EI): calcd for $C_{32}H_{22}O_4Cl_2$ (M^+): 540.0895; found: 540.0901.

4.4.3. syn-HH dimer ***2f***. Colorless crystal, mp: >300 °C; IR (KBr film): ν 1688, 1608, 1479, 1460, 1307, 1010, 756, 424 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, J=7.6, 1.2 Hz, 2H, ArH), 7.38 (d, J=8.4 Hz, 4H, ArH), 7.23–7.18 (m, 2H, ArH), 6.87 (d, J=8.4 Hz, 4H, ArH), 6.73 (t, J=8 Hz, 2H, ArH), 6.56 (d, J=8.4 Hz, 2H, ArH), 5.17 (s, 2H, CH), 4.74 (d, J=13.2 Hz, 2H, CH_2), 4.45 (d, J=13.2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.20, 161.14, 136.24, 134.36, 131.60, 131.41, 127.63, 121.21, 121.04, 119.65, 117.04, 77.55, 68.65, 54.07, 39.32. HRMS (EI): calcd for $C_{32}H_{22}O_4^{79}Br^{81}Br$ (M^+): 629.9864; found: 629.9858.

4.4.4. syn-HH dimer ***2h***. Colorless crystal, mp: 219–220 °C; IR (KBr film): ν 1689, 1608, 1478, 1306, 1219, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, J=8, 1.6 Hz, 2H, ArH), 7.24–7.16 (m, 6H, ArH), 6.99 (s, 2H, ArH), 6.87 (d, J=7.6 Hz, 2H, ArH), 6.73 (t, J=7.6 Hz, 2H, ArH), 6.56 (d, J=8.4 Hz, 2H, ArH), 5.21 (s, 2H, CH), 4.77 (d, J=13.2 Hz, 2H, CH_2), 4.49 (d, J=13.2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.04, 161.14, 137.42, 136.25, 134.48, 129.76, 129.61, 127.86, 127.66, 127.28, 121.22, 119.64, 117.02, 68.63, 54.18, 39.54. HRMS (EI): calcd for $C_{32}H_{22}O_4Cl_2$ (M^+): 540.0895; found: 540.0902.

4.4.5. syn-HH dimer ***2i***. Colorless crystal, mp: 219–221 °C; IR (KBr film): ν 1688, 1608, 1479, 1307, 913, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, J=8, 1.6 Hz, 2H, ArH), 7.38 (d, J=8.4 Hz, 2H, ArH), 7.23–7.19 (m, 2H, ArH), 7.15–7.10 (m, 4H, ArH), 6.92 (d, J=7.6 Hz, 2H, ArH), 6.73 (t, J=7.6 Hz, 2H, ArH), 6.56 (d, J=8.4 Hz, 2H, ArH), 5.20 (s, 2H, CH), 4.77 (d, J=13.2 Hz, 2H, CH_2), 4.48 (d, J=13.1 Hz, 2H, CH_2);

^{13}C NMR (100 MHz, CDCl3): δ 190.02, 161.15, 137.68, 136.26, 132.68, 130.23, 129.88, 128.31, 127.67, 122.66, 121.24, 119.65, 117.03, 68.63, 54.19, 39.51. HRMS (EI): calcd for $C_{32}H_{22}O_4{}^{79}Br^{81}Br$ (M^+): 629.9864; found: 629.9856.

4.4.6. syn-HH dimer ***2j***. Colorless crystal, mp; 256–257 °C; IR (KBr film): 1690, 1608, 1481, 1461, 1307, 756, 417 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, *J*=8, 1.6 Hz, 2H, ArH), 7.25–7.17 (m, 6H, ArH), 7.05–6.98 (m, 6H, ArH), 6.73 (t, *J*=7.2 Hz, 2H, ArH), 6.53 (d, *J*=8.4 Hz, 2H, ArH), 5.39 (s, 2H, CH), 4.83 (d, *J*=12.8 Hz, 2H, CH_2), 4.58 (dd, *J*=12.8, 1.2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.38, 162.16, 161.21, 159.72, 135.91, 130.79, 130.76, 128.88, 128.80, 127.78, 123.81, 123.78, 123.56, 123.42, 121.06, 119.68, 116.86, 116.18, 115.96, 68.49, 68.451, 54.61, 34.32. HRMS (EI): calcd for $C_{32}H_{22}O_4F_2$ (M^+): 508.1486; found: 508.1493.

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Supplementary data

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