Stereocontrolled Photodimerization of (*E*)-3-Benzylidene-4-chromanones in the Crystalline State: The Effect of a Halogen Group on the Chromanone Moiety

Xue-Ming Cheng, Min Chen, Zhi-Tang Huang, Qi-Yu Zheng*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. of China
Fax +86(10)62554449; E-mail: zhengqy@iccas.ac.cn

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Abstract: A series of (*E*)-3-benzylidene-4-chromanone derivatives are synthesized, which are substituted with a halogen group on the chromanone moiety in order to control the molecular arrangement in the crystalline state. The stereoselective photoreactions of these compounds in the solid state are examined based on the crystal structures of the reactants and products. All the examples tested undergo photodimerization, except for (*E*)-3-benzylidene-6-fluorochroman-4-one. The reactants with β-structures give *syn*-head-to-head (*syn*-HH) products with high selectivity. Only (*E*)-6-chloro-3-(4-methylbenzylidene)-chroman-4-one adopted the α-form and gives an *anti*-head-to-tail (*anti*-HT) product.

Key words: photodimerization, alkenes, photochemistry, chromanones, halogens

As control of the stereoselectivity during the photodimerization of alkenes is a key issue in synthetic organic photochemistry,[1] several strategies have been directed toward the use of various organized media and supramolecular environments, such as crystals, clays, zeolites, biomolecules, micelles, self-assembled cages and artificial hosts, etc.[1a,2] Due to the highly ordered arrangement and restricted motion of molecules in the crystal lattice, alkenes satisfying topochemistry postulates may undergo highly stereoselective reactions.[3] However, it is still a challenge to stack a pair of double bonds in the crystal lattice by design, owing to the sensitivity of the crystal structure to the molecular structure and the conditions adopted for crystal growth.[4] Polymorphic crystalline forms are common phenomena, especially for organic molecules. Fluoro,[5] chloro,[6] bromo,[7] trifluoromethyl,[8] methoxy[9] and acetoxy[10] groups can act as steering groups directing aromatic molecules to pack in the desired crystalline order. With the help of these substituents the crystals of aromatic compounds tend to stack in a form characterized by a short axis, circa 4 Å (β-structure),[11] which is very important for the photocyclization of double bonds in the solid state. Halogen-bonded supramolecular architectures have been studied extensively.[12] However, the application of halogen bond assisted solid-state photodimerization is often rather limited in scope and cannot be extended to a wide range of substrates. In our previous research, we investigated the [2+2] photocycloaddition of (*E*)-3-benzylidene-4-chromanones possessing a halogen substituent on the phenyl moiety in the crystalline state.[13] We found that it was not the halogen bonds, but the electron-withdrawing properties of the halogen atoms themselves that enhanced the face-to-face π-π interactions, which favored the formation of the β-structure. Only the resulting β-structures can undergo photodimerization, which gave *syn*-head-to-head (*syn*-HH) products with high regio- and stereoselectivity. As part of our ongoing work on the photodimerization of (*E*)-3-benzylidene-4-chromanones, the useful biological activities of which have been discussed previously,[14] we herein describe the effects of halogen substituents on the chromanone moiety. Initially, the reactants, (*E*)-3-benzylidene-4-chromanones **1a**–**g**, were prepared by reaction of the corresponding 4-chromanones with an aromatic aldehyde followed by crystallization. Next, the stereoselective photoreactions of these compounds in the solid state were studied based on the crystal structures of the reactants and products.

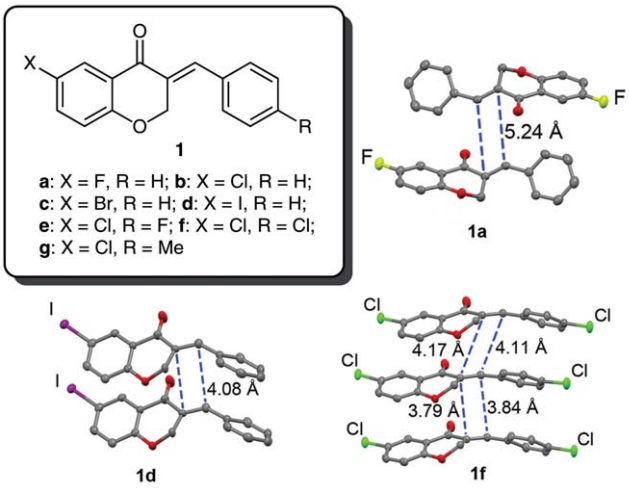

Figure 1 The structures of substituted (*E*)-3-benzylidene-4-chromanones **1a**–**g** and the arrangements of the closest neighbors in the crystal structures (ellipsoid representations) of **1a**, **1d** and **1f**

We obtained crystalline reactants **1a**–**g** from a mixture of light petroleum ether, ethyl acetate, and methanol. The single crystal structures of chromanones **1a**, **1d** and **1f** were determined by X-ray diffraction. For the photodimerization, powdered crystals of **1a**–**g** were placed be-

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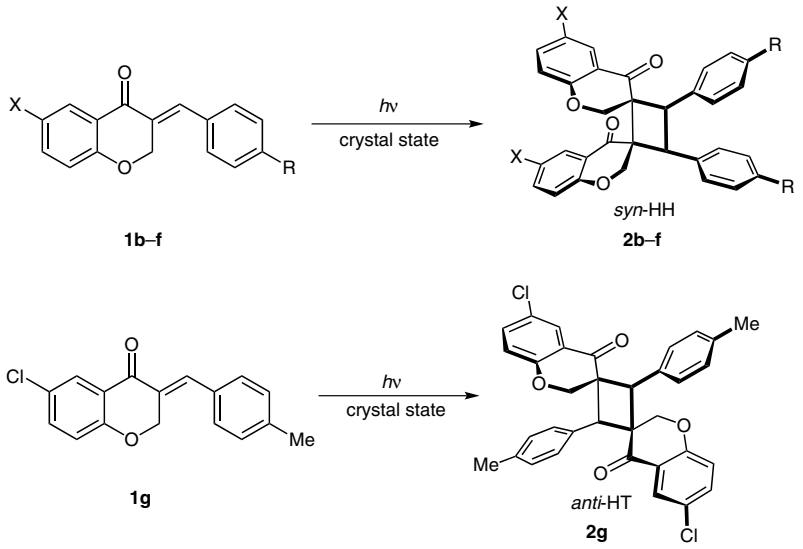

Scheme 1 Photodimerization of chromanones **1b**–**g** in the crystal state

tween two quartz slides and irradiated with a 500 W high-pressure mercury lamp using a Pyrex filter under argon at room temperature.

A knowledge of the packing arrangements of the reagents in the crystal state is a basic requirement for understanding their topochemical reactivity. Alkenes arranged in a parallel orientation with a center-to-center separation of less than 4.2 Å can undergo photocycloaddition.[3] Due to the similarity in size of fluorine and hydrogen atoms, (*E*)-3-benzylidene-6-fluorochroman-4-one (**1a**) and (*E*)-3-benzylidene-4-chromanone[15] are isostructural. On analyzing the crystal structure of **1a** (Figure 1), the closest distance between two parallel C=C bonds was found to be 5.24 Å. Therefore, chromanone **1a** was unable to undergo photodimerization in the solid state, in analogy to (*E*)-3-benzylidene-4-chromanone.[13] For compounds **1b**–**g**, clean photodimerizations occurred (Scheme 1 and Table 1).

Table 1 Photodimerization of (*E*)-3-Benzylidene-4-chromanones **1b**–**g** in the Solid State

Entry	Substrate	Time (h)[a]	Conversion (%)[b]	Yield (%)[c]	Stereochemistry
1	**1b**	20	82	51	*syn*-HH
2	**1c**	20	85	56	*syn*-HH
3	**1d**	30	78	46	*syn*-HH
4	**1e**	7	77	74	*syn*-HH
5	**1f**	10	90	57	*syn*-HH
6	**1g**	10	88	39	*anti*-HT

[a] The reaction was deemed complete on reaching a photostationary state.
[b] The conversion was determined by ^{1}H NMR spectroscopy.
[c] Yield of isolated product.

From analysis of their single crystal structures, molecules of **1d** and **1f** were arranged in a *syn*-head-to-head fashion, but with a slight offset (Figure 1). Chromanone **1d** adopted a typical β-structure and the distances between the double bonds were 4.08 Å, and crucially less than the maximum 4.2 Å. In contrast, chromanone **1f** adopted a partially distorted β-structure in which all the molecules were arranged in a *syn*-head-to-head manner, but with two sets of distances between the adjacent reactive double bonds. The distances between the first set were 4.11 Å and 4.17 Å, and those of the second set were 3.84 Å and 3.79 Å. All these lengths are less than 4.2 Å, and we are inclined to the view that the photoreaction occurs between molecules separated by the shortest distances. Halogen–halogen interactions can be ignored in compounds **1d** and **1f**, because the shortest halogen–halogen distances are greater than the sum of the van der Waals radii. Only weak C–H···O, C–H···X and π-π interactions were found in these crystals. Therefore, in analogy to compounds with a halogen substituent on the phenyl moiety, (*E*)-3-benzylidene-4-chromanones containing a halogen on the chromanone moiety prefer to adopt a β-structure. The face-to-face π-stacking was attributed to the electron-withdrawing nature of the halogen atoms,[16] which affected the arrangement of the chromanone moiety in the compounds described herein.

Although we did not obtain good quality single crystals of chromanones **1b**, **1c** and **1e** suitable for X-ray analysis, they should adopt the same arrangement as compounds **1d** or **1f**, as deduced from their similar behavior in the photodimerization reactions (Table 1). The progress of the photoreactions was monitored by ^{1}H NMR spectroscopy and thin-layer chromatography. The dimer was obtained as the major product, which was purified by column chromatography. By-products of this reaction were not isolated, nor observed by ^{1}H NMR spectroscopy. The low yield of products was due to deformation of the substrates during the reaction and the lack of molecular flexibility. X-ray

crystal structure (Figure 2) and ^{1}H NMR spectroscopic analysis indicated that the stereochemistry of dimer **2f** was *syn*-head-to-head (*syn*-HH). The ^{1}H NMR spectra of products **2b**–**e** were similar to that of **2f**, and we therefore deduce that they also adopt *syn*-head-to-head stereochemistry. The high regio- and stereoselectivity of this photodimerization reaction can be attributed to the constricted arrangement in the crystalline state.

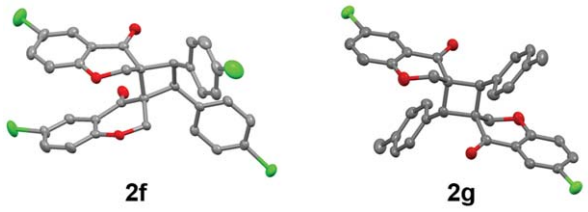

Figure 2 The X-ray crystal structures (ellipsoid representations) of dimers **2f** and **2g**

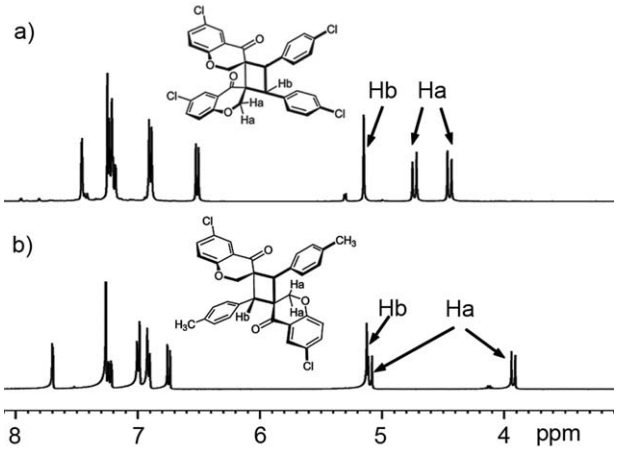

Figure 3 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of: a) **2f** and b) **2g**

However, the ^{1}H NMR spectrum of dimer **2g** was different from that of **2f** (Figure 3). The X-ray crystal structure of **2g** confirmed that it was an *anti*-head-to-tail (*anti*-HT) product (Figure 2), which may indicate that its precursor, chromanone **1g** adopted an α-structure. Although we failed to obtain single crystals of **1g** suitable for X-ray analysis, the X-ray structure of (*E*)-3-(4-methylbenzylidene)-4-chromanone[13] could provide some clues in relation to the solid-state arrangement. Steric hindrance between the methyl groups results in them orienting away from each other leading to the formation of an α-structure. The two adjacent C=C bonds in (*E*)-3-(4-methylbenzylidene)-4-chromanone are separated by distances of 4.00 Å and 4.10 Å, but they are not parallel. Therefore, this substrate cannot dimerize when subjected to irradiation. In the case of **1g**, the halogen substituent on the chromanone moiety increased the face-to-face π-π interactions between the aromatic rings. The distances between the two adjacent C=C bonds in **1g** are thus shorter than those of (*E*)-3-(4-methylbenzylidene)-4-chromanone and its photodimerization occurs easily.

In conclusion, we have synthesized a series of (*E*)-3-benzylidene-4-chromanone derivatives containing a halogen substituent on the chromanone moiety, the presence of which allows favorable face-to-face arrangement of the aromatic rings in the crystalline state. The solid-state photoreactions of these compounds possessing β-structures were examined and showed high selectivity for the formation of *syn*-head-to-head products. In addition, due to the introduction of the halogen group, (*E*)-6-chloro-3-(4-methylbenzylidene)-chroman-4-one (**1g**), which exists in the α-form, can also dimerize but gives an *anti*-head-to-tail product.

All reagents and solvents were used without any further purification. Column chromatography was performed using 200–300 mesh silica gel (Yantai, China). Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. Melting points were recorded on a Laboratory Devices X-4 apparatus and are uncorrected. IR spectra were obtained using a Nicolet 380 FT-IR spectrometer as KBr discs, wavenumbers are reported in cm^{-1}. NMR spectra were recorded on a Bruker 400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C), using $CDCl_3$ as the solvent unless otherwise specified. Chemical shifts (δ) are reported in ppm relative to TMS. High-resolution mass spectra were recorded on a Micromass UK MS spectrometer. UV irradiation experiments were conducted with an APX UV photoreaction apparatus together with a 200 V, 500 W UV lamp (Xujiang Electrical Factory), using a Pyrex filter (>300 nm) under an argon atmosphere at room temperature.

(*E*)-3-Benzylidene-4-chromanones 1a–g; General Procedure

A round-bottom flask was charged with the appropriate 4-chromanone derivative (3.4 mmol) and aromatic aldehyde (3.6 mmol). This was dissolved in MeOH (20 ml) and concd hydrochloride (10 ml). The resulting soln was heated at reflux temperature for 24 h and then diluted with H_2O. Filtration followed by crystallization from MeOH gave the pure product. Crystals suitable for X-ray analysis were grown from a mixture of PE–EtOAc–MeOH.

(*E*)-3-Benzylidene-6-fluorochroman-4-one (1a)

The title compound was prepared from 6-fluorochroman-4-one (564 mg, 3.4 mmol) and benzaldehyde (383 mg, 3.6 mmol) according to the general procedure.

Yield: 579 mg (67%); yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.67 (dd, *J* = 3.2, 8.4 Hz, 1 H), 7.48–7.42 (m, 3 H), 7.32 (d, *J* = 1.2 Hz, 1 H), 7.30 (s, 1 H), 7.23–7.18 (m, 1 H), 6.95 (dd, *J* = 4.0, 8.8 Hz, 1 H), 5.34 (d, *J* = 1.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.75, 159.03, 157.55, 156.63, 138.40, 134.43, 130.49, 130.22, 129.87, 129.00, 123.68, 123.43, 122.84, 119.83, 119.76, 113.21, 112.97, 67.95.

The spectroscopic data are in accordance with those reported.[17]

(*E*)-3-Benzylidene-6-chlorochroman-4-one (1b)

The title compound was prepared from 6-chlorochroman-4-one (619 mg, 3.4 mmol) and benzaldehyde (383 mg, 3.6 mmol) according to the general procedure.

Yield: 652 mg (71%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 2.4 Hz, 1 H), 7.89 (s, 1 H), 7.48–7.41 (m, 4 H), 7.32 (d, *J* = 1.2 Hz, 1 H), 7.30 (s, 1 H), 6.93 (d, *J* = 8.8 Hz, 1 H), 5.35 (d, *J* = 1.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.39, 159.76, 138.56, 135.89, 134.37, 130.25, 129.92, 129.01, 127.61, 127.43, 123.01, 119.87, 67.95.

The spectroscopic data are in accordance with those reported.[17]

(*E*)-3-Benzylidene-6-bromochroman-4-one (1c)
The title compound was prepared from 6-bromochroman-4-one (768 mg, 3.4 mmol) and benzaldehyde (383 mg, 3.6 mmol) according to the general procedure.

Yield: 737 mg (69% yield); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 2.4 Hz, 1 H), 7.89 (s, 1 H), 7.56 (dd, *J* = 2.4, 8.8 Hz, 1 H), 7.49–7.42 (m, 3 H), 7.32 (d, *J* = 1.2 Hz, 1 H), 7.30 (s, 1 H), 6.88 (d, *J* = 8.8 Hz, 1 H), 5.35 (d, *J* = 1.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.28, 160.22, 138.68, 138.61, 134.37, 130.57, 130.26, 129.94, 129.02, 123.50, 120.23, 114.79, 67.94.

The spectroscopic data are in accordance with those reported.[18]

(*E*)-3-Benzylidene-6-iodochroman-4-one (1d)
The title compound was prepared from 6-iodochroman-4-one (932 mg, 3.4 mmol) and benzaldehyde (383 mg, 3.6 mmol) according to the general procedure.

Yield: 739 mg (60%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 1.6 Hz, 1 H), 7.88 (s, 1 H), 7.73 (dd, *J* = 2.0, 8.4 Hz, 1 H), 7.47–7.42 (m, 3 H), 7.31 (d, *J* = 7.2 Hz, 2 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 5.35 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.07, 160.87, 144.31, 138.55, 136.72, 134.34, 130.24, 130.15, 129.92, 129.00, 123.98, 120.53, 84.46, 67.89.

The spectroscopic data are in accordance with those reported.[18]

(*E*)-6-Chloro-3-(4-fluorobenzylidene)chroman-4-one (1e)
The title compound was prepared from 6-chlorochroman-4-one (619 mg, 3.4 mmol) and 4-fluorobenzaldehyde (446 mg, 3.6 mmol) according to the general procedure.

Yield: 392 mg (40%); white solid; mp 167–168 °C.

IR (KBr): 1672, 1603, 1587, 1508, 1475, 1424, 1288, 1222, 1160, 819 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 2.4 Hz, 1 H), 7.84 (s, 1 H), 7.43 (dd, *J* = 2.4, 8.8 Hz, 1 H), 7.32–7.28 (m, 2 H), 7.15 (t, *J* = 8.4 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 1 H), 5.32 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.21, 164.80, 162.30, 159.69, 137.28, 135.96, 132.32, 132.23, 130.55, 130.11, 127.70, 127.44, 122.94, 119.88, 116.39, 116.17, 67.82.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{16}H_{10}O_2FCl$: 288.0353; found: 288.0357.

(*E*)-6-Chloro-3-(4-chlorobenzylidene)chroman-4-one (1f)
The title compound was prepared from 6-chlorochroman-4-one (619 mg, 3.4 mmol) and 4-chlorobenzaldehyde (504 mg, 3.6 mmol) according to the general procedure.

Yield: 434 mg (42%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 2.4 Hz, 1 H), 7.82 (s, 1 H), 7.45–7.42 (m, 3 H), 7.25 (s, 1 H), 7.23 (s, 1 H), 6.94 (d, *J* = 8.8 Hz, 1 H), 5.31 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.11, 159.74, 137.06, 136.10, 136.03, 132.79, 131.45, 130.78, 129.36, 127.76, 127.46, 122.91, 119.90, 67.80.

The spectroscopic data are in accordance with those reported.[19]

(*E*)-6-Chloro-3-(4-methylbenzylidene)chroman-4-one (1g)
The title compound was prepared from 6-chlorochroman-4-one (619 mg, 3.4 mmol) and 4-methylbenzaldehyde (432 mg, 3.6 mmol) according to the general procedure.

Yield: 493 mg (51%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 2.4 Hz, 1 H), 7.87 (s, 1 H), 7.42 (dd, *J* = 2.4, 8.8 Hz, 2 H), 7.28–7.20 (m, 3 H), 6.93 (d, *J* = 8.8 Hz, 1 H), 5.36 (s, 2 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.42, 159.70, 140.48, 138.67, 135.78, 131.58, 130.43, 129.77, 129.44, 127.55, 127.42, 123.07, 119.83, 68.07, 21.71.

The spectroscopic data are in accordance with those reported.[20]

Photodimerization; General Procedure
Powdered 3-benzylidene-4-chromanone derivative **1b**–**g** sandwiched between two quartz plates and placed in a Pyrex tube was irradiated with a 500 W high-pressure mercury lamp under Ar. The crude photolysate was subjected to silica gel column chromatography (PE–CH_2Cl_2, 1:2). Solid dimers were recrystallized from a mixture of PE–EtOAc.

***syn*-HH Dimer 2b**
The product was obtained from chromanone **1b** (200 mg).

Yield: 102 mg (51%); white solid; mp 234–235 °C.

IR (KBr): 1693, 1604, 1477, 1420, 1280, 1201, 704 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 2.4 Hz, 2 H), 7.24–7.18 (m, 8 H), 7.01–6.99 (m, 4 H), 6.51 (d, *J* = 8.8 Hz, 2 H), 5.22 (s, 2 H), 4.79 (d, *J* =13.2 Hz, 2 H), 4.50 (d, *J* = 13.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.49, 159.55, 136.06, 135.14, 129.77, 128.39, 126.91, 126.69, 120.48, 118.65, 68.91, 54.12, 39.63.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{32}H_{22}O_4Cl_2$: 540.0895; found: 540.0890.

***syn*-HH Dimer 2c**
The product was obtained from chromanone **1c** (200 mg).

Yield: 112 mg (56%); white solid; mp 226–228 °C.

IR (KBr): 1692, 1600, 1474, 1416, 1280, 1201, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 2.4 Hz, 2 H), 7.33 (dd, *J* = 2.4, 8.4 Hz, 2 H), 7.24–7.23 (m, 6 H), 7.01–6.99 (m, 4 H), 6.44 (d, *J* = 8.4 Hz, 2 H), 5.22 (s, 2 H), 4.79 (d, *J* = 13.2 Hz, 2 H), 4.49 (d, *J* = 13.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.36, 159.95, 138.84, 135.13, 129.83, 129.78, 128.40, 126.93, 121.02, 118.96, 113.97, 68.85, 54.09, 39.61.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{32}H_{22}O_4{}^{79}Br_2$: 627.9885; found: 627.9871; *m*/*z* [M]$^+$ calcd for $C_{32}H_{22}O_4{}^{79}Br^{81}Br$: 629.9864; found: 629.9881; *m*/*z* [M]$^+$ calcd for $C_{32}H_{22}O_4{}^{81}Br_2$: 631.9844; found: 631.9852.

***syn*-HH Dimer 2d**
The product was obtained from chromanone **1d** (200 mg).

Yield: 92 mg (46%); white solid; mp 247–249 °C.

IR (KBr): 1692, 1594, 1473, 1411, 1282, 1199, 731, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 2.0 Hz, 2 H), 7.50 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.25–7.23 (m, 6 H), 7.00 (t, *J* = 6.4 Hz, 4 H), 6.31 (d, *J* = 8.4 Hz, 2 H), 5.21 (s, 2 H), 4.78 (d, *J* = 13.6 Hz, 2 H), 4.48 (d, *J* = 13.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.21, 160.54, 144.43, 136.01, 135.12, 129.77, 128.39, 126.91, 121.58, 119.24, 83.44, 68.70, 53.97, 39.51.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{34}H_{22}O_4I_2$: 723.9608; found: 723.9616.

***syn*-HH Dimer 2e**
The product was obtained from chromanone **1e** (200 mg).

Yield: 148 mg (74%); white solid; mp 281–283 °C.

IR (KBr): 1689, 1652, 1603, 1558, 1508, 1477, 1418, 1282 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 2.0 Hz, 2 H), 7.21 (dd, *J* = 8.8, 2.4 Hz, 2 H), 6.95 (d, *J* = 6.8 Hz, 8 H), 6.53 (d, *J* = 8.4 Hz, 2 H), 5.17 (s, 2 H), 4.76 (d, *J* = 13.2 Hz, 2 H), 4.48 (d, *J* = 13.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.29, 163.03, 160.57, 159.47, 136.21, 131.32, 131.24, 130.55, 127.08, 126.70, 120.42, 118.70, 115.64, 115.43, 68.79, 54.02, 39.13.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{32}H_{20}O_4F_2Cl_2$: 576.0707; found: 576.0714.

***syn*-HH Dimer 2f**
The product was obtained from chromanone **1f** (200 mg).

Yield: 114 mg (57%); white solid; mp 291–292 °C.

IR (KBr): 1686, 1604, 1476, 1418, 1278 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 2.4 Hz, 2 H), 7.24–7.19 (m, 6 H), 6.91 (d, *J* = 8.4 Hz, 4 H), 6.52 (d, *J* = 8.8 Hz, 2 H), 5.15 (s, 2 H), 4.73 (d, *J* = 13.2 Hz, 2 H), 4.45 (d, *J* = 13.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.16, 159.45, 136.27, 133.32, 133.18, 130.98, 128.76, 127.10, 126.68, 120.33, 118.72, 68.67, 54.00, 39.17.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{32}H_{20}O_4{}^{35}Cl_4$: 608.0116; found: 608.0106; *m*/*z* $[M]^+$ calcd for $C_{32}H_{20}O_4{}^{35}Cl_3{}^{37}Cl$: 610.0086; found: 610.0078; *m*/*z* $[M]^+$ calcd for $C_{32}H_{20}O_4{}^{35}Cl_2{}^{37}Cl_2$: 612.0057; found: 612.0063.

***anti*-HT Dimer 2g**
The product was obtained from chromanone **1g** (200 mg).

Yield: 78 mg (39%); white solid; mp 285–287 °C.

IR (KBr): 1681, 1601, 1513, 1473, 1416, 1270, 1202, 1137, 1011, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.00 (d, *J* = 7.6 Hz, 4 H), 6.91 (d, *J* = 8.0 Hz, 4 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 5.13 (s, 2 H), 5.10 (d, *J* = 12.0 Hz, 2 H), 3.92 (d, *J* = 11.6 Hz, 2 H), 2.20 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.19, 159.82, 137.53, 135.87, 131.13, 129.25, 129.20, 126.83, 121.96, 119.29, 74.00, 51.53, 46.29, 21.14.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{34}H_{26}O_4Cl_2$: 568.1208; found: 568.1215.

Crystallographic Data
Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.

(*E*)-3-Benzylidene-6-fluorochroman-4-one (1a) (CCDC 895351): $C_{16}H_{11}FO_2$, *M* = 254.25, triclinic, space group $P\bar{1}$, *a* = 7.9417(16) Å, *b* = 8.5071(17) Å, *c* = 9.1657(18) Å, *α* = 90.45(3)°, *β* = 93.40(3)°, *γ* = 105.31(3)°, *V* = 596.0(2) Å^3, Z = 2, D_{calcd} = 1.417 g cm^{-3} (MoK_α, *λ* = 0.71073 Å), *T* = 173(2) K, R_1 = 0.0507, wR_2 = 0.1201.

(*E*)-3-Benzylidene-6-iodochroman-4-one (1d) (CCDC 895352): $C_{16}H_{11}IO_2$, *M* = 362.15, monoclinic, space group *P*2(1)/*n*, *a* = 4.0816(8) Å, *b* = 28.597(6) Å, *c* = 11.356(2) Å, *α* = 90.00°, *β* = 98.97(3)°, *γ* = 90.00°, *V* = 1309.3(5) Å^3, Z = 4, D_{calcd} = 1.837 g cm^{-3} (MoK_α, *λ* = 0.71073 Å), *T* = 173(2) K, R_1 = 0.0426, wR_2 = 0.1238.

(*E*)-6-Chloro-3-(4-chlorobenzylidene)chroman-4-one (1f) (CCDC 895349): $C_{16}H_{10}Cl_2O_2$, *M* = 305.14, monoclinic, space group *Pc*, *a* = 13.570(3) Å, *b* = 7.6900(15) Å, *c* = 13.205(3) Å, *α* = 90.00°, *β* = 106.25(3)°, *γ* = 90.00°, *V* = 1322.9(5) Å^3, Z = 4, D_{calcd} = 1.532 g cm^{-3} (MoK_α, *λ* = 0.71073 Å), *T* = 173(2) K, R_1 = 0.0368, wR_2 = 0.0869.

***syn*-HH Dimer 2f** (CCDC 895350): $C_{32}H_{20}Cl_4O_4$, *M* = 610.31, monoclinic, space group *P*2(1)/*n*, *a* = 14.091(3) Å, *b* = 8.1533(16) Å, *c* = 23.492(3) Å, *α* = 90.00°, *β* = 96.69(3)°, *γ* = 90.00°, *V* = 2680.58(8) Å^3, Z = 4, D_{calcd} = 1.512 g cm^{-3} (MoK_α, *λ* = 0.71073 Å), *T* = 173(2) K, R_1 = 0.0714, wR_2 = 0.1247.

***anti*-HT Dimer 2g** (CCDC 895348): $C_{34}H_{26}Cl_2O_4$, *M* = 569.45, orthorhombic, space group *Pna*2(1), *a* = 14.7893(13) Å, *b* = 8.819(2) Å, *c* = 20.761(3) Å, *α* = 90.00°, *β* = 90.00°, *γ* = 90.00°, *V* = 2707.7(8) Å^3, Z = 4, D_{calcd} = 1.397 g cm^{-3} (MoK_α, *λ* = 0.71073 Å), *T* = 173(2) K, R_1 = 0.0500, wR_2 = 0.1062.

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