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Diastereoselective Photodimerization Reactions of Chromone-2-carboxamides to Construct a C_2-Chiral Scaffold

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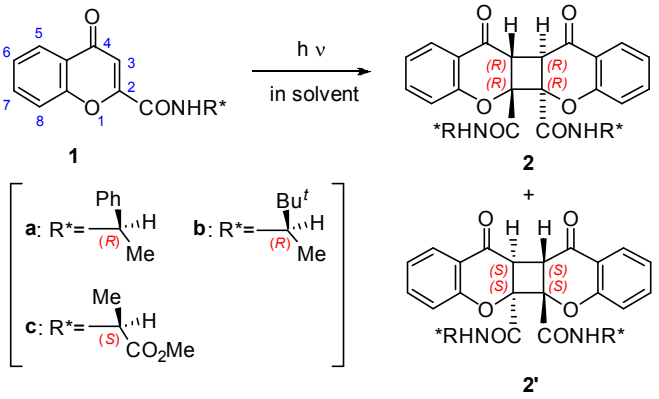
Irradiation of three chromone-2-carboxamides with a chiral auxiliary resulted in diastereoselective formation of a C_2-chiral *anti*-HH dimer scaffold. Selection of the solvent polarity and decreasing the temperature resulted in asymmetric induction with up to 84% diastereomeric excess (de).

Diastereoselectivity in photochemical reactions continues to be one of the main topics of current interest.[1] High-yield chiral induction has been achieved by the use of a chiral auxiliary and a prochiral starting material with a covalent bond.[2] The chiral auxiliary can contribute to asymmetric induction during the photochemical transformation to produce diastereomers. Recently, we reported a stereoselective photodimerization reaction of 2-chromonecarboxylic esters that exclusively formed *anti*-HH dimers among four possible dimers.[3] In most cases, controlling the selectivity of the product is difficult, since several types of photodimer are produced. In rare cases, it was reported that alkyl 2-naphthoate selectively gave C_2 chiral cubane-like photodimers.[4] In another case, coumarin and thiocoumarin in a host-guest inclusion complex also gave *anti* head-to-head (HH) dimers in a solid-state photoreaction.[5] These very rare reactions selectively lead to C_2 chiral photodimers. Materials with C_2 symmetry are widely used as ligands in catalytic asymmetric synthesis and synthetic materials. Thus, the development of a new reaction leading to C_2 chiral materials would be extremely useful.[6] In this work, we found that the intermolecular photoreaction of 2-chromonecarboxamides with chiral auxiliaries led to a highly controlled diastereoselective dimerization reaction to form a C_2-chiral scaffold.

Three chiral auxiliaries connected with amide substituents at the 2-position of the chromone structure were examined (Scheme 1). Chromonecarboxamides **1a–c** were easily prepared from 2-chromonecarboxylic acid and the corresponding optically active amines (*R*)-1-phenethylamine, (*R*)-1-*t*-butylethylamine, and (*S*)-alanine methyl ester, respectively. Table 1 shows the results of the photochemical reaction under various conditions.

When an MeCN solution of **1a** was irradiated with a Pyrex-filtered light from a 500 W high-pressure mercury lamp for 1 h at 20°C, the *anti*-HH dimer **2a** was obtained as a sole product in 93% yield and with a diasteromeric excess (de) of 52% (Table 1, entry 1). The de value increased as the reaction temperature was reduced, giving 66% de and 84% de for **2a** at –40 and –80°C, respectively (entries 2 and 3). EtCN was used instead of MeCN for low-temperature photolysis at –80°C because of the low melting point. Irradiation of **1a** in benzene also gave stereoselective *anti*-HH dimers; however, the de was quite low (entry 4) in comparison to the photoreaction in polar solvent. We examined the photoreaction in other solvents such as MeOH, ether and THF; however, complex mixture was obtained.



Scheme 1. Chromone-2-carboxamides having chiral auxiliaries with covalent bonds.

Irradiation of **1b**, which contained a bulky *t*-butyl group instead of a phenyl group, also resulted in diastereoselective formation of *anti*-HH dimers; however, the diastereoselectivity was lower than that of **1a**. Furthermore, the temperature effect was the opposite of that observed for **1a**; decreasing the temperature did not result in increased de values (entries 6–8). In this case, photolysis in non-polar benzene solution gave the best de, at 44% (entry 9).

After the photoreaction of **1c**, the de value was not particularly high; even photolysis at –40°C gave a de of –22% (entries 11 and 12). Irradiation at –80°C in EtCN solution gave only 14% de (entry 13). Furthermore, interestingly, the use of non-polar benzene as a

solvent resulted in different behavior, and **2c** was obtained as a main product (entry 14).

As the photodimerization reaction proceeds from the triplet excited state, we examined the photoreaction in the presence of the triplet sensitizer benzophenone. The photodimerization reaction proceeded more effectively and gave a higher conversion (entries 5, 10 and 15).

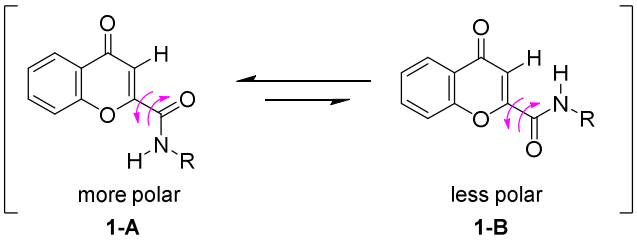
Table 1. Photodimerization reaction of chromone-2-carboxamides **1a–c** under various conditions[a]

entry	compds	solvent	temp (°C)	convn (%)	yield of **2** + **2'** (%)[b]	ratio of **2**:**2'**	de of **2** (%)
1	**1a**	MeCN	20	85	93	83:17	56
2	**1a**	MeCN	–40	91	79	88:12	66
3	**1a**	EtCN	–80	83	77	92: 8	84
4	**1a**	benzene	20	59	92	56:44	12
5	**1a**	MeCN[c]	20	97	90	83:17	56
6	**1b**	MeCN	20	91	94	69:31	38
7	**1b**	MeCN	–40	90	90	65:35	30
8	**1b**	EtCN	–80	91	78	58:42	16
9	**1b**	benzene	20	60	99	72:28	44
10	**1b**	MeCN[c]	20	97	90	63:37	26
11	**1c**	MeCN	20	92	85	43:57	–14
12	**1c**	MeCN	–40	93	91	39:61	–22
13	**1c**	EtCN	–80	94	72	43:57	–14
14	**1c**	benzene	20	76	93	72:28	44
15	**1c**	MeCN[c]	20	99	91	45:55	–10

[a]Each 0.05 M MeCN solution of **1a-c** was irradiated with a 500-W high-pressure mercury lamp for 1 h. [b]Chemical yields were determined on the basis of consumed chromones **1a–c**. [c]Benzophenone (BP) (0.1 M) was used as a triplet sensitizer.

One of the earliest rationalizations of the regiochemistry of enone cycloaddition was put forward by Corey, who proposed that a 'π complex' was formed between the photoexcited enone and a counterpart such as an alkene.[7] This is usefully predictive, and cases in which the rule breaks down can usually be accounted for by unfavourable steric interactions between the enone and the counterpart in more stable π complex orientation.[8] Theoretical approaches to 2+2 photocycloaddition of enones to alkenes were also studied.[9] In the photodimerization of chromones **1a–c** leading to *anti*-HH dimers, the regio- and stereochemistry can be reasonably explained in terms of polarization and the steric interactions of reacting species, triplet excited and ground-state molecules.

Two plausible conformations, **1-A** and **1-B**, were suggested by theoretical DFT calculation using RB3LYP/6-31G in Gaussian 09W (Scheme 2 and Table 2).[10] Planar conformations were sustained by conjugation between the chromone ring and the amide function. In all cases, conformer **1-A** is more stable than that of **1-B**, and the dipole moment of **1-A** conformer was bigger than that of **1-B** because of the orientation of two carbonyl groups. The diastereoselectivity of the photodimerization of **1** was explainable in terms of the steric interactions caused by the chiral auxiliaries (Scheme 3). The triplet excited state of **1a-A** can react with ground state of **1a-A** while avoiding steric repulsion, leading to favourable formation of **2**. As the reaction temperature was reduced, the selectivity of the reaction became higher, with a de of 84% obtained in the reaction at –80°C (Table 1, entry 3).

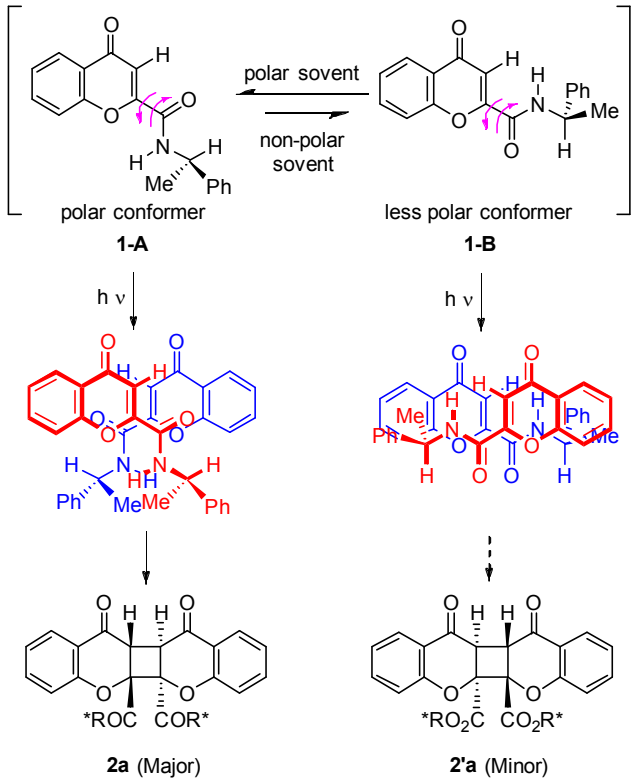


Scheme 2. Conformational change of **1**.

Table 2. Conformational analysis and the dipole moment of **1a–c**

compds	conformation	ΔH_B- ΔH_A (kcal mol^{-1})[a]	dipole moment (Deby)
1a	A (more stable)	5.78	6.75
1a	B (less stable)		2.21
1b	A (more stable)	5.98	6.88
1b	B (less stable)		2.16
1c	A (more stable)	5.80	7.01
1c	B (less stable)		3.15

[a]Differences in total energy between stable conformation A and less stable conformation B in the ground state obtained from DFT (RB3LYP/6-31G) calculation in Gaussian 09W. [b]Dipole moment obtained from DFT (RB3LYP/6-31G) calculation in Gaussian 09W.



Scheme 3. Diastereoselective photodimerization of **1a**.

On the other hand, irradiation in benzene gave a low de (Table 1, entry 4). The different polarity of the conformers may play a role for the diastereoselectivity of the photodimerization (Scheme 3). In the case of **1a-B**, the carbonyl function of the amide and the 4*H*-pyran-4-one part are orientated opposite to each other which reduces the polarity of the molecule (Table 2). Conformer **1a-B** may therefore be somewhat stabilized by the non-polar solvent and thus reduce the diastereoselectivity. This effect is certainly increased by the fact that the polarity of one carbonyl group is strengthened by electron shift from the nitrogen atom of the amide function and the polarity of the other carbonyl group by electron shift from the pyranone ring oxygen atom. In the case of **1b**, the reason for the low de of the products is unclear; however, the bulky *t*-butyl group may prevent control of the molecular conformation.

In the case of **1c**, we used the (*S*)-isomer. As the ester group was more bulky than the methyl group, the reactive chromones **1c** approached each other from the vacant site of methyl group, which meant that **2'c** was obtained as the major product in MeCN solution. However, a high de was not obtained because the steric size of both substituents was not changed significantly (entries 11–13). On the other hand, irradiation of a non-polar benzene solution of **1c** reversed the diastereoselectivity, and **2c** was produced as a main product (entry 14). As in the case of **1a**, dipole moment of **1c-A** was decreased by the bond rotation to form conformer **1c-B** which may be stabilized by the non-polar solvent and thus resulted in the inversion of the diastereoselectivity.

Unfortunately, NMR spectra in different polar solvents by changing the ratio of C_6D_6 and DMSO-$_{d6}$ did not reveal the conformational conversion between **1A** and **1B**. We cannot provide a full accounting for the diastereoselectivity; however, it seems that the conformational change depending on the solvent polarity is one of the important factors to control the stereoselectivity.

The absolute structure of diastereomeric photodimers **2a–2c**, **2'a** and **2'c** were established by single-crystal X-ray analysis. As an example, a perspective view of both diastereomeric photodimers, **2a** and **2'a**, is shown in Figure 1. The dimer **2a** shows *R* stereochemistry throughout the cyclobutane ring, while **2'a** has *S* configurations.

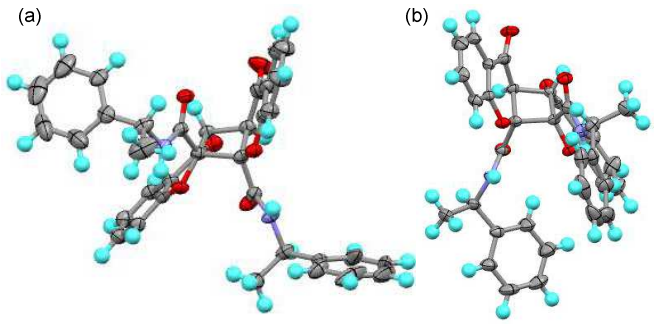


Figure 1. Perspective view of absolute configurations of diastereomeric photodimers (a) **2a** and (b) **2'a**.

Furthermore, these photodimers were easily optically resolved by recrystallization, without a cumbersome procedure. Many C_2-symmetric materials are used as ligands for catalytic asymmetric synthesis and synthetic materials. We are now developing catalytic asymmetric synthesis methods using these C_2-chiral photodimers as ligands for organometallics.

Conclusions

We achieved high chiral induction in photochemical dimerization reactions leading to a C_2 chiral scaffold through the use of chiral auxiliaries and a prochiral starting material with a covalent bond. Selection of the polarity of the solvents and reduction of the temperature resulted in asymmetric induction with up to 84% de.

Experimental

General. NMR spectra were recorded in $CDCl_3$ solution on a Bruker 300 instrument operating at 300 MHz for ^{1}H- and ^{13}C-NMR spectroscopy. Chemical shifts are reported in parts per million (ppm) relative to TMS as an internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Specific rotation was measured using a DIP 370 polarimeter (JASCO). X-ray single crystallographic analysis was conducted using a SMART APEX II or SMART APEX II ULTRA (Bruker AXS).

Preparation of 2-chromonecarboxamides **1a-c:** A toluene solution containing commercially available 1.00 g (4.90 mmol) of 2-chromonecarboxylic acid, 1.19 g (10.0 mmol) of thionylchloride, and catalytic amount of DMF was reacted for 3 h at 90 °C. After removal of the solvent and excess amount of thionylchloride *in vacuo*, crude acid chloride was obtained and used for the subsequent reaction. To a toluene solution of crude acid chloride, *(R)*-1-phenylethylamine (1.19 g, 9.80 mmol) was added drop wise at 0 °C. After the reaction mixture was stirred for 2 h at room temperature, water and ethyl acetate were added, and the organic layer was extracted in the usual manner. After evaporation of the organic solvent *in vacuo*, the residual mixture was subjected to chromatography on silica gel, and the amide 1a was obtained in 85% yield.

The other **1b** was prepared in the same manner. In the case of 1c, L-alanine methyl ester hydrochloride and triethylamine (5.0 eq) were used. The amide 1b was obtained in 97% yield and **1c** was obtained 66% yield. The structure of **1a-c** was determined on the basis of spectral data, and the crystal structure of **1a** and **1b** was also established by single crystal X-ray analysis.

(*R*)-*N*-(1-Phenylethyl)-2-chromonecarboxamide **1a**: colorless crystal; mp 123-124 °C; $[\alpha]_D^{20}$ = –1.6 (*c* = 0.47, $CHCl_3$); IR (cm^{-1}, KBr) 3295, 1677, 1646; ^{1}H NMR ($CDCl_3$) δ 1.68 (d, *J* = 6.9 Hz, 3H), 5.30-5.40 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.19 (s, 1H), 7.32-7.54 (m, 7H), 7.73 (dd, *J* = 1.6 Hz, 8.6 Hz, 1H), 8.20 (dd, *J* = 1.6 Hz, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.10, 37.37, 49.00, 61.14, 82.51, 117.20, 122.75, 125.21, 125.95, 127.52, 127.58, 128.74, 128.95, 142.07, 151.12, 166.14; EI-MS: *m*/*z* (rel. intensity) 293 (M^+, 49); HRMS (ESI-MS) *m*/*z* calcd for $C_{18}H_{15}O_3N$+H 294.1125, found 294.1114.

(*R*)-*N*-(1-*t*-Butylethyl)-2-chromonecarboxamide **1b**: colorless crystal; mp 86-87 °C; $[\alpha]_D^{20}$ = –34.0 (*c* = 0.49, $CHCl_3$); IR (cm^{-1}, KBr) 2256, 3322, 1685, 1633; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9H), 1.22

(d, *J* = 6.8 Hz, 3H), 4.05-4.15 (m, 1H), 6.74 (d, *J* = 9.3 Hz, 1H), 7.17 (s, 1H), 7.46 (t, *J* = 7.74 Hz), 7.54 (d, *J* = 8.5 Hz, 1H), 7.75 (t, *J*= 7.0 Hz), 8.22 (d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 16.01, 26.16, 34.39, 53.63, 112.17, 118.06, 124.28, 125.93, 126.08, 134.43, 154.85, 155.15, 158.52, 178.14; HRMS (ESI-MS) *m*/*z* calcd for $C_{16}H_{19}O_3N$+H 274.1438, found 274.1437.

(*S*)-*N*-(1-Methoxycarbonylethyl)-2-chromonecarboxamide **1c**: colorless crystal; mp 105-106 °C; $[\alpha]_D^{20}$ = 42.3 (*c* = 0.50, $CHCl_3$); IR (cm^{-1}, KBr) 3510, 1747, 1630; ^{1}H NMR ($CDCl_3$) δ 1.59 (d, *J* = 7.2 Hz, 3H), 3.84 (s, 3H), 4.75-4.86 (m, 1H), 7.15 (s, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.72-7.79 (m, 1H), 8.22 (dd, *J* = 1.6 Hz, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.3, 48.5, 52.8, 112.3, 118.2, 124.3, 126.0, 134.6, 154.2, 155.2, 158.7, 159.8, 172.8, 178.0; HRMS (ESI-MS) *m*/*z* calcd for $C_{14}H_{13}O_5N$+H 276.0863, found 276.0866.

X-Ray diffraction analysis data of **1a**: Colorless prismatic crystals from chloroform-hexane, trigonal space group $P3_1$, *a* = 13.4187(3) Å, *b* = 13.4187(3) Å, *c* = 28.8186(6) Å, γ = 120.0 °, *V* = 4493.9(2) $Å^3$, Z = 12, ρ = 1.301 g/cm^3, μ = 0.724 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final *R* and *wR* were 0.1240 and 0.3327 for 9005 reflections. CCDC 1010749.

X-Ray diffraction analysis data of **1b**: Colorless prismatic crystals from chloroform-hexane, triclinic space group *P*1, *a* = 5.9167(9) Å, *b* = 10.9747(17) Å, *c* = 12.2265(18) Å, α = 64.4240(19) °, β = 82.5940(19) °, γ = 89.9950(19) °, *V* = 708.78(19) $Å^3$, Z = 2, ρ = 1.28 g/cm^3, μ = 0.088 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final *R* and *wR* were 0.0398 and 0.1003 for 9005 reflections. CCDC 1010750.

Photochemical procedure of **1a-c**: A 0.02M solution of 2-chromonecarboxamides 1 was deoxygenated by bubbling argon for 20 min and was irradiated for 2 h at various temperatures. After irradiation the solvent was removed in vacuo and photoproducts were separated by flash chromatography on silica gel. The diastereoselectivity was determined on the basis of NMR spectra.

anti-HH photodimer of (*R*)-*N*-(1-phenylethyl)-2-chromonecarboxamide **2a**: colorless crystal; mp 245-246 °C; $[\alpha]_D^{20}$ = –71.0 (*c* = 0.51, $CHCl_3$); IR: (cm^{-1}, KBr) 3354, 1705, 1675; ^{1}H NMR: ($CDCl_3$) δ 1.47 (d, *J* = 6.8 Hz, 6H), 4.28 (s, 2H), 5.05 (m, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 2H), 7.26-7.33 (m, 10H), 7.45 (t, *J* =9.0 Hz, 2H), 7.94 (dd, *J* =1.7 Hz, 7.8 Hz, 2H); ^{13}C NMR: ($CDCl_3$) δ 21.58, 46.70, 49.07, 85.98, 116.38, 120.24, 122.71, 126.10, 127.20, 127.77, 128.86, 135.65, 141.71, 158.36, 166.48, 188.87; HRMS (ESI-MS) *m*/*z* calcd for $C_{36}H_{30}N_2O_6$+H 587.2165, found 587.2177.

anti-HH photodimer of (*R*)-*N*-(1-phenylethyl)-2-chromonecarboxamide **2'a**: colorless crystal; mp 248-249 °C; $[\alpha]_D^{20}$ = 139.7 (*c* = 0.47, $CHCl_3$); IR: (cm^{-1}, KBr) 3354, 1705, 1685; ^{1}H NMR: ($CDCl_3$) δ 1.46 (d, *J* = 6.9 Hz, 6H), 4.28 (s, 2H), 5.05 (m, 2H), 6.65 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 7.22-7.43 (m, 12H), 7.92 (dd, *J* = 1.7 Hz, 7.8 Hz, 2H); ^{13}C NMR: ($CDCl_3$) δ 21.10, 46.53, 48.60, 85.95, 116.56, 120.09, 122.60, 126.24, 127.06, 127.49, 128.62, 135.55, 142.42, 158.23, 166.53, 188.78; HRMS (ESI-MS) *m*/*z* calcd for $C_{36}H_{30}N_2O_6$+H 587.2165, found 587.2173.

anti-HH photodimer of (*R*)-*N*-(1-*t*-butylethyl)-2-chromonecarboxamide **2b**: colorless crystal; mp 258-259 °C; $[\alpha]_D^{20}$ = –136.0 (*c* = 0.49, $CHCl_3$); IR: (cm^{-1}, KBr) 3426, 1700, 1676; ^{1}H NMR: ($CDCl_3$) δ 0.84 (s, 18H), 1.07 (d, *J* = 6.8 Hz), 3.73-3.83 (m, 2H), 4.25 (s, 2H), 6.66 (d, *J* = 9.8 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 8.4 Hz, 2H), 7.93 (dd, *J* = 1.6 Hz, 9.1 Hz, 2H); ^{13}C NMR: ($CDCl_3$) δ 16.22, 26.02, 33.78, 46.88, 53.17, 85.83, 116.13, 120.49, 122.74, 127.26, 135.65, 158.32, 166.69, 188.84; HRMS (ESI-MS) *m*/*z* calcd for $C_{32}H_{38}O_6N_2$+H 547.2795, found 547.2803.

anti-HH photodimer of (*R*)-*N*-(1-*t*-butylethyl)-2-chromonecarboxamide **2'b**: colorless crystal; mp 216-217°C; $[\alpha]_D^{20}$ = 51.7 (*c* = 0.50, $CHCl_3$); IR: (cm^{-1}, KBr) 3419, 1704, 1680; ^{1}H NMR: ($CDCl_3$) δ 0.92 (s, 18H), 1.02 (d, *J* = 6.8 Hz), 3.71-3.82 (m, 2H), 4.27 (s, 2H), 6.60 (d, *J* = 10.0 Hz, 2H), 6.79 (brd, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.93 (brd, *J* = 7.5 Hz, 2H); ^{13}C NMR: ($CDCl_3$) δ 16.47, 26.38, 34.27, 46.93, 53.42, 86.61, 116.94, 120.73, 123.07, 127.63, 135.90, 158.65, 166.90, 189.48; HRMS (ESI-MS) *m*/*z* calcd for $C_{32}H_{38}O_6N_2$+H 547.2795, found 547.2800.

anti-HH photodimer of (*S*)-*N*-(1-methoxycarbonylethyl)-2-chromonecarboxamide **2c**: colorless crystal; mp 251-252°C; $[\alpha]_D^{20}$ = –105.7 (*c* = 0.50, $CHCl_3$); IR (cm^{-1}, KBr) 3402, 1738, 1685, 1672; ^{1}H NMR ($CDCl_3$) δ 1.35 (d, *J* = 7.1 Hz, 6H), 3.75 (s, 6H), 4.25 (s, 2H), 4.25-4.55 (m, 2H), 6.96 (d, *J* = 7.3 Hz, 2H), 7.09 (t, *J* = 7.1 Hz, 2H), 7.44-7.50 (m, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.91 (d, *J* = 6.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.80, 46.72, 48.52, 52.97, 86.07, 116.77, 120.39, 122.99, 127.28, 136.02, 158.57, 166.97, 173.16, 189.05; HRMS (ESI-MS) *m*/*z* calcd for $C_{28}H_{26}O_{10}N_2$+H 551.1657, found 551.1658.

anti-HH photodimer of (*S*)-*N*-(1-methoxycarbonylethyl)-2-chromonecarboxamide **2'c**: colorless crystal; mp 217-218°C; $[\alpha]_D^{20}$ = 69.8 (*c* = 0.52, $CHCl_3$); IR (cm^{-1}, KBr) 3354, 1751, 1697; ^{1}H NMR ($CDCl_3$) δ 1.47 (d, *J* = 7.3 Hz, 6H), 3.81 (s, 6H), 4.37 (s, 2H), 4.59-4.70 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.46-7.53 (m, 2H), 7.90 (dd, *J* =1.6 Hz, 6.3 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 17.51, 43.75, 48.07, 52.68, 84.94, 117.67, 119.87, 122.95, 127.28, 136.12, 158.32, 165.69, 174.08, 187.50; HRMS (ESI-MS) *m*/*z* calcd for $C_{28}H_{26}O_{10}N_2$+H 551.1657, found 551.1660

X-Ray diffraction analysis data of photodimer **2a**: Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, *a* = 12.2096(9) Å, *b* = 13.7443(10) Å, *c* = 18.0044(14) Å, *V* = 3021.4(4) $Å^3$, Z = 4, ρ = 1.290 g/cm^3, μ = 0.088 mm^{-1}. The structure was solved by the direct method of full matrix least-

squares, where the final *R* and *wR* were 0.0469 and 0.1150 for 5358 reflections. CCDC 1010751.

X-Ray diffraction analysis data of photodimer **2'a**: Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, a = 9.7337(10) Å, b = 13.9495(14) Å, c = 22.104(2) Å, V = 3001.3(5) Å^3, Z = 4, ρ = 1.298 g/cm^3, μ = 0.088 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final *R* and *wR* were 0.0424 and 0.0944 for 5287 reflections. CCDC 1010752.

X-Ray diffraction analysis data of photodimer **2b**: Colorless prismatic crystals from chloroform-hexane, monoclinic space group $P2_12_12_1$, a = 7.704(18) Å, b = 14.23(3) Å, c = 26.50(6) Å, V = 2906(11) Å^3, Z = 4, ρ = 1.249 g/cm^3, μ = 0.086 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final *R* and *wR* were 0.0629 and 0.1531 for 5433 reflections. CCDC 1010753. The absolute configuration could be determined on the basis of the configuration of (*R*)-1-(*t*-butyl)ethylamine.

X-Ray diffraction analysis data of photodimer **2c**: Colorless prismatic crystals, monoclinic space group $P2_12_12_1$, a = 8.021(3) Å, b = 15.273(5) Å, c = 21.484(7) Å, V = 2631.9(15) Å^3, Z = 4, ρ = 1.389 g/cm^3, μ = 0.107 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final *R* and *wR* were 0.0535 and 0.0896 for 5909 reflections. CCDC 1010754. The absolute configuration could be determined on the basis of the configuration of (*S*)-alanine.

X-Ray diffraction analysis data of photodimer **2'c**: This crystal included each one molecule of acetone and *N*-methylbenzamide. Colorless prismatic crystals, monoclinic space group $P6_5$, a = 12.380(5) Å, b = 12.380(5) Å, c = 42.393(17) Å, γ = 120.00 °, V = 5627(4) Å^3, Z = 6, ρ = 1.317 g/cm^3, μ = 0.098 mm^{-1}. The structure was solved by the direct method of full matrix least-squares, where the final *R* and *wR* were 0.0631 and 0.1416 for 6805 reflections. CCDC 1010755.

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Notes and references

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1 Y. Inoue, *Chem. Rev.* 1992, **92**, 741; Y. Inoue, *Molecular and Supramolecular Photochemistry; Chiral Photochemistry*, Y. Inoue, V. Ramamurthy, eds, Marcel Dekker, New York, 2004, vol. 11, 129; B. Grosch, T. Bach, *Molecular and Supramolecular Photochemistry; Chiral Photochemistry*, Y. Inoue, V. Ramamurthy, eds, Marcel Dekker, New York, 2004, vol. 11, 315; M. Sakamoto, *Molecular and Supramolecular Photochemistry; Chiral Photochemistry*, Y. Inoue, V. Ramamurthy, eds, Marcel Dekker, New York, 2004, vol. 11, 415.

2 N. Hoffmann, J. P. Peter, *Molecular and Supramolecular Photochemistry; Chiral Photochemistry*, ed. Y. Inoue, V. Ramamurthy, Marcel Dekker, New York, 2004, vol. 11, 179; H. Buschmann, H. D. Scharf, N. Hoffmann, M. W. Plath, J. Runsink, *J. Am. Chem. Soc.*, 1989, **111**, 5367; H. Buschmann, H. D. Scharf, N. Hoffmann, P. Esser, *Angew. Chem., Int. Ed*., 1991, **30**, 477; J. Clayden, F. E. Knowles, C. J. Menet, *J. Am. Chem. Soc.*, 2003, **125**, 9278; K. Tsutsumi, H. Nakano, A. Furutani, K. Endou, A. Merpuge, T. Shintani, T. Morimoto, K. Kakiuchi, *J. Org. Chem.,* 2004, **69**, 785.

3 M. Sakamoto, F. Yagishita, M. Kanehiro, Y. Kasashima, T. Mino, T. Fujita, *Org. Lett*., 2010, **12**, 4435; M. Sakamoto, M. Kanehiro, T. Mino, T. Fujita, *Chem. Commun*., 2009, 2379; P. Mandal, A. Nath, R.V. Venkateswaran, *Tetrahedron,* 1996, **52**, 7855; S.C. Gupta, S. K. Mukerjee, *Tetrahedron Lett.,* 1973, **51**, 5073.

4 P. J. Collin, D. B. Roberts, G. Sugowdz, D. Wells, W. H. F. Sasse, *Tetrahedron Lett.*, 1972, **13**, 321; C.-H. Tung, L.-Z. Wu, L.-P. Zhang, B. Chen, *Acc. Chem. Res.,* 2003*,* **36***, 39*; L. Lei, L.-Z. Wu, X.-L. Wu, G.-H. Liao, L.-P. Zhang, C.-H. Tung, K.-L. Ding, *Tetrahedron Lett.,* 2006, **47***,* 4725; H.-X. Xu, B. Chen, L.-P. Zhang, L.-Z. Wu, C.-H. Tung, *Tetrahedron Lett.*, 2011, **52**, 2946; S.-F. Cheng, B. Chen, X.-J. Yang, L. Luo, L.-P. Zhang, L.-Z. Wu, C.-H. Tung, *Photochem. Photobiol. Sci.* 2014, **13**, 261.

5 K. Tanaka, F, Toda, E. Mochizuki, N. Yasui, Y. Kai, I. Miyahara, K. Hirotsu, *Angew. Chem. Int. Ed*., 1999, **38**, 3523.

6 T. P. Yoon, E. N. Jacobsen, *Science,* 2003, **299**, 1691; A. Pfaltz, W. J. Drury III, *Proc. Natl. Acad. Sci. U.S.A.,* 2004, **101**, 5723.

7 E. J. Corey, S. Nozoe, *J. Am. Chem. Soc.*, 1964, 86, 5570.

8 P. de Mayo, *Acc. Chem Res.*, 1971, **4**, 41; J. –P. Pete, in *Organic Photochemistry and Photobiology*, W. Horspool, F Lenci, eds., CRC Press, Boca Raton, London, New York, Washington D. C., 2004, 71-1; D. I. Schuster, in *Organic Photochemistry and Photobiology*, W. Horspool, F Lenci, eds., CRC Press, Boca Raton, London, New York, Washington D. C., 2004, 72-1.

9 J. L. Broeker, J. E. Eksterowicz, A. J. Belk, K. N. Houk, *J. Am. Chem. Soc.*, 1995, **117**, 1847; C. Bertrand, J. Bouquant, J. P. Pete, S. Humbel, *J. Mol. Struct.*, 2001, **538**, 165; E. García-Expósito, M. J. Bearpark, R. M. Ortuño, M. A. Robb, V. Branchadell, *J. Org. Chem.*, 2002, **67**, 6070; S. Wilsey, L. González, M. A. Robb, K. N. Houk, *J. Am. Chem. Soc.*, 2000, **122**, 5866; H. I. Omar, Y. Odo, Y. Shigemitsu, T. Shimo, K. Somekawa, *Tetrahedron*, 2003, **59**, 8099.

10 Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.

Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.