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Diastereoselective photocycloaddition reactions of 2-naphthalenecarboxylates and 2,3-naphthalenedicarboxylates with furans governed by chiral auxiliaries and hydrogen bonding interactions

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ABSTRACT

By using chiral auxiliaries and hydrogen bonding interactions, we have developed diastereoselective photocycloaddition of 2-naphthalenecarboxylates and 2,3-naphthalenedicarboxylates with furan derivatives. In photoreactions of (ℓ)-menthyl 2-naphthalenecarboxylate with furan and 3-furanmethanol, respective maximum 48% and 40% diastereomeric excesses (d.e.) are observed. In photoreactions of di-8-phenyl-(ℓ)-menthyl 2,3-naphthalenedicarboxylate with 3-furanmethanol, maximum 67% d.e. is obtained. Use of solvents of low polarity, low temperatures and low furan concentration leads to increased diastereoselectivities. Variable-temperature (VT) NMR and fluorescence quenching studies indicate that hydrogen bonding interactions between the carbonyl oxygen of naphthalenecarboxylic acid esters and the OH group in 3-furanmethanol take place in both the ground and excited states. The results of computational studies show that geometries of C_2 symmetric naphthalenedicarboxylate reactants are important in governing the high diastereoselectivity in the photoreactions of 2,3-naphthalenedicarboxylates.

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1. Introduction

Photocycloaddition reactions between unsaturated compounds such as alkenes, alkynes and arenes have been extensively studied and used for synthesis of various polycyclic compounds and natural products [1–8]. The nature of short lived exciplexes, which serve as reactive intermediates in these processes, control the efficiencies, and regio-, chemo- and stereo-selectivities of the photocyloaddition reactions [9,10]. As a result, π–π, dipole [11–13] and hydrogen bonding interactions [14–27] in the exciplexes, as well as structural constraints arising in intramolecular systems [28–34] and in microcavities [35,36] have been used to govern the nature of these processes.

Photocycloadditions of cyanonaphthalenes with furan illustrate how dipole moments of exciplexes govern product distributions. For example, photoreaction of 1-cyanonaphthalene with furan generates predominantly an *endo*-[4+4] photocycloadduct [37–44], whereas the corresponding reaction of 2-cyanonaphthalene with furan produces mainly a cage product [39,41,42,44–46]. In an earlier study, we also demonstrated how dipole moments of 2-cyanonaphthalene derivatives influence the efficiencies of cage compound forming photoreactions with furan [47]. In addition, we showed that intramolecular photoreactions of cyanonaphthalene-furan linked compounds [48] and hydrogen bonding interactions in intermolecular photoreactions of cyanonaphthalenes with 3-furanmethanol [49] control the efficiencies and regioselectivities. The current study was designed to gain insight into how the stereoselectivities of photocycloadditions can be controlled by using chiral auxiliaries and hydrogen bonding interactions. As described below, we report the results of photoreactions of naphthalenecarboxylic acid esters bearing chiral auxiliaries with hydroxy-substituted furans.

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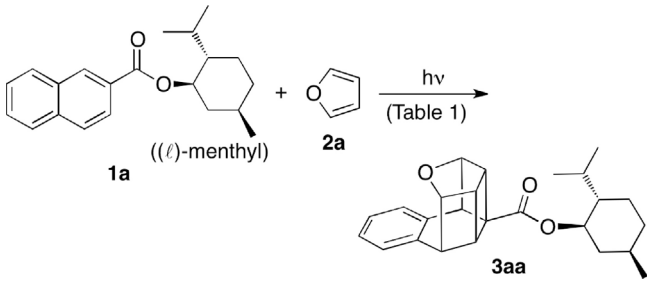
2. Results and discussion

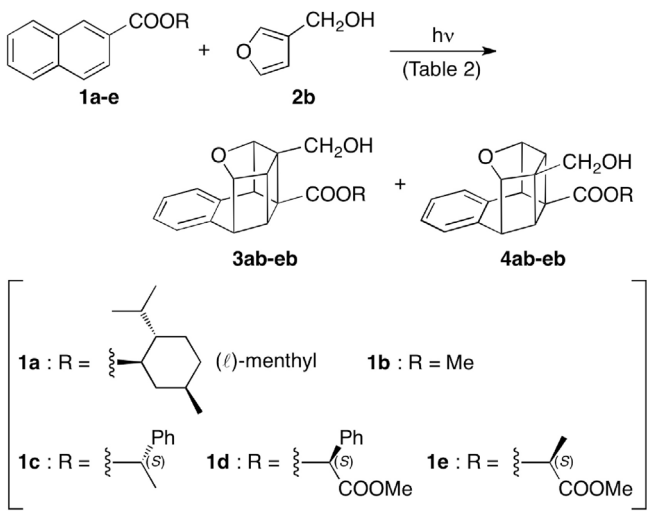
In the first phase of this investigation, the photocycloaddition reaction of the 2-naphthalenecarboxylate **1a**, possessing a (ℓ)-menthyloxycarbonyl chiral auxiliary group, with furan (**2a**) was investigated focusing on its diastereoselectivity (Scheme 1, Table 1). Solutions containing **1a** and varying concentrations of **2a** in various solvents in Pyrex vessels, under an argon atmosphere and at varying temperatures were irradiated using a high-pressure mercury lamp. ^{1}H NMR and/or HPLC analysis of the crude product mixtures showed that photoreactions promote the cycloaddition to produce cage compound **3aa** in >90% yields with the diastereomeric excesses (d.e.) shown in Table 1. Pure **3aa** was obtained by concentration of the photolysates in vacuo followed by silica gel column chromatography.

Studies of solvent effects (entries 1–6) show that the highest d.e. (39%) is observed when the least polar solvent, pentane, is employed and that reactions in aromatic solvents such as benzene and toluene result in low d.e. values. When furan (**2a**) itself is used as solvent, a lower d.e. (23%) is obtained (entry 7). Dependence of the d.e. on the concentration of **2a** in pentane shows that an increase in the concentration of **2a** leads to a decrease in d.e. (entries 1, 8–10). A study of temperature effects (r.t. to −70 °C) on d.e. showed that lowering the temperature leads to an increase in d.e. (entries 11–13). Finally, we found that the highest d.e. (48%) is attained when the reaction is carried out at −70 °C using [**2a**] = 100 mM (entry 14).

The effect of the chiral ester group of 2-naphthalenecarboxylate on diastereoselectivities of photocycloaddition reactions with 3-furanmethanol (**2b**) was explored next. These photoreactions generate regioisomeric cage products **3** and **4** as mixtures of diastereomers (Scheme 2, Table 2). Owing to spectral overlap issues, the d.e. of only **4** can be determined by using ^{1}H NMR analysis (Fig. S1). Photoreaction of (ℓ)-menthyl ester **1a** with **2b** in benzene produces **3ab** and **4ab** in >90% total yield (entry 1) and a **3ab**/**4ab** ratio of 1.20. The d.e. of **4ab** was determined to be 23%. In comparison, photoreaction of the simple methyl ester **1b** with **2b** produces **3bb** and **4bb** in >99% total yield and a **3bb**/**4bb** ratio of 1.40 (entry 2). However, reactions of esters containing other chiral auxiliaries such as (*S*)-1-phenylethyl (**1c**) and (*S*)-methyl mandelate derivative (**1d**) proceed to form the respective regioisomeric adducts **3** and **4** in <10% yields. Finally, methyl D-lactate derivative **1e** reacts with **1b** to form the corresponding regioisomers **3eb** and



Scheme 1. Photocycloaddition of (ℓ)-menthyl 2-naphthalenecarboxylate (**1a**) with furan (**2a**).



Scheme 2. Photocycloaddition of 2-naphthalenecarboxylates **1a–e** with 3-furanmethanol (**2b**).

4eb in high total yield (>90%) and in a high **3eb**/**4eb** ratio of 2.16 (entry 5). However, the d.e. of **4eb** is low (15%) compared with that of **4ab** (entry 1). The results of a study of solvent effects, using pentane, hexane, cyclohexane, ethyl acetate and acetonitrile (entries 6–10), show that the highest d.e. for formation of regioisomer **4ab** (38%) occurs when the reaction is conducted in cyclohexane (entry 8). The temperature effect on photoreactions of

Table 1
Photocycloadditions of (ℓ)-menthyl 2-naphthalenecarboxylate (**1a**) with furan (**2a**).[a]

Entry	Solvent	ε[b]	[**2a**] (mM)	Temperature (°C)	d.e. of **3aa**[c] (%)
1	Pentane	1.8[d]	50	r.t.	39
2	Cyclohexane	2.0[e]	50	r.t.	36
3	Ethyl acetate	6.0[f]	50	r.t.	19
4	Dichloromethane	8.9[f]	50	r.t.	20
5	Benzene	2.3[f]	50	r.t.	18
6	Toluene	2.4[e]	50	r.t.	17
7	Furan	2.8[g]	50	r.t.	23
8	Pentane	1.8[d]	100	r.t.	36
9	Pentane	1.8[d]	1000	r.t.	28
10	Pentane	1.8[d]	2000	r.t.	28
11	Pentane	1.8[d]	500	r.t.	29
12	Pentane	1.8[d]	500	−20	32
13	Pentane	1.8[d]	500	−70	35
14	Pentane	1.8[d]	100	−70	48

[a] 300 W high-pressure mercury lamp, Pyrex vessel, [**1a**] = 5 mM, conversion = 15–40% (^{1}H NMR and/or HPLC analysis), conversion yield >90% (GLC analysis).
[b] Dielectric constant.
[c] Determined by ^{1}H NMR and/or HPLC analyses.
[d] Data from Ref. [50].
[e] Data from Ref. [51].
[f] Data from Ref. [52].
[g] Data from Ref. [53].

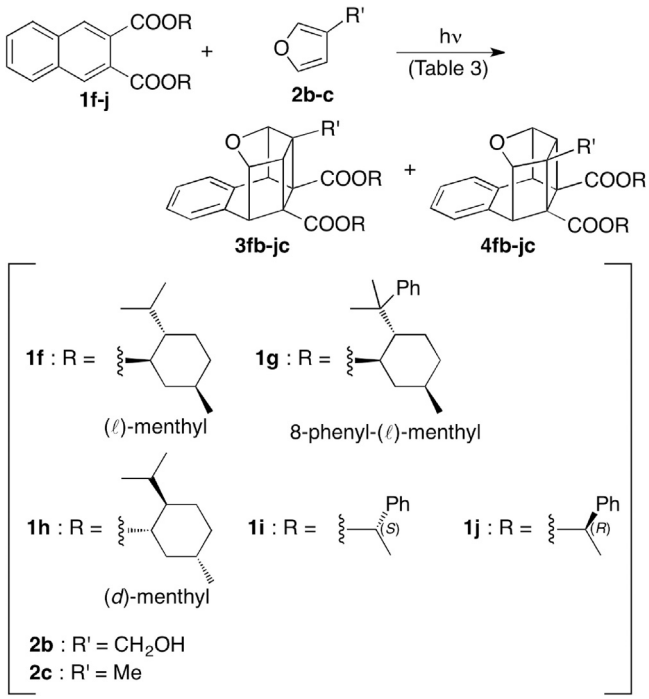
Table 2
Photocycloadditions of 2-naphthalenecarboxylates **1a–e** with 3-furanmethanol (**2b**).[a]

Entry	1	R	Solvent	ε[b]	Temperature (°C)	Total yield of **3** and **4** (%)	**3**/**4**	d.e. of **4** (%)
1	**1a**	(ℓ)-Menthyl	Benzene	2.3[c]	r.t.	>90	1.20	23
2	**1b**	Me	Benzene	2.3[c]	r.t.	>99	1.40	–[d]
3	**1c**	(*S*)-CH(Ph)CH_3	Benzene	2.3[c]	r.t.	<10	1.14	7
4	**1d**	(*S*)-CH(Ph)COOMe	Benzene	2.3[c]	r.t.	<10	1.05	5
5	**1e**	(*S*)-CH(Me)COOMe	Benzene	2.3[c]	r.t.	>90	2.16	15
6	**1a**	(ℓ)-Menthyl	Pentane	1.8[e]	r.t.	70	2.20	26
7	**1a**	(ℓ)-Menthyl	Hexane	1.9[c]	r.t.	55	1.07	18
8	**1a**	(ℓ)-Menthyl	Cyclohexane	2.0[c]	r.t.	>90	1.08	38
9	**1a**	(ℓ)-Menthyl	Ethyl acetate	6.0[c]	r.t.	<10	–[f]	–[f]
10	**1a**	(ℓ)-Menthyl	Acetonitrile	36.0[c]	r.t.	>90	1.03	16
11	**1a**	(ℓ)-Menthyl	Pentane	1.8[e]	−50	–[f]	0.83	33
12	**1a**	(ℓ)-Menthyl	Hexane	1.9[c]	50	–[f]	1.11	7
13	**1a**	(ℓ)-Menthyl	Hexane	1.9[c]	0	–[f]	0.50	26
14	**1a**	(ℓ)-Menthyl	Hexane	1.9[c]	−70	–[f]	0.40	40

[a] 300 W high-pressure mercury lamp, Pyrex vessel, 7 days, [**1a–e**] = 5 mM, [**2b**] = 50 mM.
[b] Dielectric constant.
[c] Data from Ref. [52].
[d] Single diastereomer.
[e] Data from Ref. [50].
[f] Not determined.

1a with **2b** in pentane and hexane (entries 6, 11–14) demonstrates that as the temperature is lowered the major product of the process changes from **3ab** to **4ab** and that the d.e. of **4** increases up to 40% at −70 °C.

Our attention next turned to studies of photoreactions of 2,3-chiral diesters **1f–j** with 3-furanmethanol **2b** (Scheme 3, Table 3). Because **1f–j** have C_2 symmetry, the ratios of cage products **3** and **4** correspond to diastereoselectivities of the photoreaction. Reaction of di-(ℓ)-menthyl derivative **1f** with 3-furanmethanol **2b** was utilized to study solvent effects (entries 1–5). The results showed that cage products **3fb** (minor) and **4fb** (major) are produced in this process with respective d.e. values of 36 and 34% when acetonitrile (entry 1) and dichloromethane (entry 4) are used as solvents. In addition, the efficiencies of the process are lower as the temperature is lowered (entries 6–8) but lowering temperature



Scheme 3. Photocycloadditions of 2,3-naphthalenedicarboxylates **1f–j** with furan derivatives **2b–c**.

enhances the diastereoselectivity of the process. The effects of hydrogen bonding interactions are indicated by the observation that the presence of 2.5 M H_2O in toluene (entry 9) results in lower product yields compared to the case of entry 5. In addition, photoreaction of **1f** with 3-methylfuran (**2c**), which is unable to participate in hydrogen bonding interactions, takes place in low yields (entry 10). Moreover, photoreaction of di-8-phenyl-(ℓ)-menthyl ester **1g** with **2b** proceeds slowly (155 h) but it is attended by the highest d.e. (67%) (entry 11). Di-(*d*)-menthyl ester **1h**, the enantiomer of **1f**, photochemically adds to **2b** to from **3hb** as the major product with a 17% d.e. (entry 12). Finally, (*S*)- and (*R*)-1-phenylethyl esters, **1i** and **1j**, photoreact with **2b** with low d.e. values (entries 13–17).

A variable-temperature (VT) NMR study was conducted to explore the existence of hydrogen bonding interactions [54] between the naphthalenecarboxylate ester **1b** and 3-furanmethanol **2b** (Fig. 1). Upon cooling a CD_2Cl_2 solution of **2b** (50 mM) from 20 °C to −80 °C, the resonance for the OH hydrogen shifts from 1.7 ppm to 4.3 ppm. On the other hand, cooling a CD_2Cl_2 solution containing an equimolar mixture of naphthalenecarboxylate **1b** and **2b** ([**1b**] = [**2b**] = 50 mM) from 20 °C to −80 °C causes the resonance of the OH hydrogen in **2b** to shift from 1.7 ppm to only 3.4 ppm. Similarly, when a toluene-d_8 solution of **2b** is cooled from 20 °C to −60 °C, the OH resonance shifts from 0.8 ppm to 3.8 ppm (Fig. 2) whereas this resonance in the spectrum of a toluene-d_8 solution of a mixture of **1f** and **2b** undergoes only a negligible shift from 0.2 ppm to 0.3 ppm over the same temperature range. The VT NMR spectral changes of **2b** in the presence of **1g** are similar to those when **1f** is present (Fig. S2). These observations suggest that intermolecular hydrogen bonding between molecules of **2b** is interrupted by competitive hydrogen bonding of the hydroxy group in **2b** with the carbonyl oxygens in **1b** and **1f**, and that the OH group in **2b** bonds more strongly with the carbonyl oxygen in **1f** than with that in **1b**.

In order to evaluate intermolecular hydrogen bonding interactions between **2b** and the excited states of the naphthalenecarboxylates, fluorescence quenching experiments were carried out (Fig. 3). The results showed that the fluorescence bands of **1a** and **1f** in cyclohexane are quenched by addition of furans **2a–d**, and that fluorescence emissions from exciplexes are not observed. The rate constants k_q for fluorescence quenching (Table 4) were calculated using slopes of Stern–Volmer plots of the fluorescence quenching data and fluorescence lifetimes τ of **1a** and **1f**. An analysis of the k_q values shows that fluorescence of (ℓ)-menthyl

Table 3
Effects of solvent, additives and temperature on photocycloadditions of 2,3-naphthalenedicarboxylates **1f–j** with furan derivatives **2b–c**.[a]

Entry	1	2	Solvent	Additive	Temperature (°C)	Time (h)	Yields[b] (%)		d.e.[b](%)
							3	4	
1	**1f**	**2b**	Acetonitrile	None	0	20	3	6	36
2	**1f**	**2b**	Cyclohexane	None	0	20	17	23	15
3	**1f**	**2b**	Isopropanol	None	0	20	10	12	8
4	**1f**	**2b**	Dichloromethane	None	0	41	11	22	34
5	**1f**	**2b**	Toluene	None	0	20	8	11	20
6	**1f**	**2b**	Toluene	None	15	45	20	23	9
7	**1f**	**2b**	Toluene	None	0	45	23	29	17
8	**1f**	**2b**	Toluene	None	−50	45	8	13	22
9	**1f**	**2b**	Toluene	H_2O[c]	0	20	5	9	22
10	**1f**	**2c**	Toluene	None	15	40	2	3	14
11	**1g**	**2b**	Dichloromethane	None	r.t.	155	2	13	67
12	**1h**	**2b**	Toluene	None	15	20	9	6	17
13	**1i**	**2b**	Toluene	None	0	20	11	11	0
14	**1i**	**2b**	Toluene	None	−50	45	18	17	3
15	**1i**	**2c**	Toluene	None	0	20	Trace	Trace	–[d]
16	**1j**	**2b**	Toluene	None	0	20	6	8	19
17	**1j**	**2c**	Toluene	None	0	20	Trace	Trace	–[d]

[a] 300 W high-pressure mercury lamp, Pyrex vessel, [**1f–j**] = 20 mM, [**2b–c**] = 200 mM.
[b] Determined by using ^{1}H NMR.
[c] 2.5 M. Toluene is saturated with H_2O.
[d] Not determined.

monocarboxylate ester **1a** is quenched with a larger rate by **2b** than by **2d** (entries 1, 2). Similarly, fluorescence of di-(ℓ)-menthyl dicarboxylate ester **1f** is quenched more efficiently by **2b** than by **2a** and **2c** (entries 3–5). These results indicate that hydrogen bonding takes place between the hydroxy group in **2b** and the excited states of the naphthalenecarboxylates and that these interactions facilitate fluorescence quenching.

Theorectical calculations were carried out to gain information about the interactions occurring between the naphthalenecarboxylates and furans. The structures of **1f–j** were optimized by using

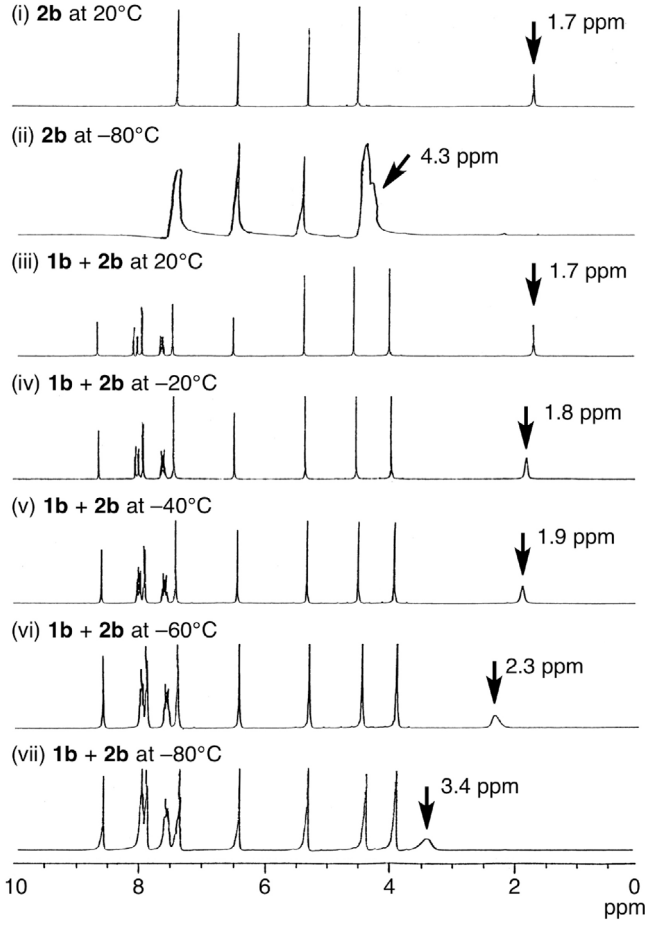


Fig. 1. Variable-temperature (VT) ^{1}H NMR spectra of (i and ii) **2b** and (iii–vii) a mixture of **1b** + **2b**, 400 MHz, [**1b**] = [**2b**] = 50 mM in CD_2Cl_2.

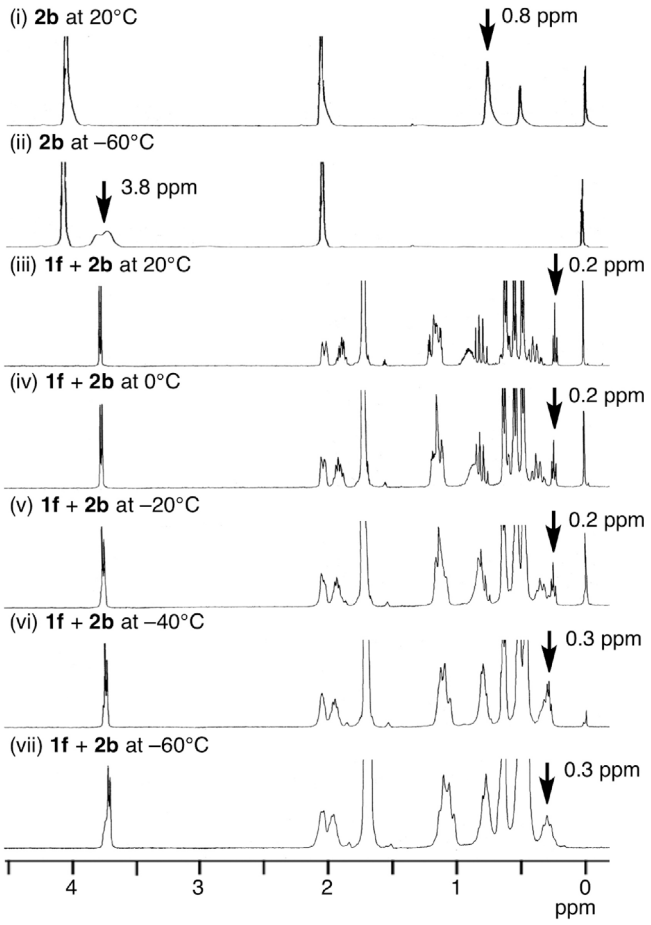


Fig. 2. VT ^{1}H NMR spectra of (i and ii) **2b** and (iii–vii) a mixture of **1f** + **2b**, 400 MHz, [**1f**] = [**2b**] = 10 mM in toluene-d_8.

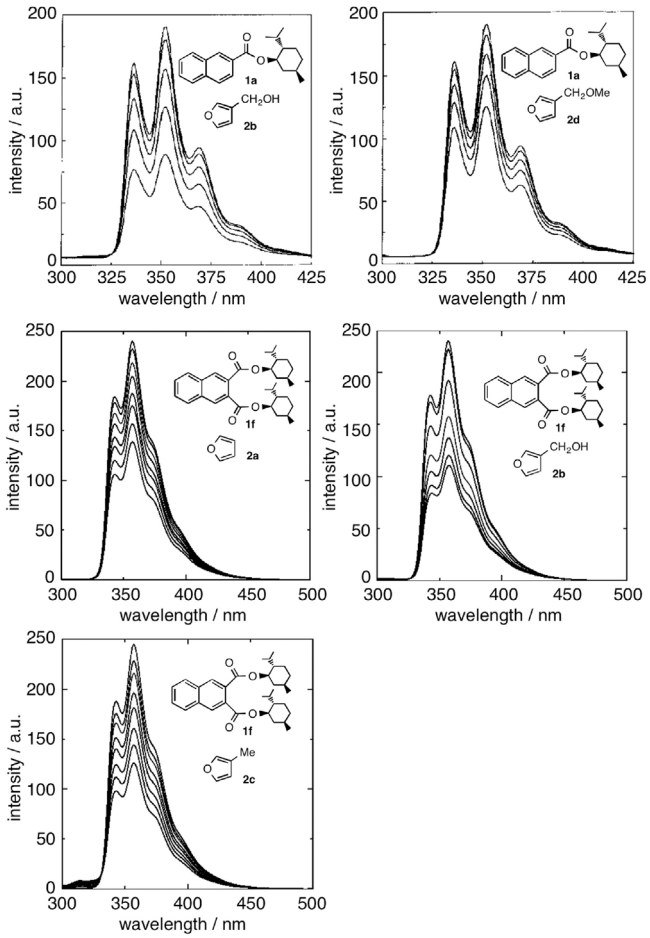


Fig. 3. Fluorescence quenching of **1a** and **1f** by furan derivatives **2a–d**, ~10^{-4} M in aerated cyclohexane, excited at 291 nm (**1a**) and 281 nm (**1f**), $[\mathbf{2a–d}]_{max}$ = 0.03–0.2 M.

PM3 (Fig. 4). The lowest energy structures of **1f** and **1g** have spatial occupancy associated with C_2 symmetric structures in which the first and third quadrants are filled, which is consistent with an earlier report [57]. In contrast, C_2 symmetrical structures of **1h–j** are collapsed and the substituents are spread overall four quadrants. Because **2** can approach the excited states of **1f** and **1g** from their vacant sites, a higher d.e. is expected for photoreactions of these substrates than those of **1h–j**.

An analysis of the calculated heats of formations of cage photoproducts indicates that **4bb** is 2.9 kcal/mol more stable than **3bb** (Fig. 5). Similarly, the data show that **4fb** is 2.1 kcal/mol more stable than **3fb**. The respective ^{1}H NMR resonances for the OH protons in **3fb** and **4fb** appear at 3.05 and 4.03 ppm in $CDCl_3$ at room temperature (Fig. S3). These chemical shifts suggest that the OH group in **4fb** participates more strongly in intramolecular hydrogen bonding than does the OH group in **3fb**.

Table 4
Rate constants for fluorescence quenching.[a]

Entry	Substrate combination	$k_q\tau$ (M^{-1})	$k_q \times 10^{-9}$ ($M^{-1}\,s^{-1}$)
1	**1a** by **2b**	33.0	4.13
2	**1a** by **2d**	19.0	2.38
3	**1f** by **2a**	5.3	0.73
4	**1f** by **2b**	19.2	2.64
5	**1f** by **2c**	7.63	1.05

[a] Calculated by using the slopes of Stern–Volmer plots. [1] = 10^{-4} M in cyclohexane, τ(**1a**) = 8.0 ns [55,56], τ(**1f**) = 7.27 ns.

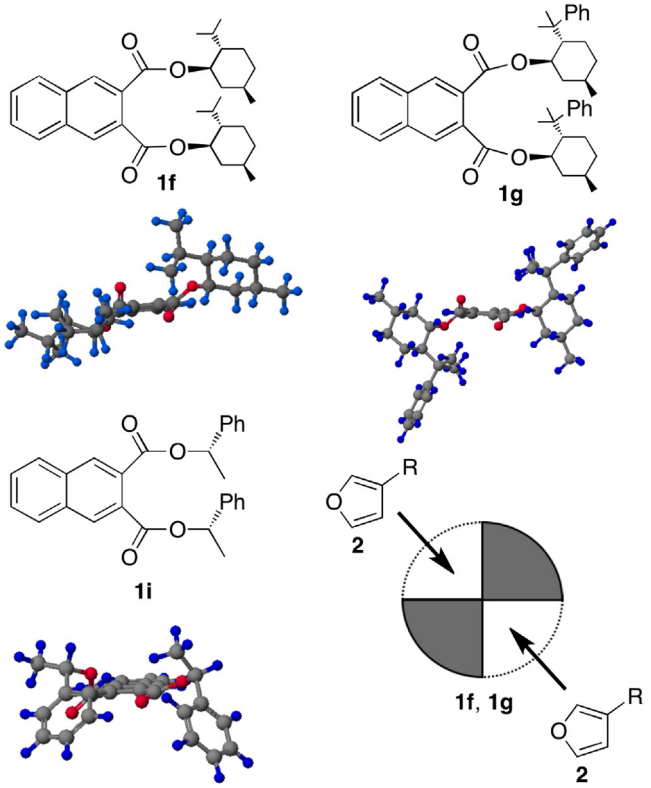


Fig. 4. Optimized structures of **1f**,**1g**, and **1i** calculated by using PM3.

The observations presented above lead to the explanation of the diastereoselectivities of the photocycloaddition reactions given pictorially in Scheme 4. In photoreaction of **1a** with **2a**, excitation of the naphthalene chromophore is followed by formation of exciplex **5**, which reacts to produce cage photoadduct **3aa**. The diastereoselectivity of this process corresponds to a face-selectivity associated with a preference for formation of one of the two exciplexes in which the furan component is located on either the upper or lower faces of the naphthalene partner. When viewed from this perspective, the decrease of diastereoselectivity seen when an aromatic solvent is used is a consequence of competitive formation of an exciplex between **1a** and the solvent or of termolecular complexes **6** and **7**, which weakens interactions of excited **1a** with the furan substrate. Although photodimerization reactions of 2-naphthalenecarboxylic acid esters are known to take place [58–60], a photodimer of **1a** does not form in this process in which an excess of the furan substrate is used. The reason why the highest level of diastereoselectivity is observed for the reactions in

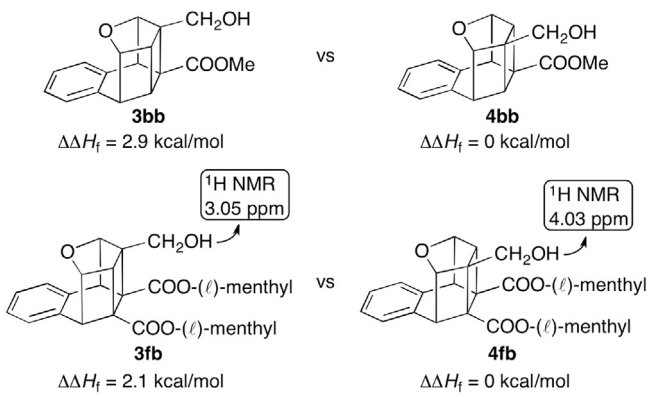
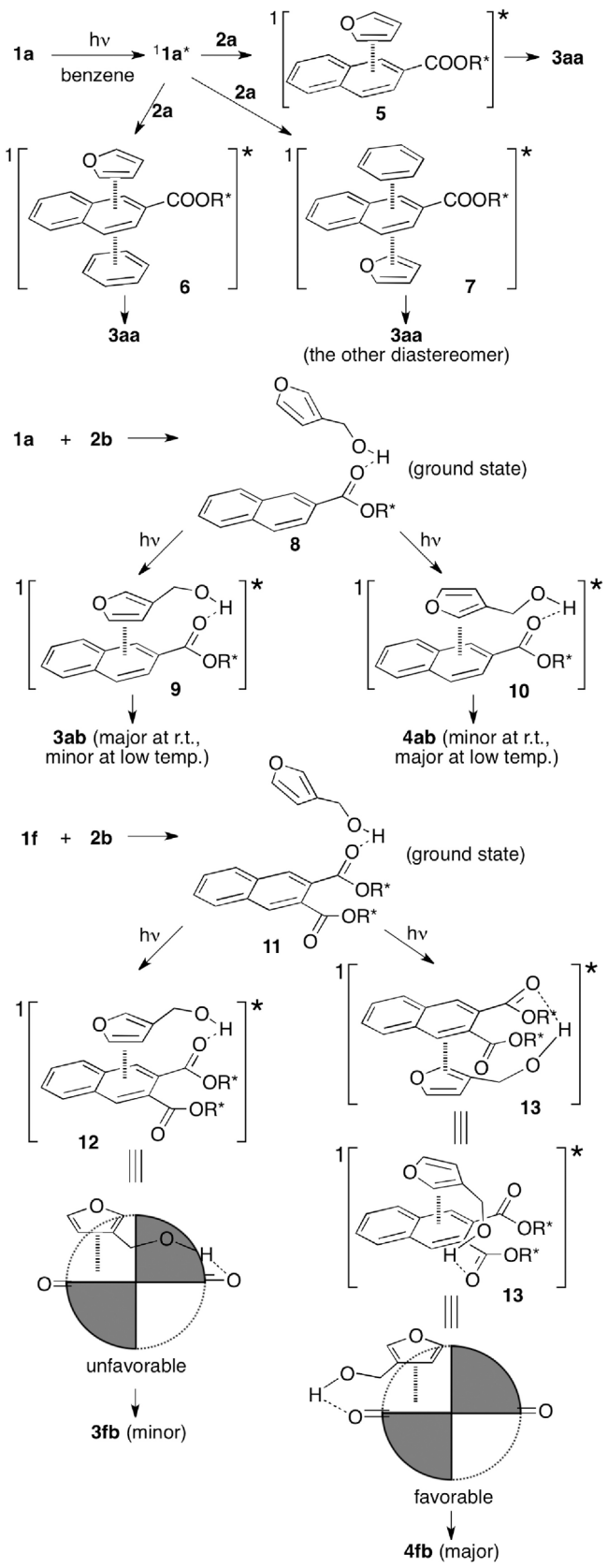


Fig. 5. Comparison of heat of formations of photoproducts calculated by using PM3.



Scheme 4. Reaction pathways and possible explanations for diastereoselectivities.

pentane is associated with the highly nonpolar aliphatic nature of this solvent that enables highly face-selective exciplex formation. The reason why an increase of concentration of furan decreases diasereoselectivity is likely associated with the formation of a termolecular complex containing two molecules of furan. The effect of decreasing temperature to increase diastereoselectivity can be seen, and it is rationalized as that it is associated with the relative rate constants for the formation of top and bottom face exciplexes, where advantage is given to formation of thermodynamically more stable exciplex when temperature decreases.

Regioselectivity is also an issue in the photoreaction of **1a** with **2b**. In this process, two diastereomers of each regiosiomer, **3ab** and **4ab**, can be produced. The results of VT NMR studies suggest that a hydrogen bonding interaction exists between **1a** and **2b** (e.g., **8** in Scheme 4). Moreover, the larger rate constant for quenching of the fluorescence of **1a** by **2b** versus by **2d** also supports participation of hydrogen bonding in formation of exciplexes **9** and **10** which give rise to the respective regioisomeric cage products **3ab** and **4ab**. The results of product distribution studies show that **3ab** is the major product when the photoreaction is carried out at room temperature but **4ab** becomes predominant in reactions at lower temperatures. In the low-temperature photoreaction, a greater preference (i.e., larger rate constant difference) should exist for formation of the lower energy exciplex, which is in accord with the theoretical calculations. The observations that the diastereoselectivity in the reaction forming **4ab** increases when nonpolar solvents such as hexane and pentane are used or the temperature is decreased are in full accord with effects on the preferential formation of the more stable exciplex.

The low photochemical reactivities of **1c** and **1d** can be attributed to competitive intramolecular interaction of the phenyl groups in the ester moieties with the excited naphthalene groups forming unreactive intramolecular excited state complexes. Support for this hypothesis comes from fluorescence quenching results (Fig. 6), which show that the fluorescence efficiency of **1d** is less than half that of **1e**, although absorbance at excitation wavelength (291 nm) is almost the same.

Because **1f** is a C_2 symmetric molecule, products arising from addition of furan substrates from the top and bottom faces of the naphthalene ring are the same. As a result, diastereoselectivity in this process corresponds to the ratio of **3** and **4**. The results of VT NMR studies indicate that a relatively strong intermolecular hydrogen bonding interaction exists between **1f** and **2b** as reflected in formation of complex **11**. Excitation of complex **11**

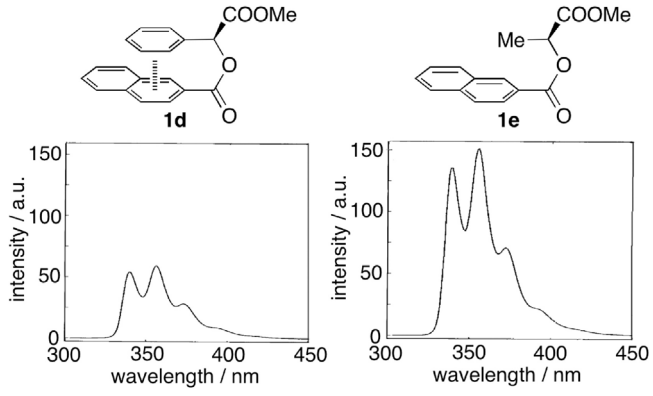


Fig. 6. Fluorescence spectra of **1d** and **1e** in cyclohexane, excited at 291 nm, 1.0×10^{-5} M.

results in formation of exciplexes **12** and **13**, which serve as precursors to the respective products **3fb** (minor) and **4fb** (major). Because the optimized molecular structure of **1f** has C_2 chirality, an exciplex in which the furan component is oriented on second and fourth quadrants is preferred. Because exciplex **13** is more stable than **12**, **4fb** is produced as a major product. Studies of solvent effects in this family indicate that photoreactions in solvents having moderate degree of polarity, dichloromethane and acetonitrile give high d.e. values. The difference of the solvent effect between Tables 1–3 might be associated with higher polarities of exciplexes **12** and **13** than those of **5**, **9** and **10**. The result that addition of H_2O decreases the yields of photoproduct formation suggests that intermolecular hydrogen bonding between **2b** and **1f** is affected by competitive hydrogen bonding with H_2O. The participation of hydrogen bonding in these photochemical reactions is also supported by the results of studies with 3-methylfuran **2c**, which show that the absence of hydrogen bonding results in low photochemical reactivity and low diastereoselectivity. The highest d.e. (67%) is observed in the photoreaction of **1g**, whose 8-phenyl-(ℓ)-menthyl groups might let the molecule be adequate C_2 symmetry having just size for diastereoselective photoreaction.

3. Conclusion

Development of asymmetric photoreactions is important from both a synthetic as well as a mechanistic view point [61–63]. Naphthalene derivatives **1a** and **1f** have been often used as chiral photosensitizers for asymmetric photoreactions in solutions [55,56,64–68]. In the study described above, we have employed these and related chiral auxiliaries containing naphthalenecarboxylic acid esters to investigate diastereoselective photocycloaddition reactions of naphthalene derivatives that are governed by hydrogen bonding interactions. The results show that photoreactions of (ℓ)-menthyl 2-naphthalenecarboxylate with furan and 3-furanmethanol proceed with 48% and 40% d.e. In addition, photoreactions of 2,3-naphthalenedicarboxylates with 3-furanmethanol take place with a maximum 67% d.e. The results of this study also show that high diastereoselectivities created by selective formation of more stable exciplexes can be governed by hydrogen bonding interactions, temperature, solvents and furan concentration. Further studies probing the development of stereoselective photoreactions are required.

4. Experimental

4.1. Materials and equipments

THF and Et_2O were distilled from CaH_2 and then from Na/Ph_2C=O. Acetonitrile was distilled from CaH_2 and then from P_2O_5. Benzene, toluene, and hexane were distilled from CaH_2 and then from Na. CH_2Cl_2 and *i*-PrOH were distilled from CaH_2. Cyclohexane was distilled from $CaCl_2$ and then from Na. Ethyl acetate was distilled from P_2O_5. Furan was distilled from Na_2SO_4. Melting points were determined on a Yanagimoto Micro Melting Point apparatus, Yanaco MP-500, and are reported uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Varian MERCURY-300 (300 MHz and 75 MHz, respectively), or a JEOL JNM-GX270 (270 MHz and 68 MHz, respectively), or a JEOL JNM-LA400 (400 MHz and 100 MHz, respectively), or a JEOL JNM-ECP500 (500 MHz and 125 MHz, respectively) spectrometer with Me_4Si as an internal standard. IR spectra were determined using a Jasco FT/IR-230 spectrometer. UV–vis spectra were recorded using a Shimadzu UV-160A spectrophotometer. Fluorescence spectra were recorded using a Jasco FP-770 spectrophotometer. Fluorescence lifetime (τ) of **1f** was measured in cyclohexane solution by using time correlation, a single photon counting methodology, with a HORIBA NAES-550 nano-second fluorometer equipped with an SSU-111A photomultiplier, an SCU-121A optical chamber, an SGM-121A monochromator, and an LPS-111 lamp power supply. Mass spectra (EI) were recorded on a SHIMADZU GCMS-QP5050 operating in the electron impact mode (70 eV) equipped with GC-17A and DB-5MS column (J&W Scientific Inc., Serial: 8696181). HPLC separations were performed on a recycling preparative HPLC equipped with Jasco PU-986 pump, Shodex RI-72 differential refractometer, Megapak GEL 201Cp and 201CP columns (GPC), or a recycling preparative HPLC equipped with Jasco PU-2086 Plus, RI-2031 Plus differential refractometer, Megapak GEL 201C columns (GPC), using $CHCl_3$ as an eluent. Column chromatography was conducted by using Kanto-Chemical Co. Ltd., silica gel 60N (spherical, neutral, 0.063–0.200 mm).

4.2. Preparation of (ℓ)-menthyl 2-naphthalenecarboxylate (**1a**)

To a stirred THF (20 mL) solution of (ℓ)-menthol (2.47 g, 16 mmol) and pyridine (few drops) was slowly added a THF (10 mL) solution of 2-naphthoyl chloride (1.92 g, 10 mmol) at 0 °C under an argon atmosphere. HCl aq. was added until the pH of the solution was 7. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to HPLC to give (ℓ)-menthyl 2-naphthalenecarboxylate (**1a**, 1.56 g, 5 mmol, 50% yield). Yellow solid; mp 70–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81–2.20 (m, 18*H*), 4.97–5.05 (m, 1*H*), 7.25–7.61 (m, 2*H*), 7.88 (d, *J* = 8.4 Hz, 2*H*), 7.97 (d, *J* = 7.1 Hz, 1*H*), 8.07 (dd, *J* = 7.0, 1.7 Hz, 1*H*), 8.60 (s, 1*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6, 20.9, 22.2, 23.8, 26.6, 31.6, 34.4, 41.1, 47.4, 75.0, 125.2, 126.4, 127.6, 128.0, 129.2, 130.7, 130.8, 132.4, 135.3, 166.1 ppm; UV (cyclohexane) λ_{max} 272, 280, 291 nm; MS (EI) *m*/*z* 127, 138, 155, 172, 310 (M^+).

4.3. Preparation of methyl 2-naphthalenecarboxylate (**1b**)

A MeOH (30 mL) solution of 2-naphthalenecarboxylic acid (863 mg, 5 mmol) and H_2SO_4 (few drops) was stirred at reflux for 12 h. After the solution was cooled to room temperature, Na_2CO_3 aq. was added until the pH of the solution was 7. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography to give methyl 2-naphthalenecarboxylate (**1b**, 702 mg, 3.8 mmol, 76% yield). Colorless solid; mp 75–77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (s, 3*H*), 7.51–7.61 (m, 2*H*), 7.88 (d, *J* = 8.4 Hz, 2*H*), 7.95 (d, *J* = 7.9 Hz, 1*H*), 8.06 (dd, *J* = 7.0, 1.7 Hz, 1*H*), 8.61 (s, 1*H*) ppm; ^{13}C NMR ($CDCl_3$) δ 52.3, 126.5, 127.3, 127.6, 128.0, 128.1, 129.2, 130.9, 131.0, 132.4, 135.4, 167.1 ppm; MS (EI) *m*/*z* 127, 155, 186 (M^+).

4.4. Preparation of (S)-1-phenylethyl 2-naphthalenecarboxylate (**1c**)

To a stirred THF (20 mL) solution of (*S*)-1-phenylethyl alcohol (1 mL, 7.5 mmol) and pyridine (few drops) was slowly added a THF (10 mL) solution of 2-naphthoyl chloride (1.01 g, 5.3 mmol) at 0 °C under an argon atmosphere. HCl aq. was added until the pH of the solution was 7. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography to give (*S*)-1-phenylethyl 2-naphthalenecarboxylate (**1c**, 1.381 g, 3.5 mmol, 66% yield). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (d, *J* = 6.6 Hz, 3*H*), 6.20 (q, *J* = 6.6 Hz, 1*H*), 7.28–7.61 (m, 7*H*), 7.87 (d, *J* = 8.4 Hz, 2*H*), 7.96 (d, *J* = 7.9 Hz, 1*H*), 8.09 (dd, *J* = 7.0, 1.7 Hz, 1*H*), 8.64 (s, 1*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.5, 73.0, 73.1, 125.2, 126.0, 126.5, 127.7, 127.8, 128.0, 128.1, 128.5, 129.2, 130.9,

131.0, 132.4, 135.4, 141.7, 165.8 ppm; MS (EI) *m*/*z* 105, 127, 155, 172, 276 (M^+).

4.5. Preparation of (*S*)-1-methoxycarbonyl-1-phenylmethyl 2-naphthalenecarboxylate (**1d**)

A MeOH (30 mL) solution of (*S*)-mandelic acid (1.52 g, 10 mmol) and H_2SO_4 (few drops) was stirred at reflux for 12 h. After the solution was cooled to room temperature, Na_2CO_3 aq. was added until the pH of the solution was 7. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography to give methyl (*S*)-mandelate (1.201 g, 7.2 mmol, 72% yield). Colorless solid; mp 54–55.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (brs, 1*H*), 3.78 (s, 3*H*), 5.18 (s, 1*H*), 7.32–7.44 (m, 5*H*) ppm; MS (EI) *m*/*z* 107, 166 (M^+).

A THF (20 mL) solution of 2-naphthalenecarboxylic acid (861 mg, 5 mmol), methyl (*S*)-mandelate (833 mg, 5 mmol), and 4-dimethylaminopyridine (488 mg, 4 mmol) was stirred at 0 °C for 5 min under an argon atmosphere. To the solution was added dicyclohexylcarbodiimide (1.7 mL, 6.6 mmol) at 0 °C, and the solution was stirred at room temperature overnight. The precipitate was removed by filtration. HCl aq. and Et_2O were added to the filtrate. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography to give (*S*)-1-methoxycarbonyl-1-phenylmethyl 2-naphthalenecarboxylate (**1d**, 1.02 g, 3.2 mmol, 64% yield). Colorless solid; mp 105.5–107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3*H*), 6.24 (s, 1*H*), 7.42–7.65 (m, 7*H*), 7.86–7.90 (m, 2*H*), 7.96 (d, *J* = 8.1 Hz, 1*H*), 8.12 (dd, *J* = 7.0, 1.7 Hz, 1*H*), 8.69 (s, 1*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.8, 75.0, 125.2, 126.3, 126.6, 127.6, 127.7, 128.2, 128.4, 128.8, 129.2, 129.3, 131.5, 131.6, 132.3, 133.9, 135.6, 169.1 ppm; UV (cyclohexane) λ_{max} 281, 292 nm; HRMS (EI) calcd for $C_{15}H_{14}O_4$: 258.0892, found: 258.0880.

4.6. Preparation of (*S*)-1-methoxycarbonylethyl 2-naphthalenecarboxylate (**1e**)

To a stirred THF (20 mL) solution of (*S*)-methyl lactate (4 mL, 36 mmol) and pyridine (few drops) was slowly added a THF (15 mL) solution of 2-naphthoyl chloride (3.93 g, 20 mmol) at 0 °C under an argon atmosphere. HCl aq. was added until the pH of the solution was 7. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography to give (*S*)-1-methoxycarbonylethyl 2-naphthalenecarboxylate (**1e**, 1.37 g, 5.3 mmol, 26% yield). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69 (d, *J* = 7.1 Hz, 3*H*), 3.79 (s, 3*H*), 5.41 (dd, *J* = 7.1, 7.0 Hz, 1*H*), 7.51–7.62 (m, 2*H*), 7.86–7.97 (m, 3*H*), 8.09 (dd, *J* = 7.0, 1.7 Hz, 1*H*), 8.66 (s, 1*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3, 52.4, 69.1, 126.5, 126.6, 127.7, 128.1, 128.3, 131.3, 131.4, 132.3, 135.6, 165.9, 171.1 ppm; UV (cyclohexane) λ_{max} 281, 291 nm; MS (EI) *m*/*z* 127, 155, 258 (M^+); HRMS (EI) calcd for $C_{20}H_{16}O_4$: 320.1049, found: 320.1049.

4.7. Preparation of di-(ℓ)-menthyl 2,3-naphthalenedicarboxylate (**1f**)

A mixture of 2,3-naphthalenedicarboxylic acid (1.051 g, 4.9 mmol), $SOCl_2$ (4 mL, 55.1 mmol), DMF (few drops) was stirred at reflux overnight under a N_2 atmosphere. Excess $SOCl_2$ was removed by distillation. The residue (2,3-naphthalenedicarbonyl dichloride) was dried under reduced pressure. To a stirred THF (20 mL) solution of (ℓ)-menthol (1.986 g, 12.7 mmol) and pyridine (4 mL) was slowly added a THF (30 mL) solution of the residue (2,3-naphthalenedicarbonyl dichloride) under a N_2 atmosphere, and the resulting solution was stirred at reflux overnight. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (toluene, Rf = 0.36) followed by HPLC (GPC) to give di-(ℓ)-menthyl 2,3-naphthalenedicarboxylate (**1f**, 1.953 g, 82% yield). Colorless solid; mp 59–60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.9 Hz, 6*H*), 0.92 (d, *J* = 6.9 Hz, 6*H*), 0.96 (d, *J* = 6.4 Hz, 6*H*), 1.10–1.20 (m, 4*H*), 1.50–1.61 (m, 6*H*), 1.72–1.75 (m, 4*H*), 2.03 (quint-d, *J* = 6.9, 2.7 Hz, 2*H*), 2.26 (m, 2*H*), 5.00 (td, *J* = 10.9, 4.4 Hz, 2*H*), 7.61 (dd, *J* = 6.0, 3.2 Hz, 2*H*), 7.93 (dd, *J* = 6.2, 3.4 Hz, 2*H*), 8.25 (s, 2*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 21.1, 22.3, 23.6, 26.4, 31.6, 34.5, 40.8, 47.3, 75.6, 128.4, 128.7, 129.7, 129.9, 133.5, 167.2 ppm; MS (FAB) *m*/*z* (relative intensity, %) 199 (84), 217 (100), 355 (19), 493 (M^++1, 29).

4.8. Preparation of bis(8-phenyl-(ℓ)-menthyl) 2,3-naphthalenedicarboxylate (**1g**) [69,70]

To a stirred mixture of Mg (1.751 g, 72.0 mmol) and Et_2O (15 mL) was added Et_2O (15 mL) solution of bromobenzene (6 mL, 57.0 mmol) at 0 °C under a N_2 atmosphere, and the solution was stirred at reflux overnight. To a stirred Et_2O (5 mL) solution of CuBr (0.817 g, 5.7 mmol) was slowly added the PhMgBr solution prepared above at −20 °C under a N_2 atmosphere, and the solution was stirred 30 min at −20 °C. To the solution was added Et_2O (5 mL) solution of (*R*)-(+)-pulegone ((*R*)-(+)-1-methyl-4-isopropylidene-3-cyclohexanone, 4 mL, 24.6 mmol) at −20 °C, and the solution was stirred at −20 °C overnight. To the solution was added HCl aq. (2.0 M, 20 mL) at −20 °C. Et_2O and $NaHCO_3$ aq. were added. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. To the residue were added H_2O (8 mL), EtOH (60 mL), and KOH (7.398 g, 131.8 mmol), and the solution was stirred at reflux for 3 h. Et_2O and brine were added. Organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo to give a residue (6.321 g, 27.4 mmol, a diastereomeric mixture of 5-methyl-2-(1-methyl-1-phenylethyl)cyclohexanone).

A mixture of Na (2.0 g, 87.0 mmol) and toluene (30 mL) was vigorously stirred at reflux under a N_2 atmosphere until a fine suspension of Na is obtained. To the mixture was simultaneously added the above residue (6.321 g, 27.4 mmol) and *i*-PrOH (5 mL). The mixture was stirred at reflux overnight. After the mixture was cooled to 0 °C, H_2O was slowly added until remained Na is decomposed. Et_2O and brine were added. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo to give a residue (4.929 g, 21.2 mmol, a mixture of 8-phenyl-(ℓ)-menthol and its diastereomer).

To a mixture of the residue (4.929 g, 21.2 mmol), *N*,*N*-dimethylaniline (4 mL, 31.7 mmol), Et_2O (10 mL) was added dropwise a Et_2O (10 mL) solution of chloroacetyl chloride (7 mL, 88.0 mmol) over 1 h at 0 °C under a N_2 atmosphere, and the mixture was stirred at reflux for 3 h. CH_2Cl_2 and H_2O were added. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by distillation under reduced pressure followed by crystallization from EtOH to give (1*R*,2*S*,5*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl chloroacetate (2.097 g, 6.8 mmol).

A mixture of (1*R*,2*S*,5*R*)-5-methyl-2-(1-methyl-1-phenylethyl) cyclohexyl chloroacetate (2.097 g, 6.8 mmol), EtOH (50 mL), H_2O (8 mL), and KOH (1.05 g, 18.7 mmol) was stirred at reflux for 2 h. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (benzene: AcOEt = 4: 1, Rf = 0.90) to give 8-phenyl-(ℓ)-menthol (1.576 g, 6.8 mmol, 27% yield).

A mixture of 2,3-naphthalenedicarboxylic acid (0.758 g, 3.5 mmol), $SOCl_2$ (2.5 mL, 34.5 mmol), and DMF (few drops) was stirred at reflux overnight under a N_2 atmosphere. Excess $SOCl_2$ was removed by distillation. The residue (2,3-

naphthalenedicarbonyl dichloride) was dried under reduced pressure. To a stirred THF (30 mL) solution of 8-phenyl-(ℓ)-menthol (1.576 g, 6.8 mmol) and pyridine (4 mL) was slowly added a THF (20 mL) solution of the residue (2,3-naphthalenedicarbonyl dichloride) under a N_2 atmosphere. The resulting solution was stirred at reflux overnight. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography ($CHCl_3$, Rf = 0.93) followed by HPLC (GPC) to give bis(8-phenyl-(ℓ)-menthyl) 2,3-naphthalenedicarboxylate (**1f**, 1.188 g, 1.9 mmol, 53% yield). Colorless solid; mp 79–82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (qd, J = 12.4, 2.8 Hz, 4*H*), 0.94 (d, J = 6.4 Hz, 6*H*), 1.08–1.22 (m, 4*H*), 1.31 (s, 6*H*), 1.38 (s, 6*H*), 1.52–1.59 (m, 2*H*), 1.63–1.66 (m, 2*H*), 2.09–2.14 (m, 2*H*), 2.24–2.26 (m, 2*H*), 5.14 (td, J = 10.8, 4.3 Hz, 2*H*), 6.86 (t, J = 7.3 Hz, 2*H*), 7.09 (t, J = 7.8 Hz, 4*H*), 7.27 (d, J = 5.5 Hz, 2*H*), 7.28 (d, J = 7.3 Hz, 2*H*), 7.59 (dd, J = 6.0, 3.2 Hz, 2*H*), 7.69 (s, 2*H*), 7.82 (dd, J = 6.2, 3.4 Hz, 2*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.1, 26.4, 27.2, 27.3, 31.5, 34.9, 40.2, 41.5, 50.9, 76.0, 125.0, 125.6, 128.0, 128.1, 128.8, 129.4, 129.7, 133.2, 151.5, 166.6 ppm; MS (FAB) m/z (relative intensity, %) 199 (35), 217 (93), 431 (11), 645 (M^++1, 13).

4.9. Preparation of di-(d)-menthyl 2,3-naphthalenedicarboxylate (**1h**)

A mixture of 2,3-naphthalenedicarboxylic acid (0.981 g, 4.5 mmol), $SOCl_2$ (4 mL, 55.1 mmol), and DMF (few drops) was stirred at reflux overnight under a N_2 atmosphere. Excess $SOCl_2$ was removed by distillation. The residue (2,3-naphthalenedicarbonyl dichloride) was dried under reduced pressure. To a stirred THF (20 mL) solution of (*d*)-menthol (1.952 g, 12.5 mmol) and pyridine (4 mL) was slowly added a THF (20 mL) solution of the residue (2,3-naphthalenedicarbonyl dichloride) under a N_2 atmosphere. The resulting solution was stirred at reflux overnight. The mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (toluene, Rf = 0.38) followed by HPLC (GPC) to give di-(*d*)-menthyl 2,3-naphthalenedicarboxylate (**1h**, 0.403 g, 0.82 mmol, 18% yield). Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (d, J = 6.9 Hz, 6*H*), 0.92 (d, J = 7.3 Hz, 6*H*), 0.96 (d, J = 6.9 Hz, 6*H*), 1.11–1.19 (m, 4*H*), 1.49–1.61 (m, 6*H*), 1.72–1.75 (m, 4*H*), 2.02 (quint-d, J = 6.9, 2.6 Hz, 2*H*), 2.25–2.27 (m, 2*H*), 5.00 (td, J = 11.0, 4.6 Hz, 2*H*), 7.61 (dd, J = 6.4, 3.2 Hz, 2*H*), 7.93 (dd, J = 6.0, 3.2 Hz, 2*H*), 8.19 (s, 2*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 21.1, 22.3, 23.6, 26.3, 31.6, 34.5, 40.8, 47.3, 75.6, 128.4, 128.7, 129.7, 129.9, 133.5, 167.2 ppm; MS (FAB) m/z (relative intensity, %) 199 (80), 217 (100), 355 (18), 493 (M^++1, 25).

4.10. Preparation of bis((S)-1-phenylethyl) 2,3-naphthalenedicarboxylate (**1i**)

A mixture of 2,3-naphthalenedicarboxylic acid (1.081 g, 4.9 mmol), (*S*)-1-phenylethanol (1.567 g, 12.8 mmol), 4-dimethylaminopyridine (1.118 g, 9.2 mmol), and CH_2Cl_2 (30 mL) was stirred for 5 min at room temperature under a N_2 atmosphere. To the solution was added a CH_2Cl_2 (30 mL) solution of dicyclohexylcarbodiimide (3.061 g, 14.8 mmol), and the solution was stirred overnight. The precipitate was removed by filtration. HCl aq. (0.5 M) and Et_2O were added to the filtrate. The organic layer was washed with sat. $NaHCO_3$ aq., separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (AcOEt:hexane = 1:1, Rf = 0.8) followed by HPLC (GPC) to give bis((*S*)-1-phenylethyl) 2,3-naphthalenedicarboxylate (**1i**, 1.402 g, 3.3 mmol, 67% yield). Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59 (d, J = 6.4 Hz, 6*H*), 6.06 (q, J = 6.7 Hz, 2*H*), 7.28–7.40 (m, 10*H*), 7.60 (dd, J = 6.4, 3.2 Hz, 2*H*), 7.90 (dd, J = 6.2, 3.4 Hz, 2*H*), 8.22 (s, 2*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 73.9, 126.4, 128.0, 128.5, 128.6, 128.8, 129.2, 130.2, 133.5, 141.6, 166.9 ppm; MS (FAB) m/z (relative intensity, %) 199 (28), 217 (48), 321 (6), 425 (M^++1, 13).

4.11. Preparation of bis((R)-1-phenylethyl) 2,3-naphthalenedicarboxylate (**1j**)

A mixture of 2,3-naphthalenedicarboxylic acid (0.432 g, 2.0 mmol), (*R*)-1-phenylethanol (0.611 g, 5.0 mmol), 4-dimethylaminopyridine (0.484 g, 4.0 mmol), and CH_2Cl_2 (15 mL) was stirred for 5 min at room temperature under a N_2 atmosphere. To the solution was added CH_2Cl_2 (15 mL) solution of dicyclohexylcarbodiimide (1.268 g, 6.1 mmol). The resulting solution was stirred overnight. The precipitate was removed by filtration. HCl aq. (0.5 M) and Et_2O were added to the filtrate. The organic layer was washed with sat. $NaHCO_3$ aq., separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography ($CHCl_3$, Rf = 0.4) followed by HPLC (GPC) to give bis((*R*)-1-phenylethyl) 2,3-naphthalenedicarboxylate (**1j**, 0.589 g, 1.4 mmol, 70% yield). Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59 (d, J = 6.9 Hz, 6*H*), 6.06 (q, J = 6.7 Hz, 2*H*), 7.27–7.30 (m, 2*H*), 7.32–7.43 (m, 8*H*), 7.61 (dd, J = 6.4, 3.2 Hz, 2*H*), 7.91 (dd, J = 6.2, 3.4 Hz, 2*H*), 8.23 (s, 2*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 74.0, 126.3, 126.4, 128.0, 128.6, 128.8, 129.2, 130.1, 133.5, 141.7, 166.9 ppm; MS(FAB) m/z (relative intensity, %) 199 (16), 217 (43), 321 (7), 425 (M^++1, 9).

4.12. Preparation of 3-methylfuran (**2c**) [71,72]

To a stirred Et_2O (500 mL) solution of 4,4-dimethoxy-2-butanone (80 mL, 0.60 mol) and methyl chloroacetate (90 mL, 1.03 mol) was added MeONa (54 g, 1.00 mol) at −5 °C under a N_2 atmosphere, and the resulting solution was stirred at −5 °C for 2 h, and at room temperature overnight. To the solution was slowly added a mixture of glacial acetic acid (7 mL) and H_2O (93 mL) at 0 °C. The organic layer was decantated. Aqueous phase was washed with Et_2O. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was distilled (bp 72–78 °C/8 mmHg) to give 2-methoxycarbonyl-3-methylfuran (71 g, 0.51 mol, 85% yield).

A mixture of 2-methoxycarbonyl-3-methylfuran (26 g, 0.19 mol) and 20% NaOH aq. (60 mL) was stirred at reflux for 2 h. After the solution was cooled to 0 °C, conc HCl (35 mL) was slowly added to give colorless crystals of 3-methylfuran-2-carboxylic acid (3.199 g, 15% yield).

A mixture of 3-methylfuran-2-carboxylic acid (3.20 g, 29 mmol), Cu (0.90 g, 14.2 mmol), and quinoline (10 mL, 84.4 mmol) was heated to 260 °C, and a fraction (bp 65.5 °C) is collected and assigned to 3-methylfuran (colorless liquid, 65–70% yield) [73].

4.13. Preparation of 3-(methoxymethyl)furan (**2d**) [74]

To a mixture of DMF (10 mL) and NaH (1.734 g, 72.3 mmol) was added DMF (40 mL) solution of 3-furanmethanol (1.4 mL, 16.3 mmol) under a N_2 atmosphere, and the suspension was stirred for 30 min at room temperature. To the mixture was added MeI (3 mL, 48.2 mmol), and the mixture was stirred for 3 h at room temperature. Et_2O and brine were added. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (petroleum ether:Et_2O = 3:1) to give 3-(methoxymethyl)furan (**2d**, 1.808 g, 16.1 mmol, 99% yield).

4.14. General procedure for photoreaction

A solution containing the reactants in a cylindrical Pyrex vessel (ϕ = 8 mm) was degassed by argon bubbling for 15–20 min and then the vessel was sealed. The solution was irradiated by using a 300 W high pressure mercury lamp (Eikosha, PIH-300) at room temperature. The solution was maintained room temperature by using circulated cooling water during irradiation. The products were separated by silica gel column chromatography and recycling preparative HPLC (GPC).

*4.14.1. (ℓ)-Menthyl 2a,4,5,9b-tetrahydro-1,5,2,4-ethanediylidenebenzo[d]cyclobut[b]oxepin-1(2H)-carboxylate (**3aa**)*

Data for one diastereomer: ^{1}H NMR ($CDCl_3$) δ 0.67–1.97 (m, 18*H*), 3.16–3.21 (m, 1*H*), 3.59–3.65 (m, 1*H*), 3.78–3.83 (m, 1*H*), 3.98–4.02 (m, 1*H*), 4.16 (d, *J* = 7.7 Hz, 1*H*), 4.59–4.67 (m, 1*H*), 4.92–4.99 (m, 2*H*), 7.17–7.28 (m, 4*H*) ppm. Data for the other diasteromer: ^{1}H NMR ($CDCl_3$) δ 0.67–1.95 (m, 18*H*), 3.12–3.14 (m, 1*H*), 3.59–3.65 (m, 1*H*), 3.81–3.85 (m, 1*H*), 3.99–4.04 (m, 1*H*), 4.09 (d, *J* = 7.5 Hz, 1*H*), 4.56–4.64 (m, 1*H*), 4.92–4.98 (m, 2*H*), 7.19–7.26 (m, 4*H*) ppm.

*4.14.2. Methyl 2-hydroxymethyl-2a,4,5,9b-tetrahydro-1,5,2,4-ethanediylidenebenzo[d]cyclobut[b]oxepin-1(2H)-carboxylate (**3bb**)*

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10–3.17 (m, 1*H*), 3.44 (t, *J* = 5.2 Hz, 1*H*), 3.64 (s, 3*H*), 3.76–3.83 (m, 1*H*), 3.98–4.07 (m, 3*H*), 4.88 (d, *J* = 10.0 Hz, 1*H*), 4.92–4.98 (m, 1*H*), 7.09–7.16 (m, 4*H*) ppm.

*4.14.3. Methyl 11-hydroxymethyl-2a,4,5,9b-tetrahydro-1,5,2,4-ethanediylidenebenzo[d]cyclobut[b]oxepin-1(2H)-carboxylate (**4bb**)*

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.17–3.22 (m, 1*H*), 3.64–3.69 (m, 1*H*), 3.66 (s, 3*H*), 3.88–3.99 (m, 3*H*), 4.19 (d, *J* = 7.5 Hz, 1*H*), 4.80 (dd, *J* = 7.5, 2.8 Hz, 1*H*), 4.97 (dd, *J* = 7.5, 2.6 Hz, 1*H*), 7.09–7.15 (m, 4*H*) ppm.

*4.14.4. Di-(ℓ)-menthyl 2-hydroxymethyl-2a,4,5,9b-tetrahydro-1,5,2,4-ethanediylidenebenzo[d]cyclobut[b]oxepin-1,10(2H)-dicarboxylate (**3fb**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.63 (d, *J* = 6.9 Hz, 3*H*), 0.75 (dd, *J* = 6.9, 5.5 Hz, 4*H*), 0.82 (d, *J* = 7.3 Hz, 3*H*), 0.87 (d, *J* = 6.4 Hz, 3*H*), 0.92 (d, *J* = 6.4 Hz, 3*H*), 0.94–1.06 (m, 2*H*), 1.22–1.31 (m, 4*H*), 1.40–1.48 (m, 4*H*), 1.62–1.68 (m, 7*H*), 1.72 (quint-d, *J* = 6.9, 2.7 Hz, 1*H*), 1.93–1.97 (m, 1*H*), 2.07–2.11 (m, 1*H*), 3.04 (t, *J* = 6.4 Hz, 1*H*), 3.78 (d, *J* = 5.0 Hz, 1*H*), 3.92 (dd, *J* = 12.4, 5.5 Hz, 1*H*), 4.00 (dd, *J* = 12.1, 7.1 Hz, 1*H*), 4.12 (dd, *J* = 7.6, 3.9 Hz, 2*H*), 4.59 (qd, *J* = 7.0, 4.4 Hz, 2*H*), 4.82 (d, *J* = 7.8 Hz, 1*H*), 4.94 (dd, *J* = 7.6, 5.3 Hz, 1*H*) 7.19–7.20 (m, 1*H*), 7.23–7.24 (m, 1*H*), 7.28–7.30 (m, 2*H*) ppm.

*4.14.5. Di-(ℓ)-menthyl 11-hydroxymethyl-2a,4,5,9b-tetrahydro-1,5,2,4-ethanediylidenebenzo[d]cyclobut[b]oxepin-1,10(2H)-dicarboxylate (**4fb**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (d, *J* = 6.87 Hz, 6*H*), 0.85 (t, *J* = 7.3 Hz, 6*H*), 0.88–1.09 (m, 4*H*), 0.91 (d, *J* = 6.9 Hz, 6*H*), 1.21–1.32 (m, 2*H*), 1.36–1.51 (m, 4*H*), 1.52–1.62 (m, 4*H*), 1.65–1.72 (m, 2*H*), 1.98–2.09 (m, 2*H*), 3.57 (d, *J* = 5.0 Hz, 1*H*), 3.84 (dd, *J* = 12.1, 8.0 Hz, 1*H*), 3.95 (d, *J* = 7.3 Hz, 1*H*), 4.03 (t, *J* = 6.9 Hz, 1*H*), 4.12 (dd, *J* = 12.4, 6.0 Hz, 1*H*), 4.32 (d, *J* = 7.3 Hz, 1*H*), 4.56 (tt, *J* = 10.9, 3.6 Hz, 2*H*), 4.87 (d, *J* = 7.8 Hz, 1*H*), 4.93 (dd, *J* = 7.6, 5.3 Hz, 1*H*), 7.15 (dd, *J* = 6.0, 2.8 Hz, 1*H*), 7.23–7.25 (m, 1*H*), 7.27–7.30 (m, 2*H*) ppm.

4.14.6. Bis((S)-1-phenylethyl) *2-hydroxymethyl-2a,4,5,9b-tetrahydro-1,5,2,4-ethanediylidenebenzo[d]cyclobut[b]oxepin-1,10(2H)-dicarboxylate (**3ib**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (d, *J* = 6.9 Hz, 3*H*), 1.54 (d, *J* = 6.4 Hz, 3*H*), 3.60 (d, *J* = 5.0 Hz, 1*H*), 3.70 (t, *J* = 6.9 Hz, 1*H*), 3.85 (dd, *J* = 11.5, 7.8 Hz, 2*H*), 4.11 (dd, *J* = 12.4, 6.0 Hz, 1*H*), 4.31 (d, *J* = 7.3 Hz, 1*H*), 4.83 (d, *J* = 7.8 Hz, 1*H*), 4.91 (dd, *J* = 7.3, 5.0 Hz, 1*H*), 5.72 (q, *J* = 6.7 Hz, 1*H*), 5.82 (q, *J* = 6.6 Hz, 1*H*), 6.94–7.06 (m, 2*H*), 7.23–7.14 (m, 12*H*) ppm.

4.14.7. Bis((S)-1-phenylethyl) *11-hydroxymethyl-2a,4,5,9b-tetrahydro-1,5,2,4-ethanediylidenebenzo[d]cyclobut[b]oxepin-1,10(2H)-dicarboxylate (**4ib**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.4 Hz, 3*H*), 1.36 (d, *J* = 6.9 Hz, 3*H*), 2.91 (t, *J* = 6.4 Hz, 1*H*), 3.69 (d, *J* = 5.0 Hz, 1*H*), 3.82 (dd, *J* = 11.9, 6.9 Hz, 1*H*), 4.07 (dd, *J* = 12.4, 6.0 Hz, 1*H*), 4.11 (d, *J* = 7.8 Hz, 1*H*), 4.14 (d, *J* = 7.3 Hz, 1*H*), 4.88 (d, *J* = 7.8 Hz, 1*H*), 4.92 (dd, *J* = 7.8, 5.0 Hz, 1*H*), 5.51 (q, *J* = 6.6 Hz, 1*H*), 5.59 (q, *J* = 6.6 Hz, 1*H*), 6.96–7.00 (m, 2*H*), 7.00–7.04 (m, 2*H*), 7.19–7.24 (m, 2*H*), 7.24–7.30 (m, 4*H*), 7.33–7.36 (m, 2*H*), 7.38 (s, 2*H*) ppm.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2017.08.052.

References

[1] J.J. McCullough, Chem. Rev. 87 (1987) 811–860.
[2] F. Müller, J. Mattay, Chem. Rev. 93 (1993) 99–117.
[3] D. De Keukeleire, S.-L. He, Chem. Rev. 93 (1993) 359–380.
[4] J. Cornelisse, Chem. Rev. 93 (1993) 615–669.
[5] K. Mizuno, H. Maeda, A. Sugimoto, K. Chiyonobu, in: V. Ramamurthy, K.S. Schanze (Eds.), Molecular and Supramolecular Photochemistry, Vol. 8, Marcel Dekker, Inc., New York, 2001, pp. 127–241.
[6] H. Maeda, K. Mizuno, in: A. Griesbeck, M. Oelgemöller, F. Ghetti (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, third ed., CRC Press, Boca Raton, 2012, pp. 489–509.
[7] S. Poplata, A. Tröster, Y.-Q. Zou, T. Bach, Chem. Rev. 116 (2016) 9748–9815.
[8] R. Remy, C.G. Bochet, Chem. Rev. 116 (2016) 9816–9849.
[9] M. Gordon, W.R. Ware (Eds.), The Exciplex, Academic Press Inc., New York, 1975.
[10] N. Mataga, Pure Appl. Chem. 69 (1997) 729–734.
[11] R.A. Caldwell, D. Creed, Acc. Chem. Res. 13 (1980) 45–50.
[12] R.A. Caldwell, L. Smith, J. Am. Chem. Soc. 96 (1974) 2994–2996.
[13] R.A. Caldwell, N.I. Ghali, C.-K. Chien, D. DeMarco, L. Smith, J. Am. Chem. Soc. 100 (1978) 2857–2863.
[14] L.K. Sydnes, K.I. Hansen, D.L. Oldroyd, A.C. Weedon, E. Jørgensen, Acta Chem. Scand. 47 (1993) 916–924.
[15] C. Zhang, X.-C. Guo, Synth. Commun. 24 (1994) 3157–3165.
[16] M.T. Crimmins, A.L. Choy, J. Am. Chem. Soc. 119 (1997) 10237–10238.
[17] S.McN. Sieburth, K.F. McGee Jr., T.H. Al-Tel, J. Am. Chem. Soc. 120 (1998) 587–588.
[18] T. Bach, H. Bergmann, K. Harms, J. Am. Chem. Soc. 121 (1999) 10650–10651.
[19] W. Adam, K. Peters, E.M. Peters, V.R. Stegmann, J. Am. Chem. Soc. 122 (2000) 2958–2959.
[20] A. Yokoyama, K. Mizuno, Org. Lett. 2 (2002) 3457–3459.
[21] T. Bach, H. Bergmann, J. Am. Chem. Soc. 122 (2000) 11525–11526.
[22] M. D'Auria, L. Emanuele, R. Racioppi, Photochem. Photobiol. Sci. 3 (2004) 927–932.
[23] K. Matsubayashi, Y. Kubo, J. Org. Chem. 73 (2008) 4915–4919.
[24] M. Nagarathinam, A.M.P. Peedikakkal, J.J. Vittal, Chem. Commun. (2008) 5277–5288.
[25] Y. Kawanami, T.C.S. Pace, J. Mizoguchi, T. Yanagi, M. Nishijima, T. Mori, T. Wada, C. Bohne, Y. Inoue, J. Org. Chem. 74 (2009) 7908–7921.
[26] Y. Yabuno, Y. Hiraga, R. Takagi, M. Abe, J. Am. Chem. Soc. 133 (2011) 2592–2604.
[27] H. Maeda, H. Takenaka, K. Mizuno, Photochem. Photobiol. Sci. 15 (2016) 1385–1392.
[28] H. Maeda, A. Sugimoto, K. Mizuno, Org. Lett. 2 (2000) 3305–3308.
[29] H. Mukae, H. Maeda, K. Mizuno, Angew. Chem. Int. Ed. 45 (2006) 6558–6560.

[30] K. Mizuno, N. Negoro, Y. Nagayama, H. Maeda, H. Ikeda, Photochem. Photobiol. Sci. 13 (2014) 145–148.
[31] H. Maeda, H. Wada, H. Mukae, K. Mizuno, J. Photochem. Photobiol. A: Chem. 331 (2016) 29–41.
[32] H. Maeda, R. Nakashima, A. Sugimoto, K. Mizuno, J. Photochem. Photobiol. A: Chem. 329 (2016) 232–237.
[33] H. Maeda, S. Matsuda, K. Mizuno, J. Org. Chem. 81 (2016) 8544–8551.
[34] H. Maeda, T. Uesugi, Y. Fujimoto, H. Mukae, K. Mizuno, J. Photochem. Photobiol. A: Chem. 337 (2017) 198–206.
[35] V. Ramamurthy, Tetrahedron 42 (1986) 5753–5839.
[36] V. Ramamurthy, S. Gupta, Chem. Soc. Rev. 44 (2015) 119–135.
[37] C. Pac, T. Sugioka, H. Sakurai, Chem. Lett. 1 (1972) 39–42.
[38] T. Sugioka, C. Pac, H. Sakurai, Chem. Lett. 1 (1972) 667–668.
[39] T. Majima, C. Pac, H. Sakurai, Bull. Chem. Soc. Jpn. 51 (1978) 1811–1817.
[40] K. Kan, Y. Kai, N. Yasuoka, N. Kasai, Bull. Chem. Soc. Jpn. 52 (1979) 1634–1636.
[41] H. Sakurai, C. Pac, Mem. Inst. Sci. Ind. Res. Osaka Univ. 37 (1980) 59–78.
[42] C. Pac, M. Yasuda, K. Shima, H. Sakurai, Bull. Chem. Soc. Jpn. 55 (1982) 1605–1616.
[43] T. Noh, D. Kim, Tetrahedron Lett. 37 (1996) 9329–9332.
[44] T. Noh, D. Kim, S. Jang, Bull. Korean Chem. Soc. 18 (1997) 357–360.
[45] T. Sugioka, C. Pac, H. Sakurai, Chem. Lett. 1 (1972) 791–792.
[46] C. Pac, H. Sakurai, Chem. Lett. 5 (1976) 1067–1072.
[47] K. Mizuno, Y. Tachibana, G. Konishi, K. Chiyonobu, H. Maeda, J. Chin. Chem. Soc. 53 (2006) 75–78.
[48] K. Chiyonobu, G. Konishi, Y. Inoue, K. Mizuno, J. Chem. Res. (S) (2001) 135–137.
[49] H. Maeda, K. Chiyonobu, K. Mizuno, Photochem. Photobiol. Sci. 10 (2011) 1445–1449.
[50] N.V. Sastry, M.K. Valand, J. Chem. Eng. Data 43 (1998) 152–157.
[51] The Chemical Society of Japan (Ed.), Handbook of Chemistry: Pure Chemistry, third ed., Maruzen, Tokyo, 1984, pp. II502–II504.
[52] U. Mayer, Coord. Chem. Rev. 21 (1976) 159–179.
[53] M. Matsumoto, S. Kondo, Nippon Kagaku Zasshi 83 (1962) 261–263.
[54] P.A. Kollman, L.C. Allen, Chem. Rev. 72 (1972) 283–303.
[55] Y. Inoue, N. Yamasaki, H. Shimoyama, A. Tai, J. Org. Chem. 58 (1993) 1785–1793.
[56] S. Asaoka, T. Wada, Y. Inoue, J. Am. Chem. Soc. 125 (2003) 3008–3027.
[57] K. Hermann, Y. Pratumyot, S. Polen, A.M. Hardin, E. Dalkilic, A. Dastan, J.D. Badjic, Chem. Eur. J. 21 (2015) 3550–3555.
[58] T. Teitei, D. Wells, W.H.F. Sasse, Aust. J. Chem. 29 (1976) 1783–1790.
[59] T. Teitei, D. Wells, T.H. Spurling, W.H.F. Sasse, Aust. J. Chem. 31 (1978) 85–96.
[60] H.-X. Xu, B. Chen, L.-P. Zhang, L.-Z. Wu, C.-H. Tung, Tetrahedron Lett. 50 (2009) 4965–4968.
[61] H. Rau, Chem. Rev. 83 (1983) 535–547.
[62] Y. Inoue, Chem. Rev. 92 (1992) 741–770.
[63] S.R.L. Everitt, Y. Inoue, in: V. Ramamurthy, K.S. Schanze (Eds.), Molecular and Supramolecular Photochemistry, Vol. 3, Marcel Dekker, Inc., New York, 1999, pp. 71–130.
[64] L. Horner, J. Klaus, Liebigs Ann. Chem. (1979) 1232–1257.
[65] Y. Inoue, T. Okano, N. Yamasaki, A. Tai, J. Photochem. Photobiol. A: Chem. 66 (1992) 61–68.
[66] Y. Inoue, H. Tsuneishi, T. Hakushi, A. Tai, J. Am. Chem. Soc. 119 (1997) 472–478.
[67] T. Kitazawa, T. Wada, Y. Inoue, J. Am. Chem. Soc. 121 (1999) 8486–8498.
[68] S. Asaoka, M. Ooi, P. Jiang, T. Wada, Y. Inoue, J. Chem. Soc. Perkin Trans. 2 (2000) 77–84.
[69] O. Ort, Org. Synth. 65 (1987) 203–214.
[70] S. Asaoka, T. Takahashi, N. Kurose, T. Koizumi, Heterocycles 36 (1993) 1601–1616.
[71] D.M. Burness, Org. Synth. Collect. 4 (1963) 649–652.
[72] D.M. Burness, J. Org. Chem. 21 (1956) 102–104.
[73] M. Okabe, H. Tamagawa, M. Tada, Synth. Commun. 13 (1983) 373–378.
[74] N. Greeves, J.S. Torode, Synthesis (1993) 1109–1112.