

Study on the environmentally-benign organic synthetic reactions using sunlight

(太陽光を利用した環境調和型有機合成反応に関する研究)

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Part 2 Organic photochemical reactions via energy transfer from excited molecules: Singlet oxygen reactions using triplet sensitizers

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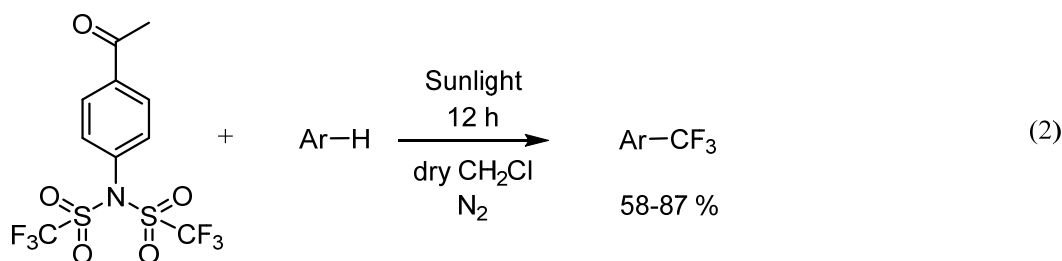
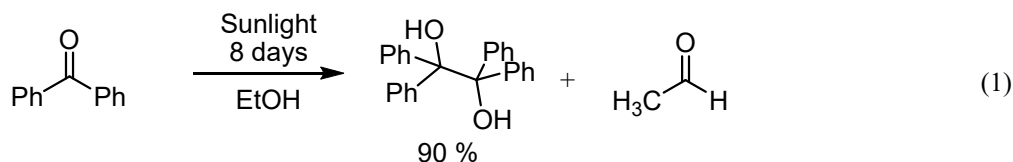
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Chapter 1

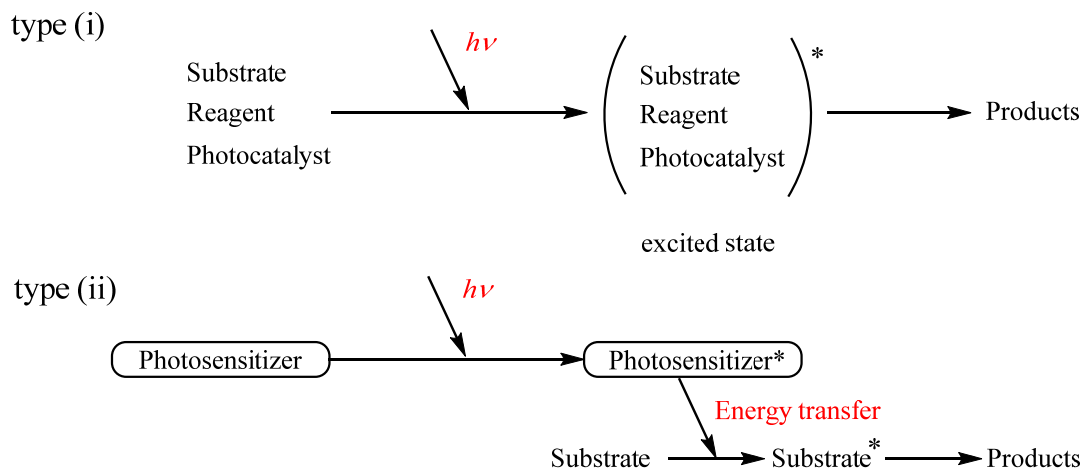
Introduction

Organic reactions are indispensable for the production of organic compounds and materials, and thermal energy is generally used in the conventional reactions. Thermal energy is often obtained by combustion of fossil fuels so that carbon dioxide, a greenhouse gas, is generated by the combustion, which causes environmental pollution and global warming. Therefore, the development of new methodologies, which are referred to as "green and sustainable chemistry,"¹ is necessary to avoid the generation of greenhouse gases.

Besides thermal energy, another type of energy can be used for the synthesis of organic compounds, namely photon energy. Organic photochemical reactions have been studied for a long time but they were generally conducted using artificial light sources²⁻¹⁰ operated by electric energy, in which a large part of the electricity is generated also by the combustion of fossil fuels. In contrast to the artificial light sources, sunlight is an infinite and most environmentally-benign ideal energy source. However, only a small number of synthetically useful photochemical reactions with limited applicability have been reported using sunlight. In addition, the efficiency of such reactions are generally unsatisfactory so that the reactions usually require long irradiation time, ranging from 10 hours to several days.¹¹⁻¹⁸ (cf. Reactions 1 and 2) Therefore, the development of sunlight-induced reactions that have wide synthetic applicability and high efficiency is necessary to replace conventional thermal reactions to reduce environmental dose in the course of the production of organic compounds and materials.



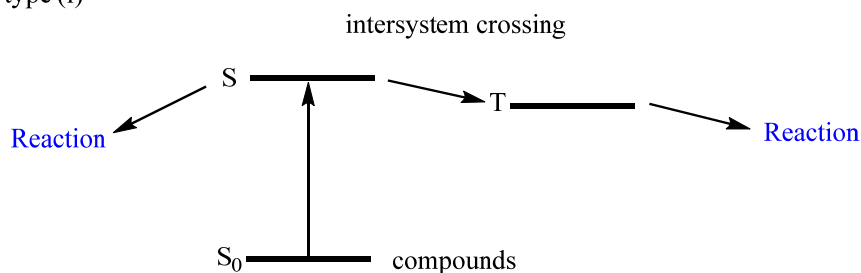
Photochemical reactions can be classified into two categories, (i) reactions via direct excitation of organic compounds and (ii) reactions via energy transfer from excited molecules (Scheme 1).



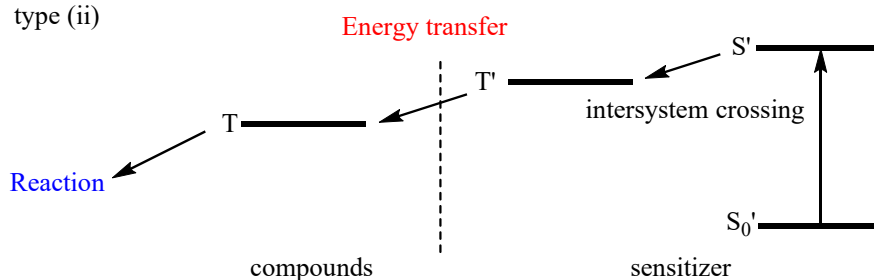
Scheme 1. Classification of photochemical processes

In the case of type (i) reactions, photons are absorbed by compounds and the compounds are excited from their ground state (S_0) to higher singlet states (S) (Scheme 2, type (i)). The reactions occur either from the singlet states (S) or from the triplet states (T) that are generated by an intersystem crossing from the singlet states (S), and lead to final products. Thus, multiple products may be formed from both S and T excited states in the type (i) reactions, and the ratio of the products should depend on the efficiency of the intersystem crossing. However, the selective reactions from the singlet states (S) can be accomplished by the addition of triplet quenchers to avoid the formation of products from the triplet states (T). On the other hand, in the type (ii) reactions, photons are absorbed by compounds, i.e. photosensitizers, which transfer photon energy to the triplet state (T) of organic molecules that form final products (Scheme 2, type (ii)). Triplet states of the sensitizers (T') are generated by an intersystem crossing from the excited singlet (S') to the triplet (T') states, and the energy is transferred from the triplet states of the sensitizers (T') to the triplet state of the compounds (T), from where the reaction occurs and lead to the final products. Type (ii) reactions initiate reactions selectively only from the triplet states of the compounds (T).

type (i)

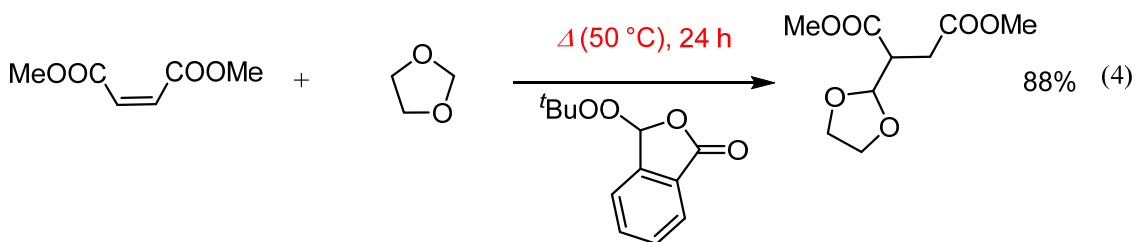
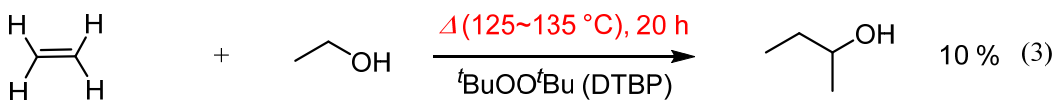


type (ii)

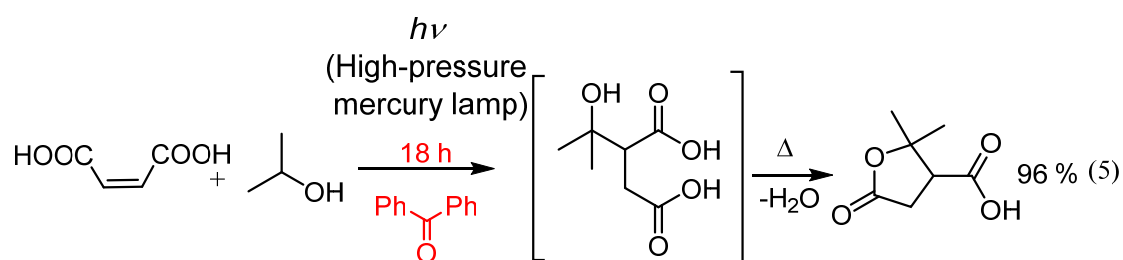


Scheme 2. Energy dissipation diagram of the type (i) and (ii) reactions.

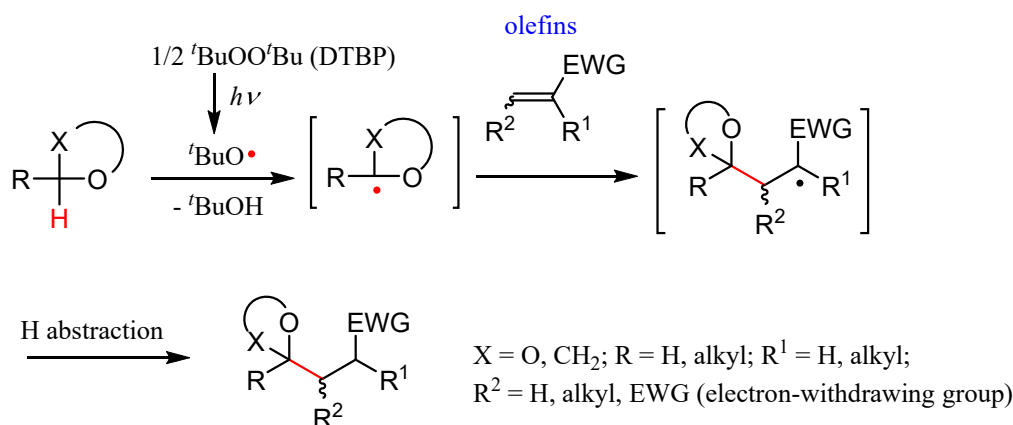
In Part 1, a C-C bond formation reaction via radical species is reported. C-C bond formation reactions are important in organic synthesis for constructing carbon skeletons of organic compounds. Various radical reactions have been developed for carbon-carbon bond formation. In contrast to ionic reactions, many functional groups are stable under radical reaction conditions, which is an advantage of using radical processes. Conventionally, two methods, thermal and photochemical processes, have been studied. However, the thermal method generally induced undesirable side reactions due to the high reaction temperature that are necessary to initiate the reactions, and giving low yield for the target product and/or require long reaction time (cf. Reactions 3 and 4).^{19, 20}



On the other hand, conventional photochemical reactions have been performed at low temperatures, so that side reactions can be reduced significantly compared to thermal processes. However, conventional photochemical C-C bond formation reactions required the use of photocatalysts such as ketones to abstract hydrogen from C-H bonds to generate carbon radicals that were added to various olefins.²¹ Benzophenone have been widely used as such ketone, but it have to be removed after reactions, which is a synthetic disadvantage (cf. Reaction 5). In addition, conventional photocatalyzed reactions generally required long reaction times, and also needed artificial light sources such as high-pressure mercury lamps.

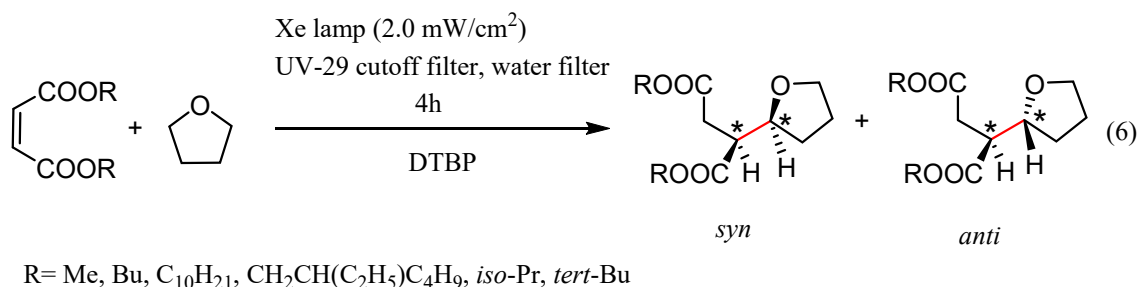


In Chapter 2, a development of a new efficient C-C bond formation reaction between cyclic ethers/cyclic acetals and olefins is reported using a xenon lamp as a light source.²² In this reaction, oxygen radical is generated by the photolysis of di-*tert*-butyl peroxide (DTBP), and thus generated oxygen radical abstracts hydrogen from a carbon adjacent to an oxygen atom to form a carbon radical. The carbon radical undergoes addition reaction to olefins to form a C-C bond. Optimization of the reaction conditions and the scope of the reaction were investigated using a xenon lamp. (Scheme 3)

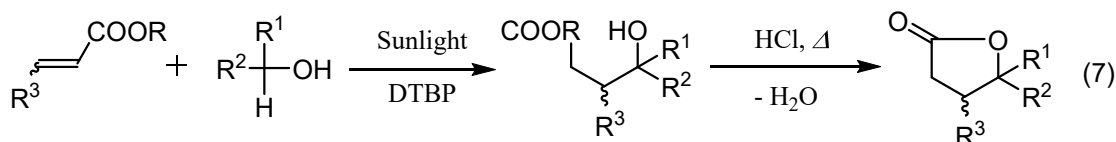


Scheme 3. A plausible reaction mechanism for the photochemical carbon-carbon bond formation reaction

In Chapter 3, diastereoselectivity in the addition of THF radicals to dialkyl maleates and the origin of the diastereoselectivity are investigated (cf. Reaction 6).²³ Diastereoselective reactions are important in organic synthesis for introducing new chiral centers into molecules. Therefore, diastereoselective reactions have been studied in the carbon radical addition to *chiral* olefins but the diastereoselectivity and its origin in the addition reaction of carbon radicals to *achiral* olefins have not been established. In the course of the study reported in Chapter 2, diastereoselectivity was observed in the addition of cyclic ethers to dimethyl malate, an *achiral* olefin, in which the formation of *syn* isomer predominated over *anti* isomer (cf. Reaction 6). In this chapter, a systematic study on the alkyl group R was conducted to clarify the origin of the diastereoselectivity.



In Chapter 4, sunlight was used as a light source for the addition of alcohols (cf. Reaction 7) and cyclic ether/cyclic acetal (Scheme 3) radicals to various olefins.²⁴ The irradiation of sunlight was conducted using Pyrex flasks without using any special equipments (Figure 1). Gram-scale photolyses were also conducted to show the possibility of industrial application of this synthetic method.



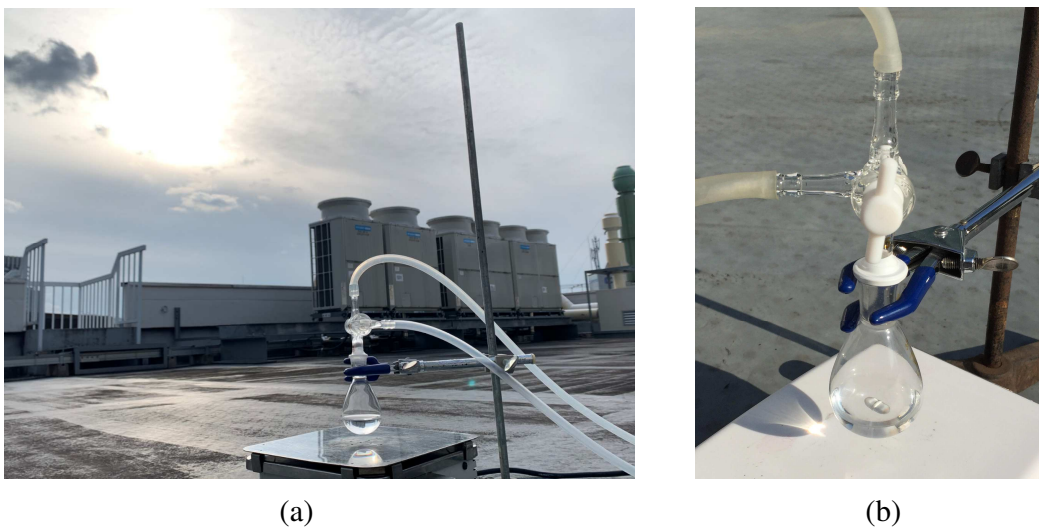
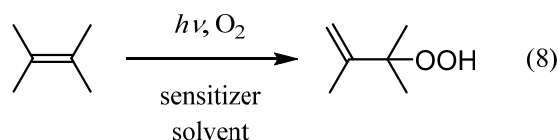


Figure 1. (a) General view of sunlight irradiation experiment. (b) Reaction vessel for sunlight irradiation

In Part 2, a functional group transformation using singlet oxygen is reported. Functional group transformation reactions are also important in organic synthesis for introducing necessary functional groups to organic compounds. Singlet oxygen has been used in industry as a mild and sustainable access to oxygenated products²⁵ and it is generally generated by an energy transfer from triplet sensitizers to the ground-state triplet oxygen. To use sunlight for organic reactions via energy transfer processes using sensitizers, the high efficiency of energy transfer is essential for achieving efficient reactions.

In Chapter 5, investigation on the efficiency of commonly used sensitizers for the generation of singlet oxygen is reported²⁶ because systematic studies on the efficiency of the sensitizers have not been reported. The efficiency is assessed by determining the kinetic constant on the generation of singlet oxygen using an ene reaction of 2,3-dimethylbutane as a probe reaction and visible light LEDs (cf. Reaction 8).



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Part 1

Photochemical reactions via direct excitation
of organic compounds:
Radical C-C bond formation reactions

Chapter 2

An addition reaction of
cyclic ethers and acetals to olefins
using di-*tert*-butyl peroxide and a Xe lamp

2-1 Introduction

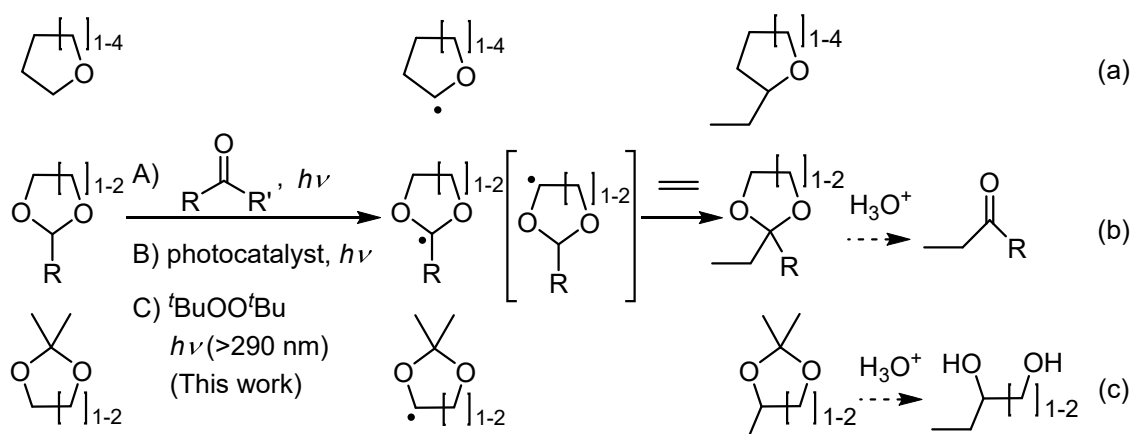
C-C bond formation is one of the most important reactions in organic synthesis and has been extensively and intensively studied. In contrast to ionic reactions, radical reactions are less studied probably due to the necessity of severe conditions, such as high temperature, for the generation of radicals, which often induce undesirable side reactions. However, many functional groups that need protection under ionic reaction conditions are tolerated in radical reactions, which is a significant advantage toward the synthesis of organic compounds. Therefore, the development of simple and efficient radical reactions for the construction of new C-C bonds is still a challenge in synthetic chemistry. The addition of carbon radicals to olefins is one of the fundamental radical C-C bond forming reactions that has been widely studied.¹ In particular, the addition of cyclic ethers and acetals to C=C bonds (Scheme 1) is of synthetic importance because the introduction of side chains at the carbon next to oxygen in cyclic ethers (Scheme 1a) can be used toward the synthesis of various bioactive natural compounds² and acetals can be used as synthons for ketones and aldehydes (Scheme 1b), and for diols (Scheme 1c). Thus, the reactions shown in Scheme 1b and c imply that the reaction involves not only C-C bond formation but also the introduction of synthetically useful functional groups.

For the generation of carbon radicals, C-heteroatom and C-H bond cleavage reactions have been widely used, in which the latter has advantage over the former because the former needs additional reactions to introduce the requisite C-heteroatom bond, which often require toxic reagents and harsh conditions.¹ Indeed, C-C bond formation using the direct activation of C-H bonds is now considered as one of the most challenging reactions. Conventional studies on the generation of carbon radicals via the abstraction of the hydrogen atom of a C-H bond can be briefly classified into three types: (i) Thermal reactions using radical initiators, (ii) photochemical reactions using ketones, and (iii) reactions using photoredox catalysts.

The first method (type i) has already been studied for the reactions shown in Scheme 1 using various radical initiators, mostly peroxides.³ However, in these early studies, high temperature and long reaction times were generally used so that the yields of the desired products were generally low. Although every effort has been made toward the improvement of these thermal reactions using di-*tert*-butyl peroxide (DTBP)⁴ and other peroxides,⁵ peracids,⁶ AIBN,⁷ and other methods,⁸ they still cannot avoid the disadvantages of using high temperatures and/or long reaction times.

The generation of carbon radicals via the photochemical excitation of ketones and

successive abstraction of α -hydrogen of heteroatoms (type ii) has also been studied for a long time.^{3b, 9, 10} Electronically excited ketones induce significant radical nature at their oxygen and carbon atoms, which enables the abstraction of a hydrogen atom from the C-H bond by the oxygen atom (Scheme 1, method A). This reaction has also been used for asymmetric reactions¹¹ and aqueous phase reactions,^{10o, p} as well as in additions to C=N bonds.¹² Recently, in the context of green chemistry, various photocatalysts using visible light irradiation have been studied for the generation of carbon radicals (type iii) and successive addition to olefins (Scheme 1, method B). Tetrabutylammonium decatungstate^{3b, 9c, 13, 14} uranyl cation,¹⁵ eosin Y,¹⁶ and cyclopropenium ion¹⁷ have been used for hydrogen abstraction from ethers/acetals. Organic¹⁸ and metal complex¹⁹ photoredox catalysts are also used for the generation of hydrogen abstracting species via single electron transfer (SET) processes. However, type ii and iii photochemical reactions generally require prolonged irradiation times, and most of the photocatalysts are very expensive and/or not commercially available. In addition, the use of ketones, aromatic ketones in most cases, in the reaction makes the purification of products difficult in many cases.



Scheme 1. Three different methods (A, B, and C) for the generation of radicals from cyclic ethers/acetals and their addition to olefins.

To overcome the disadvantages of conventional radical additions to olefins, we report a photochemical reaction using >290 nm light and DTBP, a commercially available inexpensive reagent (Scheme 1, method C). This method was applied to the reactions shown in Scheme 1, which proceeded efficiently at room temperature to give the desired products in good to excellent yield over a short reaction time; efficient reactions were completed within 0.5 h at room temperature in $>95\%$ yield. Scheme 2 shows a plausible mechanism for the reaction. The reaction was initiated by the photochemical cleavage of DTBP to form t -BuO \bullet radicals.²⁰

assigned as the *syn* isomer. The products, **3aA-*syn*** and **3aA-*anti***, were photochemically stable and did not decompose upon prolonged irradiation (Entries 2-5).

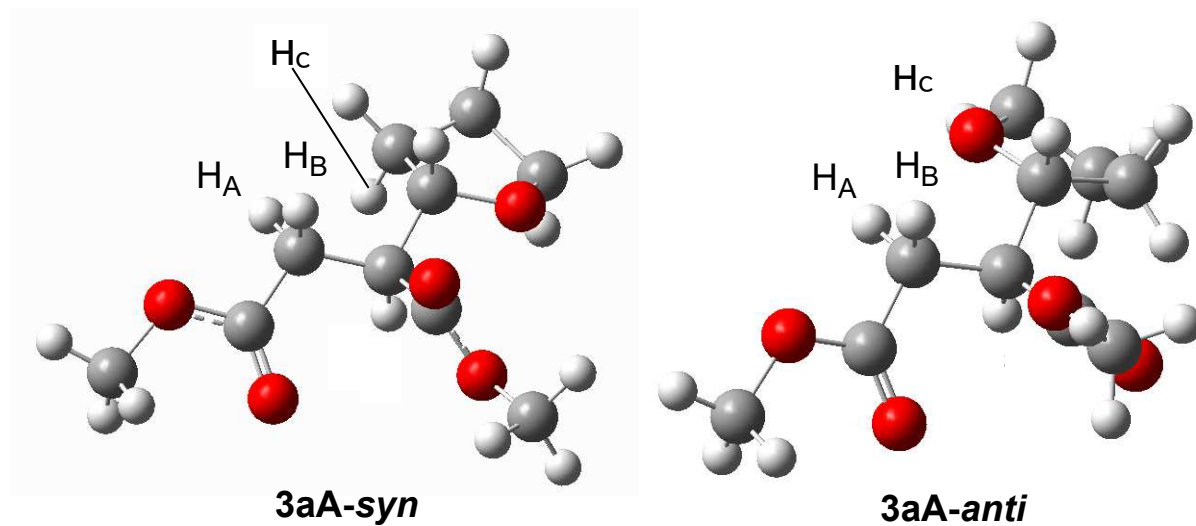


Figure 1. The stable conformation of **3aA-*syn*** and **-*anti*** calculated by DFT using B3LYP functional.

Table 1. Addition of cyclic ethers to olefins. ^a

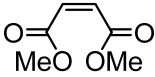

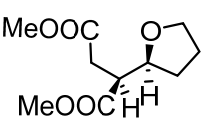
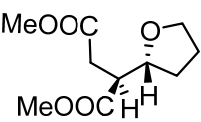

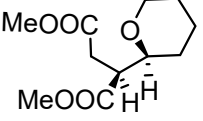
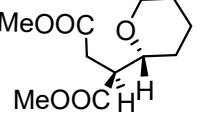

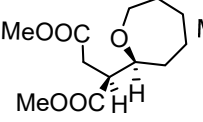
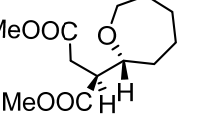

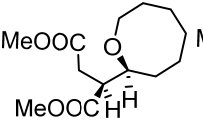
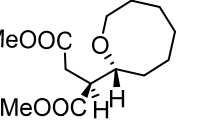

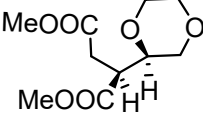
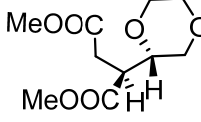
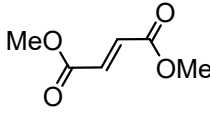
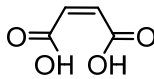
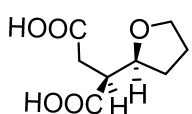
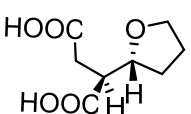
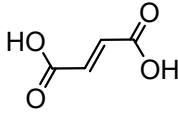
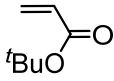
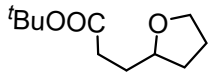
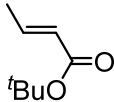
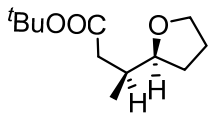
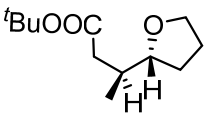
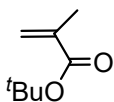
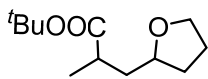
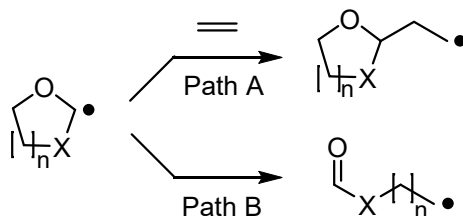
Entry	Olefin (1)	Ether (2)	Irradiation time (h)	Conversion of 1 (%)	Yield ^b (%)	
					<i>3aA-syn</i>	<i>3aA-anti</i>
1	 1a-cis	 2A	0.25	81	 3aA-syn 54	 3aA-anti 33
2			0.5	100	60 (52)	38 (30)
3			1	100	59	38
4			2	100	60	39
5			3	100	58	38
6		 2B	1	78	 3aB-syn 36	 3aB-anti 23
7			2	100	45 (38)	29 (22)
8			3	100	44	28
9		 2C	2	100	 3aC-syn 36 (29)	 3aC-anti 35 (32)
10		 2D	2	100	 3aD-syn 29 (27)	 3aD-anti 27 (26)
11		 2E	2	100	 3aE-syn 38 (31)	 3aE-anti 28 (21)
12			3	100	38	28

Table 1. Addition of cyclic ethers to olefins. ^a (continued)

13		2A	0.25	92	3aA-syn 38	3aA-anti 47
	1a-trans					
14			0.5	100	45	50
15		2A	0.5	>99		
	1b-cis				3bA-syn 45	3bA-anti 51
16		2A	0.5	100	3bA-syn 45	3bA-anti 55
	1b-trans					
17		2A	1	100		3dA 41 (33)
	1d					
18		2A	0.5	94		
	1e				3eA-syn 12	3eA-anti 11
19			1	91	26, 25	(30, <i>syn/anti</i> = 1/1) ^c
20			2	99	36, 34	
21			3	100	35, 35	
22		2A	1	100		3fA 0
	1f					

[a] Photolysis condition, substrates: olefin (0.2 mmol) and DTBP (0.1 mmol) in ether (10 mL), light source: 500-W xenon short-arc lamp fitted with an 18-cm water filter and a UV-29 cutoff filter (20 mW·cm⁻²), N₂ atm, room temp. [b] Yields are based on the consumed starting material and determined by NMR spectroscopy. The yields are the average of two (Entries 1 – 16, 21, 22), three (Entries 18, 20), five (Entry 17), and seven (Entry 19) independent runs. The yields in parentheses are those of isolated yields. [c] Isolated as a mixture of *syn* and *anti* isomers. The *syn/anti* ratio was determined by NMR spectra.

When tetrahydropyran (**2B**) was used (Entries 6-8), a similar reaction proceeded to give a diastereomeric mixture of **3aB-syn** and **3aB-anti**, which required a longer irradiation time (2 h) and with a slight decrease in the yield. The reactions using oxepane (**2C**), oxocane (**2D**), and 1,4-dioxane (**2E**) gave similar results to **2B** (Entries 9-12). The slow reaction of **2B** when compared to **2A** can be explained by (a) the slower abstraction of the α -hydrogen in **2B** by *t*-BuO• radicals compared to **2A**^{21a} and/or (b) the slower addition of the 6-membered **2B** radical to the olefin compared to the 5-membered **2A** radical.²⁵ The decrease in the yield observed for the product obtained from **2B** when compared to that from **2A** was attributed to the competition between Path A and B in Scheme 3. Cyclic ether radicals are reported to decyclize into linear radicals (Scheme 3, Path B, X = CH₂)²⁶ and the slower addition of the 6-membered compared to 5-membered radicals to olefins (Scheme 3, Path A, X = CH₂) should cause a decrease in the yield of the desired addition products for 6-membered **2B**.



Scheme 3. The addition of cyclic ether radicals to olefins (Path A) and decyclization of the radical (Path B)^{26, 28}.

To confirm the absence of any dark reactions, the reactions of **1a-cis** and **2B/2C** were conducted in the dark at room temperature for 72 h; for both **2B** and **2C**, the adducts **3aB-syn/anti** and **3aC-syn/anti** were not detected. These results indicate that light irradiation is indispensable for the reactions.

The effect of various olefins was investigated using **2A**. Olefins bearing two electron-withdrawing groups, dimethyl fumarate (**1a-trans**) (Entries 13 and 14), maleic acid (**1b-cis**) (Entry 15), and fumaric acid (**1b-trans**) (Entry 16) showed almost the same results as **1a-cis**. The isolation of **3bA-syn** and **-anti** was attempted using silica gel column chromatography, but it was unsuccessful due to the overlapping of the two isomers. The structure of the two isomers were confirmed by the hydrolysis of the **3aA-syn** and **-anti** isomers into their corresponding acids, **3bA-syn** and **-anti**, respectively.

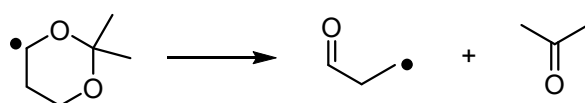
For olefins bearing a single electron-withdrawing group, the reactions of *tert*-butyl acrylate (**1d**) (Entry 17) and *tert*-butyl crotonate (**1e**) were completed within a short time and gave their corresponding products in moderate yield (Entries 18-21), but the expected product

3fA was not obtained from *tert*-butyl methacrylate (**1f**) (Entry 22). TLC analysis of these reaction mixtures after the complete consumption of the olefins showed a significant amount of products at the origin, which indicates the formation of polymers and oligomers of the starting olefins.²⁷

2-2-2 Addition of cyclic acetals to olefins

The reactions of various cyclic acetals and olefins were carried out (Table 2). The reaction of 1,3-dioxolane (**2F**) and **1a-cis** was completed within 0.5 h with the quantitative formation of three products **3aF-major**, **3aF-syn**, and **3aF-anti**, in which **3a-major** was the predominant product (Entry 1). In addition, the products did not decompose upon prolonged irradiation (Entry 2). In the case of 2-methyl-1,3-dioxolane (**2G**) (Entry 3), **3aG** was obtained in an almost quantitative yield upon 0.5 h of irradiation. When the 2-methyl substituent of **2G** was changed to *n*-hexyl (**2H**) or *iso*-propyl (**2I**), the expected products **3aH** and **3aI** were obtained in good yield, but with some decrease when compared with **3aG** (Entries 4-6). The higher regioselectivity of **2G-I** at the 2-position compared to unsubstituted **2F** can be explained by the faster α -hydrogen abstraction by *t*-BuO• radicals in the presence of the 2-alkyl substituent.^{21a} The steric effect of the 2-alkyl substituent has a significant effect on the yield of the products; larger substituents probably suppress the addition reaction (Scheme 3, Path A, X = O) and increase the ratio of the decyclization pathway²⁸ (Scheme 3, Path B, X = O).

C-C bond formation between the 4-position of 1,3-dioxolane/1,3-dioxane and **1a-cis** was attempted by blocking the 2-position with two methyl substituents in 2,2-dimethyl-1,3-dioxolane (**2J**) (Entries 7-9) and 2,2-dimethyl-1,3-dioxane (**2K**) (Entries 10, 11). Similar to that observed for cyclic ethers, a longer irradiation time was required for 6-membered **2K** when compared to 5-membered **2J**. Two sets of diastereomeric products, **3aJ-syn** and *-anti*, and **3aK-syn** and *-anti*, were obtained from **2J** and **2K**, respectively, in moderate yield. For these acetals, the expulsion of acetone has been reported via a decyclization of their corresponding cyclic radicals (Scheme 4),^{28b} which must have an effect on the yields of the desired products.



Scheme 4. Decyclization of 2,2-dimethyl-1,3-dioxane.^{28b}

The effect of various olefins was investigated using **2G** and **2J**. The trend was similar to that observed with cyclic ethers. Dimethyl fumarate (**1a-trans**) bearing two electron-withdrawing groups showed almost the same results to those observed for **1a-cis** (Entry 12). Fumaronitrile (**1c**) gave a good yield with **2G** upon 0.5 h of irradiation (Entry 13), but a moderate yield with **2J** (Entry 12). The isolation of the **3cJ-syn** and *-anti* isomers using column chromatography was also unsuccessful; only some of **3cJ-anti** was isolated and the other isomers were obtained as a *syn* and *anti* mixture. The reactions of *tert*-butyl acrylate (**1d**) (Entry 15) and *tert*-butyl crotonate (**1e**) (Entry 16) bearing a single electron-withdrawing group with **2G** were completed within 0.5 h, but showed some decrease in the product yield. In contrast, the addition of **2G** to *tert*-butyl methacrylate (**1f**) (Entry 17) did not proceed at all though **1f** was completely consumed within 0.5 h. Similar to the results with cyclic ethers, TLC analysis of the reaction mixtures showed a significant amount of products at the origin, which was also attributed to polymers and oligomers of the starting olefins.²⁷

Table 2. Addition of cyclic acetals to olefins.^a

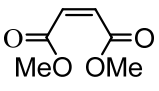

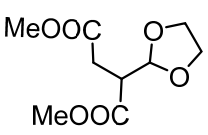
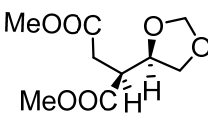

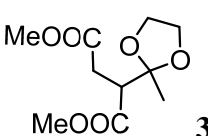
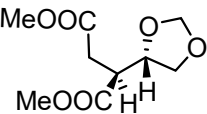
Entry	Olefin (1)	Acetal (2)	Irradiation time (h)	Conversion of 1 (%)	Yield ^b (%)
1	 1a-cis	 2F	0.5	100	 3aF-major 87
2			1	100	 3aF-syn 9
3		 2G	0.5	100	 3aG 100 (95)
					 3aF-anti 4 (95) ^c

Table 2. Addition of cyclic acetals to olefins.^a (continued)

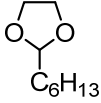
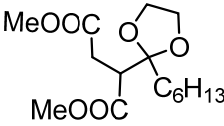
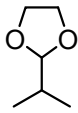
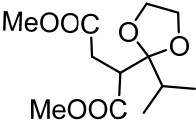

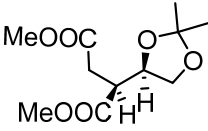
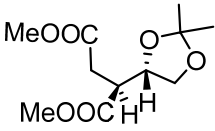

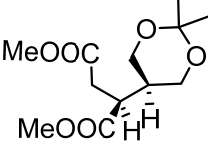
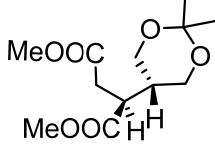
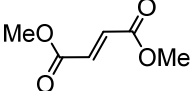
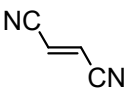
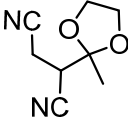
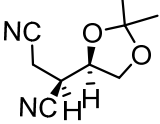
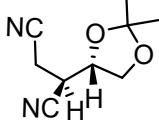
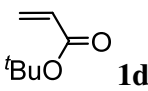
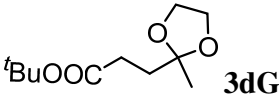
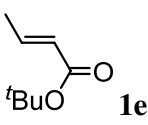
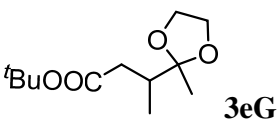
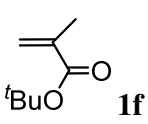
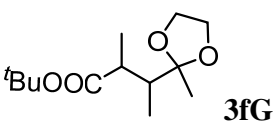
4		0.5	100		3aH	78 (75)	
5		0.75	100			69 (70)	
6		0.5	100		3aI	50 (48)	
7		0.5	83		3aJ-syn	16	
					3aJ-anti	7	
8		0.75	100			19 (15)	
9		1	100			10	
10		2	92		3aK-syn	18	
					3aK-anti	12	
11		3	100			21 (10)	
12		2G	0.5	100	3aG	91	
13		2G	0.5	100		3cG	71 (70)
14	1c	2J	2	100		3cJ-syn	12 (10)
						3cJ-anti	10 (9)

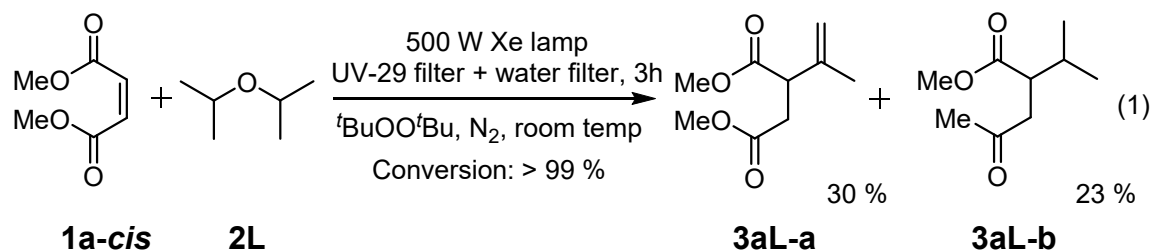
Table 2. Addition of cyclic acetals to olefins.^a (continued)

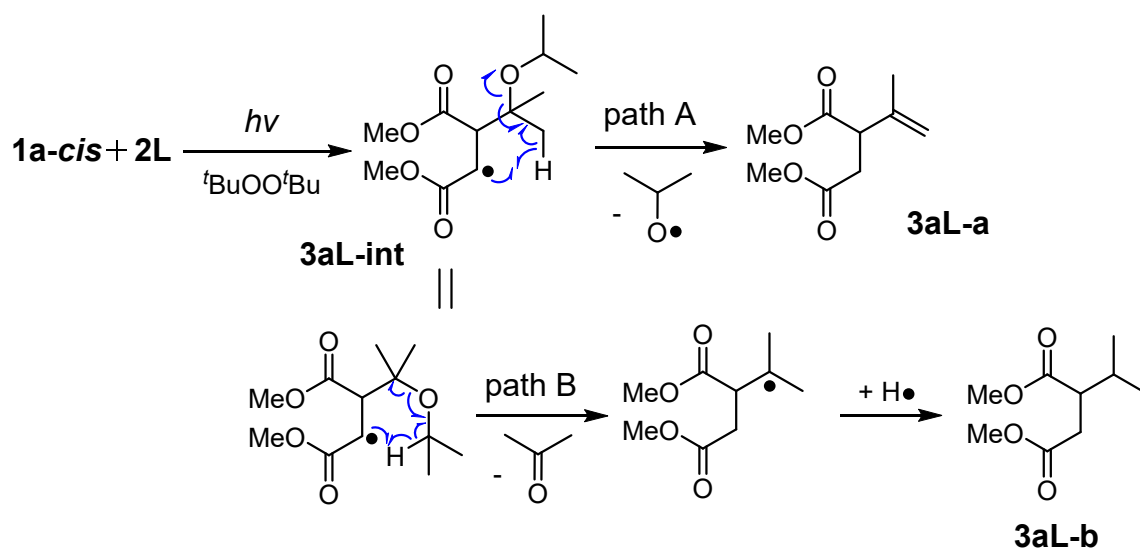
15		2G	0.5	100		37 (31)
16		2G	0.5	100		52 (47)
17		2G	0.5	100		0

[a] Photolysis condition, substrates: olefin (0.2 mmol) and DTBP (0.1 mmol) in acetals (10 mL), light source: 500-W xenon short-arc lamp fitted with an 18-cm water filter and a UV-29 cutoff filter (20 mW·cm⁻²), N₂ atm, room temp. [b] Yields are based on the consumed starting material and determined by NMR spectroscopy. The yields are the average of two (Entries 1 – 4, 6, 8, 12, 15, 17) and four (Entry 16) independent runs, and the others are of single runs. The yields in parentheses are those of isolated yields. [c] Isolated yield of the three isomers.

2-2-3 Reaction of an acyclic ether and olefin

C-C bond forming reactions have been reported between olefins and *cyclic* ethers and acetals, to the best of our knowledge, only one reaction has been reported with an *acyclic* ether, i.e., with ethyl *tert*-butyl ether,²⁷ an ether that does not have hydrogen atoms at one α -carbon of the ether. Therefore, the reaction of **1a-cis** and diisopropyl ether (**2L**) was conducted to investigate the scope of this reaction in *acyclic* ethers. The result showed the formation of two unexpected compounds **3aL-a** and **3aL-b** (Reaction 1). The most probable pathways for the formation of these products are two types of intramolecular H abstractions of intermediate radical **3aL-int**, which are shown as paths A and B in Scheme 5. A similar intramolecular H abstraction as path A has been reported during the addition of acyclic ethers to hexafluoropropene, in which the ether radicals were generated by γ -ray irradiation.²⁹





Scheme 5. Plausible reaction mechanisms for the formation of **3aL-a** and **3aL-b**.

2-3 Conclusion

A fast photochemical C-C bond forming reaction between cyclic ethers/acetal and olefins proceeds at room temperature using >290 nm light and DTBP, which gave the expected products in good to excellent yield; efficient reactions were completed within 0.5 h at room temperature in $>95\%$ yield. The acetals were used as acyl/formyl (reactions at their 2-position) and diol (reactions at their 4-position) synthons. The yields and irradiation times significantly depended on the size of the ring, in which 5-membered rings were found to be the best. The yields were also affected by the size of the 2-alkyl substituent on the cyclic acetal, which was attributed to their steric effect. The reaction with an acyclic ether, di-*iso*-propyl ether, gave two unexpected products and their plausible reaction mechanism was discussed. The reaction showed a considerable improvement to conventional carbon radical addition reactions to olefins, particularly reducing the reaction time and the use of commercially available and inexpensive DTBP.

2-4 Experimental Section

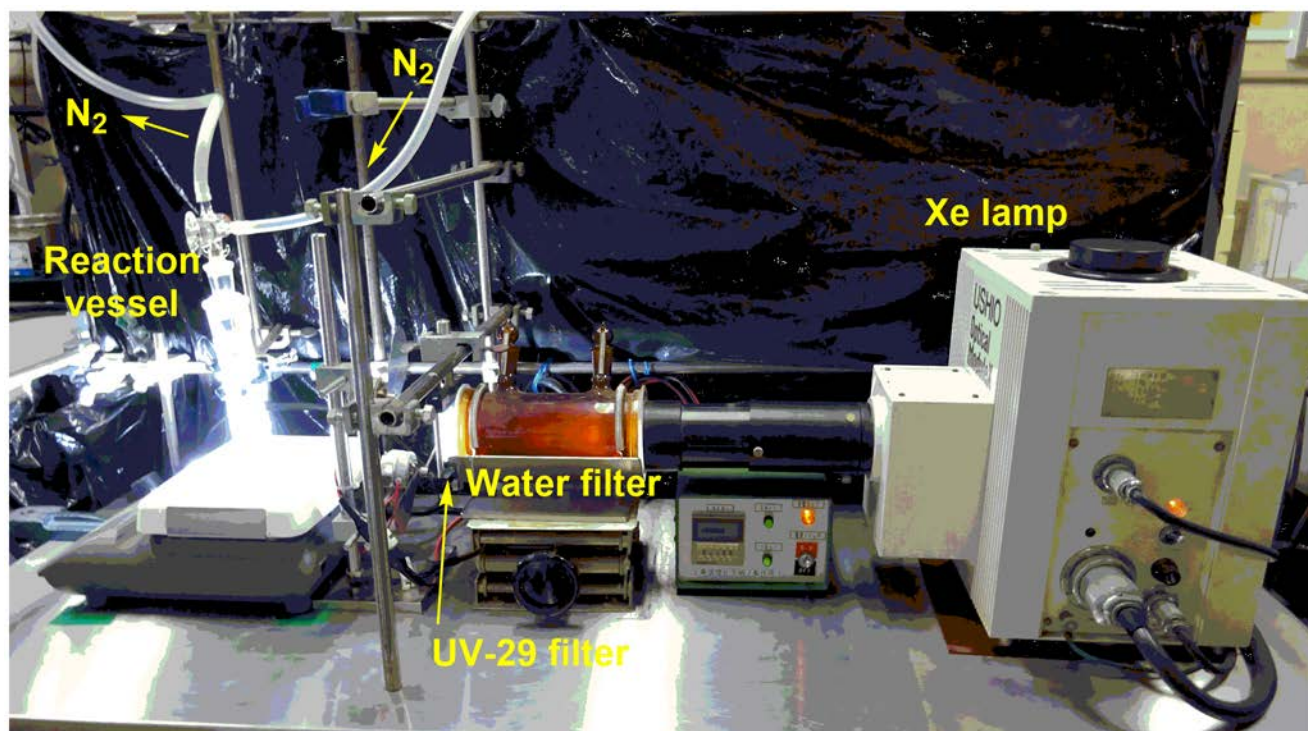
2-4-1 General Remarks

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker AVANCE 400 or a JEOL JNM-ECX400 spectrometer with CDCl₃ or acetone-d₆ as solvent. As internal standards, TMS (δ 0.0 ppm) in CDCl₃ or acetone-d₆ (δ 2.04 ppm) was used for ¹H NMR, and CDCl₃ (δ 77.0 ppm) or acetone-d₆ (δ 29.8 ppm) for ¹³C NMR analyses. HRMS spectra were recorded on an Agilent G1969 LC/MDS TOF mass spectrometer. Olefins **1a-cis**, **1a-trans**, **1b-cis**, **1b-trans**, **1c**, ethers **2A**, **2B**, **2E**, acetals **2F**, **2G**, **2J**, and DTBP were purchased and used as bought. Olefins **1d**, **1e**, **1f**, ethers **2A**, **2B**, **2E**, and acetals **2F**, **2G**, **2J** were purchased and distilled before use. Oxepane (**2C**),³⁰ oxocane (**2D**),³¹ 2-*n*-hexyl-1,3-dioxolane (**2H**),¹⁰ⁿ 2-*iso*-propyl-1,3-dioxolane (**2I**),¹⁰ⁿ and 2,2-dimethyl-1,3-dioxane (**2K**)³² were synthesized according to the reported procedures.

2-4-2 General procedure for the photolysis

An ether or acetal (**2A-L**) (10 mL) solution of olefin (**1a-f**) (0.2 mmol) and DTBP (0.1 mmol) was introduced into a quartz cylindrical cell (diameter: 3 cm) equipped with a three-way stopcock. The three-way stopcock was connected to the cell, a nitrogen source, and small vacuum pump. The solution was evacuated to about 50 mmHg under sonication for 5s and nitrogen was then introduced into the cell; this cycle was repeated 10 times. The photolysis was conducted using a 500-W xenon lamp (USHIO Optical Modulex SX-UI500XQ) fitted with an 18-cm water filter and a cut-off filter (Toshiba UV-29) under a nitrogen atmosphere. The irradiated light intensity was 20 mW/cm², which was measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with a UVD-S365 photo detector. After photolysis, the ether or acetal was removed in vacuo at 40–50 °C / < 150 Torr (most of the products were volatile under reduced pressure) and the consumption of the olefin and the products yield were determined by NMR spectroscopy using a precise amount of naphthalene as an internal standard; the yields of each product were calculated based on the consumed starting material. The isolation of the products was conducted using silica gel column chromatography.

2-4-3 Experimental setup



2-4-4 Experimental details of the reactions

2-(Tetrahydro-2-furanyl) butanedioic acid 1,4-dimethyl ester (3aA-syn**, *anti*).**^{5d, 7c, 19b, 33}

Dimethyl maleate (**1a-cis**, 28.56 mg, 0.20 mmol) and DTBP (14.36 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 0.5 h. NMR yield (CDCl₃), 98 % (*syn* / *anti* = 60 / 38) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (14/1 → 1/1).

3aA-syn: 22.17 mg (52%); colorless oil; ¹H-NMR (CDCl₃): δ = 1.59 – 1.70 (m, 1 H), 1.83 – 1.99 (m, 3 H), 2.48 (dd, *J* = 4.5, 16.6 Hz, 1 H), 2.78 (dd, *J* = 10.2, 16.6 Hz, 1 H), 3.09 (ddd, *J* = 4.5, 6.6, 10.2 Hz, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 3.74 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1 H), 3.87 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1 H), 4.06 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 25.6, 28.6, 32.5, 46.0, 51.9, 52.0, 68.4, 78.9, 172.2, 173.3 ppm. IR (KBr disk): 2953, 2876, 1740, 1730, 1460, 1439, 1414, 1360, 1346, 1317, 1263, 1196, 1165, 1069, 1020, 1005, 926, 849 cm⁻¹. MS, *m/z* (relative intensity): 45 (7), 55 (41), 59 (27), 70 (14), 71 (100), 72 (13), 97 (11), 111 (30), 114 (14), 143 (55), 153 (13), 185 (20), 216 (M⁺, 3), 217 (M⁺+1, 8).

3aA-anti: 12.83 mg (30%); colorless oil; ¹H-NMR (CDCl₃): δ = 1.67 – 1.78 (m, 1H), 1.82 – 1.94 (m, 2 H), 1.94 – 2.04 (m, 1 H), 2.70 (dd, *J* = 4.7, 16.7 Hz, 1 H), 2.80 (dd, *J* = 9.3, 16.7 Hz, 1 H), 2.92 (ddd, *J* = 4.7, 7.6, 9.3 Hz, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 3.73 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1 H), 3.81 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1 H), 4.01 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1 H)

ppm. ^{13}C -NMR (CDCl_3): $\delta = 25.6, 29.6, 33.2, 46.6, 51.8, 52.0, 68.1, 78.7, 172.6, 173.3$ ppm. IR (KBr disk): 2953, 2876, 1738, 1732, 1460, 1439, 1414, 1360, 1348, 1319, 1263, 1200, 1165, 1067, 1028, 1007, 968, 924, 891, 849 cm^{-1} . MS, m/z (relative intensity): 45 (3), 55 (16), 59 (13), 71 (100), 72 (5), 97 (4), 111 (10), 114 (3), 143 (15), 185 (6), 217 ($\text{M}^+ + 1$, 2).

2-(Tetrahydro-2H-pyran-2-yl) butanedioic acid 1,4-dimethyl ester (3aB-*syn*, *anti*).^{19b}

Dimethyl maleate (**1a-cis**, 28.83 mg, 0.20 mmol) and DTBP (14.81 mg, 0.10 mmol) in tetrahydropyran (**2B**, 10 mL). Irradiation time: 2 h. NMR yield (CDCl_3), 74 % (*syn* / *anti* = 45 / 29) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (14/1 \rightarrow 1/1).

3aB-*syn*: 17.40 mg (38 %); colorless oil; ^1H -NMR (CDCl_3): $\delta = 1.29 - 1.43$ (m, 1 H), 1.43 – 1.61 (m, 4 H), 1.81 – 1.90 (m, 1 H), 2.55 (dd, $J = 4.3, 16.8$ Hz, 1 H), 2.78 (dd, $J = 10.3, 16.8$ Hz, 1 H), 3.03 (ddd, $J = 4.3, 6.0, 10.3$ Hz, 1 H), 3.67 (s, 3 H), 3.72 (s, 3 H), 3.41 (ddd, $J = 2.6, 11.5, 11.5$ Hz, 1 H), 3.52 (ddd, $J = 1.9, 6.0, 10.9$ Hz, 1 H), 3.98 (ddd, $J = 2.0, 4.0, 11.5$ Hz, 1 H) ppm. ^{13}C -NMR (CDCl_3): $\delta = 23.3, 25.7, 28.4, 32.1, 46.9, 51.8, 51.9, 68.9, 77.7, 172.5, 173.3$ ppm. IR (KBr disk): 2951, 2849, 1738, 1437, 1414, 1368, 1356, 1333, 1258, 1209, 1194, 1165, 1138, 1088, 1051, 1009, 997, 903, 891, 843 cm^{-1} . MS (m/z , relative intensity): 41 (70), 42 (20), 43 (57), 53 (25), 55 (75), 56 (39), 57 (56), 59 (51), 67 (57), 69 (40), 83 (42), 84 (20), 85 (97), 86 (35), 87 (27), 97 (20), 111 (44), 114 (47), 115 (40), 125 (83), 138 (20), 157 (100), 158 (28), 170 (22), 199 (42), 230 (M^+ , 0.02).

3aB-*anti*: 10.10 mg (22 %); colorless oil; ^1H -NMR (CDCl_3): $\delta = 1.29 - 1.42$ (m, 1 H), 1.42 – 1.60 (m, 4 H), 1.78 – 1.91 (m, 1 H), 2.69 (dd, $J = 4.8, 16.9$ Hz, 1 H), 2.78 (dd, $J = 9.4, 16.9$ Hz, 1 H), 2.91 (ddd, $J = 4.8, 6.4, 9.4$ Hz, 1 H), 3.67 (s, 3 H), 3.71 (s, 3 H), 3.39 (ddd, $J = 3.0, 11.3, 11.3$ Hz, 1 H), 3.52 (ddd, $J = 1.9, 6.4, 10.8$ Hz, 1 H), 3.95 (ddd, $J = 2.0, 2.0, 11.3$ Hz, 1 H) ppm. ^{13}C -NMR (CDCl_3): $\delta = 23.2, 25.7, 29.5, 32.2, 47.3, 51.7, 52.0, 68.8, 77.5, 172.9, 173.5$ ppm. IR (KBr disk): 2995, 2953, 2851, 1738, 1437, 1416, 1368, 1358, 1341, 1285, 1265, 1209, 1200, 1163, 1088, 1045, 1011, 997, 899, 887, 851 cm^{-1} . MS (m/z , relative intensity): 41 (69), 42 (15), 43 (53), 44 (20), 53 (18), 55 (75), 56 (29), 57 (51), 59 (44), 67 (52), 69 (29), 83 (32), 85 (99), 86 (25), 87 (19), 111 (34), 114 (38), 115 (30), 125 (81), 157 (100), 158 (19), 170 (15), 199 (31), 230 (M^+ , 0.02). HRMS: m/z calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_5$: 230.1154; found: 230.1144.

2-(2-Oxepanyl) butanedioic acid 1,4-dimethyl ester (3aC-*syn*, *anti*).

Dimethyl maleate (**1a-cis**, 28.82 mg, 0.20 mmol) and DTBP (14.85 mg, 0.10 mmol) in oxepane (**2C**, 10 mL). Irradiation time: 2 h. NMR yield (CDCl_3), 67 % (*syn* / *anti* = 33 / 34)

(conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (40/1 → 0/1).

3aC-syn: 13.95 mg (29 %); colorless oil; ¹H-NMR (CDCl₃): δ = 1.40-1.81 (m, 8H), 2.52 (dd, *J* = 16.8, 4.4 Hz, 1H), 2.78 (dd, *J* = 16.8, 10.8 Hz, 1H), 3.01 (ddd, *J* = 10.8, 6.6, 4.4 Hz, 1H), 3.53 (ddd, *J* = 4.8, 6.8, 11.9 Hz, 1H), 3.67 (s, 3H), 3.64-3.71 (m, 1H), 3.72 (s, 3H), 3.85 (ddd, *J* = 4.8, 6.6, 11.9 Hz, 1H) ppm. ¹³C-NMR (CDCl₃): δ = 26.1, 26.3, 30.6, 32.7, 32.8, 47.6, 51.8, 51.9, 69.5, 79.4, 172.5, 173.5 ppm. IR (KBr disk): 3633, 3562, 3459, 2932, 2857, 1738, 1437, 1414, 1362, 1334, 1262, 1198, 1168, 1118, 1003, 971, 900, 873, 846, 686, 591, 534, 488, 405 cm⁻¹. MS, *m/z* (relative intensity): 41 (44), 42 (42), 43 (33), 55 (100), 57 (14), 59 (26), 69 (11), 71 (11), 81 (65), 83 (15), 87 (10), 99 (80), 114 (23), 115 (39), 139 (29), 171 (30). HRMS: *m/z* calcd. for C₁₂H₂₀O₅ + Na: 267.1208; found: 267.12028.

3aC-anti: 15.76 mg (32 %); colorless oil; ¹H-NMR (CDCl₃): δ = 1.40-1.80 (m, 8H), 2.71 (dd, *J* = 5.6, 16.8 Hz, 1H), 2.77 (dd, *J* = 8.4, 16.8 Hz, 1H), 2.92 (ddd, *J* = 5.6, 7.2, 8.4 Hz, 1H), 3.50 (ddd, *J* = 6.2, 6.8, 10.4 Hz, 1H), 3.68 (s, 3H), 3.71 (s, 3H), 3.65-3.74 (m, 1H), 3.80 (ddd, *J* = 7.2, 7.2, 10.4 Hz, 1H) ppm. ¹³C-NMR (CDCl₃): δ = 26.16, 26.24, 30.7, 32.7, 33.7, 47.8, 51.8, 52.0, 69.0, 79.1, 172.9, 173.8 ppm. IR (KBr disk): 2932, 2857, 1738, 1437, 1367, 1343, 1261, 1200, 1163, 1114, 1027, 1003, 971, 850, 537, 474, 411 cm⁻¹. MS, *m/z* (relative intensity): 41 (48), 42 (42), 43 (35), 55 (100), 57 (14), 59 (27), 69 (12), 71 (12), 81 (69), 83 (16), 87 (11), 99 (83), 114 (24), 115 (41), 139 (28), 171 (32). HRMS: *m/z* calcd. for C₁₂H₂₀O₅ + Na: 267.1208; found: 267.1209.

2-(2-Oxocanyl) butanedioic acid 1,4-dimethyl ester (3aD-syn, anti).

Dimethyl maleate (**1a-cis**, 29.00 mg, 0.20 mmol) and DTBP (14.70 mg, 0.10 mmol) in oxocane (**2D**, 10 mL). Irradiation time: 2 h. NMR yield (CDCl₃), 56 % (*syn* / *anti* = 29 / 27) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (40/1 → 0/1).

3aD-syn: 14.03 mg (27 %); colorless oil; ¹H-NMR (CDCl₃): δ = 1.38 – 1.83 (m, 10 H), 2.51 (dd, *J* = 4.4, 16.8 Hz, 1 H), 2.75 (dd, *J* = 10.6, 16.8 Hz, 1 H), 2.99 (ddd, *J* = 4.4, 6.4, 10.6 Hz, 1 H), 3.51 (ddd, *J* = 3.4, 6.2, 12.0 Hz, 1 H), 3.67 (s, 3 H), 3.62 – 3.75 (m, 1 H), 3.72 (s, 3 H), 3.83 (ddd, *J* = 3.4, 8.4, 12.0 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 24.6, 26.5, 26.9, 27.7, 32.0, 32.4, 47.8, 51.8, 51.9, 71.5, 78.8, 172.6, 173.7 ppm. IR (KBr disk): 2925, 2853, 1738, 1437, 1362, 1332, 1261, 1196, 1165, 1098, 1012, 971, 894, 848, 800, 564, 440 cm⁻¹. MS, *m/z* (relative intensity): 41 (100), 42 (24), 43 (48), 44 (10), 45 (21), 53 (13), 54 (10), 55 (65), 56 (22), 57 (19), 59 (30), 67 (23), 68 (11), 69 (39), 71 (16), 79 (11), 83 (15), 95 (66), 113 (51), 114 (20), 115 (37), 143 (11), 260 (M⁺+1 0.04). HRMS: *m/z* calcd. for C₁₃H₂₂O₅: 259.1545;

found: 259.1563.

3aD-anti: 13.51 mg (26 %); colorless oil; $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.38 - 1.85$ (m, 10 H), 2.68 (dd, $J = 4.8, 16.4$ Hz, 1 H), 2.77 (dd, $J = 9.6, 16.4$ Hz, 1 H), 2.87 (ddd, $J = 4.8, 6.4, 9.6$ Hz, 1 H), 3.46 (ddd, $J = 3.4, 6.8, 12.0$ Hz, 1 H), 3.67 (s, 3 H), 3.68 – 3.75 (m, 1 H), 3.71 (s, 3 H), 3.83 (ddd, $J = 3.2, 8.0, 12.0$ Hz, 1 H) ppm. $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 24.6, 26.4, 26.9, 28.0, 32.5, 33.1, 48.3, 51.8, 51.9, 71.6, 79.1, 172.9, 174.0$ ppm. IR (KBr disk): 2959, 2923, 2852, 1731, 1455, 1260, 1096, 1020, 799 cm^{-1} . MS, m/z (relative intensity): 41 (100), 42 (25), 43 (48), 45 (21), 53 (12), 54 (10), 55 (69), 56 (26), 57 (18), 59 (30), 67 (21), 68 (10), 69 (38), 71 (16), 79 (11), 83 (17), 87 (10), 95 (66), 113 (51), 114 (20), 115 (43), 142 (10), 143 (14), 259 (M^+ , 0.07). HRMS: m/z calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_5$: 259.1545; found: 259.1534.

2-(1, 4-Dioxan-2-yl) butanedioic acid dimethyl ester (3aE-syn, anti).^{14b, 19b, 34}

Dimethyl maleate (**1a-cis**, 28.60 mg, 0.20 mmol) and DTBP (14.54 mg, 0.10 mmol) in 1,4-dioxane (**2E**, 10 mL). Irradiation time: 2 h. NMR yield (CDCl_3), 66 % (*syn* / *anti* = 38 / 28) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (14/1 \rightarrow 1/1).

3aE-syn: 14.24 mg (31 %); colorless oil; $^1\text{H-NMR}$ (CDCl_3): $\delta = 2.53$ (dd, $J = 4.6, 16.9$ Hz, 1 H), 2.84 (dd, $J = 10.0, 16.9$ Hz, 1 H), 3.03 (ddd, $J = 4.6, 5.4, 10.0$ Hz, 1 H), 3.46 (dd, $J = 10.1, 11.5$ Hz, 1 H), 3.57 (ddd, $J = 2.9, 11.5, 11.5$ Hz, 1 H), 3.66 – 3.72 (m, 2H), 3.68 (s, 3 H), 3.74 (s, 3 H), 3.73 – 3.83 (m, 3H) ppm. $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 32.3, 43.5, 52.0, 52.2, 66.3, 67.2, 68.7, 75.3, 172.0, 172.3$ ppm. IR (KBr disk): 2957, 2914, 2859, 1738, 1439, 1414, 1366, 1337, 1302, 1277, 1258, 1234, 1200, 1169, 1119, 1043, 1005, 970, 941, 920, 905, 880, 849, 619 cm^{-1} . MS, m/z (relative intensity): 41 (52), 42 (26), 43 (65), 44 (30), 45 (49), 53 (21), 55 (83), 58 (26), 59 (75), 69 (22), 71 (28), 83 (30), 86 (50), 87 (100), 96 (46), 97 (61), 99 (26), 113 (26), 114 (90), 115 (61), 125 (29), 129(70), 146 (36), 157 (67), 172 (87), 200 (52), 201 (37), 232 (M^+ , 0.1).

3aE-anti: 9.79 mg (21 %); colorless oil; $^1\text{H-NMR}$ (CDCl_3): $\delta = 2.71$ (dd, $J = 4.7, 17.0$ Hz, 1 H), 2.80 (dd, $J = 9.2, 17.0$ Hz, 1 H), 2.93 (ddd, $J = 4.7, 7.1, 9.2$ Hz, 1 H), 3.39 (dd, $J = 10.3, 11.9$ Hz, 1 H), 3.57 (ddd, $J = 2.9, 11.7, 11.7$ Hz, 1 H), 3.66 – 3.71 (m, 2H), 3.68 (s, 3 H), 3.72 (s, 3 H), 3.74 – 3.81 (m, 3H) ppm. $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 31.9, 43.6, 51.9, 52.3, 66.3, 67.0, 69.5, 74.6, 172.47, 172.52$ ppm. IR (KBr disk): 2957, 2914, 2857, 1738, 1439, 1416, 1364, 1344, 1300, 1277, 1258, 1198, 1167, 1119, 1063, 1026, 1009, 957, 916, 905, 878, 847, 617 cm^{-1} . MS, m/z (relative intensity): 41 (44), 42 (21), 43 (60), 44 (30), 45 (39), 55 (84), 59 (72), 71 (22), 83 (23), 86 (39), 87 (100), 96 (36), 97 (52), 114 (90), 115 (52), 125 (37), 129(60), 146

(24), 157 (54), 172 (84), 200 (48), 201 (32), 232 (M⁺, 0.1).

2-(2-Tetrahydro-2-furanyl) butanedioic acid 1,4-dimethyl ester (3aA-*syn*, *anti*).^{5d, 7c, 19b, 33}

Dimethyl fumarate (**1a-*trans***, 28.86 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 0.5 h. NMR yield (CDCl₃), 95 % (*syn* / *anti* = 45 / 50) (conversion: 100 %).

2-(2-Tetrahydro-2-furanyl) butanedioic acid (3bA-*syn*, *anti*).^{33a, 35}

Maleic acid (**1b-*cis***, 23.20 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 0.5 h. NMR yield (acetone-d₆), 96 % (*syn* / *anti* = 45 / 51) (conversion: 99.9 %).

2-(2-Tetrahydro-2-furanyl) butanedioic acid (3bA-*syn*, *anti*).^{33a, 35}

Fumaric acid (**1b-*trans***, 23.11 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 0.5 h. NMR yield (acetone-d₆), 100 % (*syn* / *anti* = 45 / 55) (conversion: 100 %).

Tetrahydro-2-furan propanoic acid *tert*-butyl ester (3dA).

tert-Butyl acrylate (**1d**, 25.60 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 1 h. NMR yield (CDCl₃), 40 % (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (80/1 → 0/1).

3dA: 13.23 mg (33 %); colorless oil; ¹H-NMR (δ, CDCl₃): 1.44 (s, 9 H), 1.39 – 1.52 (m, 1 H), 1.79 (ddd, *J* = 6.4, 7.6, 7.6 Hz, 2 H), 1.82 – 1.93 (m, 2 H), 1.93 – 2.03 (m, 1 H), 2.28 (dt, *J* = 7.6, 15.2 Hz, 1 H), 2.36 (dt, *J* = 7.6, 15.2 Hz, 1 H), 3.72 (ddd, *J* = 6.4, 7.9, 7.9 Hz, 1 H), 3.78 – 3.88 (m, 2 H) ppm. ¹³C-NMR (δ, CDCl₃): 25.7, 28.1, 30.8, 31.1, 32.4, 67.6, 78.3, 80.1, 172.9 ppm. IR (KBr disk): 2974, 2870, 1726, 1457, 1391, 1365, 1256, 1148, 1113, 1070, 1020, 958, 917, 849, 756, 462, 431 cm⁻¹. MS (*m/z*, relative intensity): 41 (42), 42 (11), 43 (35), 44 (4), 55 (12), 56 (10), 57 (55), 70 (4), 71 (100), 72 (4), 73 (8), 81 (7), 84 (7), 85 (23), 97 (10), 98 (6), 101 (4), 116 (15), 125 (7), 127 (38), 143 (6), 144 (9), 145 (9). HRMS: *m/z* calcd. for C₁₁H₂₀O₃: 201.1472; found: 201.1490.

Tetrahydro-β-methyl-2-furanpropanoic acid *tert*-butyl ester (3eA-*syn*, *anti*).

tert-Butyl crotonate (**1e**, 28.37 mg, 0.20 mmol) and DTBP (14.57 mg, 0.10 mmol) in THF

(**2A**, 10 mL). Irradiation time: 1 h. NMR yield (CDCl₃), 48 % (*syn* / *anti* = 24 / 24) (conversion: 93 %). Eluent for chromatography: hexane/ethyl acetate (80/1 → 0/1). **3eA-syn** + **3eA-anti**: 10.60 mg (30 %; *syn* / *anti* = 1 / 1); colorless oil. The obtained two products were further separated by column chromatography: hexane/ethyl acetate (80/1 → 20/1). Only a part of **3eA-anti** was isolated by the second chromatographic separations and the rest of **3eA-anti** and **3eA-syn** were obtained as a mixture.

3eA-anti: ¹H-NMR (δ, CDCl₃): 0.91 (d, *J* = 6.4 Hz, 3 H), 1.45 (s, 9 H), 1.46 – 1.64 (m, 1 H), 1.80 – 1.96 (m, 3 H), 1.95 – 2.08 (m, 1 H), 2.00 (dd, *J* = 8.8, 10.0 Hz, 1 H), 2.52 (dd, *J* = 8.8, 10.0 Hz, 1 H), 3.56 (ddd, *J* = 7.1, 7.1, 7.1 Hz, 1 H), 3.72 (ddd, *J* = 6.1, 7.7, 8.4 Hz, 1 H), 3.81 (ddd, *J* = 6.8, 6.8, 8.4 Hz, 1 H) ppm.

3eA-syn + **3eA-anti**: ¹H-NMR (δ, CDCl₃): 0.99 (d, *J* = 6.4 Hz, 3 H), 1.45 (s, 9 H), 1.78 – 2.06 (m, 5 H), 2.06 – 2.18 (m, 1 H), 2.33 (dd, *J* = 4.8, 14.4 Hz, 1 H), 3.64 – 3.76 (m, 2 H), 3.79 – 3.87 (m, 1 H) ppm.

2-(1,3-dioxolan-4-yl) butanedioic acid 1,4-dimethyl ester (3aF-syn, anti) ^{19b} and **2-(1,3-dioxolan-2-yl) butanedioic acid 1,4-dimethyl ester (3aF-major)**. ^{5d, h, 19b, 36}

Dimethyl maleate (**1a-cis**, 28.99 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in 1,3-dioxolane (**2F**, 10 mL). Irradiation time: 1 h. NMR yield (CDCl₃), 100 % (*syn* / *anti* / major = 8 / 4 / 88) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (14/1 → 2/1). **3aF-major** + **3aF-syn** + **3aF-anti**: 41.64 mg (95 %). The obtained three products were further separated by column chromatography: hexane/ethyl acetate (8/1 → 1/1). Only a part of **3aF-major** was isolated by the second chromatographic separations and **3aF-syn** and **-anti**, and the rest of **3aF-major** were obtained as a mixture.

3aF-major: 19.77 mg (45 %); colorless oil; ¹H-NMR (δ, CDCl₃): 2.63 (dd, *J* = 4.8, 16.9 Hz, 1 H), 2.81 (dd, *J* = 9.2, 16.9 Hz, 1 H), 3.25 (ddd, *J* = 4.2, 4.8, 9.2 Hz, 1 H), 3.69 (s, 3 H), 3.75 (s, 3H), 3.85 – 3.92 (m, 2H), 3.92 – 4.02 (m, 2H), 5.20 (d, *J* = 4.2 Hz, 1H) ppm. ¹³C-NMR (δ, CDCl₃): 30.0, 45.6, 51.8, 52.2, 65.3, 102.7, 171.3, 172.3 ppm. IR (KBr disk): 2994, 2955, 2893, 1738, 1439, 1395, 1364, 1327, 1267, 1227, 1194, 1165, 1148, 1105, 1036, 999, 984, 945, 897, 853, 756, 667, 554, 480 cm⁻¹. MS (*m/z*, relative intensity): 40 (14), 41 (28), 42 (28), 43 (41), 44 (29), 45 (67), 46 (13), 53 (11), 54 (10), 55 (48), 56 (10), 59 (38), 69 (11), 71 (13), 73 (100), 74 (32), 75 (11), 83 (14), 87 (26), 99 (31), 103 (18), 113 (37), 114 (18), 115 (18), 127 (10), 145 (27), 157 (11), 187 (21), 219 (0.14, M⁺).

3aF-major + **3aF-syn** + **3aF-anti**: 19.77 mg (45 %, *major* / *syn* / *anti* = 71/10/19); colorless

oil.

3aF-syn: $^1\text{H-NMR}$ (δ , CDCl_3): 2.52 (dd, $J = 4.8, 16.8$ Hz, 1 H), 2.65 (dd, $J = 4.3, 16.8$ Hz, 1 H), 3.17 – 3.22 (m, 1H), 3.69 (s, 3H), 3.74 (s, 3H), 3.8 – 3.84 (m, 1H), 3.87 – 4.02 (m, 1H), 4.27 – 4.32 (m, 1H), 4.81 (s, 1H), 5.05 (s, 1H).

3aF-major + 3aF-syn + 3aF-anti: MS (m/z, relative intensity): 40 (13), 41 (30), 42 (19), 43 (59), 44 (96), 45 (100), 55 (39), 59 (31), 71 (10), 73 (45), 87 (12), 97 (20), 99 (15), 113 (24), 114 (34), 125 (16), 129 (10), 146 (10), 156 (19), 219 (0.07, M^+).

Pure **3aF-anti** was isolated from other experiment.

3aF-anti: $^1\text{H-NMR}$ (δ , CDCl_3): 2.76 (dd, $J = 5.0, 16.9$ Hz, 1 H), 2.85 (dd, $J = 7.8, 16.9$ Hz, 1 H), 2.98 (ddd, $J = 5.0, 7.8, 8.2$ Hz, 1 H), 3.69 (s, 3H), 3.72 (s, 3H), 3.79 (dd, $J = 5.5, 8.7$ Hz, 1 H), 4.03 (dd, $J = 6.4, 8.7$ Hz, 1 H), 4.25 (ddd, $J = 5.5, 6.4, 8.2$ Hz, 1 H), 4.83 (s, 1H), 5.00 (s, 1H) ppm. $^{13}\text{C-NMR}$ (δ , CDCl_3): 32.5, 45.0, 51.9, 52.3, 69.0, 74.8, 95.1, 172.2, 172.3 ppm. IR (KBr disk): 2999, 2955, 2876, 2860, 1738, 1730, 1462, 1438, 1414, 1368, 1265, 1202, 1167, 1088, 1024, 941, 851, 735 cm^{-1} . MS (m/z, relative intensity): 45 (100), 55 (43), 59 (41), 69 (13), 71 (14), 73 (61), 87 (18), 97 (20), 99 (16), 113 (32), 114 (31), 125 (18), 128 (11), 129(14), 145 (11), 146 (15), 156 (32), 187 (13), 219 (0.6, M^+).

2-(2-Methyl-1, 3-dioxolan-2-yl) butanedioic acid 1,4-dimethyl ester (3aG).^{5h, 37}

Dimethyl maleate (**1a-cis**, 28.56 mg, 0.20 mmol) and DTBP (14.51 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Irradiation time: 0.5 h. NMR yield (CDCl_3), 97 % (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (14/1 \rightarrow 2/1).

3aG: 43.72 mg (95 %); colorless oil. $^1\text{H-NMR}$ (δ , CDCl_3): 1.39 (s, 3H), 2.65 (dd, $J = 4.4, 16.9$ Hz, 1 H), 2.85 (dd, $J = 10.4, 16.9$ Hz, 1 H), 3.19 (dd, $J = 4.4, 10.4$ Hz, 1 H), 3.67 (s, 3 H), 3.74 (s, 3 H), 3.91 – 4.05 (m, 4 H) ppm. $^{13}\text{C-NMR}$ (δ , CDCl_3): 22.0, 32.4, 49.6, 51.8, 52.1, 64.85, 64.90, 108.7, 172.1, 172.5 ppm. IR (KBr): 2992, 2955, 2893, 2851, 1740, 1437, 1416, 1383, 1352, 1294, 1271, 1211, 1165, 1093, 1043, 1009, 951, 880, 853, 818, 766, 694, 650, 559, 513, 405 cm^{-1} . MS (m/z, relative intensity): 41 (17), 42 (12), 43 (81), 44 (23), 45 (29), 53 (18), 54 (8), 55 (43), 59 (35), 69 (9), 81 (6), 83 (12), 85 (16), 87 (100), 88 (44), 89 (11), 97 (13), 99 (22), 103 (15), 110 (5), 111 (12), 113 (23), 114 (7), 129 (23), 142 (5), 143 (10), 157 (56), 158 (11), 170 (15), 185 (39), 217 (5), 233 ($\text{M}^+ + 1$, 0.08).

2-(2-Hexyl-1, 3-dioxolan-2-yl) butanedioic acid 1,4-dimethyl ester (3aH).

Dimethyl maleate (**1a-cis**, 28.91 mg, 0.20 mmol) and DTBP (14.77 mg, 0.10 mmol) in 2-hexyl-1,3-dioxolane (**2H**, 10 mL). Irradiation time: 0.5 h. NMR yield (CDCl₃), 77 % (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (20/1 → 0/1).

3aH: 45.75 mg (75 %); colorless oil. ¹H-NMR (δ, CDCl₃): 0.88 (t, *J* = 6.9 Hz, 3H), 1.18–1.49 (m, 8H), 1.58–1.77 (m, 2H), 2.61 (dd, *J* = 4.6, 16.9 Hz, 1H), 2.86 (dd, *J* = 10.5, 16.9 Hz, 1H), 3.25 (dd, *J* = 4.6, 10.5 Hz, 1H), 3.67 (s, 3H), 3.74 (s, 3H) 3.90–4.07 (m, 4H) ppm. ¹³C-NMR (δ, CDCl₃): 14.0, 22.5, 22.7, 29.3, 31.7, 32.2, 35.4, 48.6, 51.8, 52.1, 65.4, 65.5, 110.4, 172.3, 172.7 ppm. IR (KBr): 2954, 2932, 2872, 2858, 1741, 1459, 1438, 1415, 1350, 1301, 1266, 1206, 1166, 1096, 1039, 1004, 950, 898, 870, 852, 822, 775, 730, 569, 422 cm⁻¹. MS (*m/z*, relative intensity): 55 (23), 99 (16), 113 (10), 157 (100), 185 (24), 217 (7), 303 (0.05, M⁺+1). HRMS: *m/z* calcd. for C₁₅H₂₆O₆ + Na: 325.1627; found: 325.1642.

2-(2-Isopropyl-1, 3-dioxolan-2-yl) butanedioic acid 1,4-dimethyl ester (3aI).

Dimethyl maleate (**1a-cis**, 28.83 mg, 0.20 mmol) and DTBP (14.95 mg, 0.10 mmol) in 2-isopropyl-1,3-dioxolane (**2I**, 10 mL). Irradiation time: 0.5 h. NMR yield (CDCl₃), 52 % (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (10/1 → 0/1).

3aI: 25.09 mg (48 %); colorless oil. ¹H-NMR (δ, CDCl₃): 0.94 (d, *J* = 6.9, 3H), 0.99 (d, *J* = 6.4, 3H), 2.05 (dq, *J* = 6.4, 6.9 Hz, 1H), 2.58 (dd, *J* = 4.1, 17.1 Hz, 1H), 2.90 (dd, *J* = 10.6, 17.1 Hz, 1H), 3.42 (dd, *J* = 4.1, 10.6 Hz, 1H), 3.67 (s, 3H) 3.73 (s, 3H), 3.94– 4.09 (m, 4H) ppm. ¹³C-NMR (δ, CDCl₃): 16.9, 17.1, 32.2, 35.9, 47.8, 51.8, 52.1, 66.4, 66.6, 112.7, 172.6, 172.7 ppm. IR (KBr): 3636, 3552, 3458, 2954, 2898, 2850, 1739, 1471, 1437, 1415, 1384, 1359, 1266, 1207, 1161, 1087, 1033, 991, 956, 900, 881, 848, 762, 686, 597, 570, 502, 469, 444 cm⁻¹. MS (*m/z*, relative intensity): 43 (81), 55 (28), 71 (15), 99 (14), 115 (100), 185 (25), 259 (0.17, M⁺). HRMS: *m/z* calcd. for C₁₂H₂₀O₆ + H: 261.1338; found: 261.1333.

2-(2, 2-Dimethyl-1, 3-dioxolan-4-yl) butanedioic acid 1,4-dimethyl ester (3aJ-syn, anti).

Dimethyl maleate (**1a-cis**, 28.69 mg, 0.20 mmol) and DTBP (14.77 mg, 0.10 mmol) in 2, 2-dimethyl-1,3-dioxolane (**2J**, 10 mL). Irradiation time: 0.75 h. NMR yield (CDCl₃), 26 % (*syn* / *anti* = 18 / 8) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (20/1→0/1).

3aJ-syn: 7.30 mg (15 %); colorless oil; ¹H-NMR (δ, CDCl₃): 1.33 (s, 3H), 1.41 (s, 3H), 2.52 (dd, *J* = 4.4, 16.8 Hz, 1H), 2.79 (dd, *J* = 9.8, 16.8 Hz, 1H), 3.20 (ddd, *J* = 4.4, 5.8, 9.8 Hz,

1H), 3.69 (s, 3H), 3.73 (s, 3H) 3.80 (dd, $J = 6.0, 8.8$ Hz, 1H), 4.01 (dd, $J = 6.4, 8.8$ Hz, 1H), 4.36 (ddd, $J = 5.8, 6.0, 6.4$ Hz, 1H) ppm. ^{13}C -NMR (δ , CDCl_3): 24.9, 26.2, 31.8, 44.2, 52.0, 52.2, 66.3, 75.1, 109.5, 172.1, 172.5 ppm. IR (KBr disk): 3855, 3630, 3457, 2988, 2954, 2359, 1737, 1438, 1372, 1257, 1210, 1164, 1063, 1007, 915, 853, 797, 642, 595, 548, 457, 431, 416 cm^{-1} . MS (m/z , relative intensity): 43 (100), 55 (11), 59 (18), 72 (17), 97 (15), 101 (13), 129 (11), 157 (33), 171 (22), 231 (13), 245 (0.2, M^+ -H). HRMS: m/z calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_6$: 246.1103; found: 246.1118.

3aJ-anti: 3.67 mg (8 %); colorless oil; ^1H -NMR (δ , CDCl_3): 1.33 (s, 3H), 1.40 (s, 3H), 2.74 (dd, $J = 4.4, 17.0$ Hz, 1H), 2.83 (dd, $J = 8.2, 17.0$ Hz, 1H), 2.97 (ddd, $J = 4.4, 8.2, 8.2$ Hz, 1H), 3.69 (s, 3H), 3.72 (s, 3H), 3.82 (dd, $J = 6.0, 8.8$ Hz, 1H), 4.12 (dd, $J = 6.4, 8.8$ Hz, 1H), 4.28 (ddd, $J = 6.0, 6.4, 8.2$ Hz, 1H) ppm. ^{13}C -NMR (δ , CDCl_3): 25.2, 26.5, 32.5, 45.4, 51.8, 52.2, 66.2, 75.0, 109.4, 172.4, 172.5 ppm. IR (KBr disk): 3630, 3461, 2988, 2954, 1738, 1439, 1414, 1372, 1258, 1211, 1167, 1064, 1007, 916, 854, 795, 758, 681, 644, 514, 430 cm^{-1} . MS (m/z , relative intensity): 43 (100), 55 (12), 59 (20), 72 (18), 97 (15), 101 (13), 111 (10), 129 (16), 157 (11), 171 (39), 246 (0.14, M^+). HRMS: m/z calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_6$: 246.1103; found: 246.1080.

2-(2, 2-Dimethyl-1, 3-dioxan-4-yl) butanedioic acid 1,4-dimethyl ester (3aK-syn, anti).

Dimethyl maleate (**1a-cis**, 28.61 mg, 0.20 mmol) and DTBP (14.93 mg, 0.10 mmol) in 2, 2-dimethyl-1,3-dioxane (**2K**, 10 mL). Irradiation time: 3 h. NMR yield (CDCl_3), 34% (*syn* / *anti* = 21 / 13) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (20/1 \rightarrow 0/1).

3aK-syn: 4.91 mg (10 %); colorless oil; ^1H -NMR (δ , CDCl_3): 1.2–1.48 (m, 1 H), 1.35 (s, 3 H), 1.44 (s, 3 H), 1.70 (dddd, $J = 5.6, 12.0, 12.4, 12.4$ Hz, 1 H), 2.60 (dd, $J = 4.8, 17.2$ Hz, 1 H), 2.75 (dd, $J = 10.0, 17.2$ Hz, 1 H), 3.08 (ddd, $J = 4.8, 5.6, 10.0$ Hz, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 3.84 (ddd, $J = 2.0, 5.6, 12.0$ Hz, 1 H), 3.94 (ddd, $J = 2.8, 12.0, 12.0$ Hz, 1 H), 4.20 (ddd, $J = 2.4, 5.6, 12.0$ Hz, 1 H) ppm. ^{13}C -NMR (δ , CDCl_3): 19.1, 27.2, 29.7, 31.1, 46.4, 51.8, 52.0, 59.6, 68.8, 98.7, 172.5, 172.6 ppm. IR (KBr disk): 2992, 2949, 2925, 2854, 1737, 1464, 1438, 1371, 1328, 1270, 1244, 1225, 1197, 1162, 1120, 1101, 1050, 1002, 970, 862, 847, 767, 524 cm^{-1} . MS (m/z , relative intensity): 41 (17), 43 (100), 55 (26), 57 (27), 58 (20), 59 (52), 67 (13), 71 (21), 93 (14), 115 (14), 125 (10), 139 (16), 153 (43), 171 (26), 245 (23), 260 (0.62, M^+). HRMS: m/z calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_6 + \text{H}$: 261.1338; found: 261.1344.

3aK-anti: 2.03 mg (4 %); colorless oil; ¹H-NMR (δ, CDCl₃): 1.34 (s, 3 H), 1.37–1.46 (m, 1 H), 1.42 (s, 3 H), 1.69 (dddd, *J* = 5.2, 11.6, 12.4, 12.4 Hz, 1 H), 2.73 (d, *J* = 7.2 Hz, 2 H), 2.90 (dt, *J* = 7.2, 7.2 Hz, 1 H), 3.67 (s, 3 H), 3.72 (s, 3 H), 3.83 (ddd, *J* = 1.6, 5.2, 12.0 Hz, 1 H), 3.94 (ddd, *J* = 3.0, 12.0, 12.4 Hz, 1 H), 4.08 (ddd, *J* = 2.8, 7.2, 11.6 Hz, 1 H) ppm. ¹³C-NMR (δ, CDCl₃): 19.1, 29.3, 29.7, 32.1, 47.3, 51.8, 52.0, 59.6, 69.0, 98.7, 172.7, 173.1 ppm. IR (KBr disk): 2993, 2953, 2925, 2871, 1737, 1438, 1381, 1338, 1267, 1245, 1199, 1165, 1131, 1092, 1049, 1025, 1009, 969, 843 cm⁻¹. MS (*m/z*, relative intensity): 41 (18), 43 (100), 44 (24), 55 (27), 57 (29), 58 (19), 59 (57), 67 (12), 71 (22), 73 (11), 93 (14), 115 (14), 125 (12), 139 (17), 153 (47), 171 (29), 245 (25). HRMS: *m/z* calcd. for C₁₂H₂₀O₆ + H: 261.1338; found: 261.1311.

2-(2-Methyl-1, 3-dioxolan-2-yl) butanedinitrile (3cG).

Fumaronitrile (**1c-cis**, 15.62 mg, 0.20 mmol) and DTBP (14.77 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Irradiation time: 0.5 h. NMR yield (CDCl₃), 71 % (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (80/1 → 0/1).

3cG: 23.40 mg (70 %); colorless oil. ¹H-NMR (δ, CDCl₃): 1.51 (s, 3H), 2.79 (dd, *J* = 8.0, 17.7 Hz, 1 H), 2.83 (dd, *J* = 6.0, 17.7 Hz, 1 H), 3.21 (dd, *J* = 6.0, 8.0 Hz, 1 H), 4.03 – 4.15 (m, 4 H) ppm. ¹³C-NMR (δ, CDCl₃): 16.5, 22.3, 38.1, 65.61, 65.63, 107.2, 116.1, 116.9 ppm. IR (KBr): 3001, 2979, 2950, 2898, 2247, 1440, 1390, 1268, 1237, 1211, 1170, 1106, 1062, 1027, 950, 891, 793, 719, 652, 559 cm⁻¹. MS (*m/z*, relative intensity): 40 (3), 41 (4), 42 (6), 43 (100), 44 (3), 45 (16), 51 (3), 52 (10), 53 (4), 54 (4), 66 (4), 79 (6), 80 (5), 87 (62), 88 (3), 93 (4), 07 (12), 151 (10). HRMS: *m/z* calcd. for C₈H₁₀O₂N₂ + Na: 189.0640; found: 189.0639.

2-(2, 2-Dimethyl-1, 3-dioxolan-4-yl) butanedinitrile (3cJ-syn, anti).

Fumaronitrile (**1c-cis**, 15.61 mg, 0.20 mmol) and DTBP (14.76 mg, 0.10 mmol) in 2, 2-dimethyl-1,3-dioxolane (**2J**, 10 mL). Irradiation time: 2 h. NMR yield (CDCl₃), 22 % (*syn* / *anti* = 12 / 10) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (1/0→0/1).

3cJ-syn: 3.9 mg (10 %); colorless oil; ¹H-NMR (δ, CDCl₃): 1.39 (s, 3H), 1.53 (s, 3H), 2.88 (d, *J* = 7.2 Hz, 2 H), 3.09 (dt, *J* = 3.2, 7.2 Hz, 1 H), 3.96 (dd, *J* = 5.6, 9.3 Hz, 1 H), 4.23 (dd, *J* = 6.4, 9.3 Hz, 1 H), 4.35 (ddd, *J* = 3.2, 5.6, 6.4 Hz, 1 H) ppm. ¹³C-NMR (δ, CDCl₃): 18.3, 25.0, 26.1, 33.0, 66.9, 73.1, 111.3, 115.5, 116.2 ppm. IR (KBr disk): 2989, 2939, 2251, 1458, 1423, 1375, 1260, 1220, 1152, 1111, 1062, 972, 933, 844, 511 cm⁻¹. MS (*m/z*, relative

intensity): 40 (49), 41 (9), 42 (11), 43 (100), 44 (5), 52 (2), 59 (3), 72 (7), 73 (3), 101 (2), 110 (4), 165 (17, M^+ -Me).

3cJ-anti: 3.4 mg (9 %); colorless oil; $^1\text{H-NMR}$ (δ , CDCl_3): 1.36 (s, 3H), 1.46 (s, 3H), 2.81 (dd, $J = 7.2, 17.2$ Hz, 1 H), 2.87 (dd, $J = 5.2, 17.2$ Hz, 1 H), 2.96 (ddd, $J = 5.2, 7.2, 7.8$ Hz, 1 H), 4.03 (dd, $J = 3.6, 9.2$ Hz, 1 H), 4.23 – 4.33 (m, 2 H) ppm. $^{13}\text{C-NMR}$ (δ , CDCl_3): 18.0, 24.8, 26.9, 33.2, 67.4, 74.0, 111.5, 115.2, 116.4 ppm. IR (KBr disk): 2988, 2937, 2250, 1456, 1423, 1375, 1259, 1215, 1151, 1059, 981, 840, 514 cm^{-1} . MS (m/z , relative intensity): 40 (4), 41 (10), 42 (12), 43 (100), 44 (6), 52 (2), 59 (3), 61 (3), 72 (7), 101 (3), 110 (4), 165 (16, M^+ -Me).

3-(2-Methyl-1, 3-dioxolan-2-yl) propionic acid *tert*-butyl ester (3dG).

tert-Butyl acrylate (**1d**, 25.43 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Irradiation time: 0.5 h. NMR yield (CDCl_3), 36 % (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (20/1 \rightarrow 0/1).

3dG: 13.45 mg (31 %); colorless oil; $^1\text{H-NMR}$ (δ , CDCl_3): 1.32 (s, 3 H), 1.44 (s, 9 H), 1.97 (t, $J = 7.8$ Hz, 2 H), 2.31 (t, $J = 7.8$, 2 H), 3.89 – 3.98 (m, 4 H) ppm. $^{13}\text{C-NMR}$ (δ , CDCl_3): 24.0, 28.0, 30.3, 34.0, 64.7, 80.1, 109.3, 172.9 ppm. IR (KBr disk): 3440, 2979, 2932, 2883, 2678, 2370, 2321, 1731, 1478, 1455, 1391, 1368, 1311, 1282, 1255, 1157, 1099, 1056, 977, 948, 866, 852, 805, 756, 650, 559, 526, 491, 439 cm^{-1} . MS (m/z , relative intensity): 41 (53), 43 (67), 57 (31), 87 (100), 99 (24), 143 (18), 145 (15), 216 (0.05, M^+). HRMS: m/z calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_4 + \text{H}$: 217.1440; found: 217.1498.

3-Methyl-3-(2-methyl-1, 3-dioxolan-2-yl) propanoic acid *tert*-butyl ester (3eG).

tert-Butyl crotonate (**1e**, 28.76 mg, 0.20 mmol) and DTBP (14.97 mg, 0.10 mmol) 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Irradiation time: 0.5 h. NMR yield (CDCl_3), 49 % (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (20/1 \rightarrow 0/1).

3eG: 21.75 mg (47 %); colorless oil; $^1\text{H-NMR}$ (δ , CDCl_3): 1.00 (d, $J = 6.9$ Hz, 3 H), 1.26 (s, 3 H), 1.45 (s, 9 H), 1.98 (dd, $J = 8.9, 14.9$ Hz, 1 H), 2.19–2.33 (m, 1 H), 2.49 (dd, $J = 5.3, 14.9$ Hz, 1 H), 3.88–3.99 (m, 4 H) ppm. $^{13}\text{C-NMR}$ (δ , CDCl_3): 15.3, 20.6, 28.1, 38.2, 38.5, 64.6, 64.7, 80.0, 111.4, 172.6 ppm. IR (KBr disk): 2979, 1730, 1458, 1368, 1296, 1256, 1154, 959, 872, 847, 760 cm^{-1} . MS (m/z , relative intensity): 41 (24), 43 (43), 57 (14), 87 (100), 113 (12), 157 (10), 231 (0.01, M^+). HRMS: m/z calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_4$: 230.1512; found: 230.1514.

2-Isopropenylbutanedioic acid 1,4-dimethyl ester (3aL-a)³⁸ and
2-isopropylbutanedioic acid 1,4-dimethyl ester (3aL-b).³⁹

Dimethyl maleate (**1a-cis**, 30.02 mg, 0.21 mmol) and DTBP (16.21 mg, 0.11 mmol) in isopropyl ether (**2L**, 10 mL). Irradiation time: 3 h. NMR yield (CDCl₃), **3aL-a**: 30 %, **3aL-b**: 23 % (conversion: 100 %). Eluent for chromatography: hexane/CH₂Cl₂ (1/0 → 1/25 and then 1/0 → 19/1). Only a part of **3aL-a** was isolated by two chromatographic separations and **3aL-b** was obtained as a mixture with **3aL-a**.

3aL-a: 8.4 mg (22 %); colorless oil; ¹H-NMR (δ, CDCl₃): 1.76 (s, 3 H), 2.52 (dd, *J* = 5.5, 16.5 Hz, 1 H), 2.95 (dd, *J* = 9.6, 16.5 Hz, 1 H), 3.55 (dd, *J* = 5.5, 9.6 Hz, 1 H), 3.68 (s, 3 H), 3.71 (s, 3H), 4.91 (d, *J* = 1.0 Hz, 1 H), 4.93 (dd, *J* = 1.0, 1.5, 1 H), ppm. ¹³C-NMR (δ, CDCl₃): 20.6, 35.1, 48.5, 51.8, 52.2, 114.3, 141.3, 172.1, 173.0 ppm. IR (KBr disk): 3082, 2953, 2847, 1738, 1647, 1437, 1339, 1296, 1260, 1217, 1163, 1096, 1003, 964, 901, 847, 772, 559 cm⁻¹. MS (*m/z*, relative intensity): 53 (27), 55 (100), 59 (61), 67 (56), 68 (23), 69 (51), 81 (13), 83 (66), 84 (46), 85 (86), 94 (16), 95 (42), 96 (14), 109 (14), 113 (26), 114 (18), 122 (24), 123 (28), 124 (31), 125 (13), 126 (20), 127 (29), 146 (42), 154 (42), 155 (98), 186 (M⁺, 6), 187 (M⁺+1, 11).

3aL-b: 13.8 mg (mixture with **3aL-a**); ¹H-NMR (δ, CDCl₃): 0.92 (d, *J* = 6.0 Hz, 3 H), 0.94 (d, *J* = 6.0 Hz, 3 H), 1.93–2.04 (m, 1 H), 2.42 (ddd, *J* = 8.7, 8.7, 12.8 Hz, 1 H), 2.68–2.78 (m, 2 H), 3.67 (s, 3 H), 3.70 (s, 3 H) ppm. ¹³C-NMR (δ, CDCl₃): 19.6, 20.1, 30.1, 32.9, 47.4, 51.6, 51.8, 172.9, 174.9 ppm. IR (mixture with **3aL-a**) (KBr disk): 2953, 2916, 1738, 1437, 1373, 1348, 1260, 1194, 1163, 1115, 1020, 1005, 899, 849 cm⁻¹. MS (mixture with **3aL-a**) (*m/z*, relative intensity): 45 (12), 54 (16), 55 (50), 59 (100), 67 (28), 68 (13), 69 (26), 83 (18), 84 (10), 85 (38), 87 (11), 94 (11), 95 (15), 97 (13), 101 (26), 113 (25), 114 (37), 115 (16), 122 (16), 126 (13), 146 (17), 154 (26), 155 (31), 157 (19), 188 (M⁺, 0.0), 189 (M⁺+1, 0.02).

2-4-5 General procedure for the hydrolysis of esters 3aA-syn and 3aA-anti

To a 20 mL round bottom flask fitted with a reflux condenser and a magnetic stirrer was added **3aA** (*syn* or *anti*), 5 mL of AcOH, and 5 mL of 6N HCl. The reaction mixture was heated at 100 °C for 3 h under a nitrogen atmosphere. After evaporation of the solvent in vacuo, the crude white solid was purified by silica gel column chromatography (ethyl acetate/acetic acid = 1/0 → 30/1).

2-(Tetrahydro-2-furanyl) butanedioic acid (*syn*) (3bA-*syn*).^{33a, 35}

3aA-*syn* (39.55 mg, 0.18 mmol) was hydrolyzed and purified to **3bA-*syn*** (8.7 mg, 25 %), white solid; ¹H NMR (acetone-*d*₆): δ = 1.65–1.77 (1H, m), 1.80–1.99 (3H, m), 2.45 (1H, dd, *J* = 3.9, 16.8 Hz), 2.68 (1H, dd, *J* = 10.3, 16.8 Hz), 3.00 (1H, ddd, *J* = 3.9, 6.3, 10.3 Hz), 3.66 (1H, ddd, *J* = 6.5, 7.7, 7.7 Hz), 3.82 (1H, ddd, *J* = 6.5, 8.2, 8.2 Hz), 4.06 (1H, ddd, *J* = 6.3, 6.5, 7.6 Hz), 10.8 (2H, br s) ppm. ¹³C NMR (acetone-*d*₆): δ = 26.3, 29.0, 32.6, 46.5, 68.6, 79.7, 173.4, 174.1 ppm. IR (KBr): 3437 (br), 3044 (br), 2984 (br), 2967 (br), 2930 (br), 2886 (br), 1773, 1699, 1437, 1408, 1314, 1275, 1254, 1219, 1192, 1138, 1114, 1070, 1020, 999, 941, 923, 841, 696, 667, 542, 444 cm⁻¹. MS, *m/z* (relative intensity): 40 (10), 41 (54), 42 (28), 43 (96), 44 (36), 45 (19), 53 (9), 55 (37), 57 (11), 67 (8), 69 (9), 71 (100), 97 (7), 111 (29), 114 (8), 125 (9), 129 (47), 143 (7), 188 (0.1, M⁺).

2-(Tetrahydro-2-furanyl) butanedioic acid (*anti*) (3bA-*anti*).^{33a, 35}

3aA-*anti* (23.20 mg, 0.11 mmol) was hydrolyzed and purified to **3bA-*anti*** (6.1 mg, 30 %), white solid; ¹H NMR (acetone-*d*₆): δ = 1.72–1.82 (1H, m), 1.82–1.94 (2H, m), 1.94–2.20 (1H, m), 2.63 (1H, dd, *J* = 5.0, 16.9 Hz), 2.69 (1H, dd, *J* = 8.5, 16.9 Hz), 2.82 (1H, ddd, *J* = 5.0, 7.3, 8.5 Hz), 3.65 (1H, ddd, *J* = 6.5, 7.4, 8.0 Hz), 3.78 (1H, ddd, *J* = 6.5, 6.6, 6.6 Hz), 3.98 (1H, ddd, *J* = 7.0, 7.0, 7.3 Hz), 10.5 (2H, br s) ppm. ¹³C NMR (acetone-*d*₆): δ = 26.2, 30.4, 33.4, 47.2, 68.3, 80.0, 173.6, 174.3 ppm. IR (KBr): 3435 (br), 2978 (br), 2957 (br), 2928 (br), 2882 (br), 1732, 1705, 1558, 1435, 1402, 1385, 1352, 1312, 1275, 1234, 1175, 1065, 1045, 1016, 991, 957, 928, 841, 698, 665, 642, 604, 567, 521, 440 cm⁻¹. MS, *m/z* (relative intensity): 40 (8), 41 (56), 42 (32), 43 (86), 44 (24), 45 (20), 53 (9), 55 (35), 57 (8), 67 (7), 69 (9), 71 (100), 72 (7), 97 (7), 100 (6), 111 (34), 114 (6), 129 (57), 188 (0.03, M⁺).

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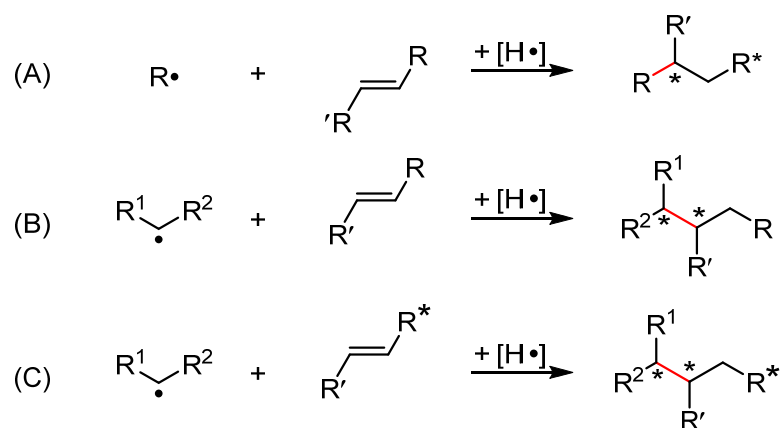
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Chapter 3

Diastereoselective
photochemical addition reaction of THF
to various dialkyl maleates

3-1 Introduction

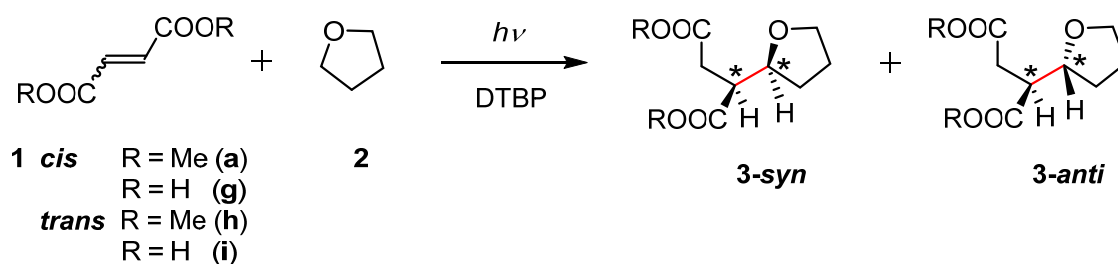
Diastereoselective reactions have been developed in order to introduce new asymmetric centers into a molecule, and these reactions have been also studied in the carbon radical addition reaction of olefins.¹⁻⁴ A typical reaction is the addition of a carbon radical to an asymmetric olefin, which generates an asymmetric carbon atom via the formation a new C-C bond in the olefin due to the steric effects of the original asymmetric center in the olefin (Scheme 1A).⁵⁻¹¹ If the addition of carbon radicals to non-asymmetric olefins proceeds diastereoselectively (Scheme 1B), i.e. the selective formation of one of the two sets of enantiomers, the introduction of two new asymmetric carbon atoms using a single reaction will be accomplished by the combination of reactions A and B (Scheme 1C). Therefore, the development of reactions that correspond to Scheme 1B is essential for realizing the reactions outlined in Scheme 1C.



Scheme 1. Diastereoselective carbon radical addition reactions of olefins: (A) Addition to asymmetric olefins, (B) addition to non-asymmetric olefins, and (C) addition to asymmetric olefins in combination with reaction type B. The asymmetric carbons are indicated using asterisks (*).

In the course of our study on the photochemical C-C bond formation reactions between cyclic ethers and olefins, we discovered an interesting diastereoselective photochemical addition of THF (**2**) to dimethyl maleate (**1a**) (Scheme 2), which corresponds to the reaction shown in Scheme 1B. The diastereomeric ratio (*d.r.*), **3a-syn**/**3a-anti**, was found to be 1.6/1.0; the *syn* and *anti* isomers were assigned according to the literature.¹² In contrast, the *d.r.* was very small during the addition of **2** to maleic acid (**1g**, 0.9/1.0 *d.r.*), dimethyl fumarate (**1h**, 0.9/1.0 *d.r.*), and fumaric acid (**1i**, 0.8/1.0 *d.r.*).¹² However, previous studies on the addition reaction of a THF radical to **1a**, using an Ir photoredox catalyst¹³ and radical initiator (PhCOCO₂H)¹⁴ have been reported to show no diastereoselectivity (1/1 *d.r.*), which are

inconsistent with our results. In the latter report, the reaction was also conducted using other dialkyl esters of maleic acid (cf. Scheme 2); although no diastereoselectivity (50/50 *d.r.*) was observed in the reactions with R = *n*-Pr, *iso*-Pr (**1e**), *sec*-Bu, allyl, methoxyethyl, and *p*-chlorobenzyl groups, those with R = Et (60/40 *d.r.*), benzyl (80/20 *d.r.*), *p*-methylbenzyl (60/40 *d.r.*), and *p*-*tert*-butylbenzyl (60/40 *d.r.*) showed diastereoselectivity.¹⁴



Scheme 2. The addition of a THF radical to various olefins (**1**). The asterisks (*) show the carbon atoms where the two new asymmetric centers were generated.

On the other hand, the addition of a THF radical to olefins **4–7** using eosin Y as a photocatalyst showed no diastereoselectivity,¹⁵ but that to **8** using neutral eosin Y and a Rh catalyst¹⁶ showed a small amount of diastereoselectivity (57/43 *d.r.*) (Figure 1).

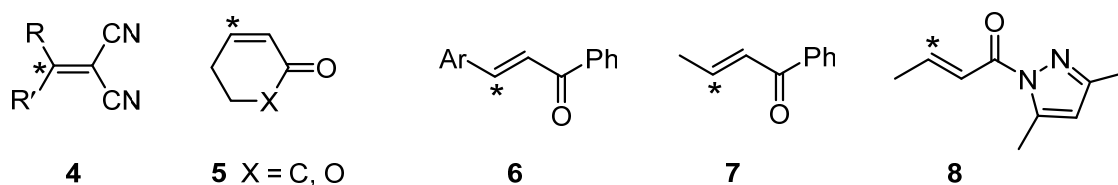


Figure 1. The olefins used for the addition of a THF radical. The asterisks (*) shows the carbon atoms where a new stereo-center was expected to be formed during the addition reaction.

As demonstrated in the literature, the diastereoselectivity of the addition reaction of a THF radical to olefins has still not been established and the origin of the diastereoselectivity has not been considered until now. In this chapter, we report clear evidence for the presence of the diastereoselectivity during the addition of a THF radical to dialkyl maleates and that the origin of the diastereoselectivity is the steric effect of the R groups.

3-2 Results and Discussion

The reactions between THF (**2**) and various maleic acid esters bearing different R groups (**1a–f**) have been conducted and the results are summarized in Table 1. The photolyses were performed using a radical initiator, di-*tert*-butyl peroxide (DTBP), and >290 nm light at room temperature under a nitrogen atmosphere.¹² The yields of the *syn*- and *anti*-isomers for each product were determined using NMR spectroscopy with naphthalene as an internal standard. The *syn*- and *anti*- isomers were isolated using column chromatography.

Table 1. Diastereomeric ratio (*d.r.*) of **3** (**3-syn**/**3-anti**) during the addition of THF (**2**) to maleic acid dialkyl esters (**1a–f**).^a

Entry	1-cis R		Yield ^b 3-syn / 3-anti (%)	<i>d.r.</i> ^b <i>syn/anti</i> ratio
1	Me	1a	60/35	1.7/1.0
2	Bu	1b	65/35 (62/34) ^c	1.8/1.0 (1.8/1.0) ^c
3		1c	60/28 (57/24) ^c	2.1/1.0 (2.4/1.0) ^c
4		1d	66/32 (59/29) ^c	2.0/1.0 (2.0/1.0) ^c
5	<i>iso</i> -Pr	1e	63/31 (60/29) ^c	2.0/1.0 (2.1/1.0) ^c
6	<i>tert</i> -Bu	1f	67/29 (65/25) ^c	2.3/1.0 (2.6/1.0) ^c

[a] Photolysis condition, substrates: **1** (0.2 mmol) and DTBP (0.1 mmol) in THF (10 mL), light source: 500-W xenon short-arc lamp fitted with an 18-cm water filter and a UV-29 cut-off filter (2.0 mW·cm⁻²), irradiation time: 4 h, N₂ atm, room temp. [b] The yield and *syn/anti* ratio were determined by NMR spectroscopy using naphthalene as an internal standard. The NMR ratios are the average of two independent runs, whose experimental errors were < 5%. [c] Yield of isolated products **3-syn** and **3-anti** isomers and their *syn/anti* ratio.

As seen in Table 1, the reactions proceed in high yield for all R groups and the *d.r.* of the addition product (**3**) increased with an increase in the length of the alkyl chain R: Me (**1a**, 1.7/1.0 *d.r.*) < Bu (**1b**, 1.8/1.0 *d.r.*) < decyl (**1c**, 2.1/1.0 *d.r.*) (Entries 1–3). The increase in the *d.r.* was also observed when the carbon adjacent to the alkoxy oxygen was varied from a *primary*, *secondary*, and *tertiary*: Bu (**1b**, 1.8/1.0 *d.r.*) < *iso*-Pr (**1e**, 2.0/1.0 *d.r.*) < *tert*-Bu (**1f**, 2.3/1.0 *d.r.*) (Entries 2, 5, and 6). The introduction of an alkyl side chain at the second carbon

atom from the alkoxy oxygen did not show any significant effect on the *d.r.*: decyl (**1c**, 2.1/1.0 *d.r.*) \approx 2-ethylhexyl (**1d**, 2.0/1.0 *d.r.*) (Entries 3 and 4). These results indicate that the steric effect of the R groups is an important factor for determining the *d.r.* (*syn/anti* ratio), in which the *d.r.* increases with an increase in the bulkiness of the R groups.

Figure 2 shows the stable ground state conformations of substrate olefins **1a–1g** obtained using DFT calculations;¹⁷ the detailed conformations and energies for each olefin are shown in the appendix of this chapter. Fumaric acid (**1i**) and its dimethyl ester (**1h**), which show no diastereoselectivity in the addition reaction, have a planar conformation (Conformer 3). On the other hand, maleic acid (**1g**) and its dimethyl ester (**1a**) showed two stable conformers with similar energies (Conformers 1 and 2). Conformer 1 has normal conjugation between the π -electron systems in the olefin and one of the ester groups, but that of the other ester is twisted out from the conjugated π -electron system. In the case of conformer 2, the π -electron systems of the two ester groups are both slightly twisted out from the π -electron system of the olefin, but considerable conjugation of the π -electron systems is maintained between the olefin and the two ester groups. The presence and absence of diastereoselectivity in the reactions of **1a** and **1g**, respectively, are probably due to the difference in the bulkiness between R = Me and H. As for linear alkyl groups, olefins **1b** and **1c** exhibited two stable conformations, conformers 1 and 2 with the same energy, which were also obtained from our DFT calculations. Linear R groups seem to have interactions similar to that of the Me groups. However, R = 2-ethylhexyl (**1d**), *iso*-Pr (**1e**), and *tert*-Bu (**1f**) only have conformer 1 as their stable conformation.

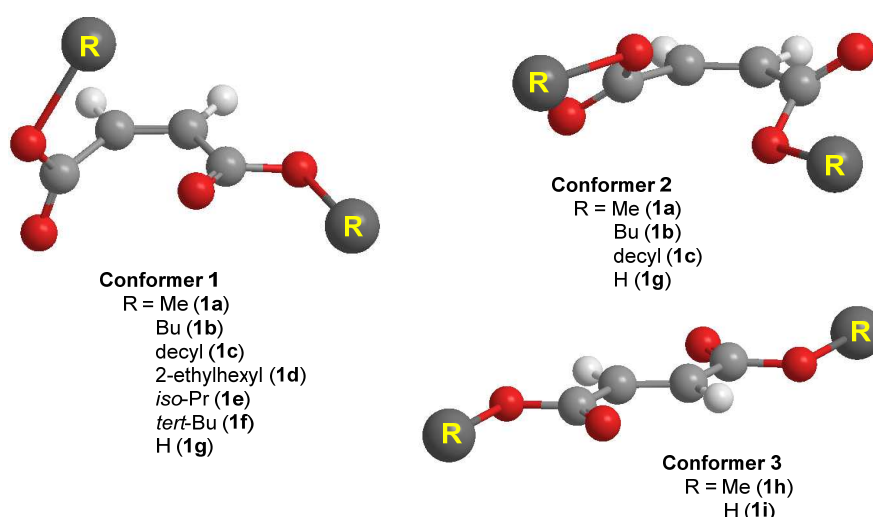


Figure 2. The stable ground state conformations of substrate olefins calculated using DFT calculations utilizing the B3LYP functional.¹⁷

These results indicate that the steric bulkiness near the carbon atom adjacent to the alkoxy oxygen atom seems to have a considerable effect on the conformation of the olefins via the interaction between the two R groups. However, it is still not clear which of the two isomers are responsible for determining the *d.r.* of the obtained products. The reactions of **1d–f** indicate that conformer 1 is responsible for determining the *d.r.* because their stable conformation is only conformer 1. On the other hand, **1c** with conformers 1 and 2 as its stable form, has a similar *d.r.* as those of **1d** and **1e**, which have only conformer 1 as their stable form. Conformers 1 and 2 of **1c** have the same energy so that both conformers are expected to exist in the same ratio, and if conformer 2 is not responsible for determining the *d.r.*, the *d.r.* of **1c** should be smaller than those of **1d** and **1e**. Therefore, these results indicate that conformer 2 is also responsible for determining the *d.r.* of the reaction adducts.

In contrast to previous reports (*vide supra*),^{13,14} clear evidence for the presence of diastereoselectivity was observed during the addition of **2** to olefin **1** in our study. The difference in the results between previous reports and our study is not clear at the moment as no explanation of the diastereoselectivity has been given in the previous reports.¹⁴ However, a comparison of the reaction procedures suggested that the difference in the reaction temperature could be the reason for the different *d.r.* Therefore, we have conducted our reaction using **1a** and **2** at 50 °C, but the *d.r.* (*syn/anti* ratio) was found to be 61/38, which was almost the same as the *d.r.* obtained at room temperature. This result indicates that the reaction temperature was not a factor for determining the *d.r.* of the reaction, and the reason for the difference in the result is still not clear at the moment.

3-3 Conclusion

The addition reactions of carbon radicals to olefins have been reported, but the stereochemistry of the carbon atoms on *both* sides of the newly formed C-C bond have not been studied in detail. In particular, the diastereoselectivity during the addition of a THF (**2**) radical to dialkyl maleates (**1**), a fundamental reaction, has not been established; both the presence and absence of diastereoselectivity has been reported in the literature. Our systematic study has shown a diastereoselective reaction took place during the addition of a THF radical to dialkyl maleates (**1a–f**), whose *d.r.* increased with the bulkiness of the alkyl groups. DFT calculations on **1a–f** showed the presence of one or two stable conformations that depend on the bulkiness of the alkyl groups.

3-4 Experimental Section

3-4-1 General Remarks

¹H and ¹³C NMR spectra were recorded on JEOL JNM-ECX400 spectrometer with CDCl₃ as solvent. As internal standards, TMS (δ 0.0 ppm) in CDCl₃ were used for ¹H NMR, and CDCl₃ (δ 77.0 ppm) for ¹³C NMR analyses. IR spectra were recorded on a JASCO FT/IR-4700 spectrometer. MS spectra were recorded on a Shimadzu GCMS-QP2010 plus spectrometer. HRMS spectra were recorded on an Agilent G1969 LC/MDS TOF mass spectrometer. Olefins **1a**, **1b**, **1d**, **1f**, THF (**2**) and DTBP were purchased and used as bought. Olefins **1c**¹⁸ and **1e**¹⁹ were synthesized according to the reported procedures. Stable ground state conformations of **1a-1i** were calculated by B3LYP/6-31++G(d,p) using Gaussian 16.¹⁷

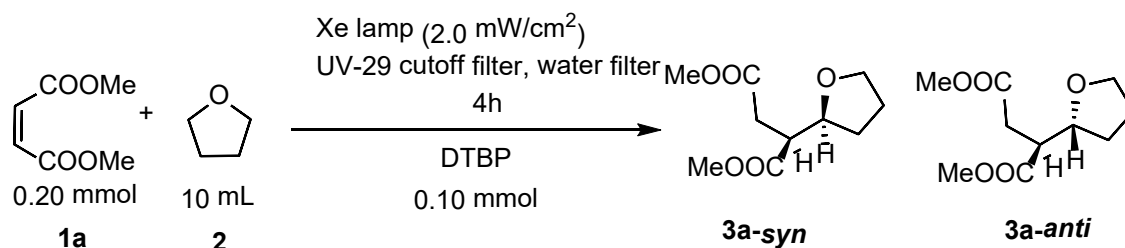
3-4-2 General procedure for the photolysis¹²

A THF (**2**) (10 mL) solution of olefin (**1a-f**) (0.2 mmol) and DTBP (0.1 mmol) was introduced into a quartz cylindrical cell (diameter: 3 cm) equipped with a three-way stopcock. The three-way stopcock was connected to the cell, a nitrogen source, and small vacuum pump. The solution was evacuated to about 50 mmHg under sonication for 5 s and nitrogen was then introduced into the cell; this cycle was repeated 10 times to remove oxygen efficiently from the solution. The photolysis was conducted using a 500-W xenon lamp (USHIO Optical Modulex SX-UI500XQ) fitted with an 18-cm water filter and a cut-off filter (Toshiba UV-29) under a nitrogen atmosphere. The irradiated light intensity was 2.0 mW/cm², which was measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with a UVD-S365 photo detector. After photolysis, THF was removed in vacuo at 40–50 °C / < 70 Torr (most of the products were volatile under reduced pressure) and the consumption of the olefin and the products yield were determined by NMR spectroscopy using a precise amount of naphthalene as an internal standard. The isolation of the products was conducted using silica gel column chromatography.

3-4-3 Experimental details of the reactions in Table 1.

3-4-3-1 Entry 1: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-dimethyl ester (**3a-cis**)

12–14



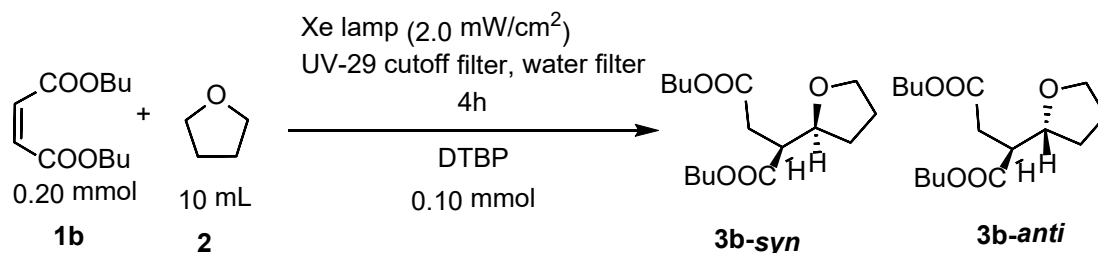
Run 1

Dimethyl maleate (**1a-cis**, 28.87 mg, 0.20 mmol) and DTBP (14.76 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3a**: quantitative % (*syn* / *anti* = 61 / 39) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a-cis**, 28.79 mg, 0.20 mmol) and DTBP (14.76 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3a**: 95 % (*syn* / *anti* = 60 / 35) (conversion: 100 %) (NMR, CDCl₃).

3-4-3-2 Entry 2: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-dibutyl ester (**3b**)



Run 1

Dibutyl maleate (**1b**, 45.52 mg, 0.20 mmol) and DTBP (15.14 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3b**: quantitative % (*syn* / *anti* = 65 / 35) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Dibutyl maleate (**1b**, 45.61 mg, 0.20 mmol) and DTBP (14.68 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3b**: quantitative % (*syn* / *anti* = 65 / 35) (conversion: 100 %) (NMR, CDCl₃).

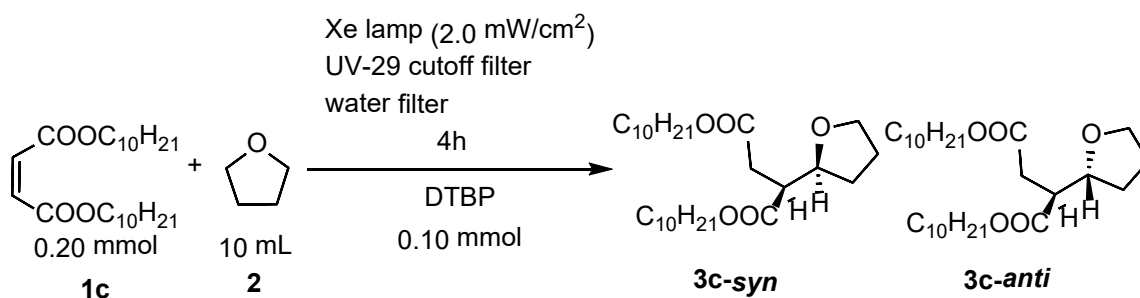
Eluent for chromatography: hexane/ethyl acetate (50/1 → 0/1).

3b-syn: 37.29 mg (62 %); colorless oil. ¹H-NMR (CDCl₃): δ = 0.92 (t, *J* 7.4 Hz, 3 H), 0.93 (t, *J* 7.4 Hz, 3 H), 1.32-1.44 (m, 4 H), 1.54-1.72 (m, 5 H), 1.83-1.97 (m, 3 H), 2.46 (dd, *J* 4.0, 16.6 Hz, 1 H), 2.76 (dd, *J* 10.0, 16.6 Hz, 1 H), 3.10 (ddd, *J* 4.0, 6.4, 10.0 Hz, 1 H), 3.74 (ddd, *J* 6.8, 6.8, 8.4 Hz, 1 H), 3.86 (ddd, *J* 6.4, 6.4, 8.4 Hz, 1 H), 4.04-4.17 (m, 5 H) ppm. ¹³C-NMR (CDCl₃): δ = 13.7 (×2), 19.1 (×2), 25.7, 28.4, 30.6 (×2), 32.5, 46.1, 64.6, 64.7, 68.4, 78.9, 171.9, 172.8 ppm. IR (KBr disk): 3451, 2960, 2874, 1736, 1465, 1392, 1259, 1168, 1068,

1023, 947, 756, 665 cm^{-1} . MS, m/z (relative intensity): 41 (35), 42 (5), 43 (31), 44 (10), 55 (8), 56 (11), 71 (100), 129 (7), 227 (1). HRMS: m/z calcd. For $\text{C}_{16}\text{H}_{28}\text{O}_5 + \text{Na}$: 323.1834; found: 323.1833.

3b-anti: 21.00 mg (34 %); colorless oil. $^1\text{H-NMR}$ (CDCl_3): δ = 0.92 (t, J 7.4 Hz, 3 H), 0.93 (t, J 7.4 Hz, 3 H), 1.38 (tq, J 7.4, 7.4 Hz, 2 H), 1.38 (tq, J 7.4, 7.4 Hz, 2 H), 1.55-1.66 (m, 4 H), 1.69-1.79 (m, 1 H), 1.82-2.04 (m, 3 H), 2.69 (dd, J 4.8, 16.4 Hz, 1 H), 2.78 (dd, J 9.6, 16.4 Hz, 1 H), 2.89 (ddd, J 4.8, 8.0, 9.6 Hz, 1 H), 3.73 (ddd, J 6.8, 7.2, 7.2 Hz, 1 H), 3.81 (ddd, J 6.4, 6.8, 8.0 Hz, 1 H), 3.99 (ddd, J 6.8, 7.2, 7.2 Hz, 1 H), 4.03-4.16 (m, 4 H) ppm. $^{13}\text{C-NMR}$ (CDCl_3): δ = 13.7 ($\times 2$), 19.08, 19.11, 25.6, 29.7, 30.58, 30.61, 33.5, 46.9, 64.5, 64.7, 68.0, 78.8, 172.3, 172.9 ppm. IR (KBr disk): 2959, 2937, 2873, 1737, 1464, 1415, 1390, 1357, 1260, 1166, 1121, 1066, 1024, 963 cm^{-1} . MS, m/z (relative intensity): 41 (41), 42 (8), 43 (32), 44 (7), 56 (17), 57 (8), 71 (100), 129 (7), 171 (5), 185 (5), 227 (2). HRMS: m/z calcd. For $\text{C}_{16}\text{H}_{28}\text{O}_5 + \text{Na}$: 323.1834; found: 323.1832.

3-4-3-3 Entry 3: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-didecyl ester (**3c**)



Run 1

Didecyl maleate (**1c**, 79.08 mg, 0.20 mmol) and DTBP (14.86 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3c**: 86 % ($\text{syn} / \text{anti} = 60 / 26$) (conversion: 100 %) (NMR, CDCl_3).

Run 2

Didecyl maleate (**1c**, 79.56 mg, 0.20 mmol) and DTBP (14.85 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3c**: 89 % ($\text{syn} / \text{anti} = 60 / 29$) (conversion: 100 %) (NMR, CDCl_3).

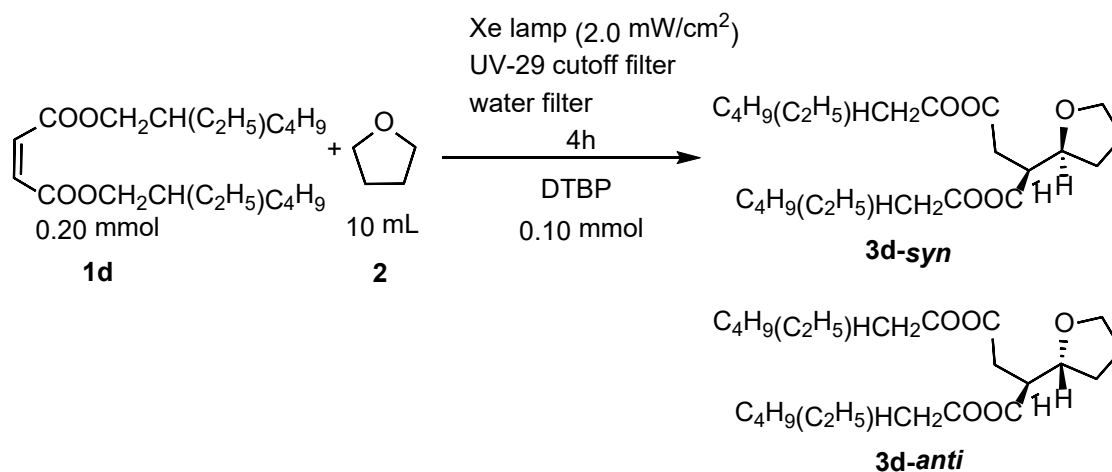
Eluent for chromatography: hexane/ethyl acetate (50/1 \rightarrow 0/1).

3c-syn: 40.20 mg (57 %); colorless oil. $^1\text{H-NMR}$ (CDCl_3): δ = 0.88 (t, J 6.6 Hz, 6 H), 1.20-1.38 (m, 28 H), 1.56-1.72 (m, 5 H), 1.84-1.97 (m, 3 H), 2.46 (dd, J 4.8, 16.4 Hz, 1 H), 2.76 (dd, J 10.0, 16.4 Hz, 1 H), 3.10 (ddd, J 4.8, 6.4, 10.0 Hz, 1 H), 3.74 (ddd, J 6.4, 6.4, 6.8 Hz, 1 H), 3.86 (ddd, J 6.4, 6.4, 8.4 Hz, 1 H), 4.00-4.18 (m, 5 H) ppm. $^{13}\text{C-NMR}$ (CDCl_3): δ =

14.1 (×2), 22.7 (×2), 25.7, 25.9 (×2), 28.4, 28.6 (×2), 29.25 (×2), 29.30 (×2), 29.5 (×4), 31.9 (×2), 32.5, 46.1, 64.9, 65.0, 68.4, 78.9, 171.9, 172.7 ppm. IR (KBr disk): 2954, 2925, 2855, 1737, 1466, 1413, 1358, 1259, 1165, 1069, 920, 733 cm⁻¹. MS, m/z (relative intensity): 41 (19), 43 (43), 44 (8), 55 (14), 57 (15), 71 (100), 129 (8), 171 (8), 269 (7). HRMS: *m/z* calcd. For C₂₈H₅₂O₅ +Na: 491.3712; found: 491.3712.

3c-anti: 24.31 mg (24 %); colorless oil. ¹H-NMR (CDCl₃): δ = 0.88 (t, *J* 6.8 Hz, 6 H), 1.26-1.35 (m, 28 H), 1.56-1.67 (m, 4 H), 1.69-1.79 (m, 1H), 1.83-2.03 (m, 3 H), 2.69 (dd, *J* 4.8, 16.4 Hz, 1 H), 2.78 (dd, *J* 9.2, 16.4 Hz, 1 H), 2.89 (ddd, *J* 4.8, 7.6, 9.2 Hz, 1 H), 3.73 (ddd, *J* 6.4, 7.2, 7.2 Hz, 1 H), 3.79 (ddd, *J* 7.2, 7.6, 8.0 Hz, 1 H), 4.01 (ddd, *J* 6.4, 7.0, 7.0 Hz, 1H), 4.01-4.15 (m, 4 H) ppm. ¹³C-NMR (CDCl₃): δ = 14.1 (×2), 22.7 (×2), 25.6, 25.9 (×2), 28.5, 28.6, 29.2, 29.26, 29.30 (×2), 29.5 (×4), 29.7, 31.9 (×2), 33.5, 46.9, 64.8, 65.0, 68.0, 78.8, 172.3, 172.9 ppm. IR (KBr disk): 2954, 2925, 2855, 1735, 1466, 1164, 1067, 913, 771, 736 cm⁻¹. MS, m/z (relative intensity): 41 (19), 43 (41), 44 (10), 55 (13), 57 (13), 71 (100), 129 (8), 171 (8), 269 (7). HRMS: *m/z* calcd. For C₂₈H₅₂O₅ +Na: 491.3712; found: 491.3712.

3-4-3-4 Entry 4: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-bis(2-ethylhexyl)ester (3d)



Run 1

Bis(2-ethylhexyl) maleate (**1d**, 68.07 mg, 0.20 mmol) and DTBP (14.79 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3d**: 99 % (*syn* / *anti* = 67/ 32) (conversion: 100 %) (NMR, CDCl₃).

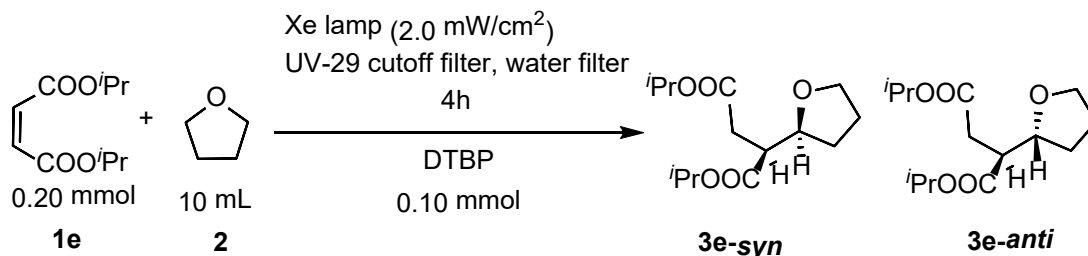
Run 2

Bis(2-ethylhexyl) maleate (**1d**, 68.18 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3d**: 96 % (*syn* / *anti* = 62/ 34) (conversion: 100 %) (NMR, CDCl₃). Eluent for chromatography: hexane/ethyl acetate (50/1 → 0/1).

3d-syn: 48.62 mg (59 %); colorless oil. ¹H-NMR (CDCl₃): δ = 0.88 (t, *J* 7.2 Hz, 6H), 0.89 (t, *J* 7.2 Hz, 6H), 1.21-1.41 (m, 16 H), 1.51-1.62 (m, 2 H), 1.63-1.72 (m, 1 H), 1.84-1.96 (m, 3 H), 2.47 (dd, *J* 4.4, 16.8 Hz, 1 H), 2.77 (dd, *J* 10.2, 16.8 Hz, 1 H), 3.14 (ddd, *J* 4.4, 6.4, 10.2 Hz, 1 H), 3.73 (ddd, *J* 7.2, 7.2, 8.0, 1 H), 3.86 (ddd, *J* 6.4, 6.4, 8.0, 1 H), 3.92-4.13 (m, 5 H) ppm. ¹³C-NMR (CDCl₃): δ = 10.89, 10.92, 10.94, 14.0 (×2), 23.0, 23.66, 23.68, 25.7, 28.3, 28.8, 28.9, 30.29, 30.34, 32.3, 38.64, 38.66, 38.68, 46.0, 67.1, 68.4, 78.8, 172.0, 172.7 ppm. IR (KBr disk): 2956, 2926, 2859, 1732, 1462, 1381, 1259, 1164, 1067, 1023, 773, 729, 676, 583, 556, 507 cm⁻¹. MS, *m/z* (relative intensity): 41 (49), 42 (11), 43 (47), 55 (37), 57 (60), 70 (24), 71 (100), 129 (15), 171 (10), 301 (0.1). HRMS: *m/z* calcd. For C₂₄H₄₄O₅ +Na: 435.3086; found: 435.3087.

3d-anti: 23.84 mg (29 %); colorless oil. ¹H-NMR (CDCl₃): δ = 0.88 (t, *J* 6.4 Hz, 6H), 0.90 (t, *J* 6.8 Hz, 6H), 1.20-1.42 (m, 16 H), 1.50-1.63 (m, 2 H), 1.69-1.79 (m, 1H), 1.82-2.03 (m, 3H), 2.70 (dd, *J* 5.0, 16.8 Hz, 1 H), 2.79 (dd, *J* 9.2, 16.8 Hz, 1 H), 2.90 (ddd, *J* 5.0, 8.0, 9.2 Hz, 1 H), 3.72 (ddd, *J* 6.8, 6.8, 7.0 Hz, 1 H), 3.81 (ddd, *J* 6.8, 6.8, 8.0 Hz, 1 H), 3.91-4.07 (m, 5 H) ppm. ¹³C-NMR (CDCl₃): δ = 10.88, 10.92, 10.95, 14.0, 23.0 (×2), 23.66, 23.69, 25.6, 28.8, 28.9, 29.7, 30.29, 30.32, 33.5, 38.62, 38.68, 46.9, 67.0, 67.2, 68.0, 78.8, 172.3, 173.0 ppm. IR (KBr disk): 2956, 2927, 2859, 1732, 1461, 1259, 1161, 1066, 1024, 773 cm⁻¹. MS, *m/z* (relative intensity): 41 (51), 42 (10), 43 (49), 44 (16), 55 (38), 56 (13), 57 (61), 70 (25), 71 (100), 129 (17), 207 (12), 342 (0.1). HRMS: *m/z* calcd. For C₂₄H₄₄O₅ +Na: 435.3086; found: 435.3086.

3-4-3-5 Entry 5: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-diisopropyl ester (**3e**)¹⁴



Run 1

Diisopropyl maleate (**1e**, 40.32 mg, 0.20 mmol) and DTBP (14.60 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3e**: 91 % (*syn* / *anti* = 61 / 30) (conversion: 100 %) (NMR, CDCl₃).

Run 2

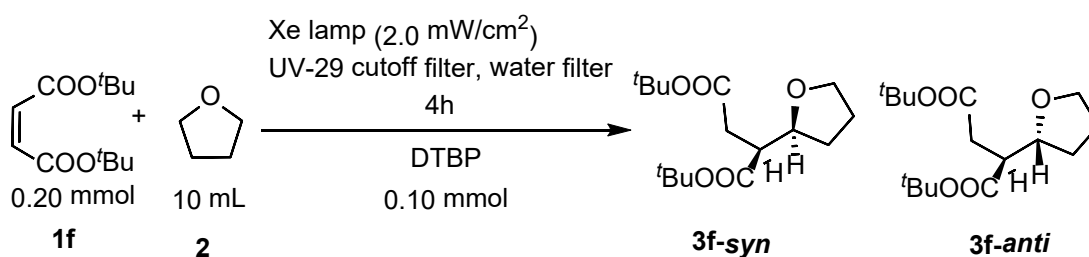
Diisopropyl maleate (**1e**, 39.98 mg, 0.20 mmol) and DTBP (14.75 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3e**: 96 % (*syn* / *anti* = 64 / 32) (conversion: 100 %) (NMR, CDCl₃).

Eluent for chromatography: hexane/ethyl acetate (50/1 → 0/1).

3e-syn: 32.80 mg (60 %); colorless oil. ¹H-NMR (CDCl₃): δ = 1.22 (d, *J* 6.4 Hz, 3 H), 1.226 (d, *J* 6.4 Hz, 3 H), 1.234 (d, *J* 6.4 Hz, 3 H), 1.25 (d, *J* 6.4 Hz, 3 H), 1.62-1.72 (m, 1 H), 1.83-1.96 (m, 3 H), 2.42 (dd, *J* 4.4, 16.4 Hz, 1 H), 2.71 (dd, *J* 10.0, 16.4 Hz, 1 H), 3.07 (ddd, *J* 4.4, 6.4, 10.0 Hz, 1 H), 3.73 (ddd, *J* 6.8, 7.2, 8.0 Hz, 1 H), 3.86 (ddd, *J* 6.4, 6.8, 8.0 Hz, 1 H), 4.08 (ddd, *J* 6.8, 6.8, 6.8 Hz, 1 H), 5.00 (dq, *J* 6.4, 6.4 Hz, 1 H), 5.05 (dq, *J* 6.4, 6.4 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 21.7, 21.76 (×2), 21.79, 25.7, 28.2, 32.7, 46.1, 67.97, 68.04, 68.3, 78.8, 171.4, 172.1 ppm. IR (KBr disk): 2979, 2931, 2874, 1731, 1468, 1374, 1263, 1173, 1107, 1068 cm⁻¹. MS, *m/z* (relative intensity): 41 (29), 43 (54), 71 (100), 129 (9), 171 (15), 229 (0.1). HRMS: *m/z* calcd. For C₁₄H₂₄O₅ +Na: 295.1521; found: 295.1521.

3e-anti: 15.60 mg (29 %); colorless oil. ¹H-NMR (CDCl₃): δ = 1.216 (d, *J* 6.4 Hz, 3 H), 1.223 (d, *J* 6.4 Hz, 3 H), 1.24 (d, *J* 6.4 Hz, 3 H), 1.25 (d, *J* 6.4 Hz, 3 H), 1.69-1.80 (m, 1 H), 1.81-2.03 (m, 3 H), 2.66 (dd, *J* 5.2, 16.4 Hz, 1 H), 2.73 (dd, *J* 9.2, 16.4 Hz, 1 H), 2.83 (ddd, *J* 5.2, 8.4, 9.2 Hz, 1 H), 3.73 (ddd, *J* 7.2, 7.2, 7.2 Hz, 1 H), 3.80 (ddd, *J* 6.8, 6.8, 8.4 Hz, 1 H), 3.96 (ddd, *J* 7.2, 7.2, 7.2 Hz, 1 H), 4.99 (dq, *J* 6.4, 6.4 Hz, 1 H), 5.04 (dq, *J* 6.4, 6.4 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 21.69, 21.73 (×2), 21.8, 25.6, 29.6, 34.0, 47.1, 67.8, 68.0, 68.1, 77.3, 171.6, 172.3 ppm. IR (KBr disk): 2979, 2937, 2874, 1731, 1468, 1374, 1262, 1172, 1108, 1067 cm⁻¹. MS, *m/z* (relative intensity): 41 (46), 42 (20), 43 (79), 45 (47), 71 (100), 129 (10), 171 (16), 213 (1). HRMS: *m/z* calcd. For C₁₄H₂₄O₅ +Na: 295.1521; found: 295.1521.

3-4-3-6 Entry 6: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-di-*tert*-butyl ester (**3f**)



Run 1

Di-*tert*-butyl maleate (**1f**, 45.50 mg, 0.20 mmol) and DTBP (14.51 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3f**: 96 % (*syn* / *anti* = 67 / 29) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Di-*tert*-butyl maleate (**1f**, 45.59 mg, 0.20 mmol) and DTBP (14.75 mg, 0.10 mmol) in THF (**2**, 10 mL). Yield of **3f**: 96 % (*syn* / *anti* = 67 / 29) (conversion: 100 %) (NMR, CDCl₃).

Eluent for chromatography: hexane/ethyl acetate (50/1 → 0/1).

3f-syn: 38.79 mg (65 %); colorless oil. ¹H-NMR (CDCl₃): δ = 1.44 (s, 9 H), 1.45 (s, 9 H), 1.58-1.74 (m, 1 H), 1.81-1.93 (m, 3 H), 2.34 (dd, *J* 4.4, 16.6 Hz, 1 H), 2.60 (dd, *J* 10.0, 16.6 Hz, 1 H), 2.99 (ddd, *J* 4.4, 6.4, 10.0 Hz, 1 H), 3.73 (ddd, *J* 6.8, 6.8, 7.2 Hz, 1H), 3.85 (ddd, *J* 6.4, 6.8, 8.0 Hz, 1 H), 4.07 (ddd, *J* 6.4, 6.4, 7.2 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 25.8, 28.0 (×7), 33.4, 46.8, 68.3, 78.9, 80.5, 80.6, 171.2, 171.8 ppm. IR (KBr disk): 2978, 2931, 2874, 1730, 1457, 1392, 1367, 1257, 1150, 1068, 848 cm⁻¹. MS, *m/z* (relative intensity): 41 (100), 43 (9), 56 (40), 57 (32), 71 (37), 188 (1.4). HRMS: *m/z* calcd. For C₁₆H₂₈O₅ +Na: 323.1834; found: 323.1833.

3f-anti: 14.76 mg (25 %); colorless oil. ¹H-NMR (CDCl₃): δ = 1.44 (s, 9 H), 1.45 (s, 9 H), 1.70-1.82 (m, 1 H), 1.82-2.02 (m, 3 H), 2.55-2.66 (m, 2 H), 2.72 (ddd, *J* 0.8, 6.4, 8.0 Hz, 1 H), 3.72 (ddd, *J* 6.8, 7.3, 8.8 Hz, 1 H), 3.79 (ddd, *J* 6.4, 6.8, 8.0 Hz, 1 H), 3.92 (ddd, *J* 6.0, 6.8, 7.3 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 25.7, 27.99 (×3), 28.03 (×3), 29.7, 35.2, 48.0, 67.9, 79.1, 80.4, 80.7, 171.5, 172.1 ppm. IR (KBr disk): 2978, 2931, 2869, 1729, 1458, 1367, 1257, 1147, 1067, 848 cm⁻¹. MS, *m/z* (relative intensity): 40 (11), 41 (100), 44 (12), 55 (17), 56 (39), 57 (33), 71 (38), 118 (5), 171 (7), 188 (1.5). HRMS: *m/z* calcd. For C₁₆H₂₈O₅ +Na: 323.1834; found: 323.1833.

3-4-3-7 Reaction of **1a** and **2** at 50 °C (**3a-cis-syn/anti**)

Dimethyl maleate (**1a**, 28.84 mg, 0.20 mmol) and DTBP (14.56 mg, 0.10 mmol) in THF (**2**, 10 mL). Irradiation time: 4h. Irradiation temperature: 50 °C. Yield of **3a**: 100 % (*syn* / *anti* = 61 / 38) (conversion: 100 %) (NMR, CDCl₃).

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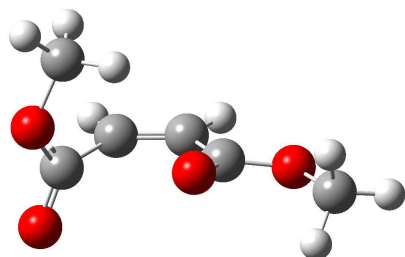
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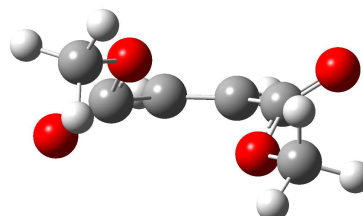
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3-6 Appendix

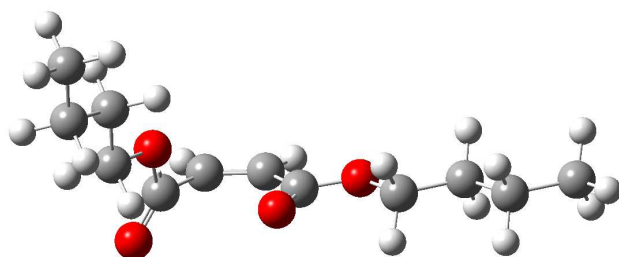
3-6-1 Calculated stable conformers and energies of maleic acid and its dialkyl esters.^{1,2}



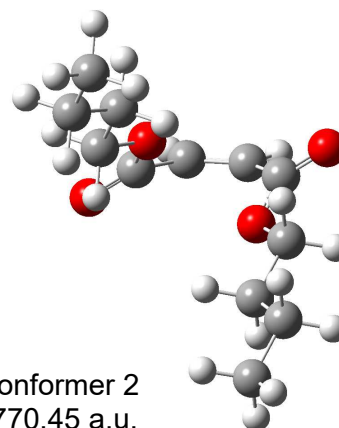
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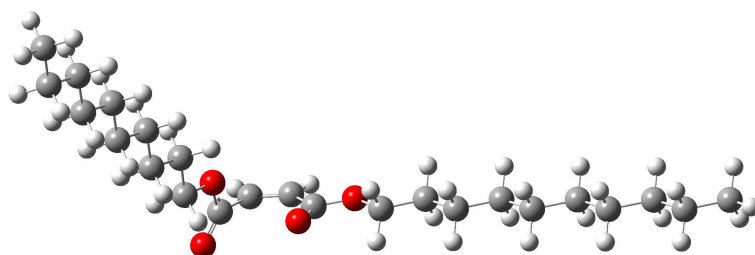
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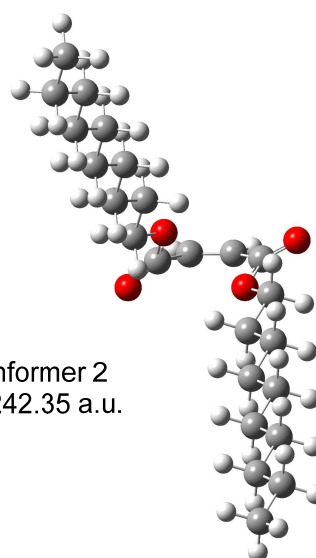
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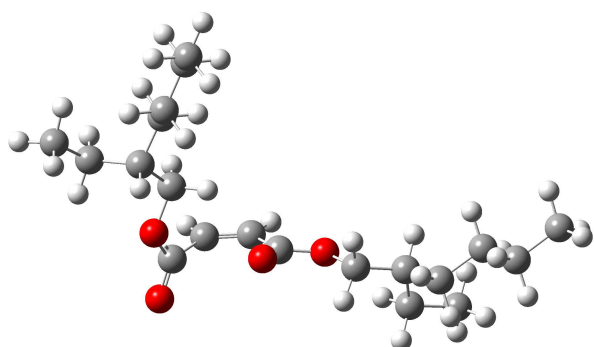
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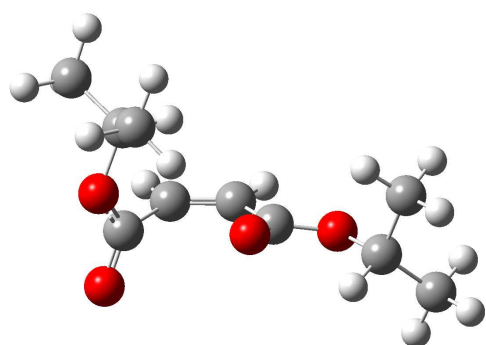
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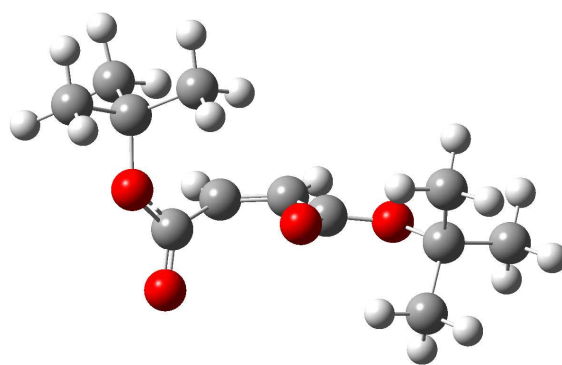
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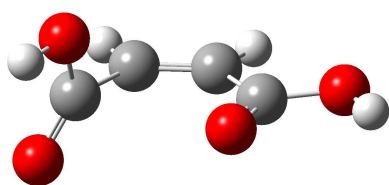
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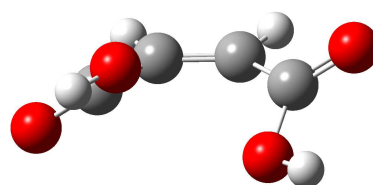
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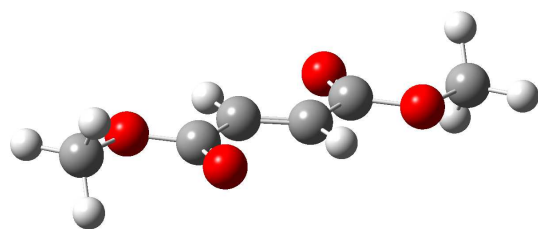
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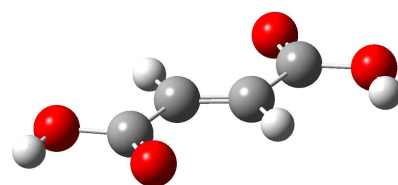
1g conformer 1
-455.88 a.u.



1g conformer 2
-455.88 a.u.



1h -534.51 a.u.



1i -455.88 a.u.

3-6-2 References

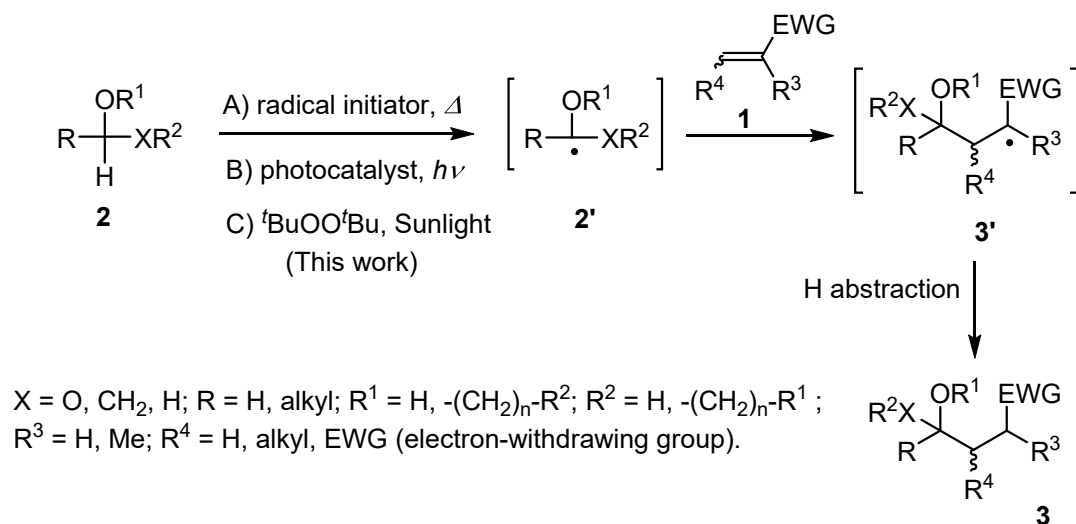
1. Stable conformations were calculated by B3LYP/6-31++G(d,p) using Gaussian 16; Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
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Chapter 4

Sunlight-induced addition reaction of
alcohols/ethers/acetal to olefins
using di-*tert*-butyl peroxide

4-1 Introduction

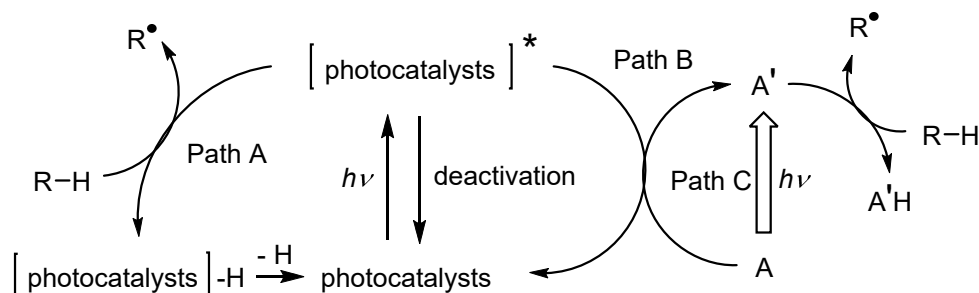
Sunlight is an infinite energy source and attempts to use this energy in organic synthesis have been investigated for a long time.¹ However, sunlight is generally not used in organic synthesis due to its limited applicability and/or low efficiency, particularly long reaction times, in the previously reported reactions. Therefore, development of widely applicable and efficient reactions is critical for using sunlight for synthetic purpose. After a period of major interest in organic photochemistry directed toward exotic molecules and reactions, interest is returning to more commonly used reactions under the concept of green chemistry.^{1c,d,2} The formation of new C-C bonds is one of the most important research areas in organic synthesis and many studies have been reported in organic photochemistry. One of these reactions is the addition of carbon radicals to olefins (Scheme 1).³ Such reactions have also been studied using thermal reactions via C-H bond cleavage using various radical initiators, mostly peroxides,⁴ but they generally require high temperature and long reaction times, and usually give low yields for the desired products (Scheme 1, condition A). Many attempts have been made to improve these thermal reactions,⁵⁻⁹ but the use of high temperature and/or long reaction times still remain as problems to be overcome.



Scheme 1. The generation of carbon radicals (type A-C) and their addition to olefins.

For photochemical C-H bond cleavage reactions used for the generation of carbon radicals, the abstraction of an α -hydrogen atom to an oxygen atom using an excited ketone has been used for a long time.^{10,11} Recently, various photocatalysts other than ketones have also been used for the same purpose (Scheme 1, condition B). Besides ketones,

tetrabutylammonium decatungstate (TBADT),^{10a, d, 12, 13} uranyl chloride and its cation,¹⁴ eosin Y,¹⁵ and cyclopropenium ion¹⁶ have been used as photocatalysts for the abstraction of the α -hydrogen atom (Scheme 2, Path A). On the other hand, the generation of reactive species (**A'**) using organic¹⁷ and metal complex¹⁸ photoredox catalysts via a SET process, and the successive abstraction of an α -hydrogen atom by **A'** has been reported (Scheme 2, Path B). However, these photocatalytic methods generally require long irradiation times and the use of organic photocatalysts frequently makes the purification of the products difficult, which are significant disadvantages for application in organic synthesis.



Scheme 2. Reaction pathways for hydrogen abstraction used toward the generation of carbon radicals.

The requirement of long irradiation times in photocatalyst induced reactions is probably due to the deactivation of the excited photocatalyst (Scheme 2). In the case of hydrogen abstraction, competition between hydrogen abstraction (Path A) and deactivation probably takes place and significantly reduces the quantum yield for Path A. A similar decrease in the quantum yield for the generation of reactive species (**A'**) (Path B) is also expected. Therefore, to increase the efficiency of the photochemical C-H bond cleavage, the direct generation of reactive species (**A'**) with a high quantum yield is necessary (Path C).

To use low intensity sunlight as a light source for organic synthesis, the reactions must be highly efficient and should proceed within a short period of time. Herein, we report an efficient sunlight-induced addition reaction of alcohols/ethers/acetal to olefins using di-tert-butyl peroxide (DTBP) (Scheme 1, condition C) that corresponds to Path C in Scheme 2.¹⁹ The reaction proceeded with shorter irradiation times when compared to many of the previously reported sunlight and conventional lamp photocatalyzed reactions, and even gave higher yields in some cases. The generation of carbon radicals is carried out by t-BuO• generated via the direct photolysis of DTBP using sunlight. The quantum yield for the generation of t-BuO• is reported to be almost unity in the liquid phase,^{20b} which minimizes the

loss of absorbed photon energy via deactivation and thus reduces the reaction time. Photochemically generated t-BuO• abstracts an α -hydrogen atom to an oxygen atom^{21, 22} to form a carbon radical (**2'**, Scheme 1), which adds to olefin **1** to give the desired product **3** via radical **3'** and its hydrogen abstraction. In addition, t-BuOH that is generated during the course of the reaction can be easily removed via simple evaporation, which can avoid difficulties in the purification process that are often caused when using organic photocatalysts.

4-2 Results and Discussion

4-2-1 Emission of sunlight and absorption of di-tert-butyl peroxide (DTBP) and olefins

The decomposition of DTBP for the generation of t-BuO• have been reported using a quartz cell and Xe lamp fitted with a UV-29 cut-off filter.¹⁹ Figure 1a shows the wavelength of light transmitted through the quartz cell and UV-29 cut-off filter is almost the same as that of a Pyrex flask. This result indicated that Pyrex flasks, generally used in organic synthesis laboratories, have a similar function as UV-29 filters, which remove light with wavelength < 290 nm from the irradiated light source to avoid considerable direct absorption of UV light by conjugated olefins. Figure 1b show the absorption wavelength of DTBP overlaps with the emission of sunlight at > 290 nm, which could induce the efficient cleavage of DTBP to generate t-BuO•.²⁰ As for the olefins used in the experiments (*vide infra*), olefins bearing one EWG did not exhibit absorption at > 290 nm, but some of those with two EWGs exhibited a slight absorption at > 290 nm.^{19a}

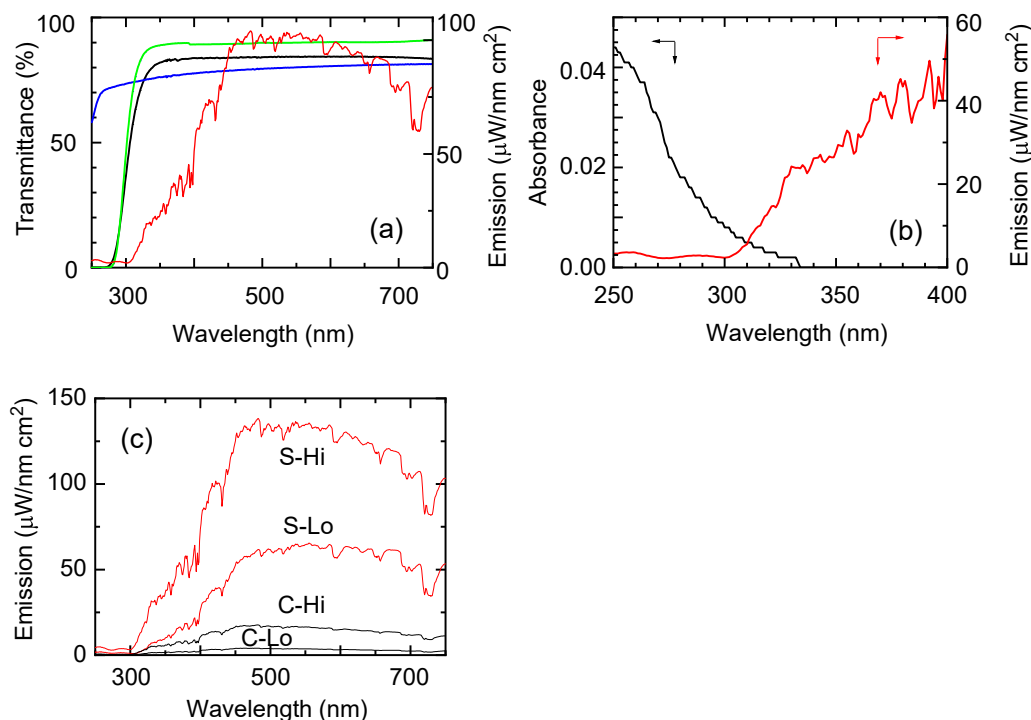


Figure 1. (a) The emission of sunlight (red, 30th August, 2020) and transmittance of a Pyrex flask (black), quartz cell (blue), and UV-29 cut-off filter (green). (b) The absorbance of DTBP (black, 5×10^{-5} M in EtOH) and emission of sunlight (red, 30th August, 2020). (c) The emission of sunlight: sunny (**S-Hi** and **S-Lo**, 9th Sept., 2020) and cloudy (**C-Hi** and **C-Lo**, 14th Sept., 2020). The emission of sunlight was measured in Tokyo (N 35°, E 139°).

The intensity of sunlight is not stable like artificial light sources. Figure 1c shows the typical emission spectra of sunlight in Tokyo (N 35°, E 139°) on a sunny and cloudy day. **S-Hi** and **S-Lo** corresponded to the highest and lowest intensity of the emission during photolysis on a sunny day. **C-Hi** and **C-Lo** were those on a cloudy day. The emission of **S-Hi**, **S-Lo**, **C-Hi**, and **C-Lo** showed light intensities of 1.50, 0.67, 0.40, and 0.25 mW/cm², respectively; this light intensity was used in Tables 1–4 (*vide infra*). The intensity of the emission changed with time and weather. In addition, seasonal variation in the maximum intensity of sunlight had to be considered, which was ~40% in 2019.²³ Details on the weather and the dates of each experiment in Tables 1–4 are shown in the appendix of this chapter.

4-2-2 Optimization of the reaction conditions

The reaction conditions were optimized using dimethyl maleate (**1a-cis**) and 2-propanol (**2A**) as a model system (Reaction 1). The ratio of **1a-cis**:DTBP was fixed at 2:1 because two

t-BuO• are generated from single DTBP molecule and the reactions were conducted at room temperature. Table 1 shows that an irradiation time of 4 h was sufficient to completely convert **1a-cis** into the desired product (**3aA**)(Entries 1 and 2); prolonged irradiation did not cause any decomposition of the product (Entry 3). The reaction also proceeded without DTBP, but a significant decrease in the conversion of **1a-cis** and yield of **3aA** was observed (Entry 4). This reaction was probably initiated via the direct excitation of **1a-cis** due to the slight absorption of sunlight by the substrate (*vide supra*) and the consecutive abstraction of the hydrogen atom from **2A** by the excited carbonyl groups in **1a-cis**.²⁴ This result indicates that DTBP is necessary for an efficient reaction, *i.e.*, reducing the irradiation time and increasing the yield of the reaction. The reaction did not form the desired product (**3aA**) without sunlight irradiation at room temperature or at 35 °C (the maximum reaction temperature during sunlight irradiation) though a slight conversion of **1a-cis** was observed (Entries 5 and 6). However, this conversion was due to the work-up procedure of the reaction and not by a thermal reaction at room temperature (Entry 7).

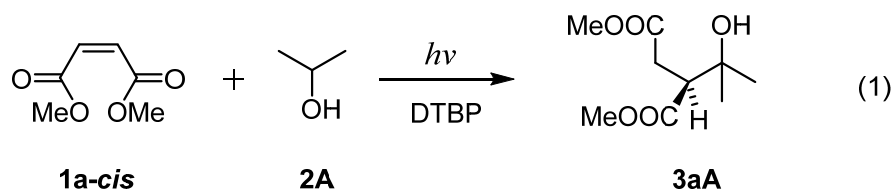


Table 1. Optimization of reaction conditions using **1a-cis** and **2A**.^a

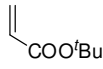
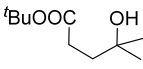
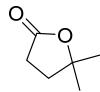
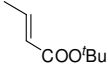
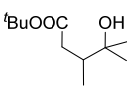
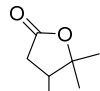

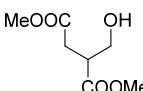
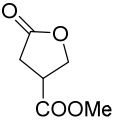
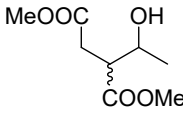
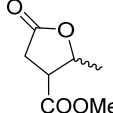
Entry	DTBP (mmol)	Reaction time (h)	Light intensity ^b (mW/cm ²)	Conversion of 1a-cis ^c (%)	Yield of 3aA ^c (%)
1	0.1	3	0.6-1.6	97	94 [91] ^e
2	0.1	4	1.5-1.6	100	100
3	0.1	5	0.8-1.7	100	97
4	0	4	1.5-1.6	22	34 [7] ^f
5 ^d	0.1	4	-	16	0 [0] ^f
6 ^{d, e}	0.1	4	-	13	0 [0] ^f
7	0.1	0	-	16	0 [0] ^f

^a Photolysis conditions: **1a-cis** (0.2 mmol) and DTBP in **2A** (10 mL), light source: sunlight, N₂ atm, room temp. Reactions were conducted using a 30 mL Pyrex eggplant-shape flask. ^b The weather, the date, and the light intensity of sunlight for each experiment are described in detail in the experimental section. ^c Yields are based on the consumed starting material and determined by NMR spectroscopy. The NMR yields are in good accord with the isolated yields.¹⁹ Result of a single run. ^d Without irradiation. ^e The reaction was conducted at 35 °C. ^f Yield based on the initial amount of the olefin.

4-2-3 Sunlight photolysis of alcohols and olefins

With the optimized reaction conditions in hand, the scope of the reaction was investigated using various alcohols and olefins (equation 2, Table 2). The light intensity indicated in Table 1 was the range between its maximum and the minimum during the photolysis reaction. The reaction of **1a-cis** and **2A** gave **3aA** in excellent yield (Entry 1), but the isolation of **3aA** using silica gel column chromatography was unsuccessful because of the partial lactonization to **3aA'** during chromatography. Therefore, **3aA** was transformed into lactone **3aA'** upon treatment with HCl gas prior to its isolation, which proceeded in excellent yield (Entry 1). Dimethyl fumarate (**1a-trans**), maleic acid (**1b-cis**), fumaric acid (**1b-trans**), and fumaronitrile (**1c**) all gave their desired products in excellent yield within 4 h (Entries 2–7). In the case of **1b-cis** and *-trans*, the generated hydroxyl carboxylic acids underwent lactonization and formed **3bA** during workup (Entries 3–6).

Table 2. Addition of alcohols to olefins.^a (continued)

8							
	1d	2A	4	0.5-2.0	100	3dA 34	3dA' 26
9							
	1e	2A	4	1.1-1.6	92	3eA 45 [41] ^h	3eA' 30 [28] ^h
10	1e	2A	5	0.3-1.6	94	3eA 53 [50] ^h	
11		MeOH	4	1.1-1.6	64		
	1a-cis	2B				3aB 71 [45] ^h	
12	1a-cis	2B	10	0.6-1.5	87	3aB 75 [65] ^h	 3aB' 65 [57] ^h (62 [54] ^h) ^g
13	1a-cis	EtOH 2C	4	1.6-2.1	100		 3aC' <i>cis/trans</i> 35/54
14 ^e	1a-cis	2C	11	0.2-1.2 ^f	100	3aC 98	3aC' <i>cis/trans</i> 34/55 (31/54) ^g

^a Photolysis conditions, substrate: olefin (**1**; 0.2 mmol) and DTBP (0.1 mmol) in alcohol (**2**, 10 mL), light source: sunlight, N₂ atm, room temp. The reactions were conducted using a 30 mL Pyrex eggplant-shape flask. ^b The weather, the date, the light intensity of sunlight, and the number of independent runs for each experiment are described in detail in the experimental section. ^c Yields are based on the consumed starting material and determined by NMR spectroscopy. The NMR yields are in good accord with the isolated yields.¹⁹ The yields are the averaged of two to five independent runs unless otherwise stated. ^d Lactonization by treatment with HCl gas at room temperature. ^e Result of a single run. ^f Light source: sunlight (cloudy). ^g Isolated yield. ^h Yield based on the initial amount of the olefin.

The reactivity of olefins bearing one EWG was investigated using *t*-butyl acrylate (**1d**) and *t*-butyl crotonate (**1e**). The reaction of **1d** with **2A** proceeded within 4 h to give adduct **3dA** in 34% yield, which was cyclized to form **3dA'** in 26% yield based on the consumed **1d** (Entry 8). The reaction of **1e** and **2A** proceeded slower than that of **1d** (Entries 9 and 10). Only a 94% conversion of **1e** was observed after 5 h with **3eA** obtained in 53% yield (Entry 10). For both **1d** and **1e**, the yield of the desired adducts were lower than those obtained from olefins bearing two EWGs,^{3c,4a} probably due to the formation of polymers and oligomers of olefins **1d** and **1e**.²⁵

The results obtained for the reaction of **1a-cis** and alcohols **2B** and **2C** are shown in Runs 11–14. The reaction using methanol (**2B**) was not completed even after 10 h of irradiation and an 87% consumption of **1a-cis** and 75% yield of **3aB** was obtained, which was cyclized into lactone **3aB'** in 65% yield (Entry 12). Ethanol (**2C**) gave **3aC** in 97% yield within 4 h with the complete consumption of **1a-cis**. Product **3aC** was cyclized into **3aC'** in 89% yield with a *cis/trans* ratio of 35/54 (Entry 13). On cloudy days, the reaction required a longer irradiation time, but the yield and the *cis/trans* ratio of the expected product was the same as those obtained on a sunny day (Entry 14). It was surprising that the yield of product **3aC** was 23% higher than that obtained using a Xe lamp as the light source (74%).^{19a}

To the best of our knowledge, the photocatalyzed addition of alcohols to olefins in neat alcohols have been conducted only using conventional lamps and not with sunlight (Table S1).²⁸ The intensity of sunlight is generally more than one order of magnitude smaller than conventional lamps, but our results show that a comparable yield of the product can be obtained in the addition reaction of **2A** to **1b-cis** and *-trans* with a shorter irradiation time (Entries 3 and 6) when compared with that of a benzophenone sensitized reaction using a high-pressure Hg lamp (18 h, 96%; Entry S1),^{11a} or a higher yield in the addition reaction of **2B** to **1a-cis** with a 1.3–3.3-fold longer irradiation time (Entries 11 and 12) compared with that of a UO₂Cl₂ sensitized reaction using a high-pressure Hg lamp (3 h, 65%; Entry S2).^{14a}

4-2-4 Effect of light intensity

The origin of the significant increase in the yield of product **3aC** in the reaction conducted under sunlight irradiation when compared with that using a Xe lamp was investigated. We surmised that the major difference between sunlight and Xe lamp irradiation was the intensity of light. Therefore, the effect of the light intensity on the yield of **3aC** was investigated using a Xe lamp (Figure 2). The yield of **3aC** was dependent on the light intensity

with the lowest yield obtained at 18 mW/cm² and two maxima at 2 and > 24 mW/cm². The yield of **3aC** at 20 mW/cm² was the same as the yield obtained in our previous report using a Xe lamp (74 %) ^{19a} and that at 2 mW/cm², which was similar to the intensity of sunlight, was in good agreement with the yield obtained using sunlight (Table 2, Entry 13). To the best of our knowledge, such a light intensity effect, increasing the yield by decreasing the light intensity, has not been reported to date. The origin of the light intensity effect is still not clear at the moment but it is probably related to the concentration of the intermediates involved in the reaction mixture.

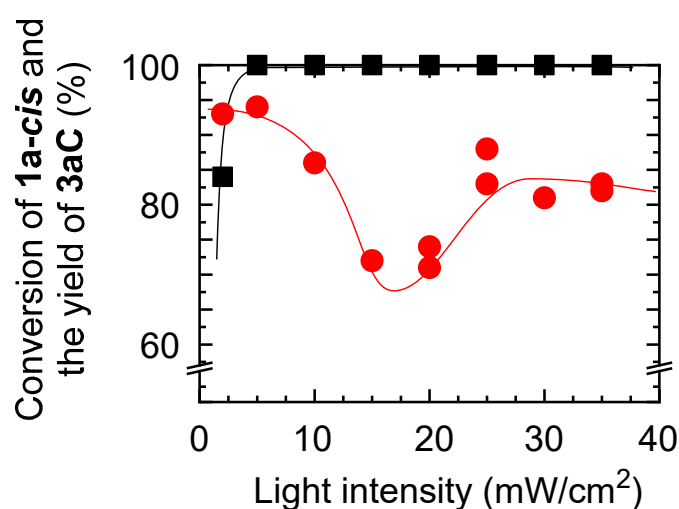


Figure 2. The effect of the light intensity on the yield of **3aC** and conversion of **1a-cis**; Symbols: **1a-cis** (■) and **3aC** (●). Reaction condition: **1a-cis** (0.2 mmol) and DTBP (0.1 mmol) in **2C** (10 mL), light source: 500 W Xenon short-arc lamp fitted with an 18-cm water filter and a UV-29 cutoff filter, irradiation time: 3 h, N₂ atm, room temp. The reactions were conducted using a quartz cylindrical cell (diameter: 3 cm).

4-2-5 Sunlight photolysis of cyclic ethers and olefins

To extend the scope of the reaction, we have investigated the use of cyclic ethers in the reaction as an alternative to alcohols (equation 3, Table 3). Most of the products obtained were a mixture of *syn* and *anti* diastereomers.^{19b} The addition of 5–7-membered cyclic ethers to **1a-cis** proceeded in good to excellent yield (Entries 1–5). However, 6- and 7-membered cyclic ethers (**2E** and **F**) require longer irradiation times for the reaction to be complete (Entries 2–5). This was probably due to the slower abstraction of the hydrogen atom from **2E** and **2F** by *t*-BuO• when compared to **2D**²¹ and/or the slower addition of the 6-membered radical of **2E** to the olefin when compared to the 5-membered radical of **2D**.²⁶ The addition of THF (**2D**) to

maleic acid (**1b-cis**), fumaric acid (**1b-trans**), and fumaronitrile (**1c**) proceeded in excellent yield within 4 h (Entries 7–9). The results on the reactions between cyclic ethers and olefins bearing two EWGs were comparable to those using a Xe lamp as the light source.^{19b}

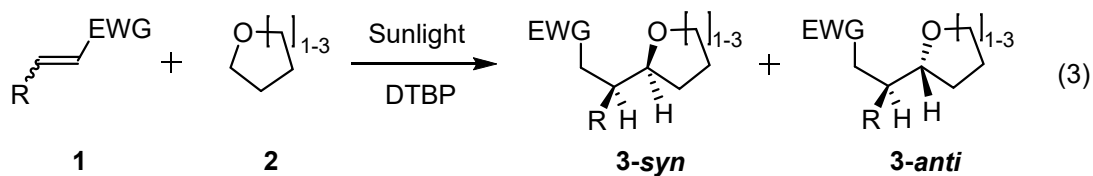
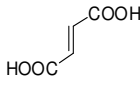
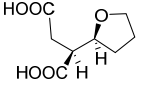
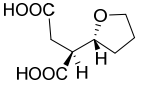

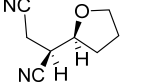
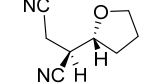
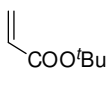
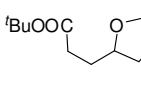
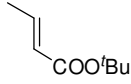
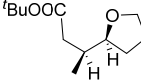
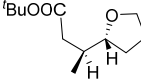


Table 3. Addition of cyclic ethers to olefins.^a

Entry	Olefin (1)	Ether (2)	Irradiation time (h)	Light intensity ^b (mW/cm ²)	Conversion of 1 (%) ^c	Yield of 3 (%) ^c
1			4	1.3-2.4	100	 3aD-syn 62 3aD-anti 34
2 ^d	1a-cis		6	0.9-1.8	52	 3aE-syn 33 [17] ^e 3aE-anti 22 [11] ^e
3 ^d			9	0.6-1.9	62	40 [25] ^e 27 [17] ^e
4 ^d			16	0.2-1.5	100	39 22
5 ^d	1a-cis		20	0.3-1.2	100	 3aF-syn 33 3aF-anti 32
6			4	1.5-2.2	100	3aD-syn 45 3aD-anti 51
7			4	1.2-2.0	100	 3bD-syn 45 3bD-anti 51

Table 3. Addition of cyclic ethers to olefins.^a(continued)

8		2D	4	0.5-2.0	100		44		51
	1b-trans					3bD-syn		3bD-anti	
9		2D	4	1.5-2.2	100		51		41
	1c					3cD-syn		3cD-anti	
10		2D	4	0.5-1.7	100		40		
	1d					3dD			
11		2D	4	1.3-1.8	91		40 [36] ^e		41 [37] ^e
	1e					3eD-syn		3eD-anti	

^a Photolysis conditions, substrate: olefin (**1**; 0.2 mmol) and DTBP (0.1 mmol) in ether (**2**, 10 mL), light source: sunlight, N₂ atm, room temp. The reactions were conducted using a 30 mL Pyrex eggplant-shape flask. ^b The weather, the date, the light intensity of sunlight, and the number of independent runs for each experiment are described in detail in the experimental section. ^c Yields are based on the consumed starting material and determined by NMR spectroscopy. The NMR yields are in good accord with the isolated yields.¹⁹ The yields are the averaged of two or three independent runs unless otherwise stated. ^d Result of a single run. ^e Yield based on the initial amount of the olefin.

The yield of **3dD** from *t*-butyl acrylate (**1d**) and **2D** was 40% (Entry 10), which was comparable to that using a Xe lamp.^{19b} In contrast, the combined yield of **3eD-syn** and *-anti* obtained from the reaction between *t*-butyl crotonate (**1e**) and **2D** was ~10% higher than that obtained using a Xe lamp (81% yield) (Entry 11).

Photocatalyzed addition reactions of cyclic ethers to olefins in neat cyclic ethers have been reported using both sunlight and conventional lamps (Table S2).²⁸ Acetophenone^{11b} and TBADT^{13b} have been used for sunlight-induced reactions. Acetophenone was used in the addition of **2D** to diethyl maleate, which required 1d of irradiation giving the desired product in 80% yield (Entry S1), whereas our reaction on the addition of **2D** to **1a-cis** only required 4 h of irradiation with a 96% yield of the desired product **3aD-syn/anti** (Entry 1). TBADT was used in the addition of 1,4-dioxane to **1a-cis**, which required 5d of sunlight irradiation to give the desired product in 59% yield (Entry S8); our similar reaction using the addition of **2E** to **1a-cis** required 16 h of irradiation (which corresponds to 2 d of irradiation in the TBADT

catalyzed reaction) to give the desired product **3aD-syn/anti** in 61% yield (Entry 2).

4-2-6 Sunlight photolysis of cyclic acetals and olefins

The addition of cyclic acetals to olefins was also investigated (equation 4, Table 4). The abstraction of the hydrogen atom from cyclic acetals was faster than that from cyclic ethers²¹ so that the reactions were completed within 3 h when using 2-methyl-1,3-dioxolane (**2G**), 1,3-dioxolane (**2H**), and 2,2-dimethyl-1,3-dioxolane (**2I**) (Entries 1–8). The reactions of **2G** and **2H** with olefins bearing two EWGs all proceeded in high yield (Entries 1–3, 7), but the product from **1d** gave only a fair yield (Entry 4), which was attributed to polymerization and oligomerization of the olefin.²⁵ However, **1c** and **1e** showed a 15 and 29% increase in the yield of **3cG** and **3eG**, respectively, when compared to that obtained under photolysis with a Xe lamp (Entry 3 and 5, respectively). In contrast, the expected product (**3fG**) was not formed from the reaction between *t*-butyl methacrylate (**1f**) and **2G** (Entry 6), probably also due to polymerization and oligomerization. In the reaction between **1a-cis** and **2I**, the product (**3aI**) was obtained as a mixture of *syn*- and *anti*-isomers in 60% yield, which was a > 2-fold increase when compared to the yield obtained under photolysis with a Xe lamp (Entry 8).

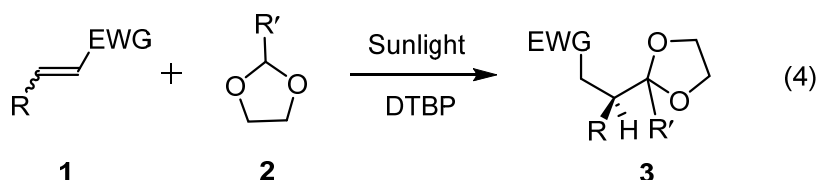
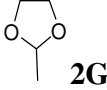
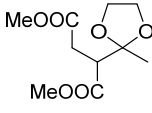
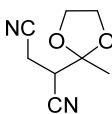
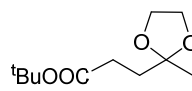
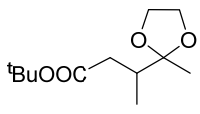
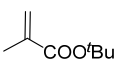
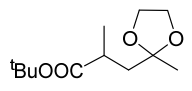

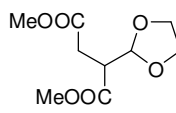
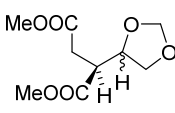
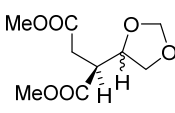

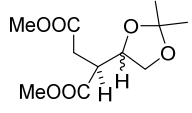
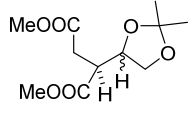


Table 4. Addition of cyclic acetals to olefins.^a

Entry	Olefin (1)	Acetal (2)	Light Intensity ^b (mW/cm ²)	Yield of 3 (%) ^c	
1	1a-cis	 2G	0.8-1.8	 3aG	98
2	1a-trans	2G	0.8-1.8	3aG	95
3	1c	2G	0.3-1.9	 3cG	86
4 ^d	1d	2G	1.8-2.0	 3dG	35
5	1e	2G	0.4-1.8	 3eG	81 (66) ^e
6	 1f	2G	0.5-2.2	 3fG	0
7	1a-cis	 2H	2.1-2.2	 3aH-major	90
				 3aH-syn	5
				 3aH-anti	3
8	1a-cis	 2I	0.3-1.6	 3aI-syn	41
				 3aI-anti	19

^a Photolysis conditions, substrate: olefin (**1**; 0.2 mmol) and DTBP (0.1 mmol) in acetal (**2**, 10 mL), light source: sunlight, irradiation time: 3 h, N₂ atm, room temp. N₂ atmosphere, room temp. Conversion of **1**: 100%. The reactions were conducted using a 30 mL Pyrex eggplant-shape flask. ^b The weather, the date, the light intensity of sunlight, and the number of independent runs for each experiment are described in detail in the experimental section. ^c Yields are based on the consumed starting material and determined by NMR spectroscopy. The NMR yields are in good accord with the isolated yields.¹⁹ The yields are the averaged of two or three independent runs unless otherwise stated. ^d Result of a single run. ^e Isolated yield.

The photocatalyzed addition of cyclic acetals to olefins in neat cyclic acetals have not been conducted using sunlight, but only using conventional lamps (Table S3).²⁸ The required sunlight irradiation time (3 h) in our experiments was comparable to conventional lamp photolyses (0.75–16 h) and the yields of the desired products were also comparable.

4-2-7 Gram-scale synthesis

To test the applicability of this sunlight reaction for use in organic synthesis, the reaction of **1a-cis** and **2A** was scaled up 50-fold. The sunlight irradiation was conducted for 4 and 6 h (0.2-0.9 mW/cm²) using **1a-cis** (1.44g, 10 mmol) and DTBP (0.73g, 5 mmol) in **2A** (500 mL) using 500-mL eggplant-shape Pyrex flasks without stirring. The yields of the **3aA** were 95% (75% conversion) and 99% (100% conversion) after 4 and 6 h of irradiation, respectively. To investigate the effect of the volume-to-surface ratio in the reaction, the reaction was conducted using **1a-cis** (2.88g, 20 mmol) and DTBP (1.46g, 10 mmol) in **2A** (1 L) using 1-L eggplant-shape Pyrex flasks with 4 h irradiation (0.4-0.9 mW/cm²) without (i) and with (ii) stirring. The yields of **3aA** were almost the same, 91% (86% conversion) (condition i) and 89% (86% conversion) (condition ii), which indicated that the volume-to-surface ratio had no effect on the efficiency of the reaction. The four conditions all gave similar yields to that observed in the small-scale experiment (cf. Table 2, Entry 1).

Additional gram-scale experiments on the reaction of **1a-cis** (1.44g, 10 mmol) and DTBP (0.73g, 5 mmol) in **2D** (500 mL), scaled up 50-fold, were conducted for 4 h under four different conditions using eggplant-shape Pyrex flasks: (i) 500 mL flask with stirring, (ii) 1 L flask with stirring, (iii) 500 mL flask without stirring, and (iv) 1 L flask without stirring. The yields of the **3aD-syn/anti** product were 62/36% (condition i), 62/36% (condition ii), 62/33% (condition iii), and 59/37% (condition iv), with 100% conversion. A considerable difference was not observed between the four conditions and all gave similar yields to that observed in the small-scale experiment (cf. Table 3, Entry 1) without extending the irradiation time.

4-3 Conclusion

The sunlight-induced addition of alcohols/ethers/acetals to olefins using DTBP proceeded efficiently, typically within 3–4 h of sunlight irradiation in excellent yields with olefins bearing two EWGs (> 95% yield) and in good to fair yield with olefins bearing one EWG. The yield observed for some of the products were higher than those obtained using a Xe

lamp as a light source, which was confirmed to be due to a light intensity effect; the lowest yield was obtained at 18 mW/cm² and two maxima were observed at 2 and > 24 mW/cm² with a ~20% difference in the product yield. The reactions proceeded faster than many of the previously reported sunlight and many conventional lamp photolyses with similar or better yields. Gram-scale experiments were conducted to test the applicability of this reaction in organic synthesis, whose results showed similar yields to those obtained for the small-scale experiments.

4-4 Experimental Section

4-4-1 General Remarks

¹H and ¹³C NMR spectra were recorded on JEOL JNM-ECX400 spectrometer with CDCl₃, acetone-d₆, or CD₃CN as a solvent. As internal standards, TMS (δ 0.0 ppm) in CDCl₃, CD₃CN (δ 1.94 ppm), or acetone-d₆ (δ 2.05 ppm) were used for ¹H NMR, and CDCl₃ (δ 77.0 ppm), CD₃CN (δ 118.26 ppm), or acetone-d₆ (δ 29.84 ppm) for ¹³C NMR analyses. IR spectra were recorded on a JASCO FT/IR-4700. Olefins **1a-cis**, **1a-trans**, **1b-cis**, **1b-trans**, **1c**, alcohols **2A**, **2B**, **2C**, acetals **2G**, **2H**, **2I**, and DTBP were purchased and used as bought. Olefins **1d**, **1e**, **1f**, and ethers **2D**, **2E** were purchased and distilled before use. Oxepane (**2F**) was synthesized according to the reported procedure.²⁷

4-4-2 General procedure for the reactions

4-4-2-1 Photolysis

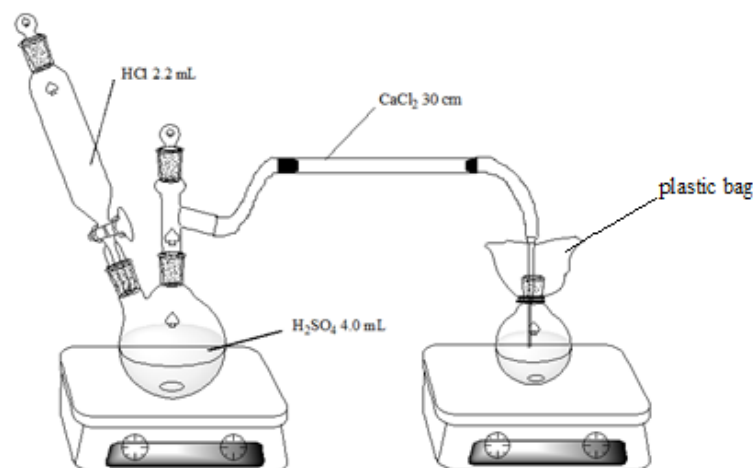
A solution of alcohol/cyclic ether/cyclic acetal (**2**) (10 mL), olefin (**1**) (0.2 mmol) and DTBP (0.1 mmol) was introduced into a quartz cylindrical cell (diameter: 3 cm) or 30 mL Pyrex eggplant-shape flask equipped with a three-way stopcock. The three-way stopcock was connected to the cell, a nitrogen source, and small vacuum pump. The solution was evacuated to about 50 mmHg under sonication for 5s and nitrogen was then introduced into the cell; this cycle was repeated 10 times. The photolysis was conducted under sunlight irradiation or a 500 W Xe lamp (USHIO Optical Modulex SX-UI500XQ) fitted with an 18-cm water filter and a cut-off filter (Toshiba UV-29) under a nitrogen atmosphere. The light intensity was measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with a UVD-S365 photo detector and emission spectra of sunlight by an Ushio USR-40D spectral radiometer. After photolysis, the alcohol/cyclic ether/cyclic acetal was removed in vacuo at 40–50 °C / < 150 Torr (most of the products were volatile under reduced pressure) and the consumption of the olefin and the products yield were determined by NMR spectroscopy using a precise amount of naphthalene as an internal standard; the yields of each product were calculated based on the consumed starting material. The isolation of products were conducted using silica gel column chromatography.

4-4-2-2 Experimental setup for sunlight photolysis

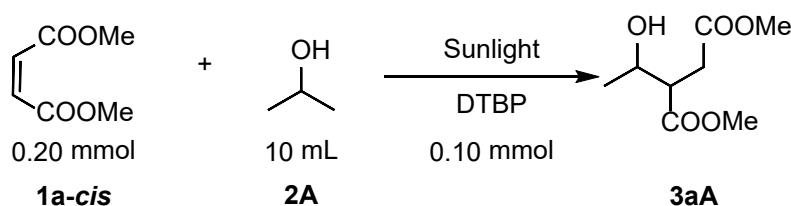


4-4-2-3 Lactonization of hydroxyl esters 3aA', 3dA', 3eA', 3aB' and 3aC'.

The crude hydroxyl ester and CHCl_3 were added to a 30 mL eggplant-shape flask and HCl gas was bubbled into the stirred solution using a setup shown in the figure below. Sulfuric acid (4 mL) was added to a two-necked flask, and hydrochloric acid (2.2 mL) was added dropwise to the sulfuric acid to generate HCl gas. The HCl gas was passed through a calcium chloride tube for drying and bubbled into the CHCl_3 solution for 25 min. After the reaction, CHCl_3 was removed using a rotary evaporator ($<50^\circ\text{C}$, $<85\text{ Torr}$). The consumption of the hydroxyl ester and the yield of the product lactone were determined by NMR spectroscopy using a precise amount of 2,7-dimethoxynaphthalene (0.10 mmol) as an internal standard; the yield of the product was calculated based on the consumption of the starting material. The isolation of the product was conducted using silica gel column chromatography.



4-4-3 Experimental details of the reactions in Tables 1



Entry 1

Dimethyl maleate (**1a-cis**, 28.63 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 0.6–1.6 mW/cm², 26th August, 2020). Irradiation time: 3 h. Yield of **3aA**: 94 % (NMR, CDCl₃) (conversion: 97 %).

Entry 2

Dimethyl maleate (**1a-cis**, 28.92 mg, 0.20 mmol) and DTBP (14.66 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 1.5–1.6 mW/cm², 17th August, 2020). Irradiation time: 4 h. Yield of **3aA**: 100 % (NMR, CDCl₃) (conversion: 100 %).

Entry 3

Dimethyl maleate (**1a-cis**, 28.75 mg, 0.20 mmol) and DTBP (14.78 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 0.8–1.7 mW/cm², 2nd March, 2020). Irradiation time: 5 h. Yield of **3aA**: 97 % (NMR, CDCl₃) (conversion: 100 %).

Entry 4

Dimethyl maleate (**1a-cis**, 28.83 mg, 0.20 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 1.5–1.6 mW/cm², 17th August, 2020). Irradiation time: 4 h. Yield of **3aA**: 34 % (NMR, CDCl₃) (conversion: 22 %).

Entry 5

Dimethyl maleate (**1a-cis**, 28.86 mg, 0.20 mmol) and DTBP (14.83 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Reaction time without irradiation of sunlight: 4 h. Yield of **3aA**: 0 % (NMR, CDCl₃) (conversion: 16 %).

Entry 6

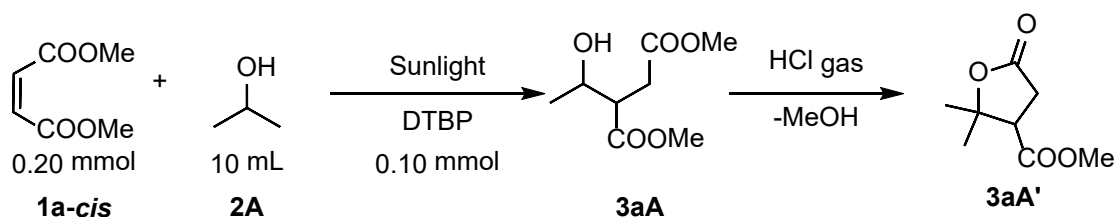
Dimethyl maleate (**1a-cis**, 28.78 mg, 0.20 mmol) and DTBP (14.48 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL) at 35 °C. Reaction time without irradiation of sunlight: 0 h. Yield of **3aA**: 0 % (NMR, CDCl₃) (conversion: 13 %).

Entry 7

Dimethyl maleate (**1a-cis**, 28.73 mg, 0.20 mmol) and DTBP (14.47 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Reaction time without irradiation of sunlight: 0 h. Yield of **3aA**: 0 % (NMR, CDCl₃) (conversion: 16 %).

4-4-4 Experimental details of the reactions in Tables 2

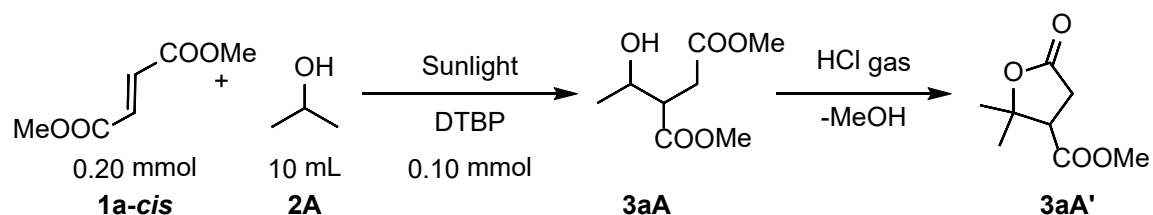
4-4-4-1 Entry 1: 2,2-Dimethyl-5-oxo-tetrahydro-3-furancarboxylic acid methyl ester (**3aA'**).^{24,29}



Dimethyl maleate (**1a-cis**, 28.78 mg, 0.20 mmol) and DTBP (14.97 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 1.5–2.2 mW/cm², 4th June, 2018). Irradiation time: 4 h. Yield of **3aA**: 98 %; **3aA'**: 97 % (NMR, CDCl₃) (conversion: 100 %). Eluent for chromatography: hexane/ethyl acetate (40/1 → 0/1).

3aA': 31.94 mg (93 %); colorless oil. ¹H-NMR (CDCl₃): δ = 1.32 (s, 3H), 1.61 (s, 3H), 2.72 (dd, *J* = 8.8, 18.0 Hz, 1 H), 3.10 (dd, *J* = 9.6, 18.0 Hz, 1 H), 3.21 (dd, *J* = 8.8, 9.6 Hz, 1 H), 3.77 (s, 3H) ppm. ¹³C-NMR (CDCl₃): δ = 23.3, 28.5, 31.8, 50.4, 52.5, 84.4, 170.3, 173.9 ppm. IR (KBr disk): 3536, 3461, 2983, 2955, 2852, 1781, 1739, 1601 1559, 1439, 1390, 1377, 1362, 1272, 1227, 1173, 1142, 1120, 1088, 1034, 1001, 966, 930, 911, 888, 851, 837, 793, 764, 738, 678, 599, 544, 540 cm⁻¹. MS, *m/z* (relative intensity): 41 (34), 43 (100), 55 (93), 59 (13), 69 (24), 97 (11), 114 (27), 129 (35), 157 (28), 172 (0.01, M⁺).

4-4-4-2 Entry 2: 2,2-Dimethyl-5-oxo-tetrahydro-3-furancarboxylic acid methyl ester (3aA').^{24, 29}



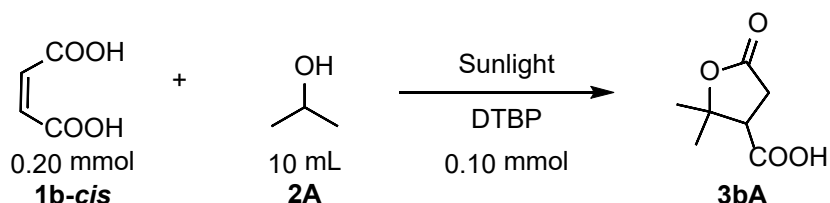
Run 1

Dimethyl fumarate (**1a-cis**, 28.82 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 1.2–1.8 mW/cm², 21st May, 2018). Irradiation time: 4 h. Yield of **3aA**: 98 %; **3aA'**: 85 % (NMR, CDCl₃) (conversion: 100 %).

Run 2

Dimethyl fumarate (**1a-cis**, 28.87 mg, 0.20 mmol) and DTBP (14.64 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 1.3–1.7 mW/cm², 27th May, 2018). Irradiation time: 4 h. Yield of **3aA**: 98 %; **3aA'**: 88 % (NMR, CDCl₃) (conversion: 100 %).

4-4-4-3 Entry 3: Tetrahydro-2,2-dimethyl-5-oxo-3-furancarboxylic acid (terebic acid, 3bA).^{19a, 29, 30}



Run 1

Maleic acid (**1b-cis**, 22.78 mg, 0.20 mmol) and DTBP (14.92 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 1.0–2.3 mW/cm², 4th May, 2016). Irradiation time: 4 h. Yield of **3bA**: 97 % (conversion: 100 %) (NMR, CD₃CN). Eluent for chromatography: hexane/ethyl acetate (100/1 → 60/1).

3bA: 26.6 mg (86 %); white solid; ¹H-NMR (CD₃CN): δ = 1.33 (s, 3H), 1.54 (s, 3H), 2.68 (dd, *J* = 17.6, 8.7 Hz, 1H), 2.90 (dd, 17.6, 8.7 Hz, 1H), 3.24 (dd, *J* = 8.7, 8.7 Hz, 1H) ppm. ¹³C-NMR (CD₃CN): δ = 23.6, 28.4, 32.7, 50.7, 85.0, 172.1, 175.3 ppm. IR (KBr disk):

3457, 3126, 3064, 3017, 2991, 2957, 2941, 2720, 2646, 2565, 2494, 2403, 1746, 1736, 1670, 1582, 1509, 1455, 1425, 1408, 1393, 1375, 1327, 1291, 1232, 1198, 1167, 1143, 1120, 1085, 1018, 982, 953, 939, 919, 858, 836, 788, 718, 604, 577, 568, 529 cm^{-1} . MS, m/z (relative intensity): 41 (27), 43 (100), 55 (40), 59 (30), 69 (14), 143 (19), 158 (M^+ , 0.1).

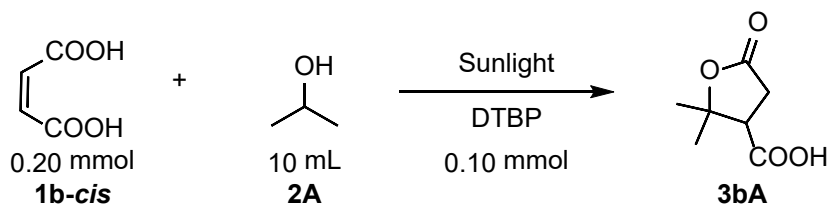
Run 2

Maleic acid (**1b-cis**, 23.26 mg, 0.20 mmol) and DTBP (14.66 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 0.5–2.2 mW/cm^2 , 29th June, 2018). Irradiation time: 4 h. Yield of **3bA**: 100 % (conversion: 100 %) (NMR, acetone- d_6).

Run 3

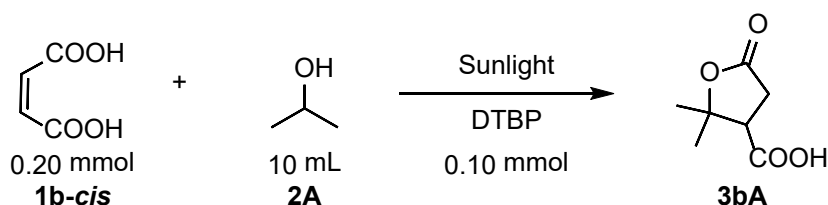
Maleic acid (**1b-cis**, 23.18 mg, 0.20 mmol) and DTBP (14.66 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 0.5–2.2 mW/cm^2 , 29th June, 2018). Irradiation time: 4 h. Yield of **3bA**: 93 % (conversion: 100 %) (NMR, acetone- d_6).

4-4-4-4 Entry 4: Tetrahydro-2,2-dimethyl-5-oxo-3-furancarboxylic acid (terebic acid, 3bA).^{19a, 29, 30}



Maleic acid (**1b-cis**, 23.22 mg, 0.20 mmol) and DTBP (14.66 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 0.5–1.3 mW/cm^2 , 13rd May, 2016). Irradiation time: 3 h. Yield of **3bA**: 92 % (conversion: 79 %) (NMR, CD_3CN).

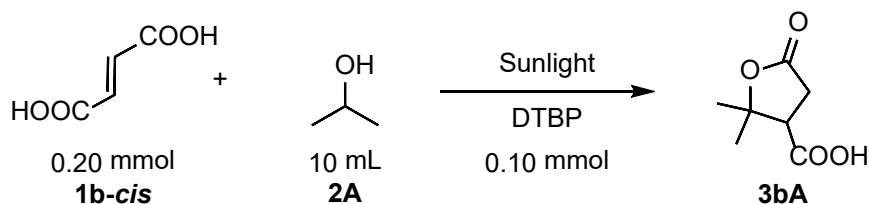
4-4-4-5 Entry 5: Tetrahydro-2,2-dimethyl-5-oxo-3-furancarboxylic acid (terebic acid, 3bA).^{19a, 29, 30}



Maleic acid (**1b-cis**, 23.23 mg, 0.20 mmol) and DTBP (14.71 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 1.7–1.8 mW/cm^2 , 17th March, 2016). Irradiation

time: 2 h. Yield of **3bA**: 93 % (conversion: 60 %) (NMR, CD₃CN).

4-4-4-6 Entry 6: Tetrahydro-2,2-dimethyl-5-oxo-3-furancarboxylic acid (terebic acid, 3bA).^{19a, 29, 30}



Run 1

Fumaric acid (**1b-trans**, 23.21 mg, 0.20 mmol) and DTBP (14.68 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 0.7–1.7 mW/cm², 22nd June, 2018). Irradiation time: 4 h. Yield of **3bA**: 94 % (conversion: 100 %) (NMR, acetone-d₆).

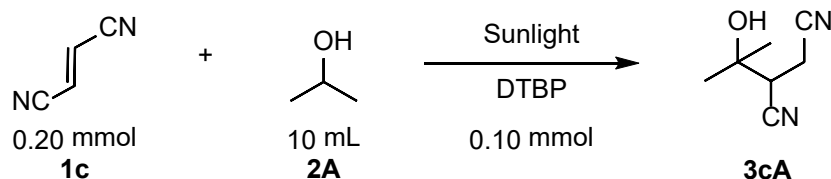
Run 2

Fumaric acid (**1b-trans**, 23.22 mg, 0.20 mmol) and DTBP (14.71 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 0.3–2.2 mW/cm², 27th June, 2018). Irradiation time: 4 h. Yield of **3bA**: 98 % (conversion: 100 %) (NMR, acetone-d₆).

Run 3

Fumaric acid (**1b-trans**, 23.22 mg, 0.20 mmol) and DTBP (14.61 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 0.3–2.2 mW/cm², 27th June, 2018). Irradiation time: 4 h. Yield of **3bA**: 100 % (conversion: 100 %) (NMR, acetone-d₆).

4-4-4-7 Entry 7: 2-(1-Hydroxy-1-methylethyl)succinonitrile (**3cA**).^{19a}



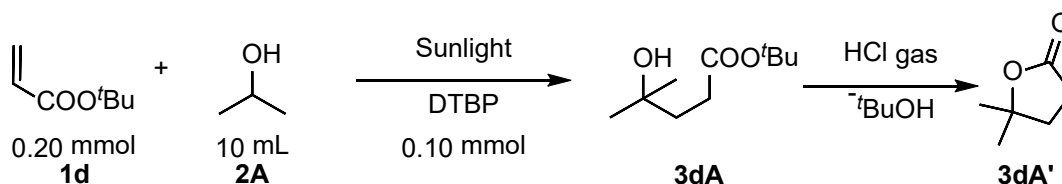
Run 1

Fumaronitrile (**1c**, 15.68 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 1.2–1.7 mW/cm², 21st May, 2018). Irradiation time: 4 h. Yield of **3bA**: 92 % (conversion: 100 %) (NMR, CDCl₃).

Run 2

Fumaronitrile (**1c**, 15.66 mg, 0.20 mmol) and DTBP (14.65 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 1.3–1.7 mW/cm², 27th May, 2018). Irradiation time: 4 h. Yield of **3bA**: 99 % (conversion: 100 %) (NMR, CDCl₃).

4-4-4-8 Entry 8: Dimethyl-tetrahydrofuran-2-one (**3dA'**).^{19a}



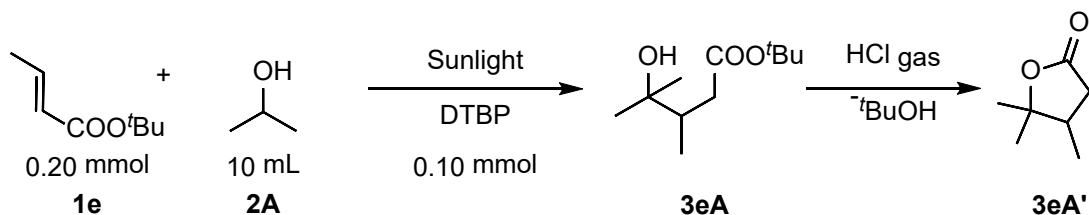
Run 1

t-Butyl acrylate (**1d**, 28.85 mg, 0.23 mmol) and DTBP (14.75 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 0.5–1.5 mW/cm², 5th June, 2018). Irradiation time: 4 h. Yield of **3dA**: 32 %; **3dA'**: 25 % (conversion: 100 %) (NMR, CDCl₃).

Run 2

t-Butyl acrylate (**1d**, 28.56 mg, 0.22 mmol) and DTBP (14.66 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: partially cloudy (light intensity: 1.3–2.0 mW/cm², 8th June, 2018). Irradiation time: 4 h. Yield of **3dA**: 36 %; **3dA'**: 27 % (conversion: 100 %) (NMR, CDCl₃).

4-4-4-9 Entry 9: Trimethyltetrahydrofuran-2-one (3eA').^{19a}



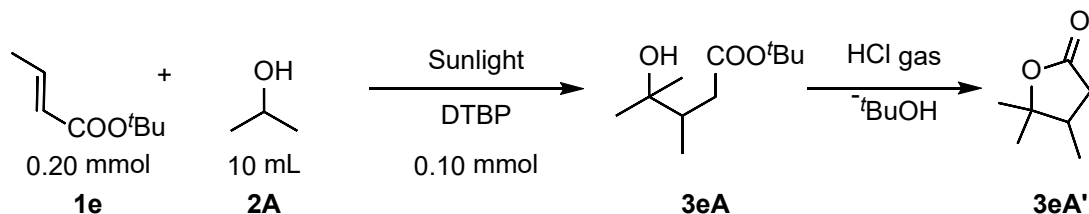
Run 1

t-Butyl crotonate (**1e**, 28.47 mg, 0.20 mmol) and DTBP (14.70 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 1.1–1.6 mW/cm², 30th August, 2020). Irradiation time: 4 h. Yield of **3eA**: 49 %; **3dA'**: 24 % (conversion: 91 %) (NMR, CDCl₃).

Run 2

t-Butyl crotonate (**1e**, 28.48 mg, 0.20 mmol) and DTBP (14.60 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 1.2–1.5 mW/cm², 9th September, 2020). Irradiation time: 4 h. Yield of **3eA**: 41 %; **3dA'**: 35 % (conversion: 92 %) (NMR, CDCl₃).

4-4-4-10 Entry 10: Trimethyltetrahydrofuran-2-one (3eA').^{19a}



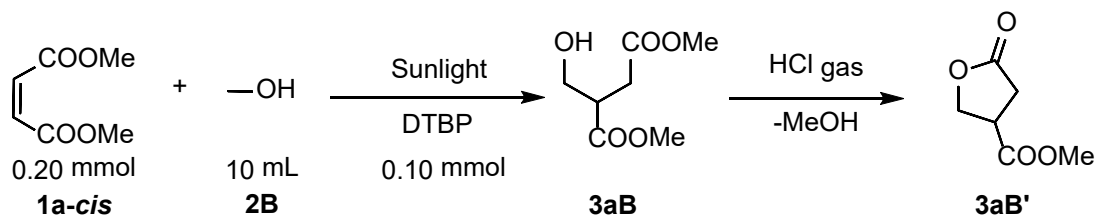
Run 1

t-Butyl crotonate (**1e**, 28.39 mg, 0.20 mmol) and DTBP (14.70 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 0.3–1.6 mW/cm², 30th August, 2020). Irradiation time: 5 h. Yield of **3eA**: 48 % (conversion: 94 %) (NMR, CDCl₃).

Run 2

t-Butyl crotonate (**1e**, 28.53 mg, 0.20 mmol) and DTBP (14.66 mg, 0.10 mmol) in 2-propanol (**2A**, 10 mL). Weather: sunny (light intensity: 1.2–1.5 mW/cm², 9th September, 2020). Irradiation time: 5 h. Yield of **3eA**: 57 % (conversion: 94 %) (NMR, CDCl₃).

4-4-4-11 Entry 11: Tetrahydro-5-oxo-3-furancarboxylic acid methyl ester (**3aB'**).³¹



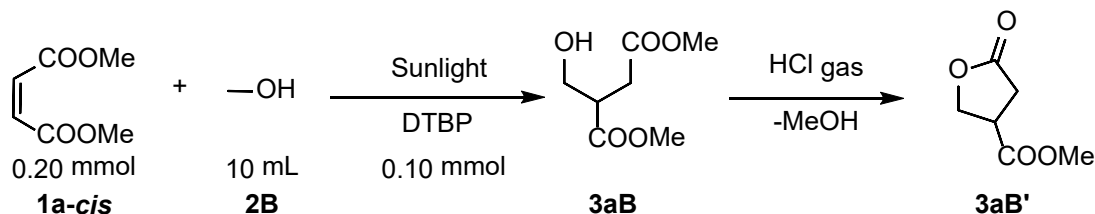
Run 1

Dimethyl maleate (**1a-cis**, 28.93 mg, 0.20 mmol) and DTBP (14.76 mg, 0.10 mmol) in Methanol (**2B**, 10 mL). Weather: sunny (light intensity: 1.1–1.6 mW/cm², 30th August, 2020). Irradiation time: 4 h. Yield of **3aB**: 71 % (conversion: 65 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a-cis**, 28.56 mg, 0.20 mmol) and DTBP (14.58 mg, 0.10 mmol) in Methanol (**2B**, 10 mL). Weather: sunny (light intensity: 1.1–1.6 mW/cm², 30th August, 2020). Irradiation time: 4 h. Yield of **3aB**: 71 % (conversion: 62 %) (NMR, CDCl₃).

4-4-4-12 Entry 12: Tetrahydro-5-oxo-3-furancarboxylic acid methyl ester (**3aB'**).³¹



Run 1

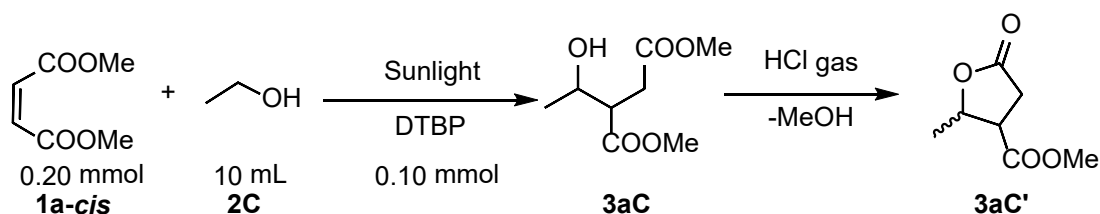
Dimethyl maleate (**1a-cis**, 28.80 mg, 0.20 mmol) and DTBP (14.69 mg, 0.10 mmol) in Methanol (**2B**, 10 mL). Weather: sunny (light intensity: 0.6–1.5 mW/cm², 9th September, 2020). Irradiation time: 10 h. Yield of **3aB**: 74 %; **3aB'**: 66 % (conversion: 89 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a-cis**, 28.67 mg, 0.20 mmol) and DTBP (14.75 mg, 0.10 mmol) in Methanol (**2B**, 10 mL). Weather: sunny (light intensity: 0.6–1.5 mW/cm², 9th September, 2020). Irradiation time: 10 h. Yield of **3aB**: 76 %; **3aB'**: 64 % (conversion: 85 %) (NMR, CDCl₃). Eluent for chromatography: hexane/ethyl acetate (40/1 → 0/1).

3aB': 15.74 mg (62 %); colorless oil; ¹H-NMR (CDCl₃): δ = 2.76 (dd, *J* = 9.6, 17.6 Hz, 1H), 2.89 (dd, *J* = 7.4, 17.6 Hz, 1H), 3.47 (dddd, *J* = 7.0, 7.4, 8.0, 9.6 Hz, 1 H), 3.78 (s, 3H), 4.46 (dd, *J* = 7.0, 9.6 Hz, 1 H), 4.50 (dd, *J* = 8.0, 9.6 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 30.9, 39.9, 52.8, 69.0, 171.5, 175.0 ppm. IR (KBr disk): 2961, 2366, 1774, 1730, 1257, 1201, 1162, 1009, 861, 791, 702, 679, 628, 607, 599, 563, 541, 528, 514, 504 cm⁻¹. MS, *m/z* (relative intensity): 41 (48), 42 (15), 43 (13), 55 (100), 59 (35), 69 (30), 84 (22), 87 (21), 102 (20), 113 (13), 116 (18), 145 (0.02, M⁺).

4-4-4-13 Entry 13: Tetrahydro-2-methyl-5-oxo-3-furancarboxylic acid methyl ester (3aC'-cis, 3aC'-trans).^{19a, 29}



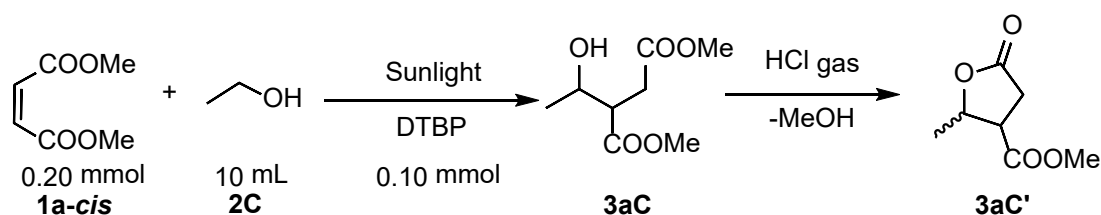
Run 1

Dimethyl maleate (**1a-cis**, 28.74 mg, 0.20 mmol) and DTBP (14.81 mg, 0.10 mmol) in Ethanol (**2C**, 10 mL). Weather: sunny (light intensity: 1.6–2.1 mW/cm², 31th July, 2018). Irradiation time: 4 h. Yield of **3aC**: 96 %; *cis*- and *trans*-**3aC'**: 36 and 55 % (conversion: 100 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a-cis**, 28.79 mg, 0.20 mmol) and DTBP (14.81 mg, 0.10 mmol) in Ethanol (**2C**, 10 mL). Weather: sunny (light intensity: 1.6–2.1 mW/cm², 31th July, 2018). Irradiation time: 4 h. Yield of **3aC**: 97 %; *cis*- and *trans*-**3aC'**: 34 and 53 % (conversion: 100 %) (NMR, CDCl₃).

4-4-4-14 Entry 14: Tetrahydro-2-methyl-5-oxo-3-furancarboxylic acid methyl ester (3aC'-cis, 3aC'-trans).^{19a, 29}



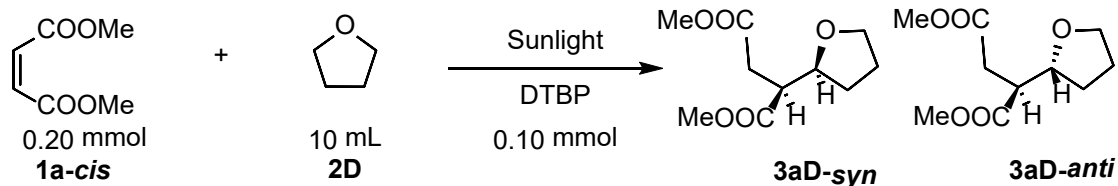
Dimethyl maleate (**1a-cis**, 28.97 mg, 0.20 mmol) and DTBP (14.80 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Weather: sunny (light intensity: 0.2–1.2 mW/cm², 31th July, 2018). Irradiation time: 11 h. Yield of **3aC**: 98 %; *cis*- and *trans*-**3aC'**: 34 and 55 % (conversion: 100 %) (NMR, CDCl₃). Eluent for chromatography: hexane/ethyl acetate (40/1 → 0/1).

3aC'-cis: 9.97 mg (31 %); colorless oil. ¹H-NMR (CDCl₃): δ = 1.52 (d, *J* = 6.4 Hz, 3 H), 2.80 (dd, *J* = 8.8, 17.2 Hz 1H), 2.94 (dd, *J* = 9.2, 17.2 Hz 1H), 3.02 (ddd, *J* = 7.6, 8.8, 9.2 Hz 1H), 3.77 (s, 3 H), 4.68 (dq, *J* = 6.4, 7.6 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 20.7, 32.3, 47.4, 52.7, 78.1, 171.1, 174.2 ppm. IR (KBr disk): 3021, 2985, 2956, 1787, 1739, 1439, 1421, 1386, 1375, 1355, 1324, 1261, 1205, 1119, 1090, 1053, 1030, 961, 946, 920, 847, 832, 758, 665 cm⁻¹. MS, *m/z* (relative intensity): 43 (21), 55 (100), 59 (18), 87 (18), 99 (9), 116 (16), 127 (4), 130 (5), 143 (M⁺, 0.1).

3aC'-trans: 17.14 mg (54 %); colorless oil; ¹H-NMR (CDCl₃): δ = 1.34 (d, *J* = 6.4 Hz, 3 H), 2.68 (dd, *J* = 9.2, 17.2 Hz 1H), 2.96 (dd, *J* = 6.4, 17.2 Hz 1H), 3.48 (ddd, *J* = 6.4, 6.8, 9.2 Hz 1H), 3.77 (s, 3 H), 4.86 (dq, *J* = 6.4, 6.8 Hz, 1 H) ppm. ¹³C-NMR (CDCl₃): δ = 16.8, 31.2, 44.5, 52.3, 76.2, 170.6, 174.7 ppm. IR (KBr disk): 3021, 2987, 2955, 1788, 1739, 1440, 1416, 1391, 1375, 1324, 1267, 1253, 1216, 1192, 1176, 1134, 1093, 1054, 995, 979, 942, 912, 892, 855, 837, 757, 664, 537 cm⁻¹. MS, *m/z* (relative intensity): 43 (18), 55 (100), 59 (17), 82 (8), 99 (19), 114 (22), 127 (5), 143 (M⁺, 0.1).

4-4-5 Experimental details of the reactions in Tables 3

4-4-5-1 Entry 1: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-dimethyl ester (**3aD-syn**, **anti**).^{19b}



Run 1

Dimethyl maleate (**1a-cis**, 28.97 mg, 0.20 mmol) and DTBP (15.18 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny later cloudy (light intensity: 1.6–2.1 mW/cm², 8th May, 2016). Irradiation time: 4 h. Yield of **3aD**: 97 % (*syn* / *anti* = 63 / 34) (conversion: 100 %) (NMR, CDCl₃).

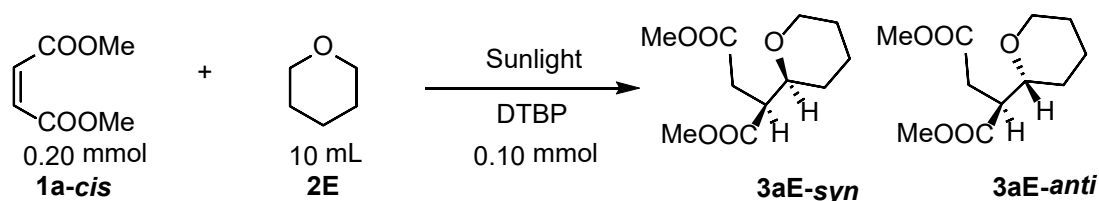
Run 2

Dimethyl maleate (**1a-cis**, 28.61 mg, 0.20 mmol) and DTBP (14.81 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny later cloudy (light intensity: 1.3–2.4 mW/cm², 8th May, 2016). Irradiation time: 4 h. Yield of **3aD**: 95 % (*syn* / *anti* = 62 / 33) (conversion: 100 %) (NMR, CDCl₃).

Run 3

Dimethyl maleate (**1a-cis**, 28.95 mg, 0.20 mmol) and DTBP (14.88 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: partially cloudy (light intensity: 2.0–2.3 mW/cm², 19th May, 2016). Irradiation time: 4 h. Yield of **3aD**: 96 % (*syn* / *anti* = 62 / 34) (conversion: 100 %) (NMR, CDCl₃).

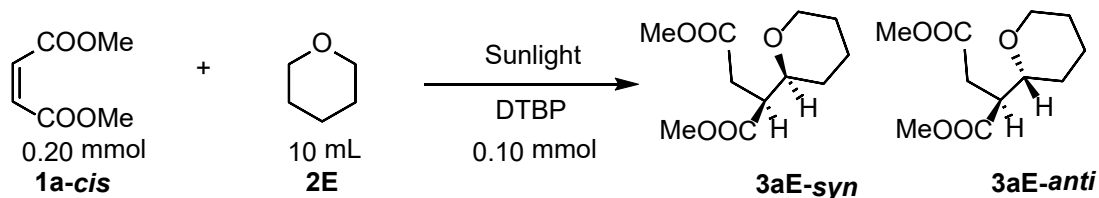
4-4-5-2 Entry 2: 2-(Tetrahydro-2H-pyran-2-yl)butanedioic acid 1,4-dimethyl ester (**3aE-syn**, **anti**).^{19b}



Dimethyl maleate (**1a-cis**, 28.60 mg, 0.20 mmol) and DTBP (14.75 mg, 0.10 mmol) in THP (**2E**, 10 mL). Weather: sunny later cloudy (light intensity: 0.9–1.8 mW/cm², 23rd May, 2016).

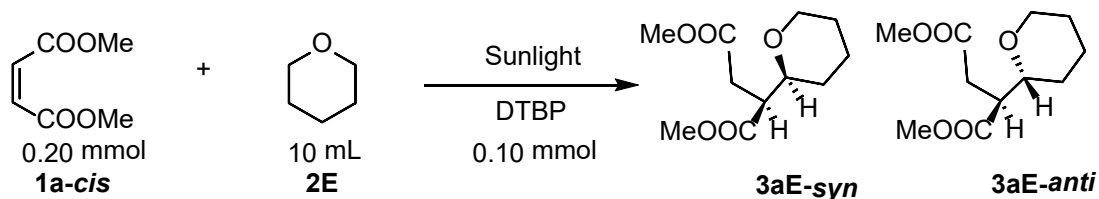
Irradiation time: 6 h. Yield of **3aE**: 55 % (*syn* / *anti* = 33 / 22) (conversion: 52 %) (NMR, CDCl₃).

4-4-5-3 Entry 3: 2-(Tetrahydro-2H-pyran-2-yl)butanedioic acid 1,4-dimethyl ester (3aE-*syn*, *anti*).^{19b}



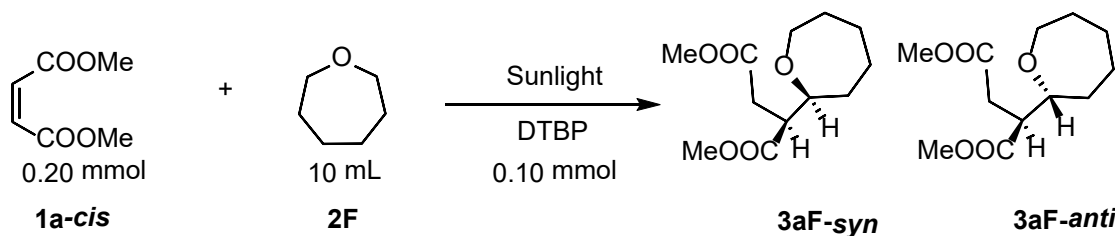
Dimethyl maleate (**1a-cis**, 28.74 mg, 0.20 mmol) and DTBP (14.58 mg, 0.10 mmol) in THF (**2E**, 10 mL). Weather: partially cloudy (light intensity: 0.6–1.9 mW/cm², 30th August, 2016). Irradiation time: 9 h. Yield of **3aE**: 67 % (*syn* / *anti* = 40 / 27) (conversion: 62 %) (NMR, CDCl₃).

4-4-5-4 Entry 4: 2-(Tetrahydro-2H-pyran-2-yl)butanedioic acid 1,4-dimethyl ester (3aE-*syn*, *anti*).^{19b}



Dimethyl maleate (**1a-cis**, 28.75 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2E**, 10 mL). Weather: cloudy later sunny (light intensity: 0.2–1.5 mW/cm², 30th August, 2016). Irradiation time: 16 h. Yield of **3aE**: 61 % (*syn* / *anti* = 39 / 22) (conversion: 100 %) (NMR, CDCl₃).

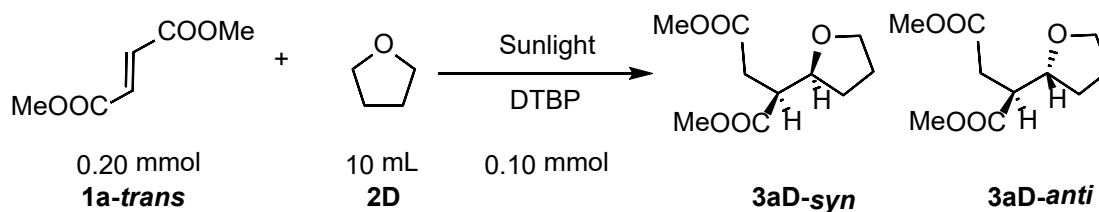
4-4-5-5 Entry 5: 2-(2-Oxepanyl)butanedioic acid 1,4-dimethyl ester (3aF-*syn*, *anti*).^{19b}



Dimethyl maleate (**1a-cis**, 28.78 mg, 0.20 mmol) and DTBP (14.71 mg, 0.10 mmol) in oxepane (**2F**, 10 mL). Weather: cloudy later sunny (light intensity: 0.3–1.2 mW/cm², 19th August, 2016). Irradiation time: 16 h. Yield of **3aF**: 61 % (*syn* / *anti* = 39 / 22) (conversion: 100 %) (NMR, CDCl₃).

May, 2016). Irradiation time: 20 h. Yield of **3aF**: 65 % (*syn* / *anti* = 33 / 32) (conversion: 100 %) (NMR, CDCl₃).

4-4-5-6 Entry 6: 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-dimethyl ester (3aD-syn, anti**)**.^{19b}



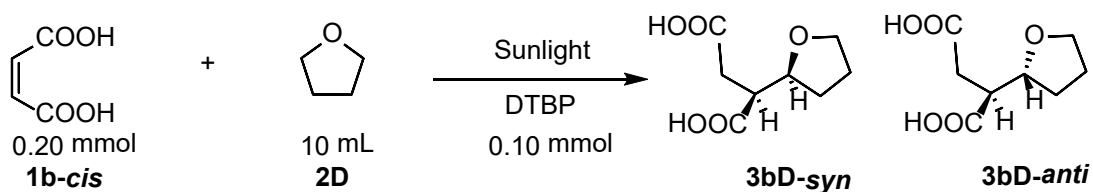
Run 1

Dimethyl fumarate (**1a-trans**, 28.93 mg, 0.20 mmol) and DTBP (14.74 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.5–1.7 mW/cm², 15th May, 2018). Irradiation time: 4 h. Yield of **3aD**: 95 % (*syn* / *anti* = 44 / 51) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Dimethyl fumarate (**1a-trans**, 28.86 mg, 0.20 mmol) and DTBP (14.66 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.7–2.2 mW/cm², 20th May, 2018). Irradiation time: 4 h. Yield of **3aD**: 95 % (*syn* / *anti* = 45 / 50) (conversion: 100 %) (NMR, CDCl₃).

4-4-5-7 Entry 7: 2-(2-Tetrahydro-2-furanyl) butanedioic acid (3bD-syn, anti**)**.^{19b}



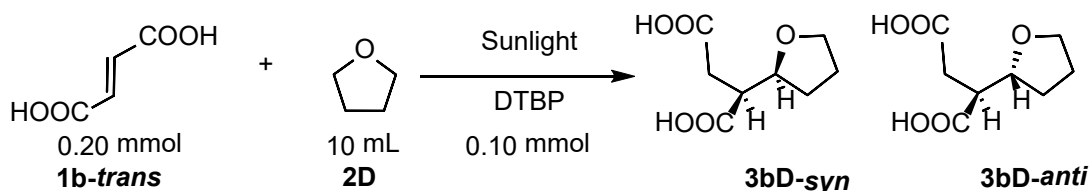
Run 1

Maleic acid (**1b-cis**, 23.20 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.2–2.0 mW/cm², 14th May, 2018). Irradiation time: 4 h. Yield of **3bD**: 98 % (*syn* / *anti* = 46 / 52) (conversion: 100 %) (NMR, acetone-d₆).

Run 2

Maleic acid (**1b-cis**, 23.27 mg, 0.20 mmol) and DTBP (14.71 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.3–1.7 mW/cm², 27th May, 2018). Irradiation time: 4 h. Yield of **3bD**: 93 % (*syn* / *anti* = 43 / 50) (conversion: 100 %) (NMR, acetone-d₆).

4-4-5-8 Entry 8: 2-(2-Tetrahydro-2-furanyl) butanedioic acid (**3bD-syn, anti**).^{19b}



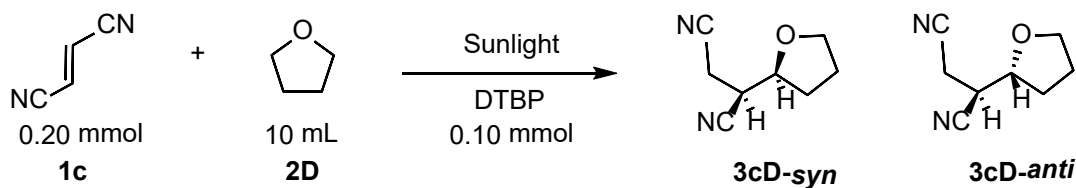
Run 1

Fumaric acid (**1b-trans**, 23.28 mg, 0.20 mmol) and DTBP (14.84 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 0.5–1.7 mW/cm², 2nd May, 2018). Irradiation time: 4 h. Yield of **3bD**: 96 % (*syn* / *anti* = 45 / 51) (conversion: 100 %) (NMR, acetone-d₆).

Run 2

Fumaric acid (**1b-trans**, 23.19 mg, 0.20 mmol) and DTBP (14.60 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 0.8–2.0 mW/cm², 14th May, 2018). Irradiation time: 4 h. Yield of **3bD**: 92 % (*syn* / *anti* = 42 / 50) (conversion: 100 %) (NMR, acetone-d₆).

4-4-5-9 Entry 9: 2-(2-Tetrahydro-2-furanyl) butanedinitrile (**3cD-syn, anti**).^{19b}



Run 1

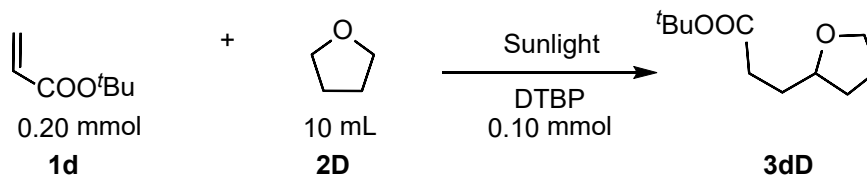
Fumaronitrile (**1c**, 15.66 mg, 0.20 mmol) and DTBP (14.70 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.5–1.7 mW/cm², 15th May, 2018). Irradiation time: 4 h. Yield of **3cD**: 91 % (*syn* / *anti* = 51 / 40) (conversion: 100 %) (NMR, acetone-d₆).

Run 2

Fumaronitrile (**1c**, 15.75 mg, 0.20 mmol) and DTBP (14.70 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.7–2.2 mW/cm², 20th May, 2018). Irradiation time: 4 h.

Yield of **3cD**: 93 % (*syn* / *anti* = 51 / 42) (conversion: 100 %) (NMR, acetone- d_6).

4-4-5-10 Entry 10: Tetrahydro-2-furanpropanoic acid *tert*-butyl ester (3dD**)..^{19b}**



Run 1

t-Butyl acrylate (**1d**, 25.76 mg, 0.23 mmol) and DTBP (14.77 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 0.5–1.5 mW/cm², 5th June, 2018). Irradiation time: 4 h. Yield of **3cD**: 45 % (conversion: 100 %) (NMR, CDCl₃).

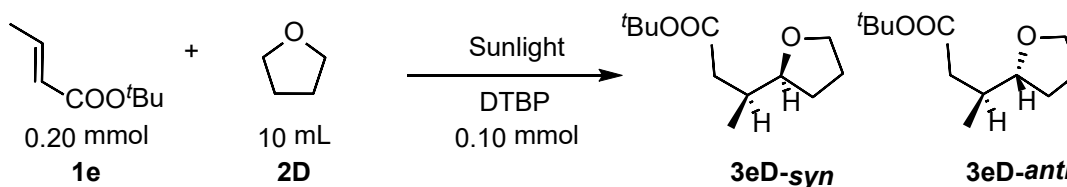
Run 2

t-Butyl acrylate (**1d**, 25.75 mg, 0.23 mmol) and DTBP (14.78 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.5–1.7 mW/cm², 25th June, 2018). Irradiation time: 4 h. Yield of **3dD**: 38 % (conversion: 100 %) (NMR, CDCl₃).

Run 3

t-Butyl acrylate (**1d**, 25.78 mg, 0.23 mmol) and DTBP (14.75 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.5–1.7 mW/cm², 25th June, 2018). Irradiation time: 4 h. Yield of **3dD**: 38 % (conversion: 100 %) (NMR, CDCl₃).

4-4-5-11 Entry 11: Tetrahydro- β -methyl-2-furanpropanoic acid *tert*-butyl ester (3eD-syn**, *anti*)..^{19b}**



Run 1

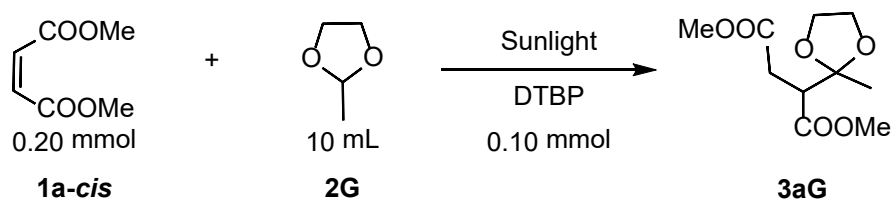
t-Butyl crotonate (**1e**, 28.61 mg, 0.20 mmol) and DTBP (14.64 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.3–1.8 mW/cm², 2nd June, 2018). Irradiation time: 4 h. Yield of **3eD**: 79 % (*syn* / *anti* = 39 / 40) (conversion: 89%) (NMR, CDCl₃).

Run 2

t-Butyl crotonate (**1e**, 28.44 mg, 0.20 mmol) and DTBP (14.61 mg, 0.10 mmol) in THF (**2D**, 10 mL). Weather: sunny (light intensity: 1.5–1.6 mW/cm², 2nd May, 2019). Irradiation time: 4 h. Yield of **3eD**: 83 % (*syn* / *anti* = 41 / 42) (conversion: 92 %) (NMR, CDCl₃).

4-4-6 Experimental details of the reactions in Tables 4

4-4-6-1 Entry 1: 2-(2-Methyl-1, 3-dioxolan-2-yl)butanedioic acid 1,4-dimethyl ester (**3aG**).^{19b}



Run 1

Dimethyl maleate (**1a-cis**, 28.86 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Weather: sunny later cloudy (light intensity: 0.8–1.8 mW/cm², 30th August, 2018). Irradiation time: 3 h. Yield of **3aG**: 97 % (conversion: 100 %) (NMR, CDCl₃).

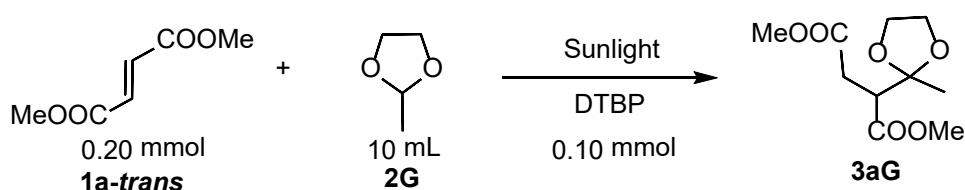
Run 2

Dimethyl maleate (**1a-cis**, 28.83 mg, 0.20 mmol) and DTBP (14.59 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Weather: sunny (light intensity: 0.8–1.5 mW/cm², 9th September, 2020). Irradiation time: 3 h. Yield of **3aG**: 100 % (conversion: 100 %) (NMR, CDCl₃).

Run 3

Dimethyl maleate (**1a-cis**, 28.72 mg, 0.20 mmol) and DTBP (14.68 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Weather: sunny (light intensity: 0.8–1.5 mW/cm², 9th September, 2020). Irradiation time: 3 h. Yield of **3aG**: 97 % (conversion: 100 %) (NMR, CDCl₃).

4-4-6-2 Entry 2: 2-(2-Methyl-1, 3-dioxolan-2-yl)butanedioic acid 1,4-dimethyl ester (3aG).^{19b}



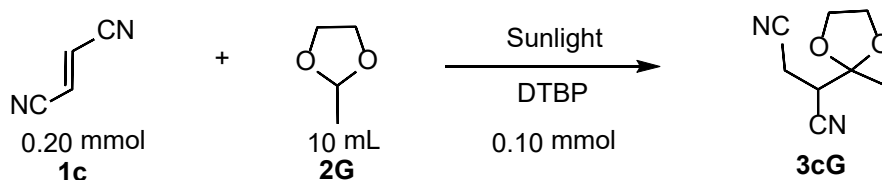
Run 1

Dimethyl fumarate (**1a-trans**, 28.83 mg, 0.20 mmol) and DTBP (14.69 mg, 0.10 mmol) in 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Weather: sunny (light intensity: 1.5–1.8 mW/cm², 3rd June, 2018). Irradiation time: 3 h. Yield of **3aG**: 95 % (conversion: 100 %) (NMR, CDCl₃).

Run 2

Dimethyl fumarate (**1a-trans**, 28.79 mg, 0.20 mmol) and DTBP (14.55 mg, 0.10 mmol) in 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Weather: partially cloudy (light intensity: 0.8–1.5 mW/cm², 5th June, 2018). Irradiation time: 3 h. Yield of **3aG**: 94 % (conversion: 100 %) (NMR, CDCl₃).

4-4-6-3 Entry 3: 2-(2-Methyl-1, 3-dioxolan-2-yl)butanedinitrile (3cG).^{19b}



Run 1

Fumaronitrile (**1c**, 15.57 mg, 0.20 mmol) and DTBP (14.61 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Weather: partially cloudy (light intensity: 0.3–1.5 mW/cm², 19th June, 2018). Irradiation time: 3 h. Yield of **3cG**: 86 % (conversion: 100 %) (NMR, CDCl₃).

Run 2

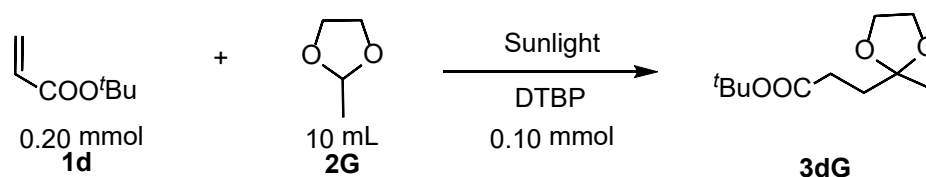
Fumaronitrile (**1c**, 15.65 mg, 0.20 mmol) and DTBP (14.70 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Weather: partially cloudy (light intensity: 1.6–1.9 mW/cm², 31st August, 2018). Irradiation time: 3 h. Yield of **3cG**: 86 % (conversion: 100 %)

(NMR, CDCl₃).

Run 3

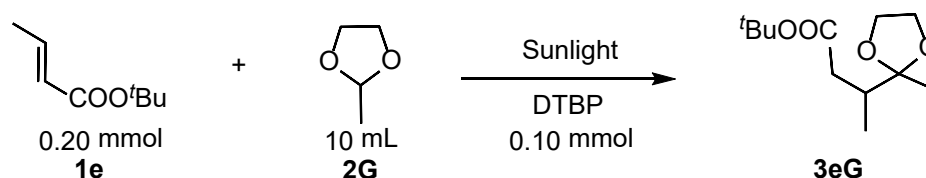
Fumaronitrile (**1c**, 15.73 mg, 0.20 mmol) and DTBP (14.70 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Weather: partially cloudy (light intensity: 1.4–1.6 mW/cm², 17th May, 2019). Irradiation time: 3 h. Yield of **3cG**: 87 % (conversion: 100 %) (NMR, CDCl₃).

4-4-6-4 Entry 4: 3-(2-Methyl-1, 3-dioxolan-2-yl)propionic acid *tert*-butyl ester (**3dG**).^{19b}



t-Butyl acrylate (**1d**, 25.90 mg, 0.20 mmol) and DTBP (14.66 mg, 0.10 mmol) in 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Weather: sunny (light intensity: 1.8–2.0 mW/cm², 14th February, 2017). Irradiation time: 3 h. Yield of **3dG**: 35 % (conversion: 100 %) (NMR, CDCl₃).

4-4-6-5 Entry 5: 3-Methyl-3-(2-methyl-1, 3-dioxolan-2-yl)propanoic acid *tert*-butyl ester (**3eG**).^{19b}



Run 1

t-Butyl crotonate (**1e**, 28.54 mg, 0.20 mmol) and DTBP (14.76 mg, 0.10 mmol) 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Weather: partially cloudy (light intensity: 0.4–1.8 mW/cm², 22nd May, 2019). Irradiation time: 3 h. Yield of **3eG**: 82 % (conversion: 100 %) (NMR, CDCl₃). Eluent for chromatography: hexane/ethyl acetate (80/1 → 0/1).

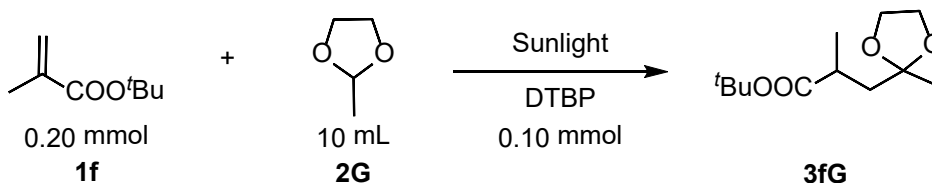
3eG: 30.6 mg (66 %); colorless oil. ¹H-NMR (δ, CDCl₃): 1.00 (d, *J* = 7.2 Hz, 3 H), 1.26 (s, 3 H), 1.45 (s, 9 H), 1.98 (dd, *J* = 9.0, 14.8 Hz, 1 H), 2.26 (ddq, *J* = 4.8, 7.2, 9.0 Hz, 1 H), 2.49 (dd, *J* = 4.8, 14.8 Hz, 1 H), 3.92–3.95 (m, 4 H) ppm. ¹³C-NMR (δ, CDCl₃): 15.3, 20.6, 28.1, 38.2, 38.5, 64.6, 64.7, 80.0, 111.4, 172.6 ppm. IR (KBr disk): 2979, 1730, 1458, 1368, 1296,

1256, 1154, 959, 872, 847, 760 cm^{-1} . MS (m/z , relative intensity): 41 (24), 43 (43), 57 (14), 87 (100), 113 (12), 157 (10), 231 (0.01, M^+).

Run 2

t-Butyl crotonate (**1e**, 28.43 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Weather: sunny (light intensity: 0.7–1.8 mW/cm^2 , 16th May, 2019). Irradiation time: 3 h. Yield of **3eG**: 79 % (conversion: 100 %) (NMR, CDCl_3).

4-4-6-6 Entry 6: 2-Methyl-3-(2-methyl-1, 3-dioxolan-2-yl)propanoic acid tert-butyl ester (**3fG**).^{19b}



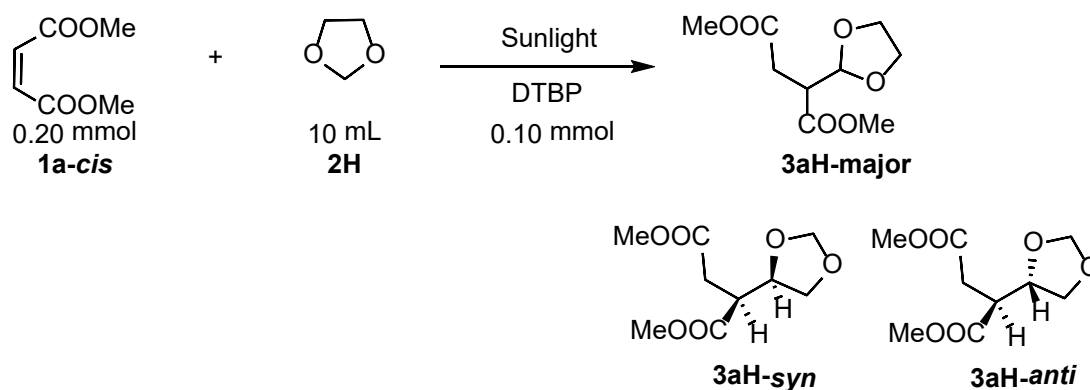
Run 1

t-Butyl methacrylate (**1f**, 28.90 mg, 0.20 mmol) and DTBP (15.18 mg, 0.10 mmol) in 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Weather: cloudy (light intensity: 0.5–1.3 mW/cm^2 , 30th September, 2016). Irradiation time: 3 h. Yield of **3fG**: 0 % (conversion: 100 %) (NMR, CDCl_3).

Run 2

t-Butyl methacrylate (**1f**, 27.73 mg, 0.20 mmol) and DTBP (14.60 mg, 0.10 mmol) in 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Weather: sunny later cloudy (light intensity: 1.3–2.2 mW/cm^2 , 6th October, 2016). Irradiation time: 3 h. Yield of **3fG**: 0 % (conversion: 100 %) (NMR, CDCl_3).

4-4-6-7 Entry 7: 2-(1,3-dioxolan-4-yl)butanedioic acid 1,4-dimethyl ester (**3aH-syn**, *anti*)^{19b} and 2-(1,3-dioxolan-2-yl)butanedioic acid 1,4-dimethyl ester (**3aH-major**).^{19b}



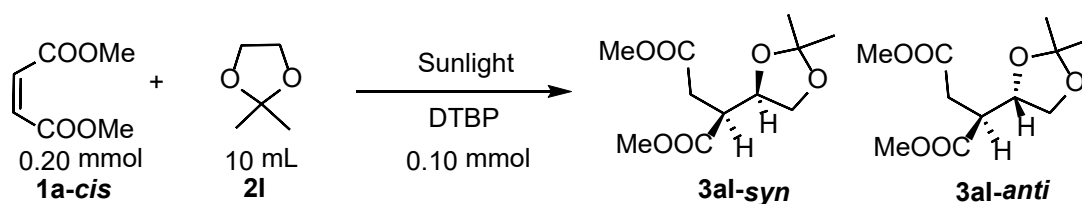
Run 1

Dimethyl maleate (**1a-cis**, 29.09 mg, 0.20 mmol) and DTBP (14.73 mg, 0.10 mmol) in 1,3-dioxolane (**2H**, 10 mL). Weather: sunny (light intensity: 2.1–2.2 mW/cm², 22nd October, 2018). Irradiation time: 3 h. Yield of **3aH**: 97 % (*syn* / *anti* / *major* = 4 / 3 / 90) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a-cis**, 29.00 mg, 0.20 mmol) and DTBP (14.78 mg, 0.10 mmol) in 1,3-dioxolane (**2H**, 10 mL). Weather: sunny (light intensity: 2.1–2.2 mW/cm², 22nd October, 2018). Irradiation time: 3 h. Yield of **3aH**: 99 % (*syn* / *anti* / *major* = 6 / 3 / 90) (conversion: 100 %) (NMR, CDCl₃).

4-4-6-8 Entry 8: 2-(2,2-Dimethyl-1,3-dioxolan-4-yl)butanedioic acid 1,4-dimethyl ester (**3aI-syn**, *anti*).^{19b}



Run 1

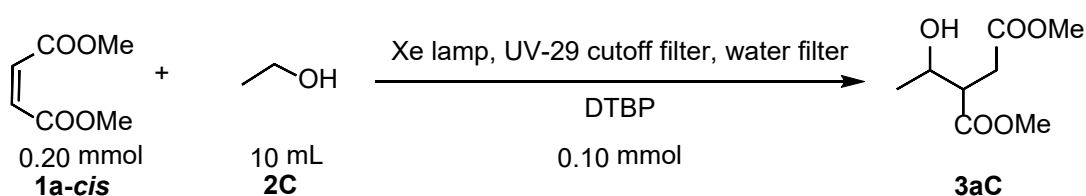
Dimethyl maleate (**1a-cis**, 28.93 mg, 0.20 mmol) and DTBP (14.68 mg, 0.10 mmol) in 2,2-dimethyl-1,3-dioxolane (**2I**, 10 mL). Weather: sunny (light intensity: 0.3–1.6 mW/cm², 23rd April, 2019). Irradiation time: 3 h. Yield of **3aI**: 61 % (*syn* / *anti* = 41 / 20) (conversion: 100 %).

100 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a-cis**, 28.89 mg, 0.20 mmol) and DTBP (14.73 mg, 0.10 mmol) in 2, 2-dimethyl-1,3-dioxolane (**2I**, 10 mL). Weather: sunny (light intensity: 0.3–1.6 mW/cm², 23rd April, 2019). Irradiation time: 3 h. Yield of **3aI**: 57 % (*syn* / *anti* = 40 / 17) (conversion: 100 %) (NMR, CDCl₃).

4-4-7 Experimental details of the reactions in Figure 2.



General procedure for the photolysis..

Dimethyl maleate (**1a-cis**) (0.2 mmol) and DTBP (0.1 mmol) in ethanol (**2C**) (10 mL) was introduced into a quartz cylindrical cell (diameter: 3 cm) equipped with a three-way stopcock. The three-way stopcock was connected to the cell, a nitrogen source, and a small vacuum pump. The solution was evacuated to about 50 mmHg under sonication for 5s and nitrogen was then introduced into the cell; this cycle was repeated 10 times. The photolysis was conducted using a 500-W xenon lamp (USHIO Optical Modulex SX-UI500XQ) fitted with an 18-cm water filter and a cut-off filter (Toshiba UV-29) under a nitrogen atmosphere. The irradiated light was measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with a UVD-S365 photo detector. After photolysis, ethanol was removed in vacuo at 40–50 °C / < 70 Torr (most of the products were volatile under reduced pressure) and the consumption of **1a-cis** and the yield of the product **3aC** were determined by NMR spectroscopy using a precise amount of naphthalene as an internal standard; the yields of each product were calculated based on the consumed starting material.

Run 1 (light intensity: 2 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.83 mg, 0.20 mmol) and DTBP (14.88 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 2 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 93 % (conversion: 84 %) (NMR, CDCl₃).

Run 2 (light intensity: 5 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.97 mg, 0.20 mmol) and DTBP (14.98 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 5 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 94 % (conversion: 100 %) (NMR, CDCl₃).

Run 3 (light intensity: 10 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.65 mg, 0.20 mmol) and DTBP (14.82 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 10 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 86 % (conversion: 100 %) (NMR, CDCl₃).

Run 4 (light intensity: 15 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.76 mg, 0.20 mmol) and DTBP (14.64 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 15 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 72 % (conversion: 100 %) (NMR, CDCl₃).

Run 5 (light intensity: 20 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.86 mg, 0.20 mmol) and DTBP (14.72 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 20 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 71 % (conversion: 100 %) (NMR, CDCl₃).

Run 6 (light intensity: 20 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.71 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 20 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 74 % (conversion: 100 %) (NMR, CDCl₃).

Run 7 (light intensity: 25 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.79 mg, 0.20 mmol) and DTBP (14.83 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 25 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 83 % (conversion: 100 %) (NMR, CDCl₃).

Run 8 (light intensity: 25 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.80 mg, 0.20 mmol) and DTBP (14.62 mg, 0.10 mmol) in ethanol

(**2C**, 10 mL). Light intensity: 25 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 83 % (conversion: 100 %) (NMR, CDCl₃).

Run 9 (light intensity: 25 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.93 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 25 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 88 % (conversion: 100 %) (NMR, CDCl₃).

Run 10 (light intensity: 30 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.81 mg, 0.20 mmol) and DTBP (14.88 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 30 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 81 % (conversion: 100 %) (NMR, CDCl₃).

Run 11 (light intensity: 35 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.84 mg, 0.20 mmol) and DTBP (14.68 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 35 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 82 % (conversion: 100 %) (NMR, CDCl₃).

Run 12 (light intensity: 35 mW/cm²)

Dimethyl maleate (**1a-cis**, 28.60 mg, 0.20 mmol) and DTBP (14.86 mg, 0.10 mmol) in ethanol (**2C**, 10 mL). Light intensity: 35 mW/cm². Irradiation time: 3 h. Yield of **3aC**: 83 % (conversion: 100 %) (NMR, CDCl₃).

4-4-8 Experimental details of the gram-scale synthesis.

4-4-8-1 General procedure

A solution of alcohol/cyclic ether (**2**) (500 mL), olefin (**1**) (10 or 20 mmol) and DTBP (5 or 10 mmol) was introduced into a Pyrex eggplant-shape flask (500 mL or 1 L) equipped with a three-way stopcock. The three-way stopcock was connected to the cell, a nitrogen source, and small vacuum pump. The solution was evacuated to about 50 mmHg under sonication for 5 s and nitrogen was then introduced into the cell; this cycle was repeated 10 times. The photolysis was conducted under sunlight irradiation under a nitrogen atmosphere. The light intensity was measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with a UVD-S365 photo detector. After photolysis, the alcohol/cyclic ether was removed in vacuo at

40–50 °C / < 150 Torr (most of the products were volatile under reduced pressure) and the consumption of the olefin and the products yield were determined by NMR spectroscopy using a precise amount of naphthalene as an internal standard; the yields of each product were calculated based on the consumed starting material.

4-4-8-2 Synthesis of 3aA

Run 1

Dimethyl maleate (**1a-cis**, 1.44 g, 10 mmol) and DTBP (0.73 g, 5 mmol) in 2-propanol (**2A**, 500 mL) using a 500 mL Pyrex eggplant-shape flasks without stirring. Weather: sunny partially cloudy (light intensity: 0.5–1.9 mW/cm², 6th October, 2020). Irradiation time: 4 h. Yield of **3aA**: 95 % (conversion: 75 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a-cis**, 1.44 g, 10 mmol) and DTBP (0.73 g, 5 mmol) in 2-propanol (**2A**, 500 mL) using a 500 mL Pyrex eggplant-shape flasks without stirring. Weather: sunny partially cloudy (light intensity: 0.2–1.9 mW/cm², 6th October, 2020). Irradiation time: 6 h. Yield of **3aA**: 99 % (conversion: 100 %) (NMR, CDCl₃).

Run 3

Dimethyl maleate (**1a-cis**, 2.88 g, 20 mmol) and DTBP (1.46 g, 10 mmol) in 2-propanol (**2A**, 1 L) using a 1 L Pyrex eggplant-shape flasks without stirring. Weather: sunny partially cloudy (light intensity: 0.5–1.9 mW/cm², 6th October, 2020).. Irradiation time: 4 h. Yield of **3aA**: 91 % (conversion: 86 %) (NMR, CDCl₃).

Run 4

Dimethyl maleate (**1a-cis**, 2.88 g, 20 mmol) and DTBP (1.46 g, 10 mmol) in 2-propanol (**2A**, 1 L) using a 1 L Pyrex eggplant-shape flasks with stirring. Weather: sunny partially cloudy (light intensity: 0.5–1.9 mW/cm², 6th October, 2020). Irradiation time: 4 h. Yield of **3aA**: 89 % (conversion: 86 %) (NMR, CDCl₃).

4-4-8-3 Synthesis of 3aD-syn/anti

Run 1

Dimethyl maleate (**1a-cis**, 1.44 g, 10 mmol) and DTBP (0.73 g, 5 mmol) in THF (**2D**, 500

mL) using a 500 mL Pyrex eggplant-shape flasks with stirring. Weather: sunny partially cloudy (light intensity: 0.6–1.6 mW/cm², 9th October, 2018). Irradiation time: 4 h. Yield of **3aD**: 98 % (*syn* / *anti* = 62 / 36) (conversion: 100 %) (NMR, CDCl₃).

Run 2

Dimethyl maleate (**1a-cis**, 1.44 g, 10 mmol) and DTBP (0.73 g, 5 mmol) in THF (**2D**, 500 mL) using a 1 L Pyrex eggplant-shape flasks with stirring. Weather: sunny partially cloudy (light intensity: 0.6–1.6 mW/cm², 9th October, 2018). Irradiation time: 4 h. Yield of **3aD**: 98 % (*syn* / *anti* = 62 / 36) (conversion: 100 %) (NMR, CDCl₃).

Run 3

Dimethyl maleate (**1a-cis**, 1.44 g, 10 mmol) and DTBP (0.73 g, 5 mmol) in THF (**2D**, 500 mL) using a 500 mL Pyrex eggplant-shape flasks without stirring. Weather: sunny partially cloudy (light intensity: 0.6–1.6 mW/cm², 9th October, 2018). Irradiation time: 4 h. Yield of **3aD**: 95 % (*syn* / *anti* = 62 / 33) (conversion: 100 %) (NMR, CDCl₃).

Run 4

Dimethyl maleate (**1a-cis**, 1.44 g, 10 mmol) and DTBP (0.73 g, 5 mmol) in THF (**2D**, 500 mL) using a 1 L Pyrex eggplant-shape flasks without stirring. Weather: sunny partially cloudy (light intensity: 0.6–1.6 mW/cm², 9th October, 2018). Irradiation time: 4 h. Yield of **3aD**: 96 % (*syn* / *anti* = 59 / 37) (conversion: 100 %) (NMR, CDCl₃).

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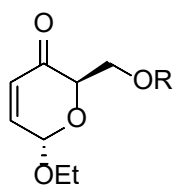
4-6 Appendix

4-6-1 Previous reports on the addition of alcohols to olefins in neat alcohols

Table A1. Previous reports on the addition of alcohols to olefins in neat alcohols.

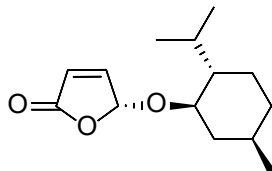
Entry	Olefin	Alcohol	Catalyst ^a	Light source ^b	Irradiation time (h)	Yield (%)	Reference
1	1b-cis & <i>-trans</i>	2A	BP	125W HP-Hg	18	96	1
2	1a-cis	2B	UO ₂ Cl ₂	450W HP-Hg (Pyrex)	3	65	2
3	1d	2B	UO ₂ Cl ₂	450W HP-Hg (Pyrex)	1	13	2
4	1e	2B	UO ₂ Cl ₂	450W HP-Hg (Pyrex)	6	47	2
5	1b-cis	2A	BP	MP-Hg	- ^c	50	3
6	S1	2B	BP	Ray	5–8.5	50–75	4
7	S2	2A	Acetone	150W HP-Hg	1	93	5

^a BP: benzophenone. ^b HP-Hg: high-pressure mercury lamp; MP-Hg: medium-pressure mercury lamp; Ray: Rayonet photochemical reactor; Phos: Phosphor-coated lamp. ^c Not indicated.



R = H, CPh₃, Ac

S1



S2

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4-6-2 Previous reports on the addition of cyclic ethers to olefins in neat cyclic ethers

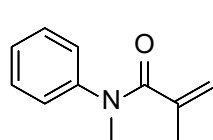
Table A2. Previous reports on the addition of cyclic ethers to olefins in neat cyclic ethers.

Entry	Olefin	Cyclic ether	Catalyst ^a	Light source ^b	Irradiation time (h)	Yield (%)	Reference
1	Diethyl maleate	2D	Acetone	HP-Hg	1	48	1
			AP	HP-Hg	- ^c	80	
			AP	Sunlight	1 day	80	
			BP	HP-Hg	- ^c	33	
2	Diethyl maleate	2E	Acetone	HP-Hg	1	16	1
			AP	HP-Hg	- ^c	78	
			AP	Sunlight	- ^c	72	
			BP	HP-Hg	- ^c	53	
3	<i>p</i> -Tolyl vinyl sulfone	2D	BP	300W HP-Hg	1	87	2
4	S3	2D	Eosin Y + ^t BuOOH	25W Blue LED	12	78	3
5	S4	2D	4-CzIPN	18W Blue LED	4	65	4
6	S5	2D	Eosin Y	18W White LED	3–24	87	5
7	S6	2D	Eosin Y	18W White LED	3–24	74	5
8	1a-cis	1,4-Dioxane	TBADT	Sunlight	5 days (8 h/day)	59	6

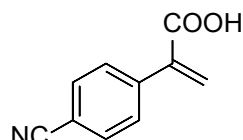
^a BP: benzophenone; AP: acetophenone; 4-CzIPN:

1,2,3,5-tetrakis-(carbazol-9-yl)-4,6-dicyanobenzene; TBADT: tetrabutylammonium

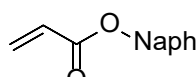
decatungstate. ^b HP-Hg: high-pressure mercury lamp; Phos: Phosphor-coated lamp. ^c Not indicated



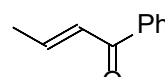
S3



S4



S5



S6

References

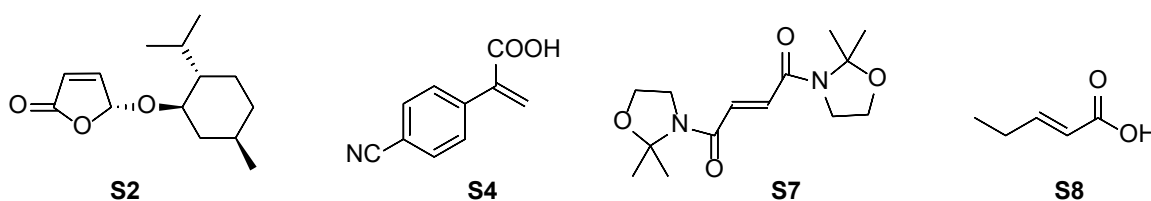
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4-6-3 Previous reports on the addition of cyclic acetals to olefins in neat cyclic acetals

Table A3. Previous reports on the addition of cyclic acetals to olefins in neat cyclic acetals.

Entry	Olefin	Cyclic acetal	Catalyst ^a	Light source ^b	Irradiation time (h)	Yield (%)	Reference
1	3-Buten-2-one	2G	BP	Six 15W Phos (quartz)	2.5	49	1
2	Butenolide	2G	BP	500W Hg	2	87	2
3	S4	2H	4-CzIPN	18W blue LED	4	50	3
4	S2	2H	Acetone	150W HP-Hg	1	70	4
5	S7	2H	BP	Four to eight 15W Phos	0.75	81.5	5
6	S8	2H	BP	750 W/m ² 365 nm LED	16 (65% conversion)	35	6

^a BP: benzophenone; 4-CzIPN: 1,2,3,5-tetrakis-(carbazol-9-yl)-4,6-dicyanobenzene; TBADT: tetrabutylammonium decatungstate. ^b HP-Hg: high-pressure mercury lamp; Hg: mercury arc lamp; Phos: Phosphor-coated lamp.



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Part 2

Organic photochemical reactions
via energy transfer from excited molecules:
Singlet oxygen reactions
using triplet sensitizers

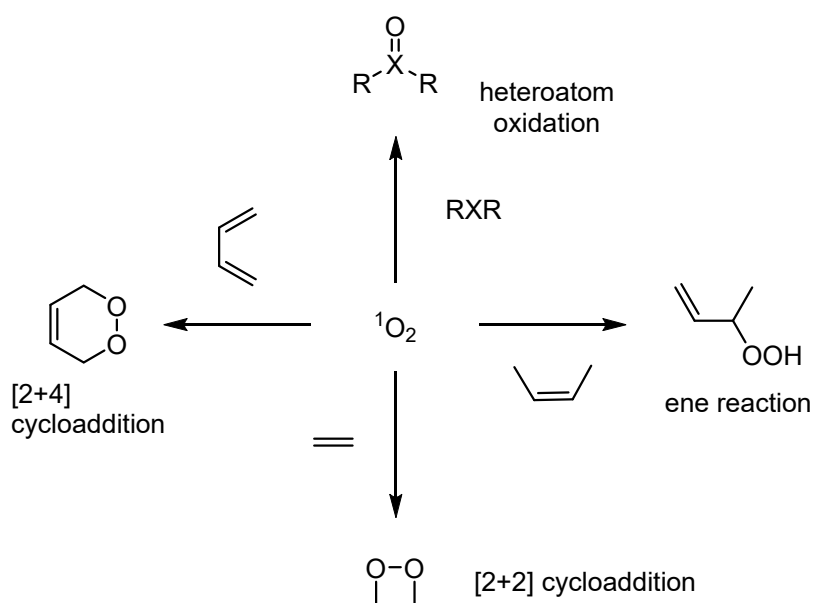
Chapter 5

Comparison on the efficiency of conventional
triplet sensitizers:

An ene-reaction of 2,3-dimethyl-2-butene

5-1 Introduction

Singlet oxygen ($^1\text{O}_2$, [$\text{O}_2(^1\Delta_g)$]) is an activated form of oxygen that is readily accessible from ground state oxygen found in air. It has been widely used toward the synthesis of organic compounds to introduce oxygen-containing functionalities, and its importance is increasing due to its small environmental impact during the course of its synthesis.¹ Since its discovery, extensive studies have been conducted and its fundamental reactions with organic compounds (ene reactions, [4+2] cycloadditions, [2+2] cycloadditions, heteroatom oxidations) (Scheme 1) have already been established in these early studies.²⁻⁴ After the initial stage of its study, the use of $^1\text{O}_2$ has been extended to the synthesis of complex organic molecules⁵⁻⁸ and many synthetic applications, and improvements have been developed^{3,9-16} together with its use in wastewater treatments¹⁷ and photodynamic therapy.¹⁸



Scheme 1. Singlet oxygen reactions.

The most common method used for the generation of $^1\text{O}_2$ utilizes a photochemical process using triplet sensitizers.¹⁹⁻²³ Because of the different spin state of singlet oxygen from the ground-state triplet oxygen, $^1\text{O}_2$ cannot be generated via the direct photochemical excitation of ground-state oxygen. Thus, energy transfer from excited triplet sensitizers to ground-state oxygen is generally used for the generation of $^1\text{O}_2$. Therefore, extensive studies on the physical properties of sensitizers, such as the quantum yield of their triplet state and $^1\text{O}_2$

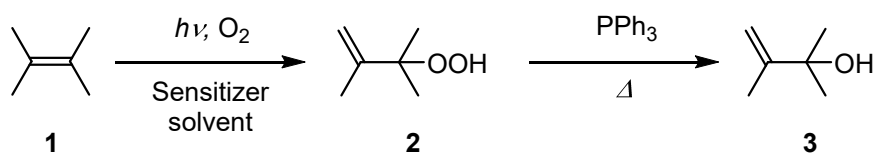
formation, and their triplet energies and lifetimes, have been conducted using various techniques and standards.^{2-4, 19-28} Various organic dyes have been used as triplet sensitizers in organic synthesis and their reactions proceed efficiently in many cases, although the irradiation time required varies from *hours* to *days*. Increasing the efficiency of the reaction is important for organic synthesis, not only by increasing the yield of the desired products but also by decreasing the reaction time. The selection of the solvent used has been reported to be important for determining the efficiency of the reaction via controlling the concentration of ¹O₂ formed in the solution. However, besides the solvent, to the best of our knowledge, it is still not clear whether the difference in the efficiency only depends on the reactivity of the substrate with ¹O₂, but also on the difference in the rate of ¹O₂ generation.

As for investigations on the reactivity of the reaction substrates, the quenching rates of ¹O₂ using various starting materials have been well studied.²⁹ On the other hand, as for the rate of ¹O₂ generation, only a limited number of results have been reported. The relative rate has been reported for methylene blue (**MB**), rose bengal (**RB**), and eosin Y (**EY**) in water using the continuous emission of a Xe lamp with filters; the rates were estimated from the development of nitroxide radicals using ESR measurements and the decomposition of deoxyguanosine using UV spectroscopy, which gave different relative rates for each sensitizer investigated.³⁰ The relative rate has also been reported for **MB**, **RB**, and **EY** in benzene/MeOH³¹ and MeOH³² using a 514.5 nm Ar laser and detecting ¹O₂ using the emission observed at 1,268 nm. The rate constants have also been reported for tetraphenylporphyrin (**TPP**) and C₆₀ in CCl₄ using a XeCl excimer laser (308 nm);³³ the authors claimed that their results were only valid in CCl₄ so that sensitizers insoluble in this solvent, such as **MB**, **RB**, and **EY**, have not been studied. However, some of these reported results on the rate of ¹O₂ generation are not consistent with each other.

On the other hand, the irradiation wavelength is one of the important factors used to control photochemical reactions. The above results on the rate of ¹O₂ generation were obtained using different light sources, which might be the reason for the inconsistency in the reported results. The quantum yield of ¹O₂ generation is expected to be a factor for controlling the efficiency of ¹O₂ reactions. The wavelength dependence on the quantum yield of ¹O₂ generation has been reported for some porphyrins and metallo porphyrins,³⁴⁻³⁶ but other studies on the quantum yield of ¹O₂ generation using various techniques and standards do not show any significant deviation in the reported values.²⁶⁻²⁸ The photodegradation of organic compounds by ¹O₂ using a pyrrole derivative³⁷ and xanthene dyes³⁸ also exhibit wavelength

dependence, but these photodegradation studies do not consider the difference in the molar extinction coefficients of the derivatives at the wavelength of irradiated light used. In contrast, the absence of wavelength dependence during the generation of $^1\text{O}_2$ has been reported for various furocoumarines and related molecules.³⁹ These results indicate that the presence of a wavelength dependence during the generation of $^1\text{O}_2$ for the commonly used triplet sensitizers is still not clear at the moment.

Therefore, a systematic study using the same method and substrate is necessary to clarify the factors for increasing the efficiency of the reaction, i.e. to determine the rate constants and obtain clear evidence for the presence or absence of a wavelength dependence during the generation of $^1\text{O}_2$ for commonly used triplet sensitizers. Herein, we report the determination of the rate constants of different sensitizers under the same conditions using the ene reaction of 2,3-dimethyl-2-butene (**1**) as a probe reaction (Scheme 2), utilizing 395 and 525 nm LEDs. The reaction of **1** \rightarrow **2** was reported to proceed almost quantitatively via triplet sensitized reactions^{40–44} and it has also been used as a probe reaction in kinetic studies on the generation of $^1\text{O}_2$ from the molybdenum-catalysed H_2O_2 reaction.⁴⁵ We have tested some widely used sensitizers, namely **MB**, **RB**, **EY**, **TPP**, and C_{60} , and determined their rate constants for the generation of $^1\text{O}_2$.



Scheme 2. The ene reaction of 2,3-dimethyl-2-butene (**1**) to give 3-hydroperoxy-2,3-dimethylbutene (**2**) and its reduction to 3-hydroxy-2,3-dimethylbutene (**3**).

5-2 Results and Discussion

5-2-1 UV absorption of various sensitizers

UV absorption spectra of the five sensitizers (**MB**, **RB**, **EY**, **TPP**, and C_{60}) and emission spectra of 395 and 525 nm LEDs are shown in Figure 1 and 2, respectively. Due to the solubility of the sensitizers, **MB**, **TPP**, and C_{60} were measured in CH_2Cl_2 , and **MB**, **RB**, and **EY** in MeOH. C_{60} was also measured in toluene. Although the absorption maximum of **MB** was the same in CH_2Cl_2 and MeOH, and showed only a small difference between the two solvents, a red shift (6 nm) in the absorption maximum of C_{60} was observed in toluene when compared with that observed in CH_2Cl_2 . Figure 1 shows that the absorbance (A_λ) of **MB**, **EY**,

and **RB** were $A_{395} < A_{525}$ (corresponding to the wavelengths of 395 and 525 nm LEDs), but those of **TPP** and **C₆₀** were $A_{395} > A_{525}$.

The absorption of **EY**, **RB**, and **MB** at 525 nm was attributed to the transition to their S_1 state and that at 395 nm to the absorption edge of their higher excited states. The emission of the 525 nm LED matched well with the absorption maximum of **EY**, but overlapped only at the absorption edge of **MB**. As for **TPP**, 525 nm light was absorbed by one of the Q bands and 395 nm light by the Soret band. As for **C₆₀**, the weak absorption at >430 nm corresponds to the orbital-forbidden electronic transitions and <430 nm to the allowed transitions.⁴⁶

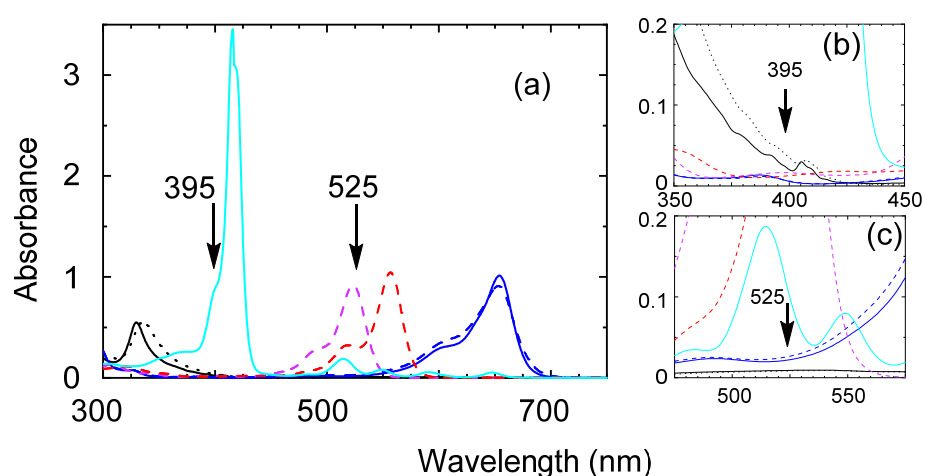


Figure 1. (a) UV absorption spectra of various sensitizers in different solvents. The wavelength at 395 and 525 nm are also shown in the figures. The concentration of the sensitizers was: (a) 1.00×10^{-5} M and (b, c) 1.00×10^{-4} M in CH_2Cl_2 (—), MeOH (- - -), and toluene (.....). Sensitizers: **MB**, blue; **EY**, violet; **RB**, red; **TPP**, light blue; **C₆₀**, black.

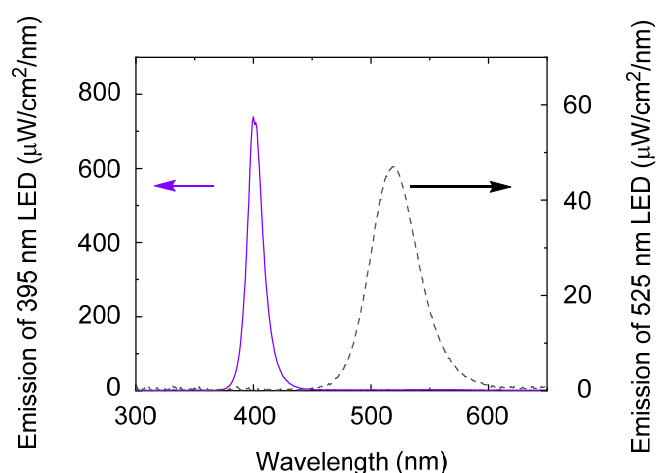


Figure 2. Emission spectra of 395 and 525 nm LEDs, measured 1.5 cm from the LED panels.

5-2-2 Ene reaction of 2,3-dimethyl-2-butene (**1**) using 395 and 525 nm LEDs

The results obtained from the ene reaction of **1** (30 mM, 10 mL) using the various sensitizers (0.12 mM) (Scheme 2) are shown in Figures 3 (395 nm LED) and 4 (525 nm LED). The reactions using **MB**, **TPP**, and **C₆₀** were conducted in CH₂Cl₂ (Figs. 3a–c and Figs. 4a, b), and those using **MB**, **RB**, and **EY** in MeOH (Figs. 3e–g and Figs. 4d–f). The reactions using **C₆₀** were also performed in toluene (Fig. 3d and Fig. 4c).

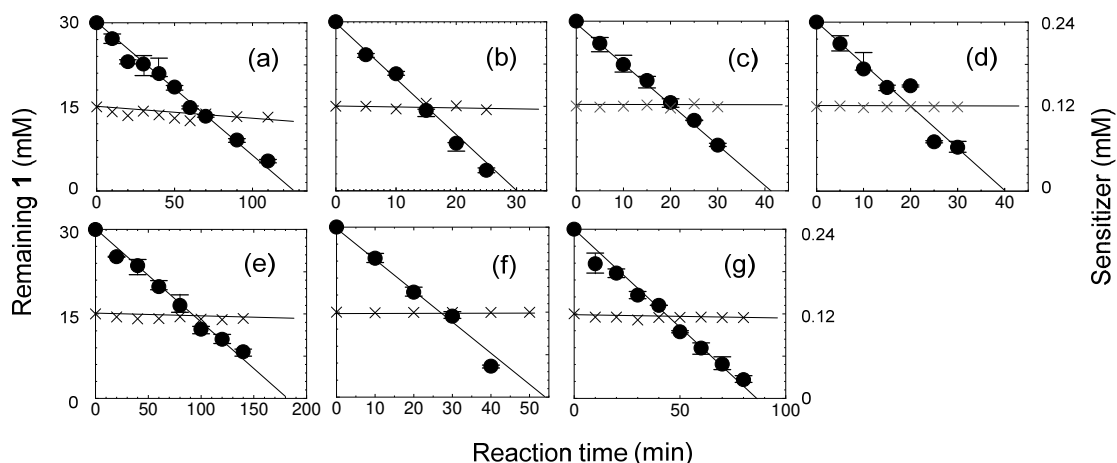


Figure 3. Ene reaction of 2,3-dimethyl-2-butene (**1**) using a 395 nm LED and various sensitizers. Symbols: **1** (●), sensitizer (×). Solvent: (a–c) CH₂Cl₂, (d) toluene, (e–g) MeOH. Sensitizer: (a, e) **MB**, (b) **TPP**, (c, d) **C₆₀**, (f) **RB**, (g) **EY**. Photolysis condition: **1** (30 mM) and sensitizer (0.12 mM) in 10 mL solution; light source, 395 nm LED (13.36 mW/cm², 370–475 nm, 1.5 cm from the LED panel); reaction vessel, quartz cylindrical cell (diameter: 3 cm); O₂ atmosphere; room temp.

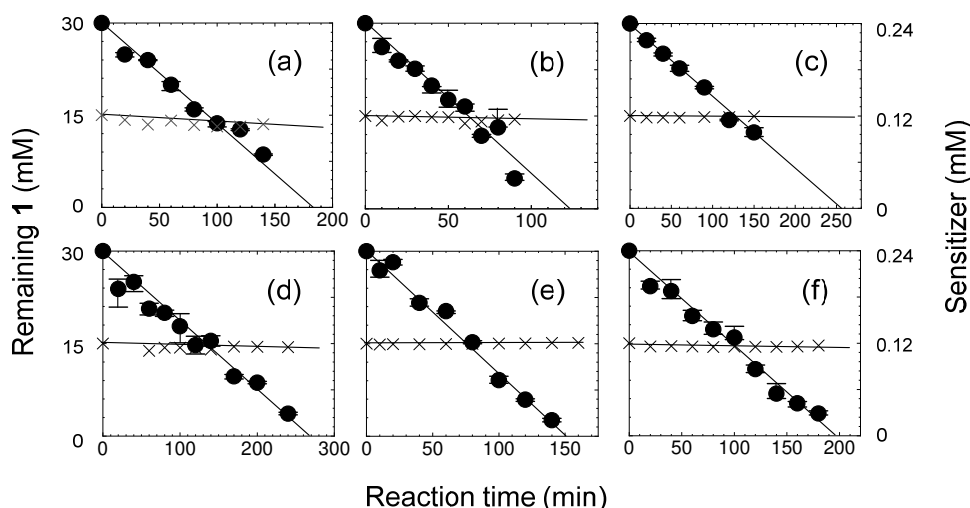


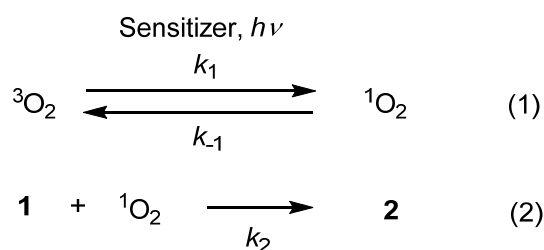
Figure 4. Ene reaction of 2,3-dimethyl-2-butene (**1**) using a 525 nm LED and various sensitizers. Symbols: **1** (●), sensitizer (×). Solvent: (a, b) CH₂Cl₂, (c) toluene, (d–f) MeOH. Sensitizer: (a, d) **MB**, (b) **TPP**, (c) **C₆₀**, (e) **RB**, (f) **EY**. Photolysis condition: **1** (30 mM) and sensitizer (0.12 mM) in 10 mL solution; light source, 525 nm LED (2.50 mW/cm², 455–620 nm, 1.5 cm from the LED panel); reaction vessel, quartz cylindrical cell (diameter: 3 cm); O₂ atmosphere; room temp.

As seen in the figures, a zero-order decay of starting material **1** was observed for all cases. The figures also showed that the decomposition of the sensitizers throughout the reaction was small. The results also showed a significant solvent effect in the reaction. As for **MB**, the reaction proceeded faster in CH₂Cl₂ than in MeOH (Fig. 3a vs 3e, and 4a vs 4d), which could be explained by the longer lifetime of ¹O₂ in CH₂Cl₂ (70–100 μs) than in MeOH (10.4 μs).^{26–28} In the case of C₆₀, the reaction did not show any significant difference between CH₂Cl₂ and toluene (Fig. 3d vs 3c).

Figures 3 and 4 show that the conversion of **1** proceeds faster under an 395 nm LED than the 525 nm LED, but it should be noted that the light intensity of the 395 nm LED (13.36 mW/cm²) was higher than that of the 525 nm LED (2.50 mW/cm²).

5-2-3 Rate constants and quantum yields for the generation of singlet oxygen for each sensitizer and wavelength studied

To compare the rate of ¹O₂ generation for each sensitizer, the rate constant was calculated for each sensitizer at an excitation wavelength of 395 and 525 nm, excluding the effects of the light intensity and molar absorption coefficient. Kinetic analysis was conducted using elementary reactions 1 and 2 shown in Scheme 3.



Scheme 3. Elementary reactions for the ene reaction of **1**.

Two kinetic equations (3 and 4) were derived from the two elementary reactions.

$$d[{}^1\text{O}_2]_t / dt = k_1 p [\text{sen}]_t [{}^3\text{O}_2]_t - k_2 [{}^1\text{O}_2]_t [\mathbf{1}]_t - k_{-1} [{}^1\text{O}_2]_t \quad (3)$$

$$- d[\mathbf{1}]_t / dt = k_2 [{}^1\text{O}_2]_t [\mathbf{1}]_t \quad (4)$$

where k_1 , k_{-1} , and k_2 are the rate constants for reactions 1 and 2, p is the number of photons absorbed by the sensitizer per unit time and sensitizer concentration,⁴⁷ and $[\mathbf{1}]_t$, $[\text{sen}]_t$, $[{}^3\text{O}_2]_t$,

and $[^1\text{O}_2]_t$ are the concentrations of **1**, sensitizer, $^3\text{O}_2$, and $^1\text{O}_2$ at time t , respectively. The reliable values of k_{-1} are reported to be $8.3 \times 10^4 - 1.1 \times 10^5$ (MeOH), $7.1 \times 10^3 - 1.9 \times 10^4$ (CH_2Cl_2), and $3.2 \times 10^4 - 5.0 \times 10^4$ (toluene) $[\text{s}^{-1}]$,²⁹ and k_2 are $3 \times 10^7 - 4 \times 10^7$ (MeOH), $4 \times 10^7 - 5.2 \times 10^7$ (CH_2Cl_2), and $3.6 \times 10^7 - 4.2 \times 10^7$ (toluene) $[\text{Ms}^{-1}]$.²⁹ As the initial concentration of **1** is 3.0×10^{-2} [M], the $k_2 [\mathbf{1}]_t$ values at $t = 0$ were calculated to be $9 \times 10^5 - 1.2 \times 10^6$ (MeOH), $1.2 \times 10^6 - 1.6 \times 10^6$ (CH_2Cl_2), $1.0 \times 10^6 - 1.3 \times 10^6$ (toluene) $[\text{s}^{-1}]$ so that $k_2 [\mathbf{1}]_t \gg k_{-1}$ near $t = 0$. Therefore, equation 3 can be approximated as follows:

$$d[^1\text{O}_2]_t / dt = k_1 p [\text{sen}]_t [^3\text{O}_2]_t - k_2 [^1\text{O}_2]_t [\mathbf{1}]_t \quad (3')$$

during the initial stage of the reaction. As p , $[^3\text{O}_2]_t$ ($\approx [^3\text{O}_2]_s$, concentration of saturated $^3\text{O}_2$), and $[\text{sen}]_t$ ($\approx [\text{sen}]_0 = 0.12$ mM, initial concentration of the sensitizers) can be considered as constant, equation 5 can be derived from equation 3' and 4 using a steady state treatment.⁴⁷

$$[\mathbf{1}]_t = -k_1 p [\text{sen}]_0 [^3\text{O}_2]_s t + 3.0 \times 10^{-2} \quad (5)$$

The calculated and observed values for the reaction using 395 and 525 nm LEDs are listed in Tables 1 and 2.⁴⁷ The $p[\text{sen}]_0$ values were calculated from the molar absorption coefficients of the sensitizers and the intensity of light from the LEDs, in which the wavelength ranges used for the calculation were 370–475 nm for the 395 nm LED and 455–620 nm for the 525 nm LED.⁴⁷ The *reaction time* was determined at the intercept of the horizontal axes in Figures 3 and 4, which corresponded to the time required for the complete consumption of **1** assuming that the reaction proceeded to completion at the initial rate. The p_{abs} value is defined by $p \times [\text{sen}]_0 \times \text{reaction time}$, which corresponds to the number of photons absorbed by the sensitizer for the complete consumption of **1**. The quantum yields for the consumption of **1** (ϕ) were calculated to be 3×10^{-4} mol (initial amount of **1**) / p_{abs} . However, the reaction of **1** \rightarrow **2** proceeded almost quantitatively via the triplet sensitized reaction^{40–43} and the ϕ values were in good agreement with the quantum yields reported for $^1\text{O}_2$ generation by each sensitizer.^{4, 23, 26–28} Therefore, we can consider that the observed ϕ values were equal to the quantum yields of $^1\text{O}_2$ generation for each sensitizer. The $k_1 p [\text{sen}]_0 [^3\text{O}_2]_s$ values for each sensitizer were obtained from the slope of the decrease of **1** in Figure 3 and 4. The rate constant (k_1) values were obtained from $k_1 p [\text{sen}]_0 [^3\text{O}_2]_s$, $p [\text{sen}]_0$, and $[^3\text{O}_2]_s$, in which the $[\text{sen}]_0$ value was 0.12 M (concentration of sensitizer) and the $[^3\text{O}_2]_s$ values, the

concentration of saturated $^3\text{O}_2$ in each solvent, were 10.2×10^{-3} (MeOH), 10.7×10^{-3} (CH_2Cl_2), and 9.88×10^{-3} (toluene) M.⁴⁸ Thus the obtained rate constants (k_1) were normalized in regards to the light intensity, molar absorption coefficient, and concentration of the sensitizer used.

Table 1. Rate constant (k_1) and quantum yield (ϕ) for the generation of $^1\text{O}_2$ using a 395 nm LED.

Sensitizer	Solvent	p [sen] $_{\text{o}} \times 10^{-6}$ (E min $^{-1}$)	Reaction time (min)	$p_{\text{abs}} \times 10^{-4}$ (E)	ϕ	$k_1 p$ [sen] $_{\text{o}}$ [$^3\text{O}_2$] $_{\text{s}}$ $\times 10^{-4}$ (M min $^{-1}$)	$k_1 \times 10^3$ (E $^{-1}$)
MB	MeOH	3.25	190	6.18	0.49	1.58	4.76
EY		6.71	86	5.77	0.52	3.48	5.10
RB		6.20	54	3.35	0.90	5.56	8.78
MB	CH_2Cl_2	3.18	126	4.00	0.75	2.38	7.01
TPP		10.69	30	3.21	0.94	10.00	8.75
C $_{60}$		7.67	41	3.15	0.95	7.32	8.92
C $_{60}$	Toluene	7.72	40	3.09	0.97	7.50	9.83

[$^3\text{O}_2$] $_{\text{s}}$ = 10.2 (MeOH), 10.7 (CH_2Cl_2), 9.88 (toluene) mM,⁴⁸ E = mol-photons.
 Photolysis condition: intensity of light, 13.36 mW/cm 2 ; wavelength range, 370–475 nm; [1] $_{\text{o}}$ = 30 mM; [sen] $_{\text{o}}$ = 0.12 mM; solution: 10 mL.

Table 2. Rate constant (k_1) and quantum yield (ϕ) for the generation of $^1\text{O}_2$ using a 525 nm LED.

Sensitizer	Solvent	p [sen] $_{\text{o}} \times 10^{-6}$ (E min $^{-1}$)	Reaction time (min)	$p_{\text{abs}} \times 10^{-4}$ (E)	ϕ	$k_1 p$ [sen] $_{\text{o}}$ [$^3\text{O}_2$] $_{\text{s}}$ $\times 10^{-4}$ (M min $^{-1}$)	$k_1 \times 10^3$ (E $^{-1}$)
MB	MeOH	2.20	268	5.89	0.51	1.12	4.99
EY		2.42	195	4.71	0.64	1.54	6.25
RB		2.57	150	3.85	0.78	2.00	7.63
MB	CH_2Cl_2	1.96	182	3.56	0.84	1.64	7.88
TPP		2.47	123	3.03	0.99	2.43	9.24
C $_{60}$	Toluene	1.18	256	3.02	0.99	1.17	10.06

[$^3\text{O}_2$] $_{\text{s}}$ = 10.2 (MeOH), 10.7 (CH_2Cl_2), 9.88 (toluene) mM,⁴⁸ E = mol-photons.
 Photolysis condition: intensity of light, 2.50 mW/cm 2 ; wavelength range, 455–620 nm; [1] $_{\text{o}}$ = 30 mM; [sen] $_{\text{o}}$ = 0.12 mM; solution: 10 mL.

As seen in Table 1 and 2, a wavelength effect on the quantum yield was observed for **EY** and **RB** in MeOH and **MB** in CH₂Cl₂, but this effect was not seen for **MB** in MeOH and **TPP** in CH₂Cl₂, which indicated that the wavelength effect was dependent on the solvent used; a solvent effect on the quantum yield of ¹O₂ generation has been reported for Mg and Zn tetrabenzoporphyrins.³⁵ In the case of **RB** in MeOH, a larger quantum yield was obtained using the shorter wavelength of irradiation, which was attributed to the presence of intersystem crossing from the higher singlet excited state(s).³⁵

The wavelength effect was also observed in the rate constants for the generation of ¹O₂. Table 3 shows the relative rate constants (*k*₁) for each sensitizer. For both 395 and 525 nm LED irradiation, the *k*₁ values were in the order of: **MB** < **EY** < **RB** (MeOH), which was consistent with the reported relative rate obtained using an Ar ion laser (514.5 nm) [**EY** < **RB** (MeOH)],³² but the order of **MB** was different in the other solvent system **EY** < **RB** < **MB** (benzene/MeOH).³¹ However, another study on the relative rate using continuous emission of a Xe lamp by monitoring the generation of ¹O₂ by decomposition of deoxyguanosine showed the order of the generation of ¹O₂ was **MB** < **EY** < **RB** (H₂O), which is consistent with our results.²⁹

Table 3. Relative rate constant for the generation of ¹O₂.

Solvent	Sensitizer	Relative <i>k</i> ₁	
		395 nm LED	525 nm LED
MeOH	MB	1.00	1.00
	EY	1.07	1.25
	RB	1.84	1.53
CH ₂ Cl ₂	MB	1.00	1.00
	TPP	1.25	1.17
	C ₆₀	1.27	-

We have observed the wavelength dependence on the quantum yield and that the wavelength effect was dependent on the solvent used. Therefore, the inconsistency in the order of the relative rates observed for the different sensitizers between the reported studies³⁰⁻³² and our results could be explained by the different solvents and wavelengths of irradiated light

used in each of the experiments.

Figure 5 shows the correlation between the rate constants (k_1) and quantum yields for $^1\text{O}_2$ generation. As shown in the figure, the rate constant was proportional to the quantum yield, irrespective of the utilized triplet sensitizer, solvent, or wavelength of irradiated light used. Therefore, the selection of sensitizers with a large quantum yield for the generation of $^1\text{O}_2$ was necessary for the larger k_1 value. On the other hand, equation 5 indicated that larger p , $[\text{sen}]_0$, and $[\text{}^3\text{O}_2]_s$ values were responsible for faster reactions. As for $[\text{sen}]_0$, it was suggested that a sensitizer concentration of $2 \times 10^{-4} - 2 \times 10^{-3}$ M resulted in a good balance between maximizing the absorption of photons and avoiding the inner filter effects.⁴ The selection of solvents having higher saturated oxygen concentration ($[\text{}^3\text{O}_2]_s$) values was preferable. As $p \propto \lambda, E, (1-10^{-a\epsilon\lambda})$ (a : constant),⁴⁷ longer irradiation wavelength (λ), higher intensity of incident light (E), and larger $\epsilon\lambda$ (the product of irradiation wavelength λ and molar extinction coefficient ϵ at λ) were required for faster reactions. The parameters indicated above were all affected by the solvent and wavelength of irradiated light used.

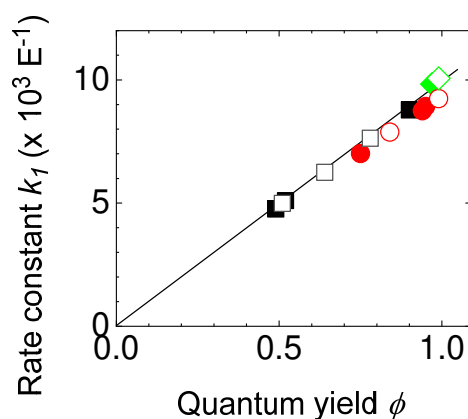


Figure 5 Correlation between the rate constant and quantum yield for $^1\text{O}_2$ generation. Solvent: MeOH (■, □), CH_2Cl_2 (●, ○), toluene (◆, ◇). Light source: 395 nm LED (■, ●, ◆), 525 nm LED (□, ○, ◇).

5-3 Conclusion

To clarify the factors for increasing the efficiency of the reaction, a systematic study determining the rate constant for the generation of $^1\text{O}_2$ using common triplet sensitizers, i.e., methylene blue (MB), rose bengal (RB), eosin Y (EY), tetraphenylporphyrin (TPP), and C_{60} , has been conducted using the ene reaction of 2,3-dimethyl-2-butene (**1**) as a probe reaction.

The wavelength effect was investigated using 395 and 525 nm LEDs. The rate constants and the quantum yields for the generation of $^1\text{O}_2$ observed for the sensitizers showed both the presence and absence of the wavelength effect, which depended on the solvent used. The wavelength effect on the quantum yield was observed for **EY** and **RB** in MeOH and **MB** in CH_2Cl_2 , but not for **MB** in MeOH and **TPP** in CH_2Cl_2 . The order of the rate constant was **MB** < **EY** < **RB** (MeOH) and **MB** < **TPP** < C_{60} (CH_2Cl_2) for both 395 and 525 nm LEDs. A faster reaction was accomplished by the larger quantum yield for the generation of $^1\text{O}_2$, longer irradiation wavelength (λ), higher intensity of incident light (E), and larger $\epsilon\lambda$ (the product of the irradiation wavelength λ and molar extinction coefficient ϵ at λ), which were all affected by the solvent and wavelength of irradiated light used.

5-4 Experimental Section

5-4-1 General information

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a JEOL ECX 400 spectrometer using CDCl_3 as solvent. As internal standards, TMS (δ 0.0 ppm) was used for ^1H NMR, and CDCl_3 (δ 77.0 ppm) for ^{13}C NMR analyses. UV measurements were conducted by using a Shimadzu UV-2400PC UV-vis spectrophotometer. GC analyses were performed by using a Shimadzu GC-2014 capillary GLC (INERT CAP1, 60 m, 0.25 mmID, $df = 0.25 \mu\text{m}$, GL Sciences Inc.) fitted with a flame-ionization detector. Emission spectra and intensity of the LEDs were measured with an Ushio Spectral Radiometer USR-40D.

2,3-Dimethyl-2-butene (**1**) ($\geq 99\%$, SIGMA-ALDRICH), triphenylphosphine (min. 98.0%, Kanto Chemical), dichloromethane (for spectroscopy, Kanto Chemical), methanol (for fluorometry, Kanto Chemical), toluene (for spectroscopy, Kanto Chemical), methylene blue (ion association reagent for spectrometric analysis, TCI), rose bengal ($>98.0\%$, TCI), eosin Y (guaranteed reagent grade, Wako Pure Chemical), TPP (ultrahigh sensitive spectrophotometric reagent for Cu, TCI), and C_{60} (99.5+%, MTR) were purchased and used as bought. 3-Hydroxy-2,3-dimethyl-1-butene (**3**) was synthesized according to the reported procedure.⁴⁹

5-4-2 General procedure for the photolysis

A solution (10 mL) of 2,3-dimethyl-2-butene (**1**) (30 mM, 0.3 mmol) and sensitizer (0.12 mM) was introduced into a quartz cylindrical cell (diameter: 3 cm) fitted with a three-way stopcock. The solution was degassed and replaced with oxygen using three vacuum-sonication- O_2 purging cycles.⁵⁰ The photolysis were conducted using a 395 or 525 nm LED (IZUMI Opto Device) under an oxygen atmosphere. The emission spectra and its intensity were measured on a Ushio Spectral Radiometer USR-40D. After the photolysis, the amount of remaining sensitizer was determined using UV spectrometry with a 1-mm optical path cell. The reaction mixture was stirred a further 2 h in the dark under an air atmosphere after the addition of PPh_3 (0.6 mmol), and the remaining **1** in the reaction mixture were then determined using glc analysis.

5-5 References

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5-6 Appendix

5-6-1 Derivation of eq 5 from eqs 3' and 4.

When we consider steady state of $[^1\text{O}_2]$, eq 3' becomes

$$d[^1\text{O}_2]_t / dt = k_1 p [\text{sen}]_t [^3\text{O}_2]_t - k_2 [^1\text{O}_2]_t [\mathbf{1}]_t = 0 \quad (3'')$$

From eq 3''

$$[^1\text{O}_2]_t = k_1 p [\text{sen}]_t [^3\text{O}_2]_t / k_2 [\mathbf{1}]_t \quad (3''')$$

By substituting 3''' to eq 4, we obtain

$$- d[\mathbf{1}]_t / dt = k_1 p [\text{sen}]_t [^3\text{O}_2]_t \quad (4')$$

As p , $[\text{sen}]_t$ ($\approx [\text{sen}]_0 = 0.12$ mM, initial concentration of the sensitizers), and $[^3\text{O}_2]_t$ ($\approx [^3\text{O}_2]_s$, concentration of saturated $^3\text{O}_2$) can be considered as constants, eq 4' is solved as

$$[\mathbf{1}]_t = - k_1 p [\text{sen}]_0 [^3\text{O}_2]_s t + C \quad (4'')$$

where C is a constant.

At $t = 0$, $[\mathbf{1}]_t$ is $[\mathbf{1}]_0 = 3.0 \times 10^{-2}$ [M], so that from eq 4''

$$[\mathbf{1}]_t = - k_1 p [\text{sen}]_0 [^3\text{O}_2]_s t + 3.0 \times 10^{-2} \quad (5)$$

5-6-2 Number of photons absorbed by the solution per unit time.

In our reactions, 10 mL of solutions were introduced in a cylindrical cell with 3.0 cm diameter. Therefore, the height of the solution in the cell (l_H) is calculated to be

$$l_H = 10 / (1.5^2 \pi) \text{ cm.}$$

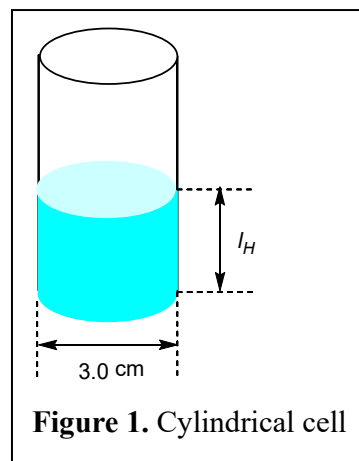


Figure 1. Cylindrical cell

Figure 2 shows the horizontal projection of the cylindrical cell. When the radius of the cell is divided into n segments, the optical path of the rectangular parallelepipeds at m th segment, l_m cm, is calculated to be

$$l_m = 2 \sqrt{1.5^2 - \left(\frac{1.5}{n} m\right)^2}$$

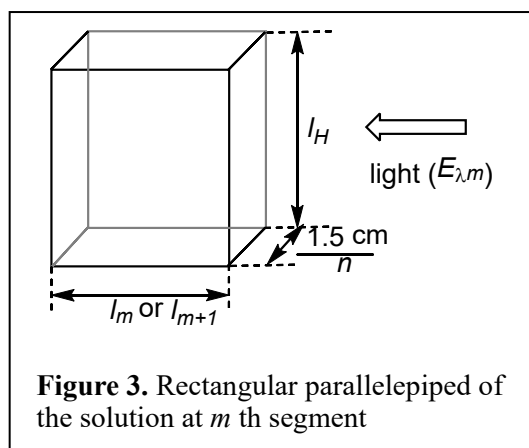
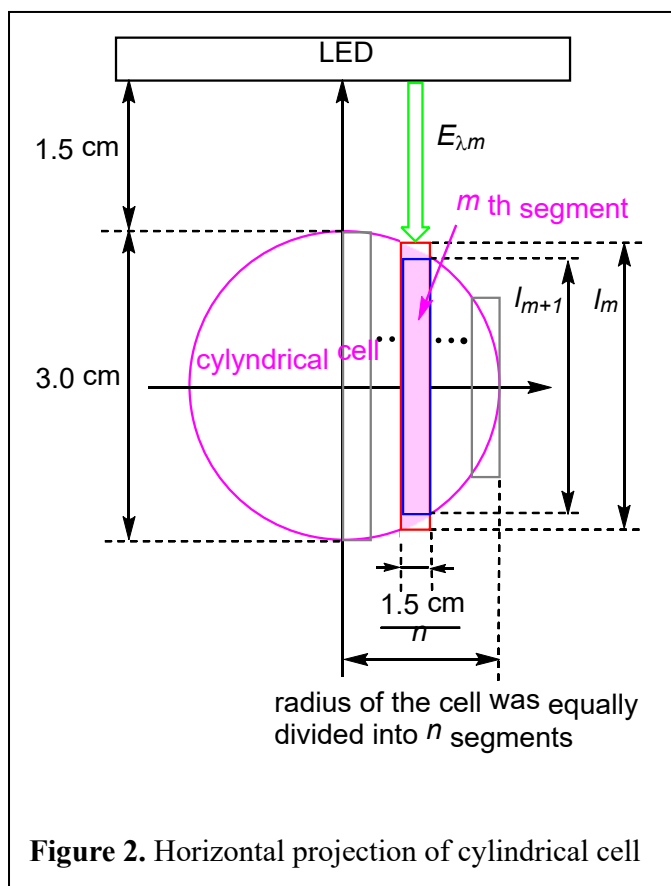
$$= \frac{3}{n} \sqrt{n^2 - m^2}$$

The number of photons (wavelength λ) absorbed by m th rectangular parallelepiped shown in Figure 3 in 1 min ($[\text{sens}]_0 p_{\lambda m}$) is,

$$[\text{sens}]_0 p_{\lambda m} = \frac{60 \times \frac{1.5}{n} l_H E_{\lambda m} \left(1 - 10^{-\varepsilon_\lambda c \frac{3}{n} \sqrt{n^2 - m^2}}\right)}{\frac{hC}{\lambda} N_A}$$

where $E_{\lambda m}$ W/cm² is the intensity of incident light (wavelength λ) at m th segment, c is the concentration of the sensitizer, h is Planck's constant, C is the speed of light, ε_λ is the molar absorption coefficient of the sensitizer at wavelength λ , and N_A is the Avogadro's number.

Figure 4 shows the relationship between the light intensities of flat panel LED 395 (370-475 nm, λ_{max} 400 nm) and LED 525 (455-600 nm, λ_{max} 518 nm), and distance from the LEDs. As shown in the figure, the light intensities decrease proportionally with the distance. Therefore, the intensity of incident light (wavelength λ) at m th segment (cf. Figure 2), $E_{\lambda m}$ W/cm², is

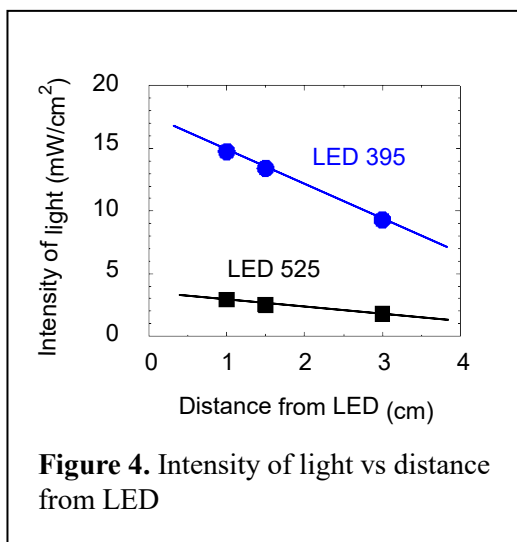


$$E_{\lambda m} = E_{\lambda 1.5} + (E_{\lambda 1.5} - E_{\lambda 3}) - (E_{\lambda 1.5} - E_{\lambda 3})/1.5 \times \left\{ 3 - \sqrt{1.5^2 - \left(\frac{1.5 m}{n}\right)^2} \right\}$$

$$= 2 E_{\lambda 1.5} - E_{\lambda 3} - (E_{\lambda 1.5} - E_{\lambda 3})/1.5 \times \left\{ 3 - \sqrt{1.5^2 - \left(\frac{1.5 m}{n}\right)^2} \right\}$$

where $E_{\lambda 1.5}$ and $E_{\lambda 3}$ are the intensities of incident light (wavelength λ) at 1.5 and 3 cm from the LED, respectively.

Therefore, the total number of photons absorbed by the solution at m th segment of the cylindrical cell in 1 min ($[\text{sen}]_0 p$) falls between the volume of rectangular parallelepipeds having lengths l_m and l_{m+1} (cf. Figure 3), which is



$$[\text{sen}]_0 p_{min} = \sum_{\lambda_1}^{\lambda_2} \sum_{m=1}^n 2[\text{sen}]_0 p_{\lambda m} < [\text{sen}]_0 p < \sum_{\lambda_1}^{\lambda_2} \sum_{m=0}^{n-1} 2[\text{sen}]_0 p_{\lambda m} = [\text{sen}]_0 p_{max}$$

where λ_1 and λ_2 are the wavelengths of the both ends of the emission of LEDs, namely, $\lambda_1 = 370$ nm and $\lambda_2 = 475$ nm for the 395 nm LED, and $\lambda_1 = 455$ nm and $\lambda_2 = 620$ nm for the 525 nm LED.

Reaction time and calculated $[\text{sen}]_0 p_{max}$ and $[\text{sen}]_0 p_{min}$ for $n = 1000$ are listed in Table S1. The ε_{λ} s in the above equations were calculated from the absorbance of each sensitizer that were measured by UV spectroscopy. $E_{\lambda 1.5}$ and $E_{\lambda 3}$ are the average emission intensities measured at 1.5 and 3 cm from the flat pannel LEDs. The value $[\text{sen}]_0 p$ was obtained as an average of $[\text{sen}]_0 p_{max}$ and $[\text{sen}]_0 p_{min}$.

Table A1. Minimum ($[sen]_0 p_{min}$), maximum ($[sen]_0 p_{max}$), and average ($[sen]_0 p$) number of photons absorbed by the sensitizer per unit time.

Sensitizer	Solvent	395 nm LED (n=1000)		525 nm LED (n=1000)	
		$[sen]_0 p_{min}$ $[sen]_0 p_{max}$ (E/min)	$[sen]_0 p$ (E/min)	$[sen]_0 p_{min}$ $[sen]_0 p_{max}$ (E/min)	$[sen]_0 p$ (E/min)
EY	MeOH	6.705×10^{-6} 6.713×10^{-6}	6.709×10^{-6}	2.418×10^{-6} 2.420×10^{-6}	2.419×10^{-6}
RB	MeOH	6.200×10^{-6} 6.207×10^{-6}	6.204×10^{-6}	2.568×10^{-6} 2.571×10^{-6}	2.569×10^{-6}
MB	MeOH	3.250×10^{-6} 3.255×10^{-6}	3.253×10^{-6}	2.196×10^{-6} 2.198×10^{-6}	2.197×10^{-6}
MB	CH ₂ Cl ₂	3.173×10^{-6} 3.177×10^{-6}	3.175×10^{-6}	1.953×10^{-6} 1.956×10^{-6}	1.955×10^{-6}
TPP	CH ₂ Cl ₂	10.682×10^{-6} 10.693×10^{-6}	10.687×10^{-6}	2.464×10^{-6} 2.467×10^{-6}	2.466×10^{-6}
C ₆₀	CH ₂ Cl ₂	7.666×10^{-6} 7.675×10^{-6}	7.670×10^{-6}	-	-
C ₆₀	Toluene	7.714×10^{-6} 7.723×10^{-6}	7.719×10^{-6}	1.178×10^{-6} 1.180×10^{-6}	1.179×10^{-6}

E = mol-photons

Chapter 6

Conclusion

Organic reactions are generally conducted using thermal energy and it is often obtained by combustion of fossil fuels, which generates carbon dioxide and causing global warming. Instead of using thermal energy for organic synthesis, development of environmentally-benign organic synthetic reactions using sunlight is reported in this thesis.

Part 1 of this thesis, from Chapter 2 to 4, is concerned with photochemical reactions via direct excitation of organic compounds; namely an efficient and widely applicable C-C bond formation reaction via radical species, which is important for the construction of carbon skeletons of organic compounds. Part 2, Chapter 5, is concerned with reactions via energy transfer from excited molecules; namely triplet sensitized generation of singlet oxygen and its use in the functional group transformation, which is also important in organic synthesis for introducing necessary functional groups to organic molecules.

In Chapter 2, a fast photochemical C-C bond formation reaction between cyclic ethers/acetals and olefins using di-*tert*-butyl peroxide (DTBP) and a xenon lamp is reported. This method provides easy access to 2-substituted cyclic ethers, and 2- or 4-substituted cyclic acetals. Acyl/formyl groups or diols can be obtained by the hydrolysis of the 2- or 4-substituted cyclic acetals, respectively. The reactions proceeded at room temperature and gave the expected products in good to excellent yields; efficient reactions were completed within 0.5 h at room temperature in >95% yield.

In Chapter 3, a diastereoselectivity in the addition of THF radicals to dialkyl maleate, which was found in the study reported in Chapter 2, and the origin of the diastereoselectivity is reported. The diastereoselectivity of the addition reaction of a THF radical to dialkyl maleates, the stereochemistry of the carbon atoms at both sides of the newly formed C-C bonds, has still not been established; both the presence and absence of diastereoselectivity have been reported in previous studies and its origin has not been discussed. A clear evidence was obtained for the presence of diastereoselectivity in the addition reaction, in which the diastereoselectivity increases with an increase in the bulkiness of the alkyl groups. DFT calculations on the maleates showed the presence of one or two stable conformations, which depend on the bulkiness of the alkyl groups.

In Chapter 4, an efficient photochemical C-C bond formation reaction between alcohols/cyclic ethers/cyclic acetals and olefins using DTBP and sunlight as a light source is reported. The reactions proceeded faster than many of the previously reported sunlight and many conventional lamp photolyses. The reactions were completed typically in 3–4 h under irradiation with sunlight and gave products in excellent yield using olefins bearing two

electron withdrawing groups (EWGs) (product yield > 95 %) and in good to fair yield with olefins bearing one EWG. The yields observed for some products were ~20 % higher than those obtained using a conventional Xe lamp as the light source, which was confirmed to be due to a light intensity effect. Gram-scale experiments showed similar yields to those observed in their corresponding small-scale experiments.

In Chapter 5, investigation on the efficiency of commonly used sensitizers for the generation of singlet oxygen ($^1\text{O}_2$) is reported. To clarify the factors for increasing the efficiency of the reaction, a systematic study has been conducted on the determination of the rate constants observed for the generation of $^1\text{O}_2$ from commonly used triplet sensitizers, i.e., methylene blue, rose bengal, eosin Y, tetraphenylporphyrin, and C_{60} , using the ene reaction of 2,3-dimethyl-2-butene as a probe reaction utilizing 395 and 525 nm LEDs. A faster reaction was accomplished by the larger quantum yield for the generation of $^1\text{O}_2$, longer irradiation wavelength, higher intensity of incident light, and larger $\varepsilon\lambda$ (the product of the irradiation wavelength λ and molar extinction coefficient ε at λ).

The results reported in this thesis provide some methodologies and examples for the development of efficient and widely applicable organic reactions using sunlight. The author believes that these methodologies and examples can contribute for the establishment of green and sustainable chemistry through minimizing environmental dose during production of organic compounds and materials.

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Publication List

Papers related to this thesis

- [1] Hayakawa, M.; Aoyama, T.; Ouchi, A., “Diastereoselective photochemical radical addition of a cyclic ether to olefins: Addition of THF radicals to dialkyl maleates,” *Arkivoc*, **2021**, (8), 145-154.
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