Synthesis B. B. Yagci et al. Feature

Access to Symmetrical and Unsymmetrical Cyclobutanes via Template-Directed [2+2]-Photodimerization Reactions of Cinnamic Acids

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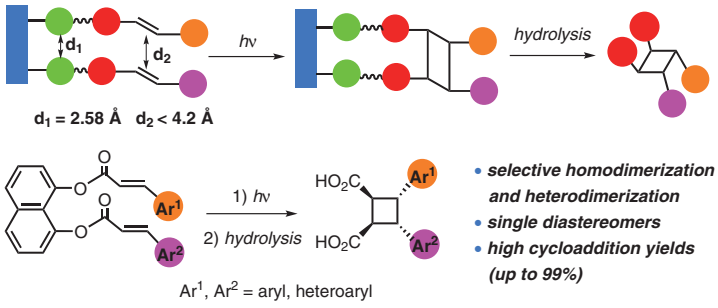

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Abstract In this work, we have developed a general and broadly applicable template-directed photochemical [2+2]-cycloaddition reaction which provides access to a wide range of symmetrical and unsymmetrical cyclobutane products. The use of 1,8-dihydroxynaphthalene as a covalent template paved the way for successful and highly selective photochemical homodimerization and heterodimerization reactions in the solid state between cinnamic acid derivatives. Notably, the method works equally well with aryl- and heteroaryl-containing substrates leading to the formation of β-truxinic acid analogues as single diastereomers and in high yields (up to 99%).

Key words cinnamic acids, [2+2] cycloaddition, cyclobutanes, heterodimerization, photochemistry, template-directed synthesis, truxinic acids

Since early studies reported in the first half of the 20th century,[1] regio- and stereoselective photodimerization reactions of cinnamic acids have continued to be of interest to the synthetic community.[2] As a consequence of the natural occurrence of many substituted cinnamic acid derivatives, it is not surprising that cinnamic acid dimers constitute a prevalent motif among cyclobutane-containing natural products. Examples of biologically active members of this class of natural products such as eucommicin A,[3] itoside N,[4] caracasandiamide,[5] and incarvillateine[6] are shown in Figure 1. The early observation that solution phase irradiation of cinnamic acids gave primarily *E* to *Z* isomerization paved the way for the advancement of studies on their solid state photochemical [2+2] cycloadditions.[7] Extensive pioneering work of Schmidt and co-workers on the crystal structure-photochemical reactivity relationship for a large number of *trans*-cinnamic acid derivatives resulted in the formulation of a number of principles currently known as the Schmidt criteria.[8] Based on these findings, it was concluded that irradiation of the α- and β-crystal polymorphs of cinnamic acids, which have distances of 3.6–4.1 Å between their parallelly oriented olefin centroids, resulted in the selective formation of α-truxillic acids (*syn*-head-to-tail dimers) and β-truxinic acids (*syn*-head-to-head dimers), respectively (Scheme 1a and 1b).[8,9] However, cinnamic acids having the γ-polymorphic structure in solid state have a distance of >4.7 Å between their olefin centroids, and as a result, they are photo-resistant under UV irradiation conditions (Scheme 1c).[9]

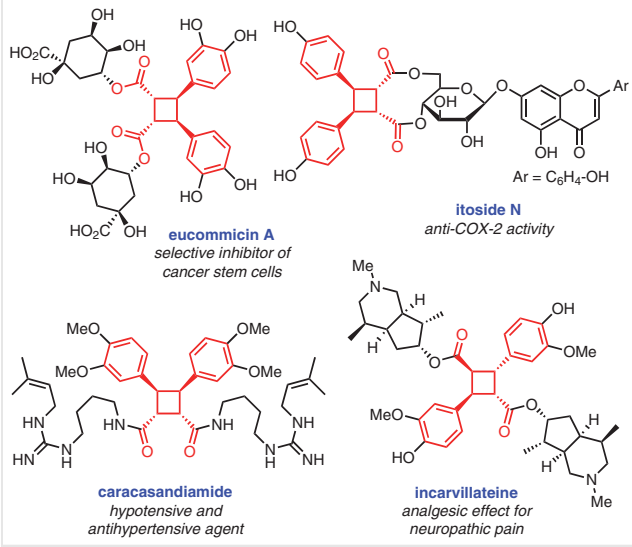

Figure 1 Examples of bioactive natural products having dimers of cinnamic acid derivatives in their structures

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This is undoubtedly a powerful synthetic approach provided that the cinnamic acid derivative of interest has the aforementioned geometrical features in solid state, and thus is in agreement with the Schmidt criteria. Such photochemical cycloaddition reactions proceed generally with very high yields and diastereoselectivities.[7,10] Moreover, this type of synthetic transformations is favored from a green chemistry perspective as they do not require the use of a solvent during the reaction.[11,12] Despite the advantages mentioned above, this approach does not provide a general

Biographical Sketches

Bilge Banu Yagci received her B.Sc. in chemistry from Bilkent University in 2018. Subsequently, she completed her M.Sc. studies under the supervision of Dr. Yunus Türkmen in 2021. Her research is focused on template-directed photochemical [2+2]-cycloaddition reactions of cinnamic acid derivatives for the diastereocontrolled synthesis of cyclobutane products.

Badar Munir studied chemistry at the University of Sargodha (Pakistan) where he obtained his B.Sc. in Chemistry. Currently, he is doing his M.Sc. in Chemistry at Bilkent University (Türkiye) under the supervision of Dr. Yunus Emre Türkmen. His research is mainly focused on photochemical dimerization reactions to access carbocyclic compounds.

Yunus Zorlu was born in İstanbul in 1982. He carried out his Ph.D. on water soluble symmetrical and asymmetrical phthalocyanine-based photosensitizers for photodynamic therapy of cancer. After studying inorganic chemistry, he was then appointed research scientist position in the field of structural chemistry in 2008, then associate professor in 2015 at Gebze Technical University. Since 2020, he has been an inorganic chemistry professor at Gebze Technical University. His primary research interests include the development of functional porous materials (metal-organic frameworks, hydrogen-bonded organic frameworks, and porous organic polymers) and non-covalent interactions (halogen and tetrel bondings).

Yunus Emre Türkmen received his B.Sc. in 2005 at the Chemistry Department of Middle East Technical University (METU) with a minor study in biology. He finished his M.Sc. studies at the same institution under the supervision of Prof. Dr. Cihangir Tanyeli. He then moved to Chicago in 2006 and did his Ph.D. in the group of Prof. Dr. Viresh Rawal at the University of Chicago. Between 2013 and 2015, he worked as a postdoctoral fellow in the group of Prof. Dr. Varinder Aggarwal FRS at University of Bristol, UK. Since 2015, he has been working at the Chemistry Department of Bilkent University as a faculty member. His research interests include the development of new catalytic methods to access carbo- and heterocycles, and template-directed photochemical cycloaddition reactions. He has been a recipient of the BAGEP (Young Scientist Awards Program) award by the Science Academy, Türkiye, in 2019, and the GEBIP (Outstanding Young Scientists) award given by the Turkish Academy of Sciences in 2022.

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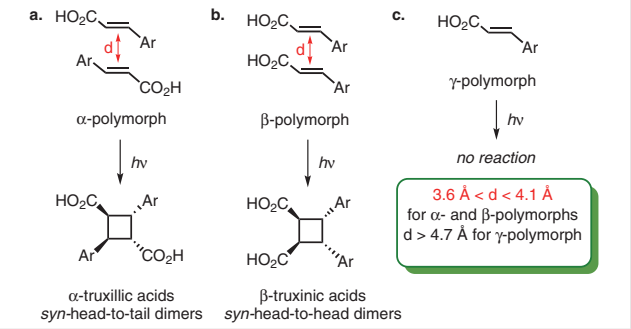
solution to the selective photodimerization of any cinnamic acid derivative regardless of its solid-state structure. In this respect, several strategies were developed to achieve the selective photochemical [2+2] cycloadditions of a variety of olefin classes including cinnamic acids. One such strategy is the use of templates in solid state which involve the utilization of metal coordination[13] and salt formation[14] as well as a diverse range of non-covalent interactions such as hydrogen,[15] halogen,[16] and chalcogen bonding.[17,18] Along these lines, a related second type of strategy is to utilize supramolecular host-guest complex formation[19] and non-covalent templates[20] for selective photochemical [2+2] cycloadditions in solution.[21] A particular advantage of these two approaches is that they operate in single synthetic reaction step as they do not involve the covalent binding of the reactants to the template. However, the first strategy requires the co-crystallization of the reactants with the template, which can be a limiting factor, whereas the second strategy requires a high binding constant between the reactants and the template in solution.

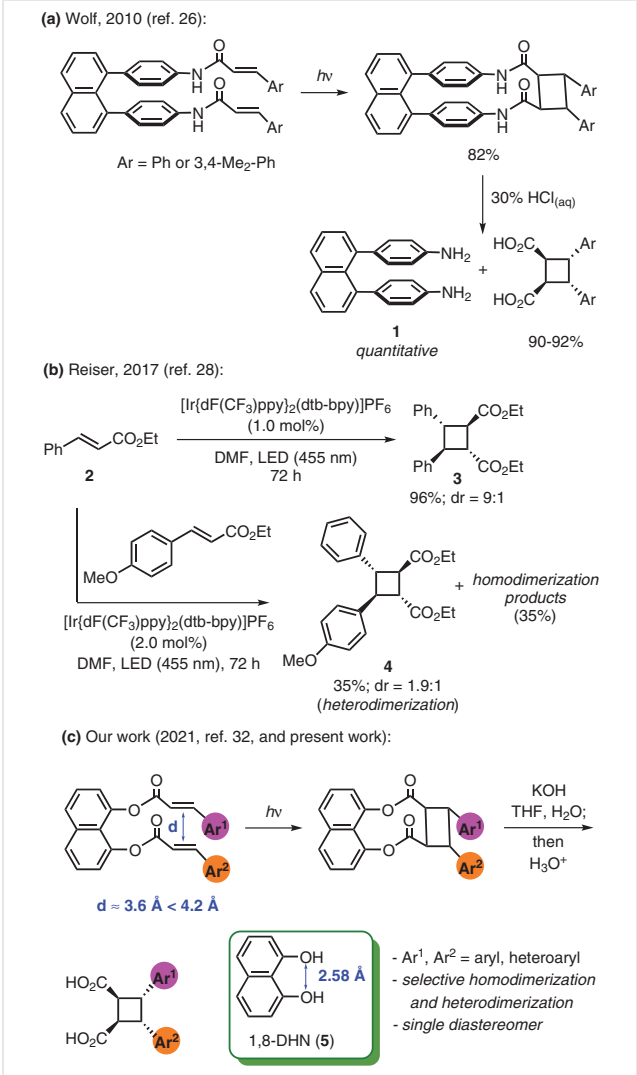


Scheme 1 Photochemical reactivity of different polymorphs of cinnamic acids

In addition to the strategies described above, a third approach is the use of covalent templates which can be used in solid state or in solution. The use of certain diols as templates in the early studies of this field resulted in the formation of diastereomeric mixtures in the investigated photodimerization reactions.[22] In 1996, König and co-workers demonstrated that 1,2-bis(hydroxymethyl)benzene was an effective diol-based covalent template for the photochemical homodimerization of *trans*-cinnamic acid in solution.[23] In the seminal studies of Hopf and co-workers, [2.2]paracyclophane core was shown to be an effective, rigid scaffold satisfying the distance criterion for a successful [2+2]-cycloaddition reaction as described by Schmidt.[8,24,25] In 2010, Wolf and co-workers developed bisaniline **1** as a covalent template for the homodimerization of two cinnamic acid derivatives to afford symmetrical β-truxinic acids in high yield (Scheme 2a).[26]

Within the past decade, visible light photocatalysis has emerged as a highly efficient method for [2+2]-cycloaddition reactions.[27] In 2017, Reiser and co-workers reported *anti*-head-to-head photodimerization of cinnamate esters giving δ-truxinates catalyzed by an Ir-based photocatalyst (Scheme 2b).[28] However, when heterodimerization reactions were tested in this study via reactions of two different cinnamates, no appreciable selectivity was observed for heterodimerization over homodimerization. Furthermore, the [2+2]-cycloaddition reactions of cinnamic acids, cinnamates, and chalcones were investigated using a variety of other visible light photocatalytic systems.[29] Despite this rich history, the photochemical dimerization reactions of cinnamic acid derivatives were mainly restricted to homodimerization,[30] and a general method for the selective heterodimerization of this compound class had yet to be discovered.[31]

In 2021, we reported the use of 1,8-dihydroxynaphthalene (1,8-DHN, **5**) as a highly effective covalent template for



Scheme 2 Selected examples of photochemical [2+2] cycloadditions of cinnamic acid derivatives

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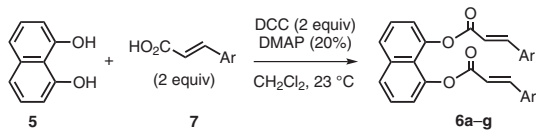
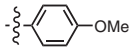
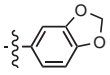
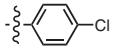
the selective photochemical homodimerization and heterodimerization reactions of cinnamic acids (Scheme 2c).[32] It should be noted that, to the best of our knowledge, this method represents the first general solution for the selective heterodimerization reactions of this compound class. During our previous work on the hydrogen bonding properties of 1,8-DHN (**5**),[33] and its use in the synthesis of the fungal natural product daldiquinone,[34] we realized the potential of compound **5** to be utilized as an ideal covalent template for the photochemical [2+2]-cycloaddition reactions of cinnamic acids. Indeed, in addition to providing the right distance between the two reacting olefins (ca. 3.6 Å)[32] so as to ensure that Schmidt's distance criterion (<4.2 Å) is satisfied, template **5** also enables the attachment of two different cinnamic acids selectively and sequentially (Scheme 2c). We should note that, Beeler and co-workers recently described the use of catechol as a covalent tether in the photochemical heterodimerization reactions of cinnamic acids in solution, and showed the application of this method to the syntheses of the natural products piperarborenines C–E.[35] Herein, we report a full account of our studies on the selective and controlled homodimerization and heterodimerization reactions of cinnamic acids via the use of 1,8-DHN (**5**) as a covalent template, and extension of its scope to the selective photodimerization of heteroaromatic substrates (Scheme 2c).

Table 1 Synthesis of the Symmetrical Diesters **6a–g**



Entry	Ar	Product	Yield (%)
1	Ph	**6a**[a]	95
2		**6b**[a]	87
3		**6c**	74
4		**6d**	81
5		**6e**	73
6		**6f**	81
7		**6g**	72

[a] The syntheses of these cycloadducts were reported previously.[32]

Our studies commenced with the investigation of the homodimerization reactions of cinnamic acid derivatives. The synthesis of the symmetrical diesters **6a–g** to be tested in the photochemical [2+2] cycloaddition was achieved via a DCC-mediated ester formation between 1,8-DHN (**5**) and the corresponding cinnamic acids **7** (Table 1). We have previously shown that phenyl- and 4-methoxyphenyl-substituted diesters **6a** and **6b** could be prepared in high yields (95% and 87%, respectively) using this method (entries 1 and 2).[32] In the present work, diester **6c** bearing the strongly electron-donating dioxolane moiety was synthesized in 74% yield (entry 3). In order to check the effect of an electron-withdrawing group on the aryl ring and assess the stability of an aryl halide group under photochemical reaction conditions, 4-chlorophenyl-substituted diester **6d** was prepared in 81% yield (entry 4). Next, we turned our attention to the synthesis of diesters with heteroaromatic rings at the β-position of the acrylate moieties. To this end, diesters **6e–g** possessing thiophene, furan and *N*-methylpyrrole rings were synthesized successfully in 73%, 81%, and 72% yields, respectively (entries 5–7).

With the successful preparation of symmetrical diesters **6a–g** in hand, we next turned our attention to the construction of unsymmetrical diesters as photochemical cycloaddition precursors (Table 2). Monoesters **8a** and **8b** were synthesized via deprotonation of 1,8-DHN (**5**) with NaH followed by treatment with one equivalent of the corresponding cinnamoyl chloride.[32] For the conversion of monoesters **8a** and **8b** to unsymmetrical diesters **6h–p** two methods were employed. Method A involves reacting monoesters **8a** or **8b** with the second cinnamic acid partner under DCC coupling conditions. Following this method, diesters **6h**, **6i**, **6m**, and **6o** were synthesized in 66–90% yields (entries 1, 2, 6, and 8).[32]

However, for some substrates method B, which involves the reaction of the monoester with an acyl chloride under basic conditions, was found to work better. During these experiments, we realized that deprotonation of monoester **8a** with one equivalent of NaH followed by treatment with one equivalent of acyl chloride of a different cinnamic acid led to the formation of a mixture of the targeted unsymmetrical diester and the symmetrical diester **6a**. In control experiments, when monoester **8a** was treated with DBU (0.1 equiv) or NaH (1.0 equiv) in the absence of additional cinnamoyl chloride, monoester **8a** was observed to undergo a non-redox disproportionation to form diester **6a** and 1,8-DHN (**5**) (Scheme 3). Pleasingly, we found that this pathway could be prevented by a simple change in the addition order of reagents. In this way, when one equivalent of NaH was added to a 1:1 mixture of monoester **8a** and (*E*)-3-(4-nitrophenyl)acryloyl chloride in THF, unsymmetrical diester **6j** was obtained in 86% yield without the formation of any symmetrical diester **6a** (Table 2, entry 3). This new protocol

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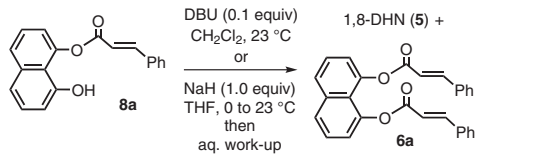
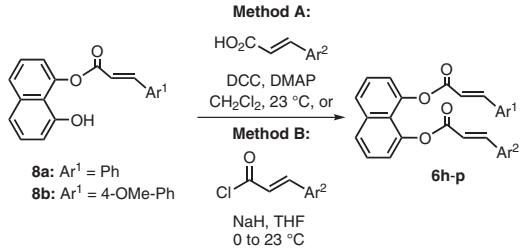
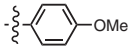
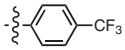
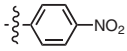
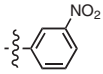
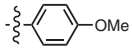
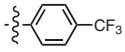
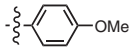
was successfully applied to the synthesis of other unsymmetrical diesters (**6k**, **6l**, **6n**, and **6p**) shown in Table 2, which were isolated in high yields (72–77%).



Scheme 3 Non-redox disproportionation of monoester **8a**

Table 2 Synthesis of the Unsymmetrical Diesters **6h–p**



Entry	Ar^1	Ar^2	Method, product, yield (%)
1	Ph		A, **6h**[a], 66
2	Ph		A, **6i**[a], 76
3	Ph		B, **6j**, 86
4	Ph		B, **6k**, 74
5	Ph		B, **6l**, 72
6	Ph		A, **6m**[a], 90
7	Ph		B, **6n**, 75
8			A, **6o**[a], 66
9			B, **6p**, 77

[a] The syntheses of these cycloadducts were reported previously.[32]

The photochemical reactivity of the diesters **6** was examined using two different irradiation conditions (Table 3). In method C, solid samples were irradiated for 8 h using a 400-W medium pressure mercury lamp, and samples were mixed thoroughly every two hours. Alternatively, in method D, a commercial nail dryer with four 9-W UV-A fluorescent lamps was used to irradiate diesters **6** in solid state for 16 h by mixing the samples every 4 h.[36] In general, both methods work comparably well with the majority of the tested cycloaddition precursors, albeit longer reaction times are required with method D. Please note that the substrates, which were investigated after our initial report,[32] were all tested with both irradiation methods. In this respect, the symmetrical template-bound β-truxinic acid esters **9a–d** bearing electron-donating and -withdrawing substituents were isolated in high yields (78–96%) and as single diastereomers (Table 3, entries 1–4). Diesters **6e–g** with heteroaromatic thiophene, furan, and *N*-methylpyrrole rings were also found to be excellent substrates under both irradiation conditions, and cycloadducts **9e–g** were obtained in 80–98% yields (entries 5–7).

Previously, we had shown that unsymmetrical β-truxinates **9h** and **9i**, which have electron-rich 4-methoxyphenyl and electron-deficient 4-(trifluoromethyl)phenyl groups, could be obtained in 99% and 88% yields, respectively, using method C.[32] In the current work, we systematically examined the effect of the position of the NO_2 group on the photochemical [2+2] cycloaddition. Whereas diesters **6j** and **6k** with NO_2 groups at the *para* and *meta* positions were successful substrates providing cycloadducts **9j** and **9k** in 77% and 88% yields, respectively (entries 10 and 11), β-truxinate **9l** with the NO_2 group at the *ortho* position was isolated in a lower yield (44% with method C, and 49% with method D; entry 12). We were pleased to confirm the structure and relative stereochemistry of cycloadduct **9j** by single-crystal X-ray analysis (Figure 2, CCDC 2265841). Mixed aryl-heteroaryl-substituted diesters **6m** and **6n** were also competent substrates affording the unsymmetrical cyclobutane diester products **9m** and **9n** in 88% and 96% yields, respectively (entries 13 and 14). The effect of having one electron-rich and one electron-deficient aryl ring on the substrate was tested with diester **6o** which gave cycloadduct **9o** in 93% yield (entry 15).[32] Finally, the presence of having two electron-rich aromatic groups was checked with diester **6p** having furyl and 4-methoxyphenyl groups. For this substrate, method D was found to be superior affording unsymmetrical cycloadduct **9p** in 84% yield, while method C resulted in a moderate yield of 57% (entry 16). Cycloadducts **9a–p** were observed to form as single diastereomers in all of the experiments shown in Table 3. Finally, we checked the reversibility of the photochemical [2+2] cycloaddition under the irradiation conditions. To this end, we subjected a sample of pure cycloadduct **9a** to irradiation using the Hg lamp (method C) for 4 h. At the end of this control experiment, cycloadduct **9a** was found to be intact

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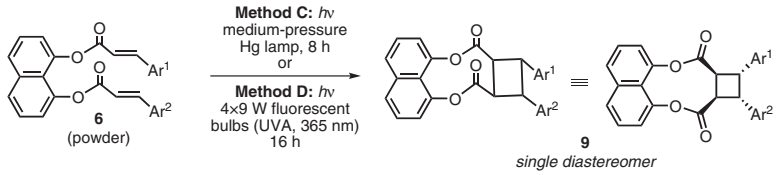
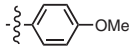
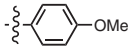
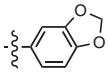
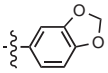
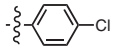
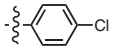
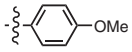
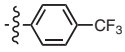
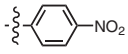
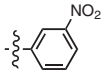
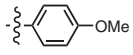
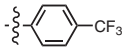
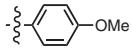
Table 3 Photochemical [2+2] Cycloadditions of Diesters **6**



Entry	Product	Ar[1]	Ar[2]	Yield (%) Method C	Method D
1	**9a**[a]	Ph	Ph	95	92
2	**9b**			78	–
3	**9c**			93	96
4	**9d**			89	90
5	**9e**			96	98
6	**9f**			86	98
7	**9g**			95	80
8	**9h**[a]	Ph		99	–
9	**9i**[a]	Ph		88	–
10	**9j**	Ph		77	61
11	**9k**	Ph		88	86
12	**9l**	Ph		44	49
13	**9m**[a]	Ph		88	–
14	**9n**	Ph		86	96
15	**9o**[a]			93	–
16	**9p**			57	84

[a] The syntheses of these cycloadducts were reported previously.[32]

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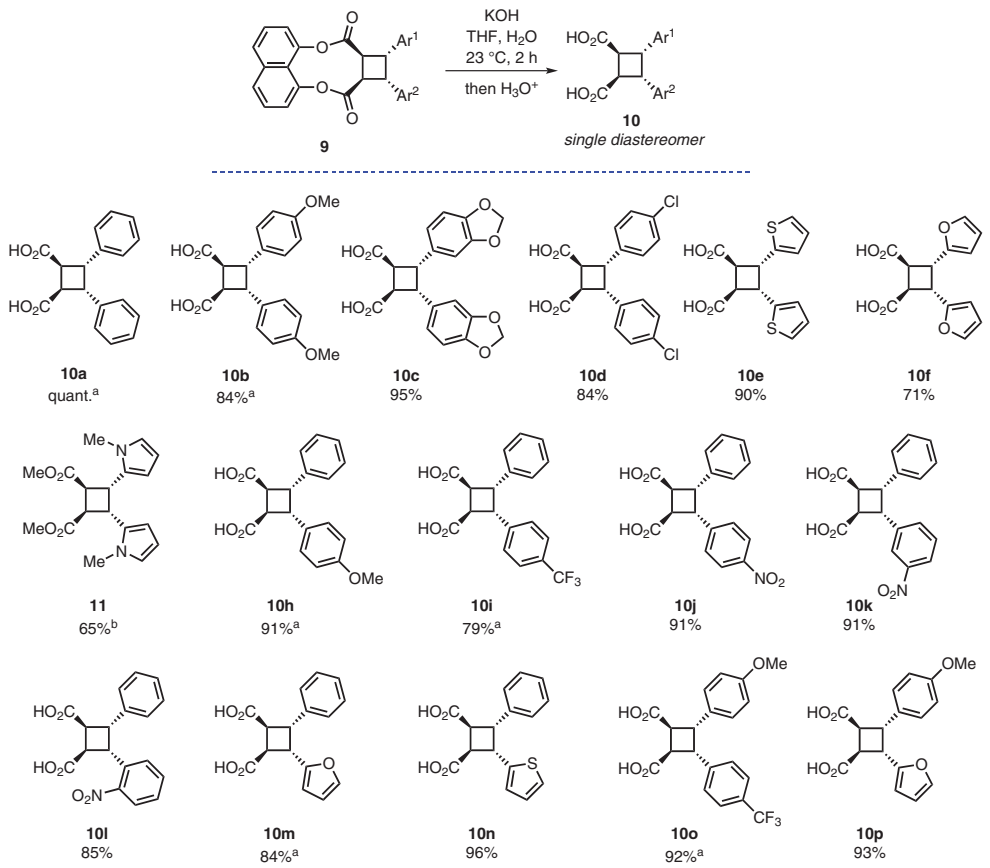

Scheme 4 Synthesis of β-truxinic acid products **10** via hydrolysis of cycloadducts **9** under basic conditions. [a] The syntheses of these β-truxinic acid products were reported previously.[32] [b] Product **11** was obtained by the reaction of **9g** with NaOMe in MeOH at 23 °C.

with no formation of diester **6a**, which indicates that the photocycloaddition reaction is irreversible under these conditions.

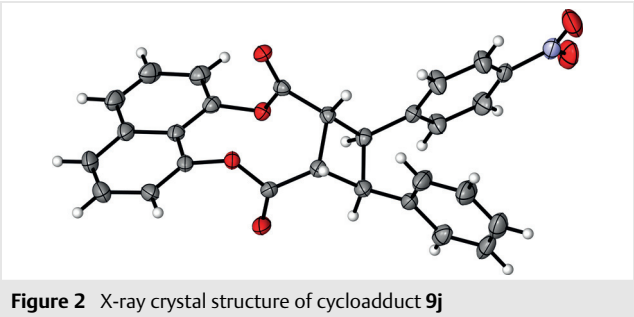

Figure 2 X-ray crystal structure of cycloadduct **9j**

In order to check the possibility of a single crystal-to-single crystal transformation[37] during the photochemical [2+2] reaction, crystals of **6d** were irradiated with UVA light using the nail dryer. While cycloadduct **9d** was found to form with full conversion upon irradiation for 16 h as determined by NMR spectroscopy, the crystals were observed to crumble during the irradiation process resulting in the formation of product **9d** in powder form (Figure S1). Regarding the interaction of diesters **6** with UV light, we have previously shown that the λ_{max} values of diester **6a** and **6o** in their UV-vis spectra in CH_2Cl_2 are 279 and 283 nm (with a shoulder at 320 nm), respectively.[32] In order to acquire more relevant data related to their solid state photochemical reactivities, we recorded their diffuse reflectance UV-vis spectra in solid powder form, which exhibited absorption below 389 nm for **6a** and 411 nm for **6o** (Figure S2). This provides an explanation for the success of both irradiation sources (methods C and D) in the photochemical [2+2]-cycloaddition reactions of diesters **6** (Table 3).

The synthesis of the β-truxinic acid products was achieved via a saponification-type basic hydrolysis of the template-bound cycloadducts **9**. In this respect, treatment of diesters **9** with KOH in a mixture of THF and H_2O at 23 °C followed by acidic workup afforded cyclobutanedicarboxylic acids **10** in high yields and as single diastereomers (Scheme 4). The unsubstituted β-truxinic acid (**10a**) was isolated in quantitative yield along with complete recovery of the template (1,8-DHN, **5**).[32] The method works successfully on diesters with electron-donating and withdrawing

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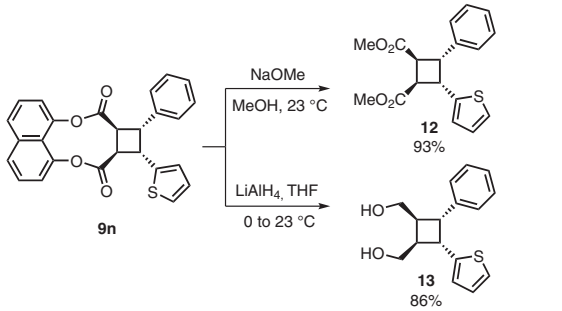
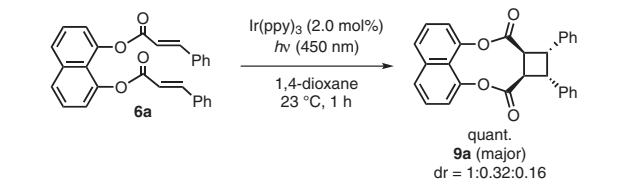
substituents affording β-truxinic acid analogues **10b–d** in 84–95% yields (Scheme 4). Thienyl- and furyl-substituted symmetrical cyclobutanedicarboxylic acids **10e** and **10f** were obtained in 90% and 71% yields, respectively. Unexpectedly, we faced problems during the isolation of *N*-methylpyrrole-substituted dicarboxylic acid. In order to circumvent this problem, cycloadduct **9g** was subjected to a transesterification reaction with the use of NaOMe in MeOH leading to the formation of cyclobutane diester **11** in 65% yield. Not surprisingly, the basic hydrolysis method works equally well with the heterodimerization products giving unsymmetrical β-truxinic acid products **10h–p** in 79–96% yields (Scheme 4). Of particular note is the little variation of reaction yield depending on the position of the NO_2 group in substrates **9j–l**. In these reactions, β-truxinic acid products **10j**, **10k**, and **10l** were obtained in 91%, 91%, and 85% yields, respectively. Finally, mixed aryl-heteroaryl-substituted cycloadducts were also competent substrates, and hydrolysis products **10m**, **10n**, and **10p** were isolated in 84–96% yields (Scheme 4).

Next, we wanted to show the synthetic utility of the photocycloaddition reaction developed in this work via other transformations (Scheme 5). First, cycloadduct **9n** was reacted with NaOMe in methanol giving dimethyl diester product **12** in 93% yield. In a second experiment, reduction of the two ester groups of **9n** with $LiAlH_4$ afforded cyclobutanedimethanol **13** in 86% yield. In these reactions, both products were obtained as single diastereomers. Finally, we opted to check the [2+2] cycloaddition of diester **6a** under visible light photocatalytic conditions.[29a] For this purpose, diester **6a** was irradiated with blue LEDs (450 nm) in 1,4-dioxane in the presence of $Ir(ppy)_3$ photocatalyst, and the reaction was observed to be complete within one hour (Scheme 6). Whereas this reaction also gave β-truxinate **9a** as the major cycloadduct, the product was found to consist of a mixture of three diastereomers (dr = 1:0.32:0.16). The same reaction was further tested in the absence of a photocatalyst but via irradiation using the medium-pressure mercury lamp in solution phase. In this experiment, when a solution of **6a** in acetone was irradiated, the reaction was complete in 2 h and afforded again a diastereomeric mixture (dr = 1:0.66:0.13) with cycloadduct **9a** being the major diastereomer. These results underscore the advantage of our solid-state photochemical cycloaddition protocol for achieving high levels of diastereoselectivity when 1,8-DHN (**5**) is used as a template.



Scheme 5 Conversion of cycloadduct **9n** to **12** and **13**



Scheme 6 Photocatalytic cycloaddition of diester **6a**

In summary, we have developed a robust and selective method for the controlled photochemical homodimerization and heterodimerization reactions of cinnamic acids leading to the formation of symmetrical and unsymmetrical cyclobutanes. The method involves the use of 1,8-dihydroxynaphthalene (**5**) as a covalent template, that enables the positioning of the two reacting olefins within a distance of <4 Å which is in agreement with Schmidt's distance criterion for a successful photochemical [2+2] cycloaddition in solid state. The photodimerization reactions work uniformly well with aryl- and heteroaryl-containing cinnamic acid derivatives affording cycloadducts in up to 99% yield and as single diastereomers. Cycloadducts were shown to be hydrolyzed easily under basic conditions at room temperature to yield symmetrical and unsymmetrical β-truxinic acids in excellent yields (71% to quant.). Research to render these photochemical [2+2] cycloadditions enantioselective is currently underway in our laboratory.

All air-sensitive solution phase reactions were run using oven-dried glassware under N_2. Reactions were monitored by TLC using aluminum-backed plates pre-coated with silica gel (Silicycle, indicator: F-254; thickness: 200 µm). UV light and/or $KMnO_4$ staining solution were used for the visualization of TLC plates. Flash column chromatographic separations were performed on Silicycle 40–63 µm (230–400 mesh) flash silica gel. ^1H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded using a Bruker Avance 400 spectrometer in $CDCl_3$ and DMSO-d_6. Internal standard signal (TMS, δ = 0) or residual solvent signals ($CDCl_3$ δ = 7.26, and DMSO-d_6 δ = 2.50 for ^1H NMR; $CDCl_3$ δ = 77.16 and DMSO-d_6 δ = 39.52 for $^{13}C\{^1H\}$-NMR spectra) were used for the calibration of ^1H and $^{13}C\{^1H\}$ NMR spectra. Infrared (FTIR) spectra were recorded on a Bruker Alpha-Platinum-ATR spectrometer with only selected peaks reported. HRMS were performed using Agilent Technologies 6224 TOF LC/MS at UNAM-National Nanotechnology Research Center and Institute of Materials Science and Nanotechnology, Bilkent University. Single crystal X-ray diffraction analysis was performed at Gebze Technical University, Turkey. Photochemical experiments for method C were carried out using a reactor obtained from Photochemical Reactors Ltd., which consists of a 400-W medium-pressure mercury lamp (3040/PX0686) and a quartz double-walled immersion well with water cooling. Regular microscope

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slides made of soda-lime glass were used for the photochemical experiments in solid state. The slides were kept at ca. 4 cm away from the lamp during the experiments. Photochemical experiments for method D were carried out using a commercial UV gel nail dryer (Elle by Beurer, MPE58) fitted with four 9-W UVA (Philips PL-S, 365 nm) fluorescent lamps. Quartz microscope slides were used in method D, and were kept at ca. 4.5 cm away from the lamps during the experiments. All photochemical reactions in method C were performed inside a fully closed safety cabinet.[38] 1,8-Dihydroxynaphthalene (1,8-DHN, **5**) was purchased from abcr Co. and used as received. Anhyd CH_2Cl_2 and THF were purchased from Acros Organics (AcroSeal®). All other commercially available reagents were used as received unless stated otherwise.

Synthesis of Symmetrical Diesters 6a–g; General Procedure I (Method A)

To a solution of 1,8-DHN (**5**; 1.0 equiv) in anhyd CH_2Cl_2 (10 mL) in a 100-mL round-bottomed flask were added sequentially *trans*-cinnamic acid derivative (2.0 equiv), DCC (2.0 equiv), and DMAP (20 mol%) at 23 °C under N_2. The resulting cloudy, heterogeneous mixture was stirred at 23 °C for 24 h. TLC analysis indicated full consumption of 1,8-DHN (**5**). The mixture was quenched with H_2O (10 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 ×) The combined organic phases were dried (anhyd Na_2SO_4), filtered, and concentrated under vacuum. The crude reaction mixture was purified by flash column chromatography.

Naphthalene-1,8-diyl (2*E*,2′*E*)-Bis(3-(benzo[*d*][1,3]dioxol-5-yl)acrylate) (6c)

Diester **6c** was synthesized using 1,8-DHN (**5**; 100 mg, 0.62 mmol), (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)acrylic acid (240 mg, 1.25 mmol), DCC (258 mg, 1.25 mmol), DMAP (15.3 mg, 0.125 mmol), and anhyd CH_2Cl_2 (10 mL) following General Procedure I. The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2) to afford pure **6c** (234 mg, 74% yield) as a white solid; mp 253–254 °C; R_f = 0.56 (CH_2Cl_2).

IR (ATR, film): 2921, 1728, 1703, 1631, 1603, 1501, 1452, 1369 cm^{-1}.

^1H NMR (DMSO-d_6, 400 MHz): δ = 7.97 (d, *J* = 8.3 Hz, 2 H), 7.65 (d, *J* = 15.9 Hz, 2 H), 7.59 (t, *J* = 7.9 Hz, 2 H), 7.29 (d, *J* = 7.5 Hz, 2 H), 7.02–7.00 (m, 4 H), 6.74 (d, *J* = 7.8 Hz, 2 H), 6.56 (d, *J* = 15.9 Hz, 2 H), 6.02 (s, 4 H).

$^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz): δ = 165.5, 149.5, 147.7, 146.4, 144.9, 136.2, 128.0, 126.6, 126.4, 125.5, 121.1, 120.9, 114.8, 108.0, 106.4, 101.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{20}NaO_8$: 531.1050; found: 531.1050.

Naphthalene-1,8-diyl (2*E*,2′*E*)-Bis(3-(4-chlorophenyl)acrylate) (6d)

Diester **6d** was synthesized using 1,8-DHN (**5**; 100 mg, 0.62 mmol), (*E*)-3-(4-chlorophenyl)acrylic acid (228 mg, 1.25 mmol), DCC (258 mg, 1.25 mmol), DMAP (15.3 mg, 0.125 mmol), and anhyd CH_2Cl_2 (10 mL) following General Procedure I. The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **6d** (245 mg, 81% yield) as a white solid; mp 247–248 °C; R_f = 0.74 (CH_2Cl_2).

IR (ATR, film): 3082, 1729, 1658, 1640, 1512 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, *J* = 8.3 Hz, 2 H), 7.76 (d, *J* = 16.1 Hz, 2 H), 7.51 (t, *J* = 7.9 Hz, 2 H), 7.21–7.18 (m, 6 H), 7.12 (d, *J* = 8.3 Hz, 4 H), 6.54 (d, *J* = 16.1 Hz, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 165.9, 146.8, 145.4, 141.9, 136.9, 135.7, 129.3, 128.8, 127.4, 126.9, 126.1, 126.0, 120.713.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{18}{}^{35}Cl_2NaO_4$: 511.0474; found: 511.0469; calcd for $C_{28}H_{18}{}^{35}Cl^{37}ClNaO_4$: 513.0445; found: 513.0438.

Naphthalene-1,8-diyl (2*E*,2′*E*)-Bis(3-(thiophen-2-yl)acrylate) (6e)

Diester **6e** was synthesized using 1,8-DHN (**5**; 50 mg, 0.31 mmol), (*E*)-3-(thiophen-2-yl)acrylic acid (96 mg, 0.62 mmol), DCC (129 mg, 0.62 mmol), DMAP (7.7 mg, 0.062 mmol), and anhyd CH_2Cl_2 (5 mL) following General Procedure I. The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **6e** (98 mg, 73% yield) as an orange solid; mp 208–209 °C; R_f = 0.17 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3060, 1726, 1623, 1603, 1422, 1363 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.95 (d, *J* = 15.7 Hz, 2 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 7.50 (t, *J* = 7.9 Hz, 2 H), 7.23 (d, *J* = 5.0 Hz, 2 H), 7.20 (d, *J* = 7.5 Hz, 2 H), 7.11 (d, *J* = 3.5 Hz, 2 H), 6.90 (app t, *J* = 4.6 Hz, 2 H), 6.42 (d, *J* = 15.7 Hz, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 165.9, 145.3, 139.44, 139.38, 136.9, 131.5, 129.3, 128.0, 127.0, 126.2, 121.6, 120.7, 116.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{17}O_4S_2$: 433.0563; found: 433.0562.

Naphthalene-1,8-diyl (2*E*,2′*E*)-Bis(3-(furan-2-yl)acrylate) (6f)

Diester **6f** was synthesized using 1,8-DHN (**5**; 100 mg, 0.62 mmol), (*E*)-3-(furan-2-yl)acrylic acid (173 mg, 1.25 mmol), DCC (258 mg, 1.25 mmol), DMAP (15.3 mg, 0.125 mmol), and anhyd CH_2Cl_2 (10 mL) following General Procedure I. The crude product was purified by flash column chromatography (SiO_2, 1% MeOH in CH_2Cl_2/hexanes 1:1) to afford pure **6f** (200 mg, 81% yield) as a brown solid; mp 179–180 °C; R_f = 0.23 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3144, 3053, 1722, 1633, 1603, 1549, 1471, 1370 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 15.7 Hz, 2 H), 7.49 (t, *J* = 7.9 Hz, 2 H), 7.27 (s, 2 H), 7.20 (d, *J* = 7.5 Hz, 2 H), 6.53–6.49 (m, 4 H), 6.36 (app s, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 166.0, 150.8, 145.34, 145.29, 136.9, 132.9, 126.9, 126.1, 121.5, 120.7, 115.5, 115.2, 112.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{17}O_6$: 401.1020; found: 401.1023.

Naphthalene-1,8-diyl (2*E*,2′*E*)-Bis(3-(1-methyl-1*H*-pyrrol-2-yl)acrylate) (6g)

Diester **6g** was synthesized using 1,8-DHN (**5**; 85 mg, 0.53 mmol), (*E*)-3-(1-methyl-1*H*-pyrrol-2-yl)acrylic acid (200 mg, 1.32 mmol), DCC (252 mg, 1.22 mmol), DMAP (16 mg, 0.13 mmol), and anhyd CH_2Cl_2 (10 mL) following General Procedure I. The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **6f** (163 mg, 72% yield) as a red solid; mp 176–177 °C; R_f = 0.26 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 2944, 1765, 1608, 1577, 1492 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (dd, *J* = 8.3, 0.8 Hz, 2 H), 7.75 (d, *J* = 15.7 Hz, 2 H), 7.49 (t, *J* = 7.9 Hz, 2 H), 7.19 (dd, *J* = 7.5, 0.9 Hz, 2 H), 6.67 (t, *J* = 2.0 Hz, 2 H), 6.48 (dd, *J* = 3.9, 1.5 Hz, 2 H), 6.33 (d, *J* = 15.7 Hz, 2 H), 6.08 (dd, *J* = 3.8, 2.6 Hz, 2 H), 3.56 (s, 6 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.0, 145.7, 136.9, 134.4, 129.1, 128.0, 126.8, 126.1, 121.9, 120.7, 113.8, 111.4, 109.8, 34.5.

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HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{26}H_{22}N_2NaO_4$: 449.1472; found: 449.1471.

Synthesis of Unsymmetrical Diesters 6j–l, 6n, and 6p; General Procedure II (Method B)

In a 50-mL round-bottomed flask, monoester **8a** or **8b** (1 equiv) was dissolved in anhyd THF (10 mL) under N_2, and the resulting solution was cooled to 0 °C in an ice bath. Cinnamoyl chloride derivative (1.0 equiv) was added, and the mixture was stirred for 5 min. Then, NaH (1.1 equiv, 60% in mineral oil) was added carefully. The ice bath was removed, and the mixture was stirred at 23 °C for 1.5 h. It was then quenched with sat. aq NH_4Cl soln (10 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 ×). The combined organic phases were dried (anhyd Na_2SO_4), filtered, and concentrated under vacuum. The crude reaction mixture was purified by flash column chromatography.

8-(Cinnamoyloxy)naphthalen-1-yl (*E*)-3-(4-Nitrophenyl)acrylate (6j)

Diester **6j** was prepared using monoester **8a** (90 mg, 0.31 mmol), NaH (13.7 mg, 0.34 mmol, 60% in mineral oil), (*E*)-3-(4-nitrophenyl)acryloyl chloride (66 mg, 0.31 mmol), and anhyd THF (15 mL) following General Procedure II. The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 2:1) to afford pure **6j** (125 mg, 86% yield) as a white solid; mp 222–223 °C; R_f = 0.33 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3058, 2930, 1731, 1634, 1600, 1512, 1344 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89–7.81 (m, 6 H), 7.55–7.50 (m, 2 H), 7.35 (d, *J* = 8.7 Hz, 2 H), 7.30–7.28 (m, 3 H), 7.22 (d, *J* = 7.5 Hz, 2 H), 7.15 (t, *J* = 7.6 Hz, 2 H), 6.71 (d, *J* = 16.1 Hz, 1 H), 6.59 (d, *J* = 16.1 Hz, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 165.8, 165.0, 148.6, 147.0, 145.2, 145.0, 143.8, 139.8, 137.0, 133.8, 131.0, 129.0, 128.6, 128.2, 127.3, 127.2, 126.4, 126.2, 124.0, 121.8, 121.3, 120.9, 120.7, 117.5.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{28}H_{19}NNaO_6$: 488.1105; found: 488.1101.

8-(Cinnamoyloxy)naphthalen-1-yl (*E*)-3-(3-Nitrophenyl)acrylate (6k)

Diester **6k** was prepared using monoester **8a** (72 mg, 0.25 mmol), NaH (11 mg, 0.27 mmol, 60% in mineral oil), (*E*)-3-(3-nitrophenyl)acryloyl chloride (55 mg, 0.26 mmol), and anhyd THF (12 mL) following General Procedure II. The crude product was purified by flash column chromatography (SiO_2, 3% MeOH in CH_2Cl_2/hexanes 1:1) to afford pure **6k** (85 mg, 74% yield) as a white solid; mp 228–229 °C; R_f = 0.35 (3% MeOH in CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3085, 3055, 1746, 1723, 1629, 1601, 1575, 1523, 1375, 1346, 1305 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.04–8.03 (m, 2 H), 7.85–7.84 (m, 4 H), 7.57–7.50 (m, 3 H), 7.31–7.26 (m, 3 H), 7.22–7.17 (m, 3 H), 7.07 (t, *J* = 7.5 Hz, 2 H), 6.72 (d, *J* = 16.0 Hz, 1 H), 6.60 (d, *J* = 16.0 Hz, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 165.7, 165.1, 148.5, 146.9, 145.2, 145.1, 143.8, 137.0, 135.5, 133.7, 133.5, 130.8, 129.8, 128.9, 128.1, 127.3, 127.1, 126.4, 126.2, 124.8, 122.5, 121.4, 120.9, 120.7, 117.5.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{28}H_{19}NNaO_6$: 488.1105; found: 488.1095.

8-(Cinnamoyloxy)naphthalen-1-yl (*E*)-3-(2-Nitrophenyl)acrylate (6l)

Diester **6l** was prepared using monoester **8a** (65 mg, 0.22 mmol), NaH (9.9 mg, 0.25 mmol, 60% in mineral oil), (*E*)-3-(2-nitrophenyl)acryloyl chloride (50 mg, 0.24 mmol), and anhyd THF (5 mL) following General Procedure II. The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **6l** (75 mg, 72% yield) as a white solid; mp 198–199 °C; R_f = 0.21 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3064, 2961, 1918, 1717, 1635, 1603, 1570, 1517, 1335 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.27 (d, *J* = 15.8 Hz, 1 H), 7.91 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.86 (d, *J* = 15.7 Hz, 1 H), 7.84 (d, *J* = 8.3 Hz, 2 H), 7.54–7.50 (m, 2 H), 7.38–7.35 (m, 3 H), 7.30–7.11 (m, 7 H), 6.67 (d, *J* = 16.1 Hz, 1 H), 6.54 (d, *J* = 15.8 Hz, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 165.7, 164.8, 148.3, 146.9, 145.3, 145.1, 141.9, 137.0, 134.0, 133.3, 130.8, 130.5, 129.9, 129.0, 128.8, 128.3, 127.2, 127.1, 126.3, 126.2, 125.0, 122.5, 121.4, 120.8, 120.7, 117.7.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{28}H_{19}NNaO_6$: 488.1105; found: 488.1092.

8-(Cinnamoyloxy)naphthalen-1-yl (*E*)-3-(Thiophen-2-yl)acrylate (6n)

Diester **6n** was prepared using monoester **8a** (88 mg, 0.30 mmol), NaH (13.3 mg, 0.33 mmol, 60% in mineral oil), (*E*)-3-(thiophen-2-yl)acryloyl chloride (55 mg, 0.32 mmol), and anhyd THF (5 mL) following General Procedure II. The crude product was purified by flash column chromatography (SiO_2, $CHCl_3$/hexanes 1:1) to afford pure **6n** (96 mg, 75% yield) as a white solid; mp 208–209 °C; R_f = 0.16 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3059, 1715, 1638, 1620, 1600, 1574, 1512 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93 (d, *J* = 15.7 Hz, 1 H), 7.85 (d, *J* = 16.0 Hz, 1 H), 7.80 (d, *J* = 8.3 Hz, 2 H), 7.47 (t, *J* = 7.7 Hz, 2 H), 7.31 (d, *J* = 7.5 Hz, 2 H), 7.25 (t, *J* = 7.3 Hz, 1 H), 7.21–7.13 (m, 5 H), 7.04 (d, *J* = 3.3 Hz, 1 H), 6.83 (t, *J* = 4.3 Hz, 1 H), 6.62 (d, *J* = 16.0 Hz, 1 H), 6.40 (d, *J* = 15.7 Hz, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 165.9, 165.8, 147.1, 145.28, 145.26, 139.3, 139.1, 136.9, 134.0, 131.5, 130.5, 129.3, 128.8, 128.3, 128.1, 126.9, 126.2, 121.5, 120.70, 120.67, 117.3, 115.9.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{26}H_{18}NaO_4S$: 449.0818; found: 449.0832.

8-(((*E*)-3-(Furan-2-yl)acryloyl)oxy)naphthalen-1-yl (*E*)-3-(4-Methoxyphenyl)acrylate (6p)

Diester **6p** was prepared using monoester **8b** (75 mg, 0.23 mmol), NaH (9.4 mg, 0.24 mmol, 60% in mineral oil), (*E*)-3-(furan-2-yl)acryloyl chloride (40 mg, 0.26 mmol), and anhyd THF (15 mL) following General Procedure II. The crude product was purified by flash column chromatography (SiO_2, 1% MeOH in CH_2Cl_2/hexanes 1:1) to afford pure **6p** (80 mg, 77% yield) as a pale brown solid; mp 138–140 °C; R_f = 0.30 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3059, 2932, 2839, 1729, 1635, 1601, 1512 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82–7.79 (m, 3 H), 7.58 (d, *J* = 15.7 Hz, 1 H), 7.50 (t, *J* = 7.9 Hz, 1 H), 7.49 (t, *J* = 7.9 Hz, 1 H), 7.33 (d, *J* = 8.7 Hz, 2 H), 7.22–7.18 (m, 3 H), 6.75 (d, *J* = 8.7 Hz, 2 H), 6.52 (d, *J* = 4.3 Hz, 1 H), 6.49–6.47 (m, 2 H), 6.33 (dd, *J* = 3.3, 1.8 Hz, 1 H), 3.82 (s, 3 H).

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$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 166.3, 166.1, 161.6, 150.7, 146.7, 145.4, 145.2, 136.9, 132.8, 130.0, 127.0, 126.9, 126.8, 126.2, 126.1, 121.6, 120.8, 120.7, 115.8, 115.2, 115.0, 114.3, 112.3, 55.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{20}NaO_6$: 463.1152; found: 463.1166.

Photochemical Cycloaddition Reactions of 6; General Procedure III (Method C)

A solid powder sample of diester **6** was placed between two soda-lime glass microscope slides. The sample was irradiated with a 400-W broadband medium-pressure Hg lamp for 8 h inside a safety box. The solid powder was mixed with a spatula to ensure homogeneity every 2 h. At the end of 8 h, the sample was analyzed by ^1H NMR spectroscopy.

Photochemical Cycloaddition Reactions of 6; General Procedure IV (Method D)

A solid powder sample of diester **6** was placed between two quartz glass microscope slides. The sample was irradiated inside a UV gel nail dryer, equipped with four 9-W UVA fluorescent bulbs, for 16 h. The solid powder was mixed with a spatula to ensure homogeneity every 4 h. At the end of 16 h, the sample was analyzed by ^1H NMR spectroscopy.

(8a*R*,9*S*,10*R*,10a*S*)-9,10-Bis(benzo[*d*][1,3]dioxol-5-yl)-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*meso*-9c)

Cycloadduct **9c** was synthesized using diester **6c** (24.9 mg, 0.049 mmol) following General Procedure III (irradiation time = 8 h) to give pure product (23.1 mg, 93% yield) as a brown solid.

Cycloadduct **9c** was also synthesized using diester **6c** (24.8 mg, 0.049 mmol) following General Procedure IV (irradiation time = 16 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9c** (23.9 mg, 96% yield) as an orange solid; mp 209–213 °C; R_f = 0.27 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3060, 2957, 2900, 1764, 1608, 1504, 1492, 1444 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (d, *J* = 8.3 Hz, 2 H), 7.50 (t, *J* = 7.9 Hz, 2 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 6.66 (d, *J* = 7.9 Hz, 2 H), 6.54 (d, *J* = 8.0 Hz, 2 H), 6.50 (s, 2 H), 5.88 (s, 4 H), 4.61 (app d, *J* = 6.0 Hz, 2 H), 4.11 (app d, *J* = 6.1 Hz, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.0, 147.8, 146.4, 145.4, 137.1, 132.1, 127.1, 126.5, 121.09, 121.05, 119.6, 108.4, 108.2, 101.1, 45.2, 44.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{20}NaO_8$: 531.1050; found: 531.1035.

(8a*R*,9*S*,10*R*,10a*S*)-9,10-Bis(4-chlorophenyl)-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*meso*-9d)

Cycloadduct **9d** was synthesized using diester **6d** (25.1 mg, 0.051 mmol) following General Procedure III (irradiation time = 8 h) to give pure product (22.3 mg, 89% yield) as a white solid.

Cycloadduct **9d** was also synthesized using diester **6d** (25.5 mg, 0.052 mmol) following General Procedure IV (irradiation time = 16 h) to give pure product (23.0 mg, 90% yield); mp 216–218 °C; R_f = 0.41 (CH_2Cl_2).

IR (ATR, film): 3060, 2925, 1765, 1607, 1577, 1366 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 8.3 Hz, 2 H), 7.52 (t, *J* = 7.9 Hz, 2 H), 7.28 (d, *J* = 7.4 Hz, 2 H), 7.16 (d, *J* = 8.3 Hz, 4 H), 6.93 (d, *J* = 8.3 Hz, 4 H), 4.72 (app d, *J* = 5.9 Hz, 2 H), 4.17 (app d, *J* = 5.9 Hz, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 169.7, 145.4, 137.1, 136.4, 132.9, 129.2, 128.7, 127.2, 126.5, 121.1, 119.5, 44.8, 43.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{18}{}^{35}Cl_2NaO_4$: 511.0474; found: 511.0461.

(8a*R*,9*S*,10*R*,10a*S*)-9,10-Di(thiophen-2-yl)-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*meso*-9e)

Cycloadduct **9e** was synthesized using diester **6e** (19.2 mg, 0.044 mmol) following General Procedure III (irradiation time = 8 h) to give pure product (18.5 mg, 96% yield).

Cycloadduct **9e** was also synthesized using diester **6e** (25.2 mg, 0.058 mmol) following General Procedure IV (irradiation time = 16 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9e** (24.8 mg, 98% yield) as a pale-yellow solid; mp 193–195 °C; R_f = 0.45 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 2926, 1763, 1608, 1577, 1365 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 8.3 Hz, 2 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 7.29 (d, *J* = 7.4 Hz, 2 H), 7.15 (d, *J* = 5.1 Hz, 2 H), 6.91 (t, *J* = 4.0 Hz, 2 H), 6.84 (d, *J* = 3.1 Hz, 2 H), 4.90 (d, *J* = 5.5 Hz, 2 H), 4.23 (d, *J* = 5.5 Hz, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 169.2, 145.3, 141.0, 137.1, 127.1, 126.9, 126.5, 125.8, 125.2, 121.1, 119.5, 46.8, 41.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{16}NaO_4S_2$: 455.0382; found: 455.0385.

(8a*R*,9*S*,10*R*,10a*S*)-9,10-Di(furan-2-yl)-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*meso*-9f)

Cycloadduct **9f** was synthesized using diester **6f** (21.6 mg, 0.054 mmol) following General Procedure III (irradiation time = 8 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9f** (18.6 mg, 86% yield).

Cycloadduct **9f** was also synthesized using diester **6f** (25.7 mg, 0.064 mmol) following General Procedure IV (irradiation time = 16 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9f** (25.2 mg, 98% yield) as a brown-orange solid; mp 164–165 °C; R_f = 0.49 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 2922, 1765, 1608, 1504, 1363 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (d, *J* = 8.3 Hz, 2 H), 7.50 (t, *J* = 7.9 Hz, 2 H), 7.28–7.25 (m, 4 H), 6.25 (dd, *J* = 3.0, 1.8 Hz, 2 H), 6.04 (d, *J* = 3.1 Hz, 2 H), 4.61 (d, *J* = 5.8 Hz, 2 H), 4.28 (d, *J* = 5.7 Hz, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 169.5, 152.0, 145.3, 142.2, 137.1, 127.1, 126.5, 121.1, 119.5, 110.5, 107.6, 44.3, 38.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{16}NaO_6$: 423.0839; found: 423.0839.

(8a*R*,9*S*,10*R*,10a*S*)-9,10-Bis(1-methyl-1*H*-pyrrol-2-yl)-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*meso*-9g)

Cycloadduct **9g** was synthesized using diester **6g** (25.3 mg, 0.059 mmol) following General Procedure III (irradiation time = 8 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9g** (24.0 mg, 95% yield) as a pale purple solid.

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Cycloadduct **9g** was also synthesized using diester **6g** (18.7 mg, 0.044 mmol) following General Procedure IV (irradiation time = 16 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9g** (15.0 mg, 80% yield) as a purple solid; mp 224–227 °C; R_f = 0.68 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3061, 2916, 1732, 1633, 1605, 1576 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 8.3 Hz, 2 H), 7.51 (t, *J* = 7.8 Hz, 2 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 6.53 (br s, 2 H), 6.04 (t, *J* = 2.7 Hz, 2 H), 5.79–5.74 (m, 2 H), 4.56 (app d, *J* = 5.3 Hz, 2 H), 4.08 (app d, *J* = 5.3 Hz, 2 H), 3.35 (s, 6 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 169.9, 145.5, 137.1, 129.8, 127.1, 126.5, 122.5, 121.1, 119.7, 107.4, 107.1, 46.2, 36.2, 33.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{22}N_2NaO_4$: 449.1472; found: 449.1462.

(8a*R*,9*S*,10*R*,10a*S*)-9-(4-Nitrophenyl)-10-phenyl-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*rac*-9j)

Cycloadduct **9j** was synthesized using diester **6j** (24.3 mg, 0.052 mmol) following General Procedure III (irradiation time = 8 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9j** (18.8 mg, 77% yield) as a gray solid.

Cycloadduct **9j** was also synthesized using diester **6j** (23.8 mg, 0.051 mmol) following General Procedure IV (irradiation time = 16 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9j** (14.4 mg, 61% yield); mp 219–220 °C; R_f = 0.24 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 2924, 2853, 1760, 1606, 1515, 1343 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.00 (d, *J* = 8.5 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.533 (t, *J* = 7.9 Hz, 1 H), 7.528 (t, *J* = 7.9 Hz, 1 H), 7.30 (d, *J* = 7.4 Hz, 2 H), 7.21–7.12 (m, 5 H), 7.02 (d, *J* = 7.1 Hz, 2 H), 4.88 (dd, *J* = 10.5, 5.5 Hz, 1 H), 4.82 (dd, *J* = 10.5, 4.9 Hz, 1 H), 4.31–4.24 (m, 2 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 169.62, 169.58, 146.7, 145.9, 145.3, 137.3, 137.1, 128.8, 128.7, 127.8, 127.5, 127.3, 127.2, 127.0, 126.5, 123.5, 121.1, 121.0, 119.4, 44.8, 44.5, 44.3, 44.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{19}NNaO_6$: 488.1105; found: 488.1115.

(8a*R*,9*S*,10*R*,10a*S*)-9-(3-Nitrophenyl)-10-phenyl-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*rac*-9k)

Cycloadduct **9k** was synthesized using diester **6k** (17.0 mg, 0.037 mmol) following General Procedure III (irradiation time = 8 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9k** (14.9 mg, 88% yield) as a white solid.

Cycloadduct **9k** was also synthesized using diester **6k** (26.7 mg, 0.057 mmol) following General Procedure IV (irradiation time = 16 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9k** (23.0 mg, 86% yield); mp 185–187 °C; R_f = 0.24 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 2954, 2921, 2852, 1761, 1746, 1606, 1526, 1347 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98–7.95 (m, 1 H), 7.91 (s, 1 H), 7.84 (d, *J* = 8.3 Hz, 2 H), 7.53 (t, *J* = 7.9 Hz, 2 H), 7.33–7.30 (m, 4 H), 7.19 (t, *J* = 7.3 Hz, 2 H), 7.11 (t, *J* = 7.3 Hz, 1 H), 7.03 (d, *J* = 7.2 Hz, 2 H), 4.88 (dd, *J* = 9.9, 4.6 Hz, 1 H), 4.82 (dd, *J* = 9.6, 3.4 Hz, 1 H), 4.33–4.27 (m, 2 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 169.7, 169.6, 148.2, 145.3, 140.4, 137.1, 134.1, 129.2, 128.8, 127.9, 127.4, 127.23, 127.19, 126.6, 126.5, 122.7, 121.9, 121.12, 121.06, 119.4, 44.48, 44.46, 44.2, 44.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{19}NNaO_6$: 488.1105; found: 488.1103.

(8a*R*,9*S*,10*R*,10a*S*)-9-(2-Nitrophenyl)-10-phenyl-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*rac*-9l)

Cycloadduct **9l** was synthesized using diester **6l** (24.7 mg, 0.053 mmol) following General Procedure III (irradiation time = 8 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9l** (10.8 mg, 44% yield) as a pale-yellow solid.

Cycloadduct **9l** was also synthesized using diester **6l** (24.3 mg, 0.052 mmol) following General Procedure IV (irradiation time = 16 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9l** (11.8 mg, 49% yield); mp 191–193 °C; R_f = 0.53 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 2922, 1761, 1606, 1574, 1525, 1359 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 8.3 Hz, 3 H), 7.59–7.50 (m, 3 H), 7.46 (d, *J* = 7.7 Hz, 1 H), 7.34–7.28 (m, 3 H), 7.15–7.08 (m, 3 H), 7.02 (d, *J* = 7.7 Hz, 2 H), 5.48 (t, *J* = 9.6 Hz, 1 H), 4.84 (dd, *J* = 10.2, 4.8 Hz, 1 H), 4.52 (t, *J* = 10.0 Hz, 1 H), 4.01 (dd, *J* = 10.8, 4.9 Hz, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 170.0, 169.8, 148.2, 145.37, 145.35, 137.9, 137.1, 134.3, 133.4, 128.8, 128.6, 128.4, 127.9, 127.3, 127.2, 127.1, 126.6, 126.5, 125.4, 121.2, 121.1, 119.4, 45.2, 44.6, 44.1, 43.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{20}NO_6$: 466.1285; found: 466.1277.

(8a*S*,9*S*,10*S*,10a*S*)-9-Phenyl-10-(thiophen-2-yl)-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*rac*-9n)

Cycloadduct **9n** was synthesized using diester **6n** (25.3 mg, 0.059 mmol) following General Procedure III (irradiation time = 8 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9n** (21.8 mg, 86% yield) as a white solid.

Cycloadduct **9n** was also synthesized using diester **6n** (25.7 mg, 0.060 mmol) following General Procedure IV (irradiation time = 16 h) to give pure product (24.8 mg, 96% yield); mp 202–203 °C; R_f = 0.30 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 3057, 2925, 1752, 1606, 1576, 1497, 1365 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 8.3 Hz, 2 H), 7.51 (t, *J* = 7.8 Hz, 1 H), 7.50 (t, *J* = 7.8 Hz, 1 H), 7.29–7.21 (m, 4 H), 7.19–7.16 (m, 1 H), 7.11 (d, *J* = 7.3 Hz, 2 H), 7.05 (d, *J* = 5.0 Hz, 1 H), 6.82 (t, *J* = 4.2 Hz, 1 H), 6.73 (d, *J* = 3.0 Hz, 1 H), 4.91 (dd, *J* = 9.9, 5.9 Hz, 1 H), 4.76 (t, *J* = 8.8 Hz, 1 H), 4.33 (dd, *J* = 10.4, 7.8 Hz, 1 H), 4.14 (dd, *J* = 10.5, 5.9 Hz, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 169.7, 169.6, 145.39, 145.37, 141.6, 137.6, 137.1, 128.4, 127.8, 127.14, 127.11, 126.5, 125.6, 124.9, 121.11, 121.05, 119.6, 47.0, 44.8, 44.4, 40.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{18}NaO_4S$: 449.0818; found: 449.0832.

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(8a*R*,9*S*,10*R*,10a*S*)-9-(Furan-2-yl)-10-(4-methoxyphenyl)-8a,9,10,10a-tetrahydrocyclobuta[*g*]naphtho[1,8-*bc*][1,5]dioxonine-8,11-dione (*rac*-9p)

Cycloadduct **9p** was synthesized using diester **6p** (25.8 mg, 0.059 mmol) following General Procedure III (irradiation time = 8 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9p** (14.7 mg, 57% yield).

Cycloadduct **9p** was also synthesized using diester **6p** (15.5 mg, 0.035 mmol) following General Procedure IV (irradiation time = 16 h). The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) to afford pure **9p** (13.0 mg, 84% yield) as a white solid; mp 154.8–155.3 °C; R_f = 0.32 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 2929, 2838, 1765, 1609, 1515, 1364 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 7.8 Hz, 2 H), 7.51 (t, *J* = 7.8 Hz, 1 H), 7.50 (t, *J* = 7.8 Hz, 1 H), 7.29–7.25 (m, 2 H), 7.22 (m, 1 H), 7.03 (d, *J* = 8.7 Hz, 2 H), 6.77 (d, *J* = 8.5 Hz, 2 H), 6.19 (t, *J* = 2.2 Hz, 1 H), 6.03 (d, *J* = 3.1 Hz, 1 H), 4.66 (t, *J* = 9.2 Hz, 1 H), 4.57 (dd, *J* = 10.1, 4.8 Hz, 1 H), 4.33 (dd, *J* = 10.5, 8.5 Hz, 1 H), 4.19 (dd, *J* = 10.6, 4.8 Hz, 1 H), 3.76 (s, 3 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 170.2, 169.6, 158.6, 152.2, 145.4, 142.2, 137.1, 130.2, 128.5, 127.08, 127.05, 126.5, 121.1, 121.0, 119.6, 113.7, 110.4, 108.2, 55.3, 45.7, 43.8, 43.6, 38.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{20}NaO_6$: 463.1152; found: 463.1160.

Hydrolysis of Cycloadducts 9; General Procedure V

To a solution of cycloadduct **9** (1.0 equiv) in THF (2.0 mL) in a 20-mL scintillation vial was added distilled water (1.0 mL) and KOH (19 equiv). The resulting mixture was stirred at 23 °C for 2 h and then quenched with 1.0 M HCl solution until pH 1–2. The aqueous phase was extracted with EtOAc (3 ×). The combined organic phases were dried (anhyd Na_2SO_4), filtered, and concentrated under vacuum. The crude mixture was purified by flash column chromatography.

(1*R*,2*S*,3*R*,4*S*)-3,4-Bis(benzo[*d*][1,3]dioxol-5-yl)cyclobutane-1,2-dicarboxylic Acid (*meso*-10c)

Dicarboxylic acid **10c** was synthesized using cycloadduct **9c** (24.2 mg, 0.048 mmol), KOH (51.2 mg, 0.91 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, EtOAc/hexanes 1:1 → 0.5% AcOH in EtOAc/hexanes 1:1) to afford pure **10c** (17.5 mg, 95% yield) as a dark brown solid; mp 151–152 °C; R_f = 0.11 (0.5% AcOH in EtOAc/hexanes 1:1).

IR (ATR, film): 3012, 2891, 1745, 1697, 1503, 1491, 1442 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.43 (br s, 2 H), 6.66 (d, *J* = 8.0 Hz, 2 H), 6.65 (d, *J* = 1.2 Hz, 2 H), 6.54 (d, *J* = 8.0, 1.2 Hz, 2 H), 5.88 (s, 4 H), 4.07 (d, *J* = 6.2 Hz, 2 H), 3.71 (d, *J* = 6.2 Hz, 2 H).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{20}H_{15}O_8$: 383.0772; found: 383.0780.

(1*R*,2*S*,3*R*,4*S*)-3,4-Bis(4-chlorophenyl)cyclobutane-1,2-dicarboxylic Acid (*meso*-10d)

Dicarboxylic acid **10d** was synthesized using cycloadduct **9d** (22.3 mg, 0.046 mmol), KOH (48.5 mg, 0.86 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, 0.5% AcOH in EtOAc/hexanes 1:1) to afford pure **10d** (14.2 mg, 84% yield) as a pale brown solid; mp 178–180 °C; R_f = 0.15 (0.5% AcOH in EtOAc/hexanes 1:1). The ^{1}H and ^{13}C NMR spectroscopic data are in agreement with those reported in the literature.[30a]

IR (ATR, film): 3123 (br), 1710, 1493, 1425 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.45 (br s, 2 H), 7.16 (d, *J* = 8.2 Hz, 4 H), 7.07 (d, *J* = 8.0 Hz, 4 H), 4.22 (app d, *J* = 5.4 Hz, 2 H), 3.80 (app d, *J* = 5.5 Hz, 2 H).

^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): δ = 173.8, 138.2, 130.7, 129.8, 127.7, 43.8, 42.4.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{18}H_{13}{}^{35}Cl_2O_4$: 363.0196; found: 363.0196; calcd for $C_{18}H_{13}{}^{35}Cl^{37}ClO_4$: 365.0167; found: 365.0166.

(1*R*,2*S*,3*R*,4*S*)-3,4-Di(thiophen-2-yl)cyclobutane-1,2-dicarboxylic Acid (*meso*-10e)

Dicarboxylic acid **10e** was synthesized using cycloadduct **9e** (24.8 mg, 0.057 mmol), KOH (48.5 mg, 0.86 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, EtOAc/hexanes 1:1 → 0.5% AcOH in EtOAc/hexanes 1:1) to afford pure **10e** (16.0 mg, 90% yield) as a pale brown solid; mp 173–175 °C; R_f = 0.13 (0.5% AcOH in EtOAc/hexanes 1:1).

IR (ATR, film): 2925, 1708, 1419, 1239 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.60 (br s, 2 H), 7.24 (d, *J* = 4.8 Hz, 2 H), 6.86–6.83 (m, 4 H), 4.31 (app d, *J* = 6.1 Hz, 2 H), 3.70 (app d, *J* = 6.1 Hz, 2 H).

^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): δ = 173.1, 142.0, 126.6, 125.4, 124.9, 45.1, 40.7.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{14}H_{11}O_4S_2$: 307.0104; found: 307.0119.

(1*R*,2*S*,3*R*,4*S*)-3,4-Di(furan-2-yl)cyclobutane-1,2-dicarboxylic Acid (*meso*-10f)

Dicarboxylic acid **10f** was synthesized using cycloadduct **9f** (24.0 mg, 0.060 mmol), KOH (62.8 mg, 1.12 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, 0.5% AcOH in EtOAc/hexanes 1:1) to afford pure **10f** (11.8 mg, 71% yield) as a pale-yellow solid; mp 175–177 °C; R_f = 0.24 (0.5% AcOH in EtOAc/hexanes 1:1). The ^{1}H NMR spectrum in DMSO-d_6 is in agreement with the spectrum reported in the literature.[30c]

IR (ATR, film): 2924, 1710, 1505, 1427 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.16 (br s, 2 H), 7.24 (app s, 2 H), 6.21 (app t, *J* = 1.4 Hz, 2 H), 5.96 (d, *J* = 2.8 Hz, 2 H), 4.29 (app d, *J* = 5.6 Hz, 2 H), 3.97 (app d, *J* = 5.4 Hz, 2 H).

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.61 (br s, 2 H), 7.41–7.40 (m, 2 H), 6.25 (dd, *J* = 3.0, 1.9 Hz, 2 H), 6.10 (d, *J* = 3.2 Hz, 2 H), 4.05 (app d, *J* = 6.1 Hz, 2 H), 3.66 (app d, *J* = 6.1 Hz, 2 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 179.2, 152.2, 142.1, 110.5, 107.4, 43.6, 38.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{12}NaO_6$: 299.0526; found: 299.0535.

Dimethyl (1*R*,2*S*,3*R*,4*S*)-3,4-Bis(1-methyl-1*H*-pyrrol-2-yl)cyclobutane-1,2-dicarboxylate (*meso*-11)

NaOMe (3.0 mg, 0.056 mmol) was added to a solution of cycloadduct **9g** (11.8 mg, 0.028 mmol) in MeOH (4 mL) at 23 °C. The resulting mixture was stirred at 23 °C for 3.5 h at which time TLC analysis indicated complete consumption of the reactant. MeOH was then evaporated

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under reduced pressure and the crude mixture was mixed with $CDCl_3$. Ionic components including the sodium salt of **5** did not dissolve in $CDCl_3$. The supernatant liquid was transferred to another flask, and all volatiles were removed under reduced pressure to afford pure **11** (6.0 mg, 65% yield) as a blackish amorphous solid; R_f = 0.43 (CH_2Cl_2/hexanes 1:1).

IR (ATR, film): 2950, 2928, 1735, 1435, 1354, 1208 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.48–6.47 (m, 2 H), 5.98 (dd, *J* = 3.5, 2.8 Hz, 2 H), 5.61 (dd, *J* = 3.6, 1.7 Hz, 2 H), 4.20 (app d, *J* = 6.0 Hz, 2 H), 3.72 (s, 6 H), 3.69 (app d, *J* = 5.9 Hz, 2 H), 3.28 (s, 6 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 173.1, 130.5, 122.2, 107.1, 106.7, 52.3, 45.2, 36.8, 33.6.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{23}N_2O_4$: 331.1652; found: 331.1666.

(1*S*,2*R*,3*S*,4*R*)-3-(4-Nitrophenyl)-4-phenylcyclobutane-1,2-dicarboxylic Acid (*rac*-10j)

Dicarboxylic acid **10j** was synthesized using cycloadduct **9j** (14.4 mg, 0.031 mmol), KOH (32.9 mg, 0.59 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, EtOAc/hexanes 1:1 → 0.5% AcOH in EtOAc/hexanes 1:1) to afford pure **10j** (9.6 mg, 91% yield) as a brownish amorphous solid.; R_f = 0.18 (0.5% AcOH in EtOAc/hexanes 1:1).

IR (ATR, film): 3030, 2925, 2854, 1707, 1601, 1517, 1425, 1345 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 10.13 (br s, 2 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.17–7.11 (m, 3 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 6.93 (d, *J* = 7.0 Hz, 2 H), 4.64 (t, *J* = 8.8 Hz, 1 H), 4.40 (dd, *J* = 9.6, 5.5 Hz, 1 H), 4.02 (t, *J* = 8.8 Hz, 1 H), 3.91 (dd, *J* = 9.2, 5.4 Hz, 1 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 179.5, 178.9, 146.7, 146.0, 137.2, 128.8, 128.5, 127.8, 127.5, 123.5, 45.0, 44.6, 44.1, 43.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{15}NNaO_6$: 364.0792; found: 364.0791.

(1*S*,2*R*,3*S*,4*R*)-3-(3-Nitrophenyl)-4-phenylcyclobutane-1,2-dicarboxylic Acid (*rac*-10k)

Dicarboxylic acid **10k** was synthesized using cycloadduct **9k** (20.0 mg, 0.043 mmol), KOH (46 mg, 0.82 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, 0.5% AcOH in EtOAc/hexanes 1:1) to afford pure **10k** (13.4 mg, 91% yield) as a yellow amorphous solid; R_f = 0.17 (0.5% AcOH in EtOAc/hexanes 1:1).

IR (ATR, film): 3030, 2925, 2855, 1706, 1527, 1422, 1346 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 8.25 (br s, 2 H), 7.93 (d, *J* = 7.9 Hz, 1 H), 7.80 (s, 1 H), 7.29–7.25 (m, 1 H), 7.22 (d, *J* = 7.7 Hz, 1 H), 7.17–7.14 (m, 2 H), 7.11–7.07 (m, 1 H), 6.96 (d, *J* = 7.2 Hz, 2 H), 4.66 (t, *J* = 9.0 Hz, 1 H), 4.41 (dd, *J* = 10.0, 5.4 Hz, 1 H), 4.04 (t, *J* = 9.1 Hz, 1 H), 3.95 (dd, *J* = 10.0, 5.7 Hz, 1 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 179.5, 178.8, 148.1, 140.5, 137.2, 134.0, 129.1, 128.8, 127.8, 127.4, 122.6, 121.9, 44.9, 44.4, 43.9, 43.5.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{18}H_{14}NO_6$: 340.0827; found: 340.0812.

(1*S*,2*R*,3*S*,4*R*)-3-(2-Nitrophenyl)-4-phenylcyclobutane-1,2-dicarboxylic Acid (*rac*-10l)

Dicarboxylic acid **10l** was synthesized using cycloadduct **9l** (20.5 mg, 0.044 mmol), KOH (46.9 mg, 0.84 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, 0.5% AcOH in EtOAc/hexanes 1:1 → 5% MeOH in EtOAc) to afford pure **10l** (12.7 mg, 85% yield) as a white solid; mp 182–185 °C; R_f = 0.25 (0.5% AcOH in EtOAc/hexanes 1:1).

IR (ATR, film): 3055, 3032, 2924, 1709, 1524, 1423, 1346 cm^{-1}.

^1H NMR (CD_3OD, 400 MHz): δ = 7.76 (d, *J* = 8.1 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.43 (d, *J* = 7.6 Hz, 1 H), 7.26 (t, *J* = 7.6 Hz, 1 H), 7.08–7.00 (m, 5 H), 5.09 (t, *J* = 10.1 Hz, 1 H), 4.33 (t, *J* = 10.2 Hz, 1 H), 4.18 (dd, *J* = 10.0, 3.7 Hz, 1 H), 3.59 (dd, *J* = 10.0, 3.7 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ = 176.6, 175.8, 149.8, 140.1, 136.1, 134.1, 130.5, 129.3, 129.2, 128.4, 127.8, 125.6, 47.0, 46.0, 44.2, 42.6.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{18}H_{14}NO_6$: 340.0827; found: 340.0825.

(1*S*,2*S*,3*S*,4*S*)-3-Phenyl-4-(thiophen-2-yl)cyclobutane-1,2-dicarboxylic Acid (*rac*-10n)

Dicarboxylic acid **10n** was synthesized using cycloadduct **9n** (19.8 mg, 0.046 mmol), KOH (49.5 mg, 0.88 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, 0.1% AcOH in EtOAc/hexanes 1:1) to afford pure **10n** (13.5 mg, 96% yield) as a pale brown solid; mp 181–182 °C; R_f = 0.30 (0.5% AcOH in EtOAc/hexanes 1:1).

IR (ATR, film): 3031, 2922, 1698, 1413, 1255 cm^{-1}.

^1H NMR (CD_3OD, 400 MHz): δ = 7.16–7.12 (m, 2 H), 7.09–7.06 (m, 3 H), 7.03 (dd, *J* = 5.1, 1.0 Hz, 1 H), 6.75 (dd, *J* = 5.0, 3.5 Hz, 1 H), 6.68 (d, *J* = 3.4 Hz, 1 H), 4.46 (dd, *J* = 9.8, 6.3 Hz, 1 H), 4.32 (t, *J* = 8.7 Hz, 1 H), 3.94 (dd, *J* = 9.7, 7.8 Hz, 1 H), 3.74 (dd, *J* = 9.9, 6.3 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ = 176.1, 175.8, 143.9, 139.9, 129.0, 128.9, 127.5, 127.4, 126.2, 125.0, 47.3, 46.8, 44.3, 42.2.

HRMS (APCI): *m*/*z* [M – H]$^-$ calcd for $C_{16}H_{13}O_4S$: 301.0540; found: 301.0521.

(1*S*,2*R*,3*S*,4*R*)-3-(Furan-2-yl)-4-(4-methoxyphenyl)cyclobutane-1,2-dicarboxylic Acid (*rac*-10p)

Dicarboxylic acid **10p** was synthesized using cycloadduct **9p** (8.2 mg, 0.019 mmol), KOH (19.8 mg, 0.35 mmol), THF (2 mL), and H_2O (1 mL) following General Procedure V. The crude product was purified by flash column chromatography (SiO_2, EtOAc/hexanes 1:1 → 0.5% AcOH in EtOAc/hexanes 1:1) to afford pure **10p** (5.5 mg, 93% yield) as a pale brown amorphous solid; R_f = 0.21 (0.5% AcOH in EtOAc/hexanes 1:1).

IR (ATR, film): 3418 (br), 2917, 2849, 1720, 1514, 1463, 1249 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 9.53 (br s, 2 H), 7.18 (s, 1 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 6.72 (d, *J* = 8.4 Hz, 2 H), 6.16 (br app s, 1 H), 5.95 (d, *J* = 2.9 Hz, 1 H), 4.41 (t, *J* = 9.4 Hz, 1 H), 4.18 (dd, *J* = 9.5, 4.7 Hz, 1 H), 4.05 (t, *J* = 9.6 Hz, 1 H), 3.82 (dd, *J* = 9.9, 4.8 Hz, 1 H), 3.73 (s, 3 H).

$^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz): δ = 173.46, 173.43, 157.7, 153.3, 141.9, 131.1, 128.4, 113.1, 110.2, 107.2, 54.9, 43.4, 43.2, 42.3, 38.4.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{17}H_{15}O_6$: 315.0874; found: 315.0871.

Dimethyl (1*S*,2*S*,3*S*,4*S*)-3-Phenyl-4-(thiophen-2-yl)cyclobutane-1,2-dicarboxylate (*rac*-12)

NaOMe (7.9 mg, 0.15 mmol) was added to a solution of cycloadduct **9n** (31.2 mg, 0.073 mmol) in MeOH (2 mL) at 23 °C. The resulting mixture was stirred at 23 °C for 2 h at which time TLC analysis indicated complete consumption of the reactant. MeOH was then evaporated under reduced pressure. The remaining crude oil was dissolved in EtOAc (10 mL), and to this solution water (10 mL) and brine (5 mL)

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were added. The two phases were partitioned in a separatory funnel. The aqueous phase was further extracted with EtOAc (3 × 15 mL). The combined organic phases were dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, EtOAc/hexanes 1:1) to afford pure **12** (22.5 mg, 93% yield) as yellow oil; R_f = 0.72 (EtOAc/hexanes 1:1).

IR (ATR, film): 2951, 1736, 1435, 1264, 1207 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.20–7.13 (m, 3 H), 7.02 (d, *J* = 7.0 Hz, 2 H), 7.00 (d, *J* = 5.1 Hz, 1 H), 6.77 (dd, *J* = 5.0, 3.6 Hz, 1 H), 6.61 (d, *J* = 3.5 Hz, 1 H), 4.55 (dd, *J* = 9.8, 6.2 Hz, 1 H), 4.41 (t, *J* = 8.8 Hz, 1 H), 3.95 (dd, *J* = 10.0, 7.7 Hz, 1 H), 3.76 (s, 3 H), 3.74 (s, 3 H), 3.78–3.71 (m, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 172.8, 172.6, 142.3, 138.1, 128.2, 127.8, 126.9, 126.6, 125.3, 124.5, 52.4, 52.3, 46.1, 45.6, 42.9, 41.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}NaO_4S$: 353.0818; found: 353.0830.

((1*S*,2*S*,3*S*,4*S*)-3-Phenyl-4-(thiophen-2-yl)cyclobutane-1,2-diyl)dimethanol (*rac*-13)

$LiAlH_4$ (25.8 mg, 0.68 mmol) was added to a solution of cycloadduct **9n** (29.1 mg, 0.068 mmol) in anhyd THF (2 mL) at 0 °C under N_2. The resulting gray-colored mixture was stirred at 23 °C for 3 h at which time TLC analysis indicated complete consumption of the reactant. The mixture was then quenched carefully with water, and gas formation was observed. The aqueous phase was extracted with EtOAc (3 ×). The combined organic phases were dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, 5% MeOH in CH_2Cl_2) to afford pure **13** (16.0 mg, 86% yield) as a brown oil; R_f = 0.23 (5% MeOH in CH_2Cl_2).

IR (ATR, film): 3317 (br), 2926, 2872, 1496, 1451, 1264 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.18–7.08 (m, 3 H), 7.04 (d, *J* = 7.0 Hz, 2 H), 6.96 (d, *J* = 5.1 Hz, 1 H), 6.75 (dd, *J* = 5.0, 3.5 Hz, 1 H), 6.57 (d, *J* = 3.3 Hz, 1 H), 4.08–3.99 (m, 2 H), 3.93–3.82 (m, 3 H), 3.63 (t, *J* = 8.5 Hz, 1 H), 3.41 (br s, 2 H), 3.29–3.22 (m, 1 H), 3.14–3.07 (m, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 144.0, 139.4, 128.2, 128.1, 126.6, 126.4, 124.7, 123.8, 62.4, 62.2, 44.8, 43.6, 40.2, 40.1.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{16}H_{17}O_2S$: 273.0955; found: 273.0972.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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(38) Please see the Supporting Information of ref. 32 for illustrations of instrumental setups of the photochemical experiments.

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