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Synthesis of Benzobicycloheptanones via the Trap of Photogenerated Ketene Methide Intermediate with Olefins

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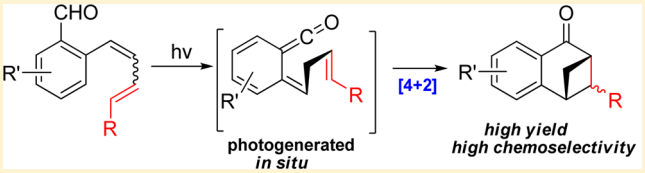
Supporting Information

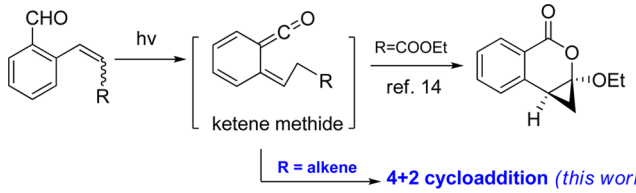
ABSTRACT: Irradiation of *ortho*-formyl dienes with UV light led to benzobicycloheptanones in high yields and chemoselectivities via a photogenerated ketene methide/Diels–Alder cascade reaction. The reaction mechanism was proposed to be a [1,5]-H shift process rather than a radical pathway based on control experiments. DFT calculations indicate that the energy of transition states is responsible for the high chemoselectivity observed in this protocol.



INTRODUCTION

Cycloaddition reactions result in the formation of a new ring from two reactants and have long played a significant role in synthetic organic chemistry.[1] A photocycloaddition reaction that involves the photon as the clean reagent for organic synthesis has a great advantage in synthesis of polycyclic or highly functionalized molecules that would be difficult to access with the standard chemistry reactions in the ground state.[2] The typical and efficient methods for syntheses of six-membered or larger-sized rings include photochemical Diels–Alder reaction,[3] [4 + 4]-photocycloaddition,[4] and photoenolization/Diels–Alder reaction.[5] Among these, the unstable dienes that generated in situ have particularly attracted the interest of organic chemists due to their high reactivity with various dienophiles to form polysubstituted six-membered building blocks. On the basis of structures of reactive diene intermediates, the unstable dienes could be categorized into three types, *ortho*-quinodimethanes,[5,6] *ortho*-quinonemethides,[7] and *ortho*-quinoid ketene methides.[8] The *ortho*-quinodimethane and its derivatives have been widely studied and utilized in natural product synthesis, such as alkaloids,[9] steroids,[10] polycyclic natural compounds,[11] anthracycline, and related quinones,[12] though the employment of the other two types is still in their early stage. Despite the advance in the preparation of *ortho*-quinoidketene methides that is usually generated from benzocyclobutenones and their derivatives through thermal methods[8] or alternative photochemical procedures,[13] a simpler and milder methodology is still desired to synthesize such a compound and its derivatives. Inspired by our previous work that UV-light irradiation of *ortho*-formyl cinnamate derivatives led to polysubstituted isochromanones through a crucial ketene methide intermediate (Scheme 1),[14] we designed and prepared a series of *ortho*-formyl dienes to investigate their chemical behaviors. We envisioned that the in situ photogenerated ketene methide intermediate could be subsequently trapped with a dienophile via an intramolecular [4 + 2] cycloaddition reaction (Scheme 1). Herein, in this paper, we present what we have achieved in this unique and interesting reaction.

Scheme 1. Pathway of Ketene Methide Generation and Its Reactivity



RESULTS AND DISCUSSION

Our initial investigation was started from the synthesis of *ortho*-formyl phenylbutadiene (**1a**, Table 1) and subjecting it to UV light irradiation. The solution of **1a** in dried benzene (0.01 M) under nitrogen was irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter to afford two products in 57% and 26% isolated yields, respectively. On the basis of spectroscopic properties, in particular, 1D and 2D NMR spectra, these two photoproducts were assigned to be the exobenzobicycloheptanone (***exo*-2a**) and endobenzobicycloheptanone (***endo*-2a**) as shown in Table 1.

Given the initial success, a more detailed study and optimization of the reaction were performed by screening solvents, atmosphere (gas), and light source. The results are outlined in Table 1. As it can be seen, the reaction proceeds efficiently in all employed conditions in 71–96% yield. Among these, the use of a Pyrex filter led to higher yield and regioselectivity, albeit a longer reaction time was applied (Table

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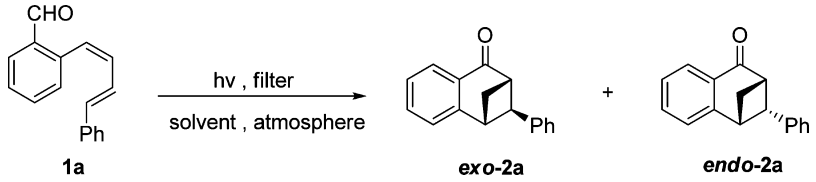
Table 1. Optimization of Reaction Conditions[a]



1a ***exo*-2a** ***endo*-2a**

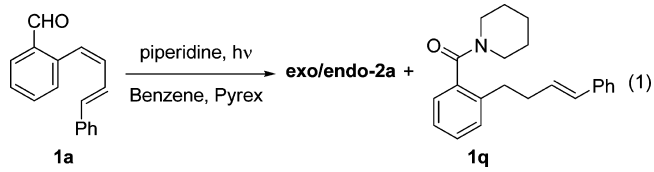
entry	solvent[b]	gas	filter	time (h)[c]	yield (%)[d](dr)[e]
1	benzene	N_2	Pyrex	8	96 (2.2:1)[f]
2	undried benzene	N_2	Pyrex	6	89 (1.5:1)
3	toluene	N_2	Pyrex	6	87 (1.1:1)
4	CH_3CN	N_2	Pyrex	6	89 (1.4:1)
5	acetone	N_2	Pyrex	11	83 (2.3:1)
6	benzene	air	Pyrex	11	71 (1.1:1)
7	benzene	N_2	Quarts	4	87 (1:1)
8	benzene	air	Quarts	4	84 (1:1)
9	undried CH_3CN	N_2	Pyrex	4	81 (1.5:1)

[a]Reactions were carried out with **1a** (0.01 M) in 2 mL of solvent under irradiation with a 500 W medium-pressure mercury lamp. [b]Dried solvent. [c]**1a** was completely consumed. [d]Yields were detected by GC. [e]Diastereomeric ratio of ***exo*-2**/***endo*-2**. [f]The ratio was calculated from isolated yield.

1, entry 1), in comparison with the cases of a Quarts filter (Table 1, entry 7). The reaction was tolerated with different solvents affording the products in high yields (Table 1, entries 3−5). Notably, the solvents with a trace amount of water slightly accelerated the reaction (Table 1, entries 2 and 9), which, on the basis of the previous literature,[15] might be due to the enforced hydrophobic interactions of water that the strong hydrogen-bonding network in water tends to exclude nonpolar solutes and force the photogenerated diene and dienophile together, resulting in higher effective concentrations and relative stabilization of the developing transition state.The deoxygenation is necessary for the reaction to avert the relatively lower yield and longer time required under the atmosphere of air (Table 1, entries 6 and 8). Finally, on the basis of GC analysis, the reaction conducted in dried benzene using a 500 W medium-pressure mercury lamp as the light source through a Pyrex filter was then utilized as the reaction conditions in further investigations. Additionally, the quantum yield (Φ = 0.05) for this conversion was determined.

To explore the scope of this cycloaddition reaction, a series of substrates were synthesized and subjected to the reaction conditions, and the results are listed in Table 2. In general, both *E*- and *Z*-dienes are reactive under the reaction conditions. The aromatic groups bearing electron-withdrawing or electron-donating substituents were tolerated in this process, leading to the corresponding products in moderate to high yields (Table 2, entries 1−11), among which the ratio of ***exo*-2** and ***endo*-2** varied from 1:1 to 4:1, except for entry 10. As a bonus, one of the products was suitable for X-ray single-crystal structural analysis, allowing unambiguous determination of its structure and relative configuration (Table2, entry 8).[16] Interestingly, the dienes substituted with a methyl group led to the highest yield and regioselectivity, respectively (Table 2, entries 12 and 13). More importantly, in the case of entry 13, a quarternary center was constructed in the reaction. When the terminal aromatic group was replaced by a cyclopropyl, the corresponding product was obtained in 34% yield with the cyclopropyl ring unopened, indicating that the [4 + 2] cycloaddition reaction might not be a radical mechanism. Additionally, the methyl instead of an aromatic group at the terminal position afforded the desired product in low yield (Table 2, entry 15). The above results suggest that the presence of an aromatic group might be responsible for stabilizing the double bond during the reaction. However, when the terminal position was substituted with an ester, the isomerization was preferentially observed (Table 2, entry 16). With regard to the different yields and ratios of the products observed in the above examples, we speculated that the steric effect plays the role in the step of [4 + 2] cycloaddition reaction.

Throughout our investigations, a series of control experiments were conducted with **1a** as a representative substrate. To add more credence to the existence of a ketene methide intermediate, a reaction was performed by subjecting an equivalent amount of **1a** and piperidine to the optimal reaction conditions, which led to a mixture of ***exo*-** and ***endo*-2a** along with an amide compound **1q** (eq 1). The formation of the amide agrees with the result observed by Kessar and co-workers in this regard.[13]



1a **1q**

To collect more information about the reaction mechanism, another control experiment was conducted by adding 3 equiv of TEMPO in the reaction of **1a**. The reaction was not prevented by TEMPO, and the photoproduct **2a** was obtained smoothly, which, in combination with our previous study on the *ortho*-formyl 3-cyclopropyl methyl cinnamate that the cyclopropyl ring fragmentation product was not obtained,[17] indicates that the formation of a ketene intermediate is through a [1,5] hydrogen-shift process rather than a radical pathway.

Another control experiment was conducted by addition of cyclohexa-1,3-diene as a triplet quencher in the solution of **1a** in benzene, which did not depress the reaction. In addition, the oxygen, dissolved in the solvent under air-saturated conditions (Table 1, entry 6), had no obvious effect on the reaction efficiency. These experiments suggest that the reaction involves a singlet state.[13a]

Moreover, we also performed the deuterium-labeled experiment and intramolecular kinetic isotope effect (KIE) experi-

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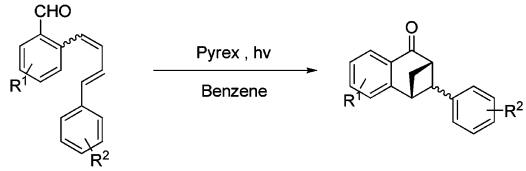
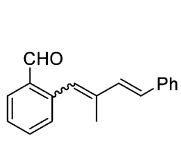
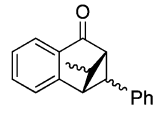
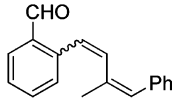
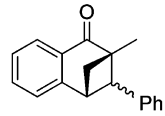
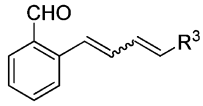
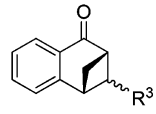
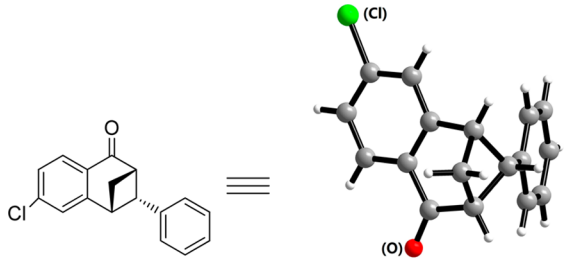
Table 2. Scope of the Photocycloaddition[a,b,c,d,e,f]

Entry	Substrate[a]	Time/h	Yield/%[b]	dr[c]
				
1	R^1= H R^2=H (**1a**)	8	83	2.2:1
2	R^1= H R^2=2′-Cl (**1b**)	20	58	1:1
3	R^1= H R^2=2′-OMe (**1c**)	9	84	1.5:1
4	R^1= H R^2=3′-Me (**1d**)	12	79	3:1
5	R^1= H R^2=3′-F (**1e**)	20	86	2.6:1
6	R^1= H R^2=4′-Me (**1f**)	7	83	2:1
7	R^1= H R^2=4′-Br (**1g**)	10	68	1.2:1
8[f]	R^1= 4-Cl R^2=H (**1h**)	10	62	1.1:1
9	R^1= 5-Cl R^2=H (**1i**)	13	69	1.2:1
10	R^1= 4-OMe R^2=H (**1j**)	13	66	1:1.6
11	R^1= 5-OMe R^2=H (**1k**)	13	50	4:1
12	 (**1l**)	 7	93	7:1
13	 (**1m**)	 8	61	1:61
				
14	R^3=Cyclopropyl(**1n**)	11	34	2.5:1
15	R^3= Me (**1o**)	26	8[d]	--
16	R^3= COOEt(**1p**)	21	--[e]	--

[a]Almost all substrates were a mixture of two isomers, except for **1a**, **1j**, **1k**, and **1p**, which were spectroscopically homogeneous. [b]Isolated yields. [c]Diastereomeric ratio value based on isolated yields of *exo*- and *endo*-type products. [d]Only *endo*-type product isolated. [e]Isomerization of olefins. [f]



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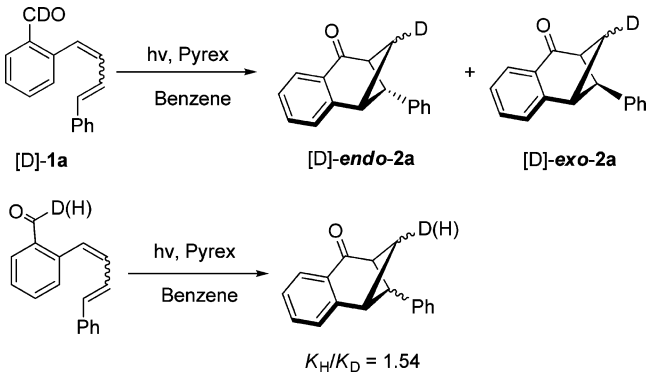
ment. As shown in Scheme 2, irradiation of partially (80%) deuterated aldehyde ([D]-**1a**) led to the corresponding

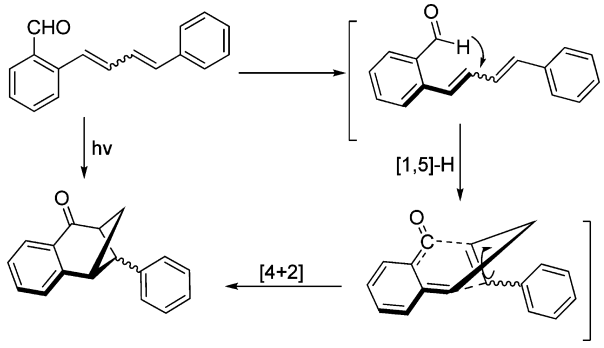
Scheme 2. Deuterium-Labeled Experiments



deuterium products [D]-***endo*-2a** and [D]-***exo*-2a**, which revealed the fact that the hydrogen of the aldehyde group was transferred to methene of the product. On the basis of NMR analysis, it was shown that two hydrogen atoms of the methene group in both diastereoisomers were equally deuterium-labeled. Such a result agrees with the ketene methide hypothesis that the intermediate formed during the reaction process possesses a long enough lifetime to allow the C−C single bond rotation to yield the products. Furthermore, the kinetic isotopic effect was observed (KH/KD = 1.54),[18] indicating that the hydrogen abstraction from the aldehyde plays a crucial role in the rate determination of the reaction.

Accordingly, the reaction mechanism was proposed as shown in Scheme 3. The hydrogen of the aldehyde was transferred to

Scheme 3. Proposed Mechanism



the double bond via a [1,5]-H shift process under irradiation to form a ketene methide intermediate, which was sequentially reacted with a built-in dienophile through intramolecular [4 + 2] cycloaddition reaction to yield the products.

A survey of the literature showed that the resultant photoproducts, benzobicycloheptanones in this protocol, are pivotal intermediates of certain bridged- and fused-type agonists of GPR40, which are generally used in the treatment or prevention or amelioration of diseases and disorders associated with the GPR40 receptor.[19] To demonstrate the synthetic potential of the reaction, a solution of 1 g of **1a** in 500 mL of acetonitrile was subsequently investigated in detail under batch and microflow conditions[20] (Table 3). Irradiation in a quartz test tube required exhaustive irradiation for 420 min to reach near completion (Table 3, entry 1), as confirmed by ^{1}H

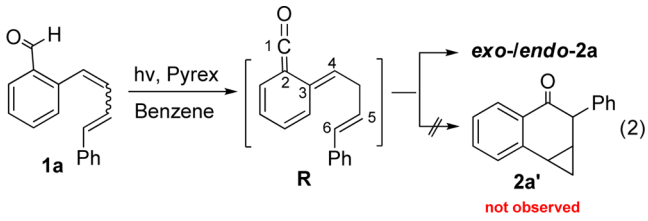
Table 3. Experimental Results for the Cycloaddtion of 1a

entry	reactor	time (min)	conversion (%)[a]
1	batch	420	100 (48)[b]
2	flow reactor	4	30
3		10	65
4		20	89
5		30	100 (58)[b]

[a]Determined by ^{1}H NMR analysis of the crude products. [b]Isolated yield.

NMR spectroscopy to afford the product in 48% yield. Under continuous flow conditions, conversion rates increased more rapidly despite irradiation from just one direction. After 30 min of irradiation, the complete conversion was effectively achieved (Table 3, entries 2−5) to yield the product in 58% .

Finally, to rationalize the excellent chemoselectivity that only the mixture of ***exo*-/*endo*-2a** obtained in the reaction (eq 2), theoretical calculations were performed from the photogenerated ketene methide intermediate **R** as the reactant.



On the basis of the density functional theory (DFT) calculations performed with the Gaussian 03 program packages (see the Supporting Information), Figure 1 shows the calculated intramolecular Diels−Alder reaction mechanism from reactant (**R**) to three different products (***endo*-2a**, ***exo*-2a**, and **2a′**). The corresponding geometries of reactant (**R**), intermediates (**Int1** and **Int2**), transition states (**TS1**−**TS5**), and predicted products (***endo*-2a**, ***exo*-2a** and **2a′**), are collected in Figure 2.

As shown in Figure 1, from the reactant (**R**), three possible pathways were found to lead to ***endo*-2a**, ***exo*-2a**, and **2a′**, which are marked in blue, black, and red, respectively. The ***endo*-2a** was predicted to be the lowest-lying in energy. A one-step transition through **TS3** contributed to the formation of ***endo*-2a**. By observing the geometrical structure of **TS3**, we found that **R** went through, first, the bonding of C1−C5, followed by the bonding of C4−C6, and finally led to ***endo*-2a**. The activation barrier is about 12.82 kcal/mol at the B3LYP/6-31G(d) level. The ***exo*-2a** has a similar geometrical structure and energy as ***endo*-2a**, which is consistent with the experimental result that a nearly 1:1 ratio of ***endo*-2a** and ***exo*-2a** was observed. Two transition states (**TS1** and **TS4**), which were connected by an intermediate (**Int1**), were located on this reaction channel. As shown in Figure 1 (black line), **TS1** is located about 2.65 kcal/mol higher than **TS4**, so the overall activation barrier for this multistep process was the energy difference from **TS1** to **R** with the value of 8.22 kcal/mol at the B3LYP/6-31G(d) level. In comparison with the pathway of ***endo*-2a** (blue line), this two-step reaction process would likely reduce the reaction velocity, but the activation barrier decreased by 4.60 kcal/mol, which might improve the branching ratio of ***exo*-2a**.

For the pathway for the formation of **2a′** via the bonding between C1−C6 and C4−C5 (Figure 1, red line), however, it

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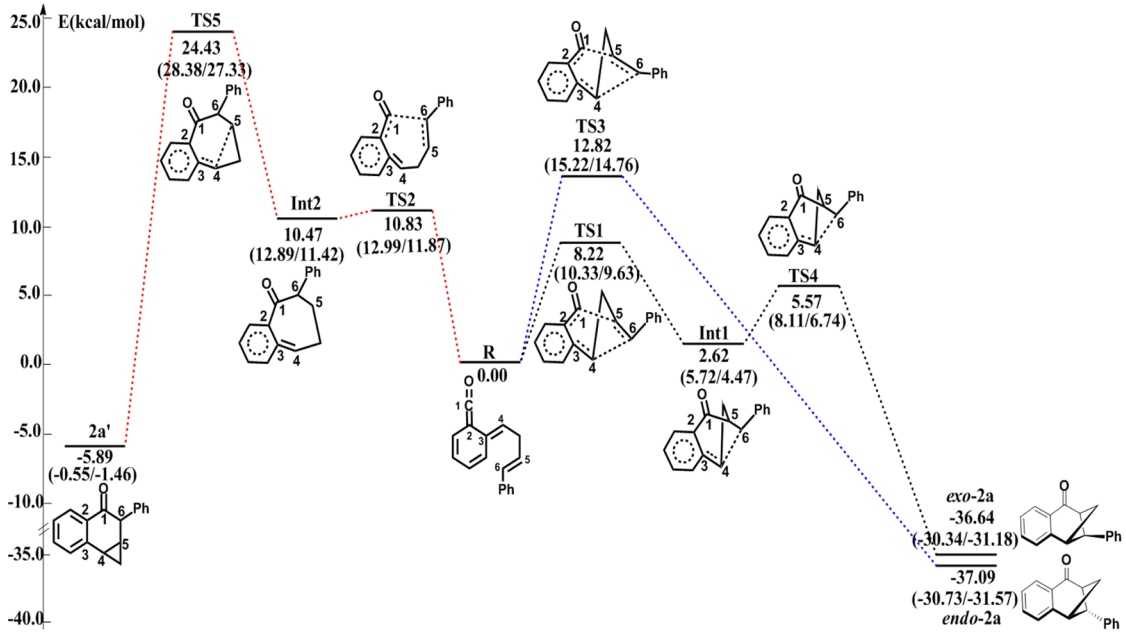

Figure 1. Calculated pathways from **R** to **2a** and **2a**′ (***endo*-2a** in blue; ***exo*-2a** in black; **2a**′ in red).

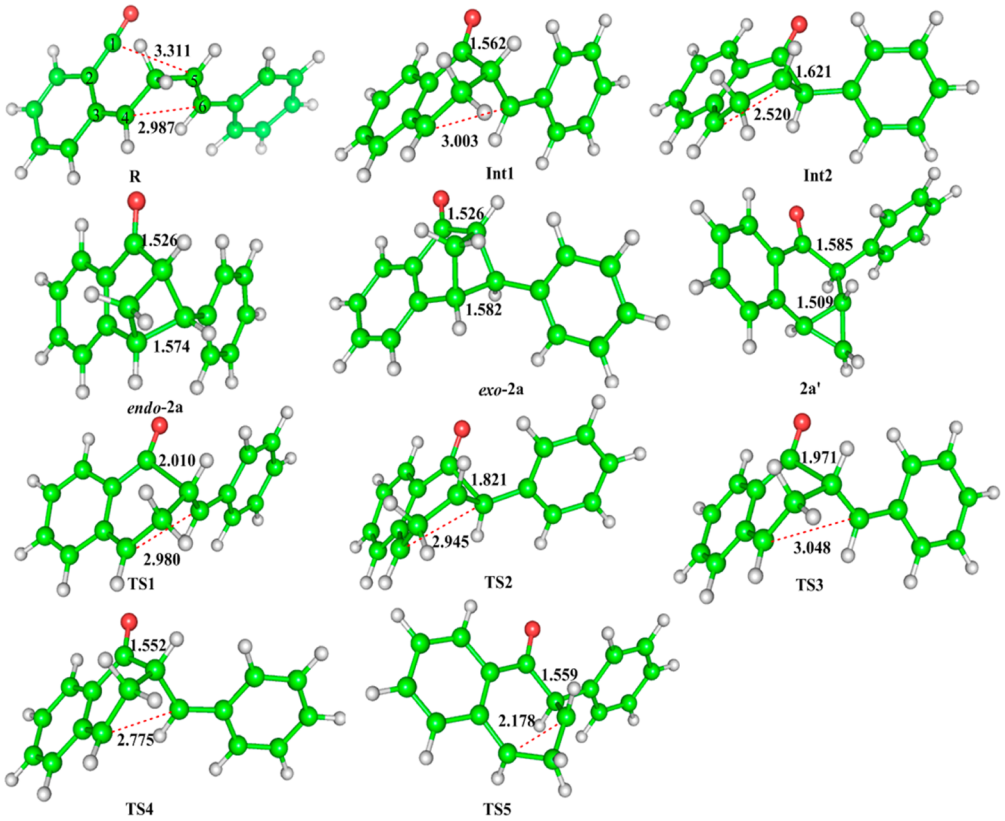

Figure 2. Corresponding geometries of reactant (**R**), intermediates (**Int1** and **Int2**), transition states (**TS1**−**TS5**), and predicted products. Key internuclear distances are denoted in angstroms.

was found that the activation barrier of this reaction pathway had reached about 24.43 kcal/mol at the B3LYP/6-31G(d) level, which was much higher than that of the other two channels. Furthermore, the **2a**′ itself has much higher energy than ***endo*-2a** and ***exo*-2a**. As a result, the reaction enthalpy of formation **2a**′ (−5.89 kcal/mol) at 298 K is much higher than that of the other two (−37.09 and −36.64 kcal/mol), which makes this reaction pathway unfavorable. Thus, both the higher activation barrier and the lower reaction enthalpy are against the formation of **2a**′, which is consistent with the experimental result that product **2a**′ was not observed in the photoreaction of **1a**.

In addition, as shown in Figure 1, the energies relative to **R** at B3LYP/6-311++G(2d,2p) and B3LYP-SCRF/6-311++G-

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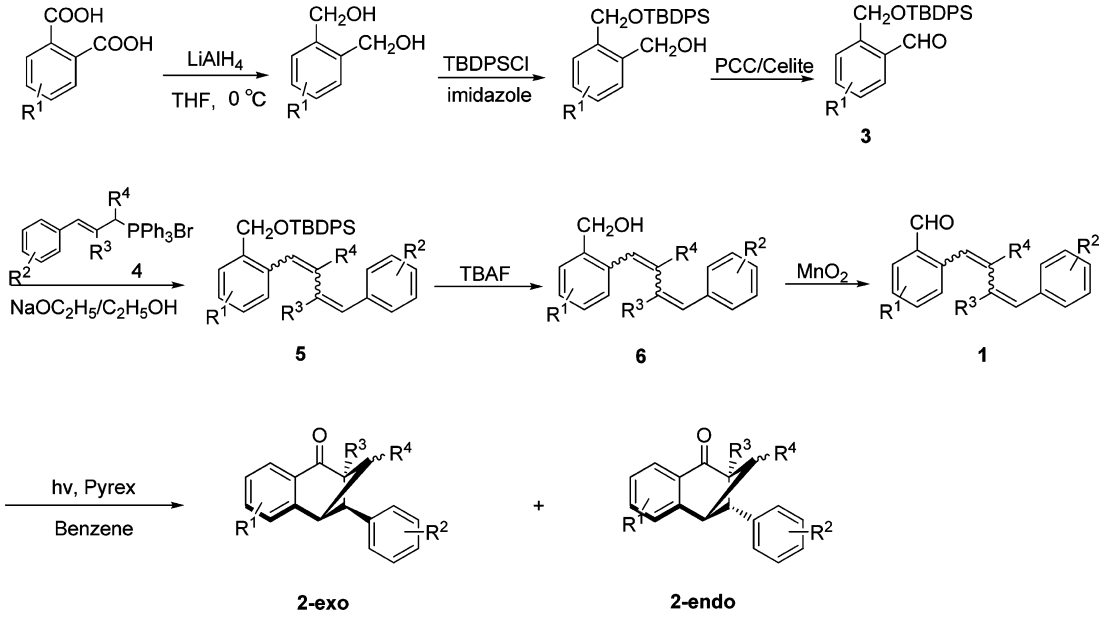
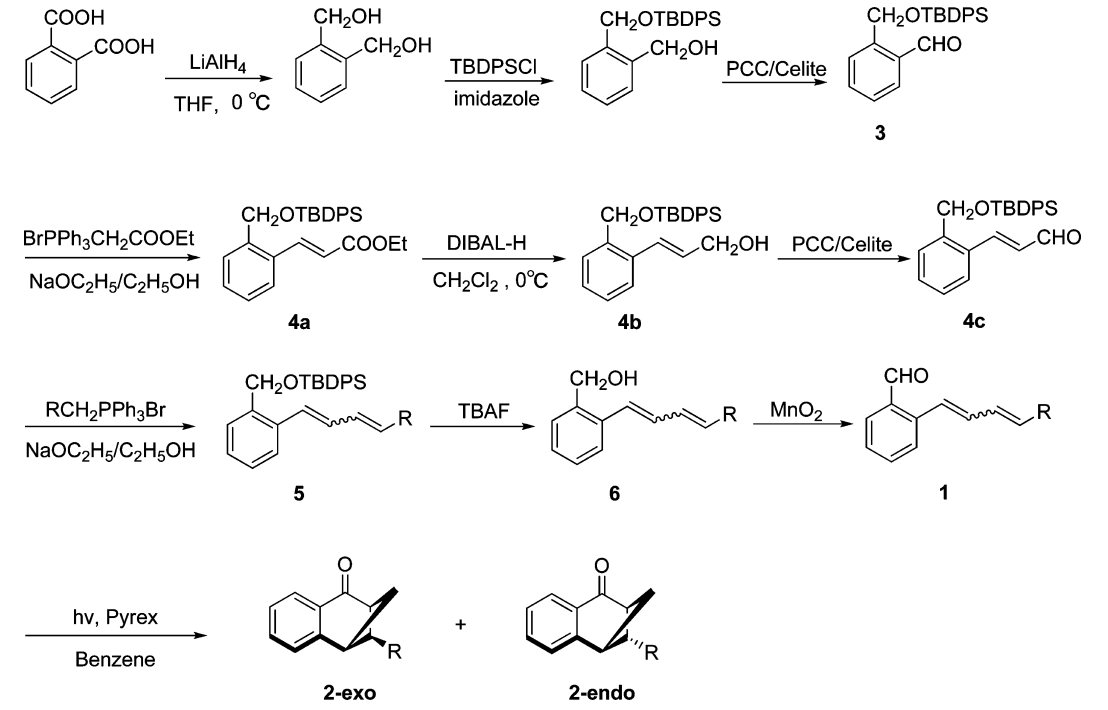
Scheme 4



Scheme 5



(2d,2p) levels are also listed in the parentheses. It shows that those relative energies at different levels are very close. On one side, it indicates that the influence from basis sets is tiny, so the results at the B3LYP/6-31G(d) level are sufficiently reliable. On the other side, the solvent benzene plays a negligible role for the reaction pathways as expected.

CONCLUSION

In summary, we have designed and successfully trapped the ketene methide diene intermediate that photogenerated in situ from *ortho*-butadienylbenzaldehyde precursors through a special [1, 5]-hydrogen shift process, with an electron-rich dienophile via the [4 + 2] cycloaddition reaction. To the best of our knowledge, the work presents the first example of a photogenerated ketene methide/Diels–Alder cascade reaction from easily made *ortho*-vinylbenzaldehyde derivatives. We expect this novel protocol to be of broad utility in the synthesis of biologically active compounds.

EXPERIMENTAL SECTION

All reactions were carried out with dry solvents using anhydrous conditions unless otherwise stated. Anhydrous tetrahydrofuran (THF), benzene, diethyl ether (Et_2O), toluene, and ethanol were dried with sodium (Na). Anhydrous dichloromethane (DCM) and *N*,*N*-dimethyformamide (DMF) were dealt with CaH_2. Reagents were purchased at the highest commercial quality and used without further

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purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.20−0.25 mm silica gel plates using UV light as the visualizing agent and phosphomolybdic acid and heat as developing agents. Silica gel was used for flash column chromatography. NMR spectra were recorded on a 400 M instrument and calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Q-TOF LC/MS system. Low-resolution mass spectra were obtained from a GC-MS system.

General Procedure for the Synthesis of 1a−1p. The target aldehydes (**1a−1p**) were generated from the corresponding compounds according to the following procedures (see Schemes 4 and 5).

General Procedure for Syntheses of Aldehyde 3. To a solution of 0.5 M *o*-phthalic acid (10.000 g, 60.2 mmol) in dry THF at 0 °C was added 5.489 g (144.5 mmol, 2.4 equiv) of $LiAlH_4$ in batches. Four hours later, the reaction was heated to 80 °C and refluxed 1 h. After reaction, the reaction was cooled to 0 °C, and then 100 mL of saturated NH_4Cl solution was added cautiously to quench the reaction. After adding 50 mL of EtOAc, the resulting mixture was filtered and the filter cake was washed with EtOAc (3 × 20 mL), the filtrate was separated, and the water phase was extracted with EtOAc (3 × 20 mL), and then the organic phase was combined, washed with saturated NaCl (2 × 50 mL), dried with anhydrous $NaSO_4$, and concentrated. The crude product (6.226 g) was dissolved in 100 mL of dimethylformamide, and then 4.602 g (67.6 mmol) of imidazole was added, followed by 12.386 g (45.1 mmol) of *tert*-butyldiphenylsilyl chloride in 50 mL of dimethylformamide. The resulting solution was stirred for 1 h, diluted with EtOAc (100 mL), washed with water (3 × 50 mL) and brine (50 mL), dried with $NaSO_4$, and concentrated in vacuo. Without further purification, the crude product (13.574 g, 36.0 mmol) was dissolved in 100 mL of dry methylene chloride, and then the mixture of pyridinium chlorochromate (PCC) (54.0 mmol, 1.5 equiv) and equivalent Celite was added. The resulting mixture was stirred at room temperature until most of the starting compound was consumed, 10 mL of diethyl ether was added to the reaction mixture, the mixture was then filtered through a pad of Celite, the pad was washed with 2 × 10 mL of methylene chloride, and the filtrate was concentrated at the rotary evaporator. The residue was chromatographed on silica gel with petroleum ether/EtOAc (20:1), and the target aldehyde **3** was obtained (12.148 g, 53% for three steps).

General Procedure for Syntheses of Aldehyde 4b. To a solution of compound **4a** (1.065 g, 2.4 mmol, 1 equiv) in 10 mL of dry DCM at 0 °C was added 5.6 mL of diisobutylaluminium hydride (DIBAL-H, 1.5 M). One hour later, 5 mL of CH_3OH was added cautiously to quench the reaction, and then 10 mL of saturated NH_4Cl was added. The resulting mixture was filtered and the filter cake was washed with DCM (3 × 10 mL), the filtrate was separated, and the water phase was extracted with DCM (3 × 10 mL). Then, the organic phase was combined, washed with saturated NaCl (2 × 25 mL), dried with anhydrous $MgSO_4$, and concentrated, and the crude product was purified via chromatography eluting with petroleum ether/EtOAc (3:1−1:1) to afford the target alcohol **4b** (772.2 mg, 80%).

General Procedure for Syntheses of Aldehyde 1. To a stirred solution of cinnamyltriphenylphosphonium bromide (674.6 mg, 1.47 mmol, 1.1 equiv) and aldehyde **3** (500 mg, 1.34 mmol, 1 equiv) in 30 mL of absolute ethanol was added dropwise a solution of sodium ethoxide (182.3 mg, 2.68 mmol, 2 equiv) in 10 mL of ethanol. Stirring was continued under a nitrogen atmosphere overnight (usually 6 h) at room temperature. Then, the solvent was removed, and water was added to the residue and extracted with EtOAc (3 × 10 mL). The EtOAc extracts were combined, dried, and concentrated. The crude reaction mixture was filtered through a short silica column. After the solvent evaporated, the crude product (604 mg) was dissolved in 10 mL of dry tetrahydrofuran. To the solution was added 998.5 mg (3.82 mmol, 3 equiv) of tetrabutylammonium fluoride. The resulting solution was stirred at room temperature for 4 h and then quenched by addition of a saturated aqueous solution of NH_4Cl (10 mL). After removal of THF, the aqueous layer was extracted with EtOAc (3 × 15 mL). The organic layers were combined, washed with brine (20 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was filtered through a short silica column. Without further purification, the residue (243.7 mg) was dissolved in 10 mL of dry methylene chloride, and then 896.3 mg of MnO_2 was added. Six hours later, the reaction mixture was filtered through a pad of silica gel, the pad was washed with methylene chloride, and the filtrate was concentrated at the rotary evaporator. The residue was chromatographed on silica gel with petroleum ether/EtOAc (10:1), and the target aldehyde **1a** was obtained (200 mg, 64% for three steps).

Compound 1a. Yellow oil; 200 mg, Yield 65%. ^{1}H NMR (400 MHz, CDCl3): δ 10.26 (s, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 7.1 Hz, 2H), 7.28 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.0 Hz, 1H), 6.93 (m, 2H), 6.75 (d, J = 15.8 Hz, 1H), 6.65 (t, J = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3): δ 192.3, 140.2, 136.9, 136.1, 133.9, 133.6, 133.4, 131.1, 129.9, 128.6, 128.0, 127.7, 126.8, 126.7, 124.3 ppm. LRMS (EI): 234(100) [M$^+$], 215, 189, 165, 151, 132, 115, 104, 91, 77, 51, 39. IR (KBr, film) ν max: 3061, 3028, 2853, 2743, 1770, 1694, 1621, 1595, 1494, 1479, 1450, 1403, 1286, 1192, 990, 750, 693 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{14}O$, [M + H]$^+$, 235.1117; found, 235.1128.

Compound 1b. Yellow solid (mp 81−85 °C); 69 mg, Yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 10.25 (s, 1H), 7.94 (dd, J = 7.7, 1.0 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.60 (dd, J = 7.6, 1.1 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.41 (d, J = 9.0 Hz, 1H), 7.39 (dd, J = 4.0, 1.9 Hz, 1H), 7.26 (t, J = 7.1 Hz, 1H), 7.15 (d, J = 15.1 Hz, 1H), 7.13−7.15(m, 1H), 7.02 (d, J = 11.3 Hz, 1H), 6.90 (dd, J = 15.5, 11.2 Hz, 1H), 6.71 (t, J = 11.3 Hz, 1H); minor: δ 10.28 (s, 1H), 7.81 (dd, J = 7.7, 1.1 Hz, 1H), 7.69−7.66 (m, 1H), 7.64 (dd, J = 9.9, 1.3 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.37−7.32 (m, 2H), 7.20 (dd, J = 7.7, 1.5 Hz, 1H), 7.18−7.12 (m, 3H), 7.06 (d, J = 12.1 Hz, 1H), 7.02 (dd, J = 15.4, 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): major: δ 192.3, 139.9, 134.9, 134.0, 133.6, 133.2, 132.8, 131.7, 131.0, 130.0, 129.8, 128.9, 127.9, 127.8, 126.8, 126.7, 126.6; minor: δ 192.8, 139.4, 134.8, 133.9, 133.7, 133.4, 132.6, 131.4, 130.2, 129.9, 129.5, 128.8, 127.7, 126.9, 126.8, 126.3 ppm. LRMS (EI): 268 [M$^+$], 233(100), 215, 202, 178, 151, 132, 115, 101, 89, 77, 63, 51. IR (KBr, film) ν_{max}: 3063, 2855, 2742, 1694, 1594, 1468, 1284, 1191, 1050, 990, 875, 752 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}ClO$, [M + H]$^+$, 269.0728; found, 269.0732.

Compound 1c. Yellow oil; 80 mg, Yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$): major: δ 10.26 (s, 1H), 7.96−7.90 (m, 1H), 7.63−7.51 (m, 3H), 7.44 (t, J = 6.7 Hz, 2H), 7.34−7.29 (m, 1H), 7.09 (m, 1H), 7.05−6.93 (m, 1H), 6.93−6.82 (m, 2H), 6.68 (t, J = 11.1 Hz, 1H), 3.83 (s, 3H); minor: δ 10.30 (s, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 8.1 Hz, 2H), 7.09 (m, 2H), 7.03−6.93 (m, 2H), 6.92−6.82 (m, 3H), 3.88 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): major: δ 192.3, 156.9, 140.5, 135.4, 134.3, 133.5, 132.2, 131.1, 131.1, 129.6, 129.1, 127.6, 126.9, 125.8, 124.9, 120.7, 110.9, 55.5; minor: δ 192.6, 156.9, 140.0, 133.8, 133.6, 132.5, 129.8, 129.7, 129.1, 127.5, 127.3, 126.8, 126.7, 125.9, 125.9, 120.8, 110.9, 55.5 ppm. LRMS (EI): 264(100) [M$^+$], 231, 202, 165, 132, 91, 77, 65. IR (KBr, film) ν_{max}: 3002, 2933, 2836, 2737, 1694, 1615, 1593, 1487, 1463, 1377, 1244, 1187, 1027, 876, 751 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O_2$, [M + H]$^+$, 265.1223; found, 265.1197.

Compound 1d. Yellow oil; 92 mg, Yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$): major: δ 10.26 (s, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.44 (m, 2H), 7.20−7.11 (m, 3H), 7.10−7.00 (m, 1H), 6.92 (m, 2H), 6.72 (d, J = 15.8 Hz, 1H), 6.64 (t, J = 11.2 Hz, 1H), 2.31 (s, 3H); minor: δ 10.29 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.4 Hz, 1H), 7.64 (m, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.44 (m, 2H), 7.27 (m, 2H), 7.20−7.11 (m, 1H), 7.06 (m, 2H), 6.72 (m, 1H), 2.37 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) major: δ 192.3, 140.3, 138.2, 136.8, 136.3, 133.8, 133.6, 133.5, 131.1, 129.9, 128.9, 128.5, 127.7, 127.4, 126.5, 124.1, 123.8, 21.4; minor: δ 192.7, 139.8, 138.3, 136.9, 135.3, 134.9, 134.5, 132.6, 132.5, 128.8, 128.6, 128.1, 127.5,

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127.3, 126.8, 124.8, 123.8, 21.4 ppm. LRMS (EI): 248(100) [M$^+$], 233, 229, 215, 189, 165, 150, 132, 105, 77, 51. IR (KBr, film) ν_{max}: 3027, 2925, 2855, 2749, 1695, 1595, 1451, 1377, 1284, 1189, 1080, 989, 872, 757, 691,660 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1275.

Compound 1e. Yellow oil; 87 mg, Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$): major: δ 10.24 (s, 1H), 7.94 (dd, J = 7.7, 1.0 Hz, 1H), 7.62 (td, J = 7.5, 1.1 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.24−7.20 (m, 1H), 7.08 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 11.5 Hz, 2H), 6.96−6.87 (m, 2H), 6.70 (d, J = 15.5 Hz, 1H), 6.63 (t, J = 11.3 Hz, 1H); minor: δ 10.28 (s, 1H), 7.82 (dd, J = 7.7, 1.1 Hz, 1H), 7.69 (s, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.43 (d, J = 8.9 Hz, 1H), 7.33−7.25 (m, 3H), 7.15 (d, J = 10.1 Hz, 1H), 6.96−6.87 (m, 2H), 6.69 (d, J = 15.7 Hz,1H). ^{13}C NMR (100 MHz, $CDCl_3$): major: δ 192.2, 163.1 (d, J = 245.6 Hz), 139.8, 139.3 (d, J = 7.6 Hz), 134.6, 134.6, 133.7, 132.7, 131.1, 130.3, 130.1 (d, J = 8.3 Hz), 127.9, 127.9, 125.6, 122.6 (d, J = 2.7 Hz), 114.8 (d, J = 21.7 Hz), 112.9 (d, J = 21.7 Hz); minor: δ 192.7, 163.1 (d, J = 245.6 Hz), 139.4, 139.3, 133.8, 133.7, 133.3 (d, J = 2.8 Hz), 132.6, 130.4, 130.2 (d, J = 8.2 Hz), 129.4, 127.9, 127.7, 126.8, 122.5(d, J = 2.8 Hz), 114.7 (d, J = 21.6 Hz), 112.9 (d, J = 21.7 Hz) ppm. LRMS (EI): 252 [M$^+$], 233, 202, 183, 157, 132, 109, 91(100), 77, 51, 39. IR (KBr, film) ν_{max}: 3064, 2856, 2741, 1770, 1695, 1605, 1580, 1479, 1253, 1189, 1145, 1074, 988, 872, 755, 682, 521 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}FO$, [M + H]$^+$, 253.1023; found, 253.1050.

Compound 1f. Yellow oil; 93 mg, Yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 10.26 (s, 1H), 7.96−7.90 (m, 1H), 7.60 (dd, J = 7.7, 6.7 Hz, 2H), 7.43 (m, 3H), 7.36 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.89 (t, J = 12.3 Hz, 3H), 6.72 (d, J = 16.0 Hz, 2H), 6.63 (t, J = 11.2 Hz, 1H), 2.31 (s, 3H); minor: δ 10.29 (s, 1H), 7.80 (dd, J = 7.7, 0.9 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 7.7 Hz,1H), 7.54 (t, J = 7.6 Hz, 1H), 7.43 (m, 1H), 7.24 (d, J = 8.3 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.01 (dd, J = 15.0, 10.6 Hz, 1H), 6.93 (dd, J = 15.1, 10.3 Hz, 1H), 6.71 (d, J = 15.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 192.3, 140.4, 138.1, 136.2, 134.8, 134.6, 133.6, 129.8, 129.5, 129.4, 127.6, 126.6, 126.6, 126.1, 123.4, 21.3; minor: δ 192.7, 139.8, 138.1, 138.1, 134.3, 134.1, 133.8, 133.6, 132.5, 132.4, 129.8, 129.7, 128.2, 127.4, 126.7, 21.3 ppm. LRMS (EI): 248(100) [M$^+$], 215, 156, 132, 105, 77, 51. IR (KBr, film) ν_{max}: 3022, 2922, 2855, 2735, 1693, 1592, 1477, 1384, 1186, 1079, 988, 798, 754 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1285.

Compound 1g. Yellow powder (mp 89.6−91.3 °C); 82 mg, Yield 61%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 10.24 (s, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.43−7.38 (m, 3H), 7.18 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 11.4 Hz, 1H), 6.91 (dd, J = 15.6, 11.2 Hz, 1H), 6.65 (dd, J = 23.4, 12.7 Hz, 2H); minor: δ 10.28 (s, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.71−7.53 (m, 3H), 7.48 (t, J = 8.0 Hz, 3H), 7.43−7.37 (m, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.08−6.99 (m, 1H), 6.96−6.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 192.2, 139.9, 135.8, 134.6, 133.8, 133.6, 132.9, 131.8, 131.0, 130.1, 128.1, 127.8, 127.6, 124.9, 121.8; minor: δ 192.7, 139.9, 133.6, 133.3, 133.2, 132.9, 132.8, 131.8, 129.8, 129.1, 128.0, 127.7, 126.8, 123.7, 120.4 ppm. LRMS (EI): 312 [M$^+$], 269, 202, 182, 169, 132(100), 117, 91, 77. IR (KBr, film) ν_{max}: 3030, 2924, 2854, 2753, 1767, 1687, 1591, 1485, 1400, 1185, 1071, 979, 876, 796, 752, 657, 495 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}BrO$, [M + H]$^+$, 313.0223; found, 313.0217.

Compound 1h. Yellow oil; 44 mg, Yield 32%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 10.19 (s, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.40 (s, 1H), δ 7.38−7.20 (m, 5H), δ 6.99−6.80 (m, 2H), 6.77 (d, J = 15.3 Hz, 1H), 6.67 (t, J = 11.1 Hz, 1H).minor: δ 10.23 (s, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 1.4 Hz, 1H), 7.56 (d, J = 14.9 Hz, 1H), δ 7.44−7.19 (m, 6H), 7.03 (dd, J = 15.1, 10.6 Hz, 1H), 6.88−6.80 (m, 1H), 6.77 (d, J = 15.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 190.9, 141.8, 140.1, 137.2, 136.6, 134.5, 132.2, 131.0, 130.8, 128.8, 128.7, 128.4, 126.8, 126.8, 123.5; minor: δ 191.3, 141.3, 140.2, 136.7, 135.9, 135.5, 133.8, 132.2, 128.6, 128.3, 128.0, 127.6, 126.6, 126.6, 124.9 ppm. LRMS (EI): 268 [M$^+$], 249, 233, 215, 202, 166, 152, 131, 115, 104, 91(100), 77, 51. IR (KBr, film) ν_{max}: 3061, 3025, 2925, 2853, 2737, 1693, 1606, 1548, 1447, 1388, 1201, 1083, 989, 813, 750, 691 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}ClO$, [M + H]$^+$, 269.0728; found, 269.0741.

Compound 1i. Yellow oil; 48 mg, Yield 29%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 10.22 (s, 1H), 7.94 (d, J = 2.2 Hz, 1H), 7.59 (dd, J = 8.2, 2.2 Hz, 1H), 7.49 (d, J = 7.4 Hz, 1H), 7.42−7.24 (m, 5H), 6.95 (dd, J = 15.6, 10.8 Hz, 1H), 6.87 (d, J = 11.2 Hz, 1H), 6.80 (d, J = 15.5 Hz, 1H), 6.70 (t, J = 11.1 Hz, 1H); minor: δ 10.27 (s, 1H), 7.80 (d, J = 2.2 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.54−7.50 (m, 2H), 7.42−7.22 (m, 4H), 7.06 (dd, J = 15.3, 10.6 Hz, 1H), 6.89 (d, J = 10.5 Hz, 1H), 6.78 (d, J = 15.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 190.7, 138.6, 136.8, 135.5, 134.9, 134.2, 133.6, 132.5, 129.2, 128.8, 128.7, 128.3, 128.3, 126.8, 125.1; minor: δ 191.0, 138.2, 136.8, 136.6, 134.9, 134.2, 134.0, 133.6, 133.5, 131.5, 128.8, 128.2, 126.8, 126.7, 123.7 ppm. LRMS (EI): 268 [M$^+$], 249, 231, 215, 202, 189, 166, 152, 131, 115, 91(100), 77, 51. IR (KBr, film) ν_{max}: 3062, 3024, 2952, 2866, 2733, 1687, 1602, 1548, 1475, 1447, 1400, 1179, 988, 897, 840, 749, 690 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}ClO$, [M + H]$^+$, 269.0728; found, 269.0734.

Compound 1j. Yellow solid (mp 87.5−90 °C); 45 mg, Yield 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (s, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 15.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 2.2 Hz, 1H), 7.08 (dd, J = 15.4, 10.6 Hz, 1H), 7.02−6.91 (m, 2H), 6.77 (d, J = 15.4 Hz, 1H), 3.95 (s, 3H). 13C NMR (100 MHz, CDCl3): δ 191.1, 163.7, 142.0, 136.9, 135.3, 134.8, 134.2, 129.0, 128.7, 128.4, 128.0, 126.6, 126.5, 113.3, 111.3, 55.6 ppm. LRMS (EI): 264 [M$^+$], 235, 202, 162(100), 148, 115, 91, 77. IR (KBr, film) ν_{max}: 3055, 3033, 2923, 2847, 2756, 1698, 1659, 1601, 1497, 1443, 1367, 1253, 1103, 1048, 877,812, 730 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O_2$, [M + H]$^+$, 265.1223; found, 265.1215.

Compound 1k. Yellow solid (mp 82.5−86.5 °C); 46 mg, Yield 25%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.46 (dd, J = 11.3, 8.1 Hz, 3H), 7.33 (dd, J = 12.2, 4.9 Hz, 3H), 7.25 (dd, J = 8.1, 6.4 Hz, 1H), 7.11 (dd, J = 8.7, 2.8 Hz, 1H), 7.01 (dd, J = 15.5, 10.6 Hz, 1H), 6.83 (dd, J = 15.3, 10.6 Hz, 1H), 6.69 (d, J = 15.5 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.77, 159.15, 137.12, 133.94, 133.46, 133.07, 132.93, 129.14, 128.73, 128.37, 127.86, 127.39, 126.54, 121.26, 113.85, 55.59 ppm. LRMS (EI): 264(100) [M$^+$], 235, 202, 162, 128, 115, 91, 77. IR (KBr, film) ν_{max}: 3054, 3021, 2956, 2849, 2756, 1661, 1602, 1499, 1453, 1369, 1072, 1021, 881, 772, 732 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O_2$, [M + H]$^+$, 265.1223; found, 265.1244.

Compound 1l. Yellow oil; 80 mg, Yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 10.22 (s, 1H), 7.93 (t, J = 7.1 Hz, 2H), 7.45−7.39 (m, 2H), 7.39−7.13 (m, 5H), 6.96 (d, J = 16.1 Hz, 1H), 6.88 (s, 1H), 6.75 (d, J = 14.1 Hz, 1H), 1.95 (s, 3H); minor: δ 10.24 (s, 1H), 7.58 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.38−7.13 (m, 5H), 7.06 (d, J = 16.4 Hz, 1H), 7.04 (s, 1H), 6.71 (d, J = 15.8 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 192.4, 140.9, 139.0, 137.2, 133.9, 133.5, 131.7, 130.7, 129.2, 128.7, 128.0, 127.8, 127.4, 126.7, 126.3, 14.1; minor: δ 192.4, 140.7, 137.9, 137.2, 133.9, 132.8, 131.5, 129.4, 129.1, 128.6, 128.0, 127.7, 127.4, 126.6, 126.3, 20.8 ppm. LRMS (EI): 248 [M$^+$], 233, 205, 178, 163, 146(100), 128, 107, 91, 77, 51, 39. IR (KBr, film) ν_{max}: 3026, 2925, 2853, 2742, 1692, 1593, 1477, 1446, 1385, 1261, 1074, 960, 888, 799, 749, 692, 564, 531 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1283.

Compound 1m. Yellow oil; 50 mg, Yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 10.31 (s, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.84−7.78 (m, 1H), 7.55 (m, 1H), 7.44−7.33 (m, 2H), 7.32−7.23 (m, 2H), 7.19 (t, J = 7.4 Hz, 2H), 6.79 (d, J = 12.2 Hz, 1H), 6.57 (d, J = 12.6 Hz, 1H), 6.52 (s, 1H), 1.66 (s, 3H); minor: δ 10.31 (s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.55 (m, 2H), 7.44−7.33 (m, 4H), 7.32−7.23 (m, 2H), 7.19 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 15.9 Hz, 1H), 6.72 (s, 1H), 2.19 (d, J = 0.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 192.4, 139.6, 138.6, 137.3, 134.2, 133.7, 133.4, 132.2, 130.7, 129.1, 128.7, 128.1, 127.5, 126.8, 125.0, 18.1; minor: δ 192.7, 141.9, 140.4, 137.6, 135.9, 134.4, 134.0, 132.8, 132.4, 129.5, 129.0, 127.3, 127.1, 126.9, 123.9, 14.1 ppm. LRMS (EI): 248 [M$^+$], 229, 215, 202, 178, 152,

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132(100), 115, 103, 91, 77, 51, 37. IR (KBr, film) ν_{max}: 3061, 3024, 2925, 2854, 1769, 1694, 1595, 1565, 1480, 1449, 1386, 1271, 1194, 1160, 1075, 967, 920, 871, 752, 699 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, $[M + H]^+$, 249.1274; found, 249.1264.

Compound 1n. Yellow oil; 73 mg, Yield 63%. ^1H NMR (400 MHz, $CDCl_3$) major: δ 10.30 (s, 1H), 7.80 (t, J = 8.4 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.60−7.48 (m, 2H), 7.42 (d, J = 15.7 Hz, 1H), 7.38−7.31 (m, 1H), 6.21 (t, J = 10.9 Hz, 1H), 4.99 (t, J = 10.5 Hz, 1H), 1.93−1.78 (m, 1H), 0.93−0.76 (m, 2H), 0.54−0.40 (m, 2H).minor: δ 10.28 (s, 1H), 7.80 (t, J = 8.4 Hz, 1H), 7.51 (m, 1H), 7.42 (d, J = 15.7 Hz, 1H), 7.38−7.32 (m, 1H), δ 7.31 (d, J = 15.4 Hz, 1H), 6.69 (dd, J = 15.5, 10.6 Hz, 1H), 6.40 (dd, J = 15.0, 10.6 Hz, 1H), 5.44 (dd, J = 15.1, 9.1 Hz, 1H), 1.57−1.43 (m, 1H), 0.92−0.80 (m, 3H), 0.53−0.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 192.5, 139.6, 133.6, 131.7, 130.3, 127.2, 127.0, 126.9, 126.9, 14.6, 10.9, 8.0; minor; δ 192.5, 142.1, 140.5, 134.6, 132.6, 132.5, 131.7, 128.1, 126.9, 126.7, 124.5, 14.6, 10.9, 7.9 ppm. LRMS (EI): 198 [M^+], 183, 165, 151, 131(100), 115, 91, 77, 63, 39. IR (KBr, film) ν_{max}: 3079, 3008, 2924, 2857, 2747, 1768, 1695, 1596, 1567, 1465, 1386, 1285, 1062, 973, 759 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{14}O$, $[M + H]^+$, 199.1117; found, 199.1121.

Compound 1o. Yellow liquid; 45 mg, Yield 60%. ^1H NMR (400 MHz, $CDCl_3$) major: δ 10.29 (s, 1H), 7.83−7.75 (m, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 8.1 Hz, 1H), 7.42 (d, J = 13.2 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.05 (ddd, J = 15.4, 11.1, 0.8 Hz, 1H), 6.36−6.24 (m, 1H), 5.72 (dq, J = 10.7, 7.2 Hz, 1H), 1.89−1.83 (m, 3H); minor: δ 10.28 (s, 1H), 7.84−7.76 (m, 1H), 7.54−7.49 (m, 2H), 7.39−7.35 (m, 1H), 7.32 (d, J = 15.6 Hz, 1H), 6.71 (dd, J = 15.5, 10.5 Hz, 1H), 6.38−6.21 (m, 1H), 5.92 (dq, J = 13.7, 6.8 Hz, 1H), 1.92−1.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 192.4, 140.3, 133.6, 132.6, 131.7, 129.5, 129.4, 127.4, 127.3, 127.0, 126.8, 13.7; minor: δ 192.5, 140.3, 134.7, 133.6, 132.7, 132.5, 131.9, 129.4, 129.3, 127.1, 125.2, 18.4 ppm. LRMS (EI): 172 [M^+], 157, 144, 131(100), 115, 103, 89, 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3071, 3003, 2930, 2860, 2756, 1696, 1596, 1480, 1384, 1079, 870, 816, 757 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{12}O$, $[M - H]^+$, 171.0815; found, 171.0831.

Compound 1p. White solid (mp 72.5−75.5 °C); 80 mg, Yield 83%. ^1H NMR (400 MHz, $CDCl_3$): δ 10.24 (s, 1H), 7.88 (d, J = 15.5 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.56−7.47 (m, 2H), 6.84 (dd, J = 15.5, 11.1 Hz, 1H), 6.04 (d, J = 15.3 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 166.7, 144.0, 138.0, 136.2, 133.7, 133.1, 133.1, 130.8, 128.8, 127.2, 123.0, 77.4, 77.1, 76.7, 60.5, 14.3 ppm. LRMS (EI): 230 [M^+], 201, 184, 156, 128(100), 102, 77, 51. IR (KBr, film) ν_{max}: 3064, 2937, 2904, 2871, 2744, 1698, 1627, 1595, 1480, 1368, 1138, 1037, 872, 839, 760, 660 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{14}O_3$, $[M + H]^+$, 231.1016; found, 231.1024.

Compound 1q. Tan oil; 11 mg, Yield 32%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35−7.25 (m, 7H), 7.25−7.14 (m, 3H), 6.41 (d, J = 15.8 Hz, 1H), 6.24 (dt, J = 15.8, 6.8 Hz, 1H), 3.87 (m, 1H), 3.64 (dd, J = 6.7, 4.0 Hz, 1H), 3.18 (m, 2H), 2.79 (dd, J = 15.9, 8.0 Hz, 2H), 2.54 (m, 2H), 1.63 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 138.1, 137.7, 136.5, 130.5, 129.9, 129.5, 128.7, 128.5, 126.9, 126.1, 126.0, 125.9, 48.2, 42.5, 34.2, 32.9, 26.5, 25.7, 24.6 ppm. LRMS (EI): 319(100) [M^+], 224, 202, 178, 146, 117, 91, 77, 65, 41. IR (KBr, film) ν_{max}: 3024, 2933, 2854, 1632, 1599, 1491, 1432, 1274, 1074, 1027, 1001, 965, 852, 744, 694, 634 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{25}NO$, $[M + H]^+$, 320.2009; found, 320.2014.

Compound 3. White solid (mp 112−115 °C); 12.148 g, Yield 53% (for three steps). ^1H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.82 (dd, J = 7.6, 1.1 Hz, 1H), 7.68 (dd, J = 7.9, 1.4 Hz, 4H), 7.63 (td, J = 7.6, 1.2 Hz, 1H), 7.49−7.34 (m, 8H), 5.20 (s, 2H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, CDCl3): δ 192.9, 143.7, 135.5, 133.9, 133.3, 132.7, 129.8, 127.8, 127.2, 126.9, 63.6, 26.9, 19.4 ppm. LRMS (EI): 374 [M^+], 317, 287, 211(100), 199, 167, 139, 119, 91, 77, 57, 39. IR (KBr, film) ν_{max}: 2958, 2645, 1767, 1695, 1589, 1437, 1219, 739, 609 cm^{-1}.

Compound 4a. Colorless oil; 9.81 g, Yield 68%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 15.9 Hz, 1H), 7.73−7.65 (m, 4H), 7.58 (d, J = 7.3 Hz, 1H), 7.46−7.27 (m, 9H), 6.36 (d, J = 15.9 Hz, 1H), 4.84 (s, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 141.7, 139.6, 135.6, 133.3, 132.9, 129.8, 129.7, 127.9, 127.8, 127.6, 126.5, 119.9, 63.9, 60.4, 26.8, 19.3, 14.3 ppm. LRMS (EI): 445 [M^+ + H], 387(100), 227, 199, 183, 115, 77, 57, 41. IR (KBr, film) ν_{max}: 3071, 2958, 2931, 2893, 2857, 1714, 1635, 1601, 1472, 1428, 1365, 1312, 1271, 1218, 1176, 1112, 1073, 977, 823, 764, 740, 702, 622, 504 cm^{-1}.

Compound 4b. Light yellow oil; 8.70 g, Yield 98%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73−7.65 (m, 4H), 7.50−7.34 (m, 8H), 7.28−7.26 (m, 1H), 6.72 (d, J = 15.7 Hz, 1H), 6.22 (dt, J = 15.7, 5.8 Hz, 1H), 4.80 (s, 2H), 4.24 (dd, J = 5.7, 4.6 Hz, 2H), 1.35 (t, J = 6.0 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 135.6, 134.8, 133.4, 130.4, 129.7, 128.2, 127.8, 127.6, 127.4, 127.3, 125.8, 63.9, 63.9, 26.8, 19.4 ppm. LRMS (EI): 402 [M^+], 345, 327, 309, 261, 249, 229, 199(100), 181, 151, 129, 115, 91, 77, 57, 39. IR (KBr, film) ν_{max}: 3338, 3070, 2957, 2930, 2857, 1589, 1471, 1427, 1379, 1361, 1188, 1112, 1070, 1007, 966, 823, 742, 702, 615, 504 cm^{-1}.

Compound 4c. White solid (mp 70.6−73.8 °C); 4.59 g, Yield 52%. ^1H NMR (400 MHz, $CDCl_3$): δ 9.65 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 15.9 Hz, 1H), 7.75 (dd, J = 7.7, 1.7 Hz, 1H), 7.71 (dd, J = 7.9, 1.4 Hz, 4H), 7.67 (d, J = 7.4 Hz, 1H), 7.50−7.46 (m, 2H), 7.43 (dd, J = 6.3, 5.0 Hz, 6H), 6.69 (dd, J = 15.8, 7.8 Hz, 1H), 4.91 (s, 2H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.9, 150.1, 139.9, 135.6, 134.8, 133.1, 132.4, 130.9, 129.9, 129.7, 129.7, 128.6, 128.0, 127.8, 127.7, 126.8, 64.0, 26.8, 19.3 ppm. LRMS (EI): 400 [M^+], 371, 343, 313, 295, 265, 247, 227, 207, 183, 165, 139, 115(100), 91, 71, 57, 39. IR (KBr, film) ν_{max}: 3071, 3050, 2930, 2857, 1962, 1892, 1824, 1682, 1624, 1600, 1471, 1428, 1289, 1192, 1111, 1073, 971, 823, 742, 702, 615, 504 cm^{-1}

General Procedure for the Synthesis of 2a−2o. The solution of aldehyde (0.15 mmol) in benzene (15 mL) was placed in a quartz tube and sealed after deoxygenating with nitrogen for 30 min prior to irradiation and then irradiated under a 500 W medium-pressure mercury lamp through a Pyrex filter. The reaction was monitored with TLC. After reaction, the solvent was removed in vacuo, and the residue was purified by flash chromatography eluting with petroleum ether/EtOAc (49:1).

Compound *exo*-2a. Yellow oil; 20 mg, Yield 57%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.5 Hz, 1H), 7.50 (t, J = 7.3 Hz, 1H), 7.47−7.38 (m, 5H), 7.36−7.28 (m, 2H), 3.84 (d, J = 6.0 Hz, 1H), 3.57 (t, J = 5.9 Hz, 1H), 3.44 (t, J = 6.1 Hz, 1H), 3.22−3.09 (m, 1H), 2.35 (dd, J = 9.7, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 151.9, 140.4, 133.4, 129.3, 128.9, 128.7, 127.4, 127.0, 127.0, 126.8, 125.0, 59.0, 53.8, 44.2, 41.0 ppm. LRMS (EI): 234(100) [M^+], 215, 202, 199, 178, 152, 132, 115, 104, 91, 77, 51, 39. IR (KBr, film) ν_{max}: 2924, 2852, 1696, 1603, 1460, 1384, 1074, 777, 761, 726, 697, 569 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{14}O$, $[M + H]^+$, 235.1117; found, 235.1116.

Compound *endo*-2a. Colorless oil; 9 mg, Yield 26%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 7.4 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 7.5 Hz, 2H), 4.47 (t, J = 5.8 Hz, 1H), 3.80 (q, J = 5.6 Hz, 1H), 3.70 (q, J = 5.7 Hz, 1H), 2.93 (dt, J = 9.3, 5.6 Hz, 1H), 2.44 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 147.8, 139.3, 133.3, 129.6, 128.0, 127.0, 126.7, 126.4, 125.9, 125.8, 55.6, 53.2, 43.9, 40.9 ppm. LRMS (EI): 234(100) [M^+], 215, 202, 199, 178, 152, 132, 115, 104, 91, 77, 51, 39. IR (KBr, film) ν_{max}: 2924, 2852, 1696, 1603, 1460, 1384, 1074, 777, 761, 726, 697, 569 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{14}O$, $[M + H]^+$, 235.1117; found, 235.1122.

Compound 2b. Light yellow oil; 23 mg, Yield 58% (mixture, *exo*/*endo* = 1:1). ^1H NMR (400 MHz, $CDCl_3$) *exo*: δ 8.11 (d, J = 7.4 Hz, 1H), 7.42−7.36 (m, 2H), 7.36−7.31 (m, 1H), 7.16−7.11 (m, 1H), 7.01−6.90 (m, 3H), 3.95 (d, J = 5.6 Hz, 1H), 3.55 (t, J = 6.0 Hz, 1H), 3.51 (t, J = 6.1 Hz, 1H), 3.13 (dt, J = 9.9, 5.9 Hz, 1H), 2.35 (dd, J = 9.8, 5.7 Hz, 1H); *endo*: δ 7.78 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.53 (td, J = 7.4, 1.3 Hz, 1H), 7.49−7.43 (m, 2H), 7.28 (t, J = 7.1 Hz, 2H), 7.20 (td, J = 7.5, 1.0 Hz, 1H), 4.45 (t, J = 5.6 Hz, 1H), 4.10 (q, J = 5.6 Hz, 1H), 3.77 (q, J = 5.6 Hz, 1H), 2.96 (dt, J = 9.2, 5.7 Hz, 1H), 2.41 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *exo*: δ

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200.6, 151.7, 137.4, 135.2, 133.4, 130.0, 129.3, 129.2, 127.9, 127.2, 126.9, 126.4, 125.7, 57.5, 52.9, 44.9, 41.3; *endo*: δ 200.6, 147.2, 136.8, 133.4, 133.0, 129.5, 129.3, 129.2, 127.5, 127.1, 126.9, 126.3, 125.2, 55.6, 51.9, 43.4, 40.1 ppm. LRMS (EI): 268 [M^+], 250, 233(100), 215, 202, 176, 151, 132, 125, 101, 89, 77, 51. IR (KBr, film) ν_{max}: 3068, 2978, 2875, 1694, 1604, 1474, 1301, 1216, 1125, 1042, 970, 886, 760, 702, 572 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}ClO$, [M + H]$^+$, 269.0728; found, 269.0743.

Compound 2c. Yellow oil; 33 mg, Yield 84% (mixture, *exo*/*endo* = 17:11). ^{1}H NMR (400 MHz, $CDCl_3$) *exo*: δ 8.06 (d, *J* = 7.2 Hz, 1H), 7.46 (dd, *J* = 11.9, 4.4 Hz, 2H), 7.38 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 3.88 (d, *J* = 5.9 Hz, 1H), 3.78 (s, 3H), 3.51−3.46 (m, 1H), 3.36 (t, *J* = 6.0 Hz, 1H), 3.12 (dt, *J* = 9.7, 5.9 Hz, 1H), 2.29 (dd, *J* = 9.6, 5.7 Hz, 1H); *endo*: δ 7.70 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 4H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 6.97 (dd, *J* = 11.5, 4.1 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 1H), 6.62 (dd, *J* = 17.0, 7.9 Hz, 2H), 4.36 (t, *J* = 5.7 Hz, 1H), 3.90−3.83 (m, 1H), 3.73 (s, 3H), 3.69 (q, *J* = 5.7 Hz, 1H), 2.90 (dt, *J* = 9.1, 5.7 Hz, 1H), 2.36 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *exo*: δ 201.6, 158.1, 152.4, 133.2, 129.4, 128.4, 128.2, 127.5, 126.9, 126.3, 125.1, 120.3, 110.3, 55.3, 53.9, 52.7, 42.9, 40.9; *endo*: δ 200.9, 157.4, 148.3, 132.9, 129.6, 128.4, 127.4, 127.2, 126.8, 126.2, 125.5, 119.9, 109.8, 55.4, 55.0, 53.4, 44.8, 41.7 ppm. LRMS (EI): 264(100) [M^+], 231, 202, 163, 145, 119, 91, 65, 39. IR (KBr, film) ν_{max}: 3068, 2946, 2836, 1694, 1603, 1461, 1350, 1180, 1028, 970, 886, 753, 574, 530 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O_2$, [M + H]$^+$, 265.1223; found, 265.1213.

Compound *exo*-2d. Yellow oil; 22 mg, Yield 59%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.5 Hz, 1H), 7.49 (dd, *J* = 10.7, 4.0 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.31 (dd, *J* = 15.2, 7.5 Hz, 2H), 7.24 (s, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 3.79 (d, *J* = 6.0 Hz, 1H), 3.56 (t, *J* = 5.9 Hz, 1H), 3.42 (t, *J* = 6.1 Hz, 1H), 3.15 (dt, *J* = 9.8, 5.9 Hz, 1H), 2.39 (s, 3H), 2.37−2.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 151.9, 140.3, 138.4, 133.4, 129.3, 128.6, 127.9, 127.5, 127.4, 127.0, 125.1, 123.9, 59.0, 53.9, 44.1, 41.1, 21.6 ppm. LRMS (EI): 248(100) [M^+], 215, 187, 178, 156, 128, 105, 77, 51. IR (KBr, film) ν_{max}: 3024, 2952, 1694, 1605, 1460, 1375, 1303, 1218, 1160, 1124, 766, 738, 701, 575 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1275.

Compound *endo*-2d. Colorless oil; 7 mg, Yield 20%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.26−7.22 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 4.42 (s, 1H), 3.78 (d, *J* = 5.6 Hz, 1H), 3.68 (d, *J* = 5.7 Hz, 1H), 2.91 (d, *J* = 9.1 Hz, 1H), 2.42 (d, *J* = 9.2 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 147.9, 139.2, 137.6, 133.3, 129.6, 127.9, 127.4, 126.9, 126.6, 126.4, 125.8, 123.7, 55.6, 53.2, 43.8, 41.1, 21.3 ppm. LRMS (EI): 248(100) [M^+], 215, 187, 178, 156, 128, 105, 77, 51. IR (KBr, film) ν_{max}: 3024, 2952, 1694, 1605, 1460, 1375, 1303, 1218, 1160, 1124, 766, 738, 701, 575 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1276.

Compound *exo*-2e. Yellow oil; 23 mg, Yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.1 Hz, 1H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.44−7.32 (m, 3H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 10.0 Hz, 1H), 7.00 (td, *J* = 8.5, 2.5 Hz, 1H), 3.81 (d, *J* = 6.0 Hz, 1H), 3.55 (t, *J* = 6.0 Hz, 1H), 3.41 (t, *J* = 6.1 Hz, 1H), 3.13 (dt, *J* = 9.8, 5.9 Hz, 1H), 2.36 (dd, *J* = 9.8, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 163.2 (d, *J* = 246.4 Hz), 151.5, 142.9 (d, *J* = 7.2 Hz), 133.5, 130.3 (d, *J* = 8.3 Hz), 129.2, 127.5, 127.1, 125.1, 122.7 (d, *J* = 2.7 Hz), 114.2 (d, *J* = 21.7 Hz), 113.8 (d, *J* = 20.8 Hz), 58.5, 53.8, 44.2, 41.1 ppm. LRMS (EI): 252 [M^+], 234, 202, 183, 170, 157, 143, 132(100), 115, 109, 101, 91, 77. IR (KBr, film) ν_{max}: 3069, 2952, 2875, 1695, 1606, 1488, 1461, 1343, 1145, 881, 770, 747 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}FO$, [M + H]$^+$, 253.1023; found, 253.1017.

Compound *endo*-2e. Colorless oil; 9 mg, Yield 24%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.37 (td, *J* = 7.5, 1.3 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.18 (td, *J* = 7.5, 1.1 Hz, 1H), 7.03 (td, *J* = 7.9, 6.1 Hz, 1H), 6.71−6.63 (m, 2H), 6.59−6.52 (m, 1H), 4.42 (t, *J* = 5.8 Hz, 1H), 3.79 (d, *J* = 5.6 Hz, 1H), 3.68 (d, *J* = 5.7 Hz, 1H), 2.93 (dt, *J* = 9.2, 5.6 Hz, 1H), 2.44 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 162.6 (d, *J* = 246.2 Hz), 147.4, 141.9 (d, *J* = 7.2 Hz), 133.5, 129.6 (d, *J* = 8.5 Hz), 129.4, 127.2, 126.4, 126.0, 122.5 (d, *J* = 2.9 Hz), 113.8 (d, *J* = 21.3 Hz), 112.9 (d, *J* = 21.2 Hz), 55.1, 53.1, 43.8, 40. 8 ppm. LRMS (EI): 252 [M^+], 234, 202, 183, 170, 157, 143, 132(100), 115, 109, 101, 91, 77. IR (KBr, film) ν_{max}: 3069, 2952, 2875, 1695, 1606, 1488, 1461, 1343, 1145, 881, 770, 747 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}FO$, [M + H]$^+$, 253.1023; found, 253.1022.

Compound *exo*-2f. Yellow oil; 20 mg, Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.5 Hz, 1H), 7.48 (dd, *J* = 10.6, 4.1 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.32 (dd, *J* = 8.0, 2.6 Hz, 3H), 7.23 (t, *J* = 6.8 Hz, 2H), 3.79 (d, *J* = 6.0 Hz, 1H), 3.53 (t, *J* = 5.9 Hz, 1H), 3.41 (t, *J* = 6.1 Hz, 1H), 3.15 (dt, *J* = 9.8, 5.9 Hz, 1H), 2.37 (s, 3H), 2.33 (dd, *J* = 9.7, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 136.3, 135.4, 132.3, 128.4, 128.2, 126.3, 125.9, 125.9, 124.0, 57.8, 52.9, 43.2, 40.0, 20.0 ppm. LRMS (EI): 248 [M^+], 233, 215, 205, 178, 156, 118, 105(100), 91, 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3024, 2948, 2921, 1697, 1605, 1514, 1460, 1381, 1297, 1015, 970, 885, 770,694 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1275.

Compound *endo*-2f. Colorless oil; 10 mg, Yield 27%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 7.6, 0.5 Hz, 1H), 7.34 (td, *J* = 7.4, 1.3 Hz, 1H), 7.29−7.21 (m, 1H), 7.15 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 2H), 4.43 (t, *J* = 5.8 Hz, 1H), 3.78 (q, *J* = 5.6 Hz, 1H), 3.67 (q, *J* = 5.7 Hz, 1H), 2.91 (dt, *J* = 9.2, 5.6 Hz, 1H), 2.42 (d, *J* = 9.2 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 146.9, 135.2, 134.2, 132.3, 128.6, 127.7, 125.9, 125.5, 125.4, 124.8, 54.5, 52.2, 42.8, 40.0, 19.9 ppm. LRMS (EI): 248 [M^+], 233, 215, 205, 178, 156, 118, 105(100), 91, 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3023, 2953, 2873, 1694, 1604, 1516, 1460, 1384, 1302, 970, 885, 768,744, 704, 568 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1278.

Compound *exo*-2g. Yellow oil; 17 mg, Yield 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.50 (td, *J* = 7.5, 1.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.76 (d, *J* = 6.0 Hz, 1H), 3.53 (t, *J* = 5.9 Hz, 1H), 3.39 (t, *J* = 6.1 Hz, 1H), 3.11 (dt, *J* = 9.9, 5.9 Hz, 1H), 2.35 (dd, *J* = 9.8, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 151.5, 139.4, 133.5, 131.8, 129.1, 128.8, 127.5, 127.1, 125.1, 120.7, 58.3, 53.7, 44.1, 40.9 ppm. LRMS (EI): 312 [M^+], 271, 233, 215(100), 203, 169, 132, 102, 77, 51. IR (KBr, film) ν_{max}: 3067, 2950, 1695, 1603, 1489, 1460, 1397, 1074, 1009, 971, 811, 777, 698, 541, 498 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}BrO$, [M + H]$^+$, 313.0223; found, 313.0219.

Compound *endo*-2g. Colorless oil; 14 mg, Yield 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.27−7.22 (m, 1H), 7.18 (dd, *J* = 7.3, 4.7 Hz, 3H), 6.74 (d, *J* = 8.1 Hz, 2H), 4.38 (t, *J* = 5.8 Hz, 1H), 3.78 (q, *J* = 5.6 Hz, 1H), 3.67 (q, *J* = 5.7 Hz, 1H), 2.92 (dt, *J* = 9.4, 5.6 Hz, 1H), 2.43 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 147.4, 138.4, 133.5, 131.2, 129.4, 128.5, 127.3, 126.4, 126.0, 119.8, 55.0, 53.0, 43.7, 40.9 ppm. LRMS (EI): 312 [M^+], 271, 233, 215(100), 203, 169, 132, 102, 77, 51. IR (KBr, film) ν_{max}: 3067, 2950, 1695, 1603, 1489, 1460, 1397, 1074, 1009, 971, 811, 777, 698, 541, 498 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}BrO$, [M + H]$^+$, 313.0223; found, 313.0217.

Compound *exo*-2h. Yellow oil; 13 mg, Yield 33%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.44−7.38 (m, 5H), 7.36 (dd, *J* = 7.0, 1.9 Hz, 2H), 3.82 (d, *J* = 6.1 Hz, 1H), 3.53 (t, *J* = 5.9 Hz, 1H), 3.44 (t, *J* = 6.0 Hz, 1H), 3.16 (dt, *J* = 9.9, 5.9 Hz, 1H), 2.33 (dd, *J* = 9.8, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 153.3, 139.8, 139.3, 128.8, 128.5, 127.7, 127.7, 127.0, 126.9, 125.4, 58.6, 53.6, 44.1, 40.6 ppm. LRMS (EI): 268 [M^+], 249, 233, 215, 202, 190, 176, 162, 139, 127, 104, 101, 91(100), 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3060, 3026, 2952, 1698, 1597, 1497, 1448, 1313, 1084, 884, 811, 736, 697, 552 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}ClO$, [M + H]$^+$, 269.0728; found, 269.0738.

Compound *endo*-2h. Colorless solid (mp 119.6−122.5 °C); 11 mg, Yield 29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.15−7.06 (m, 3H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 4.47 (t, *J* = 5.8 Hz, 1H), 3.78 (q, *J* = 5.6 Hz, 1H), 3.69 (q, *J* = 5.7 Hz, 1H), 2.93 (dt, *J* = 9.4, 5.6 Hz, 1H), 2.41

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(d, J = 9.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 149.4, 139.2, 138.8, 128.2, 128.0, 127.4, 127.4, 126.6, 126.1, 55.2, 52.9, 43.8, 40.6 ppm. LRMS (EI): 268 [M^+], 249, 233, 215, 202, 190, 176, 162, 139, 127, 104, 101, 91(100), 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3060, 3026, 2952, 1698, 1597, 1497, 1448, 1313, 1084, 884, 811, 736, 697, 552 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}ClO$, [M + H]$^+$, 269.0728; found, 269.0751.

Compound *exo*-2i. Yellow oil; 15 mg, Yield 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 2.2 Hz, 1H), 7.47−7.39 (m, 6H), 7.29 (d, J = 8.0 Hz, 1H), 3.81 (d, J = 6.1 Hz, 1H), 3.56 (t, J = 5.9 Hz, 1H), 3.44 (t, J = 6.0 Hz, 1H), 3.17 (dt, J = 9.9, 5.9 Hz, 1H), 2.32 (dd, J = 9.8, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 150.1, 139.9, 133.4, 133.0, 130.7, 128.8, 127.0, 126.6, 58.8, 53.6, 43.5, 40.8 ppm. LRMS (EI): 268 [M^+], 250, 233, 215, 202, 190, 176, 162, 127, 113, 91(100), 77, 51. IR (KBr, film) ν_{max}: 3024, 1699, 1597, 1496, 1471, 1384, 1072, 797, 773, 696, 664, 549, 457 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}ClO$, [M + H]$^+$, 269.0728; found, 269.0729.

Compound *endo*-2i. Colorless oil; 12 mg, Yield 32%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 2.1 Hz, 1H), 7.30 (dd, J = 8.0, 2.2 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 7.4 Hz, 2H), 7.01 (dd, J = 10.8, 3.8 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 4.47 (t, J = 5.8 Hz, 1H), 3.80 (q, J = 5.6 Hz, 1H), 3.71 (q, J = 5.7 Hz, 1H), 2.94 (dt, J = 9.3, 5.6 Hz, 1H), 2.40 (d, J = 9.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 146.1, 138.8, 133.1, 132.9, 130.9, 128.2, 127.9, 126.6, 126.1, 125.9, 55.3, 52.9, 43.3, 40.7 ppm. LRMS (EI): 268 [M^+], 250, 233, 215, 202, 190, 176, 162, 127, 113, 91(100), 77, 51. IR (KBr, film) ν_{max}: 3024, 1699, 1597, 1496, 1471, 1384, 1072, 797, 773, 696, 664, 549, 457 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{13}ClO$, [M + H]$^+$, 269.0728; found, 269.0725.

Compound *exo*-2j. Yellow oil; 10 mg, Yield 25%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.5 Hz, 1H), 7.42 (dd, J = 7.6, 6.0 Hz, 4H), 7.31 (td, J = 5.5, 2.9 Hz, 1H), 6.89 (dd, J = 8.5, 2.4 Hz, 1H), 6.84 (d, J = 2.3 Hz, 1H), 3.90 (s, 3H), 3.82 (d, J = 6.0 Hz, 1H), 3.52 (t, J = 5.9 Hz, 1H), 3.38 (t, J = 6.0 Hz, 1H), 3.13 (dt, J = 9.7, 5.9 Hz, 1H), 2.33 (dd, J = 9.6, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 163.5, 154.2, 140.4, 129.3, 128.7, 127.1, 126.8, 122.5, 112.4, 110.5, 58.8, 55.6, 53.5, 44.6, 40.8 ppm. LRMS (EI): 264(100) [M^+], 236, 221, 202, 178, 162, 145, 115, 91, 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3059, 3030, 2940, 2842, 1686, 1602, 1492, 1446, 1336, 1260, 1150, 1105, 1048, 871,820, 736 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O_2$, [M + H]$^+$, 265.1223; found, 265.1224.

Compound *endo*-2j. Colorless oil; 16 mg, Yield 41%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 7.7 Hz, 2H), 6.75 (d, J = 2.4 Hz, 1H), 6.63 (dd, J = 8.5, 2.4 Hz, 1H), 4.42 (t, J = 5.8 Hz, 1H), 3.81 (s, 3H), 3.75 (q, J = 5.6 Hz, 1H), 3.63 (q, J = 5.7 Hz, 1H), 2.90 (dt, J = 9.1, 5.6 Hz, 1H), 2.40 (d, J = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 163.5, 150.1, 139.5, 128.3, 128.1, 126.6, 125.8, 122.9, 112.2, 111.6, 55.4, 52.8, 44.2, 40.8, 29.7 ppm. LRMS (EI): 264(100) [M^+], 236, 221, 202, 178, 162, 145, 115, 91, 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3059, 3030, 2940, 2842, 1686, 1602, 1492, 1446, 1336, 1260, 1150, 1105, 1048, 871,820, 736 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O_2$, [M + H]$^+$, 265.1223; found, 265.1216.

Compound *exo*-2k. Yellow oil; 15 mg, Yield 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 2.7 Hz, 1H), 7.46−7.38 (m, 4H), 7.30 (td, J = 5.6, 2.8 Hz, 1H), 7.26 (d, J = 1.8 Hz, 1H), 7.05 (dd, J = 8.2, 2.7 Hz, 1H), 3.88 (s, 3H), 3.82 (d, J = 6.0 Hz, 1H), 3.52 (t, J = 5.9 Hz, 1H), 3.42 (t, J = 6.1 Hz, 1H), 3.15 (dt, J = 9.7, 5.9 Hz, 1H), 2.33 (dd, J = 9.6, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 159.1, 144.7, 140.5, 130.2, 128.7, 127.0, 126.7, 126.2, 120.5, 110.2, 59.7, 55.6, 53.8, 43.3, 41.6 ppm. LRMS (EI): 264(100) [M^+], 236, 173, 145, 128, 115, 91, 77. IR (KBr, film) ν_{max}: 3058, 3025, 2951, 2835, 1695, 1610, 1492, 1448, 1360, 1289, 1231, 1087, 1029, 975, 868, 833, 772, 698 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O_2$, [M + H]$^+$, 265.1223; found, 265.1210.

Compound *endo*-2k. Colorless oil; 4 mg, Yield 10%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 1H), 7.22 (d, J = 2.7 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 7.08 (t, J = 7.4 Hz, 2H), 7.00 (t, J = 7.0 Hz, 1H), 6.87 (d, J = 8.1 Hz, 2H), 4.45 (t, J = 5.7 Hz, 1H), 3.75 (dd, J = 11.4, 5.8 Hz, 1H), 3.73 (s, 3H), 3.68 (q, J = 5.7 Hz, 1H), 2.92 (dt, J = 9.1, 5.6 Hz, 1H), 2.41 (d, J = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 158.6, 140.4, 139.5, 130.5, 128.1, 127.5, 126.7, 125.8, 120.44, 109.2, 56.1, 55.4, 53.1, 43.0, 41.6 ppm. LRMS (EI): 264(100) [M^+], 236, 173, 145, 128, 115, 91, 77. IR (KBr, film) ν_{max}: 3058, 3025, 2951, 2835, 1695, 1610, 1492, 1448, 1360, 1289, 1231, 1087, 1029, 975, 868, 833, 772, 698 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O_2$, [M + H]$^+$, 265.1223; found, 265.1210.

Compound *exo*-2l. Yellow oil; 29 mg, Yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 8.07 (d, J = 7.4 Hz, 1H), 7.55−7.22 (m, 8H), 3.80 (d, J = 4.4 Hz, 1H), 3.56 (d, J = 6.2 Hz, 1H), 3.47 (d, J = 6.2 Hz, 1H), 2.76−2.50 (m, 1H), 1.15 (d, J = 7.3 Hz, 3H); minor: δ 8.03 (d, J = 7.5 Hz, 1H), 7.57−7.15 (m, 8H), 3.76 (s, 1H), 3.60 (t, J = 5.9 Hz, 1H), 3.53−3.48 (m, 1H), 3.41 (t, J = 6.0 Hz, 1H), 0.76 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 201.4, 153.5, 142.0, 132.9, 129.9, 128.6, 127.5, 127.1, 126.4, 126.2, 124.5, 58.2, 57.3, 52.3, 48.8, 19.0; minor: δ 200.5, 147.8, 140.3, 133.6, 130.9, 128.7, 127.3, 127.1, 126.7, 126.6, 125.8, 58.1, 56.2, 48.6, 45.5, 13.2 ppm. LRMS (EI): 248 [M^+], 233(100), 215, 205, 178, 163, 146, 131, 115, 91, 77, 51, 39. IR (KBr, film) ν_{max}: 3060, 3027, 2960, 2927, 2873, 1694, 1602, 1497, 1460, 1298, 1077, 974, 893, 775, 696 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1280.

Compound *endo*-2l. Colorless oil; 4 mg, Yield 12%. ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 7.70 (d, J = 7.6 Hz, 1H), 7.22 (dd, J = 7.1, 3.5 Hz, 2H), 7.05 (t, J = 7.4 Hz, 4H), 6.97 (dd, J = 7.2, 2.6 Hz, 2H), 4.26 (t, J = 5.6 Hz, 1H), 3.83 (q, J = 5.5 Hz, 1H), 3.52 (t, J = 5.8 Hz, 1H), 3.30 (dd, J = 12.4, 5.7 Hz, 1H), 0.87 (d, J = 6.9 Hz, 3H); minor: δ 7.65 (d, J = 7.6 Hz, 1H), 7.35 (dtd, J = 8.7, 7.5, 1.2 Hz, 2H), 7.18−7.10 (m, 2H), 6.86 (dd, J = 11.7, 8.1 Hz, 4H), 4.74 (t, J = 5.9 Hz, 1H), 3.63 (q, J = 5.6 Hz, 1H), 3.43 (t, J = 5.9 Hz, 1H), 2.76 (q, J = 7.0 Hz, 1H), 1.63 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 200.3, 143.9, 138.8, 133.1, 130.2, 127.9, 127.8, 126.8, 126.6, 126.1, 125.6, 57.6, 51.8, 48.4, 45.9, 12.4; minor: δ 199.8, 148.8, 139.8, 133.6, 131.3, 127.9, 127.0, 126.8, 126.2, 125.7, 124.7, 57.9, 53.4, 48.7, 48.4, 17.8 ppm. LRMS (EI): 248 [M^+], 233(100), 215, 205, 178, 163, 146, 131, 115, 91, 77, 51, 39. IR (KBr, film) ν_{max}: 3060, 3027, 2960, 2927, 2873, 1694, 1602, 1497, 1460, 1298, 1077, 974, 893, 775, 696 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1274.

Compound *endo*-2m. Light yellow semisolid; 22 mg, Yield 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.6 Hz, 1H), 7.32 (td, J = 7.5, 1.2 Hz, 1H), 7.20 (d, J = 7.3 Hz, 1H), 7.14 (td, J = 7.5, 1.1 Hz, 1H), 7.04 (t, J = 7.3 Hz, 2H), 6.96 (t, J = 7.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 4.21 (d, J = 6.0 Hz, 1H), 3.77 (t, J = 5.8 Hz, 1H), 2.65 (dd, J = 9.0, 5.7 Hz, 1H), 2.48 (d, J = 9.0 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 148.6, 139.5, 133.0, 129.9, 128.0, 126.7, 126.6, 126.2, 125.9, 125.9, 61.6, 56.4, 47.9, 41.5, 20.5 ppm. LRMS (EI): 248(100) [M^+], 233, 215, 205, 191, 178, 165, 152, 144, 132, 115, 103, 91, 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3027, 2962, 2868, 1692, 1602, 1496, 1477, 1377, 1300, 1198, 1101, 984, 962, 909, 746, 696, 563 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}O$, [M + H]$^+$, 249.1274; found, 249.1281.

Compound 2n. Yellow oil; 9 mg, Yield 34%. ^{1}H NMR (400 MHz, $CDCl_3$) *exo*: δ 8.03−7.87 (m, 1H), 7.45−7.39 (m, 1H), 7.34 (qd, J = 7.7, 1.1 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 3.27−3.17 (m, 2H), 3.12 (t, J = 5.9 Hz, 1H), 2.34−2.26 (m, 1H), 1.89 (dd, J = 9.1, 5.8 Hz, 1H), 1.40 (qd, J = 8.2, 4.1 Hz, 1H), 0.67−0.55 (m, 2H), 0.42−0.18 (m, 2H) ppm; *endo*: δ 8.00−7.93 (m, 1H), 7.46 (tt, J = 3.4, 1.7 Hz, 1H), 7.34 (td, J = 7.6, 1.0 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 3.37 (q, J = 5.6 Hz, 1H), 3.27−3.16 (m, 1H), 2.59 (dt, J = 9.3, 5.6 Hz, 1H), 2.34−2.20 (m, 2H), 0.41−0.18 (m, 3H), 0.17−0.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *exo*: δ 201.4, 152.6, 133.0, 130.1, 126.9, 126.8, 124.7, 62.3, 53.9, 44.2, 41.3, 13.7, 4.5, 4.3; *endo*: δ 200.9, 148.7, 133.4, 129.2, 127.0, 126.4, 125.7, 60.2, 53.7, 44.1, 40.8, 8.9, 4.5, 4.1 ppm LRMS (EI): 198 [M^+], 183, 170, 157, 144(100), 128, 115, 103, 89, 77, 63, 51, 39. IR (KBr, film) ν_{max}: 3306, 2883, 1715, 1599, 1483, 1407, 1212, 1178, 1093, 1008, 877, 825, 752 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{14}O$, [M + H]$^+$, 199.1117; found, 199.1128.

Compound *endo*-2o. Colorless liquid; 2 mg, Yield 8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.5 Hz, 1H), 7.45 (tt, J = 5.7, 2.8 Hz, 1H), 7.34 (td, J = 7.5, 0.9 Hz, 1H), 7.23−7.17 (m, 1H), 3.36−3.24

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(m, 2H), 3.13 (q, J = 5.7 Hz, 1H), 2.70 (dt, J = 10.7, 5.4 Hz, 1H), 2.28 (d, J = 9.2 Hz, 1H), 0.77 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1 147.9, 133.5, 130.2, 127.0, 126.5, 125.5, 54.0, 48.8, 44.5, 41.3, 13.4 ppm. LRMS (EI): 172 [M^+], 157, 144, 131(100), 115, 103, 89, 77, 63, 51, 39. IR (KBr, film) ν_{max}: 2924, 2853, 1697, 1601, 1463, 1384, 1075, 797, 457 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{12}O$, [M + H]$^+$, 173.0961; found, 173.0962.

Quantum Yield Determination.[21] The quantum yield for formation in benzene was determined using valerophenone actinometry (Φ = 0.33) and a merry-go-round apparatus according to the standard procedure: Equal volumes (3 mL) of each solution, 0.009 M aldehyde and actinometer (*n*-Tetradecane as internal standard), were placed in specially cleaned 13 × 100 mm Pyrex culture tubes, which were degassed and then sealed. Irradiations were conducted at around 20 °C in a merry-go-round apparatus with a 500 W medium-pressure mercury lamp housed in an immersion well. The 313 nm mercury line was isolated by a filter combination glass jacket, and an aqueous solution of 0.002 M K_2CrO_4 containing 5% K_2CO_3 by weight circulated through a Pyrex cooling jacket. Quantum yields of photoproduct formation were determined by quantitative GC relative to acetophenone formation (<10%) from parallel runs on 0.1 M valerophenone in benzene containing 1.000 g/L of tetradecane as internal standard. Quantum yields were determined at varying conversions and repeated at least three times. The quantum yield based on **1a** was 0.05.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds and the CIF file of compound ***endo*-2h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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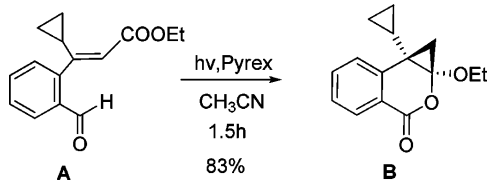
(16) CCDC 917077 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(17) Irradiation of *ortho*-formyl 3-cyclopropyl methyl cinnamate **A** in dried acetonitrile for 1.5 h led to an isochromanone **B** in 83% yield.



(18) After irradiation for 4 h, 30% of aldehyde **1a** was converted to benzobicycloheptanones, while only 19% of the partially deuterated aldehyde was consumed to form 77% deuterated products, and the rest of the aldehyde was 90% deuterium-labeled by ^{1}H NMR analysis.
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