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Journal:	*The Journal of Organic Chemistry*
Manuscript ID	jo-2019-01273y.R1
Manuscript Type:	Article
Date Submitted by the Author:	14-Jun-2019
Complete List of Authors:	Zhao, Lei-Min; Technical Institute of Physics and Chemistry, Lei, Tao; Technical Institute of Physics and Chemistry, Liao, Rong-Zhen; Huazhong University of Science and Technology, College of Chemistry and Chemical Engineering Xiao, HongYan; Technical Institute of Physics and Chemistry, Key Laboratory of Photochemical Conversion and Optoelectronic Materials Chen, Bin; Chinese Academy of Sciences, Technical Institute of Physics and Chemistry Ramamurthy, Vaidhyanathan; University of Miami, Chemistry; Tung, Chen-Ho; Technical Institute of Physics and Chemistry, Wu, Li-Zhu; Chinese Academy of Sciences, Technical Institute of Physics and Chemistry

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Visible Light Triggered Selective Intermolecular [2+2] Cycloaddition of Extended Enones: 2-Oxo-3-enoates and 2,4-Dien-1-ones with Olefins

Lei-Min Zhao,[†, ‡, Δ] Tao Lei,[†, ‡, Δ] Rong-Zhen Liao,[¶] Hongyan Xiao,[†, ‡] Bin Chen,[†, ‡] Vaidhyanathan Ramamurthy,[§] Chen-Ho Tung,[†, ‡] and Li-Zhu Wu[†, ‡, *]

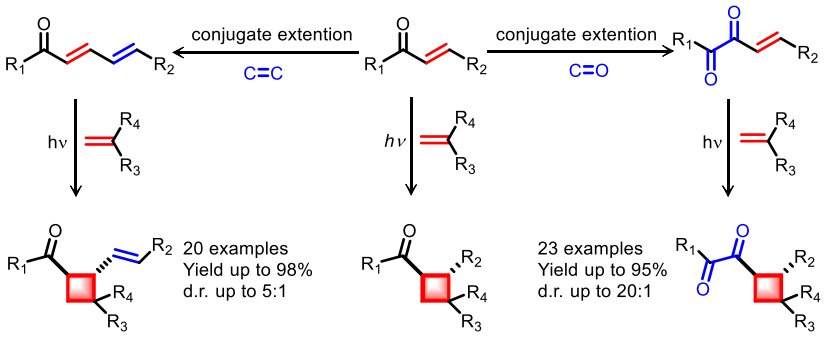
[†] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, The Chinese Academy of Sciences, Beijing, 100190, PR China

[‡] School of Future Technology, University of Chinese Academy of Sciences, Beijing, 100049, PR China

[¶] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, PR China.

[§] Department of Chemistry, University of Miami, Coral Gables, Miami, Florida 33146, USA

E-mail: lzwu@mail.ipc.ac.cn



Abstract:

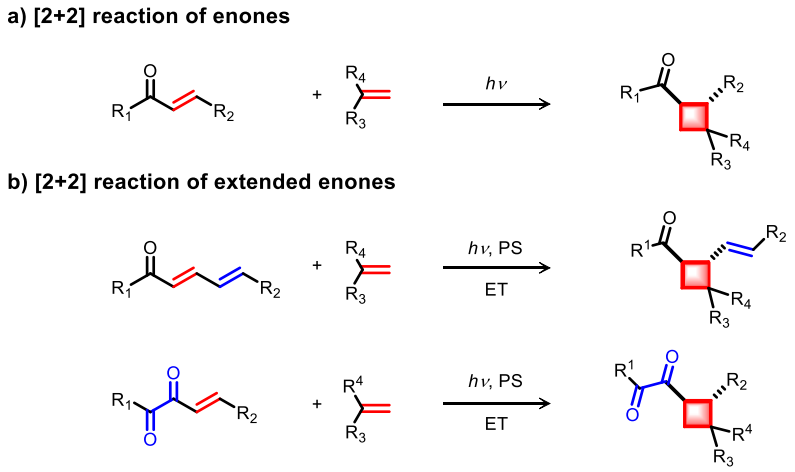
Photosensitization has recently re-emerged owing to the current interest in visible light catalysis. One of the photoreactions investigated in this context namely photo[2+2]cycloaddition of olefins is established to show high selectivity and wide generality. Here we describe the results

of our studies on selective intermolecular cycloaddition between extended enones (2,4-dien-1-ones and 2-oxo-3-enoates) and olefins under visible light sensitization. With $Ru(bpy)_3Cl_2$ as the triplet energy sensitizer, [2+2] addition of 2,4-dien-1-ones to olefins resulted in the addition to the 'ene' part of enones with high efficiency. Generality and functional group tolerance was established by examining a number of enones. 2-Oxo-3-enoates also underwent addition to olefins in presence of $Ru(phen)_3(PF_6)_2$. Both additions were more effiecient in presence of the triplet sensitizer than upon direct irradiation. No Paternò-Büchi product was detected. DFT calculation revealed the origin of high selectivity in the two extended enone systems. Together with spectroscopic studies and control experiments, the cycloaddition has been demostrated to occur from the excited triplet state of these extended enones which were generated via energy transfer process.

Introduction

Cyclobutanes and their derivatives play a predominant role in the synthesis of pharmaceutical products and commercial-valued materials.[1] One convenient and extensively employed method to build cyclobutane skeleton is the [2+2] cycloaddition between an excited and a ground state olefins.[2] Use of visible light in initiating photoreactions[3], a topic of current interest is particularly appealing in building cyclobutanes because of the following advantages: (a) the low cost and decreased energy demand of the visible light source; (b) feasibility to conduct a photoreaction without the need of specific photoreactors or quartz-wares and (c) ability to selectively excite a photosensitizer without directly exciting the reactant molecules.

Scheme 1. Intermolecular cycloadditions of extended enones



Amongst the various photocycloaddition reactions, addition of excited enones[4] to olefins have been extensively investigated. It is well known that under visible light photocatalysis (VLPC), olefins and α, β-enones undergo intra-[5-6] and intermolecular[7-8] [2+2] cycloaddition to form cyclobutanes via single electron transfer (SET)[5, 7] and energy transfer (ET)[6, 8] pathways. Given the usefulness of above cycloaddition reactions in synthesis, we thought it is important to examine the behaviour of α, β-enones with extended conjugation (extended C=C and C=O bond). It was anticipated that such an extended conjugation will shift the absorption to longer wavelengths and lower the excited singlet and triplet state energies. Thus these systems would be ideally suited for VLPC. However, one problem we foresaw with such systems behaving like a diene would offer an additional site for photoaddition. Thus far reported studies on cyclic dienones focussed on direct irradiation and the products were formed with poor selectivity.[9] An example of interest is the addition of a diene incorporated acyl imidazole to an olefin reported by Meggers.[8c] This addition is facilitated by coordination with an asymmetric Lewis acid. Extended enones like enediones/eneketoesters are known to undergo Paternò-Büchi reaction to yield oxetanes.[10] This prompted us to probe whether π-extended conjugated enone molecules would react at the C=O or

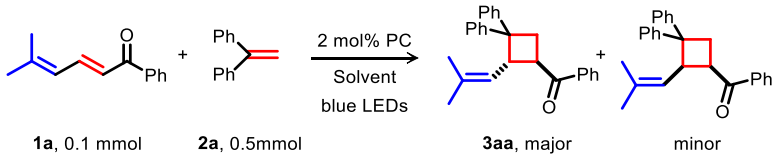
C=C end of the molecule. Here we disclose our recent results on the intermolecular [2+2] reaction of excited 2,4-dien-1-ones (enones involving additional C=C bond; dienones) and excited 2-oxo-3-enones (enediones or eneketoesters involving additional C=O bond) with ground state olefins such as 1,1-diphenylethylene (Scheme 1). When a mixture of 2,4-dien-1-ones, terminal olefin and a visible light absorbing photocatalyst was irradiated, cyclobutanes were obtained via intermolecular [2+2] addition to the α, β- C=C bond of the dienone. Similar addition also occurs when 2-oxo-3-enoates and olefins were photocatalyzed by visible light absorbing catalysts. Thus in this two cases extension of the enone with either C=C or C=O functionality did not alter the reactivity of the parent system. Results presented here for the two classes of molecules derived from α, β-enones under visible light photocatalysis (VLPC) conditions, we believe, are valuable in building complex organic molecules.

Result and Discussion

Intermolecular [2+2] reaction of 2,4-dien-1-one under VLPC condition. To avoid complications caused by geometric isomerization of the terminal double bond, we initiated the study with 2,4-dien-1-one **1a** and olefin **2a** as substrates and $Ir(ppy)_3$ as the photocatalyst. When a mixture of 0.1 mmol of **1a**, 0.5 mmol of **2a** and 2 mol % of $Ir(ppy)_3$ in acetonitrile (MeCN) was irradiated with blue LEDs (λ = 455 nm) for 10 h, a cyclobutane product derived from the C=C bond adjacent to carbonyl group was obtained in 52 % yield and 5:1 d.r. (Table 1, entry 1). Screening of several photocatalysts revealed that $Ru(bpy)_3Cl_2$ was the best (Table 1, entries 1-3). Optimization of the solvents suggested that hexafluoro-*iso*-propanol (HFIP) was most suitable (93% yield; Table 1, entries 3-7). Further control experiments confirmed the necessity of visible light

and photocatalyst. Omitting any one of the two components (photocatalyst or visible light) yielded no addition product (Table 1, entries 8-9).

Table 1. Optimizations for the [2+2] conditions of 2,4-dien-1-one.[a]



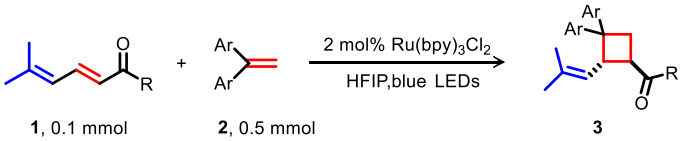
1a, 0.1 mmol **2a**, 0.5mmol **3aa**, major minor

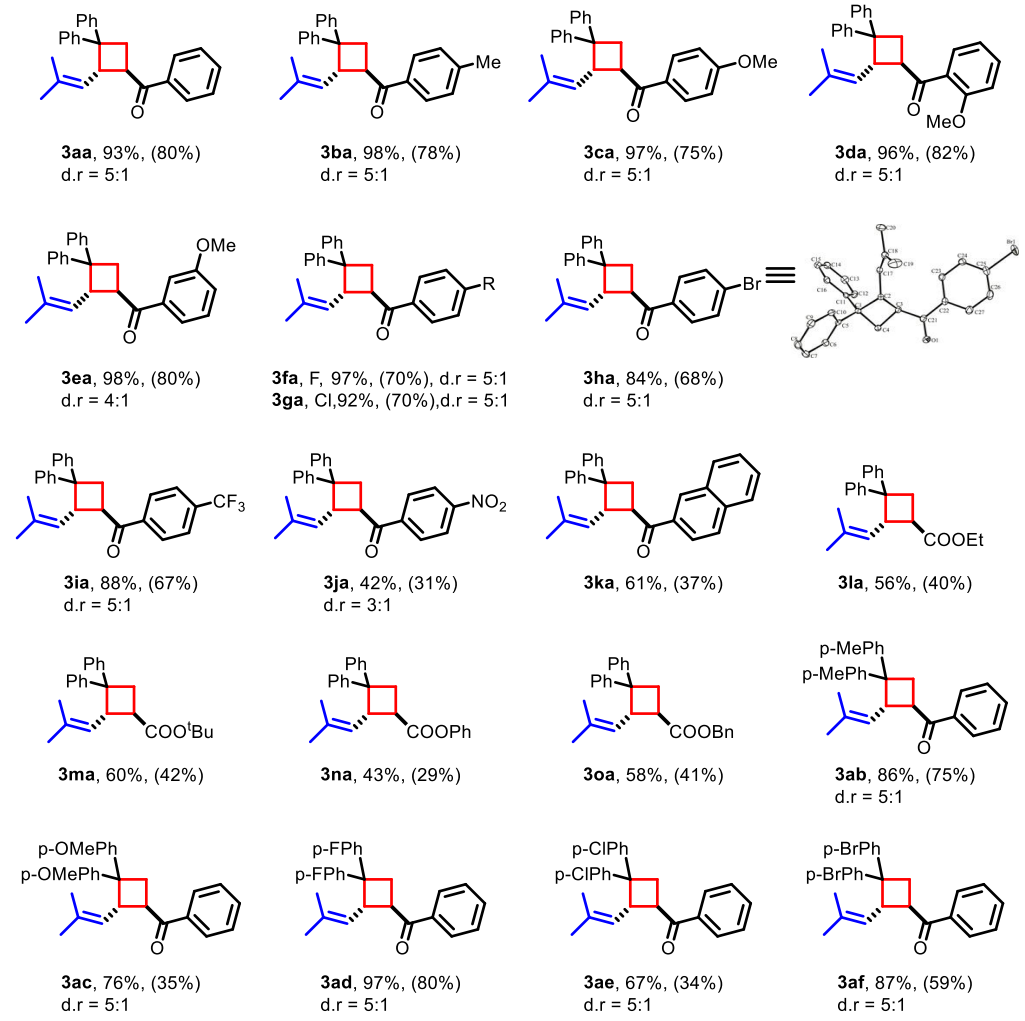
Entry	Catalyst	Solvent	Yield (%)[b]	d.r.
1	$Ir(ppy)_3$	MeCN	52	5:1
2	$Ru(bpz)_3Cl_2$	MeCN	26	3:1
3	$Ru(bpy)_3Cl_2$	MeCN	59	5:1
4	$Ru(bpy)_3Cl_2$	MeOH	69	5:1
5	$Ru(bpy)_3Cl_2$	EtOH	63	5:1
6	$Ru(bpy)_3Cl_2$	*i*-PrOH	56	5:1
7	$Ru(bpy)_3Cl_2$	HFIP	93	5:1
8[c]	$Ru(bpy)_3Cl_2$	HFIP	N.D	/
9	No PC	HFIP	N.D	/

[a] The reaction were carried out in 2.5 mL solvent with 0.1 mmol 1a, indicated 2a and 2 mol % PC (0.8 mM) under the irradiation of Blue-LEDs (λ = 455 nm) for 10 h,. [b] Yields and d.r. (anti: syn) were determined by ^{1}H-NMR using biphenylacetonitrile as internal standard. [c] Dark conditions, N.D = not detected.

Having identified the optimum reaction condition, we proceeded to explore the scope of the [2+2] reaction between 2,4-dien-1-ones and various olefins (Scheme 2). Products and their yields are summarized in Scheme 2. From the data it is clear that: a) Electronic nature of the *para*-aryl group substitution on the dienone including methyl, methoxyl, halogen atom and CF_3 had little influence on the conversion efficiency (**3aa-3ia)**. Even strongly withdrawing group NO_2 gave 31% isolated product (**3ja**). b) Position of the methoxyl substituent on the phenyl ring showed little

Scheme 2. Generality of the cycloaddition of 2,4-dien-1-ones with terminal olefin [a]





[a] Reaction condition: the reaction were carried out in 2.5 mL HFIP with 0.1 mmol **1**, 5 equiv **2** and 2 mol % $Ru(bpy)_3Cl_2$ (0.8 mM) under the irradiation of Blue-LEDs (λ = 455 nm) for 10 h. Yields and d.r. (anti: syn) were determined by ^{1}H-NMR using biphenylacetonitrile as internal standard, the ones in parenthesis were isolated yields.

difference on the conversion (*p*-OCH_3, 97% (**3ca**), *o*-OCH_3, 96% (**3da**) and 98% *m*-OCH_3, (**3ea**)) indicating the absence of steric effect caused by the substitution of aryl group. c) Introduction of

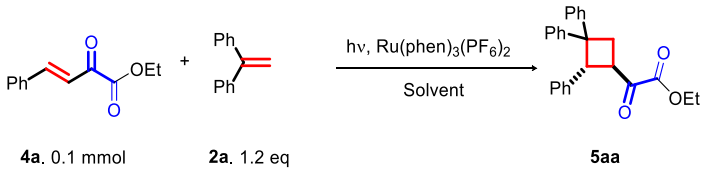
naphthalene ring led to a single isomer with moderate yield. d) More importantly, less conjugated 2,4-dienoates (non-aryl systems) were also smoothly converted to *anti*-products (**3la**, **3ma**, **3na** and **3oa**). (e) The structure of the photoproduct **3ha** was confirmed to have *anti*-configuration by X-ray diffraction. In all other cases, ^{1}H and ^{13}C NMR spectra were employed to confirm the structure of the products (see Supporting Information). (f) To probe the generality of the participating olefin, the structure of the diphenyl ethylene was modified. Different substitutions like methyl (**3ab**), F (**3ad**) and Br (**3af**) showed good tolerance. Methoxyl (**3ac**) and Cl (**3ae**) lead to moderate results due to the lower solubility in HFIP.

From the discussion above, it is clear that the cycloaddition is specific and occurred only at the α, β bond of the dienones. The reaction proceeded smoothly with the dienone containing diffferent electronic features. Similarly, the reaction was also general from the perspective of the 1,1-diaryl ethylene.

Intermolecular [2+2] cycloaddition of 2-oxo-3-enoates with olefins under VLPC condition. Recently Luo's group[11] has reported the cylcoaddition of the methyl ester of 2-oxo-3-enoates **4a** to yield the [2+2] adduct with styrenes via direct irradiation. Given the compound has virtually no absorption at 455 nm, we believed that a better approach to conduct the cycloaddition was to use a visible light absorbing catalyst, that is, a triplet sensitizer. With this in mind, we performed the photocycloaddition of 2-oxo-3-enoates by using $Ru(bpy)_3Cl_2$ as the VLPC. A mixture of 0.1 mmol of 2-oxo-3-enoates **4a**, 0.5 mmol of **2a** and 2 mol % of $Ru(bpy)_3Cl_2$ in 1,2-dichloroethane (DCE) was irradiated with blue LEDs (λ = 455 nm) for 10 h (see Supporting Information, Table S1). Isolation of the product gave a cyclobutane in moderate yield (57%, Table S1, entry 1) and high diastereoselectivity (d.r. > 20:1). In order to identify the optimum condition

for this reaction, several catalysts and solvents were examined. $Ru(phen)_3(PF_6)_2$ and acetone were found to be the best catalyst and the solvent (for details, see Supporting Information, Table S1). Experiments with varying concentrations of the olefin revealed that excess olefin was not required for this selective cross [2+2] cycloaddition under VPLC conditions. This is different from the direct irradiation conditions wherein 5-fold excess amount was required. [11]

Table 2. Importance of PC in the [2+2] reactions of 2-oxo-3-enoates with olefins under VLPC condition [a]



4a. 0.1 mmol **2a**. 1.2 eq **5aa**

Entry	Solvent	With PC		Without PC	
		Yield (%)	d.r.	Yield (%)	d.r.
1	Acetone	98	> 20:1	56	9:1
2	DCE	89	15:1	25	8:1
3	Dioxane	56	15:1	40	4:1
4	DMSO	44	10:1	20	3:1
5	MeCN	85	15:1	45	1.2:1

[a] The reaction were carried out in 2.5 mL solvent with 0.1 mmol **4a**, 1.2 equiv **2a** and 2 mol % PC (0.8 mM) (or not) under the irradiation of Blue-LEDs (λ = 455 nm) for 10 h. Yields and d.r. (anti: syn) were determined by ^{1}H-NMR using biphenylacetonitrile as internal standard. The structure of product was same with or without PC.

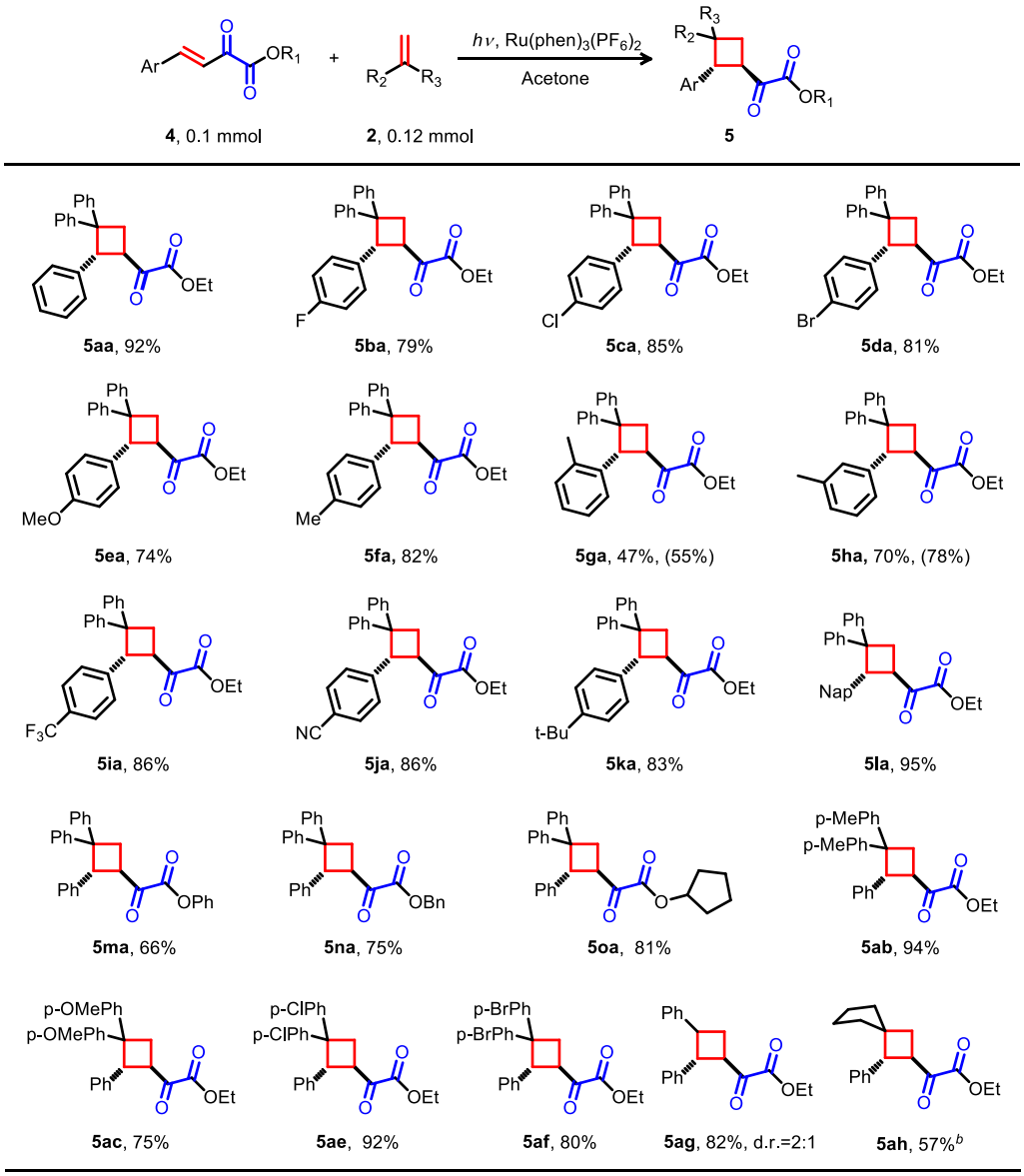
In order to prove the role of VLPC, additional reactions were carried out in different solvents with and without $Ru(phen)_3(PF_6)_2$. Under optimum condition of 1.2 eqiuv olefin **2a** in acetone, direct irradiation without the photocatalyst lead to 56% yield and 9:1 diastereoselectivity (Table 2,

entry 1). Results in other solvents like DCE, dioxane, dimethyl sulfoxide, and acetonitrile gave similar low yields. On the contrary, the presence of $Ru(phen)_3(PF_6)_2$ enhanced the yield of adduct to 98% and >20:1 d.r. in acetone. Apparent enhancement was also obtained in other tested media. These results confirmed the positive influence of VLPC on this reaction. Keeping the above solution in dark did not result in a reaction (Table S1 in SI, entry 10), confirming the necessity of visible light. More importantly, we established the synthetic value of the reaction by isolating the cyclobutane product in 82% yield upon irradiating **4a** and **2a** in gram scales in presence of $Ru(phen)_3(PF_6)_2$ (2 mol %) (Table S1, entry 13).

Generality of $Ru(phen)_3(PF_6)_2$ photocatalyzed cycloaddition was established by examining the behaviour of over two-dozen substituted 2-oxo-3-enoates towards different terminal olefins which included substituted diphenyl alkenes, styrenes and dialkylated alkenes (Scheme 3). Perusal of the product yields listed in Scheme 3 leads to the following conclusions: a) Highly efficient cycloaddition occurred between 2-oxo-3-enoates and diphenyl alkene, with different electron-donating (**5ea**, **5fa** and **5ka**) and electron-withdrawing (**5ba**, **5ca**, **5da**, **5ia** and **5ja**) groups on the phenyl ring of 2-oxo-3-enoates. This suggested that the cycloaddition was independent of the electronic effect on the aryl group substituted on the enone moiety. b) Phenyl and other alkyl modified substrates (**5ma, 5na, 5oa**) at the ester moiety showed equal efficiency as **5a**. c) Bulkiness of *o*- and *m*- methyl group on the aryl ring had moderate effect on the conversion (**5ga** and **5ha**). d) 2-Oxo-3-enoates with larger aromatic group like naphthalene (**5la**) gave the cycloadduct in 95% yield. e) As for styrene reactants, 1,1-diphenylalkenes bearing electron-donating and electron-withdrawing groups reacted with **4a** in good yields (**5ab, 5ac, 5ae** and **5af**). Mono-substituted terminal styrenes gave adduct (**5ag**) in moderate yield with 2:1 d.r. f)

Dialkylated alkenes such as methylidene-cyclopentane gave moderate yields of the cycloadducts **5ah**.

Scheme 3. Generality of the cycloaddition of 2-oxo-3-enoates with terminal olefin [a]



[a] Reaction condition: the reaction were carried out in 2.5 mL acetone with 0.1 mmol **4**, 1.2 equiv **2** and 2 mol % $Ru(phen)_3(PF_6)_2$ (0.8 mM) under the irradiation of Blue-LEDs (λ = 455 nm) for 10 h. Unless noted, yields were isolated yields, the yields in parenthesis and d.r. were determined by ^{1}H-NMR using biphenylacetonitrile as the internal standard. The configuration of aryl group and carbonyl group is *anti* (*anti*: *syn* > 20:1). As for the product **5af**, the 2:1 d.r.was introduced by another chiral center from the asymmetric olefin [b] Aliphatic olefins were added in 5 equiv and irradiated for 20 h.

In the absence of our ability to obtain crystals of the product **5**, we relied on ^{1}H NMR to characterize the structure of adducts which could be either head-to-head or head-to-tail. To ascertain the regiochemistry of the products isolated in this part, enolization and H-D exchange of **5aa** was performed in D_6-DMSO with Cs_2CO_3 as base.[12] It was anticipated that replacement of H by D would help confirm the structure of the cycloadduct (Figure 1). According to the ^{1}H-NMR

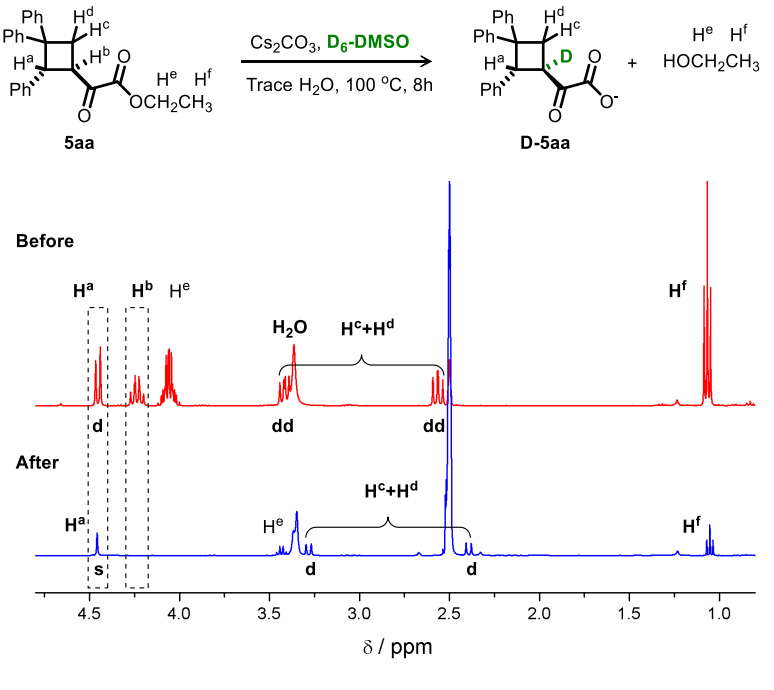


Figure 1. Identification for the structure of **5aa** via H-D exchange experiment.

spectrum displayed in Figure 1, H-D exchange of α-H of carbonyl group led to doublet-doublet peak of H^c and H^d into doublet peak, doublet peak of H^a into singlet, the decreasing of spin splitting strongly supported the structure of **5aa** (Relevant 2D ^{1}H-^{1}H COSY and HMBC spectra of **5aa** are provided in SI).

To conclude, we demonstrated that 2-oxo-3-enoates reacted at α, β C=C bond and the reaction was general in terms of both the enoates and the partner olefins. Although the reaction could be realized by direct excitation (455 nm), the yield was increased in presence of a VLPC.

Mechanistic studies of the intermolecular [2+2] reaction of extended enones under VLPC condition. Having established the value of ruthenium complexes for highly effective cycloadditions, we proceeded to probe the mechanism of the [2+2] addition of extended enones to olefins. Two pathways involving single electron transfer and energy transfer have been established in visible light induced intermolecular [2+2] cycloaddition of enones. Oftentimes, the same catalyst could act both as an electron[7a] and energy transfer[8d,8f] catalyst. The former process was established for 1-phenylalkyl-2-en-1-one derivatives[7a,7d] and the latter for chalcone and cinnamic acid esters[8d-8i]. Since the extension of enones with an additional C=C or C=O bond would lead to changes in both electronic and excited state properties, consequent changes in mechanism were likely. To probe the mechanism involved in this study, we undertook a detailed mechanistic study.

First, we studied the spectroscopic and electrochemical properties of this two extended enones. As illustrated in Supporting Information, the 2,4-dien-1-one **1a** does not absorb the blue light, only the photocatalyst absorbs the visible light. At room temperature, upon excitation, $Ru(bpy)_3Cl_2$ showed an emission with a maximal wavelength (λ_{max}) of 573 nm (Figure S1).[13] The above emission was quenched by **1a** with a rate constant of 9.70×10^8 $M^{-1} \cdot s^{-1}$ (Figure S2).[14] Based on electrochemical data [$E_{Ru(III/II^*)}$= - 1.14 V vs SCE, $E_{(1a/1a^{\cdot-})}$ < -1.2 V vs SCE, ΔG > 0.06 eV; $E_{Ru(II^*/I)}$ = 1.17 V vs SCE, $E_{(2a^{+\cdot}/2a)}$ = 1.44 V vs SCE, ΔG = 0.27 eV] (Table 3, Figure S5), SET process of the excited $Ru(bpy)_3Cl_2$ to **1a** and **2a** seemed unlikely. Similar analysis of the photophysical and electrochemical data of 2-oxo-3-enoate **4a** and $Ru(phen)_3(PF_6)_2$ indicated that

in this pair the electron transfer pathway was likely. From absorption spectra, the enoate ester **4a** absorbed the blue light weakly, while the photocatalyst did strongly (Figure S3). And the emission of excited $Ru(phen)_3(PF_6)_2$ at 600 nm was quenched by **4a** with the rate constant of 8.08×10^8 $M^{-1} \cdot s^{-1}$ (Figure S4). According to the electrochemical data in acetone [$E_{Ru(III/II^*)}$= -0.97 V vs SCE, $E_{(4a/4a^{\cdot-})}$= -0.86 V vs SCE, ΔG = -0.11 eV; $E_{Ru(II^*/I)}$= 1.52 V vs SCE, $E_{(2a^{+\cdot}/2a)}$> 1.6 V vs SCE, ΔG > 0.08 eV) (Table 3, Figure S6), the excited $Ru(phen)_3(PF_6)_2$ could reduce **4a** to generate relative anion radical theoretically. These data suggested that the addition of **1a** to olefins could proceed by energy transfer pathways and that of **4a** could proceed via both energy and electron transfer pathways.

Table 3. Redox potentials of each component [a]

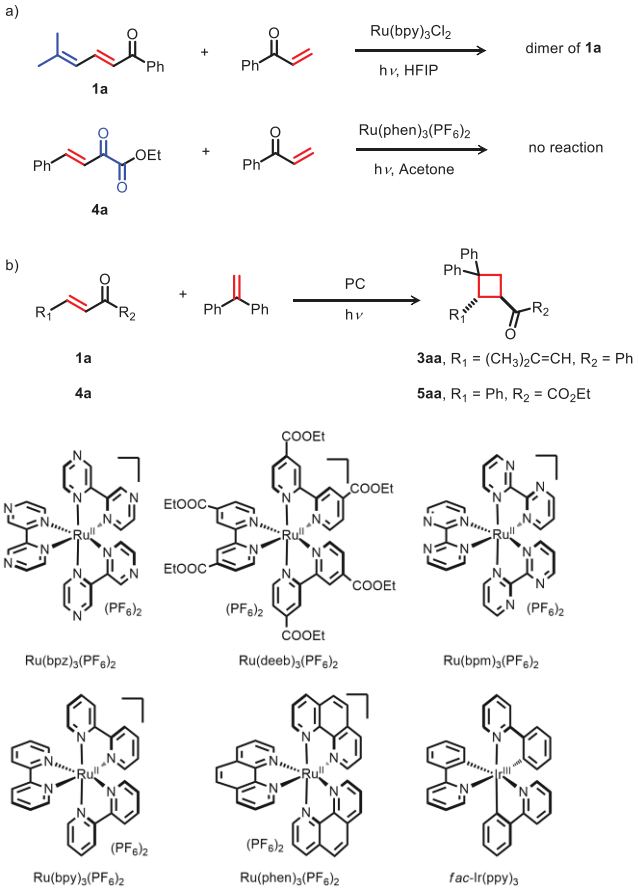
Entry	Compound	$E_{1/2}$ (M^+/M)	$E_{1/2}$ (M/M^-)	$E_{1/2}$ (M^+/M^*)	$E_{1/2}$ (M^*/M^-)
1[b]	**1a**	> 1.6	< -1.2	/	/
2[b]	**2a**	1.44	< -1.2	/	/
3[b]	$Ru(bpy)_3^{2+}$	1.23	< -1.2	-1.14	< 1.17
4[c]	**4a**	0.84	-0.86	/	/
5[c]	**2a**	> 1.6	-0.87	/	/
6[c]	$Ru(phen)_3^{2+}$	1.35	< -0.8	-0.97	< 1.52

[a] All potentials were detected in volts versus SCE. [b] Detected in hexafluoroisopropanol. [c] Detected in .actone.

In order to narrow down the energy/electron transfer pathways involved in cycloaddition reactions of extended enones, several ruthenium and iridium complexes[3c] with varied photoredox potentials and triplet energies were examined (Scheme 4). Surprisingly, electron-deficient

$Ru(deeb)_3(PF_6)_2$ could catalyse the cross [2+2] cycloaddition of 2-oxo-3-enoate **4a** and olefin **2a** at nearly quantitative conversion to cyclobutane **5aa**, indicating that an unfavourable electron transfer pathway did not arrest the reaction. On the other hand, $Ir(ppy)_3$ that enabled electron-transfer to **4a** gave cycloadduct **5aa** in lower yields (25%). These observations suggested that the electron transfer pathway for **4a** was not involved during addition and most likely the photoctalysts act as energy transfer sensitizers. Yoon has reported that if a SET process is involved in the case of enones, the generated nucleophilic species would react readily with a terminal enone like acrylophenone.[7a] The fact that the homo-dimerization of **1a** occurred when acrylophenone instead of **2a** was used as the partner olefin suggested that the reactions of 2,4-dien-1-ones do not proceed via SET process. Most likely, in this case also energy transfer plays the primary role.

Scheme 4. Control experiments



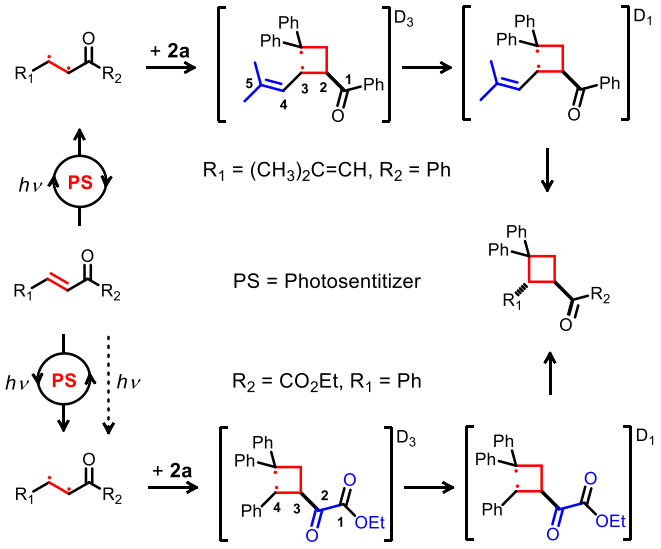
Entry	PC	E^{Ox*} (V)	E^{Red*} (V)	E_T (kJ/mol)	**3aa** (%[-])	**5aa** (%[-])
1	$Ru(bpz)_3^{2+}$	1.45	-0.26	198.32	13	42
2	$Ru(deeb)_3^{2+}$	1.07	-0.42	187.14	39	97
3	$Ru(bpm)_3^{2+}$	0.99	-0.26	190.73	22	61
4	$Ru(phen)_3^{2+}$	0.82	-0.87	201.66	73	98
5	$Ru(bpy)_3^{2+}$	0.77	-0.81	195.08	81	96
6	*fac*-$Ir(ppy)_3$	0.31	-1.73	213.03	58	25

[a] The reaction were carried out in 2.5 mL solvent with 0.1 mmol **1a** and **4a**, 10 eq acrylophenone and 2 mol % PC under the irradiation of Blue-LEDs (λ = 455 nm) for 10 h. [b] The reaction were carried out in 2.5 mL solvent with 0.1 mmol **1a** and **4a**, indicated amount of **2a** and 2 mol % PC under the irradiation of Blue-LEDs (λ = 455 nm) for 10 h. All the yields were determined by ^{1}H-NMR using biphenylacetonitrile as internal standard. The E^{Ox*} and E^{Red*} cames form literatures [10], E_T came from luminescence spectra (Figure S7).

To understand why the [2+2] reaction of 2,4-dien-1-ones **1a** selectively occur in the C=C bond adjacent to carbonyl group and why cyclobutane rather than oxetane was preferred during the addition of triplet 2-oxo-3-enoates **4a** to olefins upon sentitization, density functional theory (DFT)[15] calculations were performed (see SI). For the former system, the relevant transition state barriers for olefin additions to different positions of **1a** (C1, C2, C3, C4, C5 position in top half of Scheme 5, Figure S10) showed that the attack on C2 position had the lowest barrier with only 7.5 kcal/mol, to result in the relevant diradical intermediate. The second lowest energy barrier pathway was for the addition to C5 position (10.7 kcal/mol). Additions to other positions had much higher barriers and the resuting diradical intermediates were much less stable (Scheme S1). Besides, distortion/interaction analysis for the first C-C bond formation between **1a** and **2a** indicated a favourable interaction energy for the attack on C2 by 3.4 kcal/mol compared with C5 (Figure S11). In this case, the regioselectivity of [2+2] reaction of 2,4-dien-1-ones may stem from the interaction energy and transition state barriers to generate the first C-C bond. In terms of 2-oxo-3-enoates **4a**, the relevant transition state barriers for olefin additions to result in the diradical intermediate (C1, C2, C3, C4, C5 position in lower half of scheme 5, Figure S14) found that the addition to C3 position has the lowest 6.9 kcal/mol barrier and the addition to oxygen atom next to C2 gave the second lowest energy barrier with 8.4 kcal/mol. Other situations (add to C1 with 27.7 kcal/mol, C2 with 21.1 kcal/mol, C4 with 10.9 kcal/mol and oxygen atom in ester group with 19.6 kcal/mol) owned much higher barriers. The final cyclobutane product via lowest barrier was found to be more thermodynamic stable than the oxetane generated through second lowest barrier way with 17.7 kcal/mol. Distortion/interaction analysis for the first bond formation between **4a** and **2a** indicated a favourable interaction energy for the formation of C-C bond with

C3, which was 4.0 kcal/mol lower than the formation of C-O bond with oxygen atom in C2 (Figure S14). Therefore, the selectivity for 2-oxo-3-enoate system not only depends on the energy advantages on the first bond formation but also comes from the stability of cyclobutane skeleton.

Scheme 5. Proposed mechanism of the [2+2] crossed cycloadditions via energy transfer.



Based on the above data from theoretical computation we propose the mechanism shown in Scheme 5. Upon visible light excitation, the excited ruthenium complexes intersystem crossed to the triplet state and transferred energy to the extended enones, which led to the generation of excited enones. The excited enones further reacted with ground state terminal olefins to result in 1,4-diradical intermediate in a high-selective way and subsequently cyclized to generate cyclobutanes. It should be noted that upon direct excitation, 2-oxo-3-enoates could be directly excited to undergo [2+2] reaction to get 56% yield and 9:1 d.r. The paticipitation of sensitizer $Ru(phen)_3(PF_6)_2$ led to higher efficiency in both yield and selectivity.

Conclusion

In conclusion, several 2,4-dien-1-ones and 2-oxo-3-enoates were designed to investigate the excited state behaviour of extended enones towards terminal olefins. Under carefully optimized conditions, these two substrates undergo intermolecular cross [2+2] cycloaddition with olefins to produce cyclobutanes with high regio- and diasteroseletivities. Mechanistic studies involving spectral, electrochemical data and control experiments confirmed the energy transfer from photocatalyst to extended enones, playing an important role in the cycloaddition process. DFT calculation demonstrated the origin of high selectivity of this [2+2] process. We believe this detailed study of the cross [2+2] reaction of extended enones (extension with C=C and C=O bond) would provide much possibility for the elaborate construction of highly functional cyclobutanes. Further exploration on visible light induced [2+2] reaction is underway in our laboratory.

Experimental Section

General Information: ^{1}H NMR spectra were recorded using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals. Blue LEDs (3 W, $\lambda = 450 \pm 10$ nm, 145 lm @700mA) were used as the irradiation light source. Mass spectra were recorded using a Trio-2000 GC-MS spectrometer and an ApexIII (7.0 tesla) FTICR mass spectrometer (Bruker). Excitation was provided by using an Nd:YAG laser (third harmonic, 10 ns) at 405 nm. The detector was a Xenon lamp on the Edingburgh LP920 apparatus from Analytical Instruments. The values of lifetime were calculated by exponential function fitting with luminescence spectrometer software L900. UV-Vis absorption spectra were recorded with a Shimadzu 1601PC

spectrophotometer. Photoluminescence (PL) measurements were performed at room temperature using a Hitachi 4500 fluorescence spectrophotometer and a Perkin–Elmer LS50B spectrofluorimeter. Commercially available reagents and solvents were used without further purification. Reaction substrates 2,4-dien-1-ones[16], 2-oxo-3-enoates[17] and photocatalyst **Ru(deeb)$_3$(PF$_6$)$_2$**[18] were prepared according to the procedures in the literatures. For the irradiation, the material of the reaction vessel is common glass; the distance from the light source to the irradiation is about 0.5 cm. No use of filters was used in the general procedures.

General procedure for the cross intermolecular [2 + 2] cycloaddition of 2,4-dien-1-ones and olefins: A 10 mL Pyrex tube equipped with a magnetic stirring bar was charged with 2,4-dien-1-one (**1**, 0.1 mmol), 1,1-disubstituted olefins (**2**, 0.12 mmol), Ru(bpy)$_3$Cl$_2$ (2 mol%) in 2.5 mL HFIP. The mixture was degassed with Nitrogen and irradiated by blue LEDs (λ = 450 nm) for 10 hours at room temperature, then the solution was concentrated *in vacuo*. The diastereomer ratios were determined by ^{1}H-NMR analysis of the crude reaction mixture, and the yield was determined using diphenylacetonitrile as an internal standard. The residue was purified by column chromatography on silica gel to get the isolated [2+2] products.

*DL-((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)(phenyl)methanone (**3aa**):* Isolated yield : 29.4 mg, 80%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 – 7.90 (m, 2H), 7.60 – 7.53 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.36 (m, 4H), 7.36 – 7.24 (m, 3H), 7.22 – 7.15 (m, 3H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.13 (dd, *J* = 19.8, 9.9 Hz, 1H), 3.97 – 3.88 (m, 1H), 3.25 (dd, *J* = 11.8, 7.7 Hz, 1H), 2.92 (dd, *J* = 11.7, 10.5 Hz, 1H), 1.63 (d, *J* = 0.9 Hz, 3H), 1.58 (d, *J* = 1.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 200.2, 151.3, 143.1, 136.5, 134.6, 133.0, 128.7, 128.42,

128.36, 128.2, 126.2, 125.8, 124.6, 51.8, 47.4, 45.2, 33.7, 26.0, 18.4. HRMS (ESI) calculated for $C_{27}H_{26}NaO^+$ $[M+Na]^+$: 389.1876, found: 389.1862.

*DL-((1S,2S,3S,4S)-3,4-bis(2-methylprop-1-en-1-yl)cyclobutane-1,2-diyl)bis(phenylmethanone) (**dimer of 1a**):* Isolated yield : 16.4 mg, 44%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 4H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 4H), 5.35 (d, *J* = 7.3 Hz, 2H), 4.25 – 4.12 (m, 2H), 3.10 – 2.99 (m, 2H), 1.68 (s, 6H), 1.31 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.5, 136.1, 135.3, 133.1, 128.9, 128.3, 126.6, 46.7, 42.9, 25.7, 18.3. HRMS (ESI) calculated for $C_{26}H_{28}NaO_2^+$ $[M+Na]^+$: 395.1982, found: 395.1967.

*DL-((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)(p-tolyl)methanone (**3ba**)*: Isolated yield : 29.7 mg, 78%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.20 – 7.08 (m, 5H), 7.07 – 7.01 (m, 3H), 4.63 (d, *J* = 10.5 Hz, 1H), 3.98 (t, *J* = 10.0 Hz, 1H), 3.76 (dd, *J* = 18.0, 9.7 Hz, 1H), 3.09 (dd, *J* = 11.7, 7.8 Hz, 1H), 2.76 (t, *J* = 11.1 Hz, 1H), 2.29 (s, 3H), 1.50 (s, 3H), 1.46 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.6, 150.2, 142.6, 142.0, 133.3, 132.9, 127.9, 127.7, 127.3, 127.2, 127.0, 125.1, 125.0, 124.6, 123.6, 50.7, 46.2, 43.9, 32.6, 24.9, 20.6, 17.3. HRMS (ESI) calculated for $C_{28}H_{28}NaO^+$ $[M+Na]^+$: 403.2032, found: 403.2017.

*DL-(4-methoxyphenyl)((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)methanone (**3ca**):* Isolated yield : 32.5 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) 1H NMR (400 MHz, CDCl3) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.28 – 7.19 (m, 3H), 7.17 – 7.09 (m, 3H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.71 (d, *J* = 10.5 Hz, 1H), 4.05 (t, *J* = 10.1 Hz, 1H), 3.86 – 3.75 (m, 4H), 3.16 (dd, *J* = 11.8, 7.8 Hz, 1H), 2.86 (t, *J* = 11.1 Hz, 1H), 1.58 (s, 3H), 1.55 (s, 3H). ^{13}C{^{1}H} NMR (101

MHz, $CDCl_3$) δ 198.5, 163.4, 151.3, 143.1, 134.4, 130.9, 129.5, 128.4, 128.3, 128.1, 126.2, 126.1, 125.7, 124.7, 113.5, 55.4, 51.7, 47.3, 44.8, 33.5, 25.9, 18.4. HRMS (ESI) calculated for $C_{28}H_{28}NaO_2^+$ $[M+Na]^+$: 419.1982, found: 419.1965.

*DL-(2-methoxyphenyl)((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)methanone (**3da**):* Isolated yield : 32.5 mg, 82%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.15 (m, 7H), 7.15 – 7.09 (m, 3H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.56 (d, *J* = 10.2 Hz, 1H), 4.11 – 3.89 (m, 2H), 3.82 (s, 3H), 3.23 (dd, *J* = 11.5, 7.7 Hz, 1H), 2.61 (t, *J* = 10.9 Hz, 1H), 1.56 (s, 3H), 1.51 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.0, 158.5, 151.4, 143.3, 133.2, 132.9, 130.4, 128.3, 128.2, 127.9, 126.2, 125.9, 125.7, 125.1, 120.5, 111.2, 55.4, 51.6, 48.5, 46.6, 34.7, 26.0, 18.1. HRMS (ESI) calculated for $C_{28}H_{28}NaO_2^+$ $[M+Na]^+$: 419.1982, found: 419.1966.

*DL-(3-methoxyphenyl)((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)methanone (**3ea**):* Isolated yield : 31.7 mg, 80%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 2H), 7.40 – 7.34 (m, 4H), 7.34 – 7.28 (m, 3H), 7.28 – 7.22 (m, 1H), 7.20 – 7.15 (m, 3H), 7.13 – 7.05 (m, 1H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.13 (t, *J* = 10.0 Hz, 1H), 3.94 – 3.85 (m, 1H), 3.83 (s, 3H), 3.24 (dd, *J* = 11.8, 7.8 Hz, 1H), 2.95 – 2.88 (m, 1H), 1.64 (s, 3H), 1.62 (s, 3H). ^{13}C {1H} NMR (101 MHz, $CDCl_3$) δ 199.9, 159.9, 151.3, 143.2, 138.1, 134.6, 129.4, 128.5, 128.4, 128.2, 126.2, 125.8, 124.9, 121.4, 119.5, 113.1, 55.5, 51.9, 47.4, 45.4, 33.9, 26.0, 18.5. HRMS (ESI) calculated for $C_{28}H_{28}NaO_2^+$ $[M+Na]^+$: 419.1982, found: 419.1967.

*DL-(4-fluorophenyl)((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)methanone (**3fa**):* Isolated yield : 27.0 mg, 70%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.8, 5.5 Hz, 2H),

7.38 (d, *J* = 4.3 Hz, 4H), 7.35 – 7.24 (m, 3H), 7.22 – 7.16 (m, 3H), 7.09 (t, *J* = 8.6 Hz, 2H), 4.80 (d, *J* = 10.6 Hz, 1H), 4.10 (t, *J* = 10.1 Hz, 1H), 3.89 (td, *J* = 10.0, 7.9 Hz, 1H), 3.24 (dd, *J* = 11.8, 7.7 Hz, 1H), 2.95 (t, 1H), 1.65 (s, 3H), 1.59 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.5, 165.9 (d, J_{C-F} = 254.5 Hz), 151.3, 143.2, 134.8, 133.1 (d, J_{C-F} = 0.13 Hz), 131.4 (d, J_{C-F} = 9.2 Hz), 128.6, 128.5, 128.3, 126.4, 126.3, 126.0, 124.8, 115.5 (d, J_{C-F} = 21.8 Hz), 52.0, 47.8, 45.2, 33.6, 26.1, 18.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -105.48 (s). HRMS (ESI) calculated for $C_{27}H_{25}NaFO^+$ $[M+Na]^+$: 407.1782, found: 407.1766.

DL-(4-chlorophenyl)((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)methanone (**3ga**): Isolated yield : 28.1 mg, 70%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.36 (m, 6H), 7.36 – 7.24 (m, 3H), 7.24 – 7.16 (m, 3H), 4.81 (d, *J* = 10.6 Hz, 1H), 4.11 (t, *J* = 10.1 Hz, 1H), 3.94 – 3.82 (m, 1H), 3.24 (dd, *J* = 11.8, 7.7 Hz, 1H), 3.00 – 2.90 (m, 1H), 1.66 (s, 3H), 1.60 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.9, 151.3, 143.1, 139.6, 135.1, 134.9, 130.2, 128.8, 128.6, 128.5, 128.3, 126.4, 126.3, 126.0, 124.8, 52.0, 47.8, 45.3, 33.6, 26.1, 18.6. HRMS (ESI) calculated for $C_{27}H_{25}NaClO^+$ $[M+Na]^+$: 423.1486, found: 423.1471.

*DL-(4-bromophenyl)((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)methanone (**3ha**):* Isolated yield : 30.3 mg, 68%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.34 – 7.23 (m, 3H), 7.22 – 7.12 (m, 3H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.07 (t, *J* = 10.1 Hz, 1H), 3.91 – 3.79 (m, 1H), 3.21 (dd, *J* = 11.8, 7.7 Hz, 1H), 2.98 – 2.88 (m, 1H), 1.64 (s, 3H), 1.57 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 199.0, 151.1, 143.0, 135.4, 134.8, 131.7, 131.0, 130.2, 128.43, 128.42, 128.2, 126.3, 126.2, 125.9, 124.7, 51.9, 47.7, 45.2, 33.5, 26.0, 18.5. HRMS (ESI) calculated for $C_{27}H_{25}NaBrO^+$ $[M+Na]^+$: 467.0981, found: 467.0965.

*DL-((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)(4-(trifluoromethyl)phenyl)methanone (**3ia**):* Isolated yield : 29.1 mg, 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.24 (m, 7H), 7.22 – 7.16 (m, 3H), 4.80 (d, *J* = 10.6 Hz, 1H), 4.11 (t, *J* = 10.1 Hz, 1H), 3.91 (td, *J* = 9.9, 7.9 Hz, 1H), 3.26 (dd, *J* = 11.8, 7.7 Hz, 1H), 2.95 (dd, *J* = 11.7, 10.5 Hz, 1H), 1.64 (s, 3H), 1.57 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 151.1, 142.9, 139.4, 135.0, 134.4 (q, J_{C-F} = 32.6 Hz), 129.0, 128.44, 128.41, 128.2, 126.3, 126.1, 126.0, 125.4 (q, J_{C-F} = 3.7 Hz), 124.6, 123.8 (q, J_{C-F} = 272.7 Hz), 52.0, 47.7, 45.6, 33.4, 25.9, 18.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.08 (s). HRMS (ESI) calculated for $C_{28}H_{25}NaF_3O^+$ $[M+Na]^+$: 457.1750, found: 457.1737.

*DL-((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)(4-nitrophenyl)methanone (**3ja**):* Isolated yield: 12.7 mg, 31%..^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.15 (m, 7H), 7.12 – 7.01 (m, 3H), 4.67 (d, *J* = 10.5 Hz, 1H), 3.95 (t, *J* = 10.1 Hz, 1H), 3.79 (dd, *J* = 17.7, 9.7 Hz, 1H), 3.13 (dd, *J* = 11.9, 7.6 Hz, 1H), 2.84 (t, *J* = 11.1 Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 197.6, 149.7, 149.2, 141.4, 139.8, 134.2, 128.6, 127.3, 127.18, 127.15, 125.3, 124.91, 124.88, 123.2, 122.4, 50.8, 46.8, 44.6, 31.8, 24.9, 17.4. HRMS (ESI) calculated for $C_{27}H_{25}NO_3Na^+$ $[M+Na]^+$: 434.1727, found: 434.1714 .

*DL-((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutyl)(naphthalen-2-yl)methanone (**3ka**):* Isolated yield : 15.4 mg, 37%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 4.2 Hz, 4H), 7.20 – 7.12 (m, 3H), 7.08 – 7.01 (m, 3H), 4.74 (d, *J* = 10.3 Hz, 1H), 4.04 – 3.83 (m, 2H), 3.13 (dd, *J* = 11.9, 7.5 Hz, 1H), 2.89 (t, *J* = 11.0 Hz, 1H), 1.48 (s, 3H), 1.32 (s, 3H). ^{13}C{1H}

NMR (101 MHz, $CDCl_3$) δ 200.0, 151.3, 143.1, 135.6, 134.8, 133.8, 132.5, 130.7, 129.5, 128.45, 128.40, 128.3, 128.2, 127.82, 127.79, 126.7, 126.2, 126.1, 125.8, 124.8, 124.3, 51.8, 47.9, 45.3, 33.1, 26.0, 18.4. HRMS (ESI) calculated for $C_{31}H_{28}NaO^+$ $[M+Na]^+$: 439.2032, found: 439.2019.

*DL-(1R,2S)-ethyl 2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutanecarboxylate (**3la**):* Isolated yield : 13.4 mg, 40%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 6H), 7.07 – 6.97 (m, 4H), 4.51 (d, *J* = 10.3 Hz, 1H), 4.05 – 3.94 (m, 3H), 3.09 (dd, *J* = 11.4, 8.1 Hz, 1H), 2.87 (dd, *J* = 18.4, 9.9 Hz, 1H), 2.52 (t, *J* = 11.1 Hz, 1H), 1.72 (s, 3H), 1.52 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.1, 150.0, 141.4, 132.6, 127.2, 127.1, 126.9, 125.0, 124.7, 123.4, 59.3, 51.1, 45.8, 40.6, 33.2, 24.9, 17.4, 13.2. HRMS (ESI) calculated for $C_{23}H_{26}O_2Na^+$ $[M+Na]^+$: 357.1825, found: 357.1813.

*DL-(1R,2S)-tert-butyl 2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutanecarboxylate (**3ma**):* Isolated yield : 15.2 mg, 42%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 6H), 7.10 – 7.02 (m, 4H), 4.51 (d, *J* = 10.4 Hz, 1H), 3.93 (t, *J* = 10.1 Hz, 1H), 3.11 – 2.97 (m, 1H), 2.79 (dd, *J* = 18.3, 9.9 Hz, 1H), 2.49 (t, *J* = 11.1 Hz, 1H), 1.74 (s, 3H), 1.54 (s, 3H), 1.32 (s, 9H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.6, 151.3, 142.7, 133.2, 128.3, 128.2, 127.9, 126.1, 126.0, 125.7, 124.8, 80.1, 52.0, 47.1, 42.6, 34.1, 28.1, 26.0, 18.6. HRMS (ESI) calculated for $C_{25}H_{30}O_2Na^+$ $[M+Na]^+$: 385.2138, found: 385.2124.

*DL-(1R,2S)-phenyl 2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutanecarboxylate (**3na**):* Isolated yield : 11.1 mg, 29%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 8H), 7.26 – 7.20 (m, 5H), 7.11 – 7.06 (m, 2H),, 4.75 (d, *J* = 10.4 Hz, 1H), 4.30 (t, *J* = 10.0 Hz, 1H), 3.37 (dd, *J* = 11.3, 8.0 Hz, 1H), 3.32 – 3.24 (m, 1H), .2.83 (t, *J* = 10.8 Hz, 1H), 1.94 (s, 3H), 1.71 (s, 3H). $^{13}C\{1H\}$

NMR (101 MHz, $CDCl_3$) δ 172.7, 151.1, 151.0, 142.5, 134.3, 129.5, 128.5, 128.3, 128.2, 126.3, 126.2, 126.0, 125.8, 124.4, 121.6, 52.6, 47.3, 42.0, 34.5, 26.1, 18.7. HRMS (ESI) calculated for $C_{27}H_{26}O_2Na^+$ $[M+Na]^+$: 405.1825, found: 405.1811.

*DL-(1R,2S)-benzyl 2-(2-methylprop-1-en-1-yl)-3,3-diphenylcyclobutanecarboxylate (**3oa**):* Isolated yield : 16.2 mg, 41%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 5H), 7.38 – 7.31 (m, 6H), 7.29 – 7.21 (m, 4H), 5.21 (q, *J* = 12.4 Hz, 2H), 4.73 (d, *J* = 10.4 Hz, 1H), 4.21 (t, *J* = 10.1 Hz, 1H), 3.30 (dd, *J* = 11.4, 7.9 Hz, 1H), 3.20 – 3.10 (m, 1H), 2.77 (t, *J* = 11.0 Hz, 1H), 1.84 (s, 3H), 1.71 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.1, 151.2, 142.6, 136.4, 134.0, 128.7, 128.5, 128.4, 128.3, 128.23, 128.16, 126.3, 126.2, 126.0, 124.7, 66.3, 52.6, 47.3, 41.8, 34.4, 26.1, 18.6. HRMS (ESI) calculated for $C_{28}H_{28}O_2Na^+$ $[M+Na]^+$: 419.1982, found: 419.1964.

*DL-((1R,2S)-2-(2-methylprop-1-en-1-yl)-3,3-di-p-tolylcyclobutyl)(phenyl)methanone (**3ab**):* Isolated yield : 29.7 mg, 75%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.91 (d, *J* = 10.5 Hz, 1H), 4.17 (t, *J* = 10.1 Hz, 1H), 4.04 – 3.95 (m, 1H), 3.29 (dd, *J* = 11.7, 7.7 Hz, 1H), 2.96 (dd, *J* = 11.5, 10.6 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H), 1.74 (s, 3H), 1.66 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 201.0, 149.4, 141.2, 137.6, 136.4, 135.9, 135.1, 133.7, 129.8, 129.7, 129.5, 129.2, 129.1, 126.8, 125.8, 52.1, 48.2, 46.1, 34.8, 26.7, 21.9, 21.8, 19.2. HRMS (ESI) calculated for $C_{29}H_{30}ONa^+$ $[M+Na]^+$: 417.2189, found: 417.2173.

*DL-((1R,2S)-3,3-bis(4-methoxyphenyl)-2-(2-methylprop-1-en-1-yl)cyclobutyl)(phenyl)methanone (**3ac**):* Isolated yield : 15.5 mg, 35%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H),

6.90 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.77 (d, *J* = 10.4 Hz, 1H), 4.01 (t, *J* = 10.0 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.13 (dd, *J* = 11.7, 7.7 Hz, 1H), 2.90 – 2.78 (m, 1H), 1.61 (s, 3H), 1.53 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.2, 158.0, 157.7, 143.9, 136.7, 135.8, 134.4, 132.9, 129.4, 128.7, 128.3, 127.1, 124.9, 113.8, 113.5, 55.3, 50.7, 47.5, 45.2, 34.1, 29.8, 25.9, 18.4. HRMS (ESI) calculated for $C_{29}H_{30}O_3Na^+$ $[M+Na]^+$: 449.2087, found: 449.2072.

*DL-((1R,2S)-3,3-bis(4-fluorophenyl)-2-(2-methylprop-1-en-1-yl)cyclobutyl)(phenyl)methanone (**3ad**):* Isolated yield : 32.2 mg, 80%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.20 – 7.10 (m, 4H), 7.09 – 7.02 (m, 2H), 4.77 (d, *J* = 10.4 Hz, 1H), 4.10 (t, *J* = 10.0 Hz, 1H), 4.01 – 3.83 (m, 1H), 3.21 (dd, *J* = 11.9, 7.7 Hz, 1H), 2.94 (dd, *J* = 11.8, 10.5 Hz, 1H), 1.69 (d, *J* = 0.6 Hz, 3H), 1.61 (d, *J* = 0.7 Hz, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.6, 162.3 (d, J_{C-F} = 245.7 Hz), 162.0 (d, J_{C-F} = 244.7 Hz), 147.6 (d, J_{C-F} = 3.3 Hz), 139.6 (d, J_{C-F} = 3.1 Hz), 137.3, 136.0, 133.9, 130.7 (d, J_{C-F} = 7.8 Hz), 129.5, 129.2, 128.4 (d, J_{C-F} = 7.8 Hz), 125.0, 116.0 (d, J_{C-F} = 21.3 Hz), 115.8 (d, J_{C-F} = 21.1 Hz), 51.8, 48.2, 45.7, 34.8, 26.7, 19.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.93 (s), -117.00 (s). HRMS (ESI) calculated for $C_{27}H_{24}F_2ONa^+$ $[M+Na]^+$: 425.1687, found: 425.1673.

*DL-((1R,2S)-3,3-bis(4-chlorophenyl)-2-(2-methylprop-1-en-1-yl)cyclobutyl)(phenyl)methanone (**3ae**):* Isolated yield : 14.8 mg, 34%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.57 – 7.50 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.19 (m, 4H), 7.08 – 7.01 (m, 2H), 4.71 (d, *J* = 10.5 Hz, 1H), 4.02 (t, *J* = 10.0 Hz, 1H), 3.89 – 3.78 (m, 1H), 3.12 (dd, *J* = 11.9, 7.7 Hz, 1H), 2.84 (dd, *J* = 11.9, 10.4 Hz, 1H), 1.61 (d, *J* = 0.9 Hz, 3H), 1.53 (d, *J* = 1.1 Hz, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.5, 150.0, 142.1, 137.3, 136.3, 133.9, 133.3, 132.7, 130.6,

129.5, 129.3, 129.2, 128.4, 124.9, 52.0, 48.1, 45.7, 34.5, 26.4, 19.3. HRMS (ESI) calculated for $C_{27}H_{24}OCl_2Na^+$ $[M+Na]^+$: 457.1096, found: 457.1082.

DL-((1R,2S)-3,3-bis(4-bromophenyl)-2-(2-methylprop-1-en-1-yl)cyclobutyl)(phenyl)methanone ***(3af)****:* Isolated yield : 31.0 mg, 59%. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.69 (d, *J* = 10.5 Hz, 1H), 3.99 (t, *J* = 10.0 Hz, 1H), 3.82 (dd, *J* = 18.0, 9.5 Hz, 1H), 3.09 (dd, *J* = 11.9, 7.7 Hz, 1H), 2.81 (t, *J* = 11.1 Hz, 1H), 1.59 (s, 3H), 1.50 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 199.6, 149.1, 141.6, 136.1, 135.0, 133.2, 131.3, 131.0, 130.1, 128.4, 128.0, 127.2, 123.0, 120.5, 119.9, 51.4, 47.1, 44.8, 33.4, 25.3, 18.4. HRMS (ESI) calculated for $C_{27}H_{24}OBr_2Na^+$ $[M+Na]^+$: 545.0086, found: 545.0071.

General procedure for the cross intermolecular [2 + 2] cycloaddition of 2-oxo-3-enoates and olefins: A 10 mL Pyrex tube equipped with a magnetic stirring bar was charged with 2-oxo-3-enoates (**4**, 0.1 mmol), 1,1-disubstituted olefins (**2**, 0.12 mmol), $Ru(phen)_3(PF_6)_2$ (2 mol%) in 2.5 mL Acetone. The mixture was degassed with Nitrogen and irradiated by blue LEDs (λ = 450 nm) for 10 hours at room temperature, then the solution was concentrated *in vacuo*. The diastereomer ratios were determined by ^{1}H-NMR analysis of the crude reaction mixture, and the yield was determined using diphenylacetonitrile as an internal standard. The residue was purified by column chromatography on silica gel to get the isolated [2+2] products.

Gram-scale reaction of the cross intermolecular [2 + 2] cycloaddition of 2-oxo-3-enoates and olefins: A 50 mL Pyrex tube equipped with a magnetic stirring bar was charged with 2-oxo-3-enoates (**4a**, 5 mmol), 1,1-disubstituted olefins (**2a**, 6 mmol), $Ru(phen)_3(PF_6)_2$ (2 mol%) in 25 mL Acetone. The mixture was degassed with Nitrogen and irradiated by blue LEDs (λ = 450

nm) for 24 hours at room temperature, then the solution was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to get the isolated [2+2] product in yield of 82% (1.6 g).

H-D Exchange experiment of product *5aa*: In an argon-filled glove box, ***5aa*** (38.4 mg, 0.1 mmol, 1.0 equiv), Cs_2CO_3 (98 mg, 0.3 mmol, 3.0 equiv) and DMSO-d_6 (1 mL) were added into a dry 10-mL Schlenk tube. The reaction mixture was capped tightly and vigorously stirred in an oil bath maintained at 100 °C for 8 h. After cooled down to RT, the reaction mixture was filtered through a celite pad. The filtrate was analyzed by ^{1}H NMR and ^{13}CNMR spectroscopy. The hydrolysis of ester gourp was caused by trace water in system which was detected by ^{1}H NMR before reaction. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 – 7.28 (m, 2H), 7.29 – 7.23 (m, 2H), 7.19 – 7.13 (m, 1H), 7.10 – 7.00 (m, 5H), 6.94 – 6.83 (m, 4H), 4.44 (s, 1H), 3.27 (d, J = 11.5 Hz, 1H), 2.38 (d, J = 11.6 Hz, 1H). ^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ 205.7, 168.6, 151.1, 142.3, 139.5, 128.5, 128.3, 127.44, 127.42, 126.1, 126.0, 125.61, 125.59, 79.1, 56.0, 53.0, 50.7, 42.3 (t, $J_{C\text{-}D}$ = 21.1 Hz), 34.8, 18.4.

*DL-ethyl 2-oxo-2-((1R,2R)-2,3,3-triphenylcyclobutyl)acetate (**5aa**):* Isolated yield : 35.4 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 4H), 7.27 – 7.12 (m, 7H), 7.12 – 7.06 (m, 2H), 7.02 – 6.94 (m, 2H), 4.67 (d, J = 10.5 Hz, 1H), 4.36 (dt, J = 10.4, 8.6 Hz, 1H), 4.23 – 4.07 (m, 2H), 3.48 (dd, J = 11.6, 8.3 Hz, 1H), 2.80 (t, J = 11.1 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 194.4, 161.6, 150.7, 141.6, 138.4, 129.2, 128.9, 128.7, 128.1, 128.0, 127.2, 126.5, 126.4, 126.3, 62.4, 54.1, 52.7, 44.1, 34.0, 14.0. HRMS (ESI) calculated for $C_{26}H_{24}O_3Na^+$ $[M + Na]^+$: 407.1618, Found: 407.1622.

*DL-ethyl 2-((1R,2R)-2-(4-fluorophenyl)-3,3-diphenylcyclobutyl)-2-oxoacetate (**5ba**):* Isolated yield : 31.8 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.25 – 7.12 (m, 4H), 7.07 – 7.01 (m, 2H), 6.91 – 6.78 (m, 4H), 4.58 (d, *J* = 10.5 Hz, 1H), 4.31 – 4.08 (m, 3H), 3.44 (dd, *J* = 11.7, 8.3 Hz, 1H), 2.74 (t, *J* = 11.0 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 162.6 (d, J_{C-F} = 246.0 Hz), 161.9, 161.4, 150.8, 141.8, 134.7 (d, J_{C-F} = 3.0 Hz), 131.1 (d, J_{C-F} = 8.0 Hz), 129.4, 129.1, 128.6, 127.1, 126.8, 115.3 (d, J_{C-F} = 21.2 Hz), 63.0, 54.5, 52.3, 44.8, 34.4, 14.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.32 (s). HRMS (ESI) calculated for $C_{26}H_{23}FO_3Na^+$ $[M+Na]^+$: 425.1523, found: 425.1517.

*DL-ethyl 2-((1R,2R)-2-(4-chlorophenyl)-3,3-diphenylcyclobutyl)-2-oxoacetate (**5ca**):* Isolated yield : 35.6 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 4H), 7.23 – 7.12 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.54 (d, *J* = 10.5 Hz, 1H), 4.26 – 4.07 (m, 3H), 3.42 (dd, *J* = 11.7, 8.3 Hz, 1H), 2.72 (t, *J* = 11.1 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 194.4, 161.8, 150.7, 141.6, 137.4, 133.6, 130.9, 129.2, 129.1, 128.7, 128.6, 127.1, 126.8, 126.7, 63.1, 54.5, 52.3, 44.6, 34.5, 14.5. MALDI-TOF calculated for $C_{26}H_{23}ClO_3Na^+$ $[M+Na]^+$: 441.1228, found: 441.1232.

*DL-ethyl 2-((1R,2R)-2-(4-bromophenyl)-3,3-diphenylcyclobutyl)-2-oxoacetate (**5da**):* Isolated yield : 37.5 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.25 – 7.18 (m, 4H), 7.18 – 7.07 (m, 4H), 6.99 (d, *J* = 7.1 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 4.49 (d, *J* = 10.5 Hz, 1H), 4.25 – 4.05 (m, 3H), 3.39 (dd, *J* = 11.6, 8.4 Hz, 1H), 2.68 (t, *J* = 11.1 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 193.8, 161.1, 150.1, 140.9, 137.3, 130.9, 130.7, 128.57, 128.55, 128.1, 126.6, 126.2, 126.1, 121.1, 62.5, 53.7, 51.7, 43.9, 33.8, 13.9. MALDI-TOF calculated for $C_{26}H_{23}BrO_3Na^+$ $[M+Na]^+$: 485.0723, found: 485.0726.

*DL-ethyl 2-((1R,2R)-2-(4-methoxyphenyl)-3,3-diphenylcyclobutyl)-2-oxoacetate (**5ea**):* Isolated yield : 30.6 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 4H), 7.22 – 7.11 (m, 4H), 7.09 – 6.99 (m, 2H), 6.85 – 6.76 (m, 2H), 6.70 – 6.61 (m, 2H), 4.50 (d, *J* = 10.6 Hz, 1H), 4.27 – 4.08 (m, 3H), 3.73 (s, 3H), 3.39 (dd, *J* = 11.6, 8.1 Hz, 1H), 2.71 (t, *J* = 11.2 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 194.9, 162.1, 159.4, 151.2, 142.0, 131.0, 130.7, 129.3, 129.0, 128.5, 126.9, 126.8, 126.6, 113.9, 62.9, 55.8, 54.5, 52.8, 45.0, 34.1, 14.4. MALDI-TOF calculated for $C_{27}H_{26}O_4Na^+$ $[M+Na]^+$: 437.1723, found: 437.1729.

*DL-ethyl 2-((1R,2R)-3,3-diphenyl-2-(p-tolyl)cyclobutyl)-2-oxoacetate (**5fa**):* Isolated yield : 32.6 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.25 – 7.12 (m, 4H), 7.11 – 7.06 (m, 2H), 7.00 – 6.93 (m, 2H), 6.85 – 6.79 (m, 2H), 4.57 (d, *J* = 10.5 Hz, 1H), 4.35 – 4.24 (m, 1H), 4.24 – 4.10 (m, 2H), 3.44 (dd, *J* = 11.6, 8.2 Hz, 1H), 2.76 (t, *J* = 11.2 Hz, 1H), 2.28 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 194.9, 162.1, 151.3, 142.1, 137.2, 135.8, 129.5, 129.3, 129.2, 129.1, 128.5, 126.9, 126.7, 62.9, 54.5, 53.1, 44.8, 34.4, 30.4, 21.6, 14.4. MALDI-TOF calculated for $C_{27}H_{26}NaO_3^+$ $[M+Na]^+$: 421.1774, found:421.1776.

*DL-ethyl 2-((1R,2R)-3,3-diphenyl-2-(o-tolyl)cyclobutyl)-2-oxoacetate (**5ga**):* Isolated yield : 18.7 mg, 47%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.34 – 7.27 (m, 4H), 7.22 – 7.11 (m, 5H), 7.11 – 7.06 (m, 2H), 7.03 – 6.96 (m, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.35 (d, *J* = 7.7 Hz, 1H), 4.85 (d, *J* = 10.2 Hz, 1H), 4.21 – 4.03 (m, 3H), 3.56 (dd, *J* = 11.9, 8.6 Hz, 1H), 2.74 (dd, *J* = 11.9, 10.1 Hz, 1H), 2.45 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Acetone-d_6) δ 194.3, 161.3, 150.3, 141.2, 137.2, 136.2, 130.0, 129.2, 129.1, 128.2, 127.7, 126.5, 126.2, 126.0, 125.0, 61.7, 54.4, 48.6, 44.8, 34.4, 20.0, 13.2. MALDI-TOF calculated for $C_{27}H_{26}NaO_3^+$ $[M+Na]^+$: 421.1774, found: 421.1779.

*DL-ethyl 2-((1R,2R)-3,3-diphenyl-2-(m-tolyl)cyclobutyl)-2-oxoacetate (**5ha**):* Isolated yield : 27.9 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 4H), 7.10 – 6.99 (m, 4H), 6.96 – 6.86 (m, 3H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 4.42 (d, *J* = 10.5 Hz, 1H), 4.17 – 4.09 (m, 1H), 4.09 – 3.97 (m, 2H), 3.31 (dd, *J* = 11.6, 8.2 Hz, 1H), 2.60 (t, *J* = 11.1 Hz, 1H), 2.06 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 194.3, 161.4, 150.5, 141.4, 138.0, 137.3, 129.9, 128.7, 128.5, 127.9, 127.8, 127.7, 126.3, 126.3, 126.2, 126.1, 62.4, 53.8, 52.4, 44.1, 33.8, 21.4, 13.8. MALDI-TOF calculated for $C_{27}H_{26}NaO_3^+$ $[M+Na]^+$: 421.1774, found: 421.1780.

*DL-ethyl 2-((1R,2R)-3,3-diphenyl-2-(4-(trifluoromethyl)phenyl)cyclobutyl)-2-oxoacetate (**5ia**):* Isolated yield : 38.9 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 6H), 7.25 – 7.14 (m, 4H), 7.06 – 6.99 (m, 4H), 4.66 (d, *J* = 10.4 Hz, 1H), 4.36 – 4.23 (m, 1H), 4.23 – 4.11 (m, 2H), 3.48 (dd, *J* = 11.7, 8.4 Hz, 1H), 2.76 (t, *J* = 11.2 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 194.2, 161.7, 150.5, 143.0, 141.5, 129.9 (q, J_{C-F} = 32.4 Hz), 129.9, 129.2, 129.1, 128.7, 127.3, 126.9, 126.7, 125.4 (q, J_{C-F} = 3.7 Hz), 125.2 (q, J_{C-F} = 273.0 Hz), 63.1, 54.6, 52.3, 44.4, 34.8, 14.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.43 (s). MALDI-TOF calculated for $C_{27}H_{23}F_3NaO_3^+$ $[M+Na]^+$: 475.1492, found: 475.1491.

*DL-ethyl 2-((1R,2R)-2-(4-cyanophenyl)-3,3-diphenylcyclobutyl)-2-oxoacetate (**5ja**):* Isolated yield : 35.2 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.16 (m, 3H), 7.16 – 7.09 (m, 3H), 7.00 – 6.93 (m, 4H), 4.62 (d, *J* = 10.4 Hz, 1H), 4.30 – 4.12 (m, 3H), 3.44 (dd, *J* = 11.6, 8.6 Hz, 1H), 2.70 (t, *J* = 11.2 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 193.3, 160.8, 149.5, 143.7, 140.7, 131.6, 129.6, 128.6, 128.4,

128.2, 126.8, 126.4, 126.1, 118.8, 110.7, 62.6, 54.0, 51.5, 43.3, 34.2, 13.9. MALDI-TOF calculated for $C_{27}H_{23}NNaO_3^+$ $[M+Na]^+$: 432.1570, found: 432.1570.

*DL-ethyl 2-((1R,2R)-2-(4-(tert-butyl)phenyl)-3,3-diphenylcyclobutyl)-2-oxoacetate (**5ka**):* Isolated yield : 36.6 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 4H), 7.17 – 7.06 (m, 6H), 7.02 – 6.95 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 4.51 (d, *J* = 10.5 Hz, 1H), 4.28 – 4.15 (m, 1H), 4.15 – 4.00 (m, 2H), 3.37 (dd, *J* = 11.5, 8.3 Hz, 1H), 2.68 (t, *J* = 11.1 Hz, 1H), 1.22 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 194.3, 161.4, 150.6, 149.9, 141.4, 135.1, 128.7, 128.4, 127.8, 126.25, 126.23, 126.0, 124.6, 62.3, 53.8, 52.3, 44.1, 34.4, 33.6, 31.4, 13.8 MALDI-TOF calculated for $C_{30}H_{32}NaO_3^+$ $[M+Na]^+$: 463.2244, found: 463.2246.

*DL-ethyl 2-((1R,2R)-2-(naphthalen-2-yl)-3,3-diphenylcyclobutyl)-2-oxoacetate (**5la**):* Isolated yield : 29.2 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.83 (m, 2H), 7.77 (d, *J* =8.5, 1H), 7.65 (s, 1H), 7.63 – 7.56 (m, 4H), 7.53 (t, *J* =7.6, 2H), 7.39 (t, *J* =7.2, 1H), 7.34 – 7.24 (m, 5H), 7.15 (dd, *J* =8.4, 1.0, 1H), 4.97 (d, *J* =10.5, 1H), 4.69 – 4.56 (m, 1H), 4.39 – 4.19 (m, 2H), 3.70 (dd, *J* =11.6, 8.2, 1H), 3.02 (t, *J* =11.1, 1H), 1.28 (t, *J* =7.1, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 194.4, 161.6, 150.7, 141.6, 136.1, 133.4, 132.8, 128.9, 128.8, 128.4, 128.2, 128.1, 127.7, 127.5, 127.2, 126.6, 126.5, 126.4, 126.2, 126.0, 62.5, 54.2, 53.1, 44.5, 34.1, 14.0. HRMS (ESI) calculated for $C_{30}H_{26}NaO_3^+$ [M+Na]+: 457.1774, found: 457.1756.

*DL-phenyl 2-oxo-2-((1R,2R)-2,3,3-triphenylcyclobutyl)acetate (**5ma**):* Isolated yield : 28.5 mg, 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 9H), 7.21 – 7.13 (m, 6H), 7.09 – 7.04 (m, 2H), 6.95 – 6.89 (m, 2H), 6.55 (d, *J* = 16.3 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 4.00 – 3.85 (m, 1H), 3.35 (dd, *J* = 11.8, 8.0 Hz, 1H), 2.87 (dd, *J* = 11.6, 10.6 Hz, 1H). ^{13}C{1H} NMR (101 MHz,

$CDCl_3$) δ 199.6, 150.9, 143.2, 142.0, 139.1, 134.6, 130.3, 129.1, 128.8, 128.7, 128.3, 128.1, 127.9, 127.8, 126.9, 126.3, 126.1, 125.8, 125.1, 53.7, 53.4, 45.9, 33.0. HRMS (ESI) calculated for $C_{30}H_{24}NaO_3^+$ $[M + Na]^+$: 455.1618, Found: 455.1638.

*DL-benzyl 2-oxo-2-((1R,2R)-2,3,3-triphenylcyclobutyl)acetate (**5na**):* Isolated yield : 33.5 mg, 75%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.32 – 7.24 (m, 6H), 7.21 – 7.06 (m, 7H), 7.02 – 6.96 (m, 2H), 6.90 – 6.83 (m, 2H), 5.16 (d, *J* = 12.1 Hz, 1H), 5.06 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 10.4 Hz, 1H), 4.31 – 4.19 (m, 1H), 3.39 (dd, *J* = 11.7, 8.3 Hz, 1H), 2.69 (t, *J* = 11.2 Hz, 1H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.7, 161.2, 150.3, 141.3, 138.0, 134.5, 128.9, 128.7, 128.62, 128.55, 128.5, 128.4, 127.78, 127.76, 126.9, 126.22, 126.16, 126.0, 67.8, 53.8, 52.3, 43.8, 33.9. HRMS (ESI) calculated for $C_{31}H_{26}NaO_3^+$ $[M+Na]^+$: 469.1774, found: 469.1772.

*DL-cyclopentyl 2-oxo-2-((1R,2R)-2,3,3-triphenylcyclobutyl)acetate (**5oa**):* Isolated yield : 34.4 mg, 81%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 4.3 Hz, 4H), 7.20 – 7.03 (m, 7H), 7.02 – 6.94 (m, 2H), 6.91 – 6.82 (m, 2H), 5.17 – 5.06 (m, 1H), 4.53 (d, *J* = 10.5 Hz, 1H), 4.20 (dd, *J* = 19.1, 10.0 Hz, 1H), 3.36 (dd, *J* = 11.6, 8.3 Hz, 1H), 2.71 (t, *J* = 11.1 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.67 – 1.56 (m, 2H), 1.57 – 1.44 (m, 4H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.6, 161.5, 150.5, 141.3, 138.1, 129.0, 128.6, 128.5, 127.90, 127.86, 127.1, 126.3, 126.2, 126.1, 79.7, 53.8, 52.6, 43.9, 33.5, 32.5, 32.4, 23.8, 23.7. MALDI-TOF calculated for $C_{29}H_{28}NaO_3^+$ $[M+Na]^+$: 447.1931, found: 447.1930.

*DL-ethyl 2-oxo-2-((1R,2R)-2-phenyl-3,3-di-p-tolylcyclobutyl)acetate (**5ab**):* Isolated yield : 38.9 mg, 94%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.20 – 7.11 (m, 5H), 7.03 – 6.92 (m, 6H), 4.59 (d, *J* = 10.5 Hz, 1H), 4.35 – 4.26 (m, 1H), 4.25 – 4.10 (m, 2H), 3.41 (dd, *J* =

11.6, 8.2 Hz, 1H), 2.73 (t, *J* = 11.0 Hz, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.3, 161.4, 147.8, 138.5, 138.4, 135.8, 135.5, 129.12, 129.06, 128.6, 128.5, 127.8, 127.0, 126.1, 62.4, 53.3, 52.5, 43.9, 34.0, 21.05, 20.97, 13.8. MALDI-TOF calculated for $C_{28}H_{28}NaO_3^+$ $[M+Na]^+$: 435.1931, found: 435.1933.

*DL-ethyl 2-((1R,2R)-3,3-bis(4-methoxyphenyl)-2-phenylcyclobutyl)-2-oxoacetate (**5ac**):* Isolated yield : 33.3 mg, 75%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.09 (m, 3H), 6.92 (d, *J* = 7.8 Hz, 4H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 4.51 (d, *J* = 10.4 Hz, 1H), 4.25 (dd, *J* = 18.9, 10.2 Hz, 1H), 4.20 – 4.04 (m, 2H), 3.78 (s, *3*H), 3.73 (s, *3*H), 3.32 (dd, *J* = 11.2, 8.5 Hz, 1H), 2.68 (t, *J* = 11.0 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.9, 162.0, 158.6, 158.4, 143.6, 139.0, 134.5, 130.3, 129.6, 128.4, 127.8, 127.6, 114.5, 113.9, 62.9, 55.9, 55.8, 53.3, 53.2, 44.4, 34.9, 14.4. MALDI-TOF calculated for $C_{28}H_{28}NaO_5^+$ $[M+Na]^+$: 467.1829, found: 467.1829.

*DL-ethyl 2-((1R,2R)-3,3-bis(4-chlorophenyl)-2-phenylcyclobutyl)-2-oxoacetate (**5ae**):* Isolated yield : 41.7 mg, 92%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.25 – 7.19 (m, 2H), 7.18 – 7.06 (m, 5H), 6.96 – 6.86 (m, 4H), 4.54 (d, *J* = 10.4 Hz, 1H), 4.33 – 4.21 (m, 1H), 4.21 – 4.05 (m, 2H), 3.34 (dd, *J* = 11.8, 8.3 Hz, 1H), 2.69 (t, *J* = 11.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.3, 161.8, 148.9, 140.3, 138.1, 133.2, 132.8, 130.6, 129.4, 129.4, 128.7, 128.2, 128.0, 63.0, 53.7, 53.0, 43.9, 34.5, 14.4. MALDI-TOF calculated for $C_{26}H_{22}Cl_2NaO_3^+$ $[M+Na]^+$: 475.0838, found: 475.0838.

*DL-ethyl 2-((1R,2R)-3,3-bis(4-bromophenyl)-2-phenylcyclobutyl)-2-oxoacetate (**5af**):* Isolated yield : 43.4 mg, 80%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 8.5 Hz, 2H), 7.26 (d, *J* =

8.5 Hz, 2H), 7.21 – 7.07 (m, 5H), 6.94 – 6.87 (m, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.52 (d, *J* = 10.5 Hz, 1H), 4.30 – 4.20 (m, 1H), 4.20 – 4.09 (m, 2H), 3.32 (dd, *J* = 11.8, 8.3 Hz, 1H), 2.67 (t, *J* = 11.1 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.3, 161.7, 149.3, 140.7, 138.0, 132.4, 131.7, 131.0, 129.4, 128.7, 128.6, 128.0, 121.3, 120.9, 63.1, 53.8, 52.9, 43.9, 34.4, 14.4. MALDI-TOF calculated for $C_{26}H_{22}Br_2NaO_3^+$ $[M+Na]^+$: 564.9807, found: 564.9808.

*DL-ethyl 2-((1R,2R,3S)-2,3-diphenylcyclobutyl)-2-oxoacetate (**5ag**):* Isolated yield : 25.3 mg, 82%, d.r.=2:1. ^1H NMR (400 MHz, $CDCl_3$, major product as standard) δ 7.26 – 7.08 (m, 6.72H), 7.06 – 6.91 (m, 2.04H), 6.90 – 6.85 (m, 0.66H), 6.84 – 6.78 (m, 0.68H), 4.25 (dd, *J* = 16.9, 8.6 Hz, 0.34H), 4.21 – 4.05 (m, 2.29H), 3.90 – 3.81 (m, 1.02H), 3.77 (t, *J* = 9.6 Hz, 0.66H), 3.58 (dd, *J* = 18.4, 9.7 Hz, 0.66H), 2.74 – 2.58 (m, 1.31H), 2.29 (dd, *J* = 20.5, 10.2 Hz, 0.67H), 1.20 – 1.12 (m, 3.00H),. $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.4, 194.1, 161.2, 161.1, 142.8, 141.6, 139.9, 138.7, 128.6, 128.5, 128.02, 127.97, 127.9, 127.8, 127.0, 126.9, 126.7, 126.3, 126.1, 62.5, 62.4, 50.0, 46.8, 46.0, 44.8, 43.3, 41.6, 29.4, 26.2, 13.93, 13.90. HRMS (ESI) calculated for $C_{20}H_{20}NaO_3^+$ $[M+Na]^+$: 331.1305, found: 331.1299.

*DL-ethyl 2-oxo-2-((1S,2R)-1-phenylspiro[3.4]octan-2-yl)acetate (**5ah**):* Isolated yield : 16.3 mg, 57%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.3 Hz, 2H), 7.17 – 7.09 (m, 3H), 4.18 – 4.10 (m, 2H), 4.06 (dd, *J* = 18.8, 9.3 Hz, 1H), 3.63 (d, *J* = 9.9 Hz, 1H), 2.11 – 1.94 (m, 2H), 1.67 – 1.58 (m, 2H), 1.48 – 1.29 (m, 4H), 1.26 – 1.12 (m, 5H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.6, 161.5, 139.0, 128.2, 127.6, 126.6, 62.3, 50.4, 48.7, 41.4, 39.8, 35.7, 33.6, 23.5, 23.4, 13.9. MALDI-TOF calculated for $C_{18}H_{22}NaO_3^+$ $[M+Na]^+$: 309.1461, found: 309.1466.

ASSOCIATED CONTENT

Supporting information

Condition optimization table, crystal structural data of **3ha** (Compound_3ha. cif), ^{1}H-^{1}H COSY spectrum, HMBC spectrum and H-D exchange spectra of **5aa**, Spectroscopic and electrochemical data, DFT calculation, ^{1}H and ^{13}C NMR spectra of all products.

Experimental details and the spectral characterization of catalytic reaction are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*lzwu@mail.ipc.ac.cn

Author Contributions

Δ These authors contributed equally.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

Financial support from the Ministry of Science and Technology of China (2017YFA0206903), the National Natural Science Foundation of China (21861132004 and 21473227), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17000000), the Key Research Program of Frontier Sciences of the Chinese Academy of Sciences (QYZDY-SSW-JSC029) and K. C. Wong Education Foundation is gratefully acknowledged. V. Ramamurthy acknowledges the Chinese Academy of Sciences for a fellowship and the U.S. National Science Foundation (CHE-1807729) for the research support.

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