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Visible-Light-Mediated Ring-Opening Strategy for the Regiospecific Allylation/Formylation of Cycloalkanols

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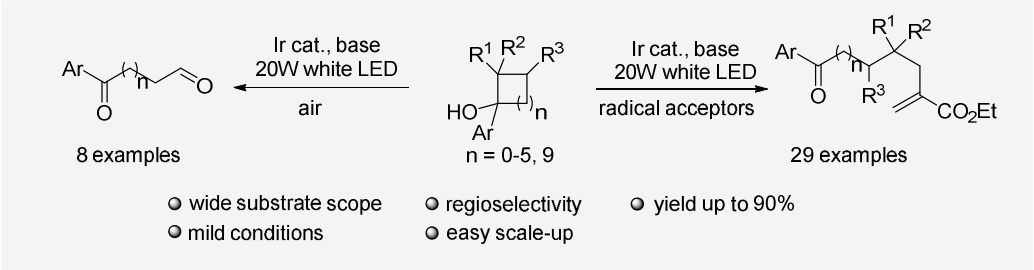


Abstract

Here we describe a straightforward and efficient approach for regiospecific introduction of an allyl group into cycloalkanol molecules employing a visible-light-mediated ring-opening strategy. A wide range of distally allylated or formylated ketones are furnished from 1-aryl cycloalkanol precursors of variable ring sizes, providing a concise and practical access for the modification of complex natural products. Preliminary mechanistic studies demonstrate that the key O-centered radicals mediate the sequential ring cleavage and allylation/formylation.

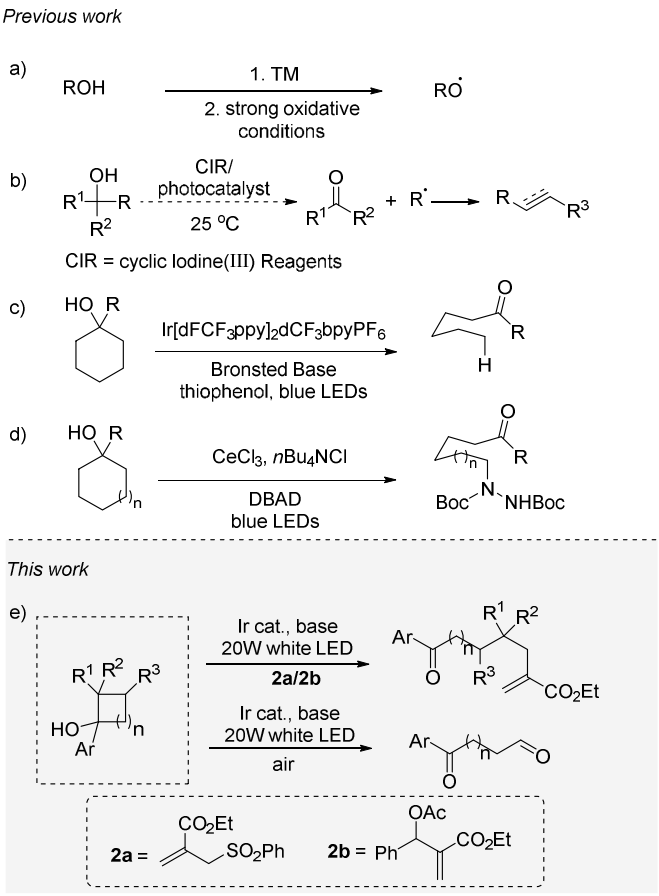
Introduction

Alkoxyl radicals are vital synthetic intermediates which are not only extensively applied in mechanistic investigations but also served as versatile reaction intermediates in activation of unfunctionalized alkanes as well as their adjacent C-C bonds.[1] However, the production of an

alkoxyl radical via direct homolysis of an O-H bond with high dissociation energy is remarkably challenging.[2] In this regard, considerable efforts have been made in the catalytic oxidation of alcohols to produce alkoxyl radicals.[3] To date, transition-metal catalyzed methods for alcohol activation under strong oxidative conditions are widely used for the generation of alkoxyl radicals (Scheme 1a).[4] In 2016, Chen and co-workers reported a visible-light-induced alcohol oxidation strategy for alkynylation/alkenylation employing a cyclic iodine(III) reagent as the oxidant (Scheme 1b).[5]

Tertiary cycloalkanols can serve as valuable precursors for regiospecific construction of distally functionalized ketones through selective homolysis of the strained cyclic C-C bonds.[6] In 2016, Knowles and co-workers reported a cyclic alkanols to linear ketones enabled by Proton-Coupled Electron Transfer process (Scheme 1c).[7] Recently, the group of Zuo described a simple cerium(III) chloride/base catalyzed intermolecular C-C bond cleavage/ amination sequence for cyclic alcohols (Scheme 1d).[8] In spite of these elegant contributions, novel catalytic processes to enrich the scope and utility of this category of transformations are still challenging and in great demand. Proton-Coupled Electron Transfer (PCET), a process occurs when both an electron and a proton transfer in a concerted step upon the combined effect of one-electron oxidation and Bronsted base, has emerged as a powerful approach across the biochemistry and material domains.[9] PCET is of great potential in the activation of unactivated bonds, which is difficult to achieve using traditional HAT (Hydrogen Atom Transfer) methods.[10, 11, 12] As a part of ongoing work of our group, here we report an effective, regioselective transformation of cyclic aryl alkanols to a wide range of linear ketones via alkoxyl intermediates under mild reaction conditions (Scheme 1e).

Scheme 1. Methods for the generation of alkoxyl radical. TM = Transition Metals.

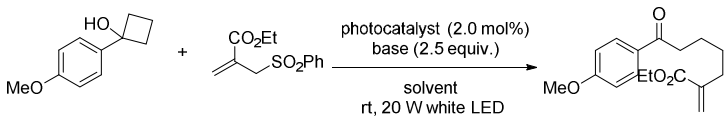


Results and Discussion

Our initial attempt was started by testing the reaction between 1-(4-methoxyphenyl)cyclobutanol (**1a**) (Ep = 1.22 V vs Fc/Fc+) and ethyl 2-((phenylsulfonyl)methyl)acrylate (**2a**) in the presence of $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (2.0 mol%) in dichloromethane (DCM) under the irradiation of a 20 W white LED (Table 1). A ring-opening product (**3a**) was isolated in 18% yield (entry 1). Then several photocatalysts were surveyed, among which $Ir[dF(CF_3)ppy]_2(dCF_3bpy)PF_6$ (2.0 mol%) gave the best result (entries 2-4). Further screening on bases such as 4-dimethylaminopyridine (DMAP), Et_3N, DBU and collidine indicated that collidine is the most effective one, affording **3a** in 73% yield (entries 5-8). The influence of solvents was also examined in which N,N-Dimethylformamide (DMF) and $PhCF_3$ led to moderate yields (entries 9, 10). Control

experiments showed that photocatalyst, base, visible light and inert atmosphere are necessary for this photoredox process (entries 11-14).

Table 1. The optimization of reaction conditions.[a]



1a **2a** **3a**

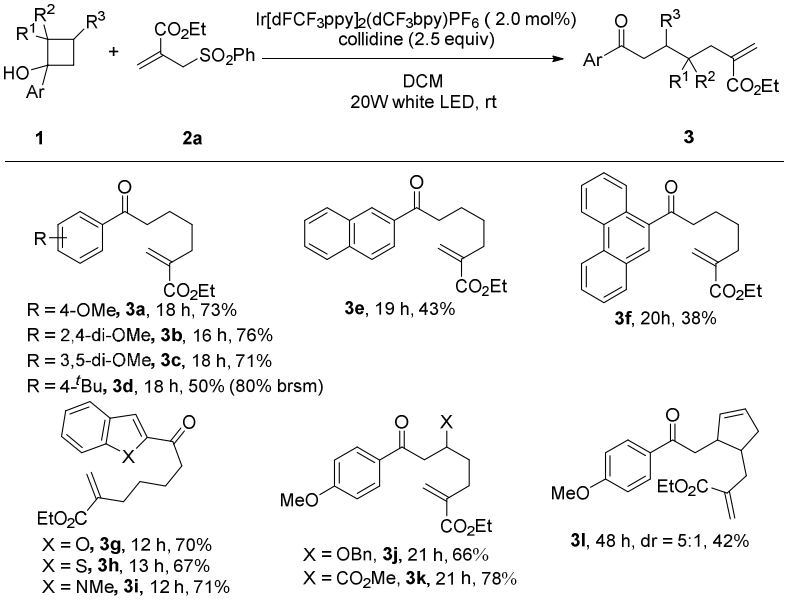
entry[a]	photocatalyst	solvent	base	yield(%)[b]
1	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	DCM	lutidine	18
2	$Ir[dF(CF_3)(ppy)]_2(bpy)PF_6$	DCM	lutidine	trace
3	$Ir(ppy)_2(bpy)PF_6$	DCM	lutidine	18
4	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DCM	lutidine	67
5	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DCM	DMAP	trace
6	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DCM	Et_3N	0
7	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DCM	DBU	0
8	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DCM	collidine	73
9	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DMF	collidine	47
10	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	$PhCF_3$	collidine	58
11	--	DCM	collidine	0
12	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DCM	--	0
13[c]	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DCM	collidine	0
14[d]	$Ir(dFCF_3ppy)_2(dCF_3bbpy)PF_6$	DCM	collidine	0

[a] Unless otherwise noted, reactions were conducted with 0.1 mmol **1a**, 0.2 mmol **2a**, 0.25 mmol base, 0.002 mmol photocatalyst in 1.0 mL solvent, under the irradiation of a 20 W white LED and N_2 atmosphere. [b] Isolated yield. [c] Reaction performed in the dark. [d] Reaction conducted without degassing. Lutidine = 2, 6-dimethylpyridine. Collidine = 2,4,6-trimethylpyridine.

With the optimized conditions established, we next investigated the ring opening/allylation protocol. The transformation was proved effective to various cycloalkanols, affording allylation products in moderate to good yields (Scheme 2). Electron-rich groups, e.g. methoxyl, substituted cyclobutanols afforded the corresponding products in moderate yields (**3a**-**3c**). The alkyl groups, such as ^{t}Bu, substituted cyclobutanol also proceeded smoothly to provide the desired products 3d in good yield. For substrates with fused benzene rings, lower yields were obtained in reaction systems (**3e**, **3f**). Moreover, a range of cyclobutanols attached to heterocycles were found suitable

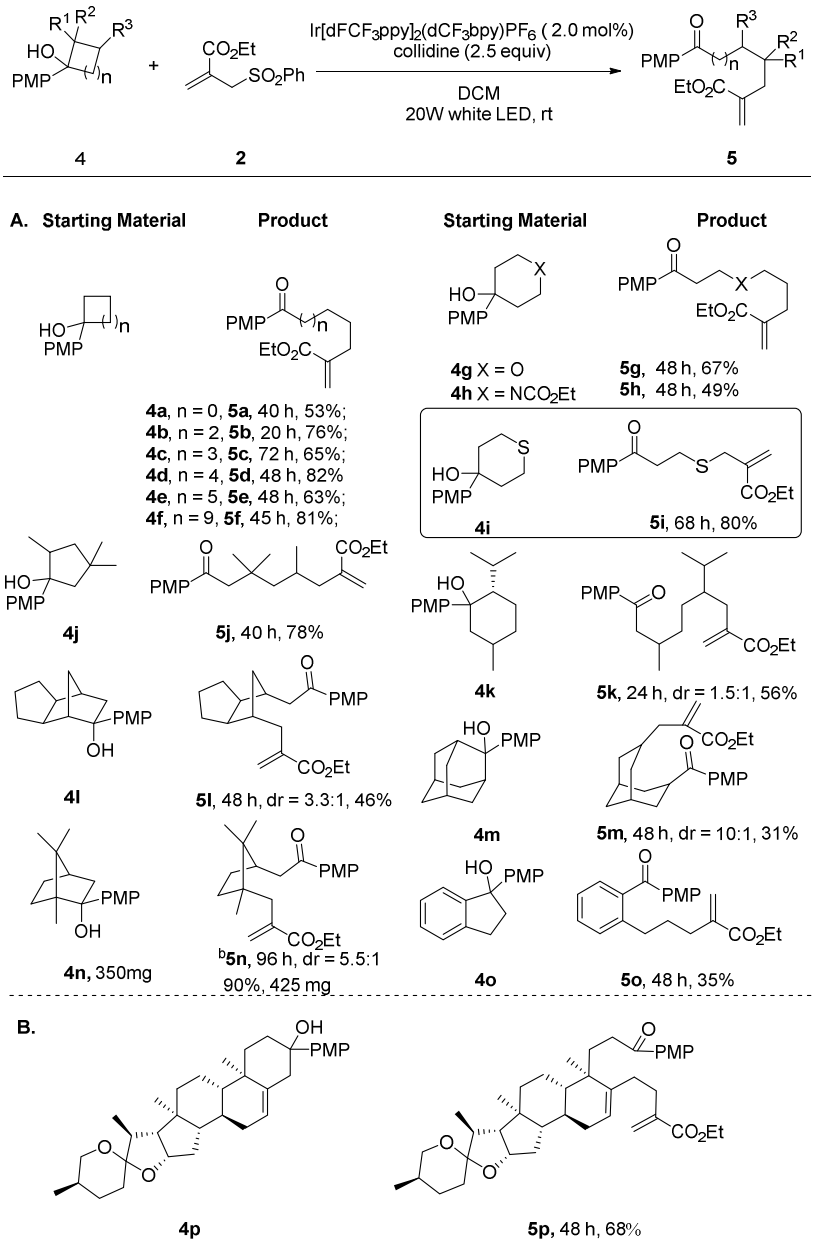
for the procedure, and the corresponding products were acquired in modest yields (**3g-3i**). The ring-opening products of multisubstituted cyclobutanols, which were difficult to synthesize via traditional routes owing to the Thorpe-Ingold Effects,[13] were also furnished in moderate to excellent yields in this protocol (**3j-3l**).

Scheme 2. Scope of Different Aryls.[a]



[a] Reaction conditions: 0.1 mmol **1a**, 0.2 mmol **2a**, 0.25 mmol collidine, 2.0 mol % photocatalyst in 1.0 mL DCM, N_2 circumstance, 20 W white LED. Isolated yields are shown.

Scheme 3. Scope of Different Cycloalkanols.[a]

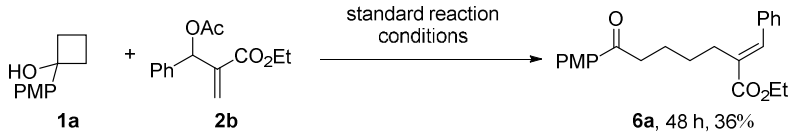


[a] Reaction conditions: 0.1 mmol **4**, 0.2 mmol **2a**, 0.25 mmol collidine, 2.0 mol % photocatalyst in 1.0 mL DCM, N_2 circumstance, 20 W white LED. Isolated yields are shown. [b] 0.5 mol % photocatalyst.

Subsequently, the scope of various ring-sized cycloalkanols bearing different functional groups was examined (Scheme 3A). A series of cycloalkanols with different sized rings were compatible with the reaction conditions, generating the distally allylation products in good efficiency (**5a-5f**). Substrates containing a heteroatom in the ring could also undergo the transformation successfully, providing ring-opening products in moderate to good yields (**5g**, **5h**). Interestingly, in the

reaction of sulfur-contained substrate **4i**, **5i** was isolated instead with an exceptional deethylation process. Substrates bearing an alkyl substitution at the α-position of the hydroxyl group were also proved viable, furnishing the corresponding products in moderate to good yields (**5j**-**5m**). Scaled-up synthesis of **5n** was conducted, with the desired product obtained in excellent yield even with lowered photocatalyst loading to 0.5 mol%. The dihydroindenol derivative **4o** was then examined, and **5o** was obtained in 35% yield. To highlight the synthetic utility of this protocol, further exploration of practicality in the derivative of diosgenin **4p** was also carried out, the allylation reactions took place smoothly on the specific location to give the desired product **5p** in good yield (Scheme 3B).

Scheme 4. Morita−Baylis−Hillman Acetate as a source of allyl.

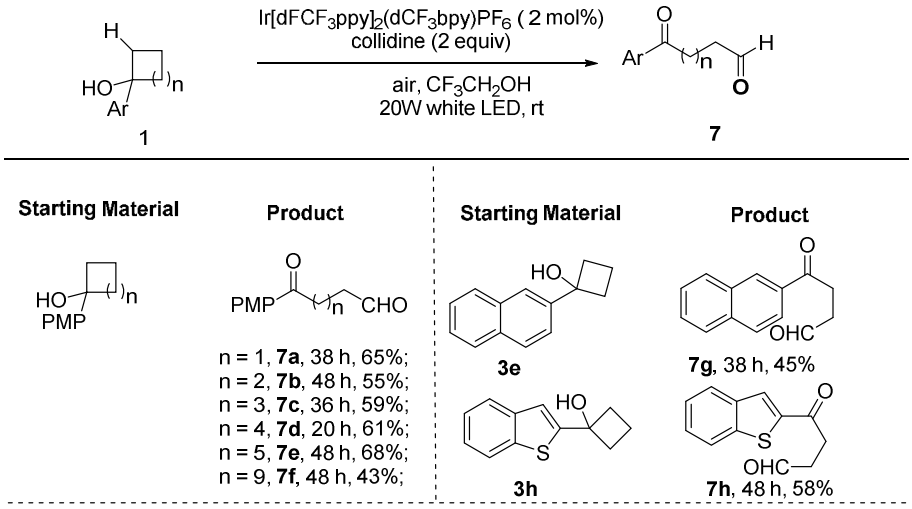


To further explore the application of the new strategy, we found that Morita−Baylis−Hillman reaction partner[14] **2b** could also be accommodated in this process (Scheme 4). Preliminary studies revealed that the model substrate **1a** and **2b** are compatible with the reaction conditions, providing the desired product **6a** in 36% yield.

Encouraged by the previous study,[15] we wonder whether air could be used as the oxidant in this ring-opening strategy. We were pleased to find that the distally formylated products **7a** was successfully afforded in 45% when DCM was switched to 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Scheme 5), whereas no reaction was observed in DCM. We then examined other reaction media using air as the oxidant and found CF_3CH_2OH was the ideal solvent (Table S4). Under optimized conditions, cycloalkanols of different ring sizes (**1a**, **1e**, **4b**-**4f**) all reacted well to

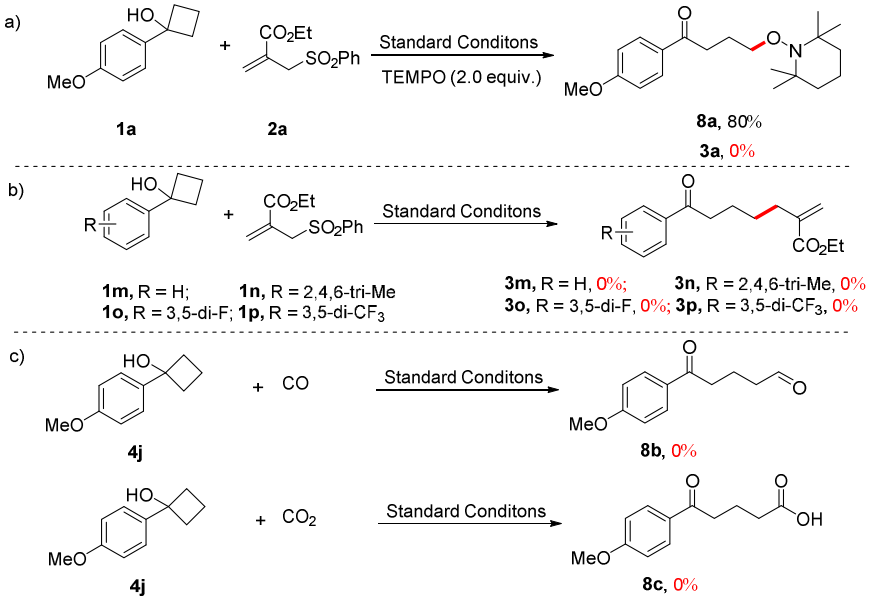
provide the corresponding products in moderate to good yields (Scheme 5). For substrates with fused benzene and hetercycle rings, moderate yields are provided in this procedure (**7g**, **7h**).

Scheme 5. Air as a Green Reaction Partner.[a]



[a] Reaction conditions: 0.1 mmol **1**, 0.2 mmol **2b**, 0.20 mmol lutidine, 2.0 mol % photocatalyst in 1.0 mL CF_3CH_2OH, air, 20 W white LED, r.t. Isolated yields are shown.

Scheme 6. Control experiments.

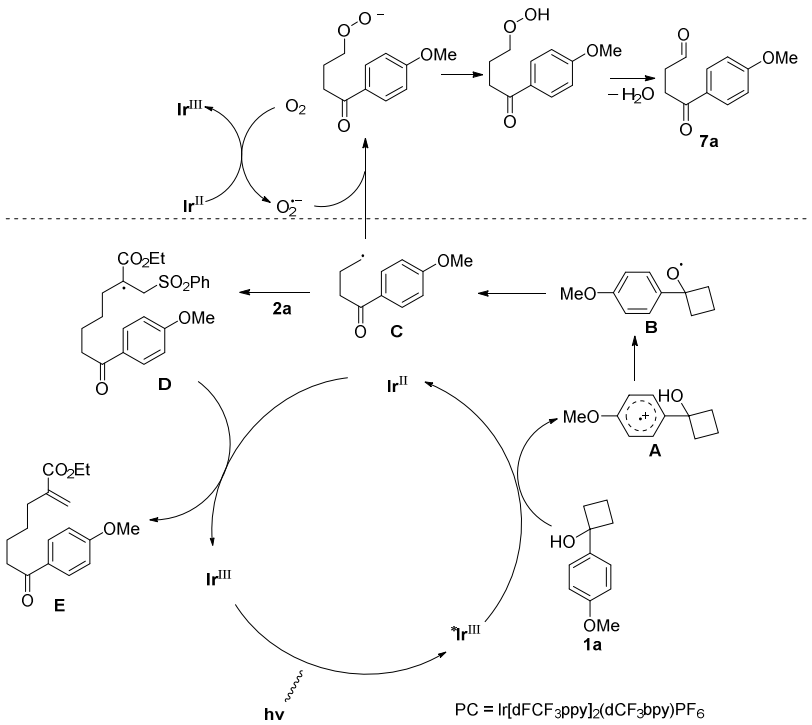


To gain further insights into the mechanism, a radial intermediate trapping experiment was conducted (Scheme 6a), the reaction was completely inhibited by the radical scavenger

2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), indicating a radical pathway of this process. It is noteworthy that substrates with aryl substituents that are generally difficult to be oxidized by the photocatalyst to produce radical cations failed to form allylated products (Scheme 6b). Alternative reaction partners such as CO and CO_2 could not undergo this ring-opening process (Scheme 6c).

A detailed description of the mechanism based on the above mechanistic studies as well as current literature was outlined in Scheme 7.[15,16,17] Excitation of the photocatalyst $Ir^{III}[dF(CF_3)ppy]_2(dCF_3bpy)PF_6$ followed by the process of single electron oxidation of **1a** afforded transient radical cation **A** and $Ir^{II}[dF(CF_3)ppy]_2(dCF_3bpy)PF_6$. An intramolecular proton-coupled electron transfer process occured with the concomitant formation of the key alkoxy radical intermediate **B** by donating a proton to base. Aryl ketone with a distal alkyl radical **C** was generated smoothly from the ring-opening process owing to the ability of the alkoxyl radicals that could weaken the adjacent C−C bonds. Radical **C** could further be trapped by **2a** to give the intermediate **D**, which was then reduced by $[Ir]^{II}[dF(CF_3)ppy]_2(dCF_3bpy)PF_6$ to afford the product **E** and $PhSO2^{2-}$. In the other process, Ir^{II} was oxdized to Ir^{III} by the oxygen in air with the concomitant formation of $[O2]^{\bullet-}$,and the oxygen radical anion was easily trapped by **C** to yield the aldehyde product **7a**.

Scheme 7. Proposed reaction mechanism.



Conclusion

In summary, an efficient and straightforward method for the construction of distally allylated and formylated ketones has been developed using photoredox cycle under mild reaction conditions. We envision that this ring-opening strategy will find further applications in synthesis of natural products and biomolecule studies. Further studies and investigations towards novel application of alkoxyl radical processes are under way in our laboratory.

Experimental Section

General Information

Commercial reagents were obtained from Aldrich and Energy Chemical Chemicals without further purification unless otherwise stated. ^{1}H NMR, ^{13}C NMR were recorded on a Bruker AV-400 or 600 (^{1}H NMR at 400 MHz or 600 M, ^{13}C NMR at 100 MHz or 151 M) spectrometers using tetramethylsilane (TMS) as internal standard. Data are reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz,

integration). High resolution mass spectra (HRMS) were collected on Q-TOF LC/MS system. GC-MS analysis was conducted on a 7890A-5975C/Agilent.

General Procedure for the Synthesis of substrates.

(1) For substrates **1a-1e**, **1j-1l**, **4a-4o**, **5p**:

In a two-neck bottle, a mixture of ArBr (10 mmol, 1 equiv), Mg (15 mmol, 1.5 equiv) and catalytical amount of iodine in anhydrous THF (25 mL) under N_2 atmosphere, subsequently the mixture was string until the complete formation of the aryl Grignard reagent. And relevant ketone was added into the reaction mixture at 0 ^{o}C, and then the reaction was removed to room temperature. When the starting materials completely consumed monitored by TLC, the reaction was quenched using saturated aqueous ammonium chloride solution and extracted with EtOAc. The organic layers were combined and washed with brine, dried over Na_2SO_4, concentrated in vacuo. The residue was purified by a silica gel column (petroleum ether/EtOAc:, 10:1) to afford the corresponding products.

(2) For substrates **1f**, **1g**, **1h** and **1i**:

In a two-neck bottle, ArH (10 mmol, 1 equiv.) was added in anhydrous THF (25 mL) under N_2 atmosphere, 4.8 mL BuLi (12 mmol, 1.2 equiv.) was added to the solution at -78 °C, an hour later, the reaction system was transfered to room temperature. When the starting materials completely consumed, reactions were quenched using saturated aqueous ammonium chloride solution and extracted with EtOAc. The organic layers was combined and washed with brine, dried over Na_2SO_4, concentrated in vacuo. The residue was purified by a silica gel column (petroleum ether/EtOAc:, 10:1) to afford cycloalkanols.

1-(4-methoxyphenyl)cyclobutan-1-ol (1a). Colorless oil, 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 2.54 (ddd, J = 13.2, 8.7, 4.9 Hz, 2H), 2.42-2.28 (m, 2H), 2.18-1.89 (m, 2H), 1.64 (dp, J = 11.1, 8.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.8, 138.6, 126.6, 113.8, 76.7, 55.4, 36.9, 13.0; GC-MS (EI, QMS, m/z): 92.1, 108.1, 135.1, 150.1, 178.1. The spectroscopic data is in agreement with the literature.[3d]

1-(2,4-dimethoxyphenyl)cyclobutan-1-ol (1b). Colorless oil, 80% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.22 (d, J = 8.3 Hz, 1H), 6.50 (s, 1H), 6.46 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.47 (s, 1H), 2.52-2.45 (m, 2H), 2.38-2.30 (m, 2H), 2.05-1.97 (m, 1H), 1.67-1.59 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 160.3, 158.5, 126.1, 126.1, 103.5, 99.4, 76.4, 55.5, 55.4, 35.3, 14.2; GC-MS (EI, QMS, m/z): 122.1, 152.1, 165.1, 180.1, 208.1; HRMS (ESI): calcd for $C_{12}H_{17}O_3^+$, $(M+H)^+$, 209.1172, found, 209.1179.

1-(3,5-dimethoxyphenyl)cyclobutan-1-ol (1c). Colorless oil, 72% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.65 (d, J = 2.2 Hz, 1H), 6.38 (t, J = 2.1 Hz, 1H), 3.80 (s, 3H), 2.59-2.48 (m, 1H), 2.35 (ddd, J = 17.0, 9.9, 6.1 Hz, 1H), 2.16 (s, 1H), 2.07-1.95 (m, 1H), 1.77-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.0, 149.0, 103.3, 99.1, 77.2, 55.5, 36.9, 13.2; GC-MS (EI, QMS, m/z): 137.1, 152.1, 165.1,180.1, 208.1; HRMS (ESI): calcd for $C_{12}H_{17}O_3^+$, $(M+H)^+$, 209.1172, found, 209.1169.

1-(4-(tert-butyl)phenyl)cyclobutan-1-ol (1d). White Solid, 83% isolated yield . ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (q, J = 8.6 Hz, 4H), 2.63 - 2.54 (m, 2H), 2.37 (ddd, J = 12.5, 9.4, 7.7 Hz, 2H), 2.13 (s, 1H), 2.07-1.96 (m, 1H), 1.76-1.63 (m, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 150.2, 143.4, 125.4, 124.9, 76.9, 36.8, 34.6, 31.5, 13.1; GC-MS (EI, QMS, m/z): 134.0, 147.0, 161.1, 176.0, 204.1. The spectroscopic data is in agreement with the literature.[3d]

1-(naphthalen-2-yl)cyclobutan-1-ol (1e). Colorless oil, 80% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.95-7.81 (m, 4H), 7.65 (d, J = 8.5 Hz, 1H), 7.49 (dd, J = 12.3, 6.3 Hz, 2H), 2.76-2.63 (m, 2H), 2.52-2.39 (m, 2H), 2.07 (ddd, J = 14.8, 10.4, 5.0 Hz, 2H), 1.80-1.71 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 141.4, 131.2, 130.8, 126.7, 126.3, 125.7, 124.3, 124.1, 122.1, 121.2, 34.9, 11.2; GC-MS (EI, QMS, m/z): 128.1, 141.1, 155.1, 170.1, 198.1. The spectroscopic data is in agreement with the literature.[3c]

1-(phenanthren-9-yl)cyclobutan-1-ol (1f). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.77 (d, J = 8.1 Hz, 1H), 8.69 (d, J = 8.2 Hz, 1H), 8.40 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.80 (s, 1H), 7.73 -7.61 (m, 4H), 2.95 (dd, J = 14.9, 10.9 Hz, 2H), 2.69 (dd, J = 18.8, 9.1 Hz, 2H), 2.38 (s, 1H), 2.27-2.14 (m, 1H), 1.85-1.71 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 138.3, 131.7, 131.1, 130.5, 129.7, 129.1, 127.2, 127.1, 126.9, 126.4, 126.4, 124.2, 123.4, 122.5, 78.6, 36.7, 14.6; GC-MS (EI, QMS, m/z): 165.1, 203.1, 215.1, 232.1, 248.1. The spectroscopic data is in agreement with the literature.[7]

1-(benzofuran-2-yl)cyclobutan-1-ol (1g). Colorless oil, 59% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.58 (dd, J = 7.5, 0.7 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.28 (dtd, J = 21.3, 7.3, 1.1 Hz, 2H), 6.70 (d, J = 0.6 Hz, 1H), 2.73-2.56 (m, 3H), 2.53-2.37 (m, 2H), 2.05-1.93 (m, 1H), 1.82 (dp, J = 11.2, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_H 160.8, 155.1, 128.3, 124.3, 122.9, 121.2, 111.3, 101.6, 72.7, 35.7, 12.9; GC-MS (EI, QMS, m/z): 118.1, 131.1, 145.0, 160.1, 188.1. The spectroscopic data is in agreement with the literature. [3c]

1-(benzo[b]thiophen-2-yl)cyclobutan-1-ol (1h). White solid, 68% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.84 (d, J = 7.8 Hz, 1H), 7.79-7.73 (m, 1H), 7.35 (dtd, J = 16.4, 7.2, 1.2 Hz, 2H), 7.29 (d, J = 2.7 Hz, 1H), 2.64 (dddd, J = 11.3, 9.0, 4.5, 2.5 Hz, 2H), 2.57-2.46 (m, 2H), 2.44 (s,

1H), 2.02 (dtt, J = 11.3, 9.3, 4.5 Hz, 1H), 1.85 (dp, J = 11.3, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 152.2, 139.8, 139.8, 124.4, 124.3, 123.6, 122.6, 119.3, 75.3, 38.3, 12.9; GC-MS (EI, QMS, m/z): 89.0, 134.0, 147.0, 176.0, 204.1. The spectroscopic data is in agreement with the literature.[7]

1-(1-methyl-1H-indol-2-yl)cyclobutan-1-ol (1i). White solid, 20% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.4 Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 2.40-2.21 (m, 4H), 1.99-1.85 (m, 2H), 1.78- 1.66 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 137.0, 134.1, 128.7, 127.6, 126.9, 126.6, 75.3, 36.6, 12.4; GC-MS (EI, QMS, m/z): 144.1, 154.1, 168.1, 183.1, 201.1. The spectroscopic data is in agreement with the reported literature.[7]

3-(benzyloxy)-1-(4-methoxyphenyl)cyclobutan-1-ol (1j). Colorless oil, 47% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 4.3 Hz, 4H), 7.30 (dt, J = 9.2, 4.6 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 4.47 (d, J = 6.3 Hz, 2H), 3.84-3.73 (m, 4H), 2.97-2.89 (m, 2H), 2.50 -2.41 (m, 2H), 2.29 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 159.0, 138.2, 137.6, 128.6, 128.0, 127.8, 126.8, 114.0, 70.6, 70.0, 65.4, 55.4, 45.3; GC-MS (EI, QMS, m/z): 199.1, 214.2, 244.2，277.2,,284.1; HRMS (ESI): calcd for $C_{18}H_{21}O_3^+$, $(M+H)^+$, 285.1485, found, 285.1494.

methyl 3-hydroxy-3-(4-methoxyphenyl)cyclobutane-1-carboxylate (1k). White solid, 48% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.42 (d, J = 8.6 Hz, 2H), 6.91 (d, 2H), 3.96-3.80 (s, 3H), 3.73 (s, J = 9.0 Hz, 3H), 2.90 (s, 1H), 2.89-2.84 (m, 2H), 2.79 (dd, J = 15.4, 7.3 Hz, 2H), 2.67-2.59 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 176.6, 159.1, 137.0, 126.6, 114.0, 73.3, 55.4, 52.2, 40.9, 29.6; HRMS (ESI): calcd for $C_{13}H_{16}O_4Na^+$, $(M+ Na)^+$, 259.0941, found, 259.0934.

6-(4-methoxyphenyl)bicyclo[3.2.0]hept-2-en-6-ol (1l). Colorless oil, 72% isolated yield. ^{1}H

NMR (400 MHz, $CDCl_3$): δ_H 7.45-7.35 (m, 2H), 6.90 (d, J = 8.7 Hz, 2H), 5.96 (s, 2H), 3.81 (s, 3H), 3.36 (t, J = 7.9 Hz, 1H), 3.19 (t, J = 7.7 Hz, 1H), 2.94 (dd, J = 13.0, 8.4 Hz, 1H), 2.88-2.79 (m, 1H), 2.52 (dd, J = 17.4, 8.7 Hz, 1H), 2.14 (s, 1H), 2.08 (dd, J = 13.0, 3.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.6, 139.9, 135.7, 133.0, 126.2, 113.7, 76.5, 55.4, 48.0, 44.5, 39.6, 33.1; GC-MS (EI, QMS, m/z): 148.1,173.1,188.2, 201.2, 216.2; HRMS (ESI): calcd for $C_{14}H_{17}O_2^+$, $(M+H)^+$, 217.1223, found, 217.1228.

1-phenylcyclobutan-1-ol (1m). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.51 (d, J = 7.7 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 2.68-2.52 (m, 2H), 2.50-2.32 (m, 2H), 2.16 (s, 1H), 2.09-1.99 (m, 1H), 1.79-1.60 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 146.3, 128.5, 127.3, 125.1, 77.08, 36.9, 13.1; GC-MS (EI, QMS, m/z): 78.1, 105.1, 120.1, 148.1; The spectroscopic data is in agreement with the reported literature.[3d]

1-mesitylcyclobutan-1-ol (1n). White Solid, 75%isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.81 (s, 2H), 2.80-2.70 (m, 2H), 2.55-2.46 (m, 2H), 2.34 (s, 6H), 2.26 (s, 3H), 2.00 (s, 1H), 1.87-1.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 139.6, 136.7, 136.6, 130.6, 81.6, 39.4, 21.7, 20.7, 17.0; GC-MS (EI, QMS, m/z): 115.1, 129.1, 144.1, 157.1, 190.0; HRMS (ESI): calcd for $C_{13}H_{19}O^+$, $(M+H)^+$, 191.1430, found, 191.1434.

1-(3,5-difluorophenyl)cyclobutan-1-ol (1o). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 (s, 2H), 7.80 (s, 1H), 2.58 (ddd, J = 12.9, 8.9, 5.6 Hz, 2H), 2.49-2.38 (m, 2H), 2.31 (d, J = 6.3 Hz, 1H), 2.21-2.08 (m, 1H), 1.90-1.74 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 164.1 (d, J = 12.6 Hz), 162.4 (d, J = 12.7 Hz), 150.7 (s), 108.1 (dd, J = 20.4, 5.1 Hz), 102.6 (t, J = 25.4 Hz), 76.6, 37.3, 13.0; GC-MS (EI, QMS, m/z): 105.1, 120.1, 148.1, 156.1, 184.1; HRMS (ESI): calcd for $C_{10}H_{11}F_2O^+$, $(M+H)^+$, 185.0772, found, 185.0773.

1-(3,5-bis(trifluoromethyl)phenyl)cyclobutan-1-ol (1p). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.04 (t, J = 6.5 Hz, 2H), 6.72 (t, J = 8.8 Hz, 2H), 2.55-2.46 (m, 2H), 2.43-2.33 (m, 2H), 2.29 (s, 1H), 2.14-2.01 (m, 1H), 1.84-1.71 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 149.0, 131.8 (q, J = 33.1 Hz), 125.4, 125.4, 123.6 (q, J = 272.7 Hz), 121.2 (dd, J = 7.5, 3.8 Hz), 121.3, 121.2, 121.2, 76.6, 37.6, 13.1; GC-MS (EI, QMS, m/z): 142.1, 157.1, 241.0, 256.1, 284.1; HRMS (ESI): calcd for $C_{12}H_{11}F_6O^+$, $(M+H)^+$, 285.0709, found, 285.0712.

1-(4-methoxyphenyl)cyclopropan-1-ol (4a). Colorless oil, 76% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29 (d, J = 7.5 Hz, 2H), 6.90 (d, J = 6.7 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 1H), 1.22 (s, 2H), 0.99 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.5, 136.3, 126.5, 113.9, 56.8, 55.5, 16.9; GC-MS (EI, QMS, m/z): 64.1, 92, 107.1, 135.0, 164.0. The spectroscopic data is in agreement with the literature.[3d]

1-(4-methoxyphenyl)cyclopentan-1-ol (4b). Colorless oil, 88% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.40 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 7.6 Hz, 2H), 3.79 (s, 3H), 1.96 (s, 6H), 1.80 (t, 2H), 1.65 (t, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.5, 139.3, 126.5, 113.6, 83.3, 55.4, 41.6, 23.8; GC-MS (EI, QMS, m/z): 115.1, 128.1, 159.1, 174.1, 192.1. The spectroscopic data is in agreement with the literature.[7]

1-(4-methoxyphenyl)cyclohexan-1-ol (4c). Colorless oil, 74% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.43 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 1.87-1.67 (m, 8H), 1.60 (s, 2H), 1.35-1.24 (m, 1H); ^{13}C NMR (151 MHz, CDCl3): δ_C 158.4, 125.9, 113.6, 72.9, 55.4, 55.4, 39.0, 25.6, 22.4; GC-MS (EI, QMS, m/z): 135.1, 150.1, 163.1, 188.2, 206.2. The spectroscopic data is in agreement with the literature.[7]

1-(4-methoxyphenyl)cycloheptan-1-ol (4d). Colorless oil, 66% isolated yield. ^{1}H NMR (400

MHz, $CDCl_3$): δ_H 7.44 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 2.08 (dd, J = 14.2, 10.8 Hz, 2H), 1.92 (dd, J = 14.5, 8.1 Hz, 2H), 1.81 (dd, J = 23.9, 11.4 Hz, 2H), 1.75-1.69 (m, 2H), 1.65-1.53 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.3, 143.0, 125.9, 113.5, 76.7, 55.4, 43.4, 29.3, 22.6; GC-MS (EI, QMS, m/z): 135.0, 159.1, 174.1, 202.1, 220.0. The spectroscopic data is in agreement with the literature. [7]

1-(4-methoxyphenyl)cyclooctan-1-ol (4e). Colorless oil, 58% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.43 (d, J = 7.1 Hz, 2H), 6.87 (d, J = 7.1 Hz, 2H), 3.80 (s, 3H), 2.03 (dd, J = 14.8, 8.0 Hz, 2H), 1.99-1.92 (dd, 2H), 1.71 (m, 5H), 1.54 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.4, 141.3, 126.4, 113.5, 76.5, 55.4, 37.9, 28.5, 24.6, 22.2; GC-MS (EI, QMS, m/z): 155.1, 167.1, 183.1, 198.1, 234.1. The spectroscopic data is in agreement with the literature.[7]

1-(4-methoxyphenyl)cyclododecan-1-ol (4f). White solid, 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H), 1.87 (t, J = 7.2 Hz, 4H), 1.40 (d, J = 9.9 Hz, 16H), 1.23 (d, J = 10.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.4, 140.7, 126.5, 113.3, 76.3, 55.4, 35.6, 26.5, 26.2, 22.6, 22.3, 20.1; GC-MS (EI, QMS, m/z): 135.1, 150.1, 245.1, 272.1, 290.1. The spectroscopic data is in agreement with the literature.[7]

4-(4-methoxyphenyl)tetrahydro-2H-pyran-4-ol (4g). White solid, 58% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.40 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.91 (td, J = 11.8, 2.0 Hz, 2H), 3.84 (dd, J = 11.3, 4.0 Hz, 2H), 3.80 (s, 3H), 2.13 (td, J = 13.1, 5.1 Hz, 2H), 1.77 (dd, J = 7.8, 3.8 Hz, 1H), 1.72-1.65 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.8, 140.4, 125.8, 113.8, 70.30, 64.1, 55.4, 38.9; GC-MS (EI, QMS, m/z): 77.1, 135.0, 150.1, 190.1, 208.1; HRMS (ESI): calcd for $C_{12}H_{17}O_3^+$, $(M+H)^+$, 209.1172, found, 209.1167.

ethyl 4-hydroxy-4-(4-methoxyphenyl)piperidine-1-carboxylate (4h). White solid, 35% isolated

yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 4.06 (s, 2H), 3.82 (s, 3H), 3.30 (t, J = 11.7 Hz, 2H), 1.98 (s, 2H), 1.85-1.67 (m, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.8, 155.7, 140.3, 125.8, 113.8, 71.1, 61.4, 55.4, 40.1, 38.1, 14.8; GC-MS (EI, QMS, m/z): 121.1, 145.1, 232.2, 261.1, 279.1; HRMS (ESI): calcd for $C_{15}H_{21}NO_4Na^+$, $(M+Na)^+$, 302.1363, found, 302.1363.

1-(4-methoxyphenyl)cyclobutan-1-ol (4i). Red solid, 48% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H), 3.19 (t, J = 13.0 Hz, 2H), 2.46 (d, J = 13.6 Hz, 2H), 2.20-2.08 (m, 2H), 2.01 (d, J = 14.0 Hz, 2H), 1.53 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.7, 141.5, 125.6, 113.8, 71.6, 55.4, 39.8, 24.4; GC-MS (EI, QMS, m/z): 135.1, 163.1, 177.1, 196.1, 224.1; HRMS (ESI): calcd for $C_{12}H_{17}O_2S^+$, $(M+H)^+$, 225.0944, found, 225.0938.

1-(4-methoxyphenyl)-2,4,4-trimethylcyclopentan-1-ol (4j). Colorless oil, 64% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.40-7.34 (m, 1H), 6.87 (d, J = 8.8 Hz, 1H), 3.80 (s, 2H), 2.47-2.33 (m, 1H), 1.93 (d, J = 14.4 Hz, 1H), 1.86 (d, J = 14.4 Hz, 1H), 1.72-1.65 (m, 1H), 1.51 (s, 1H), 1.19 (s, 1H), 1.12 (s, 2H), 0.80 (d, J = 6.7 Hz, 1H), ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.2, 138.5, 126.2, 113.5, 85.1, 58.8, 55.4, 48.2, 44.5, 35.8, 32.2, 11.7; GC-MS (EI, QMS, m/z): 135.1, 150.1, 191.1, 219.2, 234.2; HRMS (ESI): calcd for $C_{15}H_{23}O_2^+$, $(M+H)^+$, 235.1693, found, 235.1692.

2-isopropyl-1-(4-methoxyphenyl)-5-methylcyclohexan-1-ol (4k). Colorless oil, 55% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 (d, J = 7.5 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 3.81 (s, 3H), 1.85 (t, J = 12.4 Hz, 2H), 1.67-1.49 (m, 6H), 1.41 (t, J = 13.0 Hz, 1H), 1.04 (q, J = 12.2 Hz, 1H), 0.89 (d, J = 6.2 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.0, 141.0, 125.8, 113.5, 78.3, 55.3, 51.9, 50.1, 35.3, 28.7, 26.7, 23.9, 22.4,

21.4, 18.5; GC-MS (EI, QMS, m/z): 107.1, 135.1, 177.1, 262.1. The spectroscopic data is in agreement with the literature.[7]

(3aS,4S,5S,7S,7aS)-5-(4-methoxyphenyl)octahydro-1H-4,7-methanoinden-5-ol (4l). Colorless oil, 65% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.51-7.40 (d, 2H), 6.91-6.82 (d, 2H), 3.80 (s, 3H), 2.78 (q, J = 8.7 Hz, 1H), 2.33 (dd, J = 13.1, 5.1 Hz, 2H), 2.07 (q, J = 8.7 Hz, 1H), 2.02 (d, J = 5.0 Hz, 1H), 1.98-1.88 (m, 2H), 1.71 (dd, J = 12.2, 6.2 Hz, 1H), 1.67 (s, 1H), 1.41 (d, J = 11.3 Hz, 2H), 1.34-1.24 (m, 1H), 1.22 (d, J = 10.3 Hz, 1H), 1.08-1.00 (m, 1H), 0.96 (tdd, J = 12.6, 8.9, 6.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.4, 141.3, 127.4, 113.6, 80.2, 55.4, 51.7, 47.8, 46.1, 42.1, 39.5, 32.7, 32.4, 32.0, 27.5; GC-MS (EI, QMS, m/z): 135.1, 150.1, 172.1, 241.2, 258.1; HRMS (ESI): calcd for $C_{17}H_{22}O_2Na^+$, $(M+Na)^+$, 281.1512, found, 281.1502.

(1r,3r,5r,7r)-2-(4-methoxyphenyl)adamantan-2-ol (4m). White solid, 88% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.46 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 3.81 (s, 3H), 2.53 (s, 2H), 2.39 (d, J = 12.2 Hz, 2H), 1.90 (s, 1H), 1.72 (d, J = 13.4 Hz, 9H), 1.48 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.7, 137.7, 126.8, 114.0, 75.4, 55.4, 37.8, 35.9, 35.0, 33.2, 27.6, 27.0; GC-MS (EI, QMS, m/z): 121.1, 150.1, 227.2, 241.2, 258.1; HRMS (ESI): calcd for $C_{17}H_{22}O_2Na^+$, $(M+Na)^+$, 281.1512, found, 281.1513.

(1S,2R,4R)-2-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (4n). White solid, 88% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 2.30 (d, J = 13.9 Hz, 1H), 2.26-2.15 (m, 1H), 1.91 (t, J = 4.3 Hz, 1H), 1.82 (s, 1H), 1.75 (ddt, J = 16.9, 12.8, 3.8 Hz, 1H), 1.29 (s, 3H), 1.27-1.16 (m, 2H), 0.93 (d, J = 2.8 Hz, 6H), 0.91-0.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 158.5, 138.4, 128.0, 112.9, 83.4, 55.4, 53.6, 50.4, 45.7, 31.4, 26.7, 21.8, 21.8, 10.0; GC-MS (EI, QMS, m/z): 135.1, 150.1, 214.2, 242.2,

260.1. The spectroscopic data is in agreement with the literature.[7]

1-(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-ol (4o). Colorless oil, 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38-7.29 (m, 4H), 7.28-7.19 (m, 1H), 7.12 (d, J = 7.4 Hz, 1H), 6.86 (d, J = 7.9 Hz, 2H), 3.81 (s, 3H), 3.21-3.07 (m, 1H), 3.00-2.85 (m, 1H), 2.57-2.39 (m, 2H), 2.07 (s, 1H); ^{13}C NMR (151 MHz, CDCl3): δ_C 158.6, 148.2, 144.1, 138.6, 128.5, 127.1, 127.1, 125.1, 124.07, 113.5, 85.3, 55.4, 44.9, 29.9; GC-MS (EI, QMS, m/z): 152.1, 178.1, 207.1, 222.1, 240.1; HRMS (ESI): calcd for $C_{16}H_{16}O_2\,Na^+$, $(M+H)^+$, 263.1043, found, 263.1039.

(5'R,6aR,6bS,8aS,8bR,9S,11aS,12aS,12bS)-4-(4-methoxyphenyl)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-ol (4p). Colorless oil, 50% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 5.48 (d, J = 4.8 Hz, 1H), 4.45 (dd, J = 14.9, 7.5 Hz, 1H), 3.83 (d, J = 5.5 Hz, 3H), 3.55-3.47 (m, 1H), 3.41 (t, J = 10.9 Hz, 1H), 2.82 (d, J = 14.4 Hz, 1H), 2.16-2.00 (m, 1H), 1.98 (s, 1H), 1.93-1.88 (t, 1H), 1.88-1.79 (m, 3H), 1.79-1.75 (m, 1H), 1.74-1.69 (m, 2H), 1.68-1.58 (m, 7H), 1.57-1.44 (m, 3H), 1.32 (ddd, J = 16.9, 12.0, 5.8 Hz, 2H), 1.25-1.11 (m, 6H), 1.01 (d, J = 6.9 Hz, 3H), 0.86-0.79 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 158.5, 140.5, 140.0, 125.9, 124.3, 113.6, 109.4, 80.9, 73.4, 67.0, 62.2, 56.6, 55.4, 50.4, 46.58, 41.7, 40.4, 39.9, 36.9, 35.5, 34.9, 32.3, 32.0, 31.6, 31.5, 30.4, 28.9, 20.9, 18.9, 17.3, 16.4, 14.7; HRMS (ESI): calcd for $C_{34}H_{48}O_4Na^+$, $(M+Na)^+$, 543.3445, found, 543.3445.

General Procedures for Allylation of Cycloalkanols

Procedure A: Allylation of cycloalkanol reactions were conducted as follows: In a 10 mL bottom flask, containing a magnetic stirring bar, the respective cycloalkanols (0.1 mmol, 1 equiv), ethyl 2-((phenylsulfonyl)methyl)acrylate **2a**/**2b** (0.2 mmol, 2 equiv), collidine (0.25 mmol, 2 equiv) and

$Ir[dF(CF_3)ppy]_2(dCF_3bpy)PF_6$ was dissolved in 1 mL DCM, and the reaction system was irradiated under the 20 W White LED at room temperature. After the reaction, the solvents was removed under reduced pressure and purified by flash column chromatography (10% EtOAc/hexane-30% EtOAc/hexane) to give the allylation products.

Procedure B : Formylation of Cycloalkanol reactions were conducted as follows: In a 10 mL bottom flask, containing a magnetic stirring bar, the respective Cycloalkanols (0.1 mmol, 1 equiv), 2,6-Lutidine (0.25 mmol, 2.5 equiv) and $Ir[dF(CF_3)ppy]_2(dCF_3bpy)PF_6$ (2.0 mol%)was dissolved in 1 mL CF_3CH_2OH, and the reaction system was irradiated under the 20 W White LED at room temperature. After the reaction, the solvents was removed under reduced pressure and purified by flash column chromatography (10% EtOAc/hexane-30% EtOAc/hexane) to give the allylation products.

ethyl 7-(4-methoxyphenyl)-2-methylene-7-oxoheptanoate (3a). Procedure A: yellow oil, 21.2 mg, 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98-7.88 (m, 2H), 6.97-6.88 (m, 2H), 6.13 (d, J = 1.3 Hz, 1H), 5.53 (d, J = 1.3 Hz, 1H), 4.27 - 4.13 (t, 2H), 3.86 (s, 3H), 2.93 (t, J = 7.4 Hz, 2H), 2.34 (t, J = 7.5 Hz, 2H), 1.82- 1.68 (m, 2H), 1.62 -1.49 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 198.9, 167.4, 163.4, 140.7, 130.4, 130.2, 124.7, 113.8, 60.7, 55.5, 38.1, 31.8, 28.2, 24.1, 14.3; GC-MS (EI, QMS, m/z): 135.1, 150.1, 245.1, 272.1, 290.1; HRMS (ESI): calcd for $C_{17}H_{22}NaO_4^+$, $(M+Na)^+$, 313.1410, found, 313.1411.

ethyl 7-(2,4-dimethoxyphenyl)-2-methylene-7-oxoheptanoate (3b). Procedure A: yellow oil, 24.3 mg, 76% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.77 (d, J = 8.7 Hz, 1H), 6.50 (d, J = 8.7 Hz, 1H), 6.43 (s, 1H), 6.12 (s, 1H), 5.51 (s, 1H), 4.18 (q, J = 7.0 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 2.94 (t, J = 7.3 Hz, 2H), 2.32 (t, J = 7.6 Hz, 2H), 1.73-1.65 (m, 2H), 1.57-1.48 (m, 2H),

1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 200.6, 167.4, 164.3, 160.7, 140.8, 132.7, 124.5, 121.3, 105.1, 98.4, 60.6, 55.6, 55.5, 43.5, 31.8, 28.2, 24.2, 14.3; GC-MS (EI, QMS, m/z): 135.0, 163.0, 229.1, 302.1, 320.1; HRMS (ESI): calcd for $C_{18}H_{25}O_5^+$, $(M+H)^+$, 321.1697, found, 321.1693.

ethyl 7-(3,5-dimethoxyphenyl)-2-methylene-7-oxoheptanoate (3c). Procedure A: colorless oil, 22.7 mg, 71% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.09 (s, 2H), 6.64 (s, 1H), 6.15 (s, 1H), 5.54 (s, 1H), 4.26-4.12 (q, 2H), 3.84 (s, 6H), 2.95 (t, J = 6.6 Hz, 2H), 2.36 (t, J = 7.1 Hz, 2H), 1.81-1.72 (m, 2H), 1.62-1.52 (m, 2H), 1.30 (t, J = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 200.0, 167.4, 161.0, 140.7, 139.1, 124.8, 106.0, 105.2, 60.7, 55.7, 38.5, 31.8, 28.1, 24.0, 14.3; GC-MS (EI, QMS, m/z): 165.0, 180.0, 229.1, 302.1, 320.1; HRMS (ESI): calcd for $C_{18}H_{25}O_5^+$, $(M+H)^+$, 321.1697, found, 321.1695.

ethyl 7-(4-(tert-butyl)phenyl)-2-methylene-7-oxoheptanoate (3d). Procedure A: colorless oil, 25.3 mg, 80% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.89 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 6.14 (s, 1H), 5.54 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.97 (t, J = 7.2 Hz, 2H), 2.35 (t, J = 7.4 Hz, 2H), 1.80-1.73 (m, 2H), 1.57 (dd, J = 15.8, 8.0 Hz, 2H), 1.34 (s, 9H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 200.1, 167.4, 156.8, 140.7, 134.6, 128.2, 125.7, 124.8, 60.7, 38.4, 35.2, 31.9, 31.2, 28.2, 24.1, 14.4; GC-MS (EI, QMS, m/z): 118.0, 161.1, 176.1, 271.1, 316.3; HRMS (ESI): calcd for $C_{20}H_{29}O_3^+$, $(M+H)^+$, 317.2111, found, 317.2115.

ethyl 2-methylene-7-(naphthalen-2-yl)-7-oxoheptanoate (3e). Procedure A: Colorless oil, 14.0 mg, 45% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.47 (s, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.92- 7.85 (m, 2H), 7.57 (dt, J = 14.7, 6.7 Hz, 2H), 6.16 (s, 1H), 5.56 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.13 (t, J = 7.3 Hz, 2H), 2.39 (t, J = 7.6 Hz, 2H), 1.90-1.79 (m, 2H),

1.64 (dt, J = 15.2, 7.5 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 200.3, 167.4, 140.7, 135.7, 134.4, 132.7, 129.8, 129.7, 128.5, 128.5, 127.9, 126.9, 124.8, 124.0, 60.7, 38.5, 31.9, 28.2, 24.1, 14.3; GC-MS (EI, QMS, m/z): 127.0, 155.0, 170.0, 265.1, 310.2; HRMS (ESI): calcd for $C_{20}H_{22}O_3Na^+$, $(M+H)^+$, 333.1461, found, 333.1462.

ethyl 2-methylene-7-oxo-7-(phenanthren-9-yl)heptanoate (3f). Procedure A: colorless oil, 14.0 mg, 39% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 8.72 (d, J = 8.2 Hz, 1H), 8.68 (d, J = 8.5 Hz, 1H), 8.50 (d, J = 8.2 Hz, 1H), 8.09 (s, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.3 Hz, 2H), 6.16 (s, 1H), 5.56 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.16 (t, J = 7.3 Hz, 2H), 2.39 (t, J = 7.4 Hz, 2H), 1.95-1.79 (m, 2H), 1.65 (dd, J = 15.1, 7.6 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 204.9, 167.3, 140.5, 135.6, 131.7, 130.8, 130.1, 129.7, 128.9, 128.7, 128.4, 127.5, 127.1, 126.5, 124.7, 122.9, 122.7, 60.7, 42.1, 31.8, 28.1, 24.2, 14.2; GC-MS (EI, QMS, m/z): 151.1, 177.1, 205.1, 220.1, 360.2; HRMS (ESI): calcd for $C_{24}H_{25}O_3^+$, $(M+H)^+$, 361.1798, found, 361.1794.

ethyl 7-(benzofuran-2-yl)-2-methylene-7-oxoheptanoate (3g). Procedure A: yellow solid, 21.0 mg, 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.70 (d, J = 7.8 Hz, 1H), 7.57 (dd, J = 8.4, 0.6 Hz, 1H), 7.52-7.42 (m, 2H), 7.35-7.28 (m, 1H), 6.15 (s, 1H), 5.54 (d, J = 1.3 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.98 (t, J = 7.4 Hz, 2H), 2.37 (t, J = 7.5 Hz, 2H), 1.81 (dt, J = 15.1, 7.5 Hz, 2H), 1.64-1.54 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 191.5, 167.3, 155.7, 152.7, 140.5, 128.3, 127.2, 124.8, 124.0, 123.4, 112.7, 112.6, 60.7, 38.8, 31.7, 28.1, 23.8, 14.3; GC-MS (EI, QMS, m/z): 145.0, 160.0, 226.1, 282.1, 300.1; HRMS (ESI): calcd for $C_{18}H_{21}O_4^+$, $(M+H)^+$, 301.1434, found, 301.1444.

ethyl 7-(benzo[b]thiophen-2-yl)-2-methylene-7-oxoheptanoate (3h). Procedure A: White solid,

21.2 mg, 67% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.95 (s, 1H), 7.87 (t, J = 8.4 Hz, 2H), 7.42 (dtd, J = 14.8, 7.2, 1.2 Hz, 2H), 6.15 (s, 1H), 5.55 (d, J = 1.3 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.02 (t, J = 7.4 Hz, 2H), 2.37 (t, J = 7.5 Hz, 2H), 1.82 (dt, J = 15.1, 7.5 Hz, 2H), 1.65-1.54 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 199.4, 168.6, 163.4, 139.8, 130.5, 130.4, 127.7, 113.8, 60.8, 55.5, 47.7, 45.9, 43.4, 40.7, 36.5, 32.2, 28.0, 21.6, 20.0, 19.9, 14.2; GC-MS (EI, QMS, m/z): 161.0, 176.0, 242.0, 298.1, 316.1; HRMS (ESI): calcd for $C_{18}H_{21}O_3S^+$, $(M+H)^+$, 317.1206, found, 317.1201.

ethyl 7-(1-methyl-1H-indol-2-yl)-2-methylene-7-oxoheptanoate (3i). Procedure A: colorless oil, 22.2 mg, yield 71%. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.69 (d, J = 8.0 Hz, 1H), 7.38 (s, 2H), 7.30 (s, 1H), 7.19-7.11 (m, 1H), 6.15 (s, 1H), 5.55 (s, 1H), 4.21 (q, J = 7.0 Hz, 2H), 4.08 (s, 3H), 2.99 (t, J = 7.4 Hz, 2H), 2.37 (t, J = 7.5 Hz, 2H), 1.85-1.75 (m, 2H), 1.64-1.56 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 194.5, 167.4, 140.7, 140.2, 134.9, 126.0, 125.9, 124.8, 123.0, 120.8, 111.3, 110.5, 60.8, 39.8, 32.4, 31.9, 28.3, 24.8, 14.4; GC-MS (EI, QMS, m/z): 158.1, 173.1, 268.1, 295.1, 313.2; HRMS (ESI): calcd for $C_{19}H_{24}O_3N^+$, $(M+H)^+$, 314.1751, found, 314.1745.

ethyl 5-(benzyloxy)-7-(4-methoxyphenyl)-2-methylene-7-oxoheptanoate (3j). Procedure A: colorless oil, 26.1 mg, yield 66%. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.95 (d, J = 8.1 Hz, 2H), 7.34-7.23 (m, 5H), 6.93 (d, J = 8.1 Hz, 2H), 6.15 (s, 1H), 5.52 (s, 1H), 4.53 (s, 1H), 4.28- 4.16 (m, 3H), 3.87 (s, 3H), 3.37 (dd, J = 16.0, 6.5 Hz, 1H), 2.98 (dd, J = 16.0, 5.5 Hz, 1H), 2.54-2.39 (m, 2H), 1.82 (ddd, J = 16.3, 10.2, 6.0 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 197.4, 167.3, 163.7, 140.6, 138.6, 130.7, 130.5, 128.4, 127.9, 127.7, 124.8, 113.9, 75.6, 71.9, 60.8, 55.6, 43.4, 33.7, 27.8, 14.3; GC-MS (EI, QMS, m/z): 77.1, 135.1, 216.1, 305.1, 396.1;

HRMS (ESI): calcd for $C_{24}H_{29}O_5^+$, $(M+Na)^+$, 397.2010, found,397.2013.

1-ethyl 6-methyl 5-(2-(4-methoxyphenyl)-2-oxoethyl)-2-methylenehexanedioate (3k). Procedure A: colorless oil, 30.0 mg, 86% isolated yield containing 8% of 2a. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.94 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.18 (s, 1H), 5.58 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.70 (s, 3H), 3.48-3.40 (m, 1H), 3.06 (dt, J = 12.8, 5.7 Hz, 2H), 2.37 (t, J = 7.9 Hz, 2H), 1.93-1.73 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 196.6, 176.0, 167.1, 163.7, 139.9, 130.5, 129.8, 125.5, 113.9, 60.9, 55.6, 52.0, 40.1, 40.0, 31.0, 29.6, 14.3; GC-MS (EI, QMS, m/z): 135.0, 150.0, 303.1, 317.2, 348.2; HRMS (ESI): calcd for $C_{19}H_{24}NaO_6^+$, $(M+H)^+$, 371.1465, found, 371.1456.

ethyl 2-(((1S)-2-(2-(4-methoxyphenyl)-2-oxoethyl)cyclopent-3-en-1-yl)methyl)acrylate (3l). Procedure A: colorless oil, 13.8 mg, 42% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 6.15 (d, J = 1.4 Hz, 1H), 5.67 (s, 2H), 5.52 (d, J = 1.2 Hz, 1H), 4.20 (qd, J = 7.1, 1.2 Hz, 2H), 3.86 (s, 3H), 3.01 (dd, J = 13.8, 4.1 Hz, 1H), 2.98-2.83 (m, 2H), 2.53 (ddd, J = 21.6, 9.1, 6.0 Hz, 2H), 2.32 (dd, J = 14.0, 9.0 Hz, 1H), 2.22-2.11 (m, 1H), 2.06-1.95 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δc 198.3, 167.4, 163.5, 139.8, 133.7, 130.5, 130.4, 129.9, 125.8, 113.8, 60.8, 55.6, 47.6, 43.9, 42.4, 38.0, 37.9, 14.4; GC-MS (EI, QMS, m/z): 135.0, 149.0, 167.0, 279.1, 328.2; HRMS (ESI): calcd for $C_{20}H_{25}O_4^+$, $(M+H)^+$, 329.1747, found, 329.1749.

ethyl 6-(4-methoxyphenyl)-2-methylene-6-oxohexanoate (5a). Procedure A: Colorless oil, 14.6 mg, 53% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.93 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 6.17 (s, 1H), 5.56 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 2.94 (t, J = 7.3 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2H), 2.00-1.88 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$):

δ_C 198.6, 167.3, 163.5, 140.4, 130.4, 130.2, 125.1, 113.8, 60.8, 55.6, 37.5, 31.4, 23.1, 14.3; GC-MS (EI, QMS, m/z): 135.1, 150.1, 207.0, 231.1, 276.1; HRMS (ESI): calcd for $C_{16}H_{20}O_4Na^+$, $(M+Na)^+$, 299.1254, found, 299.1260.

ethyl 8-(4-methoxyphenyl)-2-methylene-8-oxooctanoate (5b). Procedure A: yellow oil, 21.2 mg, 70% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.93 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.12 (s, 1H), 5.50 (s, 1H), 4.19 (q, J = 7.1 Hz, 1H), 3.85 (s, 2H), 2.90 (t, J = 7.4 Hz, 1H), 2.30 (t, J = 7.6 Hz, 1H), 1.80-1.69 (m, 1H), 1.78-1.70 (m, 1H), 1.51 (dt, J = 15.2, 7.6 Hz, 1H), 1.40 (dt, J = 15.0, 7.7 Hz, 1H), 1.28 (t, J = 7.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.1, 167.4, 163.4, 141.0, 130.4, 130.2, 124.5, 113.8, 60.7, 55.5, 38.2, 31.8, 29.1, 28.4, 24.4, 14.3; GC-MS (EI, QMS, m/z) : 135.0, 150.0, 230.1, 286.4, 304.1; HRMS (ESI): calcd for $C_{18}H_{24}NaO_4^+$, $(M+Na)^+$, 327.1567, found, 327.1575.

ethyl 9-(4-methoxyphenyl)-2-methylene-9-oxononanoate (5c). Procedure A: colorless oil, 20.7 mg, 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 6.11 (d, J = 1.1 Hz, 1H), 5.49 (d, J = 1.4 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 2.89 (t, J = 7.4 Hz, 2H), 2.33-2.24 (t, 2H), 1.75-1.67 (m, 2H), 1.47 (dt, J = 14.7, 7.3 Hz, 2H), 1.38 (dt, J = 10.5, 3.5 Hz, 4H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 199.3, 167.5, 163.4, 141.1, 130.4, 130.3, 124.38, 113.8, 60.7, 55.6, 38.3, 31.9, 29.3, 29.2, 28.4, 24.6, 14.3; GC-MS (EI, QMS, m/z): 135.1, 155.1, 254.1, 273.1, 318.2; HRMS (ESI): calcd for $C_{19}H_{27}O_4^+$, $(M+H)^+$, 319.1904, found, 319.1906.

10-(4-methoxyphenyl)-2-methylene-10-oxodecanoate (5d). Procedure A: colorless oil, 27.2 mg, 82% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.92 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.1 Hz, 2H), 6.10 (s, 1H), 5.48 (s, 1H), 4.18 (q, J = 7.0 Hz, 2H), 3.85 (s, 3H), 2.89 (t, J = 7.3 Hz, 2H), 2.27

(t, J = 7.4 Hz, 2H), 1.73-1.68 (m, 2H), 1.50-1.40 (m, 2H), 1.34 (s, 6H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.3, 167.5, 163.4, 141.2, 130.4, 130.3, 124.3, 113.8, 60.6, 55.5, 38.4, 31.9, 29.4, 29.4, 29.2, 28.4, 24.7, 14.3; GC-MS (EI, QMS, m/z): 135.1, 150.1, 241.2.0, 287.1, 332.3; HRMS (ESI): calcd for $C_{20}H_{29}O_4^+$, $(M+H)^+$, 333.2060, found, 333.2062.

ethyl 11-(4-methoxyphenyl)-2-methylene-11-oxoundecanoate (5e). Procedure A: yellow oil, 21.8 mg, 63% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.94 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.11 (s, 1H), 5.49 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 2.90 (t, J = 7.4 Hz, 2H), 2.28 (t, J = 7.6 Hz, 2H), 1.75-1.65 (m, 2H), 1.44 (d, J = 6.4 Hz, 2H), 1.39-1.27 (m, 11H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.4, 167.5, 163.4, 141.2, 130.4, 130.3, 124.3, 113.8, 60.6, 55.6, 38.4, 31.9, 29.5, 29.5, 29.4, 29.3, 28.5, 24.7, 14.3; GC-MS (EI, QMS, m/z): 135.0, 150.1, 163.0, 255.2, 346.2; HRMS (ESI): calcd for $C_{21}H_{30}NaO_4^+$, $(M+Na)^+$, 369.2036, found, 369.2039.

ethyl 15-(4-methoxyphenyl)-2-methylene-15-oxopentadecanoate (5f). Procedure A: colorless oil, 32.5 mg, 81% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.93 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.10 (s, 1H), 5.49 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 2.89 (t, J = 7.4 Hz, 2H), 2.27 (t, J = 7.6 Hz, 2H), 1.74-1.64 (m, 2H), 1.43 (dd, J = 14.3, 7.0 Hz, 2H), 1.38-1.18 (m, 20H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.3, 167.5, 163.4, 141.2, 130.4, 130.3, 124.2, 113.7, 60.6, 55.5, 38.4, 31.9, 29.7, 29.7, 29.7, 29.6, 29.5, 29.5, 29.3, 28.5, 24.7, 14.3; GC-MS (EI, QMS, m/z): 135.1, 150.1, 328.2, 384.3, 402.3; HRMS (ESI): calcd for $C_{25}H_{39}O_4^+$, $(M+H)^+$, 403.2843, found, 403.2847.

ethyl 5-(3-(4-methoxyphenyl)-3-oxopropoxy)-2-methylenepentanoate (5g). Procedure A: colorless oil, 23.4 mg, 73% isolated yield containing 6% of 2a. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.96 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 6.14 (s, 1H), 5.52 (s, 1H), 4.20(q, 2H), 3.87 (s,

3H), 3.84 (t, J = 6.6 Hz, 2H), 3.48 (t, J = 6.3 Hz, 2H), 3.20 (t, J = 6.6 Hz, 2H), 2.35 (t, J = 7.5 Hz, 2H), 1.77-1.70 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 197.1, 167.2, 163.5, 140.3, 130.5, 130.2, 129.1, 128.8, 124.8, 113.7, 70.3, 66.2, 60.6, 55.5, 38.5, 28.5, 28.3, 14.2; GC-MS (EI, QMS, m/z): 150.1, 163.1, 241.1, 287.1, 320.2; HRMS (ESI): calcd for $C_{18}H_{25}O_5^+$, $(M+H)^+$, 321.1697, found, 321.1706.

ethyl 5-((ethoxycarbonyl)(3-(4-methoxyphenyl)-3-oxopropyl)amino)-2-methylenepentanoate (5h). Procedure A: colorless oil, 28.5 mg, 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.95 (s, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.16 (s, 1H), 5.54 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.0 Hz, 2H), 3.87 (s, 3H), 3.62 (t, J = 7.1 Hz, 2H), 3.37-3.09 (m, 4H), 2.29 (s, 2H), 1.73 (s, 2H), 1.34-1.18 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 197.6, 167.0, 163.7, 140.0, 130.5, 130.4, 124.9, 124.7, 113.8, 61.2, 60.7, 55.5, 47.6, 43.8, 37.3, 29.1, 27.4, 14.7, 14.2; GC-MS (EI, QMS, m/z): 135.1, 168.1, 241.2, 318.2, 391.3; HRMS (ESI): calcd for $C_{21}H_{30}NO_6^+$, $(M+H)^+$, 392.2068, found, 392.2061.

ethyl 2-(((3-(4-methoxyphenyl)-3-oxopropyl)thio)methyl)acrylate (5i). Procedure A: colorless oil, 24.6 mg, 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.22 (s, 1H), 5.71 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.44 (s, 2H), 3.21 (t, J = 7.4 Hz, 2H), 2.86 (t, J = 7.4 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 196.9, 166.3, 163.8, 137.2, 130.5, 129.8, 126.1, 113.9, 61.2, 55.6, 38.4, 33.4, 26.2, 14.3; GC-MS (EI, QMS, m/z): 135.0, 163.0, 195.0, 275.1, 308.1; HRMS (ESI): calcd for $C_{16}H_{21}O_4S^+$, $(M+H)^+$, 309.1155, found, 309.1148.

ethyl (R)-8-(4-methoxyphenyl)-4,6,6-trimethyl-2-methylene-8-oxooctanoate (5j). Procedure A: colorless oil, 27.0 mg, 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (d, J = 8.9 Hz,

2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.15 (d, *J* = 1.7 Hz, 1H), 5.46 (s, 1H), 4.17 (qd, *J* = 7.1, 0.7 Hz, 2H), 3.85 (s, 3H), 2.82 (q, *J* = 14.5 Hz, 2H), 2.36 (dd, *J* = 13.3, 5.4 Hz, 1H), 2.04 (dd, *J* = 13.4, 8.5 Hz, 1H), 1.85-1.74 (m, 1H), 1.43 (dd, *J* = 14.1, 3.9 Hz, 1H), 1.34-1.24 (m, 4H), 1.03 (d, *J* = 4.3 Hz, 6H), 0.89 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.1, 167.5, 163.3, 139.9, 131.9, 130.6, 126.4, 113.7, 60.7, 55.5, 49.6, 48.5, 42.3, 34.7, 28.1, 27.9, 22.5, 14.4; GC-MS (EI, QMS, m/z): 135.0, 150.1, 191.1, 263.1, 346.2; HRMS (ESI): calcd for $C_{21}H_{30}NaO_4^+$, $(M+Na)^+$, 369.2036, found, 369.2040.

ethyl (4R)-4-isopropyl-9-(4-methoxyphenyl)-7-methyl-2-methylene-9-oxononanoate (5k). Procedure A: colorless oil, 20.9 mg, 56% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (d, J = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.14 (s, 1H), 5.46 (d, *J* = 3.8 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 2.94-2.80 (m, 1H), 2.68 (dd, *J* = 15.5, 8.1 Hz, 1H), 2.39-2.25 (m, 1H), 2.19-2.02 (m, 2H), 1.81-1.65 (m, 1H), 1.43-1.33 (m, 2H), 1.31-1.10 (m, 6H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.88-0.78 (m, 6H); 13C NMR (151 MHz, CDCl3): δ 199.2, 167.6, 163.4 , 140.5, 130.7 (d, J = 3.2 Hz), 125.8, 113.8 , 60.7, 55.6, 45.8(d, J = 8.2 Hz), 42.5 (d, J = 16.4 Hz), 35.0 (d, J = 8.1 Hz), 33.5 (d, J = 17.3 Hz), 30.6 (d, J = 3.0 Hz), 28.6 (d, J = 24.3 Hz), 27.2 (d, J = 18.3 Hz), 20.2 (d, J = 3.0 Hz), 19.1 (d, J = 15.0 Hz), 18.7 (d, J = 8.5 Hz), 14.3; GC-MS (EI, QMS, m/z): 135.0, 150.1, 207.0, 346.1, 374.2; HRMS (ESI): calcd for $C_{23}H_{35}O_4^+$, $(M+H)^+$, 375.2530, found, 375.2520.

ethyl-2-(((1R,3S,3aS,6aR)-3-(2-(4-methoxyphenyl)-2-oxoethyl)octahydropentalen-1-yl)methyl)acrylate (5l). Procedure A: colorless oil, 17.0 mg, 46% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.93 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.09 (s, 1H), 5.49 (s, 1H), 4.25-4.12 (m, 2H), 3.87 (s, 3H), 3.02 (dd, *J* = 15.0, 4.8 Hz, 1H), 2.87 (dd, *J* = 14.8, 8.3 Hz, 1H), 2.47 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.22 (dd, *J* = 13.5, 8.6 Hz, 1H), 2.13 (m, *J* = 6.8 Hz, 1H), 2.04 (dd, *J* = 15.4,

7.2 Hz, 1H), 1.97-1.86 (m, 2H), 1.61 (dd, *J* = 25.9, 19.0 Hz, 2H), 1.53 (dd, *J* = 18.6, 9.8 Hz, 1H), 1.46 (s, 2H), 1.40 (d, *J* = 5.2 Hz, 2H), 1.33-1.26 (m, 3H), 0.90-0.76 (q, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.1, 167.4, 163.3, 140.3, 130.7, 130.5, 130.3, 125.3, 113.7, 60.5, 55.5, 50.1, 49.7, 46.2, 44.1, 43.3, 41.1, 37.9, 32.4, 32.2, 25.3, 14.2; GC-MS (EI, QMS, m/z): 135.0, 207.0, 220.1, 325.1, 370.2; HRMS (ESI): calcd for $C_{23}H_{30}NaO_4^+$, $(M+Na)^+$, 393.2036, found, 393.2028.

ethyl 2-(((1R,3r,5S,7r)-7-(4-methoxybenzoyl)bicyclo[3.3.1]nonan-3-yl)methyl)acrylate (5m). Procedure A: colorless oil, 11.5 mg, 31% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.99-7.91 (d, 2H), 6.96-6.87 (d, 2H), 6.16 (d, *J* = 1.6 Hz, 1H), 5.49 (d, *J* = 1.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 3.53-3.43 (m, 1H), 2.20 (d, *J* = 6.8 Hz, 2H), 2.16 (d, *J* = 8.2 Hz, 2H), 2.10-1.98 (m, 3H), 1.82 (dd, *J* = 8.7, 4.2 Hz, 1H), 1.56 (d, *J* = 12.1 Hz, 2H), 1.52-1.44 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.18-1.13 (m, 1H), 1.04 (td, *J* = 12.8, 3.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 203.0, 167.7, 163.3, 139.4, 130.5, 129.9, 125.7, 113.8, 60.8, 55.6, 40.2, 39.5, 37.6, 30.0, 29.3, 26.6, 25.5, 14.4; GC-MS (EI, QMS, m/z): 135.0, 189.0, 207.0, 296.1, 370.2; HRMS (ESI): calcd for $C_{23}H_{31}O_4^+$, $(M+H)^+$, 371.2217, found, 371.2210.

ethyl-2-(((1R,3R)-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2,2-trimethylcyclopentyl)methyl)acrylate (5n). Procedure A: colorless oil, 33.5 mg, 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.20 (d, *J* = 1.7 Hz, 1H), 5.41 (d, *J* = 0.6 Hz, 1H), 4.24-4.09 (m, 1H), 3.86 (s, 3H), 2.98 (dd, *J* = 15.1, 3.3 Hz, 1H), 2.72 (dd, *J* = 15.1, 10.6 Hz, 1H), 2.55-2.44 (m, 1H), 2.37 (d, *J* = 13.0 Hz, 1H), 2.26 (d, *J* = 12.9 Hz, 1H), 1.99- 1.86 (m, 1H), 1.57-1.45 (m, 1H), 1.26 (dd, *J* = 15.4, 8.3 Hz, 5H), 0.92 (s, 3H), 0.78 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 194.8, 167.3, 143.9, 142.5, 140.5, 139.3, 129.0, 127.5, 126.0, 125.1, 124.9, 123.1, 60.7, 39.1, 31.8, 28.2, 24.3, 14.3; GC-MS (EI, QMS, m/z): 135.1, 203.1, 259.1,

298.1, 372.3; HRMS (ESI): calcd for $C_{23}H_{32}NaO_4^+$, $(M+Na)^+$, 395.2193, found, 395.2197.

ethyl 5-(2-(4-methoxybenzoyl)phenyl)-2-methylenepentanoate (5o). Procedure A: colorless oil, 12.3 mg, 35% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.86-7.77 (m, 2H), 7.45-7.39 (m, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.27 (dd, J = 5.9, 2.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 6.10 (s, 1H), 5.45 (d, J = 1.3 Hz, 1H), 4.22-4.12 (m, 2H), 3.90 (s, 3H), 2.73-2.63 (m, 2H), 2.28 (t, J = 7.6 Hz, 2H), 1.81-1.69 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 197.5, 167.3, 163.9, 140.7, 140.5, 139.2, 132.7, 130.8, 130.1, 123.0, 128.2, 125.4, 124.7, 113.8, 60.7, 55.7, 32.9, 31.7, 30.3, 14.3; GC-MS (EI, QMS, m/z): 135.0, 149.0, 167.0, 279.1, 353.2; HRMS (ESI): calcd for $C_{22}H_{24}NaO_4^+$, $(M+Na)^+$, 375.1567, found, 375.1576.

ethyl-4-((4R,4aS,5'R,6aS,6bR,7S,9aS,10aS,10bS)-4-(3-(4-methoxyphenyl)-3-oxopropyl)-4,5',6a,7-tetramethyl-1,3',4,4a,4',5,5',6,6a,6b,6',7,9a,10,10a,10b-hexadecahydrospiro[benzo[4,5]indeno[2,1-b]furan-8,2'-pyran]-3-yl)-2-methylenebutanoate (5p). Procedure A: colorless oil, 42.9 mg, 68% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.15 (s, 1H), 5.58 (d, J = 5.2 Hz, 1H), 5.53 (s, 1H), 4.44 (dd, J = 15.0, 7.4 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 3.50 (d, J = 7.0 Hz, 1H), 3.40 (t, J = 10.9 Hz, 1H), 2.82 (ddd, J = 16.7, 10.6, 6.1 Hz, 1H), 2.62-2.52 (m, 1H), 2.49-2.41 (m, 2H), 2.19-2.10 (m, 2H), 2.07 (d, J = 7.3 Hz, 1H), 2.02 (dd, J = 10.9, 6.2 Hz, 1H), 1.93- 1.83 (m, 2H), 1.78 (dd, J = 15.3, 8.5 Hz, 2H), 1.73-1.57 (m, 7H), 1.56-1.44 (m, 3H), 1.34 (dd, J = 13.5, 6.5 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.25-1.11 (m, 3H), 1.04 (s, 3H), 0.99 (d, J = 6.9 Hz, 3H), 0.81 (t, J = 2.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.4, 167.4, 163.4, 142.0, 141.0, 130.4, 130.3, 124.8, 122.6, 113.8, 109.5, 81.0, 67.0, 62.2, 60.7, 56.8, 55.6, 43.7, 41.7, 41.1, 40.3, 40.0, 33.4, 32.3, 32.0, 31.68, 31.5, 30.4, 30.0, 29.4, 28.9, 22.8, 21.2, 17.3, 16.4, 14.7, 14.3; HRMS (ESI): calcd for $C_{40}H_{56}NaO_6^+$, $(M+Na)^+$,

655.3969, found, 655.3968.

ethyl (E)-2-benzylidene-7-(4-methoxyphenyl)-7-oxoheptanoate (6a). Procedure A: colorless oil, 13.2 mg, 36% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (d, J = 8.2 Hz, 2H), 7.67 (s, 1H), 7.43-7.30 (m, 5H), 6.92 (d, J = 8.2 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 2.91 (t, J = 7.3 Hz, 2H), 2.61-2.54 (m, 2H), 1.84-1.74 (m, 2H), 1.69-1.57 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.0, 168.5, 163.5, 139.0, 135.9, 133.5, 130.4, 130.2, 129.3, 128.6, 128.4, 113.8, 60.9, 55.6, 38.0, 29.0, 27.4, 24.5, 14.5; HRMS (ESI): calcd for $C_{23}H_{27}O_4^+$, $(M+H)^+$, 367.1904, found, 367.1912.

4-(4-methoxyphenyl)-4-oxobutanal (7a). Procedure B: colorless oil, 12.5 mg, 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.90 (s, 1H), 7.97 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.28 (t, J = 6.4 Hz, 2H), 2.91 (t, J = 6.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 201.1, 196.5, 163.8, 130.5, 129.6, 113.9, 55.6, 37.8, 30.8; GC-MS (EI, QMS, m/z): 92.1, 107.1, 135.1, 164.1, 192.1; HRMS (ESI): calcd for $C_{11}H_{13}O_3^+$, $(M+H)^+$, 193.0859, found, 193.0860.

5-(4-methoxyphenyl)-5-oxopentanal (7b). Procedure B: colorless oil, 11.3 mg, 55% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.83 (s, 1H), 7.96 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 3.01 (t, J = 7.0 Hz, 2H), 2.60 (td, J = 7.0, 1.0 Hz, 2H), 2.09 (p, J = 7.1 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 202.3, 198.1, 163.7, 130.4, 130.0, 113.9, 55.6, 43.3, 37.1, 16.8; GC-MS (EI, QMS, m/z): 107.1, 135.1, 150.1, 178.1, 206.1; HRMS (ESI): calcd for $C_{12}H_{15}O_3^+$, $(M+H)^+$, 207.1016, found, 207.1018.

6-(4-methoxyphenyl)-6-oxohexanal (7c). Procedure B: colorless oil, 12.8 mg, 59% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.81 (s, 1H), 7.96 (d, J = 8.3 Hz, 2H), 6.96 (d, J = 8.2 Hz, 2H), 3.89 (s, 3H), 2.97 (t, J = 6.9 Hz, 2H), 2.52 (t, J = 6.8 Hz, 1H), 1.85-1.71 (m, 3H), 1.61 (s, 1H); ^{13}C

NMR (151 MHz, $CDCl_3$): δ_C 202.3, 198.4, 130.3, 129.9, 113.7, 55.5, 43.8, 37.8, 23.8, 21.8; GC-MS (EI, QMS, m/z): 135.1, 150.1, 163.1, 192.1, 220.1; HRMS (ESI): calcd for $C_{13}H_{17}O_3^+$, $(M+H)^+$, 221.1172, found, 221.1169.

7-(4-methoxyphenyl)-7-oxoheptanal (7d). Procedure B: colorless oil, 14.3 mg, 61% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.76 (s, 1H), 7.93 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 2.92 (t, J = 7.3 Hz, 2H), 2.45 (td, J = 7.3, 1.4 Hz, 2H), 1.75 (dt, J = 12.4, 6.1 Hz, 2H), 1.72-1.64 (m, 2H), 1.47-1.35 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 202.8, 198.9, 163.5, 130.4, 130.2, 113.8, 55.6, 43.9, 38.0, 29.0, 24.3, 22.0; GC-MS (EI, QMS, m/z): 135.1, 150.1, 163.1, 206.1, 234.1; HRMS (ESI): calcd for $C_{14}H_{19}O_3^+$, $(M+H)^+$, 235.1329, found, 235.1326.

8-(4-methoxyphenyl)-8-oxooctanal (7e). Procedure B: colorless oil, 16.5 mg, 68% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.78 (s, 1H), 7.96 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 3.89 (s, 3H), 2.93 (t, J = 7.3 Hz, 2H), 2.41 (dt, J = 30.1, 7.3 Hz, 2H), 1.80-1.72 (m, 2H), 1.70 -1.62 (m, 2H), 1.41 (d, J = 2.8 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 202.9, 199.1, 178.6, 163.4, 130.3, 113.7, 55.5, 43.8, 38.1, 33.8, 29.0, 24.3, 21.9; GC-MS (EI, QMS, m/z): 135.1, 150.1, 163.1, 202.1, 248.2; HRMS (ESI): calcd for $C_{15}H_{21}O_3^+$, $(M+H)^+$, 249.1485, found, 249.1490.

12-(4-methoxyphenyl)-12-oxododecanal (7f). Procedure B: colorless oil, 13.1 mg, 43% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.78 (s, 1H), 7.96 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.92 (t, J = 7.4 Hz, 2H), 2.43 (td, J = 7.4, 1.7 Hz, 2H), 1.79-1.69 (m, 2H), 1.63 (dd, J = 13.6, 6.2 Hz, 1H), 1.43-1.27 (m, 13H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 203.2, 199.4, 163.4, 130.4, 130.3, 113.8, 55.6, 44.0, 38.4, 29.6, 29.5, 29.5, 29.5, 29.3, 24.7, 22.2; GC-MS (EI, QMS, m/z): 135.1, 150.1, 261.1, 276.3, 304.3; HRMS (ESI): calcd for $C_{19}H_{28}NaO_3^+$, $(M+Na)^+$, 327.1931, found, 327.1928.

4-(naphthalen-2-yl)-4-oxobutanal (7g). Procedure B: colorless oil, 9.5 mg, 45% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.94 (s, 1H), 8.52 (s, 1H), 8.04 (dd, J = 8.6, 1.5 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.89 (t, J = 8.3 Hz, 2H), 7.64-7.52 (m, 2H), 3.47 (t, J = 6.4 Hz, 2H), 2.99 (t, J = 6.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 200.9, 197.9, 135.8, 133.8, 132.6, 130.0, 129.7, 128.7, 128.6, 127.9, 127.0, 123.9, 37.9, 31.2; HRMS (ESI): calcd for $C_{14}H_{13}O_2^+$, $(M+H)^+$, 213.0910, found, 213.0905.

4-(benzo[b]thiophen-2-yl)-4-oxobutanal (7h). Procedure B: colorless oil, 12.6 mg, 58% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.91 (s, 1H), 8.03 (s, 1H), 7.96 - 7.77 (m, 2H), 7.44 (dt, J = 22.5, 7. 2 Hz, 2H), 3.38 (t, J = 6.3 Hz, 2H), 2.98 (t, J = 6.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.3, 192.4, 143.0, 142.6, 139.2, 129.4, 127.7, 126.1, 125.2, 123.1, 37.8, 31.6; GC-MS (EI, QMS, m/z): 133.0, 161.0, 190.0, 207.0, 218.0; HRMS (ESI): calcd for $C_{12}H_{11}SO_2^+$, $(M+H)^+$, 219.0474, found, 219.0469.

Control Experiment with TEMPO

the reactions were conducted as follows: In a 10 mL bottom flask, containing a magnetic stirring bar, **3a** (0.1 mmol, 1 equiv), ethyl 2-((phenylsulfonyl)methyl)acrylate **2a** (0.2 mmol, 2 equiv), TEMPO (0.2 mmol, 2 equiv), collidine (0.2 mmol, 2 equiv) and $Ir[dF(CF_3)ppy]_2(dCF_3bpy)PF_6$ was dissolved in 1 mL DCM, and the reaction system was irradiated under the 20 W White LED at room temperature. After the reaction, the solvents was removed under reduced pressure and purified by flash column chromatography to give the product.

1-(4-methoxyphenyl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butan-1-one. colorless oil, 26.6 mg, 80% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.82 (t, J = 6.2 Hz, 2H), 3.09-2.95 (m, 2H), 2.02-1.90 (m, 2H), 1.60 (s,

2H), 1.43 (d, J = 5.3 Hz, 4H), 1.12 (d, J = 20.1 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 199.0, 163.5, 130.5, 130.3, 113.8, 75.7, 59.8, 55.6, 39.7, 35.3, 33.2, 24.0, 20.3, 17.3; GC-MS (EI, QMS, m/z): 135.1, 177.1, 281.1, 310.1, 331.1; HRMS (ESI): calcd for $C_{20}H_{32}O_3N^+$, $(M+H)^+$, 334.2377, found, 334.2371.

ASSOCIATED CONTENT

^{1}H and ^{13}C NMR spectra for all compounds. 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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