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Visible-Light-Mediated Manganese-Catalyzed Allylation Reactions of Unactivated Alkyl Iodides

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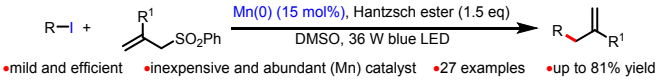
Supporting Information Placeholder

ABSTRACT: Herein, we report a protocol for visible-light-mediated allylation reactions between unactivated alkyl iodides and allyl sulfones under mild conditions with catalysis by inexpensive and readily available $Mn_2(CO)_{10}$. This protocol is compatible with a wide array of sensitive functional groups and has a broad substrate scope with regard to both the alkyl iodide and the allyl sulfone



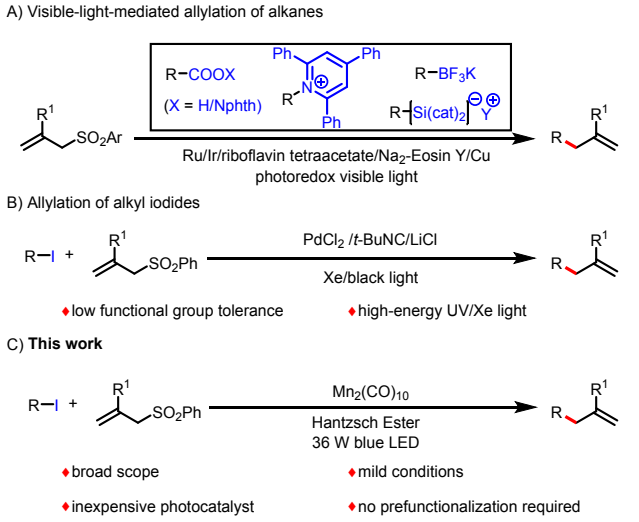
INTRODUCTION

Radical allylation is an efficient method for constructing $C(sp^3)$–$C(sp^3)$ bonds and is particularly useful for organic synthesis because it introduces an allyl group, which is a versatile handle for further functionalization.[1] Most of the reported free radical allylation reactions use allylstannane as the source of the allyl group,[2] but this organotin reagent is toxic and difficult to remove from product mixture. Interest in the use of photoredox catalysis in organic synthesis has grown rapidly in recent years,[3] and there have been several reports of visible-light-mediated photoredox radical allylation reactions with alkyl carboxylic acids,[4] carboxylic acid active esters,[5] alkyl trifluoroborates,[6] Katritzky pyridinium salts, [7] or silicates[8] as free radical precursors with allyl sulfones as radical acceptors (Scheme 1A). Although these allylation processes are much simpler and use less-toxic reagents than previously reported reactions, most of them require the use of noble metals such as iridium and ruthenium, and the radical precursors often must be prefunctionalized. Therefore, it would be a significant advance if these expensive catalysts could be replaced with a cheap, earth-abundant 3d transition metal, such as manganese, and if the substrate scope could be expanded to include widely available organic compounds that are commonly used as building blocks in medicinal chemistry, such as alcohols and alkyl iodides.

In 2018, the Ryu group reported the use of alkyl iodides as radical precursors for photocatalytic allylation reactions (Scheme 1B),[9] but high-energy xenon or ultraviolet lamps are required, which limits the functional group tolerance and thus the substrate scope of the process. Because alkyl iodides are readily available and inexpensive, we wished to develop a practical, mild protocol with a broader functional group tolerance and without the requirement for high-energy UV light. To do so, we needed to overcome the challenge posed by the fact that efficient excited-state quenching of ruthenium- and iridium-based photoredox catalysts with unactivated alkyl iodides (ca. −1.67 V vs. SCE for ethyl iodide) to generate alkyl radicals is difficult.[10]

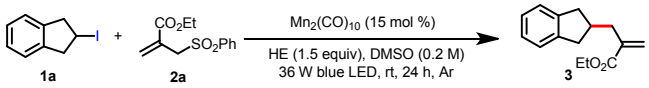
Photoirradiation of decacarbonyldimanganese, $Mn_2(CO)_{10}$, is known to cause homolytic cleavage of the weak Mn–Mn bond (~150 kJ mol^{-1}) to form two manganese-centered pentacarbonyl radicals [$\cdot Mn(CO)_5$].[11] These radicals can extract iodine atoms from alkyl iodides in a process that is not limited by the reduction potential of the metal or the redox properties of the catalyst.[12,13] Therefore, the use of $Mn_2(CO)_{10}$ as a catalyst would solve the problem posed by the low reduction potential of alkyl iodides, which hampers their reduction by common photocatalysts to generate alkyl radicals.[14] However, for successful catalytic turnover, the active catalyst, [$\cdot Mn(CO)_5$], would have to be regenerated from $Mn(CO)_5I$ under the reaction conditions. Herein we report that we have succeeded in developing a protocol for efficient visible-light-mediated allylation reactions of unactivated alkyl iodides with $Mn_2(CO)_{10}$ as catalyst via a unique mechanism (Scheme 1C).

Scheme 1. Photoredox-mediated allylation reactions.



RESULTS AND DISCUSSION

Table 1. Optimization of Reaction Conditions.[a]



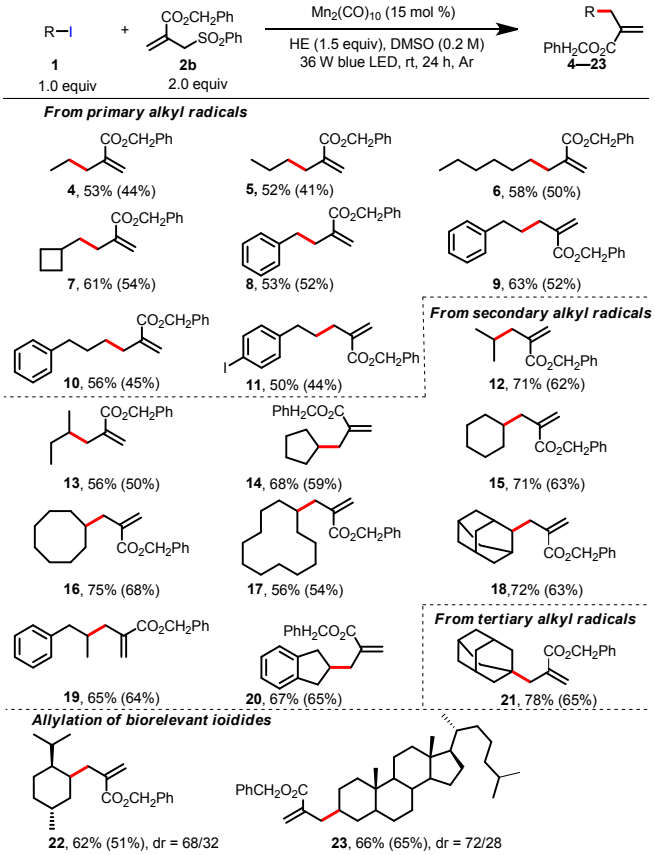
entry	photocatalyst	solvent	yield (%)[b]
1	**$Mn_2(CO)_{10}$**	**DMSO**	**81 (66[c])**
2	$Ir(ppy)_3$	DMSO	NR
3	$[Ru(bpy)_3]Cl_2·6H_2O$	DMSO	NR
4	$[Ru(bpy)_3](PF_6)_2$	DMSO	NR
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMSO	NR
6	$Mn_2(CO)_{10}$	MeOH	73
7	$Mn_2(CO)_{10}$	Acetone	55
8	$Mn_2(CO)_{10}$	DMF	53
9[d]	$Mn_2(CO)_{10}$	DMSO	NR
10	—	DMSO	NR
11[e]	$Mn_2(CO)_{10}$	DMSO	16

[a]Reaction conditions, unless otherwise noted: **1a** (0.3 mmol) and **2a** (0.6 mmol) photocatalyst (0.045 mmol), Hantzsch ester (HE, 0.45 mmol), and solvent (1.5 mL) under Ar atmosphere. [b]Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. NR = no reaction. [c]Isolated yield. [d]Performed in the absence of light. [e]Performed in the absence of HE..

We commenced our studies using 2-iodo-2,3-dihydro-1*H*-indene (**1a**) and ethyl 2-((phenylsulfonyl)methyl)acrylate (**2a**) as model substrates to investigate the optimal reaction conditions (Table 1). We were pleased to find that in the presence of 15 mol % $Mn_2(CO)_{10}$ and 1.5 equiv of Hantzsch ester (HE) as a reducing agent, irradiation of **1a** and **2a** in DMSO with a 36 W blue LED at room temperature under argon provided an excellent yield of desired product **3** (entry 1). Screening of various photocatalysts revealed that $Ir(ppy)_3$, $[Ru(bpy)_3](PF_6)_2$, $[Ru(bpy)_3]Cl_2·6H_2O$, or $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ failed to afford the target product (entries 2–5). MeOH, acetone, and DMF proved to be inferior solvents to DMSO (entries 6–8). Control experiments demonstrated that $Mn_2(CO)_{10}$, and visible light were essential for the success of the reaction (entries 9 and 10), while the absence of HE were proven detrimental for the whole protocol (entry 11).

With satisfactory conditions in hand, we explored the substrate scope of the reaction, beginning with the unactivated alkyl iodide (Scheme 2). A wide range of primary alkyl iodides **1** reacted with allyl sulfone **2b** to give desired products **4**–**11** in moderate yields. Specifically, primary iodides of linear alkanes gave **4**–**6** in 52%–58% yields; and (iodomethyl)cyclobutane gave **7**, with an intact cyclobutane ring, in 61% yield. Benzyl iodide, phenethyl iodide, and phenylpropyl iodide were also suitable substrates, giving **8**, **9,** and **10** in 53%, 63%, and 56% yields, respectively. Notably, the reaction of 4-iodophenethyl iodide occurred selectively at the sp^3 C–I bond to afford **11** in 50% yield. Next, we examined the suitability of secondary iodoalkanes. The yields obtained with these substrates were higher than those with the primary iodides because secondary alkyl radicals are more stable and more nucleophilic than primary radicals. Acyclic secondary iodides afforded target products **12** and **13** in yields of 71% and 56%, respectively. Subsequently we explored various cyclic iodoalkanes to determine the effects of ring size; five-, six-, eight-, and twelve-membered-ring iodoalkanes all gave the corresponding products (**14**–**17**) in moderate to good yields. The sterically bulky substrate 2-iodoadamantane afforded **18** in 72% yield. This reaction was also applicable to secondary alkanes containing an aryl moiety (**19** and **20**). In addition, reaction of 1-iodoadamantane, a tertiary iodoalkane, proceeded smoothly, leading to the formation of **21** in 78% yield. Finally, we investigated the applicability of the protocol for biologically relevant substrates and found that the allylation reactions of iodomenthol and 3-iodocholesterol, which were prepared in one step from the corresponding alcohols, smoothly afforded target products **22** and **23** in moderate yields. Product of this reaction will underwent a Giese reaction with alkyl iodide[15] account for a modest yield.

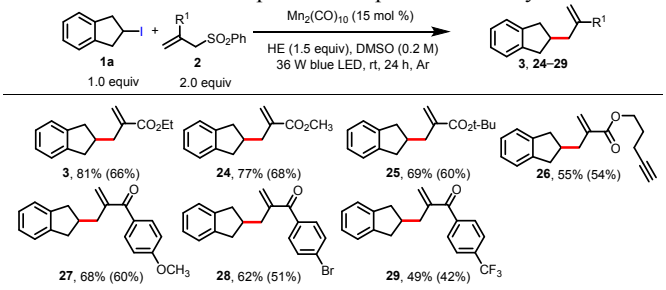
Scheme 2. Substrate scope with respect to the alkyl iodide.[a]



[a]Unless otherwise noted, reactions were performed on a 0.3 mmol scale under the conditions listed in entry 1 of Table 1. Isolated yields are given in parentheses.

Furthermore, we explored various allyl sulfone substrates to determine their suitability for this radical allylation reaction (Scheme 3). When 2-iodo-2,3-dihydro-1*H*-indene (**1a**) was used as the radical precursor, the yields were satisfactory, ranging from 49% to 81%. Allyl sulfones with various substituents (Me, Et, ^{t}Bu and alkyne esters) smoothly delivered the corresponding allylated products (**3** and **24**–**26**) in good yields. In addition to the esters, benzoyl compounds containing either an electron-donating methoxy group (**27**) or an electron-withdrawing bromine atom (**28**) or trifluoromethyl group (**29**) were viable allyl sulfone substrates.

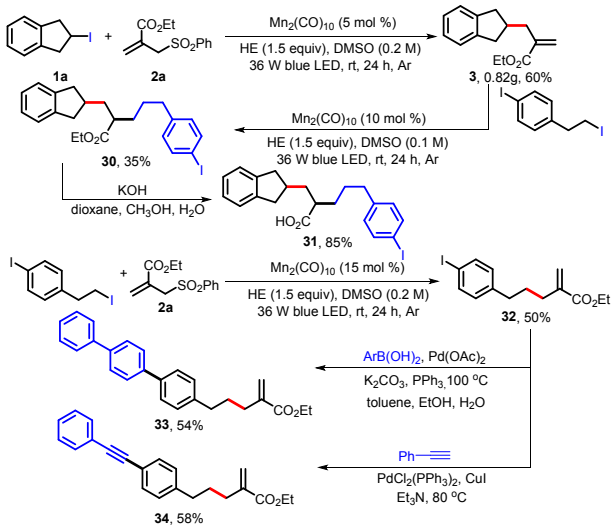
Scheme 3. Substrate scope with respect to the allyl sulfone.[a]



[a]Unless otherwise noted, reactions were performed on a 0.3 mmol scale under the conditions shown in entry 1 of Table 1. Isolated yields are given in parentheses.

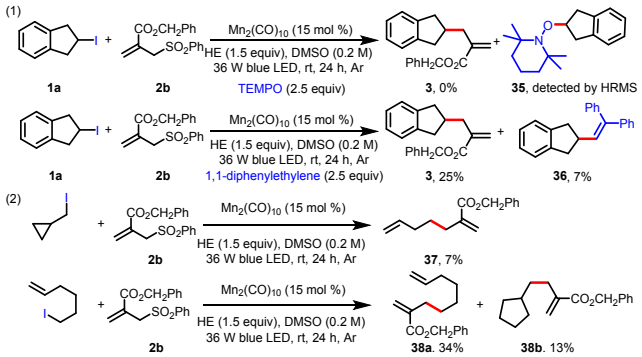
To demonstrate the synthetic applications of the method (Scheme 4), we carried out a gram-scale reaction (6.0 mmol) between **1a** with **2a**, which was complete within 24 h under the standard conditions (except that the amount of catalyst was decreased to 5 mol %) and gave **3** in 60% yield (0.82g). Acrylate **3**, which is a Michael receptor, underwent a Giese reaction with 4-iodophenethyl iodide to afford **30**;[15] and subsequent hydrolysis with KOH afforded carboxylic acid **31**; that is, we were able to use the method described herein to synthesize structurally complex carboxylic acids. Finally, iodide **32**(obtained by reaction of 4-iodophenethyl iodide and **2a**) smoothly underwent Suzuki coupling with an arylboronic acid or Sonagashira coupling with phenylacetylene to provide moderate yields of corresponding products **33** and **34**, respectively.

Scheme 4. Applications of the protocol.



Having explored the substrate scope of this visible-light-mediated reaction, we turned our attention to its mechanism (Scheme 5). (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and 1,1-diphenylethylene were used as radical scavengers to determine whether the reaction proceeded via a radical process. We found that TEMPO (2.5 equiv) completely inhibited the formation of **3**, and TEMPO adduct 2,6-di-*tert*-butyl-4-methyl phenoxy-2,3-dihydro-1*H*-indene **35** was detected by mass spectrometry. In addition, the corresponding product of radical trapping, 2-(2,2-diphenylvinyl)-2,3-dihydro-1*H*-indene (**36**), was isolated from the reaction in the presence of 1,1-diphenylethylene, further supporting the intermediacy of an alkyl radical. To confirm the mechanism, we next performed a radical clock experiment; specifically, allylation of **2b** with (iodomethyl)cyclopropane gave ring-opened product **37**, and allylation with 6-iodohex-1-ene gave a 2.7:1 mixture of **38a** and **38b** in 47% yield via a 5-*exo* radical cyclization. Taken together, the results of these experiments clearly point to a radical pathway. Moreover, a light/dark experiment showed that coupling product **3** could be formed in the dark (see ESI), which implies a radical chain propagation mechanism.

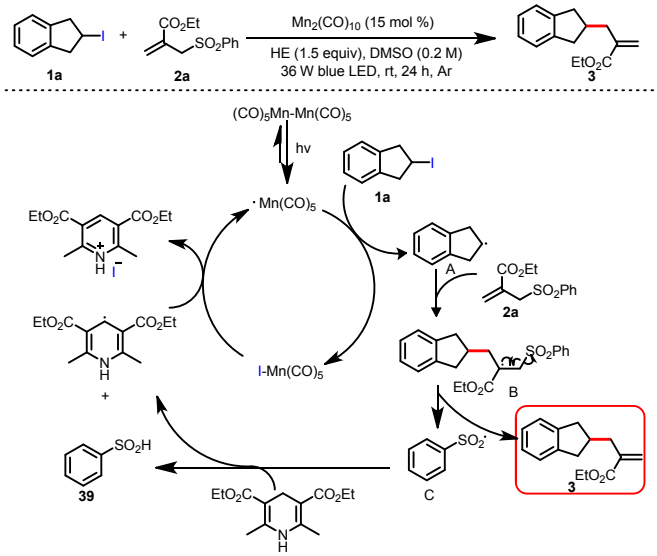
Scheme 5. Mechanistic Experiments.



[a]See ESI for experimental details.

On the basis of these mechanistic experiments and previous reports, we propose the mechanism depicted in Scheme 6. First, upon irradiation with the blue LED, $Mn_2(CO)_{10}$ is homolyzed to form [·$Mn(CO)_5$], which abstracts iodine from 2-iodo-2,3-dihydro-1*H*-indene (**1a**) to generate nucleophilic radical species **A** and $Mn(CO)_5I$. The iodine-abstraction step is irreversible, owing to the difference between the dissociation energies of the Mn–I bond of $Mn(CO)_5I$ (67 kcal mol^{-1}) and the C(sp^3)–I bond of 2-iodo-2,3-dihydro-1*H*-indene (60 kcal mol^{-1}).[12] Radical **A** then adds to allyl sulfone **2a** to afford radical intermediate **B**, which undergoes β-fragmentation to give allylated product **3** and phenylsulfonyl radical ($PhSO_2$·, **C**). Sulfonyl radical **C** abstracts the hydrogen atom from HE to afford benzenesulfinic acid **39** or loss of sulfur dioxide to form a phenyl radical, which then abstracts the hydrogen atom from HE. And the resulting dienyl radical may react with $Mn(CO)_5I$ to regenerate the active catalyst [·$Mn(CO)_5$]. A ionic reduction of $Mn(CO)_5I$ by HE may also occur.

Scheme 6. Proposed Mechanism



In conclusion, we have developed a new protocol for visible-light-mediated allylation reactions of unactivated alkyl iodides with catalysis by $Mn_2(CO)_{10}$, an inexpensive complex of an earth-abundant metal, and with HE as reducing agent. This versatile protocol tolerates a variety of functional groups and has a broad scope with regard to both the alkyl iodide and the allyl sulfone. Moreover, the allylated products contain a reactive terminal olefin moiety that can act as a handle for further functionalization.

EXPERIMENTAL SECTION

General Method and Materials. Reagents were purchased from commercial sources and were used as received. Blue light-emitting diode (LED) (36 W, max = 455 nm) purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature. The material of the irradiation vessel was borosilicate glass. ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh).

General Procedures for Synthesis of Alkyl Iodides. According to literature reports,[16] alkyl iodides are prepared by the corresponding alcohols. The spectral data of the alkyl iodides are consistent with the literature data.[16]

Preparation of Allyl Sulfone. According to literature reports,[17] The spectral data of the allyl sulfone are consistent with the literature data.[17] **2a** and **2b** is prepared according to the same literature[17] and spectral data of them are consistent with the literature data. [17]

Radical trapping experiments. To a 8 mL glass vial was added $Mn_2(CO)_{10}$ (17.55 mg, 0.045 mmol, 15 mol %), **1a** (73 mg, 0.3 mmol, 1.0 equiv), **2b** (190 mg, 0.6 mmol, 2.0 equiv), TEMPO (117 mg, 0.75 mmol, 2.5 equiv) or 1,1-dipheny -lethylene (135 mg, 0.75 mmol, 2.5 equiv), HE (114 mg, 0.45 mmol, 1.5 equiv) and 1.5mL of DMSO. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h.

Procedure for Giese reaction (synthesis of 30). To a 8 mL glass vial was added $Mn_2(CO)_{10}$ (11.7 mg, 0.03 mmol, 10 mol %), **3** (69 mg, 0.3 mmol, 1.0 equiv), 1-iodo-4-(2-iodoethyl)benzene (215 mg, 0.6 mmol, 2.0 equiv), HE (114 mg, 0.45 mmol, 1.5 equiv) and 3.0 mL of DMSO. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The mixture was diluted with 10 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

Hydrolysis of ester (synthesis of 31). To an oven dried Schlenk tube was added synthesized pure ester 30 (268 mg, 0.58 mmol, 1.0 equiv)， KOH (98 mg, 1.74 mmol, 3.0 equiv), the solvent(6 ml) is 1/1/1 by volume of dioxane, methanol and water. The tube was evacuated and backfilled with Ar (this process was repeated three times). The mixture was then stirred rapidly and warm up to 110 °C for 24h. After finishing the reaction, added 1M HCl to adjust the system pH to 2, and extracted with ethyl acetate (3 × 25 mL). The combined organic extracts were washed with brine (75 mL), dried over Na_2SO_4, and concentrated in vacuum to get pure product.

Procedure for Suzuki coupling reaction (synthesis of 33). Synthesized pure compound **32** (69 mg, 0.2 mmol, 1.0 equiv), phenylboronic acid(44 mg, 0.22 mmol, 1.1 equiv), K_2CO_3 (55 mg,

0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5.0 mol %), PPh_3 (9 mg, 0.03mmol, 0.15 equiv), toluene (2.3 mL, 0.113M), equal mixture of ethanol/water (0.113 mL, 0.565 M) were taken into a re-sealable pressure tube (13 x 100 mm) and was allowed it to stir at 100 °C with heating mantle for 24h. After finishing the reaction, the solvent mixture was evaporated and again diluted with dicholomethane (20 mL). This diluted mixture was then passed through a celite bed followed by the washing of this bed with additional amount of dicholomethane (20 mL). This combined organic layer was washed with water (1 x 20 mL) using a separating funnel. The collected organic layer was dried over $MgSO_4$ and solvent was evaporated under reduced pressure. This crude product was then subjected to purification using flash column chromatography to get pure product.

Procedure for Sonagashira coupling reaction (synthesis of 34). Synthesized pure compound **32** (69 mg, 0.2 mmol, 1.0 equiv), phenylacetylene (31 mg, 0.3 mmol, 1.5 equiv), CuI(3.8 mg, 0.02 mmol, 0.1 equiv), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol, 5.0 mol %), Et_3N (2 ml) were taken into a re-sealable pressure tube (13 x 100 mm) and was allowed it to stir at 80 °C with heating mantle for 24h. After finishing the reaction, add water to quench the reaction, the solvent mixture was evaporated and again diluted with ethyl acetate (20 mL x 3). This combined organic layer was washed with water (1 x 20 mL) using a separating funnel. The collected organic layer was dried over Na_2SO_4 and solvent was evaporated under reduced pressure. This crude product was then subjected to purification using flash column chromatography to get pure product.

Gram-scale Reaction. To a 100 ml oven dried Schlenk tube was added $Mn_2(CO)_{10}$ (117 mg, 0.3 mmol, 5 mol %), **1a** (1.45g, 6.0 mmol, 1.0 equiv), **2a** (3.051g, 12.0 mmol, 2.0 equiv), HE (2.28 g, 9.0 mmol, 1.5 equiv) and 30 mL of DMSO. The tube was evacuated and backfilled with Ar three times. The mixture was then stirred rapidly and irradiated under 36W blue LED at room temperature for 24 h. The mixture was diluted with 50 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over Na_2SO_4, and concentrated in vacuum. After purification by flash column chromatography on silica gel, the product **3** was obtained in 60% yield (0.82g).

Experimental Procedures and Product Characterization

General Procedure for the allylation of unactivated alkyl iodides. To a 8 mL glass vial was added $Mn_2(CO)_{10}$ (17.55 mg, 0.045 mmol, 15 mol %), **1** (0.3 mmol, 1.0 equiv), **2** (0.6 mmol, 2.0 equiv), HE (114 mg, 0.45 mmol, 1.5 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The mixture was diluted with 10 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3× 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

Product Characterization

*ethyl 2-((2,3-dihydro-1H-inden-2-yl)methyl)acrylate **(3)***

According to the general procedure. Colorless oil (45.8 mg, 66%) Yield determined by ^{1}H NMR: 81%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (dd, J = 5.2, 3.6 Hz, 2H), 7.11 (dd, J = 5.6, 3.2 Hz, 2H), 6.20 (d, J = 0.8 Hz, 1H), 5.56 (d, J = 0.8 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.03 (dd, J = 15.2, 7.2 Hz, 2H), 2.71 (dd, J = 14.4, 7.2 Hz, 1H), 2.62 (dd, J = 15.2, 6.8 Hz, 2H), 2.47 (d, J = 7.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 143.1, 139.8, 126.2, 125.6, 124.5, 60.7, 38.8, 38.3, 37.8, 14.2. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}NaO_2$ 253.1199; Found 253.1198

*benzyl 2-methylenepentanoate **(4)***

According to the general procedure. Colorless oil (27.2 mg, 44%) Yield determined by ^{1}H NMR: 53%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 6.20 (s, 1H), 5.55 (d, J = 1.2Hz, 1H), 5.20 (s, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.55 – 1.44 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 140.6, 136.2, 128.6, 128.1, 128.0, 125.0, 66.3, 33.9, 21.5, 13.7. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}NaO_2$ 227.1043; Found 227.1042

*benzyl 2-methylenehexanoate **(5)***

According to the general procedure. Colorless oil (26.7 mg, 41%) Yield determined by ^{1}H NMR: 52%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 6.18 (s, 1H), 5.54 (s, 1H), 2.32 (t, J = 7.6 Hz, 2H), 1.50 – 1.40 (m, 2H), 1.37 – 1.28 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 140.9, 136.2, 128.5, 128.1, 128.0, 124.8, 66.3, 31.6, 30.6, 22.3, 13.9.**HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}NaO_2$ 241.1199; Found 241.1197

*benzyl 2-methylenenonanoate **(6)***

According to the general procedure. Colorless oil (39.1 mg, 50%) Yield determined by ^{1}H NMR: 58%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 6.18 (d, J = 0.8 Hz, 1H), 5.54 (d, J = 1.2 Hz, 1H), 5.20 (s, 2H), 2.36 – 2.27 (m, 2H), 1.50 – 1.42 (m, 2H), 1.32 – 1.23 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 140.8, 136.2, 128.6, 128.1, 128.0, 124.8, 66.3, 31.9, 31.82, 29.2, 29.1, 28.4, 22.7, 14.1. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{25}O_2$261.1849; Found 261.1845

*benzyl 4-cyclobutyl-2-methylenebutanoate **(7)***

According to the general procedure. Colorless oil (39.3 mg, 54%) Yield determined by ^{1}H NMR: 61%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 5H), 6.18 (d, J = 4.0 Hz, 1H), 5.54 (d, J = 3.2 Hz, 1H), 5.20 (d, J = 4.8 Hz, 2H), 2.26 – 2.17 (m, 2H), 2.08 – 1.98 (m, 2H), 1.87 – 1.75 (m, 2H), 1.65 – 1.51 (m, 4H), 1.31 – 1.21 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 140.8, 136.2, 128.6, 128.1, 128.0, 124.7, 66.3, 35.7, 35.6, 29.6, 28.2, 18.4. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{20}NaO_2$ 267.1356; Found 267.1354

*benzyl 2-methylene-4-phenylbutanoate **(8)***

According to the general procedure. Colorless oil (41.7 mg, 52%) Yield determined by ^{1}H NMR: 53%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 5H), 7.22 – 7.14 (m, 2H), 7.13 – 7.04 (m, 3H), 6.13 (s, 1H), 5.44 (s, 1H), 5.13 (s, 2H), 2.76 – 2.66 (m, 2H), 2.61 – 2.52 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 166.9, 141.4, 139.9, 136.1, 128.6, 128.5, 128.4, 128.2, 128.1, 126.0, 125.8, 66.5, 34.9, 34.0.**HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O_2$ 267.1380; Found 267.1379

*benzyl 2-methylene-5-phenylpentanoate **(9)***

According to the general procedure. Colorless oil (44.3 mg, 52%) Yield determined by ^{1}H NMR: 63%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 7.29 – 7.22 (m, 2H), 7.20 – 7.12 (m, 3H), 6.21 (s, 1H), 5.55 (s, 1H), 5.19 (s, 2H), 2.63 (t, J = 7.6 Hz, 2H), 2.37 (t, J = 7.6 Hz, 2H), 1.86 – 1.75 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.1, 142.1, 140.4, 136.1, 128.6, 128.5, 128.4, 128.2, 128.1, 125.9, 125.3, 66.4, 35.5, 31.6, 30.1. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}NaO_2$ 303.1356; Found 303.1352

*benzyl 2-methylene-6-phenylhexanoate **(10)***

According to the general procedure. Colorless oil (39.5 mg, 45%) Yield determined by ^{1}H NMR: 56%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 7.29 – 7.23 (m, 2H), 7.19 – 7.11 (m, 3H), 6.18 (s, 1H), 5.52

(s, 1H), 5.18 (s, 2H), 2.60 (t, J = 7.2 Hz, 2H), 2.35 (t, J = 7.2 Hz, 2H), 1.69 – 1.60 (m, 2H), 1.56 – 1.48 (m, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.1, 142.5, 140.6, 136.2, 128.6, 128.4, 128.3, 128.2, 128.1, 125.7, 125.1, 66.4, 35.8, 31.8, 31.0, 28.1. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}NaO_2$ 317.1512; Found 317.1510

*benzyl 5-(4-iodophenyl)-2-methylenepentanoate **(11)***

According to the general procedure. Colorless oil (53.9 mg, 44%) Yield determined by ^1H NMR: 50%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.40 – 7.29 (m, 5H), 6.89 (d, J = 8.4 Hz, 2H), 6.21 (s, 1H), 5.54 (s, 1H), 5.19 (s, 2H), 2.56 (t, J = 7.6 Hz, 2H), 2.38 – 2.30 (m, 2H), 1.82 – 1.72 (m, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.0, 141.7, 140.2, 137.4, 136.1, 130.6, 128.6, 128.2, 128.1, 125.4, 90.9, 66.5, 34.9, 31.5, 29.9. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}INaO_2$ 429.0322; Found 429.0319

*benzyl 4-methyl-2-methylenepentanoate **(12)***[18]

According to the general procedure. Colorless oil (53.9 mg, 62%) Yield determined by ^1H NMR: 71%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 5H), 6.14 (d, J = 1.6 Hz, 1H), 5.44 (d, J = 1.2 Hz, 1H), 5.11 (s, 2H), 2.12 (dd, J = 7.2, 0.8 Hz, 2H), 1.78 – 1.68 (m, 1H), 0.81 (d, J = 6.8 Hz, 6H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.2, 140.6, 136.2, 128.6, 128.1, 128.0, 125.0, 66.3, 33.9, 21.5, 13.7.**HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1380; Found 219.1377

*(R)-benzyl 4-methyl-2-methylenehexanoate **(13)***

According to the general procedure. Colorless oil (36.7 mg, 50%) Yield determined by ^1H NMR: 56%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 6.21 (s, 1H), 5.51 (s, 1H), 5.18 (s, 2H), 2.44 – 2.33 (m, 1H), 2.12 – 2.01 (m, 1H), 1.63 – 1.52 (m, 1H), 1.43 – 1.29 (m, 1H), 1.19 – 1.07 (m, 1H), 0.90 – 0.81 (m, 6H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.3, 139.7, 136.2, 128.5, 128.1, 128.0, 126.1, 66.3, 39.4, 33.5, 29.3, 18.8, 11.4. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}O_2$ 233.1536; Found 233.1532

*benzyl 2-(cyclopentylmethyl)acrylate **(14)***

According to the general procedure. Colorless oil (43.1 mg, 59%) Yield determined by ^1H NMR: 68%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 6.18 (s, 1H), 5.54 (s, 1H), 5.19 (s, 2H), 2.33 (d, J = 7.2 Hz, 2H), 2.09 – 1.99 (m, 1H), 1.79 – 1.66 (m, 2H), 1.66 – 1.56 (m, 2H), 1.55 – 1.46 (m, 2H), 1.19 – 1.05 (m, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.3, 140.4, 136.2, 128.5, 128.1, 128.0, 125.4, 66.3, 38.6, 38.2, 32.4, 25.0. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}O_2$ 245.1536; Found 245.1533

*benzyl 2-(cyclohexylmethyl)acrylate **(15)***

According to the general procedure. Colorless oil (48.7 mg, 63%) Yield determined by ^1H NMR: 71%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 5H), 6.20 (d, J = 1.6 Hz, 1H), 5.50 (d, J = 1.2 Hz, 1H), 5.19 (s, 2H), 2.21 (d, J = 7.2 Hz, 2H), 1.70 – 1.65 (m, 4H), 1.50 – 1.40 (m, 1H), 1.25 – 1.07 (m, 4H), 0.92 – 0.83 (m, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.3, 139.2, 136.2, 128.5, 128.1, 128.0, 126.1, 66.3, 40.0, 36.6, 33.1, 26.5, 26.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{23}O_2$ 259.1693; Found 259.1690

*benzyl 2-(cyclooctylmethyl)acrylate **(16)***

According to the general procedure. Colorless oil (58.3 mg, 68%) Yield determined by ^1H NMR: 75%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.23 (m, 5H), 6.20 (d, J = 1.6 Hz, 1H), 5.50 (d, J = 1.2 Hz, 1H), 5.19 (s, 2H), 2.21 (d, J = 7.2 Hz, 2H), 1.79 – 1.68 (m, 1H), 1.63 – 1.37 (m, 12H), 1.30 – 1.18 (m, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 166.4, 138.9, 135.3, 127.6, 127.2, 127.1, 125.2, 65.4, 39.6, 35.1, 31.0, 26.3, 25.3, 24.4. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{27}O_2$ 287.2006; Found 287.2002

*benzyl 2-(cyclododecylmethyl)acrylate **(17)***

According to the general procedure. Colorless oil (55.2 mg, 54%) Yield determined by ^1H NMR: 56%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.21 (d, J = 1.6 Hz, 1H), 5.51 (d, J = 1.2 Hz, 1H), 5.19 (s, 2H), 2.23 (d, J = 7.2 Hz, 2H), 1.72 – 1.62 (m, 1H), 1.36 – 1.19 (m, 22H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.3, 139.8, 136.2, 128.6, 128.1, 128.1, 126.2, 66.4, 38.0, 32.6, 29.0, 24.5, 23.9, 23.5, 23.4, 21.8. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{35}O_2$ 343.2632; Found 343.2627

*benzyl 4-(adamantan-2-yl)-2-methylenebutanoate **(18)***

According to the general procedure. Colorless oil (59 .0mg, 63%) Yield determined by ^1H NMR: 72%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 6.20 (s, 1H), 5.51 (s, 1H), 5.19 (s, 2H), 2.47 (d, J = 7.2 Hz, 2H), 1.94 – 1.79 (m, 7H), 1.69 (d, J = 12.5 Hz, 6H), 1.50 (d, J = 12.6 Hz, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.3, 139.7, 136.2, 128.6, 128.1, 128.0, 125.8, 66.4, 43.1, 39.2, 38.4, 35.3, 31.5, 31.4, 28.2, 28.0. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}O_2$ 311.2006; Found 311.2001

*(S)-benzyl 4-methyl-2-methylene-5-phenylpentanoate **(19)***

According to the general procedure. Colorless oil (56.5 mg, 64%) Yield determined by ^1H NMR: 65%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 7.24 (t, J = 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 7.2 Hz, 2H), 6.24 (s, 1H), 5.53 (s, 1H), 5.23 – 5.12 (m, 2H), 2.67 (dd, J = 13.2, 5.6 Hz, 1H), 2.44 (dd, J = 13.6, 5.6 Hz, 1H), 2.35 (dd, J = 13.6, 8.4 Hz, 1H), 2.13 (dd, J = 13.6, 8.4 Hz, 1H), 2.06 – 1.93 (m, 1H), 0.81 (d, J = 6.4 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.2, 141.0, 139.4, 136.2, 129.2, 128.6, 128.2, 128.1, 126.6, 125.3, 66.4, 43.4, 39.6, 34.0, 19.0. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}NaO_2$ 317.1512 ; Found 317.1508

*benzyl 2-((2,3-dihydro-1H-inden-2-yl)methyl)acrylate **(20)***

According to the general procedure. Colorless oil (57.3 mg, 65%) Yield determined by ^1H NMR: 67%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.27 (m, 5H), 7.15 (d, J = 2.4 Hz, 2H), 7.11 (d, J = 2.8 Hz, 2H), 6.25 (s, 1H), 5.59 (s, 1H), 5.20 (s, 2H), 3.01 (dd, J = 15.2, 7.5 Hz, 2H), 2.70 (dt, J = 14.4, 7.2 Hz, 1H), 2.60 (dd, J = 15.6, 6.8 Hz, 2H), 2.49 (d, J = 7.2 Hz, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.1, 143.1, 139.6, 136.1, 128.6, 128.2, 128.1, 126.2, 124.5, 66.5, 38.9, 38.1. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}NaO_2$ 315.1356; Found 315.1352

*benzyl 2-(adamantan-1-ylmethyl)acrylate **(21)***

According to the general procedure. Colorless oil (60.6 mg, 65%) Yield determined by ^1H NMR: 78%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 6.23 (s, 1H), 5.44 (s, 1H), 5.18 (s, 2H), 2.17 (s, 2H), 1.91 (s, 3H), 1.66 (d, J = 12.0 Hz, 3H), 1.57 (d, J = 11.6 Hz, 3H), 1.43 (s, 6H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 168.0, 137.3, 136.2, 128.5, 128.2, 128.1, 127.5, 66.5, 45.5, 42.1, 37.0, 33.3, 28.7. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{30}NaO_2$ 333.1825; Found 333.1819

*benzyl 2-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)methyl)acrylate **(22)***

According to the general procedure. Colorless oil (50.0 mg, 51%) Yield determined by ^1H NMR: 62%. dr = 68/32. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 6.22 (d, J = 1.2 Hz, 1H), 5.52 (d, J = 6.0 Hz, 1H), 5.49 (s, 1H), 5.24 – 5.14 (m, 2H), 2.85 (dd, J = 13.2, 2.8 Hz, 0.68H), 2.38 (dd, J = 13.6, 2.8 Hz, 0.32H), 2.25 (t, J = 12.8 Hz, 0.32H), 2.09 (dd, J = 7.6, 3.2 Hz, 0.32H), 2.04 (ddd, J = 13.6, 6.8, 2.8 Hz, 0.68H), 1.74 – 1.69 (m, 1.29H), 1.63 (ddd, J = 10.8, 10.4, 4.0 Hz, 2.75H), 1.45 (d, J = 11.2 Hz, 0.32H), 1.43 – 1.37 (m, 0.68H), 1.25 (s, 0.32H), 1.21 (ddd, J = 11.6, 6.6, 3.6 Hz, 0.68H), 1.07 (dd, J = 12.8, 9.2 Hz, 0.32H), 0.98 (d, J = 2.8 Hz, 0.32H), 0.95 (dd, J = 9.2, 6.0 Hz, 0.68H), 0.93 – 0.86 (m, 5H), 0.85 (d, J = 2.8 Hz, 0.68H), 0.82 (d, J = 6.4 Hz, 2H), 0.78 (d, J = 6.4 Hz, 1H),

0.73 (d, J = 6.8 Hz, 2H), 0.45 (dd, J = 24.4, 11.6 Hz, 0.68H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 140.1, 139.7, 136.1, 128.6, 128.2, 128.2, 126.6, 126.1, 66.4, 66.4, 47.9, 40.9, 37.8, 37.6, 36.3, 35.8, 35.3, 33.6, 32.6, 29.4, 28.1, 26.6, 25.7, 25.0, 24.3, 22.8, 21.8, 21.6, 20.6, 15.1. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{31}O_2$ 315.2319; Found 315.2314

benzyl 2-(((3S,10S,13R,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)methyl)acrylate ***(23)***

According to the general procedure. Colorless oil (74.8 mg, 65%) Yield determined by ^{1}H NMR: 66%. dr = 72/28. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.22 (s, 0.72H), 6.19 (s, 0.28H), 5.50 (s, 1H), 5.18 (s, 2H), 2.42 (t, J = 6.6 Hz, 1.44H), 2.29 – 2.15 (m, 0.55H), 2.01 – 1.87 (m, 2H), 1.84 – 1.76 (m, 1H), 1.67 – 1.60 (m, 2H), 1.55 – 1.44 (m, 4H), 1.39 – 1.30 (m, 5H), 1.26 – 1.19 (m, 4H), 1.09 (dd, J = 20.0, 7.0 Hz, 9H), 1.02 – 0.96 (m, 3H), 0.90 (d, J = 6.3 Hz, 4H), 0.86 (d, J = 6.5 Hz, 8H), 0.77 (s, 2H), 0.74 (s, 1H), 0.64 (s, 4H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 140.2, 136.2, 128.5, 128.1, 128.0, 126.0, 66.4, 66.3, 56.7, 56.6, 56.4, 54.7, 54.7, 46.6, 42.6, 40.3, 40.1, 40.0, 39.6, 38.5, 37.2, 36.4, 36.2, 36.0, 35.9, 35.6, 35.4, 34.6, 33.1, 32.5, 32.2, 32.0, 29.0, 28.8, 28.3, 28.1, 24.8, 24.2, 23.9, 23.9, 22.9, 22.6, 21.1, 20.8, 18.7, 12.4, 12.1, 11.8. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{58}NaO_2$ 569.4329 ; Found 569.4330

methyl 2-((2,3-dihydro-1H-inden-2-yl)methyl)acrylate ***(24)***

According to the general procedure. Colorless oil (43.9 mg, 68%) Yield determined by ^{1}H NMR: 77%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 2H), 7.15 – 7.09 (m, 2H), 6.21 (s, 1H), 5.57 (s, 1H), 3.76 (s, 3H), 3.03 (dd, J = 15.2, 7.2 Hz, 2H), 2.69 (dd, J = 14.4, 7.2 Hz, 1H), 2.61 (dd, J = 15.2, 6.8 Hz, 2H), 2.47 (d, J = 7.2 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.8, 143.1, 139.6, 126.2, 125.9, 124.5, 51.9, 38.8, 38.2, 37.8. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}NaO_2$ 239.1043; Found 239.1043

tert-butyl 2-((2,3-dihydro-1H-inden-2-yl)methyl)acrylate ***(25)***

According to the general procedure. Colorless oil (46.2 mg, 60%) Yield determined by ^{1}H NMR: 69%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 2H), 7.15 – 7.07 (m, 2H), 6.11 (d, J = 1.6 Hz, 1H), 5.48 (d, J = 1.2 Hz, 1H), 3.02 (dd, J = 14.8, 7.2 Hz, 2H), 2.69 (dt, J = 14.0, 7.1 Hz, 1H), 2.61 (dd, J = 15.2, 6.8 Hz, 2H), 2.44 (d, J = 6.8 Hz, 2H), 1.50 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 166.6, 143.2, 141.3, 126.2, 124.7, 124.5, 80.6, 38.9, 38.5, 37.9, 28.1. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{22}NaO_2$ 281.1512; Found 281.1513

pent-4-yn-1-yl 2-((2,3-dihydro-1H-inden-2-yl)methyl)acrylate ***(26)***

According to the general procedure. Colorless oil (46.0 mg, 54%) Yield determined by ^{1}H NMR: 55%. R_f = *0.40* (Petroleum ether/EtOAc, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 2H), 7.15 – 7.09 (m, 2H), 6.21 (s, 1H), 5.58 (s, 1H), 4.26 (t, J = 6.4 Hz, 2H), 3.03 (dd, J = 14.8, 7.2 Hz, 2H), 2.70 (dt, J = 14.0, 7.2 Hz, 1H), 2.62 (dd, J = 15.2, 6.8 Hz, 2H), 2.47 (d, J = 7.2 Hz, 2H), 2.32 (td, J = 7.2, 2.4 Hz, 2H), 1.97 (t, J = 2.4 Hz, 1H), 1.91 (d, J = 6.8 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 143.0, 139.6, 126.2, 125.9, 124.5, 83.0, 69.1, 63.3, 38.8, 38.3, 37.8, 27.6, 15.4. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}NaO_2$ 291.1356; Found 291.1355

2-((2,3-dihydro-1H-inden-2-yl)methyl)-1-(4-methoxyphenyl)prop-2-en-1-one ***(27)***

According to the general procedure. Colorless oil (52.2 mg, 60%) Yield determined by ^{1}H NMR: 68%. R_f = *0.40* (Petroleum ether/EtOAc, 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.5 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 2H), 7.23 (d, J = 8.5 Hz, 2H), 6.06 (s, 1H), 5.84 (s, 1H), 4.16 (s, 3H), 3.39 – 3.29 (m, 2H), 2.99 (d, J = 5.3 Hz, 1H), 2.95 (s, 4H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 197.0, 163.3, 147.5, 143.1, 132.1, 130.2, 126.2, 124.5, 124.2, 114.0, 113.6, 55.5, 39.0, 39.0, 38.3. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}O_2$ 293.1536; Found 293.1531

1-(4-bromophenyl)-2-((2,3-dihydro-1H-inden-2-yl)methyl)prop-2-en-1-one ***(28)***

According to the general procedure. Colorless oil (51.9 mg, 51%) Yield determined by ^{1}H NMR: 62%. R_f = *0.40* (Petroleum ether/EtOAc, 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (q, J = 8.4 Hz, 4H), 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 5.99 (s, 1H), 5.73 (s, 1H), 3.15 (dd, J = 10.4, 6.4 Hz, 2H), 2.80 (s, 1H), 2.78 (s, 4H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 197.0, 147.1, 142.9, 136.5, 131.6, 131.1, 127.4, 126.6, 126.3, 124.5, 124.4, 39.0, 38.3, 38.2. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}BrNaO$ 363.0355; Found 363.0349

2-((2,3-dihydro-1H-inden-2-yl)methyl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one ***(29)***

According to the general procedure. Colorless oil (42.0 mg, 42%) Yield determined by ^{1}H NMR: 49%. R_f = *0.40* (Petroleum ether/EtOAc, 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 4.0 Hz, 2H), 7.23 (dd, J = 5.2, 3.2 Hz, 2H), 6.07 (s, 1H), 5.77 (s, 1H), 3.24 – 3.13 (m, 2H), 2.82 (s, 1H), 2.79 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 197.0, 147.0, 142.9, 141.0, 133.6 (q, J = 32.7 Hz), 129.7, 128.5, 126.3, 125.3 (q, J = 3.7 Hz), 124.5, 39.0, 38.2, 38.0. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}F_3NaO$ 353.1124; Found 353.1123

(R)-ethyl 2-((2,3-dihydro-1H-inden-2-yl)methyl)-5-(4-iodophenyl)pentanoate ***(30)***

According to the general procedure. Colorless oil (48.2 mg, 35%) R_f = *0.40* (Petroleum ether/EtOAc, 20/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.4 Hz, 2H), 7.16 (dd, J = 8.4, 4.0 Hz, 2H), 7.14 – 7.08 (m, 2H), 6.90 (d, J = 8.4 Hz, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.02 (ddd, J = 26.8, 15.6, 7.6 Hz, 2H), 2.55 (dt, J = 13.2, 6.4 Hz, 4H), 2.47 (td, J = 9.2, 4.8 Hz, 1H), 2.43 – 2.34 (m, 1H), 1.93 – 1.83 (m, 1H), 1.71 – 1.63 (m, 1H), 1.62 – 1.54 (m, 3H), 1.53 – 1.44 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 176.2, 143.2, 143.1, 141.7, 137.4, 130.6, 126.2, 126.2, 124.4, 124.4, 60.3, 44.6, 39.5, 39.0, 38.6, 38.4, 35.3, 32.4, 29.0, 14.4. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{28}IO_2$ 463.1128; Found 463.1131

(R)-2-((2,3-dihydro-1H-inden-2-yl)methyl)-5-(4-iodophenyl)pentanoic acid ***(31)***

According to the general procedure. Yellow solid (214.1 mg, 85%) M.p. = 80 – 82 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 2H), 7.13 – 7.01 (m, 4H), 6.84 (d, J = 7.6 Hz, 2H), 3.05 – 2.87 (m, 2H), 2.55 – 2.44 (m, 4H), 2.44 – 2.34 (m, 2H), 1.91 – 1.77 (m, 1H), 1.68 – 1.47 (m, 5H), 1.18 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 142.0, 141.9, 140.5, 136.3, 129.5, 125.2, 123.4, 123.3, 89.9, 43.4, 38.4, 37.8, 37.3, 37.1, 34.2, 31.0, 28.7, 27.8. **HRMS** (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{27}INO_2$ 452.1081; Found 452.1072

ethyl 5-(4-iodophenyl)-2-methylenepentanoate ***(32)***

According to the general procedure. Colorless oil (51.6 mg, 50%) R_f = *0.40* (Petroleum ether/EtOAc, 20/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.6 Hz, 2H), 6.94 (d, J = 7.6 Hz, 2H), 6.15 (s, 1H), 5.52 (s, 1H), 4.20 (dd, J = 14.0, 6.8 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H), 2.32 (t, J = 7.2 Hz, 2H), 1.77 (dt, J = 14.4, 7.2 Hz, 2H), 1.29 (t, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.2, 141.7, 140.5, 137.4, 130.6, 124.7, 90.8, 60.7, 34.9, 31.4, 29.9, 14.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}IO_2$ 345.0346; Found 345.0344

ethyl 5-([1,1':4',1''-terphenyl]-4-yl)-2-methylenepentanoate ***(33)***

According to the general procedure. White solid (40.1 mg, 54%) M.p. = 104 – 106 °C. R_f = *0.40* (Petroleum ether/EtOAc, 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 5H), 7.62 (s, 1H),

7.56 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 6.17 (s, 1H), 5.55 (s, 1H), 4.21 (q, J = 7.2 Hz, 2H), 2.69 (t, J = 7.6 Hz, 2H), 2.39 (t, J = 7.6 Hz, 2H), 1.92 – 1.79 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.3, 141.4, 140.8, 140.7, 140.0, 139.9, 138.2, 129.0, 128.8, 127.5, 127.4, 127.3, 127.1, 127.0, 124.7, 60.7, 35.1, 31.6, 30.1, 14.3. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{27}O_2$ 371.2006; Found 371.2003

*ethyl 2-methylene-5-(4-(phenylethynyl)phenyl)pentanoate **(34)***

According to the general procedure. Colorless oil (36.8 mg, 58%). *R_f = 0.40* (Petroleum ether/EtOAc, 4/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.30 – 7.20 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), 6.07 (s, 1H), 5.44 (s, 1H), 4.12 (q, J = 7.2 Hz, 2H), 2.56 (t, J = 7.6 Hz, 2H), 2.26 (t, J = 7.6 Hz, 2H), 1.78 – 1.65 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.2, 142.6, 140.6, 131.6, 131.6, 128.5, 128.4, 128.1, 124.7, 123.5, 120.7, 89.6, 88.9, 60.7, 35.4, 31.5, 29.9, 14.3. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}NaO_2$ 341.1512; Found 341.1511

*2-(2,2-diphenylvinyl)-2,3-dihydro-1H-indene **(36)***[19]

According to the general procedure. White solid (6.0 mg, 7%) M.p. = 63 – 65 °C. R_f = 0.50 (Pure petroleum ether). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.22 (m, 5H), 7.21 – 7.19 (m, 1H), 7.18 – 7.13 (m, 2H), 7.12 – 7.08 (m, 2H), 6.20 (dd, J = 10.0, 2.8 Hz, 1H), 3.21 (dt, J = 24.0, 8.0 Hz, 1H), 3.03 (dd, J = 15.2, 8.0 Hz, 2H), 2.87 (dd, J = 15.2, 8.4 Hz, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 143.1, 142.4, 141.5, 140.3, 133.6, 129.9, 128.5, 128.2, 127.9, 127.3, 127.1, 127.1, 126.3, 124.4, 40.7, 40.5. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}$ 297.1638; Found 297.1633

*benzyl 2-methylenehept-6-enoate **(37)***

According to the general procedure. Colorless oil (5.0 mg, 7%) Yield determined by ^1H NMR: 10%. R_f = 0.40 (Petroleum ether/EtOAc, 40/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 5H), 6.13 (s, 1H), 5.73 (ddt, J = 16.8, 10.0, 6.4 Hz, 1H), 5.49 (s, 1H), 5.13 (s, 2H), 4.91 (dd, J = 20.4, 13.6 Hz, 2H), 2.35 – 2.21 (m, 2H), 2.05 – 1.94 (m, 2H), 1.52 – 1.47 (m, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.1, 140.5, 138.4, 136.1, 128.6, 128.1, 128.0, 125.2, 114.8, 66.4, 33.2, 31.3, 27.6. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O_2$ 231.1380; Found 231.1382

*benzyl 2-methylenenon-8-enoate **(38a)** benzyl 4-cyclopentyl-2-methylenebutanoate **(38b)***

According to the general procedure. Colorless oil (35.8 mg, 47%) Yield determined by ^1H NMR: 54%. R_f = 0.40 (Petroleum ether/EtOAc, 20/1). **^1H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 6.18 (d, J = 4.4 Hz, 0.92H), 5.80 (ddd, J = 17.0, 6.7, 3.5 Hz, 0.75H), 5.55 (s, 1H), 5.20 (s, 2H), 4.96 (dd, J = 21.8, 13.7 Hz, 1.5H), 2.38 – 2.27 (m, 2H), 2.03 (dd, J = 13.7, 6.8 Hz, 1.56H), 1.81 – 1.72 (m, 0.86H), 1.51 – 1.44 (m, 2.17H), 1.42 – 1.29 (m, 3.21H), 1.26 (s, 0.34H), 1.09 (s, 0.65H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 167.2, 141.1, 140.8, 139.0, 136.2, 128.6, 128.1, 128.0, 124.9, 124.7, 114.3, 66.4, 39.7, 35.0, 33.7, 32.6, 31.8, 31.2, 28.7, 28.2, 25.2. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{22}NaO_2$ 259.1693 ; Found 259.1692

ASSOCIATED CONTENT

Supporting Information Available: Experimental procedures and spectroscopic data for all new 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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