Ti(OiPr)₄-Enabled Dual Photoredox and Nickel-Catalyzed Arylation and Alkenylation of Cyclopropanols

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In this article, we report an application of cyclopropanols as coupling partners in the dual photoredox/nickel catalyzed reaction with aryl and vinyl bromides. We found that this cross-coupling proceeds smoothly in the presence of Ti(OiPr)₄ as an additive to provide β-aryl or γ,δ-unsaturated ketones.

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Ti(OiPr)₄-enabled dual photoredox and nickel-catalyzed arylation and alkenylation of cyclopropanols

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ABSTRACT. Readily available from esters and ketones, cyclopropanols are inclined to undergo diverse ring-opening reactions. Their one-electron oxidation is a conventional way to β -carbonyl radicals. However, despite this fact, their application as a coupling partner in dual photoredox and nickel-catalyzed reactions with organic halides remains underdeveloped. Here, we report that Ti(OiPr)₄ additive enables this elusive cross-coupling with aryl and alkenyl bromides affording β -substituted ketones.

Nickel-catalyzed coupling of the photochemically generated alkyl radicals¹ with aryl, alkenyl or alkyl halides has recently emerged as a powerful tool for the C-C bond construction (Scheme 1A).² Proceeding under mild conditions, these reactions generally tolerate sensitive functional groups and moreover, can be deployed for the formation of an asymmetric stereocenter.³ The scope of the radical precursors used in the coupling is exceptionally broad. After the pioneering reports on the arylation of organotrifluoroborates, aliphatic carboxylic acids and N,N-dimethylaniline by Molander⁴ and MacMillan and Doyle,⁵ various alternative coupling partners were utilized including alkylsilicates,⁶ monoalkyl oxalates,⁷ dihydropyridines,^{8,9} alkyl halides,¹⁰ alkanes,¹¹ oxiranes,¹² aziridines,¹³ cycloalkanone oxime-carboxylates,¹⁴ N-hydroxyphthalimide esters,¹⁵ Katritzky salts,¹⁶ alkylsulfinate salts,¹⁷ xanthate esters,¹⁸ boracene-based alkyl borates,¹⁹ linear²⁰ and cyclic alcohols.²¹ Being a source of β -ketoradicals **3**,²² cyclopropanols **1** can also undergo the photoredox/nickel dual catalyzed reaction to provide β -substituted ketones (Scheme 1B).²¹ However, scope of cyclopropanols that can be engaged in this coupling is rather narrow. Shenvi reported arylation and alkenylation of tricyclic silyloxycyclopropanes **4** promoted by an iridium photocatalyst and a nickel complex.^{21a} One of the obtained β -substituted ketones **5** was further efficiently applied in a concise synthesis of natural alkaloid GB-22.^{21a} Another example of the photoredox initiated ring-opening arylation was described by Rueping.^{21b} The presence of PMP group in **6** was crucial because the formation of alkoxy radical **2** was initiated by the one-electron oxidation of this moiety. Here, we report that limitations in the scope of photoredox and nickel dual-catalyzed cyclopropanol arylation and alkenylation can be overcome when the reaction is carried out in the presence of Ti(O*i*Pr)₄ as an additive. Under these conditions, β -substituted ketones **10** can be obtained from cyclopropanols **8** and aryl- or vinyl- bromides **9**.

Scheme 1. Reactions of cyclopropanols under dual photoredox and nickel catalysis

Transformation of cyclopropanol **1** ($E^{\text{ox}} = +1.66 \text{ V}$)²³ to oxycyclopropyl radical **2** require a relatively strong oxidant. For comparison, the reduction potential of the excited photocatalysts commonly used in the cooperative photoredox and nickel catalysis lays between +0.77 and +1.35 V.^{2c} Thus, either a photocatalyst with a stronger oxidative properties or an alternative way of oxycyclopropyl radical **2** generation was required. Recently we found that cyclopropanols undergo

one-electron oxidation by the photoexcited acridinium salts ($E_{1/2}(\text{P}^*/\text{P}^-) = +2.08 \text{ V}$),²⁴ but our attempts to use them in the ring-opening arylation of **8** with **9** were unsuccessful. Nevertheless, we found that addition of $\text{Ti}(\text{OiPr})_4$ to the reaction mixture enables the reaction even when 4CzIPN ($E_{1/2}(\text{P}^*/\text{P}^-) = +1.35 \text{ V}$)²⁵ is employed as a photocatalyst. The highest yield in the arylation of **11a** with *p*-bromoanisole (**12a**) was achieved when the reaction was run in acetone in the presence of the photocatalyst, nickel chloride bipyridine complex, potassium carbonate as a base and titanium isopropoxide as an additive. Changing the solvent with acetonitrile and DMA resulted in a slight drop in yield, but in THF, the arylation was significantly less efficient. When di-*tert*-butylbipyridine, batophenanthroline, neocuproine or dimethoxybipyridine were used as alternative ligands, the yield of **13a** diminished. While inorganic salt K_3PO_4 can be employed as a base of choice, the reaction in the presence of 2,6-lutidine proceeded giving the product in a low 23% yield. The yield of **10a** in the reaction promoted by $\text{Ti}(\text{OtBu})_4$ additive with bulk *tert*-butoxide ligands was slightly lower than that under the standard conditions. Trimethyl borate also promoted the cross-coupling, though, significantly less efficiently. No reaction was observed when aluminum isopropoxide was used as an additive or when the arylation was carried out in the absence of $\text{Ti}(\text{OiPr})_4$ or a photocatalyst.

Table 1. Optimization of the reaction conditions.^a

entry	reaction conditions	yield of 13a (%) ^b
1	standard conditions	60%
2	THF instead of acetone	28%

3	MeCN instead of acetone	49%
4	DMA instead of acetone	51%
5	NiCl ₂ ·DME and dtbbpy instead of NiCl ₂ ·bpy	47%
6	BPhen·NiCl ₂ ·2DMF instead of NiCl ₂ ·bpy	47%
7	NiCl ₂ ·DME and neocuproine instead of NiCl ₂ ·bpy	21%
8	NiCl ₂ ·DME and dMeObpy instead of NiCl ₂ ·bpy	30%
9	K ₃ PO ₄ instead of K ₂ CO ₃	56%
10	2,6-lutidine instead of K ₂ CO ₃	23%
11	Ti(<i>O</i> <i>t</i> Bu) ₄ instead of Ti(<i>O</i> <i>i</i> Pr) ₄	47%
12	B(OMe) ₃ instead of Ti(<i>O</i> <i>i</i> Pr) ₄	19%
13	Al(<i>O</i> <i>i</i> Pr) ₃ instead of Ti(<i>O</i> <i>i</i> Pr) ₄ or no Ti(<i>O</i> <i>i</i> Pr) ₄ or no 4CzIPN	0%

^aReaction conditions: **11a** (0.1 mmol), **12a** (0.2 mmol), photocatalyst (0.005 mmol), NiCl₂·bpy (0.005 mmol) or NiCl₂·DME (0.005 mmol), ligand (0.005 mmol), additive (0.2 mmol), base (0.3 mmol) and solvent (1 mL), blue LEDs, 15h. ^bCrude ¹H NMR yield with CH₂Br₂ as internal standard; 4CzIPN = 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile; bpy = 2,2'-bipyridine; dtbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine; BPhen = 4,4'-diphenyl-2,2'-bipyridine; DME = 1,2-dimethoxyethane; DMA = N,N-dimethylacetamide; dMeObpy = 4,4'-dimethoxy-2,2'-bipyridine.

Having optimized the reaction conditions, we next investigated the scope of the reaction. Aryl bromides with donor or acceptor functional groups, as well as an ortho-substituent reacted with **11a** giving desired β-arylketones **13a-f**. Silylated hydroxyl group, alkenyl and diethylacetal units in the cyclopropanol substrate were tolerated but formation of **13h** and **13i** was slightly less efficient. The reaction of the 1,2-disubstituted cyclopropanol afforded arylketone **13j** as a single β-branched regioisomer. In contrast to the palladium-catalysed arylation which leads to α-branched products,²⁶ the investigated radical reaction proceeded with cleavage of the more substituted bond of the three-carbon ring.

Next, cross-coupling of cyclopropanols with vinyl halides was investigated. Generally, yields of the alkenylation were better when the reaction was carried out in the presence of neocuproine instead of bipyridine ligand. The reaction between cyclopropanol **11a** and 2-bromoalkenes

provided ketones **14a** and **14b** in 84% and 55% yields, respectively. Alkenylation of **11a** with vinyl triflate also proceeded efficiently to produce β -cyclohexenylketone **14c**. In synthesis of γ,δ -unsaturated ketones **14d** and **14e** from 2-alkylsubstituted vinyl bromides and cyclopropanol **11a**, bipyridine ligand was more favorable than neocuproine and the products were isolated in 45% and 46% yields, respectively. Formation of *Z*-alkenylketone **14e** was accompanied by a little isomerization of the double bond, which caused drop in *Z/E* ratio to 8:1. Diminishing of the isomeric purity was more significant for the products **14g** and **14h** bearing the alkene unit conjugated with an electron-rich aromatic ring. After completion of the coupling, **14g** was isolated as a 6:1 mixture of *E/Z* stereoisomers. This ratio further dropped to 1.7:1 when the reaction time was increased to 48h. Ketone product **14f** with the unsubstituted benzene ring was obtained as a single *E*-isomer. Aryl chloride units were found to be inert under the reaction conditions and ketone **14h** was prepared from the corresponding vinyl bromide in a good 61% yield. Then, diverse 1-mono and 1,2-disubstituted cyclopropanols were tested in the reaction with 2-bromopropene. The substrate bearing two hydroxycyclopropyl groups underwent smooth coupling giving diketone **14i** in 51% yield. Silylated and unprotected hydroxyl groups, alkenyl unit and acetal protecting groups were tolerated and corresponding products **14j-n** were isolated in 41-75% yields. The reaction conditions were mild enough for the preparation of enantiomerically pure alkenylketones **14o-p** that contain sensitive α -stereocenters. Alkenylation of 1,2-disubstituted cyclopropanols provided regioisomerically pure β -branched products **14q-s** in 41-64% yields. These reactions proceeded more efficiently in the presence of bipyridine ligand instead of neocuproine. Finally, β -isopropenylcycloheptanone **14t** was obtained from the bicyclic cyclopropanol in 57% yield.

Table 2. The scope of the reaction ^{a,b}

^aReaction conditions A: **11** (0.25 mmol), **12** (0.5 mmol), 4CzIPN (0.0125 mmol), NiCl₂·bpy (0.0125 mmol), Ti(OiPr)₄ (0.5 mmol), K₂CO₃ (0.75 mmol), acetone (2.5 mL), blue LEDs, 15h;

^bReaction conditions B: the same as reaction conditions A, but NiCl₂·DME (0.00625 mmol) and neocuproine (0.00625 mmol) were used instead of NiCl₂·bpy (0.0125 mmol).

To get insight into the role of $\text{Ti}(\text{OiPr})_4$ in the ring-opening cross-coupling, additional control experiments were carried out (Scheme 2A). First, the reaction between cyclopropane **11a** and $\text{Ti}(\text{OiPr})_4$ in acetone- d^6 was investigated. We observed a fast exchange between the isopropoxyde and cyclopropyloxy ligands leading to 1:3 mixture of **11a** and **15**. Initially, we assumed that the formed titanium cyclopropoxide complex **15** could undergo one-electron oxidation by the photoexcited 4CzIPN* more efficiently than free cyclopropanol **11a**. However, voltamperograms of **11a** and its 1:1 mixture with $\text{Ti}(\text{OiPr})_4$ were nearly identical suggesting that the additive played another role in the reaction. Alternatively, $\text{Ti}(\text{OiPr})_4$ could serve as a co-catalyst that assists formation of cyclopropyloxy nickel(III) complexes.²⁷ Homolytic cleavage of RO-Ni^{III} bond could provide cyclopropyloxy radicals, which could further undergo the ring-opening and cross-coupling.^{28,29,30} Bering in mind that formation of RO-Ni^{III} intermediates is possible even in the absence of a photocatalyst and this reaction proceeds more efficiently under the irradiation with 390-395 nm LEDs,^{27e} we carried out additional control experiments without 4CzIPN. When blue LEDs were used as a source of light, the alkenylation of **11a** by 2-bromopropene gave product **14a** in 10% yield, while no reaction was observed in the absence of $\text{Ti}(\text{OiPr})_4$. Under the irradiation with purple LEDs, the yield increased significantly to 38% and 1% of the product was formed in the absence of $\text{Ti}(\text{OiPr})_4$. Based on these experiments, we proposed a catalytic cycle in which 4CzIPN* oxidizes the nickel complex rather than cyclopropanol or its titanium alkoxide while $\text{Ti}(\text{OiPr})_4$ assists the formation of RO-Ni^{III} intermediates (Scheme 2B). After the oxidative addition of aryl or vinyl bromide to **16**, aryl nickel complex **17** would undergo oxidation by the photoexcited 4CzIPN* and ligand exchange with titanium alkoxide **18** to provide Ni^{III} complex **19**. Next, Ni^{III}-O bond in **19** would break providing Ni^{II} complex **20** and oxycyclopropyl radical **21**. Ring-opening of **21** would give β -ketoradical **22** which would further react with **20** affording

Ni^{III} complex **23**. Reductive elimination from **23** would lead to coupling product **24** and Ni^I species **25**, reduction of which would close the catalytic cycle.

Scheme 2. Control experiments and plausible catalytic cycle

In conclusion, we have developed a general approach to β -aryl and β -alkenylketones from cyclopropanols and aryl or alkenyl bromides or triflates. We found, that this photoredox and nickel dual catalyzed reaction becomes general for a broad scope of 1-mono- and 1,2-disubstituted

cyclopropanols when carried out in the presence of $\text{Ti}(\text{OiPr})_4$ additive. The cross-coupling is compatible with functional groups including unprotected hydroxyl and proceeds under conditions mild enough for the preparation of enantiomerically pure ketones bearing a sensitive α -stereocenter.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures and characterization of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Ti(OiPr)₄-enabled dual photoredox and nickel-catalyzed arylation and alkenylation of cyclopropanols

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1. General information

All solvents were purchased from commercial sources and, unless otherwise noted, used without further purification. If necessary, solvents were distilled and dried before use by standard methods. Flash column chromatography was performed through silica gel (200–300 mesh). Thin layer chromatography (TLC) was performed using Silica gel 60 F254 plates and visualized using UV light or phosphoromolybdic acid. Photochemical reactions were carried with two 20W blue light (400 nm) projectors or with three 10W purple (395 nm) light projectors. The organic dye 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) and $\text{NiCl}_2\cdot\text{bpy}$ catalyst were synthesized using reported procedures^{1,2}. NMR spectra were obtained on a Bruker AVANCE 500 spectrometer and calibrated using residual solvent as an internal reference [^1H NMR: CDCl_3 (7.26); ^{13}C NMR: CDCl_3 (77.16)]. Chemical shifts (δ) are given in ppm and coupling constants (J) are given in Hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet) m (multiplet), bs (broad singlet), or combinations thereof. High resolution MS were obtained on Agilent technologies 6550 iFunnel Q-TOF LC/MS system using electrospray ionization (ESI) method. Optical rotations were measured using an Autopol III automatic polarimeter (2-mL cell, 1 dm path length; concentration (c) is in g/100mL and $[\alpha]_{\text{D}}$ values are in degrees.). Gas chromatography (GC) was performed on an Agilent 8860 GC instrument using Astec CHIRALDEX B-DM (30 m $\times$ 0.25 mm) column. Cyclic voltammetry was performed in a conventional three-electrode one compartment closed cell with Pt wire working electrode, Pt sheet counter electrode, and Ag wire pseudoreference electrode; potential of Ag pseudoreference electrode was calibrated by ferrocenium/ferrocene redox couple (the measurements were performed under dry Ar atmosphere, the electrolyte solution was 0.1 M NBu_4OTf in acetonitrile).

2. Synthesis of starting cyclopropanols

General procedure A:

To a stirred solution of ester (1 eq.) and $\text{Ti}(\text{OiPr})_4$ (1 eq.) in dry THF or Et_2O (0.5 M) a solution of a Grignard reagent in dry THF or Et_2O (1-1.4 M, 4 eq.) was added over 0.5 h at room temperature under argon atmosphere. The reaction was stirred for 30 min and quenched with saturated aqueous NH_4Cl (0.14 mL per 1 mmol of Grignard reagent) at 0 °C. The suspension was stirred for 15 min, filtered through Celite® and the precipitate was washed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using PE and EtOAc as the eluent.

General procedure B:

To a stirred solution of ester (1 eq.), alkene (1 eq.) and $\text{Ti}(\text{OiPr})_4$ (1 eq.) in dry THF or Et_2O (0.5 M) a solution of a Grignard reagent in dry THF or Et_2O (1-1.4 M, 4 eq.) was added over 0.5 h at room temperature under argon atmosphere. The reaction was stirred for 30 min and quenched with saturated aqueous NH_4Cl (0.14 mL per 1 mmol of Grignard reagent) at 0 °C. The suspension was stirred for 15 min, filtered through Celite® and the precipitate was washed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using PE and EtOAc as the eluent.

1-(2-phenylethyl)cyclopropan-1-ol (11a): Synthesized according to the general procedure A from methyl 3-phenylpropionate and ethylmagnesium bromide in THF. The crude product was purified by flash column chromatography on silica gel (5→10% EtOAc/PE) to provide a colorless oil (633 mg, 3.91 mmol, 64% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 2.90 – 2.83 (m, 2H), 1.92 – 1.85 (m, 2H), 1.85 (br. s, 1H), 0.82 – 0.70 (m, 2H), 0.53 – 0.41 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.3, 128.6 (2C), 128.6 (2C), 126.0, 56.0, 40.6, 32.6, 13.8 (2C). Data are consistent with those reported in the literature.³

1-(3-(*tert*-butyldiphenylsilyloxy)propyl)cyclopropan-1-ol (11b): Synthesized according to the general procedure A from isopropyl 4-((*tert*-butyldiphenylsilyloxy)butanoate and ethylmagnesium bromide in THF. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/PE) to provide a colorless oil (804 mg, 2.27 mmol, 87% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.71 – 7.67 (m, 4H), 7.47 – 7.37 (m, 6H), 3.76 (t, J = 5.7 Hz, 2H), 3.26 (br. s, 1H), 1.81

– 1.75 (m, 2H), 1.69 (t, $J = 6.8$ Hz, 2H), 1.05 (s, 9H), 0.80 – 0.75 (m, 2H), 0.47 – 0.43 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 135.7 (4C), 133.6 (2C), 129.9 (2C), 127.9 (4C), 64.6, 55.6, 36.1, 31.2, 29.6, 26.9 (3C), 19.3, 13.7. HRMS (ESI⁺): m/z calc'd for $\text{C}_{22}\text{H}_{31}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 355.2088, found 355.2084.

1-(4-methylpent-3-en-1-yl)cyclopropane-1-ol (11c): Synthesized according to the general procedure A from ethyl 5-methylhex-4-enoate and ethylmagnesium bromide in THF. The crude product was purified by flash column chromatography on silica gel (15% EtOAc/PE) to provide a colorless oil (605 mg, 4.31 mmol, 67% yield); ^1H NMR (500 MHz, CDCl_3) δ 4.79 (t, $J = 5.9$ Hz, 1H), 3.72 (dq, $J = 9.4, 7.0$ Hz, 2H), 3.59 (s, 1H), 3.56 (dq, $J = 9.5, 7.1$ Hz, 2H), 1.89 (d, $J = 5.8$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 6H), 0.81 – 0.70 (m, 2H), 0.49 – 0.39 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 103.1, 61.9, 53.3, 41.1, 15.5, 12.6.

1-(2,2-diethoxyethyl)cyclopropane-1-ol (11d): Synthesized according to the general procedure A from ethyl 3,3-diethoxypropanoate and ethylmagnesium bromide in THF. The crude product was purified by flash column chromatography on silica gel (10→20% EtOAc/PE) to provide a colorless oil (357 mg, 2.05 mmol, 39% yield); ^1H NMR (500 MHz, CDCl_3) δ 4.79 (t, $J = 5.9$ Hz, 1H), 3.72 (dq, $J = 9.5, 7.1$ Hz, 2H), 3.59 (s, 1H), 3.56 (dq, $J = 9.5, 7.1$ Hz, 2H), 1.89 (d, $J = 5.9$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 6H), 0.81 – 0.70 (m, 2H), 0.49 – 0.39 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 103.1, 61.9, 53.3, 41.1, 15.5, 12.6. Data are consistent with those reported in the literature.⁴

2-methyl-1-phenethylcyclopropan-1-ol (11e): Synthesized according to the general procedure A from methyl 3-phenylpropionate and propylmagnesium bromide in THF. The crude product was purified by flash column chromatography on silica gel (5→10% EtOAc/PE) to provide a colorless oil (157 mg, 0.89 mmol, 80% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 2.92 – 2.85 (m, 2H), 1.93 – 1.85 (m, 2H), 1.80 (s, 1H), 1.13 – 1.05 (m, 1H), 1.02 (d, $J = 6.1$ Hz, 3H), 0.86 (dd, $J = 9.7, 5.3$ Hz, 1H), 0.10 – 0.04 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.6, 128.6, 128.6, 126.0, 59.0, 36.4, 32.7, 20.9, 20.1, 14.3. Data are consistent with those reported in the literature.³

1,1'-(propane-1,3-diyl)bis(cyclopropan-1-ol) (11f): Synthesized according to the general procedure A from dimethyl glutarate and

ethylmagnesium bromide (8 equiv.) in THF. The crude product was purified by flash column chromatography on silica gel (30% EtOAc/PE) to provide white crystals (402 mg, 2.57 mmol, 42% yield); ^1H NMR (500 MHz, CDCl_3) δ 2.05 (s, 2H), 1.80 – 1.71 (m, 2H), 1.66 – 1.56 (m, 4H), 0.80 – 0.70 (m, 4H), 0.51 – 0.41 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 55.9, 38.3, 22.5, 13.7. Data are consistent with those reported in the literature.⁵

1-(5-hydroxypentyl)cyclopropan-1-ol (11g): Synthesized according to the general procedure A from caprolactone and ethylmagnesium bromide in THF. The crude product was purified by flash column chromatography on silica gel (10→15% EtOAc/PE) to provide a colorless oil (1.04 g, 7.19 mmol, 55% yield); ^1H NMR (500 MHz, CDCl_3) δ 3.65 (t, J = 6.6 Hz, 2H), 1.65 – 1.49 (m, 6H), 1.48 – 1.35 (m, 2H), 0.79 – 0.66 (m, 2H), 0.51 – 0.35 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 63.0, 55.8, 38.4, 32.8, 25.8, 13.7. Data are consistent with those reported in the literature.⁶

1-((2-methyl-1,3-dioxolan-2-yl)methyl)cyclopropane-1-ol (11h): Synthesized according to the general procedure A from ethyl 2-(2-methyl-1,3-dioxolan-2-yl)acetate and ethylmagnesium bromide in THF. The crude product was purified by flash column chromatography on silica gel (15% EtOAc/PE) to provide a colorless oil (180.4 mg, 1.14 mmol, 40% yield); ^1H NMR (500 MHz, CDCl_3) δ 4.06 – 3.97 (m, 4H), 3.85 (br. s, 1H), 1.94 (s, 2H), 1.44 (s, 3H), 0.78 – 0.73 (m, 2H), 0.51 – 0.47 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 111.3, 64.7 (2C), 53.3, 45.2, 24.9, 12.7 (2C). Data are consistent with those reported in the literature.⁷

1-[(1S)-1-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]ethyl]cyclopropan-1-ol (11i): Synthesized according to the general procedure A from ethyl (2S)-2-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]propanoate and ethylmagnesium bromide in THF. The crude product was purified by flash column chromatography on silica gel (5% EtOAc/PE) to provide a colorless oil (275 mg, 1.27 mmol, 60% yield); $[\alpha]_D^{20}$ = +4.58 (c=0.50 in CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 3.41 (q, J = 6.3 Hz, 1H), 2.47 (br. s, 1H), 1.24 (d, J = 6.3 Hz, 3H), 0.90 (s, 9H), 0.82 – 0.78 (m, 1H), 0.76 – 0.72 (m, 1H), 0.49 – 0.46 (m, 2H), 0.07 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 73.2, 59.6, 26.0 (3C), 19.9, 18.2, 13.6, 10.0, -4.4, -4.4.

(S)-1-(1-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)cyclopropan-1-ol (11j): Synthesized according to the general procedure A from methyl (2*S*)-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2-methylpropanoate and ethylmagnesium bromide in THF. The crude

product was purified by flash column chromatography on silica gel (5% EtOAc/PE) to provide a colorless oil (361 mg, 1.57 mmol, 73% yield); $[\alpha]_D^{20} = +3.64$ ($c=0.53$ in CHCl_3) $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 3.91 (dd, $J = 9.6, 4.0$ Hz, 1H), 3.68 (dd, $J = 9.6, 5.0$ Hz, 1H), 3.60 (br. s, 1H), 1.41 – 1.34 (m, 1H), 1.02 (d, $J = 7.1$ Hz, 3H), 0.91 (s, 9H), 0.75 (ddd, $J = 10.9, 5.8, 4.8$ Hz, 1H), 0.67 (ddd, $J = 10.8, 5.8, 5.3$ Hz, 1H), 0.47 (ddd, $J = 10.8, 5.9, 4.8$ Hz, 1H), 0.37 (ddd, $J = 10.9, 5.9, 5.3$ Hz, 1H), 0.09 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 68.5, 59.7, 40.8, 26.0 (3C), 18.3, 13.3, 13.0, 11.4, -5.4, -5.5. Data are consistent with those reported in the literature.⁸

2-(4-((*tert*-butyldiphenylsilyl)oxy)butyl)-1-phenethylcyclopropan-1-ol (11k): Synthesized according to the general procedure B from ethyl 3-phenylpropionate, *tert*-butyl(hex-5-en-1-

yl)oxy)diphenylsilane and cyclopentylmagnesium chloride in THF. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/PE) to provide a colorless oil (730 mg, 1.54 mmol, 51% yield); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.72 – 7.61 (m, 4H), 7.45 – 7.33 (m, 6H), 7.32 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 3.66 (t, $J = 6.4$ Hz, 2H), 2.93 – 2.80 (m, 2H), 2.00 – 1.91 (m, 1H), 1.82 – 1.73 (m, 2H), 1.67 – 1.38 (m, 6H), 1.05 (s, 9H), 0.94 – 0.79 (m, 2H), 0.11 – 0.05 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.6, 135.7, 134.3, 129.7, 128.6, 128.6, 127.7, 126.0, 64.0, 59.0, 36.6, 32.7, 32.5, 29.4, 27.0, 26.3, 26.0, 19.8, 19.4. **HRMS** (ESI⁺): m/z calc'd for $\text{C}_{31}\text{H}_{40}\text{NaO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$: 495.2690, found 495.2686.

1-(2-hydroxy-2-phenethylcyclopropyl)butan-2-yl pivalate ((±)-11l):

To a stirred solution of methyl 3-phenylpropionate (492 mg, 3 mmol, 1 eq.), pent-4-en-2-ol (300 mg, 3 mmol, 1 eq.) and $\text{Ti}(\text{O}i\text{Pr})_4$ (0.89 mL, 3 mmol, 1 eq.) in dry Et_2O (25 mL) a solution of PrMgBr in Et_2O (22 mL, 24 mmol, 1.1 M, 8 eq.) was added

over 1 h at room temperature under argon atmosphere. The reaction was stirred for 30 min and quenched with saturated aqueous NH_4Cl solution (3.5 mL) at 0 °C. The suspension was stirred for 15 min, filtered through Celite® and the precipitate was washed with EtOAc (5×5 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (10→15% EtOAc/PE) to give cyclopropanol (±)-**S1** as a colorless oil (313 mg, 1.33 mmol, 45% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 3.71 – 3.66 (m, 1H), 2.91 – 2.82 (m, 2H), 1.96 (dt, J = 14.9, 4.5 Hz, 1H), 1.91 – 1.83 (m, 1H), 1.83 – 1.75 (m, 1H), 1.65 – 1.53 (m, 3H), 0.95 (t, J = 7.4 Hz, 3H), 0.80 – 0.71 (m, 1H), 0.66 (dd, J = 9.3, 5.1 Hz, 1H), 0.46 – 0.41 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.7, 128.5 (2C), 128.5 (2C), 125.8, 72.9, 57.4, 42.0, 34.2, 32.4, 28.8, 19.9, 19.5, 10.5.

To a solution of cyclopropanol (±)-**S1** (587 mg, 2.5 mmol) and pyridine (0.44 mL, 5.5 mmol, 2.2 eq.) in DCM (9 mL) pivaloyl chloride (0.61 mL, 5 mmol, 2 eq.) was added at 0 °C. The reaction mixture was stirred overnight at room temperature, then quenched with saturated aqueous NaHCO_3 solution (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (10% EtOAc/PE) to provide cyclopropanol (±)-**11I** as a colorless oil (557 mg, 70%). ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 4.96 – 4.87 (m, 1H), 2.89 – 2.77 (m, 2H), 2.14 (br s, 1H), 1.90 – 1.81 (m, 1H), 1.80 – 1.54 (m, 5H), 1.21 (s, 9H), 0.89 (t, J = 7.5 Hz, 3H), 0.65 – 0.58 (m, 2H), 0.46 – 0.37 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 178.5, 142.4, 128.5 (4C), 125.9, 75.5, 58.2, 41.6, 39.0, 32.5, 32.4, 27.4, 27.2, 20.7, 19.1, 9.7. Data are consistent with those reported in the literature.⁹

5-methoxy-1,1a,2,3-tetrahydro-7bH-cyclopropa[a]naphthalen-7b-ol (11m):

To an ice-cold solution of ketone **S2** (500 mg, 2.8 mmol, 1 eq.) and Et_3N (1.6 mL, 11.4 mmol, 4 eq.) in dry DCM (7 mL) TMSOTf (1.5 mL, 8.5 mmol, 3 eq.) was added

dropwise. After stirring for 1 h at 0°C, the reaction mixture was diluted with saturated aqueous NaHCO₃ solution (5 mL) and water (5 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 5 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure to give TMS enol ether **S3** as an oil which was used in the next step without further purification.

To an ice-cold solution of the above TMS enol ether **S3** in dry DCM (10 mL) solution of Et₂Zn in toluene (9.3 mL, 6.5 mmol, 0.7 M, 2.3 eq.) was added under argon atmosphere followed by CH₂I₂ (0.68 mL, 8.4 mmol, 3 eq.). The reaction mixture was stirred overnight at room temperature, then quenched with saturated aqueous NH₄Cl (5 mL) and extracted with DCM (3×5 mL). Combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure to give TMS-protected cyclopropanol **S4** as a colorless oil which was used in the next step without additional purification.

To a solution of the above TMS-protected cyclopropanol **S4** in MeOH (2.8 mL) PPTS (704 mg, 2.8 mmol, 1 eq.) was added. After stirring for 10 min at room temperature, pyridine (0.23 mL, 2.8 mmol, 1 eq.) was added, and the mixture was evaporated under reduced pressure. The residue was then purified by column chromatography on silica gel (15→25% EtOAc/PE) to provide cyclopropanol **11m** as a colorless oil (388 mg, 2.0 mmol, 73% yield over three steps). ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 8.5 Hz, 1H), 6.82 (ddd, *J* = 8.5, 2.7, 0.9 Hz, 1H), 6.66 – 6.61 (m, 1H), 3.79 (s, 3H), 2.61 – 2.54 (m, 1H), 2.42 – 2.29 (m, 2H), 1.98 (ddt, *J* = 13.2, 6.4, 2.2 Hz, 1H), 1.77 (tdd, *J* = 13.2, 5.5, 3.2 Hz, 1H), 1.73 – 1.65 (m, 1H), 1.20 (dd, *J* = 9.9, 5.7 Hz, 1H), 1.02 – 0.95 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 157.8, 134.5, 132.8, 125.3, 114.1, 111.7, 55.4, 54.6, 26.5, 24.2, 18.8, 16.4. Data are consistent with those reported in the literature.⁹

3. Selected optimizations studies on Ni/photoredox catalyzed alkenylation

General procedure: condition screening

A 1.5 mL vial equipped with a stirring bar was charged with cyclopropanol **11a** (20 mg, 0.12 mmol, 1 eq.), NiCl₂·bpy (1.8 mg, 6.2 μmol, 5 mol %), 4CzIPN (4.9 mg, 6.2 μmol, 5 mol %), K₂CO₃ (51.2 mg, 0.37 mmol, 3 eq.) and Ti(O*i*Pr)₄ (73 μL, 0.25 mmol, 2 eq.). The vial was purged with Ar for 5 min followed by addition of 2-bromoprop-1-ene (21 μL, 0.25 mmol, 2 eq.) solution in acetone (1.2 mL). The resulting mixture was set to stir (1200 rpm) and irradiated with two 20W blue LED spotlights (5 cm away) for 15 h. Upon reaction complete the crude mixture was poured into 5% H₂SO₄ solution (2 mL) and extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with water (2 mL), saturated solution of NaHCO₃ (2 mL), dried over Na₂SO₄ and concentrated under reduced pressure. Crude NMR with internal standard (dibromomethane) was recorded.

Table S1: Solvent screening

Deviation from standard conditions	Conversion	NMR Yield of 14a
none	62	58
MeCN	77	58
THF	57	45
DMA	53	43
acetone/ <i>i</i> PrOH (60:1)	56	54
acetone/ <i>i</i> PrOH (6:1)	60	60
<i>i</i> PrOH	-	trace

Table S2: Condition evaluation

Deviation from standard conditions	Conversion, %	Yield 14a, % ^a
10 mol % of 4CzIPN instead of 5 mol % ^b	82	59
10 mol % of NiCl ₂ ·bpy instead of 5 mol % ^c	61	53
CPTi(OiPr) ₃ 15 (1 eq.) ^d instead of 11a (1 eq.) + Ti(OiPr) ₄ (2 eq.)	52	41
NiCl ₂ ·DME (5 mol %) + 2,9-Neocuproine (5 mol %) instead of NiCl ₂ ·bpy	92	82 (71) ^e
NiCl ₂ ·DME (5 mol %) + 6,6'-Dimethyl-2,2'- bipyridine (5 mol %) instead of NiCl ₂ ·bpy	76	45
NiCl ₂ ·DME (2.5 mol %) + 2,9-Neocuproine (2.5 mol %) instead of NiCl ₂ ·bpy	nd	nd (84) ^e
Ti(OtBu) ₄ instead of Ti(OiPr) ₄	43	33

^a Yields were determined by ¹H NMR spectroscopy using dibromomethane as an internal standard;

^b MeCN was used as a solvent;

^c The reaction was carried out with 5% of NiCl₂·bpy and additional 5% were added after 7h;

^d CP – 1-phenethylcyclopropoxy substituent.

^e Isolated yields are given in parentheses (the reactions were carried out with 0.25 mmol of starting material);

4. Arylation and alkenylation of cyclopropanols

General procedure A:

A 4 mL vial equipped with a stirring bar was charged with cyclopropanol (0.25 mmol, 1 eq.), aryl halide (0.50 mmol, 2 eq.), 4CzIPN (9.9 mg, 12.5 μ mol, 5 mol %), NiCl₂·bpy (3.6 mg, 12.5 μ mol, 5 mol %), Ti(O*i*Pr)₄ (148 μ L, 0.50 mmol, 2 eq.) and K₂CO₃ (103.5 mg, 0.75 mmol, 3 eq.). The vial was purged with Ar for 10 min, followed by addition of acetone (2.5 mL). The resulting mixture was set to stir (1200 rpm) and irradiated with two 20W blue LED spotlights (5 cm away) for 15 h. Upon reaction complete the crude mixture was poured into 5% H₂SO₄ solution (5 mL) and extracted with EtOAc (3 $\times$ 2 mL). The combined organic layers were washed with water (2 mL), saturated solution of NaHCO₃ (2 mL) and dried over Na₂SO₄. After removal of the solvent in vacuum, the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc as the eluent to yield the corresponding products.

General procedure B:

A 4 mL vial equipped with a stirring bar was charged with cyclopropanol (0.25 mmol, 1 eq.), NiCl₂·DME (1.4 mg, 6.25 μ mol, 2.5 mol %), 2,9-neocuproine (1.3 mg, 6.25 μ mol, 2.5 mol %), 4CzIPN (9.9 mg, 12.5 μ mol, 5 mol %), K₂CO₃ (103.5 mg, 0.75 mmol, 3 eq.) and Ti(O*i*Pr)₄ (148 μ L, 0.50 mmol, 2 eq.). The vial was purged with Ar for 5 min followed by addition of vinyl bromide (0.50 mmol, 2 eq) solution in acetone (2.5 mL). The resulting mixture was set to stir (1200 rpm) and irradiated with two 20W blue LED spotlights (5 cm away) for 15 h. Upon reaction complete the crude mixture was poured into 5% H₂SO₄ solution (5mL) and extracted with EtOAc (3 $\times$ 2 mL). The combined organic layers were washed with water (2 mL), saturated solution of NaHCO₃ (2 mL) and dried over Na₂SO₄. After removal of the solvent in vacuum, the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc as the eluent to yield the corresponding products.

1-(4-methoxyphenyl)-5-phenylpentan-3-one

(13a): Obtained according to the general procedure A from cyclopropanol **11a** and 4-bromoanisole. The crude product was purified by flash column chromatography on silica gel (5% EtOAc/PE) to

provide a colorless oil (38.5 mg, 0.144 mmol, 58% yield). The yields of the product obtained from 4-methoxyphenyl trifluoromethanesulfonate and 1-chloro-4-methoxybenzene were 18% and 0%, respectively; ¹H NMR (500 MHz, CDCl₃) δ 7.28 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.08 (d, *J* = 8.7 Hz,

2H), 6.82 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 3H), 2.89 (t, $J = 7.6$ Hz, 2H), 2.84 (t, $J = 7.6$ Hz, 2H), 2.71 (t, $J = 7.6$ Hz, 1H), 2.68 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.4, 158.1, 141.2, 133.2, 129.4 (2C), 128.6 (2C), 128.4 (2C), 126.2, 114.0 (2C), 55.4, 44.9, 44.7, 29.8, 29.0. HRMS (ESI⁺): m/z calc'd for $\text{C}_{18}\text{H}_{20}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 291.1356, found 291.1364.

isopropyl 4-(3-oxo-5-phenylpentyl)benzoate

(13b): Obtained according to the general procedure A from cyclopropanol **11a** and isopropyl 4-bromobenzoate. The crude product was purified by flash column chromatography on silica gel (3%

EtOAc/PE) to provide a colorless oil (38.5 mg, 0.119 mmol, 48% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, $J = 8.3$ Hz, 2H), 7.30 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 7.17 – 7.13 (m, 2H), 5.24 (hept, $J = 6.3$ Hz, 1H), 2.93 (t, $J = 7.5$ Hz, 2H), 2.89 (t, $J = 7.5$ Hz, 2H), 2.71 (t, $J = 7.5$ Hz, 4H), 1.36 (d, $J = 6.3$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.7, 166.1, 146.4, 141.0, 129.9 (2C), 129.0, 128.6 (2C), 128.4 (2C), 128.4 (2C), 126.3, 68.3, 44.6, 44.1, 29.8, 29.7, 22.1 (2C). HRMS (ESI⁺): m/z calc'd for $\text{C}_{21}\text{H}_{24}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 347.1618, found 347.1618.

1-(naphthalen-2-yl)-5-phenylpentan-3-one (13c):

Obtained according to the general procedure A from cyclopropanol **11a** and 2-bromonaphthalene. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/PE) to

provide a colorless oil (40.0 mg, 0.139 mmol, 56% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.83 – 7.80 (m, 1H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.61 (s, 1H), 7.50 – 7.41 (m, 2H), 7.31 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.13 (m, 2H), 3.07 (t, $J = 7.6$ Hz, 2H), 2.91 (t, $J = 7.6$ Hz, 2H), 2.81 (t, $J = 7.6$ Hz, 2H), 2.74 (t, $J = 7.6$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 209.2, 141.1, 138.6, 133.7, 132.2, 128.6 (2C), 128.4 (2C), 128.2, 127.7, 127.6, 127.2, 126.6, 126.2, 126.1, 125.5, 44.7, 44.5, 30.0, 29.9. HRMS (ESI⁺): m/z calc'd for $\text{C}_{21}\text{H}_{20}\text{NaO}$ $[\text{M}+\text{Na}]^+$: 311.1406, found 311.1400.

1-phenyl-5-(o-tolyl)pentan-3-one (13d):

Obtained according to the general procedure A from cyclopropanol **11a** and 1-bromo-2-methylbenzene. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/PE) to provide a colorless oil (28.9 mg, 0.115

mmol, 46% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16

(m, 3H), 7.16 – 7.07 (m, 4H), 2.91 (t, $J = 7.6$ Hz, 2H), 2.88 (t, $J = 7.9$ Hz, 2H), 2.74 (t, $J = 7.6$ Hz, 2H), 2.66 (t, $J = 7.9$ Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.4, 141.1, 139.2, 136.0, 135.7, 130.4, 128.7, 128.6 (2C), 128.4 (2C), 126.4, 126.3, 44.6, 43.3, 30.0, 27.2, 19.4. **HRMS** (ESI $^{+}$): m/z calc'd for $\text{C}_{18}\text{H}_{20}\text{NaO}$ $[\text{M}+\text{Na}]^{+}$: 275.1406, found 275.1410.

isopropyl 2-(2-(3-oxo-5-phenylpentyl)phenyl)acetate (13e): Obtained according to the general procedure A from cyclopropanol **11a** and 1-methylethyl 2-bromobenzeneacetate. The crude product was purified by flash column chromatography on silica gel (6% EtOAc/PE)

to provide a colorless oil (43.7 mg, 0.129 mmol, 52% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.27 (m, 1H), 7.23 – 7.11 (m, 8H), 4.99 (hept, $J = 6.3$ Hz, 1H), 3.61 (s, 2H), 2.93 – 2.87 (m, 4H), 2.75 – 2.68 (m, 4H), 1.22 (d, $J = 6.3$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.1, 171.3, 141.1, 139.7, 132.7, 130.7, 129.4, 128.6 (2C), 128.4 (2C), 127.7, 126.6, 126.3, 68.4, 44.6, 44.0, 39.0, 29.9, 26.8, 21.9 (2C). **HRMS** (ESI $^{+}$): m/z calc'd for $\text{C}_{22}\text{H}_{26}\text{NaO}_3$ $[\text{M}+\text{Na}]^{+}$: 361.1774, found 361.1779.

1-(phenanthren-9-yl)-5-phenylpentan-3-one (13f):

Obtained according to the general procedure A from cyclopropanol **11a** and 9-bromophenanthrene. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/PE) to provide a colorless oil (42.7

mg, 0.126 mmol, 51% yield); ^1H NMR (500 MHz, CDCl_3) δ 8.75 (dd, $J = 8.4, 0.9$ Hz, 1H), 8.66 (d, $J = 8.0$ Hz, 1H), 8.02 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.82 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.71 – 7.58 (m, 4H), 7.57 (s, 1H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.16 (d, $J = 7.0$ Hz, 2H), 3.40 (t, $J = 8.3$ Hz, 2H), 2.93 (t, $J = 7.6$ Hz, 2H), 2.89 (t, $J = 8.3$ Hz, 2H), 2.75 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.3, 141.1, 135.2, 131.9, 130.9, 130.9, 129.8, 128.6 (2C), 128.4 (2C), 128.2, 126.8 (2C), 126.5, 126.4, 126.3, 126.2, 124.2, 123.5, 122.6, 44.6, 43.4, 30.0, 27.2. **HRMS** (ESI $^{+}$): m/z calc'd for $\text{C}_{25}\text{H}_{22}\text{NaO}$ $[\text{M}+\text{Na}]^{+}$: 361.1563, found 361.1562.

6-((tert-butyldiphenylsilyl)oxy)-1-(4-methoxyphenyl)hexane-3-one (13g):

Obtained according to the general procedure A from cyclopropanol **11b** and 4-bromoanisole. The crude product was purified by flash column

chromatography on silica gel (3% EtOAc/PE) to provide a colorless oil (63.0 mg, 0.137 mmol, 55% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.67 – 7.63 (m, 4H), 7.45

– 7.36 (m, 6H), 7.10 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.78 (s, 3H), 3.66 (t, $J = 6.1$ Hz, 2H), 2.84 (t, $J = 7.6$ Hz, 2H), 2.70 (t, $J = 7.6$ Hz, 2H), 2.51 (t, $J = 7.3$ Hz, 2H), 1.87 – 1.78 (m, 2H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.2, 158.1, 135.7 (4C), 133.9 (2C), 133.3, 129.8 (2C), 129.4 (2C), 127.8 (4C), 114.0 (2C), 63.1, 55.4, 44.7, 39.5, 29.1, 27.0 (3C), 26.7, 19.3. HRMS (ESI+): m/z calc'd for $\text{C}_{29}\text{H}_{36}\text{NaO}_3\text{Si}$ $[\text{M}+\text{Na}]^+$: 483.2326, found 483.2321.

1-(4-methoxyphenyl)-7-methyloct-6-en-3-one

(13h): Obtained according to the general procedure A from cyclopropanol **11c** and 4-bromoanisole. The crude product was purified by flash column chromatography on silica gel (2% EtOAc/PE) to provide a colorless oil (27.5 mg, 0.112 mmol, 45% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.09 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 5.06 – 5.00 (m, 1H), 3.78 (s, 3H), 2.84 (t, $J = 7.6$ Hz, 2H), 2.69 (t, $J = 7.6$ Hz, 2H), 2.40 (t, $J = 7.4$ Hz, 2H), 2.28 – 2.19 (m, 2H), 1.67 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.2, 158.1, 133.3, 129.4 (2C), 127.8, 122.9, 114.0 (2C), 55.4, 44.7, 43.1, 29.1, 25.8, 22.6, 17.8. HRMS (ESI+): m/z calc'd for $\text{C}_{16}\text{H}_{22}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 269.1512, found 269.1512.

1,1-diethoxy-5-(4-methoxyphenyl)pentan-3-one

(13i): Obtained according to the general procedure A from cyclopropanol **11d** and 4-bromoanisole. Upon reaction complete the crude mixture was poured into 5 mL saturated aqueous solution of NH_4Cl and extracted with EtOAc (3×2 mL). The crude product was purified by flash column chromatography on silica gel (5% EtOAc/PE) to provide a colorless oil (30.1 mg, 0.107 mmol, 43% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.09 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 4.89 (t, $J = 5.7$ Hz, 1H), 3.78 (s, 3H), 3.65 (dq, $J = 9.3, 7.1$ Hz, 2H), 3.50 (dq, $J = 9.3, 7.1$ Hz, 2H), 2.86 – 2.80 (m, 2H), 2.78 – 2.73 (m, 2H), 2.72 (d, $J = 5.7$ Hz, 2H), 1.17 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 207.2, 158.1, 133.2, 129.4 (2C), 114.0 (2C), 100.1, 62.5 (2C), 55.4, 47.8, 45.9, 28.6, 15.4 (2C). HRMS (ESI+): m/z calc'd for $\text{C}_{16}\text{H}_{24}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 303.1567, found 303.1561.

5-(4-methoxyphenyl)-1-phenylhexan-3-one (13j):

Obtained according to the general procedure A from cyclopropanol **11e** and 4-bromoanisole. The crude product was purified by flash column chromatography

on silica gel (2% EtOAc/PE) to provide a colorless oil (33.9 mg, 0.120 mmol, 48% yield); **¹H NMR** (500 MHz, CDCl₃) δ 7.23 – 7.28 (m, 2H), 7.22 – 7.16 (m, 1H), 7.13 – 7.08 (m, 4H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.27 (h, *J* = 7.0 Hz, 1H), 2.85 – 2.79 (m, 2H), 2.71 – 2.55 (m, 4H), 1.22 (d, *J* = 7.0 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 209.2, 158.2, 141.2, 138.3, 128.6 (2C), 128.4 (2C), 127.8 (2C), 126.2, 114.0 (2C), 55.4, 51.8, 45.1, 34.9, 29.7, 22.3. **HRMS** (ESI⁺): *m/z* calc'd for C₁₉H₂₂NaO₂ [M+Na]⁺: 305.1512, found 305.1526.

6-methyl-1-phenylhept-6-en-3-one (14a): Obtained according to the general procedure B from cyclopropanol **11a** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (1% EtOAc/PE) to provide a colorless oil (42.5 mg, 0.210 mmol, 84% yield);

¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 4.72 (s, 1H), 4.63 (s, 1H), 2.94 – 2.87 (m, 2H), 2.79 – 2.73 (m, 2H), 2.57 – 2.50 (m, 2H), 2.31 – 2.24 (m, 2H), 1.71 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 209.6, 144.6, 141.2, 128.6, 128.5, 126.2, 110.3, 44.4, 41.3, 31.5, 29.9, 22.8. **HRMS** (ESI⁺): *m/z* calc'd for C₁₄H₁₉O [M+H]⁺: 203.1430, found 203.1433.

6-methylene-1-phenyldecan-3-one (14b): Obtained according to the general procedure B from cyclopropanol **11a** and 2-bromohex-1-ene. The crude product was purified by flash column chromatography on silica gel (1→1.5% EtOAc/PE) to provide a colorless

oil (33.6 mg, 0.137 mmol, 55% yield); **¹H NMR** (500 MHz, CDCl₃) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 4.72 (s, 1H), 4.65 (s, 1H), 2.93 – 2.88 (m, 2H), 2.78 – 2.73 (m, 2H), 2.56 – 2.50 (m, 2H), 2.31 – 2.24 (m, 2H), 2.03 – 1.97 (m, 2H), 1.43 – 1.36 (m, 2H), 1.35 – 1.25 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 209.7, 148.8, 141.3, 128.6, 128.5, 126.2, 109.1, 44.5, 41.5, 36.2, 30.1, 29.9, 29.8, 22.6, 14.1. **HRMS** (ESI⁺): *m/z* calc'd for C₁₇H₂₅O [M+H]⁺: 245.1900, found 245.1901.

1-(cyclohex-1-en-1-yl)-5-phenylpentan-3-one (14c): Obtained according to the general procedure B from cyclopropanol **11a** and cyclohex-1-en-1-yl trifluoromethanesulfonate. The crude product was purified by flash column chromatography on silica gel (1%

EtOAc/PE) to provide a colorless oil (36.4 mg, 0.150 mmol, 60% yield); **¹H NMR** (500 MHz, CDCl₃) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 5.39 – 5.33 (m, 1H),

2.90 (t, $J = 7.6$ Hz, 2H), 2.74 (t, $J = 7.6$ Hz, 2H), 2.52 – 2.46 (m, 2H), 2.23 – 2.15 (m, 2H), 1.99 – 1.92 (m, 2H), 1.92 – 1.86 (m, 2H), 1.64 – 1.57 (m, 2H), 1.56 – 1.50 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.1, 141.3, 136.4, 128.6, 128.5, 126.2, 121.5, 44.4, 41.5, 32.0, 29.9, 28.5, 25.3, 23.0, 22.5. HRMS (ESI⁺): m/z calc'd for $\text{C}_{17}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 243.1743, found 243.1746.

(E)-1-phenylundec-6-en-3-one (14d): Obtained according to the general procedure B from cyclopropanol **11a** and (*E*)-1-bromohex-1-ene. The crude product was purified by flash column chromatography on silica gel (1→1.5% EtOAc/PE) to provide a colorless oil (27.5 mg, 0.113 mmol, 45% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 5.47 – 5.31 (m, 2H), 2.93 – 2.87 (m, 2H), 2.76 – 2.70 (m, 2H), 2.47 – 2.42 (m, 2H), 2.28 – 2.22 (m, 2H), 2.00 – 1.92 (m, 2H), 1.34 – 1.24 (m, 4H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.7, 141.3, 131.8, 128.6, 128.4, 128.3, 126.2, 44.5, 43.0, 32.3, 31.8, 29.8, 27.0, 22.3, 14.1. HRMS (ESI⁺): m/z calc'd for $\text{C}_{17}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$: 245.1900, found 245.1899.

(Z)-1-phenyloct-6-en-3-one (14e): Obtained according to the general procedure A from cyclopropanol **11a** and (*Z*)-1-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (2% EtOAc/PE) to provide a colorless oil as 1:8 mixture of *E/Z* isomers (23.2 mg, 0.115 mmol, 46% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 5.51 – 5.27 (m, 2H), 2.90 (t, $J = 7.7$ Hz, 2H), 2.73 (t, $J = 7.7$ Hz, 2H), 2.44 (t, $J = 7.4$ Hz, 2H), 2.35 – 2.27 (m, 2H), 1.62 – 1.58 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.8, 141.3, 128.8, 128.6 (2C), 128.5 (2C), 126.2, 125.2, 44.5, 42.8, 29.9, 21.4, 12.8. HRMS (ESI⁺): m/z calc'd for $\text{C}_{14}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$: 203.1430, found 203.1431.

(E)-1,7-diphenylhept-6-en-3-one (14f): Obtained according to the general procedure B from cyclopropanol **11a** and (*E*)-(2-bromovinyl)benzene. The crude product was purified by flash column chromatography on silica gel (1→2% EtOAc/PE) to provide a colorless oil (51.6 mg, 0.195 mmol, 78% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.24 (m, 6H), 7.19 (t, $J = 7.4$ Hz, 4H), 6.39 (d, $J = 15.9$ Hz, 1H), 6.17 (dt, $J = 15.9, 6.9$ Hz, 1H), 2.92 (t, $J = 7.6$ Hz, 2H), 2.76 (t, $J = 7.6$ Hz, 2H), 2.57

(t, J = 7.2 Hz, 2H), 2.51 – 2.45 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.3, 141.2, 137.5, 130.9, 129.0, 128.6, 128.5, 127.2, 126.3, 126.2, 44.6, 42.6, 29.9, 27.2. HRMS (ESI⁺): m/z calc'd for $\text{C}_{19}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$: 265.1587, found 265.1590.

(E)-7-(4-methoxyphenyl)-1-phenylhept-6-en-3-one (14g): Obtained according to the general procedure B from cyclopropanol **11a** and (*E*)-1-(2-bromovinyl)-4-methoxybenzene. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/PE) to provide a colorless oil as 6:1 mixture of *E/Z* isomers (30.2 mg, 0.103 mmol, 41% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.24 (m, 5H), 7.20 – 7.17 (m, 2H), 6.86 – 6.82 (m, 2H), 6.34 (d, J = 15.8 Hz, 1H), 6.03 (dt, J = 15.8, 6.9 Hz, 1H), 3.80 (s, 3H), 2.92 (t, J = 7.6 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.56 (t, J = 7.3 Hz, 2H), 2.50 – 2.42 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.4, 159.0, 141.2, 130.4, 130.3, 128.6 (2C), 128.4 (2C), 127.2 (2C), 126.7, 126.2, 114.1 (2C), 55.4, 44.5, 42.8, 29.9, 27.2. HRMS (ESI⁺): m/z calc'd for $\text{C}_{20}\text{H}_{22}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 305.1512, found 305.1512.

(E)-7-(2,4-dichlorophenyl)-1-phenylhept-6-en-3-one (14h): Obtained according to the general procedure B from cyclopropanol **11a** and (*E*)-1-(2-bromovinyl)-2,4-dichlorobenzene. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/PE) to provide a colorless oil as 6:1 mixture of *E/Z* isomers (50.8 mg, 0.153 mmol, 61% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 2.1 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.20 – 7.17 (m, 3H), 6.68 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.8, 6.8 Hz, 1H), 2.92 (t, J = 7.6 Hz, 2H), 2.77 (t, J = 7.6 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 2.55 – 2.48 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.0, 141.1, 134.2, 133.2, 133.0, 132.6, 129.4, 128.6 (2C), 128.4 (2C), 127.6, 127.3, 126.3, 126.1, 44.5, 42.3, 29.9, 27.3. HRMS (ESI⁺): m/z calc'd for $\text{C}_{19}\text{H}_{19}\text{Cl}_2\text{O}$ $[\text{M}+\text{H}]^+$: 333.0807, found 333.0804.

2,12-dimethyltrideca-1,12-diene-5,9-dione (14i): Obtained according to the general procedure B from cyclopropanol **11f**, and 2-bromoprop-1-ene (4 eq.) with $\text{NiCl}_2\cdot\text{DME}$ (5%), 2,9-neocuproine (5%), 4CzIPN (10%), $\text{Ti}(\text{OiPr})_4$ (4 eq.), K_2CO_3 (6 eq.). The crude product was purified by flash column chromatography on silica gel (5→6% EtOAc/PE) to provide a colorless oil (30.1 mg, 0.127 mmol, 51% yield); ^1H NMR (500 MHz, CDCl_3) δ 4.71 (s, 2H), 4.63

(s, 2H), 2.56 – 2.48 (m, 4H), 2.45 (t, $J = 7.1$ Hz, 4H), 2.26 (t, $J = 7.6$ Hz, 4H), 1.84 (p, $J = 7.1$ Hz, 2H), 1.72 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.1, 144.6, 110.3, 41.7, 41.0, 31.6, 22.7, 17.8. HRMS (ESI⁺): m/z calc'd for $\text{C}_{15}\text{H}_{24}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 259.1669, found 259.1665.

1-((*tert*-butyldiphenylsilyl)oxy)-7-methyloct-7-en-4-one (14j): Obtained according to the general procedure B from cyclopropanol **11b** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (2% EtOAc/PE) to provide a colorless oil (74.0 mg, 0.188 mmol, 75% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.68 – 7.62 (m, 4H), 7.46 – 7.34 (m, 6H), 4.73 (s, 1H), 4.65 (s, 1H), 3.67 (t, $J = 5.9$ Hz, 2H), 2.58 – 2.50 (m, 4H), 2.27 (t, $J = 7.5$ Hz, 2H), 1.88 – 1.78 (m, 2H), 1.73 (s, 3H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.5, 144.7, 135.7, 134.0, 129.8, 127.8, 110.3, 63.2, 41.1, 39.3, 31.7, 27.0, 26.8, 22.8, 19.4. HRMS (ESI⁺): m/z calc'd for $\text{C}_{25}\text{H}_{35}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 395.2401, found 395.2394.

10-hydroxy-2-methyldec-1-en-5-one (14k): Obtained according to the general procedure B from cyclopropanol **11g** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (30% EtOAc/PE) to provide a colorless oil (30.8 mg, 0.167 mmol, 67% yield); ^1H NMR (500 MHz, CDCl_3) δ 4.72 (s, 1H), 4.64 (s, 1H), 3.64 (t, $J = 6.6$ Hz, 2H), 2.56 – 2.50 (m, 2H), 2.43 (t, $J = 7.3$ Hz, 2H), 2.29 – 2.23 (m, 2H), 1.72 (s, 3H), 1.65 – 1.52 (m, 4H), 1.51 (br s, 1H), 1.40 – 1.30 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.7, 144.7, 110.2, 62.8, 42.8, 41.1, 32.6, 31.6, 25.5, 23.5, 22.8. HRMS (ESI⁺): m/z calc'd for $\text{C}_{11}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$: 185.1536, found 185.1533.

2,9-dimethyldeca-1,8-dien-5-one (14l): Obtained according to the general procedure B from cyclopropanol **11c** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (2% EtOAc/PE) to provide a colorless oil (29.3 mg, 0.163 mmol, 65% yield); ^1H NMR (500 MHz, CDCl_3) δ 5.10 – 5.02 (m, 1H), 4.72 (s, 1H), 4.64 (s, 1H), 2.57 – 2.50 (m, 2H), 2.44 (t, $J = 7.5$ Hz, 2H), 2.31 – 2.21 (m, 4H), 1.72 (s, 3H), 1.67 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.4, 144.7, 132.8, 122.9, 110.2, 42.9, 41.1, 31.6, 25.8, 22.8, 22.7, 17.8. HRMS (ESI⁺): m/z calc'd for $\text{C}_{12}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$: 181.1587, found 181.1587.

5-methyl-1-(2-methyl-1,3-dioxolan-2-yl)hex-5-en-2-one (14m): Obtained according to the general procedure B from cyclopropanol **11h** and 2-bromoprop-1-ene. Upon reaction complete the crude mixture was poured into 5 mL saturated aqueous solution of NH_4Cl and extracted with EtOAc (3×2 mL).

The crude product was purified by flash column chromatography on silica gel (5% EtOAc/PE) to provide a colorless oil (20.1 mg, 0.102 mmol, 41% yield); ^1H NMR (500 MHz, CDCl_3) δ 4.71 (s, 1H), 4.65 (s, 1H), 4.00 – 3.91 (m, 4H), 2.76 (s, 2H), 2.69 – 2.61 (m, 2H), 2.26 (t, $J = 7.6$ Hz, 2H), 1.72 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 207.2, 144.7, 110.2, 108.1, 64.7 (2C), 51.8, 42.6, 31.3, 24.6, 22.8. HRMS (ESI⁺): m/z calc'd for $\text{C}_{11}\text{H}_{18}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 221.1148, found 221.1141.

1,1-diethoxy-6-methylhept-6-en-3-one (14n): Obtained according to the general procedure B from cyclopropanol **11d** and 2-bromoprop-1-ene. Upon reaction complete the crude mixture was poured into 5 mL saturated aqueous solution of

NH_4Cl and extracted with EtOAc (3×2 mL). The crude product was purified by flash column chromatography on silica gel (3→4% EtOAc/PE) to provide a colorless oil (34.8 mg, 0.162 mmol, 65% yield); ^1H NMR (500 MHz, CDCl_3) δ 4.89 (t, $J = 5.7$ Hz, 1H), 4.71 (s, 1H), 4.64 (s, 1H), 3.66 (dq, $J = 9.3, 7.1$ Hz, 2H), 3.52 (dq, $J = 9.3, 7.1$ Hz, 2H), 2.73 (d, $J = 5.7$ Hz, 2H), 2.63 – 2.56 (m, 2H), 2.27 (d, $J = 7.7$ Hz, 2H), 1.71 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 207.4, 144.5, 110.2, 100.2, 47.7, 42.3, 31.1, 22.8, 15.4. HRMS (ESI⁺): m/z calc'd for $\text{C}_{12}\text{H}_{22}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 237.1461, found 237.1459.

(S)-2-((tert-butyldimethylsilyl)oxy)-6-methylhept-6-en-3-one (14o): Obtained according to the general procedure B from cyclopropanol **11i** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (2% EtOAc/PE) to provide a colorless oil (30.8 mg, 0.120 mmol, 48%

yield); $[\alpha]_{\text{D}}^{20} = -5.05$ ($c=0.55$ in CHCl_3) ^1H NMR (500 MHz, CDCl_3) δ 4.72 (s, 1H), 4.66 (s, 1H), 4.15 (q, $J = 6.8$ Hz, 1H), 2.82 – 2.65 (m, 2H), 2.25 (t, $J = 7.7$ Hz, 2H), 1.73 (s, 3H), 1.28 (d, $J = 6.8$ Hz, 3H), 0.92 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 213.8, 144.9, 110.0, 75.0, 35.3, 31.0, 25.9, 22.9, 21.0, 18.2, -4.5, -4.9. *ee* determined by the Mosher method was 93%. Selected ^1H NMR chemical shifts for (S)-6-methyl-3-oxohept-6-en-2-yl (S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate: δ 5.28 (q, $J = 7.0$ Hz, 1H, CH_3CHO), 1.45 (d, $J = 7.0$ Hz, 3H, CH_3CHO). Selected ^1H NMR chemical shifts for (S)-6-methyl-3-oxohept-6-en-2-yl

(R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate: δ 5.32 (q, J = 7.0 Hz, 1H, CH₃CHO), 1.51 (d, J = 7.0 Hz, 3H, CH₃CHO). **HRMS** (ESI⁺): m/z calc'd for C₁₄H₂₈NaO₂Si [M+Na]⁺: 279.1751, found 279.1754.

(S)-1-((tert-butyldimethylsilyl)oxy)-2,6-dimethylhept-6-en-3-one (14p): Obtained according to the general procedure B from cyclopropanol **11j** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (2% EtOAc/PE) to provide a colorless oil (37.2 mg, 0.138 mmol, 55% yield); $[\alpha]_D^{20}$ = +29.28 (c =0.69 in CHCl₃), **¹H NMR** (500 MHz, CDCl₃) δ 4.71 (s, 1H), 4.66 (s, 1H), 3.72 (dd, J = 9.8, 7.7 Hz, 1H), 3.61 (dd, J = 9.8, 5.4 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.71 – 2.57 (m, 2H), 2.26 (t, J = 7.7 Hz, 2H), 1.73 (s, 3H), 1.02 (d, J = 6.9 Hz, 3H), 0.86 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 213.3, 144.9, 110.1, 65.8, 48.7, 41.2, 31.2, 26.0, 22.8, 18.3, 13.2, -5.4. **HRMS** (ESI⁺): m/z calc'd for C₁₅H₃₁O₂Si [M+H]⁺: 271.2088, found 271.2086.

Fragments of ^1H NMR spectra of (S)-6-methyl-3-oxohept-6-en-2-yl (R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (up) and (S)-6-methyl-3-oxohept-6-en-2-yl (S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (under):

Retention of *ee* was observed for **14p**.

Racemic product **rac-14p**: Astec CHIRALDEX B-DM, He at 12 psi, 0.75 mL/min, 110 °C, FID.

Signal: FID1A						
RT [min]	Type	Width [min]	Area	Height	Area%	Name
75.306	MM m	0.36	6.23	0.20	49.97	
76.464	MM m	0.37	6.24	0.20	50.03	
		Sum	12.48			

Chiral product **14p**: Astec CHIRALDEX B-DM, He at 12 psi, 0.75 mL/min, 110 °C, FID.

Racemic product **rac-14p** was obtained from corresponding chiral ketone according previously reported procedure with Al_2O_3 .¹⁰

5,6-dimethyl-1-phenylhept-6-en-3-one (14q): Obtained according to the general procedure A from cyclopropanol **11e** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (2% EtOAc/PE) to provide a colorless oil (28.7 mg, 0.133 mmol, 53% yield);

¹H NMR (500 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 4.71 – 4.68 (m, 2H), 2.89 (t, J = 7.6 Hz, 2H), 2.75 – 2.66 (m, 3H), 2.54 (dd, J = 15.9, 6.4 Hz,

1H), 2.34 (dd, *J* = 15.9, 7.9 Hz, 1H), 1.70 (s, 3H), 1.01 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 209.3, 149.2, 141.3, 128.6 (2C), 128.5 (2C), 126.2, 109.7, 48.9, 44.9, 36.7, 29.8, 20.2, 19.7. HRMS (ESI⁺): *m/z* calc'd for C₁₅H₂₁O [M+H]⁺: 217.1587, found 217.1587.

9-((tert-butyldiphenylsilyl)oxy)-1-phenyl-5-(prop-1-en-2-yl)nonan-3-one (14r): Obtained according to the general procedure A from cyclopropanol **11k** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (2% EtOAc/PE) to

provide a colorless oil (82.1 mg, 0.160 mmol, 64% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.69 – 7.64 (m, 4H), 7.45 – 7.35 (m, 6H), 7.30 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 4.74 (s, 1H), 4.69 (s, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.70 (td, *J* = 7.4, 2.9 Hz, 2H), 2.65 – 2.55 (m, 1H), 2.46 (dd, *J* = 15.5, 7.9 Hz, 1H), 2.37 (dd, *J* = 15.5, 6.5 Hz, 1H), 1.62 (s, 3H), 1.57 – 1.45 (m, 2H), 1.31 – 1.20 (m, 4H), 1.05 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 209.3, 146.7, 141.3, 135.7 (4C), 134.3, 129.6 (2C), 128.6 (2C), 128.5 (2C), 127.7 (4C), 126.2 (2C), 111.9, 63.9, 47.8, 44.8, 42.8, 33.1, 32.6, 29.7, 27.0 (3C), 23.6, 19.4, 19.0. HRMS (ESI⁺): *m/z* calc'd for C₃₄H₄₅O₂Si [M+H]⁺: 513.3183, found 513.3177.

7-oxo-9-phenyl-5-(prop-1-en-2-yl)nonan-3-yl pivalate (14s): Obtained according to the general procedure A from cyclopropanol (±)-**11l** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (3%

EtOAc/PE) to provide **14s** as a 1:1 mixture of diastereomers, colorless oil (36.4 mg, 0.102 mmol, 41% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 4.79 – 4.77 (m, 0.5H), 4.75 – 4.72 (m, 0.5H), 4.71 (s, 0.5H), 4.67 (s, 0.5H), 2.90 – 2.83 (m, 2H), 2.77 – 2.61 (m, 3H), 2.50 (dd, *J* = 15.8, 7.4 Hz, 0.5H), 2.47 – 2.44 (m, 1H), 2.39 (dd, *J* = 15.8, 7.0 Hz, 0.5H), 1.70 (s, 1.5H), 1.68 – 1.64 (m, 1H), 1.62 (s, 1.5H), 1.58 – 1.41 (m, 3H), 1.21 (s, 4H), 1.19 (s, 5H), 1.18 – 1.14 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 1.5H), 0.84 (t, *J* = 7.4 Hz, 1.5H). ¹³C NMR (126 MHz, CDCl₃) δ 208.8, 208.7, 178.4, 178.2, 146.3, 145.8, 141.2, 128.6 (2C), 128.4 (2C), 126.2, 126.2, 112.9, 112.1, 73.1, 72.8, 47.9, 47.2, 44.7, 39.4, 39.1, 39.0, 37.2, 37.0, 29.8, 29.7, 29.7, 27.5, 27.4 (3C), 27.3 (3C), 26.6, 19.2, 19.1, 9.4, 9.4. HRMS (ESI⁺): *m/z* calc'd for C₂₃H₃₄NaO₃ [M+Na]⁺: 381.2400, found 381.2402.

2-methoxy-7-(prop-1-en-2-yl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (14t): Obtained according to the general procedure A from cyclopropanol **11m** and 2-bromoprop-1-ene. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/PE) to provide a colorless oil (33.0 mg, 0.143 mmol, 57% yield); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.7$ Hz, 1H), 6.82 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.68 (d, $J = 2.5$ Hz, 1H), 4.83 (s, 1H), 4.74 (s, 1H), 3.85 (s, 3H), 3.01 – 2.86 (m, 2H), 2.79 (dd, $J = 14.1, 3.8$ Hz, 1H), 2.63 – 2.54 (m, 1H), 2.22 – 2.15 (m, 1H), 2.11 (dd, $J = 14.1, 10.1$ Hz, 1H), 1.80 – 1.70 (m, 4H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 198.8, 163.6, 146.6, 143.6, 130.1, 126.3, 113.2, 112.6 (2C), 55.5, 45.0, 38.0, 28.8, 27.7, 22.1. **HRMS** (ESI $^+$): m/z calc'd for $\text{C}_{15}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 231.1380, found 231.1378.

triisopropoxy(1-phenethylcyclopropoxy)titanium (15): Prepared by stirring cyclopropanol **11a** (1 eq.) and $\text{Ti}(\text{OiPr})_4$ (1 eq.) at room temperature under reduced pressure for 1 hour. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 – 7.14 (m, 5H), 4.59 – 4.45 (m, 3H), 2.97 – 2.89 (m, 2H), 1.94 – 1.86 (m, 2H), 1.27 (d, $J = 6.1$ Hz, 18H), 0.96 – 0.83 (m, 2H), 0.58 – 0.45 (m, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 143.0, 128.6, 128.4, 125.7, 41.4, 32.9, 26.7, 25.5, 15.6.

5. Mechanistic investigation

General procedure: w/o photocatalyst

A 1.5 mL vial equipped with a stirring bar was charged with cyclopropanol **11a** (20 mg, 0.12 mmol, 1 eq.), NiCl₂·DME (1.4 mg, 6.25 μmol, 2.5 mol %), 2,9-neocuproine (1.3 mg, 6.25 μmol, 2.5 mol %), K₂CO₃ (51.2 mg, 0.37 mmol, 3 eq.) and Ti(OiPr)₄ (73 μL, 0.25 mmol, 2 eq., for entry 1, 3). The vial was purged with Ar for 5 min followed by addition of 2-bromoprop-1-ene (21 μL, 0.25 mmol, 2 eq.) solution in acetone (1.2 mL). The resulting mixture was set to stir (1200 rpm) and irradiated with light source (5 cm away) for 22 h. Upon reaction complete the crude mixture was poured into 5% H₂SO₄ solution (2 mL; for entry 1 and 3) or H₂O (2 mL; for entry 2 and 4) and extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with water (2 mL; for entry 1 and 3), saturated solution of NaHCO₃ (2 mL; for entry 1 and 3), dried over Na₂SO₄ and concentrated under reduced pressure. Crude NMR with internal standard (dibromomethane) was recorded.

Entry	Light source	Ti(OiPr) ₄ , equiv.	NMR Yield of 14a , %
1	blue LEDs	2	10
2	blue LEDs	-	-
3	purple LEDs	2	38
4	purple LEDs	-	1

Cyclic Voltammetry

The blank curve (**Figure S1**) indicates no considerable oxidation current, whereas addition of cyclopropanol **11a** leads to appearance of anodic peak around 1.7 V vs Fc^+/Fc which is attributed to cyclopropanol oxidation. A further addition of 1 equivalent of $\text{Ti}(\text{OiPr})_4$ does not change shape of the voltammogram noticeably, only slight current increase is observed

Thus, addition of $\text{Ti}(\text{OiPr})_4$ to reaction mixture does not change oxidation potential of **11a** and appear not to affect oxidative ability of initial state of the compound.

Figure S1. Cyclic voltammograms of Pt wire electrode in blank electrolyte (black curve), electrolyte with cyclopropanol **11a** (red curve), electrolyte with cyclopropanol **11a** and 1 equivalent of $\text{Ti}(\text{OiPr})_4$ (blue curve). Potential scan rate 0.1 V/s

IPA/Cyclopropanol ligand exchange experiment

To a solution of cyclopropanol **11a** (10 mg, 0.062 mmol) in acetone- d_6 (0.7 mL) $Ti(OiPr)_4$ (0.018 mL, 0.062 mmol) was added and 1H NMR was recorded after 10 min at room temperature. Formation of 1:3 mixture of **11a** and **15** was observed.

Figure S2. 1H NMR (500 MHz, acetone- d_6) of compound **11a** (A) and 1:1 mixture of **11a** and $Ti(OiPr)_4$ after 10 min at room temperature (B).

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6. ^1H NMR and ^{13}C NMR Spectra

^1H NMR (500 MHz, CDCl_3) of compound **11a**

^{13}C NMR (126 MHz, CDCl_3) of compound **11a**

¹H NMR (500 MHz, CDCl₃) of compound **11c**

¹³C NMR (126 MHz, CDCl₃) of compound **11c**

¹H NMR (500 MHz, CDCl₃) of compound **11d**

¹³C NMR (126 MHz, CDCl₃) of compound **11d**

¹H NMR (500 MHz, CDCl₃) of compound **11e**

¹³C NMR (126 MHz, CDCl₃) of compound **11e**

^1H NMR (500 MHz, CDCl_3) of compound **11f**

^{13}C NMR (126 MHz, CDCl_3) of compound **11f**

¹H NMR (500 MHz, CDCl₃) of compound **11k**

¹³C NMR (126 MHz, CDCl₃) of compound **11k**

¹H NMR (500 MHz, CDCl₃) of compound S1

¹³C NMR (126 MHz, CDCl₃) of compound S1

¹H NMR (500 MHz, CDCl₃) of compound **111**

¹³C NMR (126 MHz, CDCl₃) of compound **111**

¹H NMR (500 MHz, CDCl₃) of compound **11m**

¹³C NMR (126 MHz, CDCl₃) of compound **11m**

^1H NMR (500 MHz, CDCl_3) of compound **13e**

^{13}C NMR (126 MHz, CDCl_3) of compound **13e**

¹H NMR (500 MHz, CDCl₃) of compound 13f

¹³C NMR (126 MHz, CDCl₃) of compound 13f

^1H NMR (500 MHz, CDCl_3) of compound **13g**

^{13}C NMR (126 MHz, CDCl_3) of compound **13g**

^1H NMR (500 MHz, CDCl_3) of compound **13i**

^{13}C NMR (126 MHz, CDCl_3) of compound **13i**

^1H NMR (500 MHz, CDCl_3) of compound **13j**

^{13}C NMR (126 MHz, CDCl_3) of compound **13j**

¹H NMR (500 MHz, CDCl₃) of compound **14b**

¹³C NMR (126 MHz, CDCl₃) of compound **14b**

14c

^1H NMR (500 MHz, CDCl_3) of compound **14c**

14c

^{13}C NMR (126 MHz, CDCl_3) of compound **14c**

^1H NMR (500 MHz, CDCl_3) of compound **14d**

^{13}C NMR (126 MHz, CDCl_3) of compound **14d**

^1H NMR (500 MHz, CDCl_3) of compound **14f**

^{13}C NMR (126 MHz, CDCl_3) of compound **14f**

^1H NMR (500 MHz, CDCl_3) of compound **14h**

^{13}C NMR (126 MHz, CDCl_3) of compound **14h**

^1H NMR (500 MHz, CDCl_3) of compound **14i**

^{13}C NMR (126 MHz, CDCl_3) of compound **14i**

^1H NMR (500 MHz, CDCl_3) of compound **14j**

^{13}C NMR (126 MHz, CDCl_3) of compound **14j**

¹H NMR (500 MHz, CDCl₃) of compound **14k**

¹³C NMR (126 MHz, CDCl₃) of compound **14k**

^1H NMR (500 MHz, CDCl_3) of compound **14l**

^{13}C NMR (126 MHz, CDCl_3) of compound **14l**

¹H NMR (500 MHz, CDCl₃) of compound **14n**

¹³C NMR (126 MHz, CDCl₃) of compound **14n**

^1H NMR (500 MHz, CDCl_3) of compound **14p**

^{13}C NMR (126 MHz, CDCl_3) of compound **14p**

^1H NMR (500 MHz, CDCl_3) of compound **14r**

^{13}C NMR (126 MHz, CDCl_3) of compound **14r**

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