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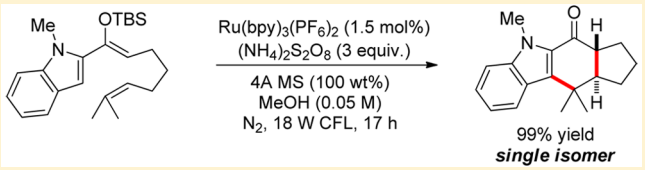
Visible-Light-Promoted Oxidative [4 + 2] Cycloadditions of Aryl Silyl Enol Ethers

Bo Yang and Zhan Lu*

Department of Chemistry, Zhejiang University, 866 Yuhangtang Road, Hangzhou 310058, China

Supporting Information

ABSTRACT: Visible-light-promoted oxidative [4 + 2] cycloadditions of ε,3-unsaturated silyl enol ethers have been developed to efficiently and diastereoselectively construct polycyclic skeletons under mild conditions. The diastereoselectivities were dependent on the stereoconfiguration of silyl enol ether, substitutions on the link, as well as electric properties of substitutions on aryl rings. The intermediates could be trapped by TEMPO, oxygen or methanol. Mechanistic studies indicated the reaction was initiated by one-electron oxidation of the silyl enol ether.



Polycyclic cyclohexanone is a core skeleton in natural products (Scheme 1).[1] Biogenetically, it can be hypothesized that the phenyl substituted enols formed by enolization of ε,3-unsaturated 1,3-dicarbonyl compounds undergo an intramolecular cyclization followed by oxidation of intermediates.[1g]

Oxidative [4 + 2] cycloaddition is one of the useful methods to construct this structure (Scheme 2). The Diels−Alder reactions of both electron-rich dienes and alkenes are forbidden. When the electron-rich diene was oxidized to be radical cation whose HOMO did match with the LUMO of electron-rich alkenes, the formal [4 + 2] reaction could undergo smoothly following by one-electron oxidation of the intermediate to give the cyclization product. Snider reported an elegant oxidative cyclization of ε,3-unsaturated silyl enol ethers using the stoichiometric amount of copper(II) or cerium(IV).[2] Visible light as a clean reagent has been shown wide utility in organic synthesis.[3] [4 + 2] Cycloaddition reactions could be also promoted by visible light through a redox-neutral pathway.[4] However, to the best of our knowledge, visible light promoted oxidative [4 + 2] cycloaddition reactions are still limited. Our group has previously reported a visible light-promoted nitro-initiated [3 + 2] cycloaddition via one-electron reduction process.[5] Inspired by the biogenetic process and oxidative cycloadditions, here, we reported a visible-light-promoted oxidative [4 + 2] cycloaddition of ε,3-unsaturated silyl enol ethers initiated by one-electron oxidation process.

We chose silyl enol **2a** as a model substrate[6] which could be easily obtained from the corresponding phenyl ketone **1a** through deprotonation by LDA and then trapped by trifluoromethanesulfonic acid *tert*-butyldimethylsilyl ester (TBDMSOTf) (Scheme 3). The synthesis using known procedures was starting from commercially available tetrahydro-2-pyran through bromination, oxidation[7] and wittig reaction[8] to afford **S2**. The corresponding Grignard reagent prepared by **S2** and meganisum turnings in Et_2O reacted with acyl chloride in the prescence of CuI to give **1a**. Another strategy is the reactions of the corresponding Grignard reagent with arylaldehydes following oxidation by PCC to give **1a**.

The reaction of ε,3-unsaturated enol silyl ether **2a** in the presence of $Ru(bpy)_3(PF_6)_2$ as photosentisizer and dioxygen as a terminal oxidant using 4 Å MS as a desiccant under the irradiation of 18W CFL in a solution of methanol afforded the desired cycloaddition product **3a** but only in 8% yield (entry 1, Table 1). Various oxidants such as TBHP, *m*-CPBA, $Na_2S_2O_8$, $(NH_4)_2S_2O_8$ were used instead of dioxygen, $(NH_4)_2S_2O_8$ is particularly suitable to afford **3a** in 91% yield with 5:1 *dr* (entry 5).[9] Using iridium-photosentisizers or organic dyes instead of $Ru(bpy)_3(PF_6)_2$, rare products were observed (entries 6−9). Interestingly, the $Fe(phen)_3(PF_6)_2$ as a visible light photosentisizer[10] could promote the cycloaddition to give **3a** in 23% yield (entry 10). Additionally, acetone, acetonitrile, dichloromethane, dimethylformamide, and dimethyl sulfoxide were used as solvents to dramatically inhibit reactions. The control experiments indicated that all essentials such as photosentisier, $(NH_4)_2S_2O_8$, or visible light were necessary.

With optimal conditions in hands, the scope of the substrates was shown in Table 2. The reaction of *para*-mehoxy substrate **2b** afforded **3b** in 75% yield with 7:1 *dr*. Due to difficult separation of two diastereoisomers, the condensation reaction of the crude mixture with 2,4-dinitrophenylhydrazine followed by filtrated and washed by methanol gave the pure major condensation product **4b** in 61% isolated yield. When *meta*-methoxyphenyl silyl enol ether **2c** was subjected to this process, two regioisomers were isolated in 66% and 23% yields, respectively, with excellent diastereoselectivities. Steric hindered *othro*-methoxy substitution **2d** was also tolerated to generate **3d** in 55% yield with 20:1 *dr*. Various silyl protecting groups were investigated that the larger silyl groups were used,

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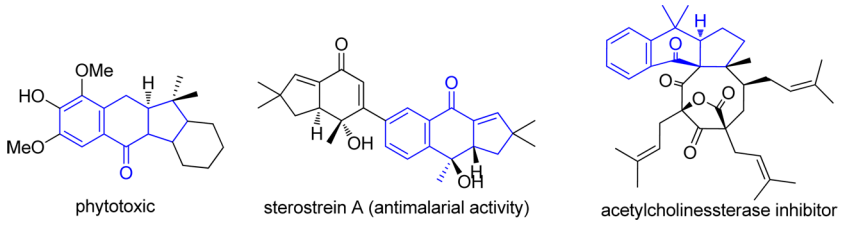
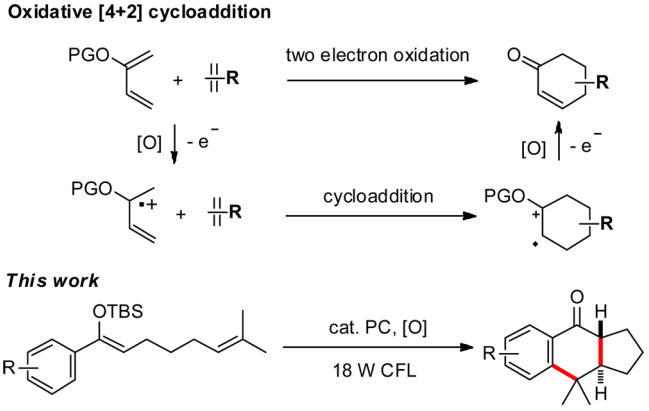
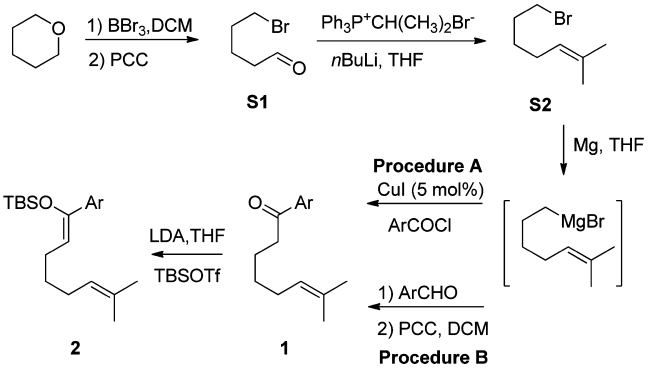
Scheme 1. Selected Natural Products Containing Polycyclic Cyclohexanone



Scheme 2. Oxidative [4 + 2] Cycloadditions

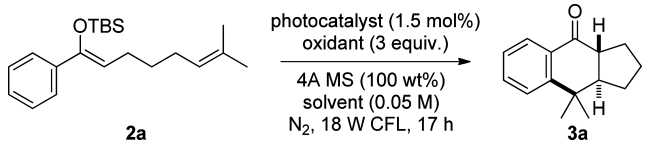


Scheme 3. Synthesis of Silyl Enol Ether 2



the higher yields and diastereoselectivities were observed. Morever, halides were also tolerated to give the corresponding cyclization products **3f–g** in 58–64% yield with moderate diastereoselectivities. The pure major diastereoisomers could be obtained after condensation with 2,4-dinitrophenylhydrazine in 40–49% yields. An excellent diastereoselectivity can be achieved in the formation of 2,5-dimethoxy product **2h** in 93% yield. The reaction of 2-naphthyl silyl enol ether gave **3i** in 32% yield. Notably, 2-indyl silyl enol ethers were applicable to deliver **3j–k** in high yields with one single diastereoisomer. Using stoichiometric CAN or visible light iron-photocatalyst, reactions of **2j** underwent smoothly, however, were not efficient. The diester (**3l**) or a methyl substitution (**3m**) on the link dramatically diminished the diastereselectivity. The substitutions on the link might decelerate the ring-closing step which delivered divergent diastereoselectivities. The stereochemistry was determined by compared the data of known compounds **3m** and **3m′** to those reported in the literature.[2] Due to a similar reason, the reaction of **2n** was too messy to identify the diastereoselectivity, and only the bicyclohexane product **3n** was isolated in 13% yield. The δ,ε-unsaturated silyl

Table 1. Optimizations



2a 3a

entry	photocatalyst	oxidant	solvent	yield (%)[a]
1	$Ru(bpy)_3(PF_6)_2$	O_2	MeOH	8
2	$Ru(bpy)_3(PF_6)_2$	TBHP	MeOH	0
3	$Ru(bpy)_3(PF_6)_2$	*m*-CPBA	MeOH	7
4	$Ru(bpy)_3(PF_6)_2$	$Na_2S_2O_8$	MeOH	21
5	$Ru(bpy)_3(PF_6)_2$	$(NH_4)_2S_2O_8$	MeOH	91[b]
6	$Ir(ppy)_3$	$(NH_4)_2S_2O_8$	MeOH	0
7	$Ir(ppy)_2(dtbbpy)PF_6$	$(NH_4)_2S_2O_8$	MeOH	6
8	Rosebengal	$(NH_4)_2S_2O_8$	MeOH	0
9	EosinY	$(NH_4)_2S_2O_8$	MeOH	<5
10	$Fe(phen)_3(PF_6)_2$	$(NH_4)_2S_2O_8$	MeOH	23
11	$Ru(bpy)_3(PF_6)_2$	$(NH_4)_2S_2O_8$	DCM	<5
12	$Ru(bpy)_3(PF_6)_2$	$(NH_4)_2S_2O_8$	MeCN	9
13	$Ru(bpy)_3(PF_6)_2$	$(NH_4)_2S_2O_8$	acetone	0
14	$Ru(bpy)_3(PF_6)_2$	$(NH_4)_2S_2O_8$	DMF	0
15	$Ru(bpy)_3(PF_6)_2$	$(NH_4)_2S_2O_8$	DMSO	<5
16[c]	$Ru(bpy)_3(PF_6)_2$	$(NH_4)_2S_2O_8$	MeOH	0
17	–	$(NH_4)_2S_2O_8$	MeOH	0
18	$Ru(bpy)_3(PF_6)_2$	–	MeOH	0

[a]Yields were determined by ^1H NMR using mesitylene as an internal standard. [b]Isolated yield with 5:1 *dr*. [c]Without light.

enol ether **2o** did be converted to α-mehoxylation product **5o** in 33% yield without any cyclic product. These results suggested that a five-membered ring was easily formed, and the newly formed radical could be oxidized to cation if cyclization reaction did not efficiently occur. The reaction of **2p** containing 1,2-disubstituted alkene afforded **3p** in 39% yield with 12:1 *dr*.[2]

Various polycycles **6–8** could be easily obtained from the product **3j** by vinylation or removal of the carbonyl group (Scheme 4).

To gain further understanding of the mechanism, some experiments conducted were showed in Scheme 5. The radical intermediate was captured by addition of TEMPO to afford **9** in 21% yield which elucidated that one-electron oxidation of silyl enol to radical cation was the initiated step. The reaction of silyl enol ether **10** with oxygen in the presence of $Ru(bpy)_3(PF_6)_2$ in a solution of acetonitrile under the irradiation of 18 W CFL afforded the silyl peroxide **11** in 82% yield.[11] It was possible that the excited state of $Ru(bpy)_3(PF_6)_2$ might oxidize the silyl enol; however, direct oxygen-participated oxidation of silyl enol could not be ruled out. Interestingly, the reaction of a *Z*/*E* mixture of **2j** was carried out to afford the cycloaddition products **3j** and **3j′** in 99% combined yield with 4:1 diastereoselectivity which

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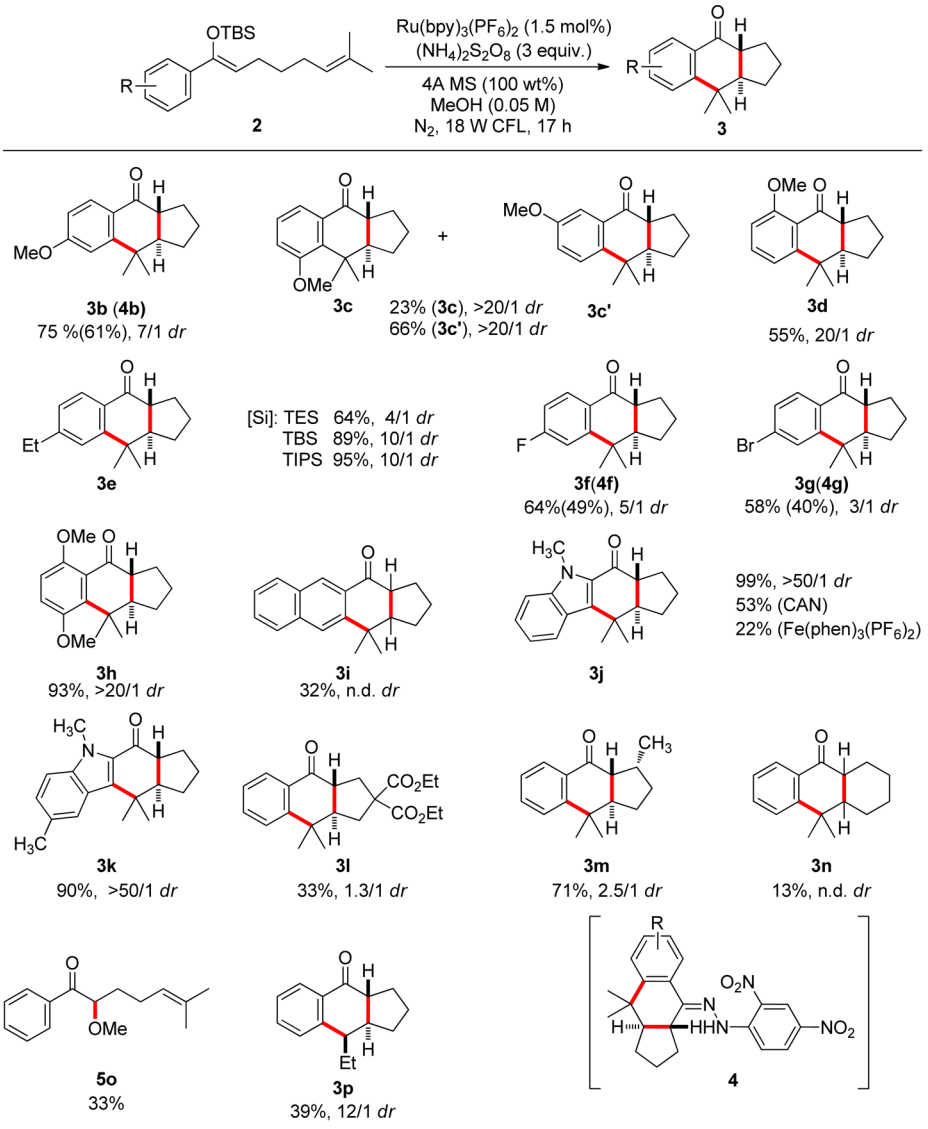
Table 2. Substrate Scope[a]



[a]Standard conditions: 0.3 mmol of **2**, 1.5 mol % of $Ru(bpy)_3(PF_6)_2$, 3 equiv of $(NH_4)_2S_2O_8$, 100 wt % of 4 Å MS in a solution of MeOH (0.05 M) under the irradiation of 18 W CFL for 17 h. Isolated yield of products **3** or **5o**. The data in the parentheses is the isolated yield of the corresponding compound **4**.

indicated that the new formed radical cation was not exclusively distonic and did not easily undergo the configuration-reversible reaction. The reaction of **2a** was performed for 40 min to afford **3a** in 3% yield. Additionally, the same reaction was conducted for 40 min then stirred without light for 16 h to give **3a** in 5% yield. These fluorescence quenching experiments indicated that reaction is visible light photocatalysis, however, the radical chain reaction cannot exclusively be ruled out.

On the basis of above results and others previously reported in literatures, plausible mechanisms for the oxidative [4 + 2] reactions are proposed in Scheme 6. The $[Ru]^{II}$ obsorbs the visible light to produce excited state $*[Ru]^{II}$ which could be oxidized by persulfate to generate sulfate radical anion **12** and $[Ru]^{III}$. The oxidation potential of **2** measured is +1.424 V (SCE) which is higher than the oxidation potential of Ru^{III}/Ru^{II} (1.29 V, SCE). This means that **2** could not be oxidized by Ru^{III} directly. Oxidation of silyl enol by **12** can lead to radical cation **13** which can undergo intramolecular radical cyclization to give **17**. Either way, the newly formed radical species **13** is susceptible to be oxidized by sulfate radical anion **12** to give the methoxylation product followed by nucleophilic trapping by methanol. Further radical cyclization following oxidation of **17** gave **3a** followed by elimination of proton. Another pathway involving oxidation of **17** to the corresponding cation followed by cyclization could not be ruled out conclusively; however, nucleophilic trapping of **17** with methanol was not observed. The stereochemical information in the reactants was mainly retained in the products. This phenomenon could be explained by the model proposed by Snider.[2] In the three possible Newman configurations (Scheme 7), configuration **a** is more favorable for **13** because the number of gauche interactions are minimized.

In summary, visible-light-promoted oxidative [4 + 2] cycloadditions of ε,3-unsaturated silyl enol ethers to access various polycyclic rings have been reported. This protocol features mild conditions and a broad scope without stoichiometric transition-metal oxidants. Additionally, some intermediates could be trapped by TEMPO, oxygen or

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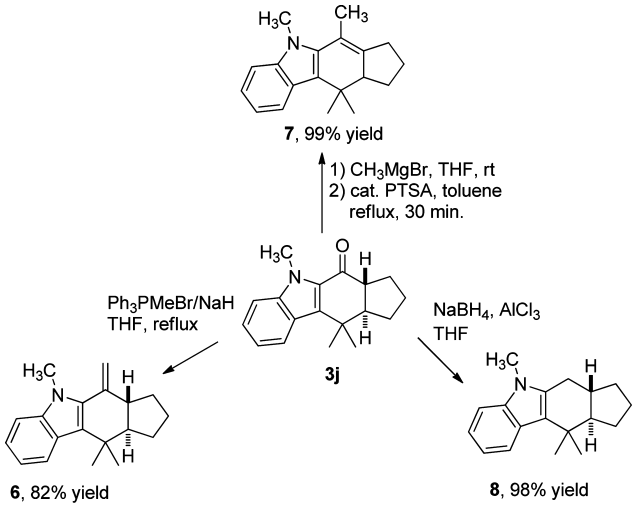
Scheme 4. Further Derivatizations



methanol to elucidate the mechanism. The diastereoselectivities were dependent on stereoconfiguration of silyl enol ether, substitutions on the link, as well as electric properties of substitutions on aryl rings.

EXPERIMENTAL SECTION

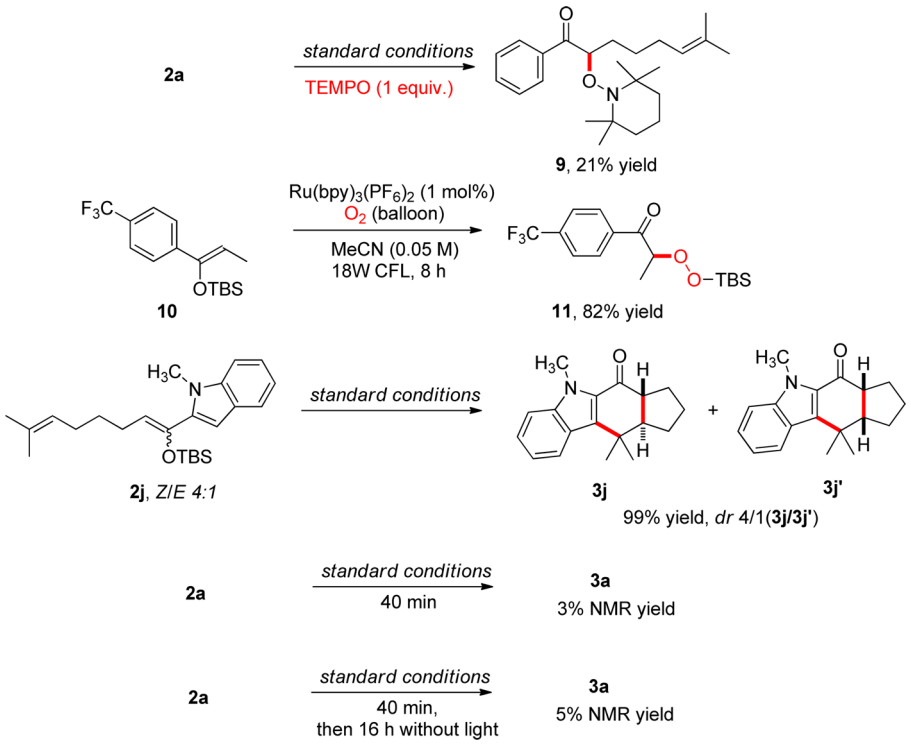
Ether, THF and toluene were distilled from sodium benzophenone ketyl prior to use. DCM and NEt_3 were distilled from calcium hydride. Methanol was distilled from sodium. Lithium diisopropylamide (LDA) (1.0 mol/L in THF) and TBDMSOTf (Trifluoromethanesulfonic acid *tert*-butyldimethylsilyl ester) were purchased from Energy Chemical. The other commercial available chemicals were used as received. NMR spectra were recorded on a 400 or 300 MHz instrument. ^{1}H NMR chemical shifts were referenced to the solvent resonance (7.26 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet. IR spectra were recorded on a FTIR spectrometer with diamond ATR accessory. High-resolution mass spectra (HRMS) were recorded on EI-TOF (electrospray ionization-time-of-flight). Element analyses were performed on Vario Micro elemental analyzer.

5-Bromopentanal. Prepared according to literature methods.[12] To a solution of BBr_3 (7.1 mL, 74 mmol) in dichloromethane (70 mL) was added dropwise tetrahydropyran (17.2260 g, 200 mmol) at 0 °C. The mixture was then heated to reflux for 1 h. After allowing this mixture to cool, it was transferred via syringe to a flask containing PCC (47.4232 g, 220 mmol) and dichloromethane (200 mL). The resulting dark solution was then heated to reflux for 1 h and allowed to cool. Et_2O was added and the mixture was filtered through a pad of silica gel. The filtrate was evaporated in vacuo to give a crude brown liquid which was then distilled in vacuo to give 17.4690 g (53% yield) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (t, J = 1.5 Hz, 1H), 3.43 (t, J = 6.4 Hz, 2H), 2.50 (td, J = 7.0, 1.5 Hz, 2H), 1.97−1.73 (m, 4H).

1-Bromo-6-methyl-hept-5-ene. Prepared according to the modified literature methods.[13] Isopropyl triphenyl phosphonium bromide[12] (52.3981 g, 136 mmol) was suspended in 200 mL THF. After cooling to 0 °C, the mixture was added with *n*-BuLi (50.0 mL, 2.4 M in hexane, 118.0 mmol). The simulation was stirred for 30 min at 0 °C and for another 30 min at room temperature. The mixture was cooled to −78 °C and slowly injected the aldehyde (15.12 g, 90.9 mmol)). After completion of the addition, the mixture was stirred for 10 min at −78 °C, warmed to room temperature and then stirred at 30 °C overnight. Then petroleum ether was added and filtered through a pad of Celite, the residue was concentrated and distilled in vacuo to give the title compound (13.4309 g, 77% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) 5.13−5.07 (m, 1H), 3.41 (t, J = 6.9 Hz, 2H), 2.01 (q, J = 7.3 Hz, 2H), 1.91−1.81 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.51−1.42 (m, 2H).

General Procedure A for Synthesis of Aryl Ketones.[13] 1-Bromo-6-methyl-hept-5-ene (10 mmol, 1.0 equiv) was added to a suspension of Mg turnings (360 mg, 15 mmol, 1.5 equiv) in THF (12

Scheme 5. Mechanistic Studies



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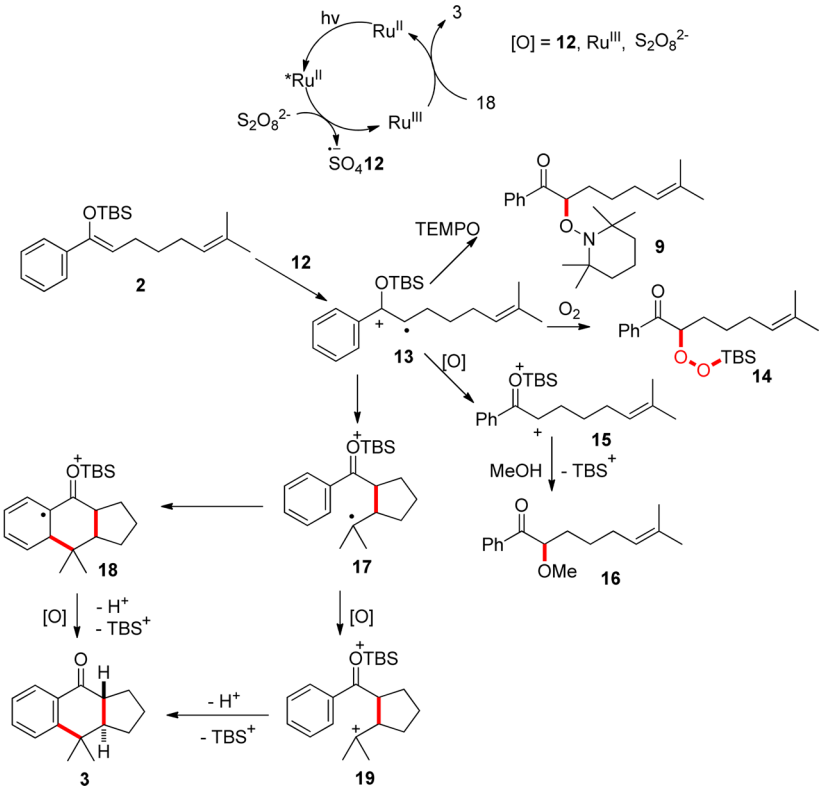
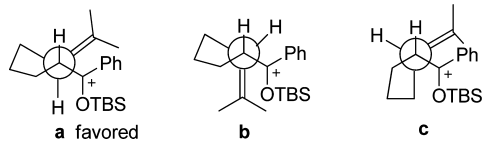
Scheme 6. Plausible Mechanism



Scheme 7. Primary Newman Models to Predict the Stereochemistry of Products



mL) at room temperature. The resulting mixture was then refluxed for 40 min. In another flask, CuI (0.05 equiv) was added to a solution of benzoyl chloride (1.0 equiv) in THF (10 mL) at −15 °C. The Grignard reagent previously prepared was then added dropwise over 30 min at −15 °C. The mixture was stirred at −10 °C for additionally 1 h and then allowed to warm to room temperature and stirred overnight. THF was removed under reduced pressure and the residue was treated with CH_2Cl_2 (20 mL) and aqueous HCl (1.0 M, 10 mL). The two layers were separated and the aqueous one was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with aqueous $NaHCO_3$ (saturated), dried over $MgSO_4$, filtered, concentrated and purified by column chromatography (SiO_2, PE/EtOAc) to afford the corresponding ketones.

General Procedure B for Synthesis of Aryl Ketones. Prepared according to a previously reported literature method.[13] 1-bromo-6-methyl-hept-5-ene (10 mmol, 1.0 equiv) was added to a suspension of Mg turnings (1.5 equiv) in Et_2O (12 mL) at room temperature. The resulting mixture was then refluxed for 40 min. The mixture was cooled to room temperature and added dropwise to a solution of aryl aldehyde in Et_2O (20 mL) at 0 °C. The mixture was treated with saturated NH_4Cl, The two layers were separated and the aqueous one was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated and used directly without further purification. The residue was dissolved in DCM followed by adding PCC (1.5 equiv). The mixture was stirred at room temperature and monitored by TLC. Et_2O was added and the mixture was filtered through a pad of silica gel. The residue was concentrated and purified by column chromatography (SiO_2, PE/EtOAc) to afford the corresponding aryl ketones.

*7-Methyl-1-phenyloct-6-en-1-one (**1a**).* Prepared according to the general procedure A using benzoyl chloride (1.5500 g, 11.0 mmol), 1-bromo-6-methyl-hept-5-ene (1.9996 g, 10.4 mmol), Mg turnings (0.3850 g, 16.0 mmol), CuI (0.1052 g, 0.5 mmol) and THF (22 mL) as starting materials to afford **1a** (1.2686 g, 5.9 mmol, 56% yield). IR ν 3061, 2928, 2857, 1687, 1598, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−7.93 (m, 2H), 7.57−7.52 (m, 1H), 7.45 (t, J = 8.0 Hz, 2H), 5.15−5.09 (m, 1H), 2.96 (t, J = 7.6 Hz, 2H), 2.03 (q, J = 7.2 Hz, 2H), 1.80−1.70 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.47−38 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 137.1, 132.8, 131.6, 128.5, 128.0, 124.3, 38.5, 29.5, 27.8, 25.7, 24.0, 17.7; HRMS (EI-TOF) Calcd for $C_{15}H_{20}O$ $[M]^+$: 216.1514, found 216.1514.

*1-(4-Methoxyphenyl)-7-methyloct-6-en-1-one (**1b**).* Prepared according to the general procedure A using 4-methoxybenzoyl chloride (1.7055 g, 10.0 mmol), 1-bromo-6-methyl-hept-5-ene (1.9061 g, 10.0 mmol), Mg turnings (0.3587 g, 15.0 mmol), CuI (0.1066 g, 0.5 mmol) and THF (22 mL) as starting materials to afford **1b** (1.3062 g, 5.3 mmol, 53% yield) as a colorless oil. IR ν 2931, 2856, 1677, 1601, 1511, 1258 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 9.3 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 5.03−4.98 (m, 1H), 3.70 (s, 3H), 2.76 (t, J = 7.2 Hz, 2H), 1.91 (q, J = 7.2 Hz, 2H), 1.68−1.52 (m, 2H), 1.57 (s, 3H), 1.49 (s, 3H), 1.36−1.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 162.9, 130.9, 129.8, 129.7, 124.0, 113.2, 54.8, 37.7, 29.2, 27.5, 25.3, 23.8, 17.2; HRMS (EI-TOF) Calcd for $C_{16}H_{22}O_2$ $[M]^+$: 246.1620, found 246.1618.

*1-(3-Methoxyphenyl)-7-methyloct-6-en-1-one (**1c**).* Prepared according to the general procedure A using 3-methoxybenzoyl chloride (1.3695 g, 8.0 mmol), CuI (0.0706 g, 0.37 mmol), Mg turnings (0.2661 g, 11.1 mmol), 1-bromo-6-methyl-hept-5-ene (1.2995 g, 6.8 mmol) and THF (18 mL) as starting materials to afford **1c** (0.9570 g, 3.9 mmol, 57% yield) as a colorless oil. IR ν 2928, 2857, 1686, 1594, 1258 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 5.7 Hz, 1H), 7.49 (dd, J = 2.1, 1.2 Hz, 1H), 7.36 (t, J = 6.0 Hz, 1H), 7.10 (ddd, J = 6.3, 2.1, 0.6 Hz, 1H), 5.15−5.09 (m, 1H), 3.86 (s, 3H), 2.94 (t, J = 5.7 Hz, 2H), 2.03 (q, J = 5.4 Hz, 2H), 1.79−1.70 (m, 2H), 1.68 (s, 3H),

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1.61 (s, 3H), 1.47−1.37 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 159.8, 138.5, 131.6, 129.5, 124.3, 120.7, 119.3, 112.3, 55.4, 38.6, 29.5, 27.8, 25.7, 24.1, 17.7; HRMS (EI-TOF) Calcd for $C_{16}H_{22}O_2$ $[M]^+$: 246.1620, found 246.1618.

*1-(2-Methoxyphenyl)-7-methyloct-6-en-1-one (**1d**).* Prepared according to the general procedure A using 2-methoxybenzoyl chloride (1.2208 g, 7.1 mmol), 1-bromo-6-methyl-hept-5-ene (1.3457 g, 7.0 mmol), Mg turnings (0.2644 g, 11.0 mmol), CuI (0.0670 g, 0.35 mmol) and THF (18 mL) as starting materials to afford **1d** (0.5288 g, 2.1 mmol, 30% yield) as a colorless oil. IR ν 2930, 2856, 1675, 1598, 1485, 1288, 1245 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.6, 2.0 Hz, 1H), 7.46−7.39 (m, 1H), 7.02−6.91 (m, 2H), 5.15−5.07 (m, 1H), 3.88 (s, 3H), 2.95 (t, J = 7.2 Hz, 2H), 2.00 (q, J = 7.2 Hz, 2H), 1.73−1.64 (m, 5H), 1.59 (s, 3H), 1.43−1.33 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 158.2, 133.0, 131.3, 130.0, 128.8, 124.4, 120.5, 111.4, 55.4, 43.6, 29.6, 27.8, 25.6, 24.0, 17.6; HRMS (EI-TOF) Calcd for $C_{16}H_{22}O_2$ $[M]^+$: 246.1620, found 246.1618.

*1-(4-Ethylphenyl)-7-methyloct-6-en-1-one (**1e**).* Prepared according to the general procedure B using 1-bromo-6-methyl-hept-5-ene (2.1410 g, 11.2 mmol), Mg turnings (0.5403 g, 22.5 mmol) 4-ethylbenzaldehyde (1.3446 g, 10.0 mmol), Et_2O (40 mL), PCC (3.2691 g, 15.2 mmol) and DCM (60 mL) as starting materials to afford **1e** (2.0576 g, 8.4 mmol, 84% yield) as a colorless oil. IR ν 3349, 2966, 2931, 2860, 1683, 1608, 1454 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 5.15−5.08 (m, 1H), 2.97−2.90 (t, J = 7.2 Hz, 2H), 2.70 (q, J = 7.6 Hz, 2H), 2.03 (q, J = 7.2 Hz, 2H), 1.78−1.69 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.46−1.37 (m, 2H), 1.25 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 149.7, 134.8, 131.5, 128.2, 128.0, 124.3, 38.4, 29.5, 28.9, 27.8, 25.7, 24.1, 17.6, 15.2; HRMS (EI-TOF) Calcd for $C_{17}H_{24}O$ $[M]^+$: 244.1827, found 244.1824.

*1-(4-Fluorophenyl)-7-methyloct-6-en-1-one (**1f**).* Prepared according to the general procedure B using 4-fluorobenzaldehyde (1.2469 g, 10.0 mmol), 1-bromo-6-methyl-hept-5-ene (2.1410 g, 11.2 mmol), Mg turnings (0.5403 g, 22.5 mmol), Et_2O (40 mL), PCC (3.2951 g, 15.3 mmol) and DCM (60 mL) as starting materials to afford **1f** (1.5017 g, 6.4 mmol, 64% yield) as a colorless oil. IR ν 2929, 2858, 1686, 1598, 1506, 1410, 1231 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.90 (m, 2H), 7.11 (t, J = 8.8 Hz, 2H), 5.11 (t, J = 7.2 Hz, 1H), 2.92 (t, J = 7.2 Hz, 2H), 2.02 (q, J = 7.2 Hz, 2H), 1.78−1.69 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.47−1.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 165.6 (d, J = 241.4 Hz), 133.5 (d, J = 2.9 Hz), 131.7, 130.6 (d, J = 36.0 Hz), 124.2, 115.6 (d, J = 22.2 Hz), 38.4, 29.5, 27.8, 25.7, 24.0, 17.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −105.76; HRMS (EI-TOF) Calcd for $C_{15}H_{19}OF$ $[M]^+$: 234.1420, found 234.1422.

*1-(4-Bromophenyl)-7-methyloct-6-en-1-one (**1g**).* Prepared according to the general procedure B using 4-bromobenzaldehyde (1.8527 g, 10.0 mmol), 1-bromo-6-methyl-hept-5-ene (2.1410 g, 11.2 mmol), Mg turnings (0.5403 g, 22.5 mmol), Et_2O (40 mL), PCC (3.2579 g, 15.1 mmol) and DCM (60 mL) as starting materials to afford **1g** (2.3506 g, 8.0 mmol, 80% yield) as a white solid. mp = 46−48 °C. IR ν 3028, 2961, 2929, 1649, 1463, 1255 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 5.09 (t, J = 6.8 Hz, 1H), 2.89 (t, J = 7.2 Hz, 2H), 2.00 (q, J = 6.4 Hz, 2H), 1.76−1.67 (m, 2H), 1.66 (s, 3H), 1.58 (s, 3H), 1.45−1.34 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 135.7, 131.8, 131.7, 129.5, 127.9, 124.2, 38.4, 29.4, 27.7, 25.7, 23.9, 17.6; HRMS (EI-TOF) Calcd for $C_{15}H_{19}OBr$ $[M]^+$: 294.0619, found 294.0611.

*1-(2,5-Dimethoxyphenyl)-7-methyloct-6-en-1-one (**1h**).* Prepared according to the general procedure B using 2,5-dimethoxybenzaldehyde (1.6689 g, 10.0 mmol), 1-bromo-6-methyl-hept-5-ene (2.1410 g, 11.2 mmol), Mg turnings (0.5403 g, 22.5 mmol), PCC (2.6770 g, 15.0 mmol), Et_2O (40 mL) and DCM (60 mL) as starting materials to afford **1h** (2.0023 g, 7.2 mmol, 72% yield) as a colorless oil. IR ν 2931, 2856, 1675, 1495, 1278, 1222 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 3.2 Hz, 1H), 7.01−6.97 (m, 1H), 6.88 (d, J = 8.8 Hz, 1H) 5.14−5.08 (m, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.96 (t, J = 7.2 Hz, 2H), 2.00 (q, J = 7.2 Hz, 2H), 1.73−1.62 (m, 5H), 1.59 (s, 3H), 1.42−1.33 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 153.4, 152.8, 131.4, 128.9, 124.5, 119.4, 113.9, 113.1, 56.0, 55.8, 43.6, 29.6, 27.9, 25.7, 24.1, 17.6; HRMS (EI-TOF) Calcd for $C_{17}H_{24}O_3$ $[M]^+$: 276.1725, found 276.1726.

*7-Methyl-1-(naphthalen-2-yl)oct-6-en-1-one (**1i**).* Prepared according to the general procedure A using 2-naphthoyl chloride (1.9197 g, 10.1 mmol), 1-bromo-6-methyl-hept-5-ene (1.9197 g, 10.0 mmol), Mg turnings (0.3841 g, 16.0 mmol), CuI (0.0963 g, 0.5 mmol) and THF (22 mL) as starting materials to afford **1i** (1.8444 g, 6.9 mmol, 69% yield) as a colorless oil. IR ν 2925, 2856, 1682, 1461 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.04 (dd, J = 8.4, 1.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.91−7.85 (m, 2H), 7.62−7.51 (m, 2H), 5.18−5.12 (m, 1H), 3.13−3.06 (t, J = 7.6 Hz, 2H), 2.06 (q, J = 7.2 Hz, 2H), 1.87−1.76 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.53−1.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 135.5, 134.4, 132.5, 131.6, 129.6, 129.5, 128.34, 128.27, 127.7, 126.7, 124.3, 123.9, 38.6, 29.6, 27.8, 25.7, 24.2, 17.7; HRMS (EI-TOF) Calcd for $C_{19}H_{22}O$ $[M]^+$: 266.1671, found 266.1674.

Methyl 1*H*-indole-2-carboxylate. Prepared according to a previously reported literature method[14] using 1*H*-indole-2-carboxylic acid (8.06 g, 50.0 mmol) and MeOH (20 mL) as starting materials to afford methyl 1*H*-indole-2-carboxylate (8.4800 g, 48.4 mmol, 97% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (br, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 8.0, 7.2 Hz, 1H), 7.25−7.23 (m, 1H), 7.17 (t, J = 7.2 Hz, 1H), 3.96 (s, 3H).

Methyl 1-methyl-1*H*-indole-2-carboxylate. Prepared according to a previously reported literature method[1] using methyl 1*H*-indole-2-carboxylate (5.2658 g, 30 mmol), CH_3I (2.2 mL, 36 mmol), NaH (60%, 0.8651 g, 36 mmol) and THF (60 mL) as starting materials to afford the title compound (3.7198 g, 19.7 mmol, 65% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 1H), 7.41−7.32 (m, 2H), 7.29 (s, 1H), 7.18−7.11 (m, 1H), 4.09 (s, 3H), 3.92 (s, 3H).

1-Methyl-1*H*-indole-2-carboxylic acid. Prepared according to a previously reported literature method[15] using methyl 1-methyl-1*H*-indole-2-carboxylate (3.1408 g, 16.6 mmol) and KOH (12%, 150 mL) as starting materials to afford the title compound (2.8708 g, 16.4 mmol, 99% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74−7.69 (m, 1H), 7.48 (s, 1H), 7.43−7.36 (m, 2H), 7.17 (ddd, J = 8.0, 6.0, 2.4 Hz, 1H), 4.11 (s, 3H).

1-Methyl-1*H*-indole-2-carbonyl chloride. Prepared according to a general procedure using 1-methyl-1*H*-indole-2-carboxylic acid (2.6312 g, 15.0 mmol) and thionyl chloride (2.9 mL) as starting materials refluxing in dichloromethane for 2 h. The solvent was removed under reduced pressure and dried in vacuo to afford the desired product. The crude product was used directly without further purification.

Methyl 5-methyl-1*H*-indole-2-carboxylate. Prepared according to a similar procedure for synthesis of methyl 1-methyl-1*H*-indole-2-carboxylate using 5-methyl-1*H*-indole-2-carboxylic acid (1.9211 g, 11.0 mmol) and MeOH (18 mL) as starting materials to afford the title compound (1.6240 g, 8.6 mmol, 78% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.47 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.15 (dd, J = 10.0, 1.2 Hz, 1H), 3.94 (s, 3H), 2.44 (s, 3H).

Methyl-1,5-dimethyl-1*H*-indole-2-carboxylate. Prepared according to a similar procedure for synthesis of methyl 1-methyl-1*H*-indole-2-carboxylate using methyl 5-methyl-1*H*-indole-2-carboxylate (1.5087 g, 8.0 mmol), NaH (0.2155 g, 10.5 mmol), MeI (0.74 mL, 9.6 mmol) and THF (20 mL) as starting materials to afford the title compound (1.0187 g, 5.0 mmol, 63% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.26 (d, J = 8.6 Hz, 1H), 7.21−7.15 (m, 2H), 4.04 (s, 3H), 3.89 (s, 3H), 2.44 (s, 3H).

1,5-Dimethyl-1*H*-indole-2-carboxylic acid. Prepared according to a similar procedure for synthesis of 1-methyl-1*H*-indole-2-carboxylic acid using methyl-1,5-dimethyl-1*H*-indole-2-carboxylate (1.0176 g, 5.0 mmol) and KOH (12% in water) as starting materials to afford the title compound (0.8731 g, 4.6 mmol, 92% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.37 (s, 1H), 7.30 (d, J = 8.6 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 4.07 (s, 3H), 2.45 (s, 3H).

1,5-Dimethyl-1*H*-indole-2-carbonyl chloride. Prepared according to the same procedure for synthesis of methyl-1*H*-indole-2-carbonyl chloride.

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*7-Methyl-1-(1-methyl-1H-indol-2-yl)oct-6-en-1-one (**1j**).* Prepared according to the general procedure A using 1-methyl-1*H*-indole-2-carbonyl chloride[16] (1.9482 g, 10.0 mmol), 1-bromo-6-methyl-hept-5-ene (2.0797 g, 109 mmol), Mg turnings (0.3613 g, 15.0 mmol), CuI (0.1043 g, 0.55 mmol) and THF (22 mL) as starting materials to afford **1j** (1.7365 g, 6.4 mmol, 64% yield) as a colorless oil. IR ν 2928, 2857, 1663, 1614, 1514, 1464, 1392 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 3.6 Hz, 2H), 7.29 (s, 1H), 7.20−7.14 (m, 1H), 5.16 (t, J = 6.6 Hz, 1H), 4.08 (s, 3H), 3.01−2.93 (t, J = 7.6 Hz, 2H), 2.07 (q, J = 7.2 Hz, 2H), 1.84−1.75 (m, 2H), 1.72 (s, 3H), 1.64 (s, 3H), 1.51−1.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 139.9, 134.8, 131.5, 125.71, 125.65, 124.3, 122.7, 120.6, 111.0, 110.2, 39.8, 32.1, 29.5, 27.8, 25.7, 24.8, 17.6; HRMS (EI-TOF) Calcd for $C_{18}H_{23}NO$ $[M]^+$: 269.1780, found 269.1775.

*1-(1,5-Dimethyl-1H-indol-2-yl)-7-dimethyloct-6-en-1-one (**1k**).* Prepared according to the general procedure A using 1,5-dimethyl-1*H*-indole-2-carbonyl chloride (0.9800 g, 4.7 mmol), 1-bromo-6-methyl-hept-5-ene (0.6734 g, 3.5 mmol), CuI (0.0362 g, 0.19 mmol), Mg turnings (0.1434 g, 6.0 mmol) and THF (20 mL) as starting materials to afford **1k** (0.4753 g, 1.2 mmol, 35% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.24 (d, J = 1.6 Hz, 1H), 7.19 (d, J = 1.2 Hz, 1H), 7.17 (s, 1H), 5.11 (t, J = 7.2 Hz, 1H), 4.03 (s, 3H), 2.95−2.89 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.02 (q, J = 7.2 Hz, 2H), 1.79−1.69 (m, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.47−1.35 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 138.6, 134.9, 131.6, 129.9, 127.8, 126.0, 124.3, 122.0, 110.6, 110.0, 39.9, 32.2, 29.6, 27.8, 25.7, 25.0, 21.3, 17.7; IR ν 2923, 2856, 1660, 1523, 1459, 1177, 732 cm^{-1}; HRMS (EI-TOF) Calcd for $C_{19}H_{25}NO$ $[M]^+$: 283.1936, found 283.1935.

Diethyl 2-(3-methylbut-2-en-1-yl)malonate. Prepared according to a previously reported procedure[17] using 1-bromo-3-methylbut-2-ene (3.6339 g, 22 mmol), diethyl malonate (5.5368 g, 20 mmol), K_2CO_3 (5.5368 g, 40 mmol) and acetons (50 mL) as atarting materials. The mixture was refluxed overnight. Then K_2CO_3 was filtered and the solvent was removed. The residue was purified by flash column chromatography (PE/EtOAc, 30:1) to give the title compound as a colorless oil (3.9206 g, 17.2 mmol, 86% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 5.11−5.02 (m, 1H), 4.18 (q, J = 7.2 Hz, 4H), 3.32 (t, J = 7.6 Hz, 1H), 2.58 (t, J = 7.6 Hz, 2H), 1.68 (s, 3H), 1.63 (s, 3H), 1.25 (t, J = 7.1 Hz, 6H).

*Diethyl 2-(3-Methylbut-2-en-1-yl)-2-(3-oxo-3-phenylpropyl)-malonate (**1l**).* Prepared according to a similar procedure.[18] To a suspension of NaH (0.2400 g, 6.0 mmol) in THF/DMF (1:1, 6 mL) was added diethyl 2-(3-methylbut-2-en-1-yl)malonate (1.1506 g, 5.04 mmol) dropwise at 0 °C under N_2 atmosphere and stirred for another 10 min. Then the reaction mixture was warmed to room temperature and stirred for 1 h. Then 3-chloropropiophenone (1.0211g, 6 mmol) and NaI (0.0750 g, 0.5 mmol) was added and the mixture was refluxed at 80 °C for 18 h. The resulting suspension was diluted with ether, and quenched with saturated aqueous NH_4Cl. The organic layer was washed with saturated aqueous NH_4Cl. The aqueous was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified by flash column chromatography on silica gel (PE/EtOAc 30:1) to afford the title compound (1.0989 g, 3.0 mmol, 61% yield) as a colorless oil. IR ν 2978, 2926, 1730, 1688, 1449, 1182 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 5.00 (t, J = 7.2 Hz, 1H), 4.17 (q, J = 7.2 Hz, 4H), 3.01−2.94 (m, 2H), 2.66 (d, J = 7.2 Hz, 2H), 2.32−2.26 (m, 2H), 1.68 (s, 3H), 1.62 (s, 3H), 1.22 (t, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 171.3, 136.7, 135.6, 133.0, 128.5, 128.0, 117.6, 61.2, 57.0, 33.8, 32.2, 27.1, 25.9, 17.9, 14.0; HRMS (EI-TOF) Calcd for $C_{21}H_{28}O_5$ $[M]^+$: 360.1937, found 360.1938.

*3,7-Dimethyl-1-phenyloct-6-en-1-one (**1m**).* Prepared according to the general procedure B using phenylmagnesium bromide (1 M in THF, 20 mL), 2,6-dimethyl-5-heptena (2.7 mL, 15.0 mmol), PCC (6.8200 g, 31.6 mmol) and DCM (80 mL) as starting materials to afford **1m** (1.9110 g, 8.3 mmol, 55% yield) as a colorless oil. IR ν 3060, 2962, 2854, 1729, 1686, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.55 (dd, J = 7.2, 7.2 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 5.14−5.06 (m, 1H), 2.96 (dd, J = 15.6, 5.2 Hz, 1H), 2.74 (dd, J = 15.6, 8.0 Hz, 1H), 2.25−2.14 (m, 1H), 2.11−1.91 (m, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.45−1.40 (m, 1H), 1.35−1.23 (m, 1H), 0.97 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 137.4, 132.8, 131.5, 128.5, 128.1, 124.4, 45.9, 37.2, 29.5, 25.7, 25.5, 19.9, 17.6; HRMS (EI-TOF) Calcd for $C_{16}H_{22}O$ $[M]^+$: 230.1671, found 230.1675.

6-Bromohexanal.[19] Prepared according to a general procedure using 6-bromohexan-1-ol (4.8732 g, 26.9 mmol), PCC (12.5900 g, 58.4 mmol) and DCM (160 mL) as starting materials. The mixture was stirred for 24 h at room temperature. Et_2O was added and the mixture was filtered through a pad of silica gel. The residue was concentrated and distilled in vacuo (with oil pump) to afford the title compound (2.7416 g, 15.3 mmol, 57% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.80−9.74 (m, 1H), 3.42 (t, J = 6.8 Hz, 2H), 2.47 (td, J = 7.2, 1.6 Hz, 2H), 1.95−1.83 (m, 2H), 1.73−1.60 (m, 2H), 1.54−1.43 (m, 2H).

1-Bromo-7-methyloct-6-ene.[20] Prepared by a procedure smiliar to 1-bromo-6-methyl-hept-5-ene using 6-bromohexanal (2.7400 g, 15.3 mmol), isopropyl triphenyl phosphonium bromide (9.1200 g, 23.7 mmol) and THF (100 mL) as atarting materials to afford the title compound (2.0646 g, 10.1 mmol, 66% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.14−5.06 (m, 1H), 3.40 (t, J = 7.2 Hz, 2H), 1.98 (q, J = 7.2 Hz, 2H), 1.91−1.82 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.49−1.30 (m, 4H).

*8-Methyl-1-phenylnon-7-en-1-one (**1n**).* Prepared according to the general procedure A using benzoyl chloride (1.3970 g, 10.0 mmol), 1-bromo-7-methyl-hept-5-ene (2.0640 g, 10.0 mmol), Mg turnings (0.3710 g, 15.5 mmol), CuI (0.0957 g, 0.5 mmol) and THF (40 mL) as starting materials to afford **1n** (1.7469 g, 7.6 mmol, 76% yield) as a colorless oil. IR ν 2926, 2855, 1686, 1449, 1222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.55 (dd, J = 7.6, 7.2 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 5.17−5.07 (m, 1H), 2.96 (t, J = 7.6 Hz, 2H), 2.05−1.91 (m, 2H), 1.79−1.70 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.42−1.34 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 137.0, 132.8, 131.3, 128.5, 128.0, 124.6, 38.5, 29.7, 29.0, 27.8, 25.7, 24.3, 17.6; HRMS (EI-TOF) Calcd for $C_{16}H_{22}O$ $[M]^+$: 230.1671, found 230.1671.

4-Bromobutanal.[21] Prepared by a procedure smiliar to synthesis of 5-bromopentanal using tetrahydrofuran (8.1 mL, 100 mmol), BBr_3 (3.6 mL, 37.0 mmol), PCC (23.7400 g, 110.1 mmol) and DCM (135 mL) as starting materials to afford the title compound (7.6563 g, 51% yield, purity 68%) as a colorless oil. The ^1H NMR is in accordance to the literature.[13]

6-Bromo-2-methylhex-2-ene. Prepared by a procedure smiliar to synthesis of 1-bromo-6-methyl-hept-5-ene using 4-bromobutanal (7.6560 g, 50.7 mmol), isopropyl triphenyl phosphonium bromide (28.9500 g, 75.1 mmol), *n*-BuLi (2.4 M in hexane, 27.5 mL, 66.0 mmol) and THF (250 mL) as starting materials to afford the title compound (2.2179 g, 12.5 mmol, 25% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.10−5.03 (m, 1H), 3.40 (t, J = 6.8 Hz, 2H), 2.13 (q, J = 7.2 Hz, 2H), 1.93−1.84 (m, 2H), 1.69 (s, 3H), 1.63 (s, 3H).

*6-Methyl-1-phenylhept-5-en-1-one (**1o**).* Prepared according to the general procedure A using benzoyl chloride (1.4 mL, 12.0 mmol), 1-bromo5-methyl-hept-5-ene (2.0895 g, 11.8 mmol), Mg turnings (0.4893 g, 20.0 mmol), CuI (0.1169 g, 0.6 mmol) and THF (50 mL) as starting materials to afford **1o** (1.2412 g, 6.1 mmol, 52% yield) as a colorless oil. IR ν 2926, 2856, 1687, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 6.8 Hz, 2H), 7.58−7.52 (m, 1H), 7.49−7.43 (m, 2H), 5.17−5.10 (m, 1H), 2.99−2.93 (m, 2H), 2.08 (q, J = 7.6 Hz, 2H), 1.84−1.74 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 137.1, 132.8, 132.5, 128.5, 128.0, 123.8, 37.9, 27.5, 25.7, 24.5, 17.7; HRMS (EI-TOF) Calcd for $C_{14}H_{18}O$ $[M]^+$: 202.1358, found 202.1355.

*(Z/E)-1-Phenylnon-6-en-1-one (**1p**).*[13] Prepared according to the general procedure A using benzoyl chloride (1.4244 g, 10.1 mmol), 1-bromo5-methyl-hex-4-ene (*Z*/*E* mixture) (1.9603 g, 10.2 mmol), Mg turnings (0.3703 g, 15.4 mmol), CuI (0.1055 g, 0.5 mmol) and THF (35 mL) as starting materials to afford **1p** (1.5983 g, 7.4 mmol, 74%

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J. Org. Chem. 2016, 81, 7288−7300

yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 7.2, 7.2 Hz, 2H), 5.51−5.26 (m, 2H), 2.97 (t, J = 7.2 Hz, 2H), 2.14−1.97 (m, 4H), 1.81−1.70 (m, 2H), 1.50−1.40 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H). Anal. Calcd $C_{15}H_{20}O$ for C, 83.28; H, 9.32. Found C, 82.84; H, 9.01.

General Procedure C for Synthesis of Silyl Enol Ethers. To a 50 mL flame-dried Schlenk flask cooled under N_2, LDA (2 M in THF) and THF (3 mL) was added. The Schlenk was placed at −78 °C and **1** (5 mmol, in 6 mL THF) was added dropwise via syringe. The mixture was stirred for another 30 min at −78 °C, and then TBDMSOTf (7.5 mmol, 1.5 equiv) was added via syringe and stirred for 30 min at −78 °C and stirred overnight at 0 °C. The reaction mixture was diluted with Et_2O, quenched with saturated aqueous $NaHCO_3$ and separated. The aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel to afford the silyl enol ethers.

*(Z)-tert-Butyldimethyl((7-methyl-1-phenylocta-1,6-dien-1-yl)-oxy)silane (**2a**).* Prepared according the general procedure C employing **1a** (0.7775 g, 3.6 mmol), LDA (2 M in THF, 2.4 mL, 4.7 mmol), TBDMSOTf (1.26 mL, 5.4 mmol) and THF (6 mL) as starting materials to afford **2a** (0.9745 g, 2.9 mmol, 82% yield) as a colorless oil. IR ν 3031, 2957, 2929, 1649, 1447, 1283 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 2H), 7.30−7.19 (m, 3H), 5.14 (t, J = 7.2 Hz, 1H), 5.10 (t, J = 7.2 Hz, 1H), 2.23−2.15 (m, 2H), 2.08−1.98 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.50−1.39 (m, 2H), 0.98 (s, 9H), −0.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 139.9, 131.5, 127.9, 127.3, 125.9, 124.6, 111.9, 29.9, 27.9, 25.9, 25.8, 25.7, 18.3, 17.7, −4.1; HRMS (EI-TOF) Calcd for $C_{21}H_{34}OSi$ $[M]^+$:330.2379, found 330.2382.

*(Z)-tert-Butyl((1-(4-methoxyphenyl)-7-methylocta-1,6-dien-1-yl)-oxy)dimethylsilane (**2b**).* Prepared according to the general procedure C employing **1b** (0.9722 g, 3.95 mmol), LDA (2 M in THF, 2.4 mL), TBDMSOTf (1.3 mL, 5.5 mmol) as starting materials to afford **2b** (1.0615 g, 2.9 mmol, 75% yield) as a colorless oil. IR ν 2930, 2857, 1650, 1609, 1510, 1248 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 5.16 (t, J = 7.2 Hz, 1H), 5.00 (t, J = 7.1 Hz, 1H), 3.81 (s, 3H), 2.21−2.16 (m, 2H), 2.07−2.01(m, 2H), 1.71 (s, 3H), 1.62 (s, 3H), 1.49−1.41 (m, 2H), 0.99 (s, 9H), −0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 148.9, 132.6, 131.4, 127.1, 124.7, 113.2, 110.4, 55.2, 30.0, 27.9, 25.9, 25.8, 25.7, 18.3, 17.6, −4.1; HRMS (EI-TOF) Calcd for $C_{22}H_{36}O_2Si$ $[M]^+$:360.2485, found 360.2484.

*(Z)-tert-Butyl((1-(3-methoxyphenyl)-7-methylocta-1,6-dien-1-yl)-oxy)dimethylsilane (**2c**).* Prepared according to the general procedure C employing **1c** (0.7427 g, 3.0 mmol), LDA (2 M in THF, 2 mL, 4.0 mmol), TBDMSOTf (1.1 mL, 4.5 mmol) and THF (7 mL) as starting materials to afford **2c** (0.7827 g, 2.2 mmol, 72% yield) as a colorless oil.IR ν 2930, 2857, 1649, 1600, 1256 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.16 (m, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.00 (s, 1H), 6.79 (dd, J = 8.0, 2.4 Hz, 1H), 5.20−5.10 (m, 2H), 3.81 (s, 3H), 2.23−2.18 (m, 2H), 2.08−2.02 (m, 2H), 1.71 (s, 3H), 1.63 (s, 3H), 1.50−1.43 (m, 2H), 1.00 (s, 9H), −0.01 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 149.0, 141.4, 131.5, 128.9, 124.6, 118.4, 113.1, 112.1, 111.1, 55.1, 29.8, 27.9, 25.9, 25.80, 25.76, 18.3, 17.7, −4.1; HRMS (EI-TOF) Calcd for $C_{22}H_{36}O_2Si$ $[M]^+$: 360.2485, found 360.2487.

*(Z)-tert-Butyl((1-(2-methoxyphenyl)-7-methylocta-1,6-dien-1-yl)-oxy)dimethylsilane (**2d**).* Prepared according to the general procedure C employing **1d** (0.4611 g, 1.82 mmol), LDA (2 M in THF, 1.2 mL, 2.4 mmol), TBDMSOTf (0.66 mL, 2.8 mmol) and THF (5 mL) as starting materials to afford **2d** (0.5292 g, 1.47 mmol, 78% yield, 86% purity) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.10 (m, 2H), 6.85−6.77 (m, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.08 (t, J = 7.2 Hz, 1H), 4.83 (t, J = 6.8 Hz, 1H), 3.74 (s, 3H), 2.18−2.12 (m, 2H), 1.99−1.94 (m, 2H), 1.62 (s, 3H), 1.54 (s, 3H), 1.42−1.31 (m, 2H), 0.83 (s, 9H), −0.21 (s, 6H). Anal. Calcd for $C_{22}H_{36}O_2Si$: C, 73.28; H, 10.06. Found C, 72.89; H, 9.81.

*(Z)-tert-Butyl((1-(4-ethylphenyl)-7-methylocta-1,6-dien-1-yl)oxy)-dimethylsilane (**2e**).* Prepared according to the general procedure C employing **1e** (0.7609 g, 3.1 mmol), LDA (2 M in THF, 1.9 mL, 3.7 mmol), TBDMSOTf (1.1 mL, 4.6 mmol) as starting materials to afford **2e** (0.6498 g, 2.7 mmol, 86% yield) as a colorless oil. IR ν 2931, 2858, 1603, 1283 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 5.17−5.12 (m, 1H), 5.06 (t, J = 7.2 Hz, 1H), 2.63 (q, J = 7.6 Hz, 2H), 2.2−2.16 (m, 2H), 2.06−2.01 (m, 2H), 1.70 (s, 3H), 1.61 (s, 3H), 1.48−1.40 (m, 2H), 1.23 (t, J = 7.6 Hz, 3H), 0.98 (s, 9H), −0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 143.3, 137.3, 131.4, 127.3, 125.8, 124.7, 111.2, 29.9, 28.5, 27.9, 25.9, 25.8, 25.7, 18.3, 17.7, 15.5, −4.0; HRMS (EI-TOF) Calcd for $C_{23}H_{38}OSi$ $[M]^+$: 358.2692, found 358.2690.

*(Z)-Triethyl((1-(4-ethylphenyl)-7-methylocta-1,6-dien-1-yl)oxy)-silane (**2ea**).* Prepared according to the general procedure C employing **1e** (0.5732 g, 2.3 mmol), LDA (2 M in THF, 2.0 mmol), chlorotriethylsilane (0.67 mL, 4.0 mmol) as starting materials to afford **2ea** (0.4440 g, 1.2 mmol, 41% yield) as a colorless oil. IR ν 3028, 2960, 2878, 1686, 1649, 1458 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.16 (t, J = 6.8 Hz, 1H), 5.10 (t, J = 7.2 Hz, 1H), 2.64 (q, J = 7.6 Hz, 2H), 2.24−2.18 (m, 2H), 2.08−2.02 (m, 2H), 1.71 (s, 3H), 1.63 (s, 3H), 1.48−1.42 (m, 2H), 1.24 (t, J = 7.6 Hz, 3H), 0.94 (t, J = 7.9 Hz, 9H), 0.62 (q, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 143.4, 137.1, 131.5, 127.4, 125.5, 124.6, 110.6, 30.0, 28.5, 27.9, 25.8, 25.7, 17.7, 15.4, 6.7, 5.4; HRMS (EI-TOF) Calcd for $C_{23}H_{38}OSi$ $[M]^+$: 358.2692, found 358.2690.

*(Z)-((1-(4-Ethylphenyl)-7-methylocta-1,6-dien-1-yl)oxy)-triisopropylsilane (**2eb**).* Prepared according to the general procedure C employing **1e** (0.7360 g, 3.0 mmol), HMDS (2 M in THF, 2.0 mL, 4.0 mmol) instead of LDA, triisopropylsilyl chloride (0.85 mL, 4.0 mmol) and THF (8 mL) as starting materials to afford **2eb** (0.8925 g, 2.2 mmol, 74% yield) as a colorless oil. IR ν 2926, 1648, 1462, 1329 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.15 (t, J = 7.2 Hz, 1H), 4.94 (t, J = 7.2 Hz, 1H), 2.64 (q, J = 7.6 Hz, 2H), 2.25−2.20 (m, 2H), 2.07−2.02 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.49−1.42 (m, 2H), 1.24 (t, J = 7.6 Hz, 3H), 1.11−1.02 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 143.4, 137.8, 131.4, 127.3, 126.0, 124.7, 110.6, 29.9, 28.5, 27.9, 25.9, 25.8, 17.9, 17.6, 15.5, 13.5; HRMS (EI-TOF) Calcd for $C_{26}H_{44}OSi$ $[M]^+$: 400.3161, found 400.3163.

*(Z)-tert-Butyl((1-(4-fluorophenyl)-7-methylocta-1,6-dien-1-yl)-oxy)dimethylsilane (**2f**).* Prepared according to the general procedure C employing **1f** (1.1885 g, 5.0 mmol), LDA (2 M in THF, 3 mL, 6.0 mmol), TBDMSOTf (1.73 mL, 7.5 mmol) and THF (8 mL) as starting materials to afford **2f** (1.6154 g, 4.6 mmol, 91% yield) as a colorless oil. IR ν 2930, 2857, 1651, 1507, 1228 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.36 (m, 2H), 7.01−6.93 (m, 2H), 5.14 (t, J = 7.2 Hz, 1H), 5.04 (t, J = 7.2 Hz, 1H), 2.21−2.16 (m, 2H), 2.07−2.01 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.49−1.41 (m, 2H), 0.98 (s, 9H), −0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 247.5 Hz), 148.4, 136.1 (d, J = 3.0 Hz), 131.6, 127.5 (d, J = 7.1 Hz), 124.5, 114.7 (d, J = 21.2 Hz), 111.8, 29.8, 27.9, 25.83, 25.80, 25.75, 18.3, 17.7, −4.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.2; HRMS (EI-TOF) Calcd for $C_{21}H_{33}OSiF$ $[M]^+$: 348.2285, found 348.2289.

*(Z)-tert-Butyl((1-(4-bromophenyl)-7-methylocta-1,6-dien-1-yl)-oxy)dimethylsilane (**2g**).* Prepared according to the general procedure C employing **1g** (0.8827 g, 3.0 mmol), LDA (2 M in THF, 1.6 mL, 3.3 mmol), TBDMSOTf (1.0 mml, 4.5 mmol) and THF (6 mL) as starting materials to afford **2g** (0.5298 g, 1.3 mmol, 43% yield) as a colorless oil. IR ν 2956, 2857, 1647, 1483, 1256 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H), 5.13−5.06 (m, 2H), 2.18−2.12 (m, 2H), 2.03−1.98 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.49−1.38 (m, 2H), 0.96 (s, 9H), −0.07 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 138.8, 131.5, 131.0, 127.4, 124.5, 121.1, 112.6, 29.7, 27.9, 25.8, 25.7, 18.3, 17.7, −4.0; HRMS (EI-TOF) Calcd for $C_{21}H_{33}OSiBr$ $[M]^+$: 408.1484, found 408.1486.

*(Z)-tert-Butyl((1-(2,5-dimethoxyphenyl)-7-methylocta-1,6-dien-1-yl)oxy)dimethylsilane (**2h**).* Prepared according to the general procedure C employing **1h** (1.1886 g, 4.3 mmol), LDA (2 M in THF, 4.0 mL, 8 mmol), TBDMSOTf (1.6 mL, 7.0 mmol) and THF (6 mL) as starting materials to afford **2h** (1.4530 g, 3.7 mmol, 74% yield) as a colorless oil. IR ν 2932, 2856, 1658, 1496, 1216, 1053 cm^{-1}; ^{1}H

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J. Org. Chem. 2016, 81, 7288−7300

NMR (400 MHz, $CDCl_3$) δ 6.88 (dd, J = 2.0, 1.6 Hz 1H), 6.76 (d, J = 2.0 Hz, 2H), 5.18−5.17 (m, 1H), 4.98 (t, J = 7.2 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.22−2.19 (m, 2H), 2.07−2.01 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.4−1.10 (m, 2H), 0.93 (s, 9H), −0.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 151.2, 146.2, 131.3, 130.0, 124.8, 115.9, 114.2, 113.4, 112.1, 55.9, 55.7, 29.9, 27.9, 25.7, 25.9, 25.5, 18.3, 17.6, −4.5; HRMS (EI-TOF) Calcd for $C_{23}H_{38}O_3Si$ $[M]^+$: 390.2590, found 390.2592.

(Z)-tert-Butyldimethyl((7-methyl-1-(naphthalen-2-yl)octa-1,6-dien-1-yl)oxy)silane ***(2i)***. Prepared according to the general procedure C employing **1i** (1.0964 g, 4.1 mmol), LDA (2 M in THF, 2.6 mL, 5.2 mmol), TBDMSOTf (1.4 mL, 6.0 mmol) and THF (8 mL) as starting materials to afford **2i** (0.9371 g, 2.4 mmol, 60% yield) as a colorless oil. IR ν 2929, 2856, 1646, 1467, 1255 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.84 (dd, J = 6.8, 6.0 Hz, 2H), 7.79 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.51−7.45 (m, 2H), 5.33 (t, J = 7.2 Hz, 1H), 5.22 (t, J = 6.8 Hz, 1H), 2.34−2.29 (m, 2H), 2.15−2.10 (m, 2H), 1.76 (s, 3H), 1.68 (s, 3H), 1.59−1.51 (m, 2H), 1.08 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 137.2, 133.2, 132.8, 131.5, 128.1, 127.6, 127.4, 126.0, 125.7, 124.6, 124.34, 124.33, 112.7, 29.9, 27.9, 26.0, 25.9, 25.8, 18.4, 17.7, −4.0; HRMS (EI-TOF) Calcd for $C_{25}H_{36}OSi$ $[M]^+$: 380.2535, found 380.2531.

(Z)-2-(1-((tert-Butyldimethylsilyl)oxy)-7-methylocta-1,6-dien-1-yl)-1-methyl-1H-indole ***(2j)***. Prepared according to the general procedure C employing **1j** (1.1314 g, 4.2 mmol), LDA (2 M in THF, 2.3 mL, 5.5 mmol), TBDMSOTf (1.4 mL, 6.3 mmol) and THF (8 mL) as starting materials to afford **2j** (1.1184 g, 2.9 mmol, 69% yield) as a colorless oil. IR ν 2929, 2857, 1661, 1465, 1254 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 1H), 7.33−7.21 (m, 2H), 7.21 (t, J = 7.6 Hz, 1H), 6.44 (s, 1H), 5.20 (t, J = 7.2 Hz, 1H), 5.12 (t, J = 7.2 Hz, 1H), 3.74 (s, 3H), 2.29−2.23 (m, 2H), 2.-2.06 (m, 2H), 1.74 (s, 3H), 1.66 (s, 3H), 1.54−1.46 (m, 2H), 0.97 (s, 9H), −0.13 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 139.7, 137.6, 131.6, 127.5, 124.5, 121.7, 120.6, 119.5, 116.8, 109.2, 101.4, 30.9, 29.7, 27.8, 25.8, 25.7, 25.3, 18.1, 17.7, −5.1; HRMS (EI-TOF) Calcd for $C_{24}H_{37}NOSi$ $[M]^+$: 383.2644, found 383.2643.

(Z)-2-(1-((tert-Butyldimethylsilyl)oxy)-7-methylocta-1,6-dien-1-yl)-1,5-dimethyl-1H-indole ***(2k)***. Prepared according to the general procedure C employing **1k** (0.4757 g, 1.24 mmol), LDA (2 M in THF, 0.8 mL, 1.6 mmol), TBDMSOTf (0.5 mL, 1.9 mmol) and THF (6 mL) as starting materials to afford **2k** (0.4091 g, 1.0 mmol, 83% yield) as a colorless oil. IR ν 2928, 2856, 1661, 1253 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.06 (dd, J = 8.4, 1.2 Hz, 1H), 6.36 (s, 1H), 5.23−5.19 (m, 1H), 5.11 (t, J = 7.4 Hz, 1H), 3.72 (s, 3H), 2.47 (s, 3H), 2.29−2.23 (m, 2H), 2.012−2.06 (m, 2H), 1.75 (s, 3H), 1.66 (s, 3H), 1.54−1.47 (m, 2H), 0.98 (s, 9H), −0.12 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 139.7, 136.1, 131.5, 128.6, 127.7, 124.6, 123.3, 120.3, 116.5, 108.9, 100. 9, 30.9, 29.7, 27.8, 25.8, 25.7, 25.3, 21.4, 18.1, 17.7, −5.1; HRMS (EI-TOF) Calcd for $C_{25}H_{39}NOSi$ $[M]^+$: 397.2801, found 397.2807.

(Z)-Diethyl-2-(3-((tert-butyldimethylsilyl)oxy)-3-phenylallyl)-2-(3-methylbut-2-en-1-yl)malonate ***(2l)***. Prepared according to the general procedure C employing **1l** (0.9682 g, 2.7 mmol), LDA (2 M in THF, 1.6 mL, 3.2 mmol), TBDMSOTf (0.87 mL, 3.8 mmol) and THF (6 mL) as starting materials to afford **2l** (1.1175 g, 2.4 mmol, 88% yield) as a colorless oil. IR ν 2931, 2859, 1731, 1648, 1253 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.0, 1.6 Hz, 2H), 7.28−7.26 (m, 3H), 5.10−5.07 (m, 1H), 5.00 (t, J = 7.2 Hz, 1H), 4.21 (q, J = 6.4 Hz, 4H), 2.85 (d, J = 7.2 Hz, 2H), 2.66 (d, J = 7.6 Hz, 2H), 1.74 (s, 3H), 1.65 (s, 3H), 1.27 (t, J = 7.2 Hz, 6H), 1.04 (s, 9H), −0.00 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 151.8, 139.4, 135.2, 127.8, 127.6, 125.9, 118.1, 105.0, 61.0, 57.6, 31.4, 29.4, 27.0, 25.8, 18.2, 17.8, 14.0, −4.1; HRMS (EI-TOF) Calcd for $C_{27}H_{42}O_5Si$ $[M]^+$: 474.2802, found 474.2804.

(Z)-tert-Butyl((3,7-dimethyl-1-phenylocta-1,6-dien-1-yl)oxy)-dimethylsilane[13] ***(2m)***. Prepared according to the general procedure C employing **1m** (0.9192 g, 4.0 mmol), LDA (2 M in THF, 2.6 mL, 5.2 mmol), TBDMSOTf (1.4 mL, 6.0 mmol) and THF (6 mL) as starting materials to afford **2m** (1.1077 g, 3.2 mmol, 81% yield) as a colorless oil. IR ν 2957, 2858, 1648, 1255 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.30−7.22 (m, 3H), 5.18−5.14 (m, 1H), 4.88 (d, J = 9.6 Hz, 1H), 2.77−2.66 (m, 1H), 2.06−2.00 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.41−1.31 (m, 2H), 1.03 (d, J = 6.8 Hz, 3H), 1.00 (s, 9H), −0.02 (s, 3H), −0.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 140.1, 131.0, 127.8, 127.3, 126.2, 125.0, 118.4, 37.9, 30.0, 26.0, 25.9, 25.7, 20.8, 18.3, 17.6, −4.0, −4.1; HRMS (EI-TOF) Calcd for $C_{22}H_{36}OSi$ $[M]^+$: 344.2535, found 344.2534.

(Z)-tert-Butyldimethyl((8-methyl-1-phenylnona-1,7-dien-1-yl)-oxy)silane ***(2n)***. Prepared according to the general procedure C employing **1n** (0.5868 g, 2.5 mmol), LDA (2 M in THF, 1.5 mL, 3.0 mmol), TBDMSOTf (0.8 mL, 3.5 mmol) and THF (5 mL) as starting materials to afford **2n** (0.7785 g, 2.2 mmol, 89% yield) as a colorless oil. IR ν 2928, 2856, 1689, 1256 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.41 (m, 2H), 7.29−7.19 (m, 3H), 5.15−5.08 (m, 2H), 2.22−2.17 (m, 2H), 2.02−1.97 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.44−1.36 (m, 4H), 0.98 (s, 9H), −0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 139.9, 131.2, 127.8, 127.3, 125.9, 124.8, 112.0, 29.8, 29.4, 28.0, 26.1, 25.9, 25.7, 18.3, 17.7, −4.1; HRMS (EI-TOF) Calcd for $C_{22}H_{36}OSi$ $[M]^+$: 344.2535, found 344.2534.

(Z)-tert-Butyldimethyl((6-methyl-1-phenylhepta-1,5-dien-1-yl)-oxy)silane ***(2o)***. Prepared according to the general procedure C employing **1o** (1.0135 g, 5.0 mmol), LDA (2 M in THF, 2.2 mL, 4.5 mmol), TBDMSOTf (1.05 mL, 4.5 mmol) and THF (6 mL) as starting materials to afford **2o** (1.0713g, 3.0 mmol, 66% yield) as a colorless oil. IR ν 2929, 2857, 1650, 1255 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.45 (m, 2H), 7.31−7.21 (m, 3H), 5.19 (t, J = 6.8 Hz, 1H), 5.12 (t, J = 7.2 Hz, 1H), 2.27−2.22 (m, 2H), 2.14−2.08 (m 2H), 1.72 (s, 3H), 1.64 (s, 3H), 0.99 (s, 9H), −0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 139.9, 131.7, 127.9, 127.3, 125.9, 124.3, 111.6, 28.2, 26.5, 25.9, 25.8, 18.3, 17.8, −4.0; HRMS (EI-TOF) Calcd for $C_{20}H_{32}OSi$ $[M]^+$: 316.2222, found 316.2222.

tert-Butyldimethyl(((1Z,5E/Z)-1-phenylocta-1,5-dien-1-yl)oxy)-silane[13] ***(2p)***. Prepared according to the general procedure C employing(*Z*/*E*)-1-phenylnon-6-en-1-one (1.0166 g, 4.7 mmol), LDA (2 M in THF, 3.1 mL, 6.2 mmol), TBDMSOTf (1.5 mL, 7.0 mmol) and THF (9 mL) as starting materials to afford the title compound (1.1343 g, 3.4 mmol, 73% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.0 Hz, 2H), 7.32−7.25 (m, 3H), 5.49−5.32 (m, 2H), 5.12 (t, J = 7.2 Hz, 1H), 2.29−2.20 (m, 2H), 2.15−1.98 (m, 4H), 1.56−1.46 (m, 2H), 1.03−0.95 (m, 12H), −0.04 (s, 6H). Anal. Calcd for $C_{21}H_{34}OSi$: C, 76.30; H, 10.37. Found C, 76.15; H, 10.04.

General Procedure for Oxidative [4 + 2] Cycloaddition of Aryl Silyl Enol Ethers. To a 50 mL flame-dried Schlenk flask containing 4 Å MS (100 wt %) cooled under N_2, $(NH_4)_2S_2O_8$ (3 equiv), $Ru(bpy)_3(PF_6)_2$ (1.5 mol %), **2** (0.3 mmol) and MeOH (6 mL) were added. The mixture was degassed through three freeze−pump−thaw cycles under N_2. The reaction was placed at room temperature and stirred in front of a 18W compact fluorescent lamp at a distance of 15 cm for 17 h. The reaction was diluted with Et_2O and filtered through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo before it was purified by flash chromatography on silica gel to afford **3**.

To a 50 mL flame-dried Schlenk flask cooled under N_2, 2,4-dinitrofenylhydrazin, Cat.H_2SO_4 (con.) (two drops), MeOH (3 mL) was added. The mixture was stirred at 50 °C for 15 min. Then **3** (without purification) dissolved in MeOH (6 mL) was added via syringe. The mixture was stirred for another 4 h at 50 °C. After cooled to room temperature, the solid was filtered and washed by small amount of MeOH, dried in vacuo, affording the title compound **4**.

(E)-1-(9,9-Dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]-naphthalen-4(2H)-ylidene)-2-(2,4-dinitrophenyl)hydrazine ***(4a)***. Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2122 g, 0.92 mmol), 4 Å MS (0.0902 g), $Ru(bpy)_3(PF_6)_2$ (0.0043 g, 0.005 mmol), **2a** (0.0866 g, 0.29 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^{1}H NMR (*dr* = 5:1), and then condensed with DNP (0.1123 g, 0.57 mmol) in MeOH (9 mL) affording **4a** as a red solid (0.6557 g, 0.164 mmol, 57% yield) by filtration and washed

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by MeOH. mp = 206−208 °C; IR ν 3331, 3109, 1615, 1589, 1335 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 1H), 9.14 (d, J = 2.4 Hz, 1H), 8.34 (dd, J = 9.6, 2.4 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 9.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.39 (dd, J = 7.6, 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 2.97−2.91 (m, 1H), 2.75−2.67 (m, 1H), 2.09−1.75 (m, 6H), 1.45 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 150.4, 145.0, 137.9, 132.2, 130.1, 129.9, 129.6, 126.2, 126.1, 125.0, 123.5, 116.8, 53.2, 40.5, 36.3, 27.3, 23.9, 22.9, 22.1; HRMS (EI-TOF) Calcd for $C_{21}H_{22}N_4O_4$ $[M]^+$: 394.1641, found 394.1642.

*(E)-1-(2,4-Dinitrophenyl)-2-(7-methoxy-9,9-dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-ylidene)hydrazine (**4b**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2065g, 0.90 mmol), 4 Å MS (0.1132 g), $Ru(bpy)_3(PF_6)_2$ (0.0042 g, 0.005 mmol), 2b (0.1023 g, 0.28 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated *in vacuo*. The crude mixture was monitored by ^1H NMR (dr = 7:1) and then condensed with DNP (0.1123 g, 0.57 mmol) in MeOH (9 mL) to afford the red solid (0.0754 g, 0.172 mmol, 61% yield) by filtration and washed by MeOH. mp = 156−157 °C; IR ν 3314, 2958, 1614, 1589, 1334 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 1H), 9.15 (s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 9.2 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 6.95−6.75 (m, 2H), 3.88 (s, 3H), 3.56−3.36 (m, 1H), 2.73−2.55 (m, 1H), 2.41−2.25 (m, 1H), 1.87−1.72 (m, 1H), 1.70−1.50 (m, 3H), 1.44 (s, 3H), 1.18 (s, 3H), 1.06−0.85 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 157.9, 148.5, 144.8, 137.6, 129.9, 129.3, 128.2, 124.0, 123.6, 116.7, 111.5, 111.1, 55.3, 51.9, 37.3, 36.6, 32.3, 31.1, 29.4, 26.3, 25.8; HRMS (EI-TOF) Calcd for $C_{22}H_{24}N_4O_5$ $[M]^+$: 424.1747, found 424.1743.

*(3a*R,9a*R)-8-Methoxy-9,9-dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-one (**3c**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2002 g, 0.88 mmol), 4 Å MS (0.0912 g), $Ru(bpy)_3(PF_6)_2$ (0.0046 g, 0.005 mmol), **2c** (0.1039 g, 0.29 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (dr > 20:1), and then purified by flash column chromatography using 50:1 PE/EtOAc as the eluent to give **3c** (0.0161 g, 0.066 mmol, 23% yield) as a white solid and **3c′** (0.0467 g, 0.191 mmol, 66% yield) as a white solid. mp = 108−110 °C; IR ν 2959, 2874, 1694, 1664, 1260 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 1H), 7.27 (dd, J = 8.0, 8.0 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H), 2.74−2.60 (m, 1H), 2.10−1.85 (s, 5H), 1.84−1.73 (m, 1H), 1.72−1.64 (m, 1H), 1.53 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 158.5, 140.8, 134.7, 127.1, 119.6, 116.2, 55.4, 54.2, 48.3, 38.0, 27.5, 26.4, 23.4, 22.6, 17.8; HRMS (EI-TOF) Calcd for $C_{16}H_{20}O_2$ $[M]^+$: 244.1463, found 244.1467.

*(3a*R,9a*R)-6-Methoxy-9,9-dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-one (**3c′**).* mp = 102−104 °C; IR ν 2874, 2839, 1691, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 2.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.09 (dd, J = 8.8, 2.8 Hz, 1H), 3.84 (s, 3H), 2.76−2.63 (m, 1H), 2.11−1.85 (m, 4H), 1.84−1.75 (m, 1H), 1.74−1.62 (m, 1H), 1.55−1.47 (m, 1H), 1.40 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 157.8, 146.4, 133.4, 127.6, 121.4, 109.1, 55.4, 53.2, 49.3, 37.1, 29.1, 26.5, 24.0, 23.1, 22.2; HRMS (EI-TOF) Calcd for $C_{16}H_{20}O_2$ $[M]^+$: 244.1463, found 244.1468.

*(3a*R,9a*R)-5-Methoxy-9,9-dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-one (**3d**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.1999 g, 0.88 mmol), 4 Å MS (0.1073 g), $Ru(bpy)_3(PF_6)_2$ (0.0041 g, 0.005 mmol), **2d** (0.1068 g, 0.30 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (dr = 20:1), and then purified by flash column chromatography using 10:1 PE/EtOAc as the eluent to give **3d** (0.0399 g, 0.1633 mmol, 55% yield) as a white solid. mp = 106−108 °C; IR ν 2962, 2874, 1693, 1592, 1467 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.0, 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 3.86 (s, 3H), 2.77−2.65 (m, 1H), 2.17−2.06 (m, 1H), 2.06−1.96 (m, 1H), 1.91−1.81 (m, 2H), 1.80−1.61 (m, 2H), 1.60−1.49 (m, 1H), 1.39 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 159.4, 156.0, 133.3, 122.7, 118.8, 109.5, 56.0, 53.8, 50.6, 38.4, 29.9, 27.0, 23.9, 23.2, 22.4; HRMS (EI-TOF) Calcd for $C_{16}H_{20}O_2$ $[M]^+$: 244.1463, found 244.1459.

*(3a*R,9aR)-7-Ethyl-9,9-dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-one (**3e**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2108 g, 0.88 mmol), 4 Å MS (0.1132 g), $Ru(bpy)_3(PF_6)_2$ (0.0048 g, 0.005 mmol), **2eb** (0.1132 g, 0.28 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (dr = 10:1), and then purified by flash column chromatography using 60:1 PE/EtOAc as the eluent to give **3e** (0.0649 g, 0.268 mmol, 95% yield, dr = 10:1) as a white solid.

When employing $(NH_4)_2S_2O_8$ (0.2021 g, 0.88 mmol), 4 Å MS (0.1013 g), $Ru(bpy)_3(PF_6)_2$ (0.0040 g, 0.005 mmol), **2ea** (0.1013 g, 0.28 mmol) and MeOH (6 mL) as starting materials, affording **3e** (0.0441 g, 0.18 mmol, 64% yield, dr = 4:1).

When employing $(NH_4)_2S_2O_8$ (0.2104 g, 0.88 mmol), 4 Å MS (0.1113 g), $Ru(bpy)_3(PF_6)_2$ (0.0042 g, 0.005 mmol), **2** (0.1007 g, 0.28 mmol) and MeOH (6 mL) as starting materials, affording **3e** (0.0608 g, dr = 10:1, 0.25 mmol, 89% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 1.2 Hz, 1H), 7.13 (dd, J = 8.0, 1.6 Hz, 1H), 2.73−2.63 (m, 3H), 2.09−1.99 (m, 2H), 1.98−1.84 (m, 2H), 1.83−1.63 (m, 2H), 1.61−1.48 (m, 1H), 1.42 (s, 3H), 1.30−1.22 (m, 6H). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found C, 83.90; H, 8.91.

*(E)-1-(2,4-Dinitrophenyl)-2-(7-fluoro-9,9-dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-ylidene)hydrazine (**4f**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2063g, 0.90 mmol), 4 Å MS (0.1050 g), $Ru(bpy)_3(PF_6)_2$ (0.0044 g, 0.005 mmol), **2f** (0.1002 g, 0.288 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (dr = 5:1), and then condensed with DNP (0.1181 g, 0.60 mmol) in MeOH (9 mL) affording the red solid (0.0601 g, 0.146 mmol, 49% yield) by filtration and washed by MeOH. mp = 241−243 °C; IR ν 3335, 2963, 1617, 1589, 1337 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 1H), 9.15 (s, 1H), 8.36 (d, J = 9.2 Hz, 1H), 8.27 (dd, J = 8.8, 6.4 Hz, 1H), 8.11 (d, J = 9.6 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 7.04−6.94 (m, 1H), 3.02−2.86 (m, 1H), 2.77−2.61 (m, 1H), 2.08−1.71 (m, 6H), 1.43 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (d, J = 251.5 Hz), 154.3, 153.2 (d, J = 7.1 Hz), 145.0, 138.0, 130.0, 129.6, 128.5, 128.4, 123.6, 116.7, 113.7 (d, J = 22.2 Hz), 111.7 (d, J = 22.2 Hz), 53.1, 40.5, 36.6, 30.9, 27.2, 23.9, 22.8 22.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.2; HRMS (EI-TOF) Calcd for $C_{21}H_{21}O_4N_4F$ $[M]^+$: 412.1547, found 412.1549.

*(E)-1-(7-Bromo-9,9-dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-ylidene)-2-(2,4-dinitrophenyl)-hydrazine (**4g**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2038 g, 0.90 mmol), 4 Å MS (0.1161 g), $Ru(bpy)_3(PF_6)_2$ (0.0044 g, 0.005 mmol), **2g** (0.1262 g, 0.308 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (dr = 3:1), and then condensed with DNP (0.1179 g, 0.60 mmol) in MeOH (9 mL) affording **4g** (0.0582 g, 0.123 mmol, 40% yield) as a red solid by filtration and washed by MeOH. mp = 195−198 °C; IR ν 3329, 2923, 2855, 1724, 1614, 1589, 1334 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.48 (s, 1H), 9.15 (s, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.12 (dd, J = 9.6, 8.0 Hz, 2H), 7.56 (s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 3.03−2.85 (m, 1H), 2.77−2.58 (m, 1H), 2.10−1.72 (m, 6H), 1.44 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 152.2, 144.8, 138.1, 131.3, 130.0, 129.7, 129.5, 128.3, 127.8, 124.7, 123.5, 116.8, 53.0, 40.4, 36.6, 27.3, 27.2, 23.9, 22.8, 22.0; HRMS (EI-TOF) Calcd for $C_{21}H_{21}O_4N_4Br$ $[M]^+$: 472.0746, found 472.0744.

*(3a*R,9a*R)-5,8-Dimethoxy-9,9-dimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-one (**3h**).* Prepared according to

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the general procedure employing $(NH_4)_2S_2O_8$ (0.2101 g, 0.92 mmol), 4 Å MS (0.1073 g), $Ru(bpy)_3(PF_6)_2$ (0.0042 g, 0.005 mmol), **2h** (0.1038 g, 0.266 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (*dr* > 20:1), and then purified by flash column chromatography using 5:1 PE/EtOAc as the eluent to give **3h** (0.0676 g, 0.246 mmol, 93% yield) as a white solid. mp = 159−160 °C; IR ν 2957, 2924, 1700, 1465, 1262 cm^{-1}; 1H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 9.2 Hz, 1H), 6.83 (d, *J* = 9.2 Hz, 1H), 3.828 (s, 3H), 3.825 (s, 3H), 2.79−2.69 (m, 1H), 2.25−2.16 (m, 1H), 2.01−1.91 (m, 1H), 1.91−1.82 (m, 1H), 1.81−1.70 (m, 2H), 1.68−1.55 (m, 2H), 1.50 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 153.1, 152.2, 142.1, 125.0, 116.8, 111.4, 56.8, 55.84, 55.78, 50.1, 38.6, 27.8, 26.9, 23.1, 22.5, 18.6; HRMS (EI-TOF) Calcd for $C_{17}H_{22}O_3$ $[M]^+$: 274.1569, found 274.1571.

*(3a*R,11a*R)-11,11-Dimethyl-3,3a,11,11a-tetrahydro-1H-cyclopenta[b]anthracen-4(2H)-one (**3i**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2120 g, 0.93 mmol), 4 Å MS (0.1060 g), $Ru(bpy)_3(PF_6)_2$ (0.0042 g, 0.005 mmol), **2i** (0.1059 g, 0.278 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (*dr* > 20:1), and then purified by flash column chromatography using 60:1 PE/EtOAc as the eluent to give **3i** (0.0234 g, 0.088 mmol, 32% yield) as a white solid. mp = 113−115 °C; IR ν 2960, 2875, 1689, 1463, 1221 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 9.2 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 7.90−7.83 (m, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.57−7.50 (m, 2H), 2.85−2.74 (m, 1H), 2.20−1.92 (m, 4H), 1.91−1.79 (m, 1H), 1.76 (s, 3H), 1.74 (s, 3H), 1.73−1.66 (m, 1H), 1.62−1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 151.3, 137.2, 131.14, 131.12, 129.6, 127.9, 127.5, 127.2, 125.3, 123.3, 55.7, 47.5, 39.1, 30.6, 26.6, 23.6, 22.7, 20.1; HRMS (EI-TOF) Calcd for $C_{19}H_{20}O$ $[M]^+$: 264.1514, found 264.1513.

*(3a*R,10a*R)-5,10,10-Trimethyl-1,2,3,3a,10,10a-hexahydrocyclopenta[b]carbazol-4(5H)-one (**3j**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2091 g, 0.92 mmol), 4 Å MS (0.1082 g), $Ru(bpy)_3(PF_6)_2$ (0.0040 g, 0.005 mmol), **2j** (0.1061 g, 0.277 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (*dr* > 50:1), and then purified by flash column chromatography using 50:1 PE/EtOAc as the eluent to give **3j** (0.0733 g, 0.274 mmol, 99% yield) as a white solid. mp = 174−176 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.40−7.33 (m, 2H), 7.15−7.10 (m, 1H), 4.06 (s, 3H), 2.84−2.74 (m, 1H), 2.25 (ddd, *J* = 13.6, 12.0, 6.4 Hz, 1H), 2.11−1.99 (m, 1H), 1.98−1.68 (m, 4H), 1.64 (s, 3H), 1.62−1.54 (m, 1H), 1.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 138.9, 136.8, 130.3, 128.9, 127.5, 123.6, 121.9, 110.3, 56.0, 50.4, 35.5, 31.3, 28.7, 25.4, 23.6, 22.2, 21.6, 20.9; HRMS (EI-TOF) Calcd for $C_{18}H_{21}NO$ $[M]^+$: 267.1623, found 267.1624.

*(3a*R,10a*R)-5,8,10,10-Tetramethyl-1,2,3,3a,10,10a-hexahydrocyclopenta[b]carbazol-4(5H)-one (**3k**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2057 g, 0.90 mmol), 4 Å MS (0.1061 g), $Ru(bpy)_3(PF_6)_2$ (0.0040 g, 0.005 mmol), **2k** (0.1151 g, 0.29 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (*dr* > 50:1), and then purified by flash column chromatography using 50:1 PE/EtOAc as the eluent to give **3k** (0.0734 g, 0.261 mmol, 90% yield) as a white solid. mp = 128−129 °C; IR ν 2958, 2929, 1666, 1512, 1460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.20 (d, *J* = 8.8 Hz, 1H), 4.03 (s, 3H), 2.82−2.72 (m, 1H), 2.48 (s, 3H), 2.23 (ddd, *J* = 13.6, 12.0, 6.4 Hz, 1H), 2.10−1.99 (m, 1H), 1.97−1.70 (m, 4H), 1.64 (s, 3H), 1.61−1.51 (m, 1H), 1.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 138.9, 136.8, 130.3, 128.9, 127.5, 123.6, 121.9, 110.3, 55.9, 50.4, 35.5, 31.3, 28.7, 25.4, 23.6, 22.2, 21.6, 20.9; HRMS (EI-TOF) Calcd for $C_{19}H_{23}NO$ $[M]^+$: 281.1780, found 281.1782.

*(3a*R,9a*R)-Diethyl-4,4-dimethyl-9-oxo-3a,4,9,9a-tetrahydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (**3l**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2077 g, 0.90 mmol), 4 Å MS (0.1470 g), $Ru(bpy)_3(PF_6)_2$ (0.0042 g, 0.005 mmol), **2l** (0.1393 g, 0.293 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (*dr* = 1:2), and then purified by flash column chromatography using PE/EtOAc (20:1) as the eluent to give **3l** and **3l′** (0.0351 g, 0.10 mmol, 33% yield, *dr* = 1:2) as a colorless oil. IR ν 2977, 2900, 1731, 1681, 1264 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 (td, *J* = 8.0, 1.6 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.35−7.27 (m, 1H), 4.27−4.15 (m, 2H), 4.12−4.01 (m, 2H), 3.19−3.12 (m, 1H), 2.79−2.73 (m, 2H), 2.53−2.41 (m, 1H), 2.40−2.30 (m, 1H), 1.84 (t, *J* = 13.2 Hz, 1H), 1.46 (s, 3H), 1.33 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 172.4, 171.5, 149.6, 134.1, 130.4, 127.8, 126.7, 125.8, 61.7, 61.5, 58.9, 50.6, 47.6, 37.2, 36.6, 35.5, 34.1, 26.7, 14.0, 13.9; HRMS (EI-TOF) Calcd for $C_{21}H_{26}O_5$ $[M]^+$: 358.1780, found 358.1771.

*(3a*S,9a*R)-Diethyl-4,4-dimethyl-9-oxo-3a,4,9,9a-tetrahydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (**3l′**).* IR ν 2970, 2934, 1730, 1693, 1258, 1063 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57−7.50 (m, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.34−7.27 (m, 1H), 4.29−4.12 (m, 4H), 2.97−2.79 (m, 2H), 2.65 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.45 (dd, *J* = 14.0, 10.4 Hz, 1H), 2.36−2.25 (m, 1H), 2.14−2.05 (m, 1H), 1.44 (s, 3H), 1.31−1.22 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 172.5, 172.1, 153.2, 133.7, 131.8, 127.2, 126.4, 126.2, 61.7, 61.6, 57.5, 51.50, 48.4, 37.5, 35.2, 33.6, 28.7, 23.2, 14.04, 14.00; HRMS (EI-TOF) Calcd for $C_{21}H_{26}O_5$ $[M]^+$: 358.1780, found 358.1771.

*(3a*R,9a*R)-3,9,9-Trimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-one (**3m**).*[2] Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2068 g, 0.90 mmol), 4 Å MS (0.1042 g), $Ru(bpy)_3(PF_6)_2$ (0.0041g, 0.005 mmol), **2m** (0.1013 g, 0.294 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (*dr* = 2.5:1), and then purified by flash column chromatography using 50:1 PE/EtOAc as the eluent to give **3m** and **3m′** (0.0477 g, 0.209 mmol, 71% yield) as a white solid. IR ν 2962, 2871, 1691, 1604, 1462, 1227 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.54−7.48 (m, 1H), 7.46 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.31−7.24 (m, 1H), 2.45−2.30 (m, 1H), 2.25 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.21−2.11 (m, 1H), 2.02−1.90 (m, 1H), 1.86−1.76 (m, 1H), 1.69−1.56 (m, 1H), 1.39 (s, 3H), 1.38−1.30 (m, 1H), 1.26 (s, 3H), 1.24 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 153.7, 133.3, 132.5, 127.0, 126.3, 126.1, 55.8, 53.3, 37.7, 33.4, 31.7, 28.6, 24.7, 23.2, 21.5; HRMS (EI-TOF) Calcd for $C_{16}H_{20}O$ $[M]^+$: 228.1514, found 228.1516.

*(3a*R,9a*S)-3,9,9-Trimethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]naphthalen-4(2H)-one (**3m′**).*[13] IR ν 2958, 2870, 1678, 1600, 1455, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.51 (td, *J* = 8.0, 1.6 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 2.66 (dd, *J* = 8.4, 5.2 Hz, 1H), 2.47−2.36 (m, 1H), 2.24−2.11 (m, 1H), 1.87−1.80 (m, 1H), 1.77−1.70 (m, 1H), 1.43 (s, 3H), 1.25 (s, 3H), 1.20 (d, *J* = 8.0 Hz, 3H), 1.17- 1.01 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 150.2, 133.4, 132.0, 127.4, 126.3, 125.3, 55.7, 50.4, 40.6, 36.0, 34.6, 34.1, 29.4, 26.1, 21.4; HRMS (EI-TOF) Calcd for $C_{16}H_{20}O$ $[M]^+$: 228.1514, found 228.1512.

*(4a*R,9a*R)-10,10-Dimethyl-1,3,4,4a,9a,10-hexahydroanthracen-9(2H)-one (**3n**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2129 g, 0.93 mmol), 4 Å MS (0.1059 g), $Ru(bpy)_3(PF_6)_2$ (0.0042 g, 0.005 mmol), **2n** (0.0957 g, 0.278 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (*dr* unknown), and then purified by flash column chromatography using 60:1 PE/EtOAc as the eluent to give **3n** (0.0075 g, 0.033 mmol,

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13% yield) as a white solid. IR ν 2925, 2856, 1679, 1598, 1314 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05−7.99 (m, 1H), 7.55−7.48 (m, 2H), 7.31−7.26 (m, 1H), 2.54−2.45 (m, 1H), 2.41−2.32 m, 1H), 2.07−1.98 (m, 1H), 1.92−1.81 (m, 2H), 1.80−1.71 (m, 1H), 1.42 (s, 3H), 1.31−1.22 (m, 4H), 1.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 153.2, 133.6, 130.7, 127.3, 126.2, 125.8, 47.5, 46.2, 37.0, 27.1, 26.9, 26.5, 26.0, 25.7, 25.0; HRMS (EI-TOF) Calcd for $C_{16}H_{20}O$ $[M]^+$: 228.1514, found 228.1518.

*2-Methoxy-6-methyl-1-phenylhept-5-en-1-one (**5o**).* Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2042 g, 0.90 mmol), 4 Å MS (0.0972 g), $Ru(bpy)_3(PF_6)_2$ (0.0040 g, 0.005 mmol), **2o** (0.0914 g, 0.289 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo and purified by flash column chromatography using 50:1 PE/EtOAc as the eluent to give **5o** (0.0188 g, 0.093 mmol, 32% yield) as a colorless oil. IR ν 2925, 1694, 1449, 1122 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.2 Hz, 2H), 7.60−7.54 (m, 1H), 7.46 (dd, J = 7.6, 7.6 Hz, 2H), 5.11 (t, J = 8.0 Hz, 1H), 4.44 (dd, J = 7.6, 5.2 Hz, 1H), 3.36 (s, 3H), 2.28−2.06 (m, 2H), 1.85−1.77 (m, 2H), 1.70 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 135.2, 133.3, 133.1, 128.63, 128.59, 123.1, 84.1, 57.8, 33.2, 25.7, 24.0, 17.6; HRMS (EI-TOF) Calcd for $C_{15}H_{20}O_2$ $[M]^+$: 232.1463, found 232.1459.

*(3a*R,9*R,9a*S)-9-ethyl-3,3a,9,9a-tetrahydro-1H-cyclopenta[b]-naphthalen-4(2H)-one (**3p**).*[13] Prepared according to the general procedure employing $(NH_4)_2S_2O_8$ (0.2102 g, 0.93 mmol), 4 Å MS (0.1009 g), $Ru(bpy)_3(PF_6)_2$ (0.0041 g, 0.005 mmol), **2p** (0.0913g, 0.276 mmol) and MeOH (6 mL). After 17 h, the reaction was diluted with Et_2O and passed through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^1H NMR (dr = 12:1), and then purified by flash column chromatography using 60:1 PE/EtOAc as the eluent to give **3p** (0.0229 g, 0.107 mmol, 39% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.6, 1.2 Hz, 1H), 7.54−7.49 (m, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 2.99−2.92 (m, 1H), 2.51 (ddd, J = 13.63, 10.0, 8.0 Hz, 1H), 2.30−1.66 (m, 8H), 1.48 (q, J = 10.0 Hz, 1H), 0.76 (t, J = 7.6 Hz, 3H).

*(3a*R,10a*R)-5,10,10-Trimethyl-4-methylene-1,2,3,3a,4,5,10,10a-octahydrocyclopenta[b]carbazole (**6**).* According to a known procedure.[22] To a 50 mL flame-dried Schlenk flask cooled under N_2, methyltriphenylphosphonium bromide (0.4307 g, 1.2 mmol) THF (10 mL) and NaH (60%) (0.0502 g, 1.2 mmol) was added. The mixture was refluxed for 30 mim and then **3j** dissolved in THF (5 mL) was added dropwise. The mixture was refluxed for another 13 h. Petroleum ether was added and passed through a short pad of silica with Et_2O as eluent. The filtrate was concentrated and in vacuo and purified by flash column chromatography using PE/EtOAc (100:1) as the eluent to afford **6** (0.0843 g, 0.3 mmol, 82% yield). mp = 104−106 °C; IR ν 2958, 2870, 1625, 1464, 1241 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−7.81 (m, 1H), 7.35 (d, J = 6.8 Hz, 1H), 7.31−7.23 (m, 1H), 7.17−7.09 (m, 1H), 5.31 (s, 1H), 5.14 (s, 1H), 3.88 (d, J = 1.6 Hz, 3H), 2.61−2.48 (m, 1H), 2.11−1.99 (m, 1H), 1.98−1.74 (m, 5H), 1.73−1.65 (m, 1H), 1.62 (d, J = 3.2 Hz, 3H), 1.37 (d, J = 3.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 139.9, 134.4, 125.0, 124.1, 121.9, 120.8, 118.8, 109.5, 105.6, 56.5, 44.7, 34.7, 32.2, 29.1, 27.5, 24.3, 22.9, 22.8; HRMS (EI-TOF) Calcd for $C_{19}H_{23}N$ $[M]^+$: 265.1830, found 265.1829.

*4,5,10,10-Tetramethyl-1,2,3,5,10,10a-hexahydrocyclopenta[b]-carbazole (**7**).* According to a known procedure.[23] To a 50 mL flame-dried Schlenk flask cooled under N_2, methylmagnesium bromide (3 M in THF) (0.6 mmol) was added dropwise to a solution of **3j** in THF (5 mL) at 0 °C. The mixture was stirred at room temperature overnight. The mixture was treated with saturated NH_4Cl, The two layers were separated and the aqueous one was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to afford the crude product. The crude product was dissoloved in toluene (10 mL), and p-toluenesulfonic acid monohydrate (0.0104 g, 0.06 mmol) was added under N_2. The mixture was refluxed overnight. The mixture was treated with saturated $NaHCO_3$ and separated. The aqueous layers was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography using PE/EtOAc (50:1) as eluent to afford **7** (0.0830 g, 99% yield) as a slight yellow oil. IR ν 2963, 2844, 1468, 1368 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.6, 5.6 Hz, 1H), 7.37−7.31 (m, 1H), 7.25−7.18 (m, 1H), 7.17−7.09 (m, 1H), 3.73 (d, J = 3.2 Hz, 3H), 3.61−3.48 (m, 1H), 2.76−2.62 (m, 1H), 2.61−2.48 (m, 2H), 2.44−2.29 (m, 1H), 2.09−1.95 (m, 2H), 1.63−1.52 (m, 6H), 1.41−1.34 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 138.2, 134.1, 125.1, 120.3, 120.0, 118.41, 118.40, 116.7, 108.9, 35.1, 33.7, 30.5, 29.7, 28.6, 27.3, 22.7, 20.9; HRMS (EI-TOF) Calcd for $C_{19}H_{23}N$ $[M]^+$: 265.1830, found 265.1831.

*(3a*S,10a*R)-5,10,10-Trimethyl-1,2,3,3a,4,5,10,10a-octahydrocyclopenta[b]carbazole (**8**).* According to a known procedure.[24] To a 50 mL flame-dried Schlenk flask cooled under N_2, $NaBH_4$ (40.5 mg, 1.07 mmol) and **3j** (0.0613 g, 0.23 mmol), $AlCl_3$ (0.0800 g, 0.60 mmol), and THF (6 mL) was added, respectively. The mixture was refluxed for 2 h. When cooled to room temperature, the mixture was quenched by water and extracted by ethyl acetate. The combined organic layers were dried by sodium sulfate, filtered, concentrated and purified by flash chromatography through silica gel to afford **8** (0.0569 g, 1.0 mmol, 98% yield) as a white solid. mp = 130−131 °C; IR ν 3412, 2957, 2925, 1466, 1090, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81−7.74 (m, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.23−7.15 (m, 1H), 7.15−7.07 (m, 1H), 3.63 (d, J = 1.6 Hz, 3H), 3.02 (ddd, J = 15.6, 5.2, 2.0 Hz, 1H), 2.48−2.36 (m, 1H), 2.18−2.05 (m, 1H), 2.05−1.94 (m, 1H), 1.94−1.77 (m, 3H), 1.78−1.66 (m, 1H), 1.59 (s, 3H), 1.51−1.38 (m, 2H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 135.4, 125.5, 120.0, 119.7, 119.5, 118.3, 108.8, 55.3, 37.7, 34.1, 31.6, 29.5, 29.0, 28.9, 24.1, 23.2, 23.1; HRMS (EI-TOF) Calcd for $C_{18}H_{23}N$ $[M]^+$: 253.1830, found 253.1831.

*7-Methyl-1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)oct-6-en-1-one (**9**).* To a 50 mL flame-dried Schlenk flask containing 4 Å MS (100 wt %) cooled under N_2, $(NH_4)_2S_2O_8$ (0.2101 g, 0.90 mmol), $Ru(bpy)_3(PF_6)_2$ (0.0045 g, 0.0045 mmol), **2a** (0.0993 g, 0.30 mmol), TEMPO (0.0469 g, 0.30 mmol) and MeOH (6 mL) were added. The mixture was degassed through three freeze−pump−thaw cycles under N_2. The reaction was placed at room temperature and stirred in front of a 18W compact fluorescent lamp at a distance of 15 cm for 17 h. The reaction was diluted with Et_2O and filtered through a short pad of silica using Et_2O. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel using PE/EtOAc (50:1) as eluent to afford **9** (0.0221 g, 0.06 mmol, 20% yield) as a yellow oil. IR ν 2927, 2860, 1685, 1457, 1376 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 8.0, 7.2 Hz, 2H), 4.98 (t, J = 7.2 Hz, 1H), 4.87 (dd, J = 9.2, 5.2 Hz, 1H), 2.07−1.83 (m, 4H), 1.61 (s, 3H), 1.60−1.54 (m, 1H), 1.52 (s, 3H), 1.51−1.44 (m, 2H), 1.43−13.4 (m, 2H), 1.33−1.14 (m, 9H), 1.03 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 136.1, 132.9, 131.8, 129.3, 128.4, 124.0, 89.7, 59.8, 40.4, 33.9, 32.6, 27.8, 25.6, 24.9, 20.3, 17.6, 17.1; HRMS (EI-TOF) Calcd for $C_{15}H_{18}O$ $[M-C_9H_{19}NO]^+$: 214.1358, found 214.1363.

*(Z)-tert-Butyldimethyl((1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)oxy)silane (**10**).* To a 50 mL flame-dried Schlenk flask cooled under N_2, KH (0.2092 g, 5.0 mmol), 1-(4-(trifluoromethyl)phenyl)propan-1-one (0.9680 g, 5.0 mmol) and THF (10 mL) was added. The mixture was stirred for 1 h at room temperature and then TBSCl (0.9123 g, 6.0 mmol) was added. The mixture was stirred overnight and filtered through a short pad of silica gel, concentrated and purified by flash column chromatography using petroleum ether as eluent to afford **10** (1.4131 g, 4.47 mmol, 93% yield) as a colorless oil. IR ν 2934, 2861, 1324, 1127, 1067, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 4H), 5.32 (q, J = 6.9 Hz, 1H), 1.76 (d, J = 6.9 Hz, 3H), 1.00 (s, 9H), −0.03 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 143.3, 129.3 (q, J = 32.4 Hz), 125.7, 125.0 (q, J = 3.7 Hz), 123.0, 108.1, 25.8, 18.3, 11.8, −4.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.4; HRMS (EI-TOF) Calcd for $C_{16}H_{23}OSiF_3$ $[M]^+$: 316.1470, found 316.1467.

*2-((tert-butyldimethylsilyl)peroxy)-1-(4-(trifluoromethyl)phenyl)-propan-1-one (**11**).* To a 50 mL flame-dried Schlenk flask cooled under O_2 balloon, (Z)-*tert*-butyldimethyl((1-(4-(trifluoromethyl)-

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J. Org. Chem. 2016, 81, 7288−7300

phenyl)prop-1-en-1-yl)oxy)silane (0.1264 g, 0.4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.0037 g, 0.004 mmol) and MeCN (8 mL) was added. The reaction was placed at room temperature and stirred in front of a 18W compact fluorescent lamp at a distance of 15 cm for 8 h. The reaction was diluted with Et$_2$O and passed through a short pad of silica using Et$_2$O. The filtrate was concentrated and in vacuo and purified by flash chromatography on silica gel to afford **11** (0.1136 g, 82% yield) as a colorless oil. IR ν 2934, 2860, 1323, 1133 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 5.14 (d, J = 6.8 Hz, 1H), 1.47 (d, J = 6.8 Hz, 3H), 0.85 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.5, 138.1, 134.2 (d, J = 32.6 Hz), 129.3, 125.4 (q, J = 3.7 Hz), 84.0, 26.0, 25.7, 18.1, 15.5, −6.0; ^{19}F NMR (376 MHz, CDCl$_3$) δ −63.2; HRMS (ESI) Calcd for C$_{16}$H$_{23}$F$_3$O$_3$Si [M-H]$^-$: 347.1290, found 347.1288.

*(3a*R,10a*S)-5,10,10-Trimethyl-1,2,3,3a,10,10a-hexahydrocyclopenta[b]carbazol-4(5H)-one (**3j′**).* Prepared according to a general procedure using **2j** (*Z*/*E* 4:1, 0.0963 g, 0.25 mmol), (NH$_4$)$_2$S$_2$O$_8$ (0.2102 g, 0.92 mmol), 4 Å MS (0.0963 g), Ru(bpy)$_3$(PF$_6$)$_2$ (0.0041 g, 0.005 mmol), MeOH (6 mL). After 17 h, the reaction was diluted with Et$_2$O and passed through a short pad of silica using Et$_2$O. The filtrate was concentrated in vacuo. The crude mixture was monitored by ^{1}H NMR (*dr* = 4:1) and then purified by flash column chromatography using PE/EtOAc (50:1) as the eluent to give **3j** and **3j′** (total: 0.0681 g, 0.25 mmol, 99% yield, 4/1 *dr*) as white solids.

3j′: mp = 86−88 °C; IR ν 2957, 2926, 1653, 1467, 1053, 742 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, J = 8.4 Hz, 1H), 7.40−7.33 (m, 2H), 7.11 (ddd, J = 8.1, 6.0, 1.6 Hz, 1H), 4.06 (s, 3H), 3.06−3.01 (m, 1H), 2.53 (ddd, J = 13.2, 7.6, 1.2 Hz, 1H), 2.26−2.18 (m, 1H), 1.89−1.75 (m, 2H), 1.68 (s, 3H), 1.66−1.60 (m, 2H), 1.54 (s, 3H), 1.46−1.37 (m, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.0, 140.4, 133.9, 128.1, 126.0, 124.3, 123.1, 119.7, 110.5, 55.0, 49.5, 34.8, 32.5, 31.5, 28.0, 27.5, 26.7, 22.4; HRMS (EI-TOF) Calcd for C$_{18}$H$_{21}$NO [M]$^+$: 267.1623, found 267.1626.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01016.

Characterization data for all new compounds. (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: luzhan@zju.edu.cn.

Notes

The authors declare no competing financial interest.

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