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ARTICLE

Direct construction of 4-aryl tetralones via visible-light-induced cyclizations of styrenes with molecular oxygen

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Kuai Wang,[a] Ling-Guo Meng,*[,a] Qi Zhang[a] and Lei Wang*[,a,b]

A direct synthesis of 4-aryl tetralones from aromatic alkenes and O_2 under visible light irradiation was developed. An organic dye, acridinium was used as photocatalyst in this transformation, providing a facile and environmental platform to a wide range of 4-aryl tetralones.

Introduction

Tetralone and its derivatives, containing prominent biological activity, are usually studied in medicinal chemistry. For this reason, tetralone core widely found in the structure of pharmaceutically active molecular, exhibiting significant activity, such as against hepatitis C Virus, potential antipsychotic, retinoic acid metabolism blocking and monoamine oxidases inhibitor et al (Figure 1).[1] So tetralone and its derivatives attracted more attention from chemists toward achieving it and abundant of platforms are applied to synthesize them. A few works have concerned the synthesis of 4-aryl tetralones,[2] for example, traditional methods for 4-aryl tetralones synthesis involved Friedel–Crafts cyclization of more complicated starting materials, and usually requiring acidic medium, multiple steps and complex operation (Scheme 1a–c),[3] and recent reports by use of 1-naphthol as substrate with high temperature, long reaction time and environmentally-unfriendly metal salts in the most of cases (Scheme 1d).[4] Therefore, the development of simple and green protocol for the preparation of 4-aryl tetralones is highly desirable.

Recent a few decades, photoredox catalysis driven by visible light has emerged as power tools for the construction of organic molecules,[5] and many photocatalyzed annulations, for example intermolecular cyclizations,[6] transition-metal assisted cycloaddition,[7] [3+2]-[8] and [4+2]-annulations,[9] were developed to form a wide range of carbo- and heterocycles. Compared with the reported idiomatic cyclization modes, such as metallo- or organocatalytic cycloaddtions,[10,11] free-radical[12] and Diels-Alder cyclizations,[13] those synthetic methods have following merits, such as sustainability, utilization of a clean energy source, according with green chemistry, etc.

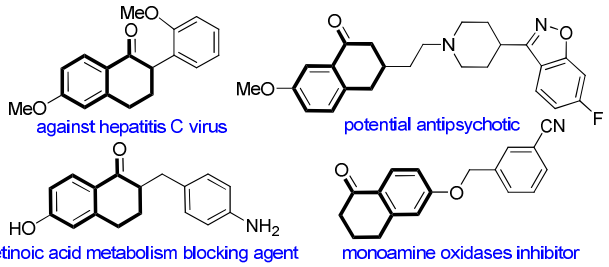
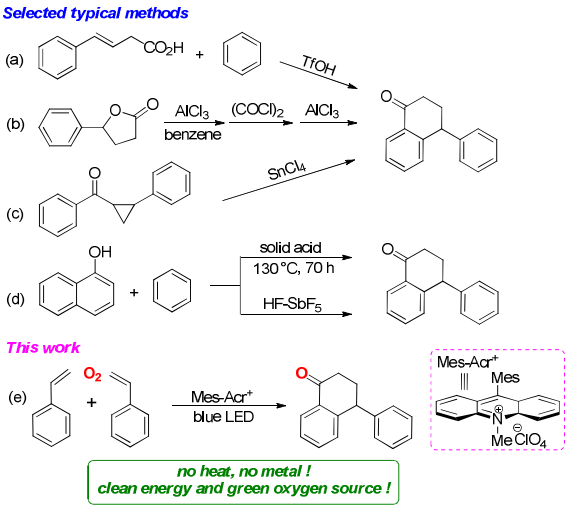


Figure 1 Biological molecular containing tetralone core unit.



Scheme 1 Different methods for the synthesis of 4-aryl tetralones.

[a] Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China; E-mail: milig@126.com, leiwang@chnu.edu.cn.
Tel.: +86-561-380-2069; fax: +86-561-309-0518
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

† Footnotes relating to the title and/or authors should appear here.
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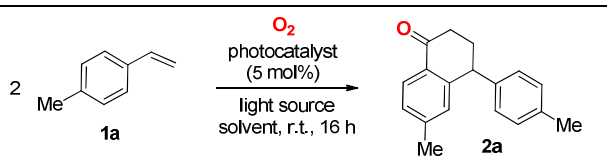
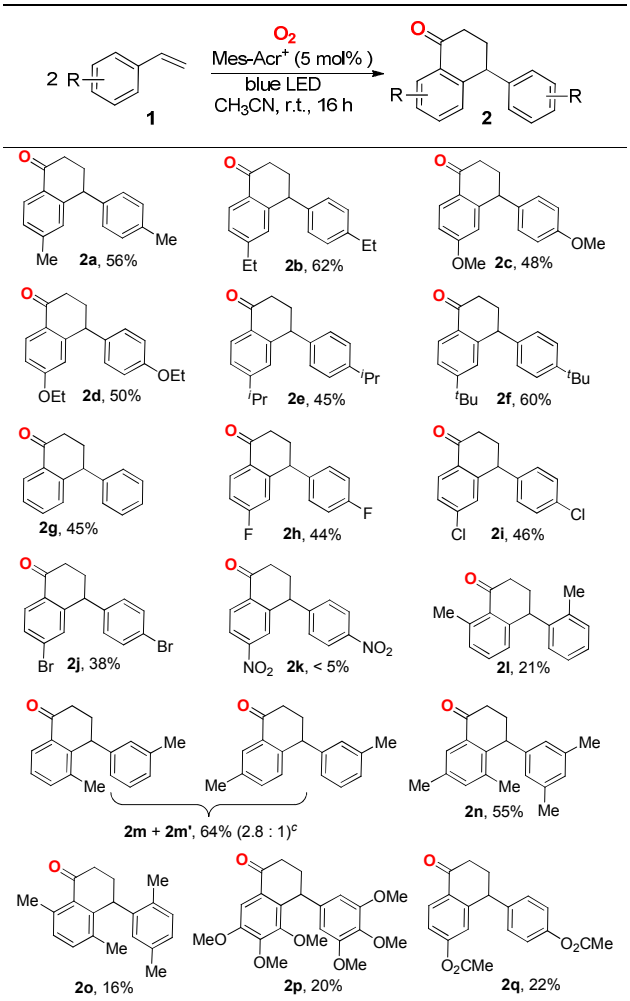
Table 1 Optimized reaction conditions.[a]



Entry	Photocatalyst	Light source	Solvent	Yield[b] (%)
1	Mes-Acr$^+$	15 W light bulb	CH_3CN	35[c]
2	Mes-Acr$^+$	—	CH_3CN	NR[d]
3	—	15 W light bulb	CH_3CN	NR
4	Mes-Acr$^+$	15 W light bulb	CH_3CN	40
5	Mes-Acr$^+$	blue LED	CH_3CN	56
6	Mes-Acr$^+$	green LED	CH_3CN	10
7	9-Phenylacridine	blue LED	CH_3CN	8
8	TPP-TFB[e]	blue LED	CH_3CN	< 5
9	Eosin Y	blue LED	CH_3CN	NR
10	Rose Bengal	blue LED	CH_3CN	NR
11	Rhodamine B	blue LED	CH_3CN	NR
12	Methylene blue	blue LED	CH_3CN	NR
13	$Ru(phen)_3(PF_6)_2$	blue LED	CH_3CN	NR
14	$Ir(PPy)_3$	blue LED	CH_3CN	NR
15	Mes-Acr$^+$	blue LED	DCE	32
16	Mes-Acr$^+$	blue LED	CH_2Cl_2	16
17	Mes-Acr$^+$	blue LED	$CHCl_3$	13
18	Mes-Acr$^+$	blue LED	EtOH	12
19	Mes-Acr$^+$	blue LED	Acetone	10
20	Mes-Acr$^+$	blue LED	THF	10
21	Mes-Acr$^+$	blue LED	DMF	< 5
22	Mes-Acr$^+$	blue LED	DMSO	< 5

[a] Reaction conditions: **1a** (0.50 mmol), photocatalyst (0.0125 mmol), light source, solvent (2.0 mL), in O_2 atmosphere at room temperature for 16 h. [b] Isolate yield. [c] In air. [d] NR = No reaction. [e] TPP-TFB = 2,4,6-Triphenylpyrylium tetrafluroborate. Mes-Acr$^+$ = 9-mesityl-10-methylacridinium perchlorate. PPy = 2-phenylpyridine

Scheme 2 The scope of styrenes.[a,b]



[a] Reaction conditions: **1** (0.50 mmol), Mes-Acr$^+$ (0.0125 mmol), blue LED, CH_3CN (2.0 mL), in O_2 atmosphere at room temperature for 16 h. [b] Isolate yield. [c] The ratio was determined by ^1H NMR.

As we known, dioxygen generally is considered as a green oxidant, but is also as ideal, cheap and clean oxygen source for introducing oxygen into organic molecules. But in photocatalyzed chemistry, it frequently used as oxidant and assisted photocatalyst to complete cycle,[14] but was rarely appeared as starting materials involving in photocatalytic reactions.[15] Styrene, an important photo-chemical reactant, was used in difunctionalization reactions with halohydrocarbons.[16] But there is a few reports using styrenes as substrates in photocatalytic annulations.[15a] In order to establish a new annulation on the basis of styrenes, 9-mesityl-10-methylacridinium perchlorate (Mes-Acr$^+$) with high catalytic activity, was employed as photocatalyst and tested to induce new cyclizations of styrenes. To our delight, a novel visible-light-induced O_2 assisted cyclizations of styrenes was developed and this method provided a direct route to 4-aryl tetralones under simple reaction conditions (Scheme 1e). Herein, we wish to report this novel Mes-Acr+ catalyzed photoinduced cyclization of styrenes with molecular oxygen for the construction of 4-aryl tetralones.

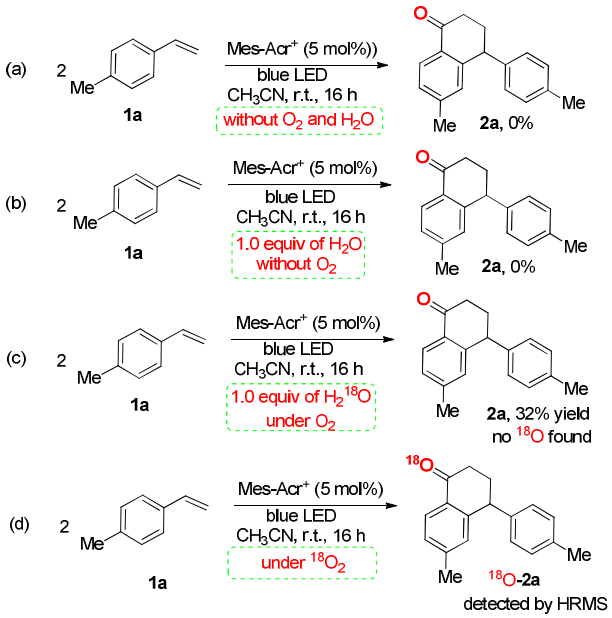
Results and discussion

Our studies were initiated at the addition of 5 mol% of organic dye Mes-Acr$^+$ to a solution of 4-methylstyrene and the results are listed in Table 1. When the reaction was carried out in CH_3CN and exposure to air at room temperature for 16 h by using a 15 W light bulb as light source, afforded cyclic compound **2a** as colorless oil in 35% yield (Table 1, entry 1), and this compound was characterized by ^1H and ^{13}C NMR spectroscopy and HRMS analysis. The experiments indicated that photocatalyst and visible-light are essential in the reaction system, because the reaction was halted immediately in the absence of in either one of them (Table 1, entries 2 and 3). The

desired product yield of **2a** was improved to 40% when the reaction was carried out in the presence of O_2, instead of air (Table 1, entry 4 vs 1). To our delight, the yield was obvious improved under blue LED irradiation (replacing light bulb as light source) and gave **2a** in 56% yield (Table 1, entry 5); but only 10% yield of **2a** was observed under green LED irradiation (Table 1, entry 6). The yield of the model reaction was deceased sharply when using 9-phenylacridine or 2,4,6-triphenylpyrylium tetrafluroborate (TPP-TFB) as catalyst (Table 1, entries 7 and 8). Further investigations on other organic dyes, such as Eosin Y, Rose Bengal, Rhodamine B or Methylene blue, the reaction can not occur (Table 1, entries 9–12). When the general Ru- and Ir-complexes, such as $Ru(phen)_3(PF_6)_2$ and $Ir(PPy)_3$ were used as photocatalyst instead of the above organic dyes, the negative results were obtained (Table 1, entries 13 and 14). After investigation of the effect of the solvent on the model reaction, CH_3CN was found to be the best medium, low yields (10–32%) of cyclic product **2a** were obtained when DCE, CH_2Cl_2, $CHCl_3$, EtOH, acetone, or THF was used as solvent (Table 1, entries 15–20). With the utilization of polar solvent (DMF or DMSO), only a trace amount of the desired product was detected by TLC (Table 1, entries 21 and 22).

With the optimized reaction conditions in our hand, a series of 4-aryl tetralones were prepared after examining the substrate scope. Overall, styrenes bearing either electron-rich or electron-poor groups led to the desired cycloadducts, as shown in Scheme 2. Generally, substrates **1** with an electron-rich group, such as Me, Et, MeO or EtO on the benzene rings, provided the corresponding products in 48–62% yields (**2a**–**d**). Even using substrates **1** with a bulk group (^{i}Pr or ^{t}Bu) on the phenyl ring, were tolerated rather well, provided **2e** and **2f** in 45 and 60% yields, respectively. Conversely, the product yields (**2h**–**j**) of the reactions were slight decreased when the electron-deficient groups (F, Cl or Br) were introduced in the substrates. Notably, the reaction was halted when 4-nitrostyrene was used as substrate under the present reaction conditions. For a 2-methyl-substituted styrene involved in the reaction, only 21% yield of the desired product **2l** was isolated owing to the steric effect. When a *meta*-methyl derivative was employed in the reaction, providing two regio-isomers **2m** and **2m'** in a ratio of 2.8 : 1. Disubstituted substrate, such as 3,5-dimethyl styrene, generated the corresponding product **2n** in 55% yield. However, for a substrate with 2,5-dimethyl or 3,4,5-trimethoxy groups on the benzene ring gave the corresponding products (**2o** and **2p**) in low yields. It is important to note that a sensitive functional group, such as acetoxy, also produced desired product, albeit the yield was so low (**2q**). The configuration of 4-aryl tetralone **2n** was further confirmed by X-ray diffraction.[17]

To elaborate the reaction mechanism clearly and find the oxygen atom in final product from O_2 or H_2O, several control experiments were performed, as depict in Scheme 3. When 4-methylstyrene (**1a**) was carried out in the absence of O_2 and H_2O, no cycloadduct **2a** was observed (Scheme 3a). Furthermore, the model reaction also can not occur when only 1.0 equiv of H_2O was involved in the reaction (Scheme 3b).



Scheme 3 Control experiments.

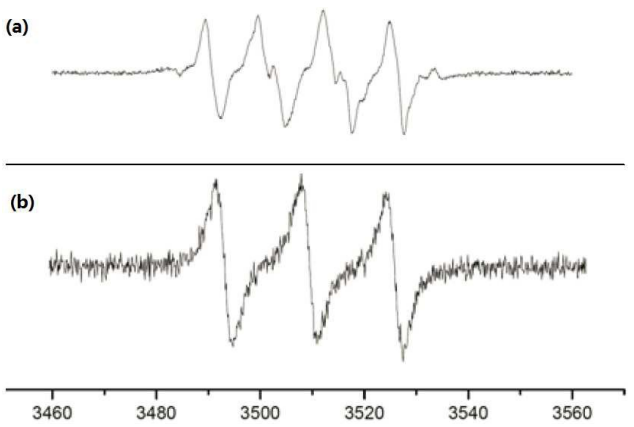
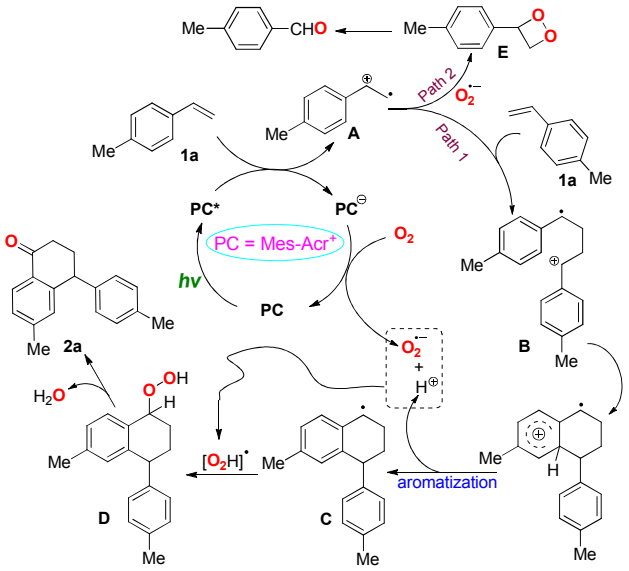


Figure 2 EPR studies. (a) EPR spectrum of a solution of Mes-Acr$^+$ (2×10^{-3} mol/L), **1a** (8×10^{-2} mol/L), and DMPO (3.4×10^{-2} mol/L) in air-saturated CH_3CN under blue LED irradiation for 30 s. (b) EPR spectrum of a solution of Mes-Acr$^+$ (2×10^{-3} mol/L), **1a** (8×10^{-2} mol/L), and TEMP (2.4×10^{-2} mol/L) in air-saturated CH_3CN under blue LED irradiation for 30 s.

These facts imply that oxygen atom in the product did not come from water but from O_2. It was further confirmed by the control experiments in Scheme 3c and 3d.

Further evidence for in what form involved in the reaction of O_2 ($^1O_2$ or $O_2^{\bullet-}$), 2,2,6,6-tetramethylpiperidine (TEMP) and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were employed as capture agents to trap $^1O_2$ or $O_2^{\bullet-}$ by electron paramagnetic resonance (EPR) spectrometer, respectively. As shown in Figure 2, when a solution of Mes-Acr$^+$ and **1a** in air-saturated CH_3CN was tested under blue LED irradiation, both signals of $^1O_2$ and $O_2^{\bullet-}$ were observed when DMPO and TEMP were used as scavenger, respectively.[18] On the other hand, only signal of $^1O_2$ was appeared when Methylene blue or Rose Bengal was in place of Mes-Acr$^+$ (detailed EPR studies, in ESI), but these catalysts were ineffective on this reaction (as shown in Table



Scheme 4 Proposed mechanism.

1), which indirectly indicated $O_2^{\bullet-}$ is an active species in the annulation.

On the basis of the above control experiments and reported literature, a possible mechanism for this photo-annulation is proposed, shown as Scheme 4. Under blue light irradiation, the ground state of photocatalyst (**PC**) is pumped to its excited state **PC***, which reacted with **1a** to generate anion of catalyst (**PC**$^-$) and a cation radical **A** (cyclic voltammetry measurements, in ESI).[19] Then the formed intermediate **A** adds to another **1a** to give intermediate **B** (Path 1), which further transforms into intermediate **C** through an intermolecular electrophilic addition and aromatization processes. It is important to note that intermediate **C** can be confirmed by a trapping experiment with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, details in ESI). Meanwhile, the photoredox cycle is completed by a reduction of **PC**$^-$ with $\mathbf{O_2}$ to give the original state of photocatalyst (**PC**) and anion radical $\mathbf{O_2}$ ($\mathbf{O_2}^{\bullet-}$). Then, $[\mathbf{O_2H}]^{\bullet}$, generated from $\mathbf{O_2}^{\bullet-}$ with $\mathbf{H}^+$, reacts with **C** to produce intermediate **D**. Finally, the desired product **2a** is generated from the reductive elimination of H_2O of **D**.[15b,15d] On the other hand, when $\mathbf{O_2}^{\bullet-}$ reacts with **1a** (Path 2), dioxetane intermediate **E** is formed, providing *p*-tolualdehyde as side product (detected by HRMS in ESI) finally.[14a,20]

Conclusions

In conclusion, we have developed a facile synthesis of 4-aryl tetralones through a photo-catalytic cyclization of styrenes under very simple reaction conditions. Although this transformation generated the corresponding products with modest yields, the synthetic method utilized green oxygen source and clean energy, which accord with requirement of green and eco-sustainable chemistry. There are advantages with catalytic amount of Mes-Acr$^+$ as catalyst, commercial available starting materials, green oxidant, clean energy, simple operation and mild reaction conditions by comparing with the reported methods (Table S1 of ESI for detail).[3b,3c,4] Meanwhile, this one-pot platform could expect to be as high synthetic utility. Further development of other photocatalytic annulations is currently underway.

Experimental section

General remarks

All reactions were conducted in clean glassware with magnetic stirring. CH_3CN was dried and freshly distilled from calcium hydride under nitrogen atmosphere. Chromatographic purification was performed on silica gel (100–200 mesh) and analytical thin layer chromatography (TLC) on silica gel 60-F_{254} (Qindao, China), which was detected by fluorescence. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured with a Bruker AC 400 spectrometer with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet). High resolution mass spectra were obtained with an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI. EPR spectra were recorded at room temperature using a Bruker A300 spectrometer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

Typical procedure for the synthesis of 4-aryl tetralones

To a stirred solution of styrene (0.50 mmol) in 2.0 mL of CH_3CN, Mes-Acr$^+$ (0.0125 mmol) was added. The reaction mixture was carried out under O_2 atmosphere with blue LED irradiation at room temperature for 16 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (30:1 petroleum ether/EtOAc) to give the pure product.

Characterization data for all products

Compound 2a. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 3H), 6.99 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 4.23 (dd, J = 4.8, 6.8 Hz, 1H), 2.72–2.64 (m, 1H), 2.59–2.52 (m, 1H), 2.46–2.38 (m, 1H), 2.33 (s, 3H), 2.27–2.19 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 146.4, 144.4, 140.7, 136.3, 130.6, 129.9, 129.3, 128.4, 128.0, 127.2, 44.8, 36.4, 31.9, 21.7, 21.0. HRMS (ESI) calcd for $C_{18}H_{18}O$ $(M+H)^+$: 251.1436; Found: 251.1430.

Compound 2b. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.19–7.13 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 4.26 (dd, *J* = 4.8, 6.8 Hz, 1H), 2.71–2.52 (m, 6H), 2.48-2.40 (m, 1H), 2.29–2.20 (m, 1H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.17 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 150.6, 146.4, 142.5, 140.9, 130.8, 128.8, 128.4, 128.0, 127.3, 126.7, 44.8, 36.3, 31.9, 29.0, 28.4, 15.4, 15.0. HRMS (ESI) calcd for $C_{20}H_{22}O$ $(M+H)^+$: 279.1749; Found: 279.1753.

Compound 2c. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.87–5.85 (m, 3H), 6.43 (d, *J* = 2.0 Hz, 1H), 4.21 (dd, *J* = 4.4, 8.0 Hz 1H), 3.80 (s, 3H), 3.74 (s, 3H), 2.70–2.63 (m, 1H), 2.59–2.52 (m, 1H), 2.45–2.37 (m, 1H), 2.28–2.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 163.7, 158.4, 149.1, 135.5, 129.6, 129.5, 126.5, 114.0, 113.6, 113.2, 55.3, 55.2, 44.8, 36.4, 31.9. HRMS (ESI) calcd for $C_{18}H_{18}O_3$ $(M+H)^+$: 283.1334; Found: 283.1330.

Compound 2d. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.85–6.82 (m, 3H), 6.42 (d, *J* = 2.0 Hz, 1H), 4.18 (dd, *J* = 4.4, 8.0 Hz, 1H), 4.04–3.92 (m, 4H), 2.70–2.63 (m, 1H), 2.59–2.51 (m, 1H), 2.43–2.36 (m, 1H), 2.27–2.18 (m, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 163.1, 157.7, 149.2, 135.4, 129.5, 129.4, 126.3, 114.5, 114.1, 113.6, 63.6, 63.4, 44.8, 36.5, 32.0, 14.8, 14.5. HRMS (ESI) calcd for $C_{20}H_{22}O_3$ $(M+H)^+$: 311.1647; Found: 311.1644.

Compound 2e. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.23–7.21 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 4.28–4.25 (m, 1H), 2.93–2.79 (m, 2H), 2.70–2.62 (m, 1H), 2.58–2.51 (m, 1H), 2.49–2.41 (m, 1H), 2.29–2.21 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 6H), 1,17 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 155.1, 147.1, 146.3, 140.9, 131.0, 128.4, 127.6, 127.3, 126.5, 125.2, 44.8, 36.2, 34.2, 33.6, 31.9, 23.9, 23.9, 23.6, 23.4. HRMS (ESI) calcd for $C_{22}H_{26}O$ $(M+H)^+$: 307.2062; Found: 307.2069.

Compound 2f. White solid. Mp: 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.04–6.99 (m, 3H), 4.31–4.28 (m, 1H), 2.68–2.60 (m, 1H), 2.57–2.43 (m, 2H), 2.31–2.23 (m, 1H), 1.31 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 157.2, 149.4, 145.9, 140.4, 130.6, 128.1, 126.9, 126.4, 125.3, 124.3, 44.7, 36.0, 35.1, 34.4, 31.7, 31.3, 30.9. HRMS (ESI) calcd for $C_{24}H_{30}O$ $(M+H)^+$: 335.2375; Found: 335.2373.

Compound 2g. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.37–7.30 (m, 3H), 7.26–7.24 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 4.32 (dd, *J* = 4.8, 8.0 Hz, 1H), 2.77–2.70 (m, 1H), 2.66–2.58 (m, 1H), 2.51–2.43 (m, 1H), 2.34–2.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 146.2, 143.7, 133.5, 132.8, 129.5, 128.6, 128.6, 127.1, 127.0, 126.8, 45.3, 36.7, 31.8. HRMS (ESI) calcd for $C_{16}H_{14}O$ $(M+H)^+$: 223.1123; Found: 223.1122.

Compound 2h. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 6.4, 8.8 Hz, 1H), 7.11–7.01 (m, 5H), 6.62 (dd, *J* = 2.0, 8.8 Hz, 1H), 4.26 (dd, *J* = 4.0, 8.4 Hz, 1H), 2.76–2.69 (m, 1H), 2.66–2.58 (m, 1H), 2.48–2.40 (m, 1H), 2.31–2.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 167.1 (d, *J* = 254.3 Hz), 163.0 (d, *J* = 244.5 Hz), 149.3 (d, *J* = 8.4 Hz), 138.6 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 9.7 Hz), 130.0 (d, *J* = 8.0 Hz), 129.4 (d, *J* = 2.8 Hz), 115.8 (d, *J* = 22.0 Hz), 115.8 (d, *J* = 21.2 Hz), 114.9 (d, *J* = 21.9 Hz), 44.9 (d, *J* = 1.1 Hz), 36.7, 31.1 (d, *J* = 0.9 Hz). HRMS (ESI) calcd for $C_{16}H_{12}F_2O$ $(M+H)^+$: 259.0934; Found: 259.0933.

Compound 2i. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.34–7.31 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 0.8 Hz, 1H), 4.25 (dd, *J* = 4.4, 8.0 Hz, 1H), 2.75–2.68 (m, 1H), 2.65–2.58 (m, 1H), 2.48–2.40 (m, 1H), 2.30–2.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 147.3, 141.3, 140.1, 133.0, 131.1, 129.8, 129.2, 129.0, 128.9, 127.8, 44.7, 36.5, 31.6. HRMS (ESI) calcd for $C_{16}H_{12}Cl_2O$ $(M+H)^+$: 291.0343; Found: 291.0348.

Compound 2j. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.51–7.46 (m, 3H), 7.10 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 4.24 (dd, *J* = 4.4, 8.0 Hz, 1H), 2.74–2.67 (m, 1H), 2.65–2.57 (m, 1H), 2.47–2.40 (m, 1H), 2.29–2.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 147.2, 141.8, 132.2, 132.0, 131.5, 130.8, 130.1, 129.0, 129.0, 121.1, 44.6, 36.4, 31.6. HRMS (ESI) calcd for $C_{16}H_{12}Br_2O$ $(M+H)^+$: 378.9333; Found: 378.9329.

Compound 2l. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.21 (m, 2H), 7.17–7.07 (m, 3H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 4.52–4.49 (m, 1H), 2.78–2.59 (m, 5H), 2.41–2.34 (m, 4H), 2.27–2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 147.7, 142.1, 141.1, 135.9, 132.4, 131.8, 130.7, 130.6, 128.6, 127.4, 126.5, 126.2, 42.4, 38.6, 29.4, 23.3, 19.5. HRMS (ESI) calcd for $C_{18}H_{18}O$ $(M+H)^+$: 251.1436; Found: 251.1437.

Compound 2m+2m'. Coloress oil. δ 8.06 (d, *J* = 7.6 Hz, 1H, 2m), 7.93 (s, 1H, 2m'), 7.40 (d, *J* = 7.6 Hz, 1H, 2m), 7.34 (t, *J* = 7.6 Hz, 1H, 2m), 7.27–7.20 (m, 2H, 2m'), 7.17 (t, *J* = 7.6 Hz, 1H, 2m), 7.09 (d, *J* = 7.6 Hz, 1H, 2m'), 7.04 (d, *J* = 7.6 Hz, 1H, 2m), 6.94 (s, 1H, 2m'), 6.90–6.88 (m, 2H, 2m'), 6.84 (s, 1H, 2m), 6.78 (d, *J* = 7.6 Hz, 1H, 2m), 4.44 (s, 1H, 2m), 4.24 (s, 1H, 2m'), 2.76–2.70 (m, 1H, 2m'), 2.63–2.51 (m, 2H, 2m'), 2.63–2.51 (m, 2H, 2m), 2.48–2.42 (m, 1H, 2m'), 2.48–2.42 (m, 1H, 2m), 2.39 (s, 3H, 2m'), 2.33 (s, 3H, 2m'), 2.29–2.25 (m, 1H, 2m), 2.29 (s, 3H, 2m), 2.11 (s, 3H, 2m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 198.4, 143.8, 143.6, 143.4, 141.5, 138.2, 138.1, 137.0, 136.7, 135.7, 134.5, 133.3, 132.5, 129.5, 129.2, 128.9, 128.4, 128.3, 127.4, 127.3, 127.1, 126.9, 125.6, 125.3, 125.0, 44.9, 40.9, 36.8, 33.3, 31.9, 30.8, 21.4, 21.4, 20.9, 19.2. HRMS (ESI) calcd for $C_{18}H_{18}O$ $(M+H)^+$: 251.1436; Found: 251.1435.

Compound 2n. Coloress solid. Mp: 141–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.19 (s, 1H), 6.83 (s, 1H), 6.58 (s, 2H), 4.34 (s, 1H), 2.57–2.51 (m, 2H), 2.44–2.37 (m, 4H), 2.22 (s, 7H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 141.7, 140.7, 137.8, 136.9, 136.7, 136.4, 133.1, 128.1, 126.0, 125.1, 40.6, 33.5, 30.9, 21.3, 20.9, 19.2. HRMS (ESI) calcd for $C_{20}H_{22}O$ $(M+H)^+$: 279.1749; Found: 279.1748.

Compound 2o. Coloress solid. Mp: 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 6.8 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.33 (s, 1H), 4.54–4.53 (m, 1H), 2.70–2.66 (m, 4H), 2.48–2.42 (m, 5H), 2.10–2.05 (m, 4H), 1,97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 145.4, 139.5, 138.8,

135.2, 134.7, 134.3, 132,5, 132.3, 130.7, 130.6, 128.5, 127.1, 38.5, 35.3, 27.4, 23.6, 21.0, 19.2, 18.8. HRMS (ESI) calcd for $C_{20}H_{22}O$ $(M+H)^+$: 279.1749; Found: 279.1751.

Compound 2p. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 1H), 6.23 (s, 2H), 4.57–4.56 (m, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.81 (s, 3H), 3.74 (s, 6H), 3,53 (m, 3H), 2.63–2.44 (m, 3H), 2.24–2.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 153.1, 152.7, 150.7, 147.5, 138.9, 136.7, 132.7, 128.3, 105.4, 104.9, 60.8, 60.7, 56.1, 56.1, 56.0, 37.9, 33.6, 30.8. HRMS (ESI) calcd for $C_{22}H_{26}O_7$ $(M+H)^+$: 403.1757; Found: 403.1759.

Compound 2q. Coloress oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.14–7.07 (m, 5H), 6.69 (s, 1H), 4.30 (dd, *J* = 4.4, 8.4 Hz, 1H), 2.77–2.70 (m, 1H), 2.66–2.58 (m, 1H), 2.48–2.40 (m, 1H), 2.30–2.28 (m, 4H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 169.4, 168.7, 154.6, 149.5, 148.0, 140.6, 130.5, 129.5, 129.1, 122.2, 121.8, 120.8, 45.0, 36.8, 31.9, 21.1, 21.0. HRMS (ESI) calcd for $C_{20}H_{18}O_5$ $(M+H)^+$: 339.1232; Found: 339.1239.

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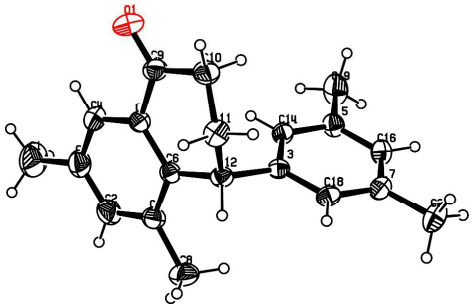

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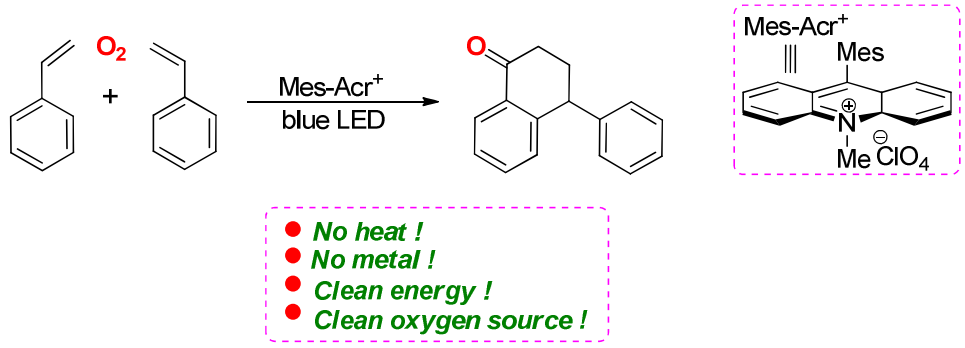
Direct construction of 4-aryl tetralones via visible-light-induced cyclizations of styrenes with molecular oxygen

Kuai Wang,[a] Ling-Guo Meng,*[,a] Qi Zhang,[a] and Lei Wang*[,a,b]

Abstract: A direct synthesis of 4-aryltetralones from aromatic alkenes and O_2 using acridinium as photocatalyst under visible light irradiation was developed.



[a] *Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P R China; E-mail: leiwang@chnu.edu.cn*

Tel.: +86-561-380-2069; fax: +86-561-309-0518

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P R China*