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Photoredox-Catalyzed Dimerization of Arylalkenes *via* an Oxidative [4+2] Cycloaddition Sequence: Synthesis of Naphthalene Derivatives

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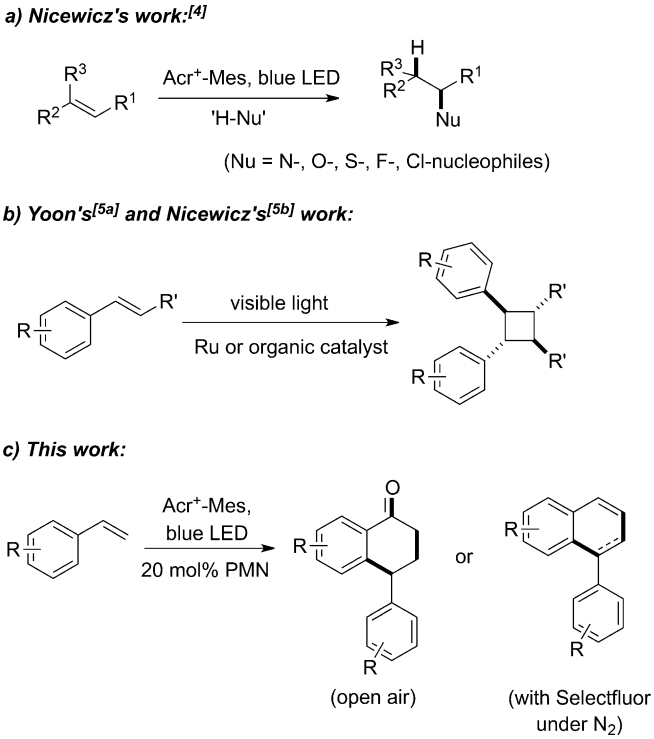
Abstract: We report a radical cation [4+2] annulation of arylalkenes to afford naphthalene derivatives using an organic photosensitizer (9-mesityl-10-methylacridinium perchlorate) under visible light photocatalysis. In the presence of oxygen (in the air), the oxidative dimerization/intramolecular [4+2] cycloaddition of two alkene molecules provides 3,4-dihydronaphthalen-1(2*H*)-ones in good to high yields. Under a nitrogen atmosphere, (dihydro)naphthalenes were attained in moderate to excellent yields by using Selectfluor as the oxidant. The transformation proceeds *via* a tandem dimeric electrophilic addition/Friedel–Crafts cyclization/radical coupling/elimination sequence. This approach represents a mild and straightforward assembly of the naphthalene skeleton using a visible light photocatalytic cascade strategy.

Keywords: cascade reaction; [4+2] cycloaddition; naphthalene derivatives; radical cations; styrene derivatives; visible light photocatalysis

Introduction

Alkenes are important building blocks in synthetic chemistry, as they generally undergo addition and polymerization reactions under thermal conditions.[1] In the past decade, visible light photocatalysis has attracted considerable attention due to the environmental compatibility and versatility in promoting a large number of synthetically important reactions.[2] Under photocatalytic conditions, alkene precursors are readily oxidized or reduced to polar radical species *via* photoinduced electron transfer (PET) processes.[3] For electron-rich alkenes, the radical cations that are generated are expected to possess unusual reactivities compared to neutral alkenes. For example, a carbocation is responsible for an electrophilic reaction, and a carbon radical can undergo radical addition or coupling. As such, Nicewicz and co-workers developed an elegant anti-Markovnikov olefin hydrofunctionalization under photochemical conditions, employing a dual catalyst system comprised of an organic single electron photooxidant and a redox-active H-atom donor (Scheme 1a).[4] In 2012, Yoon and co-workers



Scheme 1. Photocatalyzed reactions of alkenes based on radical cation intermediate.

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reported on visible light-mediated transition metal (Ru)-catalyzed [2+2] cycloaddition reactions based on radical cation intermediates.[5a] Afterwards, the [2 + 2] dimerization of alkenes *via* an organic single electron oxidant-electron relay system was presented by Nicewicz et al. (Scheme 1b).[5b] As claimed in their work, when a photocatalyst with a high reduction potential was used, cycloreversion was accompanied in the [2+2] cycloaddition reactions of alkenes. In our research, we wish to achieve the oxidative linear homocoupling of alkenes and further transformations through the selection of an appropriate photocatalyst. As a result, we found a new, formal [4+2] annulation of arylalkenes under photoirradiated conditions with an organic photosensitizer, Acr^+-Mes (9-mesityl-10-methylacridinium perchlorate).[6] With the incorporation of a keto functionality during the annulation cascade sequence, 3,4-dihydronaphthalen-1(2*H*)-ones were assembled in the open air whereas, under an N_2 atmosphere, (dihydro)naphthalenes were constructed efficiently by using Selectfluor as the oxidant (Scheme 1c).[7] 3,4-Dihydronaphthalen-1(2*H*)-ones (1-tetralones) are found in natural products that exhibit interesting biological, pharmaceutical and medicinal properties.[8] 3,4-Dihydronaphthalen-1(2*H*)-one and its substituted derivatives are also important starting materials and intermediates in organic synthesis.[9] On the other hand, the (1,2-dihydro)naphthalene skeleton can be found in many lignans, a class of natural products existing in plants.[10] Due to their biological importance and application as organic synthons, their synthesis has attracted considerable attention.[11] Herein, a mild and straightforward assembly of the naphthalene skeleton starting from simple styrene derivatives, via a photocatalyzed cascade process of electrophilic addition/Friedel–Crafts cyclization/radical coupling/elimination, has been developed.

Results and Discussion

Initially, we performed the reaction of styrene **1a** ($E_{ox} = +1.97$ V *vs.* SCE)[12] in the open air under different reaction conditions (Table 1). With 1 mol% of Acr^+-Mes ($E^*_{red} = +2.08$ V *vs.* SCE)[12] as the organic photocatalyst, various solvents were screened (entries 1–6). No reaction occurred in polar solvents such as DMSO (entry 1), and only a benzaldehyde side product was observed in DMF solution (entry 2). In THF, we detected the formation of the addition/cyclization product **2a**, although the yield was low (entry 3). Dichloromethane and nitromethane gave improved yields (entries 4 and 5), and an even better yield of 62% was obtained in acetonitrile (entry 6). Considering that dioxygen is required in the catalytic cycle (see the Supporting 1nformation), we used an

Table 1. Optimization of the reaction conditions[a]

1a **2a**

Entry	Catalyst	Co-oxidant	Solvent	Time [h]	Yield [%][b]
1	Acr^+-Mes	air	DMSO	48	n.r.
2	Acr^+-Mes	air	DMF	48	0
3	Acr^+-Mes	air	THF	48	21
4	Acr^+-Mes	air	DCM	48	30
5	Acr^+-Mes	air	$MeNO_2$	48	59
6	Acr^+-Mes	air	MeCN	40	62
7	Acr^+-Mes	O_2 balloon	MeCN	24	60
8	**Acr^+-Mes**	**air, PMN**	**MeCN**	**40**	**87**
9	Acr^+-Mes	air, PMN	MeCN (0.1 M)	40	84
10	Acr^+-Mes	air, PMN	MeCN (1.0 M)	24	71
11	Acr^+-Mes (5 mol%)	air, PMN	MeCN	40	76
12	TPT	air, PMN	MeCN	40	32
13	none	air, PMN	MeCN	48	n.r.
14[c]	Acr^+-Mes	air, PMN	MeCN	48	n.r.
15[d]	Acr^+-Mes	PMN	MeCN	48	n.r.

[a] Reactions were conducted with **1a** (0.5 mmol), catalyst (1 mol%), and PMN (20 mol%) in 1.0 mL of dry solvent (0.5 M) at room temperature in the open air with a 12 W blue LED irradiated, unless otherwise noted. n.r. = no reaction.
[b] Isolated yield.
[c] The reaction was conducted in the dark.
[d] The reaction was conducted under an N_2 atmosphere.

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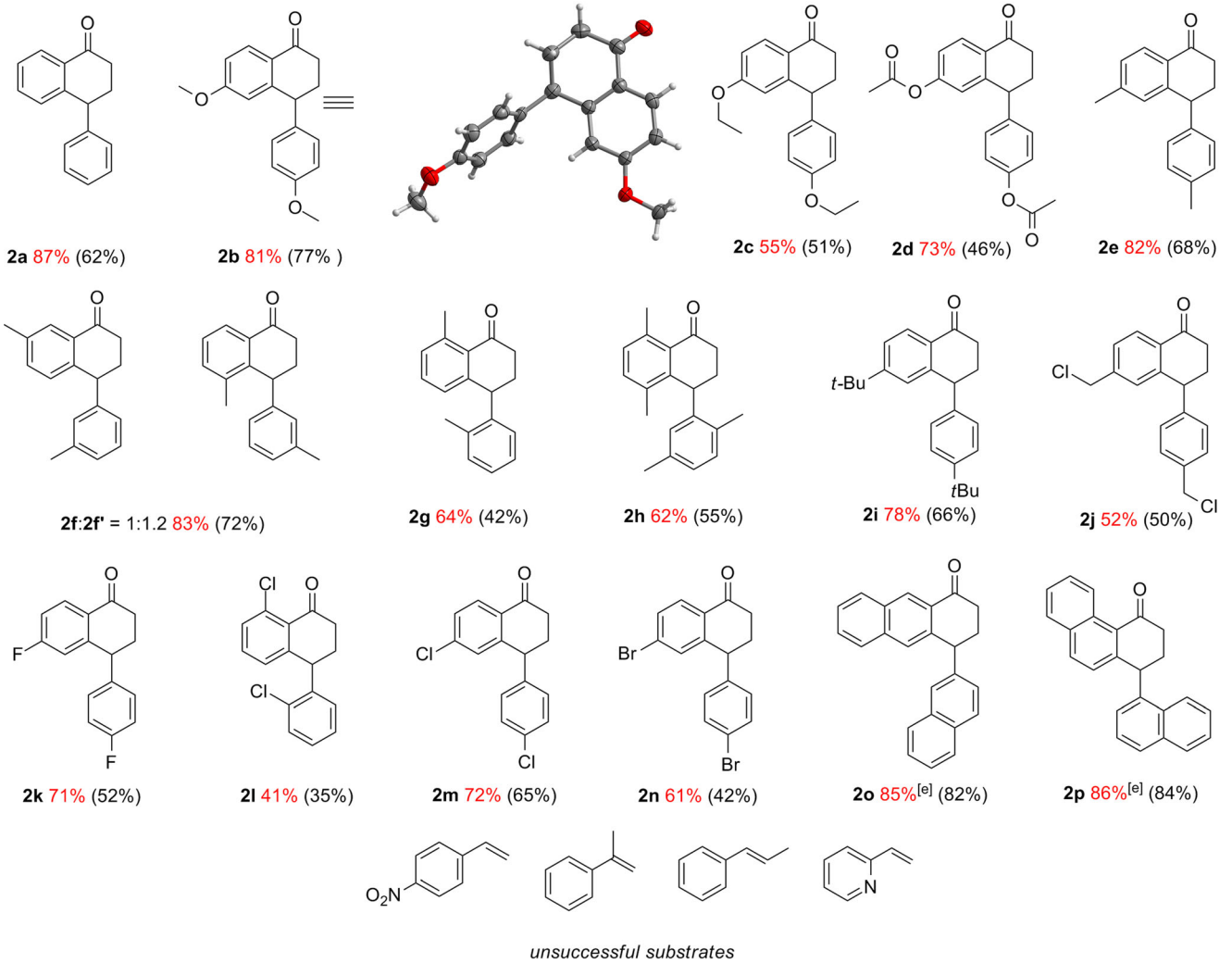
O_2 balloon to perform the reaction. However, a large amount of aldehyde side product was produced within 24 h (entry 7). We surmised that a high O_2 concentration may quench the radical cation intermediate rapidly. With the introduction of PMN (2-phenylmalononitrile) as a co-oxidant, the reaction in the open air afforded product **2a** in 87% yield (entry 8). Encouraged by these results, the solution concentration was changed. It was found that both higher and lower concentrations led to decreased yields (entries 9 and 10). On increasing the catalyst amount to 5 mol%, the reaction turned out to be complicated, with **2a** being

Table 2. Radical cation [4+2] annulation: synthesis of dihydronaphthalenones **2**.[a,b,c,d]



[a] Reactions were conducted with 1 mol% Acr+-Mes, and 20 mol% PMN in 0.5 M MeCN in the open air with a 12 W blue LED.
[b] Isolated yield.
[c] Data in the parenthesis corresponds to the yield in the absence of PMN.
[d] Arylaldehyde by-products can be observed in the reactions.
[e] With DCM as the solvent.

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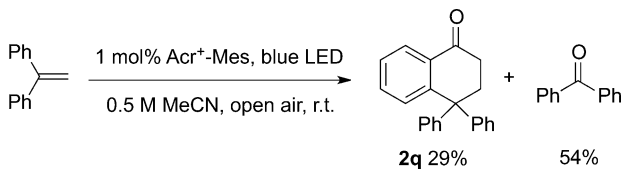
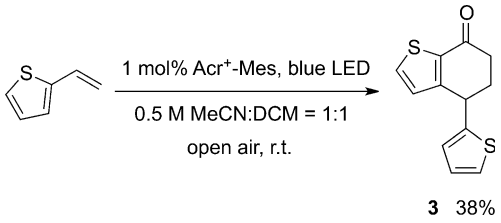
formed only in 76% yield (entry 11). The use of 2,4,6-triphenylpyrylium tetrafluoroborate (TPT, 1 mol%) ($E^*_{red} = +2.28$ V *vs.* SCE)[12] was also examined as the organic photosensitizer, rather than Acr^+-Mes, but the yield decreased significantly (entry 12). Comparatively, in the absence of the photosensitizer, light or air, no target molecule was observed, validating the photocatalytic nature of this process (entries 13–15).

We next investigated the scope of the radical cation [4+2] annulation reaction. It was found that various substituted styrenes ($E_{ox} = +1.15 \sim 2.50$ V *vs.* SCE for general alkenes)[12] are suitable precursors for the explored reaction (Table 2).[13] Substrates with electron-donating methoxy, ethoxy and acetyloxy groups at the 4-position of the styrene gave the desired products, **2b–d**, in moderate to high yields. The structure of **2b** was confirmed by X-ray single-crystal diffraction.[14] Alkyl substituents on the phenyl ring include *o*-, *m*-, *p*-methyl, 2,4-dimethyl, *tert*-butyl and chloromethyl (**2e–j**). Note that an inseparable regioisomer mixture of **2f** and **2f′** was obtained with a 3-methylstyrene substrate. Halogens (F, Cl, and Br) were well tolerated, giving the corresponding dihalogenated products **2k–n** in good yields. Interestingly, 1-vinyl- and 2-vinylnaphthalene also worked well, affording the corresponding 2,3-dihydrophenanthrenone and 3,4-dihydroanthracenone (**2o** and **2p**) in 85% and 86% yield, respectively.[15]

Styrenes containing a strong electron-withdrawing group, such as a nitro group, were unable to react under the standard conditions. Only trace amounts of 4-nitrobenzaldehyde were produced. This indicates that the generation of the corresponding radical cation is feasible but that the intermolecular electrophilic addition is difficult due to the electron-poor character of 4-nitrostyrene. α-Methylstyrene and β-methylstyrene were not competent partners. Acetophenone and benzaldehyde were generated, along with intact substrates. It seems that the quenching of the resulting radical cation by molecular oxygen to give the aldehyde product is much faster than the [4+2] annulation reaction in this case. 1,1-Diphenylethene could afford 4,4-diphenyl-3,4-dihydronaphthalen-1(2*H*)-one (**2q**), but in low yield (Scheme 2). Heteroarylalkenes were also subjected to the reaction sequence. As a result, the reaction of 2-thienylethene performed in the open air gave 4-(thiophen-2-yl)-5,6-dihydrobenzo[*b*]thiophen-7(4*H*)-one (**3**) in 38% yield



Scheme 2. The cation radical [4+2] annulation of 1,1-diphenylethene.

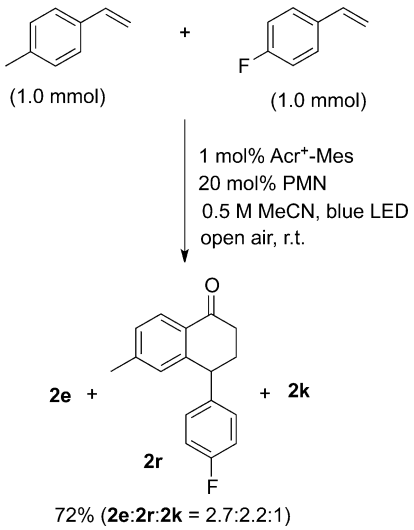


Scheme 3. The cation radical [4+2] annulation of 2-thienylethylene.

(Scheme 3).[16,17] However, electron-poor 2-pyridylethylene failed to afford the corresponding [4+2] annulation product, similar to the result observed for 4-nitrostyrene. In the reaction of a non-terminal styrene and a conjugated diene such as *trans*-stilbene or (*E*)-buta-1,3-dien-1-ylbenzene, oxidative cleavage of the C=C double bond to yield the corresponding benzaldehydes and cinnamaldehyde was observed. No reaction takes place when an enyne (e.g., but-3-en-1-yn-1-ylbenzene) was used as the substrate under otherwise identical conditions.

The cross-over radical cation [4+2] reaction using two styrenes with different substituents on the phenyl ring (e.g., a 1:1 mixture of 4-methylstyrene and 4-fluorostyrene) was also conducted (Scheme 4). The corresponding homodimerized and cross-dimerized products **2e**, **2r** and **2k** were obtained as an inseparable mixture in a 72% total isolated yield.[18]

To reveal the source of the ketone oxygen, we performed the photoredox reaction of **1a** in the presence of $H_2{}^{18}O$ (5.0 equiv.) (Scheme 5). As a result, dihydronaphthalenone **2a** was produced in 79% yield without any ^{18}O enrichment of its ketone oxygen. Together with the experimental results of the reaction conduct-



Scheme 4. Cross-over radical cation [4+2] reaction. Yields refer to the combined yields of all tetralone products. Ratio was determined by ^{1}H NMR analysis of the crude product.

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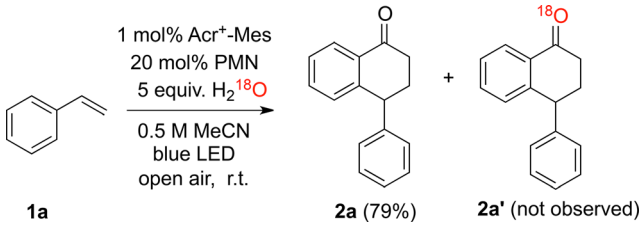
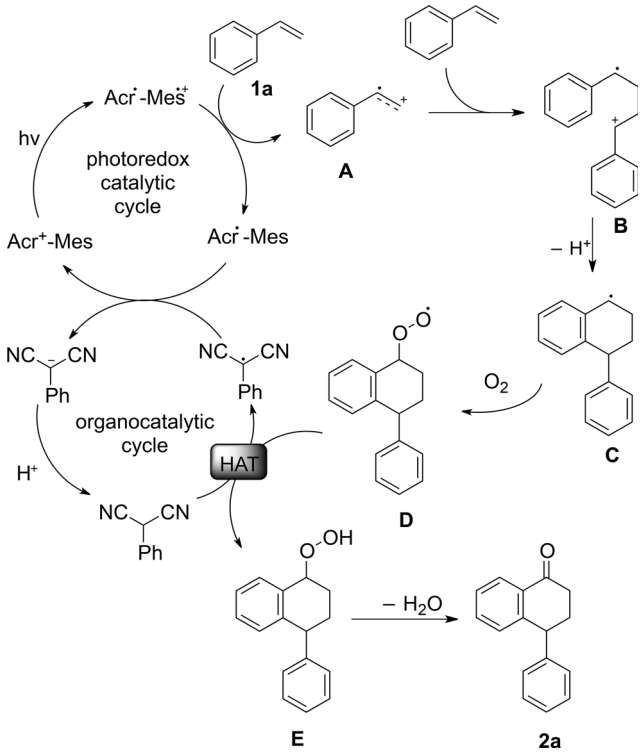


Scheme 5. Control experiments.

ed under an N_2 atmosphere (Table 1, entry 15), it was concluded that the ketone oxygen originates from molecular oxygen in the air (see the Supporting Information, Scheme S1).

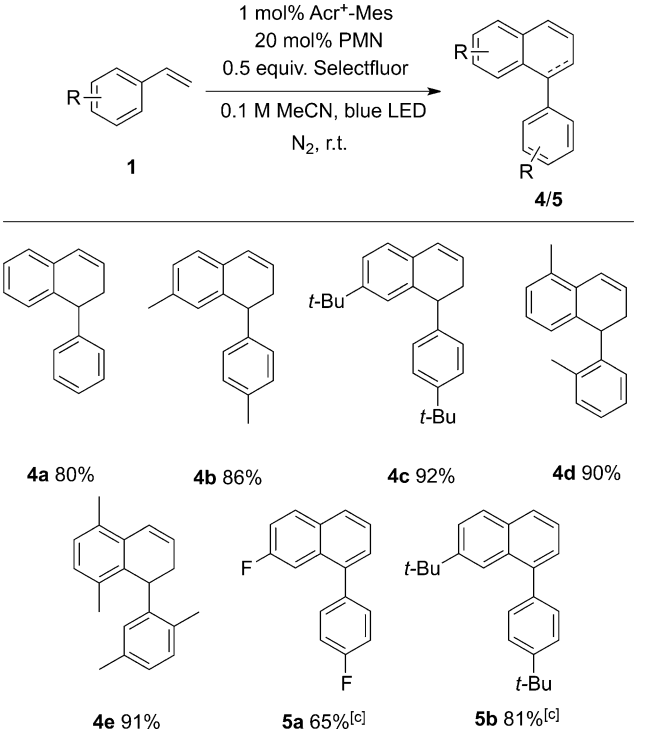
On the basis of all the results described above and previous work by Nicewicz[4] and Yoon,[5] we propose a plausible mechanism for the formation of naphthalenones (Scheme 6). Under irradiation, the acridinium catalyst is excited to (Acr$^+$-Mes)* which oxidizes the alkene **1a**, generating a 1,2-radical cation **A** and the reduced acridine radical. Electrophilic trapping of intermediate **A** by a neutral alkene molecule gives rise to distal 1,4-radical cation **B**, which readily undergoes Friedel–Crafts annulation to form intermediate **C** *via* deprotonation. Radical **C** would further react with triplet O_2 to produce peroxide radical **D**.[19] The H-atom transfer from PMN to intermediate **D** followed by the elimination of water[20] affords naphthalenone **2a** as the final product. On the other hand, the malononitrile radical that is derived from the H-atom donor PMN would oxidize the organic photosensitizer to finish the photoredox catalytic cycle. The malononitrile anion would then accept a proton to complete the organocatalytic cycle.



Scheme 6. Proposed cascade mechanism for the formation of dihydronaphthalenones **2**. HAT = hydrogen atom transfer.

We also investigated the oxidative [4+2] cycloaddition reaction under an N_2 atmosphere (for the optimization conditions, see the Supporting Information, Table S1). In the presence of Selectfluor (0.5 equiv.), various dihydronaphthalenes **4a–e** were obtained in good to high yields (80–92%, Table 3). It was found that naphthalenes **5a** and **5b** were produced when 1.0 equiv. of Selectfluor was used. Similar to the results mentioned above, only electron-rich terminal alkynes are efficient for the radical cation [4+2] annulations. The possible mechanism for the formation of 1,2-dihydronaphthalenes **4** and naphthalenes **5** is depicted in Scheme 7. The reaction involves a sequential electrophilic addition, Friedel–Crafts cyclization, fluorination and HF elimination. In the case of 1.0 equiv. of Selectfluor, 1,2-dihydronaphthalenes **4** were oxidized to yield naphthalenes **5** *via* dehydrogenative aromatization. A fluorine atom transfer[21] was proposed as the key factor for the formation of (1,2-dihydro)-

Table 3. Radical cation [4+2] annulation: synthesis of (dihydro)naphthalenes **4** and **5**.[a,b]



[a] Reactions were conducted with 1 mol% Acr$^+$-Mes, 20 mol% PMN, 0.5 equiv. Selectfluor in 0.1 M MeCN under N_2 with a 12 W blue LED for 12 h.
[b] Isolated yield.
[c] 1.0 equiv. Selectfluor was used.

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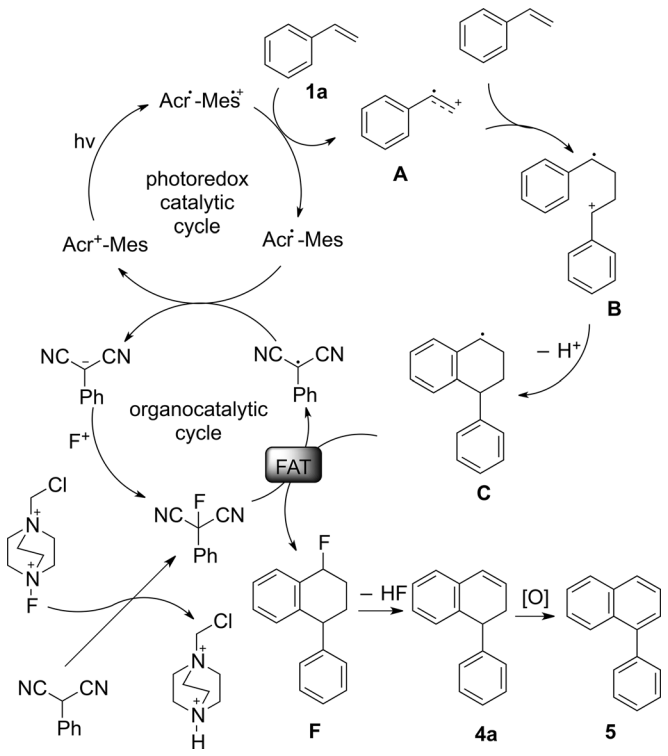

Scheme 7. Proposed cascade mechanism for the formation of (dihydro)naphthalenones **4** and **5**. FAT = fluorine atom transfer.

naphthalenes. In an isolated reaction of 2-phenylmalononitrile with Selectfluor (1.0 equiv.), 2-fluoro-2-phenylmalononitrile could be obtained in 60% yield (see the Supporting Information, Figure S1), which partly supports the involvement of 2-fluoro-2-phenylmalononitrile in the proposed mechanism.

Finally, we tried to synthesize the bioactive bisnorlignans pachypostaudin-A and pachypostaudin-B[22] utilizing the photocatalytic cascade protocol, but were unsuccessful (see the Supporting Information, Scheme S2).

Conclusions

In conclusion, we have developed a mild and straightforward approach for the construction of naphthalene derivatives starting from simple styrene derivatives under visible light photoredox conditions. A variety of substituted arylalkenes and 2-thienylethylene afforded the corresponding formal [4+2] annulation products in high efficiency. A mechanism involving electrophilic addition/Friedel–Crafts cyclization/radical coupling/elimination was proposed. On the one hand, in the presence of oxygen (in the air), the oxidative dimerization/[4+2] cycloaddition of two alkene molecules provided dihydronaphthalenones in good to high yields. On the other hand, under an N_2 atmosphere and with Selectfluor as the oxidant, (dihydro)naphthalenes were attained in moderate to excellent yields. The photocatalytic cascade protocol represents a novel, mild and straightforward approach towards synthesizing naphthalene derivatives including 3,4-dihydronaphthalen-1(2*H*)-ones, dihydronaphthalenes and naphthalenes starting from simple styrene derivatives.

Experimental Section

General

Dry reagents were purchased from commercial sources and used without further treatment. The products were purified by column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Varian spectrometer at 500 MHz and 125 MHz, respectively, with TMS as the internal standard. Elemental analyses were measured on an E-2400 analyzer (Perkin–Elmer). Mass spectra were recorded on an Agilent 1100 LCMsD mass spectrometer.

Synthesis and Analytical Data of 2–5

General procedure for the preparation of 2a–q and 3 (2a as an example): To a solution of 9-mesityl-10-methylacridinium perchlorate (1 mol%, 4.2 mg) and 2-phenylmalononitrile (20 mol%, 28.4 mg) in dry MeCN (2.0 mL, with 4 Å MS), styrene **1a** (1.0 mmol, 104.2 mg) was added. The reaction mixture was stirred at room temperature and irradiated by a 12 W blue LED for 40 h. After the starting material **1a** had been consumed as indicated by TLC, the reaction mixture was poured into water and then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, petroleum ether:ethyl acetate = 100:1) to give **2a** as a white solid; yield: 96.6 mg (87%).

General procedure for the preparation of 4 (4b as an example): To a solution of 9-mesityl-10-methylacridinium perchlorate (1 mol%, 4.2 mg), 2-phenylmalononitrile (20 mol%, 28.4 mg) and Selectfluor (0.5 equiv., 177.1 mg) in dry MeCN (10 mL), 4-methylphenylene **1e** (1.0 mmol, 118.2 mg) was added. The mixture was degassed using three freeze-pump-thaw cycles under nitrogen. The reaction mixture was stirred at room temperature and irradiated by a 12 W blue LED for 12 h. After the starting material **1e** had been consumed as indicated by TLC, the reaction mixture was poured into water and then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, petroleum ether) to give **4b** as a colorless oil; yield: 100.7 mg (86%).

4-Phenyl-3,4-dihydronaphthalen-1(2*H*)-one (2a): White solid; yield: 97 mg (87%); mp 70–72 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.29–2.34 (m, 1H), 2.44–2.51 (m, 1H), 2.59–2.65 (m, 1H), 2.70–2.76 (m, 1H), 4.29–4.32 (m,

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1H), 6.98 (d, J=7.5 Hz, 1H), 7.11 (d, J=7.5 Hz, 2H), 7.25–7.27 (m, 1H), 7.31–7.37 (m, 3H), 7.43 (t, J=7.0 Hz, 1H), 8.12 (d, J=7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 31.8, 36.7, 45.3, 126.8, 127.0, 127.1, 128.6, 128.6, 129.5, 132.8, 133.6, 143.7, 146.3, 198.1; HR-MS (ESI): m/z=223.1118, calcd. for $C_{16}H_{14}O$ $[M+H]^+$: 223.1123.

6-Methoxy-4-(4-methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2b): White solid; yield: 114 mg (81%); mp 119–120 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.23–2.28 (m, 1H), 2.40–2.44 (m, 1H), 2.54–2.60 (m, 1H), 2.64–2.70 (m, 1H), 3.75 (s, 3H), 3.81 (s, 3H), 4.19–4.21 (m, 1H), 6.44 (d, J= 2.5 Hz, 1H), 6.87 (d, J=8.5 Hz, 3H), 7.04 (d, J=8.5 Hz, 2H), 8.09 (d, J=8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=32.0, 36.4, 44.8, 55.3, 55.4, 113.2, 113.6, 114.0, 126.5, 129.5, 129.6, 135.5, 149.1, 158.4, 163.7, 197.1; HR-MS (ESI): m/z=283.1343, calcd. for $C_{18}H_{18}O_3$ $[M+H]^+$: 283.1334.

6-Ethoxy-4-(4-ethoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2c): White solid; yield: 85 mg (55%); mp 95–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.37 (t, J=8.0 Hz, 3H), 1.42 (t, J=7.0 Hz, 3H), 2.20–2.27 (m, 1H), 2.37–2.43 (m, 1H), 2.53–2.59 (m, 1H), 2.64–2.70 (m, 1H), 3.93–3.98 (m, 2H), 4.00–4.04 (m, 2H), 4.16–4.19 (m, 1H), 6.42 (d, J= 2.0 Hz, 1H), 6.83–6.86 (m, 3H), 7.02 (d, J=9.0 Hz, 2H), 8.07 (d, J=9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 14.6, 14.8, 32.0, 36.5, 44.8, 63.4, 63.6, 113.5, 114.1, 114.5, 126.3, 129.5, 129.5, 135.4, 149.2, 157.7, 163.1, 197.1; HR-MS (ESI): m/z=311.1641, calcd. for $C_{20}H_{22}O_3$ $[M+H]^+$: 311.1647.

4-(7-Acetoxy-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)-phenyl acetate (2d): White solid; yield: 123 mg (73%); mp 62–63 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.25 (s, 3H), 2.27–2.30 (m, 1H), 2.31 (s, 3H), 2.43–2.47 (m, 1H), 2.60–2.67 (m, 1H), 2.72–2.77 (m, 1H), 4.28–4.31 (m, 1H), 6.69 (d, J=2.0 Hz, 1H), 7.07 (d, J=9.0 Hz, 2H), 7.09–7.11 (m, 1H), 7.14 (d, J=8.5 Hz, 2H), 8.16 (d, J=9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.1, 21.1, 32.0, 36.9, 45.0, 120.9, 121.9, 122.2, 129.2, 129.5, 130.5, 140.7, 148.0, 149.5, 154.6, 168.8, 169.5, 196.7; HR-MS (ESI): m/z=339.1226, calcd. for $C_{20}H_{18}O_5$ $[M+H]^+$: 339.1232.

6-Methyl-4-(*p*-tolyl)-3,4-dihydronaphthalen-1(2*H*)-one (2e): Colorless oil; yield: 103 mg (82%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.23–2.27 (m, 1H), 2.92 (s, 3H), 2.35 (s, 3H), 2.41–2.46 (m, 1H), 2.55–2.60 (m, 1H), 2.66–2.72 (m, 1H), 4.22–4.24 (m, 1H), 6.81 (s, 1H), 6.99 (d, J=8.0 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 7.17 (s, 1H), 8.01 (d, J= 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.0, 21.8, 31.9, 36.4, 44.8, 127.2, 128.0, 128.5, 129.3, 129.9, 130.5, 136.3, 140.7, 144.5, 146.4, 198.1; HR-MS (ESI): m/z=251.1443, calcd. for $C_{18}H_{18}O$ $[M+H]^+$: 251.1436.

7-Methyl-4-(*m*-tolyl)-3,4-dihydronaphthalen-1(2*H*)-one (2f) and 5-methyl-4-(*m*-tolyl)-3,4-dihydronaphthalen-1(2*H*)-one (2f'): White solid; yield: 104 mg (83%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.10 (s, 3H), 2.23–2.27 (m, 2H), 2.28(s, 3H), 2.32 (s, 3H), 2.38 (s, 3H), 2.40–2.46 (m, 2H), 2.56–2.58 (m, 2H), 2.59–2.63(m, 1H), 2.69–2.75 (m, 1H), 4.21–4.23 (m, 1H), 4.42 (d, J=2.5 Hz, 1H), 6.76 (d, J= 7.5 Hz, 1H), 6.83 (s, 1H), 6.88 (t, J=7.5 Hz, 2H), 6.93 (s, 1H), 7.02 (d, J=7.5 Hz, 1H), 7.07 (d, J=7.5 Hz, 1H), 7.14 (t, J=7.5 Hz, 1H), 7.20 (t, J=7.5 Hz, 1H), 7.24–7.26 (m, 1H), 7.31 (t, J=7.5 Hz, 1H), 7.38 (d, J=7.0 Hz, 1H), 7.92 (s, 1H), 8.04(d, J=8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=19.3, 20.9, 21.4, 21.4, 30.7, 31.9, 33.3, 36.8, 40.9, 44.9, 125.0, 125.3, 125.6, 126.9, 127.1, 127.3, 127.4, 128.3, 128.4, 128.9, 129.2, 129.5, 132.5, 133.2, 134.5, 135.7, 136.6, 137.0, 138.1, 138.2, 141.4, 143.4, 143.5, 143.8, 198.5, 198.9; HR-MS (ESI): m/z=251.1445, 251.1441, calcd. for $C_{18}H_{18}O$ $[M+H]^+$: 251.1436.

8-Methyl-4-(*o*-tolyl)-3,4-dihydronaphthalen-1(2*H*)-one (2g): Colorless oil; yield: 80 mg (64%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.22–2.25 (m, 1H), 2.36–2.40 (m, 1H), 2.42 (s, 3H), 2.61–2.66 (m, 1H), 2.71 (s, 3H), 2.72–2.76 (m, 1H), 4.50–4.53 (m, 1H), 6.76 (d, J=8.0 Hz, 1H), 6.81 (d, J= 7.5 Hz, 1H), 7.08–7.17 (m, 3H), 7.22–7.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=19.6, 23.5, 29.3, 38.6, 42.4, 126.2, 126.6, 127.4, 128.6, 130.6, 130.8, 131.8, 132.4, 135.9, 141.1, 142.1, 147.7, 200.3; HR-MS (ESI): m/z=251.1429, calcd. for $C_{18}H_{18}O$ $[M+H]^+$: 251.1436.

4-(2,5-Dimethylphenyl)-5,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one(2h): White solid; yield: 86 mg (62%); mp 96–98 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.98 (s, 3H), 2.04–2.09 (m, 1H), 2.11 (s, 3H), 2.42–2.45 (m, 1H), 2.46 (s, 3H), 2.47–2.49 (m, 1H), 2.64–2.69 (m, 1H), 2,71 (s, 3H), 4.53–4.55 (m, 1H), 6.34 (s, 1H), 6.92 (d, J=7.5 Hz, 1H), 7.10 (t, J=7.5 Hz, 2H), 7.20 (d, J=7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=18.9, 19.2, 21.1, 23.7, 27.4, 35.3, 38.5, 127.1, 128.5, 130.6, 130.7, 132.3, 132.6, 134.4, 134.7, 135.2, 138.8, 139.5, 145.4, 201.2; HR-MS (ESI): m/z=279.1758, calcd. for $C_{20}H_{22}O$ $[M+H]^+$: 279.1749.

6-(*tert*-Butyl)-4-[4-(*tert*-butyl)phenyl]-3,4-dihydronaphthalen-1(2*H*)-one (2i): White solid; yield: 130 mg (78%); mp 99–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.24 (s, 9H), 1.32 (s, 9H), 2.26–2.31 (m, 1H), 2.45–2.57 (m, 2H), 2.61–2.67(m, 1H), 4.29–4.31 (m, 1H), 7.00 (d, J=8.5 Hz, 2H), 7.05 (s, 1H), 7.32 (d, J=8.0 Hz, 2H), 7.39–7.41(m, 1H), 8.05 (d, J=8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=30.9, 31.3, 31.7, 34.4, 35.1, 36.0, 44.6, 124.3, 125.3, 126.4, 126.9, 128.1, 130.5, 140.4, 145.9, 149.4, 157.3, 198.2; HR-MS (ESI): m/z=335.2366, calcd. for $C_{24}H_{30}O$ $[M+H]^+$: 335.2375.

6-(Chloromethyl)-4-[4-(chloromethyl)phenyl]-3,4-dihydronaphthalen-1(2*H*)-one (2j): Colorless oil; yield: 83 mg (52%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.27–2.31 (m, 1H), 2.45–2.49 (m, 1H), 2.59–2.65 (m, 1H), 2.69–2.75 (m, 1H), 4.31–4.33 (m, 1H), 4.49 (s, 2H), 4.60 (s, 2H), 6.99 (s, 1H), 7.11 (d, J=7.5 Hz, 2H), 7.37 (d, J=8.0 Hz, 2H), 7.40 (d, J= 8.0 Hz, 1H), 8.12 (d, J=8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.7, 36.4, 44.9, 45.3, 45.8, 127.4, 127.8, 128.9, 129.0, 129.4, 132.6, 136.1, 142.9, 143.6, 146.2, 197.3; HR-MS (ESI): m/z=319.0651, calcd. for $C_{18}H_{16}Cl_2O$ $[M+H]^+$: 319.0656.

6-Fluoro-4-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2k): White solid; yield: 92 mg (71%); mp 67–69 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.24–2.31 (m, 1H), 2.42–2.47 (m, 1H), 2.60–2.66 (m, 1H), 2.70–2.76 (m, 1H), 4.24–4.27 (m, 1H), 6.60–6.62 (m, 1H), 7.02–7.07 (m, 3H), 7.08–7.11 (m, 2H), 8.13–8.16 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.9, 36.7, 44.9, 114.9, 115.6, 115.8, 129.3, 130.0, 130.3, 138.6, 149.3, 161.8, 165.9, 196.3; HR-MS (ESI): m/z= 259.0942, calcd for $C_{16}H_{12}F_2O$ $[M+H]^+$: 259.0934.

8-Chloro-4-(2-chlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2l): Colorless oil; yield: 59 mg (41%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.34–2.37 (m, 1H), 2.42–2.44 (m, 1H), 2.68–2.71 (m, 2H), 4.82–4.84 (m, 1H), 6.83 (d, J= 7.5 Hz, 1H), 6.89 (d, J=7.5 Hz, 1H), 7.16 (t, J=7.0 Hz, 1H), 7.22 (t, J=7.0 Hz, 1H), 7.30 (t, J=7.5 Hz, 1H), 7.39

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(d, J=8.0 Hz, 1H), 7.45 (d, J=8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=28.5, 37.7, 42,6, 127.1, 128.3, 128.3, 130.0, 130.0, 130.6, 131.0, 133.0, 134.0, 134.3, 140.5, 147.9, 196.4; HR-MS (ESI): m/z=291.0348, calcd. for $C_{16}H_{12}Cl_2O$ $[M+H]^+$: 291.0343.

6-Chloro-4-(4-chlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2m): White solid: yield: 105 mg (72%); mp 64–65 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.25–2.28 (m, 1H), 2.42–2.46 (m, 1H), 2.59–2.66 (m, 1H), 2.69–2.74 (m, 1H), 4.23–4.26 (m, 1H), 6.93 (d, J=1.0 Hz, 1H), 7.06 (d, J=10.0 Hz, 2H), 7.31–7.35 (m, 3H), 8.05 (d, J=8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.6, 36.5, 44.6, 127.8, 128.9, 129.0, 129.2, 129.8, 131.1, 132.9, 140.1, 141.3, 147.3, 196.6; HR-MS (ESI): m/z=291.0350, calcd. for $C_{16}H_{12}Cl_2O$ $[M+H]^+$: 291.0343.

6-Bromo-4-(4-bromophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2n): White solid; yield: 116 mg (61%); mp 86–88 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.24–2.27 (m, 1H), 2.42–2.46 (m, 1H), 2.62–2.65 (m, 1H), 2.68–2.71 (m, 1H), 4.22–4.24 (m, 1H), 6.99 (d, J=8.5 Hz, 2H), 7.11 (s, 1H), 7.47–7.52 (m, 3H), 7.97 (d, J=8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.6, 36.5, 44.7, 121.1, 129.0, 129.1, 130.2, 130.8, 131.5, 132.0, 132.2, 141.8, 147.3, 196.7; HR-MS (ESI): m/z=380.9303, calcd. for $C_{16}H_{12}Br_2O$ $[M+H]^+$: 380.9313.

4-(Naphthalen-2-yl)-3,4-dihydroanthracen-1(2*H*)-one (2o): White solid; yield: 137 mg (85%); mp 124–126 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.50–2.54 (m, 1H), 2.56–2.60 (m, 1H), 2.63–2.71 (m, 1H), 2.73–2.80 (m, 1H), 5.23–5.24 (m, 1H), 7.26 (d, J=8.5 Hz, 1H), 7.34–7.43 (m, 4H), 7.52 (t, J=7.5 Hz, 1H), 7.57 (d, J=8.0 Hz, 1H), 7.78–7.82 (m, 2H), 7.87–7.91 (m, 3H), 8.28 (d, J=8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.0, 33.2, 40.7, 122.6, 125.8, 126.0, 126.2, 126.6, 126.9, 126.9, 127.5, 127.7, 128.1, 128.3, 128.6, 128.8, 130.8, 131.1, 132.2, 133.2, 136.2, 139.6, 143.0, 198.7; HR-MS (ESI): m/z=323,1425, calcd. for $C_{24}H_{18}O$ $[M+H]^+$: 323.1436.

1-(Naphthalen-1-yl)-2,3-dihydrophenanthren-4(1*H*)-one (2p): White solid; yield: 138 mg (86%); mp 124–125 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.53–2.56 (m, 1H), 2.70–2.81 (m, 3H), 5.31–5.32 (m, 1H), 6.89 (d, J=7.0 Hz, 1H), 7.14 (m, J=8.5 Hz, 1H), 7.30 (t, J=7.5 Hz, 1H), 7.53–7.59 (m, 3H), 7.70 (t, J=7.5 Hz, 1H), 7.77 (d, J=8.5 Hz, 1H), 7.82 (d, J=8.0 Hz, 1H), 7.89 (d, J=8.5 Hz, 1H), 7.93 (d, J=8.0 Hz, 1H), 8.17. (d, J=8.5 Hz, 1H), 9.51 (d, J=8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=29.3, 37.8, 42.8, 123.3, 125.3, 125.8, 126.3, 126.4, 127.0, 127.2, 127.6, 127.7, 128.3, 128.4, 129.0, 129.2, 131.1, 131.4, 133.0, 134.2, 134.6, 138.7, 148.1, 200.7; HR-MS (ESI): m/z=323,1431, calcd. for $C_{24}H_{18}O$ $[M+H]^+$: 323.1436.

4,4-Diphenyl-3,4-dihydronaphthalen-1(2*H*)-one (2q): White solid; yield: 43 mg (29%); mp 168–169 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.53 (t, J=6.5 Hz, 2H), 2.97 (t, J=6.5 Hz, 2H), 6.74–6.76 (m, 1H), 7.03–7.04 (t, 4H), 7.22–7.31 (m, 6H), 7.37–7.44 (m, 2H), 8.13–8.15 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=35.7, 36.9, 53.3, 126.8, 127.2, 127.6, 128.2, 129.2, 130.9, 132.8, 133.1, 145.7, 149.6, 197.9; HR-MS (ESI): m/z=299.1440, calcd. for $C_{22}H_{18}O$ $[M+H]^+$: 299.1436.

7-(Thiophen-2-yl)-6,7-dihydrobenzo[*b*]thiophen-4(5*H*)-one (3): White solid; yield: 45 mg (38%); mp 95–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.37–2.41 (m, 1H), 2.55–2.67 (m, 2H), 2.75–2.80 (m, 1H), 4.52–4.55 (m, 1H), 6.82 (d, J=3.5 Hz, 1H), 6.86 (d, J=5.0 Hz, 1H), 6.96–6.98 (m, 1H), 7.22–7.23 (m, 1H), 7.60 (d, J=5.0 Hz 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=34.0, 36.6, 38.1, 124.3, 125.3, 126.8, 128.6, 133.9, 136.6, 145.6, 153.6, 191.5; HR-MS (ESI): m/z=235.0244, calcd. for $C_{12}H_{10}OS_2$ $[M+H]^+$: 235.0251.

1-Phenyl-1,2-dihydronaphthalene (4a): Colorless oil; yield: 82 mg (80%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.62–2.67 (m, 2H), 4.14 (t, J=8.5 Hz, 1H), 5.98–6.02 (m, 1H), 6.54 (d, J=9.5 Hz, 1H), 6.81 (d, J=7.5 Hz, 1H), 7.07–7.11 (m, 2H), 7.18 (t, J=7.5 Hz, 1H), 7.22–7.25 (m, 3H), 7.31 (t, J=7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.9, 43.8, 126.1, 126.4, 126.8, 127.2, 127.2, 127.8, 128.0, 128.4, 128.4, 134.1, 137.8, 144.4; HR-MS (ESI): m/z=207.1169, calcd. for $C_{16}H_{14}$ $[M+H]^+$: 207.1174.

7-Methyl-1-(*p*-tolyl)-1,2-dihydronaphthalene (4b): Colorless oil; yield: 101 mg (86%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.22 (s, 3H), 2.34 (s, 3H), 2.56–2.59 (m, 1H), 2.61–2.65 (m, 1H), 4.05 (t, J=8.5 Hz, 1H), 5.90–5.93 (m, 1H), 6.51 (d, J=10 Hz, 1H), 6.66 (s, 1H), 6.97–7.01 (m, 2H), 7.07–7.13 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.0, 21.3, 32.2, 43.4, 126.0, 126.1, 127.3, 127.8, 128.2, 128.6, 129.1, 131.5, 135.9, 137.0, 137.9, 141.6; HR-MS (ESI): m/z=235.1495, calcd. for $C_{18}H_{18}$ $[M+H]^+$: 235.1487.

7-(*tert*-Butyl)-1-[4-(*tert*-butyl)phenyl]-1,2-dihydronaphthalene (4c): White solid; yield: 146 mg (92%); mp 71–72 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.22 (s, 9H), 1.31 (s, 9H), 2.57–2.62 (m, 1H), 2.67–2.72 (m, 1H), 4.10 (t, J=8 Hz, 1H), 5.89–5.93 (m, 1H), 6.51 (d, J=9.5 Hz, 1H), 6.93 (s, 1H), 7.05 (d, J=8 Hz, 1H), 7.11 (d, J=8 Hz, 2H), 7.21 (dd, J=2 Hz, J=8 Hz, 1H), 7.30 (d, J=8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.2, 31.4, 32.0, 34.4, 34.6, 43.2, 123.5, 125.1, 125.3, 125.7, 126.3, 127.7, 127.8, 131.5, 137.3, 141.5, 148.9, 150.2; HR-MS (ESI): m/z=319.2430, calcd. for $C_{24}H_{30}$ $[M+H]^+$: 319.2426.

5-Methyl-1-(*o*-tolyl)-1,2-dihydronaphthalene (4d): Colorless oil; yield: 105 mg (90%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.36 (s, 3H), 2.39 (s, 3H), 2.53–2.58 (m, 2H), 4.34–4.38 (m, 1H), 6.06–6.10 (m, 1H), 6.54 (d, J=7.5 Hz, 1H), 6.78 (d, J=10 Hz, 1H), 6.95 (t, J=7.5 Hz, 1H), 7.02 (d, J=7.5 Hz, 1H), 7.10 (t, J=5 Hz, 1H), 7.12–7.17 (m, 2H), 7.21 (t, J=4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=19.3, 19.8, 30.1, 40.0, 124.7, 125.3, 126.1, 126.2, 126.9, 127.6, 128.3, 128.5, 130.4, 132.6, 133.1, 136.2, 138.0, 142.1; HR-MS (ESI): m/z=235.1480, calcd. for $C_{18}H_{18}$ $[M+H]^+$: 235.1487.

5-Methyl-1-(*o*-tolyl)-1,2-dihydronaphthalene (4e): White solid; yield: 119 mg (91%); mp 107–108 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.96 (s, 3H), 2.10 (s, 3H), 2.34–2.38 (m, 1H), 2.40 (s, 3H), 2.45 (s, 3H), 2.80–2.86 (m, 1H), 4.35 (d, J=9 Hz, 1H), 5.76–5.79 (m, 1H), 6.42 (s, 1H), 6.77 (dd, J=3 Hz, J=10 Hz, 1H), 6.86 (d, J=7.5 Hz, 1H), 6.91 (d, J=7.5 Hz, 1H), 6.99 (d, J=7.5 Hz, 1H), 7.05 (d, J=8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=18.8, 19.1, 19.3, 21.2, 29.7, 34.6, 124.9, 125.2, 126.7, 128.3, 128.7, 129.1, 130.1, 130.9, 131.6, 132.7, 133.4, 134.9, 135.7, 141.0; HR-MS (ESI): m/z=263.1792, calcd. for $C_{20}H_{22}$ $[M+H]^+$: 263.1800.

7-Fluoro-1-(4-fluorophenyl)naphthalene (5a): White solid; yield: 78 mg (65%); mp 54–55 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.18–7.22 (t, 2H), 7.27–7.30 (m, 1H), 7.42–7.50 (m, 5H), 7.86 (d, J=8.5 Hz, 1H), 7.89–7.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=109.2, 115.4, 116.2, 124.6, 127.7, 130.7, 131.4, 132.6, 136.2, 138.7, 160.0, 161.4, 161.9,

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163.4; HR-MS (ESI): $m/z = 241.0824$, calcd. for $C_{16}H_{10}F_2$ $[M+H]^+$: 241.0829.

7-(*tert*-Butyl)-1-[4-(*tert*-butyl)phenyl]naphthalene (5b): Colorless oil; yield: 128 mg (81%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.33$ (s, 3H), 1.42 (s, 3H), 7.04 (d, $J = 6.5$ Hz, 1H), 7.44–7.52 (m, 5H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.79 (d, $J = 7.5$ Hz, 1H), 7.85 (d, $J = 8.5$ Hz, 1H), 7.96 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 31.2$, 31.5, 34.6, 35.0, 121.1, 124.5, 124.8, 125.1, 126.9, 127.1, 127.9, 129.7, 131.4, 132.1, 137.9, 140.1, 148.5, 150.0; HR-MS (ESI): $m/z = 317.2262$, calcd. for $C_{24}H_{28}$ $[M+H]^+$: 317.2269.

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References

[1] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry*, 5th edn., Springer, **2007**.

[2] For recent reviews on visible-light photocatalysis, see: a) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322; b) D. M. Schultz, T. P. Yoon, *Science* **2014**, *343*, 1239176; c) J. Xuan, W.-J. Xiao, *Angew. Chem.* **2012**, *124*, 6934; *Angew. Chem. Int. Ed.* **2012**, *51*, 6828; d) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102; e) D. Ravelli, M. Fagnoni, A. Albini, *Chem. Soc. Rev.* **2013**, *42*, 97; f) S. Fukuzumi, K. Ohkuboa, *Chem. Sci.* **2013**, *4*, 561; g) S. Fukuzumi, K. Ohkuboa, *Org. Biomol. Chem.* **2014**, *12*, 6059; h) Y. Xi, H. Yi, A. Lei, *Org. Biomol. Chem.* **2013**, *11*, 2387.

[3] In addition to polar radicals, diradicals may be produced from alkenes *via* an energy transfer mechanism. For representative examples, see: a) R. R. Islangulov, F. N. Castellano, *Angew. Chem.* **2006**, *118*, 6103; *Angew. Chem. Int. Ed.* **2006**, *45*, 5957; b) Z. Lu, T. P. Yoon, *Angew. Chem.* **2012**, *124*, 10475; *Angew. Chem. Int. Ed.* **2012**, *51*, 10329; c) Y.-Q. Zou, S.-W. Duan, X.-G. Meng, X.-Q. Hu, S. Gao, J.-R. Chen, W.-J. Xiao, *Tetrahedron* **2012**, *68*, 6914; d) E. P. Farney, T. P. Yoon, *Angew. Chem.* **2014**, *126*, 812; *Angew. Chem. Int. Ed.* **2014**, *53*, 793; e) K. Singh, S. J. Staig, J. D. Weaver, *J. Am. Chem. Soc.* **2014**, *136*, 5275; f) A. E. Hurtley, Z. Lu, T. P. Yoon, *Angew. Chem.* **2014**, *126*, 9137; *Angew. Chem. Int. Ed.* **2014**, *53*, 8991.

[4] a) D. S. Hamilton, D. A. Nicewicz, *J. Am. Chem. Soc.* **2012**, *134*, 18577; b) T. M. Nguyen, D. A. Nicewicz, *J. Am. Chem. Soc.* **2013**, *135*, 9588; c) A. J. Perkowski, D. A. Nicewicz, *J. Am. Chem. Soc.* **2013**, *135*, 10334; d) T. M. Nguyen, N. Manohar, D. A. Nicewicz, *Angew. Chem.* **2014**, *126*, 6312; *Angew. Chem. Int. Ed.* **2014**, *53*, 6198; e) D. J. Wilger, J.-M. Grandjean, T. R. Lammert, D. A. Nicewicz, *Nat. Chem.* **2014**, *6*, 720; f) N. A. Romero, D. A. Nicewicz, *J. Am. Chem. Soc.* **2014**, *136*, 17024.

[5] Radical cation [2+2] cycloaddition: a) M. A. Ischay, M. S. Ament, T. P. Yoon, *Chem. Sci.* **2012**, *3*, 2807; b) M. Riener, D. A. Nicewicz, *Chem. Sci.* **2013**, *4*, 2625; radical cation [4+2] cycloaddition: c) S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 19350; d) S. Lin, C. E. Padilla, M. A. Ischay, T. P. Yoon, *Tetrahedron Lett.* **2012**, *53* 3073; radical cation [2+2+2] cycloaddition: e) J. D. Parrish, M. A. Ischay, Z. Lu, S. Guo, N. R. Peters, T. P. Yoon, *Org. Lett.* **2012**, *14*, 1640.

[6] The organic photocatalyst Acr^+-Mes has found wide applications in visible light-mediated reactions. For selected examples, see: a) T.-T. Zeng, J. Xuan, W. Ding, K. Wang, L.-Q. Lu, W.-J. Xiao, *Org. Lett.* **2015**, *17*, 4070; b) J. Xuan, X.-D. Xia, T.-T. Zeng, Z.-J. Feng, J.-R. Chen, L.-Q. Lu, W.-J. Xiao, *Angew. Chem.* **2014**, *126*, 5759; *Angew. Chem. Int. Ed.* **2014**, *53*, 5653; c) X. Wu, C. Meng, X. Yuan, X. Jia, X. Qian, J. Ye, *Chem. Commun.* **2015**, *51*, 11864; d) J. D. Griffin, M. A. Zeller, D. A. Nicewicz, *J. Am. Chem. Soc.* **2015**, *137*, 11340.

[7] During our own investigations, a similar work was reported by Wang and co-workers, see: K. Wang, L.-G. Meng, Q. Zhang, L. Wang, *Green Chem.* **2016**, *18*, 2864.

[8] a) C. F. Schwender, S. Farber, C. Blaum, J. Shavel, *J. Med. Chem.* **1970**, *13*, 684; b) T. da Silva, L. M. X. Lopes, *Phytochemistry* **2004**, *65*, 751; c) V. F. de Andrade-Neto, T. Da Silva, L. M. Xavier Lopes, V. E. Do Rosário, F. De Pilla Varotti, A. U. Krettli, *Antimicrob. Agents Chemother.* **2007**, *51*, 2346; d) T-S. Wu, Y-L. Tsai, A. G. Damu, P-C. Kuo, P-L. Wu, *J. Nat. Prod.* **2002**, *65*, 1522; e) D. N. Quang, T. Hashimoto, M. Tanaka, M. Baumgartner, M. Stadler, Y. J. Asakawa, *Nat. Prod.* **2002**, *65*, 1869; f) D. A. Whiting, *Nat. Prod. Rep.* **1987**, *4*, 499.

[9] a) S. Ge, J. F. Hartwig, *J. Am. Chem. Soc.* **2011**, *133*, 16330; b) X.-J. Li, M. Li, W. Yao, H.-Y. Lu, Y. Zhao, C.-F. Chen, *RSC Adv.* **2015**, *5*, 18609; c) P. S. Poon, L. Bedoya, G. J. Churio, A. K. Banerjee, *Nat. Prod. Res.* **2014**, *28*, 1747; d) L. M. Deck, Q. Mgani, A. Martinez, A. Martinic, L. J. Whalen, D. L. V. Jagt, R. E. Royer, *Tetrahedron Lett.* **2012**, *53*, 373; e) W. Quaglia, M. Pigini, A. Piergentili, M. Giannella, F. Gentili, G. Marucci, A. Carrieri, A. Carotti, E. Poggesi, A. Leonardi, C. Melchiorre, *J. Med. Chem.* **2002**, *45*, 1633; f) K. Vukics, T. Fodor, J. Fischer, I. Fellegvári, S. Lévai, *Org. Process Res. Dev.* **2002**, *6*, 82.

[10] a) B. L. Yvon, P. K. Datta, T. N. Le, J. L. Charlton, *Synthesis* **2001**, *10*, 1556; b) P. K. Datta, C. Yau, T. S. Hooper, B. L. Yvon, J. L. Charlton, *J. Org. Chem.* **2001**, *66*, 8606; c) D. A. Whiting, *Nut. Prod. Rep.* **1990**, *7*, 349; d) E. C. N. Nono, P. Mkounga, V. Kuete, K. Marat, P. G. Hultin, A. E. Nkengfack, *J. Nat. Prod.* **2010**, *73*, 213; e) S. Suzuki, T. Umezawa, *J. Wood Sci.* **2007**, *53*, 273; f) B. T. Ngadjui, D. Lontsi, J. F. Ayafor, B. L. Sondengam, *Phytochemistry* **1989**, *28*, 231.

[11] For the synthesis of 1-tetralones, see: a) D.-M. Cui, M. Kawamura, S. Shimada, T. Hayashi, M. Tanaka, *Tetrahedron Lett.* **2003**, *44*, 4007; b) J. Vercouillie, M. Abarbri, J-L. Parrain, A. Duchêne, J. Thibonnet, *Synth. Commun.* **2004**, *34*, 3751; c) J. C. T. Reddel, K. E. Lutz,

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A. B. Diagne, R. J. Thomson, *Angew. Chem.* **2014**, *126*, 1419; *Angew. Chem. Int. Ed.* **2014**, *53*, 1395; d) W. S. Murphy, S. Wattanasin, *J. Chem. Soc. Perkin Trans. 1* **1981**, 2920; e) V. A. Koptyug, T. P. Andreeva, *J. Org. Chem. USSR* **1971**, *7*, 2490; f) I. B. Repinskaya, N. A. Koryabkina, Z. S. Makarova, V. A. Koptyug, *J. Org. Chem. USSR* **1982**, *18*, 754; g) I. B. Repinskaya, D. D. Barkhutova, Z. S. Makarova, A. V. Alekseeva, V. A. Koptyug, *J. Org. Chem. USSR* **1985**, *21*, 759; h) I. B. Repinskaya, K. Y. Koltunov, M. M. Shakirov, L. N. Shchegoleva, V. A. Koptyug, *Russ. J. Org. Chem.* **1993**, *29*, 803; i) K. Y. Koltunov, *Tetrahedron Lett.* **2008**, *49*, 3891; j) K. Y. Koltunov, A. N. Chernov, G. K. S. Prakash, G. A. Olahc, *Chem. Pharm. Bull.* **2012**, *60*, 722; k) A. Liard, B. Quiclet-Sire, R. N. Saicic, S. Z. Zard, *Tetrahedron Lett.* **1997**, *38*, 1759. For the synthesis of (Dihydro)naphthalenes: l) F. R. Mayo, *J. Am. Chem. Soc.* **1968**, *90*, 1289; m) K. Maeda, E. J. Farrington, E. Galardon, B. D. John, J. M. Brown, *Adv. Synth. Catal.* **2002**, *344*, 104; n) H. Ikeda, T. Nomura, K. Akiyama, M. Oshima, H. D. Roth, S. Tero-Kubota, T. Miyashi, *J. Am. Chem. Soc.* **2005**, *127*, 14497; o) C. E. Rye, D. Barker, *J. Org. Chem.* **2011**, *76*, 6636; p) J. K. Rout, C. V. Ramana, *J. Org. Chem.* **2012**, *77*, 1566; q) J. Freudenberg, A. C. Uptmoor, F. Rominger, U. H. F. Bunz, *J. Org. Chem.* **2014**, *79*, 11787; r) W. Li, H. Liu, J. Xu, P. Zang, Q. Liu, W. Li, *Eur. J. Org. Chem.* **2014**, *16*, 3475.

[12] For the redox potential of the photocatalysts and alkene substrates, see: H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett* **2016**, *27*, 714.

[13] In the absence of PMN, product **2** can be obtained, albeit in lower yields. In this case, molecular oxygen participates the catalytic cycle. Please see the Supporting Information.

[14] CCDC 1064103 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[15] a) F. M. Hauser, Y-J. Xu, *Org. Lett.* **1999**, *1*, 335; b) J. G. Allen, S. J. Danishefsky, *J. Am. Chem. Soc.* **2001**, *123*, 351; c) C. J. Abelt, T. Sun, R. K. Everett, *Photochem. Photobiol. Sci.* **2011**, *10*, 618; d) A. M. Green, C. J. Abelt, *J. Phys. Chem. B* **2015**, *119*, 3912.

[16] a) S. S. Samanta, S. C. Ghosh, A. De, *J. Chem. Soc. Perkin Trans. 1* **1997**, 3673; b) J. Messinger, L. Hirvelä, B. Husen, L. Kangas, P. Koskimies, O. Pentikäinen, P. Saarenketo, H. Thole, *Mol. Cell. Endocrinol.* **2006**, *248*, 192.

[17] 2-Thienylethene has poor solubility in MeCN. Thus, DCM was added to enhance the solubility.

[18] The formation of the homodimerized and cross-dimerized products may be due to the existence of the following equilibrium in the reaction system.

[19] a) S. Zhu, A. Das, L. Bui, H. Zhou, D. P. Curran, M. Rueping, *J. Am. Chem. Soc.* **2013**, *135*, 1823; b) Y. Su,

L. Zhang, N. Jiao, *Org. Lett.* **2011**, *13*, 2168; c) K. Ohkubo, S. Fukuzumi, *Org. Lett.* **2000**, *2*, 3647; d) K. Ohkubo, K. Mizushima, R. Iwata, K. Souma, N. Suzuki, S. Fukuzumi, *Chem. Commun.* **2010**, *46*, 601.

[20] a) N. Tada, Y. Ikebata, T. Nobuta, S.-I. Hirashima, T. Miura, A. Itoh, *Photochem. Photobiol. Sci.* **2012**, *11*, 616; b) N. Tada, K. Hattori, T. Nobuta, T. Miura, A. Itoh, *Green Chem.* **2011**, *13*, 1669.

[21] For examples of photoredox reactions involving fluorine atom transfer, see: a) J.-B. Xia, C. Zhu, C. Chen, *J. Am. Chem. Soc.* **2013**, *135*, 17494; b) M. Rueda-Becerril, O. Mahé, M. Drouin, M. B. Majewski, J. G. West, M. O. Wolf, G. M. Sammis, J.-F. Paquin, *J. Am. Chem. Soc.* **2014**, *136*, 2637.

[22] D. A. Whiting, *Nat. Prod. Rep.* **1990**, *7*, 345.

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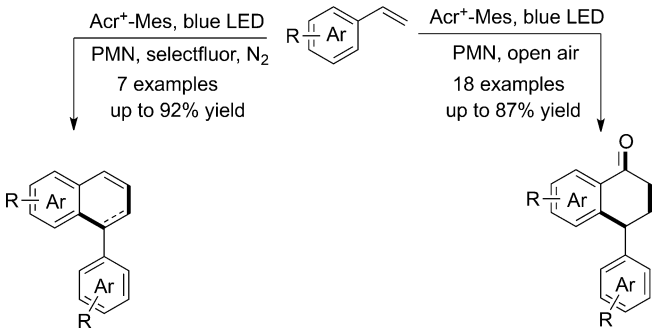

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