

Facile access to synthetically challenging aryl-naphthalenes *via* photoenolization/Diels–Alder/aromatization one-pot sequence

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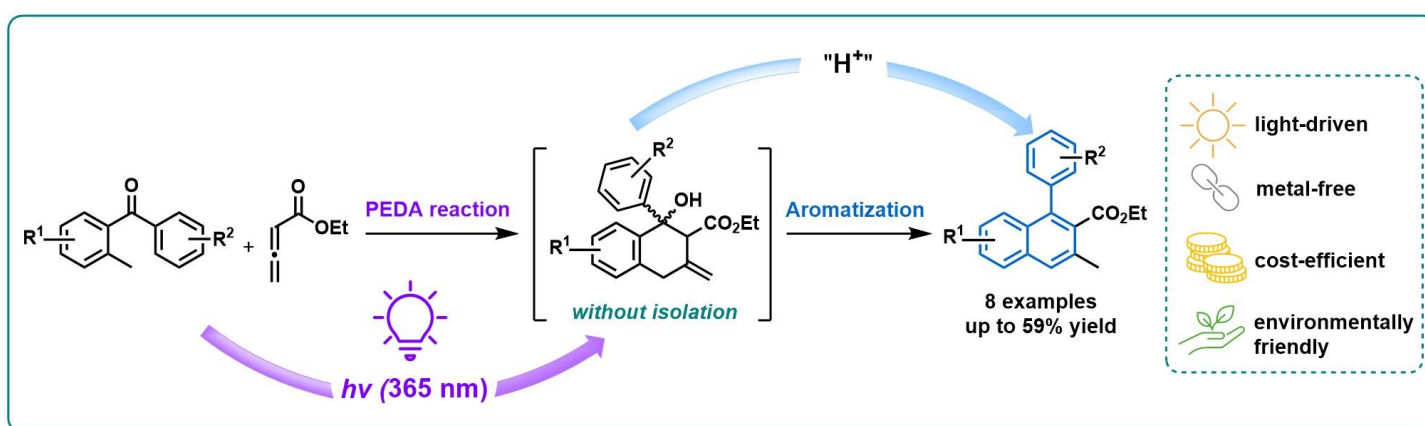
Received 02-12-2026

Accepted 03-22-2026

Published on line 04-22-2026

Abstract

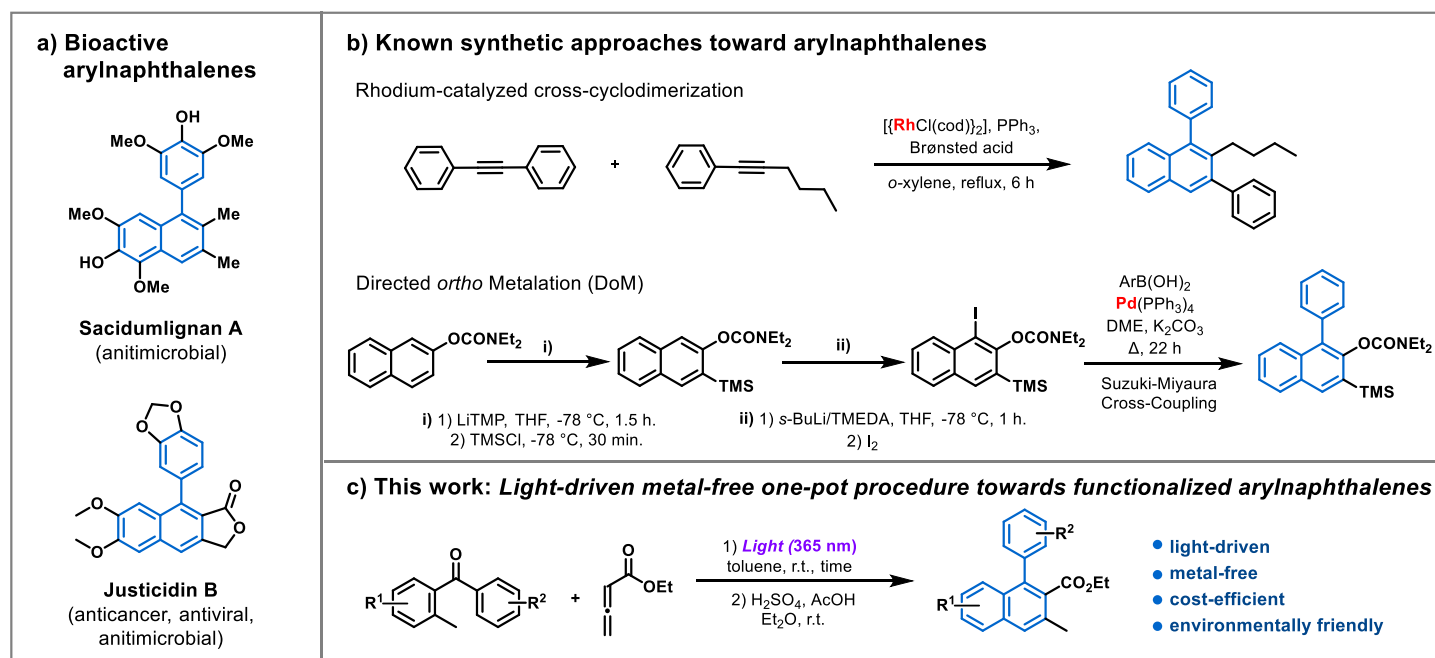
Arylnaphthalenes are valuable structural motifs in bioactive compounds with anticancer, antioxidant, and antiviral activities. Despite their importance, existing synthetic approaches typically rely on expensive transition-metal catalysts or harsh reaction conditions, limiting functional-group tolerance and sustainability. Here we report a first light-driven, metal-free strategy for the synthesis of highly substituted aryl-naphthalenes *via* a photoenolization/Diels–Alder (PEDA) domino process followed by *in situ* aromatization. Upon UV irradiation (365 nm), 2-methylbenzophenones generate reactive photoenols that engage in cycloaddition and subsequent aromatization, delivering functionalized aryl-naphthalenes in overall yields of up to 59%. This operationally simple, one-pot protocol provides a cost-efficient and versatile alternative for constructing aryl-naphthalene architectures under mild conditions.



Keywords: Photoenolization, Diels–Alder reaction, Aromatization, One-pot synthesis, Arylnaphthalenes

Introduction

Naphthalenes are privileged scaffolds found in numerous natural products and pharmacologically active compounds. Their derivatives exhibit broad therapeutic effects, including antimicrobial¹, anticancer² and anti-inflammatory³ properties, making them valuable building blocks for synthetic drugs. In particular, aryl naphthalenes have attracted increased interest due to their pharmacological effects in cancer chemotherapy and their antioxidant and antiviral properties.⁴ Examples of such biologically active aryl naphthalenes include Sacidumlignan A (Scheme 1a), which exhibits antimicrobial activities against two Gram-positive bacteria *in vitro*.⁵ Another very popular representative of aryl naphthalenes is Justicidin B, which can be isolated from plants like *Justicia*⁶ or perennial *Linum perenne*.⁷ It exhibits not only activity against cervical cancer cells⁸ and the Zika virus⁹ but also antiviral¹⁰ and antimicrobial¹¹ activities.



Scheme 1. a) Selected representatives of bioactive aryl naphthalenes. b) Representative synthetic methods to access aryl naphthalenes. c) Light-driven photoenolization/Diels–Alder/aromatization one-pot procedure toward functionalized aryl naphthalenes presented in this work.

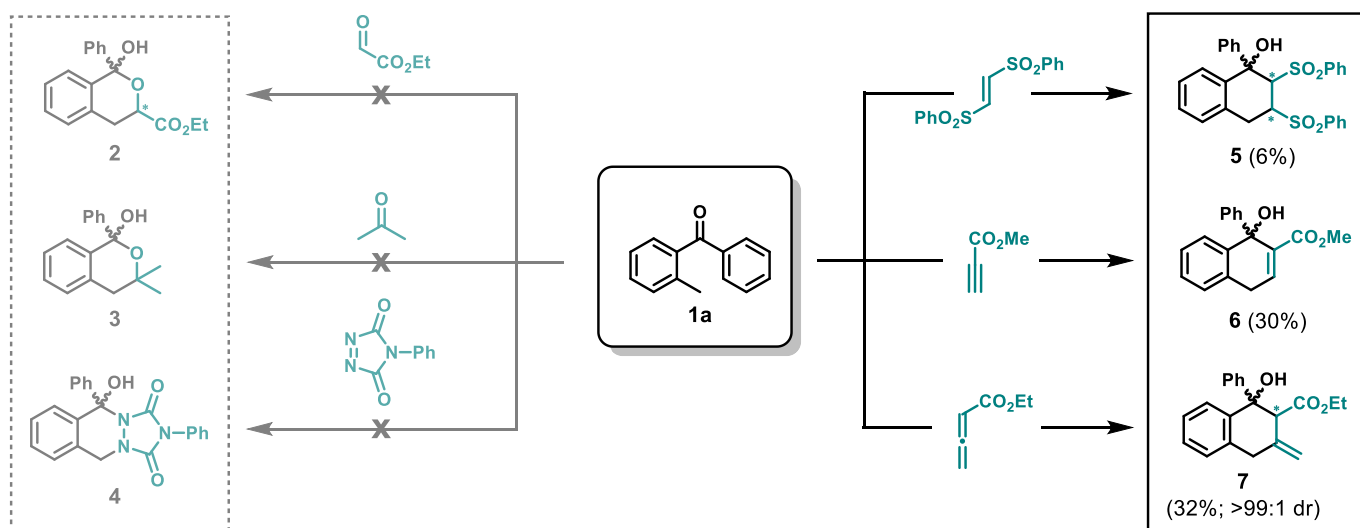
Current strategies towards highly substituted aryl naphthalenes often rely on transition metal-catalyzed coupling reactions, such as the rhodium-catalyzed dimerization of two internal alkynes (Scheme 1b).¹² However, these products are limited to the use of two substituted internal alkynes and require an expensive rhodium catalyst.¹³ Another approach involves directed *ortho*-metalation *via* elimination reactions (Scheme 1b), which has the drawbacks of harsh reaction conditions and requiring very low reaction temperatures. Additionally, two steps are required to form 1,2,3-substituted naphthalenes, followed by a Suzuki reaction to obtain the final aryl naphthalenes.¹⁴ Therefore, the development of more straightforward, cost-efficient, waste-reducing, sustainable methods toward aryl naphthalenes are highly desirable.

Notably, the concept of domino reactions is a powerful tool in organic synthesis for economically and sustainably installing molecular complexity from simple compounds.^{15–24} Building on the concept of a light-driven domino strategy, the photoenolization of 2-methylbenzophenones represents a particularly attractive

platform. Under UV irradiation, these substrates generate highly reactive o-quinodimethane intermediates that act as transient dienes and readily undergo subsequent cycloaddition reactions, enabling the efficient construction of complex ring systems.²⁵⁻²⁷ In our previous work, we demonstrated the utility of this approach for the synthesis of phthalazines *via* photoenolization of 2-methylbenzophenone derivatives.²⁸ Encouraged by these findings, we sought to further expand the synthetic scope of this transformation toward the preparation of functionalized aryl naphthalenes. Given the broad applicability of such scaffolds, we envisioned a one-pot sequence combining photoenolization/Diels–Alder cycloaddition with subsequent aromatization, thereby enabling streamlined and sustainable access to highly substituted aryl naphthalenes (Scheme 1c). Accordingly, we report herein the first light-driven, metal-free, and environmentally benign approach to highly substituted aryl naphthalenes, featuring a photoenolization/Diels–Alder (PEDA) domino reaction as the key step.

Results and Discussion

To develop and optimize the proposed one-pot procedure, we began a screening of various dienophiles. 2-Methylbenzophenone **1** was reacted with six different dienophiles under UV irradiation (365 nm) for 18 h (Scheme 2). While no product formation was observed for ethyl glyoxylate, acetone, or 4-phenyl-1,2,4-triazole-3,5-dione, reactions with (*E*)-1,2-bis(phenylsulfonyl)ethene and methyl propiolate afforded the Diels–Alder adducts **5** and **6** in 6% and 30% yield, respectively. The best result was obtained with ethyl buta-2,3-dienoate, which afforded compound **7** in 32% yield with an excellent diastereomeric ratio (>99:1). The structure of compound **7** was confirmed by 1D and 2D NMR techniques (see Figures S1–S4 of the Supporting Information). HSQC and COSY spectra confirmed key proton–carbon correlations and coupling patterns.



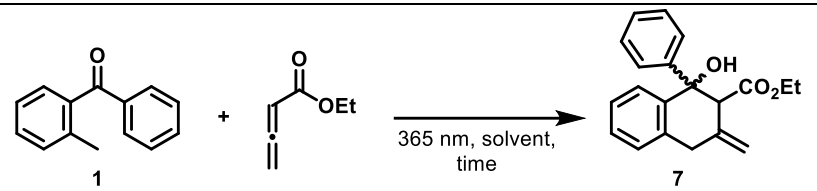
Scheme 2. Screening of different dienophiles. Reaction conditions: 200 μ mol of 2-methylbenzophenone, 5.00 equiv. of dienophile, toluene, 365 nm, 18 h.

After identifying buta-2,3-dienoate as a promising dienophile, the PEDA reaction was optimized, starting with reaction conditions previously reported by our group using 5.0 equiv. of buta-2,3-dienoate in 4 mL of toluene.²⁸ After 18 h, TLC indicated complete consumption of 2-methylbenzophenone (**1**), and compound **7** was obtained reproducibly in 32% yield after workup and purification (Table 1, entry 1). Next, the concentration of

1 was increased by reducing the solvent volume to 1 mL, which afforded **7** in 52% yield after 14 h of irradiation (Table 1, entry 2). Reducing the amount of dienophile to 1.0 equiv. and 2.0 equiv. decreased the yield to 26% and 39%, respectively (Table 1, entries 3 and 4). In further optimization experiments, different polar solvents were screened, including MeCN, DMF, and MeOH. While MeCN and MeOH gave slightly lower yields of 46% and 49%, respectively (Table 1, entries 5 and 7), DMF led to a dramatically decreased yield of 8% (Table 1, entry 6). This is likely due to the fact that the light absorption of compound **1** is optimal in toluene.

Next, the reaction time was varied, since previous PEDAs reactions in our group toward phthalazines required only 3 h,²⁸ which we also applied to this reaction. Under these conditions in toluene, the yield increased to 76% (Table 1, entry 8). Extending the reaction time to 3.5 h and 4 h further affected the yield, giving 78% and 57%, respectively (Table 1, entries 9 and 10). Therefore, the optimal reaction time was selected as 3.5 h (Table 1, entries 9).

Table 1. Optimization of the reaction conditions for the PEDAs reaction toward compound **7**



Entry	Solvent volume (mL)	Dienophile (equiv.)	Solvent	Time (h)	Yield (%)
1	4	5	toluene	18	32
2	1	5	toluene	14	52
3	1	1	toluene	18	26
4	1	2	toluene	18	39
5	1	5	MeCN	14	46
6	1	5	DMF	14	8
7	1	5	MeOH	14	49
8	1	5	toluene	3	76
9	1	5	toluene	3.5	78
10	1	5	toluene	4	57

With the optimized conditions of the photoenolization, we proceeded with the optimization of the aromatization step of compound **7** towards arynaphthalene derivative **8** using different acids and oxidants (Table 2). Based on our previous work,²⁸ TFA was initially applied. Treatment of the Diels-Alder adduct **7** with excess TFA at 140 °C for 15 h gave compound **8** in 46% yield (Table 2, entry 1). In another approach, triethylsilane and boron trifluoride were added instead of TFA, according to the work of Kraus and Wu.²⁹ The two reagents were added at -78 °C, and the mixture was stirred at room temperature overnight, to receive **8** in a 32% yield (Table 2, entry 2). In a further attempt, thionyl chloride in pyridine was examined according to a literature-known procedure for the synthesis of arynaphthofuranone derivatives.³⁰ After addition of excess SOCl₂ at 0 °C and stirring at room temperature overnight, naphthalene derivative **8** was obtained in a poor yield of 6% (Table 2, entry 3). Similarly, the use of excess DDQ³¹ in toluene at 100 °C only resulted in trace amounts of product (Table 2, entry 4). Finally, the combination of H₂SO₄ and AcOH in Et₂O improved the yield of compound **8** to 74% after stirring for 22 h at room temperature (Table 2, entry 5).³² Longer reaction times or absence of AcOH led to decreased yields of 68% and 63%, respectively. The lower yield observed in the absence of AcOH may be

attributed to its role in facilitating proton transfer and stabilizing intermediates during the reaction, while H₂SO₄ acts as a Brønsted acid and dehydrating agent, helping to remove excess water.

Table 2. Reaction screening for the aromatization of compound 7 to naphthalene derivative 8

Entry	Reagent 1 (equiv.)	Reagent 2 (equiv.)	Solvent	Time (h)	T (°C)	Yield (%)
1	CF ₃ COOH (56)	-	DCM	15	140	46
2	Et ₃ SiH (1.5)	BF ₃ *Et ₂ O (1.10)	Toluene	o/n	-78→rt	32
3	SOCl ₂ (2.4)	-	Pyridine	o/n	0→rt	6
4	DDQ (3.5)	-	Toluene	22	100	traces
5	H ₂ SO ₄ (1.0)	AcOH (3.5)	Et ₂ O	22	rt	74
6	H ₂ SO ₄ (1.0)	AcOH (3.5)	Et ₂ O	144	rt	68
7	H ₂ SO ₄ (1.0)	-	Et ₂ O	22	rt	63

Subsequently, the optimized conditions for both reaction steps were combined into a one-pot procedure to generate a reaction scope. Hereby, the unsubstituted 2-methylbenzophenone gave **8a** in an overall yield of 59% (Figure 1). The introduction of electron-donating substituents in the form of methyl **8b**, methoxy **8c** and benzyloxy **8d** groups, resulted in yields of 42%, 12% and 34%, respectively. In the case of electron-withdrawing substituents such as the cyano **8e** group, the PEDAs reactions were successful, however, the aromatization step remained incomplete, resulting in diminished yields of 10% and trace amounts, respectively. For the bromo **8f,g** and chloro **8h** substituents, the PEDAs and aromatization step did not finish after prolonged irradiation leading to similar yields of 25%, 9% and 20%.

In summary, the one-pot PEDAs/aromatization protocol was applied to a range of 2-methylbenzophenone derivatives. The unsubstituted substrate **8a** gave the highest overall yield (59% over three steps). The electron-donating substituents (**8b-d**) were also tolerated (up to 42% yield over three steps). In contrast, electron-withdrawing (**8e**) and halogenated (**8f-8h**) derivatives led to incomplete aromatization and significantly reduced yields (up to 25% over three steps), indicating that substituent electronic effects strongly influence the efficiency of the one-pot transformation. Overall, the reaction scope highlights the method's applicability to the cost-efficient, straightforward synthesis of new aryl-naphthalene derivatives.

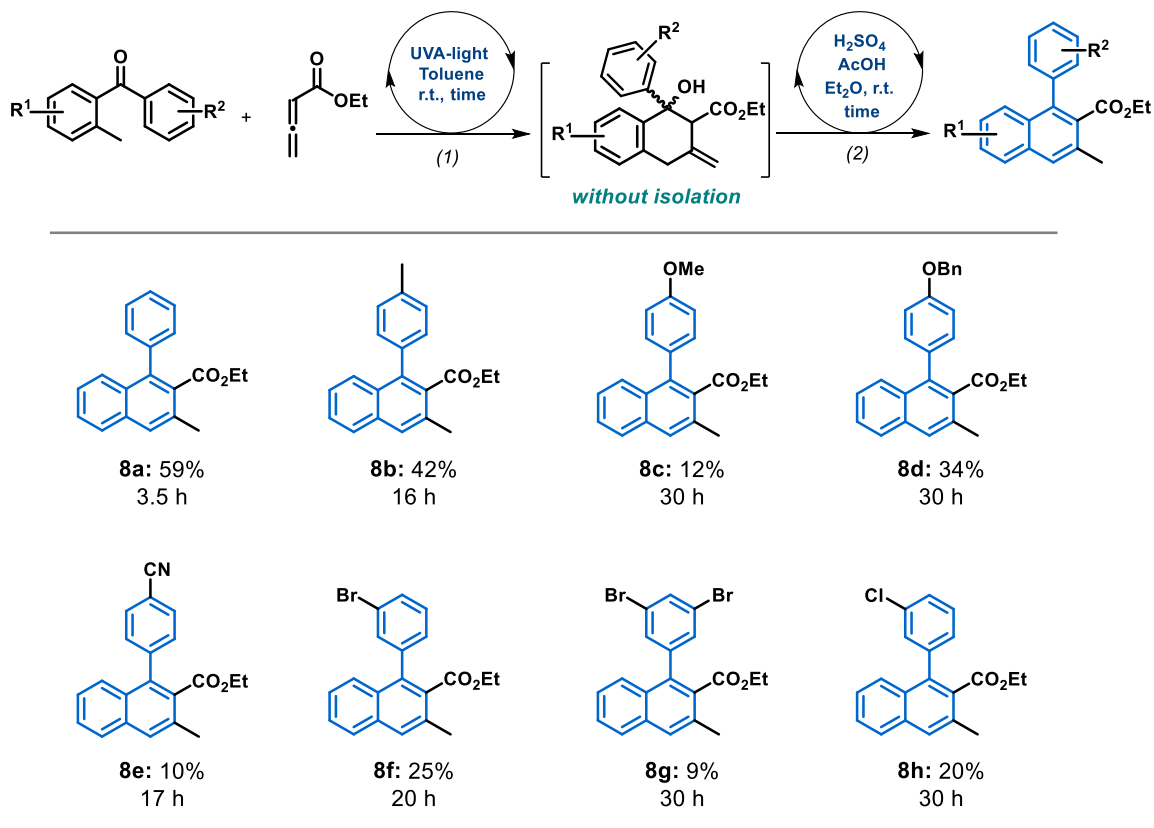


Figure 1. Substrate scope. Conditions: (1) Degassed toluene (1 mL, 0.2 M); (2) H₂SO₄ (1.00 equiv.), AcOH (3.50 equiv.), Et₂O (200 μL, 1 M).

The mechanism of this one-pot reaction, which consists of photoenolization, a Diels-Alder reaction, and aromatization, is presented in Figure 2. Hereby, the photoenolization starts with the irradiation of the starting material **1** in the ground state (S_0) towards the singlet excited state (S_1). Followed by intersystem crossing (ISC), the relatively long-lived triplet state (T_1) is reached. After 1,5-hydrogen atom transfer (1,5-HAT), the excited triplet ketone yields the triplet 1,4 biradical (3E). The free rotation of the ketyl group, leads to the initial formation of both the (*Z*)- and the (*E*)-photoenols in about equal yield. While the short-lived (*Z*)-photoenol rapidly reverts to starting material **1** through efficient intramolecular 1,5-HAT, the (*E*)-photoenol is a longer-lived intermediate and can readily react with the dienophile - ethyl buta-2,3-dienoate - to form compound **7** via a Diels-Alder reaction. Finally, addition of H₂SO₄ and AcOH leads to the formation of the desired aryl naphthalene **8** via aromatization.

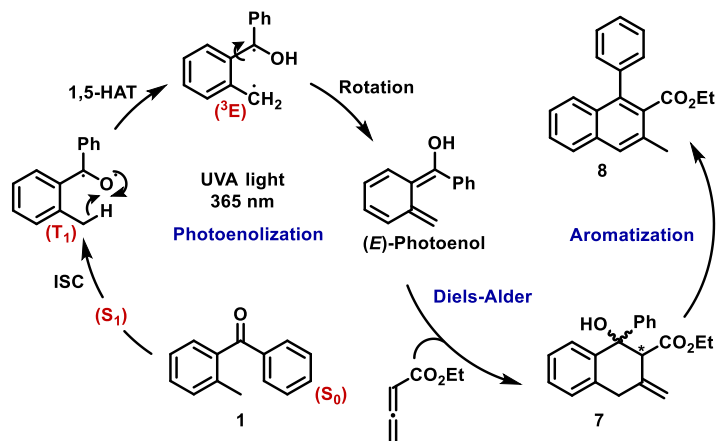


Figure 2. Detailed mechanism of the photoenolization/Diels–Alder (PEDA) reaction and the subsequent aromatization.

Conclusions

In summary, we have established a light-driven, transition-metal-free, one-pot strategy for the synthesis of functionalized aryl naphthalenes *via* a photoenolization/Diels–Alder domino process followed by *in situ* aromatization. This operationally simple approach offers an atom-economical and environmentally benign alternative to conventional multistep, transition metal-catalyzed routes. Reaction efficiency is governed by the electronic properties of the benzophenone precursors: unsubstituted 2-methylbenzophenone affords the highest overall yield (up to 59%), whereas electron-donating substituents red-shift absorption, necessitating prolonged irradiation and diminishing efficiency, and electron-withdrawing groups impede the aromatization step. These insights define key design principles for substrate selection and highlight the potential of photochemical domino reactions as sustainable tools for constructing complex polycyclic aromatic frameworks.

Experimental Section

General. All chemicals used for synthesis were purchased from commercial sources and were used without further purification. Nitrogen served as a protective gas. All solvents were purified by distillation or were purchased in HPLC-grade-quality. All products were dried in a high vacuum (up to 10^{-3} mbar). 2-Methylbenzophenone **1a** was purchased from BLD Pharmatech. 2-Methylbenzophenone substrates for the photoinduced naphthalene synthesis were synthesized according to literature known procedure or were available in our group ((3-bromophenyl)(*o*-tolyl)methanone **1f**, 4-(2-methylbenzoyl)benzointrile **1e**, (2-fluorophenyl)(*o*-tolyl)methanone **1i** and (3,5-dibromophenyl)(*o*-tolyl)methanone **1g**).²⁸

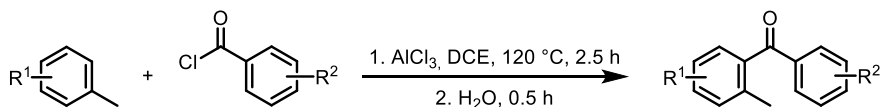
Thin layer chromatography (TLC). Thin layer chromatography (TLC) was performed on silica gel TLC cards (Alugramm® SIL G/UV254, layer thickness 0.20 mm, Macherey-Nagel) with fluorescence indicator (wavelength: 254 nm).

Mass spectrometry (MS). ESI and APPI mass spectra were recorded on a Bruker Daltonik maXis 4G, a Bruker Daltonik micrOTOF II focus or a Bruker Daltonics ultraflexTOF/TOF.

NMR spectroscopy. ^1H -NMR and ^{13}C -NMR spectra were recorded at rt on a Bruker Avance 300, 400, 500 or 600 spectrometer operating at 300 MHz, 400 MHz, 500 MHz or 600 MHz. All chemical shifts are given in the ppm scale and refer to the non-deuterized proportion of the solvent.

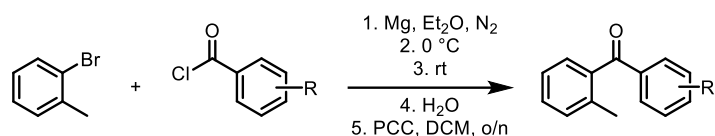
Synthetic Procedures

General procedure 1 (GP1)



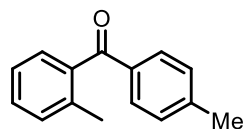
A solution of AlCl_3 (760 mg, 5.70 mmol, 1.14 equiv.) and benzoylchloride derivative (10.0 mmol, 2.00 equiv.) in DCE (4 mL) was added to a round bottom flask. To this solution, a mixture of 3,4-dichlorotoluene (644 μL , 5.00 mmol, 1.00 equiv.) in DCE (2.5 mL) was added. After heating to 120 $^\circ\text{C}$ for 2.5 h, the mixture was poured on crushed ice and stirred for 30 minutes. Then, the mixture was extracted with DCM (3x40 mL). The combined organic phases were washed with water (30 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. Afterward, the residue was purified *via* column chromatography (SiO_2 ; Hexane:EtOAc; 40:1).

General procedure 2 (GP2)



A two-neck flask equipped with a reflux condenser and dropping funnel was flushed with nitrogen for 10 minutes. After adding magnesium (209 mg, 8.60 mmol, 1.07 equiv.) and absolute Et_2O (600 μL), a solution of 2-bromotoluene (973 μL , 8.00 mmol, 1.00 equiv.) in abs. Et_2O (6 mL) was filled into the dropping funnel. This solution was slowly added to the flask and refluxed until most of the magnesium was dissolved. After cooling the reaction mixture to 0 $^\circ\text{C}$, a solution of aldehyde (907 μL , 8.00 mmol, 1.00 equiv.) in absolute Et_2O (2 mL) was added dropwise. Then, the mixture was allowed to warm to room temperature until the end of the reaction. The reaction was quenched with water, and the biphasic system was extracted with Et_2O (3x25 mL). Afterward, the organic phases were collected, dried with Na_2SO_4 , filtered, and the solvent was removed under reduced pressure. The residue was dissolved in DCM (77 mL), PCC (2.59 g, 12.0 mmol, 1.50 equiv.) was added, and the mixture was stirred at rt. After TLC indicated complete alcohol consumption, the mixture was concentrated under reduced pressure and filtered through a short pad of celite. The filtrate solvent was removed under reduced pressure, and the crude product was purified *via* column chromatography.

o-Tolyl(*p*-tolyl)methanone (1b)



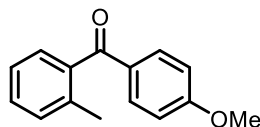
The reaction was performed according to **GP1** using toluene and 2-methylbenzoyl chloride.

Column chromatography: Hexane:EtOAc 10:1; Yield: 91%, 961 mg, 4.57 mmol.

¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.75 – 7.65 (m, 2H), 7.42 – 7.33 (m, 1H), 7.32 – 7.17 (m, 5H), 2.43 (s, 3H), 2.32 (s, 3H) ppm.

The obtained spectroscopic data are in accordance with the literature.³³

(4-Methoxyphenyl)(*o*-tolyl)methanone (1c)



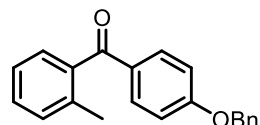
The reaction was performed according to **GP2** using 2-bromotoluene and 4-methoxybenzaldehyde.

Column chromatography: Hexane:EtOAc 40:1; Yield: 33%, 597 mg, 2.64 mmol.

¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.90 – 7.70 (m, 2H), 7.42 – 7.33 (m, 1H), 7.33 – 7.21 (m, 3H), 7.01 – 6.85 (m, 2H), 3.88 (s, 3H), 2.30 (s, 3H) ppm.

The obtained spectroscopic data are in correspondence with the literature.³⁴

(4-(Benzyloxy)phenyl)(*o*-tolyl)methanone (1d)



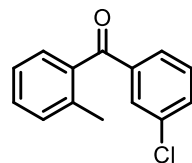
The reaction was performed according to a procedure known in the literature using 2-bromotoluene and 4-(benzyloxy)benzaldehyde.²⁸

Column chromatography: Hexane:EtOAc 20:1; Yield: 7%, 178 mg, 587 μ mol.

¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.86 – 7.71 (m, 2H), 7.51 – 7.31 (m, 6H), 7.31 – 7.16 (m, 3H), 7.09 – 6.94 (m, 2H), 5.14 (s, 2H), 2.30 (s, 3H) ppm.

The obtained spectroscopic data are in correspondence with the literature.²⁸

(3-Chlorophenyl)(*o*-tolyl)methanone (1h)



The reaction was performed according to **GP2** using 2-bromotoluene and 3-chlorobenzaldehyde.

Column chromatography: Hexane:EtOAc 40:1; Yield: 44%, 817 mg, 3.54 mmol.

¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.78 (t, *J* = 1.9, 1H), 7.66 (dt, *J* = 7.8, 1.4, 1H), 7.55 (ddd, *J* = 7.9, 2.1, 1.1, 1H), 7.46 – 7.36 (m, 2H), 7.29 (ddd, *J* = 14.0, 7.4, 1.4, 3H), 2.34 (s, 3H) ppm.

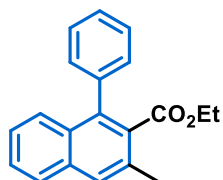
The obtained spectroscopic data are in correspondence with the literature.

General Procedure 3 (GP3)

A HPLC vial with magnetic stirring bar was filled with toluene (1 mL), 2-methylbenzophenone derivative **1** (200 μ mol, 1.00 equiv.) and ethyl buta-2,3-dienoate (95%, 122 μ L, 1.00 mmol, 5.00 equiv.) and was degassed with N₂ for 5 minutes. The vial was sealed with a teflon band and irradiated with an LED (365 nm, Hepatochem PhotoRedOx Box) until TLC indicated complete consumption of

the 2-methylbenzophenone derivative. Afterward, the solution was transferred to a 10 ml flask, and the solvent was removed under reduced pressure. The residue was treated with Et₂O (200 μl), H₂SO₄ (95%, 11.3 μL, 200 μmol, 1.00 equiv.) and AcOH (40.0 μL, 200 μmol, 1.00 equiv.). This mixture was stirred for 30 h, and then the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography (SiO₂, Hexane:EtOAc).

Ethyl 3-methyl-1-phenyl-2-naphthoate (8a)



The reaction was performed according to **GP3** using 2-methylbenzophenone **1a**.

Irradiation time: 3.5 h.

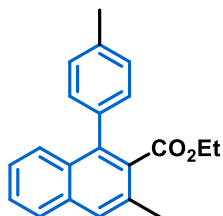
Column chromatography: Hexane:EtOAc 25:1; Yield: 59%, 34.3 mg, 118 μmol.

¹H-NMR (300 MHz, Chloroform-*d*) δ = 7.80 (dt, *J* = 8.2, 0.9, 1H), 7.70 (d, *J* = 1.1, 1H), 7.61 – 7.30 (m, 8H), 4.01 (q, *J* = 7.1, 2H), 2.54 (s, 3H), 0.94 (t, *J* = 7.1, 3H) ppm.

¹³C-NMR (101 MHz, Chloroform-*d*) δ = 169.7, 138.2, 137.8, 133.9, 133.0, 131.5, 130.6, 130.4, 128.1, 127.7, 127.5, 126.9, 126.9, 125.9, 61.0, 20.1, 13.8 (three signals are missing or coincident) ppm.

HRMS (ESI) exact mass calculated for C₂₀H₁₉O₂ [M+H]⁺ 291.1380, found 291.1392.

Ethyl 3-methyl-1-(*p*-tolyl)-2-naphthoate (8b)



The reaction was performed according to **GP3** using *o*-tolyl(*p*-tolyl)methanone **1b**. Irradiation time: 16 h.

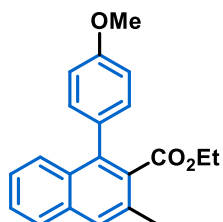
Column chromatography: Hexane:EtOAc 25:1; Yield: 42%, 25.3 mg, 83.1 μmol.

¹H-NMR (400 MHz, Chloroform-*d*) δ = 7.83 – 7.75 (m, 1H), 7.68 (d, *J* = 1.0, 1H), 7.58 (dd, *J* = 8.5, 1.1, 1H), 7.47 (ddd, *J* = 8.1, 6.8, 1.3, 1H), 7.34 (ddd, *J* = 8.3, 6.8, 1.3, 1H), 7.26 (d, *J* = 1.7, 4H), 4.05 (q, *J* = 7.1, 2H), 2.53 (s, 3H), 2.44 (s, 3H), 0.99 (t, *J* = 7.1, 3H) ppm.

¹³C-NMR (101 MHz, Chloroform-*d*) δ = 169.8, 137.9, 137.4, 135.2, 133.9, 133.1, 131.4, 130.8, 130.2, 128.8, 127.9, 127.4, 126.9, 126.8, 125.8, 61.0, 21.4, 20.1, 13.9 (two signals are missing or coincident) ppm.

HRMS (APPI) exact mass calculated for C₂₁H₂₁O₂ [M+H]⁺ 305.1535, found 305.1537.

Ethyl 1-(4-methoxyphenyl)-3-methyl-2-naphthoate (8c)



The reaction was performed according to **GP3** using (4-methoxyphenyl)(o-tolyl)methanone **1c**. Irradiation time: 30 h.

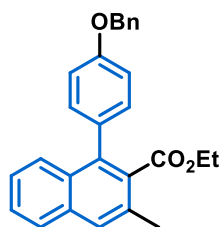
Column chromatography: Hexane:EtOAc 15:1; Yield: 12%, 9.40 mg, 23.9 μmol .

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) δ = 7.79 (d, J = 8.1, 1H), 7.67 (s, 1H), 7.58 (d, J = 8.5, 1H), 7.47 (ddd, J = 8.2, 6.8, 1.3, 1H), 7.35 (ddd, J = 8.3, 6.7, 1.3, 1H), 7.32 – 7.27 (m, 2H), 7.03 – 6.95 (m, 2H), 4.06 (q, J = 7.2, 2H), 3.88 (s, 3H), 2.52 (s, 3H), 1.01 (t, J = 7.1, 3H) ppm.

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ = 169.8, 159.3, 137.4, 133.9, 133.3, 131.5, 131.4, 131.0, 130.4, 127.9, 127.5, 126.9, 126.8, 125.9, 113.6, 61.0, 55.5, 20.1, 14.0 (two signals are missing or coincident) ppm.

HRMS (ESI) exact mass calculated for $\text{C}_{21}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$ 321.1485, found 321.1488.

Ethyl 1-(4-(benzyloxy)phenyl)-3-methyl-2-naphthoate (**8d**)



The reaction was performed according to **GP3** using (4-(benzyloxy)phenyl)(o-tolyl)methanone **1d**. Irradiation time: 30 h.

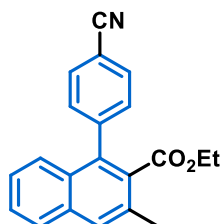
Column chromatography: Hexane:EtOAc 15:1; Yield: 34%, 27.2 mg, 68.6 μmol .

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) δ = 7.79 (dd, J = 8.2, 1.3, 1H), 7.67 (d, J = 1.0, 1H), 7.59 (dd, J = 8.5, 1.1, 1H), 7.51 – 7.27 (m, 9H), 7.11 – 7.01 (m, 2H), 5.15 (s, 2H), 4.04 (q, J = 7.1, 2H), 2.52 (d, J = 0.9, 3H), 0.98 (t, J = 7.2, 3H) ppm.

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ = 169.8, 158.5, 137.4, 137.1, 133.9, 133.3, 131.5, 131.4, 130.9, 130.7, 128.8, 128.2, 127.9, 127.7, 127.5, 126.9, 125.9, 114.5, 70.2, 61.0, 20.1, 14.0 (five signals are missing or coincident) ppm.

HRMS (ESI) exact mass calculated for $\text{C}_{27}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$ 397.1798, found 397.1801.

Ethyl 1-(4-cyanophenyl)-3-methyl-2-naphthoate (**8e**)



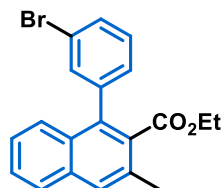
The reaction was performed according to **GP3** using 4-(2-methylbenzoyl)benzointrile **1e**. Irradiation time: 17 h.

Column chromatography: Hexane:EtOAc 25:1; Yield: 10%, 6.20 mg, 19.7 μmol .

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) δ = 7.85 – 7.81 (m, 1H), 7.79 – 7.73 (m, 3H), 7.55 – 7.47 (m, 3H), 7.40 – 7.35 (m, 2H), 4.04 (q, J = 7.2, 2H), 2.54 (d, J = 0.9, 3H), 0.99 (t, J = 7.1, 3H) ppm.

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ = 169.0, 143.5, 135.7, 133.9, 132.8, 131.9, 131.7, 131.3, 129.9, 129.1, 127.7, 127.3, 126.5, 126.1, 118.9, 111.8, 61.3, 20.1, 13.9 (two signals are missing or coincident) ppm.

HRMS (APPI) exact mass calculated for $\text{C}_{21}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 316.1332, found 316.1324.

Ethyl 1-(3-bromophenyl)-3-methyl-2-naphthoate (8f)

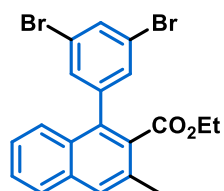
The reaction was performed according to **GP3** using (3-bromophenyl)(o-tolyl)methanone **1f**. Irradiation time: 20 h.

Column chromatography: Hexane:EtOAc 25:1; Yield: 25%, 18.4 mg, 49.8 μmol .

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) δ = 7.81 (dd, J = 8.5, 1.4, 1H), 7.71 (d, J = 1.1, 1H), 7.62 – 7.55 (m, 2H), 7.55 – 7.46 (m, 2H), 7.46 – 6.93 (m, 3H), 4.08 (q, J = 7.1, 2H), 2.53 (s, 3H), 1.02 (t, J = 7.1, 3H) ppm.

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ = 169.3, 140.4, 136.1, 133.8, 133.3, 133.0, 131.5, 130.9, 130.3, 129.7, 129.1, 128.6, 127.6, 127.1, 126.5, 126.2, 122.2, 61.2, 20.1, 13.9 ppm.

HRMS (ESI) exact mass calculated for $\text{C}_{20}\text{H}_{18}\text{BrO}_2$ [$\text{M}+\text{H}$] $^+$ 369.0485, found 369.0492.

Ethyl 1-(3,5-dibromophenyl)-3-methyl-2-naphthoate (8g)

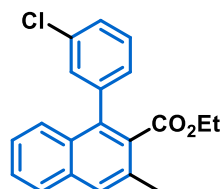
The reaction was performed according to **GP3** using (3,5-dibromophenyl)(o-tolyl)methanone **1g**. Irradiation time: 30 h.

Column chromatography: Hexane:EtOAc 25:1; Yield: 9%, 8.30 mg, 18.5 μmol .

$^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ = 7.90 – 7.78 (m, 1H), 7.78 – 7.66 (m, 2H), 7.64 – 7.33 (m, 5H), 4.13 (q, J = 7.2, 2H), 2.53 (s, 3H), 1.09 (t, J = 7.1, 3H) ppm.

$^{13}\text{C-NMR}$ (101 MHz, Chloroform-*d*) δ = 169.0, 141.8, 134.6, 133.8, 133.4, 133.1, 132.2, 131.6, 130.0, 129.1, 127.7, 127.3, 126.5, 126.2, 122.7, 61.3, 20.1, 14.0 (two signals are missing or coincident) ppm.

HRMS (APPI) exact mass calculated for $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{O}_2$ [$\text{M}+\text{H}$] $^+$ 446.9590, found 446.9595.

Ethyl 1-(3-chlorophenyl)-3-methyl-2-naphthoate (8h)

The reaction was performed according to **GP3** using (3-chlorophenyl)(o-tolyl)methanone **1h**. Irradiation time: 30 h.

Column chromatography: Hexane:EtOAc 40:1; Yield: 20%, 12.8 mg, 39.4 μmol .

$^1\text{H-NMR}$ (400 MHz, Chloroform-*d*) δ = 7.81 (dd, J = 8.7, 1.4, 1H), 7.71 (s, 1H), 7.58 – 7.46 (m, 2H), 7.46 – 7.34 (m, 4H), 7.33 – 7.26 (m, 1H), 4.07 (q, J = 7.1, 2H), 2.53 (s, 3H), 1.01 (t, J = 7.1, 3H) ppm.

¹³C-NMR (101 MHz, Chloroform-*d*) δ = 169.2, 139.9, 136.1, 133.9, 133.7, 132.9, 131.4, 130.4, 130.2, 129.3, 128.6, 128.5, 127.8, 127.4, 127.0, 126.4, 126.1, 61.0, 20.0, 13.8 ppm.

HRMS (ESI) exact mass calculated for C₂₀H₁₈ClO₂ [M+H]⁺ 325.0990, found 325.0993.

Acknowledgements

S.B.T. gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft (DFG, grant TS 87/28-1).

Supplementary Material

Copies of ¹H, ¹³C, COSY and HSQC NMR spectra of compound **7** and **8a-8h** are available in the Supporting Information file associated with this paper.

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