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Porphyrins as Photoredox Catalysts in Csp²-H Arylations: Batch and Continuous Flow Approaches

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Graphical Abstract



ABSTRACT

We have investigated both batch and continuous flow photoarylations of enolacetates to yield different α-arylated aldehyde and ketone building blocks by using diazonium salts as the aryl-radical source. Different porphyrins were used as SET photocatalysts, and photophysical as well as electrochemical studies were performed to rationalize the photoredox properties and suggest mechanistic insights. Notably, the most electron-deficient porphyrin (mesotetra(pentafluorophenyl)porphyrin) shows the best photoactivity as an electrondonor in the triplet excited-state, which was rationalized by the redox potentials of excited states and the turnover of the porphyrins in the photocatalytic cycle. Scope, a two-step continuous protocol and multigram-scale reactions are also presented revealing a robust, cost-competitive and easy methodology, highlighting the significant potential of porphyrins as SET photocatalysts.

INTRODUCTION

Although photochemical reactions have been known for a long time,^{1,2} only in the last century have significant chemical transformations been widely performed using visible light to promote catalysis.^{3,4,5,6,7,8} Among various C-H (sp²) functionalizations, arylation reactions have gained importance in methodology studies due to their application in active pharmaceutical ingredient (API) and natural product syntheses.^{9,10,11,12} Metal complexes based on Ru(II) and Ir(III) have been used to perform these photoarylations, especially by single electron transfer (SET), generating aryl-radicals thus from arylsystems.^{13,14} diazonium/iodonium salts and other activated aromatic Ruthenium(II) and Iridium(III) compounds usually have triplet excited states with high reduction potentials (0.7-2.0 V) and long lifetimes (over 1000 ns), which make them very useful for many organic SET photocatalyzed reactions. However, Ru and Ir based complexes are expensive and with no prospect for sustainable use in scaled up applications. An alternative to these transition metal-photocatalysts is the use of organic dyes, whose photocatalytic properties can match or even surpass the efficiency of metal-complexes, with advantageous low cost, availability and easier residual clean-up of the products, opening up many possibilities in chemical synthesis.^{9,15}

Given this background, porphyrins are useful tetra-pyrrolic organic dyes with great potential to replace many metal-complexes, working as oxidizing or reducing agents and presenting similar lifetimes of the triplet state when compared to some metallo-complexes.^{15,16} Metal-free porphyrins have been only recently explored as SET photoredox catalysts, probably due to the relative

difficulty to access their excited state redox potentials, the relative old-fashioned and inefficient synthetic routes to obtain these compounds,¹⁷ and their conditional use as ligands of transition metals for catalysis; ¹⁸ however, many of these issues have been currently solved,¹⁹ making porphyrin derivatives very promising and cost-competitive photocatalysts.^{15,16,20} Regarding the use of porphyrins as SET catalysts, Kanai and coworkers²¹ have reported an electron rich porphyrin derivative in coumarin arylation, though they did not investigate if the reactions are just thermal or also photocatalyzed by ambient light. Two recent and seminal applications of porphyrins as SET photocatalysts were published by Gryko and coworkers reporting in the first tetraphenylporphyrin (TPP) as photoredox catalyst in reactions of aldehydes with diazo compounds¹⁶ and in the second different porphyrins in photoarylations of heteroarenes.²² However, in this second publication they did not clearly explain the high SET photoactivity of the meso-tetra(pentafluorophenyl)porphyrin (TPFPP), which worked as an excellent photo-reducer despite containing twenty fluorine atoms attached to the aryl groups surrounding the porphyrin core. In addition, this last methodology was only applied on a very low scale (0.25 mmol), with a reduced scope and utilizing batch conditions. Normally, methodologies on radical photoarylation are performed by using arenediazonium salts²³ on very low scales, since these salts are considered to present safety and experimental concerns due to their low stabilities.²⁴ An alternative to avoid this safety concern is the use of reactors operating under continuous flow conditions, 25, 26, 27, 28, 29 which allows safe and precise reaction control, scale up, automation and sustainability. In addition, the in-situ generation of these compounds has been

used in multigram and end-to-end approaches in flow,³⁰ with no need for stocking diazonium salts.

In this present study, we have considered all these concerns, and evaluated two different porphyrins as photoredox catalysts in Csp²-H photoarylations of enol-acetates in both batch and continuous flow conditions. Thus we describe an efficient, safe and cost competitive methodology using very low loadings of porphyrin derivatives, shorter reaction times, scalability and scope, when compared to $[Ru(bpy)_3]Cl_2$ or organic dyes such as Eosin Y and Rose Bengal (Scheme 1).³¹



Scheme 1. Visible light mediated photoarylations.

RESULTS AND DISCUSSION

The proof of concept that porphyrin derivatives work as SET photocatalysts in photoarylations of enol-acetates was performed in batch with the diazonium salt **1a** and the enol-acetate **2a** using the *meso*-tetraphenylporphyrin (**TPP**) (Scheme 2, Table 1).



Scheme 2. Reaction model in batch conditions.

Table 1: Reactions with TPP in batch at 25 °C.

entry ^a	TPP (mol%)	time (h)	LEDs (28 W) ^b	yield 3a (%) ^c
1	5	2	White	44
2	2	2	White	45
3	1	2	White	42
4	5	2	Blue	53/57 ^d
5	5	4	Blue	55
6	2	2	Blue	55
7	1	2	Blue	54
8	0.5	2	Blue	55
9	0	2	Blue	32 ^e
10	0	2	Dark	16 ^e

^a 1 mmol of **1a** and 15 mmol of **2a** in 6 mL of CH_2CI_2 :DMF (3.5:2.5) mixture (total volume 8 mL)

^b homemade batch reactor – see supporting information

^c isolated yields

^d Double checked reaction

 $^{\circ}$ Experiments were performed in the presence of DMF/CH₂Cl₂ mixture, with or without light (see ref 32, p. 775 for details on the background reaction).

As shown in Table 1 (entries 1–3) the α -aryl-ketone **3a** was obtained in 42–45% yield, independent of the **TPP** charge (1–5 mol%) using white LEDs. However, using blue LEDs (entries 4–8, Table 1) **3a** was isolated in 53–55%

yield independent of the charge of **TPP** (0.5–5 mol%). Surprisingly, reaction without **TPP** under blue LEDS (entry 9, Table 1), or no **TPP** and no light yielded **3a** in 32 and 16% yield, respectively. These are background reaction conditions and the occurrence of the product **3a** is explained by the different manners in which aryl radicals are slowly generated in the presence of DMF and thermal conditions.³² According to the literature, aryl radicals can be generated from arenediazonium salts through many different approaches using metals (Cu(I), Fe(II), etc), anion induced dediazotization, photoinduced electron transfer and solvent induced dediazotization.³² Our background results from entries 9 and 10 (Table 1) can be explained by these last two cases (Scheme 3). However, these are only competitive reactions for radical generation, and we have found a significant increase in the yields in the presence of **TPP** also indicating the occurrence of SET photocatalysis, as previously evidenced by Gryko's group in the arylation of heteroaromatics.²²



Scheme 3: Proposal based on the literature³² for the background reaction.

After testing the **TPP** SET photoactivity we then decided to test the meso-tetrakis(pentafluorophenyl)porphyrin (**TPFPP**) as photocatalyst. Improved yields were obtained in all entries (Table 2) using **TPFPP**, and the best result was found by using blue LEDs, **TPFPP** at 0.5 mol% and 0 °C (entry 5, Table 2)

obtaining compound **3a** in 74% yield. The evident effect of the temperature was demonstrated in this last experiment, also highlighting the better photocatalytic SET effect of **TPFPP**. As is well-known, triplet life-times of porphyrins are increased at lower temperatures improving the efficiency of these photocatalysts.³³ A control experiment (entry 6, Table 2) was performed using the same conditions of entry 5, however, without **TPFPP** showing that the product **3a** can be obtained in 40% yield. This result corroborates with the photo-induced radical generation and arylation, but definitely does not equal the SET photocatalytic effect of **TPFPP** (74% yield, entry 5, Table 2).

Table 2: Reactions with TPFPP in D	atch.
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entry ^{a,b}	TPFPP (mol%)	LEDs (28 W)	Temperature (°C)	yield 3a (%) ^c
1	2	Blue	25	69
2	1	Blue	25	69
3	0.5	Blue	25	68
4	0.5	White	25	64
5	0.5	Blue	0	74/74 ^{d,e}
6	0	Blue	0	40 ^d

^a 1 mmol of **1a** and 15 mmol of **2a** in 6 mL of CH₂Cl₂:DMF (3.5:2.5) mixture (total volume 8 mL)

^b all the reactions were performed in 2h.

^c isolated yields

^d reaction performed inside a temperature-controlled freezer

e double checked reaction

Subsequently, the solvent effect was also investigated since photocatalyzed reactions are very solvent-dependent. As presented in Table 3, different mixtures were tested always considering the modulation of the polarity and the reagent solubilities. The mixture $CH_2Cl_2:CH_3NO_2:DMF$ (3.5:2.0:0.5)

(entry 1, Table 3), using **TPFPP** at 0.5 mol%, 0 °C and using white LEDs gave **3a** in 71% yield. Nevertheless, using these same conditions, but with blue LEDs (entry 2, Table 3), compound **3a** was obtained in 79–80% yield in a double-checked experiment, thus indicating the higher efficiency of blue light for exciting **TPFPP**. Regarding this result, we have shown how the blue LEDs emission spectra fits better with the absorption band of this porphyrin (see the supporting information). In addition, an experiment (entry 3, Table 3) clearly showed the SET photocatalytic effect of **TPFPP**, since under dark conditions and at 0 °C (background) only traces of compound **3a** were found. This result also corroborates with the previously presented background reactions (entries 9–10, Table 1), since the temperature effect (0 °C) is decisive to inhibit the chemical aryl-radical formation, while only the photocatalytic effect is present.

Table 3: Reactions with TPFPP in batch at 0 °C.

entry ^{a,b}	solvent (ratio)	LEDs (28 W)	yield 3a (%) ^c
1	CH ₂ Cl ₂ :CH ₃ NO ₂ :DMF (3.5:2.0:0.5)	white	71
2	CH ₂ Cl ₂ :CH ₃ NO ₂ :DMF (3.5:2.0:0.5)	blue	79/80 ^d
3	CH ₂ Cl ₂ :CH ₃ NO ₂ :DMF (3.5:2.0:0.5)	no light	1
4	DMF ^e	blue	69
5	CH ₃ NO ₂ :DMF (2.5:3.5)	blue	76
6	CH ₃ NO ₂ :DMF (5:1)	Blue	82/81 ^d

^a 1 mmol of **1a** and 15 mmol of **2a** in 6 mL of solvent/mixture using **TPFPP** (0.5 mol%) (total volume 8 mL)

 $^{\rm b}$ all the reactions were performed in 2h at 0°C.

^c isolated yields

^d double checked reaction

^e reactions in pure CH₂Cl₂ or CH₃NO₂ were not considered due to the low solubility of **1**a.

The use of only DMF as solvent (entry 4, Table 3) allowed the isolation of compound **3a** in 69% yield, and the mixtures of nitromethane and DMF (entries 5 and 6, Table 3) gave **3a** in 76 and 82% yield, respectively, demonstrating CH₃NO₂:DMF 5:1 as the best solvent mixture (double-checked experiment).

After finding some optimized conditions and the best solvent mixture (CH₃NO₂:DMF 5:1), the temperature effect was checked again, as well as the reaction time and lower excesses of enol acetate 2a (Table 4).

entry ^a	ratio 1a:2a	TPFPP	LEDs (28	temperature	reaction	yield 3a	
	(mmol)	(mol%)	W)	(°C)	time (h)	(%) ^b	
1	1:15	0.5	Blue	0	2	82	
2	1:15	0.5	Blue	25	2	72	
3	1:15	0.5	no light	25	8	28	
5	1:5	0.5	Blue	0	2	57	
6	1:1	0.5	Blue	0	2	44	

Table 4: Reactions with **TPFPP** in batch with CH₃NO₂:DMF (5:1).

^a in 6 mL of CH₃NO₂:DMF (5:1)

^b isolated yields

 Entry 1 (Table 4) presents the same result as entry 6 (Table 3) and was repeated only for easy comparison with different parameters from Table 4. The temperature effect (0 °C, 82% yield) is relevant as demonstrated by entry 2 (Table 4) in which an experiment at 25 °C gave **3a** in 72% yield. The 8h experiment in the dark (entry 3, Table 4) gave **3a** in 28% yield, in agreement with the thermal solvent induced de-diazotization.

Smaller excesses of **2a** were also evaluated giving **3a** in 57% yield by when using 5 eqv (entry 5, Table 4) and 44% yield when using 1 eqv (entry 6,

 Table 4). For these last results we have detected the presence of aryl-dimers by CG-MS indicating that the use of **2a** in large excess is crucial.

After optimizing the photoarylations of **2a** with the diazonium salt **1a** in batch, we adapted this protocol to continuous flow conditions using a homemade PFA tubing photo-reactor (Scheme 4) (see the supporting information for construction details).



Scheme 4. Continuous photo-flow setup.

Therefore, we decided to start with the optimized conditions from Table 3 (entry 6). All the tested total flow rates (0.1–1.0 mL.min⁻¹) (Table 5) furnished the compound **3a** in the range 73–92%, but with very different throughputs (g/day). Considering that the idea is to apply the continuous protocol for different aryldiazonium salts we adopted entry 5 (Table 5) with 0.4 mL.min⁻¹ total flow as the optimized condition (88% yield, 11.4 g/day and residence time

= 50 min). It is important to highlight that all the optimizations in flow were developed using the same amounts of substrates and solvent mixture (1 mmol of **1a** and 15 mmol of **2a** in 6 mL of CH_3NO_2 :DMF (5:1) - 8 mL total volume) for comparison with batch conditions. For batch experiments we used a glass tube, and for continuous flow conditions the reaction mixture was directly pumped using at the end the proper solvent mixture to push all the reaction through the photo-flow reactor.

entry ^{a,b}	flow (mL.min ⁻¹)	residence time (min)	yield 3a (%) ^c	throughput (g/day)
1	1.0	20	73	23.5
2	0.8	25	86	22.2
3	0.6	33	92	17.8
4	0.5	40	84/85 ^d	13.5/13.7
5	0.4	50	88	11.4
6	0.3	67	84	8.0
7	0.2	100	83	5.4
8	0.1	200	84	2.7

Table 5: Reactions under continuous flow conditions.

^a mixture of 1 mmol of **1a** and 15 mmol of **2a** in 6 mL of CH₃NO₂:DMF (5:1), **TPFPP** (0.5 mol%) (total volume 8 mL)

^b Homemade 20 mL PFA continuous photoreactor, blue LEDs (28W) with PFA tubes cooled to 0 ^oC – check the supporting information for details.

^c isolated yields

^d double checked experiment

Subsequently, the scope of different aryldiazonium salts was studied under continuous flow, thus obtaining compounds 3b-n (Scheme 5). The three substrates containing NO₂ groups (3b-c) were obtained in 70–88% yields, confirming the efficiency of the protocol and the reactivities of nitro-aryl-radicals.

 The group containing fluorine atoms (**3e–g**) was obtained in moderate yields (34–54%), and the other electron-withdrawing substituted diazonium salts **1h–j** led to the corresponding arylated products in 57–76% yields. The non-substituted arylated product **3d** and others substituted with electron-donating groups (**3k–n**) were obtained in 33–48% yields. For comparison, batch experiments (50 min) with the diazonium salts **1f** and **1k** gave **3f** and **3k** in 13 and 30% yield, respectively, confirming that our continuous protocol is more efficient. There was no formation of the products **3o** and **3p**, probably due to the higher reactivity of their radicals, with evidence of radical dimerization (as detected by GC-MS).



Scheme 5. Scope with different aryl-diazonium salts.

After exploring the scope of aryldiazonium salts, we investigated different enol acetates (**2b**–**g**) with **1a** as radical source using our optimized photo-flow continuous conditions (Scheme 6). The aldehyde **4b** was obtained in 45% yield, the arylated ketones **4c–4g** in yields from 26–77%.



Two-step Protocol for Photoarylations

Aiming at exploring a two-step protocol for photoarylations with **TPFPP** we constructed a setup for *in-situ* aryl diazonium salt generation (Scheme 7, Table 6).



Scheme 7. End-to end protocol for photoarylations.

Table 6: Two-step protocol under contir	nuous flow conditions.
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Entry	NaNO ₂ (mmol)	acid (mmol)	overall Yield 3 (%) ^b	throughput (g/day)
1 ^a	2	TFA (1.3)	28	4.5
2 ^a	2	TFA (0.65)	49	7.9
3ª	1	TFA (0.65)	36	5.8
4 ^a	2	PTSA (0.5)	-	-
5	2	HBF ₄ (1.3)	53	6.8
6 ^c	2	HBF ₄ (1.3)	43/45 ^d	8.3/8.7

^a PUMP 1 at 0.2 mL.min⁻¹: mixture of 4 (1 mmol), 2 (15 mmol), TFA, TPFPP (0.5 mol%) and DMF (1.3 mL). PUMP 2 at 0.2 mL.min⁻¹: NaNO₂ and DMF (3.5 mL) (overall flow at 0.4 mL.min⁻¹)
^b isolated yields

c PUMP 1 at 0.3 mL.min⁻¹: mixture of **4** (1 mmol), **2a** (15 mmol), **TPFPP** (0.5 mol%) and DMF (1.3 mL). PUMP 2 at 0.3 mL.min⁻¹: NaNO₂ and DMF (3.5 mL) (overall flow at 0.6 mL.min⁻¹) ^d double checked experiment

The use of 2 equiv of NaNO₂ and TFA (1.3 equiv) for the diazotization of **4** (entry 1, Table 6) furnished the corresponding product **3a** in 28% overall yield; however, using 0.65 equiv of TFA a significant increase was observed obtaining **3a** in 49% yield. Lower amounts of NaNO₂ (1 equiv, entry 3, Table 6) gave **3a**, but in 36% overall yield. PTSA does not work in this two-step protocol probably due to deactivation by protonation of **TPFPP**. The experiment with HBF₄ (entry 5, Table 6) gave compound **3a** in 53% yield and a throughput of 6.8 g/day. With a 0.6 mL.min⁻¹ overall flow, but maintaining the other reaction conditions, compound **3a** was obtained in 43–45% yield in double checked experiments (8.3–8.7 g/day). In addition, we tested the process intensification of this two-step protocol, carrying out a long-running experiment for 8h in a continuous steady state mode, obtaining compound **3a** in 48% yield (3.03 g, 16.9 mmol). This last result was obtained using the same reaction conditions of entry 6 (Table 6), and shows an easy process intensification of the protocol with the same efficiency of the standard protocol.

In summary, we have found that the two-step protocol is efficient considering that the overall 45% yield means almost 70% for each step.

Photophysical and Electrochemical Measurements and Mechanistic Insights

We then evaluated the photophysical and excited state electrochemical aspects of this protocol to rationalize the SET process of porphyrins in photoarylations. The results obtained with **TPFPP** were better than the photocatalyzed experiments with **TPP**, and no clear explanation is reported in

the literature. Therefore, why does a very electron deficient SET photocatalyst (**TPFPP**, with 20 fluorine atoms) work better than the corresponding neutral porphyrin (**TPP**)? It is important to highlight that a similar effect was previously observed by Gryko and co-workers²² in photoarylations of heterocycles, but no clear rationalization was provided.

First, we measured the photophysical and electrochemical properties of **TPP**, **TPFPP** and **1a** in order the estimate the thermodynamics of the SET processes (for the electrochemical and photoelectrochemical measurements and details, see the supporting information).

The $E_{ox}*[TPP^+/TPP^*]$ and $E_{ox}*[TPFPP^+/TPFPP^*]$ and E_{red} of **1a** were determined according to literature protocols. ^{15,34} As shown in Scheme 8 the triplet $E_{ox}*$ determined for **TPP** is -0.35V against +0.13V for **TPFPP**. However, considering the E_{red} of **1a** (+0.58V), both photocatalysts can efficiently reduce **1a** and yield the corresponding aryl radical, with ΔG_{SET} -21.4 and -10.4 kcal.mol⁻¹, respectively. If only the Gibbs energy of the radical generation (ΔG_{SET}) is considered, no explanation for the better efficiency of **TPFPP** can be found. However, considering all the photocatalytic cycle we found a significantly more favored turnover of **TPFPP**⁺⁻ to **TPFPP**, since its steady state oxidation potential (+1.77V) is 0.52V higher than for **TPP** (1.25V), thus justifying the improved photocatalytic efficiency of **TPFPP** can efficiently generate aryl radicals from aryldiazonium salts, but **TPFPP** is the best since its turnover is more efficient.



Scheme 8. Proposed photocatalytic cycle with experimental photo and electrochemical measurements.

The mechanistic proposal (Scheme 9) is very similar to the previously described by Köning³¹ which used different photocatalysts. Essentially, the photocatalytic cycle starts with the blue light exciting of **TPFPP** from the steady state (PS) to the singlet state (¹PS*) with a free decay to the triplet sate (³PS*), which presents an adequate E_{ox}* and longer lifetime as well. As demonstrated by our photo-electrochemical measurements (Scheme 8) in the triplet state, **TPFPP** is able to reduce the diazonium salt **1a**, thus generating the aryl radicals **A** which are trapped by **2a** to yield **B**. The intermediate **B** can be promptly oxidized giving the cation **C** and, subsequently, **3a**. Aiming to add more support to our mechanistic proposal we performed an experiment in the presence of 1eqv of TEMPO and detected the coupled product **6** by GC-MS (supporting Information).



Scheme 9. Mechanistic Proposal

CONCLUSIONS

 A protocol for the synthesis of α -aryl-ketones/aldehyde by photoarylation with diazonium salts is described using two different porphyrins (**TPP** and **TPFPP**) as SET photocatalysts. Batch and continuous flow optimized conditions are presented with significant yields (up to 92%), including a multigram scale experiment (3.03 g) performed under continuous flow conditions. The scope containing different diazonium salts and different enol-acetates is demonstrated, with a two-step protocol for the continuous photoarylations. Finally, photophysical and electrochemical studies provides a plausible rationalization

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for the better **TPFPP** efficiency as photocatalyst, and radical trapping experiments gave us some mechanistic insights on the photocatalytic cycle.

EXPERIMENTAL SECTION

Generalities: The starting materials were purchased from Sigma-Aldrich and used without any purification, and the solvents were used after distillation. Thinlayer chromatography (TLC) in silica gel 60 with F₂₅₄ (0.25 mm) was used to identify product formation, and the purification of products was carried out by column chromatography (silica gel, pore size 60 Å, 230 – 400 mesh). ¹H NMR and ¹³C NMR spectra were acquired with a Bruker Avance 400 spectrometer, operating at 400.15 and 100.62 MHz, respectively, using $CDCI_3$, acetone- d_6 or dimethylsufoxide- d_6 as solvents and tetramethylsilane as internal reference. Chemical shifts are reported in δ (ppm) relative to tetramethylsilane and the coupling constants (J) in Hertz (Hz). The multiplicities were assigned as: singlet (s), doublet (d), triplet (t), quadruplet (q), double doublet (dd), double triplet (dt), triple doublet (td) and multiplet (m). The continuous flow reactors are homemade and a KNAUER HPLC pump (AZURA P 4.1S) used for pumping the solutions. A Chiller RTE 101 (NESLAB) with a water / ethylene glycol mixture, operating at 0 °C was used in the jacketed reactions, and a back-pressure regulator (250 psi) connected at the end of the systems. The irradiation was conducted with 28W blue and white LEDs.

Experimental Procedures

Aryldiazonium tetrafluoroborate salts were prepared according to the literature.²³

4-nitrobenzenediazonium tetrafluoroborate (1a).³¹ Obtained as a light-yellow solid in 86% yield (8.6 mmol, 2.04 g). ¹**H NMR** (400 MHz, DMSO-*d6*): $\delta_{\rm H}$ 8.72 (d, *J* = 9.0 Hz, 2H), 8.94 (d, *J* = 9.0 Hz, 2H). ¹³**C {**¹**H} NMR** (100 MHz, DMSO-*d6*): $\delta_{\rm C}$ 121.8, 126.0, 134.4, 153.2.

2-nitrobenzenediazonium tetrafluoroborate (1b).³¹ Obtained as a white solid in 87% yield (8.7 mmol, 2.06 g). ¹**H NMR** (400 MHz, DMSO-*d6*): $\delta_{\rm H}$ 8.41 (t, *J* = 8.0 Hz, 1H), 8.53 (t, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.0 Hz, 1H), 9.11 (d, *J* = 8.0 Hz, 1H). ¹³**C {**¹**H} NMR** (100 MHz, DMSO-*d6*): $\delta_{\rm C}$ 111.1, 128.0, 136.5, 142.2, 144.5.

3-nitrobenzenediazonium tetrafluoroborate (1c).³¹ Obtained as a white solid in 43% yield (4.3 mmol,1.02 g). ¹H NMR (400 MHz, DMSO-*d6*): δ_H 8.24 (t, *J* = 8.3 Hz, 1H), 8.98 – 9.04 (m, 2H), 9.62 (t, *J* = 2.0 Hz, 1H). ¹³C {¹H} NMR (100 MHz, DMSO-*d6*): δ_C 118.2, 128.1, 132.7, 135.0, 137.9, 147.6.

Benzenediazonium tetrafluoroborate (1d).^{23a} Obtained as a white solid in 70% yield (7.0 mmol, 1.34 g). ¹H NMR (400 MHz, DMSO-*d6*): $\delta_{\rm H}$ 7.98 (t, *J* = 8.0 Hz, 2H), 8.26 (t, *J* = 8.0 Hz, 2H), 8.66 (t, *J* = 8.0 Hz, 1H). ¹³C {¹H} NMR (100 MHz, DMSO-*d6*): $\delta_{\rm C}$ 116.0, 131.2, 132.6, 140.8.

4-fluorobenzenediazonium tetrafluoroborate (1e).^{23a} Obtained as a white solid in 79% yield (7.9 mmol,1.66 g). ¹**H NMR** (400 MHz, DMSO-*d*6): $\delta_{\rm H}$ 7.85 – 7.91 (m, 2H), 8.91 – 8.96 (m, 2H). ¹³**C {¹H} NMR** (100 MHz, DMSO-*d*6): $\delta_{\rm C}$ 112.2, 120.6 (d, *J* = 25.6 Hz), 138.0 (d, *J* = 12.8 Hz), 170.5 (d, *J* = 268.8 Hz).

2-fluorobenzenediazonium tetrafluoroborate (1f).³⁵ Obtained as a white solid in 80% yield (8.0 mmol,1.68 g). ¹**H NMR** (400 MHz, DMSO-*d6*): $\delta_{\rm H}$ 7.82 (t, *J* = 8.0 Hz, 1H), 8.01 (t, *J* = 8.0 Hz, 1H), 8.35 – 8.41 (m, 1H), 8.71 – 8.7 (m, 1H). ¹³C {¹**H**} NMR (100 MHz, DMSO-*d6*): $\delta_{\rm C}$ 105.5 (d, *J* = 12.80 Hz), 118.6 (d, *J* =

15.0 Hz), 127.4 (d, *J* = 2.2 Hz), 133.4 (d, *J* = 3.7 Hz), 144.6 (d, *J* = 9.0 Hz), 160.2 (d, *J* = 273.3 Hz).

3-fluorobenzenediazonium tetrafluoroborate (1g).³⁶ Obtained as a white solid in 82% yield (8.2 mmol, 1.72 g). ¹**H NMR** (400 MHz, $(CD_3)_2CO-d6$): δ_H 8.15 – 8.20 (m, 1H), 8.22 – 8.27 (m, 1H), 8.70 – 8.73 (m, 1H), 8.75 – 8.78 (m, 1H). ¹³C {¹H} NMR (100 MHz, $(CD_3)_2CO-d6$): δ_C 117.8 (d, *J* = 12.0 Hz); 120.5 (d, *J* = 30.1 Hz), 130.6 (d, *J* = 21.0 Hz), 130.8 (d, *J* = 3.7 Hz), 134.8 (d, *J* = 9.0 Hz), 162.2 (d, *J* = 253.7 Hz).

4-chlorobenzenediazonium tetrafluoroborate (1h).^{23a} Obtained as a white solid in 75% yield (7.5 mmol,1.70 g).¹H NMR (400 MHz, $(CD_3)_2CO-d6$): δ_H 8.14 – (d, *J* = 9.0 Hz, 2H), 8.84 (d, *J* = 9.0 Hz, 2H). ¹³C {¹H} NMR (100 MHz, $(CD_3)_2CO-d6$): δ_C 115.0, 132.9, 135.4, 149.0.

2-trifluoromethylbenzenediazonium tetrafluoroborate (1i).³¹ Obtained as a white solid in 86% yield (8.6 mmol, 2.23 g).¹H NMR (400 MHz, $(CD_3)_2CO-d6$): $\delta_H 8.46$ (t, J = 8.0 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.68 (t, J = 8.0 Hz, 1H), 9.21 (d, J = 8.0 Hz, 1H). ¹³C {¹H} NMR (100 MHz, $(CD_3)_2CO-d6$): δ_C 113.8, 122.0 (d, J = 274.0 Hz), 130.7 (d, J = 36.1 Hz), 131.6 (d, J = 3.0 Hz); 136.5, 137.2; 143.4. **3-trifluoromethylbenzenediazonium tetrafluoroborate (1j).**^{23a} Obtained as a white solid in 83% yield (8.3 mmol, 2.16 g). ¹H NMR (400 MHz, DMSO-*d6*): δ_H 8.24 (t, J = 8.0 Hz, 1H), 8.68 (d, J = 8.0 Hz, 1H), 8.97 (d, J = 8.0 Hz, 1H), 9.22 (s, 1H). ¹³C {¹H} NMR (100 MHz, DMSO-*d6*): δ_C 118.3, 122.0 (d, J = 273.3 Hz), 130.1 (d, J = 3.7 Hz), 130.1 (d, J = 34.6 Hz), 132.7, 136.5, 137.2 (d, J = 3.0 Hz). **4-ethylbenzenediazonium tetrafluoroborate (1k).**³⁷ Obtained as a white solid in 78% yield (7.8 mmol, 1.71 g).¹H NMR (400 MHz, DMSO-*d6*): δ_H 1.25 (t, J = 7.0 Hz, 3H), 2.83 – 2.90 (m, 2H), 7.85 (d, J = 8.0 Hz, 2H), 8.58 2H). ¹³C {¹H} NMR (100 MHz, DMSO-*d6*): δ_C 14.4, 29.0, 112.1, 130.7 132.8, 159.3.

4-methoxybenzenediazonium tetrafluoroborate (11).³¹ Obtained as a grey solid in 85% yield (8.5 mmol,1.88 g). ¹H NMR (400 MHz, DMSO-*d6*): $\delta_{\rm H}$ 4.04 (s, 3H), 7.48 (d, *J* = 9.4 Hz, 2H), 8.60 (d, *J* = 9.4 Hz, 2H). ¹³C {¹H} NMR (100 MHz, DMSO-*d6*): $\delta_{\rm C}$ 57.4, 103.2, 117.2, 136.0, 168.8.

2-methoxybenzenediazonium tetrafluoroborate (1m).³⁸ Obtained as a light orange solid in 74% yield (7.4 mmol,1.64 g).¹**H NMR** (400 MHz, DMSO-*d6*): $\delta_{\rm H}$ 4.19 (s, 3H), 7.43 – 7.57 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 8.21 – 8.25 (m, 1H), 8.51 (dd, *J* = 8.4 and 1.6 Hz, 1H). ¹³**C {**¹**H} NMR** (100 MHz, DMSO-*d6*): $\delta_{\rm C}$ 58.6, 102.2, 114.8, 122.8, 132.3, 143.7, 162.0.

3-methoxybenzenediazonium tetrafluoroborate (1n).^{23a} Obtained as a white solid in 78% yield (7.8 mmol,1.73 g). ¹**H NMR** (400 MHz, $(CD_3)_2CO-d6$): δ_H 4.02 (s, 3H), 7.90 – 7.93 (m, 1H), 7.98 (m, 1H), 8.37 (t, *J* = 2.3 Hz, 1H), 8.44 – 8.47 (m, 1H). ¹³C {¹H} NMR (100 MHz, $(CD_3)_2CO-d6$): δ_C 57.3, 116.3, 117.0, 126.6, 130.0, 133.4, 161.5.

4-(dimethylamino)benzenediazonium tetrafluoroborate (10).³⁹ Obtained as a white solid in 70% yield (7.0 mmol,1.64 g). ¹**H NMR** (400 MHz, DMSO-*d*6): $\delta_{\rm H}$ 3.26 (s, 6H), 7.06 (d, *J* = 9.8 Hz, 2H), 8.21 (d, *J* = 9.8 Hz, 2H). ¹³**C {**¹**H} NMR** (100 MHz, DMSO-*d*6): $\delta_{\rm C}$ 40.4, 88.9, 113.8, 134.0, 156.1.

3,4-(Methylenedioxy) benzenediazonium tetrafluoroborate (1p).³⁸ Obtained as a solid in 45% yield (4.5 mmol,1.06 g). ¹**H NMR** (400 MHz, DMSO-*d*6): $\delta_{\rm H}$ 6.45 (s, 2H), 7.48 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 2.1 Hz, 1H), 8.04 (dd, *J* = 8.7 and 2.1 Hz, 1H). ¹³**C {**¹**H} NMR** (100 MHz, DMSO-*d*6): $\delta_{\rm C}$ 104.4, 105.5, 109.4, 110.6, 134.1, 148.4, 158.8. **General procedure for the preparation of non-commercial enol-acetates.**⁴⁰ To a flask containing PTSA (0.5 g), a mixture of the ketones (1.0 equiv.,160 mmol), and isopropenyl acetate (1.8 equiv, 288 mmol) was added and subsequently heated at 100 °C. After 24 hours, the reaction mixture was diluted in ethyl acetate (30 mL) and washed with water (3 x 50 mL) and saturated NaHCO₃ solution (50 mL). The organic layer was separated and dried with Na₂SO₄, filtered and concentrated under reduced pressure. All products were purified by column chromatography using toluene/ethyl acetate (9.8:0.2) as eluent.

1-phenylvinyl acetate (2c).⁴⁰ Obtained in 50% yield (23.5 g, 144.9 mmol). ¹**H NMR** (400 MHz, (CD₃)₂CO-*d*6): $\delta_{\rm H}$ 2.28 (s, 3H), 5.03 (d, *J* = 2.3 Hz, 1H), 5.61 (d, *J* = 2.3 Hz, 1H), 7.61 – 7.41 (m, 2H), 7.58 – 7.58 (m, 2H). ¹³**C {¹H} NMR** (100 MHz, (CD₃)₂CO-*d*6): $\delta_{\rm C}$ 20.9, 102.5, 125.7, 129.4, 129.7, 135.4, 154.0, 169.3.

1-cycloheptenyl acetate (2d).⁴¹ Obtained in 60% yield (26.6 g, 172.6 mmol). ¹**H NMR** (400 MHz, CDCl₃): $\delta_{\rm H}$ 1.58 – 1.72 (m, 6H), 2.07 – 2.10 (m, 5H), 2.29 – 2.32 (m, 2H), 5.45 (t, J = 6.45 Hz, 1H). ¹³**C {**¹**H**} **NMR** (100 MHz, CDCl₃): $\delta_{\rm C}$ 20.9, 25.2, 25.2, 26.9, 30.9, 33.0, 117.9, 153.1, 169.7.

1-cyclohexenyl acetate (2e).⁴⁰ Obtained in 80% yield (32.3 g, 230.4 mmol). ¹**H NMR** (400 MHz, CDCl₃): δ_{H} 1.58 – 1.61 (m, 2H), 1.72 – 1.75 (m, 2H), 2.09 – 2.13 (m, 7H), 5.34 – 5.36 (m, 1H). ¹³**C {¹H} NMR** (100 MHz, CDCl₃): δ_{C} 21.0, 21.6, 22.5, 23.5, 26.7, 113.9, 148.3, 169.4.

1-cyclopentenyl acetate (2f).⁴² Obtained in 65% yield (23.6 g, 187.2 mmol).¹**H NMR** (400 MHz, DMSO-*d6*): δ_H 1.84 – 1.88 (m, 2H), 2.09 (s, 3H), 2.26 – 2.28 (m, 2H), 2.35 – 2.37(m, 2H), 5.34 – 5.37 (m, 1H). ¹³C {¹H} NMR (100 MHz, DMSO-*d6*): $\delta_{\rm C}$ 20.9, 20.9, 28.4, 30.9, 112.7, 151.1, 168.4.

2-pentenyl acetate (2g).⁴⁰ Obtained in 72% yield (26.5 g, 206.7 mmol). Mixture E/Z. ¹H NMR (400 MHz, DMSO-*d6*): $\delta_{\rm H}$ 0.91–0.96 (m, 3H), 1.39 – 1.41 (m, 2H), 1.57–1.59 (m, 1H), 2.06–2.23 (m, 5H), 5.01– 5.07 (m, 1H). ¹³C {¹H} NMR (100 MHz, DMSO-*d6*): $\delta_{\rm C}$ 10.6, 11.2, 11.3, 11.4, 20.6, 20.8, 21.8, 26.4, 109.2, 111.2, 150.4, 150.5, 168.3, 169.4.

General procedure for enol-acetate photoarylation in batch.

 TPFPP (4.87 mg, 0.5 mol%, 0.005 mmol) and DMF (1 mL) were added to a screwcap glass tube (15 mL). Nitromethane (5.0 mL), enol acetate (15 equiv, 1.65 mL) and 4-nitrobenzenediazonium tetrafluoroborate (1 equiv, 236.0 mg) were added and the tube closed with a rubber septum, fully protected from light and degassed for five minutes under argon and with ultrasound. The reaction mixture was stirred for 2 hours at 0 °C (freezer) with irradiation by the blue LEDs. The workup was performed with water (20 mL) and extracted with toluene (3 x 30 mL). The organic layer was dried over Na₂SO₄, filtered and concentered under reduced pressure. The reaction was purified by column chromatography using hexane:ethyl acetate (9:1) as eluent.

General procedure for enol-acetate photoarylation under continuous flow conditions. TPFPP (4.87 mg, 0.5 mol%, 0.005 mmol) and DMF (1 mL) were added to a glass tube (15 mL). Nitromethane (5.0 mL), enol acetate (15 equiv, 1.65 mL) and 4-nitrobenzenediazonium tetrafluoroborate (1 equiv, 236.0 mg) were added and the tube closed with a rubber septum, fully protected from light and degassed for five minutes under argon and with ultrasound. The reaction mixture was transferred to a PFA loop (9.0 mL), cooled at 0 °C and pumped

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(0.4 mL.min⁻¹) through the blue LED reactor (20 mL total volume), also maintained at 0°C using a cooled jacketed glass reactor. The solvent mixture 5:1 nitromethane/dimethylformamide was used for pumping the reaction mixture. All products were purified on silica gel using a hexane/ethyl acetate solvent gradient (from 9.5:0.5 to 9.0:1.0).

1-(4-nitrophenyl)propan-2-one (3a).³¹ Obtained as a yellow oil in 88% yield (0.88 mmol, 156 mg) ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.25 (s, 3H), 3.87 (s, 2H), 7.37 (d, *J* = 9.0 Hz, 2H), 8.19 (d, *J* = 9.0 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.8, 49.8, 123.6, 130.5, 141.7, 146.9, 204.3.

1-(2-nitrophenyl)propan-2-one (3b).³¹ Obtained as a yellow oil in 74% yield (0.74 mmol, 132.5 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.30 (s, 3H), 4.12 (s, 2H), 7.27 (dd, J = 8.0 and 1.0 Hz,1H), 7.44 (td, J = 8.0 and 1.3 Hz, 1H), 7.58 (td, J = 8.0 and 1.0 Hz, 1H), 8.09 (dd, J = 8.0 and 1.3 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 30.0, 48.6, 125.2, 128.4, 130.4, 133.6, 133.7, 148.6, 203.7.

1-(3-nitrophenyl)propan-2-one (3c).³¹ Obtained as a yellow oil in 70% yield (0.70 mmol, 125 mg). ¹H NMR (400 MHz, CDCl₃): δ_H 2.26 (s, 3H), 3.88 (s, 2H), 7.50 – 7.55 (m, 2H), 8.06 (s, 1H), 8.12 – 8.15 (m, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ_C 29.9, 49.6, 122.1, 124.5, 129.5, 135.9, 136.0, 148.3, 204.5.

1-phenylpropan-2-one (3d).⁴³ Obtained as a yellow oil in 30% yield (0.30 mmol, 40.2 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.07 (s, 3H), 3.61 (s, 2H), 7.14 – 7.12 (m, 2H), 7.17 – 7.21 (m, 1H), 7.24 – 7.28 (m, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.3, 51.0, 127.1, 128.8, 129.4, 134.2, 206.4.

1-(4-fluorophenyl)propan-2-one (3e).⁴⁴ Obtained as a yellow oil in 47% yield (0.47 mmol, 71.4 mg). ¹H NMR (400 MHz, CDCl₃): δ_{H} 2.08 (s, 3H), 3.60 (s, 2H),

6.94 (t, J = 8.3 Hz, 2H), 7.06 – 7.10 (m, 2H). ¹³**C** {¹H} **NMR** (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.3, 49.9, 115.6 (d, J = 21.8 Hz), 129.9 (d, J = 2.3 Hz), 131.0 (d, J = 8.0 Hz), 161.8 (d, J = 245.4 Hz), 206.0.

1-(2-fluorophenyl)propan-2-one (3f).⁴⁵ Obtained as a yellow oil in 43% yield (0.43 mmol, 65.4 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.13 (d, *J* = 0.3 Hz, 3H), 3.67 (s, 2H), 6.97 – 7.00 (m, 1H), 7.03 (td, *J* = 7.5 and 2.0 Hz, 1H), 7.10 (td, *J* = 7.5 and 2.0 Hz, 1H), 7.16 – 7.22 (m, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.4, 43.9, 115.4 (d, *J* = 21.8 Hz), 121.6 (d, *J* = 16.6 Hz), 124.2 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 8.3 Hz), 131.6 (d, *J* = 4.5 Hz), 161.0 (d, *J* = 245.4 Hz), 205.0.

1-(3-fluorophenyl)propan-2-one (3g).⁴⁶ Obtained as a yellow oil in 54% yield (0.54 mmol, 82.1 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.09 (s, 3H), 3.62 (s, 2H), 6.82 – 6.90 (m, 2H), 7.21 (m, Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.41, 50.39, 113.95 (d, *J* = 20.3 Hz), 116.40 (d, J = 21.8 Hz), 125.15 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 8.3 Hz), 136.5 (d, *J* = 7.0 Hz), 163.0 (d, *J* = 246.2 Hz), 205.5.

1-(4-chlorophenyl)propan-2-one (3h).³¹ Obtained as a yellow oil in 76% yield (0.76 mmol, 128 mg). ¹H NMR (400 MHz, CDCl₃): δ_H 2.16 (s, 3H), 3.67 (s, 2H), 7.12(d, *J*= 8.2 Hz, 2H), 7.29 (d, *J*= 8.2 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ_C 29.4, 50.0, 128.8, 130.8, 132.6, 133.0, 205.7.

1-(2-(trifluoromethyl)phenyl)propan-2-one (3i).³¹ Obtained as a yellow oil in 57% yield (0.57 mmol, 115 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.21 (s, 3H), 3.92 (s, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.6, 47.4, 124.5 (d, *J* = 273.3 Hz), 126.2 (d, *J* = 5.3 Hz), 127.3, 131.9, 132.7, 132.8, 204.7.

1-(3-(trifluoromethyl)phenyl)propan-2-one (3j).⁴⁴ Obtained as a yellow oil in 67% yield (0.67 mmol, 135 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.20 (s, 3H), 3.78 (s, 2H), 7.38 (m, 1H), 7.45 (m, 2 H), 7.53 (m, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.6, 50.2, 123.9 (d, *J* = 20.3 Hz), 124.3 (d, *J* = 21.8 Hz), 126.2 (d, *J* = 3.0 Hz), 129.1, 130.9 (d, *J* = 7.0 Hz), 133.0, 135.0 (d, *J* = 246.2 Hz); 205.2.

1-(4-ethylphenyl)propan-2-one (3k).⁴⁷ Obtained as a yellow oil in 43% yield (0.43 mmol, 69.7 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 1.22 (t, *J* = 7.7 Hz, 3H), 2.13 (s, 3H), 2.63 (q, *J* = 7.7 Hz, 2H), 3.65 (s, 2H), 7.11(d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 15.6, 28.5, 29.2, 50.7, 128.3, 129.4, 131.4, 143.0, 206.8.

1-(4-methoxyphenyl)propan-2-one (3I).³¹ Obtained as a yellow oil in 48% yield (0.48 mmol, 78.7 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.06 (s, 3H), 3.56 (s, 2H), 3.72 (s, 3H), 6.80 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.1, 50.1, 55.3, 114.2, 126.3, 130.4, 158.7, 206.9.

1-(2-methoxyphenyl)propan-2-one (3m).⁴⁸ Obtained as a yellow oil in 40% yield (0.40 mmol, 65.6 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.05 (s, 3H), 3.58 (s, 2H), 3.72 (s, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.84 (td, *J* = 8.0 and 1.2 Hz, 1H), 7.04 (dd, *J* = 8.0 and 1.2 Hz, 1H), 7.17 (td, *J* = 8.0 and 1.2 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 29.3, 45.6, 55.3, 110.5, 120.7, 123.6, 128.6, 131.1, 157.4, 207.1.

1-(3-methoxyphenyl)propan-2-one (3n).⁴⁴ Obtained as a yellow oil in 33% yield (0.33 mmol, 54.1 mg). ¹H NMR (400 MHz, CDCl₃): δ_{H} 2.08 (s, 3H), 3.59 (s, 2H), 3.73 (s, 3H), 6.67 – 6.68 (m, 1H), 6.71–6.76 (m, 2H), 7.16–7.20 (m, 1H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ_{C} 29.2, 51.1, 55.2, 112.5, 115.0, 121.8, 129.8, 135.7, 159.9, 206.4.

2-(4-nitrophenyl)acetaldehyde (4b).³¹ Obtained as a yellow oil in 45% yield (0.45 mmol, 74.3 mg). ¹H NMR (400 MHz, CDCl₃): δ_H 3.81 (d, J = 1.7 Hz, 2H), 7.33 (d, J = 8.7Hz, 2H), 8.15 (d, J = 8.7Hz, 2H), 9.75 (t, J = 1.7 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ_C 50.0, 124.0, 130.6, 139.4, 147.4, 197.3.

2-(4-nitrophenyl)-1-phenylethanone (4c).³¹ Obtained as a yellow solid in 77% yield (0.77 mmol, 186 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 4.42 (s, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.48 – 7.52 (m, 2H), 7.59 – 7.61 (m, 1H), 8.00 – 8.03 (m, 2H), 8.19 (d, J = 8.7 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 44.9, 123.6, 128.4, 128.8, 130.6, 133.7, 136.1, 142.0, 147.0, 195.9.

2-(4-nitrophenyl)cycloheptanone (4d).⁴⁹ Obtained as a yellow oil in 40% yield (0.40 mmol, 93.2 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 1.43 – 1.76 (m, 3H), 1.96 – 2.14 (m, 5H), 2.63 – 2.66 (m, 2H), 3.91 (dd, *J* = 11.0 and 3.2 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 8.17(d, *J* = 8.8 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 24.4, 29.1, 29.4, 32.4, 43.4, 58.0, 123.5, 129.1, 146.8, 148.1, 211.8.

2-(4-nitrophenyl)cyclohexanone (4e).³¹ Obtained as a yellow oil in 49% yield (0.26 mmol, 57.0 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 1.81 – 2.06 (m, 4H), 2.19 – 2.34 (m, 2H), 2.46 – 2.59 (m, 2H), 3.75 (dd, *J* = 12.5 and 5.1 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 25.3, 27.7, 35.2, 42.2, 57.3, 123.5, 129.6, 146.4, 148.9, 208.9.

2-(4-nitrophenyl)cyclopentanone (4f).⁴⁹ Obtained as a yellow oil in 31% yield (0.31 mmol, 63.5 mg). ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 1.98 – 2.38 (m, 4H), 2.51 – 2.61 (m, 2H), 3.45 (dd, J_1 , J_2 = 8.7 and 12.0 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H),

8.18 (d, *J* = 8.5 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ_C 20.8, 31.2, 38.2, 55.0, 123.7, 129.1, 145.7, 146.9, 216.2.

2-(4-nitrophenyl)pentan-3-one (4g).³¹ Obtained as a yellow oil (mixture *E/Z*) in 50% yield (0.45 mmol, 74.3 mg). ¹**H NMR** (400 MHz, CDCl₃): $\delta_{\rm H}$ 1.00 (t, *J* = 7.3 Hz 3H), 1.45 (d, *J* = 7.0 Hz, 3H), 2.40–2.47 (m, 2H), 3.93 (q, *J* = 7.0 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 7.9, 17.7, 34.9, 52.3, 124.1, 128.8, 147.1, 148.1, 209.9.

Two-step protocol for photoarylations.

TPFPP (4.87 mg, 0.5 mol%, 0.005 mmol), 1.0 mmol of 4-nitroaniline (138 mg, 1.0 equiv), 2.0 mL of DMF, enol acetate (15 equiv, 1.65 mL) and tetrafluoroboric acid solution 48 w% (1.3 equiv, 0.26 mL) were mixed in a flask. In another flask NaNO₂ (2.0 equiv, 138.0 mg in 0.5 mL of H₂O) and 3.5 mL de DMF were mixed. Both solutions were degassed for five minutes. Two 4.0 mL loops were separately filled with the solutions and pumped (0.2 mL.min⁻¹) through a T mixer connected in the photoreactor inlet. Product purification was performed as previously described.

Compound 6³¹ GC-MS. EM *m/z*: 278 (5%), 206(10%), 179(10%), 69 (100%).

ASSOCIATED CONTENT

Supporting information: The supporting information is available free of charge on the ACS Publications website at DOI: 101021/acs.joxxxx. Supporting information contains ¹H and ¹³C{¹H} NMR spectra, photo and electrochemical measurements and all the details of the homemade engineered flow-chem and batch setups.

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