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Direct C–H photoarylation of diazines using aryldiazonium salts and visible-light†

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In this study, direct C–H photoarylation of pyrazine with aryldiazonium salts under visible-light irradiation (blue-LEDs) is described, and additional examples including photoarylations of pyrimidine and pyridazine are also covered. The corresponding aryl-diazines were prepared in yields up to 84% only by mixing and irradiating the reaction with no need for an additional photocatalyst. We demonstrate the efficacy of this protocol by the scope with electron-donor, -neutral, and -withdrawing groups attached at the *ortho*, *meta*, and *para* positions of the aryldiazonium salts; the results are better than those reported for ruthenium-complex mediated photoarylations. Additionally, we demonstrate the robustness of this methodology with a 5 mmol scaled-up experiment. Mechanistic studies were carried out giving support to the proposal of a photocatalyzed approach by an electron donor–acceptor (EDA) complex, also highlighting the crucial role that solvents play in the formation of the EDA complex.

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Introduction

The 1,*n*-diazines, such as pyridazines (*n* = 2), pyrimidines (*n* = 3) and pyrazines (*n* = 4), are six-membered aromatic rings containing two nitrogen atoms. These building blocks are electron-deficient common *N*-heteroarenes present in natural products,^{1–3} active pharmaceutical ingredients (APIs),^{4,5} agrochemicals,⁶ and functionalized materials.^{7,8} Arylated diazines moieties can be found in many blockbuster drugs, such as rosuvastatin (Crestor®), sildenafil (Viagra®), and imatinib (Gleevec®), besides others such as minaprine, gabazine, and botryllazine (Fig. 1). Therefore, the development of methodologies for the formation of C–C bonds between aryl groups and diazines is fundamental to the pharmaceutical industry, and still a challenge for organic chemists.

Metal-catalyzed cross-coupling reactions have been widely employed in the arylation of electron-deficient *N*-heteroarenes, mainly for the azines (pyridines and their derivatives).^{9–11} In comparison with pyridines, the presence of a second *N*-atom in the diazines decreases significantly the electron density of these compounds, which limits the use of such protocols.¹² Typically, metal-catalyzed protocols depend on either electrophilic substitution or sequential metalation/deprotonation mechanism, which restrict their application to only electron-rich substrates or acidic C–H bond containing compounds, respectively.^{13–15}

In 2006, Fagnou and co-workers reported a methodology for the synthesis of a series of (*N*-hetero)bis-aryl scaffolds using diazine *N*-oxides and aryl halides, catalyzed by palladium and copper complexes at high temperatures¹² (Scheme 1, eqn (a)).

Other metals, including gold,¹⁶ nickel,¹³ and manganese¹⁷ were successfully applied to the cross-coupling between the aryl halide or arylboronic acid and diazines. In 2010, Baran and co-workers reported a silver-catalyzed Minisci-type reaction for the arylation of azines and some diazines *via* radical coupling using arylboronic acids, the silver salt, and potassium persulfate¹⁵ (Scheme 1, eqn (b)). Vishwakarma, Singh, and co-workers reported a similar protocol for the arylation of pyrazines (1,4-diazine) with a wide variety of arylboronic acids using an iron complex¹⁸ (Scheme 1, eqn (c)). The same group, in 2016, also reported a metal-free approach for this transformation, generating the aryl radical at 160 °C (neat) in the presence of potassium persulfate and the arylboronic acid (Scheme 1, eqn (d)).¹⁹ Xue and co-workers demonstrated that visible-light can be employed in the arylation of diazines using a Ru(bpy)₂Cl₂ complex and aryldiazonium tetrafluoroborate as the source of aryl radicals (Scheme 1, eqn (e)).²⁰

Herein, we report a protocol for the direct C–H photoarylation of pyrazine, pyrimidine, and pyridazine nuclei using a variety of aryldiazonium salts substituted with electron-donor, neutral and acceptor groups. Our methodology was developed without additives such as strong oxidants nor additional photocatalysts; only the substrates, solvents, and visible-light irradiation (blue LEDs) were used. We postulate that the reaction proceeds by a photoactive electron donor–acceptor (EDA) complex between the diazines and the aryldiazonium salts, thus

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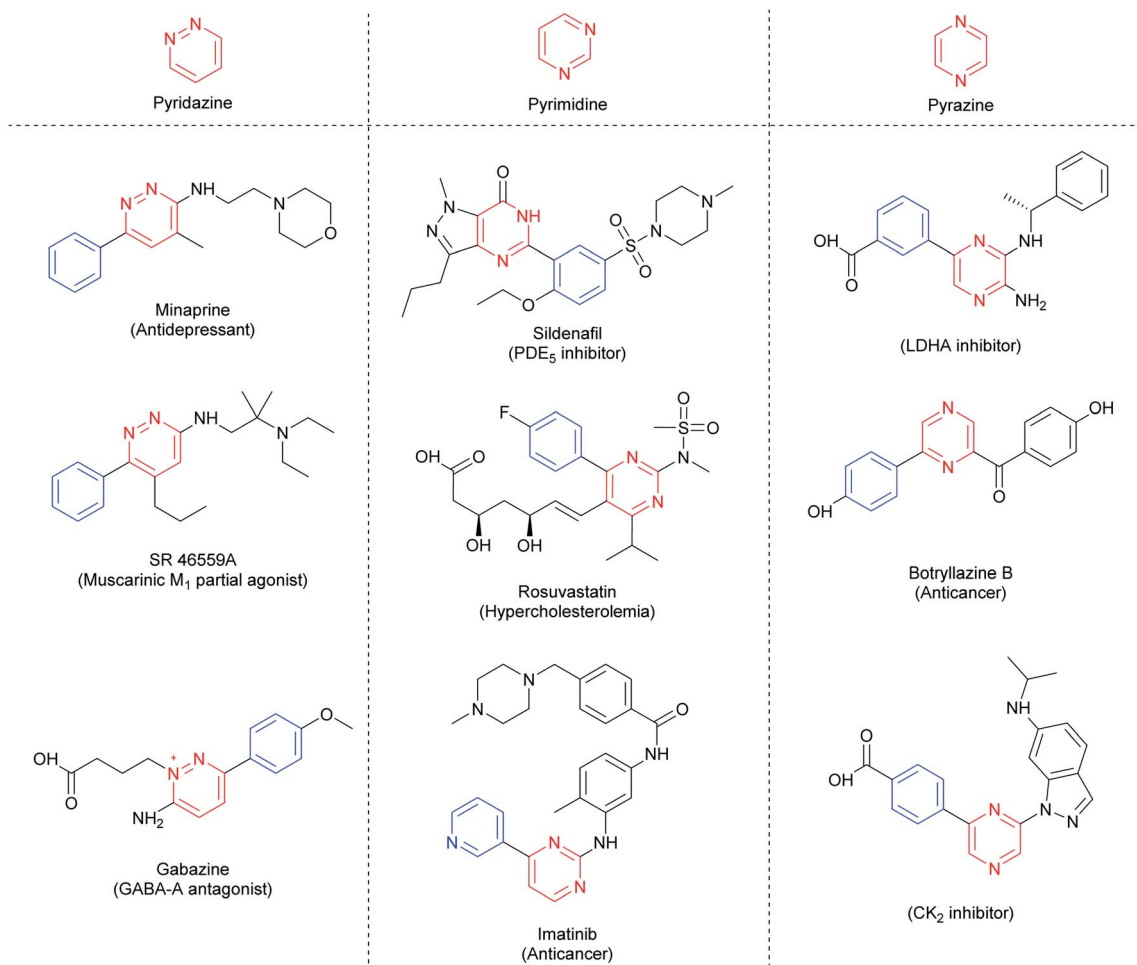


Fig. 1 Representative drugs containing diazine moieties.

allowing photocatalytic aryl radical generation and subsequent reaction with the diazines (Scheme 1, eqn (f)).

Results and discussion

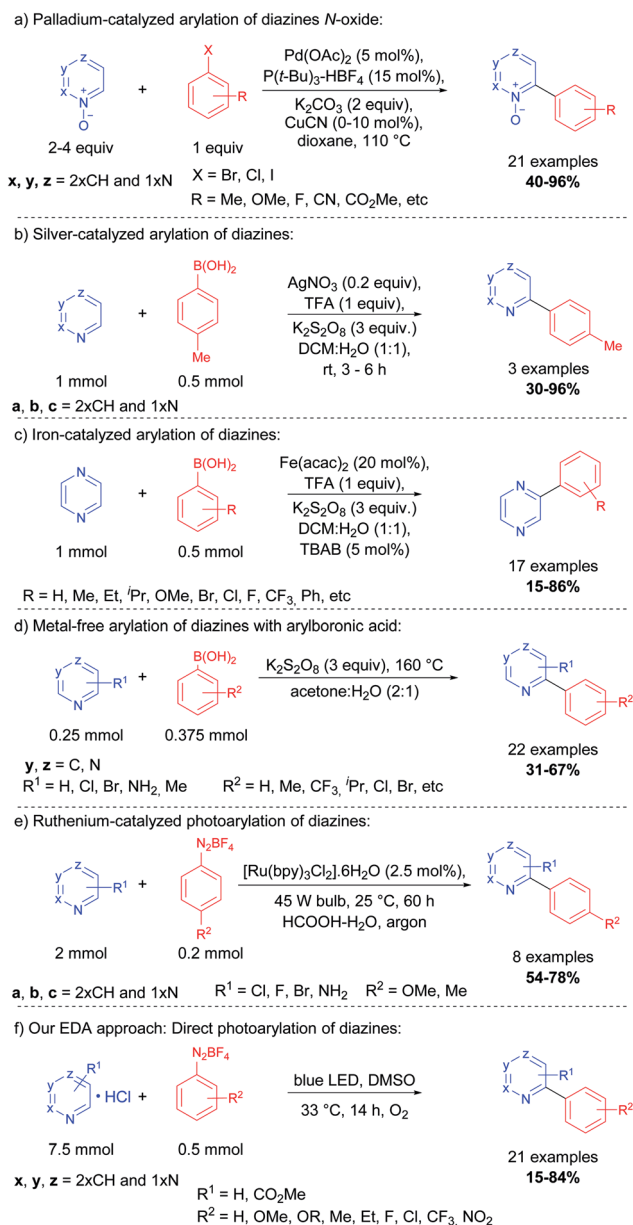
Initially, pyrazine free base (**1a**) and *p*-methoxybenzenediazonium tetrafluoroborate (**2a**) were selected as model substrates. A homemade blue LED (120 W) photoreactor was used and the setup was equipped with a control system (Arduino) to monitor both irradiation time and the internal temperature of the photoreactor (details of the photoreactor and control system are shown in the ESI, Fig. S2–S4†). The reaction between (**1a**) (0.75 mmol) and (**2a**) (0.1 mmol) in water (0.6 mL) was tested under an oxygen atmosphere in the absence of light at 40 °C, thus furnishing 2-(4-methoxyphenyl)pyrazine (**3a**) as traces (2% of yield) after 14 h (Table 1, entry 1). Subsequently, the product (**3a**) was obtained in 20% yield under blue LED irradiation (14 h) at 33 °C (temperature controlled photoreactor), thus suggesting that this transformation is potentially photoinduced (Table 1, entry 2).

Attempts to improve the protocol efficiency were tested using 15, 25, and 30 equiv. of **1a** in comparison to **2a**, thus obtaining

3a in 43, 52, and 59%, respectively (Table 1, entries 3–5). Using an excess of **2a** instead of **1a** allowed us to obtain **3a** in only 2% yield (Table 1, entry 6). Ruthenium-mediated photoarylation reaction of diazines with aryldiazonium salts, reported by Xue and co-workers,²⁰ also required a relevant excess (10 equiv.) of diazines for this transformation, suggesting that the use of excesses of diazines are crucial in photoarylation protocols. Consequently, further screenings of the reaction conditions were performed with the use of 15 equiv. of **1a** in comparison to **2a**.

The increase of the irradiation time from 14 to 24 h did not lead to better results (44% yield, Table 1, entry 7), while a decrease of the yield (31%) was observed with 8 h of irradiation (Table 1, entry 8). We have recently shown that protonated pyridines can be efficiently employed in photoarylations by EDA-complexes in water under visible-light irradiation.²¹ Therefore, we decided to test the use of pyrazine hydrochloride (**1b**) (1.5 mmol) in water. In these conditions, **3a** was obtained in 8% yield (14 h, Table 1, entry 9). However, an excellent result was obtained using DMSO as the solvent, giving **3a** in 81% yield (78% isolated yield) under the same reaction conditions (Table 1, entry 10).



Scheme 1 Representative protocols for C–H arylation of 1,*n*-diazines.

Continuing with our evaluation of solvents, the low solubility of pyrazine hydrochloride limited the choice to DMF and a mixture of DMSO with acetonitrile (1 : 1), thus giving **3a** in 9 and 44% yields, respectively (Table 1, entries 11 and 12). Attempts to generate the pyrazinium cation *in situ* starting from **1a** were carried out using *p*-toluenesulfonic acid as the proton source. However, a slight reduction in the yields was observed when 15 and 20 equiv. of PTSA were used (65 and 66% yield, Table 1, entries 13 and 14, respectively).

Considering the possibility of an EDA mechanism, the low electron density of the diazines reduces their ability as donor species. One strategy much employed to avoid this limitation is to use sacrificial donor compounds that promote the efficient formation of the EDA complex with the acceptor species.^{22,23} A variety of sacrificial donor compounds have been used in the

literature such as *N,N*-dimethylaniline,²⁴ triethylamine,²⁵ 1,3,5-trimethoxybenzene (TMB),²⁶ and pyridine.²⁷ Thus, the photoarylation of pyrazine hydrochloride (**1b**) with *p*-methoxybenzenediazonium tetrafluoroborate (**2a**) was carried out using TMB or pyridine as sacrificial donors. However, product **3a** was obtained in 28 and 33% yields, respectively (Table 1, entries 15 and 16).

Subsequently, the effect of the temperature was evaluated. The photoarylation of **1b** with **2a** was carried out at –22 °C using a mixture of DMSO and acetonitrile to avoid the freezing of DMSO. The yields were 51 and 54% for the mixtures of DMSO/acetonitrile (1 : 1) and (3 : 1), respectively (Table 1, entries 17 and 18). These results are superior to those performed with DMSO/acetonitrile (1 : 1) at 33 °C (44% yield, Table 1, entry 12), but not better than when pure DMSO at 33 °C was used (81%, Table 1, entry 10). The improvements in these photoarylations at low temperatures have already been demonstrated²⁸ since this increases the excited-state lifetime of the EDA complexes. However, a limitation of using only DMSO (mp = 19 °C) as an optimal solvent in this protocol restricts the use of low temperatures.

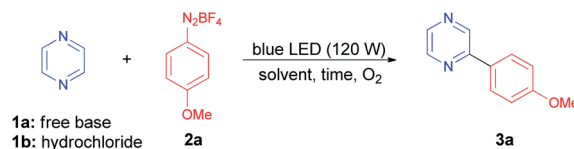
Since the mixture between molecular oxygen and DMSO has been proved by Liu and co-workers²⁹ to be an efficient radical oxidative reagent under thermal conditions (high temperatures), we decided to evaluate if DMSO + O₂ exerts influence and can also justify the high efficiency of DMSO as solvent in our photocatalyzed protocol. Therefore, the background reaction was tested in the dark, maintaining all the optimized reaction conditions between **1b** and **2a** at 40 °C; in these conditions, the product **3a** was obtained in only 9% yield (Table 1, entry 19). The requirement of an O₂ atmosphere was also evaluated. The DMSO solution was sonicated and purged with an argon atmosphere for 30 min and the reaction was performed under the optimized conditions, giving **3a** in 66% yield (Table 1, entry 20). Additionally, the crude reaction product **3a** obtained as described in entry 10, Table 1 was carefully analysed by GC-MS with no evidence of dimethylsulfone formation as verified in Liu's protocol. With all these results in hand, we have no evidence that the exceptional efficiency of DMSO as solvent is due to the radical oxidant power of DMSO + O₂. Thus, we have proved the necessity of light to promote the reaction and postulate that the influence of DMSO is related to the formation of photoactive intermediates or their excited states.

Finally, the robustness of the methodology was evaluated under the optimized conditions (Table 1, entry 21) using **2a** in 5 mmol scale, thus obtaining **3a** in 74% yield (0.7 g).

Then, we used the optimized protocol (Table 1, entry 10) to explore the scope and limitations of these photoarylations. A variety of aryldiazonium salts with different substitution patterns was evaluated, together with substituted pyrazines and other diazines, such as pyrimidine (1,3-diazine) and pyridazine (1,2-diazine) (Scheme 2).

The protocol afforded yields between 71% (4-methylbenzenediazonium) and 75% (4-ethyl-benzenediazonium) for alkyl electron-donor groups (Scheme 2, **3o** and **3g**, respectively) and 72% for the neutral group H (benzenediazonium, Scheme 2, **3l**), which are very close to the optimized reaction model (4-



Table 1 Screening of the reaction conditions^a

Entry	Pyrazine (mmol)	2a (mmol)	Solvent	Additive	Light	Temp. (°C)	Time (h)	Yield ^b (%)
1	1a (0.75)	0.1	H ₂ O	—	Dark	40	14	2
2	1a (0.75)	0.1	H ₂ O	—	Blue	33	14	20
3	1a (1.5)	0.1	H ₂ O	—	Blue	33	14	43
4	1a (2.5)	0.1	H ₂ O	—	Blue	33	14	52
5	1a (3.0)	0.1	H ₂ O	—	Blue	33	14	59
6	1a (0.3)	0.6	H ₂ O	—	Blue	33	14	2
7	1a (1.5)	0.1	H ₂ O	—	Blue	33	24	44
8	1a (1.5)	0.1	H ₂ O	—	Blue	33	8	31
9	1b (1.5)	0.1	H ₂ O	—	Blue	33	14	8
10	1b (1.5)	0.1	DMSO	—	Blue	33	14	81 (78) ^c
11	1b (1.5)	0.1	DMF	—	Blue	33	14	9
12	1b (1.5)	0.1	DMSO : CH ₃ CN (1 : 1)	—	Blue	33	14	44
13	1a (1.5)	0.1	DMSO	PTSA (15 equiv.)	Blue	33	14	65
14	1a (1.5)	0.1	DMSO	PTSA (20 equiv.)	Blue	33	14	66
15	1b (1.5)	0.1	DMSO	TMB (2 equiv.)	Blue	33	14	28
16	1b (1.5)	0.1	DMSO	Pyridine (2 equiv.)	Blue	33	14	33
17 ^d	1b (1.5)	0.1	DMSO : CH ₃ CN (1 : 1)	—	Blue	-22	14	51
18 ^d	1b (1.5)	0.1	DMSO : CH ₃ CN (3 : 1)	—	Blue	-22	14	54
19	1b (1.5)	0.1	DMSO	—	Dark	40	14	9
20 ^e	1b (1.5)	0.1	DMSO	—	Blue	33	14	66
21	1b (75)	5.0	DMSO	—	Blue	33	14	74 (0.7 g)

^a Reaction conditions: pyrazine free base (**1a**) (0.3, 0.75, 1.5, 2.5, 3.0 mmol), *p*-methoxybenzenediazonium tetrafluoroborate (0.1, 0.2, 0.6 mmol), in solvent (0.6 mL) at temperature (-22, 33, 40 °C) under an O₂ atmosphere for 14 or 24 h. ^b Yield determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. ^c Isolated yield obtained in triplicate (average). ^d Reaction performed inside a freezer at -22 °C.

^e Solvent was previously deoxygenated and maintained under an argon atmosphere.

OMe-benzenediazonium, **3a**, 78% isolated yield, Scheme 2). Electron-withdrawing groups present in aryldiazonium salts at the 4-position (Cl, F, NO₂) also gave the corresponding products (**3p**, **3d**, and **3j**) in similar yields (75, 72 and 60% yields, respectively). However, the expected product **3t** was not obtained when the reaction was performed with 4-(dimethylamino)-benzenediazonium salt (**2t**). Similar results were observed for the photoarylation of azines using both catalyst-free²¹ and metal-catalysis³⁰ approaches, suggesting that the salt **2t** is inappropriate for radical C–H arylation protocols. The σ -acceptor group (CF₃) in the *meta*-position of the diazonium salt **2m** also gave the respective product **3m** in a similar yield (74%), however, the CF₃ group at *ortho*-position **2n** gave the corresponding product in only 15% yield. In general, all the products from *ortho*-substituted diazonium salts were obtained in very low to moderate yields (5–45% yields for **3c**, **3f**, **3i**, **3n**, **3r** and **3s**) regardless of the electronic nature of the substituent in the diazonium salts. These last results suggest that besides the electronic effect, the steric effect is also important for this protocol and, overall, the yields were superior for *para*-substituted aryldiazonium salts followed by *meta*- and *ortho*-positions. Finally, the substituted pyrazine **1c** was also reacted with **2a** giving a regioisomeric mixture (**3v**) with arylation in

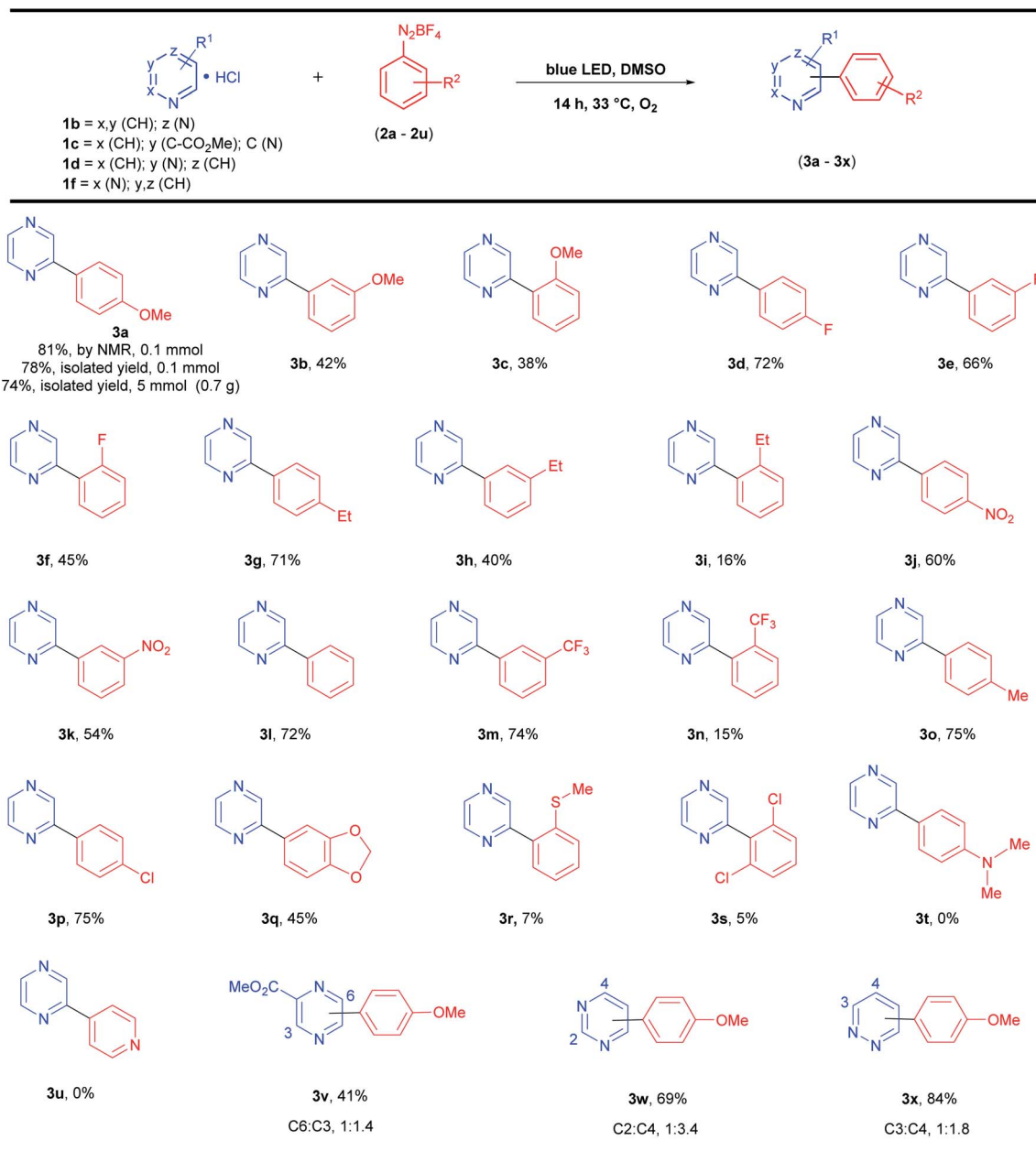
both C-6 and C-3 positions (1 : 1.4 ratio) and 41% overall yield. Pyrimidine **1d** also afforded a regioisomeric mixture after the photoarylation with **2a** giving **3w** in 69% overall yield (C-2 : C-4 in 1 : 3.4 ratio), and pyridazine **1f** yielded **3x** (84% overall yield, isomeric mixture, C3 : C4 in 1 : 1.8 ratio).

Thus, we have established a protocol for photoarylations of pyrazines with aryldiazonium salts. Reactions involving photoarylations of pyrimidines, and pyridazines are also demonstrated making this protocol valuable. The reactions are all promoted by visible-light and do not require additional photocatalysts, metals, additives or high temperatures, occurring *via* an electron donor–acceptor (EDA) complex, as evidenced below.

Mechanistic considerations

In our previous studies on direct C–H photoarylation of pyridine hydrochlorides with aryldiazonium salts, an EDA complex was proposed for the photocatalytic step.²¹ The crucial step involves the formation of an aryl radical through a single-electron transfer (SET) process in the excited state of a photoactive EDA complex, which is formed between the pyridine free-base and the aryldiazonium salt. Therefore, we propose that a similar mechanism also operates for the direct C–H photoarylation of diazines.





Scheme 2 Scope and limitation of the reaction. ^aReaction conditions: pyrazine hydrochloride (**1b–1f**, 7.5 mmol), aryldiazonium salt (**2a–2u**, 0.5 mmol) in DMSO (3 mL) at 33 °C under an O₂ atmosphere and blue LEDs (120 W) for 14 h. Isolated yield after column chromatography.

Initially, the reaction was performed in the presence of 2 equiv. of the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), using the optimized conditions. In this case, the pyrazine free base **1a** was used instead of its hydrochloride **1b** ($pK_{aH} = 0.6$)³¹ to avoid the well-known acid-promoted disproportionation reaction of TEMPO.³² In these conditions, the TEMPO-trapped-*O*-aryl adduct was detected by GC-MS, supporting the photocatalyzed aryl radical generation (Fig. S6, ESI[†]). Indeed, the use of pyrazine hydrochloride (**1b**) in the optimized protocol proved to be crucial for the efficiency of the reaction, and we postulate that the aryl radical addition to

the activated pyrazine (**1b**) is favored, similarly to the proposed in our pyridine hydrochloride approach.²¹ On the other hand, for the EDA complex formation, an electron donor specie in solution such as **1a** is necessary, which is possible due to the acid–base equilibrium between **1b** and **1a**.

Intriguingly, the reaction between **2a** and **1a** (free base) or **2a** and **1b** (hydrochloride), using water as the solvent did not furnish satisfactory yields (20–59%). However, excellent results were obtained when DMSO was used (up to 81%, Table 1, entry 10) which supports the idea and the importance of the equilibrium between **1b** and **1a** depending on the solvent. In this



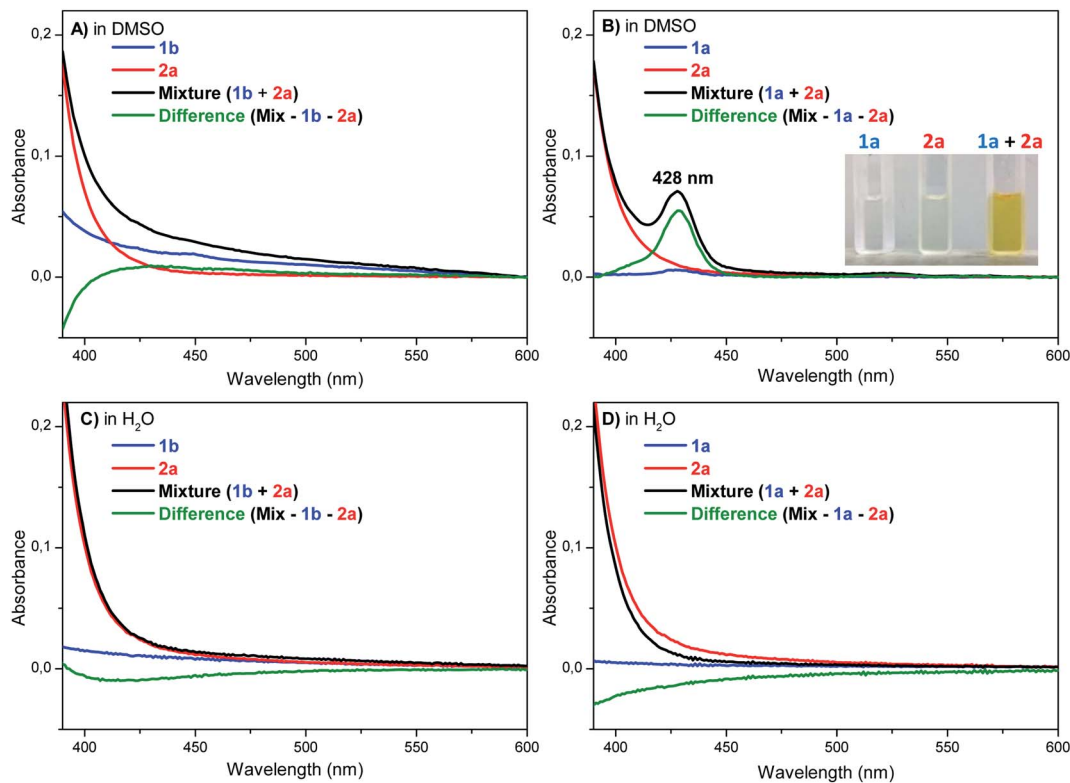
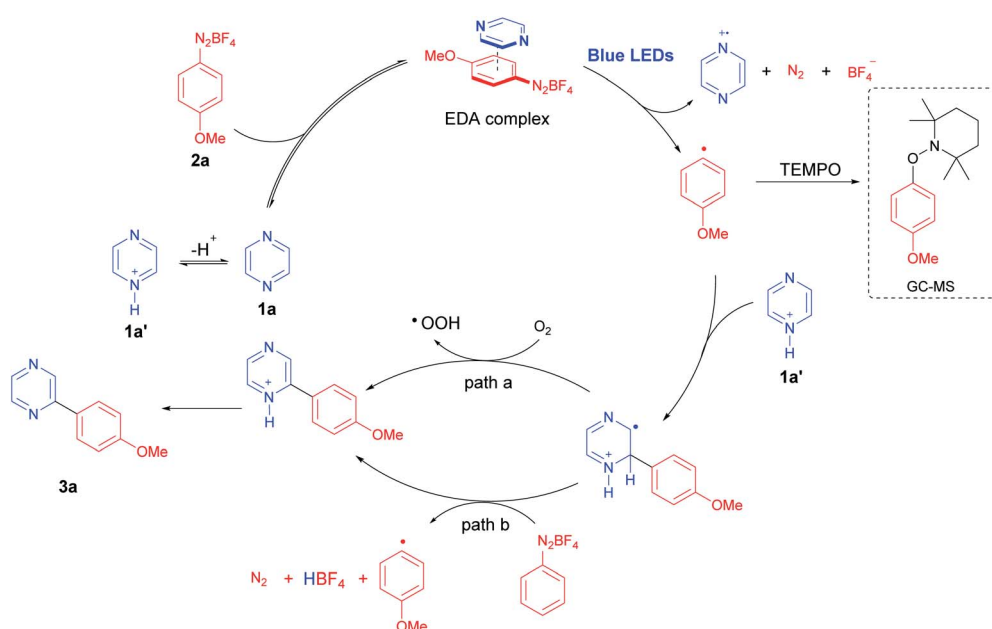


Fig. 2 UV-Vis absorption spectra of **1b** (1.5 mmol), **2a** (0.1 mmol), the mixture of **1b** with **2a**, and the difference of the mixture with **1b** and **2a** in (A) DMSO and (C) H_2O . UV-Vis absorption spectra of **1a** (1.5 mmol), **2a** (0.1 mmol), the mixture of **1a** with **2a**, and the difference of the mixture with **1a** and **2a** in (B) DMSO and (D) H_2O .

case, the lower dielectric constant of DMSO probably reduces the ionization of **1b**, and simultaneously allow an ideal concentration of protonated pyrazine **1b** (radical addition step) and free base **1a** (EDA complex formation step) to favor the role

process. Thus, the last challenge on this mechanism would be to prove the EDA complex formation in solution.

Typically, the EDA complex presents a strong colored solution after mixing two non-colored compounds, thus



Scheme 3 Proposed mechanism for the visible-light mediated C–H direct arylation of diazines with aryldiazonium salts.



characterized by the appearance of a charge-transfer (CT) absorption band.^{21,22,27} The UV-Vis experiments were carried out in water and DMSO using *p*-methoxybenzenediazonium tetrafluoroborate (**2a**) with both pyrazine hydrochloride (**1b**) and pyrazine free base (**1a**), respectively (Fig. 2). The UV-Vis spectra obtained for **1b**, **2a**, and their mixtures in DMSO, showed that no evident new CT band was observed in the tested concentrations (Fig. 2A). Conversely, a new band was clearly detected at 428 nm for the mixture between **1a** and **2a** in DMSO (Fig. 2B), proving the formation of an EDA complex. In water, no CT band was observed between **2a** and **1a** or **1b** (Fig. 2C and D), suggesting that the EDA concentration in water, even using **1a** (free base) is really low, thus justifying the lower efficiency of the protocol in this solvent. Overall, these results corroborate with the proposal of an equilibrium between the protonated pyrazine **1b** and the free base form **1a**, while both species are important in the catalytic cycle, being **1a** critical for the EDA complex formation, and **1b** a reactive starting material for the posterior aryl radical attack (Scheme 3). To complete the catalytic cycle, we suggest that the radical intermediate can be oxidized to the corresponding arylated pyrazine by molecular oxygen (path a) or by another aryldiazonium salt molecule (path b), as we have shown that the removal of molecular oxygen from the reaction mixture caused a slight reduction in yields, but did not completely inhibit the reaction (Scheme 3).

Conclusions

A direct C–H photoarylation of pyrazines with a scope of diazonium salts is described, and additional experiments with pyrimidine and pyridazine are also presented. We have demonstrated that different diazines can be easily arylated by using visible light, DMSO as the solvent, and diazonium salts, with no need for additional photocatalysts. We have shown that diazines and diazonium salts form a visible-light photoactive electron donor–acceptor (EDA) complex in solution, and allow aryl radical generation with further arylation of the diazines. The protocol was explored in up to 0.7 g-scale (74% yield) in a simple home-made batch photoreactor. The methodology was efficient for both electron-donor, -neutral, and electron-withdrawing groups attached mainly in the *para*-positions of the aryldiazonium salts, with moderate results for groups in *meta*, and lower results for groups in the *ortho*-position. Mechanistic investigations were carried out to give support for the proposed mechanism *via* an EDA complex.

Conflicts of interest

There are no conflicts to declare.

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