Preprint Title	Photocatalyzed Arylation of Isonitriles by Diaryliodonium Salts towards N-Substituted Benzamides
Authors	Nadezhda M. Metalnikova, Nikita S. Antonkin, Tuan K. Nguyen, Natalia S. Soldatova, Alexander V. Nyuchev, Mikhail A. Kinzhalov and Pavel S. Postnikov
Publication Date	16 Apr. 2025
Article Type	Full Research Paper
Supporting Information File 1	ESI.pdf; 8.2 MB
ORCID® iDs	Nadezhda M. Metalnikova - https://orcid.org/0000-0002-4498-0982; Tuan K. Nguyen - https://orcid.org/0000-0002-7881-7630; Natalia S. Soldatova - https://orcid.org/0000-0002-1738-4747; Alexander V. Nyuchev - https://orcid.org/0000-0002-0460-0543; Mikhail A. Kinzhalov - https://orcid.org/0000-0001-5055-1212; Pavel S. Postnikov - https://orcid.org/0000-0001-9713-1290

Photocatalyzed Arylation of Isonitriles by Diaryliodonium Salts towards N-Substituted Benzamides

Nadezhda M. Metalnikova‡1, Nikita S. Antonkin‡1, Tuan K. Nguyen[2], Natalia S. Soldatova[1], Alexander V. Nyuchev[3], Mikhail A. Kinzhalov*2, Pavel S. Postnikov*1.

Address: [1]Research School of Chemistry and Applied Biomedical Sciences, Tomsk Polytechnic University, Lenina Avenue 30, Tomsk, 634050, Russian Federation.
[2]Saint Petersburg State University, 7–9 Universitetskaya Nab., Saint Petersburg, 199034, Russian Federation.
[3]Department of Organic Chemistry, Lobachevsky State University of Nizhny Novgorod, Gagarina Avenue 23, Nizhny Novgorod, 603950, Russian Federation.

Email: Pavel S. Postnikov - postnikov@tpu.ru
Mikhail A. Kinzhalov - m.kinzhalov@spbu.ru
* Corresponding author
‡ Equal contributors

Abstract

The arylation of isonitriles by diaryliodonium salts under photoredox conditions has been proposed for the first time. The suggested procedure allows preparing the broad range of N-substituted arylamides using both symmetric and unsymmetric diaryliodonium salts in mild conditions. The plausible mechanism for the reaction and the selectivity of aryl transfer in case of asymmetrical iodonium salts was studied.

Keywords

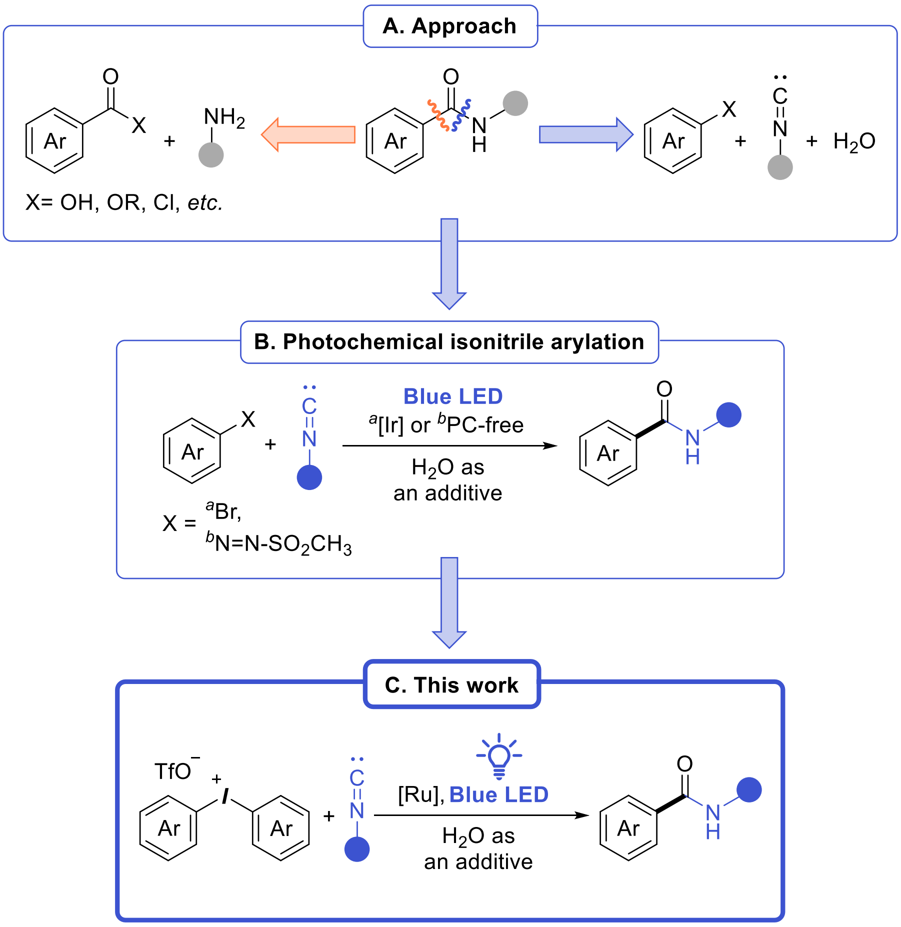
Diaryliodonium salts; isonitriles; arylation; benzamides; photoredox.

Introduction

Amides represent a crucial and ubiquitous structural motif in essential biomolecules including proteins and peptides [1], as well as in a wide array of bioactive compounds. According to the DrugBank there were more than 250 approved anesthetic drugs classified as amides [2]. Just recently, between 2021 and June 2022, sixteen anticancer drugs containing amide bond had been approved by U.S. FDA [3]. The COCONUT database gave more than 20 000 examples of N-substituted benzamides as natural products [4,5]. Consequently, the preparation of amides has garnered significant attention within organic and medicinal chemistry. Commonly, amide bonds have been formed *via* the reaction of carboxylic acids or their derivatives with appropriate amines (Scheme 1, A) [6]. Although conventional approach is effective and straightforward, it usually suffers from harsh conditions and low tolerance to sensitive functional groups. Due to this reason, the alternative routes toward the preparation of amides are in great demand in modern synthetic chemistry [7].

The arylation of isonitriles was introduced nearly a decade ago as an alternative synthetic pathway for the preparation of N-substituted benzamides (Scheme 1, A) [8]. Over the years, the basic reaction has been modified to imply various metal-containing catalysts [9-20] or at least metal-free transformations. Metal-free approaches often employ heteroarenes under harsh conditions [21] or diazonium salts as arylating agents [22,23]. However, diazonium salts are distinguished by inherent instability complicating the use in such transformations. Moreover, among the various arylation strategies, photochemical methods remain relatively underexplored, with only a few examples reported [24,25]. These methods often face limitations such as the significant excess of isonitrile [24] or a restricted scope of aryl bromides (Scheme 1, B) [25].

In contrast, diaryliodonium salts, representing stable, robust and efficient arylating agents [26-28], have not been explored yet for the synthesis of benzamides from isonitriles. To bridge this gap, we propose a photoredox-mediated strategy for the synthesis of arylamides via the arylation of isonitriles with diaryliodonium salts under blue light irradiation (Scheme 1, C).



Scheme 1: Background and conception.

Results and Discussion

We commenced our investigation by the optimization of reaction conditions. Diphenyliodonium triflate ***1a*** and *p*-isocyanotoluene were used as model substrates. Taking into account the possibility of iodonium salts decomposition under irradiation alone we carried out an initial experiment without a catalyst observing only traces of the benzamide ***2aa*** (Table 1, entry 1). Despite the fact that there is no arylations of isonitrile by diaryliodoniums toward amides so far, a few examples of photochemical cascade arylation-cyclization of isonitriles with diaryliodonium salts have been published [29-31]. Thus, we settled with the similar conditions to the ones published [29-31] introducing the photocatalyst $[Ru(bpy)_3](PF_6)_2$ which successfully initiated the reaction under blue light irradiation afforded benzamide ***2aa*** in 36% yield (Table 1, entry 2). Inspired by the first positive results, we tested various cyanoarene-based catalytic systems. Unfortunately, 4CzTPN, 4CzIPN, and 3DPAFIPN did not demonstrate increased efficiency and yields of target product were slightly lower than for $[Ru(bpy)_3](PF_6)_2$ (Table 1, entries 3–5). Thus, all other optimization has been done using $[Ru(bpy)_3](PF_6)_2$ as a catalyst.

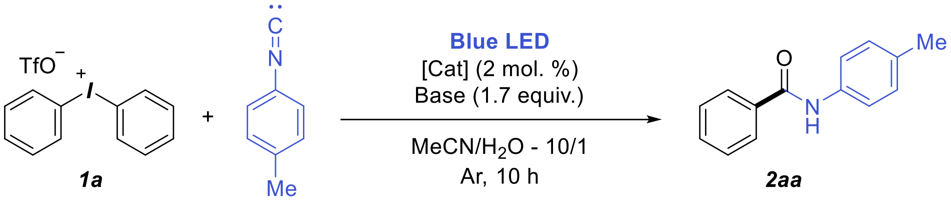
After, we moved to the screening of bases and their potential role in the arylation process. Firstly, the reaction without base or the use of weaker bases, such as sodium phosphates, resulted in reduced yields of ***2aa*** (Table 1, entries 6–8) due to the acidic hydrolysis of the isonitrile to formamide [32]. Stronger bases such as Cs_2CO_3 (Table 1, entry 9) and KOH (Table 1, entry 10) led to diminished yields, reducing the product formation to 30% and 11%, respectively. In both cases we observed sufficient decomposition of iodonium salt affecting the yield of desired product.

Afterwards, we evaluated the other crucial parameters for photochemical reactions such as the reagents concentration and their ratio. Surprisingly, both dilution of the reaction mixture to 0.05 M and concentration to 0.2 M led to reduced yields (Table 1, entries 11–12) compared to the optimal concentration of 0.1 M. Furthermore, the yield of ***2aa*** exhibited minimal dependence on the molar ratio of iodonium salt to isonitrile (Table 1, entries 13–19). In case of significant excess of the isonitrile we observed the multiple addition of isonitrile forming oligomerized products detected by GCMS.

Finally, control experiments without irradiation gave traces of the benzamide ***2aa*** showing no activation by Ru-complex at room temperature (Table 1, entry 20). An experiment conducted under an air atmosphere yielded only 9% of ***2aa*** (Table 1, entry 21) indicating that the presence of atmospheric oxygen significantly inhibited the reaction.

Based on these findings, the optimal conditions for further studies were established as the use of equimolar amounts of diaryliodonium salt and isonitrile, Na_2CO_3 as the base, and $[Ru(bpy)_3](PF_6)_2$ as the photocatalyst, under an Ar atmosphere with irradiation by blue LED light (Table 1, entry 2).

Table 1: Optimization of the reaction conditions.[a]



#	Isonitrile/iodonium salt ratio	C(isonitrile), M	Catalyst	Base	Yield, %[b]
Variation of Catalysts					
1	1 / 1	0.1	-	Na_2CO_3	n.d.
2	**1 / 1**	**0.1**	**$[Ru(bpy)_3](PF_6)_2$**	**Na_2CO_3**	**36 (31)[c]**
3	1 / 1	0.1	4CzTPN	Na_2CO_3	20
4	1 / 1	0.1	4CzIPN	Na_2CO_3	30
5	1 / 1	0.1	3DPAFIPN	Na_2CO_3	30
Variation of Bases					
6	1 / 1	0.1	$[Ru(bpy)_3](PF_6)_2$	Na_2HPO_4	21
7	1 / 1	0.1	$[Ru(bpy)_3](PF_6)_2$	NaH_2PO_4	24
8	1 / 1	0.1	$[Ru(bpy)_3](PF_6)_2$	-	22
9	1 / 1	0.1	$[Ru(bpy)_3](PF_6)_2$	Cs_2CO_3	30
10	1 / 1	0.1	$[Ru(bpy)_3](PF_6)_2$	KOH	11

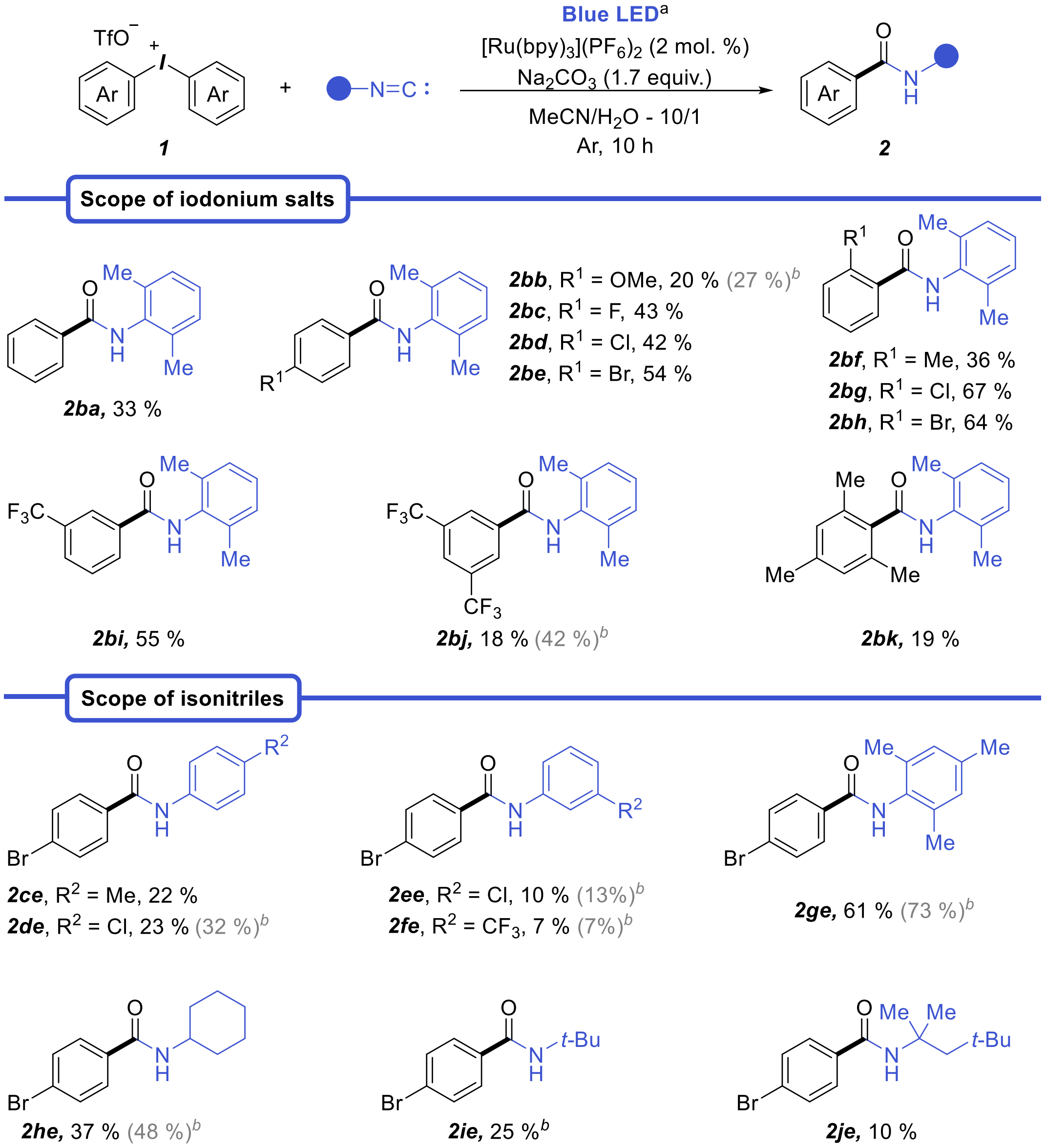
Variation of Reagents Concentration					
11	1 / 1	0.2	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	32
12	1 / 1	0.05	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	28
Variation of Isonitrile / Iodonium Salt Ratio					
13	1 / 2	0.1	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	31
14	1 / 3	0.1	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	20
15	1.5 / 1	0.05	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	28
16	2 / 1	0.05	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	34
17	3 / 1	0.05	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	34
18	4 / 1	0.05	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	36
19	4 / 1	0.1	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	30
Control Experiments					
20[d]	1 / 1	0.1	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	traces
21[e]	1 / 1	0.1	$[Ru(bpy)_3](PF_6)_2$	Na_2CO_3	9

[a]Reaction conditions: MeCN (1 mL), H_2O (100 μL), irradiation by blue LED (465 nm, 20 W) for 10 h. [b]Determined by ^{1}H NMR using 1,3,5-isopropylbenzene as an internal standard. [c]Isolated yield. [d]In the dark. [e]On air.

With optimized conditions in hands, a series of benzamides ***2aa*–*2je*** were synthesized using various symmetrical diaryliodonium salts ***1a*–*1k*** and isocyanides (Scheme 2). The analysis of reaction yields allowed to establish the dependency from the electronic effects of substituents in the diaryliodonium salts. Diaryliodonium salts containing electron-deficient aryls afforded products ***2*** in higher yields compared to those bearing EDG. Specifically, the reaction with EWG-substituted iodonium salts produced benzamides ***2bc*–*2be***, ***2bg*–*2bj*** in 18–67% yields. The benzamide ***2bj*** was isolated in only 18% yield probably due to low solubility of bis(3,5-ditrifluoromethyl)iodonium triflate ***1j*** in MeCN/H_2O mixture. The highest yields were achieved in case of *ortho*-halo-substituted diaryliodonium salts providing 64% and 67% for amides ***2bg*** and ***2bh***, respectively. In contrast, iodonium salts with electron-rich aryls afforded the corresponding benzamides ***2aa***, ***2ba***, ***2bb***, ***2bf*** and ***2bk*** in significantly lower 19–36% yields.

Subsequently, various isonitriles were evaluated in the reaction with bis(4-bromophenyl)iodonium triflate ***1e*** under optimized conditions**.** Amides were successfully synthesized from both aliphatic and aromatic isonitriles, with yields reaching up to 61%. The highest yields were observed for benzamides ***2be*** and ***2ge*** in the reaction with sterically hindered aromatic isonitriles, such as 2,4,6-trimethylphenyl isocyanide and 2,6-dimethylphenyl isocyanide.

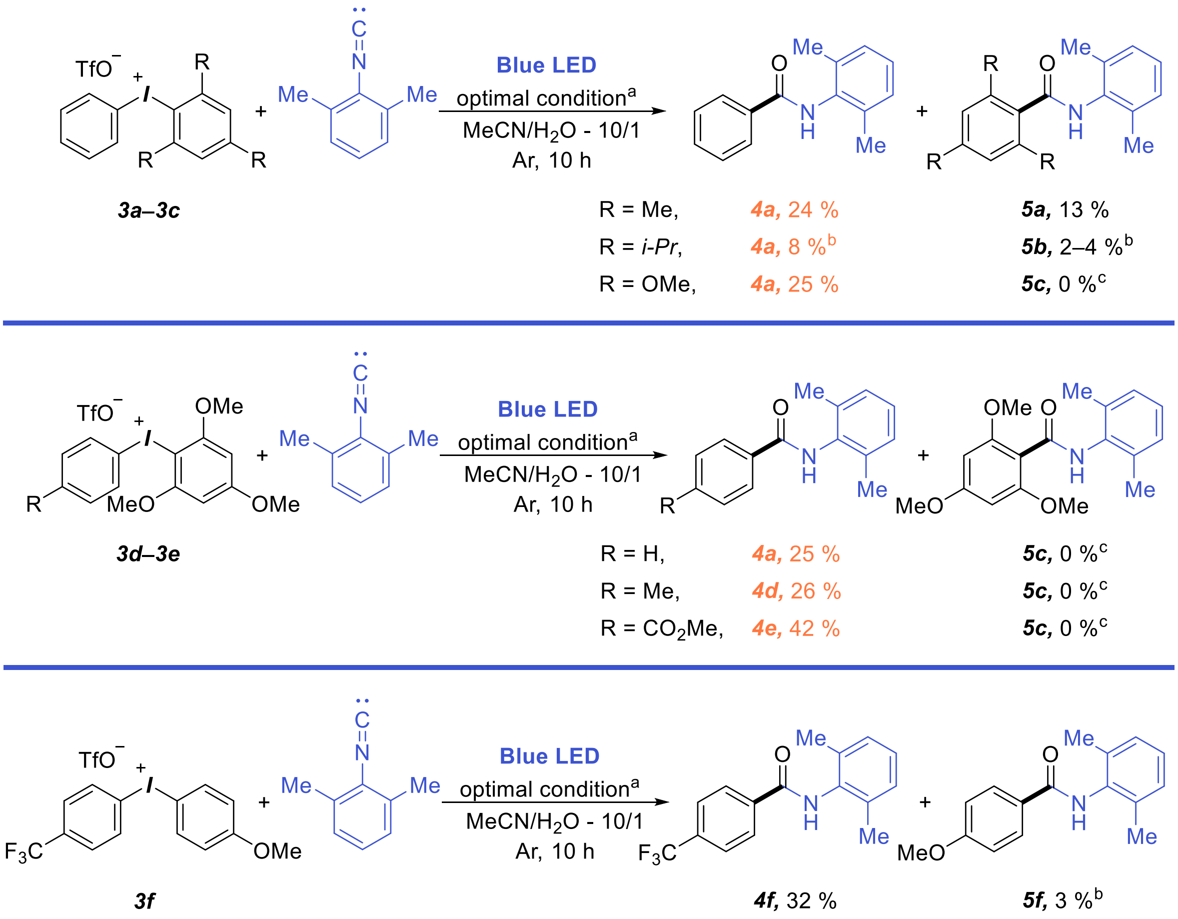
The use of 2 equivalents of iodonium salt ***1e*** further improved the yields of certain amides (***2bb***, ***2bj***, ***2de***, ***2ee***, ***2ge*** and ***2he***), as significant amounts of unreacted isonitrile remained when only 1 equivalent was employed.



Scheme 2: Reaction scope of iodonium salts **1** and isocyanides. ^a^Reaction condition: isocyanide (0.2 mmol), iodonium salt ***1*** (0.2 mmol), Na_2CO_3 (0.34 mmol),

$[Ru(bpy)_3](PF_6)_2$ (0.004 mmol), MeCN (2 mL), H_2O (200 μL) irradiation by blue LED (465 nm, 20 W) for 10 h. [b]2 equiv. of iodonium salt ***1*** and 3.4 equiv. of Na_2CO_3 were used (yields in grey are for standard conditions[a]).

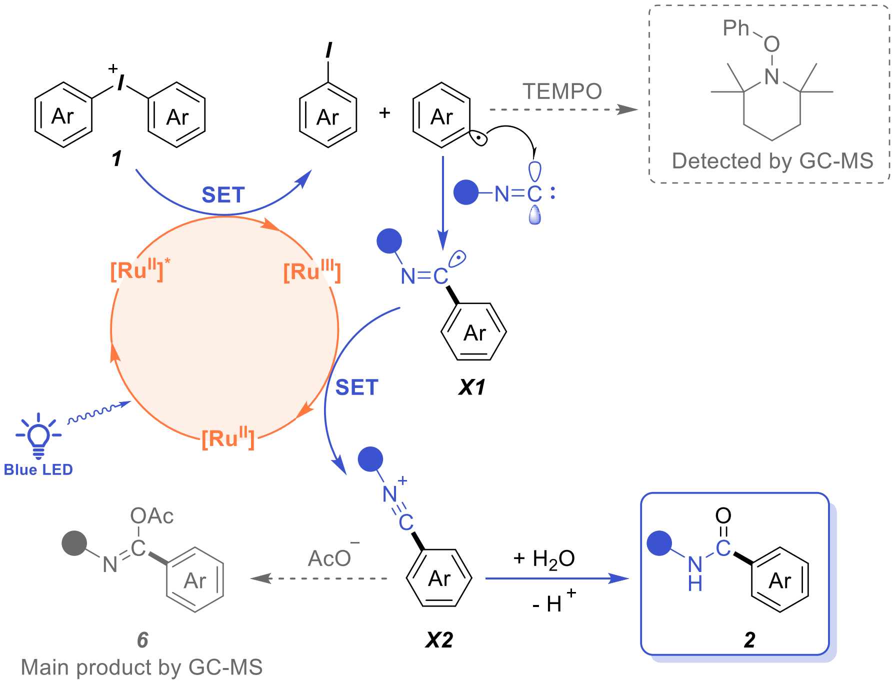
The limited scope of iodonium salts for arylations usually arose from the poor range of synthetically accessible symmetrical salts compared to their asymmetrical analogues. However, the selective transfer of one of the aryls is a main challenge for asymmetrical iodonium salts. Therefore, we moved to the asymmetrical iodonium salts to test the selectivity of aryl transfer under proposed conditions. Since iodonium salts prone to repeat the selectivity pattern of nucleophilic substitution in the photoredox processes [33-39], we evaluated iodonium salts with common dummy ligands such as 2,4,6-trimethoxypehnyl (TMP) [40,41], sterically hindered 2,4,6-triisopropylphenyl and mesityl ligands. *Codes for amides **2ba**, **2bk** and **2bb** were changed in this section to **4a**, **5a** and **5f** respectively for the sake of clarity.* The highest selectivity was achieved using aryl(2,4,6-trimethoxyphenyl)iodonium triflates ***3c*****–*****3e*** yielding desired amides ***4a***, ***4d***, ***4e*** in 25–42% yield. Competing amide ***5c*** was not detected in the reaction mixture even by GC-MS. In contrast, the mesityl-substituted salt ***3a*** gave both competing products ***4a*** and ***5a*** in a ≈2:1 ratio, while the 2,4,6-triisopropylphenyl derivative ***3b*** yielded a mixture of products ***4a*** and ***5b*** in low yield (Scheme 3).



Scheme 3: Selectivity experiment and scope of asymmetrical iodoniums salts. [a]Reaction conditions: 2-isocyano-1,3-dimethylbenzene (0.2 mmol), iodonium salt ***3*** (0.2 mmol), Na_2CO_3 (0.34 mmol), $[Ru(bpy)_3](PF_6)_2$ (0.004 mmol), MeCN (2 mL), H_2O (200 µL) under irradiation by blue LED (465 nm, 20 W) for 10 h. [b]Determined by ^1H NMR using 1,2-dibromoethane as an internal standard. [c]Not detected by GC-MS.

Our experiments clearly demonstrated that electron-poor aryls gave better yields in case of both symmetrical and asymmetrical iodonium salts. However, the radical stability or philicity for aryl radicals known to be mostly indifferent to the substituents in the aryl ring [42]. Additionally, such reactivity pattern could not be explained only by steric factors since the yield dramatically dropped for *ortho*-methyl-substituted iodonium salt ***1f*** compared to *ortho*-halo-substituted salts ***1g*** and ***1h*** providing the best yields in the scope. Moreover, the strong correlation of the yield with the electronic effects in aryl rings was clearly shown in the experiment with iodonium salt ***3f*** (Scheme 3). We believe that the reason for the primarily transfer of the electron-poor ligands under given conditions is favorable formation of EWG-substituted aryl radicals from iodonium cation based on their reduction potentials and bond dissociation energies calculated by Romanczyk and Kurek [43] .The reduction potential in SET reactions for iodonium salts with EWG-substituted aryls significantly differs from the ones with electron-rich aryls with 0.36 eV gap between $(4\text{-}NO_2C_6H_4)_2I^+$ and $(4\text{-}OMeC_6H_4)_2I^+$ iodonium cations. If asymmetrical iodonium cations are considered where one of the aryls is phenyl and the other is 4-substituted phenyl the bond dissociation energy is 4.0 kcal/mol lower in case of $(4\text{-}NO_2C_6H_4)$ compared to $(4\text{-}OMeC_6H_4)$ [43].

To gain a comprehensive understanding of the reactivity pattern in the current transformation, a reaction mechanism was proposed taking into the account the known data and controlled experiments (Scheme 4). Upon irradiation with blue light, the Ru(II) catalyst undergoes photoexcitation, followed by an oxidative single-electron transfer (SET) process with the iodonium salt, leading to the generation of an aryl radical, aryl iodide, and Ru(III). The formation of the aryl radical was corroborated through a trapping experiment utilizing TEMPO as a radical scavenger (Scheme 4 and ESI, 4. Control experiments). The resulting aryl radical is subsequently captured by an isonitrile molecule, forming an imidoyl radical intermediate ***X1***. The intermediate ***X1*** facilitates the reduction of the Ru(III) species back to Ru(II) thereby completing the photoredox cycle, with the formation of the cationic intermediate ***X2***. We propose that bulky isonitriles effectively shielded the radical or cationic centers in intermediates ***X1*** or ***X2***, thereby preventing multiple additions of isonitrile to give the highest yields for benzamides ***2be*** and ***2ge*** among the scope of isonitriles. In the final step of the reaction, the addition of a water molecule from the reaction medium to ***X2*** occurred culminating in the formation of the final product ***2*** after deprotonation and tautomerization. The proposed mechanistic pathway was formally validated by conducting the reaction in the presence of NaOAc as a base resulted in the formation of the acetoxy derivative ***6*** attributable to the addition of acetate instead of water in the final step (Scheme 4). Additional control experiment excluded the possible arylation of formamide ***7*** by iodonium salt (ESI, 4. Control experiments).



Scheme 4: Proposed reaction mechanism.

Conclusion

In conclusion, a novel synthetic methodology for the preparation of *N*-substituted arylamides from isonitriles and diaryliodonium salts had been proposed utilizing visible-light photoredox ruthenium-based catalysis. Both symmetrical and asymmetrical diaryliodonium salts were evaluated and their reactivity was systematically analyzed in relation to the structural features of the iodonium salts and isonitriles. The study revealed that EWG-substituted diaryliodonium salts exhibited superior performance compared to EDG-substituted ones. Furthermore, the potential for selective transfer of a single aryl group from asymmetrical diaryliodonium salts was demonstrated through the use of dummy ligands, such as 2,4,6-trimethoxyphenyl.

Supporting Information

Supporting Information File 1:

File Name: ESI

File Format: pdf

Title: Supporting information. Photocatalyzed Arylation of Isonitriles by Diaryliodonium Salts towards N-Substituted Benzamides

Acknowledgements

Authors acknowledge the valuable advices from Yulia A. Vlasenko. TKN and MAK express their gratitude to the Center for Magnetic Resonance and the Center for Chemical Analysis and Materials Research at St Petersburg State University for providing access to analytical instrumentation essential for this research.

Funding

This work was supported by the Russian Science Foundation (№ 23-73-10091).

Conflicts of interest

There are no conflicts to declare.

References

1. Greenberg, A.; Breneman, C. M.; Liebman, J. F. (Eds.) The Amide Linkage: Structural Significance in Chemistry, Biochemistry, and Materials Science; John Wiley & Sons, Inc.: New York, 2000.

2. DrugBank Online, *codes for search: advanced search -> "approved" and "category: N01BB — Amides"*, https://go.drugbank.com/unearth/advanced/drugs#results (accessed February 25, 2025).

3. Asif, M.; Srivastava, R.; Fatima, A.; Shakeel, M.; Hassan, F; Nasibullah, M. A *Russ. J. Bioorg. Chem.*, **2023**, *49*, 1165–1176.

4. Sorokina, M.; Merseburger, P.; Rajan, K.; Yirik, M. A.; Steinbeck, C. *J. Cheminform.*, **2021**, *13*, 2.

5. COCONUT Database, https://coconut.naturalproducts.net/search?type=substructure&q=CNC(c1ccccc1)%3DO (accessed March 15, 2025).

6. Acosta-Guzmán, P.; Ojeda-Porras, A.; Gamba-Sánchez, D. *Adv. Synth. Catal.* **2023**, *365*, 4359–4391.

7. Pattabiraman, V.; Bode, J. *Nature* **2011**, *480*, 471–479.

8. Jiang, H.; Liu, B.; Li, Y.; Wang, A.; Huang. H. *Org. Lett.* **2011**, *13*, 1028–1031.

9. Huang, L.; Guo, H.; Pan, L.; Xie, C. *Eur. J. Org. Chem.* **2013**, 6027–6031.

10. Yavari, I.; Ghazanfarpour-Darjani, M.; Bayat, M. J. *Tetrahedron Lett.* **2014**, *55*, 4981–4982.

11. Khairnar, B. J.; Bhanage, B. M. *Synthesis* **2014**, *46*, 1236–1242.

12. Sarkar, S.; Pal, R.; Roy, M.; Chatterjee, N.; Sarkar, S.; Sen, A. K. *Tetrahedron Lett.* **2015**, *56*, 623–626.

13. Li, Y.; Cao, J.; Zhu, Q.; Zhang, X.; Shi, G. *Russ. J. Gen. Chem.* **2016**, *86*, 668–671.

14. Lu, F.; Chen, Z.; Li, Z; Wang, X.; Peng, X.; Li, C.; Fang, L.; Liu, D.; Gao, M.; Lei, A. *Org. Lett.* **2017**, *19*, 3954–3957.

15. Liu, J. Q.; Shen, X.; Liu, Z.; Wang, X. S. *Org. Biomol. Chem.* **2017**, *15*, 6314–6317.

16. Khalaj, M.; Taherkhani, M.; Mousavi-Safavi, S. M.; Akbari, J. *Synlett* **2018**, *29*, 94–98.

17. Sharma, P.; Jain, N. *Adv. Synth. Catal.* **2018**, *360*, 1932–1937.

18. Yasaei, Z.; Mohammadpour, Z.; Shiri, M.; Tanbakouchian, Z.; Fazelzadeh, S. *Front. Chem.* **2019**, *7*, 433.

19. Li, Q.; Cai, Y.; Jin, H.; Liu, Y.; Zhou, B. *Tetrahedron Lett.* **2020**, *61*, 152605.

20. Yan, Q.; Yuan, Q. J.; Shatskiy, A.; Alvey, G. R.; Stepanova, E. V.; Liu, J. Q.; Kärkäs, M. D.; Wang, X. S. *Org. Lett.* **2024**, *26*, 3380–3385.

21. Zhou, Z.; Ji, H.; Li, Q.; Zhang, Q.; Li, D. *Org. Biomol. Chem.* **2021**, *19*, 2917–2922.

22. Basavanag, U. M. V.; Dos Santos, A.; El Kaim, L.; Gámez-Montaño, R.; Grimaud, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 7194–7197.

23. Xia, Z.; Zhu, Q. *Org. Lett.* **2013**, *15*, 4110–4113.

24. Malacarne, M.; Protti, S.; Fagnoni, M. *Adv. Synth. Catal.* **2017**, *359*, 3826–3830.

25. Cannalire, R.; Amato, J.; Summa, V.; Novellino, E.; Tron, G. C.; Giustiniano, M. *J. Org. Chem.* **2020**, *85*, 14077–14086.

26. Merritt, E. A.; Olofsson, B. *Angew.Chem. Int. Ed.*, 2009, *48*, 9052–9070.

27. Olofsson, B. Arylation with Diaryliodonium Salts. In *Hypervalent Iodine Chemistry. Topics in Current Chemistry*; Wirth, T., Ed.; Springer, Cham, **2015**; Vol. 373, 135–166.

28. Pan, C.; Wang, L.; Han, J. *Chem. Rec.* **2023**, *23*, e202300138.

29. Wang, R.; Jiang, H.; Cheng, Y.; Kadi, A. A.; Fun, H. K.; Zhang, Y.; Yu, S. *Synthesis* **2014**, *46*, 2711−2726.

30. Jiang, H.; Cheng, Y.; Wang, R.; Zhang, Y.; Yu, S. *Chem. Commun.* **2014**, *50*, 6164−6167.

31. Chen, J. Y.; Wu, H. Y.; Song, H. Y.; Li, H. X.; Jiang, J.; Yang, T. B.; He, W. M. *J. Org. Chem.* **2023**, *88*, 8360−8368.

32. Sung, K.; Chen, C. C. *Tetrahedron Lett.* **2001**, *42*, 4845−4848.

33. Samanta, R. K.; Meher, P.; Murarka, S. *J. Org. Chem.* **2022**, *87*, 10947–10957.

34. Chen, Z.; Liu, N. W.; Bolte, M.; Rena, H.; Manolikakes, G. *Green Chem.* **2018**, *20*, 3059–3070.

35. Liu, N. W.; Liang, S.; Manolikakes, G. *Adv. Synth. Catal.* **2017**, *359*, 1308–1319.

36. Senapati, S.; Parida, S. K.; Karandikar, S. S.; Murarka, S. *Org. Lett.* **2023**, *25*, 7900–7905.

37. Meher, P.; Samanta, R. K.; Manna, S.; Murarka, S. *Chem. Commun.* **2023**, *59*, 6092–6095.

38. Thombare, K. R.; Parida, S. K.; Meher, P.; Murarka, S. *Chem. Commun.* **2024**, *60*, 13907–13910.

39. Galicia, J.; McDonald, N. R.; Bennett, C. W.; He, J.; Glossbrenner, M. D.; Romero, E. A. *Chem. Commun.* **2024**, *60*, 6929–6932.

40. Stuart, D. R. *Chem. Eur. J.* **2017**, *23*, 15852–15863.

41. Sandtorv, A. H.; Stuart, D. R. *Angew. Chem. Int. Ed.* **2016**, *55*, 15812–15815.

42. Parsaee, F.; Senarathna, M. C.; Kannangara, P. B.; Alexander, S. N.; Arche, P. D. E.; Welin, E. R. *Nat. Rev. Chem*. **2021**, *5*, 486–499.

43. Romańczyk, P. P.; Kurek, S. S. *Electrochim. Acta* **2020**, *351*, 136404.