Iron Photocatalysis Applied to Oxidative Amidation of Aldehydes with NaCl

WILEY VCH

RESEARCH ARTICLE

Iron Photocatalysis Applied to Oxidative Amidation of Aldehydes with NaCl

Andrea Dellisanti,[a] Luisa Pisano,[a] Massimo Carraro,[a] Andrea Porcheddu,[b] Lidia De Luca*[a] and Silvia Gaspa,[a]

[a] A. Dellisanti, Dr. L. Pisano, Dr. M. Carraro, Prof. L. De Luca, Dr. S. Gaspa
Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali
Università degli Studi di Sassari
Via Vienna 2, 07100 Sassari, Italy
E-mail: ldeluca@uniss.it

[b] Prof. A. Porcheddu
Dipartimento di Scienze Chimiche e Geologiche
Università degli Studi di Cagliari
Cittadella Universitaria, 09042 Monserrato, Italy

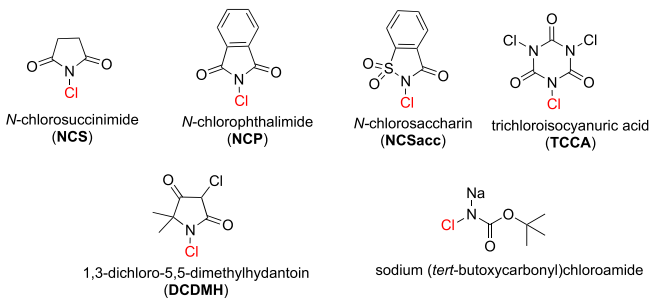
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate.))

Abstract: A synthesis of amides from aldehydes promoted by the photoactive complex of Fe_2SO_4 with 2-picolinic acid, NaCl as chlorine source, $Na_2S_2O_8$ as a benign oxidant is reported. The reaction is mediated by visible-light and is carried out at room temperature in absence of additives. Fe_2SO_4 is a readily available earth-abundant metal (EAMs) salt, not needed to be prepared and is environmentally sustainable. Both aliphatic and aromatic aldehydes and mono- and disubstituted amines have been texted in this transformation. This report opens intriguing perspectives for extending application of photoactive complex iron salts toward halogenation processes as well as for C-H activations and gives a contribution to the field of earth-abundant metals based-catalysis.

Introduction

Development of new methodologies induced by visible light is a current trend in organic chemistry [1]. Photosynthesis can be meant as the conversion of light into chemical energy, efficiently employed to promote chemical transformations, thus allowing the development of sustainable and efficient synthetic methodologies. Visible light can be intended as a clean reagent: it activates the substrates without leaving any by-products in the reaction mixture, with considerable simplification of the work-up and purification steps. Furthermore, the use of visible light, instead of thermal energy, to accomplish chemical processes, allows a great energy saving. The use of photosensitizers has given a great impulse to photochemistry [2]. Photocatalytic processes have provided new safe and more accessible methodologies characterized by high atom economy, selectivity, and ~~to~~ introduced new reactivity modes in organic synthesis, playing an impactful part in green methodologies. The majority of photochemical reactions require catalysts based on heavy or rare metals, usually Ru(II) and Ir(III) [3]. However, the high cost, scarceness and high toxicity of these noble metals have promoted the necessity to replace Ru- and Ir-based photocatalysts with more sustainable, easily accessible and cheaper metals [4].

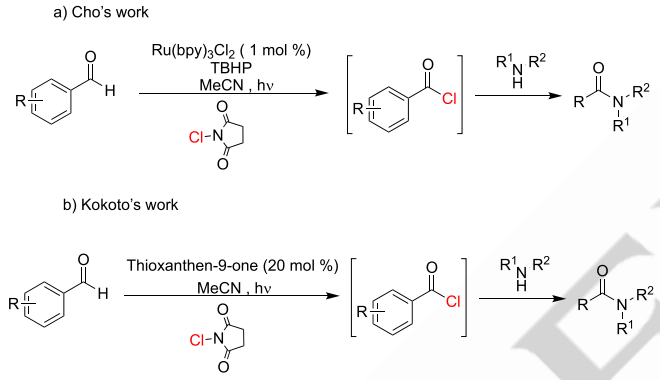
Earth abundant metals (EAM_S), have greater terrestrial abundance than precious metals, therefore their use in synthetic chemistry would lead to reduce both cost and environmental footprint. Furthermore EAM_S-based catalysts display different reactivity profiles, allowing alternative chances to open new reaction pathways [5]. Chlorinated compounds are not only pervasive in nature but also important in many areas as pharmaceuticals, polymers, agrochemicals and crucial intermediates for preparing complex molecules [6]. Many chlorination methodologies have been developed but most of them require harsh reaction conditions, excesses of chlorinating agents, initiators and ~~on~~ the use of toxic and hazardous chlorinating reagents as the corrosive Cl_2 and HCl, or *N*-chloroimides such as *N*-chlorosuccinimide (NCS), *N*-chlorophthalimide (NCP), *N*-chlorosaccharin (NCSacc), Trichloroisocyanuric acid (TCCA), 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) and *N*- chloro -*N*-sodio-carbamates. All of these reagents are prepared from Cl_2 and lead to the formation of significant amounts of organic waste (Scheme 1) [7].



Scheme 1. Common chlorinating agents.

Among chlorinated compounds, acyl chlorides are versatile and reactive molecules. They are used as synthetic intermediates for the preparation of many useful organic moieties as carboxylic anhydrides, esters, hydroxamic acids and amides. Conventionally, acyl chlorides are prepared from carboxylic acids employing oxalyl chloride, thionyl chloride, phosphorous trichloride or phosphorous pentachloride [8], which are unsafe and toxic and unsuitable for large scale synthesis.

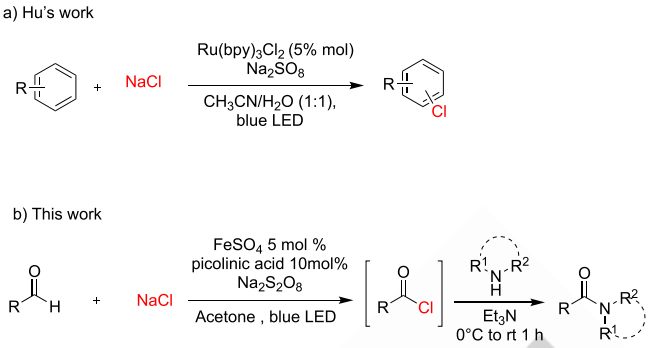
Recent studies have focused on the use of visible light to prepare acyl chloride. Cho and co-workers have developed an efficient one-pot amide visible-light mediated synthesis from aromatic aldehydes *via* the formation of acyl chloride, by the use of $Ru(bpy)_3Cl_2$ as a photocatalyst, *tert*-butyl hydrogen peroxide as an oxidant and NCS as a chlorine source (Scheme2-a) [9]. In 2021 Kokotos and co-workers have proposed a proficient synthesis of amides from aromatic aldehydes mediated by visible-light, through acyl chloride generation, using thioxanthene-9-one as an organic photocatalyst and NCS as chlorinating reagent (Scheme 2-b) [10].



Scheme 2. Photocatalyzed synthesis of amides.

However, these methods employ NCS as chlorine source which lead to the formation of significant amounts of organic waste. Therefore, there is still a need for greener and readily accessible protocols for the activation of carbonyl derivatives that make use of accessible and more sustainable chlorinating agents.

In 2017, Hu and coworkers reported a convenient photocatalyzed oxidative C-H chlorination by using NaCl as a chlorine source, $Na_2S_2O_8$ as an oxidant and $Ru(bpy)_3Cl_2$ as a photocatalyst (Scheme 3-a) [11]. This photocatalyzed oxidative chlorination is one of rare methods which employ abundant, cheap and non-toxic NaCl as a chlorine source.



Scheme 3. NaCl as a chlorine source in photocatalyzed reactions.

Iron is the second most abundant metal on hearth and chemists have had a long-standing interest in replacing the Ru and Ir present in classical photocatalysts with earth abundant metal [12]. The earth-abundant iron offers an economical and sustainable alternative to precious and toxic Ru and Ir [13]. However, the photoexcited metal to ligand charge transfer states of many iron complexes relax at the picosecond time scale to low energy lying ligand field states, resulting in ineffective electron-transfer reactivity [14]. Jin has reported an *in situ* generation of photoactive complex of Fe_2SO_4 with 2-picolinic acid, in order to improve the excited-state lifetime of the photocatalyst for the decarboxylative alkylation of heteroarenes in the presence of $NaBrO_3$ or $NaClO_3$ as an oxidant [15].

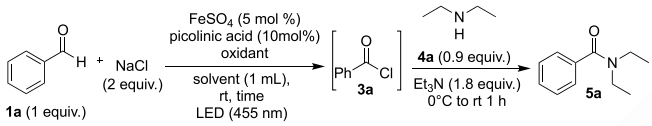
Due to our interest in the use of EAM_s-based salts as photocatalysts [16] and in chlorination of organic compounds [17], we studied the possibility to use NaCl as a chlorinating agent in a procedure photocatalyzed by Fe_2SO_4 with 2-picolinic acid as ligand, to convert aldehydes into acyl chlorides as intermediates for obtaining amides (Scheme 3-b).

Results and Discussion

The investigation started reacting benzaldehyde **1a** (1 equiv.) and NaCl (1.2 equiv.), in the presence of 5 mol% $FeSO_4.7H_2O$, 10% mol 2-picolinic acid, in 1 mL of acetonitrile (MeCN) under blue LED irradiation (centered at 455 nm) for 48 h (until the complete transformation of the starting aldehyde **1a**). The resulting mixture, containing the acyl chloride **2** generated in situ, was added with NEt_3 (1.8 equiv.) and diethylamine **3a** (0.9 equiv.), after 1 hour at room temperature the corresponding *N*,*N*-diethylbenzamide **4a** was formed in 33% yield (Table 1, entry 1). Several parameters have been studied and the complete optimization process is summarized in Table 1. To optimize the product yield, the amount of NaCl was increased to 2 equivalent, obtaining the product in 51% yield (Table 1, entry 2). The same reaction was carried out employing 2 equiv. (Table 1, entry 3) and 1 equiv. (Table 1, entry 4) of $Na_2S_2O_8$ and the amide **4a** has been obtained in 60% and 72% yield respectively. A screening of oxidants was carried out: Oxone (Table 1, entry 5), O_2 (Table 1, entry 6), TBHP in decane (Table 1, entry 7) and H_2O_2 (Table 1, entry 8) were tested and only Oxone have furnished the product in 55% yield, in the other

cases no formation of *N*,*N*-diethylbenzamide **4a** was detected. Then a screening of solvents has been carried out in order to substitute acetonitrile with a more sustainable one, and cyclopentyl methyl ether (CPME) (Table 1, entry 9), ethyl acetate (AcOEt) (Table 1, entry 10), 2-methyltetrahydrofuran (2-MeTHF) (Table 1, entry 11) and dioxolane (Table 1, entry 12) were employed, but no formation of product was detected. When acetone, a green conventional solvent, has been used, the product was obtained with an increase of yield to 89% (Table 1, entry 13). Then the irradiation time was reduced to 24 h with a decrease of yield to 39% (Table 1, entry 14). The same reaction was carried out in the dark (Table 1, entry 15), in the absence of 2-picolinic acid (Table 1, entry 16), in the absence of $Na_2S_2O_8$ (Table 1, entry 17) and in the absence of $FeSO_4$ (Table 1, entry 18), but no reaction has been observed.

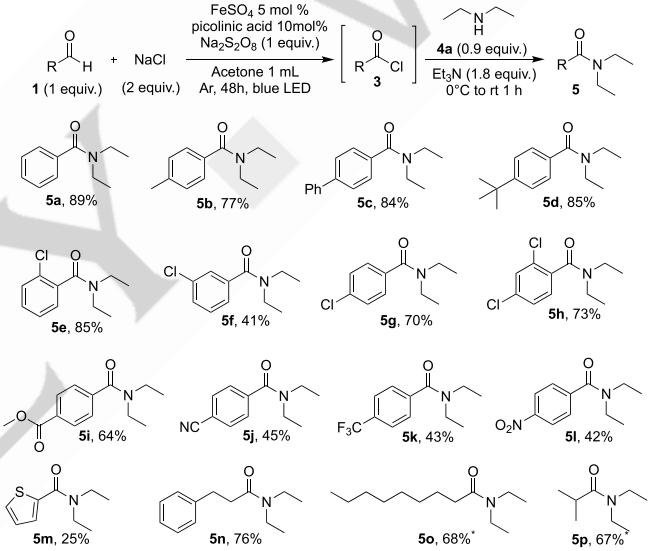
Table 1. The effect of amounts of reagents, solvents and time in the model reaction.



Entry[a]	NaCl [eq.]	Oxidant [eq.]	Solvent	Time [h]	Yield [%][b]
1	1.2	$Na_2S_2O_8$ (3)	MeCN	48	33%
2	2	$Na_2S_2O_8$ (3)	MeCN	48	51%
3	2	$Na_2S_2O_8$ (2)	MeCN	48	60%
4	2	$Na_2S_2O_8$ (1)	MeCN	48	72%
5	2	Oxone (1)	MeCN	48	55%
6	2	O_2	MeCN	48	0%
7	2	TBHP	MeCN	48	0%
8	2	H_2O_2	MeCN	48	0%
9	2	$Na_2S_2O_8$ (1)	CPME	48	0%
10	2	$Na_2S_2O_8$ (1)	AcOEt	48	0%
11	2	$Na_2S_2O_8$ (1)	2-MeTHF	48	0%
12	2	$Na_2S_2O_8$ (1)	Dioxolane	48	0%
13	2	$Na_2S_2O_8$ (1)	Acetone	48	89%
14	2	$Na_2S_2O_8$ (1)	Acetone	24	39%
15	2	$Na_2S_2O_8$ (1)	Acetone	48	0%[c]
16	2	$Na_2S_2O_8$ (1)	Acetone	48	0%[d]
17	2	-	Acetone	48	0[e]
18	2	Na_2SO_8 (1)	Acetone	48	0[f]

[a] Unless otherwise shown, the reaction was performed using aldehyde **1a** (1 equiv.), NaCl (2 equiv.), in solvent (1 mL), and in the presence of oxidant $FeSO_4$ (5 mol%), picolinic acid (10 mol%), under blue LED (455 nm) irradiation. Then, the resulting mixture was cooled to 0°C, and diethyl amine 3a (0.9 equiv.) and NEt_3 (1.8 equiv.) were added, and after 1h at room temperature, the desired amide **4a** was obtained. See supporting information for details. [b] Isolated yields. [c] Reaction carried out in the dark. [d] Reaction carried out in the absence of 2-picolinic acid. [e] Reaction carried out in the absence of Na_2SO_8. [f] Reaction carried out in the absence of $FeSO_4$.

With the optimized conditions in hand (Table 1, entry 13), the applicability and functional group tolerance were explored. And array of aromatic and aliphatic aldehydes **1**, while keeping the reactant **4a** fixed, were employed and tested.

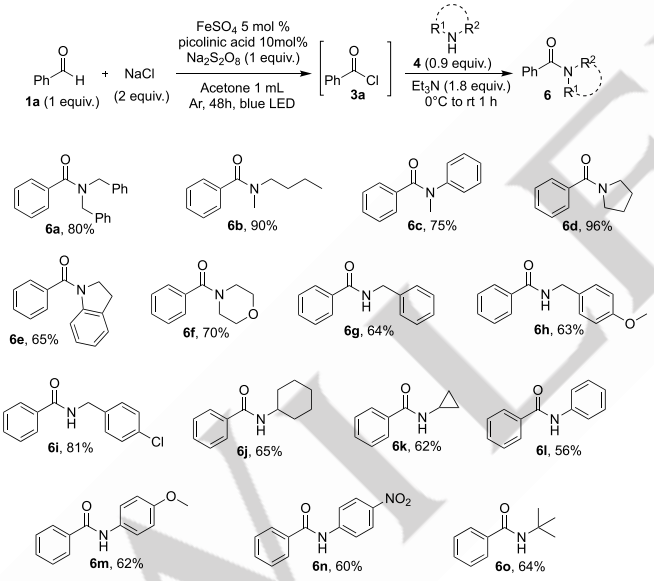


Scheme 4. Investigation of the scope of the reaction with respect to the aldehyde

**the reactions were performed in MeCN*

In general, the corresponding amides (**5a**-**5p**) were obtained in satisfying yields. Different functional groups on aromatic ring both electron donating and electron withdrawing were tested. Electron donating substituents in para position, as methyl, phenyl and *tert*-butyl showed good results furnishing the amides **5b**, **5c** and **5d** in respectively 77%, 84% and 85% yields. Benzaldehydes with halide substituents, as chlorine in ortho, meta, para positions were subjected to this procedure giving the resultants amides **5e**, **5f**, **5g** and **5h** in good yields, which could be further transformed by traditional cross-coupling reactions. Moderate electron withdrawing group as COOMe was well tolerated furnishing the corresponding amide **5i** in 64% yield. Strong electron-withdrawing groups, as CN, CF_3, and NO_2 provided the corresponding amides **5j**, **5k** and **5l** in moderate yields. Thiophen-2-carbaldehyde was subjected to optimized reactions conditions but the desired heteroaryl amide **5m** was obtained in 25% yield. To demonstrate

the versatility of the procedure aliphatic aldehydes, including both linear and branched, which usually cannot survive under oxidative conditions, were tested and converted to the desired amides **5n**, **5o** and **5p** in respectively 76%, 68% and 67% yields. The scope of the reaction was further explored with a selection of secondary, primary and aromatic amines. Secondary aliphatic amines as dibenzylamine, *N*-methylbutylamine and *N*-methylaniline furnished the corresponding amides **6a**, **6b** and **6c** in very high yields, secondary aliphatic cyclic amines as pyrrolidine, indoline and morpholine works well giving the amides **6d**, **6e** and **6f** in respectively 96% 65% and 70% yields. The reaction was carried out with benzylamine and 4-methoxybenzylamine and the amides **6g** and **6h** were obtained in good yields. Benzyl amine with halide substituent as chlorine was used to obtain *N*-(4-chlorobenzyl) benzamide **6i**, which can be further transformed by cross-coupling reactions. Primary α–branched amines, which are fundamental building blocks in natural products and pharmaceuticals, as cyclohexylamine, cyclopropylamine, and *tert*-butylamine have been employed, giving the corresponding amides **6j, 6k** and **6o** in satisfying yields. Finally aniline, a weak nucleophile, and anilines with an electron donating substituent, as OMe, and with a strong electron-withdrawing group, as NO_2 were employed giving the expected amides **6l**, **6m** and **6n** in respectively 56% 62% and 60% yields.

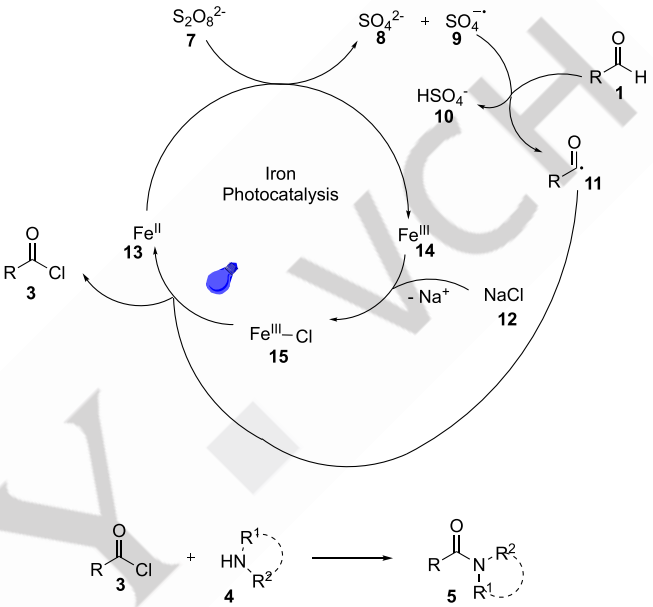


Scheme 5 Investigation of the scope of the reaction with respect to the amine

Based on previous studies [18-21] and our experimental observations, a description of a possible mechanism is reported in Scheme 6. Peroxydisulfate anion **7** oxidizes Fe^{II} giving sulfate ion **8** and sulfate radical anion **9** via single electron reduction as previously reported in literature [18]. Sulfate radical anion **9** abstracts a hydrogen atom from the aldehyde **1** furnishing the corresponding acyl radical **11** and hydrogen sulfate **10** [19]. Coordination of the chloride anion to ~~the~~ Fe^{III} forms the iron complex **15** [20]. Photoexcitation of iron complex **15** should promote chlorine transfer to the acyl radical, generating the reduced Fe^{II} and acyl chloride **3** according to Li [19] and Jin [20].

In the end, acyl chloride **3** reacts with amine **4** to give the corresponding amide **5**. To validate this hypothesis, the presence of the acyl radical was confirmed through a radical scavenger experiment and its trapping with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) [21].

Scheme 6. Proposed reaction mechanism.



Conclusion

In summary, we have developed a synthesis of amides starting directly from aldehydes under visible light using NaCl, as chlorine source, sodium peroxydisulfate as an oxidant and a photoactive complex of Fe_2SO_4 with 2-picolinic acid, an earth-abundant metal (EAMs) salt, as a sustainable photocatalyst. Fe_2SO_4 is readily commercially available, not needed to be prepared and is environmentally sustainable. Sodium chlorine is a greener chlorine source than those typically used. Sodium peroxydisulfate is a cost-effective oxidant characterized by long shelf lives. Acetone was used as a solvent, is classified among the greener conventional solvents. This works opens perspectives for the extended application of iron salts toward halogenation processes as well as for C-H activations thereby making a significant contribution to the field of catalysis with earth-abundant metals.

Experimental Section

In a round bottom flask of 10 mL, NaCl (2 mmol), $FeSO_4 \cdot 6H_2O$ (5% mol) and picolinic acid (10 mol%), $Na_2S_2O_8$ (1 mmol) were added to a solution of aldehyde (1 mmol) in 1 mL acetone (MeCN for aliphatic aldehyde) under argon atmosphere and at room temperature. The mixture was stirred under blue led irradiation for 48 hours (the reaction was monitored by TLC until disappearance

of aldehyde). Then the reaction mixture was cooled to 0 °C and an amine (0.91 mmol) and NEt_3 (1.82 mmol) was added. The reaction mixture was left to stir from 0°C to room temperature for 1h until disappearance of the intermediate acyl chloride (monitored by TLC). Then, the reaction mixture was quenched with water and extracted with AcOEt. The combined organic layers were washed three times with a solution of 5% citric acid solution and then three times with a solution of 5% $NaHCO_3$; the organic phase was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude products were purified by flash chromatography on silica gel.

Supporting Information

The authors have cited additional references within the Supporting Information.[22, 63]

Acknowledgements

We acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.1, Call for tender No. 1409 published on 14.9.2022 by the Italian Ministry of University and Research (MUR), funded by the European Union – NextGenerationEU– Project Title: The Second Life of Posidonia Oceanica: Sustainability-guided Isolation and Valorization of its Main Constituents – CUP J53D23014680001- Grant Assignment Decree No. 1064 adopted on 18.07.2023 by the Italian Ministry of Ministry of University and Research (MUR).

Keywords: aldehydes • C-H activation • earth-abundant metal salts • photocatalysis • sodium chloride

[1] C. R. J. Stephenson, T. P. Yoon, D. W. C. MacMillan, *Visible light photocatalysis in organic chemistry*, Wiley-VCH Verlag, Weinheim, **2017**, p. 444.

[2] a) B. König, *Eur. J. Org. Chem.* **2017**, 1979, b) K. L. Skubi,T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035, c) I.K. Sideri, E. Voutyritsa, C. G. Kokotos, *Org. Biomol. Chem*. **2018**,*16*, 4596, d) L. Capaldo, D. Ravelli, M. Fagnoni, *Chem. Rev.* **2022**, *122*, 1875, e) N. F. Nikitas, P. L. Gkizis, C. G. Kokotos, *Org. Biomol. Chem.*, **2021**,*19*, 5237, f) P.L. Gkizis, *Eur.J. Org.Chem.* **2022**, e202201139.

[3] a) L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* **2018**, *57*, 10034; b) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev*. **2013**, *113*, 5322.

[4] a) K. P. S. Cheung, S. Sarkar, V. Gevorgyan, *Chem. Rev.* 2022, *122,* 1543; b) P. Herr, C. Kerzig, C.B. Larsen, D. Haüssinger, O. S. Wenger, *Nat. Chem*. **2021**, *13*, 956; c) Y. Abderrazak, A. Bhattacharyya, O. Reiser, *Angew. Chem. Int. Ed*. **2021**, *60*, 21100; d) J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan, *Nature Rev. Chem.* **2017**, *1*, 0052.

[5] R. M. Bullock, J. G. Chen, L. Gagliardi, P. J. Chirik, O. K. Farha, C. H. Hendon, C. W. Jones, J. A. Keith, J. Klosin, S. D. Minteer, R. H. Morris, A. T. Radosevich, T. B. Rauchfuss, N. A. Strotman, A. Vojvodic, T. R. Ward, J. Y. Yang, Y. Surendranath, *Science* **2020**, *369*, eabc3183.

[6] a) G. W. Gribble, *Acc. Chem. Res.* **1998**, *31*, 141; b) B. G. Wang, J. B. Gloer, N. Y. Ji, J. C. Zhao, *Chem. Rev.* **2013**, *113*, 3632; c) N. V. Zhukova, T. A. Gloriozova, V. V. Poroikov, V. M. Dembitsky, *Pharma Innov. J.* **2017**, *6*, 456.

[7] S. Parisotto, E. Azzi, A. Lanfranco, P. Renzi, A. Deagostino, *Reactions* **2022**, *3*, 233.

[8] a) G. W. Brown, *The Chemistry of the Hydroxyl Group*, Interscience, London, **1971**, 592– 622; b) M. F. Antell, *The Chemistry of Acyl Halides*, Interscience, London, **1972**; c) H. C. J. Ottenheijm, J. H. M. De Man, *Synthesis* **1975**, *3*, 163.

[9] N. Iqbal, E. J. Cho, *J. Org. Chem.* **2016**, *81*, 1905.

[10] N. F. Nikitas, M. K. Apostolopoulou, E. Skolia, A. Tsoukaki, C. G. Kokotos, *Chem. Eur. J.* **2021**, *27*, 7915.

[11] L. Zhang, X. Hu, *Chem. Sci.* **2017**, *8*, 7009.

[12] a) C. B. Larsen, O. S. Wenger, *Chem. Eur. J.* **2018**, *24*, 2039; b) O. S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 13522; c) Y. Qiao, E. J. Schelter, *Acc. Chem. Res.* **2018**, *51*, 2926; d) B. M. Hockin, C. Li, N. Robertson, E. Zysman-Colman, *Catal. Sci. Technol.* **2019**, *9*, 889; e) O. S. Wenger, *Chem. Eur. J.* **2019**, *25*, 6043; f) A. Hossain, A. Bhattacharyya, O. Reiser, *Science* **2019**, 364, eaav9713.

[13] a) Z. Li, X. Wang, S. Kia, J. Jin, *Org. Lett.* **2019**, *21*, 4259; b) O. Baslé, *Curr. Opin. Green Sustain.* **2021**, *32*,100539; c) Y. Abderrazak, A. Bhattacharyya, O. Reiser, *Angew. Chem. Int. Ed.* **2021**, *60*, 21100; d) L. H. M. de Groot, A. Ilic, J. Schwarz, K. Warnmark, *J. Am. Chem. Soc.* **2023**, *145,* 9369.

[14] G. Feng, X. Wang, J. Lin, *Eur. J. Org. Chem*. **2019**, 6728.

[15] Z. Li, X. Wang, S. Xia, J. Jin, *Org. Lett.* **2019**, *21*, 4259.

[16] a) S. Gaspa, L. Ledda, D. d'Atri, A. Porcheddu, L. Pisano, M. Carraro, L. De Luca, Adv. Synth. Catal. **2023**, *365*, 508; b) S. Gaspa, G. Sciortino, A. Porcheddu, C. Dell'Osa, G. Satta, U. Azzena, L. Pisano, M. Carraro, D. Sanna, E. Garribba, L. De Luca, *Mol. Catal*. **2023**, *541*, 113054.

[17] a) S. Gaspa, M. Carraro, L. Pisano, A. Porcheddu, L. De Luca, *Eur. J. Org. Chem.* **2019**, 3544; b) S. Gaspa, A. Valentoni, G. Mulas, A. Porcheddu, L. De Luca, *Chemistry Select* **2018**, 3, 7991; c) S. Gaspa, I. Amura, A. Porcheddu, L. De Luca, *New J. Chem.* **2017**, *41*, 931; d) S. Gaspa, A. Porcheddu, A. Valentoni, S. Garroni, S. Enzo, L. De Luca, *Eur. J. Org. Chem.* **2017**, 5519; e) S. Gaspa, A. Porcheddu, L. De Luca, *Tetrahedron Lett.* **2017**, *58*, 2533.

[18] a) D. Kiejza, U. Kotowska, W. Polińska, J. Karpińska, *Sci. Total Environ.* **2021**, *790*, 148195; b) C. Liang, I. L. Lee, I. Y. Hsu, C. P. Liang, Y. L. Lin, *Chemosphere* **2008**, *70*, 426.

[19] P. Zhang, H. Shen, L. Zhu, W. Cao, C. Li, *Org. Lett.* **2018**, *20*, 7062.

[20] Z. Li, X. Wang, S. Xia, J. Jin, *Org. Lett.* **2019**, *21*, 4259.

[21] For details see Supporting Information.

[22] M. A. Short, J. M. Blackburn, J. L. Roizen, *Angew. Chem. Int. Ed.* **2018**, *57*, 296.

[23] M. Teders, L. Pitzer, S. Buss, F. Glorius, *ACS Catal.* **2017**, *7*, 4053.

[24] S. Sultan, M. A. Rizvi, J. Kumar, B. A. Shah, *Chem. Eur. J.* **2018**, *24*, 10617.

[25] M. A. Cismesia, T. P. Yoon, *Chem. Sci.* **2015**, *6*, 5426.

[26] C. G. Hatchard, C. A. Parker, J. Bowen Edmund, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **1956**, *235*, 518.

[27] H. J. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl. Chem.* **2004**, *76*, 2105.

[28] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Chemical Actinometry. Handbook of Photochemistry*, 3rd Ed., **2006**.

[29] G. Hatchard, C. A. Parker, J. Bowen Edmund, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **1956**, *235*, 518.

[30] S. Gaspa, A. Farina, M. Tilocca, A. Porcheddu, L. Pisano, M. Carraro, U. Azzena, L. De Luca, *J. Org. Chem.* **2020**, *85*, 11679.

[31] I. Cohen, A. K. Mishra, G. Parvari, R. Edrei, M. Dantus, Y. Eichen, A. M. Szpilman, *Chem. Commun.* **2017**, 53, 10128.

[32] Z. Li, L. Liu, K. Xu, T. Huang, X. Li, B. Song, T. Chen, *Org. Lett.* **2020**, *22*, 5517.

[33] W. Kawahata, T. Asami, T. Kiyoi, T. Irie, H. Taniguchi, Y. Asamitsu, T. Inoue, T. Miyake, M. Sawa, *J. Med. Chem.* **2018**, *61*, 8917.

[34] S. S. Shah, M. Shee, Y. Venkatesh, A. K. Singh, S. Samanta, N. D. P. Singh, *Chem. Eur. J.* **2020**, *26*, 3703.

[35] N. N. Li, M. Li, J. N. Gao, Z. Zhang, J.B. Xie, *J. Org. Chem.* **2022**, *87*, 10876.

[36] A. Leggio, A. Comandè, E. L. Belsito, M. Greco, L. L. Feudo, A. Liguori, *Org. Biomol. Chem*. **2018**, *16*, 5677.

[37] T. H. Ding, J. P. Qu, Y. B. Kang, *Org. Lett.* **2020**, *22*, 3084.

[38] K. Shichijo, M. Fujitsuka, Y. Hisaeda, H. Shimakoshi, *J. Organomet. Chem.* **2020**, *907*, 121058.

[39] W. Li, X. F. Wu, *Org. Lett*. **2015**, 17, 1910.

[40] C. Liu, H. N. Chen, T. F. Xiao, X. Q. Hu, P. F. Xu, G. Q. Xu, Chem. Commun. **2023**, *59*, 2003.

[41] H. Lin, S. Liu, Q. Li, Q. Zhang, L. Yang, T. Wang, J. Luo, *Synth. Commun.* **2023**, *53*, 1412.

[42] X. Kong, Y. Chen, X. Chen, Z. X. Lu, W. Wang, S. F. Ni, Z. Y. Cao*, Org. Lett.* **2022**, *24*, 2137.

[43] C. Hu, X. Yan, X. Zhou, Z. Li, *Org. Biomol. Chem.* **2013**, *11*, 8179.

[44] C. Liu, H. N. Chen, T. F. Xiao, X. Q. Hu, P. F. Xu, G. Q. Xu, *Chem. Commun.* **2023**, *59*, 2003.

[45] S. Nagano, K. Maruoka, *Adv. Synth. Catal.* **2023**, 365, 295.

[46] A. Fusano, S. Sumino, S. Nishitani, T. Inouye, K. Morimoto, T. Fukuyama, I. Ryu, *Chem. Eur.J.* **2012**, *18*, 9415.

[47] T. Bathini, V. S. Rawat, S. Bojja*, Tetrahedron Lett.* **2015**, *56*, 5656.

[48] S. Gaspa, A. Porcheddu, L. De Luca, *Org. Biomol. Chem.* **2013**, *11*, 3803.

[49] J. F. Soulé, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.* **2011**, *133*, 18550.

[50] A. Banerjee, T. Hattori, H. Yamamoto, *Synthesis* **2023**, *55*, 315.

[51] B. Pan, D. M. Huang, H. T. Sun, S. N. Song, X. B. Su, *J. Org. Chem.* **2023**, *88*, 2832.

[52] Z. Fu, X. Wang, S. Tao, Q. Bu, D. Wei, N. Liu, *J. Org. Chem.* **2021**, *86*, 2339.

[53] Q. Zhao, H. Li, L. Wang, *Org. Biomol. Chem.* **2013**, *11*, 6772.

[54] S. C. Ghosh, J. S. Y. Ngiam, C. L. L. Chai, A. M. Seayad, T. T. Dang, A. Chen, *Adv. Synth. Catal.* **2012**, *354*, 1407.

[55] V. K. Pandey, C. S. Tiwari, A. Rit, *Org. Lett.* **2021**, *23*, 1681.

[56] S. N. Rao, D. C. Mohan, S. Adimurthy, *Org. Lett.* **2013**, *15*, 1496.

[57] Q. Yang, Z. Wang, T. Kato, Y. Liu, K. Maruoka, *Org. Lett.* **2023**, *25*, 2958.

[58] C. Wang, Y. Wang, J. Wu, Q. Hu, H. Luo, Z. Wang, Y. Wang, D. Li, J. Liang, J. Yang, *Org. Biomol. Chem.* **2023**, *21*, 5185.

[59] C. Q. O'Broin, P. J. Guiry, *Org. Lett.* **2020**, *22*, 879.

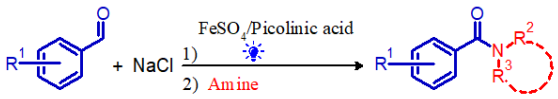
[60] I. A. P. S. Rajan, S. Rajendran, *New J. Chem.* **2023**, *47*, 10480.

[61] C. R. Shugrue, J. R. DeFrancisco, A. J. Metrano, B. D. Brink, R. S. Nomoto, B. R. Linton, *Org. Biomol. Chem.* **2016**, *14*, 2223.

[62] H. M. R. Hoffmann, K. Haase, *Synthesis* **1981**, 715.

[63] C. Zhou, P. Li, X. Zhu, L. Wang, *Org. Lett.* **2015**, *17*, 6198.

Entry for the Table of Contents



A visible-light mediated oxidative amidation of aldehydes promoted by photoactive complex of Fe_2SO_4 with 2-picolinic acid, NaCl as chlorine source, Na_2SO_8 as an oxidant, and acetone as a solvent is reported. Fe_2SO_4 is an earth-abundant metal (EAMs) salt, commercially readily available and environmentally sustainable. Sodium chloride is a green and sustainable chlorine source.