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A Visible-Light Driven Esterification of Aldehydes Catalyzed by $VOSO_4$

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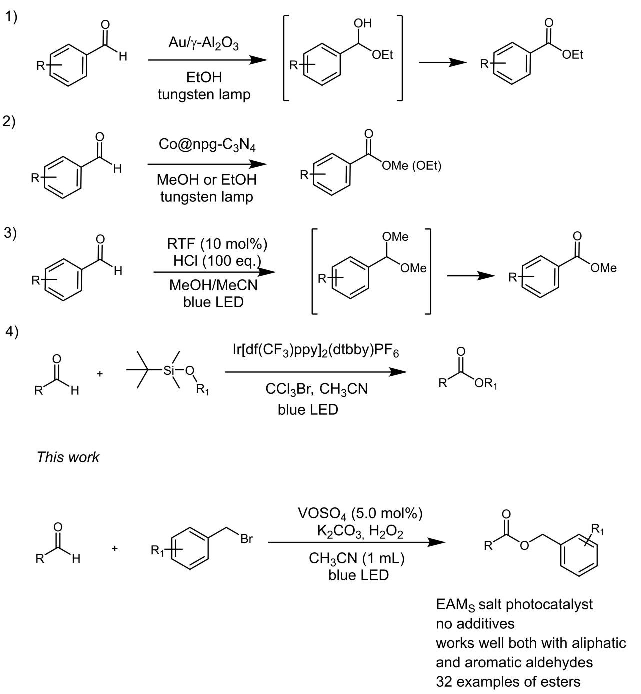
Abstract: An esterification of the C–H bond of aldehydes promoted by oxidovanadium(IV) sulfate, $V^{IV}OSO_4$, is reported. The process is mediated by visible-light, is carried out at room temperature, in absence of additives and using H_2O_2 as a benign oxidant. $VOSO_4$ is a commercially available, earth-abundant metal (EAM_s) salt, that does not require to be prepared. This report opens intriguing perspectives for the extended application of vanadium salts toward halogenation processes as well as for C–H activations and gives a contribution in the field of earth-abundant metals based-catalysis.

Keywords: Aldehydes; C–H activation; Esterification; Photocatalysis; Vanadium, EAM_s salts.

Esters are one of the most meaningful functional groups in organic chemistry and are present in several natural products, polymers, pharmaceuticals and synthetic intermediates.[1] Traditionally, esters are achieved via the acid-catalyzed esterification reaction of carboxylic acids with alcohols or transesterification of esters,[2,1a] but these procedures usually require the excess use of alcohols or removal of water via azeotropic distillation to drive the equilibrium to get esters in good yield. Otherwise, esters can be synthesized through the consecutive activation of carboxylic acids (e.g., via acyl chlorides, anhydrides, and activated esters),[3] followed by the addition of alcohols, which is achieved with harsh reaction conditions.[4] Even if this is the common synthetic pathway employed in the industrial synthesis of pharmaceuticals, it presents many disadvantages as two additional steps, use of hazardous reagents and production of stoichiometric amount of waste products.[5] The direct access to benzyl esters from benzoic acids and benzyl bromides has unfrequently been reported because benzoate is not much reactive. Roque and co-workers have been reported a synthesis of benzyl esters form benzyl bromide and bismuth(III) benzoate. The bismuth(III) benzoate needs to be previously prepared from triphenylbismuth and is used in stoichiometric ratio with the carboxylic acid, therefore, the methodology make use of stoichiometric amount of triphenylbismuth and benzyl bromide.[6] Benzyl esters have been also synthesized by reacting potassium arene carboxylates and benzyl bromide in acetonitrile as a solvent at reflux. The potassium carboxylates have been prepared by heating a mixture of the acid, potassium hydroxide and the ammonium salt.[7] Zao et al. have achieved benzyl acetate by reacting benzyl bromide with an excess of potassium acetate in the presence of crown ether-based covalent organic frameworks (CE-COFs) acetonitrile at reflux.[8]

The oxidative esterification of the aldehyde group is an appealing alternative approach to the synthesis of esters: unlike classical routes to esters, it does not involve the direct activation of a carboxylic acid,[9] and aldehydes are cheaper than carboxylic acids and can also be obtained from renewable resources.[10]

The direct conversion of aldehydes to esters is well known,[11] but most of these methods require stoichiometric amount of heavy metallic oxidant which generate huge amount of undesired waste. The direct transformation of aldehydes mediated by visible light is little explored. Visible-light-mediated photoreactions have been shown to display a safe, sustainable and accessible alternative to traditional methods, and to introduce new reactivity modes in organic synthesis.[12] In this context, esterification of substituted benzaldehydes with alcohols (principally methanol and ethanol) used as a solvent under visible light irradiation in the presence of supported gold nanoparticles as a catalyst (Scheme 1, path 1) has been reported.[13] The reaction proceeds *via* a hemiacetal intermediate. In 2017, Jain and co-workers have reported a visible light mediated esterification of aromatic aldehydes using a cobalt complex immobilized on nanoporous graphitic carbon nitride (Co@npg–C_3N_4) as a photocatalyst, in alcohols (methanol or ethanol) as both solvent and reactant (Scheme 1, path 2).[14] Wolf and co-workers carried out a photooxidation of aldehydes to methyl esters catalyzed by riboflavin tetraacetate (RFT) mediated by blue light (Scheme 1, path 3).[15] The reaction proceeds on aromatic aldehydes in methanol, under acidic conditions, via an acetal intermediate, providing the corresponding methyl esters. In 2018 Pandey and co-workers proposed a cross-dehydrogenating coupling of aldehydes with *tert*-butyldimeththylsilyl ethers mediated by visible-light photoredox catalysis. The reaction is carried out by the use of a photoredox catalyst based on iridium, an equimolecular quantity of CCl_3Br and an excess of R-OTBS ethers (Scheme 1, path 4).[16]



Scheme 1. Synthesis of esters from aldehydes mediated by visible light.

Recently Bath and co-workers proposed an oxidative esterification of aldehydes with α-bromocarbonyl compounds to α-acyloxycarbonyl compounds under visible light in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate as a photocatalyst and $AgBF_4$ as an additive,[17] and Li and co-workers reported an oxidative esterification of aldehydes with phenols photopromoted by a Ni(II)-based complex.[18]

The methodologies hitherto described provide mainly methyl or ethyl esters, obtained with highly reactive aromatic aldehydes, and make use of alcohols (methanol and ethanol) as both solvents and reactants. Consequently, these procedures suffer of limited substrate scopes and of unfavourable stoichiometric ratios of the reagent (related to the formation of hemiacetal or acetal intermediates). Moreover, the use of transition metal-based catalysts often immobilized on nanoporous materials, hard to prepare as well as or the use of riboflavin tetraacetate which needs to be synthsized[19] limits the accessibility of these methodologies and their improvement in view of industrial scale application. It is thus advisable to explore the opportunity to find a new photocatalyst more sustainable, easily and directly accessible and cheaper. Therefore the development of a new methodology using novel benign catalyst, driven by a green energy source for effective conversion of aldehydes to esters would be highly desirable.

Here we report a new class of photocatalytic system based on oxidovanadium(IV) sulfate, $V^{IV}OSO_4$, a stable, inexpensive and commercially available salt. Vanadium is part of the family of earth abundant elements (EAM_S), which have greater terrestrial abundance than precious metals, and thus their application in synthetic chemistry would lead to reduce both cost and environmental footprint. Moreover (EAM_S) display different reactivity profiles, affording alternative scientific opportunities for new catalysts design and opening new reaction pathways.[20] Reports on of earth-abundant metals (EAM_S) based-photocatalysts have been reported recently and include inorganic and organometallic complexes based on vanadium(V),[21] chromium(III),[22] iron(II),[23] cobalt(III),[24] copper(I),[25] zinc(II),[26] zirconium(IV),[27] and tungsten(VI),[28] but this field undoubtedly still needs to be explored massively. Particularly, $V^VO(O^iPr)_3$ has been reported as an example of V-based homogenous photocatalyst which, in presence of O_2, selectively oxidizes the Cα–Cβ bond of lignin β-1 at room temperature and under visible light irradiation[29] Furthemore, mixed-valence vanadium oxide particles grafted on oxide supports were used to allow oxidation of aliphatic alcohols.[30]

In relation to our interest in the synthesis of esters,[31] we evaluated the possibility to directly use EAMs-based salts as photocatalysts for selective esterification of aldehydes.

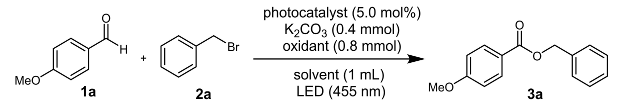
In this report the efficiency of $V^{IV}OSO_4$ has been compared with that of other inorganic salts of first raw transition metals and metal complexes in the synthesis of esters from benzyl bromides and aldehydes. This The catalyst well tolerates both aromatic and aliphatic aldehydes and benzyl bromides with diverse functional groups. Selective C–H activation remains a highly suitable target in organic synthesis, and this work supplements the range of available methods with a procedure mediated by visible-light and a catalyzed by a non-noble metal salt.[26a, 32] Ref. [26c] does not exist

The investigation started reacting 4-methoxybenzaldehyde **1 a** with benzyl bromide **2 a** as the model substrates, using a selection of EAMs salts as V, Fe, Ni, Cu, Mn, and Co under light irradiation by blue (455 nm) or green (535 nm) LEDs (Table 1). In the first reaction, benzaldehyde (Table 1, **1 a**, 0.8 mmol), benzyl bromide (Table 1, **2 a**, 0.4 mmol) and $VOSO_4$ (Table 1, 5 mol%), K_2CO_3 (Table 1, 0.4 mmol), *tert*-butyl hydroperoxide (TBHP) (Table 1, 0.4 mmol) in 1 mL of CH_3CN were irradiated for 72 h with blue LED_S afforded benzyl benzoate **3 a** in 95%. For comparison, a stable $V^{IV}O$ complex, $V^{IV}O(acac)_2$, where acac is acetylacetonate ligand, and a vanadate(V) salt, $NH_4V^VO_3$, have been tested, yielding **3 a** in 40% and 38%, respectively (Table 1, entries 2 and 3). Using as catalysts iron salts $Fe^{II}Cl_2$ and $Fe^{III}Cl_3$, the product **3 a** was formed in 24% and 19% yield, respectively, under blue LED irradiation (Table 1, entries 4 and 5). $Ni^{II}SO_4$ has shown comparable results, affording the desired ester in 18% yield (Table 1, entry 6). Salts based on copper, as Cu^ICl and Cu^{II}-$(OAc)_2$ were employed furnishing the product **3 a** in 21% and 10% respectively (Table 1, entries 7 and 8). Other salts based on EAM_S like $Mn^{II}Cl_2$, $Co^{II}Cl_2$ and $V^{III}Cl_3$ with maximum absorbance around 535 nm (green led), were tested but did not lead to the product (Table 1, entries 9, 10 and 11). Relating to all the systems, $V^{IV}OSO_4$ afforded the product **3 a** with the most promising yield of the set achieving 95% (Table 1, entry 1). Classical photocatalysts Ru^{II}-$(bpy)_3Cl_2$ was also tested and the product **3 a** have been obtained in 43% yield (Table 1, entry 12). With this result in hand, a solvent screening has been achieved. In ethyl acetate (AcOEt), cyclopentyl methyl ether (CPME), 2-Mmethyltetrahydrofuran (2Me-THF) and tetrahydrofuran (THF) the yields were respectively 65%, 0%, 0% and 20% (Table 1, entries 13, 14, 15 and 16), showing an important enhancement in acetonitrile. Hydrogen peroxide (H_2O_2) has been tested as an oxidant, giving the product **3 a** in 95% yield (Table 1, entry 17). It is to highlight that hydrogen peroxide is considered a green oxidant reagent while satisfies the principles of green chemistry.

Even if molecular oxygen is considered to be an ideal oxidant, its employ sometimes is difficult since it needs harsh reaction conditions as high temperature or pressure and it often displays poor selectivity.[33]

Among the common oxidant reagents, hydrogen peroxide (H_2O_2) with 47% oxygen content has been found to be suitable and hands-on to use. Additionally, in the oxidation reaction one oxygen atom is transferred to the substrate and at the same time one equivalent of H_2O is formed as an ideal and green by-product.[34] In addition, due to its good solubility in water and many organic solvents, hydrogen peroxide is a very widely usable oxidant.[34d,35] Moreover, it has is safe for storage, operation, transportation and is commercially available, inexpensive and highly effective and selective. For these characteristics it has wide applications.[36] The same reaction conditions were employed using $Ru^{II}(bpy)_3Cl_2$ as a photocatalyst, giving the product **3 a** in 38% yield (Table 1, entry 18), showing a performance worse than $V^{IV}OSO_4$. The reaction in presence of $V^{IV}OSO_4$ was performed in the dark and under green LEDs irradiation (Table 1, entries 19 and 20) obtaining the product only in trace. This finding confirms a blue LEDs light-activation process. Finally, the reaction was carried out without

Table 1. Screening of reaction conditions.



Entry[a]	Catalyst	Oxidant	λ (nm)	Solvent	Yield[b]
1	$VOSO_4$	TBHP	455	CH_3CN	95%
2	$VO(acac)_2$	TBHP	455	CH_3CN	40%
3	NH_4VO_3	TBHP	455	CH_3CN	38%
4	$FeCl_2$	TBHP	455	CH_3CN	24%
5	$FeCl_3$	TBHP	455	CH_3CN	19%
6	$NiSO_4$	TBHP	455	CH_3CN	18%
7	CuCl	TBHP	455	CH_3CN	21%
8	$Cu(OAc)_2$	TBHP	455	CH_3CN	10%
9c)	$MnCl_2$	TBHP	535	CH_3CN	0
10c)	$CoCl_2$	TBHP	535	CH_3CN	0
11c)	VCl_3	TBHP	535	CH_3CN	0
12	$Ru(bpy)_3Cl_2$	TBHP	455	CH_3CN	43%
13	$VOSO_4$	TBHP	455	AcOEt	65%
14	$VOSO_4$	TBHP	455	CPME	0%
15	$VOSO_4$	TBHP	455	2Me-THF	0%
16	$VOSO_4$	TBHP	455	THF	20%
17	$VOSO_4$	H_2O_2	455	CH_3CN	95%
18	$Ru(bpy)_3Cl_2$	H_2O_2	455	CH_3CN	38%
19	$VOSO_4$	H_2O_2	dark	CH_3CN	trace
20[c]	$VOSO_4$	TBHP	535	CH_3CN	0%
21	–	H_2O_2	455	CH_3CN	0%

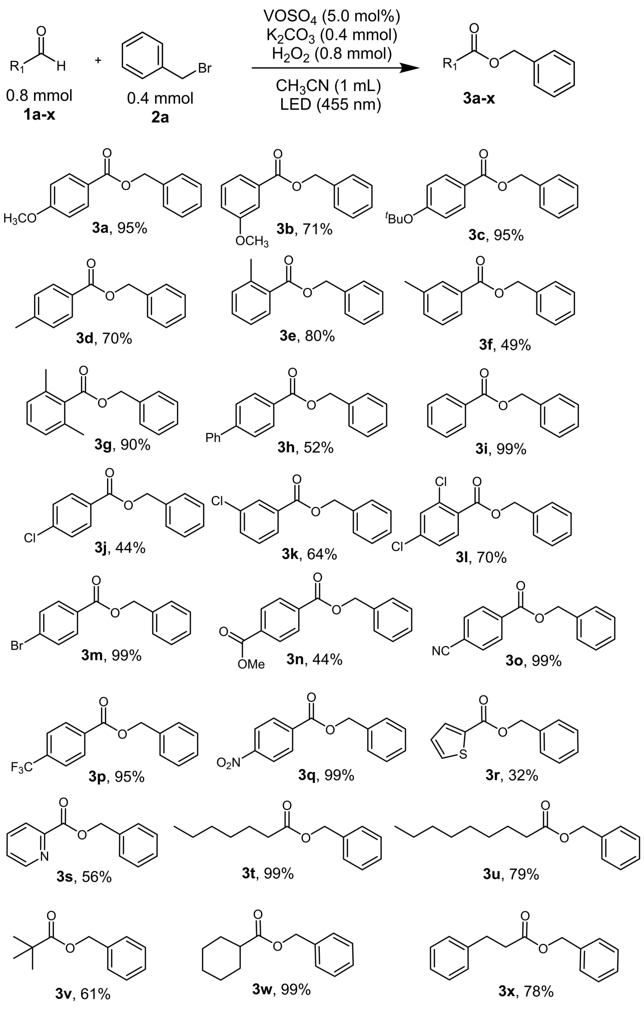
[a] Reaction conditions: aldehyde (0.8 mmol), benzyl bromide (0.4 mmol), oxidant (0.8 mmol), K_2CO_3 (0.4 mmol), solvent (1 mL), photocatalyst (5% mol), blue LED_S (455 nm), 72 h.
[b] Isolated yields.
[c] The reaction mixture was irradiated for 72 h with green LED_S (535 nm).

the catalyst and no product was obtained (Table 1, entry 21). Also, at the end of the reaction 60% of unreacted aldehyde was recovered.[37]

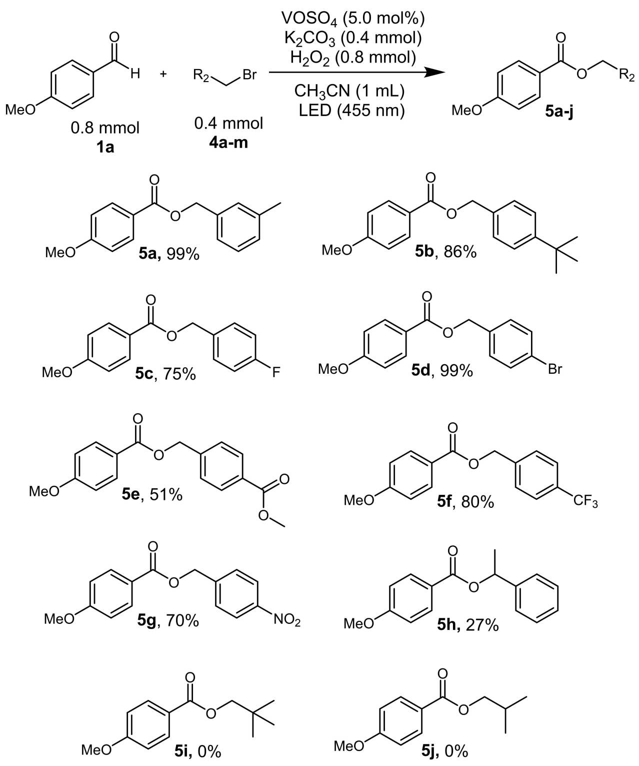
With the optimized conditions in hand (Table 1, entry 17), the aldehyde scope has been investigated. An array of aromatic and aliphatic aldehydes has been tested. In general, the corresponding esters were obtained in good yields (Scheme 2, **3a**–**x**). Different functional groups on aromatic rings both electron donating and electron withdrawing were examined. Neither the electronic properties nor the steric effects of substituents on the ring of aromatic aldehydes were found to have any effect on the reaction yields.

Strong electron donating groups as OMe in para and e meta positions and O^{t}Bu in para position (Scheme 2, **3a**, **3b** and **3c**) showed very good results. Benzaldehydes with moderate electron donating substituents as methyl in orto, meta and para positions (Scheme 2, **3d**, **3e** and **3f**) and phenyl (Scheme 2, **3h**) were tested with satisfactory results. Benzaldehyde with halide substituents, such as chlorine in meta and para positions and bromide were subjected to this procedure giving the corresponding esters, which could be further transformed by traditional cross-coupling reactions (Scheme 2, **3j**, **3k**, **3l**, and **3m**). Moderate electron withdrawing groups as COOMe (Scheme 2, **3n**) was well tolerated. Strong electron withdrawing groups as CN, CF_3 and NO_2 provided the desired esters with very good results, in respectively 99%, 95% and 99% yields (Scheme 2, **3o**, **3p**, and **3q**). The reactions with sterically demanding disubstituted aldehyde was performed and the corresponding ester (Scheme 2, **3g**) was obtained in high yield despite steric hindrance. To prove the synthetic utility of the procedure thiophen-2-carbaldehyde and picolinaldehyde (Scheme 2, **1r** and **1s**) were subjected to optimized reactions conditions, giving the desired heteroaryl esters (Scheme 2, **3r** and **3s**). Aliphatic aldehydes, both linear and branched, which typically cannot survive under oxidative conditions, were converted to the desired esters in very high yields (Scheme 2, **3t**, **3u**, **3v**, **3w** and **3x**).

To investigate the scope of the method, the reaction was tested with an array of benzyl bromides. The electronic properties of substituents on the aromatic ring of benzyl bromide were found to have any influence on the reaction. Both electro-donating groups, such as benzylic C–H and *tert*-butyl (Scheme 3, entries **5a** and **5b**), and withdrawing groups, such as ester, CF_3 and NO_2 (Scheme 3, entry



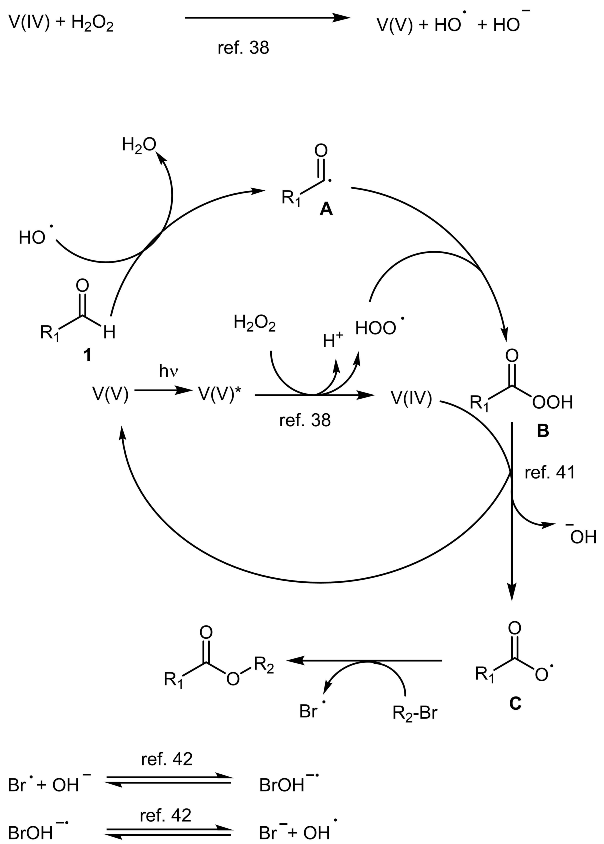
Scheme 2. Investigation of the aldehyde scope of the reaction.



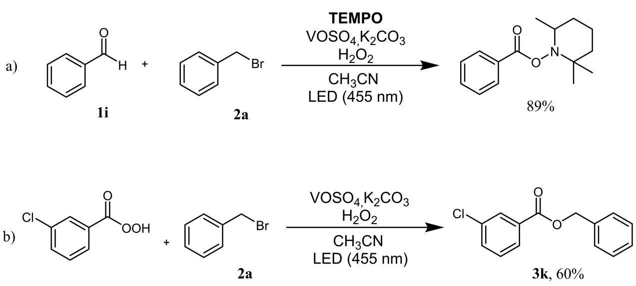
Scheme 3. Investigation of the benzyl bromide scope of the reaction.

5f and **5g**), were well tolerated providing the desired esters in good yields. Benzyl bromide with carbonyl substituents like ester gave good results too (Scheme 3, **5e**). The reaction carried out on benzyl bromides with halide substituents on the aromatic ring gave the corresponding esters, which could be further transformed by traditional cross-coupling reactions (Scheme 3, entries **5c** and **5d**).

When aliphatic bromide, such as 1-bromo-2,2-dimethylpropane and 1-bromo-2-methylpropane, were employed as the substrates, no desired products were obtained (Scheme 3, entries **5i** and **5j**).



Scheme 4. Proposed reaction mechanism.



Scheme 5. Mechanistic investigations supporting the formation of acyl radical and 3-chlorobenzoperoxoic acid intermediate.

Based on the previous studies[38] and our experimental observations, a possible mechanism is proposed in Scheme 4. Firstly, V(IV) reacts with H_2O_2 forming a hydroxyl radical ·OH, V(V) and anion $^{-}$OH.[38b] The hydroxyl radical ·OH abstracts a hydrogen atom from aldehyde affording an acyl radical A and H_2O.[38] To confirm this hypothesis, the acyl radical was supported by a radical scavenger experiment and was trapped with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (Scheme 5, path a).[39] Subsequently V(V)[40] reacts with H_2O_2 to generate V(IV) and peroxyl radical HOO·.[38] The latter reacts with the acyl radical A to form the peroxy acid B, which is cleaved by SET to give carboxyl radical C and anion $^{-}$OH.[41] This was confirmed carrying out the reaction with the peracid instead of the aldehyde under identical reaction conditions and the **3k** product was obtained (Scheme 5, path b).

Finally, intermediate C reacts with benzyl bromide providing the corresponding ester.

In summary, we have developed the synthesis of esters starting directly from aldehydes under visible light and using $VOSO_4$, an earth-abundant metal (EAM_s) salt, as a sustainable photocatalyst. $VOSO_4$ is readily commercially available, not needed to be prepared and is environmentally sustainable. This works opens perspectives for the extended application of vanadium salts toward halogenation processes as well as for C–H activations and gives a contribution in the field of catalysis with earth-abundant metals.

Experimental Section

In a round bottom flask of 25 mL, aldehyde (0.8 mmol), $VOSO_4$*$5H_2O$ (0.005 g, 5% mol), K_2CO_3 (0.4 mmol) and H_2O_2 (30% sol. aq., 0.8 mmol) were added to a solution of a benzyl bromide (0.4 mmol) in 1 mL CH_3CN under Ar atmosphere and at room temperature. The mixture was stirred under blue led irradiation for 72 hours under Ar (the reaction was monitored by TLC until disappearance of benzyl bromide). 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 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.

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