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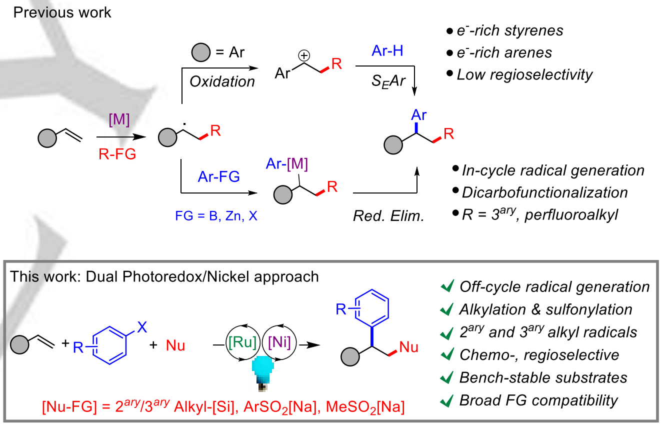
Dual Photoredox/Nickel-Catalyzed Three-Component Carbofunctionalization of Alkenes[5]

Andrés García-Domínguez, Rahul Mondal, Cristina Nevado*[a]

Abstract: The potential of merging photoredox and nickel catalysis to perform multicomponent alkene difunctionalizations under visible light irradiation is demonstrated here. Secondary and tertiary alkyl groups as well as sulfonyl moieties can be added to the terminal position of the double bond with simultaneous arylation of the internal carbon atom in a single step under mild conditions. The process, devoid of stoichiometric additives, benefits from the use of bench-stable and easy-to-handle reagents, is operationally simple and tolerates a wide variety of functional groups.

The intermolecular difunctionalization of alkenes represents a powerful strategy to construct complex aliphatic structures by concomitant formation of C-C and/or C-X bonds across the π-system.[1] The use of radicals in this context has become particularly attractive due to their ability to rapidly add onto unsaturated moieties under mild conditions.[2] Because of their synthetic utility, alkene dicarbofunctionalization reactions, i.e. transformations involving the simultaneous formation of two new C-C bonds have been thoroughly studied in this context.[3-5] Typically, these strategies utilize tertiary or perfluoroalkyl radical precursors that are combined either with electron-rich styrenes and arenes[3] or, alternatively, with activated olefins and functionalized aromatics (arylmetal Ar-M or haloarenes Ar-X) in the presence of a metal catalyst (Scheme 1, top).[4] The need for activated tertiary or perfluoroalkyl derivatives and for electronically biased substrates together with the use of sensitive organometallic reagents under harsh conditions, still limits the synthetic potential of these methods.

Photoredox catalysis has emerged as a powerful tool to enable single electron transfer (SET) reactions under mild conditions.[5] On the other hand, the ability of nickel catalysts to forge C-C and C-X bonds involving Csp^3 partners is also well established.[6] The combination of these two strategies has bared fruit, and thus novel alkyl-alkyl and alkyl-aryl cross coupling reactions have been developed under such paradigm.[7] However, and despite its potential, three-component dicarbofunctionalizations of alkenes exploiting the synergy between photoredox and Ni catalysis are still scarce.[4c, 7l] Given our ongoing interest in the radical difunctionalization of π-systems,[8] we set out to explore a photoredox/nickel dual catalysis towards a flexible three-component difunctionalization of alkenes. We envisioned that an off-cycle radical generation by the excited photocatalyst would enable the addition of several groups (both, carbon- and heteroatom-based) across the olefin under analogous reaction conditions. Herein, we report the first examples of photoredox alkene carbosulfonylations and alkylarylations by combination of aromatic halides with both, secondary and tertiary alkyl silicates and sulfonyl derivatives, respectively (Scheme 1, bottom). These reactions proceed with complete chemo- and regiocontrol employing bench-stable starting materials under mild conditions. In addition to its operational simplicity, this method significantly broadens the scope of existing strategies[3-5] both in terms of the compatible olefins (acrylates, acrylonitriles, vinylboronic esters, allylic acetates) and addition partners (secondary and tertiary alkyl as well as alkyl and arylsulfonyl groups), which highlights the synergistic potential of dual photoredox/Ni catalysis beyond the cross-coupling realm.



Scheme 1. Three-component carbofunctionalizations of alkenes. FG = Functional Group.

First, we focused our efforts on the activation of secondary alkyl silicates (E_{ox}= 0.3 - 0.9 V *vs* SCE in DMF)[9a-c] by the photoexcited ruthenium (II) tris(bypiridine) complex (E_{red}= 0.77 V *vs* SCE in MeCN)[9d] in order to address one of the main limitations in current methods. Alkyl silicates are produced in three steps from the corresponding trichlorosilanes according to previously described procedures.[9] Further, aryl iodides were selected as Csp^2 partners given their facile reaction with nickel catalysts.[10] The reaction of *tert*-butylacrylate with diisopropylammonium cyclohexylbis-(catecholato)silicate and 4-*tert*-butyliodobenzene in the presence of a nickel precatalyst, bipyridine type ligands and Ru(bpy)$_3$Cl$_2$·6H$_2$O under blue light irradiation was investigated first (Table 1).[11] The molar ratio between the reaction partners was found to be crucial for a successful outcome. A slight excess of alkene and alkyl silicate significantly favored the difunctionalization product minimizing the direct alkyl-arene cross-coupling. After initial optimization, the use of NiCl$_2$·6H$_2$O/dtbbpy (10 mol%) in DMF (0.1 M) provided **1** in 68%

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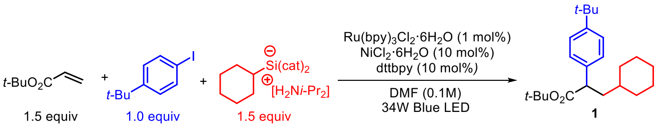
isolated yield (Table 1, entry 1). Other bipyridine ligands led to lower yields (Table 1, entries 2-3), whereas the use of a preformed nickel catalyst did not improve the reaction outcome (Table 1, entry 4). An hexafluorophosphate ruthenium salt gave similar results (Table 1, entry 5) while tris(phenathroline)ruthenium(II) dichloride monohydrate as photocatalyst gave lower yields (Table 1, entry 6). The presence of oxygen was detrimental for the reaction as demonstrated by the results shown in entries 7 and 8. Further, control experiments confirmed the need for nickel, photocatalyst and light irradiation to produce the desired difunctionalized product **1** (entry 9).

Table 1. Optimization of the reaction conditions for the alkene dicarbofunctionalization reaction.

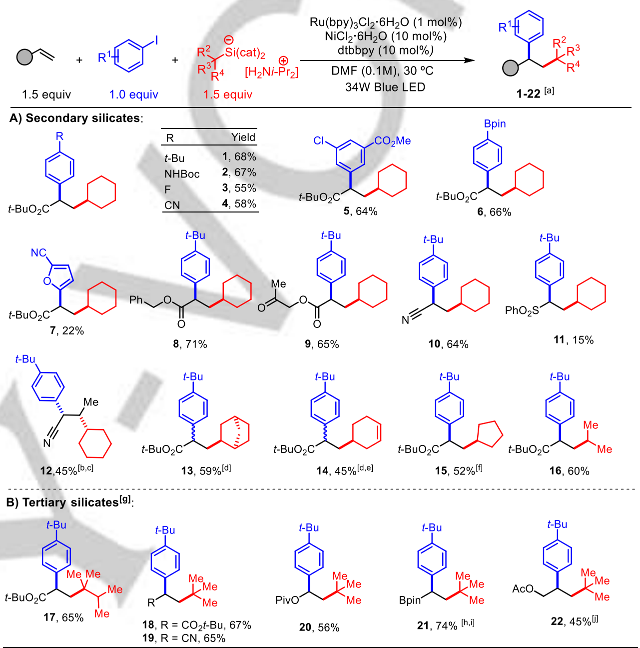


Entry	Deviations from Above	NMR Yield of **1** (%)[a]
1	none	69 (68)
2	diMeObpy (10 mol%)	58
3	bpy (10 mol%)	55
4	Using Ni(dtbbpy)(H_2O)$_4$$Cl_2$ (10 mol%)	64
5	Using Ru(bpy)$_3$(PF_6)$_2$ (1 mol%)	68
6	Using Ru(phen)$_3$$Cl_2$·$H_2O$ (1 mol%)	50
7	Under air	34
8	Not degassed DMF	43
9	No nickel / No photocatalyst / No light	0

[a] NMR yields using 4-nitroacetophenone as internal standard. In brackets: Isolated yield after column chromatography on silica gel. DMF: *N,N*-dimethylformamide; dttbpy: 4,4'-di-tert-butyl-2,2'-bipyridine; diMeObpy: 4,4'-dimethoxy-2,2'-bipyridine; bpy: 2,2'-bipyridine; phen: 1,10-phenantroline.

With the optimized conditions in hand, we set out to explore the scope of this transformation (Scheme 2). Both, electron-rich as well as electron-deficient substituted aryl iodides delivered the desired products **1**-**6** in moderate to good yields. The reaction is orthogonal with respect to classical cross-coupling procedures as the C-Boron bond remained intact in product **6**, which could be isolated in 66% yield. A 5-cyanofurane derivative **7** could only be isolated in 22% yield. However, other acrylates containing benzyl or ketone groups in their structures as well as acrylonitriles and vinylsulfones could be successfully engaged in the reaction (**8**-**11**), highlighting the functional group compatibility of this method. In addition, an internal olefin (*E*:*Z* = 4:1) delivered the highly congested product **12** with exquisite diastereoselectivity (dr > 20:1).

Different alkyl silicates were evaluated next. Cyclic derivatives as well as species containing double bonds in their structures were well tolerated as demonstrated by the efficient isolation of products **13**-**15**. Additionally, the method is not only restricted to the incorporation of cycloalkyl groups but also isopropyl and tertiary linear alkyl silicates could be engaged with similar efficiencies under the standard reaction conditions (**16**-**19**). To our delight, the use of tertiary alkyl silicates completely avoided the formation of Hiyama-type coupling products allowing the dicarbofunctionalization of a wider range of olefins. In this manner, electron rich olefins, vinyl boranes and even unactivated alkenes could be successfully transformed into desired dicarbofunctionalization products **20**-**22**.



[a] Unless otherwise stated, the reactions were run at 0.2 mmol scale and the products isolated after column cromatography on silica gel. [b] dr > 20:1. [c] Using crotonitrile (4.0 equiv, *E*:*Z* = 4:1). Hiyama-type coupling product was produced in 25% yield as judged by NMR. [d] dr = 1:1. [e] Using isopropyl ammonium silicate derivative. [f] Using triethylammonium derivative. [g] Using tetraethylammonium derivative. [h] Isolated as alcohol after oxidation of the crude with $NaBO_3·4H_2O$ (5 equiv) in THF/H_2O (v/v = 1/1, 0.1 M). [i] Yield over two steps. [j] Using allylacetate (5.5 equiv).

Scheme 2. Scope of the dual photoredox/nickel catalyzed dicarbofunctionalization.

Difunctionalizations incorporating simultaneously both, sulfonyl and aryl groups across simple olefins have been mainly explored on intramolecular settings.[12] Thus, encouraged by the above-mentioned results and the feasibility of oxidizing sodium arenesulfinates (E_{ox} = 0.3-0.6 vs SCE in MeCN)[13] by the Ru-photocatalyst,[14] we set out to expand the utility of our protocol in this context. When the previous standard conditions (Table 1, entry 1) were applied to the reaction of *tert*-butylacrylate with 4-*tert*-butyliodobenzene and sodium benzenesulfinate, an encouraging 41% yield of compound **23** was obtained together with 28% of the undesired biarylsulfone **23´** (Table 2, entry 1). Increasing the amount of aryl iodide led to a slight improvement of the yield (48%) on the desired product (Table 2, entry 2). The use of 10 mol% $NiCl_2Py_4$ led to the formation of **23** in 44% yield (Table 2, entry 3). Further improvement was observed when DMF was replaced by DMSO, as **23** and **23´** could be obtained in 53 and 18% yield, respectively (Table 2, entry 4). Finally, the use of a more electron-rich bipyridine ligand (diMeObipy) furnished **23** in 72% yield together with 13% of **23´** (Table 2, entry 5). Reducing the catalyst loading proved to be beneficial so that, under the newly optimized reaction conditions, compound **23** could be isolated in 69% yield and less than 10% of **23´** was detected in

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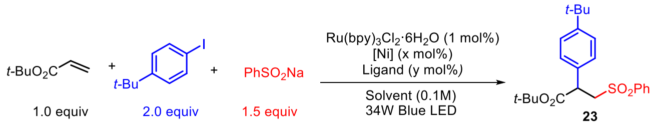
the reaction media (Table 2, entry 6. For additional optimization experiments, see SI).[11]

The reaction scope was investigated next (Scheme 3). Under the optimized conditions, different substitutions and functionalities in the ester moiety were tolerated, furnishing the desired arylsulfonylated products **24**-**39** in good yields. Remarkably the reaction proved not only suitable for the use of aryl iodides, but also for aryl bromides thus expanding the synthetic utility of the method (**30**-**35**).

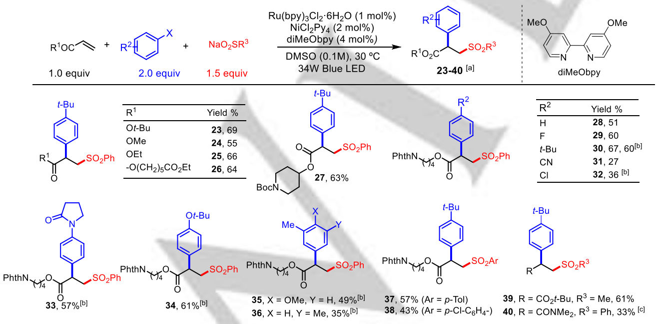
Table 2. Optimization of the reaction conditions for the alkene carbosulfonylation reaction.



Entry	Reaction conditions	NMR yield of **23** (%)[a]
1	As in Scheme 2	41[b]
2	$NiCl_2·6H_2O$ (10 mol%), dtbbpy (10 mol%) in DMF (0.1 M)	48[c]
3	$NiCl_2Py_4$ (10 mol%), dtbbpy (10 mol%) in DMF (0.1 M)	44
4	$NiCl_2Py_4$ (10 mol%), dtbbpy (10 mol%) in DMSO (0.1 M)	53[d]
5	$NiCl_2Py_4$ (10 mol%), diMeObpy (10 mol%) in DMSO (0.1 M)	72[e]
6	$NiCl_2Py_4$ (10 mol%), diMeObpy (4 mol%) in DMSO (0.1 M)	76 (69)[f]

[a] NMR yields using 4-nitroacetophenone as internal standard. In brackets: Isolated yield after column chromatography on silica gel. [b] 28% of diarylsulfone $tBuC_6H_4SO_2Ph$ **23´** was obtained. [c] 20% **23´** [d] 18% of **23´** [e] 13% of **23´** [f] 8% of **23´**

In addition, sulfinates with different electronic features were nicely engaged in the reaction giving products **37**-**39** in moderate to high efficiencies. Vinyl amides could also be incorporated in the reaction scope, as demonstrated by the successful isolation of difunctionalized product **40**.

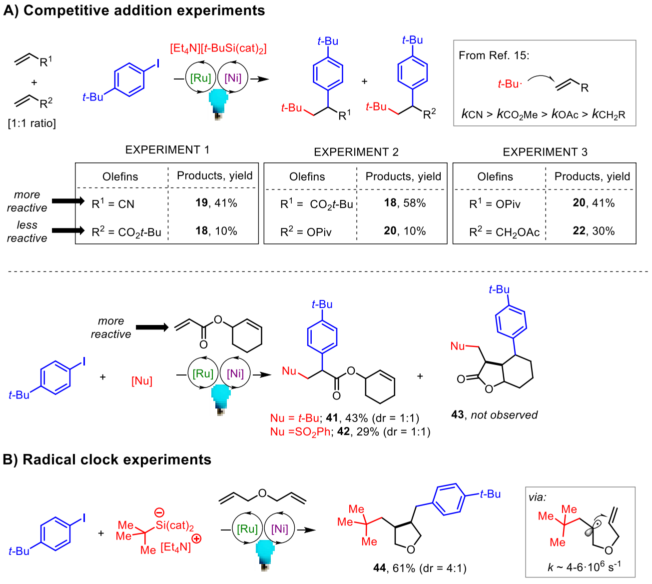


[a] Unless otherwise stated, the reactions were run at 0.2 mmol scale using aryl iodides. The products were isolated by column cromatography on silica gel; [b] Using Ar-Br (2.0 equiv), $NiCl_2Py_4$ (20 mol%) and diMeObpy (40 mol%). [c] [Ni] (20 mol%)

Scheme 3. Scope of the dual photoredox/nickel catalyzed carbosulfonylation.

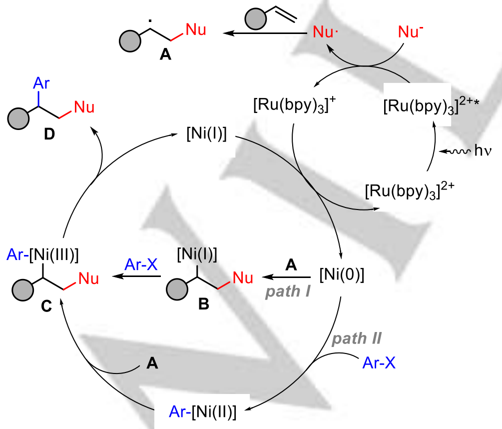
To further showcase the synthetic potential of these transformations, the reactions to produce adducts **2**, **28** and **30** were carried out in 1 mmol scale. Under the standard reaction conditions, these products could be isolated in 58, 65 and 59% yield, respectively.

After the successful development of both transformations, several control experiments were designed to interrogate the reaction pathway. First, the use of radical scavengers such as TEMPO or 1,1-diphenylethylene decreased reaction efficiencies, which suggests a radical based mechanism (for details, see SI).[11] Further, competitive intermolecular experiments were carried out combining two different olefins at an equimolar ratio in the presence of the *tert*-butyl silicate derivative and 4-*tert*-butyl iodobenzene (Scheme 4A, top). A mixture of difunctionalization products from both olefins was obtained, favoring, in all cases, the adducts stemming from the most reactive olefinic acceptor towards the *tert*-butyl radical (**19** vs. **1**; **1** vs. **20**; **20** vs. **22**).[15] Besides, when both olefins were located within the same substrate, the addition of the alkyl or the sulfonyl group took place exclusively onto the more activated one to give 1,2-carbofunctionalization products **41**-**42** (Scheme 4A, bottom). These competition experiments suggest the formation of radicals from the ‘nucleophilic’ reaction partner and its subsequent addition to the olefin on the outset of the reaction. These conclusions were further supported by radical clock experiments using a diallyl ether probe, which revealed the sole formation of the tetrahydrofuran derivative **44** in 61% yield as a 4:1 mixture of diastereoisomers (Scheme 4B). As the rate of the cyclization of similar substrates has been reported (k ~ 4-6·10^6 s^{-1}),[16] these results indicate that the reaction of secondary radicals with the intermediates responsible to deliver the C-Ar bond at last may be a much slower process.[17] Further, the fact that cyclized product **43** is not observed reflects the preference of the secondary C-centered radical in α position to the ester group to recombine with the corresponding ArNi(II) complex. In contrast, upon addition of the *t*Bu radical to the double bond on the diallylether radical clock, the secondary radical undergoes cyclization with the vicinal double bond rather than recombination with the Ni(II) species to give cyclized product **44**. These results showcase the effect that the different stabilization of the secondary C-centered radical intermediates can have on the reaction outcome.



Scheme 4. Control experiments.

Based on these control experiments and existing evidence gathered in the literature,[6,7] the following mechanism is proposed (Scheme 5). The excited photocatalyst oxidizes the nucleophile delivering the corresponding radical which, in an off-cycle process, adds to the terminal carbon of the olefin to give secondary C-centered radical **A**. The reaction of **A** with Ni(0) generates a transient alkyl-Ni(I) complex **B**, that upon oxidative addition with the aromatic halide produces the key Ar-Ni(III)-alkyl intermediate **C** (Scheme 5, path I). Alternatively, the same species can be formed as a result of the oxidative addition of the aromatic halide onto Ni(0) followed by radical recombination with **A** (path II).[15] In both cases, a C-C reductive elimination from **C** delivers the product **D** together with a Ni(I) complex. Both catalytic cycles are closed by oxidation of Ru(I) species by Ni(I), which regenerates both, the Ru(II) photocatalyst and the Ni(0) catalyst, respectively.[19]



Scheme 5. Proposed catalytic pathways towards product formation.

In summary, we showcase here the potential of merging photoredox and nickel catalysis under visible light to perform three-component carbofunctionalizations of alkenes. As the generation of radicals is independ from the nickel complex, the use of an affordable photocatalyst has allowed the utilization of sulfinates and alkylsilicates to generate sulfonyl and both, secondary and tertiary alkyl radicals, respectively, with minor changes in the reaction conditions. In addition, the stability and ease of handling of all precursors confers excellent functional group compatibility and operational simplicity to this approach, while significantly expanding the scope of existing alkene carbofunctionalization methods.

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Keywords: photoredox catalysis • nickel catalysis • carbosulfonylation • dicarbofunctionalization • three-component reaction

[1] For recent reviews, see: a) E. Merino, C. Nevado *Chem. Soc. Rev.* **2014**, *43*, 6598; b) D. A. Petrone, J. Ye, M. Lautens, *Chem. Rev.* **2016**, *116*, 8003; c) R. K. Dhungana, S. KC, P. Basnet, R. Giri, *Chem. Rec.* **2018**, *18*, 1314;d) T. Fujihara, Y. Tsuji, *Synthesis* **2018**, *50*, 1737; e) J.-S. Zhang, L. Liu, T. Chem, L.-B. Han, *Chem. Asian J.* **2018**, *13*, 2277.

[2] For selected publications, see: a) M. Hartmann, Y. Li, A. Studer, *J. Am. Chem. Soc.* **2012**, *134*, 16516; b) B. Ovadia, F. Robert, Y. Landais, *CHIMIA* **2016**, *70*, 34; c) X.-W. Lan, N.-X. Wang, Y. Xing, *Eur. J. Org. Chem.* **2017**, 5821; d) S. N. Gockel, T. L. Buchanan, K. L. Hull, *J. Am. Chem. Soc.* **2018**, *140*, 58; e) Y. Cheng, C. Mück-Lichtenfeld, A. Studer, *J. Am. Chem. Soc.* **2018**, *140*, 6221.

[3] For selected examples, see: a) A. Carboni, G. Dagousset, E. Magnier, G. Masson, *Chem. Commun.* **2014**, *50*, 14197; b) Y. Ma, D. Zhang, Z. Yan, M. Wang, C. Bian, X. Gao, E. E. Bunel, A. Lei, *Org. Lett.* **2015**, *17*, 2174; c) X.-H. Ouyang, R.-J. Song, M. Hu, Y. Yang, J.-H. Li, *Angew. Chem. Int. Ed.* **2016**, *55*, 3187; d) M. Li, J. Yang, X.-H. Ouyang, Y. Yang, M. Hu, R.-J. Song, J.-H. Li, *J. Org. Chem.* **2016**, *81*, 7148; e) Y. Duan, W. Li, P. Xu, M. Zhang, Y. Chenga, C. Zhu, *Org. Chem. Front.* **2016**, *3*, 1443; f) G. Dagousset, C. Simon, E. Anselmi, B. Tuccio, T. Billard, E. Magnier, *Chem. Eur. J.* **2017**, *23*, 4282; g) X. Yong, Y-F. Han, Y. Li, R.-J. Song, J.-H. Li, *Chem. Commun.* **2018**, *54*, 12816; h) J.-S. Lin, T.-T. Li, J.-R. Liu, G.-Y. Jiao, Q.-S. Gu, J.-T. Cheng, Y.-L. Guo, X. Hong, X.-Y. Liu, *J. Am. Chem. Soc.* **2019**, *141*, 1074; i) F. J. R. Klauck, H. Yoon, M. J. James, M. Lautens, F. Glorious, *ACS Catal.* **2019**, *9*, 236.

[4] a) F. Wang, D. Wang, X. Mu, P. Chen, G.Liu, *J. Am. Chem. Soc.* **2014**, *136*, 10202; b) L. Wu, F. Wang, Xi. Wan, D.Wang, P. Chen, G. Liu, *J. Am. Chem. Soc.* **2017**, *139*, 2904; For a dual Cu/Ir photoredox dicarbofunctionalization see, c) X.-L. Lv, C. Wang, Q.-L. Wang, W. Shu, *Org. Lett.* **2019**, *21*, 56; d) J. Terao, F. Bando, N. Kambe, *Chem Commun.* **2009**, 7336; e) T. Qin, J. Cornella, C. Li, L. R. Malins, J. T. Edwards, S. Kawamura, B. D. Maxwell, M. D. Eastgate, P. S. Baran, *Science* **2016**, *352*, 801; f) J.-W. Gu, Q.-Q. Min, L.-C. Yu, X. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 12270; g) A. García-Domínguez, Z. Li, C. Nevado, *J. Am. Chem. Soc.* **2017**, *139*, 6835; h) A. García-Domínguez, C. Nevado, *CHIMIA* **2018**, *4*, 212; i) L. Guo, F. Song, S. Zhu, H. Li, L. Chu, *Nature Commun.* **2018**, *9*, 45.

[5] For selected reviews, see: a) J. M. R. Narayanam, C. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102; b) C. K. Prier, D. A. Rankic, D. W. C. Macmillan, *Chem. Rev.* **2013**, *113*, 5322; c) T. P. Yoon, C. R. J. Stephenson, *Adv. Synth. Catal.* **2014**, *356*, 2739; d) J.-R. Chen, X.-Q. Hu, L.-Q. Lu, W.-J.Xiao, *Chem. Soc. Rev.* **2016**, *45*, 2044.

10.1002/anie.201906692

[6] For reviews, see: a) T. Moragas, A. Correa, R. Martin, R. *Chem. Eur. J.* **2014**, *20*, 8242; b) C. E. I Knappke,.S. Grupe, D. Gärtner, M. Corpet, C. Gosmini, J. von Wangelin, *Chem. Eur. J.* **2014**, *20*, 6828; c) J. Gu, X. Wang, W. Xue, H. Gong, *Org. Chem. Front.* **2015**, *2*, 1411; d) D. J. Weix, *Acc. Chem. Res.* **2015**, *48*, 1767.

[7] For selected reviews, see: a) J. Twilton, C. C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan, *Nature Rev. Chem.* **2017**, *1*, 0052; b) J. K. Matsui, S. B. Lang, D. R. Heitz, G. A. Molander, *ACS Catal.* **2017**, *7*, 2563; c) Y.-Y. Gui, L. Sun, Z.-P. Lu, D.-G. Yu, *Org. Chem. Front.* **2016**, *3*, 522. d) J. C. Tellis, C. B. Kelly, D. N. Primer, M. Jouffroy, N. R. Pattel, G. A. Molander, *Acc. Chem. Res.* **2016**, *49*, 1429; e) J. A. Milligan, J. P. Phelan, S. O. Badir, G.A. Molander, *Angew. Chem. Int. Ed.* **2019**, *DOI: 10.1002/anie.201809431.*For selected examples, see: f) Z. Zuo, D. T. Ahneman, L. Chu, J. A. Terrett, A. G. Doyle, D. W. C. MacMillan, *Science* **2014**, *345*, 437; g) J. Twilton, M. Christensen, D. A. DiRocco, R. T. Ruck, I. W. Davies, D. W. C. MacMillan, *Angew. Chem. Int. Ed.* **2018**, *57*, 5369; h) R. Alam, G. A. Molander, *J. Org. Chem*. **2017**, *82*, 13728; i) B. A. Vara, N. R. Patel, G. A. Molander, *ACS Catal*. **2017**, *7*, 3955; j) Z. Zuo, H. Cong, W. Li, J. Choi, G. C. Fu, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2016**, *138*, 1832; k) Z. Duan, W. Li, A. Lei, *Org. Lett.* **2016**, *18*, 4012; For an indoline synthesis under Nickel/Photoredox Dual Catalysis: l) S. Z. Tasker, T. F. Jamison, *J. Am. Chem. Soc.* **2015**, *137*, 9531.

[8] a) N. Fuentes, W. Kong, L. Fernández-Sánchez, E. Merino, C. Nevado, *J. Am. Chem. Soc.* **2015**, 137, 964; b) Z. Li, A. García-Domínguez, C. Nevado, *J. Am. Chem. Soc.* **2015**, *137*, 11610; c) Z. Li, A. García-Domínguez, C. Nevado, *Angew. Chem Int. Ed.* **2016**, *55*, 6938; d) W. Shu, A. Lorente, E. Gómez-Bengoa, C. Nevado, *Nature Commun.* **2017**, *8*, 13832; e) A. García-Domínguez, S. Müller, C. Nevado*, Angew. Chem. Int. Ed.* **2017**, *56*, 9949; f) W. Shu, E. Merino, C. Nevado*, ACS Catal.* **2018**, 8 6401.

[9] a) V. Corcé, L.-M. Chamoreau, E. Derat, J.-P. Goddard, C. Ollivier, L. Fensterbank, *Angew. Chem. Int. Ed.* **2015**, *54*, 11414; b) Y. Nishigaichi, A. Suzuki, A. Takuwa, *Tetrahedron Lett.* **2007**, *48*, 211; c) D. Matsuoka, Y. Nishigaichi, *Chem. Lett.* **2014**, *43*, 559. For redox potential of common photocatalysts, see: d) C. K. Prier, D. A. Rankic, D. W. C. Macmillan, *Chem. Rev.* **2013**, *113*, 5322.

[10] For selected examples on alkyl-aryl cross-couplings using dual ruthenium/nickel catalysis, see: a) M. Jouffroy, D. N. Primer, G. A. Molander, *J. Am. Chem. Soc.* **2016**, *138*, 475; b) N. R. Patel, G. A. Molander, *J. Org. Chem.* **2016**, *81*, 7271; c) K. Lin, R. J Wiles, C. B. Kelly, G. H. M. Davies, G. A. Molander, *ACS Catal.* **2017**, *7*, 5129; d) B. A. Vara, M. Jouffroy, G. A. Molander, *Chem. Sci*. **2017**, 8, 530.

[11] See Supporting Information for further details.

[12] For selected examples, see: a) X. Li, X. Xu, P. Hu, X. Xiao, C. Zhou, *J. Org. Chem.* **2013**, *78*, 7343; b) D. Xia, T. Miao, P. Li, L. Wang, *Chem. Asian. J.* **2015**, *10*, 1919; c) H. Wang, S. Sun, J. Cheng, *Org. Lett*. **2017**, 19, 5844; d) X.-Q. Chu, H. Meng, X.-P. Xu, S.-J. Ji, Shun-Jun, Chem. Eur. J. 2015, 21, 11359; e) S.-F. Wang, C.-P. Chuang, J.-H. Lee, S.-T. Liu, *Tetrahedron* **1999**, *55*, 2273. For three-component vicinal carbosulfonylations involving C-Ar bond formation on allenes: f) N. Vicart, B. Gazes, J. Gore, *Tetrahedron* **1996**, *52*, 9101; g) Y. Hou, Q. Shen, Z. Li, S. Chen, Y. Zhao, M. Qin, P. Gon *Adv. Synth. Catal.* **2018**, *360*, 631.

[13] a) A. U. Meyer, K. Straková, T. Slanina, B. König, *Chem. Eur. J.* **2016**, *22*, 8694. For a review on the use of sulfinates in organic synthesis, see: b) J. Aziz, S. Messaoudi, M. Alami, A. Hamze, *Org. Biomol. Chem.* **2014**, *12*, 9743 and references therein.

[14] For recent examples of coupling reactions using haloarenes with sulfinates under photoredox catalysis, see: a) M. J. Cabrera-Alfonso, Z.-P. Lu, C. B. Kelly, S. B. Lang, R. Dykstra, O. Gutierrez, G. A. Molander, *Chem. Sci.* **2018**, *9*, 3186; b) N.-W. Liu, K. Hofman, A. Herbert, G. Manolikakes, *Org. Lett.* **2018**, *20*, 760; c) H. Yue, C. Zhu, A. Rueping, *Angew. Chem. Int. Ed.* **2018**, *57*, 1371; d) T. Knauber, R. Chandrasekaran, J. W. Tucker, J. M. Chen, M. Reese, D. A. Rankic, N. Sach, C. Helal, *Org. Lett.* **2017**, *19*, 6566.

[15] H. Fischer, L. Radom, *Angew. Chem. Int. Ed.* **2001**, *40*, 1340.

[16] M. Newcomb, *Tetrahedron* **1993**, *49*, 1151.

[17] A previous study on Csp^3-Csp^3 Negishi cross-coupling suggests that the key C-C bond formation process may happen at a higher rate: V. B. Phapale, E. Buñuel, M. García-Iglesias, D. J. Cárdenas, *Angew. Chem. Int. Ed.* **2007**, *46*, 8790.

[18] For studies showing the favourable addition of benzyl radicals to Ni(0), see: O. Gutierrez, J. C. Tellis, D. N. Primer, G. A. Molander, M. C. Kozlowski, *J. Am. Chem. Soc.* **2015**, *137*, 4896.

[19] Based on photophysical characterization experiments, an alternative mechanism involving a photoredox induced radical-chain mechanism in which, after an initiation cycle by the Ru-catalyst, Ni species serve as oxidant for the formation of the Nu-type radicals cannot be ruled out. See ref. 11.

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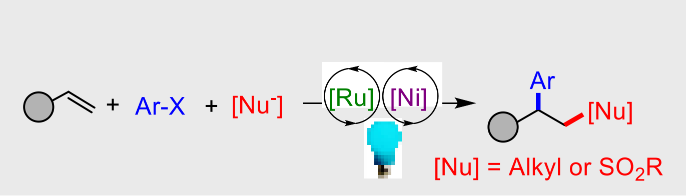
COMMUNICATION



Herein, we demonstrate the use of a dual Ru/Ni catalytic system in a three-component carbofunctionalization of alkenes under visible light irradiation. The method allows the simultaneous and regiocontrolled addition of aromatic groups together with sulfonyl or alkyl groups across the π-system with readily available, bench-top stable sulfinates and alkylsilicates partners.

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