Photoredox/Nickel Dual Catalysis for C(sp2)-C(sp3) Cross Electrophile Coupling Reaction Using Phenols and Alcohols as the Latent Electrophile Sources

Sayan K. Jana, Rayan Bhattacharya‡, Purusattam Dey‡, Sunit Chakraborty and Biplab Maji *
Department of Chemical Sciences, Indian Institute of Science Education and Research
Kolkata, Mohanpur 741246 (India)

* Email: bm@iiserkol.ac.in

Abstract

Introducing alkyl groups, particularly through innovative C(sp2)-C(sp3) bond-forming methods utilizing abundant feedstocks, holds promise for expanding chemical diversity, especially in drug discovery programs. Herein, we employed biomass-derived abundant phenols and alkyl alcohols as the coupling partners for the C(sp2)-C(sp3) cross-electrophile coupling reactions. Our innovation involved activating both the coupling partner via the same activator and designing a catalytic system that activates stronger bonds while ensuring coss-selectivity. The visible-light photoredox/nickel dual catalytic systems accommodate large substrate scope tolerating diverse functional groups. Besides, both the activation and cross-coupling reaction could be performed in one pot, and the reaction could be scaled up. Preliminary mechanistic studies involving luminescence quenching, cyclic voltammetry, radical quenching, and radical clock studies elucidated the proposed reaction mechanism.

Introduction

The C(sp2)-C(sp3) bonds are privileged in pharmaceuticals, natural products, and other biological products.[1, 2] Innovative methods for incorporating an alkyl group, particularly using abundant feedstock, would provide opportunities to expand chemical space, principally for drug discovery programs.[3-5] Traditionally, C(sp2)-C(sp3) fragments are built via transition metal-catalyzed cross-coupling reaction employing an organometallic nucleophile and an aryl or alkyl halide electrophiles.[6-8] Recently, reductive cross-coupling of two radially available electrophiles that avoid the concern associated with the delicate organometallic reagents have been popularized.[9, 10] However, the cross-selectivity remains one of the significant challenges in these reactions, especially when the electrophiles are similar.[11-13]

https://doi.org/10.26434/chemrxiv-2024-mlh9c **ORCID:** https://orcid.org/0000-0001-5034-423X

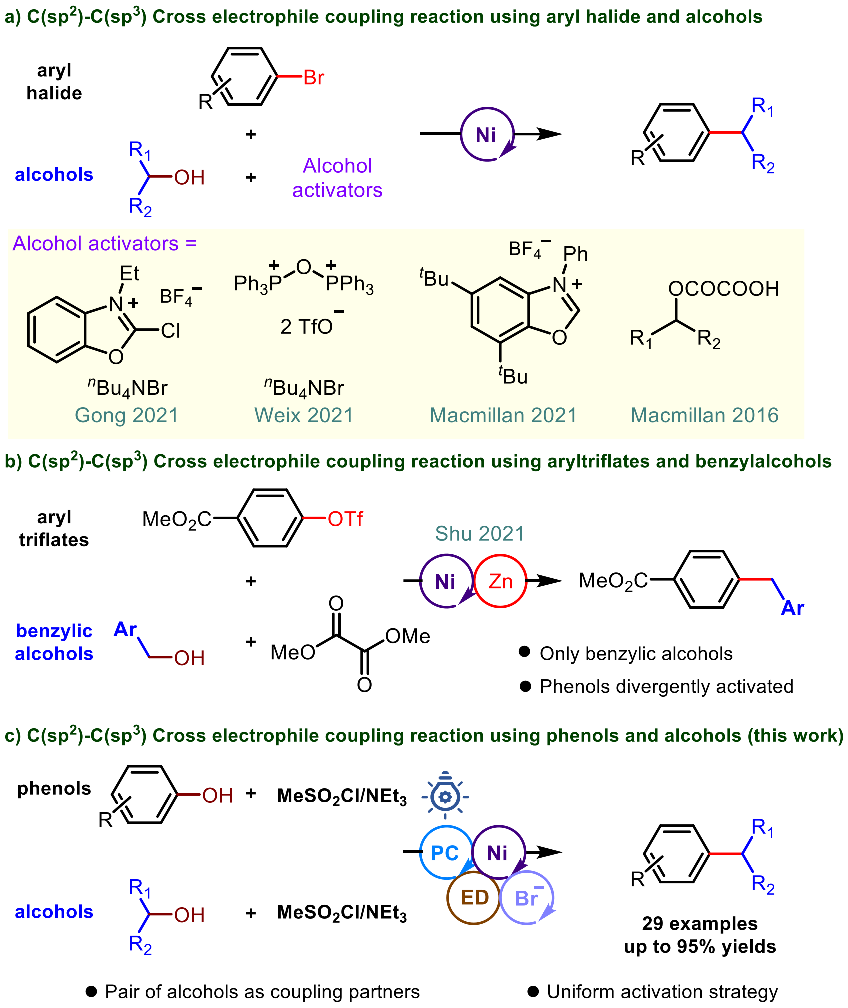
Primarily, aryl halides are reacted with different alkyl precursors to make the C(sp2)-C(sp3) bond.[7, 8] [14-20]Aryl and alkyl alcohols are well-established ‘native’ functional groups and are abundant chemicals from diverse sources compared to the traditional coupling partners.[21, 22] Using alcohols as carbon components in C(sp2)-C(sp3) bond-forming reactions is advantageous regarding economics and sustainability.[22, 23] However, the use of these feedstocks in these reactions is minimal compared to the number of strategies available with organohalides, mainly due to the challenges associated with activating strong C–O bonds. In this context, using aryl halide as C(sp2)-electrophile, diverse cross-coupling strategies were developed using alkanols as the C(sp3)-partner in the presence of stoichiometric alcohol activators (Scheme 1a).[24, 25] However, it is scarce to employ phenol derivatives as the C(sp2)-source in the C(sp2)-C(sp3) cross-coupling reaction,[26-28] and a pool of phenol derivates, mainly from lignin biomass,[13, 24] has been left out. Noticeably, the use of both aryl and alkyl alcohols as two coupling partners in C(sp2)-C(sp3) bond-forming reactions is rare.

Our literature survey shows that only one report described the utilization of alcohols as both coupling partners for the reductive C(sp2)-C(sp3) coupling reaction (Figure 1b).[27] Dimethyl oxalate was employed to activate benzyl alcohols in situ for coupling with preformed aryl triflates at slightly elevated temperatures. While the activation of two coupling agents by two distinct activators enabled high cross-selectivity, it constrained its valuation for its sustainability. Besides, the method is only applicable to activated benzylic alcohols.

Results and discussion

Herein, we attempted a challenge to activate phenols and non-activated alkanols by the same activating group and engage it in a reductive C(sp2)-C(sp3) coupling reaction (Scheme 1c). We envision that both the alcohols could be activated by mesitylation, making them low-reactive starting materials.[29] However, a suitable reaction condition and metal/ligand combination are necessary to selectively react with aryl mesylate over alkyl mesylate for the fruitful conversion to cross-coupled product over the unproductive homodimerizations.8 We recently studied the reactivity of alkyl mesylate for cyclopropanation reactions, where a bromide salt additive enables a steady concentration of alkyl bromide for generating alkyl radicals.[30] Herein, we found that an engineered visible-light photoredox/nickel dual catalyst system can overcome the abovementioned challenges, enabling selective cross-coupling of a diverse pool of

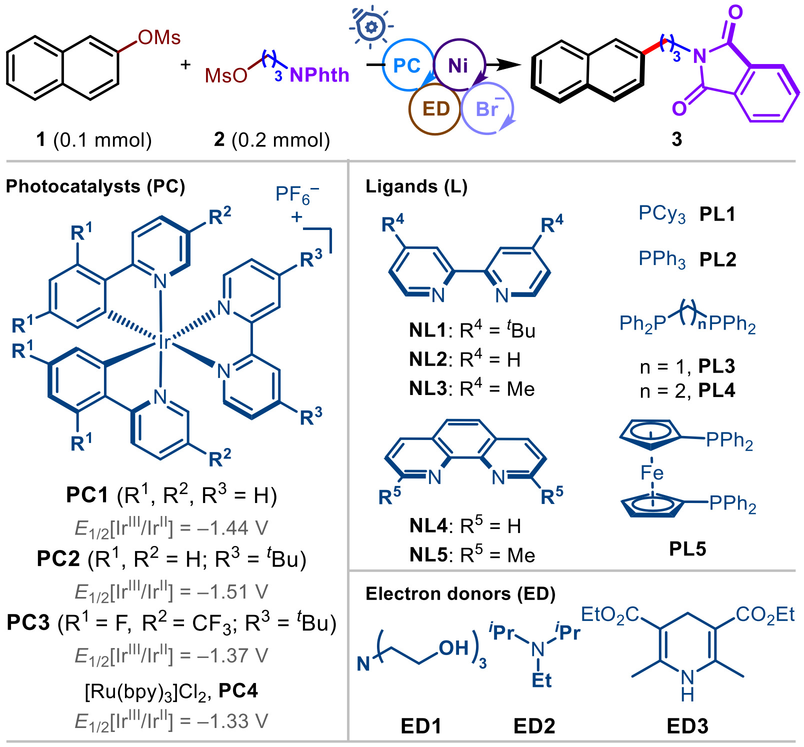
Scheme 1. Introduction



feedstock alcohols at room temperature. Identifying a dual ligand system and bromide additive was crucial for the catalysis. The low reactivity of mesylates was leveraged by introducing it early in the synthetic scheme and utilized for iterative and programmable cross-coupling sequences to enhance the chemical space and three-dimensionality.

We began investigating the reductive cross-electrophile coupling of mesylates **1** and **2** as the model substrates (Tables 1, S1-S7). After systematically screening various reaction parameters, we found NiCl2·glyme (10 mol%) in combination with dual ligands **NL1** (10 mol%) and **PL1** (10 mol%) catalyzed the reaction in DMAc solvent (0.4 M) in the presence of nBu4NBr and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1 equiv.) as additives and PC1 (1 mol%) with **ED1** (2 equiv.) as the terminal reductant at 427 nm blue light emitting diode (LED) irradiation at 30 °C for 24h gave the best result, affording **3** in 89% yield (Table 1, entry 1). Investigation of the reaction with individual ligands produced lower yields of **3** (entries 2,3). We also kinetically monitored these

Table 1. Reaction Development: Key Optimizations.[a]

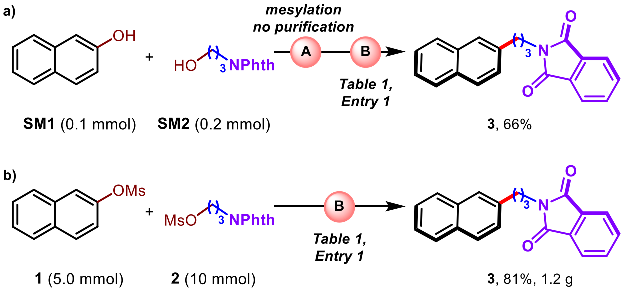


entry	Deviations from conditions [a]	% yield of **3**
1	none	89 (85)
2	without **PL1**	62
3	without **NL1**	11
4	**NL2**-**NL5** instead of **NL1**	up to 31
5	**PL2**-**PL5** instead of **PL1**	up to 19
6	no $NiCl_2$.glyme/**L**	0
7	no **PC1**	0
8	no **ED1**	0
9	no light at 60-80 °C	0
10	no $^nBu_4NBr$	trace
11	$^nBu_4NI$ instead of $^nBu_4NBr$	13
12	no DBU	53
13	tetramethylguanidine, tetramethylethylenediamine, 2,6-lutidine instead of DBU	up to 71
14	**PC2**-**PC4** instead of **PC1**	up to 66
15	**ED2**-**ED3** instead of **ED1**	up to 19
16	Zn, Mn, and In (3 equiv.) at 60 °C instead of **PC1**/**ED1**/light	<5%

[a] Reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol), **PC1** (1 mol%), $NiCl_2$·glyme (10 mol%), **NL1** (10 mol%), **PL1** (10 mol%), **ED1** (0.2 mmol), $^nBu_4NBr$ (0.1 mmol), DBU (0.1 mmol), DMAc (0.4 M) under 427 nm blue LED irradiation at 30 °C. Yields determined by GC-FID analysis using mesitylene as an internal standard. Isolated yield in the parenthesis.

reactions by analyzing the aliquots over time integrals (see S11-13 for details). The **NL1**-ligated Ni completely consumed the aryl mesylate **1** and produced 62% of **3**, along with the reduced product naphthalene **4** as the major side product in 34% yield within 24 h (entry 2). Conversely, **PL1**-ligated nickel-catalyst reacted sluggishly (80% conversion of 1) and gave only 11% of **3** after 24 h (entry 3). The majority of consumed **1** is converted to naphthalene **4** (57%). These results confirmed the complementary reactivity of the dual ligands in enhancing the catalytic activity and improving product selectivity. Notably, other bipyridine and phenanthroline ligands **NL2-NL5**, combined with **PL1** (entry 4) or without **PL1** (Table S1), gave a meager yield of **3**. Similar observations were made with phosphines **PL2-5** (entry 5, Table S2). These again suggest the enhanced reactivity of mixed-ligand system **NL1** and **PL1** in selectively producing cross-coupled product **3**. Control experiments prove that each component of the reaction conditions is compulsory for obtaining a high yield of **3** (entries 6-10). No reaction occurred without light, even when heated at 60-80 °C (entry 9). Bromide additive was crucial for the success of the reaction (entry 10). During kinetic monitoring, we observed the conversion of alkyl mesylate **2** to bromide, which remained in steady concentration during the reaction. However, using $^{n}Bu_4NI$ as an additive reduced the reaction yield, producing higher amounts of demesitylation products **4** and **5** (entry 11). While previously iodides were used to enhance the reactivity of alkyl electrophiles, our findings suggest that using bromide is more practical. The presence of DBU is beneficial for the high reaction yield (entry 12). However, the use of other bases is detrimental (entry 13). A few other photocatalysts PC2-PC4, capable of reducing Ni(II)-centers, could also be used, albeit at a lower efficiency (entry 14). However, the reaction was susceptible to the electron donor. A meager yield was observed by changing other electron donors (entry 15). Noticeably, a poor <5% yield of **3** was obtained when the reaction was performed thermally at 60 °C in the presence of Zn, Mn, and In (3 equiv.) as the terminal reductant (entry 16). It thus highlighted the delicate role of the visible-light photoredox cycle in generating the reducing equivalents in a controlled manner for controlling the reactivity and selectivity of the catalyst.

Scheme 2. Synthetic utility. a) Telescope reaction, b) Gram-scale reaction.

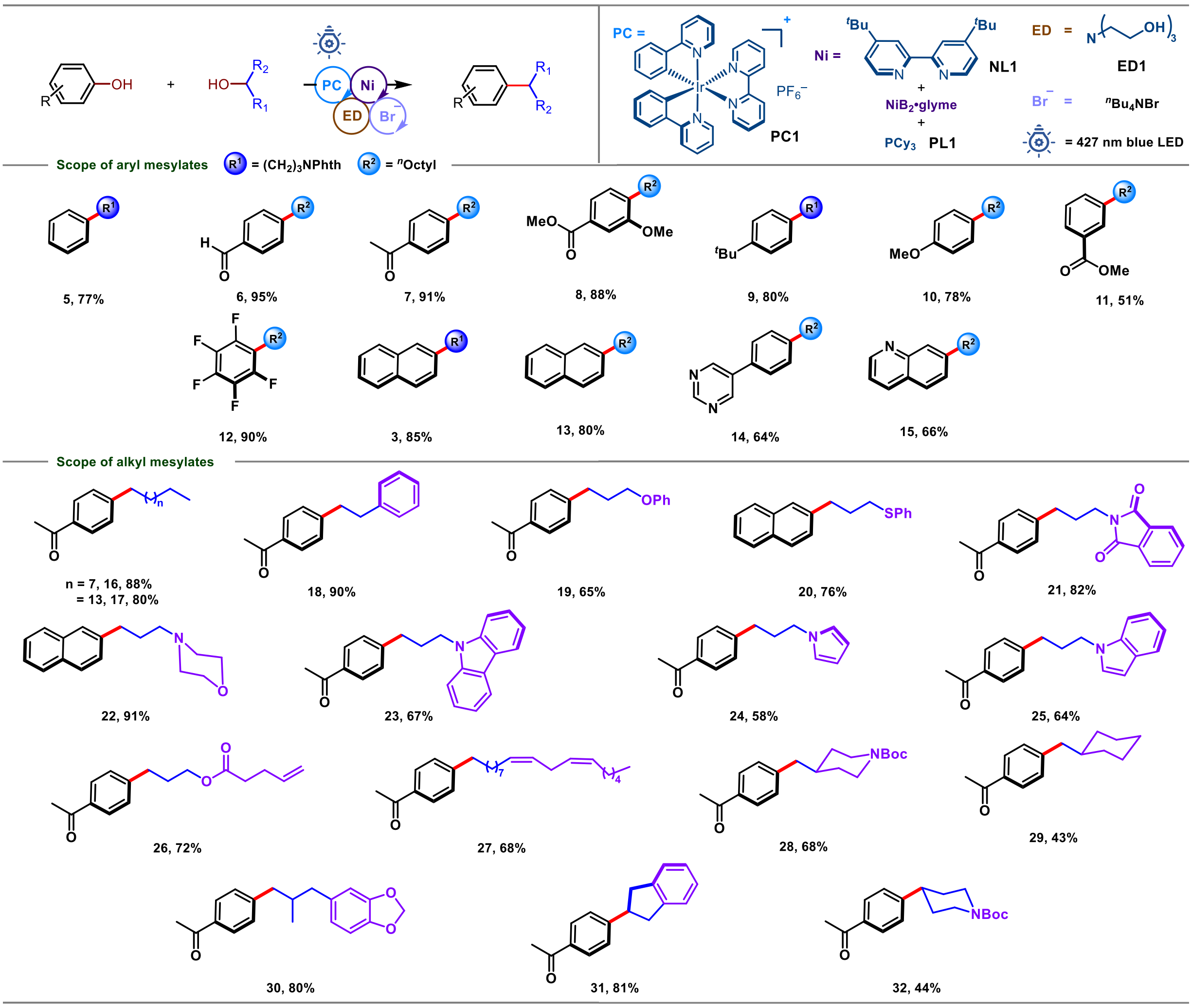


Since the starting material of this reaction is readily available and has a large and abundant feedstock, a telescoped protocol is investigated (Scheme 2a). Commercially available β-naphthol **SM1** and 3-phthalimide propanol **SM2** were taken as a mixture, and in situ mesitylation was done. The crude mixture, after workup without purification, was subjected to the photocatalytic reaction conditions in Table 1, entry 1. The desired product **3** was isolated in 66% yield. A gram scale reaction was carried out for further synthetic applicability of this protocol. We got an excellent outcome, furnishing **3** in 81% yield (1.2 g), providing a proof of concept for this process to be used on a larger scale.

Using optimized reaction conditions in our hand (Table 1, entry 1), we explored the generality of the reductive cross-coupling of two similar electrophiles. As shown in Table 2, we first varied different aryl mesylates derived from their corresponding phenol derivatives. Initially, we attempted to accommodate different lignin-derived phenol derivatives as C(sp2)-electrophiles. The mesylates derived from phenol (**5**), 4-hydroxy benzaldehyde (**6**), 4-hydroxy acetophenone (**7**), and apocynin (**8**) smoothly took part in the light-mediated C(sp2)-C(sp3) coupling reactions, yielding the corresponding products 5-8 in high 77-95% yields. Similar high yields of the products (**9-11**) were also obtained for aryl mesylates containing diverse electrically biased functional groups at different positions of the aryl ring. The pentafluoroaryne (**12**) also participated in the reaction with high efficiency. We then performed this cross-coupling strategy with naphthalene (**3, 13**) and different heteroaryl mesylates (**14, 15**). Notably, heteroarenes, including pyrimidine and quinoline were well tolerated in these reaction conditions and provided 64-66% yields of the desired cross-coupled product (**14, 15**).

We then started exploring the scope of the alkyl coupling partner. First, we checked aliphatic alcohols with different alkyl chain lengths. Mesylates of biomass-derived decanol and cetyl alcohol are well tolerated in our reaction condition, furnishing excellent 88% and 80% yields of the desired cross-coupled products **16**, and **17**, respectively. To illustrate the functional group compatibility, we prepared alkyl mesylates decorated with diverse functional groups and subjected them under photoredox/nickel dual catalysis. Pleasingly, the mild reaction conditions accommodated a sizeable functional group. A high 65-90% yields of the cross-coupled products were obtained for alkyl electrophiles containing aryl (**18**), ether (**19**), thioether (**20**), and protected amine (**21**) groups. We then took the alkanols with various heterocycles. The cross-coupled products having morpholine (**22**), carbazole (**23**), pyrrole (**24**), and indole (**25**) were isolated in high 58-91% yields. Alkyl electrophiles containing terminal (**26**) and internal (**27**) olefinic functionality were also retained under these conditions, delivering 72% and 68% yields of the desired products, respectively. β-Branching does not influence the reaction significantly, and the products containing piperidine (**28**), cyclohexyl (**29**), and helional (**30**) fragments were isolated in good yields. Notably, secondary alkyl electrophiles were also accommodated under these conditions. Mesylates derived from indanol (**31**) and N-Boc-piperidinol (**32**) provided 81% and 44% yield of desired cross-products, respectively.

Table 2. Scope of the Reaction.a

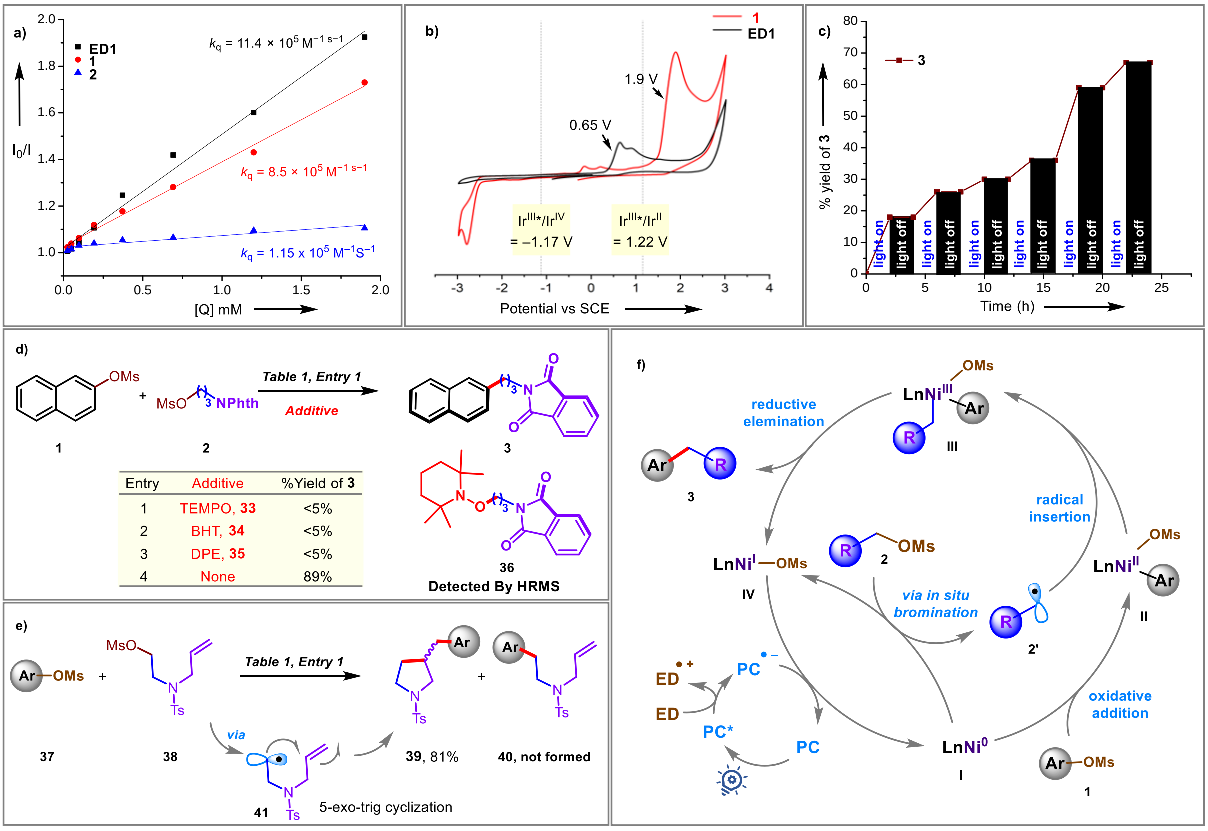


a Reaction conditions: Table 1, entry 1. Isolated yield.

Preliminary mechanistic experiments were conducted further to investigate the reaction mechanism (Figure 1). A Stern-Volmer quenching experiment was performed to gain insight into the photoredox catalytic cycle (Figure 1a). The luminescence quenching of **PC1** at a high rate ($k_q = 11.4 \times 10^5$ M^{-1} s^{-1}) by **ED1** has validated the role of **ED1** as a terminal reductant during catalysis. We have also found a luminescence quenching in the presence of **1** (k_q = 8.5 × 10^5 M^{-1} s^{-1}). To gain more insight a cyclic voltammetry experiment was performed and we have found that an electron transfer to the excited **PC1** ($E_{1/2}[Ir^{III*}/Ir^{II}]$ =+1.22 V vs saturated calomel electrode, SCE) from **1** (reduction potentials = +0.65 V vs SCE) is not thermodynamically feasible (Figure 1b). Previously, we and others observed triplet energy transfer EnT from the excited **PC1** to naphthalenes.[31, 32] The luminescence quenching by **1** could thus be attributed to off-cycle EnT. A light-on-off experiment was performed, and it highlighted the need for continuous irradiation in the reaction and revealed that the reactive intermediates are not accumulated under the given reaction conditions (Figure 1c). Moreover, the system's stability under darkness reflects its potential for practical use.

When photoredox reaction was conducted in the presence of various radical quenchers like 2,2,6,6-tetramethyl piperidinyl oxy (TEMPO, **33**), 2,6-di-tert-butyl-4-methylphenol (BHT, **34**), and 1,1-diphenyl styrene (DPE, **35**), the formation of **3** is shut down (Figure 1d). It indicated the existence of free radicals in the catalytic cycle. Notably, a TEMPO adduct of **2** with the following composition $C_{20}H_{29}N_2O_3$ ([M+H]+ = 345.2174) and plausible structure **36** is detected by high-resolution mass spectrometry (HRMS) analysis. It confirms the presence of alkyl radicals in the reaction mixture. Additionally, when a radical clock reaction was performed with an olefin-tethered alkyl mesylate 38, the desired cross-coupled product **40** was not formed (Figure 1e). Instead, a pyrrolidine product **39**, produced via an intramolecular radical 5-exo-trig cyclization reaction (plausibly via **41**), was isolated in a high 81% yield. This experiment confirms the intermediacy of alkyl radicals in the reaction medium and highlights the synthetic utility of the method in producing complex molecules.

We have drawn a plausible reaction mechanism based on the preliminary mechanistic studies and previous reports (Figure 1f). We have hypothesized that the photoredox catalyst **PC1** will be excited upon irradiation with visible light. The organic electron donor, **ED1**, ($E_{1/2}$ = 0.65 V vs SCE) can reductively quench the excited state of the photoredox catalyst PC*($E_{1/2}[Ir^{III}/Ir^{II}]$ = +1.22 V vs SCE).[33, 34] The resulting $\mathbf{PC^{\bullet -}}$ ($E_{1/2}[Ir^{III,*}/Ir^{II}]$ = –1.44 V vs SCE) could reduce the Ni(II)-complex to its low valent Ni(0) state ($E_{1/2}$ $[Ni^{II}/Ni^{0}]$ = –1.2 V vs SCE). At this stage, alkyl bromide forming from **2** via in situ bromination can undergo a single electron transfer with Ni(0) to form a free alkyl radical **2'**. At the same time, aryl mesylate **1** can undergo an oxidative addition with Ni(0) species. The resulting aryl-Ni(II) species **II** could be intercepted instantly by the alkyl radical **2’** generated in the previous cycle to form Ni(III) species. The reductive elimination yields the C(sp2)-C(sp3) cross-coupled product **3** and Ni(I) species **IV**. Then, two catalytic cycles merge again and close the catalytic cycle.



Entry	Additive	%Yield of **3**
1	TEMPO, **33**	<5%
2	BHT, **34**	<5%
3	DPE, **35**	<5%
4	None	89%

Figure 1. Mechanistic Studies and Proposed Mechanism. (a) Stern-Volmer Luminescence Quenching Experiment. (b) Cyclic Voltammetry studies. (c)Light On-off Experiment. (d) Radical Trapping Experiment (e) Radical Clock Experiment (f) Proposed mechanism.

Conclusion

In summary, we have successfully executed a cross-electrophile coupling using a visible-light photoredox/Ni dual catalysis system, employing aryl and alkyl mesylates as coupling partners. Notably, our approach utilizes a plentiful and large-scale alcohol feedstock for both reactants. The versatility of the reaction is evident, accommodating various unactivated primary alcohols with diverse heterocycles, electron-rich and poor arenas, and heteroarenes. The process is efficiently conducted in a single pot, thanks to the effectiveness of alcohol activation. Additionally, it provides a complementary and gentle approach to synthesizing desirable products, facilitating easy scalability. To the best of our knowledge, this work represents the first demonstration of a photo-redox metal dual-catalyzed cross-electrophile coupling with abundant alcohol coupling partners. We anticipate that our findings will open avenues for further exploration in the promising realm of alcohol activation.

Author information

Corresponding Author

Biplab Maji – Department of Chemical Sciences, Indian Institute of Science and Research Kolkata, Mohanpur – 741246, West Bengal, India; Email: bm@iiserkol.ac.in

Author

Sayan Kr. Jana - Department of Chemical Sciences, Indian Institute of Science and Research Kolkata, Mohanpur – 741246, West Bengal, India

Rayan Bhattacharya - Department of Chemical Sciences, Indian Institute of Science and Research Kolkata, Mohanpur – 741246, West Bengal, India

Purusattam Dey - Department of Chemical Sciences, Indian Institute of Science and Research Kolkata, Mohanpur – 741246, West Bengal, India

Sunit Chakraborty - Department of Chemical Sciences, Indian Institute of Science and Research Kolkata, Mohanpur – 741246, West Bengal, India

Author Contributions

All authors have given approval to the final version of the paper. [#]These authors contributed equally to this work.

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Notes

The authors declare no competing financial interest.

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