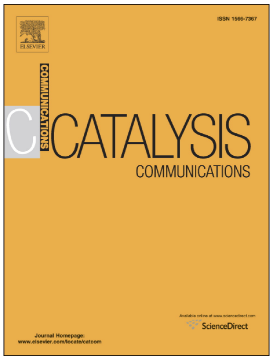

One-pot Negishi cross-coupling reaction of aryldiazonium salts via Ni catalysis induced by visible-light

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One-pot Negishi Cross-Coupling Reaction of Aryldiazonium Salts via Ni Catalysis Induced by Visible-Light

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Abstract

Visible-light induced catalysis is of high interest for its mild and environmentally benign properties. Herein, a general Ni catalysis accelerated by visible-light was successfully developed for one-pot Negishi coupling reactions at room temperature in a short reaction time (< 2 hours), using diazonium salts with Ar_2Zn generated *in situ* from Grignard reagents and $ZnBr_2$. This protocol provides a convenient access to C-C bond formation for important biaryl components. It tolerates various functional groups, and Hammett study illuminates the possiblility of Ni(III)/Ni(I) redox catalytic cycle.

Keywords

Negishi coupling, Visible-light induced Ni-catalysis, Aryldiazonium Salts, Room temperature

1. Introduction

The biaryl components are ubiquitous in the structure of natural products, pharmaceutical agents and functional materials.[1-2] Tremendous efforts have been extended to construct biaryls. Over the past decade, the aryl-aryl bond formation catalyzed by transition-metal has been particularly studied, and there has been numerous elegant methodologies developed in this research area.[3-4] However, despite these progress, the oxidation of metal catalyst from low valence to high valence in its catalytic process still remains a big challenge under mild conditions.[5-7] Photocatalysis has emerged as a powerful tool to accelerate transition-metal catalysis.[8] Notably, in 2011, Sanford group reported visible-light photocatalysis successfully accelerated the rate of Pd-catalyzed C-H arylation using aryldiazonium salt as arylation reagent.[9] In 2015, Kobayashi group proved that visible-light irradiation conspicuously decreased the Cu-catalyzed C-N coupling reaction temperature.[10] Visible-light as a green energy attracted our attention to facilitate oxidation of tough transition-metal in its redox-catalytic cycle.[11]

Ni catalysis induced by visible-light has been well explored for $C(sp^3)$-$C(sp^2)$ bond formation at room temperature.[12-17] However, Ni-catalyzed $C(sp^2)$-$C(sp^2)$ bond formation at room temperature was rarely reported to date.[18-20] Negishi coupling as a C-C bond formation reaction has won its Noble prize. Although Pd-catalyzed Negishi reaction under mild conditions has been widely reported to construct biaryls,[21] nickel catalyst has usually been employed in Negishi reaction only with well-designed ligand

and at high temperature (>60 ^oC).[22-25] Inspired by Sanford's work, we questioned if visible-light photocatalysis could be used to convert low valence to high valence of nickel in its catalytic cycle at room temperature.

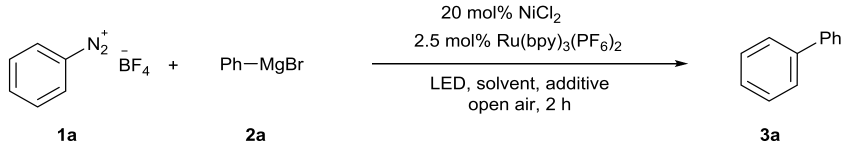
2. General procedure for the Ru/Ni catalyzed reaction

$Ru(bpy)_3(PF_6)_2$ (5.37 mg, 0.00625 mmol, 0.025 equiv), and $NiCl_2$ (6.48 mg, 0.05 mmol, 0.20 equiv) were added into a 20 mL Fisherbrand Glass Threaded vial with a stir bar, and then PhN_2BF_4 (**1a**, 48.0 mg, 0.25 mmol, 1.0 equiv) and EtOH (3.0 mL) were added. On the other hand, Ph_2Zn was prepared using PhMgBr (1 M in ether, 0.5 mmol, 2.0 equiv), $ZnBr_2$ (0.25 mmol), LiBr (0.38 mmol) and THF (5 mL) in a 15 mL flask stirring for 30 min at room temperature, after solvent was removed, and then a solution of the residue in toluene (3 mL) was transferred to light-irradiation vial. The vial was sealed with a Teflon cap, and placed on a stir plate with two 12 W blue LEDs (one on either side of the vial about 5 cm away). The reaction mixture was allowed to stir at room temperature for 2 h. The reaction was then quenched with water (5 mL) and EtOAc (10 mL). The GC yield of the crude product was determined to be 73% (using hexadecane as the standard). The reaction mixture was further diluted with additional EtOAc (30 mL) and H_2O (20 mL) and extracted three times with EtOAc (40 mL). Finally, the combined organic layers were washed with brine (1 x 30 mL), dried over $NaSO_4$, filtered, concentrated, and purified by flash chromatography column (eluent: 5% - 30% hexanes in ethyl acetate) to get the product **3a** as a white solid (28.2 mg, 73%).

3. Results and Discussion

We began our initial investigations by examining the Ni-catalyzed C-C bond formation at room temperature, using phenyldiazonium tetrafluoroborate (**1a**) and phenylmagnesium bromide (**2a**) as substrates, in presence of $ZnBr_2$ and under a Ru-based photocatalysis (Table 1). Promising results were obtained, when THF was used as solvent and $NiCl_2$ (20 mol%) as catalyst, the reaction gave 14% biphenyl (**3a**) in open air after 2 hours (entry 1). Screening of different solvents resulted in highest yield 63%, where toluene was used to generate organozinc reagent, and then EtOH was added to furnish photocatalyzed cross-coupling step (entry 7 of entries 1-9). Furthermore, different additives were utilized to determine the best combination of $ZnBr_2$ (1 equiv.) and LiBr (1.5 equiv.) to provide 73% yield (entry 12 of 10 - 12). LiBr may lead to a multimetallic synergistic effect in the reaction. [26-28] The incomplete reaction gave 57% yield after 1 hour (entry 13). Due to the occurance of side reaction, when the reaction time was extended to 15 h, the 71% yield was obtained (entry 14). Direct use of Gregnard reagent led to no desired product (entry 15). Logically, the control experiments were performed to illustrate that photoredox catalyst and LED irradiation were all essential for this coupling reaction (entries 16-17). Finally, a reaction under argon was performed to exclude the possibility of oxidization of oxygen (entry 18), and the absence of Ni catalyst caused no target product (entry 19).

Table 1 Optimization of Ni-catalyzed Negishi Reaction of Phenyldiazonium Tetrafluoroborate (**1a**) and Phenylmagnesium Bromide (**2a**) under LED Irradiation.[a]



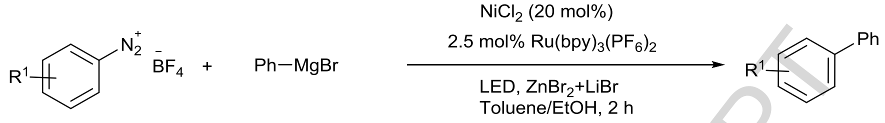
Entry	Additive	Solvent	Yield (%) [b]
1	$\mathrm{ZnBr_2}$	THF	14
2	$\mathrm{ZnBr_2}$	Toluene	21
3	$\mathrm{ZnBr_2}$	1,4-dioxane	11
4	$\mathrm{ZnBr_2}$	THF+MeOH	6
5	$\mathrm{ZnBr_2}$	THF+EtOH	13
6	$\mathrm{ZnBr_2}$	Toluene+MeOH	26
7	$\mathrm{ZnBr_2}$	Toluene+EtOH	63
8	$\mathrm{ZnBr_2}$	1,4-dioxane+MeOH	21
9	$\mathrm{ZnBr_2}$	1,4-dioxane+ EtOH	58
10	$\mathrm{ZnCl_2}$	Toluene + EtOH	53
11	$\mathrm{ZnCl_2}$+LiCl	Toluene + EtOH	64
12	$\mathrm{ZnBr_2}$+LiBr	Toluene + EtOH	73(73)
13 [c]	$\mathrm{ZnBr_2}$+LiBr	Toluene + EtOH	57
14 [d]	$\mathrm{ZnBr_2}$+LiBr	Toluene + EtOH	71
15	--	Toluene + EtOH	<1
16[e]	$\mathrm{ZnBr_2}$+LiBr	Toluene + EtOH	<1
17[f]	$\mathrm{ZnBr_2}$+LiBr	Toluene + EtOH	<1
18[g]	$\mathrm{ZnBr_2}$+LiBr	Toluene + EtOH	73
19[h]	$\mathrm{ZnBr_2}$+LiBr	Toluene + EtOH	0

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), $\mathrm{NiCl_2}$ (0.05 mmol, 20 mol%), $\mathrm{Ru(bpy)_3(PF_6)_2}$ (0.00625 mmol, 2.5 mol%), solvent (6.0 mL or 3.0 mL/3.0 ml indicated mixture) at room temperature in open air under blue LED irradiation. [b]Yield based on **1a** and determined by GC analysis using hexadecane as an internal standard, isolated yield in parentheses. [c]Reaction time: 1 hours. [d]Reaction time: 15 hours. [e]Without photoredox Ru catalyst. [f]Without LED irradiation. [g]Under Ar. [h]Without Ni catalyst

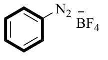
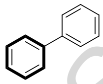
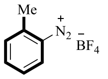
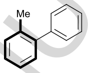
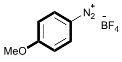
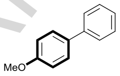
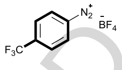
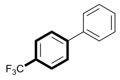
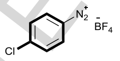
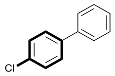
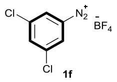
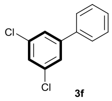
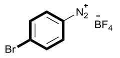
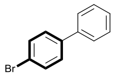
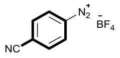
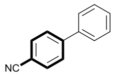
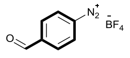
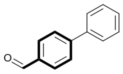
As can be deduced from the results listed on Table 2, a wide variety of aryldiazonium salts were proved to be suitable substrates and provided the desired products in moderate to good yields (**3a**-**3k**). The steric had a negative effect by decreasing the yield to 48% (**3b**). When the reactant with electron-donating group was used, the reaction afforded 68% yield (**3c**). On the other hand, electron-withdrawing 4-$\mathrm{CF_3}$ group had minimal deleterious effect resulting in 55% yield (**3d**). Starting compounds containing Cl or Br on the aromatic ring reacted chemoselectively through diazonium side (entries 5-7): 4-Cl and

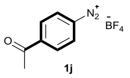
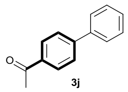
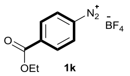
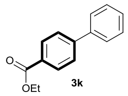
3,5-dichloro compounds gave moderate yields (**3e**: 60% and **3f**: 64%), and the yield of 4-bromo fragment was a bit lower (**3g**: 41%). To our delight, 4-nitrile substrate was tolerated, affording 49% yield (**3h**). Besides, the substrates with labile functional groups such as aldehyde, ketone or ester (**1l-1k**) were also compatible in this reaction, giving the desired coupling products in 33%, 57% and 62% yields, respectively.

Table 2 Scope of Aryldiazonium Salts for Ni-catalyzed Negishi Reaction under LED Irradiation.[a]



1 **2a** **3**

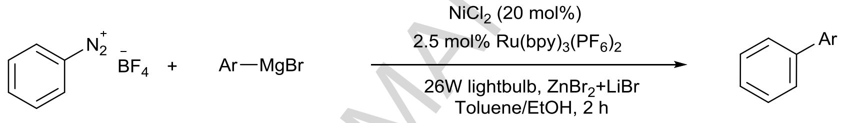
Entry	[Aryl-N2]BF$_4$ (**1**)	Product (**3**)	Isolated Yield
1	 **1a**	 **3a**	73
2	 **1b**	 **3b**	48
3	 **1c**	 **3c**	68
4	 **1d**	 **3d**	55
5	 **1e**	 **3e**	60
6	 **1f**	 **3f**	64
7	 **1g**	 **3g**	41
8	 **1h**	 **3h**	49
9	 **1i**	 **3i**	33

10	 1j	 3j	57
11	 1k	 3k	62

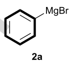
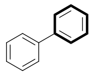
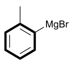
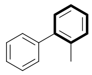
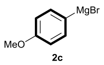
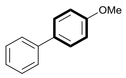
[a]Reaction conditions: **1** (0.25 mmol), **2a** (0.5 mmol), $NiCl_2$ (0.05 mmol, 20 mol%), $ZnBr_2$ (0.25 mmol), LiBr (0.38 mmol), $Ru(bpy)_3(PF_6)_2$ (0.00625 mmol, 2.5 mol%), 3.0 mL toluene/3.0 ml ethanol at room temperature in open air under blue LED irradiation.

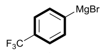
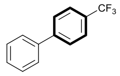
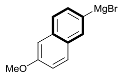
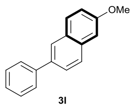
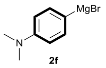
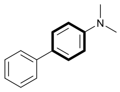
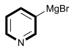
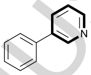
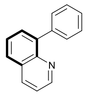
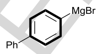
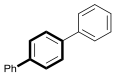
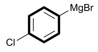
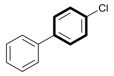
Next, experiments were performed to investigate the scope of Grignard reagents (Table 3). The sterically hindered substrate (**2b**) afforded a bit lower yield (entry 2, 46%). As expected, both 4-methoxyl and 4-CF_3 generated the desired products in good yields (entry 3 and 4). Naphthalene was compatible in this reaction with 66% yield (**3l**). Notably, the compounds containing basic groups such as dimethylamino, pyridinyl and quinolin-8-yl groups were well tolerant for this protocol, resulting in 45%, 64% and 71% yields, respectively (entries 6-8). Biphenyl compound gave a good yield, and 4-Cl reagent afforded the target product in 61% yield (entries 9-10).

Table 3 Scope of Grignard Reagent for Ni-catalyzed Negishi Reaction under light Irradiation.[a]



1a **2** **3**

Entry	ArMgBr (**2**)	Product (**3**)	Isolated Yield
1	 2a	 3a	73
2	 2b	 3b	46
3	 2c	 3c	70

4	 **2d**	 **3d**	64
5	 **2e**	 **3l**	66
6	 **2f**	 **3m**	45
7	 **2g**	 **3n**	64
8	 **2h**	 **2o**	71
9	 **2i**	 **3p**	70
10	 **2j**	 **3e**	61

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[a] Reaction conditions: **1a** (0.25 mmol), **2** (0.5 mmol), $NiCl_2$ (0.05 mmol, 20 mol%), $ZnBr_2$ (0.25 mmol), LiBr (0.38 mmol), $Ru(bpy)_3(PF_6)_2$ (0.00625 mmol, 2.5 mol%), 3.0 mL toluene/3.0 ml ethanol at room temperature in open air under blue LED irradiation.

Hammett study was performed to get insight into the mechanism of this photoredox reaction (**Figure 1**).[29] Using different-substitutent diazoniums (4-MeO, 4-Cl, 4-COOEt, 4-CF_3, -CN *vs* 4-H), it is showed that this reaction is sensitive to the substituents (ρ = 0.75, **Figure 1a**), indicating that diazonium salts had built up a partial negative charge or lost a partial positive charge in their transition states, which could be elucidated by one electron trap of ArN_2^+ to form $ArN_2^{\cdot}$ radical, and by the low oxidation valence redox cycle of Ni(III)/Ni(I) instead of Ni(IV)/Ni(II). The Ni(IV)/Ni(II) cycle usually requires a haloalkane coupling partner.[30, 31] On the other side, the competition experiments between different Grignard reactants (4-NMe_2, 4-MeO, 4-Ph, 4-Cl, 4-CF_3 *vs* 4-H) illuminates that these substrates had been building up positive charge (or lost negative charge) on their intermediates (ρ = -0.45, **Figure 1b**), [32] this may be due to the more efficient transmetalation of electron-rich zinc reagent with $NiCl_2$.

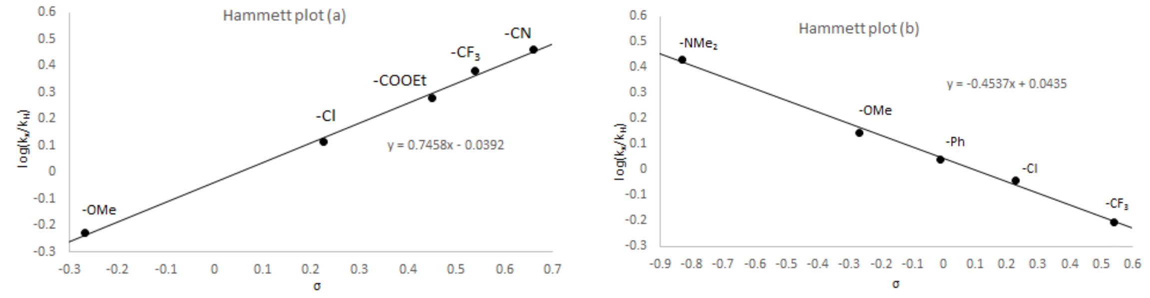

Figure 1. (a) Plot of log (k_X/k_H) vs σ for ArN_2BF_4 with PhMgBr. (b) Plot of log (k_X/k_H) vs σ for PhN_2BF_4 with ArMgBr.

A plausible catalytic cycle of this Ni/Ru photocatalyzed Negishi coupling is shown in **Figure 2**. The key steps of Ni catalytic cycle include [31]: (i) generation of Ph_2Zn from $ZnBr_2$ and Grignard reagent PhMgBr; (ii) transmetalation of NiX_2 (**A**) with Ph_2Zn to form PhNi(II)X (**B**); (iii) one-electron oxidation of PhNi(II)X (**B**) by $Ar^{\cdot}$ radical to generate PhArNi(III)X (**C**); (iv) C-C bond formation by reductive elimination to release the biaryl product and Ni(I)X (**D**); (v) one-electron oxidation of Ni(I)X (**D**) by $Ru(bpy)_3^{3+}$ to regenerate the initial Ni(II)X_2 (**A**), consistent with Hammett study. The steps on Ru catalytic cycle are as reported [9] [33]: (i) light-irradiation of the Ru catalyst to generate excited $Ru(bpy)_3^{2+}$*; (ii) oxidation of the Ru center to $Ru(bpy)_3^{3+}$ with concomitant reduction of aryldiazonium salt to $ArN_2^{\cdot}$ radical; [34] (iii) N_2 releasing of $ArN_2^{\cdot}$ to produce $Ar^{\cdot}$ radical; (iv) one-electron reduction of $Ru(bpy)_3^{3+}$ to regenerate the photocatalyst.

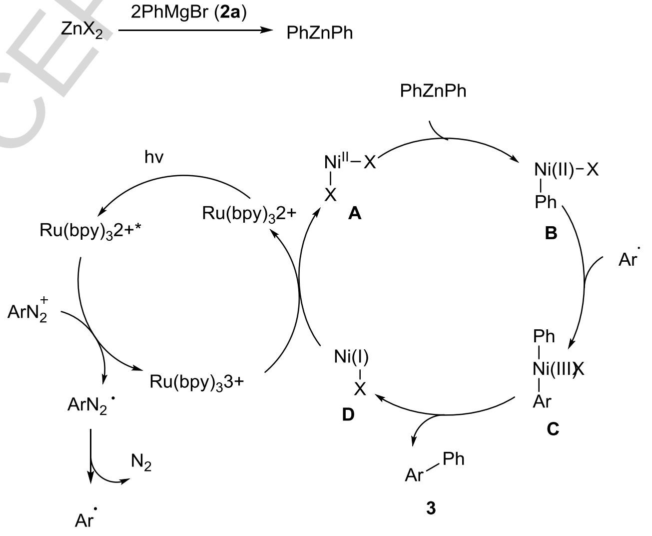

Figure 2 Plausible Mechanism for Ni/Ru-catalyzed One-pot Negishi-Coupling Reaction

4. Conclusion and Future Directions

In sum, we reported a mild one-pot approach for nickel-catalyzed Negishi reaction, being accelerated by photocatalysis. These reactions proceeded smoothly at room temperature and were compatible with a range of functional groups. This protocol successfully utilized visible-light photoredox to facilitate Ni redox catalysis. We anticipate that this new approach will benefit other Ni-catalyzed synthetic transformations.

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References and notes

1. J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359-1470.
2. G. Bringmann, T. Gulder, M. Breuning, Chem. Rev. 111 (2010) 563-639.
3. A. Fihri, M. Bouhrara, B. Nekoueishahraki, J. Basset, V. Polshettiwar, Chem. Soc. Rev. 40 (2011) 5181-5203.
4. F. Han, Chem. Soc. Rev. 42 (2013) 5270-5298.
5. M. Hopkinson, A. Tlahuext-Aca, F. Glorius. Acc. Chem. Res. 49 (2016) 2261−2272.
6. X. Zhang, D. W. C. MacMillan, J. Am. Chem. Soc. 139 (2017), 11353−11356.
7. E. B. McLean, A. Lee, Tetrahedron, 74 (2018) 4881-4902.
8. C. K. Prier, D. A. Rankic, D. W. C. MacMillan Chem. Rev. 113 (2013) 5322-5363.
9. D. Kalyani, K. McMurtrey, S. Neufeldt, M. Sanford, J. Am. Chem. Soc. 133 (2011) 18566-18569.
10. W. Yoo, T. Tsukamoto, S. Kobayashi, Angew. Chem. Int. Ed. 54 (2015) 6587-6590.
11. M. Hopkinson, A. Tlahuext-Aca, F. Glorius, Acc. Chem. Res. 49 (2016) 2261 - 2272.
12. J. Twilton, C. Le, P. Zhang, M. H. Shaw, R.W. Evans, D. W. C. MacMillan, Nat. Rev. Chem. 1 (2017) 1-18.
13. R. T. Smith, X. -H Zhang, J. A. Rincón, J. Agejas, C. Mateos, M. Barberis, S. García-Cerrada, O. Frutos, D. W. C. MacMillan J. Am. Chem. Soc. 140 (2018) 17433−17438.
14. V. Bacauanu, S. Cardinal, M. Yamauchi, M. Kondo, D. F. Fernández, R. Remy, D. W. C. MacMillan Angew. Chem. Int. Ed. 57 (2018) 12543 –12548.
15. I. B. Perry, T. F. Brewer, P. J. Sarver, D. M. Schultz, D. A. DiRocco, D. W. C. MacMillan Nature 560 (2018) 70-75.
16. I. Abdiaj, A. Fontana, M. V. Gomez, A. Hoz, J. Alcázar, Angew. Chem.Int. Ed. 57 (2018) 8473 –8477.
17. G. Lise-Lotte in *Targets in Heterocyclic Systems, Vol. 14* (Eds.: O. Attanasi, D. Spinelli), Wiley-VCH, Weinheim, 2008, pp. 85-119.
18. S. Z. Tasker1, E. A. Standley, T. F. Jamison Nature 509 (2014) 299-309.
19. A. Fihri, M. Bouhrara, B. Nekoueishahraki, J. Basset, V. Polshettiwar, Chem. Soc. Rev. 40 (2011) 5181-5203.
20. F. Han, Chem. Soc. Rev. 42 (2013) 5270-5298.
21. F. -X. Felpin, S. Sengupta, Chem. Soc. Rev. 48 (2019), 1150—1193.
22. V. Phapale, D. Cárdenas, Chem. Soc. Rev. 38 (2009) 1598–1607.
23. K. Yamamoto, S. Otsuka, K. Nogi, H. Yorimitsu, ACS Catal. 7 (2017) 7623−7628.
24. R. Gerber, C. Frech, Chem. Eur. J. 17 (2011) 11893 – 11904.
25. J. M. Bhojane, S. A. Sarode, J. M. Nagarkar New J. Chem. 40 (2016) 1564—1570.
26. J.-L. Tao, B. Yang, Z.-X. Wang, J. Org. Chem. 80 (2015) 12627−12634.
27. D. R. Armstrong, W. Clegg, P. García-Álvarez, A. R. Kennedy, M. D. McCall, L. Russo, E. Hevia, Chem. Eur. J. 17 (2011) 8333 – 8341.
28. L. C. McCann, H. N. Hunter, J. A. C. Clyburne, M. G. Organ, Angew. Chem. Int. Ed. 51 (2012) 7024 –7027.
29. L. Hammett, J. Am. Chem. Soc. 59 (1937) 96–103.
30. Y. –Z. Li, L. –F. Zou, R. -P Bai, Y. Lan, Org. Chem. Front. 5 (2018) 615–622.

31. V. B. Phapale, M. Guisán‐Ceinos, E. Buñuel, D. J. Cárdenas, Chem. Eur. J. 15 (2009) 12681 – 12688.
32. A. Stein, M. Tencer, E. Moffatt, R. Dawe, J. Sweet, J. Org. Chem. 45 (1980) 3539–3540.
33. H. Cano-Yelo, A. Deronzier, J. Chem. Soc., Faraday Trans. 1. 80 (1984) 3011-3019.
34. The addition of 1.0 equivalent TEMPO completely quenched the reaction, no desired product was obtained. This reaction procedure: Ru(bpy)$_3$(PF$_6$)$_2$ (5.37 mg, 0.00625 mmol, 0.025 equiv), and NiCl$_2$ (6.48 mg, 0.05 mmol, 0.20 equiv) were added into a 20 mL Fisherbrand Glass Threaded vial with a stir bar, and then PhN$_2$BF$_4$ (**1a**, 48.0 mg, 0.25 mmol, 1.0 equiv), TEMPO (39 mg, 0.25 mmol, 1.0 equiv.) and EtOH (3.0 mL) were added, and then followed the general procedure for the rest of operation.

Highlights

- A Negishi reaction for C(sp^2)-C(sp^2) bond formation was achieved.
- This room-temperature transformation completed in 2 hours.
- Visible-light induced this Ni-catalyzed cross-coupling reaction.
- Aryldiazonium salts were used as coupling partners with Ar_2Zn.
- The labile functional groups were tolerated.