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Photochemical Nickel-Catalyzed Reductive Migratory Cross-Coupling of Alkyl Bromides with Aryl Bromides

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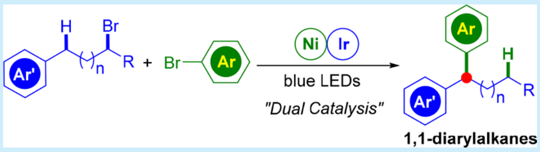
Supporting Information



ABSTRACT: A novel method to access 1,1-diarylalkanes from readily available, nonactivated alkyl bromides and aryl bromides via visible-light-driven nickel and iridium dual catalysis, wherein diisopropylamine ($^i\mathrm{Pr}_2\mathrm{NH}$) is used as the terminal stoichiometric reductant, is reported. Both primary and secondary alkyl bromides can be successfully transformed into the migratory benzylic arylation products with good selectivity. Additionally, this method showcases tolerance toward a wide array of functional groups and the presence of bases.

1,1-Diarylalkanes are a significant class of pharmacophores present in drugs and many other relevant biologically active molecules.[1] Therefore, the synthesis of this framework has aroused enormous interest and attention. Transition-metal-catalyzed cross-coupling reactions of benzylic electrophiles with arylmetallic reagents or aryl halides are the most common strategy to construct this class of compounds.[2] The direct catalytic arylation of benzylic C−H bonds is a more attractive protocol to access this skeleton, and progress has been made by Walsh[3] with palladium and by Stahl[4] and Liu[5] with copper. Very recently, further progress toward avoiding the use of activated but potentially unstable benzylic halides as well as arylmetallic reagents was made independently by us[6] and Zhu and co-workers.[7] We demonstrated that 1,1-diarylalkanes can be efficiently prepared from nonactivated alkyl electrophiles and aryl electrophiles under nickel catalysis in the presence of a stoichiometric reducing agent (Figure 1a, top). However, this approach still relied on the use of a stoichiometric amount of a metal reductant such as manganese or zinc metal dust to complete the catalytic cycle.[8] Efforts toward exploring alternative reducing agents and new catalytic systems would therefore be highly beneficial to broaden the synthetic utility of this strategy further.

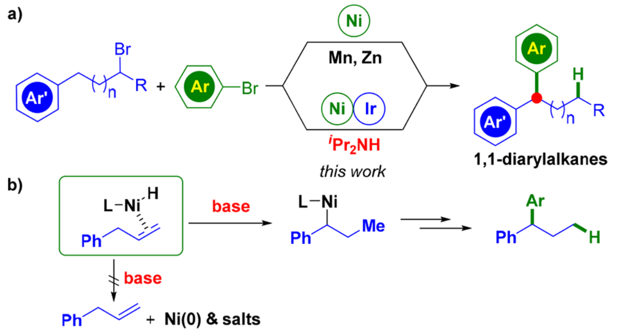


Figure 1. Nickel-catalyzed reductive migratory cross-coupling reactions.

Visible-light-driven photoredox catalysis has been well-established as a powerful tool in the construction of carbon−carbon and carbon−heteroatom bonds in organic synthesis over the past decade.[9] The merging of photoredox catalysis with transition metal catalysis has shed new light on transition metal catalysis, by not only providing new coupling partners but also altering the catalytic cycles.[10] Numerous studies on the redox neutral and oxidative systems[11] have previously been described. However, in comparison, reports on the transformation involving photochemical transition-metal catalysis under reductive conditions have to date remained scarce.[12,13] Herein, we report a photochemical, nickel-catalyzed migratory cross-coupling of nonactivated, aryl substituted alkyl bromides with aryl bromides using a cheap organic amine as the terminal electron donor,[14] allowing access to 1,1-diaraylalkanes with high efficiency and selectivity under mild conditions (Figure 1a, bottom). It is noteworthy that, even in the presence of a large amount of organic base, the reaction selectively affords the migratory cross-coupling products, rather than olefins or the Heck type products,[15] probably due to the reductive elimination from the Ni−H species being reversible[16] (Figure 1b).

We initiated this study with the cross-coupling of (3-bromopropyl)benzene (**1a**) with bromobenzene (**2a**). By extensive screening of the reaction parameters, we found that the combination of [Ir]-**1**, $\mathrm{NiBr_2{\cdot}DME}$, bathocuproine (BC),[17] $\mathrm{MgBr_2}$ (as an additive), and $^i\mathrm{Pr}_2\mathrm{NH}$ as the stoichiometric reductant at room temperature in DMF under blue LEDs irradiation for 24 h leads to the migratory cross-coupling product 1,1-diphenylpropane (**3a**) in 84% yield with a 32/1 regioisomeric ratio (*remote*/*ipso* coupling). The ligand screening efforts again showed that the migratory product **3a** is preferred when 6,6′-dimethyl-2,2′-bipyridine (6,6′-dmbpy) or neocuproine was used as a ligand (Table 1, entries 2 and 3), while using 4,4′-di(*tert*-butyl)-2,2′-bipyridine (4,4′-dtbbpy)

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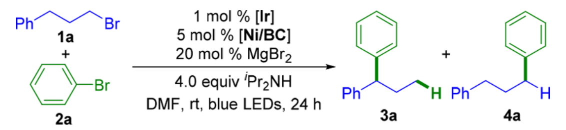
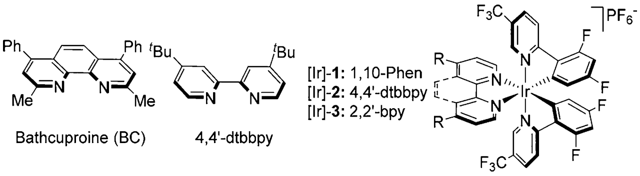
Table 1. Effects of Reaction Parameters[a]



entry	variation of standard conditions	yield/% (3a/4a)[b]
1	none	92[c] (32/1)
2	6,6′-dmbpy instead of BC	71 (44/1)
3	neocuproine instead of BC	79 (16/1)
4	4,4′-dtbbpy instead of BC	74 (1/92)
5	[Ir]-**2** instead of [Ir]-**1**	85 (28/1)
6	[Ir]-**3** instead of [Ir]-**1**	83 (36/1)
7	$MgCl_2$ instead of $MgBr_2$	81 (42/1)
8	$^nBu_4NBr$ instead of $MgBr_2$	86 (42/1)
9	no $MgBr_2$	83 (33/1)
10	Et_3N instead of $^iPr_2NH$	35 (13/1)
11	Et_2NH instead of $^iPr_2NH$	2 (3/1)
12	no $^iPr_2NH$	0
13	no $NiBr_2$·DME/BC	0
14	no Ir complex or light	0

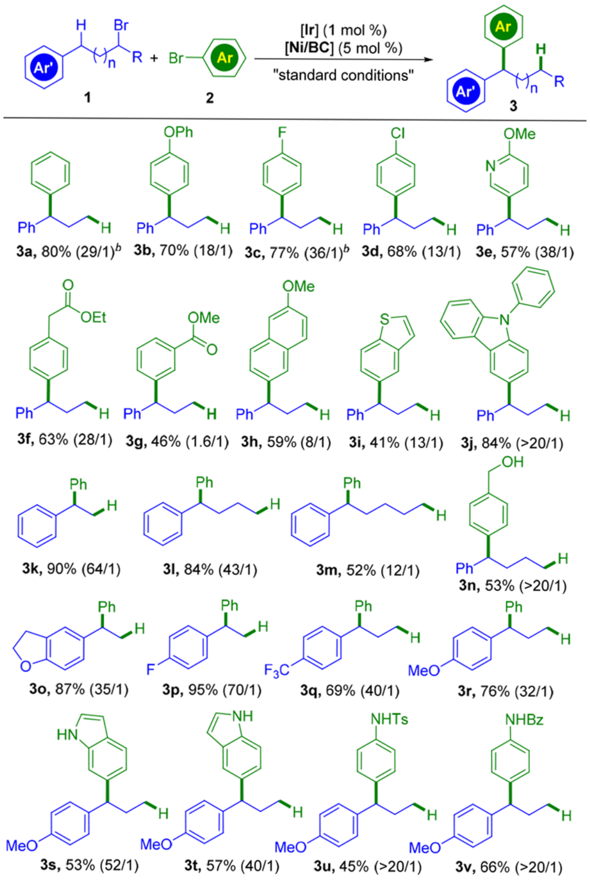
[a] General conditions: [Ir]-**1** (1 mol %), $NiBr_2$·DME (5 mol %), BC (5 mol %), $MgBr_2$ (20 mol %), **1a** (0.45 mmol), **2a** (0.3 mmol), $^iPr_2NH$ (1.2 mmol), DMF (3 mL), rt, 24 h. [b] Yields and regioisomeric ratios are determined by GC-FID with naphthalene as the internal standard. [c] 84% isolated yield.



yielded predominantly the *ipso*-product **4a** (Table 1, entry 4). Replacing the iridium photocatalyst [Ir]-**1** with [Ir]-**2** or [Ir]-**3** resulted in a slight decrease in the reaction yield (Table 1, entries 5 and 6). The addition of $MgBr_2$ led to a further increase in the yield (Table 1, compare entries 1, 7, 8, and 9). The choice of electron donor also turned out to be crucial for the photochemical transformation, as replacing $^iPr_2NH$ with Et_3N or Et_2NH led to a significant drop in the yield (Table 1, compare entries 1, 10, and 11), maybe due to less steric hindrance.[18] Finally, control experiments showed that the nickel, ligand, organic electron donor, iridium complex, and light are all required for the coupling reaction to occur (Table 1, entries 12, 13, and 14).

With the optimal conditions in hand, we then turned our attention to the generality of these migratory cross-coupling conditions. As shown in Scheme 1, a series of aryl bromides were first examined, and as a result, both aryl and heteroaryl bromides were converted to the corresponding cross-coupling products in moderate to high yields under the standard conditions. Notably, low selectivity was observed with electron-deficient or π-extended aryl bromides (**3g**, **3h**, and **3i**), probably due to the fact that the reductive elimination offering the *ipso*-products is faster than the electron-rich ones. Primary alkyl bromides with aliphatic chains consisting of two to five carbons and a terminal aryl substituent were tested next for the cross-coupling reaction. The results show that the electronic property of aromatic rings attached to the alkyl bromides had no obvious influence on either the reactivity or selectivity of the reductive cross-coupling reactions. Furthermore, functional groups such as electron-rich pyridine (**3e**), esters (**3f**), alcohol

Scheme 1. Investigation of Substrate Scope[a]



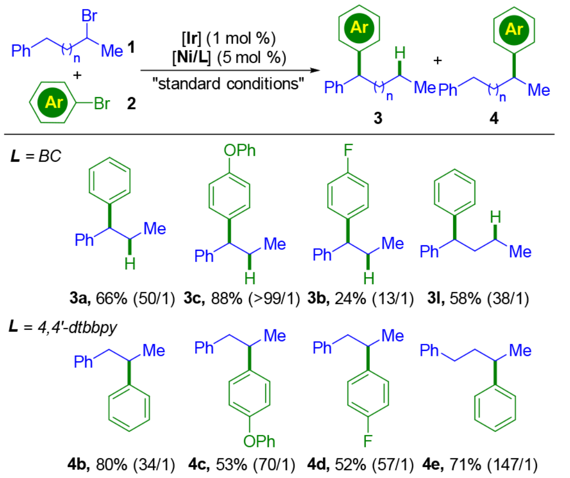
[a] Standard conditions: [Ir]-**1** (1 mol %), $NiBr_2$·DME (5 mol %), BC (5 mol %), $MgBr_2$ (20 mol %), aryl bromide (0.3 mmol), alkyl bromide (0.45 mmol), $^iPr_2NH$ (1.2 mmol), DMF (3 mL), rt, 24–36 h. Isolated yields, by average of two runs. Regioisomeric ratios are determined by GC-FID. [b] 1.0 mmol scale reaction.

(**3n**), unprotected indoles (**3s**, **3t**), and amides (**3u**, **3v**) were all compatible under the photochemical reductive coupling conditions.

Attention was then turned to the reactivity of the secondary alkyl bromides under these coupling conditions. As shown in Scheme 2, the choice of ligand was also able to successfully dictate the selectivity of the cross-coupling product. Bathocuproine promotes coupling at the *remote*-site, while using 4,4′-dtbbpy the *ipso*-site products are preferred, which is consistent with the report of Lei and co-workers.[12b] It is worth pointing out that the 4-bromofluorobenzene exhibited poor reactivity in the migratory coupling reaction (Scheme 2, **3b**). The construction of a quaternary steric center is still a challenge for the current reductive system (Scheme 3, eq 1). As a final note, a mixture of primary and secondary alkyl bromides **1a** and **1w** provided the migratory benzylic product in 87% yield (Scheme 3, eq 2).

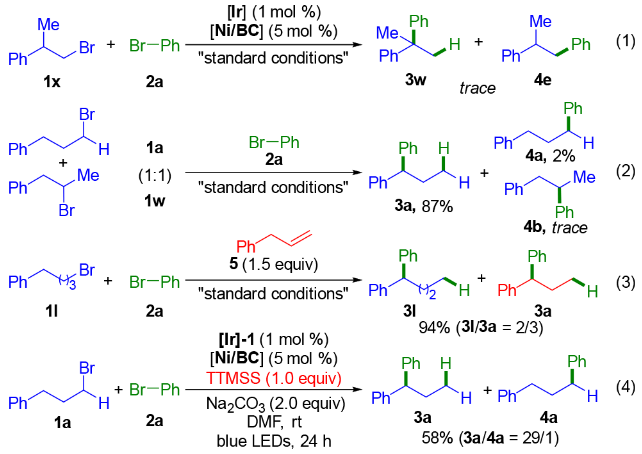
To gain further insights into the transformation, additional control experiments were conducted. A stoichiometric amount of nonactivated olefin **5** was added to the cross-coupling of 4-carbon alkyl bromide **1l** with **2a**, and a mixture of products formed with the olefin-based **3a** being the major one (Scheme 3, eq 3). These results indicate that the nickel chain-walking is not limited to an intramolecular process. Furthermore, catalytic conditions similar to those for MacMillan's reductive photo-

Scheme 2. Investigation of Secondary Alkyl Bromides[a]

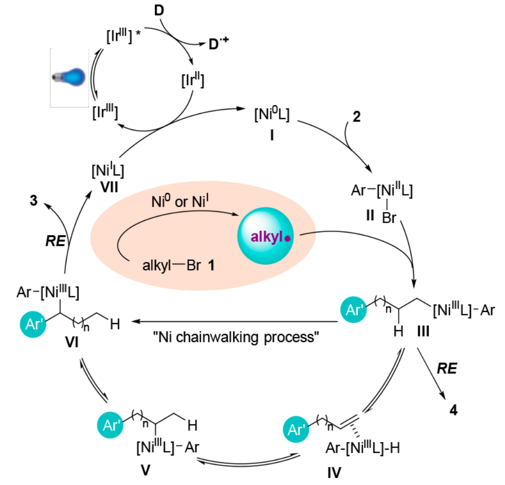


[a] Standard conditions: [Ir]-**1** (1 mol %), $NiBr_2$·DME (5 mol %), BC (5 mol %), $MgBr_2$ (20 mol %), aryl bromide (0.3 mmol), alkyl bromide (0.45 mmol), $^iPr_2NH$ (1.2 mmol), DMF (3 mL), rt, 36 h. Isolated yields, average of two runs. Regioisomeric ratios are determined by GC-FID.

Scheme 3. More Details on the Photochemical Reductive Migratory Cross-Coupling Reaction



Scheme 4. Proposed Mechanism



catalytic system,[12a] using tris(trimethysilyl)silane (TTMSS) as the stoichiometric reducing agent, were also effective in the migratory cross-coupling, giving a 58% yield and a 29/1 regioisomeric ratio (Scheme 3, eq 4).

Based on the current literature, a radical chain mechanism[19] is proposed to rationalize the light-driven nickel-catalyzed reductive migratory cross-coupling reaction. As illustrated in Scheme 4, an aryl bromide oxidative addition to nickel(0) **I** resulted in the formation of Ni(II) complex **II**. Meanwhile, a single-electron transfer process generates an alkyl radical from an alkyl bromide, which binds to the complex **II**, leading to the formation of the Ni(III) intermediate **III**. Then a nickel chain-walking process[20] occurs until the thermodynamically most stable benzylic-nickel complex **VI** is formed. Reductive elimination from Ni(III) affords the benzylic arylation product **3** along with the corresponding Ni(I) species. The latter is reduced back to the Ni(0) catalyst by reductive quenching. The formation of *ipso*-product **4** is rationalized by the direct reductive elimination from the intermediate **III**. At this stage, we cannot rule out the possibility of chain-walking via a Ni(I)[7] or Ni(II)[21] mediated process.

In summary, a visible-light-driven reductive redox-relay cross-coupling reaction by nickel catalysis has been developed. Cheap organic electron-donor diisopropylamine is used as the terminal stoichiometric reducing agent. The pharmaceutically important 1,1-diarylalkanes can be synthesized from the nonactivated alkyl bromides and aryl bromides efficiently. This robust reductive migratory coupling reaction tolerant of some of the more common functional groups and also the presence of an organic base. A radical chain mechanistic profile with nickel chain-walking as a key step is tentatively proposed to rationalize this transformation. Further mechanistic investigation is currently ongoing in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00413.

Details on the conditions investigation, extended data about the photoreaction, NMR data and characterization (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) A review on 1,1-diarylalkanes: (a) Vanjari, R.; Singh, K. N. *Chem. Soc. Rev.* **2015**, *44*, 8062. Selected examples: (b) Hills, C. J.; Winter, S. A.; Balfour, J. A. *Drugs* **1998**, *55*, 813. (c) Silva, D. H. S.; Davino, S. C.; de Moraes Barros, S. B.; Yoshida, M. *J. Nat. Prod.* **1999**, *62*, 1475. (d) McRae, A. L.; Brady, K. T. *Expert Opin. Pharmacother.* **2001**, *2*, 883. (e) Malhotra, B.; Gandelman, K.; Sachse, R.; Wood, N.; Michel, M. C. *Curr. Med. Chem.* **2009**, *16*, 4481.

(2) Selected examples on preparation of 1,1-diarylalkanes: (a) Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2011**, *133*, 389. (b) Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 3307. (c) Do, H.-Q.; Chandrashekar, E. R. R.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 16288. (d) Zhou, Q.; Cobb, K. M.; Tan, T.; Watson, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 12057. (e) Poremba, K. E.; Kadunce, N. T.; Suzuki, N.; Cherney, A. H.; Reisman, S. E. *J. Am. Chem. Soc.* **2017**, *139*, 5684. (f) Xiao, L.-J.; Cheng, L.; Feng, W.-M.; Li, M.-L.; Xie, J.-H.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2018**, *57*, 461.

(3) (a) Zhang, J.; Bellomo, A.; Creamer, A. D.; Dreher, S. D.; Walsh, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 13765. (b) Montel, S.; Jia, T.; Walsh, P. J. *Org. Lett.* **2014**, *16*, 130. (c) Sha, S. C.; Zhang, J.; Walsh, P. J. *Org. Lett.* **2015**, *17*, 410. (d) Kim, B. S.; Jiménez, J.; Gao, F.; Walsh, P. J. *Org. Lett.* **2015**, *17*, 5788.

(4) Vasilopoulos, A.; Zultanski, S. L.; Stahl, S. S. *J. Am. Chem. Soc.* **2017**, *139*, 7705.

(5) Zhang, W.; Chen, P.; Liu, G. *J. Am. Chem. Soc.* **2017**, *139*, 7709.

(6) Peng, L.; Li, Y.; Li, Y.; Wang, W.; Pang, H.; Yin, G. *ACS Catal.* **2018**, *8*, 310.

(7) Chen, F.; Chen, K.; Zhang, Y.; He, Y.; Wang, Y.-M.; Zhu, S. *J. Am. Chem. Soc.* **2017**, *139*, 13929.

(8) Reviews on reductive cross-electrophile couplings: (a) Everson, D. A.; Weix, D. J. *J. Org. Chem.* **2014**, *79*, 4793. (b) Moragas, T.; Correa, A.; Martin, R. *Chem. - Eur. J.* **2014**, *20*, 8242. (c) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi von Wangelin, A. *Chem. - Eur. J.* **2014**, *20*, 6828. (d) Gu, J.; Wang, X.; Xue, W.; Gong, H. *Org. Chem. Front.* **2015**, *2*, 1411. (e) Weix, D. J. *Acc. Chem. Res.* **2015**, *48*, 1767. (f) Wang, X.; Dai, Y.; Gong, H. *Top. Curr. Chem.* **2016**, *374*, 43.

(9) Selected reviews on photocatalysis: (a) Bach, T.; Hehn, J. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 1000. (b) Xuan, J.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2012**, *51*, 6828. (c) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322. (d) Xuan, J.; Lu, L.-Q.; Chen, J.-R.; Xiao, W.-J. *Eur. J. Org. Chem.* **2013**, *2013*, 6755. (e) Xi, Y.; Yi, H.; Lei, A. *Org. Biomol. Chem.* **2013**, *11*, 2387. (f) Hopkinson, M. N.; Sahoo, B.; Li, J.-L.; Glorius, F. *Chem. - Eur. J.* **2014**, *20*, 3874. (g) Du, J.; Skubi, K. L.; Schultz, D. M.; Yoon, T. P. *Science* **2014**, *344*, 392. (h) Nicewicz, D. A.; Nguyen, T. M. *ACS Catal.* **2014**, *4*, 355. (i) Beatty, J. W.; Stephenson, C. R. J. *Acc. Chem. Res.* **2015**, *48*, 1474. (j) Tan, F.; Xiao, W.-J. *Huaxue Xuebao* **2015**, *73*, 85. (k) Xuan, J.; Zhang, Z.-G.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2015**, *54*, 15632. (l) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. *Chem. Soc. Rev.* **2016**, *45*, 2044. (m) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075. (n) Liu, Y.; Dong, W. *Chin. J. Chem.* **2017**, *35*, 1491.

(10) Reviews on the merge of photoredox and transtion metal catalysis: (a) Twilton, J.; Le, C.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W. C. *Nat. Rev. Chem.* **2017**, *1*, 0052. (b) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. *Acc. Chem. Res.* **2016**, *49*, 1429. (c) Gui, Y.-Y.; Sun, L.; Lu, Z.-P.; Yu, D.-G. *Org. Chem. Front.* **2016**, *3*, 522. Selected examples: (d) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. *Science* **2014**, *345*, 437. (e) Terrett, J. A.; Cuthbertson, J. D.; Shurtleff, V. W.; MacMillan, D. W. C. *Nature* **2015**, *524*, 330. (f) Shaw, M. H.; Shurtleff, V. W.; Terrett, J. A.; Cuthbertson, J. D.; MacMillan, D. W. C. *Science* **2016**, *352*, 1304. (g) Welin, E. R.; Le, C.; Arias-Rotondo, D. M.; McCusker, J. K.; MacMillan, D. W. C. *Science* **2017**, *355*, 380.

(11) Reviews on photochemical transition metal catalysis in oxidative conditions: (a) Zhong, J.-J.; Meng, Q.-Y.; Chen, B.; Tung, C.-H.; Wu, L.-Z. *Huaxue Xuebao* **2017**, *75*, 34. (b) Pei, P.-k.; Zhang, F.; Yi, H.; Lei, A. *Huaxue Xuebao* **2017**, *75*, 15 Selected examples:. (c) Zhong, J.-J.; Meng, Q.-Y.; Liu, B.; Li, X.-B.; Gao, X.-W.; Lei, T.; Wu, C.-J.; Li, Z.-J.; Tung, C.-H.; Wu, L.-Z. *Org. Lett.* **2014**, *16*, 1988. (d) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. *Science* **2015**, *349*, 1326. (e) Zhang, G.; Liu, C.; Yi, H.; Meng, Q.; Bian, C.; Chen, H.; Jian, J.-X.; Wu, L.-Z.; Lei, A. J. *J. Am. Chem. Soc.* **2015**, *137*, 9273. (f) Margrey, K. A.; McManus, J. B.; Bonazzi, S.; Zecri, F.; Nicewicz, D. A. J. *J. Am. Chem. Soc.* **2017**, *139*, 11288.

(12) Examples on photochemical cross-electrophiles coupling: (a) Zhang, P.; Le, C.; MacMillan, D. W. C. J. *J. Am. Chem. Soc.* **2016**, *138*, 8084. (b) Duan, Z.; Li, W.; Lei, A. *Org. Lett.* **2016**, *18*, 4012.

(13) More examples on photochemical transition metal catalysis in reductive conditions: (a) Murata, K.; Numasawa, N.; Shimomaki, K.; Takaya, J.; Iwasawa, N. *Chem. Commun.* **2017**, *53*, 3098. (b) Shimomaki, K.; Murata, K.; Martin, R.; Iwasawa, N. J. *J. Am. Chem. Soc.* **2017**, *139*, 9467. (c) Meng, Q.-Y.; Wang, S.; König, B. *Angew. Chem., Int. Ed.* **2017**, *56*, 13426.

(14) (a) Schoenebeck, F.; Murphy, J. A.; Zhou, S.-Z.; Uenoyama, Y.; Miclo, Y.; Tuttle, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 13368. (b) Doni, E.; Mondal, B.; O'Sullivan, S.; Tuttle, T.; Murphy, J. A. J. *J. Am. Chem. Soc.* **2013**, *135*, 10934.

(15) Reviews on Heck reactions: (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (b) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2. (c) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (d) Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945.

(16) Lin, B.-L.; Liu, L.; Fu, Y.; Luo, S.-W.; Chen, Q.; Guo, Q.-X. *Organometallics* **2004**, *23*, 2114.

(17) The steric hindrance of the methyl groups is thought to play a key role; for more studies on bathocurpoine, see: (a) Zheng, C. W.; Wang, D.; Stahl, S. S. J. *J. Am. Chem. Soc.* **2012**, *134*, 16496. (b) Wang, D.; Weinstein, A. B.; White, P. B.; Stahl, S. S. *Chem. Rev.* **2018**, *118*, 2636.

(18) No C−N bond formation products were observed.

(19) Examples on radical chain mechanism in nickel catalysis: (a) Biswas, S.; Weix, D. J. J. *J. Am. Chem. Soc.* **2013**, *135*, 16192. (b) Zhao, C.; Jia, X.; Wang, X.; Gong, H. J. *J. Am. Chem. Soc.* **2014**, *136*, 17645. (c) Schley, N. D.; Fu, G. C. J. *J. Am. Chem. Soc.* **2014**, *136*, 16588. (d) Breitenfeld, J.; Ruiz, J.; Wodrich, M. D.; Hu, X. J. *J. Am. Chem. Soc.* **2013**, *135*, 12004.

(20) Reviews on transformations involving transition metal chain-walking process: (a) Vasseur, A.; Bruffaerts, J.; Marek, I. *Nat. Chem.* **2016**, *8*, 209. (b) Sommer, H.; Juliá-Hernández, F.; Martin, R.; Marek, I. *ACS Cent. Sci.* **2018**, *4*, 153. Selected examples: (c) Werner, E. W.; Mei, T.-S.; Burckle, A. J.; Sigman, M. S. *Science* **2012**, *338*, 1455. (d) Mei, T.-S.; Patel, H. H.; Sigman, M. S. *Nature* **2014**, *508*, 340. (e) Buslov, I.; Becouse, J.; Mazza, S.; Montandon-Clerc, M.; Hu, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 14523. (f) Buslov, I.; Keller, S. C.; Hu, X. *Org. Lett.* **2016**, *18*, 1928. (g) Dupuy, S.; Zhang, K.-F.; Goutierre, A.-S.; Baudoin, O. *Angew. Chem., Int. Ed.* **2016**, *55*, 14793. (h) Zhu, S.; Niljianskul, N.; Buchwald, S. L. *Nat. Chem.* **2016**, *8*, 144. (i) Juliá-Hernández, F.; Moragas, T.; Cornella, J.; Martin, R. *Nature* **2017**, *545*, 84. (j) Singh, S.; Bruffaerts, J.; Vasseur, A.; Marek, I. *Nat. Commun.* **2017**, *8*, 14200.

(21) D'Aniello, M. J.; Barefield, E. K. *J. Am. Chem. Soc.* **1978**, *100*, 1474. An alternative possible Ni(II)-chain-walking mechanism involving a bimolecular transmetallation is suggested by the reviewer; please see Scheme S3.