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Nickel-Catalyzed Cyclization Strategy for the Synthesis of Pyrroloquinolines, Indoloquinolines, and Indoloisoquinolines

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01055 Read Online

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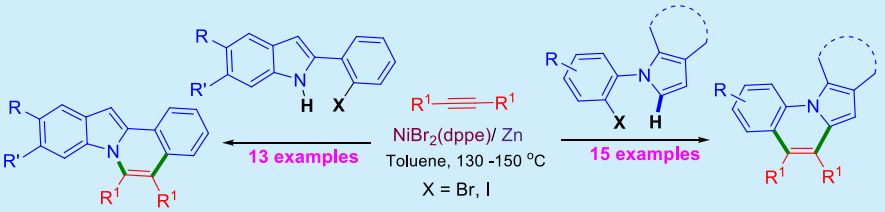
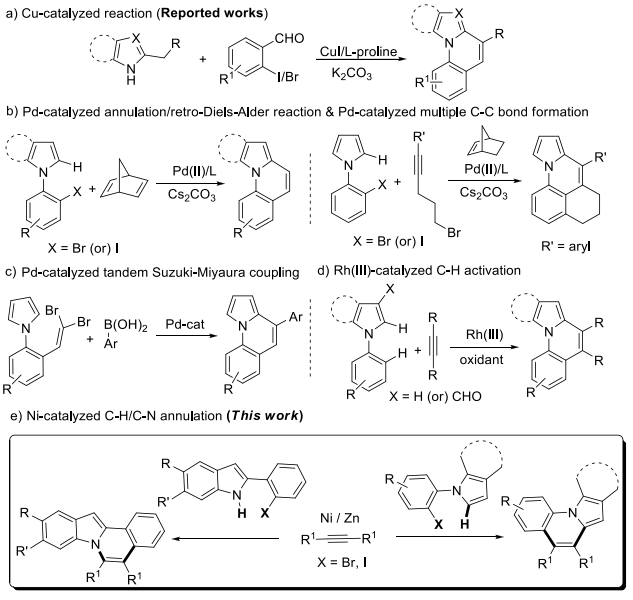


ABSTRACT: An inexpensive and benchtop stable Ni-catalyst/Zn system for the synthesis of pyrrolo/indoloquinolines and indolo[2,1-*a*]isoquinolines is explored. This platform provides a one-pot entry for the preparation of various pyrrolo and indoloquinolines/isoquinolines, which involves successive C−C and C−N bond formation, respectively. In addition, we have also performed the preliminary photophysical studies for the synthesized compounds.

Pyrrolo/indoloquinolines are an important class of heterocycles widely found in many bioactive naturally occurring compounds and pharmaceuticals.[1] In addition, these compounds shows interesting photophysical properties, with regard to applications such as semiconductors,[2a,b] dyes,[2c] and dye-sensitized solar cells (DSSCs).[2d]

Despite their great significance, the synthesis of pyrroloquinolines and indoloquinolines were rarely explored, because of the requirement of multistep and restricted availability of starting materials.[2a,3] However, a metal catalyst provides a great entry for the synthesis of various heterocyclic compounds. So far, only a few metal-catalyzed syntheses of pyrrolo/indoloquinolines are known. Thus, an example of pyrroloquinolines by copper-catalyzed Ullmann coupling, followed by condensation of aldehydes has been reported in 2010 (Scheme 1a).[4] Lautens group's sequentially utilized intermolecular and intramolecular reactions for the construction of pyrrolo/indoloquinolines by using $Pd(OAc)_2$/PPh_3/norbornadiene/Cs_2CO_3 mediated C−H annulations followed by in situ retro-Diels−Alder reaction.[5a] A palladium-catalyzed domino reaction of 1-(2-iodophenyl)-1*H*-pyrrole with bromoalkyl-aryl alkynes (Scheme 1b)[5b] and efficient Pd-catalyzed tandem reaction of *gem*-dibromoolefins with organoboronic acids are also known to provide pyrrolo/indoloquinolines frameworks (Scheme 1c).[5c] Later on, Dong and Chen et al. reported a rhodium-catalyzed dual C−H activation reaction of 2-substituted imidazoles with alkynes to form aza-fused quinolines.[6] Recently, the group of Lan and You co-workers reported facile access to various indolo[1,2-*a*]quinolines by a rhodium-catalyzed C−H activation with indolyl aldehydes and alkynes (Scheme 1d).[7]

Scheme 1. Metal-Catalyzed Synthesis of Pyrrolo/indoloquinolines



Received: March 23, 2020

https://dx.doi.org/10.1021/acs.orglett.0c01055
Org. Lett. XXXX, XXX, XXX−XXX

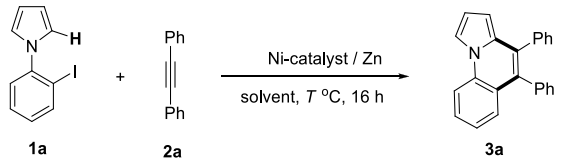
Among the above existing methodologies, the most of them required costly metal complex and tedious reaction conditions. Nowadays, the development of inexpensive, environmentally benign alternative metal catalysts is most sought in organic synthesis. In this regard, to our knowledge, so far, Ni/Zn combination of C−H annulations is not explored. Herein, we wish to report a first Ni/Zn system for construction of pyrrolo/indoloquinolines and indolo[2,1-*a*]isoquinolines through C−H and C−N annulations, respectively (Scheme 1e). Note that Cheng's group developed a series of Ni/Zn-system for easy access to various carbocyclic and heterocyclic compounds.[8]

The reaction of 1-(2-iodophenyl)-1*H*-pyrrole (**1a**, 0.30 mmol) with diphenyl acetylene (**2a**, 0.60 mmol) in the presence of $NiBr_2$(dppe)/Zn in toluene at 130 °C for 16 h gave 4,5-diphenylpyrrolo[1,2-*a*]quinoline **3a** in 90% isolated yield. The product **3a** was confirmed by its ^1H and ^{13}C NMR analyses, as well as MS analysis.

To examine the feasibility of annulations reaction, we began our optimization study of 1-(2-iodophenyl)-1*H*-pyrrole **1a** with diphenyl acetylene **2a**. When the starting materials **1a** and **2a** was treated in the presence of Zn alone in acetonitrile at 90 °C for 16 h, desired compound **3a** was not formed (Table 1, entry 1). Then, the combination of $NiBr_2$/Zn did not give the desired product (Table 1, entry 2). Upon employing $NiBr_2$/PPh_3 and $NiBr_2$/dppe system with Zn powder, we started to observe the product **3a** in 12% and 26% yields, respectively (Table 1, entries 3 and 4). The $NiBr_2(PPh_3)_2$ and $NiBr_2$(dppe) complexes were also effective for the cyclization reaction (Table 1, entries 5 and 6). Furthermore, increasing the reaction temperature as well as Zn equivalent increased the yield of product (Table 1, entries 7 and 8). Instead of CH_3CN, the use of toluene solvent improves the product yield **3a** in 60% (Table 1, entry 9). To our delight, after several optimization studies, we found that the **1a** (0.30 mmol), **2a** (0.60 mmol), $NiBr_2$(dppe) (10 mol %), and Zn (3 equiv), in toluene at 130 °C for 16 h, is the most appropriate condition for the formation of **3a** in 90% isolated yield (Table 1, entry 10). Until now, the best solvent has been toluene. Other solvents such as tetrahydrofuran (THF), 1,4-dioxane, 1,2-dichloroethane (1,2-DCE), and dimethylformamide (DMF) were ineffective for this catalytic reaction (Table 1, entries 11−15).

Under the optimized reaction conditions, 4-substituted 2-iodoarylpyrroles **1b**−**1d** with **2a** were tested; those results are summarized in Scheme 2. Thus, electron-donating 4-methyl-2-iodophenylpyrrole (**1b**) underwent annulations effectively with **2a** to give 4,5-diphenylpyrrolo[1,2-*a*]quinolines (**3b**) in 87%

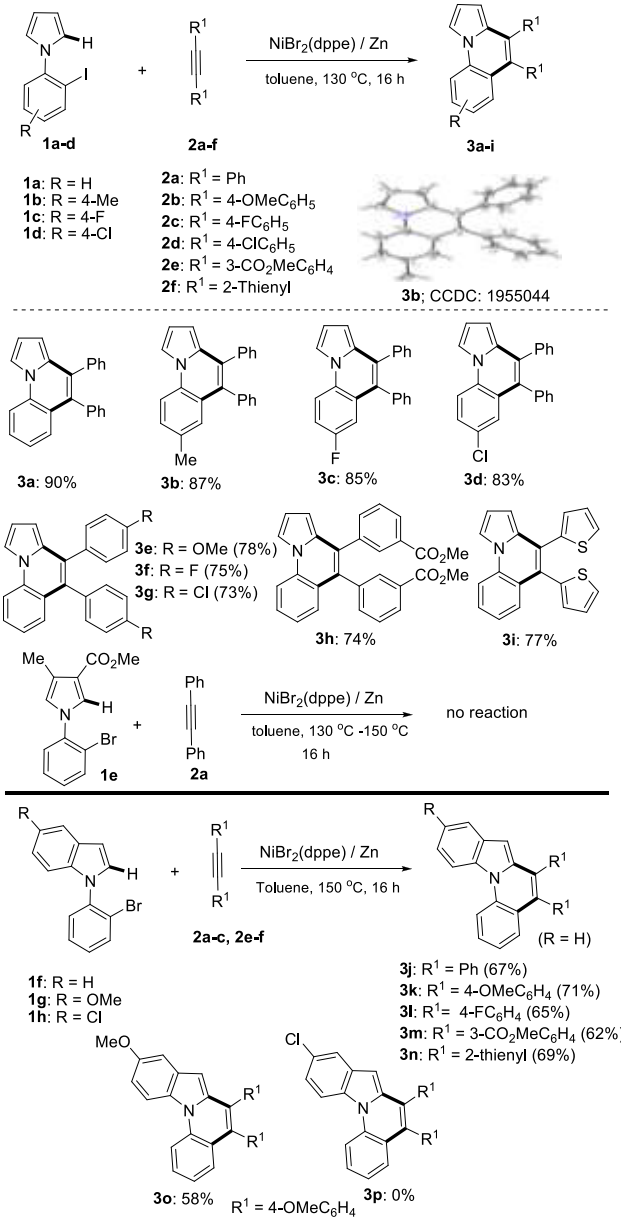
Table 1. Optimization Studies[a,b]



entry	catalyst	Zn (x equiv)	solvent	temperature, T (°C)	yield[b] (%)
1	–	1.5	CH_3CN	90	–
2	$NiBr_2$	1.5	CH_3CN	90	–
3	$NiBr_2/PPh_3$	1.5	CH_3CN	90	12
4	$NiBr_2$/dppe	1.5	CH_3CN	90	26
5	$NiBr_2(PPh_3)_2$	1.5	CH_3CN	90	20
6	$NiBr_2$(dppe)	1.5	CH_3CN	90	31
7	$NiBr_2$(dppe)	1.5	CH_3CN	110	45
8	$NiBr_2$(dppe)	2.5	CH_3CN	110	52
9	$NiBr_2$(dppe)	3	toluene	110	60
10	**$NiBr_2$(dppe)**	**3**	**toluene**	**130**	**90**
11	$NiBr_2$(dppe)	3	THF	110	trace
12	$NiBr_2$(dppe)	3	1,4-dioxane	110	trace
13	$NiBr_2$(dppe)	3	1,2-DCE	110	–
14	$NiBr_2$(dppe)	3	xylenes	130	–
15	$NiBr_2$(dppe)	3	DMF	130	trace

[a]Reactions were conducted using **1a** (0.30 mmol), **2a** (0.60 mmol), catalyst (10 mol %), and Zn (x equiv), in solvent (2 mL) at 130 °C for 16 h. [b]Isolated yield.

Scheme 2. Results of Annulation of 1-(2-iodophenyl)-1*H* pyrroles with Alkynes[ab]



[a]Reaction conditions: **1** (0.30 mmol), **2** (0.60 mmol), and Zn (3 equiv), in toluene (2 mL) at 130−150 °C for 16 h. [b]Isolated yield.

https://dx.doi.org/10.1021/acs.orglett.0c01055
Org. Lett. XXXX, XXX, XXX−XXX

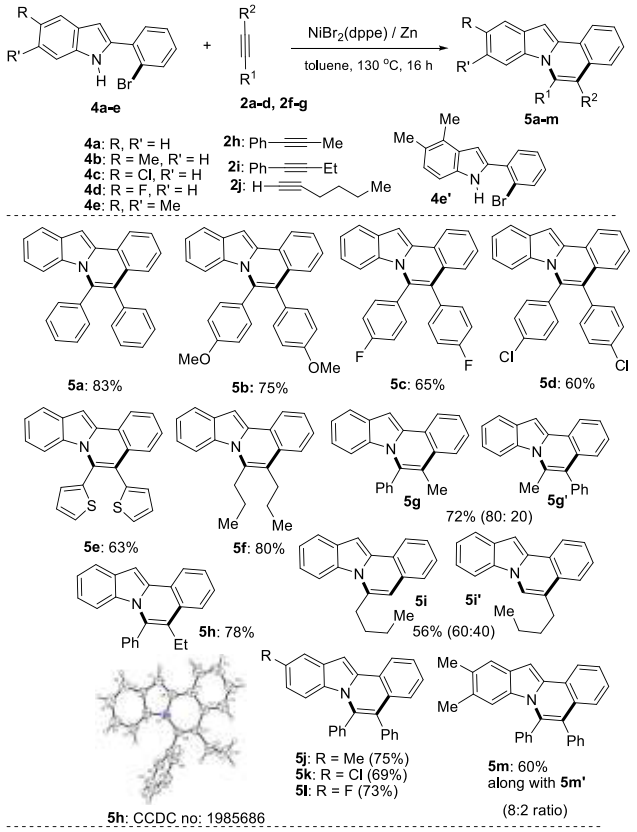
yield. Similarly, 4-fluoro-2-iodophenylpyrrole (**1c**) and 4-chloro-2-iodophenylpyrrole (**1d**) are also reacted nicely with **2a** to provide products **3c** and **3d** in 85% and 83% yields, respectively. In addition to **2a**, substituted alkynes (**2b**−**2f**) were investigated for the cyclization reactions. Thus, alkynes having both electron-rich and electron-deficient groups reacted nicely with **1a** to furnish expected cyclized products **3e**−**3h** in good yields. Similarly, di(2-thienyl)acetylene **2f** with **1a** gave 4,5-di(thiophen-2-yl)pyrrolo[1,2-*a*]quinoline **3i** in 77% yield. Unfortunately, the 3,4-disubstituted pyrrole **1e** with **2a** failed to give a cyclized product under standard reaction conditions (130 °C −150 °C), because of the steric (or) electronic effect of ester and methyl groups on the 3,4-position of pyrrole **1e**. However, we recovered both of the starting materials, along with partial debromination of 3,4-disubstituted pyrrole **1e**.

To evaluate the scope of the present reaction, treatment of 1-(2-bromoaryl)-1*H*-indole **1f** reacted well with **2a** in the presence of $NiBr_2$(dppe) (10 mol %), Zn (3 equiv), toluene at 150 °C for 16 h to give 5,6-diphenylindolo[1,2-*a*]quinoline **3j** in 67% yield (Scheme 2 bottom). Under similar reaction conditions, various internal alkynes **2b**, **2c**, **2e**, **2f** effectively reacted with **1f** to afford the corresponding 5,6-diarylindoloquinolines **3k**−**3n** in 71%−69% yields (Scheme 2). In addition to **1f**, substituted indoles (**1g** and **1h**) were also tested for this cyclization reaction. Thus, the 1-(2-bromophenyl)-5-methoxy-1*H*-indole (**1g**) nicely reacted with alkyne (**2b**) to give cyclized product **3o** in 58% yield. However, 1-(2-bromophenyl)-5-chloro-1*H*-indole (**1h**) unfortunately failed to give an expected product **3p** with alkynes (**2a** or **2b**) under standard reaction conditions.

Furthermore, the scope of the present Ni/Zn annulations reaction can also be applied to 2-(2-bromophenyl)-1*H*-indoles with alkynes and the results are summarized in Scheme 3. The reaction of 2-(2-bromophenyl)-1*H*-indole (**4a**) with diphenylacetylene (**2a**), $NiBr_2$(dppe) (10 mol %), and Zn (3 equiv), in toluene at 130 °C for 16 h afforded 5,6-diphenylindolo[2,1-*a*]isoquinoline **5a** in 83% yield.

Note that, so far, a few examples of Ni/Zn-catalyzed C−C/C−N bond formation have been explored for the synthesis of heterocyclic compounds.[8,9] The ruthenium- and rhodium-catalyzed C−H/N-H activation for the construction of indolo[2,1-*a*]isoquinolines has been reported.[10] However, very recently, Chatani and co-workers reported a Ni-catalyzed synthesis of 5,6-disubstituted indolo[2,1-*a*]isoquinolines via oxidative C−H/N−H coupling of 2-phenylindoles with alkynes.[11] Thus, the development of efficient alternative catalysts/approaches for the synthesis of useful 5,6-diarylindolo[2,1-*a*]isoquinolines is still desirable. Under similar reaction conditions, other internal alkynes (**2b**, **2c**, **2d**, and **2f**) nicely participated with **4a** to give corresponding annulated products **5b**−**5e** in 60%−75% yields. Interestingly, oct-4-yne (**2g**) also reacted with **4a** to afford the expected compound **5f** in 80% yield. To understand the regioselectivity of this reaction, we performed using the unsymmetrical alkynes as substrates for the reaction with **4a**. For example, 1-phenyl-1-propyne (**2h**) underwent cyclization with **4a** at 130 °C for 16 h to afford two regioisomers **5g** and **5g′** (80:20 ratio) in 72% combined yield (Scheme 3). Similarly, the reaction between **4a** and 1-phenyl-1-butyne (**2i**), to afford product **5h** in 78% yield, along with a trace of isomer **5h′** (observed in ^{1}H NMR). Furthermore, the regiochemistry of product **5h** was confirmed by single-crystal X-ray diffraction. Encouraged by these results, the terminal alkyne 1-hexyne (**2j**) reacted with **4a** to give

Scheme 3. Results of Annulations of 4 with Alkynes[a,b]



[a]Reaction conditions: **4** (0.30 mmol), **2** (0.60 mmol), and Zn (3 equiv), in toluene (2 mL) at 130 °C for 16 h. [b]Isolated yield.

regioisomeric products **5i** and **5i′** in 56% combined yield with a 60:40 ratio. However, under similar reaction conditions, phenylacetylene with **4a** failed to give expected product, rather we could observe only a complex mixture on the TLC. In addition to **4a**, 2-(2-bromophenyl)-5-methyl-1*H*-indole (**4b**), 2-(2-bromophenyl)-5-chloro-1*H*-indole (**4c**) and 2-(2-bromophenyl)-5-fluoro-1*H*-indole (**4d**) worked well with **2a** to give products **5j**−**5l** in good yields. Similarly, the regioisomeric 2-(2-bromophenyl)-5,6-dimethyl-1*H*-indole (**4e**)/2-(2-bromophenyl)-4,5-dimethyl-1*H*-indole (**4e′**) (8:2 ratio) effectively reacted with **2a** to give isomeric products **5m** and **5m′** in 60% yield with 8:2 ratio, respectively (Scheme 3).

The efficiency of the cyclization reaction was demonstrated through the gram-scale preparation of **5a** (Scheme 4). Thus, the reaction of 2-(2-bromophenyl)-1*H*-indole **4a** (0.5 g, 1.83 mmol) with diphenylacetylene **2a** (0.65g, 3.67 mmol), $NiBr_2$(dppe) (10 mol %), and Zn (3 equiv), in toluene at 130 °C for 16 h afforded product **5a** in 78% yield.

Furthermore, the synthetic transformations of **5a** are also explored. Thus, the treatment of 5,6-diphenylindolo[2,1-*a*]isoquinoline 5a with ethyl acrylate in the presence of $Pd(OAc)_2$/$Cu(OAc)_2$ in a mixture of solvent (DMF/DMSO) at 70 °C for 18 h gave Heck coupling product **6a** in 79% isolated yield.[12a] Next, the 1,6-conjugate addition reaction of **5a** with *p*-quinone methide in the presence of $ZnBr_2$ (10 mol %) in DCE at room temperature for 1 h gave the corresponding triarylmethane **7a** in 91% yield (Scheme 4).[12b] In addition, we have also performed preliminary photophysical studies for the synthesized pyrrolo/indoloquinoline and

https://dx.doi.org/10.1021/acs.orglett.0c01055
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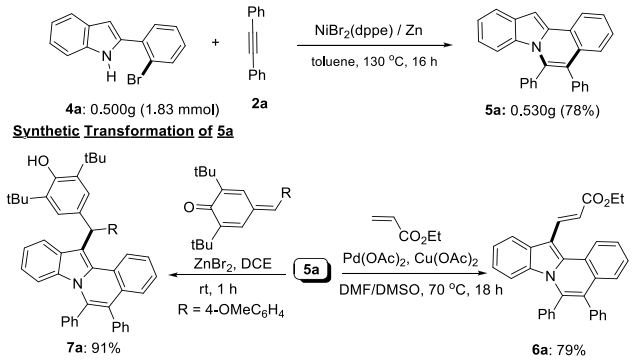
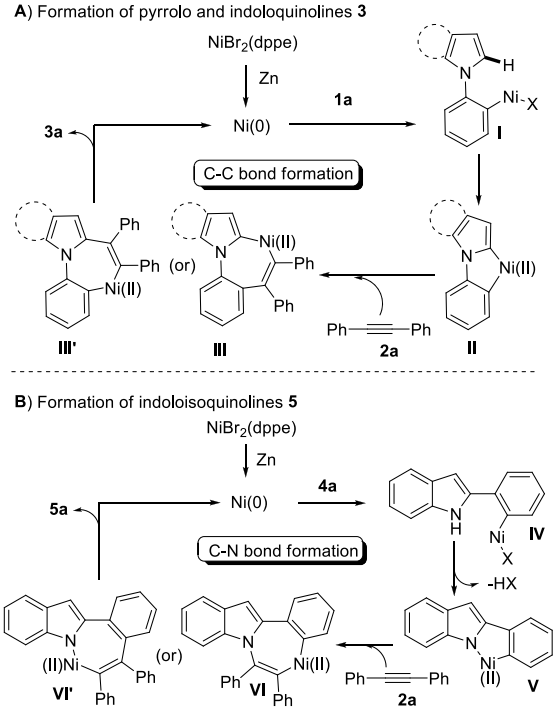
Scheme 4. Gram Scale Reaction of 4a with 2a and Synthetic Applications



indolo[2,1-*a*]isoquinoline compounds (see the Supporting Information for details).

On the basis of previous metal-catalyzed annulation reactions,[8,13] we proposed the following Ni-catalyzed reaction mechanism in Scheme 5A. First, the catalytic cycle initiated by

Scheme 5. Plausible Mechanism



Zn metal, which reduces Ni(II)-complex to active Ni(0)-complex.[8] Then, 1-(2-iodophenyl)-1*H*-pyrrole **1a** undergo oxidative addition to Ni(0) species, followed by pyrrole C(2)−H activation to a give five-membered nickelacycle **II**. Next, coordinative insertion of alkyne **2a** into the intermediate **II** generated a seven-membered nickelacycles **III** (or) **III′**. Subsequent reductive elimination of **III** (or) **III′** furnished product **3a** and the regeneration of the active nickel(0) species.

Furthermore, we also proposed a possible mechanism for the present C−N bond formation reaction in Ni-catalysis (Scheme 5B). The first step likely starts with the reduction of Ni(II) to Ni(0) species with the aid of zinc metal. Oxidative addition of 2-(2-bromophenyl)-1*H*-indole **4a** to Ni(0) leads to the formation of a five-membered azanickelacycle **V** with release of HX. Next, the coordinative insertions of the alkyne **2a** into the azanickelacycle **V** to give intermediates **VI** and **VI′**. Reductive elimination of intermediates **VI** and **VI′** affords cyclized product **5a** and regenerate Ni(0) species for the next cycle.

In conclusion, a new method for the construction of pyrrolo/indoloquinolines and indolo[2,1-*a*]isoquinolines by air-stable nickel catalyst via C−C and C−N bond connection, respectively, in one pot have been developed. This protocol provides an opportunity for the efficient synthesis of various heterocycles from simply prepared starting materials. In this transformation, which involves an activation of the C−H or N−H bond through nickel, coordinative insertion was followed by a reductive elimination approach. In addition, we have also performed preliminary photophysical studies for the synthesized compounds. Further studies toward investigation on the reaction mechanism and the application of this methodology on the organic materials are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01055.

General experimental procedure, photophysical studies, and characterization details (PDF)

Accession Codes

CCDC 1955044 and 1985686 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

K.P. gratefully acknowledge the financial support of the DST-SERB (YSS/2014/000566) New Delhi, India, and we also thank DST-FIST for NMR and HRMS facilities. We thank SAIF, IIT Madras, for X-ray crystallography analysis.

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https://dx.doi.org/10.1021/acs.orglett.0c01055
Org. Lett. XXXX, XXX, XXX−XXX