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Note

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Nickel-Catalyzed Direct Alkenylation of Methyl-Heteroarenes with Primary Alcohols

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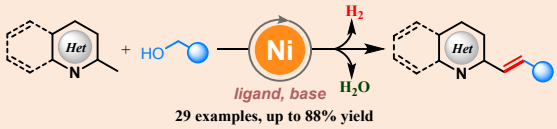
Supporting Information



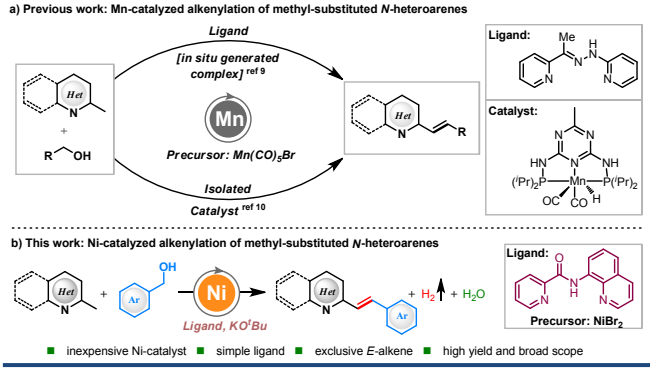
29 examples, up to 88% yield

ABSTRACT: An efficient nickel-catalyzed acceptorless dehydrogenative coupling of methyl-substituted heteroarenes with primary alcohols is achieved using an *in situ* generated complex of inexpensive $NiBr_2$ and readily available 8-aminoquinoline picolinic amide ligand. The protocol is operationally simple, scalable, and furnished a series of high-value 2-alkenyl heteroarenes in good yields (up to 88%) with exclusive *E*-selectivity. The reaction proceeds with the release of water and molecular hydrogen, which was analyzed through gas chromatography to validate the reaction mechanism.

Devising catalytic protocols to forge value-added products from feed-stock materials under environmentally benign conditions is a continuous enterprise in contemporary organic synthesis. In this context, the conversion of alcohols into important classes of chemical commodities offers a useful contribution towards the conservation of finite fossil carbon resources.[1] Specifically, catalytic dehydrogenative coupling reactions of alcohols turned out very effective to construct various carbon-carbon and carbon-heteroatom bonds with applications in the synthesis of pivotal carbocycles and heterocycles.[2] However, the majority of these transformations involve precious late-transition-metal based catalysts.[2a-c] Delicacy of the first-row-transition metals lies in the fact that they are highly abundant, less toxic, and cheaper than the late-transition-metals and thus, the utilization of first-row-transition metal based catalysis for the advancement of similar transformations is highly desirable.[2d-e]

Olefins are essential building blocks for the construction of important molecular frameworks including natural product.[3] Particularly, aryl-substituted olefins bearing *N*-heteroarene unit represent various drug molecules and agrochemicals having promising biological activities.[4] They have also found applications in the synthesis of high electron affinity polymers for light emitting diodes (LEDs).[5] Recently, as a transformative alternative to furnish functionalized alkenes, acceptorless dehydrogenative coupling (ADC) of alcohols with C–H acidic compounds, where water and hydrogen are sole byproducts, has gained significant attention.[6] Following the pioneering work of Milstein,[7] there has been a rush in the scientific community and, among the first-row transition metals, successes have primarily been accomplished with Mn-catalysis.[8] Recently, Maji group reported Mn-NNN pincer complexes for the α-olefination of methyl substituted heteroarenes using primary alcohols (Scheme 1a, top).[9]At the same time, Kempe group independently utilized isolated Mn-catalyst stabilized by PNP ligand for the olefination of heteroarene (Scheme 1a, bottom).[10] Kempe catalyst was also successfully utilized to prepare vinyl sulfone and α,β unsaturated ketones.[11] While these protocols are very effective, necessity in the use of expensive $Mn(CO)_5Br$ as the catalyst precursor and utilization of electron-rich PNP ligand are pivotal issues. Meanwhile, nickel catalysis has turned out very promising alternative to noble metal catalysis for various organic transformations and coupling processes.[12] It has also been successfully implemented in various transfer hydrogenation reactions.[2n,13] However, utilization of nickel catalysis in acceptorless dehydrogenative olefination processes is underdeveloped.[14]

Scheme 1. Transition-Metal-Catalyzed Olefination of Methyl-Substituted Heteroarenes



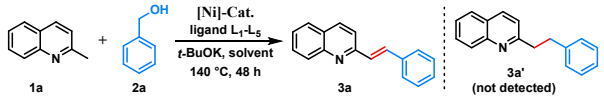
Herein, we report the α-olefination of heteroarenes with the extrusion of hydrogen gas through the development of a nickel-catalyzed acceptorless dehydrogenative coupling of primary alcohols with methyl-substituted heteroarenes (Scheme 1b).

It is worth noting that, during the preparation of our manuscript, Balaraman *et al*. communicated a nickel-NNN pincer complex for the synthesis of styrenes and stilbenes from benzyl alcohols and sulfones.[15]

We commenced our investigations by following the reaction of 2-methylquinoline **1a** and benzyl alcohol **2a** using different Ni-catalysts in combination with diverse *N*-based amide ligands (Table 1). Satisfyingly, olefination proceeded smoothly when mixture of **1a** and **2a** in *t*-BuOH was exposed to Ni-complex generated *in situ* from $NiCl_2$ and 8-aminoquinoline picolinic amide ligand $\mathbf{L_1}$ in the presence of *t*-BuOK at 140 °C and the desired product 2-styryl quinoline **3a** was isolated in 70% yield (entry 1). The reaction was also efficient with $NiCl_2$.DME (73%) and yield further improved to 88% when $NiBr_2$ was employed (entries 2-3). Notably, the alkylation product **3a'** was not detected for these cases. Further screening of ligands revealed that the reaction was unfruitful with ligand $\mathbf{L_2}$ and only 40% yield of **3a** was obtained with ligand $\mathbf{L_3}$ (entries 4-5). Screening of bidentate

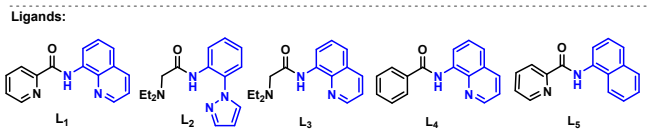
ligand **L_4–L_6** gave inferior results (entries 6-8). Changing the reaction solvent from *t*-BuOH to THF (38%), dioxane (17%), and toluene (59%) also showed detrimental effect (entries 9-11). Control experiments revealed that all the components, Ni-catalyst, ligand, and base were essential for this reaction and the reaction was ineffective in the absence of any of them (entries 12-14).

Table 1. Optimization of the Nickel-Catalyzed Olefination[a]



entry	[Ni]-catalyst	ligand (L)	solvent	yield(%)[b]
1	$NiCl_2$	L_1	*t*-BuOH	70
2	$NiCl_2$.DME	L_1	*t*-BuOH	73
3	**$NiBr_2$**	**L_1**	***t*-BuOH**	**88**
4	$NiBr_2$	L_2	*t*-BuOH	trace
5	$NiBr_2$	L_3	*t*-BuOH	40
6	$NiBr_2$	L_4	*t*-BuOH	18
7	$NiBr_2$	L_5	*t*-BuOH	22
8[c]	$NiBr_2$	L_6	*t*-BuOH	28
9	$NiBr_2$	L_1	THF	38
10	$NiBr_2$	L_1	dioxane	17
11	$NiBr_2$	L_1	toluene	59
12	-	L_1	*t*-BuOH	<10
13	$NiBr_2$	-	*t*-BuOH	<10
14[d]	$NiBr_2$	L_1	*t*-BuOH	0

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.25 mmol), [Ni]-cat. (0.025 mmol, 10 mol %), ligands L_1–L_6 (0.025 mmol, 10 mol%), *t*-BuOK (0.275 mmol, 1.1 equiv), solvent (0.5 mL), 140 °C, 48 h. [b]Isolated yield of **3a**. [c]L_6 was bipyridine. [d]In the absence of *t*-BuOK.

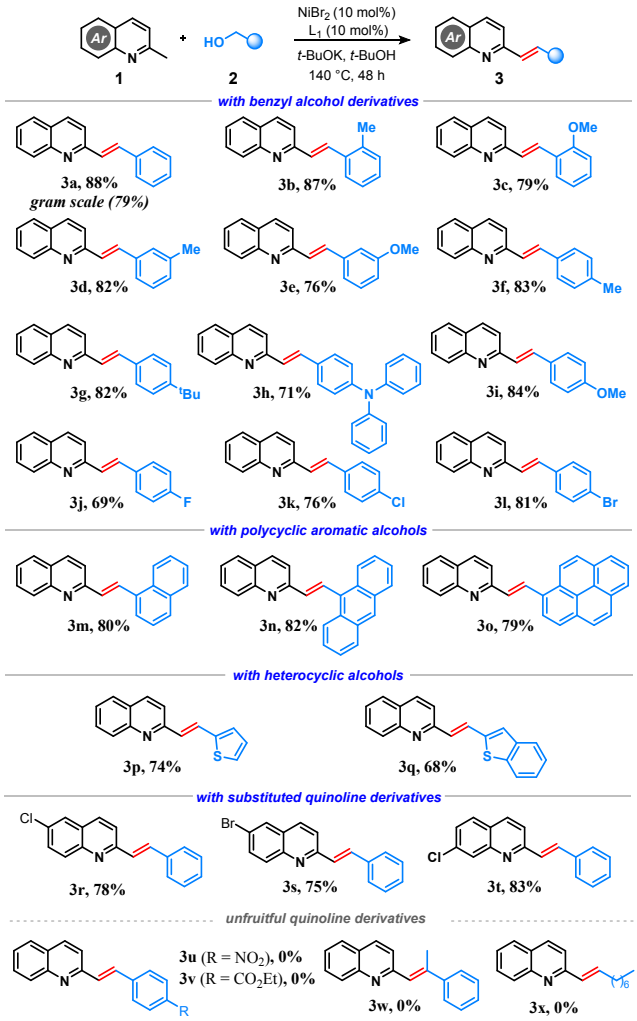


With the optimized reaction conditions in hand, we explored the scope of this olefination reaction and results are summarized in Scheme 2. The high efficiency shown by the $NiBr_2/L_1$ catalyst system in the model reaction was effectively translated to a wide variety of substituted 2-methylquinoline derivatives **1** with different alcohol derivatives **2** and exclusive *E*-selectivity was observed in all cases. Alcohols having electron-donating substituents such as methyl (**3b**,**d**,**f**), methoxy (**3c**,**e**,**i**), *t*-butyl (**3g**), diphenylamino (**3h**) and electron-deficient halogen substituents (**3j**–**l**) at *para*-, *meta*-, and *ortho*-positions of the aryl ring delivered 2-olefinated quinolines in good yields (69-88%). Interestingly, sterically hindered aromatic alcohols such as 1-napthylmethanol, 9-anthracenemethanol and 1-pyrenemethanol underwent cross-dehydrogenative coupling smoothly to afford the alkene products **3m**–**o** in high yields. Also, heterocyclic primary alcohols, for examples 2-thiophenemethanol and benzothiophene-2-methanol, furnished unsymmetrical 1,2-heteroaryl alkenes **3p** and **3q** in 74% and 68% yields, respectively. Substitutions in the quinoline ring were also considered; 6-chloro, 6-bromo, and 7-chloro substituted 2-methylquinolines gave desired products **3r**–**t** in uniformly high yields.

Unfortunately, under the present reaction conditions, benzyl alcohols with strongly electron withdrawing substituents (nitro, ester), secondary alcohol, and aliphatic alcohol such as 1-octanol did not deliver the desired alkenylation products **3u**-**x** (Scheme 2).

Scale up was also suitable; gram scale reaction of **1a** with **2a** gave the desired product **3a** in 79% yield, which is comparable to the small scale reaction (Scheme 2).

Scheme 2. Olefination Scope with 2-Methylquinolines and Primary Alcohols[a]

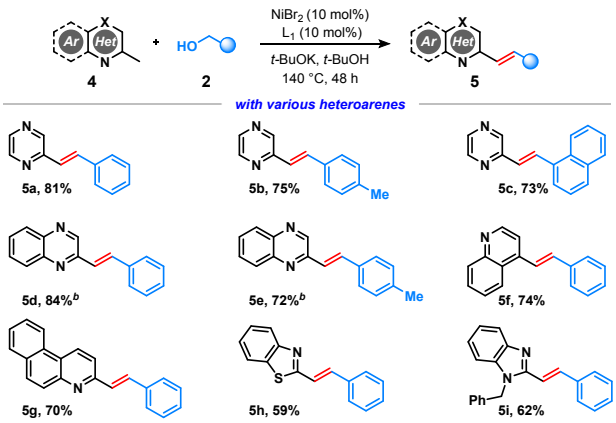


[a]Reaction conditions: **1** (0.5 mmol), **2** (0.25 mmol), $NiBr_2$ (0.025 mmol, 10 mol%), L_1 (0.025 mmol, 10 mol%), *t*-BuOK (0.275 mmol, 1.1 equiv), *t*-BuOH (0.5 mL), 140 °C, 48 h. Yields of isolated products were given.

The versatility of the protocol was further explored by studying olefination with different heteroarenes (Scheme 3). Under the standard reaction conditions, 2-methylpyrazine cleanly reacted with benzyl alcohol, *p*-tolylmethanol, and 1-naphthalenemethanol to produce corresponding 2-olefinated pyrazines **5a-c** in high yields. 2-Methylquinoxaline was also a good substrate for this process, offering **5d**–**e** in very high yields. 4-Methylquinoline and 3-methylbenzo[*f*]quinoline also rendered desired olefins **5f** and **5g**

in 74% and 70% yields, respectively. Other alkyl heteroarenes such as 2-methylbenzothiazole and 1-benzyl-2-methylbenzimidazole were also effectively participated in this cross-dehydrogenative olefination reaction, forging **5h** and **5i**, respectively, in synthetically useful yields (Scheme 3).

Scheme 3. Scope of α-Olefination with Diverse Methyl-Substituted *N*-heteroarenes[a]

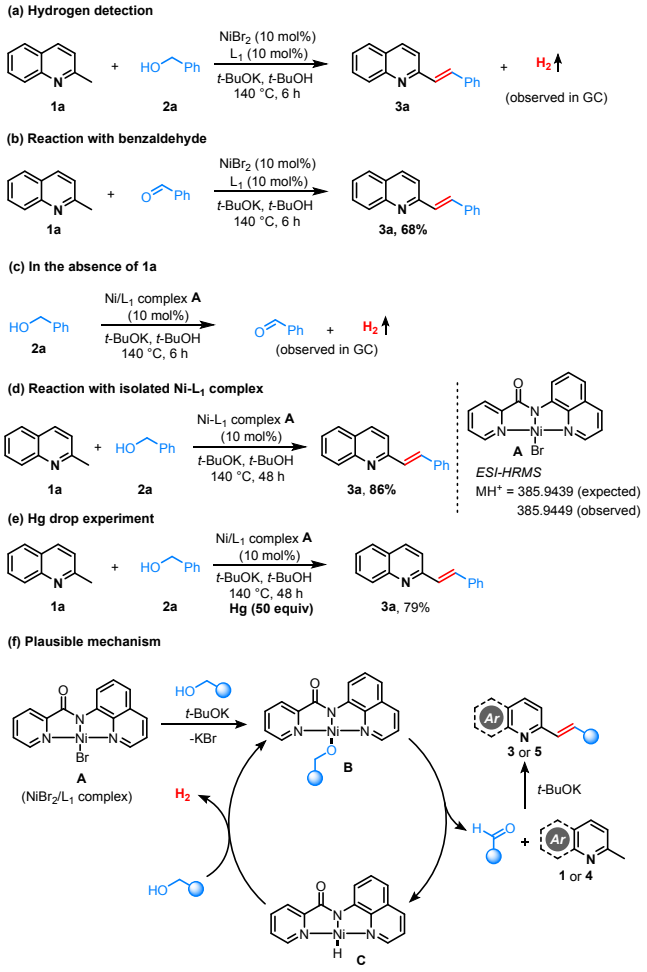


[a]Reaction conditions: **4** (0.5 mmol), **2** (0.25 mmol), $NiBr_2$ (0.025 mmol, 10 mol%), L_1 (0.025 mmol, 10 mol%), *t*-BuOK (0.275 mmol, 1.1 equiv), *t*-BuOH (0.5 mL), 140 °C, 48 h. Yields of isolated products weregiven.[b]**4** (0.25 mmol) and **2** (0.50 mmol) were used.

To gain mechanistic insight of this alkenylation reaction, various experiments were carried out. Gas chromatography analysis during the course of the reaction under optimal reaction conditions confirmed the formation of hydrogen gas and benzaldehyde (Scheme 4a). Under standard reaction conditions, **1a** also smoothly reacted with benzaldehyde to give desired product **3a** (Scheme 4b). Further, when **2a** was treated under the reaction conditions in the absence of **1a**, benzaldehyde was formed along with the liberation of hydrogen gas (Scheme 4c). These findings suggest that the present alkenylation reaction proceeds via acceptorless dehydrogenative coupling pathway. Further, Ni-L_1 complex **A** was isolated and characterized through ^{1}H-NMR, ^{13}C-NMR, and HRMS spectroscopic techniques.[16] When the benchmark reaction of **1a** with **2a** was tested using isolated Ni-L_1 complex under optimal reaction conditions, product **3a** was isolated in
86% yield (Scheme 4d). When the olefination reaction was performed in the presence of excess mercury (50 equiv), the expected product was obtained in 79% yield, confirming the homogeneity of the present catalytic system and refuting the involvement of metal nanoparticles (Scheme 4e).

Based on these findings and previous literature reports,[14a-c] a plausible reaction mechanism of Ni-NNN pincer catalyst for alkenylation of methyl-substituted heteroarene with primary alcohol is depicted in Scheme 4f. The active complex **A** thus formed from $NiBr_2$ and ligand $\mathbf{L_1}$ reacts with primary alcohol in the presence of *t*-BuOK to give Ni-alkoxide species **B**. It then undergoes β-H elimination to give the corresponding aldehyde and nickel-hydride species **C**. The liberated aldehyde condensed with 2-alkyl heteroarene (**1** or **4**) to afford alkenylated product **3** or **5**. Further, reaction of primary alcohol with nickel-hydride species **C** generates alkoxy complex **B** with the liberation of hydrogen and continues the catalytic cycle.

Scheme4. Mechanistic Investigations and Plausible Reaction Mechanism



In conclusion, we have identified a Ni(II) complex of readily available 8-aminoquinoline picolinic amide ligand for acceptorless dehydrogenative coupling (ADC) of primary alcohols with 2-methylheteroarenes. A series of high-value α-olefinated heteroarenes were prepared in good to very high yields with complete *E*-selectivity. The catalytic protocol is scalable, uses inexpensive $NiBr_2$ as the catalyst precursor, and is environmentally benign as water and molecular hydrogen are sole byproducts. Further, applications of such catalytic processes are currently ongoing in our laboratory.

EXPERIMENTAL SECTION

All non-aqueous reactions were carried out under an argon atmosphere in flame-dried glassware and were stirred using a magnetic stir plate. All the 2-Methylheteroarenes (**1** and **4**) and 4-methyquinoline were received from Aldrich and ABC labtory companies and used without further purification. All reactions were carried out using anhydrous solvent unless otherwise noted. DMSO and DMF were purchased from Acros Organic Company. Dry toluene, xylene, tetrahydrofuran and 1,4-dioxane were prepared by distilling over sodium ketyl. Anhydrous potassium tert-butoxide and anhydrous tert-Butyl alcohol was purchased from Aldrich Company.All reactions were monitored by thin layer

chromatography (TLC) on WhatmanPartisil®K6F TLC plates (silica gel 60 Å, 0.25 mm thickness) and visualized using a UV lamp (366 or 254 nm) or by use of one of the following visualization reagents: PMA: 10 g phosphomolybdic acid/ 100 mL ethanol, $KMnO_4$: 0.75 g potassium permanganate, 5 g K_2CO_3 / 100mL water. Products were isolated by column chromatography (Merck silica gel 100-200µm). Yields refer to chromatographically and spectroscopically homogenous materials unless noted otherwise. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 or Bruker 500 MHz spectrometers. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak $CDCl_3$ δ = 7.260 ppm for ^1H, δ = 77.160 ppm for ^{13}C calibrated to tetramethylsilane (δ = 0.00). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; tt, triplet of triplet; dq, doublet of quartet; br, broad; app, apparent. Mass spectra were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source. GC-TCD (Agilent-7820 A) analysis was carried out using 5A and porapak Q column connected in series using gas switching valve.Ligands (**L_1 – L_5**)[17-18] were prepared according to the literature procedure.

Procedure for Nickel-catalyzed direct alkenylation of alkyl-heteroarenes with primary alcohols:

Methyl-heteroarene **1** (0.5 mmol), primary alcohols **2** (0.25 mmol), $NiBr_2$ (0.025 mmol, 10 mol %), Ligand **L_1** (0.025 mmol, 10 mol%) and *t*-BuOK (0.275 mmol, 1.1 equiv) were taken in a dried schlenk tube with a magnetic stir bar under argon. Then, dry *t*-BuOH (0.5 mL) was added with a syringe. The reaction tube was closed and the resulting mixture was placed in a preheated oil bath at 140 ºC for 48 h. After completion, the reaction was quenched with water (3 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture (95:5 to 85:15) as eluent.

***(E)*-2-Styrylquinoline 3a[19]:** White solid, yield: 88% (51 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.64 (m, 5H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.41 – 7.39 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 1H); **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 156.2, 148.4, 136.7, 136.5, 134.6, 129.9, 129.4, 129.2, 128.9, 128.8, 127.6, 127.5, 127.4, 126.3, 119.4.

(*E*)-2-(2-Methylstyryl)quinoline 3b[20]: Colorless oil, yield: 87% (53 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 2H), 7.95 (d, *J* = 16.2 Hz, 1H), 7.80 – 7.67 (m, 5H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 16.1 Hz, 1H), 7.24 (brs, 2H), 2.53 (s, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 156.4, 148.4, 136.7, 136.5, 135.7, 132.3, 130.7, 130.3, 129.9, 129.4, 128.6, 127.6, 127.5, 126.5, 126.3, 126.0, 119.5, 20.2.

(*E*)-2-(2-Methoxystyryl)quinoline 3c[20]: Colorless oil, yield: 79% (50 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 2H), 8.03 (d, *J* = 16.6 Hz, 1H), 7.77 – 7.67 (m, 4H), 7.49 – 7.45 (m, 2H), 7.33 – 7.26 (m, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 157.5, 156.8, 148.3, 136.2, 129.9, 129.7, 129.6, 129.5, 129.2, 127.6, 127.4, 127.3, 126.1, 125.6, 120.9, 119.1, 111.1, 55.6.

(*E*)-2-(3-Methylstyryl)quinoline 3d[20]: White solid, yield: 82% (50 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.51 – 7.39 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 2.40 (s, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 156.2, 148.4, 138.5, 136.6, 136.5, 134.7, 129.9, 129.6, 129.3, 129.0, 128.8, 128.1, 127.6, 127.5, 126.3, 124.6, 119.3, 21.6.

(*E*)-2-(3-Methoxystyryl)quinoline 3e[9]:White solid, yield: 76% (49 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.11– 8.07 (m, 2H), 7.76 (d, *J* = 8 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.64 (d, *J* = 11.5 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 16.3 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.23 – 7.19 (m, 2H), 6.89 (dd, *J* = 8.1, 2.1 Hz, 1H), 3.85 (s, 3H).**$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 160.0, 156.0, 148.3, 138.0, 136.5, 134.5, 129.9 (2C), 129.4, 129.3, 127.6, 127.5, 126.3, 120.3, 119.3, 114.9, 112.0, 55.4.

(*E*)-2-(4-Methylstyryl)quinoline 3f[20]: White solid, yield: 83% (51 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.64 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 16.3 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 156.3, 148.4, 138.9, 136.4, 134.6, 133.9, 129.8, 129.7, 129.3, 128.2, 127.6, 127.4, 127.3, 126.2, 119.3, 27.6.

(*E*)-2-(4-(Tert-butyl)styryl)quinoline 3g[10]: White solid, yield: 82% (59 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.1, 6.3 Hz, 2H), 7.78 – 7.76 (m, 1H), 7.72 – 7.69 (m, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.49 (m, 1H) 7.44 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 16.4 Hz, 1H), 1.36 (s, 9H).**$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 156.4, 152.1, 148.4, 136.4, 134.4, 133.8, 129.8, 129.2, 128.4, 127.6, 127.4, 127.2, 126.2, 125.9, 119.2, 31.4.

(*E*)-N,N-Diphenyl-4-(2-(quinolin-2-yl)vinyl)aniline 3h: Yellow solid, yield: 71% (71 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.60 (m, 3H), 7.51 – 7.45 (m, 3H), 7.31 – 7.25 (m, 5H), 7.15 – 7.13 (d, *J* = 7.8 Hz, 4H), 7.08 – 7.05 (m, 4H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 156.5, 148.5, 148.4, 147.5, 136.7, 134.2, 130.3, 129.8, 129.5, 129.2, 128.3, 127.6, 127.4, 127.1, 126.1, 125.1, 123.6, 122.9, 119.2. **HRMS** (TOF MS ES+) calcd.for $C_{29}H_{22}N_2H^+$ [M + H^+] m/z 399.1861, found 399.1870.

(*E*)-2-(4-Methoxystyryl)quinoline 3i[20]: White solid, yield: 84% (55 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.12– 8.06 (m, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.58 (m, 5H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 17.5 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 2H), 3.85 (s, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 160.3, 156.5, 148.4, 136.4, 134.3, 129.8, 129.5, 129.2, 128.8, 127.6, 127.4, 127.0, 126.1, 119.3, 114.4, 55.5.

(*E*)-2-(4-Fluorostyryl)quinoline 3j[21]: White solid, yield: 69% (43 mg); **^1H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.66 (d, *J* = 9.3 Hz, 1H), 7.62 – 7.59 (m, 3H), 7.52 – 7.48 (m, 1H), 7.31 (d, *J* = 16.3 Hz, 1H), 7.09 (t, *J* = 8.6 Hz, 2H).**$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.4 Hz), 155.9, 148.4, 136.5, 133.3, 132.8 (d, *J* = 3.4 Hz), 129.9, 129.3, 129.0 (d, *J* =8.1 Hz), 128.8 (d, *J* =2.3 Hz), 127.7, 127.5, 126.3, 119.4, 116.0 (d, , *J* = 21.6 Hz).

(*E*)-2-(4-Chlorostyryl)quinoline 3k[20]: White solid, yield: 76% (50 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (t, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.33 (m, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.7, 148.4, 136.5, 135.2, 134.4, 133.1, 129.9, 129.6, 129.3, 129.1, 128.5, 127.6, 126.4, 121.0, 119.5.

(*E*)-2-(4-Bromostyryl)quinoline 3l[21]: White solid, yield: 81% (63 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.53 – 7.48 (m, 5H), 7.40 – 7.36 (m, 1H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.7, 148.4, 136.6, 135.6, 133.3, 132.1, 130.0, 129.7, 129.3, 128.8, 127.7, 127.6, 126.5, 122.7, 119.5.

(*E*)-2-(2-(Naphthalen-1-yl)vinyl)quinoline 3m[10]: White solid, yield: 80% (56 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 16.0 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 8.17 – 8.13 (m, 2H), 7.93 – 7.71 (m, 6H), 7.61 – 7.46 (m, 5H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 156.2, 148.4, 136.6, 134.2, 133.9, 131.9, 131.6, 131.5, 129.9, 129.4, 129.1, 128.8, 127.7, 127.6, 126.5, 126.4, 126.1, 125.8, 124.3, 123.9, 119.7.

(*E*)-2-(2-(Anthracen-9-yl)vinyl)quinoline 3n: Yellow solid, yield: 84% (69 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 16.5 Hz, 1H), 8.45 – 8.43 (m, 2H), 8.32 (dd, *J* = 5.7, 3.3 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.05 – 8.03 (m, 2H), 7.86 – 7.84 (m, 1H), 7.81 – 7.74 (m, 3H), 7.57 – 7.55 (m, 1H), 7.51 – 7.48 (m, 3H), 7.29 (dd, *J* = 16.4 Hz, 1H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.7, 148.5, 137.6, 136.7, 134.3, 133.6, 132.0, 131.6, 131.2, 130.0, 129.8, 129.6, 128.9, 127.7, 127.4, 127.3, 126.5, 126.1, 125.9, 125.4, 119.8. **HRMS** (TOF MS ES+) calcd.for $C_{25}H_{17}NH^+$ [M + H$^+$] m/z 332.1439, found 332.1450.

(*E*)-2-(2-(Pyren-1-yl)vinyl)quinoline 3o: Yellow solid, yield: 79% (70 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.83 (d, *J* = 15.9 Hz, 1H), 8.61 (d, *J* = 9.1 Hz, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 8.20 – 8.16 (m, 5H), 8.10 – 8.00 (m, 4H), 7.81 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 15.9 Hz, 1H), 7.54 – 7.50 (m, 1H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 156.2, 148.4, 136.6, 131.7, 131.6, 131.6, 131.4, 131.0, 131.0, 130.0, 129.4, 129.2, 128.1, 127.9, 127.7, 127.6 (2C), 126.4, 126.2, 125.7, 125.4, 125.4, 125.2, 125.0, 124.1, 123.1, 119.8. **HRMS** (TOF MS ES+) calcd.for $C_{27}H_{17}NH^+$ [M + H$^+$] m/z 356.1439, found 356.1458.

(*E*)-2-(2-(Thiophen-2-yl)vinyl)quinoline 3p[20]: White solid, yield: 74% (44 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.72 – 7.68 (m, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.30 – 7.29(m, 1H), 7.24 – 7.19 (m, 2H), 7.06 – 7.04 (m, 1H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.7, 148.4, 142.2, 136.5, 129.9, 129.2, 128.3, 128.3, 128.0, 127.6, 127.5, 127.4, 126.3, 126.2, 119.5.

(*E*)-2-(2-(Benzo[*b*]thiophen-2-yl)vinyl)quinoline 3q: White solid, yield: 68% (49 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 15.9 Hz, 1H), 7.82 – 7.70 (m, 4H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.43 (s, 1H), 7.37 – 7.32 (m, 2H), 7.26 (d, *J* = 15.9 Hz, 1H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.3, 148.5, 142.3, 140.2, 139.7, 136.6, 130.8, 130.0, 129.4, 128.0, 127.7, 127.6, 126.5, 125.7, 125.5, 124.8, 124.0, 122.5, 119.9. **HRMS** (TOF MS ES+) calcd.for $C_{19}H_{13}NSH^+$ [M + H$^+$] m/z 288.0847, found 288.0851.

(*E*)-6-Chloro-2-styrylquinoline 3r[20]: White solid, yield: 78% (52 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.99 (m, 2H), 7.74 – 7.73 (m, 1H), 7.71 – 7.62 (m, 5H), 7.42 – 7.31 (m, 4H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 156.3, 146.7, 136.5, 135.5, 135.0, 131.9, 130.9, 130.7, 129.0, 128.9, 128.6, 128.0, 127.4, 126.3, 120.3.

(*E*)-6-Bromo-2-styrylquinoline 3s[20]: White solid, yield: 75% (58 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.75 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.68 (d, *J* = 16.3 Hz, 1H), 7.66 – 7.62 (m, 3H), 7.42 – 7.32 (m, 4H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 156.4, 146.9, 136.4, 135.4, 135.1, 133.3, 131.0, 129.7, 128.9 (2C), 128.6, 128.5, 127.4.120.3, 120.0.

(*E*)-7-Chloro-2-styrylquinoline 3t[21]: White solid, yield: 83% (55 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.71 (dd, *J* = 7.3, 6.3 Hz, 1H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.65 – 7.61 (m, 3H), 7.44-7.34 (m, 5H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 157.0, 148.8, 136.5, 136.2, 135.7, 135.3, 129.0 (2C), 128.8, 128.6, 128.3, 127.5, 127.2, 125.8, 119.8.

(*E*)-2-Styrylpyrazine 5a[9]: White solid, yield: 81% (40 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 0.6 Hz, 1H), 8.55 – 8.54 (m, 1H), 8.41 (d, *J* = 2.4 Hz, 1H), 7.76 (d, *J* = 16.1 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.34 (m, 1H), 7.16 (d, *J* = 16.1 Hz, 1H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 151.4, 144.5, 143.9, 142.9, 136.2, 135.4, 129.2, 129.0, 127.5, 124.2.

(*E*)-2-(4-Methylstyryl)pyrazine 5b[9]: White solid, yield: 75% (37 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.4 Hz, 1H), 8.52 – 8.51 (m, 1H), 8.38 (d, *J* = 2.5 Hz, 1H), 7.72 (d, *J* = 16.1 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 16.1 Hz, 1H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 151.6, 144.4, 143.8, 142.6, 139.3, 135.2, 133.4, 129.7, 127.4, 123.1, 21.5.

(*E*)-2-(2-(Naphthalen-1-yl)vinyl)pyrazine 5c: White solid, yield: 73% (42 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.62 – 8.59 (m, 2H), 8.45 – 8.44 (m, 1H), 8.30 (d, *J* = 8.3 Hz, 1H), 7.90 – 7.84 (m, 3H), 7.60 – 7.50 (m, 3H), 7.22 (d, *J* = 15.7 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 151.5, 144.6, 144.1, 143.0, 133.9, 133.8, 132.4, 131.6, 129.5, 128.8, 126.8, 126.6, 126.2, 125.7, 124.3, 123.8. **HRMS** (TOF MS ES+) calcd.for $C_{16}H_{12}N_2H^+$ [M + H$^+$] m/z 233.1079, found 233.1086.

(*E*)-2-Styrylquinoxaline 5d[9]: White solid, yield: 84% (49 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.08– 8.05 (m, 2H), 7.86 (d, *J* = 16.3 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.71 – 7.64 (m, 3H), 7.44 – 7.34 (m, 4H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 150.7, 144.5, 142.5, 141.7, 136.5, 136.1, 130.4, 129.4 (2C), 129.3 (2C), 129.0, 127.6, 125.4. **HRMS** (TOF MS ES+) calcd.for $C_{16}H_{12}N_2H^+$ [M + H$^+$] m/z 233.1079, found 233.1086.

(*E*)-2-(4-Methylstyryl)quinoxaline 5e: White solid, yield: 72% (44 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.07 – 8.04 (m, 2H), 7.84 (d, *J* = 16.3 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 16.3 Hz, 1H), 7.26 – 7.22 (m, 2H), 2.39 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 151.0, 144.6, 142.6, 141.6, 139.6, 136.6, 133.4, 130.4, 129.8, 129.4,

129.2, 128.5, 127.6, 124.5, 21.6 ppm. **HRMS** (TOF MS ES+) calcd.for $C_{17}H_{14}N_2H^+$ [M + H$^+$] m/z 247.1235, found 247.1240.

(*E*)-4-Styrylquinoline 5f[9]: White solid, yield: 74% (43 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.6 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 16.1 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.65 – 7.58 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.33 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 150.2, 148.7, 143.0, 136.6, 135.2, 130.1, 129.4, 128.9, 128.8, 127.2, 126.6, 126.4, 123.5, 122.9, 117.1.

(*E*)-3-Styrylbenzo[*f*]quinoline 5g: White solid, yield: 70% (49 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.6 Hz, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 8.00 (brs, 2H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.62 (m, 6H), 7.46 – 7.40 (m, 3H), 7.35 – 7.32 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.7, 148.4, 136.8, 134.2, 131.7, 131.3 (2C), 129.8, 128.9 (2C), 128.7 (2C), 128.3, 127.4, 127.3, 127.2, 124.4, 122.7, 119.8. **HRMS** (TOF MS ES+) calcd.for $C_{21}H_{15}NH^+$ [M + H$^+$] m/z 282.1283, found 282.1287.

(*E*)-2-Styrylbenzo[*d*]thiazole 5h: White solid, yield: 59% (35 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.58 (m, 2H), 7.55 – 7.47 (m, 2H), 7.45 – 7.36 (m, 5H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 167.1, 154.0, 137.8, 135.5, 134.5, 129.6, 129.1, 127.5, 126.5, 125.5, 123.1, 122.3, 121.6. **HRMS** (TOF MS ES+) calcd for $C_{15}H_{11}NSH^+$ [M + H$^+$] m/z 238.0690, found 238.0690.

(*E*)-1-Benzyl-2-styryl-1H-benzo[*d*]imidazole 5i[9]: White solid, yield: 62% (48 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 15.8 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.19 (m, 9H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 15.8 Hz, 1H), 5.45 (s, 2H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 151.2, 143.4, 137.8, 136.2, 136.0 135.8, 129.2 (2C), 128.9, 128.1, 127.4 (2C), 126.3, 123.0, 119.6, 113.1, 109.7, 47.0.

Mechanistic Investigations:

a) Qualitative analysis of hydrogen gas liberation by GC-TCD detector: In a 15 mL Schlenk tube, 2-methylquinoline **1a** (0.50 mmol), benzyl alcohol **2a** (0.25 mmol), *t*-BuOK (0.275 mmol, 1.1 equiv), $NiBr_2$ (0.025 mmol, 10 mol %), Ligand **L_1** (0.025 mmol, 10 mol%) and *t*-BuOH (0.5 mL) were added under argon. The reaction mixture was kept for heating for 6 h. Then, the gaseous mixture was analysed on GC (TCD detector) which showed the formation of hydrogen gas (See SI page S32-S33 for Chromatogram).

d) Reaction with isolated Ni-L_1 complex:
Procedure for Synthesis of Ni-L_1 complex: To a solution of **L_1** (50 mg, 0.2 mmol, 1 equiv) in *t*-BuOH (2 mL), $NiBr_2$ (43.8 mg, 1 equiv) and *t*-BuOK (22.5 mg, 1 equiv) were added and the mixture was heated at 80 °C for 1 h. A yellow color precipitate was formed. The precipitate was filtered off and washed with hexane (2 x 4 mL). The yellow solid was dissolved in DCM (5 mL) and filtered through syringe filter. The filtrate was concentrated and dried under vacuum to afford **Ni-L_1** complex as a yellow solid in 82% yield.

Characterization of Ni-L_1 complex : ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (dd, *J* = 17.2, 5.4 Hz, 2H), 8.69 (d, *J* = 7.7 Hz, 1H), 8.24 – 8.21 (m, 1H), 7.95 – 7.92 (m, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.36 – 7.29 (m, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.7, 156.3, 154.5, 153.8, 146.8, 143.8, 140.3, 139.1, 129.6, 129.2, 127.1, 123.8, 121.9, 120.2, 120.0. **HRMS** (TOF MS ES+) calcd.for $C_{15}H_{10}BrN_3NiOH^+$ [M + H$^+$] m/z 385.9439, found 385.9449(See SI page S34-S36 for spectra).
Procedure for Reaction with isolated Ni-L_1 complex: In a 15 mL Schlenk tube, complex **A** (0.025 mmol, 10 mol%), 2-methylquinoline **1** (0.50 mmol), benzyl alcohol **2** (0.25 mmol), *t*-BuOK (0.275 mmol), and *t*-BuOH (0.5 mL) were added under argon. The reaction mixture was heated for 48 h. Then, it was cooled, quenched with water (4 mL) and extracted with ethyl acetate (3 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and volatiles were evaporated under reduced pressure. The residue was purified by column chromatography and the desired product **3a** was isolated in 86% yield.

e) Mercury drop experiment: In a 15 mL Schlenk tube, complex **A** (10 mol%), 2-methylquinoline **1a** (0.50 mmol), benzyl alcohol **2a** (0.25 mmol), *t*-BuOK (0.275 mmol), Hg (50 equiv with respect to complex **A**), and *t*-BuOH were added under argon. The reaction mixture was kept for heating for 48 h. Then, the reaction mixture was filtered through celite. The filtrate was worked up with water and ethyl acetate (3 x 10 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography and the desired product **3a** was isolated in 79% yield.

Typical experimental procedure for nickel-catalyzed directalkenylation of 2-methylquinoline with benzyl alcohol in gram scale: In a 100 mL Schlenk flask, 2-Methylquinoline **1a** (2.86g, 20 mmol), benzyl alcohol **2a** (1.08g, 10 mmol), $NiBr_2$ (0.22g, 1 mmol), Ligand L_1 (0.25g, 1 mmol) *t*-BuOK (1.23g, 11 mmol), and *t*-BuOH (20 mL) were taken under argon. The reaction tube was closed and the resulting mixture was heated at 140 ºC. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with water (30 mL) and the organic layer was extracted with ethyl acetate (3 x 40 mL). Evaporation of the combined organic layers followed by column chromatography over silica gel (mesh 100–200 mesh) with hexane/ethyl acetate mixture as eluent afforded (*E*)-2-styryl quinoline**3a** in 79% (1.82 g) isolated yield.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Copies of ^{1}H and ^{13}C NMR spectra for all compounds (PDF).

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Notes

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