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Rhodium-Catalyzed Direct C−H Bond Cyanation of Arenes with Isocyanide

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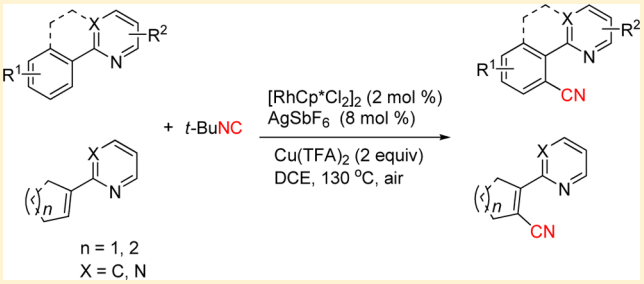
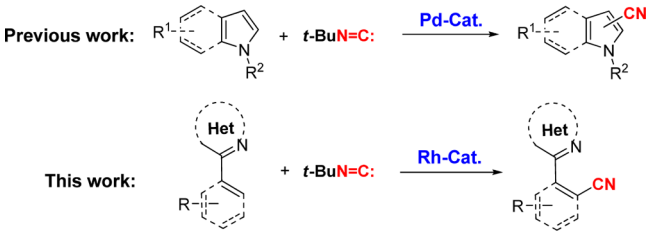
Supporting Information

ABSTRACT: An efficient rhodium-catalyzed regioselective C−H bond cyanation of arenes was developed using *tert*-butyl isocyanide as the cyanide source. A wide range of (hetero)aryl and cycloalkenyl nitriles could be afforded with high regioselectivity and good functional group tolerance.



Aryl nitriles are structural motifs that frequently occurred as the core structures of many pharmaceuticals and agrochemicals.[1] In addition, the widespread synthetic utility of nitrile moiety is highlighted by serving as a versatile building block and by its possible nitrile transformations leading to the formation of aldehydes, amides, amidines, amines, carboxyl derivatives and heterocycles.[2,3] The early synthetic efforts for the preparation of organonitriles include two traditional methods such as the Sandmeyer reaction[4] and Rosenmund−von Braun reaction,[5] which use stoichiometric amounts of copper cyanide as "CN" source. Recently, a variety of protocols on the basis of transition metal-catalyzed cyanation of aryl halides[6−11] or direct cyanation of C−H bonds[12−28] have been developed. Among them, however, some of these transformations suffered from their intrinsic drawbacks, including use of toxic reagents, poor functional group tolerance, and the need for tedious and costly preactivation steps. Compared with some toxic metal cyanide sources M−CN (M = K, Na, Zn) and user-friendly cyanation reagent $K_4[Fe(CN)_6]$, nonmetallic cyano-group sources have been fully disclosed such as using DMF,[22,23] DMSO[24] and *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide (NCTS)[25,26] as the cyano sources, which would avoid producing stoichiometric metal waste and hazardous HCN gas.[21−30] Recently, we have reported a palladium-catalyzed oxidative cyanation reaction using *tert*-butyl isocyanide as the cyanide source, in which a regioselective C2 and C3 cyanation of indoles could be achieved (Scheme 1).[31] Independently, Zhu and co-workers also disclosed the similar C3 cyanation of indoles.[32] In contrast to many reports on palladium-catalyzed and copper-mediated cyanation reactions,

Scheme 1. Metal-Catalyzed C−H Bond Cyanation Using *tert*-Butyl Isocyanide



rhodium(III)-catalyzed C−H cyanation reaction has been much less explored,[26,33] which has proved to be a good complement to other transition metals in terms of substrate scope and functional group compatibility. In this event, to expand the scope and utility of C−H cyanation reactions using nonmetallic cyano-group sources, the development of rhodium-catalyzed highly efficient, selective, and practical C−H bond cyanation methods continues to be an active and rewarding research area.

Pyrimidines and their derivatives have attracted many attentions as important motifs in materials and medicinal chemistry.[34,35] Thus, the development of readily available functionalized arylpyrimidines in a regioselective manner would find significant application in preparing this class of molecules. Previously, we have successfully demonstrated the feasibility of specific chelation effect of a pyrimidyl group in the metal-catalyzed C−H bond functionalization reactions to afford

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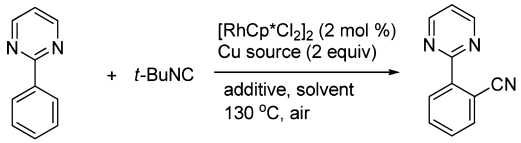
halogenated[36,37] and acetoxylated[38] arylpyrimidines regioselectively, as well as C2 cyanated *N*-pyrimidyl indoles[31] and unsymmetrical *N*-pyrimidyl ureas[39] in good to excellent yields. However, attempting to achieve cyanated arylpyrimidine products in the previous palladium-catalyzed cyanation reaction gave unsatisfactory results; for instance, *ortho*-monocyanated phenylpyrimidine **2a** was afforded in only 27% yield with 54% conversion of 2-phenylpyrimidine **1a** after reacting for 24 h at 130 °C.[31] In this context, a general, direct and selective C−H bond cyanation method would be highly desirable. Herein, we report a novel rhodium-catalyzed regioselective cyanation of (hetero)arylpyrimidines using *tert*-butyl isocyanide as an effective "CN" source. Furthermore, this protocol could be successfully applied to the vinyl C−H bond cyanation of cycloalkenes with high regioselectivity which, to our knowledge, represents the first example of metal-catalyzed direct C−H cyanation reaction of olefinic double bonds using isocyanide (Scheme 1).

At the outset of this investigation, we commenced our study by exploring the reaction of 2-phenylpyrimidine (**1a**) with *tert*-butyl isocyanide in the presence of $[RhCp^*Cl_2]_2$ (2.0 mol %) in DCE using $Cu(OAc)_2{\cdot}H_2O$ as an oxidant. Intriguingly, the *ortho*-cyanated product **2a** was isolated in 51% yield with 57% conversion of **1a** after reacting for 48 h at 130 °C (Table 1, entry 1). Better result could be achieved by addition of 1.0 equiv of PivOH after reacting for 38 h (entry 2). The use of $Cu(TFA)_2$ instead of $Cu(OAc)_2{\cdot}H_2O$ could significantly reduce the reaction time from 38 to 3 h although with decreased yield (entry 3). However, the use of $AgSbF_6$ instead of PivOH as an additive could dramatically promote this reaction and afford **2a** in 84% yield within 3 h (entry 4). Among all other solvents tested, DCE proved to be the most efficient one (entry 4), while DMF, dioxane or anisole gave much lower yields (entries 5−7), and toluene or acetic acid failed to give any product (entries 8−9). Lowering the reaction temperature gave diminished yields with lower reaction conversion (entries 10−11). Decreased yield was afforded without using $AgSbF_6$ (entry 12), and the reaction became sluggish to give **2a** in 32% yield in the absence of $[RhCp^*Cl_2]_2$ and $AgSbF_6$, which indicated that rhodium catalyst was crucial for this cyanation reaction (entry 13).

Table 1. Optimization of Reaction Conditions[a]



1a **2a**

entry	Cu source	additive (mol %)	solvent	time (h)	yield[b] (%)
1	$Cu(OAc)_2.H_2O$	–	DCE	48	51[c]
2	$Cu(OAc)_2.H_2O$	PivOH (100)	DCE	38	82
3	$Cu(TFA)_2$	PivOH (100)	DCE	3	62
4	**$Cu(TFA)_2$**	**$AgSbF_6$ (8)**	**DCE**	**3**	**84**
5	$Cu(TFA)_2$	$AgSbF_6$ (8)	DMF	8	22
6	$Cu(TFA)_2$	$AgSbF_6$ (8)	dioxane	8	33
7	$Cu(TFA)_2$	$AgSbF_6$ (8)	anisole	4	17
8	$Cu(TFA)_2$	$AgSbF_6$ (8)	toluene	24	trace
9	$Cu(TFA)_2$	$AgSbF_6$ (8)	HOAc	24	trace
10	$Cu(TFA)_2$	$AgSbF_6$ (8)	DCE	24	23[d]
11	$Cu(TFA)_2$	$AgSbF_6$ (8)	DCE	24	69[e]
12	$Cu(TFA)_2$	–	DCE	3	79
13	$Cu(TFA)_2$	–	DCE	6	32[f]

[a]Reaction conditions: **1a** (0.2 mmol), *t*-BuNC (2.0 equiv), $[RhCp^*Cl_2]_2$ (2 mol %), Cu salt (2.0 equiv) and additive (8 mol %) in solvent (1.0 mL), air, sealed tube, 130 °C. $Cu(TFA)_2$ = cupric trifluoroacetate. DCE = 1,2-dichloroethane. [b]Isolated yield. [c]With 57% conversion of **1a**. [d]At 80 °C, with 48% conversion of **1a**. [e]At 120 °C, with 86% conversion of **1a**. [f]In the absence of $[RhCp^*Cl_2]_2$.

With the optimized reaction conditions in hand, we sought to explore the reaction with a range of substrates as summarized in Scheme 2. In general, this reaction was highly efficient and showed excellent monoselectivity when substrates bearing *para*-, *meta*-, *ortho*-, or multisubstitutions on the aryl ring were employed. Substrates with electron-donating substitution at *para*- or *meta*-position could afford *ortho*-cyanated products in good to excellent yields in short reaction time (**2b**−**2d**, **2j**−**2k**), while longer time was needed to complete the reaction for those substrates with electron deficient groups (**2e**−**2i**, **2l**−**2n**). The presence of a *ortho*-methyl group on the phenyl ring resulted in the corresponding cyanated product **2o** in 47% yield and disubstituted substrate could also give **2p** in 86% yield. Furthermore, this cyanation reaction could proceed well for trisubstituted substrate with high steric hindrance, for which the combination of $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv), PivOH (1.0 equiv) and H_2O (2.5 equiv) was found to be superior to $Cu(TFA)_2$ and $AgSbF_6$, affording cyanated product **2q** in 90% yield after reacting for 36 h.

To further explore the generality and scope of this approach, a variety of substrates were investigated. As illustrated in Scheme 3, substrates with substituents on the pyrimidinyl ring also afforded cyanated products in moderate to good yields (**4a**−**4d**). This cyanation protocol was not limited to phenyl ring, the α- and β-pyrimidyl naphthalenes could afford 2- and 3-cyanation products **4e** and **4f** in 65% and 63% yield, respectively, and phenanthrene could be functionalized in the 10-position to give cyanated product **4g**. Heteroarenes such as pyrrole, indole and carbazole were also found to be suitable substrates and afforded the cyanated products in good yields (**4h**−**4j**). Moreover, this newly established protocol could extend to benzo[*h*]quinoline and gave the corresponding cyano product **4k** in 98% yield. However, 2-phenyl substituted adenine or its derivatives such as 9-benzyl-2-phenyl-9*H*-purin-6-amine failed to give any cyanated products. Notably, no significant double cyanation products or regioisomers could be isolated under the standard conditions.

It should be noted that the substrate **3c**, which has two potential *ortho*-cyanation positions derived from the coordination of rhodium and two nitrogen atoms, gave exclusive product **4c** in 41% yield (Scheme 4). The identity of **4c** was determined by spectra analysis and further confirmed by X-ray crystallographic analysis.[40]

Although there are many reports involving C−H cyanation of arenes under the assistance of various directing groups, fewer examples were successfully investigated through direct C−H cyanation of olefinic double bonds, which need prefunctionalized substrates or multistep reactions.[41,42] We were pleased to find that the vinyl C−H bond in 2-cyclohexenylpyrimidine **5a** could be also cyanated selectively to give its corresponding cyanide product **6a** in 64% yield (Scheme 5). The substrate scope was extended further to include 2-cycloalkenylpyridines providing direct access to corresponding cycloalkenyl nitriles in good yields that incorporate cyclopentenyl (**6b**) and cyclo-

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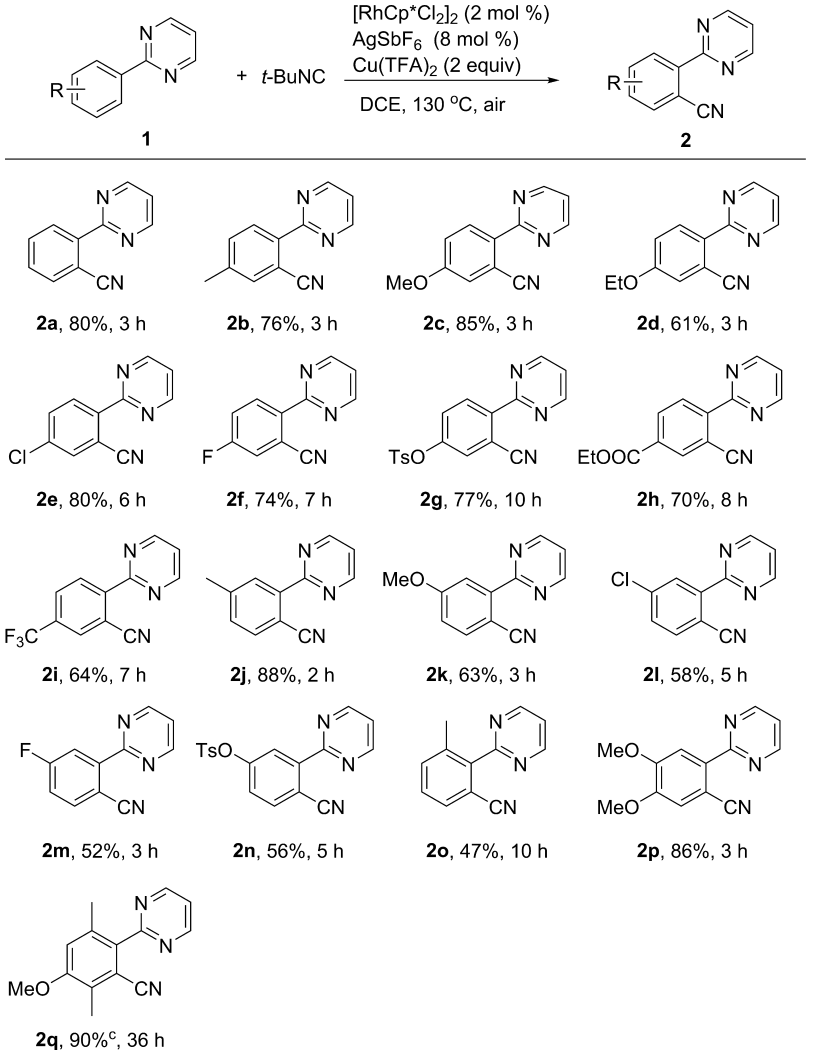
Scheme 2. Cyanation of Various Arylpyrimidines[a,b]



[a]Reaction Conditions: **1a**–**q** (0.4 mmol), *t*-BuNC (2.0 equiv), $[RhCp^*Cl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), $Cu(TFA)_2$ (2.0 equiv), DCE (2.0 mL), air, sealed tube, at 130 °C. [b]Isolated yield. [c]$Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv), PivOH (1.0 equiv), and H_2O (2.5 equiv) were used instead of $Cu(TFA)_2$ and $AgSbF_6$.

hexenyl (**6c**) functionality (Scheme 5). This reaction protocol could be very useful in the synthesis of natural products using cycloalkenyl carbonitriles as key intermediates.[43]

To define the possible intermediates and pathway of this reaction, several control experiments were carried out (Scheme 6). When **1a** was reacted with *tert*-butyl cyanide under the standard reaction conditions, only trace amount of **2a** was observed (eq 1), which suggested that the reaction might not go through the *tert*-butyl cyanide intermediate.[44,45] When 2 equiv of CuCN was used instead of *t*-BuNC and $Cu(TFA)_2$ during the reaction, **2a** was afforded in only 27% yield (eq 2), and this result implied that the reaction did not mainly proceed via the CuCN intermediate, which may be generated from *t*-BuNC and $Cu(TFA)_2$. However, when a copper carboxylate-isonitrile complex $[CF_3COO{\cdot}Cu(I)—C{\equiv}NBu\text{-}t]$ (2.0 equiv) was used instead of *t*-BuNC and $Cu(TFA)_2$, only trace amount of **2a** was detected (eq 3), which indicated that this complex might not be the key intermediate during the reaction.[31] To further confirm the origin of cyano group, aromatic isocyanide and aliphatic isocyanides were used as cyanide sources in the reaction. The cyanation reaction did not proceed when 2,6-dimethylphenyl-isocyanide and cyclohexylisocyanide were employed, while tertiary isocyanide bearing a *β*-hydrogen such as 1-adamantanylisocyanide (AdNC) could afford cyanation product **2a** in 56% yield (eq 4), which indicated that tertiary isocyanides (AdNC vs *t*-BuNC) might be crucial to give cyanation products through *β*-alkyl elimination.

Although the detailed reaction mechanism remains to be clarified, a plausible mechanism for this reaction was proposed on the basis of the above results (Scheme 7). With the direction of pyrimidyl group, electrophilic rhodation at the *ortho* position affords a rhodacycle **A**.[46] Then the following insertion of isocyanide generates an intermediate **B**,[47] which undergoes *β*-*tert*-butyl elimination to give the product **2a** together with expulsion of isobutene.[31,32] The formed Rh(I) species is reoxidized by Cu(II), which could be derived from the oxidation of Cu(I) with oxygen and regenerating the Rh(III) catalyst.

In summary, we have developed a rhodium-catalyzed C–H bond cyanation of (hetero)arylpyrimidines using *tert*-butyl isocyanide as an efficient "CN" source with good regioselectivity and functional group tolerance. The present rhodium

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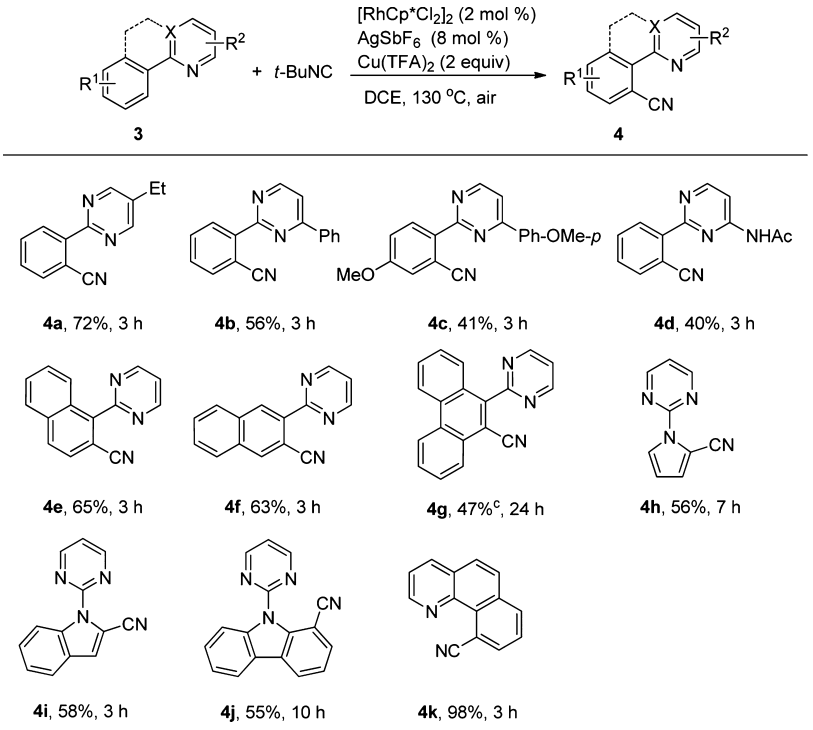
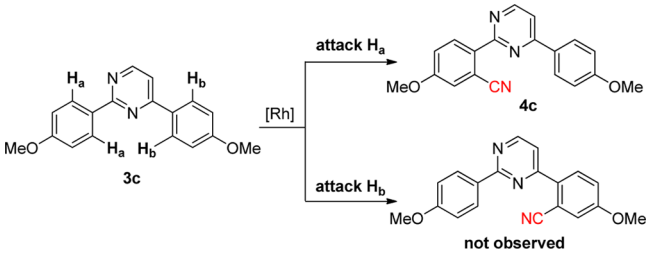
Scheme 3. Cyanation of Aromatic Heterocycles[a,b]

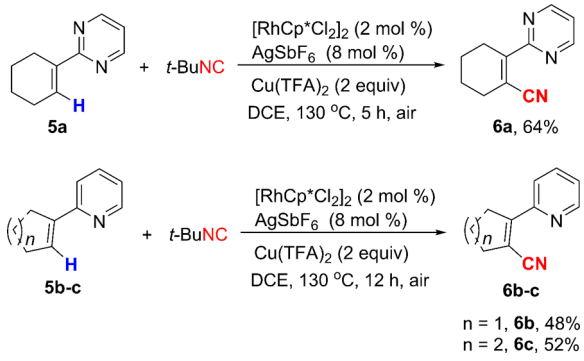


[a]Reaction Conditions: **3a–k** (0.4 mmol), *t*-BuNC (2.0 equiv), $[RhCp^*Cl_2]_2$ (2.0 mol %), $AgSbF_6$ (8 mol %), $Cu(TFA)_2$ (2.0 equiv), DCE (2.0 mL), air, sealed tube, at 130 °C. [b]Isolated yield. [c]Yield based on 57% conversion.

Scheme 4. Regioselective C–H Bond Cyanation of 3c



Scheme 5. Cyanation of Cycloalkenes



catalyst system was also successfully applied to the direct C–H cyanation of olefinic double bonds leading to cycloalkenyl nitriles in good yields. This approach offers a unique strategy and alternative route for preparation of organonitriles in good to excellent yields.

EXPERIMENTAL SECTION

General Information. All solvents were purified before use according to standard procedure. All melting points were taken on a digital melting point apparatus without correction. Infrared spectra were obtained using an FT-IR spectrometer. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 500, 125, and 470 MHz, respectively, with chemical shift values being reported in ppm relative to chloroform (δ = 7.26 ppm), dimethyl sulfoxide (δ = 2.50 ppm), or TMS (δ = 0.00 ppm) for ^1H NMR, chloroform (δ = 77.16 ppm) or dimethyl sulfoxide (δ = 39.52 ppm) for ^{13}C NMR, and C_6F_6 (δ = −164.9 ppm) for ^{19}F NMR. Mass spectra and high resolution mass spectra (HRMS) were recorded using electron impact (EI) or electrospray ionization (ESI) techniques. Elemental analyses were carried out on an elemental analyzer. X-ray structure was performed on an X-ray diffractometers. Silica gel plates GF254 were used for thin layer chromatography (TLC), and silica gel H or 300–400 mesh were used for flash column chromatography. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise indicated.

Synthesis of Starting Materials. Arylpyrimidines (**1a–1c**, **1e–1l**, **1o–1q**, **3b**, **3f**),[36] **3h–3i**,[31] and **5b–5c**[48] were synthesized as reported in the literature. Arylpyrimidines (**1m**, **3a**, **3d–3e**)[36] and **3j**[31] were prepared according to literature reported procedures. **3k** was purchased from commercial source.

2-(4-Ethoxyphenyl)-pyrimidine (1d) (General Procedure). To a round-bottom flask was added 2-chloropyrimidine (343.5 mg, 3.0 mmol), 4-ethoxyphenylboronic acid (597.6 mg, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (42.1 mg, 0.06 mmol), Na_2CO_3 (2 M, 10 mL), and dioxane (10 mL). The reaction mixture was heated at 90 °C until the 2-chloropyrimidine was consumed completely (monitored by TLC). The heterogeneous aqueous was concentrated under reduced pressure, and the residue was diluted with EtOAc (15 mL), washed by H_2O (20 mL), and brine (20 mL). The organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to afford **1d** (558.0 mg, 93%) as a white solid: mp 120–121 °C; IR (KBr, cm^{-1}) 3441, 3046, 2972, 1606, 1569, 1420, 1244, 854, 797, 641; ^1H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, J = 5.0 Hz, 2H), 8.34 (dd, J = 7.0, 2.0 Hz, 2H), 7.10 (t, J = 5.0 Hz,

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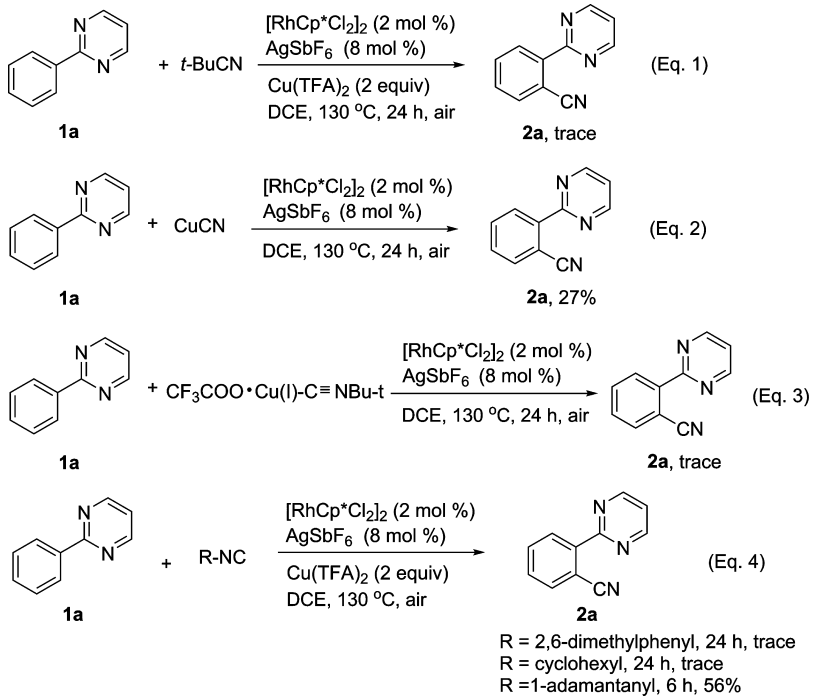
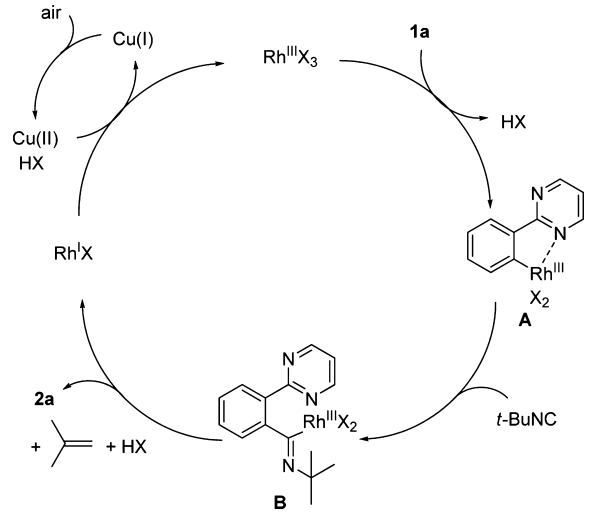
Scheme 6. Mechanistic Studies



Scheme 7. Plausible Mechanism for Synthesis of 2a from 1a



1H), 6.99–6.97 (m, 2H), 4.10 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.5, 161.5, 157.2, 129.9, 118.4, 114.6, 63.7, 14.9; EI-MS m/z 200 (59) [M^+], 172 (100), 119 (80); HRMS (EI-TOF) m/z calcd for $C_{12}H_{12}N_2O$ [M^+] 200.0950, found 200.0948.

3-(Pyrimidin-2-yl)phenyl 4-methylbenzenesulfonate (1n). The same procedure was used as for **1d** with 2-chloropyrimidine (343.5 mg, 3.0 mmol), 3-(tosyloxy)- phenylboronic acid (1051.2 mg, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (42.1 mg, 0.06 mmol), Na_2CO_3 (2 M, 10 mL) and dioxane (10 mL). After the reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) afforded **1n** (811.7 mg, 83%) as a white solid: mp 127–129 °C; IR (KBr, cm^{-1}) 3048, 1555, 1411, 1367, 1194, 1086, 899, 802, 790, 726; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.78 (d, J = 5.0 Hz, 2H), 8.34 (d, J = 7.5 Hz, 1H), 8.16 (t, J = 2.0 Hz, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 4.5 Hz, 1H), 7.08 (m, 1H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.4, 157.4, 150.2, 145.5, 139.7, 132.6, 129.9, 128.7, 126.8, 124.5, 122.4, 119.7, 21.8; EI-MS m/z (%) 326 (41) [M^+], 155 (44), 143 (30), 91 (100); HRMS (EI-TOF) m/z calcd for $C_{17}H_{14}N_2O_3S$ [M^+] 326.0725, found 326.0724.

2,4-Bis(4-methoxyphenyl)pyrimidine (3c). The same procedure was used as for **1d** with 2,4-dichloropyrimidine (447.0 mg, 3.0 mmol), 4-methoxyphenylboronic acid (1094.4 mg, 7.2 mmol), $Pd(PPh_3)_2Cl_2$ (42.1 mg, 0.06 mmol), Na_2CO_3 (2 M, 10 mL) and dioxane (10 mL). After the reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) afforded **3c** (753.4 mg, 86%) as a white solid: mp 141–143 °C; IR (KBr, cm^{-1}) 3067, 2964, 2841, 1608, 1511, 1249, 1178, 1024, 832, 820, 797, 576, 541; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.85 (d, J = 5.0 Hz, 1H), 8.56 (dd, J = 7.0, 2.0 Hz, 2H), 8.23–8.20 (m, 2H), 7.49 (d, J = 5.0 Hz, 1H), 7.07–7.03 (m, 4H), 3.92 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.9, 163.4, 162.1, 161.9, 157.0, 129.9, 129.4, 128.8, 114.2, 113.8, 112.9, 55.5, 55.4; EI-MS m/z (%) 292 (100) [M^+], 277 (10), 214 (9), 132 (17); HRMS (EI-TOF) m/z calcd for $C_{18}H_{16}N_2O_2$ [M^+] 292.1212, found 292.1210.

2-(Phenanthren-9-yl)pyrimidine (3g). The same procedure was used as for **1d** with 2-chloropyrimidine (343.5 mg, 3.0 mmol), phenanthren-9-ylboronic acid (799.2 mg, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (42.1 mg, 0.06 mmol), Na_2CO_3 (2 M, 10 mL) and dioxane (10 mL). After the reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **3g** (176.6 mg, 23%) as a yellow solid: mp 95–97 °C; IR (KBr, cm^{-1}) 3033, 1566, 1549, 1414, 813, 744, 720; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.97 (d, J = 5.0 Hz, 2H), 8.79 (d, J = 8.0 Hz, 1H), 8.73 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 8.5 Hz, 1H), 8.32 (s, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.73–7.61 (m, 4H), 7.32 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.3, 157.3, 134.6, 131.3, 131.2, 131.1, 131.0, 129.7, 129.6, 127.8, 127.0, 126.9, 126.7, 126.6, 123.0, 122.6, 119.1; EI-MS m/z (%) 256 (62) [M^+], 255 (100), 176 (26). Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93. Found: C, 84.24; H, 4.52; N, 10.73.

2-(Cyclohex-1-en-1-yl)pyrimidine (5a). The same procedure was used as for **1d** with 2-chloropyrimidine (343.5 mg, 3.0 mmol), cyclohex-1-en-1-ylboronic acid (453.6 mg, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (42.1 mg, 0.06 mmol), Na_2CO_3 (2 M, 10 mL) and dioxane (10 mL). After the reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) afforded **5a** (388.8 mg, 81%) as a colorless oil: IR (KBr, cm^{-1}) 3030, 2932, 2857, 1567, 1552,

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1419, 923, 786, 632; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.66 (d, J = 5.0 Hz, 2H), 7.29−7.27 (m, 1H), 7.05 (t, J = 5.0 Hz, 1H), 2.59−2.55 (m, 2H), 2.32−2.27 (m, 2H), 1.80−1.75 (m, 2H), 1.70−1.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.0, 156.5, 136.1, 134.2, 118.2, 26.1, 25.3, 22.6, 21.9. LC-MS (ESI) m/z 161 [M^+H]; HRMS (ESI-TOF) m/z calcd for $C_{10}H_{13}N_2$ [M+H]$^+$ 161.1079, found 161.1077.

General Procedure for the Synthesis of Cyanated Products. ***Caution!*** *Use safety glasses and nitrile gloves under a well-ventilated hood since isocyanides such as tert-butyl isocyanide have pungent odors and are known to be toxic.* To a 15 mL sealed tube was added substrates (0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). The reaction mixture was stirred at 130 °C under air atmosphere. Upon completion, the reaction was diluted by EtOAc (10 mL) and quenched with aqueous ammonia solution (3 M, 10 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined extract was dried over Na_2SO_4, filtered, and concentrated in vacuo. The given residue was purified by column chromatography to give the cyanated product.

2-Pyrimidin-2-yl-benzonitrile (2a).[31] The general procedure was followed with 2-phenylpyrimidine **1a** (62.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2a** (57.9 mg, 80%) as a white solid: mp 134−136 °C; IR (KBr, cm^{-1}) 3071, 3040, 2224, 1565, 1554, 1413, 818, 758, 628; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.91 (d, J = 5.0 Hz, 2H), 8.35 (dd, J = 7.5, 1.0 Hz, 1H), 7.84 (dd, J = 8.0, 1.0 Hz, 1H), 7.70 (td, J = 7.5, 1.0 Hz, 1H), 7.56 (td, J = 8.0, 1.0 Hz, 1H), 7.32 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.8, 157.3, 140.3, 135.0, 132.5, 130.4, 130.2, 120.1, 118.9, 111.8; EI-MS m/z 181 (100) [M^+], 128 (95).

5-Methyl-2-pyrimidin-2-yl-benzonitrile (2b).[49] The general procedure was followed with 2-(*p*-tolyl)pyrimidine **1b** (68.0 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2b** (59.3 mg, 76%) as a white solid: mp 172−174 °C; IR (KBr, cm^{-1}) 3081, 3035, 2959, 2225, 1561, 1413, 816, 801, 634; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.89 (d, J = 5.0 Hz, 2H), 8.26 (d, J = 8.5 Hz, 1H), 7.65 (s, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.29 (t, J = 5.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.9, 157.3, 140.9, 137.6, 135.5, 133.5, 130.4, 119.9, 119.2, 111.7, 21.0; EI-MS m/z 195 (100) [M^+], 143 (27), 115 (43).

5-Methoxy-2-pyrimidin-2-yl-benzonitrile (2c). The general procedure was followed with 2-(4-methoxyphenyl)pyrimidine **1c** (74.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2c** (71.7 mg, 85%) as a white solid: mp 128−129 °C; IR (KBr, cm^{-1}) 3079, 2979, 2222, 1606, 1552, 1416, 1289, 1054, 889, 803, 719; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.89 (d, J = 5.0 Hz, 2H), 8.36 (d, J = 8.5 Hz, 1H), 7.34 (d, J = 2.5 Hz, 1H), 7.28 (t, J = 5.0 Hz, 1H), 7.23 (dd, J = 9.0, 2.5 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.5, 160.8, 157.2, 132.6, 132.0, 119.8, 119.5, 118.9, 118.7, 112.9, 55.8; EI-MS m/z 211 (100) [M^+], 158 (67), 128 (18), 115 (24); HRMS (EI-TOF) m/z calcd for $C_{12}H_9N_3O$ [M^+] 211.0746, found 211.0744.

5-Ethoxy-2-(pyrimidin-2-yl)benzonitrile (2d). The general procedure was followed with 2-(4-ethoxyphenyl)-pyrimidine **1d** (80.0 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2d** (54.9 mg, 61%) as a white solid: mp 180−181 °C; IR (KBr, cm^{-1}) 3440, 2977, 2225, 1602, 1567, 1551, 1416, 1285, 1054, 827, 816, 799, 623; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.88 (d, J = 5.0 Hz, 2H), 8.34 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 2.5 Hz, 1H), 7.27 (t, J = 5.0 Hz, 1H), 7.21 (dd, J = 9.0, 2.5 Hz, 1H), 4.14 (q, J = 7.0 Hz, 2H), 1.48 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.6, 160.2, 157.2, 132.4, 132.0, 120.3, 119.5, 119.2, 118.9, 112.9, 64.2, 14.6; EI-MS m/z 225 (63) [M^+], 197 (100), 144 (87), 116 (25); HRMS (EI-TOF) m/z calcd for $C_{13}H_{11}N_3O$ [M^+] 225.0902, found 225.0904.

5-Chloro-2-pyrimidin-2-yl-benzonitrile (2e). The general procedure was followed with 2-(4-chloro-phenyl)-pyrimidine **1e** (76.2 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2e** (69.0 mg, 80%) as a white solid: mp 212−214 °C; IR (KBr, cm^{-1}) 3083, 3032, 2231, 1573, 1415, 1383, 807, 634; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.91 (d, J = 4.5 Hz, 2H), 8.36 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 2.5 Hz, 1H), 7.68 (dd, J = 9.0, 2.5 Hz, 1H), 7.33 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.9, 157.4, 138.6, 136.5, 134.6, 132.9, 131.7, 120.3, 117.6, 113.2; EI-MS m/z 217 (22) [M^+ (^{37}Cl)], 215 (74) [M^+ (^{35}Cl)], 162 (100), 127 (33), 100 (35); HRMS (EI-TOF) m/z calcd for $C_{11}H_6ClN_3$ [M^+] 215.0250, found 215.0249.

5-Fluoro-2-(pyrimidin-2-yl)benzonitrile (2f). The general procedure was followed with 2-(4-fluorophenyl)pyrimidine **1f** (69.6 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2f** (58.9 mg, 74%) as a white solid: mp 172−174 °C; IR (KBr, cm^{-1}) 3043, 2228, 1559, 1416, 1397, 903, 807; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.90 (d, J = 5.0 Hz, 2H), 8.42 (dd, J = 9.0, 5.5 Hz, 1H), 7.54 (dd, J = 8.0, 2.5 Hz, 1H), 7.43−7.39 (m, 1H), 7.32 (t, J = 5.0 Hz, 1H); ^{19}F NMR ($CDCl_3$, 470 MHz) −108.7 (m, Ar−F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.1 (d, $^1J_{C-F}$ = 252.5 Hz), 162.0, 157.4, 136.7 (d, $^4J_{C-F}$ = 3.7 Hz), 132.9 (d, $^3J_{C-F}$ = 8.7 Hz), 122.0 (d, $^2J_{C-F}$ = 25.0 Hz), 120.3, 120.2 (d, $^2J_{C-F}$ = 20.0 Hz), 117.8, 113.7 (d, $^3J_{C-F}$ = 10.0 Hz); EI-MS m/z 199 (30) [M^+], 147 (39), 146 (65), 52 (100); HRMS (EI-TOF) m/z calcd for $C_{11}H_6FN_3$ [M^+] 199.0546, found 199.0547.

Toluene-4-sulfonic Acid 3-Cyano-4-pyrimidin-2-yl-phenyl ester (2g). The general procedure was followed with 4-(pyrimidin-2-yl)phenyl 4-methylbenzenesulfonate **1g** (130.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) afforded **2g** (108.1 mg, 77%) as a white solid: mp 135−137 °C; IR (KBr, cm^{-1}) 3073, 3035, 2222, 1576, 1553, 1418, 1376, 1190, 1175, 817, 783, 714, 552; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.89 (d, J = 5.0 Hz, 2H), 8.35 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.43−7.32 (m, 5H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.7, 157.4, 150.4, 146.2, 138.9, 132.1, 131.5, 130.1, 128.5, 128.4, 126.9, 120.3, 113.1, 21.8; EI-MS m/z 351 (29) [M^+], 155 (52), 91 (100), 65 (32); HRMS (EI-TOF) m/z calcd for $C_{18}H_{13}N_3O_3S$ [M^+] 351.0678, found 351.0680.

3-Cyano-4-pyrimidin-2-yl-benzoic Acid Ethyl Ester (2h). The general procedure was followed with 4-pyrimidin-2-yl-benzoic acid ethyl ester **1h** (91.2 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2h** (70.8 mg, 70%) as a white solid: mp 128−130 °C; IR (KBr, cm^{-1}) 3089, 2991, 2224, 1720, 1554, 1413, 1278, 1179, 824, 759, 633; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.06 (d, J = 5.0 Hz, 2H), 8.47 (d, J = 8.5 Hz, 1H), 8.40 (d, J = 1.5 Hz, 1H), 8.34 (dd, J = 8.0, 1.5 Hz, 1H), 7.65 (t, J = 5.0 Hz, 1H), 4.38 (d, J = 7.5 Hz, 2H), 1.36 (t, J = 7.5 Hz, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 164.3, 161.4, 158.4, 143.6, 135.9, 133.8, 132.2, 131.3, 121.9, 118.1, 111.7, 62.1, 14.5; EI-MS m/z 253 (56) [M^+], 208 (100), 155 (27), 127 (47), 100 (29); HRMS (EI-TOF) m/z calcd for $C_{14}H_{11}N_3O_2$ [M^+] 253.0851, found 253.0852.

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2-(Pyrimidin-2-yl)-5-(trifluoromethyl)benzonitrile (2i). The general procedure was followed with 2-(4-(trifluoromethyl)phenyl)-pyrimidine **1i** (89.6 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2i** (63.7 mg, 64%) as a white solid: mp 122−123 °C; IR (KBr, cm^{-1}) 3066, 2231, 1559, 1418, 1331, 1179, 1129, 822; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.95 (d, J = 4.5 Hz, 2H), 8.56 (d, J = 9.0 Hz, 1H), 8.10 (s, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.39 (t, J = 5.0 Hz, 1H); ^{19}F NMR ($CDCl_3$, 470 MHz) −63.1 (s, Ar−CF_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.5, 157.5, 143.2, 132.5 (q, $^2J_{C-F}$ = 32.5 Hz), 131.9 (q, $^3J_{C-F}$ = 3.8 Hz), 131.1, 129.2 (q, $^3J_{C-F}$ = 3.8 Hz), 122.9 (q, $^1J_{C-F}$ = 271.3 Hz), 120.8, 117.6, 112.7; EI-MS m/z 249 (82) [M^+], 196 (99), 177 (29), 146 (58), 52 (100); HRMS (EI-TOF) m/z calcd for $C_{12}H_6F_3N_3$ [M^+] 249.0514, found 249.0515.

4-Methyl-2-(pyrimidin-2-yl)benzonitrile (2j). The general procedure was followed with 2-(*m*-tolyl)pyrimidine **1j** (68.0 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2j** (68.6 mg, 88%) as a white solid: mp 93−94 °C; IR (KBr, cm^{-1}) 3064, 3037, 2966, 2923, 2217, 1570, 1557, 1422, 1398, 816, 728; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.90 (d, J = 5.0 Hz, 2H), 8.15 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.37 (dd, J = 8.0, 1.0 Hz, 1H), 7.32 (t, J = 5.0 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.0, 157.3, 143.6, 140.1, 135.0, 131.1, 131.0, 120.1, 119.2, 108.9, 21.8; EI-MS m/z 195 (100) [M^+], 142 (54), 115 (27); HRMS (EI-TOF) m/z calcd for $C_{12}H_9N_3$ [M^+] 195.0796, found 195.0795.

4-Methoxy-2-(pyrimidin-2-yl)benzonitrile (2k). The general procedure was followed with 2-(3-methoxyphenyl)pyrimidine **1k** (74.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2k** (53.2 mg, 63%) as a white solid: mp 130−131 °C; IR (KBr, cm^{-1}) 3020, 2976, 2211, 1598, 1559, 1030, 826, 808, 635; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.90 (d, J = 5.0 Hz, 2H), 7.87 (d, J = 3.0 Hz, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.33 (t, J = 5.0 Hz, 1H), 7.06 (dd, J = 8.5, 2.5 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.8, 162.7, 157.3, 142.3, 136.7, 120.3, 119.3, 116.6, 115.3, 103.6, 55.8; EI-MS m/z 211 (72) [M^+], 210 (100), 181 (70); HRMS (EI-TOF) m/z calcd for $C_{12}H_9N_3O$ [M^+] 211.0746, found 211.0742.

4-Chloro-2-(pyrimidin-2-yl)benzonitrile (2l). The general procedure was followed with 2-(3-chlorophenyl)pyrimidine **1l** (76.2 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2l** (50.0 mg, 58%) as a white solid: mp 126−128 °C; IR (KBr, cm^{-1}) 2924, 2226, 1570, 1552, 1419, 821; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.93 (d, J = 5.0 Hz, 2H), 8.41 (d, J = 2.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.55 (dd, J = 8.5, 2.0 Hz, 1H), 7.36 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.6, 157.4, 141.7, 139.3, 136.1, 130.7, 130.5, 120.6 (2C), 110.1; EI-MS m/z (%) 217 (18) [M^+ (^{37}Cl)], 215 (50) [M^+ (^{35}Cl)], 164 (22), 162 (67), 52 (100); HRMS (EI-TOF) m/z calcd for $C_{11}H_6ClN_3$ [M^+] 215.0250, found 215.0252.

4-Fluoro-2-(pyrimidin-2-yl)benzonitrile (2m).[50] The general procedure was followed with 2-(3-fluorophenyl)pyrimidine **1m** (69.6 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2m** (41.4 mg, 52%) as a white solid: mp 154−156 °C; IR (KBr, cm^{-1}) 3112, 3085, 3053, 2226, 1606, 1560, 1423, 1209, 826; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.95 (d, J = 5.0 Hz, 2H), 8.15 (dd, J = 9.5, 2.5 Hz, 1H), 8.15 (dd, J = 8.5, 2.5 Hz, 1H), 7.38 (t, J = 5.0 Hz, 1H), 7.31−7.28 (m, 1H); ^{19}F NMR ($CDCl_3$, 470 MHz) −103.0 (m, Ar−F); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.9 (d, $^1J_{C-F}$ = 253.7 Hz), 161.7 (d, $^4J_{C-F}$ = 2.5 Hz), 157.5, 143.3 (d, $^3J_{C-F}$ = 8.8 Hz), 137.5 (d, $^3J_{C-F}$ = 8.8 Hz), 120.7, 118.3, 118.0 (d, $^2J_{C-F}$ = 23.8 Hz), 117.9 (d, $^2J_{C-F}$ = 21.2 Hz), 108.0 (d, $^4J_{C-F}$ = 3.8 Hz); EI-MS m/z (%) 199 (79) [M^+], 146 (100), 119 (25).

4-Cyano-3-(pyrimidin-2-yl)phenyl 4-Methylbenzenesulfonate (2n). The general procedure was followed with 3-(pyrimidin-2-yl)phenyl 4-methylbenzenesulfonate **1n** (130.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) afforded **2n** (78.6 mg, 56%) as a white solid: mp 162−163 °C; IR (KBr, cm^{-1}) 3091, 3048, 2922, 2223, 1558, 1421, 1378, 1163, 919, 784, 668; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.92 (d, J = 4.5 Hz, 2H), 8.19 (d, J = 2.5 Hz, 1H), 7.79 (dd, J = 8.5, 5.5 Hz, 3H), 7.37 (t, J = 5.0 Hz, 3H), 7.20 (dd, J = 8.5, 2.5 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.6, 157.5, 152.5, 146.2, 142.5, 136.7, 132.0, 128.6, 124.7, 124.1, 120.7, 110.5, 21.9; EI-MS m/z (%) 351 (35) [M^+], 207 (30), 155 (82), 91 (100); HRMS (EI-TOF) m/z calcd for $C_{18}H_{13}N_3O_3S$ [M^+] 351.0678, found 351.0681.

3-Methyl-2-(pyrimidin-2-yl)benzonitrile (2o). The general procedure was followed with 2-(*o*-tolyl)pyrimidine **1o** (68.0 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2o** (36.7 mg, 47%) as a white solid: mp 179−181 °C; IR (KBr, cm^{-1}) 2959, 2224, 1556, 1406, 819, 782, 737; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.93 (d, J = 5.0 Hz, 2H), 7.63 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 5.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.0, 157.4, 141.8, 138.0, 135.1, 131.0, 129.2, 120.1, 118.1, 112.7, 20.1; EI-MS m/z (%) 195 (70) [M^+], 194 (100), 168 (36), 114 (30); HRMS (EI-TOF) m/z calcd for $C_{12}H_9N_3$ [M^+] 195.0796, found 195.0791.

4,5-Dimethoxy-2-pyrimidin-2-yl-benzonitrile (2p). The general procedure was followed with 2-(3,4-dimethoxyphenyl)pyrimidine **1p** (86.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2p** (82.9 mg, 86%) as a white solid: mp 169−170 °C; IR (KBr, cm^{-1}) 3098, 3061, 2967, 2844, 2213, 1598, 1555, 1411, 1389, 1151, 1216, 1038, 812, 734, 634; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.89 (d, J = 5.0 Hz, 2H), 7.94 (s, 1H), 7.29 (t, J = 5.0 Hz, 1H), 7.25 (s, 1H), 4.05 (s, 3H), 3.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.5, 157.3, 152.2, 150.4, 134.4, 119.8, 119.5, 116.6, 112.5, 103.9, 56.5, 56.4; EI-MS m/z 241 (100) [M^+], 226 (47), 210 (33), 198 (32), 195 (36). Anal. Calcd. For $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.73; H, 4.47; N, 17.20.

3-Methoxy-2,5-dimethyl-6-(pyrimidin-2-yl)benzonitrile (2q). The general procedure was followed with 2-(4-methoxy-2,5-dimethylphenyl)pyrimidine **1q** (85.6 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(OAc)_2.H_2O$ (159.6 mg, 0.8 mmol), PivOH (40.8 mg, 0.4 mmol), H_2O (18.0 mg, 1.0 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **2q** (86.0 mg, 80%) as a white solid: mp 91−93 °C; IR (KBr, cm^{-1}) 3096, 2971, 2925, 2226, 1594, 1563, 1554, 1420, 1280, 1156, 1108; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.90 (d, J = 5.0 Hz, 2H), 7.31 (t, J = 5.0 Hz, 1H), 6.91 (s, 1H), 3.88 (s, 3H), 2.42 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.4, 157.6, 157.1, 136.3, 133.8, 129.5, 119.5, 117.1, 115.9, 114.0, 55.8, 20.2, 14.1; EI-MS m/z 239 (100) [M^+], 224 (36), 210 (28), 196 (42); HRMS (EI-TOF) m/z calcd for $C_{14}H_{13}N_3O$ [M^+] 239.1059, found 239.1062.

2-(5-Ethylpyrimidin-2-yl)benzonitrile (4a). The general procedure was followed with 5-ethyl-2-phenylpyrimidine **3a** (73.6 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032

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mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4a** (60.2 mg, 72%) as a white solid: mp 40−42 °C; IR (KBr, cm^{-1}) 2971, 2935, 2217, 1544, 1425, 761; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.74 (s, 2H), 8.31 (d, J = 8.0 Hz, 1H), 7.82 (dd, J = 8.0, 1.0 Hz, 1H), 7.67 (td, J = 7.5, 1.0 Hz, 1H), 7.53 (td, J = 7.5, 1.0 Hz, 1H), 2.71 (q, J = 7.5 Hz, 2H), 1.32 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.6, 156.7, 140.4, 135.4, 134.9, 132.5, 130.2, 129.8, 119.0, 111.6, 23.5, 14.7; EI-MS m/z 209 (100) [M^+], 194 (29), 181 (33), 129 (79); HRMS (EI-TOF) m/z calcd for $C_{13}H_{11}N_3$ [M^+] 209.0953, found 209.0948.

2-(4-Phenylpyrimidin-2-yl)benzonitrile (4b). The general procedure was followed with 2,4-diphenylpyrimidine **3b** (92.8 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4b** (57.6 mg, 56%) as a white solid: mp 108−110 °C; IR (KBr, cm^{-1}) 3061, 2217, 1544, 1426, 1375, 754, 685; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.91 (d, J = 5.5 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.34−8.32 (m, 2H), 7.88 (dd, J = 7.5, 1.0 Hz, 1H), 7.74−7.70 (m, 2H), 7.59−7.53 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.6, 162.7, 158.1, 140.7, 136.3, 135.3, 132.6, 131.5, 130.6, 130.3, 129.2, 127.8, 119.5, 115.5, 111.9; EI-MS m/z 257 (22) [M^+], 256 (100), 128 (29); Anal. Calcd. for $C_{17}H_{11}N_3$: C, 79.36; H, 4.31; N, 16.33. Found: C, 79.17; H, 4.15; N, 15.98.

5-Methoxy-2-(4-(4-methoxyphenyl)pyrimidin-2-yl)-benzonitrile (4c). The general procedure was followed with 2,4-bis(4-methoxyphenyl)pyrimidine **3c** (116.8 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4c** (52.0 mg, 41%) as a white solid: mp 117−119 °C; IR (KBr, cm^{-1}) 3072, 2960, 2851, 2222, 1606, 1582, 1413, 1256, 1029, 815; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.83 (d, J = 5.0 Hz, 1H), 8.56 (d, J = 8.5 Hz, 1H), 8.35 (dd, J = 7.0, 2.0 Hz, 2H), 7.63 (d, J = 5.0 Hz, 1H), 7.38 (d, J = 2.5 Hz, 1H), 7.25 (dd, J = 9.0, 2.5 Hz, 1H), 7.09 (dd, J = 7.0, 2.0 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.8, 162.3, 162.1, 160.7, 157.5, 133.1, 132.0, 129.3, 128.8, 119.8, 119.5, 118.7, 114.4, 113.9, 112.8, 55.8, 55.4; EI-MS m/z (%) 317 (30) [M^+], 316 (100), 302 (16), 273 (12); HRMS (EI-TOF) m/z calcd for $C_{19}H_{14}N_3O_2$ [M^+-H] 316.1086, found 316.1083.

***N*-(2-(2-Cyanophenyl)pyrimidin-4-yl)acetamide (4d).** The general procedure was followed with *N*-(2-phenylpyrimidin-4-yl)-acetamide **3d** (85.2 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) afforded **4d** (38.0 mg, 40%) as a white solid: mp 203−205 °C; IR (KBr, cm^{-1}) 3265, 2219, 1690, 1574, 1246, 763, 558; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.75 (d, J = 5.5 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.29 (br, 1H), 8.14 (d, J = 5.5 Hz, 1H), 7.81 (dd, J = 7.5, 1.0 Hz, 1H), 7.68 (td, J = 7.5, 1.0 Hz, 1H), 7.55 (td, J = 7.5, 1.0 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.6, 161.8, 158.9, 157.2, 139.5, 135.0, 132.6, 130.3, 130.3, 111.5, 108.8, 24.8; EI-MS m/z (%) 238 (4) [M^+], 43 (100); HRMS (EI-TOF) m/z calcd for $C_{13}H_{10}N_4O$ [M^+] 238.0855, found 238.0851.

1-(Pyrimidin-2-yl)-2-naphthonitrile (4e). The general procedure was followed with 2-(naphthalen-1-yl)pyrimidine **3e** (82.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4e** (60.1 mg, 65%) as a white solid: mp 228−230 °C; IR (KBr, cm^{-1}) 3052, 2227, 1557, 1375, 810, 742; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.03 (d, J = 5.0 Hz, 2H), 8.01 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.64 (td, J = 8.0, 1.0 Hz, 1H), 7.56 (td, J = 8.0, 1.0 Hz, 1H), 7.47 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.4, 157.5, 142.2, 135.0, 130.5, 130.1, 128.8, 128.4, 128.2, 127.0, 126.4, 120.3, 118.4, 110.2; EI-MS m/z 231 (83) [M^+], 230 (100), 204 (23), 151 (43); HRMS (EI-TOF) m/z calcd for $C_{15}H_9N_3$ [M^+] 231.0796, found 231.0802.

3-(Pyrimidin-2-yl)-2-naphthonitrile (4f). The general procedure was followed with 2-(naphthalen-2-yl)pyrimidine **3f** (82.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4f** (58.2 mg, 63%) as a white solid: mp 202−204 °C; IR (KBr, cm^{-1}) 3050, 2223, 1556, 1411, 816, 749; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.94 (d, J = 5.0 Hz, 2H), 8.85 (s, 1H), 8.41 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.68−7.62 (m, 2H), 7.32 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.2, 157.4, 137.6, 134.7, 134.3, 132.7, 131.2, 129.5, 129.1, 128.8, 128.1, 120.0, 119.4, 108.9; EI-MS m/z 231 (50) [M^+], 178 (100), 152 (15), 52 (62); Anal. Calcd. for $C_{15}H_9N_3$: C, 77.91; H, 3.92; N, 18.17. Found: C, 77.85; H, 3.82; N, 17.93.

10-(Pyrimidin-2-yl)phenanthrene-9-carbonitrile (4g). The general procedure was followed with 2-(phenanthren-9-yl)pyrimidine **3g** (102.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) afforded **4g** (30.1 mg, 47% yield based on 57% conversion of **3g**) as a yellow solid: mp 139−140 °C; IR (KBr, cm^{-1}) 3074, 3039, 2215, 1554, 1416, 748, 717; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.10 (d, J = 5.0 Hz, 2H), 8.80 (d, J = 7.5 Hz, 2H), 8.45 (dd, J = 8.0, 1.0 Hz, 1H), 7.86−7.80 (m, 3H), 7.74 (d, J = 8.5 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.54 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.0, 157.6, 143.6, 132.0, 129.6, 128.7, 128.6, 128.4, 127.7, 126.7, 123.1, 123.0, 120.5, 116.7, 110.1; EI-MS m/z (%) 281 (64) [M^+], 280 (44), 254 (23); HRMS (EI-TOF) m/z calcd for $C_{19}H_{11}N_3$ [M^+] 281.0953, found 281.0959.

1-(Pyrimidin-2-yl)-1*H*-pyrrole-2-carbonitrile (4h).[31] The general procedure was followed with 2-(1*H*-pyrrol-1-yl)pyrimidine **3h** (58.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4h** (54.4 mg, 80%) as a white solid: mp 115−118 °C; IR (KBr, cm^{-1}) 3131, 2224, 1581, 1564, 1450, 1423, 1337, 1267, 1178, 828, 814, 748; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.74 (d, J = 4.5 Hz, 2H), 7.99 (dd, J = 3.0, 2.0 Hz, 1H), 7.23 (t, J = 4.5 Hz, 1H), 7.08 (dd, J = 4.0, 1.5 Hz, 1H), 6.38 (t, J = 4.5 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 159.4, 154.3, 126.4, 125.5, 119.9, 113.8, 112.2, 101.7; LC-MS (ESI) m/z 171 [M^+H].

1-(Pyrimidin-2-yl)-1*H*-indole-2-carbonitrile (4i).[31] The general procedure was followed with 1-(pyrimidin-2-yl)-1*H*-indole **3i** (78.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4i** (51.0 mg, 58%) as a white solid: mp 120−121 °C; IR (KBr, cm^{-1}) 3101, 2225, 1572, 1531, 1449, 1427, 1256, 812, 739, 625; ^1H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, J = 5.0 Hz, 2H), 8.69 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.52−7.48 (m, 1H), 7.47 (s, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.5, 156.8, 136.8, 128.0, 127.8, 123.7, 122.2, 121.2, 118.2, 116.4, 114.4, 109.1; LC-MS (ESI) m/z 221 [M^+H].

9-(Pyrimidin-2-yl)-9*H*-carbazole-1-carbonitrile (4j). The general procedure was followed with 9-(pyrimidin-2-yl)-9*H*-carbazole **3j** (98.0 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4j** (59.4 mg, 55%) as a white solid: mp 183−185 °C; IR (KBr, cm^{-1}) 3050, 2961, 2924, 2221, 1562, 1452,

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1430, 1208, 739; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.00 (d, J = 5.0 Hz, 2H), 8.34 (t, J = 8.0 Hz, 2H), 8.12 (d, J = 8.0 Hz, 1H), 7.83 (dd, J = 7.5, 1.0 Hz, 1H), 7.56 (td, J = 7.0, 1.0 Hz, 1H), 7.45−7.42 (m, 2H), 7.36 (t, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.6, 157.0, 140.1, 138.2, 132.4, 127.8, 127.1, 124.6, 123.8, 122.8, 121.6, 120.0, 119.0, 117.7, 113.3, 98.5; EI-MS m/z (%) 270 (100) [M^+], 245 (25), 217 (9), 192 (20), 164 (14); HRMS (EI-TOF) m/z calcd for $C_{17}H_{10}N_4$ [M^+] 270.0905, found 270.0903.

Benzo[*h*]quinoline-10-carbonitrile (4k).[15] The general procedure was followed with benzo[*h*]quinoline **3k** (71.6 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **4k** (80.0 mg, 98%) as a white solid: mp 143−145 °C; IR (KBr, cm^{-1}) 3440, 3047, 2207, 1424, 832, 716, 664; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.12 (dd, J = 4.5, 1.5 Hz, 1H), 8.22 (dd, J = 8.0, 1.5 Hz, 1H), 8.14 (dd, J = 7.5, 1.5 Hz, 1H), 8.11 (dd, J = 9.0, 1.0 Hz, 1H), 7.82−7.76 (m, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.63−7.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.5, 144.5, 136.2, 135.7, 134.0, 132.7, 130.7, 127.4, 127.2, 127.1, 126.9, 123.0, 120.8, 108.9; EI-MS m/z (%) 204 (100) [M^+], 176 (11), 150 (13).

2-(Pyrimidin-2-yl)cyclohex-1-enecarbonitrile (6a). The general procedure was followed with 2-(cyclohex-1-en-1-yl)pyrimidine **5a** (64.0 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **6a** (47.4 mg, 64%) as a colorless oil: IR (KBr, cm^{-1}) 3036, 2944, 2860, 2197, 1555, 1415, 824, 799; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.83 (d, J = 5.0 Hz, 2H), 7.27 (t, J = 5.0 Hz, 1H), 2.79−2.76 (m, 2H), 2.55−2.52 (m, 2H), 1.85−1.76 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.1, 156.8, 150.7, 120.2, 119.4, 113.2, 29.7, 27.8, 21.4, 21.3. LC-MS (ESI) m/z 186 [M^+H]; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{12}N_3$ [M^+H] 186.1031, found 186.1026.

2-(Pyridin-2-yl)cyclopent-1-enecarbonitrile (6b). The general procedure was followed with 2-(cyclopentenyl)pyridine **5b** (58.0 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **6b** (32.6 mg, 48%) as a white solid: mp 126−128 °C; IR (KBr, cm^{-1}) 3059, 2973, 2949, 2206, 1577, 1473, 1426, 1345, 989, 791, 742, 610; ^{1}H NMR (Acetone-d_6, 500 MHz) δ 8.69−8.68 (m, 1H), 7.91 (td, J = 8.0, 2.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.42−7.40 (m, 1H), 3.09−3.05 (m, 2H), 2.88−2.84 (m, 2H), 2.15−2.09 (m, 2H); ^{13}C NMR (Acetone-d_6, 125 MHz) δ 157.8, 152.6, 150.4, 137.5, 124.9, 122.8, 117.9, 110.6, 37.3, 35.5, 22.9; EI-MS m/z (%) 170 (58) [M^+], 169 (100), 142 (13), 117 (8); HRMS (EI-TOF) m/z calcd for $C_{11}H_{10}N_2$ [M^+] 170.0844, found 170.0843.

2-(Pyridin-2-yl)cyclohex-1-enecarbonitrile (6c). The general procedure was followed with 2-(1-cyclohexenyl)pyridine **5c** (63.6 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (11.0 mg, 0.032 mmol), $Cu(TFA)_2$ (232.0 mg, 0.8 mmol), *t*-BuNC (66.4 mg, 0.8 mmol) and DCE (2.0 mL). After reaction was over, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) afforded **6c** (38.3 mg, 52%) as a colorless oil: IR (KBr, cm^{-1}) 3051, 2925, 2854, 2208, 1584, 1464, 1260, 1082, 1022, 802, 783; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.65−8.63 (m, 1H), 7.89 (td, J = 8.0, 2.0 Hz, 1H), 7.61 (dt, J = 7.5, 2.0 Hz, 1H), 7.43−7.40 (m, 1H), 2.61−2.59 (m, 2H), 2.42−2.39 (m, 2H), 1.74−1.67 (m, 4H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 156.7, 154.2, 149.6, 137.4, 124.3, 122.8, 119.8, 109.3, 29.1, 28.5, 21.5, 21.3; EI-MS m/z (%):184 (99) [M^+], 183 (100), 169 (47), 155 (41); HRMS (EI-TOF) m/z calcd for $C_{12}H_{12}N_2$ [M^+] 184.1000, found 184.0997.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra for all compounds, X-ray structure of compound **4c** (CIF), and details for mechanistic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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