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Rhodium(III)-Catalyzed Selective C–H Cyanation of Indolines and Indoles with an Easily Accessible Cyano Source

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Abstract: The rhodium-catalyzed selective cyanation of C–H bonds of indolines and indoles with *N*-cyano-*N*-phenyl-*para*-methylbenzenesulfonamide is described. This protocol offers a facile access to C-7 cyanated indolines and C-2 cyanated indoles with high site selectivity and excellent functional group tolerance.

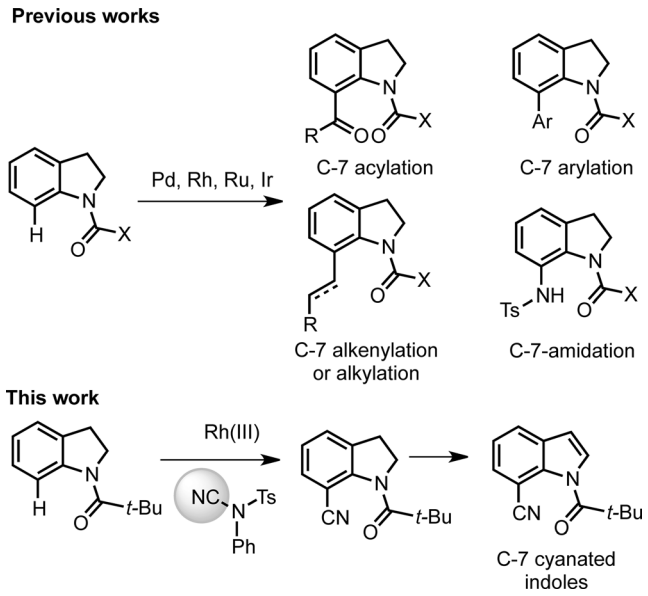
Keywords: C–H activation; cyanation; indoles; indolines; rhodium

Aromatic nitriles have been recognized as integral structural motifs of pharmaceuticals, natural products, agrochemicals, and dyes.[1] The nitrile moiety has also served as a versatile synthetic precursor for the formation of aldehydes, ketones, amines, amides, carboxylic acids, and heterocycles.[2] Traditional approaches for the synthesis of aromatic nitriles rely on Sandmeyer reactions[3] of aryldiazonium salts and Rosenmund–von Braun reactions,[4] which have inherent limitations including the stoichiometric use of metal cyanides and harsh reaction conditions as well as the generation of hazardous HCN by-products. Aryl nitriles can also be prepared from aryl amides, aryl oximes, benzylic amines, and benzylic alcohols by using conventional conditions.[5] Alternative methods are the transition metal-catalyzed cyanation of aryl halides or arylboronic acids with nucleophilic nitrile sources, such as metal cyanide salts [CuCN, KCN, NaCN, ZnCN, $K_3Fe(CN)_6$], TMSCN, and acetone cyanohydrins.[6]

Recently, a great deal of effort has been devoted to the direct cyanation of arene C–H bonds with non-metallic nitrile equivalents.[7] The selective cyanation of C–H bonds might be the most economic and benign route to the preparation of aryl nitrile derivatives. For example, Yu reported the Cu(II)-mediated C–H cyanation of arylpyridines with TMSCN or $MeNO_2$ as CN sources.[8] Chang described the Pd(II)-catalyzed cyanation of arene C–H bonds[9] and the Cu(II)-mediated cyanation of electron-rich arenes[10] using *N*,*N*-dimethylformamide (DMF) and ammonia as a combined source for the cyano unit. Jiao demonstrated the Pd(II)-catalyzed C-3 cyanation of indoles and benzofurans employing DMF as both reagent and solvent.[11] In addition, some studies on the palladium-catalyzed and cooper-mediated direct cyanations of aromatic compounds using non-metallic cyano sources, such as TMSCN,[12] isonitrile,[13] NH_4HCO_3/DMSO,[14] tosyl cyanide[15] and AIBN,[16] have been explored. Recently, Zhu demonstrated the practicable method for the formation of C-2 cyanated indoles using readily available MeCN as a cyanating agent in the presence of a copper salt.[17]

The reagent *N*-cyano-*N*-phenyl-*para*-methylbenzenesulfonamide (NCTS) can be easily prepared from phenylurea and *para*-toluenesulfonyl chloride *via* a single-step process.[18] In 2011, Wang first reported the Lewis acid-catalyzed C–H cyanation of indoles and pyrroles at the C-3 position with NCTS as a new electrophilic cyanating agent.[19] Fu[20] and Anbarasan,[21] independently, reported the Rh(III)-catalyzed direct C–H cyanations of oximes and arylpyridines with NCTS in 2013. Shortly afterwards, aryl phosphates, benzamides and azobenzenes were also investigated as directing groups in the Rh(III)- or Ru(II)-catalyzed cyanation reactions using NCTS.[22] During the preparation of our manuscript, Ackermann[23] and Glorius,[24] respectively, demonstrated the Co(III)-catalyzed selective C–H cyanation of arenes and heteroarenes with NCTS.

The indoline nucleus is a ubiquitous structural core and is widely found in heterocyclic compounds with biological and medicinal applications.[25] In particular,



Scheme 1. Catalytic C–H functionalization of indolines at the C-7 position.

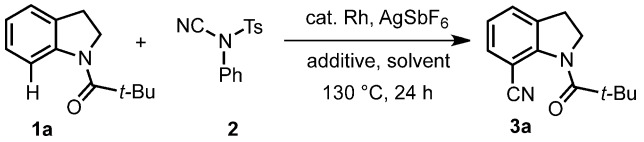
many pharmaceutical agents include the C-7 substituted indoline framework.[26] The installation of the CN group into bioactive molecules may dramatically modify their biological properties. Recently, the directing group-assisted C-7 functionalizations of indolines has been an area of intensive research with the aim to override the inherent selectivity of indoles.[27] In this context, acylation, arylation, alkenylation, alkylation, and amidation reactions were developed (Scheme 1).

In 1995, Roduit and Wellig first described the formation of 7-cyanoindoline from indoline with trichloroacetonitrile as a cyanating agent in the presence of a stoichiometric amount of BCl_3.[28] In this precedent report, only one example is given for the C-7 cynation reaction. Despite these advances, there has been no report on a catalytic C–H cyanation at the C-7 position of indolines and indoles. Herein, we described a facile approach for the C-7 selective C–H cyanation of indolines with NCTS as a user-friendly cyanation reagent. It is noteworthy that the formed C-7 cyanated indolines can be readily transformed into C-7 cyanated indoles under oxidative conditions.

We initiated our investigation by varying the reaction conditions for the envisioned C–H cyanation of *N*-pivaloylindoline **1a** with NCTS (**2**), and selected results are summarized in Table 1.

Initial experiments indicated that a cationic Rh catalyst in the presence of $Cu(OAc)_2$ in DCE solvent at 130 °C can promote the coupling of **1a** and **2** to provide the cyanated indoline **3a** in 32% yield (Table 1, entry 1). After screening a range of acetate additives, NaOAc was found to exhibit the highest reactivity (Table 1, entries 2–5). Also, a cationic Ru catalyst enabled the desired cyanation reaction to proceed to

Table 1. Optimization of the reaction conditions.[a]



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

Entry	Catalyst	Additive	Solvent	Yield [%][b]
1	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$	DCE	32
2	$[RhCp^*Cl_2]_2$	AgOAc	DCE	61
3	$[RhCp^*Cl_2]_2$	NaOAc	DCE	65
4	$[RhCp^*Cl_2]_2$	KOAc	DCE	40
5	$[RhCp^*Cl_2]_2$	CsOAc	DCE	30
6	$[Ru(p\text{-cymene})Cl_2]_2$	NaOAc	DCE	46
7	$[RhCp^*Cl_2]_2$	NaOAc	THF	30
8	$[RhCp^*Cl_2]_2$	NaOAc	MeCN	10
9	$[RhCp^*Cl_2]_2$	NaOAc	toluene	N.R.
10	$[RhCp^*Cl_2]_2$	NaOAc	*t*-AmOH	10
11	$[RhCp^*Cl_2]_2$	NaOAc	DMF	N.R.
12[c]	$[RhCp^*Cl_2]_2$	NaOAc	DCE	10
13	$[RhCp^*Cl_2]_2$		DCE	24
14[d]	$[RhCp^*Cl_2]_2$	NaOAc	DCE	50
15[e]	$[RhCp^*Cl_2]_2$	NaOAc	DCE	77

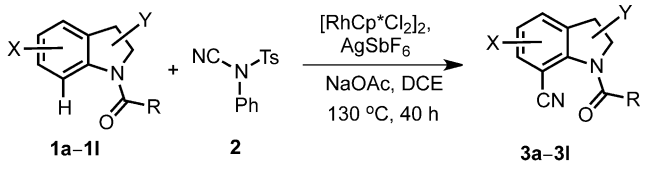
[a] *Reaction conditions*: **1a** (0.2 mmol), **2** (0.4 mmol), catalyst (5 mol%), $AgSbF_6$ (20 mol%), additive (30 mol%), solvent (1 mL) at 130 °C for 24 h in pressure tubes.
[b] Yield of product isolated by flash column chromatography.
[c] Without $AgSbF_6$.
[d] **2** (0.3 mmol, 1.5 equiv.).
[e] 40 h.

afford **3a**, albeit in relatively low yield (Table 1, entry 6). Further screening of solvents under otherwise identical conditions revealed that DCE was the most effective solvent for this coupling reaction (Table 1, entries 7–11). Exclusion of either $AgSbF_6$ or NaOAc resulted in a significantly decreased formation of the desired product **3a** (Table 1, entries 12 and 13). A decreased loading of the cyanide source **2**, under otherwise identical conditions, led to a relatively decreased formation of **3a** (Table 1, entry 14). Finally, we observed that a longer reaction time provided optimal results for the C-7 cyanation of *N*-pivaloylindoline (Table 1, entry 15).

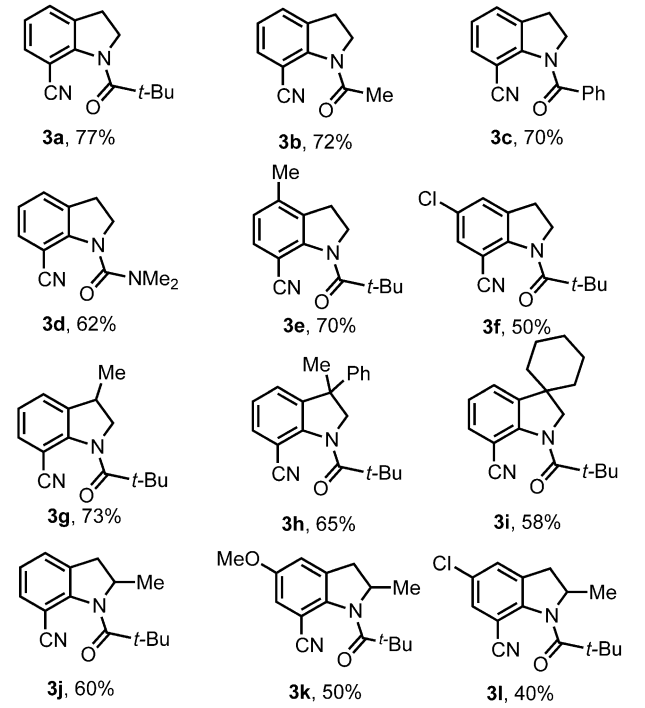
To explore the substrate scope and limitations, a range of indolines was tested under the optimal reaction conditions (Table 2). Other carbonyl or carbamoyl directing groups **1b**–**1d** were found to be effective in the C-7 cyanation reaction of indolines. The cyanation reactions of C-2, C-3 or C-4 substituted *N*-pivaloylindolines **1e** and **1g**–**1j** provided our desired C-7 cyanated products **3e** and **3g**–**3j** in moderate to good yields. However, the cyanation of C-5 substituted indolines **1f**, **1k** and **1l** was found to be relatively less efficient under the current reaction conditions.

With the results on C-7 cyanation of indolines in hand, we further explored the C-2 selective cyanation

Table 2. Scope of the C-7 cyanation of indolines.[a,b]



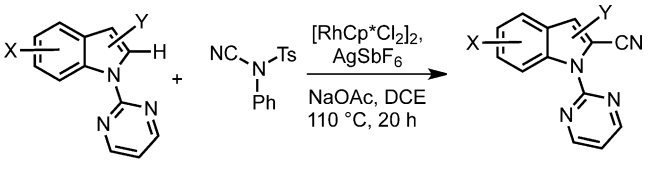
1a–1l 2 3a–3l



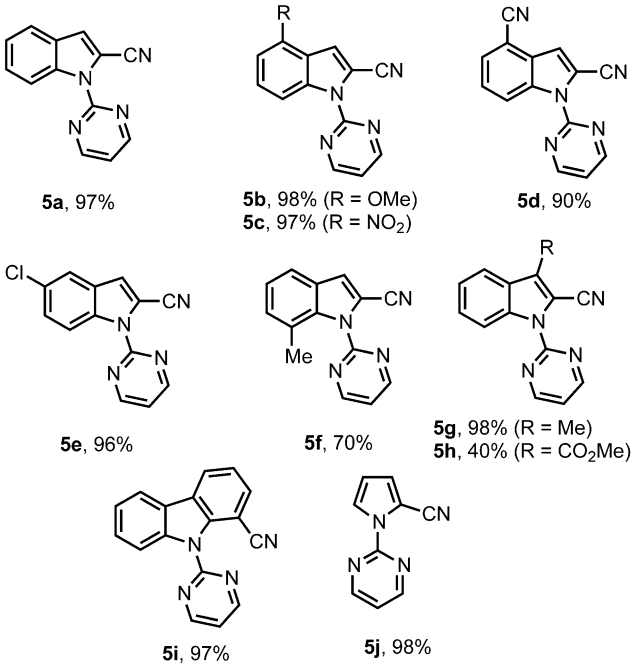
[a] *Reaction conditions*: **1a**–**1l** (0.2 mmol), **2** (0.4 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), NaOAc (30 mol%), DCE (1 mL) at 130 °C for 40 h in pressure tubes.

[b] Yield of product isolated by flash column chromatography.

Table 3. Scope of the C-2 cyanation of indoles.[a]



4a–4j 2 5a–5j



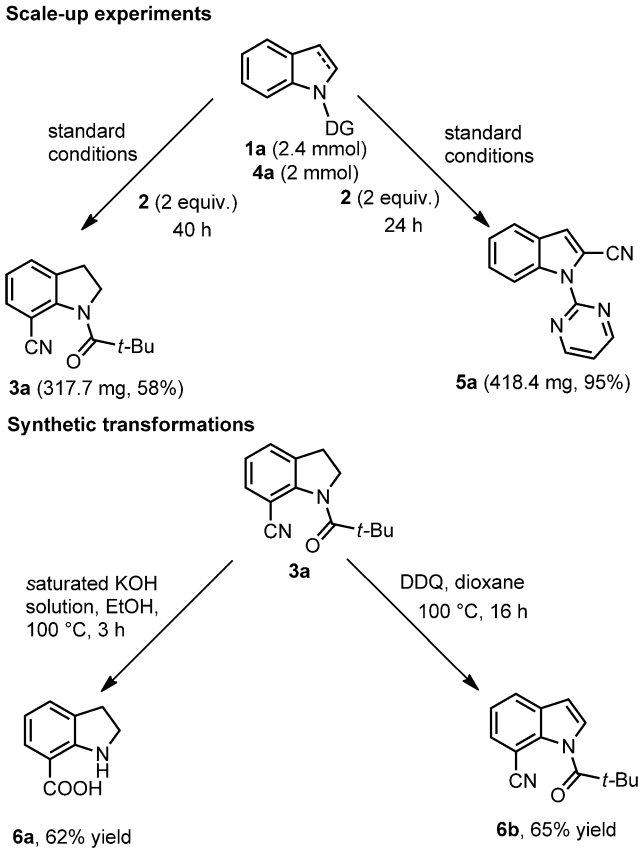
[a] *Reaction conditions*: **4a**–**4j** (0.2 mmol), **2** (0.4 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), NaOAc (30 mol%), DCE (1 mL) at 110 °C for 20 h in pressure tubes.

[b] Yield of product isolated by flash column chromatography.

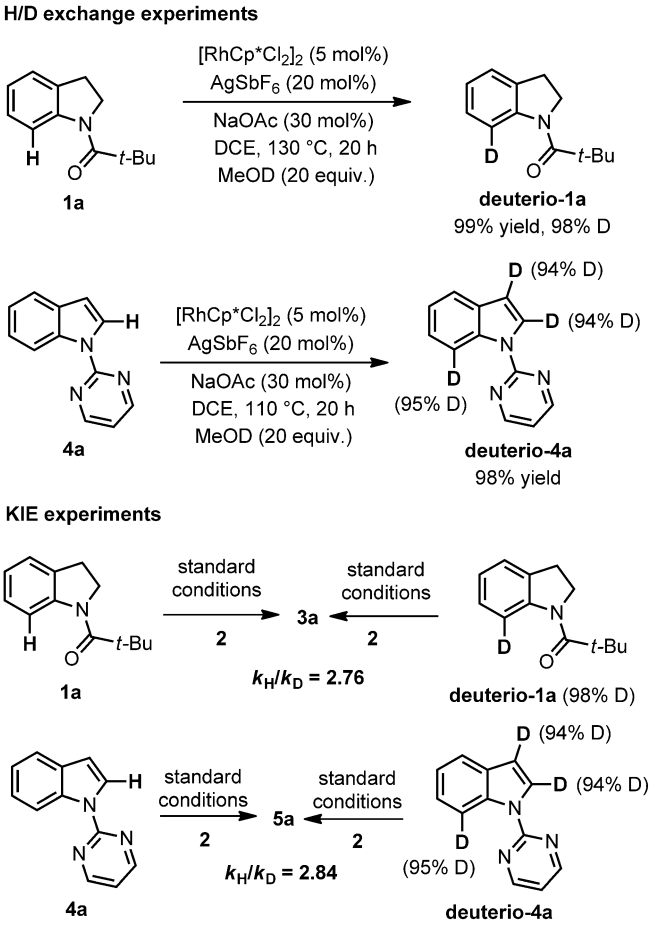
of biologically active heterocycles with a removable pyrimidine directing group (Table 3). To our delight, indole **4a** was efficiently coupled with NCTS (**2**) under very similar reaction reaction conditions to provide C-2 cyanated indole **5a** in 97% yield. In addition, indoles **4b**–**4f** bearing electron-rich and electron-deficient groups (OMe, NO_2, CN, Cl and Me) on the aromatic ring were found to be good substrates in this catalytic transformation. Notably, the sterically more congested C-3 substituted indole **4g** delivered the desired cyanated product **5g** with an excellent yield upon isolation. However, indole **4h** with an ester moiety at the C-3 position displayed a relatively decreased reactivity. Furthermore, carbazole **4i** and pyrrole **4j** also participated in this catalytic cyanation reaction to furnish the monocyanated products **5i** and **5j** in almost quantitative yields.

The scale-up reactions of indoline **1a** and indole **4a** were performed under the standard reaction conditions to afford the corresponding cyanated products **3a** (58%) and **5a** (95%), respectively (Scheme 2). To demonstrate the utility of C-7 cyanated indolines, cleavage of the *N*-pivaloyl group of **3a** under basic conditions was first attempted to afford free-(NH)-indoline **6a** in 62% yield concomitant with the hydrolysis of a nitrile group. In addition, oxidation of **3a** was performed by using of DDQ to deliver the C-7 cyanated indole **6b** in 65% yield. Meanwhile, we also carried out the deprotection of a pyrimidyl directing group on C-7 cyanated indole **5a** (Scheme 3). Treatment of **5a** with NaOEt in DMSO at 110 °C afforded 1*H*-indole-2-carbonitrile (**7a**) in 96% isolated yield, which is the key precursor for pharmaceutical agents.[29,30]

To gain some mechanistic insights into this cyanation reaction, H/D exchange experiments using indoline **1a** and indole **4a** were performed (Scheme 4). When MeOD was added to the reaction mixtures, remarkable H/D exchanges of recovered deuterio-**1a** and deuterio-**4a** were observed, which is indicative of



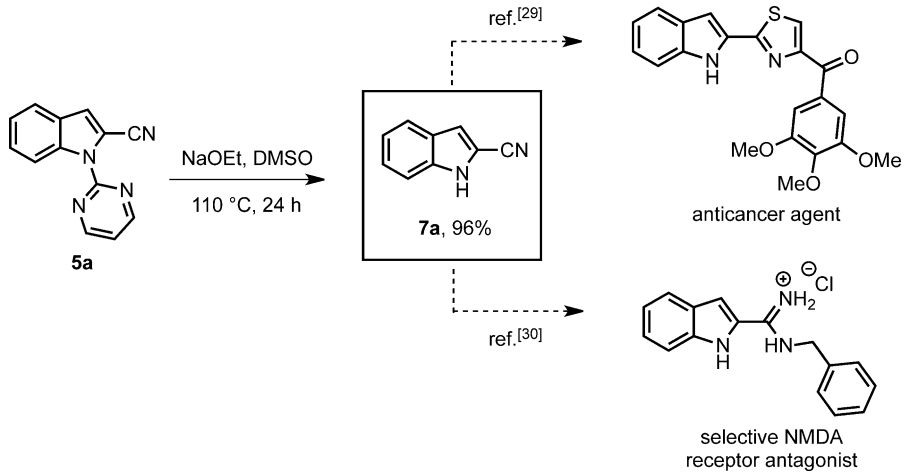
Scheme 2. Scale-up experiments and synthetic transformations.



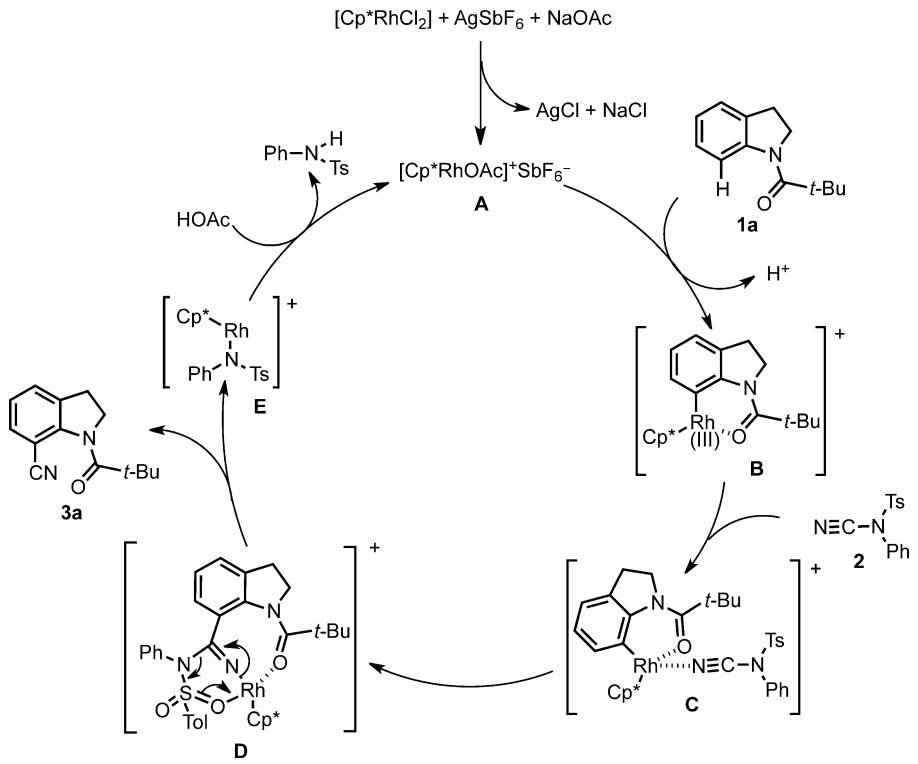
Scheme 4. H/D exchange and KIE experiments.

the reversible metalation–proto(deutero)demetallation process. Next, kinetic isotope effect (KIE) experiments on indolines (**1a** and deuterio-**1a**) and indoles (**4a** and deuterio-**4a**) with **2** were carried out under the standard reaction conditions, which resulted in the KIE values (k_H/k_D) of 2.76 and 2.84, respectively, thus indicating that C–H cleavage might be involved in the rate-limiting step.[31]

Based on our mechanistic studies, a possible catalytic cycle was proposed as shown in Scheme 5. First, treatment of $[RhCp^*Cl_2]_2$ with $AgSbF_6$ and NaOAc generate the reactive cationic Rh(III) catalyst **A**, which undergoes a reversible C–H metallation with **1a** to yield the cyclometallated complex **B**. Subsequent coordination of NCTS (**2**) with **B** provides in-



Scheme 3. Removal of a directing group and its application.



Scheme 5. Proposed reaction mechanism.

termediate **C**, followed by insertion of the CN group into the C(sp^2)–Rh bond generating the key intermediate **D**. Then rearrangement of **D** delivers the cyanated product **3a** and rhodium species **E**, which undergoes ligand exchange to afford the active rhodium species **A**.

In conclusion, we have described an efficient method for the rhodium-catalyzed direct C-7 or C-2 cyanations of highly substituted indolines or indoles with NCTS as the non-metallic cyano group source. These protocols allow the generation of an array of cyanated indoles, which are known to be crucial scaffolds of biologically active compounds.

Experimental Section

Representative Procedure for C-7 Cyanation of *N*-Pivaloylindolines with NCTS

To an oven-dried sealed tube charged with *N*-pivaloylindoline (**1a**) (40.6 mg, 0.2 mmol, 100 mol%), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol%), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol%), and NaOAc (4.9 mg, 0.06 mmol, 30 mol%) in DCE (1 mL) was added NCTS (**2**) (108.9 mg, 0.4 mmol, 200 mol%). The reaction mixture was allowed to stir at 130 °C for 40 h, and then cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated under vacuum. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 10:1) to afford **3a**; yield: 35.2 mg (77%).

Representative Procedure for C-2 Cyanation of *N*-(2-Pyrimidinyl)indoles with NCTS

To an oven-dried sealed tube charged with *N*-(2-pyrimidinyl)-indole (**4a**) (39.1 mg, 0.2 mmol, 100 mol%), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol%), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol%), and NaOAc (4.9 mg, 0.06 mmol, 30 mol%) in DCE (1 mL) was added NCTS (**2**) (108.9 mg, 0.4 mmol, 200 mol%). The reaction mixture was allowed to stir at 110 °C for 20 h, and then cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated under vacuum. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 10:1) to afford **5a**; yield: 42.9 mg (97%).

Acknowledgements

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