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Nickel Catalyzed Site Selective C–H Functionalization of α-Aryl-thioamides

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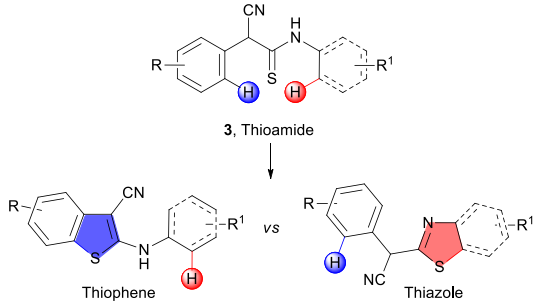
A catalytic site selective intramolecular C—S bond forming reaction is demonstrated for the first time. The C—H bond functionalization of α-aryl-thioacetanilides was efficiently catalyzed by 2 mol% $NiBr_2$ and resulting in the valuable 2-aminobenzo[*b*]thiophenes in moderate to good yields. Further, selective sp^2 C—H bond functionalization over sp^3 is exemplified.

Metal catalyzed C—H functionalization of sp^2 carbon is a powerful tool for the construction of C—C and C—X (X = O, N, S, P, B… etc.) bonds in organic synthesis.[1] Particularly, the regioselective C—H bond functionalization has received much attention among synthetic chemists.[2] In this context, the significant progress has been achieved by use of precious metals such as Pd, Rh, Ru, and Ir as catalyts.[3] However, non-precious metals such as Fe, Cu, Co, and Ni are less explored.[4] Recently, Chatani's group reported[5] an excellent combination of a nickel catalyst and an *N*,*N*'-bidentate chelating group that has been used for several C—H bonds functionalization reactions.[6] The mechanism for the nickel catalyzed reaction was also investigated by computational studies.[7] These results encouraged us to explore nickel catalysts for the site selective C—H functionalization of arenes and their applications in the synthesis of S-heterocycles.

Benzo[*b*]thiophene is an interesting class of heterocyclic compounds. This core is found in various drugs and materials.[8] In particular, 2-aminobenzo[*b*]thiophenes act as inhibitors in tubulin polymeriztion[9] and acetyl-CoA carboxylase[10] and are also used as precursors in the synthesis of the drug raloxifene and its various analogues.[11] In literature, several methods have been reported for the synthesis of 2-aminobenzo[*b*]thiophenes.[12,13] The most of the methods involve either a multi-step synthesis[12] or an intramolecular cross-coupling of C—S bond with aryl halides.[13] However, the C—H bond functionalization strategy is rarely used for the construction of the benzo[*b*]thiophene core.[8d] In 2008, Inmoto and co-workers have first reported the 2,3-diarylbenzo[*b*]thiophenes from the aryl substituted thioenols through a palladium catalyzed C—H thiolation at 120 °C.[14] Later, Antonchick's[15] and Duan's[16] groups demonstrated synthesis of dibenzothiophenes[17] via an interesting palladium catalyzed tandem C—H bond functionalization strategy. Recently, highly substituted and functionalized benzo[*b*]thiophenes were reported that involved palladium/copper mediated intramolecular C—S bond formation at 90 °C.[18] Despite good yields, these methods have their own limitations such as high reaction temperature,[14] longer reaction time,[14] and use of co-catalyst.[18b] Therefore, developing a newer catalytic method for the synthesis of benzo[*b*]thiophenes in ambient conditions is highly desirable.

The use of nickel-catalyzed C—H bond functionalization reactions for the synthesis of heterocycles have been reported recently.[5] Particularly, a number of saturated and unsaturated *N*-heterocyles, such as lactums, indoles, isoquinolones, were synthesized through nickel mediated C—N bond formation.[19] Although, nickel has been found to form C—S bond efficiently via C—H functionalization.[20] To the best of our knowledge,



Scheme 1. Site Selective C—H Functionalization of α-Aryl-thioamides **3**

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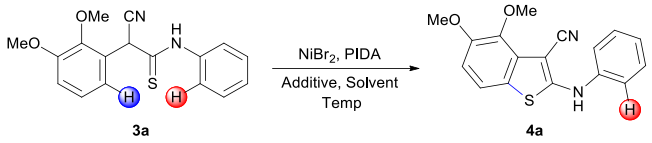
†Electronic Supplementary Information (ESI) available: [Experimental procedures and spectral characterization of compounds **3, 4, 5, and 6**. Copies of ^1H, ^{13}C NMR, and HRMS Spectra of all compounds. The X-ray data were also deposited with the CCDC (entries 1855418 & 1855419)]. See DOI: 10.1039/x0xx00000x

catalytic nickel mediated synthesis of *S*-heterocycles via intramolecular C—S bond formation is not reported.[21] In continuation of our ongoing interest in developing practical methods for the construction of heterocycles with novel physical properties,[22] we report herein the $NiBr_2$ catalyzed highly site selective C—H bond functionalization of α-aryl-thioacetanilides (Scheme 1).

Table 1. Optimization of the Nickel Catalyzed Site Selective C—H Bond Functionalization of α-Aryl-thioacetanilide **3a**[a,b]



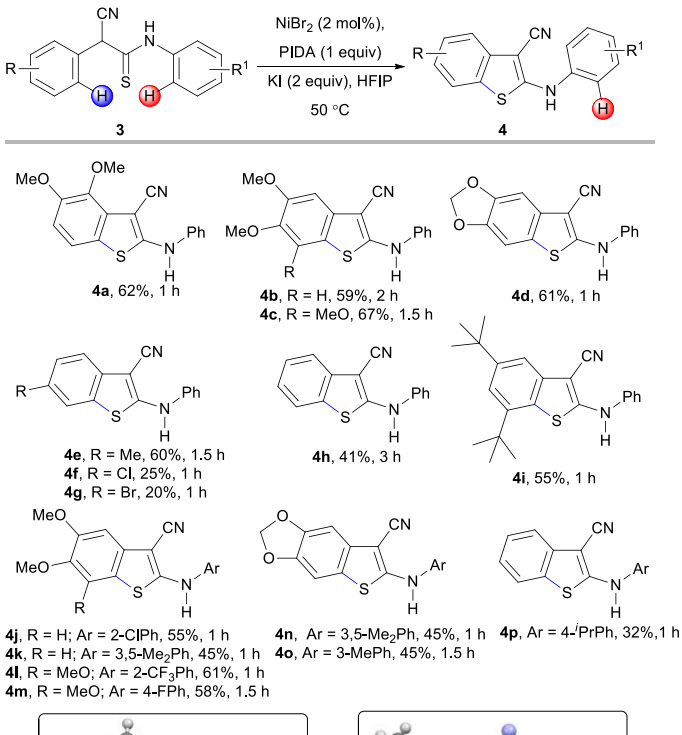
3a 4a

Entry	$NiBr_2$	Additive	Oxid	Solvent	Temp	Yield of 4a
1.	2 mol%	-	PIDA	Dioxane	rt	12%
2.	2 mol%	-	PIDA	Dioxane	60 °C	22%
3.	2 mol%	-	PIDA	Dioxane	120 °C	32%
4.	2 mol%	-	PIDA	HFIP	50 °C	35%
5.	2 mol%	KI	PIDA	HFIP	50 °C	62%[c]
6.	2 mol%	KI	PIDA	HFIP	50 °C	52%[c,d]
7.	2 mol%	-	PIDA	HFIP	50 °C	18%[d,e]
8.	5 mol%	KI	PIDA	HFIP	50 °C	60%[c]
9.	10 mol%	KI	PIDA	HFIP	50 °C	54%[c]
10.	-	KI	PIDA	HFIP	50 °C	30%[c,h]
11.	-	-	PIDA	HFIP	50 °C	10%[f]
12.	2 mol%	KI	PIDA	HFIP	50 °C	60%[c,g]

[a]Reaction conditions: **3a** (0.5 mmol), $NiBr_2$ (x mol%), PIDA (1 equiv) solvent (2.0 mL), temperature, 1-2 h. [b]Isolated yields. [c]KI (2 equiv) was used. [d]Ad_2PBu (4 mol%) was added. [e]Without KI. [f]Without $NiBr_2$.[g]Without KI and $NiBr_2$.[h]TEMPO (1 equiv) was used. HFIP-Hexafluroisopropanol. TEMPO-(2,2,6,6-Tetramethylpiperidin-1-yl)oxy

The key step of the present methodology is the nickel-catalyzed site selective C—H Functionalization of thioanilides **3**. The required thioanilides **3** were prepared by treating the anion *α*-aryl acetonitriles **1** with substituted isothiocyanates **2** in moderate to good yields (Scheme S1, ESI†). After having the thioanilides **3** in our hand, the thioanilide **3a** was chosen as model substrate for the site-selective C—H bond functionalization process (Thiophene vs Thiazole, Scheme 1). Initial experiment was performed with $NiBr_2$ affording only 12% of the product **4a** (Table 1, Entry 1). This product was characterized as 2-anilino-3-cyano-4,5-dimethoxy-benzo[*b*]thiophene (**4a**) by spectral and analytical data analysis. Further, it is confirmed by single crystal X-ray analysis (Table 2). Various conditions were examined to increase the yield of benzo[*b*]thiophene **4a** (Table 1). The reactions were performed at higher temperatures in dioxane and the yield of the product **4a** was increased to 32% at 120 °C (Table 1, Entry 3). The same reaction when carried out in HFIP, **4a** was formed at 50 °C with comparable yield (35%, Entry 4). Interestingly, with KI used as an additive, the C—H bond functionalization process was significantly improved (Table 1, Entry 5, 62%). No trace amount of benzo[*d*]thiazole was formed. To improve the yield of the 2-anilinobenzo[*b*]thiophene **4a**, the reaction was performed with the Ad_2PBu ligand (4 mol%) affording a slightly lower yield (52%, Entry 6, Table S1, ESI†). However, in the absence of KI, the yield of the product drastically dropped to 18% even in the presence ligand (Entry 7). No significant effect was found in increasing the catalyst loading from 2 mol% to 10 mol% (Entries 8 & 9). The reaction when performed in the presence of KI and HFIP, and without $NiBr_2$, the yield dropped to 30% (Entry 10). Similarly, the reaction when carried out in the presence of the oxidant only, **4a** was formed in 10% yield (Entry 11).[24] The reaction was found to be equally effective in the presence of TEMPO (Entry 12) suggesting that the C—H functionalization reaction does not involve a radical pathway. From the above studies, nickel and KI have a synergistic effect in increasing the yield of the C—H functionalized product **4a**.

Table 2. Nickel Catalyzed Site Selective C—H Functionalization of α-Aryl-thioacetanilide **3**[a]

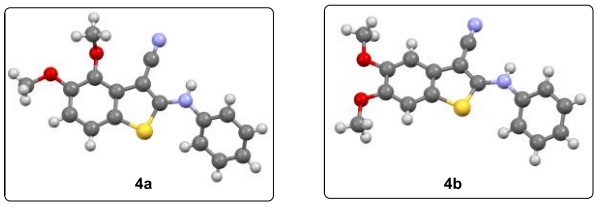


3 4

4a, 62%, 1 h
4b, R = H, 59%, 2 h
4c, R = MeO, 67%, 1.5 h
4d, 61%, 1 h

4e, R = Me, 60%, 1.5 h
4f, R = Cl, 25%, 1 h
4g, R = Br, 20%, 1 h
4h, 41%, 3 h
4i, 55%, 1 h

4j, R = H; Ar = 2-ClPh, 55%, 1 h
4k, R = H; Ar = 3,5-Me_2Ph, 45%, 1 h
4l, R = MeO; Ar = 2-CF_3Ph, 61%, 1 h
4m, R = MeO; Ar = 4-FPh, 58%, 1.5 h
4n, Ar = 3,5-Me_2Ph, 45%, 1 h
4o, Ar = 3-MePh, 45%, 1.5 h
4p, Ar = 4-^{i}PrPh, 32%,1 h



4a **4b**

[a]Isolated yields.

With the optimized conditions in our hand, we studied a series of thioanilides **3b-o** for the site selective C—H bond functionalization reactions. The electron donating substituent on aryl moieties **3b-d** smoothly underwent C—H functionalization reaction affording exclusively the benzo[*b*]thiophenes **4b-d** in

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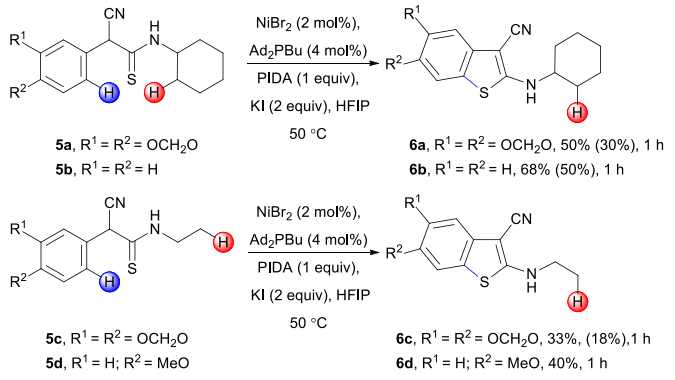
59 to 67% yields (Table 2) within 2 hours. Similarly, methyl substituted **3e** was transformed to benzo[*b*]thiophene **4e** in 60% yield under the optimized conditions. However, halo derivatives **3f-g** gave only 20-25% of the corresponding benzo[*b*]thiophenes **4f-g**. The unsubstituted thioanilide **3h** was also transformed to 2-anilino-3-cyanobenzo[*b*]thiophene (**4h**) in 41% yield. Interestingly, 1-(3,5-di^{t}butylphenyl)-1'-cyanothioacetamide **3i** smoothly underwent a highly hindered C—H bond functionalization affording 2-anilino-3-cyano-5,7-di^{t}butyl-benzo[*b*]thiophene (**4i**) in 55% yield within 1 hour under the identical reaction conditions. Various *N*-aryl substituted thioamides **3j-p** were also studied for the site selective C—H functionalization reaction (Table 2). The *N*-2-chlorophenyl substituted thioamide **3j** was transformed to benzo[*b*]thiophene **4j** (55%) without forming the thiazole derivative. Similarly, the *N*-3,5-dimethylphenyl thioamide derivative **3k** was converted to the corresponding benzo[*b*]thiophene **4k** in 45% yield. Interestingly, electron withdrawing CF_3 group containing *N*-phenyl thioamide **3l** underwent C—H bond functionalization reaction affording exclusively benzo[*b*]thiophene **4l** in 61% yield. The same trend was observed in fluoro derivative **3m** afforded the benzo[*b*]thiophene **4m** in 58% yield. The 3-methyl and 3,5-dimethyl-*N*-phenyl derivatives **3n-o** were transformed to benzo[*b*]thiophenes **4n-o** in 45% yields respectively. However, the 4-isopropyl substituted N-phenyl derivative **3o** gave only 32% benzo[*b*]thiophene **4p** (Table 2). All newly synthesized benzo[*b*]thiophenes **4b-p** were confirmed by spectral and analytical data analysis. X-ray analysis was also used to confirm the structure of one of the benzo[*b*]thiophenes (**4b**, Table 2).

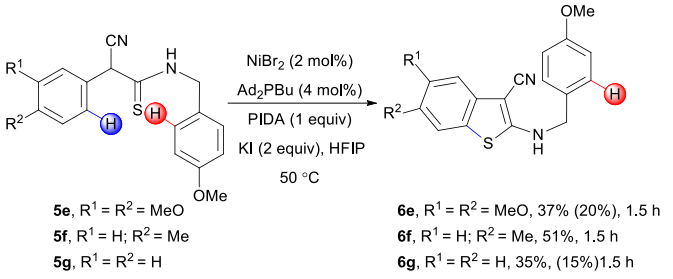
Table 3. Nickel Catalyzed Site Selective C—S Bond Formation of sp^2 C—H Bond vs sp^3 C—H Bond[a,b]



[a]Isolated yields. [b]The parenthesis is yield of product **6** without ligand.

Generally, nickel catalysts have been shown to functionalize both the sp^2 and sp^3 C—H bonds.[24] To this end, an investigation of the current catalytic system on the selectivity of sp^2 vs sp^3 C—H bond is fundamental interest. We have chosen two model substrates **5a** & **5c** for the study of site-selective process. Thus, the required thioamides **5a-d** were synthesized by treating the anion of α-aryl acetonitrile **1** with cyclohexyl and ethyl isothiocyantes (Scheme S2, ESI†). After having aliphatic thioamides **5a-d** in our hand, the first electron donating substituted *N*-cyclohexyl **5a** was subjected to a site selective C—H bond functionalization reaction under the optimized conditions. Interestingly, the benzo[*b*]thiophene **6a** was obtained in 30% yield (Table 3). No trace amount of sp^3 C—H bond functionalization was found. The yield of the product **6a** was increased to 50% by the addition of the Ad_2PBu ligand (4 mol%) (Table 3). A similar result was also observed for the unsubstituted cyclohexyl thioamide **5b** giving 68% of benzo[*b*]thiophene **6b**. Next, the *N*-ethyl thioamides **5c-d** were studied. These thioamides **5c-d** were transformed to the benzo[*b*]thiophenes **6c-d** exclusively under similar reaction conditions (Table 3). These results clearly suggested that the present nickel catalyst is highly selective for sp^2 C—H bond functionalization over sp^3 C—H bond.

Table 4. Nickel Catalyzed Controlled C—H Bond Functionalization for Synthesis of Five-membered vs Six-membered *S*-Heterocycles[a,b]



[a]Isolated yields. [b]The parenthesis is yield of product **6** without ligand

Next, we studied a controlled C—H bond functionalization for the selective synthesis of five-membered over six-membered *S*-heterocycles. The required N-benzyl substituted thioamides **5e-g** were prepared (Scheme S2, ESI†). These thioamides **5e-g** were subjected under the similar reaction conditions. The benzo[*b*]thiophenes **6e-g** were formed exclusively in moderate to good yields. No other products were detected (Table 4). The yield of products **6e** and **6g** were better in the presence of ligand (Table 4).

Conclusion

We have demonstrated the first nickel catalyzed site selective C—H bond functionalization of thioanilides for the synthesis of 2-aminobenzo[*b*]thiophenes. The present protocol is mild, low catalyst loading, and short reaction time and gives access to a variety of 2-amino-3-cyano-benzo[*b*]thiophenes in moderate to good yields. The potential application of the reaction was further extended to a highly site selective C–S bond formation of sp^2 C—H bond over sp^3 C—H bond, and 5-membered ring over 6-membered ring. Currently, metal-free site selective C—H bond functionalization reactions are in progress in our laboratory.

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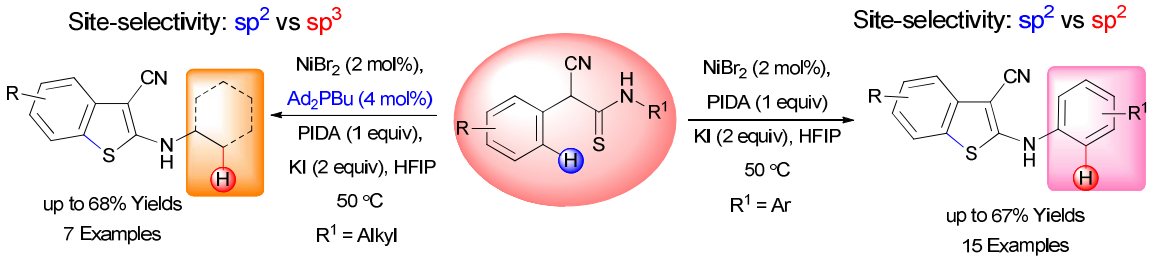
TOC Graphic



Nickel catalyzed C—H bond functionalization reaction has been used for the first time to study an intramolecular site-selective C—S bond formation of arenes.