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Palladium-Catalyzed Direct C−H Functionalization of Indoles with the Insertion of Sulfur Dioxide: Synthesis of 2-Sulfonated Indoles

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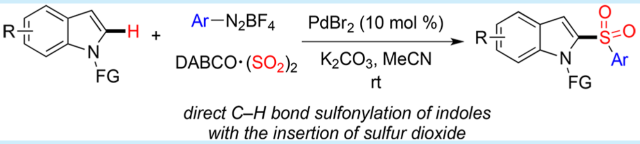
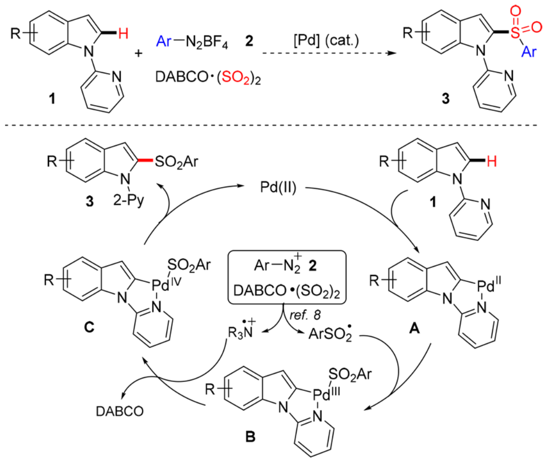
Supporting Information



ABSTRACT: A palladium-catalyzed direct C−H bond sulfonylation of indoles with the insertion of sulfur dioxide is achieved through a three-component reaction of 1-(pyridin-2-yl)indoles, DABCO·$(SO_2)_2$, and aryldiazonium tetrafluoroborates under mild conditions. Diverse 2-sulfonated indoles are generated by using 10 mol % of palladium(II) bromide as the catalyst at room temperature. This synthetic approach is efficient by merging palladium catalysis and insertion of sulfur dioxide via a radical process. 2-Pyrimidinyl can be used as the directing group well as for the C−H bond sulfonylation. Additionally, the directing group can be easily removed.

So far, significant progress for the direct C−H bond functionalization in organic synthesis has been made.[1] Breakthroughs for C−H bond activation or functionalization has been continuously observed in the past decade.[2] The important role of transition-metal catalysis in C−H bond functionalizations with diverse directing groups has been demonstrated.[1d] In the meantime, many efforts have been given for the incorporation of a sulfonyl (−SO_2−) moiety into small organic molecules[3] due to the importance of sulfonyl compounds in pharmaceuticals and materials.[4] Among the approaches developed, the insertion of sulfur dioxide into C−X bonds and C−H bonds would be a direct pathway for the generation of sulfonyl compounds. In the past few years, methods for the preparation of sulfonyl compounds by using DABCO·$(SO_2)_2$ or inorganic sulfites as the source of sulfur dioxide have emerged.[5,6] Although approaches for the direct functionalization of C−H bonds have been developed as mentioned above,[1] there are few reports for the insertion of sulfur dioxide into C−H bonds.[7] In 2014, aminosulfonylation of arenes, sulfur dioxide, and hydrazines was described in the presence of gold(III) chloride and palladium acetate as cocatalysts.[7a] In this transformation, the reaction scope for the C−H bond functionalization of arenes was limited. Recently, a copper-catalyzed *para*-selective C−H bond functionalization of 1-isoquinoline carboxamides with sulfur dioxide was reported.[7b] A copper-chelated complex was believed as the key intermediate, which triggered the reaction. Prompted by these results, we conceived that the directing groups in the substrates would facilitate the insertion of sulfur dioxide assisted by transition metal catalysis. Thus, we focused on 1-(pyridin-2-yl)indoles **1**, with an expectation to introduce sulfonyl group into 2-position of 1-(pyridin-2-yl)indoles via C−H bond functionalization with the insertion of sulfur dioxide (Scheme 1).

Scheme 1. Direct C−H Bond Sulfonylation of Indoles with the Insertion of Sulfur Dioxide



Recently, we discovered that aryldiazonium tetrafluoroborates would react with sulfur dioxide, providing arylsulfonyl radicals under mild conditions.[8] For example, vicinal difunctionalization of alkenes through a four-component reaction of aryldiazonium tetrafluoroborates, sulfur dioxide, alkenes, and hydroxylamines could be accomplished by using DABCO·$(SO_2)_2$ or potassium metabisulfite ($K_2S_2O_5$) as the source of sulfur dioxide.[8c] Encouraged by these results, we envisioned that aryldiazonium tetrafluoroborates could be applied in the C−H bond functionalization with sulfur dioxide as well. A plausible transformation via a three-component reaction of 1-(pyridin-2-yl)indoles **1**, aryldiazonium tetrafluor-

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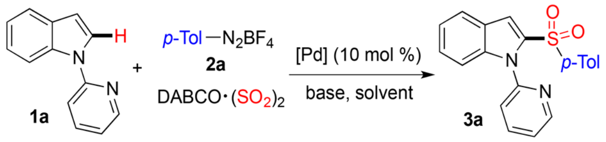
oborates **2**, and DABCO·$(SO_2)_2$ under palladium catalysis is proposed in Scheme 1. On the basis of previous reports,[8,9] we reasoned that palladium(II) catalyst would coordinate with 1-(pyridin-2-yl)indole **1**, accompanied by the C−H bond activation to produce a palladium-chelated complex **A**. Meanwhile, arylsulfonyl radical and tertiary amine radical cation would be generated from aryldiazonium tetrafluoroborates **2** and DABCO·$(SO_2)_2$.[8] Arylsulfonyl radical would then combine with complex **A** to form palladium(III) intermediate **B**, which would be oxidized by tertiary amine radical cation leading to intermediate **C**. Subsequently, 2-sulfonated indole **3** would be obtained through reductive elimination, with the release of palladium(II) catalyst. It seemed that this synthetic pathway was feasible. We therefore started to explore the palladium-catalyzed direct C−H bond sulfonylation of indoles with the insertion of sulfur dioxide.

We initiated our studies by exploring the optimal conditions for the reaction of 1-(pyridin-2-yl)indole **1a**, DABCO·$(SO_2)_2$, and 4-methylphenyldiazonium tetrafluoroborate **2a** in the presence of palladium catalyst. At the outset, the reaction was catalyzed by palladium acetate (10 mol %) in toluene at room temperature (Table 1, entry 1). However, no product was detected. Pleasingly, the desired 1-(pyridin-2-yl)-2-sulfonated indole **3a** was obtained in 21% yield when the reaction was performed in 1,2-dichloroethane (DCE) (Table 1, entry 2). The structure of 1-(pyridin-2-yl)-2-sulfonated indole **3a** was identified by X-ray diffraction analysis. Reaction in 1,4-dioxane afforded a trace amount of product (Table 1, entry 3). The transformation was hampered when the reaction occurred in DMF (Table 1, entry 4). The corresponding product **3a** was generated in 26% yield when the solvent was changed to DMSO (Table 1, entry 5). A higher yield was produced when acetonitrile was used as a replacement (Table 1, entry 6). We further screened the reaction temperature, and found that the reaction worked efficiently at 25 °C (Table 1, entries 7−9). Several palladium catalysts were then examined, which revealed that palladium bromide was the best choice (Table 1, entries 10−13). Since HBr would be released during the reaction process, different bases (1.5 equiv) were added (Table 1, entries 14−18). It was found that the yield could be improved when potassium carbonate was used as the base (Table 1, entry 15). The yield was increased to 76% when 2.0 equiv of potassium carbonate was added (Table 1, entry 19). The result was inferior when the amount of base, 4-methylphenyldiazonium tetrafluoroborate **2a**, or palladium bromide was decreased (Table 1, entries 20−22). A control experiment without the addition of palladium bromide was performed. However, no desired product was observed (Table 1, entry 23).

Table 1. Initial Studies for the Reaction of 1-(Pyridin-2-yl)indole 1a, DABCO·$(SO_2)_2$, and Phenyldiazonium Tetrafluoroborate 2a[a]



entry	[Pd]	base	solvent	temp (°C)	yield[b] (%)
1	$Pd(OAc)_2$		toluene	25	nd
2	$Pd(OAc)_2$		DCE	25	21
3	$Pd(OAc)_2$		1,4-dioxane	25	trace
4	$Pd(OAc)_2$		DMF	25	nd
5	$Pd(OAc)_2$		DMSO	25	26
6	$Pd(OAc)_2$		MeCN	25	31
7	$Pd(OAc)_2$		MeCN	0	trace
8	$Pd(OAc)_2$		MeCN	40	30
9	$Pd(OAc)_2$		MeCN	50	28
10	$Pd_2(dba)_3$		MeCN	25	30
11	$PdCl_2$		MeCN	25	25
12	$PdBr_2$		MeCN	25	35
13	$Pd(TFA)_2$		MeCN	25	13
14[c]	$PdBr_2$	Cs_2CO_3	MeCN	25	21
15[c]	$PdBr_2$	K_2CO_3	MeCN	25	60
16[c]	$PdBr_2$	Na_2CO_3	MeCN	25	41
17[c]	$PdBr_2$	$KHCO_3$	MeCN	25	46
18[c]	$PdBr_2$	K_3PO_4	MeCN	25	57
19[d]	$PdBr_2$	K_2CO_3	MeCN	25	76
20[e]	$PdBr_2$	K_2CO_3	MeCN	25	51
21[d,f]	$PdBr_2$	K_2CO_3	MeCN	25	62
22[d,g]	$PdBr_2$	K_2CO_3	MeCN	25	55
23[d]		K_2CO_3	MeCN	25	nd

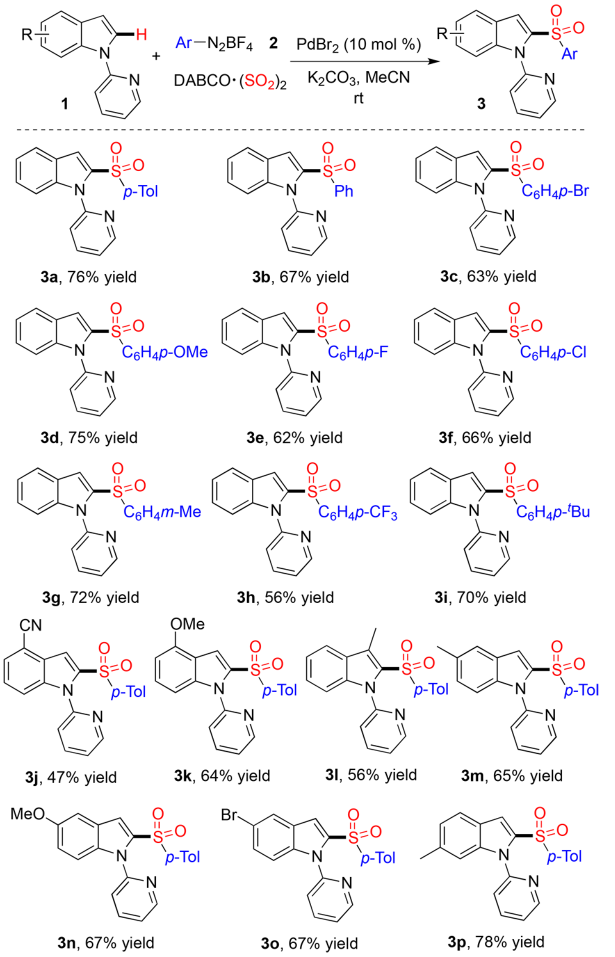
[a]Reaction conditions: 1-(pyridin-2-yl)-1*H*-indole **1a** (0.2 mmol), DABCO·$(SO_2)_2$ (0.16 mmol), *p*-methylphenyldiazonium tetrafluoroborate **2a** (0.4 mmol), solvent (2.0 mL), under N_2 protection, 8 h. [b]Isolated yield based on 1-(pyridin-2-yl)-1*H*-indole **1a**. [c]Base (0.3 mmol). [d]K_2CO_3 (0.4 mmol). [e]K_2CO_3 (0.24 mmol). [f]*p*-Methylphenyldiazonium tetrafluoroborate **2a** (0.3 mmol). [g]$PdBr_2$ (5 mol %).

With the above optimized reaction conditions in hand, we next explored the reaction scope of this C−H sulfonylation with the insertion of sulfur dioxide starting from 1-(pyridin-2-yl)indoles **1**, DABCO·$(SO_2)_2$, and aryldiazonium tetrafluoroborates **2**. The result is presented in Scheme 2. All reactions worked well to provide 2-sulfonated indoles in moderate to good yields. Various aryldiazonium tetrafluoroborates **2** were evaluated with 1-(pyridin-2-yl)indoles **1a** and DABCO·$(SO_2)_2$. Different functional groups including halo, trifluoromethyl, methoxy, and *tert*-butyl were compatible under the conditions. For example, the trifluoromethyl-substituted product **3h** was obtained in 56% yield. We subsequently examined the reactions of diverse 1-(pyridin-2-yl)indoles **1** with DABCO·$(SO_2)_2$, and 4-methylphenyldiazonium tetrafluoroborate **2a**. As expected, these transformations were efficient, giving rise to the desired products. Interestingly, the aryl bromide remained during the reaction process (compound **3o**).

We further expanded the reaction of indole with another directing group. 1-(Pyrimidin-2-yl)-1*H*-indole **4** reacted with DABCO·$(SO_2)_2$ and *p*-tolyldiazonium tetrafluoroborate **2b** leading to the corresponding product **5** in 73% yield under the standard conditions (Scheme 3).

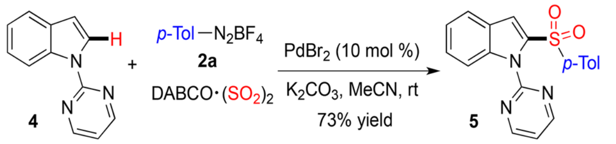
Additionally, the directing group could be easily removed. For instance, 1-(pyridin-2-yl)-2-sulfonated indole **3a** was treated with MeOTf and NaOH,[10] leading to 2-sulfonated indole **6** in 71% yield (Scheme 4). As shown in Scheme 2, we proposed that the reaction would be triggered by arylsulfonyl radical, generated in situ from aryldiazonium tetrafluoroborate **2** and DABCO·$(SO_2)_2$. To confirm the radical intermediate during the reaction process, we thus added 2.0 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in the reaction of 1-(pyridin-2-yl)indole **1a** and DABCO·$(SO_2)_2$ with 4-methylphenyldiazonium tetrafluoroborate **2a** under the standard conditions (Scheme 5, eq a). As expected, we did not detect the formation of product **3a**. In the meantime, ethene-1,1-diyldibenzene was involved in the reaction of 1-(pyridin-2-yl)indole **1a**, DABCO·$(SO_2)_2$, and 4-methylphenyldiazonium tetrafluoroborate **2a**, with an expectation to trap the in situ

Scheme 2. Reaction of 1-(Pyridin-2-yl)indoles 1, DABCO·$(SO_2)_2$, and Aryldiazonium Tetrafluoroborates 2[a,b]

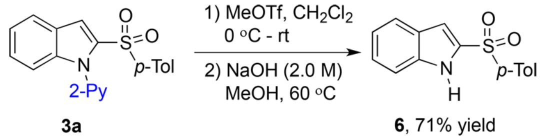


[a]Isolated yield based on 1-(pyridin-2-yl)indole **1**. [b]Reaction conditions: 1-(pyridin-2-yl)-1*H*-indole **1** (0.2 mmol), DABCO·$(SO_2)_2$ (0.16 mmol), aryldiazonium tetrafluoroborate **2** (0.4 mmol), K_2CO_3 (0.4 mmol), $PdBr_2$ (10 mol %), MeCN (2.0 mL), under N_2 protection, 25 °C, 8 h.

Scheme 3. Reaction of 1-(Pyrimidin-2-yl)-1*H*-indole 1a, DABCO·$(SO_2)_2$, and Phenyldiazonium Tetrafluoroborate 2a

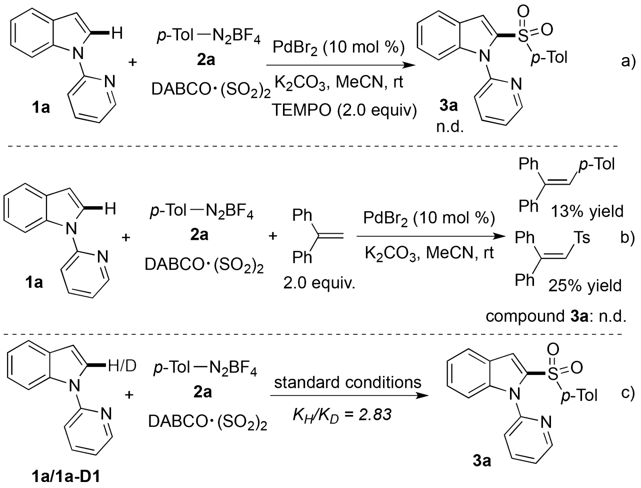


Scheme 4. Transformation of Compound 3a



formed 4-methylphenyl and 4-methylphenylsulfonyl radical. Consequently, we did observe and isolate the corresponding products in 13% and 25% yields, respectively (Scheme 5, eq b). Furthermore, kinetic isotope experiments (KIE) of substrate **1a** and its deuterated analogue **1a-D1** were performed under the standard conditions. The value of K_H/K_D was measured to be 2.83, which showed that the C−H bond cleavage might be the rate-limiting step (Scheme 5, eq c).

Scheme 5. Investigation of the Mechanism



In summary, we have reported a palladium-catalyzed direct C−H bond sulfonylation of indoles with the insertion of sulfur dioxide through a three-component reaction of 1-(pyridin-2-yl)indoles, DABCO·$(SO_2)_2$, and aryldiazonium tetrafluoroborates under mild conditions. Diverse 2-sulfonated indoles are generated by using 10 mol % of palladium(II) bromide as the catalyst at room temperature. 2-Pyrimidinyl can be used as the directing group as well for the C−H bond sulfonylation. Additionally, the directing group can be easily removed. This synthetic approach for introducing a sulfonyl ($-SO_2-$) moiety is efficient by merging palladium catalysis and arylsulfonyl radical generated from DABCO·$(SO_2)_2$ and aryldiazonium tetrafluoroborate. We believe that the insertion of sulfur dioxide into C−H bond could provide a facile and promising route to sulfonyl compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03365.

Experimental procedures, characterization data, and ^1H, ^{19}F, and ^{13}C NMR of products (PDF)

Accession Codes

CCDC 1581331 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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T.L. and W.Z. contributed equally.

Notes

The authors declare no competing financial interest.

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