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Route to *O*-aminosulfonates and Sulfonamides through Insertion of Sulfur Dioxide and Hydrogen Atom Transfer

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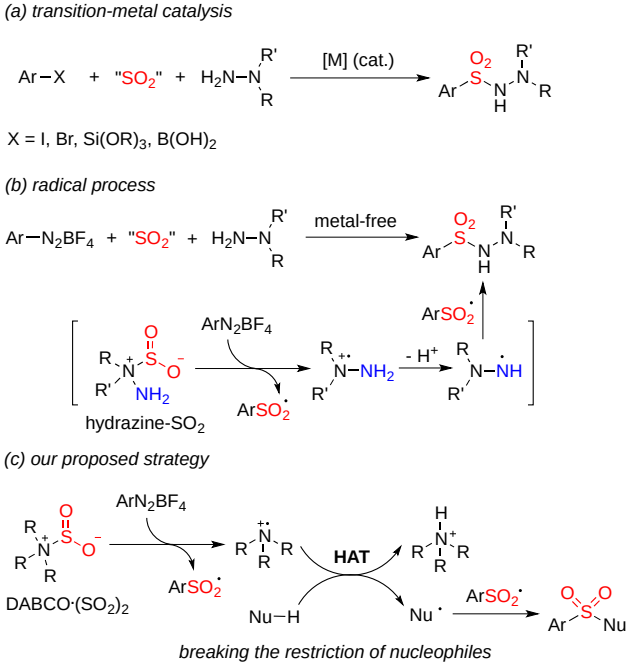
Abstract. A three-component reaction of aryldiazonium tetrafluoroborates, DABCO•$(SO_2)_2$ and hydroxylamines under catalyst-free and additive-free conditions is developed, providing aryl *O*-aminosulfonates in good yields. Sulfonamides could also be obtained via a one-pot process through a reaction of aryldiazonium tetrafluoroborates, DABCO·$(SO_2)_2$ and amines in the presence of N-hydroxybenzotriazole. A mechanism involved with the insertion of sulfur dioxide and hydrogen atom transfer is proposed, supported by theoretical calculations.

Keywords: aryldiazonium tetrafluoroborate; amine; hydrogen atom transfer; hydroxylamine; sulfur dioxide

Introduction

The sulfonyl group is widely existed in pharmaceuticals, argrochemicals, materials and synthetic intermediates.[1-4] In the past few years, sulfur dioxide insertion has been recognized as an efficient strategy for the generation of sulfonyl-containing compounds. The introduction of sulfonyl moiety from simple sources into small molecules is attractive and promising.[5-7] Early reports centered on the transition metal catalysis for the synthesis of *N*-aminosulfonamides and related compounds via the insertion of sulfur dioxide starting from aryl halides, arylboronic acids, or arylsilanes (Scheme 1a).[6a-b,6f,7a-b] Although various electrophiles have been employed, the nucleophile was limited to hydrazines and hydride. Other nucleophiles were examined in the above transformations, which were all unsuccessful. This drawback hampered the applications for the generation of sulfonyl compounds. In 2014, our group reported a metal-free coupling reaction of aryldiazonium salts, DABCO·$(SO_2)_2$ and hydrazines (Scheme 1b).[7c] This process opened a window to the radical-based transformations of sulfur dioxide, although the substrate scope was also limited, similarly to the transition-metal catalysis. We proposed that the hydrazine-SO_2 complex (generated through sulfur dioxide exchange) would proceed through a single electron transfer to produce the aryl radical, sulfur dioxide and the hydrazine radical cation. In this mechanism, the hydrazine participated in the production of sulfonyl radicals and this might explain why the nucleophile was restricted to hydrazines. Very recently, our group reported a surprising discovery that the treatment of aryldiazonium tetrafluoroborates with

Scheme 1. Proposed synthetic route via hydrogen atom transfer



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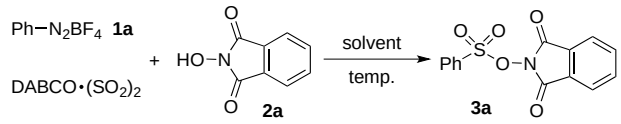
DABCO·$(SO_2)_2$ would directly generate sulfonyl radicals and tertiary amine radical cations without the participation of hydrazines.[8] The sulfonyl radicals could be trapped by aryl propiolates leading to 3-sulfonated coumarins.

In the meantime, hydrogen atom transfer (HAT) is a fundamental mechanistic step and provides an efficient route to radical intermediates in organic chemistry.[9] We noticed that recently, the MacMillan group demonstrated the tertiary amine radical cation (generated via a photoredox process) would accomplish H-atom abstraction from a range of Csp^3-H bonds.[10] The resulting radical intermediate would participate with a nickel catalysis to generate the arylated products. Moreover, the Murphy group reported that the DABCO radical cation would mediate a H-atom transfer from *N*-CH_3 groups.[11] According to these new discoveries, we supposed that the tertiary amine radical cation generated from the reaction of aryldiazonium tetrafluoroborates with DABCO·$(SO_2)_2$ would accomplish H-atom abstraction from the latent nucleophile, giving rise to the radical intermediates (Scheme 1c). The radical intermediates would be subsequently trapped by sulfonyl radicals to generate the sulfonated products. This proposed strategy took advantage of the *in situ* generated tertiary amine radical cation and the nucleophile might not be restricted to hydrazines. A variety of C, O or N nucleophiles were employed to this transformation but most of them were unsuccessful. It seemed that the HAT process might not be compatible with the existence of sulfur dioxide. Pleasingly, we were finally able to establish the construction of C-SO_2-O bonds by using *N*-hydroxyphthalimide as nucleophile. To the best of our knowledge, this represents the first successful example of oxygen nucleophiles applied in sulfur dioxide insertion reactions.

Results and Discussion

Initially, the reaction of phenyldiazonium tetrafluoroborate **1a**, DABCO·$(SO_2)_2$, with 2-hydroxyisoindoline-1,3-dione **2a** was examined in 1,2-dichloroethane (DCE) at room temperature. No desired product was observed (Table 1, entry 1). To our delight, the sulfonated product was isolated in 75% yield when the reaction temperature was increased to 80 °C (Table 1, entry 2). We further explored this reaction in different solvents. It was found that no better yields were obtained in other solvents, and DCE was demonstrated as the best choice (Table 1, entries 3-6). Gratifyingly, the yield of compound **3a** (80%) could be improved when the reaction took place at 60 °C (Table 1, entry 7). An inferior result was observed when the reaction was performed at 40 °C (Table 1, entry 8). The yield was lower when the amount of DABCO·$(SO_2)_2$ was reduced to 0.8 equiv. (Table 1, entry 9). A similar result was obtained when 1.2 equiv. of DABCO·$(SO_2)_2$ was utilized (Table 1, entry 10). The efficiency of this

Table 1. Initial studies for the reaction of phenyldiazonium tetrafluoroborate **1a**, DABCO•$(SO_2)_2$ and 2-hydroxyisoindoline-1,3-dione **2a**[a]



Entry	Solvent	T (°C)	DABCO·$(SO_2)_2$	Yield [b]
1	DCE	rt	1.0 equiv	n.d.
2	DCE	80	1.0 equiv	75
3	toluene	80	1.0 equiv	16
4	1,4-dioxane	80	1.0 equiv	21
5	DMF	80	1.0 equiv	n.d.
6	MeCN	80	1.0 equiv	42
7	DCE	60	1.0 equiv	80
8	DCE	40	1.0 equiv	48
9	DCE	60	0.8 equiv	61
10	DCE	60	1.2 equiv	81
11[c]	DCE	60	1.0 equiv	51

[a] Reaction conditions: phenyldiazonium tetrafluoroborate **1a** (0.3 mmol), DABCO•$(SO_2)_2$, 2-hydroxyisoindoline-1,3-dione **2a** (0.2 mmol), solvent (2.0 mL), under N_2 protection, 8 h. [b] Isolated yield based on 2-hydroxyisoindoline-1,3-dione **2a**. [c] Under air atmosphere

transformation was lower when the reaction occurred under air atmosphere (Table 1, entry 11).

Under the above optimized reaction conditions as shown in Table 1, scope of the catalyst-free three-component reaction of aryldiazonium tetrafluoroborates, DABCO·$(SO_2)_2$, with 2-hydroxyisoindoline-1,3-dione **2a** was next investigated. The result is presented in Table 2. Various aryldiazonium tetrafluoroborates were used as the reaction partners, giving rise to the desired sulfonated compounds in good to excellent yields (Table 2, **3a**-**m**). A minimal influence of electronic effects on the aromatic ring of aryldiazonium tetrafluoroborates was observed. Different functional groups including methyl, methoxyl, chloro, bromo, trifluoromethyl, nitro, and ester were all compatible in this transformation. Additionally, reaction of *ortho*-substituted phenyldiazonium tetrafluoroborate was workable as well, although the yield was lower (**3j**, 50% yield). Reactions of *N*-hydroxy-*N*-phenylbenzamide **2b**, aryldiazonium tetrafluoroborates with DABCO·$(SO_2)_2$ were then examined. As expected, all reactions proceeded efficiently to provide the corresponding products in good yields. Again, all substituents appended to the aromatic ring of aryldiazonium tetrafluoroborates. were tolerated under the conditions. Phenyldiazonium tetrafluoroborate **1a** reacted with DABCO·$(SO_2)_2$ and *N*-hydroxybenzamide at room temperature, leading to the desired product **3u** in 56% yield.[12] It is notable that the substrate scope could be further extended to 1*H*-benzo[*d*][1,2,3]triazol-1-ol, 3-hydroxybenzo[*d*][1,2,3]triazin-4(3*H*)-one and *N*-hydroxy-*N*,4-dimethylbenzenesulfonamide. For example, reaction of phenyldiazonium tetrafluoroborate **1a**, DABCO·$(SO_2)_2$, and 1*H*-

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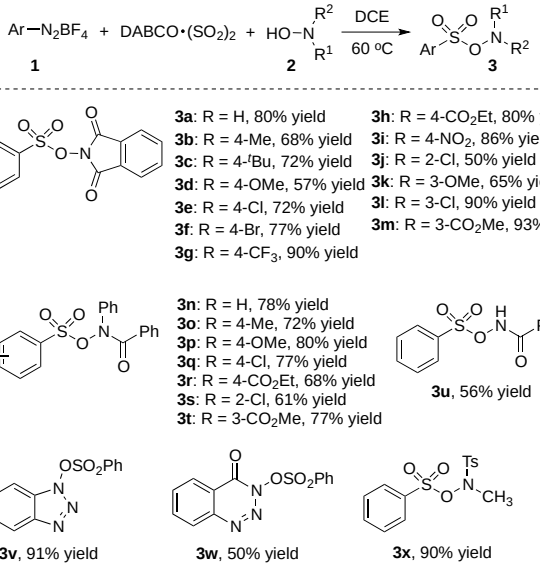
Table 2. Scope investigation for the reaction of aryldiazonium tetrafluoroborates **1**, DABCO·$(SO_2)_2$, and compound **2** [a,b]



[a] Reaction conditions: aryldiazonium tetrafluoroborate **1** (0.3 mmol), DABCO•$(SO_2)_2$ (0.2 mmol), substrate **2** (0.2 mmol), DCE (2.0 mL), under N_2 protection, 60 °C, 8 h. [b] Isolated yield based on compound **2**.

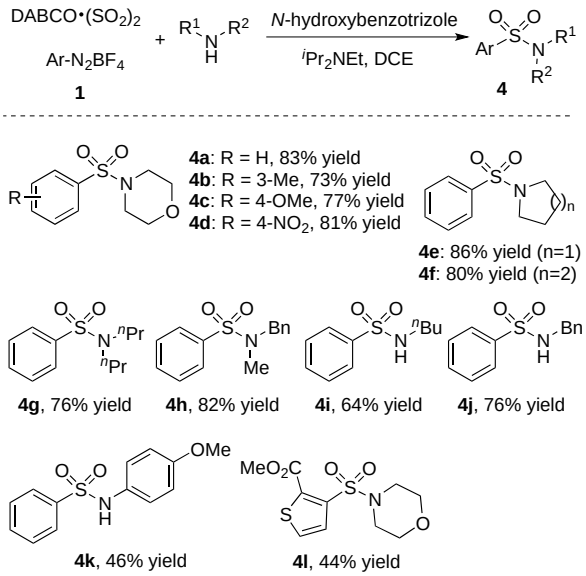
benzo[*d*][1,2,3]triazol-1-ol afforded the expected product **3v** in 91% yield.

To further extend the practicability of this process, we next explored the transformation of *O*-aminosulfonates to biologically important sulfonamides. We found that the *N*-hydroxybenzotriazole sulfonate could act as a replacement of sulfonyl chloride in amidation reactions, and react with amines in the presence of diisopropylethyl amine at room temperature to produce the corresponding sulfonamides.[13] Thus, we established a one-pot, two-step process for the synthesis of sulphonamides through the insertion of sulfur dioxide. After completion of the three-component reaction of aryldiazonium tetrafluoroborates, DABCO•$(SO_2)_2$, with *N*-hydroxybenzotriazole, amines and diisopropylethyl amine were added subsequently at room temperature. A variety of sulfonamides could be produced under the reaction conditions (Table 3). Both primary and secondary aliphatic amines were capable for this transformation, affording the desired products in moderate to good yields. Aromatic amines such as *p*-methoxyaniline gave a lower yield of 46% (**4k**). The heterocyclic thiophenediazonium tetrafluoroborates could also deliver the desired product **4l**. This procedure presents an efficient and general route for the synthesis of sulfonamides through the insertion of sulfur dioxide.

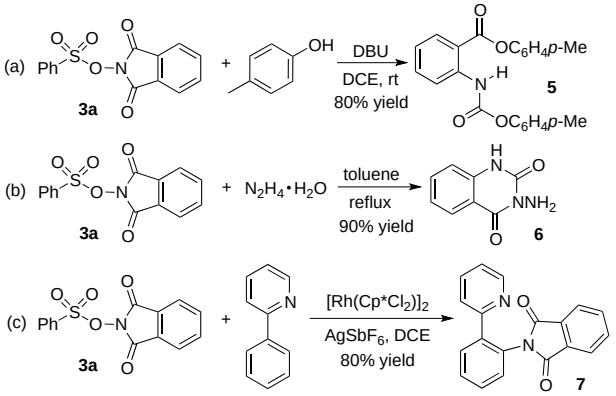
The *O*-aminosulfonate **3a** could also react with other nucleophiles to produce diverse compounds (Scheme 2, eq. a and b). For instance, 1,3-dioxoisoindolin-2-yl benzenesulfonate **3a** reacted with *p*-cresol in the presence of DBU at room temperature, affording *p*-tolyl 2-(((*p*-tolyloxy)carbonyl)amino)benzoate **5** in 80% yield.[14] Treatment of 1,3-dioxoisoindolin-2-yl benzenesulfonate **3a** with hydrazine under reflux conditions gave rise to 3-aminoquinazoline-2,4(1*H*,3*H*)-dione **6** in 90% yield.[15] Rhodium-catalyzed C-H bond activation of 2-phenylpyridine with 1,3-dioxoisoindolin-2-yl benzenesulfonate **3a** could be performed as well, leading to compound **7** in 80% yield (Scheme 2, eq. c).[16]

Several control experiments were subsequently carried out to gain more insights of the reaction mechanism (Scheme 3). The reaction was completely terminated when 2.0 equivalent of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reaction system, suggesting this reaction proceeded through a radical process (Scheme 3, eq. a). No desired product **3a** was observed as well when 3.0 equivalent of 1,1-diphenylethylene was added to the standard reaction (Scheme 3, eq. b). Ethene-1,1,2-triyltribenzene **8** and (2-(phenylsulfonyl) dibenzene **9**

Table 3. One-pot synthesis of sulfonamides[a,b]



[a] Reaction conditions: aryldiazonium tetrafluoroborate **1** (0.36 mmol), DABCO•$(SO_2)_2$ (0.2 mmol), *N*-hydroxybenzotriazole (0.24 mmol), DCE (2.0 mL), under N_2 protection, 60 °C, 1 h, then ethyldiisopropylamine (0.24 mmol), amine (0.2 mmol) was added at room temperature. [b] Isolated yield based on amine.



Scheme 2. Transformation of compound **3a**

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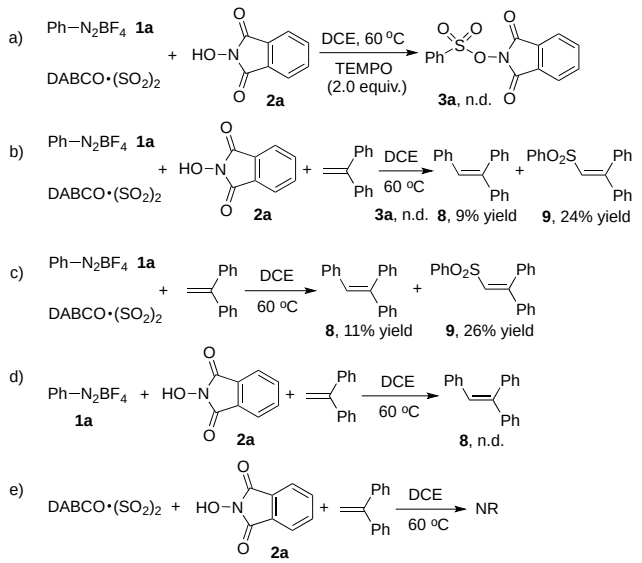


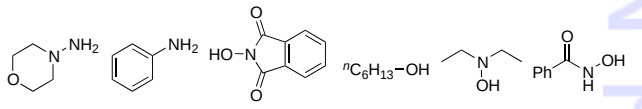
Scheme 3. Investigation of mechanism

could be isolated in 9% and 24% yields, respectively. This result indicated that this transformation experienced both aryl radical and arylsulfonyl radical as reaction intermediates. Compounds **8** and **9** could also be produced in 11% and 26% yields via the treatment of phenyldiazonium tetrafluoroborate **1a**, DABCO·$(SO_2)_2$ and 1,1-diphenylethylene in DCE (Scheme 3, eq. c). However, ethene-1,1,2-triyltribenzene **8** was not observed in the absence of DABCO·$(SO_2)_2$, which showed that DABCO·$(SO_2)_2$ was essential for the introduction of aryl radical (Scheme 3, eq. d). Furthermore, no reaction took place with the treatment of DABCO·$(SO_2)_2$, 2-hydroxyisoindoline-1,3-dione **2a** and 1,1-diphenylethylene (Scheme 3, eq. e).

To explain the unique success of *N*-acyl hydroxylamines in this transformation, the free-energy barrier and free-energy change for the hydrogen atom transfer between several *O* and *N* nucleophiles with the DABCO+· radical cation were calculated through theoretical calculations. The results were presented in Table 4. In most cases, the Gibbs free-energy barrier and free-energy change were reasonable for this transformation except the aliphatic alcohol. Comparison with the three hydroxylamines showed that the electron-rich substrate which owned a bigger free-energy change might be more reactive. The reaction of 2-hydroxyisoindoline-1,3-dione took place efficiently at 60 °C, while the reactions of *N*,*N*-diethylhydroxylamine and *N*-hydroxybenzamide became complex at the same temperature. When the reaction temperature was decreased to 25 °C, we could isolate the sulfonated product of the *N*-monoacyl substituted hydroxylamine in a moderate yield while the *N*-dialkyl hydroxylamine still failed in this process. The thermodynamic calculations and experimental results suggested that excessively reactive substrates might also be unfavourable in this transformation. Aniline was not a good partner as well in the reaction system, since aniline would react with aryldiazonium salt directly due to its strong nucleophilicity. According to the theoretical calculations, the HAT process was also reasonable for the hydrazine. In spite of this, we still thought that the previous proposed mechanism (presented in Scheme 1b) could not be excluded, considering the SO_2 exchange between hydrazine and DABCO·$(SO_2)_2$ was feasible (the hydrazine-SO_2 complex was accessible in previous report).[6b] Apparently, the electron deficient *N*-acyl hydroxylamines were unfavourable for the SO_2 exchange, suggesting that the hydrazine and hydroxylamine might undergo two different reaction routes.

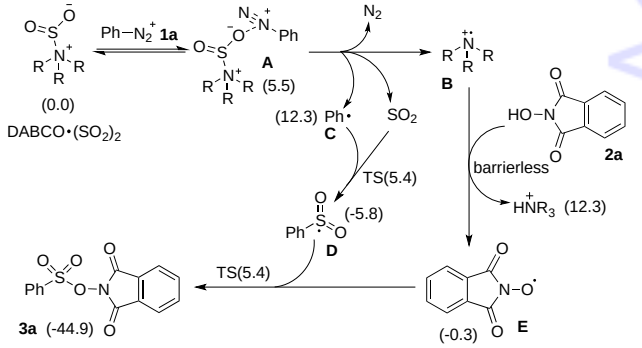
Based on the above experimental observations and theoretical calculations, a plausible mechanism was proposed in Scheme 4. As mentioned in our previous report,[7c] arydiazonium cation **1a** would react with DABCO·$(SO_2)_2$ to generate complex **A** through electrostatic interaction.[7c] The homolytic cleavage of N-S bond[17] and a single electron transfer would occur subsequently, leading to the tertiary amine radical cation **B**, SO_2 and phenyl radical **C** with the release of N_2. Then phenylsulfonyl radical **D** would be produced through the addition of phenyl radical **C** to sulfur dioxide. In the meantime, the hydrogen atom transfer (HAT) between the tertiary amine radical cation **B** and 2-hydroxyisoindoline-1,3-dione **2a** would give rise to the *O*-radical intermediate **E**, which would be trapped by the phenylsulfonyl radical

Table 4. Free-energy barrier and free-energy change (in kcal/mol) at 298.15 K for the proton exchange between various substrates with the $R_3N^{+\cdot}$ radical.



Substrate	Free-Energy Barrier	Free-Energy Change
morpholin-4-amine	NA[a]	-17.4
aniline	-0.7[b]	-1.4
2-hydroxyisoindoline-1,3-dione	NA[a]	-12.6
n-hexanol	28.2	8.2
N,*N*-diethylhydroxylamine	NA[a]	-24.4
N-hydroxybenzamide	NA[a]	-15.8

[a] The potential energy surface is so flat that no transitions state could be optimized. [b] There is a complex between $R_3N^{+\cdot}$ and the substrate before the transition state.



Scheme 4. Proposed mechanism. The numbers in brackets are the changes in Gibbs free energy relative to those of the initial reactants at 298 K. TS=transition state.

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D leading to the desired product **3a**. The overall Gibbs free energy barrier of this transformation is 17.7 kcal mol^{-1} according to theoretical calculations, indicating this route is feasible from the perspective of thermodynamics.

Conclusion

In summary, we have realized a catalyst-free three-component reaction of aryldiazonium tetrafluoroborates, DABCO·$(SO_2)_2$ and hydroxylamines under mild conditions. This transformation provides aryl *O*-aminosulfonates in good yields under catalyst-free and additive-free conditions. More importantly, this transformation could provide an efficient and convenient route to sulfonamides via a one-pot process of aryldiazonium tetrafluoroborates, DABCO·$(SO_2)_2$ and amines in the presence of *N*-hydroxybenzotrizole. A radical process is believed to be involved through the insertion of sulfur dioxide and hydrogen atom transfer, supported by theoretical calculations.

Experimental Section

General experimental procedure for the reaction of aryldiazonium tetrafluoroborates **1**, DABCO·$(SO_2)_2$, and compound **2**: Hydroxylamine **2** (0.2 mmol) was added to a solution of DABCO·$(SO_2)_2$ (0.4 mmol) and aryldiazonium tetrafluoroborate **1** (0.24 mmol) in DCE (2.0 mL) under N_2 protection. The mixture was stirred at 60 °C for 8 hours. After completion of reaction as indicated by TLC, the mixture was evaporated under reduced pressure and purified directly by flash column chromatography (EtOAc/*n*-hexane, 1:2) to give the desired product **3**.

General experimental procedure for the synthesis of sulfonamides **4**: A solution of aryldiazonium tetrafluoroborate **1** (0.36 mmol), DABCO•$(SO_2)_2$ (0.2 mmol), *N*-hydroxybenzotriazole (0.24 mmol) in DCE (2.0 mL) under N_2 protection was stirred at 60 °C for 1 h. Then the reaction was cooled to room temperature and ethyldiisopropylamine (0.24 mmol) and amine (0.2 mmol) was added and stirred for additional 2 h. After completion of reaction as indicated by TLC, the solvent was evaporated under reduced pressure and the residue was purified directly by flash column chromatography (EtOAc/*n*-hexane, 1:4) to give the desired product **4**.

Acknowledgements

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FULL PAPER

Route to *O*-aminosulfonates and Sulfonamides through Insertion of Sulfur Dioxide and Hydrogen Atom Transfer

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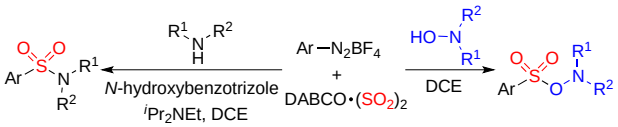

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