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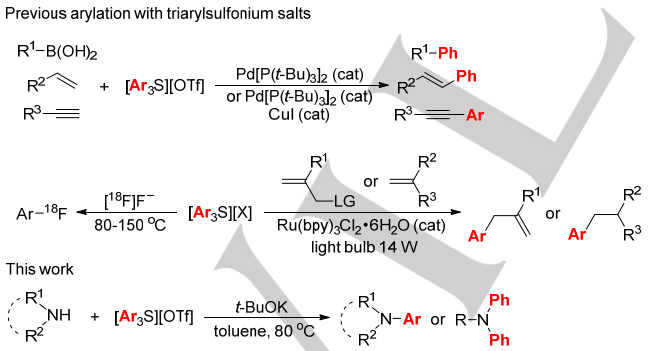
Transition Metal-Free *N*-Arylation of Amines by Triarylsulfonium Triflates

Ze-Yu Tian[a], Xiao-Xia Ming[a], Han-Bing Teng*[a], Yu-Tian Hu[a], Cheng-Pan Zhang*[a]

Abstract: A simple and efficient method for transition metal-free *N*-arylation of various amines by triarylsulfonium triflates is described. Both aliphatic and aromatic amines were smoothly converted at 80 °C in the presence of *t*-BuOK or KOH to give the corresponding mono *N*-arylated products in good to high yields. The molar ratios of the reactants and the choice of bases had a big effect on the reaction. When a large excess of [Ph_3S][OTf] and *t*-BuOK were employed for primary amines under the standard conditions, the bis(*N*-phenylated) products were predominantly formed. This method was also applicable to the synthesis of bioactive *N*-phenyl amino acid derivatives. The control experiments, the deuterium labelling study, and the presence of regioisomers of *N*-arylated products when using 4-substituted triarylsulfonium triflates suggested that the reaction might proceed through an aryne intermediate. The present protocol demonstrated that triarylsulfonium salts are versatile arylation reagents in the construction of C_{Ar}-N bonds.

Arylamines widely exist in the structural backbones of ligands, pharmaceuticals, agrochemicals, natural products, and functional materials.[1,2] Synthesis of arylamines, previously mainly relying on nitroarene reduction, has received great advancement in the transition metal-catalyzed or -free reactions of amine nucleophiles or their electrophilic analogues with appropriate arylation reagents during the last two decades.[2-7] So far, a great number of aryl chlorides, bromides, iodides, sulfonates, iodonium salts, and other pseudo halides, as well as aryne precursors, have been confirmed to be viable arylation reagents in these reactions, providing the corresponding *N*-arylated products.[1-7]



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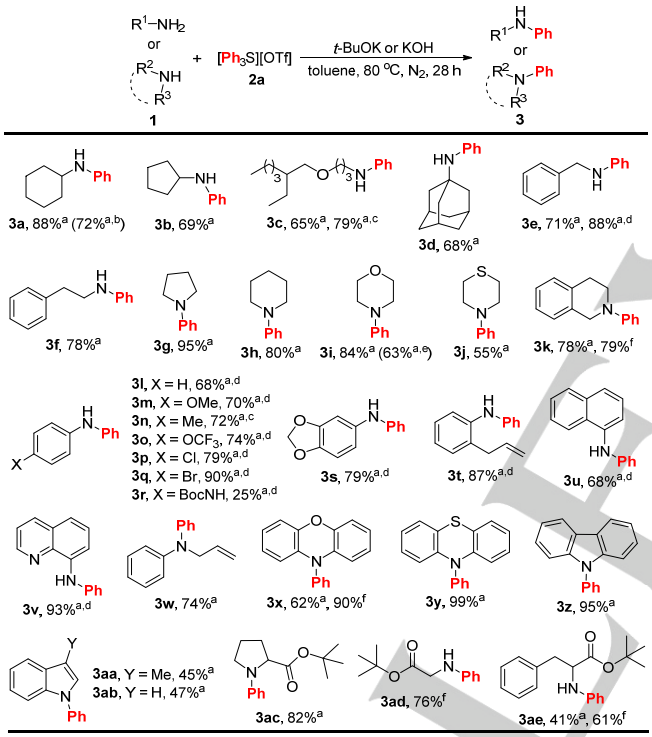
On the other hand, triarylsulfonium salts ([Ar_3S]X, X = OTf, BF_4, PF_6, etc.) are versatile agents in organic chemistry and materials science.[8,9] Recently, the Pd-catalyzed arylation of arylboronic acids, alkenes, and alkynes by [Ar_3S][OTf], the visible-light photocatalytic reduction and radical addition of [Ar_3S]X to alkenes, and the transition metal-free aromatic *ipso*-substitution of [Ar_3S][OTf] with [^{18}F]fluorides have evidenced their great usefulness in the C-C and C-F bond formation reactions.[9,10] Although the transition metal-free reactions of primary anilines and secondary aliphatic amines with diaryliodonium salts under alkaline conditions have been documented, producing various arylamines via nucleophilic aromatic substitution, aryne intermediates, or ligand exchange/reductive elimination processes[7a-d], the interactions between triarylsulfonium salts and amines or their derivatives are least studied.[11] As a class of alternative and emerging aryl transfer sources, triarylsulfonium salts have featured several advantages such as non-volatility, easy preparation, non-toxicity, moderate reactivity, and broad structural diversity. Importantly, the thermal gravimetric analysis showed that triphenylsulfonium triflate ([Ph_3S][OTf]) has a much higher onset decomposition temperature (405.8 °C) than diphenyliodonium triflate ([Ph_2I][OTf], 207.0 °C) (see supporting information), hinting at much better thermal stability of the former than the latter. Nevertheless, application of the advantageous triarylsulfonium salts as arylation reagents is to date much under developed compared to the corresponding diaryliodonium salts.[4a,6-8]

As a continuation of our interest in use of triarylsulfonium salts for arylation[8a,9], we first tested the reactions of [Ph_3S][OTf] with different types of amines under transition metal-free conditions. To our delight, the reaction of cyclohexanamine (**1a**) with triphenylsulfonium triflate (**2a**, 1.5 equiv) in toluene in the presence of *t*-BuOK (1.2 equiv) at 80 °C under a nitrogen atmosphere for 24 h gave *N*-cyclohexylaniline (**3a**) in 78% yield (Table S1). The choice of bases had a big impact on the *N*-phenylation (Table S1). *t*-BuONa, CsOH, KOH, and NaOH were moderately effective, affording **3a** in lower yields. Reaction of **1a** and **2a** with LDA or *n*-BuLi (at -78 °C to room temperature or at reflux in THF[11]) gave 7-12% of **3a**. It should be noted that, in most reactions, a small amount of *N*-cyclohexyl-*N*-phenylaniline (**4a**) was formed accompanied with **3a**, but it could be easily removed by column chromatography. Other bases such as K_2CO_3, KF, DBU, and NEt_3 were completely inert at 80 °C for the reaction, which didn't form **3a**. Moreover, if the reaction of **1a** and **2a** was run at 80 °C in the absence of base, no desired *N*-phenylation product was obtained.

Then, a brief survey of the reaction temperature showed that a temperature of 80 °C was optimal for the reaction of **1a** with **2a** and *t*-BuOK (Table S2). The solvent had a considerable influence on the conversion (Table S3). Toluene appeared to be the best solvent as the reaction of **1a**, **2a** and *t*-BuOK in CH_3CN, THF, DMF, *m*-xylene, DMSO, NMP, or 1,4-dioxane provided **3a** in a decreased yield (11-64%). Furthermore, the molar ratios of

1a, **2a** and *t*-BuOK interestingly affected the formation of **3a** (Table S4). When **2a** reacted with excess **1a** (1.11-2.0 equiv.) and *t*-BuOK (1.33-2.4 equiv.) in toluene, **3a** was formed in 75-82% yields. These yields were comparable to that obtained from the reaction of **1a** using 1.5 equiv. **2a** (78%). Notably, if **1a** was treated with 2.5 equiv. **2a** and 3.0 equiv. *t*-BuOK at 80 °C for 24 h, the doubly *N*-phenylated compound (**4a**) was obtained as the major product (91% isolated yield) (Table S4). Additionally, prolonging the reaction time of **1a**, **2a**, and *t*-BuOK (**1a**/**2a**/*t*-BuOK = 1:1.5:1.2 or 1.33:1:1.33) from 24 h to 28 h only slightly improved the yield of **3a** (Table S5). Reaction of 1.33 equiv. **1a** with **2a** in toluene in the presence of 1.33 equiv. *t*-BuOK at 80 °C for 28 h supplied **3a** in 85% yield (or 88% isolated yield on a large scale). Further extension of the reaction time did not continuously enhance the yield of **3a**.

Table 1. Mono *N*-phenylation of amines by triphenylsulfonium triflate in the presence of *t*-BuOK or KOH



[a] Reaction conditions: amine **1** (0.4 mmol), **2a** (0.3 mmol), *t*-BuOK (0.4 mmol), toluene (2 mL), 80 °C, N_2, 28 h. Isolated yield. [b] The reaction was run on a 4.5 mmol scale at 60 °C. [c] Amine **1** (0.6 mmol). [d] KOH (0.48 mmol) was used instead of *t*-BuOK (0.4 mmol). [e] The reaction was run on a 1.5 mmol scale. [f] Reaction conditions: amine **1** (0.2 mmol), **2a** (0.3 mmol), *t*-BuOK (0.24 mmol), toluene (2 mL), 80 °C, N_2, 24 h. Isolated yield.

Next, we chose an assembly of amine **1** (0.4 mmol), **2a** (0.3 mmol), *t*-BuOK (0.4 mmol), toluene (2 mL), 80 °C, N_2, and 28 h as the standard reaction conditions to probe the substrate scope of the *N*-phenylation (Table 1). Primary aliphatic amines such as cyclopentanamine (**1b**), 3-((2-ethylhexyl)oxy)propan-1-amine (**1c**), (3s,5s,7s)-adamantan-1-amine (**1d**), phenylmethanamine (**1e**), and 2-phenylethan-1-amine (**1f**) were smoothly converted to give the corresponding mono *N*-phenylated products (**3b-f**) in 65-78% yields. Similarly, secondary aliphatic amines like pyrrolidine (**1g**), piperidine (**1h**), morpholine (**1i**), thiomorpholine (**1j**), and 1,2,3,4-tetrahydroisoquinoline (**1k**) reacted with **2a** under the standard conditions to furnish respectively 95% of **3g**, 80% of **3h**, 84% of **3i**, 55% of **3j**, and 78% of **3k**. There were no bis(*N*-phenylated) products observed in the reactions of secondary amines. The scaled-up syntheses of **3a** and **3i** by reactions of **1a** and **1i** with **2a** at a 4.5 or 1.5 mmol scale gave 72% and 63% isolated yields, respectively, demonstrating the practicality of this method. Furthermore, by minor variation of the standard conditions in some reactions, e.g., use of 2 equiv. **1c** for **2a**, replacement of *t*-BuOK by KOH for **1e**, and employment of 1.5 equiv. **2a** for **1k**, the respective desired products were formed in better yields. These improvements suggested good flexibility of the conversion.

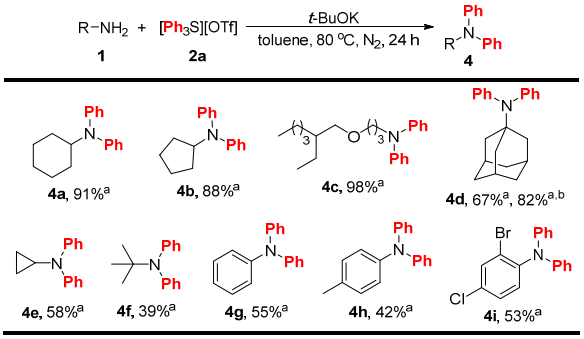
In addition, the *N*-phenylation reaction was applicable to aromatic amines (Table 1). Both KOH and *t*-BuOK were suitable bases for the *N*-phenylation of aniline (**1l**) (Table S7). Reaction of **1l** (1.33 equiv.) with **2a** in the presence of KOH (1.33 equiv.) at 80 °C for 28 h afforded **3l** in 68% yield. Aniline derivatives bearing either electron-donating or -withdrawing groups (e.g., methoxy (**1m**), methyl (**1n**), trifluoromethoxy (**1o**), chloro (**1p**), bromo (**1q**), or *tert*-butyl carbamate (BocNH, **1r**)) reacted under the same conditions to provide the mono *N*-phenylated products (**3m-r**) in 25-90% yields. The electron-withdrawing substituents on the aryl rings of anilines (**1o-q**) appeared to benefit the *N*-phenylation. Analogously, treatment of benzo[d][1,3]dioxol-5-amine (**1s**), 2-allylaniline (**1t**), naphthalen-1-amine (**1u**), and quinolin-8-amine (**1v**) with **2a**/KOH supplied the expected *N*-phenyl anilines (**3s-v**) in 68-93% yields. The electron-deficient quinolin-8-amine (**1v**) gave a higher yield of *N*-phenylated product than the electron-rich congener (**1u**) as well. Secondary aromatic amines such as *N*-allylaniline (**1w**), 10*H*-phenoxazine (**1x**), 10*H*-phenothiazine (**1y**), 9*H*-carbazole (**1z**), 3-methyl-1*H*-indole (**1aa**), and 1*H*-indole (**1ab**) reacted mildly with **2a** under the standard conditions to produce the corresponding *N*-phenylated products (**3w-ab**) in 45-99% yields. 1*H*-indoles seemed to be less effective substrates than phenoxazine, phenothiazine, and carbazole for the reaction. The BocNH group, the carbon-carbon double bonds and the heterocyclic moieties of substrates were well tolerated, illustrating good compatibility of the reaction.

To further verify the usefulness of the method, several bioactive molecules (**1ac-ae**) were examined (Table 1). It was remarkable that *tert*-butyl *L*-prolinate (**1ac**) and *tert*-butyl *L*-phenylalaninate (**1ae**) reacted with **2a** and *t*-BuOK to give desirably the racemic *N*-phenylated products (**3ac** and **3ae**) in good yields (see SI). The use of 1.5 equiv. **2a** and 1.2 equiv. *t*-BuOK to mix with *tert*-butyl glycinate (**1ad**) and **1ae** could clearly improve the yields of **3ad** and **3ae**.

Bis(*N*-phenylation) of amines by a large excess of **2a** in the presence of *t*-BuOK was also achieved. As above, reaction of **1a** with 2.5 equiv. **2a** and 3.0 equiv. *t*-BuOK at 80 °C for 24 h provided 91% of the bis(*N*-phenylated) product (**4a**). In a similar manner, treatment of **1b**, **1c**, **1d**, **1l**, **1n**, cyclopropanamine (**1af**), 2-methylpropan-2-amine (**1ag**), and 2-bromo-4-chloroaniline (**1ah**) with **2a** (2.5 equiv.)/*t*-BuOK (3.0 equiv.) gave respectively the bis(*N*-phenylated) products (**4b-i**) in moderate to high yields (Table 2). The bulky adamantanyl group in **1d** somewhat affected the bis(*N*-phenylation), affording a relatively low yield of

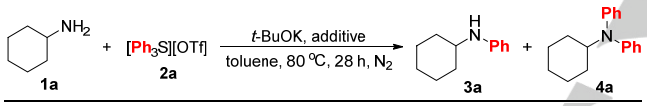
the desired product. Furthermore, the results gained from the reaction condition optimization suggested that a group of **2a**/KOH was poorly effective for the one-pot bis(*N*-phenylation) of aniline (Table S8). Reaction of **1l** with **2a** (2.5 equiv) in the presence of KOH (3.0 equiv) still gave mono *N*-phenylated amine as the main product (Table S8). All of these observations combined implied that the selective mono- and bis(*N*-phenylation) of primary amines by [Ph_3S][OTf] could be simply tuned by varying the molar equivalent of **2a** and the bases.

Table 2. Bis(*N*-phenylation) of amines by triphenylsulfonium triflate in the presence of *t*-BuOK.



[a] Reaction conditions: amine **1** (0.2 mmol), **2a** (0.5 mmol), *t*-BuOK (0.6 mmol), toluene (4 mL), 80 °C, N_2, 24 h. Isolated yield. [b] 36 h.

Table 3. Control experiments for understanding the reaction mechanism

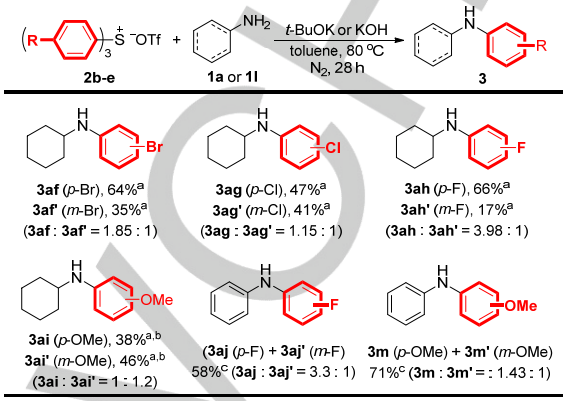


Entry	Additive	**3a** (%)	**4a** (%)
1[a]	TEMPO (1.0 equiv.)	62	4
2[b]	TEMPO (1.0 equiv.)	70	8
3[a,c]	none	81	4

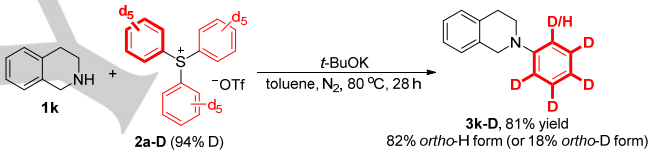
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.15 mmol), *t*-BuOK (0.2 mmol), toluene (2 mL), 80 °C, N_2, 28 h. The yields were determined by HPLC using **3a** and **4a** as external standards (**3a**: t_R = 5.930 min, **4a**: t_R = 16.823 min, λ_{max} = 249 nm (for **3a**), water / methanol = 10 / 90 (v / v)). [b] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), *t*-BuOK (0.24 mmol). [c] The reaction was run in the darkness.

It was well known that [Ar_3S]X can be readily initiated by UV-visible light or reductants to form aryl radicals for many chemical reactions.[8] *t*-BuOK is an efficient reductant in transition metal-free homolytic aromatic substitution (HAS) of aryl halides (ArX), which generates aryl radicals via a single-electron transfer (SET) between ArX and *t*-BuOK.[12] Besides, the aromatic nucleophilic *ipso*-substitution of [Ar_3S][OTf] by fluorides is also reported.[10b-c] To gain an insight into the mechanism of this *N*-phenylation reaction with [Ar_3S][OTf], several control experiments were carried out (Table 3). It was found that both the reaction of excess **1a**/*t*-BuOK with **2a** and the reaction of **1a** with excess **2a**/*t*-BuOK in the presence of TEMPO (1.0 equiv.) under the standard conditions afforded slightly lower yields of the desired product (**3a**) (entries 1 and 2). When a mixture of **1a** (0.2 mmol), **2a** (0.15 mmol), *t*-BuOK (0.24 mmol), and toluene (2 mL) was heated at 80 °C in the darkness for 28 h, **3a** was obtained in 81% yield (entry 3). These data suggested that the reaction might proceed through a non-radical pathway. Again, the standard reactions of 2-allylaniline (**1t**) and *N*-allylaniline (**1w**) with **2a**, providing **3t** and **3w** with the carbon-carbon double bonds survived, might also exclude a radical mechanism.

Table 4. *N*-Arylation of amines by triarylsulfonium triflates in the presence of *t*-BuOK or KOH



[a] Reaction conditions: cyclohexanamine (**1a**, 0.2 mmol), **2b-e** (0.15 mmol), *t*-BuOK (0.2 mmol), toluene (2 mL), 80 °C, N_2, 28 h. Isolated yield. **2b**: R = Br; **2c**: R = Cl; **2d**: R = F; **2e**: R = OMe. [b] The reaction was run at 100 °C. [c] Reaction conditions: aniline (**1l**, 0.2 mmol), **2d-e** (0.15 mmol), KOH (0.24 mmol), toluene (2 mL), 80 °C, N_2, 28 h. Isolated yield. The molar ratios of *p*- and *m*-isomers were determined by NMR spectroscopy.



Scheme 1. *N*-Phenylation of **1k** by deuterated triphenylsulfonium triflate (**2a-D**)

Further studies showed that other triarylsulfonium triflates were also available reagents for *N*-arylation of amines (Table 4). Tris(4-bromophenyl)sulfonium triflate (**2b**) reacted with **1a** in the presence of *t*-BuOK under the standard conditions to furnish 4-bromo-*N*-cyclohexylaniline (**3af**) in 64% yield and 3-bromo-*N*-cyclohexylaniline (**3af'**) in 35% yield. Similar reaction of tris(4-chlorophenyl)sulfonium triflate (**2c**), tris(4-fluorophenyl)sulfonium triflate (**2d**), and tris(4-methoxyphenyl)sulfonium triflate (**2e**) with **1a** gave mixtures of the regioisomers of the corresponding *N*-arylated products (**3ag**/**3ag'**-**3ai**/**3ai'**) in good yields. All these isomers could be easily separated by column chromatography. However, in the reactions of **2d** and **2e** with aniline (**1l**) and KOH, inseparable mixtures of *p*- and *m*-isomers of the *N*-arylated products (**3aj**/**3aj'** and **3m**/**3m'**) were obtained, the molar ratios of which were determined by NMR spectroscopy. The presence of regioisomers of products in the reactions of **2b-e** implied that the reaction might proceed via an aryne intermediate. Since the aryne intermediates have been demonstrated as highly reactive and inseparable species,[13] they are usually generated *in situ* in the reactions. Moreover, the reaction of **1k** with deuterated triphenylsulfonium triflate (**2a-D**) at 80 °C for 28 h gave **3k-D** in 81% yield with 82% *ortho*-H form (Scheme 1), suggesting a predominant N-H addition process to a benzyne intermediate. Nonetheless, the *ipso*-substitution mechanism occurring on the aromatic rings of arylsulfonium salts couldn't be fully excluded at

this stage as the *ortho*-H form of **3k-D** was not 100% produced, regardless of the H-D exchanges in the reaction system.

In conclusion, we have developed a transition metal-free method for *N*-arylation of amines by using triarylsulfonium triflates as arylation reagents and *t*-BuOK or KOH as a base. Various aliphatic and aromatic amines including primary and secondary were readily transformed to give the corresponding *N*-arylated products in good to high yields under mild conditions. The molar ratios of reactants and the types of bases greatly affected the reactions of primary amines. When a large excess of $[Ph_3S][OTf]$ was employed with using *t*-BuOK as a base, the bis(*N*-phenylated) compounds were obtained as the major products. In contrast, the secondary amines supplied only mono *N*-phenylated products even with much excess $[Ar_3S][OTf]$ and *t*-BuOK. The reaction also allowed a simple, yet powerful and reliable synthesis of bioactive *N*-phenyl amino acid derivatives. The control experiments, the deuterium labelling study, and the formation of regioisomers of *N*-arylated products using 4-substituted triarylsulfonium triflates suggested a plausible mechanism via an aryne intermediate for the reaction. Advantages of this method include a wide range of substrates, transition metal-free conditions, tunable mono- or bis(*N*-phenylation) of primary amines, and excellent thermal stability of $[Ar_3S][OTf]$ (compared to the diaryliodonium salts used for C_{Ar}-N bond formation). Application of $[Ar_3S][OTf]$ as promising arylation reagents in other transformations is currently on the way in our lab.

Experimental Section

In a nitrogen-filled glovebox, a sealed tube was charged with triphenylsulfonium triflate (**2a**, 123.6 mg, 0.3 mmol), *t*-BuOK (44.8 mg, 0.4 mmol), cyclohexanamine (**1**, 39.6 mg, 0.4 mmol), and toluene (2 mL) with vigorous stirring. The mixture was heated at 80 °C for 28 h, cooled to room temperature, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluents to give *N*-cyclohexylaniline (**3a**) as a yellow oil (46.2 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 2H), 3.52 (brs, 1H), 3.27 (m, 1H), 2.08 (dm, *J* = 12.5 Hz, 2H), 1.78 (dm, *J* = 13.5 Hz, 2H), 1.67 (dm, *J* = 13.0 Hz, 1H), 1.43-1.35 (m, 2H), 1.29-1.23 (m, 1H), 1.20-1.13 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 129.3, 116.9, 113.2, 51.7, 33.5, 26.0, 25.1.

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Keywords: transition metal-free • *N*-arylation • aryne • triarylsulfonium triflates

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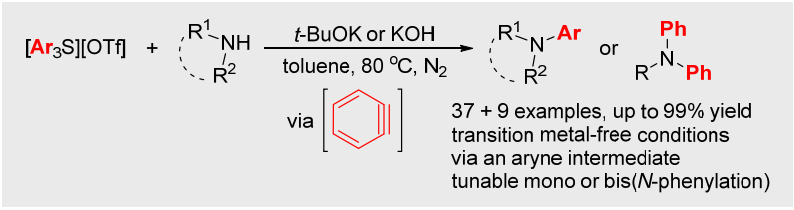

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Transition Metal-Free *N*-Arylation of Amines by Triarylsulfonium Triflates

Transition metal-free *N*-arylation of aliphatic and aromatic amines by [Ar_3S][OTf] in the presence of *t*-BuOK or KOH gave the mono *N*-arylated products in good to high yields. The reaction might proceed via an aryne intermediate. The molar ratios of the reactants and the choice of bases had a big influence on the reaction. When a large excess of [Ph_3S][OTf] and *t*-BuOK were employed for primary amines, the corresponding bis(*N*-phenylated) compounds were obtained as the major products.