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Development and Application of *O*-(Trimethylsilyl)aryl Fluorosulfates for the Synthesis of Arynes

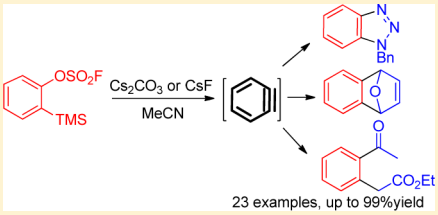
Qiao Chen,[†] Hongmei Yu,[†] Zhaoqing Xu,*[,†] Li Lin,[†] Xianxing Jiang,*[,‡] and Rui Wang*[,†]

[†]Institute of New Drugs Design and Synthesis, Key Laboratory of Preclinical Study for New Drugs of Gansu Province, School of Basic Medical Sciences, Lanzhou University, Lanzhou, China

[‡]School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou, China

Supporting Information

ABSTRACT: A class of *o*-(trimethylsilyl)aryl fluorosulfates was synthesized by a concise method and successfully used as aryne precursors for the first time. Different trapping agents such as azides, furans, and acyl acetoacetates could successfully react with the aryne precursors under mild conditions with good to excellent yields.



Since the first evidence for the existence of arynes,[1] they have attracted chemists' great attention because of their very broad synthetic utilities.[2] Their versatility in the synthesis provides organic chemists with a prodigious starting point to discover new reactions, advanced materials, and pharmaceuticals.[3] Nevertheless, the application of these versatile synthetic intermediates was limited due to their harsh preparing conditions and high synthetic cost.[4] Indeed, it was not until 1983 that arynes, motivated by Kobayashi's aryne precursors, were allowed to be generated under mild reaction conditions.[5] Although the introduction of aryl triflates have turned arynes to useful synthetic reagents from uncontrollable reactive intermediates, this kind of aryne precursor still has its own limitations, such as (i) the triflating reagents (Tf_2O and TfCl) used for the preparation of aryl triflates were relatively expensive; (ii) the aryl triflates decomposed rapidly under normal basic conditions, which restricted the use of this kind of precursors as intermediates in multistep reactions;[6] (iii) fluoride promoters used for the formation of arynes showed low selectivities over C−Si and O−Si bonds cleavage, which means that aryne precursors bearing multiple silane groups, such as C_{aryl}-SiR_3 and $C_{alkyl}O$-SiR_3, will not be expected to give highly chem- or regioselective transformation (an example is given in the following section). In 1999, Kitamura and coworkers disclosed a hypervalent iodine aryne precursor for the generation of an aryne intermediate in high yield under the treatment of Bu_4NF at room temperature.[4b] Recently, as the *o*-TMS aryl triflate analogues, a new method was developed for the preparation of arynes by the group of Akai.[7] They replaced the traditional triflating agents with nonafluorobutanesulfonyl fluoride (NfF) and cleverly conducted the arynes production and trapping reaction in one-pot. In that context, the fluoride ion released from NfF while the aryne precursor generated was directly used for the formation of aryne, and an additional fluorine source was needless. In 2012, *o*-(trimethylsilyl)aryl imidazolylsulfonates were chosen as aryne precursors by Zoltán Novák's group,[8] and the precursors do not contain any fluorine atoms themselves, and the potentially toxic of fluorinated side product was eliminated. Although these excellent aryne precursors have made notable progress in the area of aryne chemistry, the dependence of external fluoride sources, high fluoride content, or the expensive starting material still limited their employment in large-scale reactions. Nowadays, with the increasing use of arynes in synthetic chemistry, highly efficient, relatively stable, and operationally simple aryne precursors with low cost are still highly desired.

Sulfonyl halides, such as $-SO_2Cl$,[9] are highly polarized due to the electron-withdrawing property of the halogen center and can theoretically serve as leaving groups. However, the sulfur−halogen bond in sulfonyl halides is very reactive and tends to react with various chemicals ($-SO_2Br$ and $-SO_2I$ are even sensitive to light), which affects the substitution of the sulfonyl halide as a whole group in organic reactions (Figure 1, eq 1). Unlike other sulfonyl halides, the $-SO_2F$ unit is remarkably

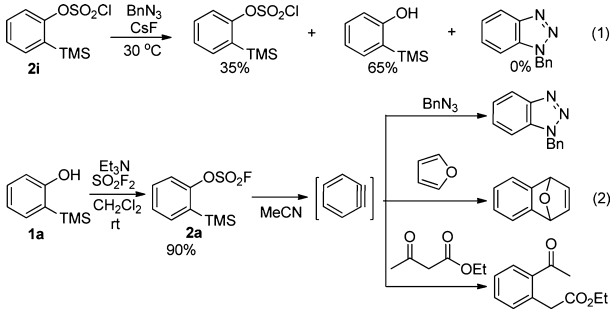


Figure 1. *O*-(TMS) phenyl fluorosulfate as precursor for the synthesis of aryne.

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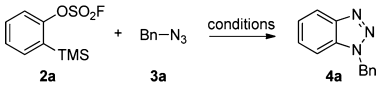
stable and redox-silent.[10] Since fluorine is the most electronegative element in the periodic table, the cleavage of the sulfonyl-fluorine bond is extremely difficult, making it hard for $-SO_2F$ to act as halogenating agents. Considering the unique property of the sulfonyl fluoride group, we envisioned that the simple $-OSO_2F$ could be used as an inexpensive -OTf alternative and serves as a leaving group for the developing of a new type of aryne precursors **2**.[11−13] As shown in Figure 1 (eq 2), **2a** was prepared in high yield by simply exposing the corresponding *o*-TMS phenol to sulfuryl fluoride in the presence of triethylamine.[14] Sulfuryl fluoride is a broad spectrum biocide, and its global production is about 3 million kilograms per year,[11,15] making it a very cheap starting material. In 2014, an excellent review published by Sharpless demonstrated the details about sulfuryl fluoride and its application in organic syntheses.[11] During the preparation of this manuscript, a series of aryl fluorosulfates were employed as coupling partners in a Suzuki reaction with remarkable yields.[16] In this note, a family of *o*-(trimethylsilyl)aryl fluorosulfates were developed and served as aryne precursors. To our delight, the new precursor designed here could smoothly facilitate the Huisgen cyclization,[8,17] Diels−Alder reaction,[7] and *σ*-bond insertion reaction[18] under very mild conditions. Furthermore, *o*-TMS aryl fluorosulfates were proved to be air- and moisture-stable and would not decompose for at least a month when placed at room temperature. This class of aryne precursors will provide economic and practical avenues toward the industrialized application of arynes.

At the outset of our investigations, by using CH_3CN as the solvent, a series of nonfluorinated bases was evaluated for the Huisgen 2 + 3 cycloaddition between *o*-TMS phenyl fluorosulfate **2a** and benzyl azide **3a** (Table 1). It was found that two equivalents of NaOH can hardly catalyze the reaction

Table 1. Optimization of the Reaction Conditions[a]



2a **3a** **4a**

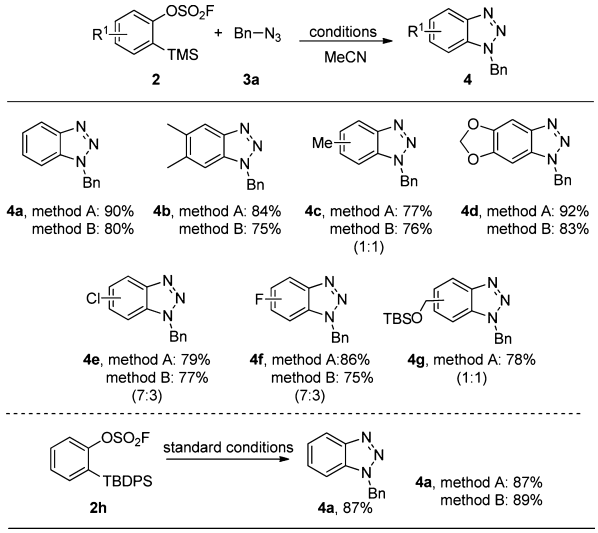
entry	base	solvent	temperature	yield[b] (%)
1	NaOH	CH_3CN	60 °C	<5
2	KOH	CH_3CN	60 °C	57
3	CsOH	CH_3CN	60 °C	76
4	Cs_2CO_3	CH_3CN	60 °C	82
5	K_3PO_4	CH_3CN	60 °C	17
6	KO^{t}Bu	CH_3CN	60 °C	40
7	K_2CO_3	CH_3CN	60 °C	29
8	DBU	CH_3CN	60 °C	<5
9	CsF	CH_3CN	60 °C	75
10	TBAF	CH_3CN	60 °C	75
11	Cs_2CO_3	CH_3CN	30 °C	78
12[c]	Cs_2CO_3	CH_3CN	30 °C	89
13[c,d]	Cs_2CO_3	CH_3CN	30 °C	97
14[c,d,e]	Cs_2CO_3	CH_3CN	30 °C	97 (90)
15[f]	CsF	CH_3CN	60 °C	88 (80)

[a]Unless otherwise noted, the reactions were carried out by using 0.24 mmol of **2a**, 0.2 mmol of **3a**, 0.4 mmol of base, and 2 mL of solvent, and stirred for 20 h. [b]Yields were detected by ^{1}H NMR with isolated yield indicated in parentheses. [c]1 equiv of 18-c-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was used. [d]0.3 mmol of **2a** was used, and the reaction was completed in 8 h. [e]0.3 mmol of Cs_2CO_3 and 1 mL of CH_3CN were used. [f]0.2 mmol of **2a**, 0.3 mmol of **3a**, and 1 mL of CH_3CN, and 36 h.

in 20 h at 60 °C (entry 1). Gratifyingly, a remarkable enhancement of reactivity was detected when KOH was used instead of NaOH, given the desired product **4a** with a promising yield (57%, entry 2). Further screening of other bases revealed that cesium salts are better candidates than potassium-containing bases (entries 3, 4, and 9 vs entries 2, and 5−7), and Cs_2CO_3 was proved to be optimal for this cycloaddition. An organic base DBU was also tested under the same conditions; however, only a trace amount of the desired product was observed (entry 8). It should be noted that the generally used F^- promoters, namely, CsF and TBAF, were also effective for the reaction (entries 9 and 10). Subsequently, Cs_2CO_3 was chosen for further investigation of the reaction conditions. Reducing the reaction temperature to 30 °C only slightly decreased the yield of **4a** (entry 11). We were happy to find that when 18-crown-6 (18-c-6) was used as an additive, the product yield was dramatically improved to 89% (entry 12).[19] A solvent survey indicated that CH_3CN is the best choice for this transformation. Modification of the ration of **2a**/**3a** to 1.5/1 improved the yield sharply (entry 13). At last, a complete conversion of **3a** was obtained by using **2a** (1.5 equiv), Cs_2CO_3 (1.5 equiv), and 18-c-6 (1 equiv) in 0.2 M CH_3CN at 30 °C for 8 h (entry 14).

Armed with the optimized conditions, several symmetrical or nonsymmetrical aryne precursors were subjected to the cycloaddition reaction with the benzyl azide **3a** (Table 2). As

Table 2. Reaction Scope with Different Aryne Precursors[a,b]



2 **3a** **4** **2h**

[a]Method A: All of the reactions were carried out with 0.3 mmol of **2**, 0.2 mmol of **3a**, 0.3 mmol of Cs_2CO_3, 0.2 mmol of 18-c-6, and 1 mL of MeCN, at 30 °C, and stirred for 12 h. Method B: 0.2 mmol of **2**, 0.3 mmol of **3a**, 0.4 mmol of CsF, and 1 mL of MeCN, at 60 °C and 36 h. [b]Isolated yields. Ratios in parentheses refer to the 5-:6-substituted product.

expected, the symmetrical aryne precursors such as **2a**, **2b**, **2d**, and **2h** afforded the single regioisomer of the products (**4a**, **4b**, **4d** and **4h**), while the nonsymmetrical aryne precursors resulted in inseparable regioisomeric mixtures of 5- and 6-substituted benzotriazoles[20] (**4c** and **4e**−**4g**). Aryne precursors with different substituent groups as well as disubstituted and heterocyclic substituted were well tolerated in the transformation and provided the desired products in good yields. It should be noted that, an aryne precursor bearing two silane-

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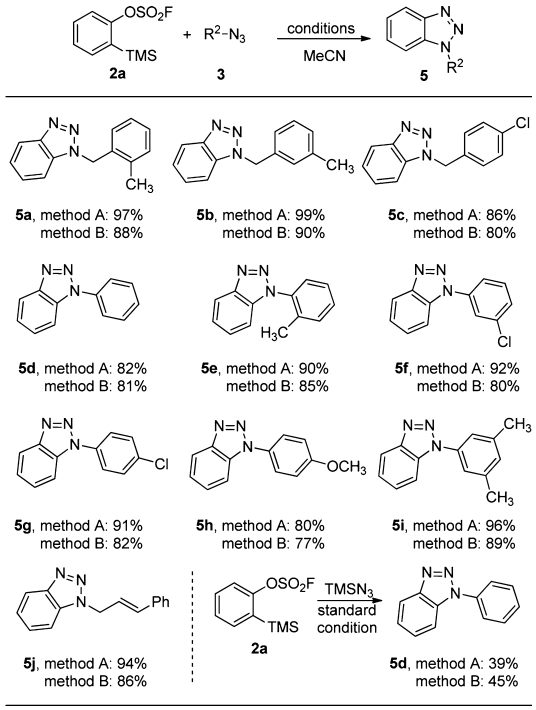
protected groups was synthesized and directly subjected to the aryne cycloaddition reaction with azide **3a**. To our delight, the corresponding **4g** was obtained in 78% yield with the *para*-silane protecting group untouched. In fact, when **4g** was exposed to one equiv of CsF, it completely desilylated to the corresponding alcohol **4g′** within 2 h. Further research indicated that the silyl substituent on the *ortho*-position of the aryne precursor was not limited to TMS, and **2h** with a TBDPS (*tert*-butyldiphenylsilyl) group also lead to the formation of **4a** with good result. Since CsF is one of the most classic desilylation reagents, the yields of the reactions catalyzed by CsF are also depicted in the table (method B).

Different azides bearing electron-donating as well as electron-withdrawing substituents also permitted an efficient access to the benzotriazoles **5a**–**5j** in good to excellent yields (Table 3).

Table 3. Reaction Scope with Different Azides[a,b]



[a]Method A: 0.3 mmol of **2a**, 0.2 mmol of **3**, 0.3 mmol of Cs_2CO_3, 0.2 mmol of 18-c-6, and 1 mL of MeCN, at 30 °C, and stirred for 12 h. Method B: 0.2 mmol of **2a**, 0.3 mmol of **3**, 0.4 mmol of CsF, and 1 mL of MeCN, at 60 °C and 36 h. [b]Isolated yields.

It is worth noting that benzyl azides bearing a methyl group exhibited even higher reactivity and yielded the corresponding benzotriazoles with outstanding results (**5a** and **5b**). While the unsubstituted azidobenzene and the methoxyl substituted azidobenzene gave slightly lower yields of the desired products, they afforded **5d** and **5h** with 82% and 80% yields, respectively. Disubstituted and allylic azides were found to be competent in the cycloaddition reaction with **2a**, thus delivering **5i** and **5j** with remarkable yields. We also examined the use of trimethylsilyl azide in this reaction; however, the desired product seems to be desilylated and then phenylated under the standard conditions and led to **5d** in a moderate yield (39%). Summarizing the results of Tables 2 and 3 (method B), we can see that CsF is also competent to generate aryne from *o*-(trimethylsilyl)aryl fluorosulfates.

Following the successful cycloaddition between the new aryne precursors and azides, we continued our investigations with other types of reactions to confirm the synthetic applicability of this novel precursor (Figure 2). To our delight,

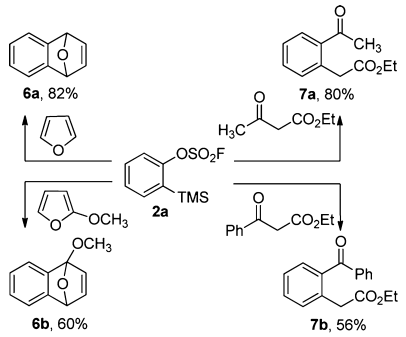
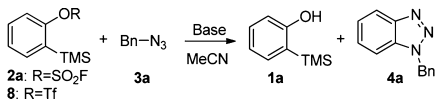


Figure 2. Application of **2a** in other reactions under the established conditions.

the Diels–Alder reaction of **2a** and furan proceeded smoothly under the standard conditions (method A), giving the corresponding Diels–Alder adducts **6a** and **6b** in 82% and 60% yields, respectively. The *σ*-bond insertion reaction of acetyl acetic ether or ethyl benzoyl acetate with **2a** were also achieved under established conditions and afforded the desired product **7a** or **7b** in good yields.

Notably, the reactivity and stability differences between Kobayashi's aryne precursor and our precursor **2a** were examined (Table 4). We were glad to find that our precursor

Table 4. Reactivity and Stability Difference between Precursors 2a and 8[a]



			yield[b] (%)		
entry	precursor	base	precursor	**1a**	**4a**
1	**2a**	CsF	8 (**2a**)	0	85
2	**8**	CsF	10 (**8**)	6	80
3[c]	**2a**	NaOH	92 (**2a**)	0	4
4	**8**	NaOH	32 (**8**)	65	1

[a]The reactions were carried out with 0.2 mmol **2a** or **8**, 0.3 mmol **3a**, and 0.2 mmol base in 1 mL of MeCN at 30 °C; stirred for 24 h. [b]Determined by ^{1}H NMR using mesitylene as an internal standard. [c]A week later, still no **1a** was detected.

demonstrated a slightly higher reactivity under the same conditions. What's more, when treated with NaOH, Kobayashi's aryne precursor seriously decomposed, while our precursor **2a** was undamaged even in a week. In order to investigate the potential of this precursor in industrial application, the Huisgen cyclization was conducted on a larger scale (10 mmol). As we had expected, both of the methods give the desired product in good yields (Figure 3).

In summary, a new class of aryne precursors was developed and successfully applied to the preparation of arynes under mild conditions. These precursors were easily approached from *o*-trimethylsilyl aryl phenols and readily available sulfuryl fluoride. Moreover, the arynes could be generated with or without an external fluoride source which smoothly underwent the

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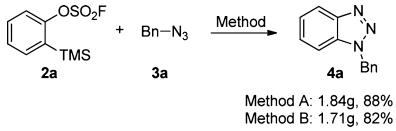

Figure 3. Peparation of **4a** with a 10 mmol scale reaction by methods A and B.

Huisgen cyclization reactions with a uniformly high yields. We believe that the design of these simple, efficient aryne precursors will benefit the application of arynes on an industrial scale. Further investigations of the applicability of the new aryne precursor as well as the mechanism studies are currently underway.

EXPERIMENTAL SECTION

General. All commercially available reagents were used without further purification unless otherwise stated. 18-c-6 was purified by recrystallization from CH_3CN. All solvents were dried according to established procedures. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a spectrometer (300 MHz, 75 and 282 MHz, respectively). The regioselectivities were determined by ^1H NMR spectra of the crude reaction mixtures. IR spectra were recorded on a FT-IR spectrometer, and only major peaks were reported in cm^{-1}. High resolution mass spectra (HRMS) were obtained by the ESI (Q-TOF or Orbitrap) or EI (TOF) ionization sources. Noncommercial azides **3** were prepared according to known procedures.[17d]

*General Procedure for the Preparation of Aryne Precursors **2**.* Starting material 2-bromophenols are commercially available, and bromosesamol[21a] was prepared from commercially available sesamol according to a literature procedure. 2-(Trimethylsilyl)phenols were prepared from the corresponding 2-bromophenols according to literature procedures.[21b] 4-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-(trimethylsilyl)phenol was prepared according to a literature procedure.[7] Aryne precursors **2** were prepared according to a modified literature procedure.[11,14] An oven-dried flask with a magnetic stirring bar, and the corresponding 2-(trimethylsilyl)phenols **1** (10 mmol) was capped with a rubber septum and then evacuated and backfilled with argon. CH_2Cl_2 (10 mL) and Et_3N (12 mmol) were added via syringes, and the mixture was stirred at room temperature for 2 h. Then the atmosphere above the solution was removed with gentle vacuum, and SO_2F_2 gas (1−1.5 equiv sulfuryl fluoride was enough. CAUTION: Sulfuryl fluoride is a chemical mainly used as a fumigant insecticide. Ingestion and other exposures to the chemical might be harmful.) was introduced by needle from a balloon filled with the gas. For large scale reactions, depletion of the sulfuryl fluoride from the balloon was easily observed, and more reagents were introduced with a fresh balloon when required. For small scale reactions, SO_2F_2 was used in excess. The reaction mixture was vigorously stirred at room temperature for 0.5−12 h, monitoring by TLC. After completion, the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel (petroleum ether−petroleum ether/ethyl acetate 10:1) to give the desired product **2a**−**2g**.

*2-(tert-Butyldiphenylsilyl)phenyl Sulfofluoridate (**2h**).* 2-(*tert*-Butyldiphenylsilyl)phenol (**1h**) was prepared according to a literature procedure.[21c] Compound **2h** was prepared from **1h** following the general procedure. White solid, 86% yield.

*2-(Trimethylsilyl)phenyl sulfochloridate (**2i**).* An oven-dried 100 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 2-(trimethylsilyl)phenol (1.66 g, 10 mmol, 1.0 equiv). The vessel was evacuated and backfilled with nitrogen. CH_2Cl_2 (20 mL) and pyridine (0.97 mL, 12 mmol, 1.2 equiv) were then added via syringes, and the solution was cooled to −40 °C. After the mixture was stirred for 1 h at −40 °C, sulfuryl chloride (0.97 mL, 12 mmol, 1.2 equiv) was added via syringe. The reaction was stirred for 2 h at this temperature and then warmed to room temperature and stirred for one more hour. After the reaction, water was added into the reaction mixture for quenching. The mixture was extracted with CH_2Cl_2, and the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give **2i** as a colorless oil; 85% yield.

*General Procedure for the Synthesis of **4**−**7**. Method A.* An oven-dried flask was charged with Cs_2CO_3 (0.3 mmol, 1.5 equiv) and 18-c-6 (0.2 mmol, 1 equiv) and capped with a rubber septum and then evacuated and backfilled with argon. Anhydrous MeCN (1 mL, 0.2 M), **2** (0.3 mmol, 1.5 equiv), and **3** (0.2 mmol, 1equiv) were added via syringes, and the reaction mixture was stirred at 30 °C for a given reaction time. After the reaction, saturated aqueous solution of NH_4Cl was added into the reaction mixture for quenching. The mixture was extracted with ethyl acetate, and the combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 10:1−6:1) to give the desired product **4** or **5**. Products **6** and **7** were synthesed using method A with the corresponding aryne trapping reagents instead of **3**.

Method B. An oven-dried flask was charged with CsF (0.4 mmol, 2 equiv) and capped with a rubber septum and then evacuated and backfilled with argon. Anhydrous MeCN (1 mL, 0.2 M), **2** (0.2 mmol, 1 equiv), and **3** (0.3 mmol, 1.5 equiv) were added via syringes, and the reaction mixture was stirred at 60 °C for 36 h. After cooling down to room temperature, the reaction mixture was concentrated in vacuo. The crude products were purified through flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1−6:1) to afford the desired product **4** or **5.**

*General Procedure for the Synthesis of **4g′**.* An oven-dried flask was charged with **4g** (35.3 mg, 0.10 mmol) and CsF (15.2 mg, 0.10 mmol) and capped with a rubber septum. The flask was evacuated and backfilled with argon. MeCN (1.0 mL) was charged via syringes, and the reaction mixture was stirred at room temperature for 2 h. Water was added into the reaction mixture for quenching. The mixture was extracted from ethyl acetate, and the combined organic phase was dried over Na_2SO_4. The organic phase was filtered and concentrated under reduce pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 2:1) to provide the titled compound **4g′** as a white solid (23.6 mg, 99%). The 5- and 6-substituted **4g′** were separable and were characterized separately. It should be noted that when one equivalent of CsF was added to the mixture of the **4g** formation reaction after **4g** was fully generated, **4g′** could also be acquired.

*2-(Trimethylsilyl)phenyl Sulfofluoridate (**2a**).* Colorless oil, R_f = 0.5 (PE), 90% yield (2.23 g). ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (dd, J = 7.5, 1.8 Hz, 1H), 7.52−7.42 (m, 1H), 7.41−7.32 (m, 2H), 0.37 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 136.2, 132.1, 131.3, 127.8, 119.0, −0.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ 42.34. IR ($CHCl_3$): 2960, 1599, 1449, 1233, 1143, 925, 845, 575 cm^{-1}. HRMS (EI): $C_9H_{13}FO_3SSi$ calcd, 248.0339; found, 248.0336.

*4,5-Dimethyl-2-(trimethylsilyl)phenyl Sulfofluoridate (**2b**).* Colorless oil, R_f = 0.5 (PE), 85% yield (2.35 g). ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.13 (d, J = 1.8 Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 0.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 140.4, 136.9, 136.4, 128.4, 119.9, 19.9, 19.2, −0.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ 41.90. IR ($CHCl_3$): 2957, 1607, 1447, 1229, 1003, 842, 803, 629 cm^{-1}. HRMS (EI): $C_{11}H_{17}FO_3SSi$ calcd, 276.0652; found, 276.0650.

*4-Methyl-2-(trimethylsilyl)phenyl Sulfofluoridate (**2c**).* Colorless oil, R_f = 0.5 (PE), 96% yield (2.52 g). ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.25 (s, 2H), 2.37 (s, 3H), 0.35 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 137.6, 136.6, 131.7, 118.7, 20.9, −0.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ 41.95. IR ($CHCl_3$): 2959, 1596, 1448, 1233, 926, 842, 803, 608 cm^{-1}. HRMS (EI): $C_{10}H_{15}FO_3SSi$ calcd, 262.0495; found, 262.0490.

*6-(Trimethylsilyl)benzo[d][1,3]dioxol-5-yl Sulfofluoridate (**2d**).* Colorless oil, R_f = 0.3 (PE), 80% yield (2.34 g). ^1H NMR (300 MHz, $CDCl_3$) δ 6.89 (d, J = 1.8 Hz, 1H), 6.88 (s, 1H), 6.04 (s, 2H), 0.33 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 149.3, 147.2, 124.3, 113.1, 102.4, 101.7, −0.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ 41.51. IR ($CHCl_3$): 2959, 1622, 1450, 1250, 1231, 993, 903, 844 cm^{-1}.

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HRMS (ESI-Orbitrap): $C_{10}H_{14}FO_5SSi$ $[M + H]^+$ calcd, 293.0310; found, 293.0313.

*4-Chloro-2-(trimethylsilyl)phenyl Sulfofluoridate (**2e**).* Colorless oil, R_f = 0.4 (PE), 78% yield (2.2 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49−7.38 (m, 2H), 7.32 (dd, J = 8.7, 1.8 Hz, 1H), 0.37 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 135.8, 134.9, 133.9, 131.1, 120.5, −1.01. ^{19}F NMR (282 MHz, $CDCl_3$) δ 42.26. IR ($CHCl_3$): 2961, 1589, 1452, 1233, 1150, 924, 844, 595 cm^{-1}. HRMS (EI): $C_9H_{12}ClFO_3SSi$ calcd, 281.9949; found, 281.9948.

*4-Fluoro-2-(trimethylsilyl)phenyl Sulfofluoridate (**2f**).* Light blue oil, R_f = 0.4 (PE), 75% yield (2.0 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (ddd, J = 9.0, 4.0, 1.9 Hz, 1H), 7.20 (dd, J = 8.0, 3.1 Hz, 1H), 7.12 (ddd, J = 9.0, 7.4, 3.2 Hz, 1H), 0.37 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C−F coupling not assigned) δ 162.9, 159.6, 150.9, 135.5, 122.5, 122.2, 121.0, 120.9, 118.0, 117.7, −1.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ 41.66, −113.80. IR ($CHCl_3$): 2960, 1583, 1452, 1233, 1135, 844, 806, 538 cm^{-1}. HRMS (EI): $C_9H_{12}F_2O_3SSi$ calcd, 266.0244; found, 266.0240.

*4-(((tert-Butyldimethylsilyl)oxy)methyl)-2-(trimethylsilyl)phenyl Sulfofluoridate (**2g**).* Colorless oil, R_f = 0.4 (PE), 80% yield (3.16 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.45−7.28 (m, 2H), 4.76 (s, 2H), 0.95 (s, 9H), 0.36 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 141.0, 133.4, 131.7, 128.7, 118.7, 64.0, 25.9, 18.3, −0.9, −5.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ 42.07. IR ($CHCl_3$): 2956, 1597, 1450, 1233, 1105, 926, 842, 804 cm^{-1}. HRMS (ESI-Orbitrap): $C_{16}H_{33}FO_4SSi_2$ N $[M + NH_4]^+$ calcd, 410.1647; found, 410.1652.

*2-(tert-Butyldiphenylsilyl)phenyl Sulfofluoridate (**2h**).* White solid, R_f = 0.6 (PE/EA = 10:1), 86% yield (3.56 g), mp 90−92 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.4, 1.8 Hz, 1H), 7.59−7.50 (m, 5H), 7.47−7.31 (m, 8H), 1.21 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0, 139.2, 136.1, 133.3, 131.9, 129.6, 127.9, 127.1, 118.7, 29.1, 18.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ 45.49. IR ($CHCl_3$): 3387, 2929, 1452, 1429, 1232, 1145, 1106, 1060, 702 cm^{-1}. HRMS (ESI-Orbitrap): $C_{22}H_{27}FO_3SSiN$ $[M + NH_4]^+$ calcd, 432.1459; found, 432.1464.

*2-(Trimethylsilyl)phenyl Sulfochloridate(**2i**).* Colorless oil, R_f = 0.6 (PE), 85% yield (2.24 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 1H), 7.57 (dt, J = 7.2, 1.8 Hz, 1H), 7.53−7.43 (m, 1H), 7.42−7.33 (m, 1H), 0.37 (d, J = 1.8 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 136.3, 132.4, 131.2, 127.8, 118.7, −0.6. IR ($CHCl_3$): 2959, 1597, 1414, 1140, 1061, 843, 594, 542 cm^{-1}. HRMS (EI): $C_9H_{13}ClO_3SSi$ calcd, 264.0043; found, 264.0039.

*Benzyl-1H-benzo[d][1,2,3]triazole (**4a**).*[8] Yellow solid, R_f = 0.3 (PE/EA = 10:1), 90% yield (37.6 mg). mp 108−110 °C (literature reported: 114−116 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.40−7.22 (m, 8H), 5.83 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 134.6, 132.7, 128.9, 128.3, 127.5, 127.3, 123.8, 119.9, 109.6, 52.1.

*1-Benzyl-5,6-dimethyl-1H-benzo[d][1,2,3]triazole (**4b**).*[17d] Yellow solid, R_f = 0.3 (PE/EA = 10:1), 84% yield (39.8 mg). mp 156−157 °C (literature reported: 158−161 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.37−7.21 (m, 5H), 7.10 (s, 1H), 5.78 (s, 2H), 2.36 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 137.7, 135.0, 133.7, 131.8, 128.9, 128.2, 127.4, 119.0, 109.0, 51.9, 20.9, 20.4.

*1-Benzyl-5(6)-methyl-1H-benzo[d][1,2,3]triazole (**4c**).*[8] Yellow solid, R_f = 0.3 (PE/EA = 10:1), 77% yield (34.2 mg), (unseparable mixture of 5- methyl and 6- methyl isomers with a 1:1 ratio). mp 95−96 °C (literature reported: 97−98 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 0.5H), 7.80 (s, 0.5H), 7.35−7.12 (m, 7H), 5.79 (s, 1H), 5.78 (s, 1H), 2.46 (s, 1.5H), 2.44 (s, 1.5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 144.8, 137.9, 134.9, 134.8, 133.8, 133.2, 131.2, 129.5, 128.8, 128.3, 128.2, 127.4, 127.3, 126.1, 119.3, 118.8, 109.1, 108.7, 52.1, 51.8, 21.9, 21.3.

*1-Benzyl-1H-[1,3]dioxolo[4′,5′:4,5]benzo[1,2-d][1,2,3]triazole (**4d**).*[8] White solid, R_f = 0.2 (PE/EA = 5:1), 92% yield (46.6 mg). mp 148−149 °C (literature reported: 148−151 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ7.35−7.20 (m, 6H), 6.61 (s, 1H), 6.01 (s, 2H), 5.71 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 146.9, 142.1, 134.5, 129.3, 128.9, 128.4, 127.4, 102.1, 97.0, 88.3, 52.2.

*1-Benzyl-5(6)-chloro-1H-benzo[d][1,2,3]triazole (**4e**).* Yellow solid, R_f = 0.5 (PE/EA = 10:1), 79% yield (38.4 mg), (unseparable mixture of 5-chloro and 6-chloro isomers with 7:3 ratio). mp 105−106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16−7.89 (m, 1H), 7.37−7.22 (m, 6H), 5.82 (s, 1.4H), 5.80 (s, 0.6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 144.8, 134.5, 134.2, 134.2, 133.8, 133.3, 131.4, 129.8, 129.1, 129.03, 128.6, 128.3, 127.5, 125.1, 122.9, 120.9, 120.6, 119.3, 110.7, 109.5, 52.5, 52.3. IR ($CHCl_3$): 3345, 2926, 1595, 1421, 1104, 1061, 845 cm^{-1}. HRMS (ESI-Q-TOF): $C_{13}H_{11}ClN_3$ $[M + H]^+$ calcd, 244.0636; found, 244.0646.

*1-Benzyl-5(6)-fluoro-1H-benzo[d][1,2,3]triazole (**4f**).*[8] Yellow solid, R_f = 0.4 (PE/EA = 10:1), 86% yield (39.0 mg), (unseparable mixture of 5-fluoro and 6-fluoro isomers with a 7:3 ratio). mp 88−89 °C (literature reported: 92−93 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (dd, J = 9.1, 4.6 Hz, 0.3H), 7.73−7.63 (m,0.7 H), 7.41−7.23 (m, 5.7H), 7.22−7.68 (m, 1H), 6.97 (dd, J = 7.9, 2.2 Hz, 0.3H), 5.83 (s, 1.4H), 5.79 (s, 0.6H). ^{13}C NMR (75 MHz, $CDCl_3$, C−F coupling not assigned) δ 163.6, 161.2, 160.4, 158.0, 146.6, 146.4, 143.1, 134.3, 134.2, 129.7, 129.0, 128.6, 127.5, 127.5, 121.5, 121.4, 117.5, 117.2, 114.1, 113.7, 110.8, 110.6, 104.6, 104.3, 95.6, 95.3, 52.5, 52.3.

*1-Benzyl-5(6)-(((tert-butyldimethylsilyl)oxy)methyl)-1H-benzo[d][1,2,3]triazole (**4g**).* Yellow wax, R_f = 0.2 (PE/EA = 10:1), 78% yield (55.1 mg), (unseparable mixture of 5-substituted and 6-substituted isomers with 1:1 ratio). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (s, 0.5H), 7.91 (d, J = 8.6 Hz, 0.5H), 7.34−7.10 (m, 7H), 5.76 (s, 2H), 4.78 (s, 1H), 4.76 (s, 1H), 0.88 (s, 4.5H), 0.86 (s, 4.5H), 0.05 (s, 3H), −0.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 145.7, 141.6, 137.8, 134.7, 133.0, 132.10, 128.9, 128.4, 127.6, 127.5, 126.3, 122.3, 119.5, 116.7, 109.4, 106.2, 64.6, 64.4, 52.2, 25.9, 25.9, 18.4, 18.3, −5.3, −5.4. IR ($CHCl_3$): 3371, 2926, 2372, 1595, 1458, 1220, 1115, 779 cm^{-1}. HRMS (ESI-Q-TOF): $C_{20}H_{28}N_3OSi$ $[M + H]^+$ calcd, 354.1996; found, 354.2007.

*(1-Benzyl-1H-benzo[d][1,2,3]triazol-5-yl)methanol (**5-Substituted 4g′**).*[21d] White solid, R_f = 0.4 (PE/EA = 1:1), 45% yield. mp 156−157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.45 (dd, J = 8.6, 1.2 Hz, 1H), 7.37−7.29 (m, 4H), 7.29−7.23 (m, 2H), 5.85 (s, 2H), 4.83 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 137.3, 134.6, 132.4, 129.0, 128.5, 127.5, 127.2, 117.8, 109.9, 65.0, 52.3. IR ($CHCl_3$): 3366, 2924, 1655, 1596, 1458, 1098, 1030, 714 cm^{-1}. HRMS (ESI-Q-TOF): $C_{14}H_{14}N_3O$ $[M + H]^+$ calcd, 240.1131; found, 240.1143.

*(1-Benzyl-1H-benzo[d][1,2,3]triazol-6-yl)methanol (**6-Substituted 4g′**).*[21d] White solid, R_f = 0.5 (PE/EA = 1:1), 45% yield. mp 119−120 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.6 Hz, 1H), 7.42 (s, 1H), 7.37−7.26 (m, 6H), 5.84 (s, 2H), 4.83 (d, J = 4.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 141.0, 134.7, 133.1, 129.0, 128.4, 127.5, 123.2, 120.0, 107.0, 64.8, 52.1. IR ($CHCl_3$): 3365, 2923, 2373, 1595, 1458, 1265, 1117, 716 cm^{-1}. HRMS (ESI-Q-TOF): $C_{14}H_{14}N_3O$ $[M + H]^+$ calcd, 240.1131; found, 240.1142.

*1-(2-Methylbenzyl)-1H-benzo[d][1,2,3]triazole (**5a**).*[21e] White solid, R_f = 0.3 (PE/EA = 10:1), 97% yield (43.2 mg). mp 77−78 °C (literature reported: 80−81 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99−7.91 (m, 1H), 7.31−7.01 (m, 6H), 6.95 (d, J = 7.5 Hz, 1H), 5.74 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 136.4, 132.9, 132.5, 130.8, 128.6, 128.4, 127.2, 126.3, 123.8, 119.9, 109.8, 50.7, 19.2.

*1-(3Methylbenzyl)-1H-benzo[d][1,2,3]triazole (**5b**).*[21e] White solid, R_f = 0.3 (PE/EA = 10:1), 99% yield (44.2 mg). mp 118−120 °C (literature reported: 119−121 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 1H), 7.43−7.27 (m, 3H), 7.24−7.15 (m, 1H), 7.08 (t, J = 8.2 Hz, 3H), 5.78 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 138.7, 134.6, 132.7, 129.1, 128.7, 128.2, 127.3, 124.6, 123.8, 119.9, 109.7, 52.1, 21.2.

*1-(4-Chlorobenzyl)-1H-benzo[d][1,2,3]triazole (**5c**).*[21e] White solid, R_f = 0.2 (PE/EA = 10:1), 86% yield (41.8 mg). mp 92−94 °C (literature reported: 87−89 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09−7.02 (m, 1H), 7.46−7.24 (m, 5H), 7.20 (d, J = 8.5 Hz, 2H), 5.80 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 134.3, 133.2, 132.5, 129.1, 128.8, 127.5, 124.0, 120.0, 109.4, 51.3.

*1-Phenyl-1H-benzo[d][1,2,3]triazole (**5d**).*[17d] Yellow solid, R_f = 0.4 (PE/EA = 10:1), 82% yield (32.0 mg). mp 90−92 °C (literature reported: 86−87 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.61 (t, J =

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7.7 Hz, 2H), 7.58−7.47 (m, 2H), 7.43 (t, J = 7.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 136.9, 132.2, 129.8, 128.6, 128.2, 124.3, 122.8, 120.2, 110.3.

*1-(o-Tolyl)-1H-benzo[d][1,2,3]triazole (**5e**).*[21f] White solid, R_f = 0.3 (PE/EA = 10:1), 90% yield (37.6 mg). mp 60−63 °C (literature reported: 66−67 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.2 Hz, 1H), 7.54−7.25 (m, 7H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 135.1, 135.1, 133.8, 131.6, 129.9, 127.9, 126.9, 126.8, 124.1, 119.9, 110.0, 17.7.

*1-(3-chlorophenyl)-1H-benzo[d][1,2,3]triazole (**5f**).* Pale gray solid, R_f = 0.3 (PE/EA = 10:1), 92% yield (42.0 mg). mp 108−110 °C (literature reported: 108−109 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 1.7 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.62−7.40 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 137.9, 135.5, 131.9, 130.8, 128.6, 124.6, 122.8, 120.6, 120.4, 110.1. IR ($CHCl_3$): 3381, 2924, 2371, 1594, 1126, 1062, 790, 740 cm^{-1}. HRMS (ESI-Q-TOF): $C_{12}H_9ClN_3$ $[M + H]^+$ calcd, 230.0480; found, 230.0490.

*1-(4-Chlorophenyl)-1H-benzo[d][1,2,3]triazole (**5g**).*[21g] White solid, R_f = 0.4 (PE/EA = 10:1), 91% yield (41.6 mg). mp 148−150 °C (literature reported: 151−152 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.3 Hz, 1H), 7.72 (t, J = 8.2 Hz, 3H), 7.56 (t, J = 8.3 Hz, 3H), 7.44 (t, J = 7.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 135.4, 134.3, 132.0, 130.0, 128.4, 124.5, 123.8, 120.3, 110.0.

*1-(4-Methoxyphenyl)-1H-benzo[d][1,2,3]triazole (**5h**).*[17c] Yellow solid, R_f = 0.2 (PE/EA = 10:1), 80% yield (36.2 mg). mp 100−101 °C (literature reported: 98−99 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.3 Hz, 1H), 7.69−7.60 (m, 3H), 7.52 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.14−7.06 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 146.2, 132.5, 129.8, 127.9, 124.4, 124.1, 120.0, 114.8, 110.2, 55.5.

*1-(3,5-Dimethylphenyl)-1H-benzo[d][1,2,3]triazole (**5i**).*[17d] Yellow solid, R_f = 0.4 (PE/EA = 15:1), 96% yield (42.8 mg). mp 58−60 °C (literature reported: 60−62 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.38 (s, 2H), 7.13 (s, 1H), 2.44 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3, 139.7, 136.7, 132.2, 130.3, 128.0, 124.2, 120.5, 120.1, 110.5, 21.3.

*1-Cinnamyl-1H-benzo[d][1,2,3]triazole (**5j**).*[17d] Yellow solid, R_f = 0.3 (PE/EA = 5:1), 94% yield (44.2 mg). mp 68−71 °C (literature reported: 72−73 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.48−7.40 (m, 1H), 7.40−7.19 (m, 6H), 6.66 (d, J = 15.9 Hz, 1H), 6.37 (dt, J = 15.8, 6.3 Hz, 1H), 5.42 (dd, J = 6.3, 1.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 135.4, 134.3, 132.8, 128.6, 128.3, 127.26, 126.5, 123.8, 122.1, 119.9, 109.7, 50.4.

*1,4-Dihydro-1,4-epoxynaphthalene (**6a**).*[8] White solid, R_f = 0.5 (PE/EA = 10:1), 82% yield (23.6 mg). mp 55−56 °C (literature reported: 53−54 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29−7.19 (m, 2H), 7.01 (s, 2H), 7.00−6.91 (m, 2H), 5.70 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 143.0, 124.9, 120.2, 82.2.

*1-Methoxy-1,4-dihydro-1,4-epoxynaphthalene (**6b**).* Clear crystal, R_f = 0.2 (PE/EA = 10:1), 60% yield (20.8 mg). mp 130−132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25−8.17 (m, 1H), 8.16−8.08 (m, 1H), 7.56−7.45 (m, 2H), 6.72 (d, J = 8.1 Hz, 1H), 6.62 (d, J = 8.2 Hz, 1H), 5.07 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 145.0, 126.3, 125.9, 125.8, 125.2, 122.0, 121.4, 107.9, 103.4, 55.8. IR ($CHCl_3$): 3277, 1598, 1268, 1090, 764 cm^{-1}. HRMS (ESI-Q-TOF): $C_{11}H_{11}O_2$ $[M + H]^+$ calcd, 175.0754; found, 175.0754.

*Ethyl 2-(2-Acetylphenyl)acetate (**7a**).*[8] White solid, R_f = 0.3 (PE/EA = 10:1), 80% yield (33.0 mg). mp 58−60 °C (literature reported: 57−59 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.6, 1.2 Hz, 1H), 7.46 (td, J = 7.4, 1.5 Hz, 1H), 7.39 (td, J = 7.5, 1.3 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.94 (s, 2H), 2.60 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 171.6, 137.2, 134.4, 132.6, 131.9, 129.9, 127.3, 60.7, 40.3, 28.8, 14.2.

*Ethyl 2-(2-Benzoylphenyl)acetate (**7b**).*[8] Yellow oil, R_f = 0.3 (PE/EA = 15:1), 56% yield (30.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85−7.78 (m, 2H), 7.62−7.53 (m, 1H), 7.52−7.28 (m, 6H), 4.02 (q, J = 7.1 Hz, 2H), 3.89 (s, 2H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 171.2, 138.2, 137.8, 134.0, 132.9, 131.7, 130.8, 130.4, 130.0, 128.3, 126.5, 60.8, 38.9, 14.0.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for the products, and single crystal data of **2h**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00923.

■ AUTHOR INFORMATION

Corresponding Authors

*(Z.X.) E-mail: zqxu@lzu.edu.cn
*(X.J.) E-mail: jiangxx5@mail.sysu.edu.cn
*(R.W.) E-mail: wangrui@lzu.edu.cn

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Roberts, J. D.; Simmons, H. E., Jr.; Carlsmith, L. A.; Vaughan, C. W. *J. Am. Chem. Soc.* **1953**, *75*, 3290−3291.

(2) (a) Goetz, A. E.; Garg, N. K. *J. Org. Chem.* **2014**, *79*, 846−851. (b) Wu, C.; Shi, F. *Asian J. Org. Chem.* **2013**, *2*, 116−125. (c) Dubrovskiy, A. V.; Markina, N. A.; Larock, R. C. *Org. Biomol. Chem.* **2013**, *11*, 191−218. (d) Yeoman, J. T. S.; Reisman, S. E. *Nature* **2012**, *490*, 179−180. (e) Bhunia, A.; Yetra, S. R.; Biju, A. T. *Chem. Soc. Rev.* **2012**, *41*, 3140−3152. (f) Bhojgude, S. S.; Biju, A. T. *Angew. Chem., Int. Ed.* **2012**, *51*, 1520−1522. (g) Yoshida, H.; Takaki, K. *Synlett* **2012**, *23*, 1725−1732. (h) Bronner, S. M.; Goetz, A. E.; Garg, N. K. *Synlett* **2011**, 2599−2604. (i) Wentrup, C. *Aust. J. Chem.* **2010**, *63*, 979−986. (j) Sanz, R. *Org. Prep. Proced. Int.* **2008**, *40*, 215−291. (k) Butenschön, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 4012−4014. (l) Peña, D.; Pérez, D.; Guitián, E. *Heterocycles* **2007**, *74*, 89−100. (m) Pellisier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701−730. (n) Sander, W. *Acc. Chem. Res.* **1999**, *32*, 669−676. (o) Kauffmann, T.; Wirthwein, R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 20−33. (p) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 543−557.

(3) (a) Goetz, A. E.; Shah, T. K.; Garg, N. K. *Chem. Commun.* **2015**, *51*, 34−45. (b) Gampe, C. M.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3766−3778. (c) Tadross, P. M.; Stoltz, B. M. *Chem. Rev.* **2012**, *112*, 3550−3577.

(4) (a) Kitamura, T. *Aust. J. Chem.* **2010**, *63*, 987−1001. (b) Kitamura, T.; Yamabe, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674−11679. (c) For a mechanistic study, see: Buxton, P. C.; Fensome, M.; Heaney, H.; Mason, K. G. *Tetrahedron* **1995**, *51*, 2959−2968. (d) Matsumoto, T.; Hosoya, T.; Katsuki, M.; Suzuki, K. *Tetrahedron Lett.* **1991**, *32*, 6735−6736. (e) Campbell, C. D.; Rees, C. W. *J. Chem. Soc.* **1969**, 742−747. (f) Friedman, L.; Logullo, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 1549−1549.

(5) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, *12*, 1211−1214.

(6) Choy, P. Y.; Chow, W. K.; So, C. M.; Lau, C. P.; Kwong, F. Y. *Chem.−Eur. J.* **2010**, *16*, 9982−9985.

(7) Ikawa, T.; Nishiyama, T.; Nosaki, T.; Takagi, A.; Akai, S. *Org. Lett.* **2011**, *13*, 1730−1733.

(8) Kovács, S.; Csincsi, Á. I.; Nagy, T. Z.; Boros, S.; Timári, G.; Novák, Z. *Org. Lett.* **2012**, *14*, 2022−2025.

(9) (a) Penney, C. L.; Perlin, A. S. *Carbohydr. Res.* **1981**, *93*, 241−246. (b) Firth, W. C. *J. Polym. Sci., Part B* **1972**, *10*, 637−641. (c) Parsons, J. S. *J. Gas Chromatogr.* **1967**, *5*, 254−256.

DOI: 10.1021/acs.joc.5b00923
J. Org. Chem. 2015, 80, 6890−6896

(10) (a) Drummond, J. N.; Kirby, A. J. *J. Chem. Soc. Perkin Trans. 2* **1986**, 579−583. (b) Zahler, W. D.; Huisgen, R. *Chem. Ber.* **1963**, *96*, 765−770. (c) Engelbrecht, A. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 641−645. (d) Traube, W. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2513−2524.
(11) Dong, J.; Krasnova, L.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2014**, *53*, 9430−9448.
(12) (a) Suter, C. M. In *The Organic Chemistry of Sulfur*; Wiley: New York, 1944; pp 453−572. (b) Lange, W. Reichspatent 532394, 27 Aug, 1931. (c) Lange, W.; Müller, E. *Chem. Ber.* **1930**, *63*, 2653−2657. (d) Steinkopf, W.; Jaeger, P. *J. Prakt. Chem.* **1930**, *128*, 63−88. (e) Steinkopf, W. *J. Prakt. Chem.* **1927**, *117*, 1−82.
(13) In **2**, -OSO2F could possibly interact with the *ortho*-TMS group and deliver fluorine to silicon as its thermodynamically favored destination, which would promote the desilylation of the precursor to generate aryne. (a) Huang, T.; Shreeve, J. M. *Inorg. Chem.* **1986**, *25*, 496−498. (b) Wlassics, I.; Tortelli, V.; Carella, S.; Monzani, C.; Marchionni, G. *Molecules* **2011**, *16*, 6512−6540.
(14) (a) Ishii, A.; Yasumoto, M. Central Glass Co., Ltd., PCT/JP2009/067841, US 20110201825 A1, 2011. (b) Ishii, A.; Ishimaru, T.; Yamazaki, T.; Yasumoto, M. Central Glass Co., Ltd., WO-2013-002040, 2013. (c) The structure of **2h** was determined by single-crystal X-ray analysis: CCDC 1053309. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
(15) (a) Andersen, S. P. S.; Blake, D. R.; Rowland, F. S.; Hurley, M. D.; Wallington, T. J. *Environ. Sci. Technol.* **2009**, *43*, 1067−1070. (b) Sulfuryl fluoride has low toxicity and has been successfully used for controlling structure infesting pests for nearly 50 years under the trade name Vikane gas fumigant. In china, SO_2F_2 is about $1/kg (CAS: 2699-79-8, MAUI (Hangzhou) Electronic Chemicals Co., Ltd.), which is relatively cheaper than traditional sulfates (trifluoromethanesulfonic anhydride, CAS: 358-23-6, $827/250g, from Alfa Aesar).
(16) Liang, Q.; Xing, P.; Huang, Z.; Dong, J.; Sharpless, K. B.; Li, X.; Jiang, B. *Org. Lett.* **2015**, *17*, 1942−1945.
(17) For selected examples: (a) Gann, A. W.; Amoroso, J. W.; Einck, V. J.; Rice, W. P.; Chambers, J. J.; Schnarr, N. A. *Org. Lett.* **2014**, *16*, 2003−2005. (b) Ikawa, T.; Takagi, A.; Goto, M.; Aoyama, Y.; Ishikawa, Y.; Itoh, Y.; Fujii, S.; Tokiwa, H.; Akai, S. *J. Org. Chem.* **2013**, *78*, 2965−2983. (c) Zhang, F.; Moses, J. E. *Org. Lett.* **2009**, *11*, 1587−1590. (d) Shi, F.; Waldo, J. P.; Chen, Y.; Larock, R. C. *Org. Lett.* **2008**, *10*, 2409−2412. (e) Reynolds, G. A. *J. Org. Chem.* **1964**, *29*, 3733−3734.
(18) Tambar, U. K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 5340−5341.
(19) (a) For an example of the activation of CsF with 18-c-6 and MeCN, see: Nishikawa, T.; Shibuya, S.; Isobe, M. *Synlett* **1994**, 482−484. (b) For the complexation of CsF with 18-c-6, see: Takeda, Y.; Kawarabayashi, A.; Endo, K.; Yahata, T.; Kudo, Y.; Katsuta, S. *Anal. Sci.* **1998**, *14*, 215−223.
(20) The regioselectivities were determined by ^{1}H NMR spectra of the crude reaction mixtures. For selected studies and reviews regarding the aryne distortion model, see: (a) Medina, J. M.; Mackey, J. L.; Garg, N. K.; Houk, K. N. *J. Am. Chem. Soc.* **2014**, *136*, 15798−15805. (b) Cheong, P. H.-Y.; Paton, R. S.; Bronner, S. M.; Im, G-Y. J.; Garg, N. K.; Houk, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 1267−1269. (c) Im, G.-Y. J.; Bronner, S. M.; Goetz, A. E.; Paton, R. S.; Cheong, P. H.-Y.; Houk, K. N.; Garg, N. K. *J. Am. Chem. Soc.* **2010**, *132*, 17933−17944.
(21) (a) Novák, Z.; Timári, G.; Kotschy, A. *Tetrahedron* **2003**, *59*, 7509−7513. (b) Nishide, K.; Miyamoto, T.; Kumar, K.; Ohsugi, S.; Node, M. *Tetrahedron Lett.* **2002**, *43*, 8569−8573. (c) Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 9760−9764. (d) Bentin, T.; Hamzavi, R.; Salomonsson, J.; Roy, H.; Ibba, M.; Nielsen, P. E. *J. Biol. Chem.* **2004**, *279*, 19839−19845. (e) Xue, Q.; Xie, J.; Li, H.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2013**, *49*, 3700−3702. (f) Liu, Q.-L.; Wen, D.-D.; Hang, C.-C.; Li, Q.-L.; Zhu, Y.-M. *Helv. Chim. Acta* **2010**, *93*, 1350−1354. (g) Zhou, J.; He, J.; Wang, B.; Yang, W.; Ren, H. *J. Am. Chem. Soc.* **2011**, *133*, 6868−6870.

DOI: 10.1021/acs.joc.5b00923
J. Org. Chem. 2015, 80, 6890−6896