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PII: S0040-4020(19)30774-4

DOI: https://doi.org/10.1016/j.tet.2019.07.020

Reference: TET 30462

To appear in: *Tetrahedron*

Received Date: 17 May 2019

Revised Date: 8 July 2019

Accepted Date: 12 July 2019

Please cite this article as: Liu Y, Wang H, Yang X, Copper-catalyzed imination of sulfoxides and sulfides, *Tetrahedron* (2019), doi: https://doi.org/10.1016/j.tet.2019.07.020.

Graphical Abstract

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Copper-catalyzed imination of sulfoxides and sulfides

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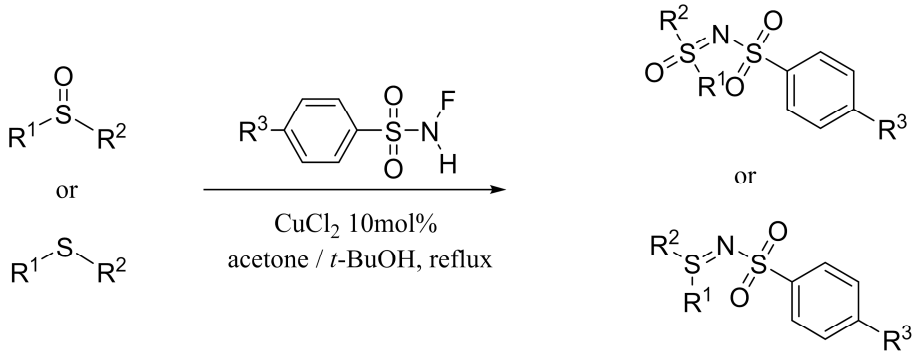

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Copper-Catalyzed
Sulfimidation
N-fluoro benzenesulfonamide
Imination
Metal-nitrene

ABSTRACT

Sulfoximines and sulfilimines have attracted considerable interest among organic chemists. The Cu(II)-catalyzed imination of sulfoxides and sulfides using various *N*-fluoro benzenesulfonamides was investigated in this study. The scope of the reaction was demonstrated by using several substituted sulfides and sulfoxides. The flow strategy for the preparation of *NH*-sulfoximines was also examined. By trapping nitrene intermediates through triphenylphosphine, we found that the reaction was conducted through a metal-nitrene intermediate mechanism.

1. Introduction

Since the discovery of sulfonimidoyl in 1949, due to their potential use in numerous applications, sulfoximines and sulfilimines have attracted considerable attention among organic chemists.[1] As a result of their wide use as building blocks for chiral ligands[2] and structural units in pseudopeptides[3], a number of synthetic approaches have been developed for their efficient preparation.

As the important moiety of the sulfoximines and sulfilimines, *N*-sulfonyl-sulfilimines have been well studied in recent years.[4] One of their key features is the variety of substitutions available to the sulfur-attached imino group. In early years, *N*-sulfonyl-sulfilimines were prepared either by treating the corresponding sulfides with chloramine-T[5] or by reaction of sulfoxides with sulfonamide[6] or sulfonylisocyanate.[7] Subsequently, other synthetic methods were developed, but most of them involved the use of toxic and potentially explosive reagents, such as hydrazoic acid (NaN_3/H_2SO_4)[8] or *O*-(mesitylenesulfonyl)hydroxylamine (MSH).[9] More recently, to avoid such reagents, metal-catalyzed methods have been described using copper or iron salts[10], manganese or ruthenium complexes[11] as catalysts. *N*-fluoro benzenesulfonamides were also shown to perform well in such reactions.[12] Here, we present the use of simple copper catalysts for the imination of sulfoxides and sulfides with *N*-fluoro benzenesulfonamides under mild conditions.

2. Results and discussion

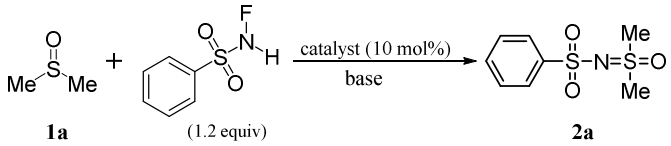
First, as a model reaction, the imination of dimethylsulfoxide **1a** with *N*-fluoro benzenesulfonamide **2a** in the presence of copper salts was investigated, and representative results are shown in Table 1. A solvent screening revealed that acetone was the most suitable solvent. Other evaluated solvents, such as DCE and *t*-BuOH, produced worse results (Table 1, entries 1-10). Next, we investigated the effects of copper salts on imination reactions. As shown in entry 11, the model imination reaction cannot occur at 70□ without copper salts. To further establish the need for copper salts in imination reactions, methyl phenyl sulfide and methyl phenyl sulfoxide were then reacted with *N*-fluoro benzenesulfonamide in the absence of copper salts (Supporting Information). No obvious product was detected when sulfoxides served as reactants, while for methyl phenyl sulfide, small amounts of products were found when the reaction time was prolonged to 20 hour. However, the yield of isolated products was only 23%. The above studies demonstrated that copper salts played a significant role in our imination reactions.

Next, we studied the effect of different kinds of copper salts on this reaction. Reactions with various Cu(I) or Cu(II) salts including CuCl, CuI, Cu_2O, $CuCl_2$, $Cu(OAc)_2$, $CuSO_4$, $CuBr_2$ and $Cu(NO_3)_2$ were then examined. Among them, $CuCl_2$ afforded the highest yield (Table 1, entries 12-17). These results indicated that both monovalent copper salts and bivalent copper salts can catalyze the reaction. The results of temperature screening revealed that imination reaction did not proceed at room temperature and 70□ was the optimal reaction temperature (Table 1, entries 18-19).

We also found that HF was produced as the reaction proceeded. Therefore, we added various bases to neutralize the HF produced in the reactions, expecting to obtain higher reaction yields. However, the results in entries 20-25 indicated that the addition of organic or inorganic bases resulted in lower reaction

yields. We surmised that *N*-fluoro benzenesulfonamides and nitrene intermediates were not able to stably exist in basic conditions, resulting in lower products yields. In summary, the optimized conditions for our imination reactions are as follows: sulfoxide **1a** (1 equiv.), $CuCl_2$ (10 mol %), $PhSO_2$-*N*(F)H (1.2 equiv.) in acetone at 70 □.

Table 1. Optimization of the Reaction Conditions.[a]



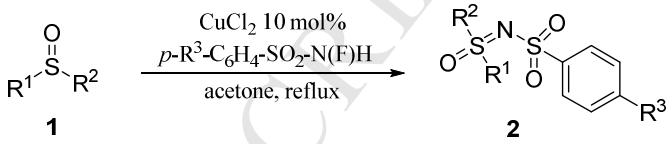
Entry	Catalyst	Base	Solvent	T (□)	Yield[b] (%)
1	Cu_2O	-	*t*-BuOH	70	44.7
2	Cu_2O	-	DCE	70	55.2
3	Cu_2O	-	acetonitrile	70	5.4
4	Cu_2O	-	alcohol	70	25.5
5	Cu_2O	-	acetone	70	66.3
6	Cu_2O	-	methanol	70	42.4
7	Cu_2O	-	toluene	70	21.5
8	Cu_2O	-	1,4-dioxane	70	<5
9	Cu_2O	-	THF	70	38.4
10	Cu_2O	-	EA	70	42.9
11	-	-	acetone	70	0
12	CuCl	-	acetone	70	61.3
13	$CuCl_2$	-	acetone	70	66.5
14	$Cu(OAc)_2$	-	acetone	70	58.6
15	$CuSO_4$	-	acetone	70	<5
16	$CuBr_2$	-	acetone	70	56.4
17	$Cu(NO_3)_2$	-	acetone	70	61.3
18	$CuCl_2$	-	acetone	rt	trace
19	$CuCl_2$	-	acetone	50	45.2
20	$CuCl_2$	DABCO	acetone	70	nr
21	$CuCl_2$	DMAP	acetone	70	24.7
22	$CuCl_2$	Pyridine	acetone	70	65.4
23	$CuCl_2$	DBU	acetone	70	16.0
24	$CuCl_2$	CH_3ONa	acetone	70	28.7
25	$CuCl_2$	K_2CO_3	acetone	70	31.0

[a] Reaction conditions: sulfoxide **1a** (1 equiv.), Cu catalyst (10 mol %), Base (1.2eq), $PhSO_2$-N(F)H (1.2 equiv.) in solvent. The reaction time is 12 hours.

[b] Yield after column chromatography.

With the optimized reaction conditions in hand, the scope of this reaction was evaluated. A variety of sulfoxides and *N*-fluoro benzenesulfonamide were subjected to the sulfimidation reaction in the presence of 10 mol % of $CuCl_2$ in acetone at 70 □ and the results are summarized in Table 2. Sulfoxides in entries 1-4 were readily converted to the corresponding sulfoximines, but the yield of **2c** was slightly lower. For sulfoxides bearing carbonyl group and cyano group, the reaction at 70 □ resulted in significant side reactions. Therefore, we carried out the reaction at 60 □ (Table 2, entries 5-6). However, sulfoxides bearing cyano group did not give the expected products, indicating that the electron-withdrawing groups on sulfoxides greatly affect the reaction. Besides, *N*-fluoro benzenesulfonamides bearing electron-withdrawing groups were found to be more reactive than those bearing electron-donating groups in the sulfimidation reaction (Table 2, entries 7-11). From this perspective, the electronic effect of substituents on *N*-fluoro benzenesulfonamides was one of the key factors in the results of imination reaction. We surmised that *N*-fluoro benzenesulfonamides with electron-withdrawing groups helped to the formation of nitrene intermediates, thereby promoting the imination reactions.

Table 2. Copper-catalyzed Imination of Sulfoxides.[a]



Entry	R^1	R^2	R^3	Product	Yield[c] (%)
1	Me	Me	H	**2a**	67
2	Ph	Ph	H	**2b**	62
3	Bn	Bn	H	**2c**	34
4	Me	Ph	H	**2d**	67
5[b]	Me	*p*-$CH_3C(O)C_6H_4$-	H	**2e**	32
6[b]	$CNCH_2$-	*p*-ClC_6H_4-	H	**2f**	nr
7	Me	Ph	Me	**2g**	45
8	Me	Ph	F	**2h**	70
9	Me	Ph	Cl	**2i**	72
10	Me	Ph	NO_2	**2j**	69
11	Ph	Ph	Me	**2k**	57

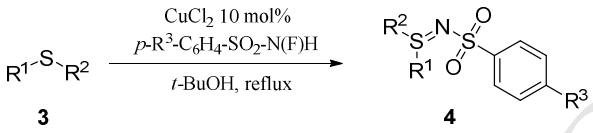
[a] Reaction conditions: sulfoxide **1** (1 mmol, 1 equiv.), $CuCl_2$ catalyst (10 mol %), *p*-R^3-C_6H_4-SO_2-N(F)H (1.2 equiv.) in acetone at 70 □. The reaction time is 12 hours. [b] Reaction in acetone at 60 □ for 12 hours.

[c] Yield after column chromatography.

Next, the reactions of sulfides catalyzed by $CuCl_2$ were evaluated (Table 3). Under similar reaction conditions, sulfides were more reactive than sulfoxides, and all the reactions listed in Table 3 were completed within 6 h. The data presented in Table 3, entries 1-4, reveal that aromatic sulfides gave higher yields than aliphatic sulfides. To expand the application of our reaction, sulfides with carbonyl, ester, amide, cyano and hydroxyl groups were further used as reactants. These sulfides only produced sulfilimines in moderate yields, revealing that substitutes on sulfides markedly influenced the reaction results. (Table 3, entries 5-9). As shown in Table 3 entries 10-13, *N*-fluoro benzenesulfonamides with electron-donating substitutes had a slightly higher yield than those bearing electron-withdrawing groups in imination reaction.

Table 3. Copper-catalyzed Imination of Sulfides.[a]

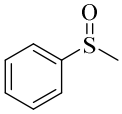
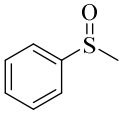
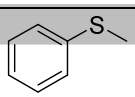
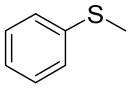
Entry	R^1	R^2	R^3	Product	Yield[d] (%)
1	Me	Me	H	**4a**	37
2	Ph	Ph	H	**4b**	65
3	Me	Ph	H	**4c**	79
4	*t*-Bu	Me	H	**4d**	63
5[b]	*p*-$CH_3C(O)C_6H_4$-	Me	H	**4e**	59
6[b]	*o*-$CH_3O(CO)C_6H_4$-	Me	H	**4f**	44
7[c]	*m*-$CH_3(CO)NHC_6H_4$-	Me	H	**4g**	38
8[b]	*p*-ClC_6H_4-	$CNCH_2$-	H	**4h**	33
9[c]	*p*-OH-C_6H_4-	Me	H	**4i**	22
10	Me	Ph	Me	**4j**	92
11	Me	Ph	F	**4k**	89
12	Me	Ph	Cl	**4l**	93
13	Me	Ph	NO_2	**4m**	81



[a] Reaction conditions: sulfide **3** (1 mmol, 1 equiv.), $CuCl_2$ catalyst (10 mol %), *p*-R^3-C_6H_4-SO_2-N(F)H (1.2 equiv.) in tert-butyl alcohol at 100 □. The reaction time is 6 hours [b]Reaction in acetone at 60□ for 6 hours. [c] Reaction in acetone at room temperature for 6 hours.
[d] Yield after column chromatography.

To highlight the advantages of our experiments, the contrast experiments were carried out using chloramine B and chloramine T as the nitrogen sources. As shown in Table 4, under the optimized conditions, the obtained reaction yield with *N*-fluoro benzenesulfonamide was higher than that with chloramine B or chloramine T. Although, *N*-fluoro benzenesulfonamide is not commercially available yet, the much increased reaction yield demonstrated the superiority and indicate the importance of our study.

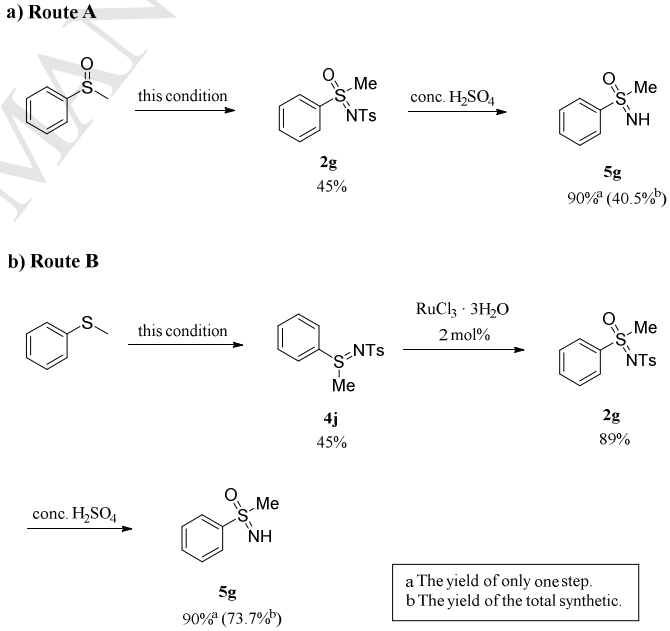
Table 4. Contrast experiment.[a]

Nitrogen Source	Sulfur Source	Yield [b] (%)
chloramine T		16.2%
chloramine B		13.6%
chloramine T		26.6%
chloramine B		15.8%

[a] Reaction conditions: sulfur source (1 equiv.), Cu catalyst (10 mol %), nitrogen source (1.2 equiv.) in DCE at 70□. The reaction time is 12 hours.
[b] Yield after column chromatography.

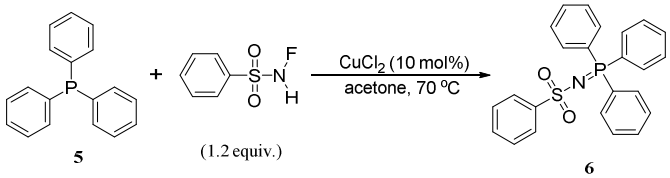
For synthetic purposes, the reactions of sulfoxides and *N*-fluoro-4-methylbenzenesulfonamide are highly valuable as the *p*-toluenesulfonyl (TS) on their products can be easily removed to give useful *NH*-sulfoximines, which are of interest in various research fields, including synthetic organic chemistry,[13] crop protection,[14] and medicinal chemistry.[15] Considering that the yield of sulfoxide in the imination reaction is much lower than that of a thioether, the following synthetic routes were designed (Scheme 1). According to the literature,[16] we used $NaIO_4$ and a catalytic amount of $RuCl_3$ for the oxidation of sulfimide **4j** to produce **2g** with a yield of 89%. After that, the *p*-toluene sulfonyl group was removed from the product with concentrated sulfuric acid. As shown in Scheme 1, the yield of the complete synthesis was much higher when the start material was a thioether than when it was a sulfoxide.

Scheme 1. Synthetic routes of *NH*-sulfoximines.



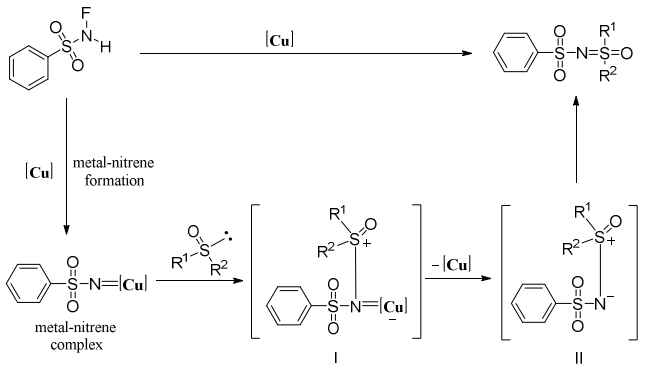
To confirm the formation of the nitrene intermediates, benzene was used to trap nitrene intermediates. However, the expected products were not found. Then, we treated *N*-fluoro benzenesulfonamide with triphenylphosphine under the imination reaction conditions.[17] After 1 hour at 70 □, **6** was obtained with a yield of 53 % (Scheme 2).

Scheme 2. Reaction of phosphorous compounds with *N*-fluoro benzenesulfonamide.



According to the previously reported literature and our experimental results, a plausible mechanism for this Cu catalyzed imination reaction is outlined in Scheme 3. First, *N*-fluoro benzenesulfonamide forms metal-nitrene complex in the presence of Cu(II) catalyst. Then, it couples with sulfoxide, forming the metal-sulfur ylide intermediate I. Eventually, the intermediate I dissociates from the metals to obtain free sulfur ylide intermediate II and is then further converted into sulfoximine.

Scheme 3. Plausible reaction mechanism.



3. Conclusions

In summary, various sulfoxides and sulfides have been converted into their corresponding sulfoximines and sulfilimines, respectively, using $CuCl_2$ as catalyst. The deprotection of the *N*-tosyl products under standard reaction conditions gives synthetically valuable ("free") *NH*-sulfoximines.

4. Experimental Section

General considerations: Unless otherwise noted, all commercially available compounds were purchased without further purification. Flash column chromatography was carried out on silica gel (300-400 mesh). Thin layer chromatography (TLC) was performed using silica gel HSGF 254 plates and visualized by UV light (254nm). NMR spectra were recorded on a Brucker AM-400 (400 MHz for ^{1}H; 100MHz for ^{13}C) spectrometer. IR spectra were recorded on a Bruker TENSOR 27 FTIR Spectrometer equipped with a Platinum ATR detector. LRMS and HRMS Mass Spectra were recorded on a Waters GCT Premier mass spectrometer with electron impact (70eV). Chemical shifts are given in parts per million (ppm) using residual solvent signals as internal standard ($CHCl_3$, δ = 7.26 ppm ^{1}H NMR, δ = 77.16 ppm for ^{13}C NMR). HRMS (EI) Mass Spectra were recorded on a Waters GCT Premier ms spectrometer with electron impact.

General procedure for the imination of sulfoxides (given in Table 2): To a suspension of the sulfoxide (1.0 mmol) and *N*-fluoro benzenesulfonamide (1.2 mmol) in acetone (5 mL) was added $CuCl_2$ (13 mg, 10 mol%) at room temperature. The resulting mixture was stirred for the period of 6-12 h at 70 □ and was monitored by TLC (Thin Layer Chromatography). Then the mixture was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate, 2:1) to afford the sulfoximines **2a-2k**.

General procedure for the imination of sulfides (given in Table 3): To a suspension of the sulfide (1.0 mmol), *N*-fluoro benzenesulfonamide (1.2 mmol) in *t*-BuOH (5 mL) was added $CuCl_2$ (13 mg, 10 mol%) at room temperature, and the mixture was stirred for 6 h at 110 □. The resulting suspension was purified by column chromatography (eluent: petroleum ether/ethyl acetate, 4:1) to give the corresponding sulfilimines **4a-4m**.

General procedure for the preparation of *N*-unsubstituted sulfoximines (given in Scheme 1): A modified procedure by Cram et al. was used. To a reaction tube charged with 4-methyl-*N*-(methyl (oxo)(phenyl)-λ^6-sulfanylidene)benzenesulfonamide **2g** (0.5 mmol, 154.52 mg) was added concentrated sulfuric acid (96%, 36 mmol, 2 mL). The mixture was stirred at room temperature for two hours. The mixture was cooled down to 0 □ and cold water (15 mL) was added carefully to quench the reaction. Then NaOH (72 mmol, 2.8 g) in water (10 mL) was added dropwise upon cooling. When the mixture became nearly neutral, Na_2CO_3 was added to adjust the pH to 9. The mixture was extracted with CH_2Cl_2 (4 ×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. Further purification by column chromatography on silica gel with ethyl acetate as eluent gave the pure *NH*-sulfoximine **5g** as a colorless oil (69.76 mg, 85% yield).

Oxidation of sulfimides to sulfoximines with $NaIO_4$/$RuCl_3$: To a reaction tube were added the sulfimide **4j** (1.0 equiv, 0.3 mmol, 87.92 mg) and $RuCl_3.3H_2O$ (2 mol%, 0.006 mmol, 1.6 mg). Then, acetonitrile (5 mL) and carbon tetrachloride (5 mL) were added successively followed by a solution of $NaIO_4$ (1.5 equiv, 0.45 mmol, 96.24 mg) in water (10 mL) while stirring. The mixture was stirred at room temperature. As indicated by TLC, the reaction finished within 1 hour. The mixture was extracted with CH_2Cl_2 (3 ×10 mL). The combined organic layers were washed with a saturated aqueous solution of $Na_2S_2O_3$ (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated to give the sulfoximine **2g** as a colorless oil (82.51 mg, 89% yield).

General procedure for the preparation of *N*-(triphenyl-5-phosphanylidene)benzenesulfonamide (given in Scheme 2): To a suspension of the pph_3 (1.0 mmol) and N-fluoro benzenesulfonamide (1.2 mmol) in acetone (5 mL) was added $CuCl_2$ (13 mg, 10 mol%) at room temperature. The resulting mixture was stirred for the period of 1 h at 70 °C and was monitored by TLC (Thin Layer Chromatography). Then the mixture was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate, 2:1) to afford the N-(triphenyl-5-phosphanylidene)benzenesulfonamide **6** as a white solid (221.16mg, 53% yield).

***N*-(Dimethyl(oxo)-λ^6-sulfanylidene)benzenesulfonamide (2a)**: White solid in 67% yield; m.p.: 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99-7.93 (m, 2H), 7.56-7.45 (m, 3H), 3.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3, 132.4, 128.8, 126.6, 44.2; IR (KBr, cm^{-1}): 3031.3, 2939.5, 1448.5, 1281.8, 779.7; HRMS (EI-TOF) m/z: M^+ Calcd for $C_8H_{11}NO_3S_2$ 233.0180; Found 233.0182.

***N*-(Diphenyl-λ^4-sulfanylidene)benzenesulfonamide (2b)**: White solid in 62% yield; m.p.: 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90-7.80 (m, 2H), 7.65-7.55 (m, 4H), 7.53-7.29 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 136.4, 132.5, 131.3, 130.0, 128.7, 127.3, 126.3. IR (KBr, cm^{-1}): 2919.6, 1445.9, 1241.6, 787.6, 583.2; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{18}H_{15}NO_3S_2$ 357.0493; Found 357.0494.

***N*-(Dimethyl(oxo)-λ^6-sulfanylidene)benzenesulfonamide (2c)**: White solid in 34% yield; m.p.: 181.3-181.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78-7.73 (m, 2H), 7.46-7.37 (m, 11H), 7.36-7.30 (m, 2H), 4.55 (d, *J* = 2.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.8, 132.0, 131.7, 129.9, 129.2, 128.6, 126.4, 125.9, 59.3. IR (KBr, cm^{-1}): 3261.2, 2931.3, 1444.3, 1222.0, 705.6, 507.1; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{20}H_{19}NO_3S_2$ 385.0806; Found 385.0803.

***N*-(Methyl(oxo)(phenyl)-λ^6-sulfanylidene)benzenesulfonamide (2d)**: White solid in 67% yield; m.p.: 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-7.92 (m, 4H), 7.74-7.68 (m, 1H), 7.63-7.56 (m, 2H), 7.54-7.50 (m, 1H), 7.48-7.43 (m, 2H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 138.4, 134.6, 132.4, 129.9, 128.8, 127.6, 126.7, 46.8. IR (KBr, cm^{-1}): 3025.8, 2929.2, 1449.4, 1239.1, 745.0, 509.2; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{13}H_{13}NO_3S_2$ 295.0337; Found 295.0338.

***N*-((4-acetylphenyl)(methyl)(oxo)- λ^6 -sulfanylidene) benzenesulfonamide (2e)**: White solid in 32% yield; m.p.: 138.5-139.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 2.0 Hz, 4H), 7.95 (dt, *J* = 7.3, 1.4 Hz, 2H), 7.57-7.50 (m, 1H), 7.46 (dd, *J* = 8.3, 6.6 Hz, 2H), 3.42 (s, 3H), 2.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.5, 143.2, 142.3, 141.5, 132.5, 129.5, 128.9, 128.1, 126.7, 46.5, 27.1; IR (KBr, cm^{-1}): 2996.0, 2915.9, 1685.8, 1397.7, 1232.4, 731.4, 609.7; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{15}H_{15}NO_4S_2$ 337.0442; Found 337.0446.

4-Methyl-*N*-(methyl(oxo)(phenyl)-λ^6-sulfanylidene)benzenesulfonamide (2g): White solid in 45% yield; m.p.: 102°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03-7.98 (m, 2H), 7.88-7.81 (m, 2H), 7.73-7.66 (m, 1H), 7.62-7.57 (m, 2H), 7.27-7.23 (m, 2H), 3.42 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 140.7, 138.5, 134.5, 129.8, 129.4, 127.6, 126.8, 46.8, 21.6.

Fluoro-*N*-(methyl(oxo)(phenyl)-λ^6-sulfanylidene)benzenesulfonamide (2h): White solid in 70% yield; m.p.: 123.4-125.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03-7.95 (m, 4H), 7.75-7.67 (m, 1H), 7.65-7.58 (m, 2H), 7.16-7.08 (m, 2H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9 (d, *J* = 253.6 Hz), 139.7 (d, *J* = 3.2 Hz), 138.3, 134.7, 129.9, 129.5 (d, *J* = 9.3 Hz), 127.6, 115.9 (d, *J* = 22.6 Hz), 46.8; ^{19}F NMR (376 MHz, CDCl3) δ: -106.32 (s, 1F). IR (KBr, cm^{-1}): 3070.3, 3958.1, 1704.3, 1156.6, 1022.9, 688.2; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{13}H_{12}FNO_3S_2$ 313.0243; Found 313.0246.

4-Chloro-*N*-(methyl(oxo)(phenyl)-λ^6-sulfanylidene)benzenesulfonamide (2i): White solid in 72% yield; m.p.: 113.8-115.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03-7.98 (m, 2H), 7.93-7.87 (m, 2H), 7.75-7.68 (m, 1H), 7.65-7.57 (m, 2H), 7.46-7.40 (m, 2H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1, 138.7, 138.2, 134.7, 130.0, 129.1, 128.3, 127.6, 46.9. IR (KBr, cm^{-1}): 3021.0, 2918.8, 1582.4, 1320.3, 1054.0, 766.4, 531.6; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{13}H_{12}ClNO_3S_2$ 328.9947; Found 328.9946.

***N*-(Methyl(oxo)(phenyl)-λ^6-sulfanylidene)-4-nitrobenzenesulfonamide (2j):** White solid in 69% yield; m.p.: 148-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34-8.29 (m, 2H), 8.19-8.13 (m, 2H), 8.03-8.01 (m, 2H), 7.78-7.73 (m, 1H), 7.68-7.63 (m, 2H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 149.1, 138.0, 135.0, 130.1, 128.2, 127.5, 124.2, 47.1.

4-Methyl-*N*-(oxodiphenyl-λ^6-sulfanylidene)benzenesulfonamide (2k): White solid in 57% yield; m.p.: 142.5-143.0 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-7.98 (m, 4H), 7.86-7.82 (m, 2H), 7.61-7.55 (m, 2H), 7.53-7.45 (m, 4H), 7.24-7.20 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 141.0, 139.9, 133.9, 129.7, 129.3, 127.9, 126.8, 21.6.

***N*-(Dimethyl-λ^4-sulfanylidene)benzenesulfonamide (4a)**: White solid in 37% yield; m.p.: 129-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88-7.80 (m, 2H), 7.49-7.38 (m, 3H), 2.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 131.5, 128.8, 126.2, 35.9.

***N*-(Diphenyl-λ^4-sulfanylidene)benzenesulfonamide (4b)**: White solid in 65% yield; m.p.: 126-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90-7.80 (m, 2H), 7.65-7.55 (m, 4H), 7.53-7.29 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 136.4, 132.5, 131.3, 130.0, 128.7, 127.3, 126.3.

***N*-(Methyl(phenyl)-λ^4-sulfanylidene)benzenesulfonamide (4c)**: White solid in 79% yield; m.p.: 107-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.77 (m, 2H), 7.66-7.62 (m, 2H), 7.51-7.41 (m, 3H), 7.39-7.30 (m, 3H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.0, 135.7, 132.5, 131.3, 130.0, 128.7, 126.1, 125.8, 39.0; IR (KBr, cm^{-1}): 3012.6, 2919.2, 1445.5, 1283.1, 754.8; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{13}H_{13}NO_2S_2$ 279.0388; Found 279.0389.

***N*-(Tert-butyl(methyl)-λ^4-sulfanylidene)benzenesulfonamide (4d)**: White solid in 63% yield; m.p.: 55.6-55.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92-7.87 (m, 2H), 7.56-7.45 (m, 3H), 1.22 (s, 9H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 132.3, 129.0, 127.1, 54.8, 30.3, 1.2. IR (KBr, cm^{-1}): 3290.4, 2980.1, 1315.1, 1148.4, 603.4; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{11}H_{17}NO_2S_2$ 259.0701; Found 259.0702.

***N*-((4-acetylphenyl)(methyl)-λ^4-sulfanylidene) benzenesulfonamide (4e)**: White solid in 59% yield; m.p.: 107.4-107.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.01-7.97 (m, 2H), 7.83-7.79 (m, 2H), 7.79 -7.75 (m, 2H), 7.43-7.38 (m, 1H), 7.38-7.33 (m, 2H), 2.86 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.7, 143.8, 140.6, 140.0, 131.6, 129.6, 128.8, 126.1 (d, *J* = 5.9 Hz), 38.9, 26.9; IR (KBr, cm^{-1}): 3002.8, 2919.9, 1689.5, 1362.8, 1285.0, 962.7, 830.2, 760.0; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{15}H_{15}NO_3S_2$ 321.0493; Found 321.0496.

Methyl-2-(S-methyl-*N*-(phenylsulfonyl)sulfinimidoyl)benzoate (4f): White solid in 44% yield; m.p.: 148.8-150.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.09 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.90-7.85 (m, 2H), 7.76 (td, *J* = 7.8, 1.4 Hz, 1H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1H), 7.44-7.36 (m, 3H), 3.96 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.9, 144.4, 140.1, 134.7, 131.8, 131.3 (d, *J* = 3.6 Hz), 128.8, 127.4, 126.6, 126.3, 53.3, 40.1; IR (KBr, cm^{-1}): 3037.5, 2955.0, 2360.4, 1711.4, 1284.3, 1140.0, 950.0, 755.7; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{15}H_{15}NO_4S_2$ 337.0442; Found 337.0445.

***N*-(3-(S-methyl-*N*-(phenylsulfonyl)sulfinimidoyl)phenyl)acetamide(4g)**: Colorless oil in 38% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (s, 1H), 8.02 (t, *J* = 1.6 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.74 (d, *J* = 2.7 Hz, 1H), 7.47-7.39 (m, 3H), 7.33-7.30 (m, 2H), 2.81 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.9, 143.6, 140.4, 136.0, 131.8, 130.5, 129.0, 126.3, 123.8, 120.5, 116.6, 77.2, 38.3, 29.8; IR (KBr, cm^{-1}): 3318.7, 3065.8, 2924.9 , 1689.8, 1592.2, 1278.5, 1141.5, 950.0, 751.9; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{15}H_{16}N_2O_3S_2$ 336.0602; Found 336.0601.

***N*-((4-chlorophenyl)(cyanomethyl)-λ^4-sulfanylidene)benzenesulfonamide (4h)**: White solid in 33% yield; m.p.: 113.9-115.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 -7.84 (m, 2H), 7.83-7.78 (m, 2H), 7.58-7.53 (m, 2H), 7.52-7.47 (m, 1H), 7.44 (dd, *J* = 8.3, 6.5 Hz, 2H), 4.08 (d, *J* = 2.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.0, 141.1, 132.3, 130.9, 129.8, 129.1, 128.3, 126.3, 110.0, 77.2, 43.0; IR (KBr, cm^{-1}): 3058.0, 2922.1, 2253.0, 1471.8, 1302.1, 1152.9, 820.2, 747.8; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{14}H_{11}ClN_2O_2S_2$ 337.995; Found 337.997.

***N*-((4-hydroxyphenyl)(methyl)-λ^4-sulfanylidene) benzenesulfonamide (4i)**: White solid in 22% yield; m.p.: 146.6-148.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.86 (m, 2H), 7.52-7.41 (m, 5H), 6.91 (d, *J* = 8.4 Hz, 2H), 2.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.5, 143.6, 131.8, 129.0, 128.4, 126.3, 124.8, 117.6, 38.2; IR (KBr, cm^{-1}): 3288.7, 2925.1, 1580.2, 1287.6, 1146.9, 841.5, 590.0; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{13}H_{13}NO_3S_2$ 295.0337; Found 295.0340.

4-Methyl-*N*-(methyl(phenyl)-λ^4-sulfanylidene)benzenesulfonamide (4j): White solid in 92% yield; m.p.: 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76-7.62 (m, 4H), 7.54-7.41 (m, 3H), 7.16-7.10 (m, 2H), 2.82 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.8, 141.2, 136.0, 132.5, 130.0, 129.3, 126.3, 125.9, 39.1, 21.5.

4-Fluoro-*N*-(methyl(phenyl)-λ^4-sulfanylidene)benzenesulfonamide (4k): White solid in 89% yield; m.p.: 68.7-68.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.77 (m, 2H), 7.70-7.64 (m, 2H), 7.57-7.45 (m, 3H), 7.05-6.97 (m, 2H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3 (d, *J* = 252.2 Hz), 140.2 (d, *J* = 3.3 Hz), 135.7, 132.8, 130.2, 128.9 (d, *J* = 9.0 Hz), 125.9, 115.7 (d, *J* = 22.3 Hz), 39.1; ^{19}F NMR (376 MHz, CDCl3) δ: -107.97 (s, 1F). IR (KBr, cm^{-1}): 3009.3, 2920.0, 1588.5, 1138.4, 959.9, 552.0; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{13}H_{12}FNO_2S_2$ 297.0293; Found 297.0297.

4-Chloro-*N*-(methyl(phenyl)-λ^4-sulfanylidene)benzenesulfonamide (4l): Colorless oil in 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76-7.71 (m, 2H), 7.68-7.64 (m, 2H), 7.54-7.51 (m, 1H), 7.50-7.44 (m, 2H), 7.32-7.28 (m, 2H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 137.5, 135.5, 132.8, 130.1, 128.9, 127.8, 125.9, 39.1. IR (Film, cm^{-1}): 3000.3, 1393.1, 1241.0, 958.6, 743.5, 533.1; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{13}H_{12}ClNO_2S_2$ 312.9998; Found 312.9997.

***N*-(Methyl(phenyl)-λ^4-sulfanylidene)-4-nitrobenzenesulfinamide (4m)**: White solid in 81% yield; m.p.: 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20-8.16 (m, 2H), 8.00-7.96 (m, 2H), 7.69-7.66 (m, 2H), 7.59-7.48 (m, 3H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 149.3, 135.2, 133.2, 130.4, 127.6, 126.0, 124.1, 39.3.

Imino(methyl)(phenyl)- λ^6-sulfanone (5g): Colorless oil in 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00-7.96 (m, 2H), 7.62-7.56 (m, 1H), 7.54-7.48 (m, 2H), 3.07 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.5, 133.1, 129.3, 127.7, 46.2.

***N*-(triphenyl-5-phosphanylidene)benzenesulfonamide (6)**: White solid in 53% yield; m.p.: 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79-7.68 (m, 6H), 7.63-7.54 (m, 5H), 7.48-7.42 (m, 6H), 7.32-7.26 (m, 1H), 7.22-7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.1 (d, *J* = 2.4 Hz), 130.4, 133.2 (d, *J* = 10.7 Hz), 132.9 (d, *J* = 2.9 Hz), 128.9 (d, *J* = 12.9 Hz), 128.1, 127.8, 125.8.

Acknowledgments

This study was financially supported by the National Natural Science Foundation of China (21372077) and by State Key Laboratory of Efficient Utilization for Low Grade Phosphate Rock and Its Associated Resources (WFKF2017-04).

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- *N*-fluoro benzenesulfonamide was first reported as a stable nitrene precursor
- Reaction was catalyzed by cheap and easily available Cu(□) catalyst
- Products were efficiently obtained without anhydrous solvents and inert gas
- Verify mechanism of metal nitrene intermediates by experiments