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Rh(III)-catalyzed, potassium acetate enabled, ketoxime-assisted direct amination of aromatic ketoximes

Lingling Liu,[a] Ning Wang,[a] Chenyang Dai,[a] Yi Han,[a] Shan Yang,[a] Zhibin Huang,*[a] Yingsheng Zhao*[a]

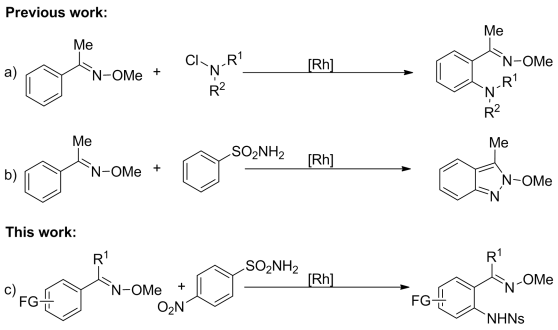
Abstract: A method to achieve rhodium(III)-catalyzed, potassium acetate enabled intermolecular C-H amination of ketoximes using various benzenesulfonamide, especially 4-nitrobenzenesulfonamide is reported. Various aryl ketoximes substituted with electron-withdrawing functional groups were all well tolerated and produced the corresponding products in moderate to good yields. A preliminary mechanistic study revealed that potassium acetate is essential to realizing intermolecular amination.

Introduction

Transition metal-catalyzed C-N bond formation has been extensively explored because these bonds are ubiquitous in natural products and pharmaceuticals. Although the Buchwald-Hartwig amination reaction and Ullmann-Goldberg coupling reaction provide powerful methods for C-N bond formation, the use of prefunctionalized arenes has limited the atomic economy of these reactions[1]. Recently, direct catalytic C-H amination has provided a high atomic economy and direct route to synthesize (hetero) aryl amines[2]. This pioneering work was first reported by Breslowet et al. who used an iron catalyst and imiono-iodane as the amidating reagent to realize the amidation of cyclohexane[3]. Since then, various groups such as Chang[4], Ackermann[5], Glorious[6], Li[7], Jiao[8] and et al. have developed efficient catalytic systems for C-H amination using Pd, Rh, Ir, and Co using miscellaneous chloramines, organic azides, and hydroxylamines as the aminating reagents. For example, Che et al. developed a palladium-catalyzed, oxime-directed C-H amination method that uses an amide as the aminating reagent[9]. Later, another group reported a Rh(III)-catalyzed oxime-direct C(sp^2)-H amination using N-chloramines (**Scheme 1a**)[10]. Recently, Zhao and co-workers disclosed the Rh(III)-catalyzed C-H bond amination of O-methyl ketoximes with sulfonamides (**Scheme 1b**)[11]. Although approaches to directly introduce an amide group at the ortho position of O-methyl ketoximes have been explored[12], nitro-substituted O-methyl ketoximes still remain a challenging class of substrates. Nitro groups are indispensable in organic synthesis because they can be easily converted to many other functional groups. Thus, the development of a general procedure for C-H amination compatible with nitro-containing substrates is highly important.

Herein, we report a Rh-catalyzed, potassium acetate enabled, ketoxime-assisted direct amination of aromatic ketoximes (**Scheme 1c**). The nitro-substituted aryl ketoximes were all well tolerated and furnished the corresponding products in moderate to good yields. A preliminary mechanistic study revealed that potassium acetate was essential to realizing intermolecular amination.

[a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Soochow Unversity
199 Renai Street, Suzhou, Jiangsu 215123, China
E-mail: yszhao@suda.edu.cn
zbhuang@suda.edu.cn

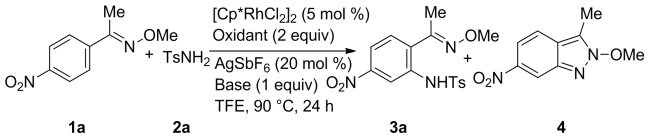


Scheme 1. Metal catalyzed oxime-directed C-H amidation.

Results and Discussion

Recently, we demonstrated the facile preparation of indazoles from ketoximes using 4-toluenesulfonamide and iodobenzene diacetate in the presence of a rhodium(III) catalyst. A wide variety of nitro-substituted ketoximes were effectively used as substrates, but the intermolecular amination product was easily transformed into indazoles when using iodobenzene diacetate[13]. We speculated that nitro-substituted ketoximes may be suitable substrates for the intermolecular amination reaction if N-N formation can be prevented during the rhodium(III) catalyzed oxidative annulation of ketoximes with sulfonamides. With these conditions in mind, we first explored the effects of oxidant to identify whether the selective intermolecular amination could be selectively realized. Thus, we firstly treated 4-nitroacetophenone oxime (**1a**) and 4-toluenesulfonamide (**2a**) with various oxidants such as $NaIO_4$, $Na_2S_2O_8$, $Cu(OAc)_2$, and AgOAc. The results showed that $NaIO_4$ provided the aminated product **3a** in 21% yield, along with 18% of the indazole product **4**. The other oxidants all provided a mixture of **3a** and **4** (**Table 1, entry 1-4**). Several bases, including K_2CO_3, $KHCO_3$, and KOAc, were employed when iodobenzene diacetate was used as the oxidant(**Table 1, entry 5-7)**. When KOAc was used as the additive, only the intermolecular amination product **3a** was obtained in 87% yield. Unfortunately, when the reaction was performed in the absence of $AgSbF_6$, only a 23% yield of **3a** was obtained (**Table 1, entry 8)**. A control experiment showed that rhodium was necessary for this transformation.

Table 1. Optimization of Reaction Conditions. [a]

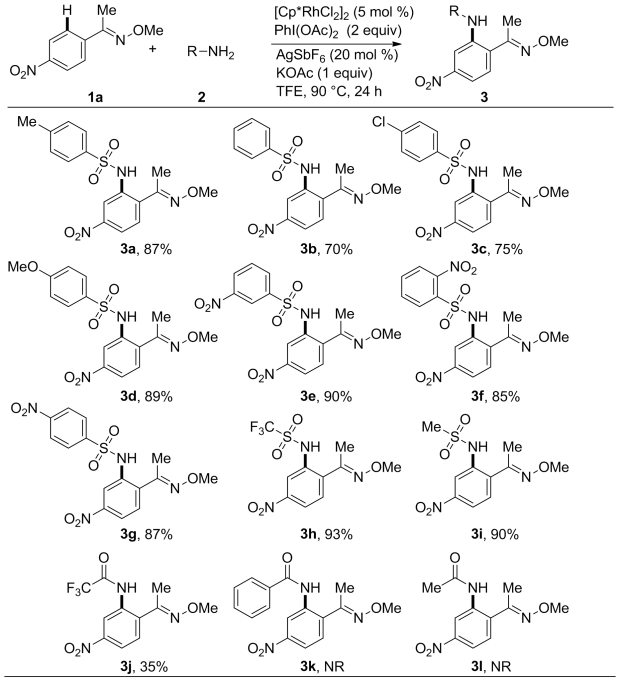


Entry	Additive	Oxidant	Base	Yield % (**3a** / **4**)
1	$AgSbF_6$	$NaIO_4$	-	21/18
2	$AgSbF_6$	$Na_2S_2O_8$	-	<5/23
3	$AgSbF_6$	$Cu(OAc)_2$	-	10/14
4	$AgSbF_6$	AgOAc	-	8/26
5	$AgSbF_6$	$PhI(OAc)_2$	K_2CO_3	26/7
6	$AgSbF_6$	$PhI(OAc)_2$	$KHCO_3$	31/12
7	$AgSbF_6$	$PhI(OAc)_2$	KOAc	87
8	-	$PhI(OAc)_2$	KOAc	23

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), Oxidant (2 equiv), Base (1 equiv), TFE (1.5 mL), 24 h; [b] isolated yields are given.

Once the optimized reaction conditions were determined, we first explored the effect of different amides on this transformation, and the data is listed in **Table 2**. Benzenesulfonamide, 4-chlorobenzenesulfonamide, and 4-methoxybenzenesulfonamideall provided the aminated products in excellent yields (**3b-3d**). The nitro-substituted sulfonamides all performed well, giving the corresponding products in greater than 85% yields (**3e-3g**). It is worth mentioning that these nitro-substituted sulfonamides could be easily removed under mild conditions to afford the aromatic amine compounds. Trifluoromethanesulfonamide was well tolerated, yielding the aminated products in 93% yield (**3h**). Unfortunately, trifluoroacetamide only provided the aminated product **3j** in 35% yield.

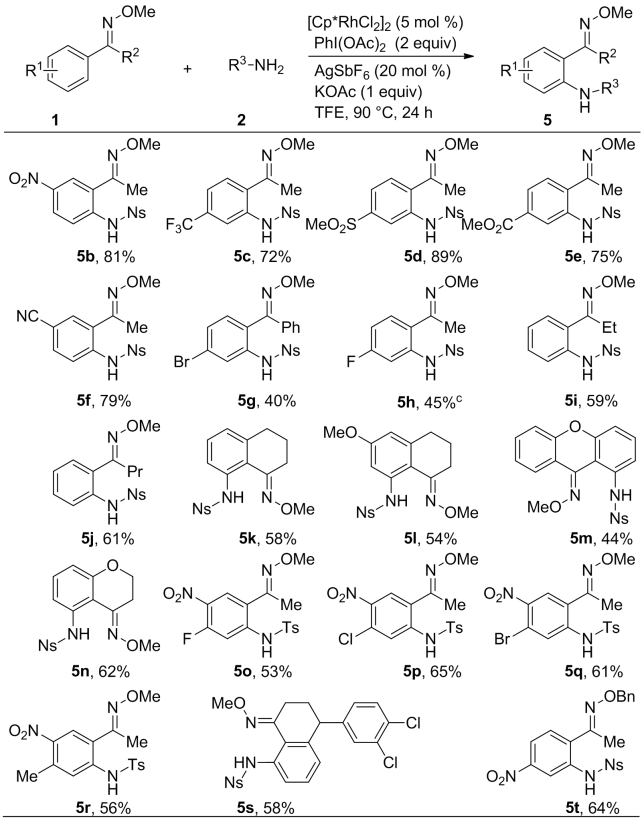
Table 2. The Amide Effect. [a]



[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), $PhI(OAc)_2$ (2 equiv), KOAc (1 equiv),TFE (1.5 mL), 24 h; [b] isolated yields are given.

Encouraged by these results, we then explored the functional group tolerance of ketoximes to 4-nitrosulfonamide, and the results are presented in **Table 3**. 3-nitroacetophenone oxime afforded **5b** in 81% yield. Other electron-withdrawing functional groups such as CF_3, SO_2Me, CO_2Me, and CN were all well tolerated (**5c-5f**), giving the aminated products in good to excellent yields. The bromide- or fluoride-substituted acetophenone oximes only provided aminated products in moderate yields (**5g-5h**), along with recovered starting material. Propiophenone oxime (**5i**) and butyrophenone oxime (**5j**) both afforded aminated products in good yields. 1-tetralone, 6-methoxy-1-tetralone, xanthone, and chroman-4-one were all effective substrates (**5k-5n**), generating the aminated products in moderate to good yields. Interestingly, all polysubstituted nitroacetophenone oximes performed well when using 4-methylbenzenesulfonamide as the aminating reagent (**5o-5r**), and gave the corresponding products in moderate to good yields. In additionally, 4-(3,4-dichloro phenyl)-tetralone (**5s**) was also a good substrate, affording the aminated product in 58% yield. When the acetophenone oxime derived from O-benzylhydroxylamine was subjected to the standard reaction conditions, the product **5t** was obtained in 64% yield.

Table 3. Substrate Scope of Ketoximes. [a]

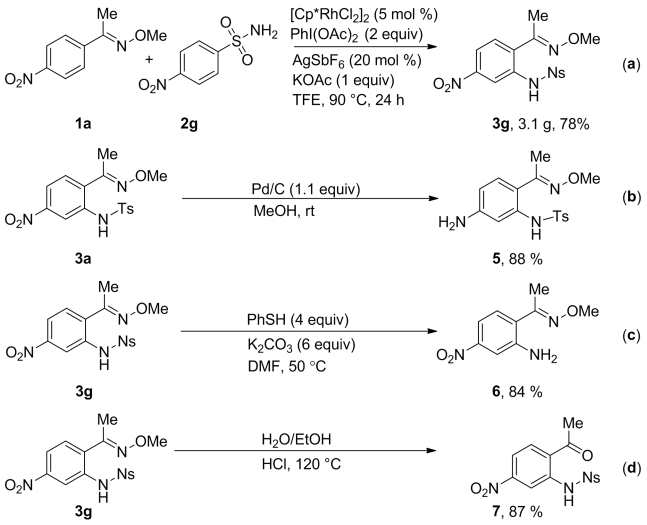


[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), $PhI(OAc)_2$ (2 equiv), KOAc (1 equiv), TFE (1.5 mL), 24 h; [b] isolated yields are given. [c] Without $AgSbF_6$ and KOAc.

To further demonstrate the synthetic utility of this method, a gram-scale reaction was performed. The product **3g** was obtained in 78% yield when the reaction was performed at a 10 mmol scale (**Scheme 2a**). The oxime directing group

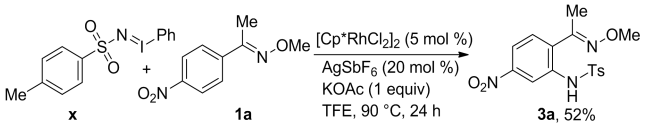
(**Scheme 2d**) and these nitro-substituted sulfonamides (**Scheme 2c**) were easily removed, and the nitro functional group (**Scheme 2b**) was easily reduced to an amine[14].

Scheme 2. Applications of the reaction.

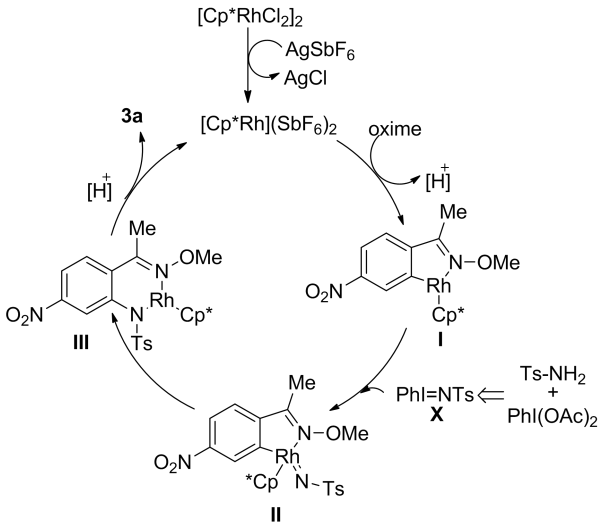


A simple mechanism experiment was performed to gain insight into this rhodium(III)-catalyzed C-H amination reaction (**Scheme 3**). When iodonium **x** was used, the corresponding product **3a** was obtained in 52% yield. This result may indicate the in situ generation of **x** from the amide with iodobenzene diacetate as the key intermediate during the catalytic cycle.

Scheme 3. Preliminary Mechanistic Study.



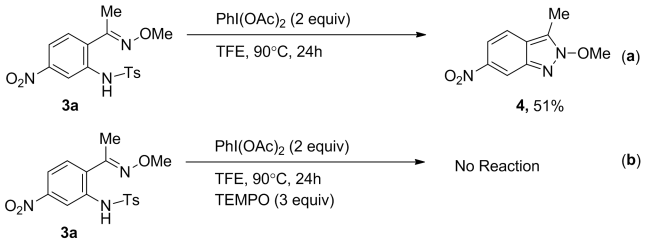
Scheme 4. Proposed Mechanism.



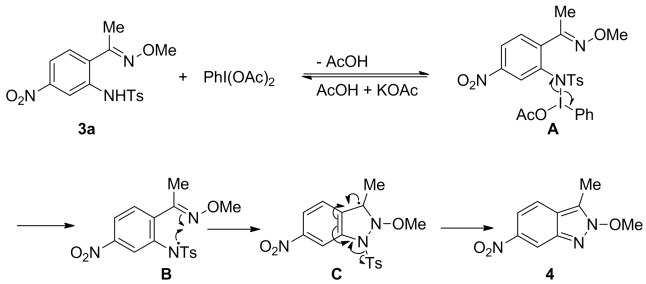
Based on a previous report and these results[15], a plausible reaction pathway is proposed in **Scheme 4**. The cationic $[Cp^*Rh^{III}]^{2+}$ complex first coordinated with the ketoxime and produced complex **I** via oxime-assisted C-H activation. The iodonium **x** was formed in situ from the sulfonamide using iodobenzene diacetate, which reacted with complex **I** to afford complex **II**, followed by migratory insertion to provide complex **III**. Subsequent protonation would release the aminated product **3a** and the catalyst precursor.

To figure out the role of potassium acetate during the catalytic cycle, several parallel experiments were carried out. When product **3a** was treated with iodobenzene diacetate, the indazole product **4** was obtained in 51% yield (**Scheme 5a**). The free radical scavenger TEMPO can completely shut down this cyclization reaction (**Scheme 5b**), indicating it undergoes an iodobenzene diacetate induced free radical pathway. Based on the previous work of Lee[13a] and these results, a plausible mechanism to form **4** was proposed in **Scheme 6.** When product **3a** is treated with iodobenzene acetate, the key intermediate **A** would be formed. The N-I bond splitting can provide the intermediate **B**, followed by N-N bond formation and electronic transfer to afford the product **4**.

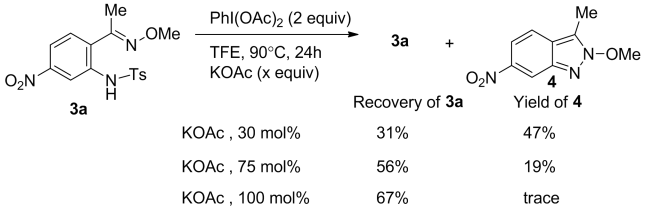
Scheme 5. Further Mechanistic Study.



Scheme 6. Plausible pathway from **3a** to **4**



Scheme 7. The role of potassium acetate.



	Recovery of **3a**	Yield of **4**
KOAc , 30 mol%	31%	47%
KOAc , 75 mol%	56%	19%
KOAc , 100 mol%	67%	trace

However, the indazole product **4** was not formed when 1 equivalent of potassium acetate was used as the additive. When the amount of potassium was reduced to less than 30 mol%, the yield of **4** is not greatly affected (**Scheme 7**).

It might be large amount of amount acetate anions would decompose key intermediate **A** to the starting material **3a (Scheme 6).**

Conclusions

Here, we have developed a practical Rh-catalyzed, potassium acetate enabled, ketoxime-assisted direct amination of aromatic ketoximes. Various aryl ketoximes substituted with electron-withdrawing functional groups were all well tolerated and gave the corresponding products in moderate to good yields. Preliminary mechanistic studies revealed the potassium acetate is essential to realize the intermolecular amination.

Experimental Section

General procedures. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. $[RhCp^*Cl_2]_2$ was prepared according to the literature procedures[16-17]. Column chromatography purifications were performed using 300–400 mesh silica gel. NMR spectra were obtained on Bruker DRX–400 instrument. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, br = broad, m = multiplet. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$, TMS or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; TMS: δ = 0.00 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.00ppm; DMSO-d_6: δ = 39.52 ppm). HRMS analyses were carried out using a Bruker MicrOTOF-Q II instrument.

Preparation of O-methyl ketoximes (1a-1l, 1n-1r, 1t): Add ketones (11.0 mmol),pyridine (2.5 mL, 30.9 mmol), H_2OMe•HCl (1.14 g, 16.5mmol), EtOH (5 mL) to a 100 mL round bottom flask equipped with a stir bar, stirred at 60 °C for 6 h. Subsequently, the mixture was quenched with water and extracted twice with ethyl acetate.The organic phases were combined, washed once with aqueous HCl and brine, dried over Na_2SO_4. The solvents were removed under reduced pressure. Recrystallization from ethyl acetate to give the O-methyl ketoximes. Spectral data matched those previously reported [11,18].

Preparation of O-methyl 9H-xanthen-9-one O-methyl oxime (1m). Add 9H-xanthen-9-one (11.0 mmol), pyridine (2.5 mL, 30.9 mmol), H_2OMe•HCl (1.14 g, 16.5mmol), EtOH (5 mL) to a 100 mL round bottom flask equipped with a stir bar, stirred at 60 °C for 6 h. Subsequently, the mixture was quenched with water and extracted twice with ethyl acetate.The organic phases were combined, washed once with aqueous HCl and brine, dried over Na_2SO_4. The solvents were removed under reduced pressure. Recrystallization from ethyl acetate to give the 9H-xanthen-9-one O-methyl oxime. 1.42 g, 57 % yield. White solid. mp: 71-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.50–7.36 (m, 2H), 7.28–7.12 (m, 4H), 4.12 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 151.3, 139.9, 131.6, 131.4, 130.3, 124.3, 123.5, 122.5, 119.3, 117.2, 116.7, 116.5, 62.9. HRMS Calcd for $C_{14}H_{11}NNaO_2$ $[M+Na]^+$: 248.0687;Found: 248.0683.

Preparation of 4-(3,4-dichlorophenyl)-3,4-dihydronaphthalen-1(2H)-one O-methyl oxime (1s). Add 4-(3,4-dichlorophenyl)-3,4-dihydronaphthalen-1(2H)-one (11.0 mmol), pyridine (2.5 mL, 30.9 mmol), H_2OMe•HCl (1.14 g, 16.5mmol), EtOH (5 mL) to a 100 mL round bottom flask equipped with a stir bar, stirred at 60 °C for 6 h. Subsequently, the mixture was quenched with water and extracted twice with ethyl acetate.The organic phases were combined, washed once with aqueous HCl and brine, dried over Na_2SO_4. The solvents were removed under reduced pressure. Recrystallization from ethyl acetate to give the 4-(3,4-dichlorophenyl)-3,4-dihydronaphthalen-1(2H)-one O-methyl oxime . 1.72 g, 49 % yield. White Solid. mp: 99-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.04 (m, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.29–7.21 (m, 2H), 7.18 (d, *J* = 2.1 Hz, 1H), 6.92–6.87 (m, 2H), 4.11–4.06 (m, 1H), 4.00 (s, 3H), 2.74–2.57 (m, 2H), 2.35–2.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 144.3, 139.7, 132.5, 130.9, 130.5 – 130.2 (m), 129.3, 128.9, 127.8, 127.2, 124.3, 62.0, 44.1, 29.3, 21.2. HRMS Calcd for $C_{17}H_{15}Cl_2NNaO$ $[M+Na]^+$: 342.0428; Found: 342.0418.

General procedure for the synthesis of products A mixture of O-methyl ketoximes **1** (0.2 mmol, 1.0 equiv), Sulfonamide derivatives **2** (0.4 mmol, 2 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.05 equiv), $AgSbF_6$ (14.0 mg, 0.2 equiv), $PhI(OAc)_2$ (128.8 mg, 2 equiv), KOAc (19.6 mg, 1 equiv) Trifluoroethanol (1.5 mL) in a 15 mL glass vial was heated at 90 °C for 24 hours. The reaction mixture was cooled to rt, filtered through diatomite and washed with 5-10 mL of ethyl acetate then concentrated in vacuo. The resulting residue was purified by column chromatography with the solvent of PE/EA= 15:1 on silica gel to give the product.

*N-(2-(1-(Methoxyimino)ethyl)-5-nitrophenyl)-4-methylbenzenesulfonamide (**3a**)* 55.9 mg, 87 % yield. Pale yellow solid; mp: 167-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.17 (br, 1H), 8.45 (d, *J* = 2.3 Hz, 1H), 7.85 (d, *J* = 2.3 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 4.0 Hz, 2H), 4.14 (s, 3H), 2.38 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 147.3, 143.8, 136.9, 135.6, 129.3, 128.8, 127.4, 126.9, 117.1, 114.1, 62.7, 21.1, 12.8. HRMS Calcd for $C_{16}H_{17}N_3NaO_5S$ $[M+Na]^+$: 386.0787; Found: 386.0784.

*N-(2-(1-(Methoxyimino)ethyl)-5-nitrophenyl)benzenesulfonamide (**3b**)* 48.8 mg, 70 % yield; Pale yellow solid. mp: 180-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.18 (br, 1H), 8.47 (d, *J* = 2.3 Hz, 1H), 7.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.86–7.80 (m, 2H), 7.54 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.52–7.44 (m, 3H), 4.14 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 147.3, 138.5, 136.7, 132.8, 128.7, 128.7, 127.8, 126.8, 117.4, 114.5, 62.7, 12.8. HRMS Calcd for $C_{15}H_{15}N_3NaO_5S$ $[M+Na]^+$: 372.0630; Found: 372.0615.

*4-Chloro-N-(2-(1-(methoxyimino)ethyl)-5-nitrophenyl)benzenesulfonamide (**3c**)* 57.4 mg, 75 % yield. Pale yellow solid; mp: 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (br, 1H), 8.45 (d, *J* = 2.3 Hz, 1H), 7.90 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.81–7.71 (m, 2H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.48–7.39 (m, 2H), 4.14 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 147.3, 139.5, 136.9, 136.5, 129.1, 129.0, 128.2, 127.5, 117.6, 114.2, 62.72, 12.8. HRMS Calcd for $C_{15}H_{14}ClN_3NaO_5S$ $[M+Na]^+$: 406.0240; Found: 406.0236.

*4-Methoxy-N-(2-(1-(methoxyimino)ethyl)-5-nitrophenyl)benzenesulfonamide (**3d**)* 67.4 mg, 89 % yield. Pale yellow solid; mp: 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (br, 1H), 8.44 (d, *J* = 2.3 Hz, 1H), 7.85 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.81–7.74 (m, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 6.94–6.87 (m, 2H), 4.14 (s, 3H), 3.82 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 155.2, 147.7, 137.5, 130.4, 129.5, 129.3, 127.8, 117.5, 114.4, 114.3, 63.2, 55.7, 13.3. HRMS Calcd for $C_{16}H_{17}N_3NaO_6S$ $[M+Na]^+$: 402.0732; Found: 402.0724.

*N-(2-(1-(Methoxyimino)ethyl)-5-nitrophenyl)-3-nitrobenzenesulfonamide (**3e**)* 70.9 mg, 90 % yield. Yellow solid; mp: 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.66 – 8.60 (m, 1H), 8.45 (d, *J* = 2.3 Hz, 1H), 8.41 – 8.37 (m, 1H), 8.19–8.14 (m, 1H), 7.94–7.89 (m, 1H), 7.74–7.68 (m, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 4.17 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 148.3, 147.8, 141.1, 136.4, 132.7, 130.6, 129.7, 128.2, 127.7, 122.3, 118.6, 114.9, 63.3, 13.2. HRMS Calcd for $C_{15}H_{14}N_4NaO_7S$ $[M+Na]^+$: 417.0481; Found: 417.0498.

*N-(2-(1-(Methoxyimino)ethyl)-5-nitrophenyl)-2-nitrobenzenesulfonamide (**3f**)* 66.9 mg, 85 % yield. Pale yellow solid; mp:185-186 °C; ^{1}H N

MR (400 MHz, $CDCl_3$) δ 11.82 (br, 1H), 8.58 (d, *J* = 2.3 Hz, 1H), 8.30–8.26 (m, 1H), 7.91 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.88–7.84 (m, 1 H), 7.79–7.74 (m, 2H), 7.58 (d, *J* = 8.8 Hz, 1H), 4.23 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 147.5, 147.2 135.9, 133.9, 132.3, 132.1, 131.2, 129.1, 127.9, 125.1, 117.3, 112.9, 62.8, 12.9. HRMS Calcd for $C_{15}H_{15}N_4O_7S$ $[M+H]^+$: 395.0661; Found: 395. 0659.

N-(2-(1-(Methoxyimino)ethyl)-5-nitrophenyl)-4-nitrobenzenesulfonamid ***e(3g)*** 68.6 mg, 87 % yield. Yellow solid; mp: 173-175 °C; ^{1}H NM R (400 MHz, $CDCl_3$) δ 11.52 (br, 1H), 8.47 (d, *J* = 2.3 Hz, 1H), 8. 35–8.28 (m, 2H), 8.07–8.00 (m, 2H), 7.93 (dd, *J* = 8.8, 2.3 Hz, 1 H), 7.57 (d, *J* = 8.8 Hz, 1H), 4.16 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 150.4, 147.9, 144.7, 136.5, 129.7, 128. 8, 127.8, 124.5, 118.4, 114.5, 63.3, 13.3. HRMS Calcd for $C_{15}H_{14}N_4$ NaO_7S $[M+Na]^+$: 417.0481; Found: 417.0498.

1,1,1-Trifluoro-N-(2-(1-(methoxyimino)ethyl)-5-nitrophenyl)methanesulfo namide ***(3h)*** 63.4 mg, 94 % yield. Pale yellow solid; mp: 66-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.18 (br, 1H), 8.62 (d, *J* = 2.3 Hz, 1H), 8.13 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 4.1 6 (s, 3H), 2.44 (s, 3H). ^{19}F NMR (400 MHz, $CDCl_3$) δ -76.43 (s). ^{13} C NMR (100 MHz, $CDCl_3$) δ 154.9, 147.5, 135.1, 129.1, 127.8, 119. 1, 114.9, 62.8, 12.8. HRMS Calcd for $C_{10}H_{10}F_3N_3NaO_5S$ $[M+Na]^+$: 3 64.0191; Found: 364.0197.

N-(2-(1-(Methoxyimino)ethyl)-5-nitrophenyl)methanesulfonamide ***(3i)*** 5 1.6 mg, 90 % yield. Pale yellow solid; mp: 175-177 °C; ^{1}H NMR (4 00 MHz, $CDCl_3$) δ 11.14 (br, 1H), 8.49 (d, *J* = 2.3 Hz, 1H), 7.95 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 4.10 (s, 3H), 3.12 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 14 7.6, 137.3, 129.3, 126.5, 116.9, 112.7, 62.7, 40.2, 12.9. HRMS Cal cd for $C_{10}H_{13}N_3NaO_5S$ $[M+Na]^+$: 310.0474; Found: 310.0458.

2,2,2-Trifluoro-N-(2-(1-(methoxyimino)ethyl)-5-nitrophenyl)acetamide ***(3j)*** 21.3 mg, 35 % yield. Pale yellow solid; mp: 135-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.64 (br, 1H), 9.46 (d, *J* = 2.4 Hz, 1H), 8.0 6 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 4.09 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 154.9 (d, *J-F* = 38.0 Hz), 147.4, 135.4, 128.8, 127.4, 118.9, 115.5, 113.8, 62.4, 12. 9. ^{19}F NMR (400 MHz, $CDCl_3$) δ -75.91. HRMS Calcd for $C_{11}H_{10}F_3$ N_3NaO_4 $[M+Na]^+$: 328.0521; Found: 364.0516.

N-(2-(1-(Methoxyimino)ethyl)-4-nitrophenyl)-4-nitrobenzenesulfonamide ***(5b)*** 63.8 mg, 81 % yield. Pale yellow solid; mp: 175-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (br, 1H), 8.36–8.30 (m, 3H), 8.13 (dd, *J* = 9.1, 2.6 Hz, 1H), 8.07–8.03 (m, 2H), 7.74 (d, *J* = 9.1 Hz, 1H), 4.15 (s, 3H), 2.32 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 155. 3, 150.0, 144.3, 142.7, 140.8, 128.0, 124.6, 124.1, 121.7, 117.9, 62. 7, 12.5. HRMS Calcd for $C_{15}H_{14}N_4NaO_7S$ $[M+Na]^+$: 417.0481; Found: 417.0491.

N-(2-(1-(Methoxyimino)ethyl)-5-(trifluoromethyl)phenyl)-4-nitrobenzenes ulfonamide ***(5c)*** 60.0 mg, 72 % yield. Pale yellow solid; mp: 120-12 2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (br, 1H), 8.30–8.24 (m, 2H), 7.96–7.94 (m, 1H), 7.93 (s, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.3 6 (d, *J* = 8.3, 1H), 4.12 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 150.3, 144.8, 135.8, 131.8 (q, *J-F* = 33.2 Hz), 12 9.3, 128.4, 126.4, 124.3, 121.0 (d, *J-F* = 3.8 Hz), 117.6 (d, *J-F* = 3.9 Hz), 63.1, 13.1. ^{19}F NMR (400 MHz, $CDCl_3$) δ -63.20(s). HRMS Calcd for $C_{16}H_{14}F_3N_3NaO_5S$ $[M+Na]^+$: 440.0504; Found: 440.0511.

N-(2-(1-(Methoxyimino)ethyl)-5-(methylsulfonyl)phenyl)-4-nitrobenzenes ulfonamide ***(5d)*** 76.0 mg, 89 % yield. Pale yellow solid; mp: 146-14 8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.48 (br, 1H), 8.33–8.27 (m, 2H), 8.17 (d, *J* = 1.8 Hz, 1H), 8.05–7.98 (m, 2H), 7.65 (dd, *J* = 8. 4, 1.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 4.14 (s, 3H), 3.06 (s, 3 H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 150.4, 144.6, 141.5, 136.4, 129.8, 128.9, 127.1, 124.4, 122.3, 118.3, 63.2, 44.2, 13.2. HRMS Calcd for $C_{16}H_{17}N_3NaO_7S_2$ $[M+Na]^+$: 450.0406; Found: 450.0390.

4-(1-(Methoxyimino)ethyl)-3-(4-nitrophenylsulfonamido)benzoate ***(5e)*** 5 2.9 mg, 75 % yield. Pale yellow solid; mp: 153-155 °C; ^{1}H NMR (4 00 MHz, $CDCl_3$) δ 11.15 (br, 1H), 8.28–8.25 (m, 2H), 8.24 (d, *J* = 1.9 Hz, 1H), 7.99–7.88 (m, 2H), 7.77 (dd, *J* = 8.3, 1.9 Hz, 1H), 7. 43 (d, *J* = 8.3 Hz, 1H), 4.11 (s, 3H), 3.93 (s, 3H), 2.10 (s, 3H). ^{13} C NMR (100 MHz, $CDCl_3$) δ 165.2, 155.3, 149.7, 144.5, 134.8, 130. 9, 128.4, 128.0, 126.9, 124.9, 123.7, 121.4, 62.5, 52.1, 12.7. HRM S Calcd for $C_{17}H_{17}N_3NaO_7S$ $[M+Na]^+$: 430.0685; Found: 430.0702.

N-(4-Cyano-2-(1-(methoxyimino)ethyl)phenyl)-4-nitrobenzenesulfonamid ***e (5f)*** 59.0 mg, 79 % yield. Pale yellow solid; mp: 155-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.88 (br, 1H), 8.32 (d, *J* = 9.0 Hz, 2H), 8.02 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.70 (d, *J* = 4.3 Hz, 1H), 7.54 (dd, *J* = 4.3, 2.3 Hz, 1H), 4.13 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 149.9, 144.4, 139.1, 132. 8, 132.4, 127.9, 124.1, 122.3, 118.7, 117.4, 107.0, 62.7, 12.4. HRM S Calcd for $C_{15}H_{14}N_4NaO_5S$ $[M+Na]^+$: 374.0685; Found: 374.0680.

N-(5-Bromo-2-((methoxyimino)(phenyl)methyl)phenyl)-4-nitrobenzenesul fonamide ***(5g)*** 39.1 mg, 40 % yield. Pale yellow solid; mp: 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (br, 1H), 8.33–8.25 (m, 2 H), 8.01–7.97 (m, 2H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.3-7.4 (m, 3H), 7.09 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.93–6.85 (m, 2H), 6.63 (d, *J* = 8.5 Hz, 1H), 4.06 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 150.3, 144.9, 136.7, 133.1, 131.4, 130.3, 129.7, 128.4, 127.7, 127.6, 124. 3, 124.5, 124.2, 122.9, 63.3. HRMS Calcd for $C_{20}H_{16}BrN_3NaO_5S$ [M +Na]$^+$: 511.9892; Found: 511.9902.

N-(5-Fluoro-2-(1-(methoxyimino)ethyl)phenyl)-4-nitrobenzenesulfonamid ***e (5h)*** 33.0 mg, 45 % yield. Yellow solid; mp: 136-137 °C; ^{1}H NM R (400 MHz, $CDCl_3$) δ 11.54 (br, 1H), 8.27 (d, *J* = 8.8 Hz, 2H), 7. 96 (d, *J* = 8.8 Hz, 2H), 7.43–7.32 (m, 2H), 6.83-6.79 (m, 1H), 4.08 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.5, 155.8, 150.2, 144.9, 137.2 (d, *J-F* = 10.9 Hz), 130.5 (d, *J-F* = 10. 0 Hz), 128.4, 124.2, 119.4, 111.4 (d, *J-F* = 21.8 Hz), 107.8 (d, *J-F* = 26.6 Hz), 62.7, 13.1. ^{19}F NMR (400 MHz, CDCl3) δ -107.81 (s). HRMS Calcd for $C1_5H_{14}FN_3NaO_5S$ $[M+Na]^+$: 390.0536; Found: 390. 0544.

N-(2-(1-(Methoxyimino)propyl)phenyl)-4-nitrobenzenesulfonamide ***(5i)*** Yellow liquid. 42.8 mg, 59 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1 1.23 (br, 1H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.34–7.27 (m, 1H), 7.19–7.09 (m, 1H), 4.07 (s, 3H), 2.58 (q, *J* = 7.6 Hz, 2H), 0.9 3 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 161.2, 150.0, 145.2, 135.5, 130.0, 128.4, 128.4, 124.9, 124.0, 122.8, 121.7, 62.7, 20.1, 11.0. HRMS Calcd for $C_{16}H_{18}N_3O_5S$ $[M+H]^+$: 364.0967; Found: 364.0958.

N-(2-(1-(Methoxyimino)butyl)phenyl)-4-nitrobenzenesulfonamide ***(5j)*** Y ellow liquid. 45.8 mg, 61 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11. 31 (br, 1H), 8.24–8.20 (m, 2H), 7.92–7.87 (m, 2H), 7.70 (m, 1H), 7. 37 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.33–7.27 (m, 1H), 7.13 (dd, *J* = 8.0, 1.4Hz, 1H), 4.06 (s, 3H), 2.64–2.47 (m, 2H), 1.39–1.21 (m, 2H), 0. 85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 150.0, 145.3, 135.5, 129.9, 128.6, 128.3, 124.7, 124.0, 122.7, 121.5, 62.7, 28.4, 20.1, 14.1. HRMS Calcd for $C_{17}H_{20}N_3O_5S$ $[M+H]^+$: 378.1124; Found: 378.1132.

N-(8-(Methoxyimino)-5,6,7,8-tetrahydronaphthalen-1-yl)-4-nitrobenzenes ulfonamide ***(5k)*** 43.4 mg, 58 % yield. White solid; mp: 204-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (br, 1H), 8.27–8.19 (m, 2H), 7. 97–7.90 (m, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.19-7.15 (m, 1H), 6.88 (dd, *J* = 7.6, 1.0 Hz, 1H), 4.07 (s, 3H), 2.70–2.59 (m, 4H), 1.70–1. 61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 149.9, 145.3, 14 2.1, 136.0, 129.9, 129.4, 128.4, 124.9, 124.7, 123.9, 118.4, 118.3,

62.7, 30.6, 24.9, 20.6. HRMS Calcd for $C_{17}H_{17}N_3NaO_5S$ $[M+Na]^+$: 398.0787; Found: 398.0777.

*N-(3-Methoxy-8-(methoxyimino)-5,6,7,8-tetrahydronaphthalen-1-yl)-4-nitrobenzenesulfonamide (**5l**)* 43.6 mg, 54 % yield. Pale yellow solid; mp: 145-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.97 (br, 1H), 8.31–8.20 (m, 2H), 8.02–7.90 (m, 2H), 7.05 (d, *J* = 2.6 Hz, 1H), 6.40 (d, *J* = 2.6 Hz, 1H), 4.04 (s, 3H), 3.78 (s, 3H), 2.65-2.61 (m, 4H), 1.69-1.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 157.4, 150.0, 145.3, 143.6, 137.9, 128.5, 124.0, 111.2, 110.1, 103.9, 62.5, 55.3, 31.0, 24.9, 20.6. HRMS Calcd for $C_{18}H_{19}N_3NaO_6S$ $[M+Na]^+$: 428.0992; Found: 428.0982.

*N-(9-(Methoxyimino)-9H-xanthen-1-yl)-4-nitrobenzenesulfonamide (**5m**)* 32.3 mg, 44 % yield. Pale yellow solid; mp: 167-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (br, 1H), 8.62 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.24–8.17 (m, 2H), 8.00–7.93 (m, 2H), 7.51–7.45 (m, 1H), 7.41 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.33-7.29 (m, 1H), 7.20 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.18–7.11 (m, 1H), 6.96 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.19 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ 152.3, 151.9, 149.6, 144.5, 143.2, 135.3, 132.4, 130.7, 130.4, 128.9, 127.9, 124.2, 123.7, 122.5, 116.7, 114.8, 114.6, 112.8, 108.1, 63.2. HRMS Calcd for $C_{20}H_{15}N_3NaO_6S$ $[M+Na]^+$: 448.0579; Found: 448.0587.

*N-(4-(Methoxyimino)chroman-5-yl)-4-nitrobenzenesulfonamide (**5n**)* 46.6 mg, 62 % yield. Pait solid; mp: 139-140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (br, 1H), 8.30–8.23 (m, 2H), 8.05–7.95 (m, 2H), 7.21–7.10 (m, 2H), 6.60 (dd, *J* = 7.8, 1.6 Hz, 1H), 4.10 (t, *J* = 6.3 Hz, 2H), 4.08 (s, 3H), 2.88 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 152.4, 150.1, 145.3, 136.8, 131.4, 128.5, 124.1, 113.4, 111.5, 106.5, 64.0, 62.9, 23.8. HRMS Calcd for $C_{16}H_{15}N_3NaO_6S$ $[M+Na]^+$: 400.0579; Found: 400.0572.

*N-(5-Fluoro-2-(1-(methoxyimino)ethyl)-4-nitrophenyl)-4-methylbenzenesulfonamide (**5o**)* 42.7 mg, 53 % yield. Pale yellow solid; mp: 172-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.00 (br, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.81–7.74 (m, 2H), 7.49 (d, *J-F* = 13.1 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.12 (s, 3H), 2.41 (s, 3H), 2.29 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 154.2, 144.5, 143.1, 135.3, 129.6, 126.8, 126.7, 116.9, 106.2 (d, *J-F* = 26.6 Hz), 99.5, 62.6, 21.1, 12.5.^{19}F NMR (400 MHz, $CDCl_3$) δ -111.54(s). HRMS Calcd for $C_{16}H_{16}FN_3NaO_5S$ $[M+Na]^+$: 404.0692; Found: 404.0704.

*N-(5-Chloro-2-(1-(methoxyimino)ethyl)-4-nitrophenyl)-4-methylbenzenesulfonamide (**5p**)* 49.9 mg, 65 % yield. Pale yellow solid; mp: 206-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (br, 1H), 8.08 (s, 1H), 7.76 (s, 1H), 7.76 (dd, *J* = 6.4, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.13 (s, 3H), 2.41 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 144.8, 141.4, 141.0, 135.8, 130.1, 129.4, 127.3, 126.7, 120.5, 120.3, 63.2, 21.6, 12.9. HRMS Calcd for $C_{16}H_{16}ClN_3NaO_5S$ $[M+Na]^+$: 420.0397; Found: 420.0406.

*N-(5-Bromo-2-(1-(methoxyimino)ethyl)-4-nitrophenyl)-4-methylbenzenesulfonamide (**5q**)* 44.9 mg, 61 % yield. Pale yellow solid; mp: 217-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (br, 1H), 8.05 (s, 1H), 7.97 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.13 (s, 3H), 2.41 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 144.8, 143.4, 140.8, 135.8, 130.0, 127.3, 126.6, 123.9, 120.9, 116.8, 63.2, 21.6, 12.8. HRMS Calcd for $C_{16}H_{16}BrN_3NaO_5S$ $[M+Na]^+$: 463.9892; Found: 463.9899.

*N-(2-(1-(Methoxyimino)ethyl)-5-methyl-4-nitrophenyl)-4-methylbenzenesulfonamide (**5r**)* 44.7 mg, 56 % yield. Pale yellow solid; mp: 226-227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (br, 1H), 8.21 (s, 1H), 7.86–7.70 (m, 2H), 7.58 (s, 1H), 7.32 (m, 2H), 4.16 (s, 3H), 2.64 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 144.4, 143.3, 140.7, 136.6, 136.2, 129.8, 127.2, 125.9, 121.8, 120.2, 62.9, 21.5, 21.4, 12.8. HRMS Calcd for $C_{17}H_{20}N_3O_5S$ $[M+H]^+$: 378.1124; Found: 378.1115.

*N-(4-(3,4-Dichlorocyclohexa-1,5-dien-1-yl)-8-(methoxyimino)-5,6,7,8-tetrahydronaphthalen-1-yl)-4-nitrobenzenesulfonamide (**5s**)* 60.4 mg, 58 % yield. Pale yellow solid; mp: 179-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.81 (br, 1H), 8.29 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.19-7.17 (m, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.74 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 4.09 (s, 3H), 4.04 (t, *J* = 5.3 Hz, 1H), 2.74-2.66 (m, 1H), 2.54-2.45 (m, 1H), 2.01-1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 150.1, 145.3, 143.7, 142.1, 136.3, 132.7, 130.8, 130.5, 130.1, 130.0, 128.5, 127.5, 125.6, 124.1, 119.2, 118.4, 62.9, 44.4, 27.9, 21.6. HRMS Calcd for $C_{23}H_{21}Cl_2N_3NaO_5S$ $[M+Na]^+$: 502.0371; Found: 502.0364.

*N-(2-(1-((Benzyloxy)imino)ethyl)-5-nitrophenyl)-4-nitrobenzenesulfonamide (**5t**)* 60.0 mg, 64 % yield. Pale yellow solid; mp: 168-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.34 (br, 1H), 8.48 (d, *J* = 2.1 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 2H), 7.89 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.54–7.41 (m, 5H), 5.35 (s, 2H), 2.28 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.2, 147.8, 144.5, 136.9, 136.6, 129.7, 129.0, 128.7, 128.6, 128.5, 127.5, 124.3, 118.2, 114.1, 13.5. HRMS Calcd for $C_{21}H_{18}N_4NaO_7S$ $[M+Na]^+$: 470.0896; Found: 470.0891.

*2-methoxy-3-methyl-6-nitro-2H-indazole (**4**)* the spectroscopic data of the product matched those previously reported.[11] 21.2 mg, 51% yield. Yellow solid; mp: 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.4 Hz, 1H), 7.90 (dd, *J* = 9.1, 1.4 Hz, 1H), 7.65 (d, *J* = 9.1 Hz, 1H), 4.34 (s, 3H), 2.65 (s, 3H). Spectral data matched those previously reported.[11]

N-(5-Amino-2-(1-(methoxyimino)ethyl)phenyl)-4-methylbenzenesulfonamide (***5***) 58.6 mg, 88 % yield. Yellow solid; mp:151-152 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 11.18 (br, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.33 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.00 (s, 3H), 3.90 (br, 2H), 2.34 (s, 3H), 1.99 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 147.8, 143.3, 137.5, 136.5, 129.8, 129.3, 127.1, 114.0, 110.2, 106.5, 62.2, 21.4, 12.7. HRMS Calcd for $C_{16}H_{19}N_3NaO_3S$ $[M+Na]^+$: 356.1045; Found: 356.1041.

*1-(2-amino-4-nitrophenyl)ethanone O-methyl oxime (**6**)* 35.2 mg, 84 % yield. Orange solid; mp: 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.8 Hz, 1H), 7.49 – 7.43 (m, 2H), 6.00 (s, 2H), 4.02 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 147.9, 146.6, 129.4, 122.7, 110.7, 110.5, 62.3, 13.0. HRMS Calcd for $C_9H_{11}N_3NaO_3$ $[M+Na]^+$: 232.0698; Found: 232.0704.

*N-(2-Acetyl-5-nitrophenyl)-4-nitrobenzenesulfonamide (**7**)* 63.4 mg, 87 % yield. Pale yellow solid; mp: 55-56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (br, 1H), 8.55 (d, *J* = 2.2 Hz, 1H), 8.38–8.30 (m, 2H), 8.17–8.11 (m, 2H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.92 (dd, *J* = 8.7, 2.2 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 150.9, 150.6, 144.6, 140.4, 133.3, 128.7, 125.2, 124.8, 117.3, 113.3, 28.7. HRMS Calcd for $C_{14}H_{17}N_3NaO_7S$ $[M+Na]^+$: 388.0215; Found: 388.0223.

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KeyWords: rhodium • potassium acetate • ketoximes• 4-nitrobenzenesulfonamide • amination

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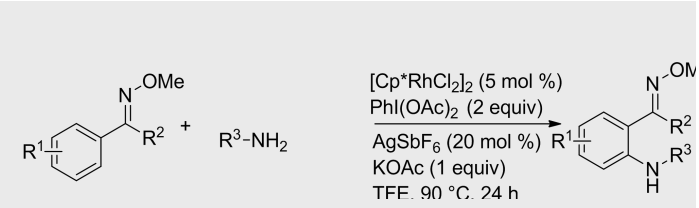
FULL PAPER



Various aryl ketoximes substituted with electron-withdrawing functional groups were all well tolerated and produced the corresponding products in moderate to good yields. A preliminary mechanistic study revealed that potassium acetate is essential to realizing intermolecular amination.

4-nitrobenzenesulfonamide • Construction of C-N

A method to achieve rhodium(III)-catalyzed, potassium acetate enabled intermolecular C-H amination of ketoximes using various benzene sulfonamide, especially 4-nitrobenzenesulfonamide is reported.

Lingling Liu,[a] Ning Wang,[a] Chenyang Dai,[a] Yi Han,[a] Shan Yang,[a] Zhibin Huang,*[a] Yingsheng Zhao*[a]

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Rh(III)-catalyzed, potassium acetate enabled, ketoxime-assisted direct amination of aromatic ketoximes