Letter

SO₂F₂-Promoted Dehydration of Aldoximes: A Rapid and Simple Access to Nitriles

Α

Yiyong Zhao^a Guangyao Mei^b Haibo Wang^b Guofu Zhang^{*a} Chengrong Ding^{*a}

^a College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. of China gfzhang@zjut.edu.cn dingcr@zjut.edu.cn

^b Zhejiang Hongyuan Pharmaceutical Co., Ltd., Linhai 317016, P. R. of China



One-pot strategy using inorganic reagents in green solvent
 Up to gram scale

Received: 20.03.2019 Accepted after revision: 04.05.2019 Published online: 25.06.2019 DOI: 10.1055/s-0037-1611840; Art ID: st-2019-w0161-l

Abstract A rapid, simple and mild process for the dehydration of aldoximes to give the corresponding nitriles, which utilizes SO_2F_2 as an efficient reagent, has been developed. A variety of (hetero)arene, alkene, alkyne and aliphatic aldoximes proceeded with high efficiency to afford nitriles in excellent to quantitative yields with great functional group compatibilities in acetonitrile under ambient conditions. Furthermore, an eco-friendly synthetic protocol to access nitriles from aldehydes with *ortho-, meta-* and *para-*nitrile groups was also described in aqueous methanol by using inorganic base Na_2CO_3 , and a one-pot synthetic strategy to generate nitriles from aldehydes was proved to be feasible.

Key words SO_2F_2 , aldoxime, nitrile, dehydration, CH_3CN , aqueous methanol

As particularly useful compounds, nitriles are not only versatile synthetic intermediates for pharmaceuticals, agricultural chemicals, and dyes,¹ but also key precursors for conversion into amides, carboxylic acids, amines, ketones, and esters.² Compared with classic strategies for the construction of nitriles,^{3a-d} especially those using highly toxic cyanides,^{3e-1} dehydration of aldoximes is an advantageous approach because of the easy availability of aldoximes, the avoidance of very toxic cyanide ion, and production of water as the side product.⁴⁻⁷ Although numerous methods for the dehydration of aldoximes to give nitriles have been reported, the limitations are still clear. For example, some methodologies require inconvenient reaction conditions and redundant work-up,⁴ the use of special reagents⁵ or a plethora of dehydrants,⁶ suffering from drawbacks of low functional group tolerance, and difficult product purification. Besides, transition-metal-catalyzed routes using Pd, Ru, Pt, Ni, Cu, and Fe catalysts have also received much attention in recent years,⁷ but most of them are confronted with obstacles of large catalyst loadings, high reaction temperatures, inert atmosphere protection, and participation of capricious ligands were mostly inevitable. Considering these issues, it is still highly desirable to develop a general, high-efficiency and mild process for the dehydration of aldoximes to nitriles.

Sulfuryl fluoride (SO₂F₂), as an inexpensive, abundant and relatively inert gas,8 has recently attracted significant attention for sulfonyl(VI) fluoride exchange (SuFEx)⁹ and other transformations.¹⁰ Especially SuFEx click chemistry, which was chiefly described by Sharpless' team in 2014, gave evidence that the proton can activate the exchange of S-F bonds for S-O bonds to make functional products,^{9a} and the sulfuryl fluoride (-SO₂F) functional group could be applied in a controllable and targeted manner for small molecules, polymers, and biomolecules because the sulfate connector is surprisingly stable toward hydrolysis.9b-h Subsequently, variant reactions were introduced by other groups.¹⁰ Notably, Qin's group demonstrated that the system of SO₂F₂/base in DMSO can be directly utilized in versatile manipulations of oxidative dehydrogenation and dehydration.^{10e-l,11}

Our research group has undertaken relevant work on deoximation and cyanidation.¹² Recently, we reported that a Fe(NO₃)₃·9H₂O-catalyzed aerobic oxidative deoximation system can be used without any other additives.^{12a} Soon afterwards, the use of aqueous ammonia (NH₃·H₂O), as the simplest N-containing ligand, was reported to effectively promote copper-catalyzed selective oxidation of alcohol to nitriles under air in water.^{12b} Inspired by the unique properties of SO₂F₂,^{9,10} we hypothesized that the proton of aldoximes **2** might activate the exchange of a S–F bond for a S–O bond to generate the corresponding sulfonyl ester **A** with the participation of SO₂F₂ and base. Given the attenuation of the N–O bond by the -SO₂F group with the assistance of base, the formation of sulfonyl ester **A** was immediately followed by β -elimination to generate the desired carbon–ni-

В

trogen triple bonds of nitrile **3** (Scheme 1). With our hypothesis, we developed a rapid, simple, and versatile dehydration of aldoximes to nitriles by using SO_2F_2 and organic base Et_3N in acetonitrile under ambient conditions. Furthermore, an eco-friendly synthetic strategy to access nitriles from the corresponding aldehydes with *ortho-*, *meta*-and *para*-nitrile functionalities could also be carried out in aqueous methanol by using inorganic alkali Na₂CO₃.



To validate our hypothesis, we embarked on the dehydration of aldoximes using SO₂F₂ and base as efficient reagents. Initially, 4-chlorobenzaldoxime (2e) was selected as model substrate to optimize the reaction conditions (Table 1, for details see Supporting Information). To our surprise, the initial result showed that the desired product **3e** was formed in almost quantitative yield when the reaction was carried out with 2.0 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), SO₂F₂ was introduced by bubbling into 2.0 mL acetonitrile (CH₃CN) via a balloon at room temperature for 10 min (entry 1). Encouragingly, other bases such as diisopropylethylamine [(*i*-Pr)₂NEt], triethylamine (Et₃N), Na₂CO₃ and K₂CO₃ were also found to be suitable in following studies (entries 2-6). Notably, although the weaker alkalinity of Et₃N led to inferior reactivity, increasing reaction time slightly could also result in nearly quantitative transformation (entries 3 and 4). It should be pointed out that, because of their low solubility in CH₃CN and alkalescence, very poor results were obtained when using inorganic bases (entries 5 and 6). We also tried to perform the reaction with less base, but the product yields decreased significantly with the loadings of Et₃N were reduced (entry 4 vs. entries 7 and 8). Several solvents, such as methanol (CH₃OH), ethyl acetate (EtOAc), dimethyl sulfoxide (DMSO) and dioxane were also screened (entries 9–12). Compared with CH₃CN, these solvents were less effective for this transformation. Furthermore, there was no generation of desired 4-chlorobenzonitrile (**3e**) without the presence of base or SO_2F_2 , respectively (entries 13 and 14). Subsequently, considering the simplified purification of intermediates,¹³ and easy preparation of aldoximes from the corresponding aldehydes without any by-product¹⁴, a series of continuous conversions, including oximation of aldehydes and cyanation of aldoximes in a system of SO₂F₂/Et₃N/CH₃CN, was tested by using 4-chlorobenzaldehyde (1e) as starting material. It was exciting to find that the final product **3e** was still generated in up to nearly quantitative yield (entry 15).

Having established the optimal reaction conditions, we further explored the generality of this transformation with respect to the aldoxime derivatives, which were quantitatively obtained from the corresponding aldehydes 1 without further purification (Scheme 2). To our delight, benzaldoxime and its derivatives bearing electron-donating groups such as methyl, methoxyl, and benzyloxy, exhibited excellent reactivity and gave almost quantitative conversions to the corresponding products (3a-c, 3j, 3r, 3t, and 3u). Similar reactivities were also observed with substrates bearing electron-withdrawing groups, including halogen, nitro and trifluoromethyl substituents (3d-h, 3o-q, and **3s**). What calls for special attention is that the isolated vields of the temperature-sensitive arylnitriles (3a, 3b, 3d, **3h**, **3w**, and **3x**) were lower than their GC yields on account of their low boiling temperature and volatility. Notably, compared with para- or meta-position substituted arvlaldehydoximes (3c, 3g, 3o, 3z), the ortho-position functionalized substrates required longer reaction time to obtain excellent vields (3p. 3r. 3aa), because the ortho-position substituent groups introduces steric hindrance that decelerates the deoximative transformation. To our delight, substrate

Letter

Table 1 Optimization of Reaction Conditions^a

	CI Ze	SO ₂ F ₂ (base, solve time	ulloon) ent, r.t. Cl ⁻	3e
Entry	Base (equiv)	Solvent	Time (min)	Isolated yield (%)
1	DBU (2.0)	CH₃CN	10	99
2	(<i>i</i> -Pr) ₂ NEt (2.0)	CH_3CN	10	98
3	Et ₃ N (2.0)	CH_3CN	10	94
4	Et ₃ N (2.0)	CH_3CN	15	99
5	Na ₂ CO ₃ (2.0)	CH_3CN	60	12
6	K ₂ CO ₃ (2.0)	CH_3CN	60	7
7	Et ₃ N (1.5)	CH_3CN	15	33 (34) ^b
8	Et ₃ N (1.0)	CH_3CN	15	9 (9) ^b
9	Et ₃ N (2.0)	CH₃OH	30	8
10	Et ₃ N (2.0)	EtOAc	30	60
11	Et ₃ N (2.0)	DMSO	30	38
12	Et ₃ N (2.0)	dioxane	15	65
13	-	CH_3CN	15	NR ^e
14 ^c	Et ₃ N (2.0)	CH_3CN	15	NR ^e
15 ^d	Et ₃ N (2.0)	CH_3CN	30	98

^a Reaction conditions: A mixture of 4-chlorobenzaldoxime **2e** (1.0 mmol, 1.0 equiv), base (2.0 mmol, 2.0 equiv), solvent (2.0 mL), and SO₂F₂ (introduced by bubbling into the solution via a balloon) was stirred at r.t. in a 25 mL Schlenk flask.

Isolated yield for 30 min in parentheses.

Without SO₂F₂

^d A series of reactions including oximation and cyanation, see Supporting Information for details.

^e NR = no reaction.

V

Syn lett

Y. Zhao et al.

С



Scheme 2 Substrate scope of dehydration of aldoximes. A mixture of aldoximes **2** (1.0 mmol, 1.0 equiv), Et₃N (2.0 mmol, 2.0 equiv), and CH₃CN (2.0 mL) was stirred at r.t. under a SO_2F_2 atmosphere (a SO_2F_2 balloon) in a 25 mL Schlenk flask; isolated yields. Aldoximes **2** were generated from the corresponding aldehydes **1** without further purification. ^a GC yields in parentheses. ^b Using 3.0 mmol of Et₃N. ^c 30 min. ^d 60 min.

bearing a *para*-COOH group, which is sensitive to alkaline systems, could also be smoothly transformed into 4-cyanobenzoic acid as the only product when 3.0 equivalent of Et₃N was used (**3m**). Remarkably, derivatives bearing oxidation-sensitive groups (methylthio and alkenyl groups) also reacted efficiently, providing excellent yields of the desired nitriles without the generation of other side products (**3n**, **3ab**). Moreover, the SO₂F₂-promoted dehydration also showed high compatibility with N/O/S-containing heterocyclic functionalities, and the desired heteroaryl nitriles **3u-v** were obtained in excellent yields. It is worth highlighting that the synthesis of 5-cvanindole **3v** containing SuFex-sensitive functionality was also achieved in 94% vield. Respectively, cinnamyl nitrile **3ac** and 3-phenylpropiolonitrile 3ad were also achieved in 95% and 87% vields from corresponding aldoximes, indicating that the alkenyl and alkynyl aldoximes were similarly appropriate for this SO₂F₂-mediated dehydration process. Besides, the conversion of aliphatic aldoximes into desired nitriles 3ae and 3af were accomplished in excellent yields by simply extending the reaction time.

Subsequently, we were excited to find that the nitrobenzaldoximes including *para-*, *meta-*, and *ortho-*positions, could be used to accomplish the dehydration to afford the corresponding nitrobenzonitriles in quantitative yields when 1.5 equiv of Na_2CO_3 was used as the base in aqueous methanol under SO_2F_2 atmosphere for 30 min (Scheme 3, method a). Meanwhile, excitingly, a one-pot process of converting nitrobenzaldehydes into the corresponding nitro-





D

Y. Zhao et al.

benzonitriles was also achieved in excellent yields (Scheme 3, method b); this was attributed to the optimized solvent of aqueous methanol, which was suitable for both oximation of aldehydes and cyanation of aldoximes (see Supporting Information for screening details). Unfortunately, other aldoximes, such as benzaldoxime (**2a**), 4-methylbenzaldehydoxime (**2b**), and 4-chlorobenzaldoxime (**2e**), were almost completely unresponsive under these adjusted conditions (see Table S2). Nevertheless, a gram-scale reaction was carried out with 4-nitrobenzaldehyde **1i** as model substrate, and product **3i** was formed in excellent yield (96%), which indicates the practicality of the application this one-pot strategy in large batch production of nitriles.

In conclusion, we have developed a rapid, simple, mild and practical process for conversion of aldoximes into nitriles promoted by the novel dehydration system of $SO_2F_2/Et_3N/CH_3CN$.^{15,16} The reaction proceeded with a range of aldoximes in excellent to near quantitative yields to afford the corresponding nitriles, demonstrating the great functional group compatibility and high efficiency of this protocol. Moreover, the eco-friendly conditions of $SO_2F_2/Na_2CO_3/aqueous$ methanol were suitable for converting nitrobenzaldoximes into nitrobenzonitriles. In addition, a one-pot synthetic strategy of obtaining nitrobenzonitriles from nitrobenzaldehydes has been confirmed to be feasible.

Funding Information

We acknowledge financial support from the National Natural Science Foundation of China (no. 20702051), the Natural Science Foundation of Zhejiang Province (LY13B020017).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611840.

References and Notes

- (a) Smith, M. B.; March, J. Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 6th ed; Wiley Interscience: Chichester, 2007. (b) Frizler, M.; Lohr, F.; Furtmann, N.; Kläs, J.; Gütschow, M. J. Med. Chem. 2011, 54, 396. (c) Bagal, D. B.; Bhanage, B. M. Adv. Synth. Catal. 2015, 357, 883. (d) Wang, M. X. Acc. Chem. Res. 2015, 48, 602. (e) Hu, P.; Chai, J. C.; Duan, Y. L.; Liu, Z. H.; Cui, G. L.; Chen, L. Q. J. Mater. Chem. A 2016, 4, 10070.
- (2) (a) Larock, R. C. Comprehensive Organic Transformations, 2nd ed;
 Wiley: New York, **1999**. (b) Anbarasan, P.; Schareina, T.; Beller,
 M. Chem. Soc. Rev. **2011**, 40, 5049.
- (3) (a) Sandmeyer, T. Ber. Dtsch. Chem. Ges. 1884, 17, 1633.
 (b) Rosenmund, K. W.; Struck, E. Ber. Dtsch. Chem. Ges. B. 1919, 52, 1749. (c) Nielsen, M. A.; Nielsen, M. K.; Pittelkow, A. Org. Process Res. Dev. 2004, 8, 1059. (d) Pradal, A.; Evano, G. Chem. Commun. 2014, 50, 11907. (e) Cristau, H. J.; Ouali, A.; Spindler, J. F.; Taillefer, M. Chem. Eur. J. 2005, 11, 2483. (f) Zhang, X.; Xia, A.; Chen, H.; Liu, Y. Org. Lett. 2017, 19, 2118. (g) Ushkov, A. V.; Grushin, V. V. J. Am. Chem. Soc. 2011, 133, 10999.

Downloaded by: Glasgow University Library. Copyrighted material

- (4) (a) Campbell, J. A.; McDougald, G.; McNab, H.; Rees, L. V. C.; Tyas,
 R. G. Synthesis 2007, 3179. (b) Hendrickson, J. B.; Hussoin, M. S.
 J. Org. Chem. 1987, 52, 4137.
- (5) (a) Luca, L. D.; Giacomelli, G.; Porcheddu, A. J. Org. Chem. 2002, 67, 6272. (b) Yadav, L. D. S.; Srivastava, V. P.; Patel, R. Tetrahedron Lett. 2009, 50, 5532. (c) Singh, M. K.; Lakshman, M. K. J. Org. Chem. 2009, 74, 3079. (d) Deton, R. M.; An, J.; Lindovska, P.; Lewis, W. Tetrahedron 2012, 68, 2899. (e) An, X. D.; Yu, S. Y. Org. Lett. 2015, 17, 5064.
- (6) (a) Loupy, A.; Régnier, S. Tetrahedron Lett. 1999, 40, 6221.
 (b) Boruah, M.; Knowar, D. J. Org. Chem. 2002, 67, 7138.
 (c) Gucma, M.; Gołębiewski, W. M. Synthesis 2008, 1997. (d) Rai, A.; Yadav, L. D. S. Eur. J. Org. Chem. 2013, 1889. (e) Song, Y. P.; Shen, D. G.; Zhang, Q. H.; Chen, B.; Xu, G. Y. Tetrahedron Lett. 2014, 55, 639. (f) Ryohei, O.; Kazutoshi, S.; Hiromi, H.; Akira, N.; Tomohiro, M.; Yasuyoshi, M. Synlett 2018, 1465.
- (7) (a) Yang, S. H.; Chang, S. Org. Lett. 2001, 3, 4209. (b) Choi, E.; Lee,
 C.; Na, Y.; Chang, S. Org. Lett. 2002, 4, 2369. (c) Yamaguchi, K.;
 Fujiwara, H.; Ogasawara, Y.; Kotani, M.; Mizuno, N. Angew.
 Chem. Int. Ed. 2007, 46, 3922. (d) Tambara, K.; Pantoş, G. D. Org.
 Biomol. Chem. 2013, 11, 2466. (e) Hyodo, K.; Kitagawa, S.;
 Yamazaki, M.; Uchida, K. Chem. Asian J. 2016, 11, 1348.
 (f) Rapeyko, A.; Climent, M. J.; Corma, A.; Concepcion, P.; Iborra,
 S. ACS Catal. 2016, 6, 4564.
- (8) Holleman-Wiberg's Inorganic Chemistry; Wiberg, N.; Holleman, A. F.; Wiberg, E., Ed.; Academic Press: New York, 2001, 550.
- (9) For the selected SuFEx chemistry, see: (a) Dong, J. J.; Krasnova, L.; Finn, M. G.; Sharpless, K. B. Angew. Chem. Int. Ed. 2014, 53, 9430. (b) Chen, W.; Dong, J. J.; Plate, L.; Mortenson, D. E.; Brighty, G. J.; Li, S.; Liu, Y.; Galmozzi, A.; Lee, P. S.; Hulce, J. J.; Cravatt, B. F.; Saez, E.; Powers, E. T.; Wilson, I. A.; Sharpless, K. B.; Kelly, J. W. J. Am. Chem. Soc. 2016, 138, 7353. (c) Gao, B.; Zhang, L.; Zheng, Q.; Zhou, F.; Klivansky, L. M.; Lu, J.; Liu, Y.; Dong, J. J.; Wu, P.; Sharpless, K. B. Nat. Chem. 2017, 9, 1083. (d) Liu, Z.; Li, J.; Li, S. H.; Li, G.; Sharpless, K. B.; Wu, P. J. Am. Chem. Soc. 2018, 140, 2919. (e) Wang, H.; Zhou, F.; Ren, G.; Zheng, Q.; Chen, H.; Gao, B.; Klivansky, L.; Liu, Y.; Wu, B.; Xu, Q.; Lu, J.; Sharpless, K. B.; Wu, P. Angew. Chem. Int. Ed. 2017, 56, 11203. (f) Marra, A.; Dong, J. J.; Ma, T. C.; Giuntini, S.; Crescenzo, E.; Cerofolini, L.; Martinucci, M.; Luchinat, C.; Fragai, M.; Nativi, C.; Dondoni, A. Chem. Eur. J. 2018, 24, 18981. (g) Guo, T. J.; Meng, G. Y.; Zhan, X. J.; Yang, Q.; Ma, T. C.; Xu, L.; Sharpless, K. B.; Dong, J. J. Angew. Chem. Int. Ed. 2018, 57, 2605. (h) Smedley, C. J.; Zheng, Q. H.; Gao, B.; Li, S. H.; Molino, A.; Duivenvoorden, H. M.; Parker, B. S.; Wilson, D. J. D.; Sharpless, K. B.; Moses, J. E. Angew. Chem. Int. Ed. 2019, 58, 4552.
- (10) (a) Revathi, L.; Ravindar, L.; Leng, J.; Rakesh, K. P.; Qin, H. L. Asian J. Org. Chem. 2018, 7, 662. (b) Epifanov, M.; Foth, P. J.; Gu, F.; Barrillon, C.; Kanani, S. S.; Higman, C. S.; Hein, J. E.; Sammis, G. M. J. Am. Chem. Soc. 2018, 140, 16464. (c) Schimler, S. D.; Cismesia, M. A.; Hanley, P. S.; Froese, R. D. J.; Jansma, M. J.; Bland, D. C.; Sanford, M. S. J. Am. Chem. Soc. 2017, 139, 1452. (d) Hanley, P. S.; Clark, T. P.; Krasovskiy, A. L.; Ober, M. S.; O'Brien, J. P.; Staton, T. S. ACS Catal. 2016, 6, 3515. (e) Zha, G. F.; Fang, W. Y.; Li, Y. G.; Leng, J.; Chen, X.; Qin, H. L. J. Am. Chem. Soc. 2018, 140, 17666. (f) Zhao, C.; Fang, W. Y.; Rakesh, K. P.; Qin, H. L. Org. Chem. Front. 2018, 5, 1835. (g) Fang, W. Y.; Huang, Y. M.; Leng, J.; Qin, H. L. Asian J. Org. Chem. 2018, 7, 751. (h) Fang, W. Y.; Leng, J.; Qin, H. L. Chem. Asian J. 2017, 12, 2323. (i) Zhao, C.; Zha, G. F.; Fang, W. Y.; Rakesh, K. P.; Qin, H. L. Eur. J. Org. Chem. 2019, 1801. (j) Revathi, L.; Ravindar, L.; Moku, B.; Qin, H. L. Org. Chem. Front. 2019, 6, 796. (k) Zhang, X.; Rakesh, K. P.; Qin, H. L.

Y. Zhao et al.

Chem. Commun. **2019**, *55*, 2845. (l) Zha G. F., Fang W. Y., Leng J., Qin H. L.; *Adv. Synth. Catal.*; **2019**, preprint; DOI: 10.1002/adsc.201900104

- (11) Almost simultaneously Qin's team published the results of a study that demonstrated a one-pot method for converting aldehydes into nitriles using 0.55 equiv of NH₂OH and 5.0 equiv of Na₂CO₃, under SO₂F₂ atmosphere in DMSO for 12 h, which exhibits differences from our dehydration conditions, see: Fang, W.-Y.; Qin, H.-L. J. Org. Chem. **2019**, *84*, 5803.
- (12) (a) Li, Y. S.; Xu, N. Z.; Mei, G. Y.; Zhao, Y.; Zhao, Y. Y.; Lyu, J. H.; Zhang, G. F.; Ding, C. R. *Can. J. Chem.* **2018**, *96*, 810. (b) Zhang, G. F.; Ma, D. T.; Zhao, Y. Y.; Zhang, G. H.; Mei, G. Y.; Lyu, J. H.; Ding, C. R.; Shan, S. *ChemistryOpen* **2018**, *7*, 885.
- (13) (a) Nicolaou, K. C.; Vourloumis, D.; Winssinger, N.; Baran, P. S. Angew. Chem. Int. Ed. 2000, 39, 44. (b) Newhouse, T.; Baran, P. S.; Hoffmann, R. W. Chem. Soc. Rev. 2009, 38, 3010.
- (14) Li, S. S.; Wu, L.; Qin, L.; Zhu, Y. Q.; Su, F.; Xu, Y. J.; Dong, L. Org. Lett. 2016, 18, 4214.
- (15) **Converting Aldoximes into the Corresponding Nitriles in Acetonitrile; Typical Procedure:** 4-Chlorobenzaldoxime **2e** (0.137 g, 1.0 mmol), CH₃CN (2.0 mL) and Et₃N (278 μ L, 2.0 mmol) were added into a 25 mL Schlenk flask equipped with magnetic stirrer and rubber stopper. Then the SO₂F₂ gas was introduced into the stirring reaction mixture by slow bubbling from a SO₂F₂ balloon, and the reaction mixture was stirred at

room temperature for 15 min. After the reaction, the mixture was diluted with water and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were then washed with brine, dried over anhydrous Na₂SO₄ and concentrated to dryness. The residue was purified by column chromatography on silica gel (300–400 mesh) with hexane and ethyl acetate to give 4-chlorobenzonitrile **3e**. ¹H NMR (500 MHz, CDCl₃): δ = 7.62 (d, *J* = 8.7 Hz, 2 H), 7.49 (d, *J* = 8.7 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃): δ = 139.6, 133.4, 129.7, 117.9, 110.9.

(16) Converting Nitrobenzaldoximes into Nitrobenzonitriles in Aqueous Methanol; Method a: 4-Nitrobenzaldoxime 2g (166 mg, 1.0 mmol), CH₃OH (2.0 mL), H₂O (0.5 mL) and Na₂CO₃ (159 mg, 1.5 mmol) were added into a 25 mL Schlenk flask equipped with magnetic stirrer and rubber stopper. The SO₂F₂ gas was introduced into the stirring reaction mixture by slow bubbling from a SO₂F₂ balloon, and the reaction mixture was stirred at room temperature for 30 min. After the reaction, the mixture was diluted with water and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were then washed with brine, dried over anhydrous Na₂SO₄ and concentrated to dryness. The residue was purified by column chromatography on silica gel (300-400 mesh) with hexane and ethyl acetate to give the 4nitrobenzonitriles **3g**. ¹H NMR (500 MHz, $CDCl_3$): δ = 8.38 (d, J = 8.9 Hz, 2 H), 7.90 (d, J = 8.9 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃): δ = 150.1, 133.5, 124.3, 118.4, 116.7.