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Transition Metal-Free Synthesis of Thiocyanato- or Nitro-arenes through Diaryliodonium Salts

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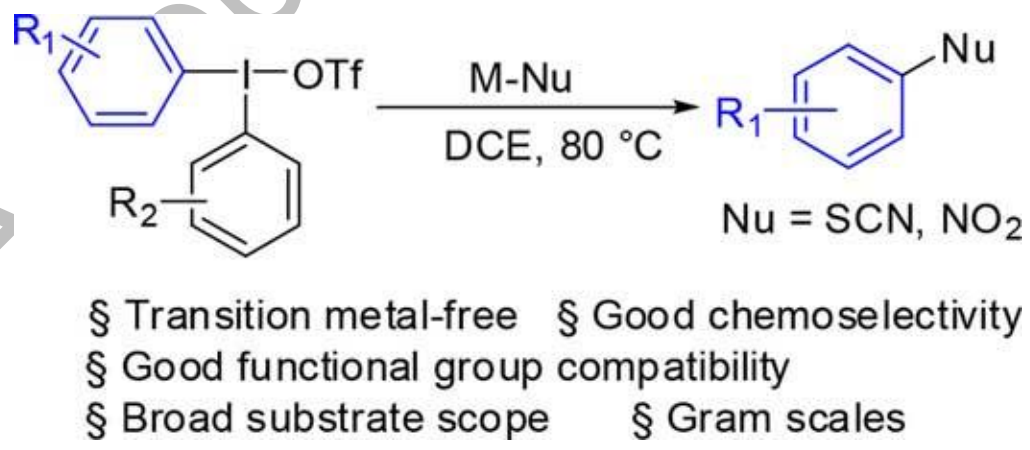
Abstract

A transition metal-free approach to facile synthesis of thiocyanato- and nitro-arenes was developed from KSCN or $NaNO_2$ with diaryliodonium salts in good yields under mild conditions. The reaction was compatible with a variety of sensitive functional substituents such as halides, nitro, and ester groups. The usefulness of arylation products has been realized.



INTRODUCTION

Thiocyanato- and nitro arenes are versatile building blocks for synthesis of organic molecules of higher complexity and these potential scaffolds are frequently found in natural products, pharmaceuticals and commonly exhibit biological activities.[1,2] Some of which are listed in Figure 1.[3] Thus, exploration of new methods for introducing thiocyanato and nitro groups into organic molecules has been of broad interest in recent years.[4,5]

The thiocyanation reaction is one of the most useful carbon−sulfur bond forming reactions.[6] Organic thiocyanates usually served as the synthetic precursors into various sulfur-containing derivatives, such as sulfur heterocycles, thioethers, disulfides, thiols and so on.[7] Traditional methods to synthesize aryl thiocyanates were direct electrophilic thiocyanation of arenes or by Sandmeyer-type reaction *via* nucleophilic substitution of aryl diazonium salts (Scheme 1A).[8] In the past few years, some approaches to synthesis of aryl thiocyanates catalyzed by transition metal catalysts have been investigated, which included the copper promoted or catalyzed nucleophilic replacement of aryl iodides with thiocyanate salts (Scheme 1B),[9] thiocyanation of aryl organometallic compounds (aryllithium, arylzinc compounds and arylboronic acids) (Scheme 1C),[10] and cyanation of organosulfur compounds under transition metal or metal-free conditions (Scheme 1D).[11]

Although great efforts have been devoted to the improvement of these transformations, most of them relied on the use of some special reagents and encountered some drawbacks, such as harsh reaction conditions, limited substrate scope, poor sensitive functional group compatibility, complicated ligands, and trace amount transition metal in the products.

In order to resolve the aforementioned drawbacks, the transition metal-free arylation strategies have been attracted much attention in recent years.[12] Diaryliodonium salts possessing two aryl groups, have been extensively applied as versatile arylation agents for a variety of nucleophiles in transition-metal free conditions due to its easy availability, high reactivity and selectivity, and less toxic reagents.[13,14] For examples, metal-free arylations of α-carban of carbonyl, alcohol, oximes, hydroxylamines, and amides with diaryliodonium salts have been developed.[15] The transformations of diaryliodonium salts with potassium thiocyanate and sodium nitrite have been studied before.[16] In 2009, Dimagno and coworkers reported a detailed effect of reductive-elimination state of diaryliodonium thiocyanate based on computational and experimental studies (Scheme 1E).[16b] Very recently, Yusubov and Zhdankin not only reported a method to prepare triisopropylsilyl-substituted aryliodonium salts but also studied the reactivity of the diaryliodonium salts with KSCN (Scheme 1F).[16c] Although Dimagno and Zhdankin have reported the studies of diaryliodonium salts with KSCN respectively, there were not a general, practical and more detailed investigations of the substrate scope and

compatibility of the functional groups in the diaryliodonium reagents. Recently, we not only reported the synthesis of *α,β*-unstratured *N*-aryl ketonitrones by the *N*-arylation of oximes with diaryliodonium salts, but also developed a tandem C-O and C-N bonds formation through *O*-arylation and [3,3]-rearrangement by diaryliodonium salts to synthesize *N*-aryl benzotriazin-4(1H)-one derivarives.[17] Continuing to investigate arylation for new nucleophiles, we surmised that to explore the substrate scope and functional group compatibility of the diaryliodonoium salts with KSCN and $NaNO_2$ would provide an efficient, practical and useful method to access these organic sulfur- or nitrogen-containing molecules.

DISCUSSION

Initially, we ran the reaction of diphenyliodonium triflate **1a** and KSCN in DMSO at 80 ˚C for 24 h. To our surprise, Phenyl thiocyanate **2a** was observed in 14% yield (Table 1, entry 1). As illustrated in Table 1, the solvents have a great effect on the yield of **2a**, which showed DCE (1,2-dichloroethane) was the best solvent for this transformation (Table 1, entries 1-8). However, the yield of **2a** decreased obviously whatever the temperature was lower or higher (Table 1, entries 8-11). Moreover, when the amount of KSCN increased to 4.0 equiv, the yield of **2a** was improved to 83% (Table 1, entry 13). The by-products of this arylation are PhI and KOTf, which make product **2a** was easily to be purified. In order to improve the solubility of KSCN, $N(n\text{-}Bu)_4F$ was added into the

reaction (Table 1, entries 14-15), we found that when N(*n*-Bu)$_4$F was added only 0.2 equiv, the product **2a** was obtained in 81% yield (Table 1, entry 14). However, increasing N(*n*-Bu)$_4$F would decrease the yield of **2a** (Table 1, entry 15). When KSCN was dropped to 1.0 equiv, the yield of **2a** was afforded in 63% (Table 1, entry 16). These results revealed that the phase-transfer catalyst could decrease the amounts of KSCN and promote the reaction.

To test the scope of the present protocols, a variety of diaryliodonium salts **1** were subjected to the optimal conditions (Table 1, entry 13). As shown in Table 2, a series of desired product **2** were obtained from moderate to good yields. This method was suitable for both electron-rich and electron-deficient either *para*-, *meta*-, or *ortho*- substituents on diaryliodonium salts **1**. Interestingly, when unsymmetric diaryliodonium salts were used, the reaction proceeded with good chemo-selectivity and the more deficient aryl moieties could be more preferably transferred to the desired products (Table 2, entries 9-16).[18] However, for diaryliodonium salt **1i**, both 4-PhO and 4-MeO substituted aryl partners were transferred to the desired products and 4-PhO substituted aryl moiety was transferred as a major product (Table 2, entry 10). The electron-rich substituents on aryl rings are preferable to get high yields than the electron-deficient substituents (Table 2, entries 1-8). This method was compatible with some important functional groups on the aryl ring of the diaryliodonium salts, such as fluorine, bromine, chlorine, methoxy, nitro,

and ester substituents, which could be used to further potential synthetic transformations. The reaction was easily scaled up to 30 mmol and analogue yield was obtained as 0.5 mmol scale (Table 2, entries 1 and 15), which provided a practical method to access these compounds easily.

To be better application of this arylation process, $NaNO_2$ was used as nucleophile in the optimal condition to synthesize nitroarenes. Various diaryliodonium salts **1** was suitable for both electron-rich and electron-deficient groups with either *meta*, *para* or *ortho* substituents in this transformation and the desired products **3** was obtained from moderate and good yields (Table 3). Especially, this method can be used to synthesize *m*-dinitrobenzene (**3g**) easily in 60% yields which was obtained in lower yield for copper-catalyzed strategies (Table 3, entry 7). This method was also compatible with some useful substituents such as halides, nitro, ester groups. Moreover, the reaction can also be easily scaled up to 30 mmol (Table 3, entry 10).

With a variety of thiocyanatoarenes **2** in hand, we decided to investigate the synthetic utility of these compounds as useful intermediates in organic synthesis (Scheme 2-1). As shown in Scheme 2-1, oxidation of **2n** with *m*-chlorobenzoperoxoic acid (*m*-CPBA) at room temperature proceeded to give product **4** in 60% yield. Treatment of **2n** with PhMgBr targeted the cyanide group afford sulphide product **5** in 74% yield, which has

been further applied into synthesis of dibenzothiophene scaffolds.[19] Nitroarenes are extensively utilized in organic synthesis, which inspired us to investigate the further application of **3n** (Scheme 2-2). When **3n** was treated with 2-methylindole proceeded substitution to afford 2,3-disubstituted indole **6** in 65% yield, which has been successfully used to prepare densely functionalized biiodoles, indoloindoles.[20]

CONCLUSIONS

We have developed a transition-metal free transformation of readily available diaryliodonium salts into the corresponding thiocyanato- or nitroarenes in good yields under mild conditions. This method features broad substrate scopes, less-toxic hypervalent iodine reagents, easily operation, gram scalability and excellent functional group compatibilities. This process is not only complementary to existing methods of thiocyanate and nitro group formation, but also extends the applications of diaryliodonium salts with diverse nucleophiles in organic synthesis.

EXPERIMENTAL

General procedure for synthesis of aryl thiocyanates 2: In Schlenk tube was charged with diaryliodonium salts **1** (0.5 mmol) and KSCN (2.0 mmol, 4.0 equiv) in air atmosphere, dissolved in DCE (5 mL). The mixture was stirred vigorously at RT for 5 min. Then, the reaction was stirred at 80 °C and monitored by TLC until **1** was consumed completely (18-24 h). At this time, the DCE was removed under reduced pressure and the

crude product was purified by flash chromatography (dry loading with SiO_2) using eluents (1:50 ethyl acetate:petroleum ether to 10:1) to provide product **2** as oil or solid.

Thiocyanatobenzene (2a),[5g] colorless oil, 56.0 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44-7.42 (m, 2H), 7.36-7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)130.1, 129.9, 129.4, 124.3, 110.4.

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REFERENCES

[1] Some examples of bioactive compounds containing SCN group, see: (a) Hill, H. A. O. In *Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives*; A. A. Newman, Ed.; Academic Press: London, **1975**; (b) Elhalem, E.; Bailey, B. N.; Docampo, R.; Ujvary, I.; Szajnman, S. H.; Rodriguez, J. B. *J. Med. Chem.* **2002**, *45*, 3984; (c) Dutta, S.; Abe, H.; Aoyagi, S.; Kibayashi, C.; Gates, K. S. *J. Am. Chem. Soc.* **2005**, *127*, 15004; (d) Pasquini, S.; Mugnaini, C.; Tintori, C.; Botta, M.; Trejos, A.; Arvela, R. K.; Larhed,

M.; Witvrouw, M.; Michiels, M.; Christ, F.; Debyser, Z.; Corelli, F. *J. Med. Chem.* **2008**, *51*, 5125.

[2] Some examples of bioactive compounds containing NO_2 group, see: (a) Priestap, H. A.; De los Santos, C.; Quirke, J. M. *J. Nat. Prod.* **2010**, *73*, 1979; (b) Piechowska, J.; Huttunen, K.; Wróbel, Z.; Lemmetyinen, H.; Tkachenko, N. V.; D. Gryko, T.; *J. Phys. Chem.* A **2012**, *116*, 9614; (c) Sosič, I.; Mirković, B.; Arenz, K.; Štefane, B.; Kos, J.; Gobec, S. *J. Med. Chem.* **2013**, *56*, 521; (d) Tiwari, R.; Moraski, G. C.; KrchňáK, V.; Miller, P. A.; Colon-Martinez, M.; Herrero, E.; Oliver, A. G.; Miller, M. J. *J. Am. Chem. Soc.* **2013**, *135*, 3539..

[3] (a) Alcaraz, M. L.; Atkinson, S. P.; Cornwall, P.; Foster, A. C.; Gill, D. M.; Humphries, L. A.; Keegan, P. S.; Kemp, R.; Merifield, E.; Nixon, R. A.; Noble, A. J.; O'Beirne, D.; Patel, Z. M.; Perkins, J.; Rowan, P.; Sadler, P.; Singleton, J. T.; Tornos, J.; Watts, A. J.; Woodland, I. A. *Org. Process Res. Dev.* **2005**, *9*, 555; (b) Pasquini, S.; Mugnaini, C.; Tintori, C.; Botta, M.; Trejos, A.; Arvela, R. K.; Larhed, M.; Witvrouw, M.; Michiels, M.; Christ, F.; Debyser, Z.; Corelli, F. *J. Med. Chem.* **2008,** *51*, 5125; (c) Asif, M. *PharmaTutor* **2015**, *3*, 15; (d) Colón, I. G.; González, F. A.; Cordero, M.; Zayas, B.; Velez, C.; Cox, O.; Kumar, A.; Alegría, A. E. *Chem. Res. Toxicol.* **2008**, *21*, 1706.

[4] Some recent examples of formation of SCN group, see: (a) Grant, M. S.; Snyder, H. R. *J. Am. Chem. Soc.* **1960**, *82*, 2742; (b) Toste, F. D.; De Stefano, V.; Still, I. W. J. *Synth. Commun.* **1995**, *25*, 1277; (c) Prakash, O.; Kaur, H.; Batra, H.; Rani, N.; Singh,

S. P.; Moriarty, R. M. *J. Org. Chem.* **2001**, *66*, 2019; (d) Bhalerao, D. S.; Akamanchi, K. G. *Synlett* **2007,** *2007*, 2952; (e) Yadav, J. S.; Reddy, B. V. S.; Murali Krishna, B. B.; *Synthesis*, **2008**, *2008*, 3779; (f) Fan, W.; Yang, Q.; Xu, F.; Li, P. *J. Org. Chem.* **2014**, *79*, 10588; (g) Zhu, D.; Chang, D.; Shi, L. *Chem. Commun.* **2015**, *51*, 7180; (h) Frei, R.; Courant, R.; Wodrich, M. D.; Waser, J. *Chem. Eur. J.* **2015,** *21*, 2662; (i) Tang, F.; Yu, J. T.; Yang, H. T.; Jiang, Y.; Cheng, J. *Chem. Commun.* **2014**, ***50***, 12139.

[5] Some recent examples of formation of NO_2 groups, see: (a) Yan, G. B.; Yang, M. H. *Org. Biomol. Chem.* **2013**, *11*, 2554; (b) Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 12898; (c) Manna, S.; Maity, S.; Rana, S.; Agasti, S.; and Maiti, D. *Org. Lett.* **2012**, *14*, 1736; (d) Zhang, W.; Lou, S. J.; Liu, Y. K.; Xu, Z. Y. *J. Org. Chem.* **2013**, *78*, 5932; (e) Zhang, W.; Zhang, J.; Ren, S. B.; Liu, Y. K. *J. Org. Chem.* **2014**, *79*, 11508; (f) Zhang, W.; Ren, S. B.; Zhang, J.; Liu, Y. K. *J. Org. Chem.* **2015**, *80*, 5973; (g) Liang, Y. F.; Li, X. Y.; Wang, X. Y.; Yan, Y. P.; Feng, P.; Jiao, N. *ACS Catal.* **2015**, *5*, 1956; (h) Liu, J.; Li, J.; Ren, J. M.; Zeng, B. B. *Tetrahedron Lett.* **2014**, *55*, 1581.

[6] (a) Guy, G. R. In *The Chemistry of Cyanates and Their Thio Derivatives*; Patai, S. Ed.; John Wiley& Sons: New York, **1977**; Part 2, P 819; (b) Mitra, S.; Ghosh, M.; Mishra, S.; Hajra, A. *J. Org. Chem.* **2015**, *80*, 8275; (c) De Mico, A.; Margarita, R.; Mariani, A.; Piancatelli, G. *Chem. Commun.* **1997**, *13*, 1237; (c) Maxwell, R. J.; Silbert, L. S.; Russell, J. R.; *J. Org. Chem.* **1977**, *42*, 1510; (d) Zhu, N.; Wang, F.; Chen, P. H.; Ye, J. X.; Liu, G. S. *Org. Lett.* **2015**, *17*, 3580; (e) Liang, Z. L.; Wang, F.; Chen, P. H.;

Liu, G. S. *Org. Lett.* **2015,** *17*, 2438; (f) Yang, H.; Duan, X. H.; Zhao, J. F.; Guo, L. N. *Org. Lett.* **2015**, *17*, 1998.

[7] Examples of thioethers, see: (a) Still, I. W. J.; Toste, F. D. *J. Org. Chem.* **1996**, *61*, 7677; (b) Ke, F.; Qu, Y.; Jiang, Z.; Li, Z.; Wu, D.; Zhou, X. *Org. Lett.* **2011**, *13*, 454; Examples of disulfides, see: (c) Prabhu, K. R.; Ramesha, A. R.; Chandrasekaran, S. *J. Org. Chem.* **1995**, *60*, 7142; (d) Sengupta, D.; Basu, B. *Tetradedron lett.* **2013**, *54*, 2277; Examples of thiols, see: (e) Houk, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 6825; (f) Linderoth, L.; Fristrup, P.; Hansen, M.; Melander, F; Madsen, R.; Andresen, T. L.; Peters, G. H. *J. Am. Chem. Soc.* **2009**, *131*, 12193. Examples of other sulphur compounds, see: (g) Pawliczek, M.; Garve, L. K. B.; Werz, D. B. *Org. Lett.* **2015**, *17*, 1716.

[8] (a) Wood, J. L.; Fieser, L. F. *J. Am. Chem. Soc.* **1941**, *63*, 2323; (b) Pilgram, K.; Phillips, D. D. *J. Org. Chem.* **1965**, *30*, 2388.

[9] Wang, Y. E.; Zhou, Y.; Wang, J. R.; Liu, L.; Guo, Q. X. *Chin. Chem. Lett.* **2006**, *17*, 1283.

[10] (a) Takagi, K.; Takachi, H.; Sasaki, K. *J. Org. Chem.* **1995**, *60*, 6552; (b) Sun, N.; Che, L. S.; Mo, W. M.; Hu, B. X.; Shen, Z. L.; Hu, X. Q. *Org. Biomol. Chem.* **2015**, *13*, 691.

[11] (a) Still, I. W. J.; Watson, I. D. G. *Synth. Commun.* **2011**, *31*, 1355; (b) Wang, Z. H.; Ji, X. M.; Hu, M. L.; Tang, R. Y. *Tetrahedron Lett.* **2015**, *56*, 5067.

[12] Transition metal-free arylation examples, see: (a) Ravi, M.; Chauhan, P.; Kant, R.; Shukla, S. K.; Yadav, R. P. *J. Org .Chem.* **2015**, *80*, 5369; (b) Wang, D. W.; Ge, B. Y.; Li, L.; Shan, J.; Ding, Y. Q. *J. Org. Chem.* **2014**, *79*, 8607; (c) Bhojgude, S. S.; Kaicharla, T.; Biju, A. T. *Org. Lett*, **2013**, *15*, 5452; (d) Basavanag, U. M. V.; Dos Santos, A.; El Kaim, L.; Gamez-Montano, R.; Grimaud, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 7194; (e) Gao, H. Y.; Ess, D. H.; Yousufuddin, M.; Kürti, L. *J. Am. Chem. Soc.* **2013**, *135*, 7086; (f) Chen, W. C.; Hsu, Y. C.; Shih, W. C.; Lee, C. Y.; Chuang, W. H.; Tsai, Y. F.; Chen, P. P. Y.; Ong, T. G. *Chem. Commun.* **2012**, *48*, 6702.

[13] A review for transition metal-free arylation with diaryliodonium salts, see: Merritt, E. A.; Olofsson, B. *Angew. Chem. Int. Ed.* **2009**, *48*, 9052.

[14] Some examples for synthesis of diaryliodonium salts, see: (a) Bielawski, M.; Aili, D.; Olofsson, B. *J. Org. Chem.* **2008**, *73*, 4602; (b) Bielawski, M.; Zhu, M.; Olofsson, B. *Adv. Synth. Catal.* **2007**, *349*, 2610.

[15] Some examples of O or N-arylation process, see: (a) Dey, C.; Lindsted, E.; Olofsson, B. *Org. Lett.* **2015**, *17*, 4554; (b) Monastyrskyi, A.; Namelikonda, N. K.; Manestsch, R. *J. Org. Chem.* **2015**, *80*, 2513; (c) Lindstedt, E.; Ghosh, R.; Olofsson, B. *Org. Lett*. **2013**, *15*, 6070; (d) Ghosh, R.; Olofsson, B. *Org. Lett*. **2014**, *16*, 1830; (e) Gao, H. Y.; Xu, Q. L.; Keene, C.; Kürti, L. *Chem. Eur. J.* **2014**, *20*, 8883; (f) Ghosh, R.; Stridfeldt, E.; Olofsson, B. *Chem. Eur. J.* **2014**, *20*, 8888; (g) Yang, Y.; Wu, X. S.; Han, J. W.; Mao, S.; Qian, X. F.; Wang, L. M. *Eur. J. Org. Chem.* **2014**, *2014*, 6854; (h) Guo, F. L.; Wang, L.

M.; Wang, P. Q.; Yu, J. J.; Han, J. W. *Asian J. Org. Chem.* **2012**, *1*, 218; (i) Jalalian, N.; Petersen, T. B.; Olofsson, B. *Chem. Eur. J.* **2012**, *18*, 14140.

[16] (a) Lubinkowski, J. J.; Gomez, M.; Calderon, J. L.; McEwen, W. E. *J. Org. Chem.* **1978**, *43*, 2432; (b) Wang, B. J.; Graskemper, J. W.; Qin, L. L.; Dimagno, S. G. *Angew. Chem. Int. Ed*. **2010**, *49*, 4079; (c) Yusubov, M. S.; Svitich, D. Y.; Yoshimura, A.; Kastern, B. J.; Nemylin, V. N.; Zhdankin, V. V. *Eur. J. Org. Chem.* **2015**, 4831.

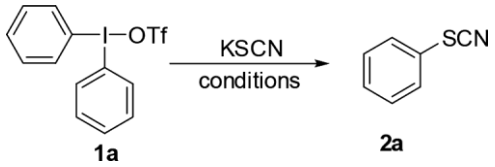
[17] (a) Ma, X. P.; Shi, W. M.; Mo, X. L.; Li, X. H.; Li, L. G.; Pan, C. X.; Chen, B.; Su, G. F.; Mo, D. L. *J. Org. Chem.* **201**5, *80*, 10098; (b) Shi, W. M.; Ma, X. P.; Pan, C. X.; Su, G. F.; Mo, D. L. *J. Org. Chem.* **2015**, *80*, 11175.

[18] When unsymmetric diaryliodonium salts were used, some of the desired products were obtained in lower yields because the other aryl moieties were also transferred to the thiocyanatoarenes and the yields were 5-15%. For studies on the chemoselectivity on diaryliodonium salts, see: Malmgren, J.; Santoro, S.; Jalalian, N.; Himo, F.; Olofsson, B. *Chem. Eur. J.* **2013**, *19*, 10334

[19] Saravanan, P.; Anbarasan, P. *Org. Lett.* **2014**, *16*, 848.

[20] Kumar, S.; Rathore, V.; Verma, A.; Prasad, C. D.; Kumar, A.; Yadav, A.; Jana, S.; Meenakshi, M. S.; Kumar, S. *Org. Lett.* **2015**, *17*, 82.

Table 1. Optimization of reaction.[a]



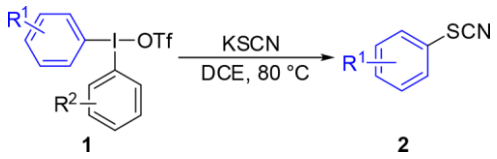
1a 2a

Entry	solvent	T (˚C)	**2a** %[b]
1	DMSO	80	14
2	DMF	80	63
3	MeCN	80	68
4	MeOH	80	20
5	THF	80	34
6	dioxane	80	31
7	toluene	80	64
8	DCE	80	74
9	DCE	60	51
10	DCE	100	57
11	DCE	120	52
12	DCE	80	80[c]

13	DCE	80	83[d]
14	DCE	80	81[e]
15	DCE	80	57[f]
16	DCE	80	63[g]

[a] Reaction conditions: **1a** (0.5 mmol), KSCN (1.0 mmol, 2.0 equiv), solvent (5 mL), 18-24 h; [b] Isolated yields; [c] KSCN (1.5 mmol, 3.0 equiv); [d] KSCN (2.0 mmol, 4.0 equiv); [e] KSCN (1.0 mmol, 2.0 equiv), N(*n*-Bu)$_4$F (0.2 equiv); [f] KSCN (1.0 mmol, 2.0 equiv), N(*n*-Bu)$_4$F (1.0 equiv); [g] KSCN (0.5 mmol, 1.0 equiv), N(*n*-Bu)$_4$F (0.2 equiv).

Table 2. The scope of diaryliodonium salts **1** with KSCN[a]



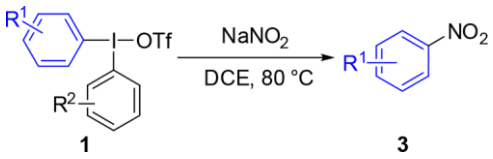
1 **2**

entry	**1**	R^1	R^2	**2**	Yield %[b]
1	**1a**	H	H	**2a**	83 (80)[c]
2	**1b**	4-MeO	4-MeO	**2b**	95
3	**1c**	4-*t*-Bu	4-*t*-Bu	**2c**	78
4	**1d**	4-Cl	4-Cl	**2d**	78
5	**1e**	4-Br	4-Br	**2e**	60
6	**1f**	4-F	4-F	**2f**	67
7	**1g**	3-NO_2	3-NO_2	**2g**	60
8	**1h**	2-Me	2-Me	**2h**	73
9	**1aa**	H	4-MeO	**2a**	65
10	**1i**	4-PhO	4-MeO	**2i**	56[d]
11	**1j**	4-Ph	4-MeO	**2j**	70
12	**1k**	4-*i*-Pr	4-MeO	**2k**	70

13	**1l**	4-CF_3	4-MeO	**2l**	69
14	**1m**	3-Br	4-MeO	**2m**	65
15	**1n**	2-Br	4-MeO	**2n**	86 (75)[e]
16	**1o**	4-CO_2Me	H	**2o**	65

[a] Reaction conditions: **1** (0.5 mmol), KSCN (2.0 mmol, 4.0 equiv), DCE (5 mL), 18-24 h; [b] Isolated yields; [c] **1a** (30 mmol) was used; [d] **2b** was also isolated with 25% yield; [e] **1n** (30 mmol) was used.

Table 3. The scope of diaryliodonium salts **1** with $NaNO_2$[a]

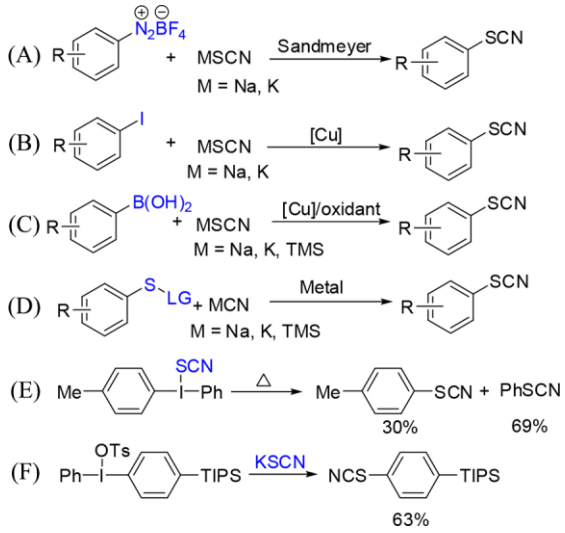


1 **3**

Entry	**1**	R^1	R^2	**3**	Yield %[b]
1	**1a**	H	H	**3a**	73
2	**1b**	4-MeO	4-MeO	**3b**	68
3	**1c**	4-*t*-Bu	4-*t*-Bu	**3c**	69
4	**1d**	4-Cl	4-Cl	**3d**	76
5	**1e**	4-Br	4-Br	**3e**	88
6	**1f**	4-F	4-F	**3f**	54
7	**1g**	3-NO_2	3-NO_2	**3g**	60
8	**1j**	4-Ph	4-MeO	**3j**	68
9	**1l**	4-CF_3	4-MeO	**3l**	63
10	**1n**	2-Br	4-MeO	**3n**	85 (78)[c]
11	**1o**	4-CO_2Me	H	**3o**	74

[a] Reaction conditions: **1** (0.5 mmol), $NaNO_2$ (2.0 mmol, 4.0 equiv), DCE (5 mL), 18-24 h; [b] Isolated yields; [c] **1n** (30 mmol) was used.

Scheme 1. Previous strategies for synthesis of thiocyanates.



Scheme 2. Transformation of **2n** and **3n**.

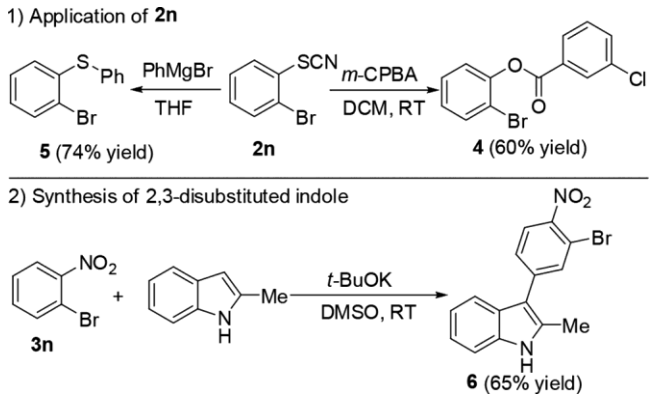
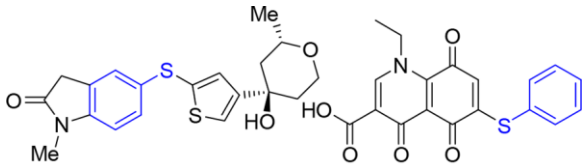
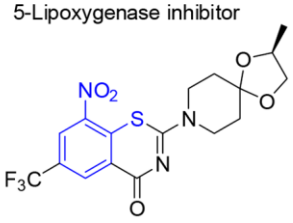


Figure 1. Selected examples of bioactive compounds with sulfides and nitro arenes.

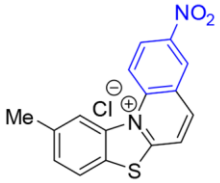


AZD4407
5-Lipoxygenase inhibitor

HIV-1 integrase inhibitor



BTZ043



NBQ-91