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三异丙基硅烷(TIPS)保护苯酚的无过渡金属催化区域选择性硫氰化反应

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摘要 芳基硫氰酸酯化合物在有机化学中非常重要, 广泛存在于农用化学品、药品和材料中. 以 NH_4SCN 为硫氰化试剂, 过氧单磺酸钾/($2KHSO_5•KHSO_4•K_2SO_4$, oxone)为氧化剂, 实现了三异丙基硅烷(TIPS)保护的苯酚衍生物无过渡金属催化区域选择性硫氰化反应. 在温和的反应条件下, 以良好至优异的收率实现了转化, 并且多种官能团对反应条件都有良好的耐受性. 该方法的实用性在麝香草酚、戊甲酚和苯乙基间苯二酚等生物活性分子的硫氰化反应中得到了很好的体现.

关键词 硫氰化; 三异丙基硅烷(TIPS)保护的苯酚; 无过渡金属催化; 自由基阳离子

Transition-Metal-Free Regioselective Thiocyanation of Triisopropylsilane (TIPS)-Protected Phenols

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Abstract Arylthiocyanate compounds are crucial in organic chemistry. They have widespread applications in agrochemicals, pharmaceuticals, and materials chemistry. Herein, the transition metal-free regioselective thiocyanation of triisopropylsilane (TIPS)-protected phenol derivatives was achieved using NH_4SCN as thiocyanation reagent and potassium peroxymonosulfonate/($2KHSO_5•KHSO_4•K_2SO_4$, oxone) as the oxidant. The conversion was achieved in good to excellent yields under mild reaction conditions. Further, various functional groups were well tolerated in these reaction conditions. The practicability of this method was demonstrated in the thiocyanation of bioactive molecules, such as thymol, amylcresol, and phenethyl resorcinol.

Keywords thiocyanation; triisopropylsilane (TIPS)-protected phenols; transition-metal-free ; radical cation

1 Introduction

Aryl thiocyanate compounds are common intermediates in synthesizing target molecules in pharmaceutical and materials chemistry.[1] Many aryl thiocyanates exhibit highly potent biological and pharmacological activities and are essential building blocks of many bioactive heterocycles and agrochemicals.[2] Additionally, aryl thiocyanates are versatile precursors for preparing various useful organosulfur compounds, such as benzonitrile,[3] trifluoromethyl sulfide,[4] *S*-thiocarbamate,[5] thiophenol,[6] disulfide compounds,[7] thioethers,[8] thioesters,[9] and sulfonyl cyanides.[5] Because of their importance, a substantial amount of research is dedicated to developing various methods to synthesize these aryl thiocyanates. Traditionally, aryl thiocyanate compounds are obtained by cross-coupling aryl halides,[10] aryl diazonium salts (Sandmeyer reaction),[11] and aryl boronic acids.[12] Although these traditional methods facilitate the synthesis of various aryl thiocyanates, the widespread application of these methods is hindered by using toxic transition metal reagents, prefunctionalized substrates, and harsher reaction conditions. Therefore, the

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direct thiocyanation of aromatic compounds is one of the most important and convenient methods to form carbon-sulfur bonds. Some reports of direct thiocyanation conditions of aromatic compounds at an early stage include antimony $SbCl_5/Pb(SCN)_2$,[13] $Zn(SCN)_2/Cl_2$,[14] $Mn(OAc)_3/NH_4SCN$,[15] $Cu(SCN)_2/Cl_2$,[16] and such others. These methods also rely heavily on toxic metals, eventually generating large amounts of heavy metal waste, which is harmful to the environment. A perfect alternative to this problem is a practical, efficient, highly selective strategy involving transition-metal-free catalysis.[17] Consequently, chemists have been striving to achieve transition metal-free direct C—H functionalization of organic molecules.[18]

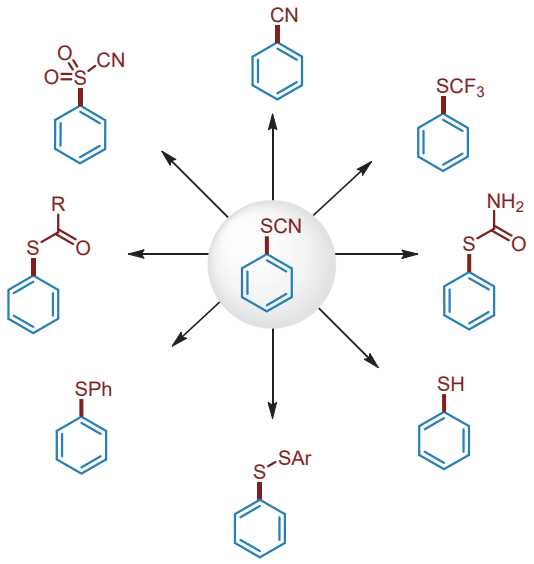


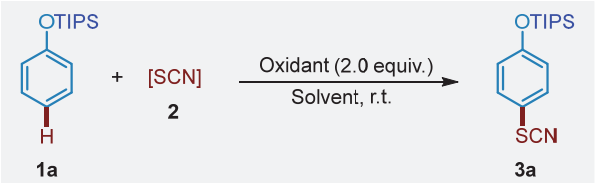
Figure 1 Arylthiocyanate compounds as key intermediates with multiple functional groups

Among the various metal-free and visible-light-catalyzed thiocyanation reactions reported, most strategies have focused on imidazole heterocycles, indoles, and nitrogen-containing activated heterocycles.[19] Further, the thiocyanation of aromatic amines and nitrogen heterocycles has also been reported to be feasible.[20] Due to their intrinsic electronic properties, there are relatively few systematic studies on the thiocyanation of phenol derivatives.[21] Phenol derivatives are common building blocks in bioactive molecules, agrochemicals, and natural products, so developing safe and efficient synthetic methods for their highly selective thiocyanation is essential.[22] Compared with other thiocyanation reagents, NH_4SCN is inexpensive and commercially available.[23] This study reports a method for the transition metal-free regioselective thiocyanation of triisopropylsilane (TIPS)-protected phenols under mild conditions using commercially available and inexpensive NH_4SCN as the cyano group source and oxone as the oxidant. This method systematically studies the thiocyanation of phenolic compounds and can tolerate a variety of TIPS-protected phenolic compounds, including pharmaceutical molecules and bioactive compounds.

2 Results and discussion

TIPS-protected phenol **1a** was selected as a model substrate for optimizing the reaction conditions and exploring the effects of different thiocyanation reagents, oxidants, and solvents on the reaction (Table 1). Initially, different thiocyanation reagents were screened using oxone (potassiumperoxomonosulfate) as the oxidizing agent and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the solvent. KSCN reacted rapidly at room temperature within 1 h to give *para*-selective thiocyanation products in 95% yield (Entry 1). In sharp contrast, the AgSCN reaction did not yield the expected product (Entry 2). When NH_4SCN was used as the thiocyanate source, the reaction yield was 96% with excellent regioselectivity (Entry 3). Next, the effects of different oxidants on the reaction were screened. When oxone was replaced by $K_2S_2O_8$ or H_2O_2, the product yield decreased slightly (Entries 4, 5). Using oxygen and *tert*-butyl hydroperoxide (TBHP) as oxidants did not result in product formation (Entries 5, 6). Finally, various solvents were screened. Solvent optimization proved to be the key to high conversion and selectivity with HFIP producing the best yields. The reaction did not proceed smoothly when 1,2-dichloroethane (DCE), EtOH, dimethyl sulfoxide (DMSO), dioxane, and CH_3CN were used as solvents (Entries 7～15). Notably, the reaction could not proceed without oxone as the oxidant (Entry 16), indicating that oxone

Table 1 Optimization of the reaction conditions[a]

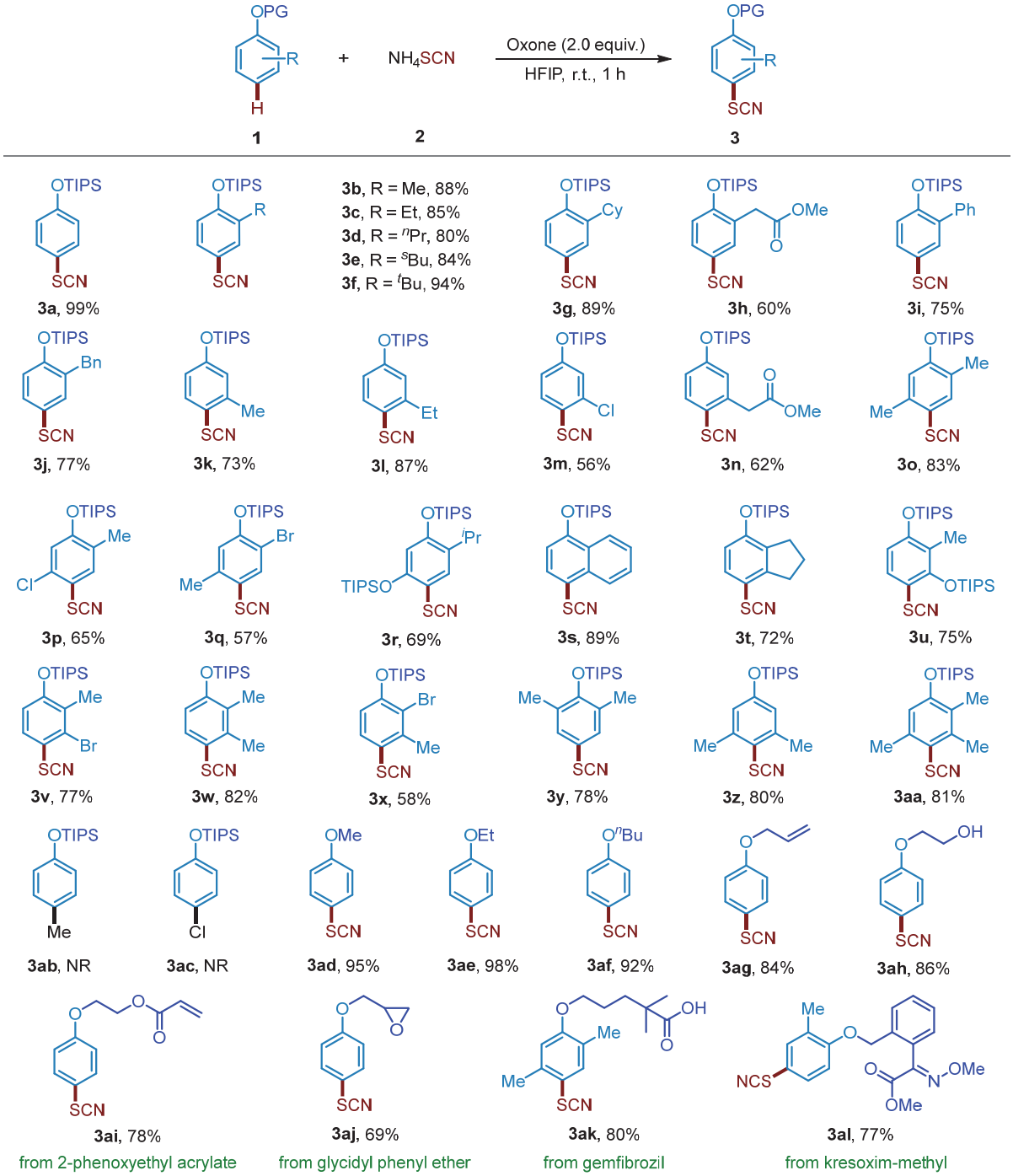


Entry	Oxidant	Solvent	[SCN] source	Yield/%
1	Oxone	HFIP	KSCN	92
2	Oxone	HFIP	AgSCN	NR
3	Oxone	HFIP	NH_4SCN	99
4	$K_2S_2O_8$	HFIP	NH_4SCN	86
5	H_2O_2	HFIP	NH_4SCN	83
6	O_2	HFIP	NH_4SCN	Trace
7	TBHP	HFIP	NH_4SCN	NR
8	Oxone	H_2O	NH_4SCN	NR
9	Oxone	DCE	NH_4SCN	NR
10	Oxone	EtOH	NH_4SCN	NR
11	Oxone	DMSO	NH_4SCN	NR
12	Oxone	DMF	NH_4SCN	NR
13	Oxone	Dioxane	NH_4SCN	NR
14	Oxone	THF	NH_4SCN	NR
15	Oxone	CH_3CN	NH_4SCN	NR
16	—	HFIP	NH_4SCN	NR

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), oxidant (2.0 equiv.), HFIP (1.0 mL) at room temperature for 1 h in a sealed tube, isolated yield. TBHP＝*tert*-butyl hydroperoxide. HFIP＝1,1,1,3,3,3-Hexafluoro-2-propanol. Oxone＝Potassiumperoxomonosulfate ($2KHSO_5•KHSO_4•K_2SO_4$).

is key to forming a radical, cationic intermediate critical in the oxidation of TIPS-protected phenol.

Delightfully, various substrates underwent facile direct and regioselective thiocyanation under optimized reaction conditions, affording the desired products in good to excellent yields (Scheme 1). Notably, direct thiocyanation occurred at the *para*-position of the phenol derivative with high selectivity, and no thiocyanation at other sites was observed. The thiocyanation of various *ortho*-substituted phenols was also investigated. The reaction of phenols, bearing electron-donating groups of methyl, ethyl (**3c**), propyl (**3d**), butyl (**3e**), *tert*-butyl (**3f**), and cyclohexyl (**3g**), proceeded smoothly to obtain the corresponding thiocyanated products in moderate to excellent yields. The *para*-thiocyanated products were also delivered in moderate yields when with methyl acetate (**3h**), phenyl (**3i**), and benzyl (**3j**) groups as *ortho*-substituents. Further, the *meta*-methyl (**3k**) or *meta*-ethyl (**3l**) substituted phenols provided the thiocyanated products with good yields and high *para*-selectivity. Due to the electron-withdrawing effect of the



Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), oxone (2.0 equiv.), HFIP (1.0 mL) at room temperature for 1 h in a sealed tube, isolated yield.

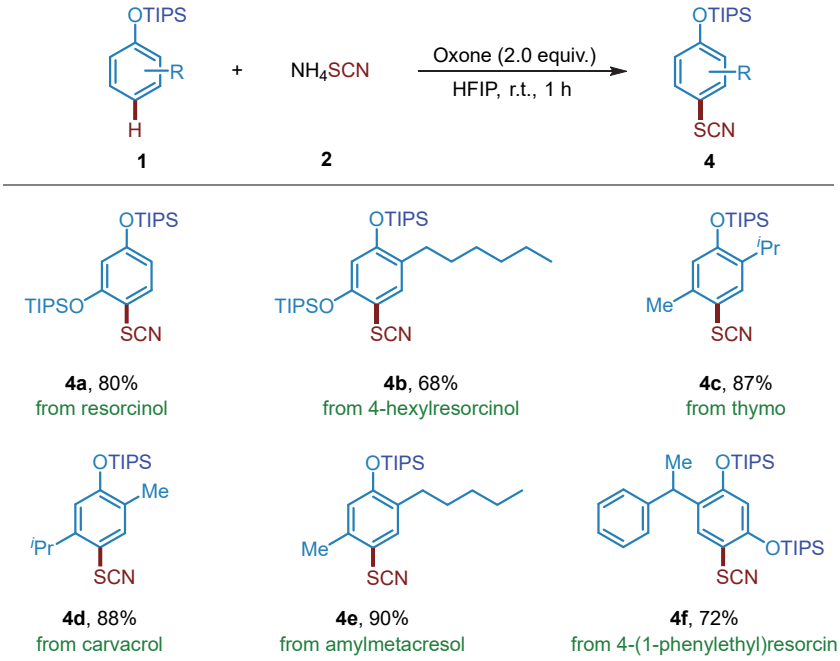
Scheme 1 Scope of thiocyanation with phenol derivatives

substituent, a decrease in the product yield was observed using TIPS-protected 3-chlorophenol (**3m**) and 3-methylphenol acetate (**3n**). Various 2,5-disubstituted phenols (**3o**～**3r**) also provided the corresponding products in moderate to good yields, highlighting the synthetic importance of this thiocyanation reaction. Both 1-naphthol (**3s**) and 4-hydroxyhydrindene (**3t**) were well tolerated and generated the corresponding thiocyanation products. Likewise, various 2,3-disubstituted phenols (**3u**～**3x**) delivered the desired thiocyanation products with excellent regioselectivity and reactivity. On the other hand, 2,6-disubstituted (**3y**), 3,5-disubstituted (**3z**), and 2,3,5-trisubstituted (**3aa**) phenols also showed good thiocyanation activity. The reaction cannot occur when the *para*-position of the aromatic hydrocarbon substrates contain substituents such as methyl and chlorine (**3ab**～**3ac**). In addition to triisopropylsilane-protected substrates, the suitability of different protected phenol derivatives was also investigated. Alkyl-protected substrates such as anisole, phenetole, and phenylbutyl ether all proceeded smoothly with excellent yields and regioselectivities (**3ad**～**3ag**). Protecting groups containing hydroxyl and alkenyl structural units, such as propenylphenyl ether (**3ah**), 2-phenoxyethan-1-ol (**3ai**) and 2-phenoxyethyl acrylate (**3aj**) are also suitable for this reaction. Through this protocol, thiocyanate functional groups can be easily introduced into bioactive molecules and drug molecules, such as phenyl glycidyl ether (**3aj**), gemfibrozil (**3ak**) and kresoxim-methyl (**3al**). It suggests that this protocol has potential applications in new drug development and discovery of drug-like molecules.

The late modification and functionalization of existing drug molecules must be considered while developing novel drugs and discovering drug-like molecules.[24] The application value of this strategy was further demonstrated by performing regioselective thiocyanation reactions on a variety of biologically active phenolic compounds, all of which showed good compatibility. TIPS-protected resorcinol **4a** (pesticide intermediate), 4-hexylresorcinol **4b** (anthelmintic), thymol **4c** (fungicide), carvacrol **4d** (sanitary fungicide) and amylmetacresol **4e** (treatment of mouth and throat infections) proceeded smoothly in the reaction, providing thiocyanated product in good yield and high para-selectivity. Importantly, phenylethylresorcinol **4f** (skin whitening agent) with multiple aromatic structures also achieved single-site thiocyanation in good yields (Scheme 2).

A gram-scale reaction was performed under standard conditions to examine the scalability of this protocol. The reaction proceeded smoothly, leading to thiocyanated product **3a** in 99% yield (Scheme 3A). The TIPS protecting group was easily removed under basic conditions with excellent yield (**5**). The deprotected product was further transformed, and the thiocyano group was converted to a thiotrifluoromethyl group (**6**) with excellent yield in the presence of $TMSCF_3$ and Cs_2CO_3 (Scheme 3B). These synthetic transitions further demonstrate the practical value of this reaction.

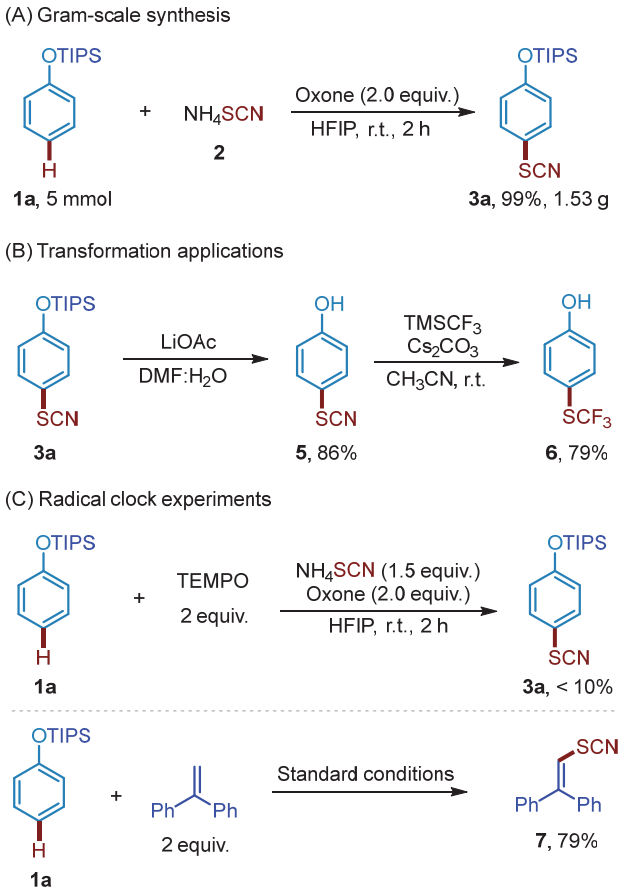
A free radical trapping experiment was conducted to explore the mechanism of thiocyanation reaction. Under standard conditions, ＜10% the thiocyanate product was obtained after adding 2 equiv. of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Oxone decomposes to produce strong oxidant sulfate anions ($SO_4^{-\bullet}$ or $HSO_5^{-\bullet}$).[25] It is known that sulfate anions interact with low ionization potential aromatics to generate free radical cations.[26] After adding TEMPO, the yield of thiocyanation products



Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), oxone (2.0 equiv.), HFIP (1.0 mL) at room temperature for 1 h in a sealed tube, isolated yield.

Scheme 2 Late-stage C—H thiocyanation of pharmaceutically important molecules

decreased significantly, which certified that free radical cations in the reaction system were effectively removed. Subsequently, the radical scavenger 1,1-stilbene was added under standard conditions. Likewise, no corresponding product was detected, but compound **7** was obtained in 79% yield (Scheme 3C). We speculate that this is due to excess 1,1-stilbene reacting with thiocyanate anions. These experimental results indicated that the reaction involves a free radical process.

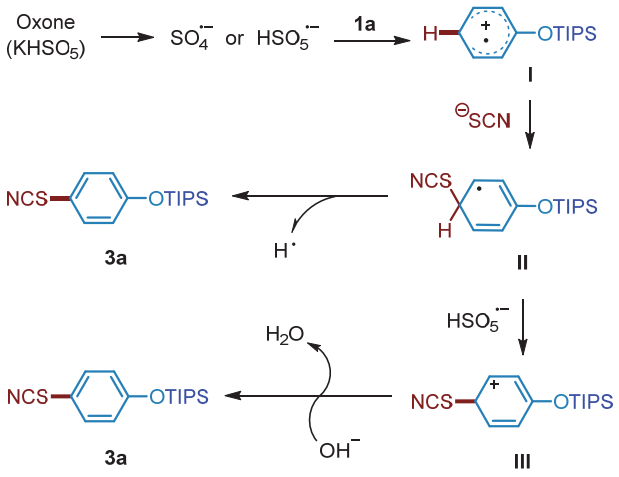


Scheme 3 Synthetic applications and radical clock experiments

Based on the findings of this study and previous literature, a plausible reaction mechanism was proposed (Scheme 4).[20a,27] First, oxone decomposes to produce a strong oxidant sulfate radical anion ($SO_4^{\cdot-}$ or $HSO_5^{\cdot-}$), which in turn oxidizes aromatic compounds to form a free radical cation intermediate **I**. Subsequently, the thiocyanate anion undergoes nucleophilic addition to the cationic intermediate 4-H to form free radical intermediate **II**. Ultimately, the loss of hydrogen radicals in **II** will yield the desired compound **3a**. Alternatively, further oxidation of intermediate **II** will lead to the formation of cationic intermediate **III**. Finally, H^+ is removed by OH^- in the system to obtain the desired product **3a**.

3 Conclusions

In summary, we systematically studied the thiocyanation reaction of TIPS-protected phenols under mild conditions with excellent yield and regioselectivity without transition metal catalysis. Simple and efficient thiocyanation was performed using commercially available and inexpensive oxone and NH_4SCN to tolerate a variety of functional groups and successfully applied to the modification of various bioactive compounds. Most importantly, the protocol was shown to be easily scalable to gram-scale reactions, demonstrating its practical utility in organic synthesis.



Scheme 4 Possible mechanism of phenol thiocyanation

4 Experimental section

4.1 General experimental information

All reactions were carried out under an air atmosphere (*ca.* 15 mL volume) equipped with a magnetic stirring element. Unless otherwise stated, all commercial reagents were used without additional purification. Column chromatography was undertaken on silica gel (200～300 mesh) using a proper eluent system. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Inova-400 MHz, Inova-300 MHz, Bruker DRX-400 or Bruker DRX-500 instruments with $CDCl_3$ as solvent. High-resolution mass spectrometry (HRMS) was performed on a Bruker micro TOF-Q instrument using electrospray ionization (ESI). TIPS-protected phenol derivatives were prepared according to references. The solvents and reagents were obtained from commercial suppliers and used without further purification.

4.2 General synthesis procedure

A mixture of triisopropyl(phenoxy)silane (**1a**, 0.2 mmol), NH_4SCN (0.3 mmol) and oxone (2.0 equiv.) in HFIP (1 mL) in a sealed tube was stirred at room temperature for 1 h. After the reaction, the HFIP was removed through evaporation. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (V ∶ V = 1 ∶ 25) to afford the pure desired product **3a** (Caution: HFIP is highly toxic and corrosive. It should be used in a fume cupboard with all appropriate precautions taken).

4.3 Gram scale reaction for synthesis of **3a**

A mixture of triisopropyl(phenoxy)silane (**1a**, 5.0 mmol), NH_4SCN (6.5 mmol) and oxone (2.0 equiv.) in HFIP (20 mL) in a sealed tube was stirred at room temperature for 1 h. After the reaction, the HFIP was removed through evaporation. The residue was extracted with ethyl acetate and washed with water. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (V∶V=1∶25) to afford the pure desired product **3a**.

4.4 Characterization of compounds

Triisopropyl(4-thiocyanatophenoxy)silane (**3a**): Colorless oil. 60.9 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J=8.8 Hz, 2H), 6.92 (d, J=8.8 Hz, 2H), 1.29～1.24 (m, 3H), 1.10 (d, J=7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 133.7, 121.9, 114.3, 111.7, 17.9, 12.8. HRMS (ESI) calcd for $C_{16}H_{25}NNaOSSi$ $[M+Na]^+$ 330.1318, found 330.1321.

Triisopropyl(2-methyl-4-thiocyanatophenoxy)silane (**3b**): Yellow oil. 56.6 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J=2.2 Hz, 1H), 7.25 (dd, J=8.4, 2.6 Hz, 1H), 6.80 (d, J=8.5 Hz, 1H), 2.24 (s, 3H), 1.35～1.26 (m, 3H), 1.11 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.5, 134.7, 131.5, 130.9, 119.5, 113.5, 111.9, 18.1, 17.1, 13.1. HRMS (ESI) calcd for $C_{17}H_{27}NNaOSSi$ $[M+Na]^+$ 344.1475, found 344.1481.

Triisopropyl(2-ethyl-4-thiocyanatophenoxy)silane (**3c**): Yellow oil. 57.1 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J=2.5 Hz, 1H), 7.26 (dd, J=8.5, 2.6 Hz, 1H), 6.81 (d, J=8.5 Hz, 1H), 2.65 (q, J=7.5 Hz, 2H), 1.38～1.25 (m, 3H), 1.21 (t, J=7.5 Hz, 3H), 1.12 (d, J=7.5 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.0, 137.2, 133.2, 130.9, 119.5, 113.6, 111.9, 23.7, 18.1, 13.9, 13.1. HRMS (ESI) calcd for $C_{18}H_{29}NNaOSSi$ $[M+Na]^+$ 358.1631, found 358.1637.

Triisopropyl(2-propyl-4-thiocyanatophenoxy)silane (**3d**): Yellow oil. 55.9 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J=2.5 Hz, 1H), 7.25 (dd, J=8.5, 2.5 Hz, 1H), 6.80 (d, J=8.5 Hz, 1H), 2.62～2.55 (m, 2H), 1.66～1.56 (m, 2H), 1.38～1.24 (m, 3H), 1.11 (d, J=7.4 Hz, 18H), 0.96 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 135.7, 134.1, 130.9, 119.6, 113.5, 112.0, 32.8, 23.1, 18.1, 14.1, 13.1. HRMS (ESI) calcd for $C_{19}H_{31}NNaOSSi$ $[M+Na]^+$ 372.1788, found 372.1791.

Triisopropyl(2-(*sec*-butyl)-4-thiocyanatophenoxy)silane (**3e**): Yellow oil. 61.1 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J=2.6 Hz, 1H), 7.25 (dd, J=8.5, 2.6 Hz, 1H), 6.81 (d, J=8.5 Hz, 1H), 3.16 (q, J=7.0 Hz, 1H), 1.70～1.47 (m, 2H), 1.39～1.24 (m, 3H), 1.19 (d, J=7.0 Hz, 3H), 1.12 (dd, J=7.5, 2.0 Hz, 18H), 0.86 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 140.4, 131.2, 130.6, 119.6, 113.8, 112.0, 33.7, 29.8, 20.4, 18.1, 13.2, 12.1. HRMS (ESI) calcd for $C_{20}H_{33}NNaOSSi$ $[M+Na]^+$ 386.1944, found 386.1950.

Triisopropyl(2-(*tert*-butyl)-4-thiocyanatophenoxy)silane (**3f**): Colorless oil. 68.5 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J=2.5 Hz, 1H), 7.29 (dd, J=8.5, 2.5 Hz, 1H), 6.79 (d, J=8.4 Hz, 1H), 1.44～1.35 (m, 12H), 1.15 (d, J=7.5 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 141.7, 131.7, 131.1, 120.4, 113.3, 112.1, 35.3, 29.5, 18.3, 13.5. HRMS (ESI) calcd for $C_{20}H_{33}NNaOSSi$ $[M+Na]^+$ 386.1944, found 386.1947.

Triisopropyl(2-cyclohexyl-4-thiocyanatophenoxy)silane (**3g**): Yellow oil. 69.3 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J=2.5 Hz, 1H), 7.25 (dd, J=8.5, 2.6 Hz, 1H), 6.80 (d, J=8.5 Hz, 1H), 3.05～2.94 (m, 1H), 1.90～1.82 (m, 4H), 1.80～1.72 (m, 1H), 1.41～1.25 (m, 8H), 1.12 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.3, 140.6, 131.1, 130.6, 119.6, 113.8, 112.1, 37.3, 33.1, 27.0, 26.3, 18.1, 13.1. HRMS (ESI) calcd for $C_{22}H_{35}NNaOSSi$ $[M+Na]^+$ 412.2101, found 412.2108.

Methyl 2-(5-thiocyanato-2-((triisopropylsilyl)oxy)phenyl)acetate (**3h**): Yellow oil. 45.5 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J=2.5 Hz, 1H), 7.36 (dd, J=8.5, 2.6 Hz, 1H), 6.85 (d, J=8.5 Hz, 1H), 3.68 (s, 3H), 3.64 (s, 2H), 1.34～1.26 (m, 3H), 1.10 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.2, 156.4, 135.2, 132.6, 127.5, 119.5, 113.8, 111.7, 52.1, 36.0, 18.0, 13.1. HRMS (ESI) calcd for $C_{19}H_{29}NNaO_3SSi$ $[M+Na]^+$ 402.1530, found 402.1534.

Triisopropyl((5-thiocyanato-[1,1'-biphenyl]-2-yl)oxy)-silane (**3i**): Colorless oil. 57.5 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J=2.6 Hz, 1H), 7.46～7.32 (m, 6H), 6.95 (d, J=8.5 Hz, 1H), 1.18～1.07 (m, 3H), 0.95 (d, J=7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.3, 137.5, 135.6, 134.8, 132.2, 129.6, 128.2, 127.7, 121.1, 114.4, 17.9, 12.9. HRMS (ESI) calcd for $C_{22}H_{29}NNaOSSi$ $[M+Na]^+$ 406.1631, found 406.1638.

Triisopropyl(2-benzyl-4-thiocyanatophenoxy)silane (**3j**): Colorless oil. 61.2 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.27 (m, 3H), 7.23 (d, J=7.3 Hz, 1H), 7.20～7.13 (m, 3H), 6.87 (d, J=8.5 Hz, 1H), 4.00 (s, 2H), 1.37～1.23 (m, 3H), 1.09 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 139.6, 134.7, 134.1, 131.6, 128.9, 128.7, 126.4, 119.7, 113.9, 111.9, 36.1, 18.1, 13.2. HRMS (ESI) calcd for $C_{22}H_{31}NNaOSSi$ $[M+Na]^+$ 420.1788, found 420.1791.

Triisopropyl(3-methyl-4-thiocyanatophenoxy)silane (**3k**): Colorless oil. 47.0 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J=8.5 Hz, 1H), 6.83 (d, J=2.4 Hz, 1H), 6.75 (dd, J=8.5, 2.4 Hz, 1H), 2.48 (s, 3H), 1.32～1.20 (m, 3H), 1.10 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 142.8, 135.5, 123.1, 119.2, 113.7, 21.0, 17.9, 12.8. HRMS (ESI) calcd for $C_{17}H_{27}NNaOSSi$ $[M+Na]^+$ 344.1475, found 344.1484 .

Triisopropyl(3-ethyl-4-thiocyanatophenoxy)silane (**3l**): Colorless oil. 58.4 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J=8.5 Hz, 1H), 6.84 (d, J=2.7 Hz, 1H), 6.76 (dd, J=8.5, 2.8 Hz, 1H), 2.82 (q, J=7.5 Hz, 2H), 1.31～1.22 (m, 6H), 1.10 (d, J=7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.9, 148.4, 135.9, 121.5,

119.3, 113.2, 111.9, 27.6, 18.0, 14.7, 12.8. HRMS (ESI) calcd for $C_{18}H_{29}NNaOSSi$ $[M+Na]^+$ 358.1631, found 358.1633.

Triisopropyl(3-chloro-4-thiocyanatophenoxy)silane (**3m**): Colorless oil. 38.3 mg, 56% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, J=8.7 Hz, 1H), 7.01 (d, J=2.6 Hz, 1H), 6.86 (dd, J=8.7, 2.6 Hz, 1H), 1.31～1.23 (m, 3H), 1.10 (d, J=7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 135.9, 133.4, 122.3, 120.3, 114.4, 110.2, 17.9, 12.7. HRMS (ESI) calcd for $C_{16}H_{24}ClNNaOSSi$ $[M+Na]^+$ 364.0929, found 364.0932.

Methyl 2-(2-thiocyanato-5-((triisopropylsilyl)oxy)phenyl)acetate (**3n**): Colorless oil. 47.0 mg, 62% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, J=8.4 Hz, 1H), 6.89～6.84 (m, 2H), 3.84 (s, 2H), 3.72 (s, 3H), 1.30～1.22 (m, 3H), 1.09 (d, J=7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.7, 158.9, 138.9, 136.7, 123.5, 120.8, 114.7, 111.6, 52.5, 39.9, 17.9, 12.8. HRMS (ESI) calcd for $C_{19}H_{29}NNaO_3SSi$ $[M+Na]^+$ 402.1530, found 402.1532.

Triisopropyl(2,5-dimethyl-4-thiocyanatophenoxy)silane (**3o**): White solid, m.p. 64～65 ℃. 55.7 mg, 83% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37 (s, 1H), 6.71 (s, 1H), 2.44 (s, 3H), 2.20 (s, 3H), 1.35～1.25 (m, 4H), 1.12 (d, J=7.4 Hz, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 139.7, 136.5, 128.7, 120.9, 112.7, 111.6, 20.7, 18.1, 16.5, 13.1. HRMS (ESI) calcd for $C_{18}H_{29}NNaOSSi$ $[M+Na]^+$ 335.1739, found 335.1732.

Triisopropyl(5-bromo-2-methyl-4-thiocyanatophenoxy)-silane (**3p**): Yellow oil. 52.1 mg, 65% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47 (s, 1H), 7.03 (s, 1H), 2.21 (s, 3H), 1.35～1.25 (m, 3H), 1.11 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 134.1, 130.9, 123.0, 121.7, 115.7, 110.7, 18.1, 16.8, 13.0. HRMS (ESI) calcd for $C_{17}H_{26}BrNNaOSSi$ $[M+Na]^+$ 422.0580, found 422.0585.

Triisopropyl(2-bromo-5-methyl-4-thiocyanatophenoxy)-silane (**3q**): Colorless oil. 45.6 mg, 57% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 6.98～6.60 (m, 1H), 2.44 (s, 3H), 1.37～1.27 (m, 3H), 1.13 (d, J=7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 141.7, 138.4, 122.1, 114.6, 113.5, 110.7, 20.9, 18.1, 13.1. HRMS (ESI) calcd for $C_{17}H_{26}BrNNaOSSi$ $[M+Na]^+$ 422.0580, found 422.0583.

((4-Isopropyl-6-thiocyanato-1,3-phenylene)bis(oxy))bis-(triisopropylsilane) (**3r**): Colorless oil. 70.2 mg, 69% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30 (s, 1H), 6.37 (s, 1H), 3.25 (p, J=6.9 Hz, 1H), 1.36～1.23 (m, 6H), 1.19 (d, J=6.9 Hz, 6H), 1.13 (dd, J=9.1, 7.3 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.8, 153.2, 133.8, 129.6, 111.9, 109.2, 104.9, 26.6, 22.9, 18.1, 18.1, 13.4, 13.3. HRMS (ESI) calcd for $C_{28}H_{51}NNaO_2SSi_2$ $[M+Na]^+$ 544.3071, found 544.3071.

Triisopropyl((4-thiocyanatonaphthalen-1-yl)oxy)silane (**3s**): Yellow oil. 63.7 mg, 89% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, J=8.3 Hz, 1H), 8.29 (d, J=8.4 Hz, 1H), 7.79 (d, J=8.1 Hz, 1H), 7.71 (ddd, J=8.3, 6.9, 1.2 Hz, 1H), 7.60 (ddd, J=8.0, 6.8, 0.9 Hz, 1H), 6.88 (d, J=8.1 Hz, 1H), 1.50～1.37 (m, 3H), 1.18 (d, J=7.5 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.0, 135.2, 134.5, 129.0, 128.7, 126.5, 124.9, 123.9, 112.2, 111.6, 110.6, 18.2, 13.2. HRMS (ESI) calcd for $C_{20}H_{27}NNaOSSi$ $[M+Na]^+$ 380.1475, found 380.1477.

Triisopropyl((7-thiocyanato-2,3-dihydro-1*H*-inden-4-yl)oxy)silane (**3t**): Colorless oil. 50.1 mg, 72% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, J=8.7 Hz, 1H), 6.66 (d, J=8.4 Hz, 1H), 3.08 (t, J=7.5 Hz, 2H), 2.96 (t, J=7.5 Hz, 2H), 2.13 (p, J=7.6 Hz, 2H), 1.33～1.22 (m, 3H), 1.10 (d, J=7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.0, 149.8, 136.8, 132.6, 118.2, 111.4, 109.7, 33.5, 30.9, 24.2, 18.1, 13.0. HRMS (ESI) calcd for $C_{19}H_{29}NNaOSSi$ $[M+Na]^+$ 370.1631, found 370.1636.

((2-Methyl-4-thiocyanato-1,3-phenylene)bis(oxy))bis-(triisopropylsilane) (**3u**): Yellow oil. 74.1 mg, 75% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, J=8.7 Hz, 1H), 6.55 (d, J=8.7 Hz, 1H), 2.17 (s, 3H), 1.47～1.35 (m, 3H), 1.33～1.25 (m, 3H), 1.12 (dd, J=12.7, 7.4 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4, 154.9, 129.4, 121.4, 113.5, 111.8, 106.2, 18.1, 14.5, 13.1, 11.7. HRMS (ESI) calcd for $C_{26}H_{47}NaO_2SSi_2$ $[M+Na]^+$ 516.2758, found 516.2763.

Triisopropyl(3-bromo-2-methyl-4-thiocyanatophenoxy)-silane (**3v**): Colorless oil. 61.7 mg, 77% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J=8.6 Hz, 1H), 6.79 (d, J=8.6 Hz, 1H), 2.67 (s, 3H), 1.39～1.28 (m, 3H), 1.13 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.7, 142.4, 133.4, 120.1, 117.8, 114.7, 111.1, 22.5, 18.1, 13.1. HRMS (ESI) calcd for $C_{17}H_{26}BrNNaOSSi$ $[M+Na]^+$ 422,0580, found 422,0582.

Triisopropyl (2,3-dimethyl-4-thiocyanatophenoxy)-silane (**3w**): Colorless oil. 55.0 mg, 82% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J=8.6 Hz, 1H), 6.72 (d, J=8.6 Hz, 1H), 2.48 (s, 3H), 2.23 (s, 3H), 1.35～1.26 (m, 3H), 1.12 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 141.1, 132.3, 129.9, 117.1, 113.9, 111.9, 18.3, 18.1, 13.6, 13.1. HRMS (ESI) calcd for $C_{18}H_{29}NNaOSSi$ $[M+Na]^+$ 358.1631, found 358.1635.

Triisopropyl(2-bromo-3-methyl-4-thiocyanatophenoxy)-silane (**3x**): Yellow oil. 46.4 mg, 58% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43 (dd, J=5.0, 2.5 Hz, 1H), 6.84 (d, J=8.7 Hz, 1H), 2.38 (s, 3H), 1.34～1.25 (m, 3H), 1.11 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.8, 131.9, 128.8, 127.2, 118.4, 117.2, 111.0, 18.1, 17.7, 13.1. HRMS (ESI) calcd for $C_{17}H_{26}BrNNaOSSi$ $[M+Na]^+$ 422.0580, found 422.0579.

Triisopropyl(2,6-dimethyl-4-thiocyanatophenoxy)silane (**3y**): Colorless oil. 55.5 mg, 78% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.16 (s, 2H), 2.26 (s, 6H), 1.35～1.26 (m, 3H), 1.12 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 132.2, 130.8, 113.8, 18.1, 17.9, 14.4. HRMS (ESI) calcd for $C_{18}H_{29}NNaOSSi$ $[M+Na]^+$ 358.1631, found 358.1636.

Triisopropyl(3,5-dimethyl-4-thiocyanatophenoxy)silane (**3z**): White solid, m.p. 42～43 ℃. 53.7 mg, 80% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.69 (s, 2H), 2.53 (s, 6H), 1.30～1.22 (m, 3H), 1.10 (d, J=7.3 Hz, 18H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ: 158.6, 144.7, 120.7, 113.4, 111.3, 22.3, 18.0, 12.8. HRMS (ESI) calcd for $C_{18}H_{29}NNaOSSi$ $[M+Na]^+$ 358.1631, found 358.1634.

Triisopropyl(2,3,5-trimethyl-4-thiocyanatophenoxy)-silane (**3aa**): Yellow colloid. 56.6 mg, 81% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.65 (s, 1H), 2.53 (d, J=11.6 Hz, 6H), 2.20 (s, 3H), 1.35～1.26 (m, 3H), 1.12 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 143.0, 141.0, 127.2, 118.7, 113.6, 111.7, 22.5, 19.2, 18.1, 13.6, 13.2. HRMS (ESI) calcd for $C_{19}H_{31}NNaOSSi$ $[M+Na]^+$ 372.1788, found 372.1791.

1-Methoxy-4-thiocyanatobenzene (**3ad**): Colorless liquid. 31.4 mg, 95% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.52～7.46 (m, 2H), 6.96～6.91 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.3, 133.8, 115.9, 113.8, 111.7, 55.6.

1-Ethoxy-4-thiocyanatobenzene (**3ae**): Colorless liquid. 35.1 mg, 98% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.48～7.44 (m, 2H), 6.93～6.88 (m, 2H), 4.01 (q, J=7.0 Hz, 2H), 1.40 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.7, 133.8, 116.3, 113.4, 111.7, 63.9, 14.6.

1-Butoxy-4-thiocyanatobenzene (**3af**): Yellowish liquid. 38.1 mg, 92% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.49～7.43 (m, 2H), 6.95～6.89 (m, 2H), 3.95 (t, J=6.5 Hz, 2H), 1.82～1.68 (m, 2H), 1.54～1.43 (m, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9, 133.8, 116.3, 113.4, 111.7, 68.1, 31.1, 19.2, 13.8.

1-(Allyloxy)-4-thiocyanatobenzene (**3ag**): Yellowish liquid. 32.1 mg, 84% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.50～7.45 (m, 2H), 6.98～6.91 (m, 21H), 6.02 (ddd, J=22.4, 10.5, 5.3 Hz, 1H), 5.41 (dd, J=17.3, 1.6 Hz, 1H), 5.31 (dd, J=10.5, 1.5 Hz, 1H), 4.54 (dt, J=5.3, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 133.7, 132.4, 118.2, 116.6, 113.9, 111.8, 69.0.

2-(4-Thiocyanatophenoxy)ethan-1-ol (**3ah**): Yellowish liquid. 33.6 mg, 86% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.53～7.45 (m, 2H), 6.99～6.93 (m, 2H), 4.13～4.03 (m, 2H), 3.97 (t, J=4.5 Hz, 2H), 2.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.5, 133.9, 116.5, 114.4, 111.7, 69.7, 61.3. HRMS (ESI) calcd for $C_9H_9NNaO_2S$ $[M+Na]^+$ 218.0246, found 218.0241.

2-(4-Thiocyanatophenoxy)ethyl acrylate (**3ai**): Yellowish liquid. 38.9 mg, 78% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51～7.46 (m, 2H), 6.98～6.93 (m, 2H), 6.43 (dd, J=17.3, 1.4 Hz, 1H), 6.14 (dd, J=17.3, 10.4 Hz, 1H), 5.86 (dd, J=10.4, 1.4 Hz, 1H), 4.52～4.48 (m, 2H), 4.23～4.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.0, 160.2, 133.8, 131.6, 127.9, 116.5, 114.5, 111.5, 66.2, 62.6. HRMS (ESI) calcd for $C_{12}H_{11}NNaO_3S$ $[M+Na]^+$ 272.0352, found 272.0355.

2-((4-Thiocyanatophenoxy)methyl)oxirane (**3aj**): Yellowish liquid. 28.6 mg, 69% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51～7.47 (m, 2H), 6.99～6.94 (m, 2H), 4.27 (dd, J=11.1, 2.9 Hz, 1H), 3.93 (dd, J=11.1, 5.9 Hz, 1H), 3.35 (ddt, J=5.7, 4.2, 2.7 Hz, 1H), 2.91 (dd, J=4.9, 4.1 Hz, 1H), 2.75 (dd, J=4.9, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 133.8, 116.6, 114.7, 111.6, 69.1, 50.0, 44.6. HRMS (ESI) calcd for $C_{10}H_9NNaO_2S$ $[M+Na]^+$ 230.0246, found 230.0245.

5-(2,5-Dimethyl-4-thiocyanatophenoxy)-2,2-dimethyl-pentanoic acid (**3ak**): White solid, m.p. 61～63 ℃; 49.1 mg, 80% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34 (s, 1H), 6.71 (s, 1H), 3.94 (t, J=6.0 Hz, 2H), 2.48 (s, 3H), 2.17 (s, 3H), 1.87～1.78 (m, 2H), 1.77～1.70 (m, 2H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.7, 159.2, 140.1, 135.9, 126.7, 113.6, 111.9, 111.6, 68.2, 42.0, 36.7, 25.0, 24.9, 20.9, 15.6. HRMS (ESI) calcd for $C_{16}H_{21}NnaO_3S$ $[M+Na]^+$ 330.1134, found 330.1138.

Methyl (*E*)-2-(methoxyimino)-2-(2-((2-methyl-4-thiocyanatophenoxy)methyl)phenyl)acetate (**3al**): Yellow solid, 104～106 ℃; 57.0 mg, 77% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51 (dd, J=7.6, 1.6 Hz, 1H), 7.48～7.35 (m, 2H), 7.36～7.28 (m, 2H), 7.22 (dd, J=7.4, 1.6 Hz, 1H), 6.80 (d, J=8.6 Hz, 1H), 5.00 (s, 2H), 4.01 (d, J=0.7 Hz, 3H), 3.82 (d, J=0.8 Hz, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.1, 158.1, 149.1, 134.7, 134.1, 131.0, 129.1, 128.7, 127.9, 127.5, 113.5, 112.6, 111.6, 68.5, 63.8, 52.9, 16.1. HRMS (ESI) calcd for $C_{19}H_{18}N_2NaO_4S$ $[M+Na]^+$ 393.0879, found 393.0885.

((4-Thiocyanato-1,3-phenylene)bis(oxy))bis(triisopropylsilane) (**4a**): Colorless oil. 76.8 mg, 80% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, J=8.6 Hz, 1H), 6.56 (dd, J=8.6, 2.5 Hz, 1H), 6.45 (d, J=2.4 Hz, 1H), 1.33 (dt, J=14.8, 7.4 Hz, 3H), 1.28～1.18 (m, 3H), 1.14 (d, J=7.4 Hz, 18H), 1.09 (d, J=7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 155.4, 132.2, 114.7, 111.6, 111.1, 106.2, 18.1, 18.0, 13.1, 12.8. HRMS (ESI) calcd for $C_{25}H_{45}NNaO_2SSi_2$ $[M+Na]^+$ 502.2602, found 502.2605.

(4-Hexyl-6-thiocyanato-1,3-phenylene)bis(oxy))bis-(triisopropylsilane) (**4b**): Yellow oil. 76.7 mg, 68% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26 (s, 1H), 6.38 (s, 1H), 2.58～2.50 (m, 2H), 1.55 (p, J=7.8, 7.4 Hz, 2H), 1.37～1.24 (m, 12H), 1.18～1.06 (m, 36H), 0.94～0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.3, 153.2, 132.5, 128.3, 111.8, 109.3, 104.8, 31.9, 30.3, 30.2, 29.4, 22.7, 18.1, 18.1, 14.2, 13.3, 13.2. HRMS (ESI) calcd for $C_{31}H_{57}NNaO_2SSi_2$ $[M+Na]^+$ 586.3541, found 586.3542.

Triisopropyl(2-isopropyl-5-methyl-4-thiocyanato-phenoxy)silane (**4c**): Colorless oil. 63.3 mg, 87% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.40 (s, 1H), 6.71 (s, 1H), 3.30 (p, J=6.9 Hz, 1H), 2.45 (s, 3H), 1.38～1.29 (m, 3H), 1.21 (d, J=6.9 Hz, 6H), 1.13 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.8, 139.7, 138.8, 132.7, 120.9, 113.0, 111.7, 26.8, 22.7, 20.8, 18.2, 13.2. HRMS (ESI) calcd for $C_{20}H_{33}NNaOSSi$ $[M+Na]^+$ 386.1944, found 386.1950.

Triisopropyl(5-isopropyl-2-methyl-4-thiocyanato-phenoxy)silane (**4d**): Colorless oil. 64.3 mg, 88 % yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.41 (s, 1H), 6.79 (s, 1H), 3.41 (hept, J=6.8 Hz, 1H), 2.21 (s, 3H), 1.34～1.27 (m, 3H), 1.24 (d, J=6.8 Hz, 6H), 1.13 (d, J=7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3, 149.9, 136.7, 128.6, 116.7, 112.3, 111.7, 31.4, 23.6, 18.1, 16.4, 13.1. HRMS (ESI) calcd for $C_{20}H_{33}NNaOSSi$ $[M+Na]^+$ 386.1944,

found 386.1951.

Triisopropyl(5-methyl-2-pentyl-4-thiocyanatophenoxy)-silane (**4e**): Colorless oil. 70.5 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (s, 1H), 6.71 (s, 1H), 2.60～2.54 (m, 2H), 2.44 (s, 3H), 1.62～1.52 (m, 2H), 1.39～1.28 (m, 7H), 1.12 (d, J=7.4 Hz, 18H), 0.90 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.5, 139.7, 135.9, 133.3, 120.9, 112.7, 111.7, 31.9, 30.4, 29.7, 22.7, 20.8, 18.1, 14.2, 13.2. HRMS (ESI) calcd for $C_{22}H_{37}NNaOSSi$ $[M+Na]^+$ 414.2257, found 414.2262.

((4-(1-Phenylethyl)-6-thiocyanato-1,3-phenylene)bis-(oxy))bis(triisopropylsilane) (**4f**): Yellow oil. 84.1 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.31 (m, 3H), 7.29～7.23 (m, 3H), 6.48 (s, 1H), 4.59 (q, J=7.2 Hz, 1H), 1.65 (d, J=7.2 Hz, 3H), 1.44～1.38 (m, 3H), 1.37～1.28 (m, 3H), 1.23 (d, J=7.1 Hz, 18H), 1.15 (d, J=6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 153.8, 145.7, 131.8, 131.4, 128.4, 127.6, 126.1, 111.7, 109.1, 104.9, 37.5, 21.5, 18.1, 18.0, 13.4, 13.3. HRMS (ESI) calcd for $C_{33}H_{52}NNaO_2SSi_2$ $[M+Na]^+$ 606.3228, found 606.3231.

4-((Trifluoromethyl)thio)phenol (**6**): Colorless solid, 56～59 °C; 30.7 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58～7.52 (m, 2H), 6.90～6.85 (m, 2H), 5.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 138.7, 129.7 (q, J=308.1 Hz), 116.7, 115.6 (d, J=2.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −43.9.

Supporting Information Experimental procedures and full spectroscopic data for all new compounds (**3a**～**3al**, **4a**～**4f**). The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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