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电化学促进的五元芳香杂环与硫氰酸铵氧化交叉脱氢偶联反应

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摘要 报道了一种无化学氧化剂、无外加电解质条件下电化学促进的五元芳香杂环化合物(吡唑、咪唑、呋喃和噻吩)与硫氰酸铵发生氧化交叉脱氢偶联反应合成硫氰基五元芳香杂环化合物的方法. 反应中, 硫氰酸铵发挥着电解质和硫氰化试剂的双重作用, 简化了反应体系.

关键词 五元芳香杂环化合物; 电化学合成; 脱氢偶联反应; 双作用; 绿色化学

Electrochemical Oxidative Cross-Dehydrogenative Coupling of Five-Membered Aromatic Heterocycles with NH_4SCN

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Abstract A practical method for the synthesis of various thiocyanated 5-membered aromatic heterocycles through electrochemical cross-coupling of heterocycles (pyrazoles, pyrroles, furans and thiophenes) with NH_4SCN under chemical oxidant- and exogenous electrolyte-free conditions was developed. NH_4SCN played dual roles of a supporting electrolyte and a thiocyanated reagent, and thus simplify the reaction system.

Keywords five-membered heterocycles; electrochemical synthesis; cross-dehydrogenative coupling reaction; dual roles; green chemistry

1 Introduction

The sustainable and efficient construction of functionalized heterocycles is an important task in synthetic chemistry.[1] 5-Membered aromatic heterocycles, including pyrazoles, pyrroles, furans and thiophenes widely distributed in a large spectrum of natural products and synthetic pharmaceuticals.[2] It is worth noting that pharmaceutical studies have shown that the interaction between various functional groups in the molecule, mainly including the heteroaromatic nucleus and its functional group. This interplay has a significant impact on the biological activity of the molecule or its medicinal value *in vivo*. Chemists have also focused the study of structure-activity relationships on the integration of various functional groups into heterocycles. Among various heterocycle derivatives, the thiocyanated heterocycles not only exhibit a broad range of valuable biological and pharmaceutical activities,[3] but also act as versatile synthetic intermediates for synthetic transformations.[4] Therefore, methodologies for synthesizing such derivatives have been widely investigated.[5]

The oxidative cross-dehydrogenative coupling reaction is regarded as one of the powerful methodologies for forging carbon-carbon/heteroatom bonds given its atom-, step-economy and the easy availability of raw materials.[6] On the basis of this synthetic strategy, a series of synthetic methods for thiocyanated 5-membered heterocycles have been developed with low cost inorganic thiocyanate salts as the thiocyanate source over the past years (Scheme 1a).[7]

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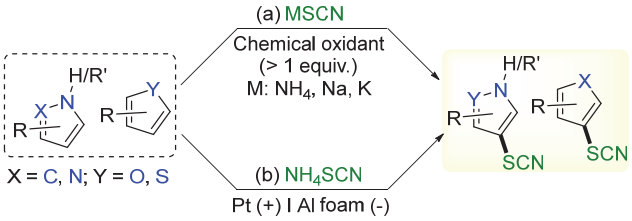
Despite these advances, the usage of excess chemical oxidants reduces the atom economy of the whole process and causes safety concerns, especially for large-scale production. In addition, the strong oxidation conditions can narrow the functional group tolerance and limit the substrate scope. Therefore, an environment-friendly and practical method for the synthesis of such compounds under mild and strong oxidant-free conditions would be highly desirable.



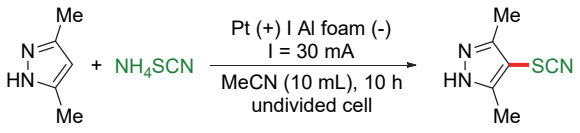
Scheme 1 Synthesis of thiocyanated five-membered heterocycles

Electrochemical organic synthesis is seeing a substantial resurgence as a greener alternative to traditional synthetic strategies involving redox processes.[8] As traceless electrons are essentially the reagent utilized for the redox process, the employment of large amounts of often harmful oxidants or reductants can be avoided. Therefore, electrochemical syntheses are considered "inherently green" and impressive achievements have been made over the past years.[9] However, the atom economy and efficiency of most of the electrochemical reactions are compromised by the requirement of stoichiometric amount of supporting electrolytes. As a consequence, it is highly desirable to exploit exogenous electrolyte-free electrochemical reaction. As part of our continuous efforts to develop green synthesis reactions,[10] we report herein on an eco-friendly and practical method for the synthesis of thiocyanated five-membered heterocycles through electrochemical cross-coupling reactions under chemical oxidant- and exogenous electrolyte-free conditions (Scheme 1b).

2 Results and discussion

Our research began by the exploration of coupling reaction between 3,5-dimethylpyrazole (**1a**) and NH_4SCN (**2a**) in a simple undivided cell equipped with a platinum plate anode Pt (+) and an aluminium foam plate cathode Al foam (−) as the working electrode pairs (Table 1). To our delight, the electrochemical reaction proceeded selectively and efficiently in MeCN under 30 mA constant current electrolysis at ambient temperature and gave the target 4-thiocyanated product **3aa** in 91% GC yield (88% isolated yield, Table 1, Entry 1). Next, a series of electrode pairs were investigated and the effect of the Pt (+)/Al foam (−) electrode pair on the transformation was better than the other electrode pairs (Entries 2～9). Performing the reaction with KSCN or NaSCN as the thiocyanate source resulted in lower yields of **3aa** (Entries 10 and 11). Subsequently, a series of solvents were tested, and replacement of MeCN with DMF delivered a 16% yield of **3aa**, while only a trace amount of **3aa** was detected when employing DMSO, EtOH or acetone as the reaction medium (Entries 12～15). Decreasing the constant current from 30 mA to 15 mA affected the reaction slightly (Entry 16). Finally, no reaction took place without the electric current under otherwise equal conditions. Thus, the conversion could be precisely controlled by switching the electric current on or off (Entry 17).

Table 1 Optimization of reaction conditions[a]



1a **2** **3a**

Entry	Condition	Yield[b]/%
1	No change	91 (88)[c]
2	Pt(+)|Pt(−) instead of Pt(+)|Al foam (−)	72
3	Pt(+)|C(−) instead of Pt(+)|Al foam (−)	82
4	Pt(+)|Fe(−) instead of Pt(+)|Al foam (−)	84
5	Pt(+)|Cu(−) instead of Pt(+)|Al foam (−)	16
6	C (+)|Pt(−) instead of Pt(+)|Al foam (−)	89
7	C(+)|C(−) instead of Pt(+)|Al foam (−)	38
8	C(+)|Al foam (−) instead of C(+)|Pt(−)	75
9	RVC(+)|Al foam (−) instead of Pt(+)|Al foam (−)	85
10	KSCN instead of NH_4SCN	67
11	NaSCN instead of NH_4SCN	82
12	DMF instead of MeCN	16
13	DMSO instead of MeCN	Trace
14	EtOH instead of MeCN	Trace
15	Acetone instead of MeCN	Trace
16	15 mA, 15 h	87
17	Without electric current	N.R.

[a] Conditions: Pt (15 mm×10 mm×0.1 mm) as the anode, Al foam (15 mm×8 mm×2 mm) as the cathode, constant current=30 mA, **1a** (0.5 mmol), **2** (1.5 mmol), MeCN (10 mL), room temperature, in air, 10 h, undivided cell; [b] GC yields using dodecane as an internal reference; [c] isolated yields.

Under the optimal reaction conditions, the coupling of a variety of five-membered heterocycles with NH_4SCN was investigated (Table 2). Firstly, *N*-unsubstituted pyrazoles were tested in the present reaction and the desired products (**3a** and **3b**) were afforded in 88% and 86% yields. Pyrazoles modified with alkyl, cycloalkyl, alkenyl, and benzyl groups at the nitrogen atom reacted with NH_4SCN efficiently and produced the corresponding products (**3c**～**3x**) in good yields. No matter whether the phenyl ring of *N*-phenyl-1*H*-pyrazole substrate **1** was substituted with either sterically hindered, electron-donating or electron-withdrawing group, all of them underwent this coupling reaction efficiently and formed the target products (**3o**～**3v**) in good to excellent yields. Both disubstitutedphenyl- and naphthalen-2-yl-1*H*-pyrazoles were well tolerated in this transformation, providing the corresponding products **3w** and **3x** in 73% and 75% yields, respectively. Importantly,

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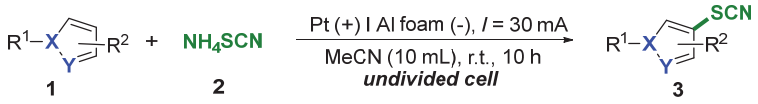
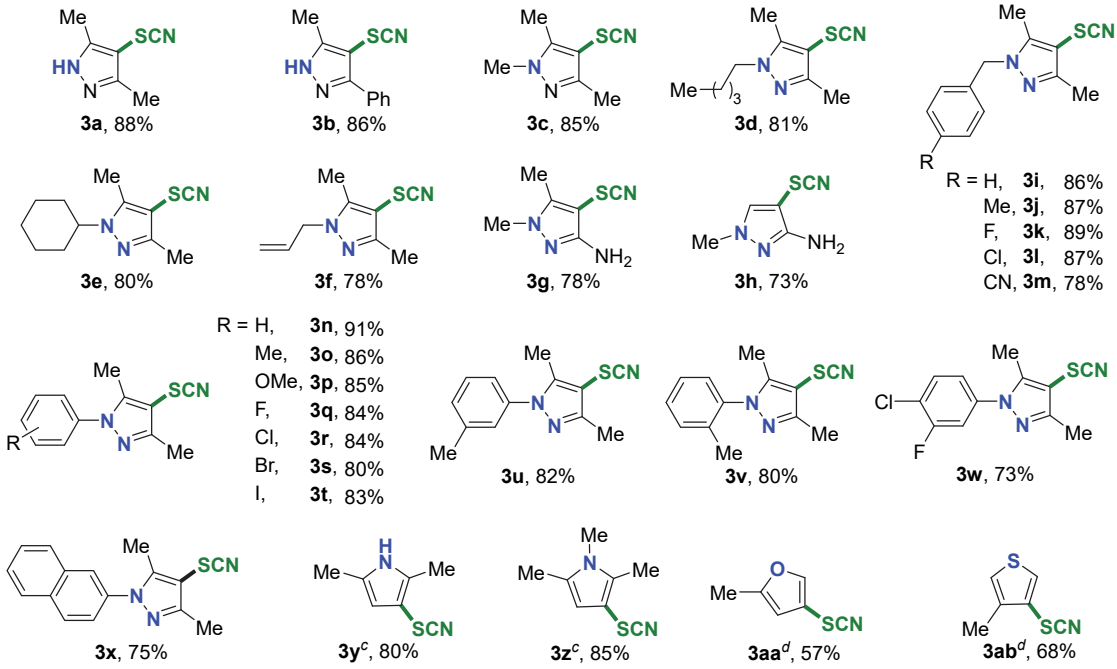
Table 2 Substrate Scope of the thiocyanation[a,b]

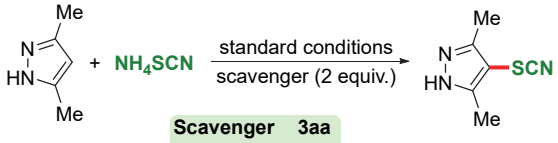




[a] Conditions: Pt (15 mm×10 mm×0.1 mm) as the anode, Al foam (15 mm×8 mm×2 mm) as the cathode, constant current=30 mA, **1** (0.5 mmol), **2** (1.5 mmol), MeCN (10 mL), room temperature, in air, 10 h, undivided cell; [b] isolated yields; [c] constant current=15 mA, 2 h; [d] constant current=15 mA, 10 h.

the resulting products bearing halogens (F, Cl, Br and I) and cyano group (CN) could be further utilized for the synthesis of more complex organic compounds. Gratifyingly, the electrochemical cross-coupling reaction can be successfully extended to pyrroles, furan and thiophene affording the desired products **3y**～**3ab** in good yields. When thiazole was used as the substrate, only a complicated reaction mixture of unidentified products was observed under the standard conditions. Changing KSCN to KSeCN led to no reaction.

To gain mechanistic insight into the electrochemical coupling reaction, both the radical trapping experiments and cyclic voltammetry experiments were carried out. As shown in Scheme 2a, the present coupling reactions were completely inhibited in the presence of the radical scavenger (TEMPO or BHT). The results indicated that the radical process was presumably involved in the electrochemical transformation. The power on/off experimental results that continuous electric current was indispensable for this transformation. Subsequently, the cyclic voltammetry experiments were conducted (Figure 1). Pyrazole **1a** presented an oxidative peak at E=1.78 V vs Ag/AgCl, which was much higher than that of NH_4SCN (E=1.34 V vs Ag/AgCl). Furthermore, the CV curves of a mixture of pyrazole and NH_4SCN showed similar oxidative peak with a slightly higher oxidation potential (E=1.44 V vs Ag/AgCl) than NH_4SCN. These results manifested that the anodic oxidation of NH_4SCN might occur preferentially.



Scavenger	3aa
TEMPO	trace
BHT	trace

Scheme 2 Control experiments

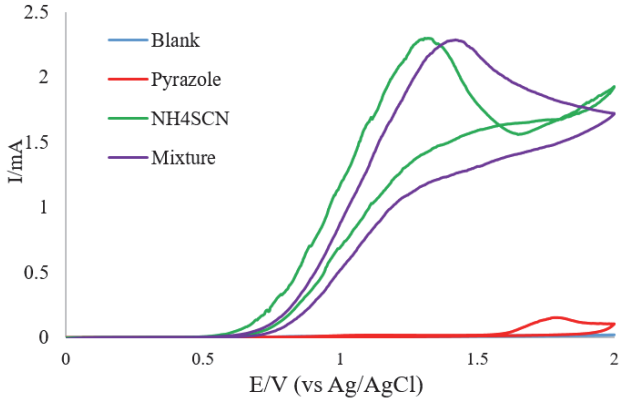


Figure 1 Cyclic voltammetry experiments

On the basis of the above-mentioned experimental results and previously related publications[11], a plausible mechanism for the electrochemical coupling reaction was

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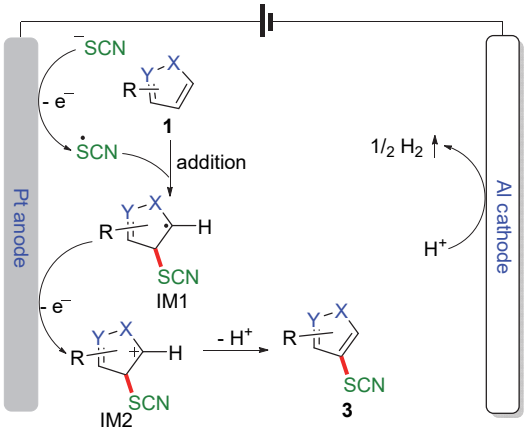
proposed. As shown in Scheme 3, the thiocyanate ion (SCN^-) was firstly oxidized at the surface of graphite plate anode to form a thiocyanate radical (SCN•), which regioselectively attacked the C—C double bond of five-membered aromatic heterocycle (**1**) to yield a carbon-centered radical IM1. Subsequently, the radical IM1 underwent anodic oxidation to afford the pyrazole cation intermediate IM2 and loss of one electron. Finally, the deprotonation of intermediate IM2 provided the desired thiocyanated heterocycle (**3**). At the same time, the hydrogen ions were reduced at the the surface of platinum plate cathode with the release of H_2.



Scheme 3 Proposed reaction mechanism

3 Conclusions

In summary, a green and efficient electrochemical cross-coupling of five-membered aromatic heterocycles (pyrazoles, pyrroles, furans and thiophenes) with NH_4SCN was realized, which provided a practical method to prepare various thiocyanated heterocycles. The present transformation can be achieved via a traceless electricity, featuring good functional-group tolerance and an eco-friendly manner, thereby under chemical oxidant- and exogenous electrolyte-free conditions. NH_4SCN played dual roles of a supporting electrolyte and a thiocyanated reagent, and thus simplify the reaction system. Under the optimal conditions, a variety of thiocyanated heterocycles (28 examples) were obtained in good to excellent yields with good regioselectivity, which could serve as a handle for future late-stage synthesis in fine chemistry and pharmaceutical chemistry.

4 Experimental section

4.1 General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anode electrode is Pt (50 mm×10 mm×0.1 mm), and Al foam (50 mm×8 mm×2 mm) is the cathode. All electrodes were purchased from Beijing Instrument Electric Technology Co. Ltd and used directly. All reagents were purchased from Energy Chemical (China) and used directly. The instrument for cyclic voltammetrys is CHI 660E potentiostat, and the conditions are as follow: a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 mol/L in CH_3CN) as counter and reference electrode. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200～300 mesh silica gel. ^1H NMR spectra were recorded at 500 MHz, ^{13}C NMR spectra were recorded at 125 MHz and ^{19}F NMR spectra were recorded at 471 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^1H NMR: $CDCl_3$ δ 7.26, ^{13}C NMR: $CDCl_3$ δ 77.0). HRMS were performed on a spectrometer operating on ESI-TOF.

4.2 Experimental section

4.2.1 General experimental procedure for compounds 3

In an undivided reaction tube equipped with a stir bar, heterocycles **1** (0.5 mmol), NH_4SCN (1.5 mmol) and MeCN (10 mL) were added. The reaction tube was equipped with platinum electrode (15 mm×10 mm×0.1 mm) as anode, Al foam (15 mm×8 mm×2 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 30 mA under room temperature for 10 h. After completion, the solvent was concentrated under reduced pressure, and the pure products **3a**～**3ab** were obtained by flash chromatography on silica gel.

4.2.2 Characterization data of products 3

3,5-Dimethyl-4-thiocyanato-1*H*-pyrazole (**3a**):[12a] ^1H NMR (500 MHz, $CDCl_3$) δ: 11.49 (s, 1H), 2.41 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.58, 110.98, 94.89, 11.09.

5-Methyl-3-phenyl-4-thiocyanato-1*H*-pyrazole (**3b**): ^1H NMR (500 MHz, $CDCl_3$) δ: 8.92 (s, 1H), 7.68～7.66 (m, 2H), 7.47～7.45 (m, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.97, 148.84, 129.80, 129.51, 128.97, 128.25, 111.28, 94.04, 10.55; HRMS calcd for $C_{11}H_{10}N_3S$ $[M+H]^+$ 216.0595, found 216.0593.

1,3,5-Trimethyl-4-thiocyanato-1*H*-pyrazole (**3c**): ^1H NMR (500 MHz, $CDCl_3$) δ: 3.68 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.70, 142.87, 110.12, 93.28, 35.87, 10.83, 9.17; HRMS calcd for $C_{12}H_{12}N_3S$ $[M+H]^+$ 230.0752, found 230.0750.

3,5-Dimethyl-1-pentyl-4-thiocyanato-1*H*-pyrazole (**3d**): ^1H NMR (500 MHz, $CDCl_3$) δ: 3.98 (t, J=7.5 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H), 1.82～1.76 (m, 2H), 1.38～1.26 (m, 4H), 0.90 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.74, 143.29, 111.29, 93.93, 50.08, 29.72, 28.73, 22.28, 13.93, 11.96, 10.15; HRMS calcd for $C_{16}H_{20}N_3S$ $[M+H]^+$ 286.1378, found 286.1375.

1-Cyclohexyl-4-thiocyanato-1*H*-pyrazole (**3e**): ^1H NMR (500 MHz, $CDCl_3$) δ: 3.96-3.92 (m, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.93～1.86 (m, 6H), 1.72 (d, J=12.5 Hz, 1H), 1.40～1.26 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.44, 142.45, 111.40, 93.56, 58.73, 32.51, 25.59, 25.03, 12.02, 10.05; HRMS calcd for $C_{12}H_{18}N_3S$ $[M+H]^+$ 136.1221, found 236.1226.

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1-Allyl-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3f**):[12a] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.86～5.78 (m, 1H), 5.14 (d, J=10.0 Hz ,1H), 4.96 (d, J=17.0 Hz, 1H), 4.53 (d, J=5.5 Hz, 2H), 2.05 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.81, 129.76, 129.12, 128.97, 128.80, 127.84, 125.71, 36.72, 31.60.

1,5-Dimethyl-4-thiocyanato-1*H*-pyrazol-3-amine (**3g**):[12b] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.04 (s, 2H), 3.64 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.06, 144.07, 111.13, 80.65, 36.48, 10.28.

1-Methyl-4-thiocyanato-1*H*-pyrazol-3-amine (**3h**): ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.44 (s, 1H), 6.31 (s, 2H), 3.61 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 150.70, 142.16, 113.17, 73.83, 35.59; HRMS calcd for $C_5H_7N_4S$ $[M+H]^+$ 155.0386, found 155.0381.

1-Benzyl-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3i**):[12a] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27-7.19 (m, 3H), 7.04 (d, J=7.5 Hz, 2H), 5.17 (s, 2H), 2.30 (s 3H), 2.24 (s 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.08, 142.96, 134.60, 127.93, 127.06, 125.84, 110.06, 94.12, 76.27, 10.99, 9.27.

3,5-Dimethyl-1-(4-methylbenzyl)-4-thiocyanato-1*H*-pyrazole (**3j**): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12 (d, J=7.5 Hz, 2H), 7.01 (d, J=7.5 Hz, 2H), 5.18 (s, 2H), 2.36 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.97, 143.93, 137.89, 132.66, 129.64, 126.99, 111.22, 94.98, 53.85, 21.17, 12.08, 10.35; HRMS calcd for $C_{19}H_{18}N_3S$ $[M+H]^+$ 320.1221, found 320.1218.

1-(4-Fluorobenzyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3k**): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.13-7.10 (m, 2H), 7.01 (d, J=8.5 Hz, 2H), 5.20 (s, 2H), 2.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.36 (d, J=247.3 Hz), 151.22, 143.93, 131.47 (d, J=3.1 Hz), 128.78 (d, J=8.3 Hz), 115.91 (d, J=21.5 Hz), 111.11, 95.27, 53.20, 12.04, 10.29; HRMS calcd for $C_{18}H_{15}FN_3S$ $[M+H]^+$ 324.0971, found 324.0968.

1-(4-Chlorobenzyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3l**): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30 (d, J=8.0 Hz, 2H), 7.05 (d, J=8.0 Hz, 2H), 5.20 (s, 2H), 2.37 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.33, 144.00, 134.15, 134.02, 129.16, 128.35, 111.07, 95.40, 53.25, 12.08, 10.32; HRMS calcd for $C_{18}H_{15}ClN_3S$ $[M+H]^+$ 340.0675, found 340.0672.

4-((3,5-Dimethyl-4-thiocyanato-1*H*-pyrazol-1-yl)methyl)benzonitrile (**3m**): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64 (d, J=8.0 Hz, 2H), 7.21 (d, J=8.0 Hz, 2H), 5.31 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.68, 144.22, 140.97, 132.77, 127.57, 118.35, 112.06, 110.85, 95.83, 53.20, 12.03, 10.25; HRMS calcd for $C_{19}H_{15}N_4S$ $[M+H]^+$ 331.1017, found 311.1014.

3,5-Dimethyl-1-phenyl-4-thiocyanato-1*H*-pyrazole (**3n**):[5j] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.50 (t, J=7.5 Hz, 2H), 7.44 (d, J=7.5 Hz, 1H), 7.41～7.39 (m, 2H), 2.44 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.99, 144.34, 139.07, 129.38, 128.64, 124.98, 110.84, 96.60, 12.02, 11.52.

3,5-Dimethyl-4-thiocyanato-1-(*p*-tolyl)-1*H*-pyrazole (**3o**):[12a] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.20(s, 4H), 2.34 (d, J=5.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.76, 143.27, 137.69, 135.57, 128.87, 123.80, 109.91, 95.15, 20.13, 10.98, 10.42.

1-(4-Methoxyphenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3p**):[5j] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30(d, J=8.5 Hz, 2H), 6.99 (d, J=9.0 Hz, 2H), 3.86 (s, 3H), 2.42 (s, 3H); 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.67, 151.67, 144.44, 132.08, 126.48, 114.46, 110.98, 95.90, 55.61, 12.00, 11.35.

1-(4-Fluorophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3q**):[12a] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36～7.30(m, 2H), 7.12 (t, J=8.0 Hz, 2H), 2.35 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.45 (d, J=247.9 Hz), 151.07, 143.42, 134.12 (d, J=3.1 Hz), 125.89 (d, J=8.6 Hz), 115.32 (d, J=23.0 Hz), 109.72, 95.72, 10.96, 10.40.

1-(4-Chlorophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3r**):[12b] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48(d, J=8.5 Hz, 2H), 7.36 (d, J=8.5 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.32, 144.37, 137.55, 134.48, 129.59, 126.11, 110.67, 97.20, 12.03, 11.58.

1-(4-Bromophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3s**):[12b] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55(d, J=8.5 Hz, 2H), 7.23 (d, J=8.5 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.31, 143.29, 137.01, 131.52, 125.30, 121.37, 109.60, 96.23, 10.99, 10.55.

1-(4-Iodophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3t**):[5j] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.75 (d, J=8.0 Hz, 2H), 7.09 (d, J=8.0 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.33, 143.24, 137.69, 137.48, 125.42, 109.59, 96.27, 92.72, 11.00, 10.58.

3,5-Dimethyl-4-thiocyanato-1-(*m*-tolyl)-1*H*-pyrazole (**3u**):[12b] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30 (t, J=8.0 Hz, 1H), 7.17 (d, J=8.0 Hz, 2H), 7.10 (d, J=8.0 Hz 1H), 2.36-2.35 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.88, 144.32, 139.67, 138.98, 129.43, 129.08, 125.70, 121.93, 110.92, 96.37, 21.35, 12.03, 11.53.

3,5-Dimethyl-4-thiocyanato-1-(*o*-tolyl)-1*H*-pyrazole (**3v**):[5j] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (t, J=7.5 Hz, 1H), 7.27～7.22 (m, 2H), 7.12 (d, J=8.0 Hz 1H), 2.35 (s, 3H), 2.14 (s 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.69, 144.17, 136.79, 134.72, 130.18, 128.84, 126.46, 125.84, 110.01, 94.07, 16.19, 11.04, 9.56.

1-(4-Chloro-3-fluorophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole (**3w**):[5j] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54～7.52 (m, 1H), 7.33～7.26 (m 2H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.90 (d, J=250.4 Hz), 152.46, 144.54, 135.54 (d, J=3.9 Hz), 127.45, 124.67 (d, J=7.5 Hz), 122.07 (d, J=19.0 Hz), 117.19 (d, J=22.5 Hz), 110.56, 97.48, 12.02, 11.56.

3,5-Dimethyl-1-(naphthalen-2-yl)-4-thiocyanato-1*H*-pyrazole (**3x**):[5j] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (d, J=5.0 Hz, 1H), 7.91～7.87 (m, 2H), 7.85 (d, J=5.0 Hz, 1H), 7.57～7.52 (m, 3H), 2.48 (s, 3H), 2.46 (s, 3H); ^{13}C NMR

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(125 MHz, $CDCl_3$) δ: 152.18, 144.63, 136.43, 133.05, 132.71, 129.56, 128.21, 127.91, 127.24, 127.09, 123.37, 122.87, 110.92, 96.75, 12.12, 11.72.

2,5-Dimethyl-3-thiocyanato-1*H*-pyrrole (**3y**): ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.05 (s, 1H), 5.75 (s, 1H), 2.09 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 133.16, 127.91, 113.42, 110.05, 92.66, 12.94, 11.20; HRMS calcd for $C_7H_9N_2S$ $[M+H]^+$ 153.0486, found 153.0485.

1,2,5-Trimethyl-3-thiocyanato-1*H*-pyrrole (**3z**): ^{1}H NMR (500 MHz, DMSO-d_6) δ: 5.94 (s, 1H), 3.34 (s, 3H), 2.20 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 134.68, 130.02, 113.36, 110.00, 91.99, 31.52, 12.38, 10.68; HRMS calcd for $C_8H_{11}N_2S$ $[M+H]^+$ 167.0643, found 167.0640.

2-Methyl-4-thiocyanatofuran (**3aa**): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.79 (d, J=3.5 Hz, 1H), 6.12 (d, J=3.0 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.43, 127.67, 123.49, 109.22, 108.91, 14.11; HRMS calcd for C_6H_6NOS $[M+H]^+$ 140.0170, found 140.0165.

3-Methyl-4-thiocyanatothiophene (**3ab**): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, J=5.5 Hz, 1H), 6.99 (d, J=5.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.22, 131.68, 130.57, 112.63, 110.25, 14.90; HRMS calcd for $C_6H_6NS_2$ $[M+H]^+$ 155.9942, found 155.9938.

4.2.3 Cyclic voltammetry experiment

CV measurements were performed on a CHI 660E potentiostat, and the conditions are as follow: a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 mol/L in CH_3CN) as counter and reference electrode. Cyclic voltammograms of reactants and their mixtures in 0.1 mol/L Bu_4NBF_4/CH_3CN using a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 mol/L in CH_3CN) as counter and reference electrode at 50 mV/s scan rate: (a) Blank (20 mmol/L), (b) **1a** (20 mmol/L), (c) NH_4SCN (20 mmol/L), (d) **1a** (20 mmol/L) and NH_4SCN (20 mmol/L).

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of compounds. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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