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**Authors:** Weisi Guo, Qian Wang, and Jieping Zhu



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# Selective 1,2-Aminoisothiocyanation of 1,3-Dienes Under Visible Light Photoredox Catalysis

Weisi Guo,[a, b] Qian Wang,[a] Jieping Zhu*[a]

[a] Dr. W. Guo, Dr. Q. Wang, Prof. Dr. J. Zhu
Laboratory of Synthesis and Natural Products
Institute of Chemical Sciences and Engineering
Ecole Polytechnique Fédérale de Lausanne
EPFL-SB-ISIC-LSPN, BCH 5304, 1015 Lausanne (Switzerland)
E-mail: jieping.zhu@epfl.ch
Homepage: http://lspn.epfl.ch

[b] College of Chemistry & Molecular Engineering
Qingdao University of Science & Technology
53 Zhengzhou Road, Qingdao, P. R. China

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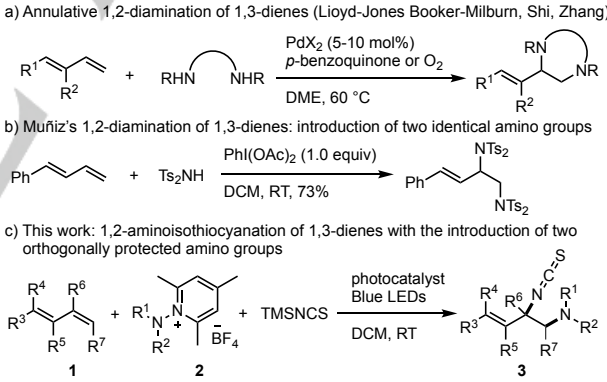
**Abstract:** Selective three-component 1,2-diamination of 1,3-dienes with concurrent introduction of two orthogonally protected amino groups remains unknown in spite of its significant synthetic potential. We report herein that reaction of conjugated dienes with *N*-aminopyridinium salts and TMSNCS affords 1,2-aminoisothiocyanation products in a highly chemo- and regio-selective manner under mild photoredox catalytic conditions. Mechanistic studies indicate that the facile isomerization of allyl thiocyanates to allyl isothiocyanates under photocatalytic conditions is responsible for the selective formation of the observed products. The mild isomerization protocol is expected to find applications in the synthesis of allyl isothiocyanates in a broad sense.

Selective functionalization of 1,3-dienes is a challenging yet highly valued synthetic transformation as it converts the easily available chemicals to the highly functionalized molecules.[1] Due to the omnipresence of nitrogen-containing compounds in bioactive natural products and pharmaceuticals, the difunctionalization of 1,3-dienes incorporating an amino or its equivalent functions has attracted great recent attention. Thus, diamination,[2,3] aminothiolation,[4] amino oxygenation,[5] aminofluorination,[6] aminomethylamination[7] and aminoalkylation/arylation[8,9] have been developed allowing the ready access to the highly functionalized alkenes.[10] Despite the significant progress recorded in this field, selective incorporation of two easily manipulable and orthogonally protected amino groups remains challenging. For example, the annulative 1,2-diamination of conjugated dienes using ureas, diaziridinones and *N,N*-ditosyl *o*-phenylenediamines has been developed into a powerful synthetic tool for the synthesis of cyclic ureas/tetrahydroquinazolines. However, the two amino groups of these reagents have to be protected by the same function in order to avoid the regioselectivity issue (Scheme 1a). The only report on the acyclic 1,2-diamination of 1,3-dienes developed by Muñiz[2d] afforded the products with two identical sulfonamide groups (Scheme 1b).[11]

Isothiocyanate (NCS) and thiocyanate (SCN) are prevalent functional groups found in natural products and bioactive compounds.[12,13] They are also important building blocks for the construction of nitrogen- and sulfur-containing derivatives.[14,15] Selective thiocyanation of alkenes including dithiocyanation,[16] trifluoromethylthiocyanation,[17] aminothiocyanation[18] thiocyanodiphenylphosphinoylation,[19] and isothiocyanatoalkylthiation[20] of alkenes have been developed. However, to the best of our knowledge, aminoisothiocyanation of 1,3-dienes has never been reported. As a continuation of our research program dealing with the development of radical based difunctionalization of alkenes[21] and remote C($sp^3$)-H functionalization,[22] we report herein that reaction of conjugated dienes **1** with readily available *N*-aminopyridinium salts **2**[23,24] afforded, under mild visible light photoredox catalytic conditions, the 1,2-aminoisothiocyanation products **3** in good yields with excellent chemo- and regio-selectivities (Scheme 1c). Facile reductive isomerization of allyl thiocyanates to allyl isothiocyanates under photoredox conditions is evidenced to account for the observed chemoselectivity.

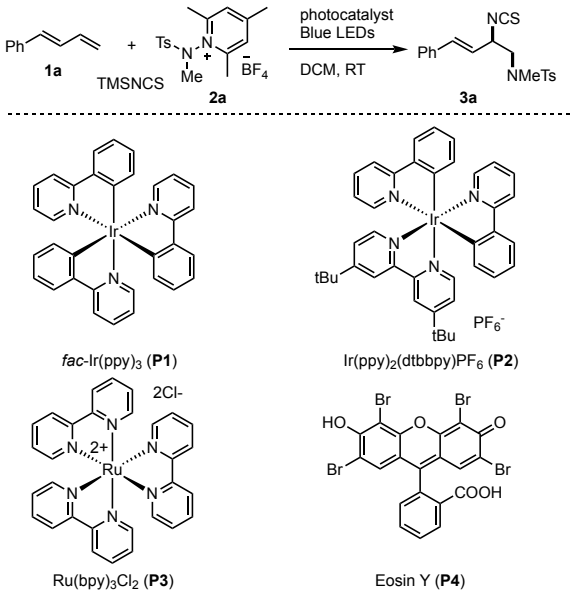



***Scheme 1***. Challenges in selective 1,2-diamination of 1,3-dienes: introducing two orthogonally protected amino groups. *Abbreviations*: DCM = dichloromethane.

We commenced our studies using (*E*)-1-phenyl-1,3-butadiene (**1a**) and *N*-aminopyridinium salt **2a** as model substrates. Systematic survey of reaction conditions allowed us to identify the following optimum conditions: *fac*-Ir(ppy)$_3$ (1.0 mol%) as a photoredox catalyst in dichloromethane (DCM) under irradiation with blue LEDs at room temperature (Table 1, entry 1).[25] Under these conditions, the 1,2-aminoisothiocyanation product **3a** was formed as single isomer in 75% isolated yield. While **3a** was formed in similar yield with Ir(ppy)$_2$(dtbbpy)(PF$_6$) (entry 2), other commonly used photocatalysts, such as Ru(bpy)$_3$Cl$_2$·6H$_2$O and eosin Y, gave inferior results (entries 2-4). Lower yields of **3a** was obtained when the reaction was performed in MeCN and DCE under otherwise identical conditions (entries 1 vs 5, 6). Control

experiments revealed that both photoredox catalyst and light are indispensable for the reaction (entries 7,8). Finally, addition of TEMPO to the reaction mixture inhibited completely the reaction (entry 9).

**Tale 1**. Optimization of reaction conditions[a]

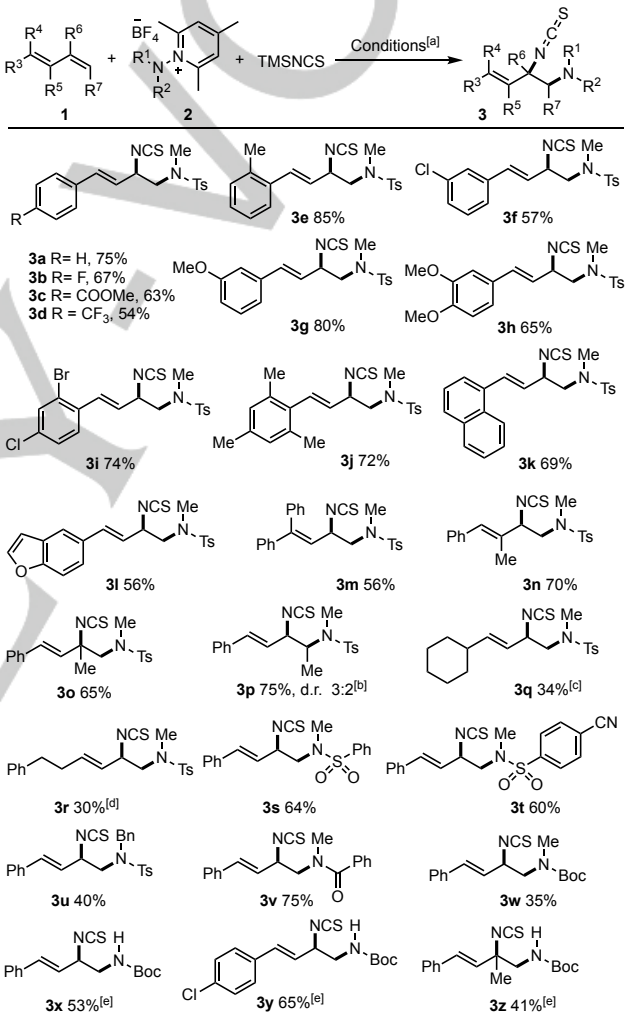



| Entry | Conditions | Yield **3a** (%)[b] |
|---|---|---|
| 1 | *fac*-Ir(ppy)$_3$ (**P1**), DCM | 75 |
| 2 | Ir(ppy)$_2$(dtbbpy)(PF$_6$) (**P2**), DCM | 72 |
| 3 | Ru(bpy)$_3$Cl$_2$·6H$_2$O (**P3**), DCM | 18 |
| 4 | Eosin Y (**P4**), DCM | 0 |
| 5 | *fac*-Ir(ppy)$_3$, CH$_3$CN | 65 |
| 6 | *fac*-Ir(ppy)$_3$, DCE | 68 |
| 7 | No PC, DCM | 0 |
| 8 | *fac*-Ir(ppy)$_3$, DCE, in the dark | 0 |
| 9 | *fac*-Ir(ppy)$_3$, DCE, TEMPO (2.0 equiv) | 0 |

[a] Conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol, 1.0 equiv), TMSNCS (0.2 mmol, 2.0 equiv), photocatalyst (0.001 mmol, 0.01 equiv), solvent (1.0 mL), blue LEDs, room temperature, $N_2$. [b] Isolated yields. *Abbreviations*: DCE = dichloroethane; TEMPO = 2,2,6,6-Tetramethyl-1-piperidinyloxy.

With the optimized conditions in hands, we proceeded to explore the substrate scope of this methodology starting with the conjugated dienes (Scheme 2). For 1-aryl-1,3-butadienes, the presence of electron withdrawing (F, Cl, Br, COOMe, and $CF_3$) and electron donating groups (Me, OMe) at different positions of the phenyl ring is well tolerated (**3a**-**3j**). Naphthalene (**3k**) and heterocycle such as benzofuran (**3l**) are compatible with the reaction conditions. The 1,1-, 1,2- and 1,3-disubstituted 1,3-dienes participated in the reaction to afford the corresponding diamination products (**3m**-**3o**) in good yields. Notably, compound **3o** containing a tetrasubstituted carbon was isolated in 65% yield. Reaction of 1-phenyl-1,3-pentadiene displayed high chemo- and regio-selectivity to furnish product **3p** in 75% yield as a mixture of two diastereomers (d.r. = 3:2). The lack of diastereoselectivity in this case is nevertheless not unexpected. Alkyl substituted dienes, including cyclohexyl and phenethyl substituted dienes, participated in the reaction to afford **3q** and **3r** in yields of 34% and 30%, respectively. In these two cases, the 1,4-aminoisothiocyanation products were also isolated in about 25% yields.

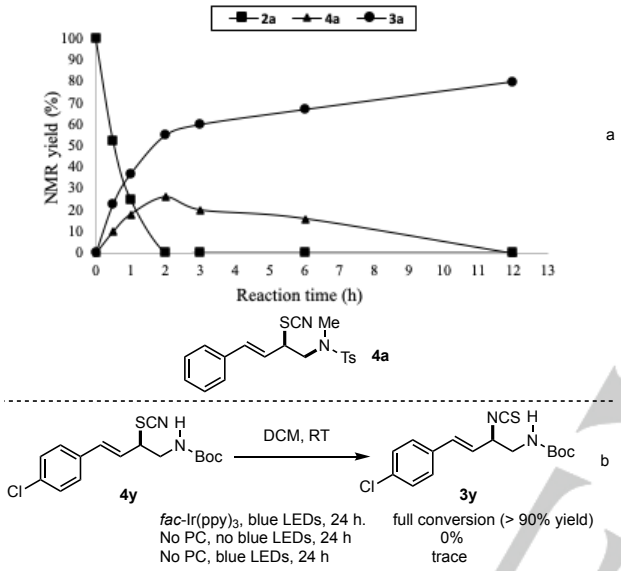
The scope of pyridinium salts was next investigated. As it is seen, the amidyl radicals ($RSO_2N^{\bullet}R^1$, $RCON^{\bullet}R^1$, $t$BuOCON$^{\bullet}$R$^1$) derived from the corresponding *N*-aminopyridinium salts participated in the reaction to afford the corresponding three-component adducts (**3s**-**3z**) in good yields. The ready formation of compounds **3x**-**3z** is particularly noteworthy as the primary amino function could be released easily after removal of *N*-Boc group. It is worth noting that only the *E*-alkene was isolated when a mixture of *E/Z* dienes were used as starting materials. Finally, similar yield of **3a** (1.05g, 76%) was obtained when the reaction was performed at a gram scale.




***Scheme 2***. [a] Conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol, 1.0 equiv), TMSNCS (0.2 mmol, 2.0 equiv), *fac*-Ir(ppy)$_3$ (0.001 mmol, 0.01 equiv), dichloromethane (1.0 mL), blue LEDs, room temperature, $N_2$, 12 h. [b] The d.r. was determined by $^1$H NMR. [c] The 1,4-aminoisothiocyanation product was isolated in 24% yield, see SI. [d] The 1,4-aminoisothiocyanation product was isolated in 25% yield, see SI. [e] 24 h. *Abbreviations*: Ts = 4-toluenesulfonyl; Boc = *tert*-butoxycarbonyl

The chemoselective introduction of isothiocyanate function in the above 1,2-aminoisothiocyanation reaction is intriguing as thiocyanation is generally a dominating pathway in related transformations.[15-19, 22b] To understand the reaction course, the progress of reaction between **1a**, **2a** and TMSNCS was

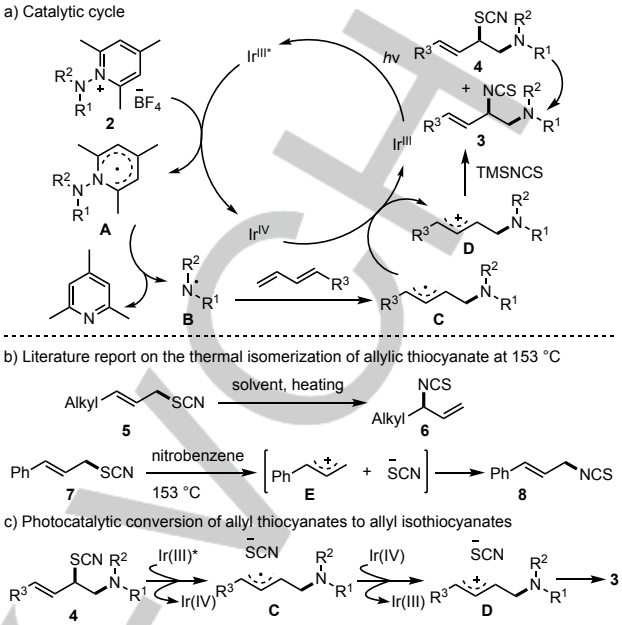
monitored by $^1$H NMR spectroscopy and the results are shown in Scheme 3a. The plot revealed that both 1,2-aminoisothiocyanation and 1,2-aminothiocyanation products **3a** and **4a** were formed at the initial stage of the reaction. After 2 h, all the *N*-aminopyridinium salt **2a** was consumed leading to **3a** and **4a** in NMR yields of 56% and 26%, respectively. Continued irradiation of the reaction mixture led to the gradual conversion of **4a** to **3a**. To further confirm this observation, pure aminothiocyanation product **4y** was isolated. Irradiation of a DCM solution of **4y** in the presence of *fac*-Ir(ppy)$_3$ provided cleanly the aminoisothiocyanation product **3y**. Additional control experiments indicated that both the photoredox catalyst and the blue LEDs irradiation are essential for this isomerization (Scheme 3b).




***Scheme 3.*** Reaction course of **1a, 2a** with TMSNCS monitored by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard and the results of the control experiment.

The light ON/OFF experiments showed that the product was formed only under blue LEDs irradiation (Figure S2). The quantum yield of the reaction between **1a** and **2a** was determined to be 0.11 (see the Supporting Information). These results indicated that the radical chain mechanism might not be involved in the reaction. The Stern-Volmer fluorescence quenching experiments revealed that **2a**, but not TMSNCS, quenched efficiently the excited state of Ir(ppy)$_3$ (Figure S3-S5).

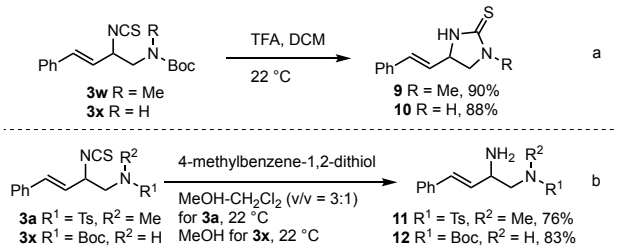
On the basis of the aforementioned results, a plausible reaction pathway is illustrated in Scheme 4. Reduction of *N*-aminopyridinium salt **2** by excited $Ir^{III*}$ species would generate radical **A** which underwent fragmentation to afford the nitrogen-centered radical **B** and 2,4,6-collidine. Regioselective addition of radical **B** to the 1,3-diene would generate the allylic radical **C**. Subsequent oxidation of radical **C** by $Ir^{IV}$ would afford carbocation intermediate **D** with concurrent re-generation of Ir(III) species. An off-catalytic cycle nucleophilic addition of TMSNCS to the allylic cation **E** is highly regioselective, albeit with low chemoselectivity, to afford a mixture of 1,2-aminoisothiocyanation and 1,2-aminothiocyanation products **3** and **4**. However, the latter was cleanly *in situ* converted to the former upon extended reaction time.




***Scheme 4***. Mechanistic proposal.

Isomerization of allyl thiocyanate is known to be highly substrate dependent.[26] While 3-alkyl substituted substrates **5** undergo sigmatropic rearrangement to afford isomeric isothiocyanates **6**, the cinnamyl thiocyanate **7** isomerizes, without 1,3-shift, to cinnamyl isothiocyanate **8** under harsh conditions (nitrobenzene, 153 °C, Scheme 4b). Detailed mechanistic studies indicated that the latter reaction went through a sequence of ionization to allyl cation **E** and thiocyanate followed by regioselective recombination.[26a] The facile isomerization of **4** to **3** under our mild photoredox catalytic conditions at room temperature was therefore surprising. We propose that the excited $Ir^{III*}$ species is capable of reducing the allylic thiocyanate **4** to the allylic radical **C** and thiocyanate. Oxidation of **C** to the allylic cation **D** by Ir(IV) followed by regio- and chemo-selective nucleophilic trapping would then afford **3** as a major product. Repeating the same cycle would afford **3** as an only isolable product (Scheme 4c). Attempts to trap the $SCN^-$ and the allylic cation **D** by BnBr and MeOH, respectively, failed indicating that **D** might form a tight ion pair with thiocyanate and the recombination could be a fast process.

The synthetic utility of these three-component adducts was next investigated. As it is shown in Scheme 5a, the vicinal aminoisothiocyanates **3w** and **3x** underwent one-pot *N*-deprotection and intramolecular cyclization to provide 2-imidazolidinethiones **9** and **10** in yields of 90% and 88%, respectively. On the other hand, treatment of **3a** (in MeOH/$CH_2Cl_2$, v/v = 3/1) and **3x** (in MeOH) with odorless 4-methylbenzene-1,2-dithiol at room temperature (22 °C, 1 h) afforded selectively protected 1,2-diamines **11** and **12** in yields of 76% and 83%, respectively.[27] Bis(tributyltin) oxide can also mediate this transformation to afford **11** and **12**, albeit with reduced yields (50%).[28]




***Scheme 5***. Post-transformations: Selective transformations of isothiocyanate.

In conclusion, we have developed a novel three-component reaction of TMSNCS, aminopyridinium salts with 1,3-dienes to access 1,2-aminoisothiocyanation products in a highly chemo-, and regio-selective manner. The isothiocyanate group can be converted to the amino group under mild conditions. To the best of knowledge, this represents the first examples of selective 1,2-diamination of 1,3-dienes with two easily manipulable and orthogonally protected amino functions being introduced. A facile isomerization of allyl thiocyanates to allyl isothiocyanates under mild photoredox catalytic conditions uncovered during this study is expected to find applications in the synthesis of allyl isothiocyanates in a broad sense.

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## *Conflict of Interest*

The authors declare no conflict of interest.

**Keywords:** Alkene difunctionalization • 1,3-diene • amino isothiocyanation • photoredox catalysis • amidyl radical

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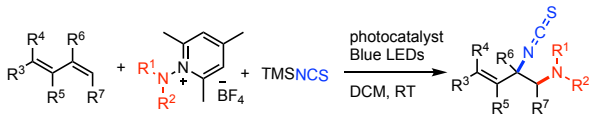
## Entry for the Table of Contents




A three-component 1,2-aminoisothiocyanation of the conjugated dienes was realized in a highly chemo- and regio-selective manner using *N*-aminopyridinium salts as donors of amidyl radicals. A facile isomerization of allyl thiocyanate to allyl isothiocyanate under photoredox catalytic conditions at room temperature is uncovered.

Institute and/or researcher Twitter usernames: ((optional))