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Letter

# Co-Catalyzed Transannulation of Pyridotriazoles with Isothiocyanates and Xanthate Esters

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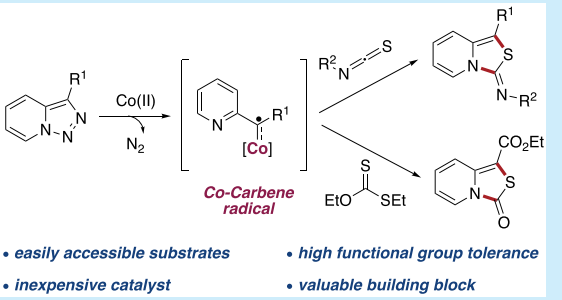
**ABSTRACT:** An efficient radical transannulation reaction of pyridotriazoles with isothiocyanates and xanthate esters was developed. This method features conversion of pyridotriazoles into two *N*-fused heterocyclic aromatic systems—imino-thiazolopyridines and oxo-thiazolopyridine derivatives—via one-step Co(II)-catalyzed transannulation reaction proceeding via a radical mechanism. The synthetic usefulness of the developed method was illustrated in the synthesis of amino acid derivatives and further transformations of obtained reaction products.

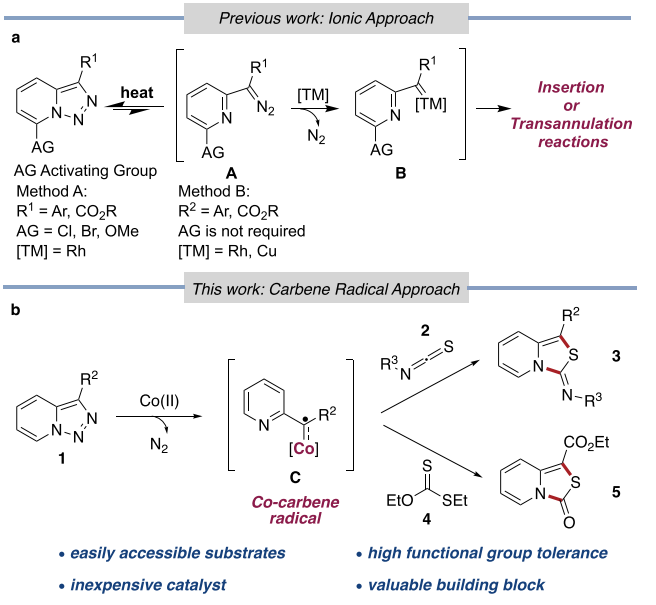





Heteroaromatic rings are paramount motifs of drugs and bioactive molecules.[1] Thus, not surprisingly that, in drug discovery research, the development of novel synthetic approaches for the rapid construction of new heterocyclic ring systems from easily available precursors is of central importance.[2] Recently, transition-metal-catalyzed denitrogenative transformations of pyridotriazoles have been emerging as a powerful tool for the synthesis of diverse *N*-heterocyclic frameworks.[3,4] These protocols take advantage of the well-known ring−chain tautomerism of the pyridotriazole core in solution into the corresponding diazo tautomer **A**, which then can be trapped by a transition-metal catalyst to form the reactive pyridyl metal carbene intermediate **B** (see Scheme 1a). First reported in 2007,[5] the transannulation reaction of pyridotriazoles was then quickly extended to other transannulations,[6] as well as X−H insertions,[7] cyclopropanation,[8] and other reactions.[9] These protocols operate through an ionic pathway, involving transition-metal carbene intermediate **B**.

Recently, metalloradical catalysis employing open-shell metalloradical complexes has been introduced as a conceptually new strategy featuring alternative trends in reactivity and selectivity. Of particular importance are stable metalloradicals of cobalt(II) porphyrins ([Co(Por)]), which form strong metal−carbon single bonds, thus behaving as carbene radical surrogates.[10] Lately, a rich chemistry of Co(II)-based metalloradicals toward a variety of useful synthetic transformations has been developed.[11,12] Surprisingly, engagement of this strategy in denitrogenative transannulation reaction is scarce.[13] In continuation of our studies on application of pyridotriazoles in synthesis of nitrogen-containing heterocycles,[5a−e] herein, we report a Co-catalyzed denitrogenative transannulation of pyridotriazoles with isothiocyanates and xanthate esters toward the synthesis of two *N*-heterocyclic aromatic systems proceeding via carbene radical intermediate **C** (see Scheme 1b).

**Scheme 1. Concepts for Transannulation of Pyridotriazoles**




First, transannulation of pyridotriazole **1a** and *t*-butyl isothiocyanate **2a**[14] en route to imino-thiazolopyridine **3a** was examined in the presence of several synthesized metal-

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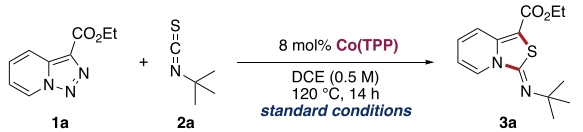
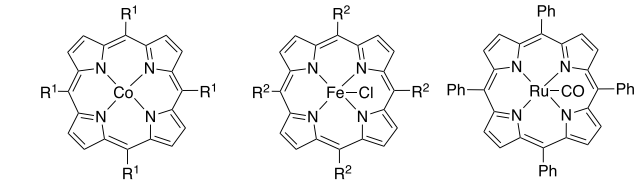
**Table 1. Optimization of Reaction Conditions**[a]

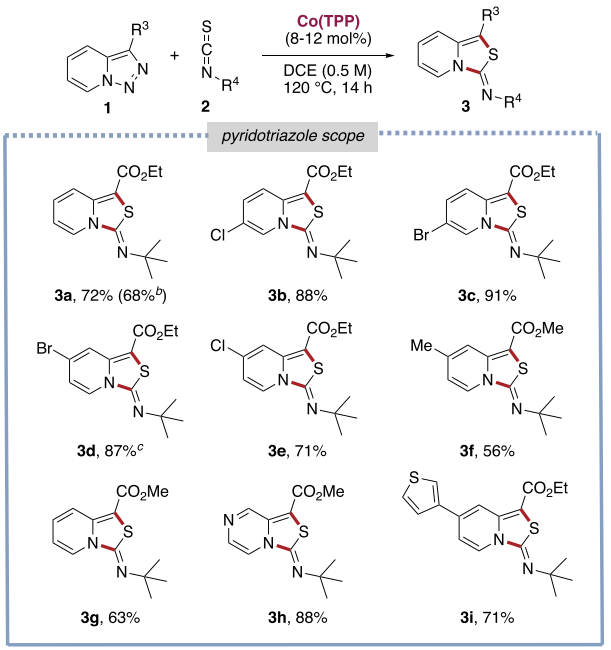



| entry | deviation from standard conditions | yield of **3a**[b] (%) |
|---|---|---|
| 1 | none | 72[c] |
| 2 | Co($F_{20}$TPP) | 64 |
| 3 | Co[(*p*-OMe)$_4$TPP] | 48 |
| 4 | Fe(TPP)Cl | 0[d] |
| 5 | Fe($F_{20}$TPP)Cl | 0[d] |
| 6 | Ru(TPP)CO | 0[d] |

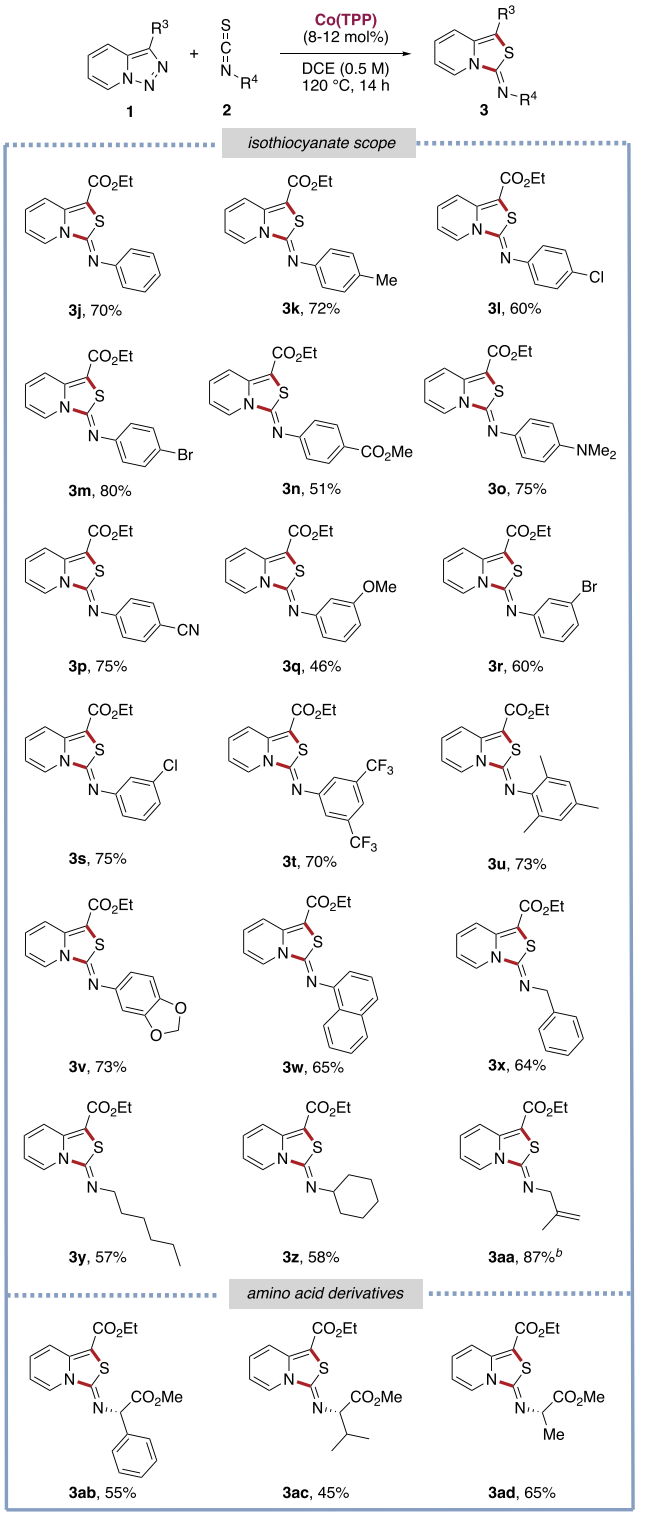
[a]0.05 mmol scale; **1**:**2** = 1:5. [b]Determined by gas chromatography/mass spectroscopy (GC/MS), using pentadecane as an internal standard with a catalyst loading of 8 mol %. [c]0.2 mmol scale, isolated yields. [d]Pyridotriazole **1a** was mostly recovered.

**Scheme 2. Scope of Pyridotriazoles**[a]




[a]0.2 mmol scale, isolated yields. See the Supporting Information for experimental details. [b]Reaction was performed in 1 mmol scale. [c]Toluene (0.5 M) used as a solvent.

**Scheme 3. Scope of Isothiocyanates**[a]




[a]0.2 mmol scale, isolated yields. See Supporting Information for experimental details. [b]Toluene (0.5 M) used as a solvent.

porphyrin-based catalysts (Table 1). It was found that Co(TPP) (TPP = tetraphenyl porphyrin) was a superior catalyst delivering **3** in 72% isolated yield (Table 1, entry 1). Employment of other Co-porphyrin-based catalysts was less efficient (Table 1, entries 2 and 3), whereas use of other Fe- and Ru-porphyrin-based catalysts was inefficient (Table 1, entries 4–6).

Next, the generality of this methodology was examined. With regard to the pyridotriazole component, several differently substituted heterocycles at C5 and C6 turned out to be capable substrates for transannulation with *t*-butyl isothiocyanate (**2a**) (Scheme 2). Thus, halogenated and methylated pyridotriazoles reacted smoothly to give the corresponding imino-thiazolopyr-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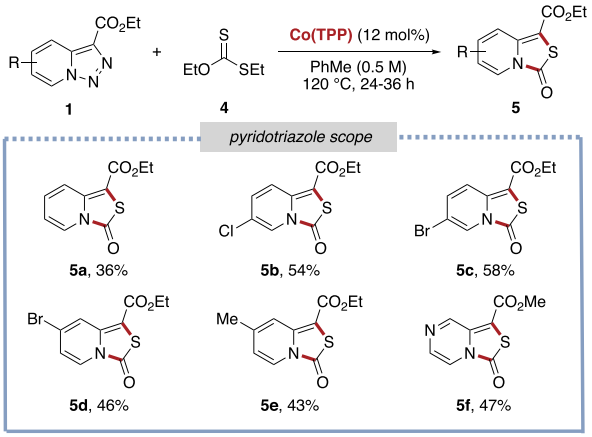
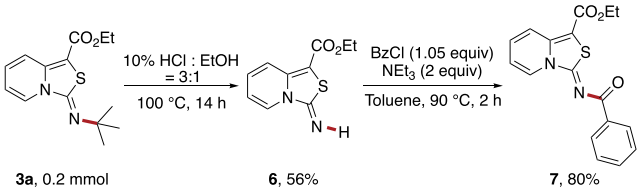
**Scheme 4. Scope of Transannulation with Xanthate Ester**[a]

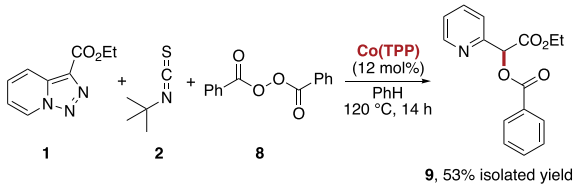



[a]0.2 mmol scale, isolated yields.

**Scheme 5. Product Transformations**

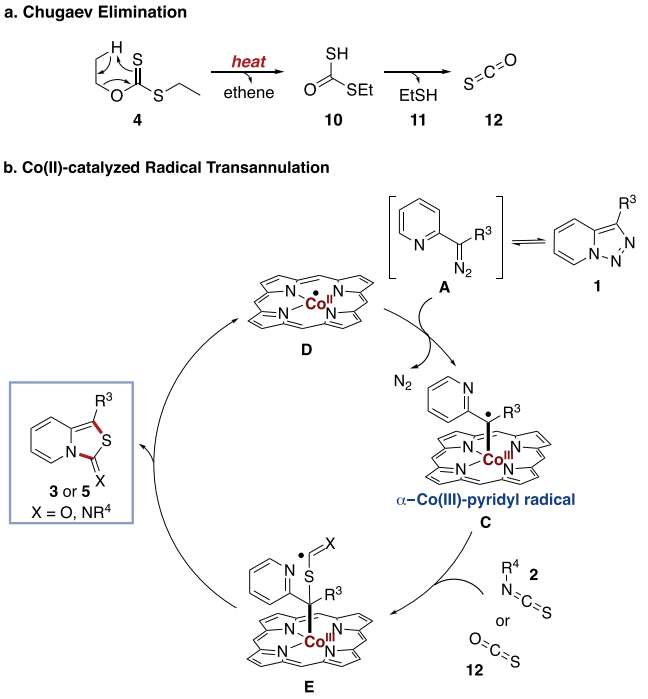



**Scheme 6. Radical Scavenging Experiment Used to Trap the Co(III)-Carbene Radical Intermediate**




idine products **3b**−**3f** in good to excellent yields. Employment of methyl ester-containing substrate **3g** and thiophene-containing pyridotriazole **3i** posed no problem. Notably, this reaction was equally efficient with *N*-fused pyrazinotriazole to deliver imino-thiazolopyrazine derivative **3h** in high yield. This reaction also appeared to be very general for isothiocyanates (see Scheme 3). A variety of functional groups was tolerated at the *para*-position of arylisothiocyanates, providing the corresponding products **3k**−**3p** in good to excellent yields. Similarly, transannulation of isothiocyanates possessing substituents at the *meta* and *ortho* positions of the arene proceeded uneventfully (**3q**−**3u**). Benzodioxolyl- and naphthyl-containing isothiocyanates smoothly underwent transannulation, affording **3v** and **3w** in good yields. In addition, it was found that alkyl isothiocyanates also are capable partners for this transformation. Thus, isothiocyanates possessing various benzyl and alkyl groups all reacted well, providing products **3x**−**3z** in good to high yields. Moreover, this reaction chemoselectively gave transannulation products **3aa** with allyl-containing isothiocyanate, the double bond moiety of which was not compromised. Notably, chiral isothiocyanates could also be efficiently employed in this reaction. Thus, isothiocyanates derived from amino acid esters smoothly underwent transannulation reaction to produce derivatives **3ab**−**3ad** in moderate yields.

**Scheme 7. Proposed Radical Activation Mechanism**




Encouraged by the successful transannulation of pyridotriazoles with isothiocyanates, we examined reactivity of carbonyl sulfide (OCS) in this transformation (Scheme 4). Because of its gaseous nature, carbonyl sulfides are experimentally difficult to handle. Hence, xanthate ester, which is a stable precursor of carbonyl sulfide that is produced via Chugaev elimination, was examined.[15] Gratifyingly, xanthate ester successfully underwent transannulation reactions with pyridotriazoles in the presence of 12 mol % Co(TPP) catalyst, providing oxo-thiazolopyridine derivatives **5a**−**5f** in moderate yields.

It was also shown that the *tert*-butyl group at imino-thiazolopyridine **3a** can easily be removed (under nonoptimized conditions) to access **6** possessing an N−H moiety, which can routinely be further functionalized, for instance, into benzoylated derivative **7** (see Scheme 5). Note that the latter cannot be accessed directly via the transannulation reaction of acylated isothiocyanates under the reaction conditions tested. It is believed that **6** can serve as a convenient synthon for a modular one-step synthesis of library of *N*-substituted imino-thiazolopyridines.

The radical nature of this transformation was validated by the following radical trapping experiment (see Scheme 6). The reaction in the presence of dibenzoyl peroxide **8** resulted in the formation of benzoyloxy-containing product **9**, thus supporting involvement of the carbene radical intermediate **C**.

On the basis of the above study and literature reports, the following plausible mechanism for this transannulation reaction is proposed. Xanthate ester **4**, which is obtained via Chugaev elimination, acts as a carbonyl sulfide (**12**) surrogate in this transformation (see Scheme 7a). Pyridotriazole **1** exist in equilibrium with its open diazo tautomer **A**, which, upon denitrogenative reaction with Co(II)-based metalloradical catalyst **D**, produces a key $\alpha$-Co(III)-pyridyl radical intermediate **C** (Scheme 7b). A subsequent trapping of this eletrophilc radical with isothiocyanate **2**[16] or the in-situ-generated carbonyl sulfide **12** produces radical intermediate **E**,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Org. Lett. XXXX, XXX, XXX−XXX

which, upon radical cyclization, leads to imino-thiazolopyridine **3** or oxo-thiazolopyridines **5** and regenerates the Co catalyst.

In summary, we have developed general and efficient Co(II)-catalyzed radical transannulation reactions of pyridotriazoles with isothiocyanates and carbonyl sulfide. This operationally simple protocol exhibits wide functional-group tolerance, efficiently producing *N*-fused imino-thiazolopyridines and oxo-thiazolopyridines.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03099.

Experimental procedures, optimization process, characterization data, and $^{1}H$ and $^{13}C$ NMR spectra of all new compounds (PDF)

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### Notes

The authors declare no competing financial interest.

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