

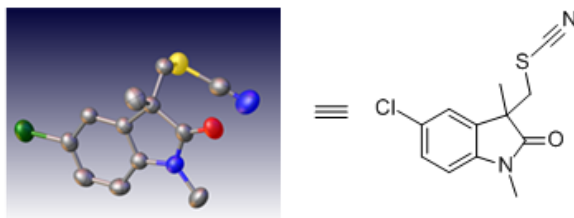
# Ag/Pyridine Co-Mediated Oxidative Arylthiocyanation of Activated Alkenes

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## 1. X-ray crystallography of compound 2g (thermal ellipsoids are shown with 30% probability)



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Table S1. Crystal data and structure refinement for 2g

Identification code	2g
Empirical formula	C <sub>12</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>s</sub>
Formula weight	266.74
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P1
a/Å, b/Å, c/Å	7.1852(2), 24.5633(6), 7.5740(2)
$\alpha$ /°, $\beta$ /°, $\gamma$ /°	90, 108.676(3), 90
Volume/Å <sup>3</sup>	1266.36(7)
Z	4
$\rho_{\text{calc}}$ /mm <sup>3</sup>	1.399
$\mu$ /mm <sup>-1</sup>	4.089
F(000)	552
Crystal size/mm <sup>3</sup>	0.26 × 0.21 × 0.18
Theta range for data collection	3.599 to 66.663°

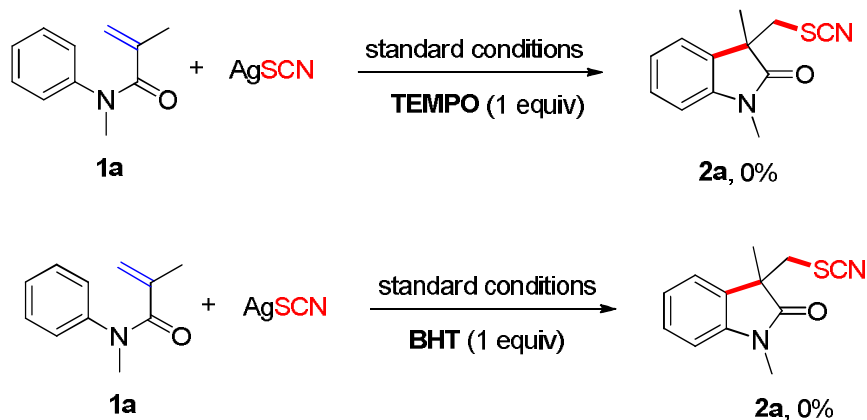
Index ranges	$-7 \leq h \leq 8, -29 \leq k \leq 29, -8 \leq l \leq 8$
Reflections collected	13972
Independent reflections	2231 [ $R(\text{int}) = 0.0483$ ]
Data/restraints/parameters	2231/0/157
Goodness-of-fit on $F^2$	1.055
Final R indexes [ $I > 2\sigma(I)$ ]	$R_1 = 0.0406, wR_2 = 0.1017$
Final R indexes [all data]	$R_1 = 0.0500, wR_2 = 0.1098$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.422/-0.284

**Crystal Data.**  $\text{C}_{12}\text{H}_{11}\text{ClN}_2\text{O}_8$ ,  $M = 266.74$ , Triclinic,  $a = 7.1852(2) \text{ \AA}$ ,  $b = 24.5633(6) \text{ \AA}$ ,  $c = 7.5740(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 108.676(3)$ ,  $\gamma = 90^\circ$ ,  $U = 1266.36(7) \text{ \AA}^3$ ,  $T = 293(2)$ , space group P1 (no. 1),  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 4.089$ , 13972 reflections measured, 2231 unique ( $R_{\text{int}} = 0.0483$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.1098 (all data).

## 2. Mechanistic Studies

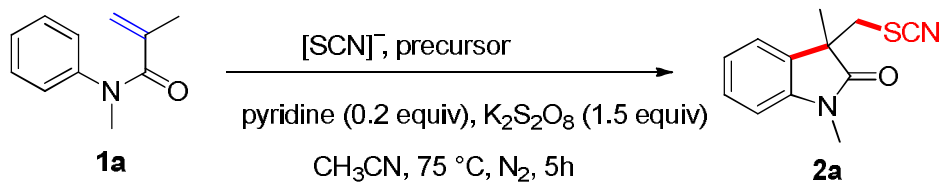
In this section, clarify several mechanistic details are clarified: 1) this transformation proceeded through a unique  $\text{NCS}\cdot$  radical addition path; 2) pyridine functioned not only as a base but also as a ligand to accelerate the oxidation of Ag(I) to Ag(II); 3) Ag(II) is the likely oxidant responsible for the formation of  $\text{NCS}\cdot$  radical.

### 2.1. Radical Verification Experiments



Compound **1a** (0.2 mmol),  $\text{K}_2\text{S}_2\text{O}_8$  (81.0 mg, 0.3 mmol), AgSCN (48 mg, 0.3 mmol), TEMPO (31.3 mg, 0.2 mmol) or BHT (44 mg, 0.2 mmol) and were combined in an oven-dried sealed tube. The vessel was evacuated and backfilled with  $\text{N}_2$  and  $\text{CH}_3\text{CN}$  (3 mL) and pyridine (3.5  $\mu\text{L}$ , 0.04 mmol) were added via syringe. The tube was then sealed with a Teflon lined cap and placed into a preheated oil bath at  $75^\circ\text{C}$  with vigorous stirring. After 8 h, the reaction mixture was cooled to room temperature and filtered through a plug of silica (eluted with EtOAc). Only trace **2a** was detected with 90% **1a** recovered. The result indicates that the radical intermediate probably be involved in the catalytic cycle of the reaction.

## 2.2 Role of Silver Experiments



CuSCN (1.5 equiv) **2a**, 0%

KSCN (1.5 equiv) **2a**, 0%

KSCN/AgNO₃ (1:1, 1.5 equiv) **2a**, 15%

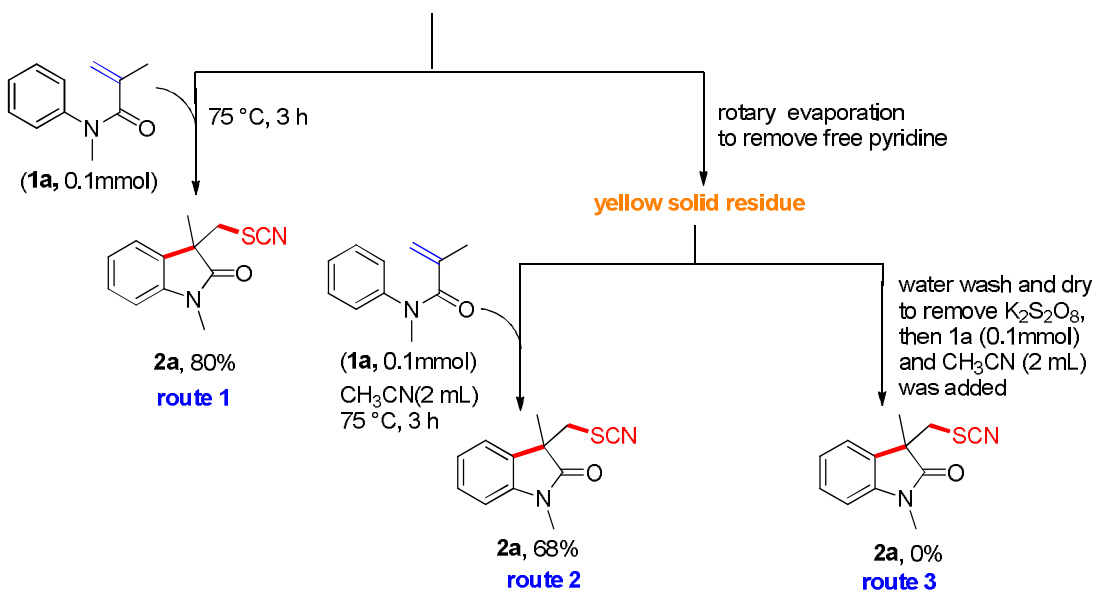
## 2.3 Role of Pyridine Experiments

AgSCN (0.15 mmol), K₂S₂O₈ (0.15 mmol), pyridine (0.05 mmol)

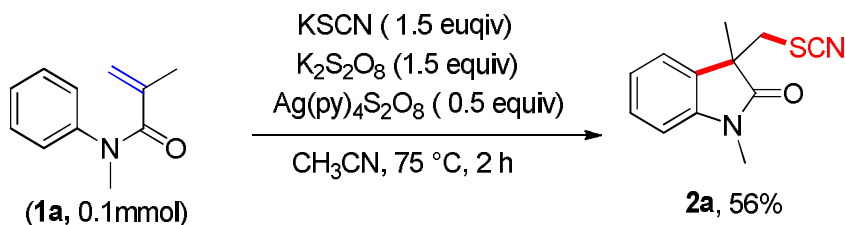
CH₃CN, 75 °C, 1 h



yellow suspension containing catalytic amount of Ag(II)-pyridine complex



In the above experiment, we found that stirring of AgSCN/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/pyridine mixture in CH<sub>3</sub>CN at 75 °C for 1 h led to the formation of colored Ag(II)–pyridine complexes, which could react with **1a** without free pyridine to give **2a** in 68% yield. However, the desired arylthiocyanation of **1a** with silver–pyridine complexes cannot proceed when K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was removed by water wash of yellow solid residue, which indicated the crucial roles of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in oxidizing Ag(I) to Ag(II).



Ag(py)<sub>4</sub>S<sub>2</sub>O<sub>8</sub>, which has been well established in the literature<sup>2</sup>, was considered to be a possible formation of the Ag(II)–pyridine complex. Accordingly, it was prepared as an orange solid.<sup>2a</sup> Treatment of **1a** with Ag(py)<sub>4</sub>S<sub>2</sub>O<sub>8</sub> (0.5 equiv), KSCN(1.5 equiv), and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.5 equiv) in CH<sub>3</sub>CN at 75 °C for 2 h led to the formation of **2a** in 56% isolated yield. In this experiment, a very quick reduction of orange-Ag(II) to colorless-Ag(I) was observed at the beginning of the reaction which suggested that Ag(II) should be the active species to oxidize NCS<sup>−</sup> to NCS• radical.

### 3. References

- [1] Mu, X.; Wu, T.; Wang, H. Y.; Guo, Y. L.; Liu, G. *J. Am. Chem. Soc.* **2012**, *134*, 878.
- [2] (a) H. Firouzabadi, P. Salehi, A. R. Sardarian and M. Seddighi, *Synthetic commun.*, 1991, **21**, 1121. (b) H. Firouzabadi, P. Salehi and I. Mohammadpour-Baltork, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2878. (c) A. Nikolaev, C. Y. Legault, M. Zhang and A. Orellana, *Org. Lett.*, 2018, **20**, 796



## 6. Copies of $^1\text{H}$ -NMR and $^{13}\text{C}$ -NMR spectra

