Electronic Supplementary Information

One-pot Synthesis of 3,5-Disubstituted 1,2,4-Thiadiazoles from

Nitriles and Thioamides via I2-Mediated Oxidative Formation of N-S

Bond

Ling Chai,^{a,‡} Yuanqing Xu,^{a,‡} Tao Ding,^{a,‡} Xiaomin Fang,^a Yanpeng Wang,^a Wenkai Zhang,^a Minghua Lu,^a Hao Xu,^{*,a} Xiaobo Yang^{*,b}

- ^a College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P. R. China.
- ^b College of Chemistry & Chemical Engineering, Shenyang Normal University, Shenyang, Liaoning, 110034, P. R. China.

E-mail : xuhao@henu.edu.cn; bxy1223@gmail.com

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General experimental procedures

All reactions were carried out under air. Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl₃ as the internal standard (¹H NMR: TMS at 0.00 ppm,CHCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.16 ppm) or were recorded using tetramethylsilane (TMS) in the solvent of d_6 -DMSO as the internal standard (¹H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ¹³C NMR: DMSO at 39.51 ppm).

Compounds 2b-j was synthesized by previous method.^[1]



Scheme S1. (A) Employing 4-acetylbenzothioamide as the substrate to react with 1g; (B) Employing amino-substituted nitriles as the substrates to react with 2a; (C) Employing pivalonitrile as the substrate to react with 2a; (D) Employing aliphatic thioamides as the substrates to react with aliphatic nitriles 1 under standard conditions; (E) Employing aromatic nitriles as substrates to react with 2a.



Figure S1. ESI-MS $[M+H]^+$ spectrum of reaction solution of *p*-methylbenzonitrile with thiobenzamide **2a**.^{*a*} [^{*a*}Reaction condition: (1) **1** (0.8 mmol), **2** [0.4 mmol, added (4×0.1 mmol per 5 min)], AlCl₃ (0.8 mmol), *n*-BuAc (1 mL), reaction time (5 h) at 70 °C in air; (2) then H₂O (0.3 mL), I₂ (0.8 mmol), reaction time (24 h) at room temperature. The resulting solution was

quenched with saturated aqueous solution of $Na_2S_2O_3$. The organic and aqueous layers were separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , concentrated and purified by column chromatography on silica gel, and the crude product is used to do the ESI-MS test.]



Figure S2. ESI-MS $[M+H]^+$ spectrum of reaction solution of *p*-chlorobenzonitrile with thiobenzamide **2a.**^{*a*} [^{*a*}Reaction condition: (1) **1** (0.8 mmol), **2** [0.4 mmol, added (4×0.1 mmol per 5 min)], AlCl₃ (0.8 mmol), *n*-BuAc (1 mL), reaction time (5 h) at 70 °C in air; (2) then H₂O (0.3 mL), I₂ (0.8 mmol), reaction time (24 h) at room temperature. The resulting solution was

quenched with saturated aqueous solution of $Na_2S_2O_3$. The organic and aqueous layers were separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , concentrated and purified by column chromatography on silica gel, and the crude product is used to do the ESI-MS test.]

References

(1) Goswami, S.; Maity, A. C.; Das, N. K. J. Sulfur Chem. 2007, 28, 233.

