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TBAI-Catalyzed Reaction between *N*-Tosylhydrazones and Sulfur: A Procedure toward 1,2,3-Thiadiazole

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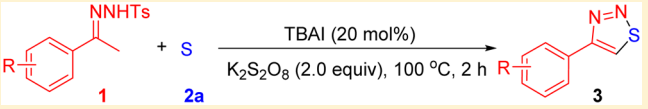
Supporting Information

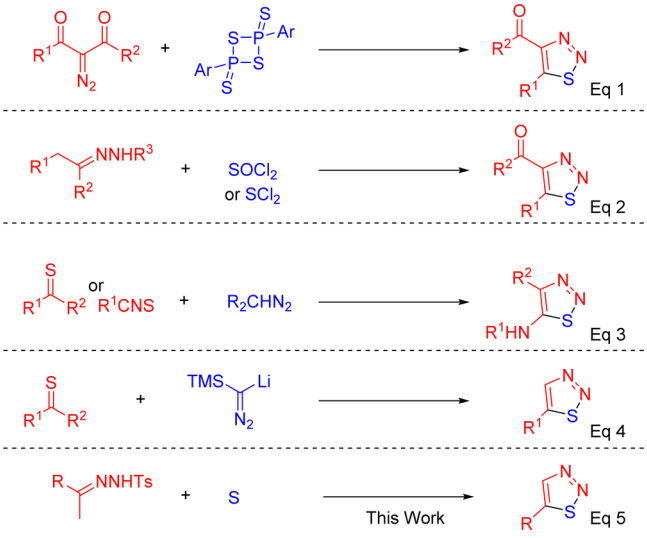
ABSTRACT: A TBAI-catalyzed reaction between *N*-tosyl hydrazone and sulfur was developed, leading to 1,2,3-thiadiazoles in moderate to good yields. It represents a facile and practical procedure to access thiadiazole under metal-free conditions. This procedure serves as an improvement for the Hurd−Mori reaction.



1,2,3-Thiadiazoles show broad pharmacological properties, such as platelet aggregation inhibitor,[1] neuroprotective regents,[2] antitumor activities,[3] antiviral activities,[4,5] and inhibitors of Hsp90 chaperone.[6,7] Moreover, they serve as intermediates in organic synthesis.[8−12]

The diazotization of α-amino ketones, followed by the reaction with Lawesson's reagent, delivered 1,2,3-thiadiazoles (Scheme 1, eq 1).[14] Meanwhile, the Hurd−Mori reaction was a powerful procedure to access such a structure (Scheme 1, eq 2).[15−17] Pechmann and Nold described the reaction of diazomethane with phenyl isothiocyanate, leading to 1,2,3-thiadiazoles (Scheme 1, eq 3).[18,19] 1,3-Dipolar cycloaddition of diazoalkanes to thiocarbonyl compounds allowed one to access 1,2,3-thiadiazoles (Scheme 1, eq 3).[20,21] Recently, Singh reported [3 + 2] cycloaddition of α-enolic dithioesters with tosyl azide, leading to 4,5-disubstituted 1,2,3-thiadiazoles.[22] The reaction of lithium (trimethylsilyl)diazomethane [TMSC(Li)═N_2] with thiocarbonyl compounds has proved to be a convenient method for the preparation of 5-substituted 1,2,3-thiadiazoles (Scheme 1, eq 4).[23] However, the diazo compounds and azide are explosive, while $SOCl_2$, SCl_2, and S_2Cl_2 react violently with water. Thus, the development of a safe methodology would be beneficial to organic chemistry. Herein, we wish to report a TBAI-catalyzed reaction between *N*-tosylhydrazones[24] and element sulfur, leading to 4-aryl-1,2,3-thiadiazoles. Sulfur powder is cheap, safe, and abundant in nature.[13] Moreover, the rigorous extrusion of moisture is not required in this procedure.

Scheme 1. Reactions toward 1,2,3-Thiadiazole



Initially, we tested the combination of acetophenone tosylhydrazone, sulfur, I_2, and $K_2S_2O_8$ in DMAC under 100 °C for 12 h. To our delight, the annulation product was isolated in 61% yield (Table 1, entry 1). KI, NH_4I, and CuI all worked to some extent with the yields ranging from 41% to 78% (Table 1, entries 2−4, and 6). However, PIDA failed to work (Table 1, entry 5). The yield further increased to 84% by employing TBAI (Table 1, entry 7). Replacing DMAC with DMF decreased the reaction efficiency (62%, Table 1, entry 7). Increasing the loading of sulfur had no positive effect on the reaction efficiency (Table 1, entry 7). Other oxidants, such as DDQ and H_2O_2, resulted in no reaction (Table 1, entries 10 and 11). The reaction did not work under toluene, acetonitrile, and dioxane (Table 1, entries 12−14). Sulfur took part in the reaction, as confirmed by the blank experiment (Table 1, entry 15). No reaction took place in the absence of TBAI or $K_2S_2O_8$ (Table 1, entries 16 and 17). Notably, the procedure was applicable to 10 mmol scale, and the product **3a** was isolated in 77% yield (Scheme 2).

After the establishment of the optimal reaction conditions, the scope of *N*-tosylhydrazone was studied, as shown in Figure 1. As expected, the procedure was applicable for substrates with both electron-donating and withdrawing-groups in the phenyl ring, providing 4-aryl-1,2,3-thiadiazoles in moderate to good

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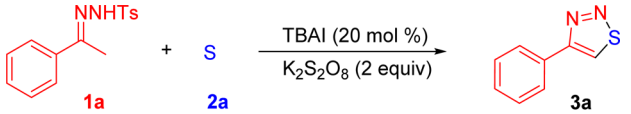
Table 1. Screening the Optimized Reaction Conditions[a]

entry	catalyst	oxidant	solvent	yield (%)[b]
1	I_2	$K_2S_2O_8$	DMAC	61
2	KI	$K_2S_2O_8$	DMAC	57
3	NH_4I	$K_2S_2O_8$	DMAC	78
4	NIS	$K_2S_2O_8$	DMAC	69
5	PIDA	$K_2S_2O_8$	DMAC	<5
6	CuI	$K_2S_2O_8$	DMAC	41
7	TBAI	$K_2S_2O_8$	DMAC	84(62)[c], (60)[d], (82)[e]
8	TBAI	$NH_4S_2O_8$	DMAC	63
9[f]	TBAI	$K_2S_2O_8$	DMAC	49
10	TBAI	DDQ	DMAC	NR
11	TBAI	H_2O_2	DMAC	NR
12	TBAI	$K_2S_2O_8$	$PhCH_3$	NR
13	TBAI	$K_2S_2O_8$	CH_3CN	NR
14	TBAI	$K_2S_2O_8$	dioxane	NR
15[g]	TBAI	$K_2S_2O_8$	DMAC	NR
16[h]	TBAI		DMAC	NR
17[i]		$K_2S_2O_8$	DMAC	NR

[a]Reaction conditions: **1a** (0.1 mmol), catalyst (20 mol %), oxidant (0.2 mmol), **2a** (0.5 mmol), and solvent (1.5 mL) at 100 °C under air for 2 h, sealed tube. [b]Isolated yield. [c]DMF. [d]**2a** (0.3 mmol). [e]**2a** (0.4 mmol). [f]**2a** (Na_2S, 0.5 mmol) [g]Without **2a**. [h]Without $K_2S_2O_8$. [i]Without TBAI. TBAI = tetrabutylammonium iodide; PIDA = iodobenzene diacetate; DMAC = dimethylacetamide.

Scheme 2



yields. The procedure tolerated the functional groups, such as bromo, trifluoromethyl, cyano, methoxy carbonyl, chloro, and acetamino well. Notably, this procedure provided a rapid access to 4-heteroaryl analogues, such as **3h**, **3k**, **3l**, and **3r**. Particularly, 4-alkenyl-1,2,3-thiadiazole **3q** was isolated in 44% yield. However, the aliphatic analogues of *N*-Ts hydrazone did not work under the procedure. The application of selenium and tellurium powder in the procedure could not provide the target product (Figure 1).

To further get some insights into the mechanism, more experiments were conducted. First, 2,2,4,4-tetramethyl-1-piperidinyloxy (TEMPO, 1 equiv), galvinoxyl free radical, and 2,6-di-*tert*-butyl-*p*-cresol (BHT, 1 equiv) were added to the standard procedure, and none of them was inhibited (Scheme 3, eq 1). The potential intermediates, such as **4**, **5**, **6**,[25] and **7**, all ran smoothly under the standard procedure with comparable yields (Scheme 3, eqs 2–4). Moreover, the reaction efficiency of **4**–**7** was hardly affected by radical inhibitor, which was consistent with the result in eq 1. However, disulfide was not formed by the reaction of α-iodo acetophenone and sulfur under the standard procedure (Scheme 3, eq 5). These results ruled out the possibility of **7** as the intermediate.

On the basis of these experimental results, a proposed mechanism was outlined in Scheme 4. First, in the presence of

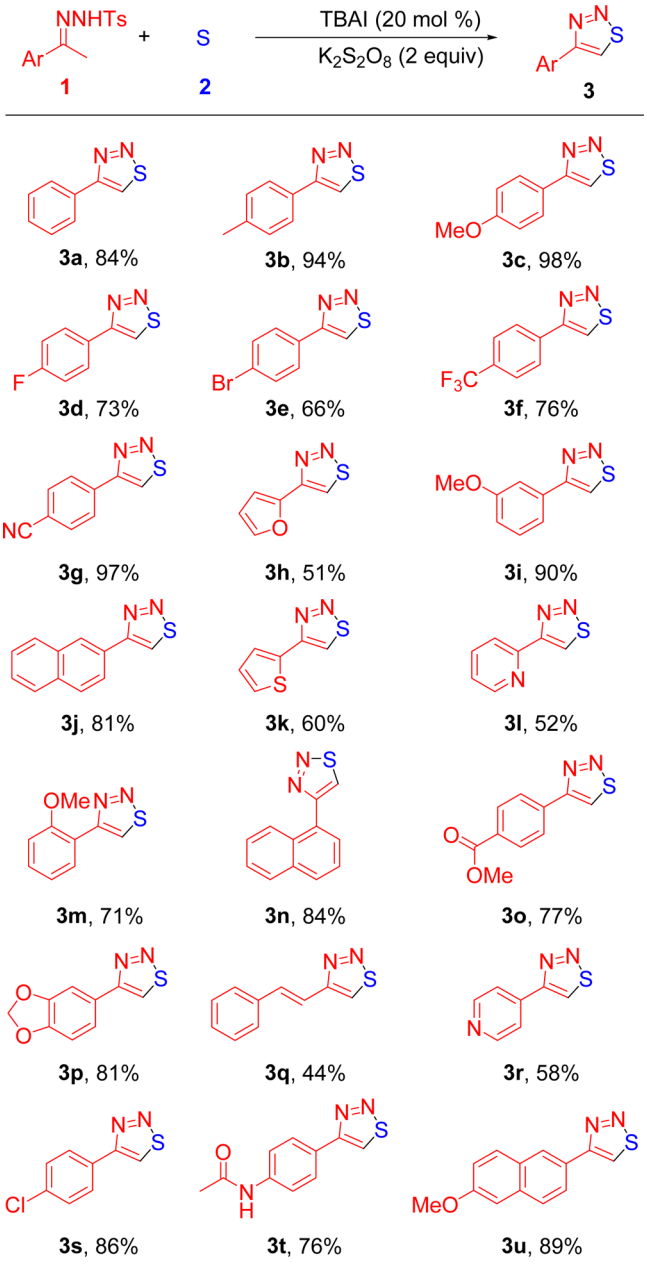


Figure 1. Scope of *N*-Ts hydrazone. Reaction conditions: **1** (0.1 mmol), **2** (sublimed sulfur, 0.5 mmol), TBAI (20 mol %), $K_2S_2O_8$ (0.2 mmol), and DMAC (1.5 mL) at 100 °C under air for 2 h, sealed tube.

$K_2S_2O_8$, I^- was oxidized to I^+. Then, the α-iodation of acetophenone tosylhydrazone took place to form intermediate **4**. Subsequently, the elimination of HI in **4** provided intermediate **5**, along with the releasing of I^-, which was oxidized to I_2 to fulfill the catalytic cycle. Second, the addition of S_8 to **5** produces intermediate **6**, which transforms to intermediate **7**. After that, the intramolecular nucleophilic attack took place to form intermediate **8**. Finally, the elimination of Ts^- and S_7 delivered 1,2,3-thiadiazoles.

In conclusion, we have developed a TBAI-catalyzed direct annulation of acetophenone tosylhydrazone and sufur powder, leading to 1,2,3-thiadiazoles in moderate to excellent yields. This procedure avoids the employment of hazardous starting materials. Furthermore, the rigorous extrusion of moisture is not required in this procedure. Thus, it represents a practical

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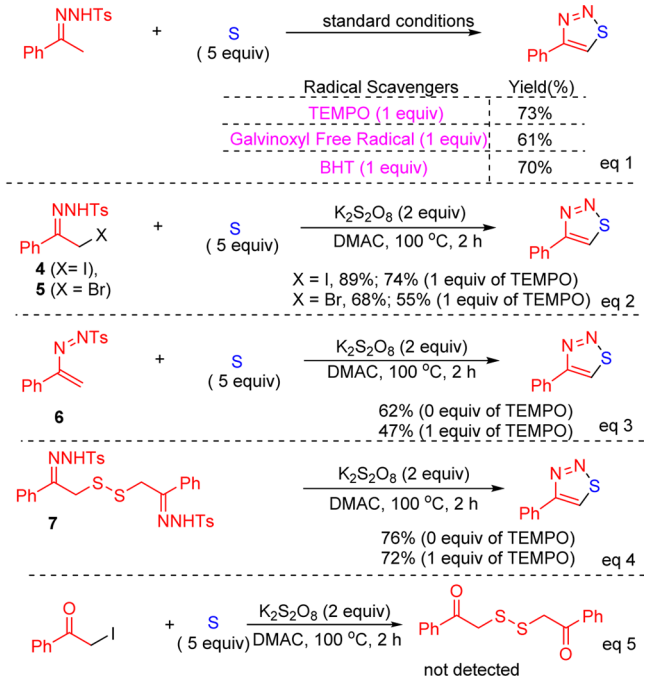
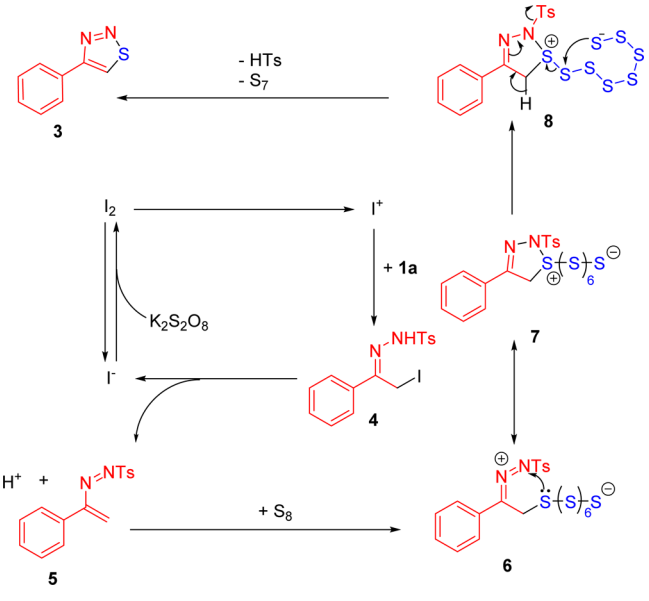
Scheme 3. Preliminary Mechanism Study



Scheme 4. A Tentative Mechanism



pathway to access such a structure as a key progress in the Hurd–Mori reaction.

EXPERIMENTAL SECTION

General Considerations. Chemicals were used as received without special purification unless stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C NMR). NMR results were reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. Melting points were taken on an electrothermal melting point apparatus and without correction. IR spectra were recorded on a spectrometer using KBr discs.

Experimental Procedure. A sealed tube was charged with *N*-tosylhydrazone (0.1 mmol), sulfur (0.5 mmol), TBAI (0.02 mmol), $K_2S_2O_8$ (0.2 mmol), and DMAC (1.5 mL). The mixture was stirring under air at 100 °C for 2 h. The mixture was washed with water and extracted by ethyl acetate and then concentrated in vacuum, and the residue was purified by preparative TLC on GF254 (petroleum ether ether/ethyl acetate) to afford the desired product.

*4-Phenyl-1,2,3-thiadiazole (**3a**).*[17] TLC on GF254 (ethyl acetate:-petroleum ether, 1:20) gave the product (13.6 mg, 84% yield) as a white solid. mp 75–77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (s, 1H), 8.05 (d, J = 7.2 Hz, 2H), 7.53–7.43 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.9, 130.8, 130.0, 129.4, 129.2, 127.4.

*4-(p-Tolyl)-1,2,3-thiadiazole (**3b**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (16.0 mg, 94% yield) as a white solid. mp 73–75 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.0, 139.5, 129.9, 129.3, 128.1, 127.3, 21.4.

*4-(4-Methoxyphenyl)-1,2,3-thiadiazole (**3c**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (17.6 mg, 98% yield) as a white solid. mp 89–93 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (s, 1H), 7.98 (d, J = 8.8 Hz, 2H), 7.03 (d, 8.8 Hz, 2H), 3.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7, 160.5, 128.7, 128.4, 123.5, 114.5, 55.4.

*4-(4-Fluorophenyl)-1,2,3-thiadiazole (**3d**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (12.5 mg, 73% yield) as a white solid. mp 185–188 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 (s, 1H), 8.05–8.01 (m, 2H), 7.22–7.18 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.4 (d, $J_{C\text{-}F}$ = 248.0 Hz), 161.8, 129.7, 129.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 127.0, 116.2 (d, $J_{C\text{-}F}$ = 21.8 Hz).

*4-(4-Bromophenyl)-1,2,3-thiadiazole (**3e**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (13.7 mg, 66% yield) as a white solid. mp 150–152 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (s, 1H), 7.92 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.7,132.3, 130.3, 129.7, 128.8, 123.6.

*4-(4-(Trifluoromethyl)phenyl)-1,2,3-thiadiazole (**3f**).* TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (15.2 mg, 76% yield) as a white solid. mp 70–72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.77 (s, 1H), 8.18 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.4 Hz 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.3, 134.0, 131.4 (q, $J_{C\text{-}F}$ = 32.6 Hz), 131.4, 126.2 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.2 (q, $J_{C\text{-}F}$ = 270.4 Hz). MS (EI): 230 (M^+); HRMS (ESI-TOF) m/z calcd for $C_9H_5F_3N_2S$ (M + COOH)$^-$ 275.0103, found 275.0108; IR (KBr) ν 3090, 2923, 2852, 1637, 1592, 1542, 1465, 1327, 1121 cm^{-1}.

*4-(1,2,3-Thiadiazol-4-yl)benzonitrile (**3g**).*[26] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (17.1 mg, 97% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.82 (s, 1H), 8.18 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.8, 134.8, 133.0, 132.1, 127.8, 118.3, 112.9.

*4-(Furan-2-yl)-1,2,3-thiadiazole (**3h**).*[27] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (7.8 mg, 51% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (s, 1H), 7.56 (s, 1H), 7.15 (d, J = 7.2 Hz, 1H), 6.59–6.57 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.7, 146.6, 143.4, 128.4, 111.9, 109.5.

*4-(3-Methoxyphenyl)-1,2,3-thiadiazole (**3i**).* TLC on GF254 (ethyl acetate:petroleum ether, 1:30) gave the product (34.8 mg, 90% yield) as a pale yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.64 (s, 1H), 7.65–7.64 (m, 1H), 7.56 (d, 7.6 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 6.98 (m, 1H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7, 160.2, 132.0, 130.2, 130.2, 119.7, 115.3, 112.7, 55.4. MS (EI): 192 (M^+); HRMS (ESI-TOF) m/z calcd for $C_9H_8N_2OS$ (M + H)$^+$ 193.0432, found 193.0430; IR (KBr) ν 3110, 3003, 2933, 1603, 1589, 1514, 1464, 1437, 1245, 1158, 1035 cm^{-1}.

*4-(Naphthalen-2-yl)-1,2,3-thiadiazole (**3j**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (15.4 mg, 81% yield) as a white solid. mp 202–206 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.76 (s, 1H), 8.60 (s, 1H), 8.10 (d, J = 10.0 Hz, 1H), 7.99–7.97 (m, 2H), 7.89–7.88 (m, 1H), 7.56–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.9, 145.6, 133.7, 133.5, 130.1, 129.0, 128.5, 128.1, 127.8, 126.9, 126.8, 124.7.

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*4-(Thiophen-2-yl)-1,2,3-thiadiazole (**3k**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:30) gave the product (10.1 mg, 60% yield) as a white solid. mp 70−73 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (s, 1H), 7.65−7.64 (m, 1H), 7.43−7.42 (m, 1H), 7.16−7.14 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.3, 133.1, 128.4, 127.9, 127.0, 126.4.

*4-(Pyridin-2-yl)-1,2,3-thiadiazole (**3l**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:10) gave the product (8.5 mg, 52% yield) as a white solid. mp 158−160 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.23 (s, 1H), 8.68 (d, 4.8 Hz 1H), 8.46 (d, J = 8.0 Hz, 1H), 7.89−7.85 (m, 1H), 7.36−7.33 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.3, 149.9, 149.8, 137.4, 133.9, 123.9, 122.5.

*4-(2-Methoxyphenyl)-1,2,3-thiadiazole (**3m**).*[28] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (12.7 mg, 71% yield) as a yellow solid. mp 94−97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.06 (s, 1H), 8.52−8.49 (m, 1H), 7.44−7.40 (m, 1H), 7.16−7.12 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 156.3, 133.3, 130.4, 130.3, 121.2, 111.2, 55.5.

*4-(Naphthalen-1-yl)-1,2,3-thiadiazole (**3n**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (16.0 mg, 84% yield) as a white solid. mp 198−200 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (s, 1H), 8.10−8.08 (m, 1H), 7.94−7.80 (m, 2H), 7.77−7.75 (m, 1H), 7.60−7.52 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.9, 134.2, 133.8, 131.4, 129.9, 128.5, 128.4, 127.1, 126.3, 125.2, 125.1.

*Methyl 4-(1,2,3-Thiadiazol-4-yl)benzoate (**3o**).* TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (15.1 mg, 77% yield) as a yellow solid. mp 144−146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.77 (s, 1H), 8.18−8.11 (m, 4H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 161.7, 134.8, 131.4, 130.8, 130.4, 127.2, 52.3; MS (EI): 220 (M^+); HRMS (ESI-TOF) m/z calcd for $C_{10}H_8N_2O_2S$ $(M + H)^+$ 221.0380, found 221.0379; IR (KBr) ν 3093, 2963, 1729, 1611, 1455, 1439, 1414 cm^{-1}.

*4-(Benzo[d][1,3]dioxol-5-yl)-1,2,3-thiadiazole (**3p**).* TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (15.0 mg, 81% yield) as a yellow solid. mp 124−126 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (s, 1H), 7.55−7.52 (m, 2H), 6.92 (d, J = 8.0 Hz 1H), 6.03 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6, 148.6, 148.3, 128.8, 124.9, 121.5, 108.9, 107.8, 101.5; MS (EI): 206 (M^+); HRMS (ESI-TOF) m/z calcd for $C_9H_6N_2O_2S$ $(M + H)^+$ 207.0222, found 207.0223; IR (KBr) ν 3091, 2922, 2360, 1629, 1608, 1522, 1464, 1445, 1244, 1039 cm^{-1}.

*(E)-4-Styryl-1,2,3-thiadiazole (**3q**).*[29] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (7.7 mg, 44% yield) as a yellow solid. mp 81−83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (s, 1H), 7.71 (d, J = 16.4 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.2, 136.1, 134.7, 130.2, 128.8, 128.7, 126.9, 117.1.

*4-(Pyridin-4-yl)-1,2,3-thiadiazole (**3r**).*[30] TLC on GF254 (ethyl acetate:petroleum ether, 1:10) gave the product (9.0 mg, 58% yield) as a white solid. mp 162−164 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.23 (s, 1H), 8.79 (s, 1H), 8.68−8.67 (m, 1H), 8.40 (d, J = 8.0 Hz, 1H), 7.47−7.44 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.7, 150.5, 148.3, 134.7, 131.0, 126.9, 124.0.

*4-(4-Chlorophenyl)-1,2,3-thiadiazole (**3s**).*[17] TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (15.6 mg, 86% yield) as a white solid. mp 136−138 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.64 (s, 1H), 7.80−7.79 (m, 2H), 7.49−7.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.7, 135.4, 130.2, 129.4, 129.2, 128.6.

*N-(4-(1,2,3-Thiadiazol-4-yl)phenyl)acetamide (**3t**).* Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:2) gave the product (14.8 mg, 76% yield) as a yellow solid. mp 216−218 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.14 (s, 1H), 9.48 (s, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.7, 161. 8, 140.3, 132.0, 127.7, 125.4, 119.4, 24.2; MS (EI): 219 (M^+); HRMS (ESI-TOF) m/z calcd for $C_{10}H_{10}N_3OS$ $(M + H)^+$ 220.0540, found 220.0539; IR (KBr) ν 3315, 3107, 2961, 1728, 1671, 1604, 1545, 1464, 1411, 1260 cm^{-1}.

*4-(6-Methoxynaphthalen-2-yl)-1,2,3-thiadiazole (**3u**).* TLC on GF254 (ethyl acetate:petroleum ether, 1:20) gave the product (18.4 mg, 89% yield) as a yellow solid. mp 150−151 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.68 (s, 1H), 8.50 (s, 1H), 8.07−8.05 (m, 1H), 7.86−7.82 (m, 2H), 7.22−7.17 (m, 2H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 158. 5, 135.0, 130.0, 129.4, 128.9, 127.7, 126.7, 126.0, 125.3, 119.7, 105.8, 55.4; MS (EI): 242 (M^+); HRMS (ESI-TOF) m/z calcd for $C_{13}H_{11}N_2OS$ $(M + H)^+$ 243.0588, found 243.0587; IR (KBr) ν 3083, 2922, 1630, 1606, 1503, 1461, 1393, 1263, 1212, 1029 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02280.

Research of mechanism and ^{1}H and ^{13}C NMR spectra of compounds **3a**−**3u** (PDF)

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Notes

The authors declare no competing financial interest.

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