

Supporting Information

Iodine-Catalyzed Cross Dehydrogenative Coupling Reaction: Sulfenylation of Enaminones Using Dimethyl Sulfoxide as an Oxidant

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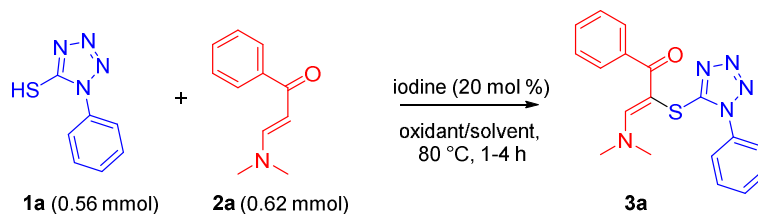
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General experimental

NMR spectra were recorded on a 400 MHz spectrometer in CDCl_3 or DMSO-d_6 . Tetramethylsilane (TMS; $\delta = 0.00$ ppm) for ^1H NMR in CDCl_3 , and residual non-deuterated solvent peak ($\delta = 2.50$ ppm) in DMSO-d_6 , served as an internal standard. The solvent signal (CDCl_3 , $\delta = 77.00$ ppm; and DMSO-d_6 , $\delta = 39.5$ ppm) was used as internal standard for ^{13}C NMR. IR spectra were measured using an FT-IR spectrometer. Mass spectra were obtained with a Q-TOF Mass Spectrometer (HRMS). Flash column chromatography was carried out by packing glass columns with commercial silica gel 230-400 mesh (commercial suppliers) and thin-layer chromatography was carried out using silica gel GF-254. All catalysts and reagents were procured from commercial suppliers. Dichloroethane was distilled over calcium hydride and stored over molecular sieves and used for all procedures. Other solvents, used for work up and chromatographic procedures were purchased from commercial suppliers.

Optimization studies for thiol-1

Optimization of solvent (Table S1)



entry	oxidant/solvent	time	isolated yield (%) ^b
1	DMSO	1 h	70
2	DCE	4 h	ND
3	EtoAc	4 h	ND
4	ACN	4 h	trace
5	Toluene	4 h	ND
6	Trifluoroethanol	4 h	ND
7	Water	4 h	ND
8	Ethanol	4 h	ND
9	DMF	2 h	18
10	DMA	4 h	trace
11	NMP	4 h	trace
12	none	4 h	trace
13	DMSO (3 equiv), DCE	2 h	33
14	DMSO (3 equiv), EtoAc	2 h	32
15	DMSO (3equiv), ACN	2 h	36
16	DMSO (3 equiv), toluene	2 h	31
17	DMSO (3 equiv), Trifluoroethanol	4 h	ND
18	DMSO (3 equiv), Water	4 h	ND
19	DMSO (3 equiv), Ethanol	4 h	ND
20	DMSO (3 equiv), DMF	2 h	28
21	DMSO (3 equiv), DMA	4 h	trace
22	DMSO (3 equiv), NMP	4 h	trace
23	DMSO (3 equiv), DCE	1.5 h	58^c
24	DMSO (5 equiv), DCE	1.5 h	61^c

ND= Not detected

^a Reaction conditions: **1a** (0.56 mmol), **2a** (0.62 mmol), iodine (20 mol%) in 1 mL of solvent at 80 °C.^b Isolated yield^c 30 mol % of iodine used at 80 °C for 1.5 h (entries 23 and 24)

In solvents such as DCE, EtoAc, ACN, Toluene, DMF, DMA and NMP decomposition of 1-phenyl-1H-tetrazole-5-thiol (**1a**) was observed with 20 mol % of iodine and (E)-3-(dimethylamino)-1-phenylprop-2-en-1-one (**2a**) was intact (entries 2-12). In TLC, only the product **3a** and starting material **2a** was observed after 2- 4 h. This could be due to the decomposition of **1a** under the reaction conditions (entries 13-24).

Optimization of catalyst or additive (Table S2)

entry	oxidant/solvent	catalyst/ additive	time	isolated yield (%)
1	DMSO	20 mol % aq. HI (55%)	2 h	41
2	DMSO	20 mol % aq. HBr	12 h	trace
3	DMSO	20 mol % NBS	12 h	trace
4	DMSO	20 mol % NCS	12 h	trace
5	DMSO	20 mol % KI	12 h	trace
6	DMSO	20 mol % KIO ₃	6 h	29
7	DMSO	none	12 h	ND

NCS = *N*-ChlorosuccinimideNBS = *N*-Bromosuccinimide

KI = Potassium iodide

Optimization of equiv of 1a and 2a and mol % of iodine (Table S3)

entry	1a (equiv)	2a (equiv)	iodine (mol %)	time	isolated yield (%)
1	1	1.5	20	1 h	72
2	1.5	1.1	20	2 h	62
3	1	1.1	30	1 h	76
4	1	1.1	50	0.5 h	77
5	1	1.1	10	2 h	62

In TLC, only the product **3a** and starting material thiol **1a** (trace) and complete consume of enaminone **2a** was observed after 1 h. The isolated yield, 62-77%, is due to the loss of product in work up or decomposition of either **1a** or **2a** under the reaction conditions. There was no other side products are formed during the reaction.

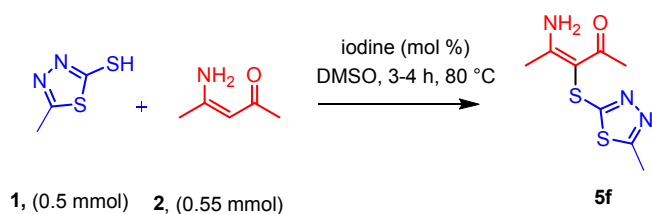
Optimization under Argon and Oxygen atmosphere (Table S4)

entry	1a (equiv)	2a (equiv)	iodine (mol %)	oxygen/ argon	isolated yield (%)
1	1	1.1	30	Reaction under O ₂ atmosphere, 1 h	76
2	1	1.1	30	Reaction under Argon atmosphere, 1 h	74

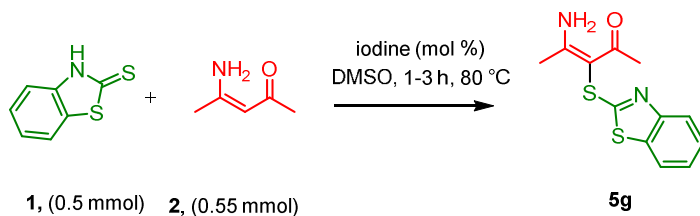
In TLC, only the product **3a** and starting material thiol **1a** (trace) and complete consume of enaminone **2a** was observed after 1 h. There was no other side products are formed during the reaction.

Effect of external additives and oxidants (Table S5)

entry	1a (equiv)	2a (equiv)	iodine (mol %)		isolated yield (%)
1	1	1.1	(30)	30 mol % of PTSA, 1 h	76
2	1	1.1	(30)	30 mol % of Et ₃ N, 1 h	trace
3	1	1.1	(30)	TBHP in decane (1 equiv), 1 h	75

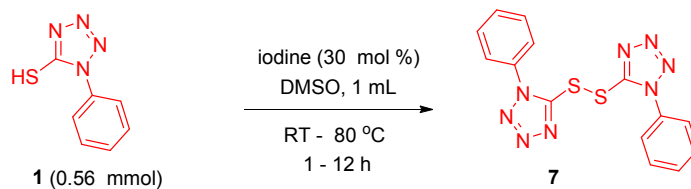
Optimization studies for 5-methyl-1,3,4-thiadiazole-2-thiol (Table S6)

entry	1a (equiv)	2 (equiv)	Iodine (mol %)	time	isolated yield (%)
1	1	1.1	(30)	4 h	32
2	1	1.1	(50)	3 h	54
3	1	1.1	(100)	3 h	72

Optimization studies for thione-2 (Table S7)

entry	1a (equiv)	2 (equiv)	iodine (mol %)	time	isolated yield (%)
1	1	1.1	(30)	3 h	72
2	1	1.1	(50)	2 h	91
3	1	1.1	(100)	1.5 h	88

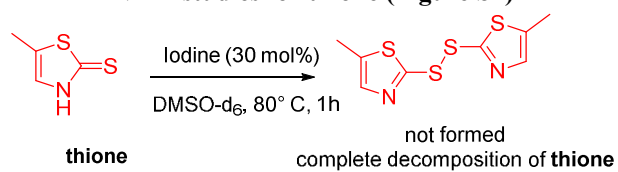
Control experiments at various temperatures (Table S8)



entry	temperature 1 mL	Time h	isolated yield
1	80 °C	1	ND
2	70 °C	1	ND
3	60 °C	1.5	ND
4	50 °C	3	ND
5	40 °C	5	ND
6	30 °C	10	ND
7	RT	12	ND

In all the cases decomposition of 1-phenyl-1H-tetrazole-5-thiol (**1**) was observed and formation of disulfide was not observed.

NMR studies for thione (Figure S1)



δ 6.52 aromatic peak completely disappears, indicates complete decomposition of 5-methylthiazole-2(3H)-thione.

