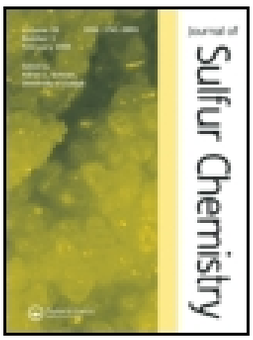

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A convenient synthesis of thiazol-2(3*H*)-one skeletons from a reaction involving terminal alkynes, elemental sulfur, and isocyanates

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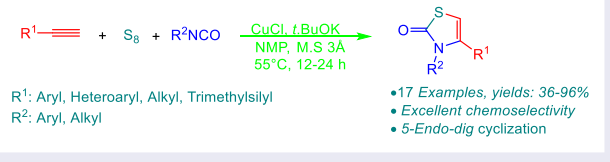
ABSTRACT

An efficient copper-catalysed tandem reaction to synthesize thiazol-2(3*H*)-one structures from readily available raw materials is described. The protocol provides a cost-effective approach to a decent range of nitrogen and sulfur bearing heterocycles in acceptable yields. The transformation takes place with CuCl as catalyst, *N*-methylpiperidine as additive, and *t*-BuOK as base in anhydrous DMF as solvent.



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Thiazol-2(3H)-one; elemental sulfur; copper-acetylide; isocyanate; cyclization

Introduction

During the last two decades, copper salts have been broadly utilized in catalytic multicomponent reactions to form a wide range of heterocyclic compounds [1–5]. In this regard, those reactions involving terminal alkynes have attracted considerable attention in preparation of synthetically important heterocycles [6–8]. The widespread application of copper salts with alkyne synthons relies on their ability to effectively activate the π-electrons of triple bonds, providing a partial positive charge on alkyne unit [9].

In this line, the additions of terminal alkynes on various type of electrophiles have been well documented [10–15]. Pioneered by Gewald [16], the nucleophilic additions of terminal alkynes on elemental sulfur in the presence of appropriate third coupling partners has emerged to form a diverse range of sulfur heterocycles [17–18].

Owing to their importance in chemical biology and medicinal chemistry, thiazole possessing molecules have attracted much attention [19–22]. Additionally, some thiazole bearing compounds like Plantazolicin exhibited pharmacologically important activity

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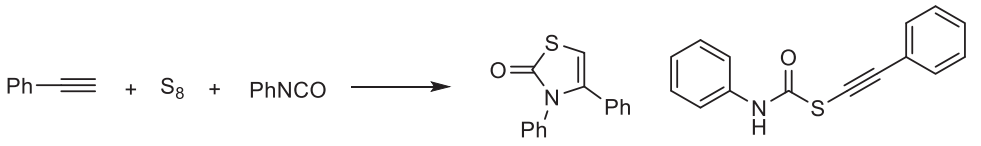
[23–25]. A number of methods have been developed for the synthesize (US format) of thiazole building-blocks with condensation reactions being among the most documented transformations [26–27]. For instance, Ghazanfarpour disclosed an organocatalytic route to thiazolidine derivatives from a reaction involving aziridines and carbon disulphide [28]. Mehrabi reported a three-component reaction between arylglyoxals with acetylthiourea and Meldrum's acid to form thiazole derivatives [29]. Khurana' laboratory has developed a novel reaction using acetic acid as mediator to form such important heterocycles [30]. A domino reaction between alkynes, elemental sulfur, and aziridines has been applied to form thiazole building blocks [17]. Recently, Domling described an Ugi-type reaction to form thiazole structures through a cyclodehydration path [31]. The recent efforts on synthesis of thiazole skeletons are very well recapitulated in a review written by Mahesh [32]. In the light of previously published methods for the synthesis of sulfur heterocycles [33–39] and in continuation of our interest on multicomponent reactions involving terminal alkynes [40–41], we herein report a catalytic multicomponent reaction between terminal alkynes, elemental sulfur, and isocyanates to form thizaole derivatives.

Results and discussion

To evaluate the suitability of the proposed catalytic multicomponent reaction, an initial attempt was performed with phenylacetylene (**1a**), elemental sulfur (**2a**), and phenyl isocyanate (**3a**) in the presence of CuI and *N*-methylpiperidine (NMP) as a sulfur activator in THF. Stirring at 55 °C for 16 h only afforded the desired compound **4a** in low yield together with *S*-(phenylethynyl) phenylcarbamothioate (**5**) in 73% yield. Increasing the reaction temperature or extending the reaction time did not affect the reaction outcome in appreciable manners. We thought that the presence of a base source may assist the reaction progress. Accordingly, the reaction with Cs_2CO_3 afforded the targeted compound **4a** in 26% yield (not shown in Table 1). To further develop the reaction conditions, the reaction was performed with various catalysts, bases, and solvents and the results are shown in Table 1. Initially, the effect of base source on reaction outcomes was examined. Tetrabutylammonium acetate (TBAAc) as an ionic inorganic base resulted in formation of **4a** in low yield (entry 1). The study also indicated that common organic bases were not effective here and only DBU afforded **4a** in acceptable yield (entries 2–6). Among the inorganic bases, *t*-BuOK exhibited much better activity in regards of the formation of **4a** (entries 7–11). Of the copper salts, CuCl was selected as the catalyst of choice based on the cost and efficiency (entries 12–19). In the cases of $Cu(CH_3CN)_4PF_6$, a higher catalyst loading was required to furnish the transformation in a similar yield (entry 15). Copper (II) salts were not suitable in this transformation (entries 17–19). Finally, the effect of solvent in this transformation was examined (entries 20–26). By comparison, the reaction in polar aprotic solvents likes DMSO, DMA, and MeCN exhibited much better productivity (entries 20–22). The reaction in protic solvent like EtOH did not afford **4a** (entry 26). The reaction conducted at lower temperatures and shorter reaction times resulted in diminished yields (not shown in Table 1).

The substrates scope toward this catalytic multicomponent reaction was then evaluated using various terminal alkynes and isocyanates (Table 2). The reaction proceeds smoothly with **1a** to afford the targeted the product **4a** in 89% yield (entry 1). Alkynes bearing *p*-methyl and *p*-methoxy as motif on aryl ring **1b-1c** reacted with acceptable yields (entries

Table 1. Optimization of reaction conditions[a].



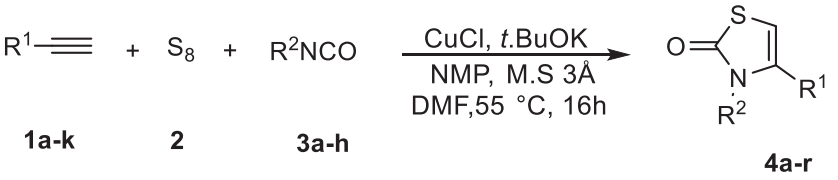
1a **2** **3a** **4a** **5**

Entry	Catalyst	Base	Solvent	Yield of **4** (%)
1	CuCl	TBAAc	DMF	25
2	CuCl	Lutidine	DMF	Traces
3	CuCl	Et_3N	DMF	27
4	CuCl	$(i\text{-}Pr)_2EtN$	DMF	18
5	CuCl	DBU	DMF	58
6	CuCl	DABCO	DMF	31
7	CuCl	K_3PO_4	DMF	NR[b]
8	CuCl	K_2CO_3	DMF	NR
9	CuCl	Cs_2CO_3	DMF	56
10	CuCl	*t*.BuOLi	DMF	70
11	CuCl	*t*.BuOK	DMF	89
12	CuI	*t*.BuOK	DMF	68
13	$CuBr.SMe_2$	*t*.BuOK	DMF	37
14	CuOAc	*t*.BuOK	DMF	27
15	$Cu(CH_3CN)_4PF_6$	*t*.BuOK	DMF	90[c]
16	CuOTf	*t*.BuOK	DMF	92
17	$Cu(OTf)_2$	*t*.BuOK	DMF	Traces
18	$Cu(BF_4)_2$	*t*.BuOK	DMF	Traces
19	$Cu(OAc)_2$	*t*.BuOK	DMF	Traces
20	CuCl	*t*.BuOK	DMSO	71
21	CuCl	*t*.BuOK	DMA	86
22	CuCl	*t*.BuOK	MeCN	63
23	CuCl	*t*.BuOK	THF	30
24	CuCl	*t*.BuOK	Toluene	43
25	CuCl	*t*.BuOK	DCM	16
26	CuCl	*t*.BuOK	EtOH	_[d]

Notes: [a]Reaction conditions: **1a** (1.2 mmol), **2** (0.2 equiv. based on **3a**), **3a** (1.0 mmol), catalyst (0.05 mmol), additive (1.5 mmol), base (1.5 mmol), 250 mg of ground 3 Å molecular sieves, solvent (3.0 mL) at 55 °C for 16 h.
[b]No reaction.
[c]With 0.10 mmol of catalyst.
[d]Ethyl phenylcarbamate was isolated in 71% yield.

2–3). Electron-deficient alkyne **1d** afforded the corresponding product in lower yield however, a decent increase in the yield occurred by extending the reaction time (entry 4). Heteroaromatic terminal alkynes **1e-1f** were also tolerated, providing the corresponding thiazol-2(3*H*)-one skeletons with good success (entries 5–6). Gratefully, alkyl terminal alkynes **1g-1j** were also compatible with this three-component reaction (entries 7–10). The reaction was also performed with a number of aryl and alkyl isocyanates (entries 11–17). The reactions conducted with isocyanates bearing electron releasing groups such as Me- and MeO- at *para* position formed the desired products in acceptable yields (entries 11–12). Chloro group was compatible with this coupling reaction, opening the door for subsequent cross-coupling reaction (entry 13). The reactions with electron-deficient isocyanates **3e-3f** proceeded with moderate yields (entries 14–15). As is typified by substrates **3 g** and **3 h**, alkyl isocyanates afforded the corresponding products **4p**-**4q** in comparatively lower yields than that of **3a** (entries 16-17), likely due to the either lack of π-electrons of the phenyl group which could act as an auxiliary coordination site to copper catalyst or

Table 2. Scope of substrates[a].



1a-k **2** **3a-h** **4a-r**

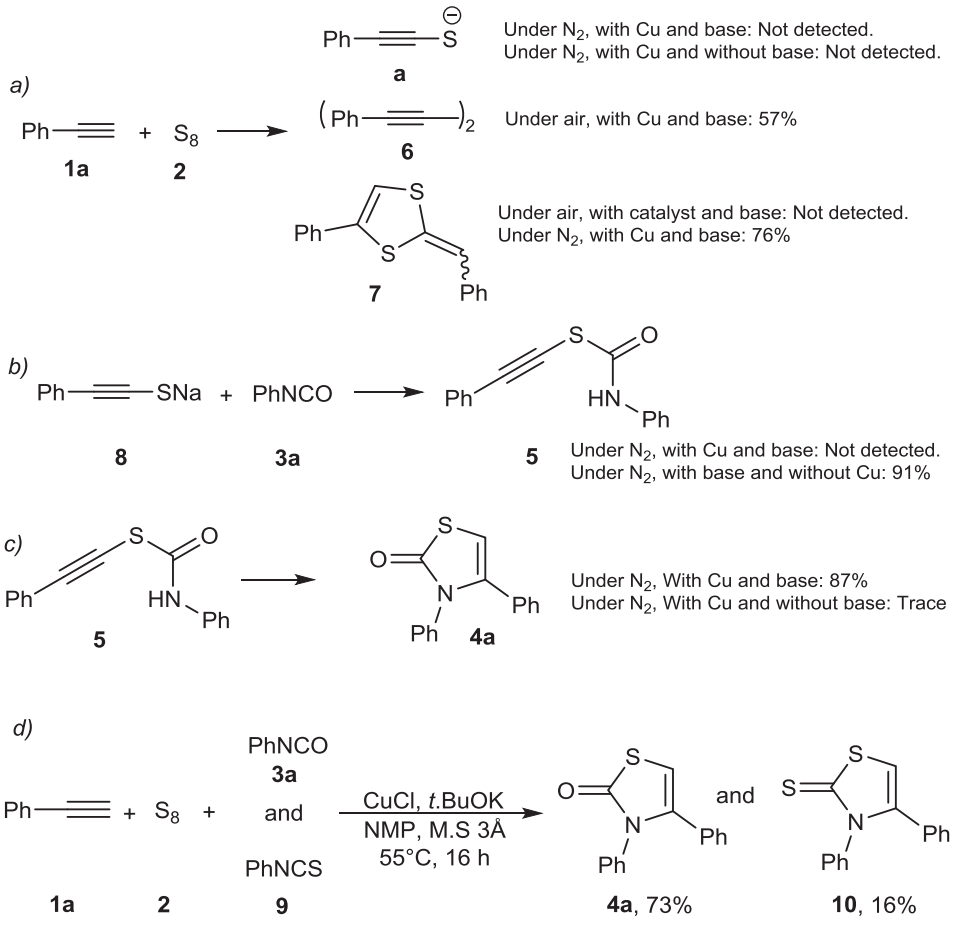
Entry	Alkyne	R^1	Isocyanate	R^2	Yield (%) of **4**
1	**1a**	Ph	**3a**	Ph	**4a**, 89
2	**1b**	4-Me-C_6H_4	**3a**	Ph	**4b**, 81
3	**1c**	4-MeO-C_6H_4	**3a**	Ph	**4c**, 78
4	**1d**	3-CF_3-C_6H_4	**3a**	Ph	**4d**, 69 (87)[b]
5	**1e**	3-Pyridyl	**3a**	Ph	**4e**, 85
6	**1f**	2-Furyl	**3a**	Ph	**4f**, 81
7	**1g**	CH_3OCH_2	**3a**	Ph	**4g**, 87[c]
8	**1h**	*t*-Bu	**3a**	Ph	**4h**, 81
9	**1i**	*n*-Bu	**3a**	Ph	**4i**, 70
10	**1j**	TMS	**3a**	Ph	**4j**, 61
11	**1a**	*t*-Bu	**3b**	4-Me-C_6H_4	**4k**, 75
12	**1a**	*t*-Bu	**3c**	4-MeO-C_6H_4	**4l**, 77
13	**1a**	*t*-Bu	**3d**	4-Cl-C_6H_4	**4m**, 87
14	**1a**	*t*-Bu	**3e**	4-MeOCO-C_6H_4	**4n**, 71
15	**1a**	*t*-Bu	**3f**	4-NO_2-C_6H_4	**4o**, 49
16	**1a**	*t*-Bu	**3g**	Cy	**4p**, 79[d]
17	**1a**	*t*-Bu	**3h**	*i*-Pr	**4q**, 75[d]

Notes: [a]For all entries except stated otherwise: **1** (1.2 mmol), **2** (0.2 equiv.), **3** (1.0 mmol), NMP (1.5 mmol), CuCl (0.05 mmol), *t*.BuOK (1.5 mmol), 3 Å molecular sieves (250 mg) dry DMF (3.0 mL), 55°C, 16 h under N_2.
[b]The digit in parentheses refers to the yield for 21 h.
[c]For entries 7–17, 0.1 mmol of CuCl was used.
[d]The yield at 70°C.

lower electrophilicity. The present transformation was not compatible with the presence of amine, hydroxyl, nitrile, and aldehyde as motif on alkynes and isocyanates structures.

To get insight on the mechanism of the reaction, the reaction was conducted in stepwise manner and the results are shown in Scheme 1. The reaction conducted with phenylacetylene and elemental sulfur to form phenylethynylthiolate **a** was unsuccessful and instead the Glaser coupling product **6** or the dimeric product **7** was obtained (Scheme 1, *a*). As such, sodium phenylacetylide **8** was prepared in a separate step using **1a** and **2** in the presence of NaH and was then reacted with isocyanate **3a**. The study indicated that the presence of copper catalyst and base was necessary to form **4a** (Scheme 1, *b*, *c*). Additionally, the reaction was conducted in competing mode with isocyanate **3a** and isothiocyanate **9** to explore the effect of electrophilicity of the third coupling partner in reaction outcome. Control experiment indicated that the reaction proceeded almost entirely through isocyanate **3a** which is most likely due to the greater potential of **3a** for nucleophilic attack of phenylethynylthiolate species **a** (Scheme 1, *d*).

Based on previous literature [15–17] and our control experiment results, a plausible mechanism is proposed in Scheme 2. Initially, species **11** was formed from phenylacetylene using CuCl and *t*-BuOK. Copper-acetylide **11** reacted with polysulfide **12** to provide alkyne polysulfide **13**. This anionic adduct further reacted with isocyanate **3a** to give the corresponding *S*-(phenylethynyl) phenylcarbamothioate complex **14**. Subsequent electrophilic cyclization of **14** through a *5-endo* path afford intermediate **15** which further reacted to form compound **4a** by the action of the conjugated acid of the base.



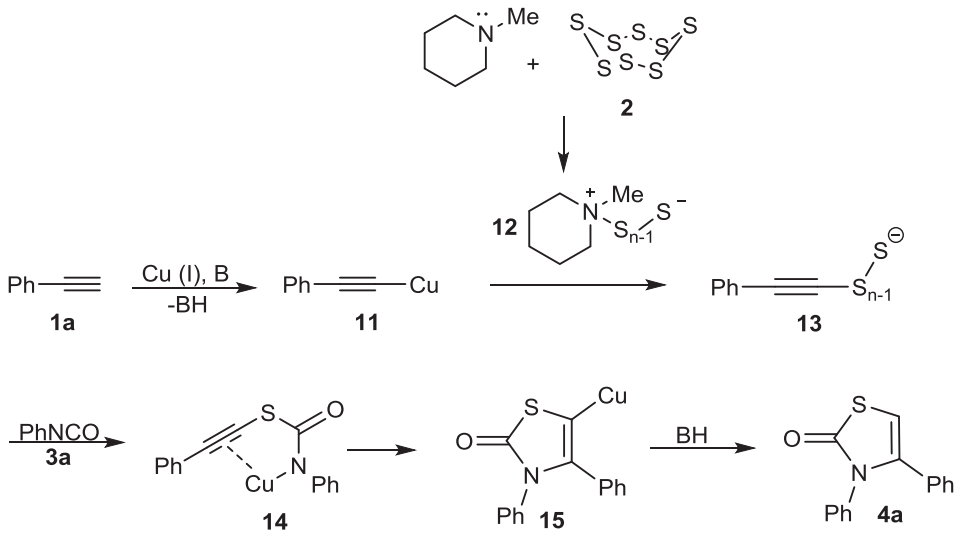
Scheme 1. Control experiments.

Conclusion

In this report, we have reported a novel catalytic three-component reaction involving terminal alkynes, elemental sulfur, and isocyanates. The reaction scope is wide and the reactions proceeded smoothly to form three covalent bonds in one pot. Control experiments were performed to explore the reaction intermediates and plausible path. A competing reaction with isocyanate and isothiocyanate was also conducted to get insight on the effect of electrophilicity of the third coupling partner on the products outcome.

Experimental

All transformations were performed in pre-dried glass tube (15 mL) under an inert atmosphere. All the substrates, copper catalysts, bases and additives were purchased from commercial sources. All the solvents were purchased from BAHERENERGY Pure Chemical Industries, and were dried before use. Melting points were recorded with Electrothermal-9100 apparatus. IR spectra were determined on a Nicolet 6700 spectrometer. ^{1}H and ^{13}C



Scheme 2. Proposed mechanism.

NMR spectra spectra were taken on a Bruker DRX-500 AVANCE spectrometer. The spectra were obtained in $CDCl_3$ at 500 and 125 MHz, resp; δ in ppm, J in Hz. Mass spectra were recorded with a EIMS (70 eV): Finnigan-MAT-8430 mass spectrometer, in m/z. Elemental analyses were performed with a Heraeus Rapid analyser. Silica gel 60 (particle size 63–200 µm or 40–100 mesh) was used for column chromatography. TLC analyses were performed on commercial glass plates of Merck Silica gel 60 (Merck, item number 116835).

General Procedure for the Preparation of Compounds 4

A pre-dried glass vessel (15 mL) was charged with elemental sulfur (0.2 mmol, 51.0 mg), NMP (1.5 mmol), and anhydrous DMF (2.0 mL). The mixture was then stirred for 40 min and terminal alkyne (as stated in Table 2), isocyanate (1.0 mmol), CuCl (as stated in Table 2), *t*.BuOK (1.5 mmol), 3 Å molecular sieves (250 mg), and anhydrous DMF (2.0 mL) were then added to the above mixture, respectively. The reaction medium was evacuated and backfilled with N_2 (twice). The mixture was stirred under the conditions described in Table 2. After the dark greenish mixture being cooled to room temperature, the mixture was passed through an alumina pad and concentrated under reduced pressure. The residue was purified by flash column chromatography with silica gel (eluent gradient of EtOAc/hexane, see spectroscopic analysis section) to give the targeted products **4**.

3,4-Diphenylthiazol-2(3H)-one (**4a**)

The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 6/1, R_f: 0.34) affording 0.22 g (89%) of **4a**; Pale yellow oil. IR (KBr): $\bar{V}$ = 3053, 2976, 1637, 1472, 1232, 1123. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 6.79 (1 H, s, CH), 7.37 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.49 (2 H, t, ^3J = 7.3 Hz, 2 CH), 7.56-7.63 (4 H, m, 4 CH), 7.76 (2 H, d, ^3J = 7.3 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 112.8 (CH), 127.6 (CH), 127.8 (CH), 128.3 (2 CH), 128.8 (2 CH), 129.7 (2 CH), 130.2 (2 CH), 133.2 (C), 135.8 (C), 149.3 (C), 172.5 (C). EI-MS (70 eV): *m/z* (%) = 253 (M^+, 1), 176 (31), 100 (62), 85 (87),

77 (100). Anal. Calcd (%) for $C_{15}H_{11}NOS$ (252.32): C, 71.12, H, 4.38, N, 5.53, S, 12.66. Found: C, 71.01, H, 4.55, N, 5.38, S, 12.52.

3-Phenyl-4-(p-tolyl)thiazol-2(3H)-one (**4b**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 6/1, R_f: 0.41) affording 0.22 g (81%) **4b**. Pale yellow oil. IR (KBr): $\bar{V}$ = 3017, 2962, 1632, 1231, 1098. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 2.35 (3 H, s, Me), 6.64 (1 H, s, CH), 7.18 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.25 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.38 (2 H, d, ^3J = 7.2 Hz, 2 CH), 7.53 (2 H, t, ^3J = 7.2 Hz, 2 CH), 7.64 (1 H, t, ^3J = 7.2 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 22.5 (Me), 112.3 (CH), 127.5 (CH), 128.2 (C), 128.2 (2 CH), 129.4 (2 CH), 129.9 (2 CH), 130.3 (2 CH), 132.7 (C), 138.8 (C), 149.5 (C), 171.3 (C). EI-MS (70 eV): *m*/*z* (%) = 267 (M^+, 3), 190 (24), 176 (31), 162 (57), 91 (72), 85 (87), 77 (100). Anal. Calcd (%) for $C_{16}H_{13}NOS$ (267.35): C, 71.88, H, 4.90, N, 5.24, S, 11.99. Found: C, 71.70, H, 4.78, N, 5.39, S, 12.11.

4-(4-Methoxyphenyl)-3-phenylthiazol-2(3H)-one (**4c**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 5/1, R_f: 0.29) affording 0.22 g (78%) **4c**. Yellow oil. IR (KBr): $\bar{V}$ = 3031, 2952,1628, 1413, 1232, 1065. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 3.76 (3 H, s, OMe), 6.46 (1 H, s, CH), 6.91 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.22 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.39 (2 H, d, ^3J = 7.8 Hz, 2 CH), 7.52 (2 H, t, ^3J = 7.8 Hz, 2 CH), 7.63 (1 H, t, ^3J = 7.8 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 54.2 (OMe), 107.7 (CH), 119.7 (2 CH), 124.2 (C), 127.1 (CH), 128.3 (2 CH), 129.2 (2 CH), 129.7 (2 CH), 135.3 (C), 148.6 (C), 160.4 (C), 174.1 (C). EI-MS (70 eV): *m*/*z* (%) = 283 (M^+, 1), 206 (9), 191 (32), 107 (100), 85 (81), 77 (83). Anal. Calcd (%) for $C_{16}H_{13}NO_2S$ (283.35): C, 67.82, H, 4.62, N, 4.94, S, 11.31. Found: C, 67.68, H, 4.80, N, 5.10, S, 11.45.

3-Phenyl-4-(3-(trifluoromethyl)phenyl)thiazol-2(3H)-one (**4d**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 4/1, R_f: 0.37) affording 0.28 g (87%) **4d**. Pale yellow oil. IR (KBr): $\bar{V}$ = 3015, 2943, 1640, 1453, 1231, 1090. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 6.81 (1 H, s, CH), 7.08 (1 H, t, ^3J = 7.5 Hz, CH), 7.39 (1 H, d, ^3J = 7.5 Hz, CH), 7.46 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.50 (1 H, s, CH), 7.55 (2 H, t, ^3J = 7.1 Hz, CH), 7.61 (1 H, t, ^3J = 7.1 Hz, CH), 7.83 (1 H, d, ^3J = 7.5 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): 114.2 (CH), 122.9 (CH, q, ^3J = 5.2 Hz), 125.1 (CF_3, q, ^1J = 276.1 Hz), 126.8 (CH, q, ^3J = 5.1 Hz), 127.2 (CH), 128.5 (2 CH), 128.9 (2 CH), 130.1 (CH), 132.4 (C, q, ^2J = 28.7 Hz), 134.1 (C), 135.9 (C), 149.5 (C), 173.9 (C). EI-MS (70 eV): *m*/*z* (%) = 321 (M^+, 1), 244 (37), 146 (25), 100 (73), 85 (81), 77 (100). Anal. Calcd (%) for $C_{16}H_{10}F_3NOS$ (321.32): C, 59.81, H, 3.14, N, 4.36, S, 9.98, F, 17.74. Found: C, 59.70, H, 3.02, N, 4.51, S, 10.11, F, 17.83.

3-Phenyl-4-(pyridin-3-yl)thiazol-2(3H)-one (**4e**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 4/1, R_f: 0.21) affording 0.22 g (85%) **4e**. Yellow oil. IR (KBr): $\bar{V}$ = 3041, 2977, 1634, 1231, 1143. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 6.72 (1 H, s, CH), 7.34 (1 H, t, ^3J = 7.7 Hz, CH), 7.42 (2 H, d, ^3J = 7.4 Hz, 2 CH), 7.53 (2 H, t, ^3J = 7.4 Hz, 2 CH), 7.64 (1 H, t, ^3J = 7.4 Hz, CH), 7.78 (1 H, d, ^3J = 7.7 Hz, CH), 8.24 (1 H, d, ^3J = 7.7 Hz, CH), 8.53 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): 119.6 (CH), 124.7 (CH), 127.3 (CH), 128.6 (2 CH), 129.15 (2 CH), 132.1 (C), 134.3 (C), 134.9 (CH), 148.7 (C), 149.1 (CH), 149.3 (CH), 174.8 (C). EI-MS

(70 eV): *m/z* (%) = 254 (M^+, 4), 177 (34), 100 (84), 85 (76), 77 (100). Anal. Calcd (%) for $C_{14}H_{10}N_2OS$ (254.31): C, 66.12, H, 3.96, N, 11.02, S, 12.61. Found: C, 66.28, H, 3.82, N, 11.24, S, 12.80.

4-(Furan-2-yl)-3-phenylthiazol-2(3H)-one (**4f**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 5/1, R_f: 0.33) affording 0.20 g (81%) **4f**. Pale yellow oil. IR (KBr): $\bar{V}$ = 3017, 2957, 1628, 1543, 1241, 1067. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 6.62 (1 H, s, CH), 6.80 (1 H, t, ^3J = 6.7 Hz, CH), 7.39 (2 H, d, ^3J = 7.8 Hz, 2 CH), 7.50 (2 H, t, ^3J = 7.8 Hz, 2 CH), 7.63 (1 H, t, ^3J = 7.8 Hz, CH), 7.78 (1 H, d, ^3J = 6.7 Hz, CH), 8.31 (1 H, d, ^3J = 6.7 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): 110.2 (CH), 114.9 (CH), 115.7 (CH), 127.3 (CH), 128.5 (2 CH), 129.1 (2 CH), 134.1 (C), 147.4 (CH), 156.2 (C), 158.7 (C), 173.1 (C). EI-MS (70 eV): *m/z* (%) = 243 (M^+, 1), 176 (45), 166 (24), 100 (83), 85 (67), 77 (100), 67 (53). Anal. Calcd (%) for $C_{13}H_9NO_2S$ (243.28): C, 64.18, H, 3.73, N, 5.76, S, 13.18. Found: C, 64.34, H, 3.60, N, 5.63, S, 13.32.

4-(Methoxymethyl)-3-phenylthiazol-2(3H)-one (**4 g**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 6/1, R_f: 0.45) affording 0.19 g (87%) **4 g**. Colorless oil. IR (KBr): $\bar{V}$ = 3018, 2962, 1636, 1311, 1262, 1106. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 3.41 (3 H, s, OMe), 4.27 (2 H, s, CH_2), 6.41 (1 H, s, CH), 7.39 (2 H, d, ^3J = 7.2 Hz, 2 CH), 7.53 (2 H, t, ^3J = 7.2 Hz, 2 CH), 7.60 (1 H, t, ^3J = 7.2 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 55.7 (OMe), 82.1 (CH_2), 101.3 (CH), 127.4 (CH), 128.6 (2 CH), 129.2 (2 CH), 134.8 (C), 153.9 (C), 171.7 (C). EI-MS (70 eV): *m/z* (%) = 221 (M^+, 1), 190 (23), 114 (64), 100 (86), 85 (70), 77 (100). Anal. Calcd (%) for $C_{11}H_{11}NO_2S$ (221.27): C, 59.71, H, 5.01, N, 6.33, S, 14.49. Found: C, 59.88, H, 5.15, N, 6.24, S, 14.62.

4-(tert-Butyl)-3-phenylthiazol-2(3H)-one (**4 h**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 1/6, R_f: 0.31) affording 0.19 g (81%) **4 h**. Colorless oil. IR (KBr): $\bar{V}$ = 3415, 3047, 2976, 1726, 1638, 1543, 1346, 1218, 1076. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.38 (9 H, s, 3 Me), 6.19 (1 H, s, CH), 7.38 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.55 (2 H, t, ^3J = 7.5 Hz, 2 CH), 7.63 (1 H, t, ^3J = 7.5 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 34.9 (3 Me), 42.2 (C), 97.2 (CH), 126.9 (CH), 128.8 (2 CH), 129.7 (2 CH), 134.6 (C), 163.4 (C), 173.8 (C). EI-MS (70 eV): *m/z* (%) = 233 (M^+, 1), 176 (31), 156 (53), 100 (81), 85 (61), 77 (84), 57 (100). Anal. Calcd (%) for $C_{13}H_{15}NOS$ (233.33): C, 66.92, H, 6.48, N, 6.00, S, 13.74. Found: C, 67.11, H, 6.31, N, 6.17, S, 13.60.

4-Butyl-3-phenylthiazol-2(3H)-one (**4i**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 7/1, R_f: 0.21) affording 0.16 g (70%) **4i**. Pale yellow oil. IR (KBr): $\bar{V}$ = 3026, 2965, 1639, 1475, 1237, 1128. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.02 (3 H, t, ^3J = 5.8 Hz, Me), 134-1.42 (4 H, m, 2 CH_2), 2.11 (2 H, t, ^3J = 5.6 Hz, CH_2), 6.19 (1 H, s, CH), 7.35 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.49 (2 H, t, ^3J = 7.1 Hz, 2 CH), 7.56 (1 H, t, ^3J = 7.1 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): 12.8 (Me), 26.3 (CH_2), 31.7 (CH_2), 37.7 (CH_2), 102.2 (CH), 127.8 (CH), 128.6 (2 CH), 129.4 (2 CH), 133.7 (C), 159.2 (C), 172.8 (C). EI-MS (70 eV): *m/z* (%) = 233 (M^+, 1), 176 (34), 156 (21), 100 (100), 85 (61), 77 (84), 57 (36). Anal. Calcd (%) for $C_{13}H_{15}NOS$ (233.33): C, 66.92, H, 6.48, N, 6.00, S, 13.74. Found: C, 66.80, H, 6.60, N, 6.17, S, 13.91.

3-Phenyl-4-(trimethylsilyl)thiazol-2(3H)-one (**4j**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 8/1, R_f: 0.41) affording 0.15 g (61%) **4j**. Colorless oil. IR (KBr): $\bar{V}$ = 3055, 2932, 1630, 1456, 1321, 1207, 640. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 0.13 (9 H, s, 3 Me), 6.49 (1 H, s, CH), 7.40 (2 H, d, ^3J = 7.7 Hz, 2 CH), 7.52 (2 H, t, ^3J = 7.7 Hz, 2 CH), 7.61 (1 H, t, ^3J = 7.7 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): 2.1 (3 Me), 117.3 (CH), 127.6 (CH), 128.9 (2 CH), 129.4 (2 CH), 131.8 (C), 134.5 (C), 173.3 (C). EI-MS (70 eV): *m*/*z* (%) = 249 (M^+, 3), 176 (19), 173 (24), 157 (83), 100 (69), 85 (81), 77 (100). Anal. Calcd (%) for $C_{12}H_{15}NOSSi$ (249.40): C, 57.79, H, 6.06, N, 5.62, S, 12.85, Si, 11.26. Found: C, 57.92, H, 6.23, N, 5.45, S, 12.96, Si, 11.35.

4-(tert-Butyl)-3-(p-tolyl)thiazol-2(3H)-one (**4k**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 5/1, R_f: 0.35) affording 0.18 g (75%) **4k**. Colorless oil. IR (KBr): $\bar{V}$ = 3051, 2937, 1636, 1476, 1236, 1092. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.35 (9 H, s, 3 Me), 2.42 (3 H, s, Me), 6.15 (1 H, s, CH), 7.23 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.29 (2 H, d, ^3J = 7.1 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 23.6 (Me), 35.2 (3 Me), 43.5 (C), 98.5 (CH), 128.3 (2 CH), 129.5 (2 CH), 130.2 (C), 138.5 (C), 165.9 (C), 174.1 (C). EI-MS (70 eV): *m*/*z* (%) = 247 (M^+, 1), 190 (56), 176 (40), 156 (23), 141 (34), 100 (83), 91 (51), 85 (86), 57 (100). Anal. Calcd (%) for $C_{14}H_{17}NOS$ (247.36): C, 67.98, H, 6.93, N, 5.66, S, 12.96. Found: C, 67.82, H, 6.81, N, 5.80, S, 13.11.

4-(tert-Butyl)-3-(4-methoxyphenyl)thiazol-2(3H)-one (**4 l**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 4/1, R_f: 0.40) affording 0.20 g (77%) **4 l**. Yellow oil. IR (KBr): $\bar{V}$ = 3044, 2966, 1641, 1511, 1470, 1232, 1176. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.37 (9 H, s, 3 Me), 3.90 (3 H, s, OMe), 6.22 (1 H, s, CH), 7.04 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.21 (2 H, d, ^3J = 7.1 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 33.8 (3 Me), 41.9 (C), 56.2 (OMe), 96.5 (CH), 115.3 (2 CH), 126.2 (C), 129.1 (2 CH), 160.2 (C), 166.3 (C), 173.5 (C). EI-MS (70 eV): *m*/*z* (%) = 263 (M^+, 1), 206 (41), 156 (25), 192 (66), 107 (94), 100 (42), 85 (37), 77 (68), 57 (100). Anal. Calcd (%) for $C_{14}H_{17}NO_2S$ (263.36): C, 63.85, H, 6.51, N, 5.32, S, 12.17. Found: C, 63.73, H, 6.68, N, 5.48, S, 12.34.

4-(tert-Butyl)-3-(4-chlorophenyl)thiazol-2(3H)-one (**4 m**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 5/1, R_f: 0.19) affording 0.23 g (87%) **4 m**. Pale yellow oil. IR (KBr): $\bar{V}$ = 3029, 2953, 1632, 1478, 1234, 1131, 810. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.40 (9 H, s, 3 Me), 6.19 (1 H, s, CH), 7.37 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.46 (2 H, d, ^3J = 7.6 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 35.2 (3 Me), 43.2 (C), 98.2 (CH), 128.7 (2 CH), 129.4 (C), 132.5 (2 CH), 135.7 (C), 166.1 (C), 173.9 (C). EI-MS (70 eV): *m*/*z* (%) = 267 (M^+, 1), 211 (34), 196 (78), 156 (19), 111 (65), 100 (87), 85 (56), 57 (100). Anal. Calcd (%) for $C_{13}H_{14}ClNOS$ (267.77): C, 58.31, H, 5.27, N, 5.23, S, 11.97, Cl, 13.24. Found: C, 58.44, H, 5.30, N, 5.12, S, 12.08, Cl, 13.30.

Methyl 4-(4-(tert-butyl)-2-oxothiazol-3(2H)-yl)benzoate (**4n**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 4/1, R_f: 0.38) affording 0.21 g (71%) **4n**. Colorless oil. IR (KBr): $\bar{V}$ = 3055, 2976, 1736, 1646, 1466, 1324, 1255, 1123. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.41 (9 H, s, 3 Me), 3.95 (3 H, s,

OMe), 6.25 (1 H, s, CH), 7.31 (2 H, d, ^3J = 7.5 Hz, 2 CH), 7.90 (2 H, d, ^3J = 7.5 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 35.2 (3 Me), 42.5 (C), 53.7 (OMe), 99.5 (CH), 126.8 (2 CH), 127.9 (C), 132.6 (2 CH), 138.5 (C), 166.1 (C), 167.4 (C), 173.8 (C). EI-MS (70 eV): *m*/*z* (%) = 291 (M^+, 1), 260 (11), 156 (38), 105 (91), 100 (73), 85 (53), 57 (100). Anal. Calcd (%) for $C_{15}H_{17}NO_3S$ (291.37): C, 61.83, H, 5.88, N, 4.81, S, 11.00. Found: C, 61.67, H, 5.72, N, 4.97, S, 11.13.

4-(tert-Butyl)-3-(4-nitrophenyl)thiazol-2(3H)-one (**4o**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 2/1, R_f: 0.43) affording 0.14 g (49%) **4o**. Yellow solid, m.p = 132-134 °C. IR (KBr): $\bar{V}$ = 3016, 2942, 1633, 1531, 1340, 1252, 1131. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.43 (9 H, s, 3 Me), 6.22 (1 H, s, CH), 7.86 (2 H, d, ^3J = 7.8 Hz, 2 CH), 8.33 (2 H, d, ^3J = 7.8 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 35.8 (3 Me), 42.9 (C), 97.2 (CH), 123.6 (2 CH), 131.8 (2 CH), 140.2 (C), 145.8 (C), 168.2 (C), 175.2 (C). EI-MS (70 eV): *m*/*z* (%) = 278 (M^+, 1), 222 (35), 207 (13), 156 (52), 100 (86), 85 (61), 57 (100). Anal. Calcd (%) for $C_{13}H_{14}N_2O_3S$ (278.33): C, 56.10, H, 5.07, N, 10.07, S, 11.52. Found: C, 56.24, H, 5.19, N, 10.22, S, 11.44.

4-(tert-Butyl)-3-cyclohexylthiazol-2(3H)-one (**4p**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 5/1, R_f: 0.21) affording 0.19 g (79%) of **4p**; Colorless oil. IR (KBr): $\bar{V}$ = 3008, 2967, 1632, 1456, 1246, 1132. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.36 (9 H, s, 3 Me), 1.40-1.95 (10 H, m, 5 CH_2), 3.72-3.77 (1 H, m, CH), 6.12 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 26.8 (CH_2), 29.1 (2 CH_2), 34.7 (3 Me), 36.3 (2 CH_2), 42.1 (C), 70.2 (CH), 101.1 (CH), 160.6 (C), 177.8 (C). EI-MS (70 eV): *m*/*z* (%) = 239 (M^+, 1), 182 (34), 156 (58), 100 (78), 85 (56), 83 (87), 57 (100). Anal. Calcd (%) for $C_{13}H_{21}NOS$ (239.38): C, 65.23, H, 8.84, N, 5.85, S, 13.39. Found: C, 65.11, H, 8.67, N, 5.73, S, 13.53.

4-(tert-Butyl)-3-isopropylthiazol-2(3H)-one (**4q**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 5/1, R_f: 0.32) affording 0.15 g (75%) of **4q**; Colorless oil. IR (KBr): $\bar{V}$ = 3029, 2943, 1639, 1435, 1251, 1126. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.40 (9 H, s, 3 Me), 1.52 (6 H, d, ^3J = 5.6 Hz, 2 Me), 4.55-4.60 (1 H, m, CH), 6.17 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 23.6 (2 Me), 34.9 (3 Me), 43.1 (C), 66.7 (CH), 103.2 (CH), 159.2 (C), 176.8 (C). EI-MS (70 eV): *m*/*z* (%) = 199 (M^+, 1), 156 (31), 140 (78), 122 (30), 100 (81), 85 (52), 57 (100). Anal. Calcd (%) for $C_{10}H_{17}NOS$ (199.31): C, 60.26, H, 8.60, N, 7.03, S, 16.09. Found: C, 60.41, H, 8.47, N, 7.19, S, 16.24.

S-(phenylethynyl) phenylcarbamothioate (**5**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 3/1, R_f: 0.26) affording 0.23 g (91%) of **5**; Colorless solid, m.p = 101-103 °C. IR (KBr): $\bar{V}$ = 3361, 3046, 2971, 1630, 1252, 1072. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 7.11 (1 H, t, ^3J = 7.7 Hz, CH), 7.27 (2 H, t, ^3J = 7.7 Hz, 2 CH), 7.36-7.44 (3 H, m, 3 CH), 7.49 (2 H, d, ^3J = 7.1 Hz, 2 CH), 7.65 (2 H, d, ^3J = 7.7 Hz, 2 CH), 8.51 (1 H, br s, NH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 81.1 (C), 94.3 (C), 119.1 (2 CH), 123.5 (C), 127.3 (CH), 127.9 (CH), 129.1 (2 CH), 129.7 (2 CH), 133.7 (2 CH), 137.7 (C), 167.4 (C). Anal. Calcd (%) for $C_{15}H_{11}NOS$ (253.32): C, 71.12, H, 4.38, N, 5.53, S, 12.66. Found: C, 71.24, H, 8.21, N, 5.70, S, 12.47.

2-Benzylidene-4-phenyl-1,3-dithiole (**7**)
The crude product was purified by column chromatography (SiO_2; Hexane/EtOAc 12/1, R_f: 0.31) affording 0.32 g (76%) of **7**. ^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta_H = 6.47$ (1 H, s, CH), 6.78 (1 H, s, CH), 7.25 (1 H, t, $^3J = 7.7$ Hz, CH), 7.30 (1 H, t, $^3J = 7.0$ Hz, CH), 7.42-7.50 (6 H, m, 6 CH), 7.67 (2 H, d, $^3J = 7.0$ Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta_C = 116.3$ (CH), 121.1 (CH), 126.8 (CH), 127.4 (CH), 128.5 (2 CH), 129.1 (2 CH), 129.6 (2 CH), 130.3 (2 CH), 135.9 (C), 137.3 (C), 140.1 (C), 143.8 (C). Anal. Calcd (%) for $C_{16}H_{12}S_2$ (363.41): C, 71.60, H, 4.51, S, 23.89. Found: C, 71.78, H, 4.63, S, 23.72.

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