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$NiSO_4$-Catalyzed C–H Activation/C–S Cross-Coupling of 1,2,3-Triazole *N*-Oxides with Thiols

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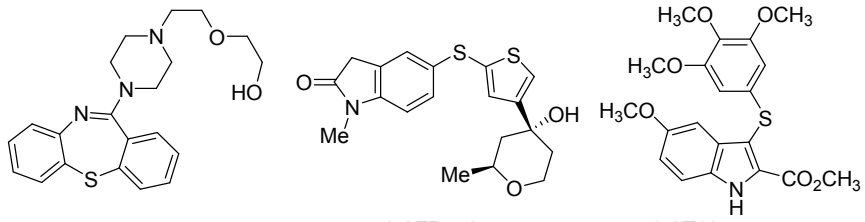
Abstract: An efficient nickel-catalyzed protocol for C–S cross-coupling through direct functionalization of 2-aryl-1,2,3-triazole *N*-oxide C–H bonds with aryl or alkyl thiols, diphenyl disulfide has been developed. The targeted N^+-O^- bond cleavage can be observed during the reaction, and thus obviate to use an additional deoxygenation step. This new protocol for the preparation of thiolated 2-aryl-1,2,3-triazoles appears to offer good yields with high regioselectivity, mild conditions, and wide substrate scope.

Keywords: 1,2,3-Triazole; Nickel; Thiolation; Cross-coupling

Introduction

Over the past few decades, transition-metal-catalyzed carbon-carbon and carbon-heteroatom bond formation has become a powerful tool to construct organic molecules. The construction of carbon-sulfur bonds and the direct functionalization of a C–H bond are central themes in organic synthesis.[1] Aryl sulfides are ubiquitous structural motifs in numerous biologically active natural products, pharmaceuticals, and materials (Figure **1**).[2] For example, Quetiapine (**1**) (branded as Seroquel, Xeroquel, and Ketipinor) is being used for the treatment of schizophrenia and bipolar disorder, and is also prescribed as an antidepressant to treat major depressive disorder.[3] Thus, there have already been some advances in aryl-sulfur bond construction,[1a,4] among which transition-metal-catalyzed cross-coupling of aryl halides and thiols played an important role. However, prefunctionalization is required for such transformation.



1 Quetiapine **2** AZD4407 **3** AT12

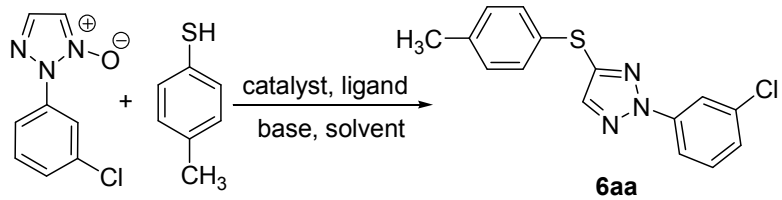
Figure **1**. Biologically active thioethers used as drugs or drug candidates.

In the area of C–H bond functionalization, much attention has been paid to C–C, C–O, and C–N bond-forming reactions.[5] In sharp contrast, the formation of a C–S bond through transition-metal catalyzed C–H activation is rare,[6] partly because of the reasoned belief that sulfur poisons metal catalysts. Fortunately, this apparent functional incompatibility has been surpassed in recent years with the emergence of new metal catalytic strategies.[7] In pioneering studies on the Cu-mediated direct thioetherification of the arene C–H bond was reported by Yu et al. in 2006.[8] Subsequently, several other groups have shown that the direct thiolation of unfunctionalized arenes or heterocyclic compounds can be achieved by employing copper salts.[9] Recently, palladium-catalyzed intramolecular[10] and intermolecular[11] aromatic C-H thiolation, rhodium-catalyzed

directed sulfenylation of arene C–H bonds,[6] and laccase-catalyzed C–S bond-forming reactions[12] have been developed. However, most of the known methods often rely on harsh conditions such as strong bases (*t*-BuOLi),[9h] high reaction temperatures (120-150 °C),[9a-f,11] and use of expensive or air-sensitive ligands and excessive reagents. Consequently, an alternative protocol is still in high demand, in particular, nickel-catalyzed C-S cross-coupling remains much less explored.

Recently, the field of nickel-catalyzed cross-coupling reactions has gained considerable attention. The low cost and high reactivity of nickel is attractive, and a range of substrates has been shown to undergo nickel-catalyzed carbon-carbon and carbon-heteroatom bond forming reactions.[13,14] Considering the promise of nickel-catalyzed couplings and the need to make industrial processes more environmentally friendly, we decided to tackle this problem and herein disclose the first versatile Ni-catalyzed cross-coupling of 1,2,3-triazole *N*-oxides with alkyl or aryl thiols under mild conditions. In addition, 1,2,3-triazole *N*-oxides are more challenging than simple *N*-oxides, such as pyridine and quinoline *N*-oxides, since they possess a free nitrogen atom that could bind and poison the catalyst.

Table **1**. Optimization of the reaction conditions[a]



4a **5a** **6aa**

entry	catalyst (equiv)	ligand	base	solvent	yield (%)[b]
1	$FeCl_3$ (0.2)	Py	K_3PO_4	DMSO	37
2	$NiSO_4$ (0.2)	Py	K_3PO_4	DMSO	47
3	$CoCl_3$ (0.2)	Py	K_3PO_4	DMSO	15
4	$CeCl_3$ (0.2)	Py	K_3PO_4	DMSO	trace
5	$AgNO_3$ (0.2)	Py	K_3PO_4	DMSO	trace
6	CuBr (0.2)	Py	K_3PO_4	DMSO	30
7	–	Py	K_3PO_4	DMSO	trace
8	$NiCl_2$ (0.2)	Py	K_3PO_4	DMSO	43
9	$Ni(NO_3)_2$ (0.2)	Py	K_3PO_4	DMSO	42
10	$Ni(OAc)_2$ (0.2)	Py	K_3PO_4	DMSO	38
11	$NiSO_4$ (0.2)	Py	K_3PO_4	CH_3CN	trace
12	$NiSO_4$ (0.2)	Py	K_3PO_4	benzene	39
13	$NiSO_4$ (0.2)	Py	K_3PO_4	NEt_3	trace
14	$NiSO_4$ (0.2)	Py	K_3PO_4	dioxane	36
15	$NiSO_4$ (0.2)	TMEDA	K_3PO_4	DMSO	53
16	$NiSO_4$ (0.2)	DMEDA	K_3PO_4	DMSO	65
17	$NiSO_4$ (0.2)	PPh_3	K_3PO_4	DMSO	trace
18	$NiSO_4$ (0.2)	DMEDA	Na_2CO_3	DMSO	trace
19	$NiSO_4$ (0.2)	DMEDA	Cs_2CO_3	DMSO	81
20	$NiSO_4$ (0.2)	DMEDA	LiOH	DMSO	trace
21	$NiSO_4$ (0.2)	DMEDA	*t*-BuOLi	DMSO	61
22	$NiSO_4$ (0.1)	DMEDA	Cs_2CO_3	DMSO	81
23 [c]	$NiSO_4$ (0.05)	DMEDA	Cs_2CO_3	DMSO	63

[a] Condition: **4a** (0.2 mmol), **5a** (0.24 mmol), ligand (0.08 mmol), base (0.4 mmol), solvent (0.6 mL), 60 °C, 12 h, under open air.
[b] Isolated yields. [c] For 36 h.

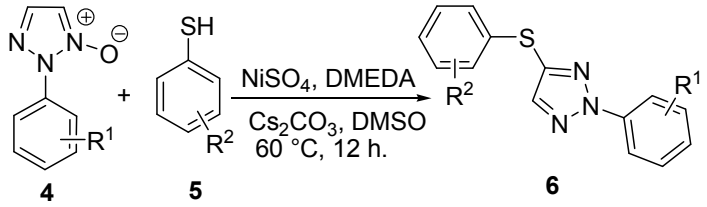
To optimize the catalysis conditions, 1,2,3-triazole *N*-oxide (**4a)**, which were prepared according to known procedures,[15] and 4-methylbenzenethiol (**5a**) were chosen as the model substrates, and some representative results are shown in Table **1**. Initially, we attempted to explore the coupling of

4a with **5a** using $FeCl_3$ as a catalyst, pyridine as a ligand, K_3PO_4 as a base, and DMSO as a solvent at 60 °C, under open air, and the desired product **6a** was obtained in 37% yield (Table **1**, entry 1). Encouraged by this result, we further examined the effect of catalyst, solvent, ligand, temperature, and base on the reaction yield. Various transition-metal compounds including Ni, Co, Ce, Ag, and Cu salts were examined, with the finding that nickel salts, especially $NiSO_4$, were the optimal choice for the coupling reaction (Table **1**, entries 1-10). In contrast, other metal salts such as $CeCl_3$ and $AgNO_3$ gave a trace of the desired product (Table **1**, entries 4 and 5). Additionally, without nickel catalyst only trace amounts of **6aa** was observed (Table **1**, entry 7). The type of solvent was vital to the present coupling reaction. DMSO was found to be the best choice (Table **1**, entries 11-14). Among various ligands screened, DMEDA (*N*,*N*'-dimethylethylenediamine) gave the best result (Table **1**, entries 15-17). The modification to the bases indicated that Cs_2CO_3 was identified as the most suitable base for the formation of **6aa** (Table **1**, entry 19). Interestingly, Na_2CO_3 and LiOH proved to be inefficient for the formation of **6aa** (Table **1**, entries 18 and 20). Further investigations revealed that there was no obvious loss in yield when catalyst loading was reduced to 10 mol % (Table **1**, entry 22). However, using 5 mol % $NiSO_4$ in the reaction led to a decreased yield of 63% (Table **1**, entry 23). Taken together, we concluded that the optimized conditions were using 10 mol % $NiSO_4$ as the catalyst, 40 mol % DMEDA as the ligand, Cs_2CO_3 as the base, DMSO as the solvent, and carrying out the reaction at 60 °C for 12 h.

Next, a range of substrates with variation in the substitution (halogen, alkyl, hydroxy) of both the 1,2,3-triazole *N*-oxides and thiols were subjected to the coupling reaction to validate its generality. As is evident from Table **2**, all of them were applicable in the coupling process, providing the deoxygenated 1,2,3-triazole derivatives **6** in yields of 56-81%.

Initially, various substituted aryl thiols were screened. Unsubstituted and alkyl-substituted substrates gave the corresponding products (**6aa-6ae**) in consistently good yields (70-81%). All halogen groups (fluoro, chloro, and bromo) at C4 position of the phenyl ring survived well in the reaction to produce (**6af-6ah**) in yields of 62-76%. The steric properties of the aryl ring did not appear to significantly affect the yield, as ortho-functionalized aryl substrates (**5b**) and (**5c**) performed equally well in the C–S cross-coupling. It was noted that 1,2,3-triazole *N*-oxide (**4a)** and 4-mercaptophenol (**5i)** was chemoselectively coupled to give the desired **6ai** in moderate yield without affecting the hydroxy group (Table **2**, entry 9). Importantly, the halo groups whether on the phenyl ring of triazole *N*-oxides or aryl thiols survived in the procedure. 4-Iodophenyl moiety (**4k)**, for instance, could successfully undergo the cross-coupling reaction with aryl substrate (**5a**) providing the corresponding product **6ka** in 58% yield (Table **2**, entry 21). In general, the thiolation of aryl halides and thiols was achieved by palladium-, copper-, and nickel-catalyzed routes.[16] Variation in the substitution on the 1,2,3-triazole *N*-oxide moiety also afforded the corresponding products in yields of 59-78%. Electron-poor triazole substrates bearing aryl groups at the N-2 position of the triazole ring furnished products with better yields (73-78%) compared with electron-rich counterpart (56-67%) (Table **2**, entries 12-18). The structure of product **6lc** was unambiguously determined by X-ray single crystal diffraction (see Supporting Information).

Table **2**. Substrate scope of the direct thiolation[a]



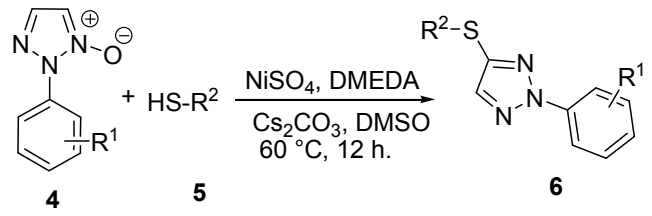
entry	R^1	R^2	product	yield (%) [b]
1	3-Cl	4-Me	**6aa**	81
2	3-Cl	2,4-Me_2	**6ab**	72
3	3-Cl	2,6-Me_2	**6ac**	70
4	3-Cl	4-Bu-*t*	**6ad**	78
5 [c]	3-Cl	H	**6ae**	71
6	3-Cl	4-F	**6af**	76
7	3-Cl	4-Cl	**6ag**	64
8	3-Cl	4-Br	**6ah**	62
9	3-Cl	4-OH	**6ai**	59
10	H	4-Cl	**6bg**	58
11	H	H	**6be**	64
12	H	4-Me	**6ba**	63
13	4-Me	4-Me	**6ca**	61
14	3,4-Me_2	4-Me	**6da**	67
15	2-Me	4-Me	**6ea**	63
16 [d]	2,5-Me_2	4-Me	**6fa**	59
17	4-OMe	4-Me	**6ga**	56
18	4-F	4-Me	**6ha**	78
19	4-Cl	4-Me	**6ia**	76
20	4-Br	4-Me	**6ja**	73
21	4-I	4-Me	**6ka**	58
22	4-CF_3	4-Cl	**6lg**	68
23	4-CF_3	2,6-Me_2	**6lc**	72
24	3-Me	4-Cl	**6mg**	64

[a] Condition: **4** (0.2 mmol), **5** (0.24 mmol), $NiSO_4$ (0.02 mmol), DMEDA (0.08 mmol), Cs_2CO_3 (0.4 mmol), DMSO (0.6 mL), under open air. [b] Isolated yields. [c] For 18 h. [d] For 24 h.

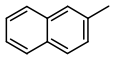
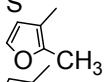
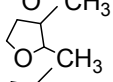
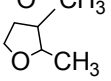
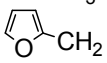
The success in using aryl thiols encouraged us to examine the reaction of 2-aryl-1,2,3-triazole *N*-oxide **4** with various thiols, and the results are summarized in Table **3**. When the nickel-catalyzed cross-coupling of **4** with naphthalene-2-thiol **5j**, thiophene-2-thiol **5k**, 2-methylfuran-3-thiol **5l**, 2-methyl-tetrahydrofuran-3-thiol **5m**, and furan-2-ylmethanethiol **5n** were performed under this reaction conditions, the corresponding thioetherification products **6aj-6an, 6ck** and **6cm** were obtained in good yields. Fortunately, the aliphatic thiols including primary, secondary, and tertiary thiols could provide the thiolation products in good to excellent yields (Table **3**, **6an-6ar**). Furthermore, we were pleased to find that steric bulk posed no problem in this reaction, as exemplified by the high yield of the thiolation product **6ar** obtained.

In addition, the thiolations of other heteroarene *N*-oxides with thiols were presented in Scheme **1**. **10a** and **10b** were formed in good yields, respectively. We were very pleased to find that the targeted N^+-O^- bond cleavage can be observed during the reaction. Disappointingly, other heteroarene *N*-oxide substrates, such as imidazole *N*-oxides, failed to work under the standard reaction conditions. The lower reactivity of those substrates observed here may be caused by their weaker acidity.[17]

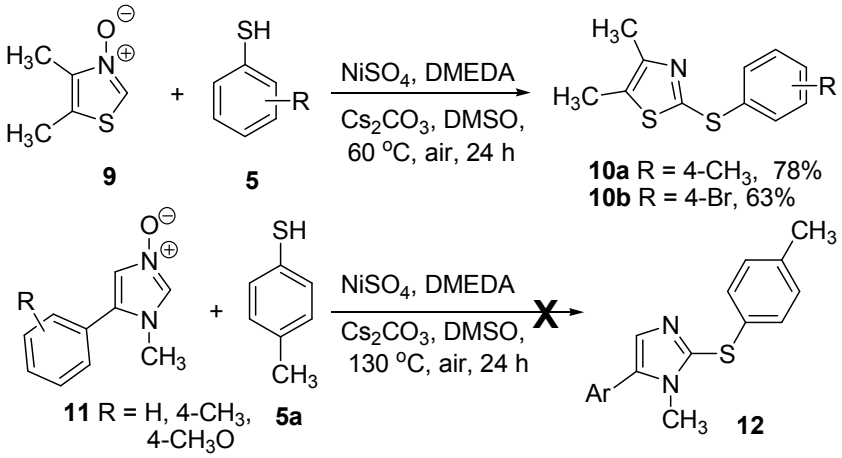
Table **3**. $NiSO_4$-catalyzed thiolation of 2-aryl-1,2,3-triazole *N*-oxide **4**[a]



4 5 6

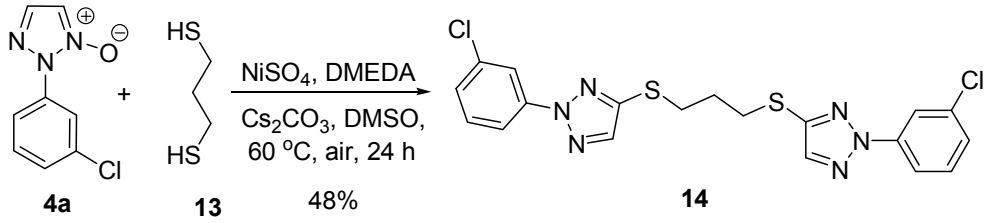
entry	R^1	R^2	product	yield (%) [b]
1	3-Cl		**6aj**	64
2	3-Cl		**6ak**	69
3	4-CH_3		**6ck**	64
4	3-Cl		**6al**	77
5 [c]	3-Cl		**6am**	73
6	4-CH_3		**6cm**	63
7	3-Cl		**6an**	72
8	3-Cl	$CH_3(CH_2)_4CH_2$	**6ao**	68
9	3-Cl	$(CH_3)_2CHCH_2CH_2$	**6ap**	72
10	3-Cl		**6aq**	79
11	3-Cl	$(CH_3)_3C$	**6ar**	86

[a] Condition: **4** (0.2 mmol), **5** (0.24 mmol), $NiSO_4$ (0.02 mmol), DMEDA (0.08 mmol), Cs_2CO_3 (0.4 mmol), DMSO (0.6 mL), under open air. [b] Isolated yields. [c] For 18 h.



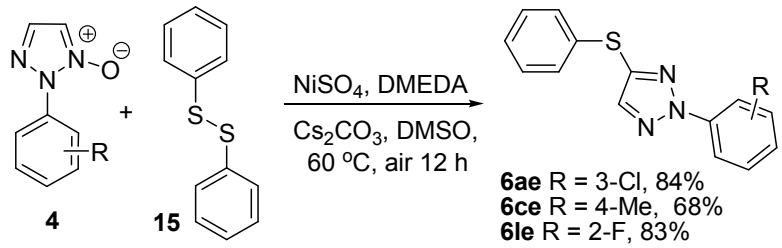
Scheme **1**. Thiolation of heteroarene *N*-oxides with thiols.

With the promising results for monoarylthiolation formation, we further explored the possibility of extending the reaction to the more challenging bisarylthiolation. We were pleased to discover that alky dithiol **13** is also active sulfenylating reagent. Reaction of 1,2,3-triazole *N*-oxides **4a** with propane-1,3-dithiol is presented in Scheme **2**.



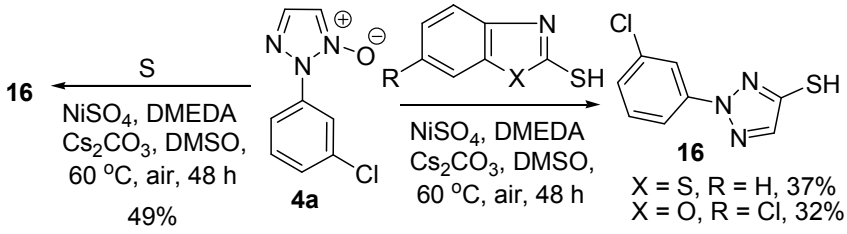
Scheme **2**. Thiolation of 1,2,3-triazole *N*-oxide **4a** with propane-1,3-dithiol **13**.

In comparison to aryl thiols, diaryl disulfides are difficult to undergo C–S coupling reactions and would perform worse as thiolating agents.[9g,9h] Thus, we examined the potential for diaryl disulfides to undergo this direct thiolation reaction. Gratifyingly, the reactions between 1,2,3-triazole *N*-oxides **4** and 1,2-diphenyldisulfane **15** using the optimized reaction conditions afforded the corresponding thioethers **6** in good to excellent yields as shown in Scheme **3.** The reason for this is not clear, although the results do indicate that the new catalytic system is more effective with diaryl disulfides as coupling partners.



Scheme **3**. Thiolation of 2-aryl-1,2,3-triazole *N*-oxides **4** with disulfide **15**.

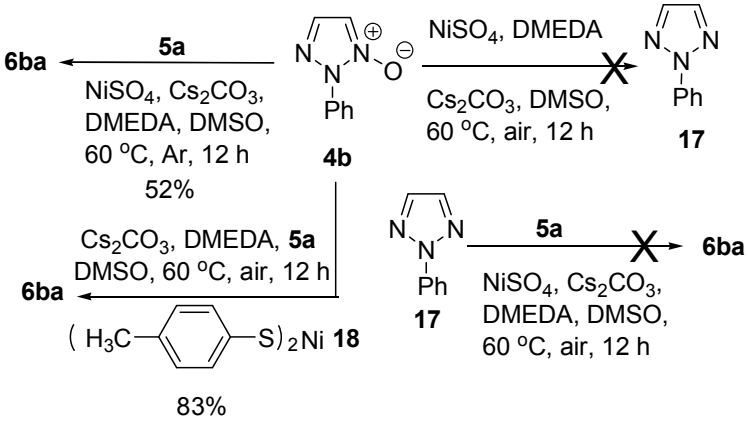
The scope of the reaction with respect to other coupling partners, such as benzothiazole-2-thiol, 6-chlorobenzooxazole-2-thiol, and sulfur, was investigated finally , and unexpectedly, under the present reaction conditions, 2-(3-Chlorophenyl)-2*H*-1,2,3-triazole-4-thiol **16** was isolated in 37%, 32%, and 49% yields, respectively (Scheme **4**).



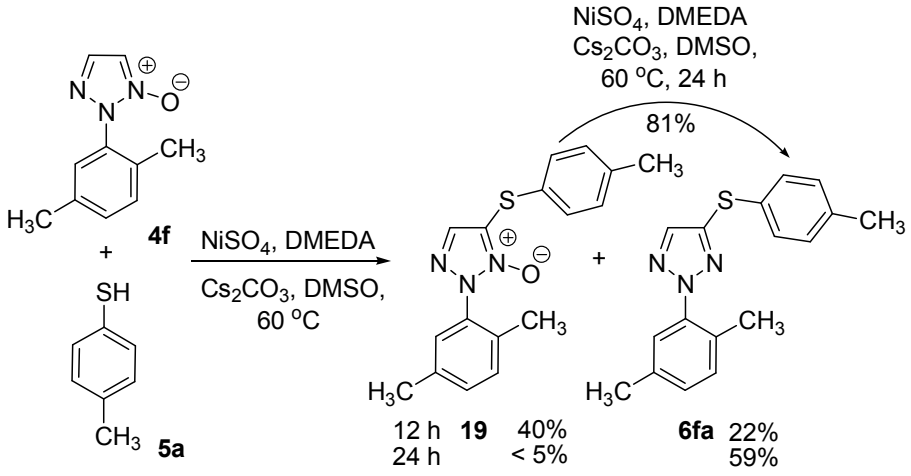
Scheme **4**. Synthesis of 2-(3-chlorophenyl)-2*H*-1,2,3-triazole-4-thiol.

On the basis of the mechanistic studies of palladium-catalyzed cross-coupling reactions *via* the C–H activation of pyridine and diazine *N*-oxides,[18] some control experiments were carried out. Firstly, we tested the reaction in the absence of the thiol as coupling partner (Scheme **5**). No deoxygenation product **17** was observed at all. Secondly, 1,2,3-triazole **17** was subjected to the standard procedures, and no corresponding thioether product was detected. These results indicated that the deoxygenation of 1,2,3-triazole *N*-oxides could occur at the same time or after the C–S bond formation step. Thirdly, the thiolation of **4b** with 4-methylbenzenethiol **5a** under an argon atmosphere (in the absence of molecular oxygen) furnished in 52% yield, indicating that molecular oxygen is not crucial for the reaction. Fourthly, the product **6ba** could be gained in 83% yield catalyzed by 10 mol % of $(ArS)_2Ni$ **18** in DMSO 60 °C for 12 h. This result indicated that **18**

may serve as an intermediate in the catalytic cycle. Fifthly, when **4f** and **5a** were subjected to the standard reaction conditions for 12 h, the corresponding product **19** and **6fa** were obtained in 40% and 22% yield, respectively (Scheme **6**). However, there was a significant increase in the yield when prolonging the reaction time to 24 h, and the deoxygenation product **6fa** was obtained in 59% yield. When **19** was subjected to the optimized conditions, the deoxygenation product **6fa** was obtained in 81% yield. These results further indicated that **19** can be reduced to its corresponding product **6fa**.

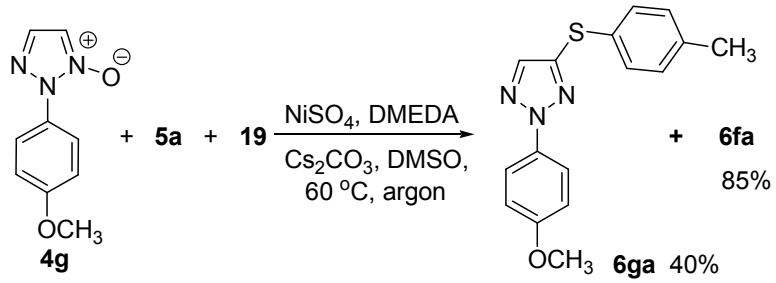


Scheme **5**. Preliminary mechanism study.



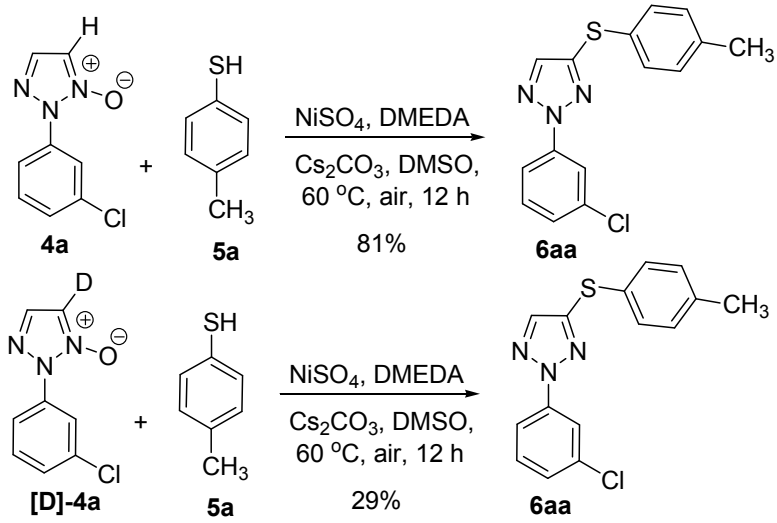
Scheme **6**. The thiolation of 1,2,3-triazole *N*-oxides **4f** with 4-methylbenzenethiol **5a**.

To further examine whether the deoxygenation of 1,2,3-triazole *N*-oxides could occur after the C–S bond formation step, a competition experiment was performed. One equivalent of thiolated *N*-oxide **19** was added to a reaction system consisting of 1 equiv of *N*-oxide **4g** and 1.2 equiv of **5a** under the optimized conditions. Products **6ga** and **6fa** were obtained in 40% and 85% yield, respectively (Scheme **7**). These results indicated that the deoxygenation of 1,2,3-triazole *N*-oxides could occur after the C–S bond formation step.



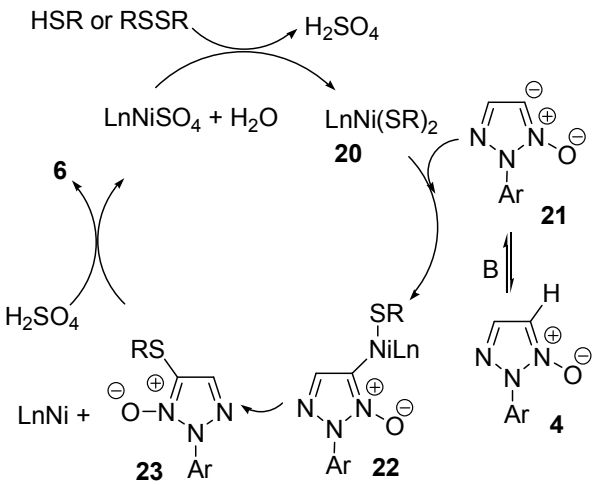
Scheme **7**. Competition experiment.

Furthermore, the intermolecular kinetic isotope effect (KIE) was also investigated by using 4-deuteriotriazole *N*-oxide **4a**. A kinetic isotope effect of 2.79 was obtained (Scheme **8**), indicated that C–H bond cleavage at the C4 position(s) of the *N*-oxides is involved in the rate-determining step. In addition, when **4a** and [D]-**4a** were run side by side in separate flasks, a significant rate difference was observed (see Supporting Information).



Scheme **8**. Kinetic isotope effect (KIE) study.

Although the mechanisms of nickel-catalyzed oxidative C–S couplings have been proposed,[19] the details remain uncertain. Based on the previous studies[19-21] and our experimental results, A plausible reaction path was outlined in Scheme **9**. First, the formation of a $Ni(SR)_2$ complex **20** gave rise to the intermediate **22**. Then, a reductive elimination produced the coupling product intermediate **23** along with a nickel species of the lower oxidation state, which would be oxidized to give Ni(II) and **6** to complete the catalytic cycle.



Scheme **9**. Plausible reaction path.

Conclusions

In conclusion, an efficient nickel-catalyzed method for C–S cross-coupling through direct functionalization of 2-aryl-1,2,3-triazole *N*-oxide C–H bonds with aryl or alky thiols, diaryl disulfide has been developed in moderate to excellent yields with high regioselectivity. We were very pleased to find that the targeted N^+-O^- bond cleavage can be observed during the reaction, and thus obviate to use an additional deoxygenation step. The advantages of this new method are broad substrate scope, operational simplicity, high atom-economy, and use of inexpensive $NiSO_4$ as the catalyst. Moreover, the high halogen compatibility of the process can provide a facile access to halo-substituted 2-aryl-4- thio-substituted triazoles.

Experimental Section

General Procedure for the Preparation of 6. To a solution of 2-aryl-1,2,3-triazole *N*-oxide (0.2 mmol), $NiSO_4$ (0.02 mmol), DMEDA (0.08 mmol) and Cs_2CO_3 (0.4 mmol) in DMSO (1 mL) was added thiol (0.24 mmol) under an air atmosphere and the mixture was stirred at 60 ^oC for 12-24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6**.

Preliminary Mechanism Study. To a solution of 2-phenyl-1,2,3-triazole *N*-oxide **4b** (32 mg, 0.2 mmol), $NiSO_4$ (31 mg, 0.02 mmol), DMEDA (7 mg, 0.08 mmol) and Cs_2CO_3 (130 mg, 0.4 mmol) in DMSO (0.6 mL) was added 4-methylbenzenethiol **5a** (30 mg, 0.24 mmol) under an argon atmosphere and the mixture was stirred at 60 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6ba** (28 mg, 52%).

To a solution of 2-phenyl-1,2,3-triazole *N*-oxide **4b** (32 mg, 0.2 mmol), bis(*p*-tolylthio)nickel **18** (6 mg, 0.02 mmol), DMEDA (7 mg, 0.08 mmol) and Cs_2CO_3 (130 mg, 0.4 mmol) in DMSO (0.6 mL) was added 4-methylbenzenethiol **5a** (30 mg, 0.24 mmol) under an air atmosphere and the mixture was stirred at 60 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6ba** (44 mg, 83%).

Competition Experiments. To a solution of 2-(4-methoxyphenyl)-5-(*p*-tolylthio)-2*H*-1,2,3-triazole *N*-oxide **4g** (31 mg, 0.1 mmol), $NiSO_4$ (2 mg, 0.013 mmol), 2-(2,5-dimethyllphenyl)-2*H*-1,2,3-triazole *N*-oxide **19** (31 mg, 0.1 mmol),

DMEDA (4 mg, 0.045 mmol) and Cs_2CO_3 (65 mg, 0.2 mmol) in DMSO (0.6 mL) was added 4-methylbenzenethiol **5a** (15 mg, 0.12 mmol) under an argon atmosphere and the mixture was stirred at 60 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6ga** (12 mg, 40%) and **6fa** (25 mg, 85%).

Kinetic Isotope Effect (KIE) Study. To a solution of 2-(3-Chlorophenyl)-1,2,3-triazole *N*-oxide **4a** (0.2 mmol) in CD_3OD (1 mL) was added Cs_2CO_3 (65 mg, 0.2 mmol) under an air atmosphere and the mixture was stirred at rt for 2 h. The reaction mixture was concentrated under reduced pressure. After the residue was dissolved in DMSO (0.6 mL), 4-methylbenzenethiol **5a** (30 mg, 0.24 mmol), $NiSO_4$ (31 mg, 0.02 mmol), DMEDA (7 mg, 0.08 mmol) and Cs_2CO_3 (130 mg, 0.4 mmol) were added. The mixture was stirred at 60 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6aa** (44 mg, 73%).

2-(3-Chlorophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6aa). Colorless liquid (49 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.16 (d, J = 7.9 Hz, 2H, Ar-H), 7.33 (dt, J = 2.0, 8.0 Hz, 1H, Ar-H), 7.38 (d, J = 8.0 Hz, 2H, Ar-H), 7.41 (t, J = 8.0 Hz, 1H, Ar-H), 7.62 (s, 1H, Ar-H), 7.96 (dt, J = 2.0, 8.0 Hz, 1H, Ar-H), 8.10 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 116.7, 119.0, 127.6, 129.0, 130.2, 130.4, 131.6, 135.2, 137.9, 138.3, 140.3, 144.7. IR (KBr) ν_{max}: 1593, 1478, 1440, 1135, 781 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}ClN_3S + H]^+$ 302.05187 (100%), 304.04892 (32%), found 302.05115 (100%), 304.04788 (32%).

2-(3-Chlorophenyl)-4-(2,4-dimethylphenylthio)-2*H*-1,2,3-triazole (6ab). Colorless liquid (45 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.00 (d, J = 7.9 Hz, 1H, Ar-H), 7.11 (s, 1H, Ar-H), 7.31 (d, J = 7.9 Hz, 1H, Ar-H), 7.34 (d, J = 7.9 Hz, 1H, Ar-H), 7.40 (t, J = 8.0 Hz, 1H, Ar-H), 7.47 (s, 1H, Ar-H), 7.93 (dd, J = 8.0, 2.0 Hz, 1H, Ar-H), 8.08 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 21.0, 116.6, 118.9, 127.5, 127.6, 127.7, 130.3, 131.7, 133.4, 135.2, 137.2, 139.0, 140.1, 140.4, 145.0. IR (KBr) ν_{max}: 1594, 1481, 1442, 1133 cm^{-1}. HRESIMS calcd for $[C_{16}H_{14}ClN_3S + H]^+$ 316.06752 (100%), 318.06457 (32%), found 316.06678 (100%), 318.06340 (32%).

2-(3-Chlorophenyl)-4-(2,6-dimethylphenylthio)-2*H*-1,2,3-triazole (6ac). Colorless liquid (44 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 6H, 2XCH_3), 7.17-7.23 (m, 3H, Ar-H), 7.24-7.32 (m, 2H, Ar-H), 7.38 (t, J = 8.1 Hz, 1H, Ar-H), 7.89 (d, J = 8.1 Hz, 1H, Ar-H), 8.03 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 116.5, 118.7, 127.2, 128.7, 128.9, 129.7, 130.3, 135.1, 135.2, 140.4, 143.5, 146.1. IR (KBr) ν_{max}: 1590, 1477, 1123, 776 cm^{-1}. HRESIMS calcd for $[C_{16}H_{14}ClN_3S + H]^+$ 316.06752 (100%), 318.06457 (32%), found 316.06672 (100%), 318.06336 (32%).

4-(4-*tert*-Butylphenylthio)-2-(3-chlorophenyl)-2*H*-1,2,3-triazole (6ad). Colorless liquid (54 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (m, 9H, 3XCH_3), 7.33 (dt, J = 1.8, 8.0 Hz, 1H, Ar-H), 7.36-7.45 (m, 5H, Ar-H), 7.66 (s, 1H, Ar-H), 7.97 (dt, J = 1.8, 9.0 Hz, 1H, Ar-H), 8.11 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.2, 34.6, 116.7, 119.0, 126.5, 127.6, 129.2, 130.4, 131.1, 135.2, 138.2, 140.4, 144.3, 151.4. IR (KBr) ν_{max}: 1593, 1483, 1133, 1010, 782 cm^{-1}. HRESIMS calcd for $[C_{18}H_{18}ClN_3S + H]^+$ 344.09882 (100%), 346.09587 (32%), found 344.09789 (100%), 346.09452 (32%).

2-(3-Chlorophenyl)-4-(phenylthio)-2*H*-1,2,3-triazole (6ae). Colorless liquid (41 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.38 (m, 4H, Ar-H), 7.42 (t, J = 8.0 Hz, 1H, Ar-H), 7.46 (d, J =

7.6 Hz, 2H, Ar-H), 7.70 (s, 1H, Ar-H), 7.98 (d, J = 8.0 Hz, 1H, Ar-H), 8.12 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.8, 119.1, 127.7, 127.8, 129.4, 130.4, 130.7, 133.1, 135.2, 138.5, 140.4, 143.6. IR (KBr) ν_{max}: 1592, 1481, 1440, 1135, 782 cm^{-1}. HRESIMS calcd for $[C_{14}H_{10}ClN_3S + H]^+$ 288.03622 (100%), 290.03327 (32%), found 288.03462 (100%), 290.03137 (32%).

2-(3-Chlorophenyl)-4-(4-fluorophenyl)thio)-2*H*-1,2,3-triazol (6af). Colorless liquid (47 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, J = 8.5 Hz, 2H, Ar-H), 7.33 (d, J = 8.0 Hz, 1H, Ar-H), 7.41 (t, J = 8.0 Hz, 1H, Ar-H), 7.48 (d, J = 8.4 Hz, 1H, Ar-H), 7.50 (d, J = 8.4 Hz, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.95 (d, J = 8.0 Hz, 1H, Ar-H), 8.09 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.5, 116.7 (d, J = 5.9 Hz), 119.1, 127.7, 127.8, 130.4, 133.7 (d, J = 8.3 Hz), 135.2, 137.9, 140.3, 144.1, 162.7 (d, J = 248.8 Hz). IR (KBr) ν_{max}: 1592, 1487, 1228, 1137, 781 cm^{-1}. HRESIMS calcd for $[C_{14}H_9ClFN_3S + H]^+$ 306.02680 (100%), 308.02385 (32%), found 306.02512 (100%), 308.02163 (32%).

2-(3-Chlorophenyl)-4-(4-chlorophenylthio)-2*H*-1,2,3-triazole (6ag). Colorless liquid (41 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.39 (m, 5H, Ar-H), 7.42 (t, J = 8.1 Hz, 1H, Ar-H), 7.72 (s, 1H, Ar-H), 7.97 (dt, J = 2.0, 8.1 Hz, 1H, Ar-H), 8.11 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.8, 119.1, 127.9, 129.5, 130.4, 131.7, 132.0, 133.9, 135.3, 138.5, 140.2, 142.8. IR (KBr) ν_{max}: 1480, 1133, 1008, 818, 754 cm^{-1}. HRESIMS calcd for $[C_{14}H_9Cl_2N_3S + H]^+$ 321.99725 (100%), 323.99430 (64%), found 321.99661 (100%), 323.99329 (32%).

4-(4-Bromophenylthio)-2-(3-chlorophenyl)-2*H*-1,2,3-triazole (6ah). Colorless liquid (46 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.5 Hz, 2H, Ar-H), 7.35 (dd, J = 8.1, 1.0 Hz, 1H, Ar-H), 7.43 (t, J = 8.1 Hz, 1H, Ar-H), 7.46 (d, J = 8.5 Hz, 2H, Ar-H), 7.73 (s, 1H, Ar-H), 7.97 (d, J = 8.1 Hz, 1H, Ar-H), 8.12 (t, J = 1.9 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 116.8, 119.1, 121.9, 127.9, 130.4, 132.0, 132.4, 132.5, 135.3, 138.6, 140.3, 142.6. IR (KBr) ν_{max}: 1591, 1478, 1080, 1004, 814, 789 cm^{-1}. HRESIMS calcd for $[C_{14}H_9BrClN_3S + H]^+$ 365.94673 (100%), 367.94469 (97%), found 365.94598 (100%), 367.94342 (97%).

4-(2-(3-Chlorophenyl)-2*H*-1,2,3-triazol-4-ylthio)phenol (6ai). Colorless liquid (36 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (s, 1H, OH), 6.86 (d, J = 8.6 Hz, 2H, Ar-H), 7.31 (d, J = 8.2 Hz, 1H, Ar-H), 7.40 (t, J = 8.2 Hz, 1H, Ar-H), 7.46 (d, J = 8.6 Hz, 2H, Ar-H), 7.53 (s, 1H, Ar-H), 7.93 (d, J = 8.2 Hz, 1H, Ar-H), 8.07 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.6, 116.7, 119.0, 122.6, 127.6, 130.3, 134.7, 135.2, 137.1, 140.4, 145.9, 156.3. IR (KBr) ν_{max}: 3420, 1592, 1487, 1436 cm^{-1}. HRESIMS calcd for $[C_{14}H_{10}ClN_3OS - H]^-$ 302.01549 (100%), 304.01254 (32%), found 302.01468 (100%), 304.01157 (32%).

4-(4-Chlorophenylthio)-2-phenyl-2*H*-1,2,3-triazole (6bg). Colorless liquid (35 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dt, J = 2.1, 8.7 Hz, 1H, Ar-H), 7.30 (s, 1H, Ar-H), 7.34-7.40 (m, 3H, Ar-H), 7.50 (t, J = 8.3 Hz, 2H, Ar-H), 7.75 (s, 1H, Ar-H), 8.08 (dd, J = 8.7, 2.1 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.8, 128.0, 129.2, 129.3, 129.4, 131.4, 131.7, 133.6, 138.5, 141.7. IR (KBr) ν_{max}: 1582, 1475, 1130, 785 cm^{-1}. HRESIMS calcd for $[C_{14}H_{10}ClN_3S + H]^+$ 288.03622 (100%), 290.03327 (32%), found 288.03523 (100%), 290.03206 (32%).

2-Phenyl-4-(phenylthio)-2*H*-1,2,3-triazole (6be). Colorless liquid (32 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.36 (m, 3H, Ar-H), 7.38 (t, J = 7.6 Hz, 1H, Ar-H), 7.43 (d, J = 7.9 Hz, 2H, Ar-H), 7.50 (t, J = 7.6 Hz, 2H, Ar-H), 7.73 (s, 1H, Ar-H), 8.09 (d, J = 8.2 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.8, 127.5, 127.8, 129.2, 129.3, 130.3, 133.7, 138.4, 139.6, 142.4. IR (KBr) ν_{max}: 1495, 1445, 1376, 1134, 750 cm^{-1}. HRESIMS calcd for $[C_{14}H_{11}N_3S + H]^+$ 254.07519 (100%), found 254.07480 (100%).

2-Phenyl-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ba). Colorless liquid (34 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 7.15 (d, J = 8.0 Hz, 2H, Ar-H), 7.35-7.40 (m, 3H, Ar-H), 7.49 (dt, J = 1.7, 8.4 Hz, 2H, Ar-H), 7.65 (s, 1H, Ar-H), 8.08 (dt, J = 1.2, 8.4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 118.8, 127.7, 129.3, 129.6, 130.1, 131.2, 137.9, 137.9, 139.6, 143.5. IR (KBr) ν_{max}: 1495, 1133, 1020, 806 cm^{-1}. HRESIMS calcd for $[C_{15}H_{13}N_3S + H]^+$ 268.09084 (100%), found 268.08997 (100%).

2-*p*-Tolyl-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ca). Colorless liquid (34 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 7.14 (d, J = 8.0 Hz, 2H, Ar-H), 7.28 (d, J = 7.9 Hz, 2H, Ar-H), 7.36 (d, J = 8.0 Hz, 2H, Ar-H), 7.64 (s, 1H, Ar-H), 7.94 (d, J = 7.9 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 21.0, 118.7, 129.8, 129.9, 130.1, 131.0, 137.5, 137.6, 137.7, 137.8, 143.0. IR (KBr) ν_{max}: 1511, 1112, 810 cm^{-1}. HRESIMS calcd for $[C_{16}H_{15}N_3S + H]^+$ 282.10649 (100%), found 282.10553 (100%).

2-(3,4-Dimethylphenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6da). Colorless liquid (40 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H, CH_3), 2.35 (s, 6H, 2XCH_3), 7.14 (d, J = 8.0 Hz, 2H, Ar-H), 7.22 (d, J = 8.2 Hz, 1H, Ar-H), 7.35 (d, J = 8.0 Hz, 2H, Ar-H), 7.64 (s, 1H, Ar-H), 7.78 (d, J = 8.2 Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 19.8, 21.0, 116.2, 119.9, 129.7, 130.0, 130.1, 130.3, 130.7, 130.9, 136.4, 137.7, 137.8, 142.8. IR (KBr) ν_{max}: 1496, 1457, 1126, 812 cm^{-1}. HRESIMS calcd for $[C_{17}H_{17}N_3S + H]^+$ 296.12214 (100%), found 296.12097 (100%).

2-*o*-Tolyl-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ea). Colorless liquid (36 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 7.15 (d, J = 8.0 Hz, 2H, Ar-H), 7.29-7.36 (m, 3H, Ar-H), 7.38 (d, J = 8.0 Hz, 2H, Ar-H), 7.58 (d, J = 7.2 Hz, 1H, Ar-H), 7.69 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 21.0, 125.1, 126.5, 128.9, 129.9, 130.0, 131.1, 131.7, 132.6, 137.4, 137.8, 139.5, 142.7. IR (KBr) ν_{max}: 1494, 1454, 1125 cm^{-1}. HRESIMS calcd for $[C_{16}H_{15}N_3S + H]^+$ 282.10649 (100%), found 282.10556 (100%).

2-(2,5-Dimethylphenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6fa). Colorless liquid (35 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H, CH_3), 2.35 (s, 6H, 2XCH_3), 7.14 (d, J = 7.9 Hz, 2H, Ar-H), 7.23 (d, J = 8.2 Hz, 1H, Ar-H), 7.35 (d, J = 7.9 Hz, 2H, Ar-H), 7.64 (s, 1H, Ar-H), 7.78 (d, J = 8.2 Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 19.8, 21.0, 116.2, 119.9, 130.0 (2C), 130.3, 130.8, 130.9, 136.4, 137.7, 137.8, 137.9, 142.8. IR (KBr) ν_{max}: 1494, 1458, 1124, 1007, 814 cm^{-1}. HRESIMS calcd for $[C_{17}H_{17}N_3S + H]^+$ 296.12214 (100%), found 296.12100 (100%).

2-(4-Methoxyphenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ga). Colorless liquid (33 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 6.99 (d, J = 9.0 Hz, 2H, Ar-H), 7.14 (d, J = 7.9 Hz, 2H, Ar-H), 7.35 (d, J = 7.9 Hz, 2H, Ar-H), 7.64 (s, 1H, Ar-H), 7.98 (d, J = 9.0 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 55.6, 114.4, 120.3, 130.0, 130.9, 133.5, 137.6, 137.7, 142.6, 159.2. IR (KBr) ν_{max}: 1510, 1250, 1167, 1134 cm^{-1}. HRESIMS calcd for $[C_{16}H_{15}N_3OS + H]^+$ 298.10141 (100%), found 298.10039 (100%).

2-(4-Fluorophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ha). Colorless liquid (45 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 7.14 (d, J = 2.7 Hz, 1H, Ar-H), 7.16 (d, J = 2.7 Hz, 2H, Ar-H), 7.18 (d, J = 8.2 Hz, 1H, Ar-H), 7.37 (d, J = 8.2 Hz, 2H, Ar-H), 7.63 (s, 1H, Ar-H), 8.03 (dd, J = 9.1, 2.2 Hz, 1H, Ar-H), 8.06 (dd, J = 9.1, 2.2 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 116.1 (d, J = 23.2 Hz), 120.5 (d, J = 8.4 Hz), 129.4, 130.1, 131.3, 135.9 (d, J = 2.9 Hz), 137.8, 138.1, 143.8, 161.9 (d, J = 247.5 Hz). IR (KBr) ν_{max}: 1509, 1451, 1133, 626 cm^{-1}.

HRESIMS calcd for $[C_{15}H_{12}FN_3S + H]^+$ 286.08142 (100%), found 286.08043 (100%).

2-(4-Chlorophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ia). Colorless liquid (46 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.16 (d, J = 8.1 Hz, 2H, Ar-H), 7.38 (d, J = 8.1 Hz, 2H, Ar-H), 7.45 (dt, J = 2.0, 6.9 Hz, 2H, Ar-H), 7.62 (s, 1H, Ar-H), 8.01(dt, J = 2.1, 6.9 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 119.9, 129.2, 129.4, 130.2, 131.5, 133.3, 137.8, 138.1, 138.2, 144.3. IR (KBr) ν_{max}: 1490, 1092, 829 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}ClN_3S + H]^+$ 302.05187 (100%), 304.04892 (32%), found 302.05139 (100%), 304.04811 (32%).

2-(4-Bromophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ja). Colorless liquid (51 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.16 (d, J = 8.0 Hz, 2H, Ar-H), 7.38 (d, J = 8.0 Hz, 2H, Ar-H), 7.60 (t, J = 8.8 Hz, 2H, Ar-H), 7.62 (s, 1H, Ar-H), 7.94 (d, J = 8.8 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 120.2, 121.2, 129.1, 130.2, 131.6, 132.4, 137.8, 138.2, 138.6, 144.4. IR (KBr) ν_{max}: 1487, 1006, 959, 826 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}BrN_3S + H]^+$ 346.00136 (100%), 347.99931 (97%), found 346.00006 (100%), 347.99757 (32%).

2-(4-Iodoophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ka). Colorless liquid (46 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.16 (d, J = 8.0 Hz, 2H, Ar-H), 7.38 (t, J = 4.1 Hz, 2H, Ar-H), 7.61 (s, 1H, Ar-H), 7.78-7.85 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 92.3, 120.4, 129.1, 130.2, 131.6, 137.8, 138.2, 138.3, 139.3, 144.4. IR (KBr) ν_{max}: 1486, 1051 953, 830 cm^{-1}. MS (EI) calcd for $[C_{15}H_{12}IN_3S]^+$ 393 (100%), found 393 (100%). Anal calcd for $C_{15}H_{12}IN_3S$: C, 45.81; H, 3.08; N, 10.69; S, 8.15. Found C, 46.13; H, 3.27; N, 10.45, S, 7.82.

4-(4-Chlorophenylthio)-2-(4-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole (6lg). Colorless liquid (48 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dt, J = 2.0, 8.6 Hz, 2H, Ar-H), 7.40 (dt, J = 2.0, 8.6 Hz, 2H, Ar-H), 7.73 (s, 1H, Ar-H), 7.76 (d, J = 8.6 Hz, 2H, Ar-H), 8.20 (d, J = 8.6 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.8, 123.8 (q, J = 272.2 Hz), 126.7 (q, J = 3.8 Hz), 129.6, 129.9, 131.4, 132.2, 134.2, 138.6, 141.7, 143.7. IR (KBr) ν_{max}: 1386, 1331, 1172, 1124, 815 cm^{-1}. HRESIMS calcd for $[C_{15}H_9ClF_3N_3S + H]^+$ 356.02361 (100%), 358.02066 (32%), found 356.02271 (100%), 358.01926 (32%).

4-(2,6-Dimethylphenylthio)-2-(4-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole (6lc). White solid (50 mg, 72%), mp 41-42 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 6H, 2XCH_3), 7.21 (d, J = 7.8 Hz, 2H, Ar-H), 7.23 (s, 1H, Ar-H), 7.26 (d, J = 7.8 Hz, 1H, Ar-H), 7.72 (d, J = 8.6 Hz, 2H, Ar-H), 8.12 (d, J = 8.6 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.4, 123.8 (q, J = 272.0 Hz), 123.9 (q, J = 3.8 Hz), 128.0, 128.6, 128.7, 129.2, 129.8, 135.4, 143.5, 146.7. IR (KBr) ν_{max}: 1615, 1385, 1324, 1125 cm^{-1}. HRESIMS calcd for $[C_{17}H_{14}F_3N_3S + H]^+$ 350.09388 (100%), found 350.09305 (100%).

4-(4-Chlorophenylthio)-2-*m*-tolyl-2*H*-1,2,3-triazole (6mg). Colorless liquid (39 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H, CH_3), 7.20 (d, J = 7.4 Hz, 1H, Ar-H), 7.26-7.31 (m, 3H, Ar-H), 7.34 (d, J = 2.1 Hz, 1H, Ar-H), 7.38 (t, J = 8.0 Hz, 1H, Ar-H), 7.74 (s, 1H, Ar-H), 7.87 (d, J = 8.0 Hz, 1H, Ar-H), 7.92 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 116.0, 119.4, 128.8, 129.2, 129.4, 131.3, 132.5, 133.5, 135.3, 138.5, 139.5, 141.5. IR (KBr) ν_{max}: 1447, 1227, 1009 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}ClN_3S + H]^+$ 302.05187 (100%), 304.04892 (32%), found 302.05112 (100%), 304.04780 (32%).

2-(3-Chlorophenyl)-4-(naphthalen-2-ylthio)-2*H*-1,2,3-triazole (6aj). Colorless liquid (43 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.3 Hz, 1H, Ar-H), 7.42 (t, J = 8.1 Hz, 1H, Ar-H), 7.47-7.53 (m, 3H, Ar-H), 7.72 (s, 1H, Ar-H), 7.75-7.86 (m, 3H, Ar-H), 7.94 (d, J = 1.0 Hz, 1H, Ar-H), 7.99 (dd, J = 8.1, 1.0 Hz, 1H, Ar-H), 8.14 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 116.8, 119.1, 126.6, 126.9, 127.5, 127.7, 127.8, 128.0, 129.2, 129.8, 130.2, 130.4, 132.5, 133.7, 135.2, 138.5, 140.4, 143.6. IR (KBr) ν_{max}: 1590, 1482, 1439, 1135, 782 cm^{-1}. HRESIMS calcd for $[C_{18}H_{12}ClN_3S + H]^+$ 338.05187 (100%), 340.04892 (32%), found 338.04941 (100%), 340.04630 (32%).

2-(3-Chlorophenyl)-4-(thiophen-2-ylthio)-2*H*-1,2,3-triazole (6ak). Colorless liquid (40 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (dd, J = 5.4, 3.6 Hz, 1H, Ar-H), 7.32 (dq, J = 8.0, 1.0 Hz, 1H, Ar-H), 7.38 (dd, J = 3.6, 1.2 Hz, 1H, Ar-H), 7.40 (t, J = 8.0 Hz, 1H, Ar-H), 7.48 (dd, J = 5.4, 1.2 Hz, 1H, Ar-H), 7.58 (s, 1H, Ar-H), 7.57 (s, 1H, Ar-H), 7.93 (dq, J = 1.0, 8.0 Hz, 1H, Ar-H), 8.07 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.7, 119.0, 127.6, 127.9, 128.9, 130.3, 131.4, 135.2, 135.6, 136.5, 140.4, 145.8. IR (KBr) ν_{max}: 1595, 1483, 1445, 1129 cm^{-1}. MS (ESI): 294 ($M+H^+$, 100), 296 ($M+H^+$, 30). Anal calcd for $C_{12}H_8ClN_3S_2$: C, 49.06; H, 2.74; N, 14.30, S, 21.83. Found C, 49.43; H, 2.95; N, 14.17, S, 21.52.

4-(Thiophen-2-ylthio)-2-*p*-tolyl-2*H*-1,2,3-triazole (6ck). Colorless liquid (35 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 7.04 (dd, J = 5.4, 3.6 Hz, 1H, Ar-H), 7.26 (d, J = 8.4 Hz, 2H, Ar-H), 7.36 (dd, J = 3.6, 1.2 Hz, 1H, Ar-H), 7.45 (dd, J = 5.4, 1.2 Hz, 1H, Ar-H), 7.58 (s, 1H, Ar-H), 7.91 (d, J = 8.4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 118.7, 127.8, 129.8, 131.0, 135.1, 136.2, 136.7, 137.5, 137.7, 144.4. IR (KBr) ν_{max}: 1512, 1127, 474 cm^{-1}. HRESIMS calcd for $[C_{13}H_{11}N_3S_2 + H]^+$ 274.04726 (100%), found 274.04564 (100%).

2-(3-Chlorophenyl)-4-(2-methylfuran-3-ylthio)-2*H*-1,2,3-triazole (6al). Colorless liquid (45 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 6.47 (d, J = 2.0 Hz, 1H, Ar-H), 7.31 (dq, J = 1.0, 8.1 Hz, 1H, Ar-H), 7.37 (d, J = 2.0 Hz, 2H, Ar-H), 7.46 (s, 1H, Ar-H), 7.91 (dq, J = 1.0, 8.1 Hz, 1H, Ar-H), 8.05 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9, 106.5, 114.9, 116.6, 118.8, 127.4, 130.3, 135.1, 135.7, 140.4, 141.2, 146.0, 156.3. IR (KBr) ν_{max}: 1593, 1483, 1131, 782 cm^{-1}. MS (ESI): 292 ($M+H^+$, 100), 294 ($M+H^+$, 30). Anal calcd for $C_{13}H_{10}ClN_3OS$: C, 53.52; H, 3.45; N, 14.40, S, 10.99. Found C, 53.89; H, 3.53; N, 14.06, S, 10.74.

2-(3-Chlorophenyl)-4-(2-methyl-tetrahydrofuran-3-ylthio)-2*H*-1,2,3-triazole (6am). Colorless liquid (43 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.36 (d, J = 6.4 Hz, 3H, CH_3), 2.08-2.17 (m, 1H, CH), 2.46-2.55 (m, 1H, CH), 3.82 (dt, J = 1.8, 8.3 Hz, 1H, CH), 4.03-4.10 (m, 2H, CH_2), 4.29 (dq, J = 8.0, 6.4 Hz, 1H, CH), 7.32 (dt, J = 1.0, 8.0 Hz, 1H, Ar-H), 7.41 (t, J = 8.0 Hz, 1H, Ar-H), 7.70 (s, 1H, Ar-H), 7.94 (dt, J = 1.0, 8.0 Hz, 1H, Ar-H), 8.07 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.9, 33.8, 50.0, 65.9, 77.1, 116.5, 118.8, 127.4, 130.4, 135.2, 136.6, 140.4, 144.4. IR (KBr) ν_{max}: 1593, 1483, 1108, 781 cm^{-1}. MS (ESI): 296 ($M+H^+$, 100), 298 ($M+H^+$, 30). Anal calcd for $C_{13}H_{14}ClN_3OS$: C, 52.79; H, 4.77; N, 14.21, S, 10.84. Found C, 53.08; H, 4.92; N, 13.97, S, 10.71.

4-(2-Methyl-tetrahydrofuran-3-ylthio)-2-*p*-tolyl -2*H*-1,2,3-triazole (6cm). Colorless liquid (35 mg , 63%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.36 (d, J = 6.3 Hz, 3H, CH_3), 2.09-2.17 (m, 1H, CH), 2.41 (s, 3H, CH_3), 2.43-2.52 (m, 1H, CH), 3.81 (dt, J = 8.2, 6.3 Hz, 1H, CH), 4.00-4.09 (m, 2H, CH_2), 4.27 (dq, J = 5.9, 6.3 Hz, 1H, CH), 7.28 (d, J = 8.5 Hz, 2H, Ar-H), 7.69 (s, 1H, Ar-H), 7.92 (d, J = 8.5 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.9, 21.0, 33.8, 50.2, 65.9, 77.1, 118.5, 129.8, 136.3, 137.4, 137.5, 142.9. IR (KBr) ν_{max}: 1513, 1381, 1109, 964 cm^{-1}. HRESIMS calcd for $[C_{14}H_{17}N_3OS + H]^+$ 276.11706 (100%), found 276.11542 (100%).

2-(3-Chlorophenyl)-4-(furan-2-ylmethylthio)-2*H*-1,2,3-triazole (6an). Colorless liquid (42 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.25 (s, 2H, SCH_2), 6.20 (t, J = 2.6 Hz, 1H, Ar-H), 6.31 (t, J

= 2.6 Hz, 1H, Ar-H), 7.33 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.38 (s, 1H, Ar-H), 7.42 (t, *J* = 8.1 Hz, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 7.95 (d, *J* = 8.1 Hz, 1H, Ar-H), 8.09 (t, *J* = 1.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.9, 107.7, 108.5, 110.6, 116.6, 118.9, 127.5, 130.4, 135.2, 137.4, 142.5, 143.5, 150.3. IR (KBr) ν_{max}: 1593, 1483, 1141, 781 cm^{-1}. HRESIMS calcd for $[C_{13}H_{10}ClN_3OS + H]^+$ 292.03114 (100%), 294.02819 (32%), found 292.03030 (100%), 294.02701 (32%).

2-(3-Chlorophenyl)-4-(hexylthio)-2*H*-1,2,3-triazole (6ao). Colorless liquid (40 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 6.9 Hz, 3H, CH_3), 1.28-1.38 (m, 4H, CH_2), 1.46 (dt, *J* = 7.1, 14.7 Hz, 2H, CH_2), 1.73 (dt, *J* = 7.4, 14.7 Hz, 2H, CH_2), 3.07 (t, *J* = 7.4 Hz, 2H, SCH_2), 7.31 (dt, *J* = 0.8, 8.1 Hz, 1H, Ar-H), 7.41 (t, *J* = 8.1 Hz, 1H, Ar-H), 7.68 (s, 1H, Ar-H), 7.94 (dt, *J* = 0.8, 8.1 Hz, 1H, Ar-H), 8.08 (t, *J* = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.5, 28.3, 29.5, 31.3, 33.7, 116.5, 118.8, 127.3, 130.3, 135.1, 136.3, 140.4, 145.2. IR (KBr) ν_{max}: 1594, 1483, 1442, 1134 cm^{-1}. HRESIMS calcd for $[C_{14}H_{18}ClN_3S + H]^+$ 296.09882 (100%), 298.09587 (32%), found 296.09810 (100%), 298.09484 (32%).

2-(3-Chlorophenyl)-4-(isopentylthio)-2*H*-1,2,3-triazole (6ap). Colorless liquid (41 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, *J* = 6.5 Hz, 6H, 2XCH_3), 1.63 (dt, *J* = 7.1, 15.0 Hz, 2H, CH_2), 1.71-1.82 (m, 1H, CH), 3.08 (t, *J* = 7.7 Hz, 2H, SCH_2), 7.31 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.41 (t, *J* = 8.1 Hz, 1H, Ar-H), 7.68 (s, 1H, Ar-H), 7.94 (d, *J* = 8.1 Hz, 1H, Ar-H), 8.08 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 27.3, 31.8, 38.5, 116.5, 118.8, 127.2, 130.3, 135.1, 136.3, 140.4, 145.1. IR (KBr) ν_{max}: 1594, 1482, 1133 cm^{-1}. HRESIMS calcd for $[C_{13}H_{16}ClN_3S + H]^+$ 282.08317 (100%), 284.08022 (32%), found 282.08237 (100%), 284.07913 (32%).

2-(3-Chlorophenyl)-4-(cyclopentylthio)-2*H*-1,2,3-triazole (6aq). Colorless liquid (44 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62-1.73 (m, 4H, CH_2), 1.78-1.86 (m, 2H, CH_2), 2.08-2.18 (m, 2H, CH_2), 3.71 (dd, *J* = 13.1, 6.5 Hz, 1H, CH), 7.31 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.41 (t, *J* = 8.1 Hz, 1H, Ar-H), 7.71 (s, 1H, Ar-H), 7.96 (d, *J* = 7.4 Hz, 1H, Ar-H), 8.09 (t, *J* = 1.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.8, 33.8, 46.6, 116.6, 118.9, 127.3, 130.3, 135.1, 137.3, 140.4, 144.9. IR (KBr) ν_{max}: 1593, 1483, 1441, 1136, 781 cm^{-1}. HRESIMS calcd for $[C_{13}H_{14}ClN_3S + H]^+$ 280.06752 (100%), 282.06457 (32%), found 280.06677 (100%), 282.06357 (32%).

4-(*tert*-Butylthio)-2-(3-chlorophenyl)-2*H*-1,2,3-triazole (6ar). Colorless liquid (46 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 9H, 3XCH_3), 7.34 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.43 (t, *J* = 8.1 Hz, 1H, Ar-H), 7.81 (s, 1H, Ar-H), 8.01 (d, *J* = 8.1 Hz, 1H, Ar-H), 8.15 (t, *J* = 1.9 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.1, 47.2, 116.9, 119.2, 127.7, 130.4, 135.2, 140.4, 141.3, 141.8. IR (KBr) ν_{max}: 1594, 1482, 1133, 782 cm^{-1}. HRESIMS calcd for $[C_{12}H_{14}ClN_3S + H]^+$ 268.06752 (100%), 270.06457 (32%), found 268.06676 (100%), 270.06362 (32%).

2-(2-Fluorophenyl)-4-(phenylthio)-2*H*-1,2,3-triazole (6ie). Colorless liquid (45 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.37 (m, 5H, Ar-H), 7.39-7.43 (m, 1H, Ar-H), 7.46 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.76 (s, 1H, Ar-H), 7.83 (t, *J* = 7.6 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.5 (d, *J* = 20.0 Hz), 124.5 (d, *J* = 4.1 Hz), 125.1, 127.7, 129.3, 129.9 (d, *J* = 7.7 Hz), 130.7, 132.2, 133.3, 138.5 (d, *J* = 0.8 Hz), 143.3, 154.5 (d, *J* = 256.0 Hz). IR (KBr) ν_{max}: 1609, 1508, 1449, 1128, 753 cm^{-1}. HRESIMS calcd for $[C_{14}H_{10}FN_3S + H]^+$ 272.06577 (100%), found 272.06536 (100%).

4-(Phenylthio)-2-*p*-tolyl-2*H*-1,2,3-triazole (6ce). Colorless liquid (36 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H, CH_3), 7.28-7.35 (m, 5H, Ar-H), 7.42 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.72 (s, 1H, Ar-H), 7.96 (d, *J* = 8.2 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 118.8, 127.3,

129.2, 129.8, 130.1, 134.0, 137.5, 137.8, 138.3, 141.9. IR (KBr) ν_{max}: 1513, 1448, 1382, 1131, 963 cm^{-1}. HRESIMS calcd for $[C_{15}H_{13}N_3S + H]^+$ 268.09084 (100%), found 268.08968 (100%).

4,5-Dimethyl-2-(*p*-tolylthio)thiazole (10a). Colorless liquid (37 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.21 (d, J = 8.0 Hz, 2H, Ar-H), 7.49 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 13.1, 21.3, 123.7, 125.9, 130.5, 130.6, 133.9, 140.3, 141.5. IR (KBr) ν_{max}: 1297, 1232, 1106, 1073 cm^{-1}. HRESIMS calcd for $[C_{12}H_{13}NS_2 + H]^+$ 236.05677 (100%), found 236.05560 (100%).

2-(4-Bromophenylthio)-4,5-dimethylthiazole (10b). Colorless liquid (38 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 7.40 (d, J = 8.4 Hz, 2H, Ar-H), 7.50 (d, J = 8.4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 13.2, 123.8, 125.5, 129.8, 132.9, 133.8, 134.0, 142.1. IR (KBr) ν_{max}: 1471, 1359, 1299, 1007 cm^{-1}. HRESIMS calcd for $[C_{11}H_{10}BrNS_2 + H]^+$ 299.95163 (100%), 301.94958 (100%), found 299.95045(100%), 301.94826 (100%).

1,3-Bis(2-(3-chlorophenyl)-2*H*-1,2,3-triazole-4-ylthio)propane (14). Colorless liquid (44 mg, 48%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.19 (dt, J = 6.9, 13.9 Hz, 2H, CH_2), 3.24 (t, J = 6.9 Hz, 4H, SCH_2), 7.30 (d, J = 8.1.0 Hz, 2H, Ar-H), 7.38 (t, J = 8.1 Hz, 2H, Ar-H), 7.69 (s, 2H, Ar-H), 7.89 (d, J = 8.1 Hz, 2H, Ar-H), 8.04 (s, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.3, 32.2, 116.5, 118.8, 127.4, 130.3, 135.2, 136.4, 140.3, 144.3. IR (KBr) ν_{max}: 1593, 1482, 1137, 1004, 1137, 1004, 963, 781 cm^{-1}. HRESIMS calcd for $[C_{19}H_{16}Cl_2N_6S_2 + H]^+$ 463.03332 (100%), 465.03037 (64%), found 463.03177 (100%), 465.02859 (64%).

2-(3-Chlorophenyl)-2*H*-1,2,3-triazole-4-thiol (16). Colorless amorphous solid (21 mg, 49%). ^1H NMR (400 MHz, DMSO-d_6): δ 7.27 (d, J = 8.1 Hz, 1H, Ar-H), 7.47 (t, J = 8.1 Hz, 1H, Ar-H), 7.86 (d, J = 8.1 Hz, 1H, Ar-H), 7.99 (s, 1H, Ar-H), 8.15 (s, 1H, Ar-H), 12.07 (s, 1H, S-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 116.5, 117.5, 125.0, 131.3, 133.9, 137.5, 139.5, 152.6. IR (KBr) ν_{max}: 3387, 1595, 1480, 1146, 785 cm^{-1}. HRESIMS calcd for $[C_8H_6ClN_3S - H]^-$ 209.98927 (100%), 211.98632 (32%), found 209.98860 (100%), 211.98547 (32%).

2-(2,5-Dimethylphenyl)-5-(*p*-tolylthio)-2*H*-1,2,3-triazole *N*-oxide (19). Colorless liquid (25 mg, 40%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.14 (d, J = 7.9 Hz, 2H, Ar-H), 7.16 (d, J = 7.9 Hz, 1H, Ar-H), 7.21 (d, J = 7.9 Hz, 1H, Ar-H), 7.37 (d, J = 7.9 Hz, 2H, Ar-H), 7.41 (s, 1H, Ar-H), 7.69 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 20.7, 21.0, 125.5, 129.4, 129.7, 130.0, 130.1, 131.0, 131.5, 136.5, 137.4, 137.7, 139.2, 142.5. IR (KBr) ν_{max}: 1502, 1452, 1128, 1010, 809 cm^{-1}. HRESIMS calcd for $[C_{17}H_{17}N_3OS + H]^+$ 312.11706 (100%), found 312.11560 (100%).

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Supporting Information Available. ^1H and ^{13}C NMR spectra of compounds **6, 10, 14, 16, and 19**; high-resolution mass spectra of compounds **6, 10, 14, 16, and 19**; and X-ray crystallographic files (CIF) for **6jc**.

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