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Copper-catalyzed cascade click/nucleophilic substitution reaction to access fully substituted triazolyl-organosulfurs†

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A novel cascade click/nucleophilic substitution reaction is developed to access 4-heterofunctionalized fully substituted triazolyl-organosulfurs using thiocyanates as both leaving groups and organosulfur precursors. This method features high regioselectivities and board substrate scope. 33 examples are shown to demonstrate the structural diversity through the synthesis of fully substituted triazolyl-organosulfurs including triazolyl-thiocyanates, triazolyl-sulfinylcyanides, triazolyl-thioethers, triazolyl-thiols and triazolyl-disulfides from internal thiocyanatoalkynes.

Introduction

Triazoles, as important structures with diverse bioactivities, have been widely applied in medicinal chemistry, agrochemicals, dyes, polymers, and materials science.[1] The Huisgen 1,3-dipolar cycloaddition reaction between azides and internal alkynes is considered to be the most straightforward and atom economical approach to prepare fully substituted 1,2,3-triazoles, but suffering from low regioselectivities, high temperature, and long reaction time.[2] In 2002, the copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction, independently developed by Sharpless, Fokin, and Meldal's group, showed the excellent performance for regioselectively preparing 1,4-disubstituted 1,2,3-triazoles. It was accomplished through the protonation of the key 5-cuprate–triazole intermediates in high yields and efficiencies under mild conditions from terminal alkynes, which has an enduring impact as the privileged example of "click chemistry".[3] 1,4,5-Fully substituted triazoles could be obtained from the post-transformations of 5-cuprate–triazole intermediates by transition-metal-catalyzed direct arylation,[4] Cu-catalyzed C–H bond functionalization,[5] and Cu-catalyzed electrophilic interrupted click reaction.[6–10] In 2005, Wu's group disclosed an electrophilic interrupted click reaction, where 5-cuprate-triazoles could be successfully trapped by electrophiles such as halides and acyl chlorides.[6] However, a stoichiometric amount of copper was required in order to avoid the protonation of Cu(I)–triazole intermediates. Later, Cai's group reported an intramolecular electrophilic interrupted click/Ullman coupling tandem reaction using copper in a catalytic amount and halides as electrophiles.[7] Recently, Xu, Song and other groups developed various electrophilic interrupted click reactions by trapping the 5-cuprate-triazoles with other electrophiles such as benzenesulfonothioates, *p*-toluenesulfono(dithioperoxoate), electrophilic amination reagents, Bu_3SnOMe, sulfoximines, boronic acids, and *N*-tosylhydrazones.[8,9] Most recently, Lautens' group disclosed the intramolecular electrophilic interrupted click/acylation domino reaction using acyl chlorides as electrophiles (Scheme 1a).[10] The structural diversity of 5-heterofunctionalized fully substituted 1,2,3-triazoles are broadly expanded by the above electrophilic interrupted click reactions. However, these transformations severely depend on the highly reactive electrophiles in order to overcome the parasitic protonation. Methods for the synthesis of 4-heterofunctionalized fully substituted triazoles by the cascade click reaction are still undeveloped.

Our group,[11] and the Fokin,[12] Mascareñas,[13] López,[13] Jia,[12,14] and Sun groups[14] addressed the diverse and regioselective issues for preparing functionalized fully substituted triazoles by chelated metal-catalyzed AAC reactions (Scheme 1b). However, the diversity of triazolyl-organosulfurs is limited only to the 5-heterofunctionalized-triazoles from the internal thioalkynes, and it is very hard to reverse the initial regioselectivities by overturning the chelation manner between the transition metal (such as Rh, Ru, and Ir) and internal thioalkyne. Recently, diversity-oriented synthesis (DOS), as a powerful strategy to access various substituted patterns of heterocyclic compounds,[15] attracted our attention. However, the strategy remains challenging and undisclosed for the DOS of different fully substituted triazolyl-organosulfurs, including

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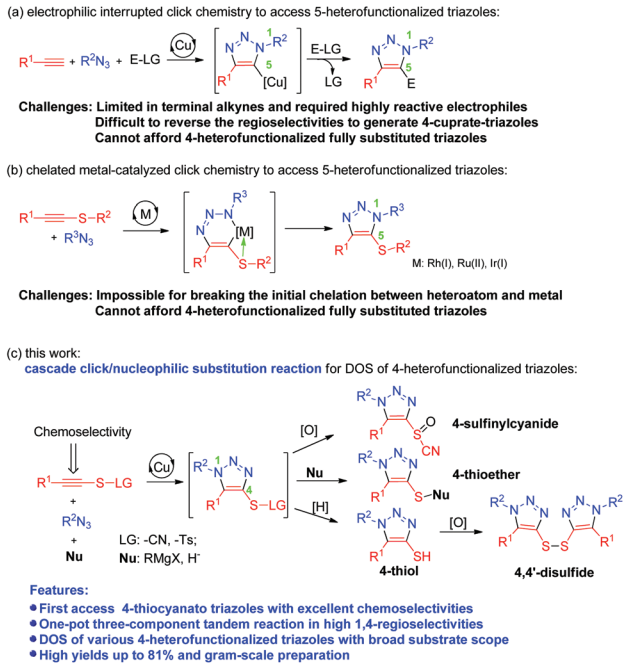


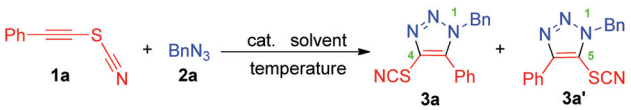
Scheme 1 Cascade click/nucleophilic substitution reaction for the synthesis of 4-heterofunctionalized triazolyl-organosulfurs.

triazolyl-thiocyanates, triazolyl-sulfinylcyanides, triazolyl-thioethers, triazolyl-thiols and triazolyl-disulfides, because most transition metal catalysts may be easily poisoned or strongly bound by sulfur. In addition, the 1 : 1 regioisomer mixture is usually obtained for the internal thioalkynes participating in the [3 + 2] cycloadditions due to their low reactivity and the difficulty in their regiocontrol by the CuAAC process.[16] Herein, we first integrate the leaving groups into the internal alkynes and develop the novel click/nucleophilic substitution cascade reaction for the DOS of triazolyl-organosulfurs in high 1,4-regioselectivity. Thiocyanate is an excellent candidate because cyanate functionalized as an ideal leaving group, and the sulfur served as a precursor.[17] Diverse fully substituted 4-heterofunctionalized-triazoles, including triazolyl-thiocyanates, triazolyl-sulfinylcyanides, triazolyl-thioethers, triazolyl-thiols and triazolyl-disulfides, could be obtained *via* the cascade click/nucleophilic substitution reactions, which remarkably expanded the structural diversity as well as simplified the preparation procedures. 33 examples are shown to demonstrate the structural diversity accomplished by this methodology (Scheme 1c).

Results and discussion

For the preparation of fully substituted 4-thiocyanato-1,2,3-triazole (**3a**), internal thiocyanatoalkyne (**1a**) and benzyl azide (**2a**) were initially chosen as the model substrates for optimizing the reaction conditions (Table 1). None of the desired AAC products were observed with CuI or Cu(II) as catalysts (Table 1, entries 1 and 2). To our delight, $(CuOTf)_2PhMe$ and $Cu(MeCN)_4PF_6$ as catalysts could supply 4-thiocyanato-1,2,3-triazole (**3a**) in moderate yields and good 1,4-regioselectivities (Table 1, entries 3 and 4). The yield could be further improved at 80 °C due to the thermodynamic control (Table 1, entry 5). The mildly decreased yield and regioselectivity were observed at 100 °C (Table 1, entry 6). Improving the catalyst loading may accelerate the catalytic cycles. The yield could be increased to 79% using 5% catalyst loading, and kept in 77% yield using 10% catalyst loading (Table 1, entries 7 and 8). High concentration (0.5 M) of solvent promoted the intermolecular reaction and gave 85% yield with good regioselectivity (11 : 1) (Table 1, entry 9). The reaction could also occur in THF and DCE

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Loading [%]	Solvent	Conc. [M]	Temperature [°C]	Yield[b,c] [%]	**3a**/**3a**'[b]
1	CuI	2.5	$CHCl_3$	0.1	60	0	—
2	$CuSO_4{\cdot}5H_2O$	2.5	$CHCl_3$	0.1	60	0	—
3	$(CuOTf)_2PhMe$	2.5	$CHCl_3$	0.1	60	60	8 : 1
4	$Cu(MeCN)_4PF_6$	2.5	$CHCl_3$	0.1	60	62	8 : 1
5	$Cu(MeCN)_4PF_6$	2.5	$CHCl_3$	0.1	80	71	8 : 1
6	$Cu(MeCN)_4PF_6$	2.5	$CHCl_3$	0.1	100	65	6 : 1
7	$Cu(MeCN)_4PF_6$	5	$CHCl_3$	0.1	80	79	8 : 1
8	$Cu(MeCN)_4PF_6$	10	$CHCl_3$	0.1	80	77	8 : 1
9	$Cu(MeCN)_4PF_6$	5	$CHCl_3$	0.5	80	85	11 : 1
10	$Cu(MeCN)_4PF_6$	5	THF	0.5	80	82	9 : 1
11	$Cu(MeCN)_4PF_6$	5	DCE	0.5	80	82	11 : 1
12	$Cu(MeCN)_4PF_6$	5	Toluene	0.5	80	Trace	—
13	$Cu(MeCN)_4PF_6$	5	H_2O	0.5	80	0	—

[a] Conditions: **1a** (1.0 equiv.), **2a** (1.5 equiv.), catalyst, solvent, for 24 h. [b] Determined by ^1H NMR of the crude mixture with toluene as an internal standard. [c] The combined yield of **3a** and **3a**′ was reported.

(Table 1, entries 10 and 11) but cannot proceed in toluene or water due to polarity and solubility issues (Table 1, entries 12 and 13).

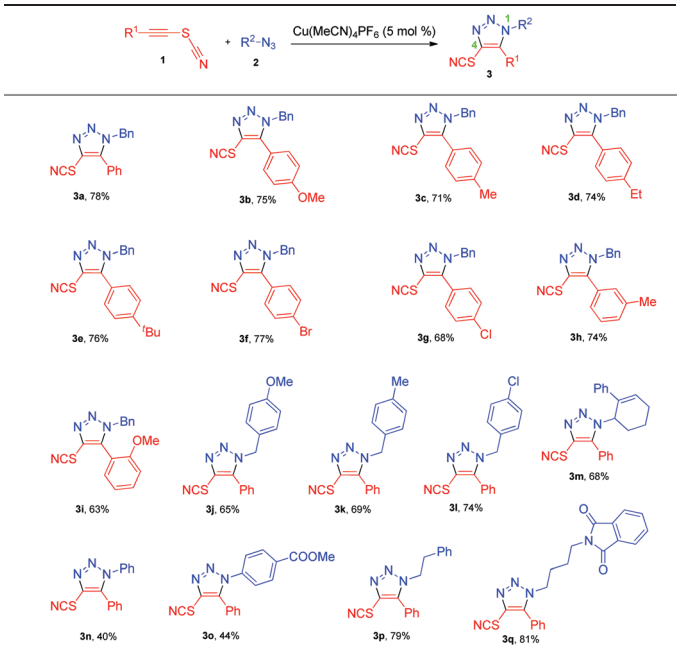
With the optimized conditions in hand, we explored the substrate scope of the azide-internal thiocyanatoalkyne cycloaddition reaction. Various internal thiocyanatoalkynes (**1**) and azides (**2**) were used as substrates to afford fully substituted 4-thiocyanato-1,2,3-triazoles (**3**) in good yields (up to 81%), chemoselectivities, and regioselectivities. Using $Cu(MeCN)_4PF_6$ as a catalyst, the synthesis of fully substituted 4-thiocyanato-1,2,3-triazoles (**3**) in $CHCl_3$ is shown in Table 2. The electronic effect was not obvious for the electron-rich and electron-deficient substrates as they showed similar yields (**3a–3h**) despite a dramatically decreased yield (63%) for the *o*-methoxylphenyl substituted derivative (**3i**). In addition to benzyl azide, the yields for electron-rich azides (**3j** and **3k**) were slightly lower than those of electron-poor azide (**3l**). To our delight, the reaction could also occur for the secondary azide, which would be used for the enantioselective CuAAC reactions in the future (**3m**).[18] Unfortunately, the utilization of aryl azides gave lower yields than that of alkyl azides in this transformation (**3n** and **3o**). **3p** was acquired from the phenylethyl azide in 79% yield. We were pleased to find that the complicated butyl azide could offer **3q** in good yields (81%).

After the fully substituted 4-thiocyanato-1,2,3-triazoles (**3**) were prepared well, the cascade click/nucleophilic substitution reaction to access fully substituted triazolyl-organosulfurs was developed in a "one-pot, three-component" manner as shown in Table 3. The preparation of fully substituted 4-thio-1,2,3-triazoles (**5**) was evaluated using a variety of Grignard reagents (**4**) as nucleophiles. THF was used as the solvent instead of $CHCl_3$ in Table 3 in order to be compatible with the following nucleophilic attacking step. The reactivity of leaving groups, –CN and –Ts, was carefully examined by the preparation of **5a**, **5b**, and **5h**. In general, internal thiocyanatoalkynes (**1**) could give higher yields compared to *S*-(phenylethynyl) 4-methylbenzenesulfonothioate (**1′**). For the primary alkyl Grignard reagents as nucleophiles, **5a–5c** were acquired in good yields. When the secondary alkyl Grignard reagents were used as nucleophiles, the yields of **5d–5f** decreased quickly because of the steric hindrance effect. **5g** was prepared in 70% yield using the benzyl Grignard reagent. Aryl Grignard reagents were also good nucleophiles to give 72–74% yields without obvious electronic effects (**5h–5j**).

The applicability of the synthesis of fully substituted 4-thiocyanato-1,2,3-triazoles was investigated in Scheme 2. It is very significant for the late-stage modifications of natural compounds by the AAC reaction to introduce the functionality. Internal thiocyanatoalkyne (**1a**) and glycosyl azide (**2r**) were used as substrates, which efficiently offered unique glycosyl thiocyanates (**3r**). It could be potentially used as a novel glycoconjugation approach (Scheme 2a). Treating with trifluoroacetic anhydride (TFAA) and H_2O_2, the controlled oxidation could produce triazolyl 4-sulfinylcyanide (**6a**) in moderate yields (Scheme 2b).

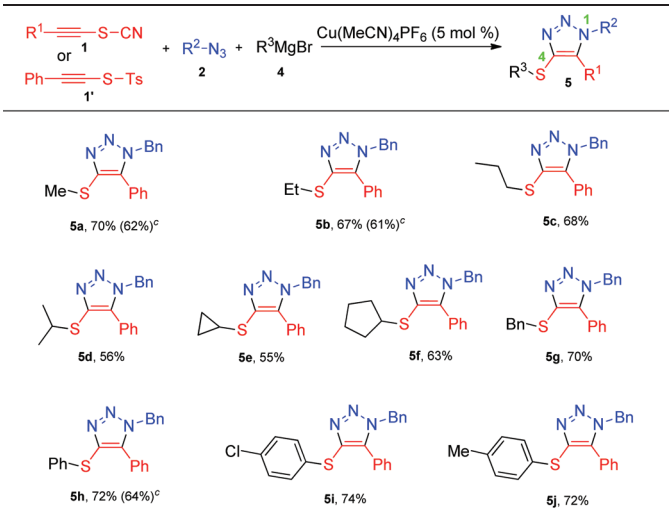
Next, we explored the applicability of the cascade click/nucleophilic substitution reaction for DOS of various fully substituted triazolyl-organosulfurs in Scheme 3. The tandem reaction could be performed on the gram scale. Treating with **1a** (6.5 mmol, 1.03 g) using methylmagnesium bromide (**4a**), **5a**

Table 2 Reaction scope of the fully substituted 4-thiocyanato-1,2,3-triazoles[a,b]

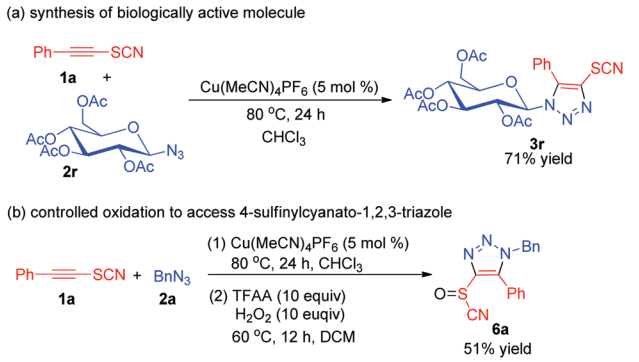


[a] Reaction conditions: **1** (1.0 equiv.), **2** (1.5 equiv.), $Cu(MeCN)_4PF_6$ (5 mol%), $CHCl_3$ (0.5 M), 80 °C in a sealed tube for 12–24 h. [b] Yield of the isolated product.

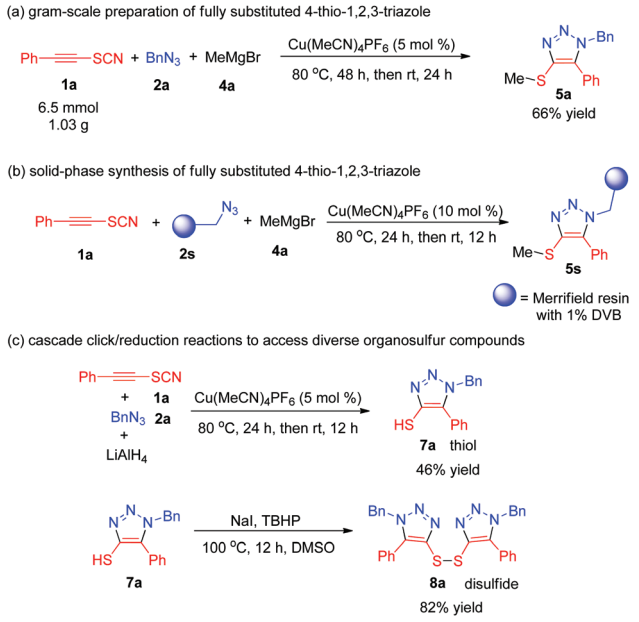
Table 3 Cascade click/nucleophilic substitution reaction to access fully substituted 4-thio-1,2,3-triazoles[a,b]



[a] Reaction conditions: **1** (1.0 equiv.), **2** (1.5 equiv.), $Cu(MeCN)_4PF_6$ (5 mol%), THF (0.5 M), 80 °C in a sealed tube for 12–24 h, then **4** (2 equiv.) was added to the mixture at 0 °C, then warmed to rt for 12 h. [b] Yield of the isolated product. [c] **1′** was used instead of **1**.



Scheme 2 The application of the synthesis of 4-thiocyanato-1,2,3-triazoles.



Scheme 3 The application of the cascade click/nucleophilic substitution reaction.

was afforded in 66% yield (4.29 mmol, 1.21 g) after column purification (Scheme 3a). The cascade click reaction could be extended to the solid-phase synthesis. (Azidomethyl) polystyrene resin (**2s**) could be employed for the preparation of fully substituted 4-thio-1,2,3-triazole (**5s**) using the Grignard reagent (**4a**) as a nucleophile. It provided a powerful methodology for surface modification and heterogeneous multicomponent catalysis (Scheme 3b). Thiocyanates could be considered as the precursors for DOS of the thioethers, thiols, and disulfides.[17] Besides organometallic reagents, hydrides were also good nucleophiles for transforming the thiocyanates into thiols. Thiol (**7a**) was obtained by cascade click/reduction reaction. The disulfide (**8a**) could be afforded by the oxidation of the related thiol (Scheme 3c). Therefore, fully substituted triazolyl-thiocyanates (**3**), triazolyl-thioethers (**5**), triazolyl-sulfinylcyanides (**6**), triazolyl-thiols (**7**) and triazolyl-disulfides (**8**) share a common internal thiocyanatoalkyne precursor by the tandem click/nucleophilic substitution reactions.

Conclusions

In summary, we first disclosed the synthesis of fully substituted 4-thiocyanato-1,2,3-triazoles in high regioselectivities, chemoselectivities, yields, and broad substrate scope by the CuAAC reaction. Beyond this research, we developed the cascade click/nucleophilic substitution reaction in a "one-pot, three-component" manner using the thiocyanates as both leaving groups and organosulfur precursors to access 4-heterofunctionalized fully substituted triazolyl-organosulfurs, such as triazolyl-thiocyanates, triazolyl-sulfinylcyanides, triazolyl-thioethers, triazolyl-thiols, and triazolyl-disulfides, from a common internal thiocyanatoalkyne precursor. More than 30 examples are shown to validate the structural diversity of this methodology for diversity-oriented synthesis (DOS) of various fully substituted triazolyl-organosulfurs. Further mechanistic studies and advanced theoretical calculations for the transition states and intermediates are underway in our laboratory.

Experimental

General methods

Unless otherwise noted, all commercially available reagents and solvents were used without further additional purification. Thin layer chromatography was performed using precoated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40–60 μm). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance II 400 MHz or Bruker Avance III 500 MHz spectrometer recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$ unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz (Hz). High resolution mass spectra (HRMS) were recorded with Agilent apparatus (TOF mass analyzer type) using an Electron Spray Injection (ESI) mass spectrometer. Melting points were determined by XP-4 melting point apparatus.

Preparation of substrates

All substrates were prepared according to the literature methods and their spectral data matched with literature studies.[9b,17b,19,20]

Representative procedure for the synthesis of fully substituted 4-thiocyanato-1,2,3-triazoles

To a vial containing (thiocyanatoethynyl)benzene **1a** (32 mg, 0.2 mmol, 1 equiv.) in $CHCl_3$ (0.4 mL) and $Cu(MeCN)_4PF_6$ (3.8 mg, 5 mol%) was added BnN_3 **2a** (40 mg, 0.3 mmol, 1.5 equiv.). The mixture was stirred at 80 °C for 24 h. The mixture was purified with flash column chromatography (20% EtOAc

in petroleum ether) to give the pure product **3a** (46 mg, 78%) as a yellow oil.

1-Benzyl-4-thiocyanato-5-phenyl-1*H*-1,2,3-triazole (3a). 45 mg, 78% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.56–7.49 (m, 3H), 7.28–7.22 (m, 5H), 7.04–7.02 (m, 2H), 5.47 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 134.1, 130.9, 129.6, 129.4, 129.0, 128.7, 127.6, 126.4, 124.2, 109.2, 53.2. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{12}N_4S$ $(M + Na)^+$ 315.0674, found 315.0680.

1-Benzyl-4-thiocyanato-5-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3b). 48 mg, 75% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.33–7.31 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 7.10–7.08 (m, 2H), 7.04 (d, J = 8.0 Hz, 2H), 5.49 (s, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 142.2, 134.3, 131.0, 129.0, 128.7, 127.5, 126.2, 115.9, 114.9, 109.4, 55.5, 53.1. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{14}N_4OS$ $(M + Na)^+$ 345.0781, found 345.0784.

1-Benzyl-4-thiocyanato-5-(*p*-tolyl)-1*H*-1,2,3-triazole (3c). 43 mg, 71% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.36–7.32 (m, 5H), 7.17 (d, J = 8.0 Hz, 2H), 7.11–7.08 (m, 2H), 5.49 (s, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 141.3, 134.3, 130.1, 129.4, 129.0, 128.7, 127.6, 126.3, 121.2, 109.3, 53.1, 21.5. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{14}N_4S$ $(M + Na)^+$ 329.0831, found 329.0836.

1-Benzyl-4-thiocyanato-5-(4-ethylphenyl)-1*H*-1,2,3-triazole (3d). 47 mg, 74% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.37 (d, J = 8.0 Hz, 2H), 7.32–7.28 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.11–7.08 (m, 2H), 5.50 (s, 2H), 2.75 (q, J = 8.0 Hz, 2H), 1.33 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 142.4, 134.3, 129.5, 129.0, 128.9, 128.7, 127.6, 126.2, 121.3, 109.3, 53.1, 28.8, 15.2. HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{16}N_4S$ $(M + Na)^+$ 343.0988, found 343.0990.

1-Benzyl-4-thiocyanato-5-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazole (3e). 53 mg, 76% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.92 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.43–7.37 (m, 5H), 5.81 (s, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 152.0, 133.5, 129.3, 129.1, 127.9, 127.4, 126.0, 125.6, 112.0, 106.4, 53.5, 34.9, 31.2. HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{20}N_4S$ $(M + H)^+$ 349.1481, found 349.1484.

1-Benzyl-4-thiocyanato-5-(4-bromophenyl)-1*H*-1,2,3-triazole (3f). 57 mg, 77% yield, yellow solid, mp = 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.67 (d, J = 12.0 Hz, 2H), 7.33–7.31 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 7.08–7.06 (m, 2H), 5.50 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 134.0, 132.7, 131.1, 129.1, 128.9, 127.5, 126.7, 125.7, 123.1, 109.0, 53.4. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{11}BrN_4S$ $(M + Na)^+$ 392.9780, found 392.9782.

1-Benzyl-4-thiocyanato-5-(4-chlorophenyl)-1*H*-1,2,3-triazole (3g). 44 mg, 68% yield, yellow solid, mp = 161–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.52 (d, J = 8.0 Hz, 2H), 7.34–7.31 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.08–7.06 (m, 2H), 5.50 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 137.5, 133.9, 130.9, 129.8, 129.1, 128.9, 127.5, 126.8, 122.6, 109.0, 53.4. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{11}ClN_4S$ $(M + Na)^+$ 349.0285, found 349.0286.

1-Benzyl-4-thiocyanato-5-(*m*-tolyl)-1*H*-1,2,3-triazole (3h). 45 mg, 74% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.45–7.38 (m, 2H), 7.33–7.31 (m, 3H), 7.10–7.07 (m, 3H), 7.02 (s, 1H), 5.49 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 139.3, 134.3, 131.7, 130.2, 129.2, 129.0, 128.7, 127.7, 126.6, 126.3, 124.1, 109.3, 53.2, 21.3. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{14}N_4S$ $(M + Na)^+$ 329.0832, found 329.0836.

1-Benzyl-4-thiocyanato-5-(2-methoxyphenyl)-1*H*-1,2,3-triazole (3i). 41 mg, 63% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.57–7.53 (m, 1H), 7.28–7.25 (m, 3H), 7.08 (d, J = 4.0 Hz, 2H), 7.04–7.00 (m, 3H), 5.43 (s, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 139.2, 134.1, 132.8, 131.2, 128.7, 128.4, 127.8, 127.3, 121.0, 113.0, 111.4, 109.1, 55.5, 53.5. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{14}N_4OS$ $(M + Na)^+$ 345.0781, found 345.0783.

1-(4-Methoxybenzyl)-4-thiocyanato-5-phenyl-1*H*-1,2,3-triazole (3j). 42 mg, 65% yield, yellow solid, mp = 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.63–7.54 (m, 3H), 7.28 (d, J = 4.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 5.44 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 142.0, 130.9, 129.6, 129.4, 129.2, 126.4, 126.1, 124.4, 114.3, 109.2, 55.3, 52.8. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{14}N_4OS$ $(M + Na)^+$ 345.0781, found 345.0783.

1-(4-Methylbenzyl)-4-thiocyanato-5-phenyl-1*H*-1,2,3-triazole (3k). 42 mg, 69% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60–7.53 (m, 3H), 7.27 (d, J = 4.0 Hz, 2H), 7.11 (d, d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 5.46 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 138.7, 131.1, 130.9, 129.7, 129.6, 129.3, 127.6, 126.3, 124.3, 109.2, 53.0, 21.1. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{14}N_4S$ $(M + Na)^+$ 329.0831, found 329.0834.

1-(4-Chlorobenzyl)-4-thiocyanato-5-phenyl-1*H*-1,2,3-triazole (3l). 48 mg, 74% yield, yellow solid, mp = 103–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.63–7.54 (m, 3H), 7.28 (d, J = 8.0 Hz, 4H), 7.01 (d, J = 8.0 Hz, 2H), 5.47 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 134.9, 132.5, 121.1, 129.5, 129.5, 129.2, 129.1, 126.6, 124.1, 109.1, 52.5. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{11}ClN_4S$ $(M + Na)^+$ 349.0285, found 349.0285.

4-Thiocyanato-5-phenyl-1-(2,3,4,5-tetrahydro-[1,1′-biphenyl]-2-yl)-1*H*-1,2,3-triazole (3m). 49 mg, 68% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.64–7.61 (m, 3H), 7.24–7.19 (m, 5H), 6.95–6.92 (m, 2H), 6.28 (t, J = 4.0 Hz, 1H), 5.38 (s, 1H), 2.52–2.45 (m, 1H), 2.27–2.22 (m, 3H), 2.16–2.10 (m, 1H), 1.82–1.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 139.2, 134.4, 132.3, 130.8, 129.7, 129.4, 128.4, 127.5, 126.3, 125.5, 124.8, 109.3, 56.5, 31.0, 25.3, 18.2. HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{18}N_4S$ $(M + Na)^+$ 381.1144, found 381.1147.

1,5-Diphenyl-4-thiocyanato-1*H*-1,2,3-triazole (3n). 22 mg, 40% yield, yellow solid, mp = 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.06 (d, J = 4.0 Hz, 2H), 7.70–7.65 (m, 5H), 7.60–7.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 135.0, 131.9, 130.9, 129.9, 129.1, 128.4, 127.9, 125.9, 113.8, 107.1. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{10}N_4S$ $(M + H)^+$ 279.0698, found 279.0703.

Methyl 4-(4-thiocyanato-5-phenyl-1*H*-1,2,3-triazol-1-yl)benzoate (3o). 30 mg, 44% yield, yellow oil. ^{1}H NMR (400 MHz,

$CDCl_3$, TMS): δ 8.12 (d, J = 8.0 Hz, 2H), 7.55–7.48 (m, 3H), 7.43 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 141.6, 139.1, 131.4, 131.0, 129.6, 129.5, 127.3, 124.6, 124.0, 108.9, 52.6. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{12}N_4O_2S$ $(M + Na)^+$ 359.0573, found 359.0575.

1-Phenethyl-4-thiocyanato-5-phenyl-1*H*-1,2,3-triazole (3p). 48 mg, 79% yield, brown solid, mp = 89–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.55–7.46 (m, 3H), 7.25–7.23 (m, 3H), 6.99 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 4.52 (t, J = 8.0 Hz, 2H), 3.20 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 136.4, 130.7, 129.3, 129.3, 128.9, 128.7, 127.3, 125.8, 124.1, 109.4, 50.7, 36.3. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{14}N_4S$ $(M + H)^+$ 307.1012, found 307.1017.

2-(4-(4-Thiocyanato-5-phenyl-1*H*-1,2,3-triazol-1-yl)butyl)isoindoline-1,3-dione (3q). 65 mg, 81% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.84 (dd, J = 8.0, 4.0 Hz, 2H), 7.74 (dd, J = 8.0, 4.0 Hz, 2H), 7.59–7.57 (m, 3H), 7.41–7.39 (m, 2H), 4.37 (t, J = 8.0 Hz, 2H), 3.64 (t, J = 8.0 Hz, 2H), 1.92–1.85 (m, 2H), 1.70–1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 141.9, 134.1, 131.9, 130.9, 129.6, 129.4, 126.1, 124.3, 123.3, 109.2, 48.8, 36.8, 26.9, 25.4. HRMS (ESI-TOF) m/z calcd for $C_{21}H_{17}N_5O_2S$ $(M + Na)^+$ 426.0995, found 426.0996.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(Acetoxymethyl)-6-(5-phenyl-4-thiocyanato-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3r). 76 mg, 71% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.68–7.61 (m, 3H), 7.56 (d, J = 8.0 Hz, 2H), 5.86 (t, J = 8.0 Hz, 1H), 5.59 (d, J = 8.0 Hz, 1H), 5.32–5.27 (m, 1H), 5.15 (t, J = 8.0 Hz, 1H), 4.27–4.22 (m, 1H), 4.19–4.12 (m, 1H), 3.89–3.85 (m, 1H), 2.14 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 169.2, 168.3, 143.4, 131.5, 129.9, 129.4, 126.5, 123.3, 108.7, 84.5, 75.0, 73.0, 69.2, 67.4, 61.7, 20.7, 20.5, 20.3. HRMS (ESI-TOF) m/z calcd for $C_{23}H_{24}N_4O_9S$ $(M + Na)^+$ 555.1156, found 555.1160.

Representative procedure for the cascade click/nucleophilic substitution reaction to access fully substituted 4-thio-1,2,3-triazoles

To a vial containing (thiocyanatoethynyl)benzene **1a** (32 mg, 0.2 mmol, 1 equiv.) in THF (0.4 mL) and $Cu(MeCN)_4PF_6$ (3.8 mg, 5 mol%) was added BnN_3 **2a** (40 mg, 0.3 mmol, 1.5 equiv.). The mixture was stirred at 80 °C for 24 h. Then, the mixture was cooled to 0 °C. MeMgBr **4a** (0.13 mL, 3.0 M, 2 equiv.) was added to the mixture at 0 °C. The mixture was warmed to rt and stirred for 12 h. The mixture was quenched with a saturated aqueous NH_4Cl solution (2 mL) and then extracted with DCM (3 × 4 mL). The organic phase was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The mixture was purified with flash column chromatography (20% EtOAc in petroleum ether) to give the pure product **5a** (39 mg, 70%) as a colorless oil.

Representative procedure for the gram-scale preparation of fully substituted 4-thio-1,2,3-triazoles

To a flask containing (thiocyanatoethynyl)benzene **1a** (1.03 g, 6.5 mmol, 1 equiv.) and $Cu(MeCN)_4PF_6$ (121 mg, 5 mol%) in THF (13 mL) was added BnN_3 **2a** (1.30 g, 9.8 mmol, 1.5 equiv.). The mixture was stirred at 80 °C for 48 h. Then, MeMgBr **4a** (4.33 mL, 3.0 M, 2 equiv.) was added to the mixture at 0 °C. The mixture was warmed to rt and stirred for 24 h. The mixture was quenched with a saturated aqueous NH_4Cl solution (50 mL) and then extracted with DCM (3 × 50 mL). The organic phase was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The mixture was purified with flash column chromatography (20% EtOAc in petroleum ether) to give the pure product **5a** (1.21 g, 66%) as a colorless oil.

Representative procedure for the solid-phase synthesis of fully substituted 4-thio-1,2,3-triazoles

To a vial containing (thiocyanatoethynyl)benzene **1a** (96 mg, 0.6 mmol) in THF (2 mL) was added $Cu(MeCN)_4PF_6$ (22.8 mg, 10 mol%) and azidomethyl polystyrene **2s** (500 mg, f = 1.20 mmol g^{-1}, 0.6 mmol) and the mixture was shaken at 80 °C. The reaction was monitored by IR. When the azide band (~2100 cm^{-1}) was disappeared (24 h), the mixture was cooled to 0 °C. MeMgBr (0.4 mL, 3.0 M, 2 equiv.) was added to the mixture at 0 °C. The mixture was warmed to rt and stirred for 12 h. The solid was filtered off, washed with THF (20 mL), H_2O (20 mL), H_2O–MeOH (20 mL), MeOH (20 mL), MeOH–$CHCl_3$ (1 : 1) (20 mL) and $CHCl_3$ (20 mL), and dried *in vacuo* at 40 °C for 24 h to afford yellow resin 1-benzyl-4-phenyl-5-(methylthio)-1*H*-1,2,3-triazole on polymer support **5s** (598 mg). Elemental analysis (%) = C, 84.47; H, 7.02; N, 4.58 (f = 1.09 mmol g^{-1}).

1-Benzyl-4-(methylthio)-5-phenyl-1*H*-1,2,3-triazole (5a). 39 mg, 70% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47–7.45 (m, 3H), 7.29–7.27 (m, 3H), 7.25–7.23(m, 2H), 7.08–7.06 (m, 2H), 5.49 (s, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 136.6, 135.2, 129.6, 129.5, 128.9, 128.8, 128.2, 127.4, 126.4, 52.5, 17.2. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{15}N_3S$ $(M + H)^+$ 282.1059, found 282.1064.

1-Benzyl-4-(ethylthio)-5-phenyl-1*H*-1,2,3-triazole (5b). 40 mg, 67% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47–7.45 (m, 3H), 7.29–7.27 (m, 3H), 7.24–7.22 (m, 2H), 7.07–7.05 (m, 2H), 5.48 (s, 2H), 2.94 (q, J = 8.0 Hz, 2H), 1.25 (t, J = 8.0 Hz, 3H). Compound **5b** is a known compound, and the proton spectrum is fully consistent with the reported literature.[16]

1-Benzyl-4-(propylthio)-5-phenyl-1*H*-1,2,3-triazole (5c). 42 mg, 68% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47–7.45 (m, 3H), 7.29–7.27 (m, 3H), 7.24–7.22 (m, 2H), 7.07–7.04 (m, 2H), 5.48 (s, 2H), 2.90 (q, J = 8.0 Hz, 2H), 1.63–1.56 (m, 2H), 0.92 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 137.9, 135.2, 129.7, 129.6, 128.8, 128.8, 128.2, 127.4, 126.5, 52.5, 36.7, 23.0, 13.1. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}N_3S$ $(M + Na)^+$ 332.1192, found 332.1193.

1-Benzyl-4-(isopropylthio)-5-phenyl-1*H*-1,2,3-triazole (5d). 35 mg, 56% yield, yellow solid, mp = 53–55 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47–7.44 (m, 3H), 7.29–7.27 (m, 3H), 7.23–7.21 (m, 2H), 7.06–7.03 (m, 2H), 5.48 (s, 2H), 3.43–2.38 (m, 1H), 1.21 (d, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 138.1, 135.2, 129.8, 129.6, 128.8, 128.8, 128.2,

127.3, 126.6, 52.6, 39.2, 23.3. HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{19}N_3S$ $(M + Na)^+$ 332.1192, found 332.1193.

1-Benzyl-4-(cyclopropylthio)-5-phenyl-1*H*-1,2,3-triazole (5e). 34 mg, 55% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47–7.44 (m, 3H), 7.29–7.27 (m, 3H), 7.24–7.22 (m, 2H), 7.07–7.05 (m, 2H), 5.48 (s, 2H), 2.23–2.18 (m, 1H), 0.82–0.79 (m, 2H), 0.62–0.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 138.5, 135.2, 129.8, 129.7, 128.8, 128.8, 128.2, 127.5, 126.6, 52.6, 15.2, 8.5. HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{17}N_3S$ $(M + Na)^+$ 330.1035, found 330.1038.

1-Benzyl-4-(cyclopentylthio)-5-phenyl-1*H*-1,2,3-triazole (5f). 42 mg, 63% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47–7.43 (m, 3H), 7.28–7.26 (m, 3H), 7.24–7.22 (m, 2H), 7.06–7.04 (m, 2H), 5.48 (s, 2H), 3.61–3.58 (m, 1H), 1.95–1.90 (m, 2H), 1.70–1.65 (m, 2H), 1.57–1.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 138.7, 135.3, 129.8, 129.6, 128.8, 128.2, 127.4, 126.6, 52.6, 47.4, 33.5, 24.5. HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{21}N_3S$ $(M + Na)^+$ 358.1348, found 358.1352.

1-Benzyl-4-(benzylthio)-5-phenyl-1*H*-1,2,3-triazole (5g). 50 mg, 70% yield, yellow solid, mp = 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.39 (t, J = 8.0 Hz, 1H), 7.32–7.28 (m, 5H), 7.17–7.12 (m, 3H), 7.05–7.03 (m, 2H), 6.98–6.95 (m, 2H), 6.77 (d, J = 8.0 Hz, 2H), 5.41 (s, 2H), 4.09 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 137.6, 137.5, 135.3, 129.6, 129.5, 129.0, 128.7, 128.5, 128.3, 128.2, 127.2, 127.0, 126.0, 52.4, 39.6. HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{19}N_3S$ $(M + Na)^+$ 380.1192, found 380.1195.

1-Benzyl-5-phenyl-4-(phenylthio)-1*H*-1,2,3-triazole (5h). 49 mg, 72% yield, yellow solid, mp = 119–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.48–7.44 (m, 1H), 7.42–7.38 (t, J = 8.0 Hz, 2H), 7.31–7.28 (m, 3H), 7.24–7.19 (m, 4H), 7.15 (d, J = 8.0 Hz, 3H), 7.09–7.05 (m, 2H), 5.52 (s, 2H). Compound **5h** is a known compound, and the proton spectrum is fully consistent with the reported literature.[16]

1-Benzyl-4-((4-chlorophenyl)thio)-5-phenyl-1*H*-1,2,3-triazole (5i). 56 mg, 74% yield, white solid, mp = 99–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.52–7.46 (m, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.31–7.28 (m, 3H), 7.21–7.18 (m, 2H), 7.15–7.10 (m, 4H), 7.09–7.06 (m, 2H), 5.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 136.1, 134.9, 134.6, 132.4, 130.0, 129.8, 129.6, 129.1, 128.9, 128.9, 128.4, 127.4, 125.8, 52.9. HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{16}ClN_3S$ $(M + Na)^+$ 400.0646, found 400.0647.

1-Benzyl-5-phenyl-4-(*p*-tolylthio)-1*H*-1,2,3-triazole (5j). 51 mg, 72% yield, white solid, mp = 84–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.46–7.42 (m, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.30–7.28 (m, 3H), 7.15 (d, J = 8.0 Hz, 4H), 7.08–7.06 (m, 2H), 7.04 (d, J = 8.0 Hz, 2H), 5.50 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 137.2, 136.5, 135.1, 132.2, 129.8, 129.7, 129.7, 129.1, 128.8, 128.8, 128.3, 127.4, 126.1, 52.8, 21.0. HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{19}N_3S$ $(M + H)^+$ 358.1372, found 358.1375.

Representative procedure for the synthesis of triazolyl sulfinylcyanides

Hydrogen peroxide (30 wt% solution in water, 10 equiv.) was added dropwise to a solution of trifluoroacetic anhydride (10 equiv.) in DCM at 0 °C. The mixture was stirred at 0 °C for 1 h. Then, **3a** (29 mg, 0.1 mmol, 1 equiv.) in DCM was added to the mixture. The mixture was stirred at 60 °C overnight. When the reaction was completed as determined by TLC, the mixture was quenched with water in 0 °C and then extracted with DCM (3 × 4 mL). The organic phase was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The mixture was purified with flash column chromatography (50% EtOAc in petroleum ether) to give the pure product **6a** (16 mg, 51%) as a colorless oil.

1-Benzyl-5-phenyl-1*H*-1,2,3-triazole-4-sulfinyl cyanide (6a). 16 mg, 51% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.69–7.67 (m, 1H), 7.62 (t, J = 8.0 Hz, 2H), 7.40–7.38 (m, 2H), 7.36–7.34 (m, 3H), 7.15–7.13 (m, 2H), 5.30 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 133.1, 132.3, 132.0, 129.7, 129.6, 129.2, 127.9, 123.1, 112.8, 106.6, 53.6. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{12}N_4OS$ $(M + Na)^+$ 331.0630, found 331.0640.

Representative procedure for the synthesis of fully substituted 4-thiol-1,2,3-triazoles

To a vial containing (thiocyanatoethynyl)benzene **1a** (32 mg, 0.2 mmol, 1 equiv.) in THF (0.4 mL) and $Cu(MeCN)_4PF_6$ (3.8 mg, 5 mol%) was added BnN_3 **2a** (40 mg, 0.3 mmol, 1.5 equiv.). The mixture was stirred at 80 °C for 24 h. Then, the mixture was cooled to 0 °C. $LiAlH_4$ (7.6 mg, 0.2 mmol, 1 equiv.) was added to the mixture at 0 °C. The mixture was warmed to rt and stirred for 12 h. The mixture was quenched with water (2 mL) and then extracted with DCM (3 × 4 mL). The organic phase was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The mixture was purified with flash column chromatography (10% MeOH in DCM) to give the pure product **7a** (25 mg, 46%) as a colorless oil.

1-Benzyl-5-phenyl-1*H*-1,2,3-triazole-4-thiol (7a). 25 mg, 46% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.44–7.40 (m, 1H), 7.34 (t, J = 8.0 Hz, 2H), 7.29–7.26 (m, 3H), 7.07–7.05 (m, 2H), 7.02–7.00 (m, 2H), 5.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 138.8, 134.8, 129.9, 129.7, 128.8, 128.6, 128.3, 127.5, 125.7, 52.6. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{13}N_3S$ $(M + Na)^+$ 290.0724, found 290.0728.

Representative procedure for the synthesis of fully substituted 4-disulfyl-1,2,3-triazoles

To a vial containing thiol **7a** (25 mg, 0.09 mmol, 1 equiv.) in DMSO (0.4 mL) was added NaI (40.5 mg, 0.27 mmol, 3 equiv.) and TBHP (0.05 mL, 5.5 M, 3 equiv.). The mixture was stirred at 100 °C for 12 h. Then, the mixture was cooled and quenched with water (2 mL) and then extracted with EtOAc (3 × 4 mL). The organic phase was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The mixture was purified with flash column chromatography (10% MeOH in DCM) to give the pure product **8a** (19 mg, 82%) as a colorless oil.

1,2-Bis(1-benzyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)disulfane (8a). 19 mg, 82% yield, white solid, mp = 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.70 (d, J = 4.0 Hz, 4H), 7.37–7.31 (m, 12H), 7.25–7.23 (m, 4H), 5.36 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 134.3, 129.2, 129.0, 128.6, 128.5, 128.1, 126.9,

124.0, 52.4. HRMS (ESI-TOF) *m*/*z* calcd for $C_{30}H_{24}N_6S_2$ $(M + H)^+$ 533.1578, found 533.1580.

Conflicts of interest

There are no conflicts to declare.

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