One-Pot Three-Component Synthesis of New Mono- and Bis-1,2,3-triazole Derivatives of 2-Benzimidazolethiol with a Promising Inhibitory Activity against Acidic Corrosion of Steel

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Abstract: A series of new mono- and bis-1,2,3-triazole derivatives of 2-benzimidazolethiol were synthesized by three-component copper(I)-catalyzed 1,3-dipolar cycloaddition. The desired heterocycles were obtained in good yields and fully characterized. The corrosion inhibition efficiency of new heterocyclic compounds was investigated on steel grade API 5L X52 in 1 M HCl using electrochemical impedance spectroscopy. The results revealed that these new organic compounds show promising inhibition properties for the corrosion of steel in acidic media.

Key words: 1,2,3-triazoles, multicomponent reaction, inhibitors, acidic corrosion, steel

1,4-Disubstituted 1,2,3-triazoles are a class of heterocyclic compounds of much interest because of their ample range of pharmacological activities.[1] In recent years, the copper(I)-catalyzed 1,3-dipolar cycloaddition (also known as Huisgen–Meldal–Sharpless reaction) is the most versatile strategy for synthesizing 1,2,3-triazoles from terminal alkynes and azides.[2] Through this reaction, a wide variety of compounds with a triazole ring could be prepared that are of interest in many areas of research.[3]

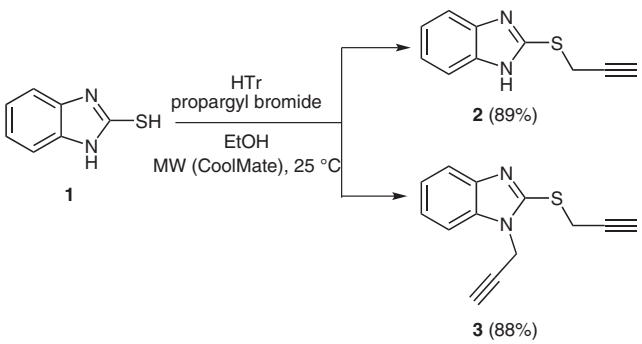
Recently, the inhibition of steel corrosion in acid solutions by different types of organic inhibitors has been extensively studied. One of the most common types of organic corrosion inhibitors are heterocyclic compounds comprising mainly a π-system (aromatic rings) and/or nitrogen, sulfur, or oxygen atoms in their structure. In this regard, 1,2,3-triazoles have been recently studied as effective corrosion inhibitors for steel in acidic media.[4]

Among the various corrosion inhibitors, benzimidazole and 2-benzimidazolethiol **1** have been tested as acidic corrosion inhibitors of steel.[5] They are not only used to abate corrosion but also are important pharmacophores because of their presence in many compounds displaying pharmacological activities.[6] Additionally, our group has reported the synthesis of 2-benzimidazolethiol and its benzylated derivative employing reconstructed hydrotalcite and their use as efficient acidic corrosion inhibitors of steel grade API 5L X52.[7,8]

Therefore, the development and study of new corrosion inhibitors are of great interest to the academic and industrial fields of corrosion. Herein, we describe the synthesis of new mono- and bis-1,2,3-triazole derivatives of 2-benzimidazolethiol and their evaluation as organic inhibitors for acidic corrosion of steel grade API 5L X52.

Synthesis

The first synthesis step involved the preparation of compounds **2** and **3** by propargylation of **1** with propargyl bromide (1 equiv for **2** and 2.3 equiv for **3**) in the presence of reconstructed hydrotalcite (HTr) following our previous procedures.[7] After workup and purification through col-



Scheme 1 Microwave-assisted synthesis of alkynes **2** and **3** in the presence of HTr

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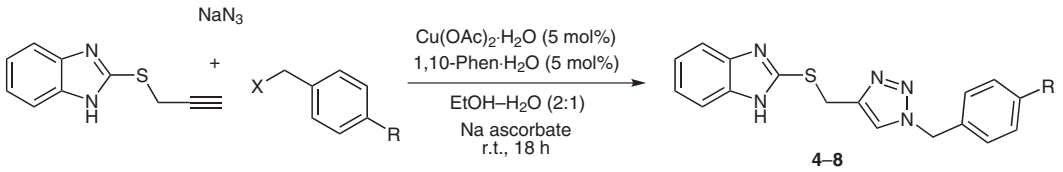
Table 1 One-Pot Three-Component Click Reaction for Compounds **4–8**



Entry[a]	Product	X	R	Yield (%)[b]
1	**4**	Cl	H	94
2	**5**	Cl	F	92
3	**6**	Cl	Cl	90
4	**7**	Br	Br	90
5	**8**	Br	I	93

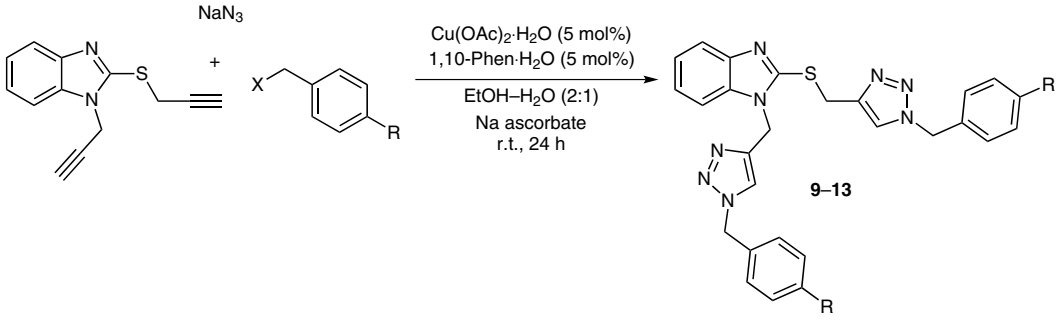
[a] Reagents: **2** (100 mg, 0.53 mmol), NaN_3 (38 mg, 0.58 mmol), and benzyl halide (0.58 mmol).
[b] Isolated yields after purification.

umn chromatography, alkynes **2** and **3** were isolated in 89 and 88% yield, respectively (Scheme 1).

With the alkyne derivative of 2-benzimidazolethiol **2**, a one-pot three-component copper(I)-catalyzed 1,3-dipolar cycloaddition was then performed for the regioselective synthesis of heterocyclic compounds **4–8**. Based on our previously reported method,[9] the reaction between **2**, sodium azide, and several benzyl halides was carried out in the presence of a catalytic amount of cupric acetate monohydrate, 1,10-phenanthroline monohydrate as ligand,[10] and sodium ascorbate as reducing agent[2a,11] in EtOH–H_2O at room temperature for 18 hours. The desired products 1,2,3-triazolobenzimidazolethiols **4–8** were isolated in 90–94% yields (Table 1).

In order to gain access to the series of bis-1,2,3-triazole derivatives of 2-benzimidazolethiol, the copper(I)-catalyzed 1,3-dipolar cycloaddition reaction was carried out with dialkyne **3** (1 equiv), sodium azide (2.1 equiv), and several benzyl halides (2.1 equiv) under the previous experimental conditions. In all cases, cycloaddition reactions showed a total conversion (TLC) after 24 hours under stirring at room temperature. The corresponding bis-1,2,3-triazoles **9–13** were isolated in 85–92% yields (Table 2).

Table 2 One-Pot Three-Component Click Reaction for Compounds **9–13**



Entry[a]	Product	X	R	Yield (%)[b]
1	**9**	Cl	H	92
2	**10**	Cl	F	86
3	**11**	Cl	Cl	85
4	**12**	Br	Br	87
5	**13**	Br	I	89

[a] Reagents: **3** (100 mg, 0.44 mmol), NaN_3 (60 mg, 0.92 mmol), and benzyl halide (0.92 mmol).
[b] Isolated yields after purification.

The structures of all newly synthesized compounds were confirmed by examination of their ^{1}H and ^{13}C NMR, IR, and mass spectra. The ^{1}H and ^{13}C NMR signals for 1,2,3-triazole derivatives of 2-benzimidazolethiol were assigned with the help of 2D heteronuclear correlation experiments (HETCOR and HMBC). The HMBC spectra showed a correlation between the CH triazole carbon atom and both hydrogen atoms of the methylene group adjacent to N-1 triazole nitrogen, whilst the quaternary carbon atom of the triazole ring correlates with both hydrogen atoms of the methylene group adjacent to N-1 benzimidazole nitrogen. The signals in the ^{1}H NMR spectra at δ = 8.04–8.09 (for **4**–**8**) and δ = 8.10–8.16 (for **9**–**13**) corresponding to the triazolyl hydrogen were supported by the signals in the ^{13}C NMR spectra at δ = 124.1–124.3 (for **4**–**8**) and δ = 124.1–124.4 (for **9**–**13**). The signals for the quaternary carbon of the triazole ring appeared at δ = 143.9–144.0 (for **4**–**8**) and δ = 142.7–143.6 (for **9**–**13**) in the ^{13}C NMR spectra. These chemical shift values are consistent with those reported for 1,4-disubstituted 1,2,3-triazoles.[4a,9,12]

Corrosion Inhibitory Activity

Electrochemical impedance spectroscopy (EIS) is a method much employed for investigation of corrosion inhibitory properties of organic compounds on metals. The compounds **4**–**13**, which incorporate the known structural features of corrosion inhibitory activity such as 2-benzimidazolethiol and the 1,2,3-triazole moiety were then evaluated as corrosion inhibitors on the steel grade API 5L X52 by EIS. The Nyquist plots obtained for the steel samples in 1M HCl solution in the presence and absence of the tested heterocycles **4**–**13** are shown in Figure 1. As can be seen from the Nyquist plots, all compounds exhibited corrosion inhibitory activity.

The blank response is shown in Figure 1 (a). Note that its impedance spectrum exhibited one single depressed semicircle, which indicates that the steel corrosion is mainly controlled by a charge transfer process. In contrast, when compounds **4**–**13** are present (30 ppm), the impedance spectra are characterized by two time constants (Figure 1, b and 1c). We can note from these figures that the spectra obtained after addition of organic compounds to the corroding media increased the impedance value (Z_{real}), and that in most cases, they are characterized by two semicircles or two time constants: one constant at high frequency and the other at low frequency, which are generally attributed to the adsorption of the organic compounds onto the metal surface. The electrochemical parameters obtained from fitting the recorded EIS data using the appropriate equivalent circuit model are listed in Table 3.

Inspection of the data of compounds **4**–**13** in Table 3 reveals that charge transfer resistance (R_{ct}) values increase prominently, while the double layer capacitance (C_{dl}) values reduced with addition of the organic compounds (30 ppm). A large R_{ct} is associated with a slower corroding

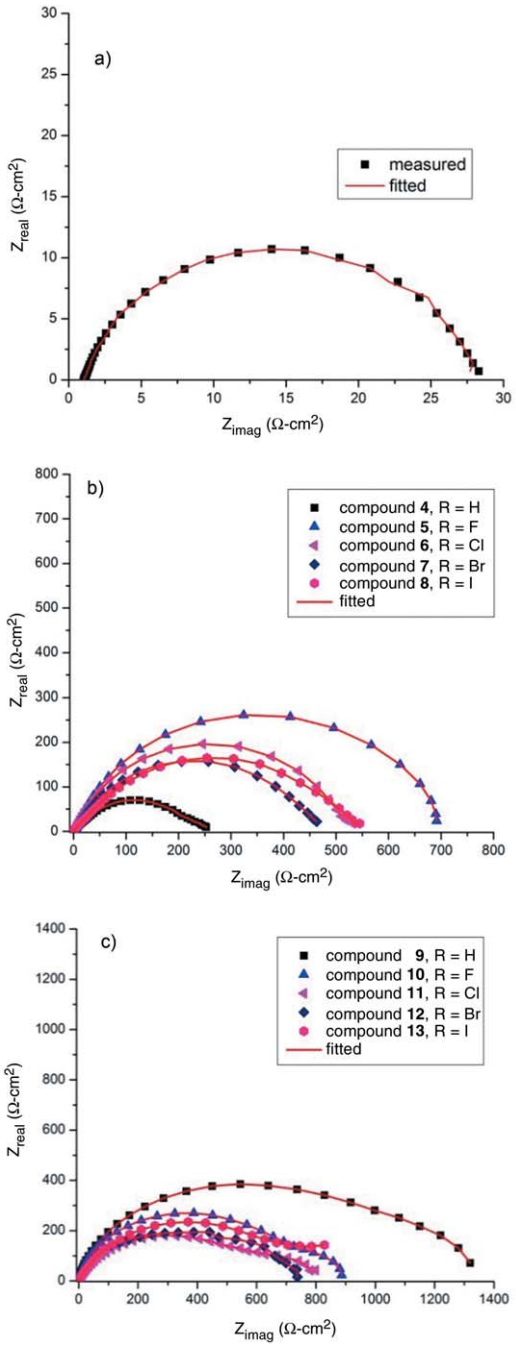


Figure 1 Experimental impedance data, Nyquist plots, recorded in the systems (**a**) steel/1 M HCl, (**b**) steel/1 M HCl + 30 ppm for compounds **4**–**8**, and (**c**) steel/1 M HCl + 30 ppm for compounds **9**–**13**

system, while the decrease in C_{dl} can be attributed to the formation of a protective layer on the metal surface.

A perusal of the literature revealed that the organic compounds containing both nitrogen and sulfur atoms in their structure are of particular importance, since these provide an excellent inhibition activity in comparison with those containing only nitrogen or sulfur atoms.[13] Therefore, it is important to remark that compounds **4**–**13** displayed corrosion inhibition efficiencies (IE) around 90% at rather low concentration values (Table 3). However, it is impor-

Table 3 Electrochemical Impedance Parameters for Steel[a]

Compound	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} (μF cm^2)	IE (%)
Blank	1.3	27	201	–
4	1.9	194	43	86
5	1.2	671	15	96
6	0.9	495	31	94
7	0.8	440	17	94
8	1.2	503	25	95
9	1.4	1250	19	98
10	1.1	900	33	97
11	1.5	756	31	96
12	1.2	680	51	96
13	1.4	900	43	97

[a] Measured in 1 M HCl solution in the presence and absence of compounds **4**–**13**, including the corrosion inhibition efficiencies (IE) at 30 ppm of the organic inhibitor.

tant to note that when halogens are included in the structure of the monotriazoles **4**–**8**, the IEs were always higher than 93%. Furthermore, for these sorts of monotriazoles the higher IE was attained by **5**, which comprises the halogen with the largest electronegativity. In contrast, in the case of the bis-triazoles **9**–**13**, the highest IE was obtained for compound **9**, which does not include halogen atoms in its structure.

In conclusion, ten new 1,2,3-triazole derivatives of 2-benzimidazolethiol were successfully synthesized in good yields through a one-pot three-component click reaction. The chemical structures of all synthesized compounds were confirmed by NMR, IR, and mass spectra. The corrosion inhibition efficiencies measured through EIS method indicate that all new heterocyclic compounds are promising corrosion inhibitors for steel in 1 M hydrochloric acid.

Commercially available reagents and solvents were used as received. Flash column chromatography was performed on silica gel 60 (230–400 mesh). Melting points were determined on a Fisher–Johns apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FT-IR/ATR spectrophotometer. NMR spectra were obtained with a Jeol ECA-500 (500 MHz) and Bruker Avance DMX-500 (500 MHz) spectrometers. Chemical shifts (δ) are given in ppm downfield from Me_4Si as an internal reference; coupling constants *J* are given in hertz. The ^{13}C NMR spectra of compounds **4**–**8** were recorded overnight. High-resolution mass spectra (HRMS) were recorded on a Jeol JMS-SX 102a and Agilent-MSD-TOF-1069A spectrometers. The electrochemical impedance study was performed at room temperature using the ZENNIUM-ZAHNER electrochemical workstation (ZAHNER-Elektrik GmbH & Co. KG), applying a sinusoidal ± 10 mV perturbation, within the 100 KHz to 0.1 Hz frequency range to an electrochemical cell with a three-electrode setup. A saturated Ag/AgCl electrode was used as reference, with a graphite bar as counter electrode, while the working electrode was the API 5L X52 steel sample with an exposed area of approximately 1 cm^2 and a chemical composition (wt%) of C: 0.080, Mn: 1.06, Si: 0.26, Ti: 0.003, V: 0.054, Nb: 0.041, P: 0.019, S: 0.003, Al: 0.039, Ni: 0.019, C_{eq}: 0.274, Fe: balance, which was prepared using standard metallographic procedures. The corrosion inhibition efficiency (IE) was evaluated by means of electrochemical impedance spectroscopy (EIS) on the API 5L X52/1 M HCl system containing 0 (blank) or 30 ppm of the organic inhibitor. Simulation of the impedance data recorded was conducted by means of electrical equivalent circuits[8b] and the electrical parameters – solution resistance (R_s), charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}) – were obtained in this way.

Mono-1,2,3-triazoles Derived from 2-Benzimidazolethiol 2; General Procedure 1 (GP1)

To a 50 mL round-bottomed flask with a magnetic stirrer, were charged $Cu(OAc)_2 \cdot H_2O$ (5 mg, 0.027 mmol, 5 mol%), 1,10-phenanthroline monohydrate (5 mg, 0.027 mmol, 5 mol%), and sodium L-ascorbate (107 mg, 0.54 mmol) in EtOH–H_2O (2:1 v/v, 6 mL), followed by stirring for 5 min at r.t. Subsequently, **2** (100 mg, 0.53 mmol), NaN_3 (38 mg, 0.58 mmol), and the required benzyl halide (0.58 mmol) were added to the reaction mixture, which was stirred for 18 h at r.t. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phases were dried (Na_2SO_4) and then the CH_2Cl_2 solvent was evaporated under vacuum. The crude product was purified by column chromatography (CH_2Cl_2–MeOH, 95:5 v/v) and recrystallized from CH_2Cl_2–hexane (1:2 v/v).

2-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methylthio]-1*H*-benzimidazole (4)

The title compound was prepared from **2** (100 mg, 0.53 mmol), NaN_3 (38 mg, 0.58 mmol), and benzyl chloride (67 μL, 0.58 mmol) according to GP1; yield: 160 mg (94%); white solid; mp 180–181 °C.

IR (ATR): 3140, 3063, 3032, 2957, 2780, 2692, 2603, 1435, 1402, 1348, 1271, 1224, 742, 708 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.61 (s, 2 H, SCH_2), 5.55 (s, 2 H, NCH_2), 7.11–7.15 (m, 2 H, ArH), 7.22–7.24 (m, 2 H, ArH), 7.28–7.33 (m, 3 H, ArH), 7.46 (br s, 2 H, ArH), 8.08 (s, 1 H, CH, triazole), 12.58 (br s, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 26.5 (SCH_2), 53.2 (NCH_2), 110.9 (ArCH), 117.9 (ArCH), 121.9 (2 × ArCH), 124.1 (CH, triazole), 128.3 (2 × ArCH), 128.5 (ArCH), 129.1 (2 × ArCH), 136.0 (C_{ipso}, benzimidazole), 136.4 (C_{ipso}), 143.9 (C_{ipso}, triazole), 144.1 (C_{ipso}, benzimidazole), 149.8 (N=CS).

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{15}N_5S$: 322.1121; found: 322.1126.

2-{[1-(4-Fluorobenzyl)-1*H*-1,2,3-triazol-4-yl]methylthio}-1*H*-benzimidazole (5)

The title compound was prepared from **2** (100 mg, 0.53 mmol), NaN_3 (38 mg, 0.58 mmol), and 4-fluorobenzyl chloride (69 μL, 0.58 mmol) according to GP1; yield: 165 mg (92%); white solid; mp 152–153 °C.

IR (ATR): 3136, 3063, 2957, 2785, 2692, 2614, 1717, 1608, 1510, 1434, 1402, 1224, 748 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.60 (s, 2 H, SCH_2), 5.54 (s, 2 H, NCH_2), 7.11–7.16 (m, 4 H, ArH), 7.29–7.32 (m, 2 H, ArH), 7.46 (br s, 2 H, ArH), 8.08 (s, 1 H, CH, triazole), 12.58 (br s, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 26.4 (SCH_2), 52.4 (NCH_2), 110.9 (ArCH), 116.0 (d, $J_{C,F}$ = 21.5 Hz, 2 × ArCH), 117.9 (ArCH), 121.8 (2 × ArCH), 124.1 (CH, triazole), 130.6 (d, $J_{C,F}$ = 8.3 Hz, 2 × ArCH), 132.6 (d, $J_{C,F}$ = 1.9 Hz, C_{ipso}), 135.9 (C_{ipso}, benzimidazole), 144.0 (2 × C_{ipso}, benzimidazole, triazole), 149.7 (N=CS), 162.3 ($J_{C,F}$ = 244.3 Hz, FC_{ipso}).

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{14}FN_5S$: 340.1027; found: 340.1031.

2-{[1-(4-Chlorobenzyl)-1*H*-1,2,3-triazol-4-yl]methylthio}-1*H*-benzimidazole (6)

The title compound was prepared from **2** (100 mg, 0.53 mmol), NaN_3 (38 mg, 0.58 mmol), and 4-chlorobenzyl chloride (93 mg, 0.58 mmol) according to GP1; yield: 170 mg (90%); white solid; mp 116–117 °C.

IR (ATR): 3132, 3071, 2967, 2883, 2808, 2697, 1719, 1490, 1420, 1404, 1348, 1269, 1225, 783, 747 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.60 (SCH_2), 5.55 (NCH_2), 7.11–7.15 (m, 2 H, ArH), 7.25 (d, J = 8.6 Hz, 2 H, ArH), 7.37 (d, J = 8.5 Hz, 2 H, ArH), 7.53 (br s, 2 H, ArH), 8.08 (s, 1 H, CH, triazole), 12.58 (br s, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 26.4 (SCH_2), 52.4 (NCH_2), 110.8 (ArCH), 117.9 (ArCH), 121.6 (ArCH), 122.1 (ArCH), 124.2 (CH, triazole), 129.1 (2 × ArCH), 130.2 (2 × ArCH), 133.3 (ClC_{ipso}), 135.4 (C_{ipso}), 135.9 (C_{ipso}, benzimidazole), 144.0 (2 × C_{ipso}, benzimidazole, triazole), 149.7 (N=CS).

HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{17}H_{14}ClN_5S$: 356.0731; found: 356.0735.

2-{[1-(4-Bromobenzyl)-1*H*-1,2,3-triazol-4-yl]methylthio}-1*H*-benzimidazole (7)

The title compound was prepared from **2** (100 mg, 0.53 mmol), NaN_3 (38 mg, 0.58 mmol), and 4-bromobenzyl bromide (145 mg, 0.58 mmol) according to GP1; yield: 190 mg (90%); white solid; mp 130–131 °C.

IR (ATR): 3125, 3063, 2972, 2879, 2807, 2692, 1718, 1488, 1397, 1345, 1269, 1224, 784, 745 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.61 (s, 2 H, SCH_2), 5.54 (s, 2 H, NCH_2), 7.12–7.16 (m, 2 H, ArH), 7.19 (d, J = 8.6 Hz, 2 H, ArH), 7.40 (br s, 1 H, ArH), 7.50 (d, J = 8.6 Hz, 2 H, ArH), 7.53 (br s, 1 H, ArH), 8.09 (s, 1 H, CH, triazole), 12.58 (br s, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 26.4 (SCH_2), 52.5 (NCH_2), 110.8 (ArCH), 117.9 (ArCH), 121.7 (ArCH), 121.8 (BrC_{ipso}), 122.1 (ArCH), 124.2 (CH, triazole), 130.5 (2 × ArCH), 132.1 (2 × ArCH), 135.8 (C_{ipso}), 136.0 (C_{ipso}, benzimidazole), 144.0 (2 × C_{ipso}, benzimidazole, triazole), 149.7 (N=CS).

HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{17}H_{14}BrN_5S$: 400.0226; found: 400.0218.

2-{[1-(4-Iodobenzyl)-1*H*-1,2,3-triazol-4-yl]methylthio}-1*H*-benzimidazole (8)

The title compound was prepared from **2** (100 mg, 0.53 mmol), NaN_3 (38 mg, 0.58 mmol), and 4-iodobenzyl bromide (172 mg, 0.58 mmol) according to GP1; yield: 220 mg (93%); white solid; mp 168–169 °C.

IR (ATR): 3129, 3075, 2968, 2887, 2812, 2693, 1719, 1484, 1417, 1398, 1269, 1226, 801, 746 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.56 (s, 2 H, SCH_2), 5.47 (s, 2H, NCH_2), 6.99 (d, J = 8.1 Hz, 2 H, ArH), 7.09–7.11 (m, 2 H, ArH), 7.32–7.36 (m, 1 H, ArH), 7.49–7.53 (m, 1 H, ArH), 7.63 (d, J = 8.1 Hz, 2 H, ArH), 8.04 (s, 1 H, CH, triazole), 12.56 (br s, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 26.5 (SCH_2), 52.7 (NCH_2), 94.9 (IC_{ipso}), 110.9 (ArCH), 118.0 (ArCH), 121.7 (ArCH), 122.3 (ArCH), 124.3 (CH, triazole), 130.6 (2 × ArCH), 136.0 (C_{ipso}, benzimidazole), 136.3 (C_{ipso}), 138.0 (2 × ArCH), 144.09 (C_{ipso}, triazole), 144.15 (C_{ipso}, benzimidazole), 149.8 (N=CS).

HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{17}H_{14}IN_5S$: 448.0087; found: 448.0090.

Bis-1,2,3-triazoles Derived from 2-Benzimidazolethiol 3; General Procedure 2 (GP2)

To a 50 mL round-bottomed flask with a magnetic stirrer, were charged $Cu(OAc)_2 \cdot H_2O$ (4 mg, 0.022 mmol, 5 mol%), 1,10-phenanthroline monohydrate (4.4 mg, 0.022 mmol, 5 mol%), and sodium L-ascorbate (87 mg, 0.44 mmol) in EtOH–H_2O (2:1 v/v, 6 mL), followed by stirring for 5 min at r.t. Subsequently, **3** (100 mg, 0.44 mmol), NaN_3 (60 mg, 0.92 mmol), and benzyl halide (0.92 mmol) were added to the reaction mixture, which was stirred for 24 h at r.t. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried (Na_2SO_4) and then the solvent was evaporated under vacuum. The crude product was purified by column chromatography (CH_2Cl_2–MeOH, 90:10 v/v) and recrystallized from CH_2Cl_2–hexane (1:2 v/v).

1-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-2-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methylthio]-1*H*-benzimidazole (9)

The title compound was prepared from **3** (100 mg, 0.44 mmol), NaN_3 (60 mg, 0.92 mmol), and benzyl chloride (106 μL, 0.92 mmol) according to GP2; yield: 200 mg (92%); white solid; mp 161–162 °C.

IR (ATR): 3136, 3064, 3022, 2940, 1719, 1494, 1447, 1378, 1045, 740, 713, 691 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.65 (s, 2 H, SCH_2), 5.40 (s, 2 H, NCH_2), 5.53 (s, 2 H, NCH_2Ph), 5.56 (s, 2 H, NCH_2Ph), 7.16–7.22 (m, 2 H, ArH), 7.24–7.36 (m, 10 H, ArH), 7.56–760 (m, 2 H, ArH), 8.12 (s, 1 H, CH, triazole), 8.15 (s, 1 H, CH, triazole).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 27.3 (SCH_2), 39.2 (NCH_2), 53.25 (NCH_2Ph), 53.26 (NCH_2Ph), 110.5 (ArCH), 118.3 (ArCH), 122.2 (ArCH), 122.3 (ArCH), 124.1 (CH, triazole), 124.4 (CH, triazole), 128.28 (2 × ArCH), 128.29 (2 × ArCH), 128.53 (ArCH), 128.56 (ArCH), 129.2 (4 × ArCH), 136.34 (C_{ipso}), 136.37 (C_{ipso}), 136.4 (C_{ipso}, benzimidazole), 142.7 (C_{ipso}, triazole), 143.4 (C_{ipso}, benzimidazole), 143.5 (C_{ipso}, triazole), 150.9 (N=CS).

HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{27}H_{24}N_8S$: 493.1917; found: 493.1913.

1-{[(4-Fluorobenzyl)-1*H*-1,2,3-triazol-4-yl]methyl}-2-{[(1-(4-fluorobenzyl)-1*H*-1,2,3-triazol-4-yl]methylthio}-1*H*-benzimidazole (10)

The title compound was prepared from **3** (100 mg, 0.44 mmol), NaN_3 (60 mg, 0.92 mmol), and 4-fluorobenzyl chloride (110 μL, 0.92 mmol) according to GP2; yield: 200 mg (86%); white solid; mp 174–175 °C.

IR (ATR): 3147, 3127, 3069, 3021, 2979, 1718, 1608, 1509, 1448, 1434, 1378, 1229, 815, 788, 739 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.64 (s, 2 H, SCH_2), 5.39 (s, 2 H, NCH_2), 5.52 (s, 2 H, NCH_2Ar), 5.54 (s, 2 H, NCH_2Ar), 7.12–7.20 (m, 6 H, ArH), 7.29–7.35 (m, 4 H, ArH), 7.56–7.59 (m, 2 H, ArH), 8.11 (s, 1 H, CH, triazole), 8.15 (s, 1 H, CH, triazole).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 27.3 (SCH_2), 39.2 (NCH_2), 52.44 (NCH_2Ar), 52.46 (NCH_2Ar), 110.4 (ArCH), 115.98 (d, $J_{C,F}$ = 21.6 Hz, 2 × ArCH), 116.0 (d, $J_{C,F}$ = 21.6 Hz, 2 × ArCH), 118.2 (ArCH), 122.2 (ArCH), 122.3 (ArCH), 124.1 (CH, triazole), 124.3 (CH, triazole), 130.6 (d, $J_{C,F}$ = 8.4 Hz, 2 × ArCH), 130.64 (d, $J_{C,F}$ = 8.4 Hz, 2 × ArCH), 132.57 (d, $J_{C,F}$ = 3.1 Hz, C_{ipso}), 132.62 (d, $J_{C,F}$ = 3.1 Hz, C_{ipso}), 136.4 (C_{ipso}), 142.7 (C_{ipso}, triazole), 143.4 (C_{ipso}, benzimidazole), 143.5 (C_{ipso}, triazole), 150.9 (N=CS), 162.3 (d, $J_{C,F}$ = 244.3 Hz, FC_{ipso}), 163.3 (d, $J_{C,F}$ = 244.4 Hz, FC_{ipso}).

HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{27}H_{22}F_2N_8S$: 529.1729; found: 529.1728.

1-{[(1-(4-Chlorobenzyl)-1*H*-1,2,3-triazol-4-yl]methyl}-2-{[1-(4-chlorobenzyl)-1*H*-1,2,3-triazol-4-yl]methylthio}-1*H*-benzimidazole (11)

The title compound was prepared from **3** (100 mg, 0.44 mmol), NaN_3 (60 mg, 0.92 mmol), and 4-chlorobenzyl chloride (148 mg, 0.92 mmol) according to GP2; yield: 210 mg (85%); white solid; mp 141–142 °C.

IR (ATR): 3148, 3125, 3065, 3016, 2956, 1716, 1491, 1448, 1434, 1376, 804, 786, 738 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.64 (s, 2 H, SCH_2), 5.40 (s, 2 H, NCH_2), 5.54 (s, 2 H, NCH_2Ar), 5.56 (s, 2 H, NCH_2Ar), 7.16–7.21 (m, 2 H, ArH), 7.26 (d, *J* = 8.8 Hz, 2 H, ArH), 7.28 (d, *J* = 8.8 Hz, 2 H, ArH), 7.37 (d, *J* = 8.7 Hz, 2 H, ArH), 7.40 (d, *J* = 8.7 Hz, 2 H, ArH), 7.56–7.59 (m, 2 H, ArH), 8.12 (s, 1 H, CH, triazole), 8.16 (s, 1 H, CH, triazole).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 27.3 (SCH_2), 39.2 (NCH_2), 52.4 (NCH_2Ar), 52.5 (NCH_2Ar), 110.4 (ArCH), 118.3 (ArCH), 122.2 (ArCH), 122.3 (ArCH), 124.2 (CH, triazole), 124.4 (CH, triazole), 129.14 (2 × ArCH), 129.16 (2 × ArCH), 130.20 (2 × ArCH), 130.24 (2 × ArCH), 133.29 (ClC_{ipso}), 133.34 (ClC_{ipso}), 135.31 (C_{ipso}), 135.36 (C_{ipso}), 136.4 (C_{ipso}, benzimidazole), 142.7 (C_{ipso}, triazole), 143.4 (C_{ipso}), 143.6 (C_{ipso}, triazole), 150.9 (N=CS).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}Cl_2N_8S$: 561.1138; found: 561.1135.

1-{[(4-Bromobenzyl)-1*H*-1,2,3-triazol-4-yl]methyl}-2-{[(1-(4-bromobenzyl)-1*H*-1,2,3-triazol-4-yl]methylthio}-1*H*-benzimidazole (12)

The title compound was prepared from **3** (100 mg, 0.44 mmol), NaN_3 (60 mg, 0.92 mmol), and 4-bromobenzyl bromide (230 mg, 0.92 mmol) according to GP2; yield: 250 mg (87%); white solid; mp 138–139 °C.

IR (ATR): 3148, 3119, 3067, 2988, 2950, 1717, 1488, 1449, 1434, 1377, 1012, 785, 737 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.64 (s, 2 H, SCH_2), 5.40 (s, 2 H, NCH_2), 5.52 (s, 2 H, NCH_2Ar), 5.54 (s, 2 H, NCH_2Ar), 7.16–7.23 (m, 6 H, ArH), 7.50 (d, *J* = 8.6 Hz, 2 H, ArH), 7.53 (d, *J* = 8.6 Hz, 2 H, ArH), 7.56–7.59 (m, 2 H, ArH), 8.12 (s, 1 H, CH, triazole), 8.16 (s, 1 H, CH, triazole).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 27.3 (SCH_2), 39.2 (NCH_2), 52.49 (NCH_2Ar), 52.52 (NCH_2Ar), 110.4 (ArCH), 118.3 (ArCH), 121.8 (BrC_{ipso}), 121.9 (BrC_{ipso}), 122.2 (ArCH), 122.3 (ArCH), 124.2 (CH, triazole), 124.4 (CH, triazole), 130.51 (2 × ArCH), 130.55 (2 × ArCH), 132.08 (2 × ArCH), 132.09 (2 × ArCH), 135.72 (C_{ipso}), 135.78 (C_{ipso}), 136.4 (C_{ipso}, benzimidazole), 142.7 (C_{ipso}, triazole), 143.3 (C_{ipso}, benzimidazole), 143.6 (C_{ipso}, triazole), 150.9 (N=CS).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}Br_2N_8S$: 649.0128; found: 649.0133.

1-{[(4-Iodobenzyl)-1*H*-1,2,3-triazol-4-yl]methyl}-2-{[(1-(4-iodobenzyl)-1*H*-1,2,3-triazol-4-yl]methylthio}-1*H*-benzimidazole (13)

The title compound was prepared from **3** (100 mg, 0.44 mmol), NaN_3 (60 mg, 0.92 mmol), and 4-iodobenzyl bromide (273 mg, 0.92 mmol) according to GP2; yield: 290 mg (89%); white solid; mp 135–136 °C.

IR (ATR): 3123, 3063, 2958, 2930, 1717, 1485, 1448, 1433, 1009, 779, 735 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.63 (s, 2 H, SCH_2), 5.39 (s, 2 H, NCH_2), 5.49 (s, 2 H, NCH_2Ar), 5.51 (s, 2 H, NCH_2Ar), 7.04 (d, *J* = 8.6 Hz, 2 H, ArH), 7.06 (d, *J* = 8.6 Hz, 2 H, ArH), 7.16–7.21 (m, 2 H, ArH), 7.55–7.58 (m, 2 H, ArH), 7.67 (d, *J* = 8.5 Hz, 2 H, ArH), 7.70 (d, *J* = 8.5 Hz, 2 H, ArH), 8.10 (s, 1 H, CH triazole), 8.14 (s, 1 H, CH triazole).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 27.3 (SCH_2), 39.2 (NCH_2), 52.65 (NCH_2Ar), 52.67 (NCH_2Ar), 94.81 (IC_{ipso}), 94.87 (IC_{ipso}), 110.4 (ArCH), 118.3 (ArCH), 122.2 (ArCH), 122.3 (ArCH), 124.2 (CH, triazole), 124.4 (CH, triazole), 130.5 (2 × ArCH), 130.6 (2 × ArCH), 136.08 (C_{ipso}), 136.13 (C_{ipso}), 136.3 (C_{ipso}, benzimidazole), 137.94 (2 × ArCH), 137.95 (2 × ArCH), 142.7 (C_{ipso}, triazole), 143.3 (C_{ipso}, benzimidazole), 143.6 (C_{ipso}, triazole), 150.8 (N=CS).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}I_2N_8S$: 744.9850; found: 744.9854.

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