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A mild protocol for efficient preparation of functional molecules containing triazole†

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The construction of a class of novel triazole molecules containing sulfonyl fluoride functionalities was achieved through Cu-catalyzed click chemistry in good to excellent yields. The sulfonyl fluoride moieties were cleaved completely under base conditions to produce *N*-unsubstituted triazoles quantitatively, which provides a strategy to combine SuFEx click chemistry with Cu-catalyzed click chemistry ingeniously.

Functionalized triazoles as core motifs are present in numerous biologically active molecules with wide applications in pharmaceuticals, agrochemicals, and other functional materials.[1–4] Many triazole derivatives have been successfully developed as drugs or drug candidates for the treatment of a variety of diseases (Fig. 1). Especially, the discovery and development of CuAAC Click Chemistry in 2001 [5] by Professor K. B. Sharpless. Based on the significance of both sulfonyl fluorides and triazoles, finding a portal to the assembly of molecules bearing both sulfonyl fluoride and triazole moieties would unquestionably increase the chance of identifying drug candidates and significantly contribute to lead compounds optimization.

On the other hand, sulfur(VI) fluoride exchange (SuFEx) has turned into a powerful chemical strategy, attracting increasing attention with wide applications in organic chemistry,[6–8] medicinal chemistry[8–11] and material science[12–14] since the great discovery developed by Professor K. B. Sharpless and coworkers in 2014.[15] The sulfonyl fluoride moiety has been the core of SuFEx methodology, which has drawn wide notice for its preparation. Aliphatic sulfonyl fluorides were a representative class of SuFEx family. The most famous methods for achieving aliphatic sulfonyl fluorides were mainly divided into two categories. The first involves ethenesulfonyl fluoride (ESF) and its olefin derivatives participated addition reactions, such as michael addition,[16–18] cycloaddition reaction,[19–21] radical addition (Fig. 2a).[22–25] The second category includes transformations of aliphatic sulfonyl fluoride reagents, which also yields aliphatic sulfonyl fluorides (Fig. 2b).[19,26] Because of the great importance of sulfonyl fluorides moieties, the development of efficient and reliable methods to synthesize sulfonyl fluoride containing scaffolds continues to be of great significance, and therefore, extensive investigations have been performed.

Under the inspiration of classic CuAAC[5] strategy and previous work of our group,[27] a series of different substituted 1-bromo-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluorides (BTESFs) **3** were synthesized by different terminal alkynes and aliphatic sulfonyl fluoride reagent **1** [27] (more details see ESI†). As illustrated in Table 1, twenty-six alkynes **2** were smoothly converted to their corresponding BTESFs **3** in good to

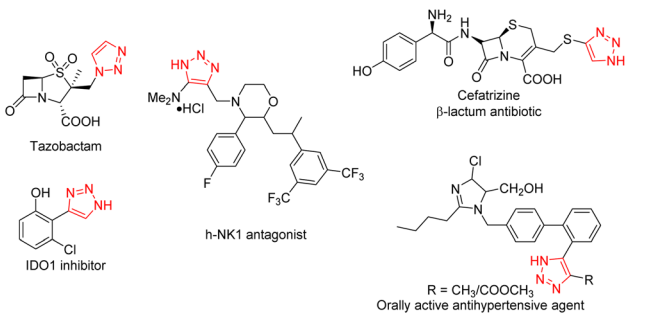

Fig. 1 Representative active molecules or drugs containing triazole.

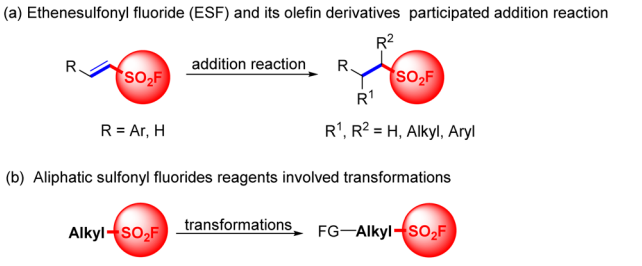

Fig. 2 General synthesis of aliphatic sulfonyl fluorides. (a) Ethenesulfonyl fluoride (ESF) and its olefin derivatives participated addition reaction; (b) aliphatic sulfonyl fluoride reagents involved transformations.

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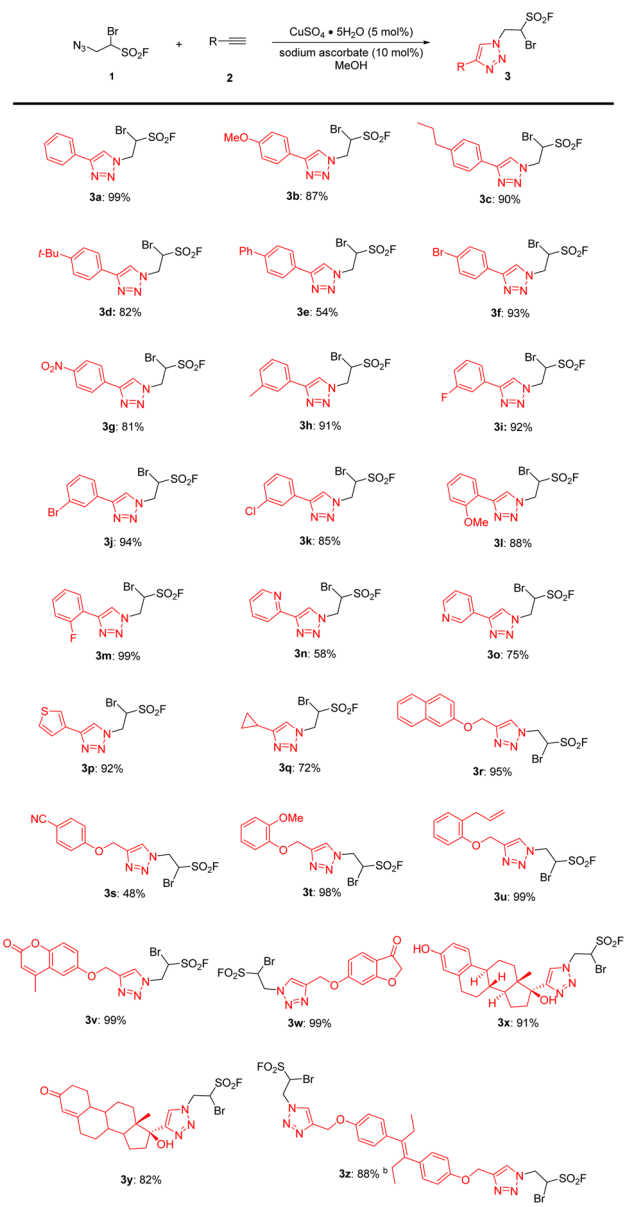
Table 1 Cu(I)-catalyzed cycloaddition for the synthesis of BTESFs **3**[a]



[a] Reaction conditions: $CuSO_4 \cdot 5H_2O$ (5 mol%, 12.5 mg), sodium ascorbate (10 mol%, 19.8 mg), **1** (1 mmol, 232 mg) and **2** (2.0 equiv., 2.0 mmol) were dissolved in MeOH (5 mL) and reacted at room temperature for 12–24 h. [b] **1** (2 mmol, 464 mg) was used.

excellent yields after Cu-catalyzed cycloaddition with azide **1**. For aromatic alkynes, no matter electron-donating groups **2b**, **2c** or electron-withdrawing groups **2f**, **2g** were all compatible. Sterically hindered substrates **2l**, **2m** did not affect the efficiency of cycloaddition. It was worth noting that heterocyclic products **3n–p** were also generated in good yields with either a nitrogen or sulfur atom. In addition, aliphatic alkynes **2q–w** were smoothly transformed into their corresponding triazoles in satisfactory yields. Especially, the alkynes derived from phenols, such as **2t–w** all gave corresponding triazoles in nearly quantitative yields. Natural products ethynyl estradiol **2x** and

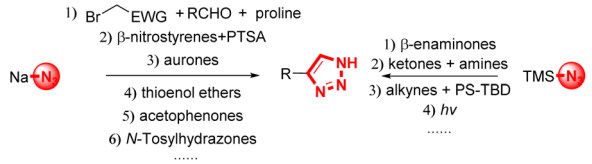


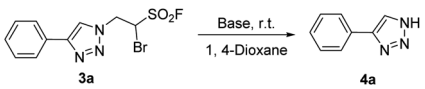
Fig. 3 Synthesis of NH-1,2,3-triazoles.

norethindrone **2y** were applicable to be modified by the cycloaddition with **1** and furnished corresponding BTESFs **3x** and **3y** in 91% and 82% yields respectively. Interestingly, when 2.0 equivalents of azide **1** was used, ditriazole substituted BTESF **3z** was generated in 88% yield after the reaction with the derivative of diethylstilbestrol **2z**.

Meaningfully, NH-1,2,3-triazoles will be obtained by the reaction of BTESFs **3** and base through the elimination step. These *N*-unsubstituted 1,2,3-triazole motifs are ubiquitous in pharmaceutical, agrochemistry and material fields (Fig. 1). And the increasing importance of NH-1,2,3-triazoles has highlighted the development of new synthetic methods for these kinds of compounds. However, most of the reports resulted in *N*-substituted 1,2,3-triazoles,[26] with only a few generating NH-triazoles,[28] which mainly involved sodium azide[29–34] and trimethylsilyl azide ($TMSN_3$)[35–38] participated cycloaddition of alkynes or alkyne precursors[39–43] (Fig. 3). With our designed BTESFs **3** in hand, NH-1,2,3-triazoles were formed facilely with excellent yields.

Afterwards, a simple condition screening was carried out using BTESF **3a** as model starting material to test the formation of 4-phenyl-1*H*-1,2,3-triazole **4a** (Table 2). The desired product **4a** was furnished with a yield of 97% when the reaction was proceeded in the presence of 2 equivalents of pyrrolidine at room temperature for 12 hours in 1,4-dioxane (entry 1). Encouraged by the result, we

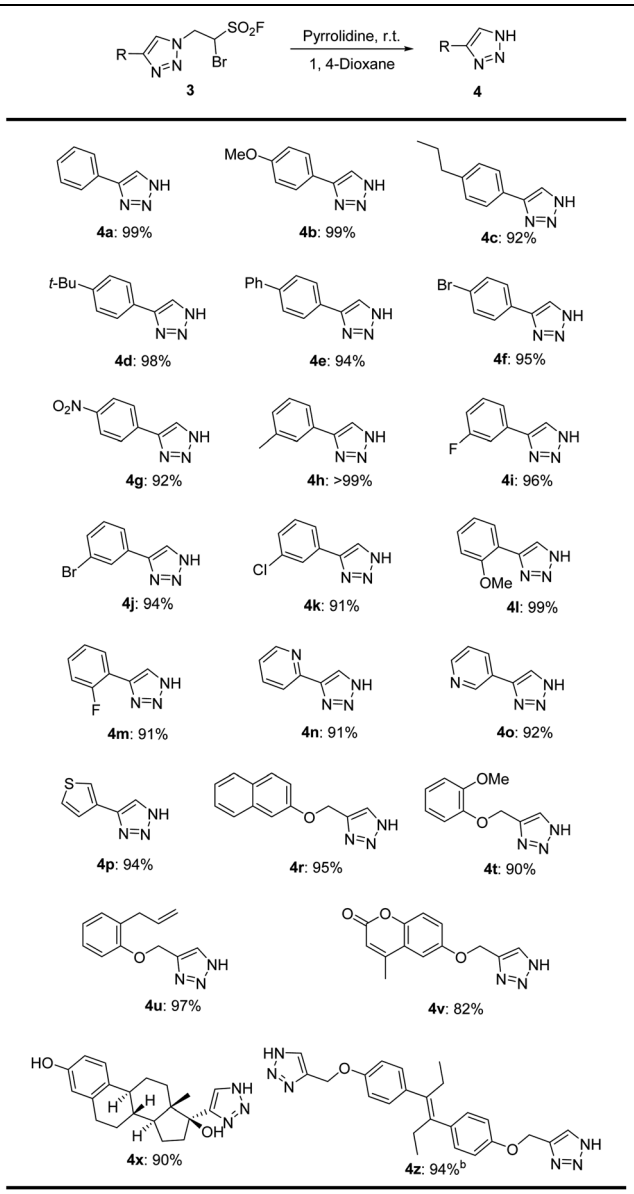
Table 2 Optimization for the synthesis of NH-1,2,3-triazoles **4**[a]



Entry	Base	Yield **4a**[b] (%)
1	Pyrrolidine	97
2	Piperidine	>99
3	Morpholine	84
4	Et_3N	26
5	DBU	23
6	DABCO	10
7	TMG	47
8	TMEDA	6
9	Na_2CO_3	12
10	NaOH	27
11	Cs_2CO_3	33
12	K_2CO_3	24

[a] Reaction condition: **3a** (0.1 mmol, 33.4 mg) and corresponding base (2 eq.) were dissolved in 1,4-dioxane (2 mL) and stirred at room temperature for 12 hours. [b] The yield was determined by HPLC using pure **4a** as external standard [t_{3a} = 2.937 min, λ_{max} = 245.2 nm, CH_3CN/water = 50 : 50 (v/v)].

Table 3 Scope of NH-1,2,3-triazoles 4[a]



[a] Reaction conditions: **3** (0.3 mmol) and pyrrolidine (0.6 mmol, 42.7 mg) were dissolved in 1,4-dioxane (2 mL) and reacted at room temperature for 12 h. [b] Pyrrolidine (1.2 mmol, 85.4 mg) was used.

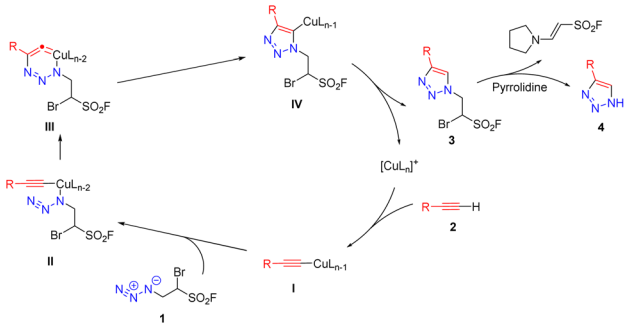


Fig. 4 Proposed mechanism.

further examined other organic and inorganic bases for the promotion of this reaction. The results indicated that secondary amines (entries 2 and 3) were beneficial for the generation of **4a** compared with other tertiary amines (entries 4–8). While inorganic bases such as Na_2CO_3, NaOH, Cs_2CO_3 and K_2CO_3 only provided the desired product in less than 30% yields (entries 9–12). Considering that pyrrolidine is more commercially available than piperidine (entry 2), finally, pyrrolidine was chosen as the suitable base for the synthesis of other NH-1,2,3-triazoles **4**.

With the optimized conditions in hand, we explored the substrate scope and functional-group tolerance for the formation of NH-1,2,3-triazoles from their corresponding BTESFs **3** (Table 3). To our delight, most BTESFs **3** were converted to their desired NH-triazoles in excellent to quantitative yields under the condition of pyrrolidine. 4-Aromatic substituted BTESFs bearing electron-donating (**3b–e**, **3h**, **3l**) or electron-withdrawing (**3f**, **3g**, **3i–k**, **3m**) groups all generated their corresponding triazoles efficiently in excellent yields. 4-Heterocyclic substituted BTESFs (**3n–p**) tolerated well and provided corresponding triazoles **4n**, **4o** and **4p** in 91%, 92% and 94% yields respectively. 4-Phenol derivatives substituted BTESFs were also amenable for the process. 2-Naphthol **3r**, guaiacol **3t**, 2-allylphenol **3u** and coumarin phenol **3v** were converted smoothly to their desired products in good to excellent yields. Especially, the derivative of diethylstilbestrol **3z** generated disubstituted triazole **4z** in 94% yield when treated with 4.0 equivalents of pyrrolidine. Ethynyl estradiol substituted triazole **4x** was also generated with yields of 90%.

A more detailed mechanism was proposed and illustrated in Fig. 4.[44] Initially, the terminal alkyne **2** coordinates with the copper(I) to give the copper(I)-alkyne intermediate **I**; then, the nitrogen atom connected with carbon atom in **1** displaces one of the ligands on the copper(I) alkyne **I** and forms a linkage with copper to form the intermediate **II**; subsequently, the terminal nitrogen atom in **II** attacks the C-2 carbon atom of the alkyne to form an unstable six-membered copper ring **III**. It has been shown that this process is an endothermic process that can form a stable five-membered triazole intermediate **IV** by releasing heat through ring contraction; finally, the intermediate **IV** undergoes hydrolysis and releases triazole product **3** to complete the catalytic cycle. Under the condition of nucleophilic base pyrrolidine,[45] the highly electrophilic sulfonyl fluoride moiety of **3** cleaved subsequently with the generation of NH-1,2,3-triazoles together with byproduct enaminyl sulfonyl fluoride.[27]

Conclusions

In conclusion, a mild method has been developed for the construction of a novel series of triazoles containing sulfonyl fluoride moiety using the sulfonyl fluoride reagent we developed. All compounds are obtained in good to excellent yields mildly. Significantly, the aliphatic sulfonyl fluoride moiety proved sensitive to bases, allowing for smooth transformation into *N*-unsubstituted triazoles under mild conditions. This offers a convenient and efficient protocol for synthesizing

sulfonyl fluorides and triazoles, both of which are versatile functionalities in medicinal discovery. Further studies of these scaffolds in organic chemistry and medicinal chemistry are ongoing in our laboratory.

Experimental section

General procedure for synthesis of 3

An oven-dried round-bottle flask (20 mL) was charged with $CuSO_4 \cdot 5H_2O$ (5 mol%, 12.5 mg), sodium ascorbate (10 mol%, 19.8 mg), alkyne **2** (2 mmol), 2-azido-1-bromoethane-1-sulfonyl fluoride **1** (1 mmol, 232 mg) and 5 mL MeOH. The mixture was stirred at room temperature for 12–24 h with monitoring by TLC. After the reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using ethyl acetate/petroleum ether = 1 : 2 to afford desired product **3**.

General procedure for synthesis of 4

An oven-dried round-bottle flask (10 mL) was charged with **3** (0.3 mmol), pyrrolidine (0.6 mmol, 42.7 mg) and 1,4-dioxane (2 mL). The mixture was stirred at room temperature for 12 h with monitoring by TLC. After the reaction was completed, the solution was concentrated to dryness and the residue was purified through silica gel chromatography using a mixture of ethyl acetate and petroleum ether from 1 : 2 to pure dichloromethane to afford desired product **4**.

1-Bromo-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3a). White solid, 331 mg, 99%. M.p. 162–163 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.66 (s, 1H), 7.85 (d, J = 7.4 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.00–6.97 (m, 1H), 5.47 (dd, J = 15.1, 5.2 Hz, 1H), 5.30 (dd, J = 15.1, 7.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 146.5 (s), 130.2 (s), 129.1 (s), 128.2 (s), 125.3 (s), 122.6 (s), 55.4 (d, J = 18.9 Hz), 50.3 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{10}H_{10}BrFN_3O_2S$ $[M + H]^+$ 333.9656, found 333.9655.

1-Bromo-2-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl) ethane-1-sulfonyl fluoride (3b). 315 mg, 87%. M.p. 131–132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.76 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 5.70–5.67 (m, 1H), 5.34 (dd, J = 14.8, 5.1 Hz, 1H), 4.96 (dd, J = 14.7, 8.4 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 159.2 (s), 146.4 (s), 126.6 (s), 122.8 (s), 121.6 (s), 114.4 (s), 55.4 (d, J = 18.7 Hz), 55.2 (s), 50.2 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 46.8 (s, 1F). ESI-MS HRMS calculated for $C_{11}H_{12}BrFN_3O_2S$ $[M + H]^+$ 363.9761, found 363.9758.

1-Bromo-2-(4-(4-propylphenyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3c). White solid, 338 mg, 90%. M.p. 128–130 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.60 (s, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 6.99–6.97 (m, 1H), 5.46 (dd, J = 15.1, 5.2 Hz, 1H), 5.29 (dd, J = 15.1, 7.6 Hz, 1H), 2.58 (t, J = 7.5 Hz, 2H), 1.65–1.57 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 146.5 (s), 142.3 (s), 129.0 (s), 127.7 (s), 125.2 (s), 122.2 (s), 55.4 (d, J = 18.8 Hz), 50.3 (s), 37.0 (s), 23.9 (s), 13.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{13}H_{16}BrFN_3O_2S$ $[M + H]^+$ 376.0125, found 376.0123.

1-Bromo-2-(4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-1-yl) ethane-1-sulfonyl fluoride (3d). White solid, 318 mg, 82%. M.p. 168–170 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.62 (s, 1H), 7.78 (d, J = 7.1 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 6.99–6.97 (m, 1H), 5.47 (dd, J = 15.1, 5.1 Hz, 1H), 5.30 (dd, J = 15.1, 7.6 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, DMSO) δ 150.7 (s), 146.5 (s), 127.4 (s), 125.7 (s), 125.1 (s), 122.2 (s), 55.4 (d, J = 18.8 Hz), 50.3 (s), 34.4 (s), 31.0 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{14}H_{18}BrFN_3O_2S$ $[M + H]^+$ 390.0282, found 390.0280.

2-(4-([1,1′-Biphenyl]-4-yl)-1*H*-1,2,3-triazol-1-yl)-1-bromoethane-1-sulfonyl fluoride (3e). White solid, 224 mg, 55%. M.p. 195–197 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.72 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 7.3 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.01–6.99 (m, 1H), 5.49 (dd, J = 15.1, 5.2 Hz, 1H), 5.32 (dd, J = 15.1, 7.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 146.1 (s), 139.8 (s), 139.5 (s), 129.3 (s), 129.0 (s), 127.6 (s), 127.3 (s), 126.6 (s), 125.8 (s), 122.7 (s), 55.4 (d, J = 18.9 Hz), 50.3 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{16}H_{14}BrFN_3O_2S$ $[M + H]^+$ 409.9969, found 409.9968.

1-Bromo-2-(4-(4-bromophenyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3f). White solid, 380 mg, 93%. M.p. 132–134 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.71 (s, 1H), 7.82 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 6.98–6.96 (m, 1H), 5.46 (dd, J = 15.2, 5.2 Hz, 1H), 5.31 (dd, J = 15.2, 7.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 145.4 (s), 132.0 (s), 129.4 (s), 127.3 (s), 123.0 (s), 121.2 (s), 55.3 (d, J = 18.9 Hz), 50.4 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{10}H_9Br_2FN_3O_2S$ $[M + H]^+$ 411.8761, found 411.8760.

1-Bromo-2-(4-(4-nitrophenyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3g). White solid, 306 mg, 81%. M.p. 156–157 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.93 (s, 1H), 8.34 (d, J = 8.9 Hz, 2H), 8.14 (t, J = 5.7 Hz, 2H), 7.01–6.98 (m, 1H), 5.51 (dd, J = 15.2, 5.2 Hz, 1H), 5.37 (dd, J = 15.2, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 146.9 (s), 144.5 (s), 136.5 (s), 126.1 (s), 124.8 (s), 124.5 (s), 55.2 (d, J = 19.1 Hz), 50.4 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.2 (s, 1F). ESI-MS HRMS calculated for $C_{10}H_9BrFN_4O_4S$ $[M + H]^+$ 378.9506, found 378.9504.

1-Bromo-2-(4-(*m*-tolyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3h). White solid, 318 mg, 91%. M.p. 127–129 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.63 (s, 1H), 7.68 (s, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 6.99–6.96 (m, 1H), 5.46 (dd, J = 15.1, 5.2 Hz, 1H), 5.30 (dd, J = 15.1, 7.5 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 146.5 (s), 138.2 (s), 130.1 (s), 128.9 (s), 128.8 (s), 125.8 (s), 122.6 (s), 122.4 (s), 55.4 (d, J = 18.9 Hz), 50.3 (s), 21.0 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{11}H_{12}BrFN_3O_2S$ $[M + H]^+$ 347.9812, found 347.9811.

1-Bromo-2-(4-(3-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3i). White solid, 323 mg, 92%. M.p. 116–117 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.74 (s, 1H), 7.71–7.65 (m, 2H), 7.54–7.50 (m, 1H), 7.20 (td, J = 8.6, 2.4 Hz, 1H), 6.98–6.95 (m, 1H), 5.46 (dd, J = 15.2, 5.2 Hz, 1H), 5.31 (dd, J = 15.2, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 162.7 (d, J = 242.2 Hz) 145.4 (d, J = 2.7 Hz), 132.6 (d, J = 8.6 Hz), 131.3(d, J = 8.6 Hz), 123.5

(s), 121.4 (d, J = 2.7 Hz), 115.0 (d, J = 21.1 Hz), 111.9 (d, J = 22.9 Hz), 55.4 (d, J = 18.8 Hz), 50.4 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.2 (s, 1F), −112.0 to −112.1 (m, 1F). ESI-MS HRMS calculated for $C_{10}H_9BrF_2N_3O_2S$ [M + H]$^+$ 351.9561, found 351.9560.

1-Bromo-2-(4-(3-bromophenyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3j). White solid, 384 mg, 94%. M.p. 101–102 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.77 (s, 1H), 8.06 (t, J = 1.6 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.58–7.55 (m, 1H), 7.44 (t, J = 7.9 Hz, 1H), 6.99–6.96 (m, 1H), 5.47 (dd, J = 15.2, 5.2 Hz, 1H), 5.31 (dd, J = 15.2, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 145.0 (s), 132.5 (s), 131.3 (s), 130.9 (s), 127.7 (s), 124.2 (s), 123.5 (s), 122.3 (s), 55.3 (d, J = 18.9 Hz), 50.4 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.2 (s, 1F). ESI-MS HRMS calculated for $C_{10}H_9Br_2FN_3O_2S$ [M + H]$^+$ 411.8761, found 411.8760.

1-Bromo-2-(4-(3-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3k). White solid, 314 mg, 85%. M.p. 117–119 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.77 (s, 1H), 7.91 (t, J = 1.7 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.44–7.42 (m, 1H), 6.98–6.95 (m, 1H), 5.47 (dd, J = 15.2, 5.2 Hz, 1H), 5.32 (dd, J = 15.2, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 145.1 (s), 133.8 (s), 132.3 (s), 131.0 (s), 128.0 (s), 124.8 (s), 123.8 (s), 123.5 (s), 55.3 (d, J = 19.0 Hz), 50.4 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.2 (s, 1F). ESI-MS HRMS calculated for $C_{10}H_9BrClFN_3O_2S$ [M + H]$^+$ 367.9266, found 367.9265.

1-Bromo-2-(4-(2-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl) ethane-1-sulfonyl fluoride (3l). White solid, 322 mg, 88%. M.p. 152–154 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.57 (s, 1H), 8.16 (dd, J = 7.7, 1.7 Hz, 1H), 7.36 (td, J = 7.8, 1.8 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.07 (td, J = 7.6, 1.0 Hz, 1H), 6.98–6.95 (m, 1H), 5.47 (dd, J = 15.0, 5.3 Hz, 1H), 5.31 (dd, J = 15.0, 7.8 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 155.5 (s), 142.2 (s), 129.4 (s), 126.7 (s), 125.2 (s), 120.9 (s), 118.7 (s), 111.8 (s), 55.7 (s), 55.6 (d, J = 18.9 Hz), 50.1 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{11}H_{12}BrFN_3O_3S$ [M + H]$^+$ 363.9761, found 363.9769.

1-Bromo-2-(4-(2-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3m). White solid, 350 mg, 99%. M.p. 132–133 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.61 (d, J = 3.7 Hz, 1H), 8.17 (td, J = 7.6, 1.6 Hz, 1H), 7.46–7.41 (m, 1H), 7.38–7.33 (m, 2H), 7.03–7.00 (m, 1H), 5.53 (dd, J = 15.0, 5.3 Hz, 1H), 5.37 (dd, J = 15.0, 7.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 158.5 (d, J = 247.2 Hz), 139.8 (d, J = 2.4 Hz), 130.0 (d, J = 8.4 Hz), 127.3 (d, J = 3.4 Hz), 125.1 (s), 125.0 (d, J = 9.6 Hz), 117.9 (d, J = 13.0 Hz), 116.1 (d, J = 21.3 Hz), 55.3 (d, J = 18.9 Hz), 50.1 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F), −114.2 to −114.3 (m, 1F). ESI-MS HRMS calculated for $C_{10}H_9BrF_2N_3O_2S$ [M + H]$^+$ 351.9561, found 351.9560.

1-Bromo-2-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3n). White solid, 194 mg, 58%. M.p. 123–124 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.72 (s, 1H), 8.62 (d, J = 4.8 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.91 (td, J = 7.8, 1.7 Hz, 1H), 7.38–7.35 (m, 1H), 7.02–6.99 (m, 1H), 5.52 (dd, J = 15.0, 5.3 Hz, 1H), 5.37 (dd, J = 15.0, 7.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 149.3 (s), 149.0 (s), 146.9 (s), 137.9 (s), 124.7 (s), 123.4 (s), 119.8 (s), 55.3 (d, J = 19.0 Hz), 50.2 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_9H_9BrFN_4O_2S$ [M + H]$^+$ 334.9608, found 334.9605.

1-Bromo-2-(4-(pyridin-3-yl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3o). White solid, 250 mg, 75%. M.p. 133–134 °C. ^{1}H NMR (500 MHz, DMSO) δ 9.08 (d, J = 1.6 Hz, 1H), 8.82 (s, 1H), 8.58 (dd, J = 4.8, 1.5 Hz, 1H), 8.26 (dt, J = 4.8, 1.5 Hz, 1H), 7.53 (dd, J = 8.3, 5.1 Hz, 1H), 7.01–6.98 (m, 1H), 5.50 (dd, J = 15.2, 5.2 Hz, 1H), 5.36 (dd, J = 15.2, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 145.8 (s), 143.1 (s), 142.5 (s), 136.4 (d, J = 3.4 Hz), 127.7 (s), 125.7 (s), 124.3 (s), 55.3 (d, J = 18.9 Hz), 50.5 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.2 (s, 1F). ESI-MS HRMS calculated for $C_9H_9BrFN_4O_2S$ [M + H]$^+$ 334.9608, found 334.9605.

1-Bromo-2-(4-(thiophen-3-yl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3p). White solid, 312 mg, 92%. M.p. 133–134 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.51 (s, 1H), 7.89 (dd, J = 2.9, 1.2 Hz, 1H), 7.66 (dd, J = 5.0, 2.9 Hz, 1H), 7.52 (dd, J = 5.0, 1.2 Hz, 1H), 6.96–6.93 (m, 1H), 5.44 (dd, J = 15.2, 5.2 Hz, 1H), 5.29 (dd, J = 15.2, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 143.1 (s), 131.5 (s), 127.5 (s), 125.8 (s), 122.4 (s), 121.5 (s), 55.5 (d, J = 18.8 Hz), 50.3 (s). ^{19}F NMR (471 MHz, DMSO) δ 46.7 (s, 1F). ESI-MS HRMS calculated for $C_8H_8BrFN_3O_2S_2$ [M + H]$^+$ 339.9220, found 339.9219.

1-Bromo-2-(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3q). White solid, 213 mg, 72%. M.p. 100–101 °C. ^{1}H NMR (500 MHz, DMSO) δ 7.92 (s, 1H), 6.88–6.84 (t, J = 6.4 Hz, 1H), 5.31 (dd, J = 15.1, 5.2 Hz, 1H), 5.14 (dd, J = 15.1, 7.7 Hz, 1H), 2.00–1.94 (m, 1H), 0.94–0.90 (m, 2H), 0.73–0.69 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 149.2 (s), 122.1 (s), 55.5 (d, J = 18.6 Hz), 50.0 (s), 7.7 (s), 6.4 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.0 (s, 1F). ESI-MS HRMS calculated for $C_7H_{10}BrFN_3O_2S$ [M + H]$^+$ 297.9656, found 297.7654.

1-Bromo-2-(4-((naphthalen-2-yloxy)methyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3r). White solid, 394 mg, 95%. M.p. 110–111 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.39 (s, 1H), 7.85–7.81 (m, 3H), 7.50 (d, J = 2.5 Hz, 1H), 7.47 (t, J = 7.0 Hz, 1H), 7.36 (t, J = 7.0 Hz, 1H), 7.20 (dd, J = 8.9, 2.5 Hz, 1H), 6.97–6.94 (m, 1H), 5.45 (dd, J = 15.1, 5.2 Hz, 1H), 5.32–5.27 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 155.9 (s), 142.9 (s), 134.2 (s), 129.4 (s), 128.7 (s), 127.5 (s), 126.8 (s), 126.5 (s), 125.9 (s), 123.8 (s), 118.7 (s), 107.4 (s), 61.1 (s), 55.4 (d, J = 18.9 Hz), 50.1(s). ^{19}F NMR (471 MHz, DMSO) δ 47.0 (s, 1F). ESI-MS HRMS calculated for $C_{14}H_{14}BrFN_3O_3S$ [M + H]$^+$ 413.9918, found 413.9915.

1-Bromo-2-(4-((4-cyanophenoxy)methyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3s). White solid, 186 mg, 48%. M.p. 102–104 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.36 (s, 1H), 7.78 (d, J = 8.9 Hz, 2H), 7.22 (d, J = 8.9 Hz, 2H), 6.95–6.92 (m, 1H), 5.44 (dd, J = 15.1, 5.2 Hz, 1H), 5.31–5.27 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 161.5 (s), 142.3 (s), 134.3 (s), 126.3 (s), 119.2 (s), 116.0 (s), 103.4 (s), 61.4 (s), 55.4 (d, J = 18.9 Hz), 50.2 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{12}H_{11}BrFN_4O_3S$ [M + H]$^+$ 388.9714, found 388.9714.

1-Bromo-2-(4-((2-methoxyphenoxy)methyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3t). White solid, 385 mg, 98%. M.p. 109–110 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.30 (s, 1H), 7.11 (dd, J = 7.9, 1.6 Hz, 1H), 6.98–6.86 (m, 4H), 5.43 (dd, J = 15.1, 5.2 Hz, 1H), 5.28 (dd, J = 15.1, 7.7 Hz, 1H), 5.15 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 149.3 (s), 147.5 (s), 143.2 (s), 125.9 (s), 121.7 (s), 120.7 (s), 114.3 (s), 112.4 (s), 61.8

(s), 55.5 (s), 55.4 (d, J = 16.3 Hz), 50.1 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.0 (s, 1F). ESI-MS HRMS calculated for $C_{12}H_{14}BrFN_3O_4S$ $[M + H]^+$ 393.9876, found 393.9876.

2-(4-((2-Allylphenoxy)methyl)-1*H*-1,2,3-triazol-1-yl)-1-bromoethane-1-sulfonyl fluoride (3u). White solid, 400 mg, 99%. M.p. 60–61 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.19–7.14 (m, 2H), 6.95–6.91 (m, 2H), 6.00–5.92 (m, 1H), 5.70 (dd, J = 8.1, 5.2 Hz, 1H), 5.30 (dd, J = 14.8, 5.1 Hz, 1H), 5.24 (s, 2H), 5.03–5.02 (m, 1H), 5.00 (s, 1H), 4.95 (dd, J = 14.8, 8.2 Hz, 1H), 3.38 (d, J = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8 (s), 145.3 (s), 136.9 (s), 130.2 (s), 129.0 (s), 127.5 (s), 124.3 (s), 121.5 (s), 115.6 (s), 112.0 (s), 62.2 (s), 55.1 (d, J = 22.4 Hz), 51.4 (s), 34.4 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ 46.8 (s, 1F). ESI-MS HRMS calculated for $C_{14}H_{16}BrFN_3O_3S$ $[M + H]^+$ 404.0074, found 404.0073.

1-Bromo-2-(4-(((4-methyl-2-oxo-2*H*-chromen-6-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3v). White solid, 443 mg, 99%. M.p. 178–180 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.35 (s, 1H), 7.36–7.29 (m, 3H), 6.95–6.93 (m, 1H), 6.39 (s, 1H), 5.44 (dd, J = 15.1, 5.2 Hz, 1H), 5.32–5.27 (m, 3H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 156.0 (s), 154.3 (s), 153.1 (s), 147.5 (s), 142.7 (s), 126.0 (s), 120.2 (s), 119.9 (s), 117.6 (s), 114.8 (s), 109.6 (s), 61.6 (s), 55.4 (d, J = 18.8 Hz), 50.1 (s), 18.2 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{15}H_{14}BrFN_3O_5S$ $[M + H]^+$ 445.9816, found 445.9816.

1-Bromo-2-(4-(((3-oxo-2,3-dihydrobenzofuran-6-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3w). White solid, 416 mg, 99%. M.p. 117–118 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.39 (s, 1H), 7.54 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 2.1 Hz, 1H), 6.95–6.92 (m, 1H), 6.76 (dd, J = 8.6, 2.1 Hz, 1H), 5.45 (dd, J = 15.1, 5.2 Hz, 1H), 5.33–5.28 (m, 3H), 4.77 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 197.3 (s), 175.7 (s), 166.3 (s), 142.1 (s), 126.3 (s), 124.8 (s), 114.4 (s), 112.0 (s), 97.8 (s), 75.6 (s), 61.7 (s), 55.4 (d, J = 18.9 Hz), 50.2 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{13}H_{12}BrFN_3O_5S$ $[M + H]^+$ 419.9660, found 419.9660.

1-Bromo-2-(4-((8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3x). White solid, 478 mg, 91%. M.p. 205–206 °C. ^{1}H NMR (500 MHz, DMSO) δ 9.01 (brs, 1H), 7.97 (s, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.92–6.89 (m, 1H), 6.46 (dd, J = 8.3, 2.1 Hz, 1H), 6.42 (s, 1H), 5.38 (dt, J = 14.9, 4.7 Hz, 1H), 5.23 (dd, J = 15.0, 7.5 Hz, 1H), 2.72–2.65 (m, 2H), 2.35–2.30 (m, 1H), 2.08–2.06 (m, 1H), 1.99–1.94 (m, 1H), 1.83–1.82 (m, 2H), 1.77–1.72 (m, 1H), 1.65–1.58 (m, 1H), 1.49–1.15 (m, 6H), 0.92 (s, 3H), 0.63–0.59 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 154.9 (s), 154.5 (d, J = 4.4 Hz), 137.3 (s), 130.5 (s), 126.1 (s), 124.0 (d, J = 7.8 Hz), 115.0 (s), 112.8 (s), 81.2 (s), 55.7 (d, J = 18.4 Hz), 55.6 (d, J = 18.4 Hz), 50.0 (d, J = 3.4 Hz), 47.7 (s), 46.9 (s), 43.3 (s), 37.3 (s), 32.5 (s), 29.3 (s), 27.3 (s), 26.2 (s), 23.6 (s), 14.4 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.2 (d, J = 22.8 Hz, 1F). ESI-MS HRMS calculated for $C_{22}H_{28}BrFN_3O_4S$ $[M + H]^+$ 528.0962, found 528.0962.

1-Bromo-2-(4-((13*S*,17*R*)-13-methyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3y). White solid, 414 mg, 82%. M.p. 97–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 6.3 Hz, 1H), 5.79–5.78 (m, 1H), 5.70–5.67 (m, 1H), 5.30–5.23 (m, 1H), 5.00–4.93 (m, 1H), 2.47–2.02 (m, 9H), 1.88–1.86 (m, 2H), 1.71–1.69 (m, 1H), 1.52–1.41 (m, 5H), 1.25–1.16 (m, 2H), 1.06 (s, 3H), 0.64–0.60 (m, 1H), 0.48–0.42 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.0 (s), 166.8 (s), 154.4 (s), 124.7 (s), 123.2 (s), 82.3 (d, J = 11.5 Hz), 55.2 (dd, J = 22.3, 15.8 Hz), 51.5 (s), 49.1 (d, J = 13.2 Hz), 48.3 (s), 47.3 (d, J = 3.5 Hz), 42.6 (s), 41.2 (s), 38.1 (s), 36.6 (s), 35.6 (s), 32.7 (s), 30.9 (s), 26.6 (s), 26.2 (s), 23.7 (d, J = 6.4 Hz), 14.3 (s). ^{19}F NMR (471 MHz, DMSO) δ 46.8 (d, J = 7.5 Hz, 1F). ESI-MS HRMS calculated for $C_{22}H_{30}BrFN_3O_3S$ $[M + H]^+$ 514.1170, found 514.1170.

(*E*)-2,2′-((((Hex-3-ene-3,4-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1*H*-1,2,3-triazole-4,1-diyl))bis(1-bromoethane-1-sulfonyl fluoride) (3z). White solid, 706 mg, 88% (when corresponding alkyne 1 mmol and **1** 2 mmol were used, **3z** was obtained in 88% yield, no **3z′** was obtained). M.p. 206–208 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.34 (s, 2H), 7.13 (d, J = 8.5 Hz, 4H), 7.05 (d, J = 8.6 Hz, 4H), 6.96–6.94 (t, J = 5.3 Hz, 2H), 5.45 (dd, J = 15.1, 5.2 Hz, 2H), 5.30 (dd, J = 15.0, 7.6 Hz, 2H), 5.20 (s, 4H), 2.09 (q, J = 7.4 Hz, 4H), 0.72 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, DMSO) δ 156.6 (s), 143.2 (s), 138.1 (s), 134.6 (s), 129.6 (s), 125.9 (s), 114.5 (s), 61.0 (s), 55.5 (d, J = 18.7 Hz), 50.1 (s), 28.1 (s), 13.3 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 2F). ESI-MS HRMS calculated for $C_{28}H_{31}Br_2F_2N_6O_6S_2$ $[M + H]^+$ 809.0055, found 809.0055.

(*E*)-1-Bromo-2-(4-((4-(4-(prop-2-yn-1-yloxy)phenyl)hex-3-en-3-yl)phenoxy)methyl)-1*H*-1,2,3-triazol-1-yl)ethane-1-sulfonyl fluoride (3z′). White solid, 140 mg, 24% (when corresponding alkyne 1 mmol and **1** 1 mmol were used, corresponding **3z** was obtained in 75% yield (300 mg), and **3z′** was obtained in 24% yield). M.p. 101–102 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.35 (s, 1H), 7.15–7.13 (m, 4H), 7.05 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.96–6.94 (t, J = 5.4 Hz, 1H), 5.45 (dd, J = 15.1, 5.2 Hz, 1H), 5.30 (dd, J = 15.1, 7.6 Hz, 1H), 5.20 (s, 2H), 4.80 (d, J = 2.1 Hz, 2H), 3.55 (s, 1H), 2.08 (q, J = 6.9 Hz, 4H), 0.71 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, DMSO) δ 156.6 (s), 155.8 (s), 143.1 (s), 138.1 (s), 138.0 (s), 134.9 (s), 134.5 (s), 129.52 (s), 129.47 (s), 125.9 (s), 114.5 (s), 114.4 (s), 79.5 (s), 78.2 (s), 61.0 (s), 55.4 (d, J = 16.6 Hz), 55.4 (s), 50.1 (s), 28.1 (s), 13.29(s), 13.27 (s). ^{19}F NMR (471 MHz, DMSO) δ 47.1 (s, 1F). ESI-MS HRMS calculated for $C_{26}H_{28}BrFN_3O_4S$ $[M + H]^+$ 576.0962, found 576.0962.

Note: In the ^{13}C NMR spectrum of **3z′**, theoretically, there should be twenty-six peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.

4-Phenyl-1*H*-1,2,3-triazole (4a).[46] White solid, 43 mg, 99%. ^{1}H NMR (500 MHz, DMSO) δ 14.98 (s, 1H), 8.24 (s, 1H), 7.86 (d, J = 7.3 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.0 Hz, 1H).

4-(4-Methoxyphenyl)-1*H*-1,2,3-triazole (4b).[46] White solid, 52 mg, 99%. ^{1}H NMR (500 MHz, DMSO) δ 14.83 (s, 1H), 8.14 (s, 1H), 7.79 (d, J = 7.9 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 3.79 (s, 3H).

4-(4-Propylphenyl)-1*H*-1,2,3-triazole (4c).[47] White solid, 52 mg, 92%. ^{1}H NMR (500 MHz, DMSO) δ 14.90 (s, 1H), 8.20 (s, 1H), 7.76 (d, J = 7.1 Hz, 2H), 7.26 (d, J = 7.3 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 1.64–1.56 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

4-(4-(*tert*-Butyl)phenyl)-1*H*-1,2,3-triazole (4d).[48] White solid, 59 mg, 98%. ^{1}H NMR (500 MHz, DMSO) δ 14.90 (s, 1H), 8.19 (s, 1H), 7.78 (d, J = 7.4 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 1.30 (s, 9H).

4-([1,1′-Biphenyl]-4-yl)-1*H*-1,2,3-triazole (4e).[49] White solid, 62 mg, 94%. ^{1}H NMR (500 MHz, DMSO) δ 15.00 (s, 1H), 8.30 (s, 1H), 7.96 (d, J = 7.7 Hz, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.1 Hz, 1H).

4-(4-Bromophenyl)-1*H*-1,2,3-triazole (4f).[50] White solid, 64 mg, 95%. ^{1}H NMR (500 MHz, DMSO) δ 15.07 (s, 1H), 8.30 (s, 1H), 7.83 (d, J = 7.9 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H).

4-(4-Nitrophenyl)-1*H*-1,2,3-triazole (4g).[46] Yellow solid, 52 mg, 92%. ^{1}H NMR (500 MHz, DMSO) δ 15.30 (s, 1H), 8.45 (s, 1H), 8.30 (d, J = 8.6 Hz, 2H), 8.13 (d, J = 8.2 Hz, 2H).

4-(*m*-Tolyl)-1*H*-1,2,3-triazole (4h).[50] White solid, 47 mg, 99%. ^{1}H NMR (500 MHz, DMSO) δ 14.92 (s, 1H), 8.22 (s, 1H), 7.69 (s, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.17 (d, J = 7.3 Hz, 1H), 2.36 (s, 3H).

4-(3-Fluorophenyl)-1*H*-1,2,3-triazole (4i).[51] White solid, 47 mg, 96%. ^{1}H NMR (500 MHz, DMSO) δ 15.08 (s, 1H), 8.34 (s, 1H), 7.93 (s, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.42–7.41 (m, 1H).

4-(3-Bromophenyl)-1*H*-1,2,3-triazole (4j).[46] White solid, 63 mg, 94%. ^{1}H NMR (500 MHz, DMSO) δ 15.12 (s, 1H), 8.34 (s, 1H), 8.07 (s, 1H), 7.89 (d, J = 7.3 Hz, 1H), 7.54–7.53 (m, 1H), 7.42 (t, J = 7.8 Hz, 1H).

4-(3-Chlorophenyl)-1*H*-1,2,3-triazole (4k).[48] White solid, 49 mg, 91%. ^{1}H NMR (500 MHz, DMSO) δ 15.11 (s, 1H), 8.34 (s, 1H), 7.93 (s, 1H), 7.85 (d, J = 7.0 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.41–7.40 (m, 1H).

4-(2-Methoxyphenyl)-1*H*-1,2,3-triazole (4l).[50] White solid, 52 mg, 99%. ^{1}H NMR (500 MHz, DMSO) δ 15.14 (s, 1H), 8.18–8.00 (m, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 8.3 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 3.90 (s, 3H).

4-(2-Fluorophenyl)-1*H*-1,2,3-triazole (4m).[52] White solid, 44 mg, 91%. ^{1}H NMR (500 MHz, DMSO) δ 15.34 (s, 1H), 8.20 (s, 1H), 8.05–8.03 (m, 1H), 7.41–7.39 (m, 1H), 7.35–7.29 (m, 2H).

2-(1*H*-1,2,3-Triazol-4-yl)pyridine (4n).[53] White solid, 40 mg, 91%. ^{1}H NMR (500 MHz, DMSO) δ 15.13 (s, 1H), 8.62–8.62 (m, 1H), 8.25 (s, 1H), 8.05–7.88 (m, 2H), 7.38–7.36 (m, 1H).

3-(1*H*-1,2,3-Triazol-4-yl)pyridine (4o).[46] White solid, 40 mg, 92%. ^{1}H NMR (500 MHz, DMSO) δ 15.16 (s, 1H), 9.09 (s, 1H), 8.69–8.37 (m, 2H), 8.23 (d, J = 7.6 Hz, 1H), 7.50–7.47 (m, 1H).

4-(Thiophen-3-yl)-1*H*-1,2,3-triazole (4p).[48] White solid, 43 mg, 94%. ^{1}H NMR (500 MHz, DMSO) δ 14.88 (s, 1H), 8.12 (s, 1H), 7.89 (s, 1H), 7.64 (s, 1H), 7.54 (d, J = 5.0 Hz, 1H).

4-((Naphthalen-2-yloxy)methyl)-1*H*-1,2,3-triazole (4r). White solid, 64 mg, 95%. M.p. 122–123 °C. ^{1}H NMR (500 MHz, DMSO) δ 14.98 (s, 1H), 7.93 (s, 1H), 7.84–7.81 (m, 3H), 7.50–7.45 (m, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 5.30 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 155.9 (s), 143.0 (s), 134.2 (s), 133.5 (s), 129.4 (s), 128.6 (s), 127.5 (s), 126.7 (s), 126.4 (s), 123.7 (s), 118.7 (s), 107.2 (s), 61.0 (s). ESI-MS HRMS calculated for $C_{13}H_{12}N_3O$ $[M + H]^+$ 226.0975, found 226.0974.

4-((2-Methoxyphenoxy)methyl)-1*H*-1,2,3-triazole (4t). White solid, 55 mg, 90%. M.p. 121–123 °C. ^{1}H NMR (500 MHz, DMSO) δ 14.94 (s, 1H), 7.84 (s, 1H), 7.11–7.09 (m, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.92 (t, J = 7.3 Hz, 1H), 6.89–6.86 (m, 1H), 5.14 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 149.3 (s), 147.5 (s), 143.2 (s), 133.6 (s), 121.5 (s), 120.6 (s), 114.1 (s), 112.3 (s), 61.6 (s), 55.4 (s). ESI-MS HRMS calculated for $C_{10}H_{12}N_3O_2$ $[M + H]^+$ 206.0924, found 206.0922.

4-((2-Allylphenoxy)methyl)-1*H*-1,2,3-triazole (4u). White solid, 62 mg, 97%. M.p. 80–82 °C. ^{1}H NMR (500 MHz, DMSO) δ 14.93 (s, 1H), 7.84 (s, 1H), 7.21–7.18 (m, 1H), 7.12–7.11 (m, 2H), 6.90 (t, J = 7.3 Hz, 1H), 5.96–5.88 (m, 1H), 5.19 (s, 2H), 5.01–4.97 (m, 2H), 3.29 (d, J = 6.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 155.7 (s), 143.4 (s), 136.8 (s), 133.1 (s), 129.6 (s), 128.2 (s), 127.4 (s), 120.8 (s), 115.5 (s), 112.2 (s), 61.4 (s), 33.9 (s). ESI-MS HRMS calculated for $C_{12}H_{14}N_3O$ $[M + H]^+$ 216.1131, found 216.1131.

6-((1*H*-1,2,3-Triazol-4-yl)methoxy)-4-methyl-2*H*-chromen-2-one (4v). White solid, 63 mg, 82%. M.p. 172–173 °C. ^{1}H NMR (500 MHz, DMSO) δ 14.98 (s, 1H), 7.89 (s, 1H), 7.36–7.29 (m, 3H), 6.39 (s, 1H), 5.28 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 159.9 (s), 154.3 (s), 153.0 (s), 147.4 (s), 142.8 (s), 133.5 (s), 120.2 (s), 119.8 (s), 117.5 (s), 114.7 (s), 109.5 (s), 61.7 (s), 18.2 (s). ESI-MS HRMS calculated for $C_{13}H_{12}N_3O_3$ $[M + H]^+$ 258.0873, found 258.0872.

(8*R*,9*S*,13*S*,14*S*,17*S*)-13-Methyl-17-(1*H*-1,2,3-triazol-4-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (4x). White solid, 91 mg, 90%. M.p. 233–235 °C. ^{1}H NMR (500 MHz, DMSO) δ 14.45 (s, 1H), 8.94 (s, 1H), 7.60 (s, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.46 (d, J = 8.3 Hz, 1H), 6.41 (s, 1H), 5.15 (s, 1H), 2.72–2.64 (m, 2H), 2.09–1.75 (m, 6H), 1.51–1.17 (m, 6H), 0.93 (s, 3H), 0.53–0.41 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 154.9 (s), 137.1 (s), 132.5 (s), 130.4 (s), 126.0 (s), 114.9 (s), 112.7(s), 81.1 (s), 50.5 (s), 47.6 (s), 46.7 (s), 43.2 (s), 37.4 (s), 32.7 (s), 29.2 (s), 27.2 (s), 26.0 (s), 23.4 (s), 14.3 (s). ESI-MS HRMS calculated for $C_{20}H_{26}N_3O_2$ $[M + H]^+$ 340.2020, found 340.2020.

(*E*)-4,4′-(((Hex-3-ene-3,4-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1*H*-1,2,3-triazole) (4z). White solid, 121 mg, 94%. M.p. 154–156 °C. ^{1}H NMR (500 MHz, DMSO) δ 14.96 (s, 2H), 7.88 (s, 2H), 7.13 (d, J = 8.6 Hz, 4H), 7.05 (d, J = 8.6 Hz, 4H), 5.19 (s, 4H), 2.09 (q, J = 7.3 Hz, 4H), 0.72 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, DMSO) δ 156.6 (s), 143.2 (s), 138.0 (s), 134.5 (s), 133.4 (s), 129.4 (s), 114.3 (s), 61.0 (s), 28.0 (s), 13.2 (s). ESI-MS HRMS calculated for $C_{24}H_{27}N_6O_2$ $[M + H]^+$ 431.2190, found 431.2189.

Conflicts of interest

There are no conflicts to declare.

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