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Silver-mediated three-component cycloaddition reaction for direct synthesis of 1-N-vinyl-substituted 1,2,3-triazoles

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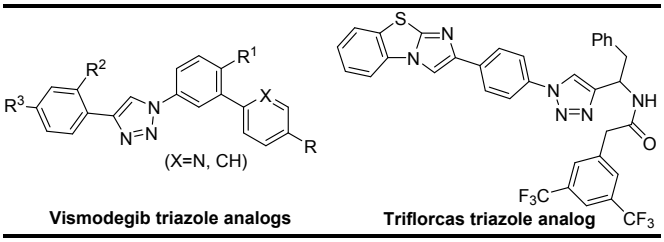
Herein, reported is a direct synthesis of 1-N-vinyl-1,2,3-triazoles via silver-mediated three-component cycloaddition reaction of phenylacetylenes, trimethylsilylazide, and 1,3-dicarbonyl compounds. The synthetic protocol proceeds with operational simplicity, good substrate and functional group compatibility, easily available feedstocks, and no need for pre-installation of vinylazide precursors, which offers a practical way for efficient elaboration of triazole derivatives.

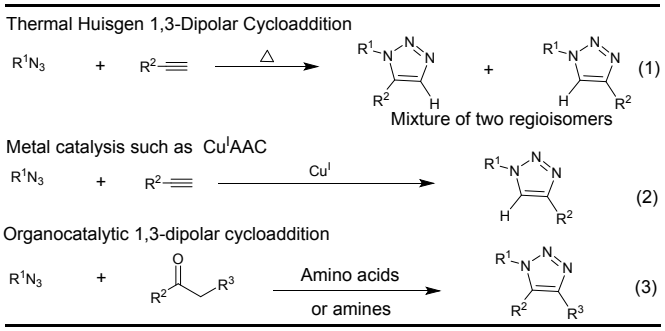
Introduction

1,2,3-Triazole constitutes the core structure of numerous functional products such as the photostabilizers,[1] agrochemicals and medicines.[2] For instance in scheme 1, two triazoles have been utilized as the anticancer agents due to the bioisosteric characterf.[3] In addition, many of the relevant compounds have been employed as specific tumor-targeting vectors, because 1,2,3-triazoles have biosimilarity with amides, including the dipole moment, relative planarity, and amphihydrogen-bonding capability. The replacement of amide units in the backbone of peptides by 1,2,3-triazole isosteres results in peptidomimetics with retained receptor affinity and cell-internalization properties, but enhanced proteolytic stability and tumor-targeting capabilities.



Scheme 1 Two examples of 1,2,3-triazole anticancer agents.

Due to the interesting functions, selective synthesis of 1,2,3-triazole compounds has long been an attractive topic in synthetic organic chemistry. In general, such a purpose is realized by employing the "click chemistry".[4] The first example on the synthesis of 1,2,3-triazoles via thermal 1,3-dipolar cycloaddition reaction was reported by Michael in the late 19th century.[5] In the 1960s, improved synthetic methods on 1,3-dipolar cycloaddition between the organoazides and alkynes have been developed by Huisgen [Scheme 2, eq (1)].[6] Nevertheless, such a reaction generally suffers from poor regioselectivity. Later, the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of organoazides and alkynes (CuAAC) has been demonstrated by the Sharpless group, and it currently becomes one of the most popular methods in the preparation of 1,4-disubstituted 1,2,3-triazoles [Scheme 2, eq (2)].[7] Interestingly, Wang the co-workers have presented an organocatalytic enamide–azide cycloaddition reaction in 2011, which allows the synthesis of 1,4,5-trisubstituted 1,2,3-triazoles under mild conditions.[8] After that, several other organocatalysts, such as amines and amino acids, have also been nicely disclosed in efficient synthesis of substituted 1,2,3-triazoles from organoazides and 1,3-dicarbonyl compounds [Scheme 2, eq (3)].[9]



Scheme 2 Various approaches for the synthesis of 1,2,3-triazoles.

Despite the significant utility the above-described transformations, the synthesis of N-vinyl-1,2,3-triazoles requires a pre-preparation to afford vinyl oganoazides as the key coupling components. Especially, vinyl oganoazides have poor stability, and they can easily undergo the cleavage of N-N, C-N, C=C, and C-C bonds to generate reactive enamine, alkene, methylene, and amide precursors, and lead to some undesired side reactions.[10] In 2013, Bi and co-workers demonstrated an efficient silver-catalyzed synthesis of vinyl azides using ethynyl carbinols. In which, the hydroxy group plays a key role in stabilizng the vinyl azides.[11]

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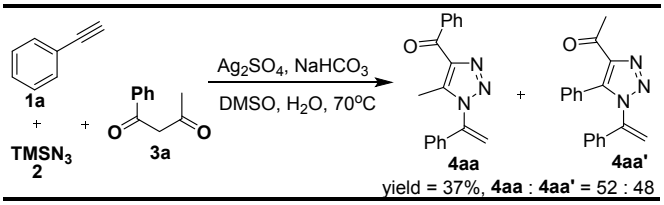
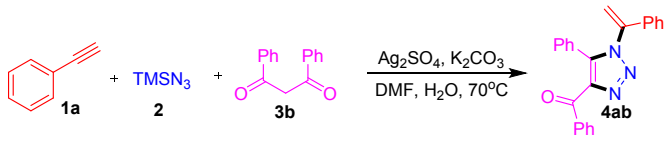
The above information and our sustained effort towards the construction of N-heterocycles[12] motivated us to employ the *in situ* formed vinyl azides as the precursors for the synthesis of N-vinyl 1,2,3-triazoles. Thus, we initially tested the reaction of phenylacetylene **1a**, stable trimethylsilylazide **2**, and 1-phenylbutane-1,3-dione **3a** in the presence of a silver salt. Gratifyingly, when the reaction was performed at 70 °C in aqueous DMF solution with 5 mol% of Ag_2SO_4 and 1 equivalent of $NaHCO_3$, two N-vinyl 1,2,3-triazole regioisomers were detected in 37% combined yield, the ratio of **4aa** and **4aa'** is 52 : 48 (Scheme 3)， and the structure of compound **4aa'** was further confirmed by single-crystal X-ray analysis. Based on the results obtained, we wished herein to report a silver-mediated three-component cycloaddition reaction for direct synthesis of 1-N-vinyl-substituted 1,2,3-triazoles.



Scheme 3 The synthesis of N-vinyl-substituted 1,2,3-triazoles.

Results and discussion

Table 1 Screening of optimal reaction conditions [a]

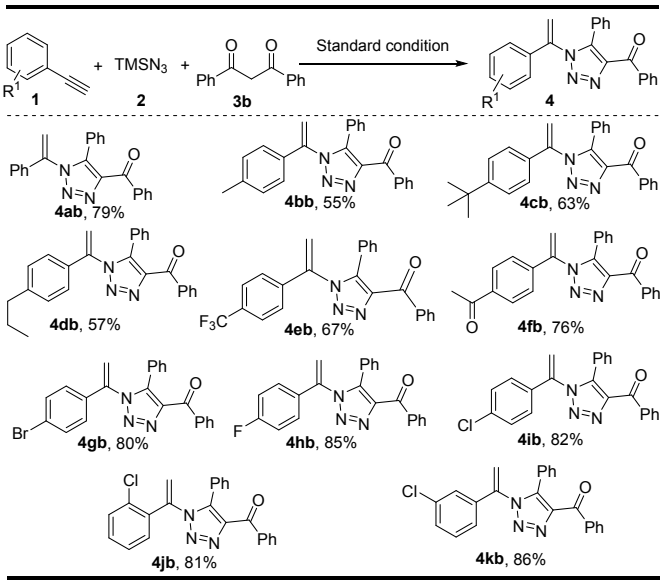


Entry	Catalyst	Solvent	Base	Yield[%][b]
1	Ag_2SO_4	DMF	K_2CO_3	76
2	Ag_2PO_4	DMF	K_2CO_3	12
3	AgOAc	DMF	K_2CO_3	trace
4	$AgSbF_6$	DMF	K_2CO_3	15
5	Ag_2SO_4	DMF	NaH	0
6	Ag_2SO_4	DMF	t-BuONa	47
7	Ag_2SO_4	DMF	$LiOH·H_2O$	0
8	Ag_2SO_4	DMF	$NaHCO_3$	44
9	Ag_2SO_4	1,4-dioxane	K_2CO_3	0
10	Ag_2SO_4	CH_3CN	K_2CO_3	50
11	Ag_2SO_4	toluene	K_2CO_3	0
12	Ag_2SO_4	THF	K_2CO_3	0
13	Ag_2SO_4	DMF	K_2CO_3	75[c]
14	Ag_2SO_4	DMF	K_2CO_3	23[d]
15	Ag_2SO_4	DMF	K_2CO_3	trace[e]
16	-	DMF	K_2CO_3	-
17	Ag_2SO_4	DMF	K_2CO_3	80[f]

[a] Unless otherwise stated, all reactions were carried out under open-to-air conditions at 70 °C for 8 h by using **1a** (0.25 mmol), **2** (0.4 mmol), **3b** (0.25 mmol), catalyst (20 mol%), base (0.25 mmol, 1 equiv), solvent (1 mL), H_2O (0.5 mmol, 2 equiv). [b] yield of isolated product. [c] temperature: 80 °C. [d] temperature: 60 °C. [e] without addition of H_2O. [f] Use of 0.1 mmol K_2CO_3.

Our initial study was focused on formulating an efficient reaction system. Here, we chose the reaction of phenylacetylene **1a**, trimethylsilylazide **2** and dibenzoylmethane **3b** as a model system. First, the reaction was performed at 70 °C for 8 h, several silver catalysts were evaluated (Table 1, entries 1–4). The results showed that Ag_2SO_4 exhibited the best performance in affording product **4ab** in 76% yield (entry 1). The screening of other bases (entries 5–8) and solvents (entries 9–12) showed that they were inferior to K_2CO_3 and DMF, respectively. Then, both increase and decrease of reaction temperature led to diminished product yields (entries 13 and 14). Further, it was found that the absence of H_2O and silver catalyst in the reaction failed to result in the desired product (entries 15 and 16), indicating that both H_2O and the silver catalyst play a crucial role in the reaction. Gratifyingly, the decrease of K_2CO_3 loading to 40 mol% was sufficient to obtain a satisfactory yield (entry 17). Thus, the optimal conditions are as described in entry 17 of Table 1 (standard conditions).

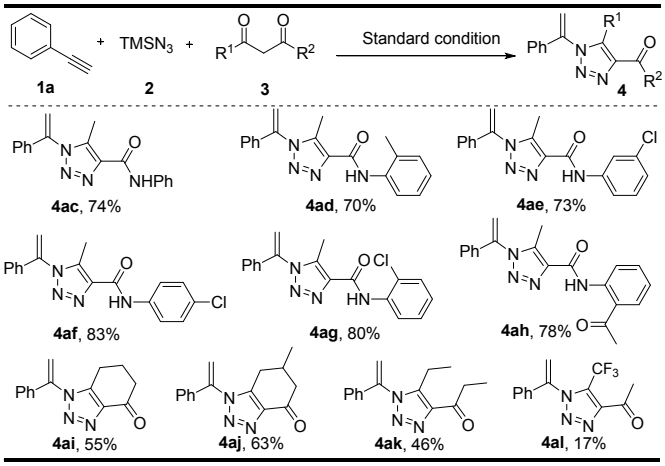
With the optimized reaction conditions in hand, we then tested the substrate scope of the reaction. First, the combination of dibenzoylmethane **3b** with various alkynes **1** was explored. As illustrated in Scheme 4, all the reactions proceeded smoothly and furnished the desired products in moderate to excellent yields upon isolation (**4ab**–**4kb**). Gratifyingly, various functional groups such as alkyl, methoxyl, –F, –Cl, –Br, and $–CF_3$ are well tolerated in the transformation, which would offer the potential for further molecular complexity via the post-functionalization. Noteworthy, it was found that the substituents on the aryl ring of alkynes **1** influenced the product formation to some extent. Especially, reactants **1** bearing an electron-withdrawing group (**4eb**–**4kb**) afforded the products in higher yields than those with an electron-donating substituent (**4ab**–**4db**), presumably because the electron-withdrawing groups can enhance the electron-density of the alkynyl group, thus favoring the formation of alkenyl azides and the subsequen the cyclization process.



Scheme 4 The variation of phenylacetylenes.

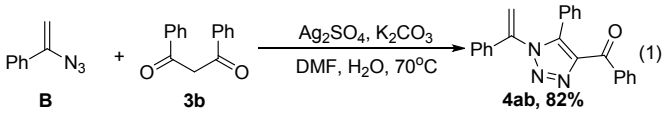
Next, we turned our attention to the variation of 1,3-dicarbonyl compounds **3**. As described in Scheme 5, all the

reactions underwent efficient cyclization to afford the desired products with excellent chemoselectivity. Interestingly, β-carbonyl amides could serve as effective coupling partners to react with phenylacetylene **1a** and azide **2**, affording the 4-carboxamide-containing 1,2,3-triazoles in high yields (**4ac**–**4ah**). The exclusive regioselectivity is attributed to the β-carbonyl group has better reactivity than the amide units. Further, both cyclic and linear 1,3-diketones were also efficiently transformed in combination with **1a** and **2** into the 4-carbonyl-5-alkyl 1,2,3-triazoles in moderate yields (**4ai**–**4al**). The retention of various functional groups on the triazole skeleton can be further applied for the elaboration of complex molecules.

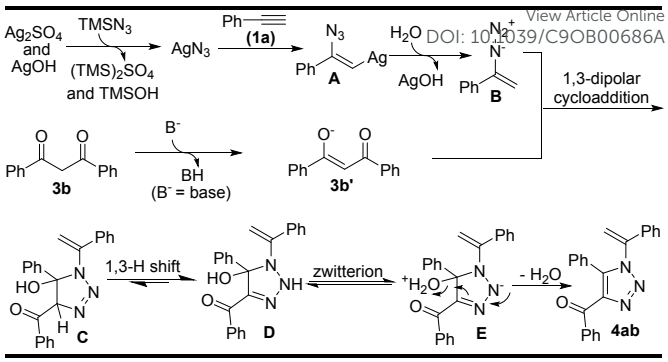


Scheme 5 The variation of 1,3-dicarbonyl substrates.

To gain mechanistic insights into the developed three component cyclization reaction, we have performed a control experiment. The pre-prepared vinylzide **B** was treated with the diketone **3b** under the standard conditions. The reaction produced the 1-N-vinyl-1,2,3-triazole **4ab** in 82% isolated yield [eq (1)], the result supports that the vinylzide **B** generated *in situ* in the reaction serves as a key reaction intermediate.



Based on the above information and the related references,[8] a plausible pathway for the formation of product **4ab** is depicted in Scheme 6. Initially, AgN_3 is generated along with the liberation of $(TMS)_2SO_4$ and TMSOH through anion exchange of $TMSN_3$ with Ag_2SO_4 and AgOH under basic solution.[13a] Then, the vinyl azide **B** is formed via the insertion of AgN_3 into the C-C triple bond of **1a** followed by protodemetalation of vinylsilver species **A** with H_2O. Then, intermediate **B** undergoes 1,3-dipolar cycloaddition with the electron-rich C-C double bond of enolate **3b'** arising from the tautomerization of 1,3-dicarbonyl compound **3b** under basic conditions, which generates the coupling adduct **C**. Further, the 1,3-hydrogen atom shift of **C** would form intermediate **D** or its zwitterion form **E**. Finally, the dehydration-driven aromatization process gives rise to the desired product **4ab**.



Scheme 6. Plausible pathway for the formation of product **4ab**.

Conclusions

In summary, we have developed a silver-mediated three-component cycloaddition reaction of phenyacetylenes, trimethylsilylazide, and 1,3-dicarbonyl compounds, which enables the preparation of various substituted 1-N-vinyl-1,2,3-triazoles in an efficient manner. The synthetic protocol proceeds with good substrate scope, easily available reagents, flexible introduction of different functionalities into the triazole skeleton, and no need for pre-preparation of vinyl azide precursors, which offers a practical way for direct construction of 1-N-vinyl-1,2,3-triazoles. Due to the significant utility of 1,2,3-trizole derivatives, the developed chemistry has the potential to be applied in various fields.

Experimental

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR and infrared spectra (IR). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400 and referenced to 7.26 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartets (q), doublet of doublets (dd), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (J&K Chemic, TCI, Fluka, Acros, SCRC), used without further purification.

General procedure for the synthesis of the product 4

The mixture of alkyne (0.25 mmol), 1,3-dicarbonyl compound (0.25 mmol), trimethylsilylazides (0.4 mmol), K_2CO_3 (0.1 mmol), H_2O (0.5 mmol) and Ag_2SO_4 (0.05 mmol) in DMF (1.5 mL) was stirred at 70 °C for 10 hours in air. After cooling down to room temperature, the resulting mixture was extracting with ethyl acetate, washed with purified water, and then concentrated by removing the solvent under vacuum. Finally,

the residue was purified by preparative TLC on silica, eluting with petroleum ether (60-90 °C) : ethyl acetate (20:1~5:1) to give 1-N-vinyl-substituted 1,2,3-triazole **4**.

Analytical data of the obtained compounds

(5-Methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)(phenyl) methanone **(4aa)**

Yield: 39%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.39 (s, 3H), 7.19 (d, *J* = 6.0 Hz, 2H), 6.07 (s, 1H), 5.64 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.57, 143.34, 141.86, 140.60, 137.46, 134.21, 133.05, 130.73, 130.07, 129.19, 128.38, 25.70, 115.38, 10.37. IR (KBr): 2926, 1651, 1541, 1369, 1264, 1170, 918, 773, 737, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{18}H_{15}N_3NaO$ [M+Na]+: 312.1107; found: 312.1112.

1-(5-Phenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)ethanone **(4aa')**

Yield: 37%, White solid, m.p: 97-98°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 8H), 7.04 (d, *J* = 6.8 Hz, 2H), 5.85 (s, 1H), 5.51 (s, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.87, 143.11, 142.29, 139.97, 134.58, 129.92, 129.67 (d, *J* = 10.3 Hz), 128.69, 128.14, 125.74 (d, *J* = 19.2 Hz), 115.66, 28.41. IR (KBr): 3059, 1690, 1650, 1548, 1486, 1448, 1416, 1285, 1247, 1155, 1025, 950, 917, 821, 770, 693, 614, 546, 505 cm^{-1}. HRMS (ESI): Calcd. for $C_{18}H_{15}N_3NaO$ [M+Na]+: 312.1107; found: 312.1111.

Phenyl(5-phenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)methanone **(4ab)**

Yield: 79%, Clear oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.22 (m, 8H), 7.09 (d, *J* = 7.2 Hz, 2H), 5.88 (s, 1H), 5.58 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.64, 143.22, 142.38, 142.11, 137.23, 134.69, 133.21, 130.80, 129.81, 129.75, 129.63, 128.71, 128.35, 128.22, 126.02, 125.90, 115.68. IR (KBr): 3054, 1660, 1483, 1448, 1257, 1178, 1008, 914, 770, 693 cm^{-1}. HRMS (ESI): Calcd. for $C_{23}H_{18}N_3O$ [M+H]+: 352.1444; found: 352.1445.

Phenyl(5-phenyl-1-(1-(p-tolyl)vinyl)-1*H*-1,2,3-triazol-4-yl)methanone **(4bb)**

Yield: 55%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.24 (m, 5H), 7.02 (dd, *J* = 24.8, 8.4 Hz, 4H), 5.83 (s, 1H), 5.47 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.70, 143.15, 142.27, 142.15, 139.84, 137.26, 133.19, 131.92, 130.80, 129.79, 129.73, 129.43, 128.34, 128.22, 126.07, 125.74, 114.76, 21.23. IR (KBr): 3057, 1660, 1484, 1450, 1420, 1258, 1179, 1009, 920, 823, 745, 695, 527 cm^{-1}. HRMS (ESI): Calcd. for $C_{24}H_{20}N_3O$ [M+H]+: 366.1601; found: 366.1600.

(1-(1-(4-(Tert-butyl)phenyl)vinyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(4cb)**

Yield: 63%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.25 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.82 (s, 1H), 5.44 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.69, 152.96, 143.17, 142.25, 142.19, 137.27, 133.19, 131.94, 130.81, 129.80, 129.74, 128.34, 128.20, 126.17, 125.79, 125.67, 114.63, 34.76, 31.18. IR (KBr): 3058, 2963, 2869, 1660, 1483, 1450, 1259, 1178, 1008, 920, 839, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{27}H_{26}N_3O$ [M+H]+: 408.2070; found: 408.2075.

Phenyl(5-phenyl-1-(1-(4-propylphenyl)vinyl)-1*H*-1,2,3-triazol-4-yl)methanone **(4db)**

Yield: 57%, Pale yellow solid, m.p: 119-120°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.23 (m, 5H), 7.02 (dd, *J* = 19.2, 8.0 Hz, 4H), 5.83 (s, 1H), 5.49 (s, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.58 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.71, 144.57, 143.23, 142.44, 142.17, 137.32, 133.20, 132.24, 130.84, 129.80, 129.76, 128.86, 128.37, 128.21, 126.18, 125.91, 114.66, 37.73, 24.35, 13.71. IR (KBr): 3055, 2952, 2925, 2868, 1655, 1483, 1452, 1418, 1257, 1179, 1007, 918, 831, 744, 695, 504 cm^{-1}. HRMS (ESI): Calcd. for $C_{26}H_{23}N_3NaO$ [M+Na]+: 416.1733; found: 416.1741.

Phenyl(5-phenyl-1-(1-(2-(trifluoromethyl)phenyl)vinyl)-1*H*-1,2,3-triazol-4-yl)methanone **(4eb)**

Yield: 67%, Brown oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 4H), 7.30 – 7.23 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.95 (s, 1H), 5.70 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.41, 143.32, 142.09, 141.18, 138.06, 137.08, 133.28, 131.38 (d, J_{C-F} = 33 Hz), 130.89, 130.74, 130.00, 129.71, 128.35, 126.36, 125.74 (q, J_{C-F} = 4 Hz), 123.69 (d, J_{C-F} = 217 Hz), 119.64, 117.76. ^{19}F NMR (376 MHz, CDCl3) δ -62.93 (s, 3F). IR (KBr): 3067, 2926, 2855, 1658, 1485, 1449, 1416, 1314, 1777, 1128, 1037, 921, 771, 694, 536 cm^{-1}. HRMS (ESI): Calcd. for $C_{24}H_{16}F_3N_3NaO$ [M+Na]+: 442.1138; found: 442.1142.

(1-(1-(4-Methoxyphenyl)vinyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(4fb)**

Yield: 76%, Brown oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.25(m, 5H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.76 (s, 1H), 5.42 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.70, 160.69, 143.19, 142.11, 141.97, 137.29, 133.20, 130.82, 129.82, 129.71, 128,36, 128.24, 127.32, 126.13, 114.15, 113.73, 55.42. IR (KBr): 3068, 1660, 1484, 1450, 1420, 1258, 1179, 1009, 920, 823, 745, 695, 531 cm^{-1}. HRMS (ESI): Calcd. for $C_{24}H_{19}N_3NaO_2$ [M+Na]+: 404.1369; found: 404.1374.

(1-(1-(4-Bromophenyl)vinyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(4gb)**

Yield: 80%, Yellow solid, m.p: 97-98°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.26 (m, 5H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.88 (s, 1H), 5.61 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.50, 143.2, 142.04, 141.41, 137.11, 133.61, 133.27, 131.92, 130.76, 129.98, 129.68, 128.36, 128.34, 127.41, 125.81, 123.92, 116.32. IR (KBr): 3058, 1486, 1449, 1420, 1256, 1179, 1072, 1107, 919, 831, 694, 529 cm^{-1}. HRMS (ESI): Calcd. for $C_{23}H_{16}BrN_3NaO$ [M+Na]+: 452.0369; found: 452.0368.

(1-(1-(4-Fluorophenyl)vinyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(4hb)**

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Yield: 85%, Yellow solid, m.p: 119-120°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.25(m, 5H), 7.15 – 7.02 (m, 2H), 6.92 (t, *J* = 8.4 Hz, 2H), 5.82 (s, 1H), 5.59 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.57, 164.35(d, J_{C-F} = 249 Hz), 143.30, 142.01, 141.47, 137.16, 133.28, 130.95(d, J_{C-F} = 3 Hz), 129.93, 129.70, 128.34 (d, J_{C-F} = 7.5 Hz), 128.00, 127.91, 125.95, 115.83 (d, J_{C-F} = 21 Hz), 115.60. ^{19}F NMR (376 MHz, CDCl3) δ -110.79 (s, 1F). IR (KBr): 2925, 1660, 1492, 1449, 1417, 1256, 1199, 1178, 1009, 920, 834, 772, 695, 530 cm^{-1}. HRMS (ESI): Calcd. for $C_{23}H_{16}FN_3NaO$ [M+Na]+: 392.1170; found: 392.1174.

(1-(1-(4-Chlorophenyl)vinyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(4ib)**

Yield: 82%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.24 (m, 5H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.86 (s, 1H), 5.60 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.51, 143.26, 142.03, 141.36, 137.13, 135.66, 133.27, 133.17, 130.76, 129.97, 129.69, 128.96, 128.36, 128.33, 127.20, 125.84, 116.23. IR (KBr): 2926, 1660, 1601, 1509, 1449, 1257, 1199, 1179, 1009, 919, 841, 773, 746, 695, 542 cm^{-1}. HRMS (ESI): Calcd. for $C_{23}H_{16}ClN_3NaO$ [M+Na]+: 408.0874; found: 408.0879.

(1-(1-(2-Chlorophenyl)vinyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(4jb)**

Yield: 81%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.21 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 2H) , 7.14 – 7.10 (m, 1H), 7.06 – 7.01 (m, 5H), 5.99 (s, 1H), 5.69 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.54, 143.64, 141.26, 140.32, 137.27, 133.33, 133.16, 132.53, 131.24, 130.81, 130.74, 130.45, 130.21, 129.69, 128.33, 128.19, 126.84, 126.27, 118.19. IR (KBr): 2926, 1657, 1503, 1448, 1255, 1201, 1179, 1009, 921, 772, 695 cm^{-1}. HRMS (ESI): Calcd. for $C_{23}H_{16}ClN_3NaO$ [M+Na]+: 408.0874; found: 408.0879.

(1-(1-(3-Chlorophenyl)vinyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(4kb)**

Yield: 86%, White solid, m.p: 133-134°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.20 (m, 6H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.09 (s, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.88 (s, 1H), 5.64 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.57, 143.36, 142.14, 141.23, 137.21, 136.48, 134.87, 133.34, 130.85, 130.07, 130.04, 129.79, 129.73, 128.44,128.40, 126.20, 125.93, 124.21, 116.94. IR (KBr): 2925, 1658, 1597, 1483, 1449, 1420, 1255, 1200, 1179, 1009, 921, 771, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{23}H_{16}ClN_3NaO$ [M+Na]+: 408.0874; found: 408.0873.

5-Methyl-N-phenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole-4-carboxamide **(4ac)**

Yield: 74%, Pale yellow solid, m.p: 79-80°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.36 (m, 5H), 7.18 – 7.16 (m, 3H), 6.05 (s, 1H), 5.62 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.29, 141.96, 138.48, 138.10, 137.77, 134.15, 130.15, 129.22, 125.73, 124.50, 119.96, 115.29, 9.57. IR (KBr): 3058, 2926, 1681, 1598, 1528, 1443, 1312, 1247, 1160, 1057, 980, 913, 883, 774, 755, 693, 587, 509 cm^{-1}. HRMS (ESI): Calcd. for $C_{18}H_{16}N_4NaO$ [M+Na]+: 327.1216; found: 327.1217.

5-Methyl-1-(1-phenylvinyl)-N-(o-tolyl)-1*H*-1,2,3-triazole-4-carboxamide **(4ad)**

Yield: 70%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 6.4 Hz, 3H), 7.26 (m, 2H), 7.18 (d, *J* = 6.4 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.05 (s, 1H), 5.62 (s, 1H), 2.43 (d, *J* = 5.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.29, 142.00, 138.67, 137.97, 135.68, 134.19, 130.65, 130.12, 129.21, 128.68, 126.90, 125.75, 124.98, 122.21, 115.24, 17.87, 9.54. IR (KBr): 2924, 1685, 1611, 1588, 1529, 1456, 1331, 1254, 1160, 887, 775, 755, 696, 627 cm^{-1}. HRMS (ESI): Calcd. for $C_{19}H_{18}N_4NaO$ [M+Na]+: 341.1373; found: 341.1377.

N-(3-chlorophenyl)-5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole-4-carboxamide **(4ae)**

Yield: 73%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.90 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 3H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.18 – 7.12 (m, 3H), 6.06 (s, 1H), 5.62 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.30, 141.91, 138.92, 138.33, 138.18, 134.90, 134.08, 130.18, 130.16, 129.24, 125.71, 124.49, 120.00, 117.84, 115.36, 9.56. IR (KBr): 2926, 1683, 1593, 1522, 1483, 1426, 1274, 1159, 1099, 912, 774, 695, 441 cm^{-1}. HRMS (ESI): Calcd. for $C_{18}H_{15}ClN_4NaO$ [M+Na]+: 361.0827; found: 361.0828.

N-(4-chlorophenyl)-5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole-4-carboxamide **(4af)**

Yield: 83%, Pale yellow solid, m.p: 136-137°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 6.8 Hz, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.05 (s, 1H), 5.61 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.25, 141.90, 138.24, 136.37, 134.08, 130.17, 129.41, 129.23, 129.21, 125.70, 121.14, 115.43, 115.33, 100.08, 9.55. IR (KBr): 2924, 1681, 1593, 1519, 1492, 1401, 1304, 1278, 1239, 1239, 1159, 1091, 1011, 828, 774, 693, 654, 505, 435 cm^{-1}. HRMS (ESI): Calcd. for $C_{18}H_{15}ClN_4NaO$ [M+Na]+: 361.0827; found: 361.0831.

N-(2-chlorophenyl)-5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole-4-carboxamide **(4ag)**

Yield: 80%, Brown solid, m.p: 88-89°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.35 (m, 4H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.05 (s, 1H), 5.63 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.35, 141.94, 138.42, 138.23, 134.68, 134.14, 130.13, 129.38, 129.21, 127.72, 125.74, 124.79, 123.54, 121.48, 115.33, 9.56. IR (KBr): 2924, 2852, 1692, 1590, 1529, 1441, 1304, 1243, 1160, 1050, 1034, 980, 886, 774, 753, 696, 631, 441 cm^{-1}. HRMS (ESI): Calcd. for $C_{18}H_{15}ClN_4NaO$ [M+Na]+: 361.0827; found: 361.0834.

2-Methoxy-N-(1-(5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)vinyl)aniline **(4ah)**

Yield: 78%, Brown oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.50 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 6.8 Hz, 3H), 7.17 (d, *J* = 6.8 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.04 (s, 1H), 5.61 (s, 1H), 3.95 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.24, 148.61, 142.00, 138.90, 137.86, 134.25, 130.06, 129.18, 127.63, 125.74, 124.01, 121.05, 119.87, 115.17, 110.23, 55.90, 9.55. IR (KBr): 2929, 2839, 1681, 1602, 1578, 1462,

1331, 1291, 1252, 1119, 1026, 889, 841, 775, 750, 695, 479 cm^{-1}. HRMS (ESI): Calcd. for $C_{19}H_{18}N_4NaO_2$ [M+Na]+: 357.1322; found: 357.1328.

1-(1-Phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazol-4(5H)-one **(4ai)**

Yield: 55%, Clear oil liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 3H), 7.23 (d, *J* = 7.2 Hz, 2H), 5.88 (s, 1H), 5.71 (s, 1H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.54 (t, *J* = 6.2 Hz, 2H), 2.16 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.29, 145.36, 142.13, 141.84, 134.03, 130.25, 129.25, 126.33, 113.92, 38.30, 23.09, 21.42. IR (KBr): 2961, 2932, 1695, 1631, 1469, 1378, 1124, 1078, 1028, 913, 775, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{14}H_{13}N_3NaO$ [M+Na]+: 262.0951; found: 262.0954.

6-Methyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazol-4(5H)-one **(4aj)**

Yield: 63%, White solid, m.p: 95-96°C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 3H), 7.22 (d, *J* = 7.2 Hz, 2H), 5.89 (s, 1H), 5.69 (s, 1H), 2,68 – 2.60(m, 2H), 2.39 – 2.33 (m, 2H), 2.26 – 2.19(m, 1H), 1.09 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.84, 145.09, 142.06, 141.81, 134.02, 130.28, 129.26, 126.26, 113.96, 46.63, 31.31, 29.09, 20.80. IR (KBr): 2958, 2924, 2873, 2851, 1697, 1634, 1471, 1398, 1306, 1268, 1136, 1088, 1028, 917, 776, 698, 638 cm^{-1}. HRMS (ESI): Calcd. for $C_{15}H_{15}N_3NaO$ [M+Na]+: 276.1107; found: 276.1111.

1-(5-Ethyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)propan-1-one **(4ak)**

Yield: 46%, Clear oil liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.0 Hz, 3H), 7.16 (d, *J* = 6.8 Hz, 2H), 6.06 (s, 1H), 5.58 (s, 1H), 3.25 (q, *J* = 7.2 Hz, 2H), 2.82 (q, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.13, 143.37, 142.63, 141.94, 134.50, 130.05, 129.08, 125.68, 115.34, 33.34, 17.26, 12.64, 7.90. IR (KBr): 2978, 2938, 1686, 1548, 1449, 1277, 1224, 1004, 942, 775, 691 cm^{-1}. HRMS (ESI): Calcd. for $C_{15}H_{17}N_3NaO$ [M+Na]+: 278.1264; found: 278.1260.

2,2,2-trifluoro-1-(5-methyl-1-(1-phenylvinyl)-1H-1,2,3-triazol-4-yl)ethanone **(4al)**

Yield: 17%, Yellow oil liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.11 (s, 1H), 5.65 (s, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.12, 145.45, 142.52, 133.86, 130.32, 129.16, 125.31, 120.21, 117.51, 116.09, 28.53. ^{19}F NMR (376 MHz, CDCl3) δ -57.05 (s, 3F).

Conflicts of interest

There are no conflicts to declare.

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Conflicts of interest

There are no conflicts to declare.

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