# Synthesis of phenylazides and 1-phenyl-1,2,3-triazoles bearing (*E*)-2-halovinyl group

*W. Zhang,[a,b] C. Su,[a] C. Kuang,[a]* and Q. Yang[c]*

*[a]Department of Chemistry, Tongji University,*
*1239 Siping Road, 200092 Shanghai, China.*
*Fax: +86 (21) 659 83191. E-mail: kuangcx@tongji.edu.cn*
*[b]Department of Chemistry, Jiaozuo Teachers College,*
*998 Shanyang Road, 450001 Jiaozuo Henan, China*
*[c]School of Pharmacy, Fudan University,*
*138 Yixueyuan Road, 200032 Shanghai, China.*
*Fax: +86 (21) 542 37692*

Treatment of (*E*)-3-(4-azidophenyl)- and (*E*)-3-(2-azidophenyl)acrylic acid with *N*-halosuccinimides in the presence of LiOAc afforded high yields of phenylazides containing (*E*)-2-halovinyl group. The latter were transformed to different phenyl-1,2,3-triazoles bearing (*E*)-halovinyl group by the $Cu^{I}$-catalyzed reaction of 1,3-dipolar cycloaddition.

**Key words:** phenylazides, 1,2,3-triazoles, (*E*)-vinyl halides, 1,3-dipolar cycloaddition.

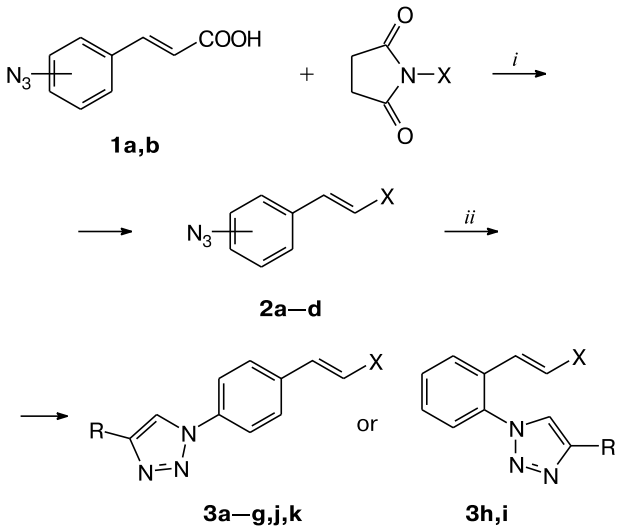
Aromatic azides are versatile synthetic intermediates in organic and bioorganic chemistry.[1] Their use as reactants for the introduction of photoaffinic label of biomolecules is especially important.[2] 1,2,3-Triazoles are widely used as pharmaceutical drugs and agrochemical materials.[3] Discovery of a $Cu^{I}$-catalyzed 1,3-dipolar cycloaddition of azides and terminal alkynes[4] provided further use of 1,2,3-triazoles for bioconjugation, search for medical drugs,[5] in material science,[6] and combinatorial chemistry[7]. In addition, a number of compounds containing 1,2,3-triazole fragment exhibited a wide range of biological activity: antibacterial,[8] herbicide and fungicide,[9] antiallergic,[10] and anti-HIV.[11]

At the same time, (*E*)-vinyl halides are extremely useful building blocks in organic synthesis and serve as vinyl-anion precursors[12] and bridging components in the transition metal catalyzed coupling reactions.[13] This stimulates requirements in the easily available 1,2,3-triazoles bearing (*E*)-halovinyl group, and, consequently, neccessity to develop reliable and efficient methods for the synthesis of phenylazides containing (*E*)-halovinyl group.

In the present work, we describe a simple method developed for the stereoselective synthesis of phenylazides **2** containing (*E*)-halovinyl group from easily available (*E*)-3-(4-azidophenyl)- and (*E*)-3-(2-azidophenyl)acrylic acids **1** (Scheme 1). Phenyl-1,2,3-triazoles **3** bearing (*E*)-halovinyl group were synthesized by the $Cu^{I}$-catalyzed reaction of 1,3-dipolar cycloaddition[4] of the corresponding azides **2** and terminal alkynes in high yields.

We started from the study of the reaction of acid **1a** with NBS. The reaction proceeds in a $MeCN—H_2O$ sol-

**Scheme 1**




**Reagents and conditions:** *i*. LiOAc, $MeCN—H_2O$ (9 : 1, v/v), ~20 or 80 °C. *ii*. R—C≡CH, CuI, sodium ascorbate, DMSO, ~20 °C.

**1:** 4-$N_3$ (**a**), 2-$N_3$ (**b**);
**2:** 4-$N_3$, X = Br (**a**); 2-$N_3$, X = Br (**b**); 4-$N_3$, X = I (**c**); 4-$N_3$, X = Cl (**d**)

| **3** | R | X | **3** | R | X |
|---|---|---|---|---|---|
| **a** | $EtO_2C$ | Br | **g** | 4-$(PhN(Me)SO_2)C_6H_4$ | Br |
| **b** | $HOH_2C$ | Br | **h** | $EtO_2C$ | Br |
| **c** | *n*-$C_5H_{11}$ | Br | **i** | $HOH_2C$ | Br |
| **d** | Ph | Br | **j** | $EtO_2C$ | I |
| **e** | 4-$BrC_6H_4$ | Br | **k** | $EtO_2C$ | Cl |
| **f** | 4-$(PhNHSO_2)C_6H_4$ | Br | | | |

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vent mixture (9 : 1, v/v) with LiOAc as a catalyst to yield phenylazide **2a** in 96% yield (Table 1, entry *1*). Though, the MeCN—$H_2O$ solvent mixture (9 : 1, v/v) has proved the most favorable reaction medium for the stereocontrolled synthesis of (*E*)-arylvinylhalides **2**, a dropwise addition of a solution of NBS in MeCN to the reaction mixture considerably increased efficiency of the reaction. The reaction of acid **1b** with NBS under the same conditions as for acid **1a** also led to compound **2b** in high yield (see Table 1, entry *2*). The reaction of compounds **1a,b** with NBS can be performed at room temperature for only 10 min after addition of NBS to obtain high yields of the corresponding phenylazides **2a,b**, in this case no irradiation with microwaves is required as in the known procedure.[14] However for the reaction of acid **1a** with NIS (NCS) yielding compounds **2c,d** in satisfactory yields, elevated temperature is required (80 °C, 1 h) (see Table 1, entries *3* and *4*).

Further, we considered a $Cu^I$-catalyzed reaction of 1,3-dipolar cycloaddition of phenylazides **2** and terminal alkynes. (*E*)-1-Azido-4-(2-bromovinyl)benzene (**2a**) was chosen as a model reactant in the reaction with ethyl propiolate. The reaction proceeded for 12 h in DMSO at room temperature under nitrogen to form triazole **3a** in 95% yield (Table 2, entry *1*).

Versatility and limitations of this method were thoroughly studied using different alkynes as an example under the same conditions as for the reaction of phenylazide **2a** with ethyl propiolate. Aliphatic alkynes (prop-2-yn-1-ol and hept-1-yne) gave triazoles **3b,c** in 89 and 87% yields, respectively (see Table 2, entries *2* and *3*). Aromatic alkynes (ethynylbenzene and 1-bromo-4-ethynylbenzene) yielded products **3d,e** in 88 and 85% yield, respectively (see Table 2, entries *4* and *5*). This method has proved very efficient even for the sterically hindered aromatic alkynes, such as *N*-phenyl-4-ethynylbenzenesulfonamide and *N*-methyl-*N*-phenyl-4-ethynylbenzenesulfonamide, from which triazoles **3f,g** were obtained in 84 and 82% yields (see Table 2, entries *6* and *7*).

**Table 1.** Synthetic conditions and yields of phenylazides **2a—d**

| Entry | Substrate | *N*-Halosuccinimide | Synthetic conditions[a] | Product[b] | Yield[c] (%) |
|---|---|---|---|---|---|
| *1* | **1a** | NBS | *A* | **2a** | 96 |
| *2* | **1b** | NBS | *A* | **2b** | 93 |
| *3* | **1a** | NIS | *B* | **2c** | 90 |
| *4* | **1a** | NCS | *B* | **2d** | 91 |

[a] *A*: **1** (1.1 mmol), LiOAc (0.2 mmol), MeCN—$H_2O$ solvent mixture (10 mL, 9 : 1, v/v), NBS (1 mmol) in MeCN (5 mL), ~20 °C, 10 min; *B*: **1** (1.1 mmol), LiOAc (0.2 mmol), MeCN—$H_2O$ solvent mixture (10 mL, 9 : 1, v/v), NIS or NCS (1 mmol) in MeCN (5 mL), 80 °C, 1 h.
[b] $E : Z > 99 : 1$ ($^1$H NMR data).
[c] Calculated on *N*-halosuccinimide.

**Table 2.** Synthetic conditions and yields of phenyl-1,2,3-triazoles **3a—k**

| Entry | Azide | R (in R—C≡CH) | Product[a,b] | Yield[c] (%) |
|---|---|---|---|---|
| *1* | **2a** | $EtO_2C$ | **3a** | 95 |
| *2* | **2a** | $HOH_2C$ | **3b** | 89 |
| *3* | **2a** | $n$-$C_5H_{11}$ | **3c** | 87 |
| *4* | **2a** | Ph | **3d** | 88 |
| *5* | **2a** | 4-$BrC_6H_4$ | **3e** | 85 |
| *6* | **2a** | 4-$(PhNHSO_2)C_6H_4$ | **3f** | 84 |
| *7* | **2a** | 4-$(PhN(Me)SO_2)C_6H_4$ | **3g** | 82 |
| *8* | **2b** | $EtO_2C$ | **3h** | 84 |
| *9* | **2b** | $HOH_2C$ | **3i** | 83 |
| *10* | **2c** | $EtO_2C$ | **3j** | 92 |
| *11* | **2d** | $EtO_2C$ | **3k** | 91 |

[a] Reaction conditions: **2** (1 mmol), R—C≡CH (1.05 mmol), DMSO (5 mL), sodium ascorbate (0.15 mmol), CuI (0.15 mmol), $N_2$, ~20 °C, 12 h.
[b] $E : Z > 99 : 1$ ($^1$H NMR data).
[c] Calculated on phenylazide **2**.

We also studied behavior of (*E*)-1-azido-2-(2-bromovinyl)benzene (**2b**) in the reactions with ethyl propiolate and prop-2-yn-1-ol. The same conditions as for **2a** produced compounds **3h,i** in 84 and 83% yields, respectively (see Table 2, entries *8* and *9*).

As we expected, the reaction of ethyl propiolate with compounds **2c,d** led to triazoles **3j,k** in good yields (see Table 2, entries *10* and *11*).

In conclusion, we developed simple method for the synthesis of phenylazides containing (*E*)-halovinyl group under mild conditions and in high yields by the reaction of easily available (*E*)-3-(4-azidophenyl)- and (*E*)-3-(2-azidophenyl)acrylic acids with *N*-halosuccinimides (NBS, NIS, and NCS). In addition, a series of phenyl-1,2,3-triazoles bearing (*E*)-halovinyl group was synthesized by the $Cu^I$-catalyzed reaction of 1,3-dipolar cycloaddition of the corresponding azides and terminal alkynes.

## Experimental

Melting points were determined on a A. Krüss Optronic GmbH KSPII apparatus and uncorrected. IR spectra were obtained on a Nexus FT-IR spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM-300 and Bruker AM-500 spectrometer using $Me_4Si$ as an internal standard. Elemental analysis was performed on a Perkin—Elmer 2400 CHNS elemental analyzer. Commercially available reactants were used as purchased. All the reactions were monitored by TLC on HuanghaiGF 254 plates with silica gel. Column chromatography was performed on silica gel (300—400 mesh) under moderate pressure.

**Synthesis of (*E*)-3-(4-azidophenyl)- and (*E*)-3-(2-azidophenyl)acrylic acids 1a,b.** Zinc powder (3.900 g, 60 mmol) was added to a stirred suspension (100 mL) of 3-(4- or 2-nitro-

phenyl)acrylic acid (5.790 g, 30 mmol) in AcOH—$H_2O$ (9 : 1, v/v) obtained from 4- or 2-nitrobenzaldehyde according to a standard procedure.[15] The reaction mixture was stirred for 0.5 h at ~20 °C and filtered. The filtrate was cooled to 0 °C in an ice bath, followed by a dropwise addition of a solution of sodium nitrite (2.484 g, 36 mmol) in water (20 mL). The mixture was stirred for 10 min at 0 °C, sodium azide (2.340 g, 36 mmol) in water (20 mL) was added dropwise to it. After the reaction was completed, the solvent was evaporated. The combined organic layers were washed with brine (2×100 mL) and cold water (100 mL) and dried with anhydrous $Na_2SO_4$. Crude product was obtained after evaporation of the solvent, which was recrystallized from AcOEt—hexane to give acid **1a** or **1b** as a brown solid residue (90%). **Compound 1a:** m.p. 197.3—197.5 °C (*cf.* Ref. 16: 195—196 °C). **Compound 1b:** m.p. 185.5—186.1 °C (*cf.* Ref. 16: 186 °C).

**Synthesis of phenylazides 2a—d containing (*E*)-halovinyl group (general procedure).** *N*-Halosuccinimide (1 mmol) in MeCN (5 mL) was added dropwise to a stirred suspension of compound **1** (1.1 mmol) in MeCN—$H_2O$ (10 mL, 9 : 1, v/v) and LiOAc (0.2 mmol). After addition of *N*-halosuccinimide was completed, the reaction mixture was stirred for 10 min at ~20 °C (for NBS) or 1 h at 80 °C (for NIS and NCS). The solvent was evaporated. The residue was diluted with AcOEt (30 mL) and filtered. The filtrate was washed with brine (2×30 mL) and cold water (30 mL) and dried with anhydrous $Na_2SO_4$. Crude product was obtained after evaporation of the solvent, which was purified by column chromatography (silica gel, light petroleum) to obtain phenylazide **2a—d**.

**(*E*)-1-Azido-4-(2-bromovinyl)benzene (2a).** Red liquid, $R_f$ 0.85 (light petroleum). Found (%): C, 42.99; H, 2.81; Br, 35.31; N, 18.90. $C_8H_6BrN_3$. Calculated (%): C, 42.88; H, 2.70; Br, 35.66; N, 18.75. $^1$H NMR (500 MHz, $CDCl_3$), δ: 6.66 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 6.91 (d, 2 H, Ar, $J$ = 8.5 Hz); 6.99 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.21 (d, 2 H, Ar, $J$ = 8.5 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 105.28, 118.38, 126.45, 131.77, 135.09, 138.86.

**(*E*)-1-Azido-2-(2-bromovinyl)benzene (2b).** Red liquid, $R_f$ 0.80 (light petroleum). Found (%): C, 43.02; H, 2.85; Br, 35.20; N, 18.93. $C_8H_6BrN_3$. Calculated (%): C, 42.88; H, 2.70; Br, 35.66; N, 18.75. $^1$H NMR (500 MHz, $CDCl_3$), δ: 6.86 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 7.08—7.05 (m, 2 H, Ar); 7.30 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.32—7.34 (m, 2 H, Ar). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 107.76, 117.64, 123.94, 126.39, 128.35, 131.31, 135.86.

**(*E*)-1-Azido-4-(2-iodovinyl)benzene (2c).** Purple liquid, $R_f$ 0.87 (light petroleum). Found (%): C, 35.33; H, 2.06; I, 46.76; N, 15.79. $C_8H_6IN_3$. Calculated (%): C, 35.45; H, 2.23; I, 46.82; N, 15.50. $^1$H NMR (500 MHz, $CDCl_3$), δ: 6.78 (d, 1 H, =C<u>H</u>I, $J$ = = 15.0 Hz); 6.96 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.27 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.37 (d, 1 H, Ar=C<u>H</u>, $J$ = 15.0 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 76.23, 119.27, 127.34, 134.57, 139.93, 143.81.

**(*E*)-1-Azido-4-(2-chlorovinyl)benzene (2d).** Yellow liquid, $R_f$ 0.87 (light petroleum). Found (%): C, 53.65; H, 3.49; Cl, 19.30; N, 23.51. $C_8H_6ClN_3$. Calculated (%): C, 53.50; H, 3.37; Cl, 19.74; N, 23.40. $^1$H NMR (500 MHz, $CDCl_3$), δ: 6.59 (d, 1 H, =C<u>H</u>Cl, $J$ = 14.0 Hz); 6.77 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 6.96 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.21 (d, 2 H, Ar, $J$ = 8.5 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 118.50, 119.36, 127.44, 131.68, 132.22, 139.71.

**Synthesis of triazoles 3a—k (general procedure).** Alkyne (1.05 mmol), sodium ascorbate (0.15 mmol), and CuI (0.15 mmol) were added to a stirred solution of phenylazide **2** (1 mmol) in DMSO (5 mL). The reaction mixture was stirred for 12 h at ~20 °C under nitrogen. The solvent was evaporated. The residue was diluted with AcOEt (30 mL) and filtered. The filtrate was washed with brine (2×30 mL) and cold water (30 mL) and dried with anhydrous $Na_2SO_4$. Crude product was obtained after evaporation of the solvent, which was purified by column chromatography (silica gel, AcOEt—light petroleum) to obtain triazole **3a—k**.

**Ethyl (*E*)-1-[4-(2-bromovinyl)phenyl]-1,2,3-triazole-4-carboxylate (3a).** Light yellow solid product, $R_f$ 0.55 (AcOEt—light petroleum, 1 : 4), m.p. 179.2—179.6 °C. Found (%): C, 48.44; H, 3.73; Br, 24.83; N, 13.02. $C_{13}H_{12}BrN_3O_2$. Calculated (%): C, 48.47; H, 3.75; Br, 24.80; N, 13.04. $^1$H NMR (500 MHz, $CDCl_3$), δ: 1.37 (t, 3 H, $CH_3$, $J$ = 7.0 Hz); 4.40 (q, 2 H, $CH_2$, $J$ = = 7.0 Hz); 6.84 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 7.09 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.42 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.67 (d, 2 H, Ar, $J$ = 8.5 Hz); 8.44 (s, 1 H, N=N-C<u>H</u>=). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 14.31, 61.55, 108.89, 121.06, 125.21, 127.46, 135.56, 135.79, 137.15, 140.97, 160.53.

**(*E*)-{1-[4-(2-Bromovinyl)phenyl]-1,2,3-triazole-4-yl}methanol (3b).** White solid product, $R_f$ 0.48 (AcOEt—light petroleum, 1 : 5), m.p. 166.8—167.2 °C. Found (%): C, 47.11; H, 3.57; Br, 28.56; N, 15.01. $C_{11}H_{10}BrN_3O$. Calculated (%): C, 47.16; H, 3.60; Br, 28.52; N, 15.00. $^1$H NMR (300 MHz, DMSO-$d_6$), δ: 4.71 (s, 2 H, $CH_2$); 7.11 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 7.18 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.56 (d, 2 H, Ar, $J$ = 9.0 Hz); 7.82 (d, 2 H, Ar, $J$ = 9.0 Hz); 8.40 (s, 1 H, —N=N-C<u>H</u>=). $^{13}$C NMR (75 MHz, $CDCl_3$), δ: 55.62, 108.69, 120.30, 120.44, 127.55, 135.78, 135.85, 136.53, 149.49.

**(*E*)-1-[4-(2-Bromovinyl)phenyl]-4-pentyl-1,2,3-triazole (3c).** White solid product, $R_f$ 0.65 (AcOEt—light petroleum, 1 : 5), m.p. 99.6—100.1 °C. Found (%): C, 56.22; H, 5.65; Br, 24.99; N, 13.09. $C_{15}H_{18}BrN_3$. Calculated (%): C, 56.26; H, 5.67; Br, 24.95; N, 13.12. $^1$H NMR (300 MHz, DMSO-$d_6$), δ: 0.91 (t, 3 H, $CH_3$, $J$ = 7.0 Hz); 1.24—1.26 (m, 2 H, $CH_3C\underline{H}_2$); 1.23—1.40 (m, 4 H, $(CH_2)_2$); 1.72—1.77 (m, 2 H, $CH_2$); 2.79 (t, 2 H, $CH_2$, $J$ = 8.0 Hz); 6.86 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 7.17 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.43 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.70 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.71 (s, 1 H, N=N—C<u>H</u>=). $^{13}$C NMR (75 MHz, $CDCl_3$), δ: 13.95, 22.39, 25.60, 29.03, 31.04, 107.96, 118.47, 120.52, 127.24, 135.81, 135.98, 136.76, 149.34.

**(*E*)-1-[4-(2-Bromovinyl)phenyl]-4-phenyl-1,2,3-triazole (3d).** Yellow solid product, m.p. 215.4—216.0 °C, $R_f$ 0.70 (AcOEt—light petroleum, 1 : 4). Found (%): C, 58.89; H, 3.70; Br, 24.56; N, 12.85. $C_{16}H_{12}BrN_3$. Calculated (%): C, 58.91; H, 3.71; Br, 24.50; N, 12.88. $^1$H NMR (500 MHz, $CDCl_3$), δ: 6.90 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 7.16 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.37—7.49 (m, 5 H, Ar); 7.78 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.91 (d, 2 H, Ar, $J$ = 8.5 Hz); 8.19 (s, 1 H, N=N—C<u>H</u>=). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 108.28, 117.25, 120.73, 125.90, 127.38, 128.53, 128.95, 130.89, 135.79, 136.41, 136.57, 146.62.

**(*E*)-1-[4-(2-Bromovinyl)phenyl]-4-(4-bromophenyl)-1,2,3-triazole (3e).** Yellow solid product, $R_f$ 0.50 (AcOEt—light petroleum, 1 : 4), m.p. 206.3—206.9 °C. Found (%): C, 47.40; H, 2.72; Br, 39.56; N, 10.33. $C_{16}H_{11}Br_2N_3$. Calculated (%): C, 47.44; H, 2.74; Br, 39.45; N, 10.37. $^1$H NMR (300 MHz, DMSO-$d_6$), δ: 7.32 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 7.46 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.72 (d, 2 H, Ar, $J$ = 8.1 Hz); 7.75 (d, 2 H, Ar, $J$ = 8.1 Hz); 7.90 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.94 (d, 2 H, Ar, $J$ = 8.5 Hz); 9.38 (s, 1 H, N=N—C<u>H</u>=). $^{13}$C NMR (75 MHz,

$CDCl_3$), δ: 109.41, 120.33, 121.63, 127.53, 127.85, 128.88, 129.81, 131.49, 132.09, 136.18, 136.37, 146.75.

**(*E*)-4-{1-[4-(2-Bromovinyl)phenyl]-1,2,3-triazol-4-yl}-*N*-phenylbenzenesulfonamide (3f).** Yellow solid product, $R_f$ 0.65 (AcOEt—light petroleum, 2 : 3), m.p. 247.2—247.7 °C. Found (%): C, 54.84; H, 3.54; Br, 16.66; N, 11.61. $C_{22}H_{17}BrN_4O_2S$. Calculated (%): C, 54.89; H, 3.56; Br, 16.60; N, 11.64. $^1$H NMR (300 MHz, DMSO-$d_6$), δ: 7.03—7.24 (m, 5 H, Ar); 7.32 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 7.45 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.75 (d, 2 H, Ar, $J$ = 8.7 Hz); 7.87 (d, 2 H, Ar, $J$ = 8.7 Hz); 7.93 (d, 2 H, Ar, $J$ = 8.4 Hz); 8.08 (d, 2 H, Ar, $J$ = 8.4 Hz); 9.43 (s, 1 H, N=N-C<u>H</u>=). $^{13}$C NMR (75 MHz, $CDCl_3$), δ: 110.14, 120.73, 120.81, 121.42, 124.66, 126.23, 128.04, 128.20, 129.61, 134.73, 136.03, 136.31, 136.59, 138.07, 139.28, 146.24.

**(*E*)-4-{1-[4-(2-Bromovinyl)phenyl]-1,2,3-triazol-4-yl}-*N*-methyl-*N*-phenylbenzenesulfonamide (3g).** Light yellow solid product, $R_f$ 0.50 (AcOEt—light petroleum, 1 : 2), m.p. 201.3—201.8 °C. Found (%): C, 55.71; H, 3.79; Br, 16.25; N, 11.27. $C_{23}H_{19}BrN_4O_2S$. Calculated (%): C, 55.76; H, 3.87; Br, 16.13; N, 11.31. $^1$H NMR (500 MHz, $CDCl_3$+ DMSO-$d_6$), δ: 3.25 (s, 3 H, $CH_3$); 6.95 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 7.11—7.12 (m, 2 H, Ar); 7.18 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.29—7.34 (m, 3 H, Ar); 7.52 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.62 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.83 (d, 2 H, Ar, $J$ = 8.5 Hz); 8.04 (d, 2 H, Ar, $J$ = 8.5 Hz); 8.61 (s, 1 H, N=N-C<u>H</u>=). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 29.30, 108.50, 119.33, 120.57, 125.82, 126.52, 127.40, 128.35, 128.87, 134.72, 135.63, 136.18, 136.43, 137.69, 138.17, 141.25, 146.51.

**Ethyl (*E*)-1-[2-(2-bromovinyl)phenyl]-1,2,3-triazole-4-carboxylate (3h).** Brown oil, $R_f$ 0.45 (AcOEt—light petroleum, 1 : 3). Found (%): C, 48.42; H, 3.74; Br, 24.88; N, 13.03. $C_{13}H_{12}BrN_3O_2$. Calculated (%): C, 48.47; H, 3.75; Br, 24.80; N, 13.04. $^1$H NMR (500 MHz, $CDCl_3$), δ: 1.45 (t, 3 H, $CH_3$, $J$ = 7.0 Hz); 4.48 (q, 2 H, $CH_2$, $J$ = 7.0 Hz); 6.84 (s, 2 H, =C<u>H</u>); 7.41 (d, 1 H, Ar, $J$ = 7.5 Hz); 7.50—7.55 (m, 2 H, Ar); 7.61 (d, 1 H, Ar, $J$ = 7.5 Hz); 8.31 (s, 1 H, N=N—C<u>H</u>=). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 14.24, 61.50, 111.30, 126.39, 127.16, 129.20, 129.33, 130.75, 130.96, 131.83, 133.37, 140.45, 160.44.

**(*E*)-{1-[2-(2-Bromovinyl)phenyl]-1,2,3-triazol-4-yl}methanol (3i).** Brown oil, $R_f$ 0.55 (AcOEt—light petroleum, 1 : 2). Found (%): C, 47.12; H, 3.58; Br, 29.08; N, 15.02. $C_{11}H_{10}BrN_3O$. Calculated (%): C, 47.16; H, 3.60; Br, 28.52; N, 15.00. $^1$H NMR (500 MHz, $CDCl_3$), δ: 4.85 (s, 2 H, $CH_2$); 6.72 (d, 1 H, =C<u>H</u>Br, $J$ = 14.0 Hz); 6.81 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.31—7.50 (m, 4 H, Ar); 7.71 (s, 1 H, N=N—C<u>H</u>=). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 56.16, 110.57, 123.99, 126.42, 127.00, 129.09, 130.15, 131.47, 131.64, 134.14, 147.97.

**Ethyl (*E*)-1-[4-(2-iodovinyl)phenyl]-1,2,3-triazole-4-carboxylate (3j).** Light yellow solid product, $R_f$ 0.55 (AcOEt—light petroleum, 1 : 4), m.p. 187.1—187.4 °C. Found (%): C, 42.25; H, 3.26; I, 34.42; N, 11.36. $C_{13}H_{12}IN_3O_2$. Calculated (%): C, 42.30; H, 3.28; I, 34.38; N, 11.38. $^1$H NMR (500 MHz, $CDCl_3$), δ: 1.44 (t, 3 H, $CH_3$, $J$ = 7.0 Hz); 4.47 (q, 2 H, $CH_2$, $J$ = 7.0 Hz); 7.02 (d, 1 H, =C<u>H</u>I, $J$ = 15.0 Hz); 7.47 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.48 (d, 1 H, ArC<u>H</u>=, $J$ = 15.0 Hz); 7.74 (d, 2 H, Ar, $J$ = 8.5 Hz); 8.52 (s, 1 H, N=N—C<u>H</u>=). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 14.28, 61.50, 79.23, 120.91, 125.19, 127.31, 135.77, 138.72, 140.91, 143.22, 160.48.

**Ethyl (*E*)-1-[4-(2-chlorovinyl)phenyl]-1,2,3-triazole-4-carboxylate (3k).** Light yellow solid product, $R_f$ 0.65 (AcOEt—light petroleum, 1 : 4), m.p. 161.3—162.7 °C. Found (%): C, 56.20; H, 4.35; Cl, 12.81; N, 15.10. $C_{13}H_{12}ClN_3O_2$. Calculated (%): C, 56.22; H, 4.36; Cl, 12.77; N, 15.13. $^1$H NMR (500 MHz, $CDCl_3$), δ: 1.44 (t, 3 H, $CH_3$, $J$ = 7.0 Hz); 4.47 (q, 2 H, $CH_2$, $J$ = 7.0 Hz); 6.77 (d, 1 H, =C<u>H</u>Cl, $J$ = 14.0 Hz); 6.88 (d, 1 H, ArC<u>H</u>=, $J$ = 14.0 Hz); 7.48 (d, 2 H, Ar, $J$ = 8.5 Hz); 7.74 (d, 2 H, Ar, $J$ = 8.5 Hz); 8.51 (s, 1 H, N=N—C<u>H</u>=). $^{13}$C NMR (125 MHz, $CDCl_3$), δ: 14.30, 61.52, 120.96, 121.04, 125.21, 127.46, 131.69, 135.72, 136.13, 140.94, 160.52.

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