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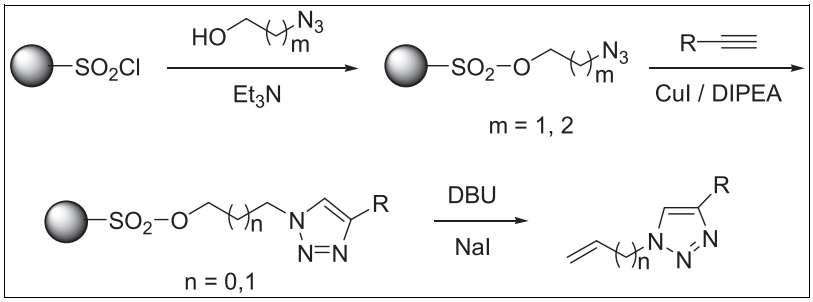

Polymer-supported 2-azidoethyl sulfonate and 3-azidopropyl sulfonate reagents have been developed and applied to the solid-phase organic synthesis of 1-vinyl- and 1-allyl-1,2,3-triazoles, respectively, by CuI-mediated azide-alkyne cycloadditions and subsequent cleavage from the polymer support through elimination reaction promoted by DBU. The advantages of this new synthetic method include simple operation and high yield of the products, as well as good stability of the reagents.

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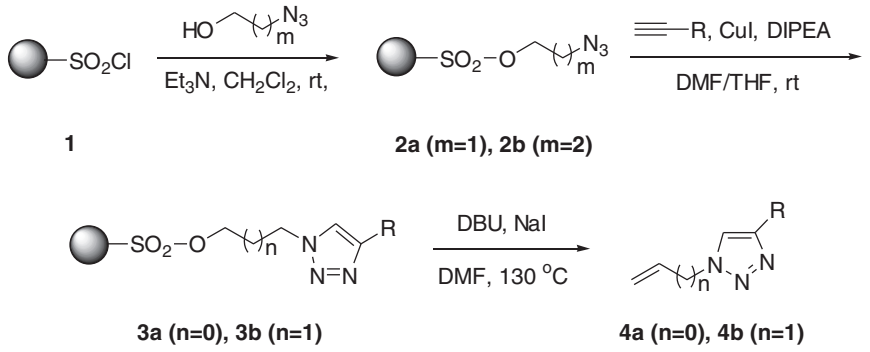
INTRODUCTION

Combinatorial chemistry, together with solid-phase organic synthesis (SPOS) technique, provides an efficient methodology for the high-speed synthesis of structurally diverse compounds for the drug discovery community [1]. The SPOS approach offers the advantages of driving the reaction to completion by the use of excess polymeric reagents and easy isolation of products by filtration from the solid support [2]. Heterocyclic compounds have attracted considerable interest because of their broad range of biological activities. Therefore, an increasing number of pharmaceutically useful heterocyclic compounds have been prepared using SPOS methodologies [3]. 1,2,3-Triazoles, as one of the most useful nitrogen-containing heterocycles [4], have received much attention because of their wide applications in many research fields such as materials, chemical, and biological sciences [5]. Owing to their importance, numerous synthesis approaches for this kind of compounds have been developed [6,7]. However, there are only a paucity of synthetic approaches for 1-vinyl- and 1-ally-1,2,3-triazoles [8]. Although some of these methods are satisfactory in terms of yield, most of the reported methods suffer at least from one of the following disadvantages: the use of expensive catalyst and reagents, tedious experimental procedures, long reaction time, or use of an additional ultrasound irradiation. As a result, a facile preparation of 1-vinyl- and 1-allyl-1,2,3-triazoles for lead discovery is highly desirable. Sulfinate-functionalized resins have been efficiently prepared and utilized in SPOS, and the resulting sulfone linker has been found to be both a robust and a versatile linker [3c,3d]. Previous and recent reports from Kurth and co-workers [9], Lam's research group [10], other laboratories [11], and ours [12] have developed sulfone-linking strategies for SPOS methods to explore sulfone-based chemical transformations. As a part of our ongoing research program focused on the use a versatile traceless sulfone linker in SPOS, we herein have explored an efficient SPOS of 1,4-*N*-vinyl- and 1,4-*N*-allyl- triazoles with the sulfonate linker. To our knowledge, this is a previously unreported method, which is shown in the Scheme 1. Compared with the reported protocols, the advantages of the present method are the use of readily available precursors, easy work-up procedure, simple monitoring technology, and high yields of the products.

RESULTS AND DISCUSSION

Firstly, polymer-supported sulfonyl chloride **1** was prepared from a commercially available 2% cross-linked benzenesulfonic acid resin by treatment it with thionyl chloride in *N*,*N*-dimethylformamide (DMF) according to a literature procedure [13]. The loading of this resin on the basis of chlorine analysis was 4.1 g/mmol. In the presence of triethylamine, 2-azidoethanol or 3-azidopropanol was reacted with sulfonyl chloride resin **1** to afford 2-azidoethyl sulfonate ester resin **2a** and 3-azidopropyl sulfonate ester resin **2b** (>98% yield, determined by elementary analysis of the nitrogen: azide loading = 3.35 mmol/g for **2a** and 3.20 mmol/g for **2b**), respectively, which were monitored

Scheme 1. Solid-phase organic synthesis of 1,4-*N*-vinyl- and 1,4-*N*-allyl- triazoles.



by the infrared absorption band at 1370 cm^{-1} (S–O stretch of $–SO_2C1$) that was shifted near to 1350 cm^{-1} ($–SO_2–O–$), as well as by the appearance of a characteristic azido absorption near 2100 cm^{-1}.

In the next step, [3 + 2] cycloaddition reaction of resin **2** with various terminal alkynes, the key for the success of this protocol, was then investigated. Recently, the advantages of using the "click" chemistry concept and specifically, the Cu(I)-catalyzed alkyne–azide cycloaddition (CuAAC) as a powerful tool in the design and synthesis of 1,4-disubstituted-1*H*-1,2,3-triazoles exclusively have been demonstrated [6,7]. On the basis of these studies, phenyl acetylene was chosen here for the template reaction with resin **2a**, and reaction conditions such as solvents (THF, DMF, and CH_2Cl_2), catalyst ($CuSO_4$/sodium ascorbate or CuI), amount of catalyst, and reaction time were evaluated. After a considerable number of experiments, the 1,3-dipolar cycloaddition of resin **2a** with phenyl acetylene proceeded smoothly in DMF/THF in the presence of diisopropylethyl amine and catalytic amounts of CuI at room temperature for 10 h to afford the 2-triazolylethyl sulfonate resin (**3aa**), which can also be monitored by the IR spectrum conveniently and precisely, in which the characteristic signal of the azido group (2100 cm^{-1}) has been distinctly shrunk after 5 h of reaction time, and then disappeared completely for another 5 h of reaction time.

Finally, the cleavage conditions with bases such as pyridine and DBU in various solvents (MeCN, DMF, THF, and 1,4-dioxane) in different reaction temperature and time were examined, and optimal result was obtained by treating resin **3aa** in DMF with DBU in the presence of NaI at 130°C for 2 h, yielding the corresponding 4-phenyl-1-vinyl-1*H*-1,2,3-triazole (**4aa**) in 86% yield on the basis of the loading of resin **2a** (entry 1, Table 1).

With an optimized CuAAC and base-catalyzed elimination cleavage protocol, the generality of the method were further evaluated using a variety of terminal alkynes with resin **2a** and **2b**, and the corresponding target compounds, 1,4-*N*-vinyl-triazoles (**4aa–4af**), and 1,4-*N*-allyl-triazoles (**4ba–4bf**) were obtained, respectively. As can be observed in Table 1, terminal alkynes including alkyl (entries 1, and 7) and aryl (entries 2–6 and 8–12) alkynes could perform efficiently with good yields (80–87%) of products (**4aa–4bf**).

CONCLUSIONS

In summary, we have developed a facile method for the solid-phase synthesis of 1,4-*N*-vinyl- and 1,4-*N*-allyl-triazoles by Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction of polymer-bound 2-azidoethyl and 3-azidopropyl sulfonate esters with terminal alkynes and subsequent base-promoted elimination reaction, respectively. This method provides a novel access to 1,4-*N*-vinyl- and 1,4-*N*-allyl- triazoles in good yields with simplification of product work-up.

EXPERIMENTAL

Melting points were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer (Bruker Corp., Billerica, MA), using $CDCl_3$ as the solvent and TMS as internal reference. IR spectra were taken on a Perkin-Elmer SP One FTIR spectrophotometer (PerkinElmer, Inc.,

Table 1

Yields of 1,4-*N*-vinyl- and 1,4-*N*-allyl-triazoles (**4aa–4bf**).

Entry	R	Product	Yield[a] (%)
1	C_6H_5	4aa	86
2	n-C_3H_7	4ab	83
3	n-C_4H_9	4ac	84
4	CH_2OH	4ad	80
5	CH_2OCH_3	4ae	86
6	$CO_2C_2H_5$	4af	85
7	C_6H_5	4ba	88
8	n-C_3H_7	4bb	84
9	n-C_4H_9	4bc	83
10	CH_2OH	4bd	80
11	CH_2OCH_3	4be	87
12	$CO_2C_2H_5$	4bf	85

[a]Isolated yields based on the azide loading of the resin **2**.

Waltham, MA). Microanalyses were performed with a Carlo Erba 1106 Elemental Analyzer (Milan, Italy). Used was 2% cross-linked benzenesulfonic acid resin for the preparation of sulfonyl chloride resin according to the reported method [13]. 2-Azidoethanol and 3-Azidopropanol were prepared by reaction of 2-chloroethanol and 3-chloropropanol with sodium azide according to literature procedure, respectively [8f,14]. The other starting materials were purchased from commercial sources and used without further purification. THF was newly stilled from sodium-benzophenone, and DMF was purified by distillation under reduced pressure over calcium hydride prior to use.

Preparation of resin 2. Under a nitrogen atmosphere, to sulfonyl chloride resin **1** (2.0 mmol, 4.1 mmol/g) swelled in CH_2Cl_2 (10 mL) for 1 h were added 2-azidoethanol or 3-azidopropanol (8.0 mmol), and triethylamine (1.1 mL, 8.0 mmol), and the resulting mixture was stirred overnight at room temperature. After this, the resin **2** was collected by filtration and washed successively with CH_2Cl_2 (2 × 10 mL), H_2O (2 × 10 mL), MeOH (2 × 10 mL), and CH_2Cl_2 (2 × 10 mL) and then dried in vacuo to give **2** as pale yellow resin. **2a**: azide loading = 3.35 mmol/g; IR (KBr): ν = 2100 ($-N_3$), 1350 ($-SO_2-O-$) cm^{-1}; **2b**: azide loading = 3.20 mmol/g; IR (KBr): ν = 2102($-N_3$), 1351($-SO_2-O-$)cm^{-1}.

General procedure for the preparation of 1,4-*N*-vinyl- and 1,4-*N*-allyl- triazoles 4. Resin **2** (2.0 mmol) was swelled in THF/DMF (15 mL, 2:1) at room temperature for 30 min under nitrogen. Then alkyne (8.0 mmol), CuI (19.0 mg; 0.1 mmol), and diisopropylethyl amine (1.0 mL, 7.7 mmol) were added, and the mixture was stirred at room temperature. This progression of the reaction was monitored by IR spectroscopy. After disappearance of the signal near 2010 cm^{-1}, the suspension was filtered through the vessel frit, and the resin was washed successively with H_2O (2 × 10 mL), MeOH (2 × 10 mL), and CH_2Cl_2 (2 × 10 mL) and dried in vacuo to give **3**. The resin **3** was then swelled in DMF (15 mL) for 30 min under a nitrogen atmosphere, and NaI (0.9 g, 0.6 mmol) and DBU (0.6 g, 4.0 mmol) were added this suspension mixture, which was heated to 130°C and kept with this temperature for 2 h. Upon completion, the mixture was cooled, and the resin was collected by filtration and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was washed with water (2 × 30 mL), dried over magnesium sulfate, and concentrated to afford products **4aa–4bf**, which were further purified via flash column chromatography eluted with hexane/ethyl acetate for their structure analysis.

4-Phenyl-1-vinyl-1H-1,2,3-triazole (4aa) [8f]. White solid, mp 50–51°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.82–7.70 (m, 2H), 7.62–7.40 (m, 3H), 7.35 (dd, *J* = 15.8, 8.7 Hz, 1H), 5.69 (dd, *J* = 15.8, 1.8 Hz, 1H), 5.15 (dd, *J* = 8.7, 1.8 Hz, 1H); IR (KBr): ν = 3133, 1645, 1460, 1230, 1010, 952, 765, 690 cm^{-1}.

4-Propyl-1-vinyl-1H-1,2,3-triazole (4ab) [8f]. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.23 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.52 (dd, *J* = 16.0, 1.8 Hz, 1H), 5.00 (dd, *J* = 8.0, 1.8 Hz, 1H), 2.68–2.65 (t, *J* = 7.6 Hz, 2H), 1.63–1.60 (m, 2H), 0.94 (t, *J* = 7.3Hz, 3H); IR (film): ν = 3135, 2960, 1648, 1375, 1040, 958, 725 cm^{-1}.

4-Butyl-1-vinyl-1H-1,2,3-triazole (4ac). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.25 (dd, *J* = 15.8, 8.8 Hz, 1H), 5.56 (dd, *J* = 15.8, 1.8 Hz, 1H), 5.03 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.72 (t, *J* = 7.7 Hz, 2H), 1.70–1.60 (m, 2H), 1.44–1.33 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 130.2, 118.3, 103.5, 31.5, 25.4, 22.5, 13.8; IR (film): ν = 3130, 2963, 1647, 1041, 1376, 954, 722 cm^{-1}; *Anal.* Calcd. for $C_8H_{13}N_3$: C, 63.54; H, 8.67; N, 27.79. Found: C, 63.43; H, 8.62; N, 27.86.

4-Hydroxymethyl-1-vinyl-1H-1,2,3-triazole (4ad). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.30 (dd, *J* = 15.6, 8.7 Hz, 1H), 5.52 (dd, *J* = 15.6, 1.6 Hz, 1H), 5.01 (dd, *J* = 8.7, 1.6 Hz, 1H), 4.78 (s, 2H), 2.41 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 130.4, 121.6, 104.5, 56.1; IR (film): ν = 3304, 3060, 2983, 1644, 1146, 1037, 886, 720 cm^{-1}; *Anal.* Calcd. for $C_5H_7N_3O$: C, 47.99; H, 5.64; N, 33.58. Found: C, 47.92; H, 5.57; N, 33.64.

4-Methoxymethyl-1-vinyl-1H-1,2,3-triazole (4ae). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.30–7.28 (m, 1H), 5.52 (dd, *J* = 15.6, 1.6 Hz, 1H), 5.00 (dd, *J* = 8.6, 1.6 Hz, 1H), 4.52 (s, 2H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 130.4, 118.6, 102.6, 65.6, 55.0; IR (film): ν = 3055, 2895, 1644, 2894, 1466, 1368, 1224, 1124, 1079, 1018, 924, 772 cm^{-1}; *Anal.* Calcd. for $C_6H_9N_3O$: C, 51.79; H, 6.52; N, 30.20. Found: C, 61.72; H, 6.48; N, 30.27.

Ethyl 1-vinyl-1H-1,2,3-triazole-4-carboxylate (4af). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.41 (dd, *J* = 16.0, 1.8 Hz, 1H), 5.52 (dd, *J* = 16.0, 1.8 Hz, 1H), 5.21 (dd, *J* = 8.8, 1.8 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 140.5, 130.7, 128.4, 118.2, 61.6, 14.1; IR (film): ν = 3198, 2927, 1725, 1644, 1450, 1378, 1230, 1170, 1085, 1025, 990, 915 cm^{-1}; *Anal.* Calcd. for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.22; H, 5.38; N, 25.22.

1-Allyl-4-phenyl-1H-1,2,3-triazole (4ba) [8a,8b]. White solid, mp 56–57°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.82 (m, 2H), 7.77 (s, 1H), 7.45–7.38 (m, 3H), 6.10–6.08 (m, 1H), 5.41–5.39 (m, 2H), 5.04–5.01 (m, 2H); IR (KBr): ν = 3130, 2972, 1645, 1449, 1240, 1015, 995, 908 cm^{-1}.

1-Allyl-4-propyl-1H-1,2,3-triazole (4bb) [8b]. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 1H), 6.04–6.02 (m, 1H), 5.35–5.31 (m, 2H), 4.98–4.95 (m, 2H), 2.72–2.69 (t, *J* = 7.6 Hz, 2H), 1.71–1.68 (m, 2H), 1.00 (t, *J* = 7.0 Hz, 3H); IR (film): ν = 3129, 2965, 1644, 1368, 1240, 1036, 994, 910 cm^{-1}.

1-Allyl-4-butyl-1H-1,2,3-triazole (4bc) [8b]. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 1H), 6.04–6.01 (m, 1H), 5.33–5.28 (m, 2H), 4.97–4.94 (m, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.68–1.64 (m, 2H), 1.41–1.35 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); IR (film): ν = 3128, 2965, 1645, 1374, 1240, 1040, 998, 910, 725 cm^{-1}.

1-Allyl-4-hydroxymethyl-1H-1,2,3-triazole (4bd) [8b]. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 1H), 6.03–6.01 (m, 1H), 5.34–5.31 (m, 2H), 4.97–4.94 (m, 2H), 4.79 (s, 2H), 2.52 (br s, 1H); IR (film): ν = 3330, 1645, 1572, 1475, 1276, 1038, 992, 922 cm^{-1}; *Anal.* Calcd for $C_6H_9N_3O$: C, 51.79; H, 6.52; N, 30.20. Found: C, 61.71; H, 6.48; N, 30.25.

1-Allyl-4-methoxymethyl-1H-1,2,3-triazole (4be). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 6.05–6.02 (m, 1H), 5.36–5.32 (m, 2H), 4.99–4.96 (m, 2H), 4.50 (s, 2H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 131.0, 120.8, 119.6, 65.5, 54.9, 52.7; IR (film): ν = 3035, 2893, 1645, 1475, 1368, 1254, 1068, 994, 912 cm^{-1}; *Anal.* Calcd for $C_7H_{11}N_3O$: C, 54.89; H, 7.24; N, 27.43. Found: C, 54.83; H, 7.19; N, 27.50.

Ethyl 1-allyl-1H-1,2,3-triazole-4-carboxylate (4bf). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 6.05–6.02 (m, 1H), 5.33–5.31 (m, 2H), 5.00–4.97 (m, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 148.1, 130.5, 121.1, 119.8, 61.2, 50.8, 13.9; IR (flim): ν = 3060, 1726, 1645, 1420, 1270, 1243, 1138, 1025, 995, 910 cm^{-1}; *Anal.* Calcd for $C_8H_{11}N_3O_2$: C, 53.03; H, 6.12; N, 23.19. Found: C, 53.00; H, 6.11; N, 23.26.

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