Liquid-phase synthesis of 4-vinyl-1*H*-1,2,3-triazoles based on polyethylene glycol supported but-3-ynyl sulfonate

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Abstract
An efficient liquid-phase synthesis of 4-vinyl-1*H*-1,2,3-triazole derivatives is developed from soluble polyethylene glycol (PEG) supported but-3-yn-1-yl sulfonate. This procedure affords the target compounds in moderate-to-excellent yields (58–91%) with mild reaction conditions and a facile work-up procedure.

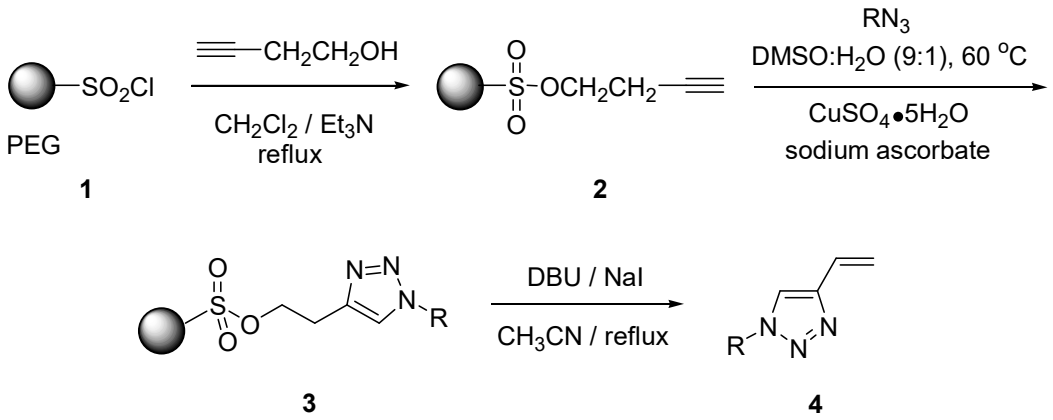
Keywords: Liquid-phase synthesis, 4-vinyl-1*H*-1,2,3-triazoles, PEG-supported but-3-yn-1-yl sulfonate, click chemistry; elimination reaction

Introduction

1,2,3-Triazoles, as an important class of nitrogen-containing heterocycles, have gained great attention and have been applied widely in pharmaceuticals, agrochemicals, dyes, corrosion inhibitors, biochemicals, polymers, and functional materials.[1–3] Since the Sharpless[4] and Meldel[5] groups independently discovered the copper-catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) reaction between azides and terminal alkynes, 'click chemistry' has received growing interest in the regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles. Following this pioneering work, many synthetic methods for producing this ring system have been developed for various purposes.[6–13] Among them, vinyl-substituted 1,2,3-triazoles are useful vinyl monomers, which have been demonstrated to take advantage of the 1,2,3-triazole subunit and combine the features found in classical monomers, such as aromaticity, polarity, and structural diversity inherent in styrenics, vinylpyridines, and acrylates, respectively, into a single building block.[14] There are, however, only a few reports concerning the synthesis of vinyl-substituted 1,2,3-triazoles.[15–19] Even up to now, only a few methods for preparation of some typical vinyl-substituted

1,2,3-triazoles, such as 1-vinyl-5,6-dihydro[1,2,3]triazolo[5,1-*a*]isoquinoline,[20] 1-benzyl-4-vinyl-1*H*-1,2,3-triazole[21] and 5-vinyl-1*H*-1,2,3-triazoles[22] have been described. Therefore, the development of a simple and practical procedure to access vinyl-substituted 1,2,3-triazoles is still highly desirable.

Recently, there has been a considerable growth in interest in the use of soluble polymer-supported catalysts and reagents in organic synthesis because of their low cost, ease of preparation and simple work-up [23, 24] Liquid-phase organic synthesis (LPOS) on soluble polymers combines the advantages of classical homogeneous solution methodology (high reactivity and simple analytical procedures) with those of solid-phase organic synthesis (SPOS) (use of excess reagents, easy isolation and purification of the final products and high stability of the system polymer-supported molecule). Herein, in continuation of our studies on the use polyethylene glycol (PEG) as support in LPOS, [25] we report a novel method for the soluble polymer-supported synthesis of 4-vinyl-1*H*-1,2,3-triazoles from PEG-supported but-3-yn-1-yl sulfonate and azides, involving sequential click and elimination reactions, as depicted in **Scheme 1**.



Scheme 1. PEG supported synthetic route to 4-vinyl-1*H*-1,2,3-triazoles.

Results and Discussion

As shown in **Scheme 1**, treatment of the difunctionalised PEG-sulfonyl chloride (**1**) with but-3-yn-1-ol in dichloromethane in the presence of triethylamine gave rise to the corresponding PEG-supported but-3-yn-1-yl sulfonate (**2**), where the polymer species were easily obtained through precipitation by addition of propan-2-ol to the reaction mixture and then simple filtration. The linking reaction to the PEG support was monitored by the infrared absorption bands at 1371 cm^{-1} (S-O stretch of SO_2C1), which was shifted to 1353 cm^{-1} (-SO_2-O-), as well as by the appearance of a typical carbon–carbon triple bond absorption at 2122 cm^{-1}. Then, the [3+2] cycloaddition reaction conditions of **2** with benzyl azide as a model substrate was investigated. Numerous experimental conditions have been reported to promote the CuAAC reaction.[3,6–8] On the basis of those results, the Cu(I) catalyst generated in situ by reduction of $CuSO_4 \cdot 5H_2O$ was chosen in our

experiment since this method was less costly and was reported to give purer material than some Cu(I) salts that are commercially available. Next, various polar solvents such as *t*-BuOH, DMF and DMSO, and their different combinations, as well as the amount of catalyst, reaction temperature and reaction time, were optimized. After varying the reaction conditions, the 1,3-dipolar cycloaddition of **2** with benzyl azide proceeded smoothly in DMSO/H_2O (9:1) in the presence of catalyst (20 mmol%) at 60 °C for 10 hours to afford the PEG-supported 2-(4-triazolyl)ethyl sulfonate (**3a**). This could also be monitored conveniently by IR spectrometry and precisely, whereby the characteristic absorption of the carbon–carbon triple bond (2122 cm^{-1}) had been distinctly shrunk after 6 h of reaction time, and disappeared completely after a further foyr hours of reaction time.

Table 1. Yields of 4-vinyl-1*H*-1,2,3-triazoles (**4a**–**4k**)

Entry	R	Product	Yield (%)[a]
1	$C_6H_5CH_2$	**4a**	88
2	4-$MeOC_6H_4CH_2$	**4b**	86
3	4-$BrC_6H_4CH_2$	**4c**	83
4	$CH_3(CH_2)_2CH_2$	**4d**	84
5	C_6H_5	**4e**	88
6	4-$MeOC_6H_4$	**4f**	90
7	3-MeC_6H_4	**4g**	91
8	2-MeC_6H_4	**4h**	62
9	2-ClC_6H_4	**4i**	58
10	4-BrC_6H_4	**4j**	86
11	4-$O_2NC_6H_4$	**4k**	85

[a] All yields refer to the isolated products after purification based on **1**.

Upon completion of the optimal click reaction conditions, PEG immobilized intermediate **3a** was separated by simple filtration after addition of diethyl ether to the reaction mixtures. Finally, conditions for cleavage from the PEG support were tested by employing different bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and potassium *t*-butoxide in various polar and non-polar solvents. It was found that the desired product, 1-benzyl-4-vinyl-1*H*-1,2,3-triazole (**4a**) was obtained in 88% isolated yield by treatment of **3a** with NaI/DBU in refluxing acetonitrile for 45 min. The structure of **4a** was confirmed on the basis of its ^1H and ^{13}C NMR spectra. Thus, compound **4a** displayed a characteristic singlet at δ = 7.45 ppm for the triazolyl C-5–H proton, and a singlet signal for the *N*–CH_2 protons appearing at δ = 5.49 ppm. Signals for the vinyl protons as a double doublet were observed at δ = 6.65, 5.85 and 5.30 ppm, respectively. Additionally, the melting point of **4a** was in agreement with the reported value.[21]

To demonstrate further the convenience of this protocol, the substrate scope of various azides was investigated. As exemplified in **Table 1**, reaction with both alkyl azides (**Table 1**, entries 1–

4) and aryl azides (**Table 1**, entries 5–11) proceeded smoothly and the corresponding products **4a**–**4k** were obtained in moderate to excellent yields. Among them, benzylic azides (**Table 1**, entries 1–3) and primary azides (**Table 1**, entry 4) were found to react readily to form the desired triazoles in high yields (83–88%) and aryl azides bearing either electron-donating (**Table 1**, entries 6–8) or electron-withdrawing (**Table 1**, entries 9–11) substituents could also be used efficiently with 58–91% yields. However, it must be pointed out that aryl azides with an electron-donating or electron-withdrawing substituent at an *ortho*-position (**Table 1**, entries 8,9), gave the corresponding triazoles (**4h** and **4i**) in relatively low yields respectively, even when the click reaction time was extended to 24 hours, possibly due to the stereo-hindrance effect of the substituents.

In the ^{1}HNMR spectra of the products **4a**–**4k**, the resonances of the vinyl protons were seen as a double doublet at δ = 6.56–6.81 (–C*H*=CH_2), 5.82–6.02 (=$CH_{cis}H_{trans}$) and 5.18–5.41 (=$CH_{cis}H_{trans}$), respectively. All products had a one-proton singlet at about δ = 7.42–7.94 ppm assignable to the triazolyl C-5–H proton. These signals clearly demonstrate the formation of the target molecules. Further support was obtained from their ^{13}C NMR spectra.

Conclusions

In summary, a novel and efficient procedure for the liquid-phase synthesis of 1-substituted-4-vinyl-1*H*-1,2,3-triazoles has been developed using PEG-supported but-3-yn-1-yl sulfonate reagent, which involved sequential click and elimination reactions. This method gives these interesting compounds in moderate to excellent yields with simple work-up and mild reaction conditions.

Experimental Section

General. Melting points are uncorrected. NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer, using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as internal standard. FTIR spectra were taken on a Perkin-Elmer SP One FTIR spectrophotometer. Microanalyses were performed with a Carlo Erba 1106 Elemental Analyzer. Difunctionalised polyethylene glycol (PEG) supported sulfonyl chloride (**1**) (loading: 0.46 mmol Cl/g) was prepared from PEG polymer (average mass 4000) according to our reported method.[26] The azides were prepared from reaction of sodium azide with the corresponding alkyl halides or aryl halides according to the procedures given in the literature.[27] The other reagents were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (60–120 mesh) using ethyl acetate/hexane mixtures as the eluent.

Preparation of PEG-supported but-3-ynyl sulfonate (2). To a solution of 3-butyn-1-ol (5.0 mmol) in anhydrous dichloromethane (10.0 mL) was added PEG 4000 disulfonyl chloride (**1**) (2.2 g, 0.05 mmol) and Et_3N (2.5 mmol), and the reaction mixture was heated at reflux for 8 h under an N_2 atmosphere. The solvent was removed in vacuo, and the crude product dissolved in hot

propan-2-ol (100 mL). The precipitation step was repeated, the combined precipitates washed with propan-2-ol (10 mL), and Et_2O (2 × 10 mL), and then dried in vacuo to afford PEG-supported but-3-yn-1-yl sulfonate (**2**) as a white solid in nearly quantitative yield. IR (KBr): ν_{max} = 3321, 2945, 2886, 2122, 1455, 1353, 1245, 1170, 695 cm^{-1}.

General procedure for the preparation of 4-vinyl-1*H*-1,2,3-triazoles (4a–4k). To a stirred solution of **2** prepared as above, azides (3.00 mmol) and sodium ascorbate (38 mg, 20 mmol%) in DMSO/H_2O (9:1, 10 mL) was added $CuSO_4 \cdot 5H_2O$ (50 mg, 20 mmol%), and the mixture was heated at 60 °C for 10 h. After completion of the reaction, the reaction mixture was cooled and the diethyl ether (100 mL) was added to cause precipitation of PEG-supported intermediate **3**. To complete the precipitation, the suspension was left at 0 ºC for another 30 min. The white precipitate was collected, washed with diethyl ether (2 × 10 mL) and dried *in vacuo*. Then, to a solution of **3** in MeCN (10 mL), NaI (450 mg, 3.00 mmol) and DBU (300 mg, 2.00 mmol) were added, and the reaction mixture was heated at reflux for 40–50 min under an N_2 atmosphere. After this, the solvent was removed under vacuum, and diethyl ether (100 mL) was added with vigorous stirring and the mixture was cooled to 0 ºC. The recovered PEG-bound sulfonic acid salt was collected by filtration, washed with cold diethyl ether (2 × 10 mL). The filtrate was washed water (each of 10 mL), dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel; hexane/EtOAc, 10:1) to afforded pure target compounds **4a–4k**.

1-Benzyl-4-vinyl-1*H*-1,2,3-triazole (4a). White solid, mp 37–38 °C (lit.[16,17,21]36–39°C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.45 (s, 1H, triazolyl *H*), 7.44–7.38 (m, 3H, Ph*H*), 7.30–7.27 (m, 2H, Ph*H*), 6.65 (dd, *J* 17.8, 10.8 Hz, 1H, C*H*=CH_2), 5.85 (d, *J* 17.8 Hz, 1H, *trans* CH=CH_2), 5.49 (s, 2H, CH_2N), 5.30 (d, *J* 10.8 Hz, 1H, *cis* CH=CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C =146.8 (NCH=*C*), 134.8 (Ph, *C*CH_2N), 129.3 (*o*-Ph, 2C), 128.8 (*C*H=CH_2), 128.2 (*m*-Ph, 2C), 125.8 (*p*-Ph), 120.3 (CH=*C*H_2), 116.1 (N*C*H=C), 54.2 (*C*H_2N).

1-(4-Methoxybenzyl)-4-vinyl-1*H*-1,2,3-triazole (4b). White solid, mp 46–47 °C (lit.[16,17] 46–47 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.42 (s, 1H, triazolyl *H*), 7.25 (d, *J* 8.0 Hz, 2H, *o*-Ph*H*), 6.95 (d, *J* 8.0 Hz, 2H, *m*-Ph*H*), 6.66 (dd, *J* 17.8, 10.6 Hz, 1H, C*H*=CH_2), 5.84 (d, *J* 17.8 Hz, 1H, *trans* CH=CH_2), 5.47 (s, 2H, CH_2N), 5.30 (d, *J* 10.6 Hz, 1H, *cis* CH=CH_2), 3.84 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 160.3 (Ph, CH_3O*C*), 146.7 (NCH=*C*), 129.9 (*o*-Ph, 2C), 126.7 (Ph, *C*CH_2N), 128.7 (*C*H=CH_2), 120.3 (N*C*H=C), 116.1 (CH=*C*H_2), 114.8 (*m*-Ar, 2C), 55.8 (*C*H_3O), 53.8 (*C*H_2N).

1-(4-Bromobenzyl)-4-vinyl-1*H*-1,2,3-triazole (4c). White solid, mp 134–135 °C (lit.[17]135–137 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.52 (s, 1H, triazolyl *H*), 7.70 (d, *J* 6.8 Hz, 2H, *m*-Ph*H*), 7.45 (d, *J* 6.8 Hz, 2H, *o*-Ph*H*), 6.68 (dd, *J* 18.2, 10.2 Hz, 1H, C*H*=CH_2), 5.82 (d, *J* 18.2 Hz, 1H, *trans* CH=CH_2), 5.23 (s, 2H, CH_2N), 5.35 (d, *J* 10.2 Hz, 1H, *cis* CH=CH_2); ^{13}C NMR ($CDCl_3$, 100

MHz): δ_C = 147.0 (NCH=*C*), 134.6 (*m*-Ph, 2C), 132.4 (*o*-Ph, 2C), 129.8 (Ph, *C*CH_2N), 129.0 (*C*H=CH_2), 123.1 (Ph, BrC), 120.5 (N*C*H=C), 116.3 (CH=*C*H_2), 53.5 (*C*H_2N).

1-(*n*-Butyl)-4-vinyl-1*H*-1,2,3-triazole (4d). Colorless oil (lit.[17]); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.48 (s, 1H, triazolyl *H*), 6.56 (dd, *J* 17.8, 10.0 Hz, 1H, C*H*=CH_2), 5.85 (d, *J* 17.8 Hz, 1H, *trans* CH=C*H*$_2$), 5.18 (d, *J* 10.0 Hz, 1H, *cis* CH=C*H*$_2$), 4.20 (t, *J* 7.2 Hz, 2H, C*H*$_2$N), 1.75–1.71 (m, 2H, C*H*$_2$$CH_2$N), 1.25–1.20 (m, 2H, C*H*$_2$$CH_3$), 0.82 (t, *J* 7.2 Hz, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 146.2 (NCH=*C*), 125.6 (*C*H=CH_2), 120.6 (N*C*H=C), 115.8 (CH=*C*H_2), 49.7 (*C*H_2N), 32.3 (*C*$H_2$$CH_2$N), 19.8 (*C*$H_2$$CH_3$), 13.3 (*C*$H_3$).

1-Phenyl-4-vinyl-1*H*-1,2,3-triazole (4e). White solid, mp 41–42 °C (lit.[17] 40–42 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.94 (s, 1H, triazolyl *H*), 7.73 (d, *J* 7.4 Hz, 2H, *o*-Ph*H*), 7.55 (t, *J* 15.5 Hz, 2H, *m*-Ph*H*), 7.44 (t, *J* 8.1 Hz, 1H, *p*-Ph*H*), 6.80 (dd, *J* 18.0, 10.2 Hz, 1H, C*H*=CH_2), 6.00 (d, *J* 18.0 Hz, 1H, *trans* CH=C*H*$_2$), 5.42 (d, *J* 10.2 Hz, 1H, *cis* CH=C*H*$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.7 (NCH=*C*), 129.8 (N*C*H=C), 128.7 (Ph, *C*N), 125.8 (*C*H=CH_2), 125.3 (*o*-Ph, 2C), 120.5 (*m*-Ph, 2C), 118.5 (*p*-Ph, C), 116.7 (CH=*C*H_2).

1-(4-Methoxyphenyl)-4-vinyl-1*H*-1,2,3-triazole (4f). White solid, mp 66–67 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.65 (s, 1H, triazolyl *H*), 7.55 (d, *J* 8.4 Hz, 2H, *o*-Ph*H*), 6.94 (d, *J* 8.4 Hz, 2H, *m*-Ph*H*), 6.71 (dd, *J* 18.4, 10.4 Hz, 1H, C*H*=CH_2), 5.94 (d, *J* 18.4 Hz, 1H, *trans* CH=C*H*$_2$), 5.43 (d, *J* 10.4 Hz, 1H, *cis* CH=C*H*$_2$), 3.79 (s, 3H, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C =159.7 (Ph, CH_3O*C*), 148.5 (NCH=*C*), 130.2 (N*C*H=C), 129.7 (Ph, *C*N), 125.7 (*C*H=CH_2), 121.7 (*o*-Ph, 2C), 116.7 (CH=*C*H_2), 114.3 (*m*-Ph, 2C), 55.6 (*C*H_3O); IR (KBr): ν_{max} = 3071, 2926, 2864, 1641, 1545, 1496, 1458, 1378, 1221, 996, 910, 826, 720 cm^{-1}; Anal. Calcd for $C_{11}H_{11}N_3O$: C 65.66, H 5.51, N 20.88; found: C 65.45 H, 5.67, N 20.75.

1-(3-Methylphenyl)-4-vinyl-1*H*-1,2,3-triazole (4g). Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.77 (s, 1H, triazolyl *H*), 7.75 (s, 1H, Ph-2*H*), 7.45 (d, *J* 7.6 Hz, 1H, Ph-6*H*), 7.34 (d, *J* 8.0 Hz, 1H, Ph-4*H*), 7.21 (d, *J* 7.2 Hz, 1H, Ph-5*H*), 6.73 (dd, *J* 18.4, 10.8 Hz, 1H, C*H*=CH_2), 5.93 (d, *J* 18.4 Hz, 1H, *trans* CH=C*H*$_2$), 5.44 (d, *J* 10.8 Hz, 1H, *cis* CH=C*H*$_2$), 2.40 (s, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.8 (NCH=*C*), 139.8 (Ph-3*C*), 136.8 (Ph-2*C*), 130.6 (N*C*H=C), 129.5 (Ph-1*C*), 128.9 (Ph-6*C*), 126.0 (*C*H=CH_2), 121.5 (Ph-4*C*), 117.7 (Ph-5*C*), 116.8 (CH=*C*H_2), 20.9 (*C*H_3); IR (film): ν_{max} = 3114, 3069, 2925, 2872, 1639, 1550, 1496, 1437, 1376, 1224, 996, 865, 694 cm^{-1}; Calcd for $C_{11}H_{11}N_3$: C 71.33, H 5.99, N 22.69; found: C 71.07, H 6.20, N 22.53.

1-(2-Methylphenyl)-4-vinyl-1*H*-1,2,3-triazole (4h). Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.70 (s, 1H, triazolyl *H*), 7.44–7.31 (m, 3H, Ph*H*), 7.21 (d, *J* 8.0 Hz, 1H, Ph-3*H*), 6.86 (dd, *J* 18.4, 10.4 Hz, 1H, C*H*=CH_2), 5.93 (d, *J* 18.4 Hz, 1H, *trans* CH=C*H*$_2$), 5.48 (d, *J* 10.4 Hz, 1H, *cis* CH=C*H*$_2$), 2.33 (s, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.4 (NCH=*C*), 136.8 (Ph-2*C*), 132.9 (Ph-6*C*), 131.2 (Ph-5*C*), 130.6 (N*C*H=C), 129.5 (Ph-1*C*), 125.9 (*C*H=CH_2), 125.3 (Ph-4*C*),

121.7 (Ph-3*C*), 116.8 (CH=*C*H$_2$), 20.9 (*C*H$_3$); IR (film): ν_{max} = 3114, 3086, 2926, 2874, 1642, 1550, 1496, 1455, 1377, 1224, 995, 868, 695 cm^{-1}; Calcd for $C_{11}H_{11}N_3$: C 71.33, H 5.99, N 22.69; found: C 71.09, H 6.21, N 22.55.

1-(2-Chlorophenyl)-4-vinyl-1*H*-1,2,3-triazole (4i). Yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H = 7.77 (s, 1H, triazolyl *H*), 7.73 (d, *J* 7.2 Hz, 1H, Ph-3*H*), 7.49–7.42 (m, 2H, Ph*H*), 7.34 (t, *J* 6.8 Hz, 1H, Ph-5*H*), 6.77 (dd, *J* 17.8, 10.4 Hz, 1H, C*H*=CH$_2$), 5.95 (d, *J* 17.8 Hz, 1H, *trans* CH=C*H*$_2$), 5.49 (d, *J* 10.4 Hz, 1H, *cis* CH=C*H*$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ_C = 149.1 (NCH=*C*), 133.4 (Ph-2*C*), 131.7 (Ph-6*C*), 130.9 (Ph-4*C*), 130.6 (N*C*H=C), 129.8 (Ph-1*C*), 128.2 (Ph-3*C*), 127.5 (Ph-5*C*), 125.9 (*C*H=CH$_2$), 116.2 (CH=*C*H$_2$); IR (film): ν_{max} = 3122, 3096, 2928, 2875, 1644, 1550, 1495, 1441, 1225, 1001, 906, 817, 696 cm^{-1}; Calcd for $C_{10}H_8N_3Cl$: C 58.41, H 3.92, N 20.43; found: C 58.21, H 4.11, N 20.30.

1-(4-Bromophenyl)-4-vinyl-1*H*-1,2,3-triazole (4j). Pale yellow solid, mp 141–142 °C (lit.[28] 141–143 °C); ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H = 7.85 (s, 1H, triazolyl *H*), 7.69 (d, *J* 8.8 Hz, 2H, *m*-Ph*H*), 7.50 (d, *J* 8.8 Hz, 2H, *o*-Ph*H*), 6.81 (dd, *J* 18.8, 11.0 Hz, 1H, C*H*=CH$_2$), 6.00 (dd, *J* 18.8, 1.2 Hz, 1H, *trans* CH=C*H*$_2$), 5.50 (dd, *J* 11.0, 1.2 Hz, 1H, *cis* CH=C*H*$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ_C = 148.9 (NCH=*C*), 134.3 (*m*-Ph, 2C), 132.2 (*o*-Ph, 2C), 130.6 (N*C*H=C), 129.8 (Ph, *C*N), 126.0 (*C*H=CH$_2$), 120.4 (Ph, BrC), 116.7 (CH=*C*H$_2$).

1-(4-Nitrophenyl)-4-vinyl-1H-1,2,3-triazole (4k). Pale yellow solid, mp 177–179 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H = 8.42 (d, *J* 8.8 Hz, 2H, *o*-Ph*H*), 8.00 (d, *J* 8.8 Hz, 2H, *m*-Ph*H*), 7.69 (s, 1H, triazolyl *H*), 6.80 (dd, *J* 18.0, 10.2 Hz, 1H, C*H*=CH$_2$), 6.02 (d, *J* 18.0 Hz, 1H, *trans* CH=C*H*$_2$), 5.51 (d, *J* 10.2 Hz, 1H, *cis* CH=C*H*$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ_C = 151.3 (Ph, NO$_2$*C*), 149.1 (NCH=*C*), 141.3 (Ph, *C*N), 130.0 (N*C*H=C), 126.4 (*C*H=CH$_2$), 125.7 (*o*-Ph, 2C), 120.5 (*m*-Ph, 2C), 117.1 (CH=*C*H$_2$); IR (KBr): ν_{max} = 3121, 1637, 1606, 1529, 1496, 1455, 1350, 1239, 1073, 993, 919, 775, 730 cm^{-1}; Calcd for $C_{10}H_8N_4O_2$: C 55.55, H 3.73, N 25.91; found: C 55.23, H 3.94, N 25.76.

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