

## Electronic Supplementary Information

# Toward a green synthesis of polymerizable vinyltriazoles: Development of an optimized one-pot strategy starting from 4- bromobutyne

A. Praud,<sup>a</sup> O. Bootzeek<sup>a</sup> and Y. Blache<sup>a\*</sup>

<sup>a</sup> Université de Toulon, MAPIEM, EA 4323, 83957 La Garde, France

### General experimental procedures:

NMR spectra were obtained at 400 MHz and 100MHz for <sup>1</sup>H and <sup>13</sup>C, respectively, on a Brüker Avance 400 MHz spectrometer. Chemical shifts were referenced to the solvent peaks. Low-resolution mass spectra were measured on a ion trap mass spectrometer fitted with an ESI interface (Esquire 6000, Brüker Daltonics).

**Typical procedure for the preparation of 1-methoxybenzyl-4-bromoethyl-(1*H*)-1,2,3-triazole (2)**<sup>8-9</sup>: azide (1) (0.04 mmol, 1 eq. purity monitored by <sup>1</sup>H-nmr) was added to a solution of H<sub>2</sub>O/EtOH (2 mL/2 mL) containing CuSO<sub>4</sub>·5H<sub>2</sub>O (0.01 eq.), 4-bromobutyne (1.5 eq.) and sodium ascorbate (0.03 eq.). The resulting mixture was stirred 12 hours at RT. A saturated solution of Na<sub>2</sub>CO<sub>3</sub> was added and the resulting solution extracted 3 times with ethylacetate. The organic layers were then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to give the compound 2, which was purified by flash chromatography on silica gel. Yellow oil, <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ : 3.15 (2H, t, *J* = 7.1 Hz), 3.50 (2H, t, *J* = 7.1 Hz), 3.68 (3H, s), 5.32 (2H, s), 6.77 (2H, d, *J* = 8.8 Hz), 7.10 (2H, d, *J* = 8.8 Hz), 7.21 (s, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 400 MHz) δ : 29.4, 31.5, 53.2, 55.3, 114.4 (2C), 121.3, 126.6, 129.6 (2C), 159.7. Found C, 48.5; H, 4.84; N, 14.22. C<sub>12</sub>H<sub>14</sub>N<sub>3</sub>OBr requires C, 48.66; H, 4.76; N 14.18.12

**Typical procedure for the preparation of 4-vinyl-(1*H*)-1,2,3-triazoles : entry 3**

Appropriate azide (0.4 mmol., 1 eq.) was added to a solution of H<sub>2</sub>O/EtOH (2 mL/2 mL) containing CuSO<sub>4</sub>·5H<sub>2</sub>O (0.01eq.), 4-bromobutyne (1.5 eq.) and sodium ascorbate (0.03 eq.). The resulting mixture was stirred 12 hours at RT. A solution of Sodium hydroxide (5 eq.) in 2 ml of water was added and the resulting mixture was stirred at the appropriate temperature for 8 hours at 45°C. After cooling and treatment with brine, the resulting solution was extracted 3 times with ethylacetate. The organic layers were then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to give the vinyl derivatives (**3**, **4**, **5**), which were purified by flash chromatography on silica gel (Si60 15-40µm n-hexane/ ethyl acetate (70/30)).

**1-methoxybenzyl-4-vinyl-(1*H*)-1,2,3-triazole (3)** : (pale yellow paste, lit.,<sup>10</sup> not reported) The structure was determined by mass spectra, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. All spectral data were in agreement with reference 10.

**1-methoxyphenyl-4-vinyl-(1*H*)-1,2,3-triazole (4)** : (mp 76°C, lit.,<sup>4</sup> 72-76°C). The structure was determined by mass spectra, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. All spectral data were in agreement with reference 4.

**1-octyl-4-vinyl-(1*H*)-1,2,3-triazole (5)**: (pale yellow oil, lit.,<sup>6</sup> transparent oil) the structure was determined by mass spectra, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. All spectral data were in agreement with reference 6.

#### **Typical procedure for the preparation of 5-vinyl-(1*H*)-1,2,3-triazoles:<sup>9</sup>**

A solution of azide (0.4 mmol., 1 eq., purity monitored by 1H-nmr), alkyne (1eq.) in dioxane (2 mL) was added under Argon to 2 mL of dioxane containing a catalytic amount of Cp\*RuCl(PPh<sub>3</sub>)<sub>2</sub> (0.02 eq.). The resulting mixture was stirred 12 hours at 60°C under Argon atmosphere. A solution of sodium hydroxide (5eq.) in a EtOH/H<sub>2</sub>O (1 mL/ 1mL) mixture was then added and the resulting solution was stirred at the appropriate temperature for 8 hours at 45°C. After cooling and treatment with brine, the resulting solution was extracted 3 times with ethylacetate. The organic layers were then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to give the

vinyl derivatives (**6**, **7**, **8**), which were purified by flash chromatography on silica gel (Si60 15-40 $\mu$ m n-hexane/ ethyl acetate (70/30)).

**1-methoxybenzyl-5-vinyl-(1*H*)-1,2,3-triazole (6)** : (yellow oil).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  : 3.67 (3H, s), 5.32 (1H, d,  $J = 11.1$  Hz), 5.39 (2H, s), 5.61 (1H, d,  $J = 16.6$  Hz), 6.35 (1H, dd,  $J = 16.6$  and 11.1 Hz), 6.63 (2H, d,  $J = 8.8$  Hz), 7.00 (2H, d,  $J = 8.8$  Hz), 7.67 (1H, s).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  : 51.4, 55.2, 114.2 (2C), 120.3, 120.4, 126.7, 128.4 (2C), 131.3, 135.4, 159.8. Found MS (ESI,  $m/z$ ) 237.88 ( $\text{M}+\text{Na}^+$ ) ; C, 67.09; H, 5.71; N,19.57.  $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}$  requires  $\text{M}^+$  214.25 ; C, 67.27; H, 5.64; N, 19.61.

**1-methoxyphenyl-5-vinyl-(1*H*)-1,2,3-triazole (7)** : (mp 65-66°C).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  : 3.65 (3H, s), 5.45 (1H, d,  $J = 11.2$  Hz), 5.79 (1H, d,  $J = 16.8$  Hz), 6.42 (1H, dd,  $J = 16.8$  and 11.2 Hz), 7.00 (2H, d,  $J = 9.0$  Hz), 7.36 (1H, d,  $J = 9$  Hz), 7.86 (1H, s).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  : 55.6, 114.5 (2C), 120.0, 121.2, 126.6 (2C), 128.9, 130.9, 136.0, 160.3. Found MS (ESI,  $m/z$ ) 223.85 ( $\text{M}+\text{Na}^+$ ), 201.87 ( $\text{M}+\text{H}$ ) ; C, 66.0; H, 5.21; N,20.89.  $\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}$  requires  $\text{M}^+$  200.22; C, 65.98; H, 5.03; N, 20.98.

**1-octyl-5-vinyl-(1*H*)-1,2,3-triazole (8)**: (yellow oil, lit.<sup>6</sup>, viscous transparent oil). The structure was determined by mass spectra,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ . all spectral data were in agreement with reference 6.