

# Phosphonated furan-functionalized poly(ethylene oxide)s using orthogonal click chemistries: Synthesis and Diels-Alder reactivity

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## 1. Materials

Acetonitrile (99.8%, Sigma-Aldrich), copper(I) bromide (Cu(I)Br, 99.99%, Sigma-Aldrich), dichloromethane (DCM, 99%, Aldrich), diethyl ether (99%, Aldrich), *N,N*-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), disodium ethylenediaminetetraacetate (EDTA.2Na, 99%, Acros), ethanol (99.8%, Sigma-Aldrich), ethyl acetate (bp<sub>760</sub> = 77°C), 2-furaldehyde (99%, Aldrich), 3-furaldehyde (99%, Aldrich), magnesium sulfate (MgSO<sub>4</sub>.7H<sub>2</sub>O, 70%, Fisher), 5-methyl-2-furaldehyde (99%, Aldrich), molecular sieves 4Å (8 to 12 mesh, Aldrich), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Sigma-Aldrich), poly(ethylene oxide) monomethyl ether 2 000 (PEO-OH, Sigma-Aldrich,  $\overline{M}_{n,NMR} = 2\ 010$  g/mol), *N*-propargylamine (99%, Acros), silica gel column chromatography (Kieselgel 60, 230-240 mesh Merck) and trimethylsilyl bromide (TMSBr, 98%, Acros) were used as received. Dimethyl hydrogenophosphonate (bp<sub>0.20 mmHg</sub> = 40 °C) was distilled in *vacuum* before use. Azido-terminated PEO monomethyl ether 2 000 (PEO-N<sub>3</sub>) was synthesized according to a literature procedure.<sup>1,2</sup>

## 2. Instrumentation

**Nuclear Magnetic Resonance Spectroscopy.** Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer operating at 400.16 MHz for <sup>1</sup>H, 100.62 MHz for <sup>13</sup>C, and 161.96 MHz for <sup>31</sup>P using either deuterated chloroform (CDCl<sub>3</sub>) or deuterated methanol (CD<sub>3</sub>OD) as the solvent. <sup>31</sup>P NMR spectra were proton decoupled. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to tetramethylsilane signals while <sup>31</sup>P NMR chemical shifts were referenced to 85% phosphoric acid as an external reference, with positive shift values

downfield from the reference. Coupling constants and chemical shifts are reported in hertz and in parts per million (ppm), respectively.

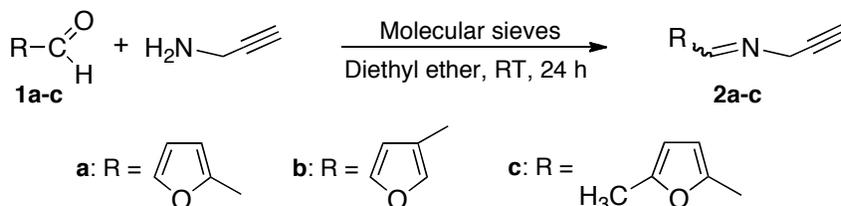
**Fourier Transform Infra-Red Spectroscopy.** Fourier transform infra-red (FT-IR) spectra were recorded using a Nicolet avatar 370 DTGS spectrometer in transmittance mode.

**High Resolution Mass Spectrometry.** High resolution mass spectra (HR-MS) were recorded on a Waters-Micromass® GCT Premier™ (GC, CI+, methane) using a HP 6890 GC apparatus equipped with a chromatographic column of 25 m, diameter 250  $\mu\text{m}$ , thickness 0.25  $\mu\text{m}$ . The sample was warmed at a temperature of 40 °C for 5 min and then further heated at a heating rate of 10 °C.min<sup>-1</sup> up to 220 °C.

**Matrix-Assisted Laser Desorption and Ionization Time Of Flight Mass Spectrometry.** Matrix-assisted laser desorption and ionization time of flight mass spectrometry (MALDI-TOF MS) analysis was performed on a Bruker Biflex III MALDI-TOF instrument equipped with a nitrogen laser operating at 337 nm, a 2GHz sampling rate digitiser, pulsed ion extraction source and reflectron. The laser pulse width is 3ns and maximum power is 200 mJ. Spectra were recorded in the linear mode with an acceleration voltage of 19 kV and delay of 200 ns. 100 single shot acquisitions were summed to give the spectra and the data were analyzed using Bruker XTOF software. Samples were prepared by dissolving the matrix (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, DCTB) in the solvent (DCM, 30 mg.mL<sup>-1</sup>) and mixing with the polymer (2 mg.mL<sup>-1</sup>) in the ratio 1:50 (v/v). 1 mL was spotted directly onto a thin layer of sodium trifluoroacetate (NaTFA) in acetone (concentration 19 mg.mL<sup>-1</sup>) that had been deposited to act as a cationizing agent.

### 3. Synthesis of the furan-functionalized phosphonic acid-terminated POE monomethyl ethers

#### 3.1. General procedure for the synthesis of Schiff bases (2a-c)



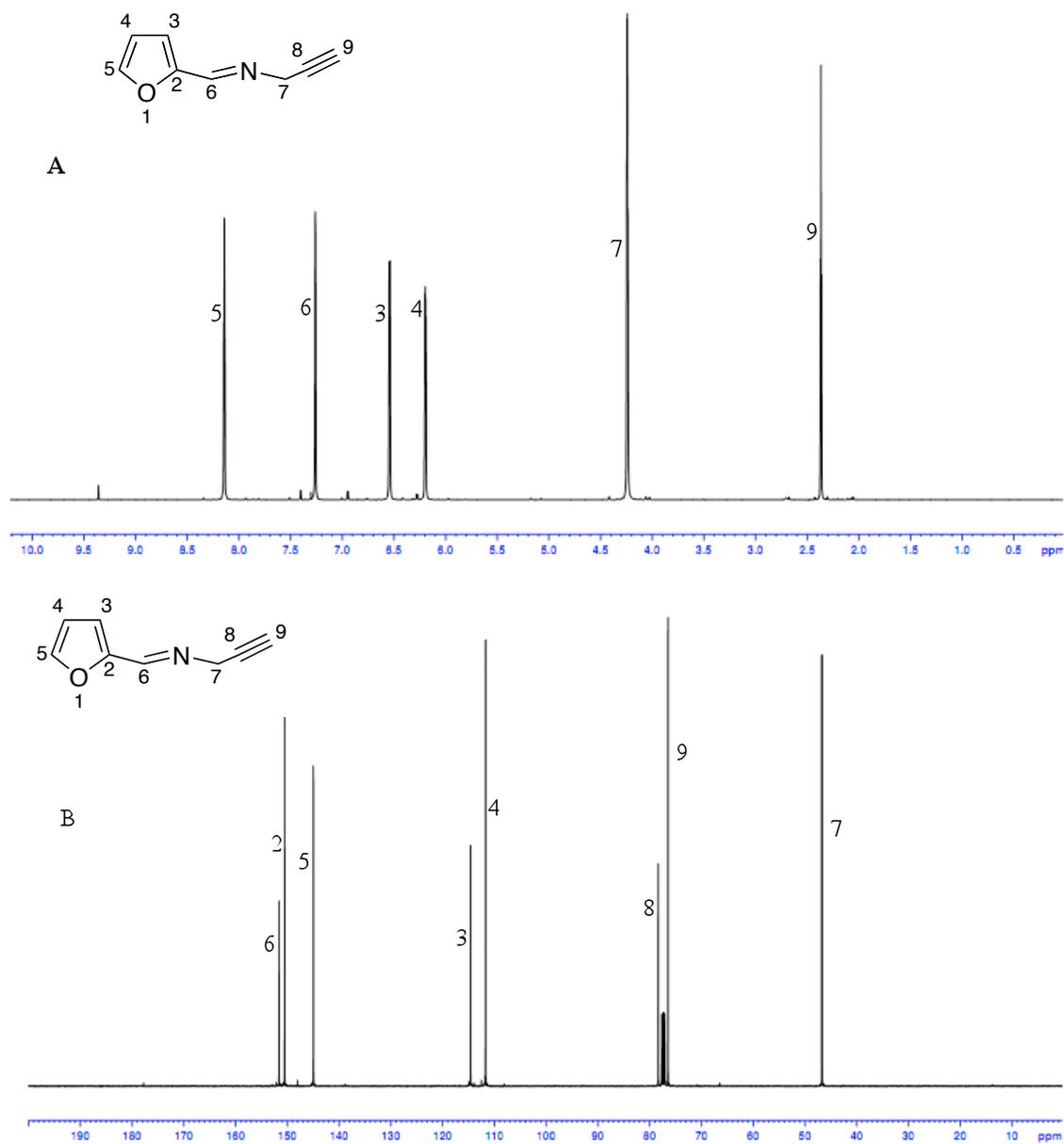
Scheme S1: Synthesis of Schiff bases (2a-c).

Aldehyde (0.05 mole), *i.e.* 2-furaldehyde (**1a**) or 3-furaldehyde (**1b**) or 5-methyl-2-furaldehyde (**1c**), anhydrous diethyl ether (15 mL) and molecular sieves 4Å (1 g) were placed in a 100 mL round-bottom flask equipped with a magnetic stirrer and a dropping funnel. A solution of *N*-propargylamine (2.75 g; 0.05 mole) in 10 mL of diethyl ether was added dropwise with stirring at room temperature. The reaction mixture was stirred for 24 h at room temperature, and then filtered. The filtrate was evaporated in vacuo, to give the crude Schiff base.

*N*-(2-furanylmethylene)prop-2-yn-1-amine (**2a**). The crude product was purified by distillation under reduced pressure ( $\text{bp}_{0.10 \text{ mmHg}} = 45^\circ\text{C}$ ) and obtained as a yellow oil in 79% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm): 8.42 (t,  $J = 3.89$  Hz, 1H,  $H_5$ ); 7.32 (t,  $J = 1.69$  Hz, 1H,  $\text{CH}=\text{N}$ ); 6.56 (d,  $J = 3.62$  Hz, 1H,  $H_3$ ); 6.28 (q,  $J = 5.31$  Hz, 1H,  $H_4$ ); 4.25 (t,  $J = 4.45$  Hz, 2H,  $\text{CH}_2$ ); 2.29 (t,  $J = 4.88$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.62 MHz),  $\delta$  (ppm): 151.62 ( $\text{CH}=\text{N}$ ); 150.54 ( $\text{C}_2$ ); 144.99 ( $\text{C}_5$ ); 114.67 ( $\text{C}_3$ ); 111.71 ( $\text{C}_4$ ); 78.37 ( $\text{C}\equiv\text{CH}$ );

76.45 (C≡CH); 46.72 (N-CH<sub>2</sub>). FT-IR (ν cm<sup>-1</sup>): 2111 (ν<sub>C=C</sub>); 1658 (ν<sub>CH=N</sub>). HRMS (CI-H<sup>+</sup>):

Calcd for C<sub>8</sub>H<sub>7</sub>NO + H<sup>+</sup>: 134.0606; Found: 134.0605.

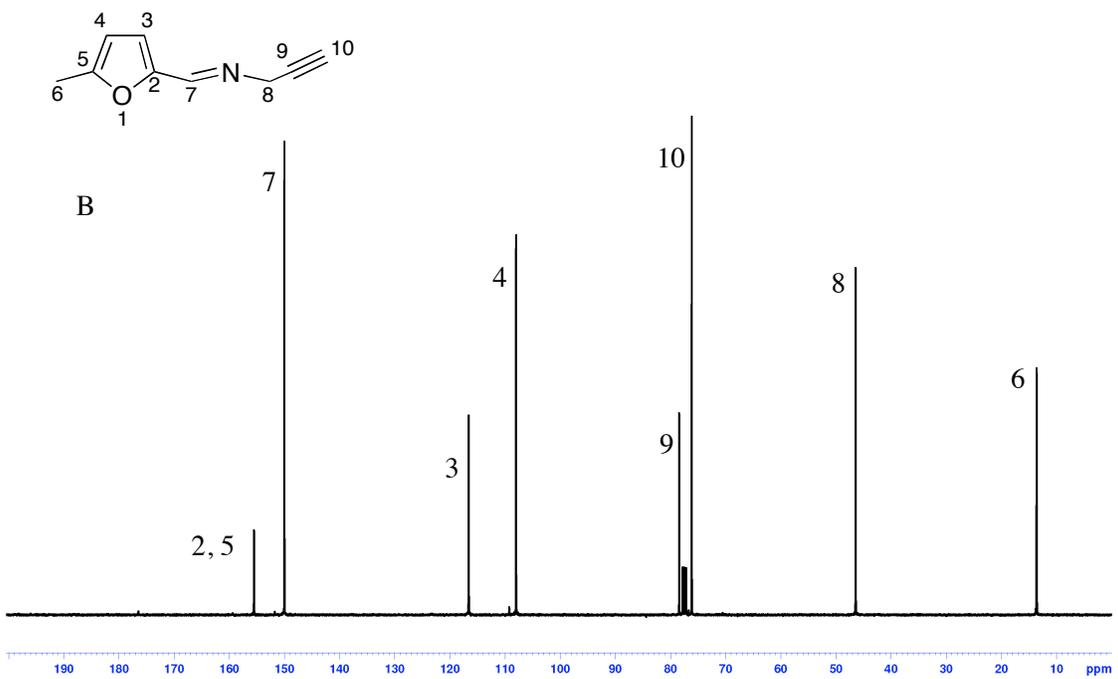
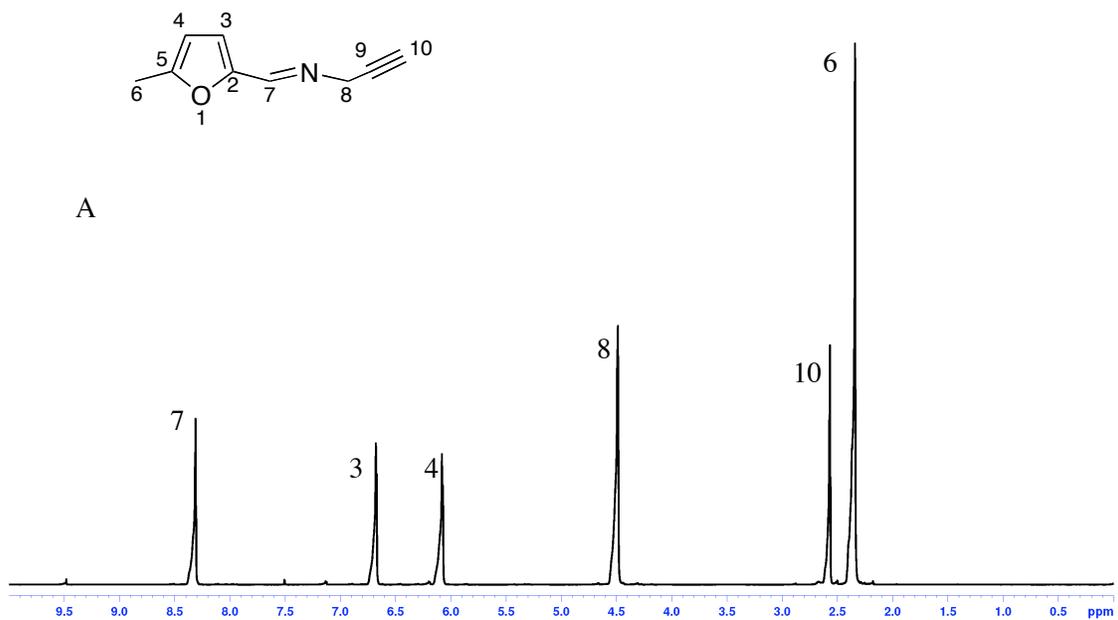


**Figure S1.** <sup>1</sup>H (A) and <sup>13</sup>C (B) NMR spectra of *N*-(2-furanylmethylene)prop-2-yn-1-amine

**2a**; solvent: CDCl<sub>3</sub>.

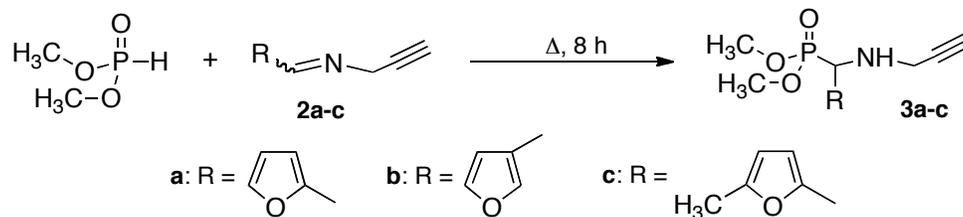
*N*-(3-furanylmethylene)prop-2-yn-1-amine (**2b**). The crude product was purified by distillation under reduced pressure (bp<sub>0.20 mmHg</sub> = 43°C) and obtained as a colorless oil in 78% yield. NMR, FT-IR and HRMS data have previously been reported in reference 3.

*N*-(5-methyl-2-furanylmethylene)prop-2-yn-1-amine (**2c**). The crude product was purified by distillation under reduced pressure (bp<sub>0.15 mmHg</sub> = 50°C) and obtained as a colorless oil in 77% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 8.32 (t, *J* = 1.64 Hz, 1H, CH=N); 6.69 (t, *J* = 3.32 Hz, 1H, *H*<sub>3</sub>); 6.09 (m, 1H, *H*<sub>4</sub>); 4.50 (t, *J* = 2.06 Hz, 2H, CH<sub>2</sub>); 2.58 (t, *J* = 2.32 Hz, 1H, C≡CH); 2.36 (m, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.62 MHz), δ (ppm): 155.55, 152.52 (C<sub>5</sub>, C<sub>2</sub>); 150.04 (CH=N); 116.60 (C<sub>3</sub>); 108.01 (C<sub>4</sub>); 78.44 (C≡CH); 76.15 (C≡CH); 46.46 (N-CH<sub>2</sub>); 13.31 (CH<sub>3</sub>). HRMS (CI-H<sup>+</sup>): Calcd for C<sub>9</sub>H<sub>9</sub>NO + H<sup>+</sup>: 148.0762; Found: 148.0763.



**Figure S2.** <sup>1</sup>H (A) and <sup>13</sup>C (B) NMR spectra of *N*-(5-methyl-2-furanylmethylene)prop-2-yn-1-amine **2c**; solvent: CDCl<sub>3</sub>.

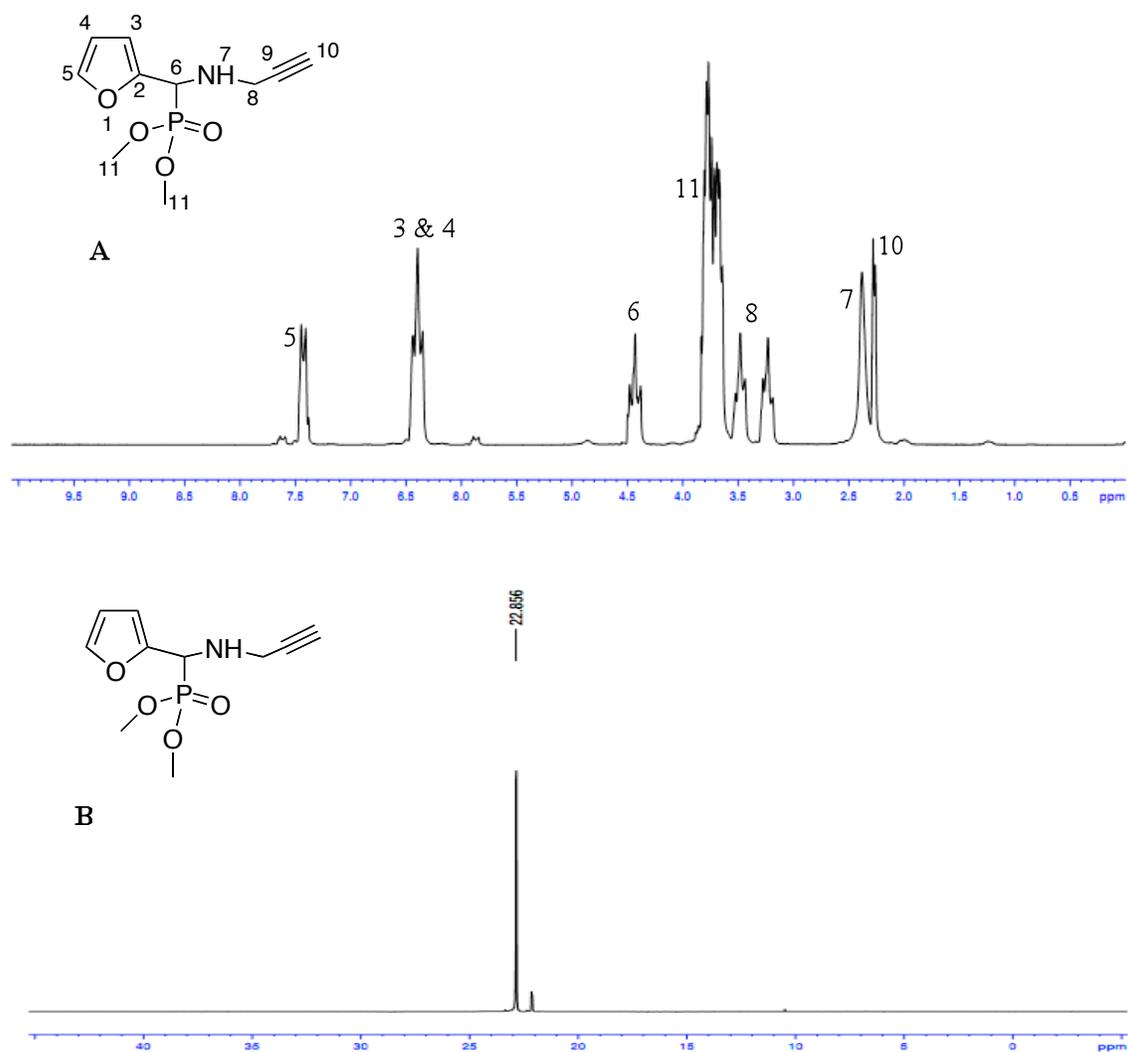
### 3.2. General procedure for the synthesis of $\alpha$ -aminophosphonates (**3a-c**)



Scheme S2: Synthesis of  $\alpha$ -aminophosphonates (**3a-c**).

Schiff base (**2a-c**; 7 mmoles) and dimethyl hydrogenophosphonate (0.77 g; 7 mmoles) were placed in a 100 mL round-bottom flask equipped with a magnetic stirrer, a reflux condenser and a dropping funnel. The reaction mixture was heated for 8 h at 60°C. The  $\alpha$ -aminophosphonates (**3a-c**) were purified by silica gel column chromatography eluted with ethyl acetate : acetonitrile (80 : 20) to give the pure products as yellow oils.

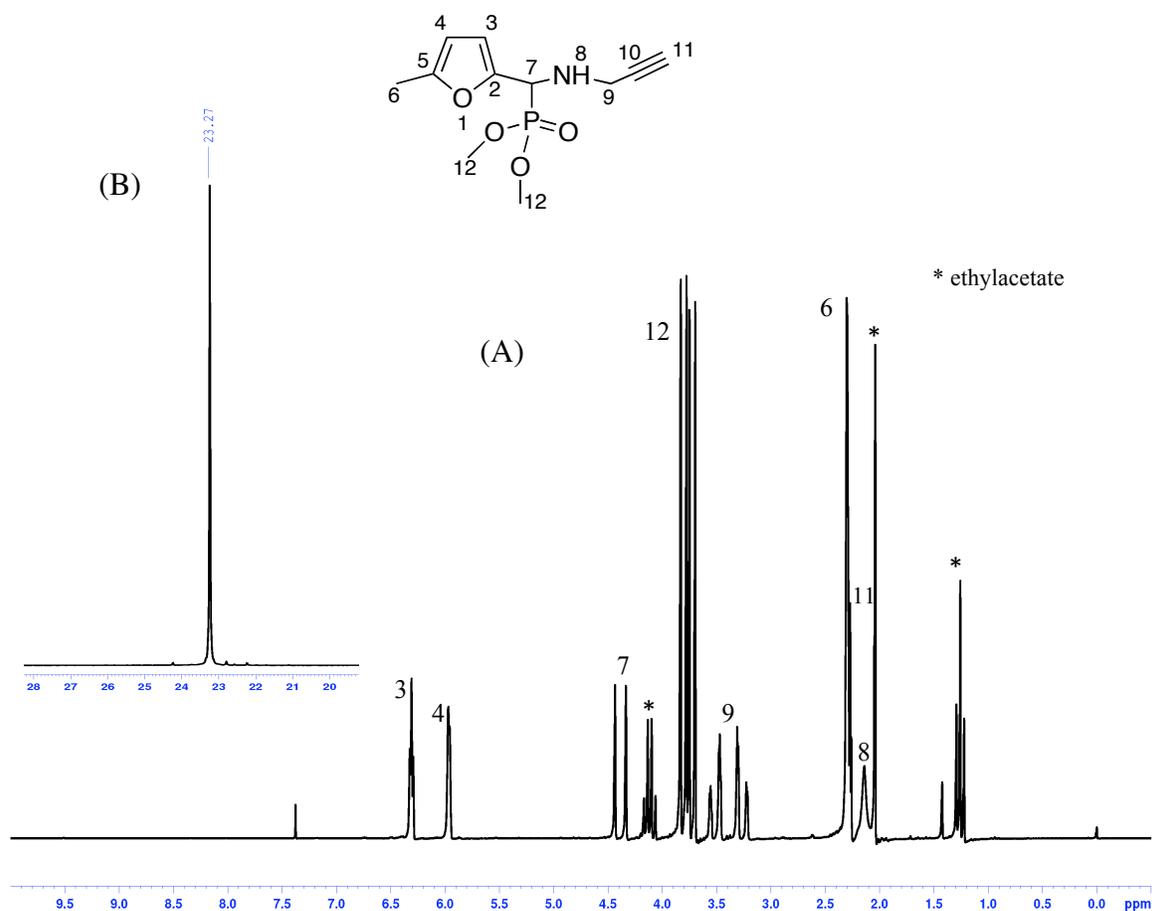
[*N*-methyl(dimethoxyphosphonyl)-(2-furanyl)]prop-2-yn-1-amine (**3a**). Yield: 90%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm): 7.43 (d,  $J = 16.04$  Hz,  $H_5$ ); 6.48-6.27 (t,  $J = 17.58$  Hz, 2H,  $H_3$  &  $H_4$ ); 4.43 (t,  $J = 18.93$  Hz, CH-P); 3.72 (m, 6H,  $\text{CH}_3$ ); 3.36 (m, 2H,  $\text{CH}_2$ ); 2.38 (s, NH); 2.27 (d,  $J = 7.26$  Hz,  $\text{C}\equiv\text{CH}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.62 MHz),  $\delta$  (ppm): 148.82 ( $\text{C}_2$ ); 148.15 ( $\text{C}_5$ ); 110.59 ( $\text{C}_3$ ); 109.95 ( $\text{C}_4$ ); 80.46 ( $\text{C}\equiv\text{CH}$ ); 72.46 ( $\text{C}\equiv\text{CH}$ ); 53.65 (CHP); 53.24 (d,  $J = 6.24$  Hz,  $\text{CH}_3$ ); 36.15 (N- $\text{CH}_2$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 161.96 MHz),  $\delta$  (ppm): 22.86. FT-IR ( $\nu \text{ cm}^{-1}$ ): 3426 ( $\nu_{\text{N-H}}$ ); 2126 ( $\nu_{\text{C}\equiv\text{C}}$ ); 1247 ( $\nu_{\text{P=O}}$ ); 1146 ( $\nu_{\text{P-O-C}}$ ). HRMS (CI- $\text{H}^+$ ): Calcd for  $\text{C}_{10}\text{H}_{14}\text{NO}_4\text{P} + \text{H}^+$ : 244.0660; Found: 244.0663.



**Figure S3.**  $^1\text{H}$  (A) and  $^{31}\text{P}$  (B) NMR spectra of [N-methyl(dimethoxyphosphonyl)-(2-furanyl)]prop-2-yn-1-amine **3a**; solvent:  $\text{CDCl}_3$ .

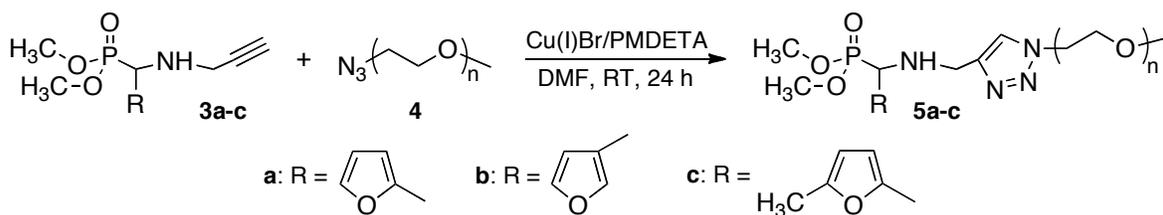
[N-methyl(dimethoxyphosphonyl)-(3-furanyl)]prop-2-yn-1-amine (**3b**). Yield: 87%. NMR, FT-IR and HRMS data have previously been reported in reference 3.

[*N*-methyl(dimethoxyphosphonyl)-(5-methyl-2-furanyl)]prop-2-yn-1-amine (**3c**). Yield: 85%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm): 6.32 (t,  $J = 3.24$  Hz, 1H,  $H_3$ ); 5.97 (m, 1H,  $H_4$ ); 4.40 (d,  $J = 19.41$  Hz,  $\text{CH-P}$ ); 3.76 (dd,  $J = 10.67, 5.46$  Hz, 6H,  $\text{CH}_3$ ); 3.39 (dd,  $J = 32.64, 17.14$  Hz, 2H,  $\text{CH}_2$ ); 2.30 (s, 3H,  $H_6$ ); 2.26 (t,  $J = 2.40$  Hz,  $\text{C}\equiv\text{CH}$ ); 2.15 (s, NH).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 161.96 MHz),  $\delta$  (ppm): 23.27. HRMS ( $\text{CI}^+$ ): Calcd for  $\text{C}_{11}\text{H}_{16}\text{NO}_4\text{P}^+$ : 257.0817; Found: 257.0811.



**Figure S4.**  $^1\text{H}$  (A) and  $^{31}\text{P}$  (B) NMR spectra of [*N*-methyl(dimethoxyphosphonyl)-(5-methyl-2-furanyl)]prop-2-yn-1-amine **3c**; solvent:  $\text{CDCl}_3$ .

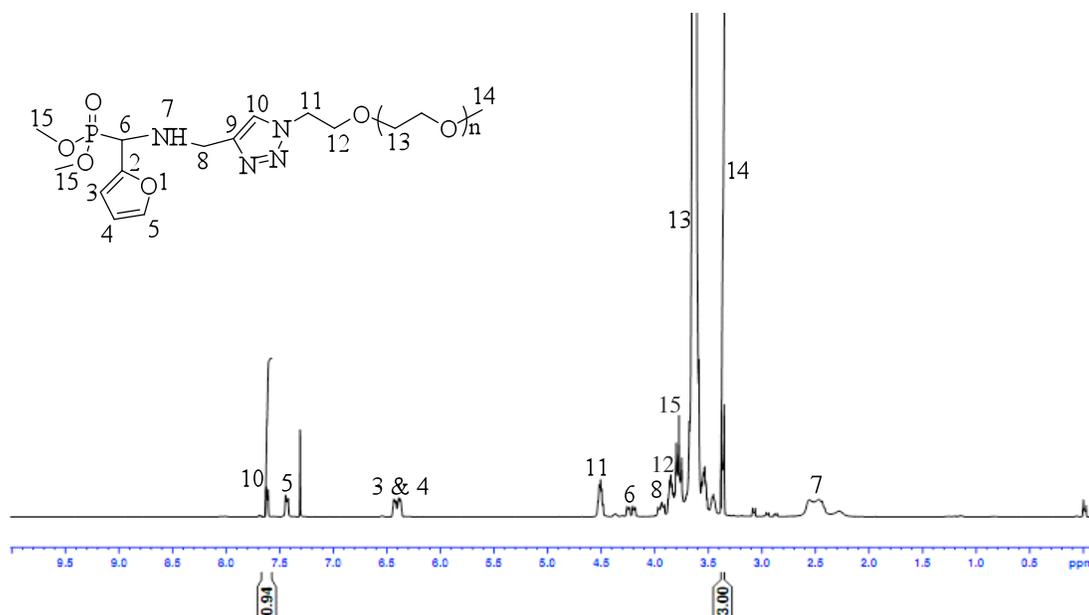
**3.3. General procedure for synthesis of dimethyl phosphonate-terminated PEO monomethyl ethers (5a-c)**



*Scheme S3: Synthesis of phosphonate-terminated furan-functionalized PEO monomethyl ethers (5a-c).*

In a typical experiment, azido-terminated PEO monomethyl ether (**4**; 1 g, 0.5 mmol),  $\alpha$ -aminophosphonate (**3a-c**; 0.5 mmol) and *N,N,N',N',N'*-pentamethyldiethylenetriamine (PMDETA; 0.1 g, 0.6 mmol) were charged to a dry Schlenk tube along with degassed DMF (5 mL). The tube was sealed with a rubber septum and subjected to six freeze-pump-thaw cycles. This solution was then cannulated under nitrogen into another Schlenk tube, previously evacuated and filled with nitrogen, containing Cu(I)Br (0.023 g, 0.16 mmol) and a stir bar. The resulting solution was subsequently stirred at room temperature for 24 h. The reaction mixture was diluted with dichloromethane (DCM, 50 mL) and then washed with  $3 \times 100$  mL of an aqueous ethylenediaminetetraacetate solution (0.03 mol/L) to remove the catalyst. The organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered and the solvent was removed under reduced pressure. The resulting phosphonate-terminated PEO monomethyl ethers **5a-c** were isolated by precipitation into cold diethyl ether.

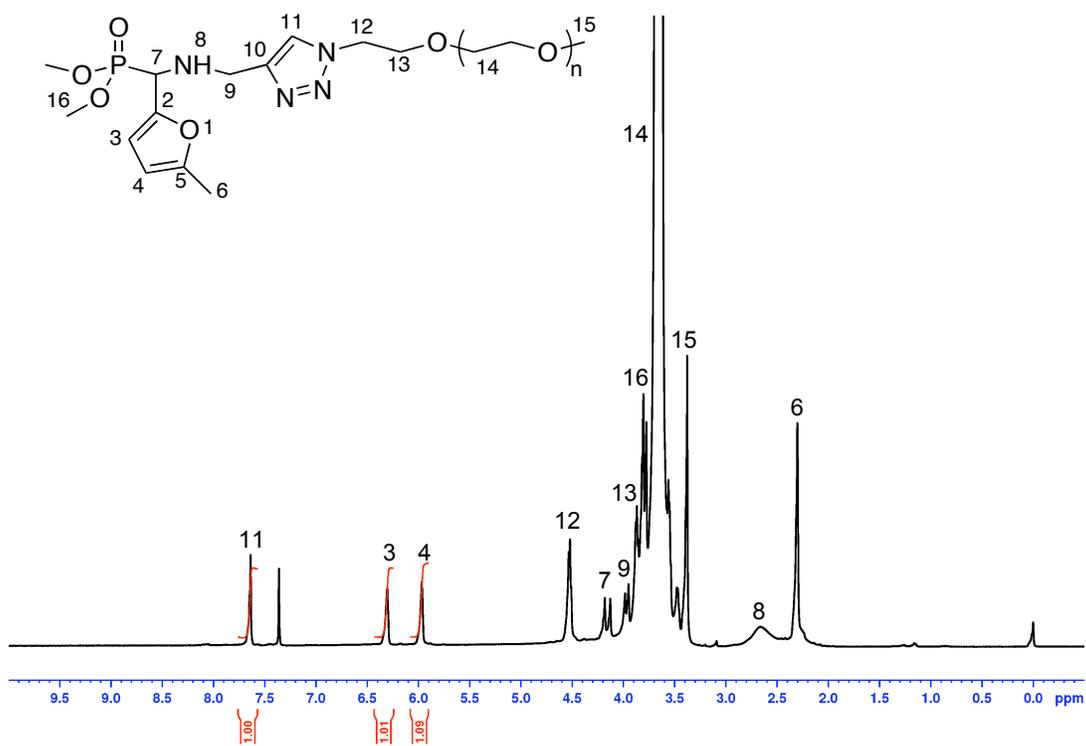
*Dimethylphosphonate-terminated 2-furan-functionalized PEO monomethyl ether (5a).*  
 Yellow powder. Yield: 76%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.62 (d,  $J = 6.66$  Hz, 1H, triazole); 7.44 (d,  $J = 6.36$  Hz, 1H,  $H_5$ ); 6.43-6.38 (m, 2H,  $H_3$  &  $H_4$ ); 4.50 (t,  $J = 2.39$  Hz, 2H,  $\text{N}_{\text{triazole}}\text{-CH}_2\text{-CH}_2\text{-O}$ ); 4.23 (dd,  $J = 11.64, 9.95$  Hz, 1H,  $\text{CHP}$ ); 3.94 (q,  $J = 7.89$  Hz, 2H,  $\text{NH-CH}_2$ ); 3.85 (t,  $J = 5.08$  Hz, 2H,  $\text{N}_{\text{triazole}}\text{-CH}_2\text{-CH}_2\text{-O}$ ); 3.78 (t,  $J = 10.41$  Hz, 6H,  $\text{P(O)O-CH}_3$ ); 3.72-3.51 (m, 172H,  $\text{CH}_2\text{-CH}_2\text{-O}$ ); 3.37 (s, 3H,  $\text{O-CH}_3$ ); 2.52 (s, 1H,  $\text{NH}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 148.94 ( $\text{C}_2$ ); 145.64 ( $\text{C}=\text{C-N}_{\text{triazole}}$ ); 142.83 ( $\text{C}_5$ ); 123.16 ( $\text{C}=\text{C-N}_{\text{triazole}}$ ); 119.81 ( $\text{C}_3$ ); 110.73 ( $\text{C}_4$ ); 71.94 ( $\text{CH}_2\text{-O-CH}_3$ ); 70.56 ( $\text{-CH}_2\text{-O-CH}_2$ ); 69.52 ( $\text{N}_{\text{triazole}}\text{-CH}_2\text{-CH}_2\text{-O}$ ); 59.02 ( $\text{CHP}$ ); 53.98 ( $\text{P(O)O-CH}_3$ ); 51.45 ( $\text{CH}_3\text{-O}$ ); 50.21 ( $\text{N}_{\text{triazole}}\text{-CH}_2\text{-CH}_2\text{-O}$ ); 42.63 ( $\text{N-CH}_2$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 161.96 MHz),  $\delta$  (ppm): 23.04. FT-IR ( $\nu$   $\text{cm}^{-1}$ ): 3452 ( $\nu_{\text{N-H}}$ ); 2883 ( $\nu_{\text{C-H}}$ ); 1467 ( $\nu_{\text{C}=\text{C}}$  triazole); 1234 ( $\nu_{\text{P=O}}$ ); 1147 ( $\nu_{\text{P-O-C}}$ ).



**Figure S5.**  $^1\text{H}$  NMR spectrum of dimethylphosphonate-terminated 2-furan-functionalized PEO monomethyl ether **5a**; solvent:  $\text{CDCl}_3$ .

*Dimethylphosphonate-terminated 3-furan-functionalized PEO monomethyl ether (5b).* Yellow powder. Yield: 70%. NMR, FT-IR and MALDI-TOF MS data have previously been reported in reference 3.

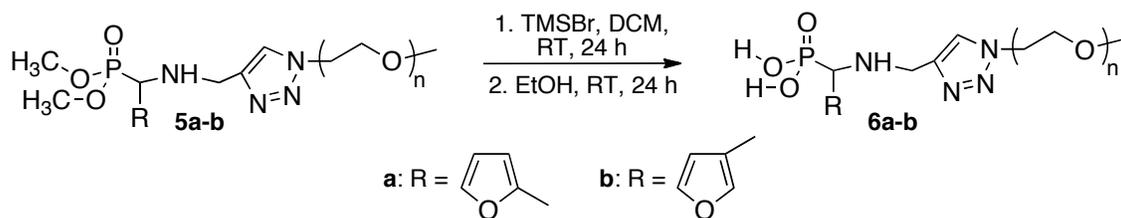
*Dimethylphosphonate-terminated 5-methyl-2-furan-functionalized PEO monomethyl ether (5c).* Yellow powder. Yield: 75%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.64 (s, 1H, triazole); 6.32 (s, 1H,  $H_3$ ); 5.98 (s, 1H,  $H_4$ ); 4.53 (m, 2H,  $\text{N}_{\text{triazole}}\text{-CH}_2\text{-CH}_2\text{-O}$ ); 4.16 (d,  $J = 10.68$  Hz, 1H,  $\text{CHP}$ ); 3.97 (d,  $J = 7.12$  Hz, 2H,  $\text{NH-CH}_2$ ); 3.88 (t,  $J = 2.56$  Hz, 2H,  $\text{N}_{\text{triazole}}\text{-CH}_2\text{-CH}_2\text{-O}$ ); 3.81 (t,  $J = 6.10$  Hz, 6H,  $\text{P(O)O-CH}_3$ ); 3.67 (m, 172H,  $\text{CH}_2\text{-CH}_2\text{-O}$ ); 3.39 (s, 3H,  $\text{O-CH}_3$ ); 2.66 (s, 1H,  $\text{NH}$ ); 2.31 (s, 3H;  $H_6$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 152.47 ( $\text{C}_2$ ); 146.74 ( $\text{C}=\text{C-N}_{\text{triazole}}$ ); 145.69 ( $\text{C}_5$ ); 123.05 ( $\text{C}=\text{C-N}_{\text{triazole}}$ ); 110.66 ( $\text{C}_3$ ); 106.68 ( $\text{C}_4$ ); 72.59 ( $\text{CH}_2\text{-O-CH}_3$ ); 70.51 ( $-\text{CH}_2\text{-O-CH}_2$ ); 69.47 ( $\text{N}_{\text{triazole}}\text{-CH}_2\text{-CH}_2\text{-O}$ ); 58.96 ( $\text{CHP}$ ); 53.66 ( $\text{P(O)O-CH}_3$ ); 52.37 ( $\text{CH}_3\text{-O}$ ); 50.14 ( $\text{N}_{\text{triazole}}\text{-CH}_2\text{-CH}_2\text{-O}$ ); 42.57 ( $\text{N-CH}_2$ ); 13.65 ( $\text{C}_6$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 161.96 MHz),  $\delta$  (ppm): 23.29.



**Figure S6.** <sup>1</sup>H NMR spectrum of dimethylphosphonate-terminated 5-methyl-2-furan-functionalized PEO monomethyl ether **5c**; solvent: CDCl<sub>3</sub>.



**3.4. General procedure for cleavage of dimethylphosphonate-terminated PEO monomethyl ethers (6a-b)**

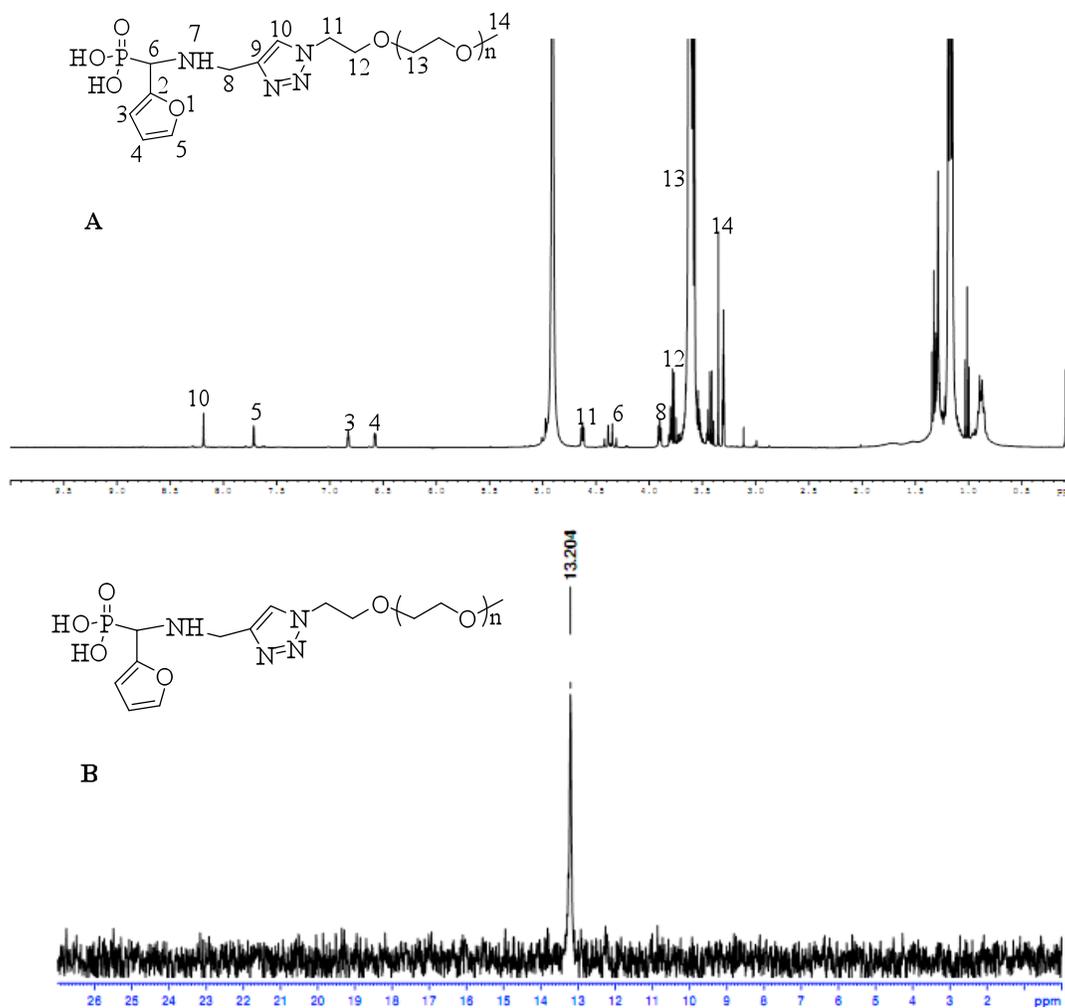


*Scheme S4: Synthesis of phosphonic acid-terminated furan-functionalized PEO monomethyl ethers (6a-b).*

A solution of the dimethylphosphonate-terminated PEO monomethyl ether (**5a-b**; 0.05 mmol) in 5 mL of DCM was added to a 100 mL two-necked flask equipped with a stir bar, a nitrogen inlet, and a dropping funnel. The solution was stirred at room temperature under nitrogen and a solution of trimethylsilyl bromide (TMSBr, 0.48 g, 3.2 mmol) in 5 mL of DCM was added dropwise via the dropping funnel. The reaction mixture was stirred for 24 h at room temperature. At the end of the reaction, the large excesses of bromosilane and DCM were removed by evaporation under low pressure. After the total elimination of bromosilane, ethanol (50 mL) was added to the flask and the stirring was continued for 24 h at room temperature. Ethanol was removed under reduced pressure to obtain the phosphonic acid-terminated PEO monomethyl ether **6a-b**.

*Phosphonic acid-terminated 2-furan-functionalized PEO monomethyl ether (6a).* Brown powder. Yield: 69%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD), δ (ppm): 8.18 (s, 1H, triazole); 7.72 (s, 1H, H<sub>5</sub>); 6.83 (t, J = 2.83 Hz, 1H, H<sub>3</sub>); 6.58 (q, J = 2.21 Hz, 1H, H<sub>4</sub>); 4.63 (t, J = 5.11 Hz, 2H, N<sub>triazole</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O); 4.37 (q, J = 15.78 Hz, 1H, CHP); 3.90 (t, J = 5.08 Hz, 2H, NH-

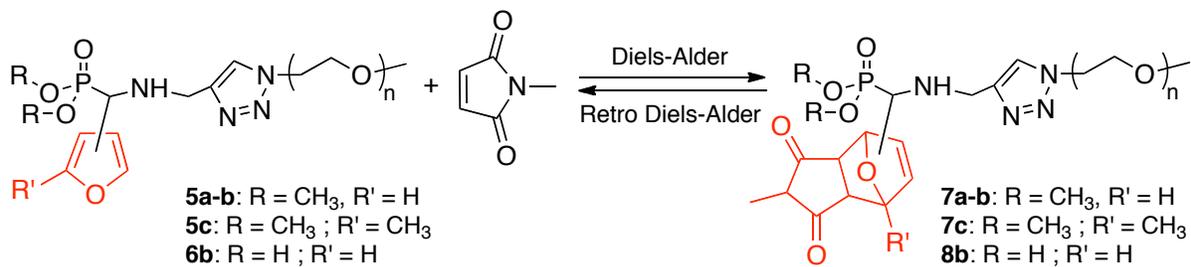
$CH_2$ ); 3.81 (d,  $J = 6.90$  Hz, 2H,  $N_{\text{triazole}}-CH_2-CH_2-O$ ); 3.75-3.40 (m, 172H,  $CH_2-CH_2-O$ );  
 3.35 (s, 3H,  $O-CH_3$ ); 2.88 (s, 1H, NH).  $^{13}C$  NMR (100 MHz,  $CD_3OD$ ),  $\delta$  (ppm): 146.26  
 ( $C_2$ ); 144.33 ( $C=C-N_{\text{triazole}}$ ); 138.68 ( $C_5$ ); 127.91 ( $C=C-N_{\text{triazole}}$ ); 115.22 ( $C_3$ ); 112.49 ( $C_4$ );  
 73.67 ( $CH_2-O-CH_3$ ); 71.45 ( $-CH_2-O-CH_2-$ ); 70.25 ( $N_{\text{triazole}}-CH_2-CH_2-O$ ); 59.12 (CHP); 58.29  
 ( $CH_3-O$ ); 50.01 ( $N_{\text{triazole}}-CH_2-CH_2-O$ ); 42.25 ( $N-CH_2$ ).  $^{31}P$  NMR ( $CD_3OD$ , 161.96 MHz),  $\delta$   
 (ppm): 13.20. FT-IR ( $\nu\text{ cm}^{-1}$ ) : 3423 ( $\nu_{OH}$ ); 2881 ( $\nu_{C-H}$ ); 1468 ( $\nu_{C=C\text{ triazole}}$ ); 1251 ( $\nu_{P=O}$ ).



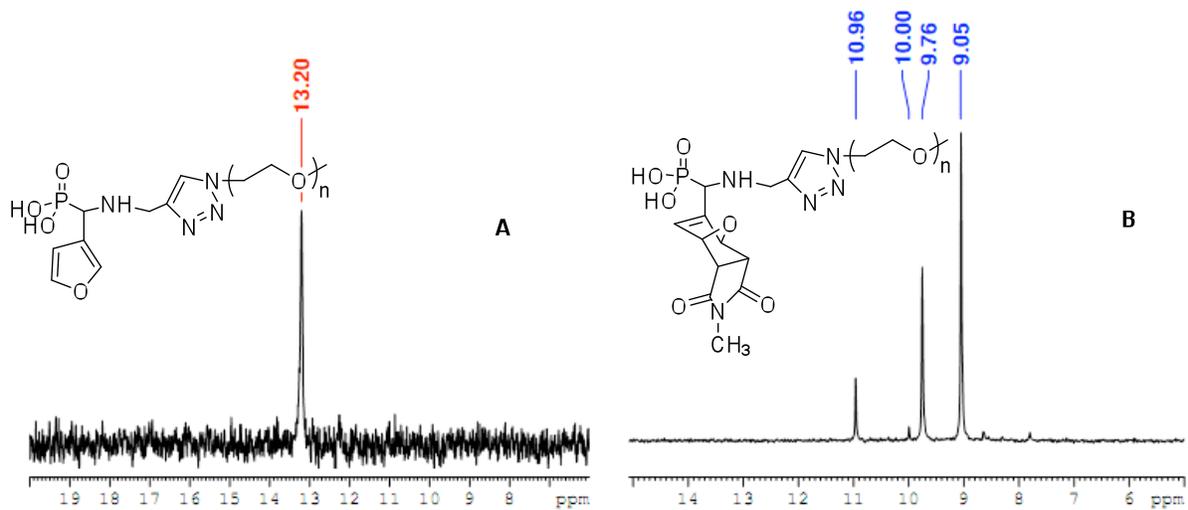
**Figure S8.**  $^1H$  (A) and  $^{31}P$  (B) NMR spectra of phosphonic acid-terminated 2-furan-functionalized PEO monomethyl ether **6a**; solvent:  $CD_3OD$ .

*Phosphonic acid-terminated 3-furan-functionalized PEO monomethyl ether (6b)*. Brown powder. Yield: 78%. NMR, FT-IR and MALDI-TOF MS data have previously been reported in reference 3.

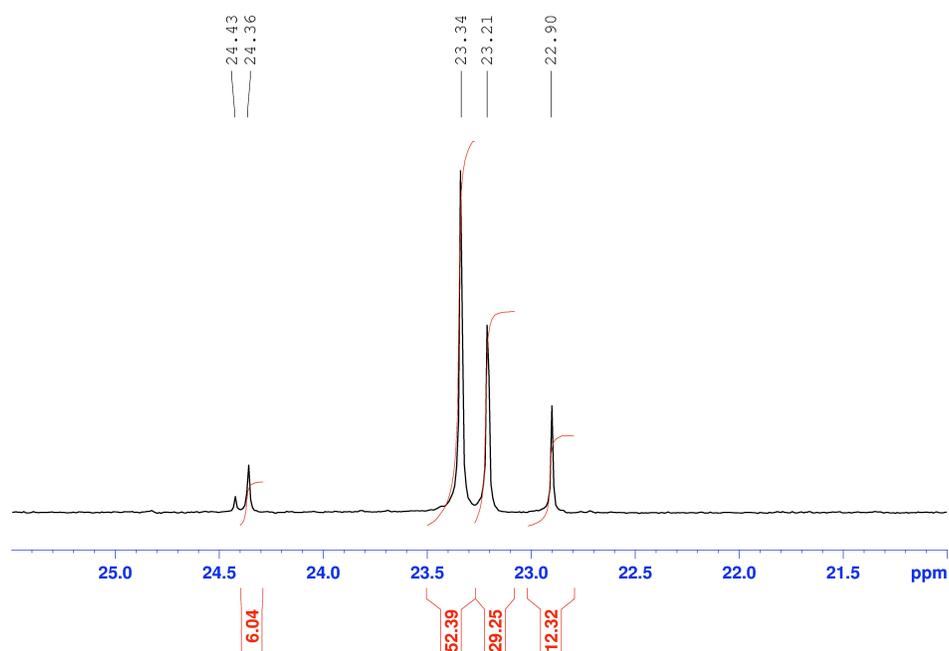
#### 4. Reactivity of the furan functionality in a Diels-Alder reaction



*Scheme S5: Diels-Alder and retro-Diels-Alder reactions between furan-functionalized PEO monomethyl ethers and N-methylmaleimide.*

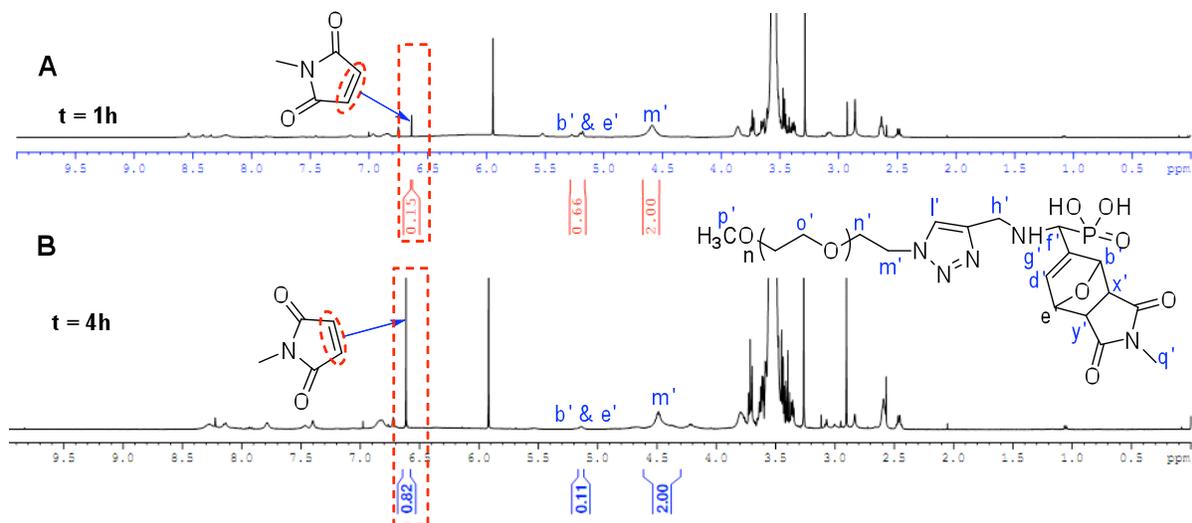


**Figure S9.** <sup>1</sup>H decoupled <sup>31</sup>P NMR spectra of (A) **6b** and (B) **8b**; solvent: CDCl<sub>3</sub>.



**Figure S10.** Quantitative  ${}^1\text{H}$  decoupled  ${}^{31}\text{P}$  NMR spectrum of **7b** acquired by a 1D sequence with inverse gated decoupling (zgif) and a relaxation delay of 30 s; solvent:  $\text{CDCl}_3$ .

## 5. Retro Diels-Alder reaction



**Figure S11.**  $^1\text{H}$  NMR spectra of the retro Diels-Alder reaction of **8b** in  $\text{TCE-d}_2$  at  $110^\circ\text{C}$  for (A)  $t = 1\text{ h}$ , (B)  $t = 4\text{ h}$ .

## 6. References

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