Electronic Supplementary Materials

Synthesis and CuAAC reactions of azidoalkylethoxysilanes; grafting CuAAC products onto silica surface

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Contents

1. Experimental details of the synthetic approaches of azidoalkylethoxysilanes (**3a-d**) and CuAAC reactions between **3b** and alkynes **4a-e**. pp2-9
2. NMR spectra (^1H , ^{13}C , ^{31}P) of new compounds pp10-19.

General Remarks

All reported boiling points are uncorrected. Silica (CARIACT Q-3, lot. No 3045071) was donated from Fuji Silysia Co. Ltd. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer operated at 400, 100 and 128 MHz, respectively. All ^1H and ^{13}C NMR spectra were referenced internally using residual chloroform signals in CDCl_3 (7.26 and 77.2 ppm, respectively). ^{31}P chemical shifts are reported externally relative to 85% aqueous H_3PO_4 (0.0 ppm). High-resolution mass spectra (HRMS) were obtained on a Hitachi M-80B operated at 75 eV using a direct inlet system. The ESI-HRMS spectrum was obtained on an Applied Biosystems Mariner system. Infrared spectra were recorded on a JASCO FT-IR4100 spectrometer. Elemental analyses were performed on a CE Instruments EA1100. Specific surface area and pore size distribution were obtained by nitrogen porosimetry using Bell Japan Inc, BELSORP-miniII.

1. Experimental details of the synthetic approaches of azidoalkylethoxysilanes.

Preparation of starting mesylate **1a**¹⁾ and tosylate **1b**²⁾ were according to the reported procedure.

Preparation of sulfonyl esters.

1-Methanesulfonyloxyhexa-5-ene (**1a**)

To a solution of ~~5-hexene-1-ol~~ ~~1-hydroxy 5-hexene~~ (2.4 mL, 20.4 mmol) and triethylamine (4.3 mL) in 80 mL of dry CH_2Cl_2 was added dropwise methanesulfonyl chloride (1.75 mL, 22.6 mmol) at 0°C under N_2 atmosphere. After completion of addition, the reaction mixture was poured into water (200 mL). The organic phase was washed with 1N HCl, saturated NaHCO_3 aqueous solution, and brine in the order. The organic phase was separated, dried with MgSO_4 , and evaporated to leave a residue. The resulting colorless liquid (3.51 g, 96%) was used for next step without further purification.

2-(~~pp-T~~ tolylsulfonyloxy)ethyl propenyl ether (**1b**)

To a solution of sodium hydroxide (4.6 g, 115 mmol) in water (25 mL) was added a solution of ethyleneglycol monoallyl ether (10.0 g, 98 mmol) in THF (50 mL) at 0 °C (ice/water bath). A solution of *p*-toluene sulfonyl chloride (17.9 g, 93 mmol) in THF (40 mL) was added dropwise to the alkaline solution at 0 °C. After completion of addition, the reaction mixture was stirred for 1 h at room temperature and poured into ice/water. The organic materials were extracted with hexane and hexane layer was washed with brine, dried with MgSO₄, and evaporated to leave a residue which was distilled under vacuum to give 22.4 g of 2-(*p*-tolylsulfonyloxy)ethyl propenyl ether (**1b**) as a colorless oil in 93% yield (22.4 g). b.p. 147-149 °C / 3.0 torr, ¹H NMR δ(400 MHz, CDCl₃) 7.80 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.80 (m, 1H), 5.30 (m, 2H), 4.10 (t, *J* = 7.1 Hz), 3.90 (d, *J* = 5.3 Hz, 2H), 3.50 (t, *J* = 7.1 Hz, 2H), 2.40 (s, 3H). This compound was used for next step without further treatment.

Preparation of azidoalkylethoxysilanes

1-Triethoxysilyl-6-azidohexane (**3a**)

To a solution of **1a** (2.66 g, 14.9 mmol) and 0.20 mL of Karstedt's catalyst xylene solution (2.1 wt% of platinum, purchased from Gelest) in dry THF (20 mL) was added dropwise a solution of triethoxysilane (3.1 mL, 17 mmol) in dry THF (20 mL) *via* syringe under N₂ atmosphere. The reaction temperature was maintained at 20 °C using a tap water bath. The reaction mixture was stirred for an additional 2 h at room temperature followed by removal of the volatiles under vacuum, which left brownish slightly viscous oil. Formation of the hydrosilylated intermediate and complete consumption of **1a** was confirmed by the upfield shift of the methylene protons adjacent to silicon and the disappearance of the olefinic protons of **1a** in the ¹H NMR measurement of the crude product. Dry DMF (40 mL) and sodium azide (1.95 g, 30 mmol) were then added to the reaction flask. After evacuation and refilling with nitrogen, the suspension was stirred at 60 °C for 12 h. The reaction mixture was filtered to remove the white solid (sodium salts and unreacted NaN₃) followed by concentration of the filtrate *in vacuo*. The crude mixture was purified by vacuum distillation (trap to trap distillation) to give 1-Triethoxysilyl-6-azidohexane (**3a**) (2.80 g, 65%) as a colorless liquid. bp 85-87 °C / 3.0 torr; ¹H NMR δ(400 MHz, CDCl₃) 3.80 (q, *J* = 7.1 Hz, 6H), 3.24 (t, *J* = 7.0 Hz, 2H), 1.58 (m, 2H), 1.45-1.32 (m, 6H), 1.21 (t, *J* = 7.1 Hz, 9H), 0.62 (m, 2H). ¹³C NMR δ(100 MHz, CDCl₃) 58.5, 51.6, 32.7, 28.9, 26.5, 22.8, 18.4, 10.5. ν_{max}(neat)/cm⁻¹ 2096 (N₃, vs). HRMS (ESI) Calcd for C₁₂H₂₇N₃O₃SiNa 312.1714; Found 312.1719.

1-Triethoxysilyl-4-oxa-6-azidohexane (**3b**)

To a solution of **1b** (20.0 g, 79 mmol) and 1.0 mL of Karstedt's catalyst xylene solution (2.1 wt% of platinum, purchased from Gelest) in dry THF (100 mL) was added dropwise triethoxysilane (19.2 g, 117 mmol) *via* syringe under nitrogen atmosphere. The reaction temperature was maintained at 20 °C using a tap water bath. The reaction mixture was stirred for an additional 2 h at room temperature followed by removal of the volatiles under vacuum, which left brownish slightly viscous oil. Formation of the hydrosilylated intermediate and complete consumption was confirmed by the upfield shift of the methylene protons adjacent to silicon and the disappearance of the olefinic protons of the starting material **1b** in the ¹H NMR measurement of the crude product. Dry DMF (100 mL) and sodium azide (10.0 g, 154 mmol) were then added to the reaction flask. After evacuation and refilling with N₂, the suspension was stirred at 60 °C for 12 h. The reaction mixture was filtered to remove the white solid followed by concentration of the filtrate *in vacuo*. The crude mixture was purified by vacuum distillation to give 1-Triethoxysilyl-4-oxa-6-azidohexane (**3b**) (14.3 g, 65%) as a colorless liquid. bp 92-93 °C / 3.0 torr; ¹H NMR δ (400 MHz, CDCl₃) 3.84 (q, *J* = 7.1 Hz, 6H), 3.63 (t, *J* = 5.0 Hz, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 3.38 (t, *J* = 5.0 Hz, 2H), 1.73 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 9H), 0.69 (m, 2H). ¹³C NMR δ (100 MHz, CDCl₃) 73.5, 69.4, 58.3, 50.8, 23.0, 18.2, 6.3. ν_{max} (neat)/cm⁻¹ 2104 (N₃, vs). Anal. Calcd for C₁₁H₂₅N₃O₄Si; C, 45.34; H, 8.65; N, 14.41; Found: C, 45.52; H, 8.66; N, 14.07.

1-(Methyldiethoxy)silyl-4-oxa-6-azidohexane (**3c**)

To a solution of **1b** (5.1 g, 20 mmol) and 0.3 mL of Karstedt's catalyst xylene solution (2.1 wt% of platinum, purchased from Gelest) in dry THF (30 mL) was added dropwise diethoxymethylsilane (4.03 g, 30.0 mmol) *via* syringe under nitrogen atmosphere. The reaction temperature was maintained at 20 °C using a tap water bath. The reaction mixture was stirred for an additional 2 h at room temperature

followed by removal of the volatiles under vacuum, which left brownish slightly viscous oil. Formation of the hydrosilylated intermediate and complete consumption was confirmed by the upfield shift of the methylene protons adjacent to silicon and the disappearance of the olefinic protons of the starting material **1b** in the ^1H NMR measurement of the crude product. Dry DMF (25 mL) and sodium azide (2.60 g, 40.0 mmol) were then added to the reaction flask. After evacuation and refilling with N_2 , the suspension was stirred at 60°C for 12 h. The reaction mixture was filtered to remove the white solid followed by concentration of the filtrate *in vacuo*. The crude mixture was purified by vacuum distillation to give 1-(methyldiethoxy)silyl-4-oxa-6-azidohexane (**3c**) (3.08 g, 59%) as a colorless liquid. bp $73 - 77^\circ\text{C} / 3$ torr; ^1H NMR δ (400 MHz, CDCl_3) 3.78 (q, $J = 7.0$ Hz, 4H), 3.63 (t, $J = 5.0$ Hz, 2H), 3.47 (t, $J = 6.6$ Hz, 2H), 3.39 (t, $J = 5.0$ Hz, 2H), 1.68 (m, 2H), 1.23 (t, $J = 7.1$ Hz, 6H), 0.66 (m, 2H), 0.14 (s, 3H). ^{13}C NMR δ (100 MHz; CDCl_3) 73.7, 69.4, 58.1, 50.8, 23.0, 18.3, 9.8, -5.0. ν_{max} (neat)/ cm^{-1} 2108 (N_3 , vs). Anal. Calcd for $\text{C}_{10}\text{H}_{23}\text{N}_3\text{O}_3\text{Si}$; C, 45.95; H, 8.87; N, 16.08; Found: C, 45.87; H, 8.92; N, 15.85.

1-(Dimethylethoxy)silyl-4-oxa-6-azidohexane (**3d**)

To a solution of **1b** (5.1 g, 20 mmol) and 0.3 mL of Karstedt's catalyst xylene solution (2.1 wt% of platinum, purchased from Gelest) in dry THF (30 mL) was added dropwise diethoxymethylsilane (3.13 g, 30.0 mmol) *via* syringe under nitrogen atmosphere. The reaction temperature was maintained at 20°C using a tap water bath. The reaction mixture was stirred for an additional 2 h at room temperature followed by removal of the volatiles under vacuum, which left brownish slightly viscous oil. Formation of the hydrosilylated intermediate and complete consumption was confirmed by the upfield shift of the methylene protons adjacent to silicon and the disappearance of the olefinic protons of the starting material **1b** in the ^1H NMR measurement of the crude product. Dry DMF (25 mL) and sodium azide (2.60 g, 40.0 mmol) were then added to the reaction flask. After evacuation and refilling with N_2 , the suspension was stirred at 60°C for 12 h. The reaction mixture was filtered to remove the white solid followed by concentration of the filtrate *in vacuo*. The crude mixture was purified by vacuum distillation to give 1-(dimethylethoxy)silyl-4-oxa-6-azidohexane (**3d**) (1.94 g, 42%), colorless liquid, bp $60 - 64^\circ\text{C} / 3$ torr; ^1H NMR δ (400 MHz, CDCl_3) 3.63 (q, $J = 7.1$ Hz, 2H), 3.58 (t, $J = 5.0$ Hz, 2H), 3.42 (t, $J = 7.1$ Hz, 2H), 3.34 (t, $J = 5.0$ Hz, 2H), 1.60 (m, 2H), 1.14 (t, $J = 7.1$ Hz, 3H), 0.59 (m, 2H), 0.08 (s, 6H). ^{13}C NMR δ (100 MHz, CDCl_3) 74.0, 69.4, 58.2, 50.8, 23.9, 18.5, 12.2, -2.1. ν_{max} (neat)/ cm^{-1} 2106 (N_3 , vs). Anal. Calcd for $\text{C}_9\text{H}_{21}\text{N}_3\text{O}_2\text{Si}$; C, 46.72; H, 9.15; N, 18.15;

Found: C, 46.04; H, 8.99; N, 17.91. HRMS (ESI) Calcd for $C_9H_{21}N_3O_2SiN_3$ 254.1301; Found 254.1295.

CuI catalyzed CuAAC reactions between **3b and alkynesd.**

1-[(1-Triethoxysilyl)-4-oxahexyl]-4-butyl-1*H*-1,2,3-triazole (5a**):**

To a suspension of **3b** (291 mg, 1.0 mmol), 1-hexyne **4a** (164 mg, 2.0 mmol), and CuI (19 mg, 0.1 mmol) in dry THF (10 mL) were added along with DIPEA (129 mg, 1.0 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was evaporated, leaving a residual pale yellow oil, which was extracted with hexane (50 mL). The hexane extract was washed with water and brine several times, dried with Mg_2SO_4 , and concentrated to leave a residue. The resulting oil was dissolved in --hexane and the solution was passed through a short silica gel column (Merck 60) using EtOAc-hexane (1/2, v/v) as an eluent to give pure **5a** (357 mg, 96%) as a colorless oil. 1H NMR δ (400 MHz, $CDCl_3$) 7.42 (s, 1H), 4.50 (td, $J = 5.2$ Hz, 2H), 3.81 (q, $J = 7.1$ Hz, 6H), 3.77 (t, $J = 5.3$ Hz, 2H), 3.40 (t, $J = 6.7$ Hz, 2H), 2.73 (t, $J = 8.0$ Hz, 2H), 1.66 (m, 4H), 1.39 (sextet, $J = 7.3$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 9H), 0.93 (t, $J = 7.3$ Hz, 3H), 0.60 (m, 2H). ^{13}C NMR δ (100 MHz, $CDCl_3$) 148.7, 122.2, 73.9, 69.4, 58.8, 50.7, 32.0, 25.8, 23.3, 22.7, 18.7, 14.2, 6.9. ν_{max} (neat)/ cm^{-1} 3155, 2972, 2929, 2876, 1551. HRMS (EI) Calcd for $C_{17}H_{35}N_3O_4Si$ 373.2397; Found 373.2407.

1-[(1-Triethoxysilyl)-4-oxahexyl]-4-(acetoxymethyl)-1*H*-1,2,3-triazole (5b**)**

To a suspension of **3b** (291 mg, 1.0 mmol), 1-propynylacetate **4b** (98 mg, 1.0 mmol), and CuI (19 mg, 0.1 mmol) in dry THF (10 mL) were added along with DIPEA (129 mg, 1.0 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was evaporated, leaving a residual pale yellow oil, which was extracted with hexane (50 mL). The hexane extract was washed with water and brine several times, dried with Mg_2SO_4 , and concentrated to leave a residue. The resulting oil was dissolved in hexane and the solution was

passed through a short silica gel column (Merck 60) using EtOAc-hexane (1/2, v/v) as an eluent to give pure **5b** (323 mg, 83%) as a colorless oil. ^1H NMR δ (400 MHz, CDCl_3) 7.74 (s, 1H), 5.21 (s, 2H), 4.53 (td, $J = 5.2$ Hz, 2H), 3.80 (q, $J = 7.0$ Hz, 6H), 3.78 (t, $J = 5.2$ Hz, 2H), 3.40 (t, $J = 6.7$ Hz, 2H), 2.07 (s, 3H), 1.65 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 9H), 0.58 (m, 2H). ^{13}C NMR δ (100 MHz, CDCl_3) 170.7, 142.5, 124.7, 73.4, 68.6, 58.3, 57.5, 50.3, 22.8, 20.7, 18.2, 6.3. ν_{max} (neat)/ cm^{-1} 3144, 3092, 2974, 2927, 2884, 1743, 1481. HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{31}\text{N}_3\text{O}_6\text{Si}$ 389.2001; Found 389.1982.

1-[(1-Triethoxysilyl)-4-oxahexyl]-4-phenyl-1H-1,2,3-triazole (**5c**)

To a suspension of **3b** (291 mg, 1.0 mmol), phenylacetylene **4c** (102 mg, 1.0 mmol), and CuI (19 mg, 0.1 mmol) in THF (10 mL) were added along with DIPEA (129 mg, 1.0 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was evaporated, leaving a residual pale yellow oil, which was extracted with hexane (50 mL). The hexane extract was washed with water and brine several times, dried with Mg_2SO_4 , and concentrated to leave a residue. The resulting oil was dissolved in hexane and the solution was passed through a short silica gel column (Merck 60) using EtOAc-hexane (1/2, v/v) as an eluent to give pure **5c** (251 mg, 64%) as a colorless oil. ^1H NMR δ (400 MHz, CDCl_3) 7.95 (s, 1H), 7.86 (d, $J = 7.2$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 1H), 4.60 (td, $J = 5.0$ Hz, 2H), 3.85 (t, $J = 5.0$ Hz, 2H), 3.81 (q, $J = 7.0$ Hz, 6H), 3.46 (t, $J = 6.6$ Hz, 2H), 1.71 (m, 2H), 1.22 (t, $J = 7.0$ Hz, 9H), 0.63 (m, 2H). ^{13}C NMR δ (100 MHz, CDCl_3) 148.1, 131.2, 129.2, 128.4, 126.1, 121.2, 73.9, 69.3, 58.8, 50.9, 23.3, 18.7, 6.9. ν_{max} (neat)/ cm^{-1} 3135, 2973, 2926, 1610, 1104, 1078. HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{31}\text{N}_3\text{O}_4\text{Si}$ 393.2084; Found 393.2066.

1-[(1-Triethoxysilyl)-4-oxahexyl]-4-(2-pyridyl)-1H-1,2,3-triazole (**5d**)

To a suspension of **3b** (281 mg, 0.96 mmol), 2-ethynylpyridine **5d** (103 mg, 1.0 mmol), and CuI (19 mg, 0.1 mmol) in THF (10 mL) were added along with DIPEA (129 mg, 1.0 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was evaporated, leaving a residual pale yellow oil, which was extracted with hexane (50 mL). The hexane extract was washed with water and brine several times, dried with Mg₂SO₄, and concentrated to leave a residue. The resulting oil was dissolved in hexane and the solution was passed through a short silica gel column (Merck 60) using EtOAc-hexane (1/2, v/v) as an eluent to give pure **5d** (168 mg, 55%) as a colorless oil. ¹H NMR δ (400 MHz, CDCl₃) 8.57 (ddd, *J* = 5.1, 1.8, 0.9 Hz, 1H), 8.22 (s, 1H), 8.16 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.22 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 4.60 (td, *J* = 5.0 Hz, 2H), 3.84 (t, *J* = 5.3 Hz, 2H), 3.78 (q, *J* = 7.1 Hz, 6H), 3.43 (t, *J* = 6.7 Hz, 2H), 1.67 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 9H), 0.60 (m, 2H). ¹³C NMR δ (100 MHz, CDCl₃) 150.4, 149.3, 148.1, 136.7, 123.0, 122.6, 120.1, 73.5, 68.7, 58.3, 50.4, 22.8, 18.2, 6.4. *v*_{max}(neat)/cm⁻¹ 3141, 2973, 2926, 2884, 1603, 1571, 1421, 1105, 1078. HRMS (EI) Calcd for C₁₈H₃₀N₄O₄Si 394.2036; Found 394.2049.

1-[(1-Triethoxysilyl)-4-oxahexyl]-4-(methyldiphenylphosphine-borane)-1*H*-1,2,3-triazole (**S-5e**)

To a suspension of **3b** (1.0 g, 3.5 mmol), **5e** (800 mg, 3.5 mmol), and CuI (64 mg, 0.1 mmol) in THF (30 mL) were added along with DIPEA (129 mg, 1.0 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was evaporated, leaving a residual pale yellow oil, which was extracted with hexane (50 mL). The hexane extract was washed with water and brine several times, dried with Mg₂SO₄, and concentrated to leave a residue. The resulting oil was dissolved in hexane and the solution was passed through a short silica gel column (Merck 60) using EtOAc-hexane (1/2, v/v) as an eluent to give pure **5e** (1.31 g, 71%) as a colorless oil. ¹H NMR δ (400 MHz, CDCl₃) 7.70-7.65 (m, 4H), 7.57 (s, 1H), 7.50-7.40 (m, 6H), 4.41 (td, *J* = 5.3 Hz, 2H), 3.82 (q, *J* = 7.1 Hz, 6H), 3.78 (d, *J* = 9.7 Hz, 2H), 3.69 (t, *J* = 5.2 Hz, 2H), 3.33 (t, *J* = 6.8 Hz, 2H), 1.63 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 9H), 0.58 (m, 2H). ¹³C NMR δ (100 MHz, CDCl₃) 132.9, 132.8, 131.9, 129.3, 129.2, 129.1, 74.0, 69.2, 58.8, 50.89, 23.326, 18.73, 6.985, 6.00. δ_p 17.7. *v*_{max}(neat)/cm⁻¹ 3149, 3057, 2973, 2924, 2883, 1543, 1105, 1077. Anal. Calcd for C₂₆H₄₁BN₃O₄PSi; C, 58.97; H, 7.81; N, 7.94; Found C, 58.94; H, 7.84; N, 7.81.

CuAAC reaction between 3b and 4c using a catalyst combination of CuSO₄ and sodium ascorbate. To a solution of **3b** (291 mg, 1.0 mmol) and phenyl acetylene **4c** (104 mg, 1.0 mmol) in THF (5 mL) was added 0.1 M CuSO₄ aqueous solution (1.0 mL) and 0.1 M sodium ascorbate aqueous solution (2.5 mL) at room temperature. The reaction mixture was stirred for 12 h followed by addition of CH₂Cl₂ (20 mL). The organic layer was washed with brine and dried over MgSO₄. The reaction products were purified by short silica gel column chromatography (Merck 60) to give 216 mg of pure **5c** (216 mg, 56%) as a colorless oil.

Grafting of 5b onto silica.

A suspension of –silica (500 mg) and **5b** (167 mg, 0.43 mmol) in dry toluene (10 mL) was heated at 60 °C for 3 h. The resulting suspension was filtered and washed with toluene and methanol then dried under vacuum. GC analysis of the filtered mother liquor showed that no unreacted **5b** was present. The color of the obtained modified silica (**7b**) was clear white, almost the same as the color of the starting silica (Q-3). The amount of 1,2,3-triazole unit introduced on the silica surface was estimated to be approximately 0.53 mmol/g from elemental analysis. Found C, 8.25; H, 1.87; N, 2.21.

Heterogeneous CuAAC reaction between 6 and 4b.

CuAAC reaction using CuI: To a suspension of azidoalkyl-modified silica (**6**) (500 mg, 0.345 mmol of N₃), propynyl acetate **4b** (69 µL, 0.70 mmol) and CuI (6.7 mg, 0.035 mmol) in THF (10 mL) was added DIPEA (61 µL, 0.35 mmol) *via* micro-syringe in one addition. The reaction mixture was stirred for 12 h at room temperature under N₂ followed by filtering and washing several times with toluene and methanol. The white material was dried under vacuum at room temperature overnight. The IR spectrum of the obtained white silica (**7aa**) showed absorption signals of both the azido and ester groups.

CuAAC reaction using CuSO₄: To a suspension of **6** and **4b** (69 µL) in THF (10 mL) was added 700 µL (0.07 mmol) of –CuSO₄·5H₂O aqueous solution (0.1 mol/L) and 1.75 mL (0.175 mmol) of 0.1 M sodium L-ascorbate aqueous solution at room temperature under N₂ atmosphere. The reaction mixture was then allowed to stir for 12 h at room temperature. The resulting yellow solid was collected by filtration, was washed with THF and methanol several times, and was dried under vacuum. The IR spectra of the obtained yellow silica (**7ab**) showed the absorption signals both of the azido- and ester groups.

References

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^1H and ^{13}C NMR spectra of **3a**

^1H and ^{13}C NMR spectra of **3b**

^1H and ^{13}C NMR spectra of **3c**.

^1H and ^{13}C NMR spectra of **3d**.

^1H and ^{13}C NMR spectra of **5a**

^1H and ^{13}C NMR spectra of **5b**

^1H and ^{13}C NMR spectra of **5c**

^1H and ^{13}C NMR spectra of **5d**

^1H , ^{13}C and ^{31}P NMR spectra of **5e**