Electronic Supplementary Information

Surface Patterning with Natural and Synthetic Polymers via an Inverse Electron Demand Diels-Alder Reaction Employing Microcontact Chemistry

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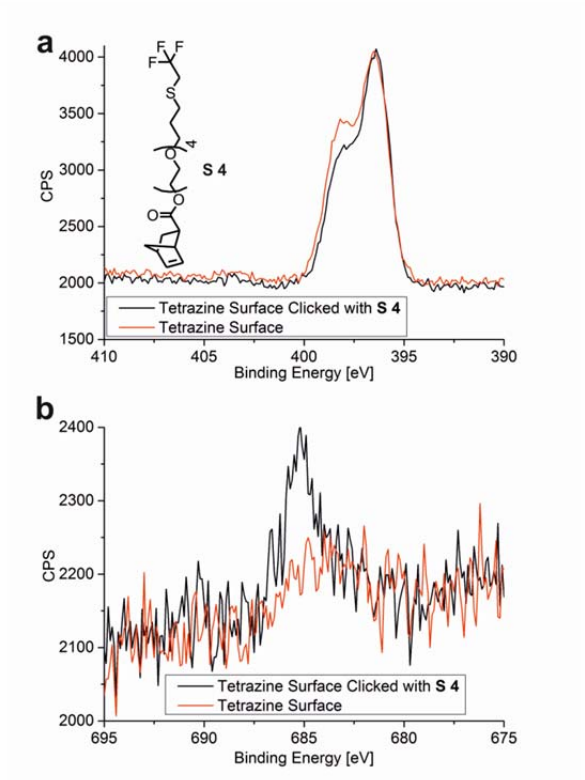


Figure S1: a) XPS Spectrum overlay of the N1s signals of a tetrazine SAM reacted with **S4** (black) and a tetrazine SAM (red) and b) XPS Spectrum overlay of the F1s signals of a tetrazine SAM reacted with **S4** (black) and a tetrazine SAM (red).

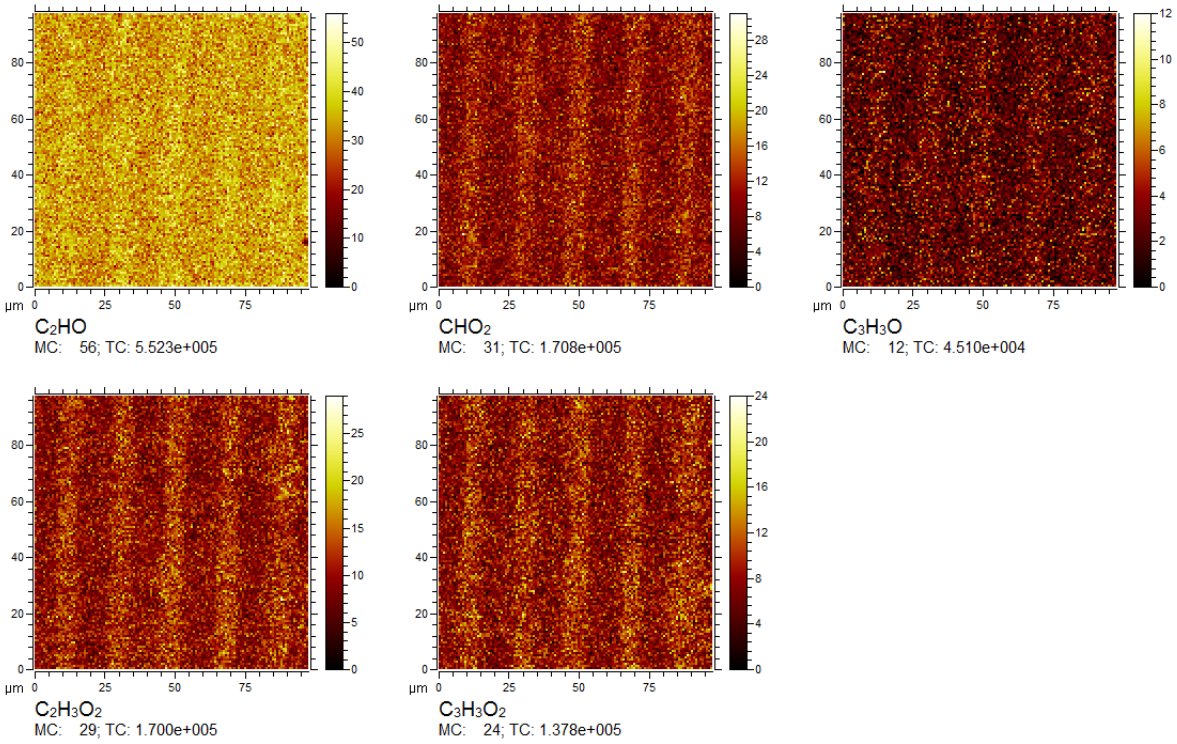


Figure S2: ToF-SIMS data of detected negative ions of a tetrazine functionalized silicon surface patterned via µCC with galactose **2** (MC: maximum counts, TC: total counts).

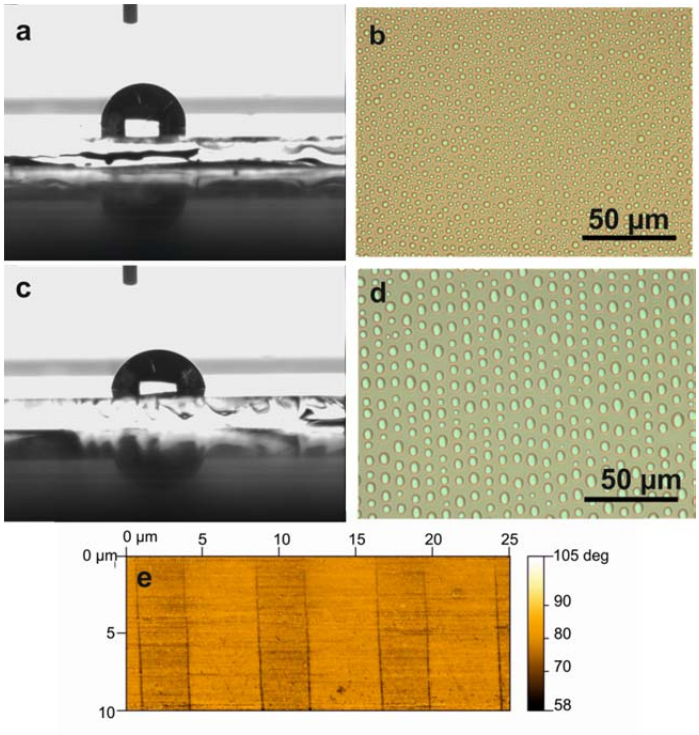
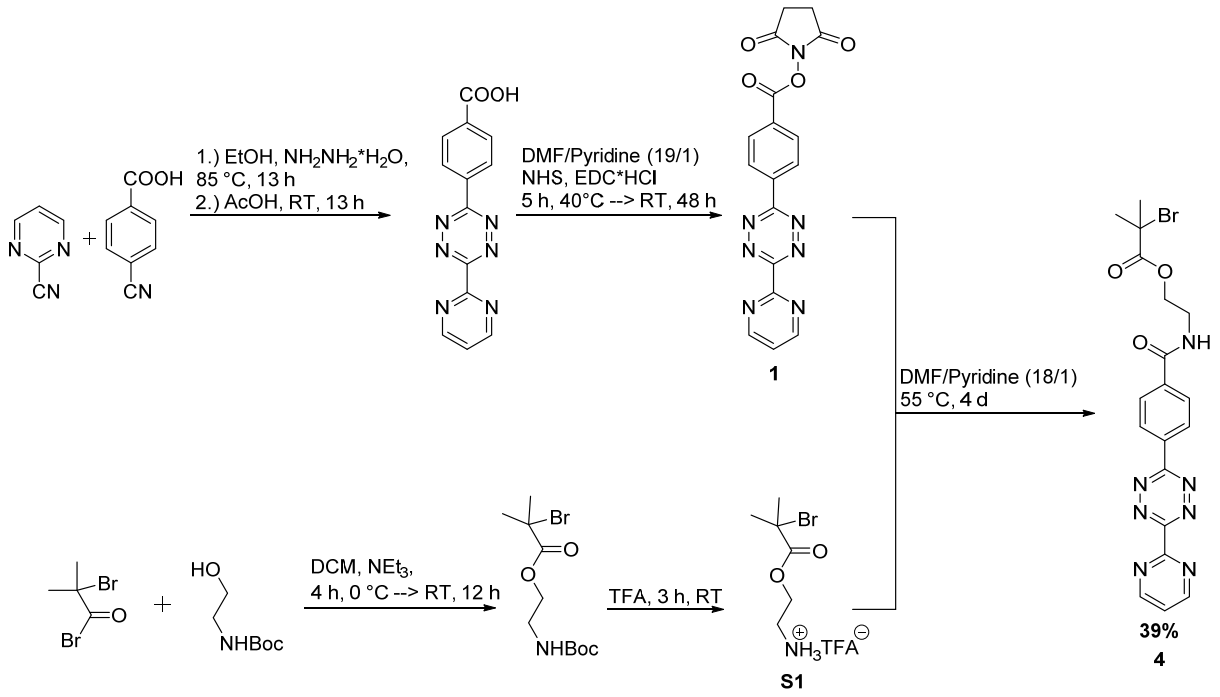


Figure S3: a) Water droplet disposed onto an 10-undecenyl trichlorosilane SAM, b) water condensation on a 10-undecenyl trichlorosilane SAM (40-fold magnification), c) water droplet disposed onto a substrate functionalized with **4** (flat stamp), d) water condensation experiments on a 10-undecenyl trichlorosilane substrate functionalized with **4** printed in 5 µm stripes spaced by 3 µm (40-fold magnification) and e) AFM phase image of a 10-undecenyl trichlorosilane functionalized silicon substrate functionalized with **4** printed in 5 µm stripes spaced by 3 µm.

Table S1: Contact angle goniometry data of an 10-undecenyl trochlorosilane SAM and the ATRP initiator **4** printed with a flat stamp.

	Alkene SAM	**Initiator 4**
Stat./°	100±1	83±1
Adv./°	106±1	85±1
Rec./°	86±1	65±2

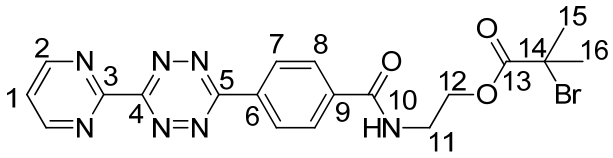
Synthesis



Scheme S1: Schematic representation of the synthesis of ATRP initiator **4**.

Compounds **1** and **S1** have been synthesized according to published routes.[1,2] The synthesis of the norbornene and cyclooctyne conjugated carbohydrates has also been reported before.[3]

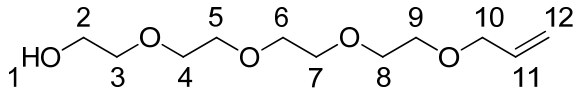
Synthesis of 4



1 (0.200 g, 0.530 mmol, 1 eq.) was dissolved in a mixture of DMF/ pyridine (18/1, 10 mL) and heated to 55 °C. Subsequently **S1** (0.222 g, 0.685 mmol, 1.3 eq.) was dissolved in DMF/pyridine (18/1, 1.25 mL) and added to **1** in portions over 3.5 h. The reaction mixture was then stirred for 4 days. The solvent was removed and the crude product was purified via column chromatography (DCM/MeOH, 97/3, R_f = 0.2) in order to yield the pure product as a violet powder (0.097 g, 0.206 mmol, 39%). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 9.13 (d, *J* = 4.9 Hz, 2H, H-2), 8.80 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.60 (t, *J* = 4.9 Hz, 1H, H-1), 6.75 (s, 1H, NH), 4.45 (t, *J* = 5.1 Hz, 2H, H-12), 3.86 (m, 2H, H-11), 1.96 (s, 6H, H-15, H-16). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 171.8 (C_q) , 166.5 (C_q), 164.0 (C_q), 163.2 (C_q), 159.5 (C_q), 158.4 (C_{Ar}), 138.4 (C_{Ar}), 129.0 (C_{Ar}), 128.0 (C_{Ar}), 122.6 (C_{Ar}), 110.0 (C_{Ar}), 64.5,

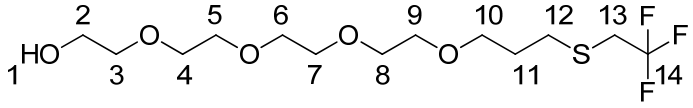
56.2, 39.3, 30.6. ESI-HRMS (m/z): calculated: $[C_{19}H_{18}BrN_7O_3Na]^+$: 494.0547, found: 494.0535.

Synthesis of allylic tetra ethylene glycol (S2)



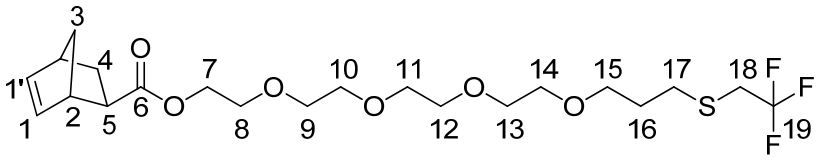
Tetra ethylene glycol (10.03 g, 51.65 mmol, 1 eq.) was dissolved in THF (60 mL) and potassium *tert*-butoxide (5.80 g, 51.65 mmol, 1 eq.) was added. The mixture was cooled to 0 °C and allyl bromide (7.50 g, 61.99 mmol, 1.2 eq.) dissolved in THF (15 mL) was added dropwise. The reaction mixture was stirred at room temperature over night. The solvent was dissolved in water (100 mL) and extracted with DCM (3x150 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed. The crude product was purified via column chromatography (DCM/MeOH, 95/5, R_f = 0.31) in order to yield the desired product as a colourless oil (4.20 g, 17.91 mmol, 35%). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 5.90 (m, 1H, H-11), 5.35 – 5.09 (m, 2H, H-12), 4.01 (m, 2H, H-10), 3.78 – 3.53 (m, 16H, H-2 to H-9). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 134.8 (C-11), 117.3 (C-12), 72.7, 72.4, 70.7, 70.4, 69.5, 61.9. ESI-HRMS (m/z): calculated: $[C_{11}H_{22}O_5Na]^+$: 257.1359, found: 257.1368

Synthesis of fluorinated tetra ethylene glycol (S3)



S2 (0.50 g, 2.13 mmol, 1 eq.), 2,2,2-trifluoro ethanethiol (0.49 g, 4.26 mmol, 2 eq.) and 2,2-dimethoxy-2-phenylacetophenone (0.05 g, 0.20 mmol, 0.09 eq.) were dissolved in MeOH (10 mL) and stirred for 48 h at room temperature under UV-irradiation (365 nm). The solvent was evaporated and the crude product purified via column chromatography (ethyl acetate, R_f = 0.27) in order to yield the desired product as an yellowish oil (0.383 g, 1.093 mmol, 51%). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 3.73 – 3.52 (m, 18H, H-2 to H-10), 3.08 (q, *J* = 10.0 Hz, 2H, H-13), 2.75 (t, *J* = 7.2 Hz, 2H, H-12), 1.91 – 1.82 (m, 2H, H-11). ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.8 , 70.7 – 70.6 (m), 70.4, 69.3 , 61.8 , 34.5 (q, *J* = 32.7 Hz, C-13), 30.1 (C-11), 29.3 (C-12). ^{19}F NMR (282 MHz, $CDCl_3$) δ/ppm = -66.46 (t, *J* = 10.0 Hz). ESI-HRMS (m/z): calculated: $[C_{13}H_{25}F_3O_5SNa]^+$: 373.1267, found: 373.1276

Synthesis of fluorinated norbornene (S4)



S3 (0.150 g, 0.428 mmol, 1.2 eq.) was dissolved in dry DMF (2 mL) and exo-5-norbornene-2-carboxylic acid (0.050 g, 0.362 mmol, 1 eq.), NMM (0.043 g, 0.425 mmol, 1.2 eq.), HOBt*H_2O (0.005 g, 0.037 mmol, 0.1 eq.) and EDC*HCl (0.082 g, 0.427 mmol, 1.2 eq.) were added. The reaction mixture was stirred at room temperature for 24 h. Subsequently the solvent was removed and the crude product was purified via column chromatography (ethyl acetat/cyclohexane, 1/1, R_f = 0.35) in order to yield the desired product as a yellowish resin (0.057 g, 0.121 mmol, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 6.14 – 6.08 (m, 2H, H-1, H-1'), 4.25 – 4.22 (m, 2H, H-7), 3.71– 3.53 (m, 16H, H-8 to H-15), 3.07 (q, *J* = 10.0 Hz, 2H, H-18), 2.91 (s, 1H), 2.75 (t, *J* = 7.3 Hz, 2H, H-17), 2.27 – 2.23 (m, 1H), 1.94 – 1.83 (m, 3H), 1.53 – 1.51 (m, 1H), 1.38 – 1.24 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm = 176.4 (C-6), 138.2 (C-1 or C-1') , 135.9 (C-1 or C-1'), 70.8 – 70.7 (m), 70.4 , 69.4 , 69.3, 63.6 , 46.8 , 46.4 , 43.2 , 41.8 , 34.6 (q, *J* = 32.5 Hz, C-18), 30.5 , 30.1 (C-16), 29.4 (C-17).
^{19}F NMR (282 MHz, $CDCl_3$) δ/ppm = -66.45 (t, *J* = 10.0 Hz). ESI-HRMS (m/z): calculated: $[C_{21}H_{33}F_3O_6SNa]^+$: 493.1842, found: 493.1847

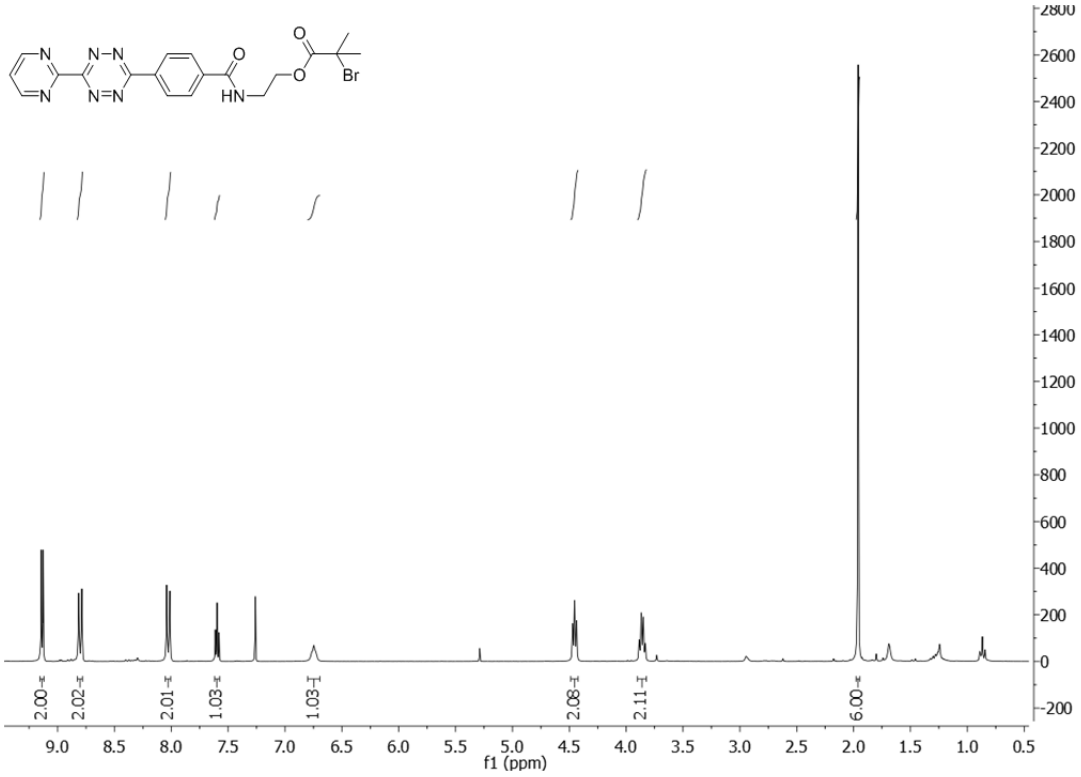


Figure S4: ^{1}H NMR (300 MHz, $CDCl_3$) of **4**

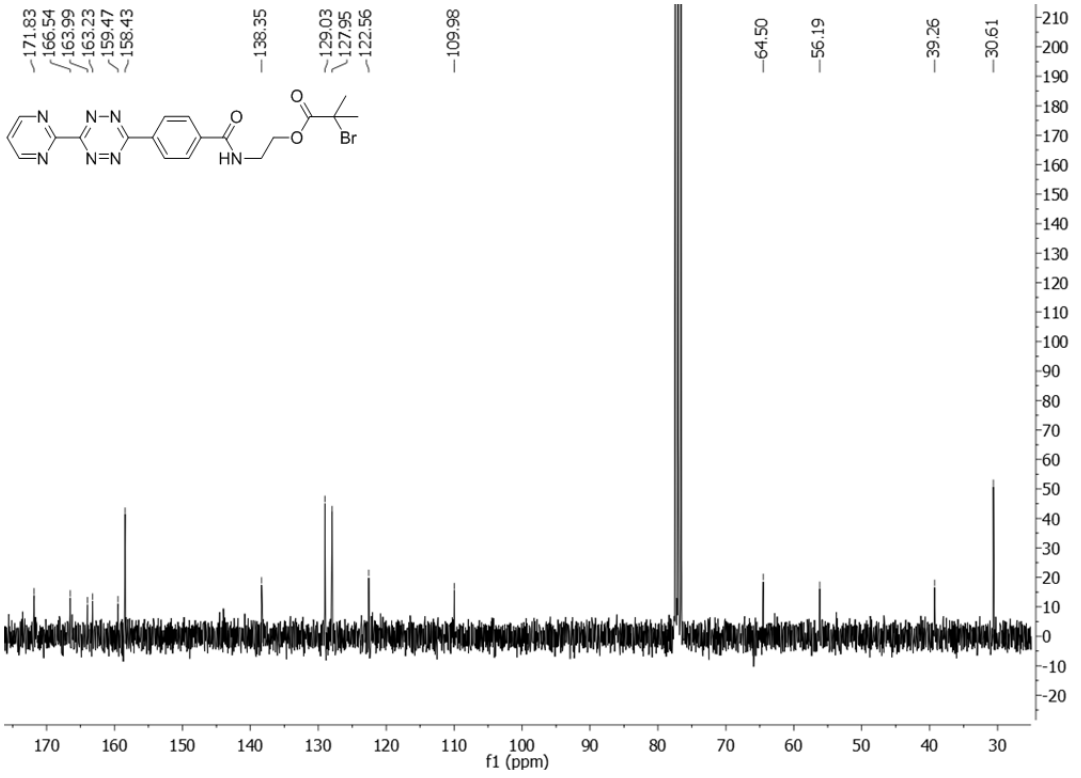


Figure S5: ^{13}C NMR (75 MHz, $CDCl_3$) of **4**

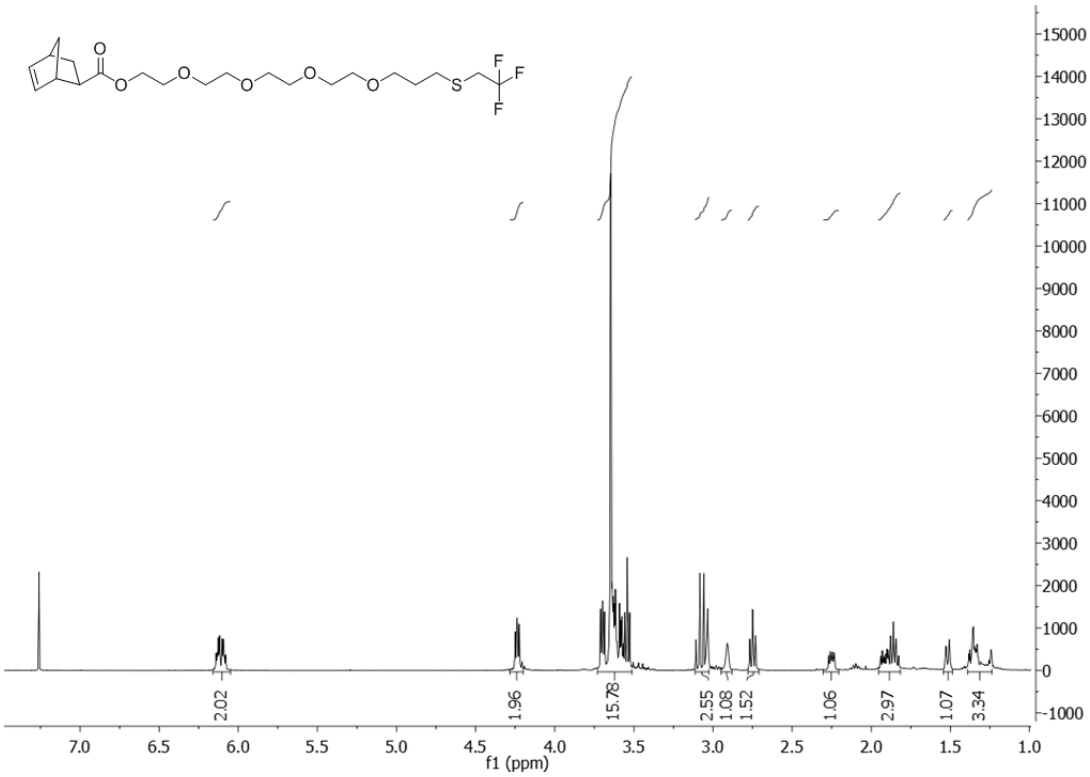


Figure S6: ^{1}H NMR (400 MHz, $CDCl_3$) of **S4**

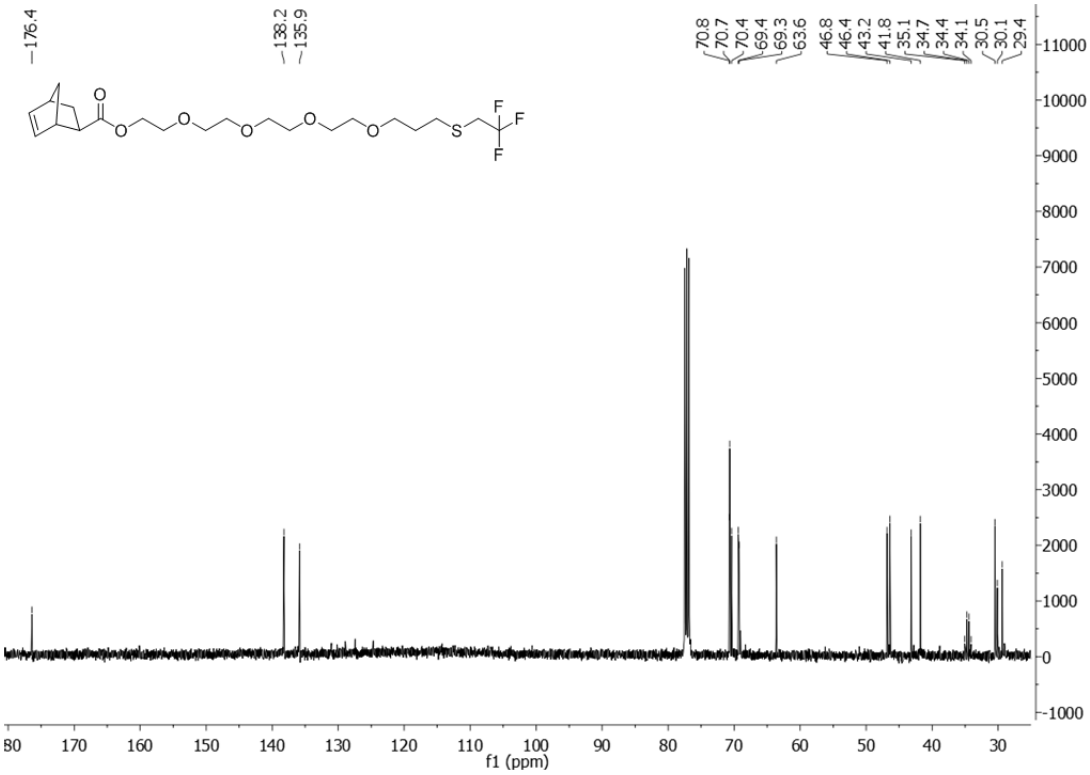


Figure S7: ^{13}C NMR (101 MHz, $CDCl_3$) of **S4**

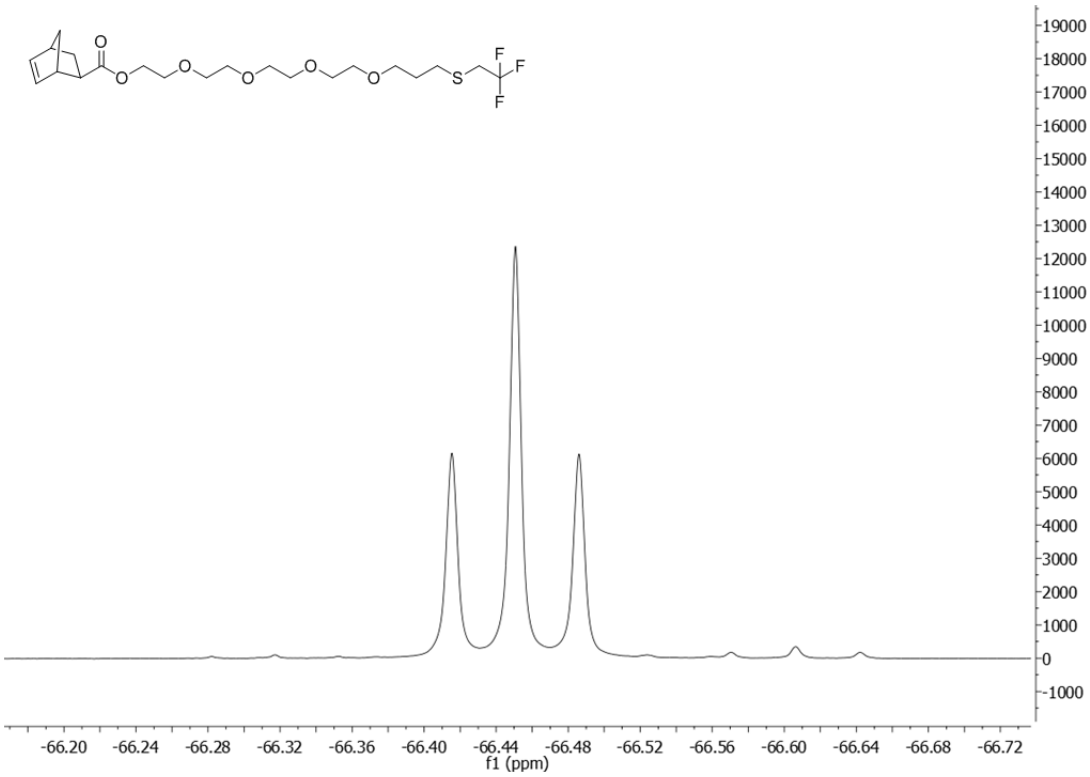


Figure S8: ^{19}F NMR (282 MHz, $CDCl_3$) of **S4**

Literature:

1 H. S. G. Beckmann, A. Niederwieser, M. Wiessler and V. Wittmann, *Chem. – Eur. J.* **2012**, *18*, 6548–6554.

2 Z. Yang, S. Zheng, W. J. Harrison, J. Harder, X. Wen, J. G. Gelovani, A. Qiao and C. Li, *Biomacromolecules* **2007**, *8*, 3422–3428.

3 C. Wendeln, I. Singh, S. Rinnen, C. Schulz, H. F. Arlinghaus, G. A. Burley and B. J. Ravoo, *Chem. Sci.* **2012**, *3*, 2479–2484.